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Rh(III)-catalyzed regioselective C–H activation dialkenylation/annulation cascade for the rapid access to 6H-isoindolo[2,1-a]indole

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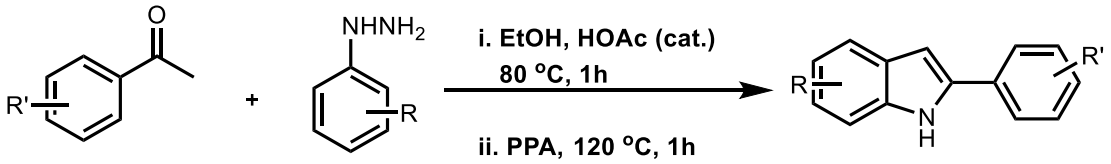
General Methods and Materials:

Unless specified, all reactions were carried out under air using commercially available solvents as received. Dichloro(η^5-pentamethylcyclopentadienyl)rhodium(III) dimer was synthesized according to a previous literature.[1] 2-phenyl indole was purchased from Alfa Aesar and used directly. All other reagents were purchased and used without further purification unless specified otherwise. Solvents for chromatography were technical grade and distilled prior to use. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). ^{1}H NMR and ^{13}C NMR data were recorded on Varian VNMR 600, Varian VNMR 400 or Mercury 300 spectrometer. Chemical shifts (δ) in ppm are reported as quoted relative to the residual signals of chloroform (^{1}H 7.26 ppm or ^{13}C 77.16 ppm). Multiplicities are described as: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet); and coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded with total proton decoupling. Mass spectra (MS-EI, 70 eV) were conducted on Finnigan MAT SSQ 700, unless otherwise specified, respectively. IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

Synthesis and Characterization of Starting Materials

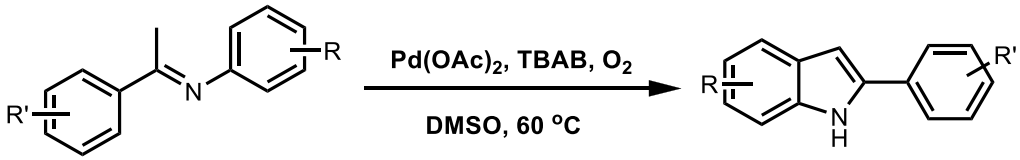
General procedure for preparation of 2-aryl indole substrates

Method A [2]



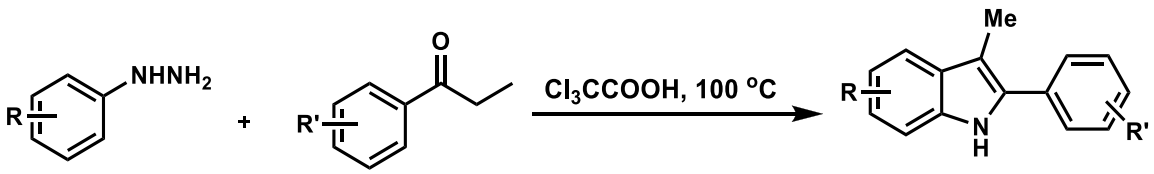
Substituted acetophenone (10 mmol) was mixed with related phenylhydrazine (10 mmol) in ethanol (25 mL) with a few drops of glacial acetic acid. The reaction was heated to 80 °C and stirred for 1 hour. Solvent was evaporated to yield the phenylhydrazone intermediate, which was added to polyphosphoric acid (20 g). Exothermic reaction was observed and the reaction mixture was slowly heated to 120 °C (keep for 1 hour). The mixtures were poured into crashed ice cube and then neutralized with 2M NaOH and extracted with EtOAc. The combined organic extracts were washed with water, dried over anhydrous Na_2SO_4, and purified by column to give to give the desired 2-aryl indole product.

Method B [3]



A Schlenk tube equipped with a stirrer bar was charged with *N*-aryl imine (2 mmol), $Pd(OAc)_2$ (45 mg, 0.2 mmol, 10 mol%) and *n*-Bu_4NBr (1.29 g, 4 mmol), followed by addition of DMSO (10 mL). The Schlenk tube was quickly evacuated, closed under vacuum, and then refilled with oxygen using an oxygen balloon. The resulting mixture was stirred at 60 °C for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 50 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford the indole product.

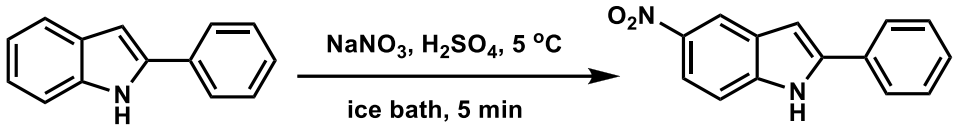
Method C [4]



A mixture of phenylhydrazine (10 mmol), ketones (10 mmol) trichloroacetic acid (30 mmol) was heated, with swirling, in test tube at 100 °C for 5 min. Water was added to the cooled

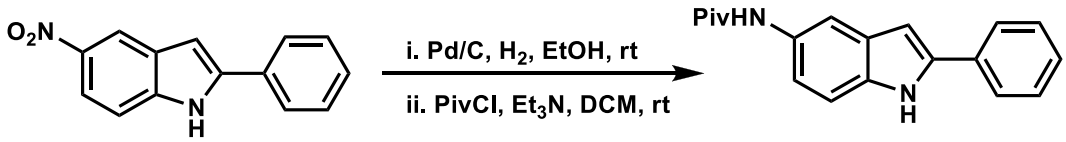
mixture which was filtered. The retentate was washed with water and dried in vacuum to give the corresponding analytically pure indoles.

Method D [5]



A solution of 2-phenyl indole in conc. H_2SO_4 (100 mL) was cooled to 5 °C in an ice bath. A solution of sodium nitrate in H_2SO_4 (50 mL), also cooled, was added, with stirring. The resulting mixture was kept for 5 min, then poured into crushed ice. The flocculent yellow precipitate was filtered and dried, crystallization by DCM-petroleum ether.

Method E

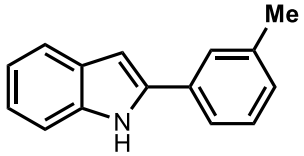


Step 1[6]

2-phenyl-5-nitro-1*H*-indole (1.63g, 6.84 mmol) and Pd/C (30% wt, 0.28 g) were added into a flask, then 50 ml EtOH was added via syringe. The vial was capped and evacuated/flushed with H_2 three times, then stirred under a hydrogen balloon for 18 h. Palladium catalyst was removed by filtration through a plug of Celite and washed thoroughly with ethyl acetate. The filtrate was concentrated under vacuum and the residue was pure enough for the next step use.

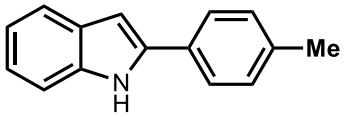
Step 2

The above obtained indole material (229 mg, 1.1 mmol) and Et_3N (318 µL, 2.18 mmol) were added into a vial containing 5 mL DCM. Then PivCl (109 μL, 1.31 mmol) was slowly added via a microsyringe at 0 °C, after addition, the mixture was stirred at rt overnight. After reaction, the product was purified by column.

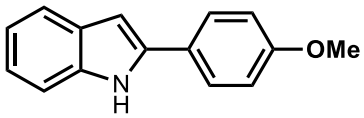


2-m-tolyl-1H-indole (**1b**)[7]: method A, yield: 72%, pale white solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ; 11.50 (s, 1H), 7.71 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.87 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 138.0, 137.7, 137.1,

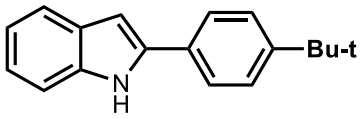
132.1, 128.7, 128.6, 128.0, 125.5, 122.2, 121.4, 120.0, 119.3, 111.3, 98.5, 21.1.



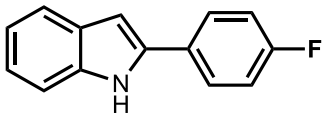
2-p-tolyl-1H-indole (**1c**)[7]: method A, yield: 93%, white solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 11.45 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.82 (s,1H), 2.33 (s, 3H); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 137.8, 137.0, 136.7, 129.4, 128.7, 124.9, 121.3, 119.8, 119.3, 111.2, 98.0, 20.8.



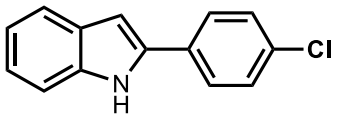
2-(4-methoxyphenyl)-1H-indole (**1d**)[7]: method B, yield: 87%, brown solid. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 11.41 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.08-6.96 (m, 4H), 6.75 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (d_6-DMSO, 100 MHz): δ 158.8, 137.8, 136.9, 128.8, 126.3, 124.9, 121.0, 119.7, 119.2, 114.3, 111.1, 97.3, 55.2.



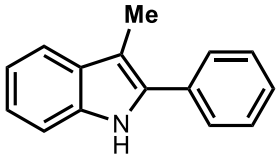
2-(4-tert-butylphenyl)-1H-indole (**1e**)[7]: method A, yield: 62%, white solid. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.28 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4, 2H), 7.50 (d, *J* = 8.4, 2H), 7.41 (d, *J* = 8.4, 1H), 7.24 (td, *J* = 7.2, 1.2, 1H), 7.18 (td, *J* = 7.8, 1.2, 1H), 6.84 (d, *J* = 1.2, 1H), 1.41 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 151.0, 138.1, 136.8, 129.6, 129.5, 126.1, 125.0, 122.2, 120.7, 120.3, 111.0, 99.6, 34.8,31.4.



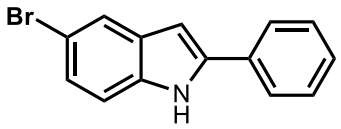
2-(4-fluorophenyl)-1H-indole (**1f**)[7]: method A, yield: 77%, white solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 11.53 (s, 1H), 7.90 (t, *J* = 5.4, 2H), 7.53 (d, *J* = 7.8, 1H), 7.41 (d, *J* = 7.8, 1H), 7.31 (t, *J* = 7.8, 2H), 7.11 (t, *J* = 7.8, 1H), 7.01 (t, *J* = 7.8, 1H), 6.86 (s, 1H); ^{19}F NMR (d_6-DMSO, 576 MHz) δ -114,7 (s); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 161.5 (d, J_F=243.0), 136.9 (d, J_F=60.0), 128.9, 128.6, 126.9 (d, J_F=9.0), 121.5, 120.0, 119.4, 115.8 (d, J_F=21.0), 111.3, 98.6.



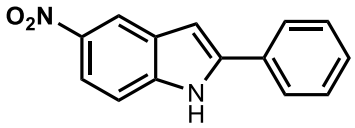
2-(4-chlorophenyl)-1H-indole (**1g**)[7]: method A, yield: 67%, brownish white solid ^{1}H NMR (d_6-DMSO, 400 MHz): δ 11.58 (s, 1H), 7.88 (d, *J* = 8.4, 2H), 7.53 (t, *J* = 8.0, 3H), 7.41 (d, *J* = 8.0, 1H), 7.12 (t, *J* = 7.2, 1H), 7.01 (t, *J* = 7.2, 1H), 6.93 (s, 1H); ^{13}C NMR (d_6-DMSO, 100 MHz): δ 137.2, 136.3, 131.7, 131.1, 128.9, 128.5, 126.6, 121.9, 120.2, 119.5, 111.3, 99.3.



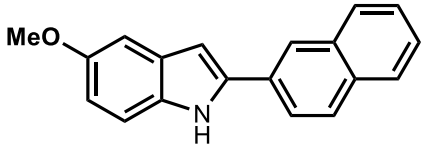
3-methyl-2-phenyl-1H-indole (**1h**)[4]: method C, yield: 82%, yellow solid. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 11.16 (s, 1H), 7.69 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.54-7.49 (m, 3H), 7.39-7.33 (m, 2H), 7.12 (td, *J* = 7.2, 0.8 Hz, 1H), 7.02 (td, *J* = 7.2, 0.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (d_6-DMSO, 100 MHz): δ 135.9, 133.7, 133.1, 129.4, 128.7, 127.5, 126.9, 121.5, 118.6, 118.4, 110.0, 106.8, 9.84.



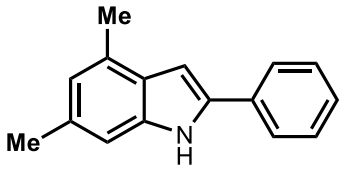
5-bromo-2-phenyl-1H-indole (**1i**)[7]: method B, yield: 93%, pale yellow white solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 11.76 (s, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.71 (s, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.38-7.33 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.89 (s, 1H); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 139.2, 135.8, 131.6, 130.5, 129.0, 127.9, 125.2, 124.0, 122.1, 113.2, 111.9, 98.3.



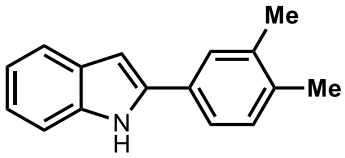
5-nitro-2-phenyl-1H-indole (**1j**)[5]: method D, yield: 95%, red solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 12.29 (s, 1H), 8.53 (d, *J* = 2.4 Hz, 1H), 8.01 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.90 (d, *J* = 7.2, Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 141.4, 141.0, 140.3, 131.0, 129.1, 128.5, 127.9, 125.4, 117.0, 111.6, 100.8.



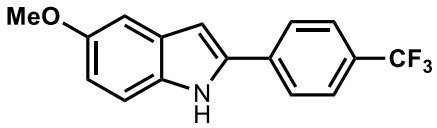
5-methoxy-2-(naphthalen-2-yl)-1H-indole (**1k**)[3]: method B, yield: 83%, pale yellow white solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 11.54 (s, 1H), 8.35 (s, 1H), 7.98 (q, *J* = 8.4 Hz, 2H), 7.92 (t, *J* = 9.0 Hz, 2H), 7.55 (t, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.06 (s, 1H), 6.96 (s, 1H), 6.78 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 153.7, 138.0, 132.5, 132.2, 129.8, 128.3, 127.8, 127.7, 126.6, 125.9, 123.7, 122.6, 112.1, 112.0, 101.6, 99.4, 55.3.



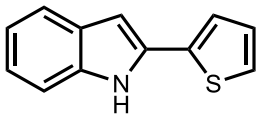
4,6-dimethyl-2-phenyl-1H-indole (**1l**)[8]: method B, yield: 61%, pale grey solid. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.27 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.02 (s, 1H), 6.84 (d, *J* = 1.2 Hz, 1H), 6.82 (s, 1H), 2.60 (s, 3H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 137.1, 136.7, 132.7, 132.4, 129.9, 129.0, 127.4, 127.1, 125.0, 122.4, 108.6, 98.5, 21.9, 18.8.



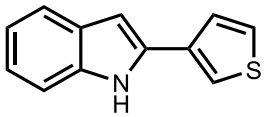
2-(3,4-dimethylphenyl)-1H-indole (**1m**)[9]: method A, yield: 57%, pale white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (s, 1H), 7.65 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.47 (s, 1H), 7.42-7.39 (m, 2H), 7.23-7.19 (m, 2H), 7.15 (td, *J* = 7.6, 0.8 Hz, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.3, 137.3, 136.8, 136.5, 130.4, 130.1, 129.5, 126.6, 122.7, 122.1, 120.6, 120.3, 110.9, 99.4, 20.1, 19.7.



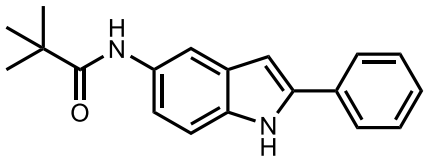
5-methoxy-2-(4-(trifluoromethyl)phenyl)-1H-indole (**1n**)[3]: method B, yield: 71%, white solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 11.58 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 9.0, Hz, 2H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.97 (d, *J* = 1.2 Hz, 1H), 6.80 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.77 (s, 3H); ^{19}F NMR (d_6-DMSO, 576 MHz) δ -60.9 (s); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 153.8, 136.2, 136.2, 132.7, 128.8, 127.1 (q, J_F=31.8), 126.6 (q, J_F=270.0), 125.8 (q, J_F=3.6), 125.1, 113.0, 112.3, 101.7, 100.5, 55.2.



2-(thiophen-2-yl)-1H-indole (**1o**)[10]: method A, yield: 51%, pale grey solid. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 11.55 (s, 1H), 7.53-7.49 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 4.0 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (d_6-DMSO, 100 MHz): δ 136.8, 135.5, 132.4, 128.5, 128.1, 125.1, 123.5, 121.7, 119.9, 119.5, 111.1, 98.7.

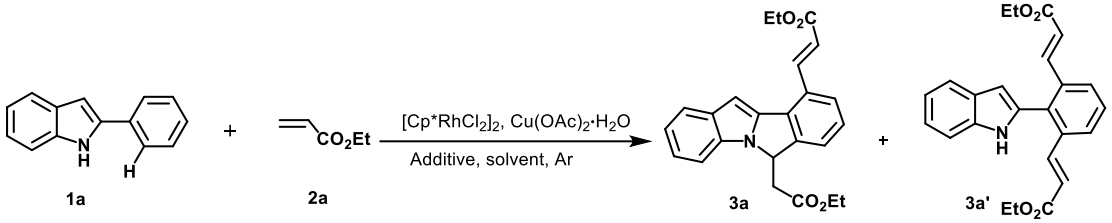


2-(thiophen-3-yl)-1H-indole (**1p**)[11]: method A, yield: 49%, white solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 11.45 (s, 1H), 7.87 (d, *J* = 1.2 Hz, 1H), 7.64-7.61 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.76 (s, 1H); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 136.6, 134.1, 134.1, 128.5, 127.0, 125.9, 121.4, 119.9, 119.6, 119.3, 110.0, 98.6.



N-(2-phenyl-1H-indol-5-yl)pivalamide (**1q**)[12]: method E, yield: 88%, red brown solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 11.42 (s, 1H), 9.03 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.82 (s, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.32-7.26 (s, 3H), 6.86 (s, 1H), 1.25 (s, 9H); ^{13}C NMR (d_6-DMSO, 150 MHz): δ 176.0, 138.0, 134.0, 132.2, 131.6, 128.8, 128.3, 127.3, 124.9, 117.0, 112.2, 110.7, 98.7, 27.4.

Condition Screening:



Entry	Temperature (°C)	Solvent	Additive	Yield[a] of **3a** (%)
1	100	DMF	–	54 (**3a'**)
2	100	*o*-xylene	Na_2CO_3	10
3	100	DMF	CsOAc	55
4	100	DMF	*t*-BuOK	–
5	100	DMF	$K_3PO_4·3H_2O$	23
6	100	DMF	NaOH	41
7[b]	100	DMF	CsOAc	trace
8[c]	100	DMF	CsOAc	<5
9[d]	100	DMF	CsOAc	–
10[e]	100	DMF	CsOAc	trace
11[f]	100	DMF	CsOAc	–
12	100	DMF	CsOAc	75
13	rt	DMF	CsOAc	trace
14	60	DMF	–	50 (**3a'**)
15[h]	80	DMF	CsOAc	40
16[h]	100	DMF	CsOAc	77
17 [h-i]	100	DMF	CsOAc	67 (45h)
18 [h-j]	100	DMF	CsOAc	81 (45h)
19 [g, j]	**100**	**DMF**	**CsOAc**	**86 (41h)**
20 [i-k]	100	DMF	CsOAc	78 (54h)
21	100	*t*-AmylOH	$AgSbF_6$ (0.15 equiv.)	trace

a. Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (1.5 equiv.), $[Cp^*RhCl_2]_2$ (3 mol%), additive (2 equiv.), $Cu(OAc)_2·H_2O$ (2 equiv.), solvent (1.5 mL), under argon, 21 h, isolated yield.

b. Without $Cu(OAc)_2·H_2O$.

c. 10 mol% $Cu(OAc)_2·H_2O$, under air.

d. Without $[Cp^*RhCl_2]_2$.

e. $[RuCl_2(p\text{-cymene})]_2$ as catalyst.

f. $[Rh(PPh_3)_3Cl]$ as catalyst.

g. 2.5 equiv. ethyl acrylate was used.

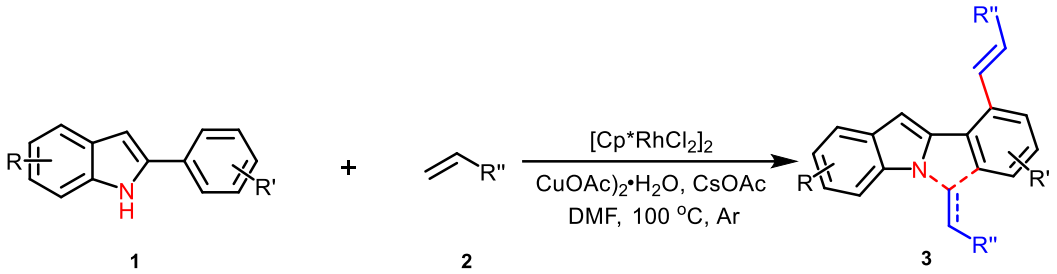
h. 1.1 equiv. CsOAc was used.

i. 4 equiv. ethyl acrylate was used.

j. 5 mol% $[Cp^*RhCl_2]_2$ was used.

k. 4 equiv. $Cu(OAc)_2·H_2O$ was used.

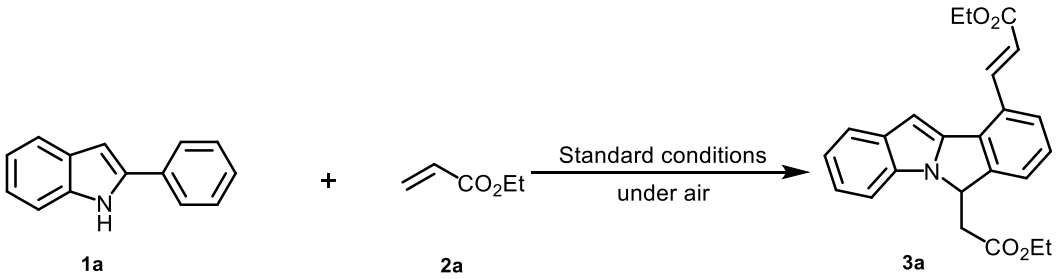
General Procedure for Rh(III)-Catalyzed C–H Activation



1 2 3

$[Cp^*RhCl_2]_2$ (0.01 mmol, 6.2 mg, 5 mol%), CsOAc (0.4 mmol, 76.8 mg, 2.0 equiv.), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol, 79.9 mg, 2.0 equiv.) and 2-aryl indole substrate **1** (0.2 mmol, 1.0 equiv.) were weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/argon-flush cycles. A solution of olefin **2** (0.5 mmol, 2.5 equiv.) in DMF (1.5 mL) was then added through the side-arm by syringe. The reaction was stirred under argon at 100 °C and the progress of the olefination annulation was monitored by TLC. Upon complete consumption of **1**, the reaction was cooled to room temperature. Volatile solvent and reagents were removed by rotary evaporation and the residue was purified by silica gel flash chromatography using *n*-Hexane/EtOAc (20:1 to 10:1) to afford product **3**.

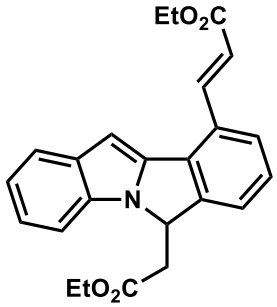
Reaction under air



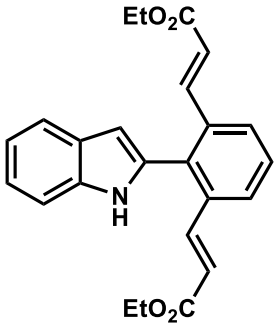
1a 2a 3a

Using a similar procedure as above: $[Cp^*RhCl_2]_2$ (0.01 mmol, 6.2 mg, 5 mol%), CsOAc (0.4 mmol, 76.8 mg, 2.0 equiv.), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol, 79.9 mg, 2.0 equiv.) and 2-phenyl indole **1a** (0.2 mmol, 38.6 mg, 1.0 equiv.) were weighed into a Schlenk tube. A solution of acrylate **2a** (0.5 mmol, 2.5 equiv.) in DMF (1.5 mL) was then added through the side-arm by syringe. The vessel was sealed with a TFE cap and the reaction was stirred at 100 °C. The progress of the olefination annulation was monitored by TLC. Upon complete consumption of **1a**, the reaction was cooled to room temperature. Volatile solvent and reagents were removed by rotary evaporation and the residue was purified by silica gel flash chromatography using *n*-Hexane/EtOAc (20:1 to 10:1) to afford product **3a**.

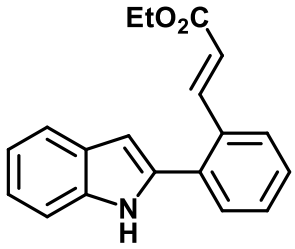
Characterization of Products:



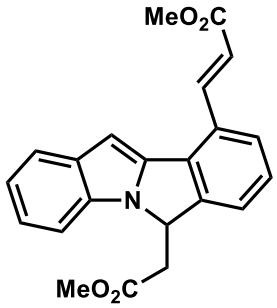
(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3a**)[13]: yield: 86%, yellow solid, melting point: 102-104 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.32 (d, *J* = 16.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.80 (s, 1H), 6.56 (d, *J* = 16.2 Hz, 1H), 5.73 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.25-4.20 (m, 2H), 3.30 (ABq, *J* = 16.8, 4.8 Hz, 1H), 2.76 (ABq, *J* = 16.2, 8.4 Hz, 1H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.7, 166.9, 146.6, 141.3, 140.7, 133.5, 133.2, 132.2, 129.0, 127.6, 125.9, 124.7, 122.5, 122.3, 120.5, 120.2, 109.7, 95.9, 61.3, 60.8, 56.5, 39.6, 14.5, 14.2.



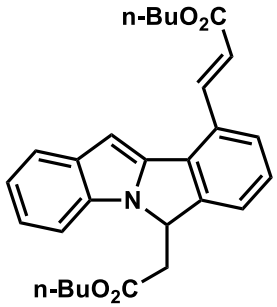
diethyl 3,3'-(2-(1H-indol-2-yl)-1,3-phenylene)(2*E*,2′*E*)-diacrylate (**3a'**)[13]: yield: 61%, yellow solid, melting point: 158-160 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.33 (s, 1H), 7.72-7.67 (m, 3H), 7.61 (d, *J* = 16.0 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.26-7.15 (m, 2H), 6.53 (s, 1H), 6.36 (d, *J* = 16.0 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.6, 142.7, 136.8, 135.8, 131.6, 129.0, 128.5, 128.0, 122.8, 121.0, 120.7, 120.4, 111.1, 107.3, 60.7, 14.3.



ethyl (*E*)-3-(2-(1H-indol-2-yl)phenyl)acrylate (**3a''**)[13]: yield: 16%, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.29 (s, 1H), 8.07 (d, *J* = 16.0 Hz, 1H),7.67 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.47-7.36 (m, 3H), 7.24 (d, *J* = 6.6 Hz, 1H), 7.20-7.12 (m, 1H), 6.60 (s, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.9, 143.6, 136.9, 135.7, 133.5, 133.3, 130.0, 129.4, 128.9, 128.2, 127.7, 122.7, 121.0, 120.3, 111.1, 105.3, 60.7, 14.4.

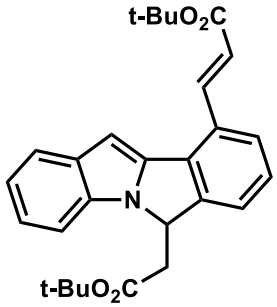


(*E*)-methyl 3-(6-(2-methoxy-2-oxoethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3b**): yield: 77%, yellow solid, melting point: 108-110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, *J* = 16.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 9.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.23 (td, *J* = 7.2, 1.2 Hz, 1H), 7.14 (td, *J* = 8.0, 1.2 Hz, 1H), 6.80 (s, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 5.75 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 3.32 (ABq, *J* = 16.4, 4.8 Hz, 1H), 2.73 (ABq, *J* = 16.4, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.3, 167.3, 146.6, 141.2, 140.9, 133.6, 133.2, 132.2, 129.0, 127.7, 126.0, 124.8, 122.6, 122.4, 120.2, 120.1, 109.6, 96.0, 56.5, 52.4, 52.1, 39.5. IR (ATR): 2950, 1720, 1431, 1164, 978, 744 cm^{-1}. EI-MS m/z (%): 361.2 (92) $[M]^+$, 288.1 (100) $[M\text{-}CH_2CO_2Me]^+$. HRMS (ESI): found: 362.1387, calcd. for $C_{22}H_{20}NO_4$ ($[M+H]^+$): 362.1392. Anal. Calcd. for $C_{22}H_{19}NO_4$: C, 73.12; H, 5.30; N, 3.88; found: C, 74.29; H, 5.16; N, 3.61.

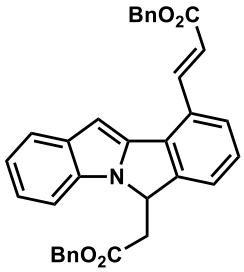


(*E*)-butyl 3-(6-(2-butoxy-2-oxoethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3c**)[13]: yield: 78%, yellow semi-solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.23 (d, *J* = 15.9 Hz, 1H), 7.61 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 6.9 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.18-7.12 (m, 1H), 7.08-7.03 (m, 1H), 6.70 (s, 1H), 6.48 (dd, *J* = 15.9, 1.2 Hz, 1H), 5.64 (dd, *J* = 7.8, 4.2 Hz, 1H), 4.21 (td, *J* = 6.3, 0.9 Hz, 2H), 4.11-4.03 (m, 2H), 3.22 (ABq, *J* = 16.2, 4.5 Hz, 1H), 2.69 (ABq, *J* = 16.2, 8.1 Hz, 1H), 1.73-1.63 (m, 2H), 1.50-1.37 (m, 4H), 1.28-1.16 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.7,

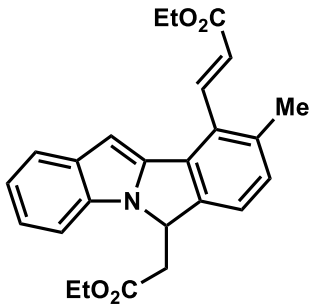
166.9, 146.6, 141.3, 140.6, 133.5, 133.2, 132.2, 129.0, 127.6, 125.9, 124.7, 122.5, 122.3, 120.4, 120.2, 109.7, 95.9, 65.2, 64.7, 56.6, 39.6, 31.0, 30.6, 19.4, 19.2, 13.9, 13.8.



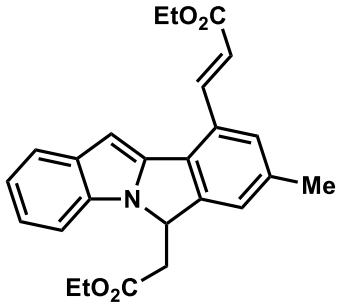
(*E*)-*tert*-butyl 3-(6-(2-tert-butoxy-2-oxoethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3d**)[13]: yield: 73%, yellow solid, melting point: 124-126 °C. ^{1}H NMR ($CDCl_3$, 3 00 MHz): δ 8.25 (d, *J* = 15.9 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7. 30 (t, *J* = 7.8 Hz, 1H), 7.22 (td, *J* = 7.2, 1.2 Hz, 1H), 7.13 (td, *J* = 7.8, 0.9 Hz, 1H), 6.80 (s, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 5.69 (dd, *J* = 7.5, 4.2 Hz, 1H), 3.21 (ABq, *J* = 16.2, 4.5 Hz, 1H), 2.79 (ABq, *J* = 16.2, 7.8 Hz, 1H), 1.61 (s, 9H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.7, 166.3, 146.7, 141.5, 139.7, 133.5, 133.3, 132.3, 129.1, 127.5, 125.7, 124.5, 122.4, 122.2, 122.1, 120.1, 109.8, 95.7, 81.7, 80.9, 56.7, 40.5, 28.4, 28.0.



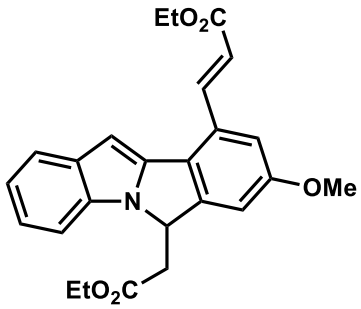
(*E*)-benzyl 3-(6-(2-(benzyloxy)-2-oxoethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3e**): yield: 57%, pale yellow solid, melting point: 120-122 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.30 (d, *J* = 16.0 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.47-7.24 (m, 12H), 7.19-7.08 (m, 3H), 6.69 (s, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 5.62 (dd, *J* = 7.8, 4.2 Hz, 1H), 5.30 (s, 2H), 5.14 (dd, *J* = 15.1, 12.2 Hz, 2H), 3.28 (ABq, *J* = 16.2, 4.4 Hz, 1H), 2.75 (ABq, *J* = 16.2, 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 166.7, 146.4, 141.3, 141.2, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 127.6, 125.9, 124.8, 122.6, 122.3, 120.2, 119.9, 109.6, 96.0, 67.2, 66.7, 56.5, 39.5. IR (ATR): 3055, 2937, 1715, 1638, 1308, 1174, 973, 736 cm^{-1}. EI-MS m/z (%): 513.3 (4) $[M]^+$, 364.2 (9) $[M\text{-}CH_2CO_2Bn]^+$. HRMS (ESI): found: 514.2012, calcd. for $C_{34}H_{28}NO_4$ ($[M+H]^+$): 514.2018. Anal. Calcd. for $C_{34}H_{27}NO_4$: C, 79.51; H, 5.30; N, 2.73; found: C, 80.02; H, 5.05; N, 2.91.



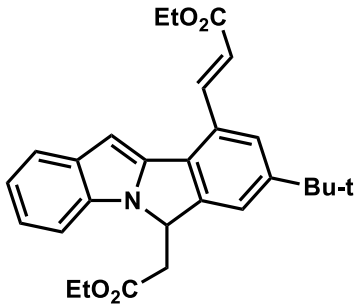
(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-9-methyl-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3f**): yield: 62%, yellow solid, melting point: 86-88 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.25 (d, *J* = 15.9 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 5.58-5.55 (m, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.05-3.98 (m, 2H), 3.13 (ABq, *J* = 16.2, 3.5 Hz, 1H), 2.81 (ABq, *J* = 16.2, 5.7 Hz, 1H), 2.37 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.5, 167.0, 144.1, 141.5, 140.6, 134.7, 133.4, 133.0, 132.4, 129.5, 126.5, 125.8, 122.3, 122.0, 120.0, 119.2, 109.9, 95.7, 61.1, 60.7, 56.2, 38.2, 18.8, 14.5, 13.9. IR (ATR): 2980, 1710, 1633, 1451, 1159, 1033, 738 cm^{-1}. EI-MS m/z (%):403.5 (1) $[M]^+$, 316.2 (3) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 404.1856, calcd. for $C_{25}H_{26}NO_4$ ($[M+H]^+$): 404.1862. Anal. Calcd. for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.47; found: C, 74.82; H, 6.05; N, 3.67.



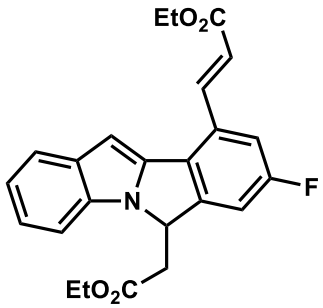
(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-8-methyl-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3g**): yield: 88%, yellow solid, melting point: 96-98 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.27 (d, *J* = 15.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 7.20 (td, *J* = 7.2, 0.6 Hz, 1H), 7.12 (td, *J* = 7.2, 0.6 Hz, 1H), 6.73 (s, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 5.65 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.26-4.18 (m, 2H), 3.26 (ABq, *J* = 16.2, 4.8 Hz, 1H), 2.73 (ABq, *J* = 16.8, 8.4 Hz, 1H), 2.41 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.8, 166.9, 146.9, 141.4, 140.7, 137.8, 133.6, 133.1, 129.8, 128.7, 126.4, 125.7, 122.2, 122.1, 120.1, 120.0, 109.5, 95.1, 61.3, 60.8, 56.4, 40.0, 21.7, 14.5, 14.2. IR (ATR): 2981, 1712, 1637, 1454, 1170, 1035, 741 cm^{-1}. EI-MS m/z (%): 403.3 (57) $[M]^+$, 316.1 (100) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 426.1676, calcd. for $C_{25}H_{25}NO_4Na$ ($[M+Na]^+$): 426.1681. Anal. Calcd. for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.47; found: C, 75.07; H, 5.85; N, 3.02.



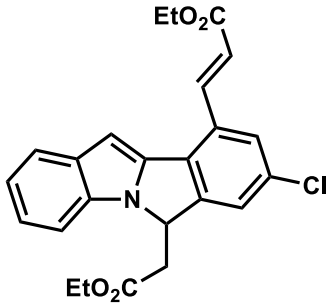
(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-8-methoxy-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3h**): yield: 80%, yellow solid, melting point: 103-105 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.25 (dd, *J* = 15.6, 3.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.10 (s, 1H), 7.06 (s, 1H), 6.67 (s, 1H), 6.52 (dd, *J* = 16.2, 2.4 Hz, 1H), 5.67-5.66 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.23 (qd, *J* = 7.2, 1.2 Hz, 2H), 3.86 (d, *J* = 3.0 Hz, 3H), 3.31-3.27 (m, 1H), 2.73 (ABq, *J* = 16.8, 8.4 Hz, 1H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.7, 166.8, 159.6, 148.5, 141.3, 140.6, 133.6, 133.2, 129.7, 125.5, 122.0, 122.0, 112.2, 110.1, 109.4, 94.4, 61.3, 60.9, 56.5, 55.8, 39.7, 14.5, 14.2. IR (ATR): 2980, 1710, 1635, 1466, 1172, 1032, 736 cm^{-1}. EI-MS m/z (%): 419.4 (100) $[M]^+$, 332.3 (37) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 442.1625, calcd. for $C_{25}H_{25}NO_5Na$ ($[M+Na]^+$): 442.1630. Anal. Calcd. for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01; N, 3.34; found: C, 72.12; H, 5.73; N, 3.05.



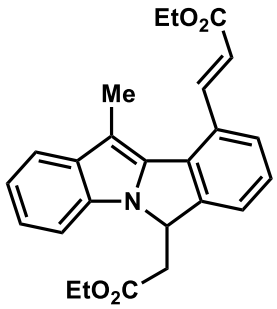
(*E*)-ethyl 3-(8-tert-butyl-6-(2-ethoxy-2-oxoethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3i**): yield: 90%, yellow solid, melting point: 142-144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, *J* = 16.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 1.6 Hz, 1H), 7.52 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.22 (td, *J* = 7.2, 1.2 Hz, 1H), 7.14 (td, *J* = 8.0, 0.8 Hz, 1H), 6.76 (s, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 5.72 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.30-4.22 (m, 2H), 3.32 (ABq, *J* = 16.0, 4.8 Hz, 1H), 2.73 (ABq, *J* = 16.0, 8.0 Hz, 1H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.39 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.9, 166.9, 151.2, 146.7, 141.3, 141.2, 133.6, 133.2, 129.7, 128.3, 122.7, 122.2, 122.2, 122.1, 120.0, 120.0, 109.6, 95.2, 61.3, 60.8, 56.6, 39.9, 35.2, 31.5, 14.5, 14.3; IR (ATR): 2963, 1731, 1636, 1452, 1308, 1181, 1034, 857, 737 cm^{-1}. EI-MS m/z (%): 445.5 (100) $[M]^+$, 388.4 (21) $[M\text{-}(CH_3)_3C]^+$, 358.4 (93) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 468.2145, calcd. for $C_{28}H_{31}NO_4Na$ ($[M+Na]^+$): 468.2151. Anal. Calcd. for $C_{28}H_{31}NO_4$: C, 75.48; H, 7.01; N, 3.14; found: C, 76.06; H, 6.76; N, 3.37.



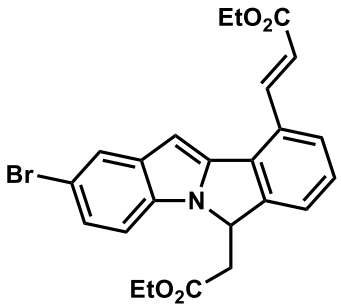
(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-8-fluoro-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3j**): yield: 57%, yellow solid, melting point: 100-102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (dd, *J* = 16.0, 1.2 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.31 (dd, *J* = 9.6, 2.0 Hz, 1H), 7.25-7.22 (m, 2H), 7.13 (td, *J* = 8.0, 0.8 Hz, 1H), 6.74 (s, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 5.71 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.23 (qd, *J* = 7.2, 1.2 Hz, 2H), 3.33 (ABq, *J* = 16.4, 4.0 Hz, 1H), 2.72 (ABq, *J* = 16.4, 8.4 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -113.1 (m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 166.5, 162.3 (J_F = 247.0), 148.7 (J_F = 9.0), 140.4, 139.5, 133.5, 133.2, 130.3, 130.2, 128.6, 122.5 (J_F = 24.0), 121.6, 120.3, 113.1 (J_F = 15.0), 112.4 (J_F = 23.0), 109.5, 95.4, 61.5, 61.0, 56.5, 39.4, 14.5, 14.2; IR (ATR): 2982, 1715, 1638, 1465, 1260, 1172, 1033, 862, 741 cm^{-1}. EI-MS m/z (%): 407.4 (100) $[M]^+$, 320.3 (82) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 430.1425, calcd. for $C_{24}H_{22}NO_4NaF$ ($[M+Na]^+$): 430.1431. Anal. Calcd. for $C_{24}H_{22}FNO_4$: C, 70.75; H, 5.44; N, 3.44; found: C, 70.01; H, 4.86; N, 3.81.



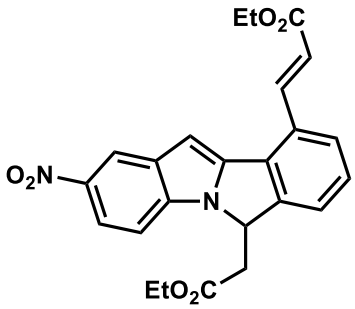
(*E*)-ethyl 3-(8-chloro-6-(2-ethoxy-2-oxoethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3k**): yield: 55%, yellow solid, melting point: 127-129 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.18 (d, *J* = 16.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.56 (s, 1H), 7.44 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.74 (s, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 5.64 (dd, *J* = 8.1, 3.9 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.25-4.18 (m, 2H), 3.28 (ABq, *J* = 16.5, 3.9 Hz, 1H), 2.71 (ABq, *J* = 16.5, 8.4 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.4, 166.5, 148.1, 140.2, 139.3, 133.4, 133.2, 130.8, 129.9, 125.9, 125.1, 122.8, 122.4, 121.6, 120.4, 109.6, 96.1, 61.5, 61.0, 56.4, 39.3, 14.5, 14.2; IR (ATR): 2982, 1716, 1638, 1449, 1310, 1172, 1032, 860, 739 cm^{-1}. EI-MS m/z (%): 423.2 (97) $[M]^+$, 336.1 (100) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 446.1130, calcd. for $C_{24}H_{22}NO_4NaCl$ ($[M+Na]^+$): 446.1135. Anal. Calcd. for $C_{24}H_{22}ClNO_4$: C, 68.00; H, 5.23; N, 3.30; found: C, 68.75; H, 4.61; N, 3.72.



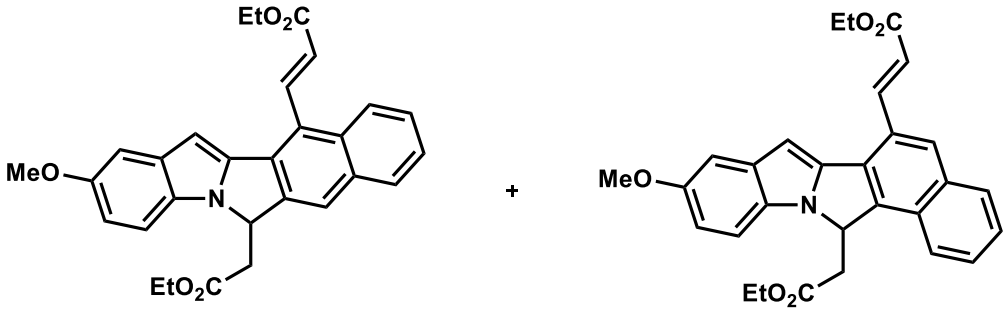
(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-11-methyl-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3l**): yield: 43%, yellow solid, melting point: 112-114 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.58 (d, *J* = 15.9 Hz, 1H), 7.67 (d, *J* = 8.1, Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 8.1 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 5.67 (dd, *J* = 7.8, 4.2 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.21 (q, *J* = 6.9 Hz, 2H), 3.26 (ABq, *J* = 16.2, 4.2 Hz, 1H), 2.73-2.65 (m, 4H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.8, 166.9, 146.9, 144.3, 138.4, 134.3, 133.4, 133.0, 128.8, 127.3, 126.8, 124.5, 122.8, 120.4, 120.1, 119.5, 109.4, 104.7, 61.3, 60.8, 55.7, 40.1, 14.5, 14.2, 11.5; IR (ATR): 2980, 1709, 1633, 1463, 1164, 1032, 865, 738 cm^{-1}. EI-MS m/z (%): 403.5 (44) $[M]^+$, 316.3 (100) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 426.1676, calcd. for $C_{25}H_{25}NO_4Na$ ($[M+Na]^+$): 426.1681. Anal. Calcd. for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.27; found: C, 75.15; H, 5.66; N, 3.54.



(*E*)-ethyl 3-(2-bromo-6-(2-ethoxy-2-oxoethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3m**): yield: 45%, yellow semi-solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.23 (d, *J* = 15.9 Hz, 1H), 7.78 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.33-7.21 (m, 3H), 6.68 (s, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 5.65 (dd, *J* = 7.2, 4.7 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 6.9 Hz, 2H), 3.18 (ABq, *J* = 16.4, 4.6 Hz, 1H), 2.77 (ABq, *J* = 16.3, 7.7 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.5, 166.8, 146.5, 142.4, 140.3, 135.1, 131.8, 131.7, 129.2, 128.1, 126.0, 125.2, 124.7, 124.5, 120.7, 113.4, 111.0, 95.2, 61.4, 60.9, 56.7, 39.6, 14.5, 14.2 ; IR (ATR): 2979, 1723, 1635, 1462, 1166, 1030, 861, 752 cm^{-1}. EI-MS m/z (%): 467.3 (55) $[M]^+$, 380.2 (66) $[M\text{-}CH_2CO_2Et]^+$, 302.2 (32) $[M\text{-}CH_3CO_2Et\text{-}Br]^+$. HRMS (ESI): found: 490.0624, calcd. for $C_{24}H_{22}BrNO_4Na$ ($[M+Na]^+$): 490.0630. Anal. Calcd. for $C_{24}H_{22}BrNO_4$: C, 61.55; H, 4.73; N, 2.99; found: C, 62.21; H, 4.31; N, 3.43.

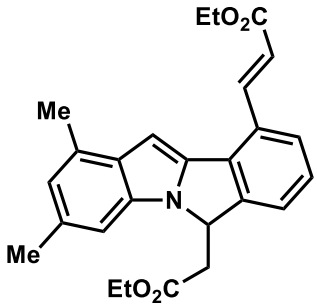


(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-2-nitro-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3n**): yield: 36%, yellow semi-solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.60 (d, *J* = 2.0 Hz, 1H), 8.22 (d, *J* = 15.9 Hz, 1H), 8.11 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.41-7.36 (m, 2H), 6.89 (s, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 5.76 (dd, *J* = 7.0, 5.1 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.21 (ABq, *J* = 16.5, 4.7 Hz, 1H), 2.88 (ABq, *J* = 16.5, 7.4 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.1, 166.5, 146.1, 144.4, 141.9, 139.7, 135.8, 132.6, 130.6, 129.7, 128.8, 126.2, 124.7, 121.2, 118.9, 118.0, 109.3, 97.6, 61.5, 61.0, 56.9, 39.4, 14.4, 14.1; IR (ATR): 2981, 1718, 1516, 1319, 1167, 1029, 805, 746 cm^{-1}. EI-MS m/z (%): 434.4 (68) $[M]^+$, 347.2 (100) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 457.1370, calcd. for $C_{24}H_{22}N_2O_6Na$ ($[M+Na]^+$): 457.1376. Anal. Calcd. for $C_{24}H_{22}N_2O_6$: C, 66.35; H, 5.10; N, 6.45; found: C, 67.12; H, 4.74; N, 6.81.

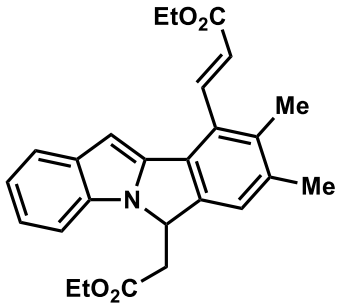


Ethyl (*E*)-3-(6-(2-ethoxy-2-oxoethyl)-2-methoxy-6H-benzo[5,6]isoindolo[2,1-a]indol-12-yl)acrylate (**3o**) and ethyl (*E*)-3-(13-(2-ethoxy-2-oxoethyl)-9-methoxy-13H-benzo[4,5]isoindolo[2,1-a]indol-6-yl)acrylate (**3o'**): isolated as an inseparable mixture (ratio = 1 : 1.7), yield: 53%, brown semi-solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41 (d, *J* = 16.4 Hz, 1H), 8.35 (d, *J* = 16.0 Hz, 1.7H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1.6H), 7.89 (d, *J* = 8.0 Hz, 1.7H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1.8H), 7.58-7.46 (m, 6H), 7.28 (d, *J* = 8.8 Hz, 2.5H), 7.15 (d, *J* = 2.0 Hz, 2.5H), 6.91-6.86 (m, 2.7H), 6.70 (s, 2.3H), 6.66 (d, *J* = 10.8 Hz, 1.7H), 6.63 (d, *J* = 16.4 Hz, 0.8H), 6.07 (dd, *J* = 6.8, 3.2 Hz, 1.7H), 5.83 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.44-4.34 (m, 5.4H), 4.24(qd, *J* = 7.2, 2.4 Hz, 2.5H), 4.16 (qd, *J* = 7.2, 2.4 Hz, 3.5H), 3.88-3.87 (m, 6.9H), 3.35-3.24 (m, 3H), 2.84-2.76 (m, 2.9H), 1.47-1.41 (m, 7.7H), 1.24 (t, *J* = 7.2 Hz, 3.6H), 1.14 (t, *J* = 7.2 Hz, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 170.8, 166.8, 154.6, 154.4, 143.5, 142.8, 141.7, 141.0, 140.6, 132.9, 130.1, 128.4, 127.4, 127.3, 127.0, 126.4, 126.3, 122.8, 120.9, 113.3, 112.6, 110.7, 110.5, 103.8, 103.5, 96.5, 95.4, 61.5, 61.3, 61.0, 60.9, 56.9, 56.1, 56.0, 40.7, 40.2, 14.6, 14.3, 14.1; IR (ATR):

2982, 1714, 1479, 1166, 1031, 856, 751 cm^{-1}. EI-MS m/z (%): 469.3 (63) $[M]^+$, 382.2 (100) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 470.1962, calcd. for $C_{29}H_{28}NO_5$ ($[M+H]^+$): 470.1967. Anal. Calcd. for $C_{29}H_{27}NO_5$: C, 74.18; H, 5.80; N, 2.98; found: C, 74.86; H, 5.24; N, 3.45.

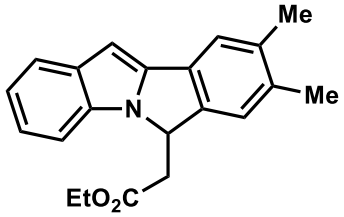


(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-1,3-dimethyl-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3p**): yield: 90%, yellow solid, melting point: 94-96 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.34 (d, *J* = 16.2 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.01 (s, 1H), 6.80 (s, 1H), 6.72 (s, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 5.66 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.26-4.21 (m, 2H), 3.30 (ABq, *J* = 16.2, 4.2 Hz, 1H), 2.70 (ABq, *J* = 16.8, 8.4 Hz, 1H), 2.58 (s, 3H), 2.47 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.8, 167.0, 146.4, 140.9, 140.0, 133.3, 132.7, 132.6, 131.5, 131.2, 128.6, 127.2, 125.8, 124.7, 122.4, 120.1, 107.2, 94.3, 61.2, 60.8, 56.4, 39.5, 22.0, 18.9, 14.5, 14.2; IR (ATR): 2979, 1714, 1632, 1421, 1166, 1031, 975, 754 cm^{-1}. EI-MS m/z (%): 417.2 (100) $[M]^+$, 330.1 (71) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 418.2013, calcd. for $C_{26}H_{28}NO_4$ ($[M+H]^+$): 418.2018. Anal. Calcd. for $C_{26}H_{27}NO_4$: C, 74.80; H, 6.52; N, 3.35; found: C, 75.23; H, 5.94; N, 6.96.

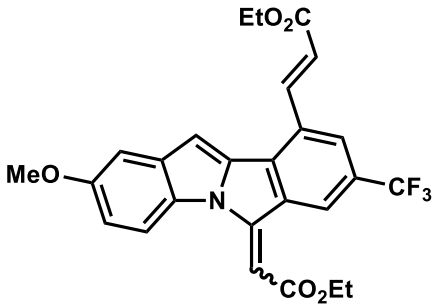


(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-8,9-dimethyl-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3q**): yield: 60%, yellowish-brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.16 (d, *J* = 15.9 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.31-7.26 (m, 2H), 7.18-7.12 (m, 2H), 6.62 (s, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 5.45 (dd, *J* = 5.4, 3.3 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.04 (ABq, *J* = 16.5, 3.0 Hz, 1H), 2.69 (ABq, *J* = 16.5, 6.0 Hz, 1H), 2.25 (s, 3H), 2.19 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 167.1, 144.9, 141.8, 140.8, 136.9, 133.8, 133.5, 133.1, 130.4, 127.1, 126.3, 122.1, 120.0, 119.1, 109.9, 95.2, 61.2, 60.7, 56.5, 39.1, 20.0, 16.1, 14.5, 14.0; IR (ATR): 2979, 1710, 1634, 1452, 1164, 1036, 860, 741 cm^{-1}. EI-MS m/z (%): 417.1 (59) $[M]^+$, 330.1 (100) $[M\text{-}CH_2CO_2Et]^+$. HRMS (ESI): found: 440.1832,

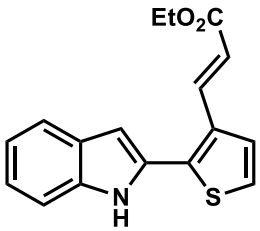
calcd. for $C_{26}H_{27}NO_4Na$ ([M+Na]$^+$): 440.1838. Anal. Calcd. for $C_{26}H_{27}NO_4$: C, 74.80; H, 6.52; N, 3.35; found: C, 75.31; H, 6.12; N, 6.83.



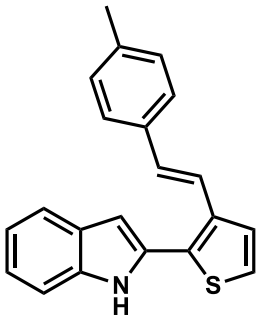
ethyl 2-(8,9-dimethyl-6H-isoindolo[2,1-a]indol-6-yl)acetate (**3q'**): yield: 25%, yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.66-7.63 (m, 1H), 7.48 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.23 (s, 1H), 7.19-7.14 (m, 1H), 7.12-7.07 (m, 1H), 6.55 (s, 1H), 5.68 (dd, *J* = 8.1, 1.5 Hz, 1H), 4.30-4.20 (m, 2H), 3.27 (ABq, *J* = 16.2, 4.8 Hz, 1H), 2.72 (ABq, *J* = 16.2, 8.1 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 171.1, 143.7, 143.4, 137.3, 136.3, 133.5, 133.3, 130.1, 124.6, 122.0, 121.7, 121.5, 119.7, 109.5, 61.2, 56.7, 39.9, 20.4, 20.2, 14.3 ; IR (ATR): 2923, 1725, 1612, 1454, 1153, 1014, 868, 739 cm^{-1}. EI-MS m/z (%): 319.1 (60) [M]$^+$, 231.9 (100) [M-CH_2CO_2Et]$^+$. HRMS (ESI): found: 342.1465, calcd. for $C_{21}H_{21}NO_2Na$ ([M+Na]$^+$): 342.1470. Anal. Calcd. for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39; found: C, 79.37; H, 6.32; N, 4.81.



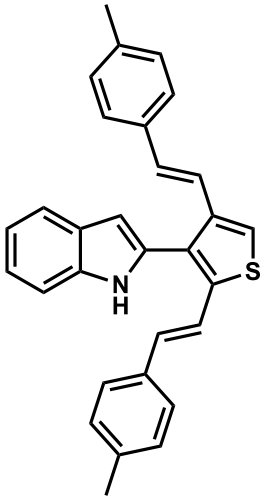
(2*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethylidene)-2-methoxy-8-(trifluoromethyl)-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3r**): yield: 58%, yellow solid, melting point: 154-156 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.38 (s, 1H), 7.90 (d, *J* = 16.2 Hz, 1H), 7.73 (s, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.58 (s, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.20 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.39 (q, *J* = 7.2 Hz, 6H); ^{19}F NMR ($CDCl_3$, 576 MHz) δ -62.5 (s); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.2, 166.2, 156.1, 144.9, 139.1, 138.3, 136.9, 136.0, 134.3,130.4 (q, J_F = 32.4), 128.4, 127.3 (q, J_F = 3.6), 125.0 (q, J_F = 3.6), 123.9 (q, J_F = 271.2), 122.0, 114.8, 112.8, 106.8, 103.5, 99.4, 61.1, 60.7, 55.7, 14.5; IR (ATR): 2926, 1708, 1631, 1477, 1296, 1034, 966, 816 cm^{-1}. EI-MS m/z (%): 485.5 (4) [M]$^+$. HRMS (ESI): found: 486.1523, calcd. for $C_{26}H_{23}F_3NO_5$ ([M+H]$^+$): 486.1528. Anal. Calcd. for $C_{26}H_{22}F_3NO_5$: C, 64.33; H, 4.57; N, 2.89; found: C, 64.86; H, 4.35; N, 3.24.



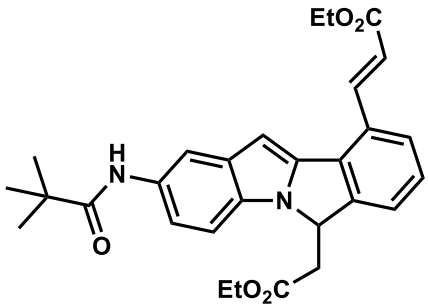
(*E*)-ethyl 3-(2-(1H-indol-2-yl)thiophen-3-yl)acrylate (**3s**): yield: 76%, yellow semi-solid. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.32 (s, 1H), 7.97 (d, *J* = 16.2 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.41 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.33 (d, *J* = 5.4 Hz, 1H), 7.30 (dd, *J* = 5.4, 0.6 Hz, 1H), 7.25 (td, *J* = 7.2, 1.2 Hz, 1H), 7.16 (td, *J* = 7.8, 0.6 Hz, 1H), 6.73 (d, *J* = 1.8 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.4, 137.1, 136.8, 133.8, 129.9, 129.0, 126.6, 125.6, 123.3, 121.1, 120.8, 119.5, 111.2, 105.1, 60.7, 14.5; IR (ATR): 3327, 2981, 1691, 1620, 1303, 1173, 1035, 862, 746 cm^{-1}. EI-MS m/z (%): 297.1 (25) $[M]^+$, 224.0 (100) $[M\text{-}CO_2Et]^+$. HRMS (ESI): found: 298.0896, calcd. for $C_{17}H_{16}SNO_2$($[M+H]^+$): 298.0902. Anal. Calcd. for $C_{17}H_{15}SNO_2$: C, 68.66; H, 5.08; N, 4.71; found: C, 69.15; H, 4.75; N, 4.54.



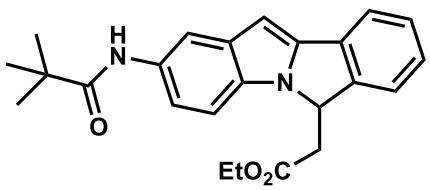
(*E*)-2-(3-(4-methylstyryl)thiophen-2-yl)-1H-indole (**3t**): yield: 54%, yellow-brown solid, melting point: 92-94 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.21 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.42-7.39 (m, 4H), 7.34 (d, *J* = 16.2 Hz, 1H), 7.31 (d, *J* = 5.4 Hz, 1H), 7.25 (td, *J* = 7.8, 1.2 Hz, 1H), 7.19-7.17 (m, 3H), 7.05 (d, *J* = 16.2 Hz, 1H), 6.73-6.72 (m, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 137.8, 136.9, 136.8, 134.6, 131.3, 130.7, 130.6, 129.6, 129.1, 126.6, 125.1, 122.8, 121.1, 120.9, 120.6, 111.1, 103.9, 21.4 ; IR (ATR): 3388, 2921, 1606, 1513, 1453, 1304, 1092, 800, 745 cm^{-1}. EI-MS m/z (%): 315.1 (100) $[M]^+$, 224.0 (54) $[M\text{-}PhCH_2]^+$. HRMS (ESI): found: 316.1155, calcd. for $C_{21}H_{18}NS$ ($[M+H]^+$): 316.1160. Anal. Calcd. for $C_{21}H_{17}NS$: C, 79.96; H, 5.43; N, 4.44; found: C, 80.52; H, 4.82; N, 4.84.



2-(2,4-bis(4-methylstyryl)thiophen-3-yl)-1H-indole (**3u**): yield: 56%, yellow solid, melting point: 212-214 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.29-7.17 (m, 8H), 7.09 (dd, *J* = 7.6, 2.8 Hz, 4H), 6.98 (d, *J* = 16.0 Hz, 1H), 6.91 (s, 2H), 6.61 (dd, *J* = 6.0, 0.8 Hz, 1H), 2.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.6, 140.3, 138.0, 137.9, 136.5, 134.4, 134.1, 131.7, 130.5, 129.9, 129.6, 129.5, 128.8, 126.6, 126.6, 122.4, 121.1, 120.9, 120.3, 120.2, 111.1, 105.2, 21.4, 21.4; IR (ATR): 3359, 2920, 1603, 1509, 1450, 1300, 1104, 957, 801, 713 cm^{-1}. EI-MS m/z (%): 431.2 (100) $[M]^+$, 340.1 (73) $[M\text{-}PhCH_2]^+$. HRMS (ESI): found: 432.1781, calcd. for $C_{30}H_{26}NS$ ($[M+H]^+$): 432.1786. Anal. Calcd. for $C_{30}H_{25}NS$: C, 83.49; H, 5.84; N, 3.25; found: C, 84.04; H, 5.35; N, 3.70.



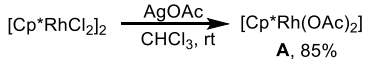
(*E*)-ethyl 3-(6-(2-ethoxy-2-oxoethyl)-2-pivalamido-6H-isoindolo[2,1-a]indol-10-yl)acrylate (**3v**): yield: 74%, yellow semi-solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (d, *J* = 16.0 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.44 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1 H), 7.33 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.29-7.25(m, 2H), 6.67 (s, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 5.63 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.22-4.14 (m, 2H), 3.19 (ABq, *J* = 16.4, 4.8 Hz, 1H), 2.73 (ABq, *J* = 16.4, 8.0 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.35 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 170.6, 166.8, 146.5, 142.0, 140.5, 133.6, 132.1, 131.1, 130.6, 128.9, 127.6, 125.8, 124.6, 120.4, 117.1, 114.0, 109.6, 95.8, 61.3, 60.8, 56.6, 39.6, 39.6, 27.9, 14.5, 14.2; IR (ATR): 3346, 2967, 1714, 1657, 1476, 1165, 1030, 866, 727 cm^{-1}. ESI-MS m/z (%): 489.2 (100) $[M+H]^+$. HRMS (ESI): found: 511.2203, calcd. for $C_{29}H_{32}N_2O_5Na$ ($[M+Na]^+$): 511.2209. Anal. Calcd. for $C_{29}H_{32}N_2O_5$: C, 71.29; H, 6.60; N, 5.73; found: C, 72.01; H, 6.36; N, 5.99.



ethyl 2-(2-pivalamido-6H-isoindolo[2,1-a]indol-6-yl)acetate (**3v'**): yield: 20%, yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.36 (s, 1H), 7.31-7.27 (m, 2H), 7.22 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.57 (s, 1H), 5.72 (dd, *J* = 7.6, 4.8 Hz, 1H), 4.26-4.18 (m, 2H), 3.22 (ABq, *J* = 16.4, 4.8 Hz, 1H), 2.76 (ABq, *J* = 16.4, 7.6 Hz, 1H), 1.35 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.6, 170.9, 145.7, 143.9, 133.6, 132.3, 130.8, 128.8, 127.5, 123.5, 121.0, 116.1, 113.9, 109.6, 92.1, 61.3, 57.0, 39.8, 27.9, 14.3; IR (ATR): 3341, 2964, 1728, 1656, 1476, 1178, 1023, 870, 752 cm^{-1}. EI-MS m/z (%): 390.4 (95) $[M]^+$, 303.3 (100) $[M-CH_2CO_2Et]^+$. HRMS (ESI): found: 413.1836, calcd. for $C_{24}H_{26}N_2O_3Na$ ($[M+Na]^+$): 413.1841. Anal. Calcd. for $C_{24}H_{26}N_2O_3$: C, 73.82; H, 6.71; N, 7.17; found: C, 74.35; H, 6.31; N, 6.87.

Mechanism study

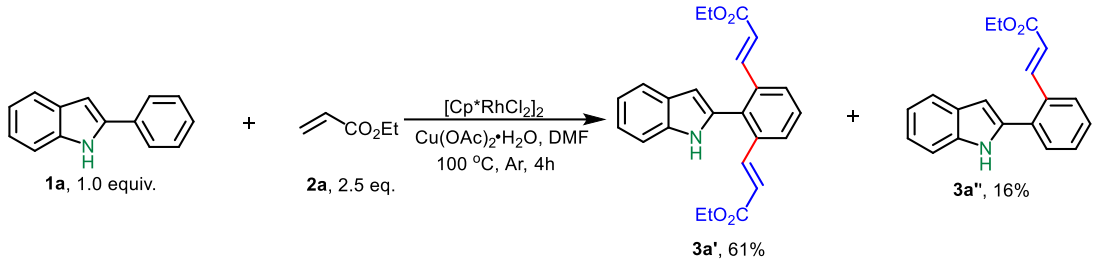
(a) Synthesis of active Rh catalyst species



Active catalytic Rh species A was synthesized according to a previous reported literature. [14] $[Cp^*RhCl_2]_2$ (750 mg, 1.0 equiv.) and AgOAc (810 mg, 4.0 equiv.) were weighed into an oven dried Schlenk tube. The reaction vessel was capped and vacuum/backfilled with argon three times. To this vessel, 20 mL $CHCl_3$ was added. The reaction was stirred at rt for two hours. The reaction mixture was filtered through a plug of celite and wished with *n*-hexane. The filtrate was concentrated by rotary evaporation and the residue yellow solid was collected as the desired catalyst (in case there is residual solvents, drying under high vacuum pump overnight might be necessary).

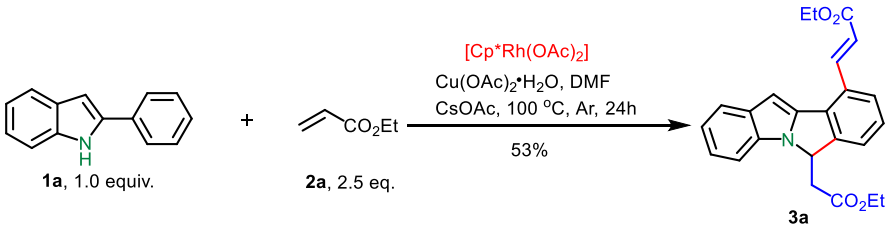
(b) Catalytic reactions

(i) In the absence of base



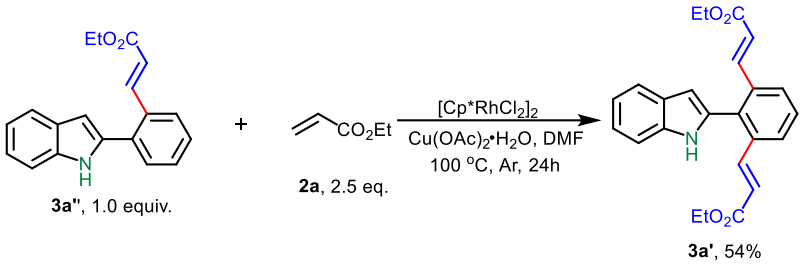
Following the ***General Procedure for Rh(III)-Catalyzed C–H Activation***, reaction is conducted on a 0.2 mmol scale, using **1a** (1.0 equiv.), ethyl acrylate **2a** (2.5 equiv.), $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.), DMF (1.5 mL).

(ii) $[Cp^*Rh(OAc)_2]$-catalyzed reaction



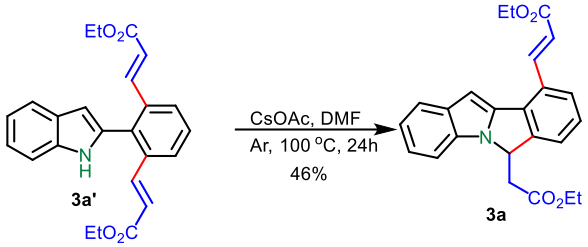
Following the ***General Procedure for Rh(III)-Catalyzed C–H Activation***, reaction is conducted on a 0.2 mmol scale, using **1a** (1.0 equiv.), ethyl acrylate **2a** (2.5 equiv.), $[Cp^*Rh(OAc)_2]$ (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.), DMF (1.5 mL).

(iii) Conversion of mono-alkenylation product to dialkenylation product



Following the ***General Procedure for Rh(III)-Catalyzed C–H Activation***, reaction is conducted on a 0.2 mmol scale, using **1a** (1.0 equiv.), ethyl acrylate **2a** (2.5 equiv.), $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.), DMF (1.5 mL).

(c) Cyclization reactions



3a' (0.2 mmol, 77.9 mg, 1.0 equiv.) and CsOAc (0.4 mmol, 76.8 mg, 2.0 equiv.) were weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/argon-flush cycles. DMF (1.5 mL) was then added through the side-arm by syringe. The reaction was stirred under argon at 100 °C for 24h. Volatile solvent and reagents were removed by rotary evaporation and the residue was purified by silica gel flash chromatography using *n*-Hexane/EtOAc (20:1 to 10:1) to afford product **3a**.

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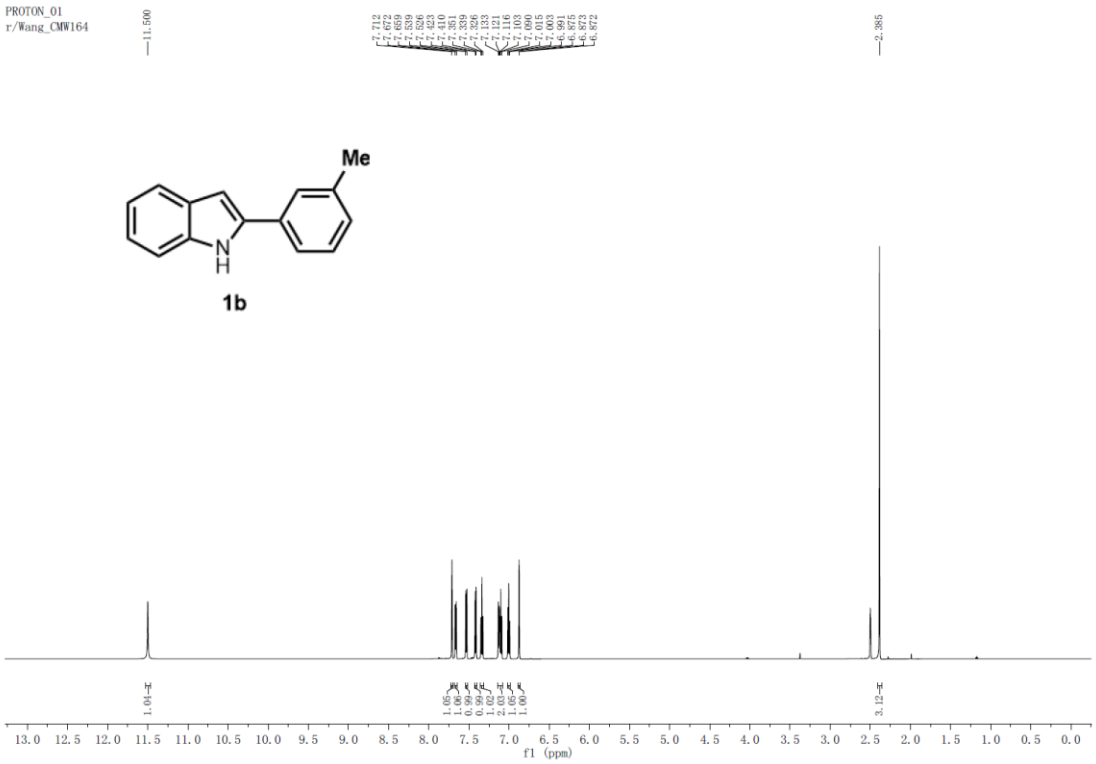
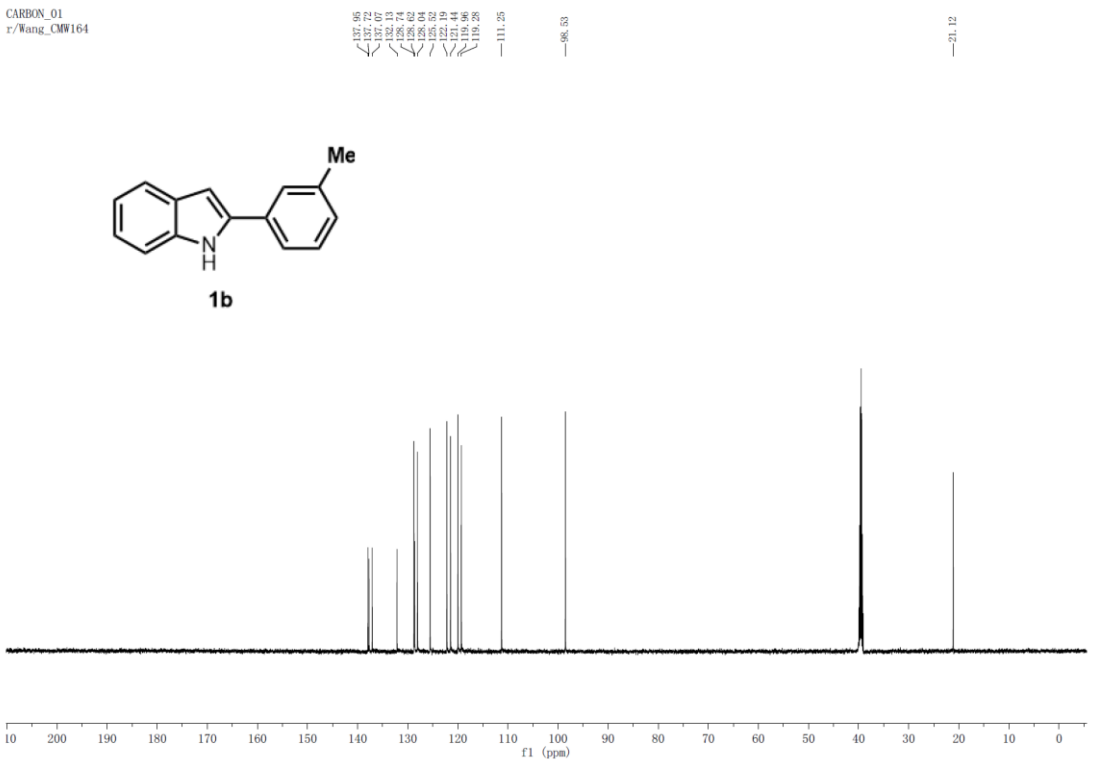
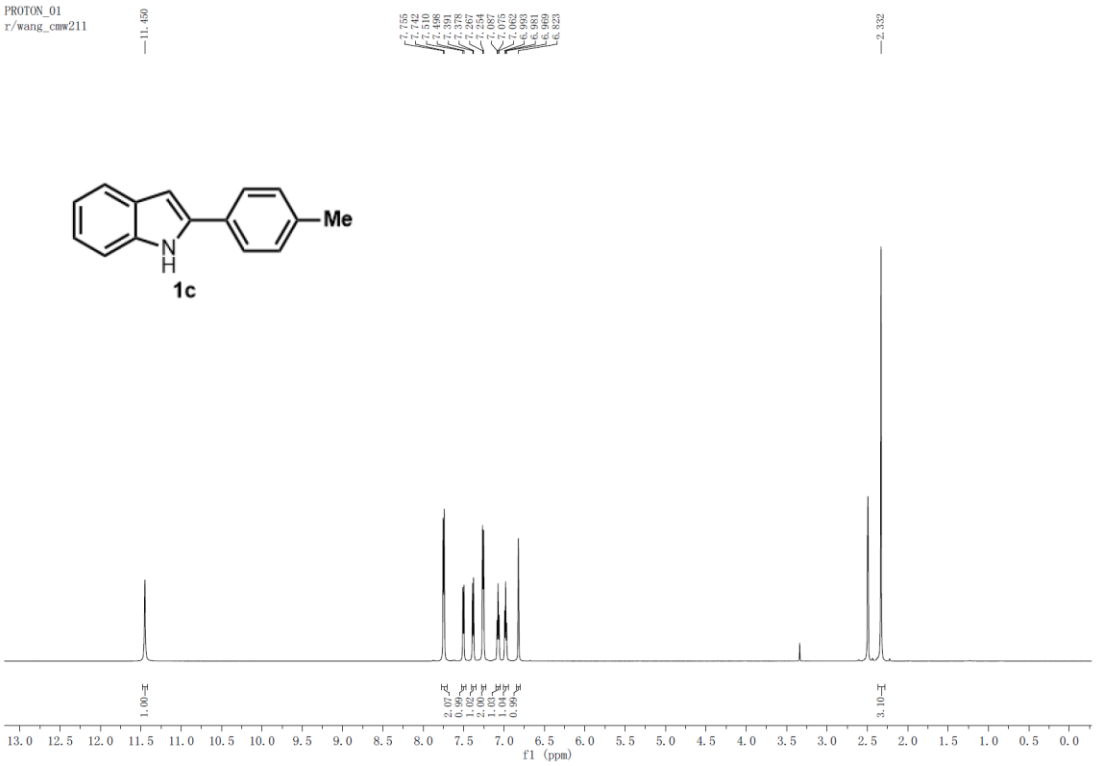
NMR Spectra Images of indole Substrates and Products



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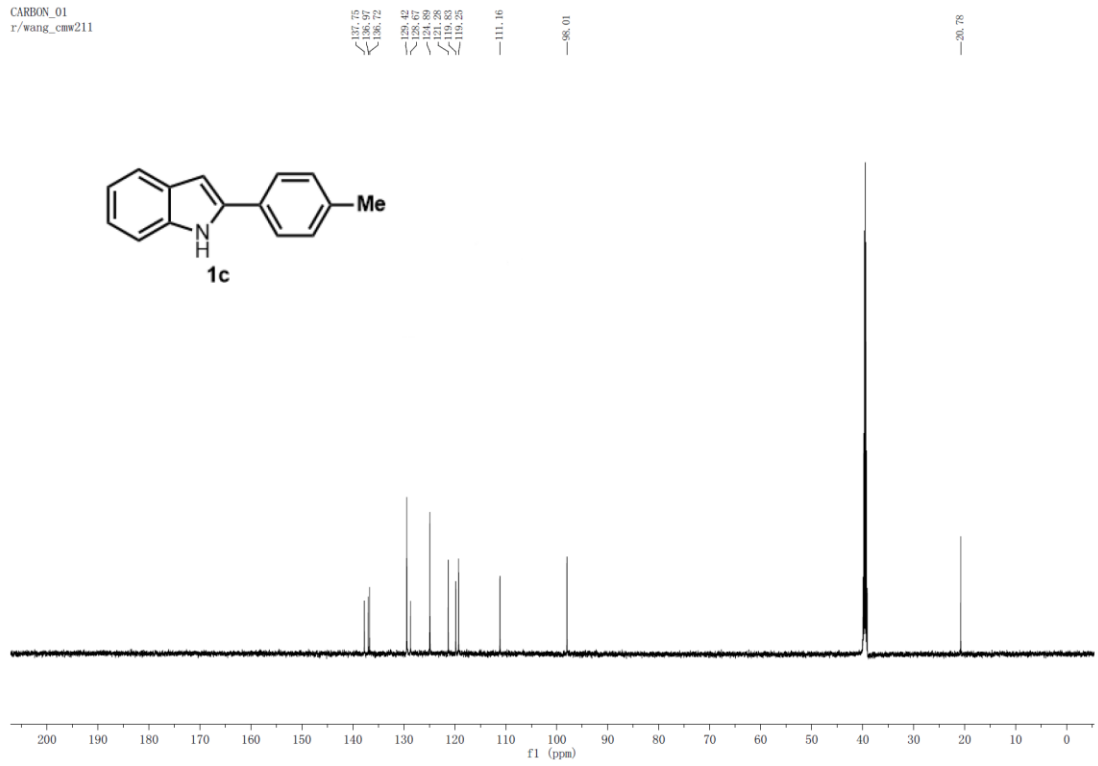
6.993
6.981
6.969
6.823
2.332
Me
N
H
1c
1.00
2.07
0.99
1.02
2.00
1.03
1.04
0.99
3.10
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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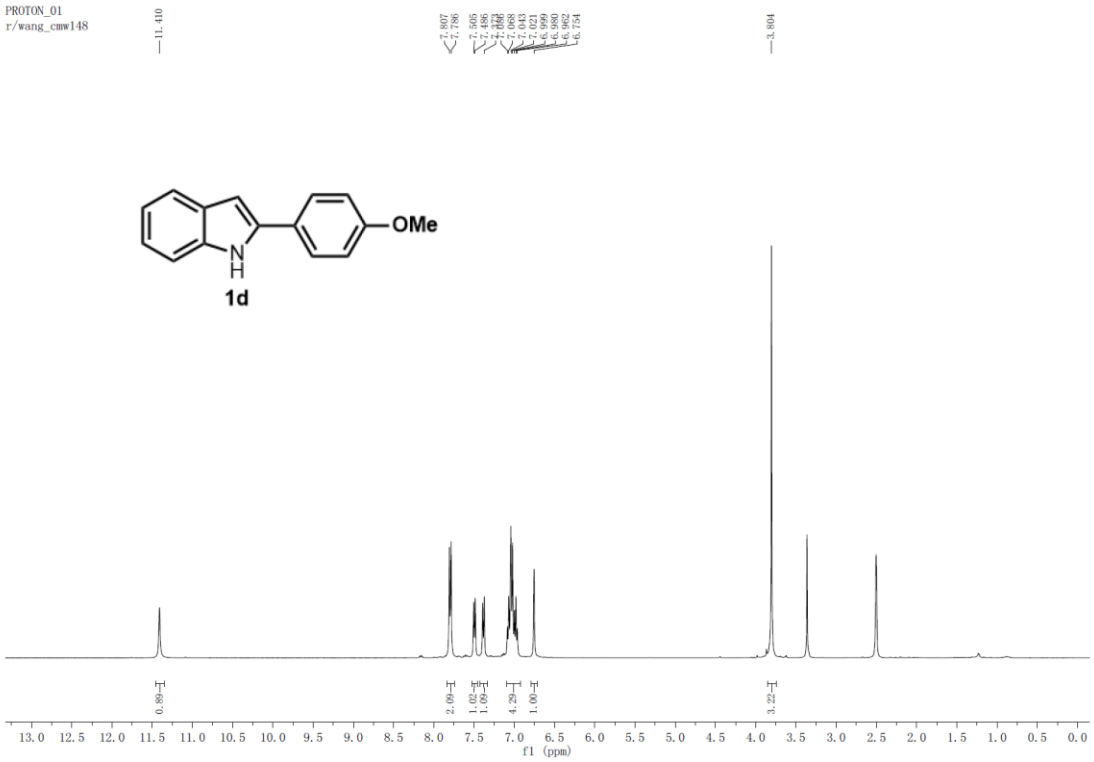
f1 (ppm)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6.754
3.804
OMe
N
H
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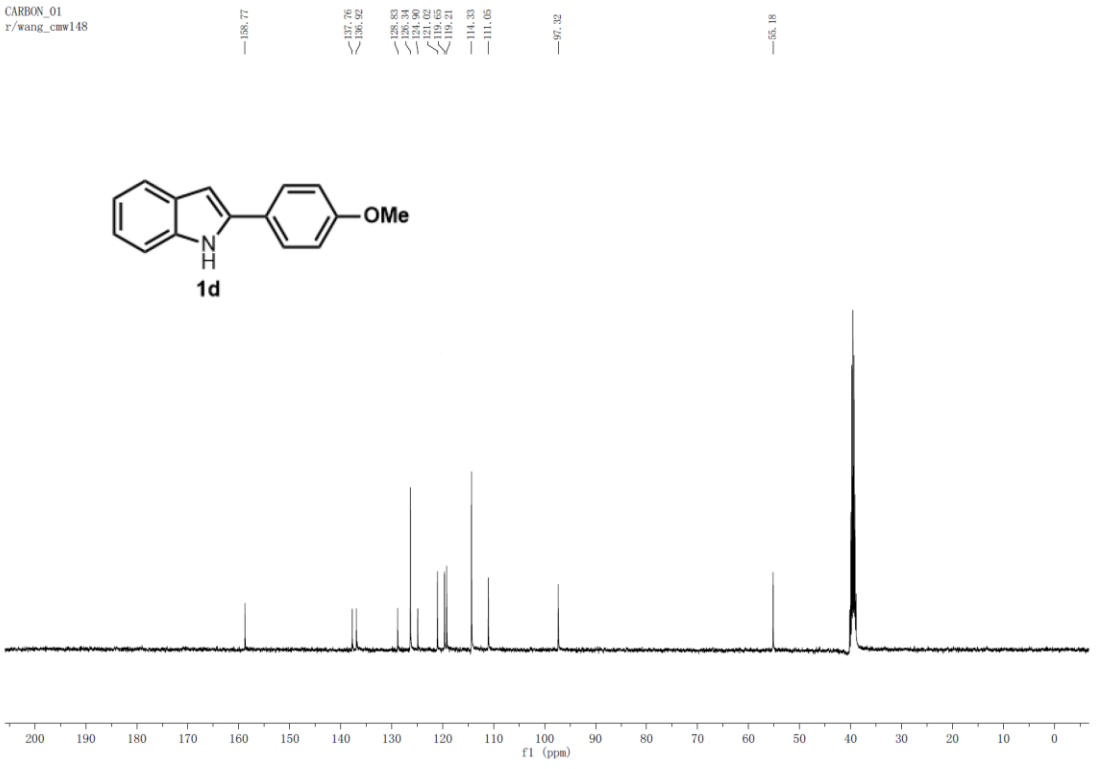
0.89
2.09
1.02
1.09
4.29
1.00
3.22
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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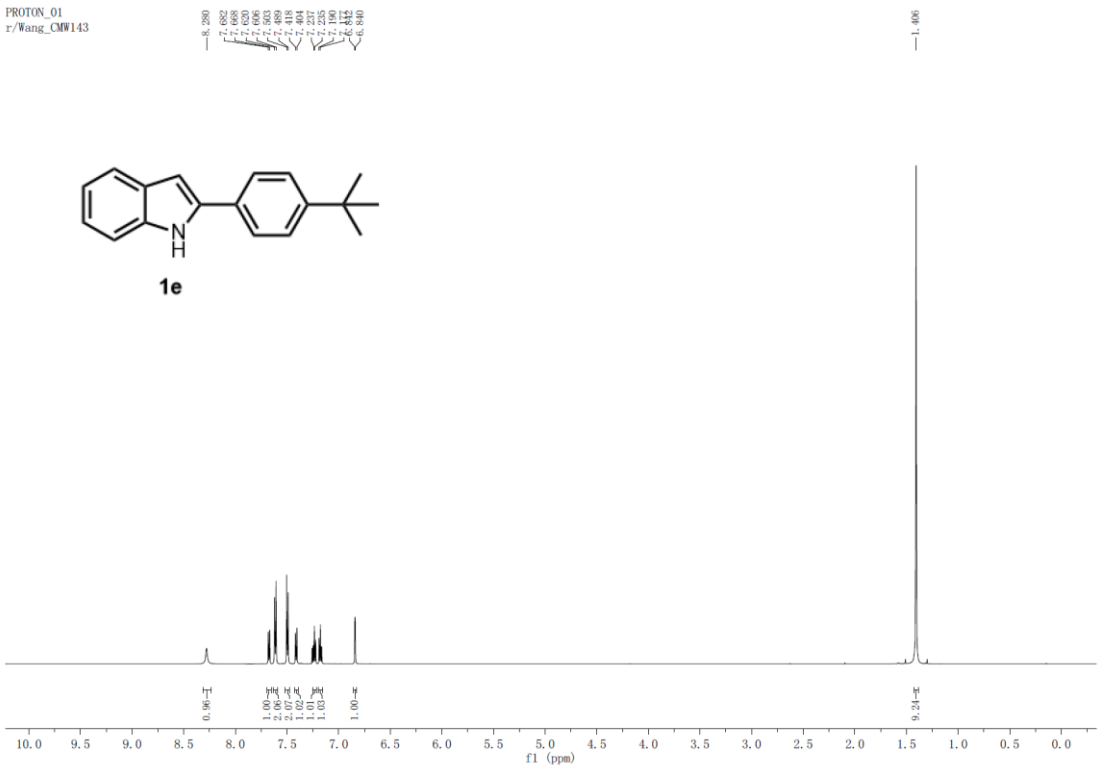
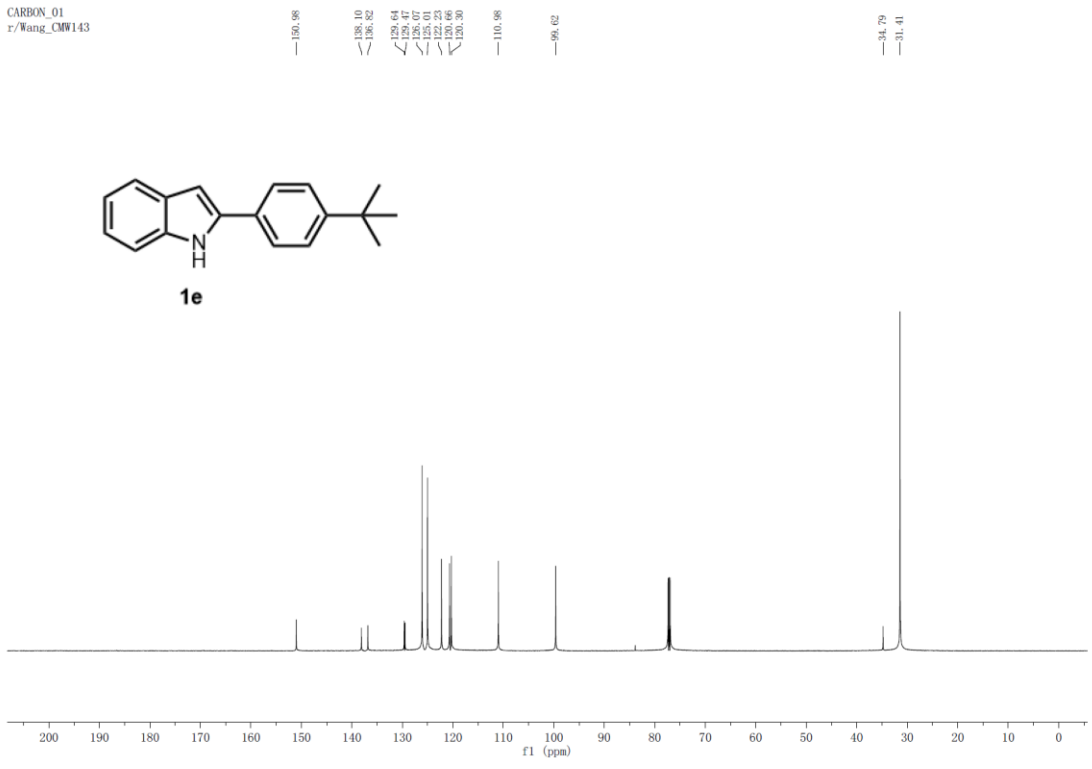
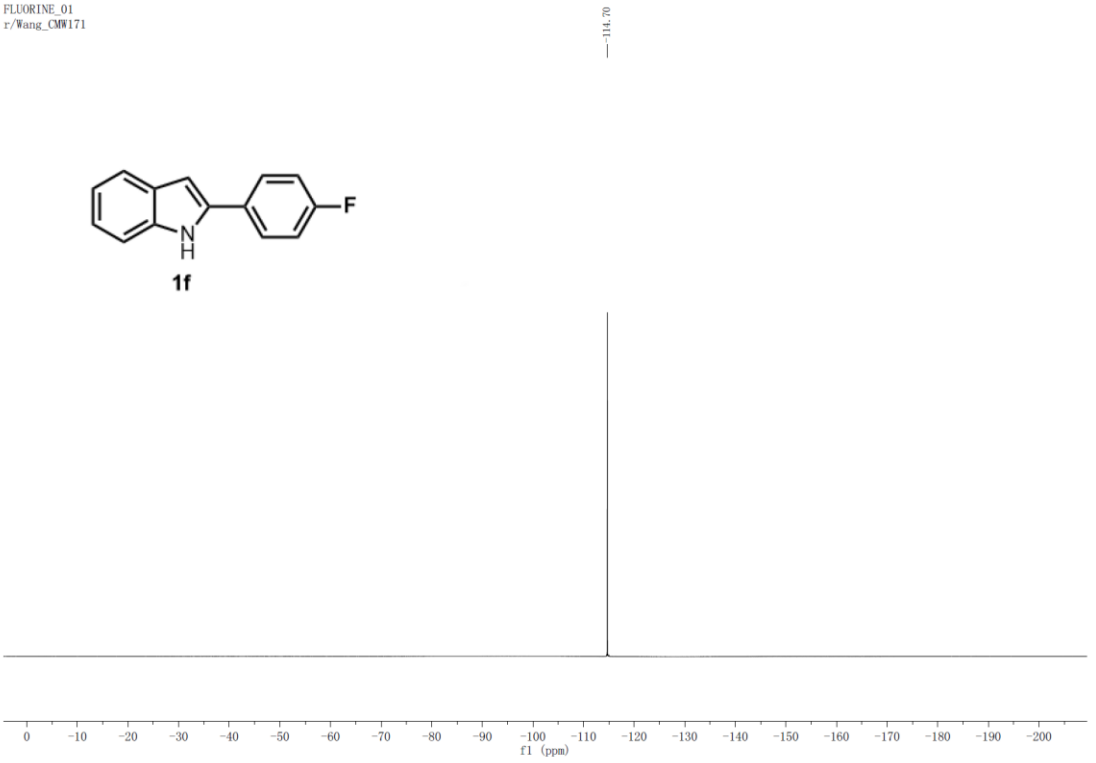
r/wang_cmw148
138.77
137.76
136.92
128.83
126.34
124.90
121.02
119.65
119.21
114.33
111.05
97.32
55.18
OMe
N
H
1d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


PROTON_01
r/Wang_CMW143
8.280
7.682
7.668
7.653
7.606
7.503
7.489
7.416
7.404
7.237
7.235
7.190
7.177
6.842
6.840
1.406
1e
0.96
1.00
2.06
2.07
1.01
1.03
1.00
9.24
f1 (ppm)

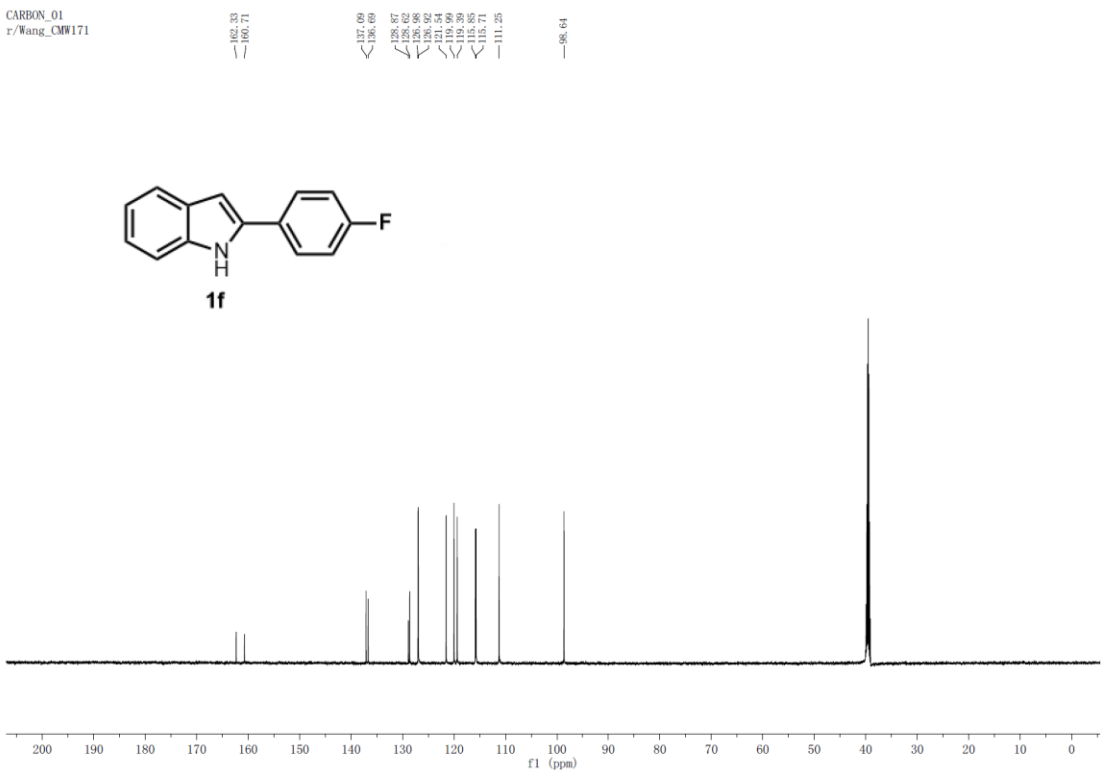

CARBON_01
r/Wang_CMW143
150.98
138.10
136.82
129.64
129.47
126.07
125.01
122.23
120.66
120.30
110.98
99.62
34.79
31.41
1e
f1 (ppm)

PROTON_01
r/Wang_CMW171

FLUORINE_01
r/Wang_CMW171

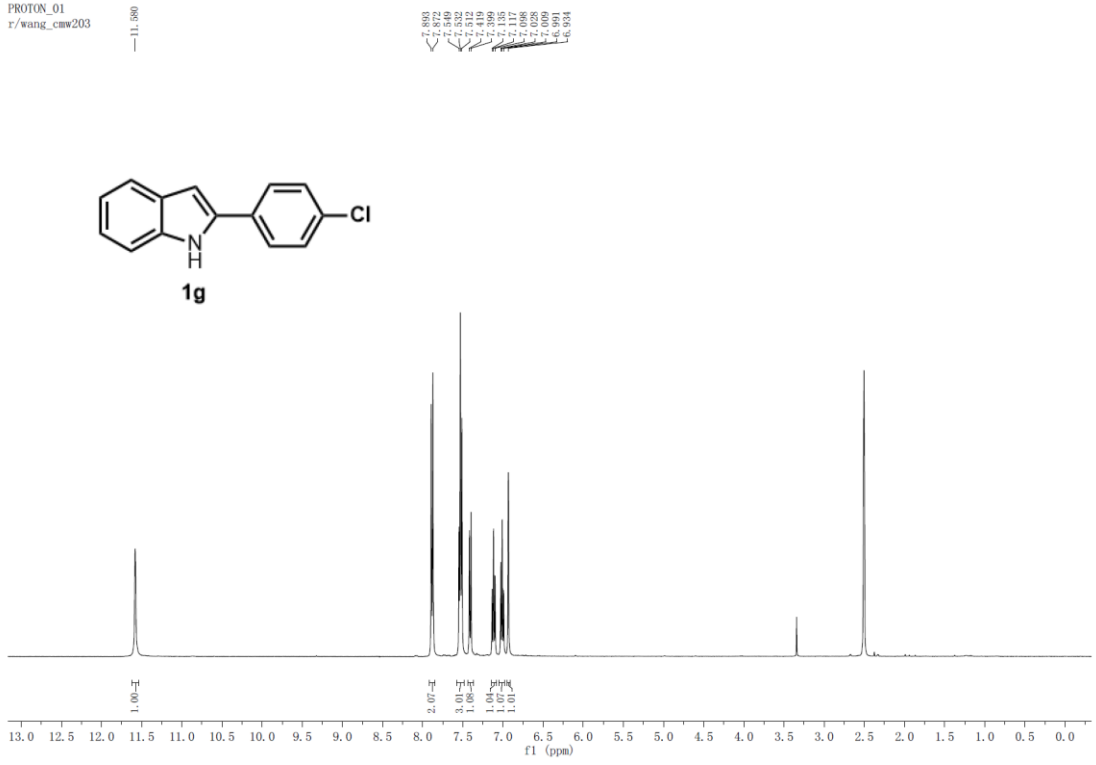


CARBON_01
r/Wang_CMW171

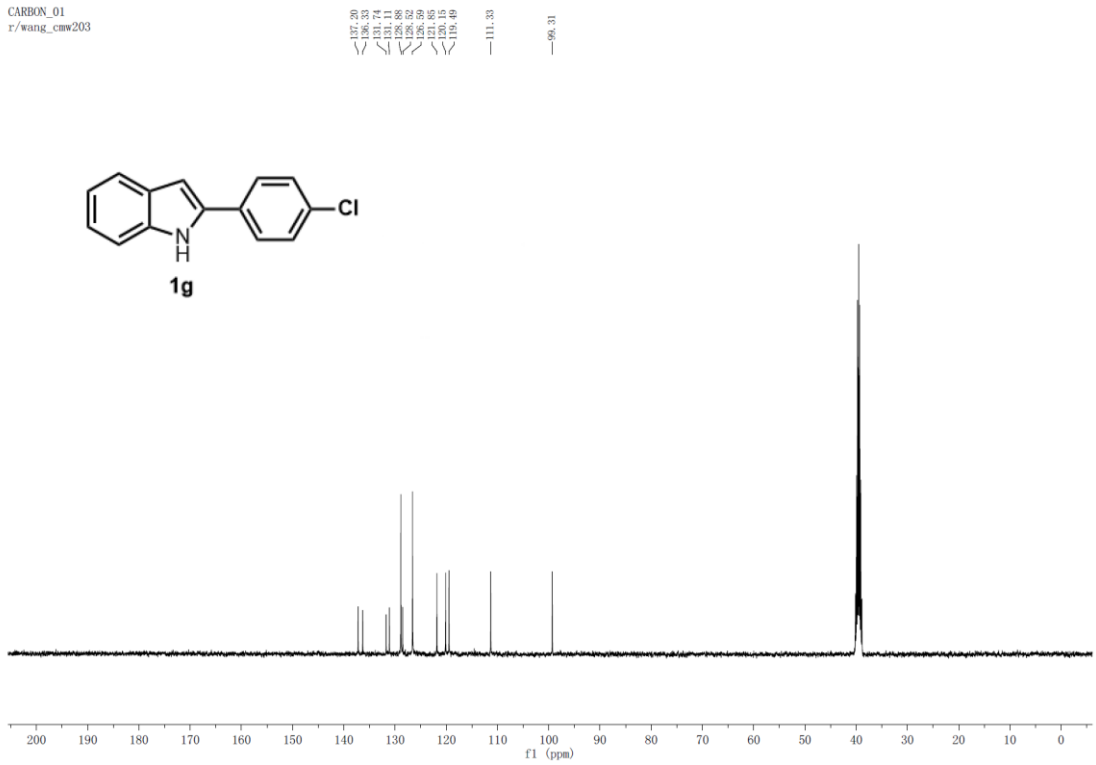


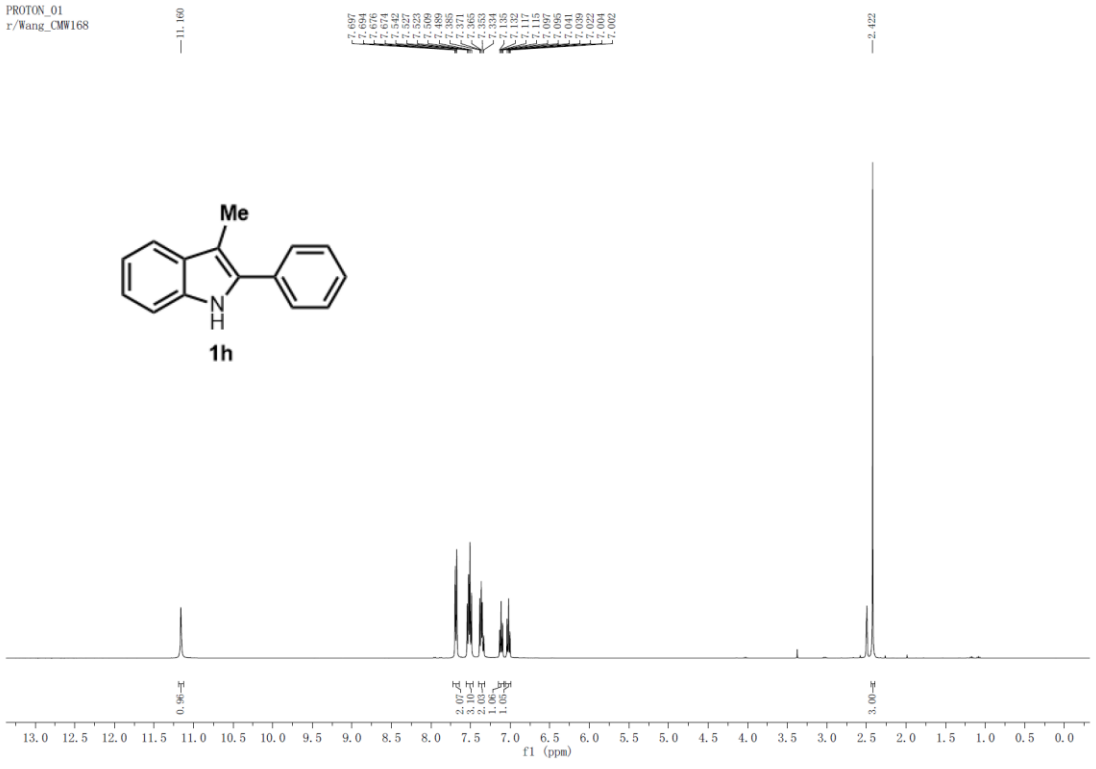
1f

PROTON_01
r/wang_cmw203



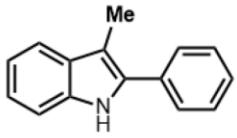
1g


CARBON_01
r/wang_cmw203
137.20
136.33
131.74
131.11
128.88
128.52
126.59
121.85
120.15
119.49
111.33
99.31
Cl
N
H
1g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

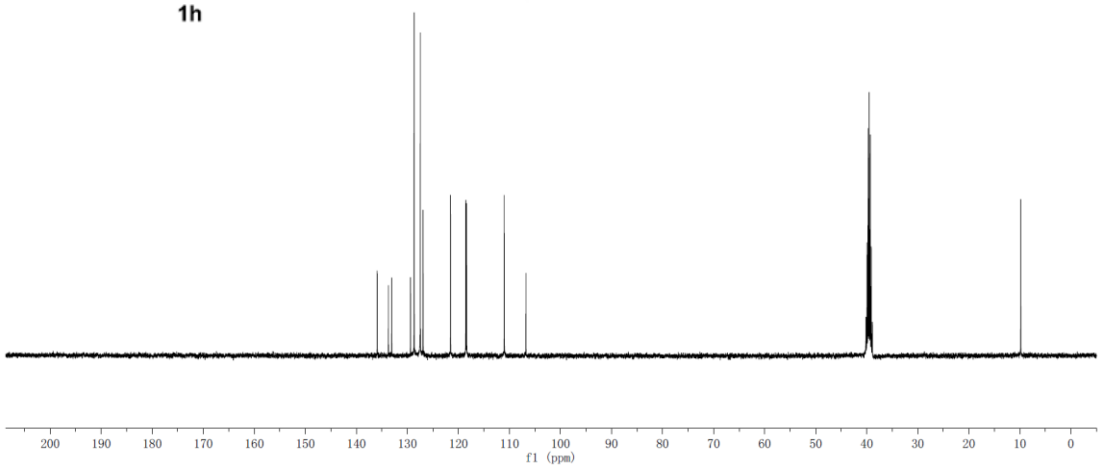

PROTON_01
r/Wang_CMW168
11.160
7.697
7.694
7.676
7.674
7.542
7.527
7.523
7.389
7.385
7.371
7.365
7.353
7.334
7.135
7.132
7.117
7.115
7.097
7.095
7.044
7.039
7.022
7.004
7.002
2.422
Me
N
H
1h
0.96
2.07
3.03
1.06
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

CARBON_01
r/Wang_CMW168

135.93
133.73
133.09
129.39
128.67
127.48
126.94
121.53
118.56
118.41
111.01
106.76
9.84

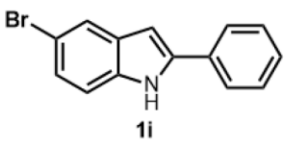


1h

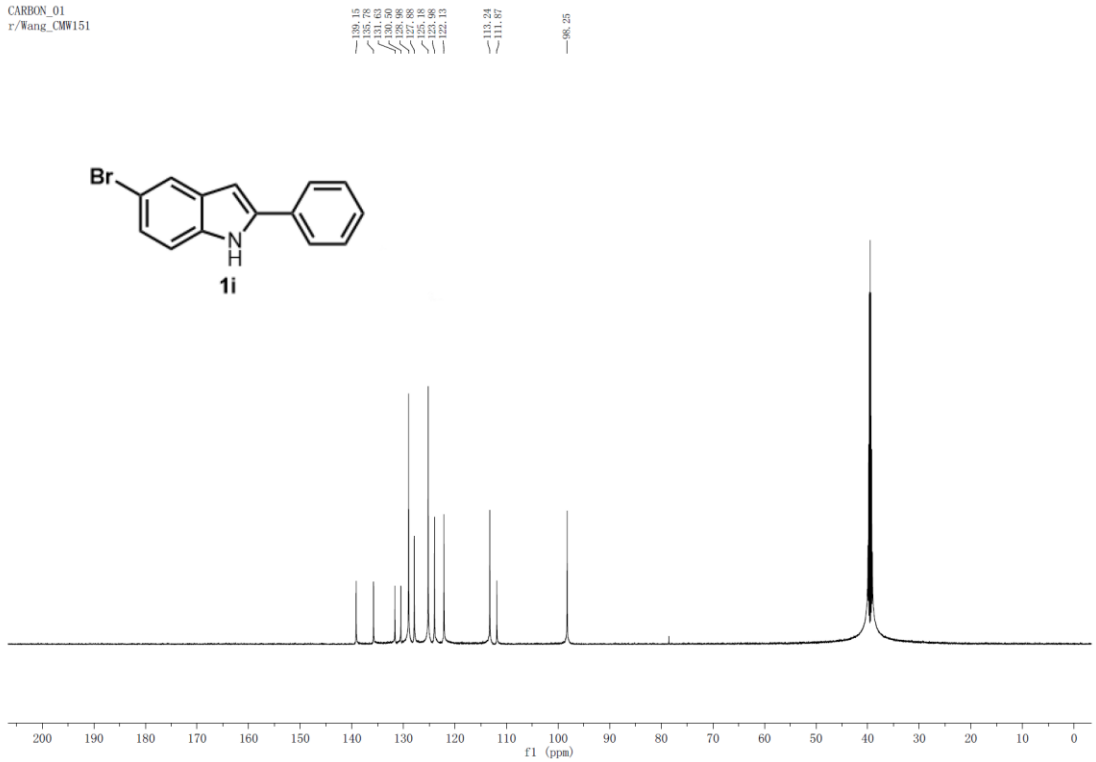


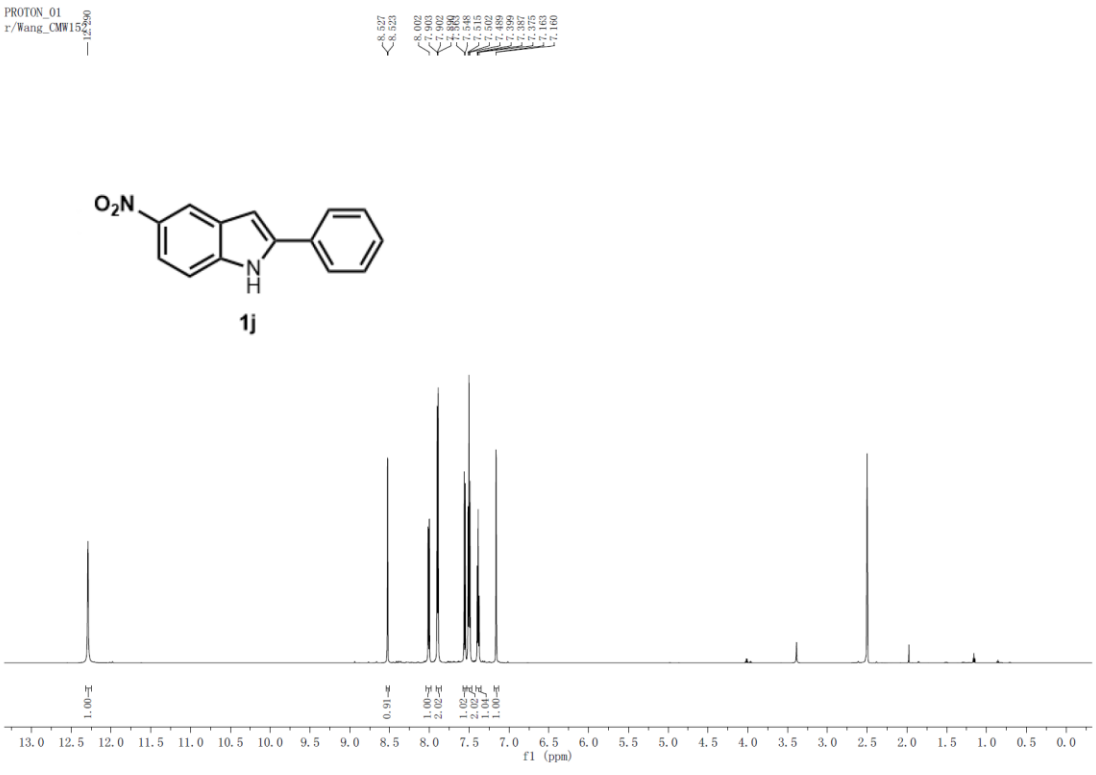
PROTON_01
r/Wang_CMW151

11.760
7.865
7.853
7.713
7.488
7.473
7.461
7.377
7.362
7.343
7.331
7.217
7.203
6.885



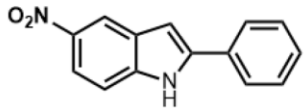
1i


CARBON_01
r/Wang_CMW151
139.15
135.28
131.63
130.50
128.98
127.98
125.18
123.98
122.13
113.24
111.87
98.25
Br
N
H
1i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

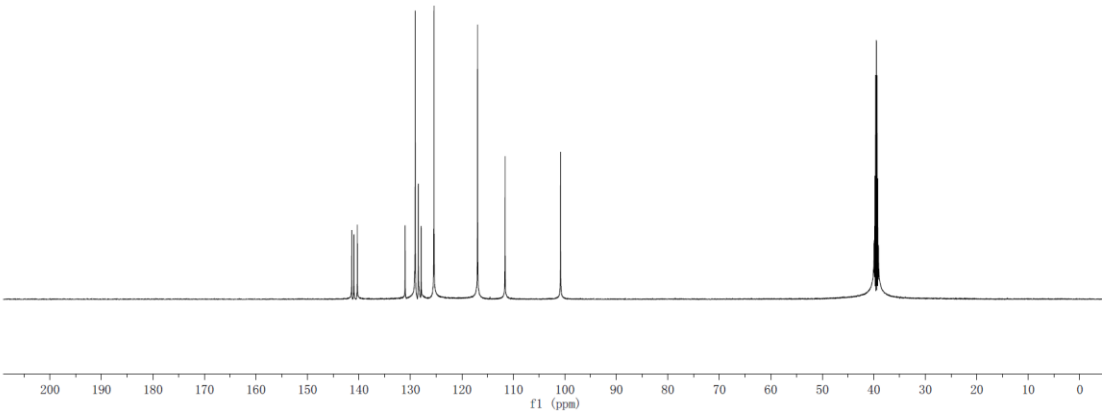

PROTON_01
r/Wang_CMW151
12.280
8.527
8.523
8.002
7.903
7.902
7.900
7.898
7.515
7.502
7.489
7.399
7.397
7.375
7.163
7.160
O2N
N
H
1j
1.00
0.91
1.00
2.02
1.02
2.02
1.04
1.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

CARBON_01
r/Wang_CMW152

141.41
140.99
140.31
131.01
129.08
128.45
127.93
125.43
116.96
111.62
100.84

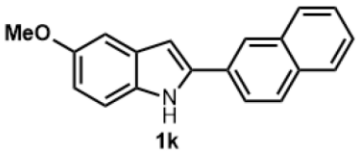


1j



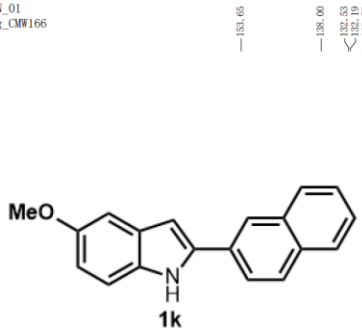
PROTON_01
r/Wang_CMW166

11.540
8.349
7.992
7.976
7.908
7.691
7.675
7.548
7.534
7.511
7.498
7.486
7.339
7.325
7.057
6.999
6.789
6.787
6.775
6.772
3.777

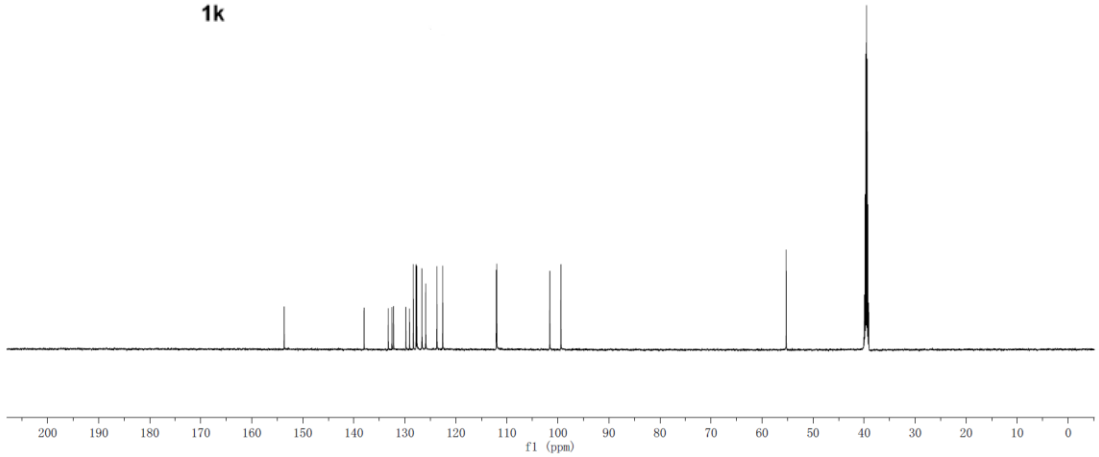


1k

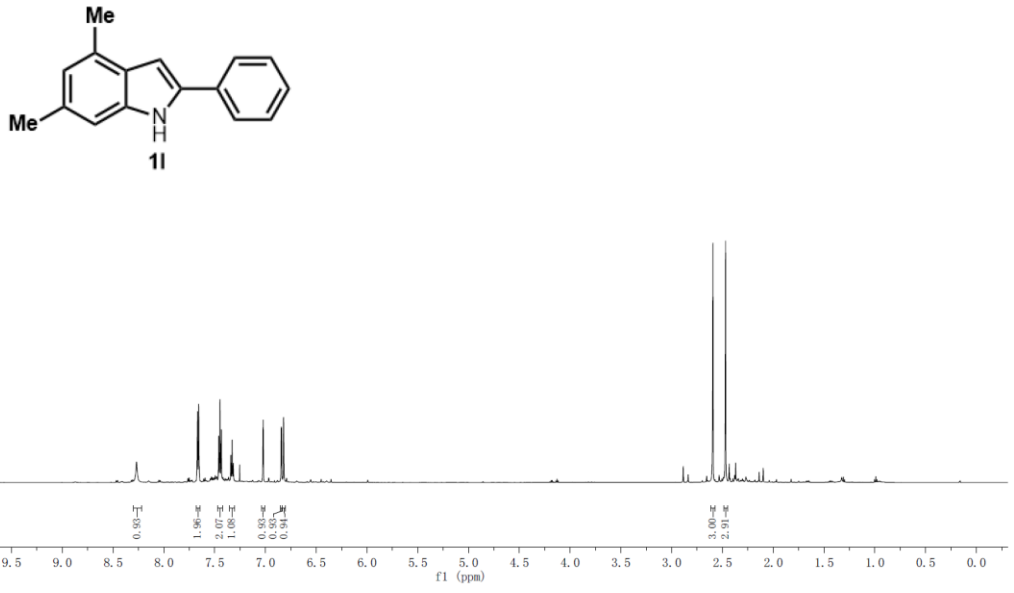
CARBON_01
r/Wang_CMW166



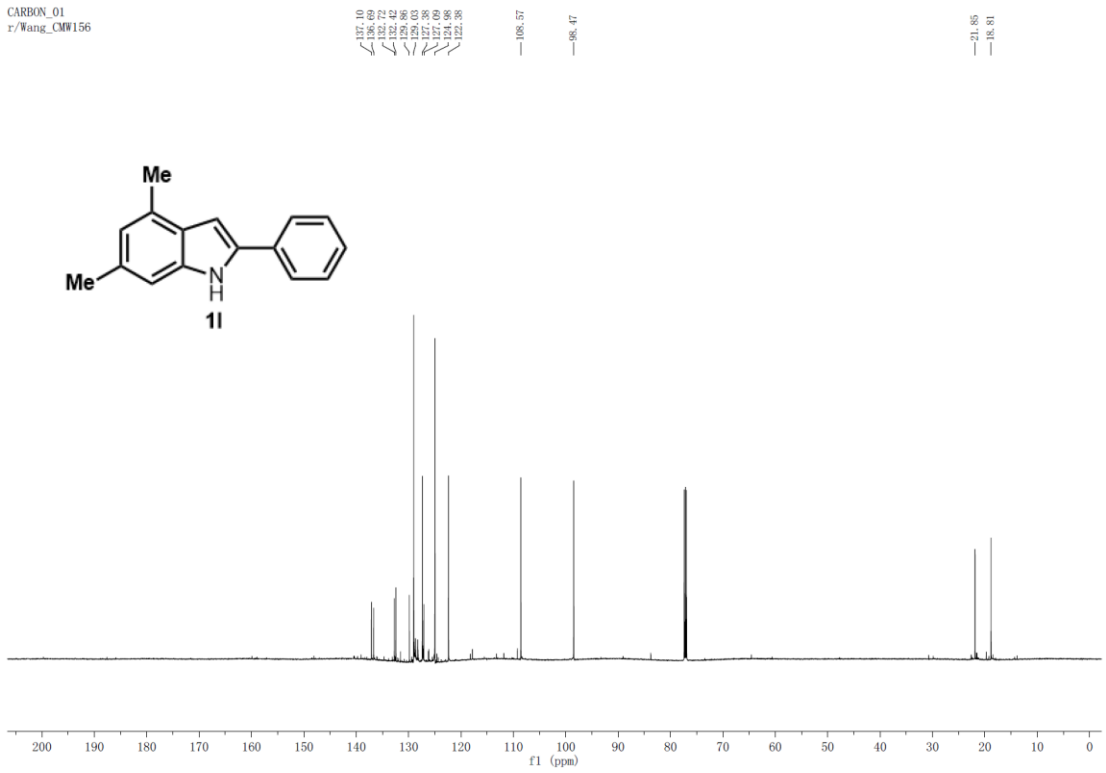
1k

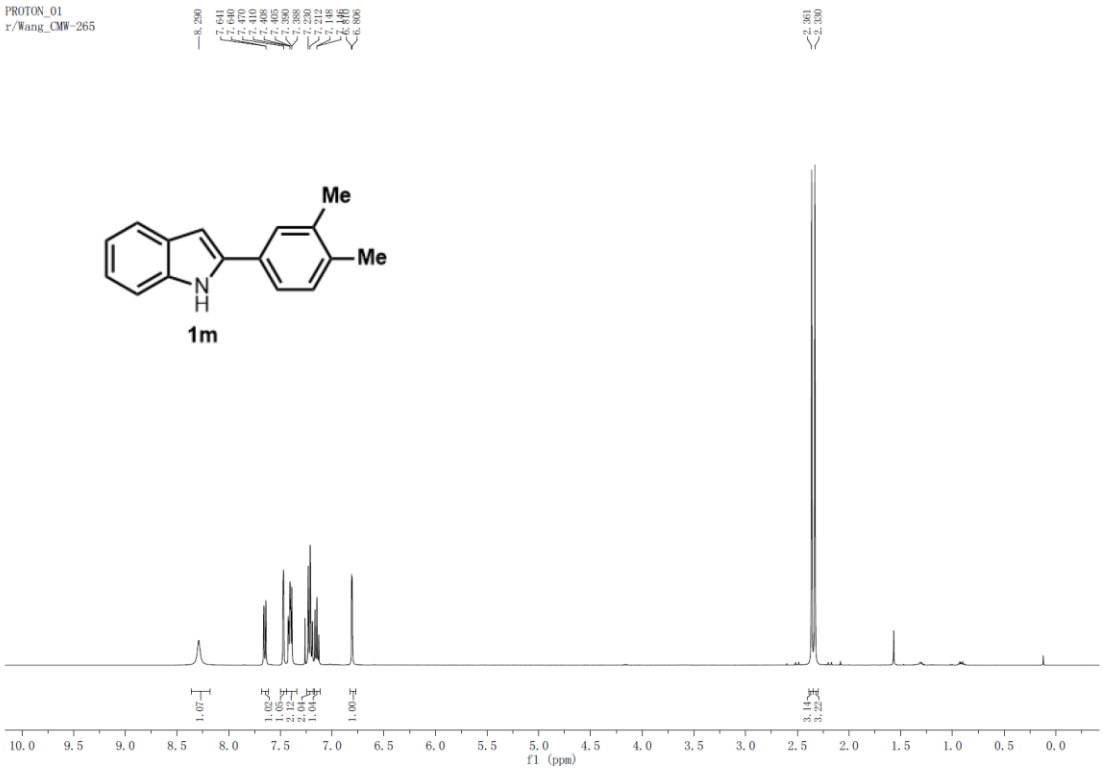


PROTON_01
r/Wang_CMW156

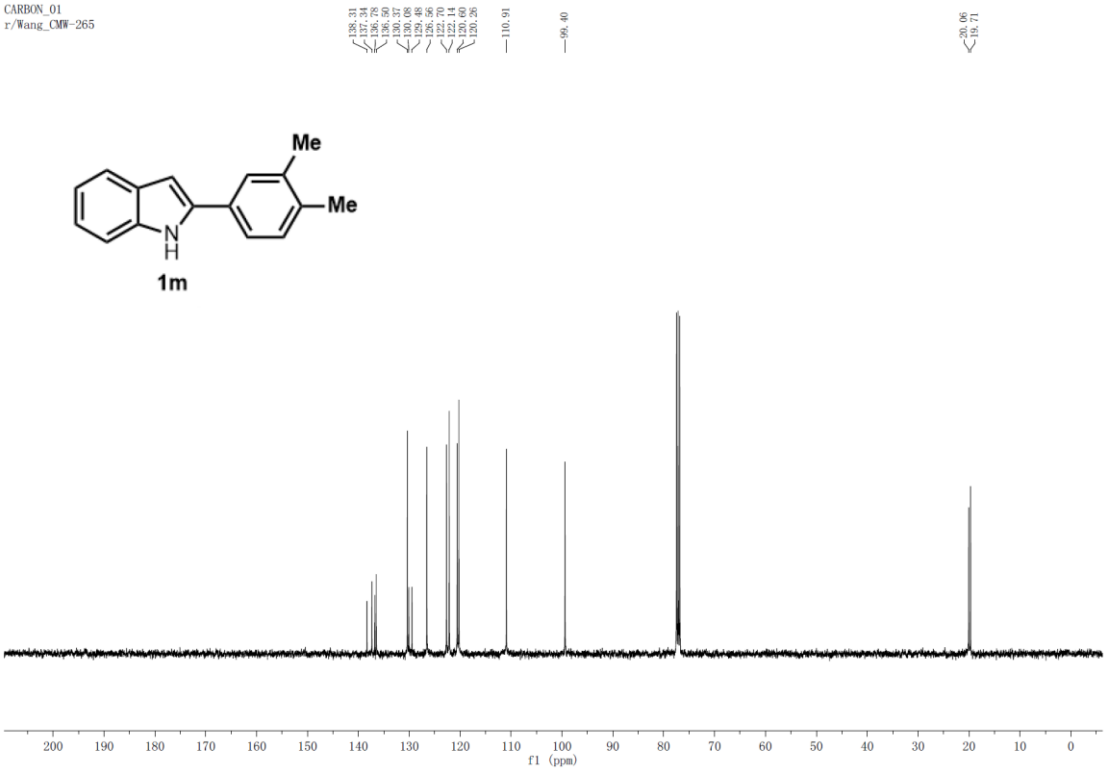


1l

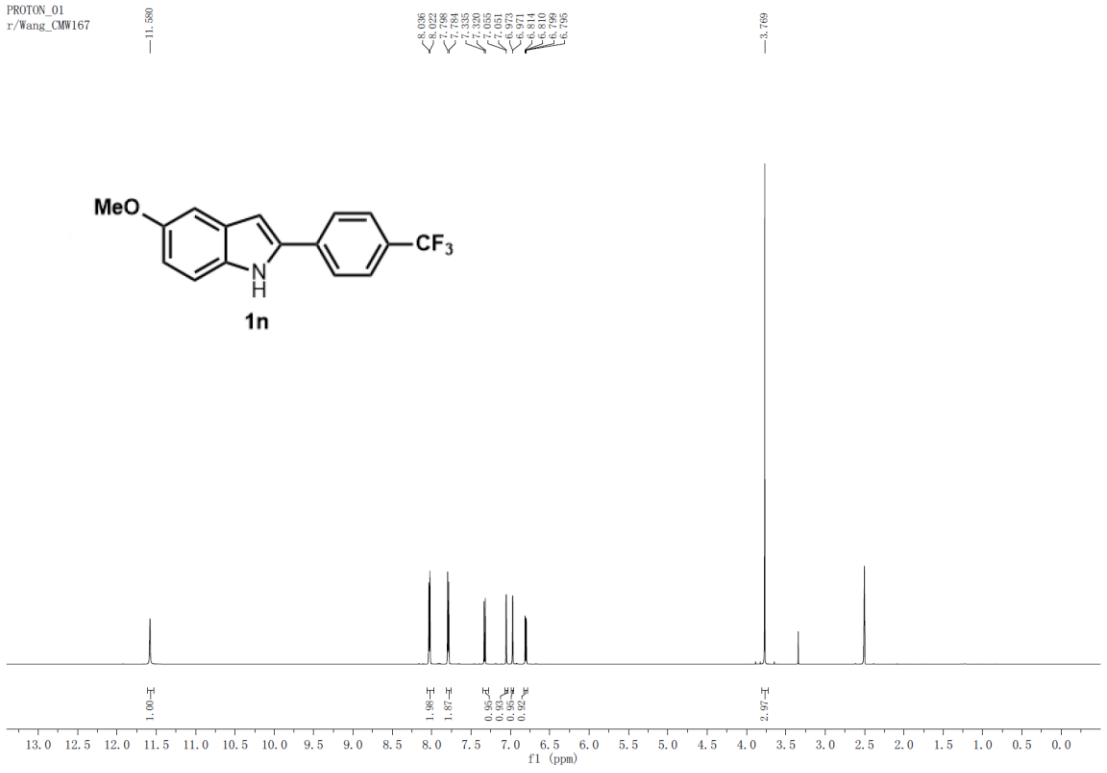

CARBON_01
r/Wang_CMW156
137.10
136.69
132.72
132.42
129.86
129.03
127.38
127.09
124.98
122.38
108.57
98.47
21.85
18.81
Me
Me
N
H
1l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


PROTON_01
r/Wang_CMW-265
8.290
7.641
7.640
7.470
7.410
7.408
7.405
7.399
7.398
7.230
7.212
7.148
7.146
6.809
6.806
2.361
2.330
Me
Me
N
H
1m
1.07
1.02
1.05
2.12
2.04
1.04
1.00
3.14
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

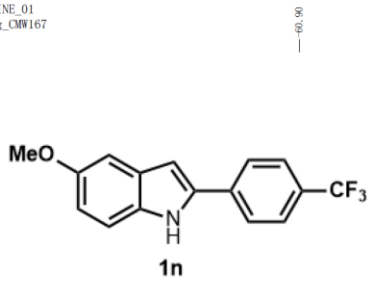
CARBON_01
r/Wang_CMW-265



PROTON_01
r/Wang_CMW167



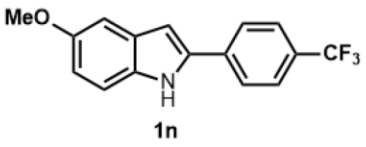
FLUORINE_01
r/Wang_CMW167



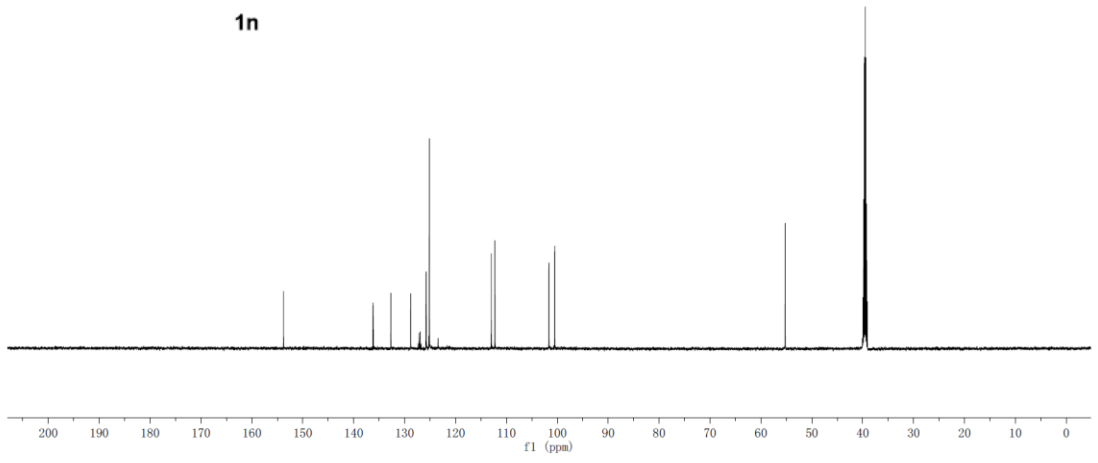
1n

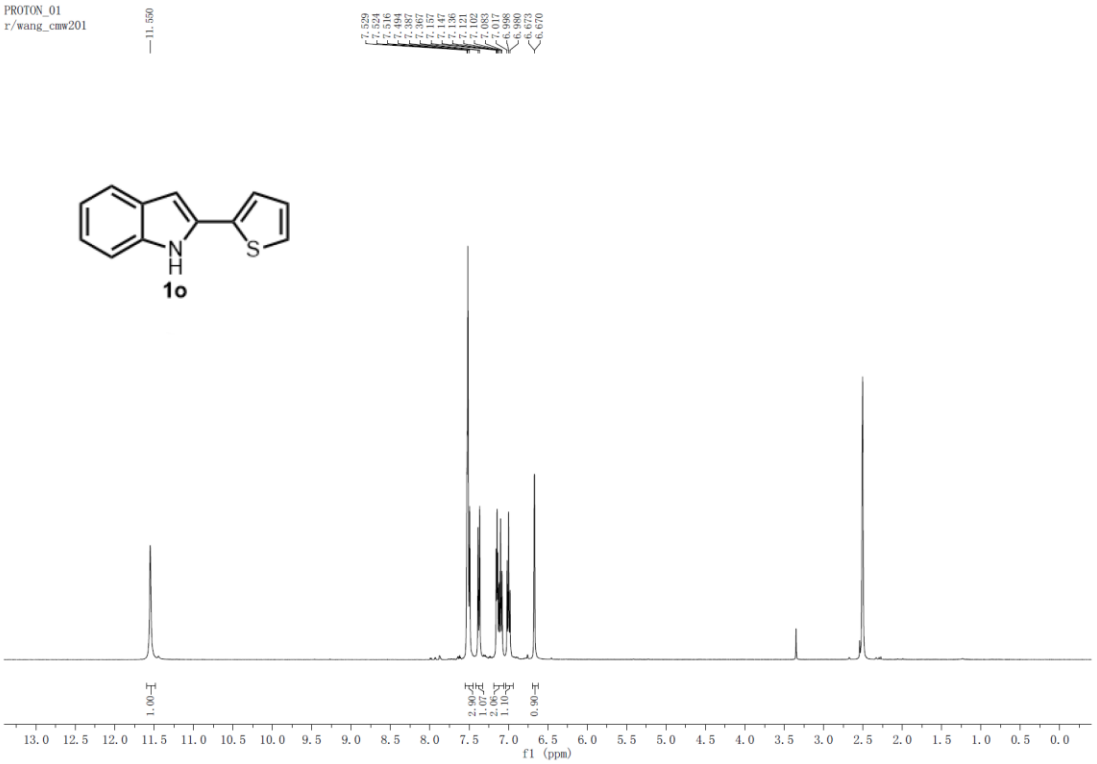
CARBON_01
r/Wang_CMW167

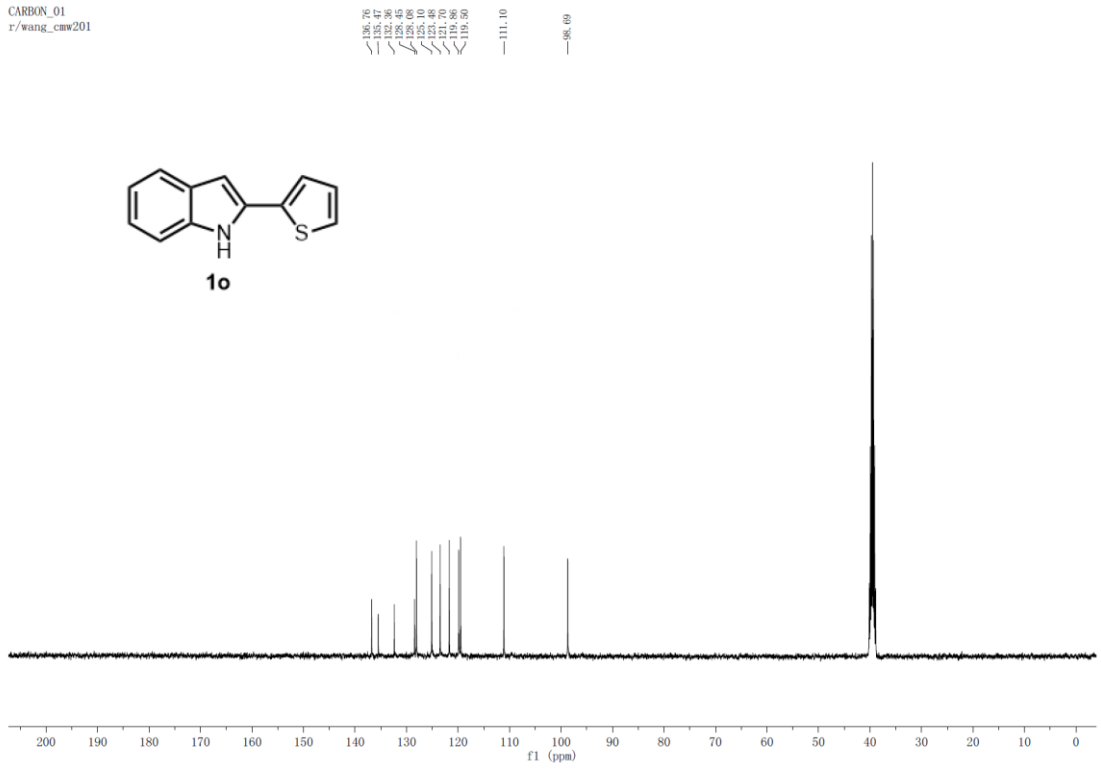
153.77
136.21
136.16
132.69
132.78
127.16
126.95
125.79
125.76
125.24
125.14
123.43
112.97
112.27
101.65
100.52
55.23

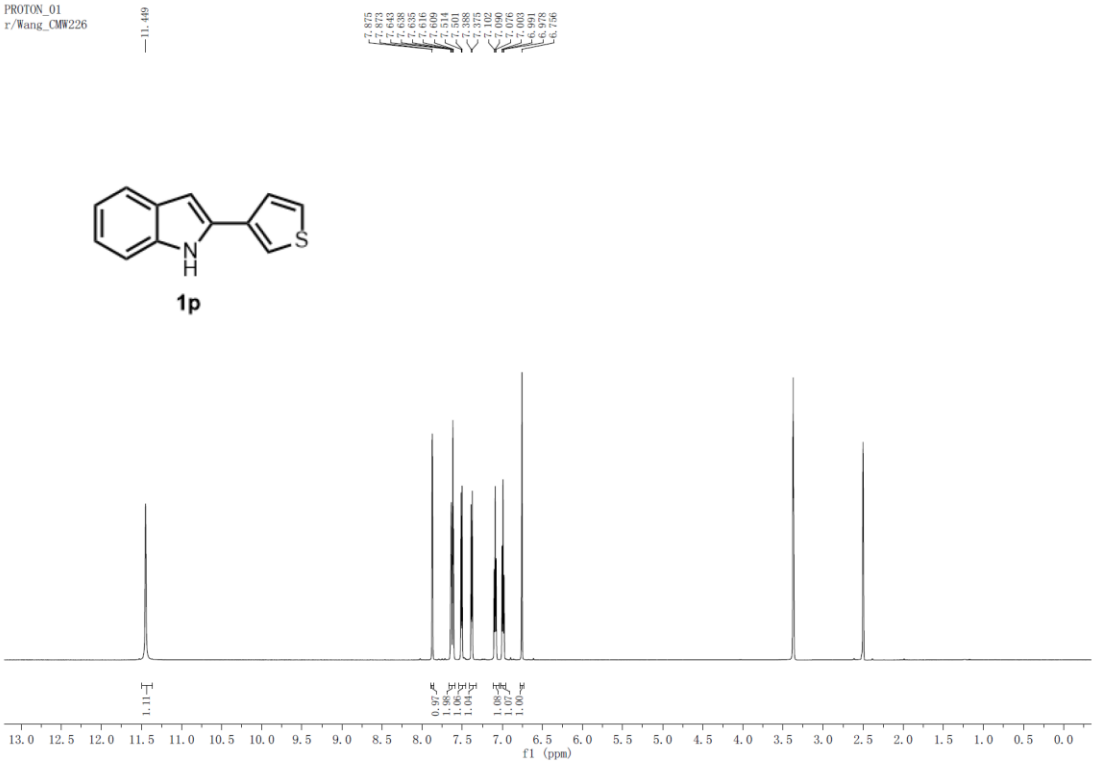


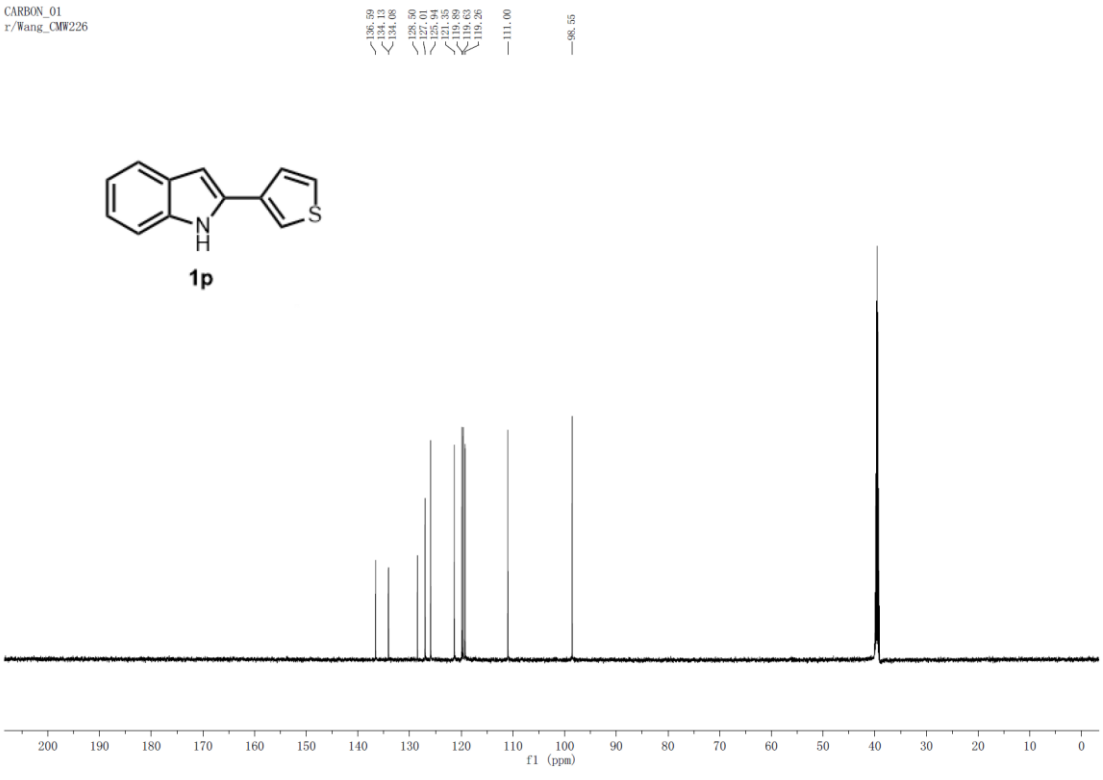
1n

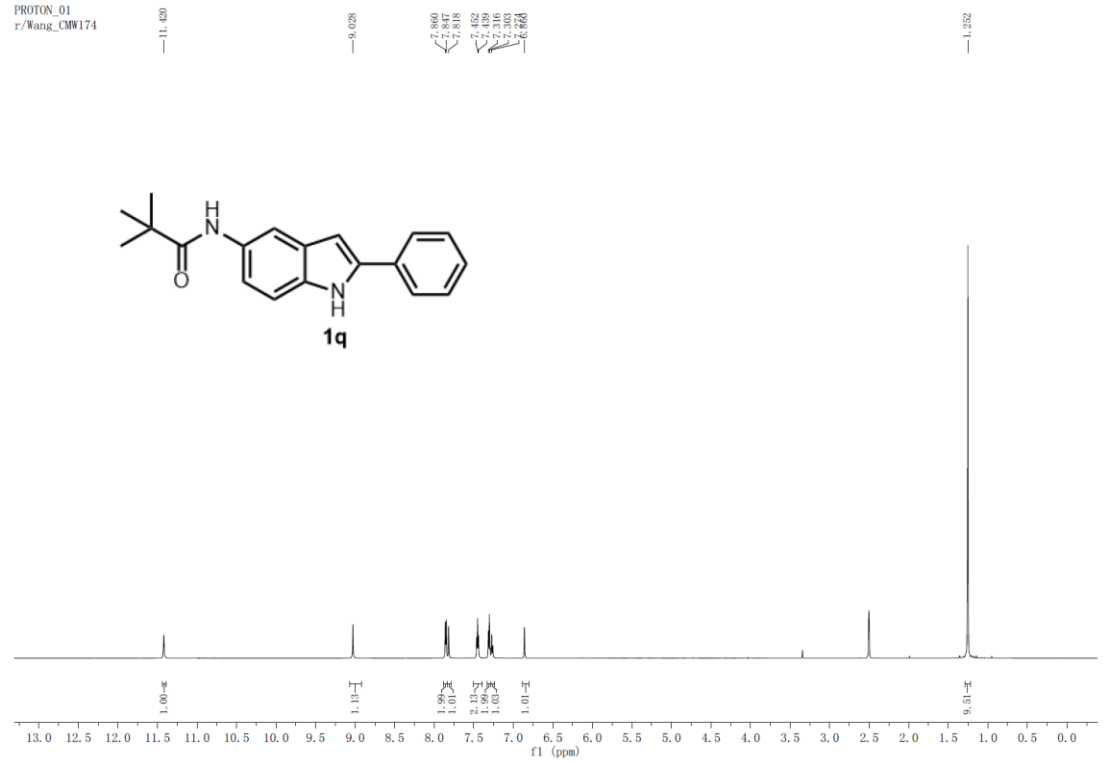


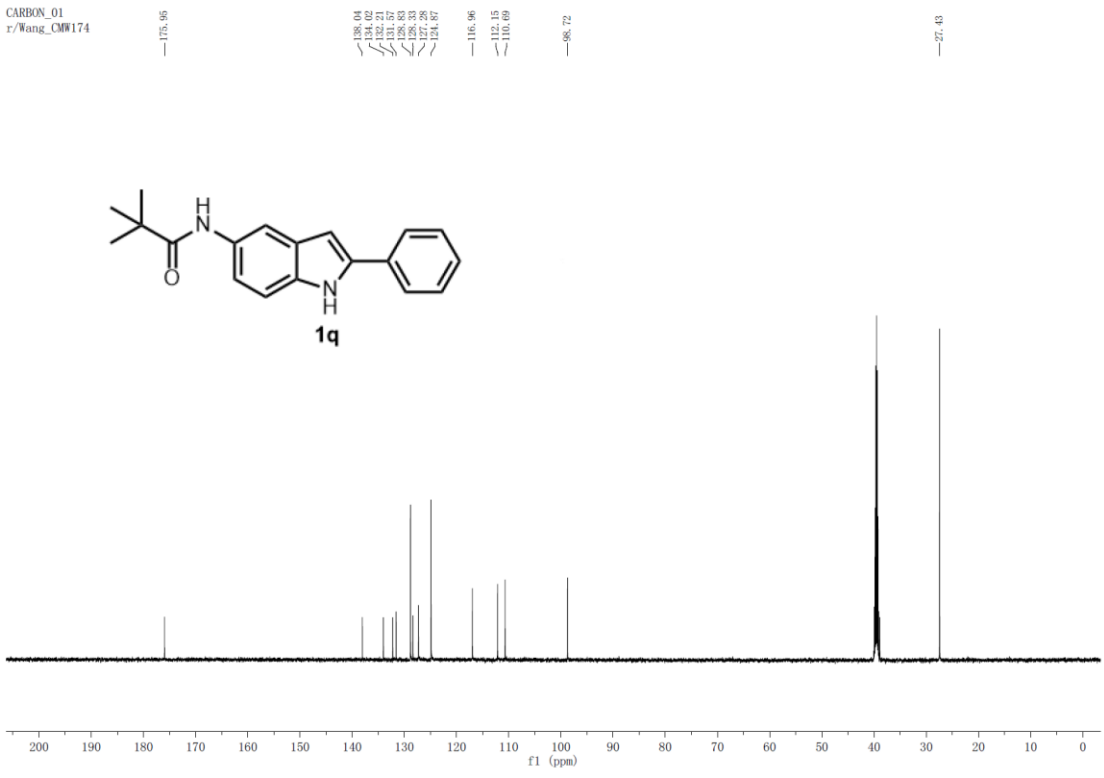

PROTON_01
r/wang_cmw201
11.560
7.529
7.524
7.516
7.494
7.387
7.367
7.157
7.147
7.136
7.121
7.102
7.083
7.017
6.998
6.980
6.673
6.670
1o
1.00
2.90
1.07
2.06
1.10
0.90
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

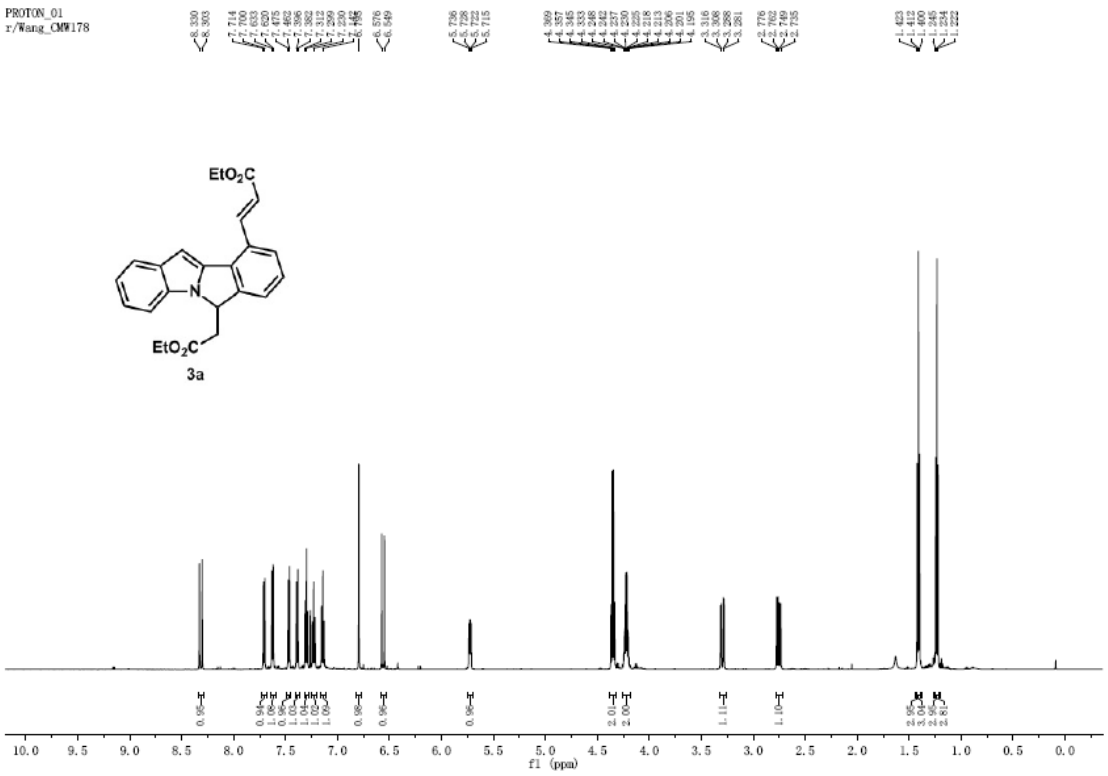

CARBON_01
r/wang_cmw201
136.76
135.47
132.36
128.45
126.86
125.10
123.48
121.70
119.96
119.50
111.10
98.69
1o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

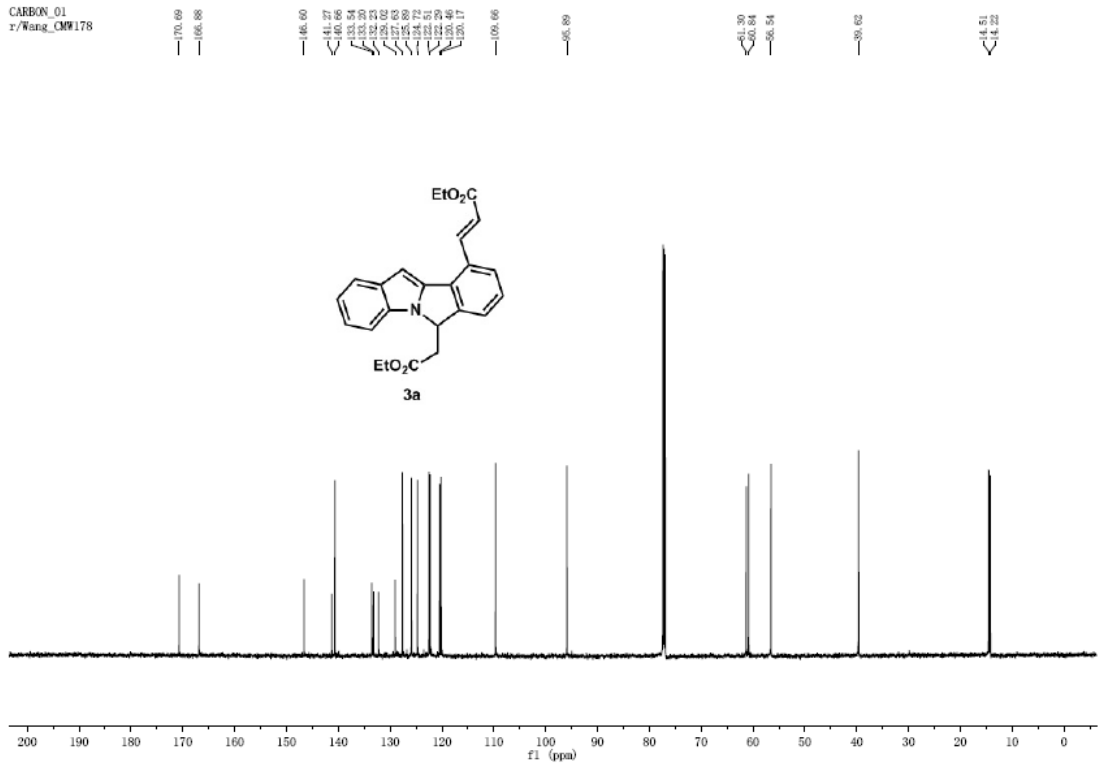

PROTON_01
r/Wang_CMW226
11.449
7.875
7.873
7.643
7.638
7.635
7.616
7.609
7.514
7.510
7.388
7.375
7.102
7.099
7.075
7.003
6.991
6.978
6.756
1p
1.11
0.97
1.98
1.06
1.04
1.08
1.07
1.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CARBON_01
r/Wang_CMW226
136.59
134.13
134.08
128.50
127.01
125.94
121.35
110.98
119.63
119.26
111.00
98.55
1p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

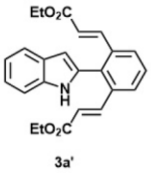

PROTON_01
r/Wang_CMW174
11.420
9.028
7.890
7.847
7.818
7.462
7.439
7.316
7.303
7.277
6.666
1.262
1q
1.00
1.13
1.99
1.01
2.13
1.99
1.03
1.01
9.51
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CARBON_01
r/Wang_CMW174
175.95
138.04
134.02
132.21
131.57
128.83
128.33
127.28
124.67
116.96
112.15
110.69
98.72
27.43
1q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

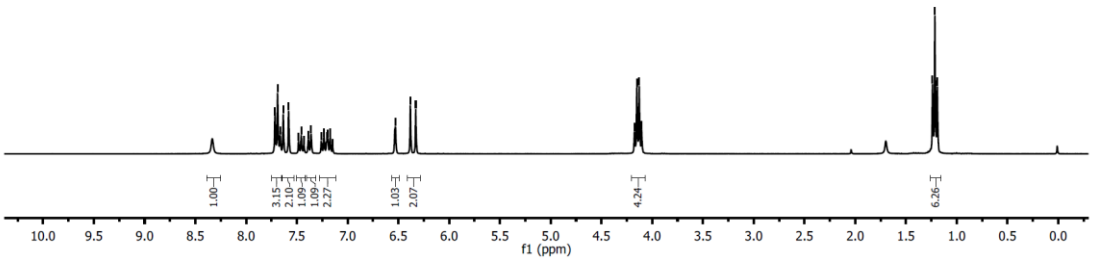

PROTON_01
r/Wang_CMW178
EtO2C
EtO2C
N
3a
f1 (ppm)


CARBON_01
r/Wang_CMW178
EtO2C
EtO2C
N
3a
f1 (ppm)

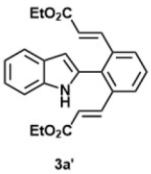
ZFM-I-56-B



3a'

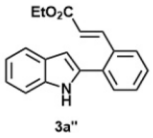


ZFM-I-56-B-C

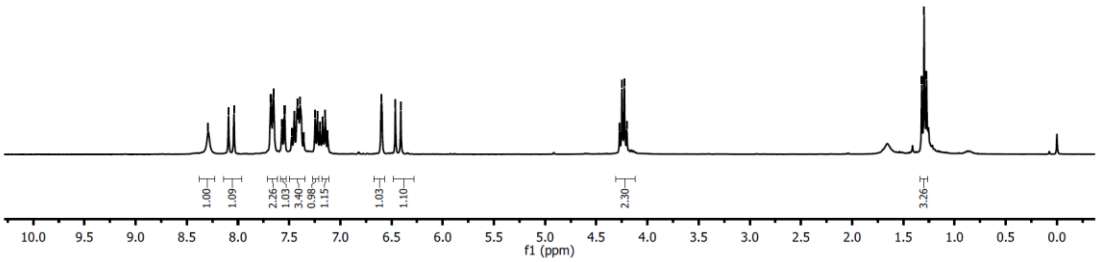


3a'

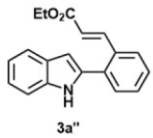
ZFM-I-56-D



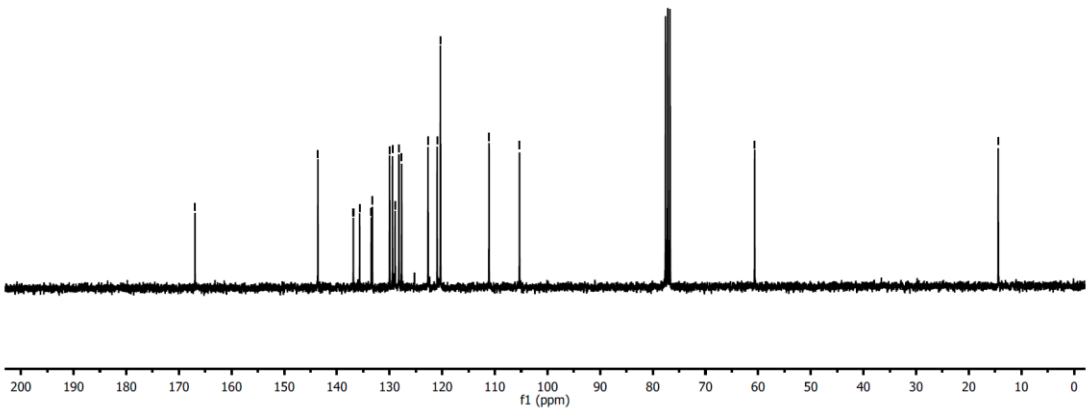
3a''

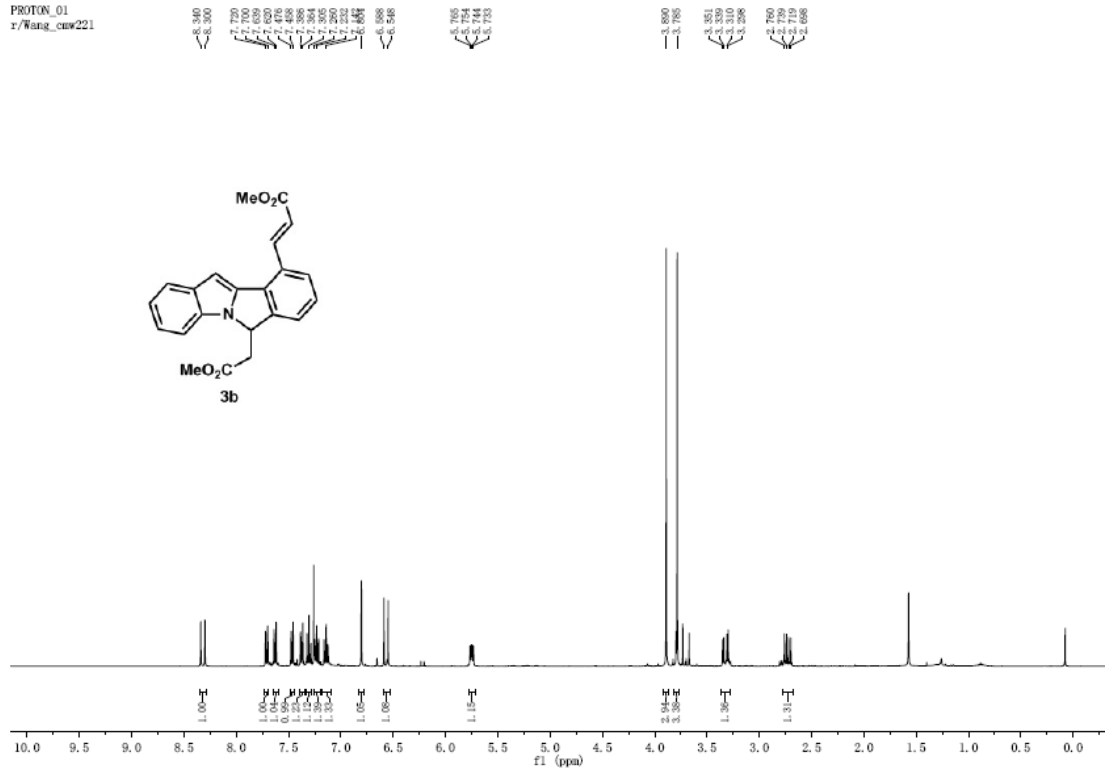


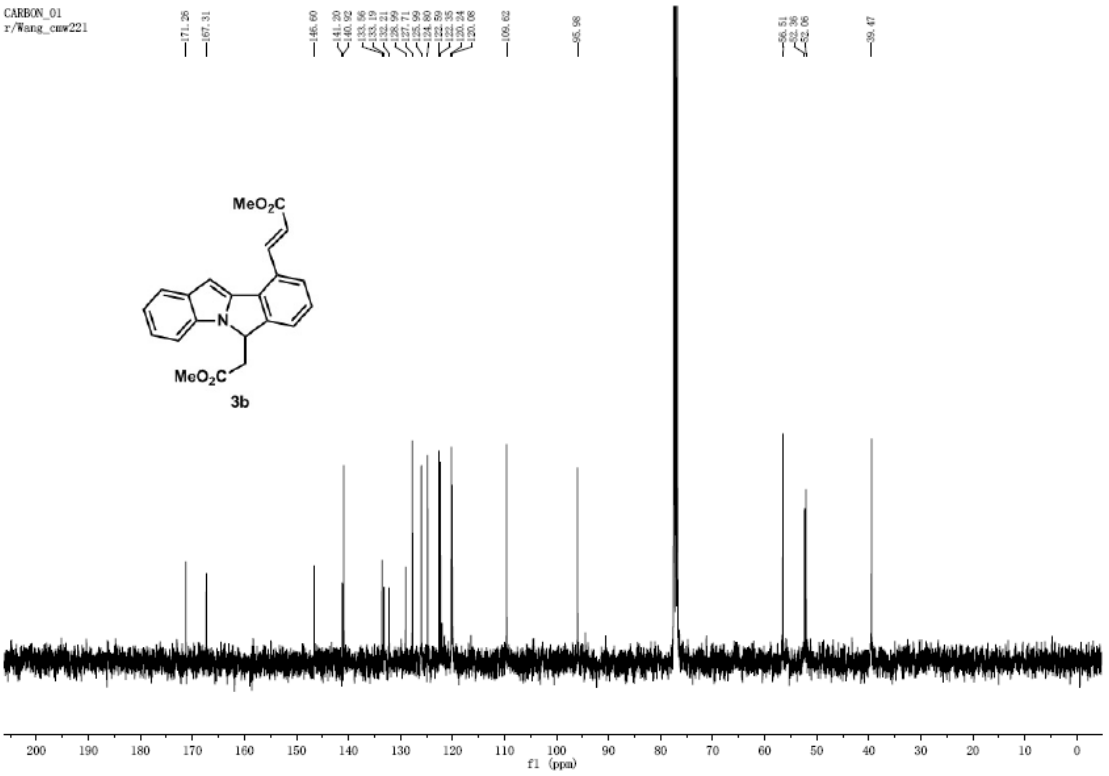
ZFM-I-56-D-C
ZFM-I-56-D-C

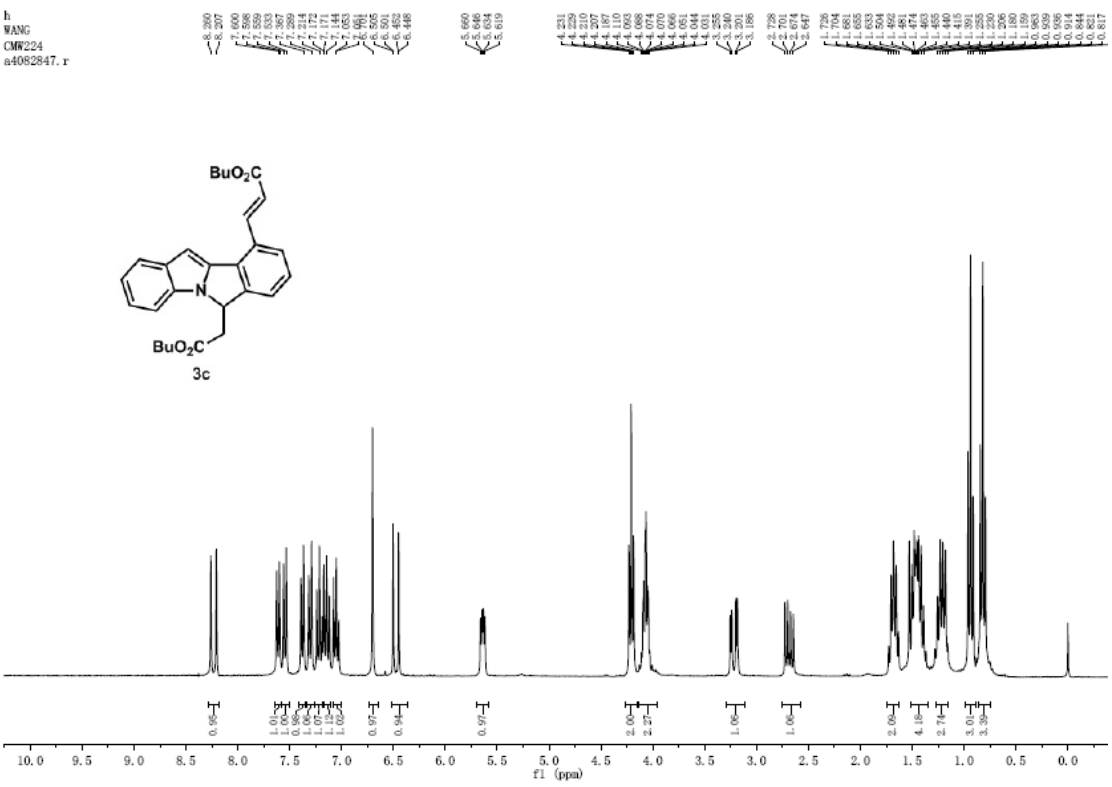


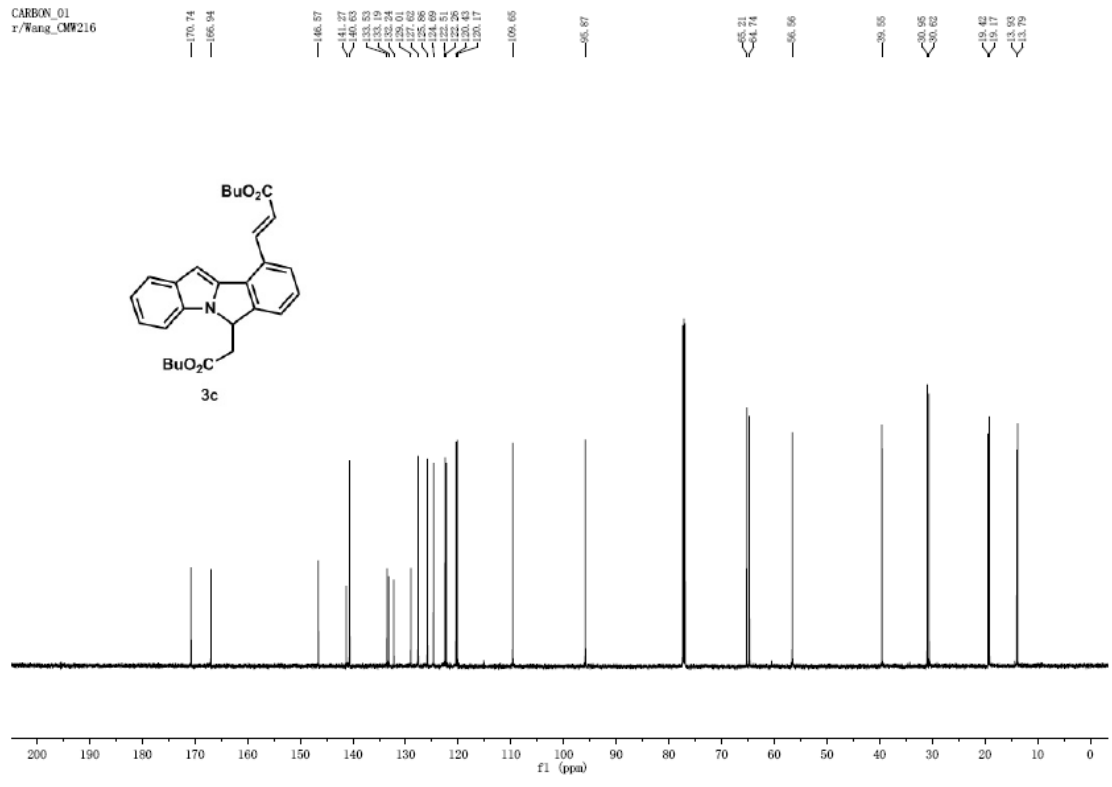
3a''

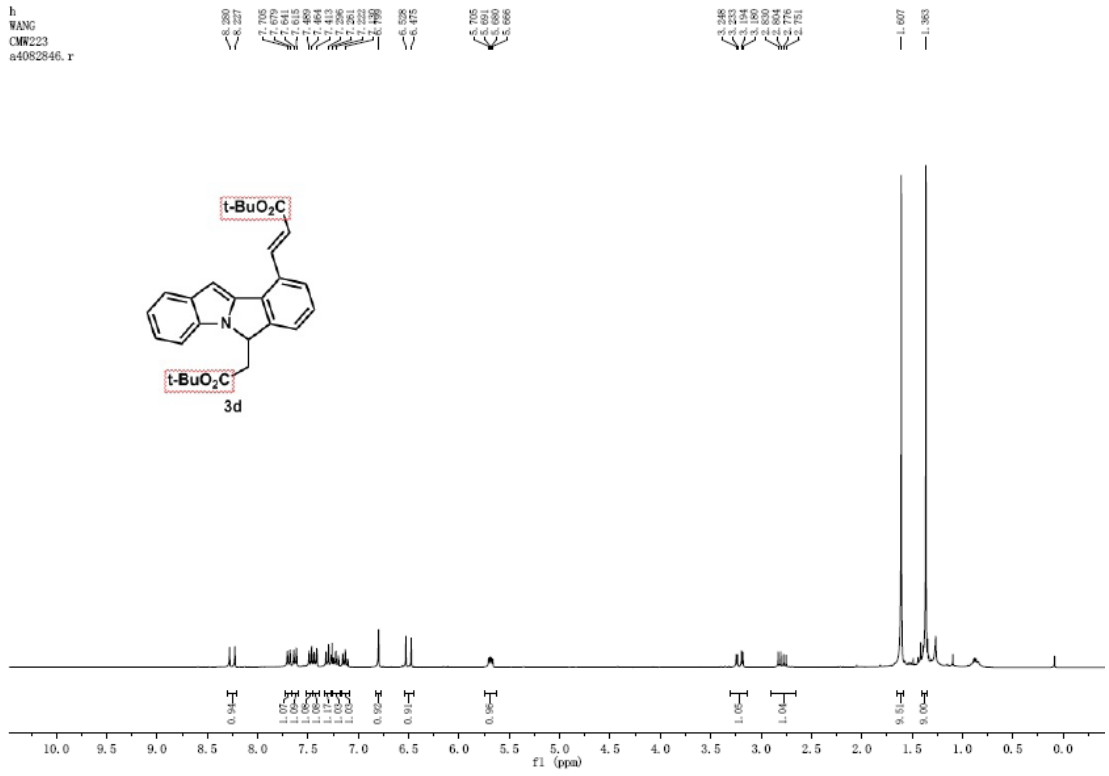


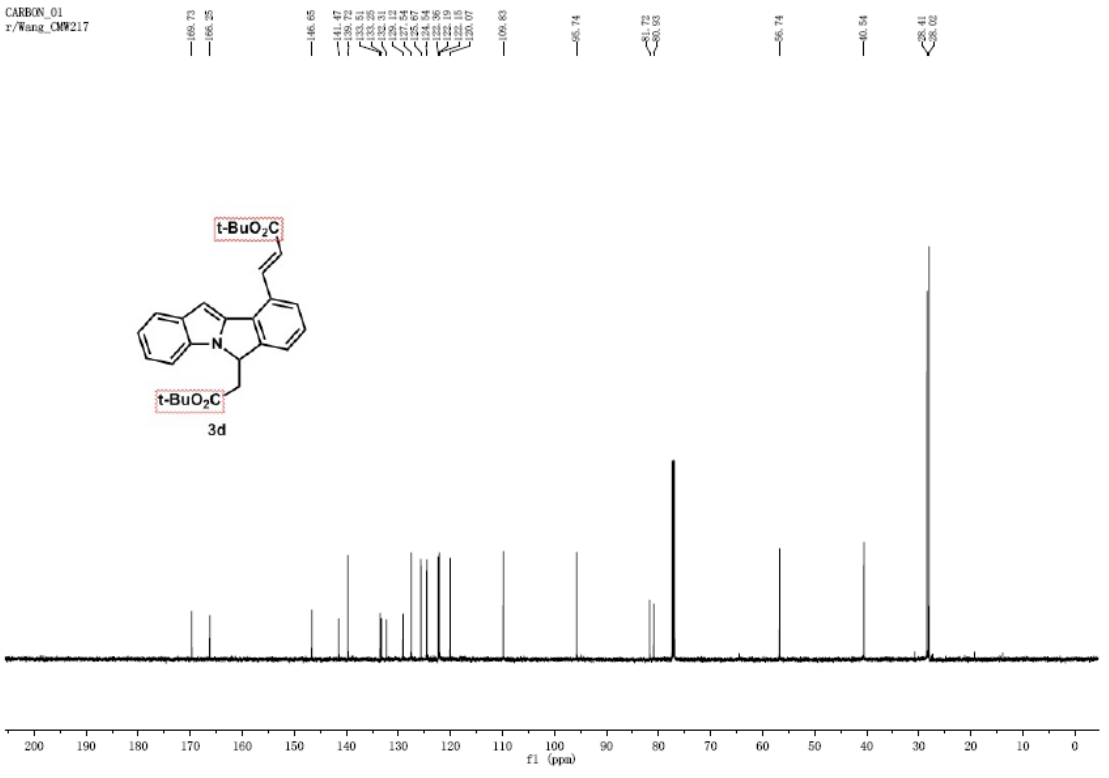

PROTON_01
r/Wang_cmw221
MeO2C
MeO2C
3b
f1 (ppm)


CARBON_01
r/Wang_cmw221
MeO2C
MeO2C
3b
f1 (ppm)

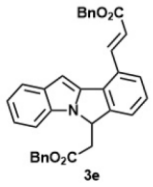

h
WANG
CMW224
a4082847.r
BuO2C
BuO2C
3c
f1 (ppm)


CARBON_01
r/Wang_CMW216
BuO2C
BuO2C
3c
f1 (ppm)

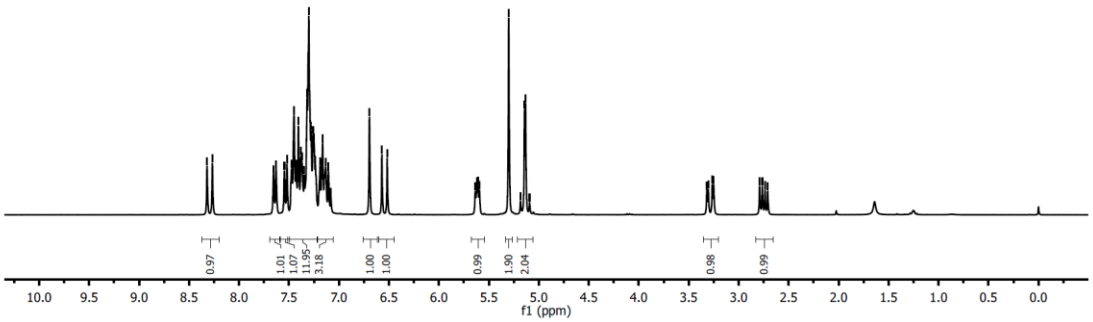

h
WANG
CMW223
a4082846.r
t-BuO2C
t-BuO2C
3d
f1 (ppm)


CARBON_01
r/Wang_CMW217
t-BuO2C
t-BuO2C
3d
f1 (ppm)

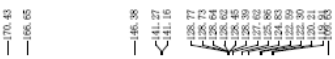
ZFM-I-104
ZFM-I-104-H

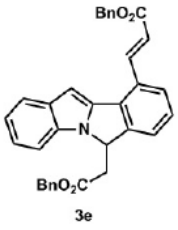


3e



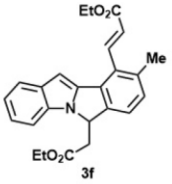
CARBON_01
r/wang_cmw204



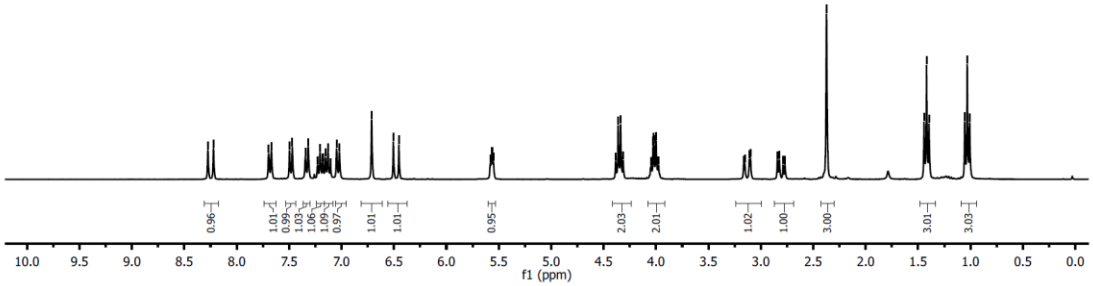


3e

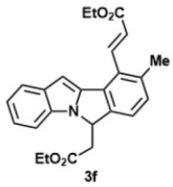
ZFM-I-105-1
ZFM-I-105-1-H



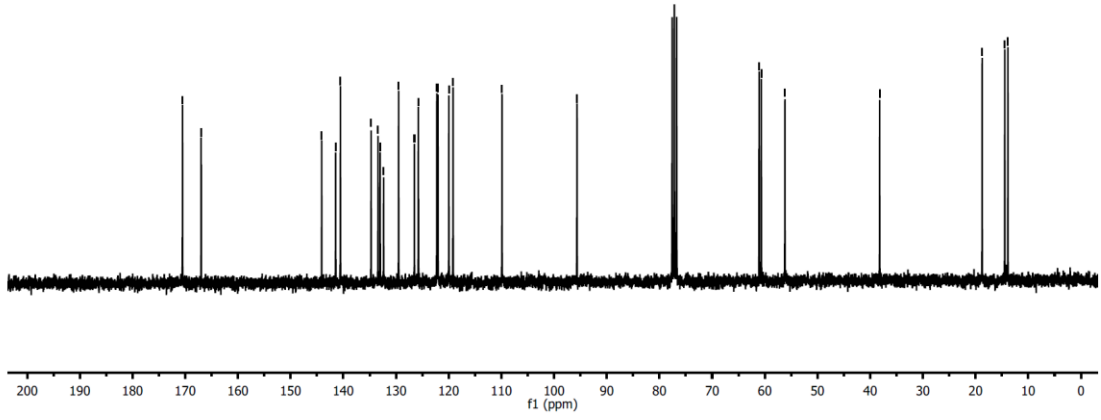
3f

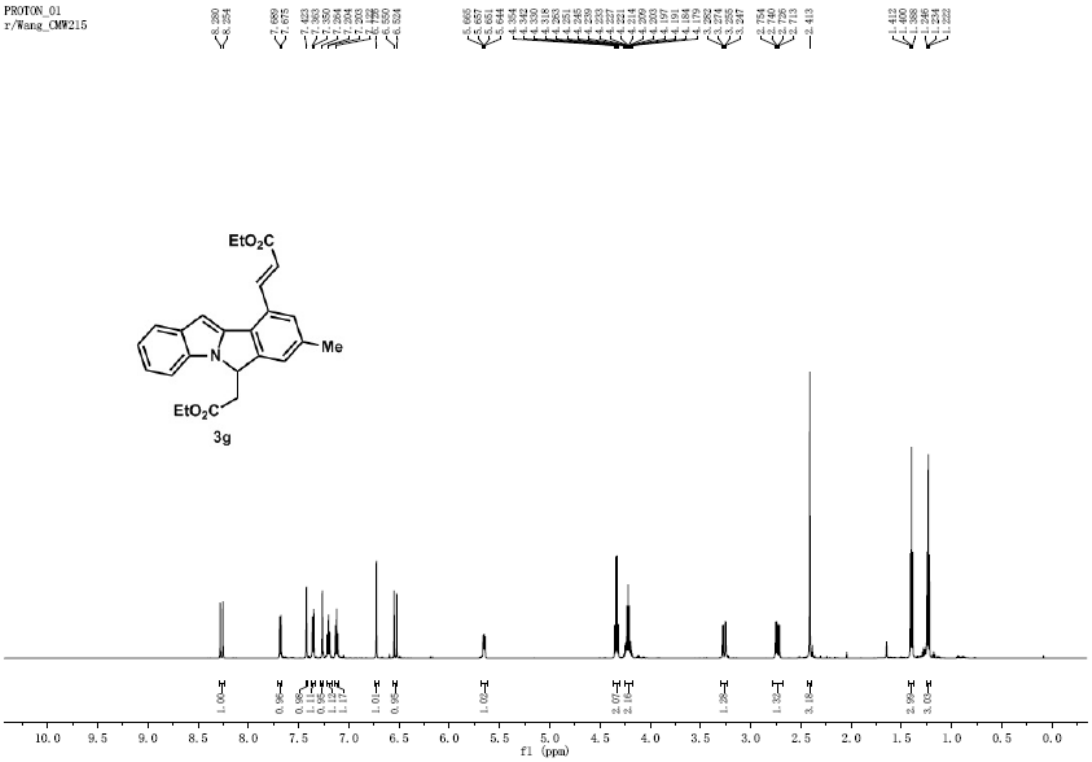


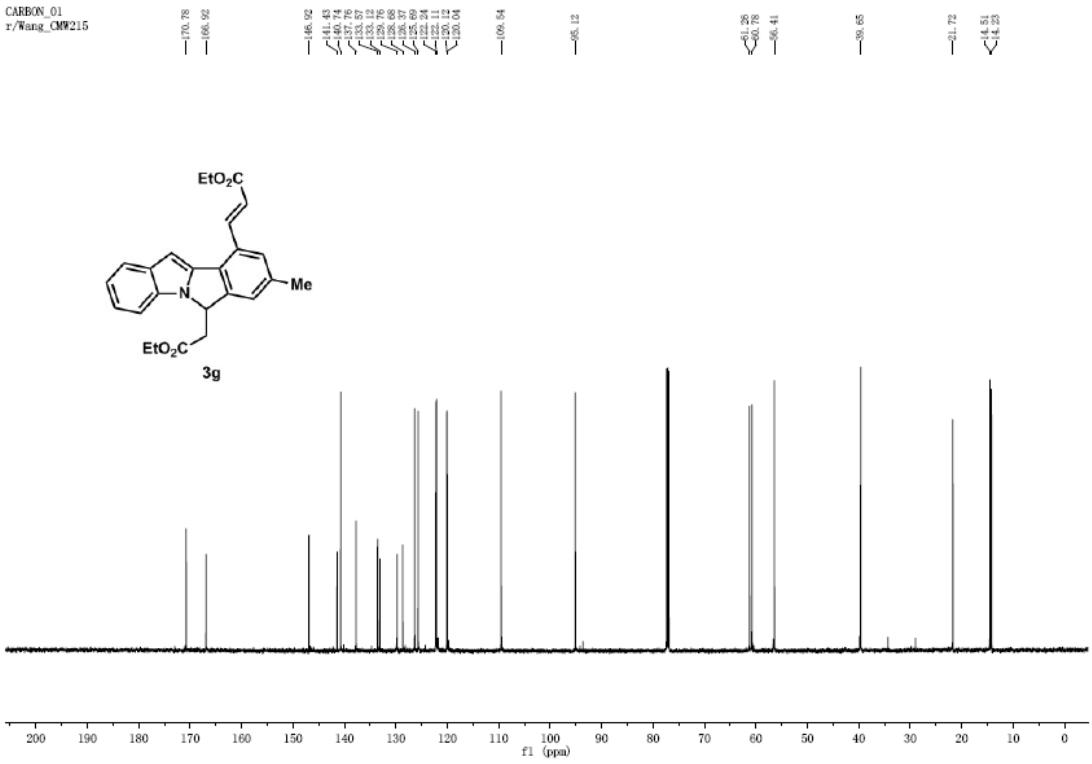
ZFM-I-105-1-C
ZFM-I-105-1-C

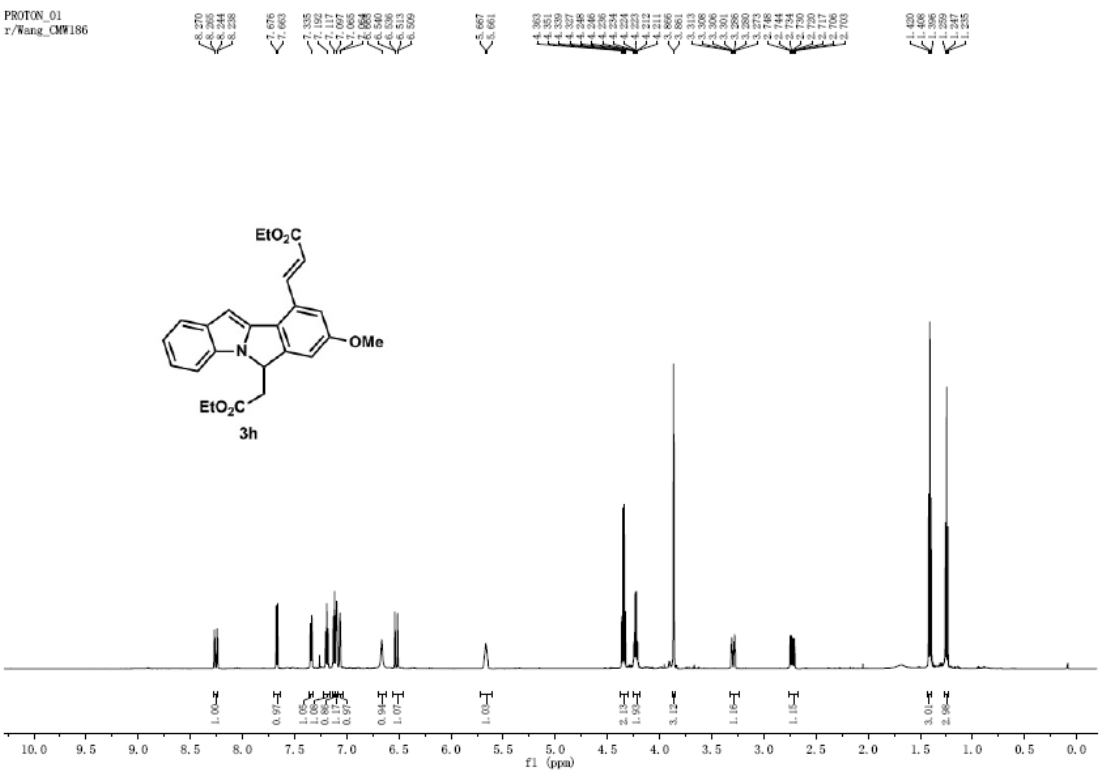


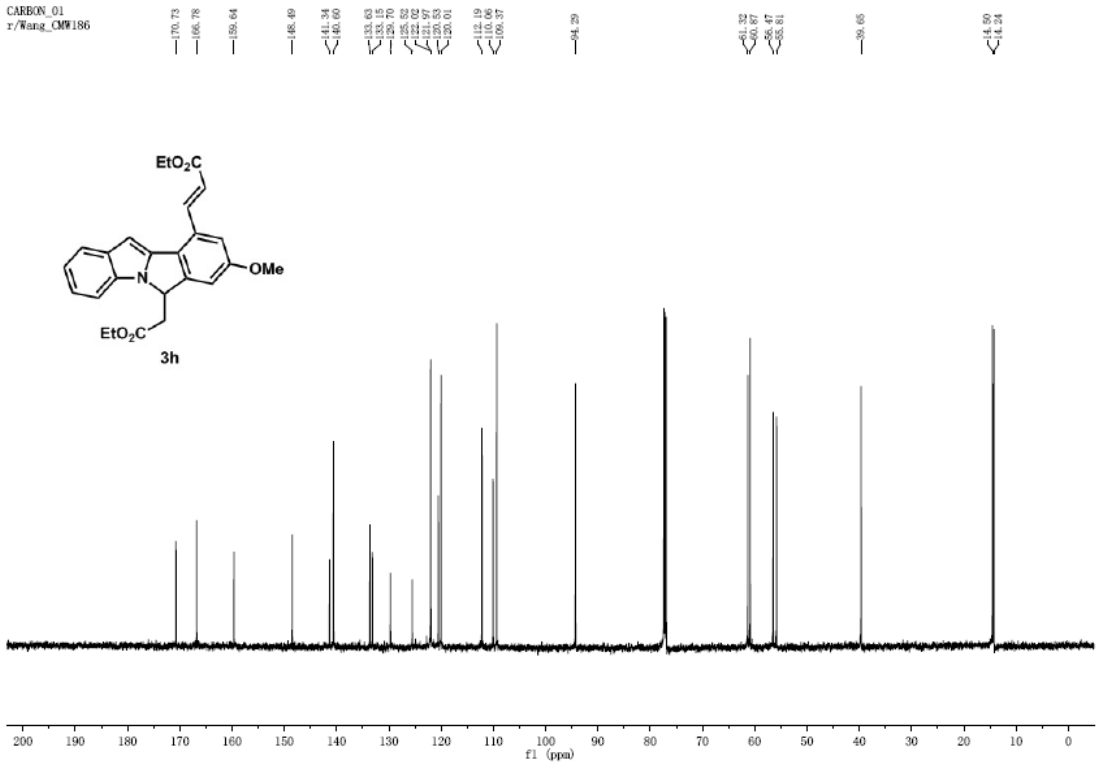
3f

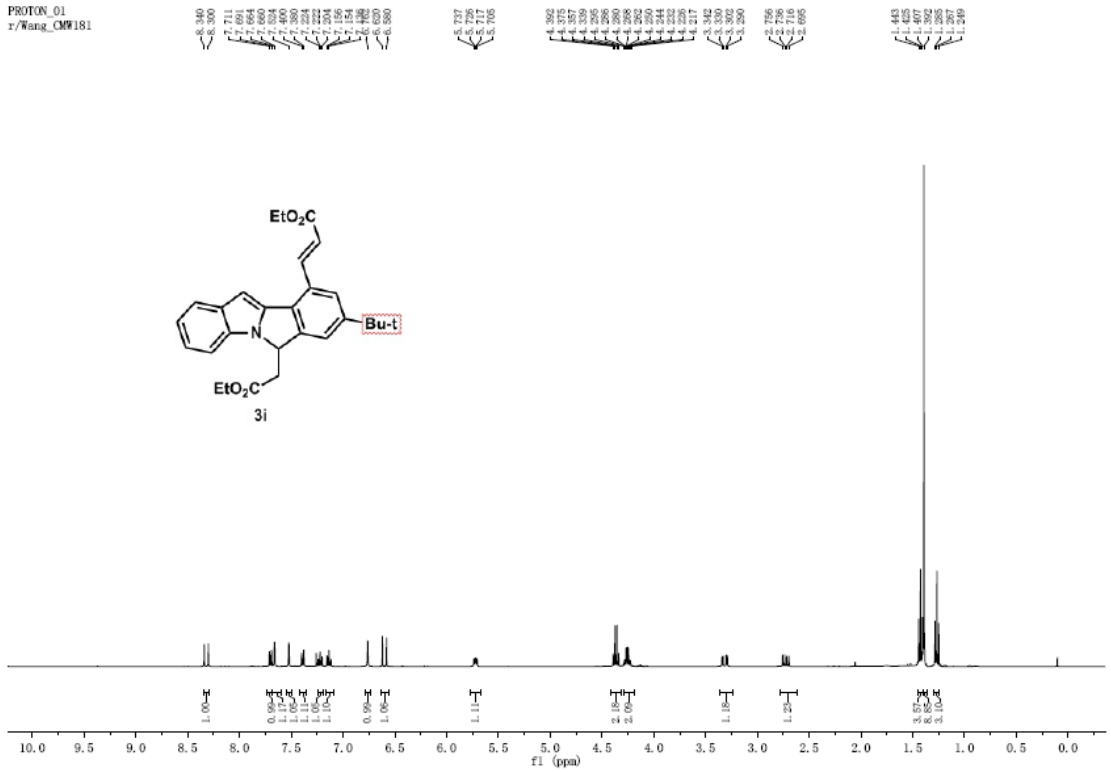


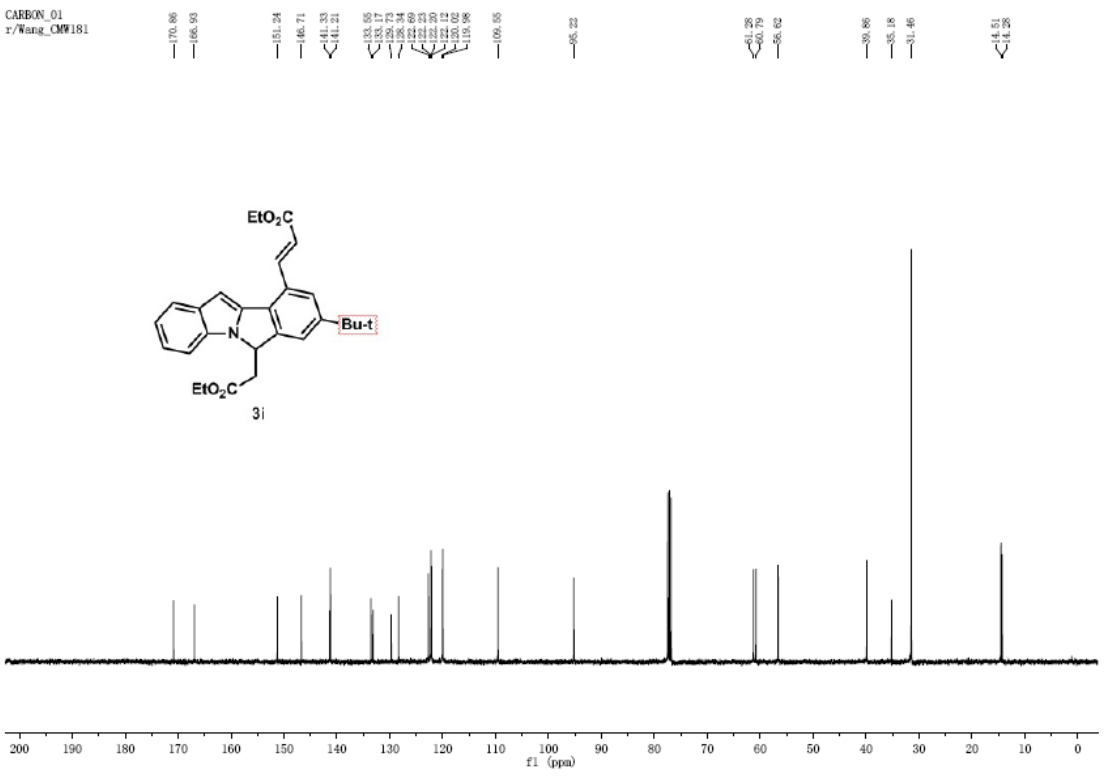

PROTON_01
r/Wang_CMW215
EtO2C
Me
N
EtO2C
3g
f1 (ppm)


CARBON_01
r/Wang_CMW215
EtO2C
Me
N
EtO2C
3g
f1 (ppm)

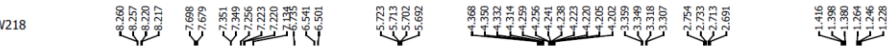

PROTON_01
r/Wang_CMW186
EtO2C
OMe
EtO2C
3h
f1 (ppm)

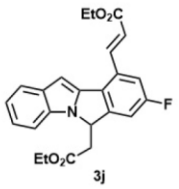

CARBON_01
r/Wang_CMW186
EtO2C
OMe
EtO2C
3h
f1 (ppm)


PROTON_01
r/Wang_CMW181
EtO2C
Bu-t
EtO2C
3i
f1 (ppm)

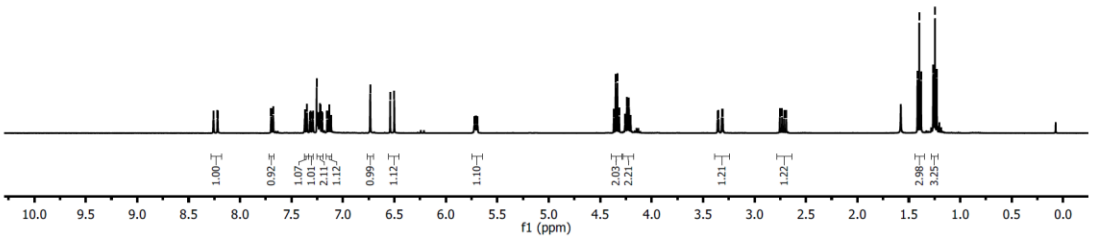

CARBON_01
r/Wang_CMW181
EtO2C
Bu-t
EtO2C
3i
f1 (ppm)

PROTON_01
r/Wang_CMW218

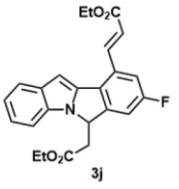




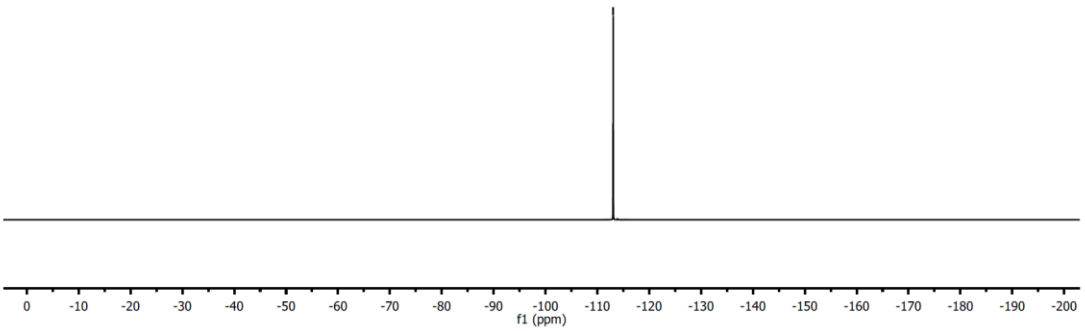
3j

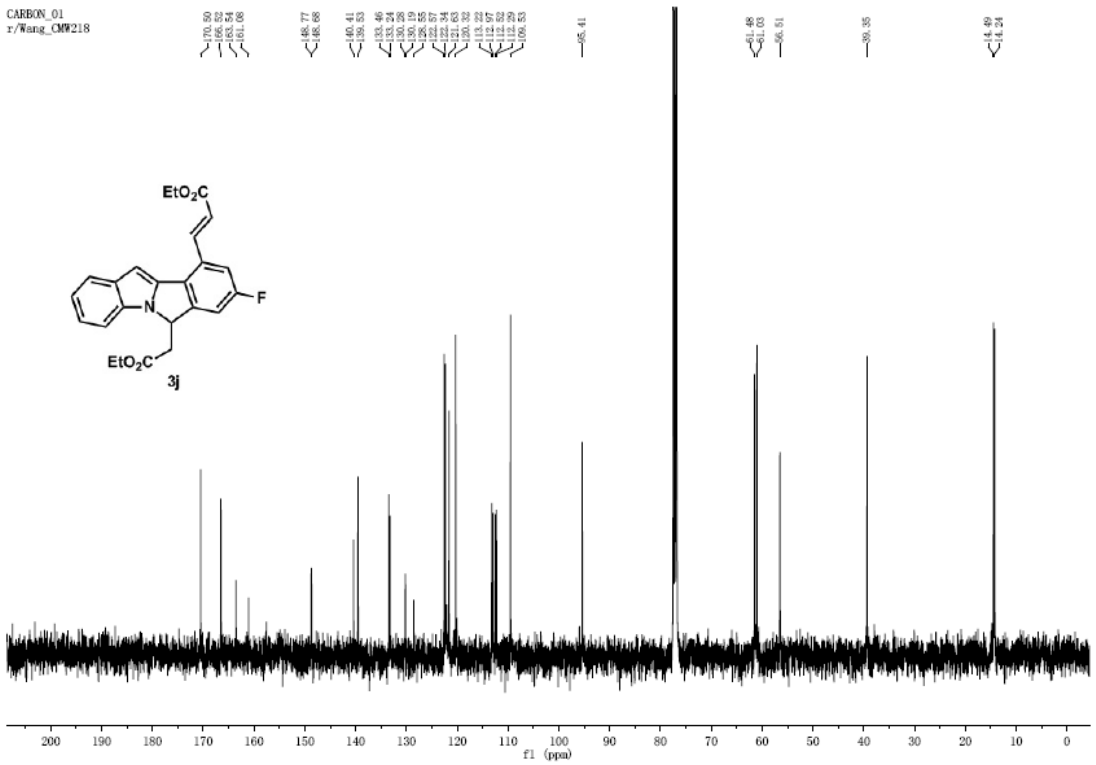


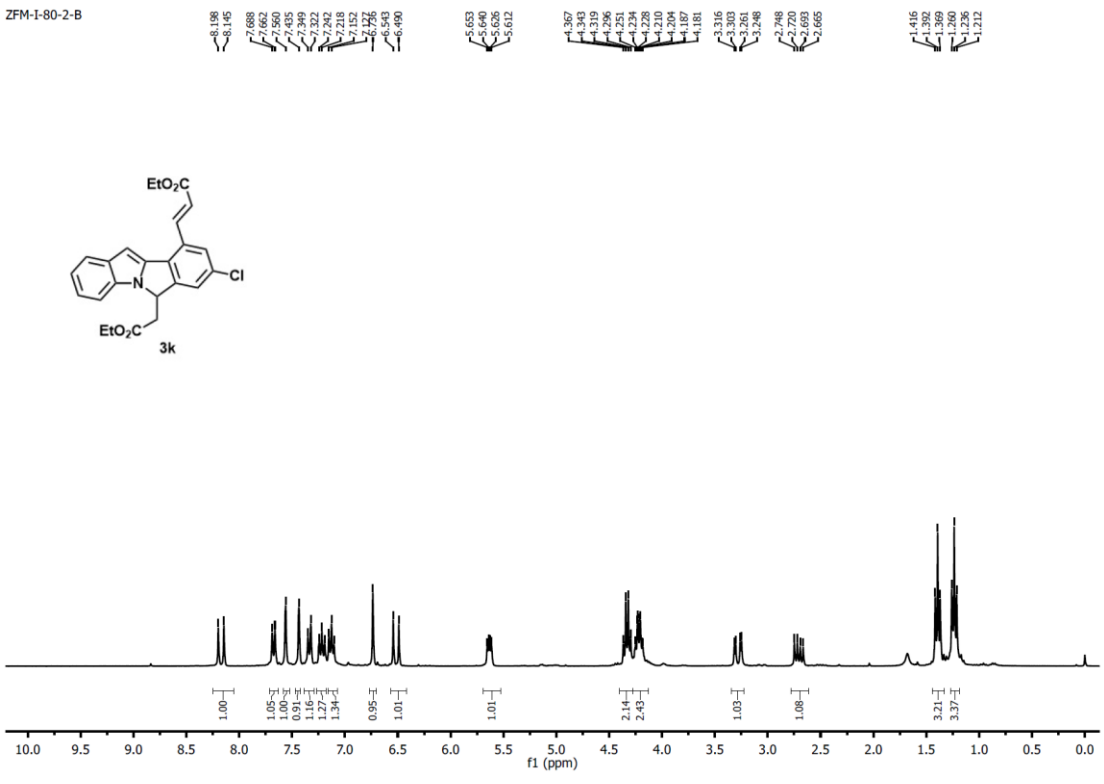
FLUORINE_01
r/Wang_CMW218

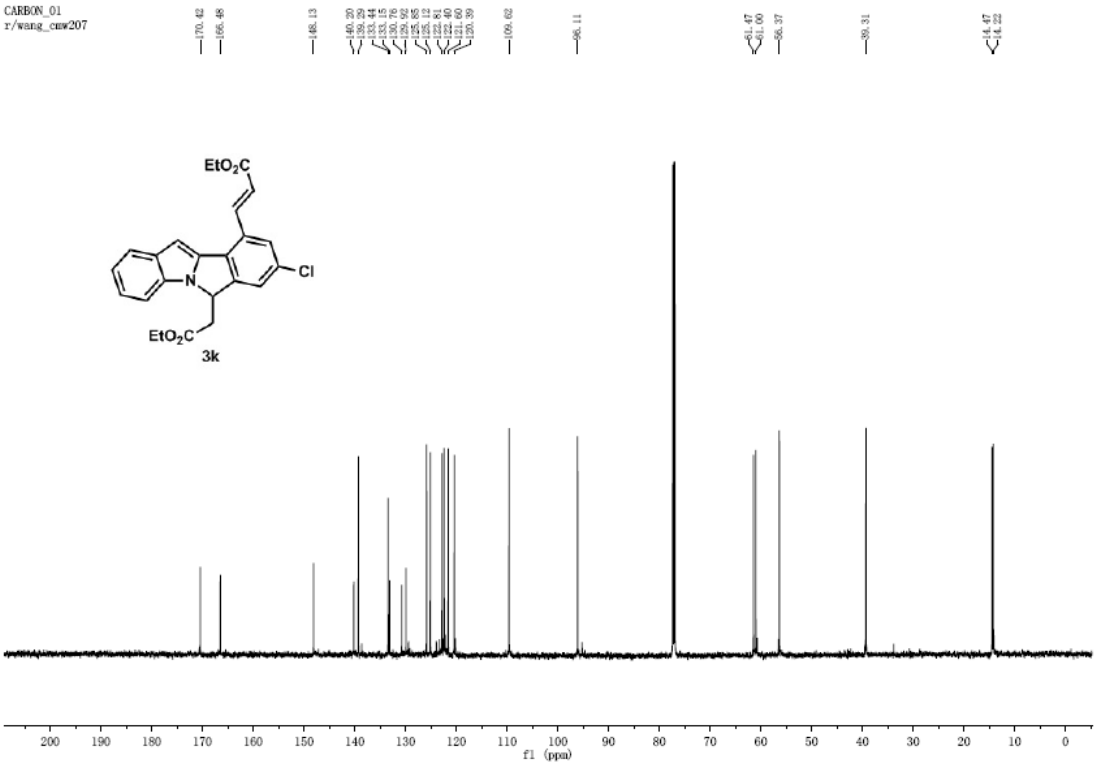


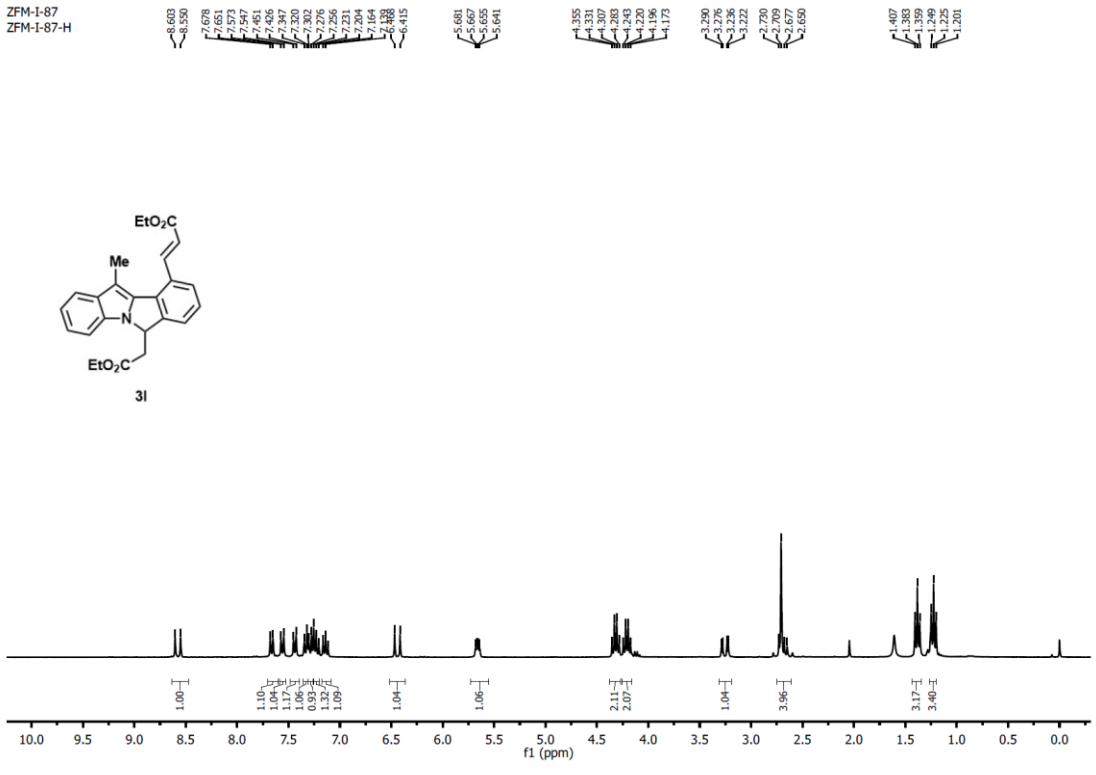
3j



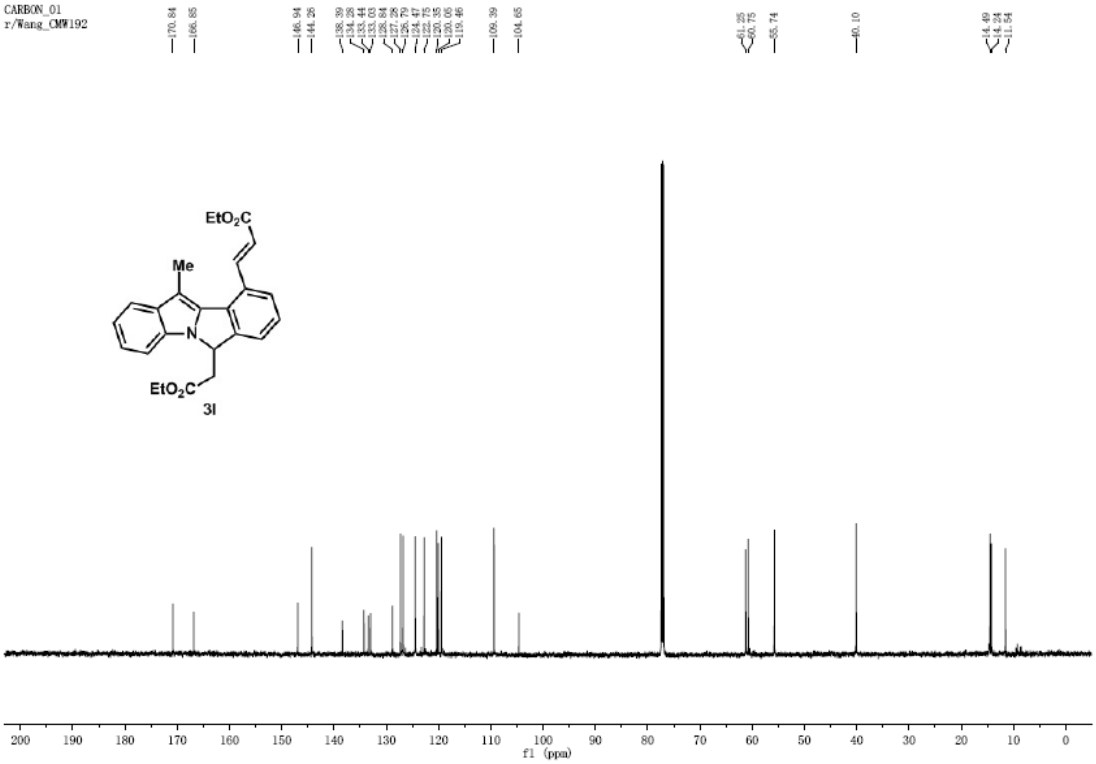

CARBON_01
r/Wang_CMW218
EtO2C
F
EtO2C
3j
f1 (ppm)


ZFM-I-80-2-B
EtO2C
Cl
EtO2C
3k
f1 (ppm)

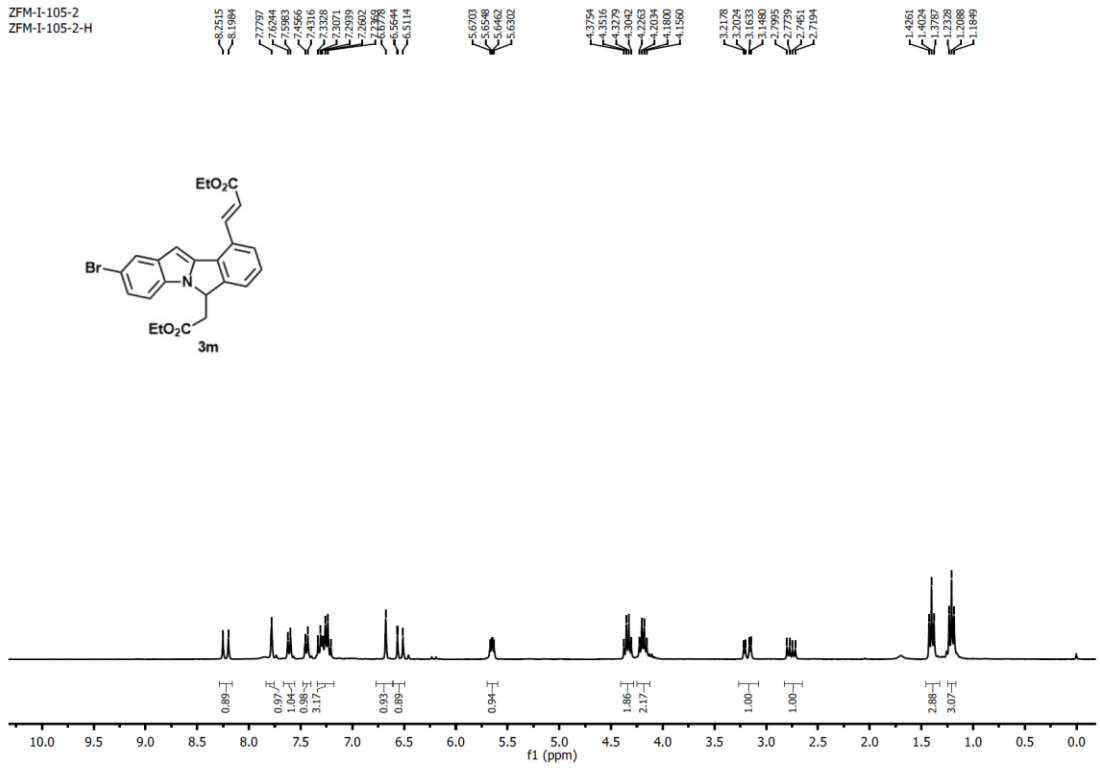

CARBON_01
r/wang_cmw207
170.42
166.48
148.13
140.20
139.29
133.44
133.15
130.76
129.92
125.68
125.33
122.84
122.40
121.60
120.39
109.62
66.11
61.47
61.00
56.37
39.31
14.47
14.22
EtO2C
Cl
N
EtO2C
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


ZFM-I-87
ZFM-I-87-H
8.603
8.590
7.678
7.661
7.657
7.547
7.451
7.426
7.347
7.320
7.302
7.276
7.256
7.231
7.204
7.164
7.138
6.468
6.415
5.681
5.667
5.655
5.641
4.355
4.331
4.307
4.283
4.243
4.220
4.196
4.173
3.290
3.276
3.236
3.222
2.730
2.709
2.677
2.650
1.407
1.383
1.359
1.349
1.225
1.201
EtO2C
Me
N
EtO2C
3l
1.00
1.10
1.04
1.17
1.06
0.93
1.32
1.09
1.04
1.06
2.11
2.07
1.04
3.96
3.17
3.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

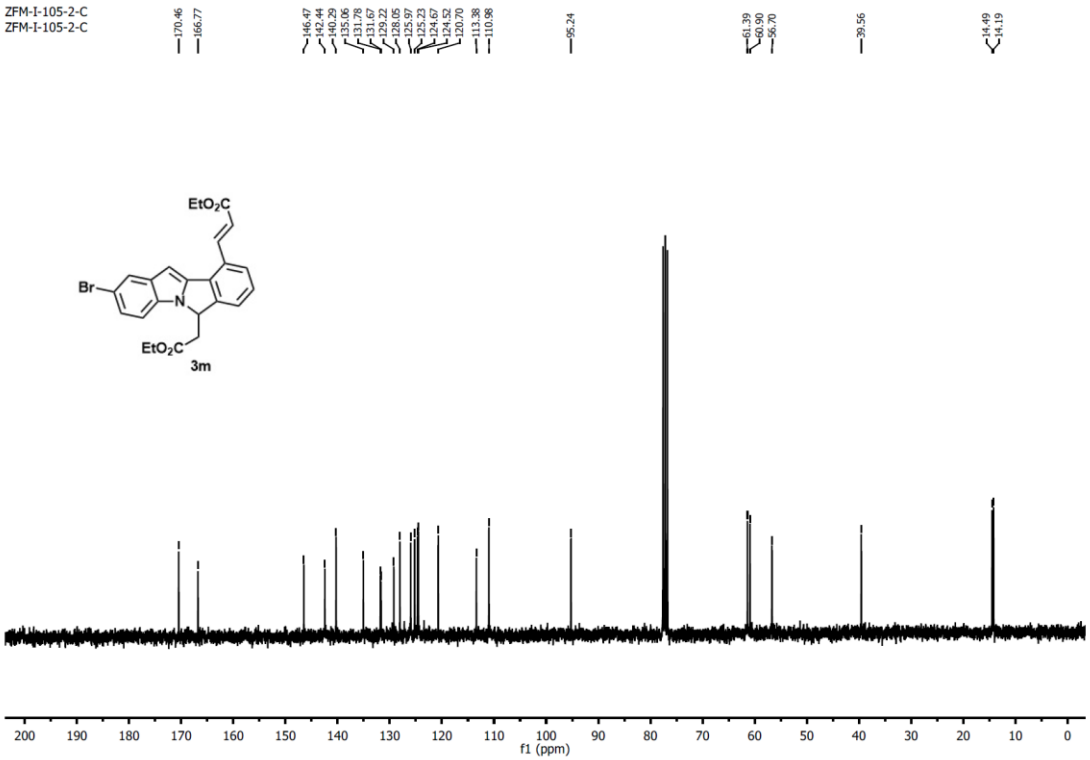
CARBON_01
r/Wang_CMW192



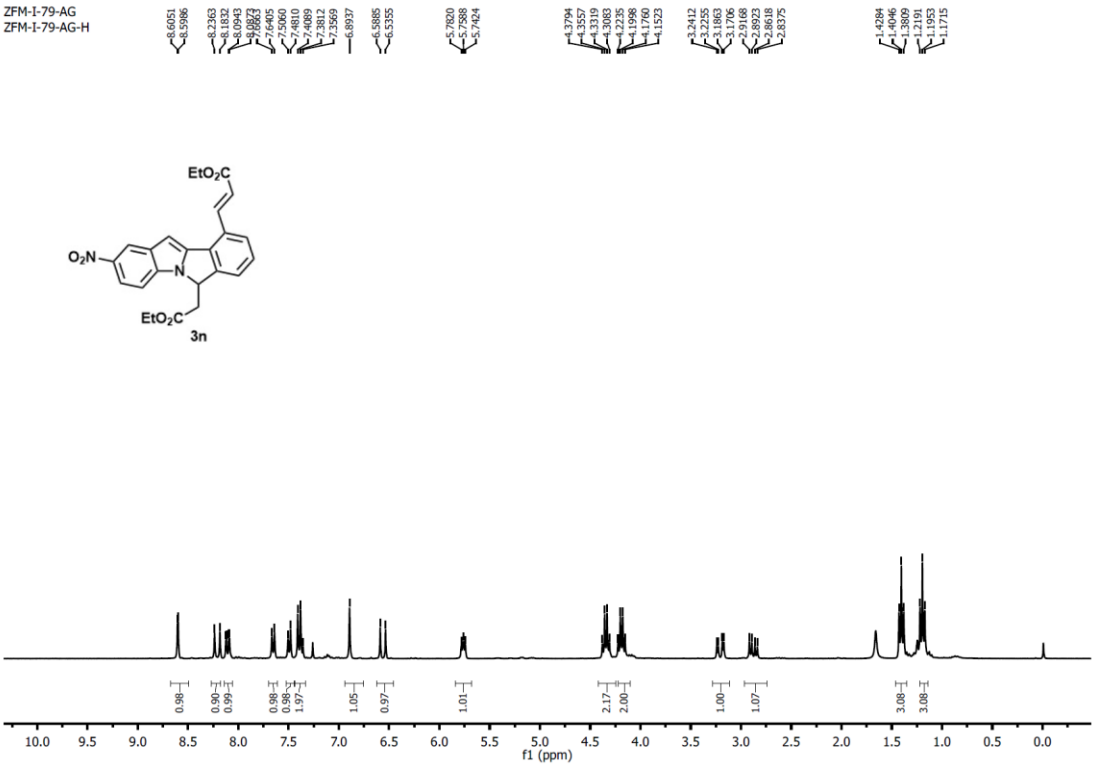
ZFM-I-105-2
ZFM-I-105-2-H

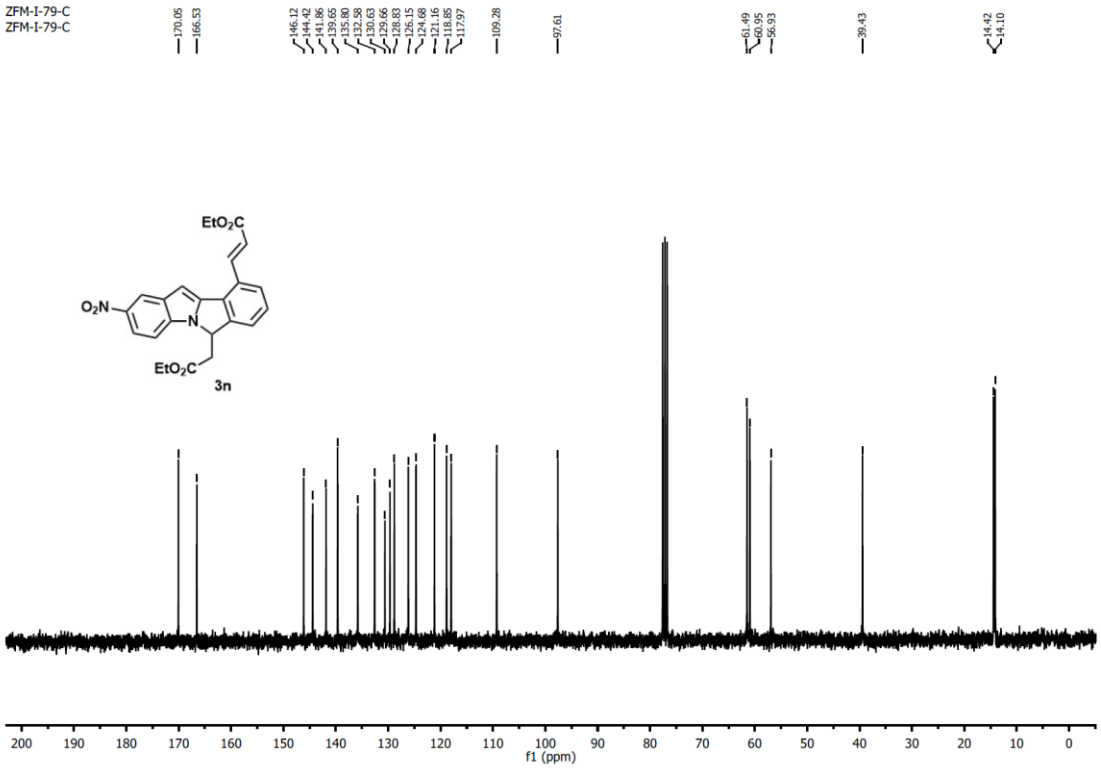


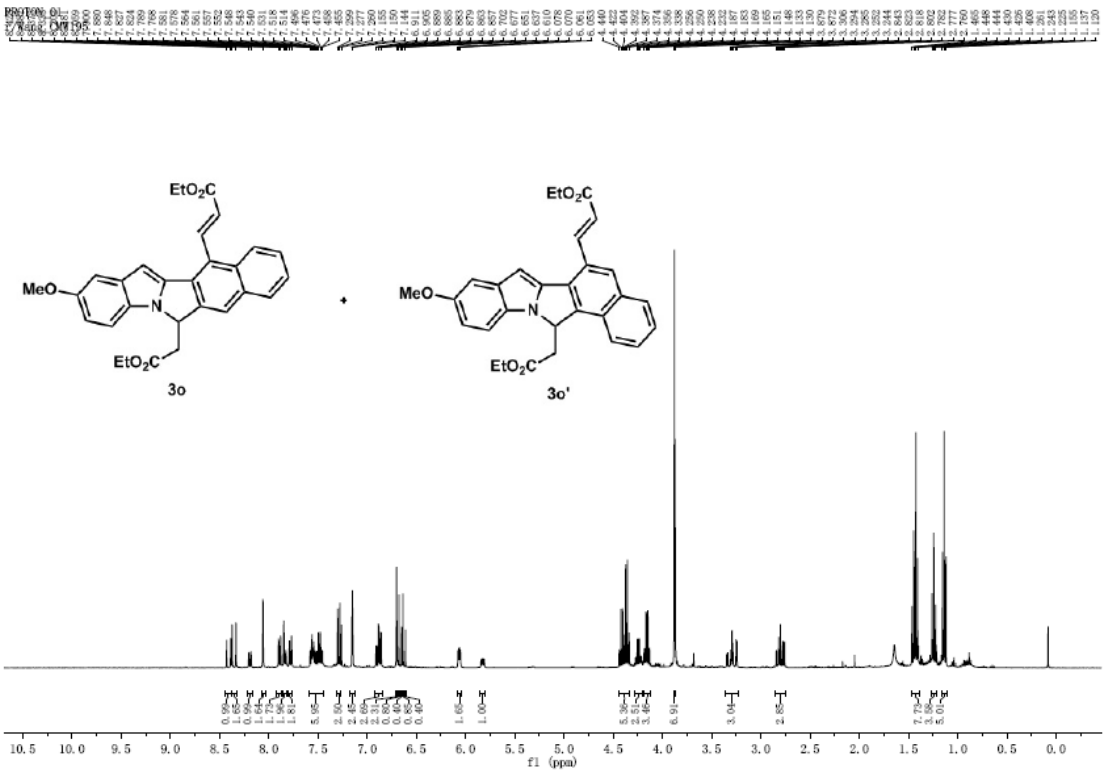
ZFM-I-105-2-C
ZFM-I-105-2-C

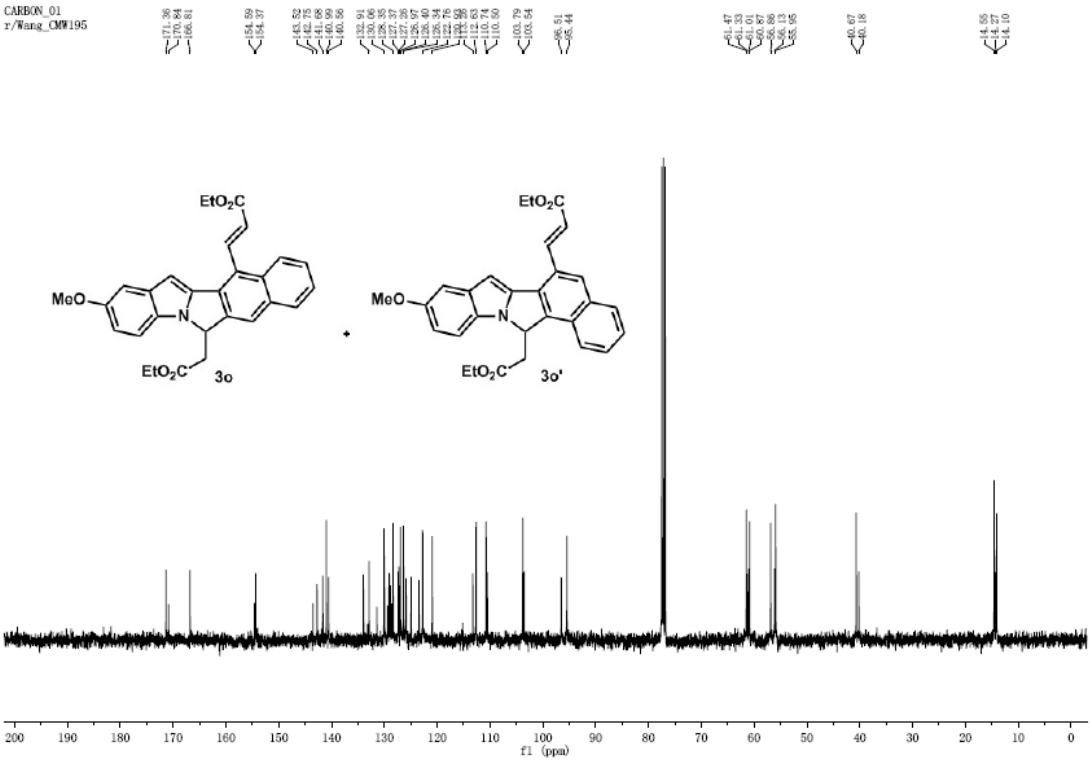


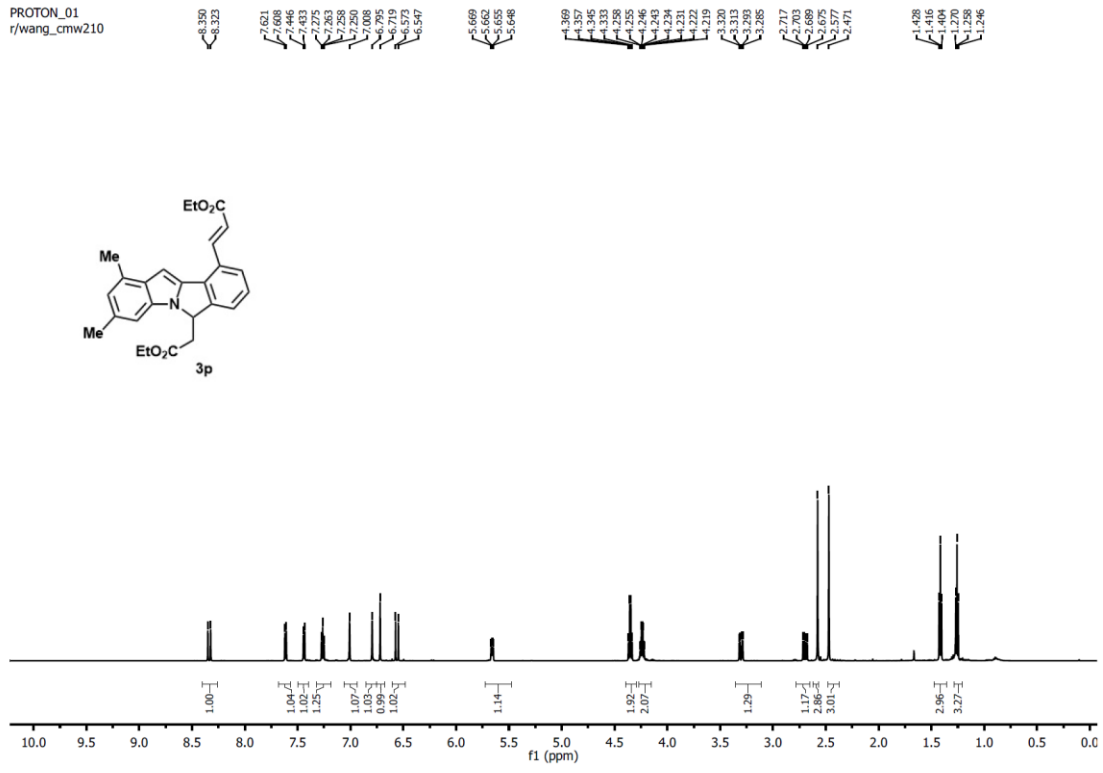
ZFM-I-79-AG
ZFM-I-79-AG-H




ZFM-I-79-C
ZFM-I-79-C
170.05
166.53
146.12
144.42
141.86
139.65
135.80
132.58
130.63
129.66
128.83
125.15
124.68
121.16
118.85
117.97
109.28
97.61
61.49
60.95
56.93
39.43
14.42
14.10
EtO2C
O2N
N
EtO2C
3n
f1 (ppm)

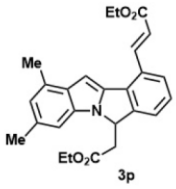

EtO2C
MeO
N
EtO2C
3o
EtO2C
MeO
N
EtO2C
3o'
f1 (ppm)


CARBON_01
r/Wang_CMW195
EtO2C
MeO
EtO2C
3o
EtO2C
MeO
EtO2C
3o'
f1 (ppm)

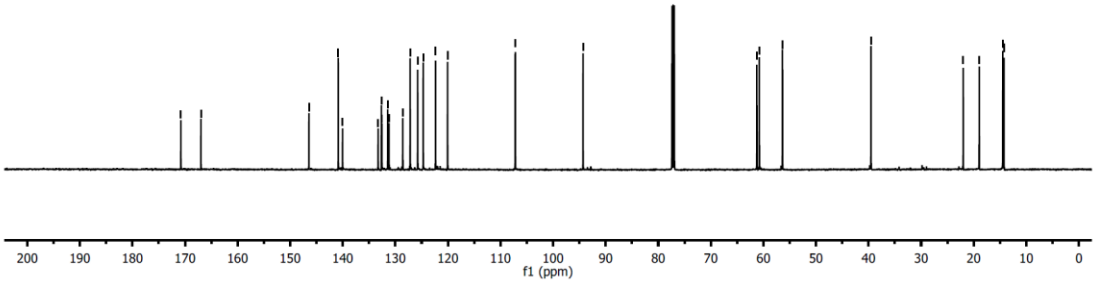

PROTON_01
r/wang_cmw210
EtO2C
Me
Me
EtO2C
3p
f1 (ppm)

CARBON_01
r/wang_cmw210

170.79 166.97 146.43 140.86 140.04 133.27 132.65 132.57 131.45 131.19 128.58 127.18 125.75 124.70 122.36 120.06 107.19 94.30 61.24 60.77 56.37 39.53 21.99 18.94 14.47 14.24

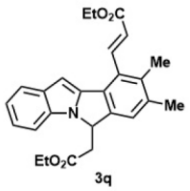


3p

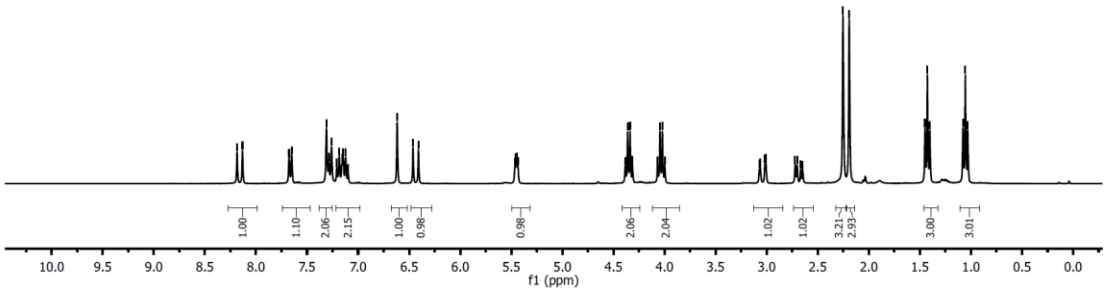


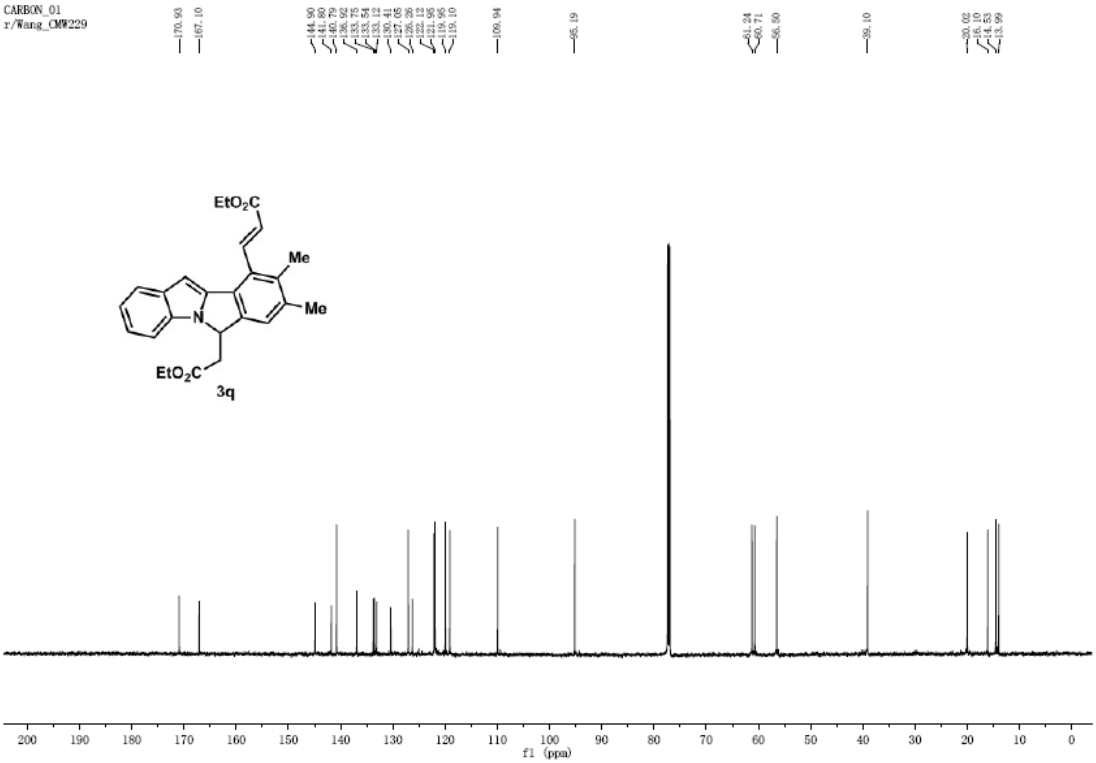
ZFM-I-83-3

8.185 8.132 7.676 7.650 7.310 7.287 7.260 7.184 7.148 7.113 6.678 6.462 6.409 5.465 5.454 5.447 5.436 4.385 4.361 4.338 4.314 4.068 4.045 4.021 3.997 3.072 3.062 3.017 3.007 2.722 2.702 2.667 2.647 2.253 2.192 1.450 1.426 1.403 1.079 1.055 1.032

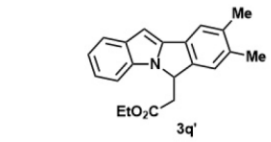


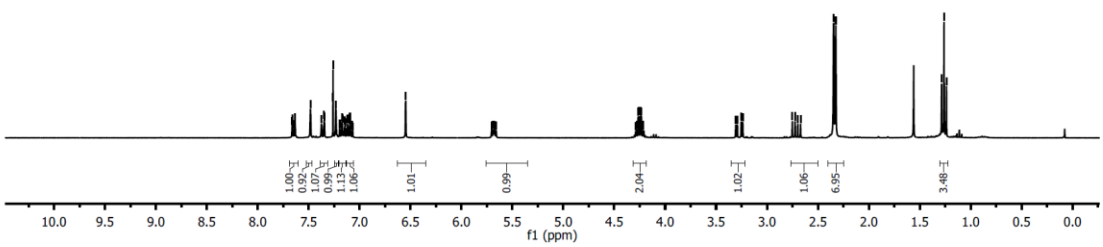
3q

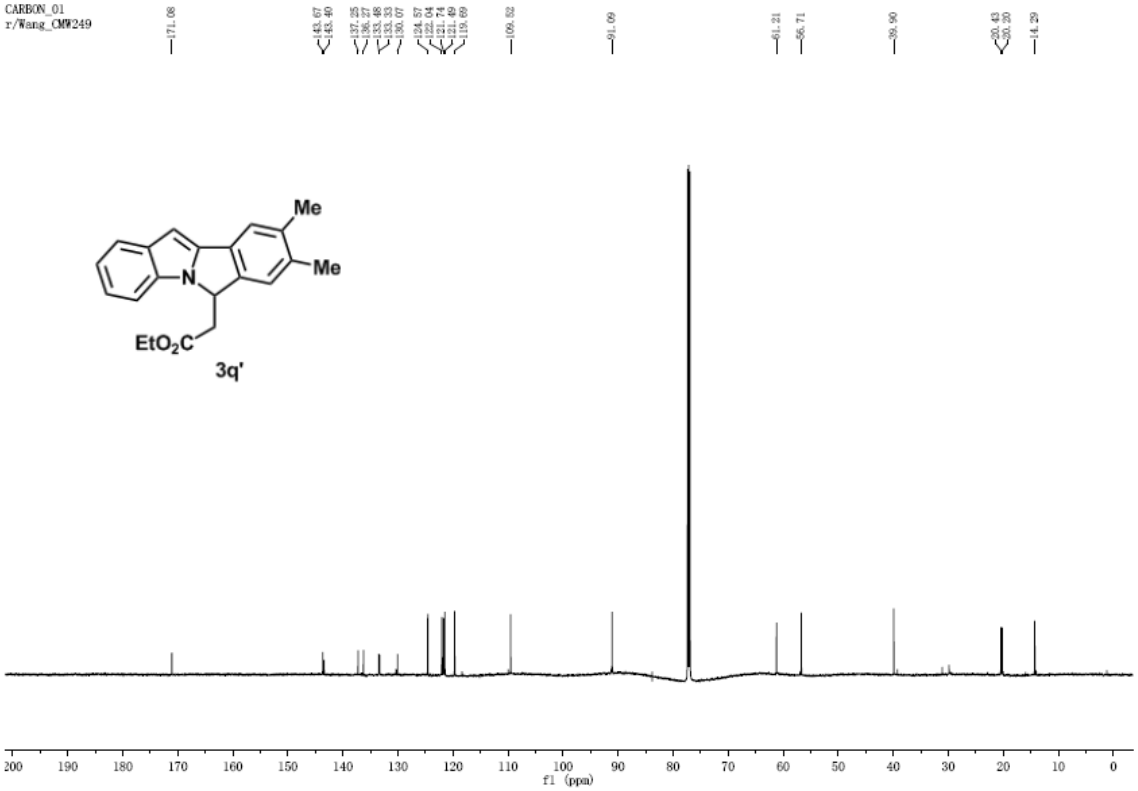


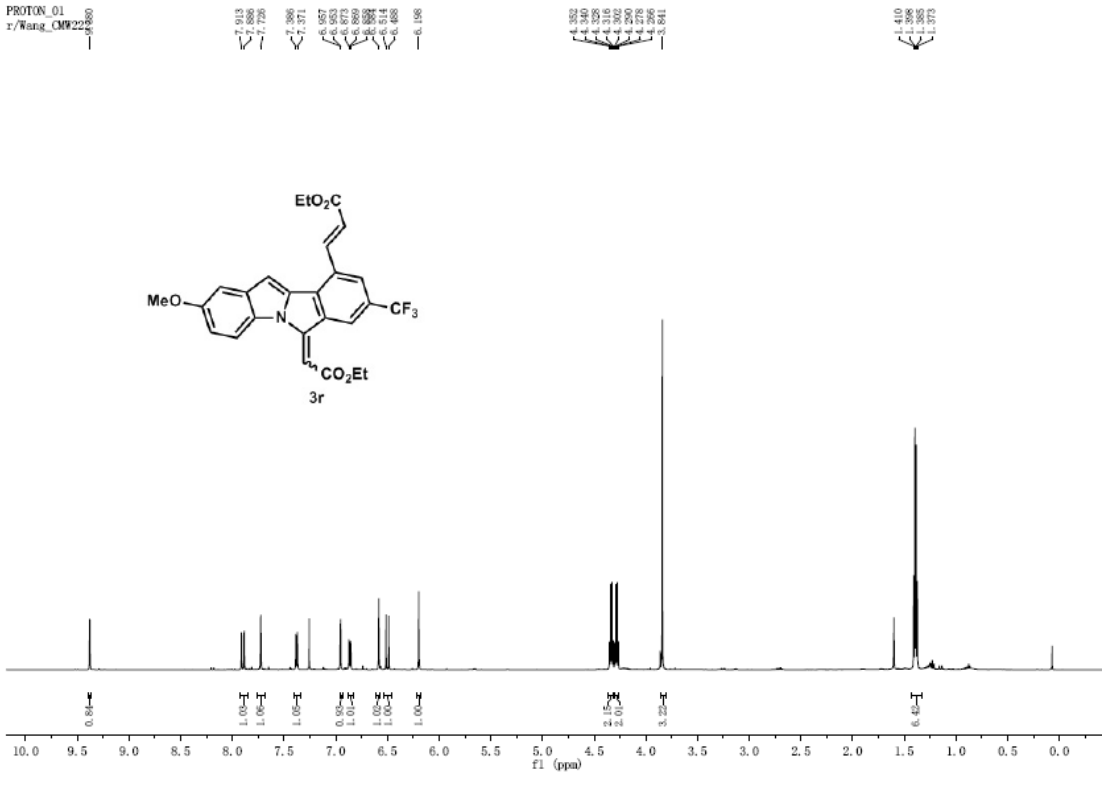

CARBON_01
r/Wang_CMW229
170.93
167.10
144.90
141.80
140.79
136.92
134.75
133.54
133.12
130.41
127.05
126.28
122.12
121.95
119.95
119.10
109.94
65.19
61.24
60.71
56.90
39.10
20.02
16.10
14.53
13.99
EtO2C
Me
Me
N
EtO2C
3q
f1 (ppm)


h
WANG
CMW231
a4090291.r
7.663
7.661
7.656
7.637
7.635
7.633
7.482
7.375
7.348
7.345
7.282
7.260
7.233
7.196
7.192
7.172
7.168
7.146
7.141
7.121
7.117
7.097
7.095
7.093
7.091
7.071
7.067
6.547
5.703
5.688
5.676
5.660
4.289
4.280
4.265
4.257
4.241
4.233
4.217
3.307
3.301
3.253
3.237
2.751
2.724
2.697
2.670
2.346
2.325
1.285
1.261
1.238

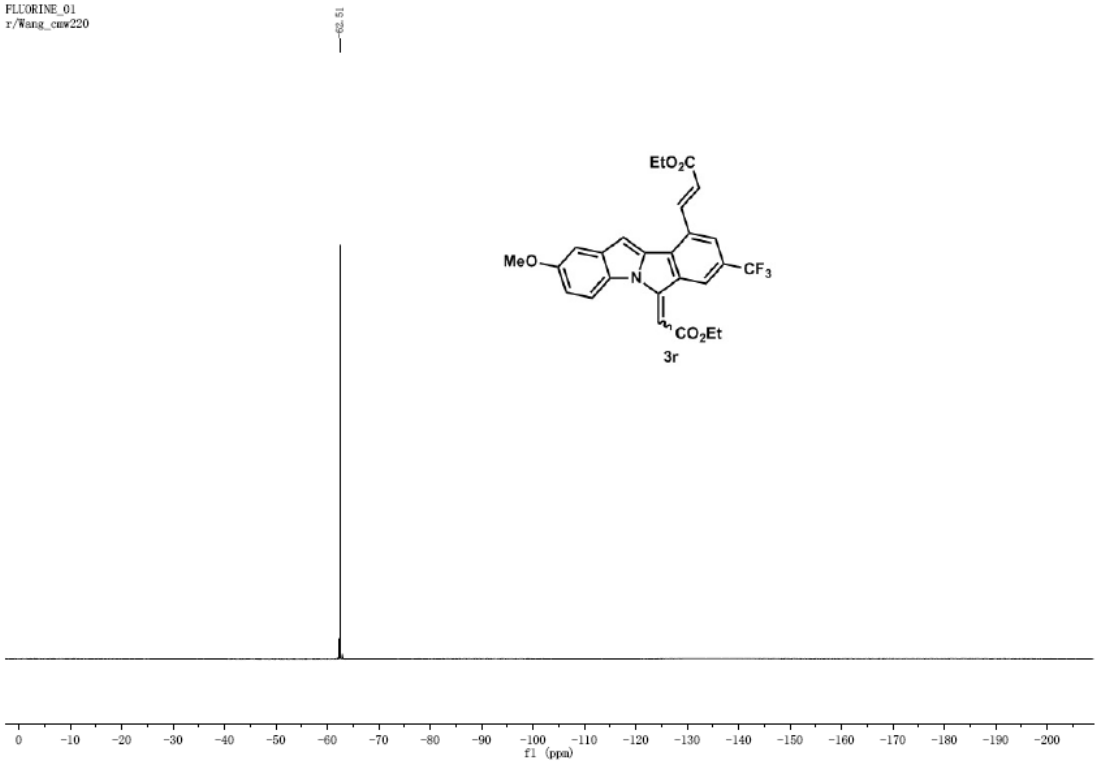

Me
Me
N
EtO2C
3q'


1.00
0.92
1.07
0.99
1.13
1.06
1.01
0.99
2.04
1.02
1.06
6.95
3.48
f1 (ppm)

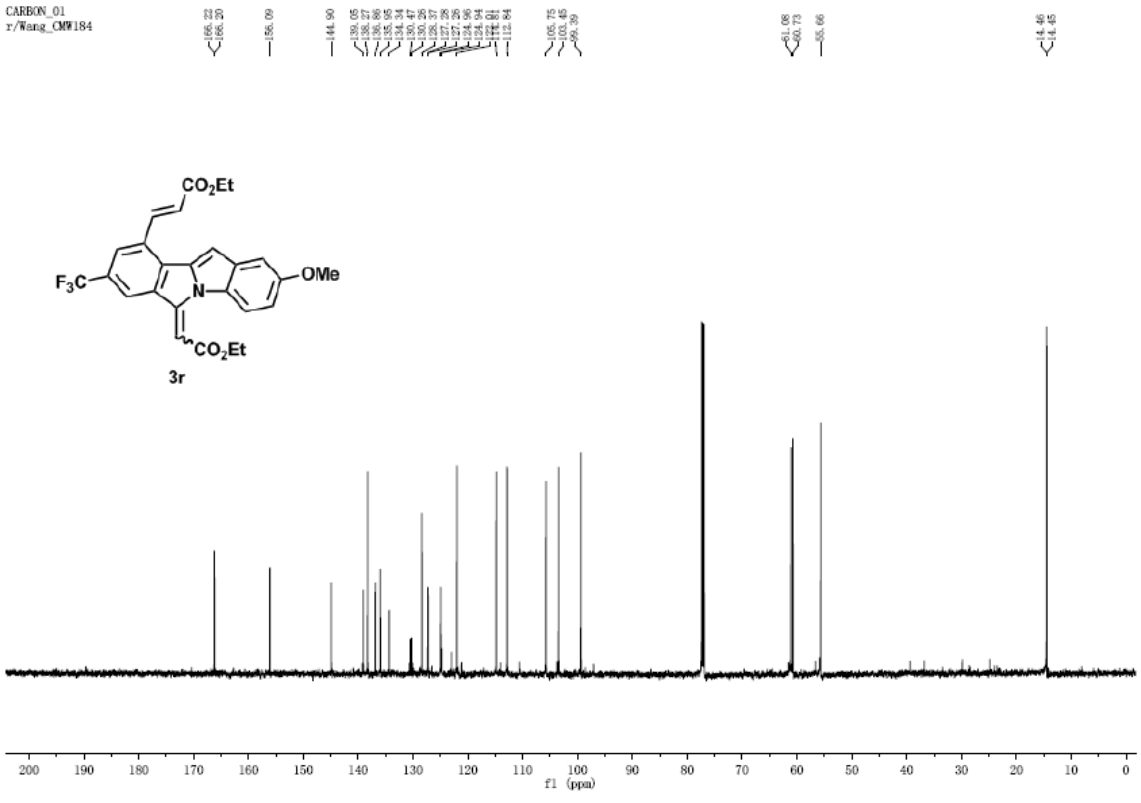

CARBON_01
r/Wang_CM9249
171.06
143.67
143.49
137.25
136.27
133.48
131.53
130.07
124.57
122.54
121.74
121.49
119.69
109.52
91.09
61.21
56.71
39.90
20.43
20.20
14.29
Me
Me
N
EtO2C
3q'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

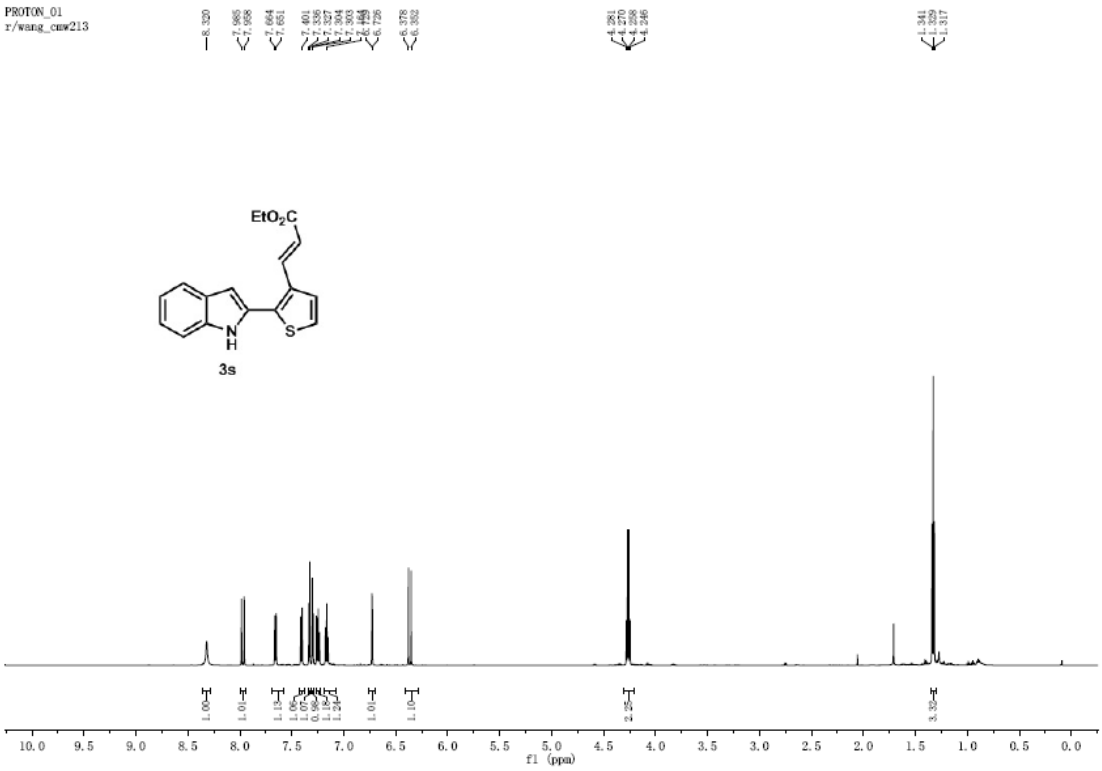

PROTON_01
r/Wang_CM9249
9.380
7.913
7.886
7.726
7.398
7.371
6.957
6.953
6.873
6.869
6.514
6.488
6.198
4.352
4.340
4.329
4.316
4.302
4.290
4.278
4.266
3.841
1.410
1.398
1.385
1.373
EtO2C
MeO
CF3
N
CO2Et
3r
0.84
1.03
1.06
1.05
0.93
1.01
1.02
1.04
1.00
2.15
2.01
3.22
6.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

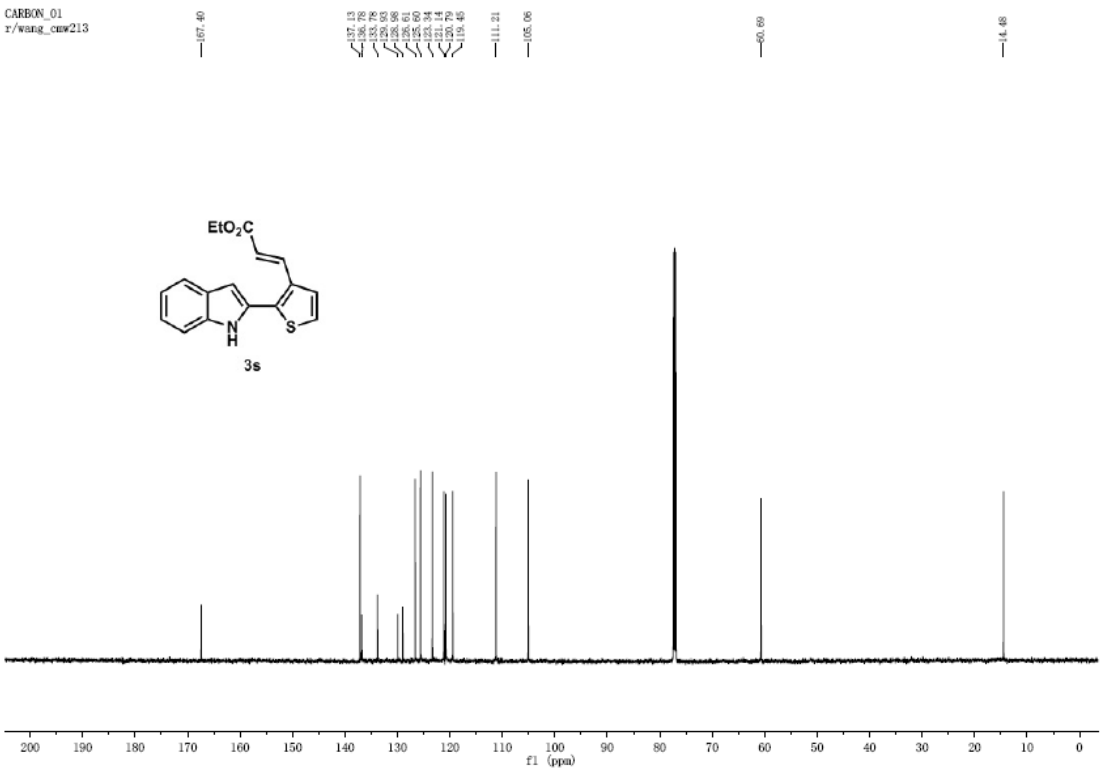
FLUORINE_01
r/Wang_cmw220

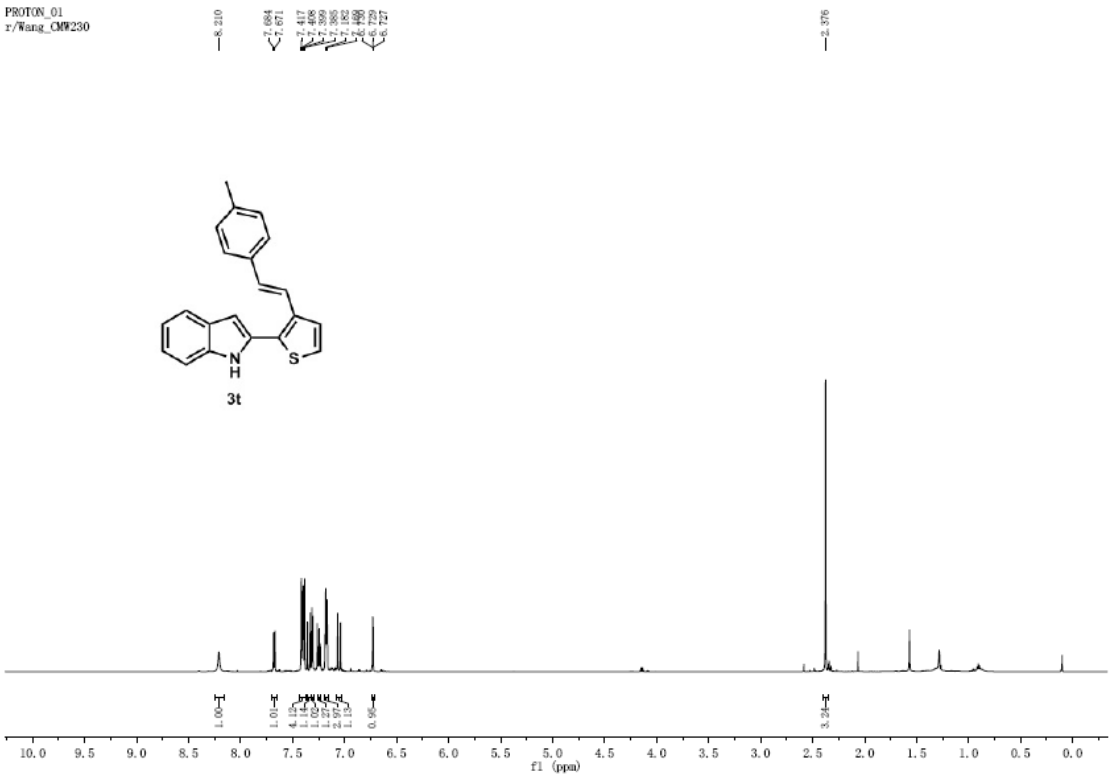


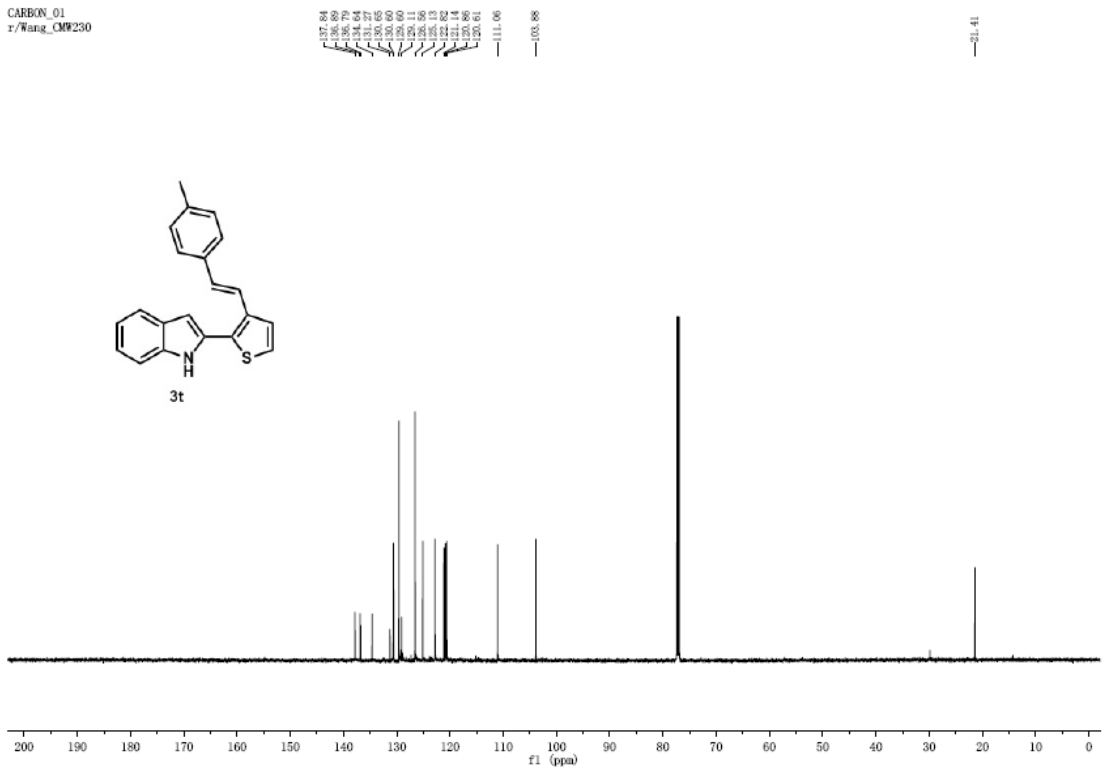
CARBON_01
r/Wang_CMW184

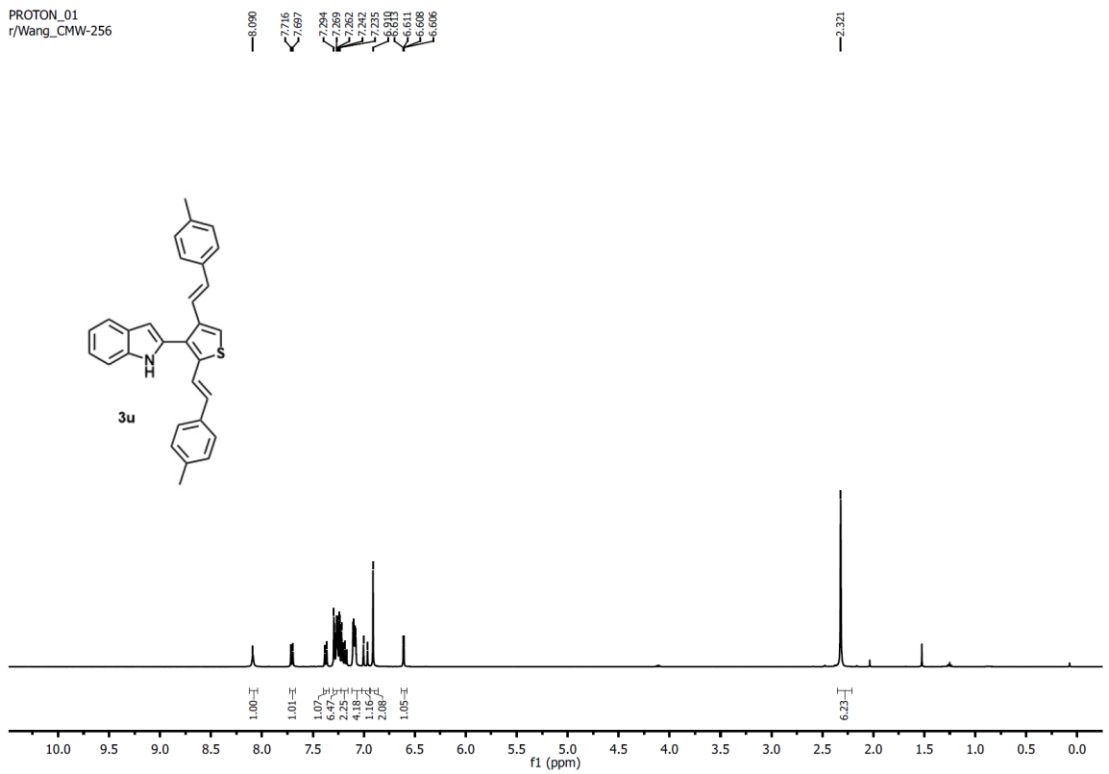


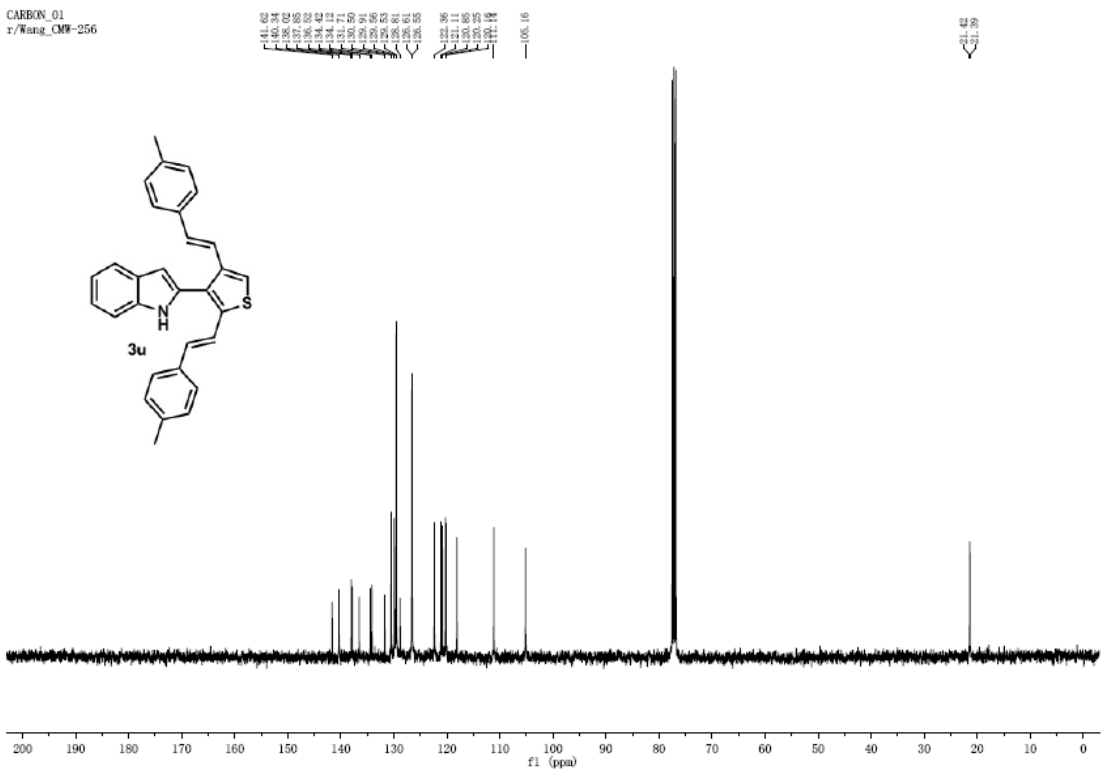

PROTON_01
r/wang_cmw213
8.320
7.988
7.958
7.664
7.651
7.401
7.336
7.327
7.317
7.304
7.303
6.726
6.378
6.352
4.281
4.270
4.258
4.246
1.341
1.329
1.317
EtO2C
N
H
S
3s
1.00
1.01
1.13
1.06
1.07
0.98
1.24
1.01
1.10
2.25
3.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

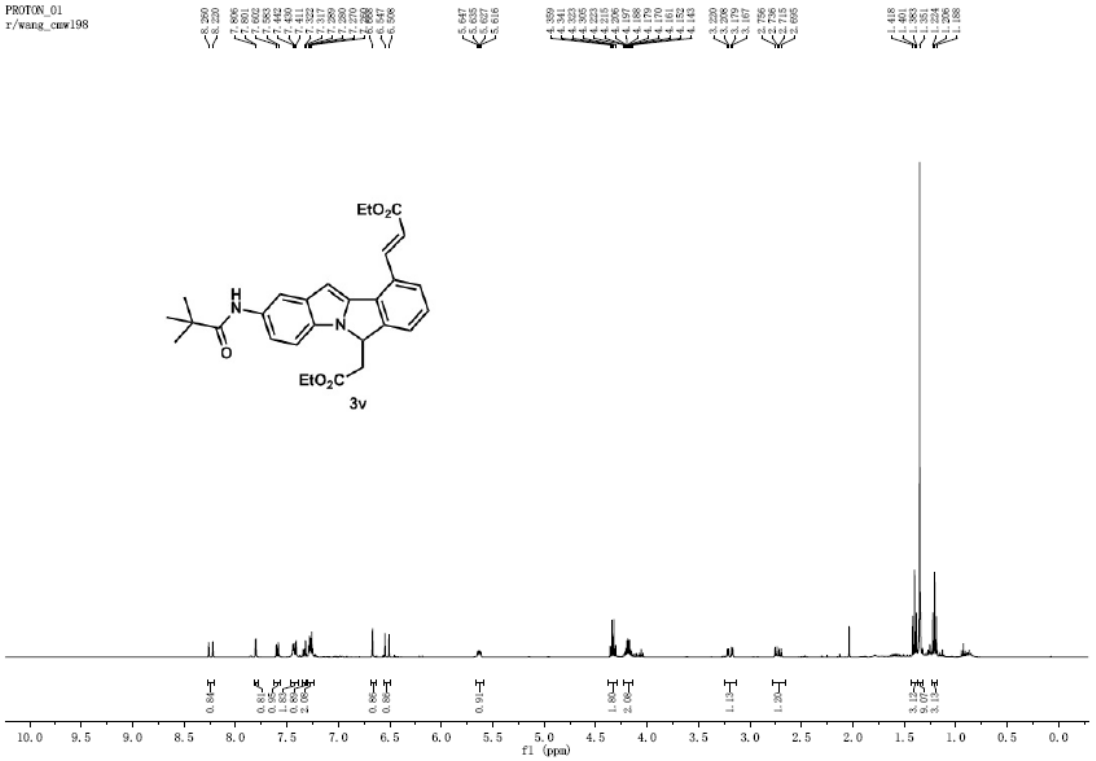

CARBON_01
r/wang_cmw213
167.40
137.13
136.78
133.78
128.98
126.61
125.60
123.34
121.14
120.79
119.45
111.21
105.06
60.69
14.48
EtO2C
N
H
S
3s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

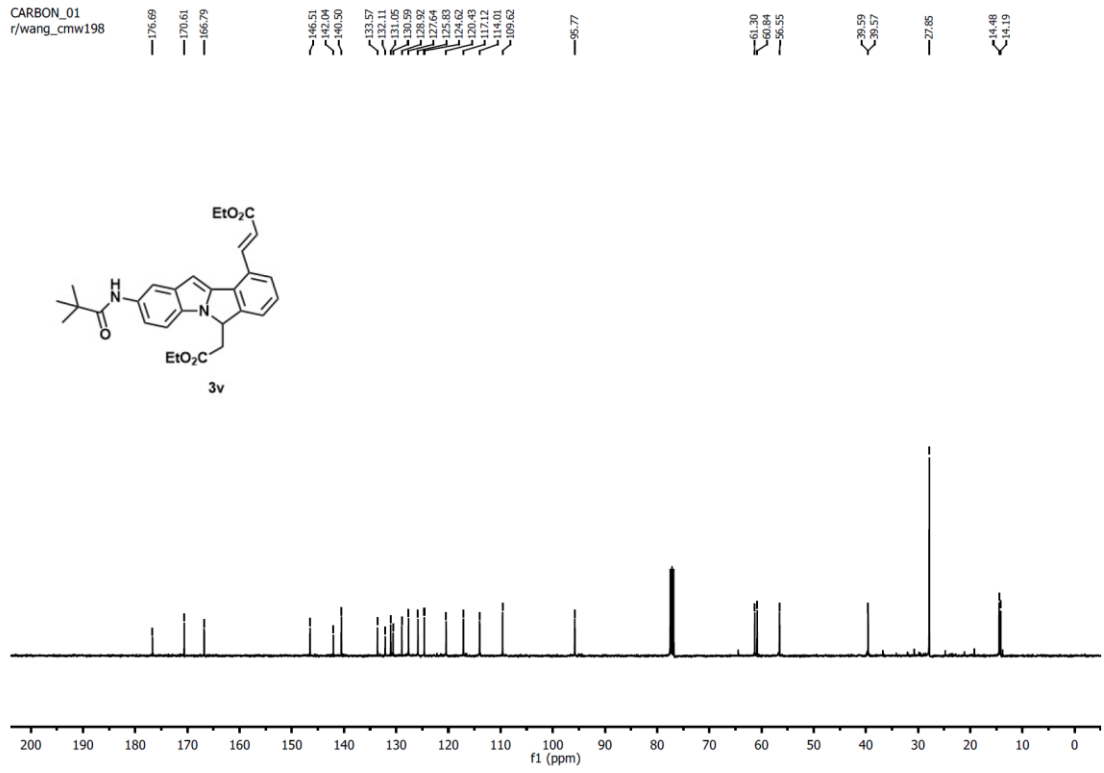

PROTON_01
r/Wang_CMW230
8.210
7.694
7.671
7.417
7.408
7.389
7.385
7.182
6.729
6.727
2.376
3t
1.00
1.01
4.10
1.14
1.02
1.27
2.97
1.15
0.96
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

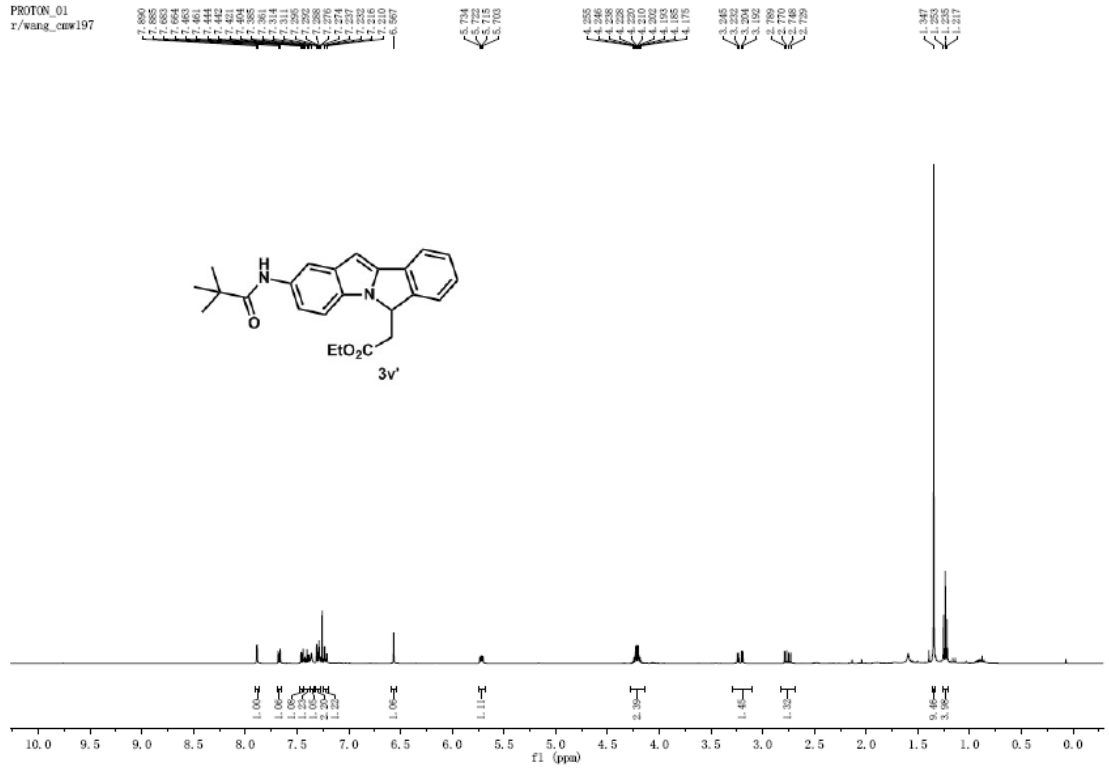

CARBON_01
r/Wang_CMW230
137.84
136.89
135.79
134.64
131.27
130.65
130.02
129.60
129.11
125.36
125.13
122.82
121.14
120.86
120.61
111.06
103.88
21.41
3t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

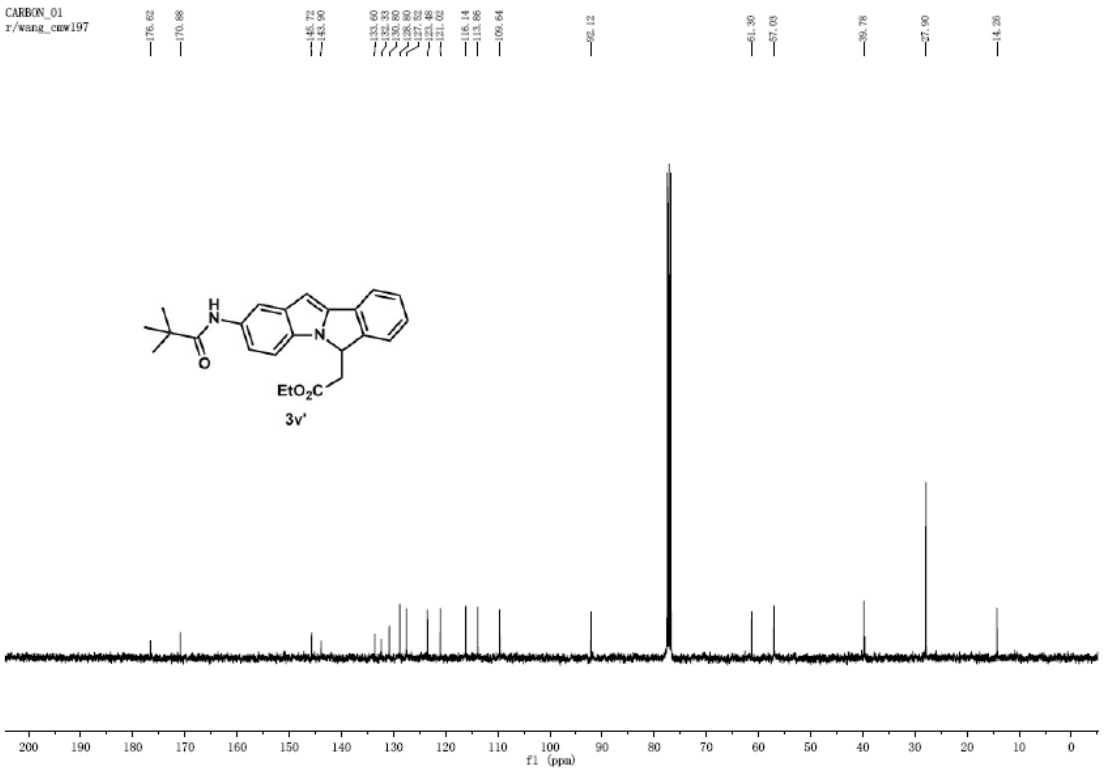

PROTON_01
r/Wang_CMW-256
8.090
7.716
7.697
7.294
7.289
7.282
7.242
7.235
6.619
6.611
6.608
6.606
2.321
3u
1.00
1.01
1.07
6.47
2.25
4.18
1.16
2.08
1.05
6.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CARBON_01
r/Wang_CMW-256
141.62
140.34
138.02
137.85
137.62
134.42
134.12
131.71
130.50
129.91
129.56
129.53
126.81
126.61
125.95
122.36
121.11
120.85
120.25
111.48
111.14
105.16
21.62
21.39
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


PROTON_01
r/wang_cmw198
EtO2C
H
N
O
EtO2C
3v
f1 (ppm)


CARBON_01
r/wang_cmw198
EtO2C
H
N
O
EtO2C
3v
f1 (ppm)


PROTON_01
r/wang_cmw197
EtO2C
3v'
f1 (ppm)


CARBON_01
r/wang_cmw197
EtO2C
3v'
f1 (ppm)