Electronic Supplementary Material (ESI) for RSC Advances.

A novel bisoxazoline/Pd composite microsphere: a highly active catalyst for the Heck reactions

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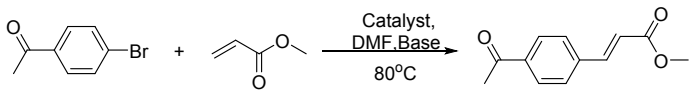
1. Materials and methods

Melting points were determined on a Perkin-Elmer differential scanning calorimeter and were uncorrected. The IR spectra were run on a Nicolete spectrometer (KBr). NMR spectra were recorded at 400 (^{1}H) and 100 (^{13}C) MHz, respectively, on a Varian Mercury plus-400 instrument using $CDCl_3$ as solvent and TMS as the internal standard. Scanning electron microscopy (SEM) was performed on a FEI Quanta 450 FEG FESEM instrument. High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). All the solvents used were strictly dried according to standard operation and stored on 4 Å molecular sieves.

All other chemicals (AR grade) were commercially available and used without further purification.

2.Optimization of the catalytic conditions

Table 1 The effect of solvents and bases[a]



Entry	Catalyst (Pd mol%)	Base	Time(h)	Yield(%)[b]
1	0.05	Na_2CO_3	2	56
2	0.05	K_2CO_3	2	72
3	0.05	KOAc	2	40
4	0.05	NaOAc	2	30
5	0.05	TEA	2	21
6	0.05	Pyridine	2	14
7	0	K_2CO_3	2	0
8	0.075	K_2CO_3	2	80
9	0.10	K_2CO_3	2	90
10	0.15	K_2CO_3	2	90
11	0.10	K_2CO_3	3	94
12	0.10	K_2CO_3	4	98
13	0.10	K_2CO_3	5	98

[a]Reaction conditions: bisoxazoline/Pd microsphere, 1 mmol of p-bromoacetophenone, 1 mmol of methyl acrylate, 2 mmol of base, 5 ml of solvent, 80 °C in air.
[b] Isolated yield.

3. Preparation and analytical data of catalyst C

Synthesis of bisacylthiourea B

To a solution of 4,4'-Oxybisbenzoyl chloride **A** (2 mmol) in CH_2Cl_2 (10 mL) was added ammonium thiocyanate (2.6 mmol) and PEG-400 (0.2 mmol). The mixture was then stirred at room temperature for 60 min and cooled to 0˚C, and the solution of 2-aminoethanol (1.8 mmol) in CH_2Cl_2 (2 mL) was added. The mixture was continuously stirred for 60 min. After the completion of the reaction, the solvent was removed by distillation, and water (10 mL) was added to obtain a white solid. The analytical sample was produced by flash chromatography(acetone and petroleum ether) to give a white solid **B**. Yield: 85%. Melting point: 209-211^{o}C. Spectral data: IR (KBr) (cm^{-1}): ν 3337, 3225, 2944, 1670, 1531. ^{1}H NMR (400 MHz, DMSO) δ 11.35 (s, 2H), 11.05 (s, 2H), 8.02 (d, *J* = 8.8 Hz, 4H), 7.17 (d, *J* = 8.8 Hz, 4H), 4.98 (s, 2H), 3.83-3.44 (m, 8H). ^{13}C NMR (100 MHz, DMSO) δ 180.71, 167.65, 159.87, 131.68, 128.22, 118.95, 58.75, 47.97, 40.38, 40.17, 39.96, 39.75, 39.54. HR-MS: m/z calcd for $C_{20}H_{21}N_2O_5S_2$ $[M+H]^+$: 433.0892; found: 433.0889.

Synthesis of bisoxazoline C

To a solution of compound **B** (1 mmol) in DMF (5 mL) was added dicyclohexylcarbodiimide (DCC) (1 mmol) and TEA(1 mmol). The mixture was stirred for 2 h at 80^{o}C, and cooled to room temperature. After the addition of water (5 mL), the white solid was obtained by the filtration. This solid was added into CH_3CN (5 mL) to be dissolved, followed by the filtration and concentration to afford the target compound **C**. Yield: 98%. Melting point: 195-196^{o}C. Spectral data: IR (KBr) (cm^{-1}): ν 3310, 2921, 1638, 1548. ^{1}H NMR (400 MHz, DMSO) δ 9.61 (s, 2H), 8.28 – 7.99 (m, 4H), 7.20 – 6.98 (m, 4H), 4.47 (t, J = 8.6 Hz, 4H), 3.78 (t, J = 8.6 Hz, 4H). ^{13}C NMR (100 MHz, DMSO) δ 180.71, 167.65, 159.87, 131.68, 128.22, 118.95, 58.75, 47.97, 40.59, 40.38, 40.17, 39.96, 39.75, 39.54, 39.33. HR-MS: m/z calcd for $C_{20}H_{19}N_4O_5$ $[M+H]^+$: 395.1355; found: 395.1395.

Synthesis of catalyst D

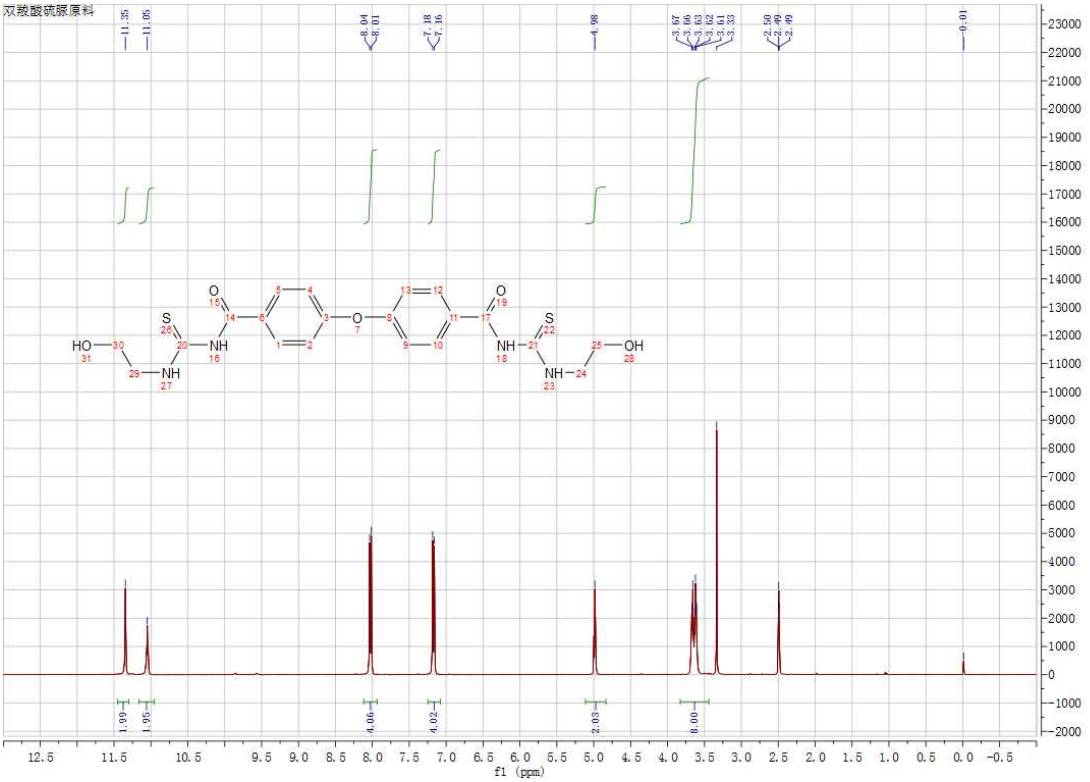
To the solution of $Pd(AcO)_2$ (2 mmol) in CH_3CN (5 mL) was added dropwise into the obtained compound **C** (1.36 g, 6 mmol) in CH_3CN (2 mL), followed by the stiring for 10 h. On completion, the filtration was conducted to a yellow solid. Washing with commercial anhydrous CH_3CN (3 × 5 mL) and drying at 50 °C overnight gave bisoxazoline/Pd microsphere as a pale yellow powder(compound **D**). IR (KBr) (cm^{-1}): ν 3443, 2907, 1592. The Pd content of the bisoxazoline/Pd microsphere catalyst is 20.01 wt% (1.8 mmol/g) measured by atomic absorption spectroscopy (AAS).

4. General Experimental Procedures for Suzuki-Miyaura Couplings

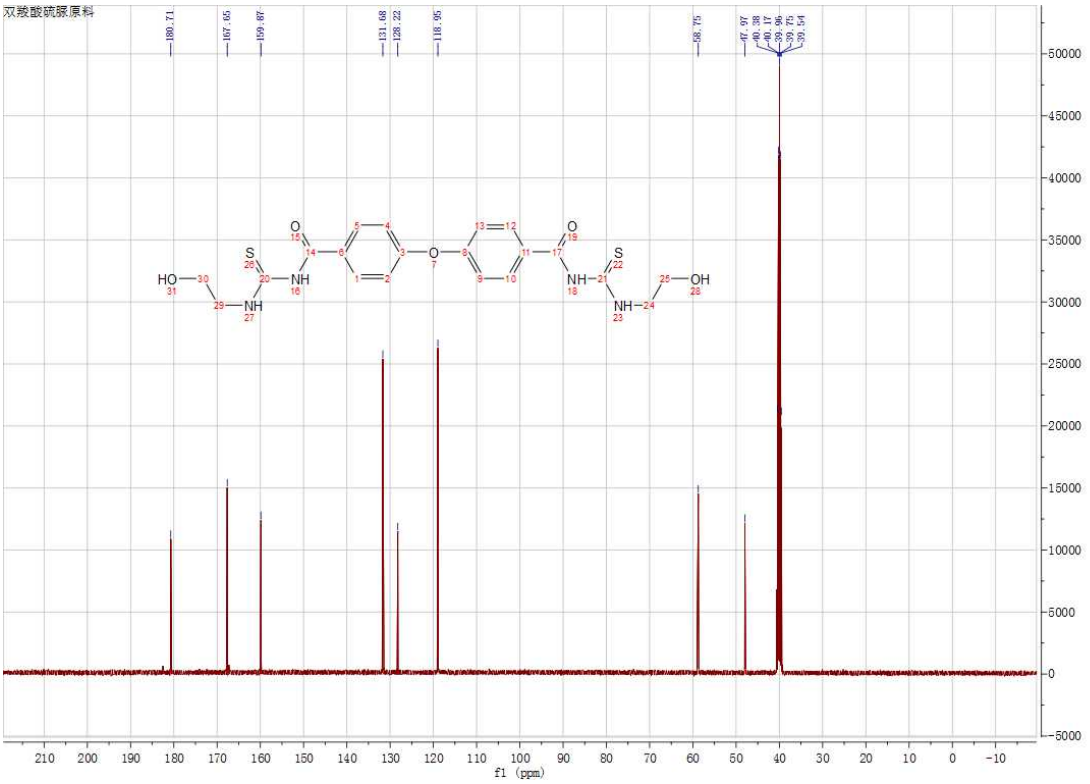
In a typical experiment, the bisoxazoline/Pd microsphere catalyst (0.10 mmol of Pd) was added to a mixture of aryl halide (1.0 mmol), olefins (1.2 mmol), and K2CO3 (1.0 mmol) in DMF (5.0 mL), and the reaction mixture was stirred at 80^{o}C. After the reaction was monitored to be complete by TLC analysis, the catalyst was removed by filtration, washed with ethanol (3 × 3 mL), and dried under vacuum for the next run. The organic fractions were then concentrated on a rotary evaporator to afford the desired compoundd in excellent yield. The crude products were purified by column chromatography on silica gel using hexane/ethyl acetate.

5. NMR spectra of the materials and products

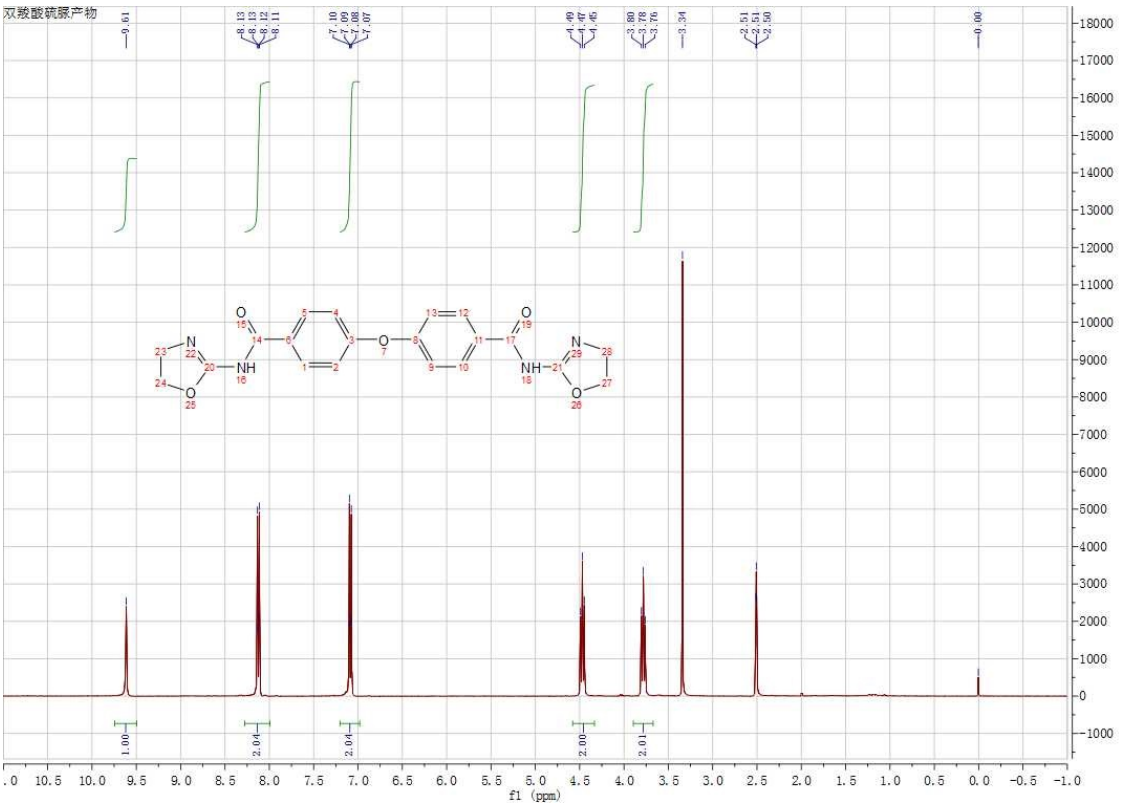
^{1}H NMR of bisacylthiourea B



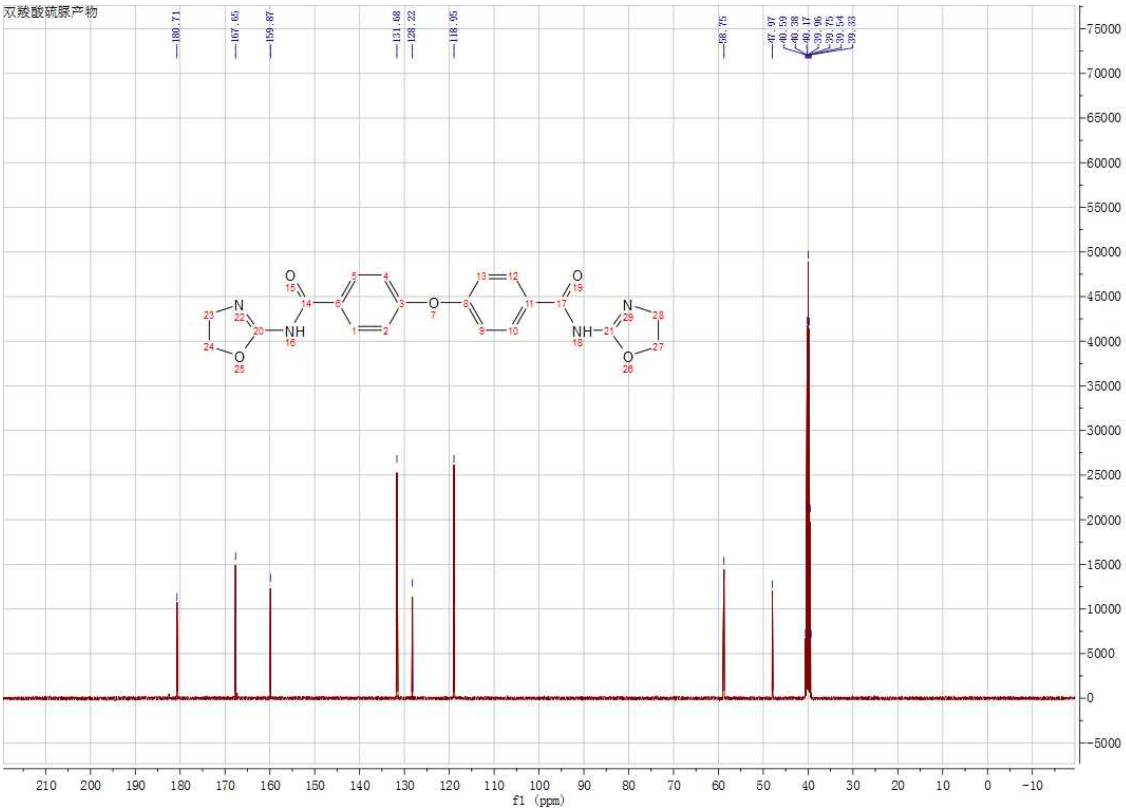
^{13}C NMR of bisacylthiourea B



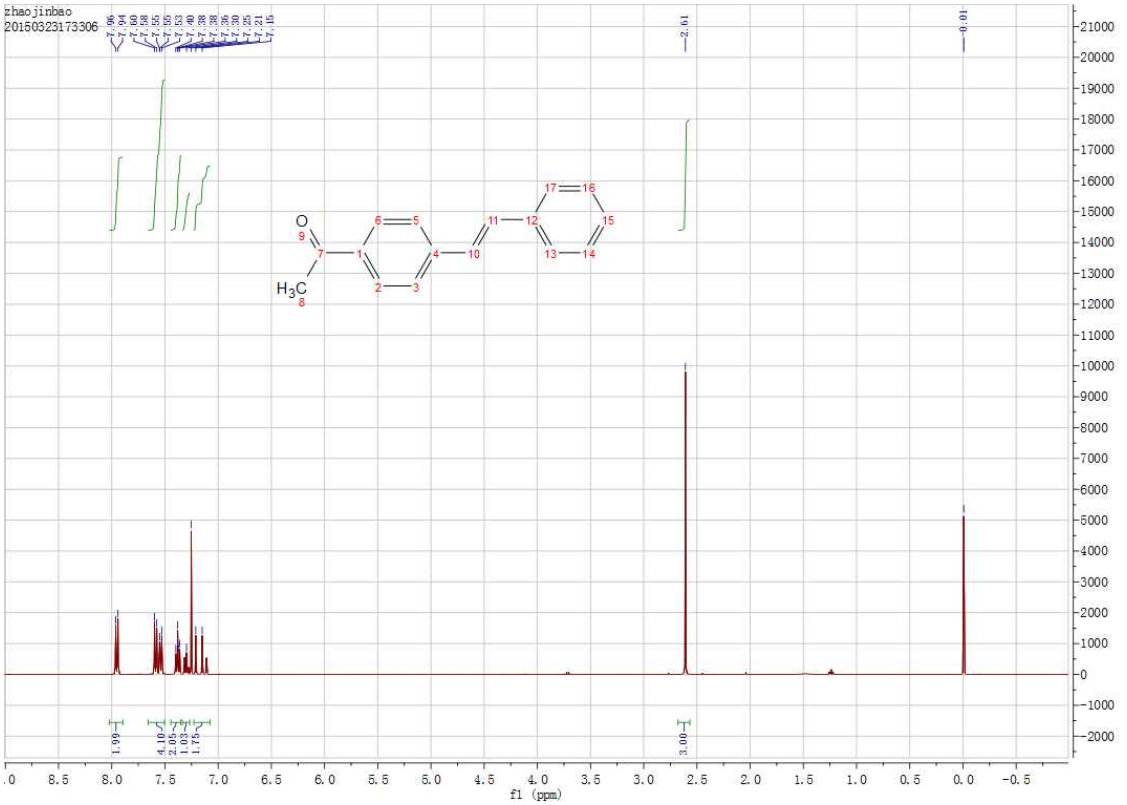
^{1}H NMR of bisoxazoline C



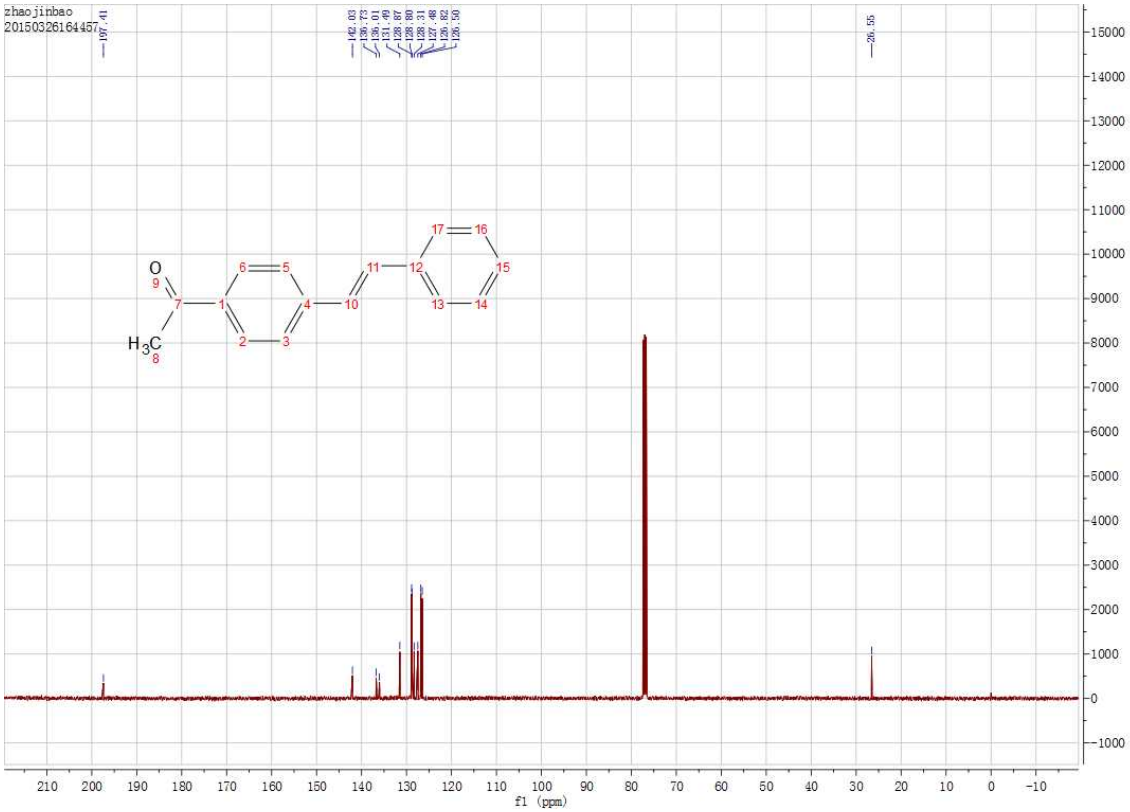
^{13}C NMR of bisoxazoline C



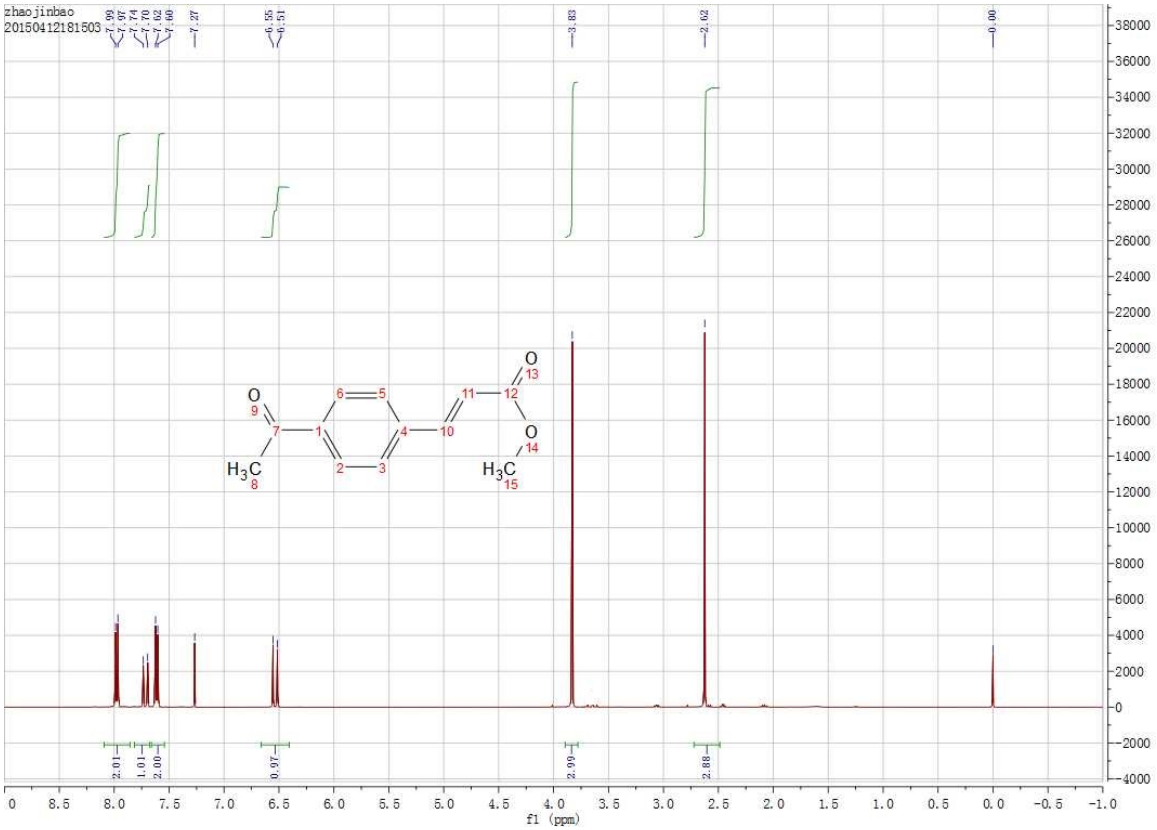
Entry 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.66 – 7.50 (m, 4H), 7.38 (dd, J = 8.1, 6.8 Hz, 2H), 7.30 (s, 1H), 7.18 (d, J = 24.2 Hz, 2H), 2.61 (s, 3H).



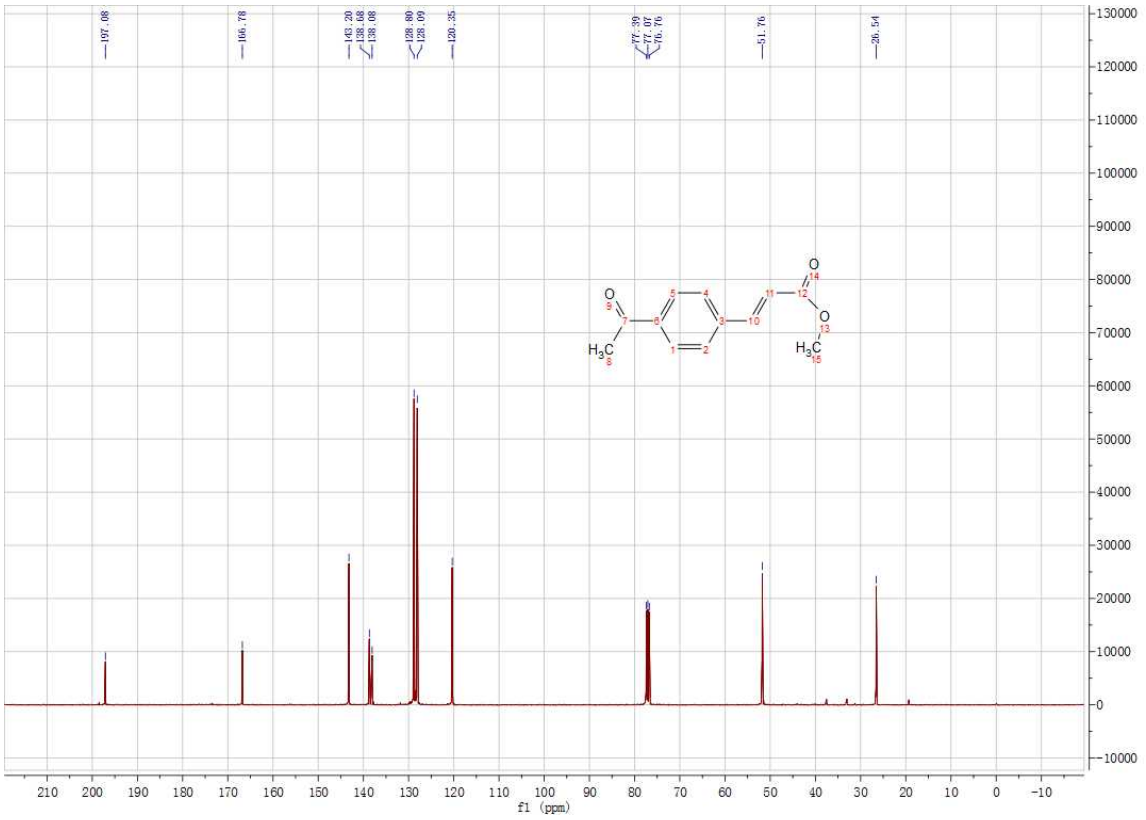
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.41 , 142.03 , 136.73 , 136.01 , 131.49 , 128.83, 128.31 , 127.48 , 126.82 , 126.50 , 26.55 .



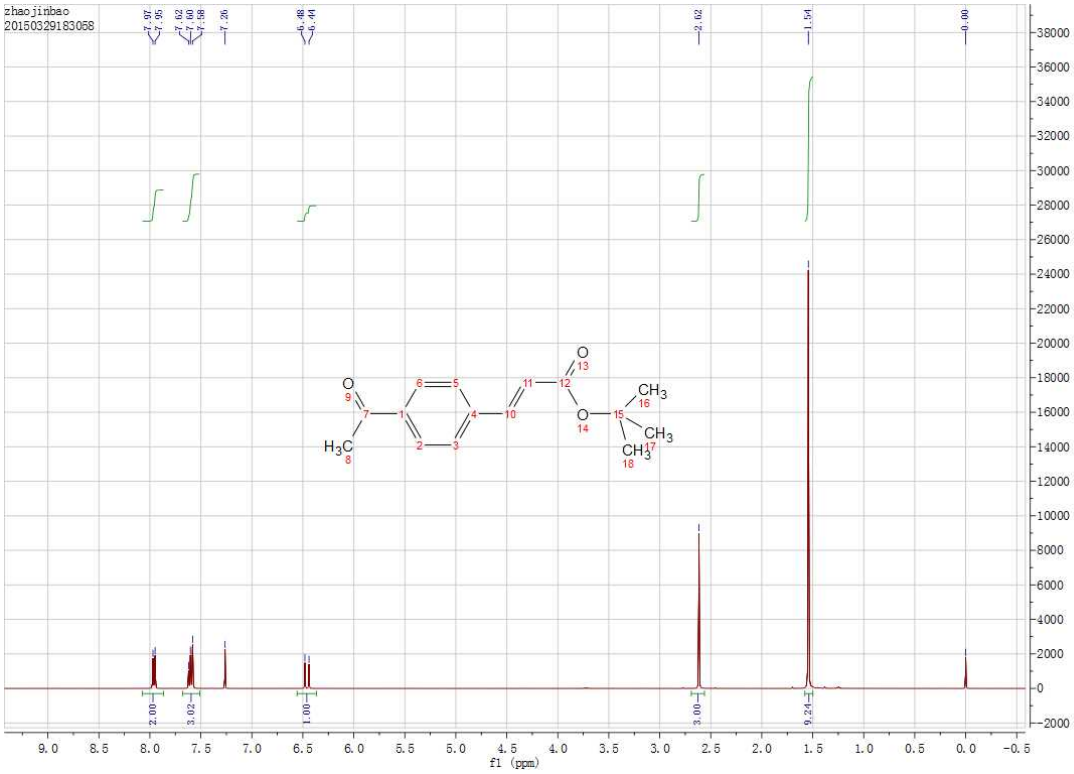
Entry 2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 16.1 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 16.1 Hz, 1H), 3.83 (s, 3H), 2.62 (s, 3H).



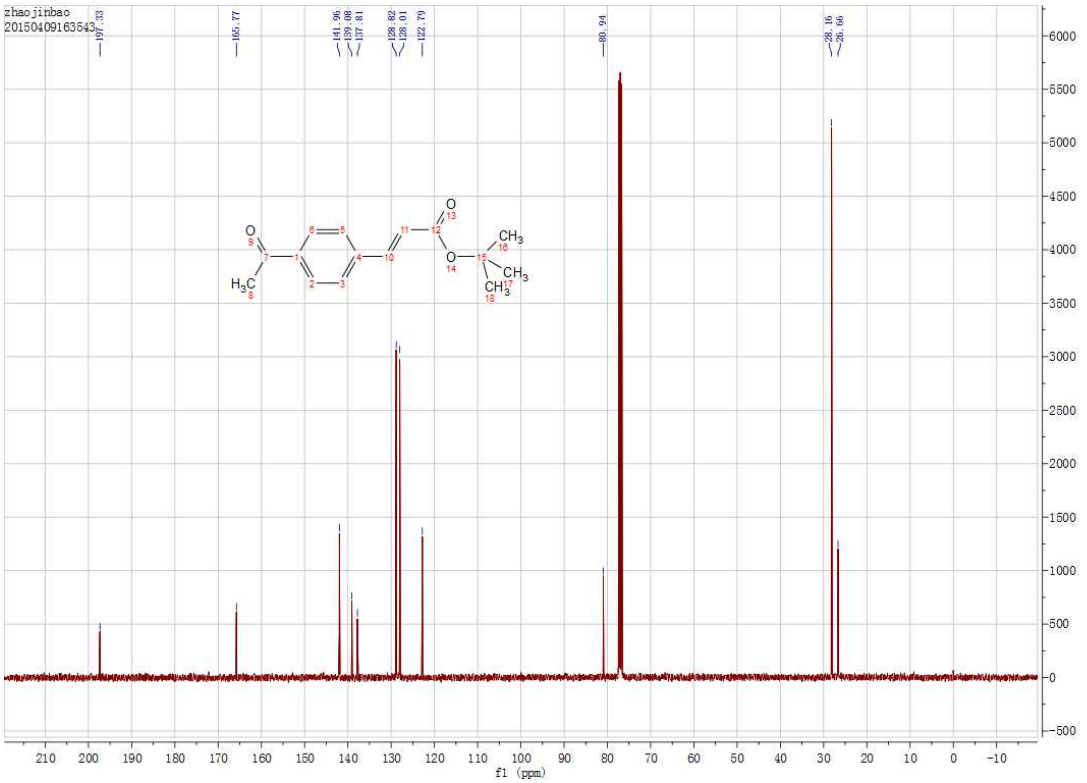
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.08 , 166.78 , 143.20 , 138.68 , 138.08 , 128.80 , 128.09 , 120.35 , 77.39 , 77.07 , 76.76 , 51.76 , 26.54 .



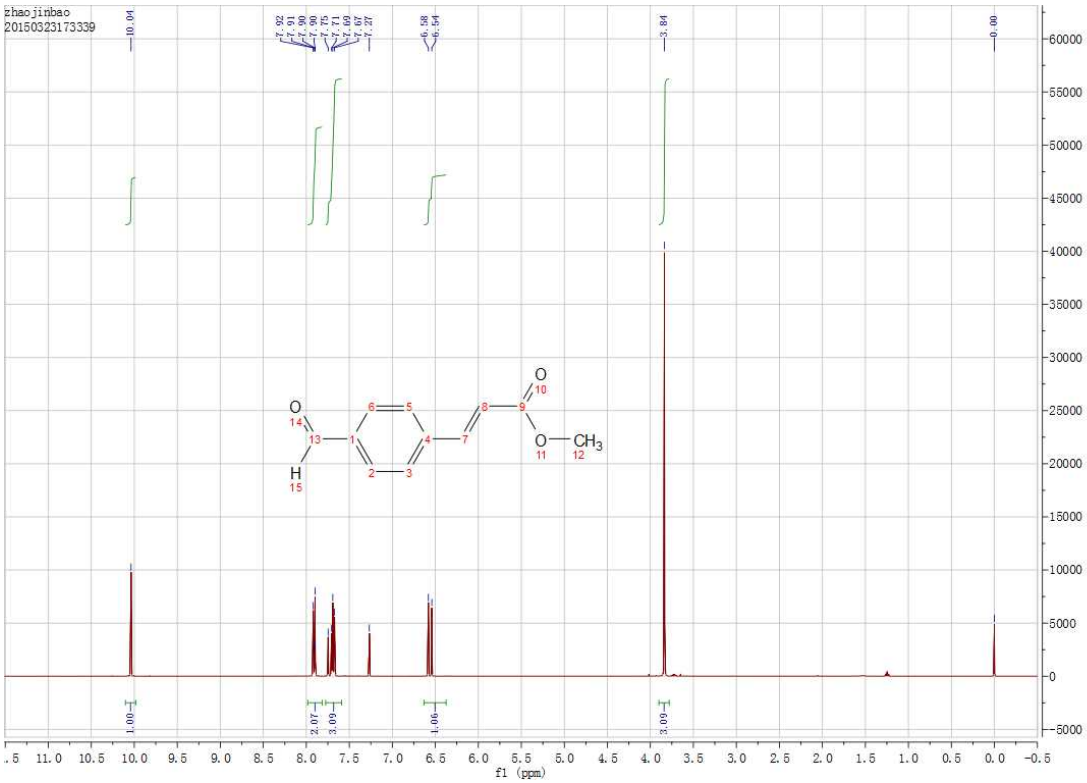
Entry 3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 2H), 7.68 – 7.51 (m, 3H), 6.46 (d, J = 16.1 Hz, 1H), 2.62 (s, 3H), 1.54 (s, 9H).



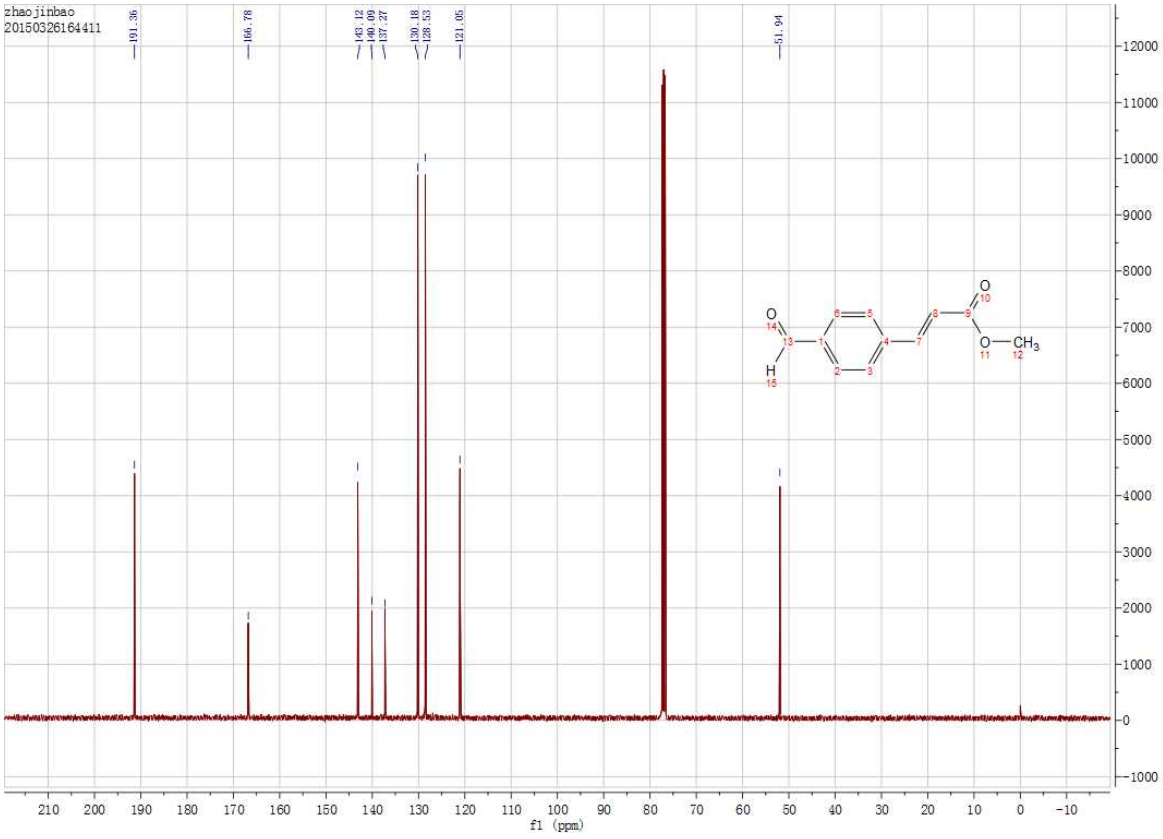
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.33 , 165.77 , 141.96 , 139.08 , 137.81 , 128.82 , 128.01 , 122.79 , 80.94 , 77.34 , 77.02 , 76.70 , 28.16 , 26.66 .



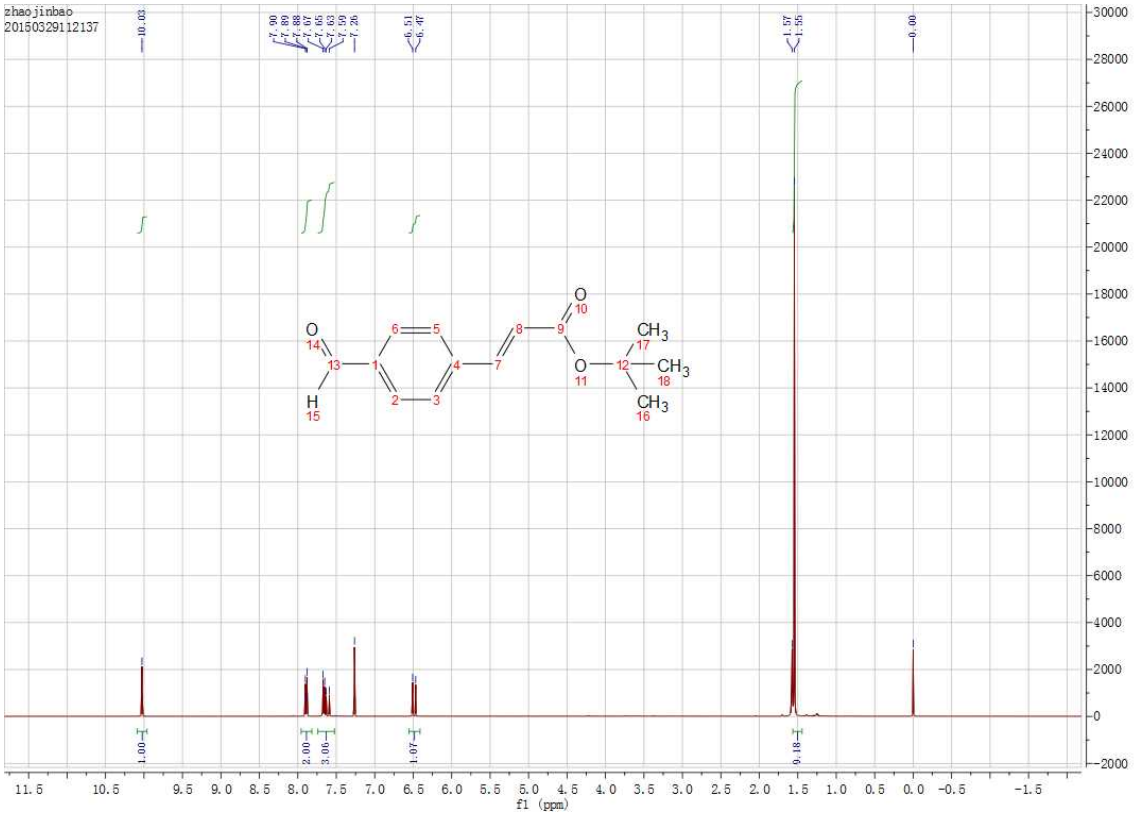
Entry 4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.98 – 7.82 (m, 2H), 7.70 (dd, *J* = 17.7, 12.2 Hz, 3H), 6.56 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H).



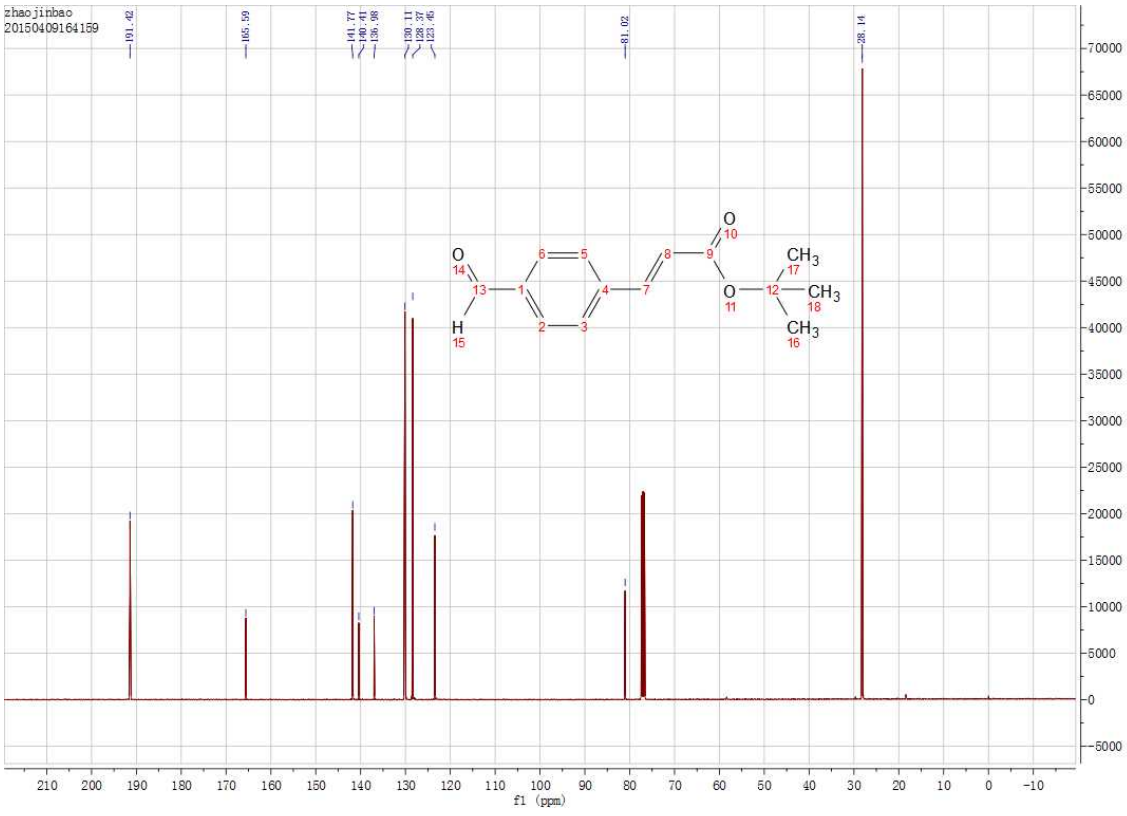
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.36 , 166.78 , 143.12 , 140.09 , 137.27 , 130.18 , 128.53 , 121.05 , 51.94 .



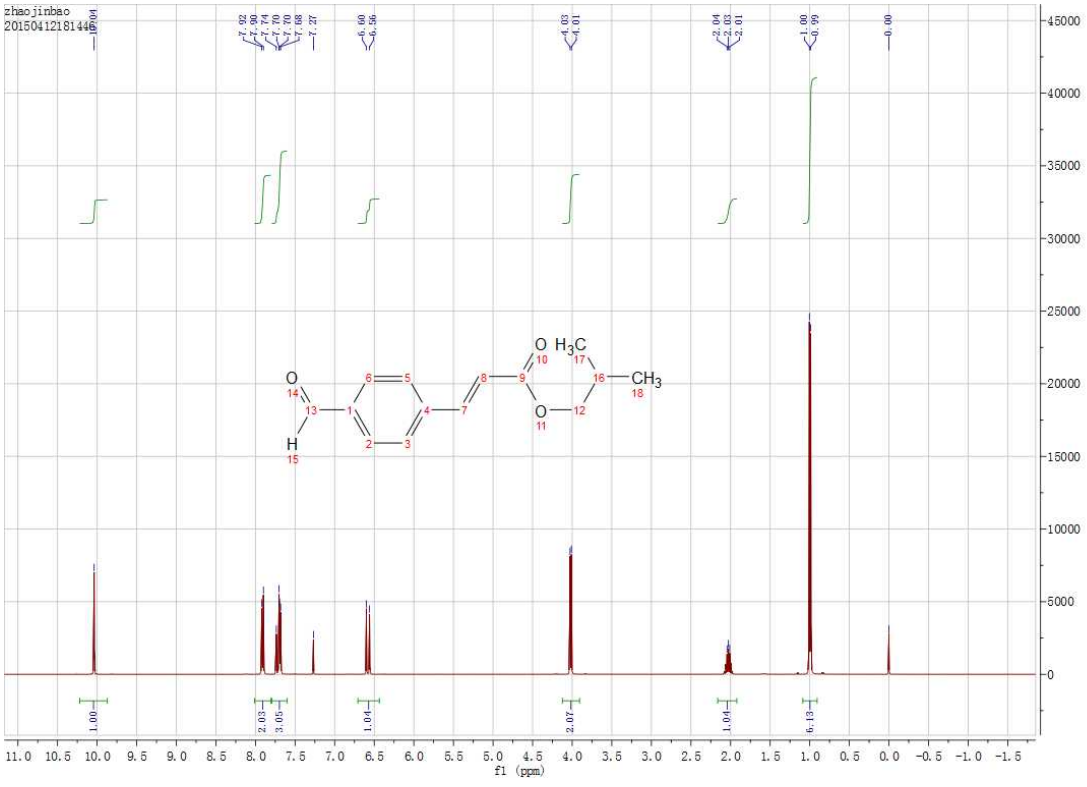
Entry 5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.96 – 7.82 (m, 2H), 7.64 (dd, J = 20.3, 12.2 Hz, 3H), 6.49 (d, J = 16.0 Hz, 1H), 1.55 (s, 9H).



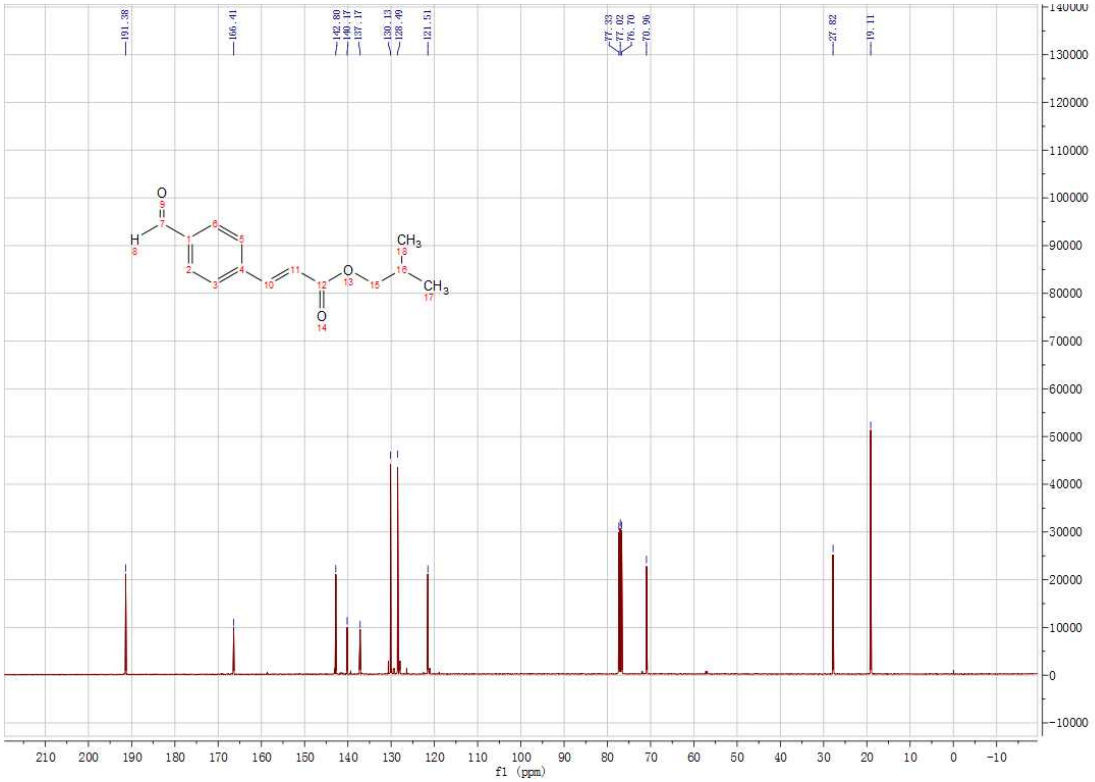
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.42 , 165.59 , 141.77 , 140.41 , 136.98 , 130.11 , 128.37 , 123.45 , 81.02 , 28.14 .



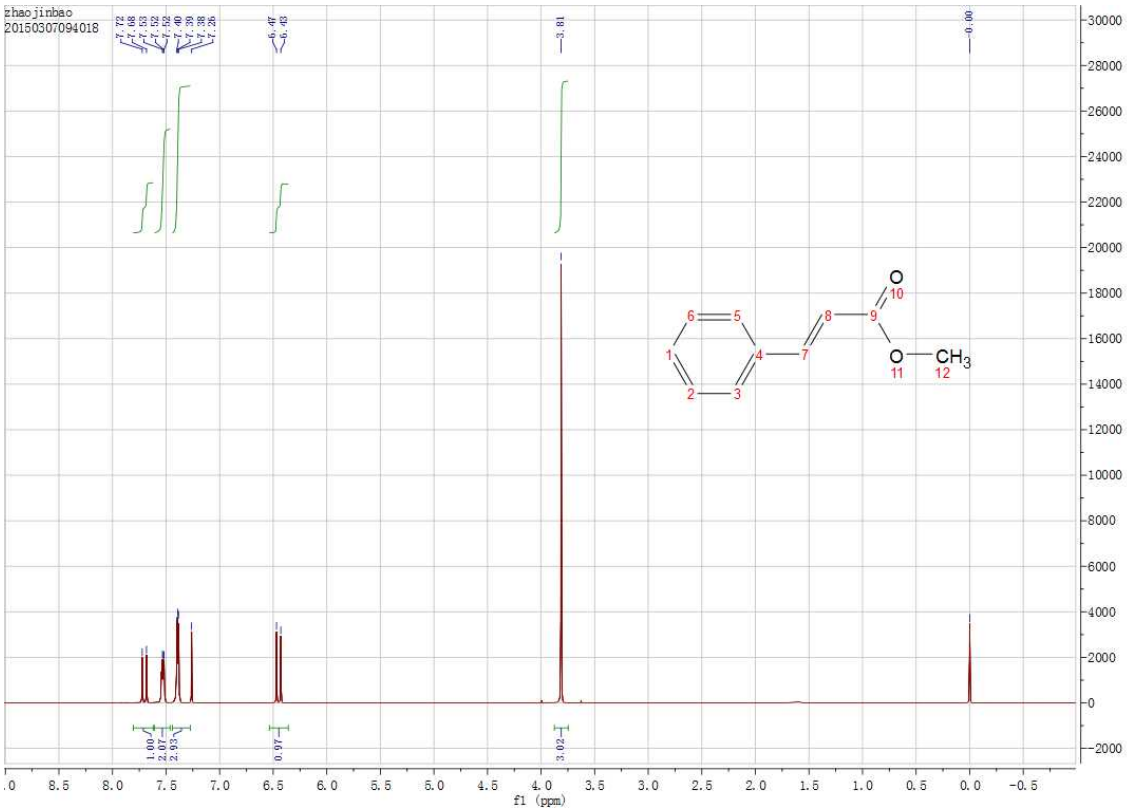
Entry 6. ^1H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.70 (dd, *J* = 12.0, 10.0 Hz, 3H), 6.58 (d, *J* = 16.1 Hz, 1H), 4.02 (d, *J* = 6.7 Hz, 2H), 2.16 – 1.92 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 6H).



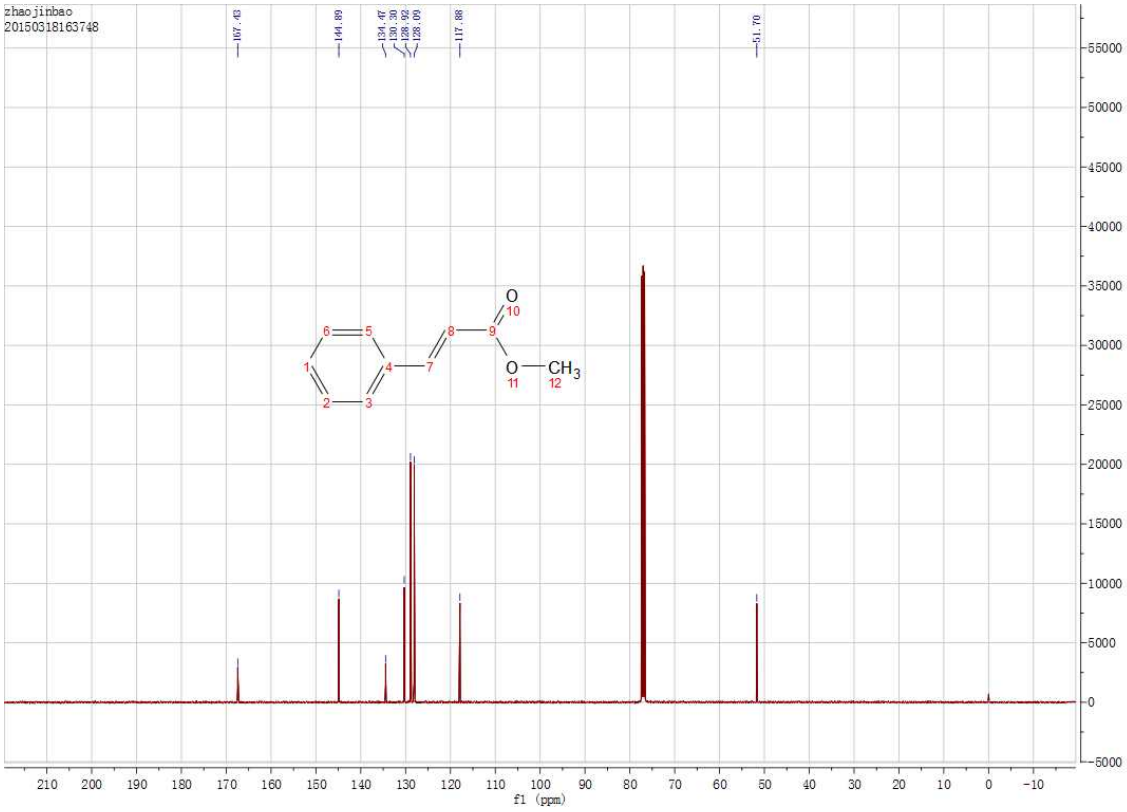
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.38 , 166.41 , 142.80 , 140.17 , 137.17 , 130.13 , 128.49 , 121.51 , 77.33 , 77.02 , 76.70 , 70.96 , 27.82 , 19.11 .



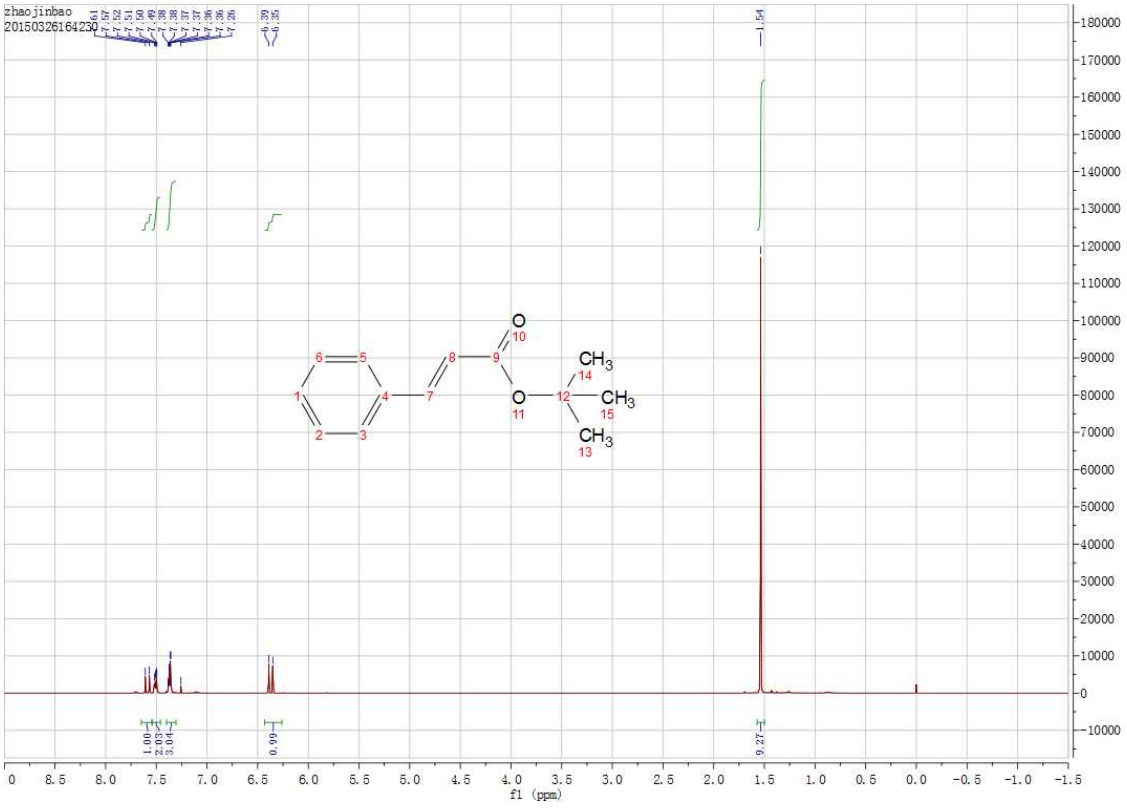
Entry 7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 16.0 Hz, 1H), 7.61 – 7.46 (m, 2H), 7.44 – 7.27 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H).



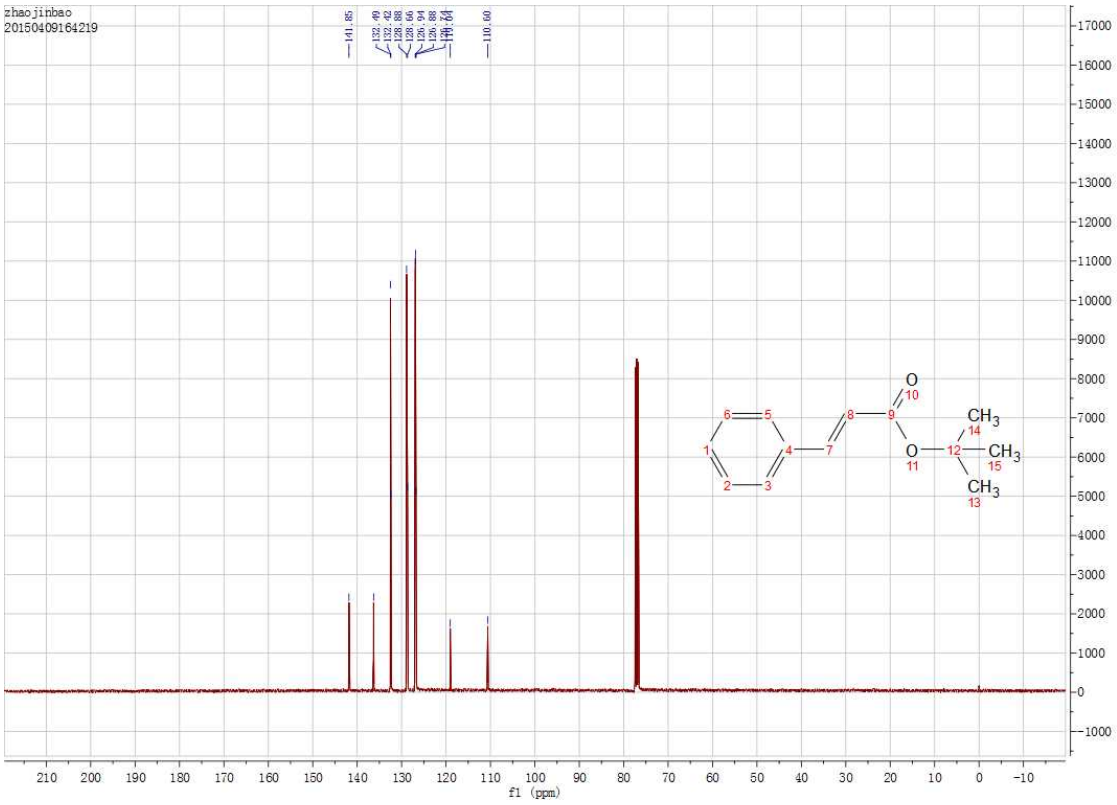
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.43 , 144.89 , 134.47 , 130.30 , 128.92 , 128.09 , 117.88 , 51.70 .



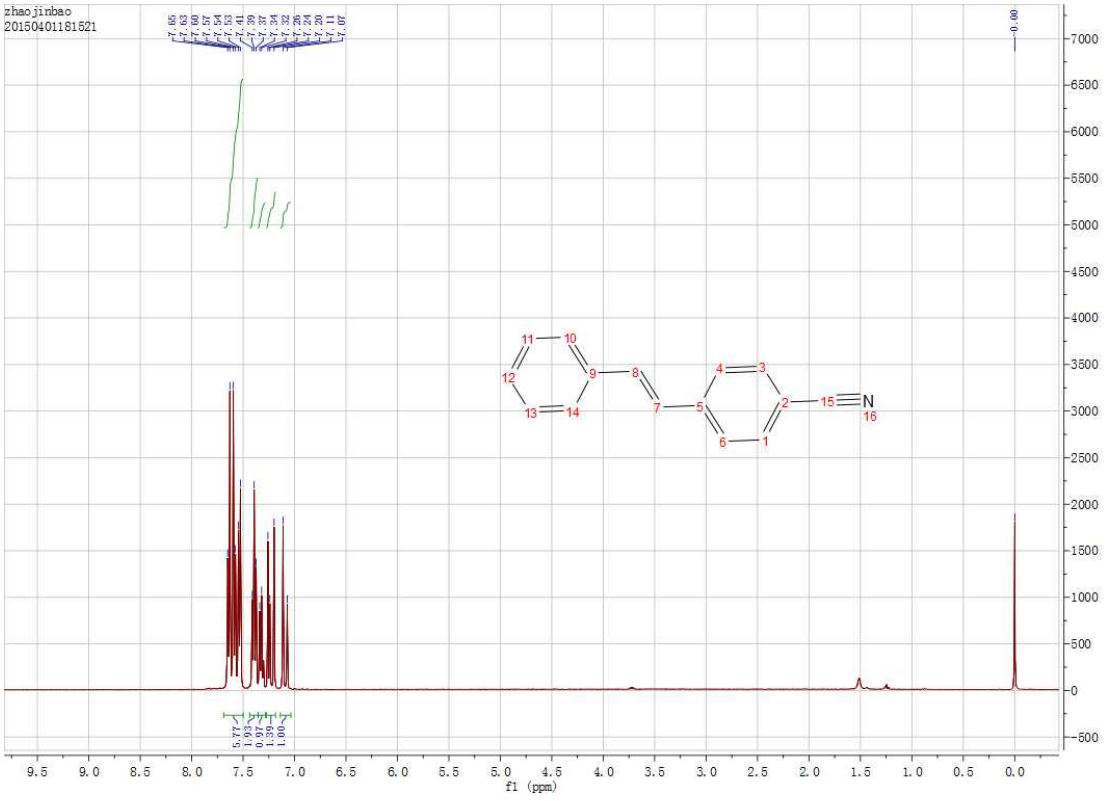
Entry 8. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 16.0 Hz, 1H), 7.51 (dd, J = 6.7, 3.3 Hz, 2H), 7.40 – 7.31 (m, 3H), 6.37 (d, J = 16.0 Hz, 1H), 1.54 (s, 9H).



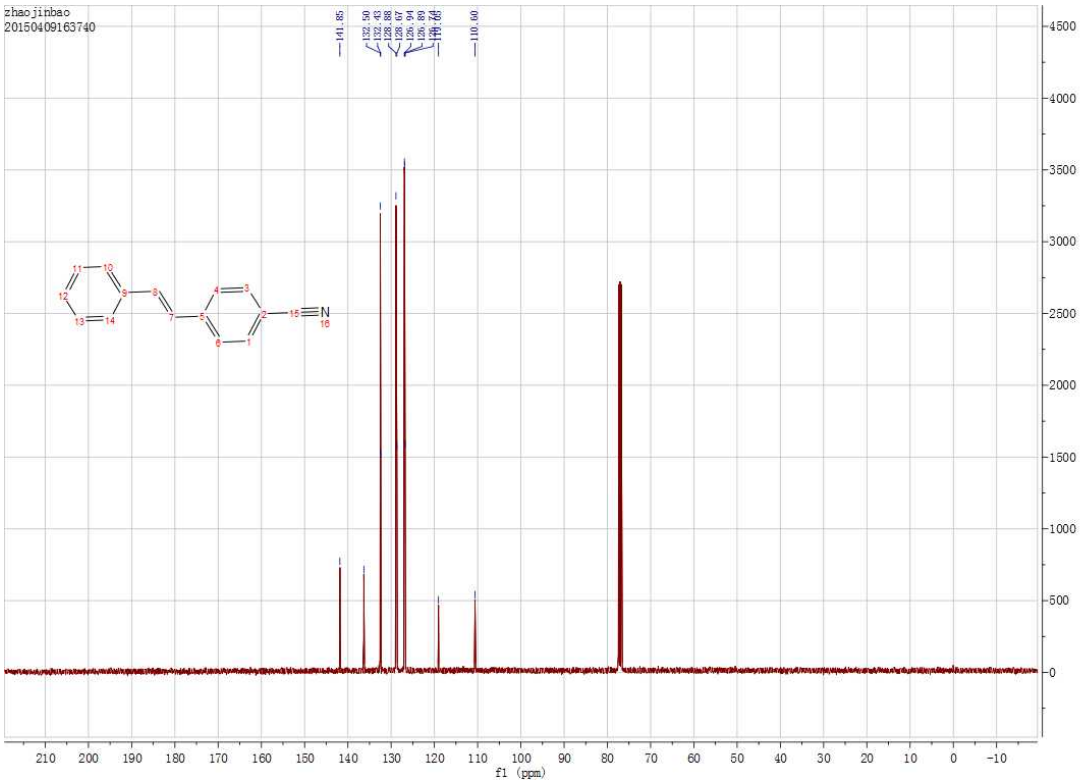
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.85 , 136.31 , 132.46 , 128.88 , 128.66 , 127.04, 126.55, 119.04 , 110.60 .



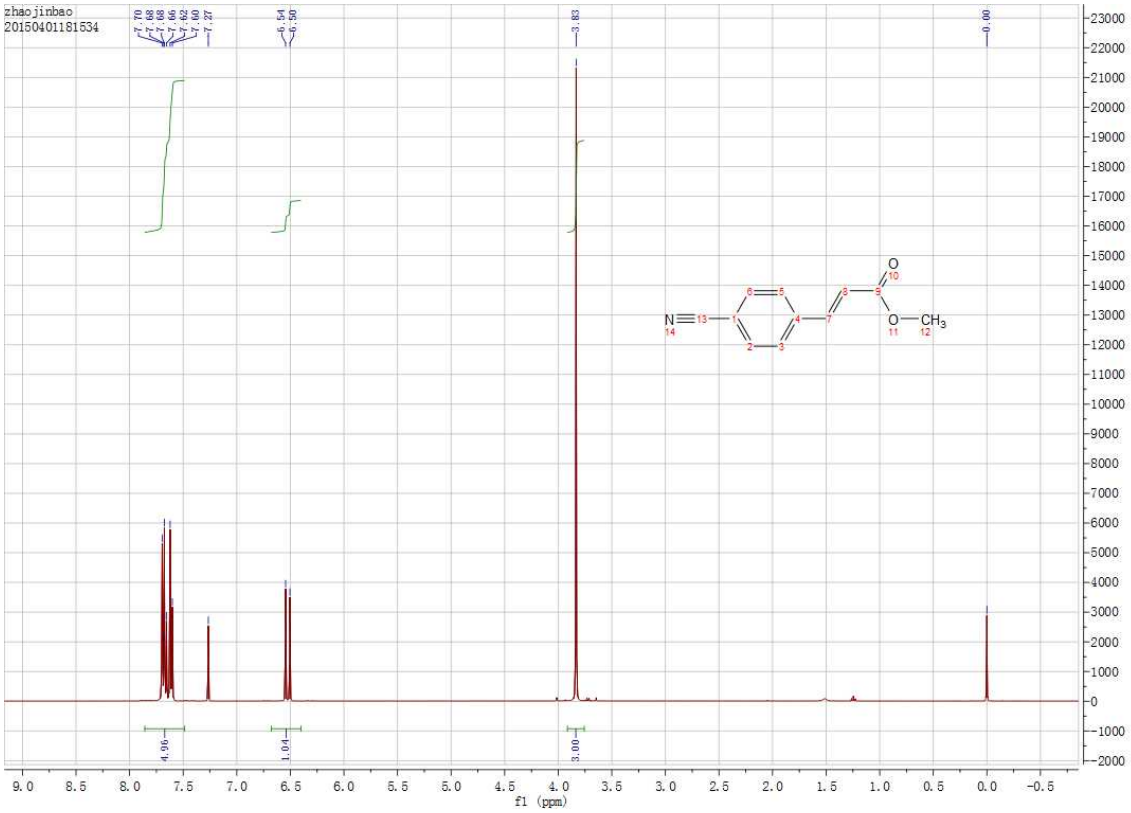
Entry 9. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.50 (m, 6H), 7.32 (ddd, J = 48.4, 19.4, 11.8 Hz, 4H), 7.09 (d, J = 16.3 Hz, 1H).



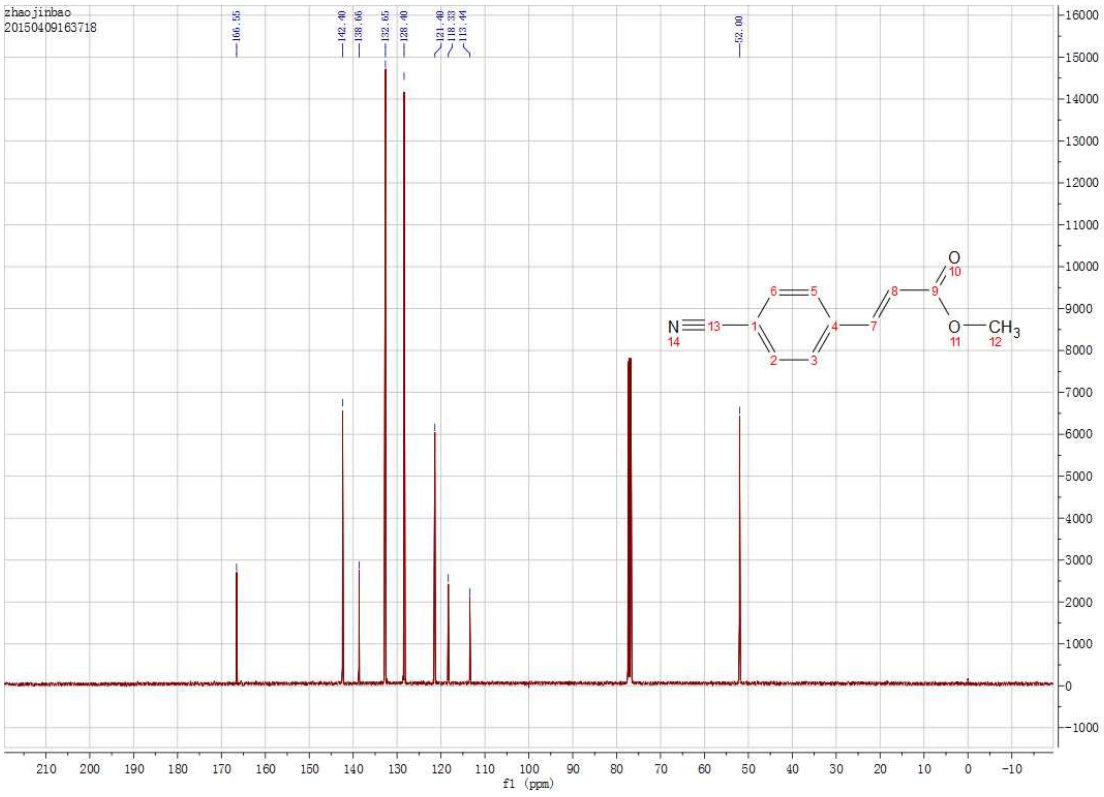
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.85 , 136.31 , 132.47 (d, J = 7.3 Hz), 128.88 , 128.67 , 127.04 , 126.60 , 119.05 , 110.60 .



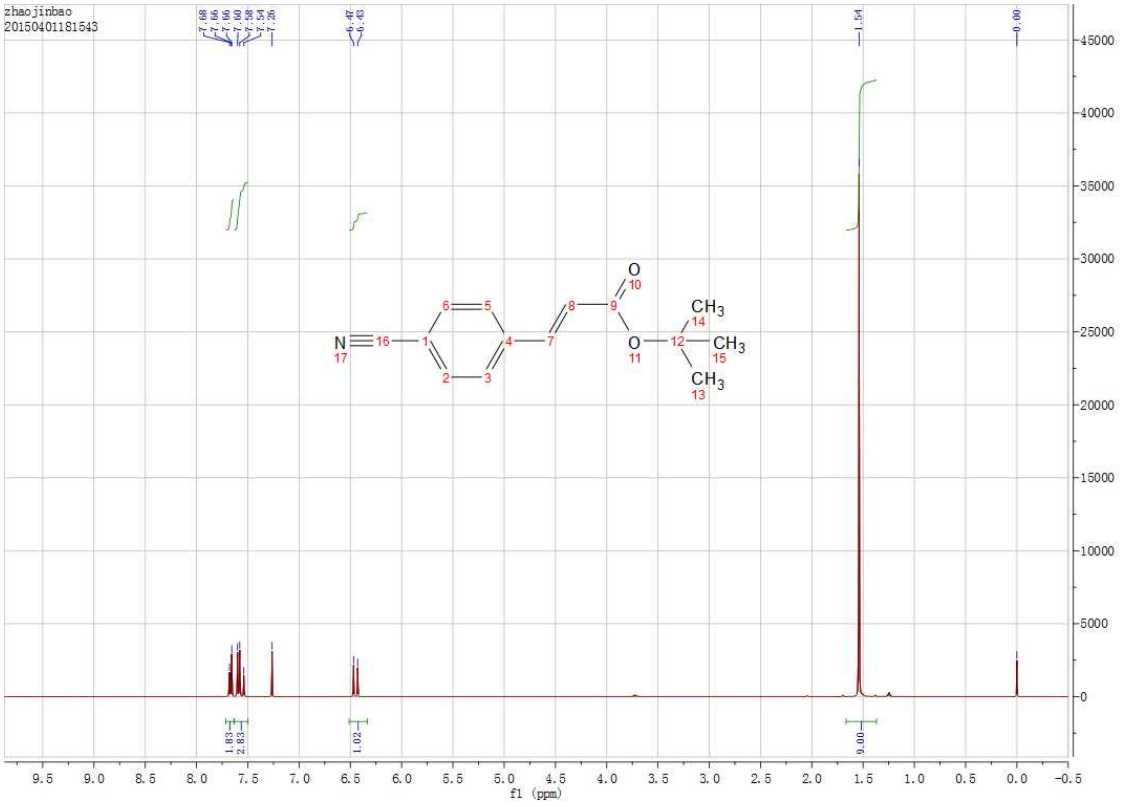
Entry 10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 9.1, 7.3 Hz, 3H), 7.61 (d, J = 8.3 Hz, 2H), 6.52 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H).



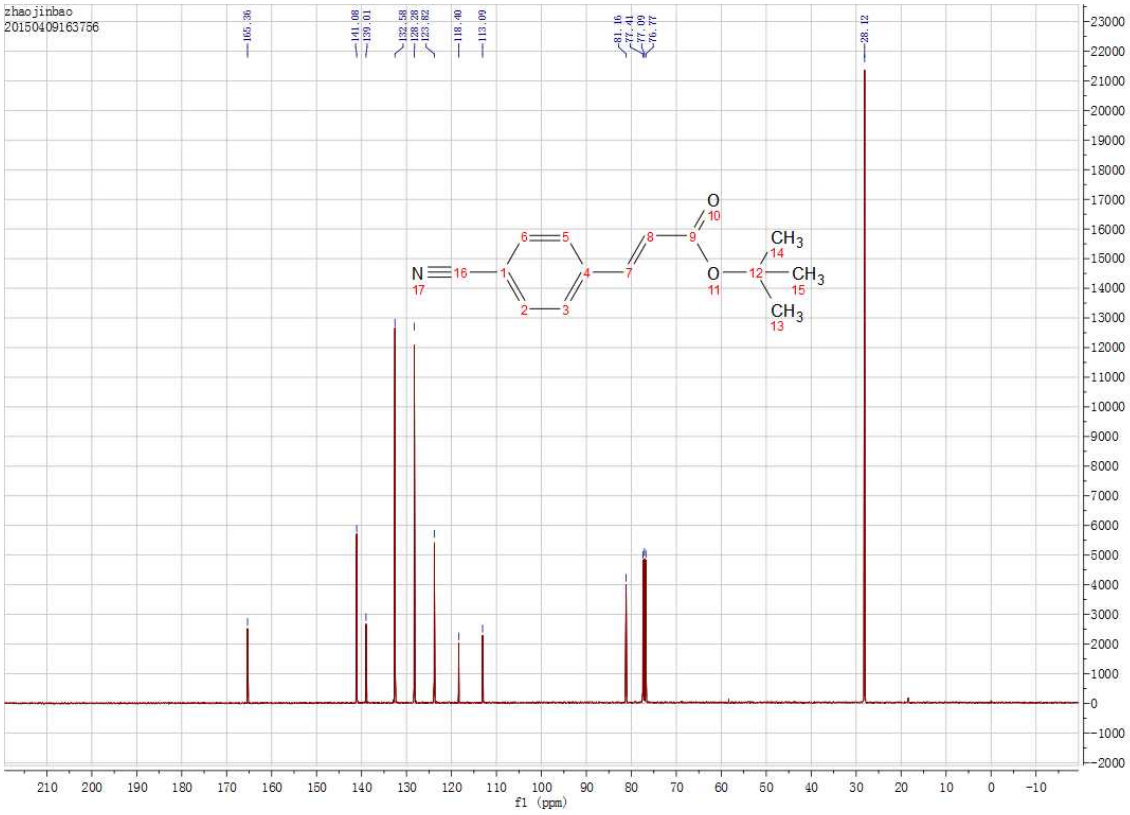
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.55 , 142.40 , 138.66 , 132.65 , 128.40 , 121.40 , 118.33 , 113.44 , 52.00 .



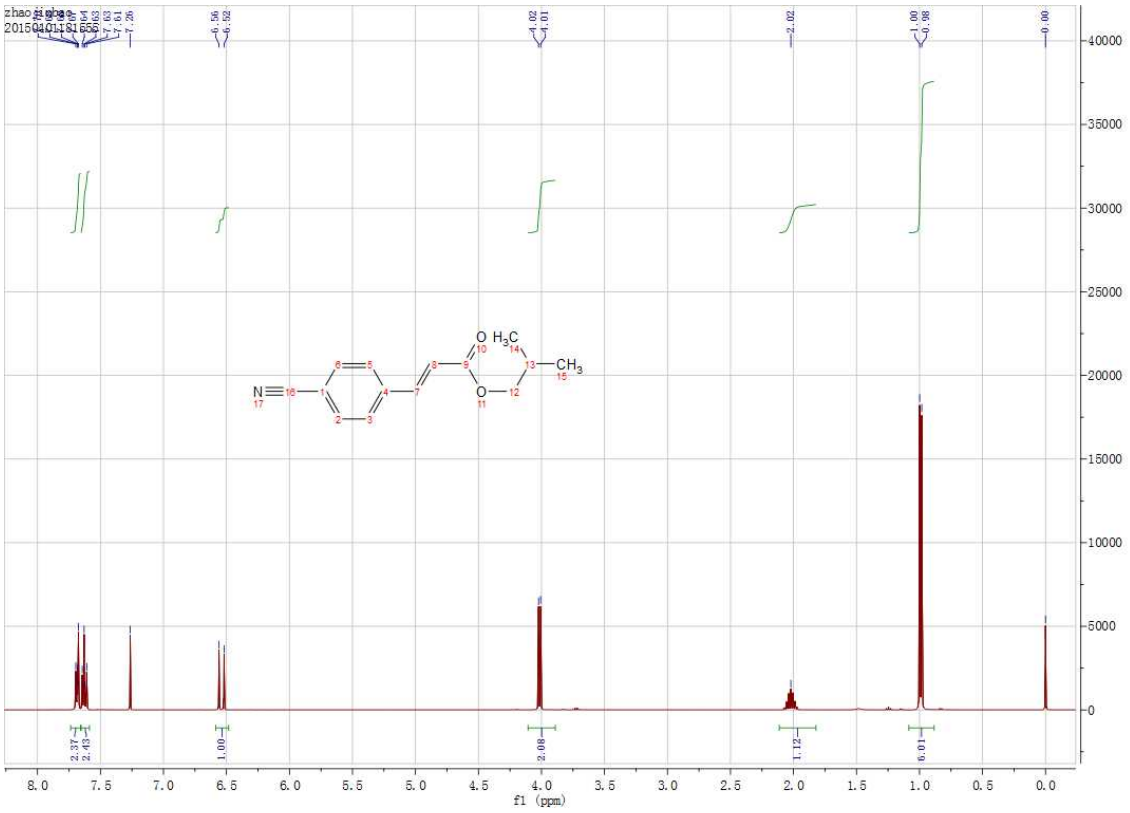
Entry 11. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.63 – 7.50 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 1.54 (s, 9H).



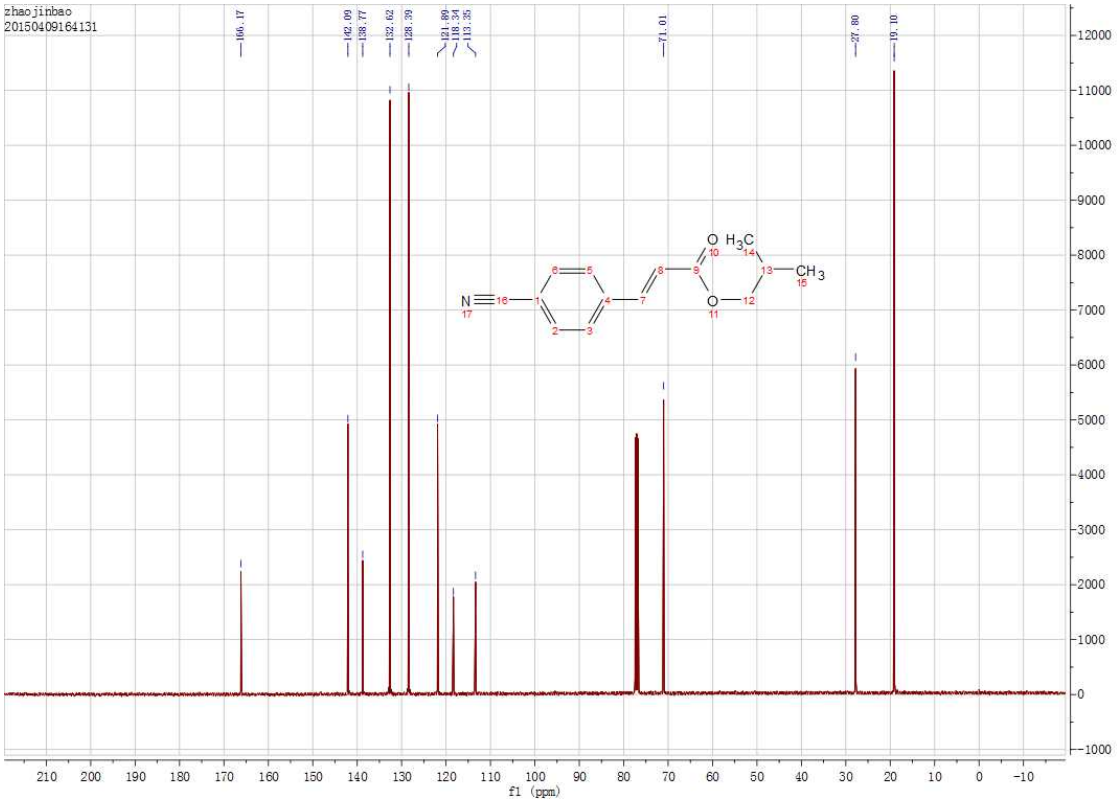
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.36 , 141.08 , 139.01 , 132.58 , 128.28 , 123.82 , 118.40 , 113.09 , 81.16 , 77.41 , 77.09 , 76.77 , 28.12 .



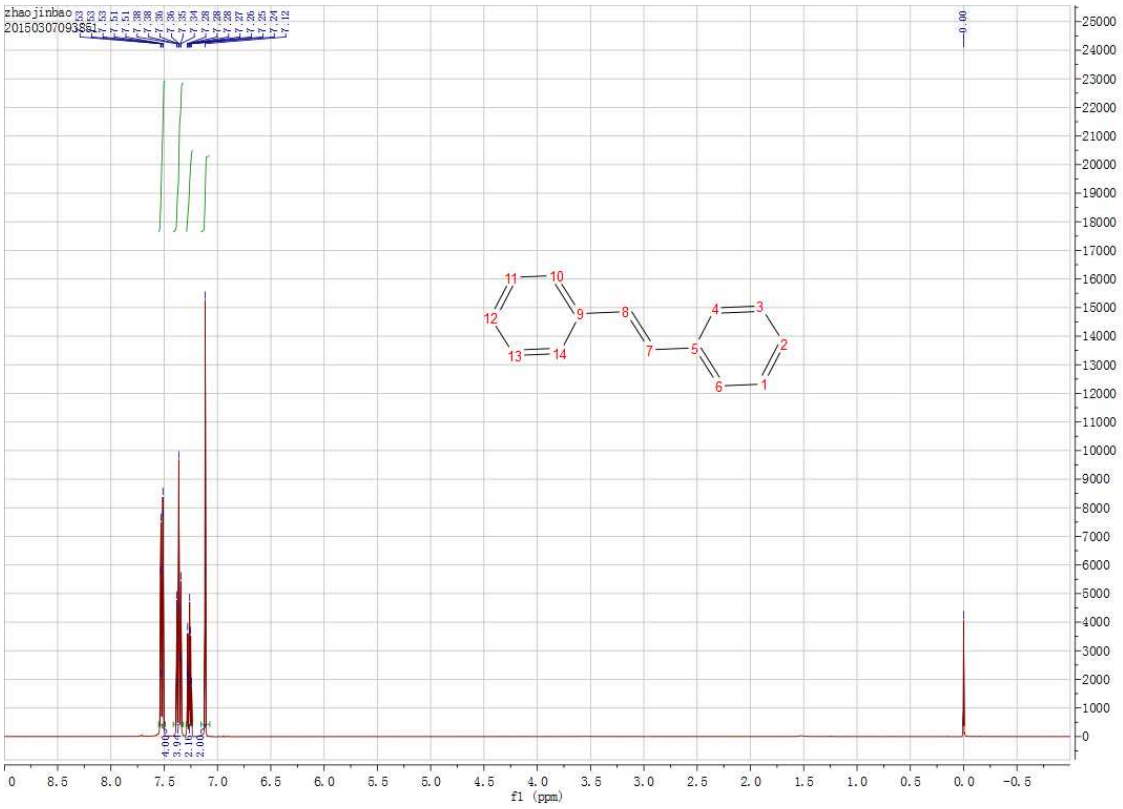
Entry 12. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 5.2, 3.2 Hz, 2H), 7.63 (dd, J = 8.0, 6.2 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 4.01 (d, J = 6.7 Hz, 2H), 2.02 (s, 1H), 0.99 (d, J = 6.7 Hz, 6H).



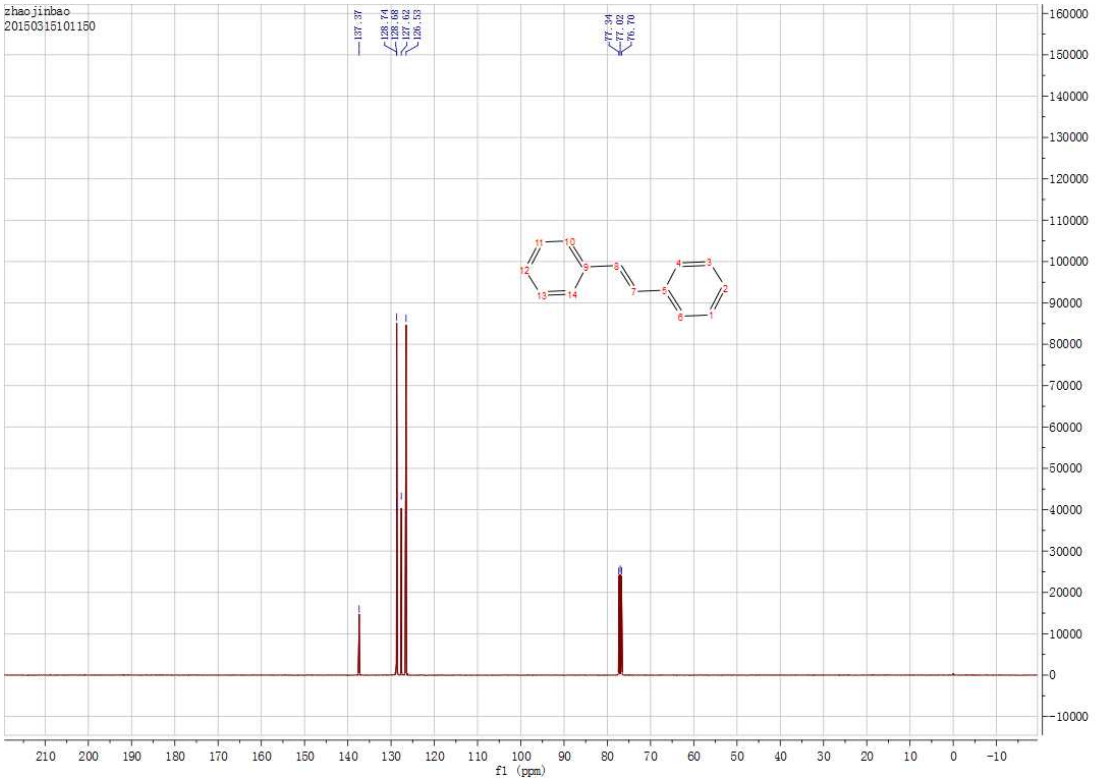
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17 , 142.09 , 138.77 , 132.62 , 128.39 , 121.89 , 118.34 , 113.35 , 71.01 , 27.80 , 19.10 .



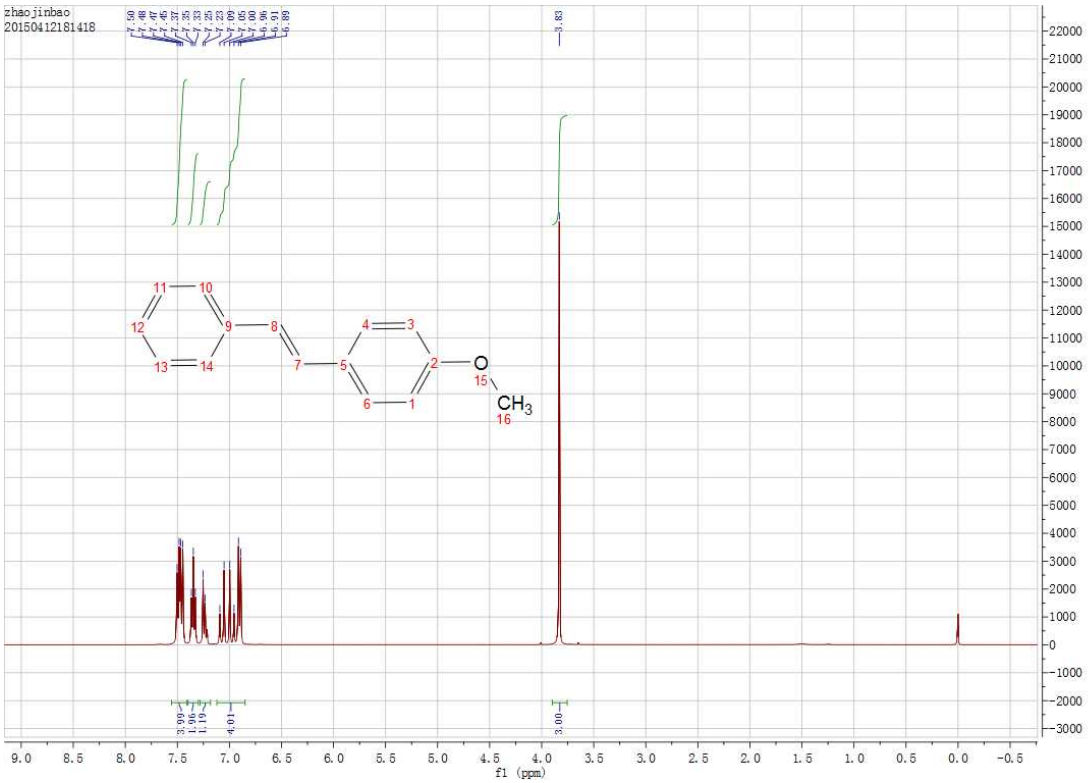
Entry 13. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 4H), 7.42 – 7.32 (m, 4H), 7.29 – 7.24 (m, 2H), 7.12 (s, 2H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 137.37 , 128.71 (d, J = 5.4 Hz), 127.62 , 126.53 , 77.34 , 77.02 , 76.70 .



Entry 14. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 13.7, 8.2 Hz, 4H), 7.35 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 7.3 Hz, 1H), 7.12 – 6.85 (m, 4H), 3.83 (s, 3H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 159.37 , 137.71 , 130.21 , 128.66 , 128.27 , 127.75 , 127.23 , 126.68 , 126.29 , 114.19 , 55.33 .