

Supporting Information

Dual Photoredox/Nickel-catalyzed Mizoroki-Heck Cross - Coupling Reactions

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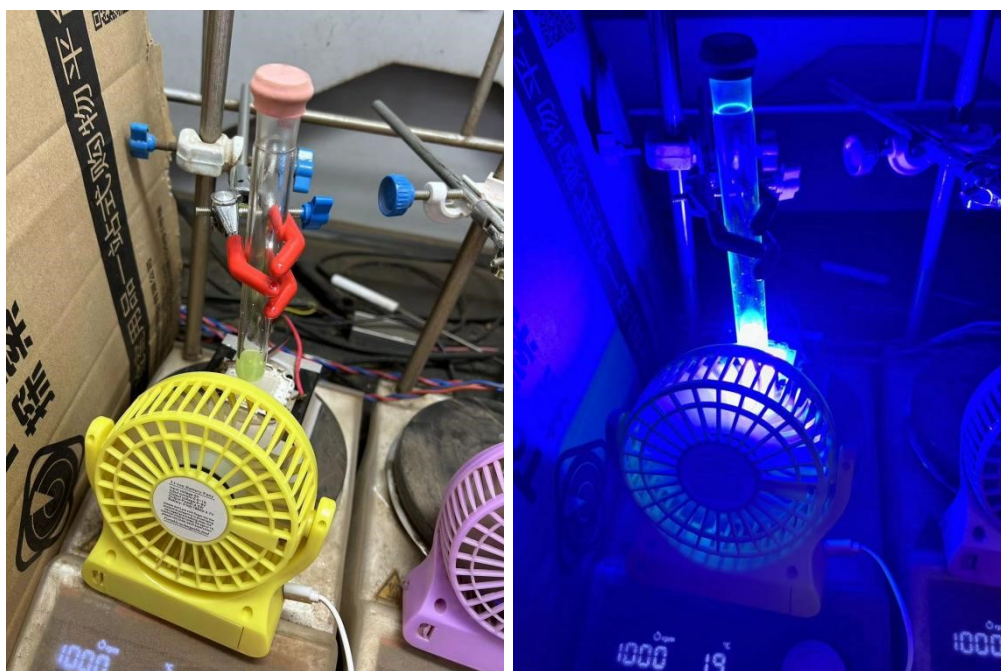
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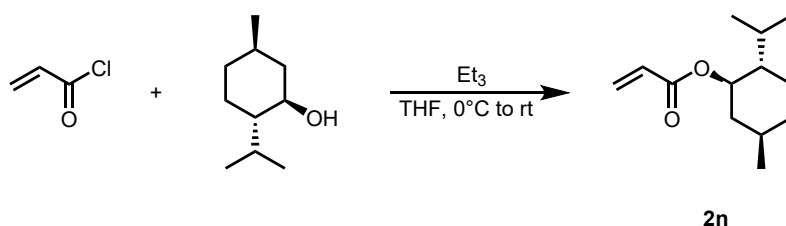
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I. General information

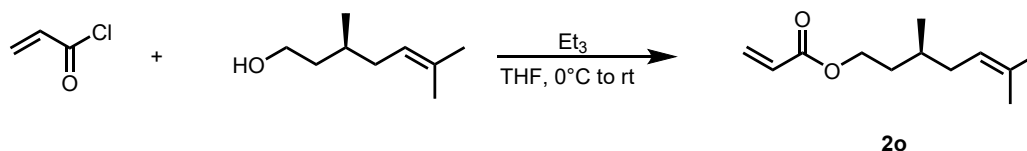
Unless stated otherwise, all reactions were carried out under argon. ^1H NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. ^{19}F NMR spectra were obtained at 376 MHz. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure with petroleum ether and ethyl acetate as eluents. Commercially available reagents were used without further purification unless indicated otherwise, all solvents were dried, super dry ethyl acetate (EA) (water ≤ 50 ppm) was purchased Energy Chemical Ltd, the following chemical reagent was purchased from Energy Chemical Ltd and Leyan Ltd: $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})(\text{PF}_6)$, $\text{Ni}(\text{dtbbpy})\text{Cl}_2$, cyclohexylboronic acid, Na_2CO_3 , **1a-1r** and **2a-2m**. The light source was 30 W Blue LED (450 nm, 1 W*30, 30-50 cd/m^2 , made in Everlight Electronics, Ltd.); borosilicate glass Schlenk tube was used as the irradiation vessel; the distance from the light source to the irradiation vessel; 2-3 cm and no filter was used.



II. Substrate synthesis



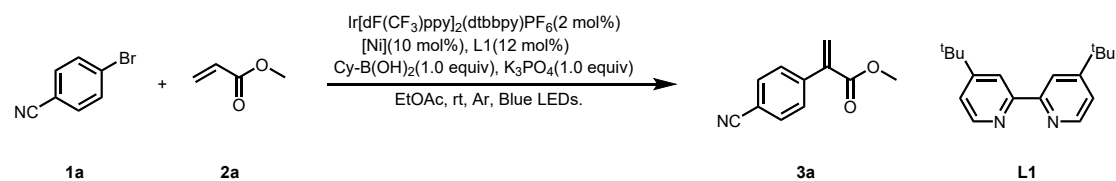
2i was synthesized according to literature report.^[1] To a stirred solution of L-menthol (1.56 g, 10.0 mmol) in THF (40 mL) at 0 °C were added acryloyl chloride (1.08 g, 12.0 mmol) and Et₃N (1.52 g, 15.0 mmol). After stirring for 12 h, acetic acid buffer (PH 4.0, 30 mL) was added to the reaction mixture, which was then extracted with EtOAc (3 × 20 mL). The combined extracts were washed with brine (20 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by chromatography (PE: EA = 80: 1 v/v) to give **2n** with 85% yield.



2o was synthesized according to literature report.^[2] To a stirred solution of (*S*)-3,6-dimethylhept-5-en-1-ol (10.0 mmol, 1.42 g) in THF (40 mL) at 0 °C were added acryloyl chloride (1.08 g, 12.0 mmol) and Et₃N (1.52 g, 15.0 mmol). After stirring for 12 h, acetic acid buffer (PH 4.0, 30 mL) was added to the reaction mixture, which was then extracted with EtOAc (3 × 20 mL). The combined extracts were washed with brine (20 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by chromatography (PE: EA = 100: 1 v/v) to give **2o** with 78% yield.

III. Optimization of reaction conditions

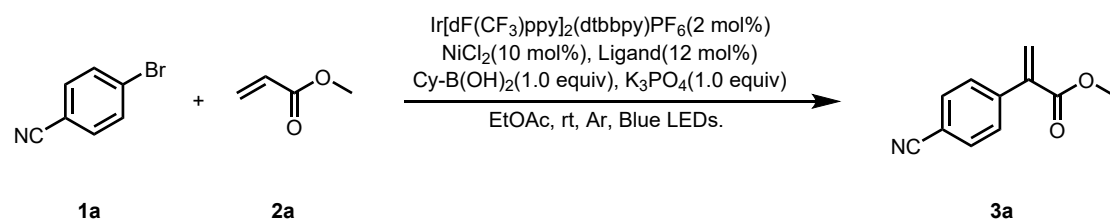
1. Screening of nickel catalyst



Entry	Nickel catalyst	Yield of 3a (%)
1	NiBr ₂ ·DME	46
2	NiCl ₂ ·DME	48
3	NiCl ₂	51
4	NiBr ₂	23
5	NiI ₂	N.R.
6	NiCl ₂ ·Py ₄	49
7	NiBr ₂ (PPh) ₃	N.R.
8	Ni(COD) ₂	44

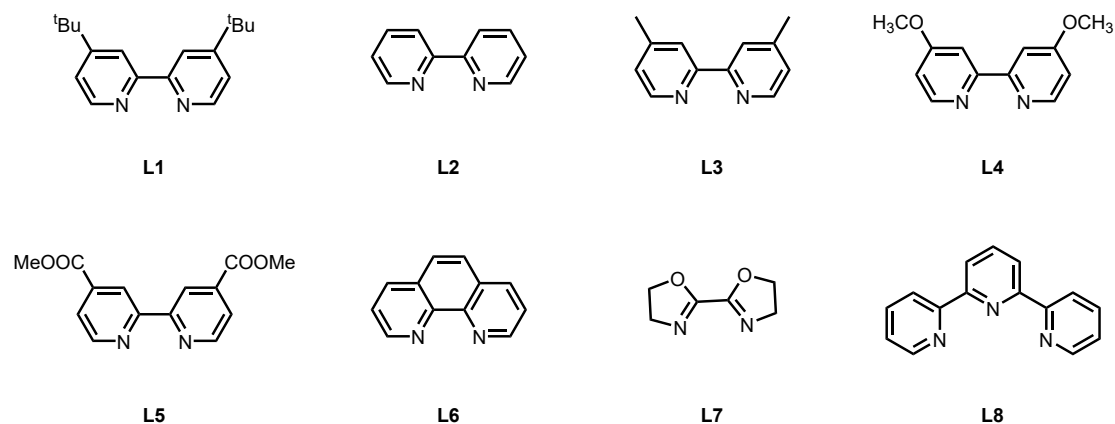
Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), [Ni] (0.02 mmol), L1 (6.5 mg, 0.024 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.4 mg, 0.004 mmol), Cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), K₃PO₄ (42.5 mg, 0.20 mmol, 1.0 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography. N.R. = no reaction. Trace = Raw material is declining but no product is being monitored. DME = Dimethoxyethane

2. Screening of ligand

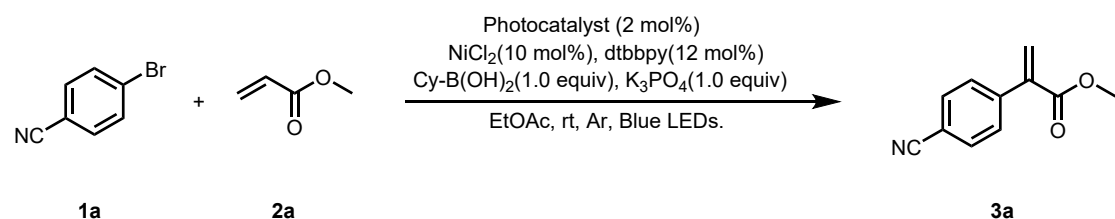


Entry	Ligand	Yield of 3a (%)
1	--	N.R.
2	L1	51
3	L2	31
4	L3	34
5	L4	N.R.
6	L5	N.R.
7	L6	N.R.
8	L7	N.R.
9	L8	N.R.

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl₂ (2.6 mg, 0.02 mmol), Ligand (0.024 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.4 mg, 0.004 mmol), Cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), K₃PO₄ (42.5 mg, 0.20 mmol, 1.0 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography. N.R. = no reaction. Trace = Raw material is declining but no product is being monitored.



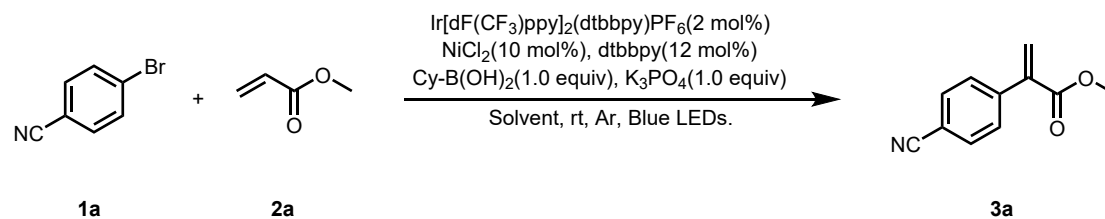
3. Screening of photocatalyst



Entry	Photocatalyst	E* _{1/2} (V vs SCE) ^[3]	Yield of 3a (%)
1	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	-0.89	51
2	4CzIPN	-1.21	N.R.
3	Ir(ppy) ₃	-1.73	N.R.
4	Ru(bpy) ₃ Cl ₂	-0.81	N.R.
5	EosinY	-1.08	N.R.

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), photocatalyst (0.004 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), K₃PO₄ (42.5 mg, 0.20 mmol, 1.0 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography. N.R. = no reaction. Trace = Raw material is declining but no product is being monitored.

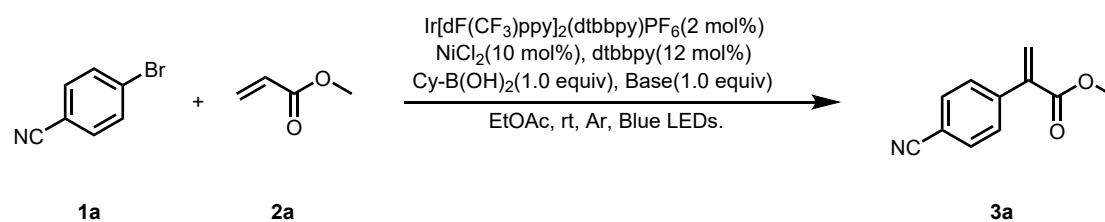
4. Screening of solvent



Entry	Solvent	Yield of 3a (%)
1	EtOAc	51
2	MeCN	N.R.
3	THF	trace
4	PhMe	N.R.
5	1,4-dioxane	22
6	DCM	trace
7	DCE	28
8	DMF	N.R.
9	DMSO	N.R.
10	DMAc	N.R.

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl_2 (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (4.4 mg, 0.004 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), K_3PO_4 (42.5 mg, 0.20 mmol, 1.0 equiv), and solvent (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography. N.R. = no reaction. Trace = Raw material is declining but no product is being monitored.

5. Screening of base

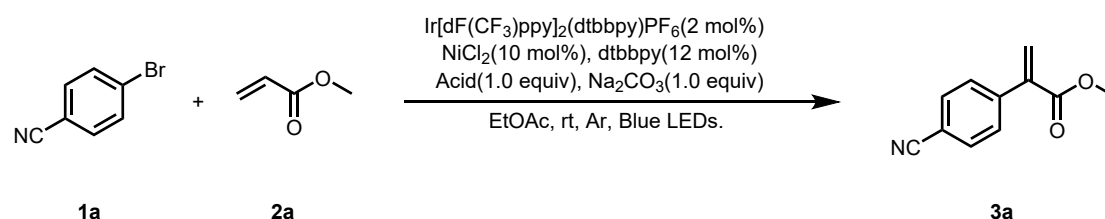


Entry	Base	Yield of 3a (%)
1	K_3PO_4	51
2	K_2HPO_4	55
3	Na_2CO_3	70
4	NaHCO_3	69
5	K_2CO_3	63
6	KHCO_3	68
7	Li_2CO_3	32
8	Cs_2CO_3	52

9	NaOAc	N.R.
10	LiOH	24
11	DBU	36

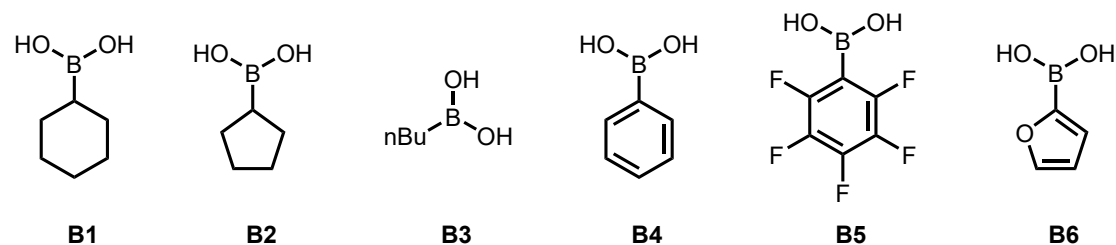
Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.4 mg, 0.004 mmol), Cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Base (0.20 mmol, 1.0 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography. N.R. = no reaction. Trace = Raw material is declining but no product is being monitored.

6. Screening of acid

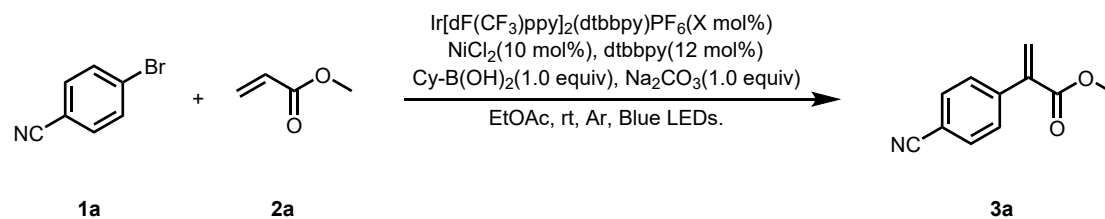


Entry	Acid	Yield of 3a (%)
1	Cyclohexylboronic acid (B1)	70
2	Cyclopentylboronic acid (B2)	63
3	Butylboronic acid (B3)	trace
4	Phenylboronic acid (B4)	34
5	Perfluorophenylboronic acid (B5)	N.R.
6	2-Furanboronic acid (B6)	trace
7	B(OH) ₃	N.R.
8	CF ₃ COOH	N.R.
9	CH ₃ COOH	N.R.
10	B ₂ pin ₂	61

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.4 mg, 0.004 mmol), acid (0.20 mmol, 1.0 equiv), Na₂CO₃ (21.2 mg, 0.20 mmol, 1.0 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography. N.R. = no reaction. Trace = Raw material is declining but no product is being monitored.



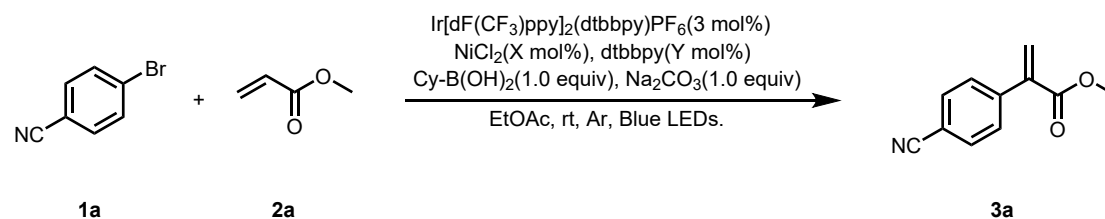
7. Screening of the amount of photocatalyst



Entry	Amount of Photocatalyst	Yield of 3a (%)
1	1 mol%	66
2	2 mol%	70
3	3 mol%	76
4	5 mol%	75

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (X mol%), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na₂CO₃ (21.2 mg, 0.20 mmol, 1.0 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography.

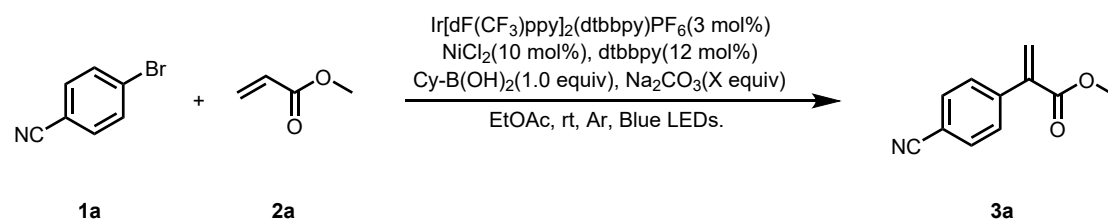
8. Screening of the amount of NiCl₂ and dtbbpy



Entry	Amount of NiCl ₂	Amount of dtbbpy(L1)	Yield of 3a (%)
1	3 mol%	5 mol%	69
2	5 mol%	7 mol%	73
3	8 mol%	10 mol%	75
4	10 mol%	12 mol%	76
5	13 mol%	15 mol%	70

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl₂ (X mol%), dtbbpy (Y mol%), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na₂CO₃ (21.2 mg, 0.20 mmol, 1.0 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography.

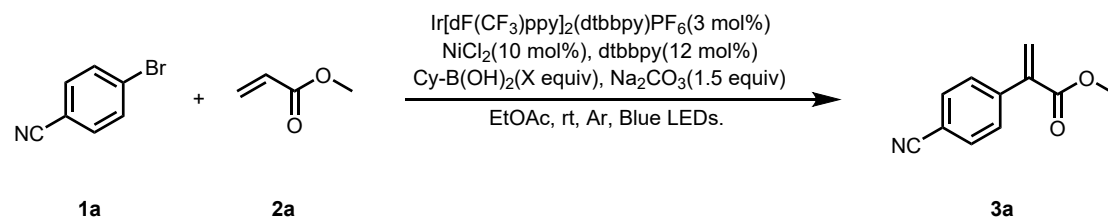
9. Screening of the amount of base



Entry	Amount of Base	Yield of 3a (%)
1	0.5 equiv	43
2	1.0 equiv	76
3	1.2 equiv	77
4	1.5 equiv	79
5	2.0 equiv	79

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na₂CO₃ (X equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography.

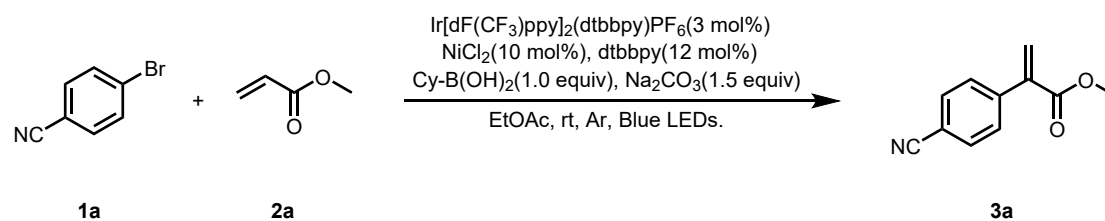
10. Screening of the amount of Cy-B(OH)₂



Entry	Amount of Cy-B(OH) ₂	Yield of 3a (%)
1	0.5 equiv	32
2	0.8 equiv	56
3	1.0 equiv	79
4	1.2 equiv	77
5	1.5 equiv	75

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (25.9 mg, 0.30 mmol, 1.5 equiv), NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (X equiv), Na₂CO₃ (31.8 mg, 0.30 mmol, 1.5 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography.

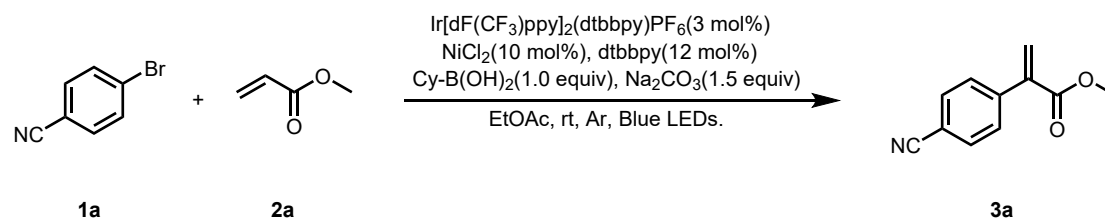
11. Screening of the amount of 2a



Entry	Amount of 2a	Yield of 3a (%)
1	1.0 equiv	68
2	1.5 equiv	79
3	2.0 equiv	86
4	3.0 equiv	85

Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (X equiv), NiCl_2 (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na_2CO_3 (31.8 mg, 0.30 mmol, 1.5 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography.

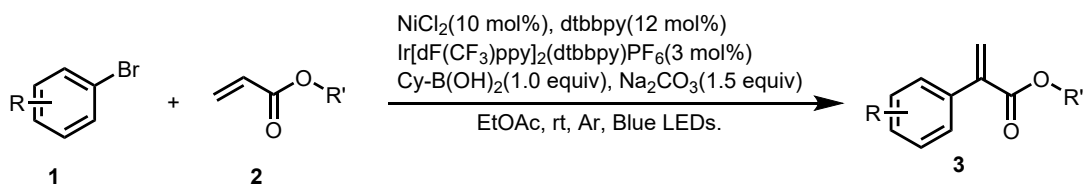
12. Control experimentes



Entry	Variation from standard conditions	Yield of 3a (%)
1	None	86
2	Without light	N.R.
3	Without $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$	N.R.
4	Without NiCl_2	N.R.
5	Without L1	N.R.
6	Without $\text{Cy-B}(\text{OH})_2$	trace
7	Without Base	N.R.

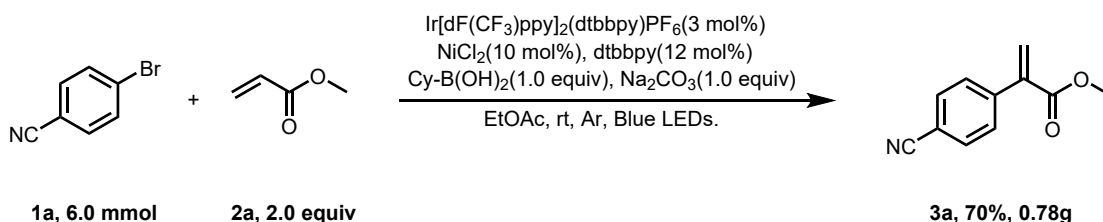
Reaction conditions: **1a** (36.4 mg, 0.20 mmol, 1.0 equiv), **2a** (34.5 mg, 0.40 mmol, 2.0 equiv), NiCl_2 (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol), $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na_2CO_3 (31.8 mg, 0.30 mmol, 1.5 equiv), and EtOAc (2.0 mL, 0.1 M) was irradiated with 30 W Blue LEDs at room temperature under argon. Yield of the isolated product after column chromatography.

IV. General procedure for Mizoroki-Heck cross-coupling of aryl bromide with aryl alkenes



In argon atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk-tube. NiCl_2 (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol) and EtOAc (1 mL) were filled into the tube for complex first. After 30min, to the oven-dried Schlenk-tube, aryl bromide (0.20 mmol, 1.0 equiv), acrylate (0.40 mmol, 2.0 equiv), $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na_2CO_3 (31.8 mg, 0.30 mmol, 1.5 equiv) and EtOAc (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W Blue LEDs (450 nm) at room temperature. After completion of the reaction, the reaction mixture was concentrated by vacuum, purified by silica gel chromatography, and eluted by petroleum ether/ethyl acetate to obtain products **3**.

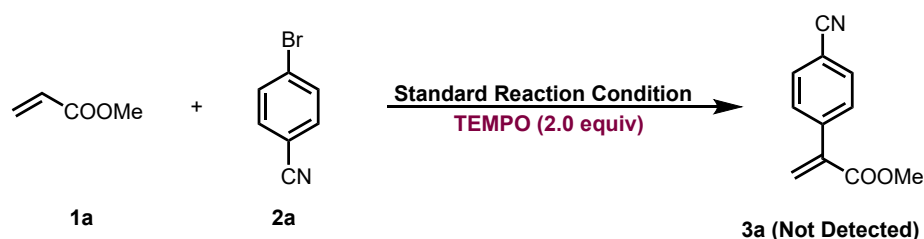
V. Gram-scale Reaction



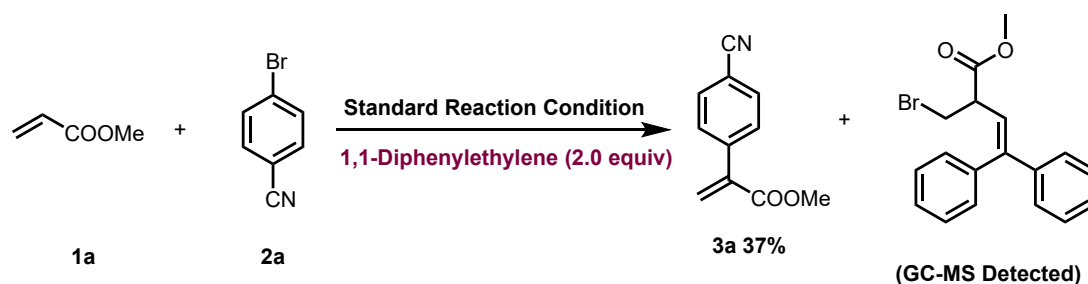
Based on the reaction system established above, in order to further prove the feasibility and practicability of this reaction system, we conducted a gram experiment on this reaction. An oven-dried 100 mL three-neck Schlenk flask with magnetic stirring bar was charged with NiCl_2 (84.0 mg, 0.60 mmol), dtbbpy (210.0 mg, 0.72 mmol) and EtOAc (15 mL) were filled into the tube for complex first. After 30min, to the oven-dried Schlenk-tube, 4-Bromobenzonitrile (1.092 g, 6.0 mmol, 1.0 equiv), methyl acrylate (1.032 g, 12.0 mmol, 2.0 equiv), $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (198.0 mg, 0.18 mmol), cyclohexylboronic acid (0.768 g, 6.0 mmol, 1.0 equiv), Na_2CO_3 (0.954 g, 9.0 mmol, 1.5 equiv) and EtOAc (15 mL) were added under argon atmosphere. The reaction mixture was degassed by bubbling with Ar. The mixture was then stirred rapidly and irradiated with 30 W 450 nm Blue LEDs at room temperature for 24 h. The reaction mixture was concentrated in vacuo to remove the EtOAc. Purified by silica gel chromatography, and eluted by petroleum ether/ethyl acetate to obtain products (0.785 g, 70%).

VI. Mechanistic studies

1. Radical-trapping experiment



In argon atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk-tube. NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol) and EtOAc (1 mL) were filled into the tube for complex first. After 30min, to the oven-dried Schlenk-tube, 4-Bromobenzonitrile (36.4 mg, 0.20 mmol, 1.0 equiv), methyl acrylate (34.5 mg, 0.40 mmol, 2.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na₂CO₃ (31.8 mg, 0.30 mmol, 1.5 equiv), TEMPO (62.6 mg, 0.4 mmol, 2.0 equiv) and EtOAc (1 mL) were added under argon atmosphere. The mixture was then stirred rapidly and irradiated with 30 W 450 nm Blue LEDs (approximately 2 cm away from the light source) at room temperature for 6 h. The reaction was fully suppressed.



In argon atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk-tube. NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol) and EtOAc (1 mL) were filled into the tube for complex first. After 30min, to the oven-dried Schlenk-tube, 4-Bromobenzonitrile (36.4 mg, 0.20 mmol, 1.0 equiv), methyl acrylate (34.5 mg, 0.40 mmol, 2.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na₂CO₃ (31.8 mg, 0.30 mmol, 1.5 equiv), 1,1'-(1,2-ethenediyl) dibenzene (0.12 mL, 0.4 mmol, 2.0 equiv) and EtOAc (1 mL) were added under argon atmosphere. The mixture was then stirred rapidly and irradiated with 30 W 450 nm LEDs (approximately 2 cm away from the light source) at room temperature for 6 h. The reaction was suppressed. The radical trapping product can be observed by GC-MS.

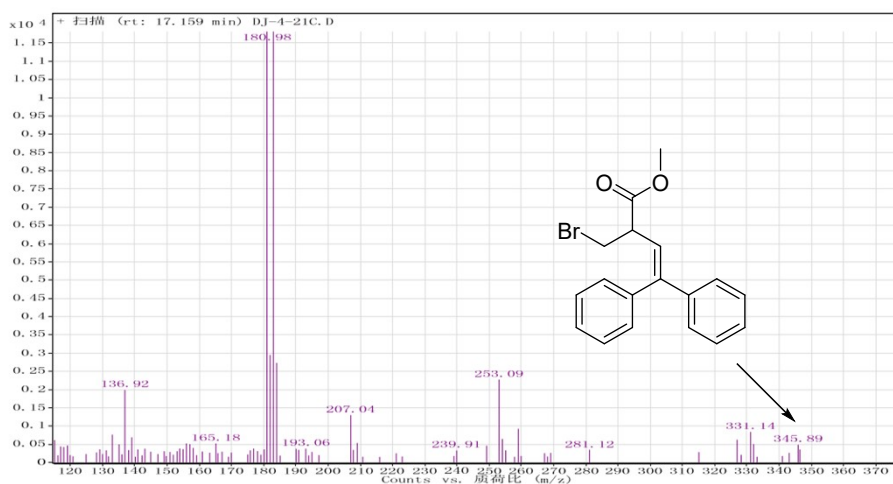
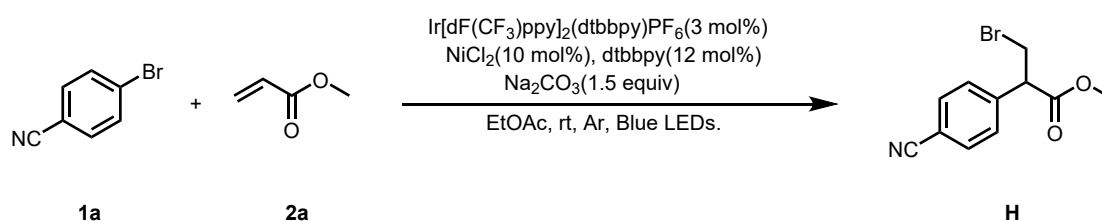
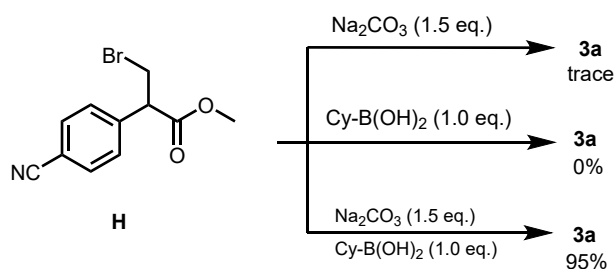


Figure S1 GC-MS analysis of radical trapping adducts

2. Experiment control of hydrogen bromide elimination



In argon atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk-tube. NiCl_2 (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol) and EtOAc (1 mL) were filled into the tube for complex first. After 30min, to the oven-dried Schlenk-tube, 4-bromobenzonitrile (36.4 mg, 0.20 mmol, 1.0 equiv), methyl acrylate (34.5 mg, 0.40 mmol, 2.0 equiv), $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (6.6 mg, 0.006 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol, 1.5 equiv) and EtOAc (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W Blue LEDs (450 nm) at room temperature. After completion of the reaction, the reaction mixture was concentrated by vacuum, purified by silica gel chromatography, and eluted by petroleum ether/ethyl acetate to obtain product precursor **H**.



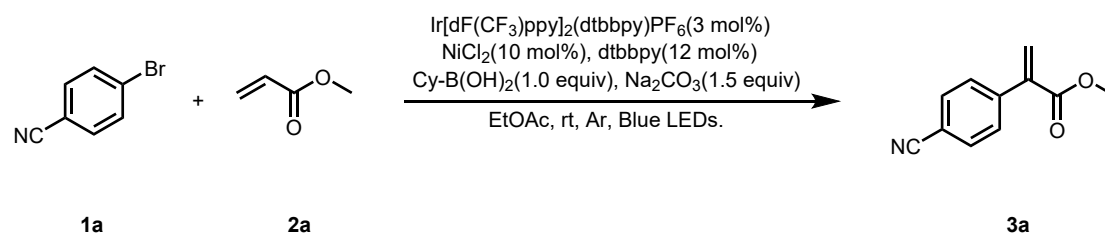
To an oven dried Schlenk-tube, product precursor **H** (26.8 mg, 0.10 mmol, 1.0 equiv), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv) and EtOAc (1 mL) were added under argon atmosphere and stirred at room temperature for 2 h. Trace product **3a** was detected.

To an oven dried Schlenk-tube, product precursor **H** (26.8 mg, 0.10 mmol, 1.0 equiv), cyclohexylboronic acid (12.8 mg, 0.10 mmol, 1.0 equiv), and EtOAc (1 mL)

were added under argon atmosphere and stirred at room temperature for 2 h. **3a** was not detected

To an oven dried Schlenk-tube, product precursor **H** (26.8 mg, 0.10 mmol, 1.0 equiv), cyclohexylboronic acid (12.8 mg, 0.10 mmol, 1.0 equiv), Na₂CO₃ (15.9 mg, 0.15 mmol, 1.5 equiv) and EtOAc (1 mL) were added under argon atmosphere and stirred at room temperature for 2 h. Purified by silica gel chromatography, and eluted by petroleum ether/ethyl acetate to obtain products (17.7 mg, 95%).

3. Light/Dark experiment



To an oven dried Schlenk-tube, NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol) and EtOAc (1 mL) were filled into the tube for complex first. After 30 min, to the oven-dried Schlenk-tube, 4-Bromobenzonitrile (36.4 mg, 0.20 mmol, 1.0 equiv), methyl acrylate (34.5 mg, 0.40 mmol, 2.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na₂CO₃ (31.8 mg, 0.30 mmol, 1.5 equiv) and EtOAc (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W Blue LEDs (450 nm) at room temperature. The reaction tube was wrapped in tin foil and a 20 μL sample of the reaction mixture was taken with a syringe and measured by GC. After being stirred for 2 hours in dark, a 20 μL sample of the reaction mixture was taken with a syringe and measured by GC. The reaction mixture was then irradiated with a 30 W Blue LEDs (450 nm) lamp and stirred for 2 hours. This process was repeated two times.

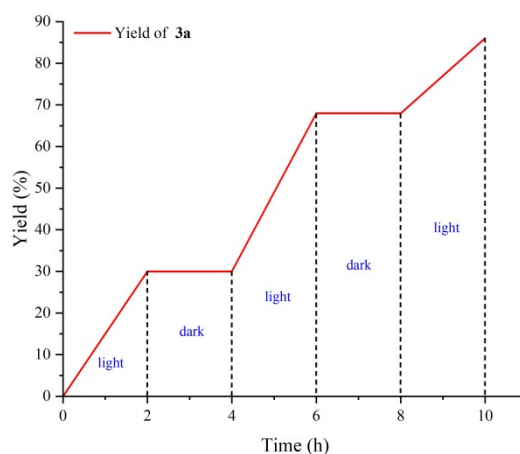


Figure S2 light on-off experiments

4. Measurement of quantum yields

The photon flux of blue LEDs was determined by standard ferrioxalate actinometry.

0.15 mol/L solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328 mg, 0.750 mmol) in 5.0 mL of 0.20 mol/L aqueous sulfuric acid.

0.15 mol/L buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg, 0.3 mmol) and sodium acetate (1.23 g, 15.0 mmol) in 20 mL of 0.20 mol/L aqueous sulfuric acid. The actinometry measurements were done as follows: To a reaction tube equipped with a stir bar was added 0.50 mL of the ferrioxalate solution. The reaction tube was sealed and placed 2 cm away from a 30 W blue LEDs. After irradiation for 5 seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution was added to the reaction tube. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50 μ L of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 mol/L aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette ($l = 1.0$ cm) at 510 nm was measured by UV-Vis spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

The amount of ferrous ion formed was calculated as follows:

$$\text{mol } Fe^{2+} = \frac{V \times \Delta A}{l \times \varepsilon}$$

where V is the total volume (0.024 L) of the solution that was analyzed, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L/(mol \cdot cm)).

The photon flux was calculated as follows:

$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f}$$

where Φ is the quantum yield for the ferrioxalate actinometer, t is the irradiation time, and f is the fraction of light absorbed at 450 nm (0.2429).

The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-A}$$

where A is the measured absorbance (0.1208) of the 0.15 mol/L solution of potassium ferrioxalate at 450 nm.

The photo flux is 3.25×10^{-7} Einstein/s.

Determination of quantum yield:

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a sample of NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol) and EtOAc (1 mL) were filled into the tube for complex first. After 30min, to the oven-dried Schlenk-tube, 4-Bromobenzonitrile (36.4 mg, 0.20 mmol, 1.0 equiv), methyl acrylate (34.5 mg, 0.40 mmol, 2.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na₂CO₃ (31.8 mg,

0.30 mmol, 1.5 equiv) and EtOAc (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W Blue LEDs at room temperature and placed 2 cm away from 30 W Blue LEDs. After 2 hours of irradiation, the molar number of the product **3a** was determined by ¹H NMR spectroscopy with (1,3-Benzodioxole) as the internal standard. The yield of **3a** was 30% (0.060 mmol).

The quantum yield was calculated as follows:

$$\Phi = \frac{\text{mol product}}{\text{photon flux} \times t \times f}$$

where flux is the photon flux determined by ferrioxalate actinometry (3.25×10^{-7} Einstein/s), t is the time, and f is the fraction of light absorbed by the irradiated reaction system at 450 nm, and the absorbance of the irradiated reaction system at 450 nm was 0.027. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-0.027} = 0.0597$.

The quantum yield was calculated: $\Phi = 0.21$

Thus, quantum yield ($\Phi = 0.21$) less than unity and results of light on-off experiment, indicate the reaction proceeds via non-chain process.

5. Fluorescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 5.0×10^{-6} M Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆, in degassed dry EtOAc at room temperature. The solutions were irradiated at 350 nm and fluorescence was measured from 440 nm to 650 nm. Control experiments showed that the excited state Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆* was mainly quenched by e⁻[(dtbbpy)Ni(Ar)(Br)]. [(dtbbpy)Ni(Ar)(Br)] solution was prepared by mixing 4-Bromobenzonitrile with Ni(dtbbpy)Cl₂ for 10 minutes in EtOAc.

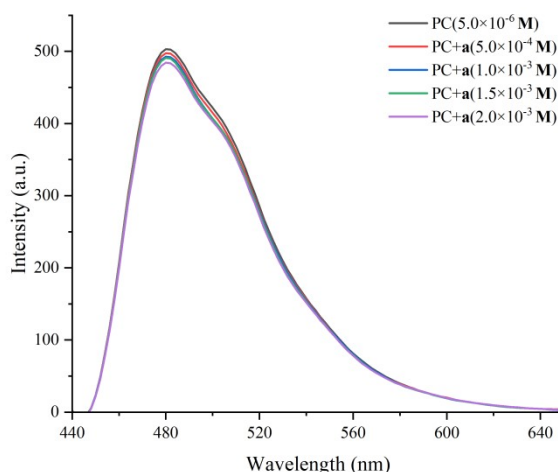


Figure S3 Fluorescence quenching data with PC and variable **a** 4-bromobenzonitrile

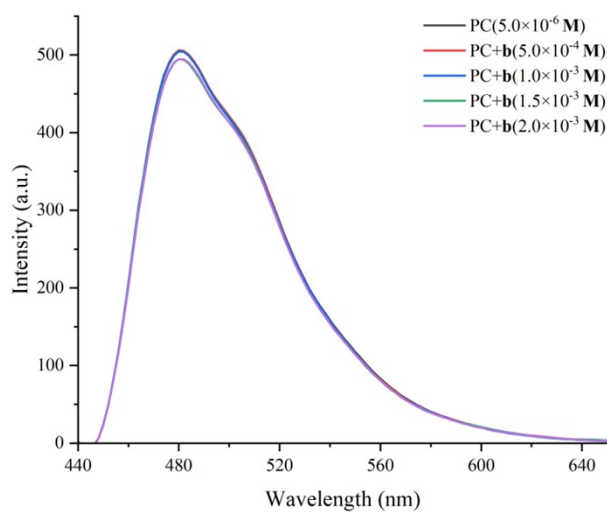


Figure S4 Fluorescence quenching data with PC and variable **b** methyl acrylate

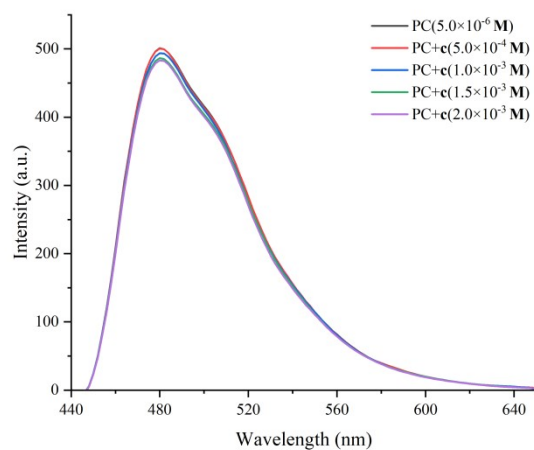


Figure S5 Fluorescence quenching data with PC and variable **c** Cyclohexylboronic acid

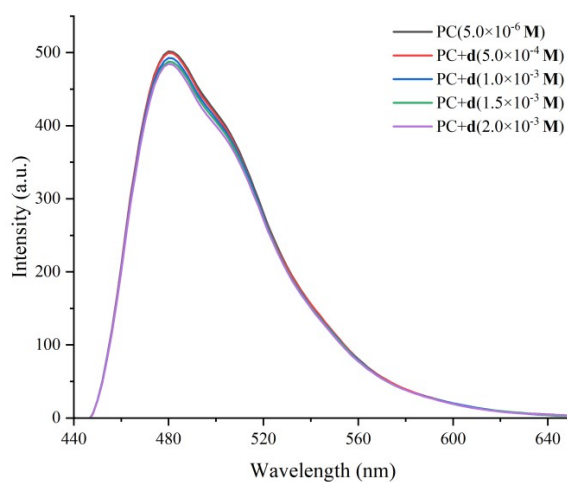


Figure S6 Fluorescence quenching data with PC and variable **d** Ni(dtbbpy)Cl₂

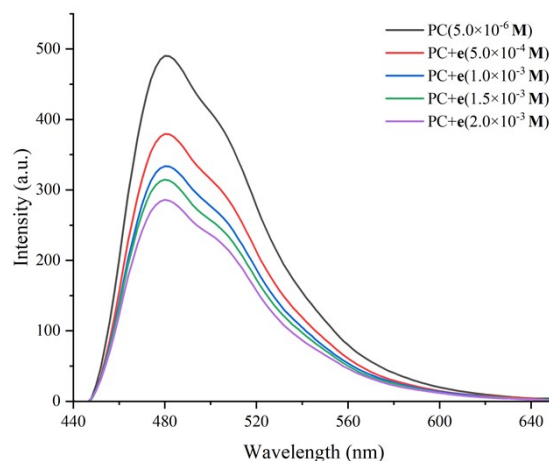
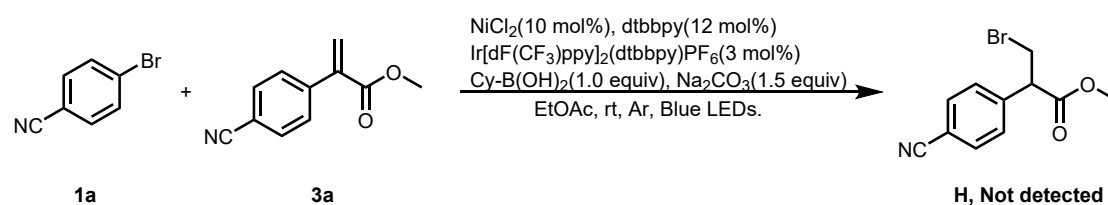


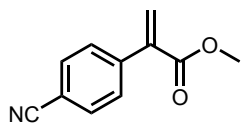
Figure S7 Fluorescence quenching data with PC and variable **e** [(dtbbpy)Ni(Ar)(Br)]

6. Control experiment of **1a** and product **3a**



In argon atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk-tube. NiCl₂ (2.8 mg, 0.02 mmol), dtbbpy (7.0 mg, 0.024 mmol) and EtOAc (1 mL) were filled into the tube for complex first. After 30min, to the oven-dried Schlenk-tube, 4-Bromobenzonitrile (0.20 mmol, 1.0 equiv), **3a** (0.20 mmol, 1.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (6.6 mg, 0.006 mmol), cyclohexylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv), Na₂CO₃ (31.8 mg, 0.30 mmol, 1.5 equiv) and EtOAc (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W Blue LEDs (450 nm) at room temperature. No production of product precursor **H** was found.

VII. Characterization data of products

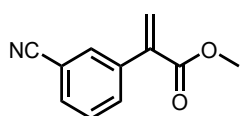


methyl 2-(4-cyanophenyl)acrylate(3a)^[4]

32.1 mg, 86% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.69 – 7.62 (m, 2H), 7.58 – 7.50 (m, 2H), 6.51 (d, *J* = 0.9 Hz, 1H), 6.00 (d, *J* = 0.9 Hz, 1H), 3.84 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 166.3, 141.4, 140.0, 132.1, 129.5, 129.3, 118.9, 112.1, 52.7.



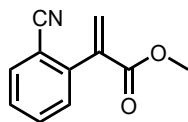
methyl 2-(3-cyanophenyl)acrylate(3b)

29.9 mg, 80% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.76 – 7.71 (m, 1H), 7.65 (ddt, *J* = 10.8, 7.8, 1.3 Hz, 2H), 7.48 (td, *J* = 7.8, 0.6 Hz, 1H), 6.51 (d, *J* = 0.9 Hz, 1H), 5.98 (d, *J* = 0.9 Hz, 1H), 3.85 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 166.4, 139.5, 138.1, 133.0, 132.3, 131.9, 129.3, 129.2, 118.8, 112.6, 52.7.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₁H₉NO₂ 188.0706, found 188.0706.

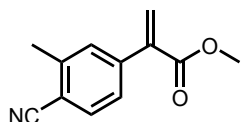


methyl 2-(2-cyanophenyl)acrylate(3c)^[5]

23.1 mg, 62% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 (td, *J* = 7.7, 1.4 Hz, 1H), 7.45 (td, *J* = 7.7, 1.3 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.72 (d, *J* = 0.9 Hz, 1H), 6.01 (d, *J* = 0.8 Hz, 1H), 3.84 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.8, 141.0, 138.7, 133.1, 132.7, 131.8, 130.4, 128.7, 118.0, 112.6, 52.8.



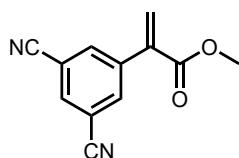
methyl 2-(4-cyano-3-methylphenyl)acrylate(3d)

35.3 mg, 88% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.32 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.48 (d, *J* = 0.9 Hz, 1H), 5.97 (d, *J* = 1.0 Hz, 1H), 3.84 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 166.5, 142.0, 141.2, 140.1, 132.5, 130.3, 129.2, 126.5, 118.2, 112.5, 52.7, 20.8.

TOFMS-ESI⁺ (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$ 202.0863, found 202.0863.



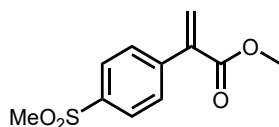
methyl 2-(3,5-dicyanophenyl)acrylate(3e)

20.3 mg, 48% yield; Colorless oil.

^1H NMR (400 MHz, CD_3Cl) δ 7.97 (d, $J = 1.5$ Hz, 2H), 7.91 (t, $J = 1.6$ Hz, 1H), 6.64 (s, 1H), 6.08 (s, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 165.4, 139.6, 137.7, 136.1, 134.7, 131.2, 116.7, 114.3, 53.1.

TOFMS-ESI⁺ (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$ 213.0659, found 213.0659.



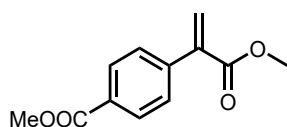
methyl 2-(4-(methylsulfonyl)phenyl)acrylate(3f)

35.0 mg, 73% yield; Colorless oil.

^1H NMR (400 MHz, CD_3Cl) δ 7.94 (d, $J = 8.5$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 6.53 (d, $J = 0.8$ Hz, 1H), 6.02 (d, $J = 0.8$ Hz, 1H), 3.85 (s, 3H), 3.07 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 166.4, 142.4, 140.3, 140.0, 129.7, 129.6, 127.5, 52.7, 44.8.

TOFMS-ESI⁺ (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{12}\text{O}_4\text{S}$ 241.0529, found 241.0529.

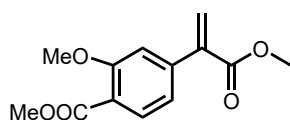


methyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)benzoate(3g)^[6]

33.8 mg, 77% yield; Colorless oil.

^1H NMR (400 MHz, CD_3Cl) δ 8.06 – 7.99 (m, 2H), 7.53 – 7.45 (m, 2H), 6.46 (d, $J = 1.1$ Hz, 1H), 5.98 (d, $J = 1.0$ Hz, 1H), 3.93 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 167.0, 166.9, 141.3, 140.7, 129.9, 129.6, 128.7, 128.6, 52.6, 52.4.



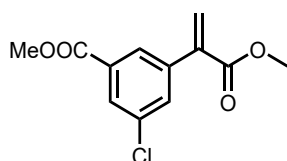
methyl 2-methoxy-4-(3-methoxy-3-oxoprop-1-en-2-yl)benzoate(3h)

37.5 mg, 75% yield; White solid. M.P : 84 °C

^1H NMR (400 MHz, CD_3Cl) δ 7.80 (d, $J = 8.1$ Hz, 1H), 7.12 – 6.97 (m, 2H), 6.46 (d, $J = 1.0$ Hz, 1H), 5.98 (d, $J = 1.1$ Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 166.8, 166.6, 159.0, 142.1, 140.6, 131.7, 128.6, 120.4, 119.6, 112.4, 56.3, 52.6, 52.3.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_5$ 251.0914, found 251.0915.



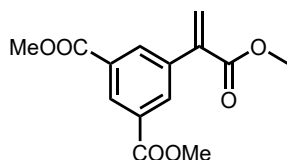
methyl 3-chloro-5-(3-methoxy-3-oxoprop-1-en-2-yl)benzoate(3i)

35.5 mg, 70% yield; White solid. M.P : 88 °C

^1H NMR (400 MHz, CD_3Cl) δ 7.98 (dt, $J = 10.8, 1.6$ Hz, 2H), 7.61 (t, $J = 1.9$ Hz, 1H), 6.49 (d, $J = 0.9$ Hz, 1H), 5.99 (d, $J = 0.9$ Hz, 1H), 3.93 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 166.4, 165.9, 139.4, 138.8, 134.5, 133.0, 131.8, 129.4, 129.2, 128.0, 52.7, 52.7.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for $\text{C}_{12}\text{H}_{11}\text{ClO}_4$ 255.0419, found 255.0419.



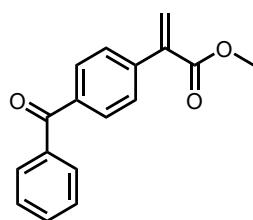
dimethyl 5-(3-methoxy-3-oxoprop-1-en-2-yl)isophthalate(3j)

31.6 mg, 57% yield; White solid. M.P : 96 °C

^1H NMR (400 MHz, CD_3Cl) δ 8.66 (t, $J = 1.7$ Hz, 1H), 8.28 (d, $J = 1.7$ Hz, 2H), 6.52 (d, $J = 0.9$ Hz, 1H), 6.03 (d, $J = 0.9$ Hz, 1H), 3.96 (s, 6H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 166.6, 166.2, 139.7, 137.7, 133.9, 130.8, 130.5, 129.2, 52.7.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for $\text{C}_{14}\text{H}_{14}\text{O}_6$ 279.0863, found 279.0863.



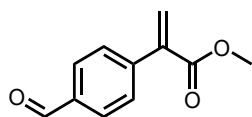
methyl 2-(4-benzoylphenyl)acrylate(3k)

39.3 mg, 74% yield; Colorless oil.

^1H NMR (400 MHz, CD_3Cl) δ 7.81 (dd, $J = 7.6, 5.7$ Hz, 4H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.56 – 7.45 (m, 4H), 6.48 (s, 1H), 6.01 (s, 1H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 196.4, 166.9, 140.9, 140.6, 137.7, 137.3, 132.7, 130.2, 130.1, 128.7, 128.5, 128.5, 52.6.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3$ 267.1016, found 267.1016.

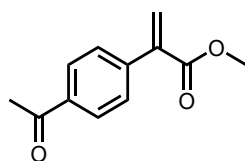


methyl 2-(4-formylphenyl)acrylate(3l)^[7]

15.9 mg, 42% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 10.04 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 6.51 (d, *J* = 0.9 Hz, 1H), 6.02 (d, *J* = 0.9 Hz, 1H), 3.85 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 192.1, 166.7, 142.9, 140.5, 136.0, 129.7, 129.3, 129.2, 52.7.

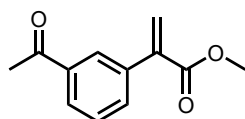


methyl 2-(4-acetylphenyl)acrylate(3m)^[8]

17.1 mg, 42% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 0.9 Hz, 1H), 5.99 (d, *J* = 0.9 Hz, 1H), 3.84 (s, 3H), 2.62 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 197.9, 166.8, 141.5, 140.6, 136.8, 128.8, 128.8, 128.4, 52.6, 26.9.



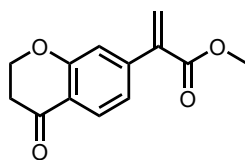
methyl 2-(3-acetylphenyl)acrylate(3n)

26.5 mg, 65% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 8.01 (t, *J* = 1.6 Hz, 1H), 7.94 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.62 (ddd, *J* = 7.7, 1.8, 1.2 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 6.47 (d, *J* = 1.1 Hz, 1H), 5.98 (d, *J* = 1.0 Hz, 1H), 3.84 (s, 3H), 2.63 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 198.1, 167.0, 140.6, 137.4, 137.2, 133.2, 128.6, 128.5, 128.4, 128.3, 52.6, 27.0.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₂H₁₂O₃ 205.0859, found 205.0859.



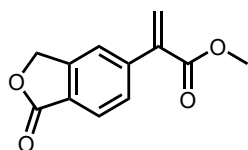
methyl 2-(4-oxochroman-7-yl)acrylate(3o)

31.0 mg, 67% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.46 (d, *J* = 0.9 Hz, 1H), 5.98 (d, *J* = 1.0 Hz, 1H), 4.59 – 4.52 (m, 2H), 3.84 (s, 3H), 2.97 – 2.73 (m, 2H).

¹³C NMR (101 MHz, CD₃Cl) δ 191.7, 166.6, 161.7, 144.5, 140.4, 129.0, 127.1, 121.8, 121.0, 118.0, 67.3, 52.7, 37.9.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₃H₁₂O₄ 233.0808, found 233.0809.



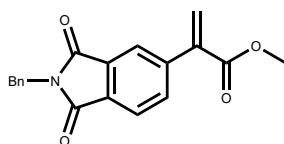
methyl 2-(1-oxo-1,3-dihydroisobenzofuran-5-yl)acrylate(3p)

29.2 mg, 67% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.53 (m, 2H), 6.55 (d, *J* = 0.9 Hz, 1H), 6.03 (d, *J* = 0.9 Hz, 1H), 5.34 (s, 2H), 3.86 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 171.0, 166.5, 146.7, 142.9, 140.3, 129.7, 125.7, 125.6, 122.3, 69.8, 52.7.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₂H₁₀O₄ 219.0652, found 219.0652.



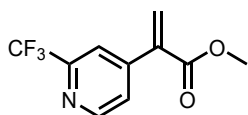
methyl 2-(2-benzyl-1,3-dioxoisindolin-5-yl)acrylate(3q)

54.5 mg, 85% yield; White solid. M.P : 108 °C

¹H NMR (400 MHz, CD₃Cl) δ 7.91 – 7.86 (m, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.36 – 7.22 (m, 3H), 6.56 (s, 1H), 6.03 (s, 1H), 4.85 (s, 2H), 3.84 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 167.9, 167.9, 166.2, 143.00, 139.9, 136.5, 134.3, 132.3, 131.6, 129.9, 128.9, 128.7, 128.0, 123.7, 123.4, 52.8, 41.9

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₉H₁₅NO₄ 322.1074, found 322.1073.



methyl 2-(2-(trifluoromethyl)pyridin-4-yl)acrylate(3r)

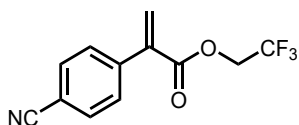
31.4 mg, 68% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 8.73 (d, *J* = 5.0 Hz, 1H), 7.76 (s, 1H), 7.57 (dd, *J* = 5.1, 1.4 Hz, 1H), 6.63 (s, 1H), 6.14 (s, 1H), 3.87 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.5, 150.2, 148.5 (d, *J* = 34.6 Hz), 146.1, 138.3, 131.2, 125.9, 121.7 (d, *J* = 274.3 Hz), 120.1 (q, *J* = 2.8 Hz), 52.9.

¹⁹F NMR (376 MHz, CD₃Cl) δ -68.01.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₀H₈F₃NO₂ 232.0580, found 232.0580.



2,2,2-trifluoroethyl 2-(4-cyanophenyl)acrylate(4a)

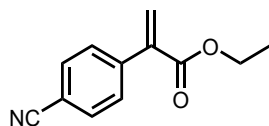
34.1 mg, 67% yield; Colorless oil.

^1H NMR (400 MHz, CD_3Cl) δ 7.68 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 6.64 (s, 1H), 6.15 (s, 1H), 4.63 (q, J = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, CD_3Cl) δ 164.1, 140.4, 138.6, 132.3, 131.4, 129.3, 123.1 (d, J = 277.3 Hz), 118.7, 112.6, 61.2 (q, J = 36.8 Hz).

^{19}F NMR (376 MHz, CD_3Cl) δ -73.65.

TOFMS-ESI $^+$ (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_8\text{F}_3\text{NO}_2$ 256.0580, found 256.0580.

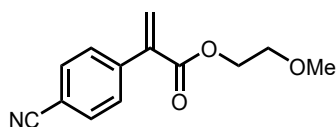


ethyl 2-(4-cyanophenyl)acrylate(4b)^[9]

32.5 mg, 81% yield; Colorless oil.

^1H NMR (400 MHz, CD_3Cl) δ 7.69 – 7.62 (m, 2H), 7.56 – 7.51 (m, 2H), 6.50 (d, J = 0.9 Hz, 1H), 5.98 (d, J = 0.9 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 165.9, 141.5, 140.3, 132.1, 129.3, 129.2, 118.9, 112.0, 61.7, 14.4.



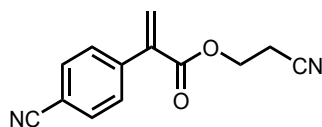
2-methoxyethyl 2-(4-cyanophenyl)acrylate(4c)

22.1 mg, 48% yield; Colorless oil.

^1H NMR (400 MHz, CD_3Cl) δ 7.69 – 7.61 (m, 2H), 7.59 – 7.51 (m, 2H), 6.54 (d, J = 0.8 Hz, 1H), 6.02 (d, J = 0.8 Hz, 1H), 4.43 – 4.36 (m, 2H), 3.70 – 3.63 (m, 2H), 3.40 (s, 3H).

^{13}C NMR (101 MHz, CD_3Cl) δ 165.9, 141.3, 139.9, 132.1, 129.7, 129.3, 118.9, 112.1, 70.5, 64.6, 59.2.

TOFMS-ESI $^+$ (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3$ 232.0968, found 232.0968.



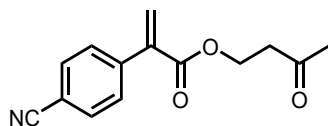
3-cyanoethyl 2-(4-cyanophenyl)acrylate(4d)

25.7 mg, 57% yield; Colorless oil.

^1H NMR (400 MHz, CD_3Cl) δ 7.71 – 7.65 (m, 2H), 7.58 – 7.53 (m, 2H), 6.61 (s, 1H), 6.10 (s, 1H), 4.46 (t, J = 6.2 Hz, 2H), 2.81 (t, J = 6.2 Hz, 2H).

^{13}C NMR (101 MHz, CD_3Cl) δ 165.1, 140.7, 139.1, 132.2, 130.9, 129.3, 118.8, 116.8, 112.4, 59.8, 18.3.

TOFMS-ESI $^+$ (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$ 227.0815, found 227.0815.



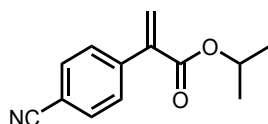
3-oxobutyl 2-(4-cyanophenyl)acrylate(4e)

31.5 mg, 65% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.67 – 7.62 (m, 2H), 7.57 – 7.47 (m, 2H), 6.47 (d, *J* = 0.8 Hz, 1H), 5.99 (d, *J* = 0.9 Hz, 1H), 4.50 (t, *J* = 6.2 Hz, 2H), 2.85 (t, *J* = 6.2 Hz, 2H), 2.20 (s, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 205.5, 165.7, 141.2, 139.9, 132.1, 129.7, 129.3, 118.9, 112.1, 60.4, 42.2, 30.5.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₄H₁₃NO₃ 244.0968, found 244.0968.

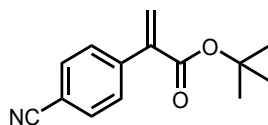
**isopropyl 2-(4-cyanophenyl)acrylate(4f)**

35.6 mg, 83% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 0.9 Hz, 1H), 5.97 (d, *J* = 0.9 Hz, 1H), 5.16 (hept, *J* = 6.3 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 6H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.4, 141.6, 140.6, 132.1, 129.3, 128.9, 118.9, 111.9, 69.4, 22.0.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₃H₁₃NO₂ 216.1019, found 216.1019.

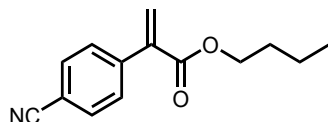
**tert-butyl 2-(4-cyanophenyl)acrylate(4g)**

35.7 mg, 78% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.69 – 7.61 (m, 2H), 7.55 – 7.49 (m, 2H), 6.40 (d, *J* = 0.9 Hz, 1H), 5.90 (d, *J* = 0.9 Hz, 1H), 1.53 (s, 9H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.1, 141.9, 141.7, 132.0, 129.4, 128.3, 119.0, 111.8, 82.2, 28.3.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₄H₁₅NO₂ 230.1176, found 230.1176.

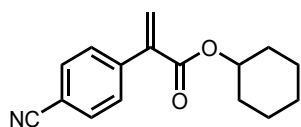
**butyl 2-(4-cyanophenyl)acrylate(4h)**

37.5 mg, 82% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 6.50 (d, *J* = 0.9 Hz, 1H), 5.98 (d, *J* = 0.9 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.69 (dq, *J* = 8.4, 6.7 Hz, 2H), 1.41 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 166.3, 141.8, 140.6, 132.4, 129.6, 129.5, 119.2, 112.3, 65.9, 31.1, 19.7, 14.2.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₄H₁₅NO₂ 230.1176, found 230.1176.



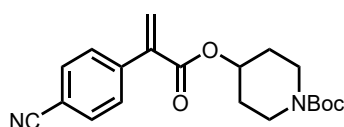
cyclohexyl 2-(4-cyanophenyl)acrylate(4i)

32.6 mg, 64% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.68 – 7.61 (m, 2H), 7.57 – 7.50 (m, 2H), 6.48 (d, *J* = 1.0 Hz, 1H), 5.96 (d, *J* = 1.0 Hz, 1H), 4.94 (tt, *J* = 8.7, 3.8 Hz, 1H), 1.95 – 1.84 (m, 2H), 1.72 (ddp, *J* = 12.4, 6.1, 3.2 Hz, 2H), 1.52 (dtt, *J* = 12.0, 9.5, 3.4 Hz, 3H), 1.40 (dtt, *J* = 12.9, 9.7, 3.1 Hz, 2H), 1.30 (dtd, *J* = 12.5, 9.2, 3.2 Hz, 1H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.3, 141.7, 140.7, 132.1, 129.3, 128.9, 119.0, 111.9, 74.1, 31.7, 25.5, 23.8.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₆H₁₇NO₂ 256.1332, found 256.1333.



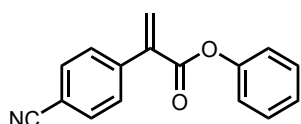
tert-butyl 4-((2-(4-cyanophenyl)acryloyl)oxy)piperidine-1-carboxylate(4j)

44.8 mg, 63% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.70 – 7.63 (m, 2H), 7.58 – 7.49 (m, 2H), 6.51 (d, *J* = 0.8 Hz, 1H), 6.00 (d, *J* = 0.8 Hz, 1H), 5.10 (tt, *J* = 7.8, 3.8 Hz, 1H), 3.70 – 3.60 (m, 2H), 3.30 (ddd, *J* = 13.6, 8.3, 3.8 Hz, 2H), 1.98 – 1.86 (m, 2H), 1.71 – 1.64 (m, 2H), 1.47 (s, 9H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.0, 154.9, 141.3, 140.3, 132.1, 129.5, 129.3, 118.8, 112.1, 80.0, 71.2, 41.4, 30.7, 28.6.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₂₀H₂₄N₂O₄ 357.1809, found 357.1808.



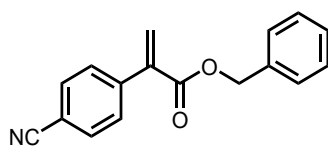
phenyl 2-(4-cyanophenyl)acrylate(4k)

35.8 mg, 72% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.71 – 7.66 (m, 2H), 7.67 – 7.60 (m, 2H), 7.47 – 7.37 (m, 2H), 7.30 – 7.25 (m, 1H), 7.18 – 7.14 (m, 2H), 6.77 (s, 1H), 6.19 (s, 1H).

¹³C NMR (101 MHz, CD₃Cl) δ 164.4, 150.7, 141.0, 139.6, 132.2, 131.0, 129.8, 129.4, 126.4, 121.6, 118.8, 112.4.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₆H₁₁NO₂ 250.0863, found 250.0863.



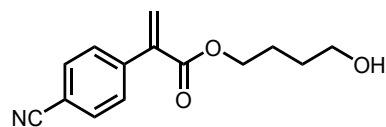
benzyl 2-(4-cyanophenyl)acrylate(4l)

27.3 mg, 52% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.32 (m, 5H), 6.55 (s, 1H), 6.01 (s, 1H), 5.28 (s, 2H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.7, 141.3, 134.0, 135.7, 132.1, 129.7, 129.3, 128.9, 128.7, 128.5, 118.9, 112.1, 67.4.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₇H₁₃NO₂ 264.1019, found 264.1020.



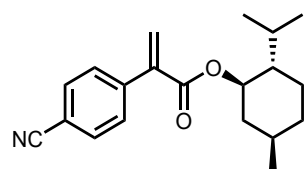
4-hydroxybutyl 2-(4-cyanophenyl)acrylate(4m)

34.7 mg, 71% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 6.51 (s, 1H), 6.00 (s, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 3.70 (t, *J* = 6.4 Hz, 2H), 1.81 (dq, *J* = 8.8, 6.5 Hz, 2H), 1.66 (dq, *J* = 10.0, 6.5 Hz, 2H), 1.54 (s, 1H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.9, 141.4, 140.1, 132.1, 129.3, 129.3, 118.9, 112.0, 65.5, 62.4, 29.2, 25.2.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₁₄H₁₅NO₃ 246.1125, found 246.1124.



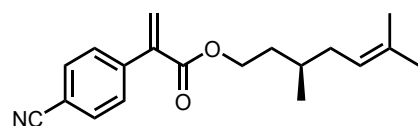
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(4-cyanophenyl)acrylate(4n)

37.9 mg, 61% yield; Colorless oil.

¹H NMR (400 MHz, CD₃Cl) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 6.46 (s, 1H), 5.96 (d, *J* = 0.8 Hz, 1H), 4.84 (td, *J* = 10.9, 4.4 Hz, 1H), 2.16 – 2.03 (m, 1H), 1.86 (pd, *J* = 7.0, 2.8 Hz, 1H), 1.76 – 1.66 (m, 2H), 1.59 – 1.39 (m, 3H), 1.16 – 1.02 (m, 2H), 0.91 (dd, *J* = 11.5, 6.8 Hz, 6H), 0.78 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CD₃Cl) δ 165.5, 141.6, 140.6, 132.1, 129.3, 128.7, 118.9, 111.9, 75.8, 47.2, 40.9, 34.3, 31.6, 26.6, 23.6, 22.2, 20.9, 16.5.

TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₂₀H₂₅NO₂ 312.1958, found 312.1959.



(R)-3,6-dimethylhept-5-en-1-yl 2-(4-cyanophenyl)acrylate(4o)

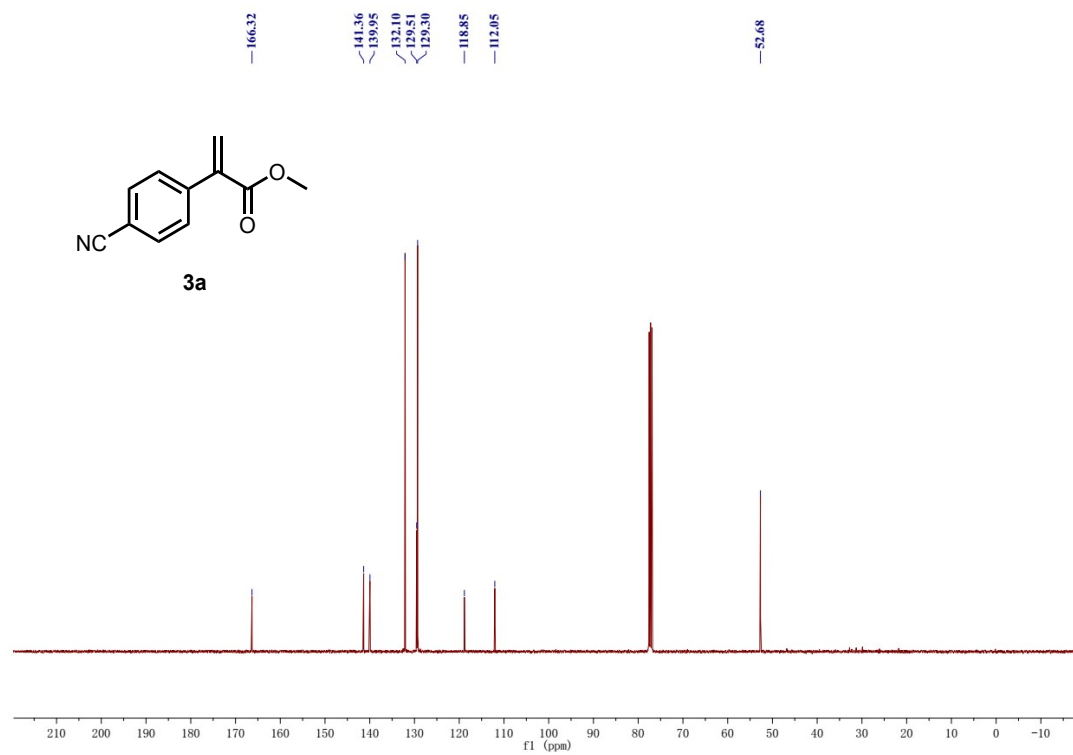
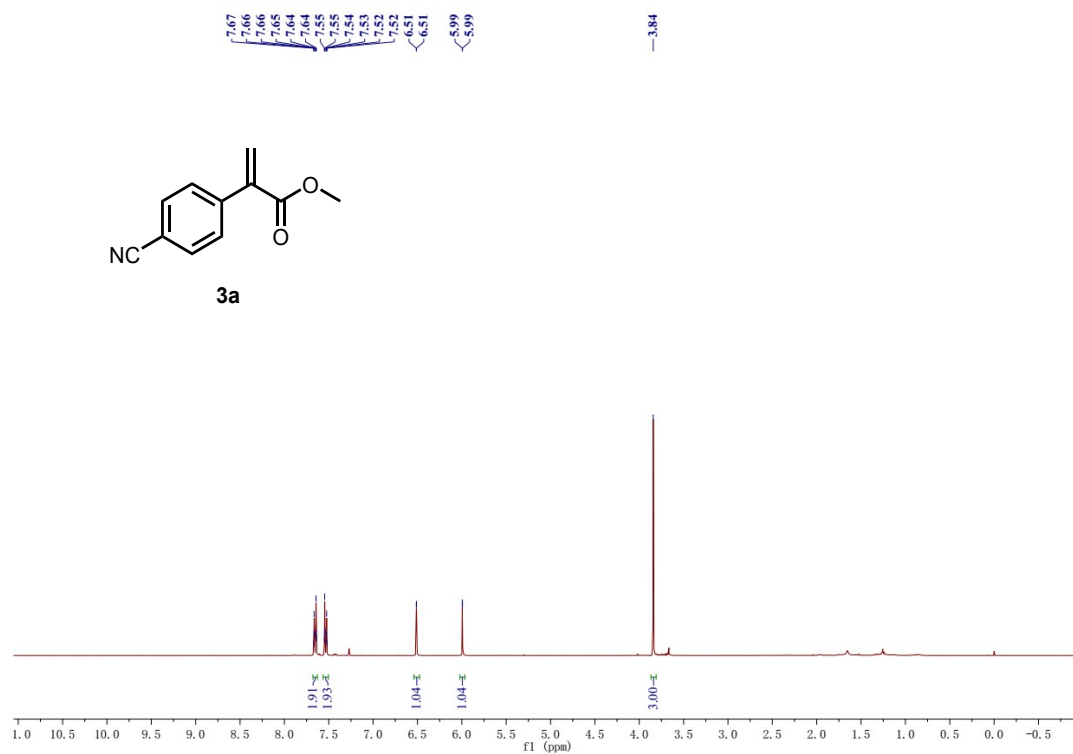
32.6 mg, 55% yield; Colorless oil.

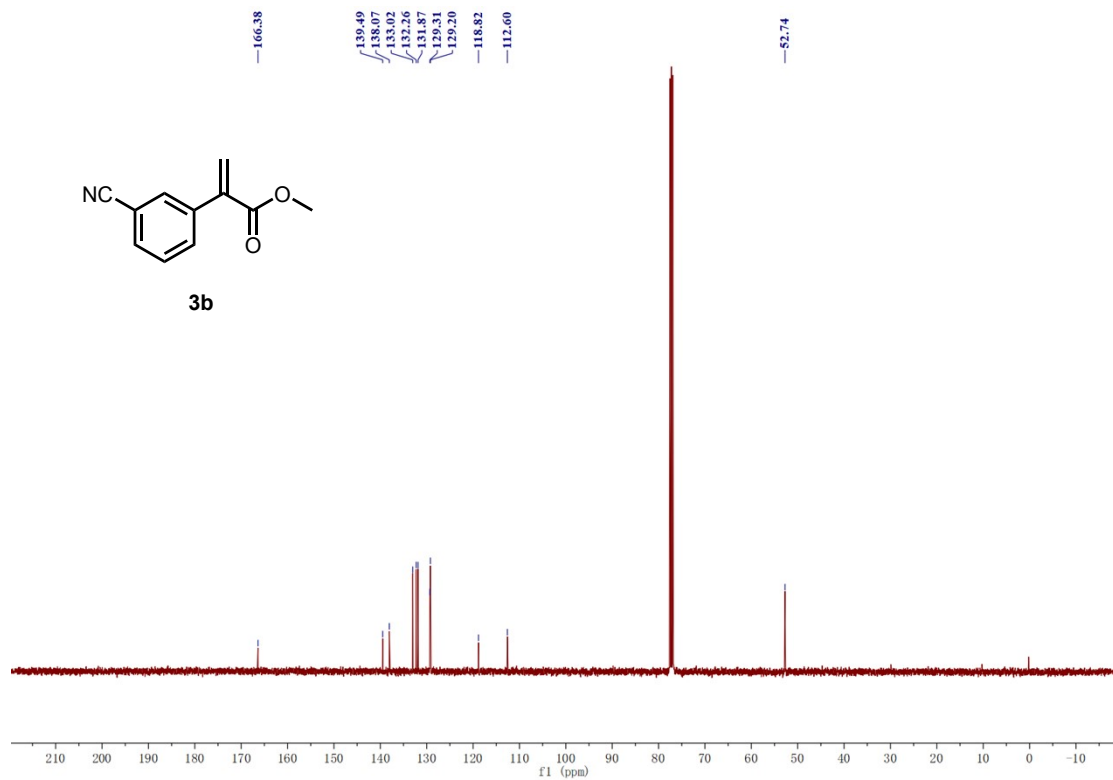
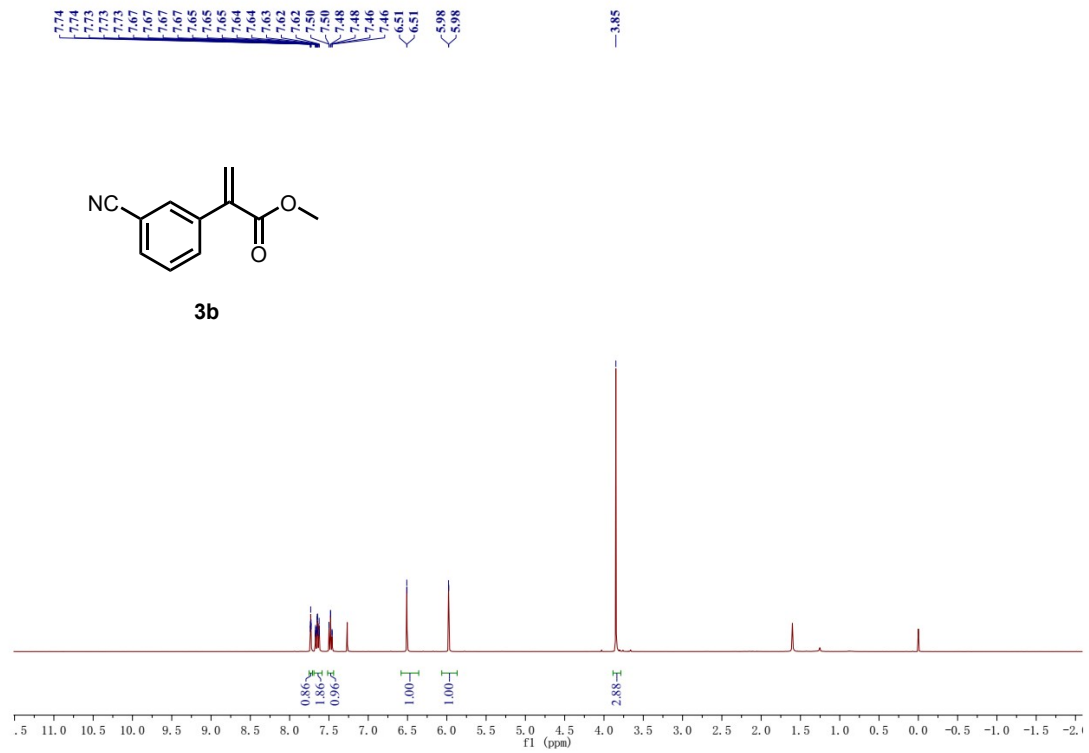
¹H NMR (400 MHz, CD₃Cl) δ 7.69 – 7.62 (m, 2H), 7.57 – 7.50 (m, 2H), 6.49 (d, *J* = 0.9 Hz, 1H), 5.98 (d, *J* = 0.9 Hz, 1H), 5.07 (ddt, *J* = 8.5, 5.7, 1.4 Hz, 1H), 4.34 – 4.22 (m, 2H), 1.97 (tq, *J* = 14.4, 7.4 Hz, 2H), 1.78 – 1.70 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.41 – 1.32 (m, 1H), 1.25 – 1.15 (m, 1H), 0.93 (d, *J* = 6.4 Hz, 3H).

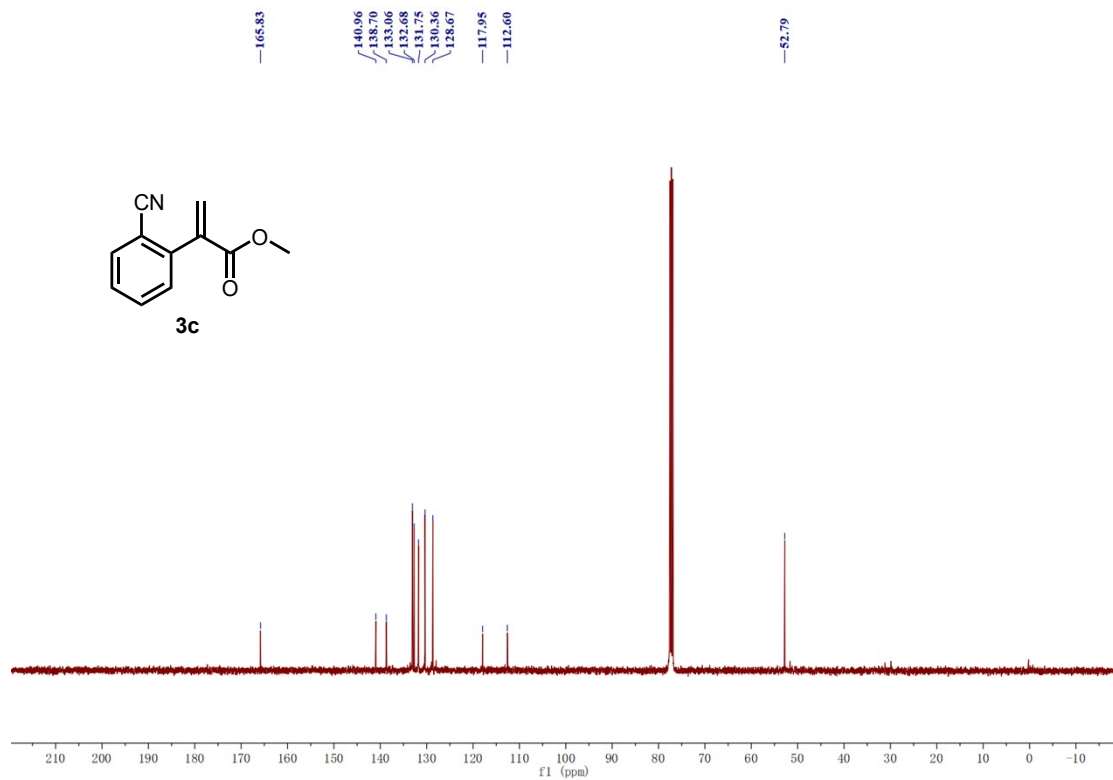
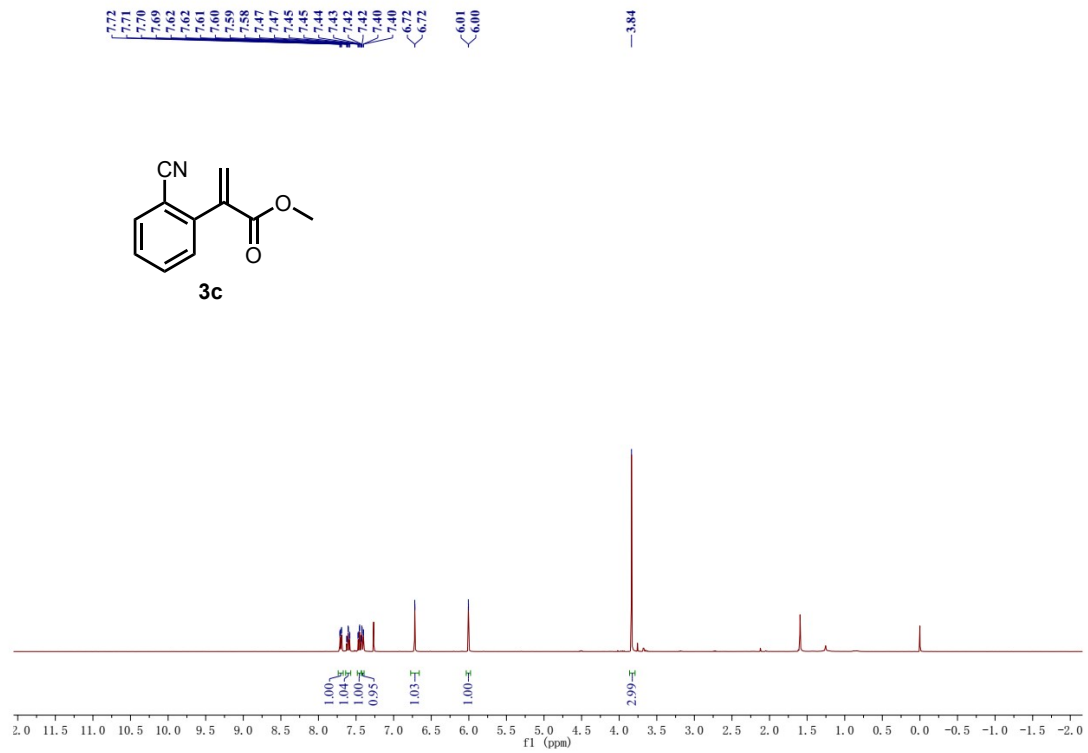
¹³C NMR (101 MHz, CD₃Cl) δ 165.9, 141.5, 140.3, 132.1, 131.7, 129.3, 129.2, 124.6, 118.9, 112.0, 64.3, 37.1, 35.5, 29.7, 26.0, 25.6, 19.6, 17.9.

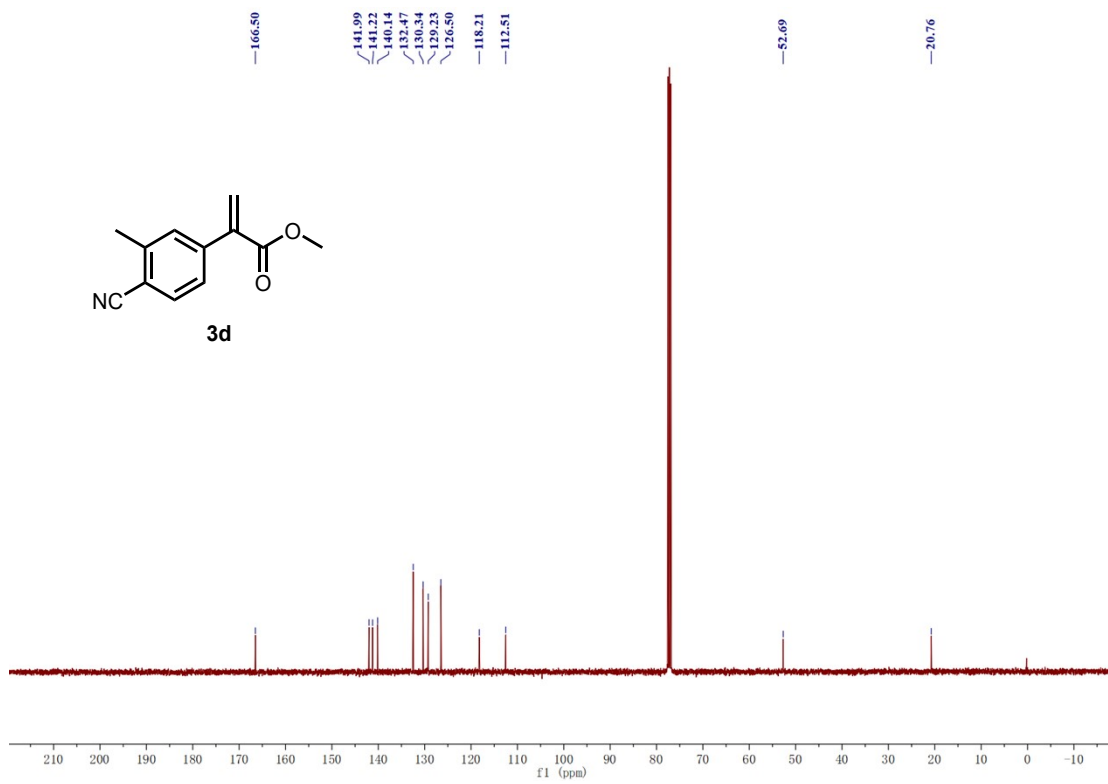
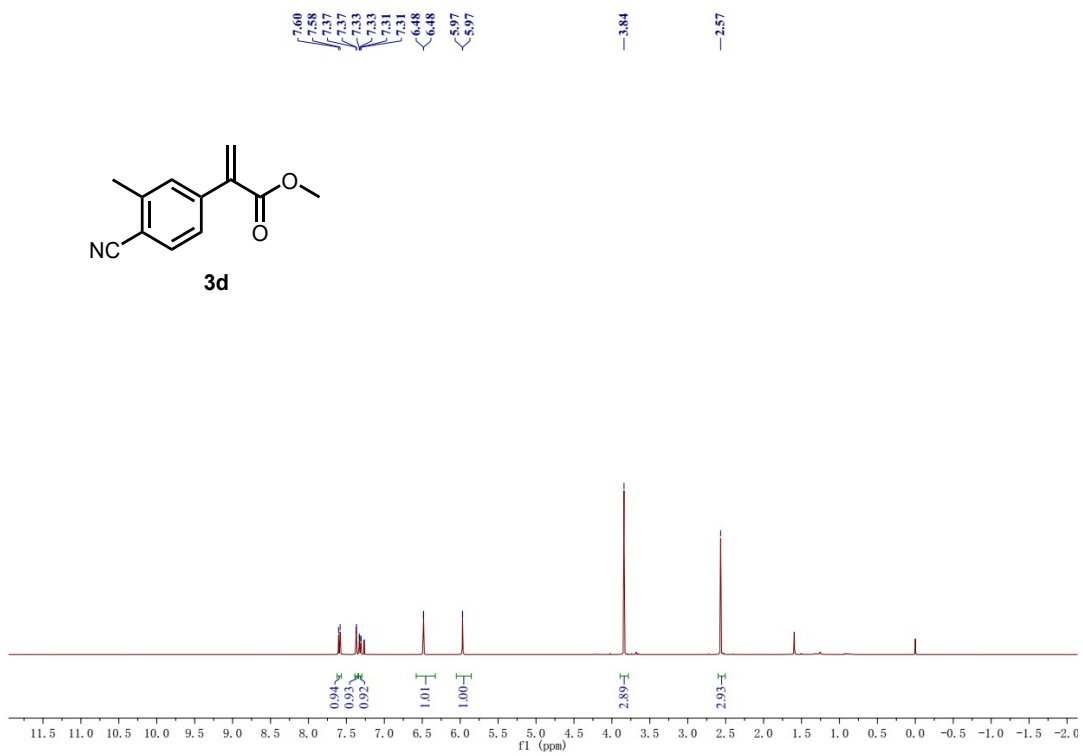
TOFMS-ESI⁺ (m/z) [M+H]⁺ calcd for C₂₀H₂₅NO₂ 312.1958, found 312.1958.

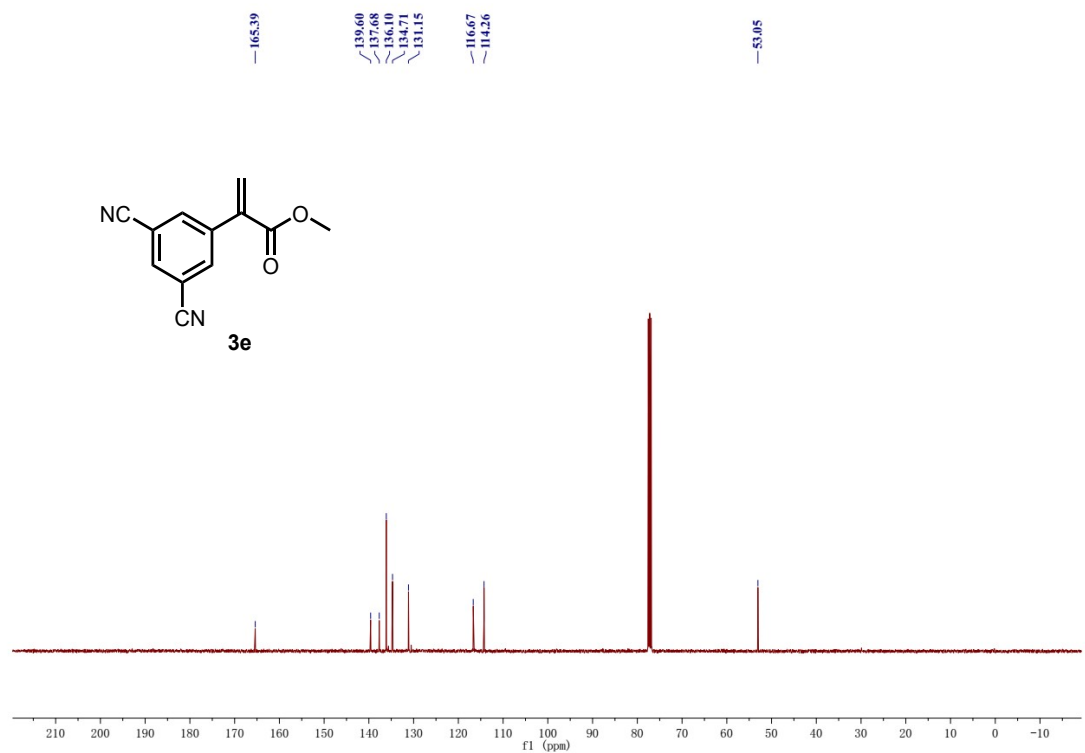
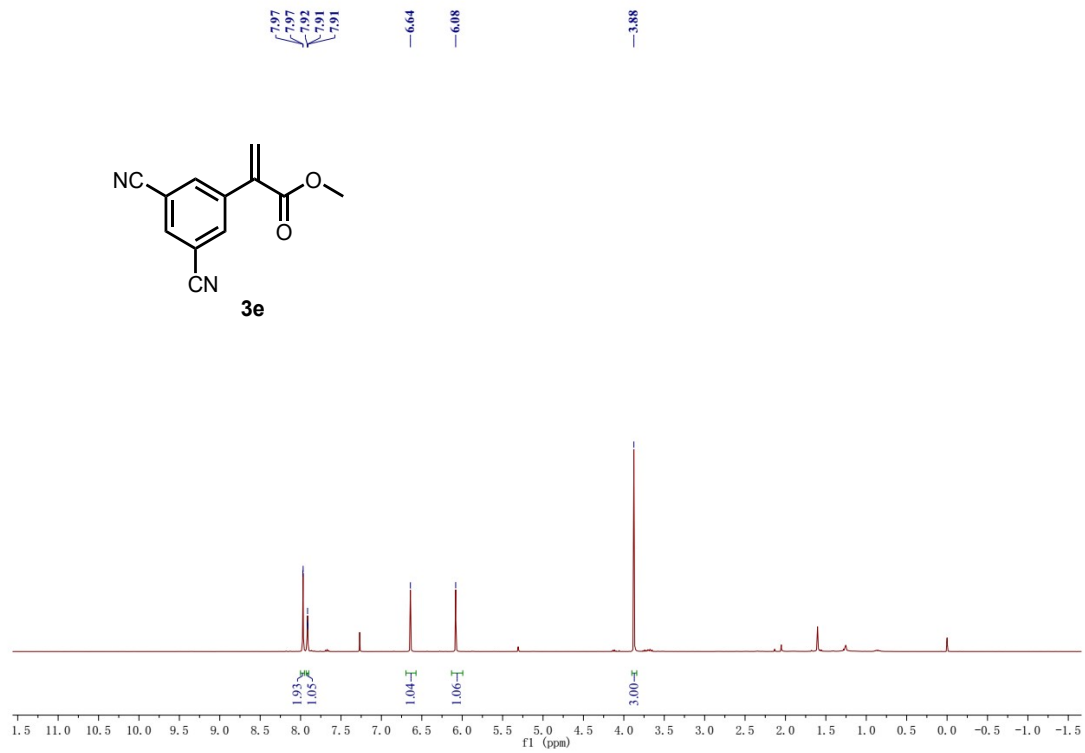
VIII. NMR Spectral Data

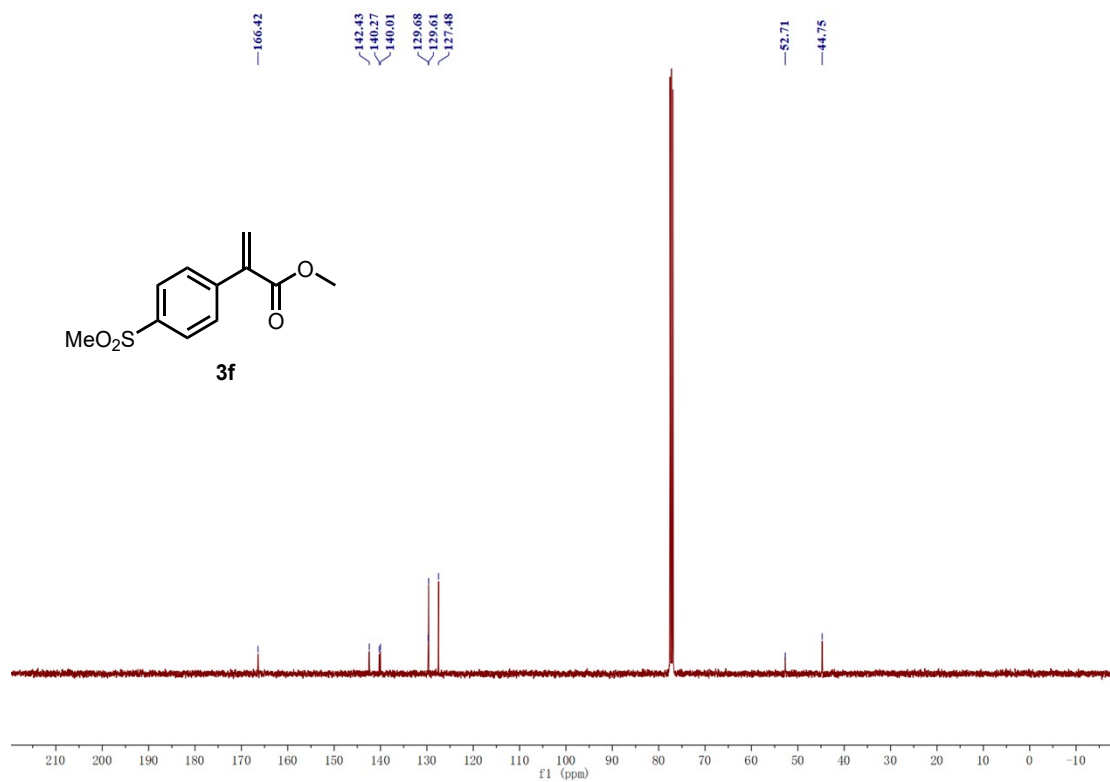
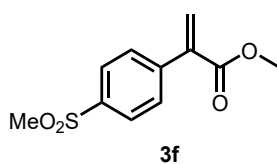
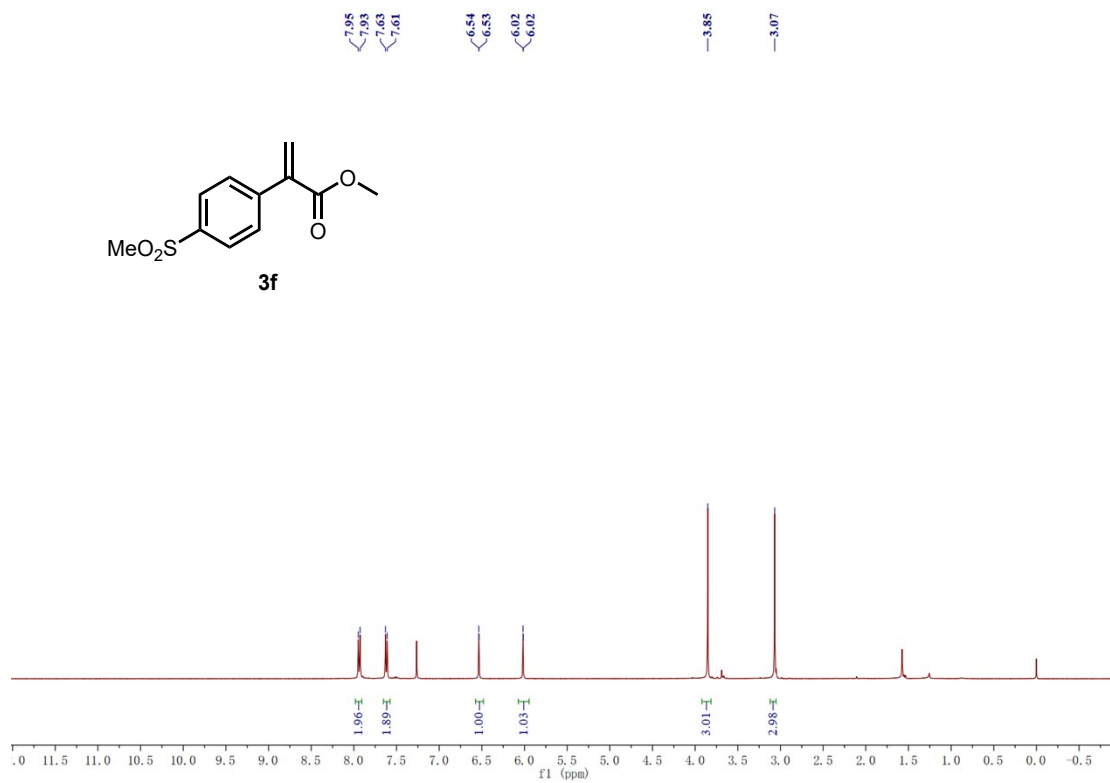
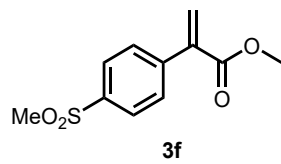


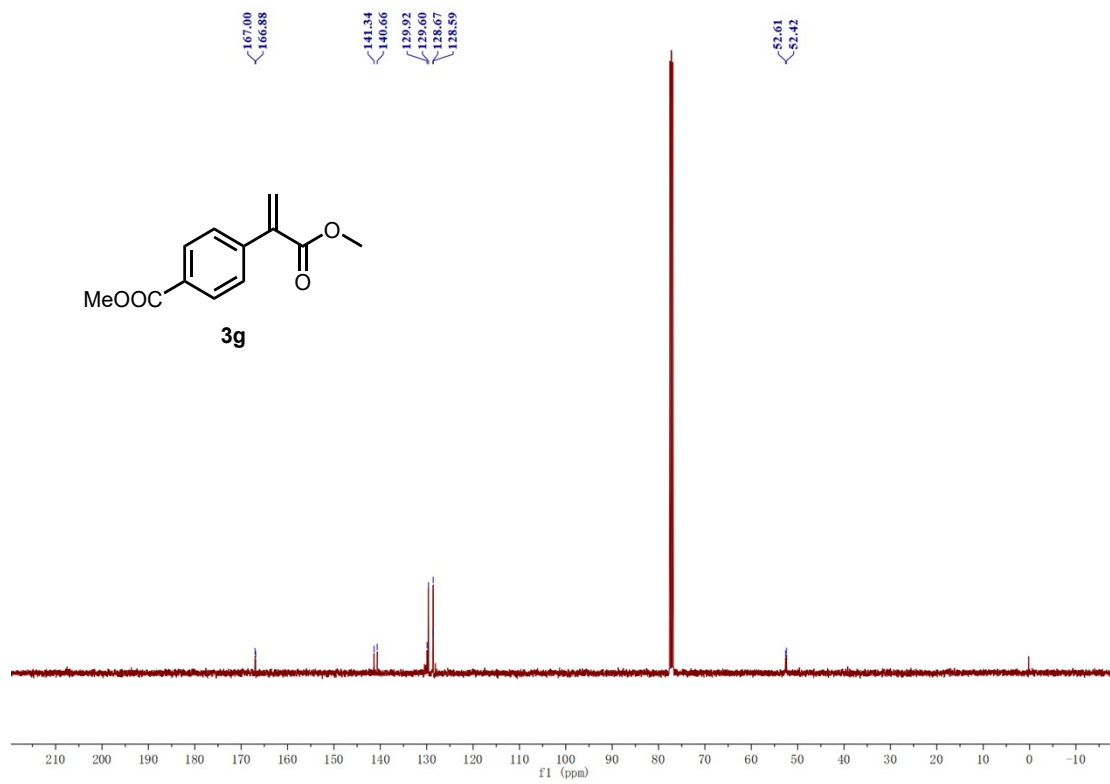
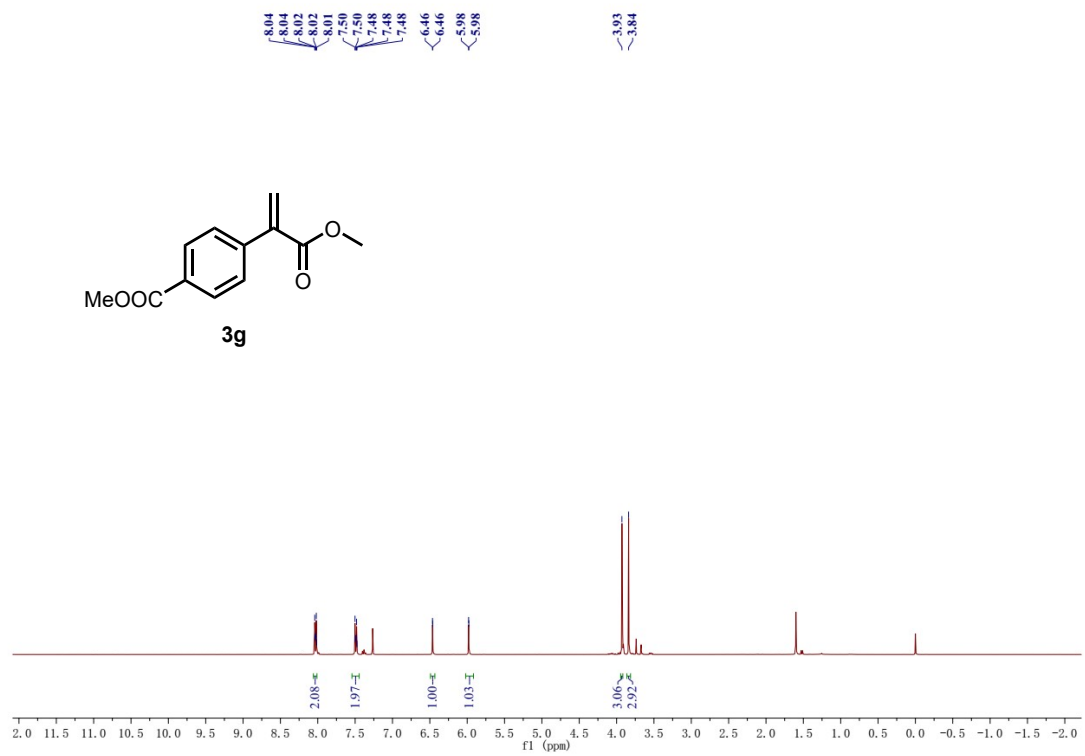


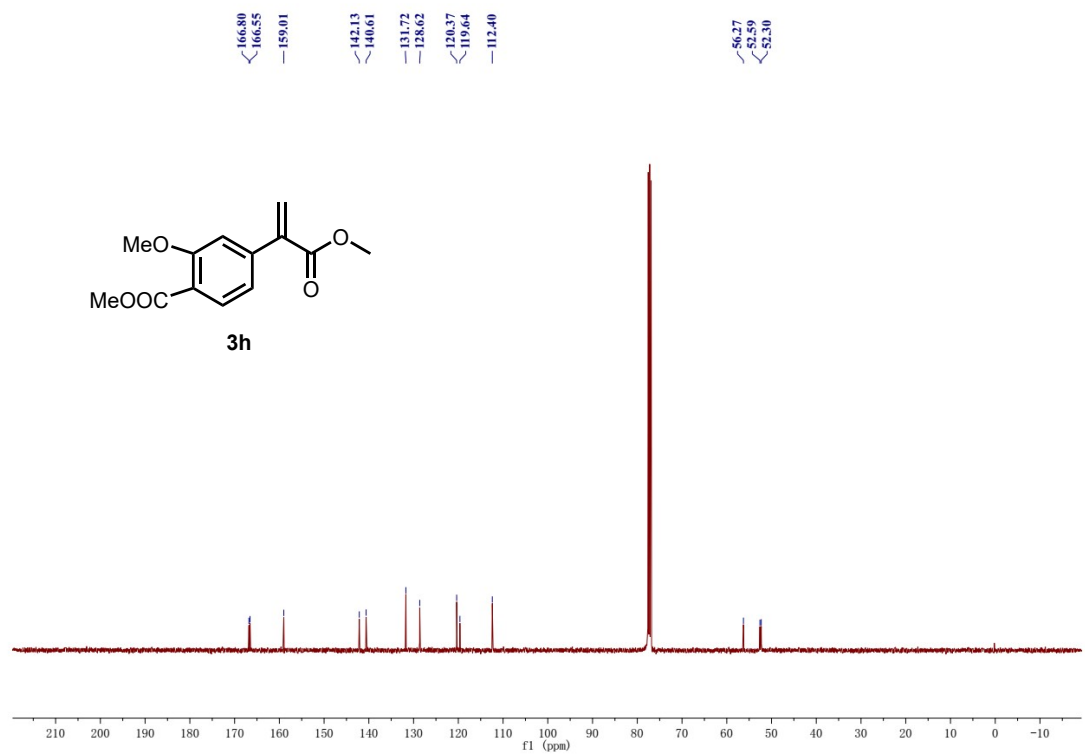
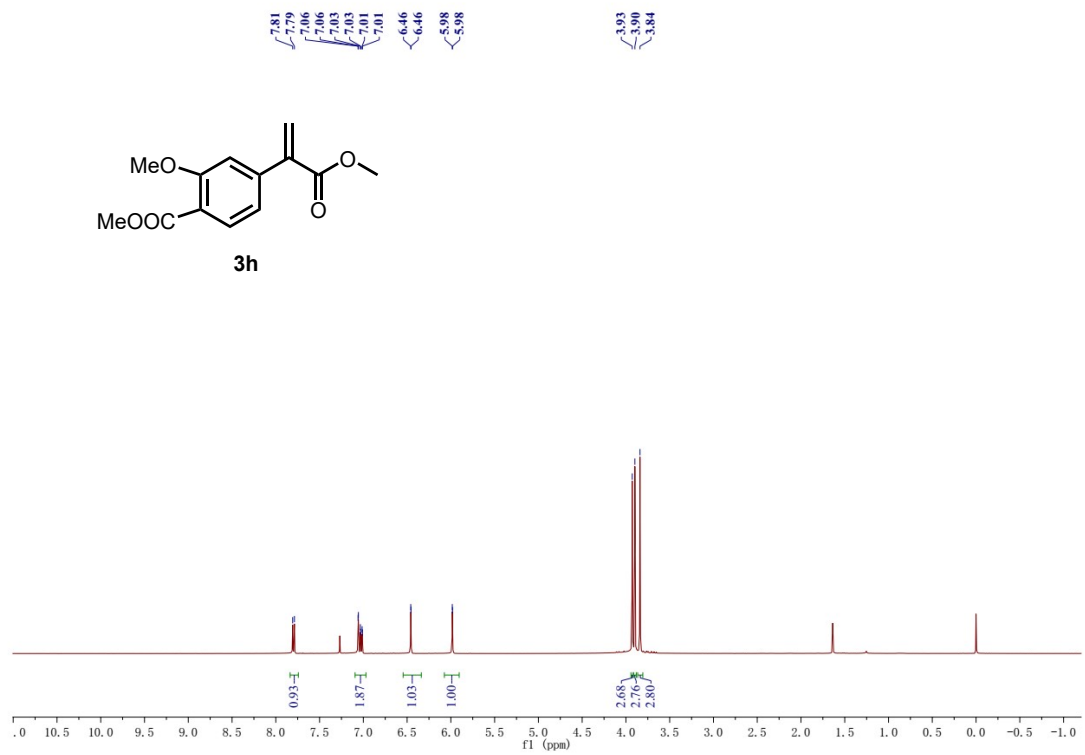


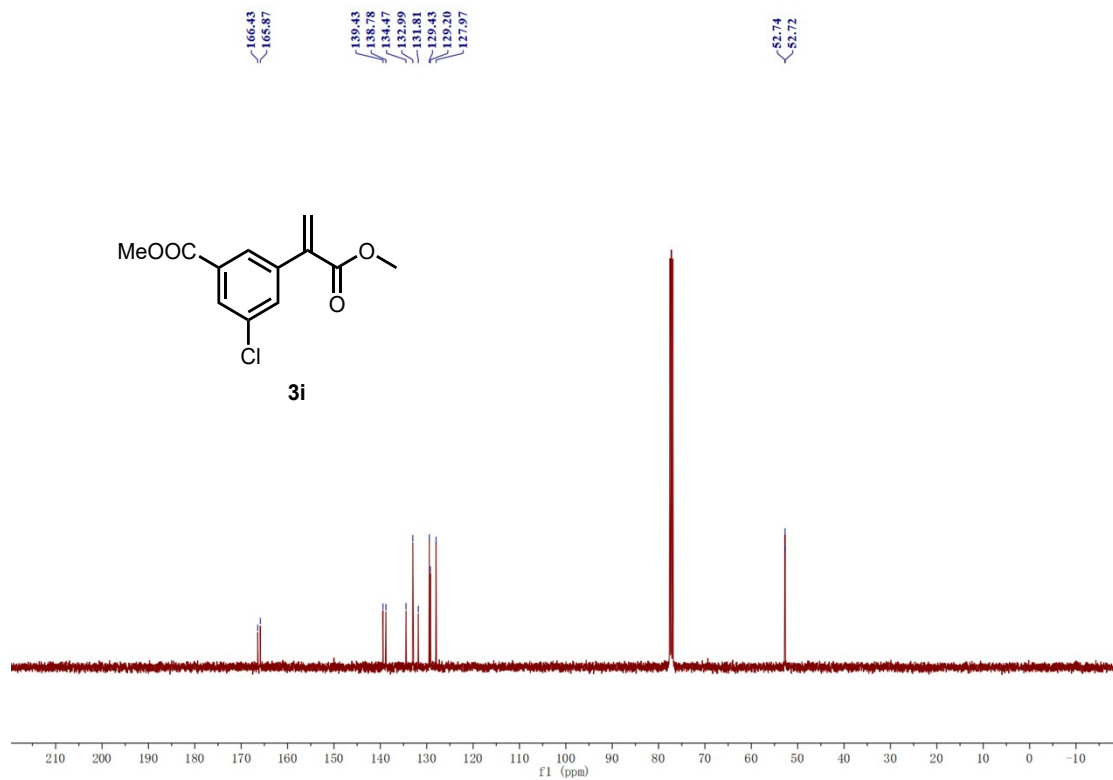
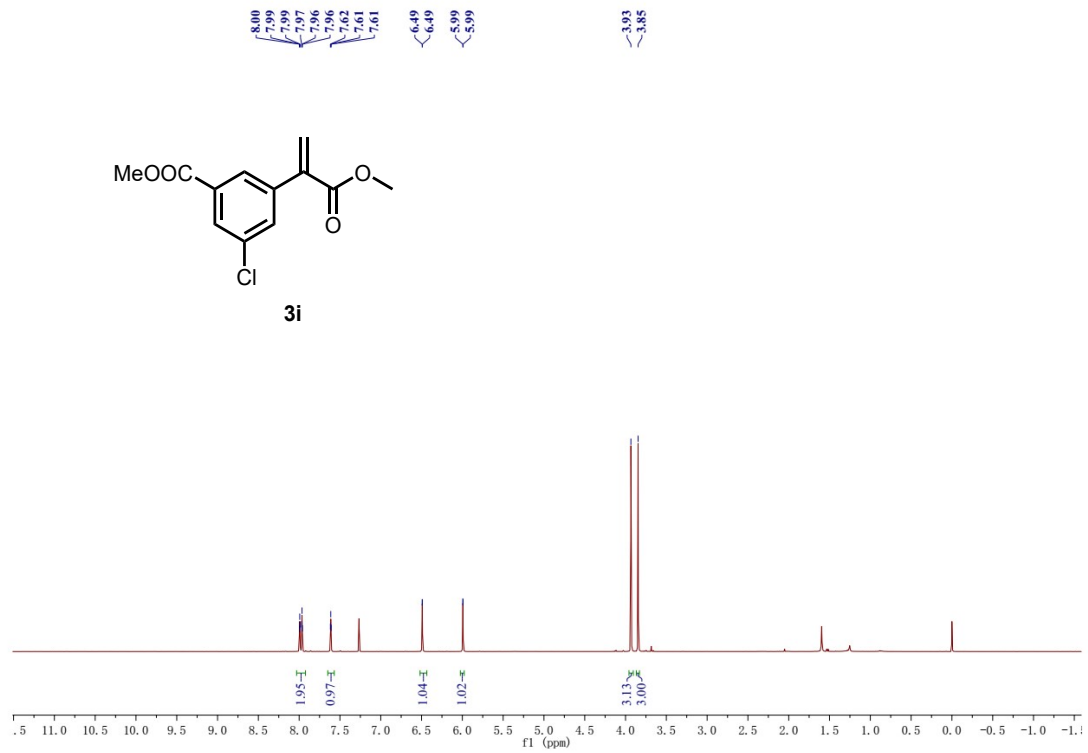


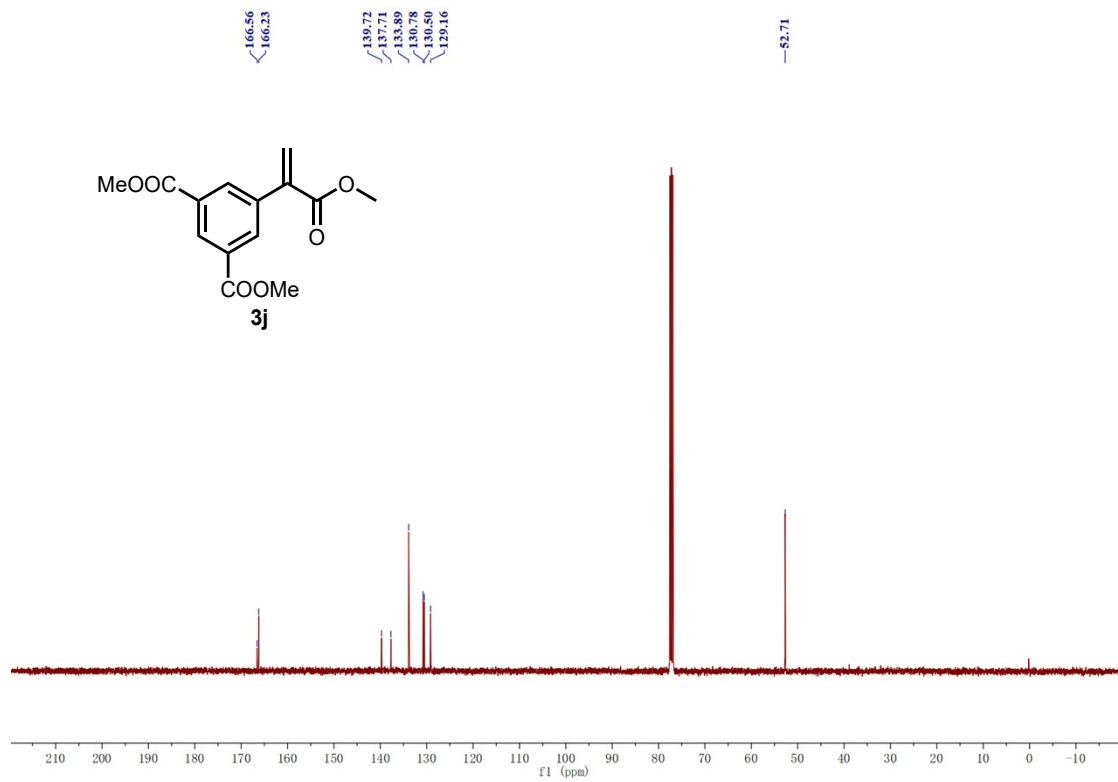
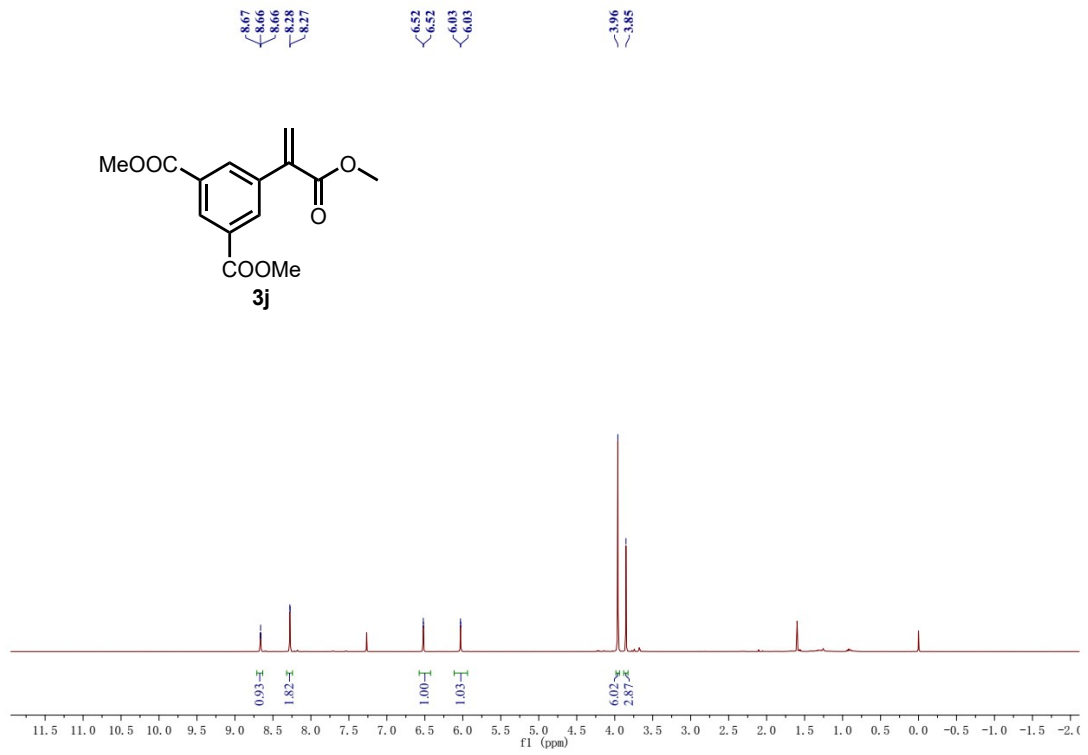


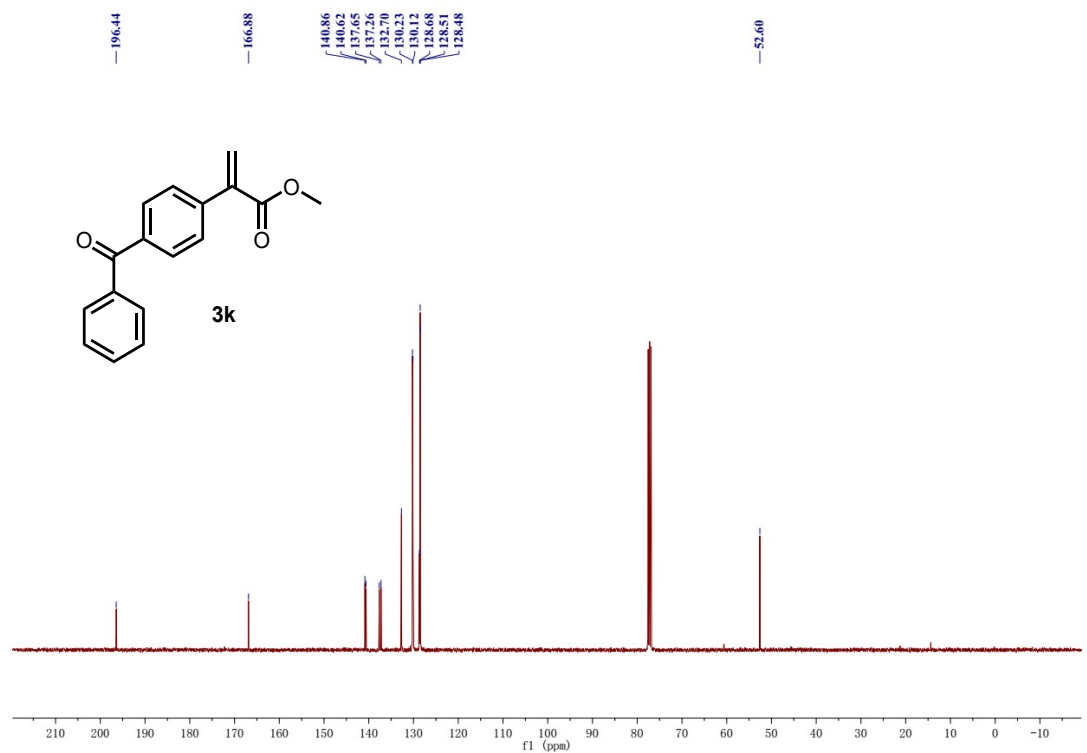
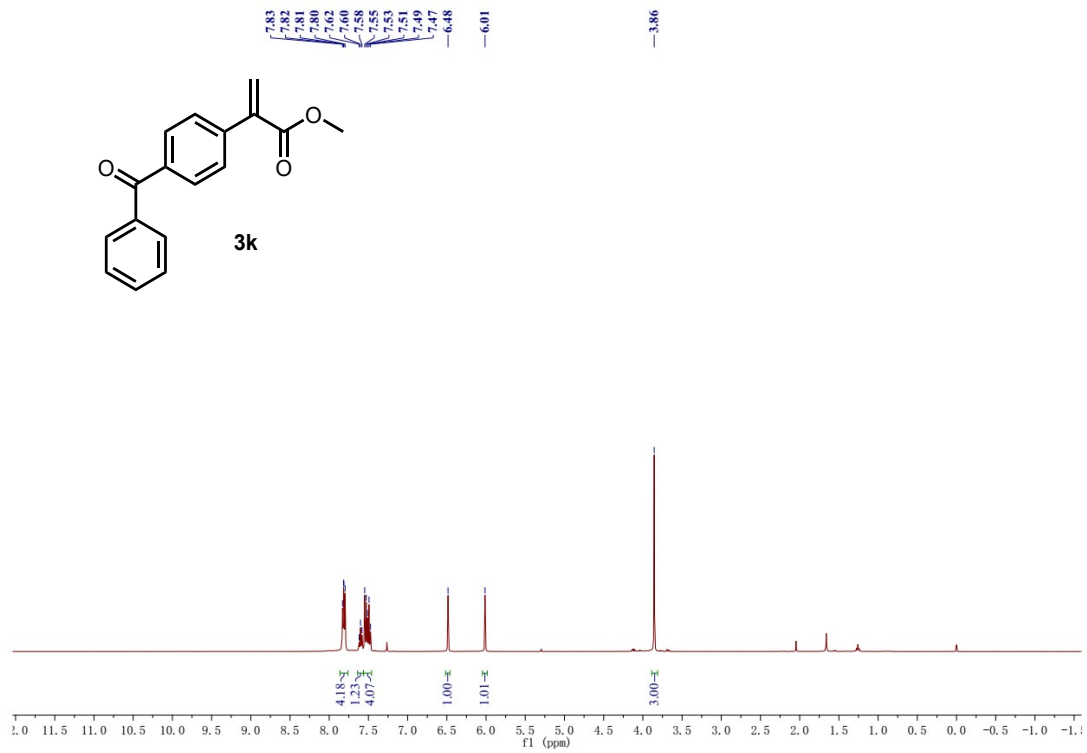


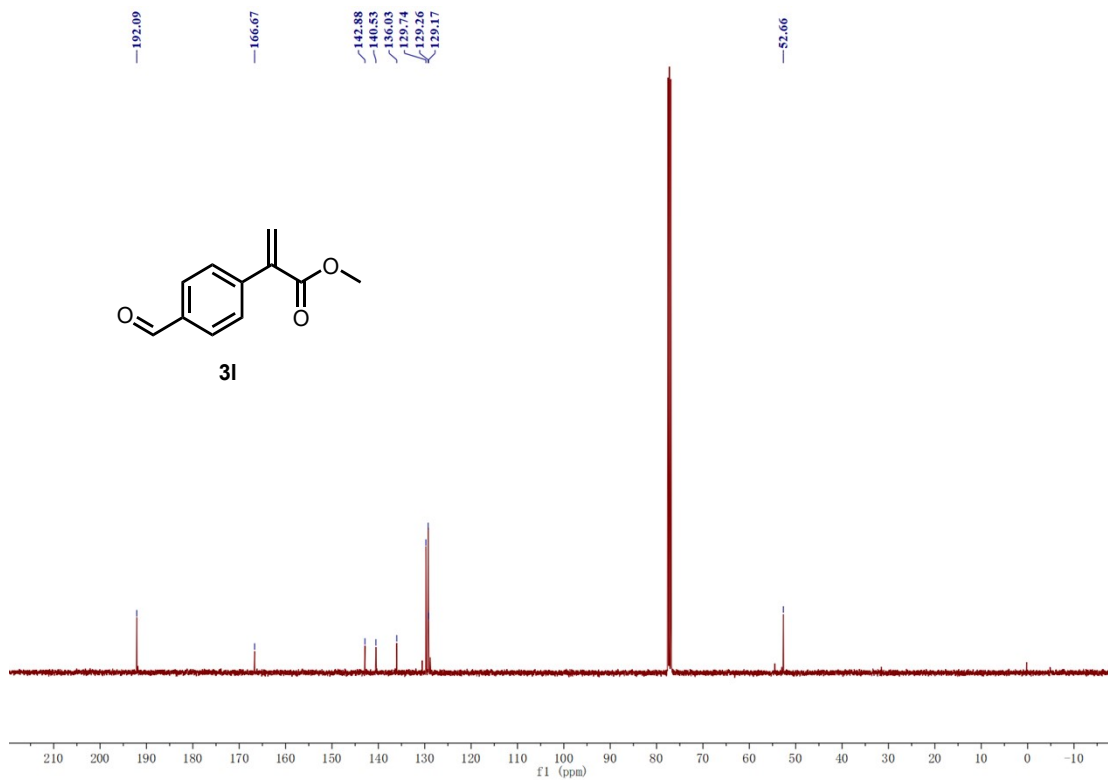
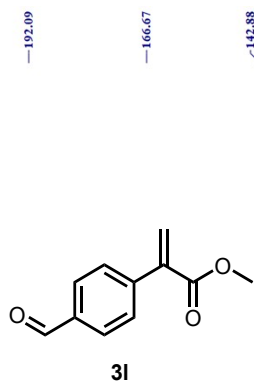
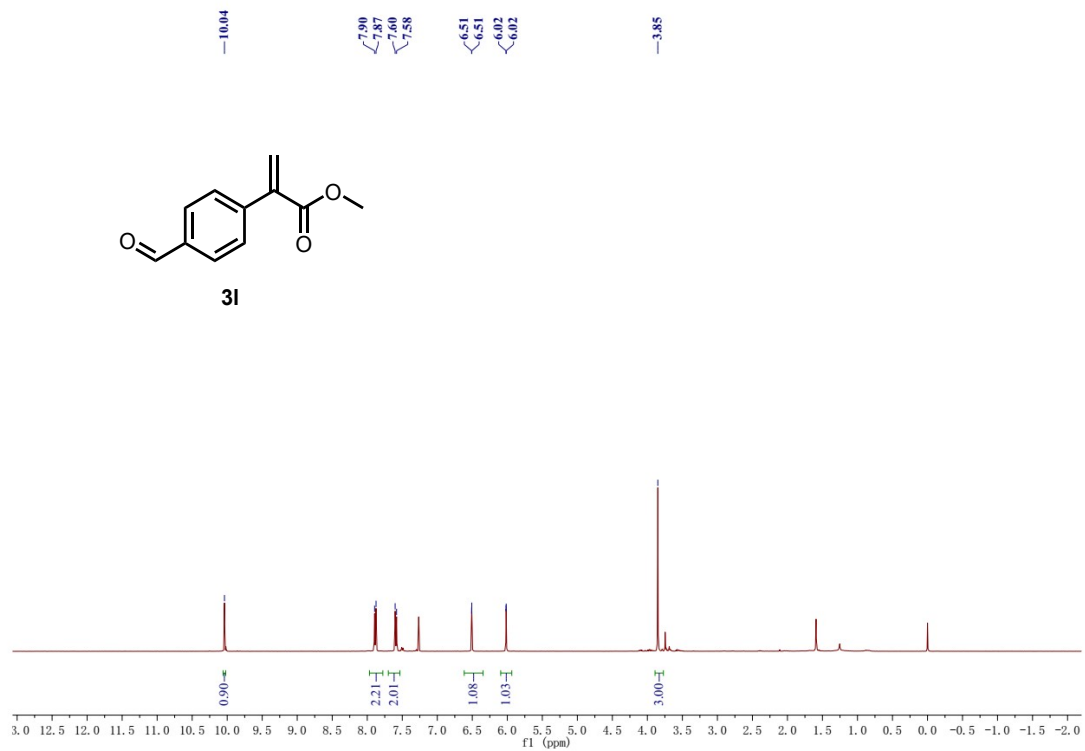
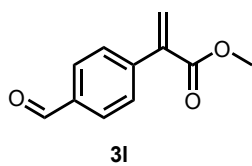


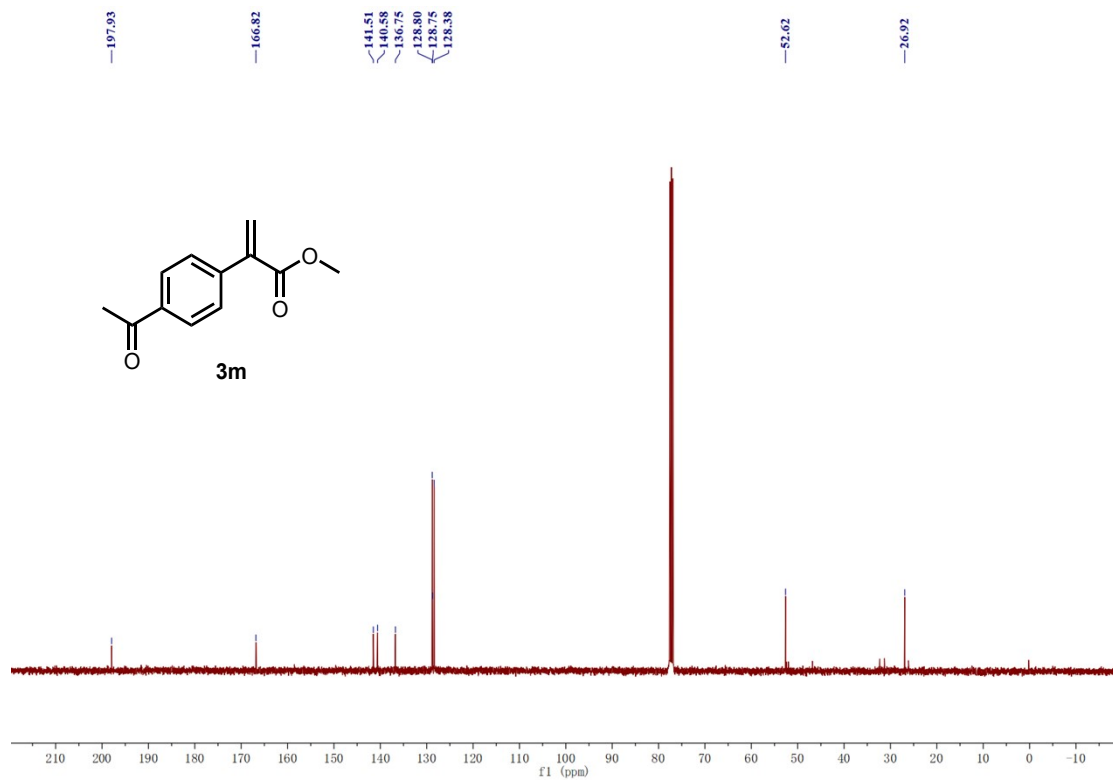
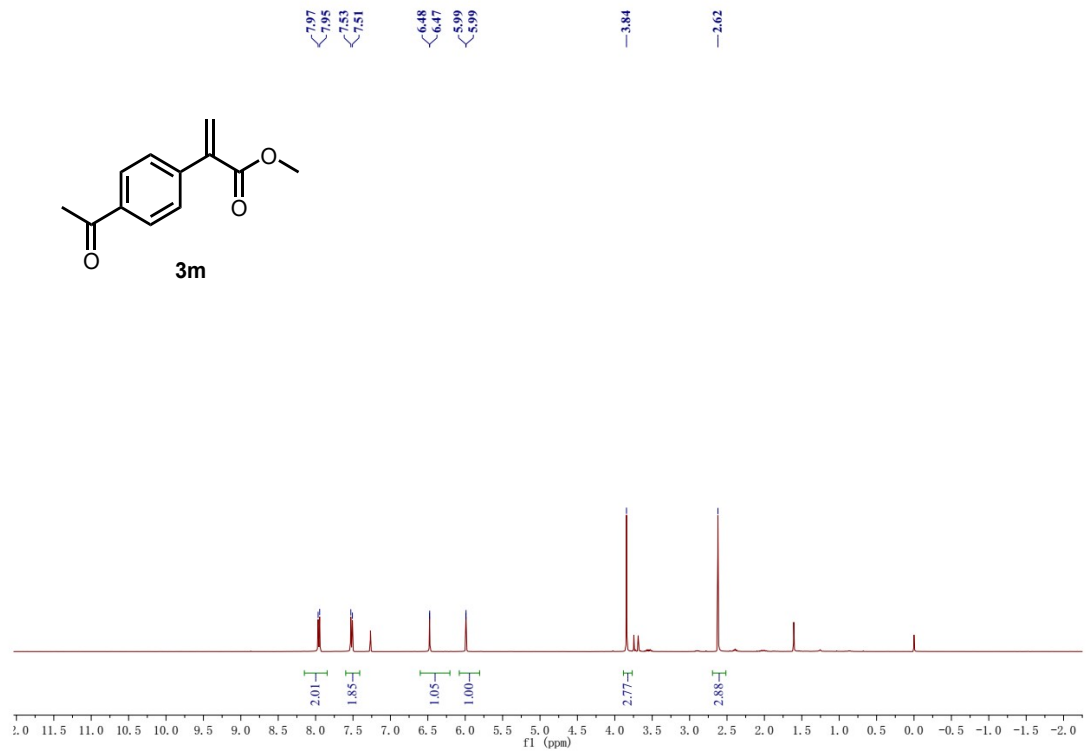


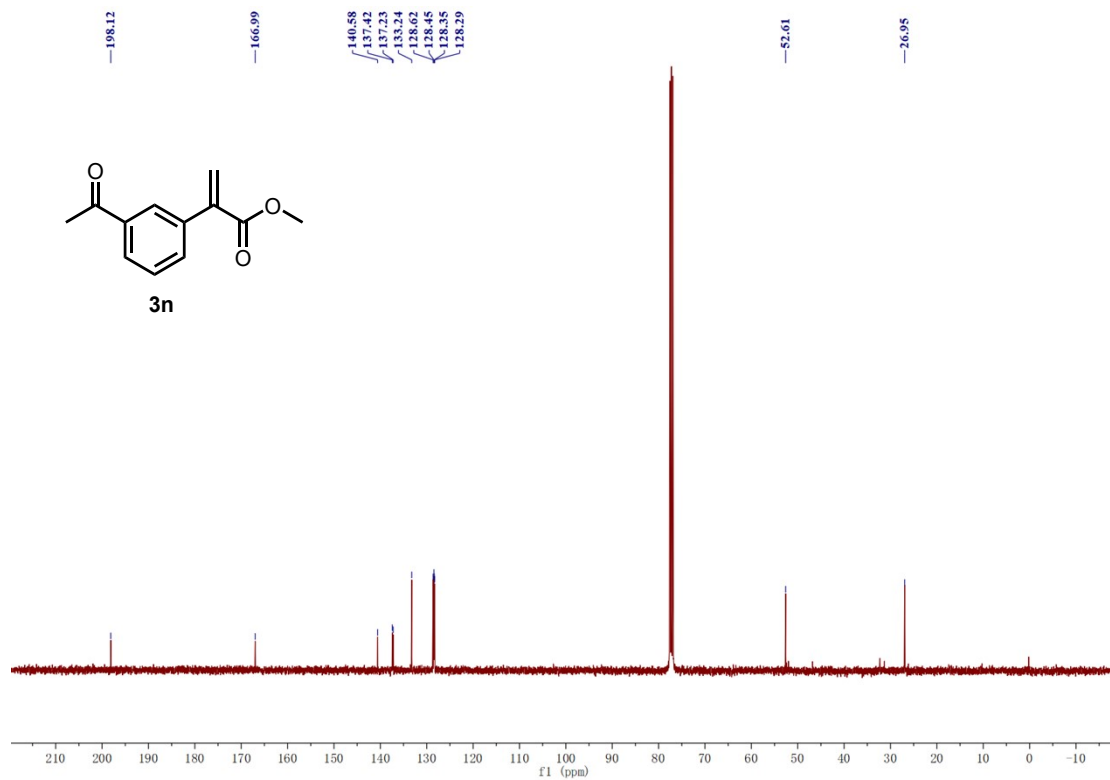
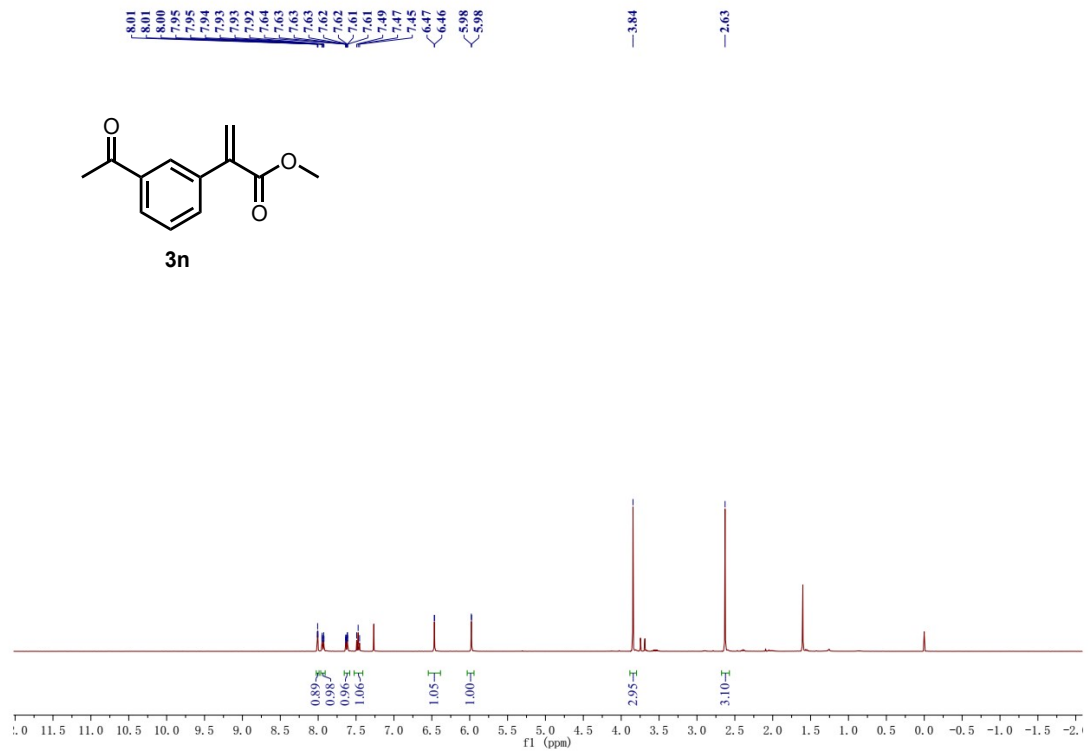


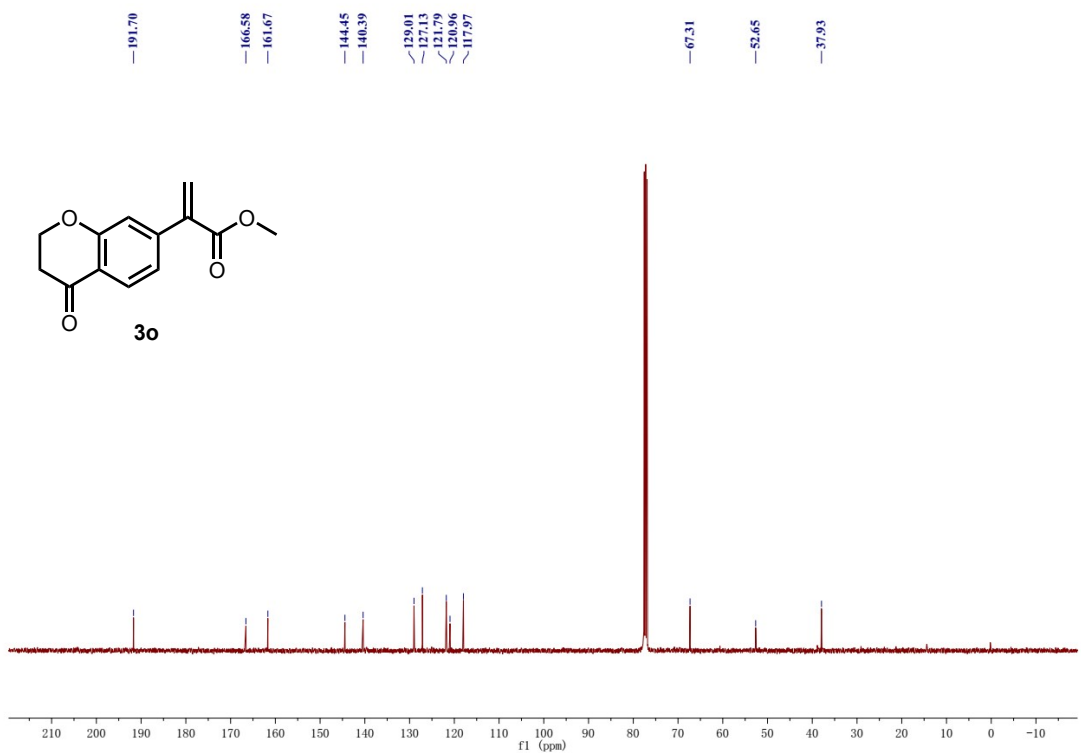
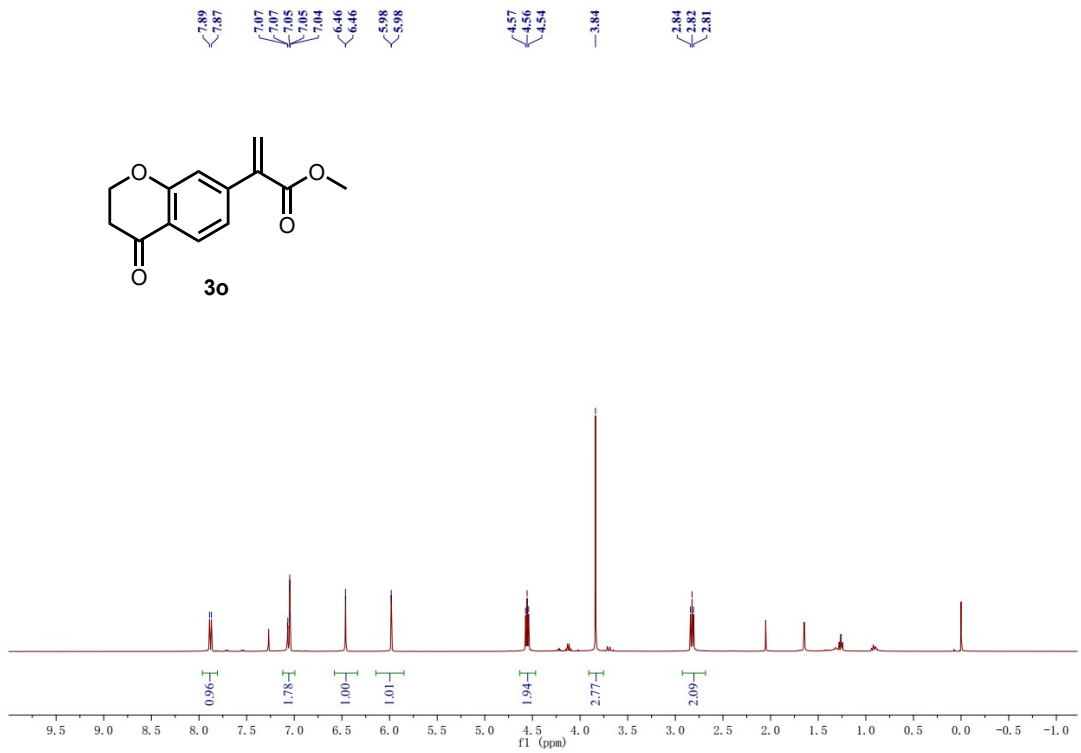


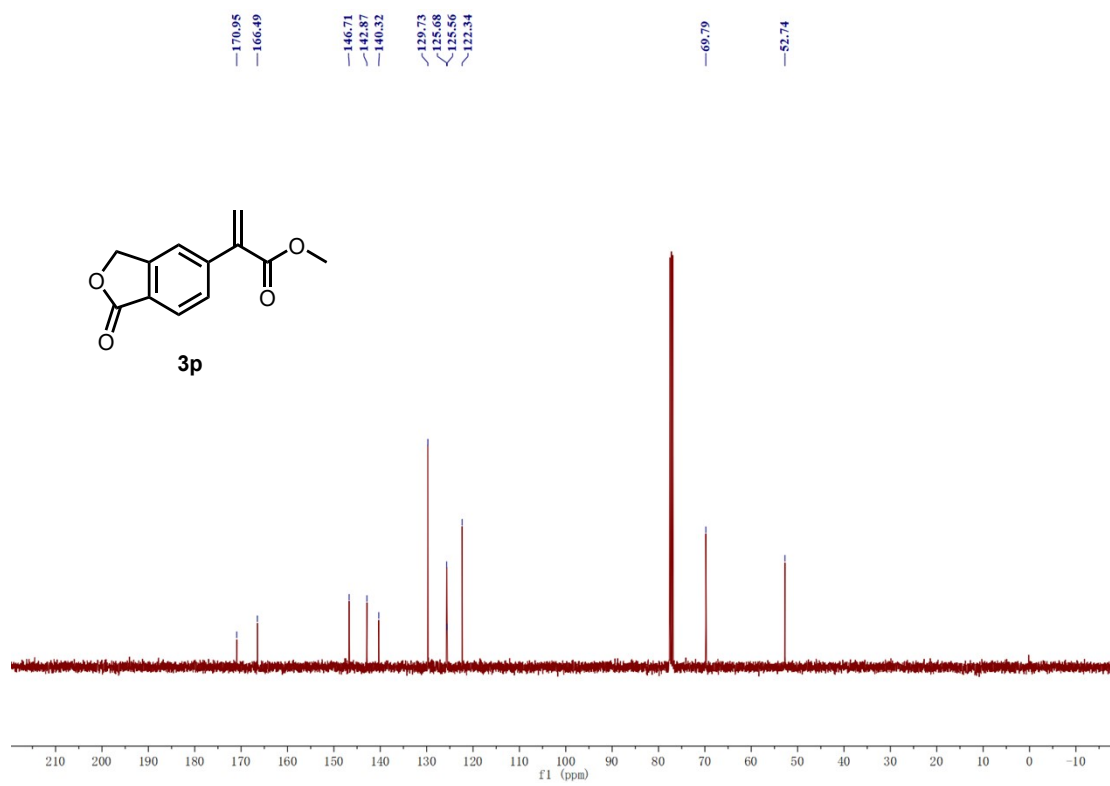
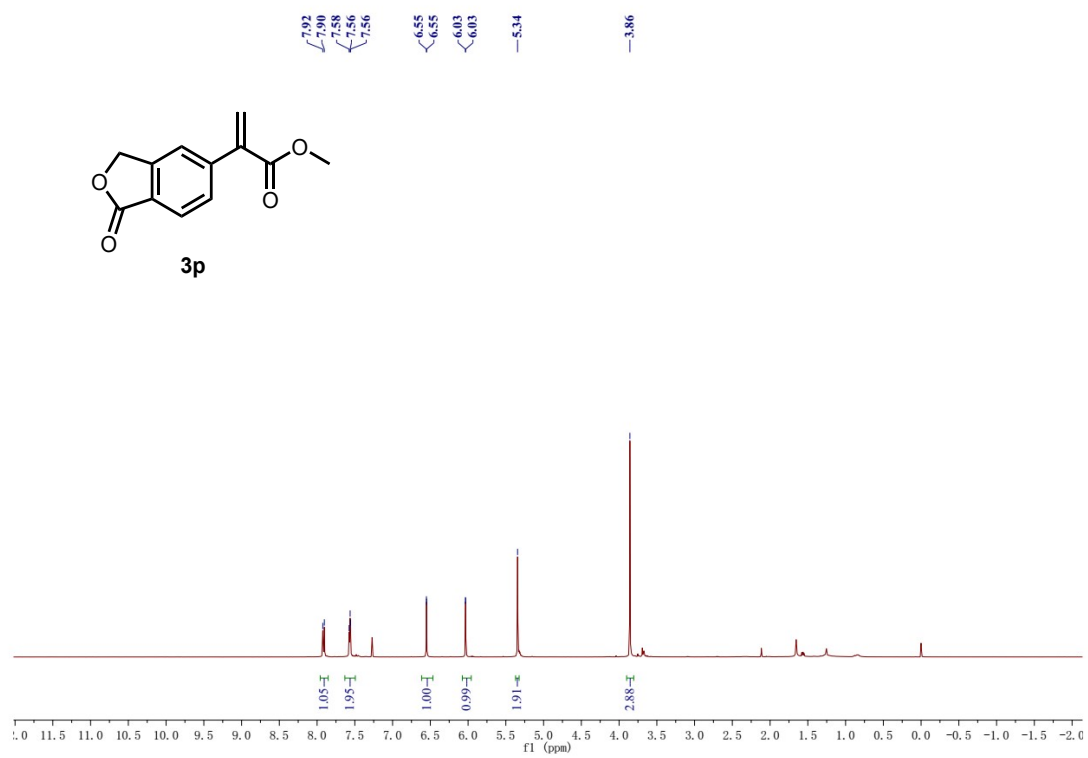


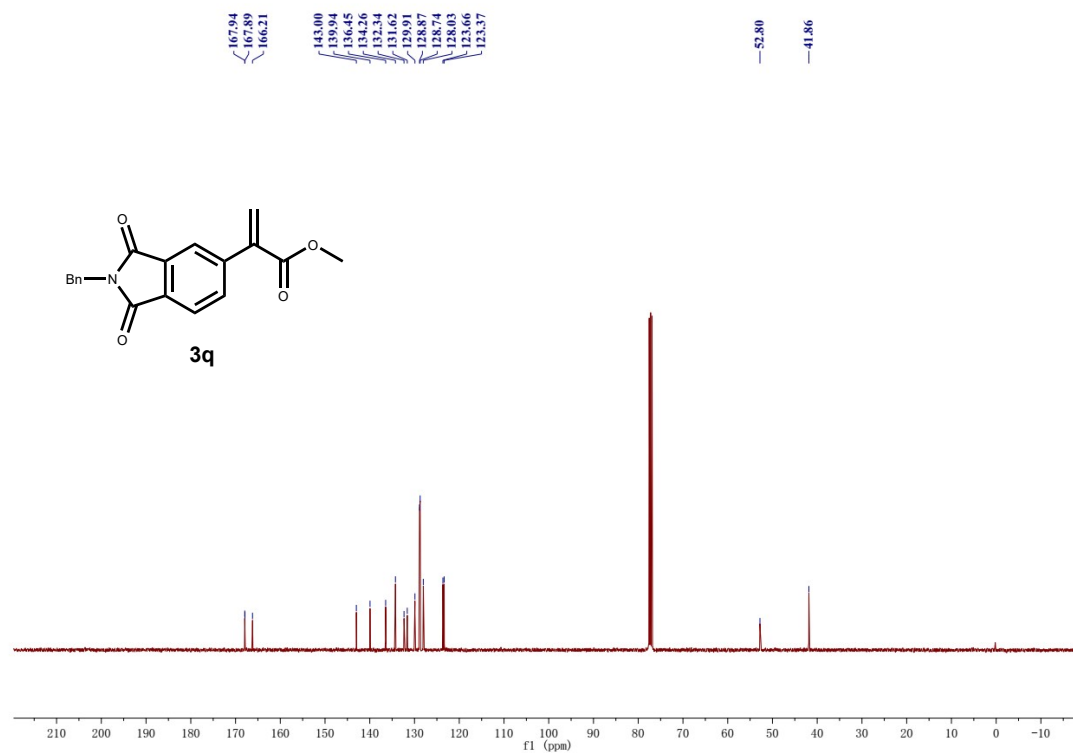
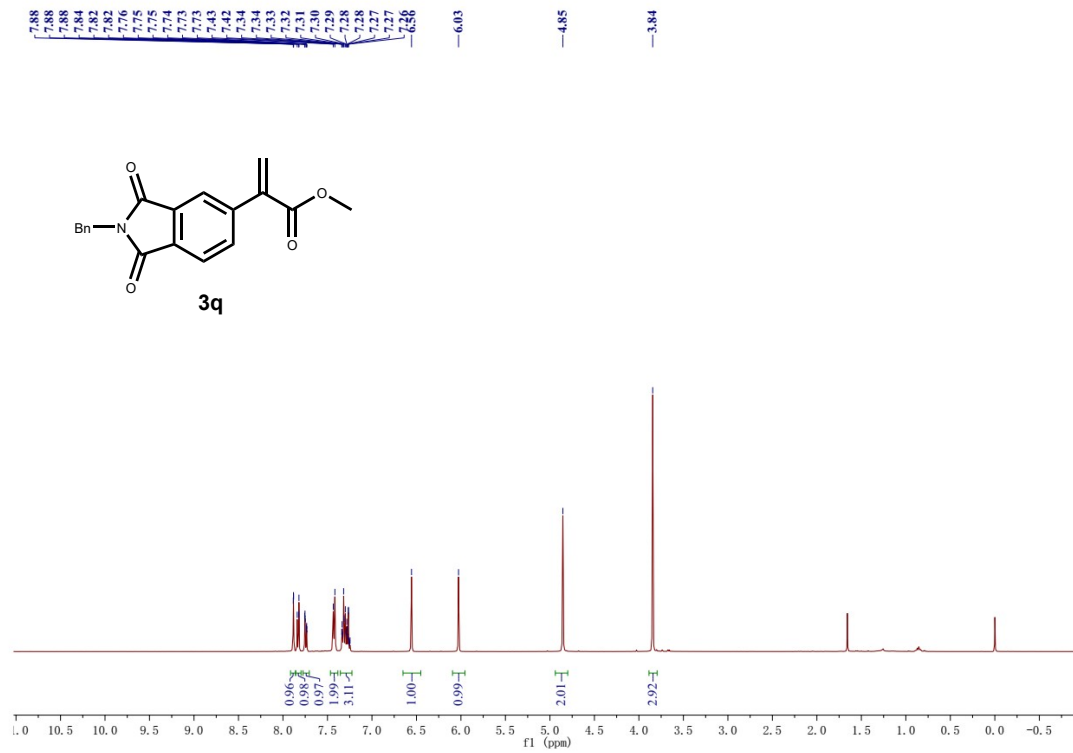


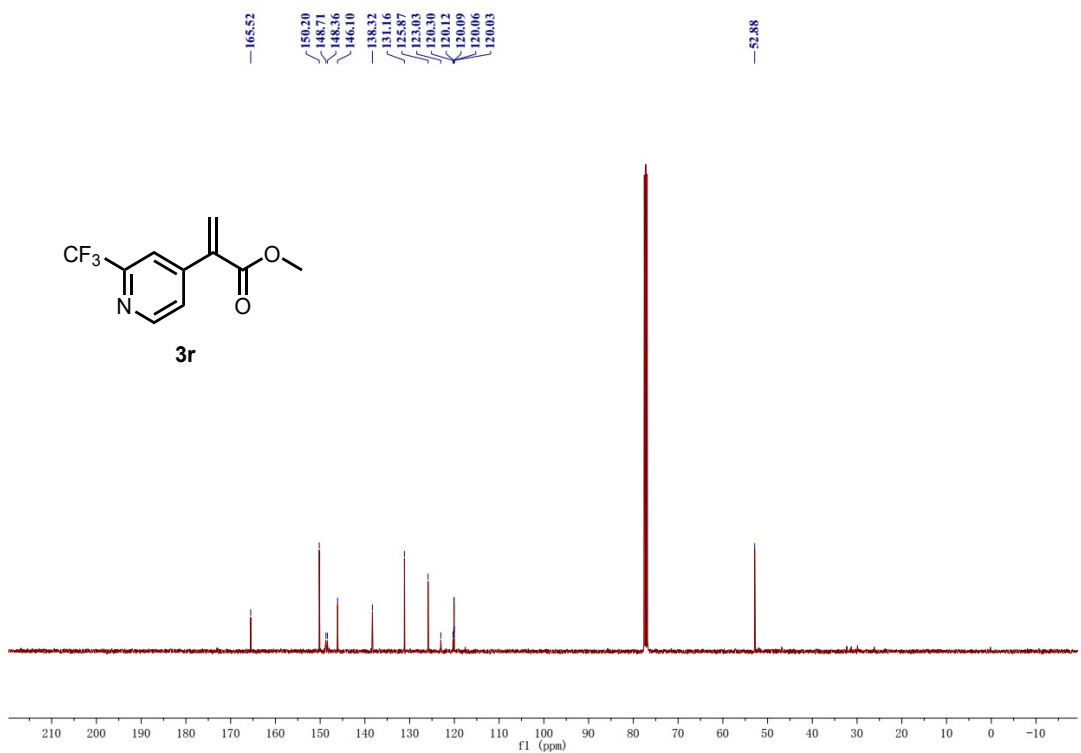
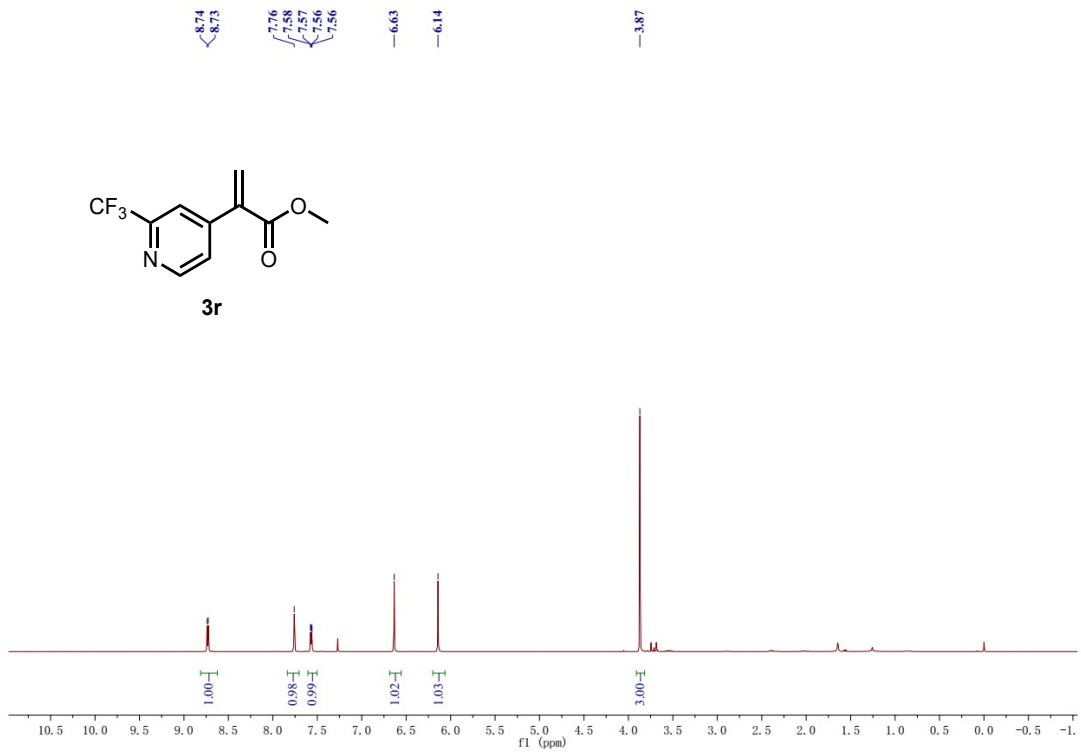


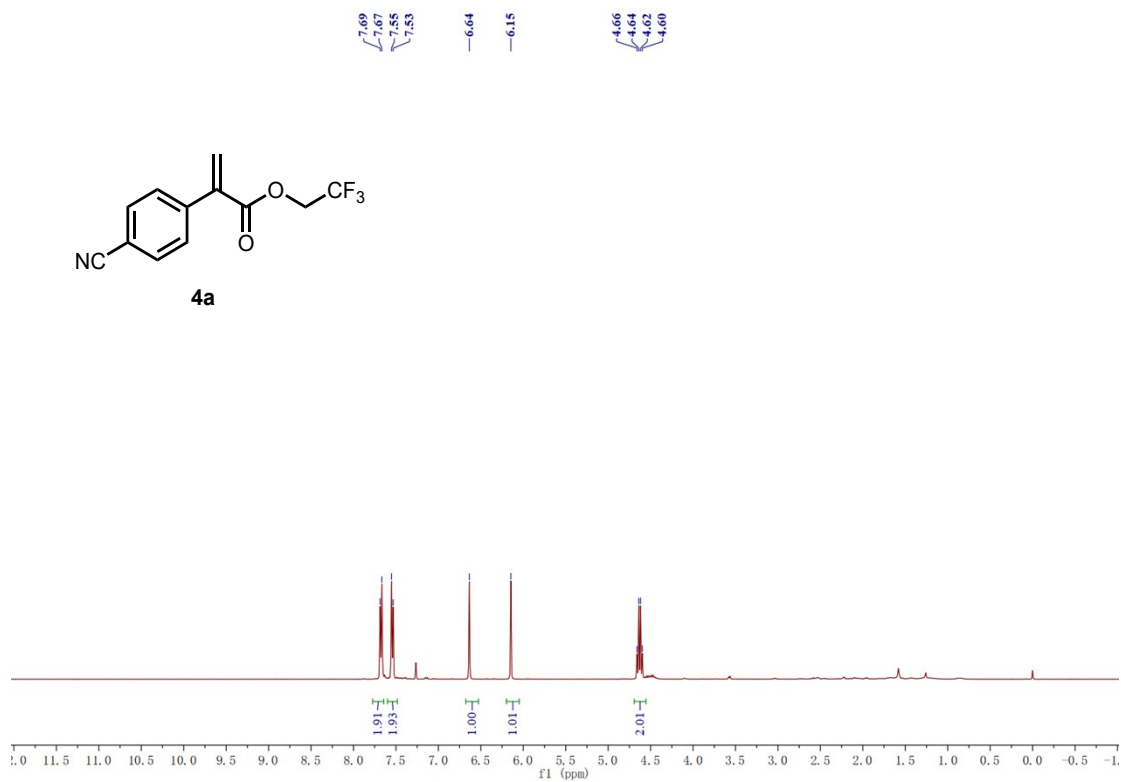
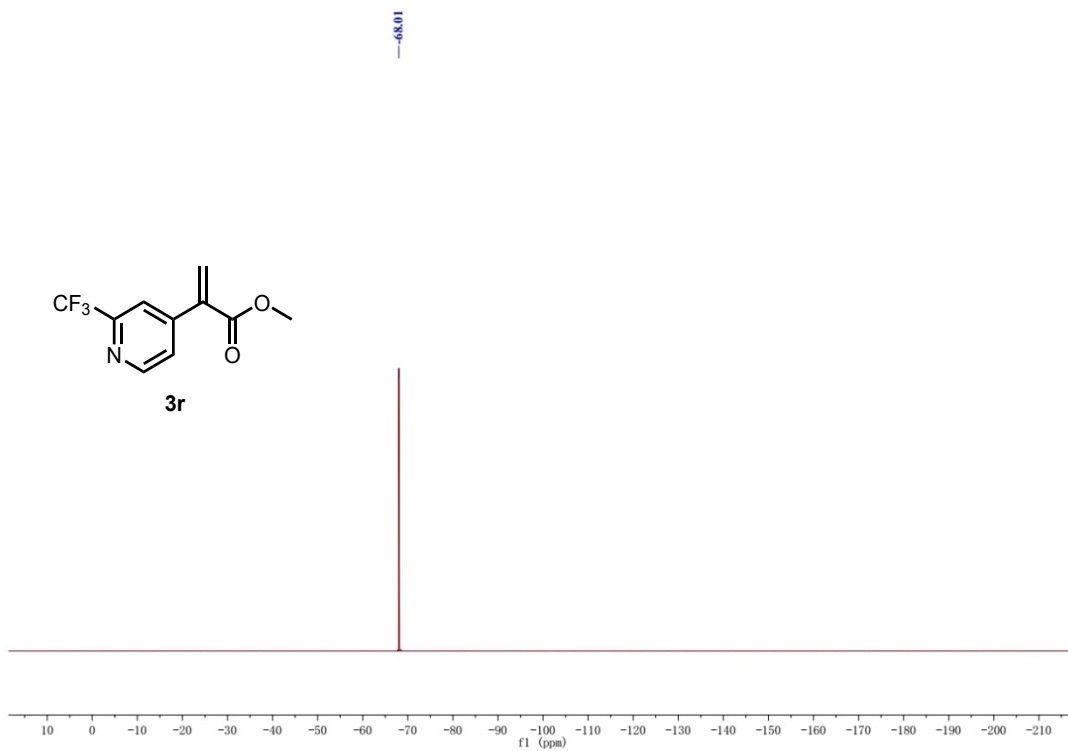


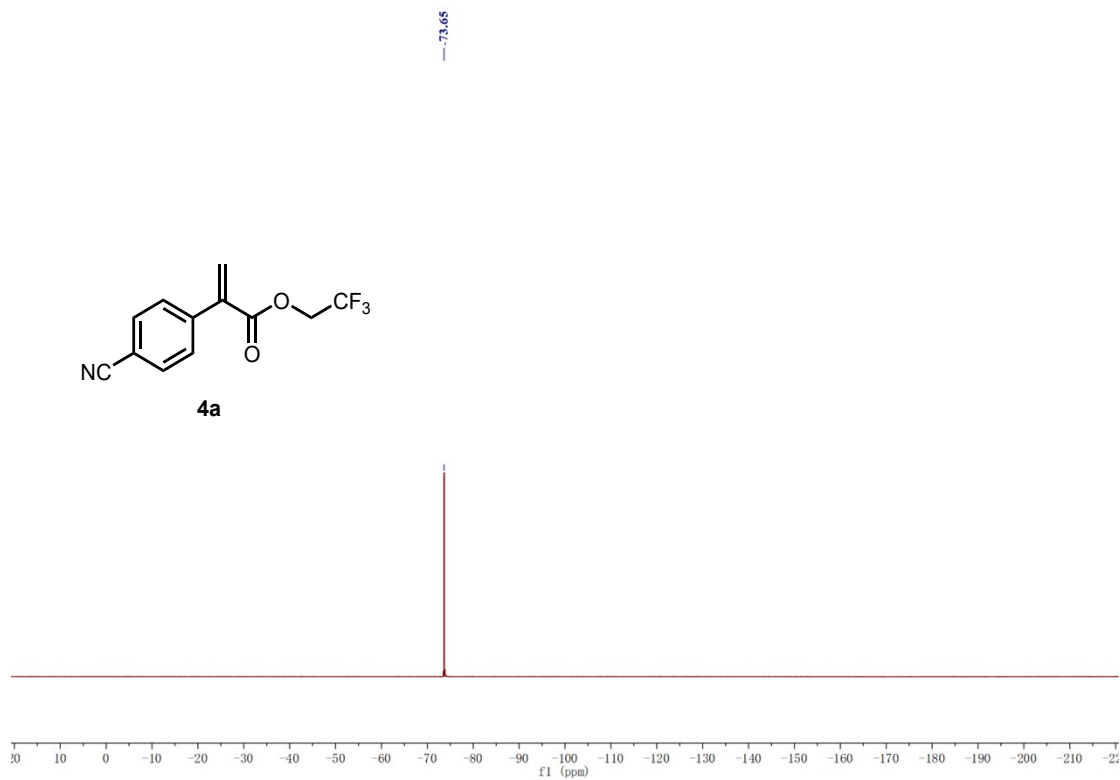
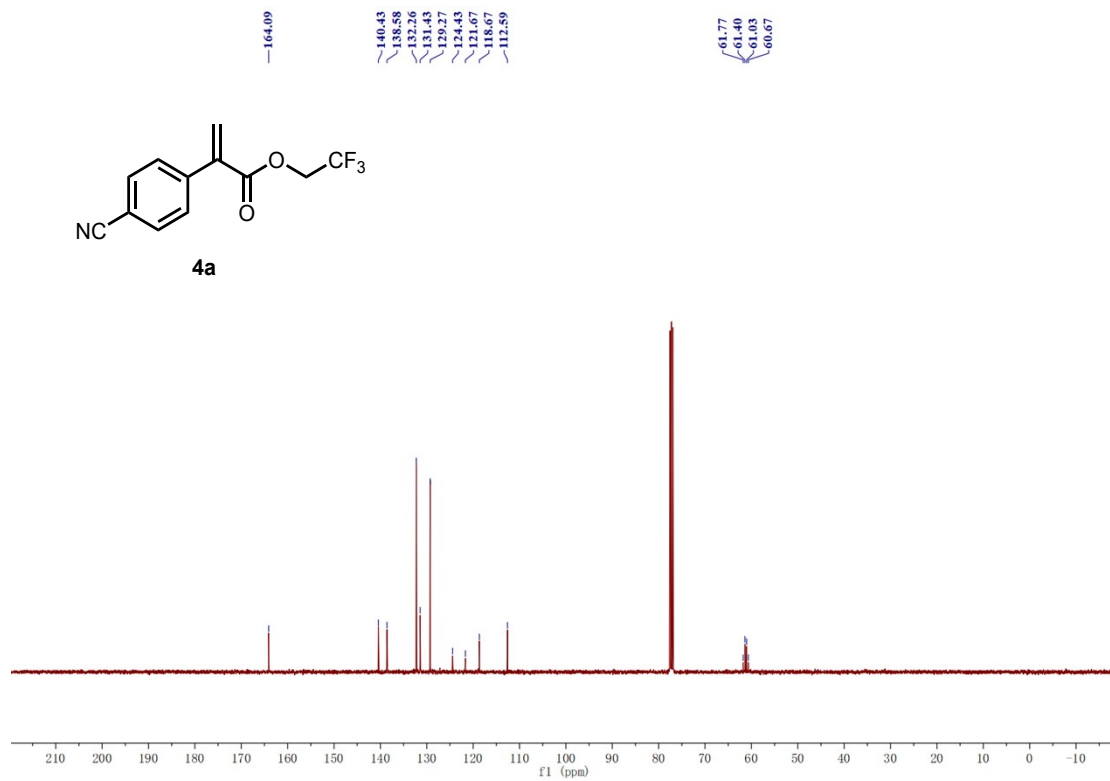


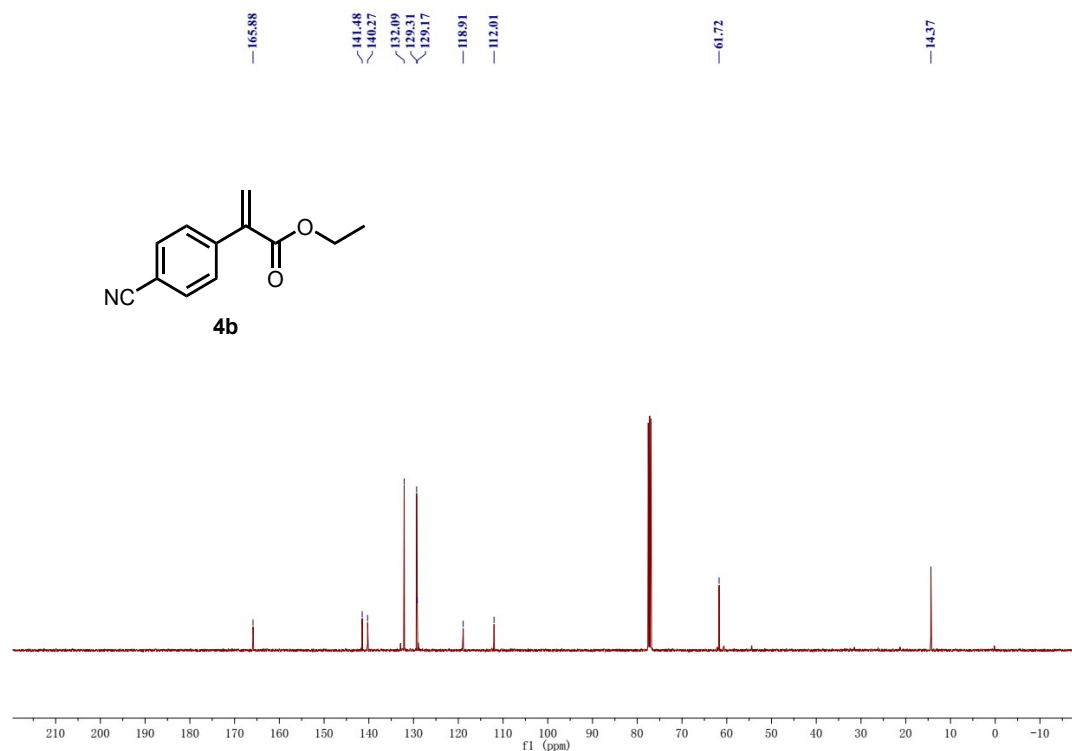
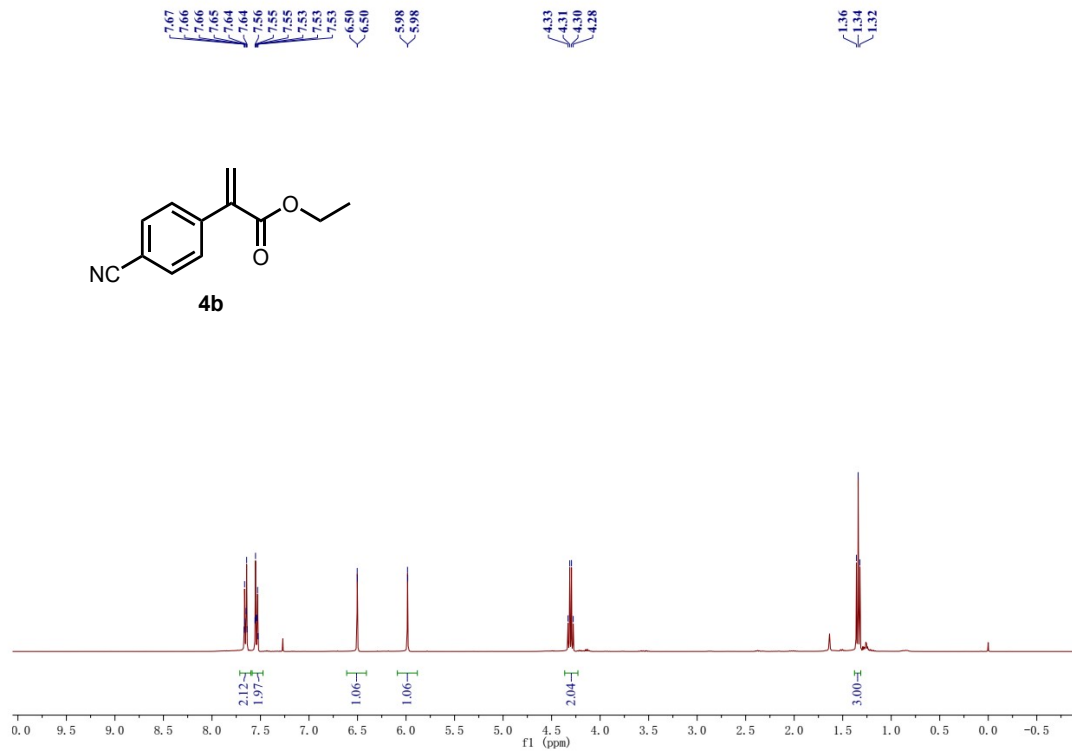


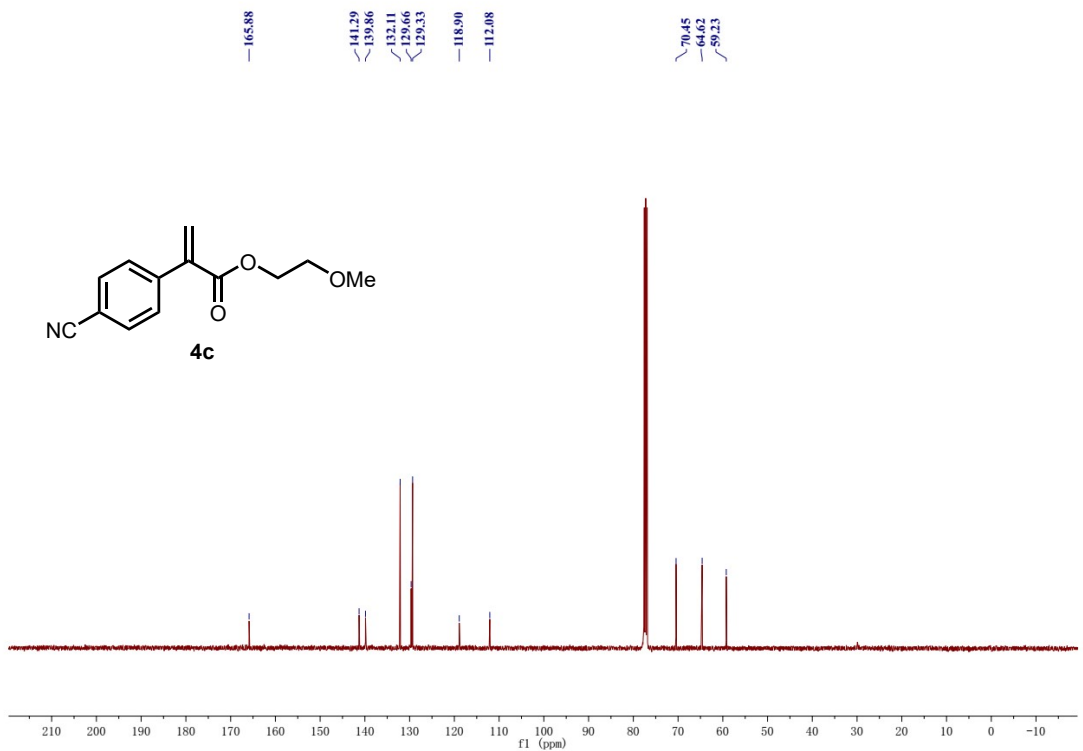
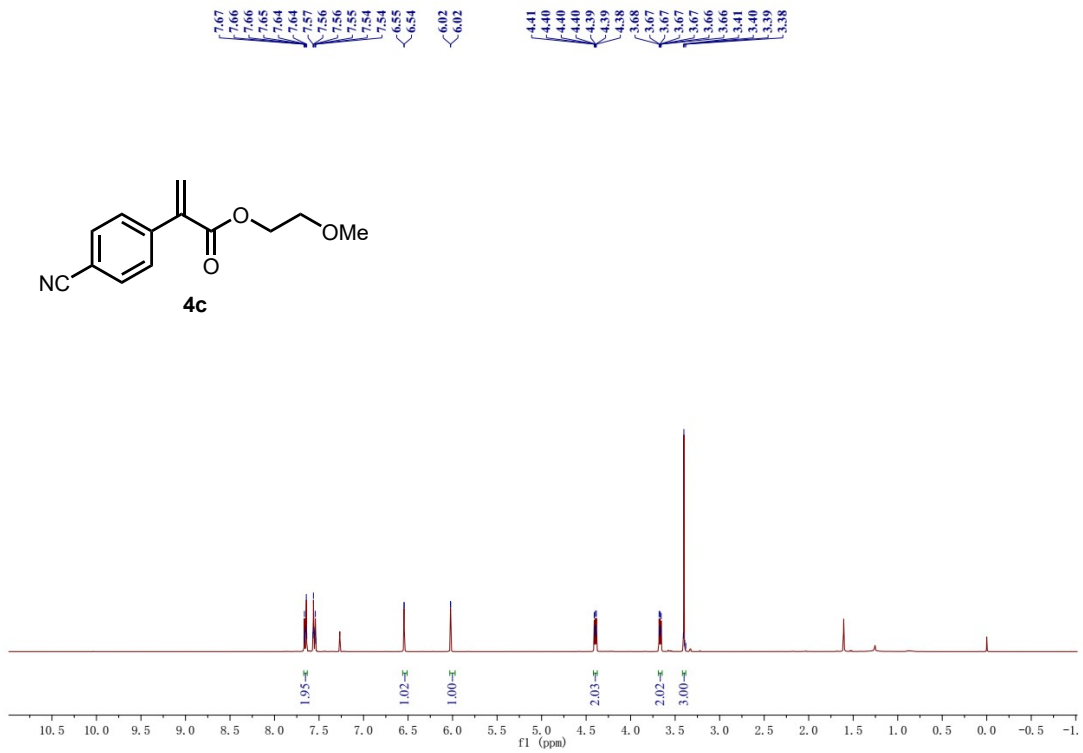


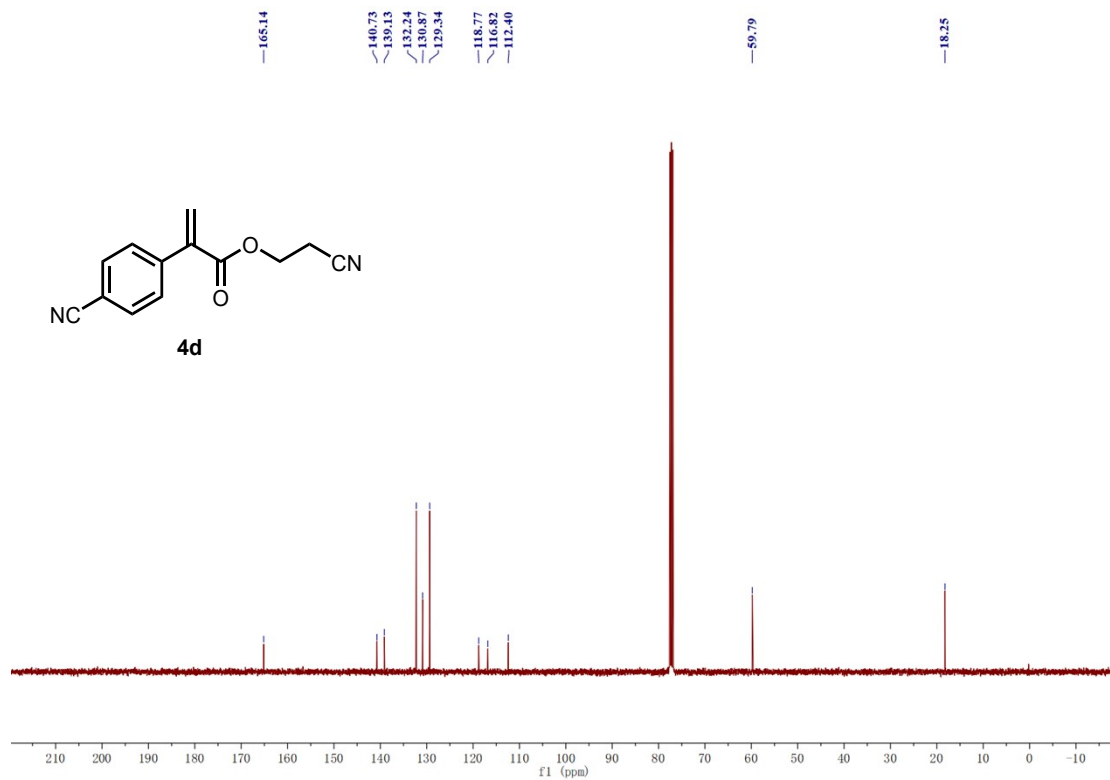
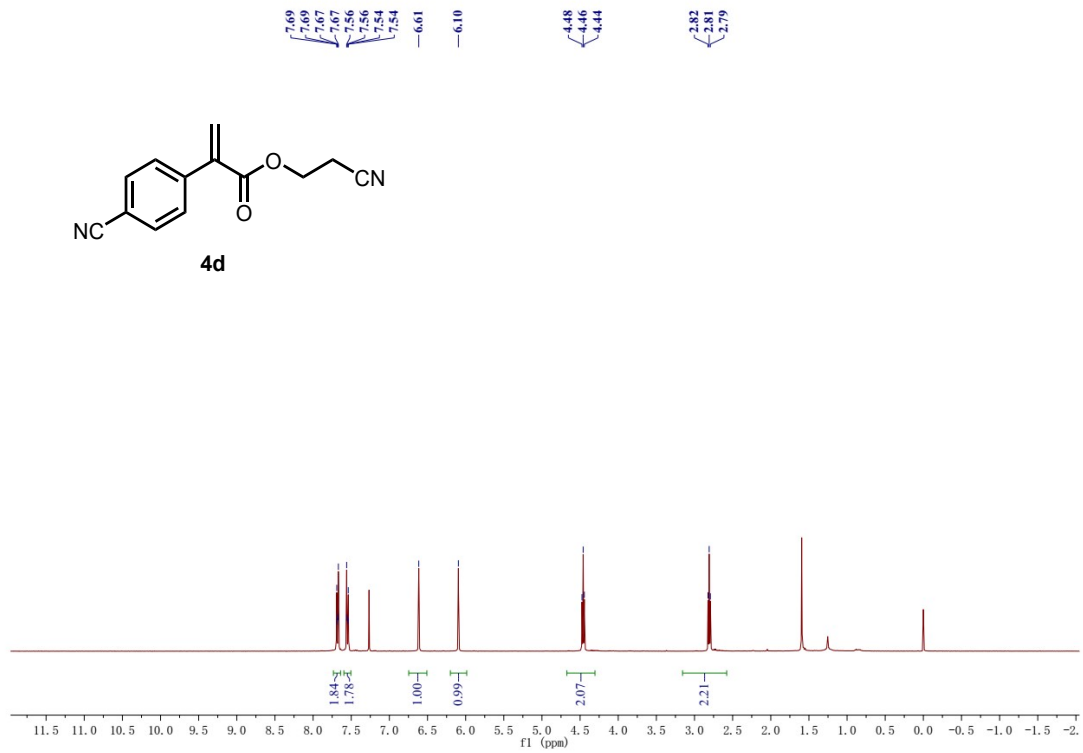


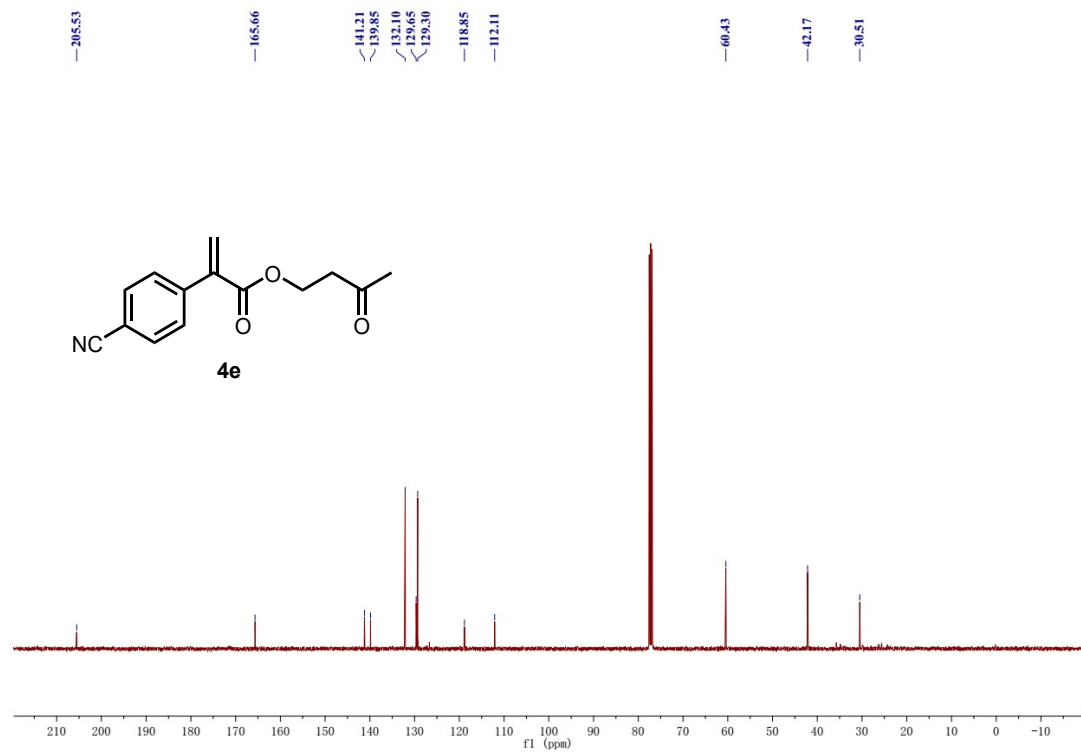
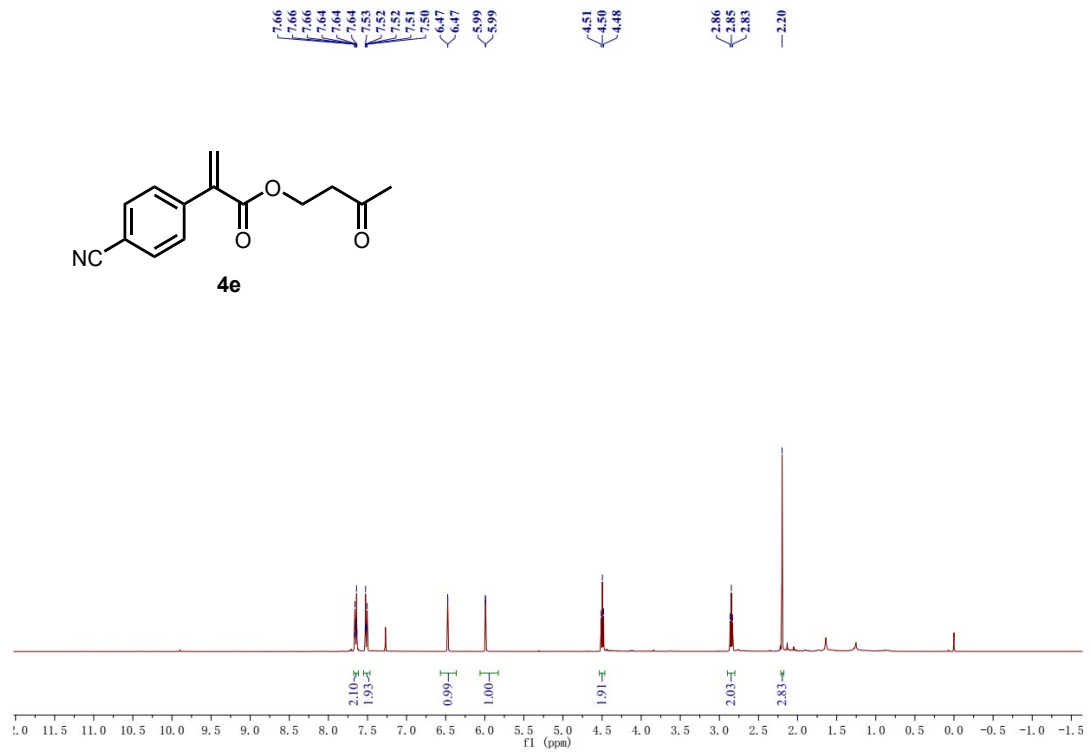


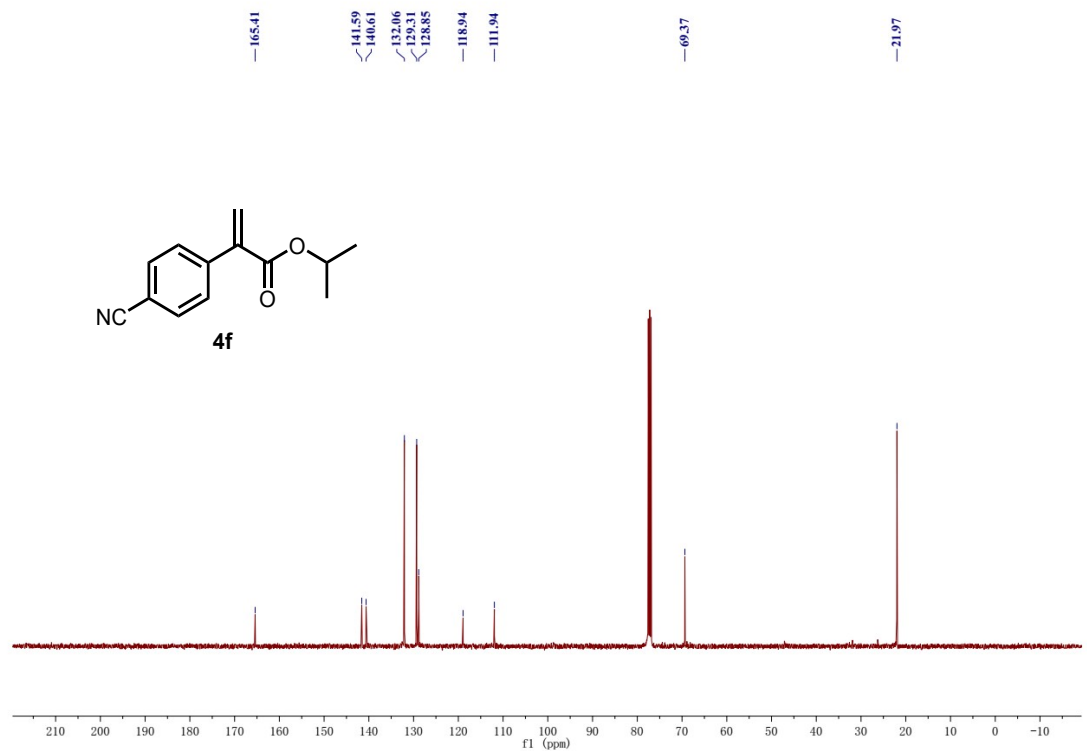
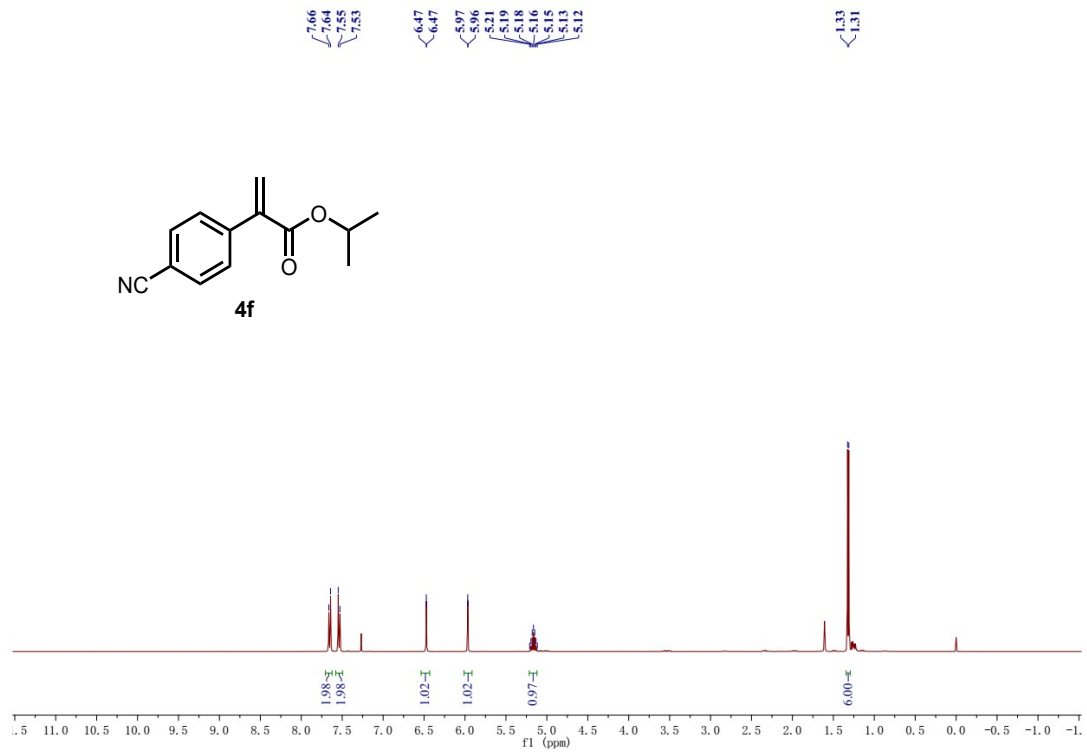


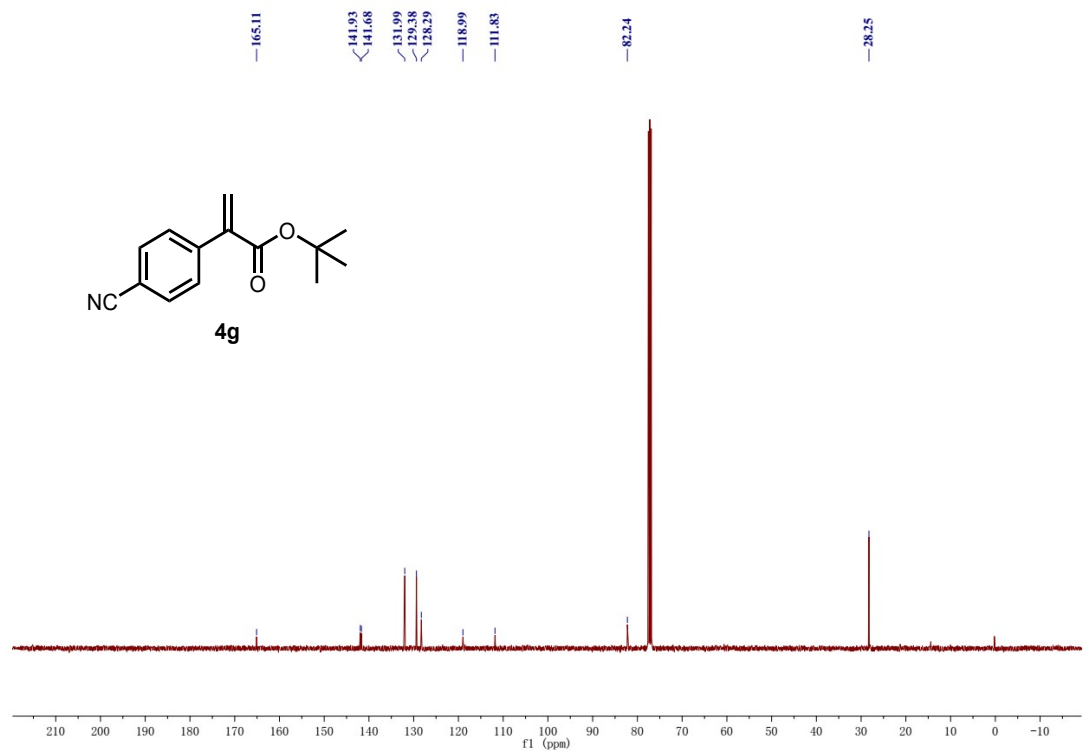
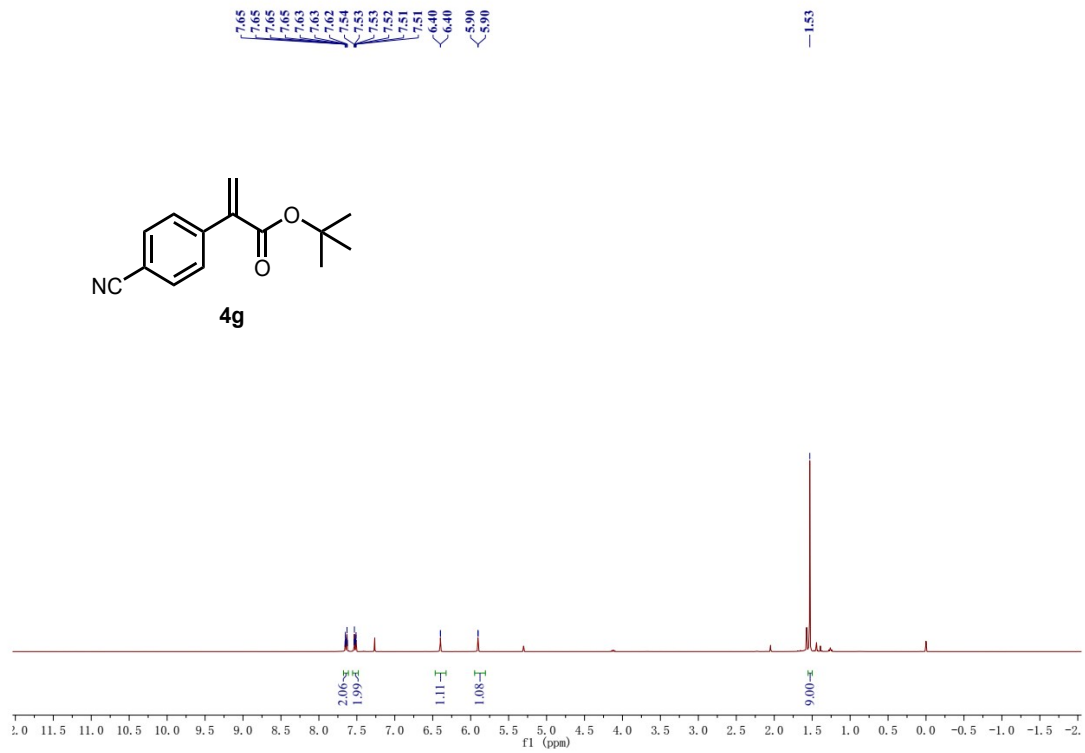


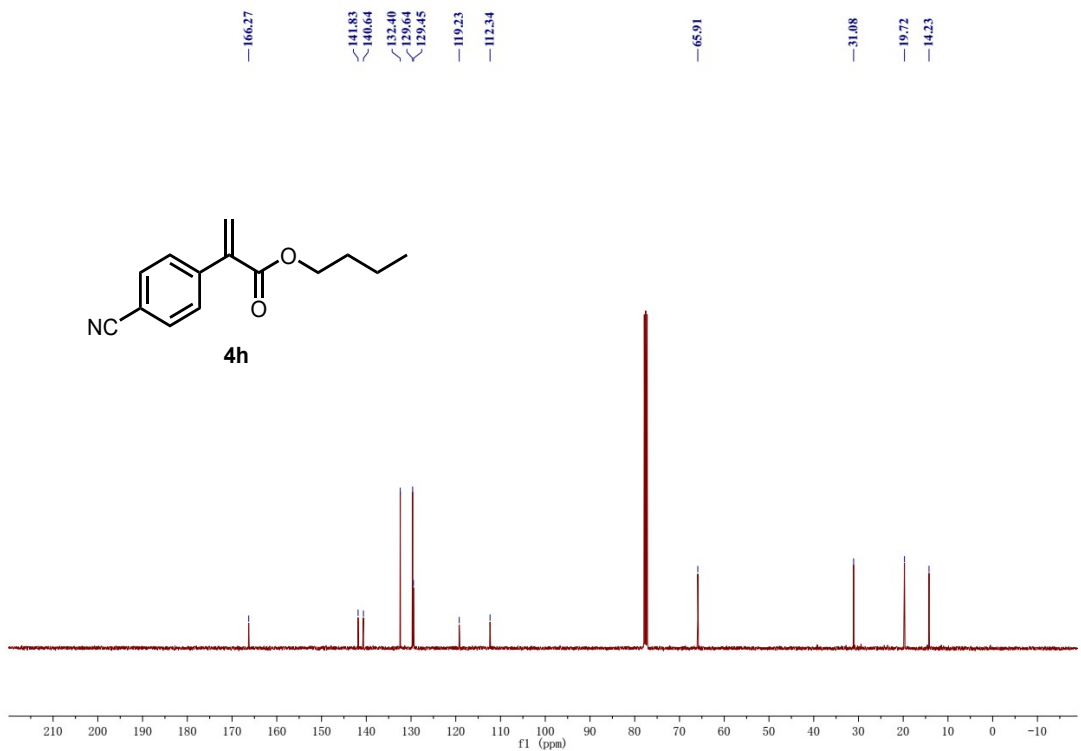
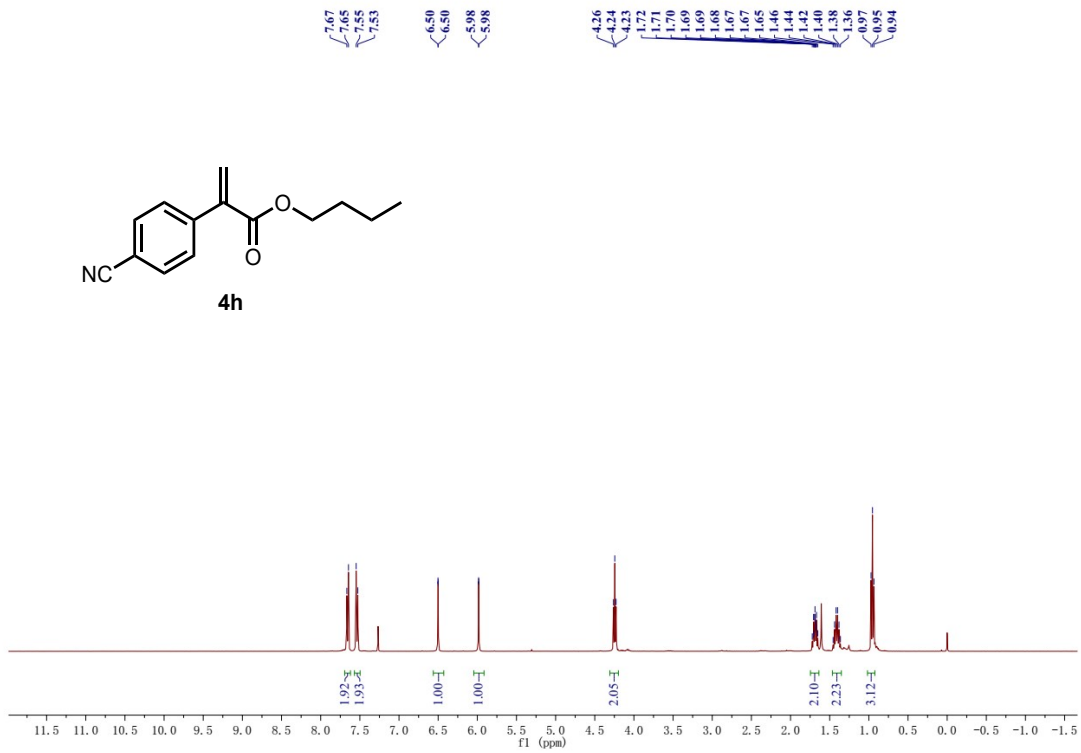




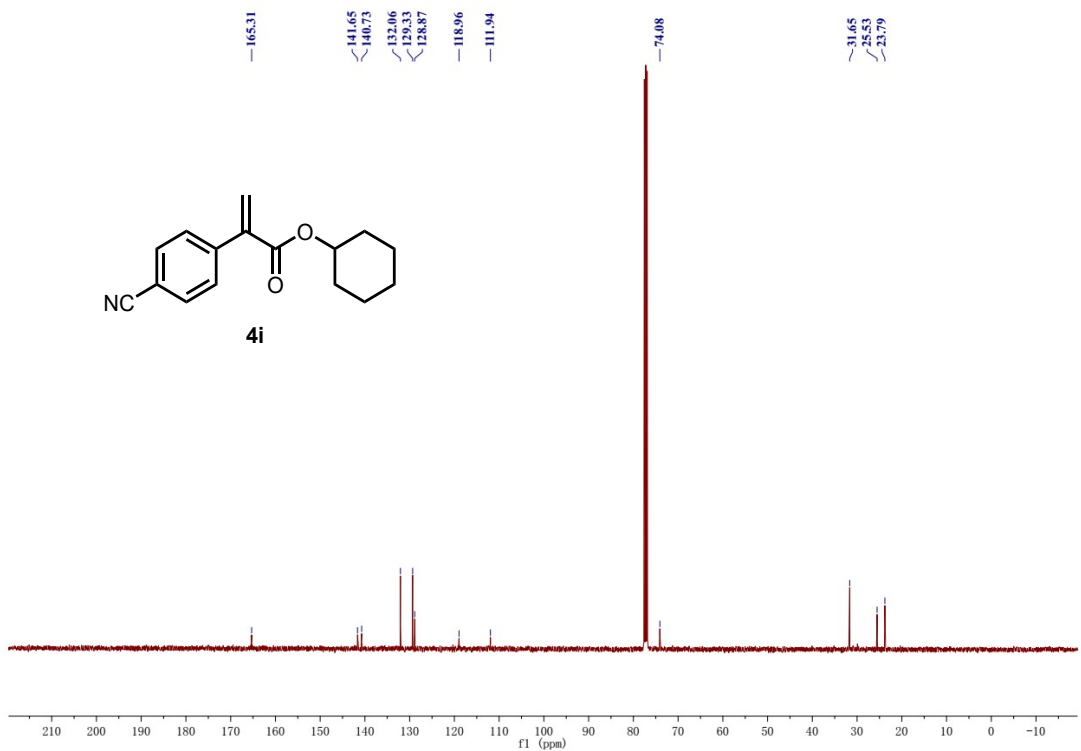
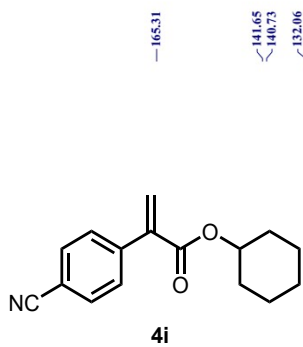
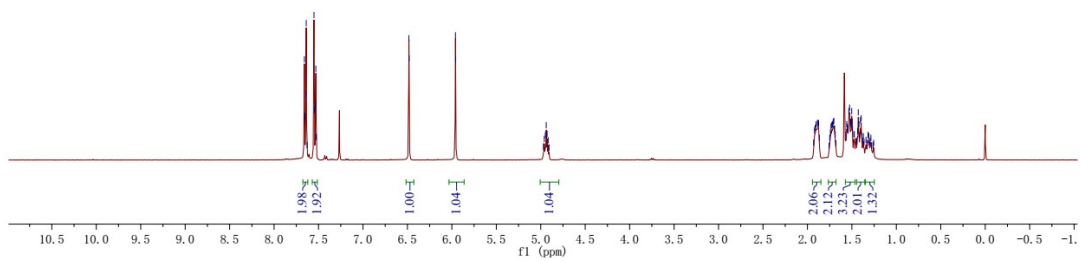
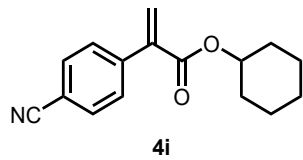


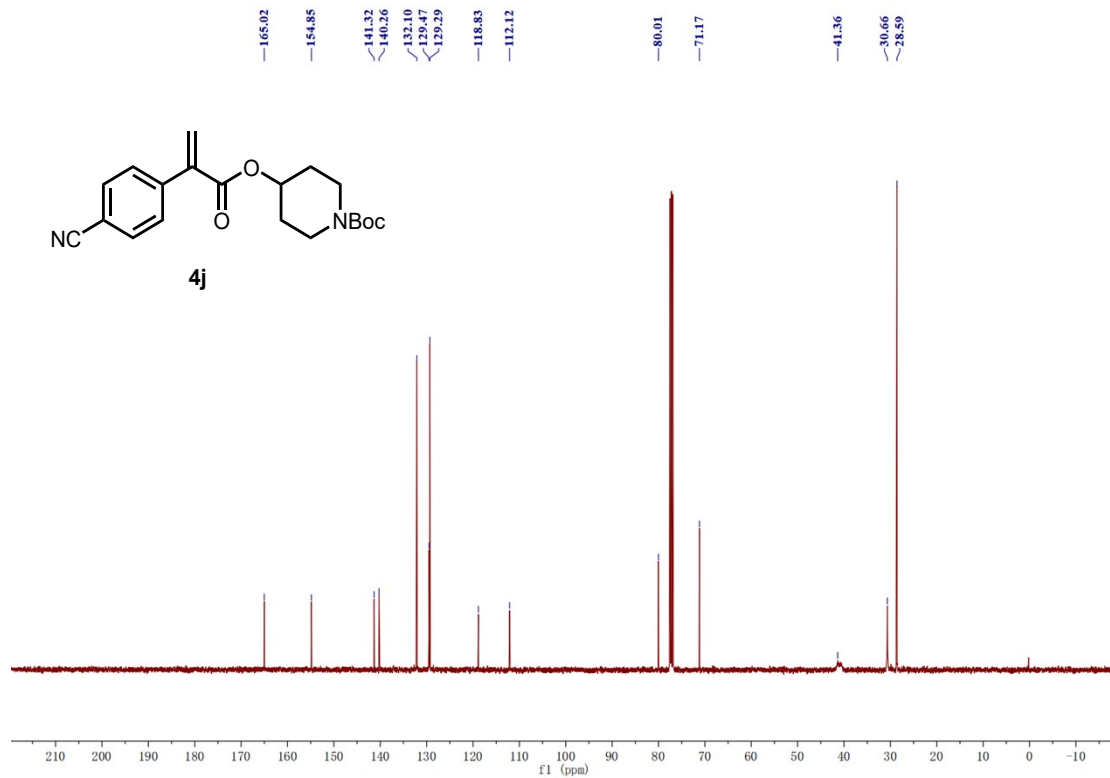
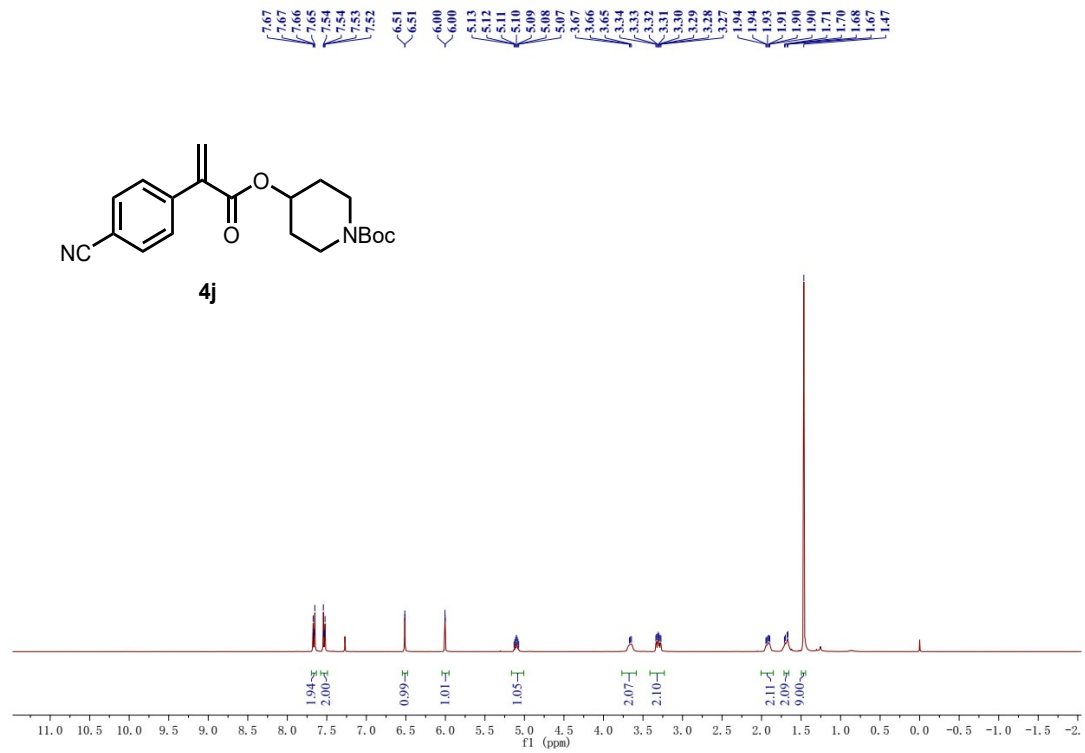




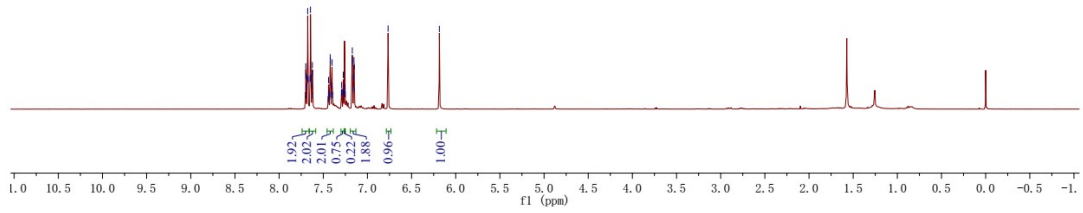
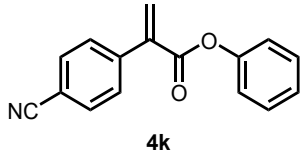


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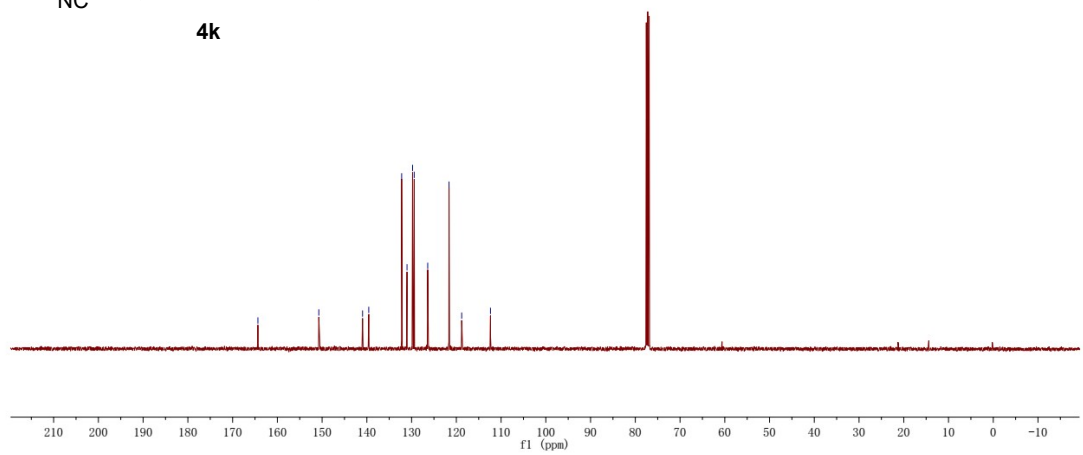
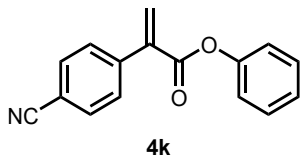


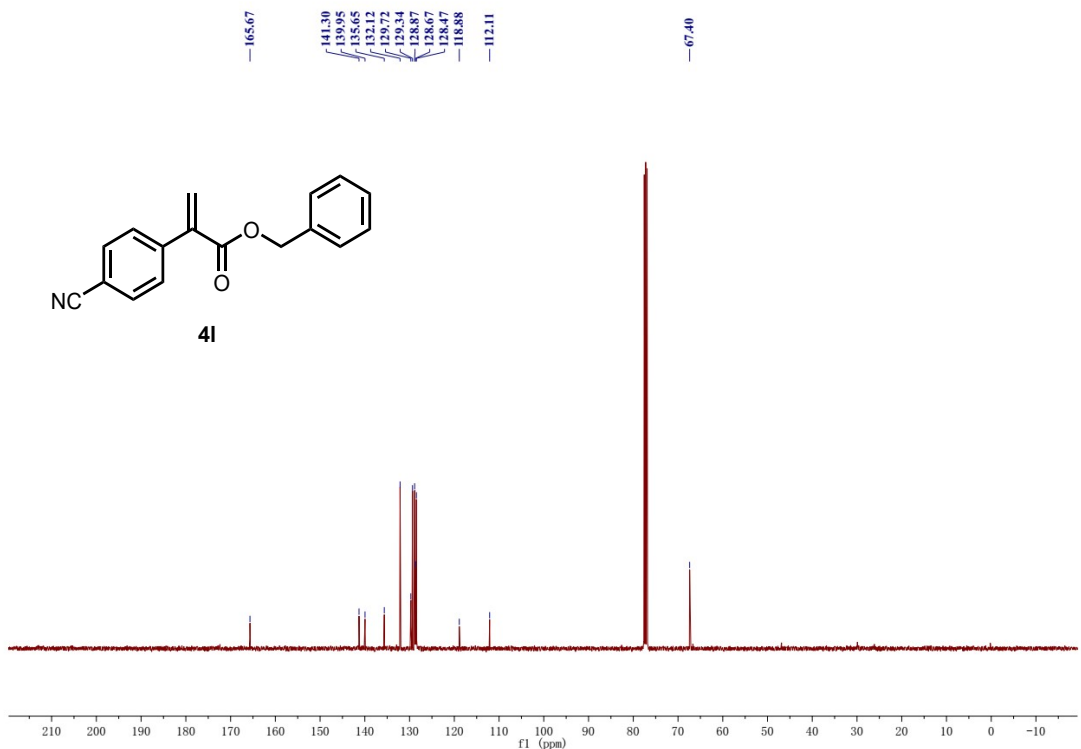
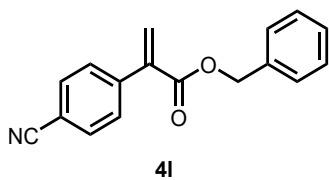
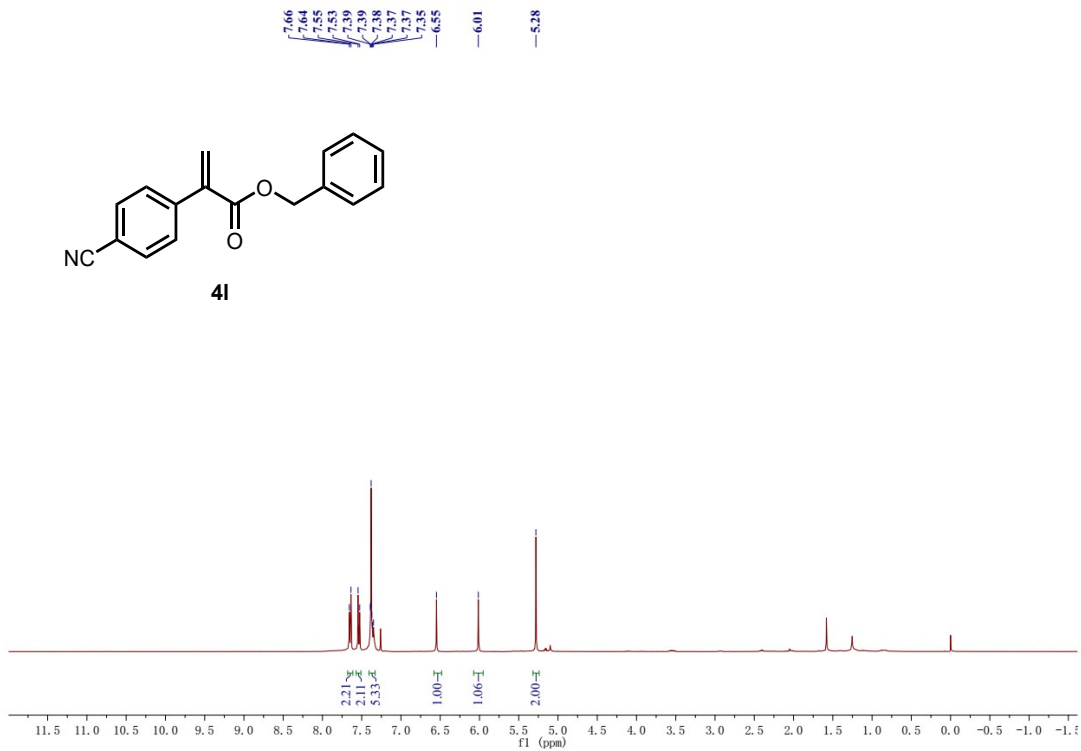
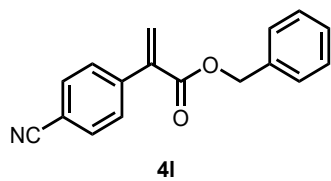


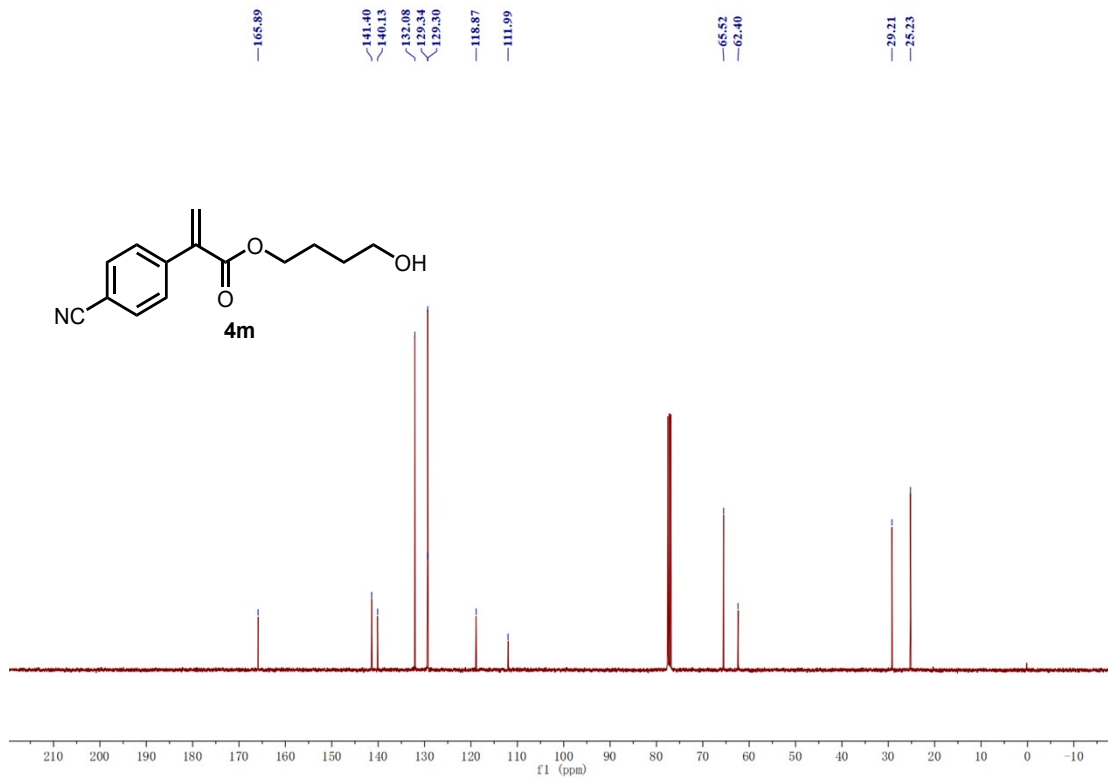
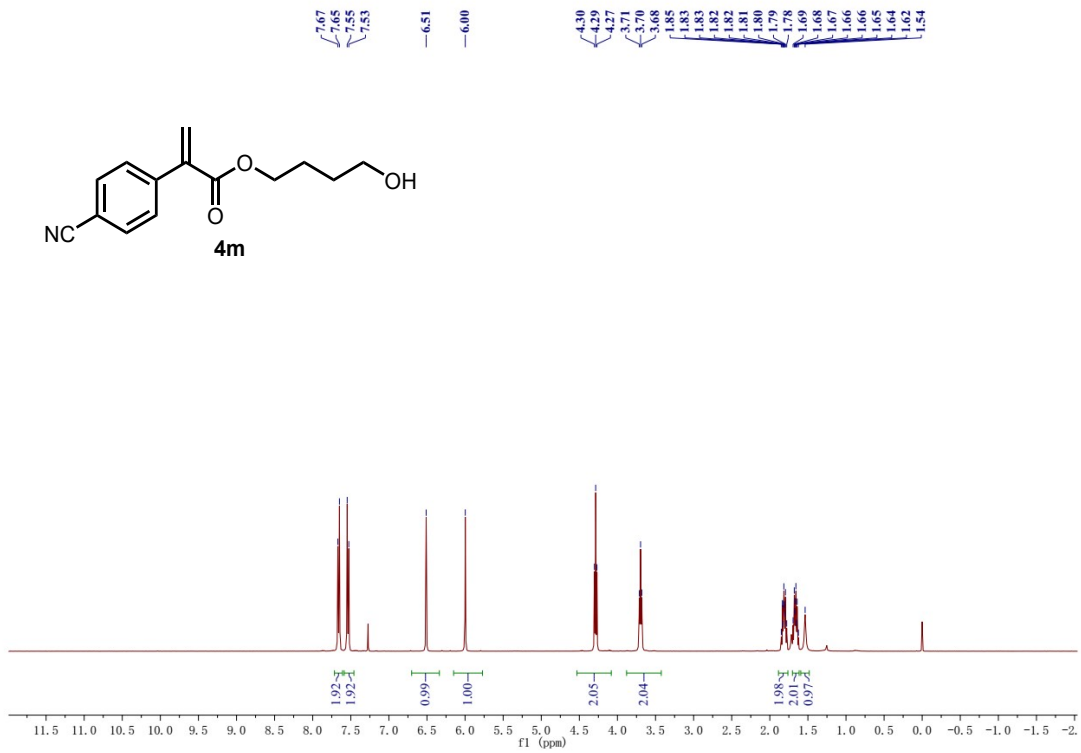
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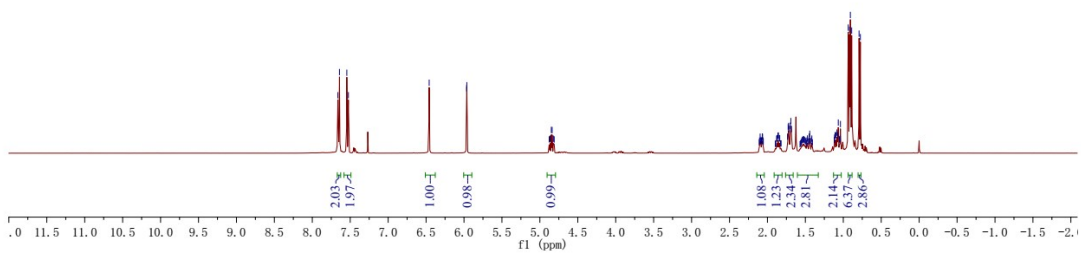
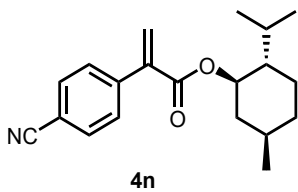
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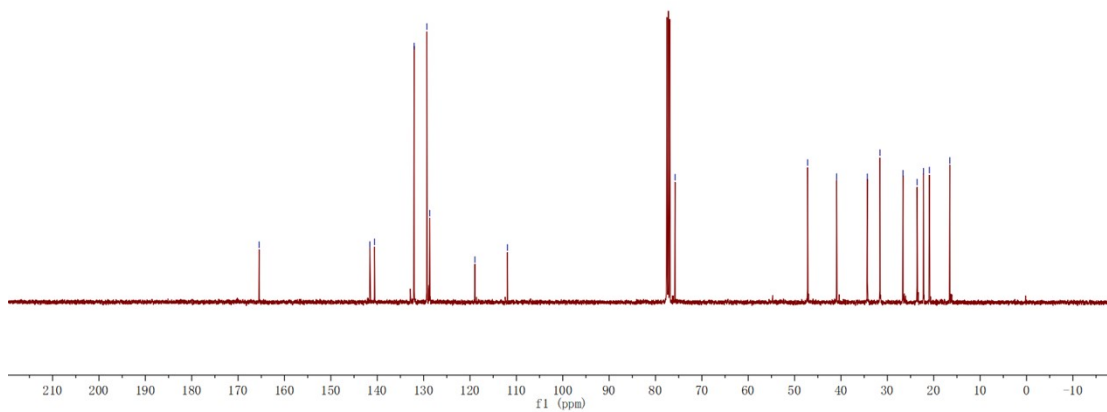
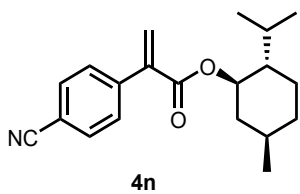




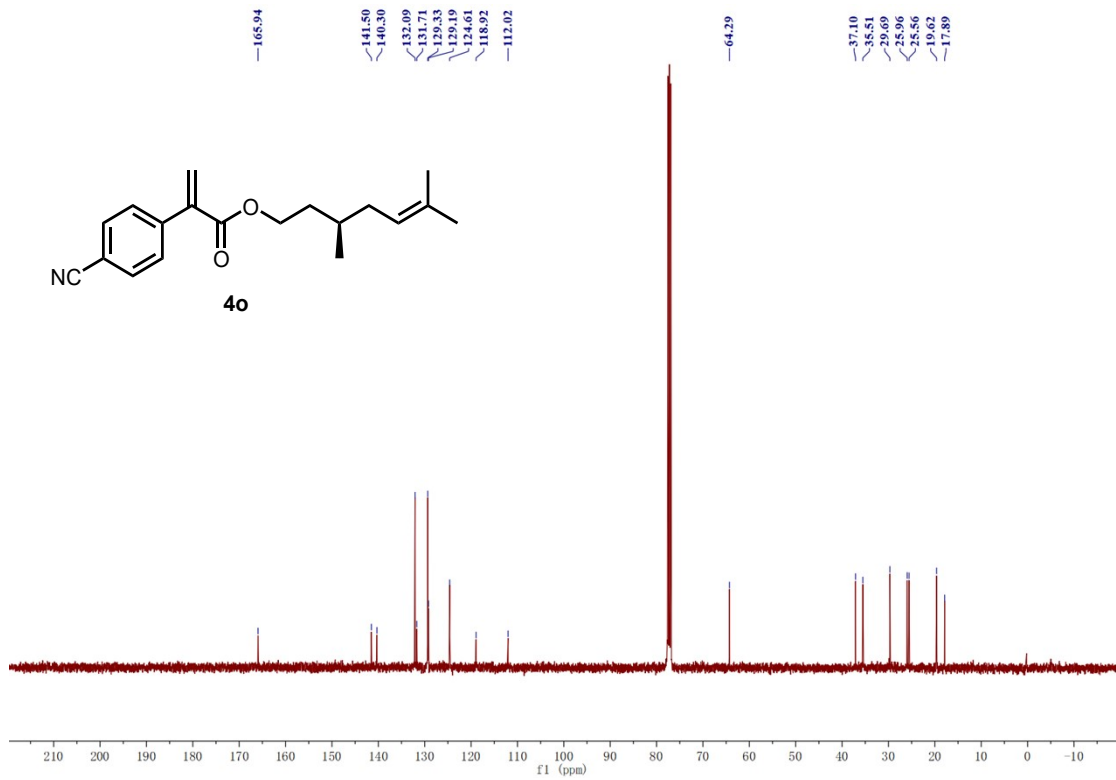
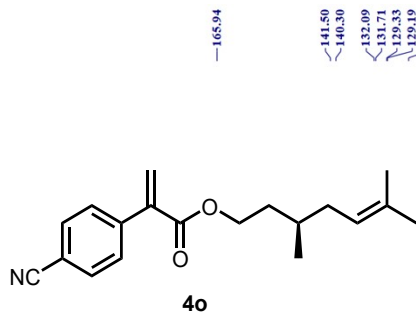
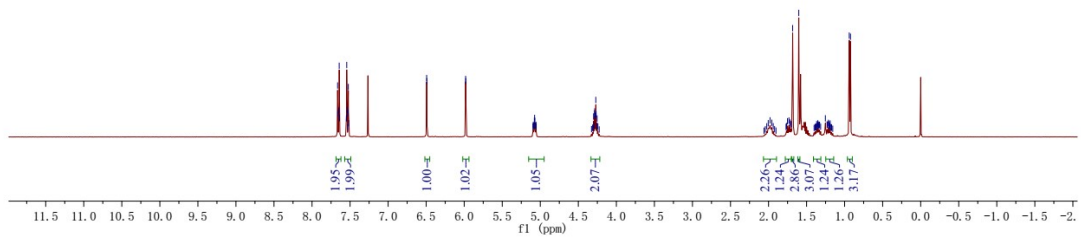
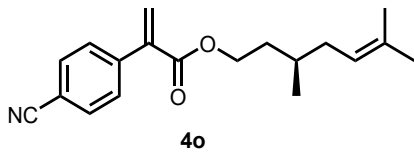
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