Supporting Information

Synthesis of 1,2,4,5 tetrasubstituted imidazole via electrochemical C(sp^3)–H Amination

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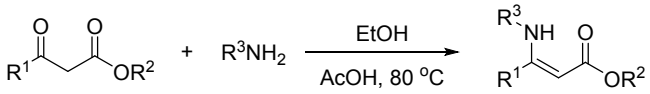
1. General Remarks

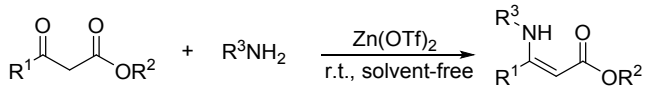
All reagents were obtained from commercial sources (purity > 99%) and used without further purification, unless otherwise indicated. Melting points were determined with a Büchi B-540 capillary melting point apparatus. The ^{1}H and ^{13}C NMR spectroscopic data were recorded with a Varian instrument at 600 and 150 MHz, respectively, and TMS was used as the internal standard. Mass spectrometry was performed with a Thermo Finnigan LCQ-Advantage instrument. High resolution mass spectral (HRMS) analyze was measured on an Agilent 1290-6540 UHPLC Q-Tof HR-MS System ESI spectrometer. Silica gel for column chromatography was purchased from Qingdao Haiyang Chemical Co., Ltd. Reactions were stirred using Teflon-coated magnetic stir bars

2. Synthetic procedures of starting materials

To a solution of substituted 1,3-dicarbonyl compound (5 mmol) in EtOH (10 mL) at rt were added aniline (15 mmol) (Naphthylamine for **1f**; cyclohexylamine for **1h**;benzylamine for **1i**) and acetic acid (1.4 mL, 25 mmol) in sequence. The reaction was heated at 80 °C until the consumption of the 1,3-dicarbonyl compound as monitored by TLC was complete. After cooling to r.t., the reaction mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and then purified by silica gel column chromatography, giving the enamine 1 in 64−99% yields.



A 50 ml single-mouth flask was charged with methyl acetoacetate (50 mmol, 5.8 g), aniline (60 mmol, 5.6 g), $Zn(OTf)_2$ (2.5 mmol, 0.9 g), stirred magnetically and monitored by TLC during the reaction (*n*-hexane: ethyl acetate = 10:1). After the reaction, the heating was stopped, cooled to room temperature, and the solution was removed by distillation under reduced pressure using a rotary evaporator to obtain a brown oily liquid, which was extracted with ethyl acetate (3 × 25 mL), the organic phases were combined, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Silica gel column chromatography (n-hexane/ethyl acetate/triethylamine = 100:1:1, v/v/v) gave a pale yellow solid. Other enamine nitrogen substitution target products were prepared as described above.



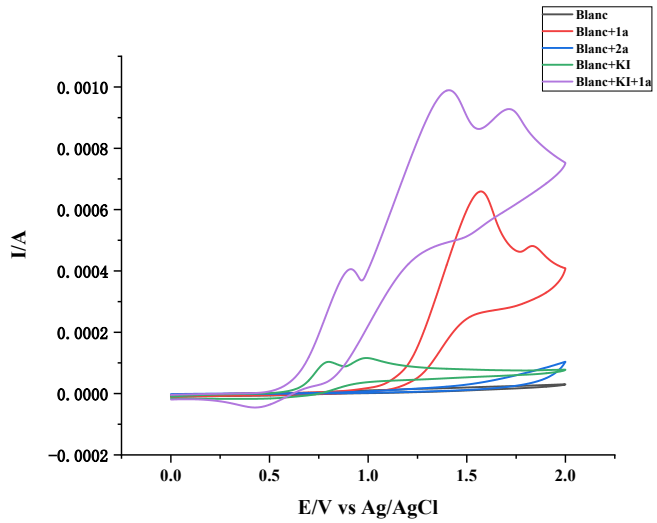
3. Synthetic procedure of compound 3aa

The electrolysis was carried out in an oven-dried undivided three-necked flask, Enamine ester **1a** (0.5 mmol, 95.5 mg), Benzylamine **2a** (1.5 mmol, 160 mg), KI (0.5 mmol, 83 mg), $^{n}Bu_4NBF_4$ (0.03 M) and DMSO (5 mL) were combined and added. The bottle was equipped with platinum plate (20 mm × 15 mm) as the anode and platinum plate (20 mm × 15 mm) as the cathode and was then charged with argon. Then the reaction mixture was stirred at a constant current of 10 mA under room temperature for 10 h. When the reaction was finished, the solution was washed with water (10 mL) and extracted with ethyl acetate (3×10 mL). The combined organic layer was dried with Na_2SO_4, filtered. The solvent was

removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petrol ether and ethyl acetate as the eluent (10/1 to 5/1).

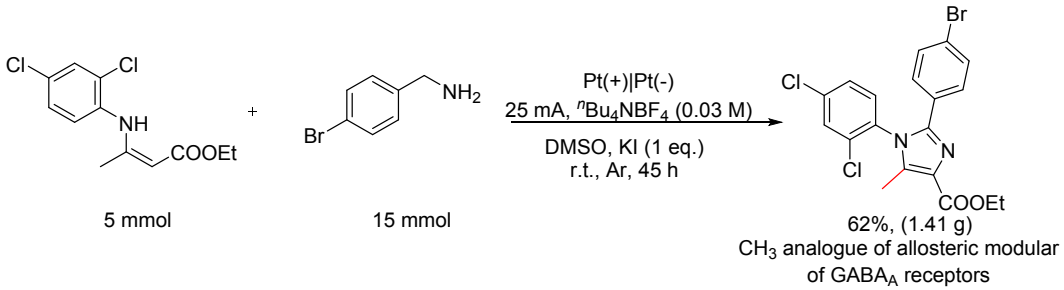
4. Cyclic voltammetry

To further understand the formation process of electrochemical oxidation of C-N bonds, cyclic voltammetry (CV) experiments were performed.relative to Ag/AgCl, no significant oxidation peaks were observed for **2a** in the range of 0.0-2.0 V (**Background+2a**), while two oxidation peaks were observed for **1a** at 1.61 V and 1.83 V (**Background+1a**). the CV of KI solution showed significant oxidation peaks at 0.81 V and 1.02 V showed distinct oxidation peaks (**Background+KI**). A significant catalytic current can be observed when the feedstock **1a** is added, with an increase in the oxidation peak from 0.001 A to 0.004 A (**Background+KI+1a**), and the increase in the peak current indicates that KI also acts as a medium for the electrochemical reaction.



Cyclic Voltammogram Recorded on (+)C/(−)Pt in *n*-Bu_4NBF_4 (1 mmol)/MeCN (10 mL) at rt;Ag/AgCl as Reference Electrode

5. Gram scale reaction



In an oven-dried undivided three-necked flask (100 mL), enamino ester (5 mmol, 1.37 g), Benzylamine **2a**(15 mmol, 2.78 g), KI (5 mmol, 0.83 g), $^{n}Bu_4NBF_4$ (0.03 M) and DMSO (30 mL) were combined and added. The bottle was equipped with platinum plate (20 mm × 15 mm) as the anode and platinum plate (20 mm × 15 mm) as the cathode and was then charged with argon. Then the reaction mixture was stirred at a constant current of 25 mA under room temperature for 45 h. When the reaction was finished, the solution was washed with water (50 mL) and extracted with ethyl acetate (3×50 mL).

The combined organic layer was dried with Na_2SO_4, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petrol ether and ethyl acetate as the eluent (7/1 to 5/1). Yellow soild was obtained in 62% isolated yield.

6. References

[1] C. A. Brandt, *Synthesis.*, 2004, **10**, 1557-1559.

[2] L. Wang, J. Zhang, M. Lang, J. Wang, *Org. Chem. Front.*, 2016, **3**, 603-608.

[3] W. Huang, C. L. Zhu, *Adv. Synth. Catal.*, 2018, **16**, 3117-3123

7. Characterization data for the products

Methyl 5-methyl-1,2-diphenyl-1H-imidazole-4-carboxylate (3aa). Pure white solid (122 mg, 80%) mp: 132-135 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (td, *J* = 2.6, 1.2 Hz, 3H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.20 (dt, *J* = 13.4, 6.2 Hz, 5H), 3.95 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 146.8, 138.3, 136.4, 129.8, 129.6, 129.3, 128.8, 128.7, 128.6, 128.0, 127.8, 51.5, 10.9. **HRMS** (ESI): m/z calcd for $C_{18}H_{16}N_2O_2$ $[M + H]^+$ 293.1285, found 293.1283.

Methyl 2-(2-chlorophenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate (3ab). Yellow solid (127 mg, 78%) mp: 135-138 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 4H), 7.27 (s, 2H), 7.22–7.16 (m, 1H), 7.16 – 7.10 (m, 2H), 3.94 (s, 3H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 144.6, 137.4, 135.0, 134.4, 132.6, 130.7, 129.8, 129.2, 129.1, 129.0, 128.6, 127.4, 126.3, 51.5, 11.0. **HRMS** (ESI): m/z calcd for $C_{18}H_{15}ClN_2O_2$ $[M + H]^+$ 327.0895, found 327.0893.

Methyl 2-(2-methoxyphenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate (3ac).Pure white solid (116 mg, 72%) mp:129-131 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 1H),7.27(s, 1H) 7.23 – 7.15 (m, 2H), 7.03 – 6.97 (m, 2H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 3.84 (s, 3H), 3.28 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 156.8, 145.1, 137.2, 136.0, 132.1, 130.8, 128.5, 128.5, 128.3, 126.9, 120.1, 119.4, 110.1, 54.5, 51.2, 11.0.**HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_3$ $[M + H]^+$ 323.1390 found 323.1395

Methyl 2-(3-bromophenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate (3ad). Pure white solid (143 mg, 77%) mp:137-140 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 1.8 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.13 (m, 3H), 7.03 (t, *J* = 7.8 Hz, 1H), 3.97 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 145.1, 138.8, 136.0, 131.7, 131.7, 131.5, 130.0, 129.7, 129.5, 129.0, 127.8, 126.9, 122.3, 51.8, 11.0. **HRMS** (ESI): m/z calcd for $C_{18}H_{15}BrN_2O_2$ $[M + H]^+$ 371.0390 found 371.0393

Methyl 5-methyl-1-phenyl-2-(m-tolyl)-1H-imidazole-4-carboxylate (3ae). Yellow viscous solid (106 mg, 70%), eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$) δ 7.49 (q, *J* = 3.4 Hz, 3H), 7.40 (s, 1H), 7.19 (p, *J* = 4.0, 3.2 Hz, 2H), 7.09 – 7.01 (m, 2H), 6.95 (d, *J* = 7.4 Hz, 1H), 3.97 (s, 3H), 2.43 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 147.0, 138.4, 137.9,

136.4, 129.8, 129.7, 129.5, 129.4, 129.3, 128.6, 127.9, 127.7, 125.4, 51.7, 21.3, 11.1. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 307.1441 found 307.1445

Methyl 2-(4-chlorophenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate (3af). Yellow solid (124 mg, 76%) mp:133-135 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.30 (s, 1H), 7.20 – 7.15 (m, 4H), 3.95 (s, 3H), 2.41 (s,3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 145.6, 138.6, 136.0, 134.7, 129.9, 129.8, 129.5, 128.8, 128.3, 128.0, 127.7, 51.6, 10.9. **HRMS** (ESI): m/z calcd for $C_{18}H_{15}ClN_2O_2$ $[M + H]^+$ 327.0895 found 327.0893

Methyl 2-(4-methoxyphenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate (3ag). Yellow solid (114 mg, 71%) mp:128-130 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 3H), 7.32 – 7.29 (m, 1H),7.28(s, 1H) 7.19 (ddq, *J* = 5.8, 3.0, 1.4 Hz, 2H), 6.75 – 6.70 (m, 2H), 3.96 (s, 3H), 3.76 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 159.7, 146.7, 138.1, 136.4, 130.0, 129.8, 129.2, 128.4, 127.8, 122.1, 113.4, 55.2, 55.1, 51.5, 11.0. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_3$ $[M + H]^+$ 323.1390 found 323.1393

Methyl 2-(2,3-dichlorophenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate (3ah). Yellow solid (132 mg, 73%) mp:136-138 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.39 – 7.37 (m, 3H), 7.31 – 7.28 (m, 1H), 7.17 – 7.12 (m, 3H), 3.94 (s, 3H), 2.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 143.9, 137.5, 134.8, 133.1, 131.9, 131.5, 130.9, 129.3, 129.2, 128.7, 127.3, 127.3, 126.8, 51.6, 10.9. **HRMS** (ESI): m/z calcd for $C_{18}H_{14}Cl_2N_2O_2$ $[M + H]^+$ 361.0505 found 361.0508

Methyl 2-(furan-2-yl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate (3ai). Pure white solid (104 mg, 74%) mp:127-129 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.8 Hz, 3H), 7.28 (dd, *J* = 7.2, 1.6 Hz, 3H), 6.26 (dt, *J* = 3.2, 1.4 Hz, 1H), 5.92 (d, *J* = 3.4 Hz, 3H), 3.95 (s, 1H), 2.37 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 143.9, 143.0, 139.0, 138.1, 135.6, 129.9, 129.9, 128.6, 127.8, 110.9, 109.8, 51.5, 10.5. **HRMS** (ESI): m/z calcd for $C_{16}H_{14}N_2O_3$ $[M + H]^+$ 283.1077 found 283.1072

Methyl 5-methyl-1-phenyl-2-(thiophen-2-yl)-1H-imidazole-4-carboxylate (3aj). Yellow solid (103 mg, 69%) mp:125-128 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 3H), 7.30 (dd, *J* = 4.8, 3.4 Hz, 2H), 7.20 (dt, *J* = 5.0, 1.4 Hz, 1H), 6.82 (ddd, *J* = 5.2, 3.6, 1.4 Hz, 1H), 6.73 (dd, *J* = 3.6, 2.0 Hz, 1H), 3.95 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 142.1, 138.5, 135.7, 132.0, 130.2, 130.1, 128.6, 128.3, 128.3, 127.1, 126.8, 51.7, 10.8. **HRMS** (ESI): m/z calcd for $C_{16}H_{14}N_2O_2S$ $[M + H]^+$ 299.0849 found 299.0850

Methyl 1-(4-chlorophenyl)-5-methyl-2-phenyl-1H-imidazole-4-carboxylate (3ba). Pure white solid (123 mg, 76%) mp:132-135 °C**, ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.38 – 7.34 (m, 2H), 7.28 – 7.21 (m, 3H), 7.16 – 7.12 (m, 2H), 3.96 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 146.7, 138.1, 135.4, 134.7, 130.1, 129.2, 129.1, 128.9, 128.8, 128.7, 128.1, 51.6, 11.0. **HRMS** (ESI): m/z calcd for $C_{18}H_{15}ClN_2O_2$ $[M + H]^+$ 327.0895 found 327.0893

Methyl 5-methyl-2-phenyl-1-(p-tolyl)-1H-imidazole-4-carboxylate (3ca). Pure white solid (111 mg, 73%) mp:136-141 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (dt, J = 6.8, 1.6 Hz, 2H), 7.27 – 7.17 (m, 5H), 7.07 – 7.04 (m, 2H), 3.95 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 146.8, 139.4, 138.6, 133.6, 130.4, 129.6, 128.6, 128.5, 128.5, 128.0, 127.5, 51.6, 21.2, 11.0. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 307.1441 found 307.1444

Methyl 5-methyl-2-phenyl-1-(m-tolyl)-1H-imidazole-4-carboxylate (3da). Yellow solid (109 mg. 71%) mp:138-141 °C**, ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 4H), 7.27 – 7.18 (m, 3H), 6.99 (d, J = 10.2 Hz, 2H), 3.96 (d, J = 1.4 Hz, 3H), 2.42 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 146.7, 140.1, 138.6, 136.3, 130.2, 129.7, 129.6, 128.6, 128.6, 128.6, 128.2, 128.0, 124.9, 51.6, 21.3, 11.1. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 307.1441 found 307.1445

methyl 5-methyl-2-phenyl-1-(o-tolyl)-1H-imidazole-4-carboxylate (3ea). Yellow viscous solid (99 mg, 65%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 4H), 7.22 (s, 1H), 7.13 (p, *J* = 7.4 Hz, 4H), 3.89 (s, 3H), 2.25 (s, 3H), 1.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 146.3, 138.1, 135.6, 135.3, 131.4, 129.8, 129.6, 128.6, 128.6, 128.2, 128.0, 127.8, 127.3, 51.5, 17.2, 10.5. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 307.1441 found 307.1446

Methyl 5-methyl-1-(naphthalen-1-yl)-2-phenyl-1H-imidazole-4-carboxylate (3fa). Pure white solid (138 mg, 81%) mp:140-143 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 14.2, 8.2 Hz, 2H), 7.55 (dt, *J* = 18.6, 7.8 Hz, 4H), 7.35 (d, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 5.8 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 2H), 4.00 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 147.5, 139.4, 134.0, 132.6, 130.1, 130.1, 129.4, 128.7, 128.6, 128.5, 128.1, 127.9, 127.9, 127.1, 126.3, 125.3, 121.9, 51.6, 10.5. **HRMS** (ESI): m/z calcd for $C_{22}H_{18}N_2O_2$ $[M + H]^+$ 343.1441 found 343.1447.

Methyl 1-butyl-5-methyl-2-phenyl-1H-imidazole-4-carboxylate (3ga). Pure white solid (78 mg, 57%) mp:.122-125 °C , **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.41 (m, 5H), 3.92 (t, *J* = 7.0 Hz, 5H), 2.64 (s, 3H), 1.65 – 1.55 (m, 2H), 1.30 – 1.17 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 147.5, 136.8, 130.5, 129.3, 129.2, 128.5, 128.3, 51.5, 44.3, 32.4, 19.7, 13.5, 10.4. **HRMS** (ESI): m/z calcd for $C_{16}H_{20}N_2O_2$ $[M + H]^+$ 273.1598 found 273.1595.

Methyl 1-cyclohexyl-5-methyl-2-phenyl-1H-imidazole-4-carboxylate (3ha). Yellow solid (80 mg, 54%) mp:140-143 °C, eluent (hexane/EtOAc = 7:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 5H), 4.11 (ddt, *J* = 10.4, 7.0, 3.4 Hz, 1H), 3.90 (s, 3H), 2.79 (s, 3H), 1.96 – 1.83 (m, 6H), 1.69 (d, *J* = 12.2 Hz, 1H), 1.29 – 1.12 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 147.9, 136.4, 131.3, 129.8, 129.3, 128.8, 128.3, 57.9, 51.4, 32.0, 26.1, 25.1, 12.0.**HRMS** (ESI): m/z calcd for $C_{18}H_{22}N_2O_2$ $[M + H]^+$ 299.1754, found 299.1757.

Methyl 1-benzyl-5-methyl-2-phenyl-1H-imidazole-4-carboxylate (3ia). white solid (93 mg, 61%) mp:130-133 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.41 – 7.32 (m, 6H), 7.00 – 6.96 (m, 2H), 5.21 (s, 2H), 3.94 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 148.1, 137.4, 135.9, 129.8, 129.4, 129.2, 129.1, 128.8, 128.6, 127.9, 125.5, 51.6, 48.1, 10.5. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 307.1441, found 307.1443.

Ethyl 5-methyl-1,2-diphenyl-1H-imidazole-4-carboxylate (3ja). Pure white solid (118 mg, 77%) mp:123-125 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (dq, *J* = 5.4, 1.8 Hz, 3H), 7.40 – 7.35 (m, 2H), 7.27 – 7.17 (m, 5H), 4.46 (dt, *J* = 7.2, 1.6 Hz,2H), 2.43 (s, 3H), 1.45 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 146.8, 138.2, 136.4, 129.8, 129.7, 129.3, 129.0, 128.8, 128.6, 128.0, 127.9, 60.5, 14.6, 11.2. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 307.1441, found 307.1445.

Tert-Butyl 5-methyl-1,2-diphenyl-1H-imidazole-4-carboxylate (3ka). Pure white solid (125 mg, 75%) mp:141-144 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.15 (m, 2H), 2.38 (s, 1H), 1.66 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 146.4, 137.0, 136.5, 130.2, 129.7, 129.7, 129.2, 128.6, 128.5, 128.0, 127.9, 80.9, 28.4, 11.3. **HRMS** (ESI): m/z calcd for $C_{21}H_{22}N_2O_2$ $[M + H]^+$ 335.1754, found 335.1756.

Ethyl 1,2,5-triphenyl-1H-imidazole-4-carboxylate (3la). Pure white solid (68 mg, 37%) mp:133-137 °C , **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.35 – 7.28 (m, 4H), 7.27 – 7.20 (m, 7H), 7.00 (dt, *J* = 6.6, 1.6 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.1, 147.4, 140.1, 136.2, 130.8, 129.9, 129.5, 129.1, 128.9, 128.8, 128.6, 128.5, 128.1, 128.0, 127.8, 127.6, 60.4, 14.2. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 369.1598, found 369.1596.

Methyl 5-ethyl-1,2-diphenyl-1H-imidazole-4-carboxylate (3ma). Pure white solid (110 mg, 72%) mp:136-138 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (tq, *J* = 4.2, 2.2, 1.6 Hz, 3H), 7.36 – 7.33 (m, 2H), 7.23 – 7.15 (m, 5H), 3.96 (s, 3H), 2.85 (q, 2H), 1.06 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 146.8, 144.3, 136.3, 129.8, 129.6, 129.5, 128.8, 128.7, 128.7, 128.1, 128.0, 51.6, 17.9, 13.9. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 307.1441, found 307.1444.

Methyl 5-isopropyl-1,2-diphenyl-1H-imidazole-4-carboxylate (3na). Pure white solid (117 mg, 73%) mp:143-147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 6.4 Hz, 3H), 7.32 (dd, *J* = 13.4, 7.0 Hz, 3H), 7.22 (d, *J* = 6.6 Hz, 4H), 3.97 (s, 3H), 3.19 – 3.08 (m, 1H), 1.34 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 147.5, 146.3, 136.6, 129.7, 129.6, 129.5, 128.8, 128.5, 128.4, 128.0, 127.9, 51.7, 25.4, 20.1. **HRMS** (ESI): m/z calcd for $C_{19}H_{18}N_2O_2$ $[M + H]^+$ 321.1598, found 321.1595.

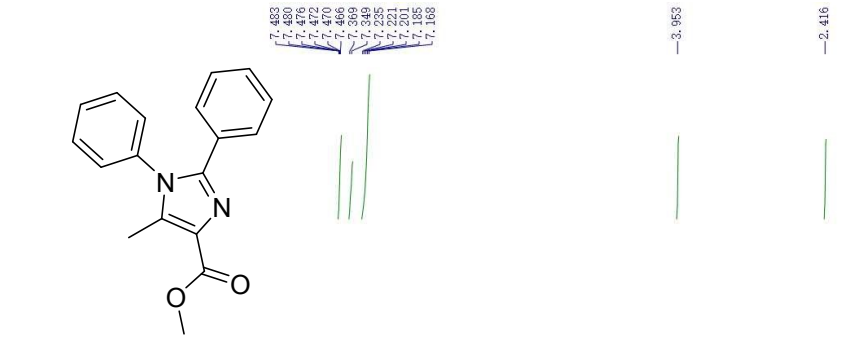
1-(5-methyl-1,2-diphenyl-1H-imidazol-4-yl)ethan-1-one (3oa) Yellow solid (88 mg, 64%) mp:127-133 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (h, *J* = 2.8 Hz, 3H), 7.39 – 7.35 (m, 2H), 7.28 – 7.18 (m, 5H), 2.71 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 145.8, 137.0, 136.7, 136.2, 129.9, 129.8, 129.3, 128.6, 128.5, 128.3, 127.8, 27.7, 11.3. **HRMS** (ESI): calcd for $C_{18}H_{16}N_2O$ $[M + H]^+$ 277.1335, found 277.1331.

Ethyl 2-(4-bromophenyl)-1-(2,4-dichlorophenyl)-5-methyl-1H-imidazole-4-carboxylate. Yellow solid (1.3 g, 58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.4 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.27 – 7.23 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 145.7, 138.3, 136.8, 133.8, 132.7, 131.6, 130.9, 130.7, 129.7, 129.7, 128.8, 128.3, 123.6, 60.7, 14.6, 10.6. **HRMS** (ESI): calcd for $C_{19}H_{15}BrCl_2N_2O_2$ $[M + H]^+$ 452.9767, found 452.9764.

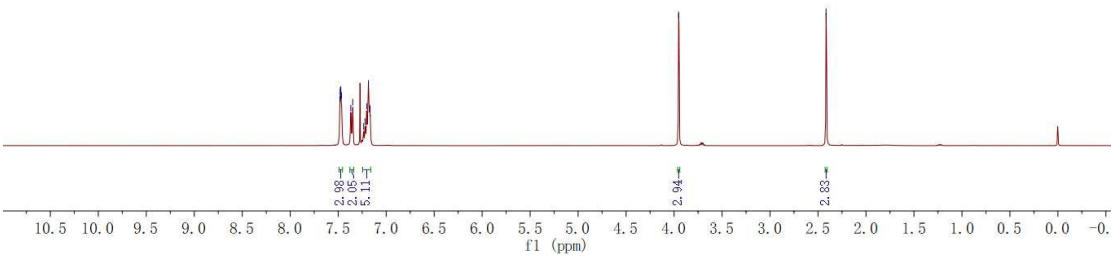
methyl 5-methyl-2-phenyloxazole-4-carboxylate (3a'a) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.47 (dd, *J* = 5.2, 1.8 Hz, 3H), 3.96 (s, 3H), 2.72 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 159.7, 156.5, 130.8, 128.8, 128.5, 126.6, 126.5, 52.1, 12.2.

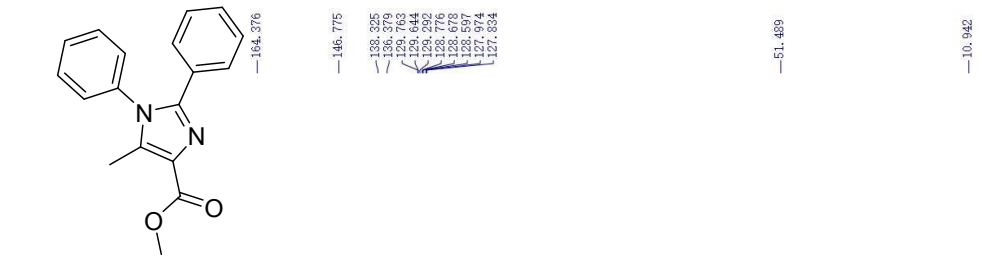
8. NMR spectra of products:

Methyl 5-methyl-1,2-diphenyl-1H-imidazole-4-carboxylate(3aa)

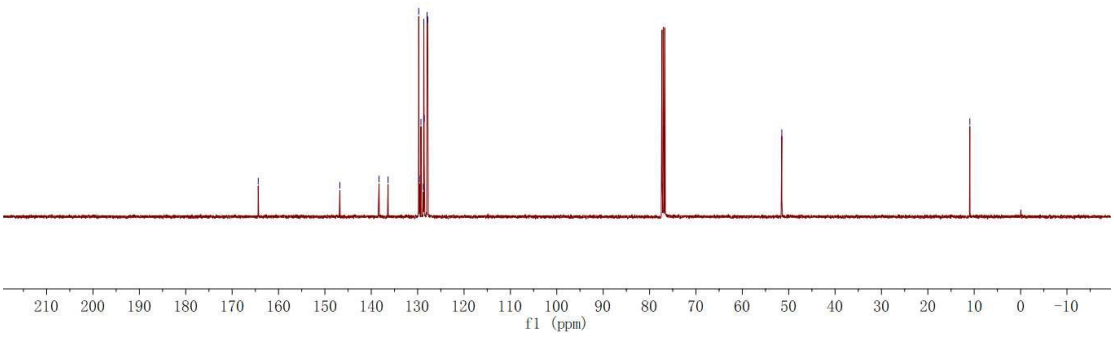


^{1}H NMR (400 MHz, $CDCl_3$)

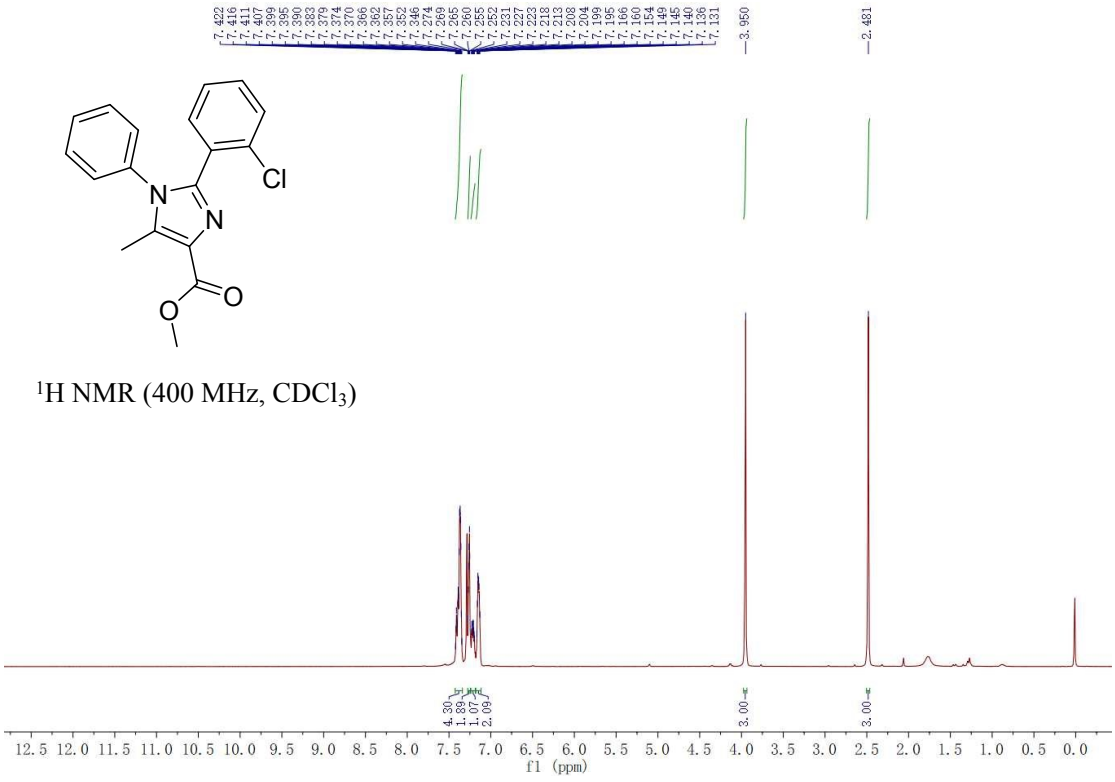




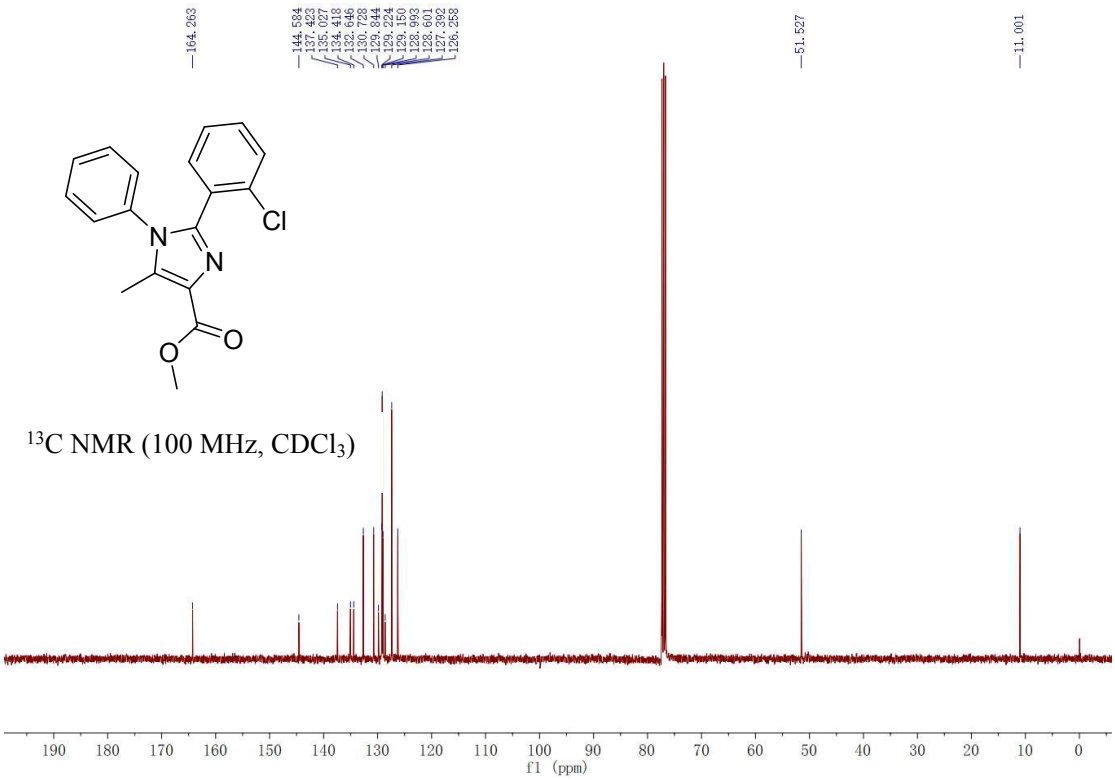
^{13}C NMR (100 MHz, $CDCl_3$)



Methyl 2-(2-chlorophenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate(3ab)

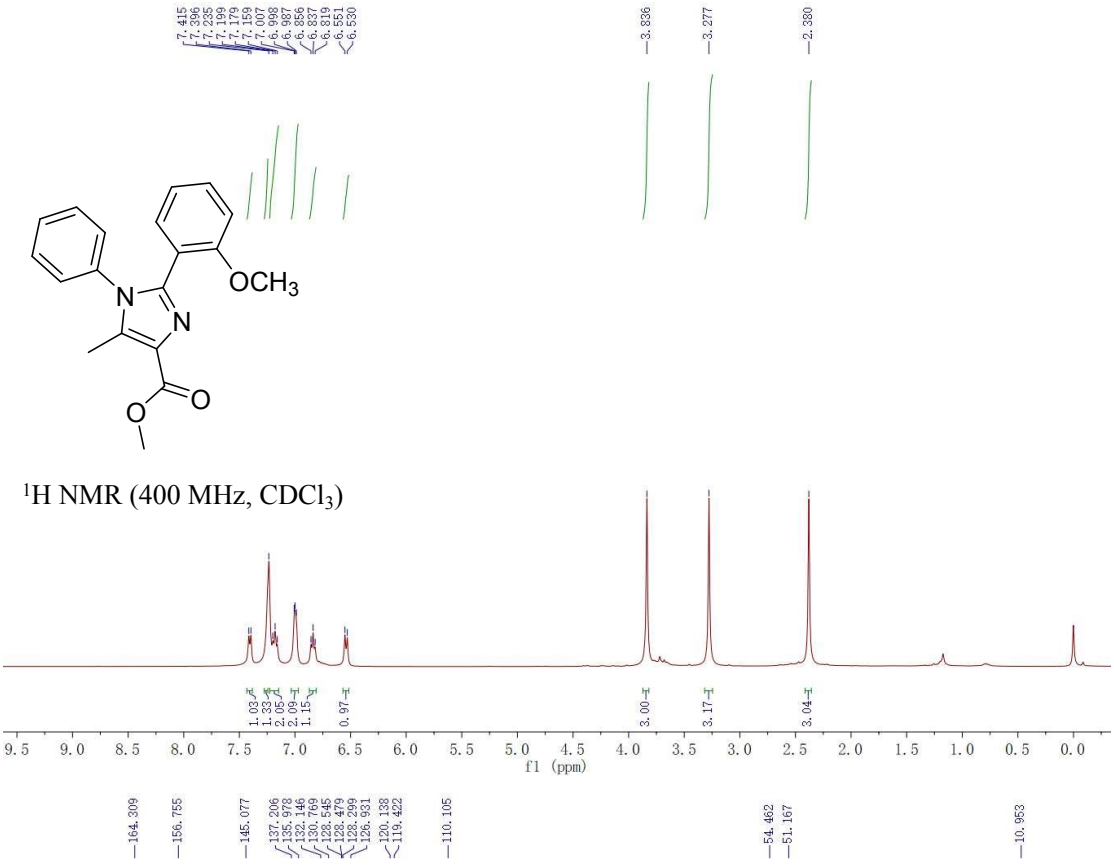


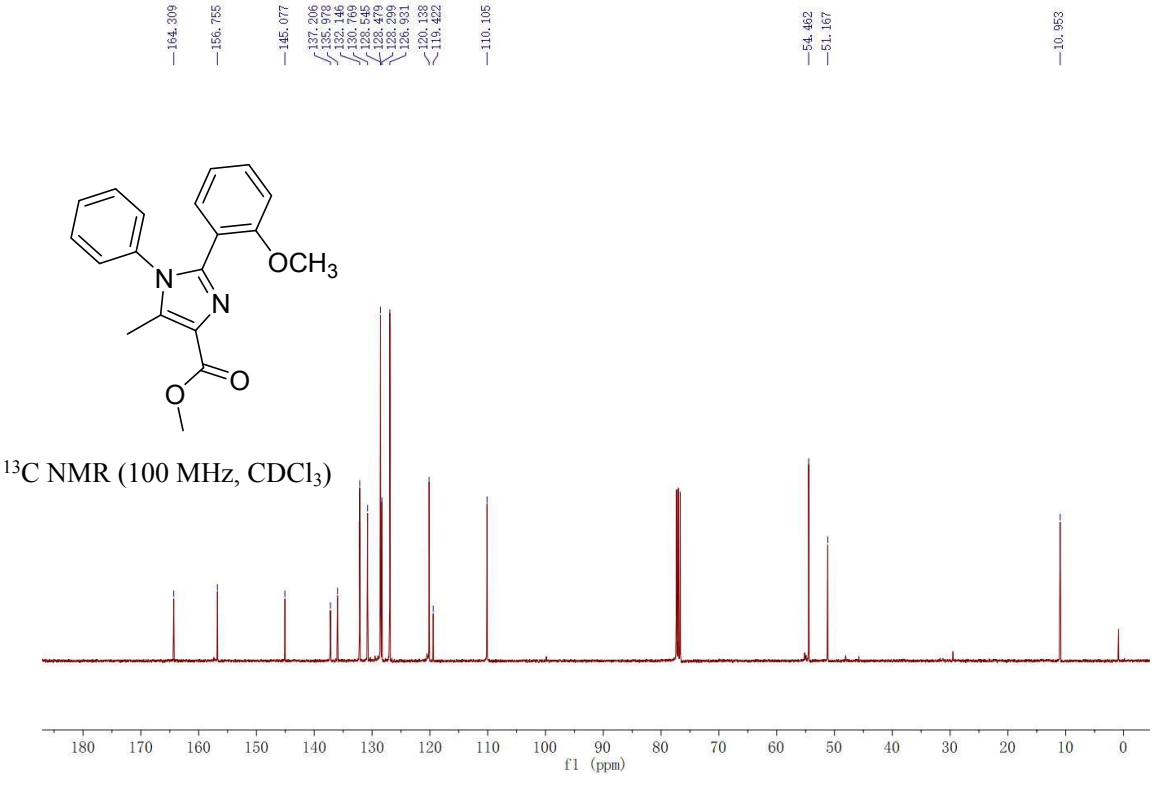
^{1}H NMR (400 MHz, $CDCl_3$)



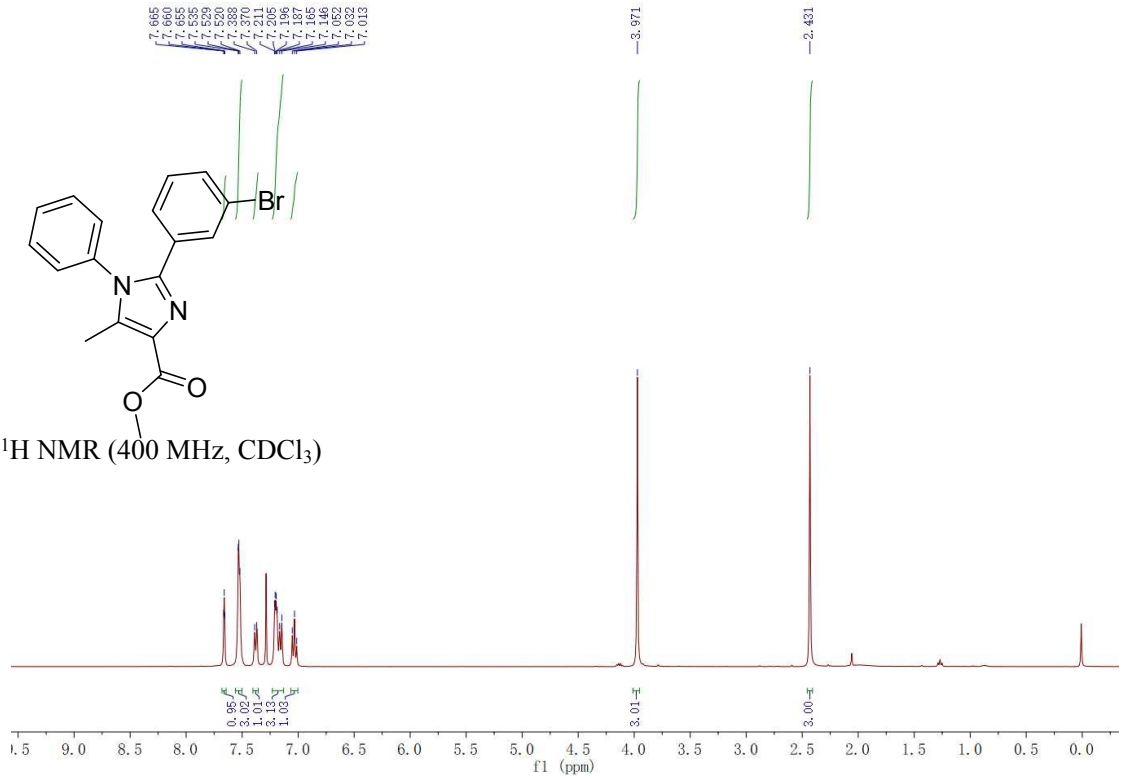
^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 2-(2-methoxyphenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate(3ac)

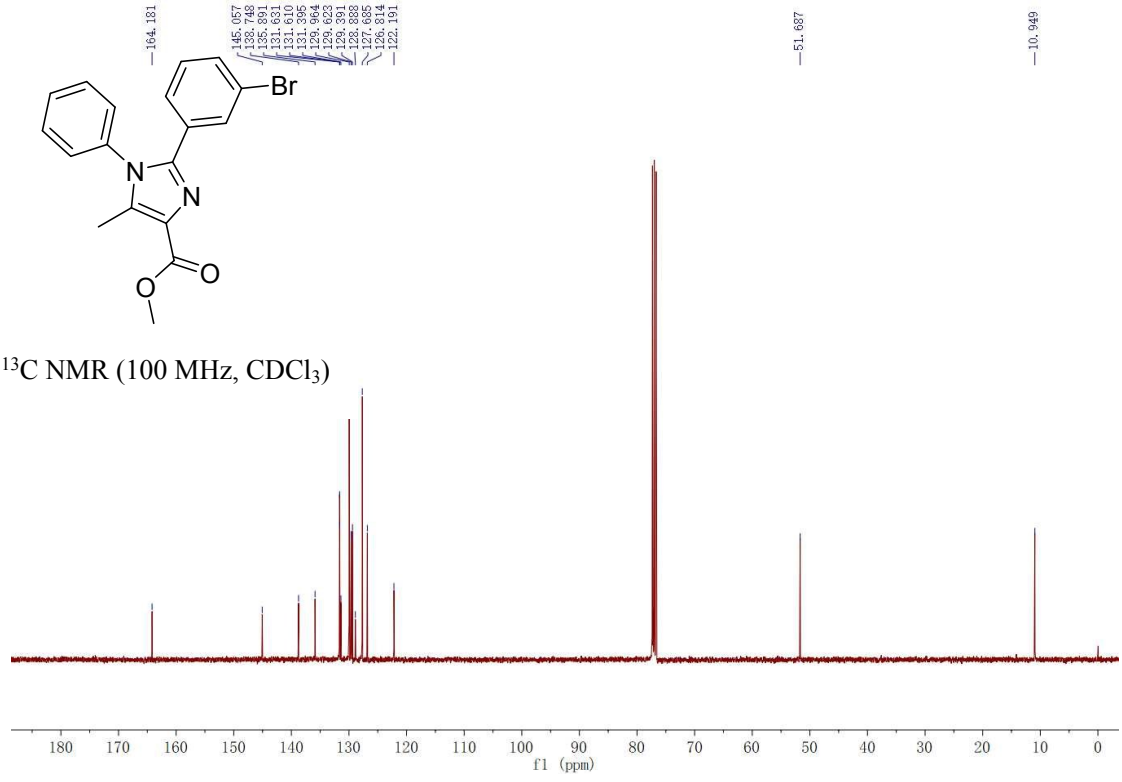




Methyl 2-(3-bromophenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate(3ad)

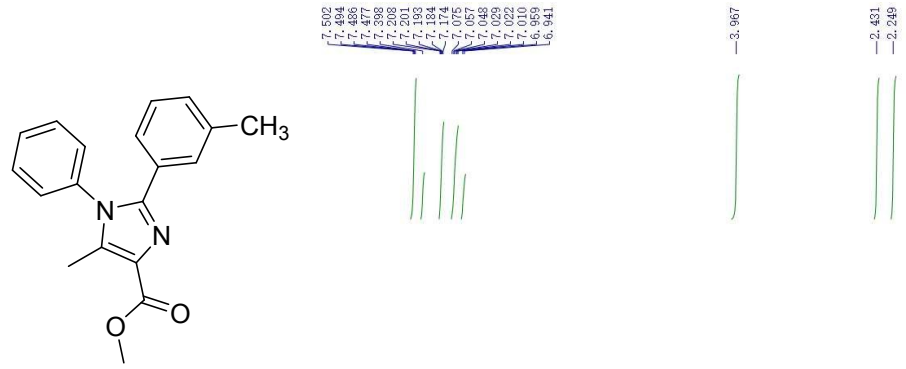


^{1}H NMR (400 MHz, $CDCl_3$)

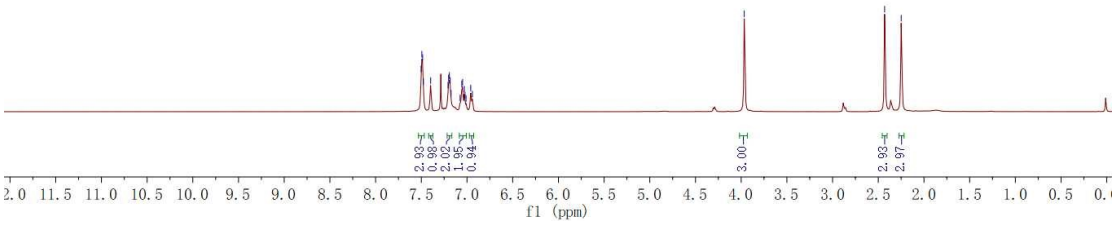


^{13}C NMR (100 MHz, $CDCl_3$)

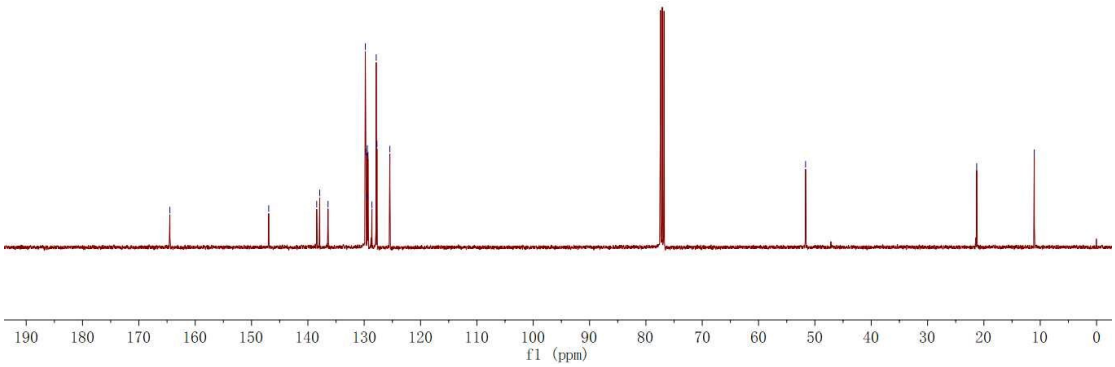
Methyl 5-methyl-1-phenyl-2-(m-tolyl)-1H-imidazole-4-carboxylate(3ae)



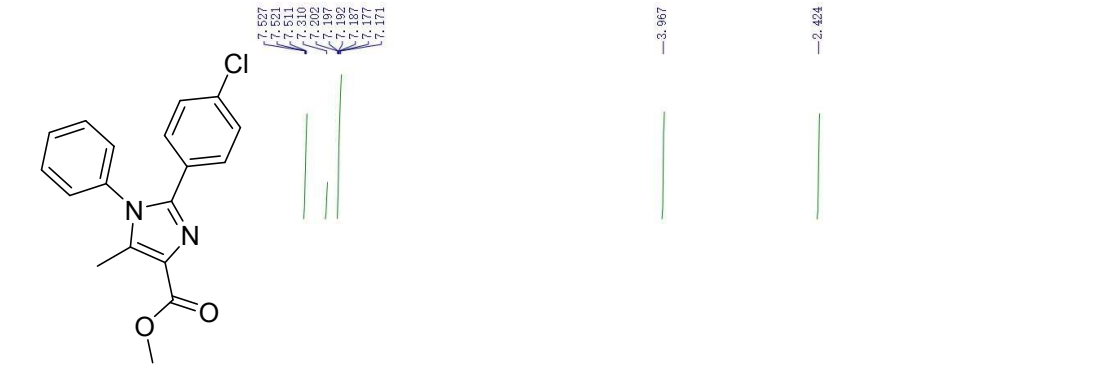
^{1}H NMR (400 MHz, $CDCl_3$)



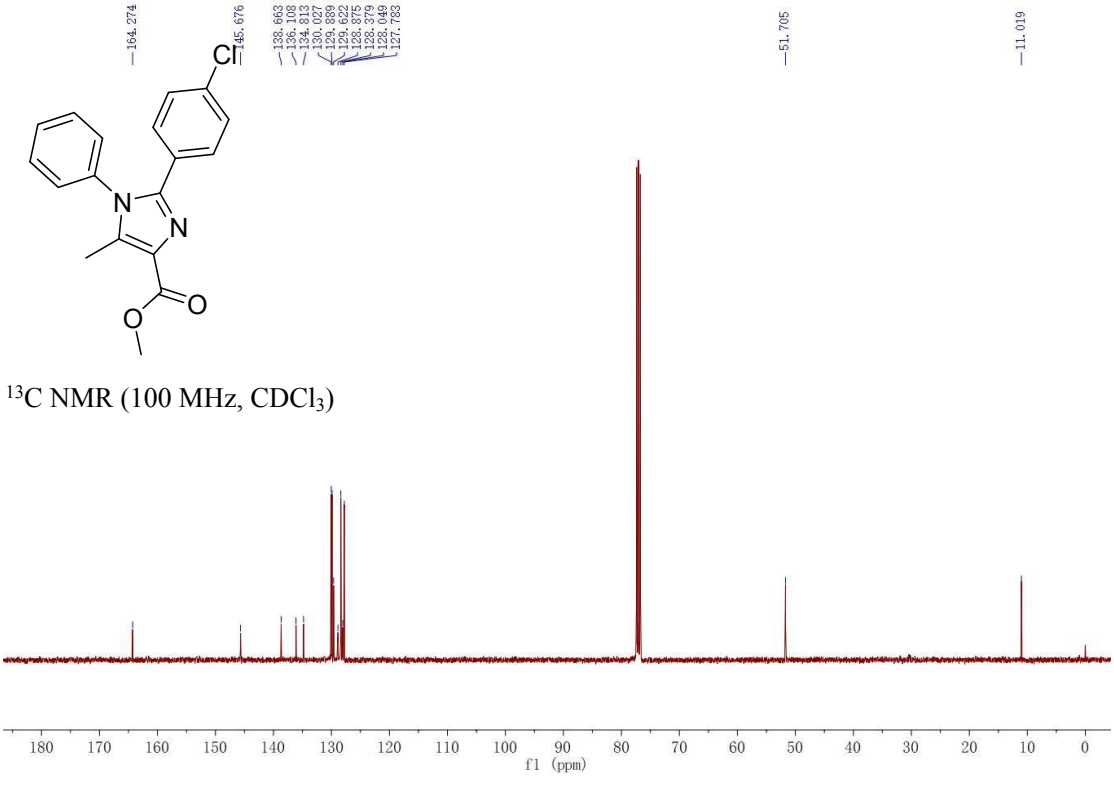
^{13}C NMR (100 MHz, $CDCl_3$)



Methyl 2-(4-chlorophenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate(3af)

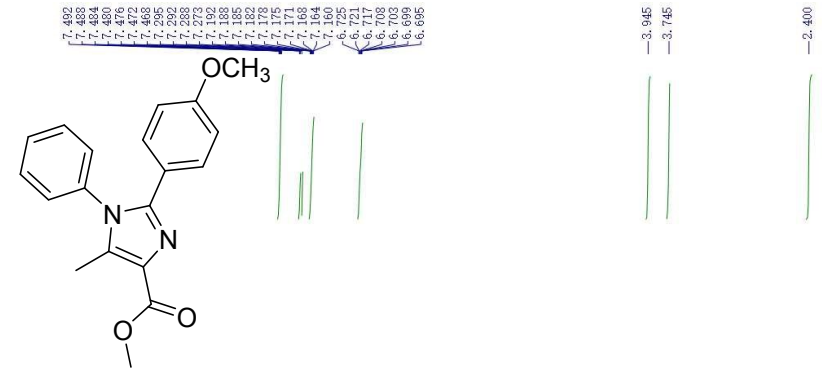


^{1}H NMR (400 MHz, $CDCl_3$)

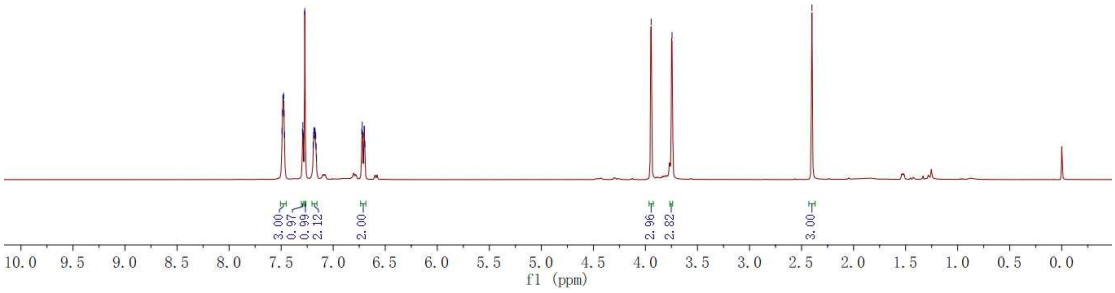


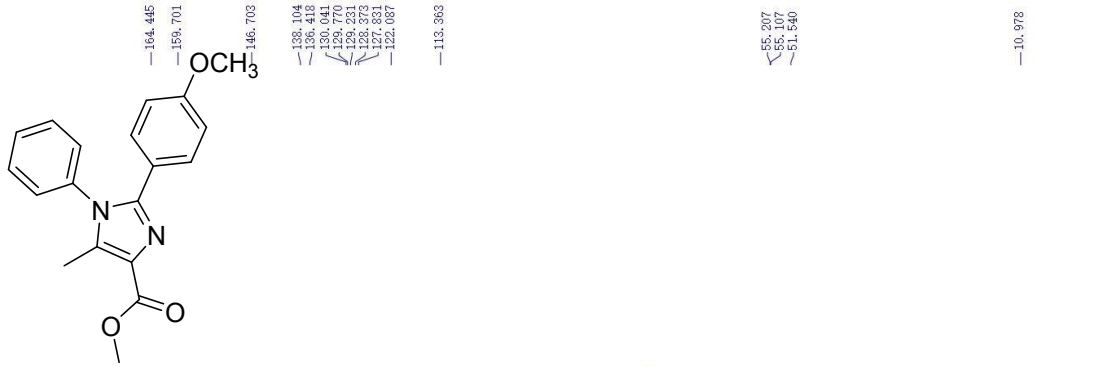
^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 2-(4-methoxyphenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate(3ag)



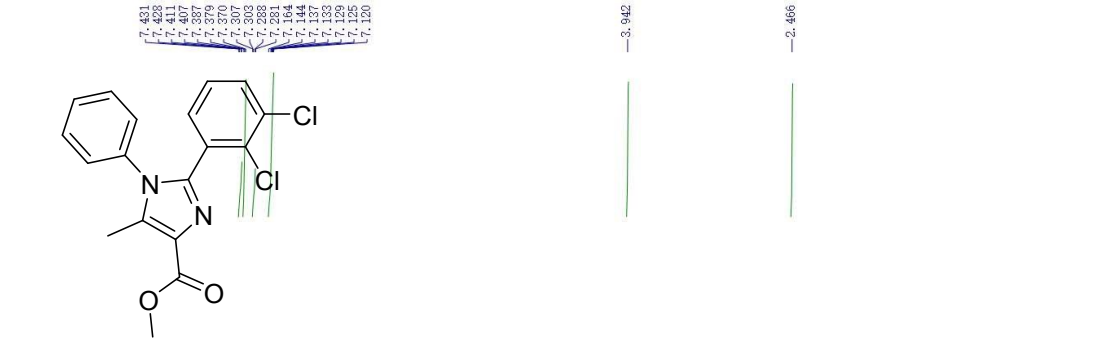
^{1}H NMR (400 MHz, $CDCl_3$)



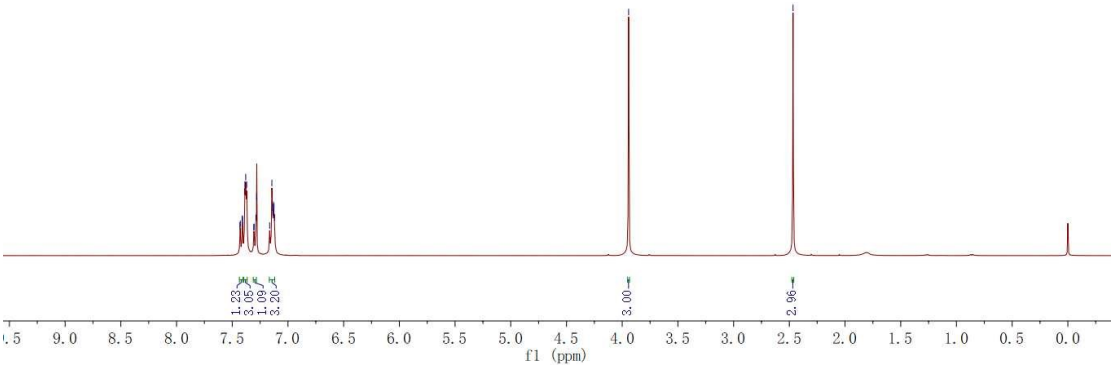


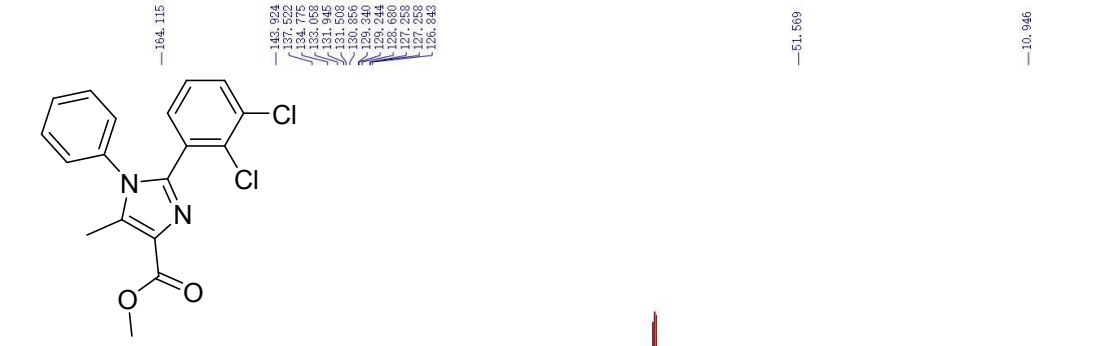
^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 2-(2,3-dichlorophenyl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate(3ah)



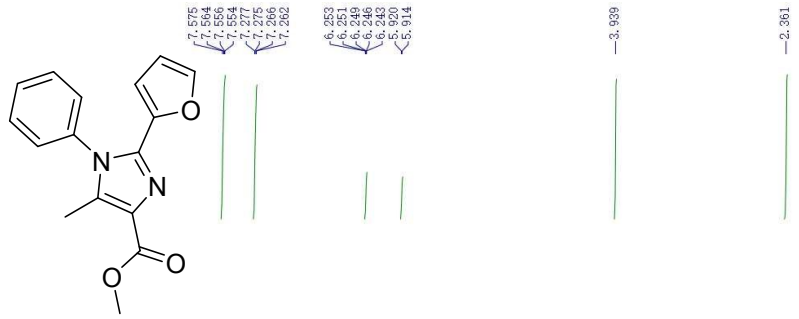
^{1}H NMR (400 MHz, $CDCl_3$)



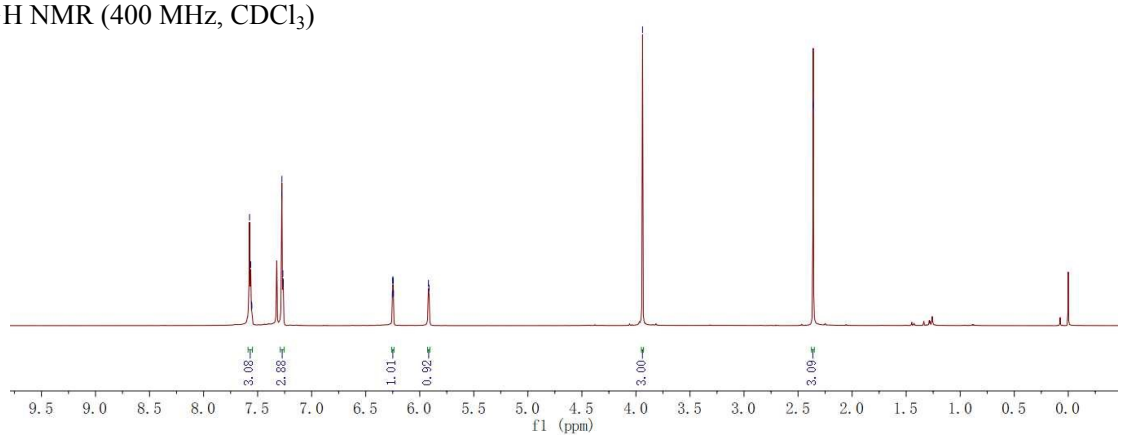


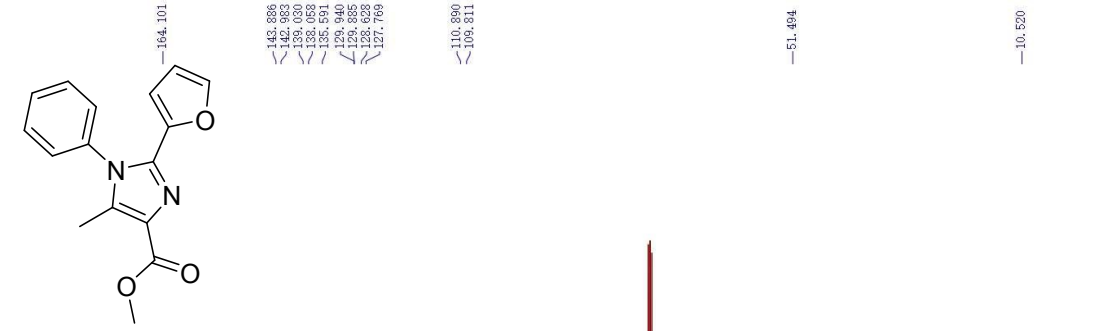
^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 2-(furan-2-yl)-5-methyl-1-phenyl-1H-imidazole-4-carboxylate(3ai)

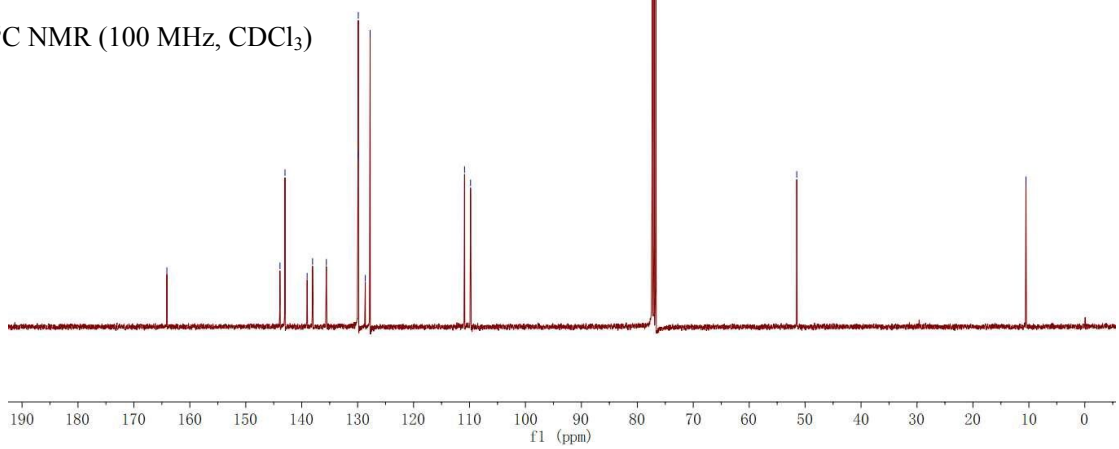


^{1}H NMR (400 MHz, $CDCl_3$)

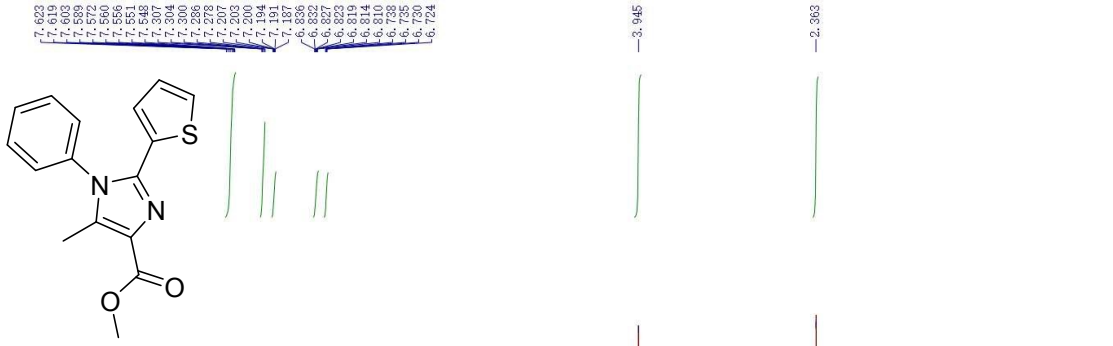




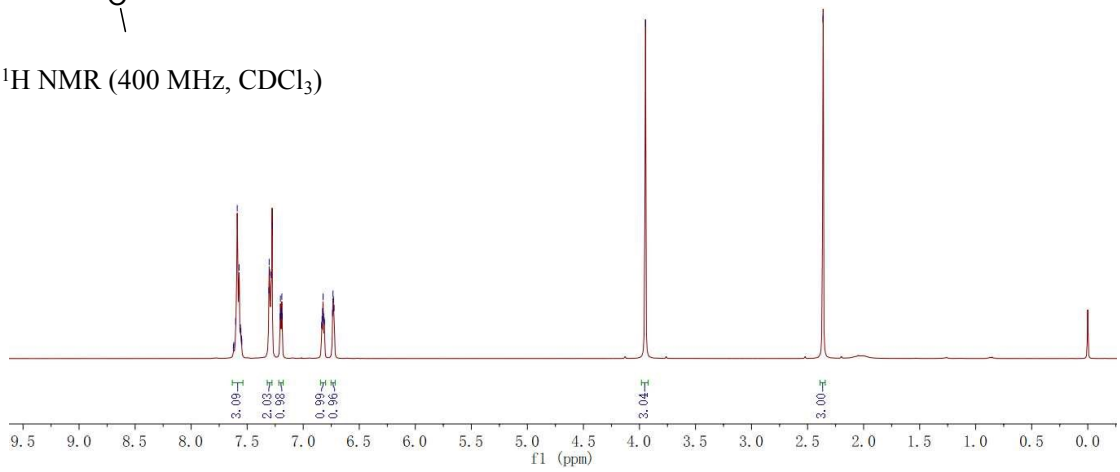
^{13}C NMR (100 MHz, $CDCl_3$)

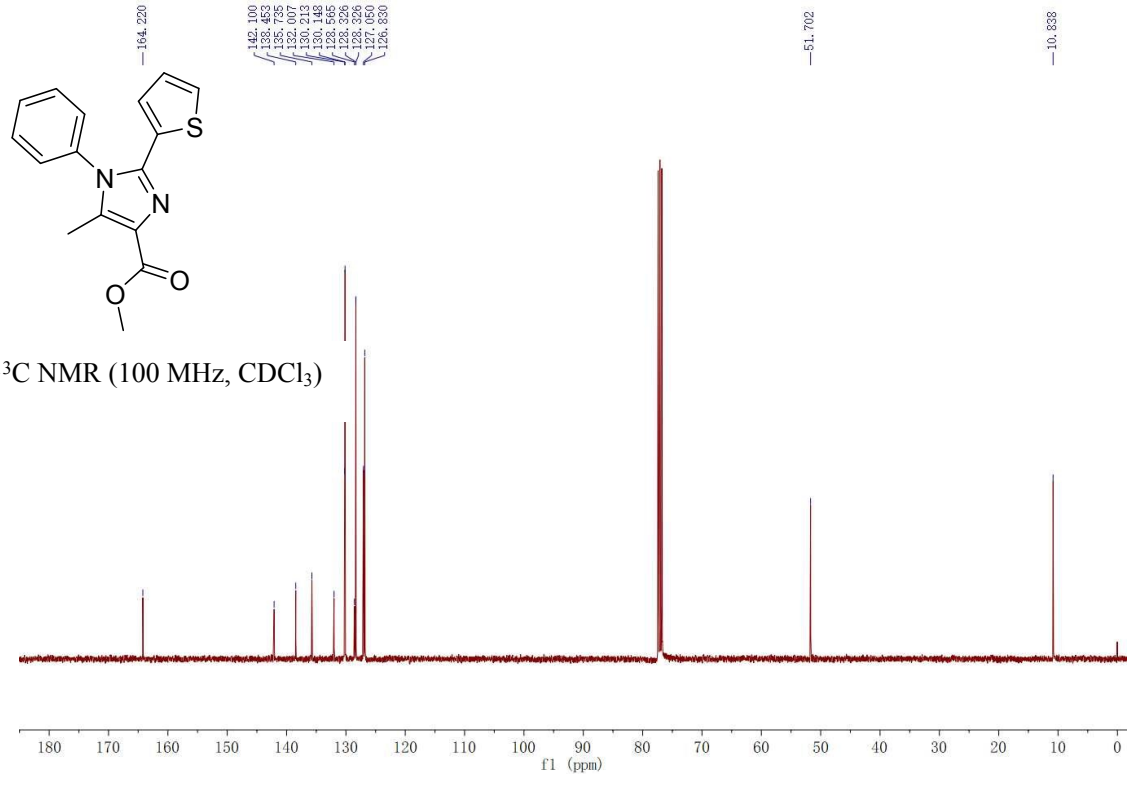


Methyl 5-methyl-1-phenyl-2-(thiophen-2-yl)-1H-imidazole-4-carboxylate(3aj)



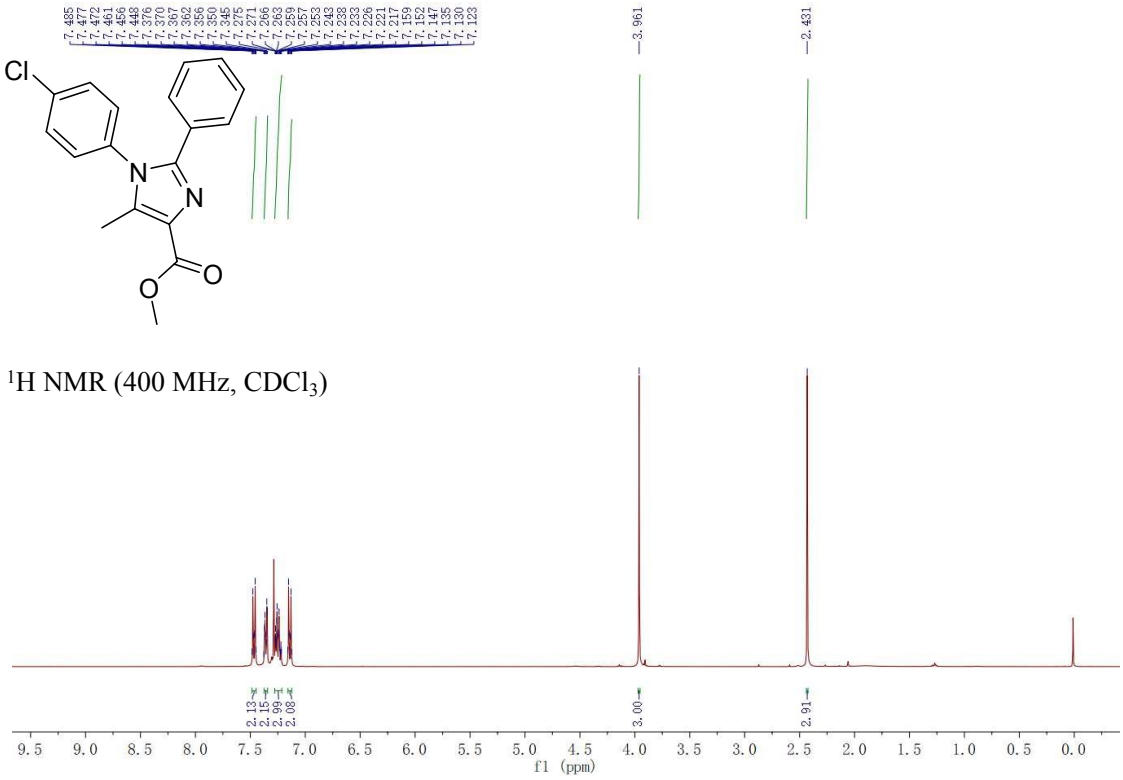
^{1}H NMR (400 MHz, $CDCl_3$)



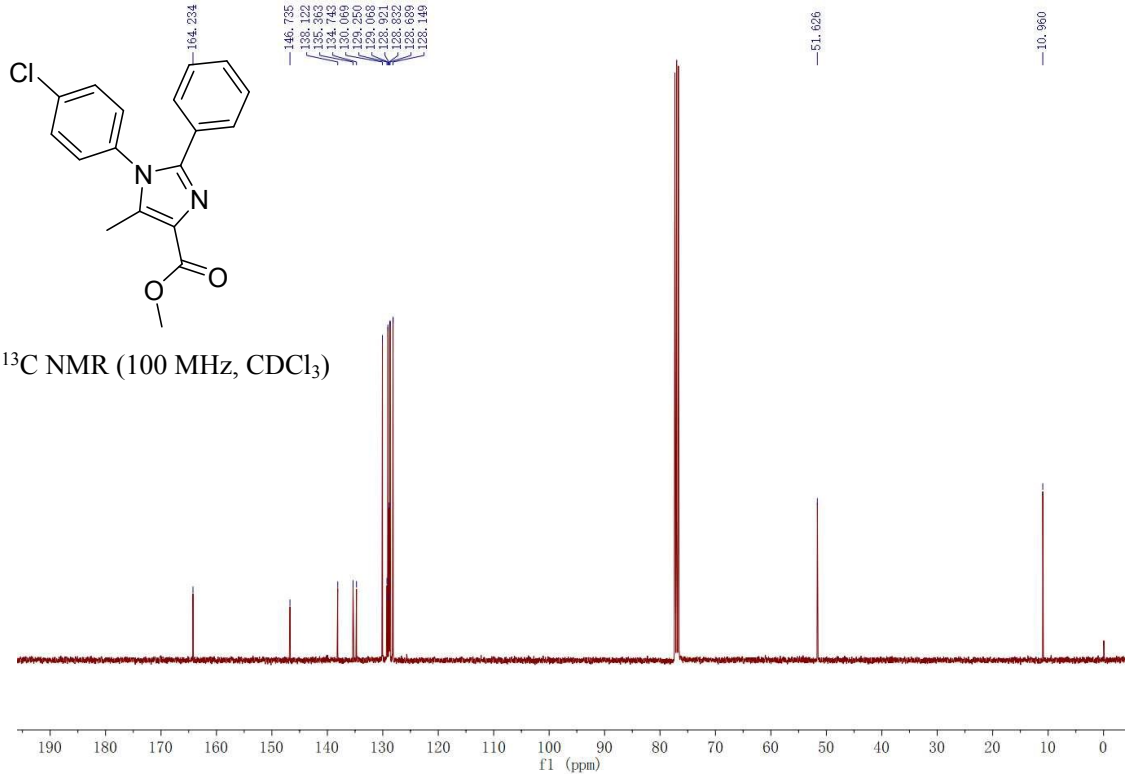


^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 1-(4-chlorophenyl)-5-methyl-2-phenyl-1H-imidazole-4-carboxylate(3ba)

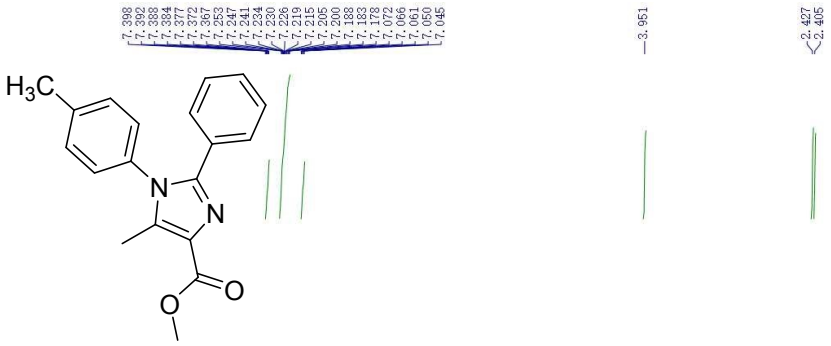


^{1}H NMR (400 MHz, $CDCl_3$)

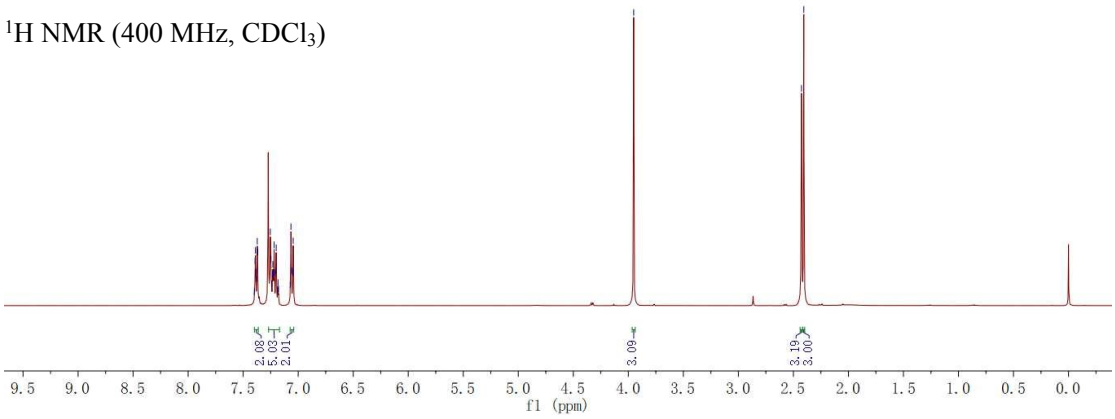


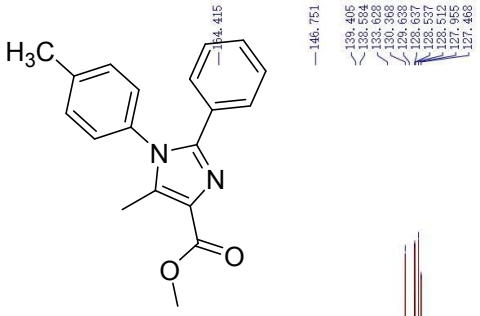
^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 5-methyl-2-phenyl-1-(p-tolyl)-1H-imidazole-4-carboxylate(3ca)



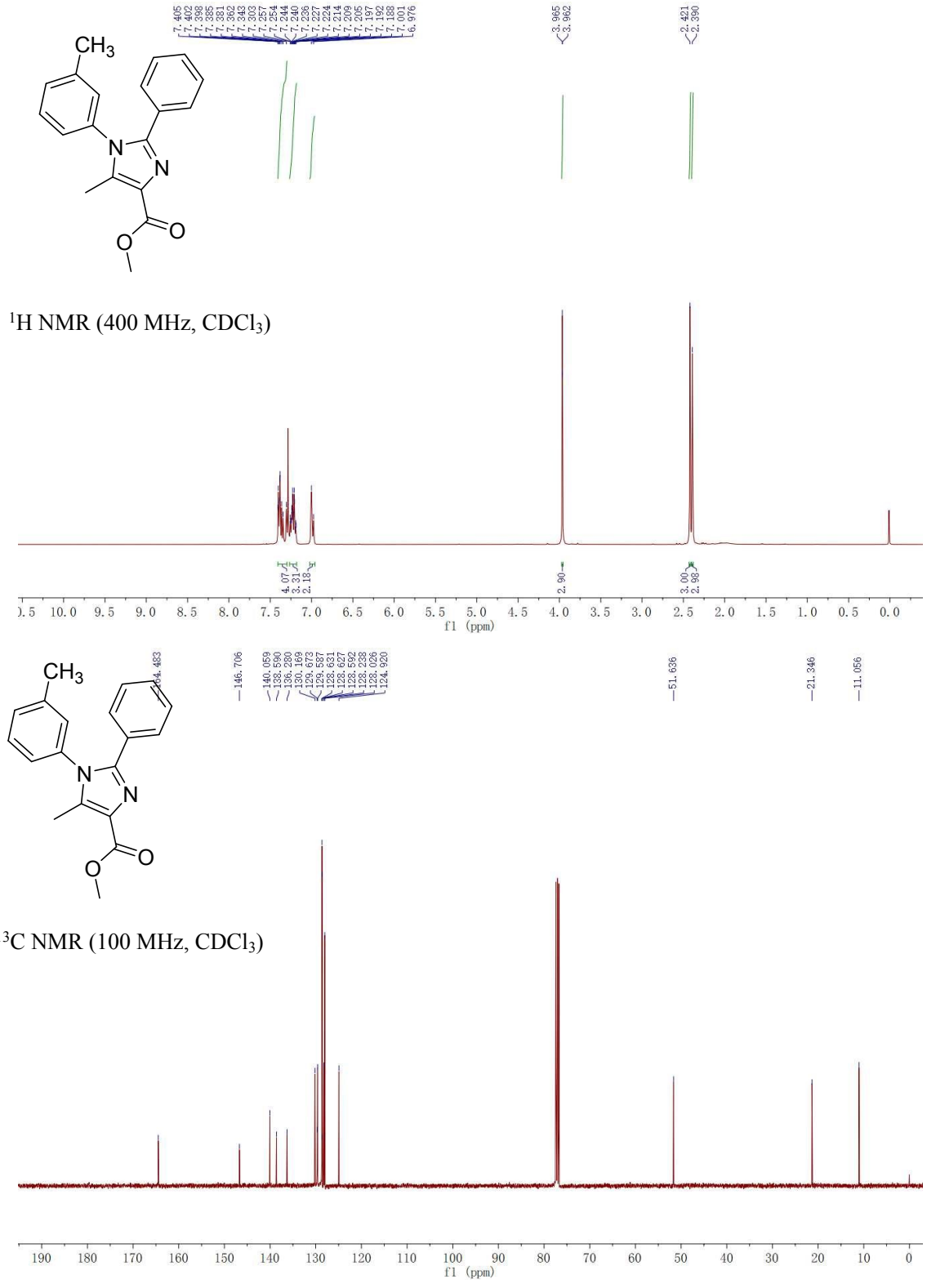
^{1}H NMR (400 MHz, $CDCl_3$)



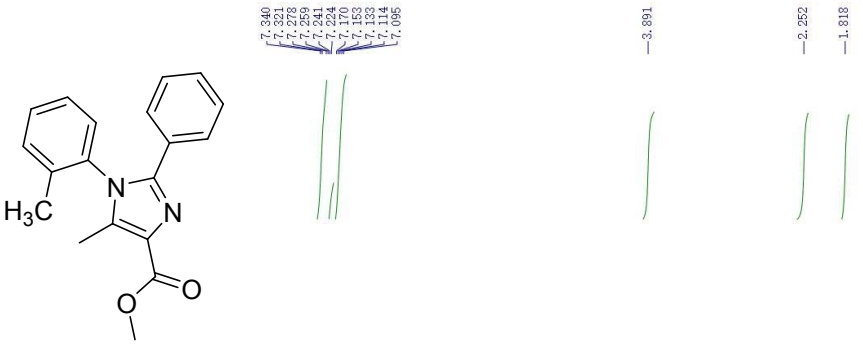


^{13}C NMR (100 MHz, $CDCl_3$)

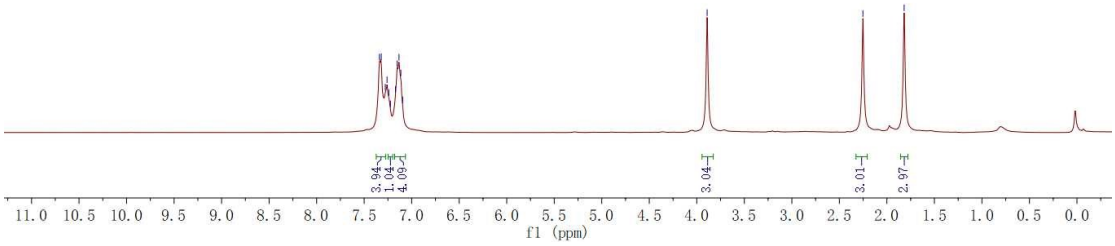
Methyl 5-methyl-2-phenyl-1-(m-tolyl)-1H-imidazole-4-carboxylate(3da)



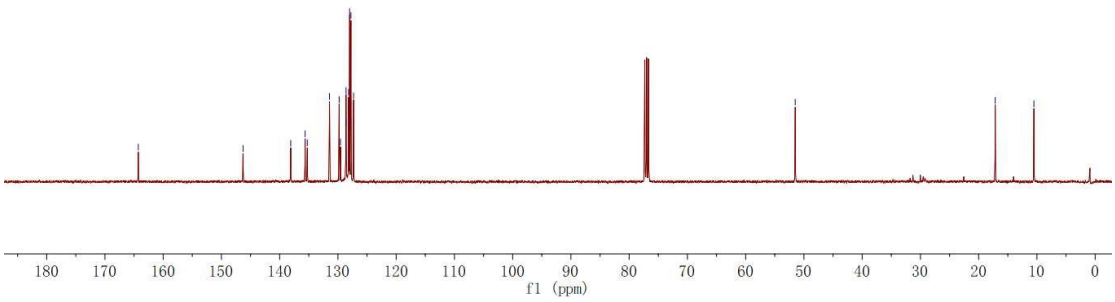
Methyl 5-methyl-2-phenyl-1-(o-tolyl)-1H-imidazole-4-carboxylate (3ea)



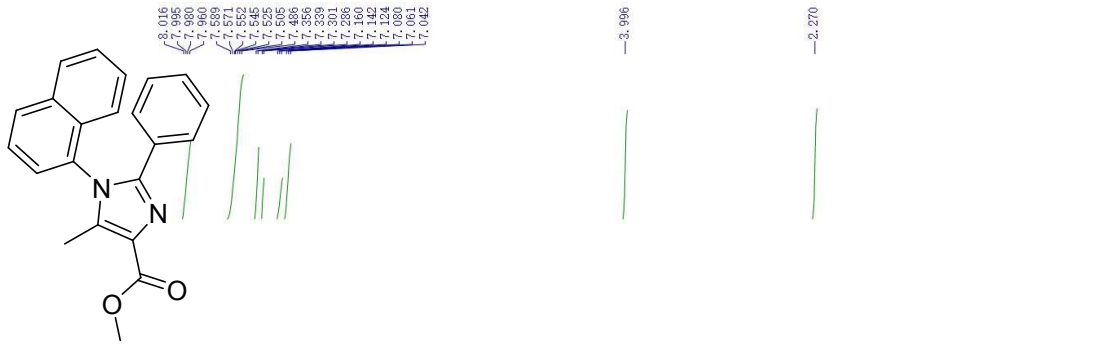
^{1}H NMR (400 MHz, $CDCl_3$)



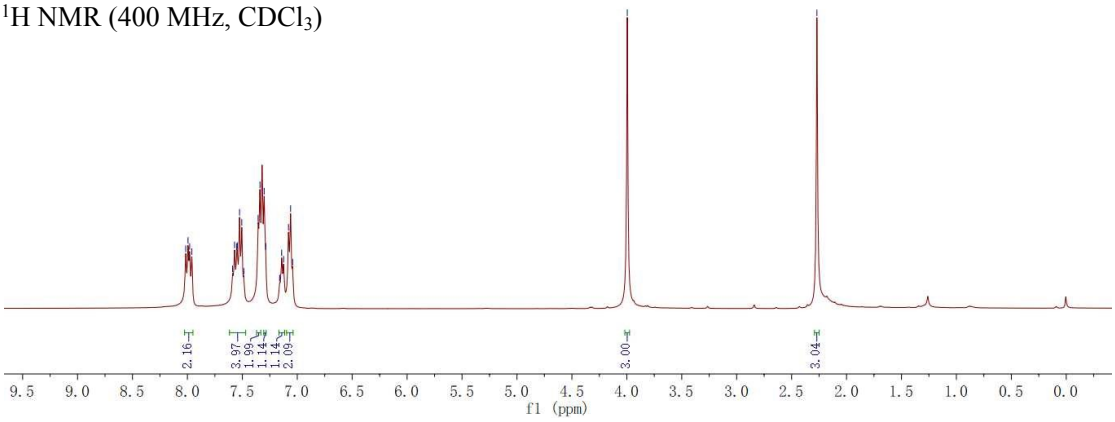
^{13}C NMR (100 MHz, $CDCl_3$)

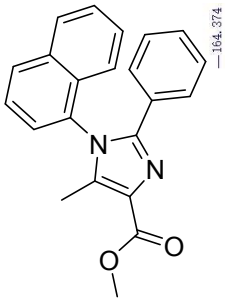


Methyl 5-methyl-1-(naphthalen-1-yl)-2-phenyl-1H-imidazole-4-carboxylate(3fa)



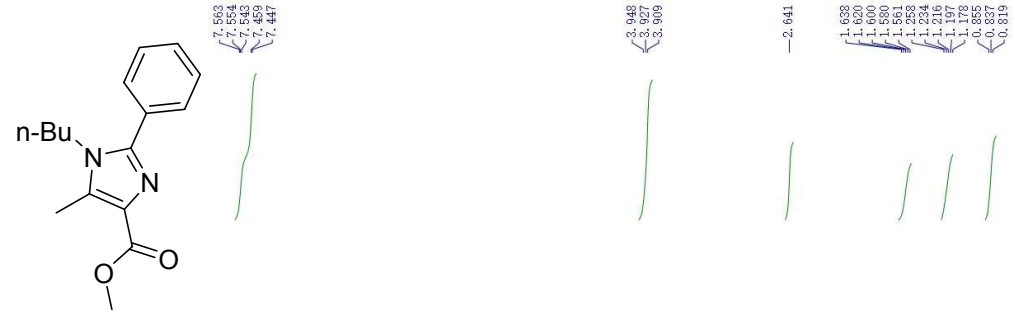
^{1}H NMR (400 MHz, $CDCl_3$)



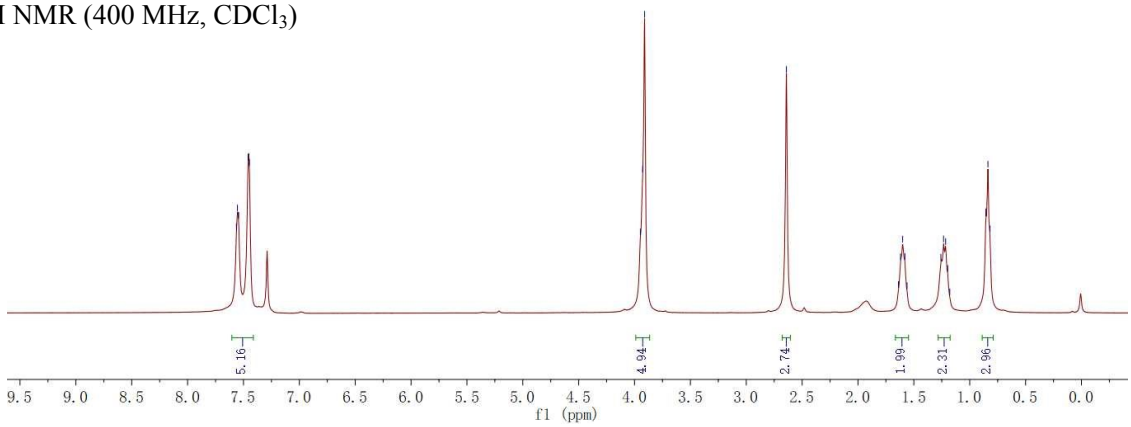


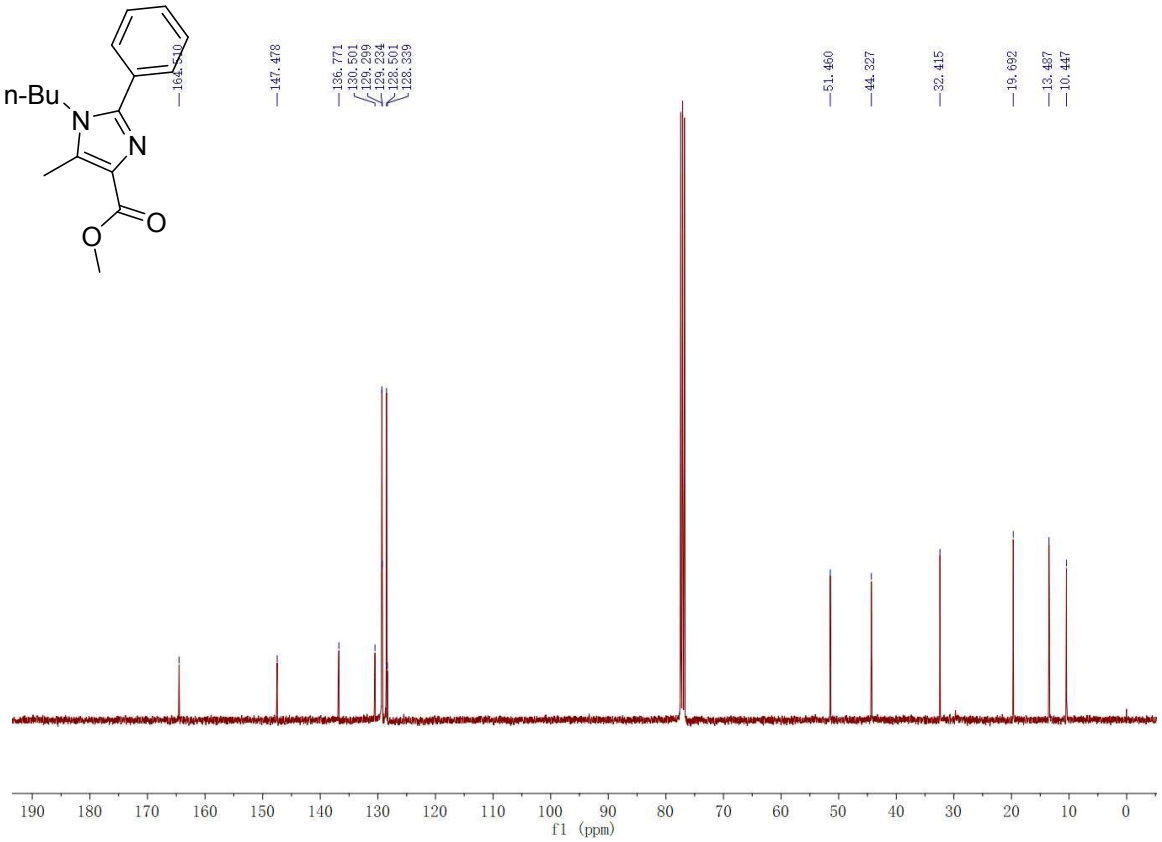
^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 1-butyl-5-methyl-2-phenyl-1H-imidazole-4-carboxylate(3ga)

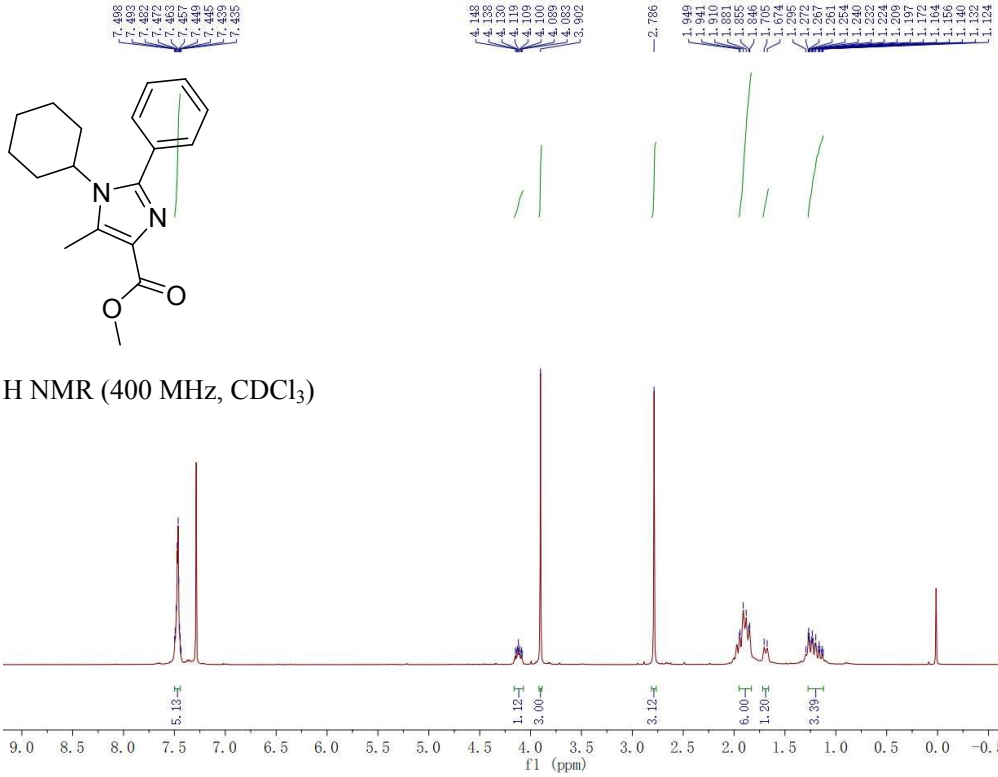


^{1}H NMR (400 MHz, $CDCl_3$)

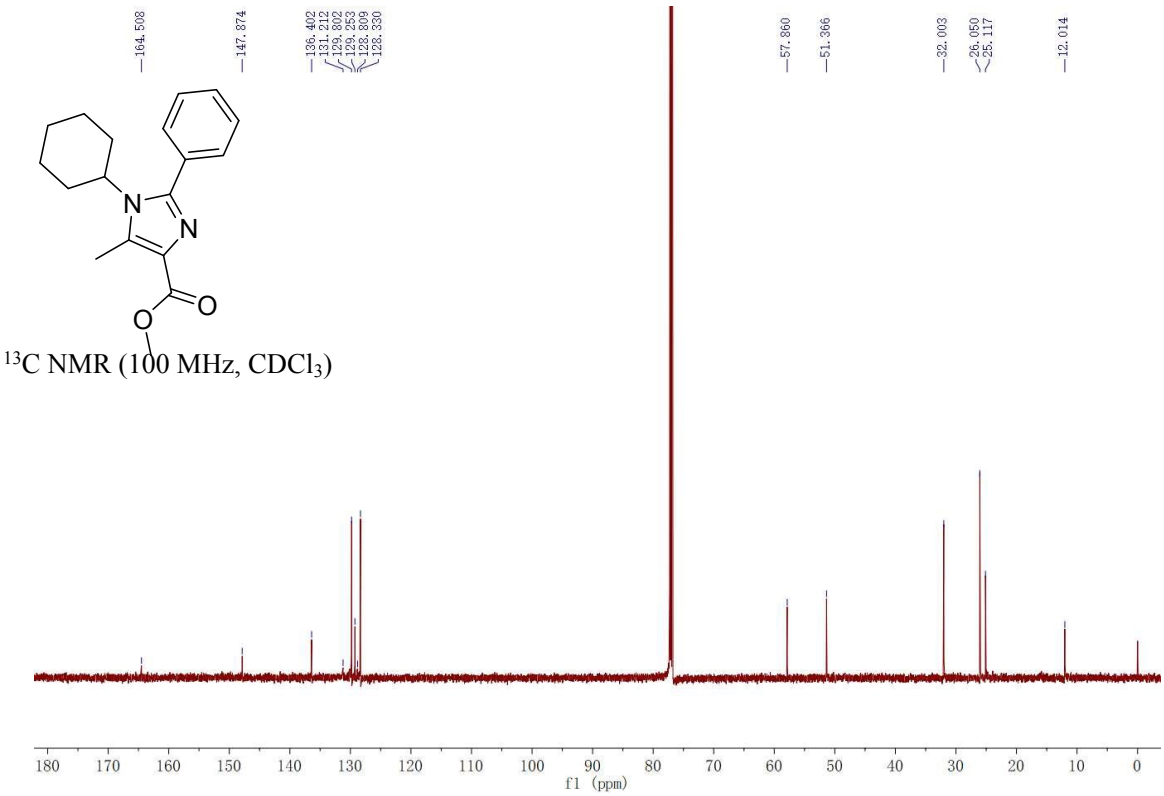




Methyl 1-cyclohexyl-5-methyl-2-phenyl-1H-imidazole-4-carboxylate(3ha)

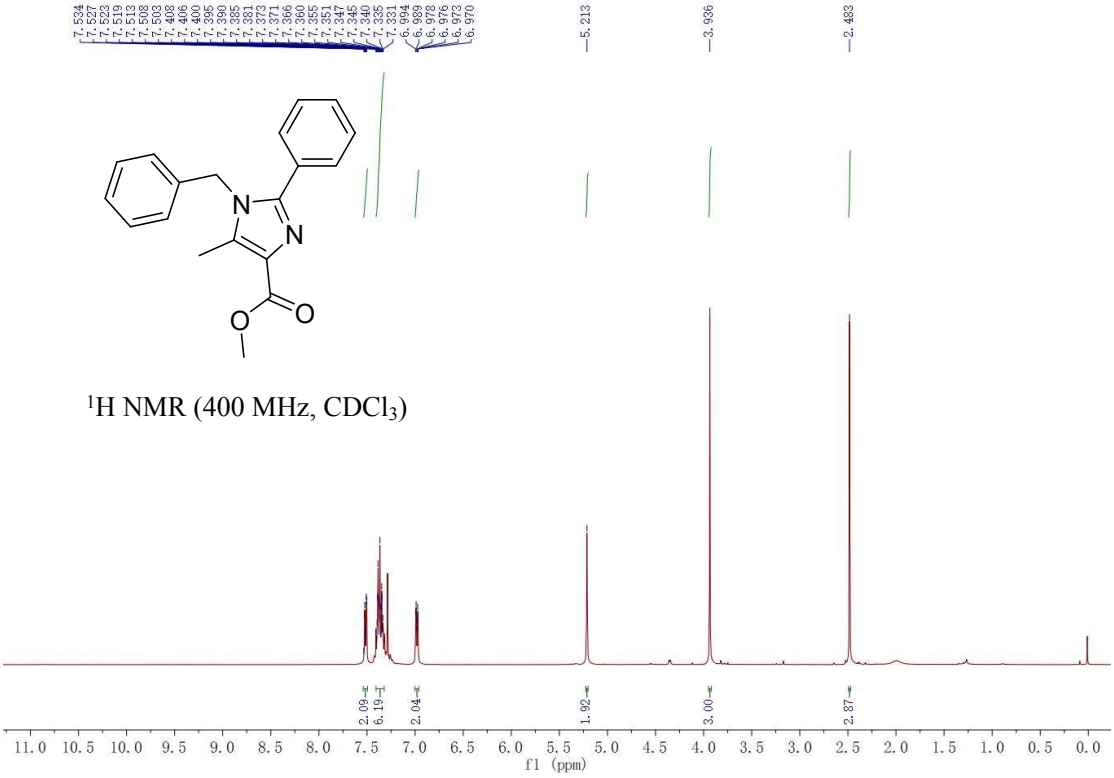


^{1}H NMR (400 MHz, $CDCl_3$)

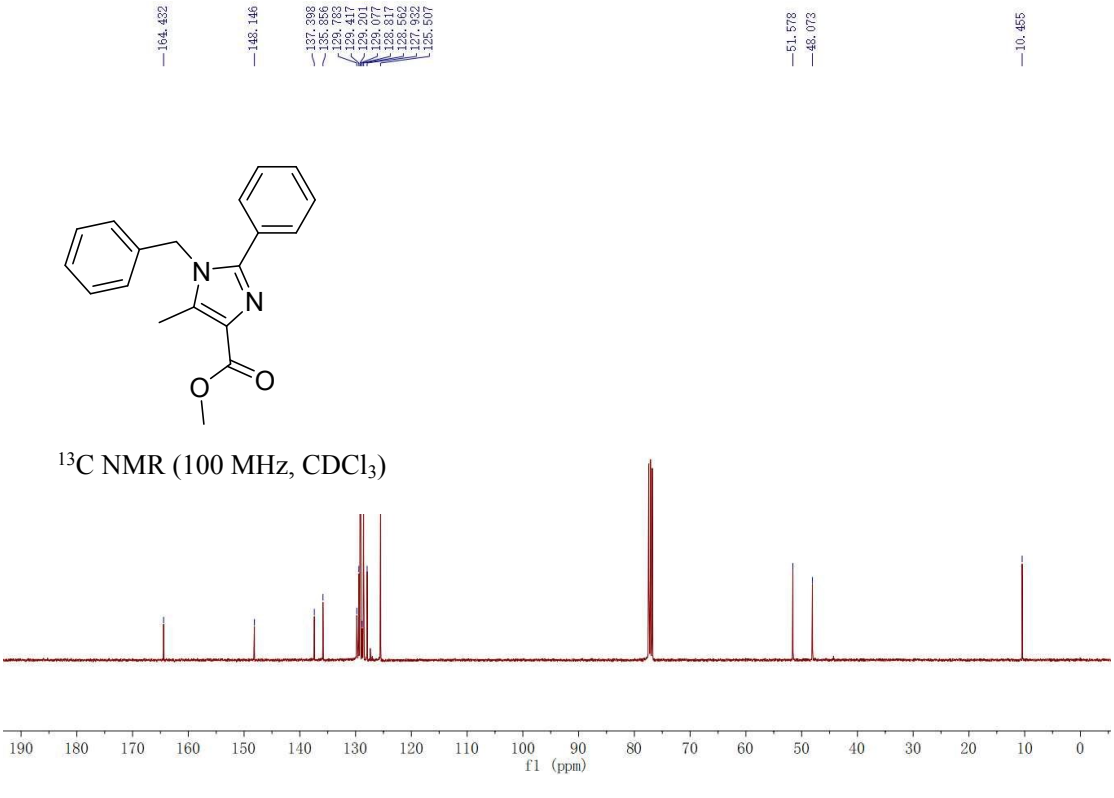


^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 1-benzyl-5-methyl-2-phenyl-1H-imidazole-4-carboxylate(3ia)

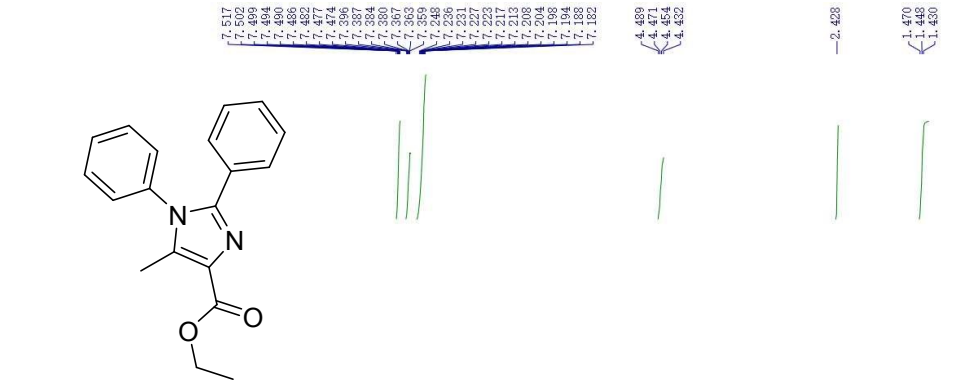


^{1}H NMR (400 MHz, $CDCl_3$)

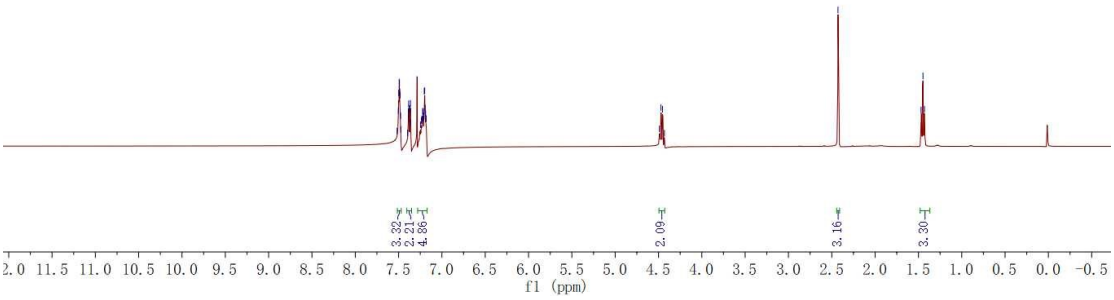


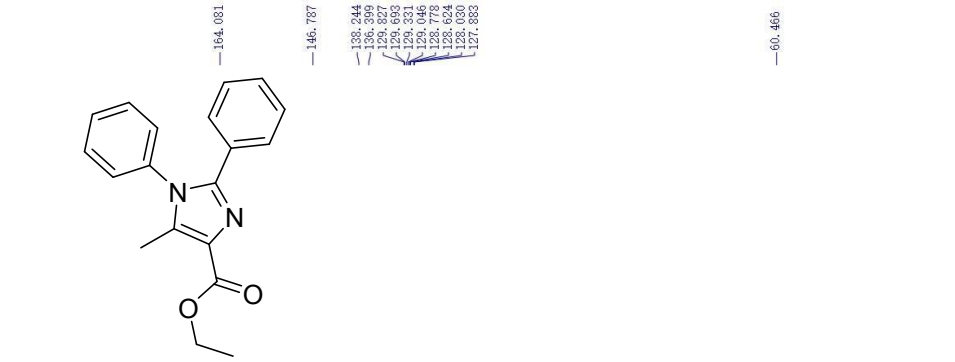
^{13}C NMR (100 MHz, $CDCl_3$)

Ethyl 5-methyl-1,2-diphenyl-1H-imidazole-4-carboxylate(3ja)



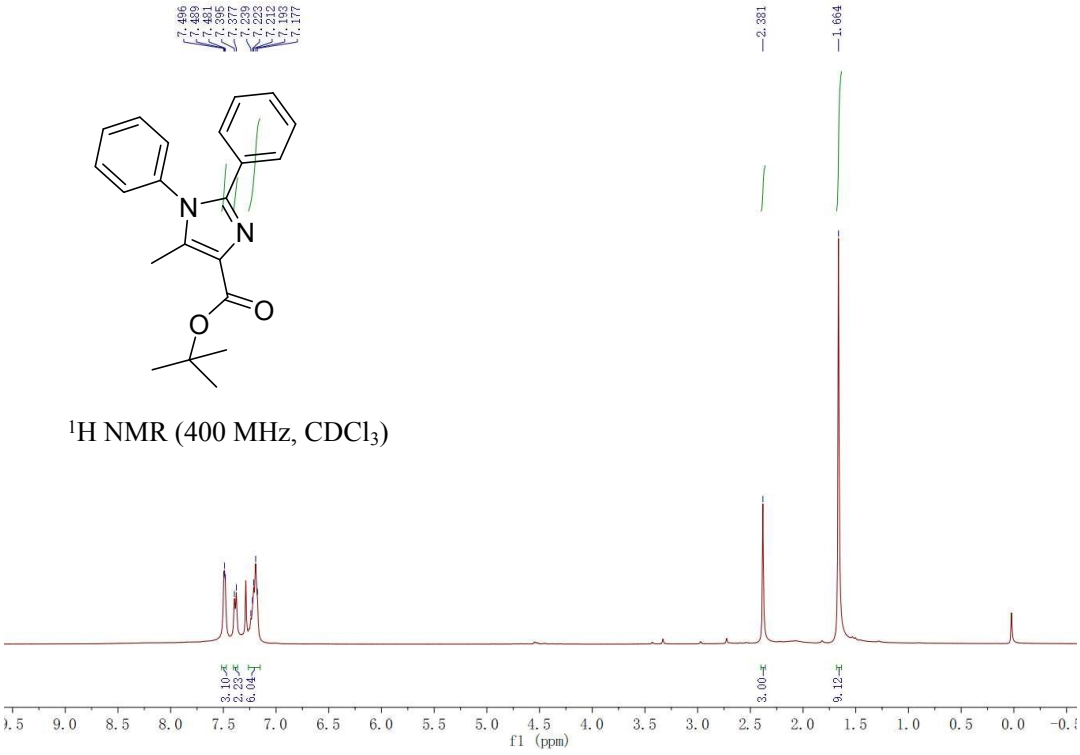
^{1}H NMR (400 MHz, $CDCl_3$)



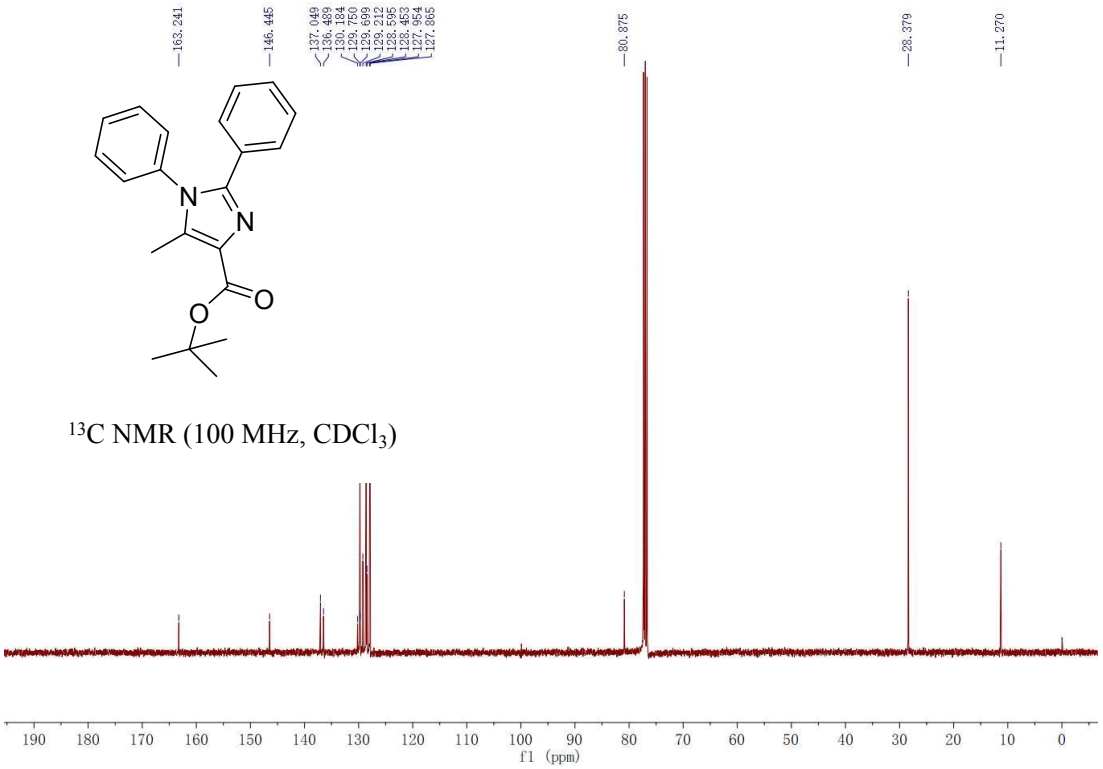


^{13}C NMR (100 MHz, $CDCl_3$)

Tert-Butyl 5-methyl-1,2-diphenyl-1H-imidazole-4-carboxylate(3ka)

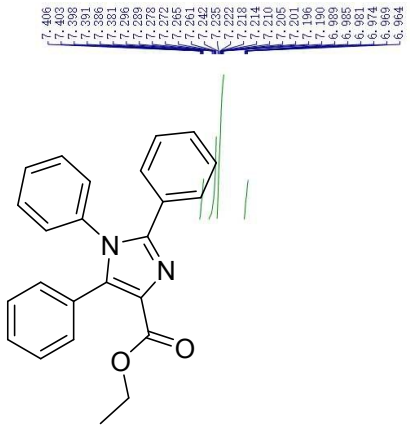


^{1}H NMR (400 MHz, $CDCl_3$)

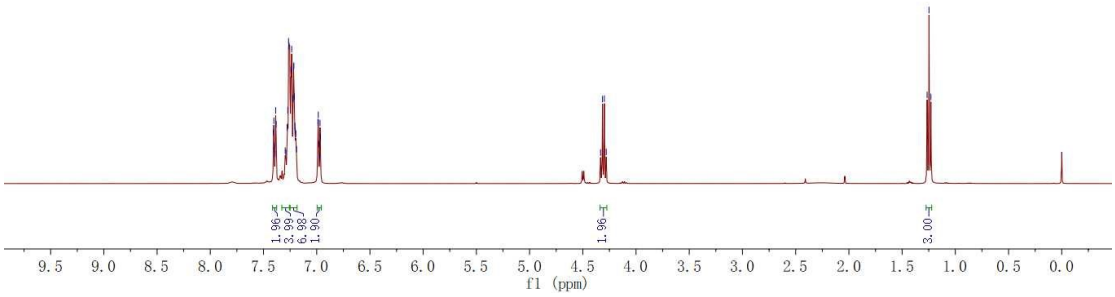


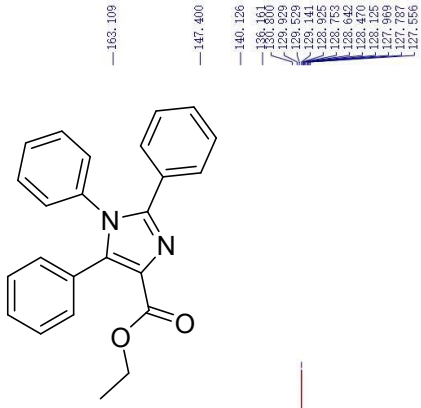
^{13}C NMR (100 MHz, $CDCl_3$)

Ethyl 1,2,5-triphenyl-1H-imidazole-4-carboxylate(3la)

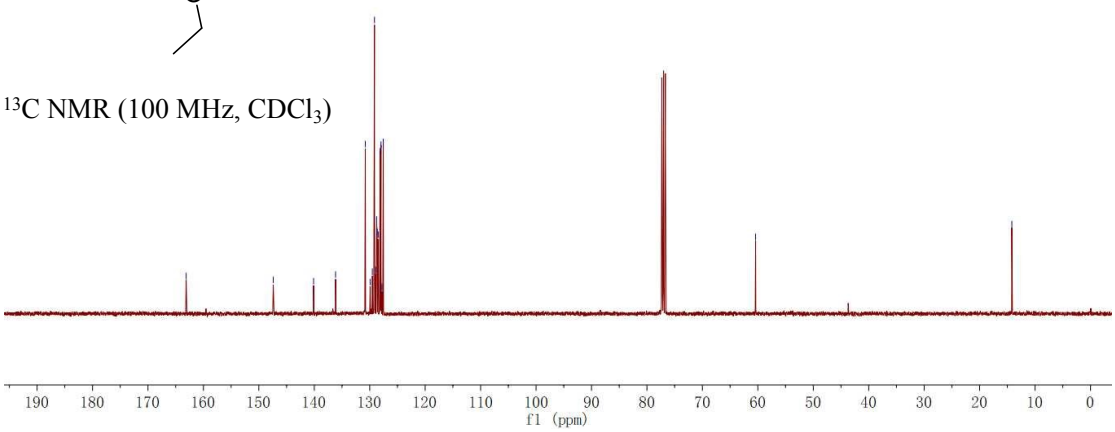


^{1}H NMR (400 MHz, $CDCl_3$)

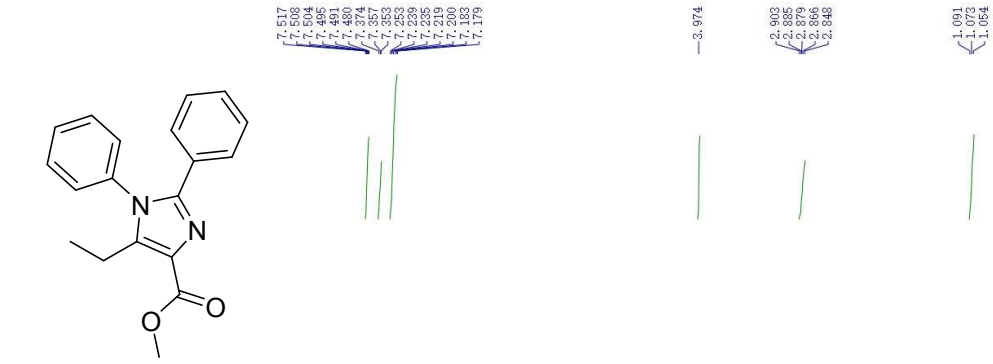




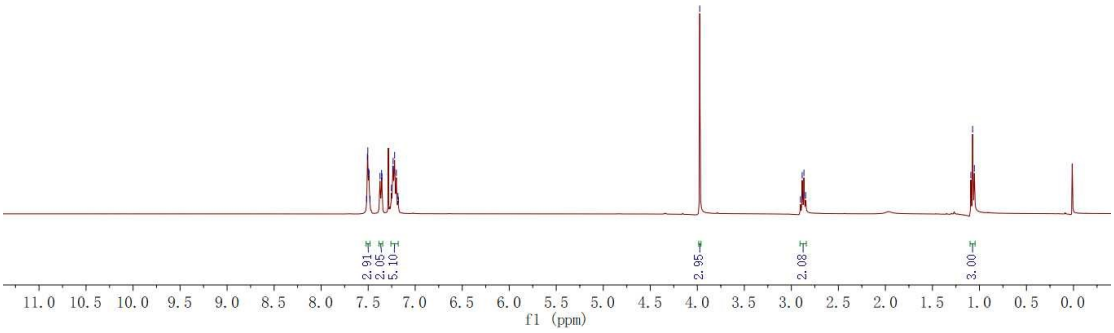
^{13}C NMR (100 MHz, $CDCl_3$)

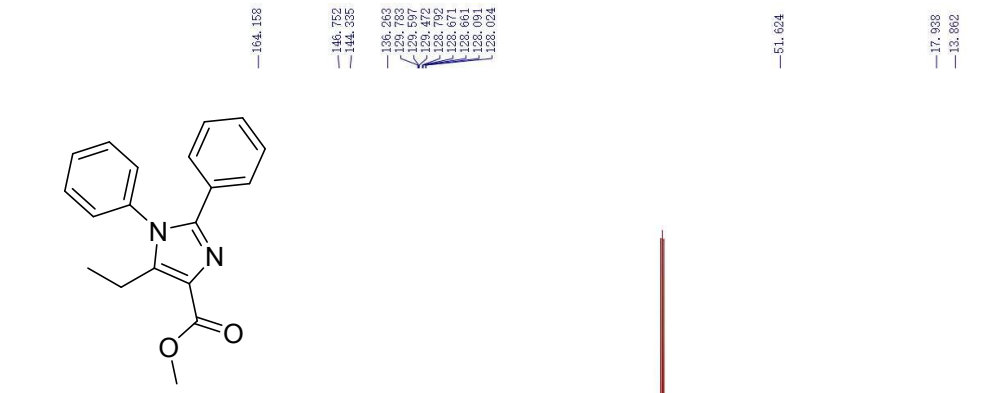


Methyl 5-ethyl-1,2-diphenyl-1H-imidazole-4-carboxylate(3ma)

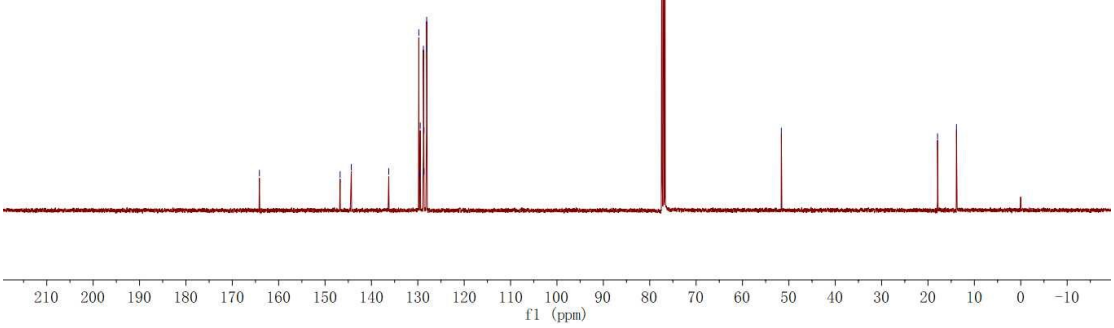


^{1}H NMR (400 MHz, $CDCl_3$)

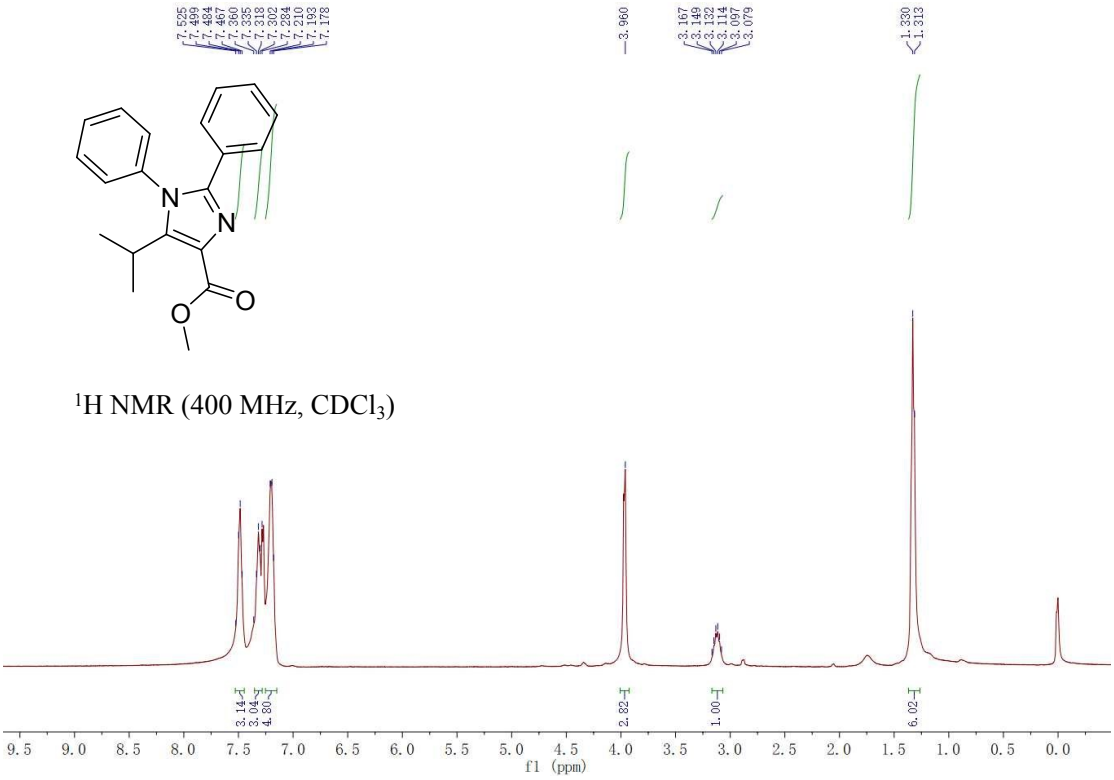




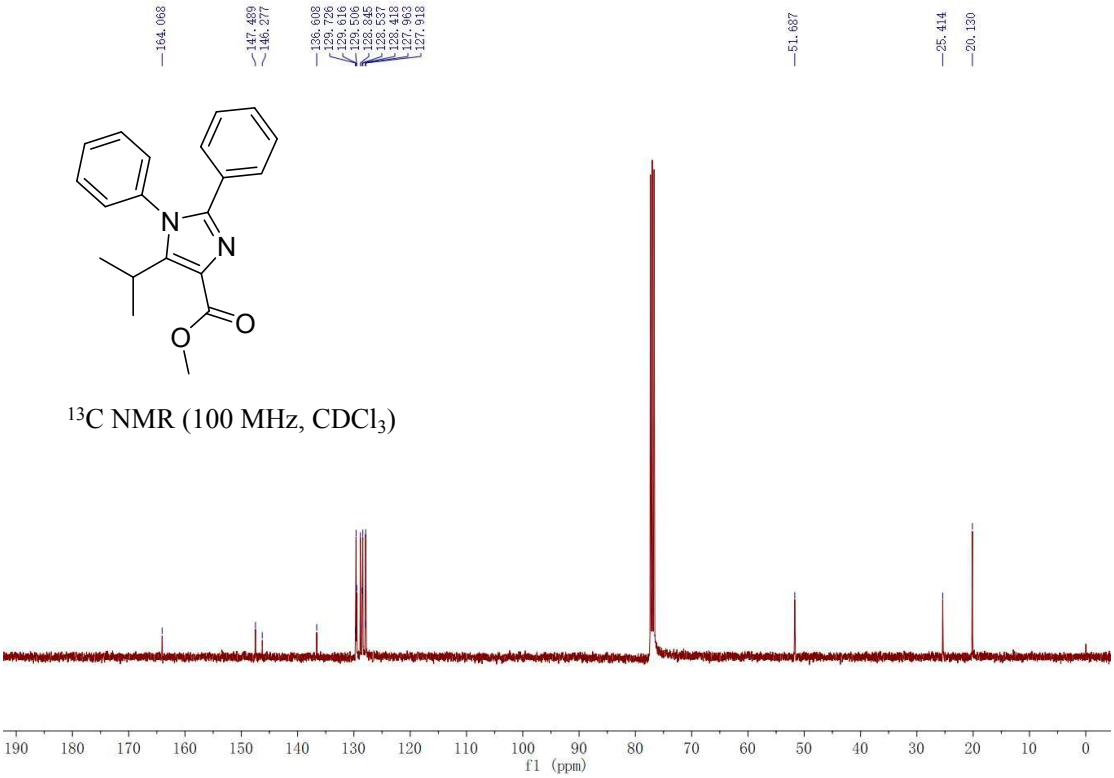
^{13}C NMR (100 MHz, $CDCl_3$)



Methyl 5-isopropyl-1,2-diphenyl-1H-imidazole-4-carboxylate(3na)

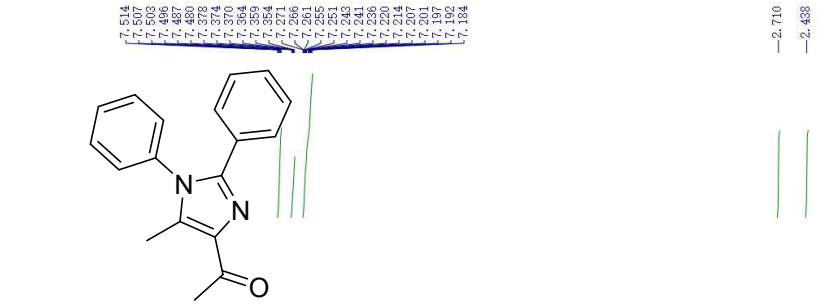


^{1}H NMR (400 MHz, $CDCl_3$)

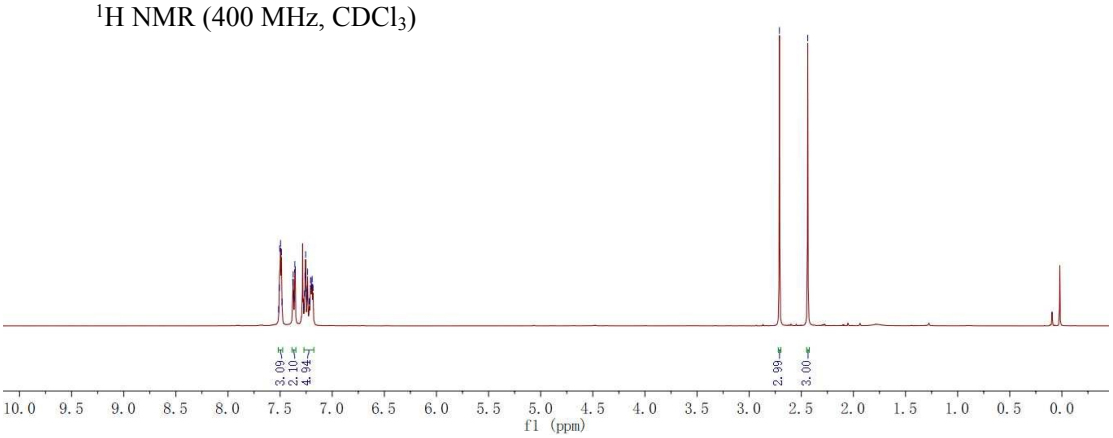


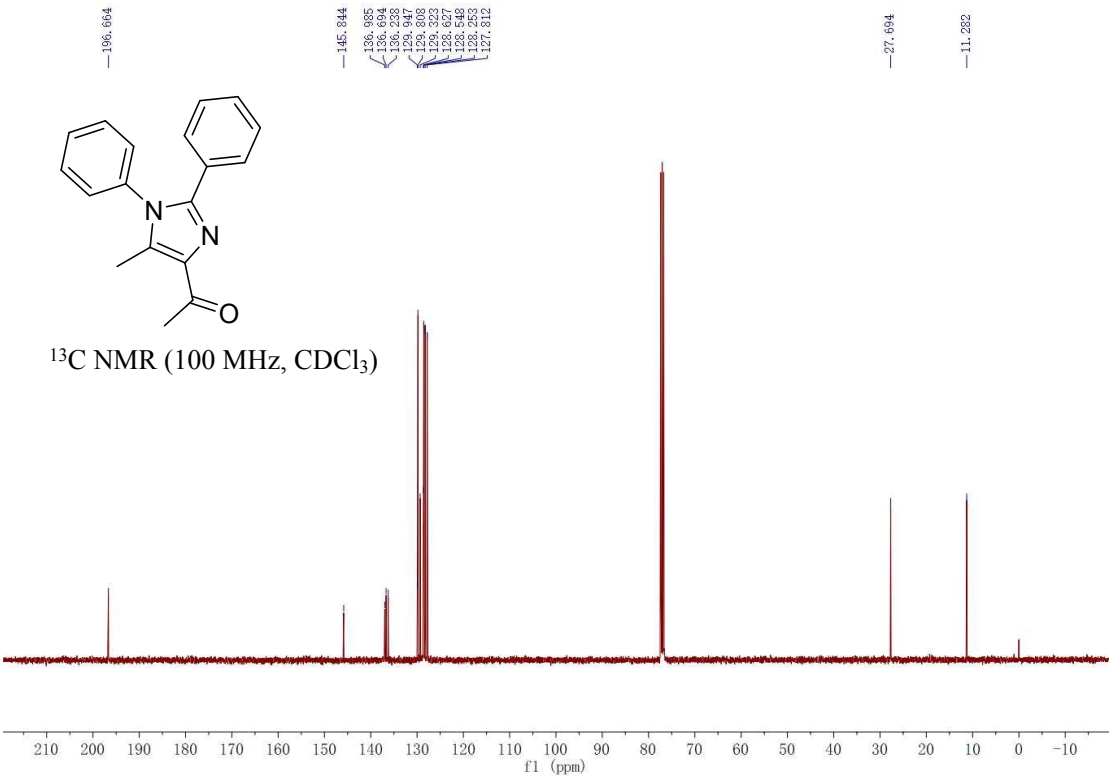
^{13}C NMR (100 MHz, $CDCl_3$)

1-(5-methyl-1,2-diphenyl-1H-imidazol-4-yl)ethan-1-one(3oa)



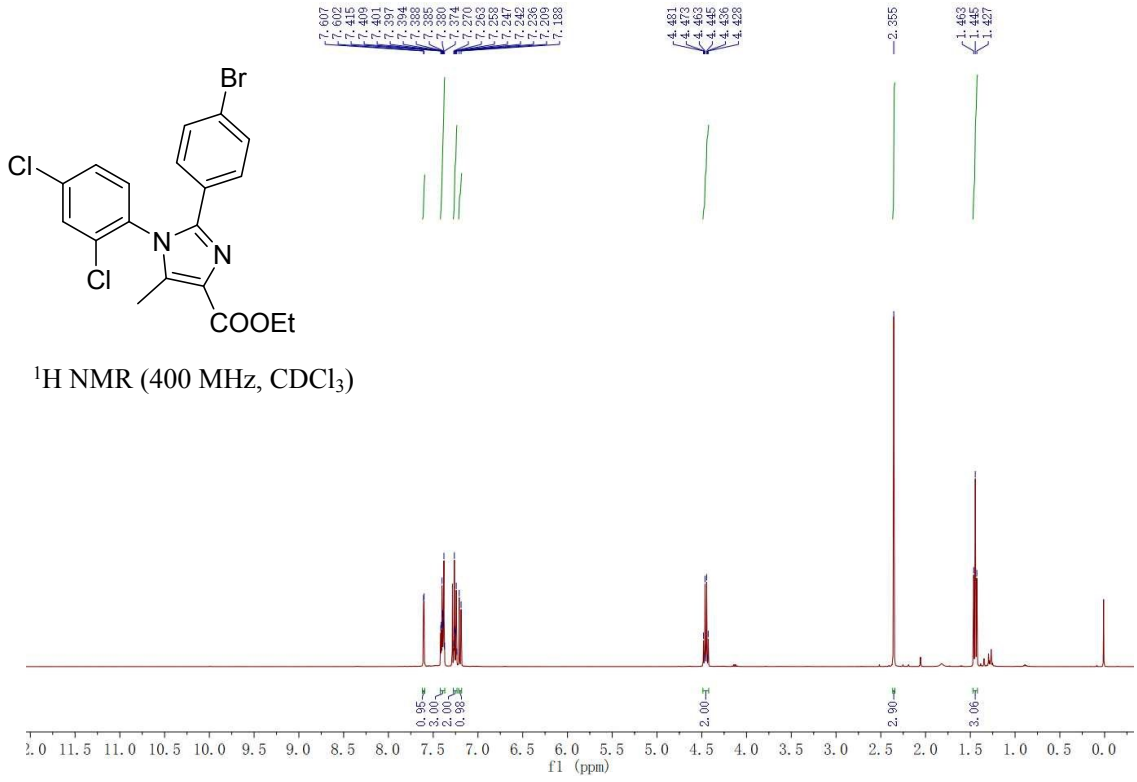
^{1}H NMR (400 MHz, $CDCl_3$)



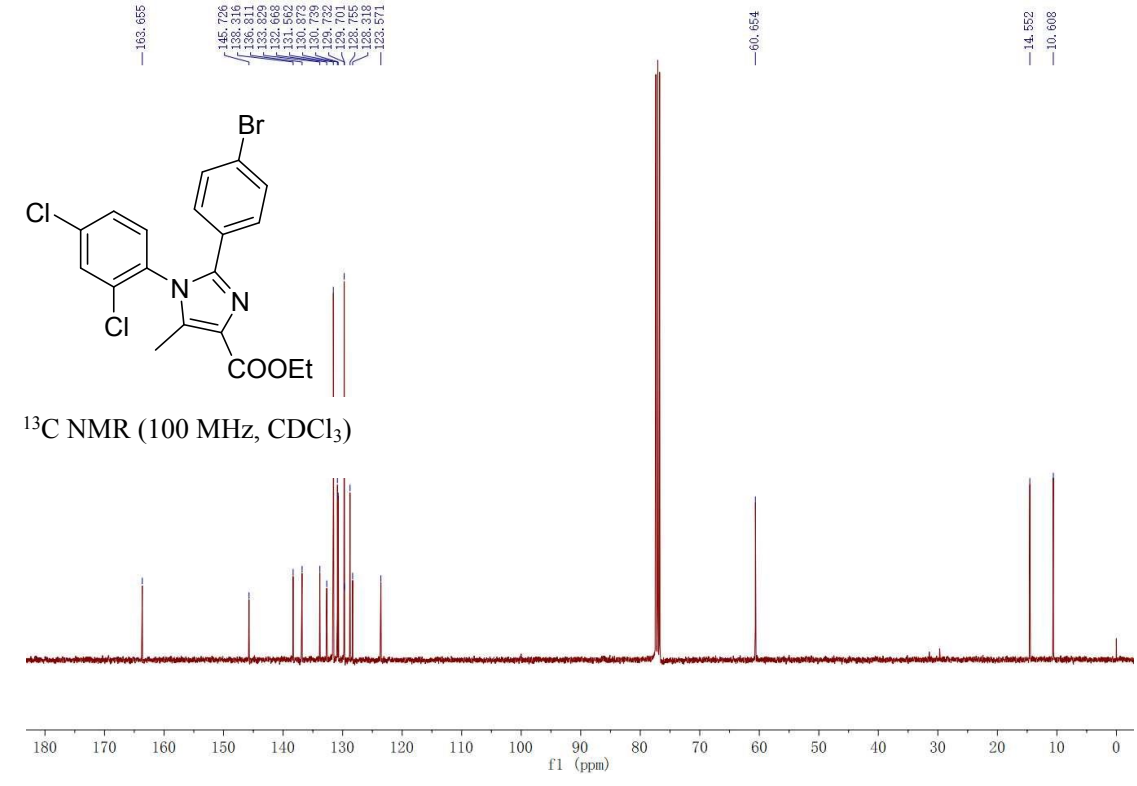


^{13}C NMR (100 MHz, $CDCl_3$)

Ethyl 2-(4-bromophenyl)-1-(2,4-dichlorophenyl)-5-methyl-1H-imidazole-4-carboxylate

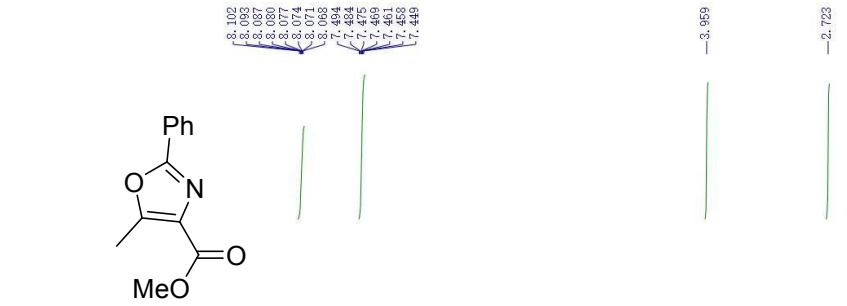


^{1}H NMR (400 MHz, $CDCl_3$)

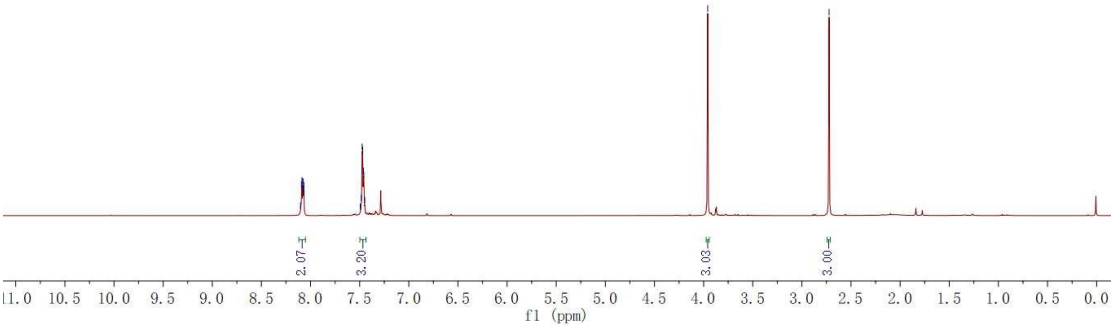


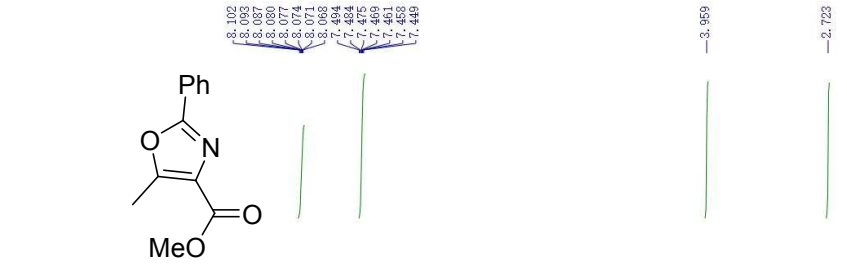
^{13}C NMR (100 MHz, $CDCl_3$)

Methyl 5-methyl-2-phenyloxazole-4-carboxylate (3a'a)

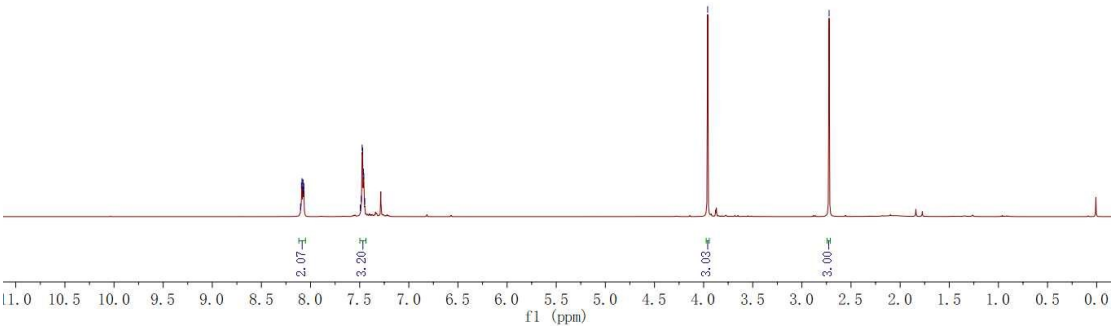


^{1}H NMR (400 MHz, $CDCl_3$)



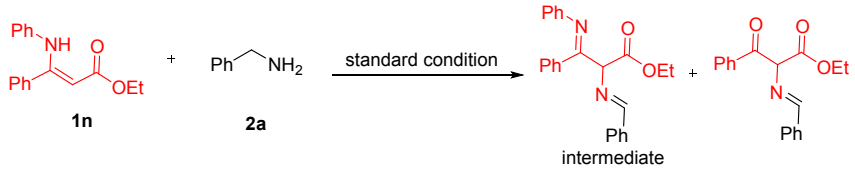


^{13}C NMR (100 MHz, $CDCl_3$)



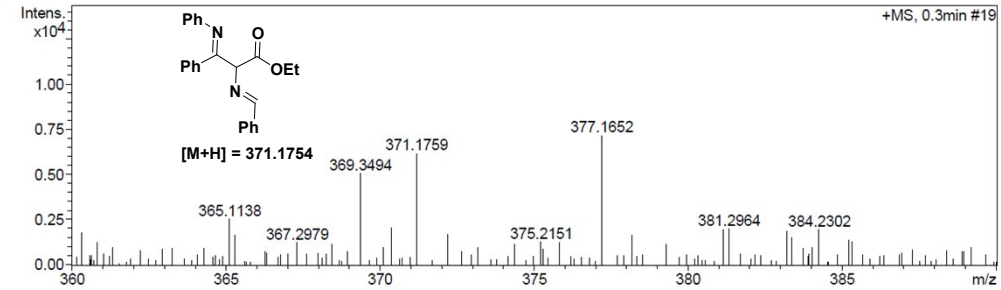
9. HRMS (ESI) of intermediates

Manuscript (Scheme 5 Control experiment)



Acquisition Parameter

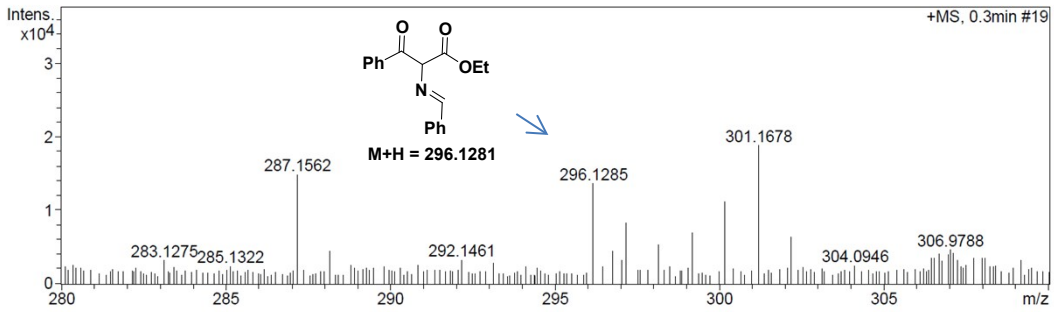
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	5500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	Formula	m/z	err [ppm]	mSigma
371.1759	C 24 H 23 N 2 O 2	371.1754	-1.2	66.7

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	5500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	Formula	m/z	err [ppm]	mSigma
296.1285	C 18 H 18 N O 3	296.1281	-1.3	67.0