Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Electrochemically promoted synthesis of polysubstituted oxazoles from *β*-diketone derivatives and benzylamines under mild conditions

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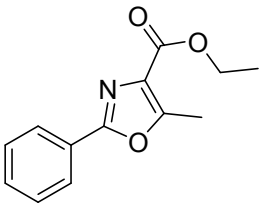
1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz). The chemical shifts were referenced to signals at 7.26 and 77.0 ppm, respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). GC-MS was obtained using electron ionization. HRMS analysis was performed in a MAT95XP high resolution mass spectrometer.

2. Typical Procedure for the Electrosynthesis of Polysubstituted Oxazoles

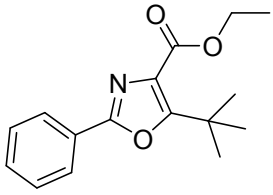
In a typical procedure, DMF (10 mL), *β*-diketones (2 mmol), benzylamine (2 mmol) and NH_4I (4 mmol) were added to the undivided cell. The electrosynthesis was performed in the undivided cell fitted with a Ni sheet cathode (2 cm × 2.5 cm × 0.02 cm) and a graphite rod anode (surface area around 5 cm^2) at a constant current 60 mA (current density 12 mA/cm^2) at room temperature. The electrolysis was ended when ketone had been completely consumed (monitored by GC-MS). After the electrolysis, the electrolyte solution was decolorized with $Na_2S_2O_3$, and then washed with distilled water (20 mL) and extracted with ethyl acetate (10 mL × 3). The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel using petroleum ether-ethyl acetate (20:1) as eluent.

3. Characterization Data for All Products



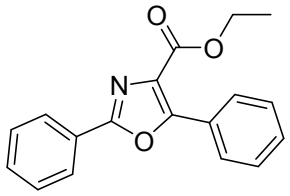
Ethyl 5-methyl-2-phenyloxazole-4-carboxylate (**3aa**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H), 7.46–7.44 (m, 3H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.71 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.49, 159.66, 156.15, 130.71, 128.83, 128.71, 126.64, 126.59, 61.02, 14.39, 12.22.



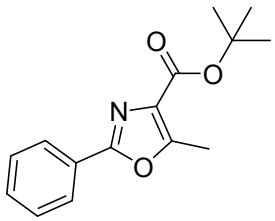
Ethyl 5-tert-butyl-2-phenyloxazole-4-carboxylate (**3ba**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–7.99 (m, 2H), 7.51–7.39 (m, 3H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.52 (s, 9H), 1.44 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.49, 162.47, 157.85, 130.56, 128.84, 128.67, 127.60, 126.77, 126.54, 61.17, 33.51, 28.26, 14.32.



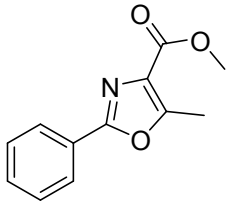
Ethyl 2, 5-diphenyloxazole-4-carboxylate (**3ca**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.05 (m, 4H), 7.52–7.39 (m, 6H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.27, 159.74, 155.01, 131.04, 130.26, 130.15, 129.30, 128.80, 128.53, 128.38, 128.30, 127.12, 126.84, 126.38, 61.44, 14.31, 13.97.



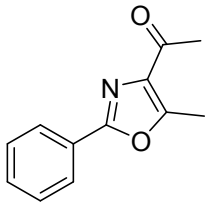
Tert-butyl 5-methyl-2-phenyloxazole-4-carboxylate (**3da**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27–7.79 (m, 2H), 7.49–7.11 (m, 3H), 2.65 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.59, 159.42, 155.05, 130.53, 129.92, 128.65, 126.79, 126.51, 28.27, 27.94, 12.31.



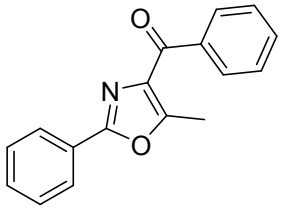
Methyl 5-methyl-2-phenyloxazole-4-carboxylate (**3ea**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H), 7.46–7.44 (m, 3H), 3.95 (s, 3H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.87, 159.70, 156.39, 130.77, 128.74, 128.55, 126.57, 126.15, 51.99, 12.11.



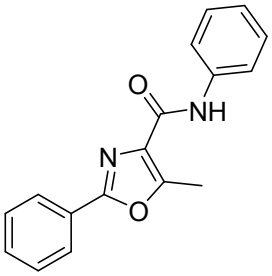
1-(5-Methyl-2-phenyloxazol-4-yl)ethanone (**3fa**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.95 (m, 2H), 7.53–7.40 (m, 3H), 2.69 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.31, 158.64, 154.43, 135.79, 130.60, 128.82, 126.90, 126.37, 27.93, 12.38.



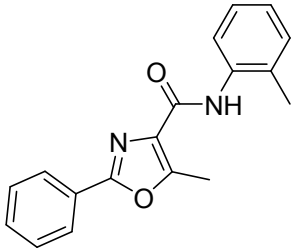
(5-methyl-2-phenyloxazol-4-yl)(phenyl)methanone (**ga**) [2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40– 8.31 (m, 2H), 8.13– 8.03 (m, 2H), 7.62–7.56 (m, 1H), 7.53–7.46 (m, 5H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.01, 158.54, 157.25, 137.53, 132.75, 130.64, 130.45, 129.03, 128.81, 128.17, 128.13, 126.91, 126.49, 12.81.



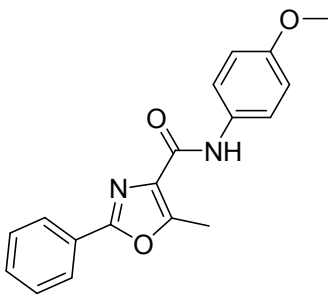
5-Methyl-N, 2-diphenyloxazole-4-carboxamide (**3ha**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.09–8.00 (m, 2H), 7.72–7.70 (m, 2H), 7.52–7.46 (m, 3H), 7.39–7.35 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.00, 158.60, 153.85, 137.77, 130.78, 130.44, 129.03, 128.89, 126.70, 126.40, 124.26, 119.77, 11.92.



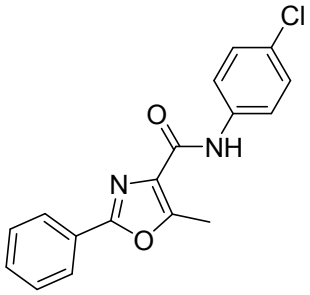
5-methyl-2-phenyl-N-o-tolyloxazole-4-carboxamide (**3ia**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.08–7.95 (m, 2H), 7.54–7.45 (m, 3H), 7.28–7.22 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.78 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.92, 158.56, 153.63, 135.78, 130.76, 130.66, 130.43, 128.87, 128.10, 126.83, 126.72, 126.38, 124.63, 121.71, 29.71, 17.66, 11.91. HRMS-EI Calcd for $C_{18}H_{16}N_2NaO_2$ $[M+Na]^+$: 315.1104; Found: 315.1103.



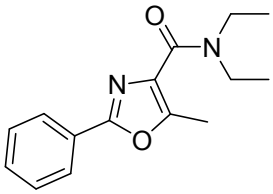
N-(4-methoxyphenyl)-5-methyl-2-phenyloxazole-4-carboxamide (**3ja**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.09–8.00 (m, 2H), 7.65–7.58 (m, 2H), 7.56–7.43 (m, 3H), 6.94–6.87 (m, 2H), 3.81 (s, 3H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.80, 158.56, 156.39, 153.59, 130.91, 130.76, 130.43, 128.89, 126.70, 126.37, 121.46, 114.19, 55.50, 11.93. HRMS-EI Calcd for $C_{18}H_{16}N_2NaO_3$ $[M+Na]^+$: 331.1053; Found: 331.1051.



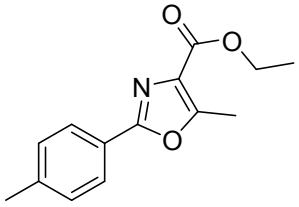
N-(4-chlorophenyl)-5-methyl-2-phenyloxazole-4-carboxamide (**3ka**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 8.07–8.01 (m, 2H), 7.70–7.65 (m, 2H), 7.52–7.47 (m, 3H), 7.36–7.30 (m, 2H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.94, 158.69, 154.04, 136.37, 130.87, 130.21, 129.18, 129.05, 128.92, 126.58, 126.40, 120.90, 29.70, 11.93. HRMS-EI Calcd for $C_{17}H_{13}ClN_2NaO_2$ $[M+Na]^+$: 335.0558; Found: 335.0559.



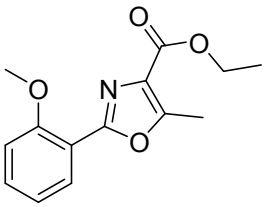
N,N-diethyl-5-methyl-2-phenyloxazole-4-carboxamide (**3la**) [3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.95 (m, 2H), 7.48–7.42 (m, 3H), 3.77 (q, *J* = 6.0 Hz, 2H), 3.49 (q, *J* =6.4 Hz, 2H), 2.63 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.97, 157.85, 153.62, 131.95, 130.20, 128.73, 127.35, 126.15, 60.36, 43.20, 40.80, 14.66, 14.18, 12.97, 12.00.



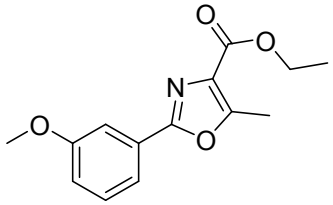
Ethyl 5-methyl-2-p-tolyloxazole-4-carboxylate (**3ab**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.30–7.20 (m, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 2.40 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.56, 159.89, 155.85, 141.06, 129.42, 128.68, 126.56, 123.94, 60.97, 21.51, 14.39, 12.19.



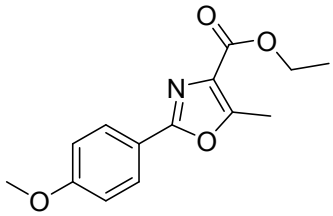
Ethyl 2-(4-methoxyphenyl)-5-methyloxazole-2-carboxylate (**3ac**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.52–7.34 (m, 1H), 7.09–6.88 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 2.70 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.59, 158.30, 157.70, 155.92, 132.04, 130.62, 128.45, 120.49, 115.88, 111.78, 60.82, 55.88, 14.35, 12.14. HRMS-EI Calcd for $C_{14}H_{15}NNaO_4$ $[M+Na]^+$: 284.0983; Found: 284.0985.



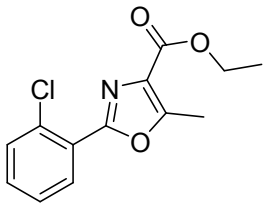
Ethyl 2-(4-methoxyphenyl)-5-methyloxazole-3-carboxylate (**3ad**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.53 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.02–6.99 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.70 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.41, 159.86, 159.54, 156.10, 129.77, 128.82, 127.81, 119.01, 117.45, 111.09, 60.98, 55.48, 14.35, 12.18. HRMS-EI Calcd for $C_{14}H_{16}NO_4$ $[M+H]^+$: 262.1074; Found: 262.1077.



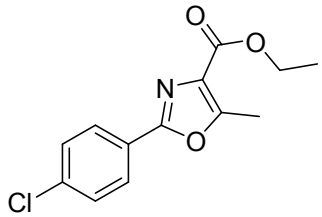
Ethyl 2-(4-methoxyphenyl)-5-methyloxazole-4-carboxylate (**3ae**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 2.68 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.61, 161.60, 159.74, 155.63, 128.55, 128.29, 119.35, 114.11, 60.96, 55.37, 14.40, 12.18.



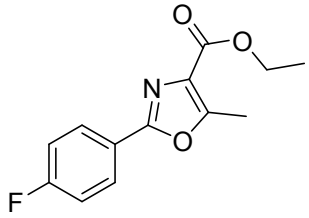
Ethyl 2-(2-chlorophenyl)-5-methyloxazole-4-carboxylate (**3af**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.43–7.30 (m, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.72 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.27, 157.73, 156.64, 132.72, 131.42, 131.36, 130.94, 128.69, 126.75, 125.85, 60.97, 14.34, 12.18.



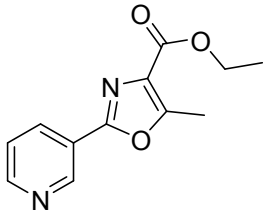
Ethyl 2-(4-chlorophenyl)-5-methyloxazole-4-carboxylate (**3ag**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.33, 158.75, 156.36, 136.90, 129.08, 128.97, 127.87, 125.10, 61.12, 14.39, 12.24.



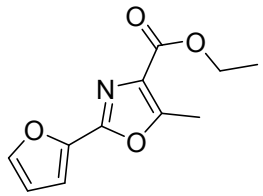
Ethyl 2-(4-fluorophenyl)-5-methyloxazole-4-carboxylate (**3ah**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.05 (m, *J* = 5.4 Hz, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.26 (*J* = 250 Hz), 162.36, 158.83, 156.12, 128.86, 128.79, 128.71, 123.03, 116.03, 115.81, 61.01, 14.35, 12.14.



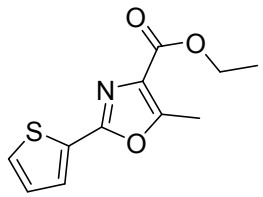
Ethyl 5-methyl-2-(pyridin-4-yl)oxazole-4-carboxylate (**3ai**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 4.4 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.85–7.81 (m, 1H), 7.41–7.38 (m, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.76 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.20, 158.33, 157.45, 149.87, 145.46, 136.99, 129.16, 125.00, 122.50, 61.10, 14.35, 12.34. HRMS-EI Calcd for $C_{12}H_{12}N_2NaO_3$ $[M+Na]^+$: 255.0740; Found: 255.0739.



Ethyl 2-(furan-2-yl)-5-methyloxazole-4-carboxylate (**3aj**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.10 (d, *J* = 3.4 Hz, 1H), 6.55–6.53 (m, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.19, 155.68, 152.30, 144.64, 142.09, 128.57, 112.26, 111.91, 61.05, 14.36, 12.04.



ethyl 5-methyl-2-(thiophen-2-yl)oxazole-4-carboxylate (**3ak**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.71 (m, 1H), 7.45–7.43 (m, 1H), 7.11–7.09 (m, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.27, 155.86, 155.65, 128.95, 128.80, 128.68, 128.50, 127.87, 61.05, 14.37, 12.12. HRMS-EI Calcd for $C_{11}H_{11}NNaO_3S$ $[M+Na]^+$: 260.0352; Found: 260.0352.

4. NMR Spectra

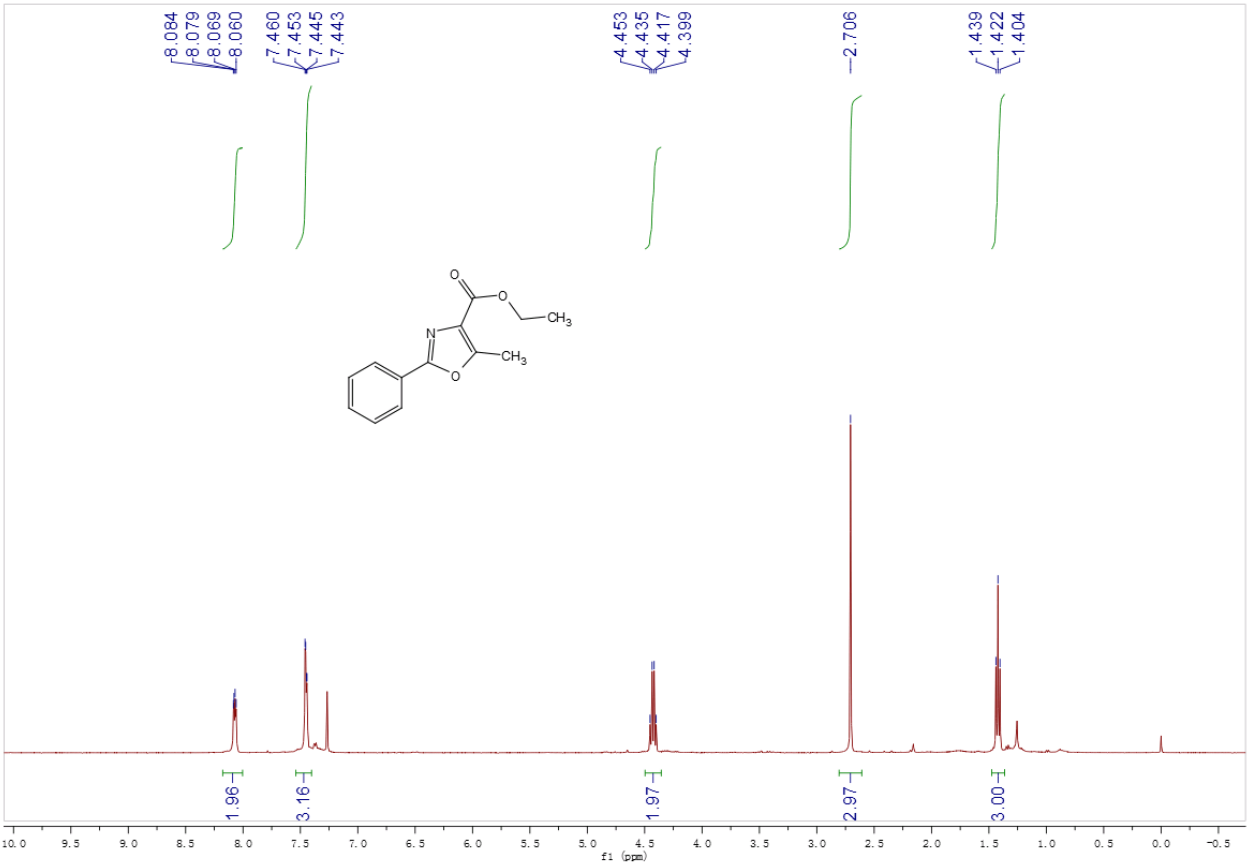


Fig. S-1. ^{1}H-NMR spectrum of (**3aa**).

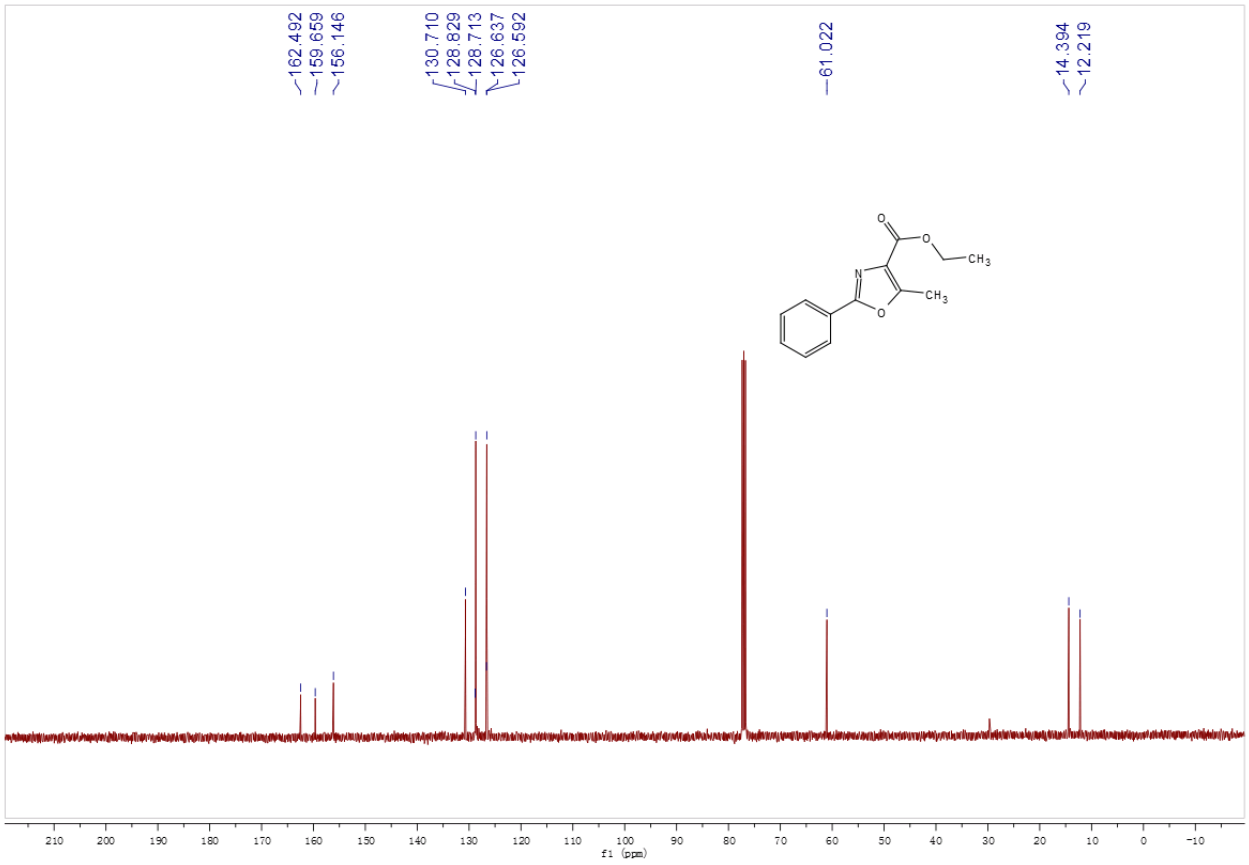


Fig. S-2. ^{13}C-NMR spectrum of (**3aa**).

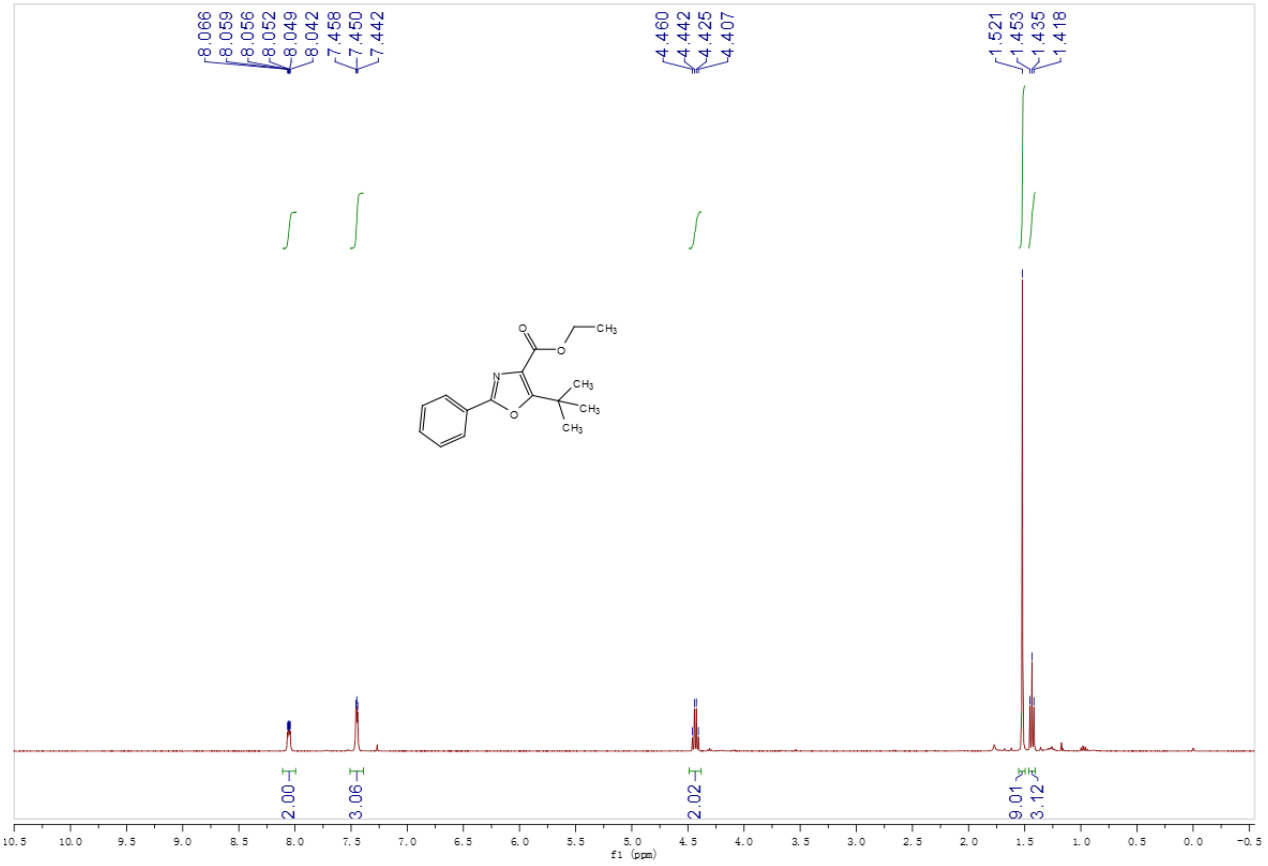


Fig. S-3. [1]H-NMR spectrum of (**3ba**).

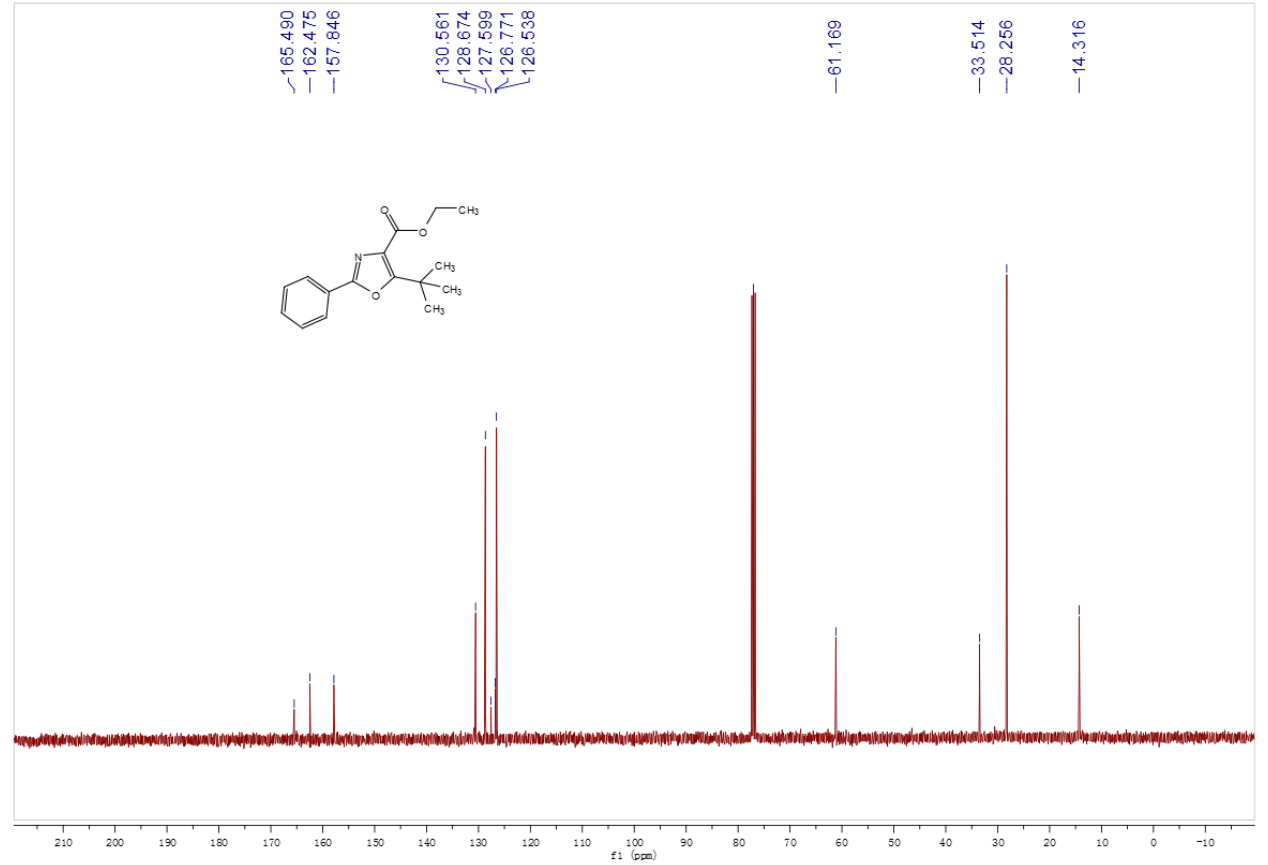


Fig. S-4. [13]C-NMR spectrum of (**3ba**).

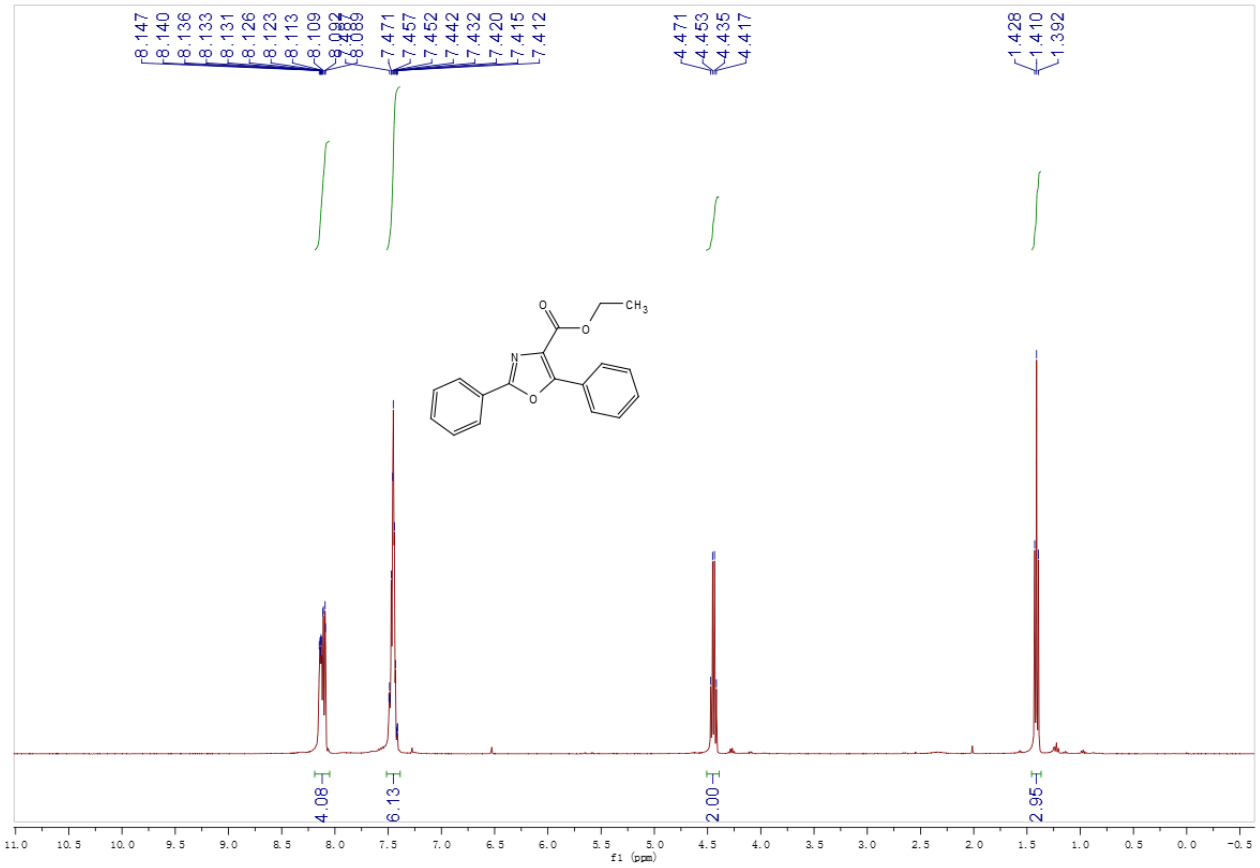


Fig. S-5. ^{1}H-NMR spectrum of (**3ca**).

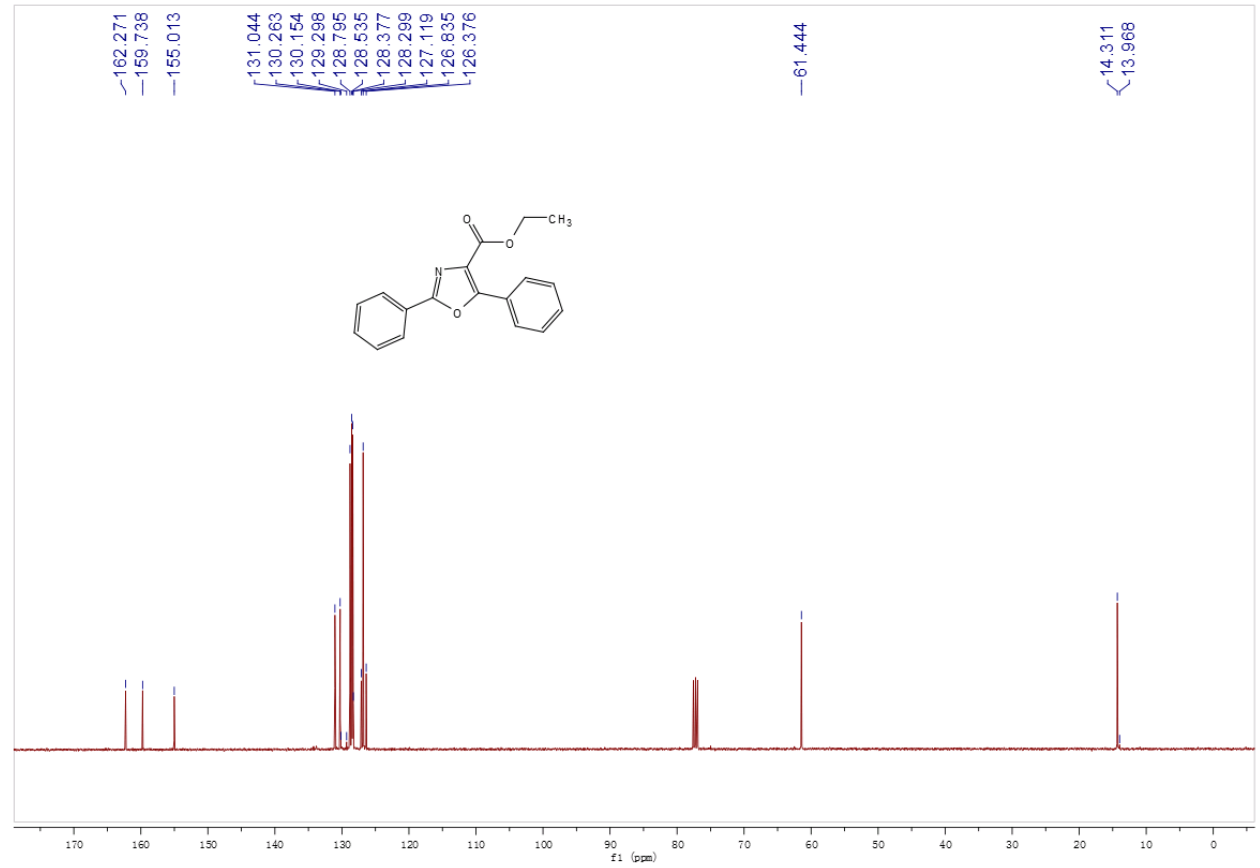


Fig. S-6. ^{13}C-NMR spectrum of (**3ca**).

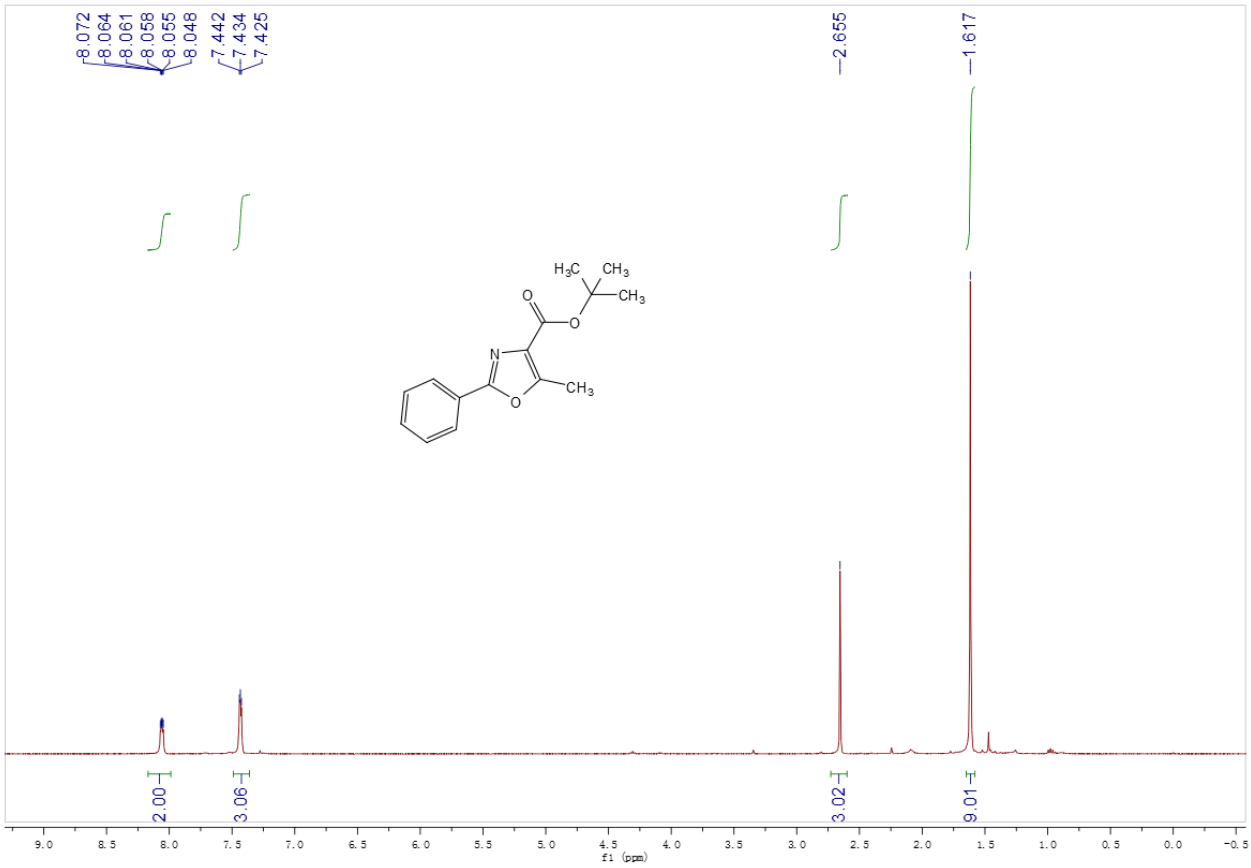


Fig. S-7. ^{1}H-NMR spectrum of (**3da**).

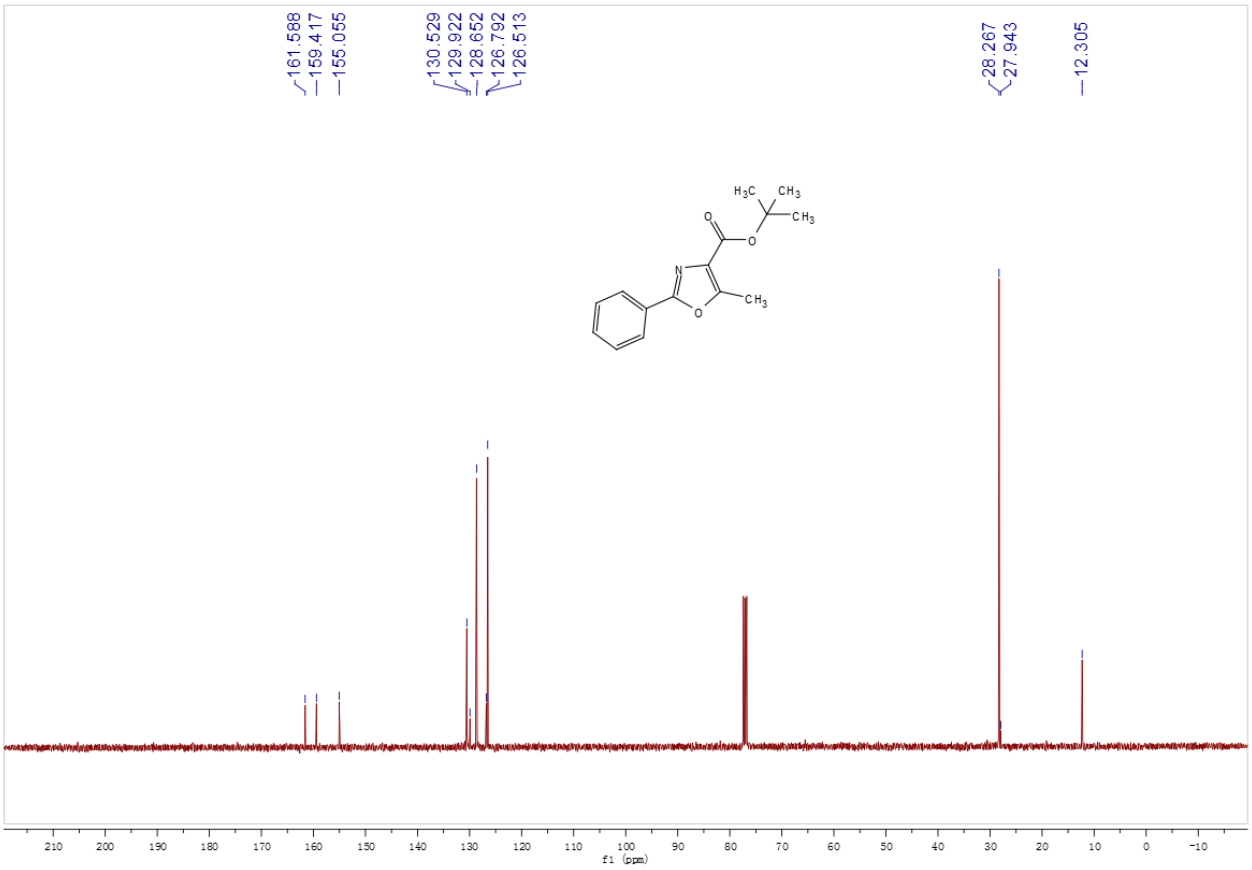


Fig. S-8. ^{13}C-NMR spectrum of (**3da**).

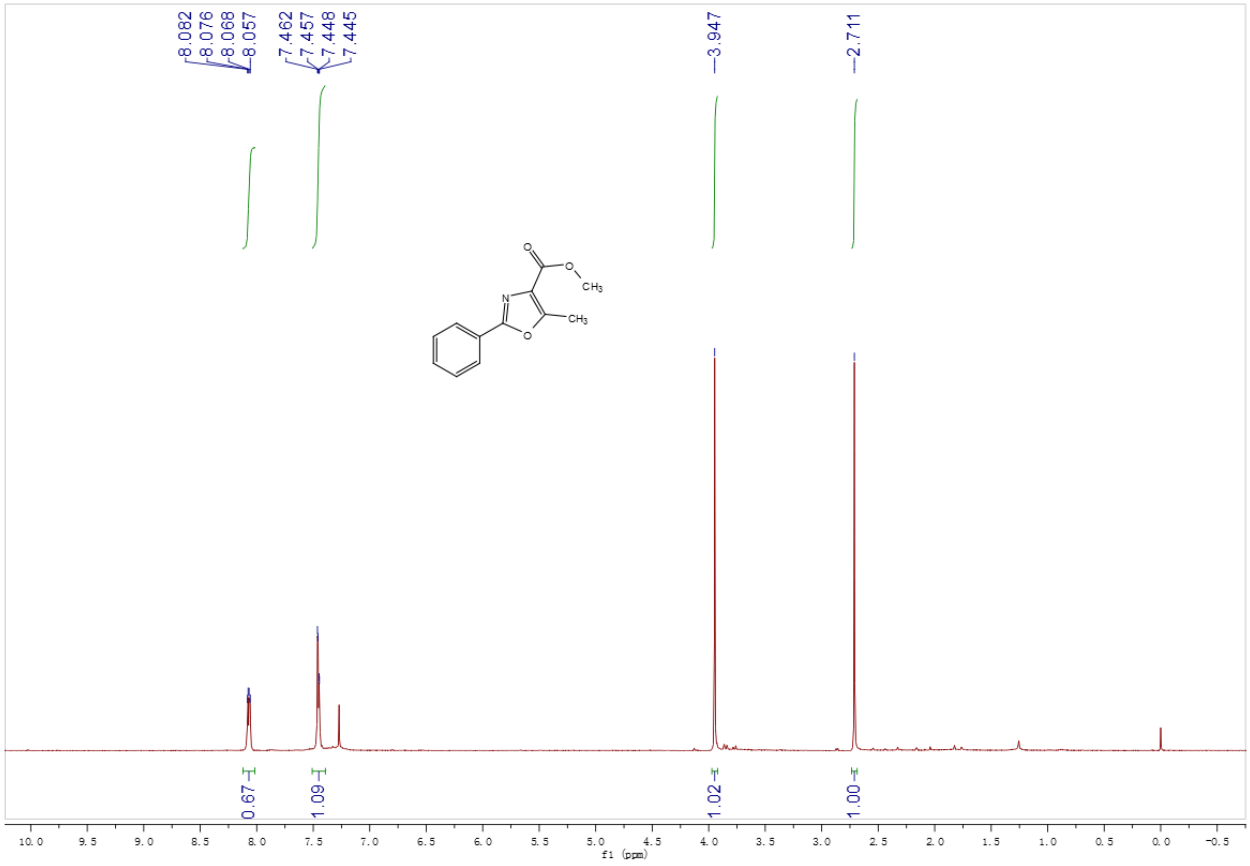


Fig. S-9. ^{1}H-NMR spectrum of (**3ea**).

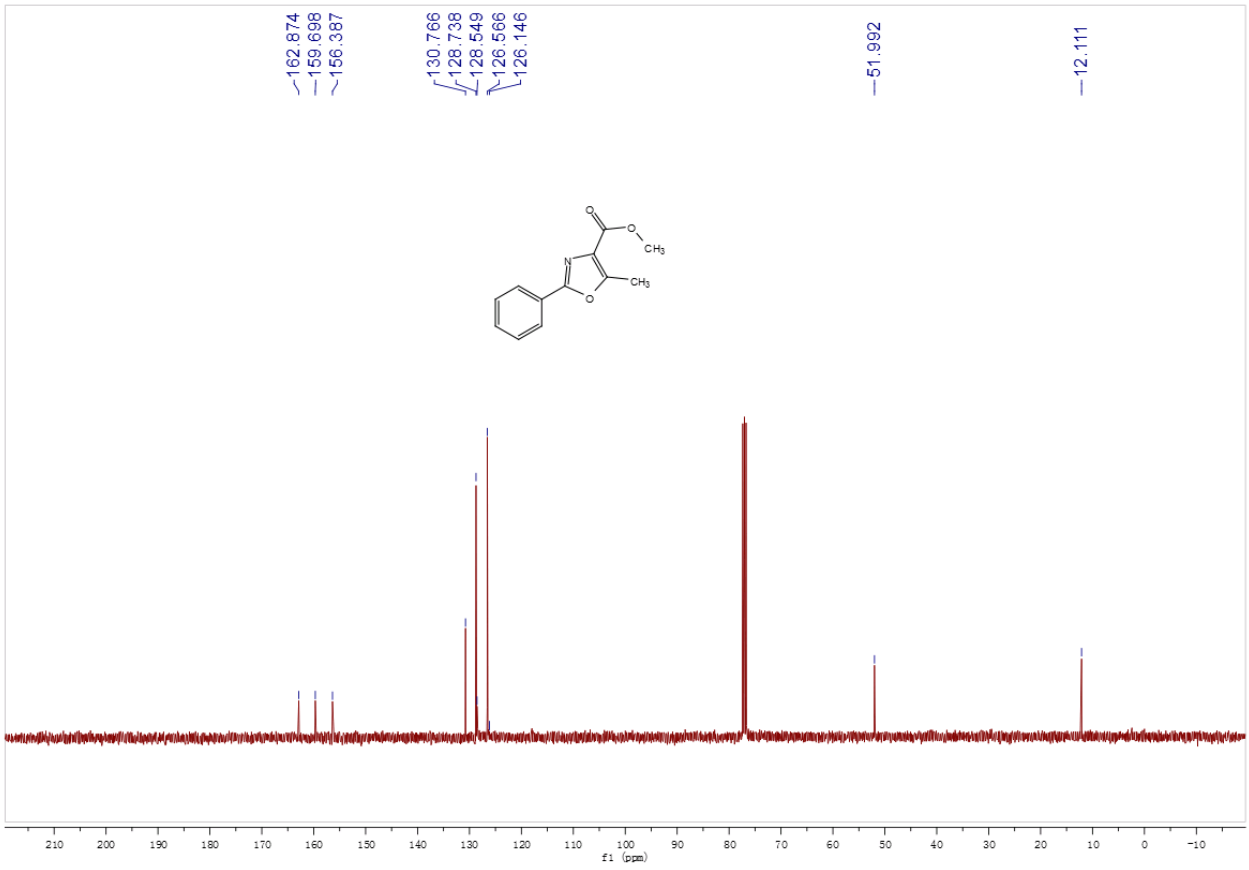


Fig. S-10. ^{13}C-NMR spectrum of (**3ea**).

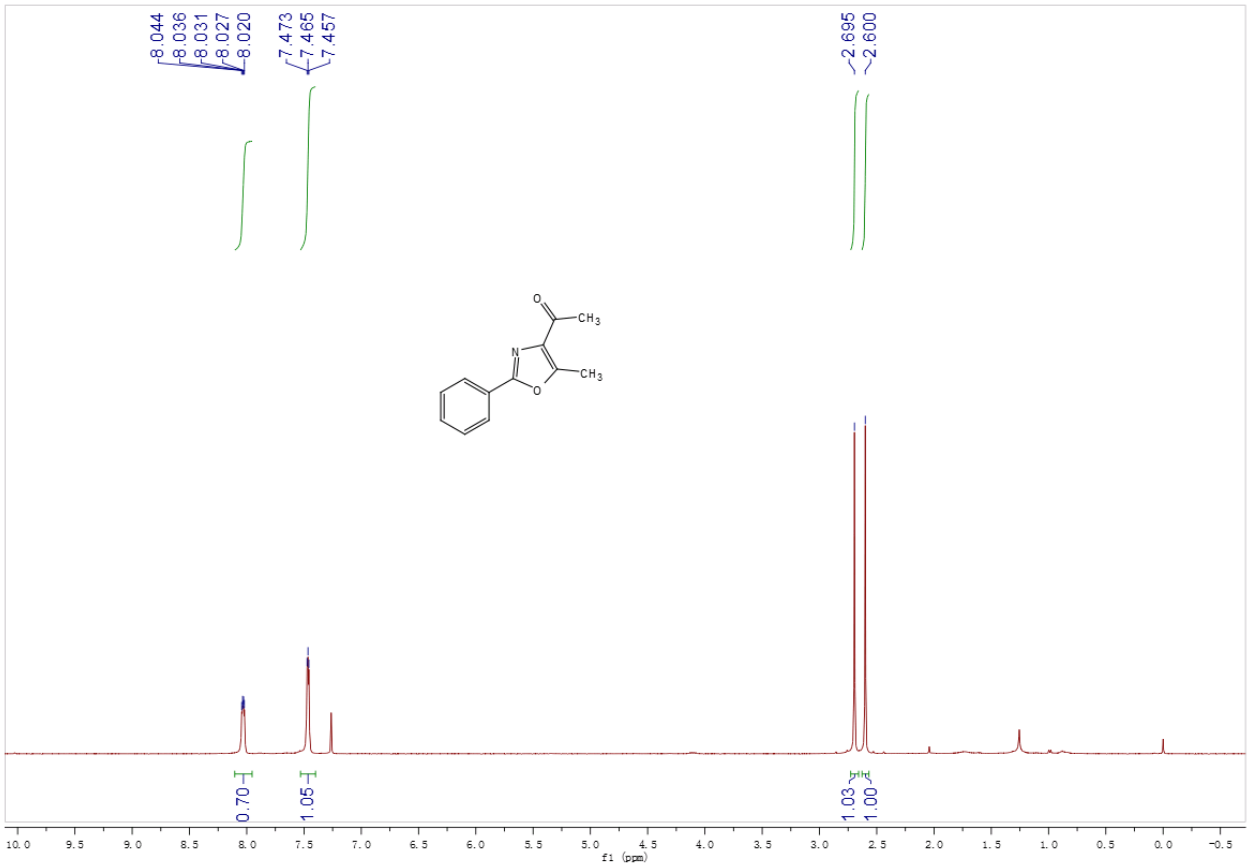


Fig. S-11. ^{1}H-NMR spectrum of (**3fa**).

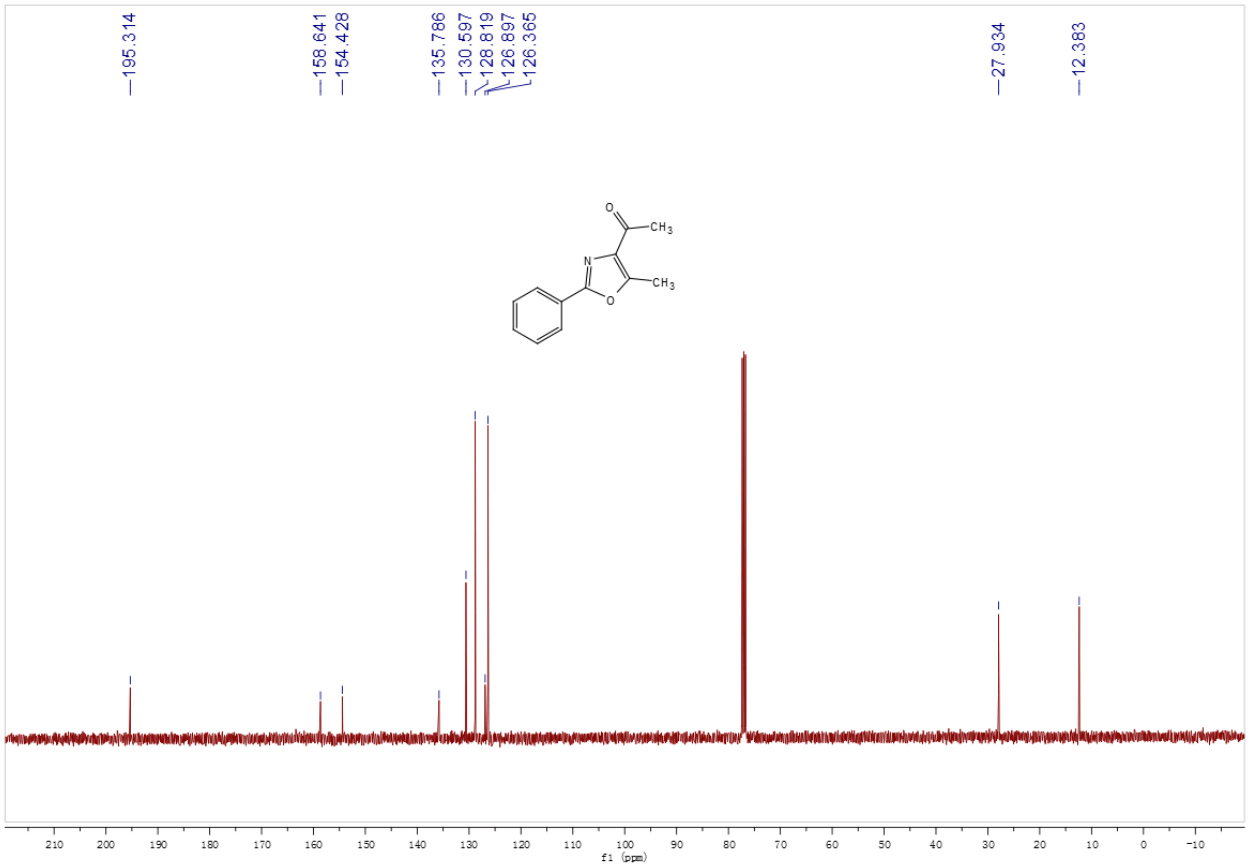


Fig. S-12. ^{13}C-NMR spectrum of (**3fa**).

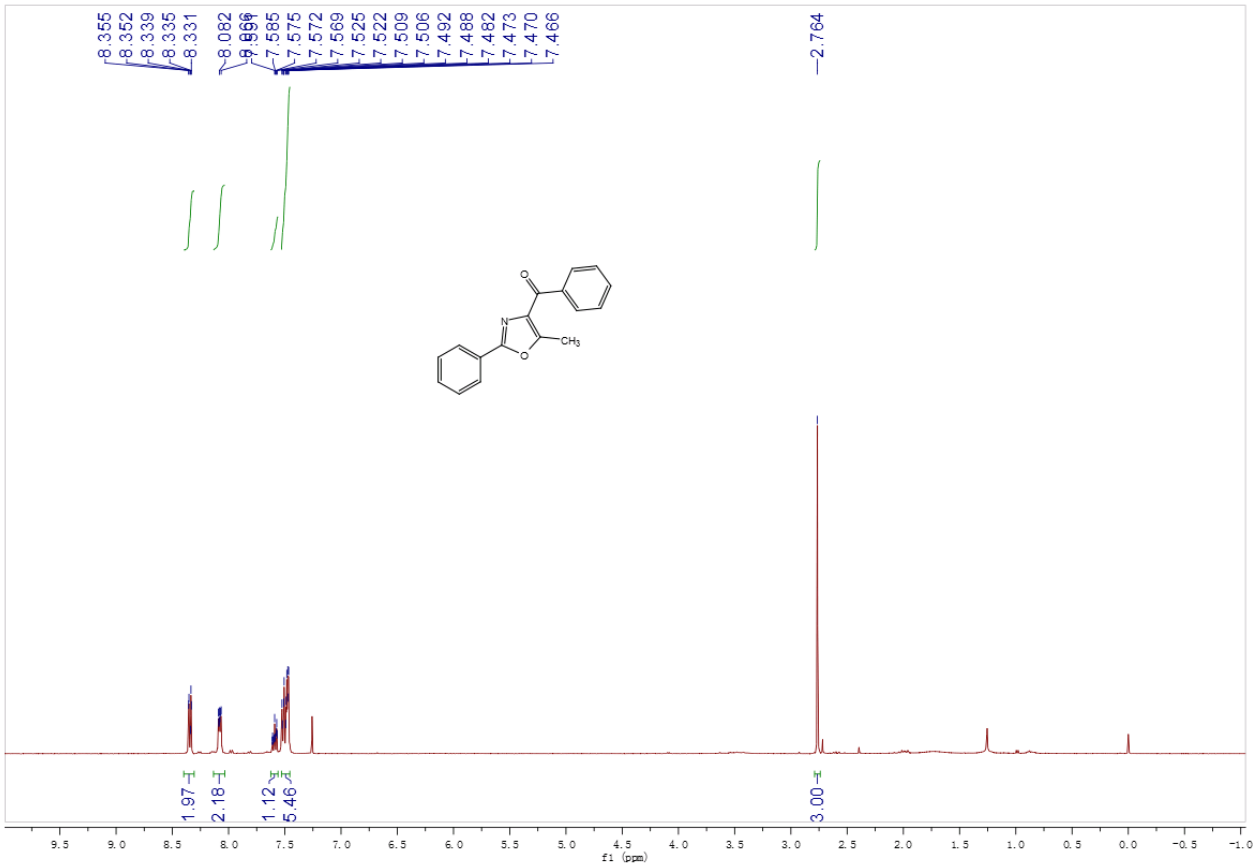


Fig. S-13. ^{1}H-NMR spectrum of (**3ga**).

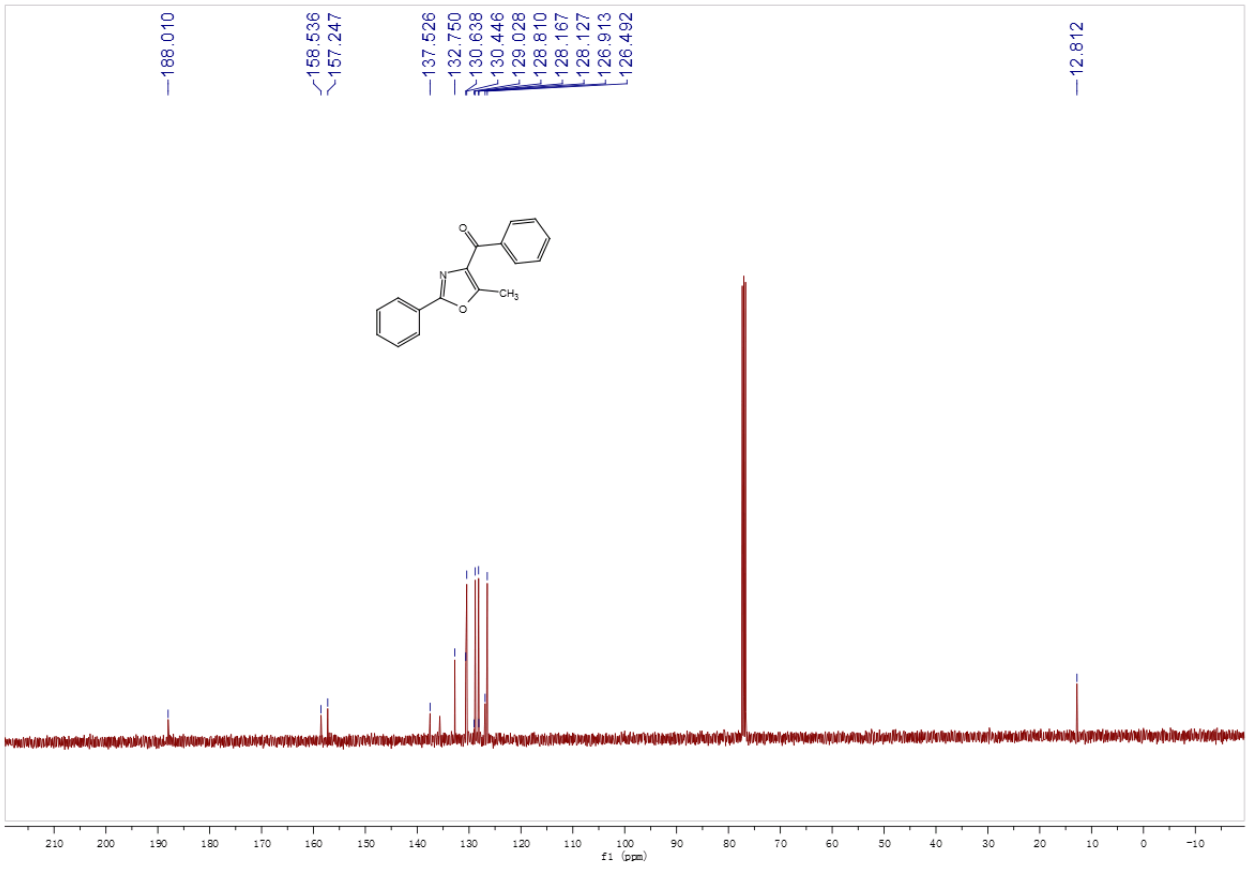


Fig. S-14. ^{13}C-NMR spectrum of (**3ga**).

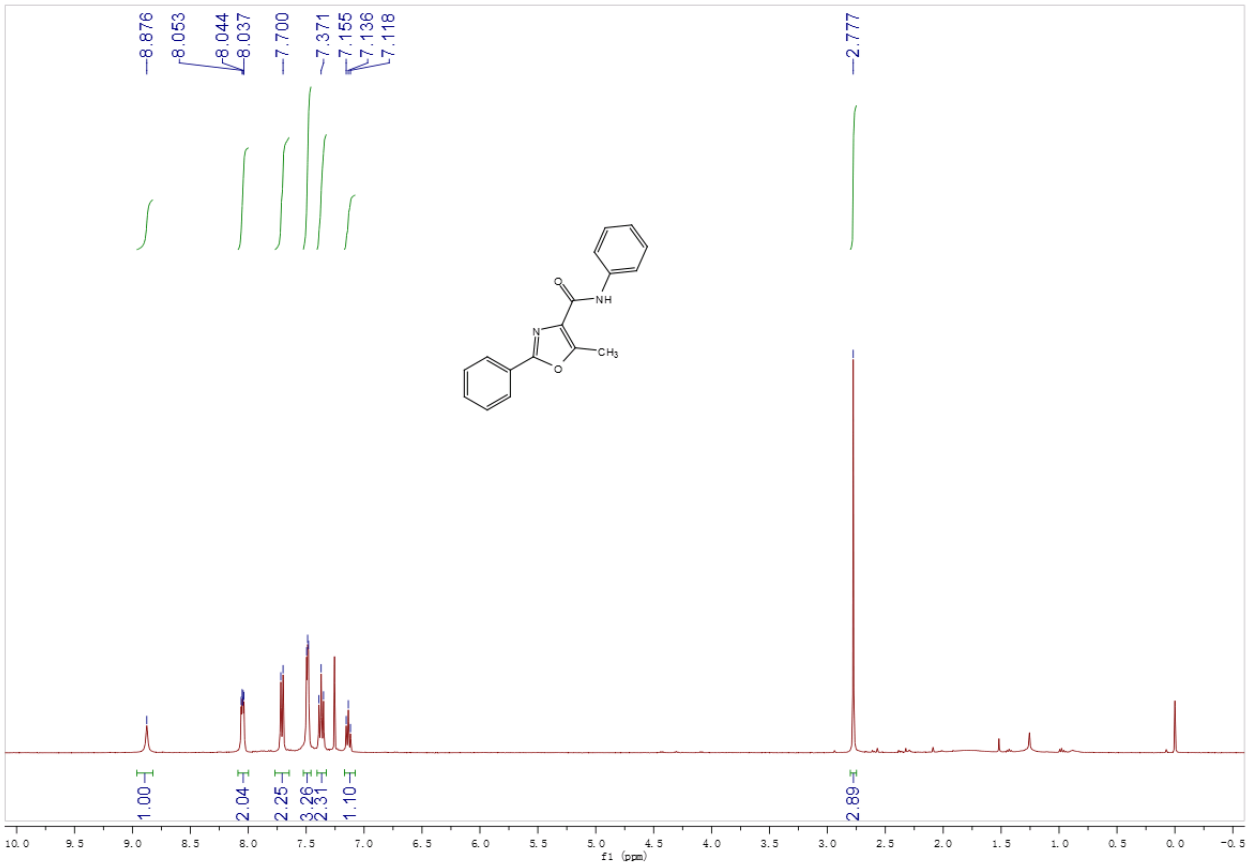


Fig. S-15. ^{1}H-NMR spectrum of (**3ha**).

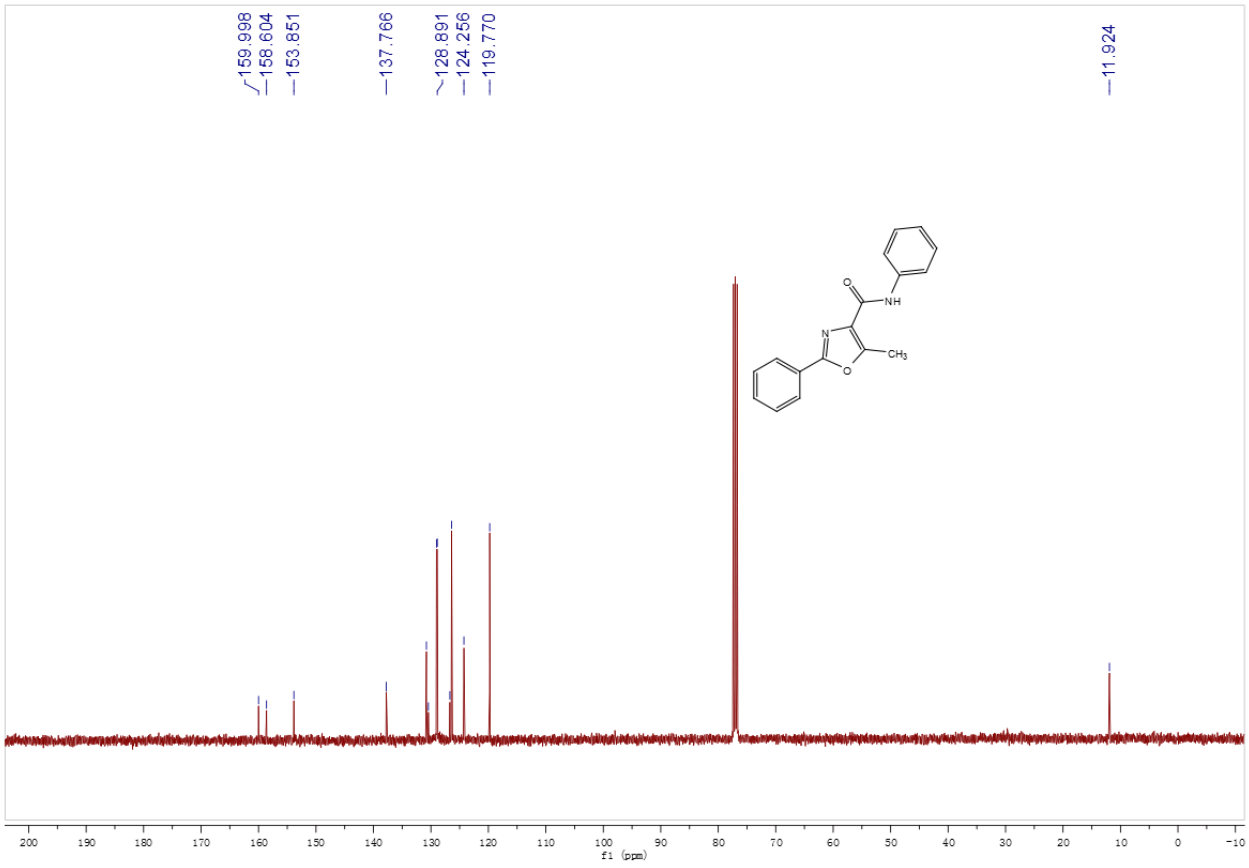


Fig. S-16. ^{13}C-NMR spectrum of (**3ha**).

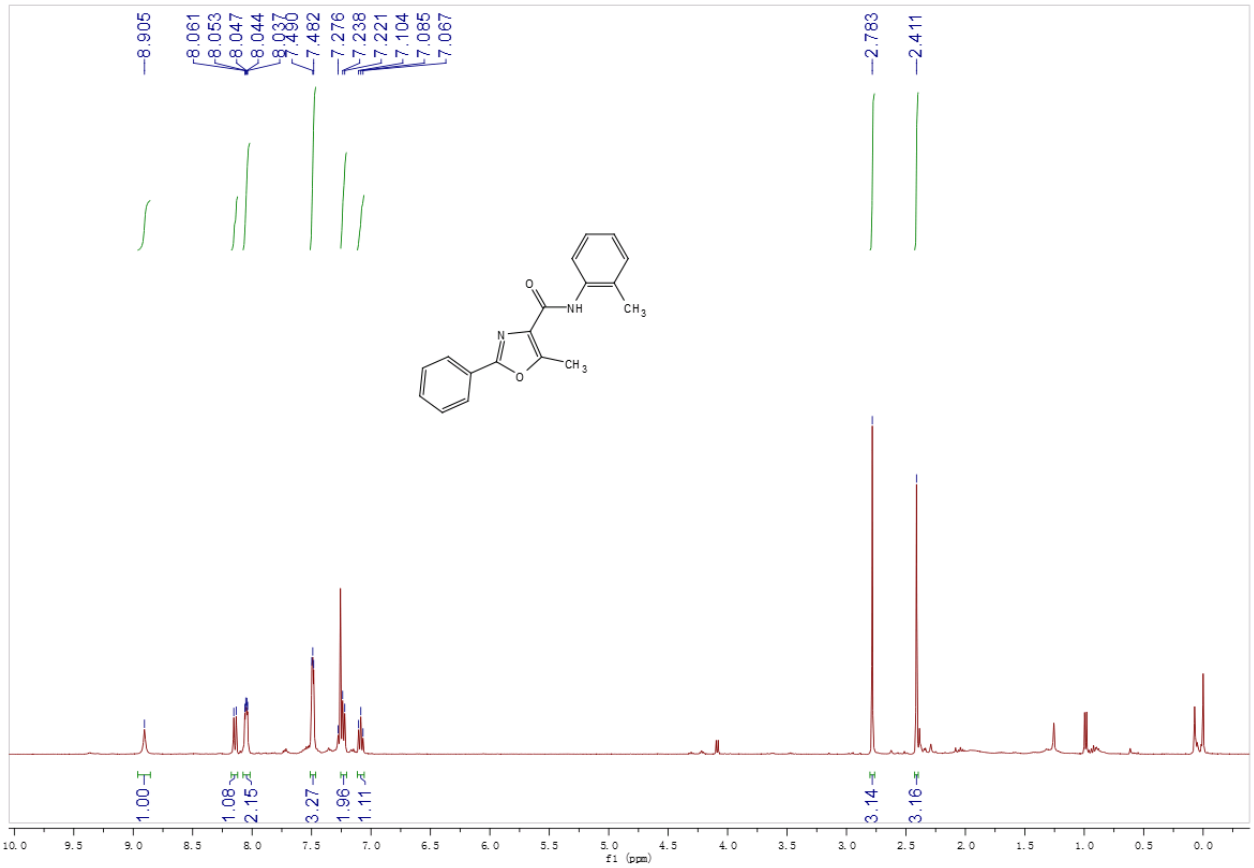


Fig. S-17. ^{1}H-NMR spectrum of (**3ia**).

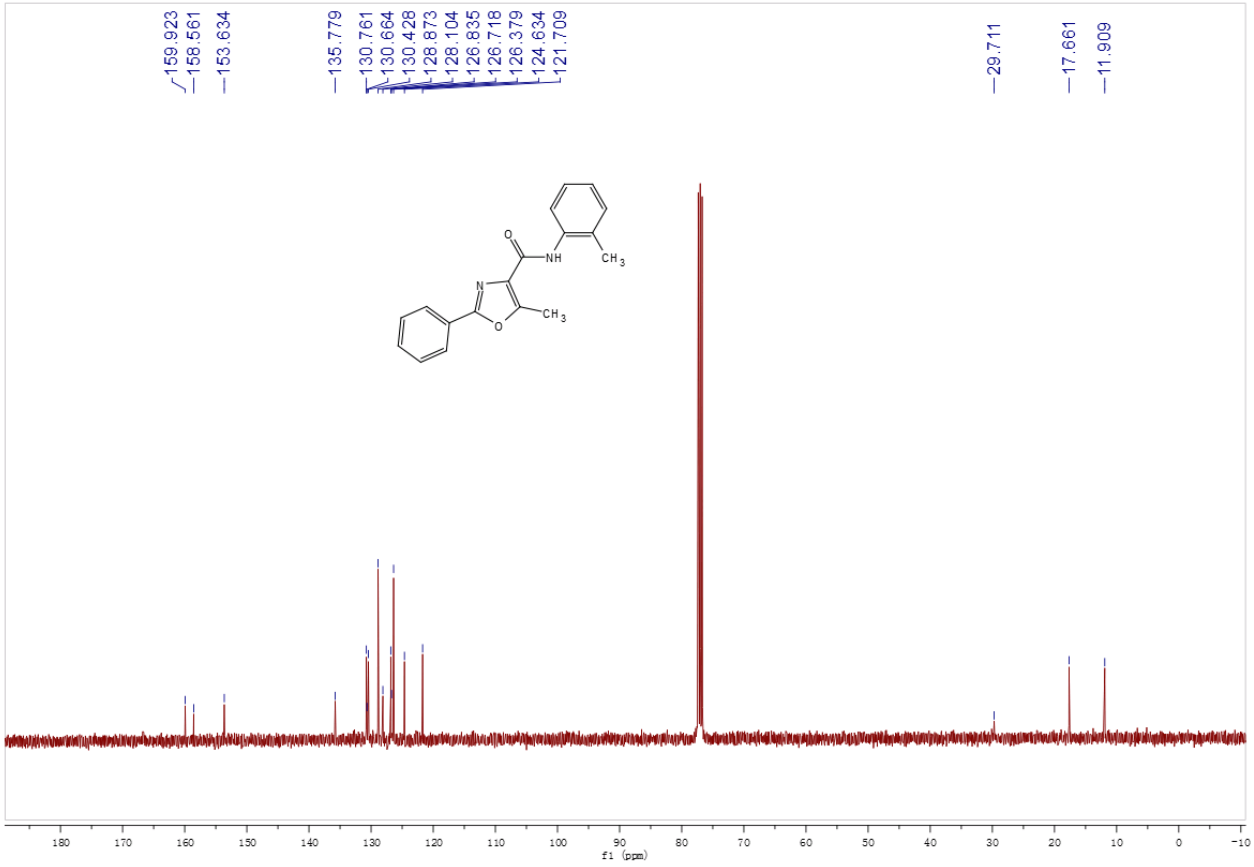


Fig. S-18. ^{13}C-NMR spectrum of (**3ia**).

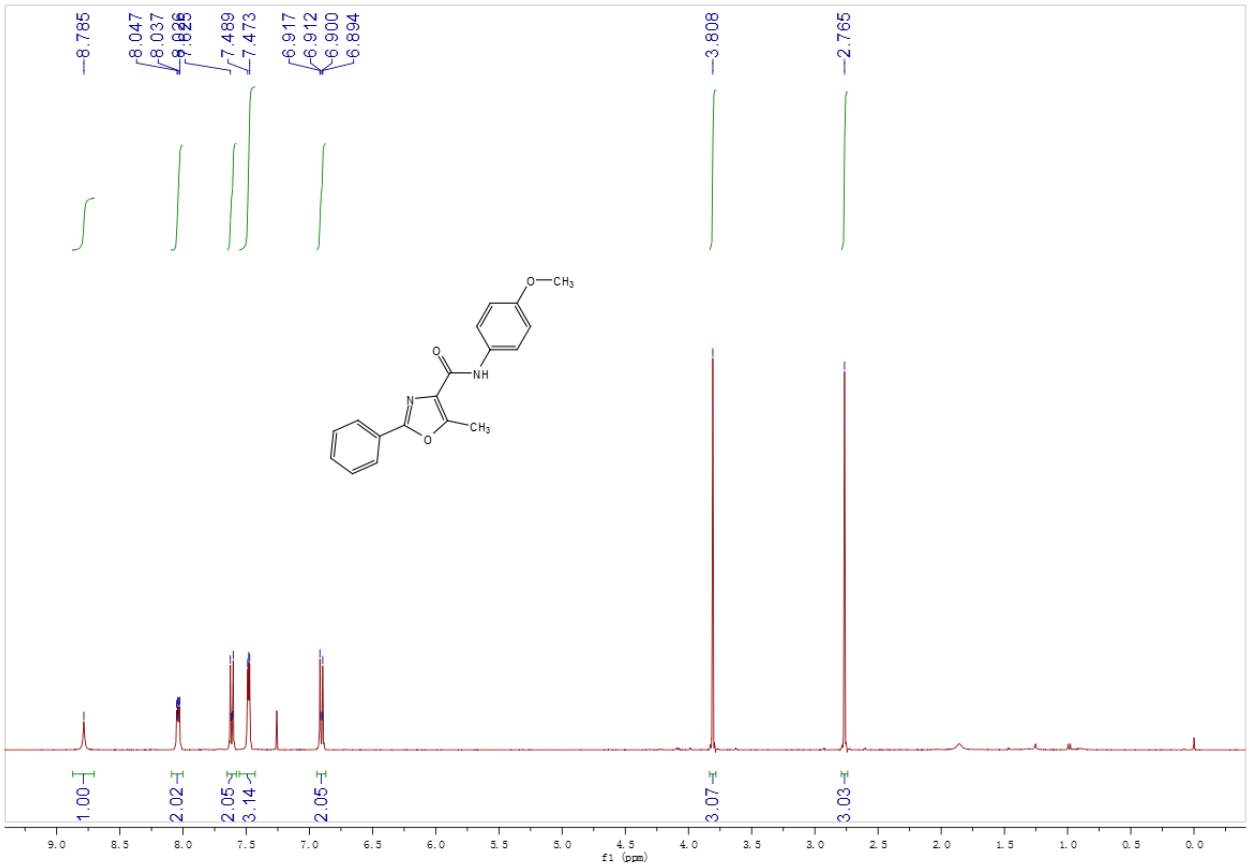


Fig. S-19. ^{1}H-NMR spectrum of (**3ja**).

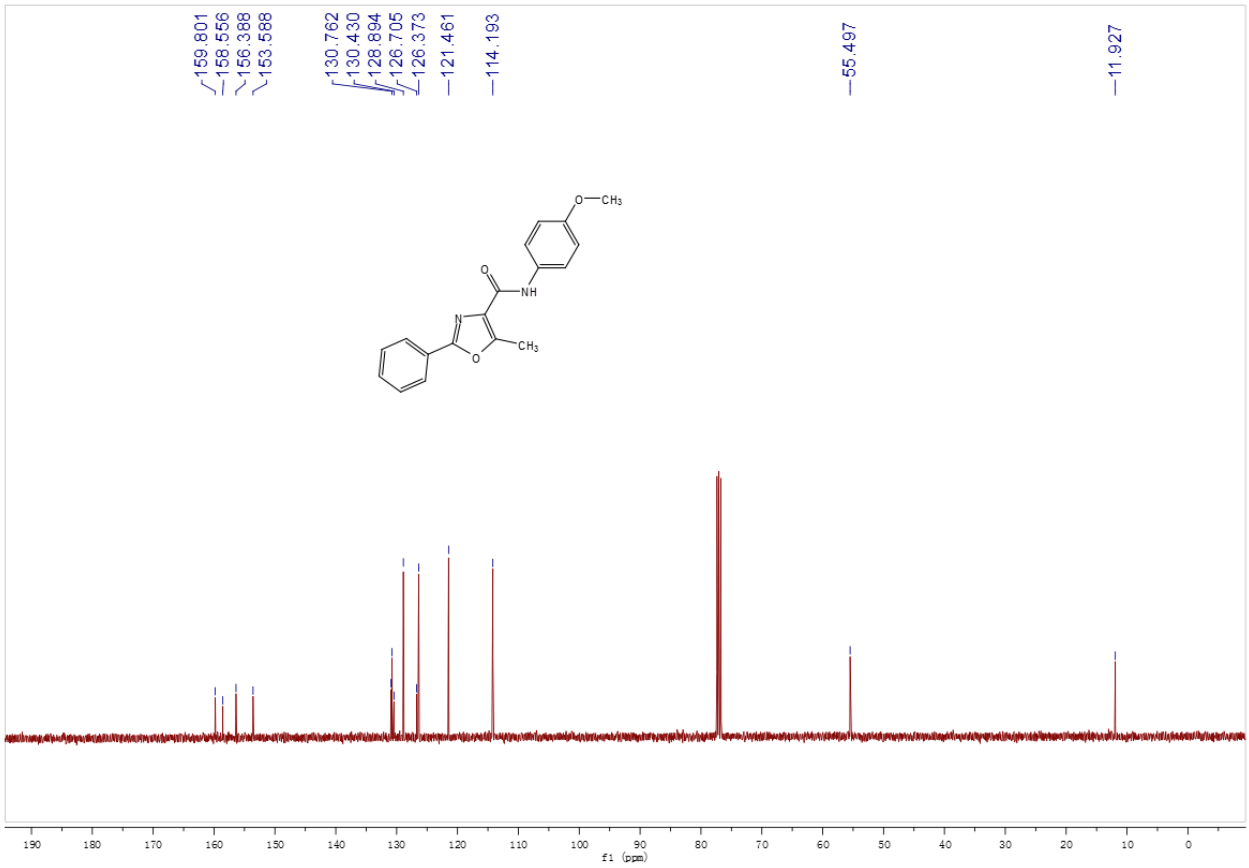


Fig. S-20. ^{13}C-NMR spectrum of (**3ja**).

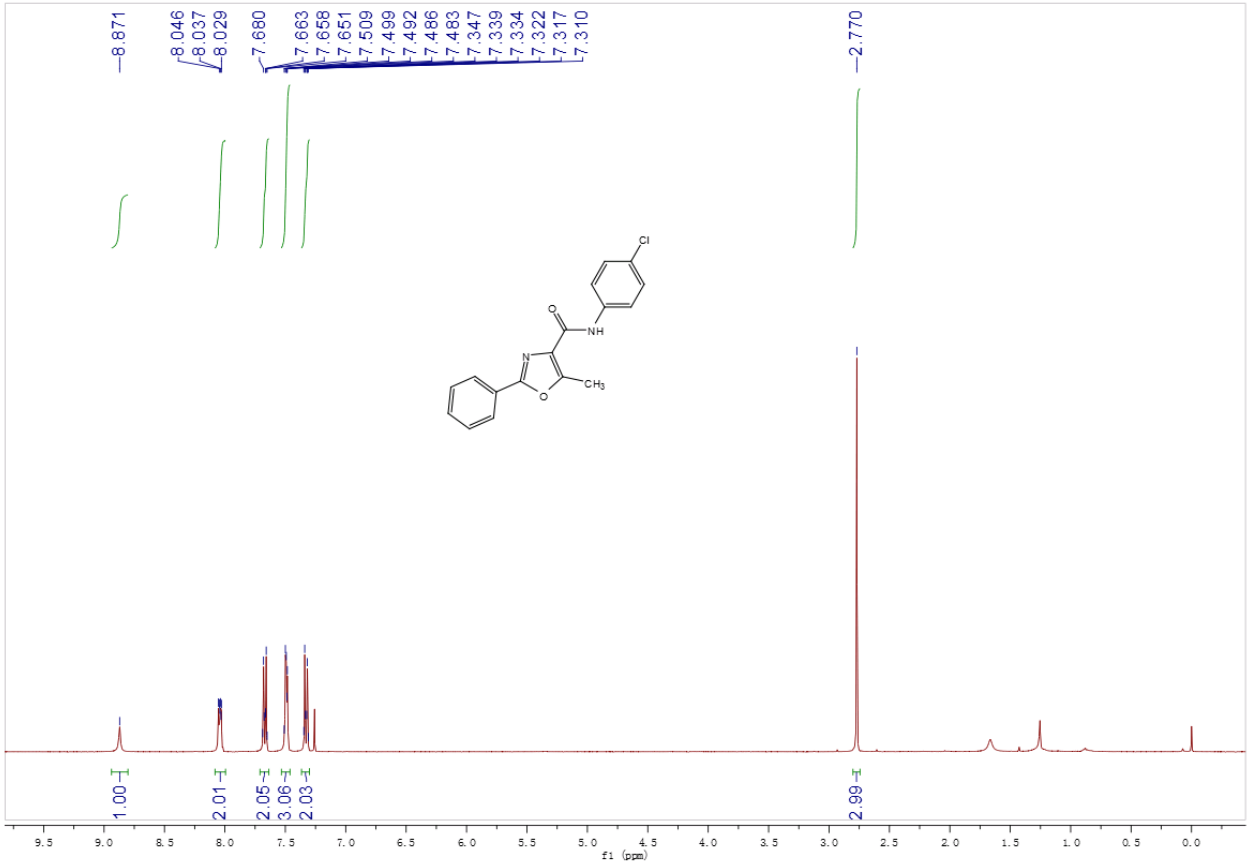


Fig. S-21. ^{1}H-NMR spectrum of (**3ka**).

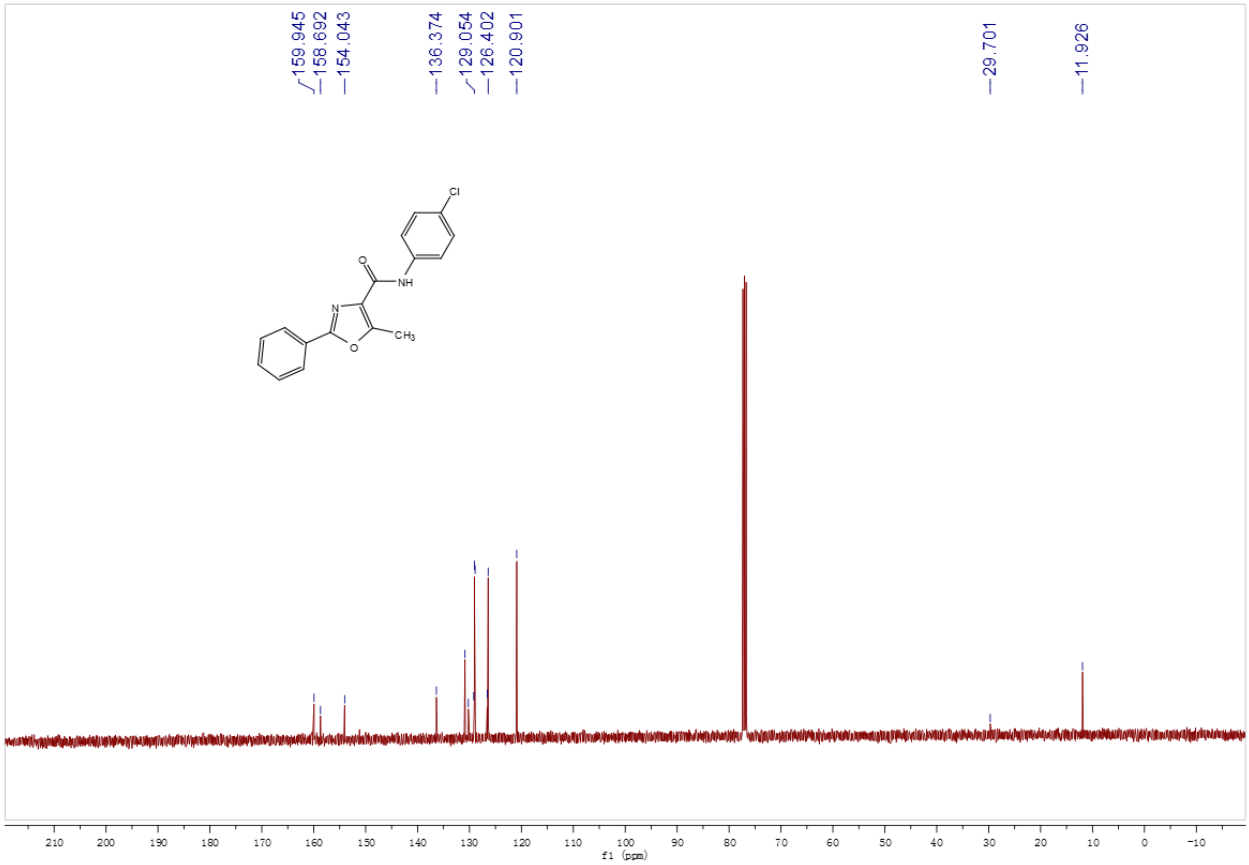


Fig. S-22. ^{13}C-NMR spectrum of (**3ka**).

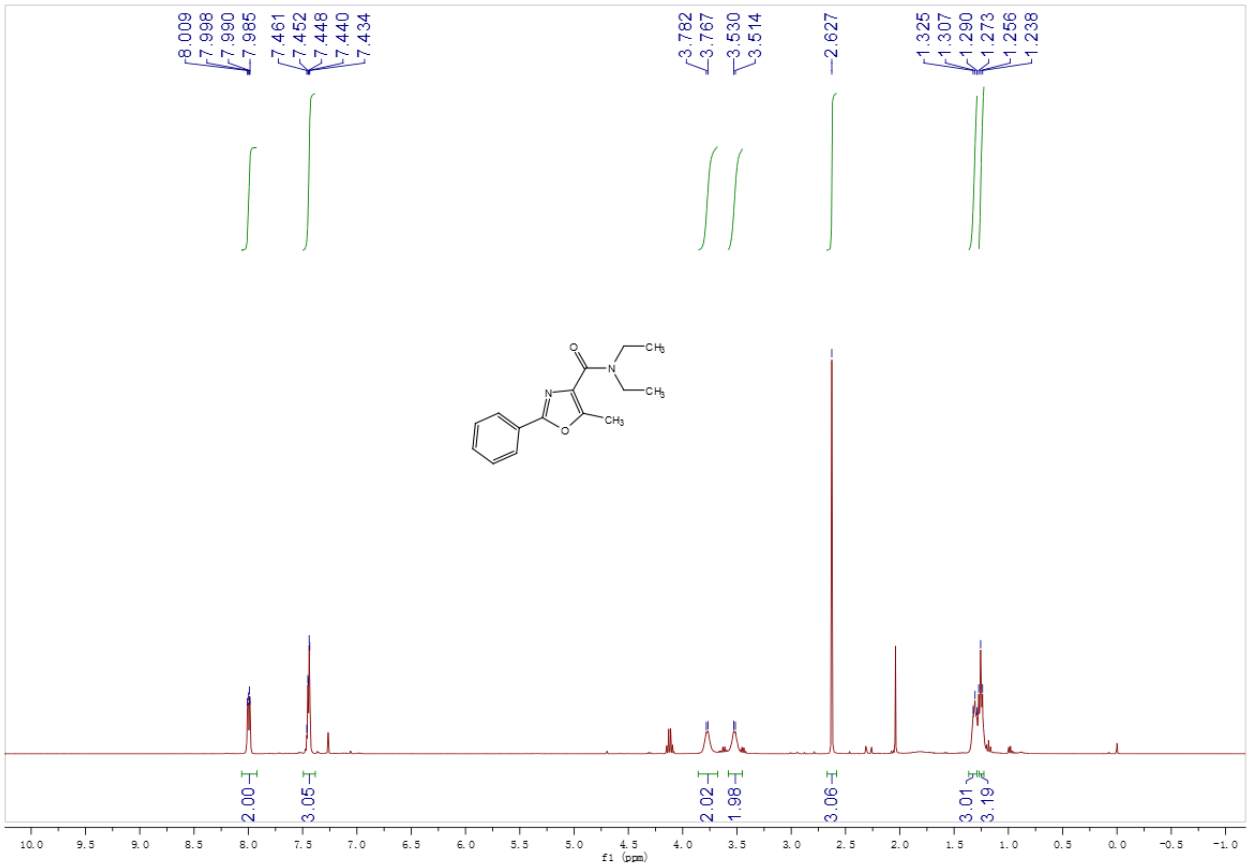


Fig. S-23. ^{1}H-NMR spectrum of (**3la**).

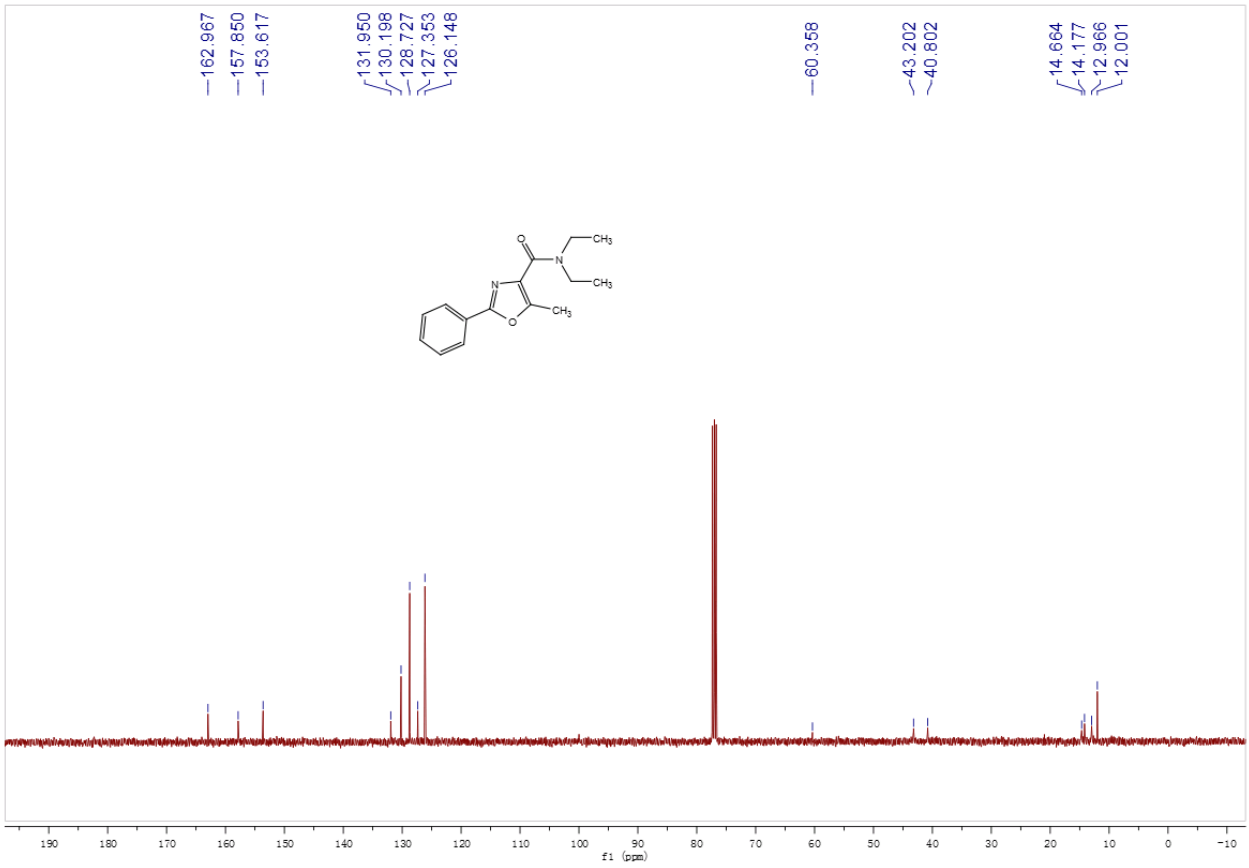


Fig. S-24. ^{13}C-NMR spectrum of (**3la**).

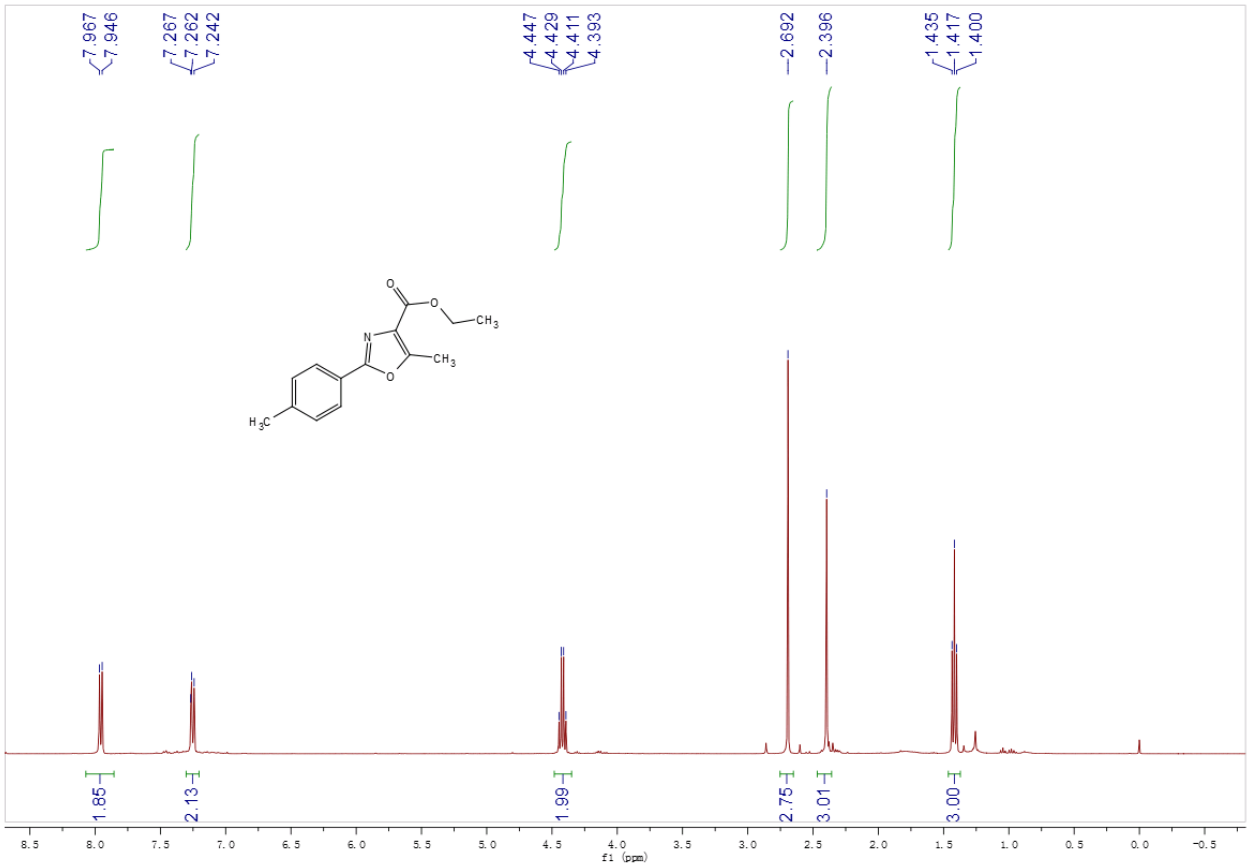


Fig. S-25. ^{1}H-NMR spectrum of (**3ab**).

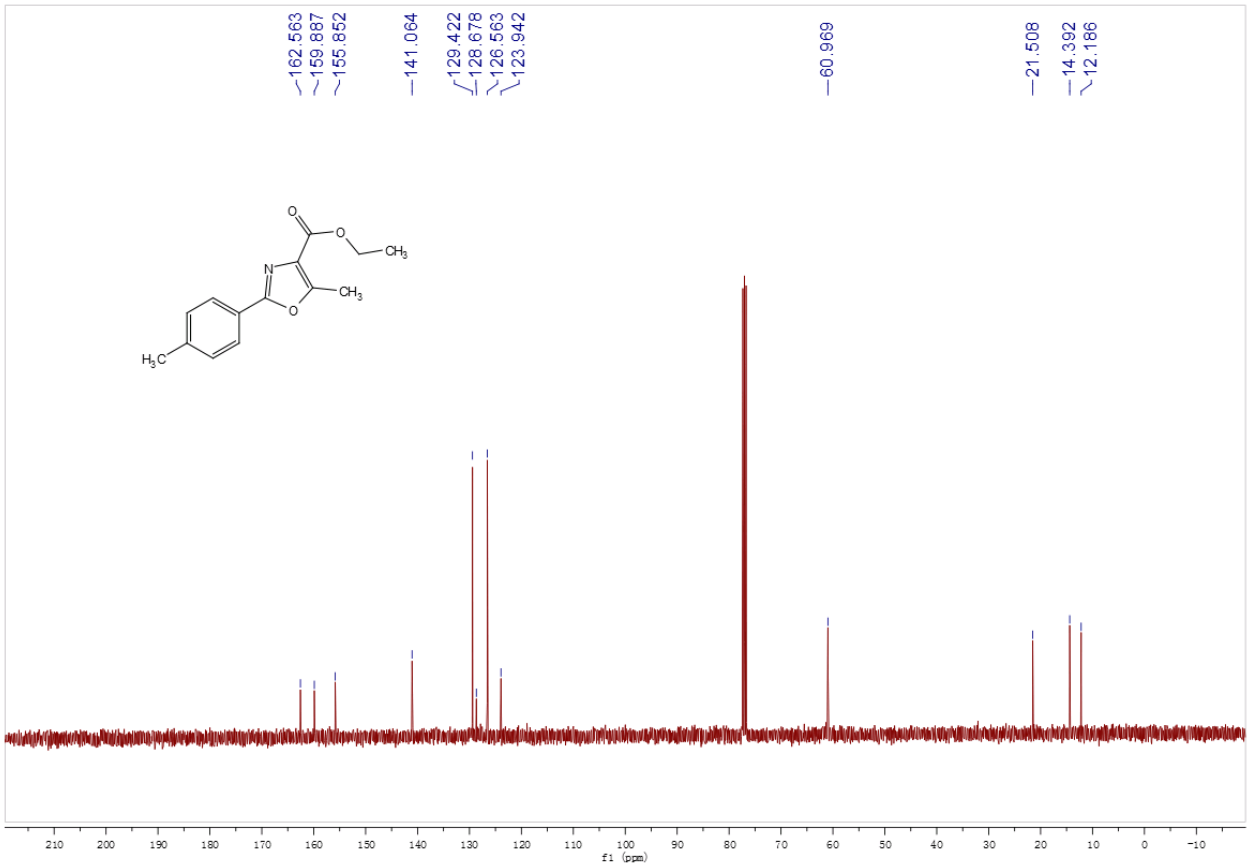


Fig. S-26. ^{13}C-NMR spectrum of (**3ab**).

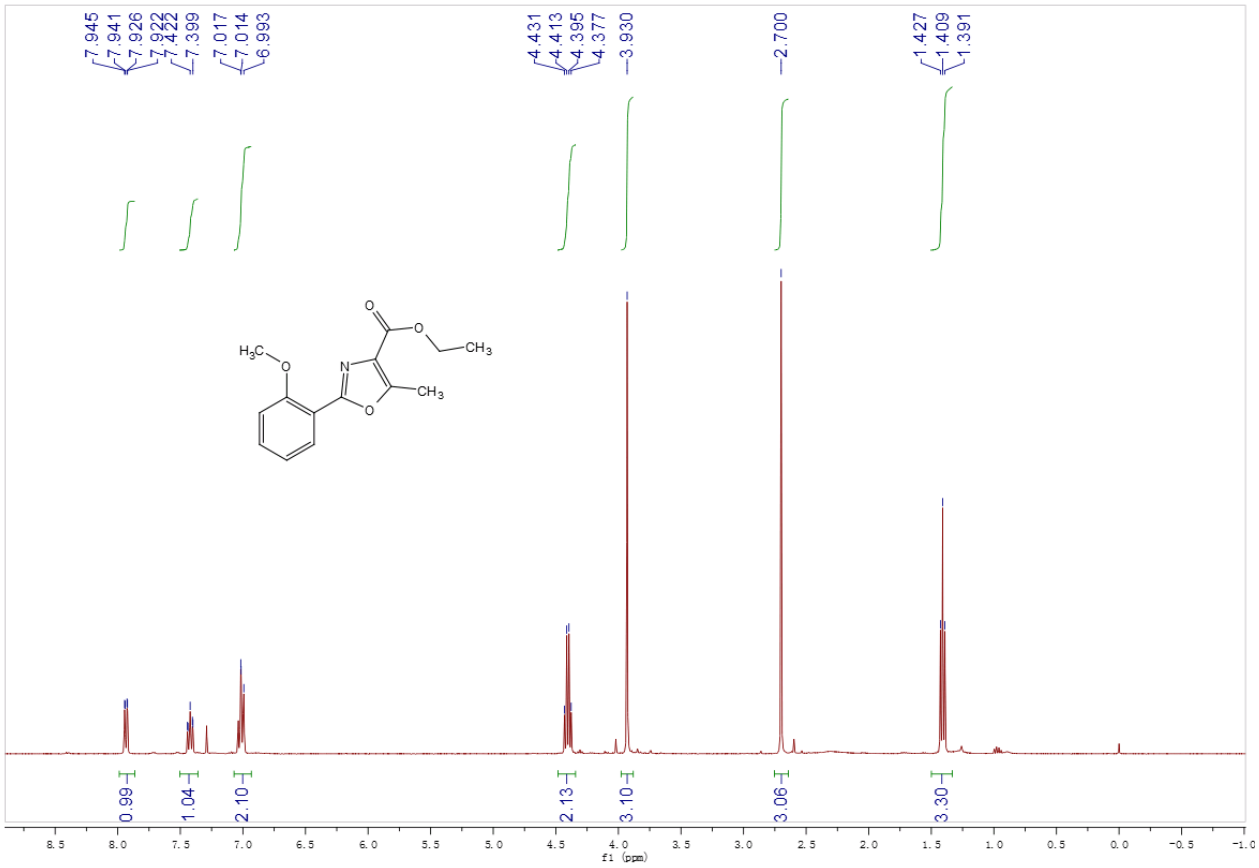


Fig. S-27. ^{1}H-NMR spectrum of (**3ac**).

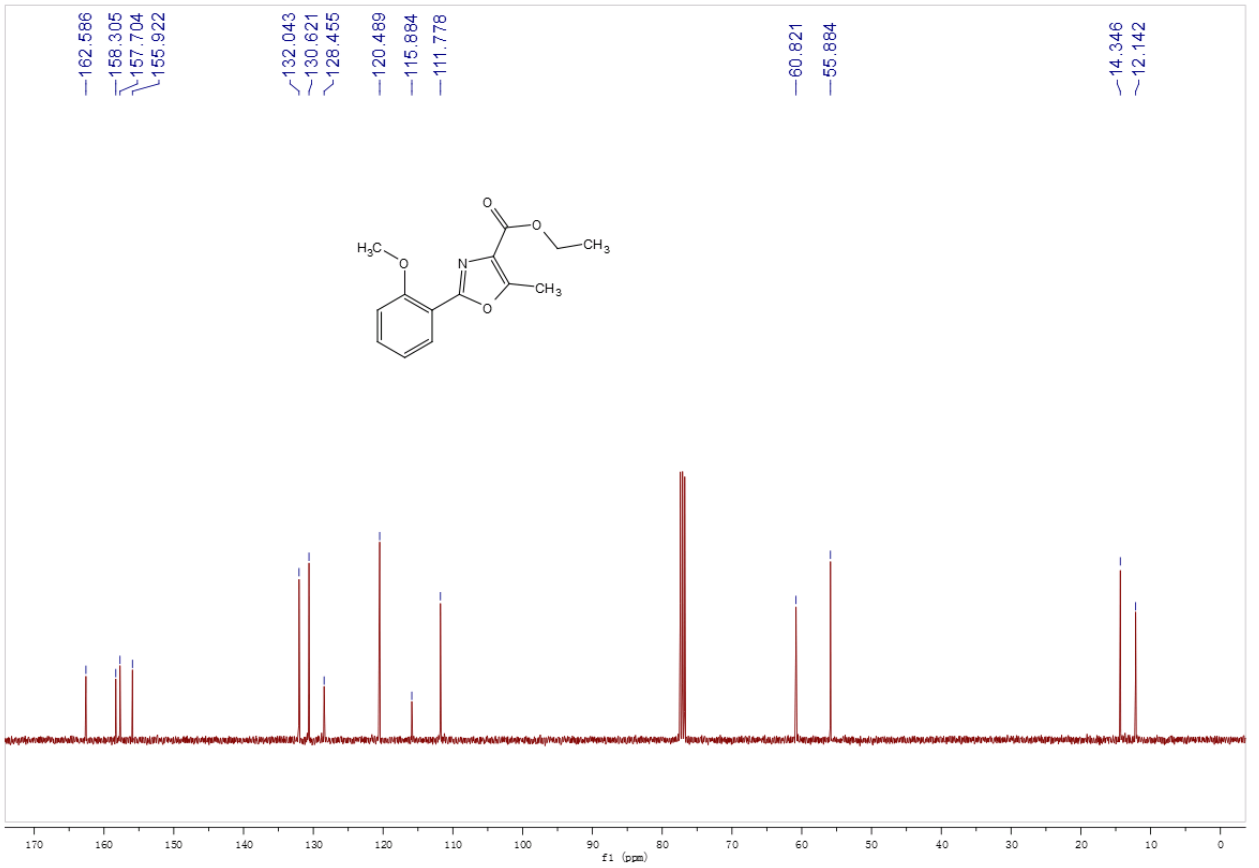


Fig. S-28. ^{13}C-NMR spectrum of (**3ac**).

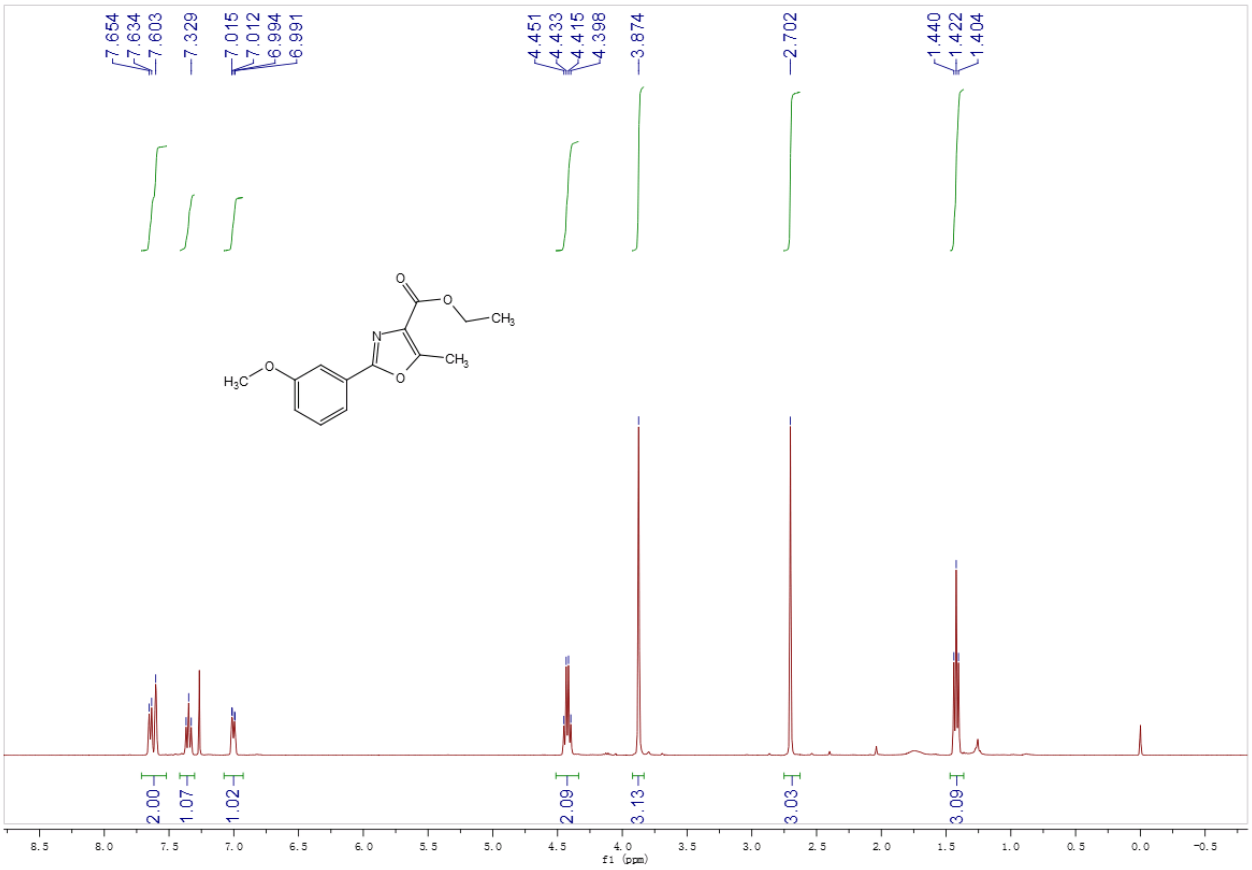


Fig. S-29. ^{1}H-NMR spectrum of (**3ad**).

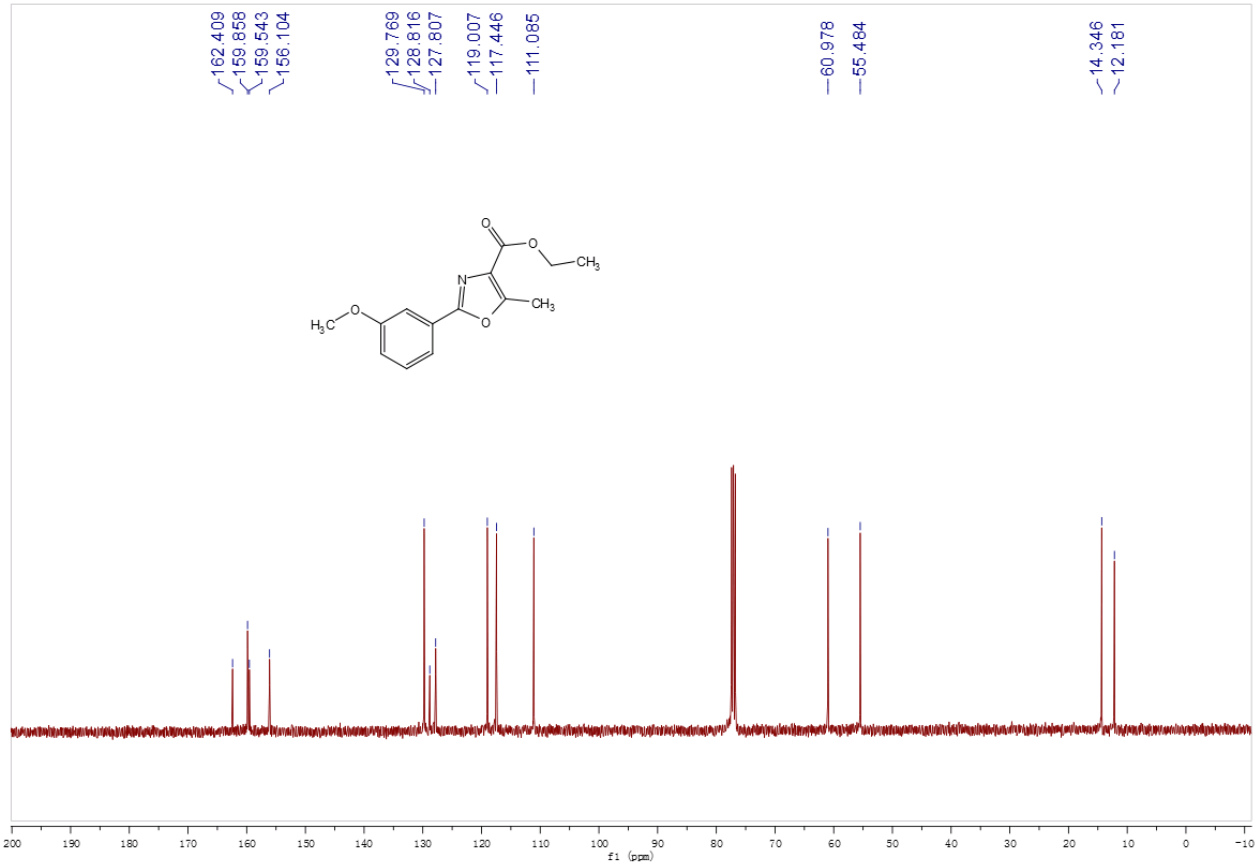


Fig. S-30. ^{13}C-NMR spectrum of (**3ad**).

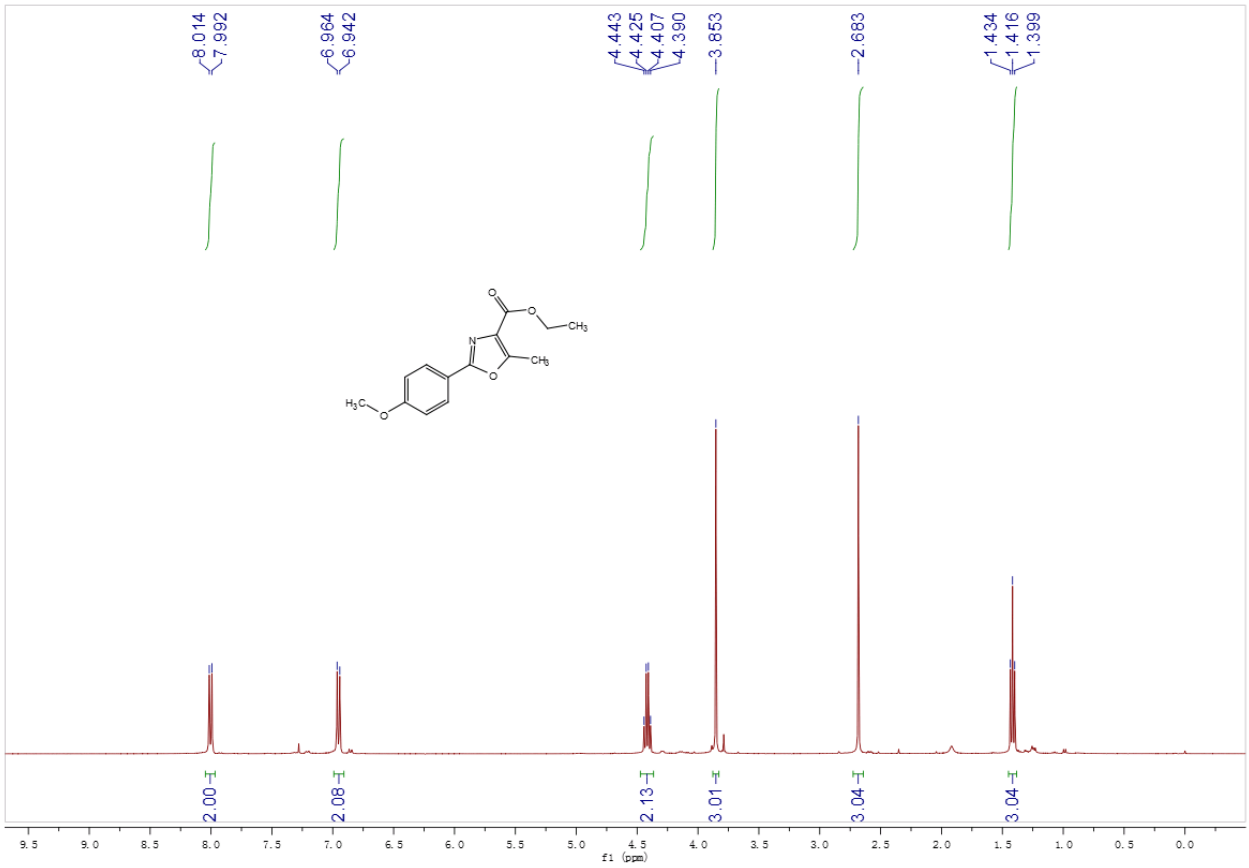


Fig. S-31. ^{1}H-NMR spectrum of (**3ae**).

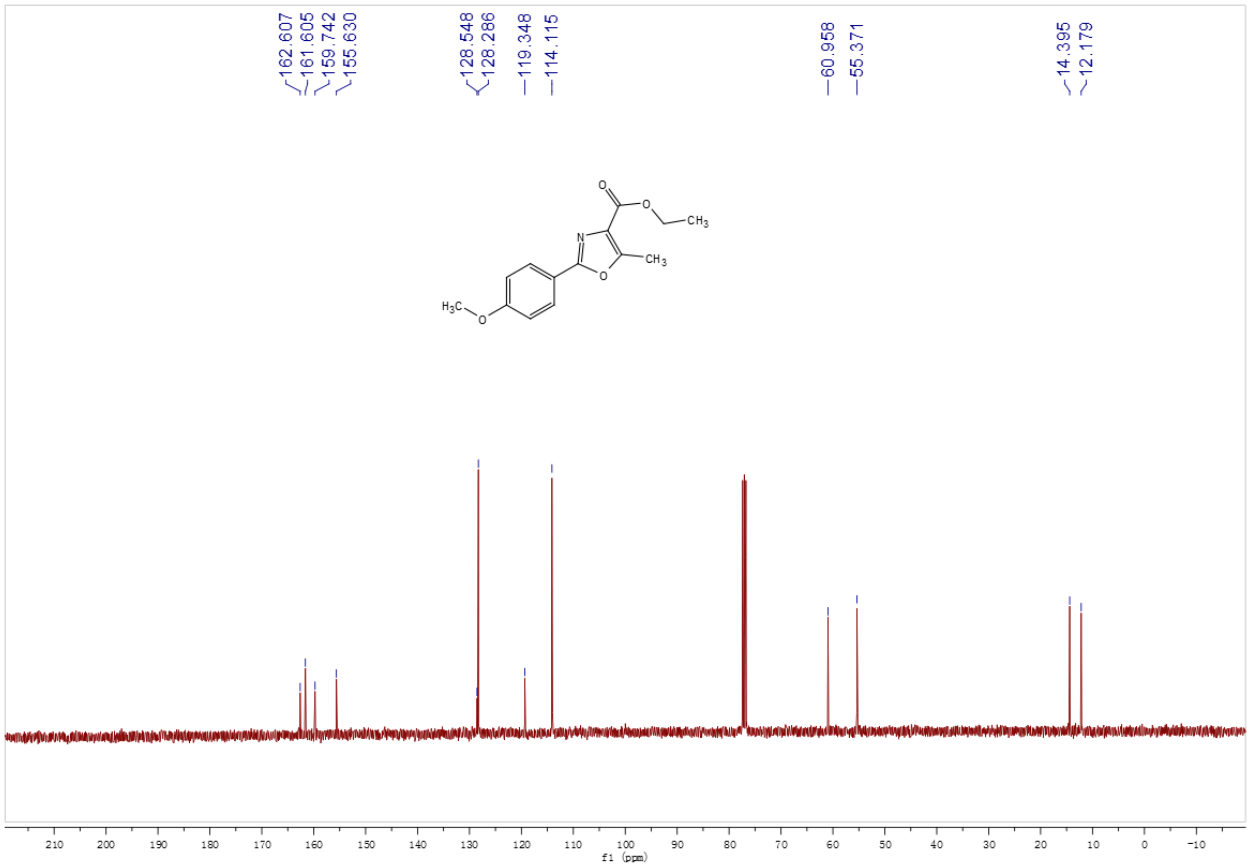


Fig. S-32. ^{13}C-NMR spectrum of (**3ae**).

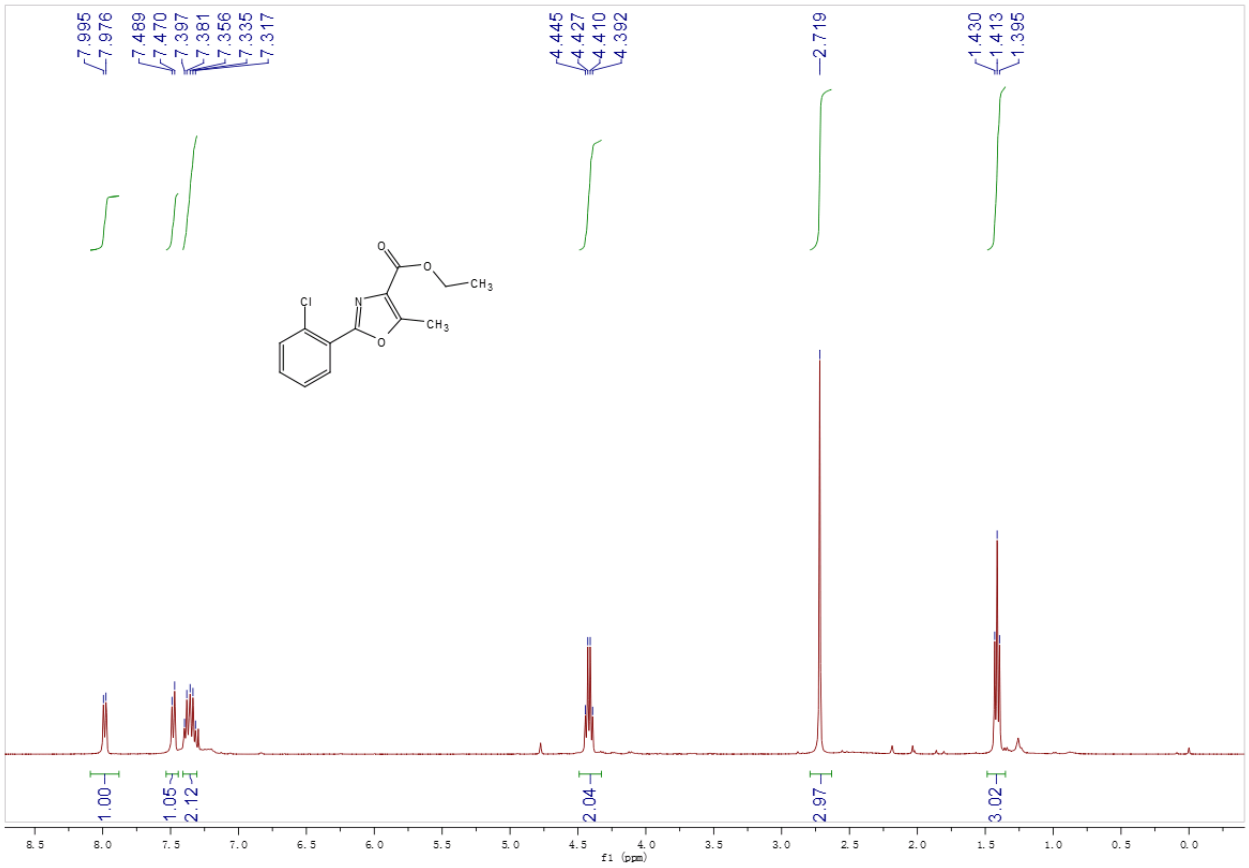


Fig. S-33. ^{1}H-NMR spectrum of (**3af**).

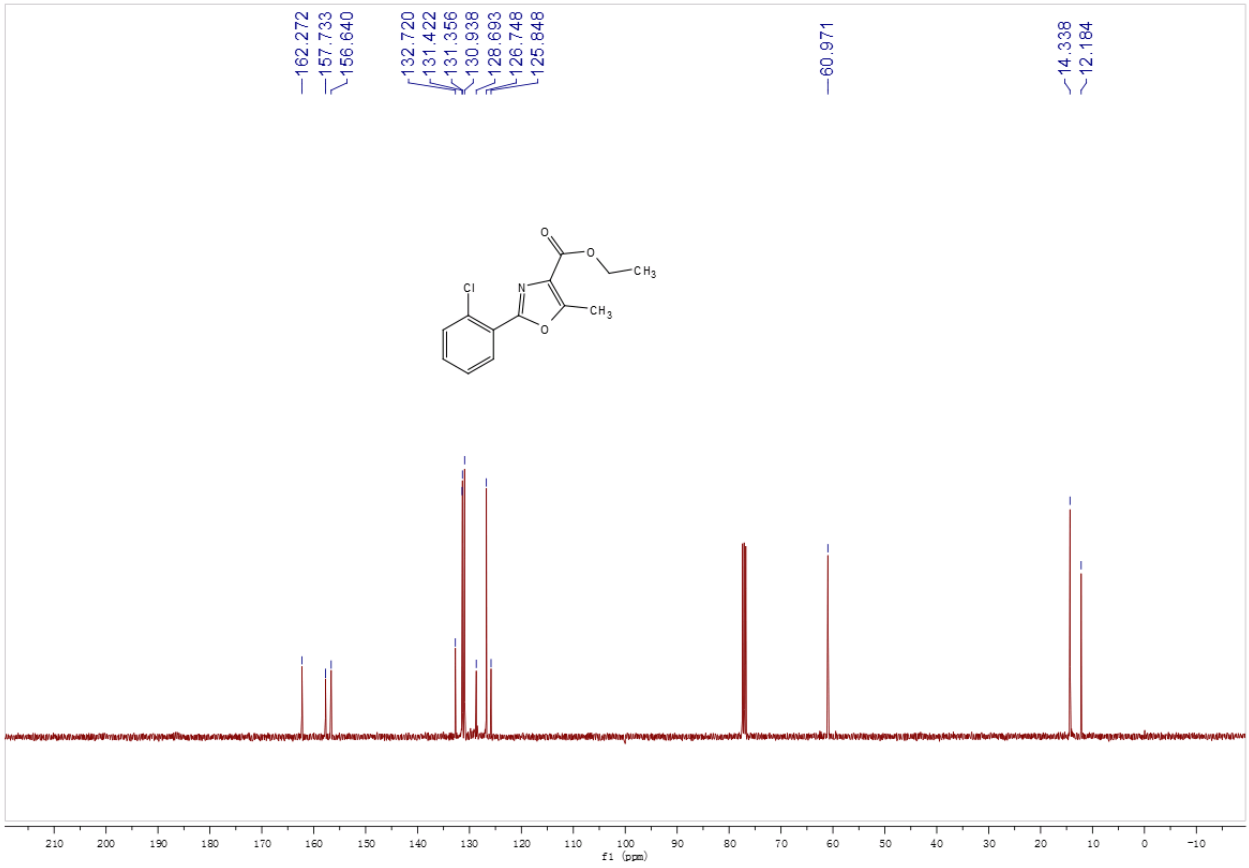


Fig. S-34. ^{13}C-NMR spectrum of (**3af**).

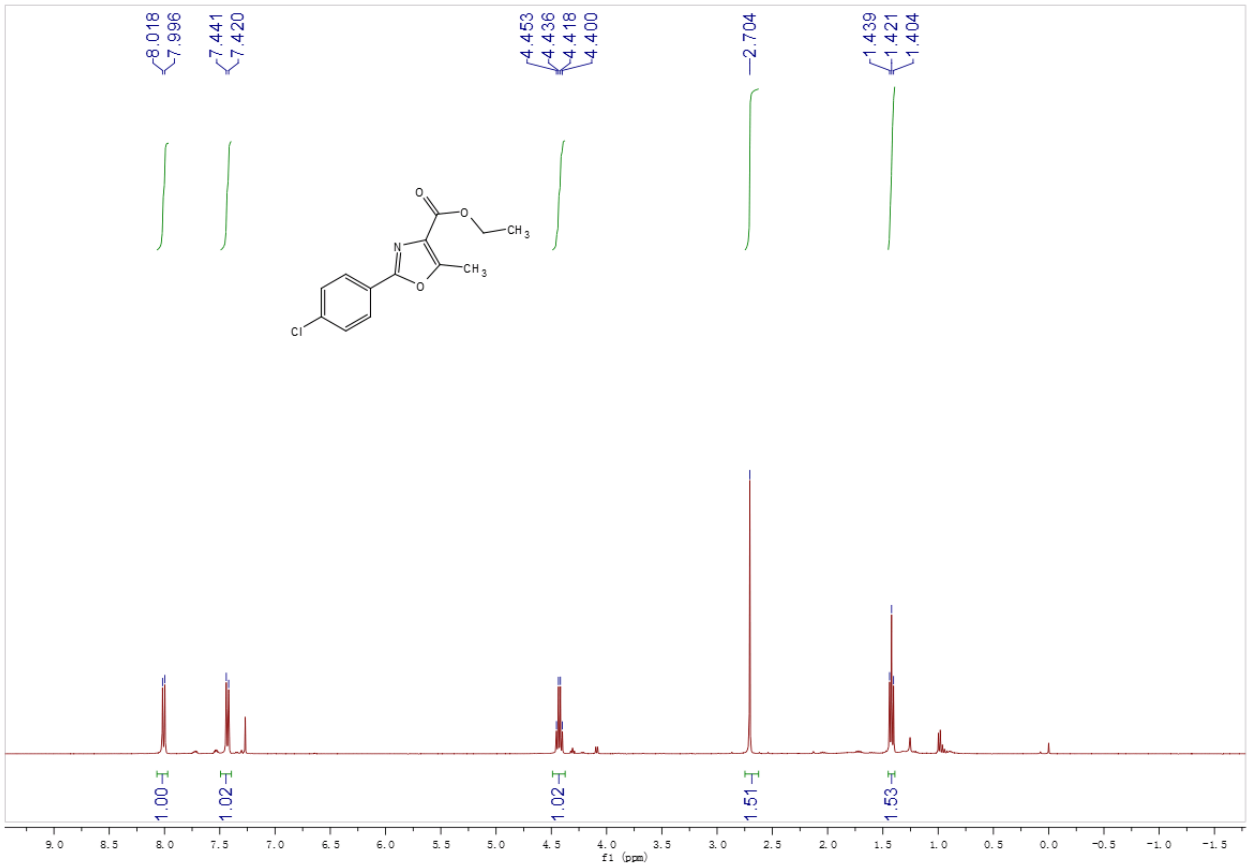


Fig. S-35. ^{1}H-NMR spectrum of (**3ag**).

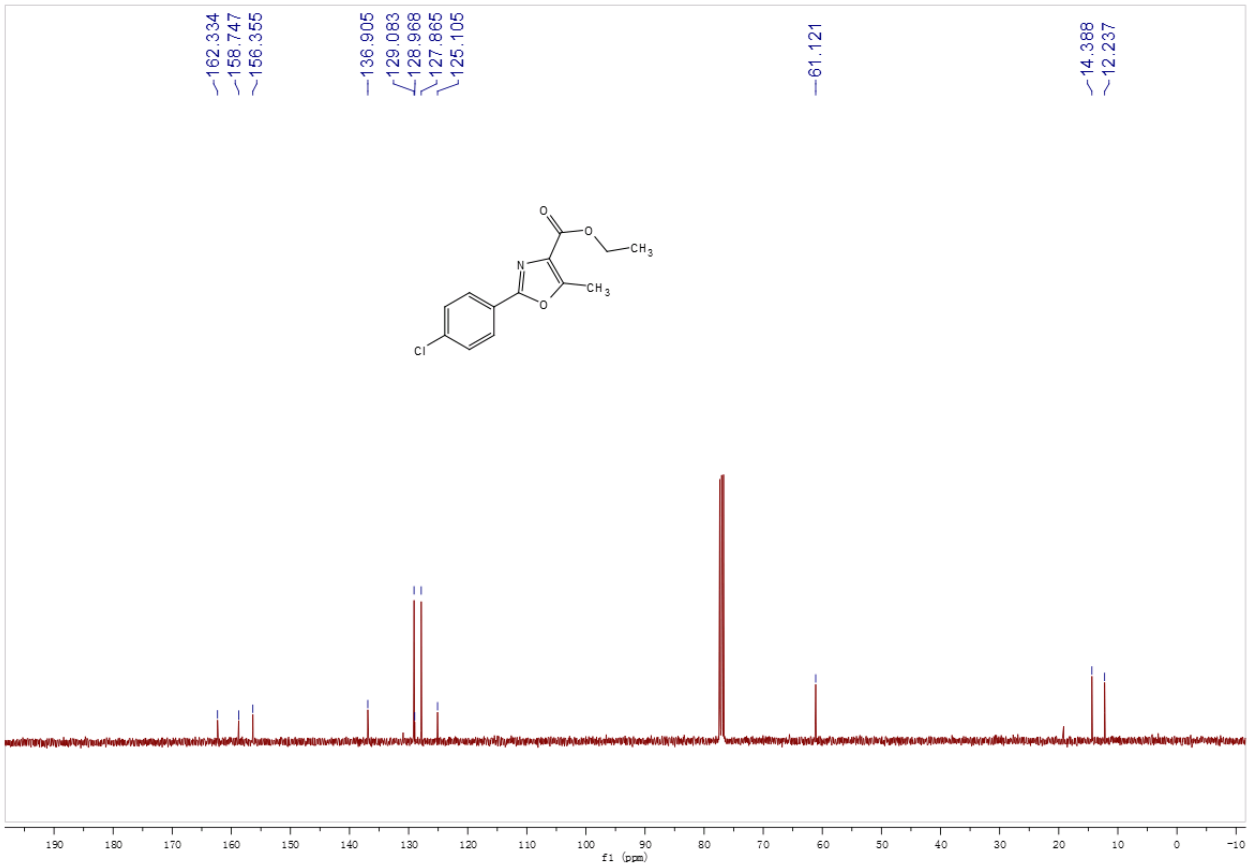


Fig. S-36. ^{13}C-NMR spectrum of (**3ag**).

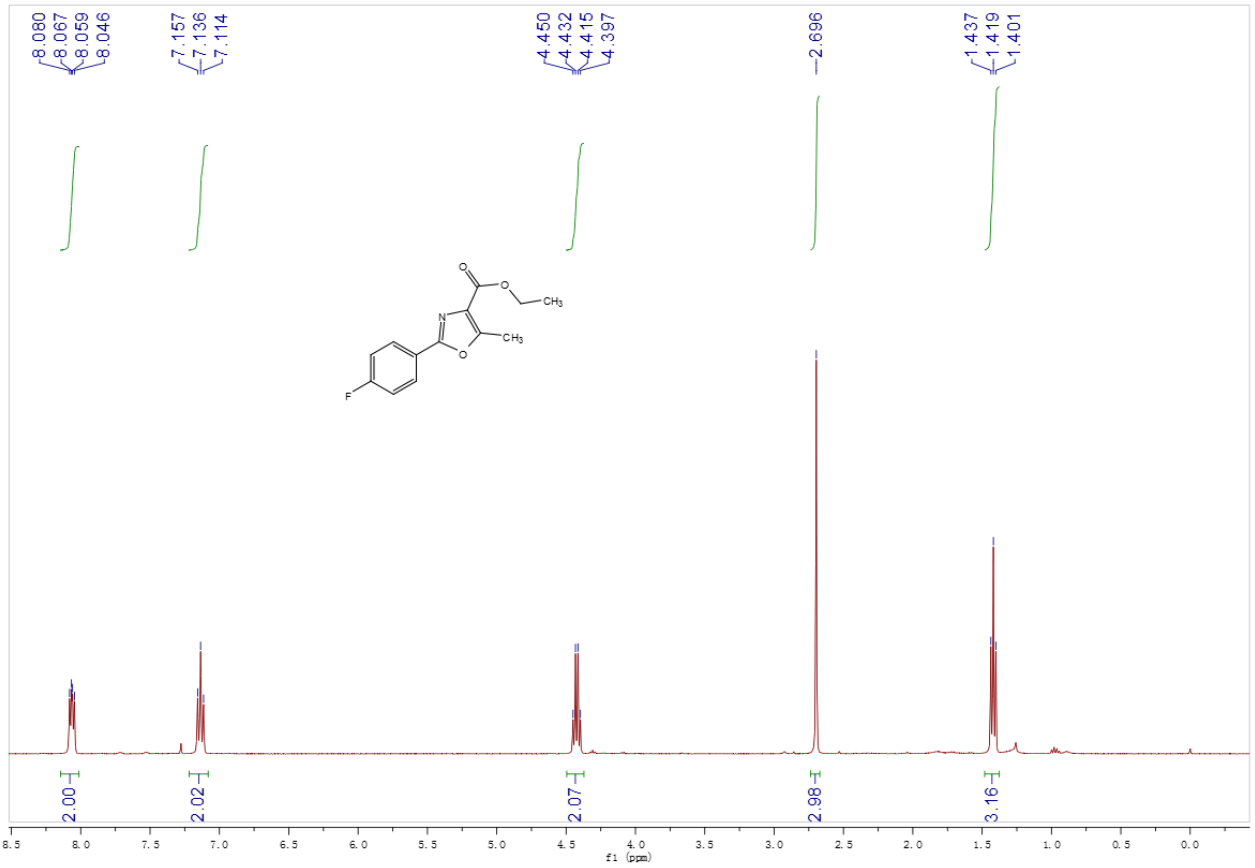


Fig. S-37. ^{1}H-NMR spectrum of (**3ah**).

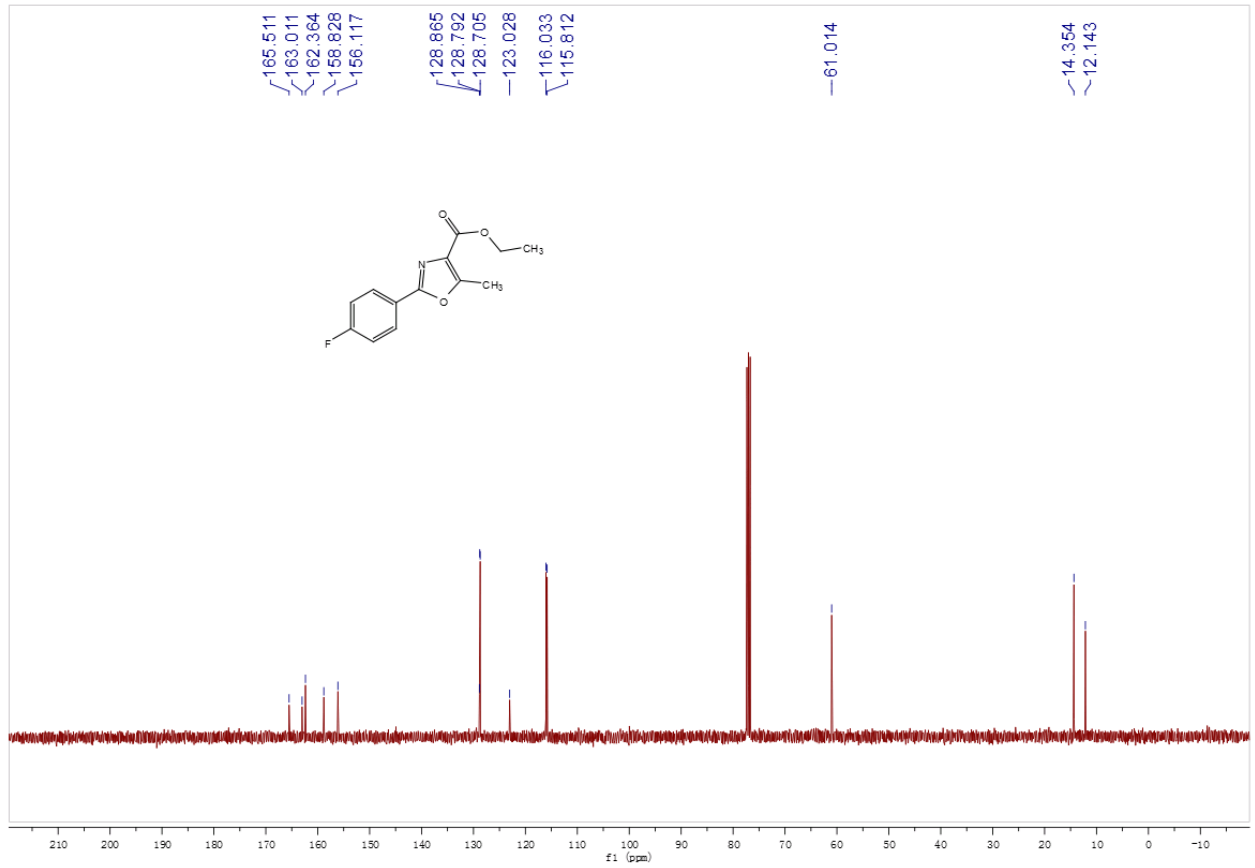


Fig. S-38. ^{13}C-NMR spectrum of (**3ah**).

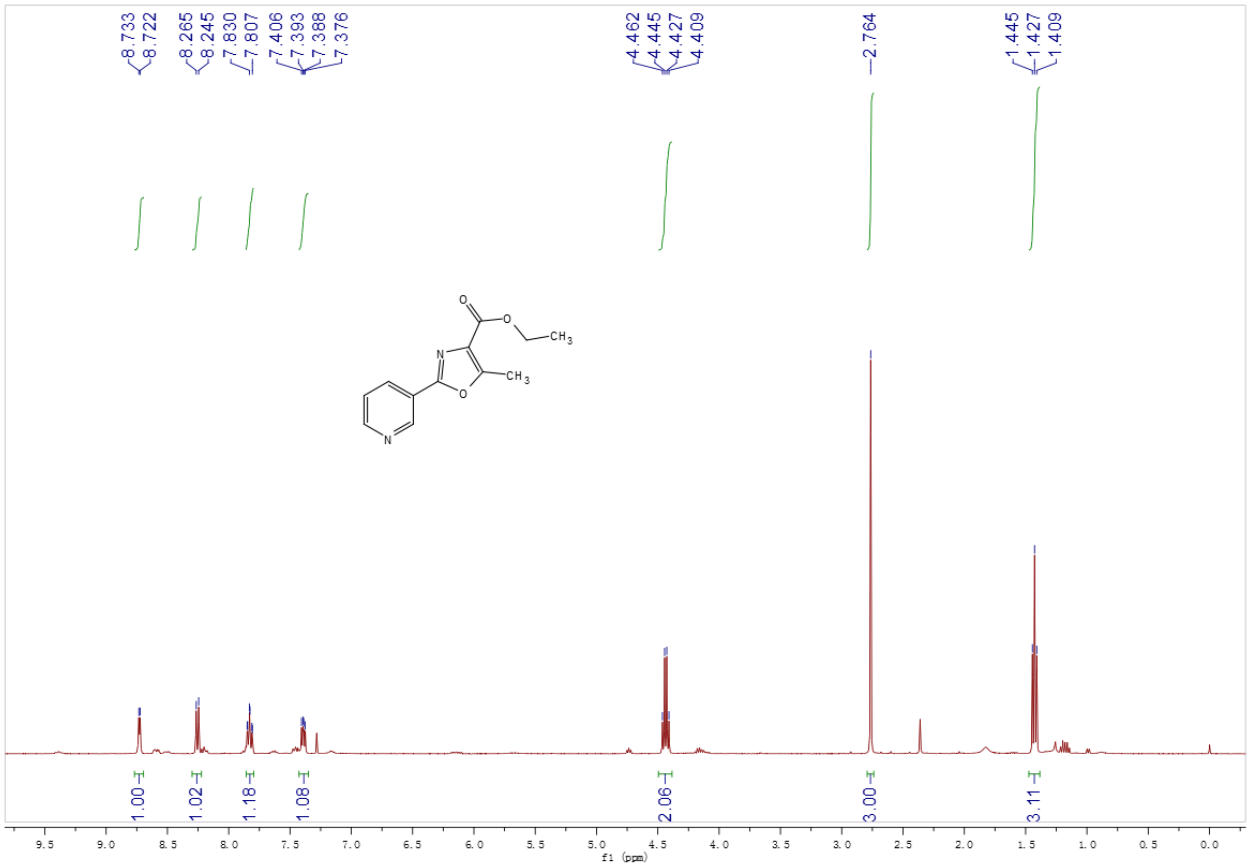


Fig. S-39. ^{1}H-NMR spectrum of (**3ai**).

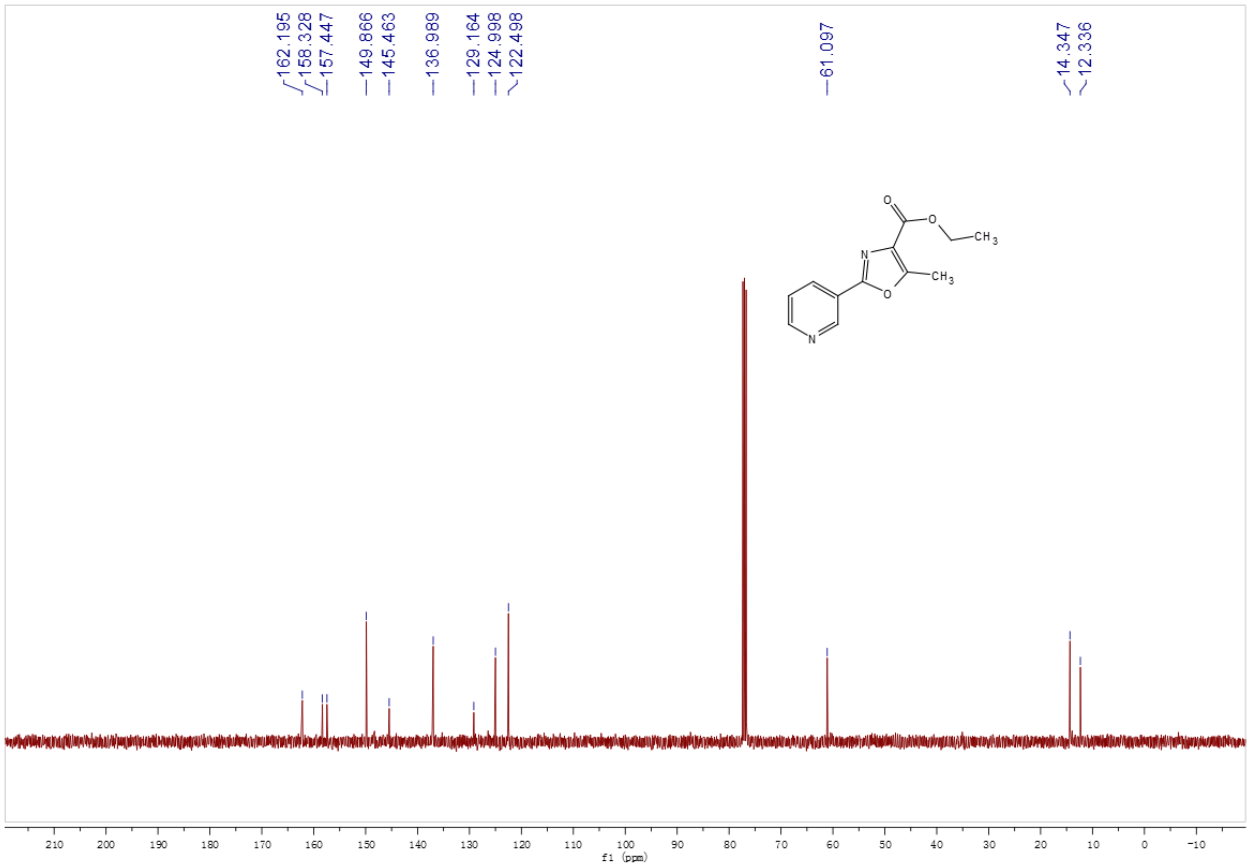


Fig. S-40. ^{13}C-NMR spectrum of (**3ai**).

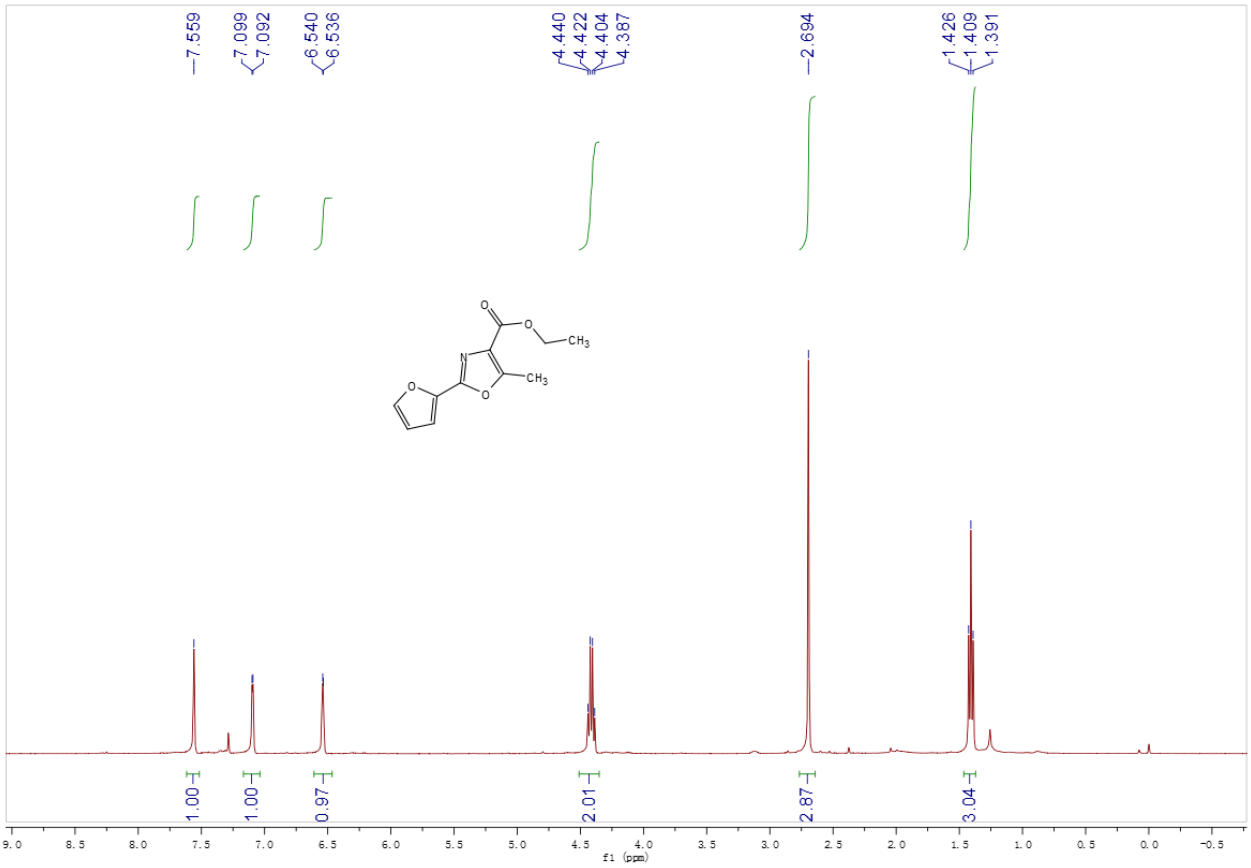


Fig. S-41. ^{1}H-NMR spectrum of (**3aj**).

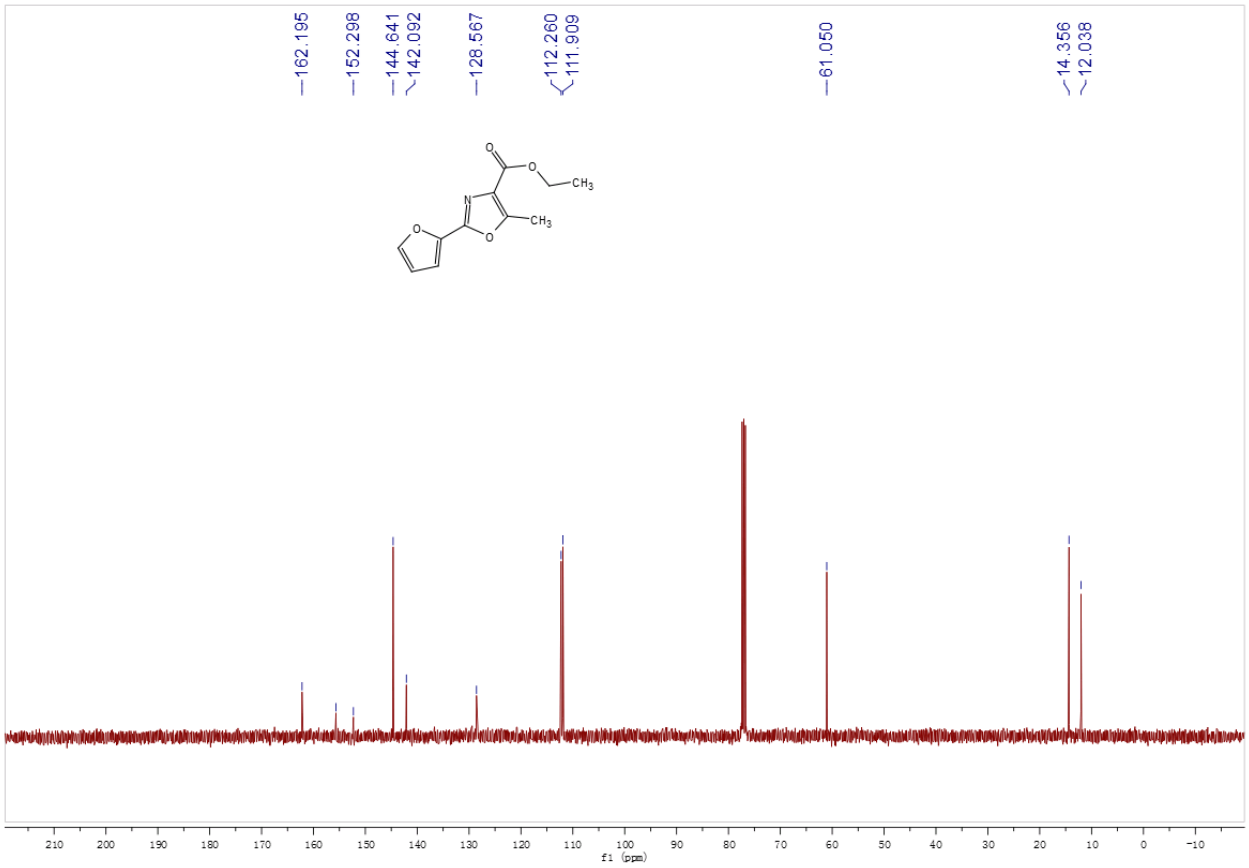


Fig. S-42. ^{13}C-NMR spectrum of (**3aj**).

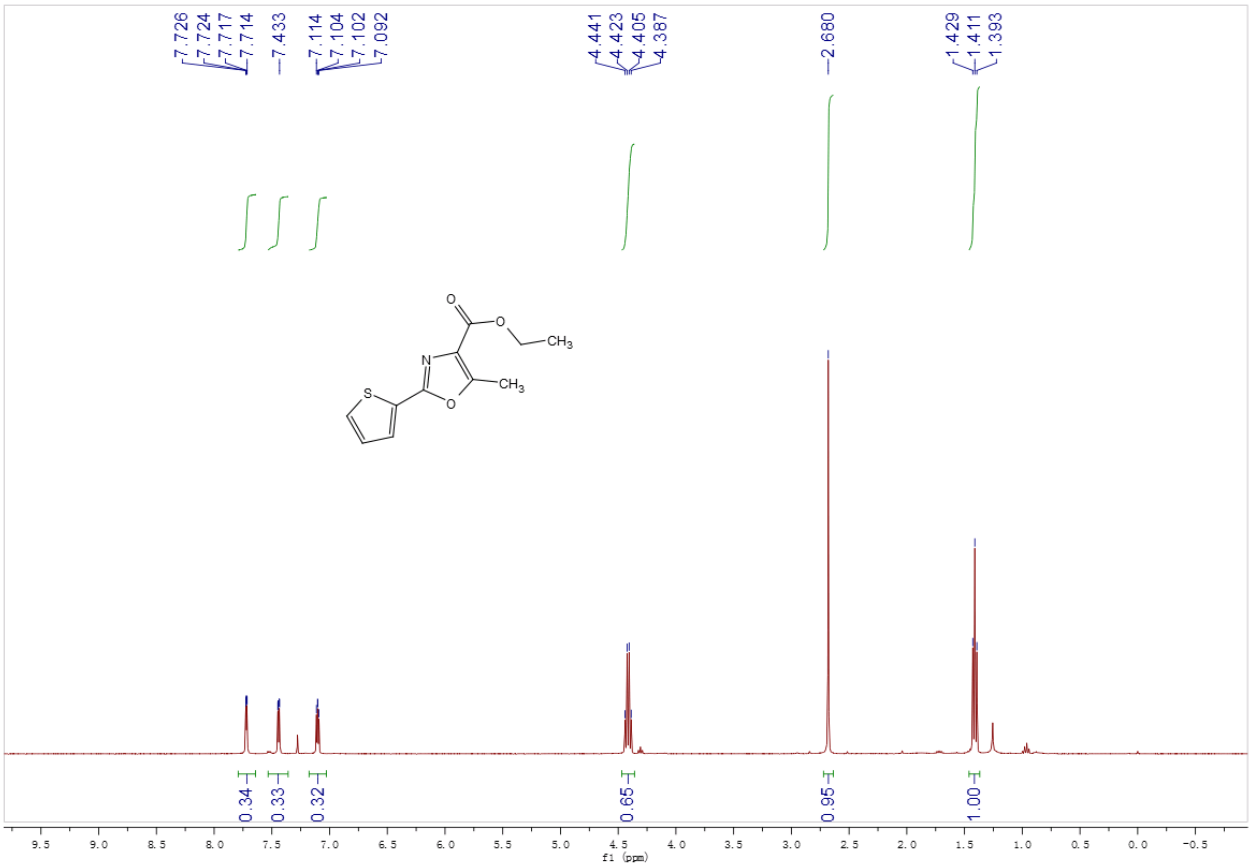


Fig. S-43. ^{1}H-NMR spectrum of (**3ak**).

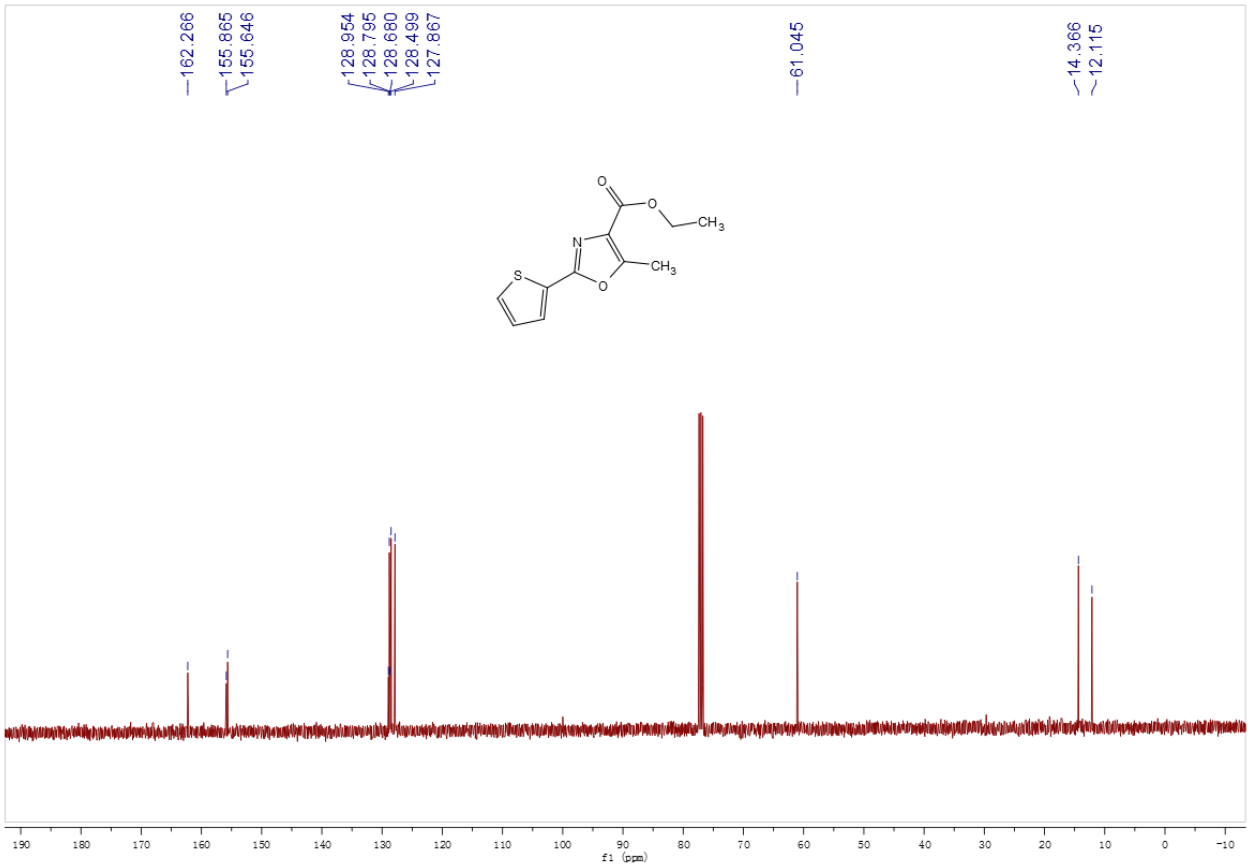


Fig. S-44. ^{13}C-NMR spectrum of (**3ak**).

5. References

[1] C.-F. Wan, J.-T. Zhang, S.-J. Wang, J.-M. Fan, Z.-Y. Wang, *Org. Lett.,* 2010, **12**, 2338.

[2] J. Xie, H.-L. Jiang, Y.-X. Cheng and C.-J. Zhu, *Chem. Commun.*, 2012, **48**, 979.

[3] C. Spanka, B. Clapham, and K. D. Janda, *J. Org. Chem.*, 2002, **67**, 3045.