Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Direct Oxidative Coupling of *N*-Acyl Pyrroles with Alkenes by Ruthenium(II)-Catalyzed Regioselective C2-Alkenylation

Weiqiang Chen,[a] Hui-Jing Li,[a,b]* Qin-Ying Li,[a,b] and Yan-Chao Wu[a,b]*

[a] School of Marine Science and Technology, Harbin Institute of Technology, Weihai 264209, P. R. China

[b] Weihai Institute of Marine Biomedical Industrial Technology, Wendeng District, Weihai 264400, P. R. China

E-mail: lihuijing@iccas.ac.cn or ycwu@iccas.ac.cn

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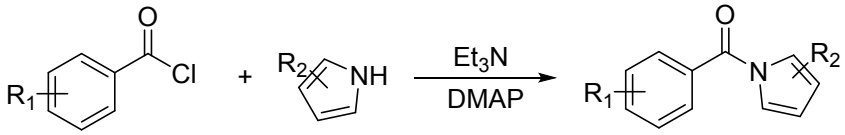
2. General Information

All reactions were carried out under an argon atmosphere except noted. Dichloromethane and toluene was distilled prior to use under a nitrogen atmosphere. Silica gel (200–300 mesh) was used for flash chromatography. The *N*-acyl pyrroles were prepared according to the literature procedures.[1–8] Formyl chloride, alkenes, and other reagents were purchased from commercial sources and used directly. High-resolution mass spectra (HRMS) were recorded by using an Electrothemal LTQ-Orbitrap mass spectrometer. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. ^{1}H and ^{13}C-NMR spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer with $CDCl_3$ as solvent. The chemical shifts are reported in ppm relative to $CDCl_3$ ($\delta = 7.26$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz. NMR data of known compounds is in agreement with literature values. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m).

3. Experimental Procedures

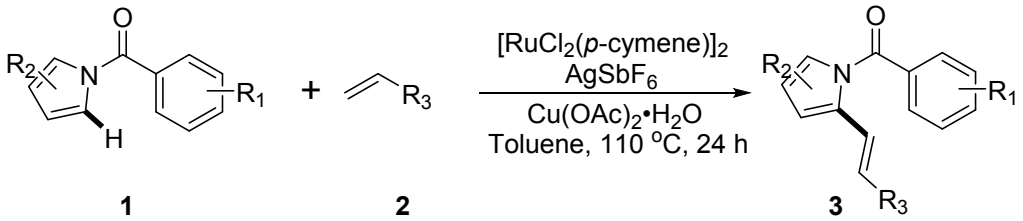
3.1 General procedure for the synthesis of *N*-acyl pyrroles **1**:



1

Benzoyl chloride (20.0 mmol) was added dropwise to a stirred solution of pyrrole (1.71 g, 25.6 mmol), triethylamine (2.60 g, 25.6 mmol) and DMAP (260 mg, 2.1 mmol) in dry dichloromethane (30 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred till the end of the reaction. The reaction mixture was then diluted with Et_2O, washed with 1 M HCl (30 mL), saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried over Na_2SO_4 and filtered. The volatiles were removed in vacuo and the residue was subjected to flash column chromatography to give the *N*-acyl pyrroles.

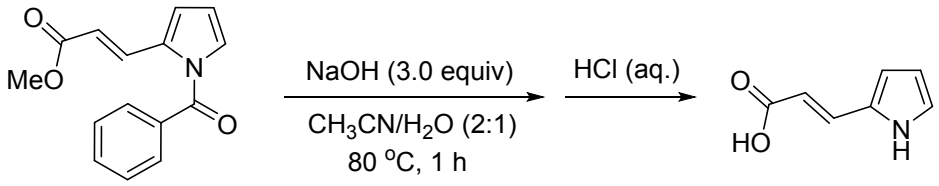
3.2 General Procedure for the Direct Oxidative Coupling between *N*-Acyl Pyrroles and alkenes



1 **2** **3**

A Schlenk reaction tube equipped with a magnetic stir bar was charged with $[RuCl_2(p\text{-cymene})]_2$ (0.05 equiv, 0.01 mmol), $AgSbF_6$ (0.10 equiv, 0.02 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.0 equiv , 0.20 mmol), *N*-acyl pyrroles **1** (1.0 equiv, 0.2 mmol) and alkenes **2** (2.0 equiv, 0.4 mmol) in toluene (2.0 mL). The tube was sealed under argon and heated to 110 °C with stirring for 24 h. After cooling down, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (ethyl acetate/petroleum ether mixtures).

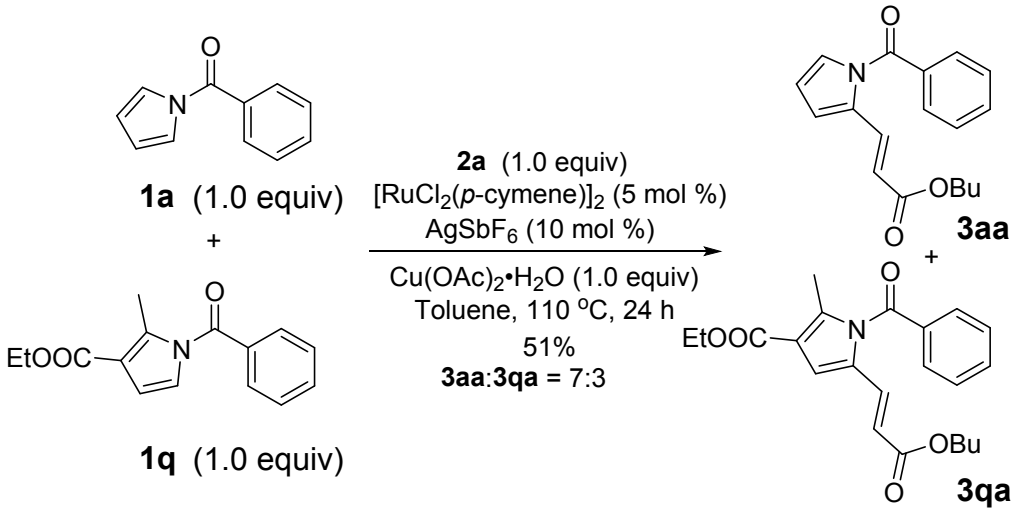
3.3 General Procedure for Deprotection and Hydrolysis of the C2-alkenylation product **3ab**



3ab (1.0 equiv) **9** (90%)

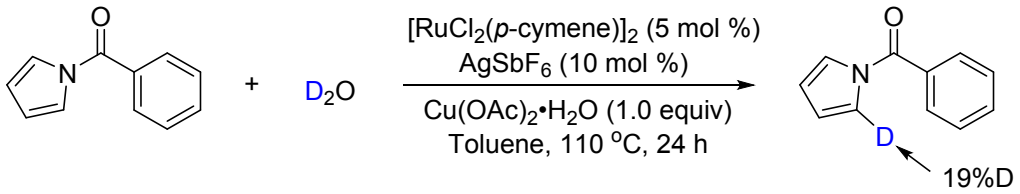
A suspension of the C2-alkenylation product **3ab** (51 mg, 0.20 mmol) and NaOH (24 mg, 0.60 mmol) in a 2:1 mixture of CH_3CN/H_2O (1 mL) was stirred at 80 °C until consumption of the starting material. After cooling down, the reaction mixture was diluted with EtOAc (5 mL), washed with 1 M HCl (5 mL) and water (3 x 5 mL), dried over Na_2SO_4 and filtered. The volatiles were removed in vacuo to obtain the product **9**.

3.4 General Procedure of Inter-molecular Competition Experiment



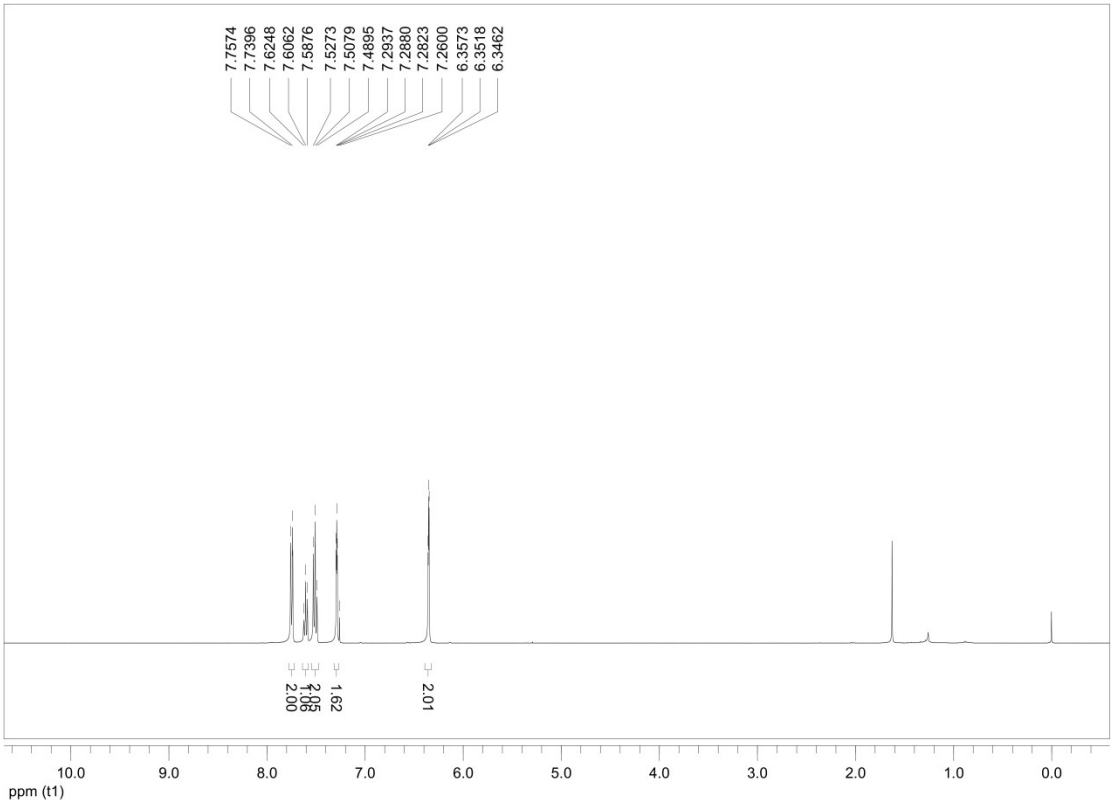
A Schlenk reaction tube equipped with a magnetic stir bar was charged with $[RuCl_2(p\text{-cymene})]_2$ (0.05 equiv, 0.01 mmol), $AgSbF_6$ (0.10 equiv, 0.02 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.0 equiv , 0.20 mmol), *N*-acyl pyrroles **1a** (1.0 equiv, 0.2 mmol) and **1q** (1.0 equiv, 0.2 mmol), alkenes **2a** (1.0 equiv, 0.2 mmol) in toluene (2.0 mL). The tube was sealed under argon and heated to 110 °C with stirring for 24 h. After cooling down, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (51%, **3aa**: **3qa** = 7:3).

3.4 General Procedure of Ru-Catalyzed H/D Exchange in **1a**



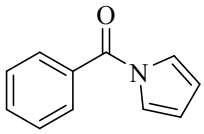
1a **1a-D**, 90% recoverd

A Schlenk reaction tube equipped with a magnetic stir bar was charged with $[RuCl_2(p\text{-cymene})]_2$ (0.05 equiv, 0.01 mmol), $AgSbF_6$ (0.10 equiv, 0.02 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.0 equiv , 0.20 mmol), *N*-acyl pyrroles **1a** (1.0 equiv, 0.2 mmol) and deuterium oxide (10.0 equiv, 2.0 mmol) in toluene (2.0 mL). The tube was sealed under argon and heated to 110 °C with stirring for 24 h. After cooling down, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (ethyl acetate/petroleum ether mixtures), providing deuterium labeled **1a** as a yellow oil in 90% yield. The D-incorporation was determined by ^1H NMR.



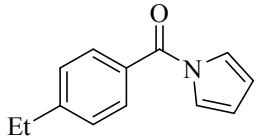
4. Characterization Data of the substrates and products

4.1 Spectral Data of Substrates **1**



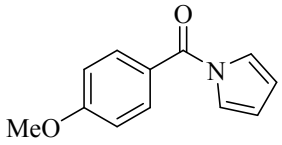
Phenyl(1*H*-pyrrol-1-yl)methanone (1a)

Synthesis carried out according to the General Procedure, compound **1a** was obtained in 91% yield as a yellow oil after purification by a silica gel column chromatography. 1H NMR (400 MHz, CDCl3) δ (ppm): 7.75 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.29 (d, J = 1.6 Hz, 2H), 6.35 (d, J = 1.6 Hz, 2H). 13C NMR (100 MHz, CDCl3) δ (ppm): 167.7, 133.2, 132.2, 129.4, 128.4, 121.2, 113.1. These spectral data correspond to previously reported data.[1]



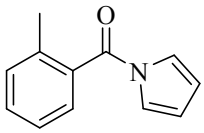
(4-Ethylphenyl)(1*H*-pyrrol-1-yl)methanone (1b)

Synthesis carried out according to the General Procedure, compound **1b** was obtained in 90% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 7.6 Hz, 2H), 7.34–7.30 (m, 4H), 6.34 (s, 2H), 2.75 (q, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.7, 149.2, 130.5, 129.8, 127.9, 121.3, 112.9, 28.9, 15.2. These spectral data correspond to previously reported data.[3]



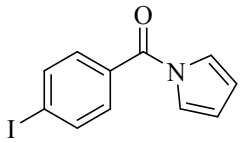
(4-Methoxyphenyl)(1*H*-pyrrol-1-yl)methanone (1c)

Synthesis carried out according to the General Procedure, compound **1c** was obtained in 93% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 2.0 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.34 (t, *J* = 2.0 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.1, 163.0, 132.0, 125.2, 121.3, 113.8, 112.7, 55.5. These spectral data correspond to previously reported data.[2]



(1*H*-Pyrrol-1-yl)(*o*-tolyl)methanone (1d)

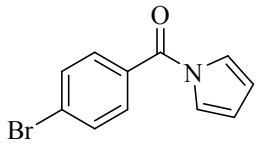
Synthesis carried out according to the General Procedure, compound **1d** was obtained in 90% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44–7.39 (m, 2H), 7.30 (t, *J* = 6.6 Hz, 2H), 7.15 (s, 2H), 6.31 (d, *J* = 1.2 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.2, 136.4, 133.7, 130.8, 130.7, 127.8, 125.5, 120.6, 113.4, 19.3. These spectral data correspond to previously reported data.[2]



(4-Iodophenyl)(1*H*-pyrrol-1-yl)methanone (1e)

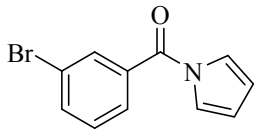
Synthesis carried out according to the General Procedure, compound **1e** was obtained in 87% yield as a white solid after purification by a silica gel column chromatography. mp 69–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 1.8 Hz, 2H), 6.36 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100

MHz, $CDCl_3$) δ (ppm): 166.9, 137.7, 132.5, 130.9, 121.1, 113.4, 99.6. These spectral data correspond to previously reported data.[4]



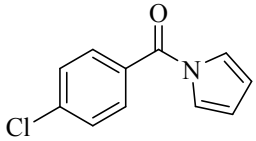
(4-Bromophenyl)(1*H*-pyrrol-1-yl)methanone (1f)

Synthesis carried out according to the General Procedure, compound **1f** was obtained in 86% yield as a white solid after purification by a silica gel column chromatography. mp 68–69°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70–7.64 (m, 4H), 7.27 (t, J = 2.2 Hz, 2H), 6.38 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.7, 132.0, 131.8, 131.0, 127.2, 121.1, 113.4. These spectral data correspond to previously reported data.[5]



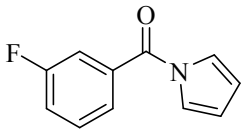
(3-Bromophenyl)(1*H*-pyrrol-1-yl)methanone (1g)

Synthesis carried out according to the General Procedure, compound **1g** was obtained in 87% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (s, 1H), 7.77–7.68 (m, 2H), 7.42 (t, J = 7.8 Hz, 1H), 7.28 (s, 2H), 6.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.1, 135.2, 135.1, 132.3, 130.0, 127.9, 122.6, 121.1, 113.6. These spectral data correspond to previously reported data.[3]



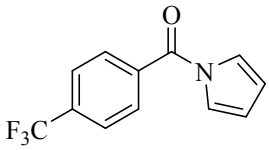
(4-Chlorophenyl)(1*H*-pyrrol-1-yl)methanone (1h)

Synthesis carried out according to the General Procedure, compound **1h** was obtained in 83% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.25 (t, *J* = 2.4 Hz, 2H), 6.36 (t, *J* = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6, 138.7, 131.5, 130.9, 128.8, 121.1, 113.4. These spectral data correspond to previously reported data.[3]



(3-Fluorophenyl)(1*H*-pyrrol-1-yl)methanone (1i)

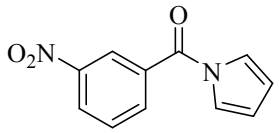
Synthesis carried out according to the General Procedure, compound **1i** was obtained in 80% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54–7.44 (m, 3H), 7.33–7.28 (m, 1H), 7.27 (t, *J* = 2.2 Hz, 2H), 6.36 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.2, 163.5, 161.0, 135.2, 135.1, 130.3, 130.2, 125.2, 125.1, 121.1, 119.4, 119.2, 116.7, 116.4, 113.5. These spectral data correspond to previously reported data.[3]



(1*H*-Pyrrol-1-yl)(4-(trifluoromethyl)phenyl)methanone (1j)

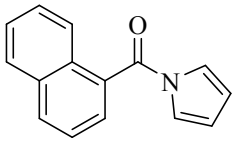
Synthesis carried out according to the General Procedure, compound **1j** was obtained in 80% yield as a yellow solid after purification by a silica gel column

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 2.2 Hz, 2H), 6.38 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.4, 136.6, 134.0, 133.7, 129.7, 125.6, 125.5, 124.8, 122.1, 121.1, 113.8. HRMS (ESI) m/z: calcd for $C_{12}H_8F_3NNaO$ $[M+Na]^+$: 262.0450, found: 262.0456.



(3-Nitrophenyl)(1*H*-pyrrol-1-yl)methanone (1k)

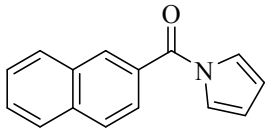
Synthesis carried out according to the General Procedure, compound **1k** was obtained in 80% yield as a yellow oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (s, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.27 (s, 2H), 6.44 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.2, 148.0, 134.9, 134.8, 129.9, 126.7, 124.3, 121.0, 114.2. These spectral data correspond to previously reported data.[6]



Naphthalen-1-yl(1*H*-pyrrol-1-yl)methanone (1l)

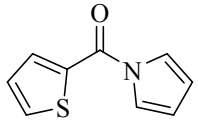
Synthesis carried out according to the General Procedure, compound **1l** was obtained in 80% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, *J* = 8.0 Hz, 1H), 7.96–7.92 (m, 2H), 7.67–7.65 (m, 1H), 7.59–7.52 (m, 3H), 7.22 (s, 2H), 6.33 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.6, 133.4, 131.4, 131.2, 130.4, 128.4, 127.6,

126.9, 126.7, 125.0, 124.4, 121.0, 113.4. These spectral data correspond to previously reported data.[7]



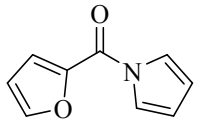
Naphthalen-2-yl(1H-pyrrol-1-yl)methanone (1m)

Synthesis carried out according to the General Procedure, compound **1m** was obtained in 83% yield as a white solid after purification by a silica gel column chromatography. mp 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.27 (s, 1H), 7.98–7.92 (m, 3H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.66–7.58 (m, 2H), 7.36 (s, 2H), 6.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.8, 134.9, 132.2, 130.7, 130.4, 129.1, 128.5, 128.4, 127.9, 127.1, 125.5, 121.4, 113.1. These spectral data correspond to previously reported data.[3]



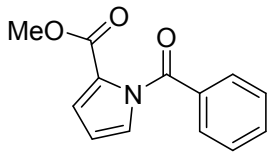
(1*H*-Pyrrol-1-yl)(thiophen-2-yl)methanone (1n)

Synthesis carried out according to the General Procedure, compound **1n** was obtained in 80% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77–7.76 (m, 1H), 7.72–7.71 (m, 1H), 7.47 (t, *J* = 2.4 Hz, 2H), 7.20–7.18 (m, 1H), 6.38 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.6, 135.8, 134.0, 133.3, 127.7, 121.0, 113.2. These spectral data correspond to previously reported data.[3]



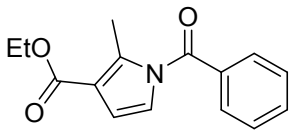
Furan-2-yl(1*H*-pyrrol-1-yl)methanone (1o)

Synthesis carried out according to the General Procedure, compound **1o** was obtained in 82% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69–7.66 (m, 3H), 7.43–7.42 (m, 1H), 6.63–6.62 (m, 1H), 6.36 (t, *J* = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.5, 146.7, 146.5, 121.2, 120.7, 113.2, 112.4. These spectral data correspond to previously reported data.[3]



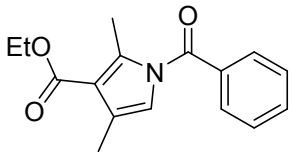
Methyl 1-benzoyl-1*H*-pyrrole-2-carboxylate (1p)

Synthesis carried out according to the General Procedure, compound **1p** was obtained in 81% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 (d, *J* = 6.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.23–7.22 (m, 1H), 7.07–7.06 (m, 1H), 6.30 (t, *J* = 3.2 Hz, 1H), 3.57 s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.2, 160.6, 133.5, 133.3, 129.8, 128.6, 127.7, 126.0, 121.2, 110.6, 51.5. HRMS (ESI) m/z: calcd for $C_{13}H_{11}NNaO_3$ $[M+Na]^+$: 252.0631, found: 252.0636.



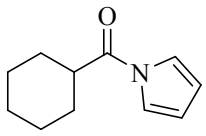
Ethyl 1-benzoyl-2-methyl-1*H*-pyrrole-3-carboxylate (1q)

Synthesis carried out according to the General Procedure, compound **1q** was obtained in 75% yield as a white solid after purification by a silica gel column chromatography. mp 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 3.6 Hz, 1H), 6.55 (d, *J* = 3.6 Hz, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 2.81 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.3, 164.9, 139.1, 133.4, 133.1, 130.1, 128.6, 121.9, 117.2, 111.2, 60.0, 14.4, 13.4. HRMS (ESI) m/z: calcd for $C_{15}H_{15}NNaO_3$ $[M+Na]^+$: 280.0944, found: 280.0941.



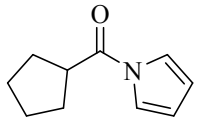
Ethyl 1-benzoyl-2,4-dimethyl-1*H*-pyrrole-3-carboxylate (1r)

Synthesis carried out according to the General Procedure, compound **1r** was obtained in 79% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 6.53 (s, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 2.77 (s, 3H), 2.16 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.1, 165.6, 139.6, 133.7, 132.8, 129.9, 128.5, 121.6, 120.2, 117.2, 59.8, 14.3, 13.9, 12.5. HRMS (ESI) m/z: calcd for $C_{16}H_{17}NNaO_3$ $[M+Na]^+$: 294.1101, found: 294.1106.



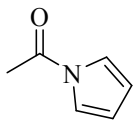
Cyclohexyl(1*H*-pyrrol-1-yl)methanone (1s)

Synthesis carried out according to the General Procedure, compound **1s** was obtained in 80% yield as a white solid after purification by a silica gel column chromatography. mp 54–55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 (t, J = 2.0 Hz, 2H), 6.29 (t, J = 2.4 Hz, 2H), 2.96–2.89 (m, 1H), 1.97–1.85 (m, 4H), 1.76–1.58 (m, 3H), 1.43–1.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.8, 118.9, 112.9, 42.8, 29.6, 25.6, 25.5. These spectral data correspond to previously reported data.[5]



Cyclopentyl(1*H*-pyrrol-1-yl)methanone (1t)

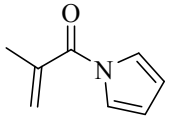
Synthesis carried out according to the General Procedure, compound **1t** was obtained in 81% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34(s, 2H), 6.29 (t, J = 2.4 Hz, 2H), 3.42–3.34 (m, 1H), 2.02–1.97 (m, 4H), 1.84–1.75 (m, 2H), 1.72–1.63 (m, 2H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.8, 119.2, 112.8, 43.0, 30.5, 26.1. HRMS (ESI) m/z: calcd for $C_{10}H_{13}NNaO$ $[M+Na]^+$: 186.0889, found: 186.0891.



1-(1*H*-pyrrol-1-yl)ethan-1-one (1u)

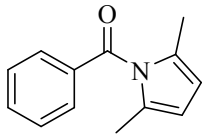
Synthesis carried out according to the General Procedure, compound **1u** was obtained

in 82% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29 (s, 2H), 6.30 (t, *J* = 2.2 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.7, 119.3, 113.2, 22.3. These spectral data correspond to previously reported data.[8]



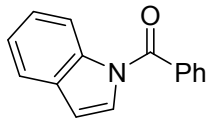
2-Methyl-1-(1*H*-pyrrol-1-yl)prop-2-en-1-one (1v)

Synthesis carried out according to the General Procedure, compound **1v** was obtained in 80% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 (t, *J* = 2.2 Hz, 2H), 6.31 (t, *J* = 2.4 Hz, 2H), 5.70 (d, *J* = 1.2 Hz, 1H), 5.52 (s, 1H), 2.11 (t, *J* = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.5, 138.6, 123.0, 120.5, 113.1, 19.8. HRMS (ESI) m/z: calcd for C_8H_9NNaO $[M+Na]^+$: 158.0576, found: 158.0573.



(2,5-Dimethyl-1*H*-pyrrol-1-yl)(phenyl)methanone (1w)

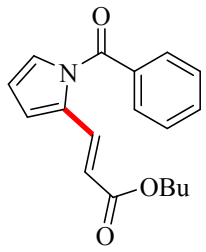
Synthesis carried out according to the General Procedure, compound **1w** was obtained in 80% yield as a yellowish oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.87 (s, 2H), 2.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.1, 135.6, 133.1, 130.3, 130.1, 128.6, 110.1, 14.6. HRMS (ESI) m/z: calcd for $C_{13}H_{13}NNaO$ $[M+Na]^+$: 222.0889, found: 222.0893.



(1*H*-indol-1-yl)(phenyl)methanone (7)

Synthesis carried out according to the General Procedure, compound **7** was obtained in 82% yield as a white solid after purification by a silica gel column chromatography. mp 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.45 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 6.8 Hz, 2H), 7.62 (t, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 6.8 Hz, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.6, 135.9, 135.0, 131.8, 130.7, 129.1, 128.5, 127.5, 124.8, 123.9, 120.8, 116.3, 108.5. HRMS (ESI) m/z: calcd for $C_{15}H_{11}NNaO$ $[M+Na]^+$: 244.0733, found: 244.0737.

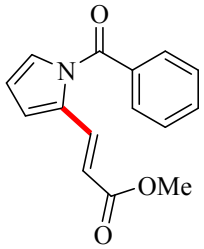
4.2 Spectral Data of products **3**



Butyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3aa)

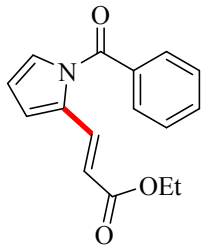
Synthesis carried out according to the General Procedure, compound **3aa** was obtained in 81% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.05 (d, *J* = 16.0 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.02–7.01

(m, 1H), 6.84 (d, J = 3.2 Hz, 1H), 6.28–6.24 (m, 2H), 4.16 (t, J = 6.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.45–1.35 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 167.0, 134.1, 133.3, 133.1, 132.2, 130.1, 128.6, 126.6, 116.8, 115.7, 111.9, 64.2, 30.7, 19.2, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{19}NNaO_3$ [M + Na]$^+$: 320.1257, found 320.1263.



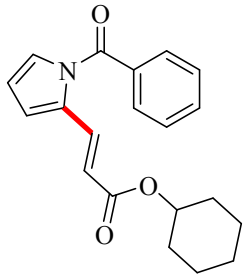
Methyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ab)

Synthesis carried out according to the General Procedure, compound **3ab** was obtained in 76% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.02 (s, 1H), 6.85 (s, 1H), 6.29–6.25 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 167.3, 134.4, 133.2, 133.1, 132.1, 130.1, 128.6, 126.7, 116.3, 115.8, 111.9, 51.5. HRMS (ESI) *m/z*: Calcd for $C_{15}H_{13}NNaO_3$ [M + Na]$^+$: 278.0788, found 278.0791.



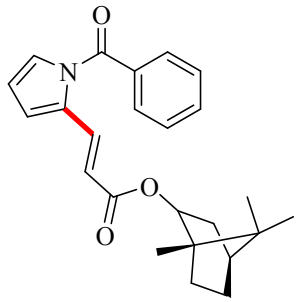
Ethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ac)

Synthesis carried out according to the General Procedure, compound **3ac** was obtained in 79% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 2.8 Hz, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 6.28–6.24 (m, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.3 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.8, 166.9, 134.2, 133.4, 133.1, 132.2, 130.1, 128.6, 126.6, 116.9, 115.7, 111.9, 60.3, 14.3. HRMS (ESI) *m/z*: Calcd for $C_{16}H_{15}NNaO_3$ $[M + Na]^+$: 292.0944, found 292.0951.



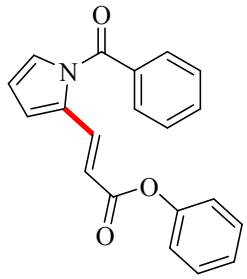
Cyclohexyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ad)

Synthesis carried out according to the General Procedure, compound **3ad** was obtained in 71% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.28–6.24 (m, 2H), 1.89–1.86 (m, 2H), 1.75–1.72 (m, 2H), 1.56–1.23 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.8, 166.3, 133.8, 133.4, 133.1, 132.3, 130.1, 128.6, 126.5, 117.5, 115.6, 111.9, 72.5, 31.7, 25.5, 23.8. HRMS (ESI) *m/z*: Calcd for $C_{20}H_{21}NNaO_3$ $[M + Na]^+$: 346.1414, found 346.1409.



(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl(*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylae (3ae)

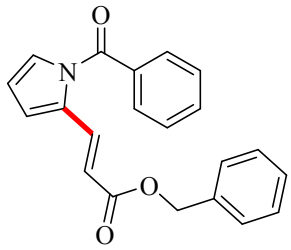
Synthesis carried out according to the General Procedure, compound **3ae** was obtained in 51% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.03–7.02 (m, 1H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.28–6.22 (m, 2H), 4.78–4.75 (m, 1H), 1.87–1.77 (m, 2H), 1.74–1.71 (m, 1H), 1.60–1.52 (m, 2H), 1.25–1.21 (m, 2H), 1.03 (s, 3H), 0.87 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 166.4, 133.8, 133.5, 133.0, 132.2, 130.0, 128.6, 126.6, 117.5, 115.6, 111.9, 80.9, 48.9, 47.0, 45.1, 38.8, 33.7, 27.1, 20.1, 20.0, 11.5. HRMS (ESI) *m/z*: Calcd for $C_{23}H_{25}NNaO_3$ [M + Na]$^{+}$: 386.1727, found 386.1731.



Phenyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3af)

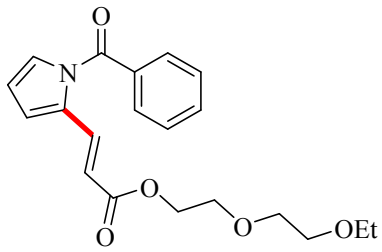
Synthesis carried out according to the General Procedure, compound **3af** was obtained in 69% yield as a colorless oil after purification by a silica gel column

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (d, *J* = 16.0 Hz, 1H), 7.78 (d, *J* = 6.8 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.09–7.07 (m, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.33 (t, *J* = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 165.3, 150.8, 135.9, 133.2, 133.1, 131.9, 130.1, 129.3, 128.7, 127.1, 125.6, 121.7, 116.5, 115.6, 112.1. HRMS (ESI) *m/z*: Calcd for $C_{20}H_{15}NNaO_3$ $[M + Na]^+$: 340.0944, found 340.0941.



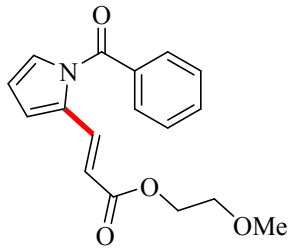
Benzyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ag)

Synthesis carried out according to the General Procedure, compound **3ag** was obtained in 66% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.38–7.33 (m, 5H), 7.04–7.03 (m, 1H), 6.86 (d, *J* = 3.2 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.28 (t, *J* = 3.4 Hz, 1H), 5.22 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 166.7, 136.2, 134.7, 133.3, 133.1, 132.1, 130.1, 128.6, 128.5, 128.2, 128.1, 126.7, 116.3, 115.9, 111.9, 66.1. HRMS (ESI) *m/z*: Calcd for $C_{21}H_{17}NNaO_3$ $[M + Na]^+$: 354.1101, found 354.1106.



2-(2-Ethoxyethoxy)ethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ah)

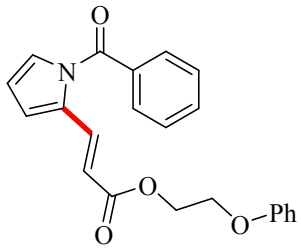
Synthesis carried out according to the General Procedure, compound **3ah** was obtained in 61% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.03–7.02 (m, 1H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.33–6.27 (m, 2H), 4.34 (t, *J* = 5.0 Hz, 2H), 3.76 (t, *J* = 4.8 Hz, 2H), 3.69–3.67 (m, 2H), 3.61–3.59 (m, 2H), 3.53 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 166.8, 134.6, 133.3, 133.1, 132.2, 130.1, 128.6, 126.7, 116.4, 115.9, 111.9, 70.7, 69.8, 69.3, 66.7, 63.6, 15.1. HRMS (ESI) *m/z*: Calcd for $C_{20}H_{23}NNaO_5$ $[M + Na]^+$: 380.1468, found 380.1491.



2-Methoxyethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ai)

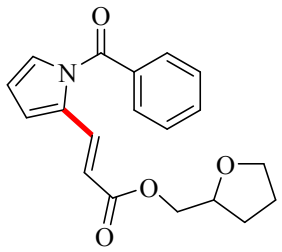
Synthesis carried out according to the General Procedure, compound **3ai** was obtained in 73% yield as a pale yellow solid after purification by a silica gel column chromatography. Mp:95–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, *J* =

16.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.03–7.01 (m, 1H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.28 (t, *J* = 3.4 Hz, 1H), 4.33 (t, *J* = 4.8 Hz, 2H), 3.65 (t, *J* = 4.6 Hz, 2H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 166.9, 134.7, 133.3, 133.1, 132.1, 130.1, 128.6, 126.7, 116.3, 115.9, 111.9, 70.6, 63.4, 59.0. HRMS (ESI) *m/z*: Calcd for $C_{17}H_{17}NNaO_4$ $[M + Na]^+$: 322.1050, found 322.1054.



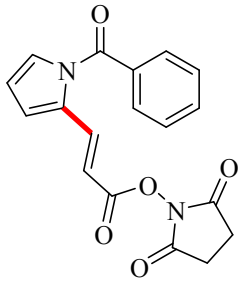
2-Phenoxyethyl *(E)*-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3aj)

Synthesis carried out according to the General Procedure, compound **3aj** was obtained in 82% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.10 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.04–7.03 (m, 1H), 6.97–6.93 (m, 3H), 6.86 (d, *J* = 3.2 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.28 (t, *J* = 3.4 Hz, 1H), 4.53 (t, *J* = 5.0 Hz, 2H), 4.22 (t, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.6, 166.8, 158.7, 134.9, 133.2, 133.1, 132.1, 130.1, 129.5, 128.6, 126.7, 121.1, 116.0, 114.6, 111.9, 65.9, 62.7. HRMS (ESI) *m/z*: Calcd for $C_{22}H_{19}NNaO_4$ $[M + Na]^+$: 384.1206, found 384.1201.



(Tetrahydrofuran-2-yl)methyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ak)

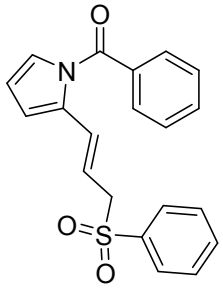
Synthesis carried out according to the General Procedure, compound **3ak** was obtained in 80% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, *J* = 16.0 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.02–7.01 (m, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.27 (t, *J* = 3.4 Hz, 1H), 4.26–4.23 (m, 1H), 4.20–4.08 (m, 2H), 3.93–3.88 (m, 1H), 3.82–3.78 (m, 1H), 2.06–1.86 (m, 3H), 1.69–1.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.6, 166.8, 134.6, 133.3, 133.1, 132.1, 130.0, 128.6, 126.7, 116.3, 115.8, 111.9, 76.6, 68.4, 66.4, 28.0, 25.6. HRMS (ESI) *m/z*: Calcd for $C_{19}H_{19}NNaO_4$ $[M + Na]^+$: 348.1206, found 348.1210.



2,5-Dioxopyrrolidin-1-yl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3al)

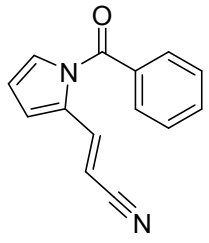
Synthesis carried out according to the General Procedure, compound **3al** was obtained in 54% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.36 (d, *J* = 16.0 Hz, 1H),

7.76 (d, *J* = 6.8 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.11–7.10 (m, 1H), 7.02 (d, *J* = 3.6 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.33 (t, *J* = 3.4 Hz, 1H), 2.86 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.4, 168.5, 162.0, 139.1, 133.3, 133.0, 131.4, 130.1, 128.7, 128.1, 117.8, 112.3, 109.2, 25.6. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{14}N_2NaO_5$ [M + Na]$^+$: 361.0795, found 361.0800.



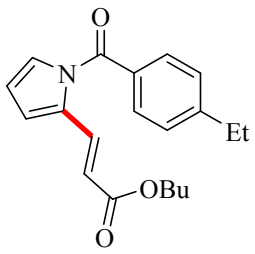
(*E*)-phenyl(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-1*H*-pyrrol-1-yl)methanone (3an)

Synthesis carried out according to the General Procedure, compound **3an** was obtained in 70% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.63–7.59 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.85–6.84 (m, 1H), 6.57 (d, *J* = 3.2 Hz, 1H), 6.19 (t, *J* = 3.4 Hz, 1H), 6.00–5.93 (m, 1H), 3.95–3.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.0, 138.5, 133.7, 133.6, 133.2, 132.8, 129.9, 129.6, 129.1, 128.5, 128.4, 124.7, 114.3, 113.0, 111.5, 60.6. HRMS (ESI) *m/z*: Calcd for $C_{20}H_{17}NNaO_3S$ [M + Na]$^+$: 374.0821, found 374.0823.



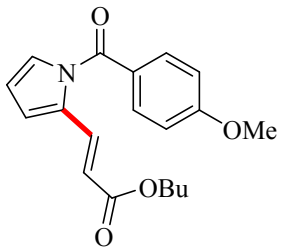
(*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylonitrile (3ao)

Synthesis carried out according to the General Procedure, compound **3ao** was obtained in 66% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (d, *J* = 16.4 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.06–7.05 (m, 1H), 6.86 (d, *J* = 3.6 Hz, 1H), 6.29 (t, *J* = 3.4 Hz, 1H), 5.70 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 140.0, 133.3, 132.9, 131.2, 130.0, 128.7, 127.5, 118.5, 116.0, 112.1, 94.0. HRMS (ESI) *m/z*: Calcd for $C_{14}H_{10}N_2NaO$ [M + Na]$^{+}$: 245.0685, found 245.0689.



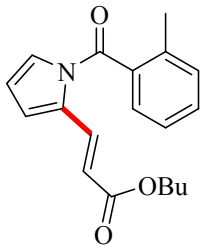
Butyl (*E*)-3-(1-(4-ethylbenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ba)

Synthesis carried out according to the General Procedure, compound **3ba** was obtained in 73% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04 (d, *J* = 16.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 1.6 Hz, 1H), 6.83 (d, *J* = 2.8 Hz, 1H), 6.27–6.23 (m, 2H), 4.16 (t, *J* = 6.6 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.45–1.35 (m, 2H), 1.28 (t, *J* = 7.6 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.6, 167.0, 150.2, 134.1, 132.0, 130.6, 130.4, 128.1, 126.6, 115.5, 111.6, 64.1, 30.7, 28.9, 19.1, 15.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{20}H_{23}NNaO_3$ [M + Na]$^{+}$: 348.1570, found 348.1573.



Butyl (*E*)-3-(1-(4-methoxybenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ca)

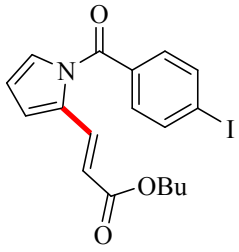
Synthesis carried out according to the General Procedure, compound **3ca** was obtained in 69% yield as a pale yellow oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (d, *J* = 16.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.28–6.23 (m, 2H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.89 (s, 3H), 1.68–1.61 (m, 2H), 1.44–1.35 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.0, 167.1, 163.7, 134.0, 132.7, 132.0, 126.5, 125.3, 116.4, 115.3, 113.9, 111.5, 64.2, 55.6, 30.7, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{19}H_{21}NNaO_4$ [M + Na]$^{+}$: 350.1363, found 350.1366.



Butyl (*E*)-3-(1-(2-methylbenzoyl)-1*H*-pyrrol-2-yl)acrylate (3da)

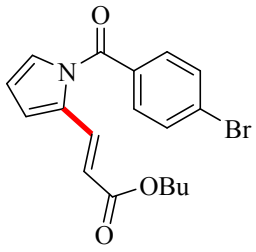
Synthesis carried out according to the General Procedure, compound **3da** was obtained in 71% yield as a yellow oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.19 (d, *J* = 16.0 Hz, 1H), 7.45–7.41 (m, 1H), 7.37 (d, *J* = 6.8 Hz, 1H), 7.29 (t, *J* = 6.6 Hz, 2H), 6.81 (t, *J* = 2.8

Hz, 2H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.22 (t, *J* = 3.4 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 1.70–1.63 (m, 2H), 1.46–1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.4, 167.0, 136.9, 134.3, 133.9, 132.0, 131.2, 131.0, 128.2, 126.1, 125.7, 117.2, 116.0, 112.3, 64.2, 30.7, 19.4, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{19}H_{21}NNaO_3$ $[M + Na]^+$: 334.1414, found 334.1410.



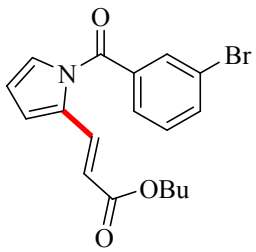
Butyl (*E*)-3-(1-(4-iodobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ea)

Synthesis carried out according to the General Procedure, compound **3ea** was obtained in 72% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, *J* = 16.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.98–6.97 (m, 1H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.29–6.24 (m, 2H), 4.17 (t, *J* = 6.8 Hz, 2H), 1.69–1.62 (m, 2H), 1.45–1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.0, 166.9, 137.9, 133.8, 132.6, 132.2, 131.3, 126.2, 117.1, 115.8, 112.2, 100.8, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{18}INNaO_3$ $[M + Na]^+$: 446.0224, found 446.0220.



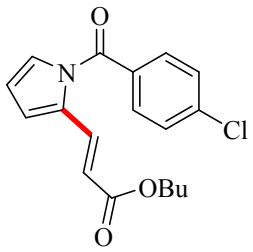
Butyl (*E*)-3-(1-(4-bromobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3fa)

Synthesis carried out according to the General Procedure, compound **3fa** was obtained in 70% yield as a yellow oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, *J* = 16.0 Hz, 1H), 7.67–7.62 (m, 4H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.29–6.24 (m, 2H), 4.16 (t, *J* = 6.6 Hz, 2H), 1.69–1.62 (m, 2H), 1.45–1.35 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.7, 166.9, 133.8, 132.2, 132.1, 132.0, 131.5, 128.2, 126.2, 117.1, 115.8, 112.2, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{18}BrNNaO_3$ $[M + Na]^+$: 398.0362, found 398.0366.



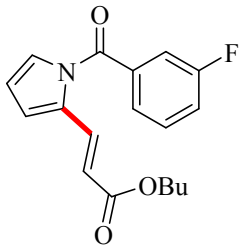
Butyl (*E*)-3-(1-(3-bromobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ga)

Synthesis carried out according to the General Procedure, compound **3ga** was obtained in 73% yield as a pale yellow oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, *J* = 16.0 Hz, 1H), 7.89 (t, *J* = 1.8 Hz, 1H), 7.77–7.74 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 6.99–6.98 (m, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 6.30–6.25 (m, 2H), 4.17 (t, *J* = 6.6 Hz, 2H), 1.69–1.62 (m, 2H), 1.45–1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.1, 166.9, 136.0, 135.2, 133.8, 132.8, 132.3, 130.1, 128.5, 126.2, 122.7, 117.2, 116.0, 112.4, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{18}BrNNaO_3$ $[M + Na]^+$: 398.0362, found 398.0360.



Butyl (*E*)-3-(1-(4-chlorobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ha)

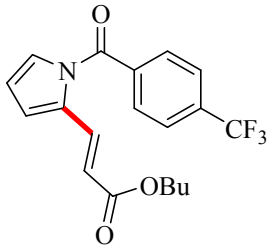
Synthesis carried out according to the General Procedure, compound **3ha** was obtained in 78% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, *J* = 16.0 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.99–6.98 (m, 1H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.30–6.24 (m, 2H), 4.17 (t, *J* = 6.8 Hz, 2H), 1.69–1.62 (m, 2H), 1.45–1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.6, 166.9, 139.7, 133.8, 132.2, 131.6, 131.5, 129.0, 126.2, 117.1, 115.8, 112.2, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{18}ClNNaO_3$ $[M + Na]^+$: 354.0867, found 354.0863.



Butyl (*E*)-3-(1-(3-fluorobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ia)

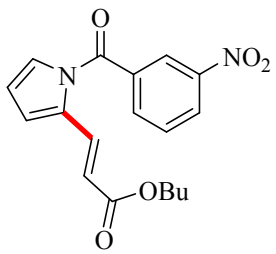
Synthesis carried out according to the General Procedure, compound **3ia** was obtained in 80% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04 (d, *J* = 16.0 Hz, 1H), 7.56–7.46 (m, 3H), 7.37–7.32 (m, 1H), 7.01–7.00 (m, 1H), 6.86 (d, *J* = 3.2 Hz, 1H),

6.31–6.25 (m, 2H), 4.18 (t, J = 6.6 Hz, 2H), 1.70–1.63 (m, 2H), 1.46–1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.4, 166.9, 163.6, 161.1, 135.4, 135.3, 133.9, 132.3, 130.5, 130.4, 126.3, 125.8, 125.7, 120.3, 120.1, 117.2, 117.1, 116.9, 116.0, 112.3, 64.3, 30.8, 19.2, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{18}FNNaO_3$ $[M + Na]^+$: 338.1163, found 338.1160.



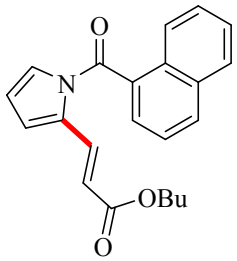
Butyl (*E*)-3-(1-(4-(trifluoromethyl)benzoyl)-1*H*-pyrrol-2-yl)acrylate (3ja)

Synthesis carried out according to the General Procedure, compound **3ja** was obtained in 76% yield as a pale yellow solid after purification by a silica gel column chromatography. Mp: 38–39 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.08 (d, J = 16.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 6.94–6.93 (m, 1H), 6.86 (d, J = 3.2 Hz, 1H), 6.31–6.27 (m, 2H), 4.18 (t, J = 6.8 Hz, 2H), 1.70–1.62 (m, 2H), 1.46–1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.5, 166.8, 136.7, 134.6, 134.3, 133.8, 132.5, 130.2, 126.1, 125.7, 125.7, 125.6, 125.6, 124.7, 122.0, 117.5, 116.1, 112.6, 64.3, 30.7, 19.2, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{19}H_{18}F_3NNaO_3$ $[M + Na]^+$: 388.1131, found 388.1133.



Butyl (*E*)-3-(1-(3-nitrobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ka)

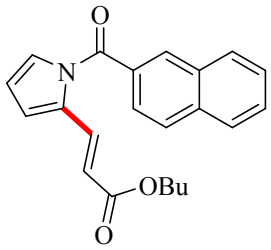
Synthesis carried out according to the General Procedure, compound **3ka** was obtained in 79% yield as a yellow oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.60 (t, *J* = 1.8 Hz, 1H), 8.51–8.48 (m, 1H), 8.11–8.09 (m, 1H), 8.04 (d, *J* = 16.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 6.95–6.94 (m, 1H), 6.89 (d, *J* = 3.2 Hz, 1H), 6.35 (t, *J* = 3.4 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.18 (t, *J* = 6.8 Hz, 2H), 1.70–1.62 (m, 2H), 1.46–1.36 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.8, 166.3, 148.1, 135.4, 135.0, 133.5, 132.6, 130.0, 127.4, 125.8, 124.8, 117.8, 116.3, 113.1, 64.4, 30.7, 19.2, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{18}N_2NaO_5$ $[M + Na]^+$: 365.1108, found 365.1106.



Butyl (*E*)-3-(1-(1-naphthoyl)-1*H*-pyrrol-2-yl)acrylate (3la)

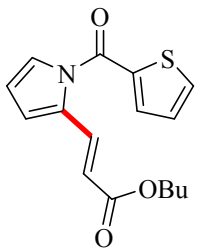
Synthesis carried out according to the General Procedure, compound **3la** was obtained in 74% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (d, *J* = 16.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.98–7.92 (m, 2H), 7.67–7.65 (m, 1H), 7.57–7.52 (m, 3H), 6.86 (d, *J* = 3.2 Hz, 1H), 6.81–6.80 (m, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.20 (t, *J* = 3.4 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 1.70–1.63 (m, 2H), 1.46–1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.9, 166.9, 134.4, 133.5, 132.3, 132.2, 131.4, 130.5, 128.5, 127.8, 127.7, 126.9, 126.6, 124.7, 124.4, 117.3, 116.1,

112.3, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{22}H_{21}NNaO_3$ $[M + Na]^+$: 370.1414, found 370.1410.



Butyl (*E*)-3-(1-(2-naphthoyl)-1*H*-pyrrol-2-yl)acrylate (3ma)

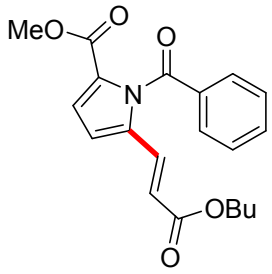
Synthesis carried out according to the General Procedure, compound **3ma** was obtained in 73% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (s, 1H), 8.10 (d, *J* = 16.0 Hz, 1H), 7.97–7.92 (m, 3H), 7.84–7.81 (m, 1H), 7.67–7.58 (m, 2H), 7.10–7.09 (m, 1H), 6.89 (d, *J* = 2.8 Hz, 1H), 6.32–6.28 (m, 2H), 4.16 (t, *J* = 6.6 Hz, 2H), 1.67–1.60 (m, 2H), 1.43–1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.8, 167.0, 135.3, 134.1, 132.3, 132.1, 131.7, 130.4, 129.2, 128.8, 128.6, 127.9, 127.2, 126.7, 125.6, 116.8, 115.7, 111.9, 64.2, 30.7, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{22}H_{21}NNaO_3$ $[M + Na]^+$: 370.1414, found 370.1411.



Butyl (*E*)-3-(1-(thiophene-2-carbonyl)-1*H*-pyrrol-2-yl)acrylate (3na)

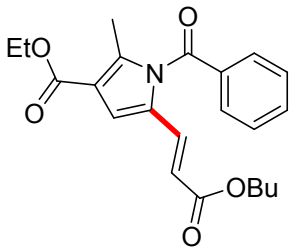
Synthesis carried out according to the General Procedure, compound **3na** was obtained in 36% yield as a pale orange oil after purification by a silica gel column

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, *J* = 16.0 Hz, 1H), 7.78–7.77 (m, 1H), 7.71–7.70 (m, 1H), 7.34–7.33 (m, 1H), 7.20–7.18 (m, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 6.32 (t, *J* = 3.6 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 4.17 (t, *J* = 6.8 Hz, 2H), 1.69–1.63 (m, 2H), 1.45–1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.0, 161.7, 136.6, 135.2, 134.8, 133.7, 132.0, 128.0, 126.0, 116.8, 115.5, 112.0, 64.3, 30.7, 19.2, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{16}H_{17}NNaO_3S$ $[M + Na]^+$: 326.0821, found 326.0823.



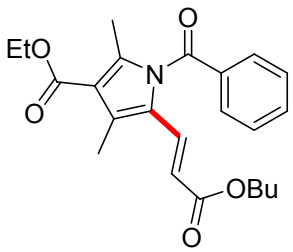
Methyl(*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-1*H*-pyrrole-2-carboxylate (3pa)

Synthesis carried out according to the General Procedure, compound **3pa** was obtained in 75% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63–7.59 (m, 3H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 15.6 Hz, 1H), 7.03 (d, *J* = 4.0 Hz, 1H), 6.77 (d, *J* = 4.0 Hz, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 4.11 (t, *J* = 6.8 Hz, 2H), 3.61 (s, 3H), 1.64–1.57 (m, 2H), 1.39–1.30 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.5, 166.2, 160.1, 135.1, 134.6, 133.8, 130.9, 129.8, 129.0, 127.4, 119.9, 118.3, 111.5, 64.5, 51.8, 30.6, 19.0, 13.6. HRMS (ESI) *m/z*: Calcd for $C_{20}H_{21}NNaO_5$ $[M + Na]^+$: 378.1312, found 378.1316.



Ethyl(*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (3qa)

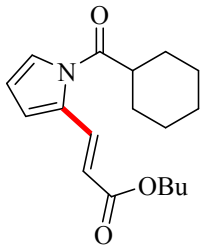
Synthesis carried out according to the General Procedure, compound **3qa** was obtained in 79% yield as a yellow oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68–7.64 (m, 3H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 15.6 Hz, 1H), 7.09 (s, 1H), 6.06 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.0 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.45 (s, 3H), 1.58–1.51 (m, 2H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.32–1.25 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.8, 166.6, 164.3, 139.9, 135.1, 133.2, 132.1, 130.7, 129.3, 129.2, 115.9, 115.6, 113.8, 64.1, 60.1, 30.6, 19.0, 14.3, 13.6, 13.0. HRMS (ESI) *m/z*: Calcd for $C_{22}H_{25}NNaO_5$ $[M + Na]^+$: 406.1625, found 406.1629.



Ethyl(*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-2,4-dimethyl-1*H*-pyrrole-3-carboxylate (3ra)

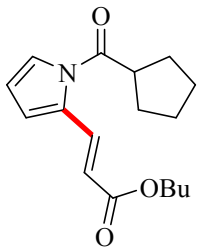
Synthesis carried out according to the General Procedure, compound **3ra** was obtained in 73% yield as a yellow oil after purification by a silica gel column

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67–7.63 (m, 3H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 16.0 Hz, 1H),5.69 (d, *J* = 16.4 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.43 (d, *J* = 2.8 Hz, 6H), 1.59–1.52 (m, 2H), 1.38 (t, *J* = 7.0 Hz, 3H), 1.34–1.27 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.8, 167.0, 165.2, 140.3, 135.0, 133.3, 131.4, 130.6, 129.2, 127.8, 119.1, 115.5, 115.3, 64.2, 60.0, 30.6, 19.1, 14.4, 13.7, 13.2, 12.1. HRMS (ESI) *m/z*: Calcd for $C_{23}H_{27}NNaO_5$ $[M + Na]^+$: 420.1781, found 420.1787.



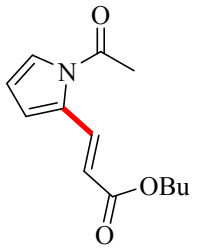
Butyl (*E*)-3-(1-(cyclohexanecarbonyl)-1*H*-pyrrol-2-yl)acrylate (3sa)

Synthesis carried out according to the General Procedure, compound **3sa** was obtained in 71% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (d, *J* = 16.0 Hz, 1H), 7.28–7.27 (m, 1H), 6.70 (d, *J* = 4.0 Hz, 1H), 6.28 (t, *J* = 3.4 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.96–2.91 (m, 1H), 1.98–1.94 (m, 2H), 1.89–1.85 (m, 2H), 1.69–1.64 (m, 4H), 1.44–1.39 (m, 6H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.5, 167.1, 135.5, 132.1, 123.0, 117.3, 115.3, 112.5, 64.2, 44.1, 30.8, 29.6, 25.6, 25.5, 19.2, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{18}H_{25}NNaO_3$ $[M + Na]^+$: 326.1727, found 326.1730.



Butyl (*E*)-3-(1-(cyclopentanecarbonyl)-1*H*-pyrrol-2-yl)acrylate (3ta)

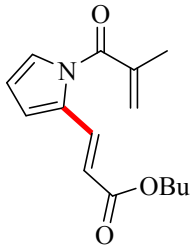
Synthesis carried out according to the General Procedure, compound **3ta** was obtained in 73% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (d, *J* = 16.0 Hz, 1H), 7.30–7.29 (m, 1H), 6.69 (d, *J* = 3.6 Hz, 1H), 6.27 (t, *J* = 3.4 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 4.17 (t, *J* = 6.8 Hz, 2H), 3.43–3.35 (m, 1H), 2.01–1.96 (m, 4H), 1.83–1.75 (m, 2H), 1.70–1.63 (m, 4H), 1.46–1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.5, 167.0, 135.5, 132.2, 123.3, 117.2, 115.2, 112.4, 64.2, 44.3, 30.8, 30.6, 26.1, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{17}H_{23}NNaO_3$ [M + Na]$^+$: 312.1570, found 312.1573.



Butyl (*E*)-3-(1-acetyl-1*H*-pyrrol-2-yl)acrylate (3ua)

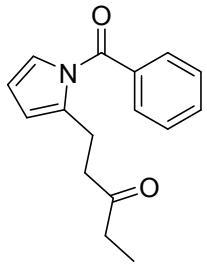
Synthesis carried out according to the General Procedure, compound **3ua** was obtained in 76% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, *J* = 16.0 Hz, 1H), 7.21–7.20 (m, 1H), 6.71 (d, *J* = 3.2 Hz, 1H), 6.28 (t, *J* = 3.4 Hz, 1H), 6.22 (d, *J* = 16.0

Hz, 1H), 4.18 (t, J = 6.8 Hz, 2H), 2.59 (s, 3H), 1.71–1.63 (m, 2H), 1.47–1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.2, 167.0, 135.1, 132.2, 123.8, 117.6, 115.4, 112.8, 64.3, 30.8, 24.2, 19.2, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{13}H_{17}NNaO_3$ $[M + Na]^+$: 258.1101, found 258.1103.



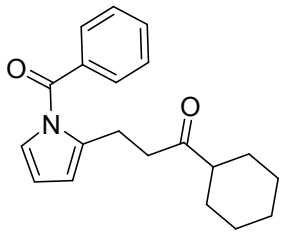
Butyl (*E*)-3-(1-methacryloyl-1*H*-pyrrol-2-yl)acrylate (3va)

Synthesis carried out according to the General Procedure, compound **3va** was obtained in 79% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04 (d, J = 16.0 Hz, 1H), 7.18–7.17 (m, 1H), 6.80 (d, J = 3.2 Hz, 1H), 6.25 (t, J = 3.4 Hz, 1H), 6.22 (d, J = 16.0 Hz, 1H), 5.80 (d, J = 1.6 Hz, 1H), 5.59 (s, 1H), 4.18 (t, J = 6.8 Hz, 2H), 2.12 (s, 3H), 1.71–1.63 (m, 2H), 1.47–1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.7, 167.0, 139.5, 134.2, 131.7, 125.9, 125.5, 116.7, 115.8, 111.8, 64.3, 30.8, 19.4, 19.2, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{15}H_{19}NNaO_3$ $[M + Na]^+$: 284.1257, found 284.1254.



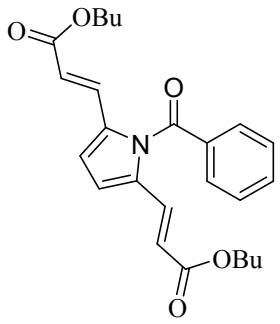
1-(1-benzoyl-1*H*-pyrrol-2-yl)pentan-3-one (4aq)

Synthesis carried out according to the General Procedure, compound **4aq** was obtained in 56% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 7.2 Hz, 2H) , 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 6.77 (t, *J* = 2.4 Hz, 1H), 6.11 (d, *J* = 2.8 Hz, 2H), 3.24 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.45 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 210.6, 169.3, 136.0, 134.3, 132.3, 129.7, 128.4, 123.4, 112.8, 110.6, 42.1, 35.9, 23.0, 7.8. HRMS (ESI) *m/z*: Calcd for $C_{16}H_{17}NNaO_2$ $[M + Na]^+$: 278.1151, found 278.1154.



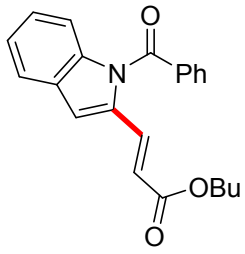
3-(1-benzoyl-1H-pyrrol-2-yl)-1-cyclohexylpropan-1-one (4ar)

Synthesis carried out according to the General Procedure, compound **4ar** was obtained in 51% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 6.8 Hz, 2H) , 7.59 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 6.77 (t, *J* = 2.6 Hz, 1H), 6.10 (d, *J* = 2.8 Hz, 2H), 3.21 (t, *J* = 7.4 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.39–2.32 (m, 1H), 1.85–1.75 (m, 4H), 1.38–1.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 213.1, 169.3, 136.2, 134.3, 132.3, 129.7, 128.4, 123.4, 112.8, 110.5, 50.8, 40.4, 28.4, 25.8, 25.7, 22.9. HRMS (ESI) *m/z*: Calcd for $C_{20}H_{23}NNaO_2$ $[M + Na]^+$: 332.1621, found 332.1616.



Dibutyl 3,3'-(1-benzoyl-1*H*-pyrrole-2,5-diyl)(2*E*,2'*E*)-diacrylate (6aa)

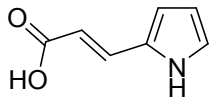
Synthesis carried out according to the General Procedure, compound **6aa** was obtained in 61% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70–7.65 (m, 3H), 7.49 (t, *J* = 7.8 Hz, 2H) , 7.27 (d, *J* = 16.0 Hz, 2H), 6.82 (s, 2H), 6.18 (d, *J* = 16.0 Hz, 2H), 4.08 (t, *J* = 6.6 Hz, 4H), 1.61–1.54 (m, 4H), 1.37–1.28 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.2, 166.5, 135.0, 134.0, 133.6, 132.0, 130.8, 129.1, 117.4, 114.0, 64.3, 30.6, 19.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_{25}H_{29}NNaO_5$ $[M + Na]^+$: 446.1938, found 446.1932.



Butyl (*E*)-3-(1-benzoyl-1*H*-indol-2-yl)acrylate (8aa)

Synthesis carried out according to the General Procedure, compound **8aa** was obtained in 80% yield as a colorless oil after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, *J* = 7.6 Hz, 2H), 7.67–7.60 (m, 2H), 7.52–7.47 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26–7.18 (m, 2H),

7.10 (s, 1H), 6.33 (d, J = 16.0 Hz, 1H), 4.12 (t, J = 6.8 Hz, 2H), 1.64–1.57 (m, 2H), 1.41–1.31 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.2, 166.2, 138.2, 136.1, 134.8, 134.3, 133.4, 130.1, 128.9, 128.7, 125.4, 123.4, 121.3, 119.0, 114.6, 110.7, 64.4, 30.6, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{22}H_{21}NNaO_3$ $[M+Na]^+$: 370.1414, found: 370.1410.



(*E*)-3-(1*H*-pyrrol-2-yl)acrylic acid (9)

Synthesis carried out according to the General Procedure, compound **9** was obtained in 90% yield as a white solid after purification by a silica gel column chromatography. ^{1}H NMR (400 MHz, DMSO) δ (ppm): 11.93 (br, 1H), 11.46 (s, 1H), 7.37 (d, J = 16.0 Hz, 1H), 6.99 (d, J = 1.2 Hz, 1H), 6.51 (s, 1H), 6.15–6.13 (m, 1H), 6.10 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ (ppm): 168.2, 134.3, 128.0, 123.0, 114.2, 111.3, 109.8. HRMS (ESI) m/z: calcd for $C_7H_7NNaO_2$ $[M+Na]^+$: 160.0369, found: 160.0366.

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5. X-ray Crystallographic Data for 3ai

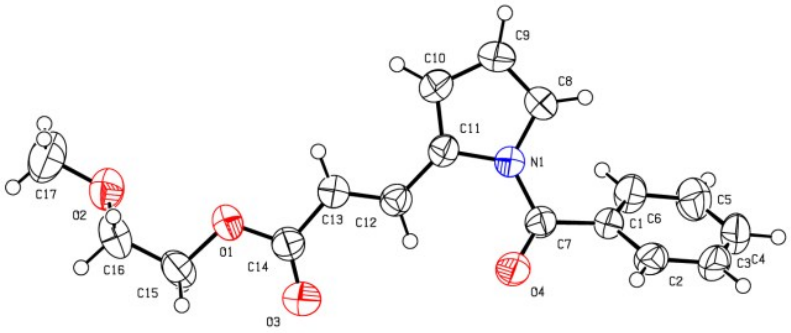


Figure S1. *X*-Ray crystal structure of **3ai**

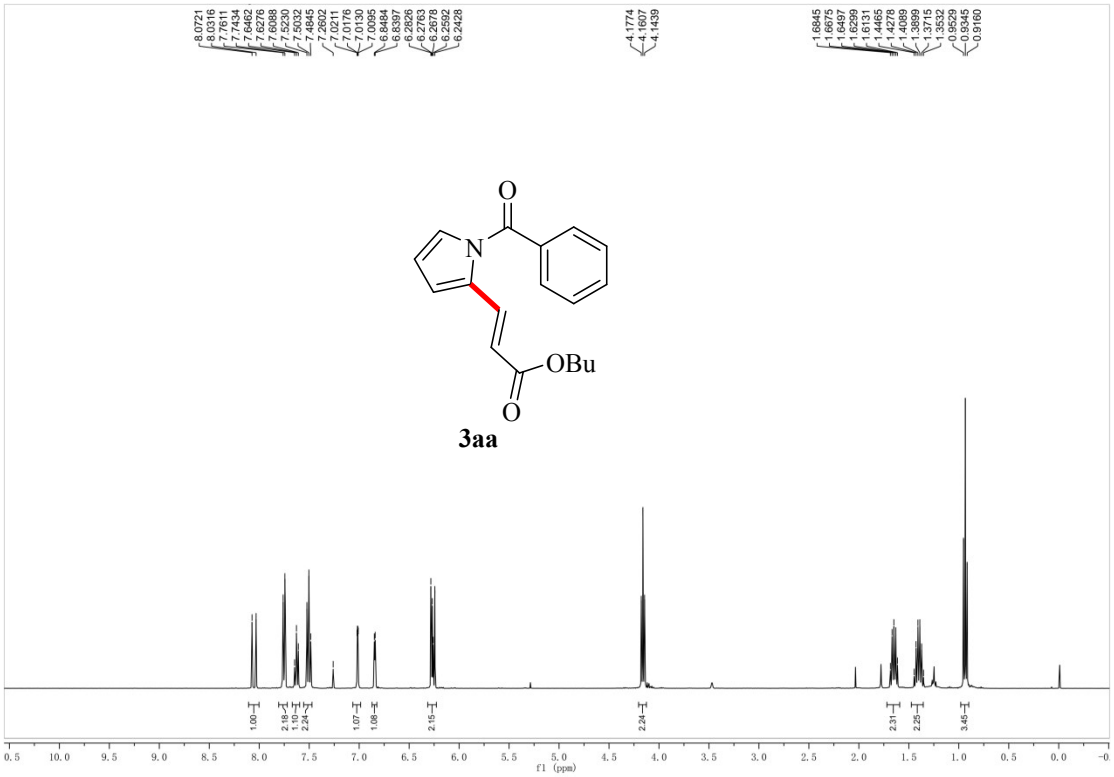
Table 1. Crystal Data and Structure Refinement for **3ai**

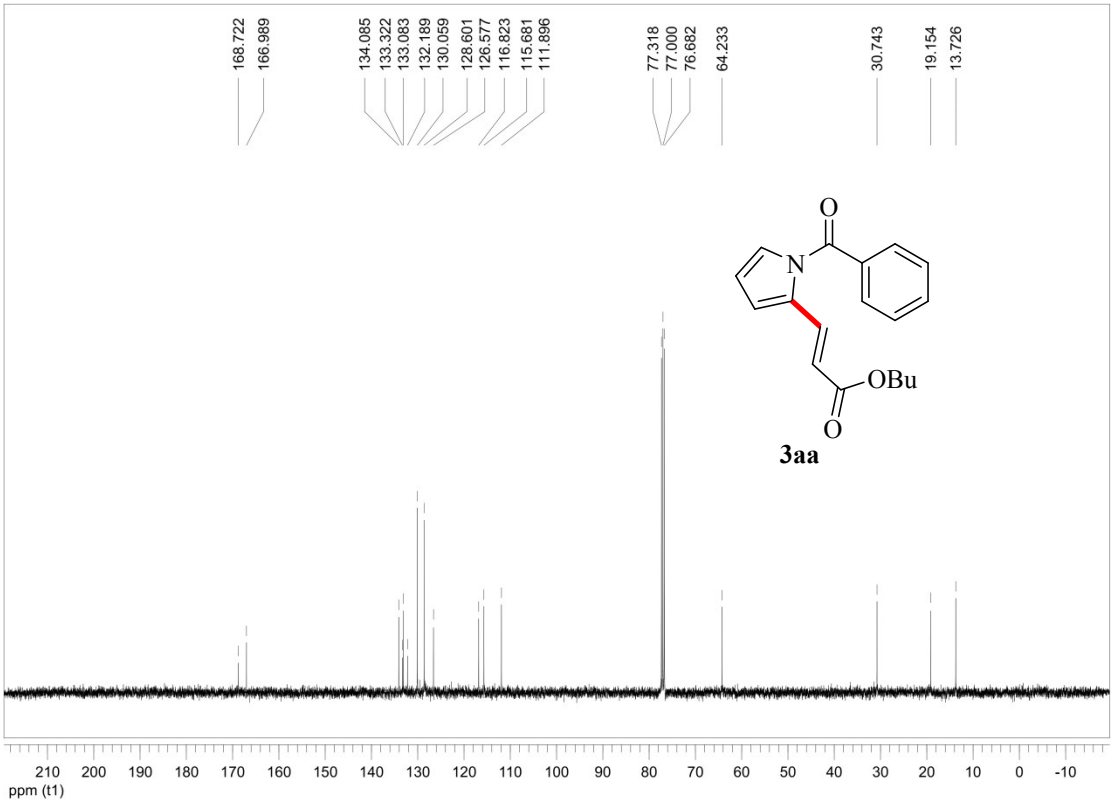
CCDC number	1915043
Empirical formula	C17 H17 N1 O4
Formula weight	299.31
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1 (14)
Unit cell dimensions	a= 10.2856(5) Å α= 90°. b= 13.4694(6) Å β= 90.662(4)°. c= 11.2174(5) Å γ= 90°.
Volume	1553.98(12) $Å^3$
Z	4
Density (calculated)	1.279 mg/m^3
Absorption coefficient	0.754 mm^{-1}
F(000)	632.0
Theta range for data collection	10.262 to 134.16°
Index ranges	$-12 \leq h \leq 9$, $-14 \leq k \leq 16$, $-13 \leq l \leq 11$

Reflections collected	5677
Independent reflections	2779 [R_{int} = 0.0163, R_{sigma} = 0.0193]
Max. and min. transmission	1.000 and 0.734
Data / restraints / parameters	2779/0/201
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.1066
R indices (all data)	R1 = 0.0478, wR2 = 0.1170
Largest diff. peak and hole	0.17 and -0.15 e $Å^{-3}$

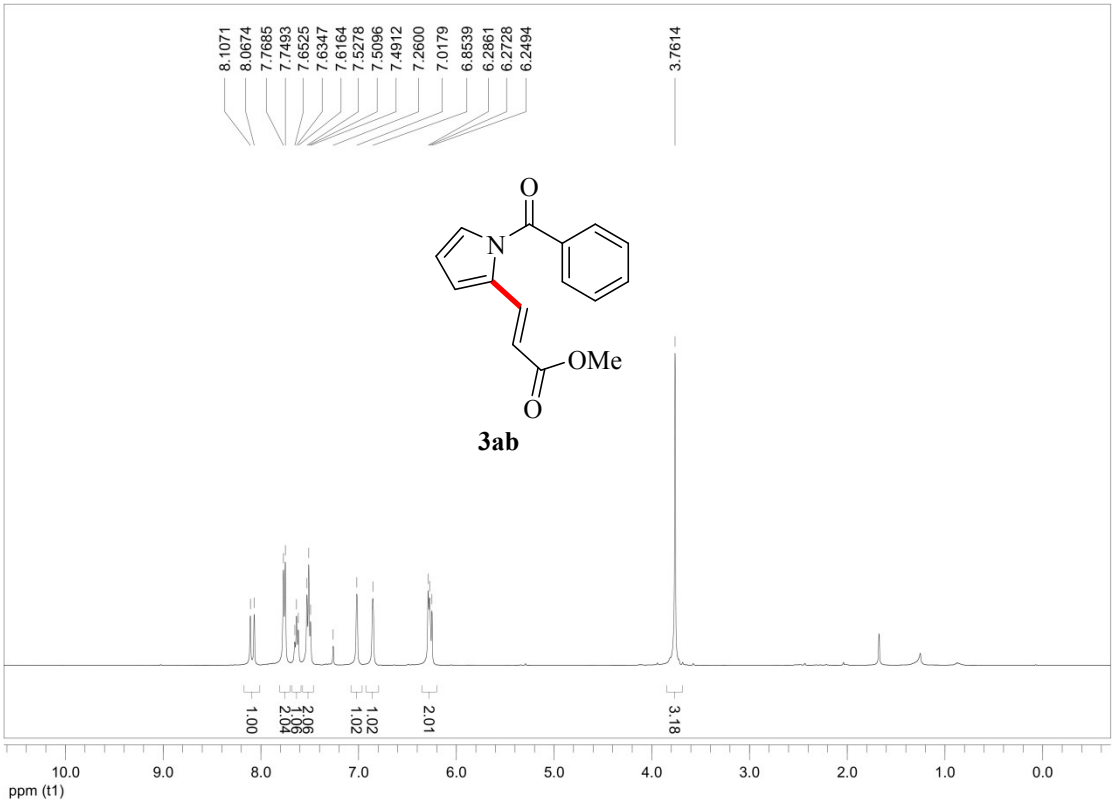
6. NMR Spectra for Products

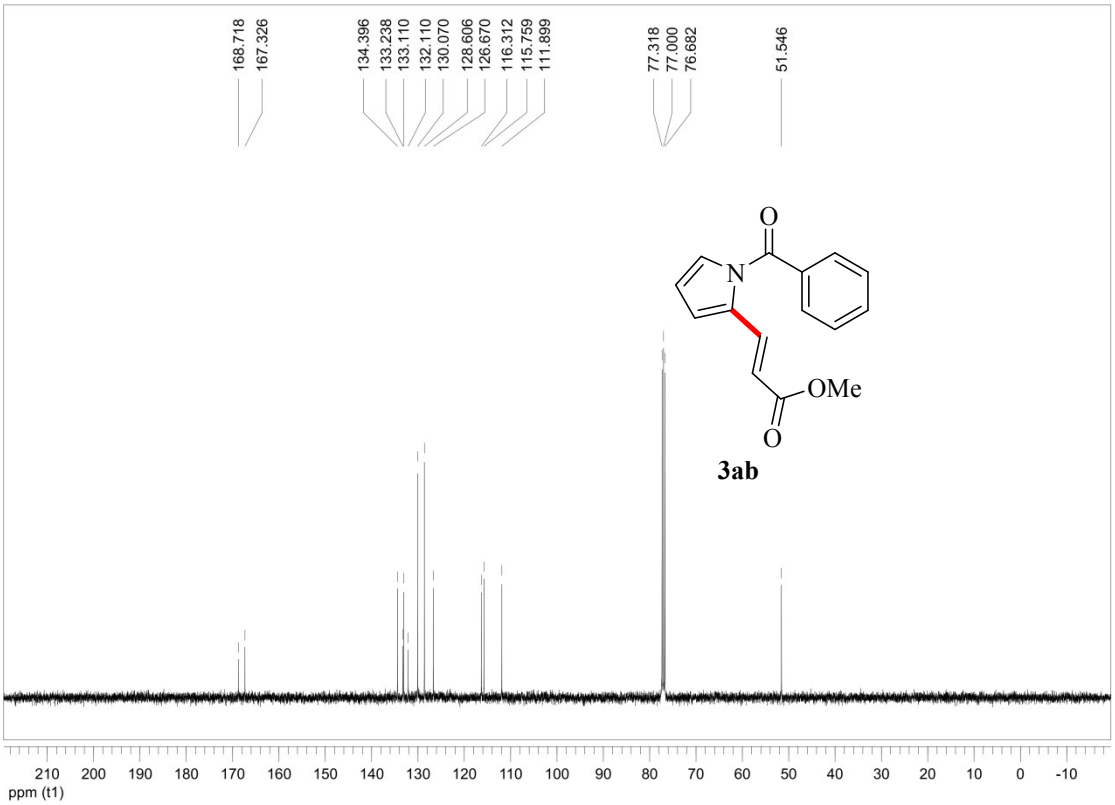
Butyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3aa)



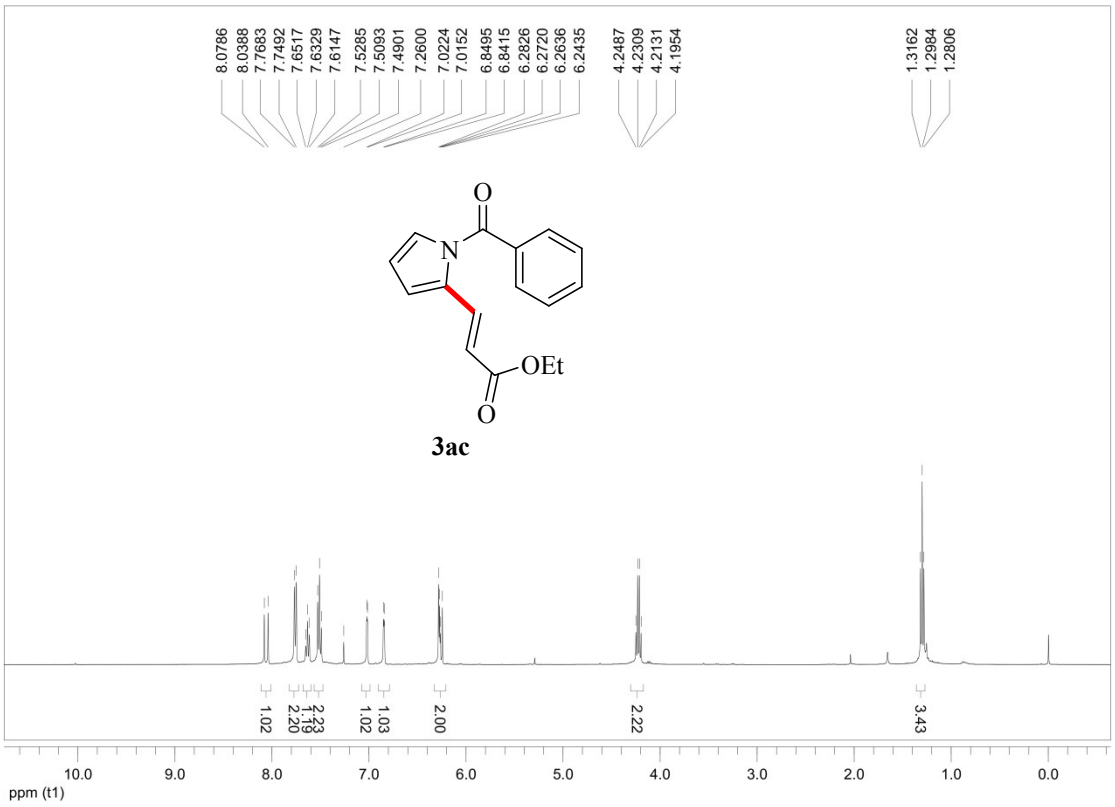


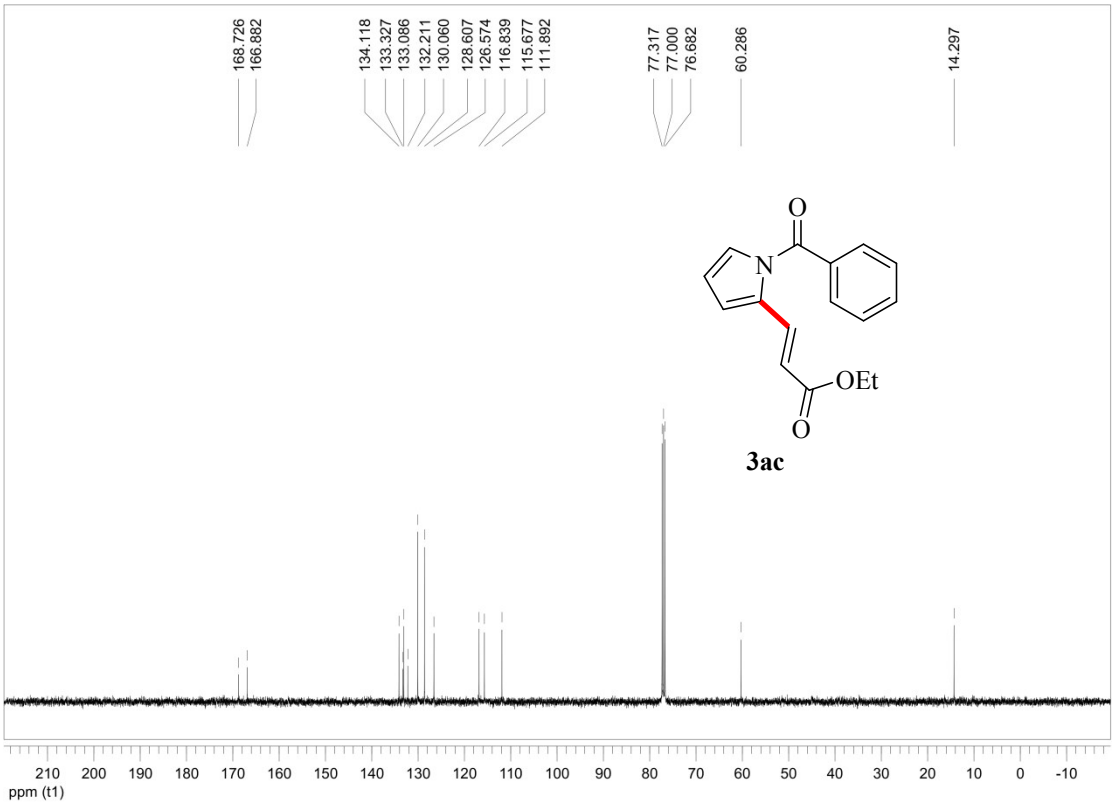
Methyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ab)



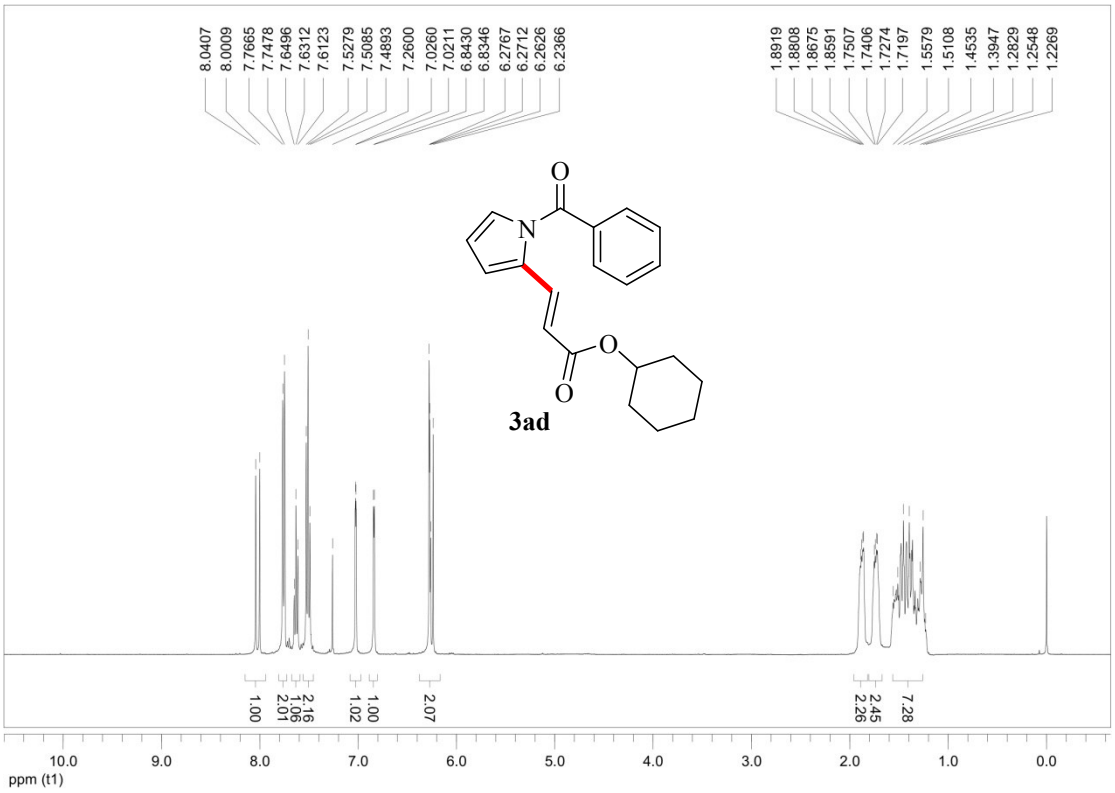


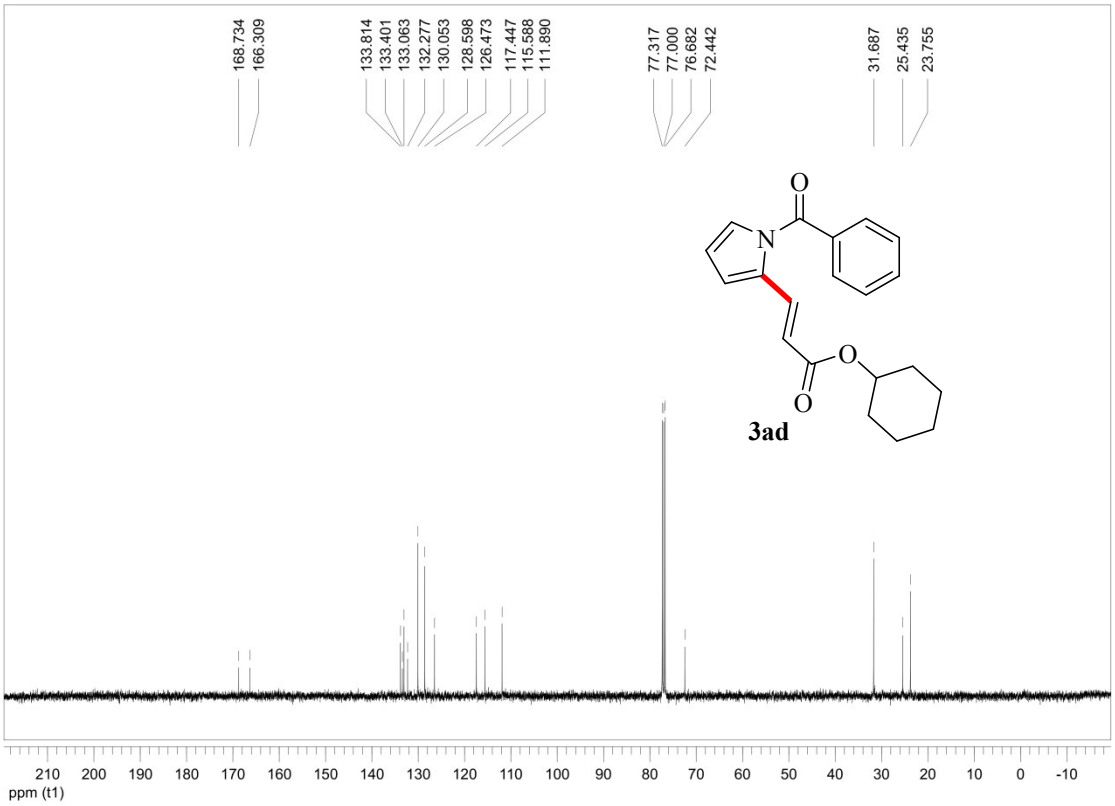
Ethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ac)



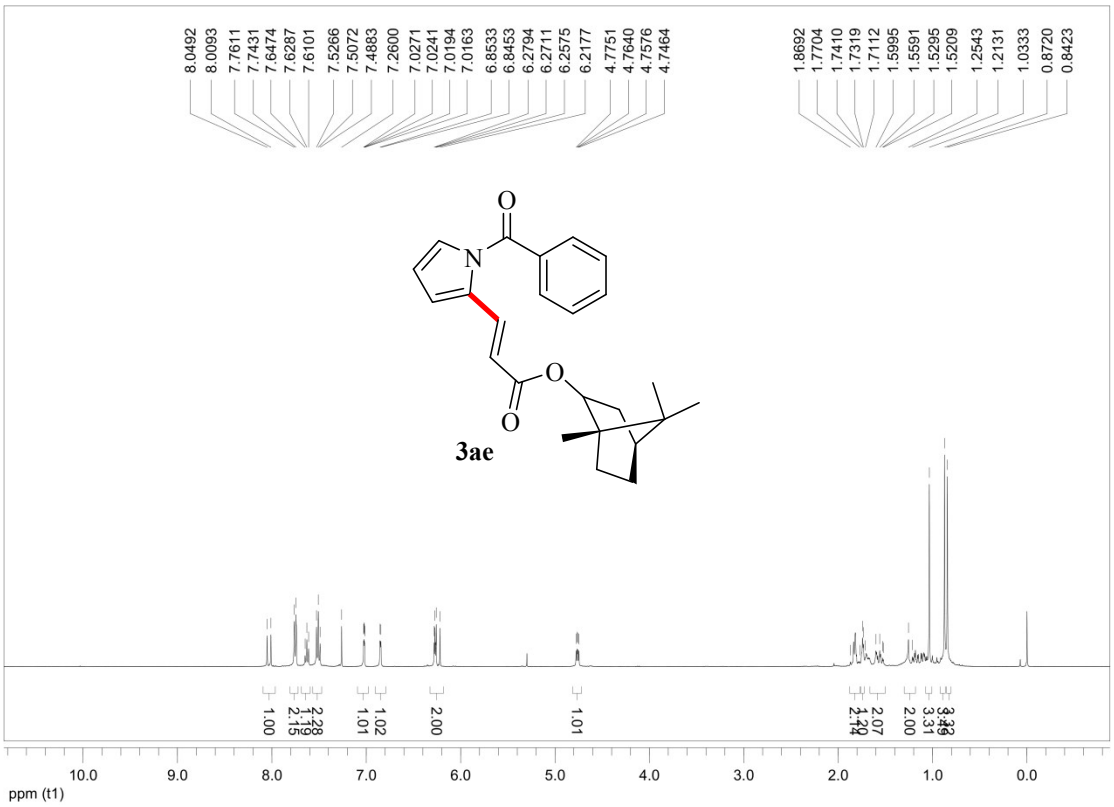


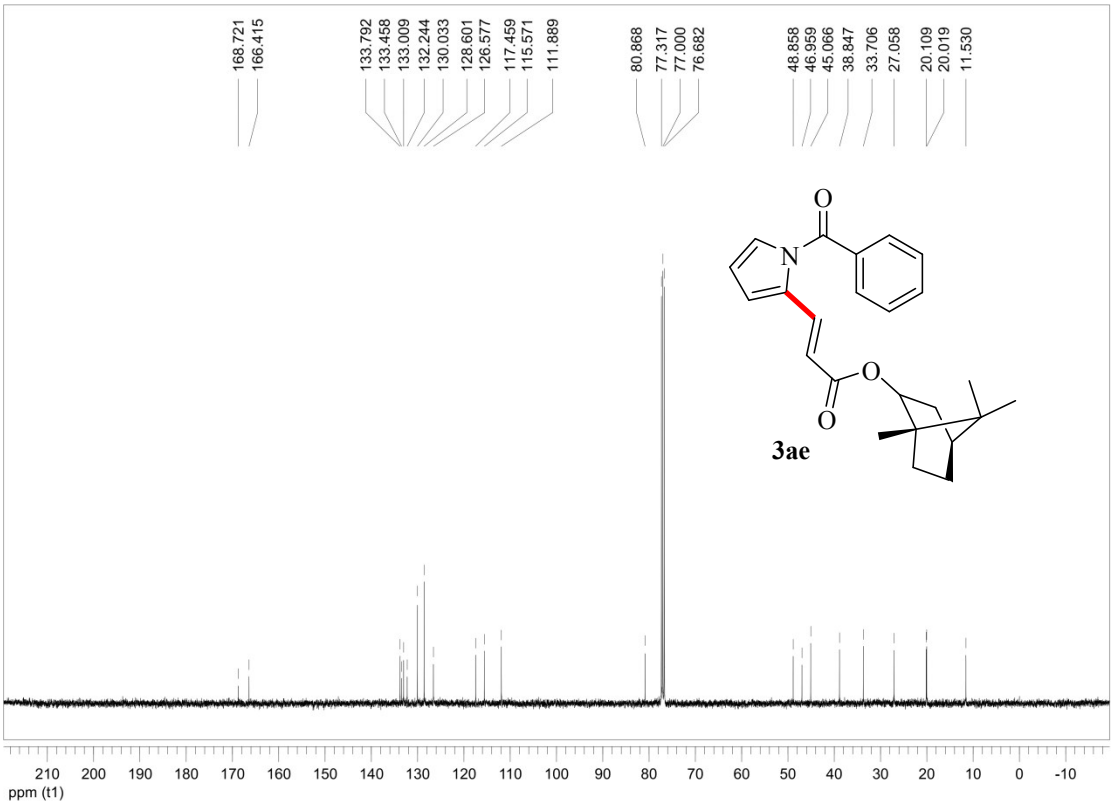
Cyclohexyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ad)



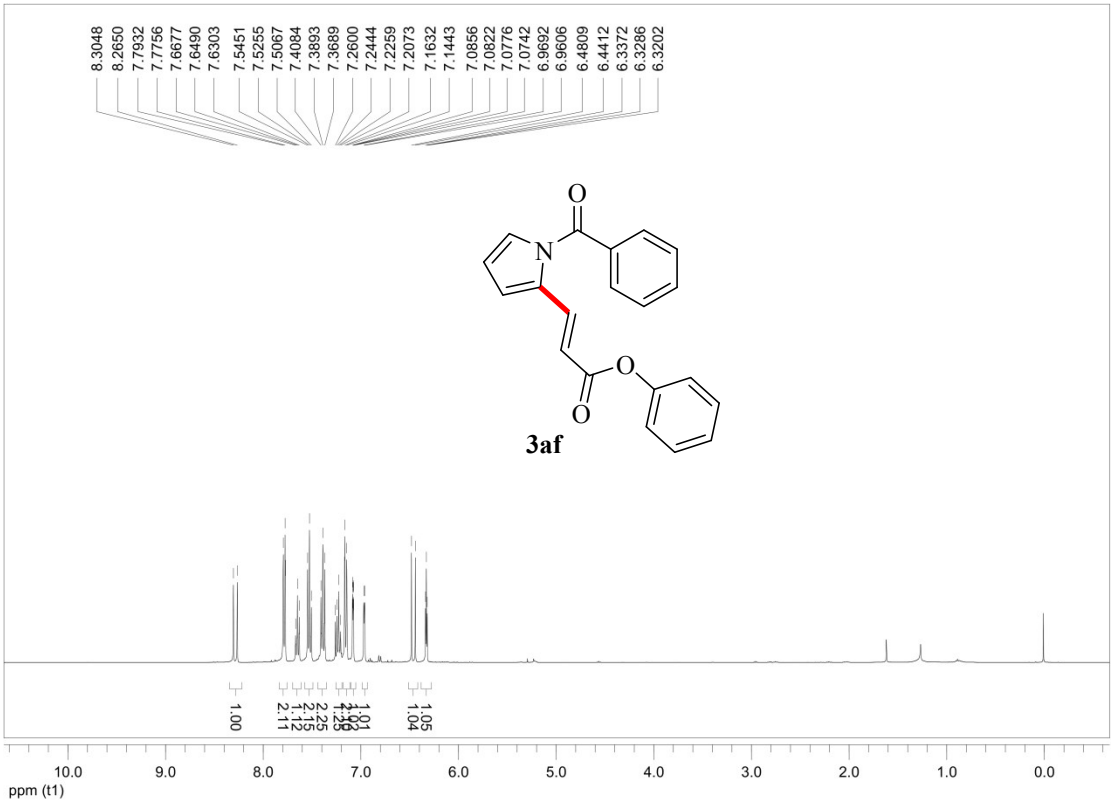


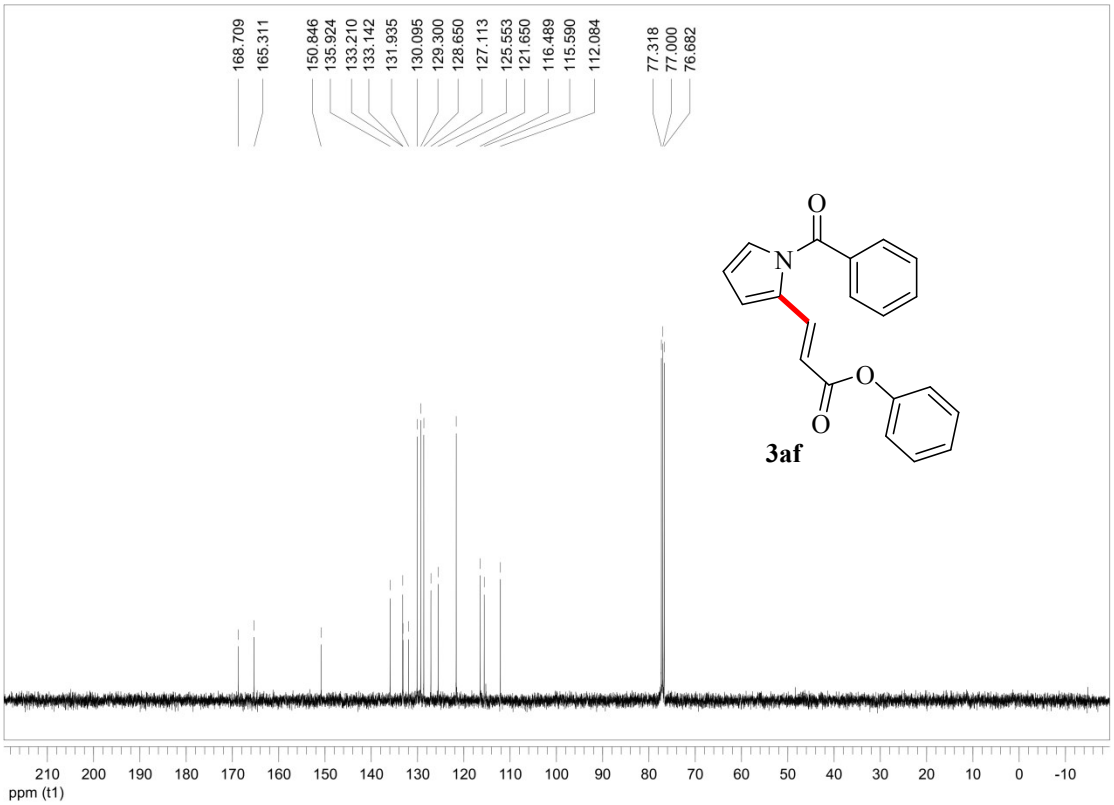
(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl(*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylae (3ae)



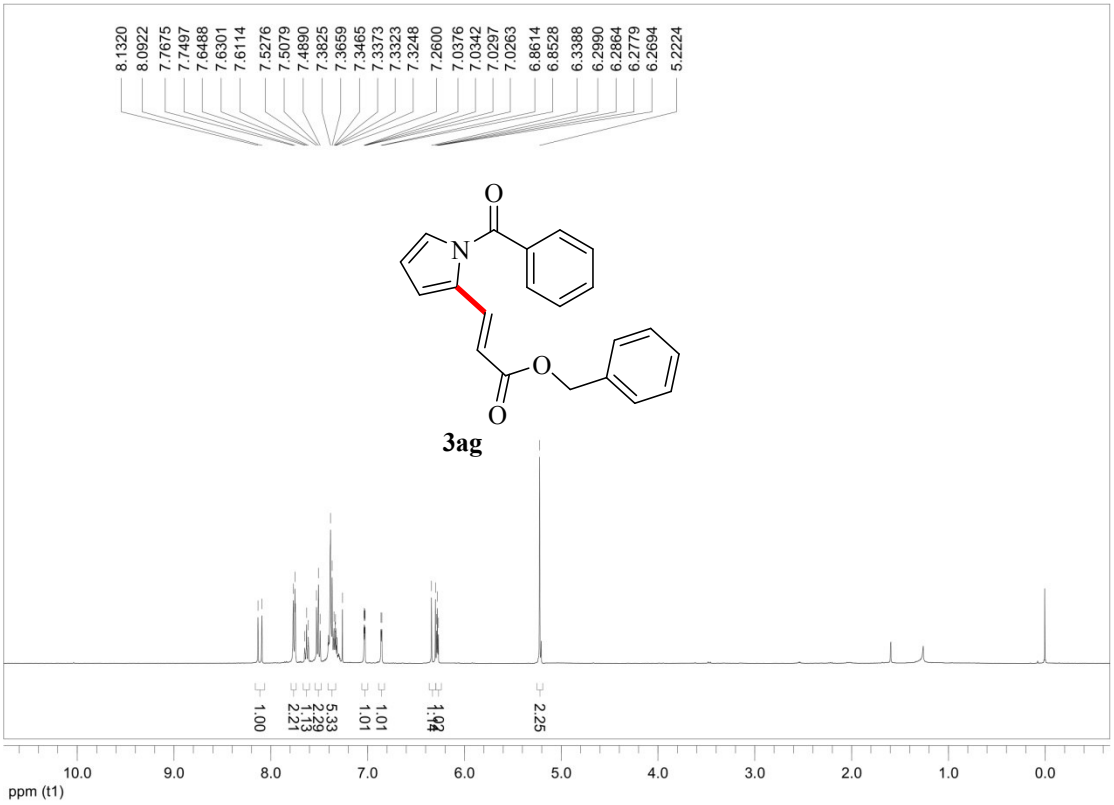


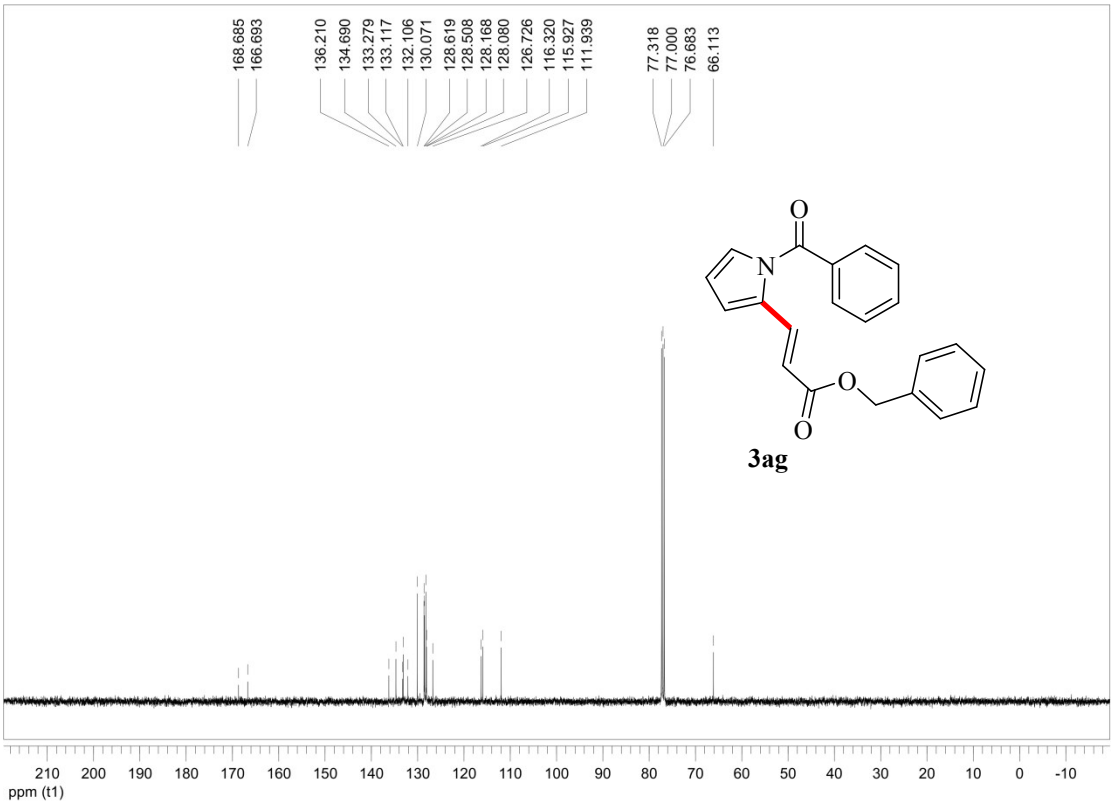
Phenyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3af)



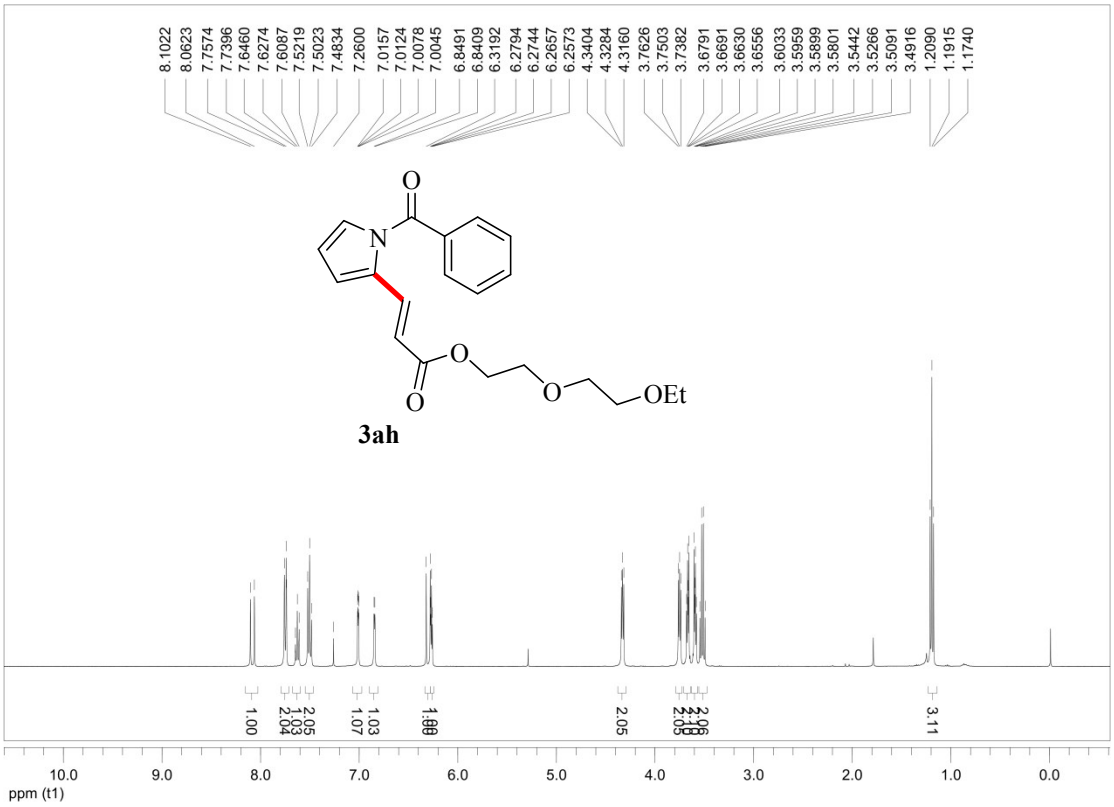


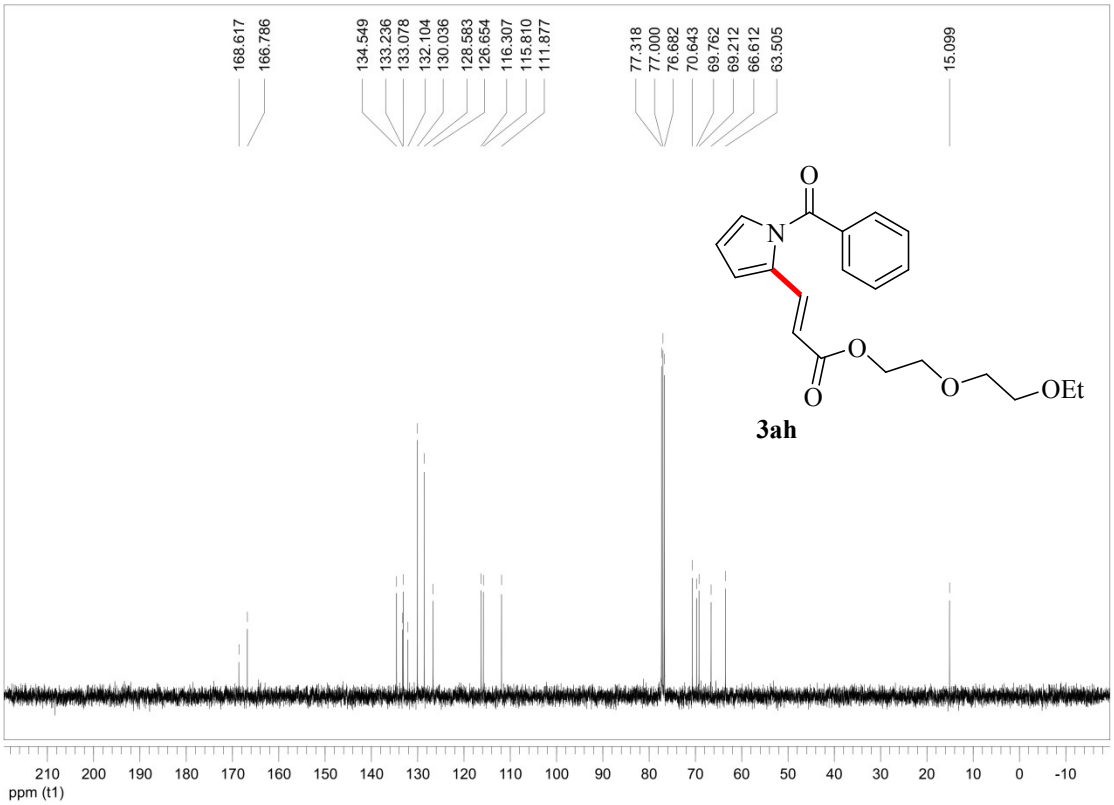
Benzyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ag)



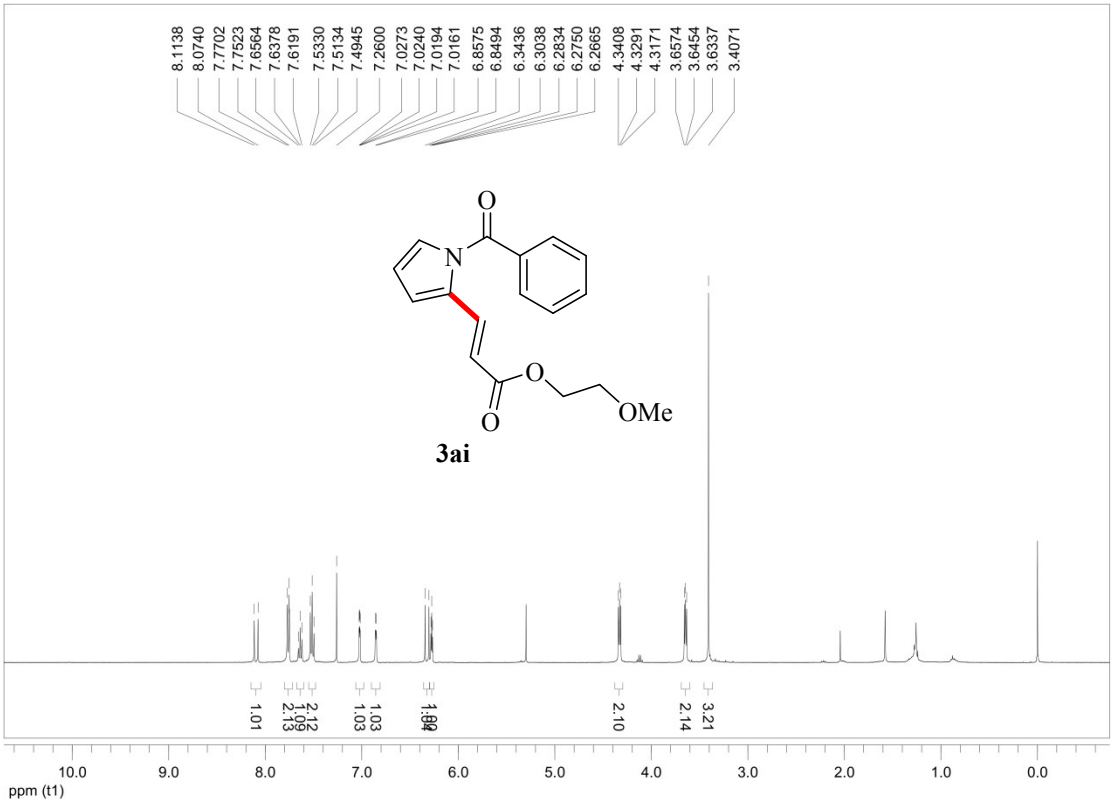


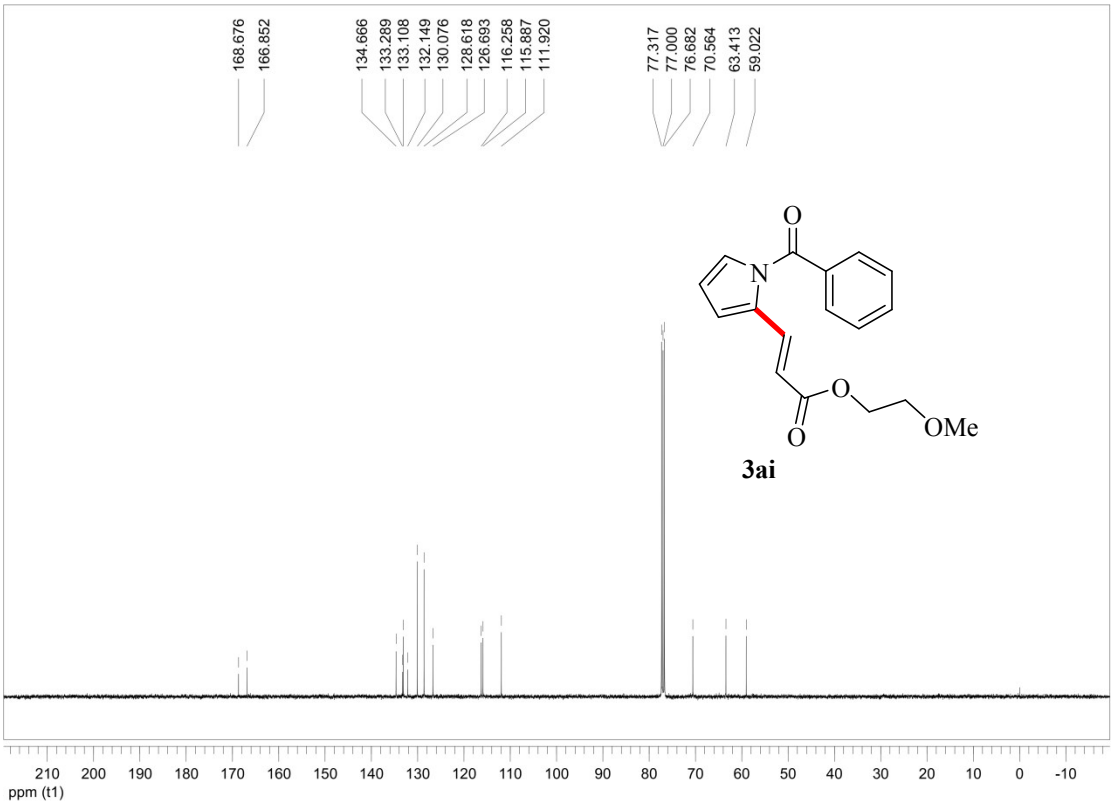
2-(2-Ethoxyethoxy)ethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ah)



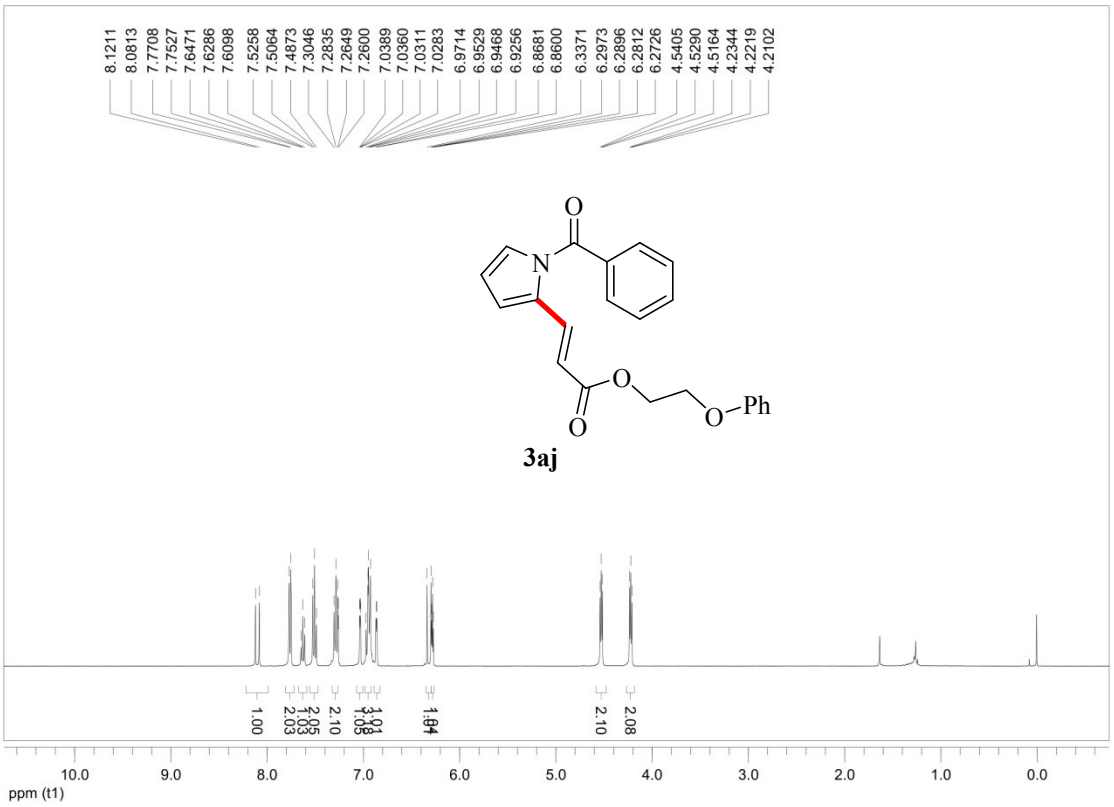


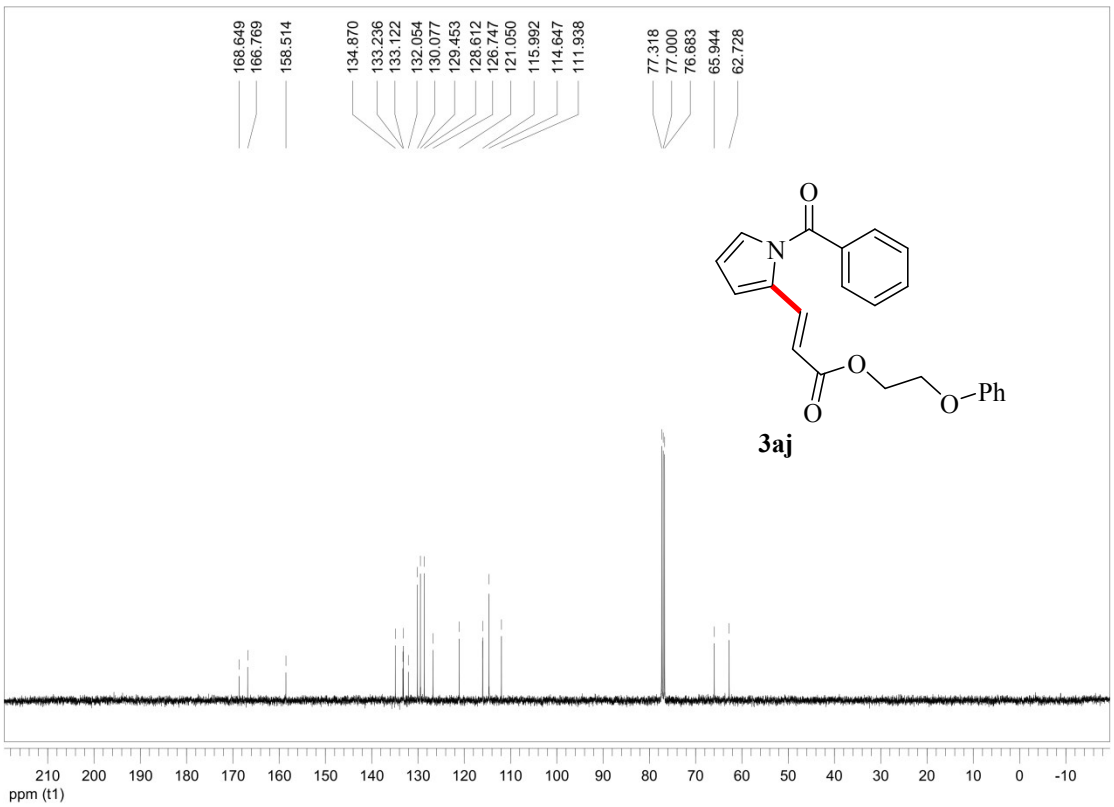
2-Methoxyethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ai)



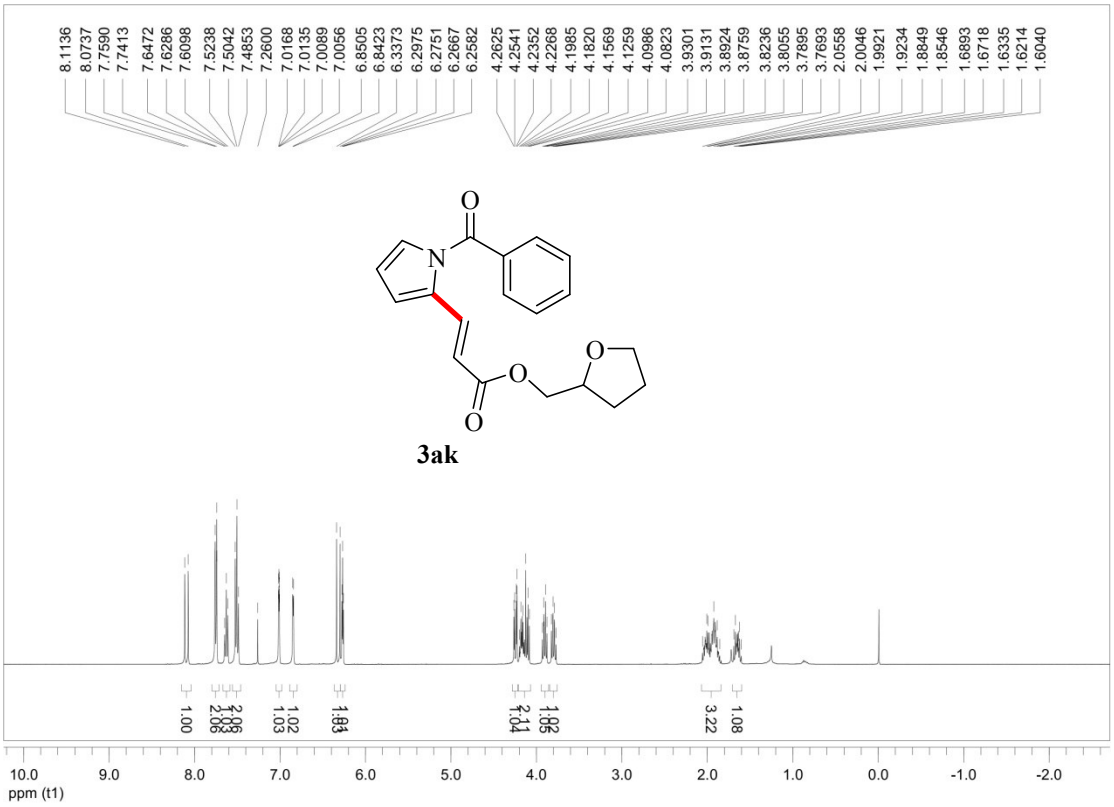


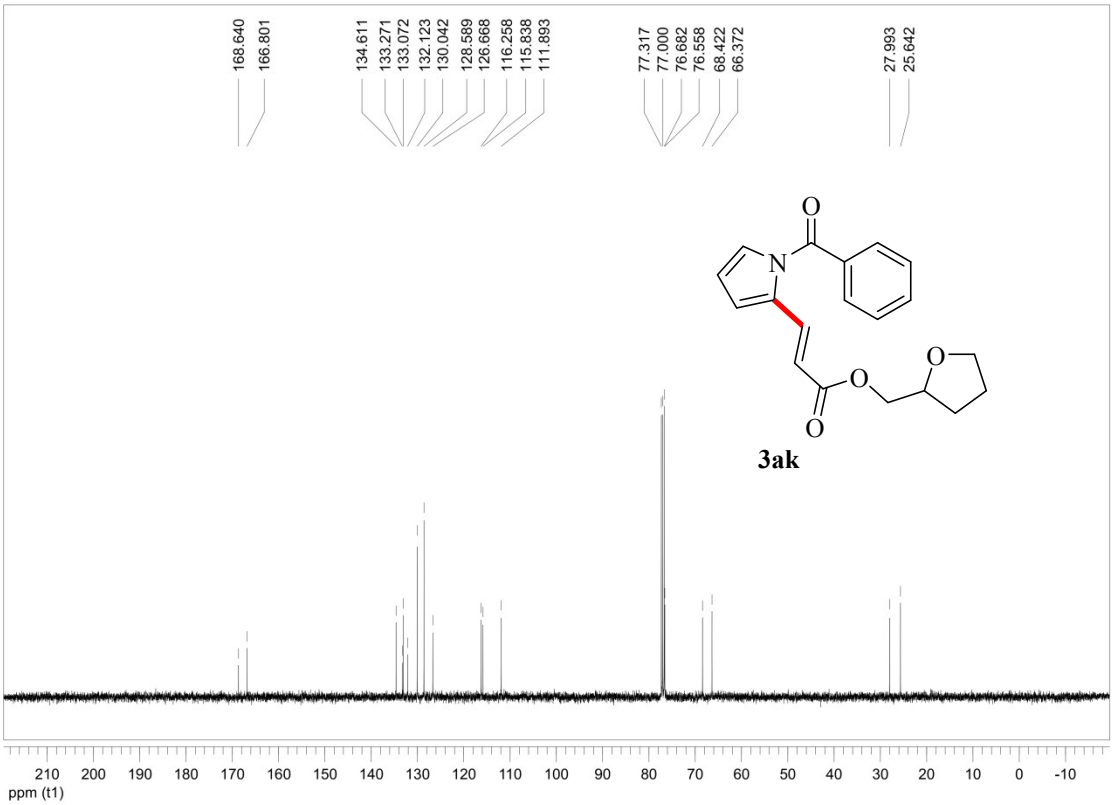
2-Phenoxyethyl *(E)*-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3aj)



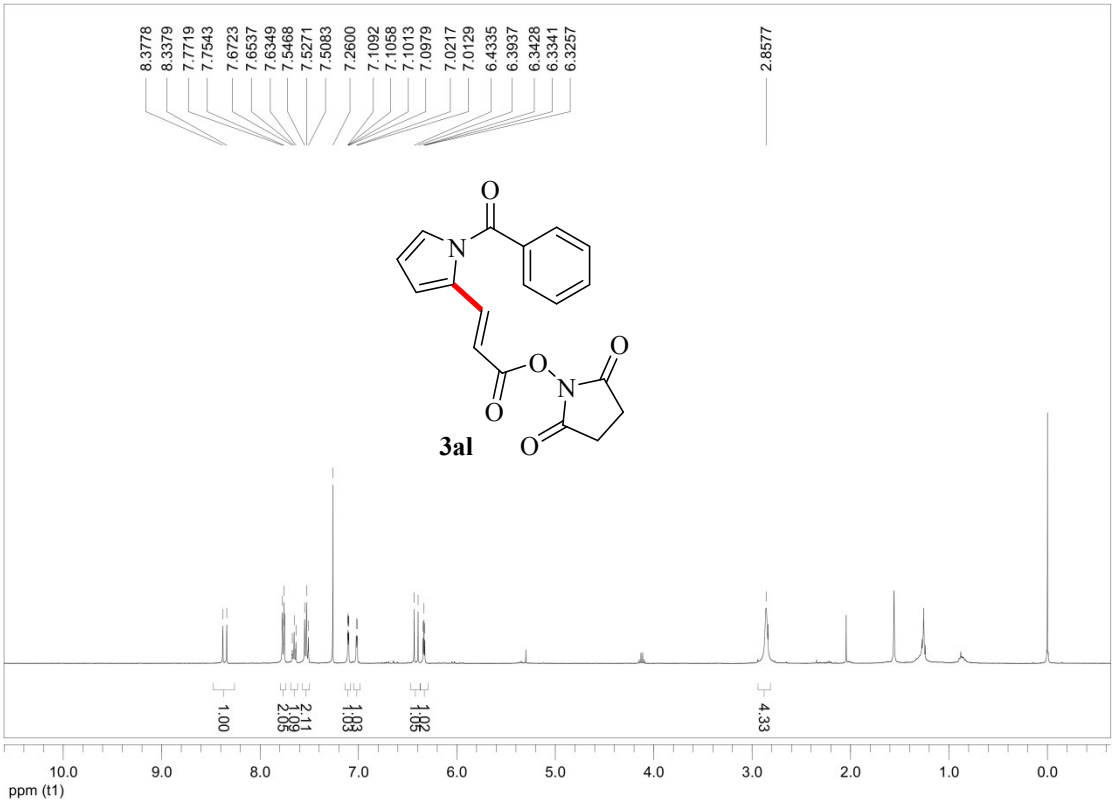


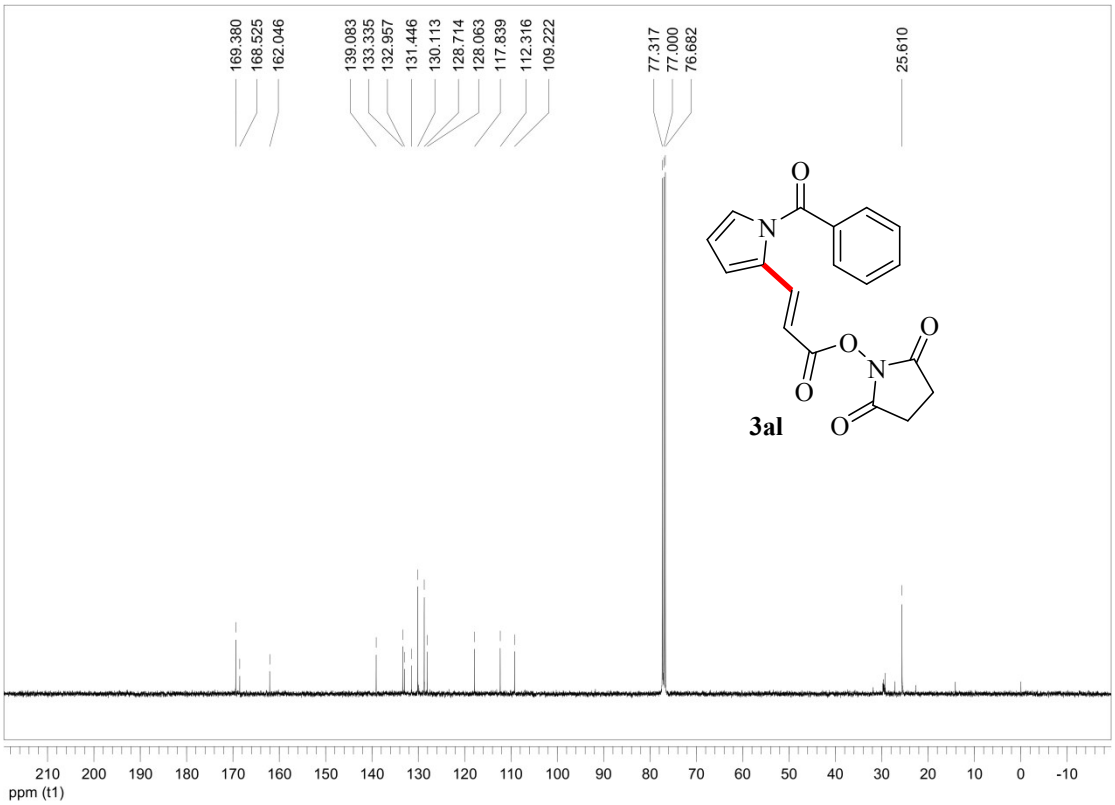
(Tetrahydrofuran-2-yl)methyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ak)



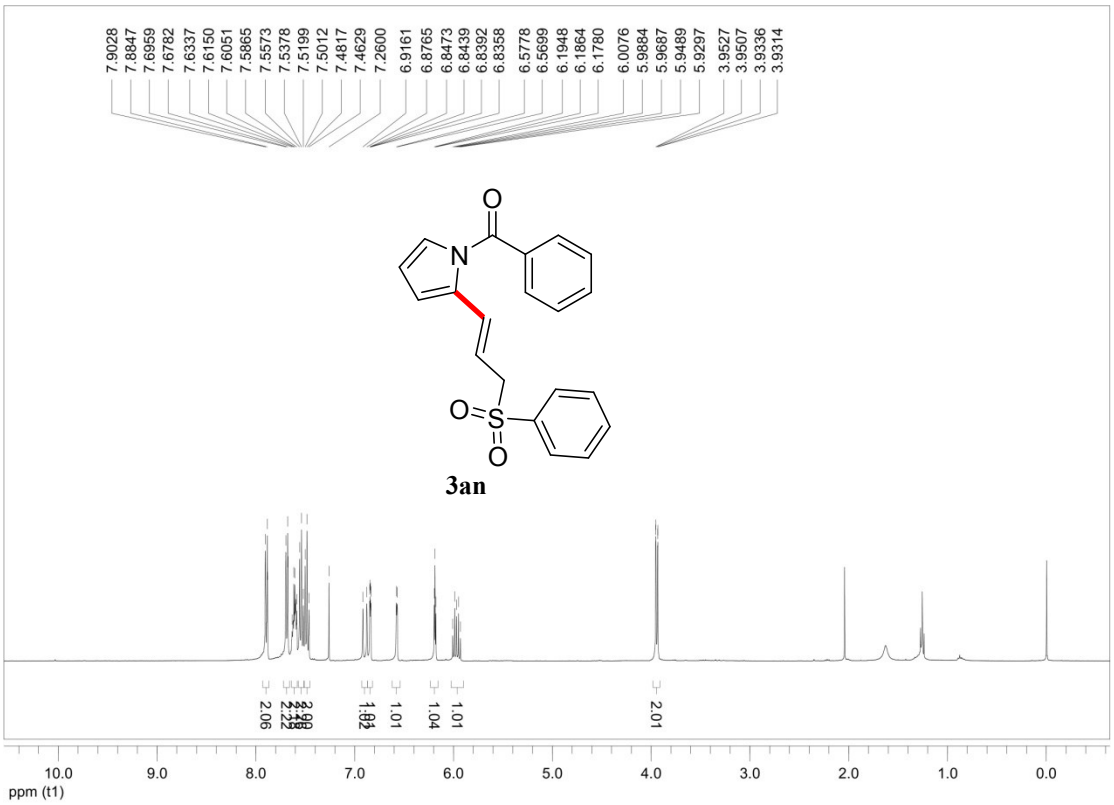


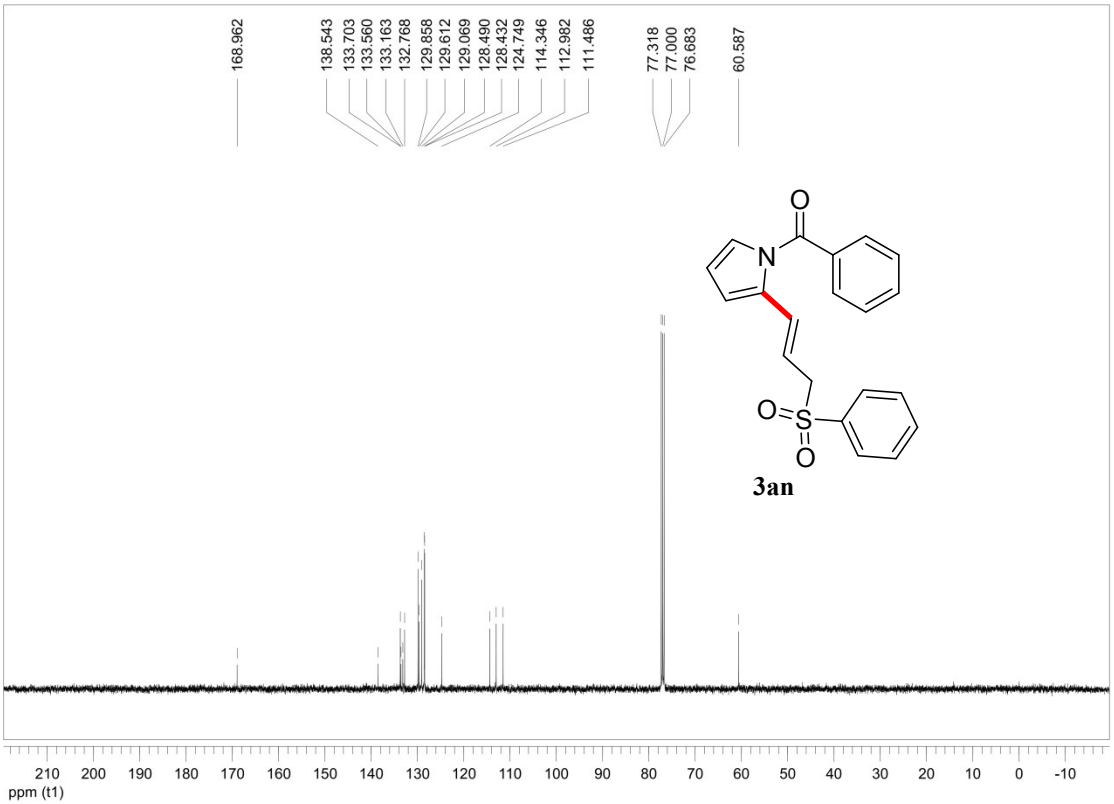
2,5-Dioxopyrrolidin-1-yl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3al)



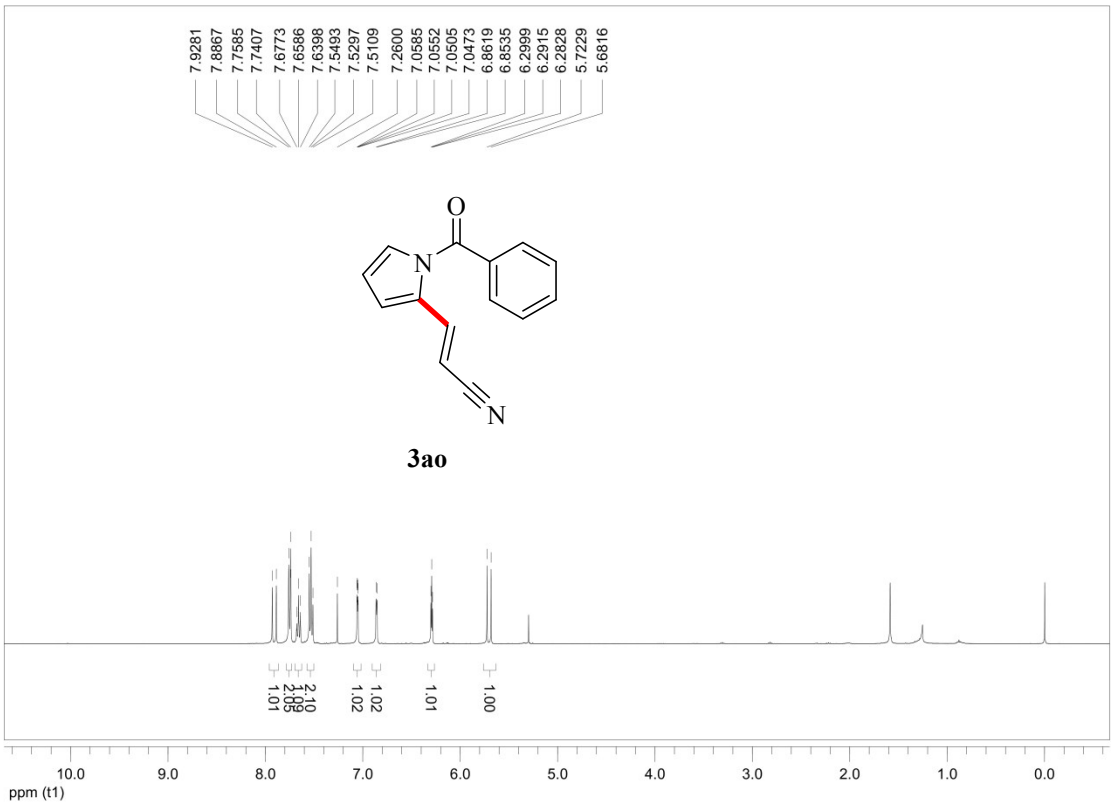


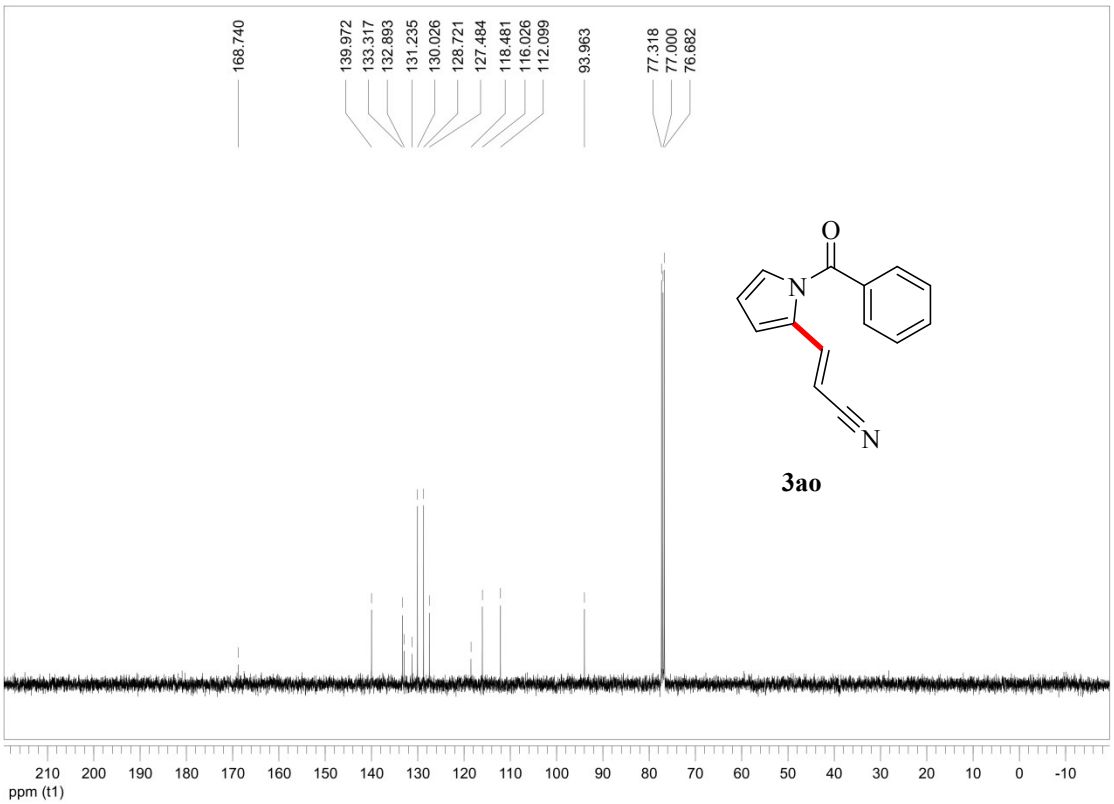
(*E*)-phenyl(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-1*H*-pyrrol-1-yl)methanone (3an)



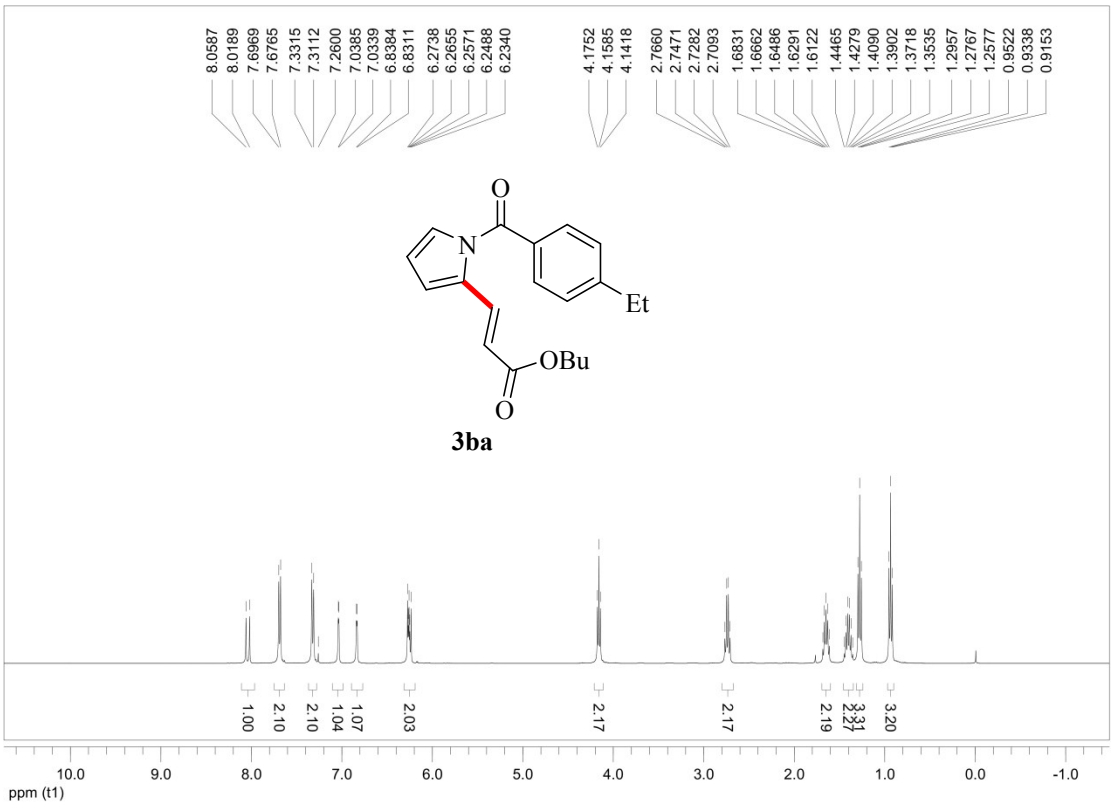


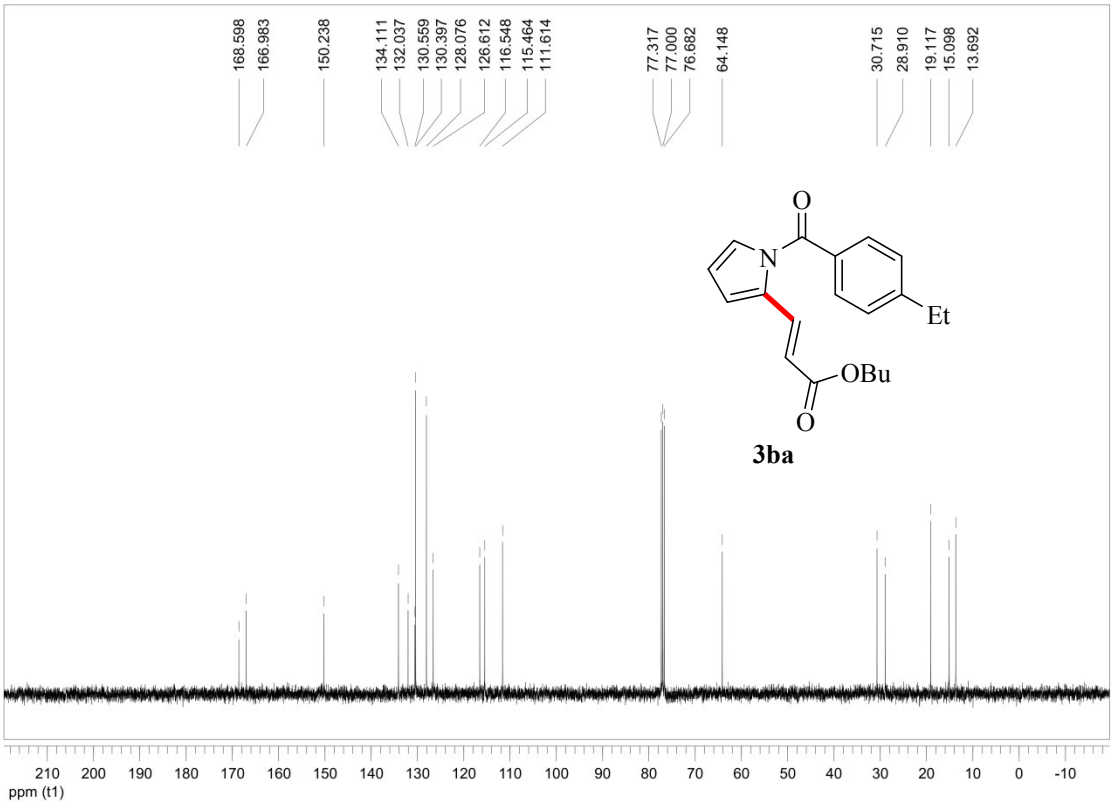
(*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylonitrile (3ao)



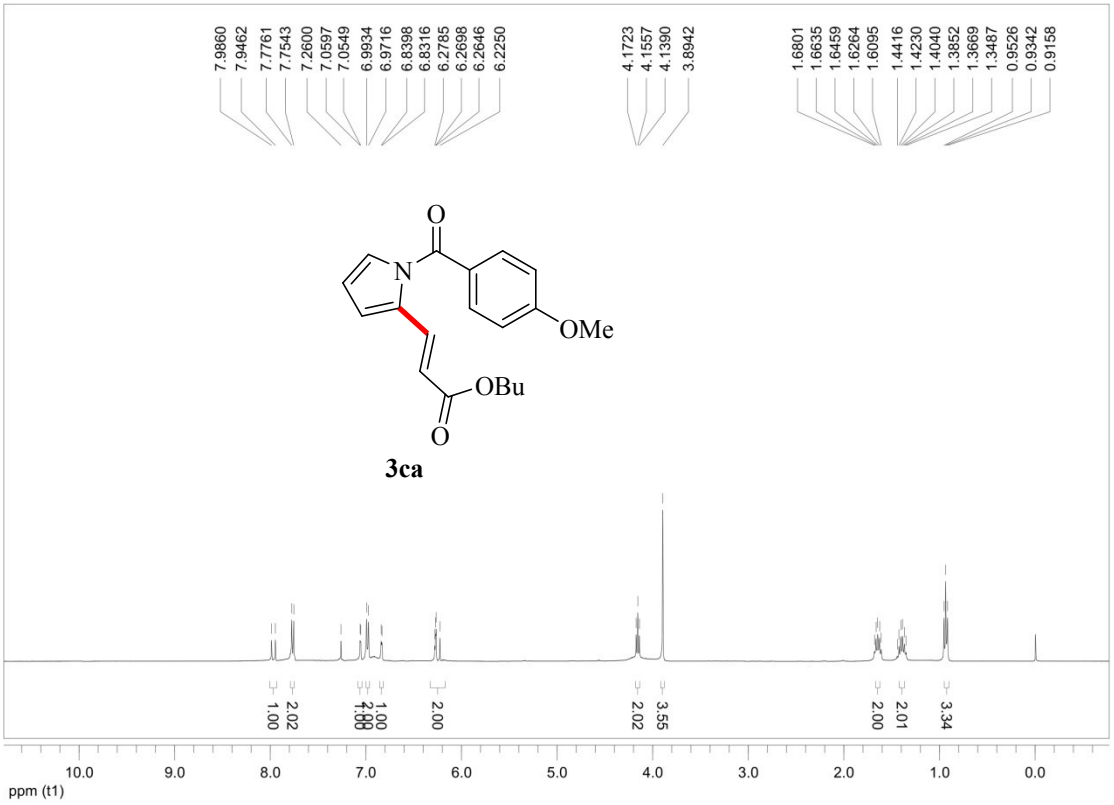


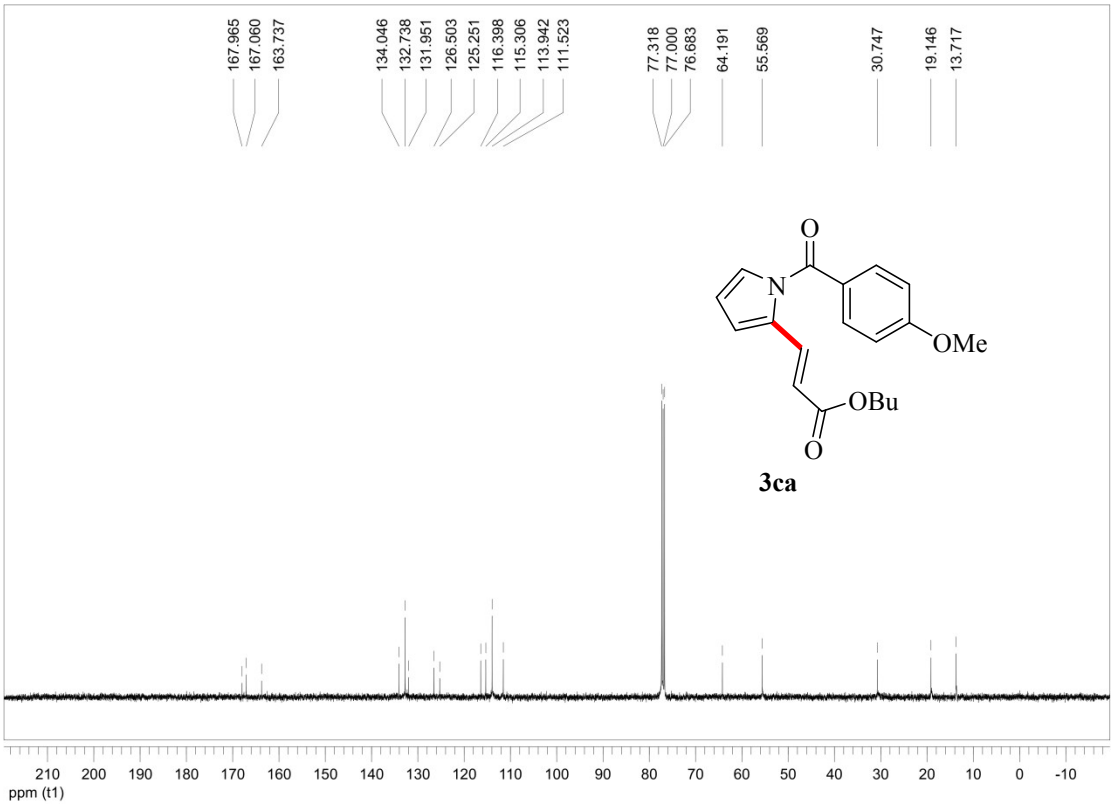
Butyl (*E*)-3-(1-(4-ethylbenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ba)



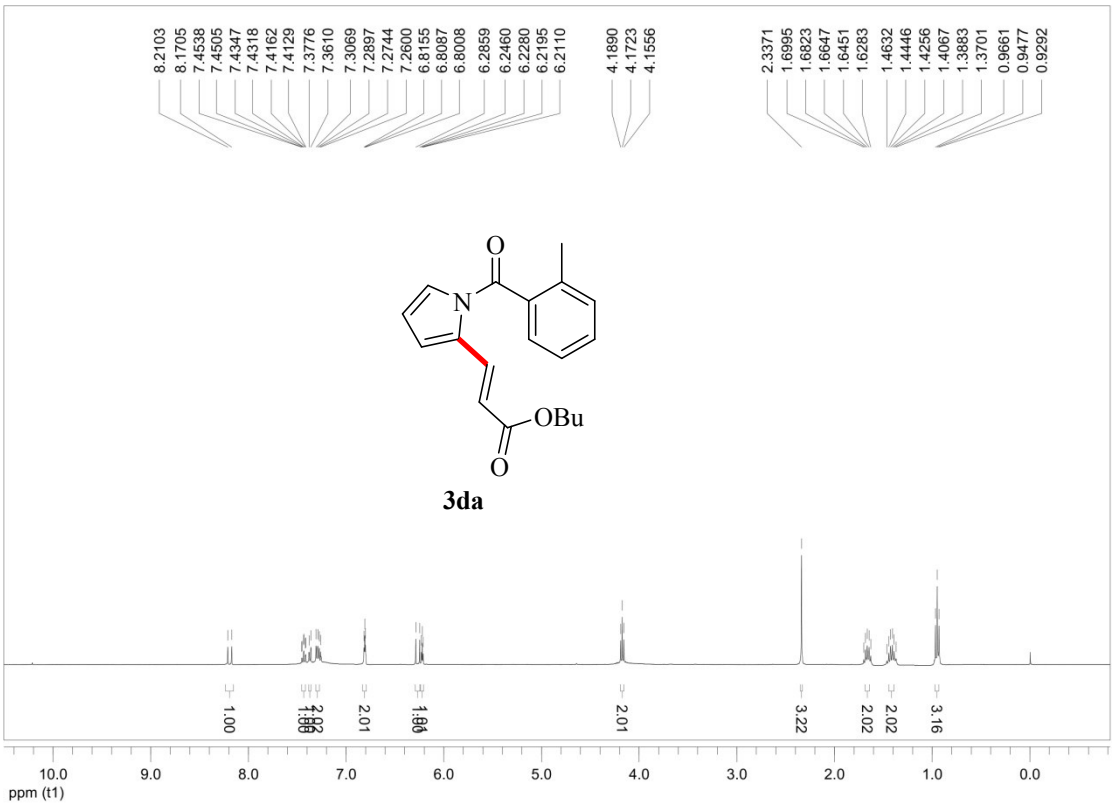


Butyl (*E*)-3-(1-(4-methoxybenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ca)

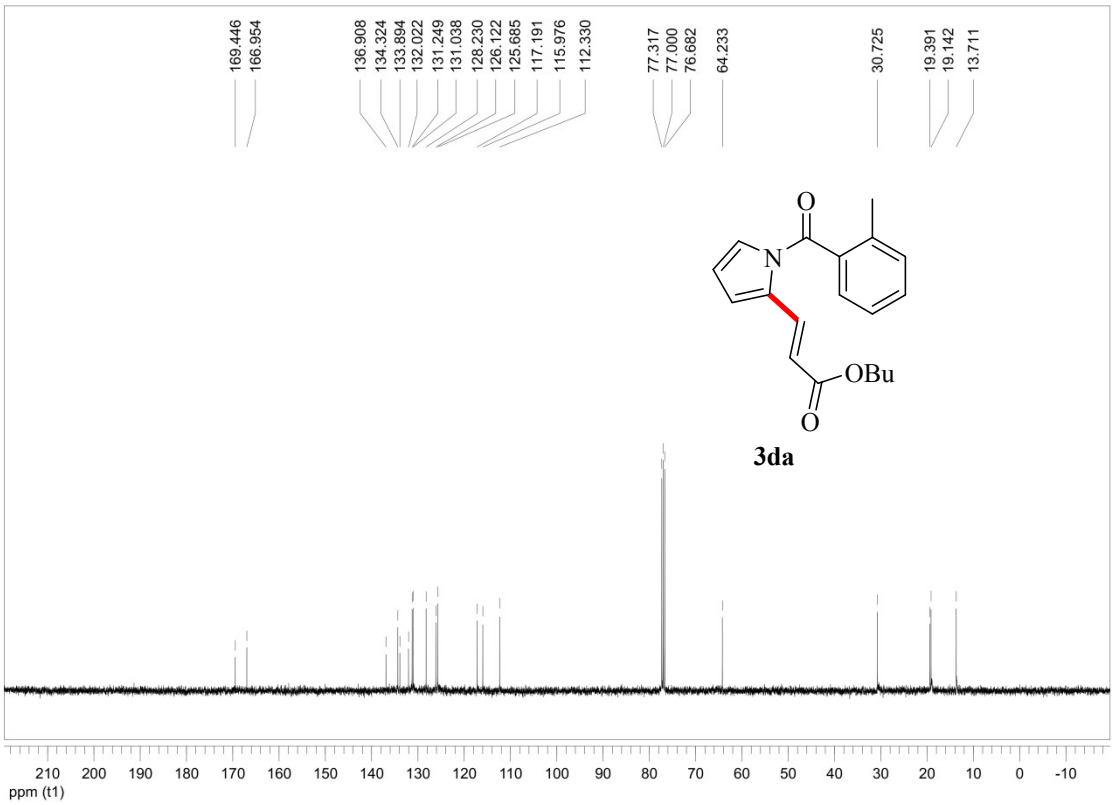




Butyl (*E*)-3-(1-(2-methylbenzoyl)-1*H*-pyrrol-2-yl)acrylate (3da)

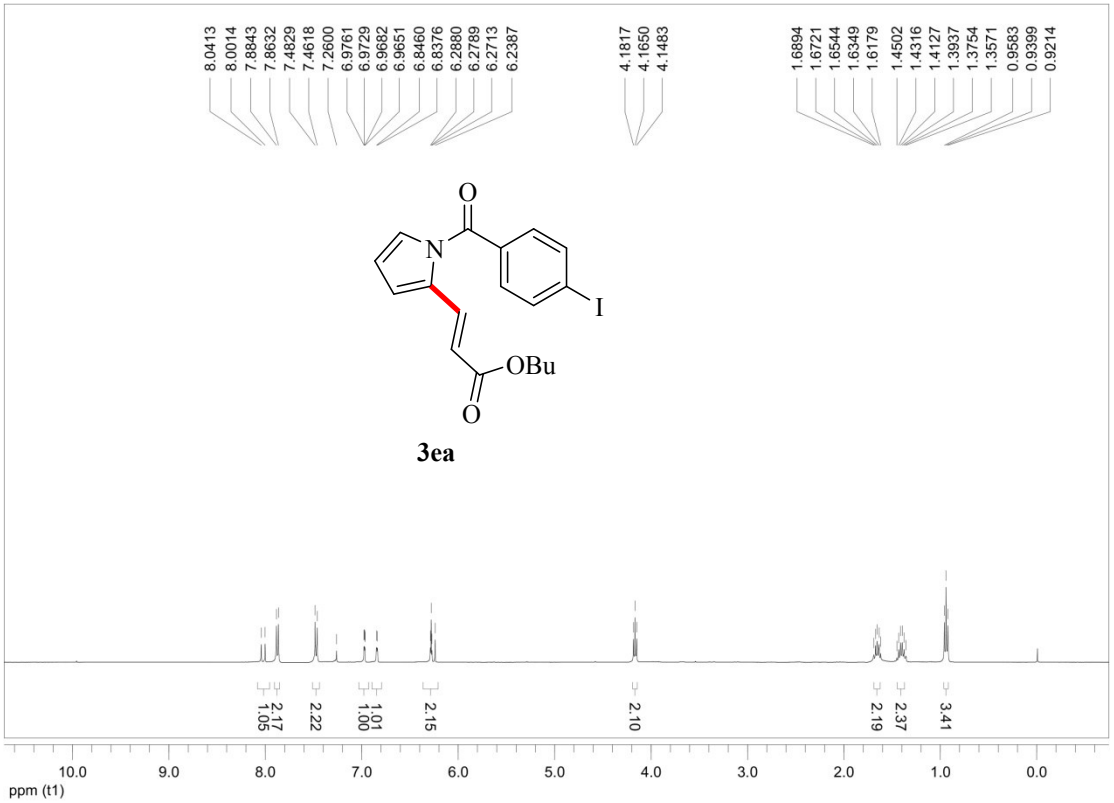


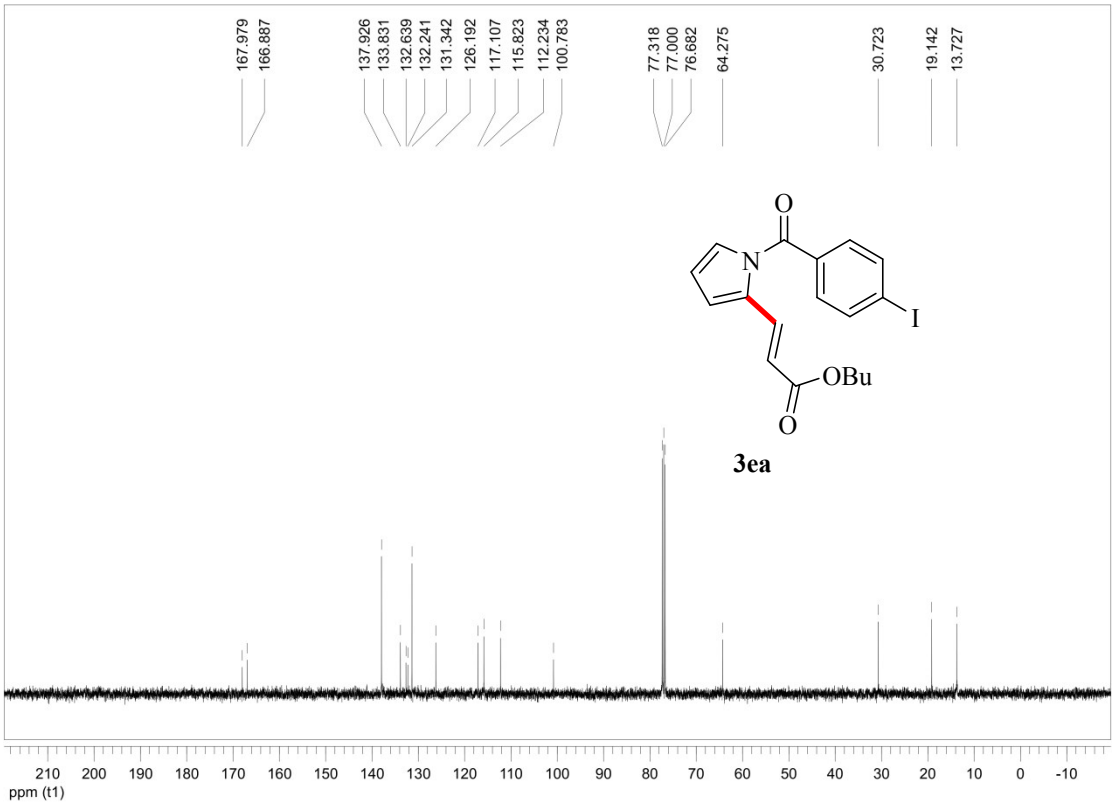
3da



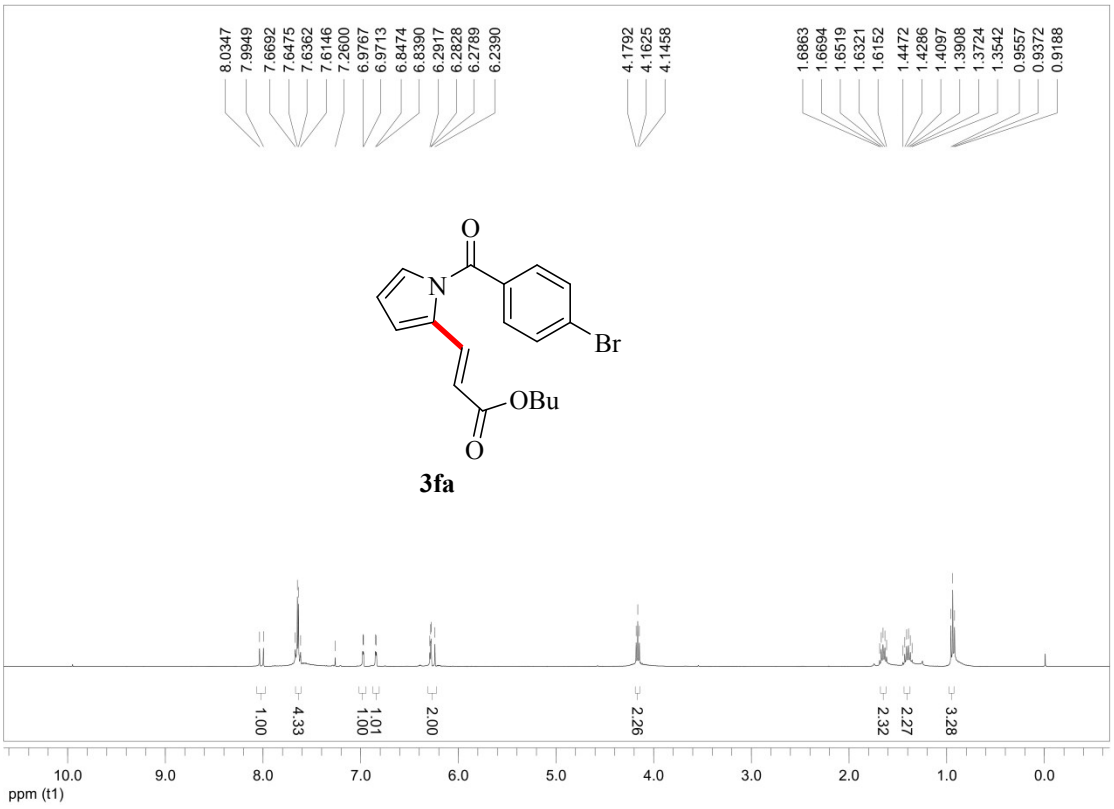
3da

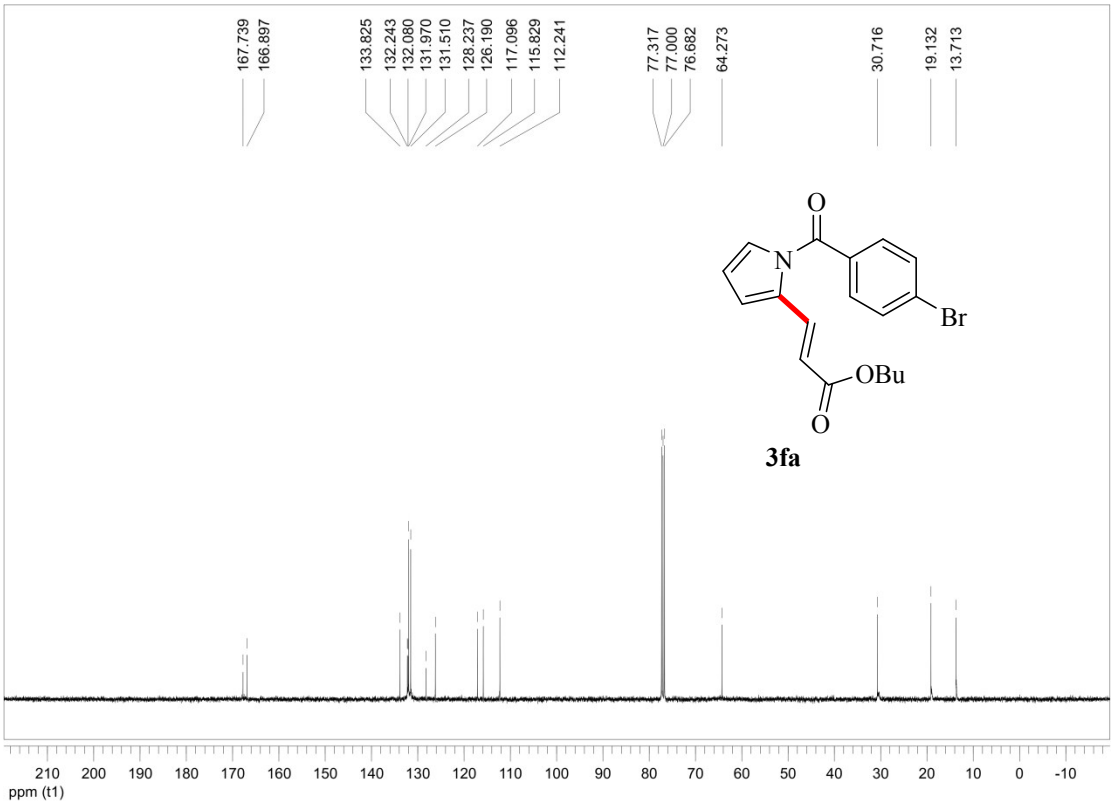
Butyl (*E*)-3-(1-(4-iodobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ea)



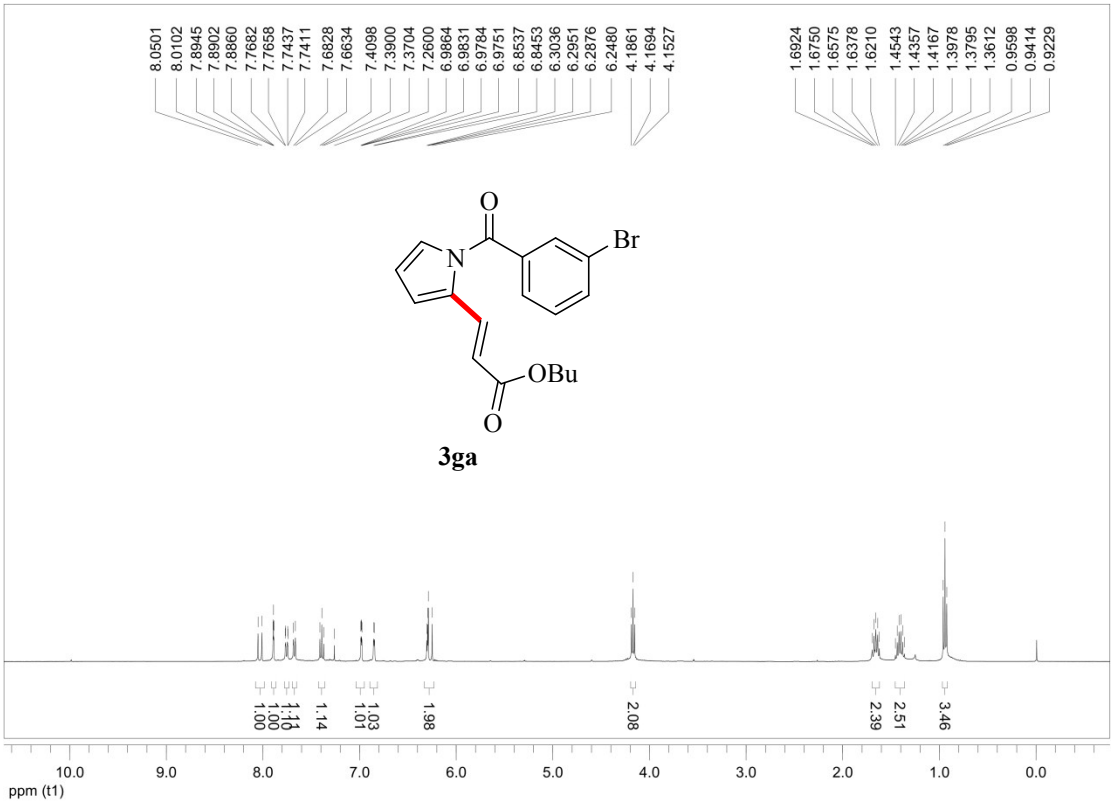


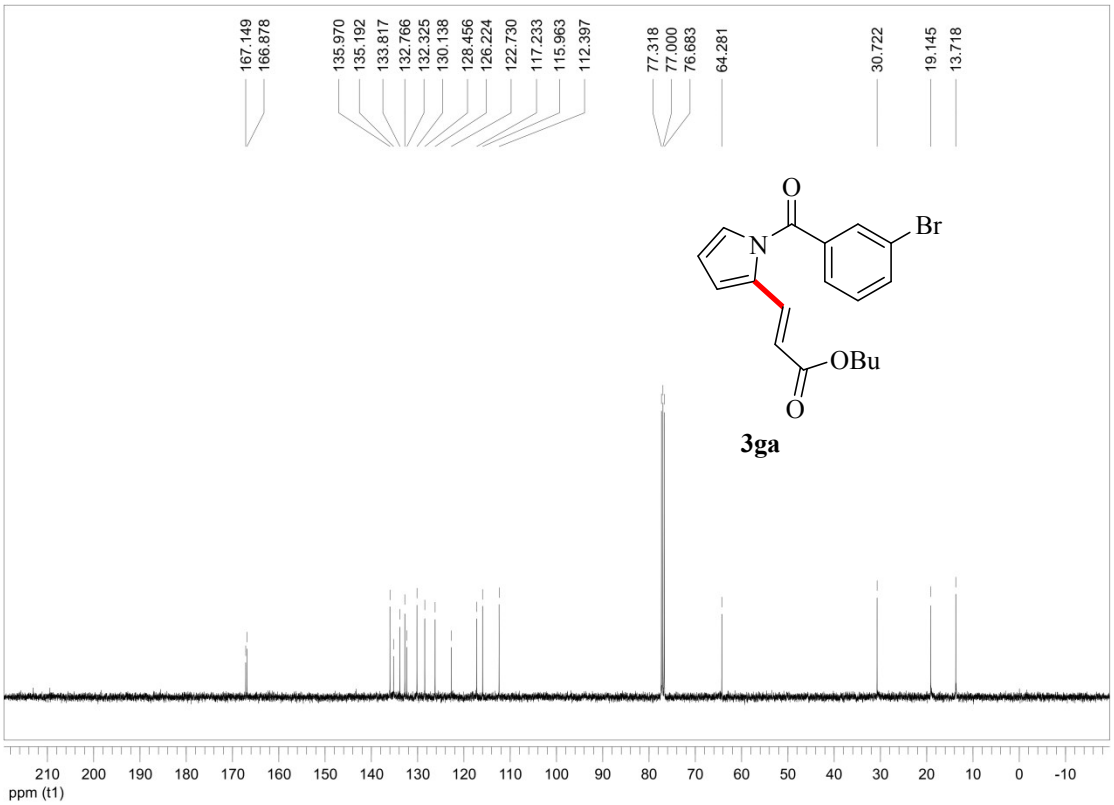
Butyl (*E*)-3-(1-(4-bromobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3fa)



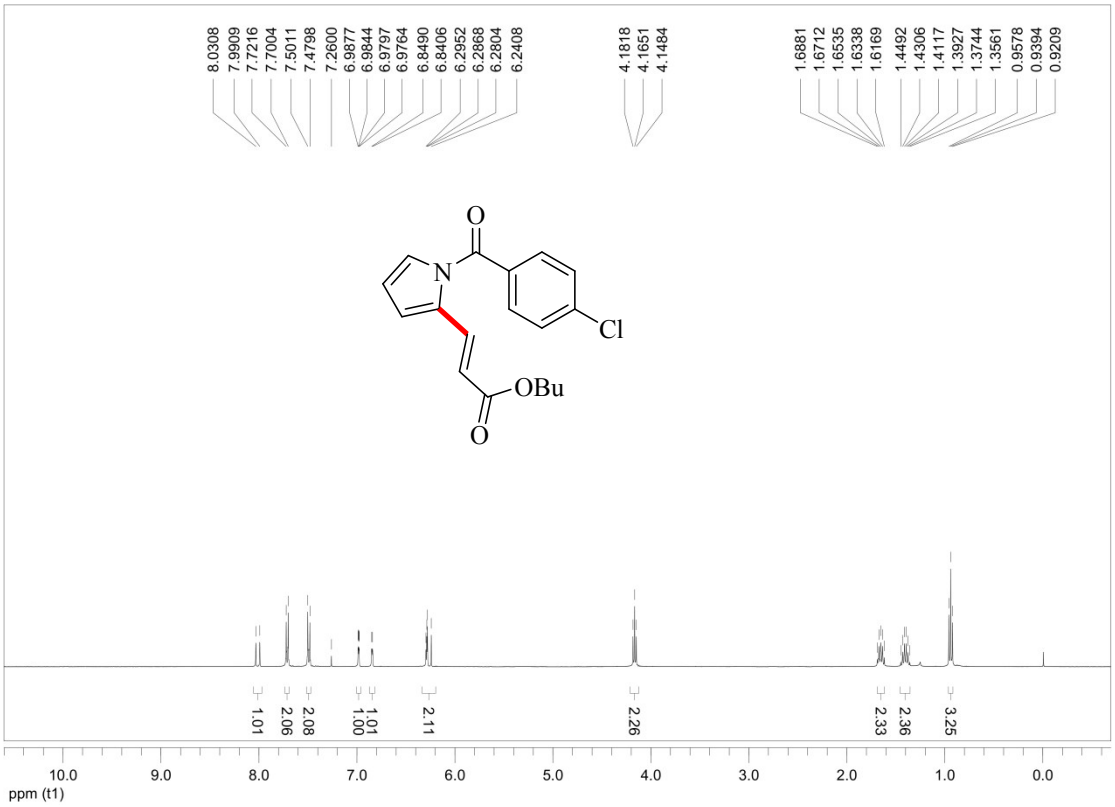


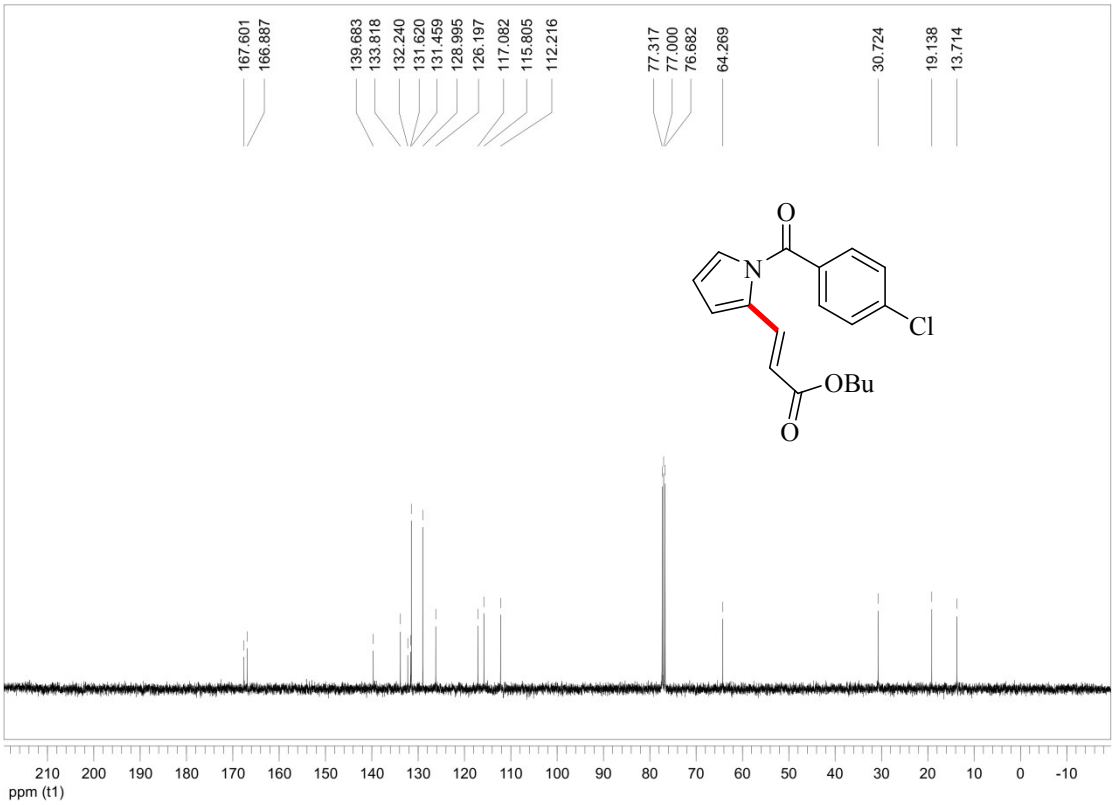
Butyl (*E*)-3-(1-(3-bromobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ga)



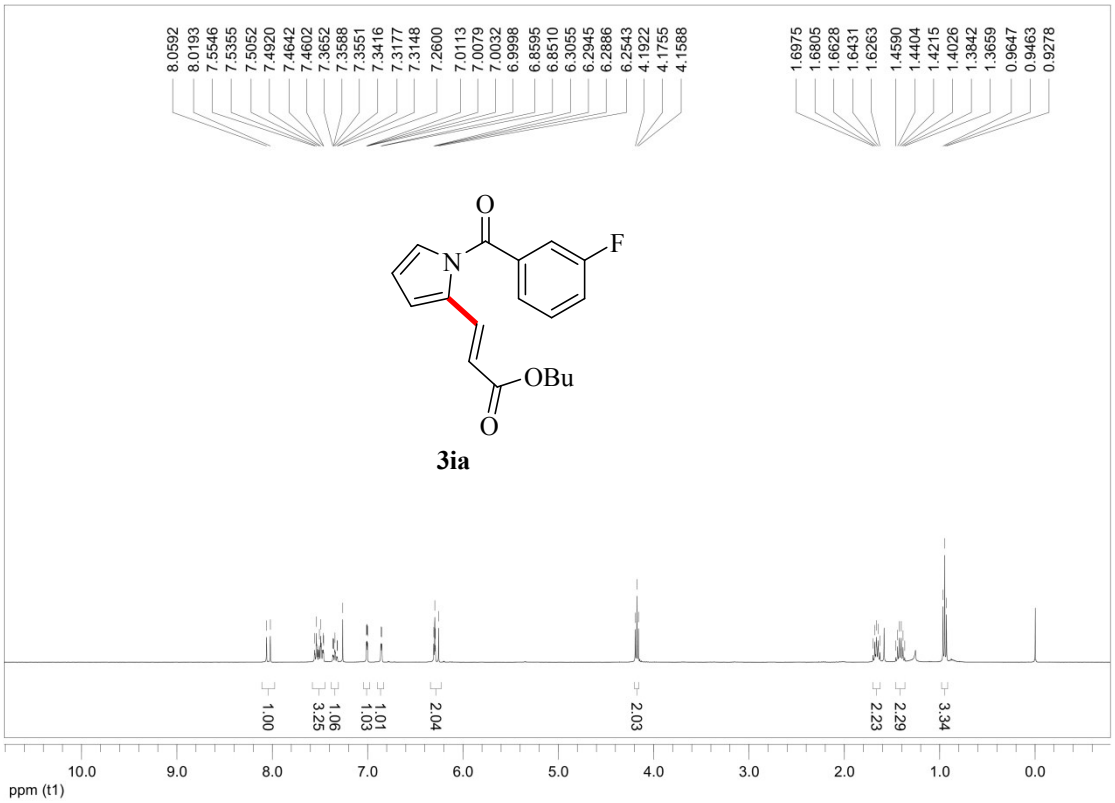


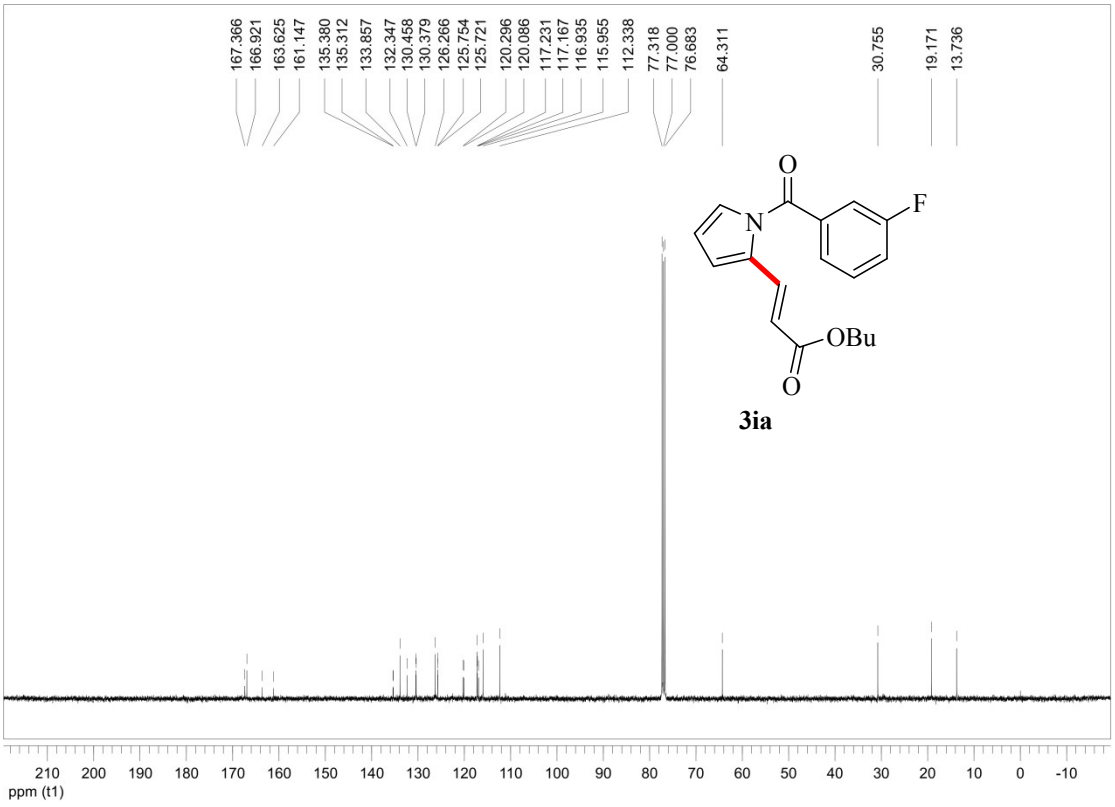
Butyl (*E*)-3-(1-(4-chlorobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ha)



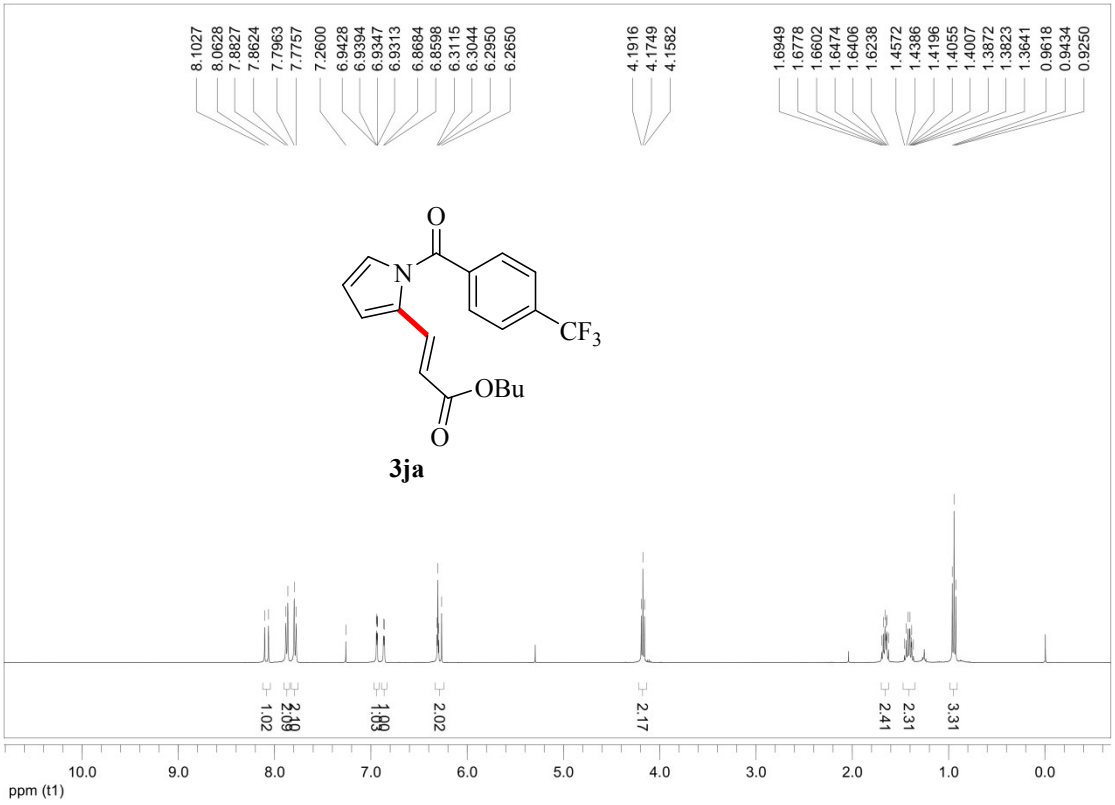


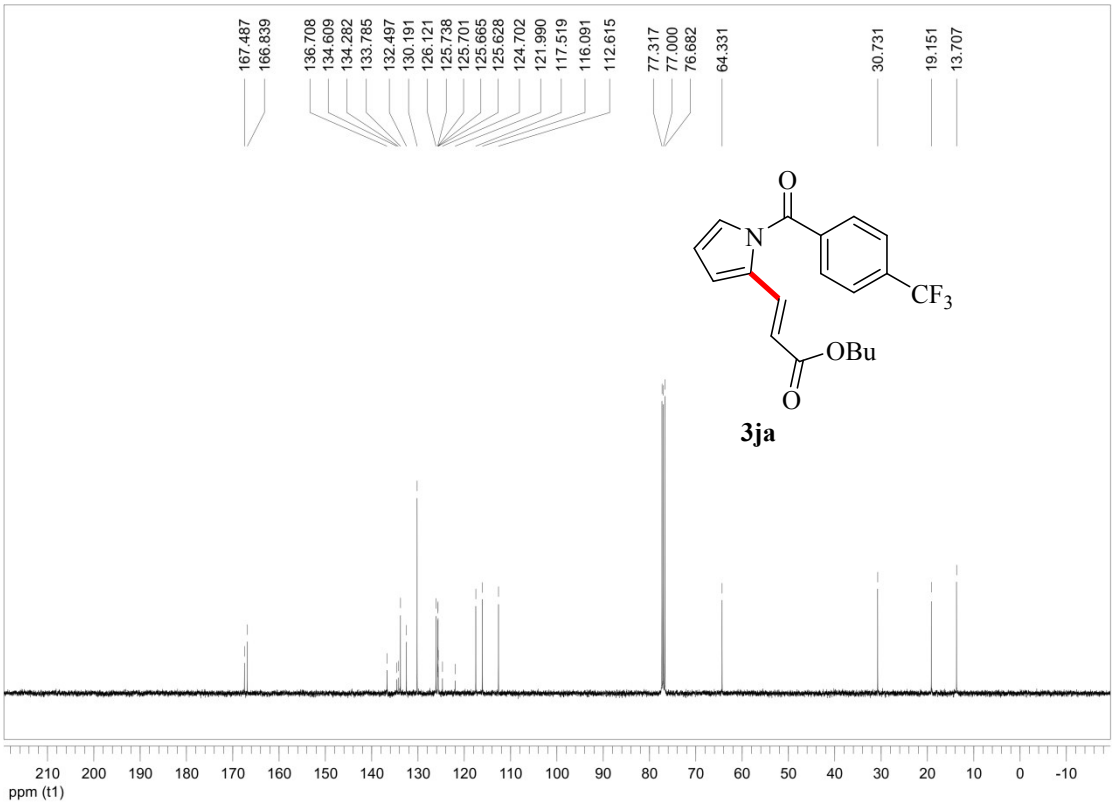
Butyl (*E*)-3-(1-(3-fluorobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ia)



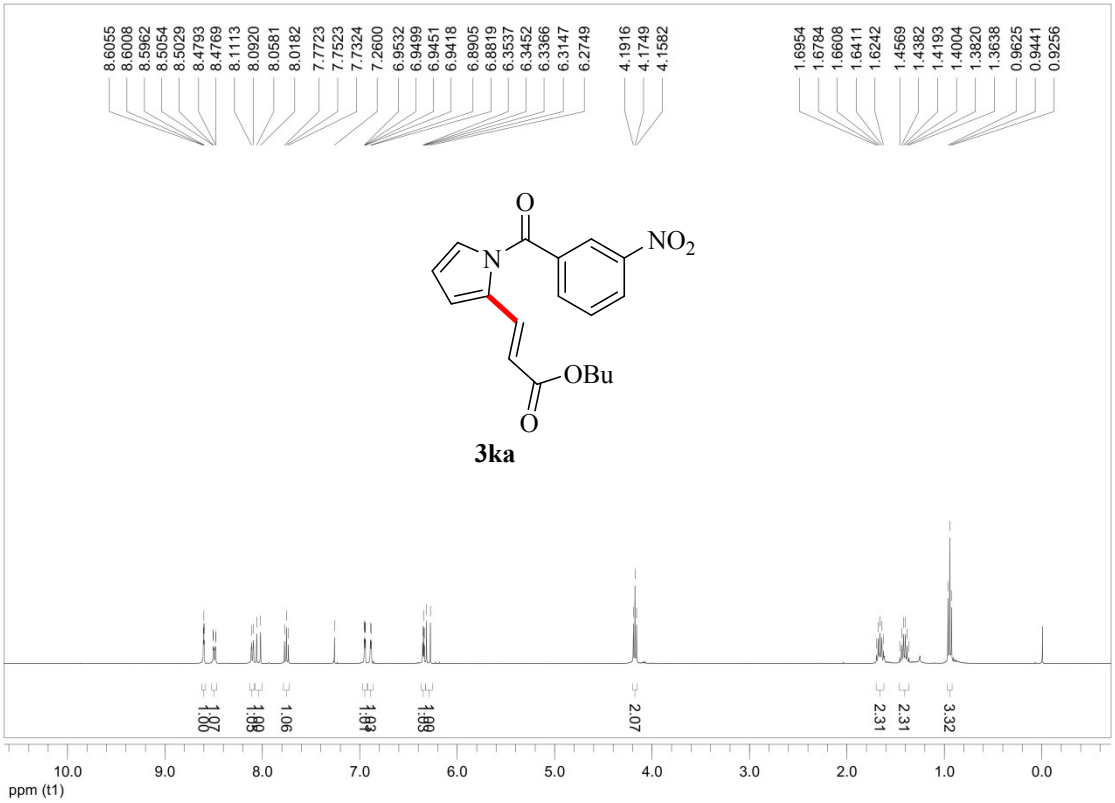


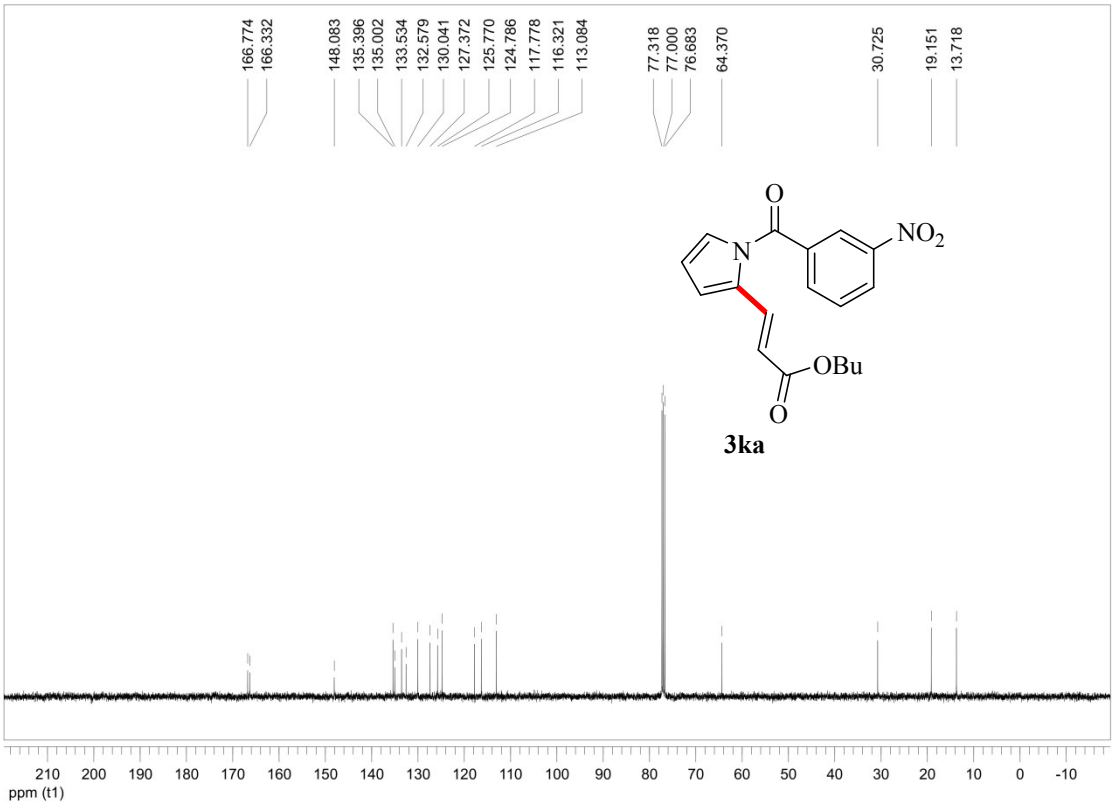
Butyl (*E*)-3-(1-(4-(trifluoromethyl)benzoyl)-1*H*-pyrrol-2-yl)acrylate (3ja)



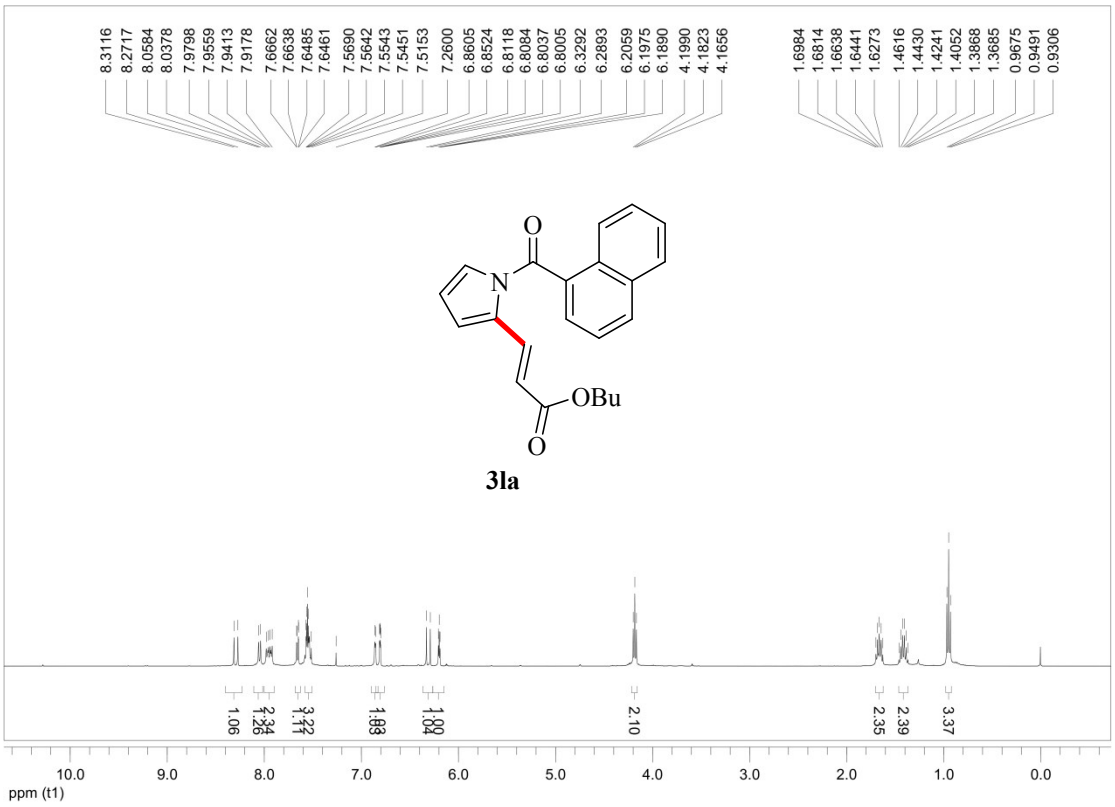


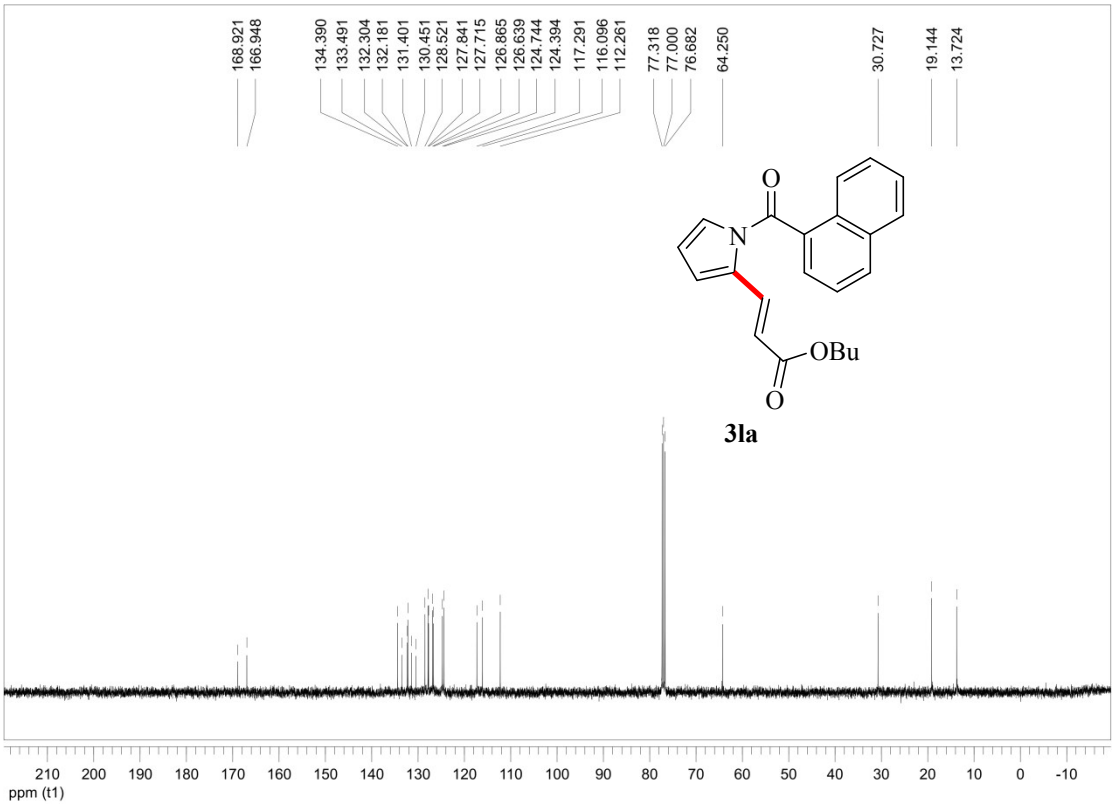
Butyl (*E*)-3-(1-(3-nitrobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ka)



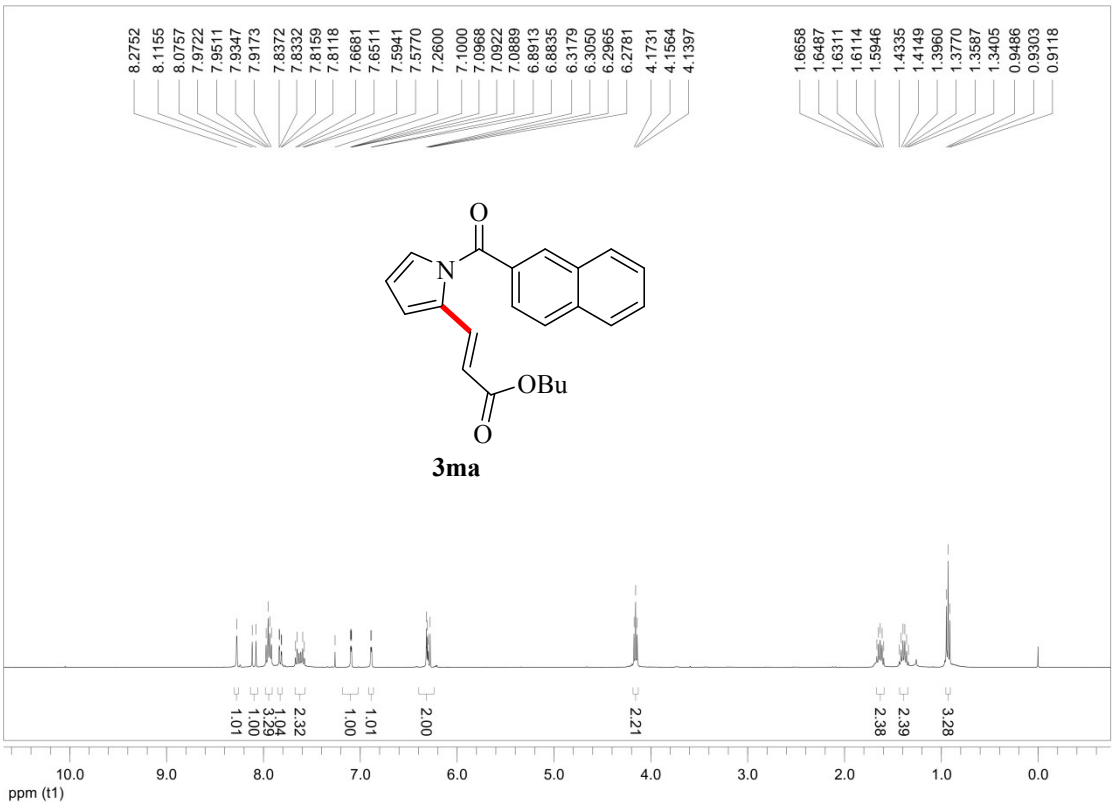


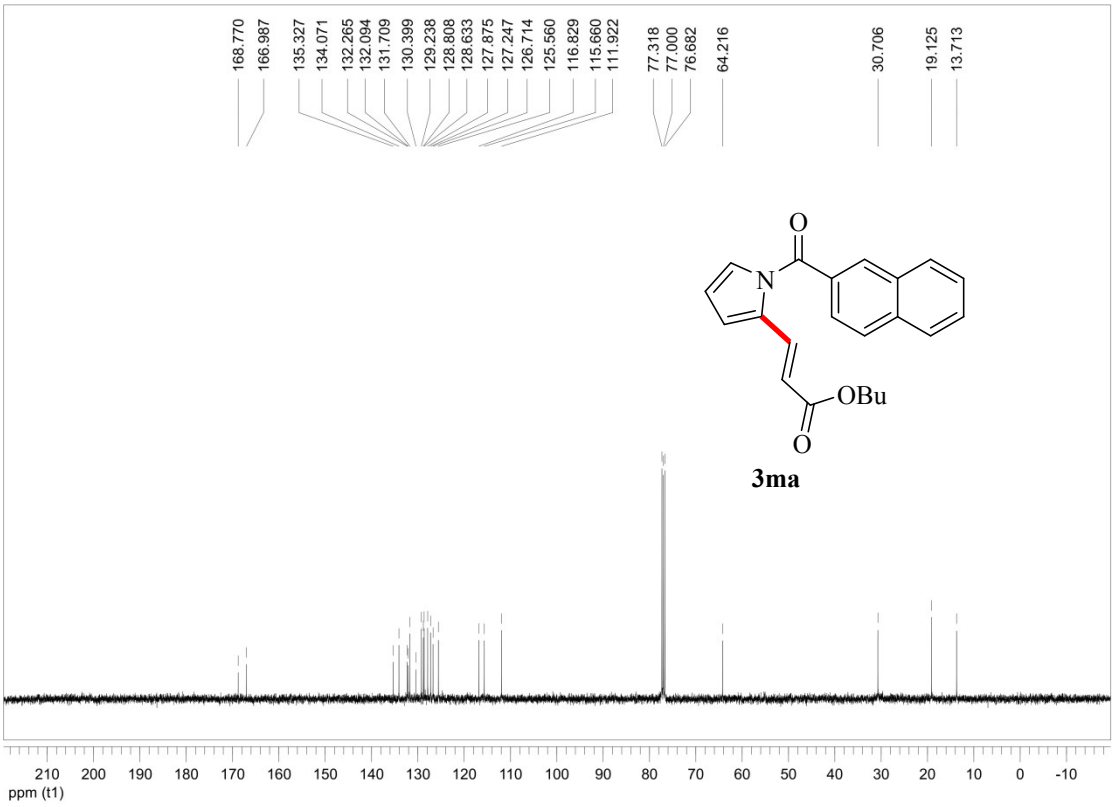
Butyl (*E*)-3-(1-(1-naphthoyl)-1*H*-pyrrol-2-yl)acrylate (3la)



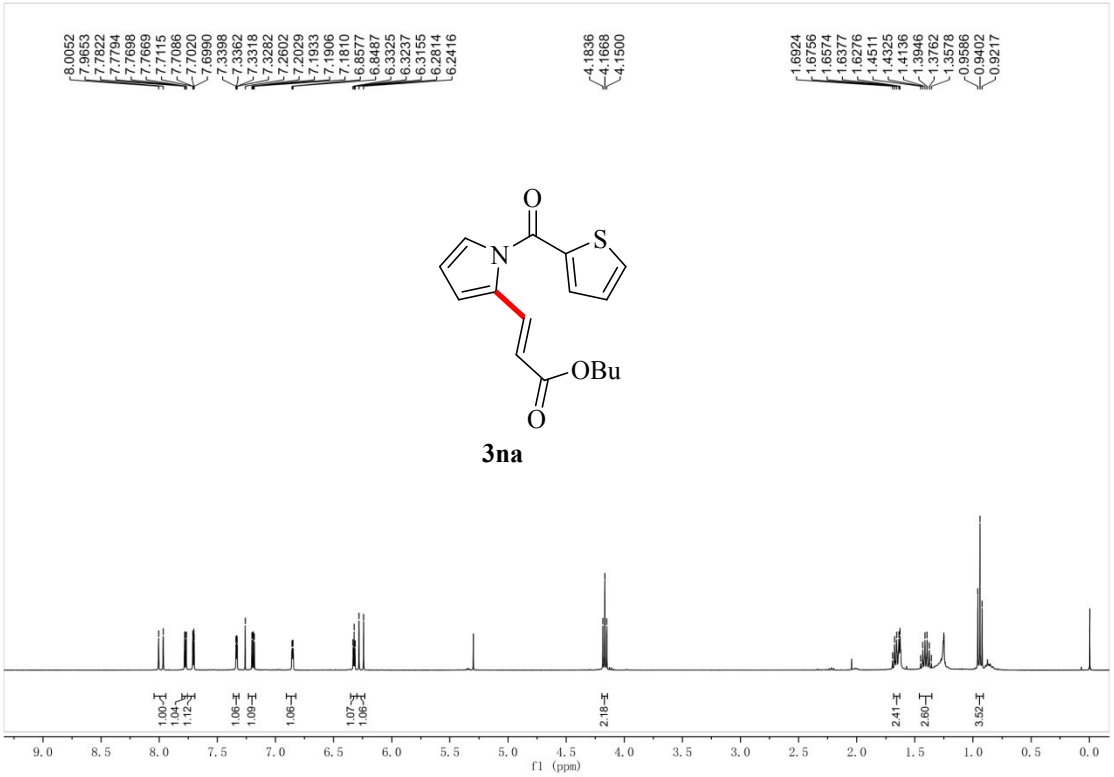


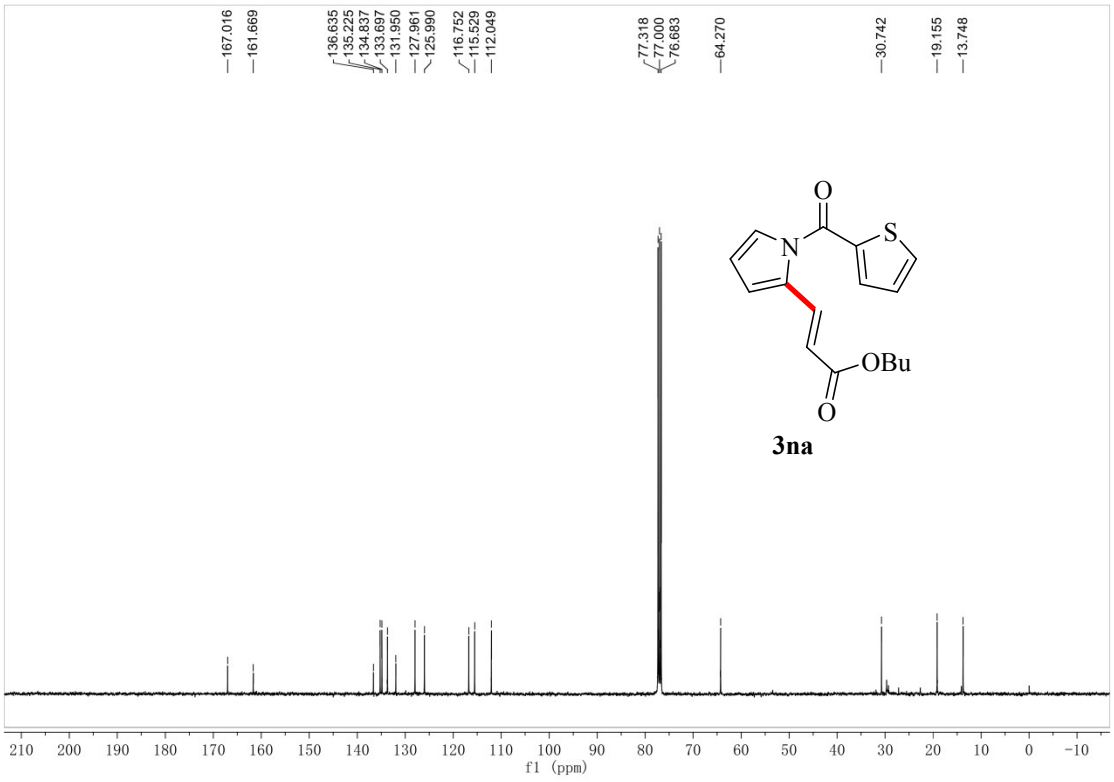
Butyl (*E*)-3-(1-(2-naphthoyl)-1*H*-pyrrol-2-yl)acrylate (3ma)



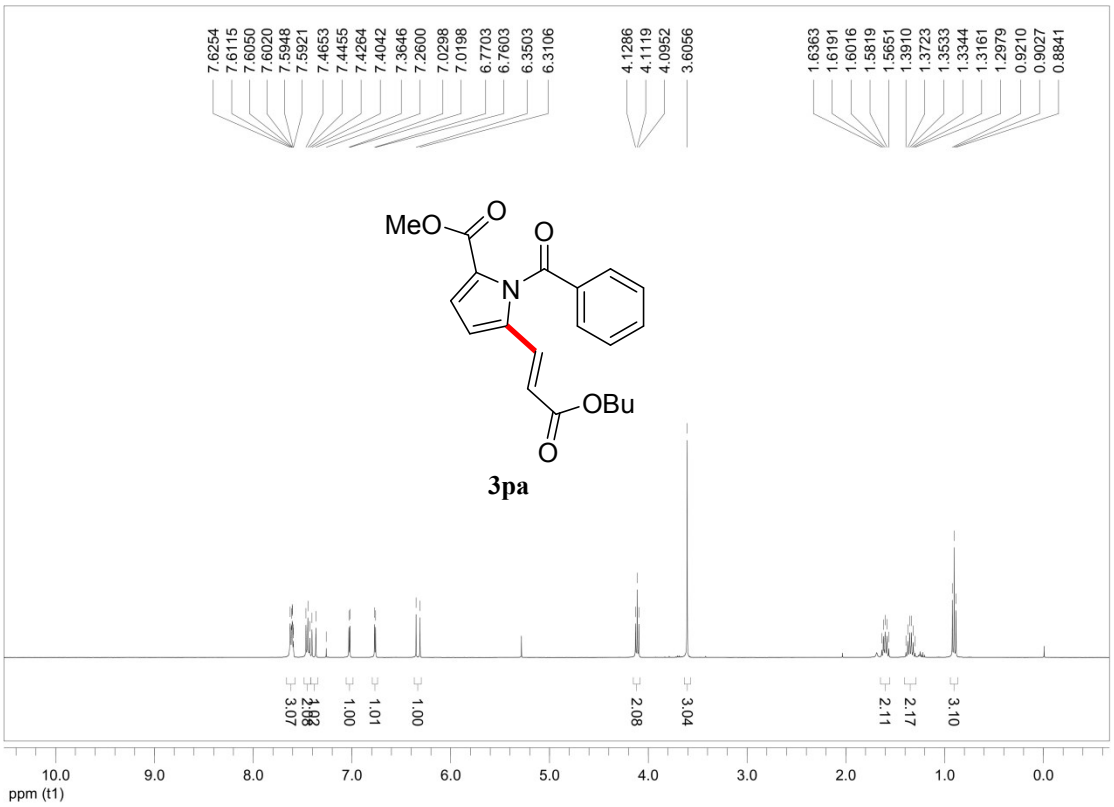


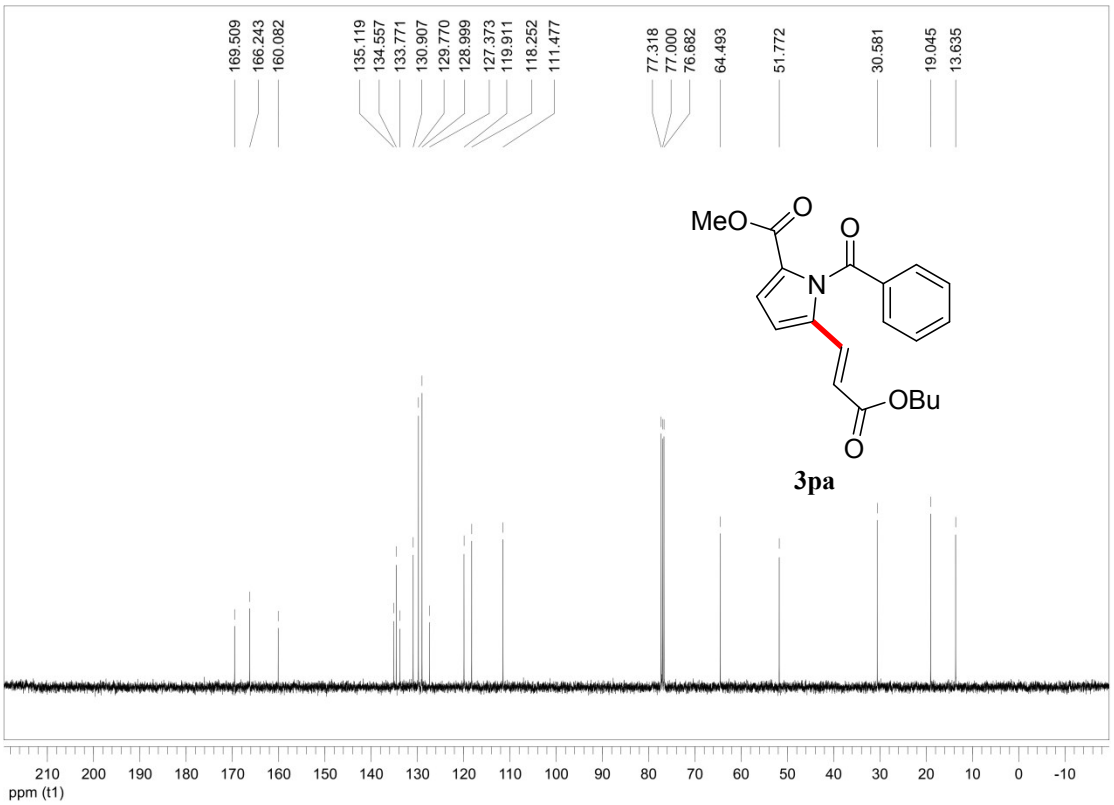
Butyl (*E*)-3-(1-(thiophene-2-carbonyl)-1*H*-pyrrol-2-yl)acrylate (3na)



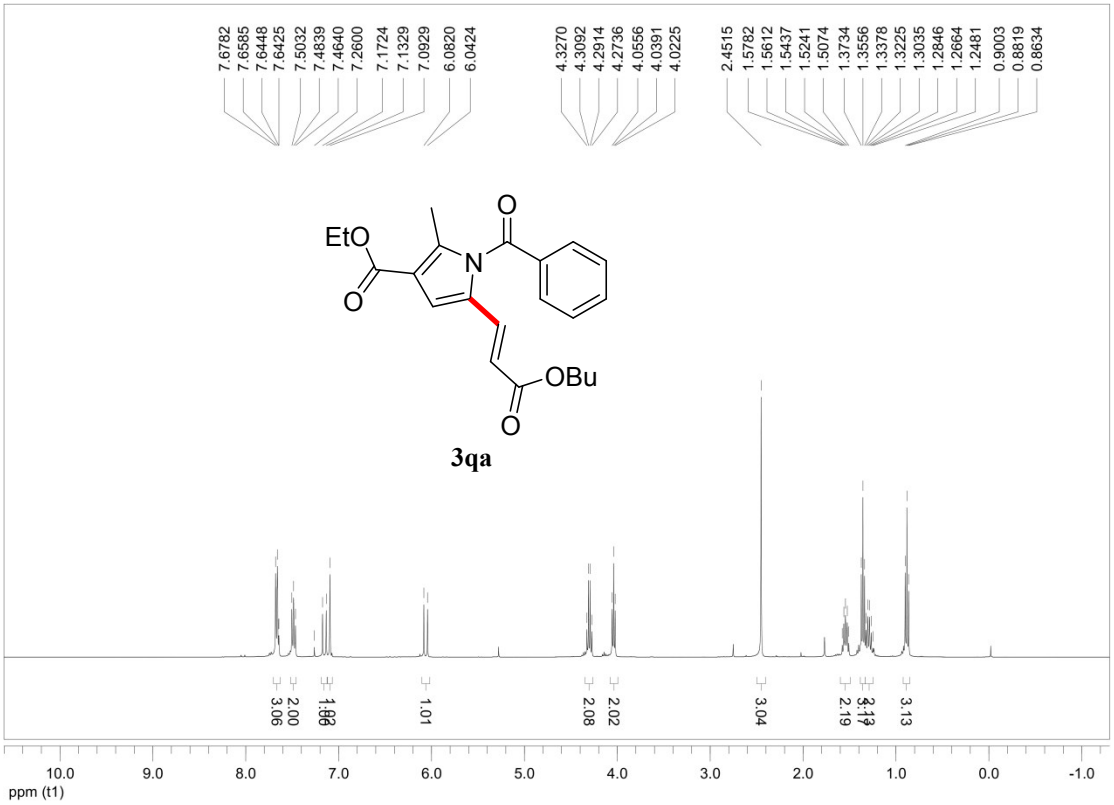


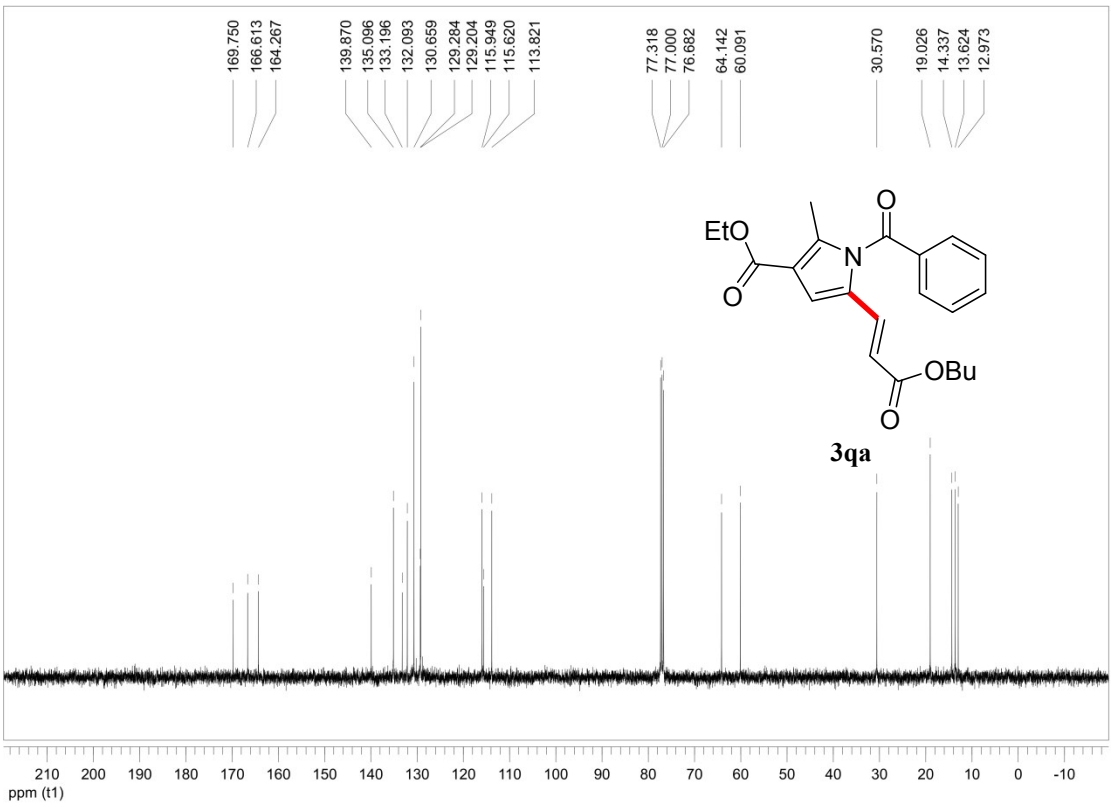
Methyl(*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-1*H*-pyrrole-2-carboxylate(3pa)



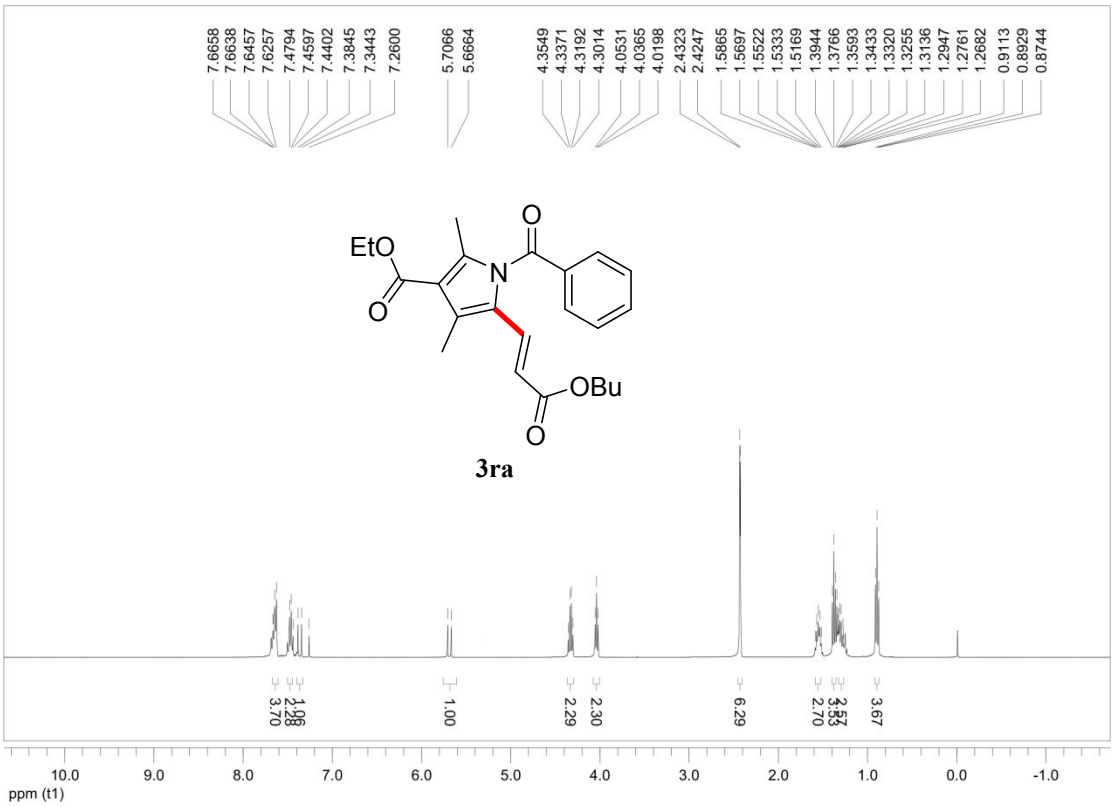


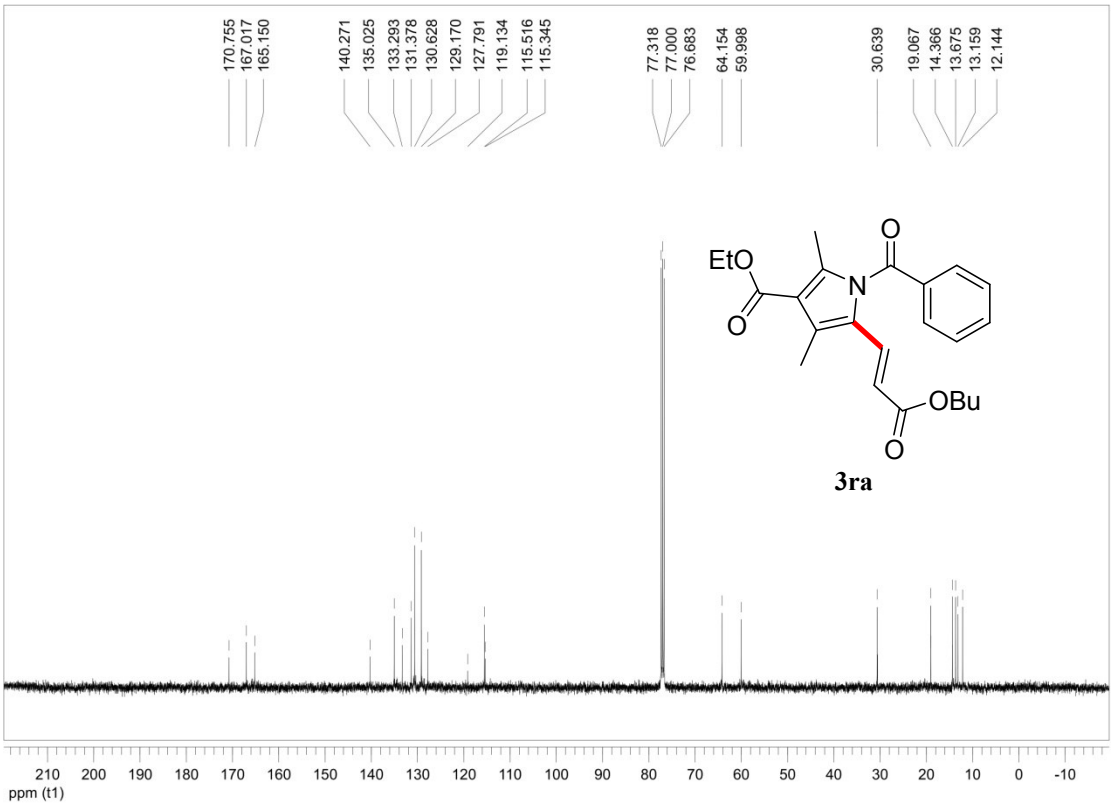
Ethyl(*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (3qa)



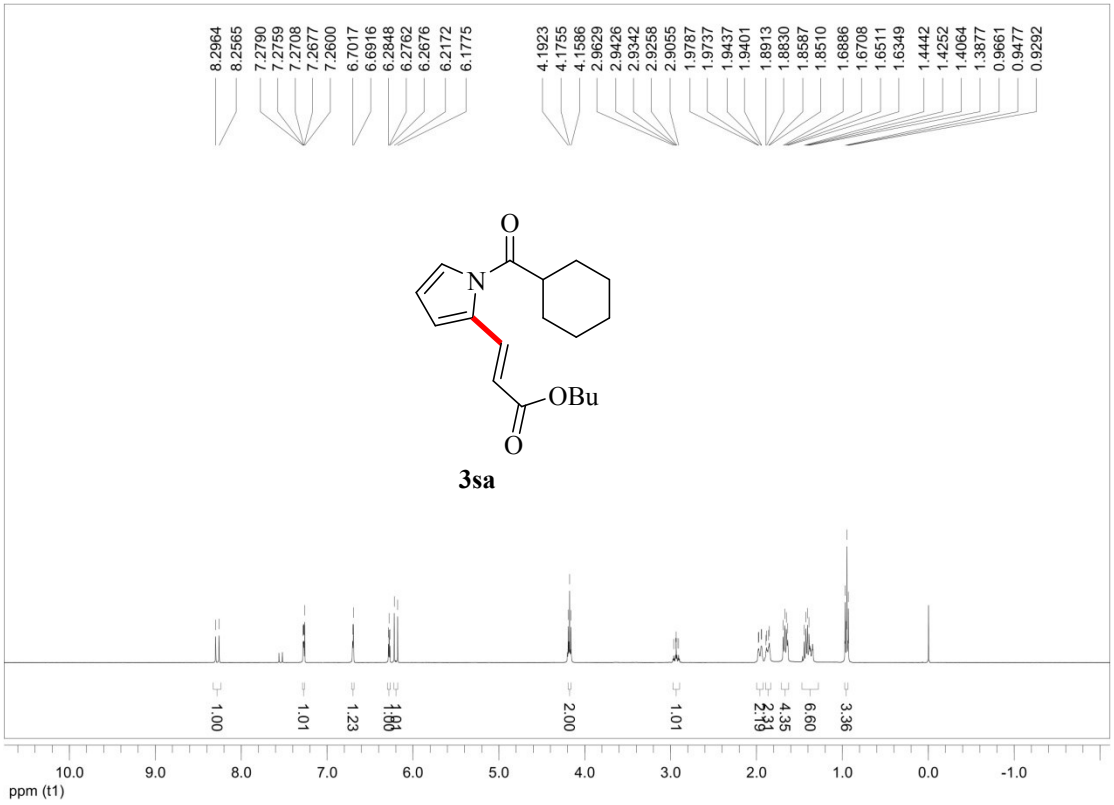


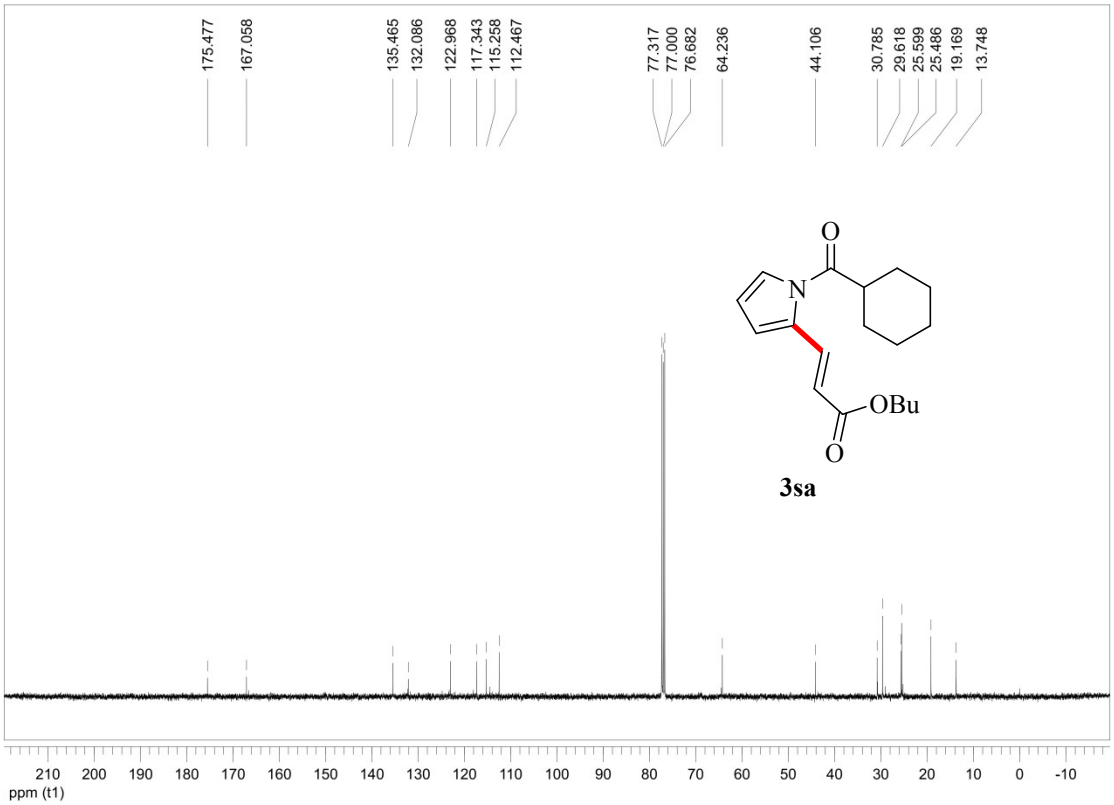
Ethyl(*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-2,4-dimethyl-1*H*-pyrrole-3-carboxylate (3ra)



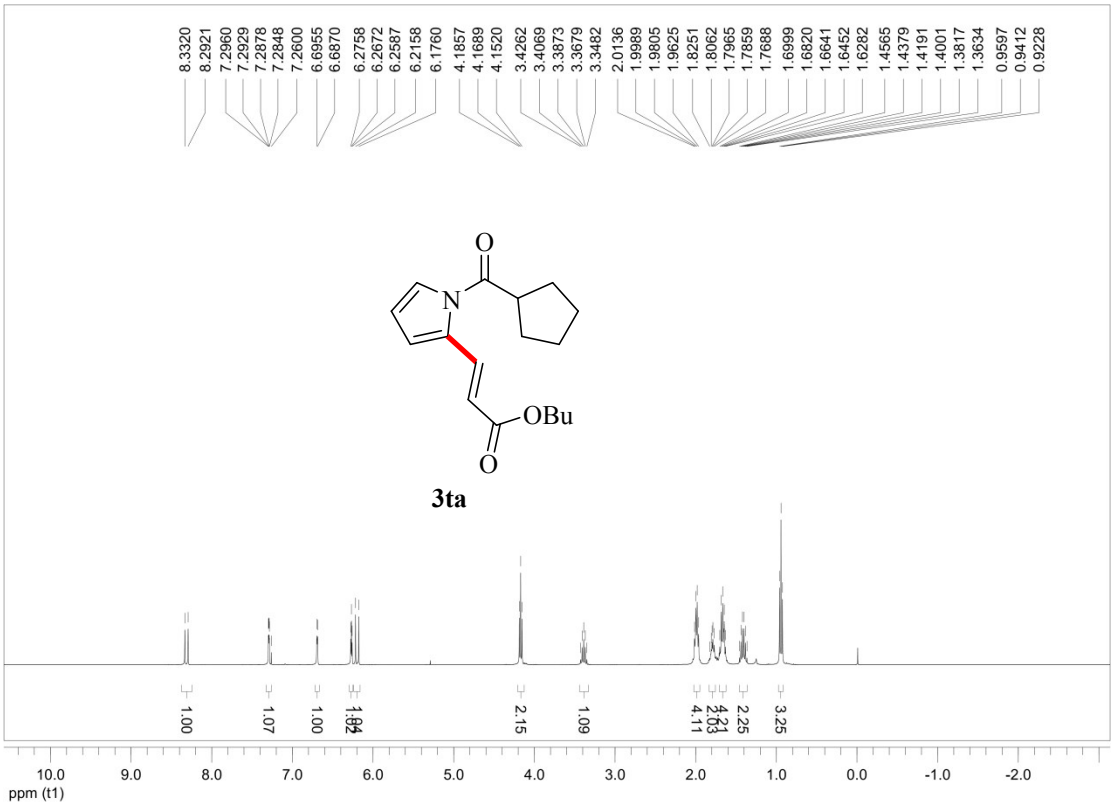


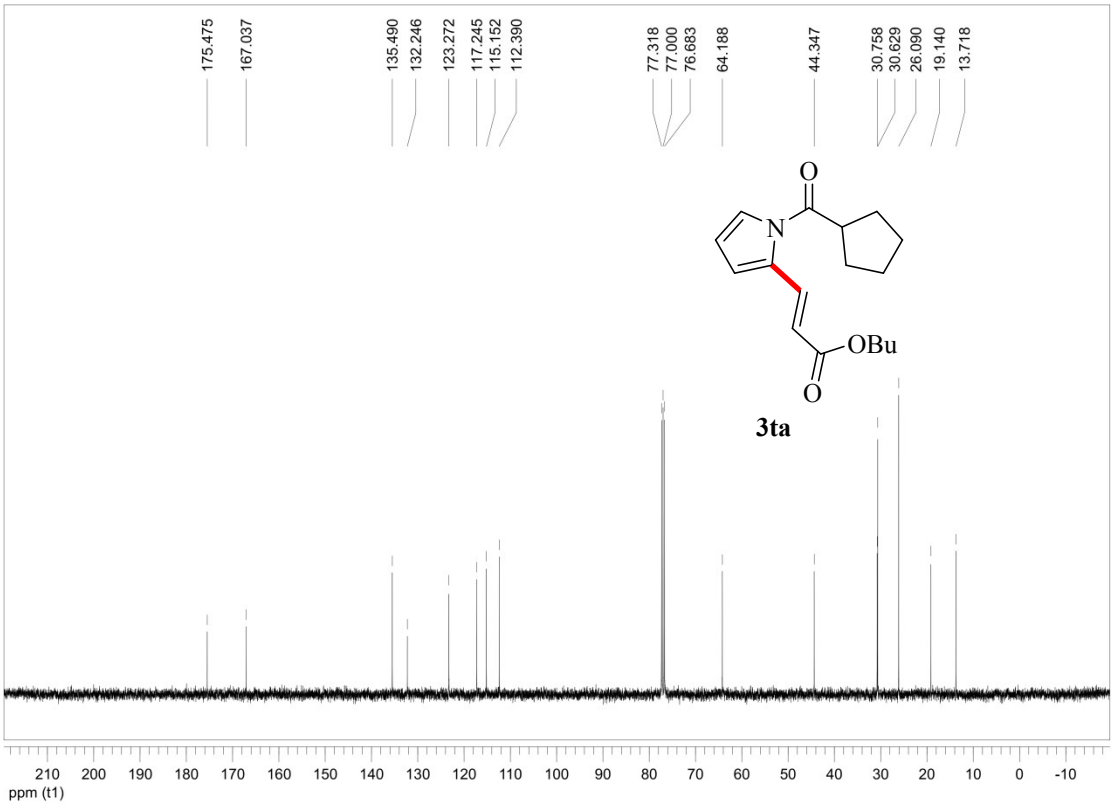
Butyl (*E*)-3-(1-(cyclohexanecarbonyl)-1*H*-pyrrol-2-yl)acrylate (3sa)



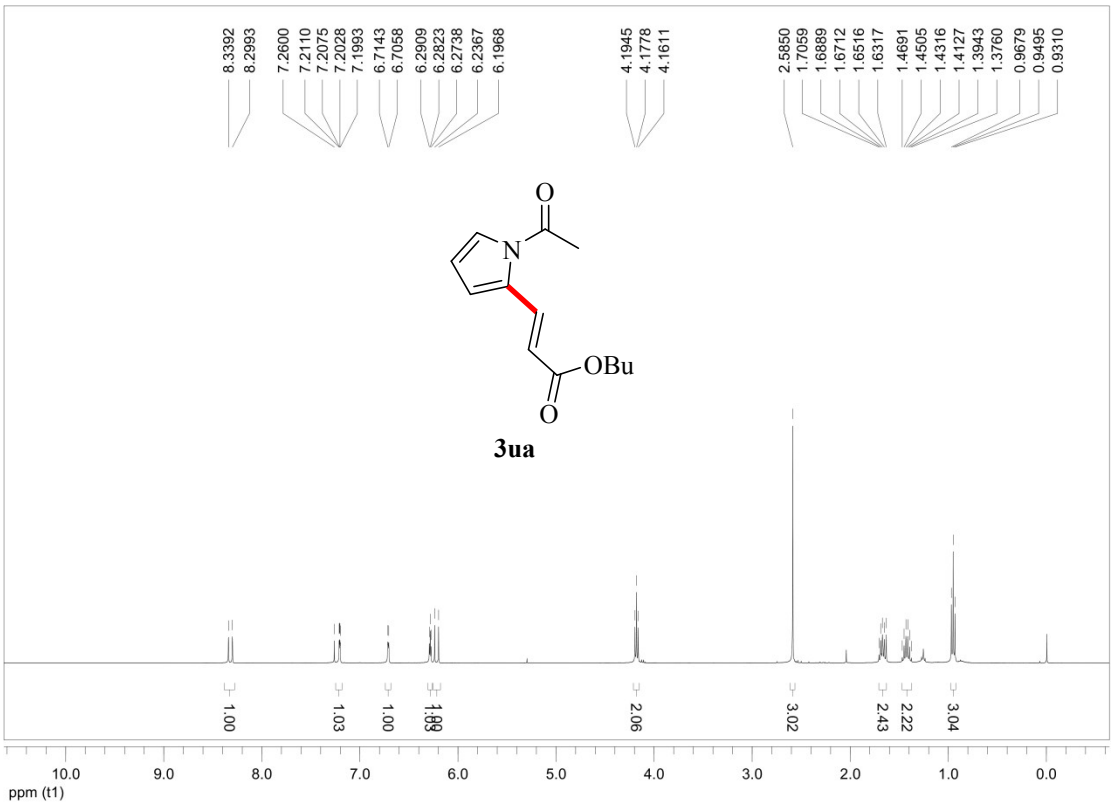


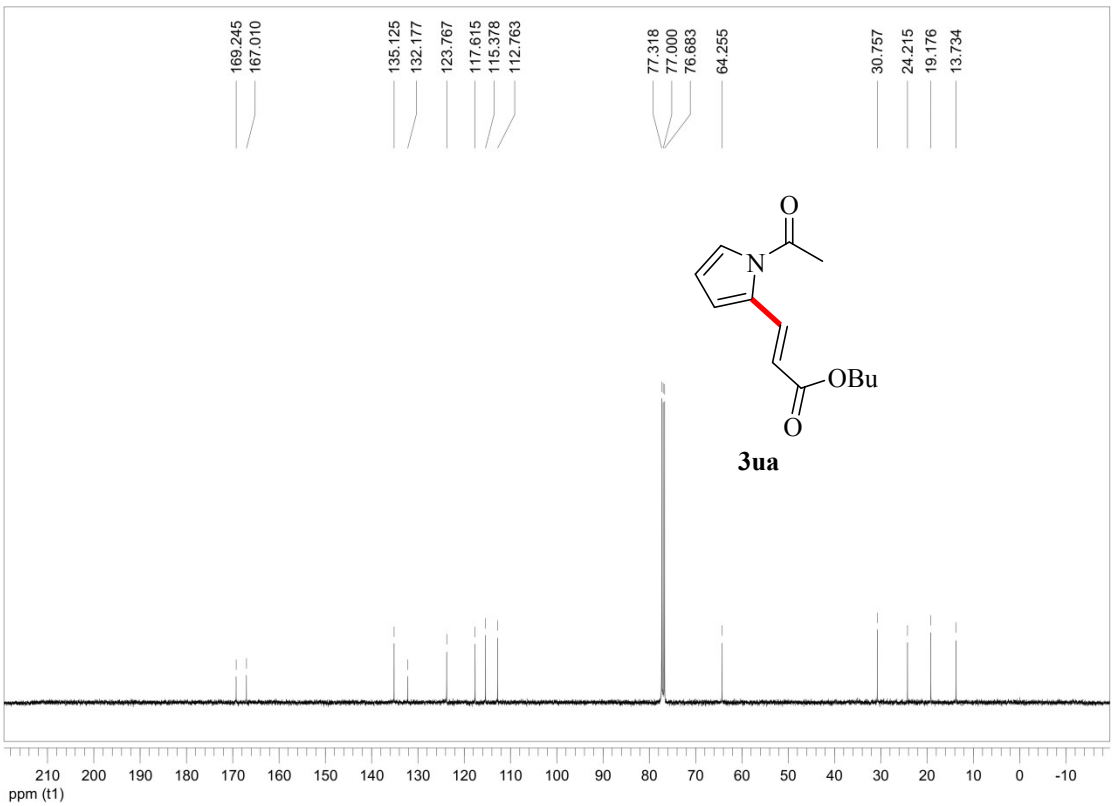
Butyl (*E*)-3-(1-(cyclopentanecarbonyl)-1*H*-pyrrol-2-yl)acrylate (3ta)



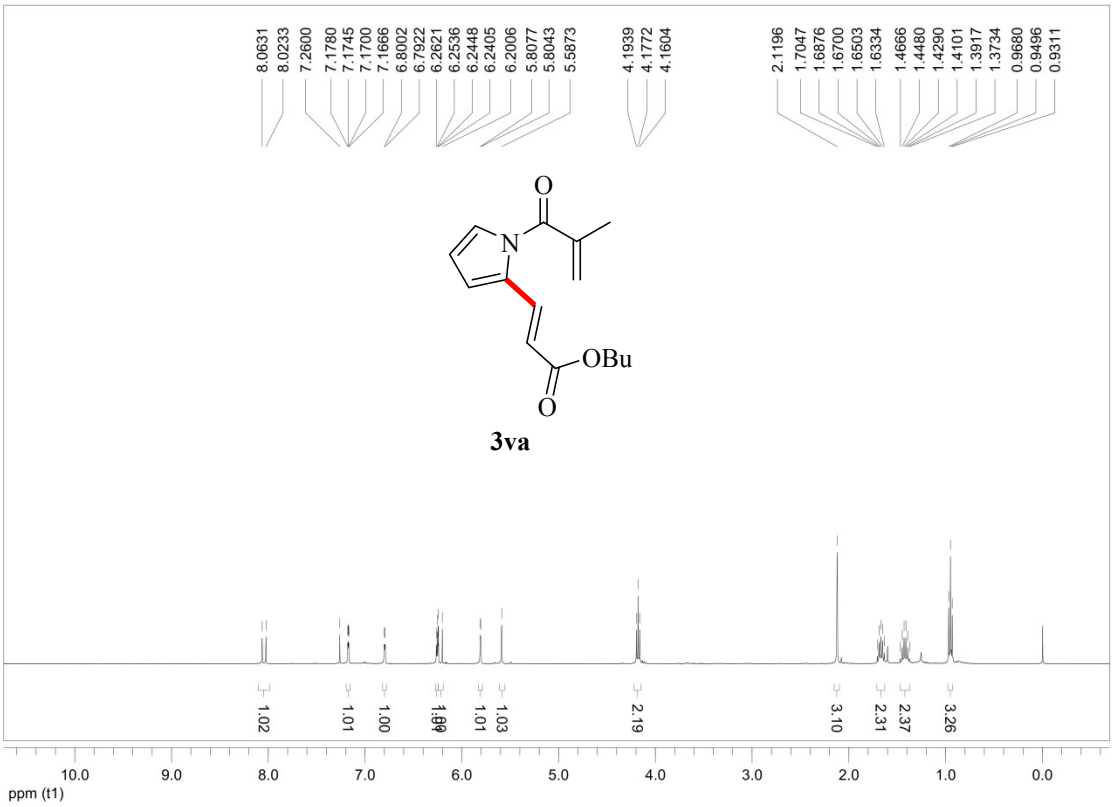


Butyl (*E*)-3-(1-acetyl-1*H*-pyrrol-2-yl)acrylate (3ua)

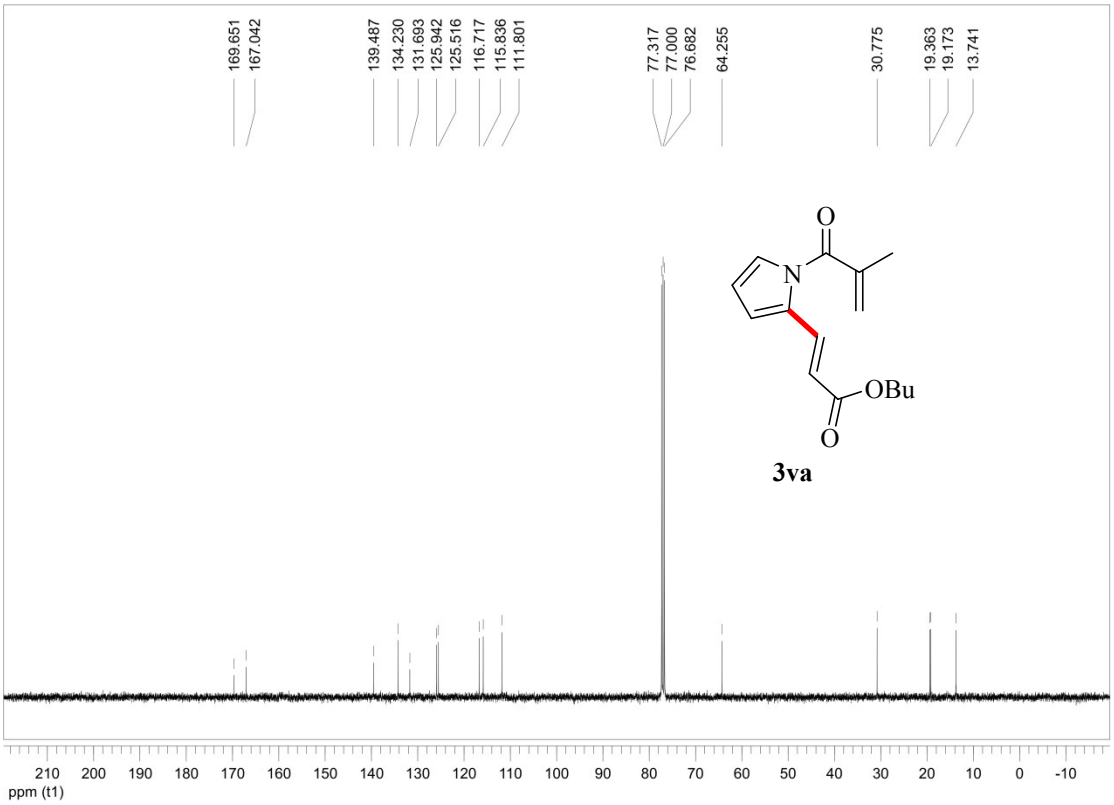




Butyl (*E*)-3-(1-methacryloyl-1*H*-pyrrol-2-yl)acrylate (3va)

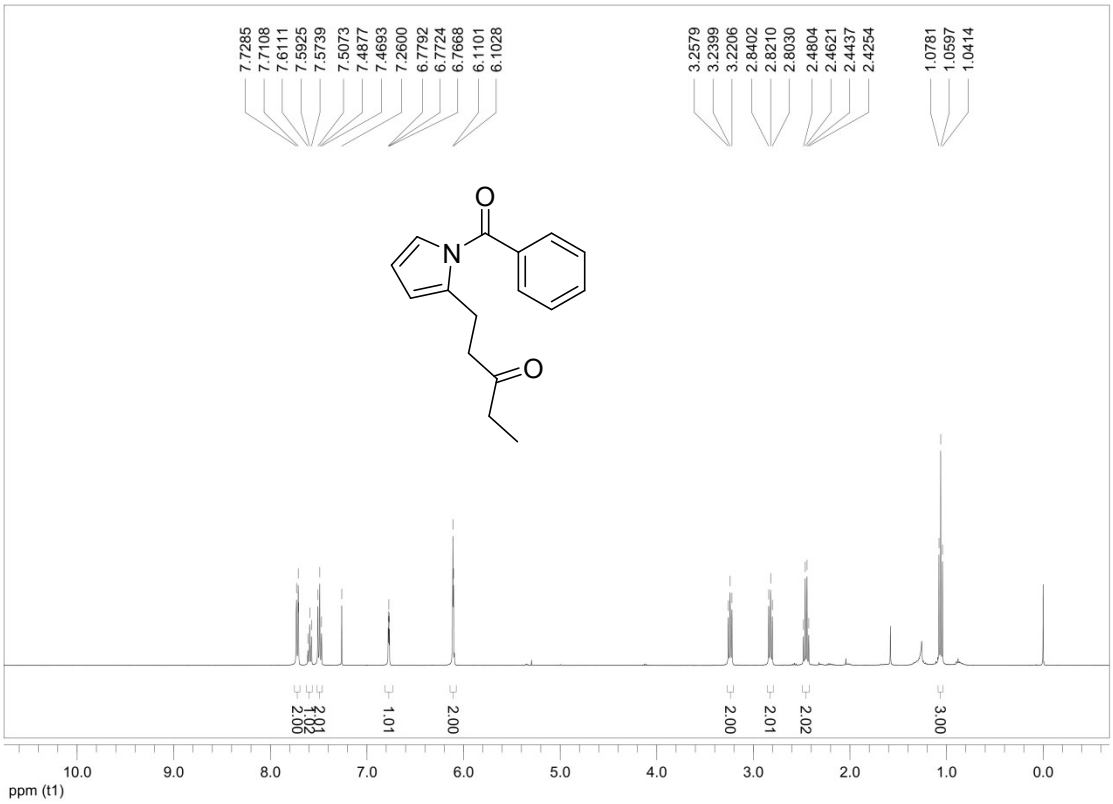


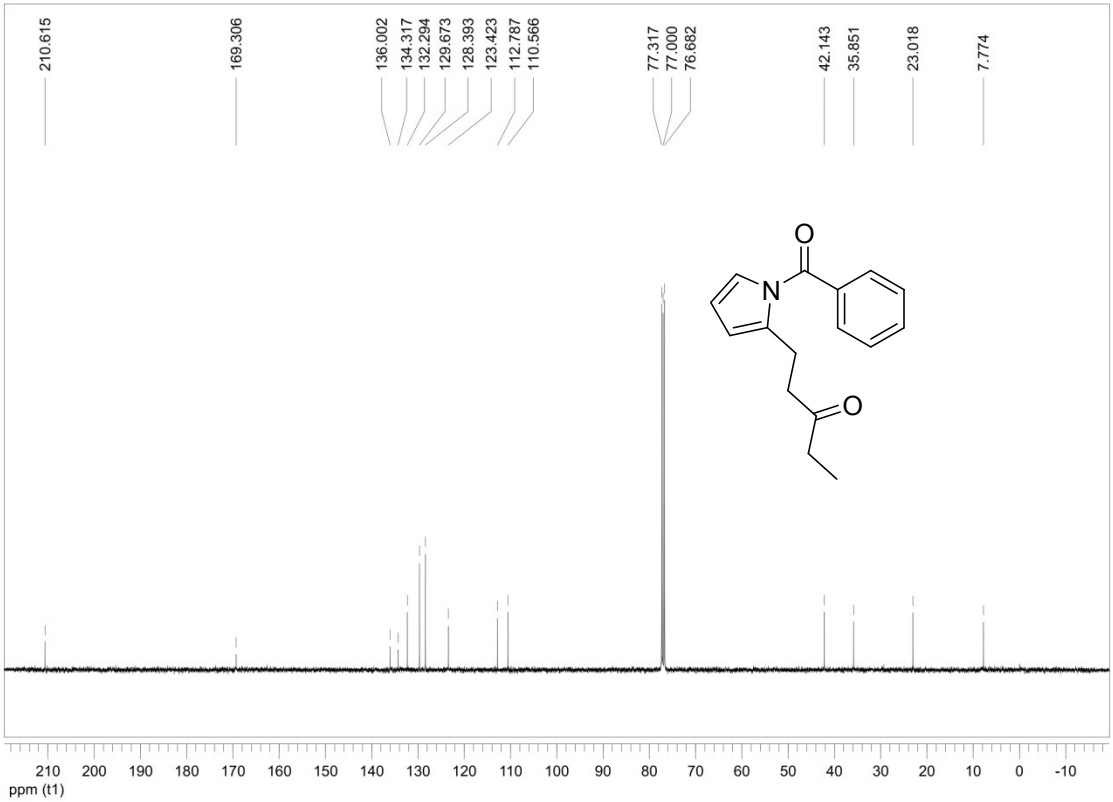
3va



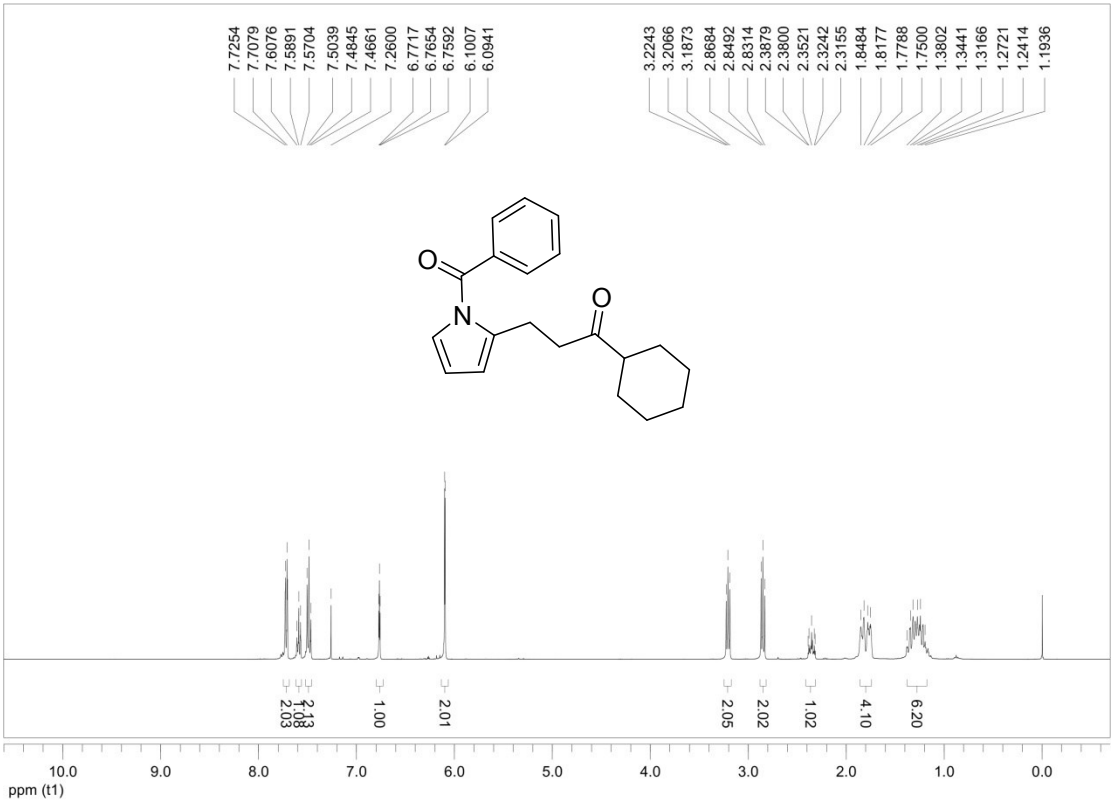
3va

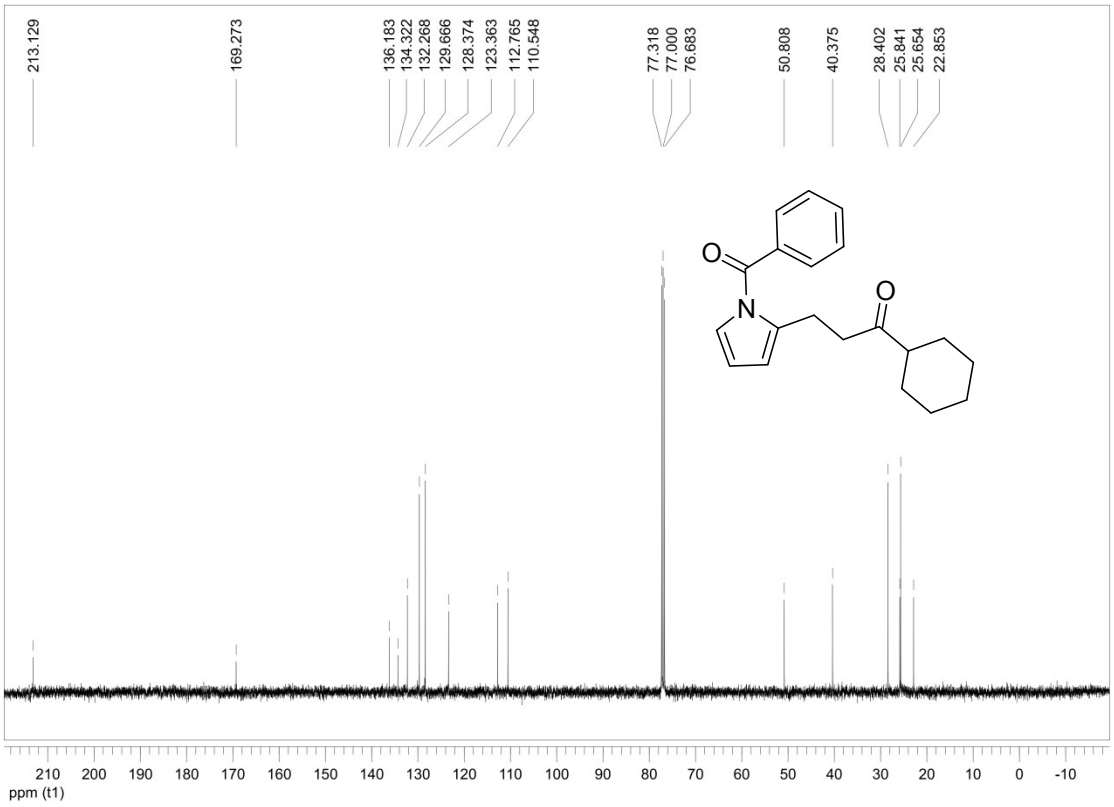
1-(1-benzoyl-1*H*-pyrrol-2-yl)pentan-3-one (4aq)



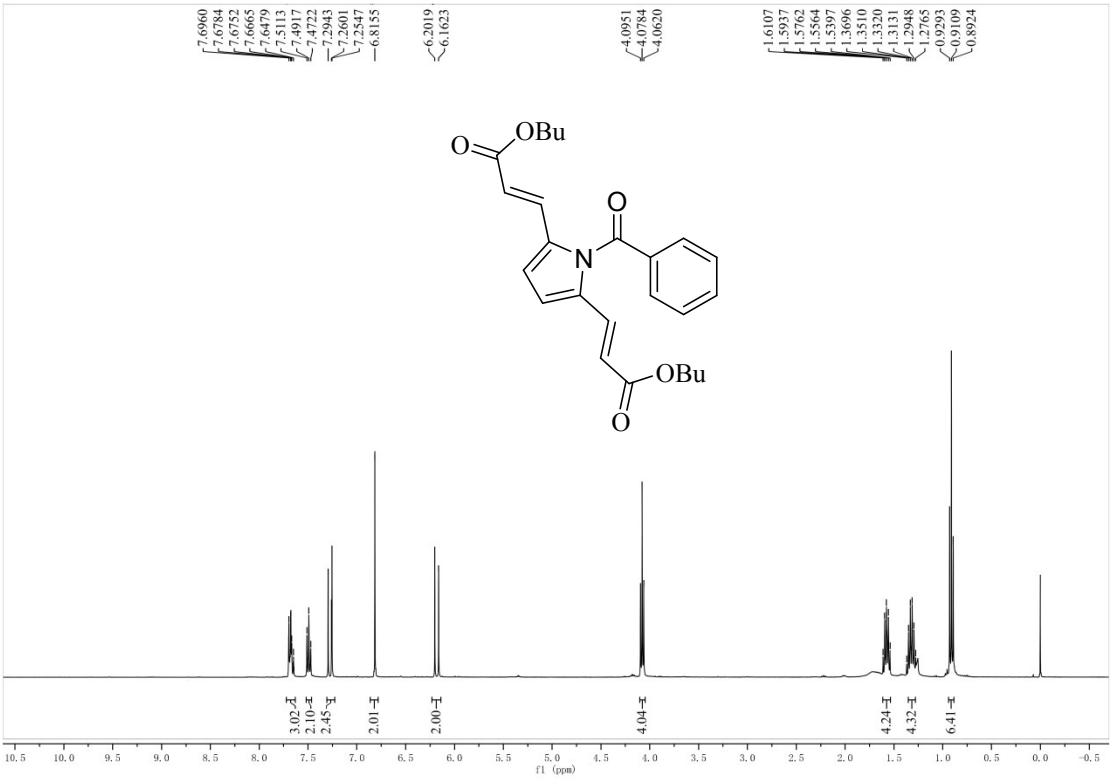


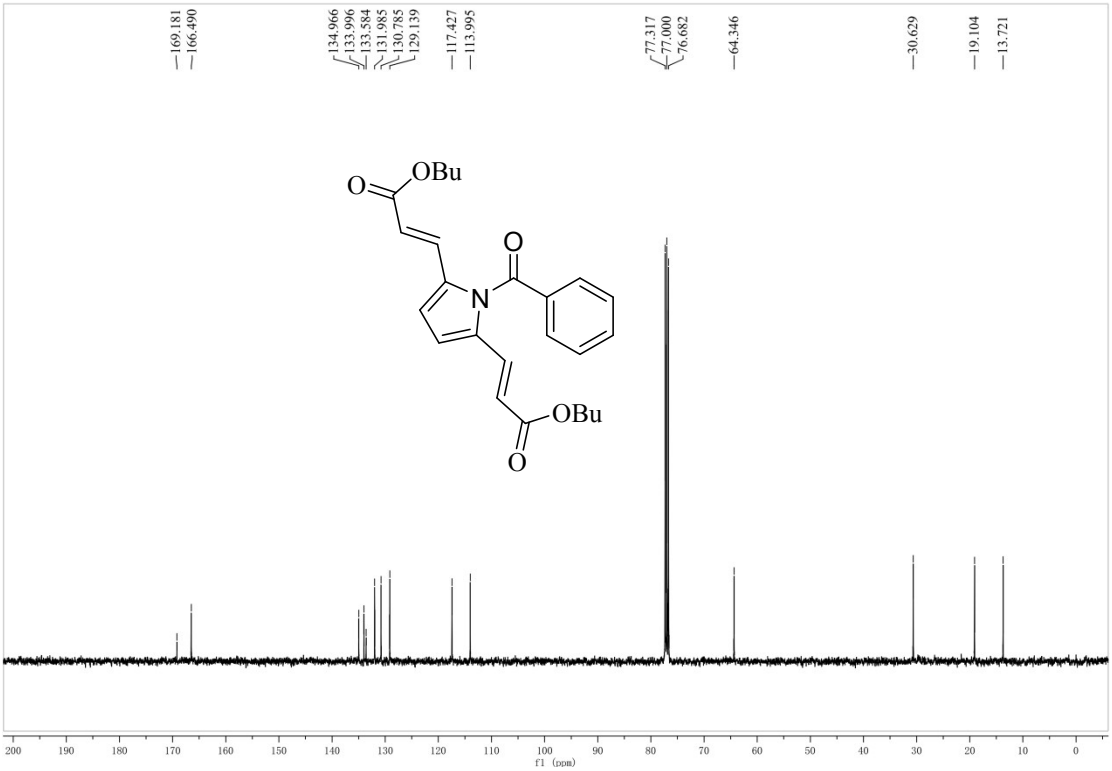
3-(1-benzoyl-1H-pyrrol-2-yl)-1-cyclohexylpropan-1-one (4ar)



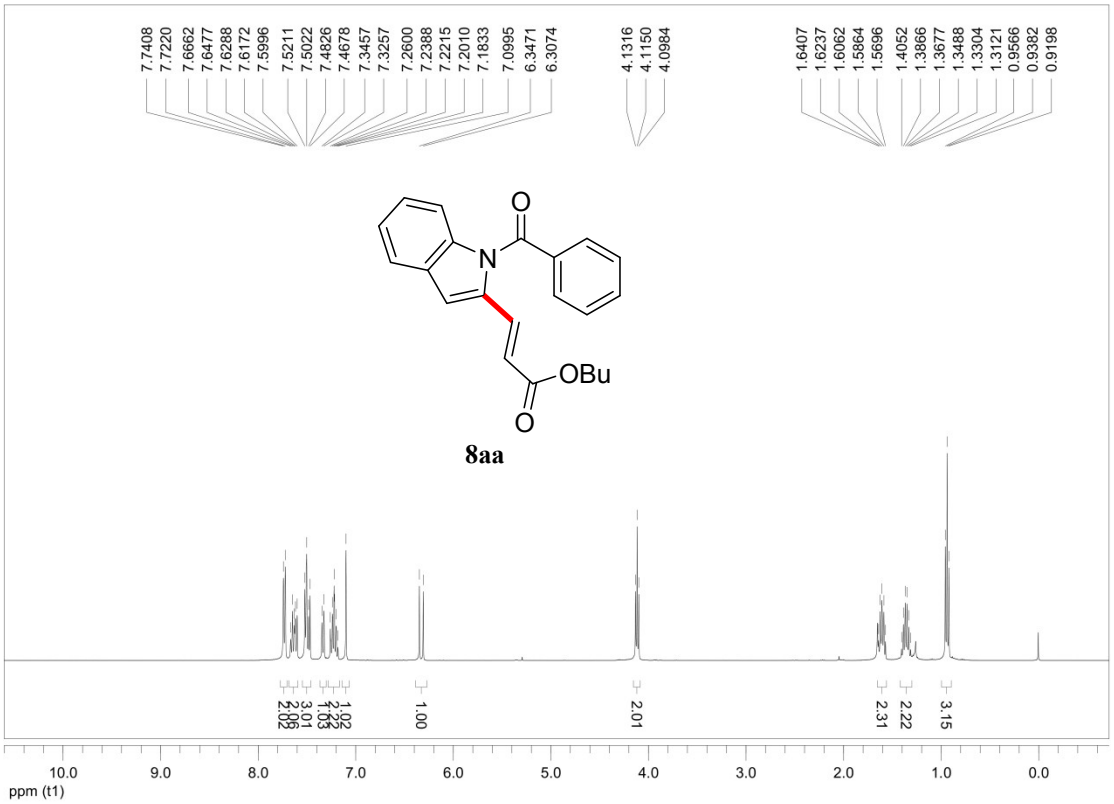


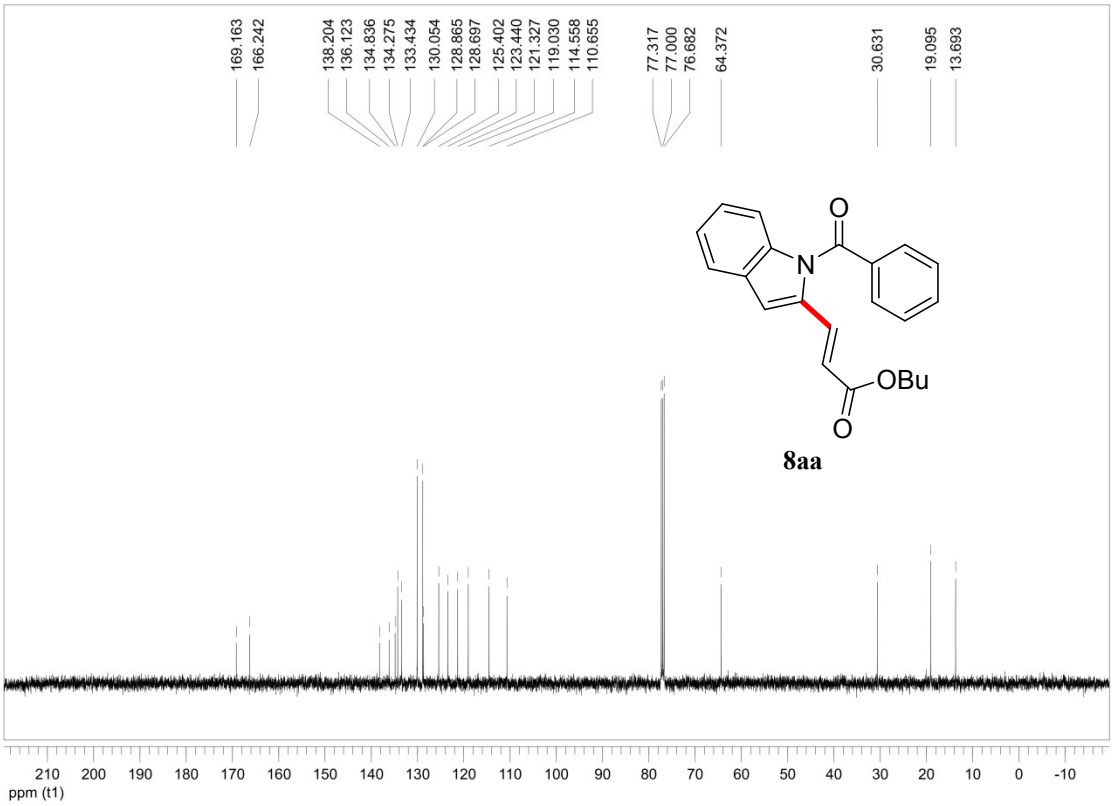
Dibutyl 3,3'-(1-benzoyl-1*H*-pyrrole-2,5-diyl)(2*E*,2'*E*)-diacrylate (6aa)



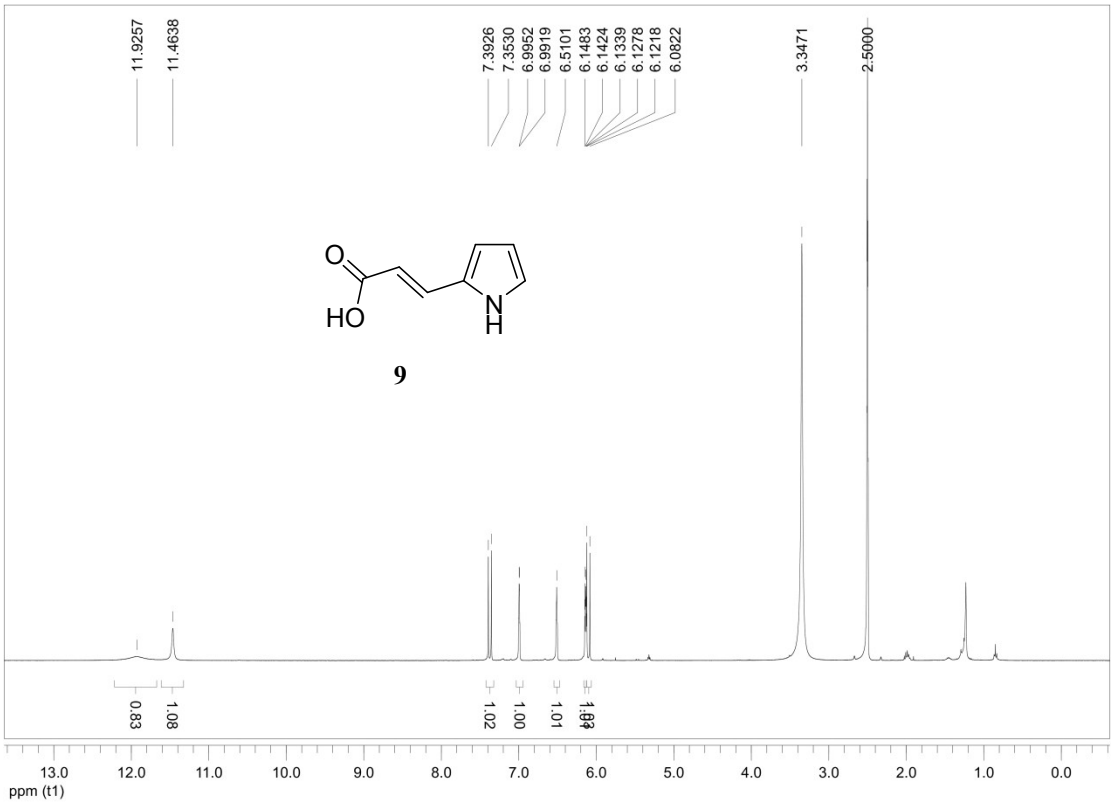


Butyl (*E*)-3-(1-benzoyl-1*H*-indol-2-yl)acrylate (8aa)





(*E*)-3-(1*H*-pyrrol-2-yl)acrylic acid (9)



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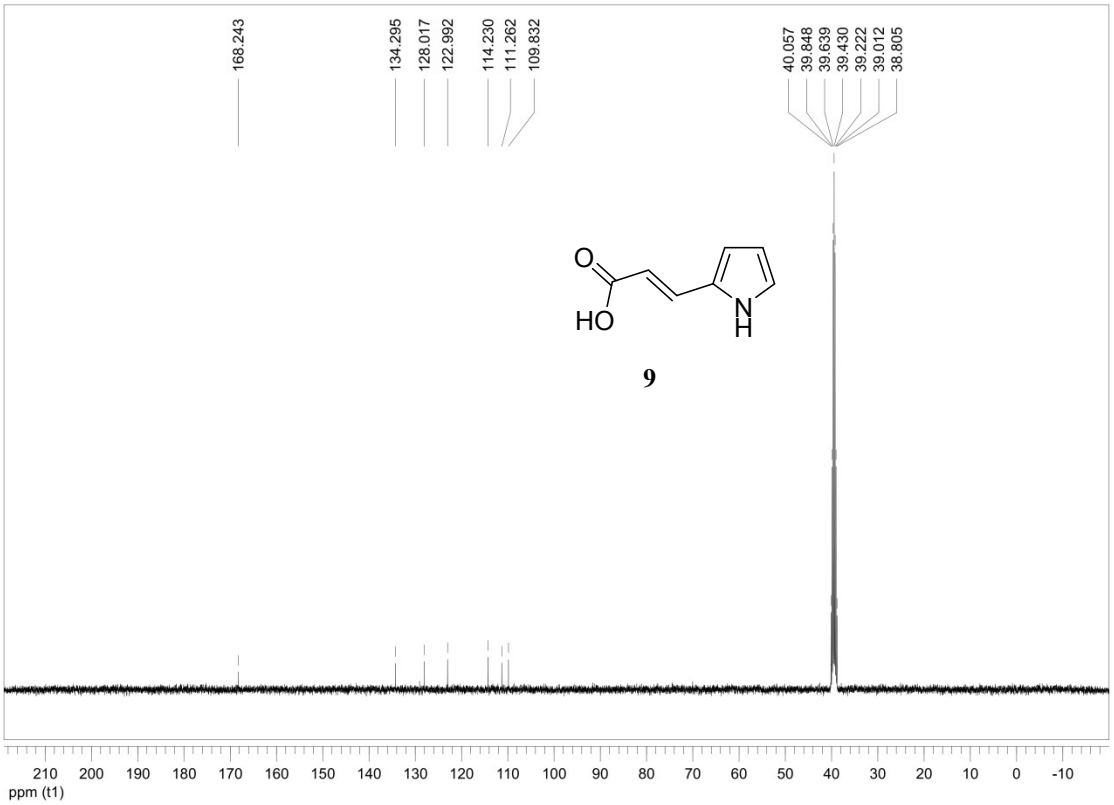

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