Supporting information

An electrochemical tandem Michael addition, azidation and intramolecular cyclization strategy for the synthesis of imidazole derivatives

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1. General information

All reagents were obtained from commercial sources and used without further purification unless otherwise indicated. Silica gel for column chromatography was purchased from Qingdao Haiyang Chemical Co., Ltd. Reactions were stirred using Teflon-coated magnetic stir bars. Thin-layer chromatography (TLC) was used to monitor the reaction. Melting points were determined using a Büchi B-540 capillary melting point apparatus. ^{1}H NMR (400/600 MHz), ^{13}C NMR (100/150 MHz) and ^{19}F NMR (376/565 MHz) spectra were recorded with $CDCl_3$. Chemical shifts are reported downfield from TMS (=0) for ^{1}H NMR. For $^{13}C\{1H\}$ NMR, chemical shifts are reported in the scale relative to $CDCl_3$ (= 77.0). High resolution mass spectrometry (HRMS) analysis was performed on an Agilent 1290–6540 UHPLC Q-Tof HR-MS System (ESI) spectrometer.

2. Typical experimental procedure [1-3]

In an oven-dried undivided three-necked bottle equipped with a stir bar were added dimethylacetylenedicarboxylate (0.5 mmol, 71 mg), DMSO (5.0 ml), benzylamine (0.5 mmol, 53.5 mg), and the reaction mixture was stirred at room temperature for 20 min. Subsequently, the formation of the allyl ester was ensured by TLC. Next, $TMSN_3$ (1.5 mmol, 172.5 mg), KI (1.0 mmol, 166.0 mg), $^{n}Bu_4NBF_4$ (0.5 mmol, 164.5 mg) were combined and added into the bottle. The bottle was equipped with platinum plate (20 mm × 15 mm) as the anode and platinum plate (20 mm × 15 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 9.0 mA for 8 hours at room temperature. When the reaction was finished, the solution was washed with saturated brines (15 mL) and extracted dichloromethane (3 × 10 mL). The combined organic layer was dried with Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residues were purified by flash column chromatography on silica gel (petroleum ether: ethyl ether = 4:1, v/v) to give the desired product.

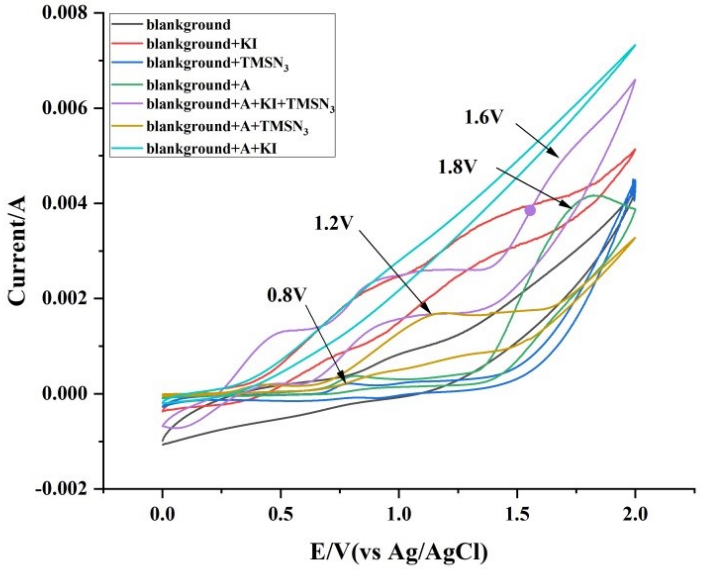
3. Large-scale experimental procedure

In an oven-dried undivided three-necked bottle equipped with a stir bar were added dimethylacetylenedicarboxylate (5.0 mmol, 710.0 mg), DMSO (35.0 ml), benzylamine (5.0 mmol, 535.0 mg), and the reaction mixture was stirred at room temperature for 2

hours. Subsequently, the formation of the allyl ester was ensured by TLC. Next, $TMSN_3$ (16.0 mmol, 1.84 g), KI (10.0 mmol, 1.66 g), $^{n}Bu_4NBF_4$ (5.0mmol, 1.65g) were combined and added into the bottle. The bottle was equipped with platinum plate (20 mm × 15 mm) as the anode and platinum plate (20 mm × 15 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 12.0 mA for 18 hours at room temperature. When the reaction was finished, the solution was washed with saturated brines (60.0 ml) and extracted dichloromethane (3 × 50 ml). The combined organic layer was dried with Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residues were purified by flash column chromatography on silica gel (petroleum ether: ethyl ether = 4:1, v/v) to give the desired product.

4. Cyclic voltammetry experiments

Cyclic voltammetry was performed in a three-electrode bottle (10.0 ml) by electrochemical analyzer at room temperature. The working electrode was a platinum electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. In all experiments, 10 mL of CH_3CN containing 0.1 M $^{n}Bu_4NBF_4$ were poured into the electrochemical cell. The scan rate is 0.03 V/s, ranging from 0.0 V to 2.0 V.



5. References

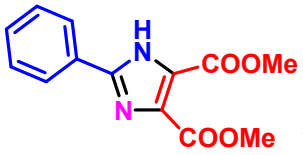
[1] S. Cossu., O. D. Lucchi., and R. Durr., Nucleophilic Addition of Highly Hindered Amines to Electron-Deficient Acetylenes. *Synth. Commun*., 1996, **26**, 4597-4601.

[2] G. Choudhary., R. K. Peddinti., Introduction of a clean and promising protocol for the synthesis of *β*-amino-acrylates and 1, 4-benzoheterocycles: an emerging innovation. *Green Chem.*, 2011, **13**, 3290-3299.

[3] A. Ziyaei-Halimehjani, M. R. Saidi. Synthesis of aza-Henry products and enamines in water by Michael addition of amines or thiols to activated unsaturated compounds. *Tetrahedron Letters.*, 2008, **49**, 1244-1248.

6. Analytical data of the synthesized derivatives

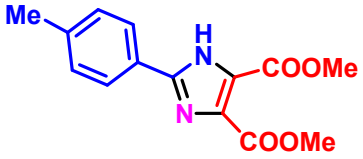
dimethyl 2-phenyl-1H-imidazole-4,5-dicarboxylate(3aa)



White solid; m.p.= 103.0- 106.1 ℃; 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.41 (qd, J = 4.2, 3.4, 1.8 Hz, 3H), 3.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 148.3, 130.3, 129.0, 128.8, 128.1, 128.0, 126.4, 52.5.

HRMS-ESI (m/z): calcd for $C_{13}H_{13}N_2O_4^+$[M+H]$^+$ 261.0870, found 261. 0871.

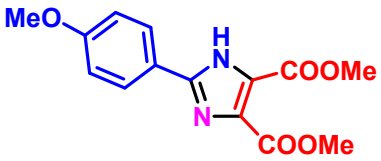
dimethyl 2-(p-tolyl)-1H-imidazole-4,5-dicarboxylate(3ba)



White solid; m.p.= 165.5-168.8 ℃; 63% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 3.92 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 148.4, 140.7, 129.6, 127.9, 126.3, 125.3, 52.5, 21.4.

HRMS-ESI (m/z): calcd for $C_{14}H_{15}N_2O_4^+$ [M+H]$^+$ 257.1026, found 257.1029.

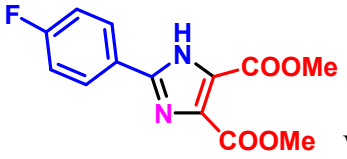
dimethyl 2-(4-methoxyphenyl)-1H-imidazole-4,5-dicarboxylate(3ca)



White solid; m.p.= 113.2-115.9℃; 63% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 6H), 3.82 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 148.3, 136.4, 129.6, 128.9, 128.0, 120.6, 114.2, 55.3, 52.5.

HRMS-ESI (m/z): calcd for $C_{14}H_{15}N_2O_5^+$ $[M+H]^+$ 291.0975, found 291.0979

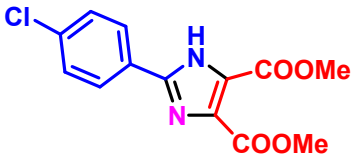
dimethyl 2-(4-fluorophenyl)-1H-imidazole-4,5-dicarboxylate(3da)



White solid; m.p.= 110.0-112.0 ℃; 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 3H), 7.09 (td, *J* = 8.0, 7.2, 2.8 Hz, 3H), 3.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 162.0 (d, *J* = 144.2 Hz), 147.4, 128.6, 128.5, 124.5 (d, *J* = 3.4 Hz), 116.2, 115.9, 52.6.

HRMS-ESI (m/z): calcd for $C_{13}H_{12}FN_2O_4^+$ $[M+H]^+$ 279.0776, found 279.0777.

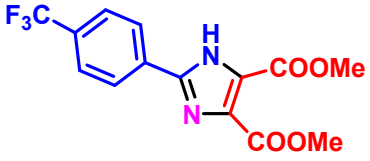
dimethyl 2-(4-chlorophenyl)-1H-imidazole-4,5-dicarboxylate (3ea)



White solid; m.p.= 155.0-157.3 ℃; 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 147.2, 137.6, 136.5, 129.1, 127.7, 126.6, 122.6, 52.6.

HRMS-ESI (m/z): calcd for $C_{13}H_{12}ClN_2O_4^+$ $[M+H]^+$ 295.0480, found 295.0485.

dimethyl 2-(4-(trifluoromethyl)phenyl)-1H-imidazole-4,5-dicarboxylate(3fa)

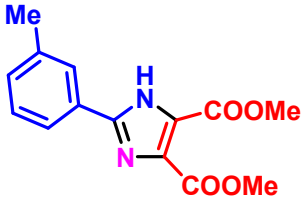


White solid; m.p.= 170.0-172.4 ℃; 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 3.96 (s, 6H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 161.1, 146.5, 132.3, 132.0, 131.3, 130.9, 126.0 (q, J = 3.8 Hz), 125.0, 122.3, 52.7.

HRMS-ESI (m/z): calcd for $C_{14}H_{12}F_3N_2O_4^+[M+H]^+$ 329.0744, found 329.0748.

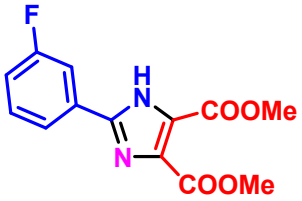
dimethyl 2-(m-tolyl)-1H-imidazole-4,5-dicarboxylate(3ga)



White solid; m.p.= 139.5-143.2°C; 53% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.27 – 7.17 (m, 2H), 3.86 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 148.5, 138.6, 131.9, 131.0, 128.6, 127.9, 127.2, 124.7, 123.3, 52.3, 21.0.

HRMS-ESI (m/z): calcd for $C_{14}H_{15}N_2O_4^+$ $[M+H]^+$ 275.1026, found 275.1029.

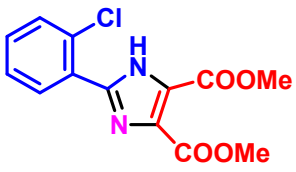
dimethyl 2-(3-fluorophenyl)-1H-imidazole-4,5-dicarboxylate(3ha)



White solid; m.p.= 134.6-138.9°C; 52% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.41 – 7.37 (m, 1H), 7.14 – 7.11 (m, 1H), 3.94 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 162.1, 161.4, 147.1 (d, J = 3.1 Hz), 130.6 (d, J = 8.2 Hz), 130.2 (d, J = 8.3 Hz), 122.2 (d, J = 3.1 Hz), 117.3 (d, J = 21.4 Hz), 113.5 (d, J = 23.8 Hz), 52.7.

HRMS-ESI (m/z): calcd for $C_{13}H_{12}FN_2O_4^+$ $[M+H]^+$ 279.0776, found 279.0779

dimethyl 2-(2-chlorophenyl)-1H-imidazole-4,5-dicarboxylate(3ia)

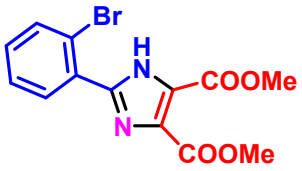


White solid; m.p.= 120.3-125.7 °C; 65% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.27 (s, 1H), 8.14 (dd, J = 7.2, 2.4 Hz, 1H), 7.43 (dd, J = 7.6, 1.8 Hz,

1H), 7.35 (m, 2H), 3.95 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 159.0, 144.9, 135.8, 131.5, 131.1, 130.8, 130.2, 127.2, 126.4, 124.2, 52.5, 52.3.

HRMS-ESI (m/z): calcd for $C_{13}H_{12}ClN_2O_4^+$ $[M+H]^+$ 295.0480, found 295.0483.

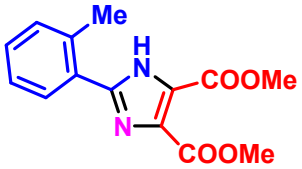
dimethyl 2-(2-bromophenyl)-1H-imidazole-4,5-dicarboxylate(3ja)



White solid; m.p.= 137.2-139.9℃; 64% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.01 (s, 1H), 8.22 (d, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 3.98 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 145.7, 133.9, 132.3, 131.5, 129.0, 128.4, 128.0, 126.3, 119.9, 52.6.

HRMS-ESI (m/z): calcd for $C_{13}H_{12}BrN_2O_4^+$ $[M+H]^+$ 338.9975, found 338.9977.

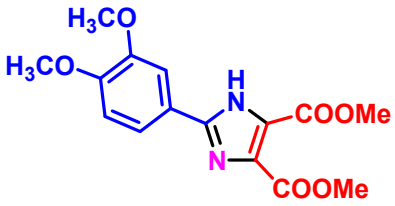
dimethyl 2-(o-tolyl)-1H-imidazole-4,5-dicarboxylate(3ka)



White solid; m.p.= 115.7-117.6℃; 61% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.26 (td, *J* = 7.6, 1.4 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 3.83 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 159.9, 148.5, 137.0, 130.7, 130.6, 129.7, 129.7, 129.4, 128.1, 125.5, 52.2, 20.2.

HRMS-ESI (m/z): calcd for $C_{14}H_{15}N_2O_4^+$ $[M+H]^+$ 275.1026, found 275.1029.

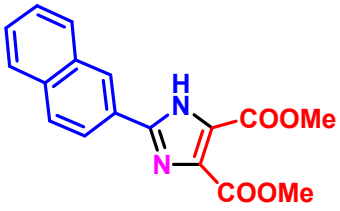
dimethyl 2-(3,4-dimethoxyphenyl)-1H-imidazole-4,5-dicarboxylate(3la)



White solid; m.p.= 117.4-121.2℃; 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.46 (m, 2H), 6.85 – 6.71 (m, 1H), 3.90 – 3.80 (m, 9H), 3.72 – 3.69 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 150.9, 149.3, 148.3, 120.9, 119.1, 111.1, 109.6, 55.9, 52.4.

HRMS-ESI (m/z): calcd for $C_{15}H_{17}N_2O_6^+[M+H]^+$ 321.1081, found 321.1085.

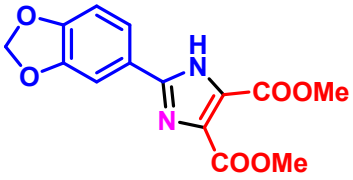
dimethyl 2-(furan-2-yl)-1H-imidazole-4,5-dicarboxylate(3ma)



White solid; m.p.= 157.6-162.1℃; 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.05 (dd, J = 8.6, 1.8 Hz, 1H), 7.86 – 7.80 (m, 3H), 7.53 – 7.46 (m, 2H), 3.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 148.2, 134.0, 133.0, 128.8, 128.5, 127.8, 127.3, 126.9, 126.3, 125.3, 123.1, 52.6.

HRMS-ESI (m/z): calcd for $C_{17}H_{15}N_2O_4^+[M+H]^+$ 311.1026, found 311.1029.

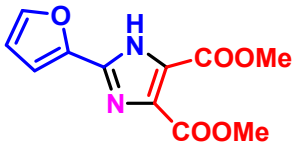
dimethyl 2-(benzo[d][1,3]dioxol-5-yl)-1H-imidazole-4,5-dicarboxylate(3na)



White solid; m.p.= 223.2-225.6℃; 67% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.54 (s, 1H), 7.67 – 7.63 (m, 2H), 7.01 (d, J = 8.2 Hz, 1H), 6.09 (s, 2H), 3.84 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.1, 159.4, 148.6, 147.7, 147.6, 136.6, 123.6, 122.7, 121.0, 108.5, 106.4, 101.5, 52.0.

HRMS-ESI (m/z): calcd for $C_{14}H_{12}O_6^+[M+H]^+$ 305.0781, found 305.0785.

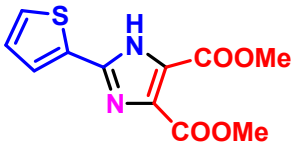
dimethyl 2-(furan-2-yl)-1H-imidazole-4,5-dicarboxylate(3oa)



White solid; m.p.= 209.7-212.5℃; 53% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.91(s, 1H), 7.86(d, J = 1.8 Hz, 1H), 7.20 (d, J = 3.4 Hz, 1H), 6.66 (dd, J = 3.4, 1.8 Hz, 1H), 3.83 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.7, 159.1, 144.5, 143.9, 140.3, 136.6, 123.4, 112.0, 110.6, 52.0.

HRMS-ESI (m/z): calcd for $C_{11}H_{11}N_2O_5^+[M+H]^+$ 251.0662, found 251.0665.

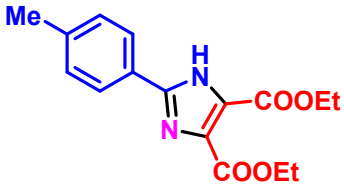
dimethyl 2-(thiophen-2-yl)-1H-imidazole-4,5-dicarboxylate(3pa)



White solid; m.p.= 213.7-216.2℃; 46% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (dq, J = 3.6, 1.2 Hz, 1H), 7.68 (dd, J = 5.0, 1.0 Hz, 1H), 7.17 (dd, J = 5.0, 3.8 Hz, 1H), 3.84(s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.3, 143.6, 135.9, 131.8, 128.6, 128.2, 127.1, 125.5, 52.1.

HRMS-ESI (m/z): calcd for $C_{11}H_{11}N_2O_4S^+$[M+H]$^+$ 267.0434, found 267.0436.

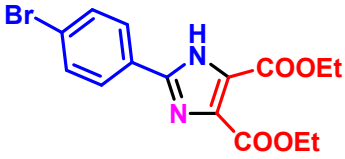
diethyl 2-(p-tolyl)-1H-imidazole-4,5-dicarboxylate(3bb)



White solid; m.p.= 170.3-172.6 ℃; 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.18 (dd, J = 7.7, 4.8 Hz, 2H), 4.41 – 4.30(m, 4H), 2.35 (d, J = 3.6 Hz, 3H), 1.35 (td, J = 7.2, 4.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 148.3, 140.3, 129.6, 129.4, 127.9, 126.3, 125.5, 61.5, 21.3, 14.1.

HRMS-ESI (m/z): calcd for $C_{16}H_{19}N_2O_4^+$[M+H]$^+$ 303.1339, found 303.1342

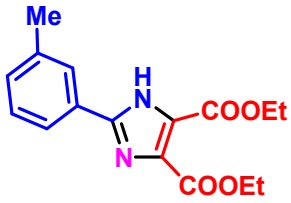
diethyl 2-(4-bromophenyl)-1H-imidazole-4,5-dicarboxylate(3rb)



White solid; m.p.= 133.1-134.7℃; 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 4.38 (q, J = 7.0 Hz, 4H), 1.36 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 147.1, 136.4, 129.1, 127.7, 126.8, 119.7, 114.3, 61.8, 14.1.

HRMS-ESI (m/z): calcd for $C_{15}H_{16}BrN_2O_4^+$[M+H]$^+$ 367.0288, found 367.0289.

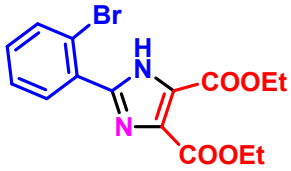
diethyl 2-(m-tolyl)-1H-imidazole-4,5-dicarboxylate(3gb)



White solid; m.p.= 126.9-129.7℃; 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.20 (dq, *J* = 16.6, 7.6, 7.2 Hz, 2H), 4.33 (q, *J* = 7.2, 6.6 Hz, 4H), 2.25 (d, *J* = 8.8 Hz, 3H), 1.30 (p, *J* = 6.8 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 148.4, 138.6, 138.6, 130.9, 130.8, 128.5, 128.1, 127.3, 123.4, 61.5, 21.1, 14.0.

HRMS-ESI (m/z): calcd for $C_{16}H_{19}N_2O_4^+[M+H]^+$ 303.1339, found 303.1344.

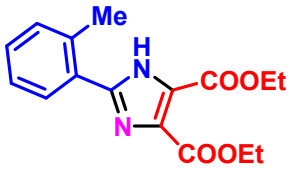
diethyl 2-(2-bromophenyl)-1H-imidazole-4,5-dicarboxylate(3jb)



White solid; m.p.= 93.3-96.7℃; 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 4.35 (q, *J* = 7.4 Hz, 4H), 1.38 – 1.29 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 145.7, 133.8, 133.5, 132.1, 131.2, 130.7, 128.8, 127.7, 120.3, 61.5, 14.1.

HRMS-ESI (m/z): calcd for $C_{15}H_{16}BrN_2O_4^+[M+H]^+$ 367.0288, found 367.0292.

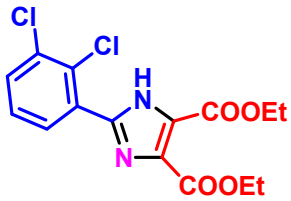
diethyl 2-(o-tolyl)-1H-imidazole-4,5-dicarboxylate(3kb)



White solid; m.p.= 95.3-97.2℃; 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.34 (s, 1H), 7.41 (dd, *J* = 11.6, 7.8 Hz, 1H), 7.28 – 7.12 (m, 3H), 4.39 – 4.27 (m, 4H), 2.40 (d, *J* = 8.6 Hz, 3H), 1.36 – 1.31 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 148.4, 137.1, 130.9, 129.7, 129.6, 129.4, 128.4, 125.7, 125.6, 61.5, 20.4, 14.1.

HRMS-ESI (m/z): calcd for $C_{16}H_{19}N_2O_4^+[M+H]^+$ 303.1339, found 303.1341.

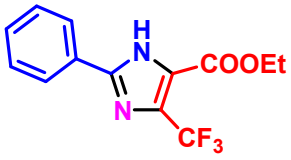
diethyl 2-(2,3-dichlorophenyl)-1H-imidazole-4,5-dicarboxylate(3sb)



White solid; m.p.= 89.7-93.2℃; 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 4H), 1.42 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 144.3, 134.1, 131.9, 130.2, 130.1, 129.3, 128.9, 127.9, 127.8, 61.8, 14.2.

HRMS-ESI (m/z): calcd for $C_{15}H_{15}Cl_2N_2O_4^+$[M+H]$^+$ 357.0403, found 357.0407

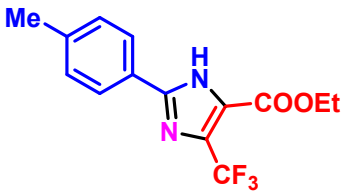
methyl 2-phenyl-4-(trifluoromethyl)-1H-imidazole-5-carboxylate(3ac)



White solid; m.p.= 168.5-171.6 ℃; 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (s, 1H), 7.97 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.49 – 7.47 (m, 3H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 147.8, 130.6, 129.1, 127.9, 126.3, 122.0, 119.3, 62.3, 13.9.

HRMS-ESI (m/z): calcd for $C_{13}H_{12}F_3N_2O_2^+$[M+H]$^+$ 285.0845, found 285.0848.

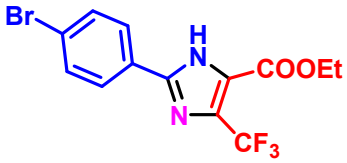
ethyl 2-(p-tolyl)-4-(trifluoromethyl)-1H-imidazole-5-carboxylate(3bc)



White solid; m.p.= 190.5-192.4 ℃; 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.85 (m, 2H), 7.26 – 7.24 (m, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 148.1, 140.9, 129.7, 126.2, 125.2, 121.6, 120.8 (q, *J* = 269.2 Hz), 62.2, 21.4, 13.9.

HRMS-ESI (m/z): calcd for $C_{14}H_{14}F_3N_2O_2^+$[M+H]$^+$ 299.1002, found 299.1005.

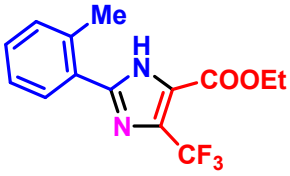
methyl 2-(4-bromophenyl)-4-(trifluoromethyl)-1H-imidazole-5-carboxylate(3rc)



White solid; m.p.= 203.8-205.8℃; 67% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.09 (s, 1H), 8.14 (d, J = 8.4 Hz, 2H), 7.57 – 7.53 (m, 2H), 4.36 (q, J = 8.0, 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.9, 146.7, 134.8, 128.9, 128.3, 127.2, 122.7, 121.0 (q, J = 268.4 Hz), 61.3, 13.9.

HRMS-ESI (m/z): calcd for $C_{13}H_{11}BrF_3N_2O_2^+$[M+H]$^+$ 362.9951, found 362.9953.

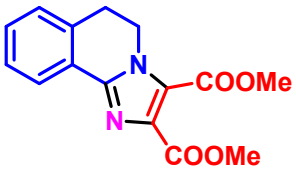
diethyl 2-(o-tolyl)-1H-imidazole-4,5-dicarboxylate (3kc)



White solid; m.p.= 156.3-159.2℃; 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.34 – 7.25 (m, 2H), 4.39 (q, J = 7.0 Hz, 2H), 2.38 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 148.2, 139.0, 131.4, 128.8, 127.8, 127.2, 124.8, 123.2, 121.8, 120.8 (q, J = 269.2 Hz), 62.3, 21.2, 13.9.

HRMS-ESI (m/z): calcd for $C_{14}H_{14}F_3N_2O_2^+$[M+H]$^+$ 299.1002, found 299.1005.

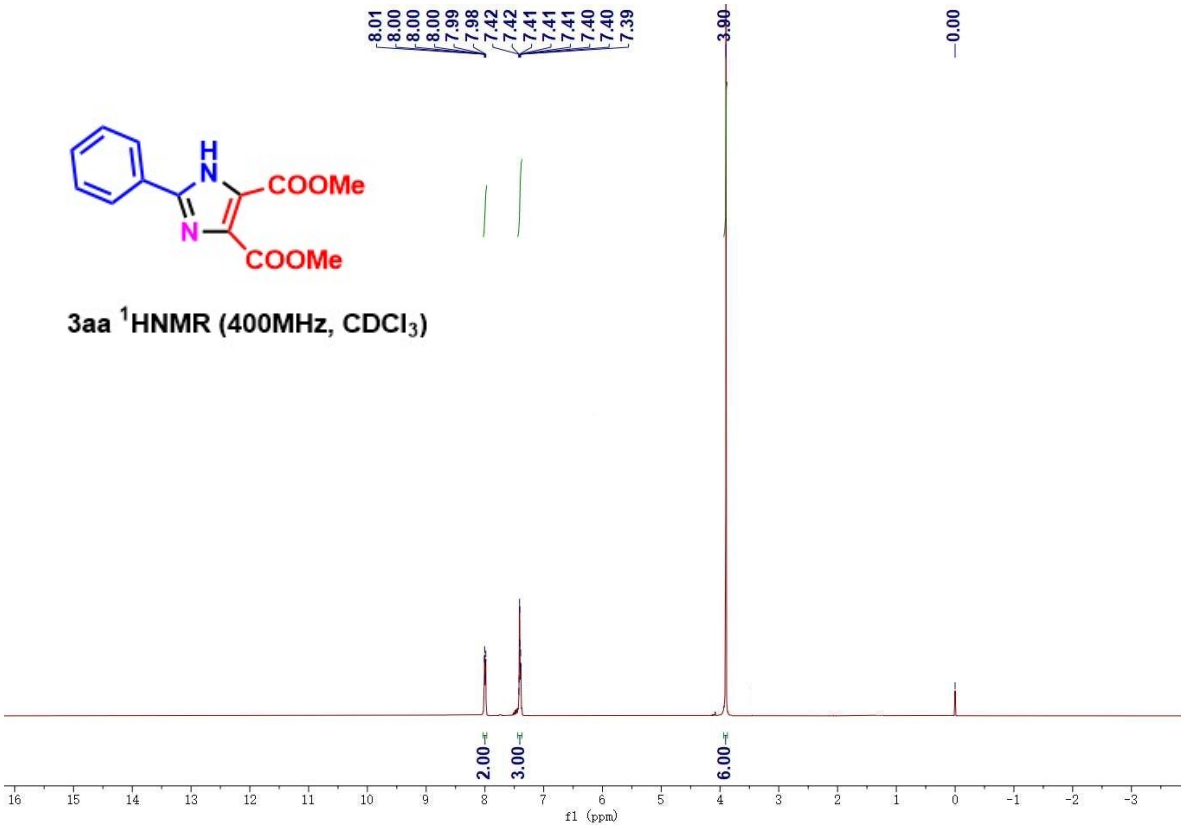
dimethyl 5,6-dihydroimidazo[2,1-a]isoquinoline-2,3-dicarboxylate(3ta)



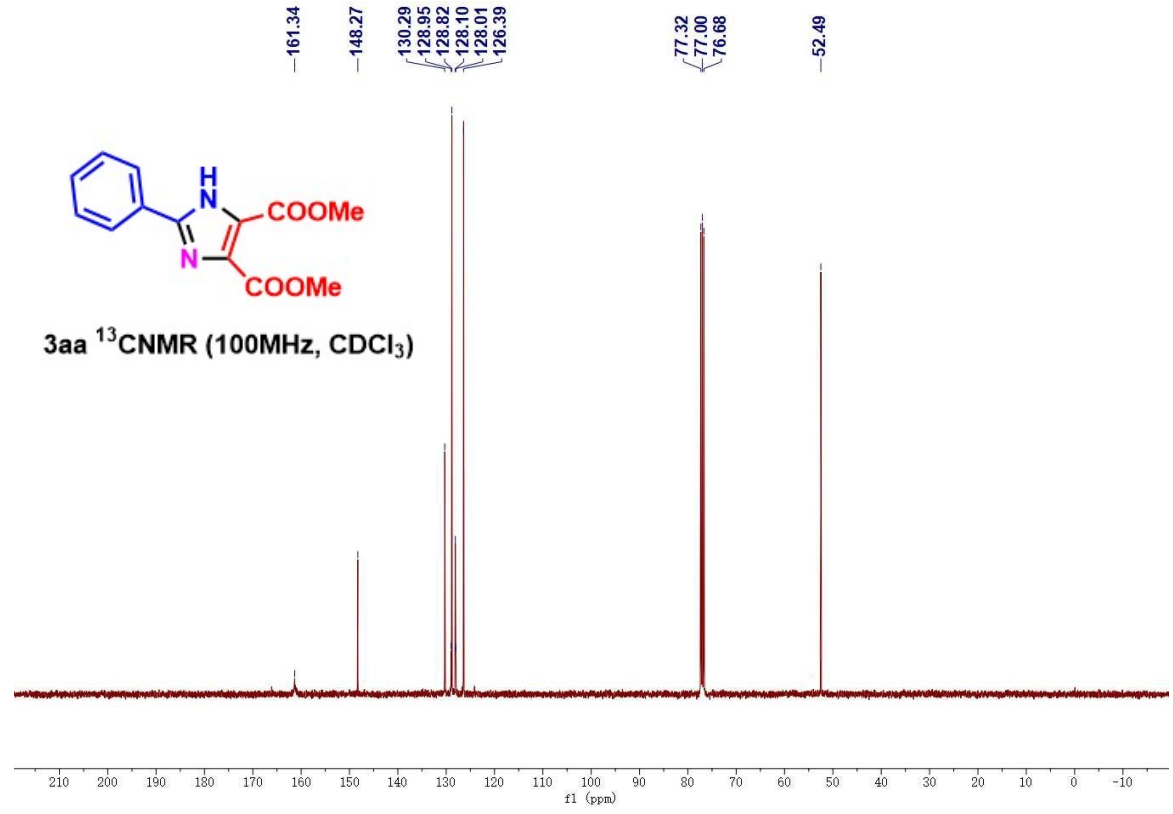
Yellow oil; 36% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.13 (m, 1H), 7.40 – 7.34 (m, 2H), 7.27 (d, J = 5.4 Hz, 1H), 4.50 (t, J = 7.0 Hz, 2H), 3.95 (d, J = 6.8 Hz, 6H), 3.18 (t, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.5, 146.3, 137.5, 133.2, 130.2, 127.7, 126.6, 125.5, 125.3, 124.0, 52.4, 42.8, 28.0.

HRMS-ESI (m/z): calcd for $C_{15}H_{15}N_2O_4^+$[M+H]$^+$ 287.1026, found 287.1029

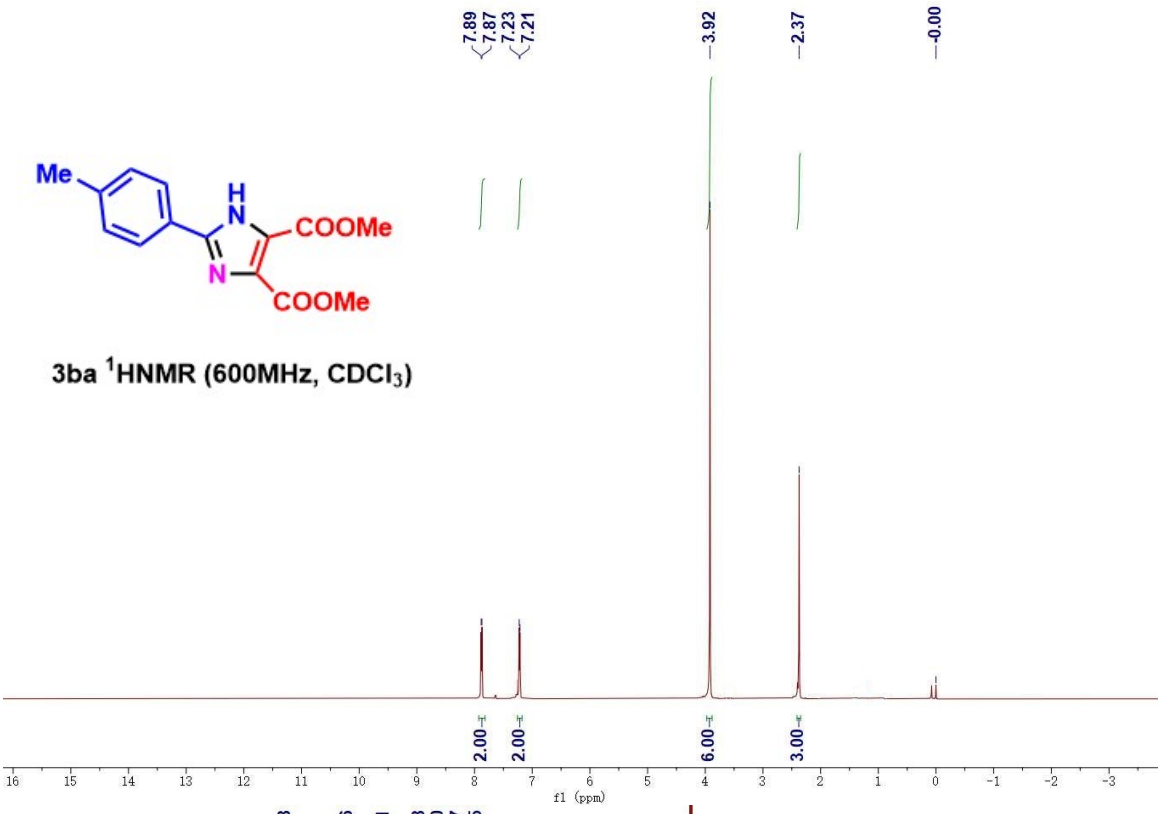
7. NMR spectra of products



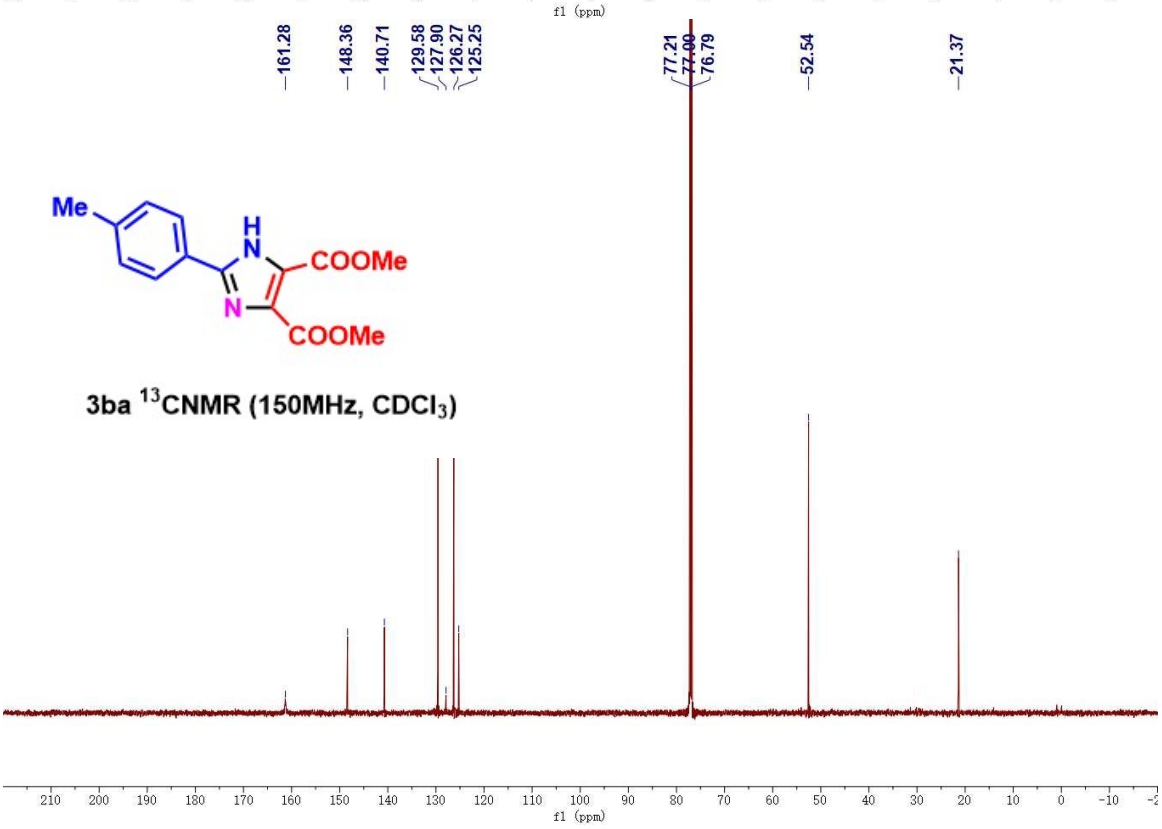
3aa ^{1}HNMR (400MHz, $CDCl_3$)



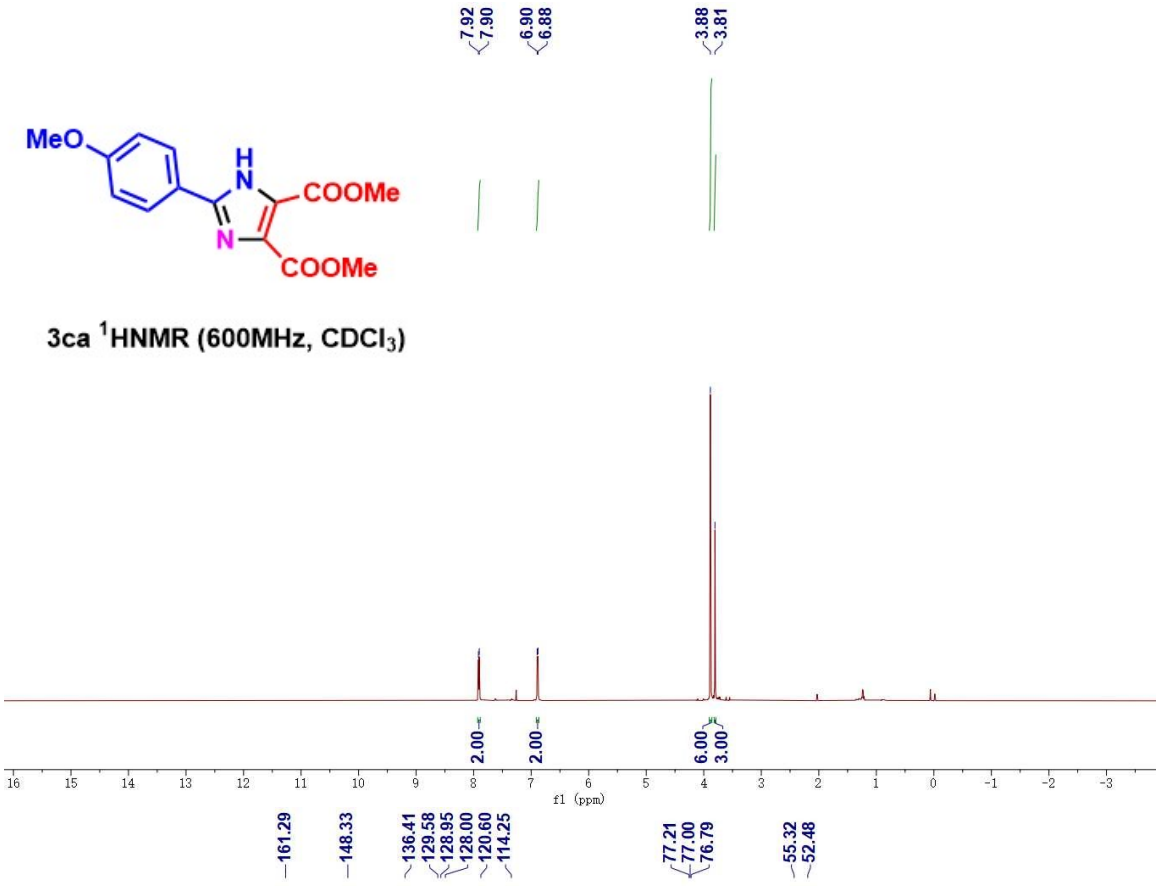
3aa ^{13}CNMR (100MHz, $CDCl_3$)



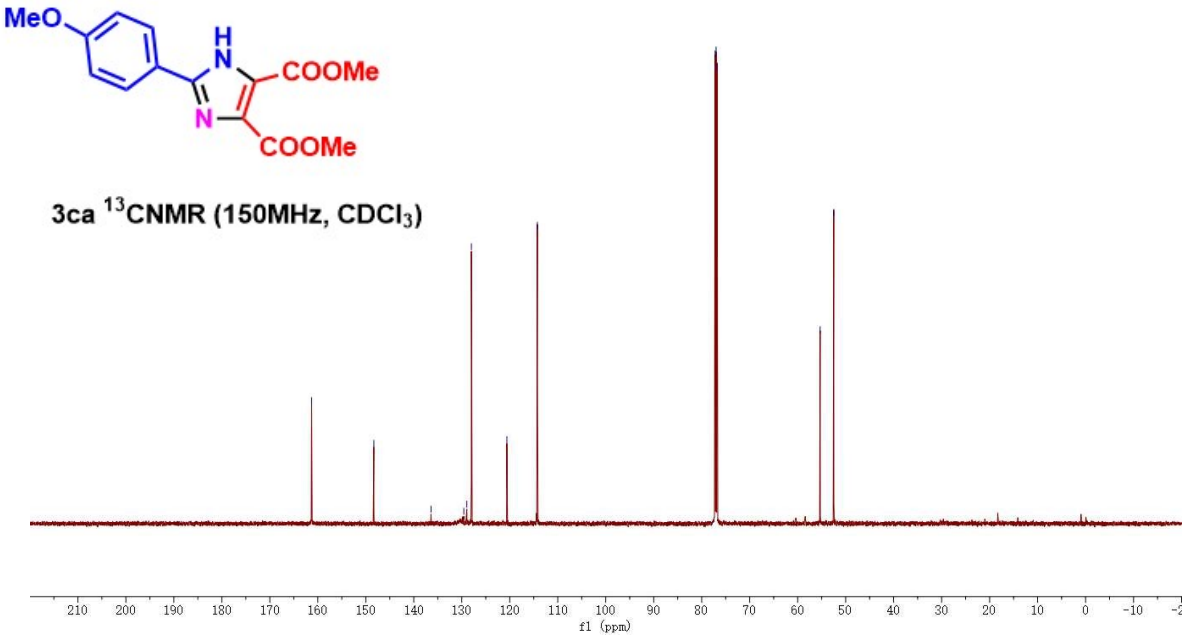
3ba ^{1}HNMR (600MHz, $CDCl_3$)



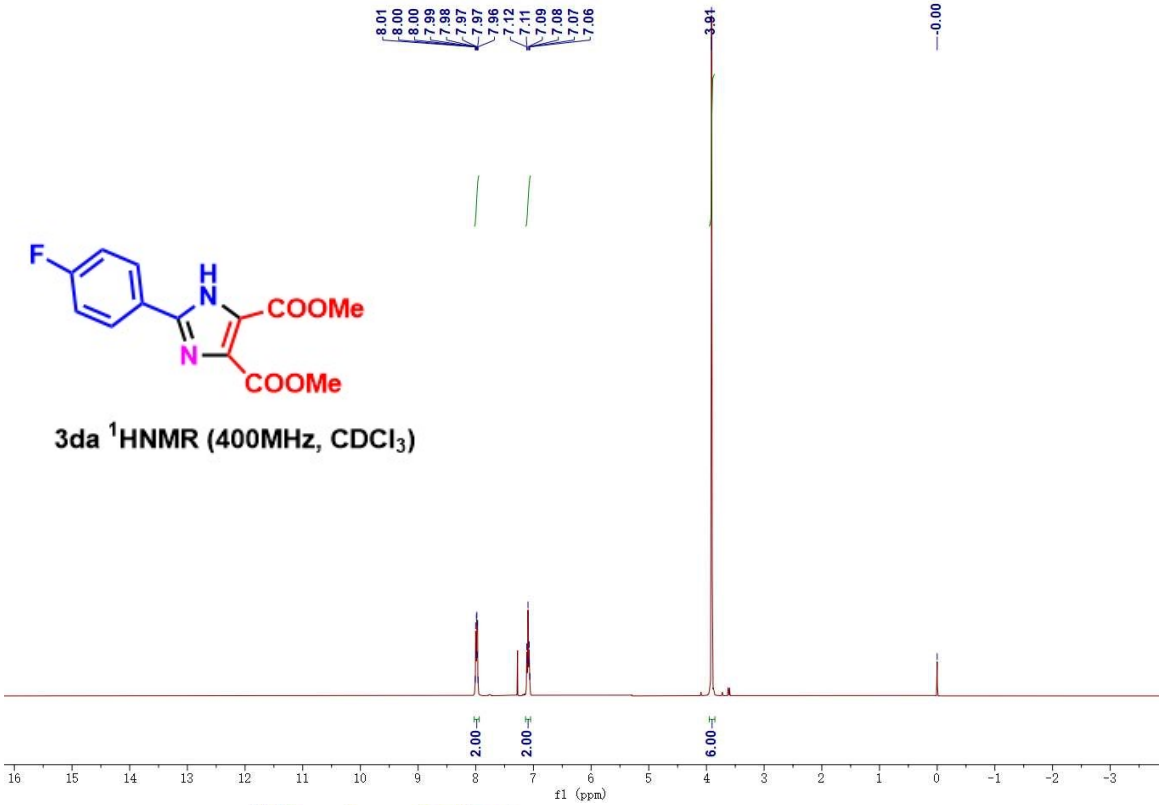
3ba ^{13}CNMR (150MHz, $CDCl_3$)



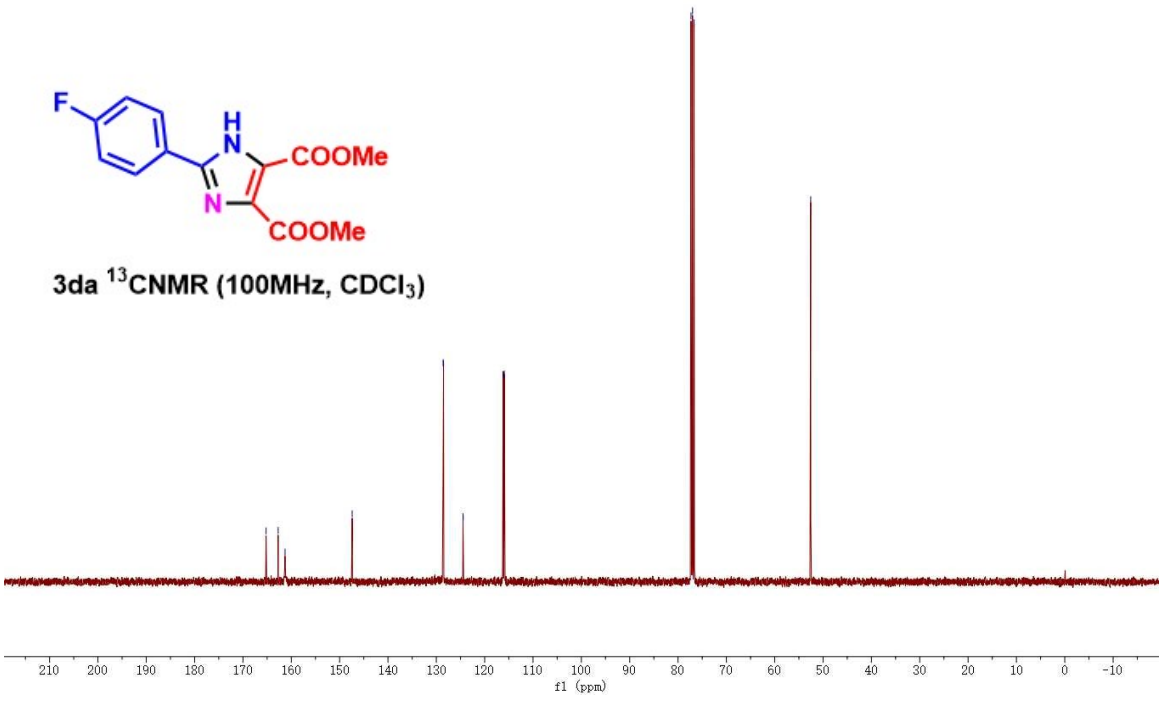
3ca ^{1}HNMR (600MHz, $CDCl_3$)



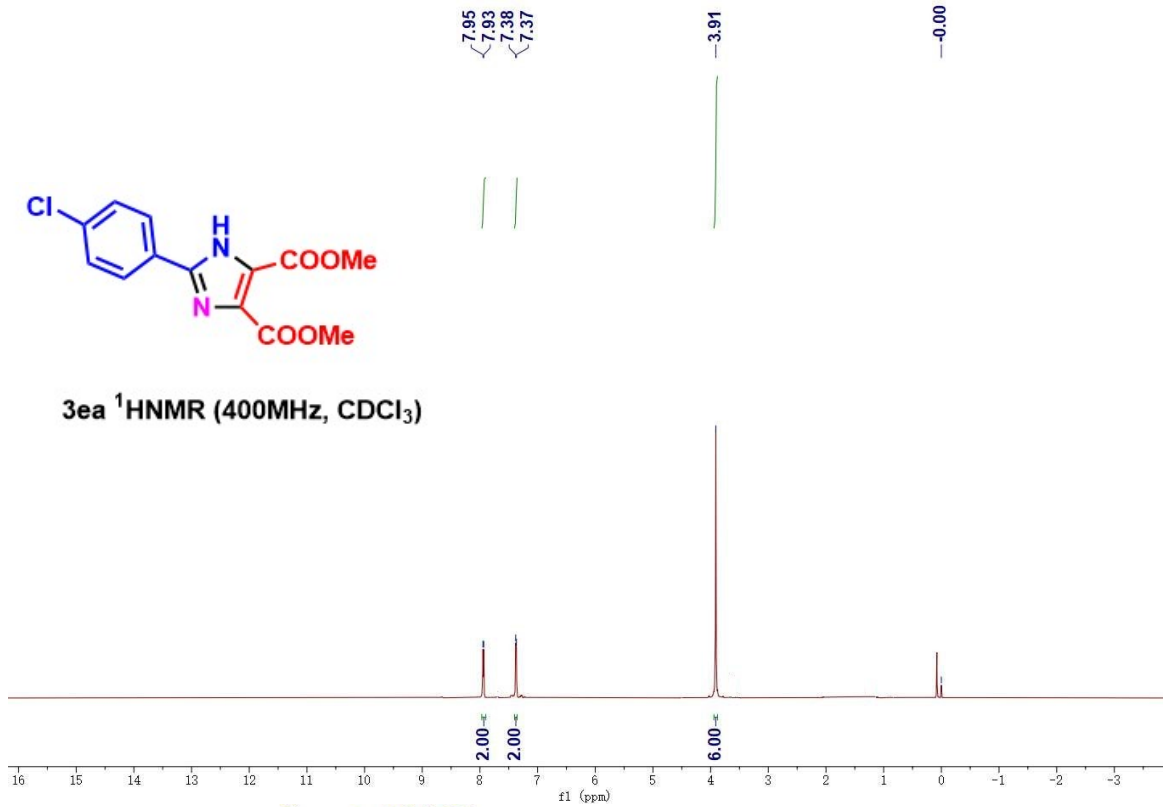
3ca ^{13}CNMR (150MHz, $CDCl_3$)



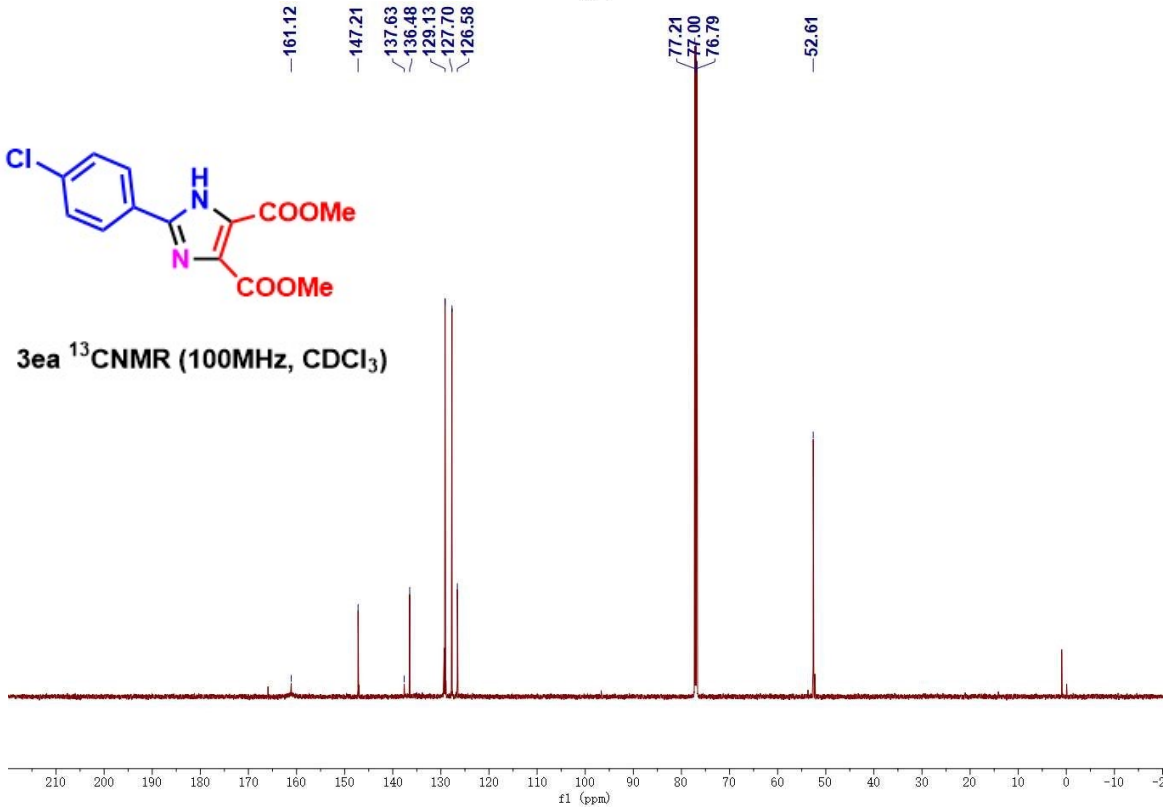
3da ^{1}HNMR (400MHz, $CDCl_3$)



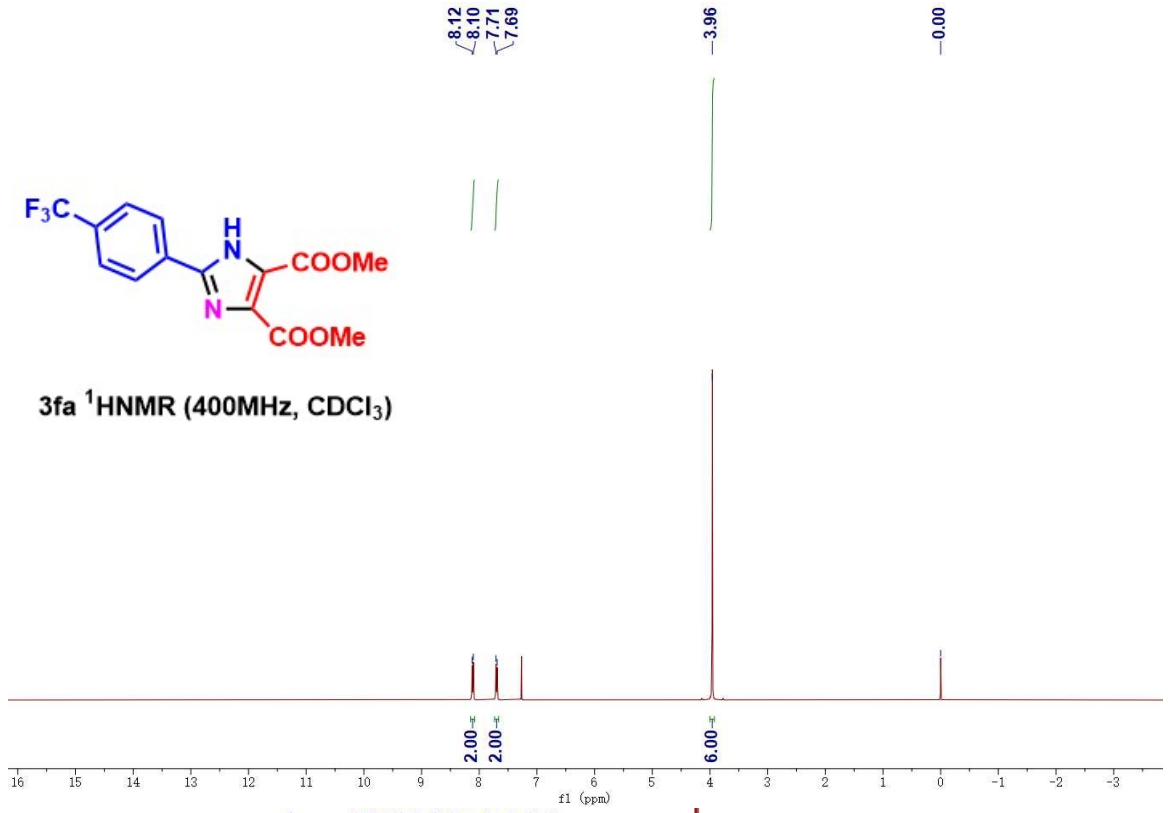
3da ^{13}CNMR (100MHz, $CDCl_3$)



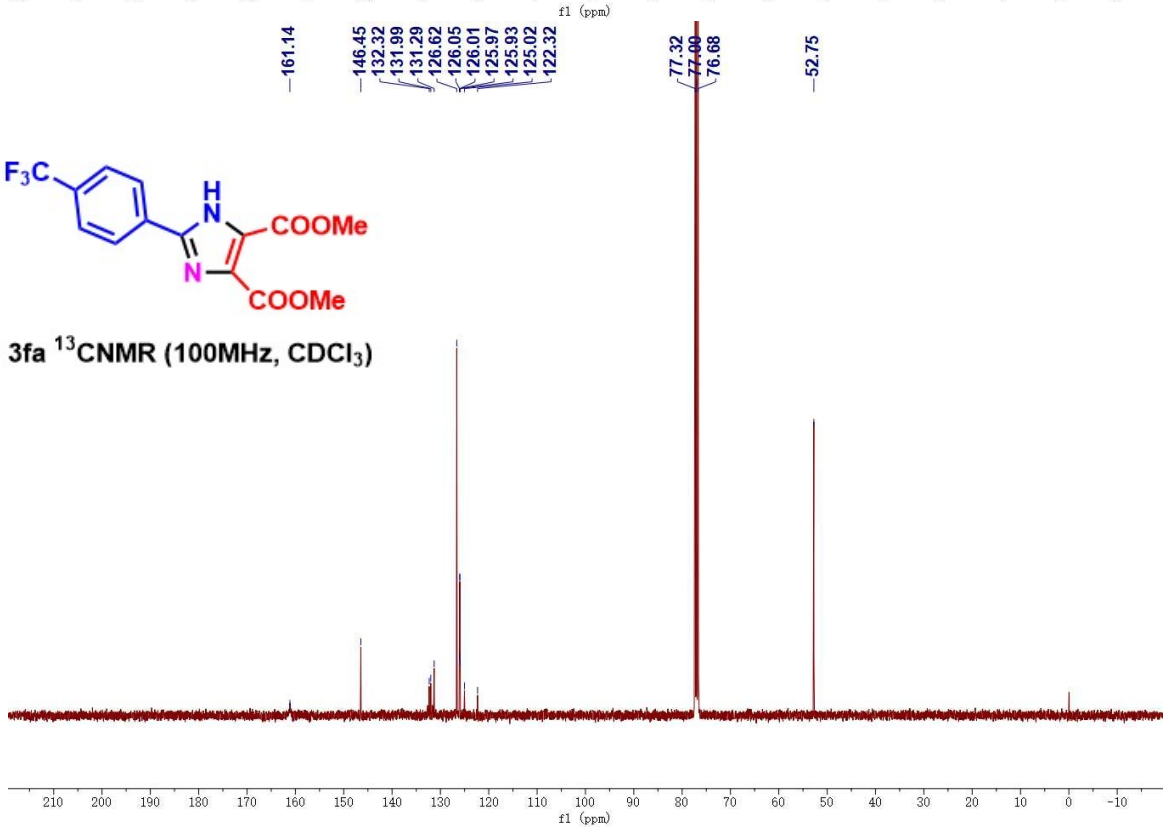
3ea ^{1}HNMR (400MHz, $CDCl_3$)



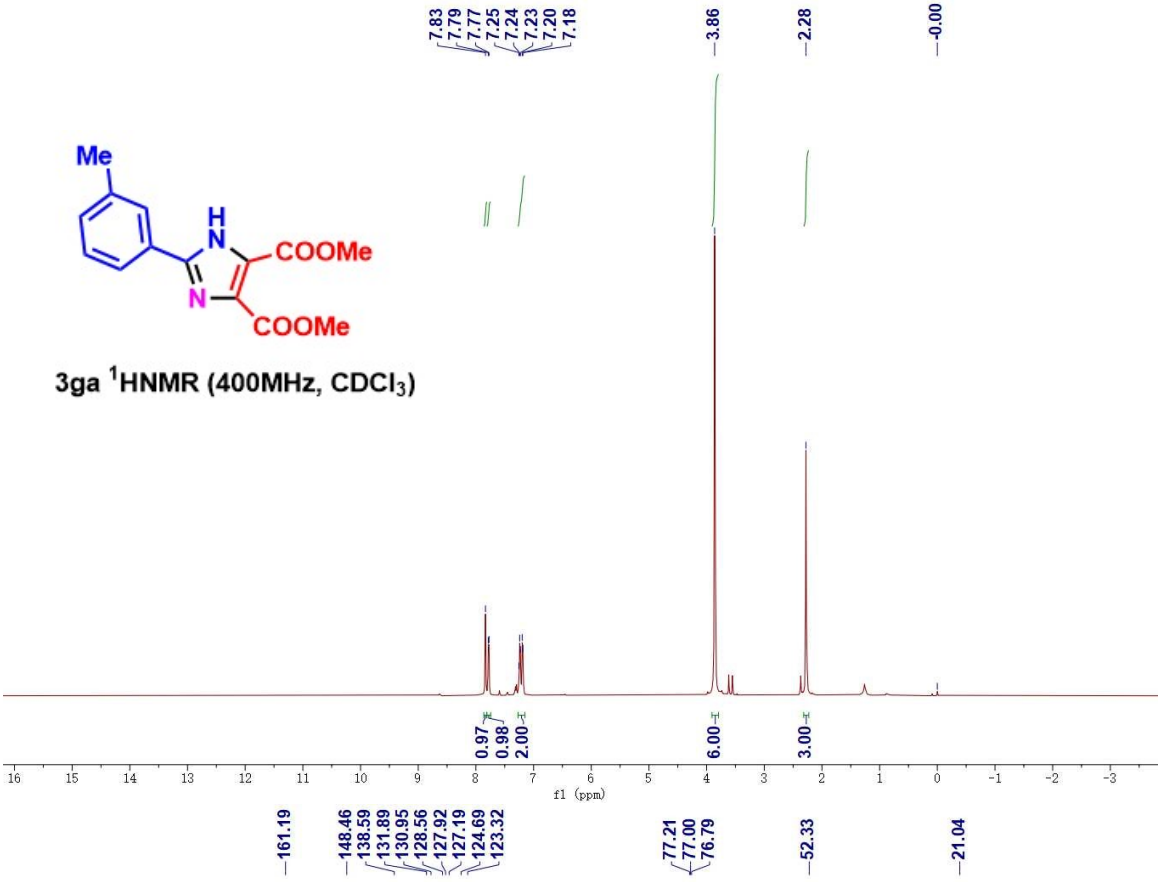
3ea ^{13}CNMR (100MHz, $CDCl_3$)



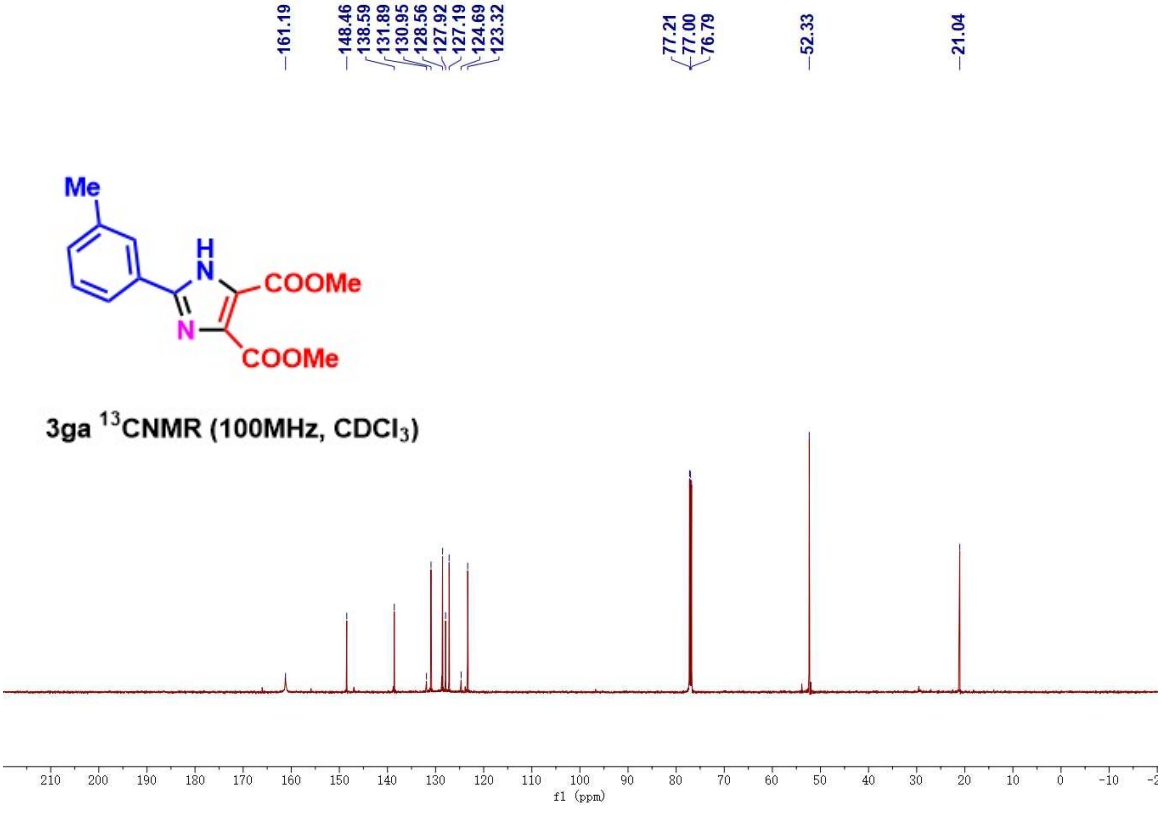
3fa ^{1}HNMR (400MHz, $CDCl_3$)



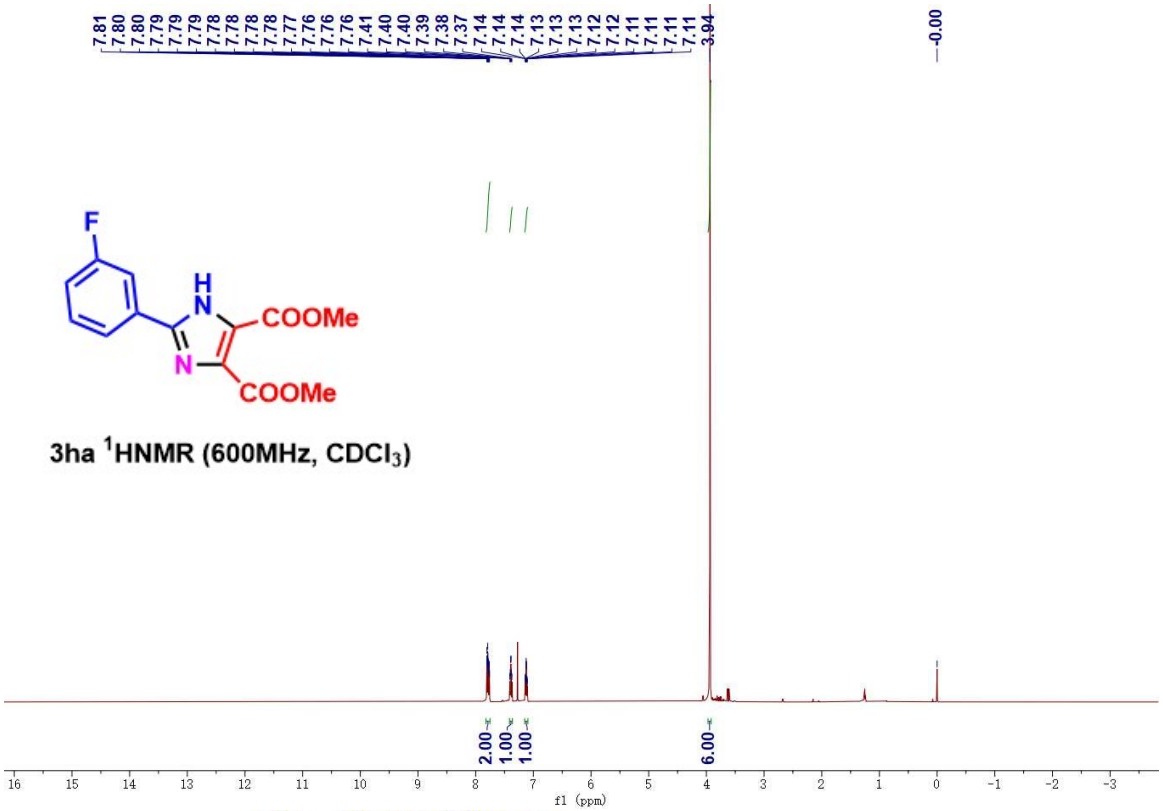
3fa ^{13}CNMR (100MHz, $CDCl_3$)



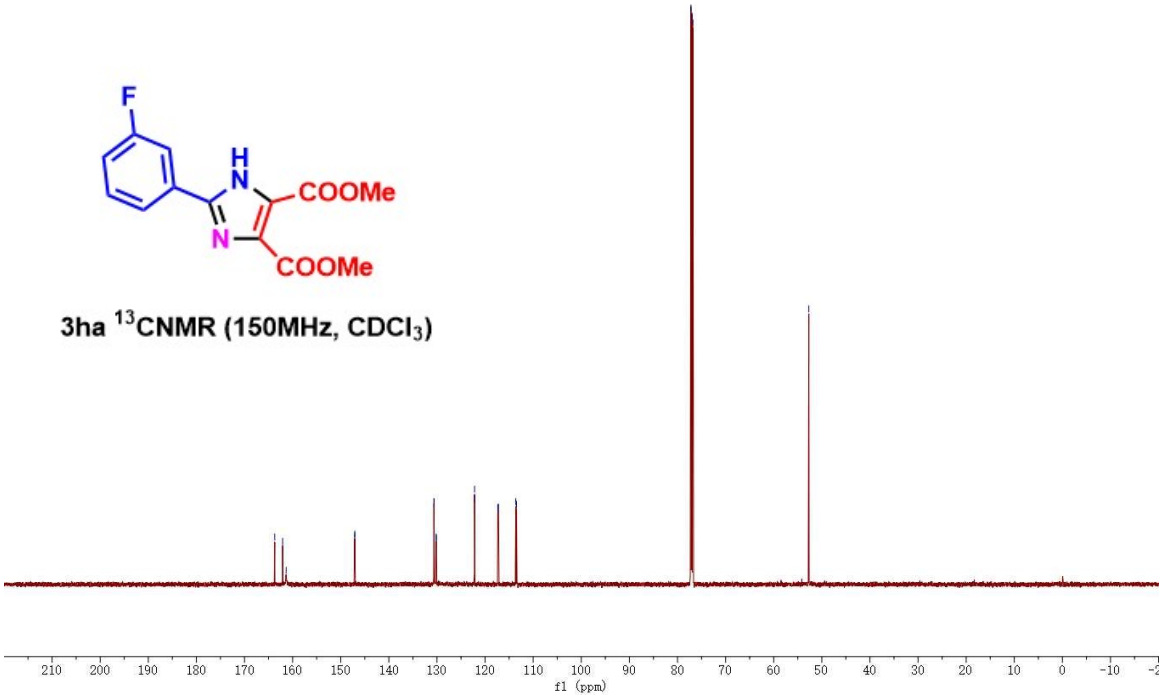
3ga ^{1}HNMR (400MHz, $CDCl_3$)



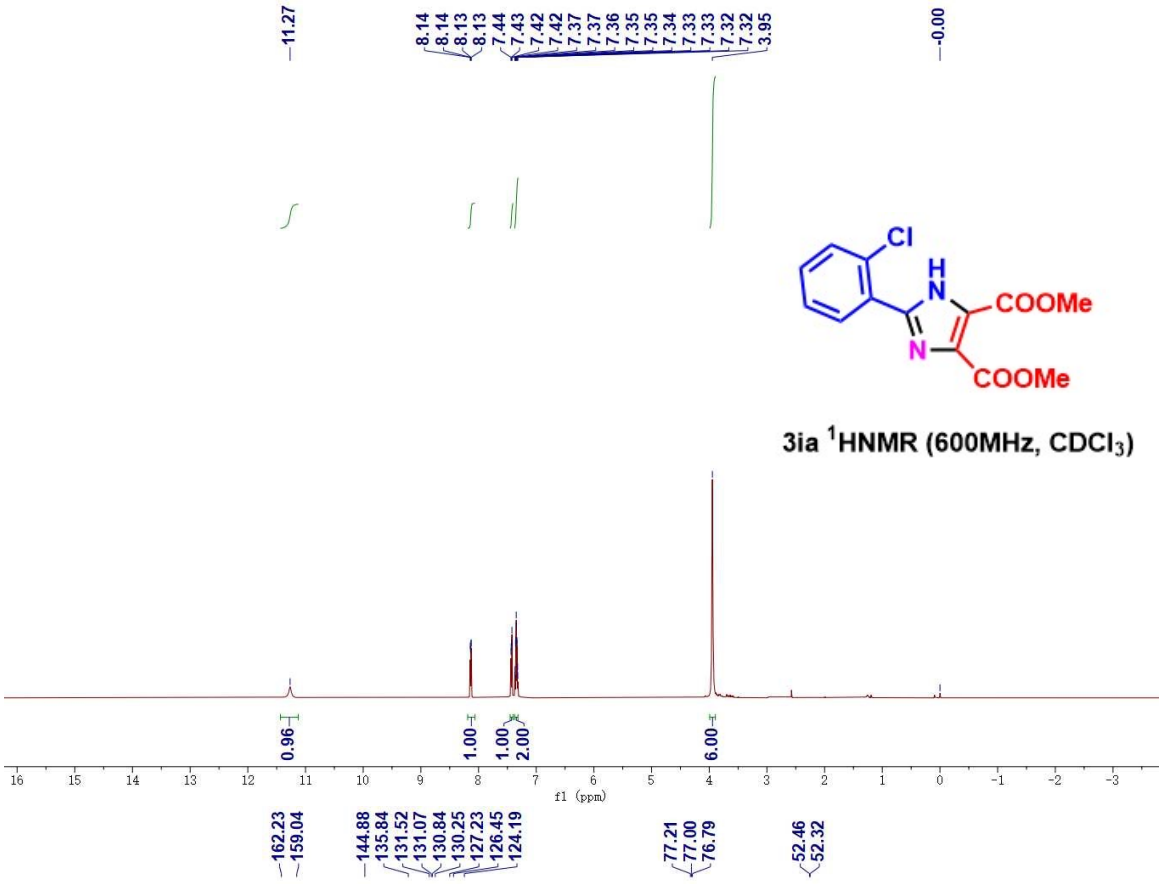
3ga ^{13}CNMR (100MHz, $CDCl_3$)



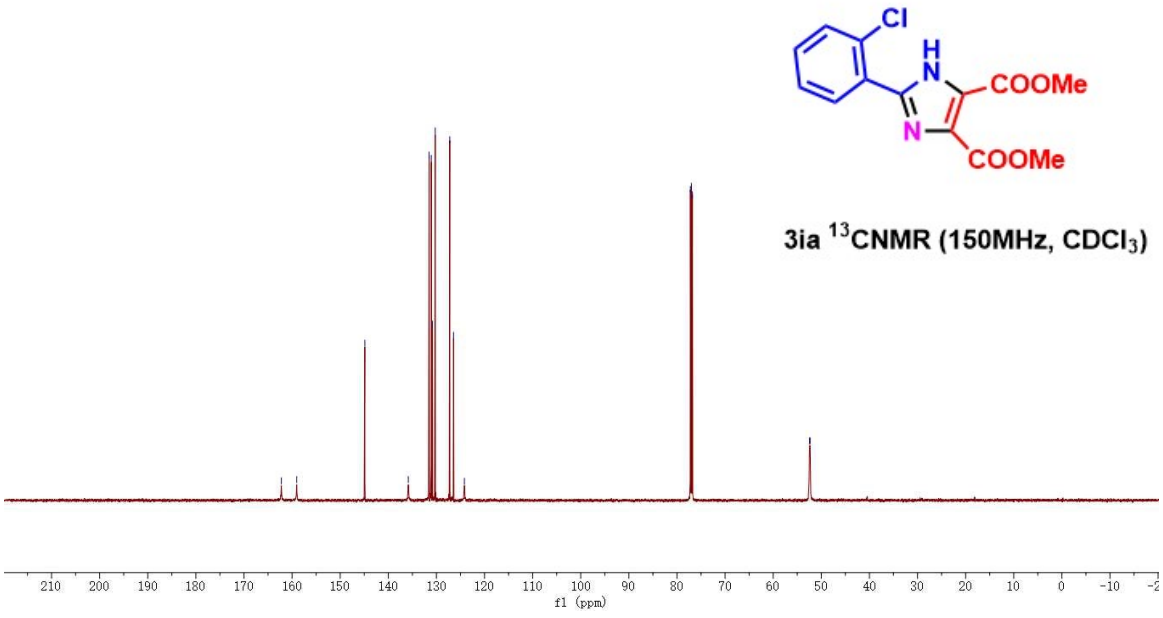
3ha ^{1}HNMR (600MHz, $CDCl_3$)



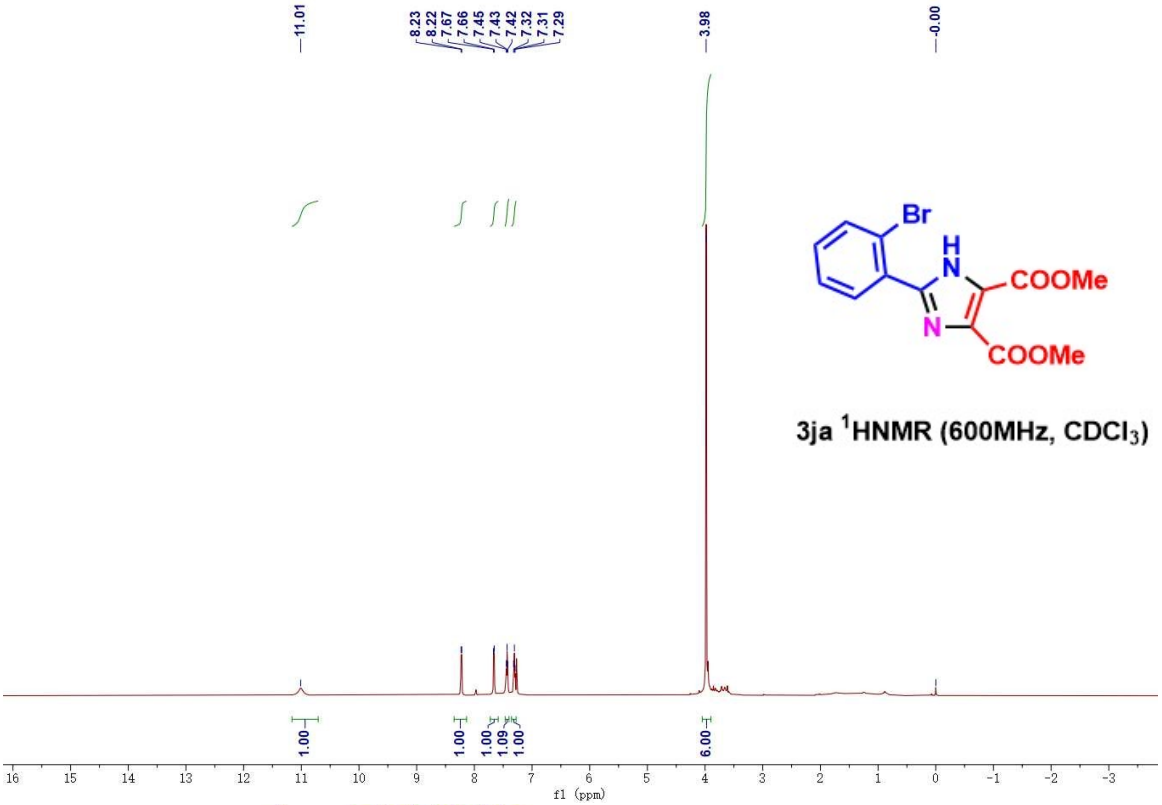
3ha ^{13}CNMR (150MHz, $CDCl_3$)



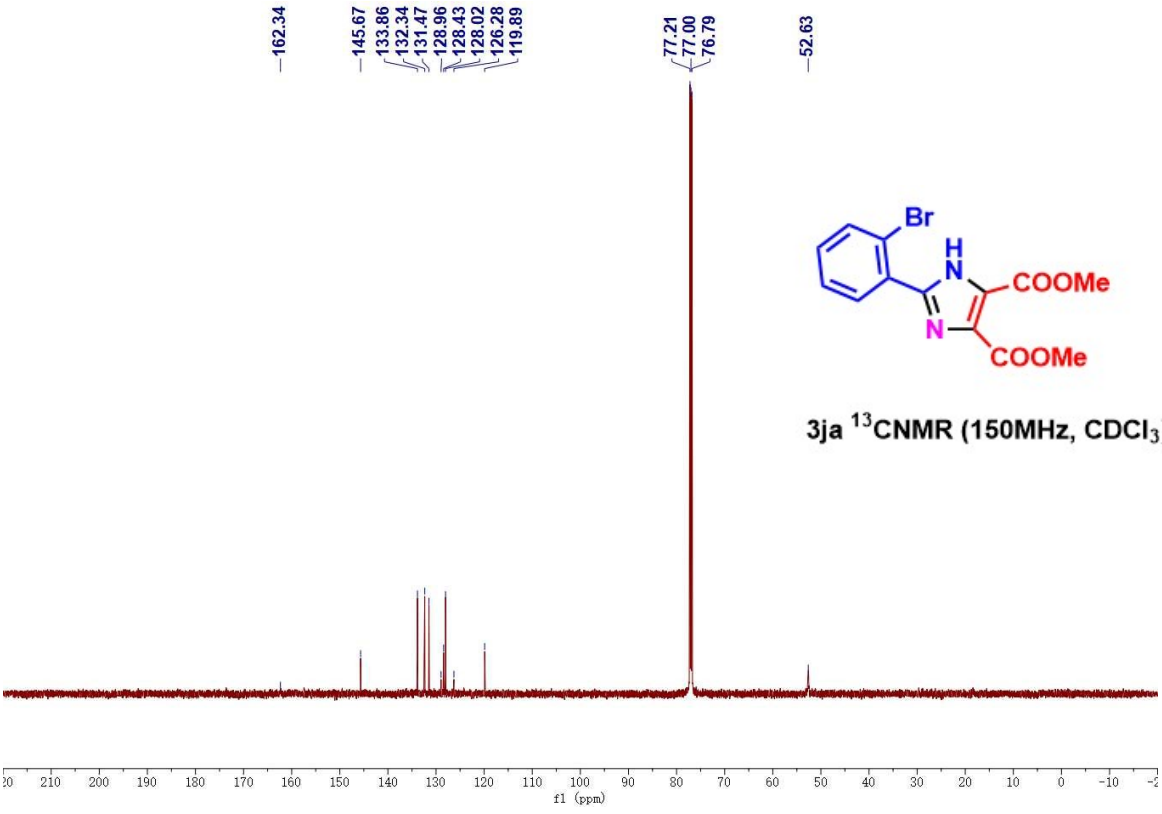
3ia ^{1}HNMR (600MHz, $CDCl_3$)



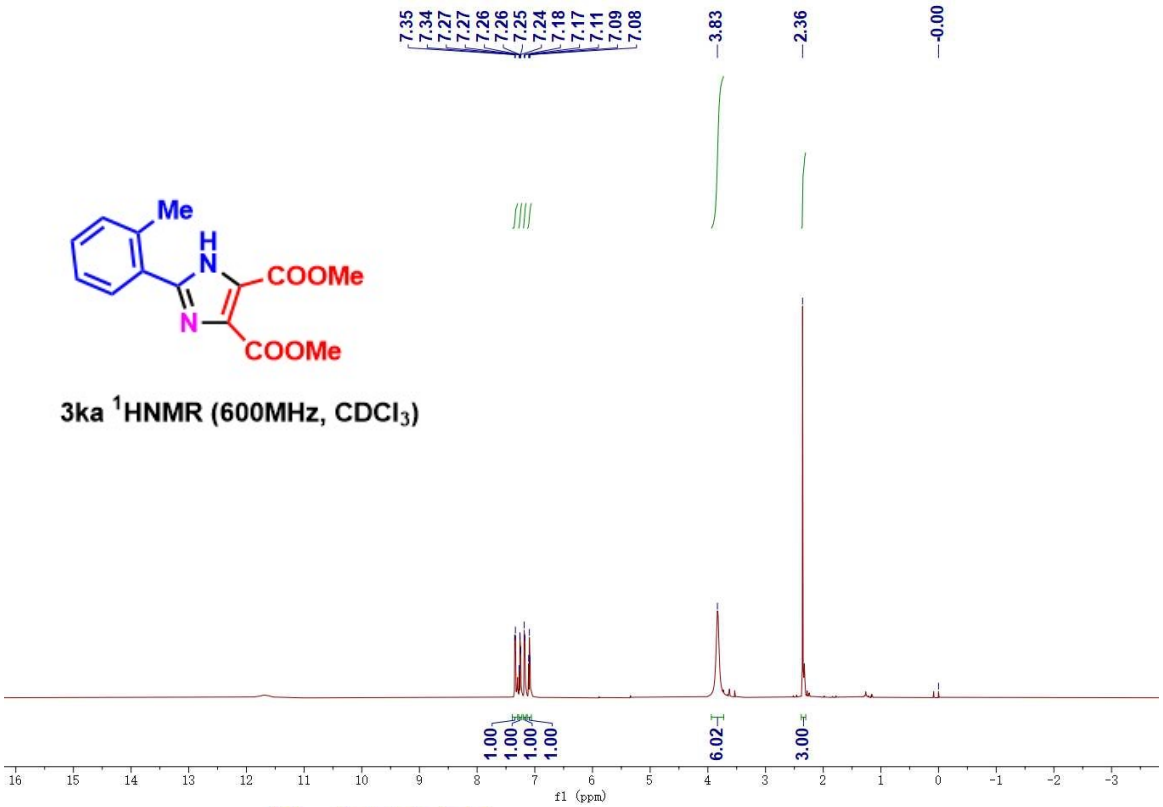
3ia ^{13}CNMR (150MHz, $CDCl_3$)



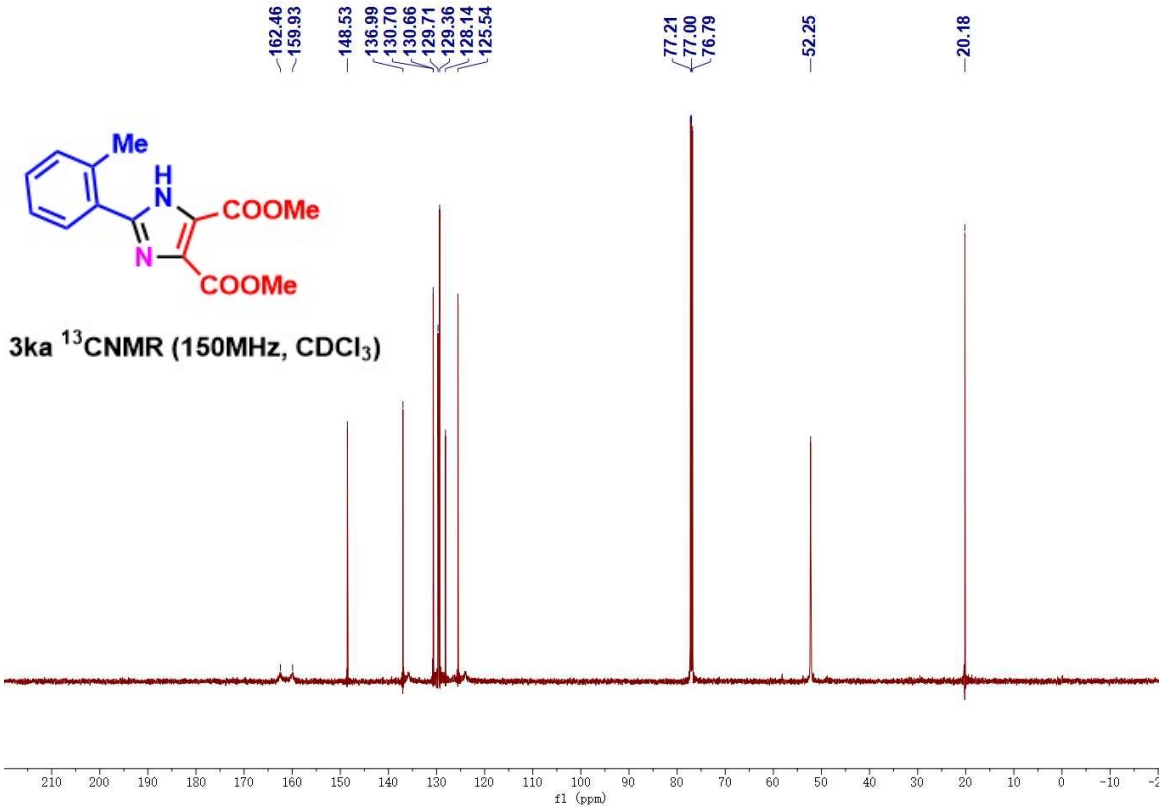
3ja ^{1}HNMR (600MHz, $CDCl_3$)



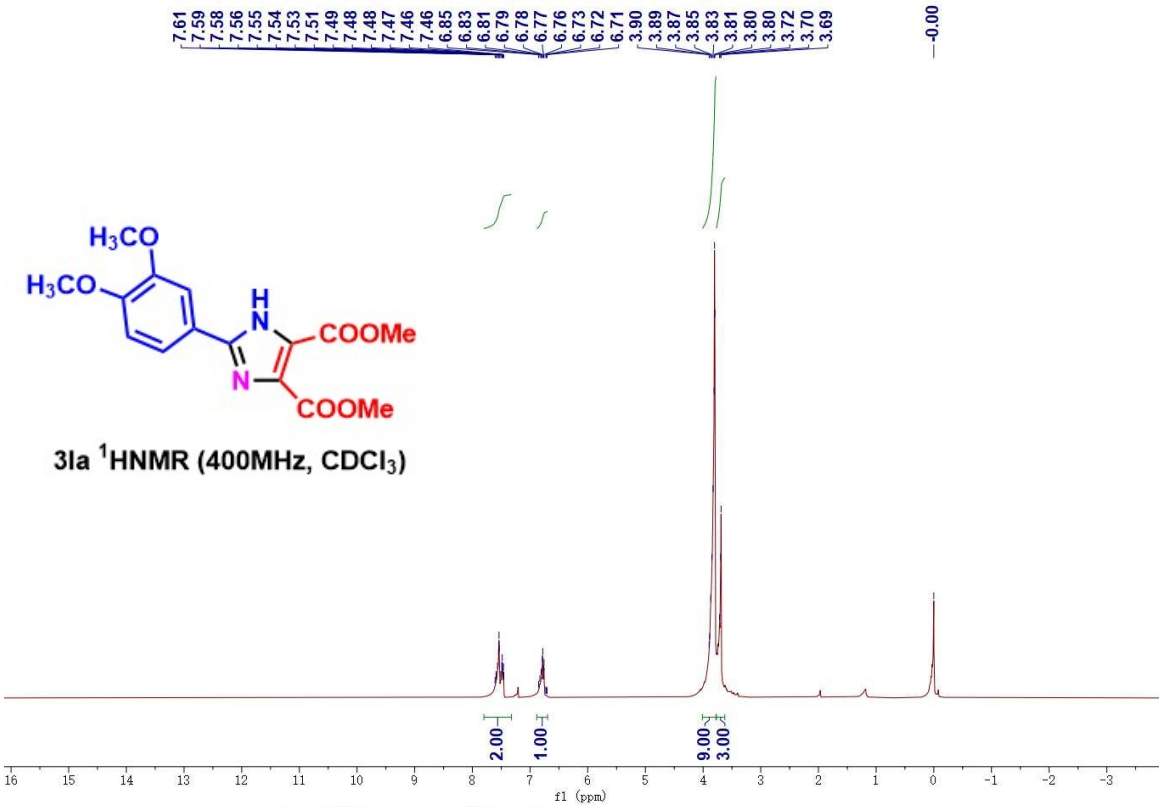
3ja ^{13}CNMR (150MHz, $CDCl_3$)



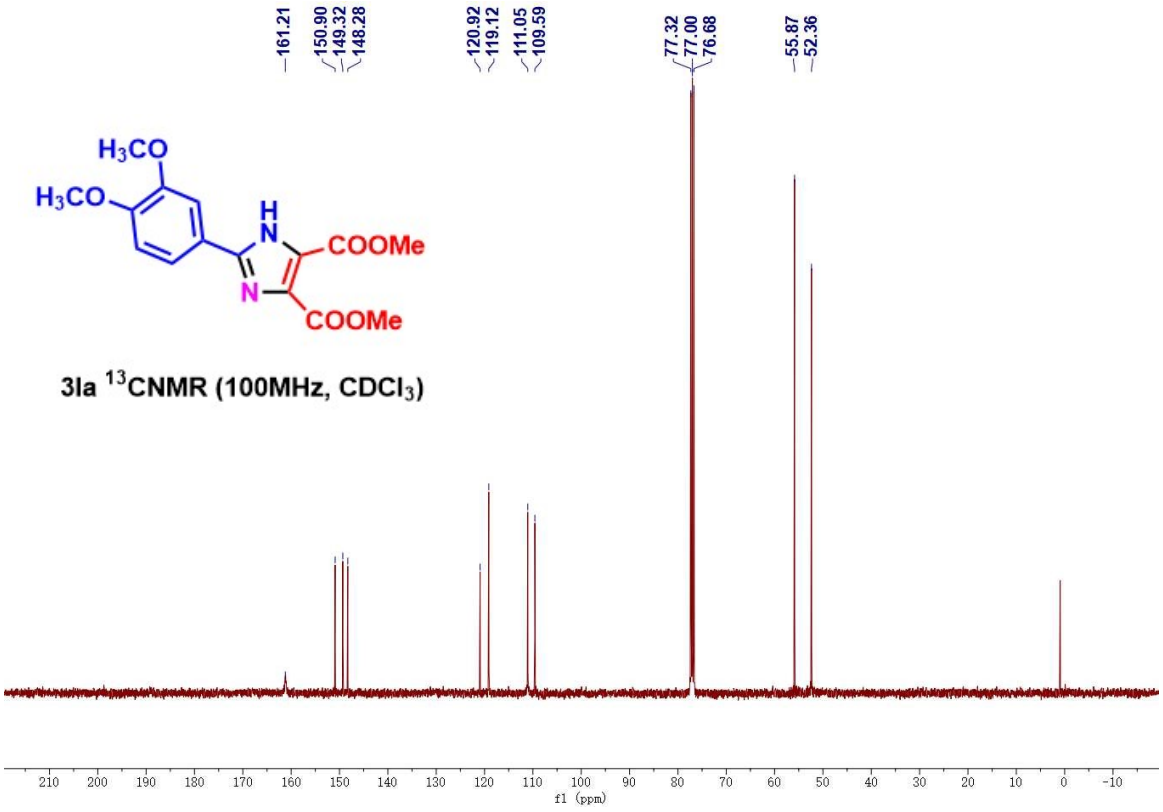
3ka ^{1}HNMR (600MHz, $CDCl_3$)



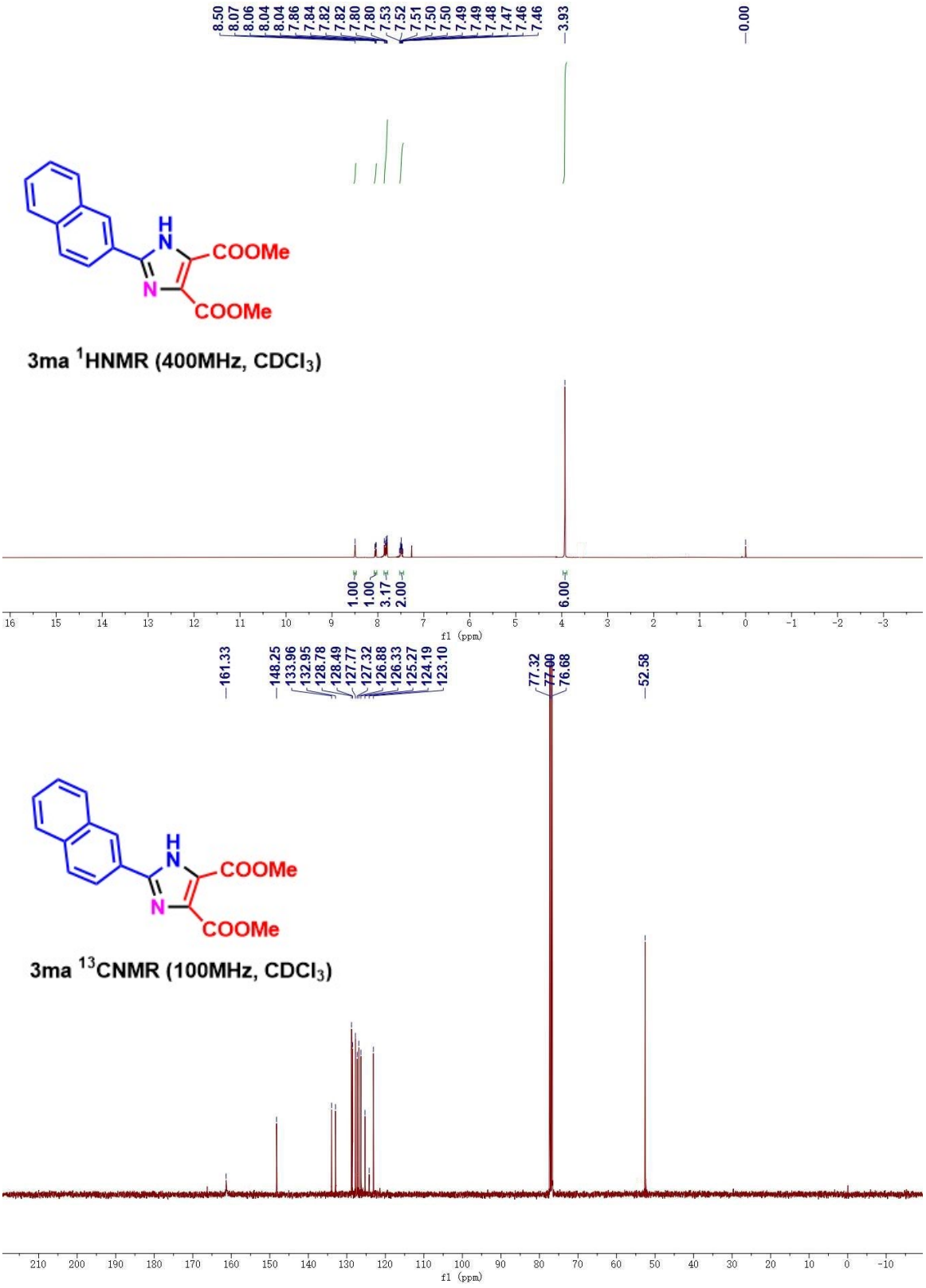
3ka ^{13}CNMR (150MHz, $CDCl_3$)



3Ia ^{1}HNMR (400MHz, $CDCl_3$)



3Ia ^{13}CNMR (100MHz, $CDCl_3$)


8.50
8.07
8.06
8.04
8.04
7.86
7.84
7.82
7.82
7.80
7.80
7.53
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.46
7.46
3.93
0.00
COOMe
COOMe
3ma 1HNMR (400MHz, CDCl3)
1.00
1.00
3.17
2.00
6.00
f1 (ppm)
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148.25
133.96
132.95
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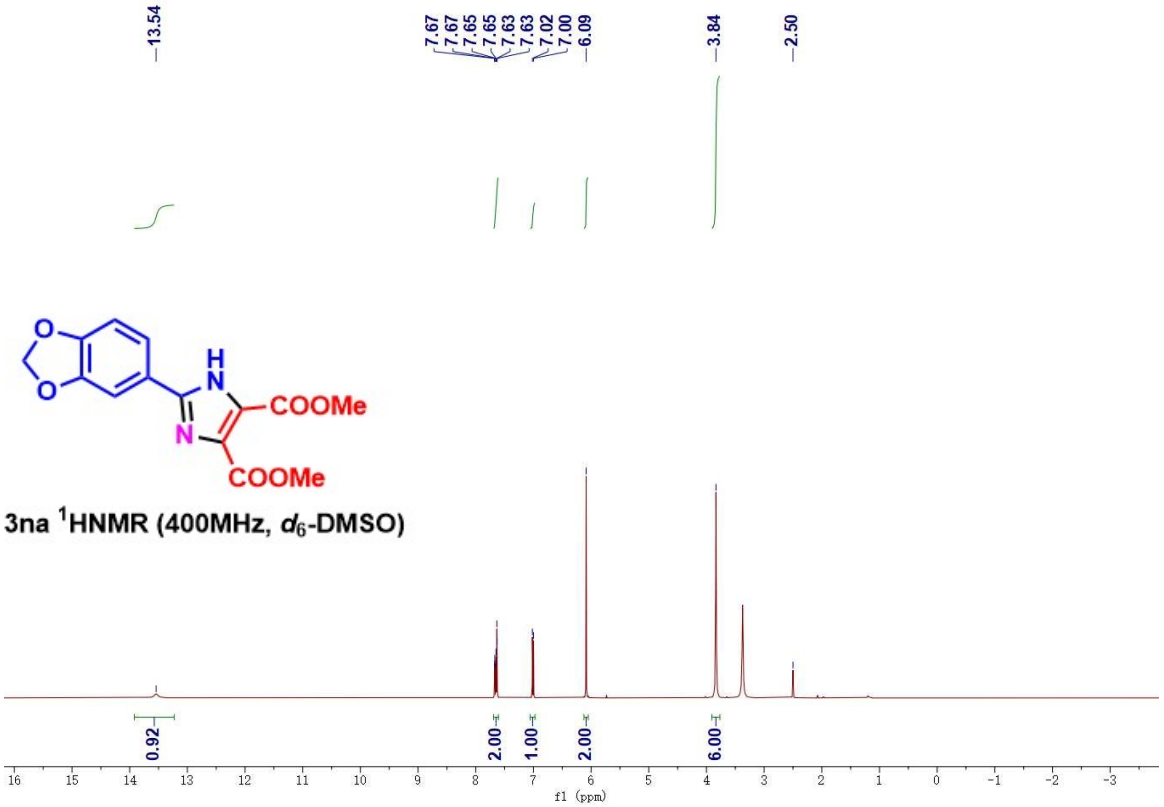
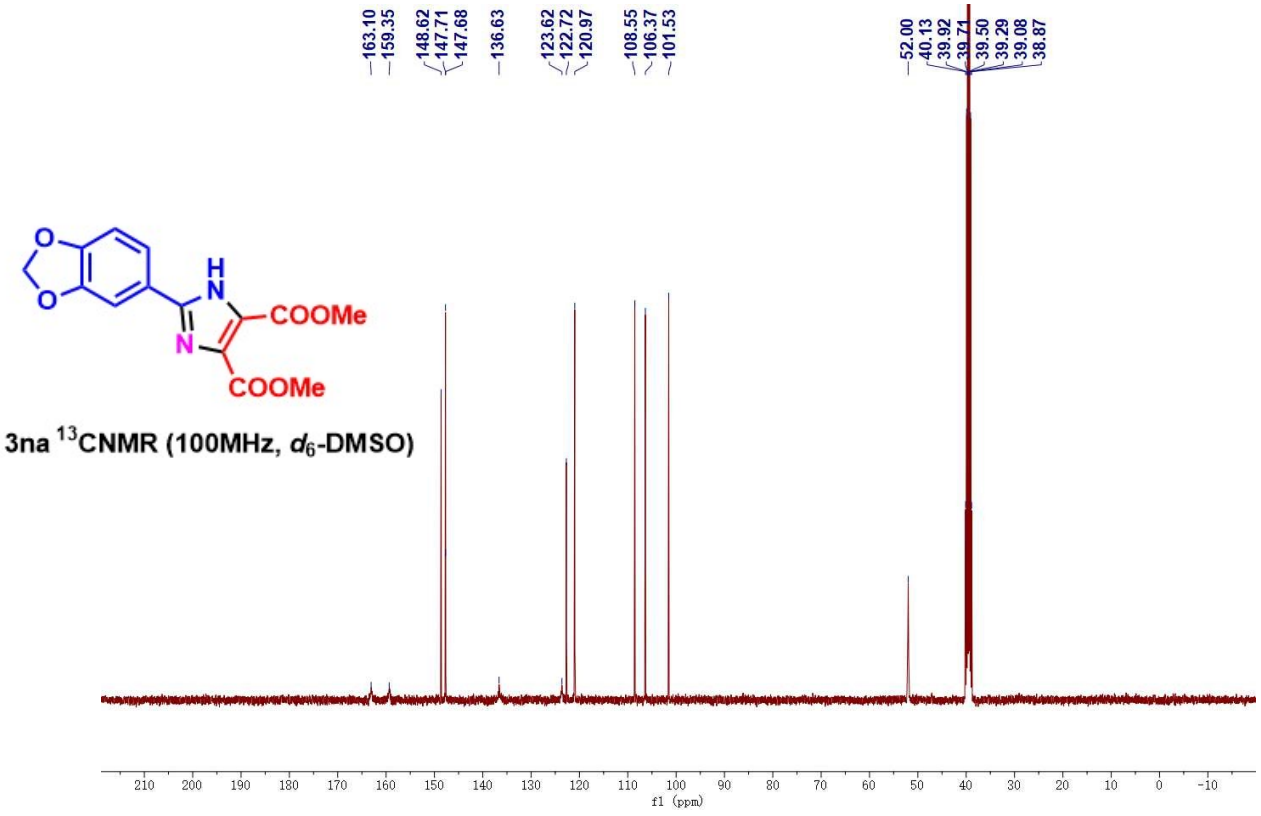
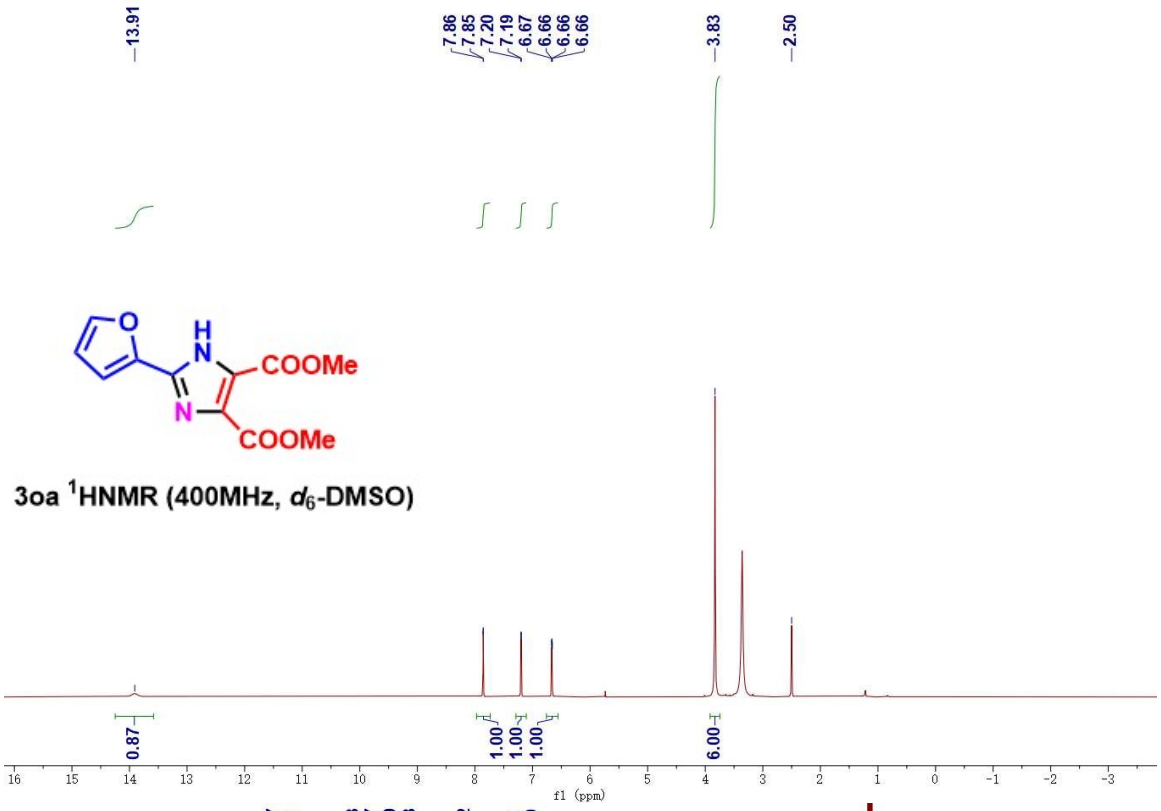
128.49
127.77
127.32
126.88
126.33
125.27
124.19
123.10
77.32
77.00
76.68
52.58
COOMe
COOMe
3ma 13CNMR (100MHz, CDCl3)
f1 (ppm)



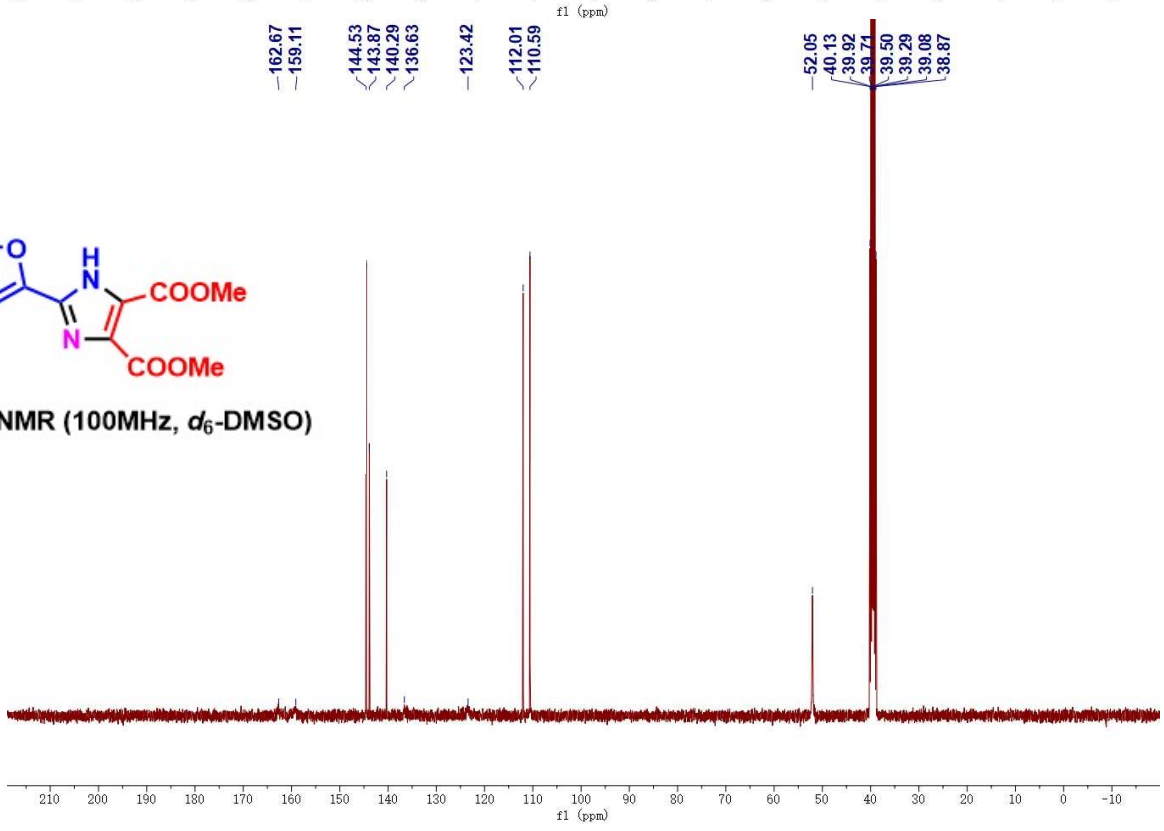
3na ^{1}HNMR (400MHz, d_6-DMSO)



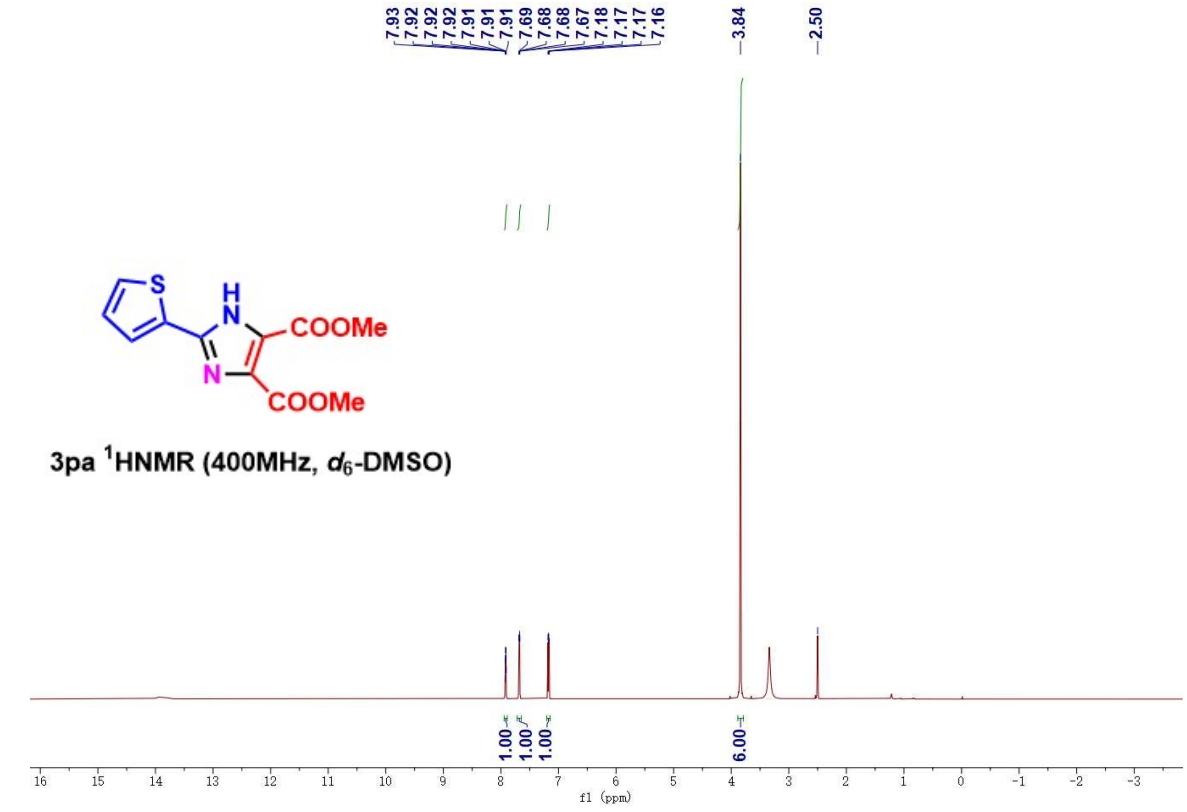
3na ^{13}CNMR (100MHz, d_6-DMSO)



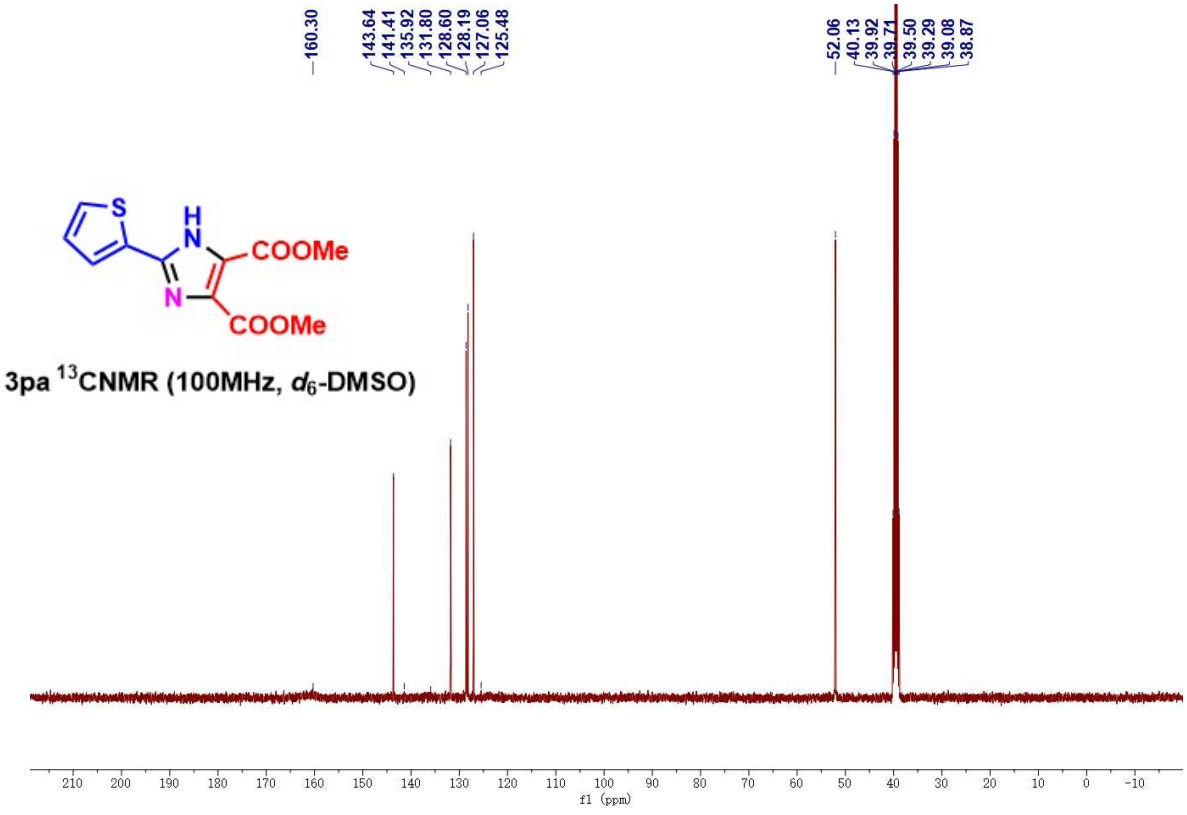
3oa ^{1}HNMR (400MHz, d_6-DMSO)



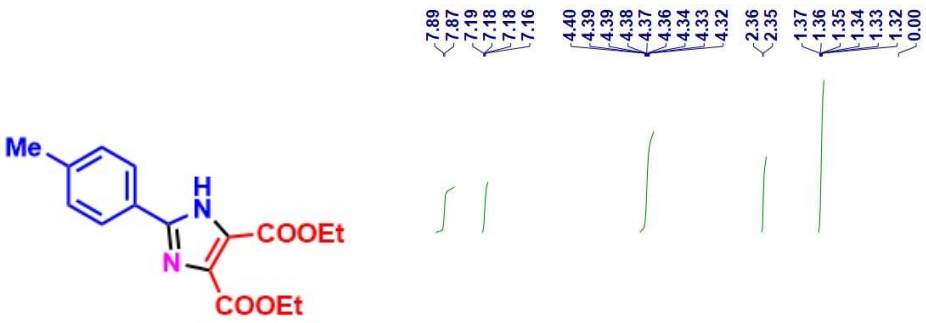
3oa ^{13}CNMR (100MHz, d_6-DMSO)



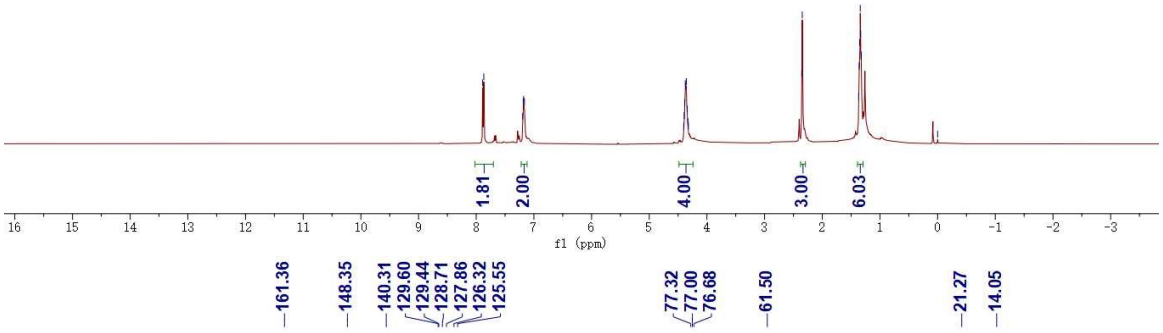
3pa ^{1}HNMR (400MHz, d_6-DMSO)



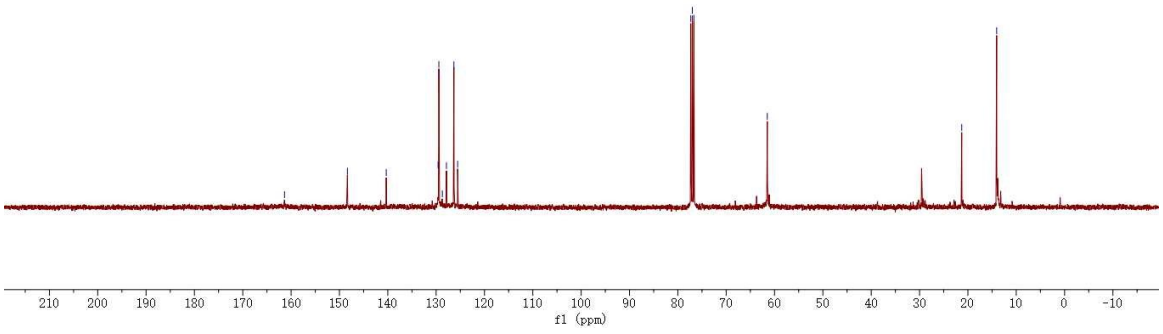
3pa ^{13}CNMR (100MHz, d_6-DMSO)

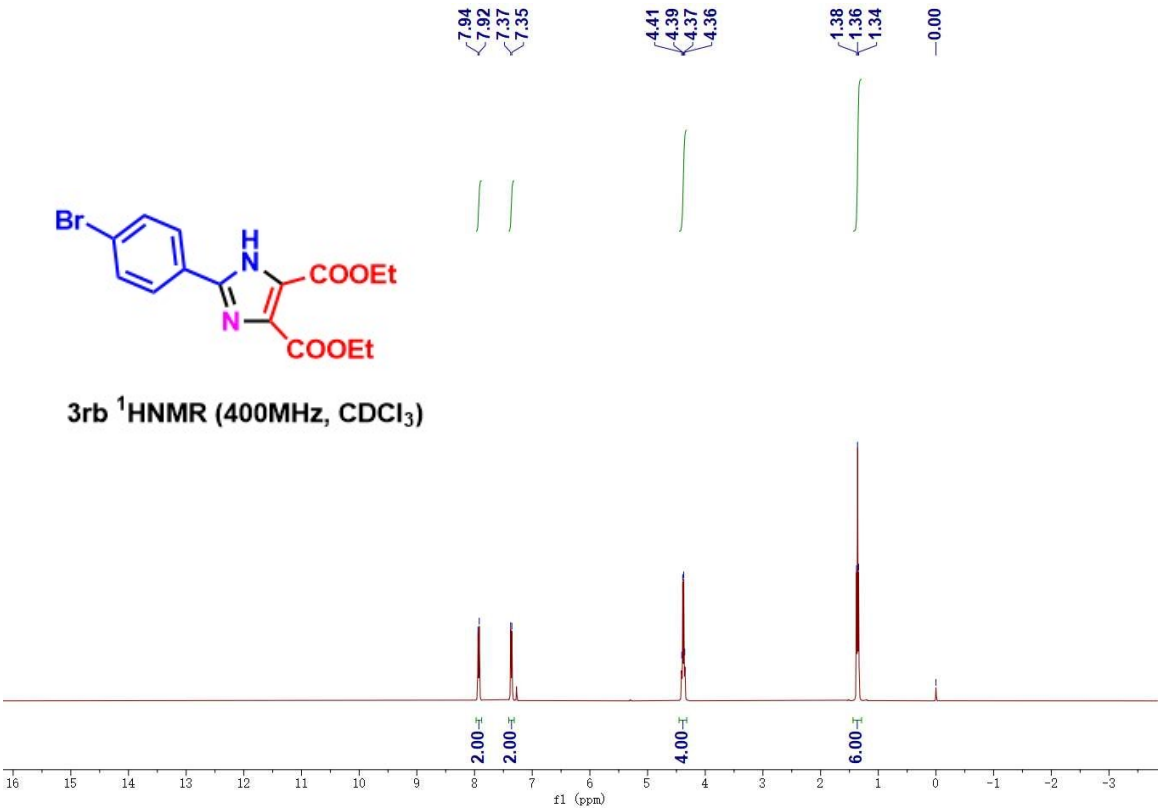


3bb ^{1}HNMR (400MHz, $CDCl_3$)

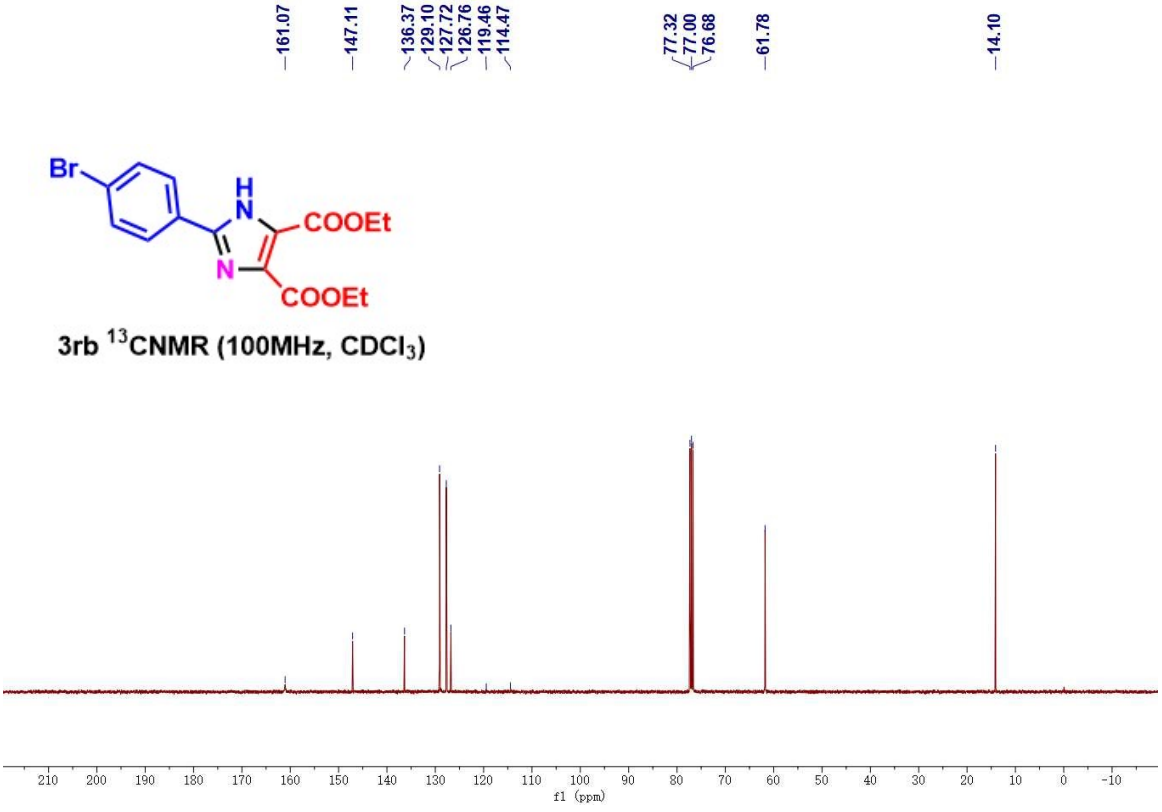


3bb ^{13}CNMR (100MHz, $CDCl_3$)

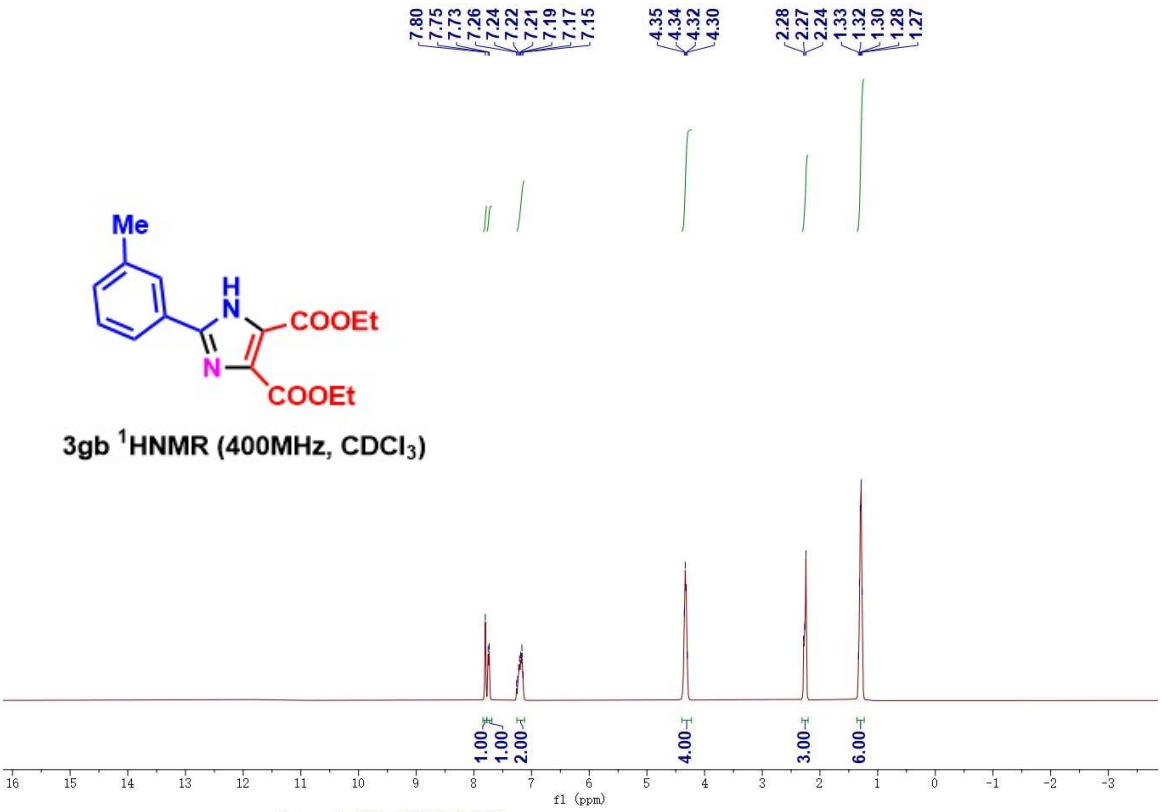




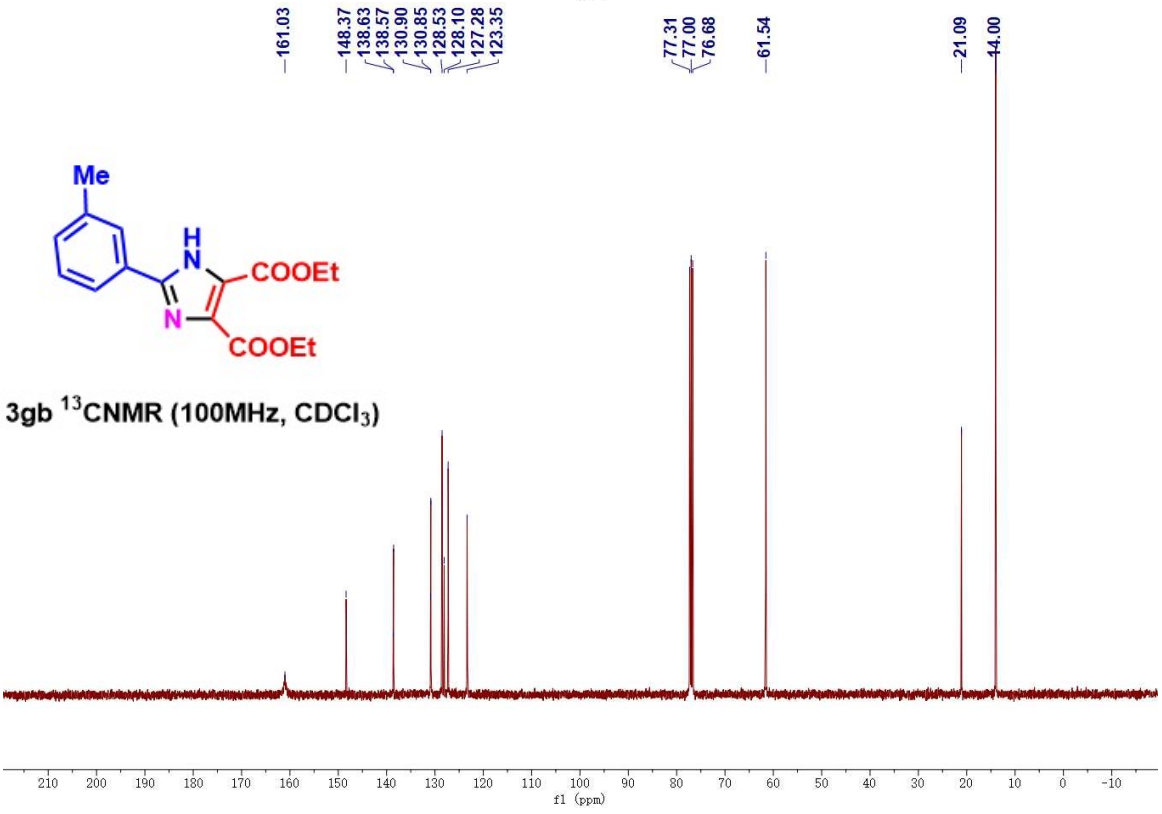
3rb ^{1}HNMR (400MHz, $CDCl_3$)



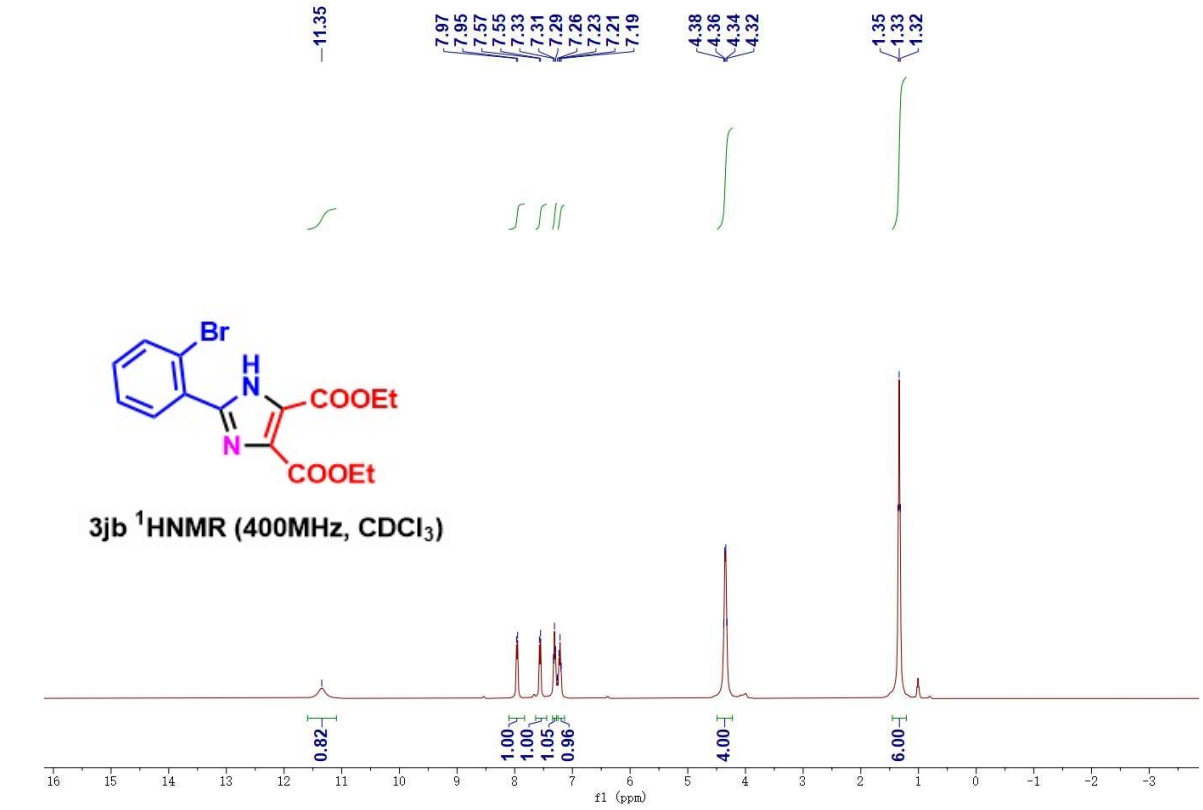
3rb ^{13}CNMR (100MHz, $CDCl_3$)



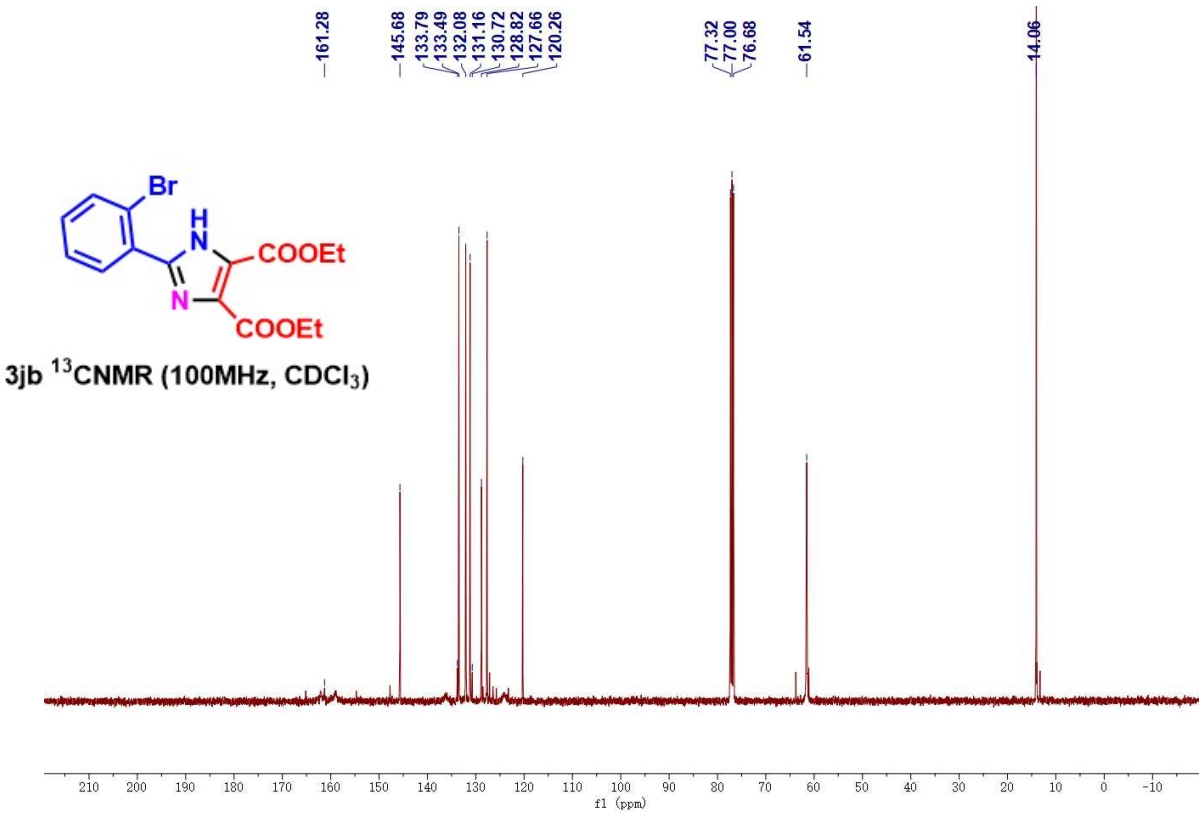
3gb ^{1}HNMR (400MHz, $CDCl_3$)



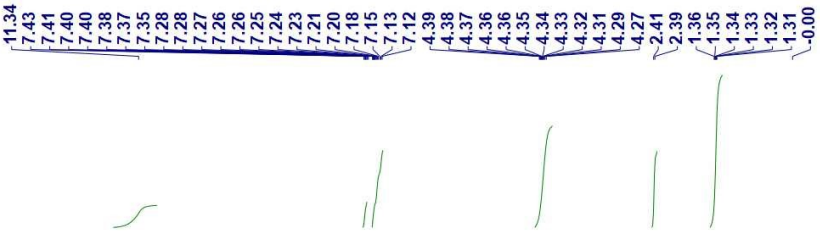
3gb ^{13}CNMR (100MHz, $CDCl_3$)



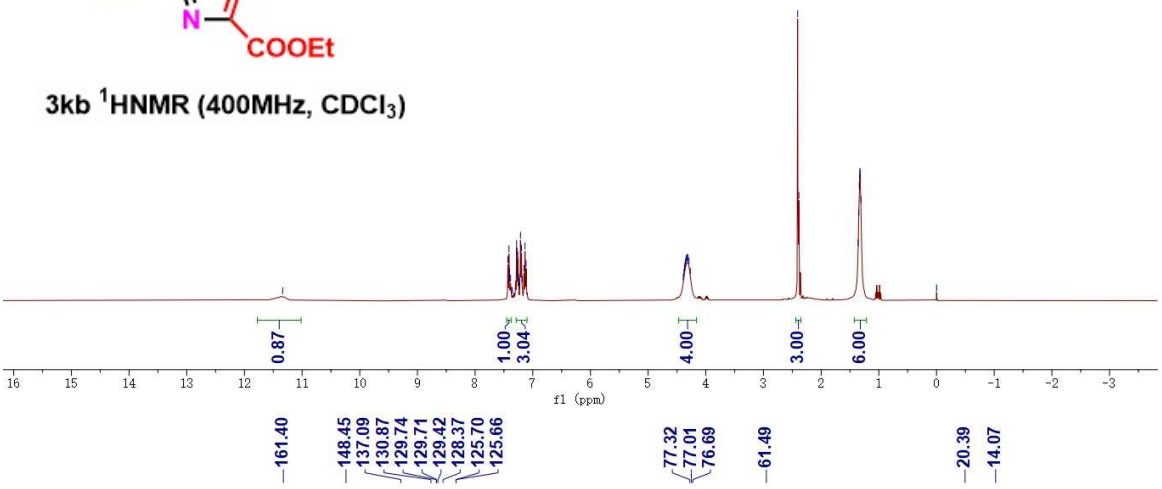
3jb ^{1}HNMR (400MHz, $CDCl_3$)

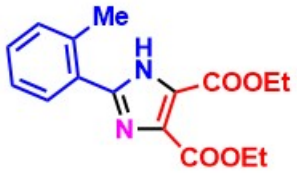


3jb ^{13}CNMR (100MHz, $CDCl_3$)

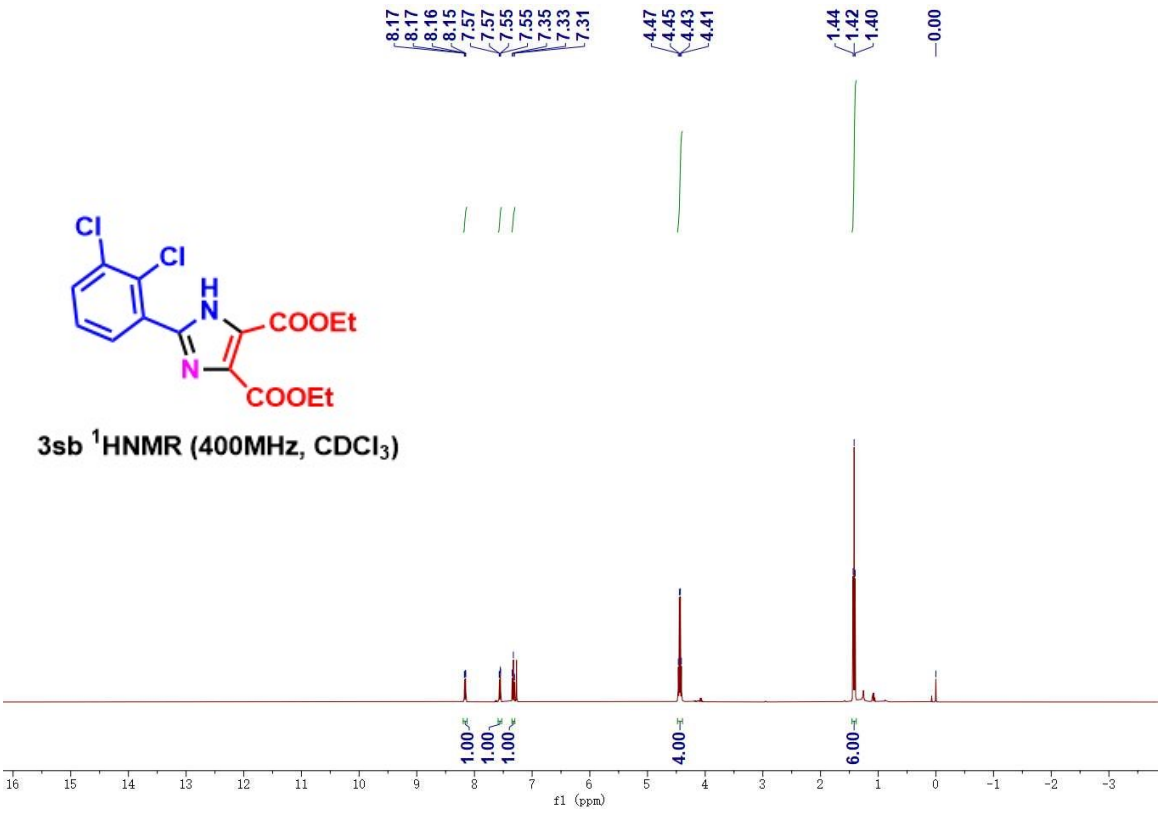


3kb ^{1}HNMR (400MHz, $CDCl_3$)

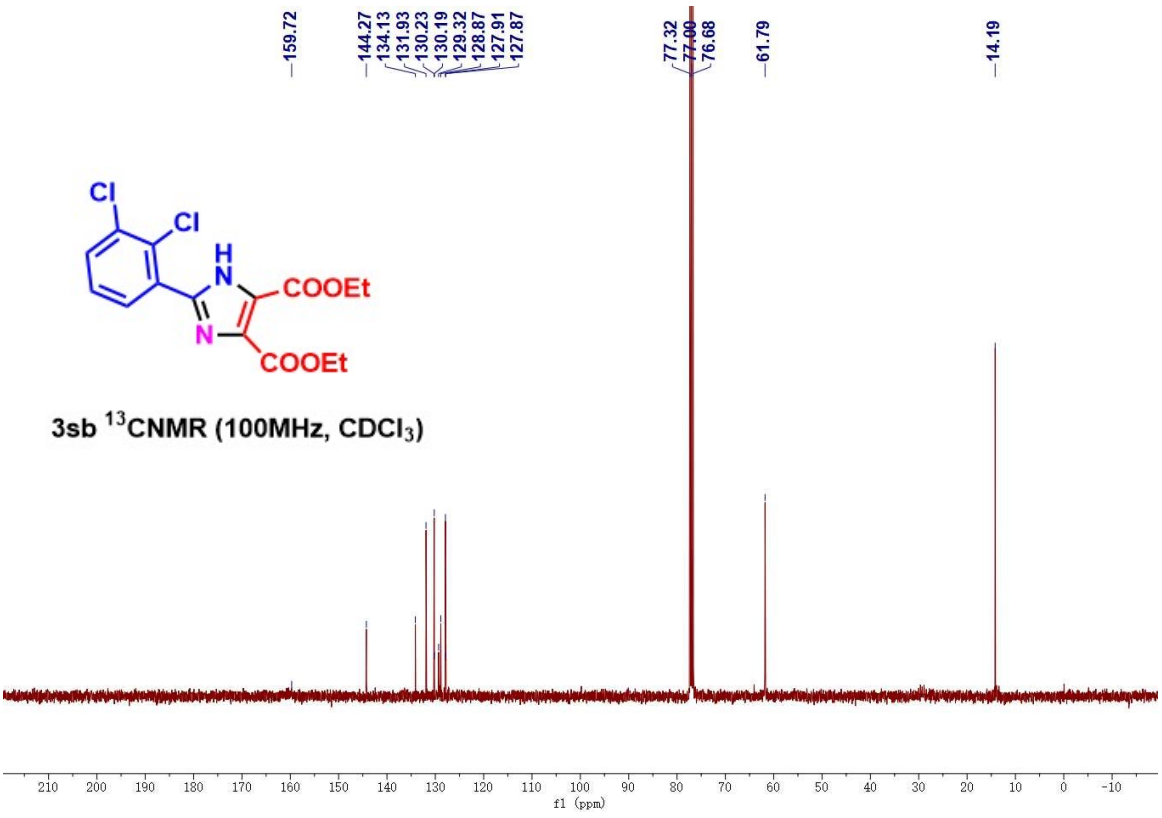




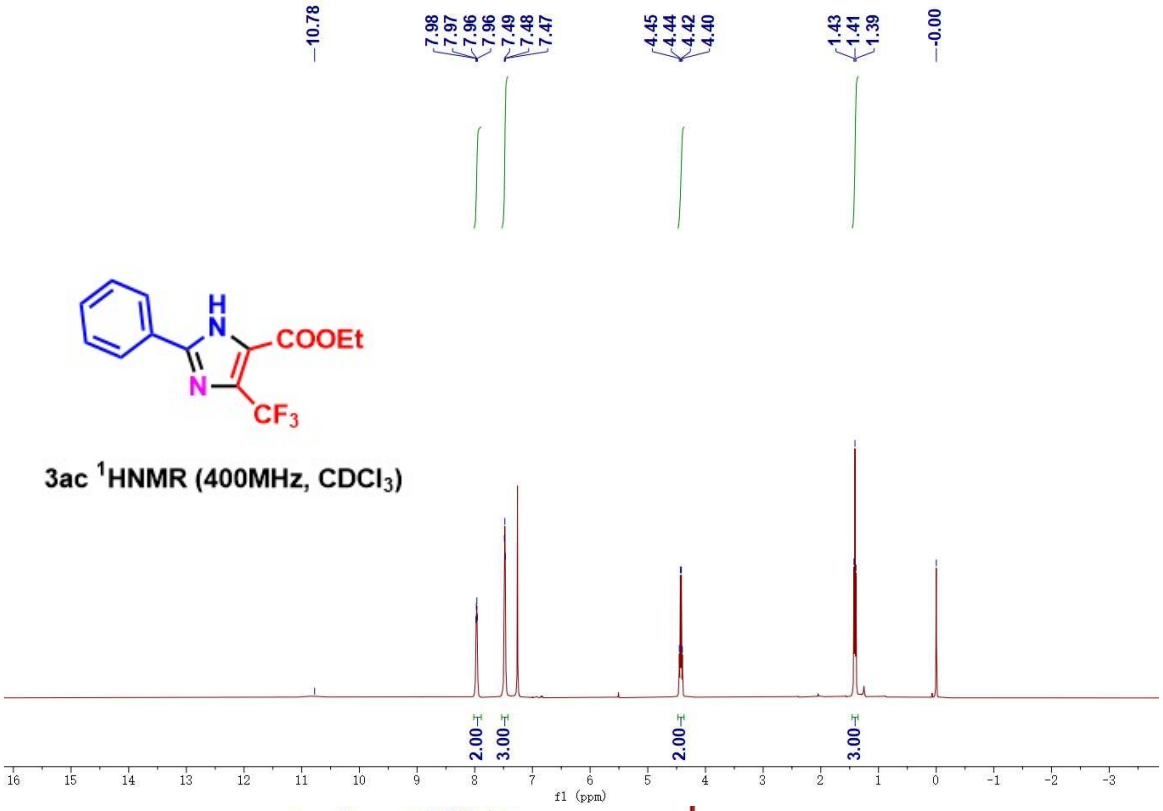
3kb ^{13}CNMR (100MHz, $CDCl_3$)

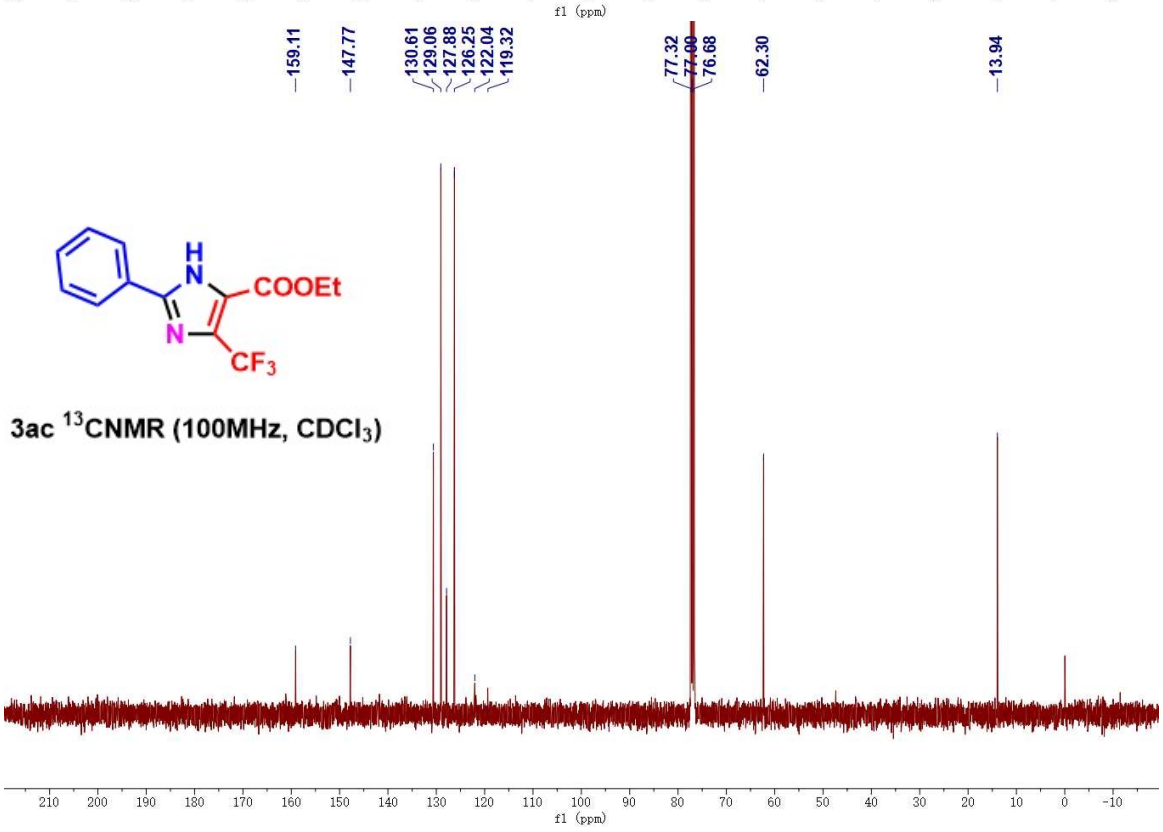


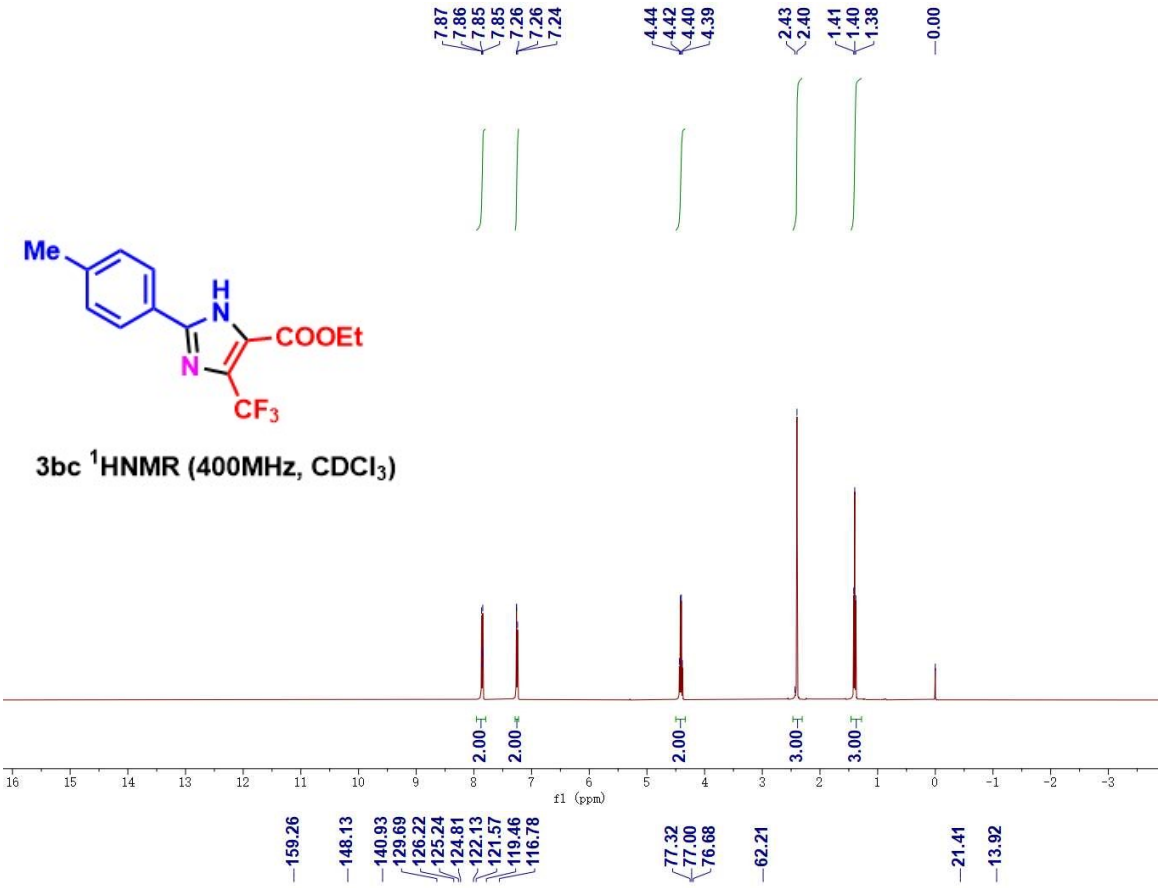
3sb ^{1}HNMR (400MHz, $CDCl_3$)



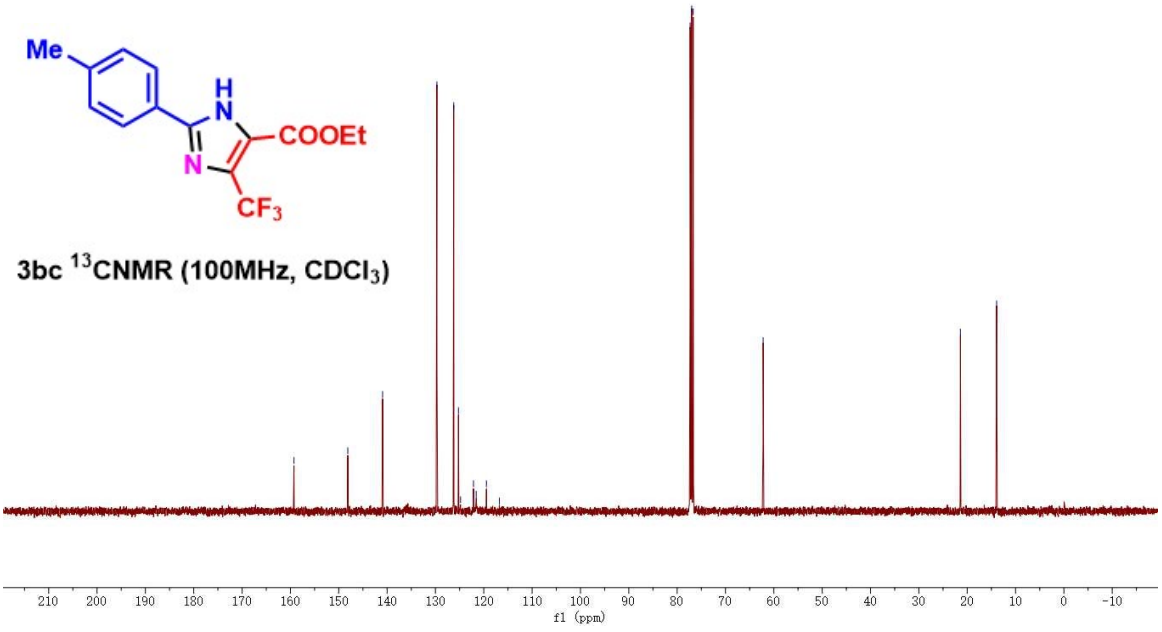
3sb ^{13}CNMR (100MHz, $CDCl_3$)


10.78
7.98
7.97
7.96
7.96
7.49
7.48
7.47
4.45
4.44
4.42
4.40
1.43
1.41
1.39
0.00
COOEt
CF3
3ac 1HNMR (400MHz, CDCl3)
2.00
3.00
2.00
3.00
f1 (ppm)

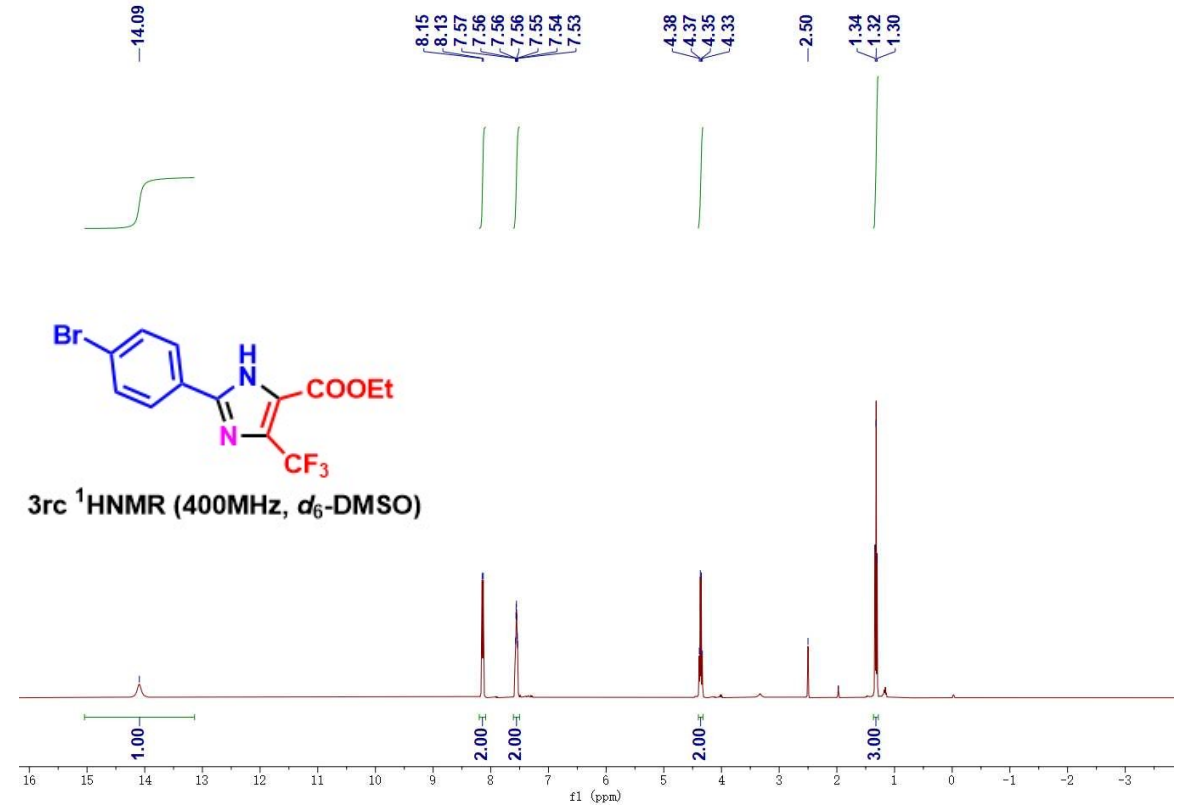

159.11
147.77
130.61
129.06
127.88
126.25
122.04
119.32
77.32
77.00
76.68
62.30
13.94
COOEt
CF3
3ac 13CNMR (100MHz, CDCl3)
f1 (ppm)



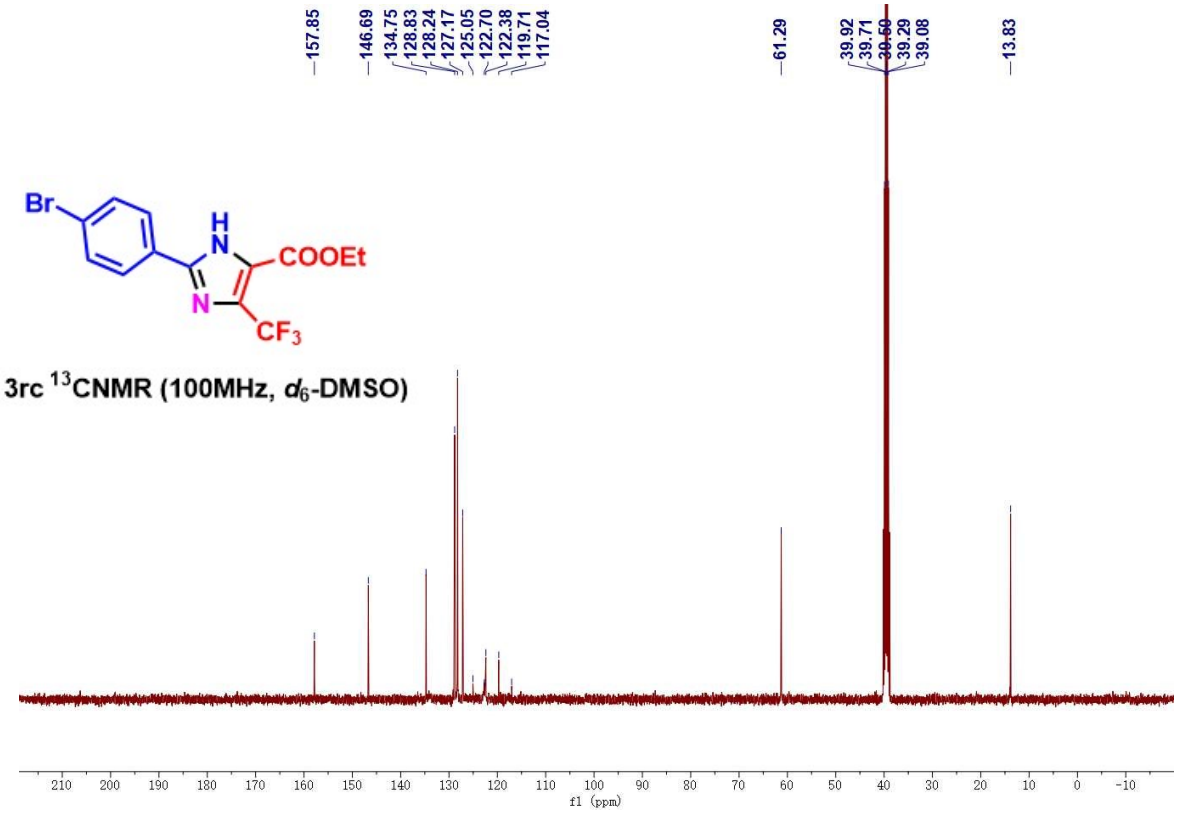
3bc ^{1}HNMR (400MHz, $CDCl_3$)



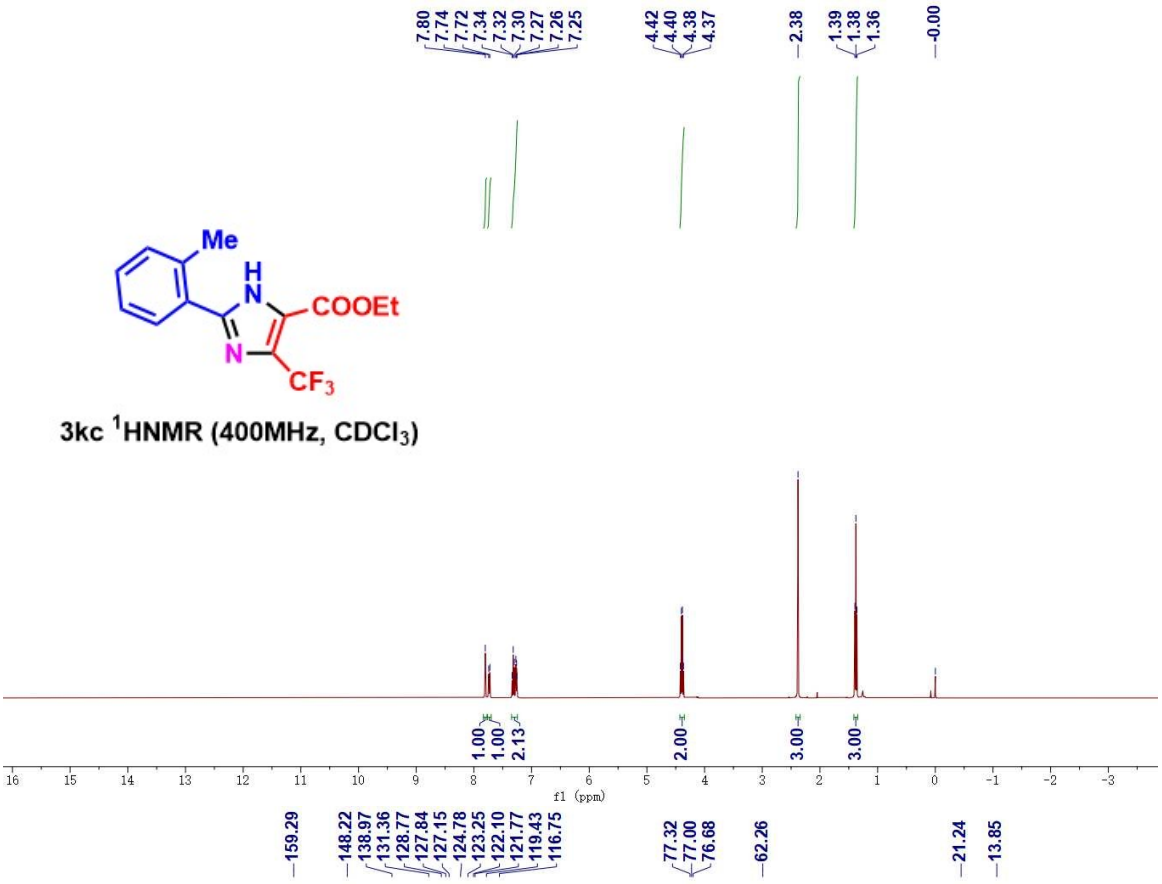
3bc ^{13}CNMR (100MHz, $CDCl_3$)



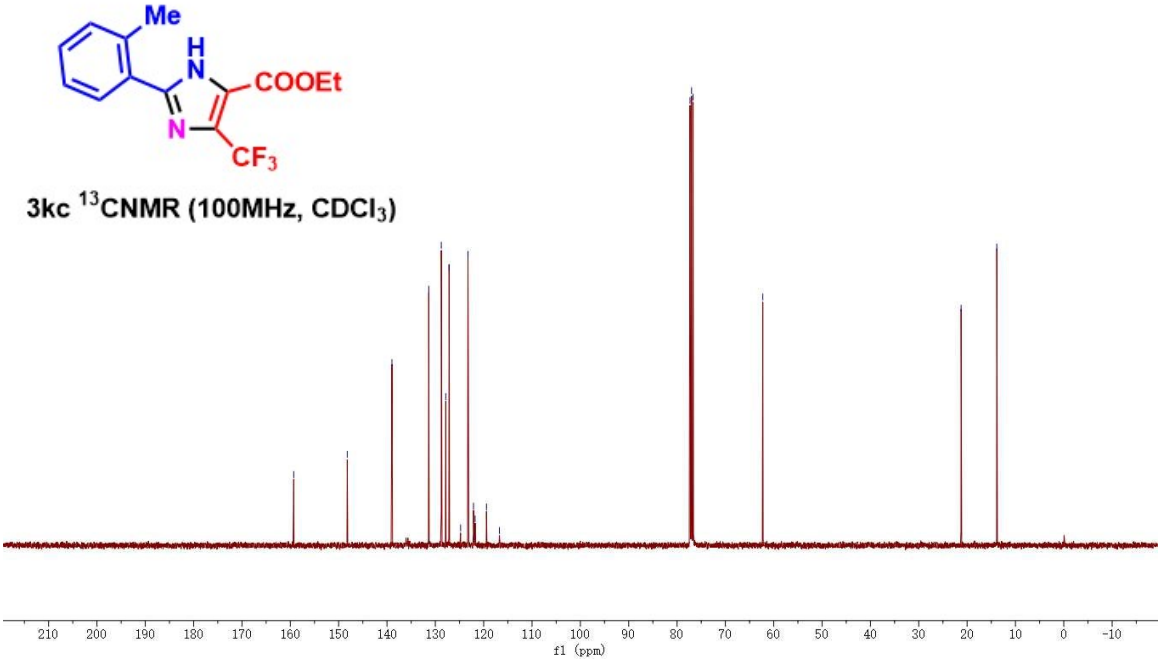
3rc ^{1}HNMR (400MHz, d_6-DMSO)



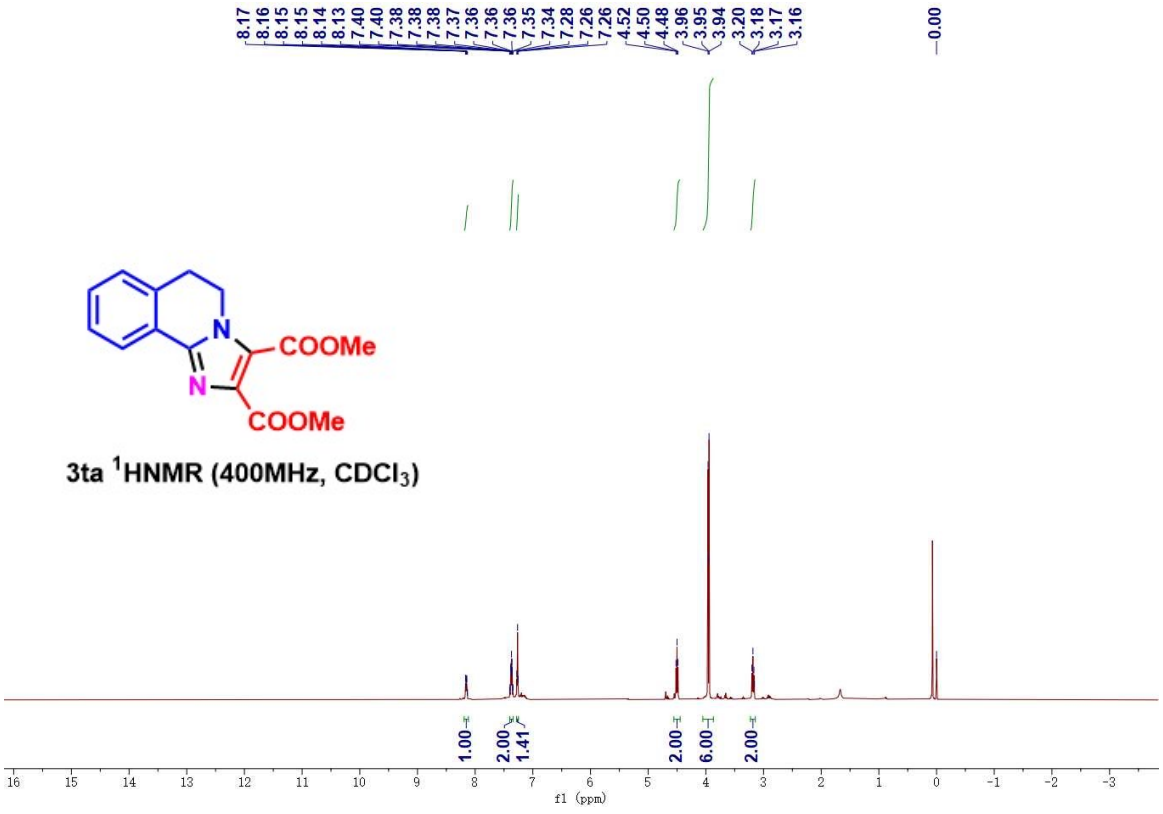
3rc ^{13}CNMR (100MHz, d_6-DMSO)



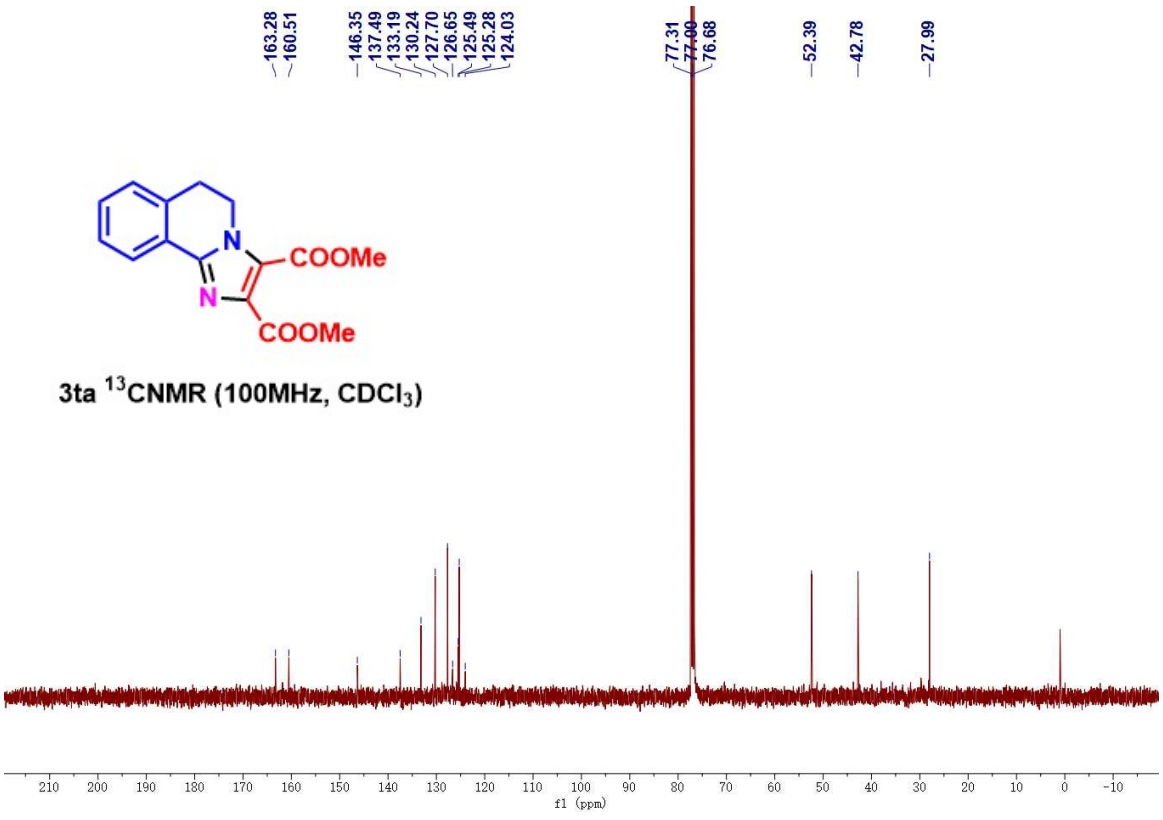
3kc ^{1}HNMR (400MHz, $CDCl_3$)



3kc ^{13}CNMR (100MHz, $CDCl_3$)



3ta ^{1}HNMR (400MHz, $CDCl_3$)



3ta ^{13}CNMR (100MHz, $CDCl_3$)