# Supporting Information

## Harnessing dipolar microenvironment engineering of PTSA for alkenylation of indole in butyl acetate

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## Contents

## General information

Unless specially indicated, all chemical reagents were purchased from commercial sources and were used as received without further purification. FT-IR spectra were obtained on Bruker Compass VERTEX 70. Steady state fluorescence spectra were recorded with a RF-6000 PC spectrophotometer. Thermogravimetric analysis (TGA) was performed using Diamond TG/DTA in $N_2$ atmosphere by heating from room temperature to 800 °C. Scanning electron microscope (SEM) was conducted with TESCAN MIRA LMS. BET surface areas were measured using Micromeritics ASAP 2460. The X-ray photoelectron spectra (XPS) were obtained with the Thermo Scientific K-Alpha paired with a monochromatic Al Kα X-ray source (1486.6 eV). $^{1}H$ and $^{13}C$ NMR spectra of organic compounds were recorded on Bruker 400. Chemical shifts are expressed in ppm relative to $Me_4Si$ in $CDCl_3$ or DMSO-$d_6$.

## Preparation of HCP materials

**Synthesis of Th-FDA**

In a typical procedure, 10 mmol thiophene, formaldehyde dimethyl acetal (FDA, 3.0 equiv.), $FeCl_3$ (3.0 equiv.), and 30 mL 1,2-dichloroethane (DCE) were added into a 100 mL round-bottom flask equipped with a magnetic stirrer. The mixture was refluxed for 24 h to give a precipitate, which was then carefully transferred into 50 mL of dilute hydrochloric acid (1.2 M in water) and stirred for 2 h. Subsequently, the polymer was subjected to Soxhlet extraction for 24 h using EtOH as solvent. Finally, the polymer was obtained by drying in a vacuum oven at 100 °C overnight.

**Synthesis of Th-FDA-O**

Typically, 10 mmol thiophene, formaldehyde dimethyl acetal (FDA, 3.0 equiv.), $FeCl_3$ (3.0 equiv.), $H_2O_2$ (1 equiv., 30 wt% in $H_2O$), and 30 mL 1,2-dichloroethane (DCE) were added into a 100 mL round-bottom flask equipped with a magnetic stirrer. The mixture was refluxed for 24 h to give a precipitate, which was then carefully transferred into 50 mL of dilute hydrochloric acid (1.2 M in water) and stirred for 2 h. Subsequently, the polymer was subjected to Soxhlet extraction for 24 h using EtOH as solvent. Finally, the polymer was obtained by drying in a vacuum oven at 100 °C overnight.

## Fluorescence spectroscopic measurements

30 mg HCP powder was soaked with 5 mL of Nile red solution DCM ($3.3 \times 10^{-3}$ M) for 24 hours.[1] Then the DCM was removed by volatilizing in fume cupboard to offer tested sample. Steady state fluorescence spectra were recorded with a RF-6000 PC spectrophotometer.

## Measurements of swelling degree *Q* (%)

60 mg ($m_1$) HCP powder was soaked with 2 mL *n*-BuOAc for 12 hours.[1] The swelling HCPs were subjected to suction filtration and weighing ($m_2$). $Q$ (%) is calculated according to the following formula：

$$Q = \frac{m_2 - m_1}{m_1} \times 100\%$$

**Table S1** $S_{BET}$ and swelling degree of different HCP materials

| Material | Th-FDA | Fresh Th-FDA-O | Used Th-FDA-O |
|---|---|---|---|
| $S_{BET}$ ($m^2/g$) | 191 | 537 | 207 |
| $Q$ (%) | 158 | 147 | 159 |

## Titration-based measurements of acid adsorption by HCP

20 mg HCP powder was impregnated in 1 mL of PTSA solution of *n*-BuOAc containing 10 mg PTSA and the mixture was stirred at room temperature in a sealed V-type flask. After 3 hours, the mixture was diluted to 10 mL by addition of *n*-BuOAc. The mixture was centrifuged and 2 mL of supernatant liquid was taken. The 2 mL liquid was mixed with 4 mL of sodium hydroxide standard solution (0.0259 M). Then the titration was conducted with oxalic acid standard solution (0.01 M) as titrant and phenolphthalein ethanol solution (0.50 wt.%) as indicator.

**Table S2** Acid adsorption capacity of HCP different materials by titration method

| Material | Th-FDA | Th-FDA-O | Recovered Th-FDA-O |
|---|---|---|---|
| Adsorbing capacity | 4.9% | 89.7% | 89.5% |

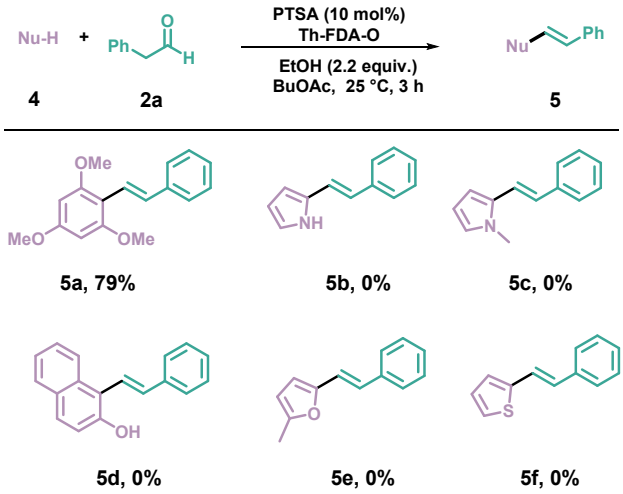
## Typical procedure for the synthesis of 3a

To a 10 mL V-type flask equipped with triangle magnetic stirring, **1a** (0.3 mmol), **2a** (0.33 mmol), EtOH (2.2 equiv.), PTSA (10 mmol%), Th-FDA-O (30 mg), and *n*-BuOAc (1 mL) was added. The mixture was then stirred for 3 hours at 25 °C. After the completion of the reaction, the reaction mixture was centrifuged and the supernatant was collected. The sediment was extracted with butyl acetate (3 mL) for 5 times. The organic liquid was combined. After concentration by rotary evaporation, the mixture was subjected preparative TLC plate for isolation with a mixed solution of petroleum ether and ethyl acetate (8/1 (v/v)) as eluent. The other compounds were prepared by the same procedure.

## The procedure for recycle experiment of Th-FDA-O

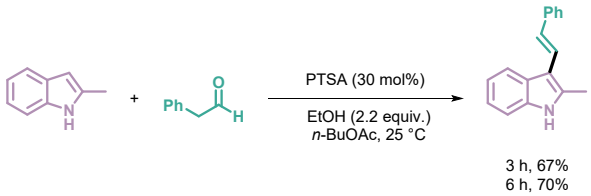
To a 10 mL V-type flask equipped with triangle magnetic stirring, **1a** (0.3 mmol), **2a** (0.33 mmol), EtOH (2.2 equiv.), PTSA (10 mmol%), Th-FDA-O (30 mg), and *n*-BuOAc (1 mL) was added. The mixture was then stirred for 3 hours at 25 °C. After the completion of the reaction, the reaction mixture was centrifuged. Then the supernatant was collected and 3mL of butyl acetate was added. The mixture was stirring for 5 minutes and the mixture was centrifuged, followed by the removing of supernatant and addition of 3mL of butyl acetate again. After the extraction procedure was repeated for 5 times, the sediment was directly used for the next cycle.

## The substrate scope of non-indole compound




**Scheme S1** The substrate scope of non-indole compound. [a] **4** (0.3 mmol), **2a** (0.33 mmol), *n*-BuOAc (1 mL), Th-FDA-O (30 mg), EtOH (2.2 equiv.), PTSA (10 mmol%), 25 °C, 3 h. [b] Isolated yield.

## Control experiments




## The scale-up procedure

To a 50 mL round-bottom flask equipped with triangle magnetic stirring, **1a** (5.0 mmol), **2a** (5.5 mmol), EtOH (11 mmol), PTSA (0.5 mmol), Th-FDA-O (500 mg), and

*n*-BuOAc (15 mL) was added. The mixture was then stirred for 5 hours at 25 °C. After the completion of the reaction, the reaction mixture was centrifuged. Then the supernatant was collected and 5 mL of butyl acetate was added. The mixture was stirring for 5 minutes and then centrifuged, followed by the removing of supernatant and addition of 5 mL of butyl acetate again. After the extraction procedure was repeated for 5 times, the organic solvent was combined. The solvent was removed by rotary evaporation. The residue was subjected to silica gel chromatography with petroleum ether and ethyl acetate (15/1 (v/v)) as eluent, which offered 1.0499 gram of product. In the rotary evaporation, 34.6 mL of butyl acetate was collected and the solvent recovery rate was calculated to be 86.5%.

## Green Metrics Analysis

Green metrics has been calculated for the basis of following equations.

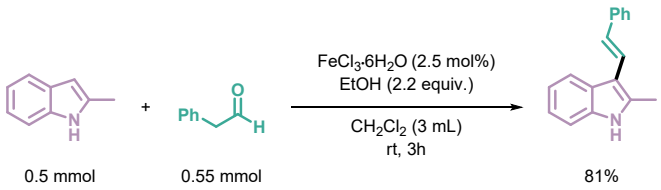
(1) *E*-factor $= \dfrac{Amount\ of\ waste}{Amount\ of\ product}$

(2) Atom economy $= \dfrac{Molecular\ mass\ of\ desired\ product}{Molecular\ mass\ of\ all\ reactants} \times 100\%$

(3) Atom efficiency $= \dfrac{Product\ yield\ \times\ atom\ economy}{100\%}$

(4) Reaction mass efficiency $= \dfrac{Mass\ of\ desired\ product}{Mass\ of\ all\ reactants} \times 100\%$

Yu's work[2]



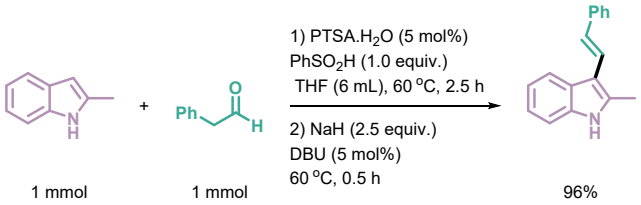

(1) *E*-factor $= \dfrac{(0.0656\ +\ 0.0661\ +\ 0.0034\ +\ 0.0507 + 3.975)\ -\ 0.0945}{0.0945} = 43.03$

(2) Atom economy $= \dfrac{233.3}{131.17\ +\ 120.15} \times 100\% = 92.8\%$

(3) Atom efficiency $= \dfrac{81\%\ \times\ 92.8\%}{100\%} = 75.2\%$

(4) Reaction mass efficiency $= \dfrac{0.0954}{0.0656\ +\ 0.0661} \times 100\% = 71.8\%$

Maji's work[3]



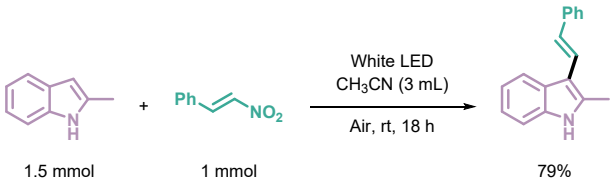

(1) *E*-factor $= \frac{(0.1312 + 0.1202 + 0.0095 + 0.1422 + 0.0600 + 0.0076 + 5.322) - 0.2240}{0.2240} = 24.86$

(2) Atom economy $= \frac{233.31}{131.17 + 120.15 + 142.18} \times 100\% = 59.3\%$

(3) Atom efficiency $= \frac{96\% \times 59.3\%}{100\%} = 56.9\%$

(4) Reaction mass efficiency $= \frac{0.2240}{0.1312 + 0.1202 + 0.1422} \times 100\% = 56.9\%$

Kapoor's work[4]



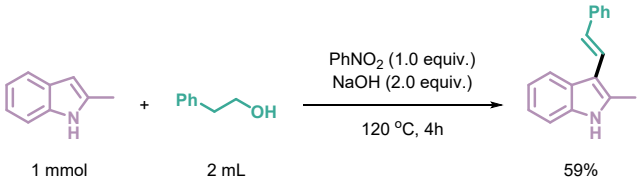

(1) *E*-factor $= \frac{(0.1968 + 0.1492 + 0.032 + 2.358) - 0.1843}{0.1843} = 13.84$

(2) Atom economy $= \frac{233.31}{131.17 + 149.15 + 32} \times 100\% = 74.7\%$

(3) Atom efficiency $= \frac{79\% \times 74.7\%}{100\%} = 59.0\%$

(4) Reaction mass efficiency $= \frac{0.1843}{0.1968 + 0.1492 + 0.032} \times 100\% = 48.8\%$

Ma's work[5]



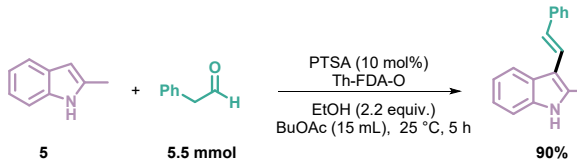

(1) *E*-factor $= \frac{(0.1312 + 2.04 + 0.1231 + 0.0800 + 2.04) - 0.1377}{0.1377} = 31.07$

(2) Atom economy $= \frac{233.31}{131.17 + 122.16} \times 100\% = 92.1\%$

(3) Atom efficiency $= \frac{59\% \times 92.1\%}{100\%} = 54.3\%$

(4) Reaction mass efficiency $= \frac{0.1377}{0.1312 + 2.04} \times 100\% = 6.3\%$

Our work




(1) *E*-factor $= \frac{(0.6559 + 0.6608 + 0.0951 + 0.5068 + 13.2) - 1.0499}{1.0499} = 13.40$

*E*-factor with solvent recovery $= \frac{(0.6559 + 0.6608 + 0.0951 + 0.5068 + 1.782) - 1.0499}{1.0499} = 2.49$

(2) Atom economy $= \frac{233.31}{131.17 + 120.15} \times 100\% = 92.8\%$

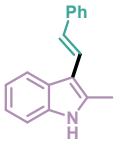
(3) Atom efficiency $= \frac{90\% \times 92.8\%}{100\%} = 83.6\%$

(4) Reaction mass efficiency $= \frac{1.0499}{0.6559 + 0.6608} \times 100\% = 79.7\%$

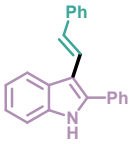
The greenness of solvent was evaluated based on the CHEM21selection guide

| | |
|---|---|
| Recommended | Water, EtOH, i-PrOH, *n*-BuOH, EtOAc, i-PrOAc, *n*-BuOAc, anisole, sulfolane. |
| Recommended or problematic? | MeOH, *t*-BuOH, benzyl alcohol, ethylene glycol, acetone, MEK, MIBK, cyclohexanone, MeOAc, AcOH, $Ac_2O$. |
| Problematic | Me-THF, heptane, Me-cyclohexane, toluene, xylenes, chlorobenzene, acetonitrile, DMPU, DMSO. |
| Problematic or hazardous? | MTBE, THF, cyclohexane, DCM, formic acid, pyridine. |
| Hazardous | Diisopropyl ether, 1,4-dioxane, DME, pentane, hexane, DMF, DMAc, NMP, methoxy-ethanol, TEA. |
| Highly hazardous | Diethyl ether, benzene, chloroform, $CCl_4$, DCE, nitromethane, $CS_2$, HMPA. |

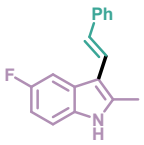
## Characterization data of the obtained compounds



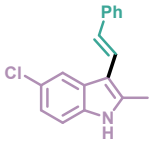
**(*E*)-2-Methyl-3-styryl-1*H*-indole (3a)[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 6.9 Hz, 1H), 7.78 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.10 (m, 5H), 7.05 (d, *J* = 16.4 Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 139.06, 135.58, 134.65, 128.69, 126.61, 126.49, 125.71, 125.28, 121.80, 121.69, 120.45, 119.74, 111.06, 110.62, 12.42.



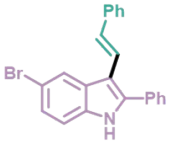
**(*E*)-2-Phenyl-3-styryl-1*H*-indole (3b)[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.15 (s, 1H), 8.11 – 8.05 (m, 1H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.50 – 7.44 (m, 4H), 7.43 – 7.17 (m, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 138.86, 137.46, 136.45, 132.56, 128.99, 128.88, 128.69, 128.26, 127.48, 126.90, 126.70, 125.92, 122.99, 122.34, 120.88, 120.86, 111.95, 111.25.



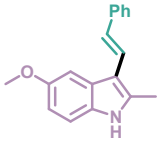
**(*E*)-5-Fluoro-2-methyl-3-styryl-1*H*-indole (3c)[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.94 (s, 1H), 7.59 (dd, *J* = 10.2, 2.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.18 – 7.12 (m, 1H), 6.98 (d, *J* = 16.5 Hz, 1H), 6.95 – 6.85 (m, 1H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 158.45 (d, $^{1}J_{C\text{-}F}$ = 234.5 Hz), 138.77, 136.40, 132.00, 128.70, 126.93 (d, $^{3}J_{C\text{-}F}$ = 10.1 Hz), 126.63, 125.71, 125.39, 121.22, 111.28 (d, $^{4}J_{C\text{-}F}$ = 4.6 Hz), 111.04 (d, $^{3}J_{C\text{-}F}$ = 9.7 Hz), 109.67 (d, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 105.08 (d, $^{2}J_{C\text{-}F}$ = 24.2 Hz), 12.50. $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -123.79 (td, *J* = 9.4, 4.4 Hz).



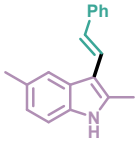
**(*E*)-5-Chloro-2-methyl-3-styryl-1*H*-indole (3d)[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 1.9 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.19 – 7.08 (m, 3H), 7.00 (d, *J* = 16.4 Hz, 1H), 2.47 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 138.68, 135.87, 133.87, 128.71, 127.68, 126.73, 126.06, 125.85, 125.78, 121.90, 120.99, 119.25, 111.48, 110.90, 12.49.



**(*E*)-5-Bromo-2-phenyl-3-styryl-1*H*-indole (3e)[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 8.17 – 8.12 (m, 1H), 7.57 – 7.51 (m, 2H), 7.49 – 7.44 (m, 4H), 7.43 – 7.40 (m, 1H), 7.36 – 7.30 (m, 3H), 7.24 – 7.19 (m, 3H), 7.14 (d, *J* = 16.5 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 138.47, 138.28, 134.99, 132.01, 129.06, 128.79, 128.71, 128.59, 128.57, 128.02, 126.94, 126.00, 125.72, 123.30, 121.63, 114.06, 112.60, 111.53.

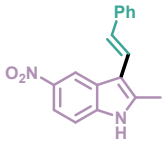


**(*E*)-5-Methoxy-2-methyl-3-styryl-1*H*-indole (3f)[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.88 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (s, 1H), 7.24 – 7.17 (m, 2H), 7.02 (d, *J* = 16.5 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.90 (s, 3H), 2.53 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 154.72, 139.03, 135.36, 130.59, 128.63, 127.17, 126.42, 125.65, 125.00, 121.76, 111.04, 110.97, 110.86, 102.79, 56.10, 12.62.

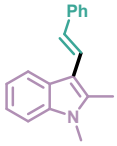


**(*E*)-2,5-Dimethyl-3-styryl-1*H*-indole (3g)[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.75 (s, 1H), 7.70 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz,

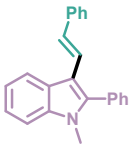
2H), 7.23 – 7.15 (m, 2H), 7.12 (d, $J$ = 8.2 Hz, 1H), 7.04 (d, $J$ = 16.4 Hz, 1H), 6.96 (d, $J$ = 8.2 Hz, 1H), 2.46 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 139.16, 134.75, 133.83, 129.71, 128.64, 126.87, 126.37, 125.67, 124.97, 123.20, 121.88, 119.59, 110.66, 110.21, 21.76, 12.47.



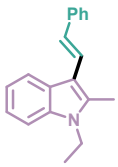

**(*E*)-2-Methyl-5-nitro-3-styryl-1*H*-indole (3h)[2]:** $^1$H NMR (400 MHz, DMSO-$d_6$) δ = 12.00 (s, 1H), 8.83 – 8.78 (m, 1H), 8.05 – 7.97 (m, 1H), 7.68 (d, $J$ = 7.6 Hz, 2H), 7.52 – 7.44 (m, 2H), 7.37 (t, $J$ = 7.5 Hz, 2H), 7.23 (t, $J$ = 7.5 Hz, 1H), 7.06 (d, $J$ = 16.7 Hz, 1H), 2.59 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 141.52, 140.10, 139.35, 138.93, 138.69, 129.04, 127.14, 126.32, 125.90, 121.27, 116.98, 116.14, 112.03, 111.69, 12.74.



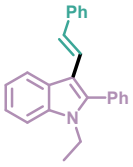

**(*E*)-1,2-Dimethyl-3-styryl-1*H*-indole (3i)[2]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, $J$ = 6.9 Hz, 1H), 7.52 (d, $J$ = 7.6 Hz, 2H), 7.35 (t, $J$ = 7.6 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 7.09 (d, $J$ = 16.3 Hz, 1H), 3.66 (s, 3H), 2.50 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 139.22, 137.25, 136.53, 128.63, 126.29, 125.77, 125.61, 124.84, 122.04, 121.41, 120.17, 119.79, 110.42, 108.98, 29.67, 10.77.



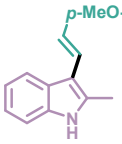

**(*E*)-1-Methyl-2-phenyl-3-styryl-1*H*-indole (3j)[2]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, $J$ = 7.8 Hz, 1H), 7.57 – 7.37 (m, 7H), 7.37 – 7.24 (m, 5H), 7.24 – 7.11 (m, 3H), 3.65 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 140.91, 139.02, 137.90, 131.29, 131.14, 128.53, 128.50, 126.31, 125.67, 125.57, 122.68, 122.46, 120.68, 112.03, 109.79, 30.55.



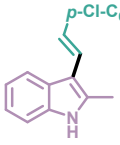

**(*E*)-1-Ethyl-2-methyl-3-styryl-1*H*-indole (3k)[2]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, $J$ = 7.7 Hz, 1H), 7.52 (d, $J$ = 7.6 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.25 – 7.15 (m, 3H), 7.10 (d, $J$ = 16.3 Hz, 1H), 4.14 (q, $J$ = 7.2 Hz, 2H), 2.51 (s, 3H), 1.34 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 139.26, 136.15, 135.70, 128.63, 126.29, 126.00, 125.62, 124.88, 122.05, 121.38, 120.11, 119.88, 110.53, 109.04, 37.92, 15.18, 10.55.




**(*E*)-1-Ethyl-2-phenyl-3-styryl-1*H*-indole (3l)[2]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, $J$ = 7.7 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.46 – 7.34 (m, 5H), 7.33 – 7.23 (m, 4H), 7.22 – 7.09 (m, 2H), 7.05 (d, $J$ = 16.5 Hz, 1H), 4.07 (q, $J$ = 7.2 Hz, 2H), 1.24 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 140.55, 139.10, 136.70, 131.65, 131.03, 128.65, 128.60, 128.56, 126.32, 125.92, 125.70, 125.51, 122.72, 122.39, 120.82, 120.63, 112.30, 110.08, 38.83, 15.30.

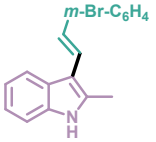



**(*E*)-3-(4-Methoxystyryl)-2-methyl-1*H*-indole (3m)[4]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.97 – 7.90 (m, 1H), 7.82 (s, 1H), 7.45 (d, $J$ = 8.7 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.20 – 7.11 (m, 3H), 7.04 (d, $J$ = 16.4 Hz, 1H), 6.90 (d, $J$ = 8.7 Hz, 2H), 3.81 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 158.50, 135.57, 134.05, 131.92, 126.81, 126.64, 124.97, 121.68, 120.30, 119.77, 119.69, 114.16, 111.14, 110.59, 55.40, 12.40.

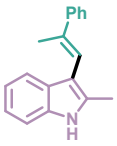



**(*E*)-3-(4-Chlorostyryl)-2-methyl-1*H*-indole (3n)[4]:** $^1$H NMR (400 MHz,

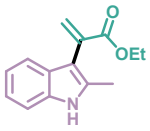
$CDCl_3$) δ = 7.95 – 7.89 (m, 1H), 7.82 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.14 (m, 4H), 7.02 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 137.58, 135.58, 135.00, 131.79, 128.76, 126.82, 126.49, 123.79, 122.30, 121.91, 120.57, 119.70, 110.84, 110.70, 12.40.



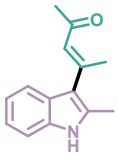

**(*E*)-3-(3-Bromostyryl)-2-methyl-1*H*-indole (3o)[4]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.88 (m, 1H), 7.84 (s, 1H), 7.65 (s, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.14 (m, 5H), 6.98 (d, *J* = 16.3 Hz, 1H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 141.33, 135.58, 135.36, 130.16, 129.13, 128.29, 126.45, 124.40, 123.38, 123.11, 122.93, 121.97, 120.65, 119.73, 110.75, 110.72, 12.43.



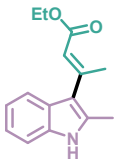

**(*E*)-2-Methyl-3-(2-phenylprop-1-en-1-yl)-1*H*-indole (3p)[3]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.81 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.17 – 7.08 (m, 2H), 6.90 (s, 1H), 2.33 (s, 3H), 2.11 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 143.36, 135.33, 132.48, 128.36, 126.98, 125.89, 121.32, 119.65, 119.41, 110.31, 18.03, 12.93.



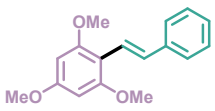

**Ethyl 2-(2-methyl-1*H*-indol-3-yl)acrylate (3q)[6]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.46 – 7.40 (m, 1H), 7.25 – 7.18 (m, 1H), 7.15 – 7.04 (m, 2H), 6.55 (d, *J* = 1.9 Hz, 1H), 5.80 (d, *J* = 1.9 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 167.64, 135.02, 134.63, 133.31, 128.02, 127.34, 121.39, 119.88, 118.89, 110.37, 109.81, 61.09, 14.27, 12.69.




**(*E*)-4-(2-Methyl-1*H*-indol-3-yl)pent-3-en-2-one (3r)[7]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 7.69 – 7.63 (m, 1H), 7.32 – 7.27 (m, 1H), 7.19 – 7.09 (m, 2H), 6.39 (s, 1H), 2.66 (s, 3H), 2.52 (s, 3H), 2.30 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 198.98, 151.39, 135.24, 133.79, 130.39, 126.99, 124.61, 121.88, 120.44, 119.55, 110.68, 32.25, 21.17, 13.71.




**Ethyl (*E*)-3-(2-methyl-1*H*-indol-3-yl)but-2-enoate (3s)[7]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.18 (s, 1H), 7.68 – 7.61 (m, 1H), 7.29 – 7.24 (m, 1H), 7.18 – 7.09 (m, 2H), 5.94 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 2.49 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 167.53, 152.30, 135.14, 133.06, 126.99, 121.75, 120.31, 119.58, 117.03, 116.72, 110.55, 59.63, 20.51, 14.47, 13.51.




**(*E*)-1,3,5-Trimethoxy-2-styrylbenzene (5a)[8]:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.53 – 7.47 (m, 2H), 7.44 (s, 1H), 7.41 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.17 (s, 2H), 3.88 (s, 6H), 3.83 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 160.23, 159.53, 139.70, 129.96, 128.42, 126.53, 126.18, 119.87, 108.19, 90.84, 55.80, 55.34.

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5. R. Zhang, R. Ma, R. Chen, L. Wang and Y. Ma, *The Journal of Organic Chemistry*, 2024, **89**, 1846-1857.
6. A. El-Harairy, M. Shaheen, J. Li, Y. Wu, M. Li and Y. Gu, *RSC Advances*, 2020, **10**, 13507-13516.
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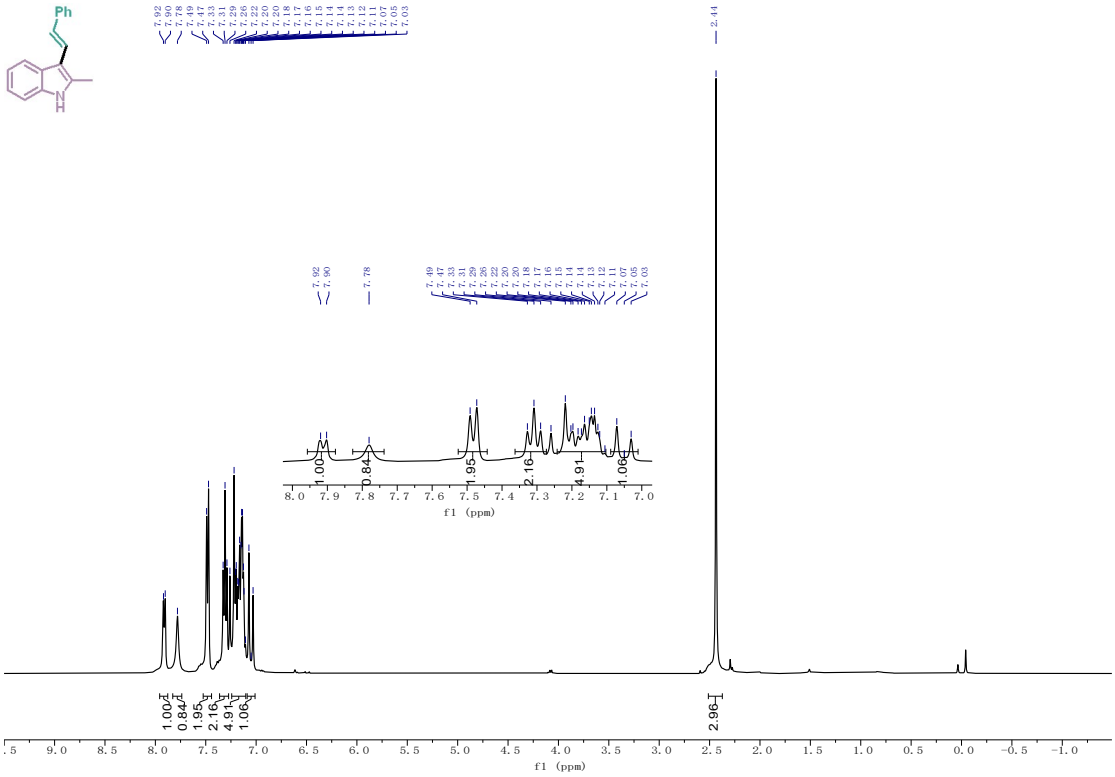
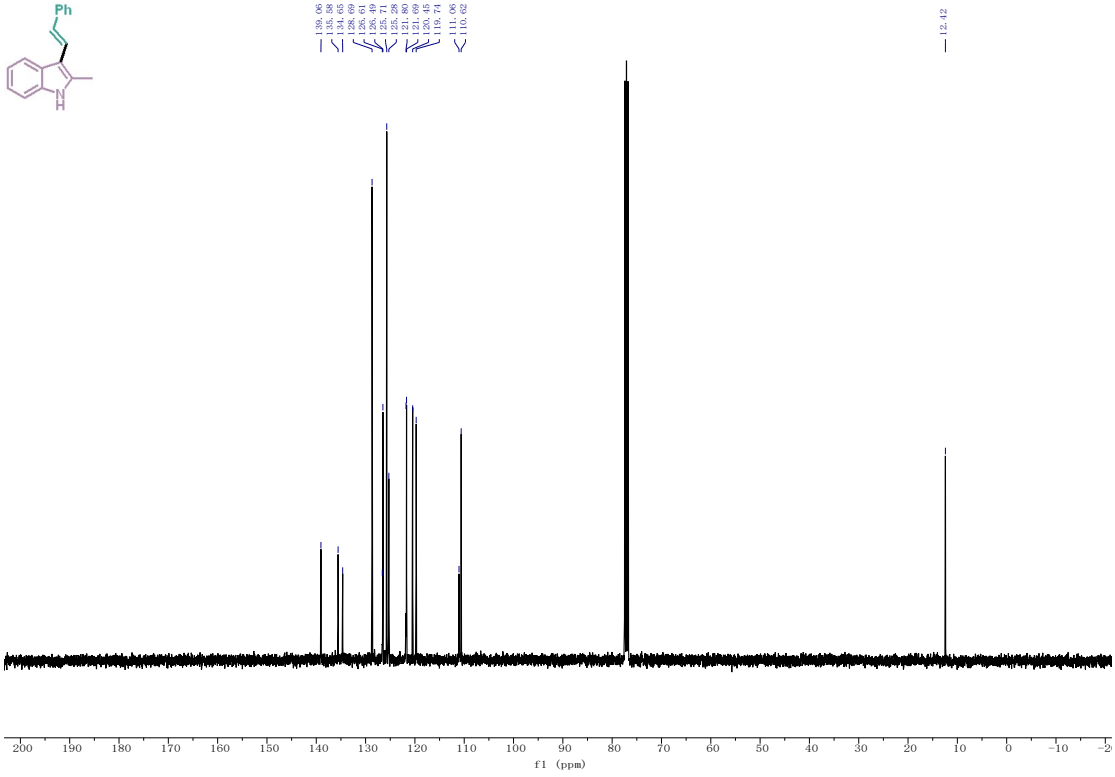
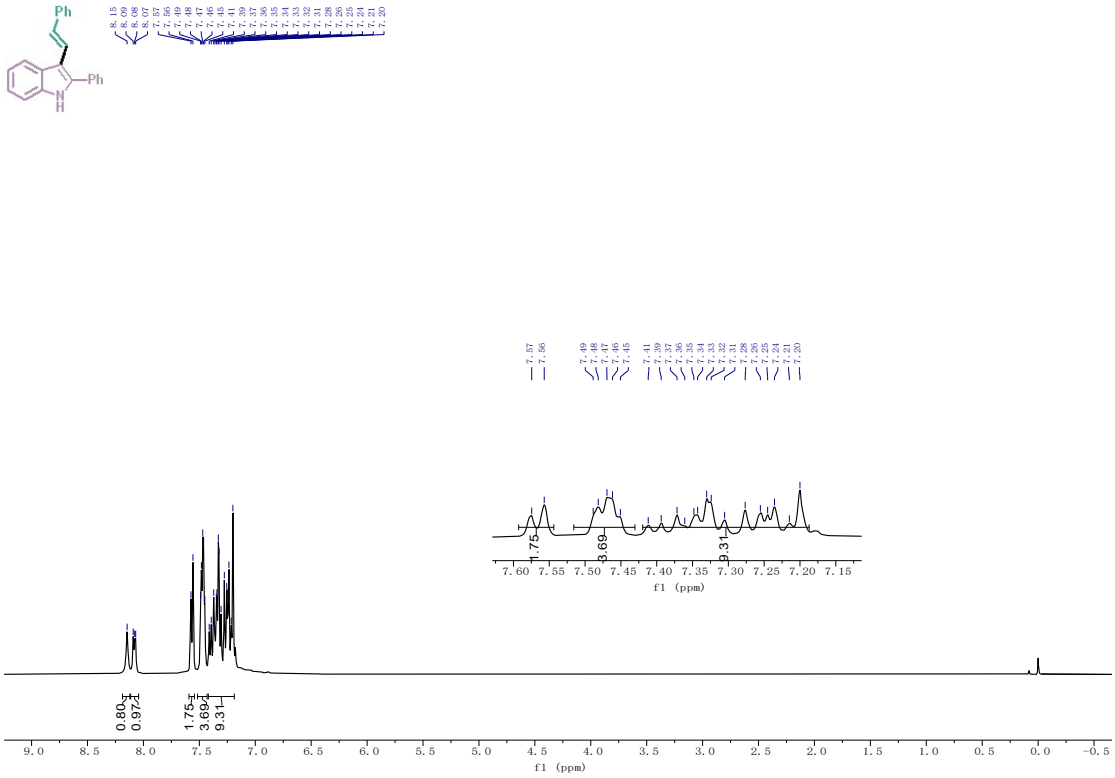
# NMR spectra of products

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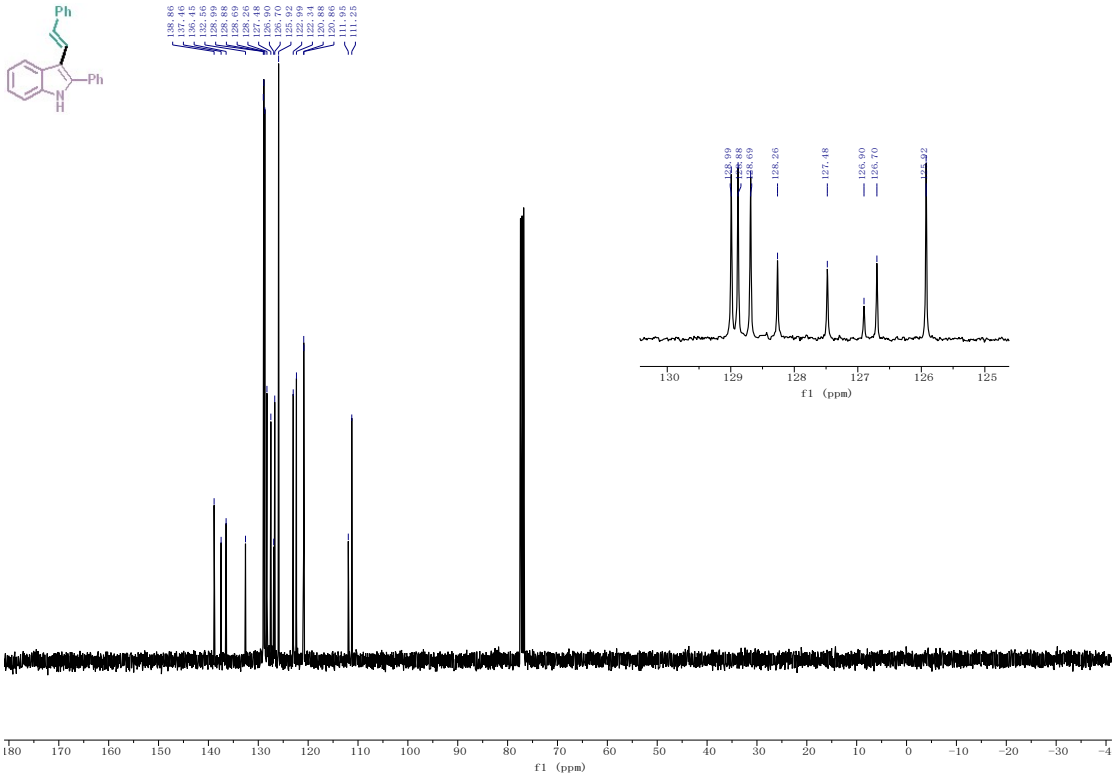
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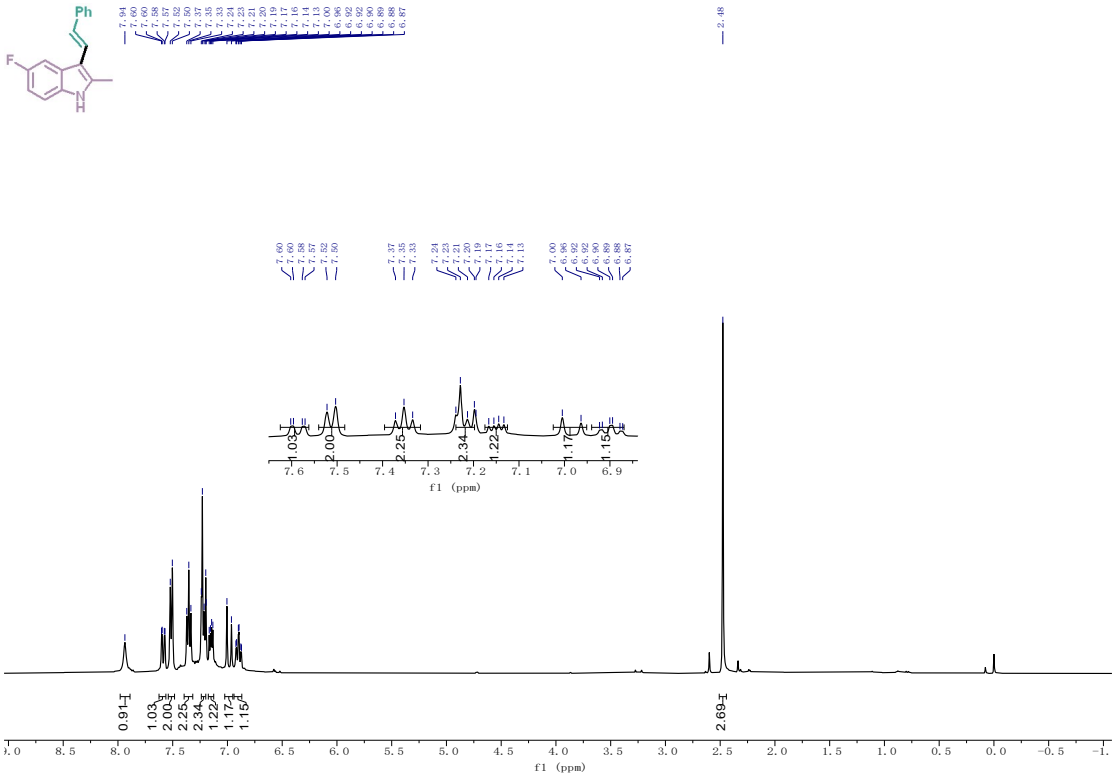
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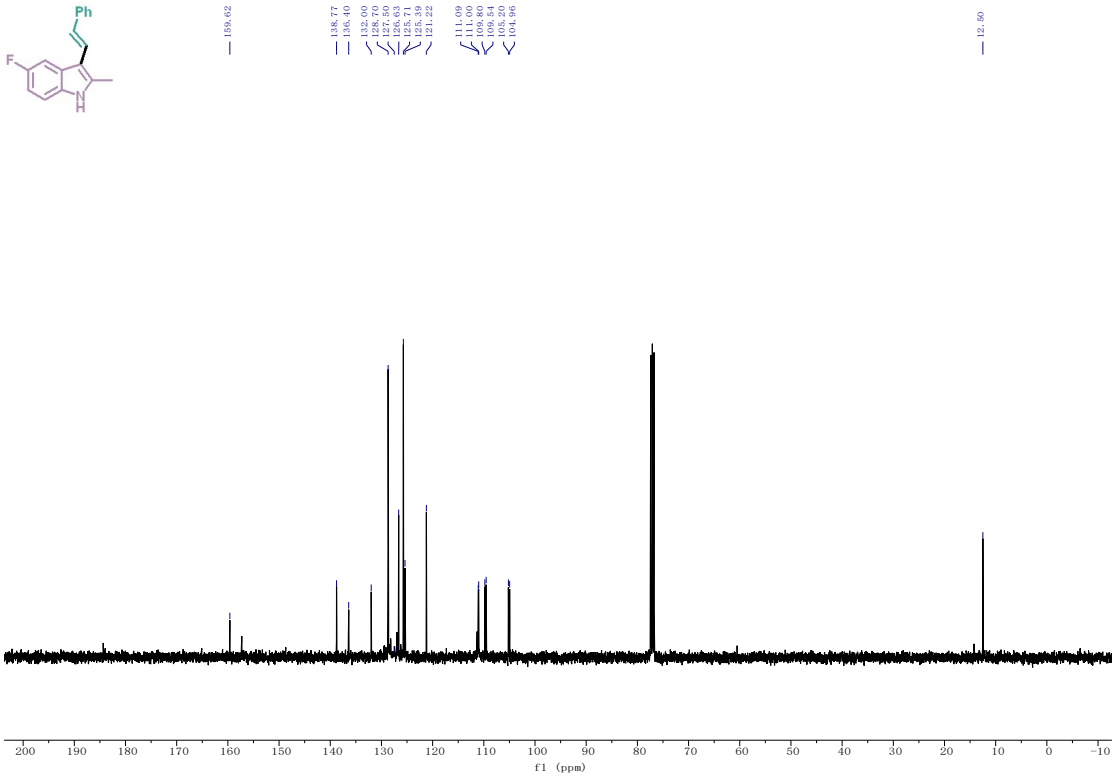
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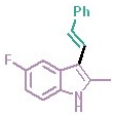
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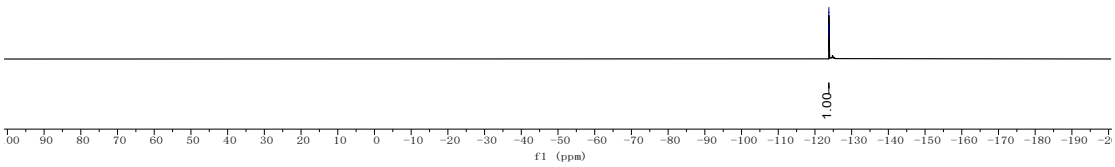
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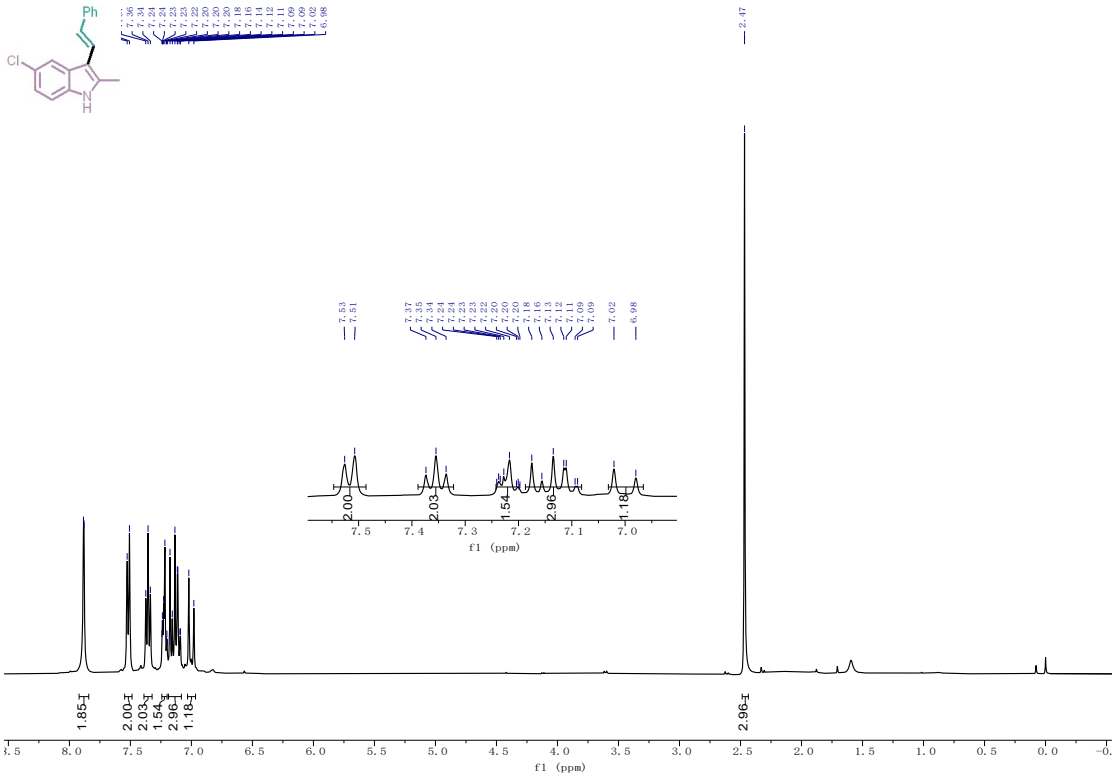
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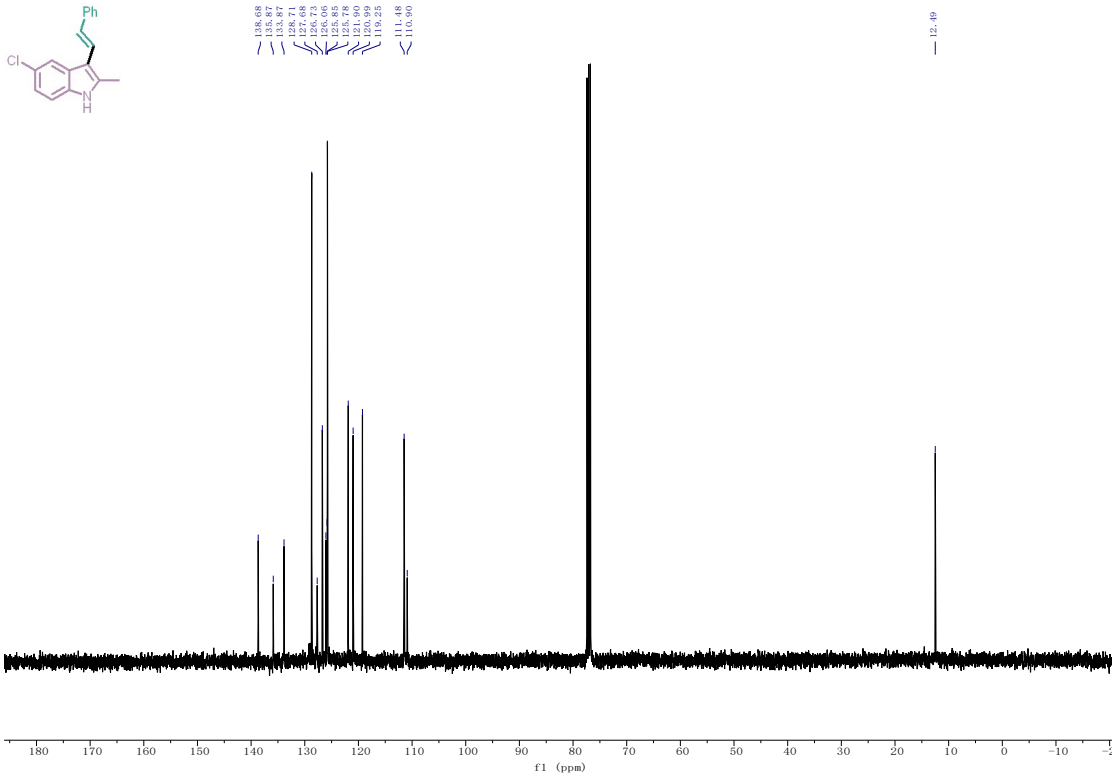
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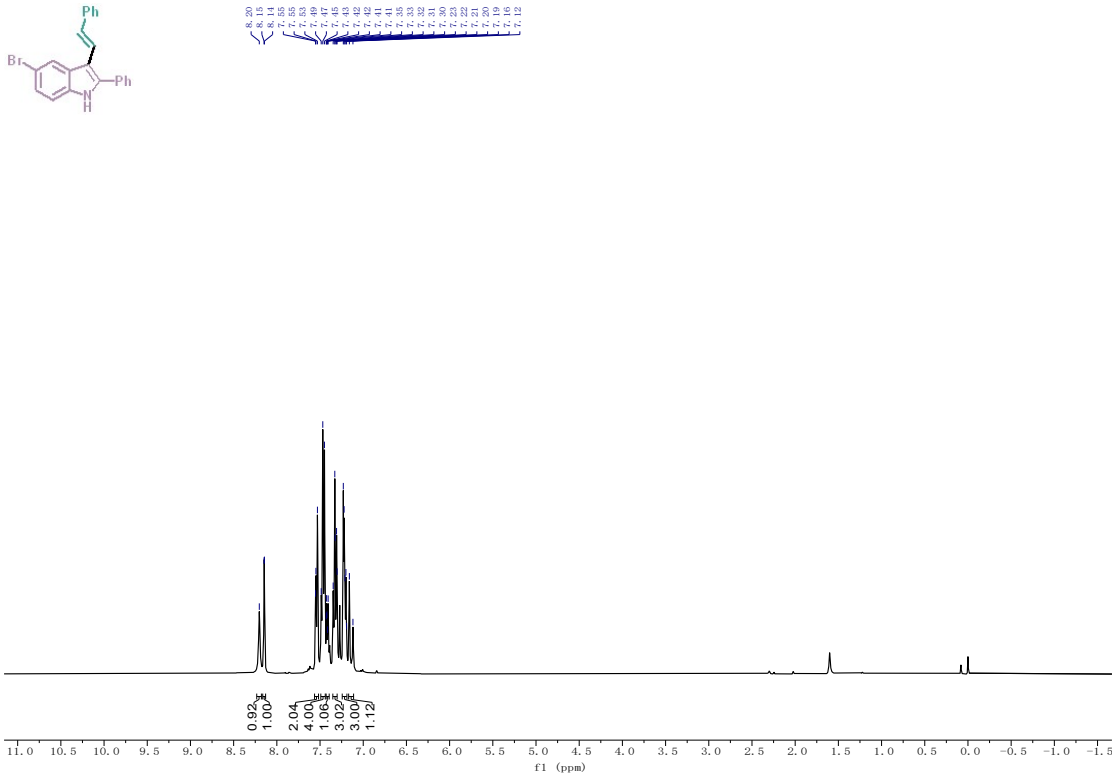
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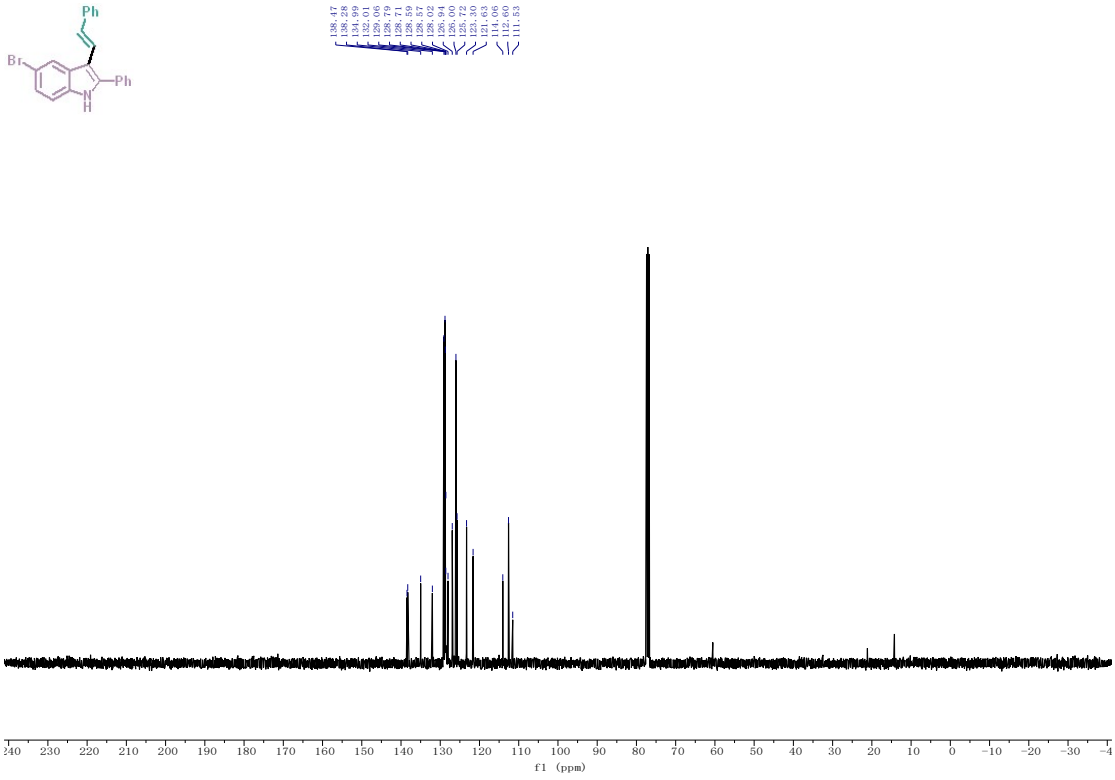
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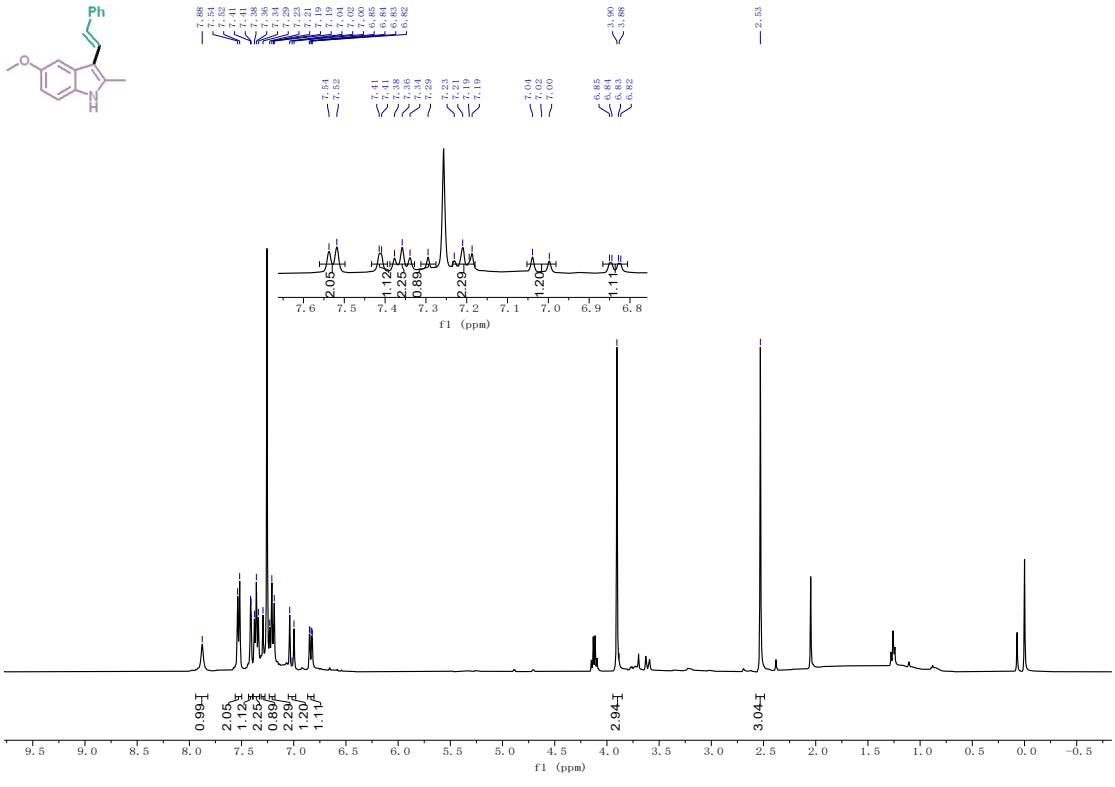
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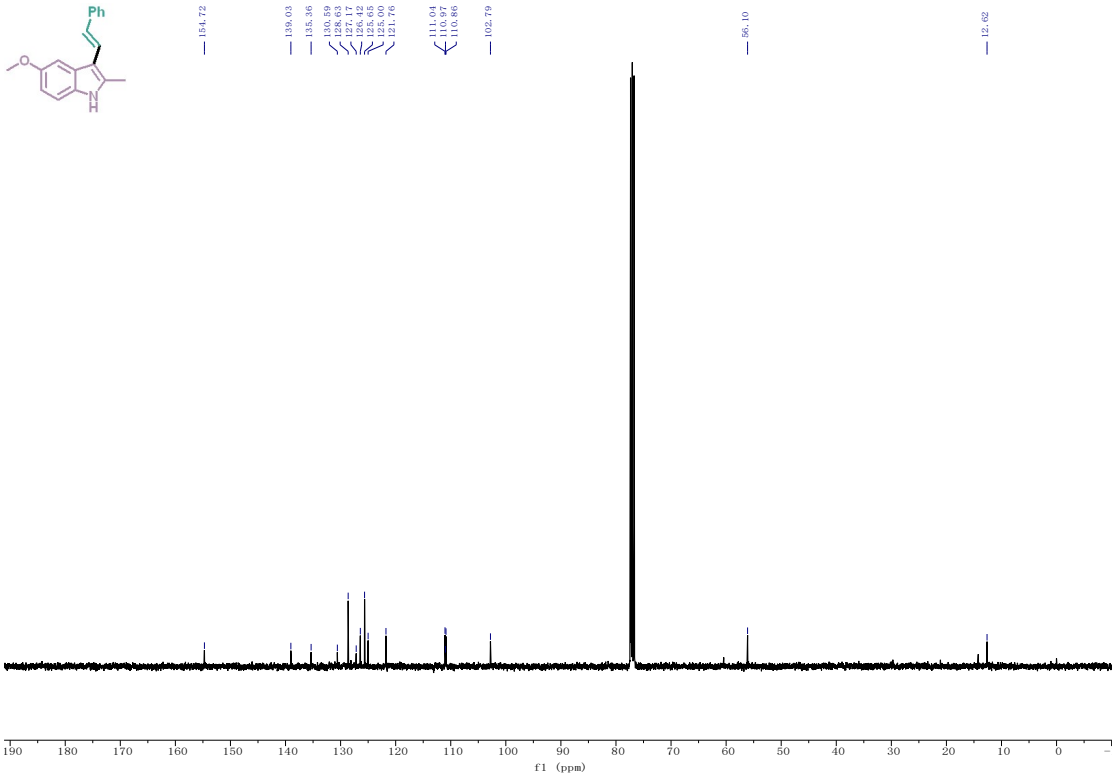
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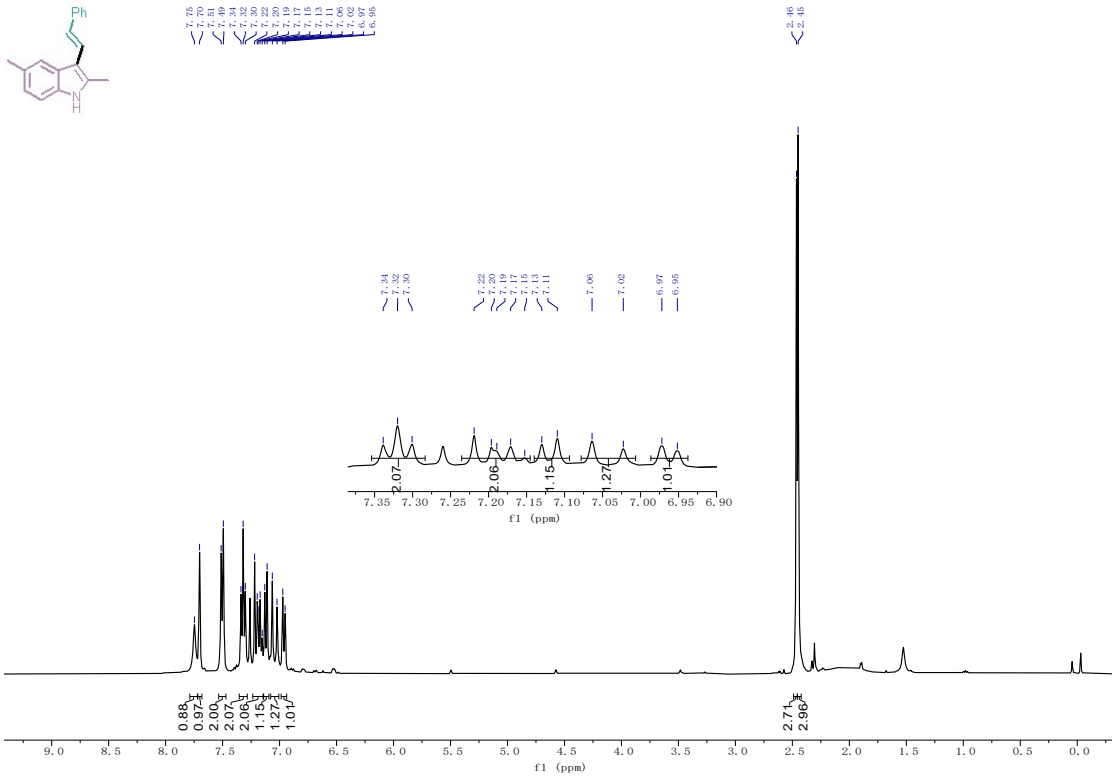
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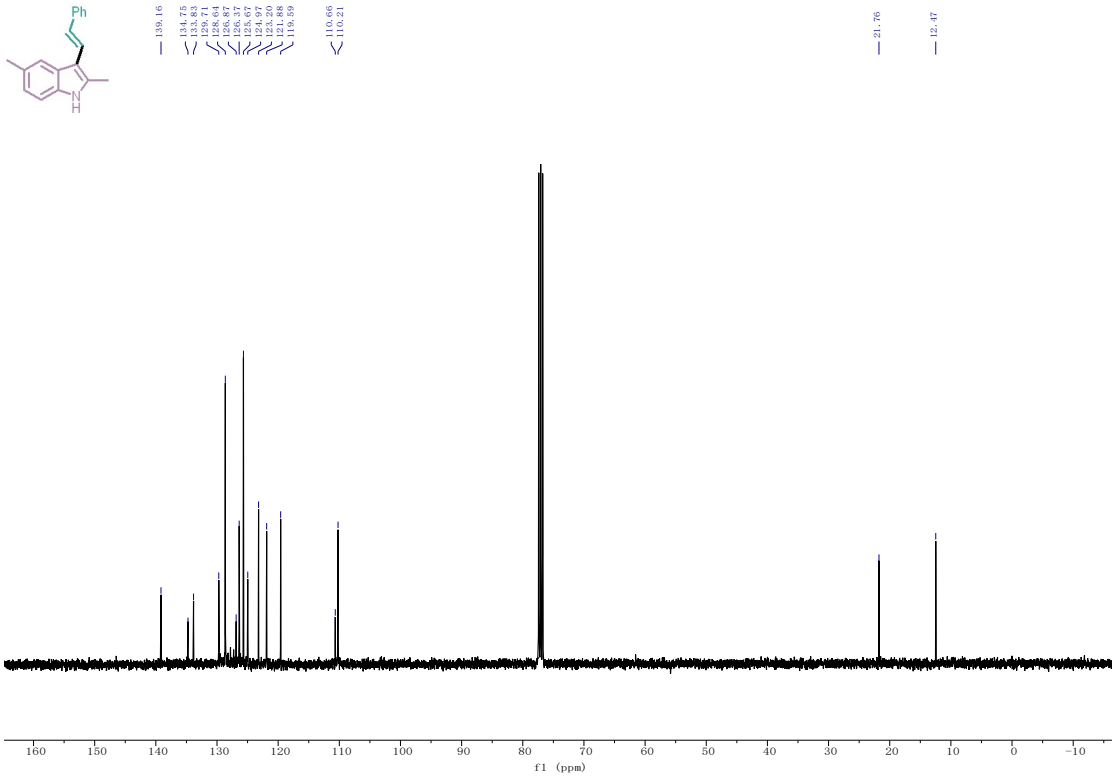
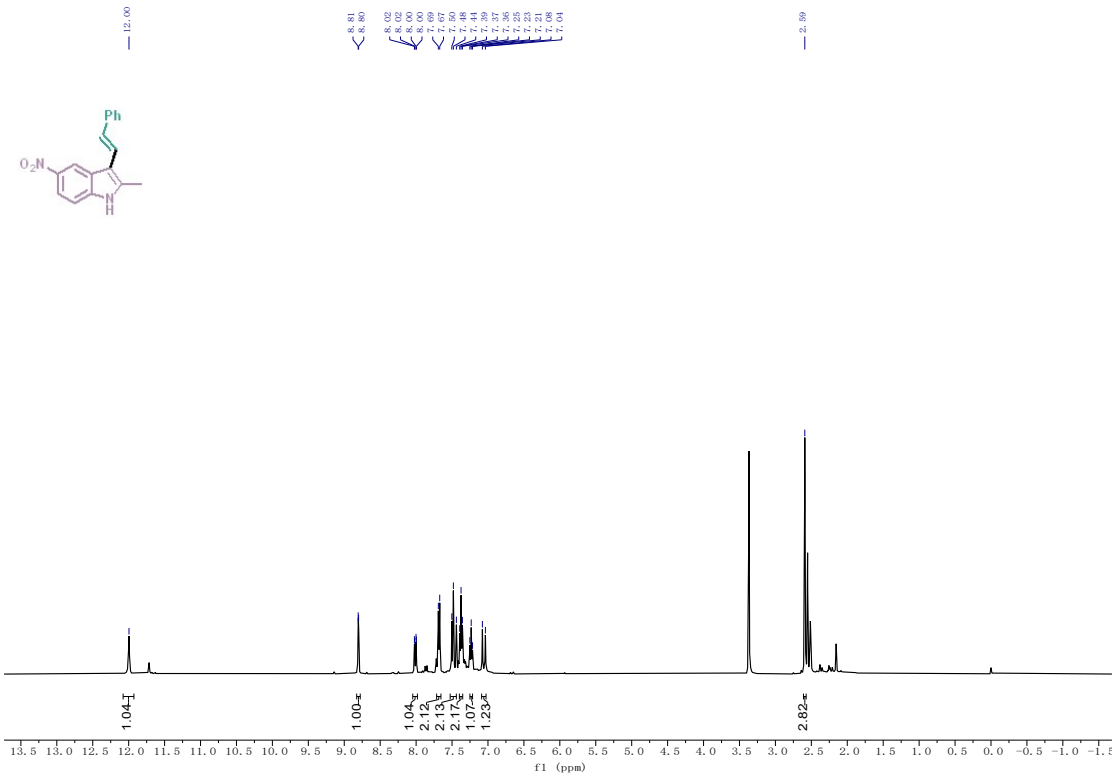
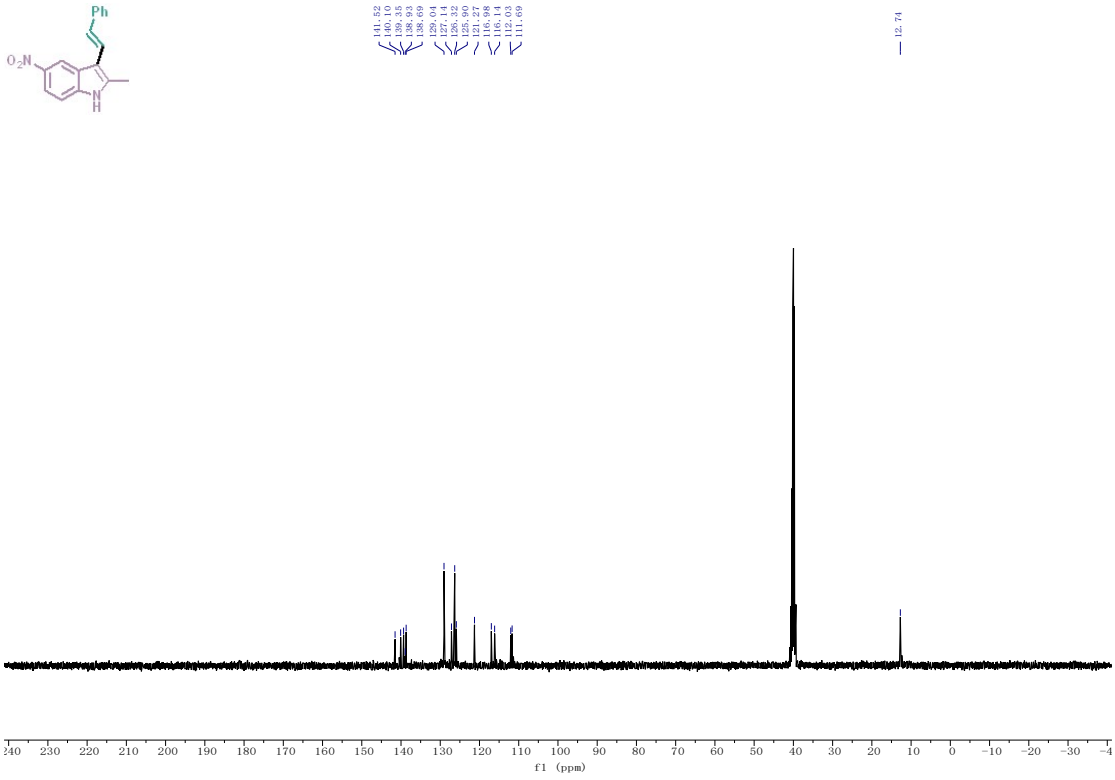
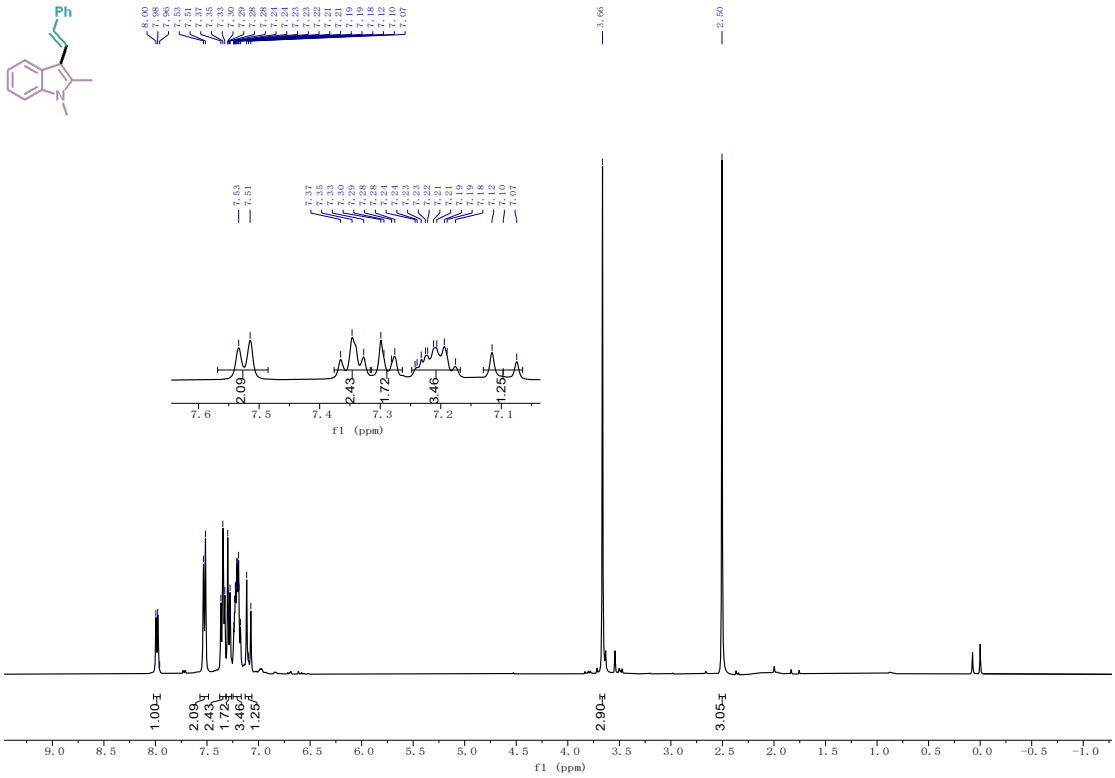
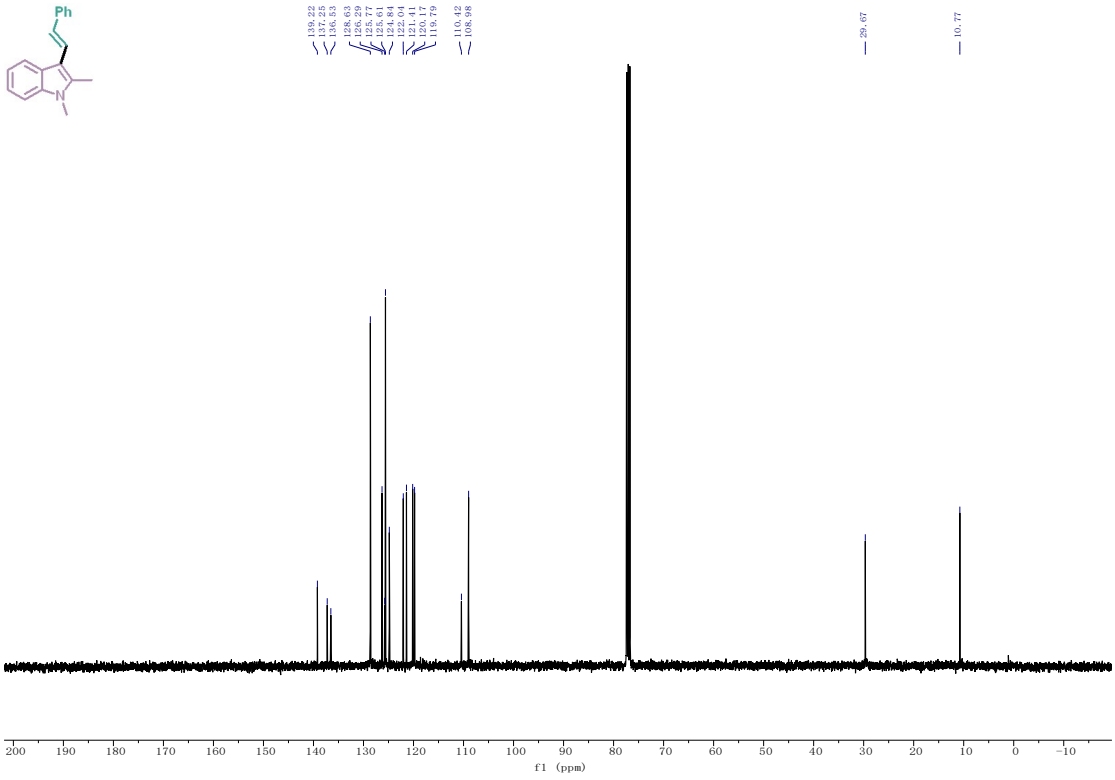
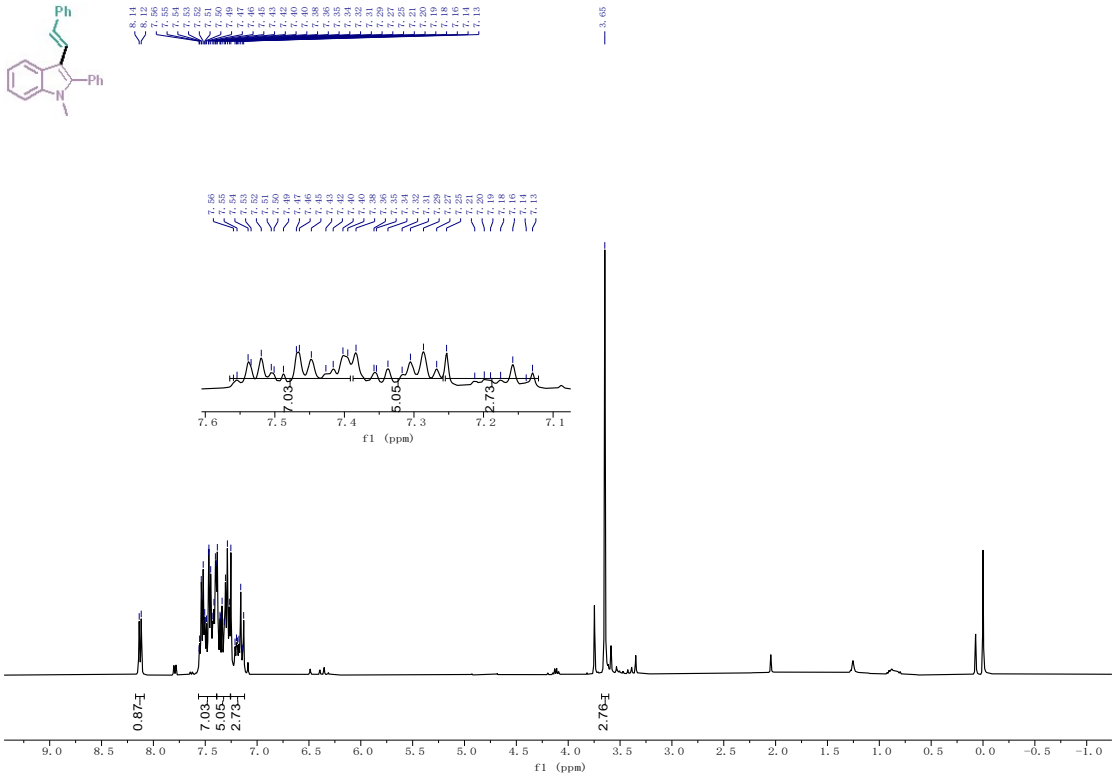

Ph
139.16
134.75
133.83
129.71
128.64
126.87
126.37
125.67
124.97
122.70
121.88
119.59
110.66
110.21
21.76
12.47
f1 (ppm)

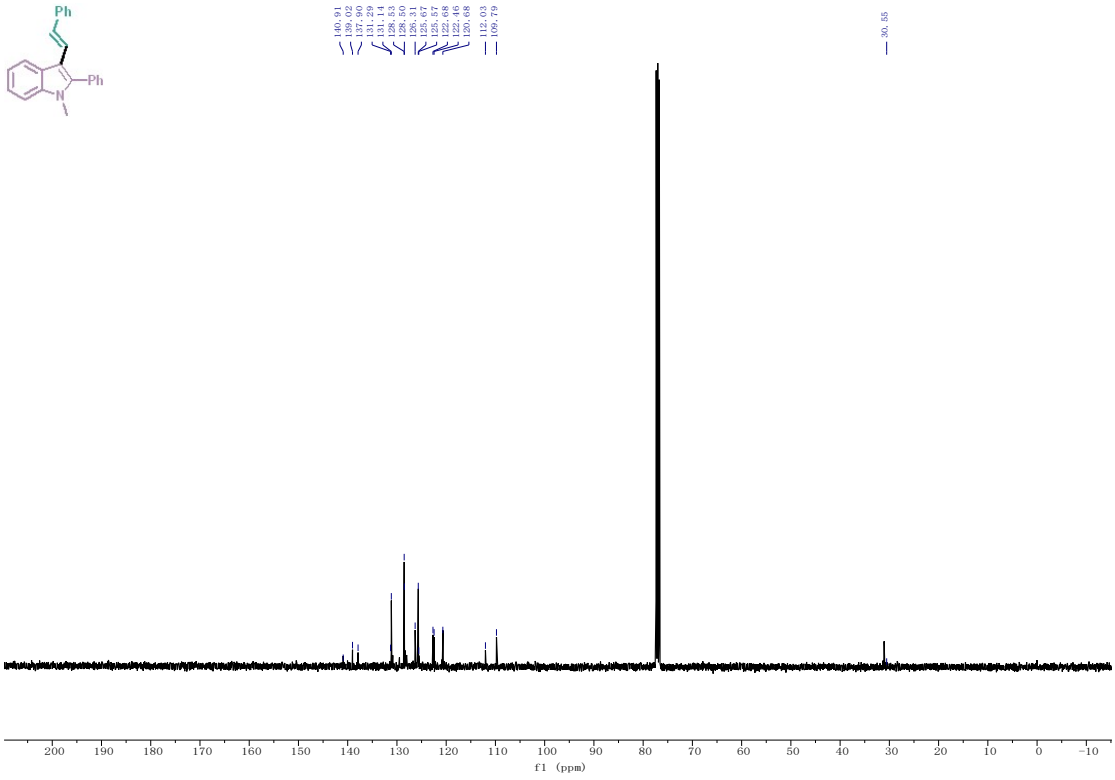

12.00
8.81
8.80
8.02
8.02
8.00
8.00
7.69
7.67
7.50
7.48
7.44
7.39
7.37
7.35
7.25
7.23
7.21
7.08
7.04
2.69
Ph
O2N
N
H
1.04
1.00
1.04
2.12
2.13
2.17
1.07
1.23
2.82
f1 (ppm)

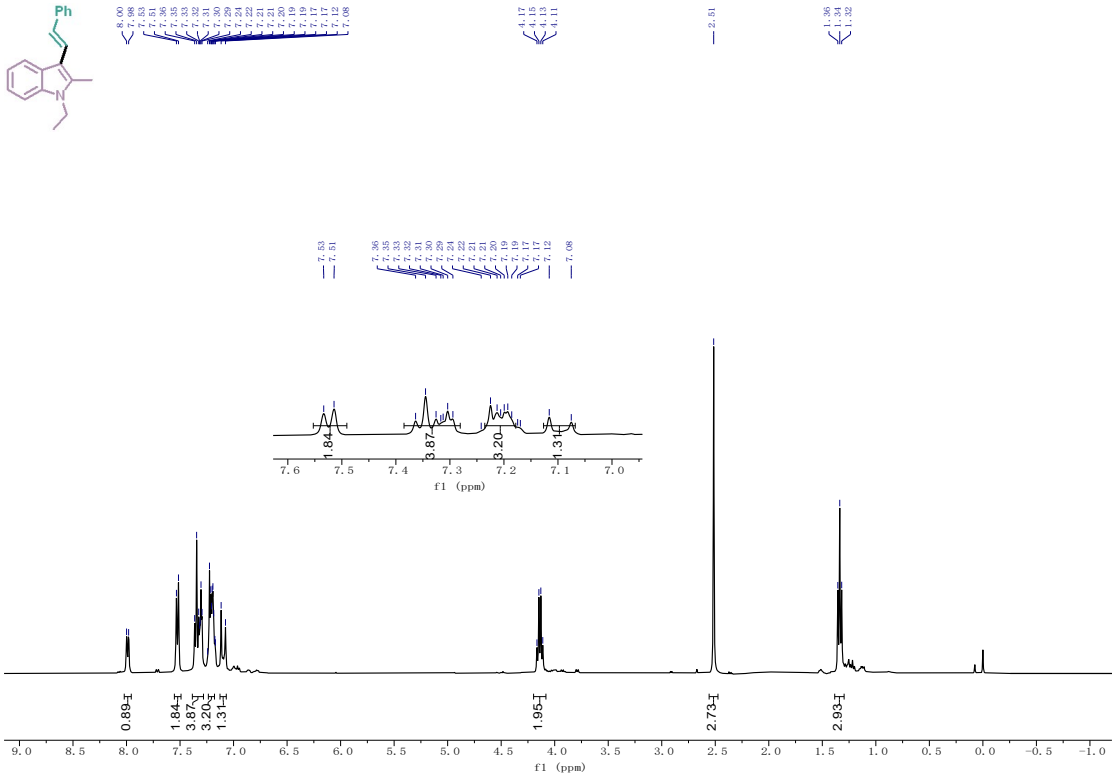

141.52
140.10
139.35
138.93
138.69
129.04
127.14
126.32
125.90
121.27
116.98
116.14
112.03
111.69
12.74
Ph
O2N
N
H
f1 (ppm)

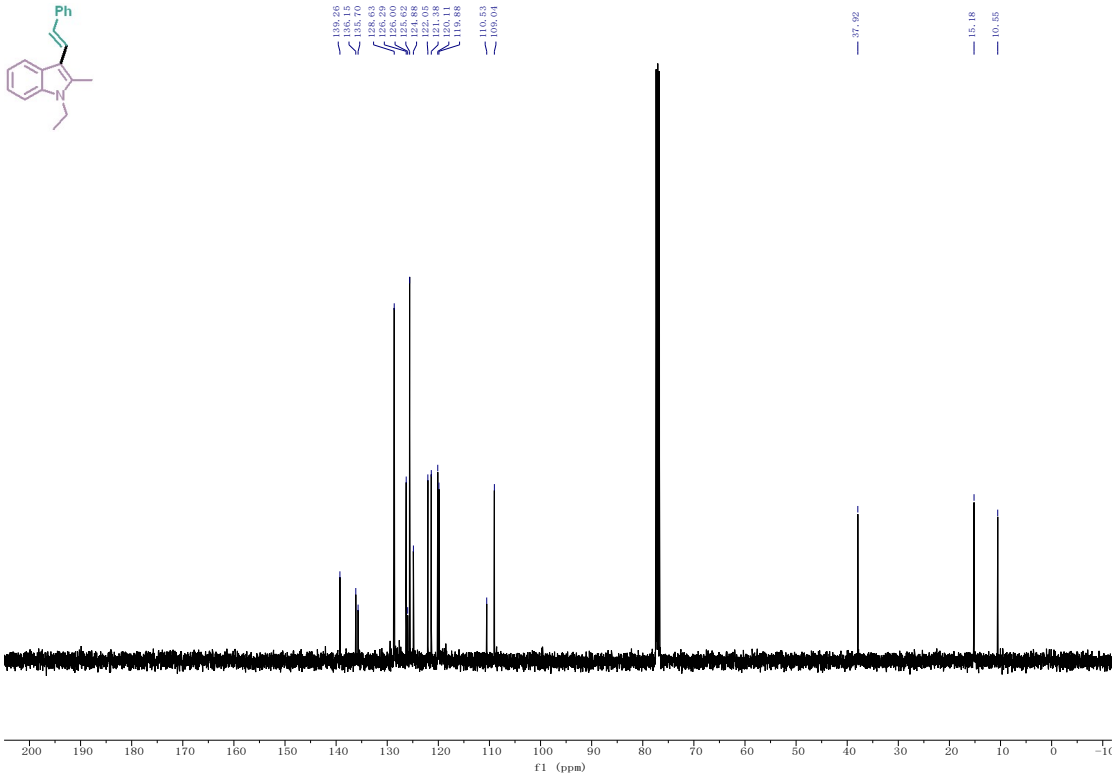

Ph
8.00
7.98
7.96
7.53
7.51
7.37
7.35
7.33
7.30
7.29
7.28
7.24
7.23
7.22
7.21
7.19
7.18
7.12
7.10
7.07
3.66
2.50
2.09
2.43
1.72
3.46
1.25
2.90
3.05
f1 (ppm)

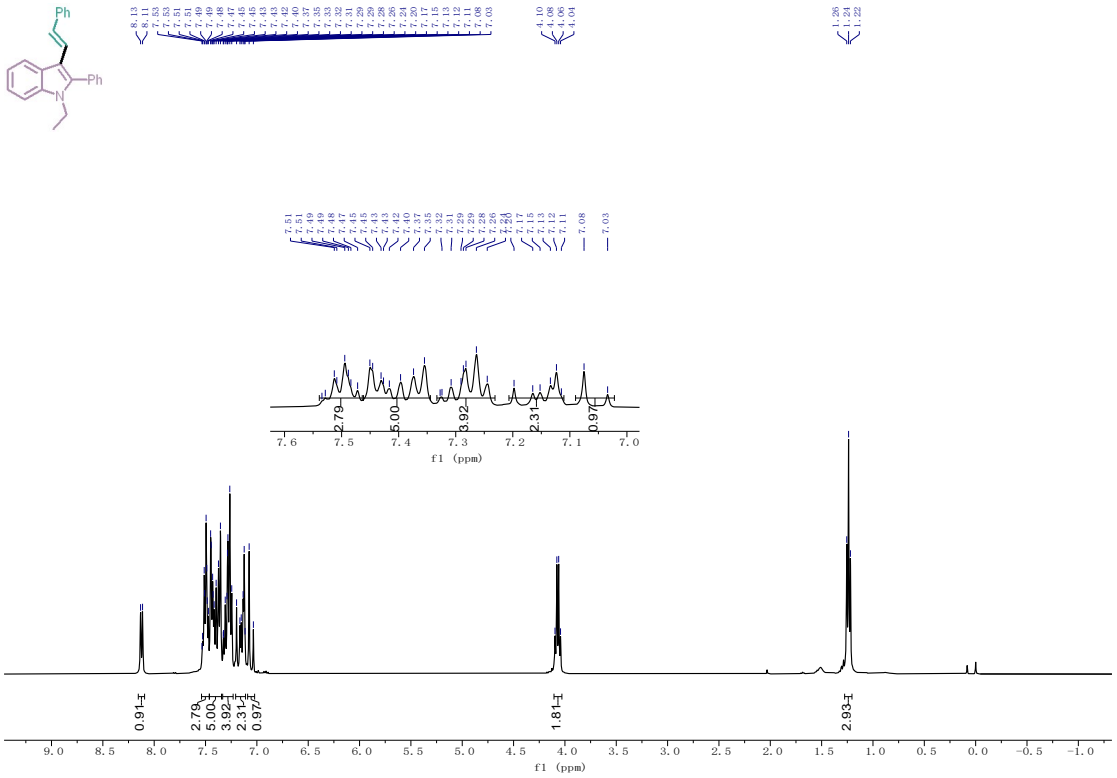

Ph
139.22
137.25
136.53
128.63
126.29
125.77
125.61
124.84
122.04
121.41
120.17
116.79
110.42
108.98
29.67
10.77
f1 (ppm)

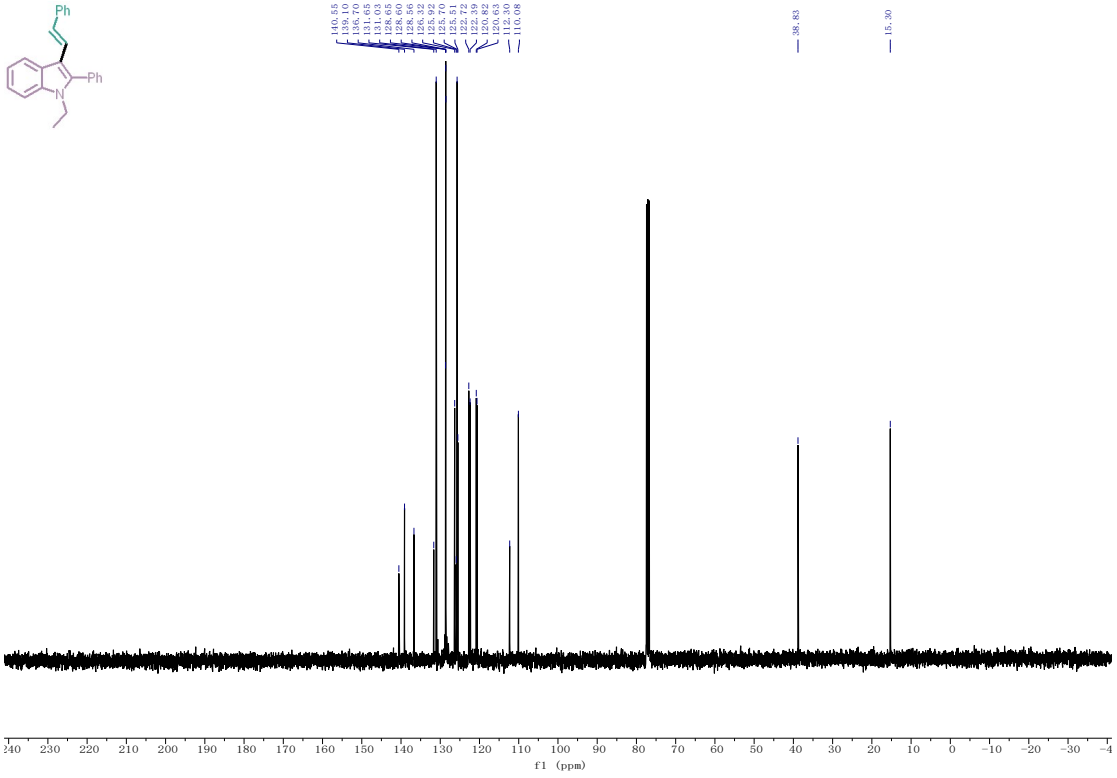

Ph
Ph
N
8.14
8.12
8.06
7.56
7.55
7.54
7.53
7.52
7.51
7.50
7.49
7.47
7.46
7.45
7.43
7.42
7.40
7.40
7.38
7.36
7.35
7.34
7.32
7.31
7.29
7.27
7.25
7.21
7.20
7.19
7.18
7.16
7.14
7.13
3.65
7.03
5.05
2.73
f1 (ppm)
0.87
7.03
5.05
2.73
2.76
f1 (ppm)


Ph
Ph
N
140.91
139.02
137.90
131.29
131.14
128.53
128.50
126.31
125.67
125.57
122.68
122.46
120.68
112.03
109.79
30.55
f1 (ppm)


Ph
8.00
7.98
7.53
7.51
7.36
7.35
7.33
7.32
7.31
7.30
7.29
7.24
7.22
7.21
7.21
7.20
7.19
7.19
7.17
7.17
7.17
7.12
7.08
4.17
4.15
4.13
4.11
2.51
1.36
1.34
1.32
1.84
3.87
3.20
1.31
0.89
1.84
3.87
3.20
1.31
1.95
2.73
2.93
f1 (ppm)


Ph
139.26
136.15
135.70
128.63
126.29
126.00
125.62
124.88
122.05
121.38
120.11
119.88
110.53
109.04
37.92
15.18
10.55
f1 (ppm)


Ph
Ph
N
8.13
8.11
7.53
7.51
7.49
7.48
7.47
7.45
7.43
7.42
7.40
7.37
7.35
7.33
7.32
7.31
7.29
7.28
7.26
7.24
7.20
7.17
7.15
7.13
7.12
7.11
7.08
7.05
4.10
4.08
4.06
4.04
1.26
1.24
1.22
2.79
5.00
3.92
2.31
0.97
1.81
2.93
f1 (ppm)


Ph
Ph
N
140.55
139.10
136.70
131.65
131.00
128.65
128.60
128.46
126.32
125.92
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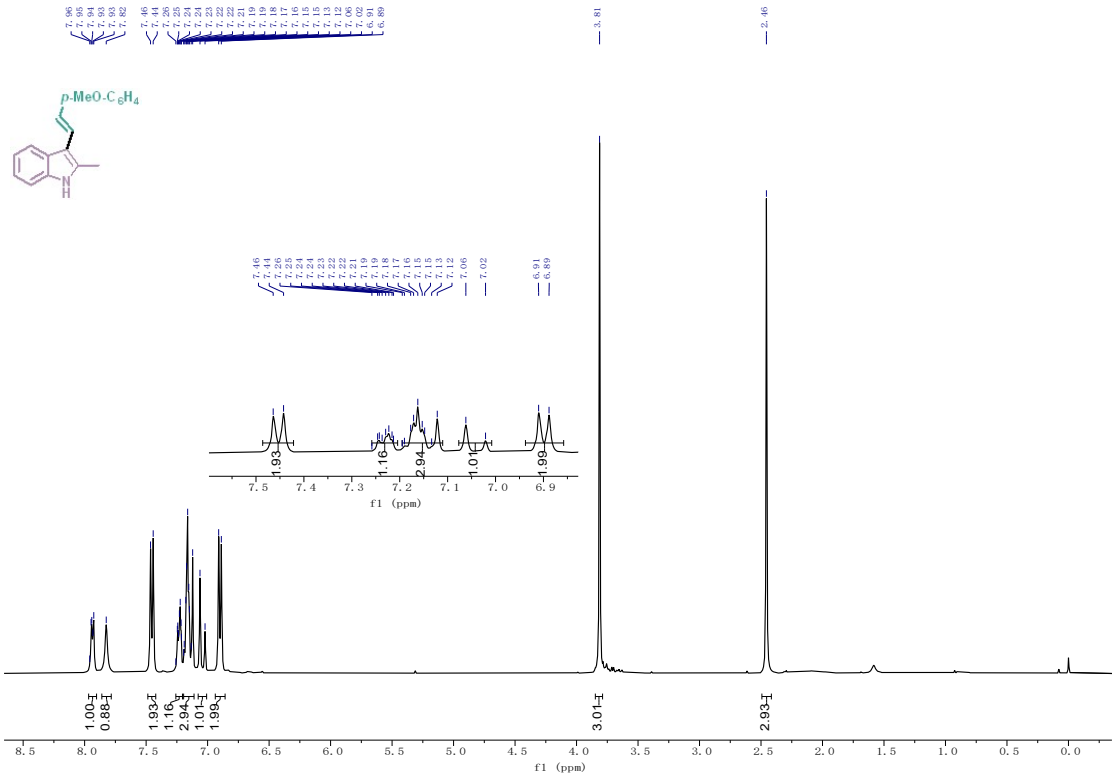
125.61
122.72
122.39
120.82
120.63
112.60
110.98
38.83
15.30
f1 (ppm)


p-MeO-C6H4
7.96
7.95
7.94
7.93
7.83
7.82
7.46
7.44
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.19
7.19
7.18
7.17
7.16
7.15
7.15
7.13
7.12
7.06
7.02
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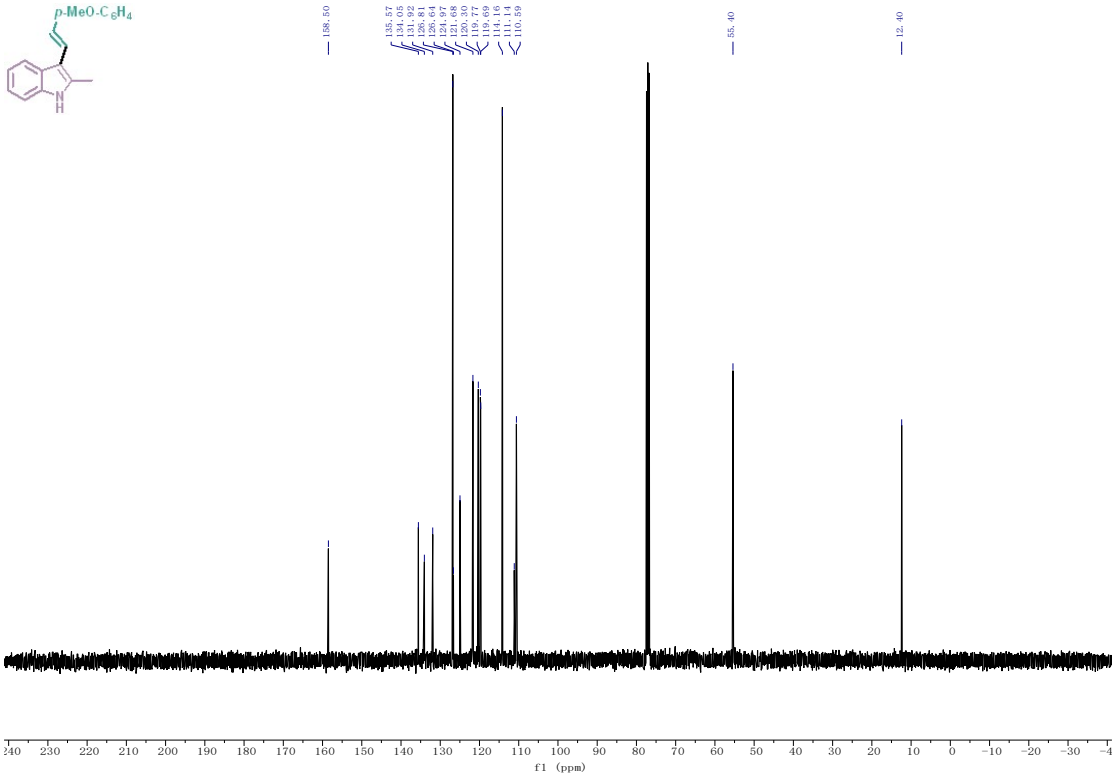
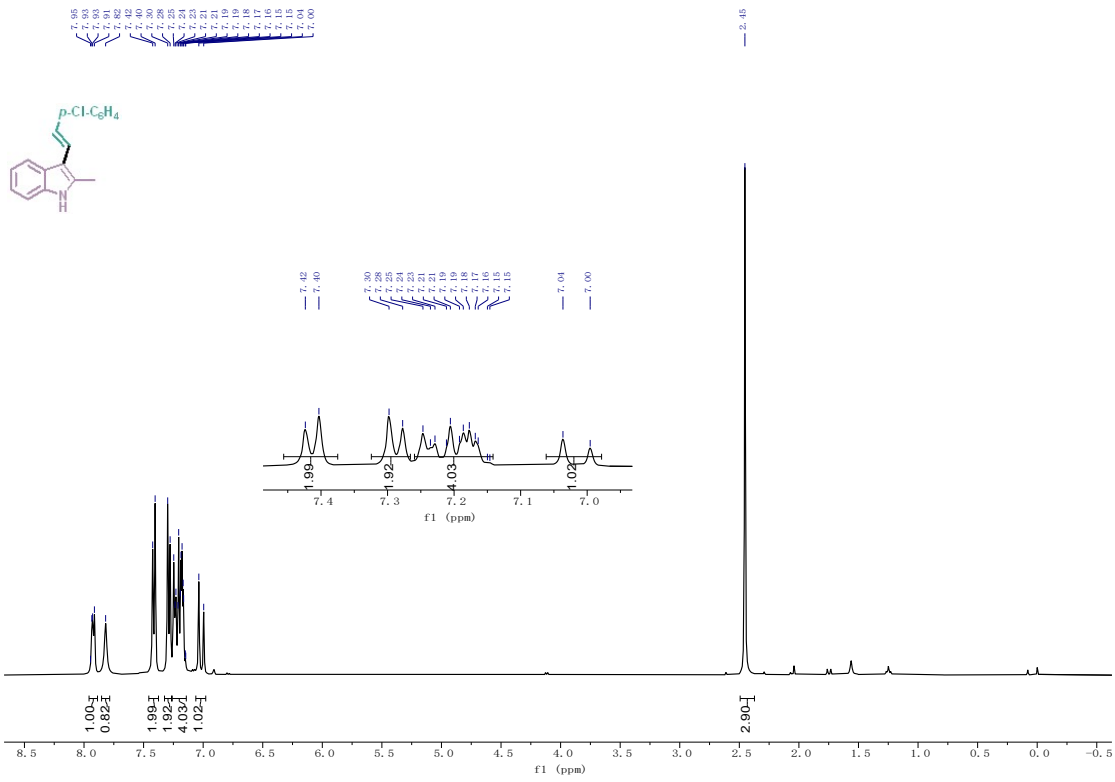
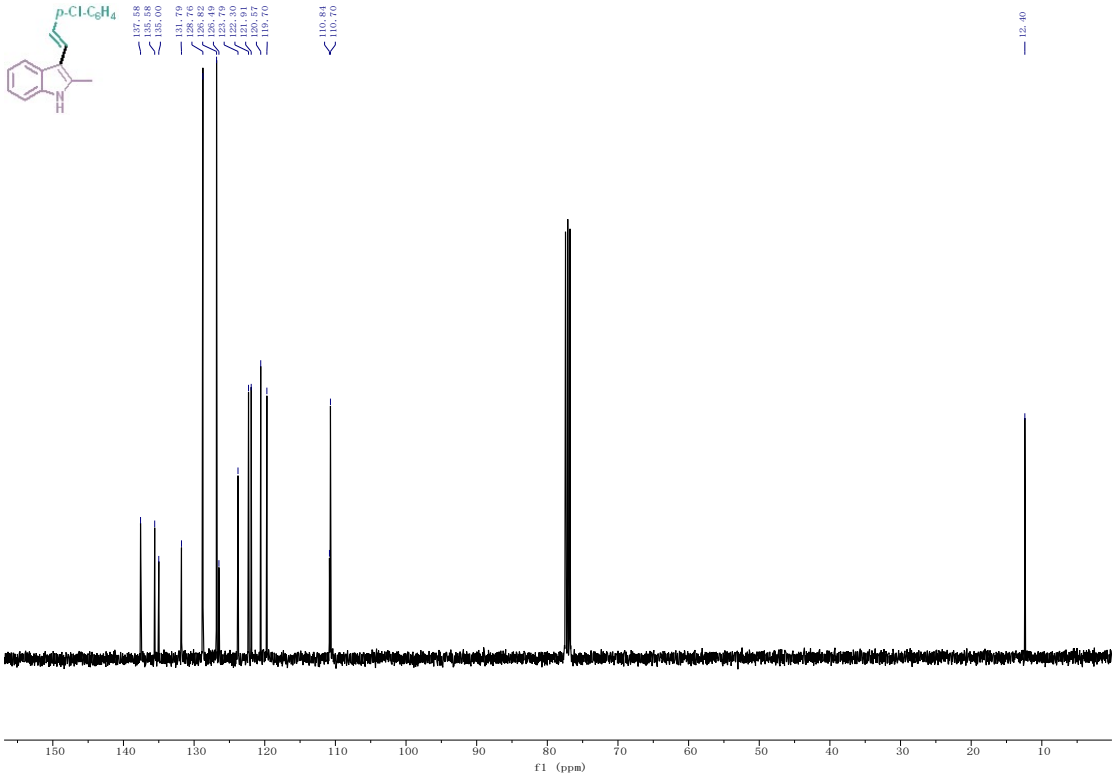
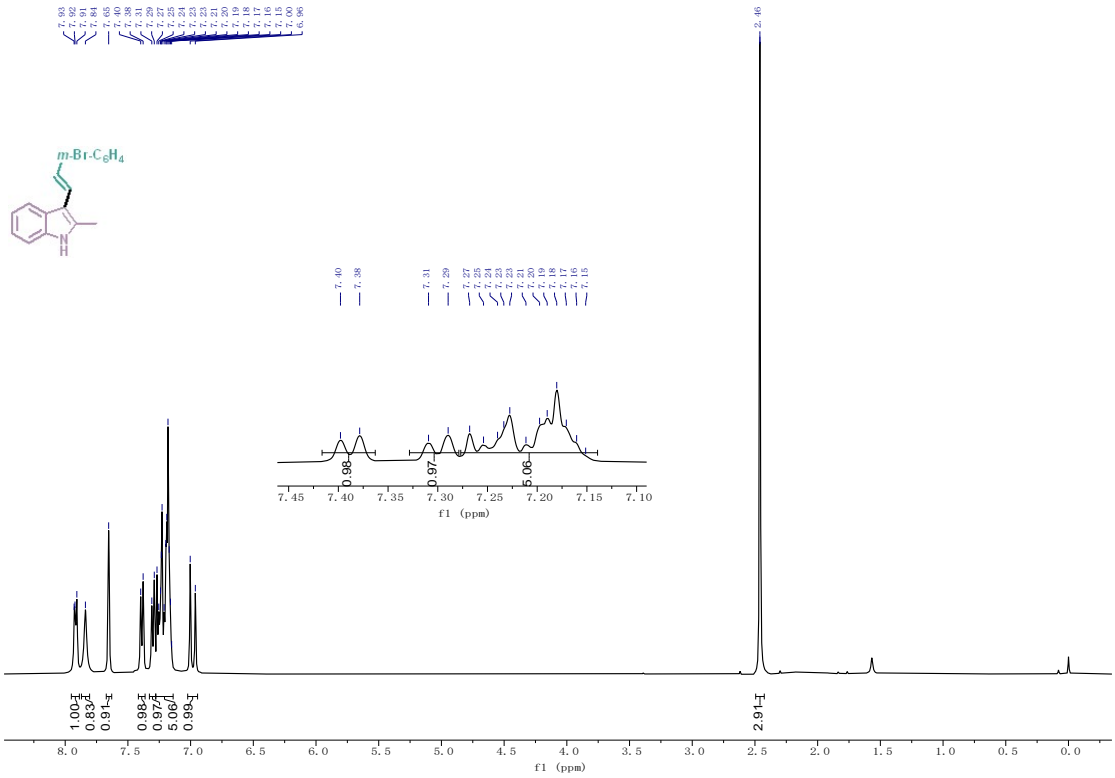
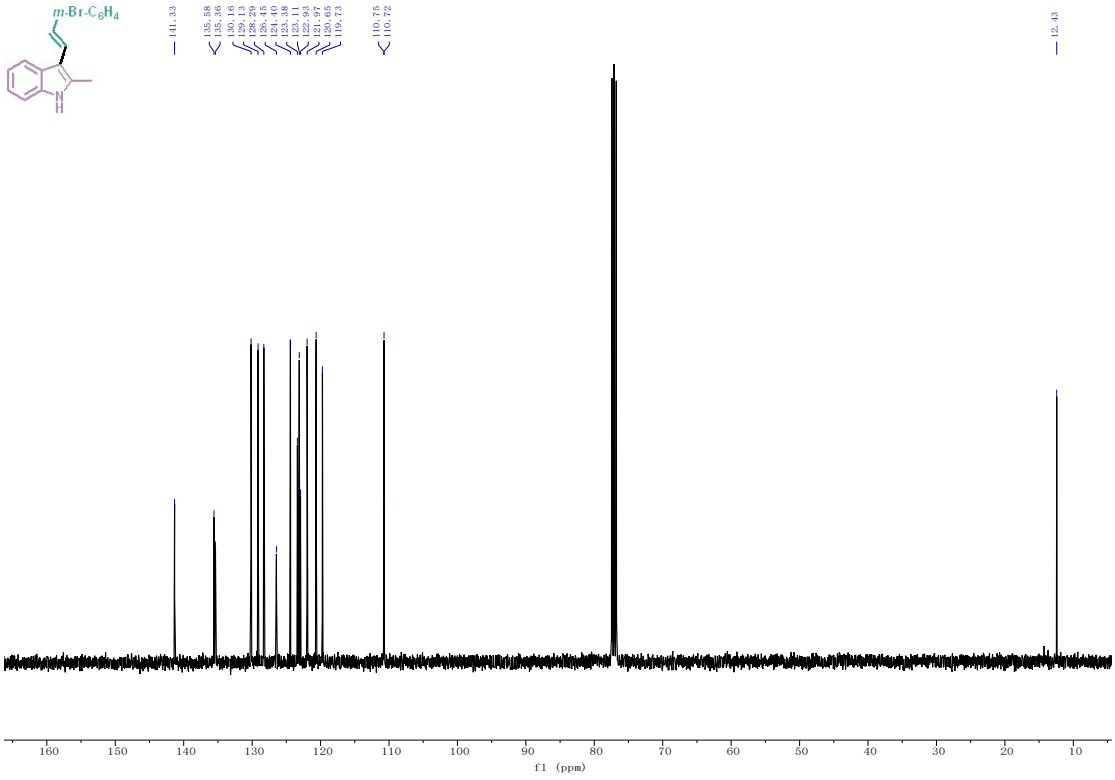
2.94
1.01
1.99
3.01
2.93
f1 (ppm)

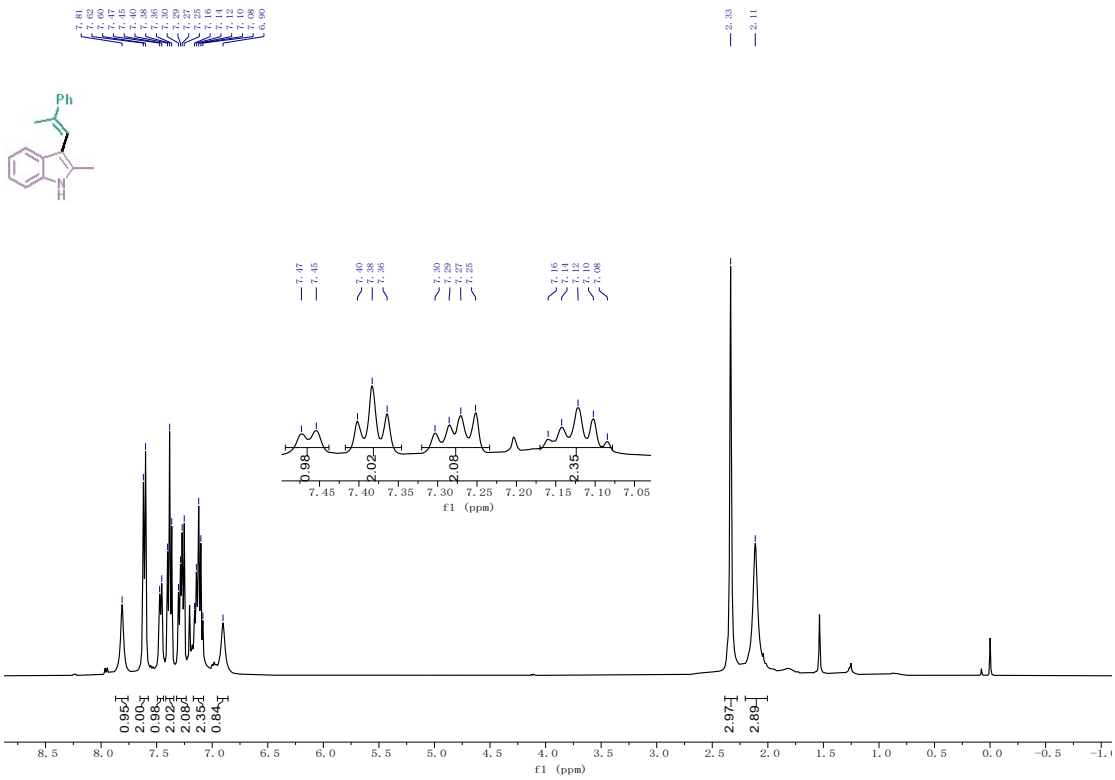

p-MeO-C6H4
158.50
135.57
134.05
131.92
128.81
126.64
124.97
121.68
120.10
119.77
119.69
114.16
111.14
110.99
55.40
12.40
f1 (ppm)

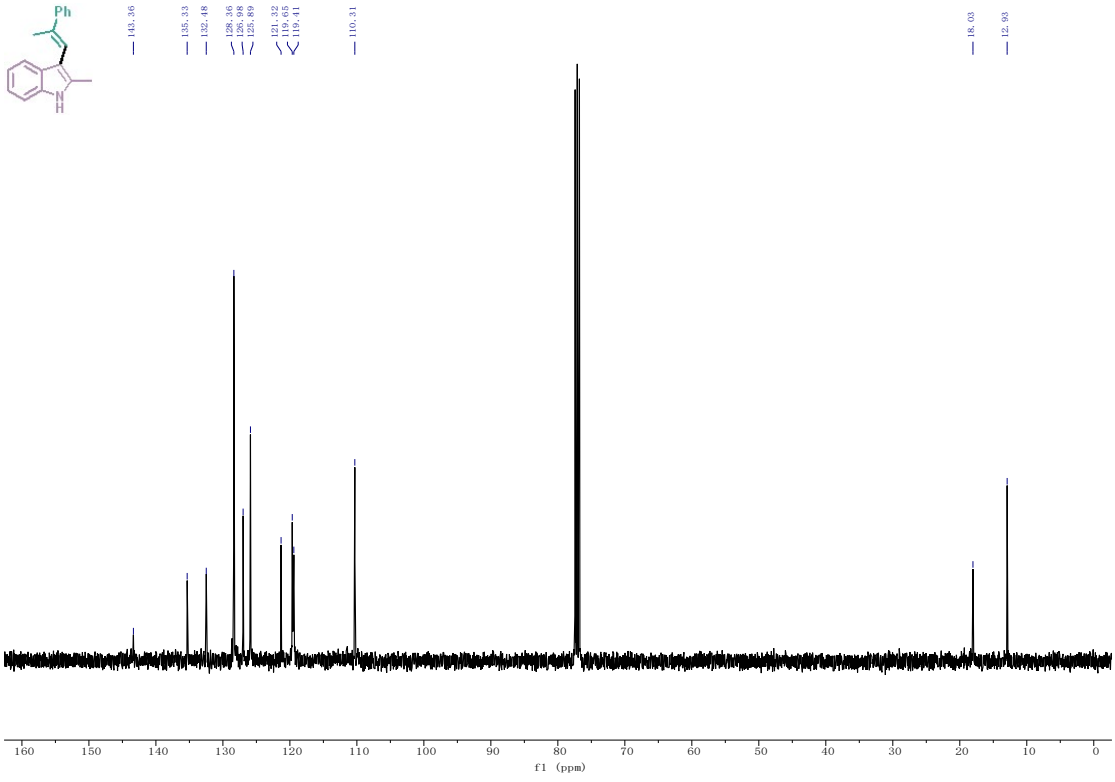

p-Cl-C6H4
7.95
7.93
7.93
7.91
7.82
7.42
7.40
7.30
7.28
7.25
7.24
7.23
7.21
7.21
7.19
7.19
7.18
7.17
7.16
7.15
7.15
7.04
7.00
2.45
1.00
0.82
1.99
1.92
4.03
1.02
2.90
f1 (ppm)

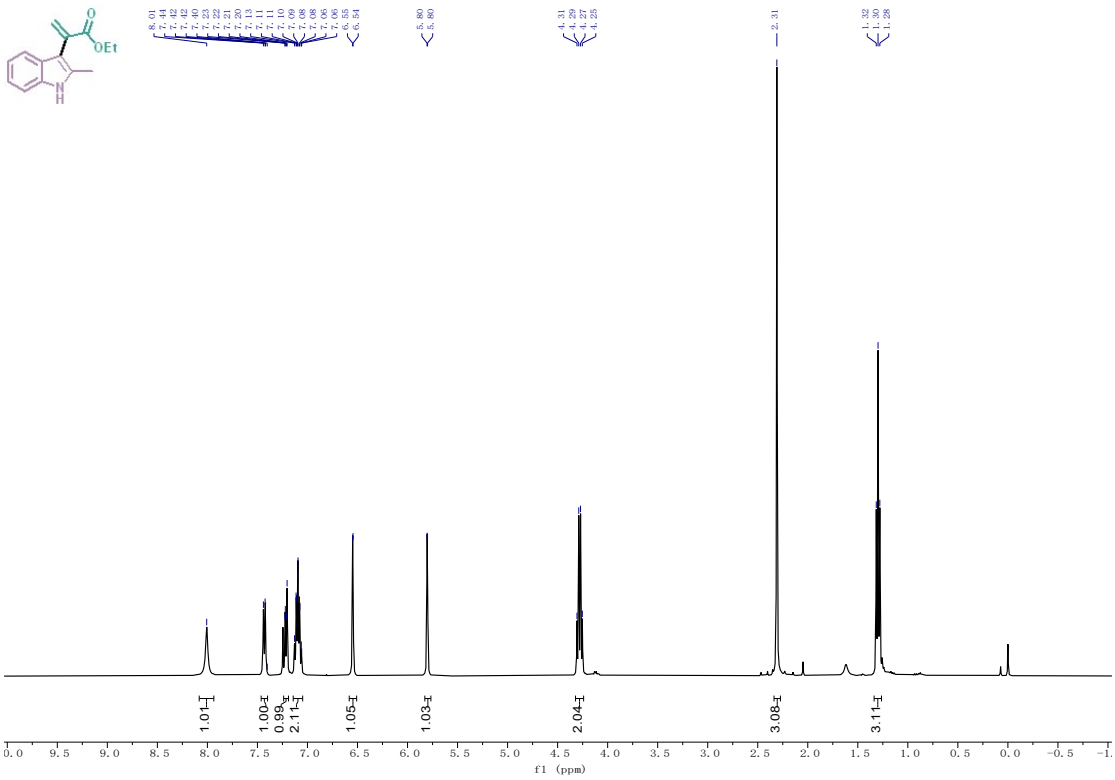

p-Cl-C6H4
137.58
135.68
135.00
131.79
128.76
126.82
126.49
123.79
122.30
121.91
120.57
119.70
110.84
110.70
12.40
f1 (ppm)

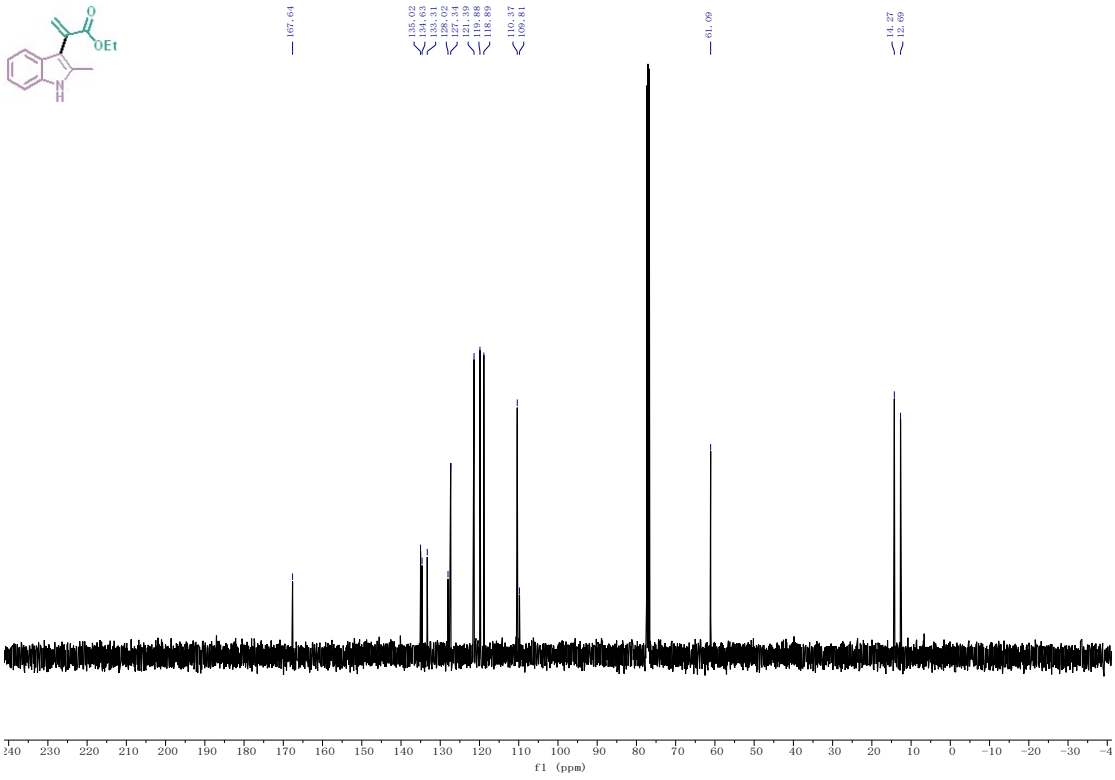

m-Br-C6H4
7.93
7.92
7.91
7.84
7.65
7.40
7.38
7.31
7.29
7.27
7.25
7.24
7.23
7.23
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.00
6.96
2.46
7.40
7.38
7.31
7.29
7.27
7.25
7.24
7.23
7.21
7.20
7.19
7.18
7.17
7.16
7.15
0.98
0.97
5.06
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
1.00
0.83
0.91
0.98
0.97
5.06
0.99
2.91
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)

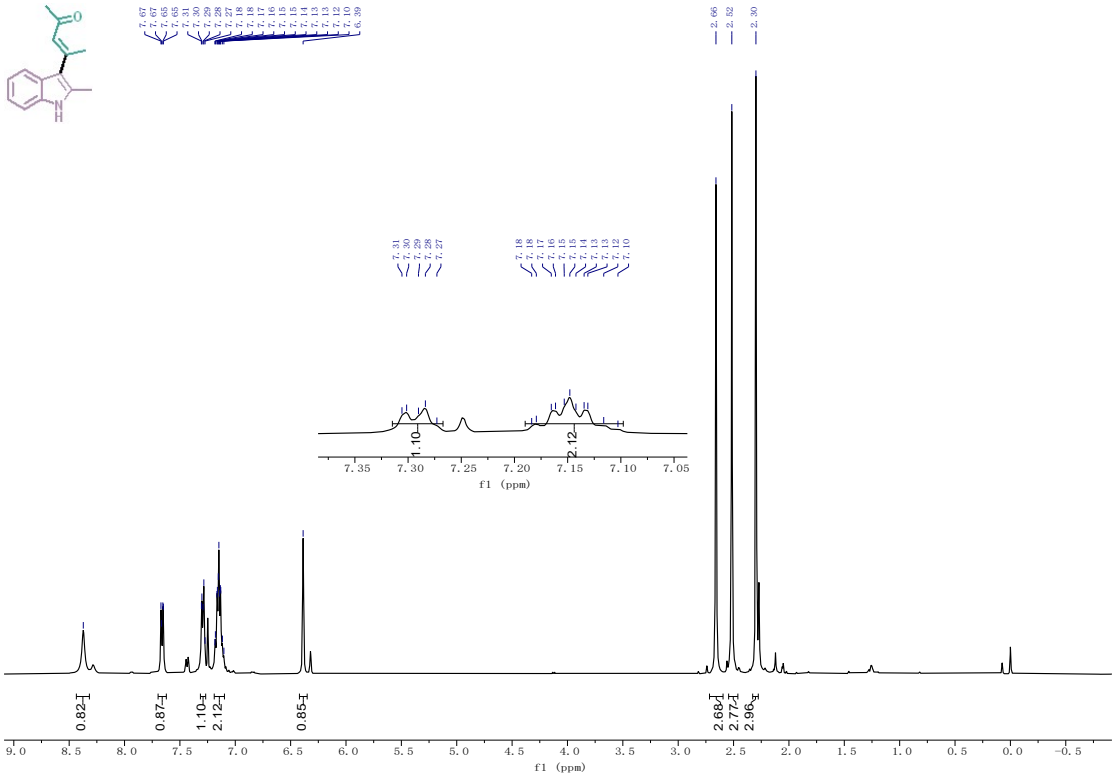

m-Br-C6H4
141.33
135.58
135.36
130.16
129.13
128.99
126.45
124.40
123.38
123.11
122.93
121.97
120.65
119.73
110.75
110.72
12.43
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

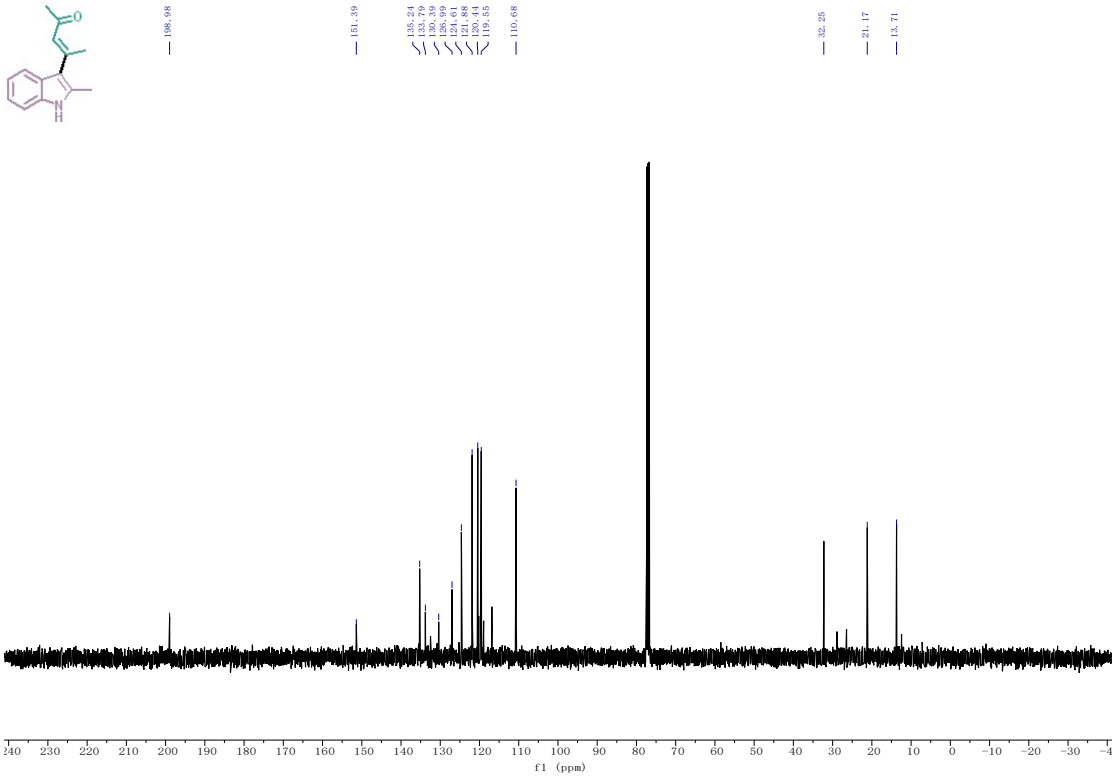

Ph
7.81
7.80
7.69
7.47
7.45
7.40
7.38
7.36
7.30
7.29
7.27
7.25
7.15
7.14
7.12
7.10
7.08
6.90
2.33
2.11
7.47
7.45
7.40
7.38
7.35
7.30
7.29
7.27
7.25
7.16
7.14
7.12
7.10
7.08
0.98
2.02
2.08
2.35
f1 (ppm)
0.95
2.00
0.98
2.02
2.08
2.35
0.84
2.97
2.89
f1 (ppm)

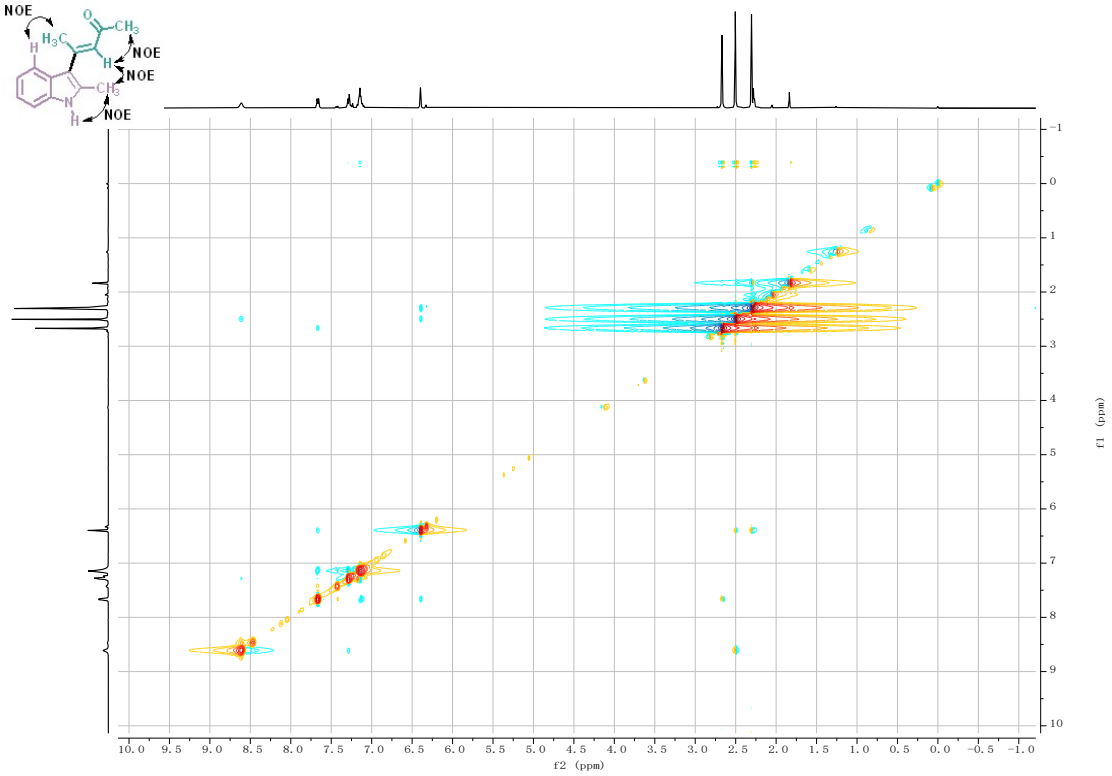

Ph
143.36
135.33
132.48
128.36
126.98
125.89
121.32
119.65
119.41
110.31
18.03
12.93
f1 (ppm)

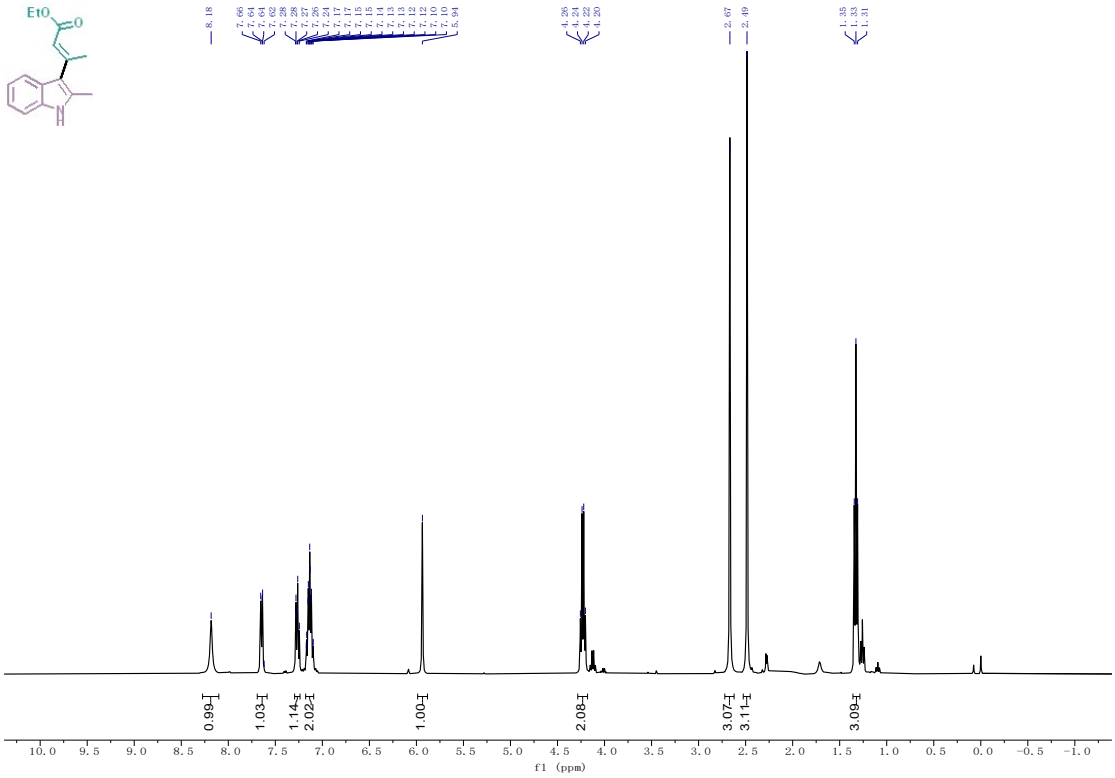

8.01
7.44
7.42
7.42
7.40
7.23
7.22
7.21
7.20
7.13
7.11
7.11
7.10
7.09
7.08
7.08
7.06
7.06
6.55
6.54
5.80
5.80
4.31
4.29
4.27
4.25
2.31
1.32
1.30
1.28
1.01
1.00
0.99
2.11
1.05
1.03
2.04
3.08
3.11
f1 (ppm)

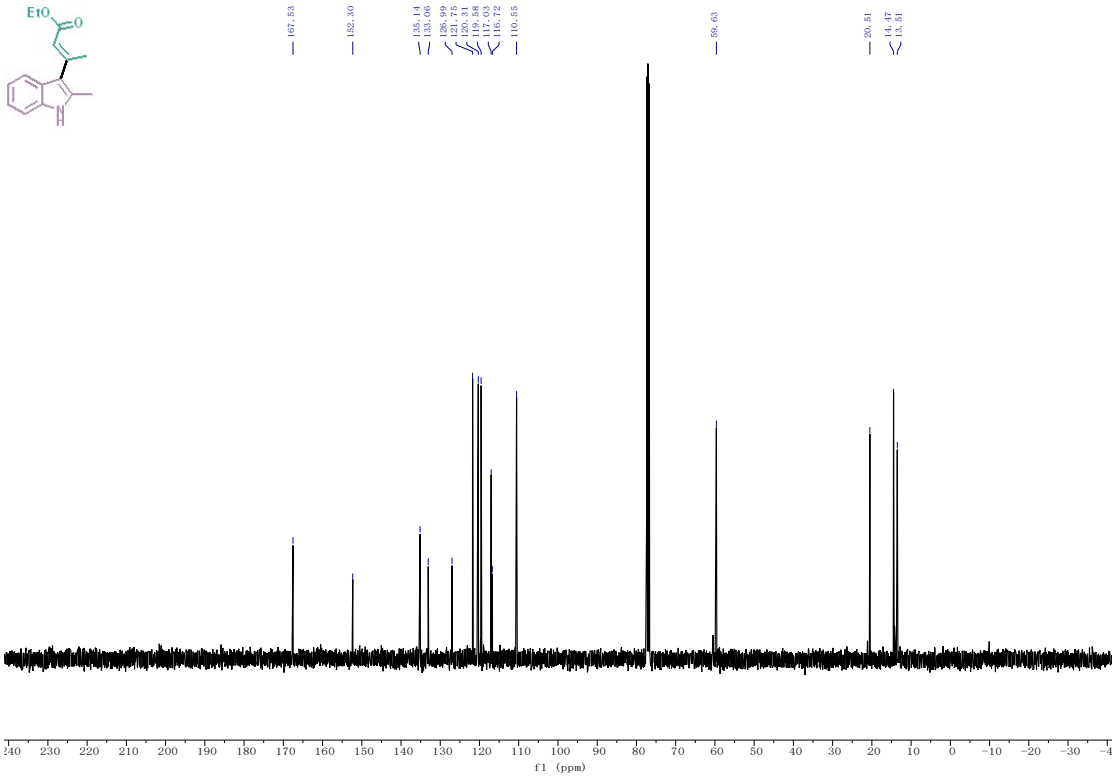

167.64
135.02
134.63
134.31
128.02
127.34
121.39
119.88
118.89
110.37
109.81
61.09
14.27
12.69
f1 (ppm)

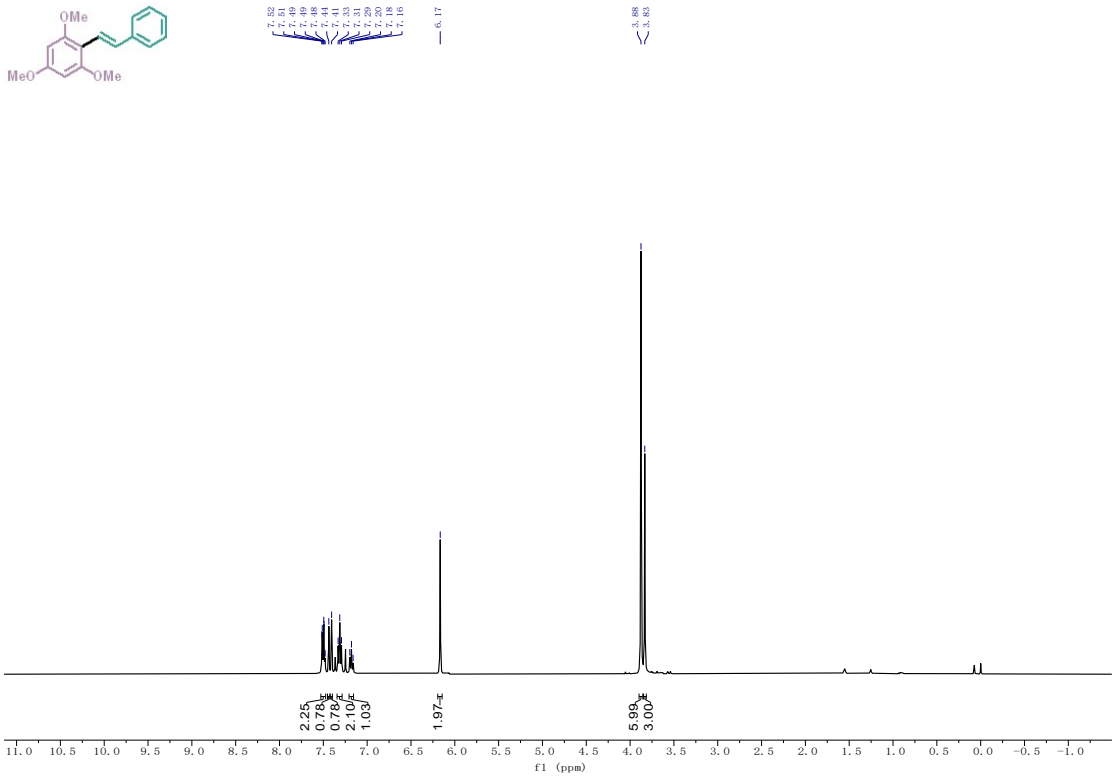


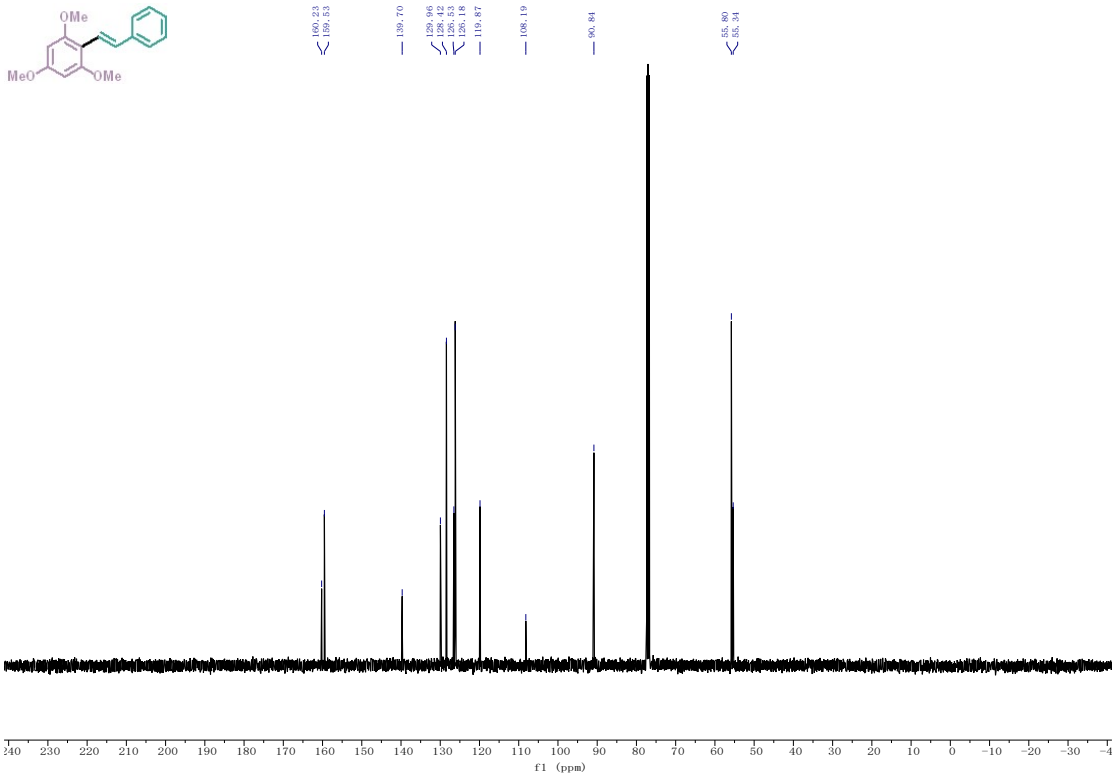



NOE
NOE
NOE
NOE
f2 (ppm)
f1 (ppm)


EtO
O
8.18
7.66
7.64
7.64
7.62
7.28
7.28
7.27
7.26
7.24
7.17
7.17
7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.10
7.10
5.94
4.26
4.24
4.22
4.20
2.67
2.49
1.35
1.33
1.31
0.99
1.03
1.14
2.02
1.00
2.08
3.07
3.11
3.09
f1 (ppm)


EtO
O
167.53
152.30
135.14
133.06
126.99
121.75
120.31
119.88
117.03
116.72
110.55
59.63
20.51
14.47
13.51
f1 (ppm)


OMe
MeO
OMe
7.52
7.51
7.49
7.49
7.48
7.44
7.41
7.33
7.31
7.29
7.20
7.18
7.16
6.17
3.88
3.83
2.25
0.78
0.78
2.10
1.03
1.97
5.99
3.00
f1 (ppm)


OMe
MeO
OMe
160.23
159.53
139.70
129.96
128.42
126.53
126.18
119.87
108.19
90.84
55.89
55.34
f1 (ppm)