Supporting Information

Cu_2O@PdCu synergistic catalysis for high-effective C-H arylation of azoles

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Materials

All organic reactions were conducted in sealed tubes under N_2 atmosphere. All chemical reagents and deuterated solvents were purchased from Sigma-Aldrich, Aladdin, Alfa, Adamas, Energy Chemical, or J&K and used without further purification, unless otherwise stated.

Instruments

Scanning electron microscope (SEM) images were taken using a FEI Inspect F50. Transmission electron microscope (TEM) images were taken using a Tecnai F30 (FEI) and Titan Cubed Themis G2 300 (FEI). X-ray diffraction (XRD) patterns were performed on Rigaku Ultima IV using Cu Kα irradiation at a scan rate of $2^{o}\cdot min^{-1}$ with the target voltage at 40 kV and current 40 mA. X-ray photoelectron spectroscopy (XPS) was performed by PHI 5000 VersaProbe III with a monochromatic Al Kα X-ray source with the beam size of 1400 um × 100 um. Charge compensation was achieved by the dual beam charge neutralization and the binding energy was corrected by setting the binding energy of the hydrocarbon C 1s feature to 284.8 eV. Frozen sections were performed with Leica UC7. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 500 MHz and 600 MHz spectrometer. Proton and carbon chemical shifts are reported relative to the solvent used as an internal reference ($CDCl_3$: δ H = 7.26 ppm; δ C = 77.16 ppm). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on an APEX II (Bruker Inc.) spectrometer with Electron Spray Ionization (ESI) resource. Flash column chromatography was performed over silica gel 200-300 mesh.

The extended X-Ray absorption fine structure measurements

The extended X-Ray absorption fine structure measurements were carried out on the sample at 21A X-ray nano-diffraction beamline of Taiwan Photon Source (TPS), National Synchrotron Radiation Research Center (NSRRC). This beamline adopted 4-bounce channel-cut Si (111) monochromator for mono-beam X-ray nano-diffraction and X-ray absorption spectroscopy. The end- station equipped with three ionization

chambers and Lytle/SDD detector after the focusing position of KB mirror for transmission and fluorescence mode X-ray absorption spectroscopy. The photon flux on the sample is range from $1x10^{11}$~$3x10^{9}$ photon/ sec for X- ray energy from 6 - 2 7 keV. The obtained XAFS data was processed in Athena (version 0.9.26) for background, pre-edge line and post-edge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.26). The k^3 weighting, k-range of 3 - 14 $Å^{-1}$ and R range of 1 - ~3 Å were used for the fitting of Cu foil; k-range of 3 - 11 $Å^{-1}$ and R range of 1 - ~2 Å were used for the fitting of samples. The four parameters, coordination number, bond length, Debye-Waller factor and E_0 shift (CN, R, ΔE_0) were fitted without anyone was fixed, the σ^2 was set. For Wavelet Transform analysis, the $\chi(k)$ exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 1 - 4 Å, k range, 0 - 12 $Å^{-1}$ for samples; k weight, 3; and Morlet function with κ=10, σ=1 was used as the mother wavelet to provide the overall distribution.

Computational method

We have employed the Vienna Ab initio Simulation Package (VASP) to perform all density functional theory (DFT) calculations with the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional. We have chosen the projected augmented wave (PAW) potentials to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Geometry optimizations were performed with the force convergency smaller than 0.05 eV/Å. A climbing image nudged elastic band (CI-NEB) method was used to locate the transition states with the same convergence standard Atoms at bottom are fixed in all the calculation. Monkhorst-Pack k-points of 1×1×1were applied for all the surface calculations.

Synthesis of Cu_2O syn

Firstly, a basic copper tartrate complex solution composed of 7 gL^{-1} of $CuSO_4 \cdot 5H_2O$, 25 gL^{-1} of potassium sodium tartrate tetrahydrate, and 4.5 gL^{-1} of KOH (Fehling's solution) was prepared. In a typical synthesis procedure,[1] 0.027 mmol $PdCl_2$ and 10 mL glucose aqueous solution (0.25 M) were added into 50 mL Fehling's solution and 450

mL water under stirring. Then the formed light-blue solution was aged at 80 ℃ under stirring for 3 h. After cooling to room temperature, the precipitates were separated at 3000 rpm, washed with water and ethanol thoroughly, and dried under vacuum overnight.

Synthesis of Octahedral Cu_2O

In a typical synthesis,[2] 4.5 g polyvinylpyrrolidone (PVP40, MW 40 000) was added into 100 mL $CuCl_2 \cdot 2H_2O$ aqueous solution (0.01 M) under constant stirring at 55 ℃ in a water bath. Then, 10 mL NaOH aqueous solution (2.0 M) was added dropwise into the above solution. After stirring for 30 min, 10 mL ascorbic acid solution (0.6 M) was added dropwise into the dark brown solution. The mixture was aged for 3 h and the solution gradually transferred into turbid red.

Synthesis of Cu_2O@PdCu

The Cu_2O@PdCu catalysts were synthesized by galvanic reaction. The whole procedure was performed at room temperature. 43.2 mg Cu_2O syn and 0.3 g PVP40 were added into 48 mL water. Then, Na_2PdCl_4 (10 mM) aqueous solution was added into the mixture under vigorously stirring. The solution turned from yellow to black quickly. After 20 min, the mixture was centrifuged at 9000 rpm, followed by washing with water and ethanol, and was dried under vacuum. In this work, five kinds of Cu_2O@PdCu catalyst were prepared by employing different molar ratio of Na_2PdCl_4 and Cu_2O syn (1:2, 2:3, 1:1, 3:2 and 2:1, respectively).

Synthesis of PdCu nanocages

The as-prepared Cu_2O@PdCu-3 described above were added into 42 mL of 25-28% $NH_3 \cdot H_2O$. The reaction was stopped after 10 h. The PdCu nanocages were obtained by centrifugation at 9000 rpm, washed with mixed water and ethanol solution and dried under vacuum overnight.

Table S1. The chemical component of Cu_2O syn, Cu_2O@PdCu-1, Cu_2O@PdCu-2, Cu_2O@PdCu-3, Cu_2O@PdCu-4, Cu_2O@PdCu-5 and PdCu nanocages.

Number	Name	Pd (mg/kg)	Cu (mg/kg)	Pd/Cu mass ratio	Pd/Cu molar ratio
1	Cu_2O syn	55584	838416[a]	0.07	0.04
2	Cu_2O@PdCu-1	240573	673943	0.36	0.22
3	Cu_2O@PdCu-2	325856	540727	0.60	0.36
4	Cu_2O@PdCu-3	469935	342357	1.37	0.82
5	Cu_2O@PdCu-4	713981	125262	5.70	3.42
6	Cu_2O@PdCu-5	725076	89751	8.08	4.85
7	PdCu nanocages	759367	107685	7.05	4.23

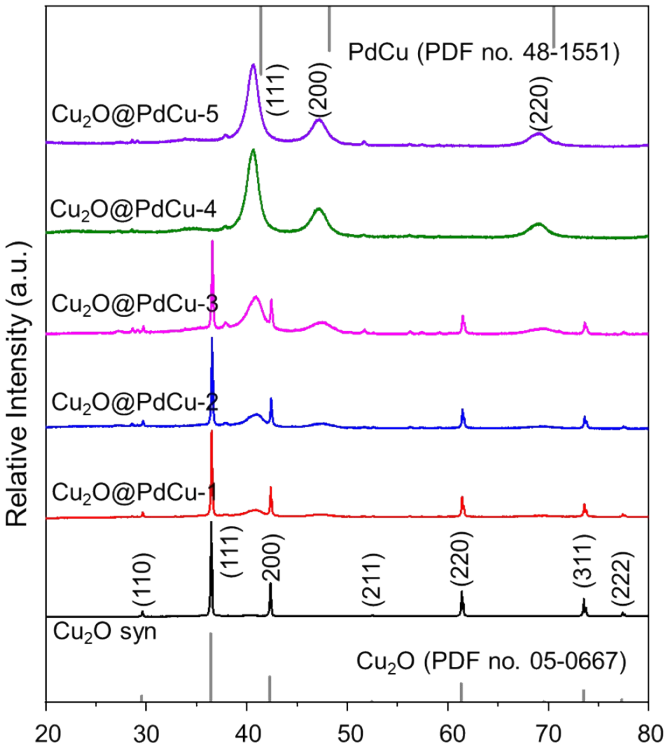


Figure S1. XRD pattern of the as-prepared catalysts.

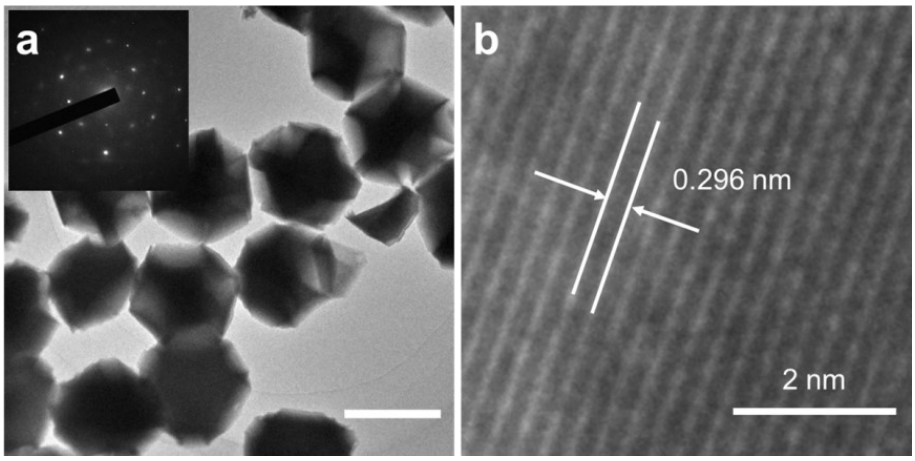


Figure S2. TEM and HR-TEM images of Cu_2O syn (a,b), the insert in c is the selected-area diffraction, scar bar in a corresponds to 500 nm.

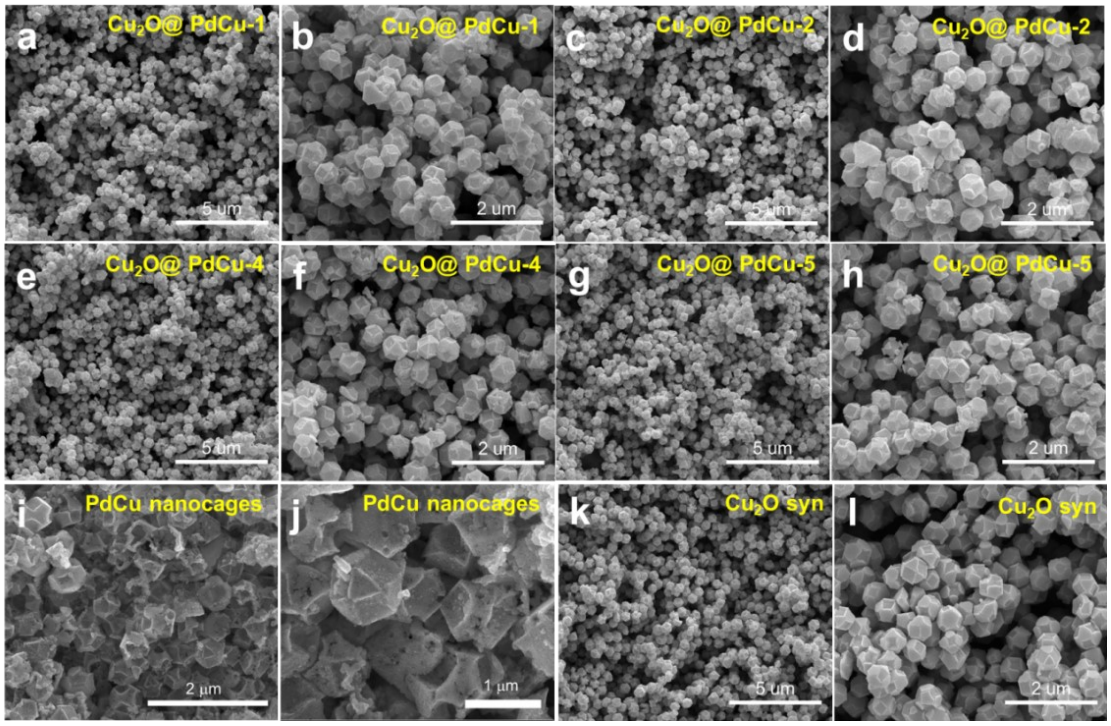


Figure S3. SEM images of Cu_2O@PdCu-1(a,b), Cu_2O@PdCu-2 (c,d), Cu_2O@PdCu-4 (e, f), Cu_2O@PdCu-5 (g, h), PdCu nanocages (i, j) and Cu_2O syn (k, l).

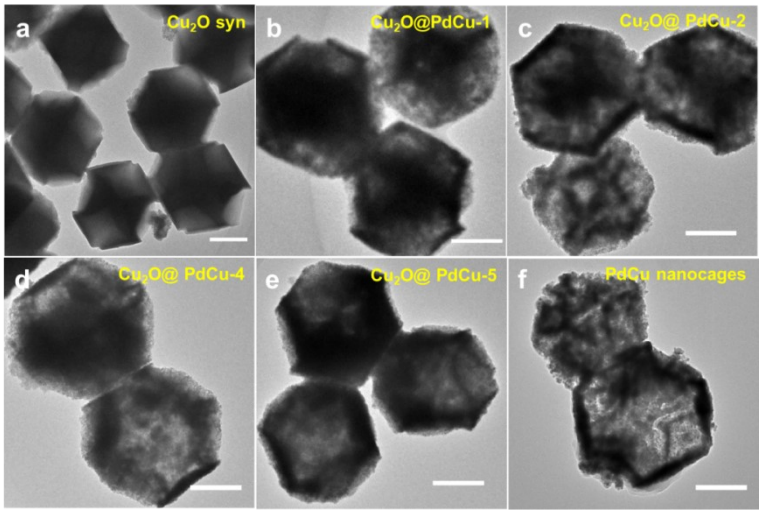


Figure S4. TEM images of Cu_2O syn (a), Cu_2O@PdCu-1 (b), Cu_2O@PdCu-2 (c), Cu_2O@PdCu-4 (d), Cu_2O@PdCu-5 (e), PdCu nanocages (f), scar bars correspond to 200 nm.

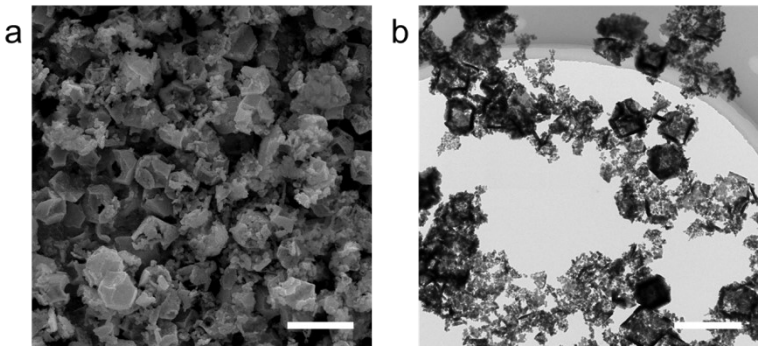


Figure S5. SEM and TEM images of Cu_2O@PdCu-3 after 3 cycle of reaction, scar bars correspond to 200 nm.

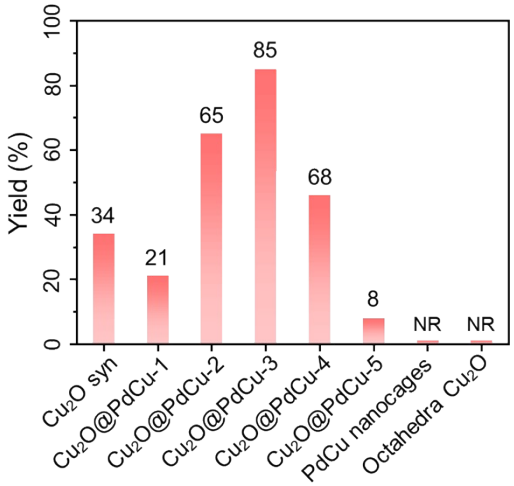
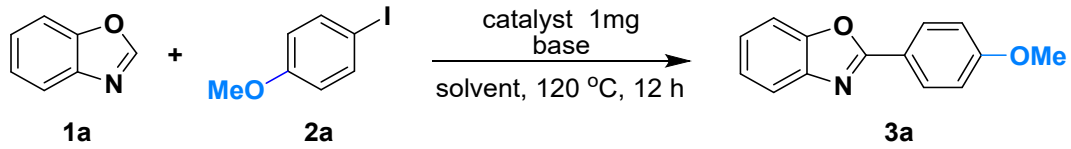


Figure S6. The catalytic performance using different catalysts towards C-H arylation of benzoxazole with 4-iodoanisole.

Table S2. Optimization of condition using benzoxazole and 4-iodoanisole



1a 2a 3a

entry	catalyst	base	solvent	yield (%)[b]
1	Cu_2O@PdCu-3	K_2CO_3	dioxane	45
2	Cu_2O@PdCu-3	K_2CO_3	DMF	95(92)
3	Cu_2O@PdCu-3	K_2CO_3	DMA	84
4	Cu_2O@PdCu-3	K_2CO_3	H_2O	38
5	Cu_2O@PdCu-3	K_2CO_3	NMP	37
6	Cu_2O@PdCu-3	Na_2CO_3	DMF	30
7	Cu_2O@PdCu-3	Cs_2CO_3	DMF	79
8	Cu_2O@PdCu-3	$NaHCO_3$	DMF	38
9	Cu_2O@PdCu-3	K_3PO_4	DMF	80
10	Cu_2O@PdCu-3	NaOAc	DMF	83
11[c]	Cu_2O@PdCu-3	K_2CO_3	DMF	82
12[d]	Cu_2O@PdCu-3	K_2CO_3	DMF	NR
13[e]	Cu_2O@PdCu-3	K_2CO_3	DMF	NR

[a]Benzoxazole (0.5 mmol), 4-iodoanisole (0.75 mmol), base (1 mmol), catalyst (1 mg) and anhydrous solvent (2 mL), under N_2 atmosphere at 120 ℃ for 18h. [b]Yield was determined by ^{1}H NMR using 1,3,5-trimethylbenzene as an internal standard (isolated yield in parentheses). [c]100 ℃. [d]1-bromo-4-methoxybenzene as reactant. [e]1-chloro-4-methoxybenzene as reactant.

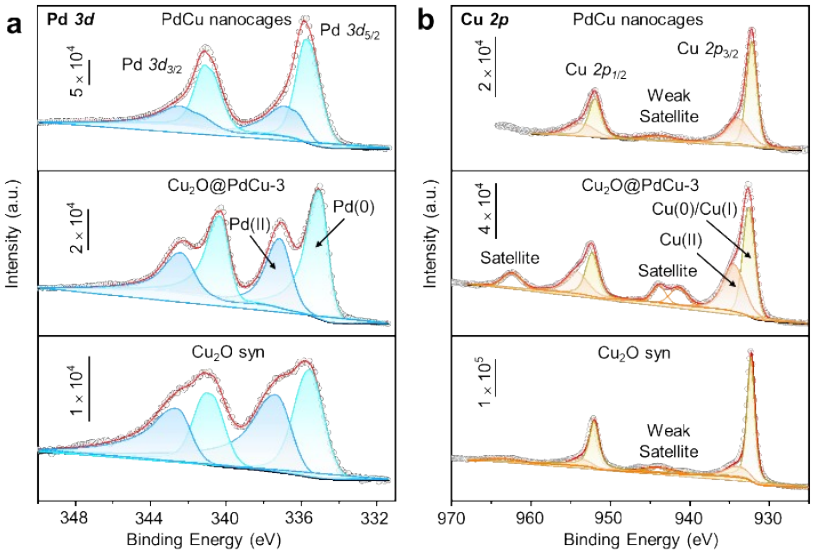


Figure S7. XPS spectra of Pd 3d (a) and Cu 2p (b) with scar bars for Cu_2O syn, Cu_2O@PdCu-3 and PdCu nanocages.

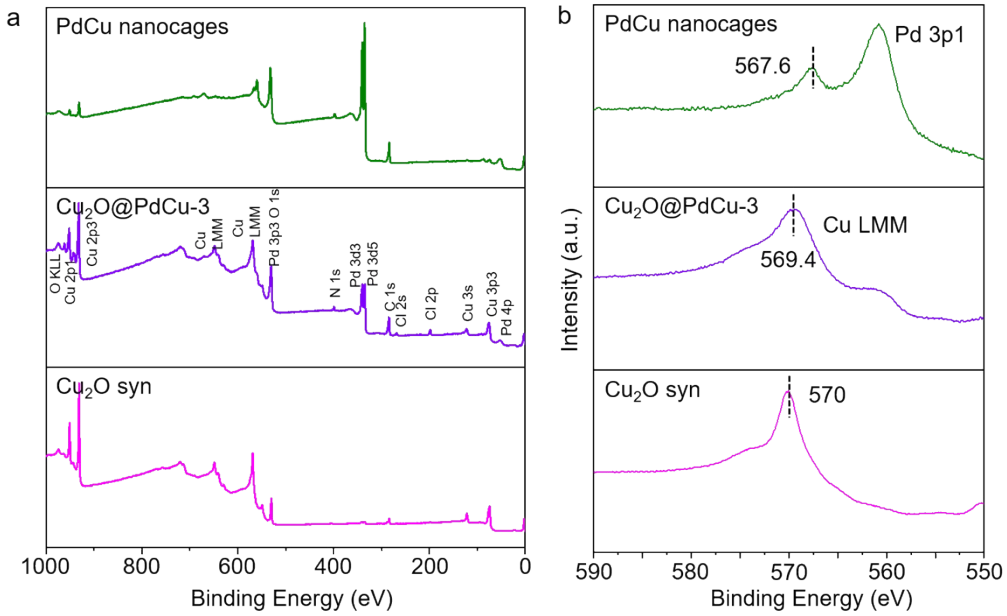


Figure S8. Survey (a) and Cu LMM spectra (b) for PdCu nanocages, Cu_2O@PdCu-3 and Cu_2O syn.

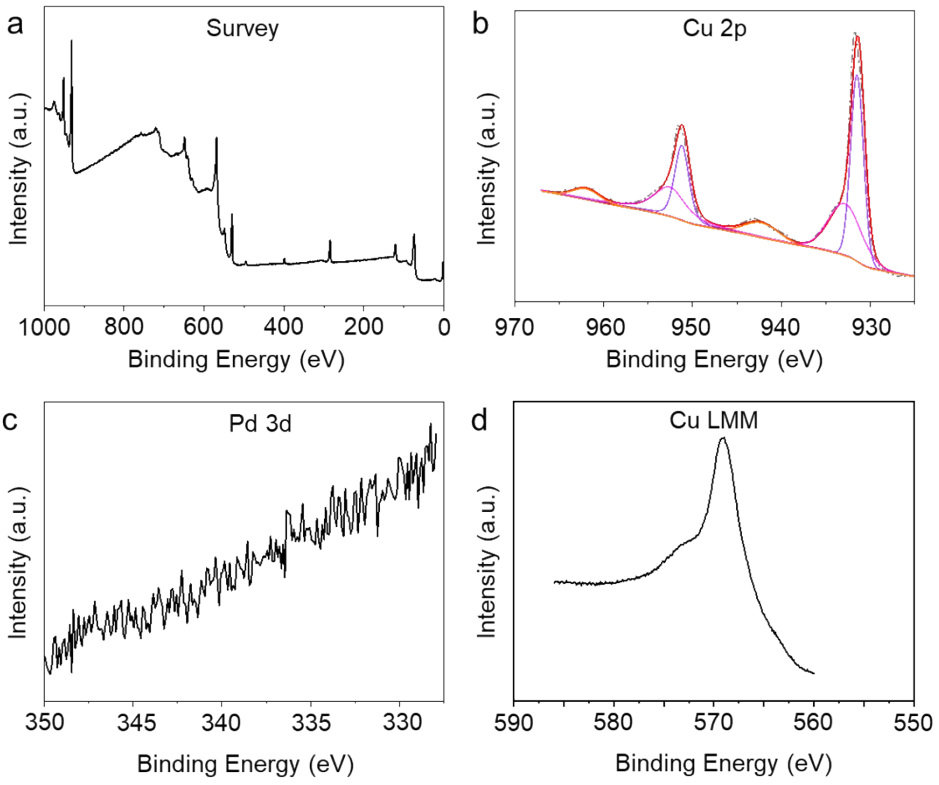


Figure S9. XPS spectra of Survey (a), Cu 2p (b), Pd 3d (c) and Cu LMM (d) for Octahedra Cu_2O.

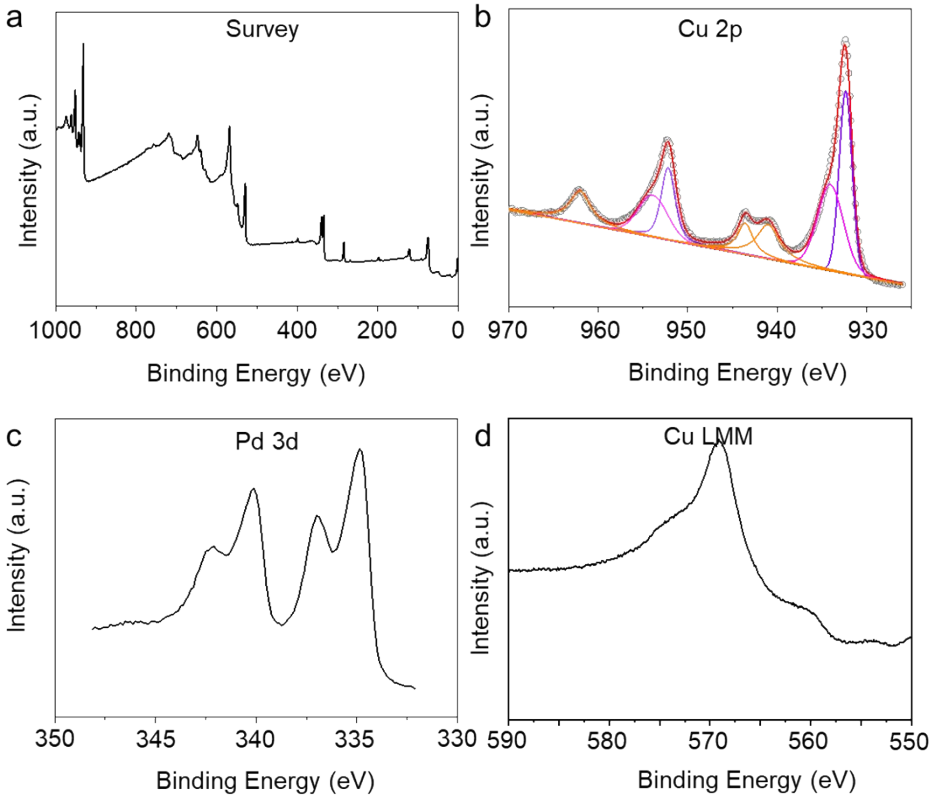


Figure S10. XPS spectra of Survey (a), Cu 2p (b), Pd 3d (c) and Cu LMM (d) for Cu_2O@PdCu-1.

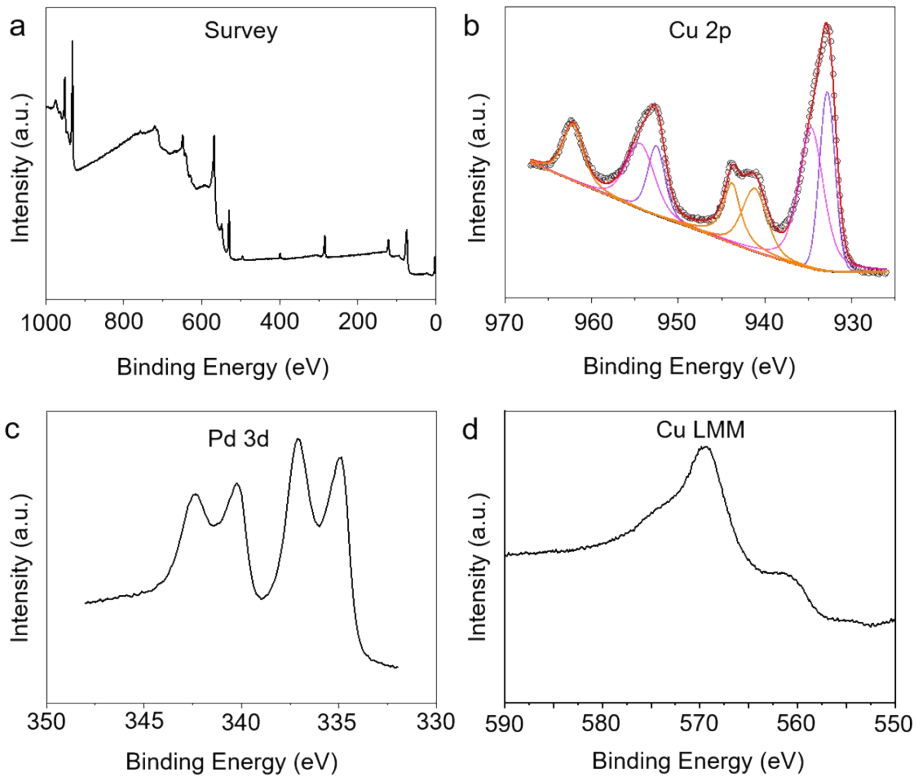


Figure S11. XPS spectra of Survey (a), Cu 2p (b), Pd 3d (c) and Cu LMM (d) for Cu_2O@PdCu-2.

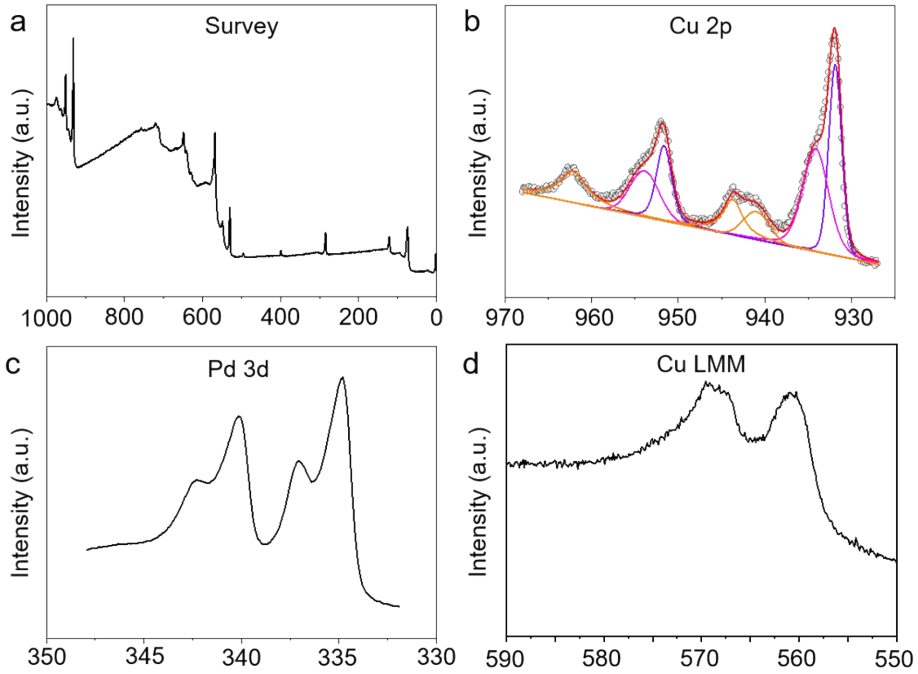


Figure S12. XPS spectra of Survey (a), Cu 2p (b), Pd 3d (c) and Cu LMM (d) for Cu_2O@PdCu-4.

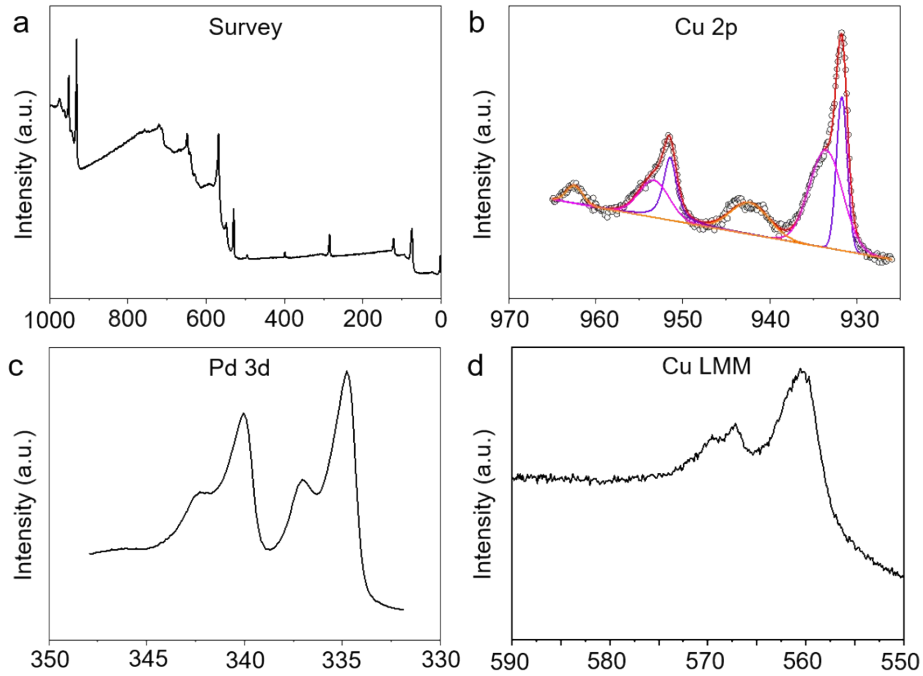


Figure S13. XPS spectra of Survey (a), Cu 2p (b), Pd 3d (c) and Cu LMM (d) for Cu_2O@PdCu-5.

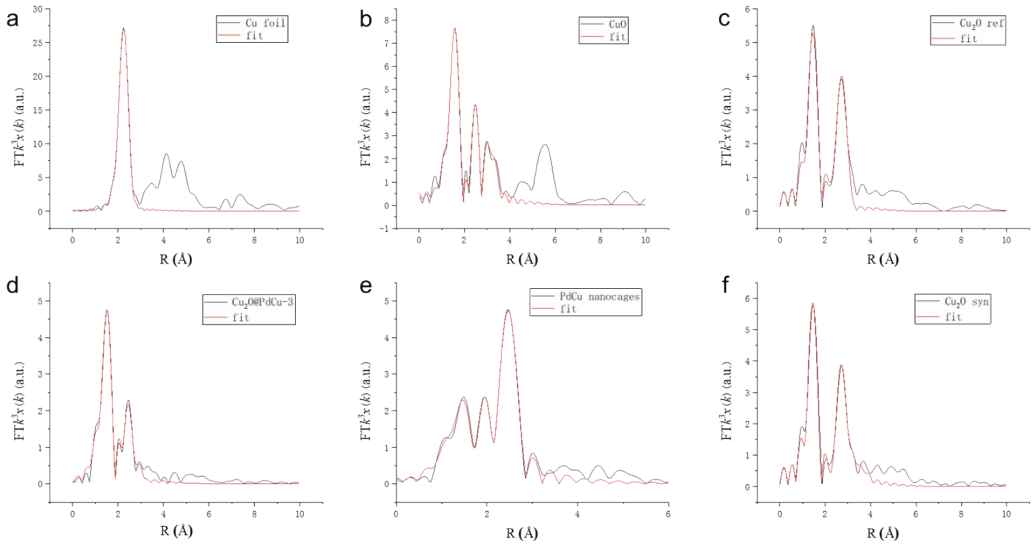


Figure S14. EXAFS fitting spectra for the k space of the Cu foil, CuO ref, Cu_2O ref, Cu_2O@PdCu-3, PdCu nanocages and Cu_2O syn.

Table S3. EXAFS fitting parameters at the Cu K-edge for various samples (S_0^2=0.86). CN: coordination numbers. R (Å): bond distance. σ^2 ($10^{-3}Å^2$): Debye-Waller factors. ΔE_0 (eV): the inner potential correction. R factor: goodness of fit.

	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Cu foil	Cu-Cu	12	2.54±0.01	0.0085	3.9±0.5	0.0026
Cu_2O	Cu-O	1.9±0.1	1.85±0.01	0.0039	6.1±1.4	0.0185
	Cu-Cu	9.4±1.0	3.02±0.01	0.0186		
CuO	Cu-O	3.5±0.1	1.96±0.01	0.0050	7.5±0.9	0.0098
	Cu-Cu	6.6±0.7	2.95±0.01	0.0121		
	Cu-Cu1	2.1±0.3	3.14±0.01	0.0032		
	Cu-O1	2.0±0.9	3.77±0.03	0.0033		
Cu_2O@ PdCu-3	Cu-O	2.4±0.1	1.93±0.01	0.0050	-3.1±0.8	0.0038
	Cu-Pd	0.8±0.1	2.69±0.01	0.0069		
	Cu-Cu	2.0±0.4	2.99±0.02	0.0165		
Cu_2O syn	Cu-O	1.8±0.1	1.84±0.01	0.0025	6.3±1.2	0.0110
	Cu-Cu	4.4±0.6	3.00±0.01	0.0131		
	Cu-O1	2.7±0.8	3.47±0.04	0.0013		
	Cu-Cu1	2.3±1.1	3.68±0.06	0.0115		
PdCu nanocages	Cu-O	1.7±0.1	1.89±0.01	0.0118	-8.0±0.6	0.0026
	Cu-Cu	0.9±0.2	2.65±0.02	0.0112		
	Cu-Pd	3.9±0.2	2.66±0.01	0.0102		

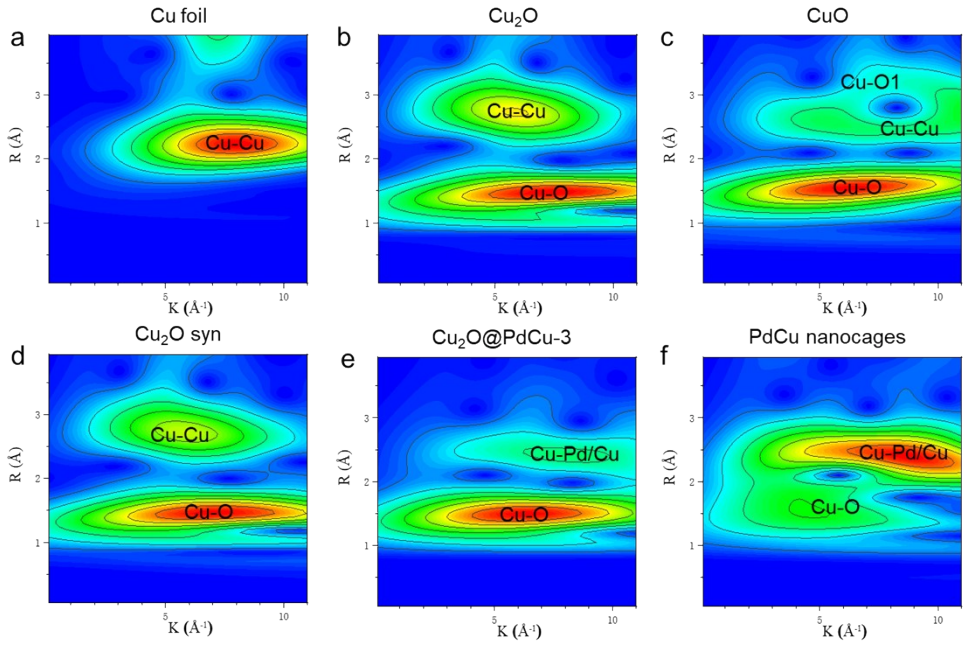


Figure S15. Morlet wavelet transformed X-ray absorption spectra of the Cu foil (a), Cu_2O ref (b), CuO ref (c), Cu_2O syn (d), Cu_2O@PdCu-3 (e) and PdCu nanocages (f).

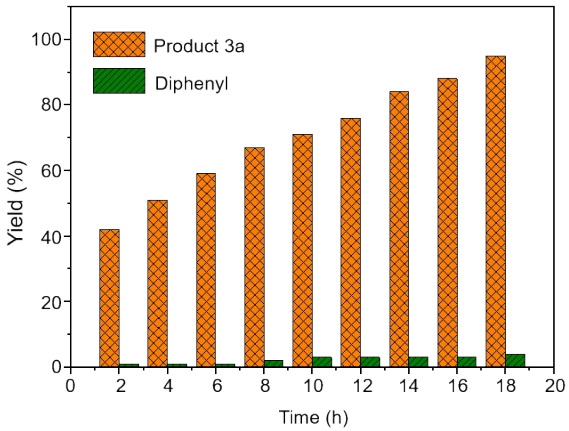


Figure S16. High selectivity.

The reaction was conducted under the standard condition, employing benzoxazole (0.5 mmol, 59.6 mg), 4-iodoanisole (0.75 mmol, 175.5 mg), K_2CO_3 (1.0 mmol, 138.0 mg), Cu_2O@PdCu-3 (1.0 mg) and anhydrous DMF (2 mL) at 120 °C. Furthermore, the result was determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard. With the extension of reaction time, the dehalogenated self-coupling byproduct of 4-iodoanisole, namely biphenyl, becomes nearly undetectable.

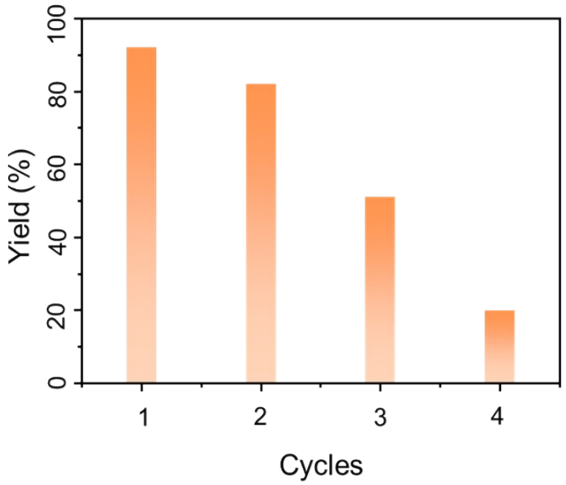


Figure S17. The catalytic stability of Cu_2O@PdCu-3.

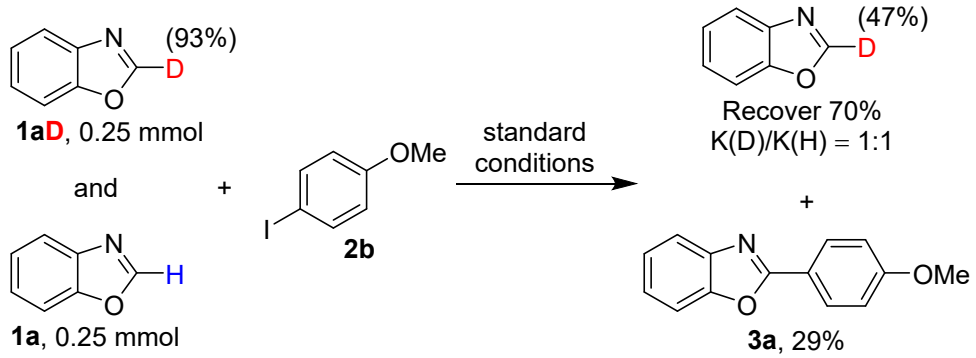


Figure S18. KIE experiment:

A dry reaction tube was charged with benzoxazole **1a** (25.0 μL, 0.25 mmol), benzoxazole-d_1 **1aD** (25.0 μL, 0.25 mmol), 4-iodoanisole **2b** (175.5 mg, 0.75 mmol), K_2CO_3 (138.2 mg, 1.0 mmol), PdCu@Cu_2O (1 mg) and anhydrous DMF (2 mL) under N_2 atmosphere. Subsequently, the mixture was subjected to ultrasonic treatment for ten minutes and stirred at 120 ℃ for 2 h. Then the mixture cooled to room temperature, added with water (5 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo. Next, the crude product was analyzed by ^{1}H NMR using mesitylene as internal standard. The result indicated that the C2-H bond cleavage of benzoxazole was not the "reaction-determining step" in this Cu_2O@PdCu-catalyzed system.

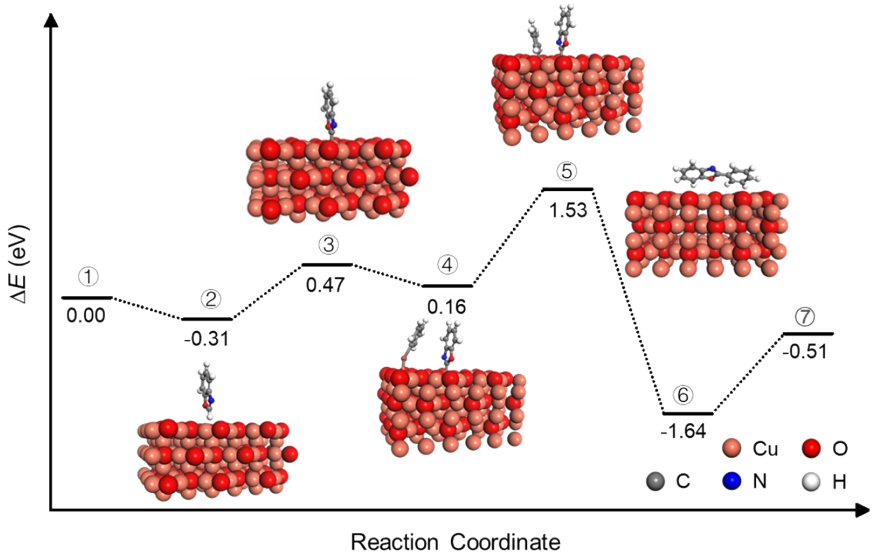
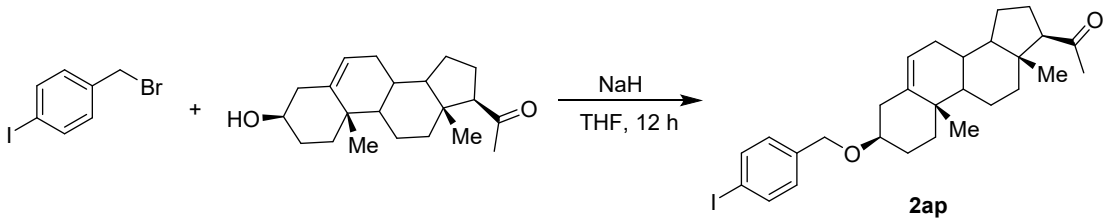


Figure S19. Energies of intermediates in the mechanism from DFT calculations with Cu_2O syn as catalyst.

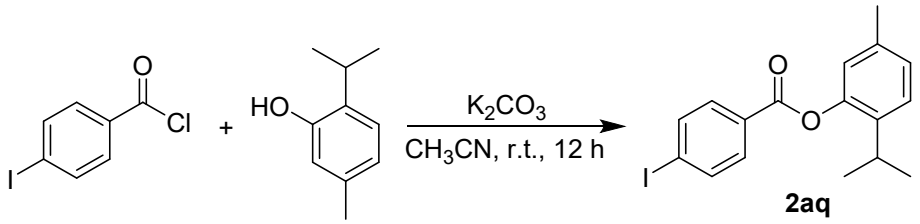
Experiment procedures for Cu_2O@PdCu-catalyzed C-H arylation of heteroarenes

Preparation of substrates2ao[4], 2ap, 2aq, 2as and 2av



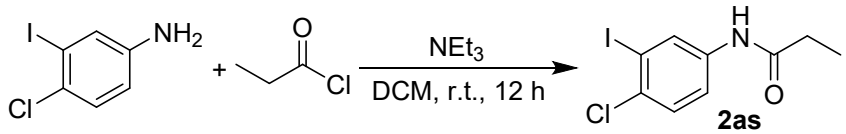
A 100 mL sealed tube was equipped with pregnenolone (1.58 g, 5 mmol), NaH (60% dispersion in mineral oil, 0.24 g, 6 mmol) and 20 mL anhydrous THF. Then under Ar atmosphere the reaction mixture was stirred at 0 ℃ for 30 min. Then a solution of 4-iodobenzyl bromide (1.78 g, 6 mmol) in 3 mL THF was dropwise added to the mixture, which was stirred at rt for another 12 h. The mixture was quenched by H_2O and extracted with ethyl acetate (3 x 20 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel chromatography: PE/AcOEt →50/1 to give **2ap** (2.3 g, 87%) as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 5.35 – 5.33 (m, 1H), 4.50 (s, 2H), 3.34 – 3.16 (m, 1H), 2.53 (t, J = 8.9 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.30 – 2.22 (m, 1H), 2.22 – 2.14 (m, 1H), 2.12 (s, 3H), 2.08 – 1.84 (m, 4H), 1.76 – 1.59 (m, 5H), 1.59 – 1.35 (m, 3H), 1.30 – 1.19 (m, 2H), 1.19 –

1.09 (m, 1H), 1.09 – 0.92 (m, 4H), 0.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 140.8, 138.8, 137.4, 129.4, 121.4, 92.8, 78.6, 69.2, 63.7, 56.9, 50.0, 44.0, 39.1, 38.9, 37.2, 36.9, 31.9, 31.8, 31.6, 28.4, 24.5, 22.8, 21.1, 19.4, 13.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{38}IO_2$ 533.1911; found 533.1903.



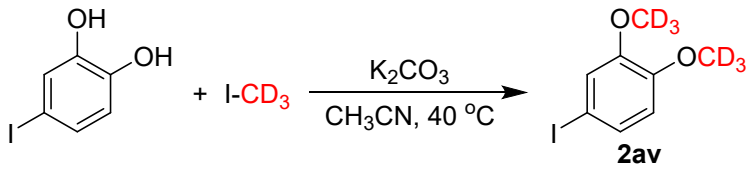
2aq

4-Iodobenzoyl chloride (1.33 g, 5 mmol), thymol (1.12 g, 7.5 mmol), K_2CO_3 (1.38g, 10 mmol) and 30 mL CH_3CN were added to a 100 mL round-bottom flask. The reaction mixture was then stirred at room temperature for 12 h. The mixture was filtered and washed with ethyl acetate. The collected filtrate was concentrated in vacuo. The crude product was purified by silica gel chromatography: PE/AcOEt →100/1 to afford **2aq** (1.75 g, 92%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 3.4 Hz, 1H), 7.07 (d, J = 7.9 Hz, 1H), 6.93 (s, 1H), 3.01 (hept, J = 6.8 Hz, 1H), 2.34 (s, 3H), 1.20 (d, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 148.0, 138.1, 137.1, 136.8, 131.6, 129.2, 127.4, 126.6, 122.8, 101.6, 27.4, 23.1, 20.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{18}IO_2$ 381.0346; found 381.0341.



2as

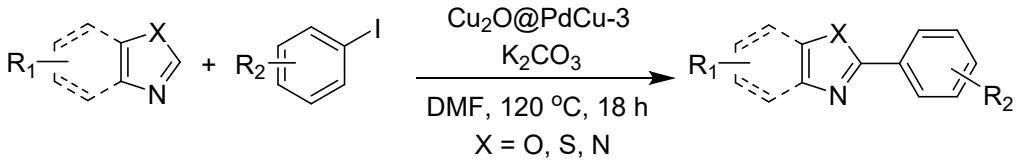
To a mixture of 3-chloro-4-iodoaniline (1.27g, 5 mmol) and NEt_3 (1.4 mL, 10 mmol) in 20 mL DCM was dropwise added propionyl chloride (0.52 mL, 6 mmol) at 0 ℃. Then the mixture was stirred at room temperature for 12 h. The violate was removed under reduce pressure. The crude product was purified by silica gel chromatography: PE/AcOEt →7/1 to afford **2as** (1.35 g, 87%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.75 (s, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.10 (d, J = 8.6 Hz, 1H), 2.38 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 140.1, 139.3, 138.8, 120.7, 119.6, 90.9, 30.7, 9.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_9H_{10}ClINO$ 309.9490; found 309.9485.



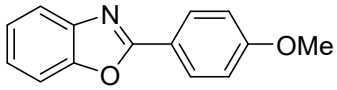
2av

A 100 mL sealed tube was charged with 3,4-dihydroxy-iodobenzene (1.18g, 5 mmol), K_2CO_3 (2,07g, 15 mmol), Iodomethane-*d*$_3$ (1.25 mL, 20 mmol), and anhydrous CH_3CN under Ar atmosphere. Then the reaction mixture was stirred at 40 °C for 12 h. After completed the reaction (monitored by TLC), the contents were then filtered, and the solid residue was washed with ethyl acetate. The combined filtrate was collected and concentrated in vacuo. The crude product was purified by silica gel chromatography: PE/AcOEt →200/1 to afford **2av** (1.03 g, 76%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 149.1, 129.7, 120.3, 113.2, 82.4, 55.3 (sept, *J* = 26.3 Hz), 55.1 (sept, *J* = 26.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_8H_4D_6IO_2$ 271.0097; found 271.0093.

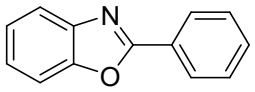
General procedure for C-H arylation of azoles



A dry reaction tube was charged with azoles (0.5 mmol), aryl iodide (0.75 mmol), K_2CO_3 (138.2 mg, 1.0 mmol), Cu_2O@PdCu-3 (1.0 mg) and anhydrous DMF (2 mL) under N_2 atmosphere. Then the mixture was subjected to ultrasonic treatment for ten minutes and stirred at 120 °C for 18 h. The reaction was added water (10 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel chromatography: PE/AcOEt →3/1 to 100/1. The reaction was carried out according to the general reaction procedure, unless otherwise stated. Isolated yields were given based on azoles.

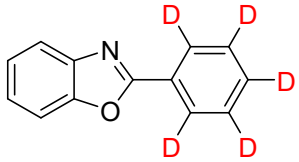


2-(4-methoxyphenyl)benzo[*d*]oxazole (**3a**).[5] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodoanisole (0.75 mmol, 175.5 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 30:1) as white solid (103.6 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.82 – 7.70 (m, 1H), 7.62 – 7.53 (m, 1H), 7.42 – 7.31 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.3, 150.7, 142.3, 129.4, 124.6, 124.4, 119.7, 119.6, 114.4, 110.4, 55.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{12}NO_2$ 226.0863; found 226.0861.

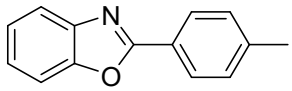


2-Phenylbenzo[*d*]oxazole (**3b**).[5] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), iodobenzene (0.75 mmol, 83.9 μL), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (92.6 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.83 – 7.74 (m, 1H), 7.59 – 7.54 (m, 1H), 7.54 – 7.47 (m, 3H), 7.39 – 7.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 150.8, 142.1, 131.5, 128.9, 127.6,

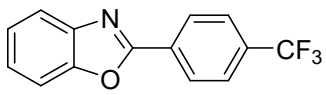
127.2, 125.1, 124.6, 120.0, 110.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{13}H_{10}NO$ 196.0757; found 196.0759.



2-(2-Methylphenyl)benzo[*d*]oxazole-d_5 (**3b-D**).[6] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), iodobenzene-d_5 (0.75 mmol, 81.9 μL), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (85.1 mg, 85% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 1H), 7.59 – 7.53 (m, 1H), 7.36 – 7.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 150.8, 142.1, 131.0 (t, J = 24.2 Hz), 128.4 (t, J = 23.4 Hz), 127.2 (t, J = 24.8 Hz), 127.0, 125.1, 124.6, 120.0, 110.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{13}H_5D_5NO$ 201.1071; found 201.1065.

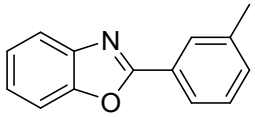


2-(4-Methylphenyl)benzo[*d*]oxazole (**3c**).[7] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodotoluene (0.75 mmol, 163.5 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (83.6 mg, 80% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.2 Hz, 2H), 7.78 – 7.73 (m, 1H), 7.60 – 7.48 (m, 1H), 7.35 – 7.31 (m, 2H), 7.30 (d, J = 8.5 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 150.7, 142.2, 142.1, 129.7, 127.6, 124.9, 124.5, 124.4, 119.9, 110.5, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{12}NO$ 210.0913; found 210.0908.

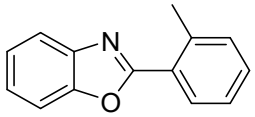


2-[4-(Trifluoromethyl)phenyl]benzo[*d*]oxazole (**3d**).[5] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodobenzotrifluoride (0.75 mmol, 110.2 μL), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 25:1) as white solid (115.8 mg, 88% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.2 Hz, 2H), 7.82 – 7.71 (m, 3H), 7.62 – 7.55 (m, 1H), 7.41 – 7.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5,

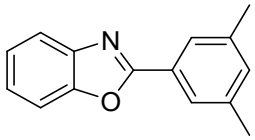
150.9, 141.9, 133.0 (q, J = 32.7 Hz), 130.4, 127.9, 125.9 (q, J = 3.8 Hz), 125.8, 124.9, 123.8 (q, J = 272.5 Hz), 120.4, 110.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_9F_3NO$ 264.0631; found 264.0642.



2-(3-Methylphenyl)benzo[*d*]oxazole (**3e**).[5] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 3-iodotoluene (0.75 mmol, 96.3 μL), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (93.1 mg, 89% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.04 (d, J = 7.7 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.57 – 7.53 (m, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.35 – 7.28 (m, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 150.8, 142.1, 138.7, 132.4, 128.8, 128.2, 127.0, 125.0, 124.8, 124.6, 120.0, 110.6, 21.4. HRMS (ESI) m/z: Calcd. $[M + H]^+$ for $C_{14}H_{12}NO$ 210.0913; found 210.0925.

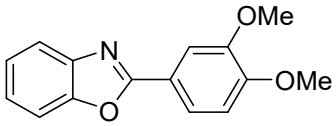


2-(2-Methylphenyl)benzo[*d*]oxazole (**3f**).[6] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 2-iodotoluene (0.75 mmol, 95.5 μL), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (53.3 mg, 51% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 7.3 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.62 – 7.54 (m, 1H), 7.41 (t, J = 7.0 Hz, 1H), 7.38 – 7.32 (m, 4H), 2.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 150.3, 142.2, 138.9, 131.8, 130.9, 130.0, 126.3, 126.1, 125.0, 124.4, 120.2, 110.5, 22.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{12}NO$ 210.0913; found 210.0926.

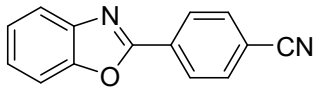


2-[(3,5-Dimethyl)phenyl]benzo[*d*]oxazole (**3g**).[6] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 1-iodo-3,5-dimethylbenzene (0.75 mmol, 108.2 μL), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified

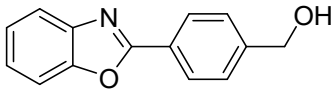
by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (95.9 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.77 – 7.73 (m, 1H), 7.59 – 7.51 (m, 1H), 7.36 – 7.31 (m, 2H), 7.14 (s, 1H), 2.40 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 150.7, 142.1, 138.6, 133.3, 126.9, 125.4, 125.0, 124.5, 119.9, 110.5, 21.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{14}NO$ 224.1070; found 224.1081.



2-(3,4-Dimethoxyphenyl)benzo[*d*]oxazole (**3h**).[8] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 1-iodo-3,4-dimethoxybenzene (0.75 mmol, 198.1 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 15:1) as yellow solid (96.9 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.70 (dd, *J* = 6.0, 2.4 Hz, 2H), 7.50 (dd, *J* = 6.4, 2.5 Hz, 1H), 7.35 – 7.25 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 152.0, 150.7, 149.2, 142.2, 124.7, 124.5, 121.2, 119.7, 119.6, 111.0, 110.4, 110.0, 56.1, 56.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{14}NO_3$ 256.0968; found 256.0961.

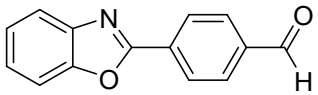


2-(4-Cyanophenyl)benzo[*d*]xazole (**3i**).[9] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodobenzonitrile (0.75 mmol, 171.8 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 35:1) as white solid (93.5 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.6 Hz, 2H), 7.81 – 7.73 (m, 3H), 7.62 – 7.56 (m, 1H), 7.45 – 7.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 150.9, 141.9, 132.7, 131.1, 127.9, 126.2, 125.1, 120.6, 118.2, 114.7, 110.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_9N_2O$ 221.0709; found 221.0702.

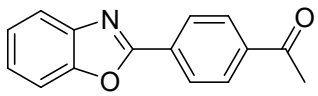


4-(Benzoxazol-2-yl)benzyl alcohol (**3j**). The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodobenzyl alcohol (0.75 mmol, 175.5 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in

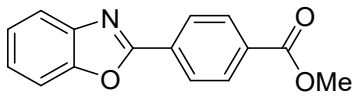
anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 25:1) as white solid (84.4 mg, 75% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17 (d, J = 8.2 Hz, 2H), 7.80 (t, J = 8.9 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.48 – 7.38 (m, 2H), 5.42 (t, J = 5.7 Hz, 1H), 4.62 (d, J = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.9, 150.6, 147.4, 142.0, 127.6, 127.5, 125.9, 125.3, 125.2, 120.2, 111.4, 62.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{12}NO_2$ 226.0863; found 226.0875.



2-[4-(Formyl)phenyl]benzo[*d*]oxazole (**3k**).[10] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodobenzaldehyde (0.75 mmol, 174.0 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 30:1) as white solid (92.5 mg, 83% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.42 (d, J = 8.2 Hz, 2H), 8.03 (d, J = 8.3 Hz, 2H), 7.83 – 7.78 (m, 1H), 7.64 – 7.59 (m, 1H), 7.45 – 7.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 161.6, 151.0, 142.0, 138.0, 132.3, 130.1, 128.1, 126.0, 125.0, 120.5, 110.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{10}NO_2$ 224.0706; found 224.0707.

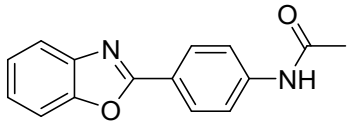


2-(4-Acetylphenyl)benzo[*d*]oxazole (**3l**).[10] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodoacetophenone (0.75 mmol, 184.6 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 25:1) as white solid (86.5 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.6 Hz, 2H), 7.85 – 7.76 (m, 1H), 7.64 – 7.54 (m, 1H), 7.43 – 7.34 (m, 2H), 2.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 150.9, 142.0, 139.0, 131.1, 128.8, 127.8, 125.8, 124.9, 120.4, 120.4, 110.8, 26.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{12}NO_2$ 238.0863; found 238.0862.

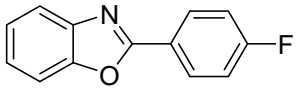


Methyl 4-(benzo[*d*]oxazol-2-yl)benzoate (**3m**).[10] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), methyl 4-

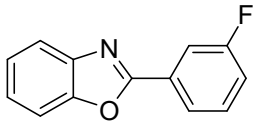
iodobenzoate (0.75 mmol, 196.5 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (94.8 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.6 Hz, 2H), 8.16 (d, *J* = 8.6 Hz, 2H), 7.82 – 7.74 (m, 1H), 7.61 – 7.55 (m, 1H), 7.40 – 7.33 (m, 2H), 3.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 161.9, 150.9, 142.0, 132.5, 131.0, 130.1, 127.5, 125.7, 124.9, 120.4, 110.8, 52.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{12}NO_3$ 254.0812; found 254.0821.



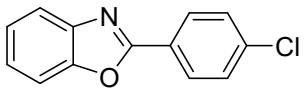
2-(4-Acetaminopyridinyl)benzo[*d*]xazole (**3n**).[11] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), *N*-(4-iodophenyl)acetamide (0.75 mmol, 195.8 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 3:1) as white solid (109.6 mg, 87% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.30 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.77 – 7.73 (m, 1H), 7.73 – 7.69 (m, 1H), 7.43 – 7.32 (m, 2H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.4, 162.7, 150.6, 143.0, 142.1, 128.6, 125.5, 125.2, 121.1, 119.9, 119.5, 111.2, 24.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{13}N_2O_2$ 253.0972; found 253.0968.



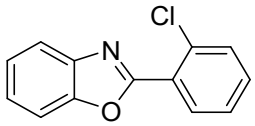
2-(4-Fluorophenyl)benzo[*d*]oxazole (**3o**).[7] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-fluoro-iodobenzene (0.75 mmol, 86.5 μL), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (93.7 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 – 8.20 (m, 2H), 7.78 – 7.71 (m, 1H), 7.59 – 7.51 (m, 1H), 7.36 – 7.30 (m, 2H), 7.18 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8 (d, *J* = 252.8 Hz), 162.2, 150.8, 142.1, 129.8 (d, *J* = 8.8 Hz), 125.1, 124.7, 123.5 (d, *J* = 3.2 Hz), 120.0, 116.2 (d, *J* = 22.2 Hz), 110.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{13}H_9FNO$ 214.0663; found 214.0666.



2-(3-Fluorophenyl)benzo[*d*]oxazole (**3p**).[12] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 1-fluoro-3-iodobenzene (0.75 mmol, 88.1 μL), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (89.5 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 9.1 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.59 – 7.54 (m, 1H), 7.50 – 7.44 (m, 1H), 7.40 – 7.33 (m, 2H), 7.21 (td, *J* = 8.3, 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (d, *J* = 246.9 Hz), 161.8 (d, *J* = 3.4 Hz), 150.8, 141.9, 130.6 (d, *J* = 8.1 Hz), 129.2 (d, *J* = 8.6 Hz), 125.5, 124.8, 123.3 (d, *J* = 3.1 Hz), 120.2, 118.5 (d, *J* = 21.3 Hz), 114.6 (d, *J* = 24.1 Hz), 110.7. HRMS (ESI) m/z: Calcd. $[M + H]^+$ for $C_{13}H_9FNO$ 214.0663; found 214.0657.

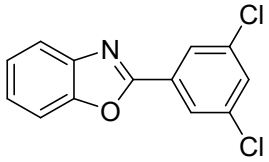


2-(4-Chlorophenyl)benzo[*d*]oxazole (**3q**).[12] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 1-chloro-4-iodobenzene (0.75 mmol, 178.8 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (96.2 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.80 – 7.70 (m, 1H), 7.57 – 7.50 (m, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 150.7, 142.0, 137.8, 129.3, 128.8, 125.7, 125.4, 124.8, 120.1, 110.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{13}H_9ClNO$ 230.0367; found 230.0374.

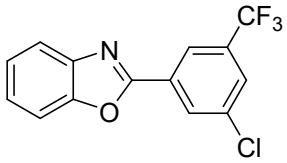


2-(2-Chlorophenyl)benzo[*d*]oxazole (**3r**).[13] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 1-chloro-2-iodobenzene (0.75 mmol, 91.6 μL), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 25:1) as yellow liquid (74.7 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.82 – 7.72 (m, 1H), 7.59 – 7.52 (m,

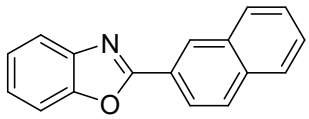
1H), 7.49 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.41 – 7.27 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161,0 150.6, 141.7, 133.5, 131.9, 131.9, 131.4, 127.0, 126.3, 125.6, 124.7, 120.5, 110.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{13}H_9ClNO$ 230.0367; found 230.0363.



2-(3,5-Dichlororomethyl)benzo[*d*]oxazole (**3s**).[13] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 1,3-dichloro-5-iodobenzene (0.75 mmol, 204.7 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (91.1 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.9 Hz, 2H), 7.83 – 7.72 (m, 1H), 7.63 – 7.54 (m, 1H), 7.49 (t, *J* = 1.9 Hz, 1H), 7.44 – 7.32 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 150.8, 141.7, 135.8, 131.2, 129.9, 125.9, 125.8, 125.1, 120.4, 110.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{13}H_8Cl_2NO$ 263.9977; found 263.9971.

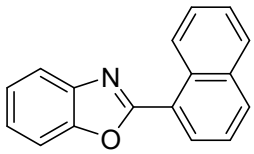


2-(3-Chloro-5-trifluoromethyl)benzo[*d*]oxazole (**3t**). The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 1-chloro-3-iodo-5-(trifluoromethyl)benzene (0.75 mmol, 229.9 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 80:1) as white solid (125.1 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 2H), 7.81 – 7.75 (m, 1H), 7.74 (s, 1H), 7.63 – 7.54 (m, 1H), 7.48 – 7.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 150.8, 141.7, 135.9, 133.1 (q, *J* = 33.7 Hz), 130.6, 129.7, 128.0 (q, *J* = 3.6 Hz), 126.2, 125.2, 122.7 (q, *J* = 271.2 Hz), 122.6 (q, *J* = 3.7 Hz), 120.5, 110.89. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_8ClF_3NO$ 298.0241; found 298.0233.

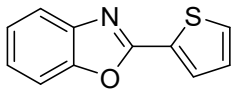


2-(2-Naphthalenyl)benzo[*d*]oxazole (**3u**).[5] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 2-iodonaphthalene (0.75 mmol, 190.6 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography

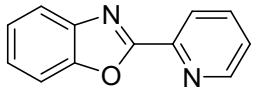
on silica gel (PE/AcOEt 100:1) as white solid (90.7 mg, 74% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.29 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.85 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.63 – 7.56 (m, 1H), 7.55 – 7.48 (m, 2H), 7.41 – 7.32 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 150.9, 142.2, 134.8, 133.0, 129.0, 128.8, 128.2, 127.9, 127.8, 126.9, 125.2, 124.7, 124.4, 124.0, 120.1, 110.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{12}NO$ 246.0913; found 246.0907.



2-(1-Naphthalenyl)benzo[*d*]oxazole (**3v**).[5] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 1-iodonaphthalene (0.75 mmol, 190.6 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 25:1) as yellow solid (105.4 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (d, *J* = 8.7 Hz, 1H), 8.43 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.72 (t, *J* = 7.3 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.37 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 150.2, 142.4, 134.0, 132.3, 130.7, 129.4, 128.7, 128.0, 126.5, 126.4, 125.3, 125.0, 124.5, 123.6, 120.3, 110.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{12}NO$ 246.0913; found 246.0916.

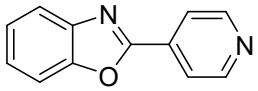


2-(2-Thienyl)benzo[*d*]oxazole (**3w**).[7] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 2-iodothiophene (0.75 mmol, 82.8 μL), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as yellow solid (32.2 mg, 32% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 3.7 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.58 – 7.51 (m, 2H), 7.35 – 7.30 (m, 2H), 7.18 (t, *J* = 3.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 150.5, 142.0, 130.3, 130.0, 129.7, 128.3, 125.1, 124.8, 119.8, 110.5. HRMS (ESI): $[M + H]^+$ m/z Calcd. for $C_{11}H_8NOS$ 202.0321; found 202.0317.

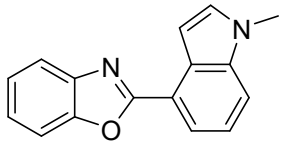


2-(2-Pyridinyl)benzo[*d*]xazole (**3x**).[5] The compound was prepared according to the

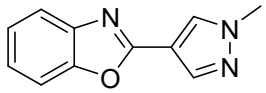
general procedure using benzoxazole (0.5 mmol, 59.6 mg), 2-iodopyridine (0.75 mmol, 153.8 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 7:1) as yellow solid (77.4 mg, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.7 Hz, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 7.82 – 7.64 (m, 2H), 7.61 – 7.47 (m, 1H), 7.39 – 7.26 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4 151.0, 150.2, 146.0, 141.7, 137.0, 126.0, 125.5, 124.9, 123.4, 120.5, 111.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{12}H_9N_2O$ 197.0709; found 197.0722.



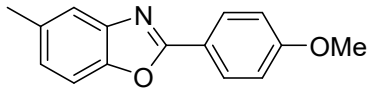
2-(4-Pyridinyl)benzo[*d*]xazole (**3y**).[7] The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodopyridine (0.75 mmol, 153.8 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 25:1) as faint yellow solid (72.6 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 6.1 Hz, 2H), 8.05 (d, *J* = 6.1 Hz, 2H), 7.84 – 7.76 (m, 1H), 7.64 – 7.55 (m, 1H), 7.43 – 7.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 150.9, 150.7, 141.7, 134.3, 126.3, 125.1, 121.0, 120.7, 111.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{12}H_9N_2O$ 197.0709; found 197.0718.



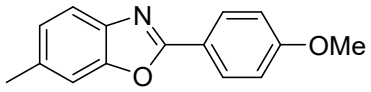
1-Methyl-4-(benzoxazol-2-yl)-1*H*-indole (**3z**). The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodo-1-methyl-1*H*-indole (0.75 mmol, 192.8 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 17:1) as white solid (102.9 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.2 Hz, 1H), 8.15 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.85 – 7.73 (m, 1H), 7.59 – 7.54 (m, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.09 (d, J = 3.1 Hz, 1H), 6.61 (dd, J = 3.1, 0.6 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 150.8, 142.6, 138.4, 130.3, 128.5, 124.3, 124.3, 121.4, 121.3, 119.5, 118.4, 110.3, 109.7, 102.4, 33.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{16}H_{13}N_2O$ 249.1022; found 249.1030.



2-(1-Methyl-1*H*-pyrazol-4-yl)benzo[*d*]oxazole (**3aa**). The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), 4-iodo-1-methyl-1*H*-pyrazole (0.75 mmol, 56.0 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 6:1) as yellow solid (58.7 mg, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.04 (s, 1H), 7.70 – 7.64 (m, 1H), 7.51 – 7.46 (m, 1H), 7.32 – 7.25 (m, 2H), 3.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 150.1, 141.9, 139.2, 130.8, 124.5, 124.5, 119.3, 111.2, 110.2, 39.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{11}H_{10}N_3O$ 200.0818; found 200.0824.

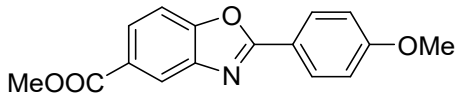


2-(4-Methoxyphenyl)-5-methyl-benzo[*d*]oxazole (**3ab**).[8] The compound was prepared according to the general procedure using 5-methylbenzoxazole (0.5 mmol, 99.9 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (77.7 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.9 Hz, 2H), 7.49 (s, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.08 (dd, J = 8.2, 0.8 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 162.2, 148.9, 142.5, 134.2, 129.3, 125.7, 119.9, 119.6, 114.3, 109.7, 55.4, 21.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{14}NO_2$ 240.1019; found 240.1023.

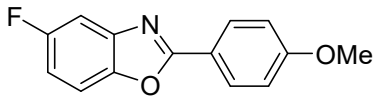


2-(4-Methoxyphenyl)-6-methyl-benzo[*d*]oxazole (**3ac**).[14] The compound was prepared according to the general procedure using 6-methylbenzoxazole (0.5 mmol, 99.8 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 70:1) as faint red solid (102.8 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.1 Hz, 1H), 7.28 (s, 1H), 7.09 (dd, J = 8.1, 0.4 Hz, 1H), 6.95 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 162.1, 150.9, 140.1, 135.0, 129.2, 125.6,

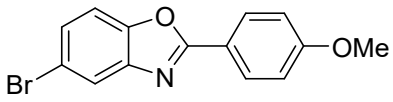
119.9, 118.9, 114.3, 110.6, 55.4, 21.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{14}NO_2$ 240.1019; found 240.1025.



Methyl 2-(4-methoxyphenyl)benzo[*d*]oxazole-5-carboxylate (**3ad**). The compound was prepared according to the general procedure using methyl 1,3-benzoxazole-5-carboxylate (0.5 mmol, 88.6 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 10:1) as white solid (79.2 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.14 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.93 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 164.4, 162.7, 153.6, 142.4, 129.6, 126.8, 126.6, 121.5, 119.0, 114.4, 110.1, 55.5, 52.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{16}H_{14}NO_4$ 284.0917; found 284.0913.

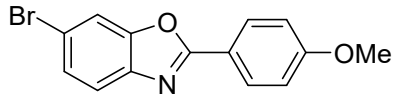


2-(4-Methoxyphenyl)-5-fluoro-benzo[*d*]oxazole (**3ae**).[15] The compound was prepared according to the general procedure using 5-fluorobenzoxazole (0.5 mmol, 68.6 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (86.3 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.0 Hz, 2H), 7.44 (dd, *J* = 8.8, 4.3 Hz, 1H), 7.39 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.06 – 6.96 (m, 3H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 162.6, 160.1 (d, *J* = 240.1 Hz), 147.0, 143.2 (d, *J* = 13.2 Hz), 129.5, 119.4, 114.4, 112.1 (d, *J* = 26.3 Hz), 110.6 (d, *J* = 10.2 Hz), 106.1 (d, *J* = 25.7 Hz), 55.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{11}FNO_2$ 244.0768; found 244.0776.

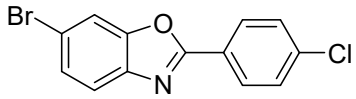


5-Bromo-2-(4-methoxyphenyl)benzo[*d*]oxazole (**3af**).[16] The compound was prepared according to the general procedure using 5-bromobenzooxazole (0.5 mmol, 99.0 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 200:1) as white solid (69.0 mg, 46% yield).

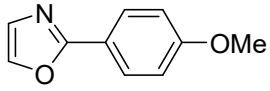
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.9 Hz, 2H), 7.84 (s, 1H), 7.40 (s, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 162.7, 149.7, 144.0, 129.6, 127.5, 122.6, 119.1, 117.1, 114.4, 111.6, 55.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{11}BrNO_2$ 303.9968; found 303.9963.



6-Bromo-2-(4-methoxyphenyl)benzo[*d*]oxazole (**3ag**). The compound was prepared according to the general procedure using 6-bromobenzooxazole (0.5 mmol, 99.0 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 10:1) as white solid (94.2 mg, 62% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.43 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 162.6, 151.2, 141.5, 129.5, 127.8, 120.5, 119.1, 117.4, 114.5, 113.9, 55.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{11}BrNO_2$ 303.9968; found 303.9961.

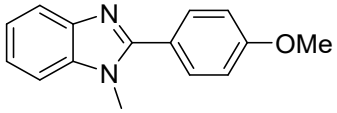


6-Bromo-2-(4-chlorophenyl)benzo[*d*]oxazole (**3ah**).[17] The compound was prepared according to the general procedure using 6-bromobenzo[*d*]oxazole (0.5 mmol, 99.0 mg), 1-chloro-4-iodobenzene (0.75 mmol, 178.8 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 200:1) as white solid (109.6 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.43 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.2, 138.2, 129.4, 128.9, 128.2, 125.1, 121.0, 118.3, 114.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{13}H_8BrClNO$ 307.9472; found 307,9468.

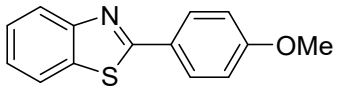


2-(4-Methoxyphenyl)oxazole (**3ai**).[18] The compound was prepared according to the general procedure using oxazole (0.5 mmol, 49.4 μL), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel

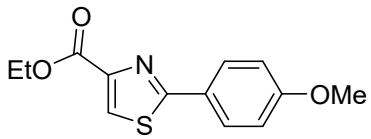
(PE/AcOEt 30:1) as colorless liquid (39.4 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.65 (s, 1H), 7.18 (s, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 161.3, 138.0, 128.2, 128.0, 120.4, 114.2, 55.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{10}H_{10}NO_2$ 176.0706; found 176.0702.



2-(4-Methoxy-phenyl)-1-methyl-1*H*-benzoimidazole (**3aj**).[9] The compound was prepared according to the general procedure using 1-methyl-1*H*-benzo[d]imidazole (0.5 mmol, 66.1 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_3PO_4 (1.0 mmol, 212.3 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 3:1) as yellow solid (77.4 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.33 – 7.26 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 153.8, 143.0, 136.6, 130.9, 122.6, 122.5, 122.3, 119.6, 114.2, 109.5, 55.4, 31.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{15}N_2O$ 239.1179; found 239.1176.

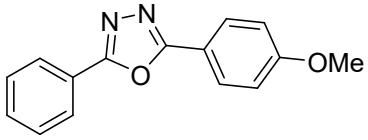


2-(4-Methoxyphenyl)benzo[*d*]thiazole (**3ak**).[9] The compound was prepared according to the general procedure using benzothiazole (0.5 mmol, 54.6 μL), 4-iodoanisole (0.75 mmol, 184.6 mg), K_3PO_4 (1.0 mmol, 212.3 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 100:1) as white solid (65.1 mg, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.9 Hz, 3H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 161.9, 154.2, 134.9, 129.1, 126.5, 126.2, 124.8, 122.8, 121.5, 114.4, 55.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{12}NOS$ 242.0634; found 242.0627.

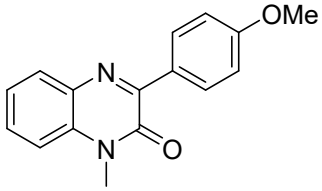


Ethyl 2-(4-methoxyphenyl)thiazole-4-carboxylate (**3al**). The compound was prepared according to the general procedure using ethyl thiazole-4-carboxylate (0.5 mmol, 78.6 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1.0 mmol, 138.2 mg) and

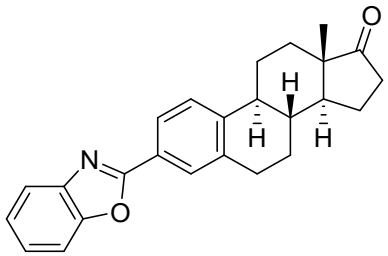
Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 10:1) as faint yellow solid (56.6 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 161.7, 161.5, 147.9, 128.5, 126.2, 125.8, 114.3, 61.4, 55.4, 14.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{13}H_{14}NO_3S$ 264.0689; found 264.0693.



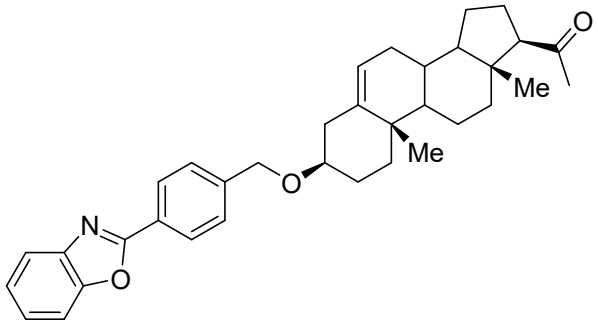
2-(4-Methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (**3am**). The compound was prepared according to the general procedure using 2-phenyl-1,3,4-oxadiazole (0.5 mmol, 73.1 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1.0 mmol, 138.2 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 5:1) as faint yellow solid (64.3 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.44 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.1, 162.4, 131.5, 129.0, 128.7, 126.8, 124.1, 116.4, 114.5, 55.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{13}N_2O_2$ 253.0972; found 253.0980.



3-(4-Methoxyphenyl)-1-methylquinoxalin-2(*1H*)-one (**3an**). The compound was prepared according to the general procedure using quinoxolone (0.5 mmol, 80.1 mg), 4-iodoanisole (0.75 mmol, 184.6 mg), K_2CO_3 (1.0 mmol, 138.2 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 5:1) as faint yellow solid (122.5 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.9 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 154.9, 153.2, 133.2, 133.2, 131.4, 130.2, 129.8, 128.8, 123.7, 113.5, 113.4, 55.4, 29.3.HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{16}H_{15}N_2O_2$ 267.1128; found 267.1129.

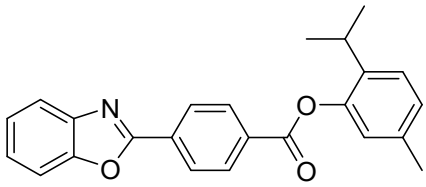


3-(Benzoxazol-2-yl)-1,3,5(10)-trien-17-one (**3ao**). The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), iodoestrone **2ao** (0.75 mmol, 285.2 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 15:1) as white solid (98.3 mg, 53% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.78 – 7.69 (m, 1H), 7.59 – 7.48 (m, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.28 (m, 2H), 3.18 – 2.73 (m, 2H), 2.49 (dd, *J* = 18.9, 8.7 Hz, 1H), 2.43 (dd, *J* = 13.2, 3.0 Hz, 1H), 2.31 (td, *J* = 11.2, 4.0 Hz, 1H), 2.20 – 2.08 (m, 1H), 2.08 – 2.00 (m, 2H), 1.97 (d, *J* = 12.5 Hz, 1H), 1.74 – 1.53 (m, 3H), 1.53 – 1.40 (m, 3H), 0.91 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 150.7, 143.8, 142.1, 137.4, 128.2, 128.1 126.0, 125.0, 124.9, 124.6, 124.5, 119.9, 110.5, 50.5, 47.9, 44.6, 37.9, 35.8, 31.6, 29.3, 26.3, 25.6, 21.6, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{25}H_{26}NO_2$ 372.1958; found 372.1951.

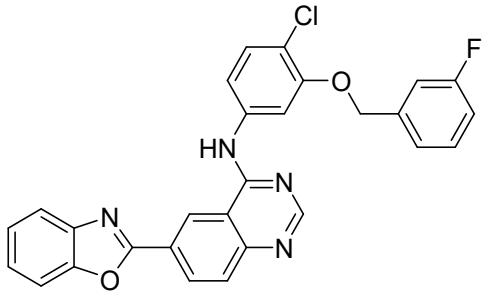


1-((*3R*,*10S*,*13R*,*17R*)-3-((4-(Benzo[d]oxazol-2-yl)benzyl)oxy)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one (**3ap**). The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), **2ap** (0.75 mmol, 399.4 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 30:1) as white solid (120.3 mg, 46% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 2H), 7.81 – 7.74 (m, 1H), 7.60 – 7.55 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.31 (m, 2H), 5.36 (d, *J* = 5.1 Hz, 1H), 4.64 (s, 2H), 3.39 – 3.22 (m, 1H), 2.52 (t, *J* = 8.9 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.37 – 2.24 (m, 1H), 2.22 – 2.16 (m, 1H), 2.12 (d, *J* = 3.3 Hz,

3H), 2.06 – 1.96 (m, 3H), 1.93 – 1.80 (m, 1H), 1.68 – 1.56 (m, 3H), 1.54 – 1.41 (m, 3H), 1.30 – 1.21 (m, 3H), 1.08 – 0.99 (m, 4H), 0.98 – 0.86 (m, 2H), 0.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 163.0, 150.7, 143.0, 142.1, 140.8, 127.8, 127.7, 126.2, 125.1, 124.6, 121.5, 120.0, 110.6, 79.0, 69.5, 63.7, 56.9, 50.0, 44.0, 39.1, 38.8, 37.2, 36.9, 31.9, 31.8, 31.6, 28.4, 24.5, 22.8, 21.1, 19.4, 13.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{35}H_{42}NO_3$ 524.3159; found 524.3153.

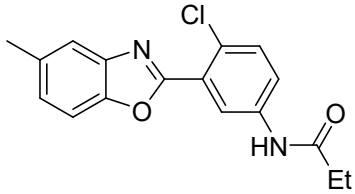


2-Isopropyl-5-methylphenyl 4-(benzo[d]oxazol-2-yl)benzoate (**3aq**). The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), **2aq** (0.75 mmol, 285.2 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 10:1) as white solid (137.4 mg, 74% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 8.4 Hz, 2H), 8.38 (d, J = 8.4 Hz, 2H), 7.91 – 7.80 (m, 1H), 7.66 – 7.58 (m, 1H), 7.45 – 7.36 (m, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 6.99 (s, 1H), 3.10 (sept, J = 6.9 Hz, 1H), 2.37 (s, 3H), 1.26 (d, J = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 161.8, 150.9, 148.1, 142.1, 137.2, 136.8, 132.0, 131.6, 130.7, 127.7, 127.4, 126.6, 125.9, 125.0, 122.8, 120.5, 110.9, 27.3, 23.1, 20.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{22}NO_3$ 372.1594; found 372.1590.

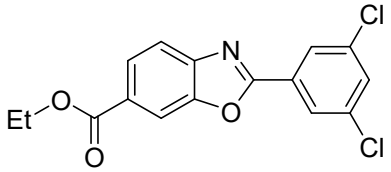


6-(Benzo[*d*]oxazol-2-yl)-N-(3-chloro-5-((3-fluorobenzyl)oxy)phenyl)quinazolin-4-amine (**3ar**). The compound was prepared according to the general procedure using benzoxazole (0.5 mmol, 59.6 mg), **2ar** (0.75 mmol, 379.3 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 3:1) as yellow solid (106.8 mg, 43% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.17 (s, 1H), 9.27 (d, J =

1.3 Hz, 1H), 8.57 (s, 1H), 8.43 (dd, *J* = 8.7, 1.6 Hz, 1H), 8.02 (d, *J* = 2.6 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.77 (dd, *J* = 9.1, 2.3 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.42 – 7.36 (m, 2H), 7.35 – 7.26 (m, 2H), 7.21 (dd, *J* = 9.0, 3.6 Hz, 1H), 7.16 (dt, *J* = 8.3, 4.3 Hz, 1H), 5.21 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 163.6, 162.2, 161.7, 157.3 (d, *J* = 239.9 Hz), 151.8, 150.8, 150.3, 142.0, 140.1 (d, *J* = 7.5 Hz), 133.4, 131.2, 131.0 (d, *J* = 8.3 Hz), 129.3, 126.2, 125.5, 124.7, 124.3, 123.7 (d, *J* = 2.7 Hz), 123.4, 122.8, 121.5, 120.3, 115.2, 115.0, 114.5, 114.4, 111.3, 69.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{19}ClFN_4O_2$ 497.1175; found 497.1168.

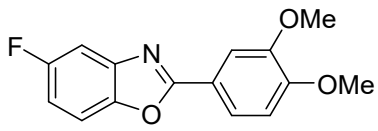


2-(4-Propionamido-4-chlorophenyl)-5-methyl-benzo[*d*]oxazole (**3as**).[19] The compound was prepared according to the general procedure using 5-methylbenzo[*d*]oxazole (0.5 mmol, 66.6 mg), **2as** (0.75 mmol, 232.1 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 5:1) as white solid (70.8 mg, 45% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.34 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 1.9 Hz, 1H), 7.67 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.58 (s, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.3, 160.7, 148.6, 143.2, 141.9, 134.7, 132.9, 132.7, 127.1, 120.8, 120.1, 119.7, 117.9, 110.7, 30.1, 21.5, 9.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{16}ClN_2O_2$ 315.0895; found 315.0885.

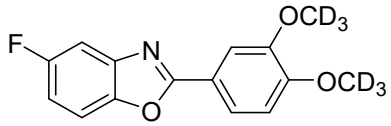


Ethyl 2-(3,5-dichlorophenyl)benzo[*d*]oxazole-6-carboxylate (**3at**).[20] The compound was prepared according to the general procedure using ethyl benzo[d]oxazole-6-carboxylate (0.5 mmol, 95.6 mg), 1,3-dichloro-5-iodobenzene (0.75 mmol, 204.7 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (5.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 10:1) as white solid (109.3 mg, 65% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 1.0 Hz, 1H), 8.14 – 8.04 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 1.9 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9,

162.7, 150.4, 145.4, 135.9, 131.8, 129.3, 128.3, 126.7, 126.1, 119.9, 112.4, 61.4, 14.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{16}H_{12}Cl_2NO_3$ 336.0189; found 346.0181.



2-(3,4-Dimethoxyphenyl)-5-fluoro-benzo[*d*]oxazole (**3au**).[21] The compound was prepared according to the general procedure using 5-fluoro-1,3-benzoxazole (0.5 mmol, 68.6 mg), 4-iodo-1,2-dimethoxybenzene (0.75 mmol, 198.1 mg), K_2CO_3 (1 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 15:1) as white solid (84.7 mg, 62% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.64 (d, *J* = 1.9 Hz, 1H), 7.38 (dd, *J* = 8.8, 4.3 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.97 (td, *J* = 9.1, 2.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 160.1 (d, *J* = 240.1 Hz), 152.2, 149.2 (s), 147.0, 143.0 (d, *J* = 13.3 Hz), 121.3, 119.3, 112.1 (d, *J* = 26.3 Hz), 111.0, 110.5 (d, *J* = 10.1 Hz), 109.9, 106.0 (d, *J* = 25.6 Hz), 56.1, 55.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{13}FNO_3$ 274.0874; found 274.0867.



2-(3,4-Dimethoxyphenyl)-5-fluoro-benzo[*d*]oxazole-d_6 (**3av**).[21] The compound was prepared according to the general procedure using 5-fluoro-1,3-benzoxazole (0.5 mmol, 68.6 mg), 4-iodo-1,2-dimethoxybenzene-d_6 **2av** (0.75 mmol, 202.6 mg), K_2CO_3 (1.0 mmol, 138.0 mg) and Cu_2O@PdCu-3 (1.0 mg) in anhydrous DMF (2 mL). The crude product was purified by column chromatography on silica gel (PE/AcOEt 15:1) as white solid (88.0 mg, 63% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.69 (d, *J* = 1.5 Hz, 1H), 7.44 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.03 (td, *J* = 9.0, 2.5 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 160.1 (d, *J* = 240.2 Hz), 152.2, 149.2, 146.9, 143.1 (d, *J* = 13.2 Hz), 121.9, 119.4, 112.1 (d, *J* = 26.2 Hz), 111.0, 110.6 (d, *J* = 10.2 Hz), 109.9, 106.0 (d, *J* = 25.7 Hz), 55.4 (sept, *J* = 11.4 Hz), 55.1 (sept, *J* = 10.9 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_7D_6FNO_3$ 280.1251; found 280.1246.

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Copies of ^{1}H and ^{13}C NMR Spectra

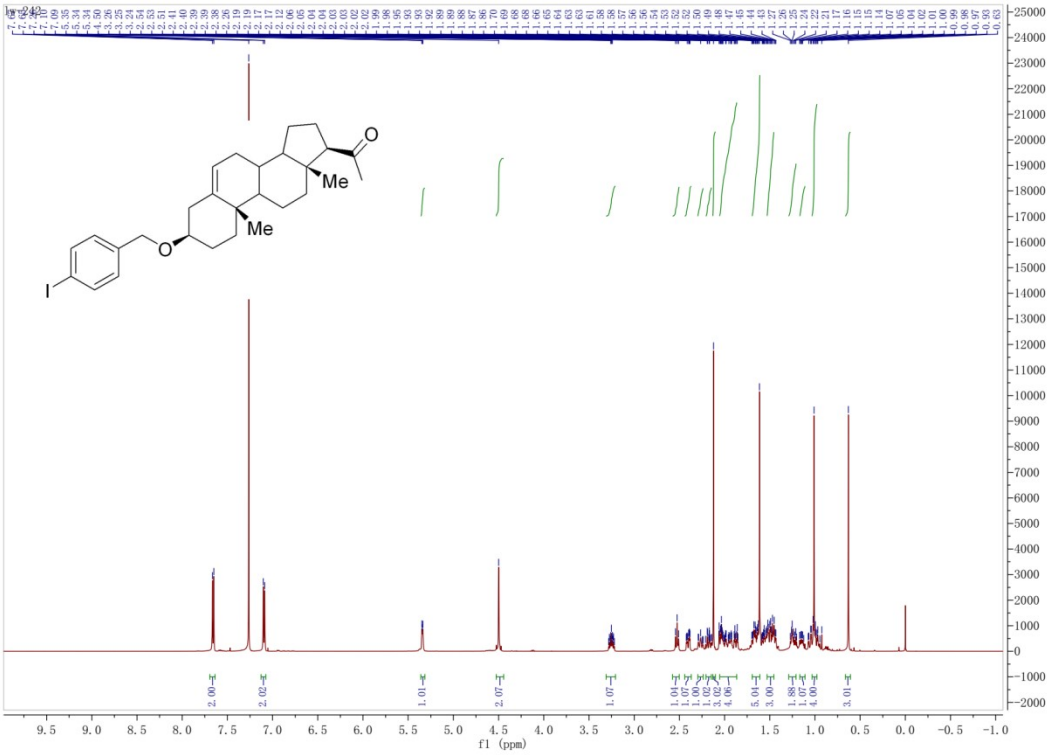

Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **2ap**

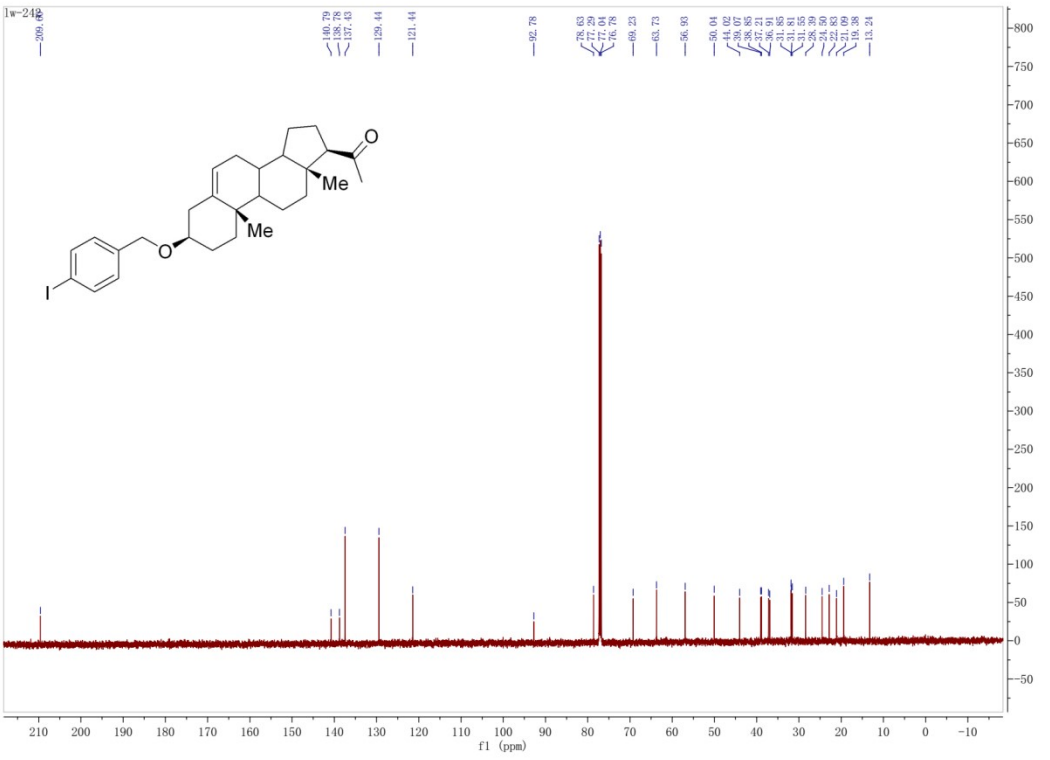

Figure S21. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **2ap**

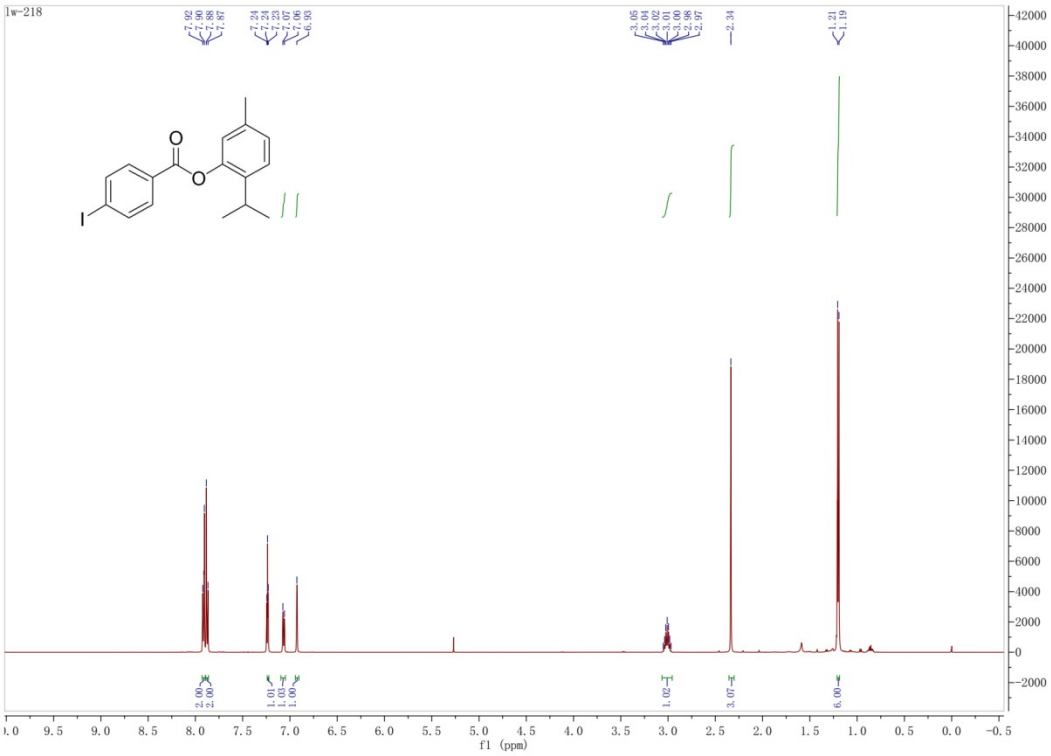

Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **2aq**

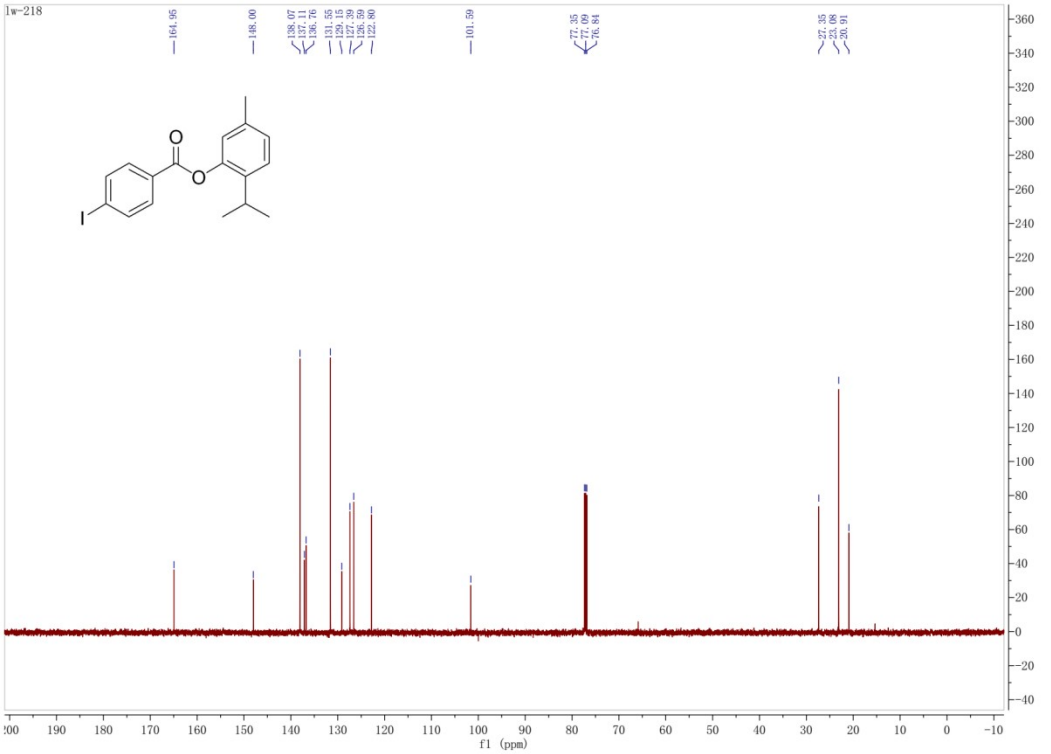

Figure S23. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **2aq**

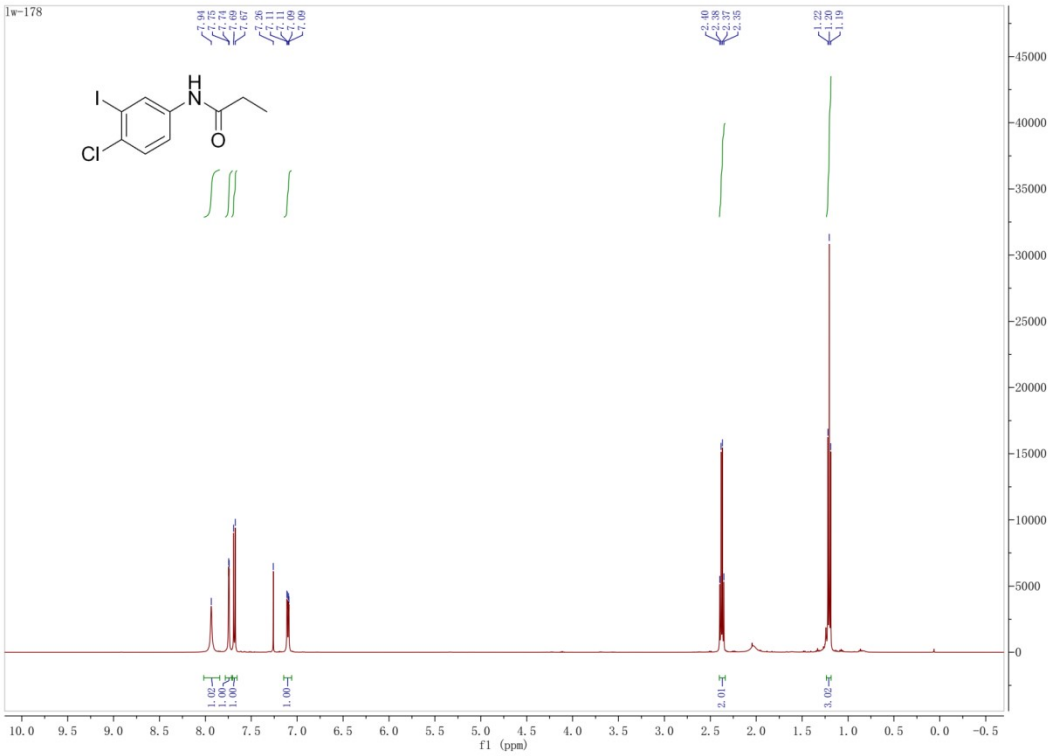

Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **2as**

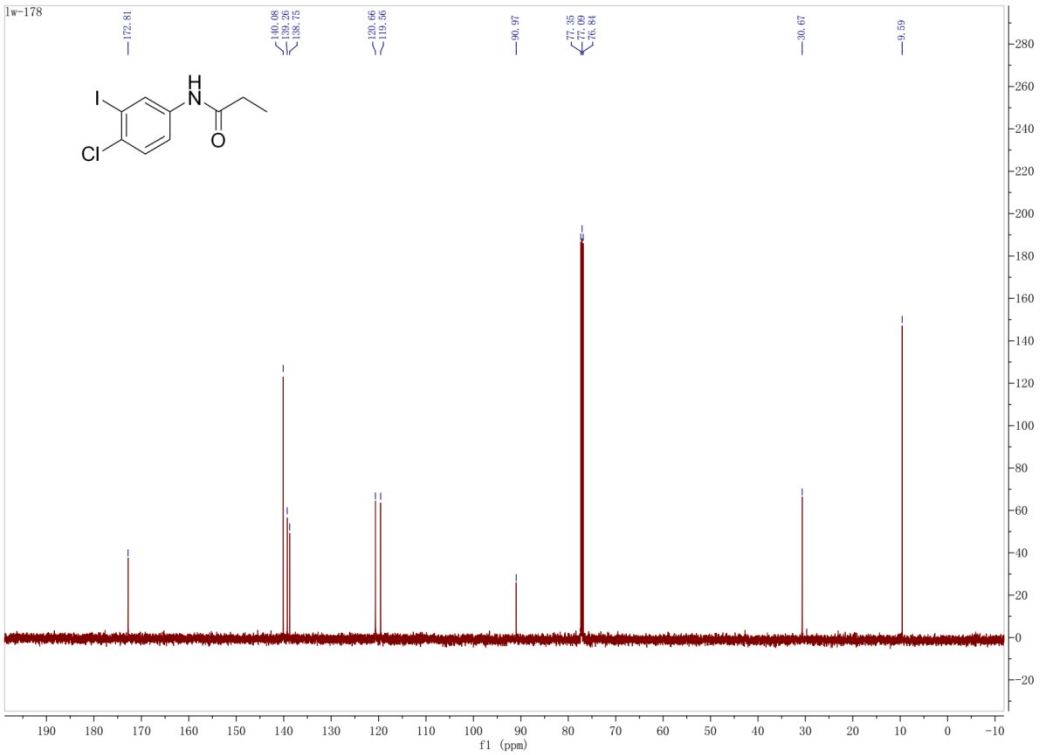

Figure S25. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **2as**

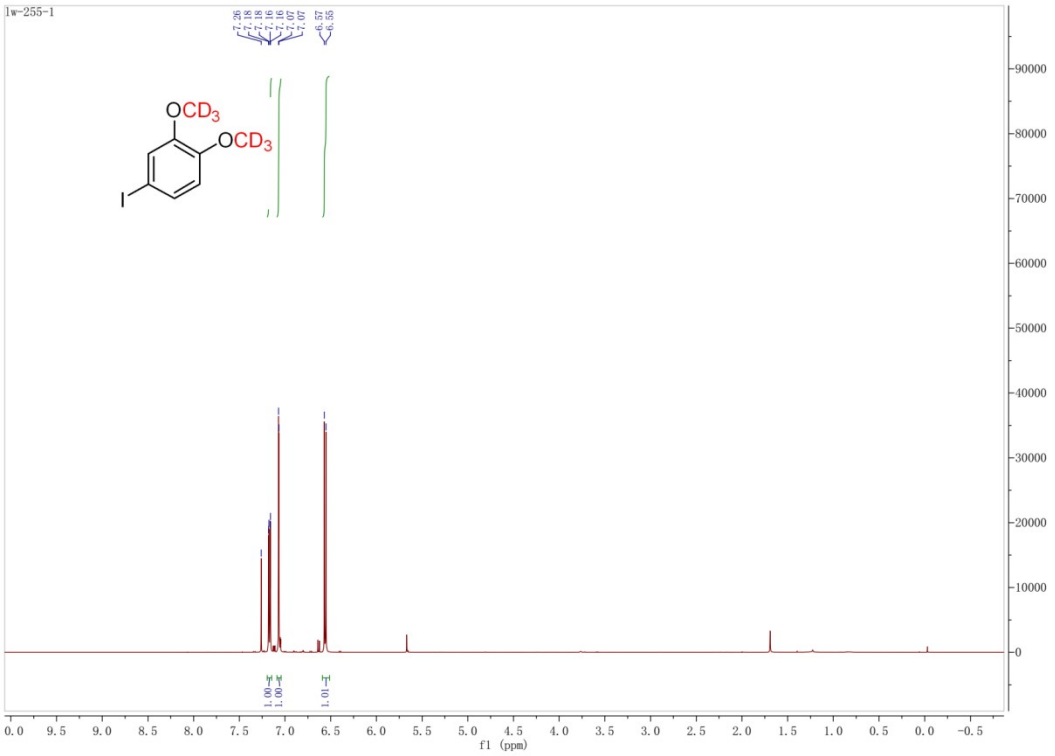

Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **2av**

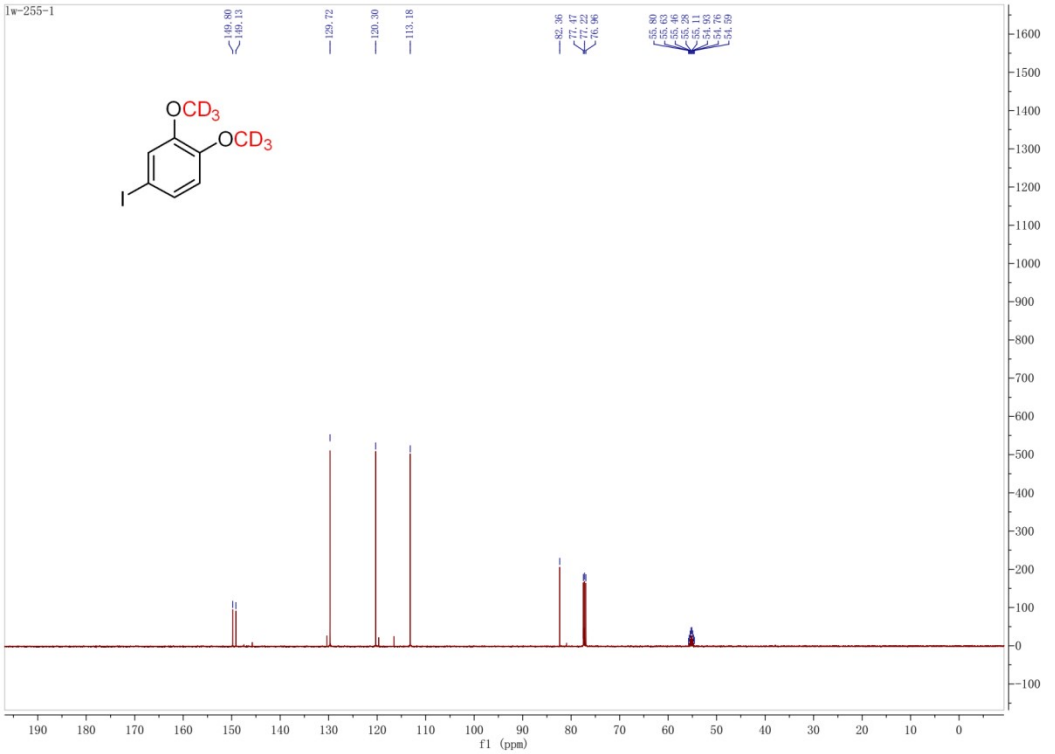

Figure S27. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **2av**

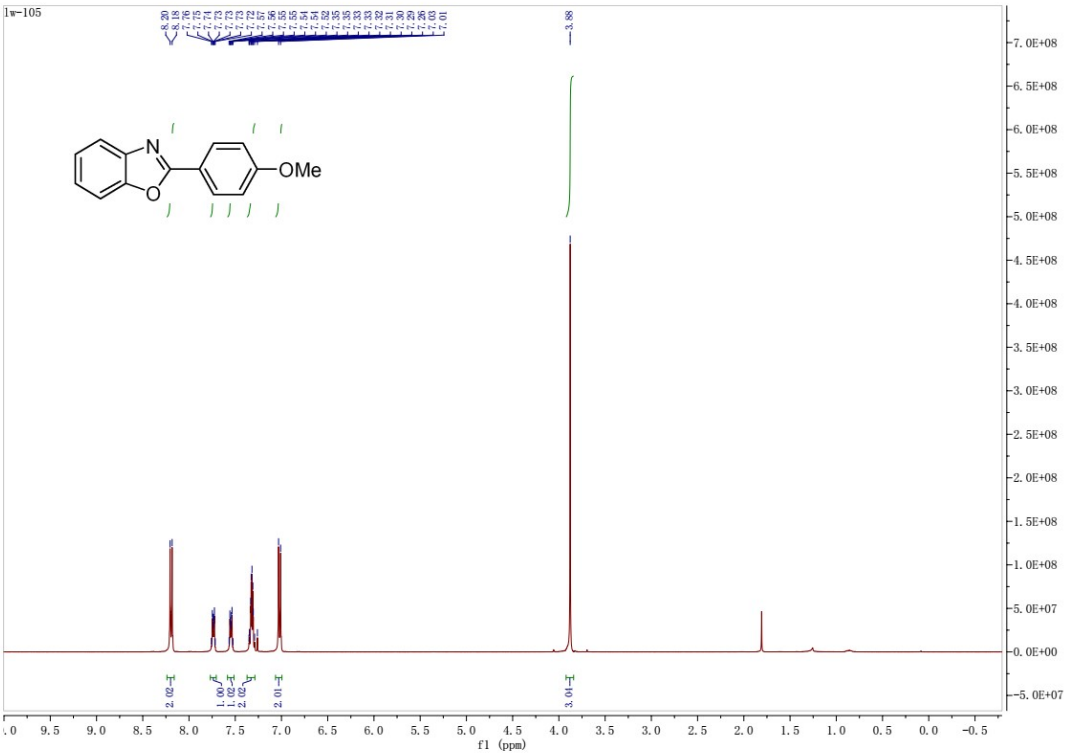

Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3a**

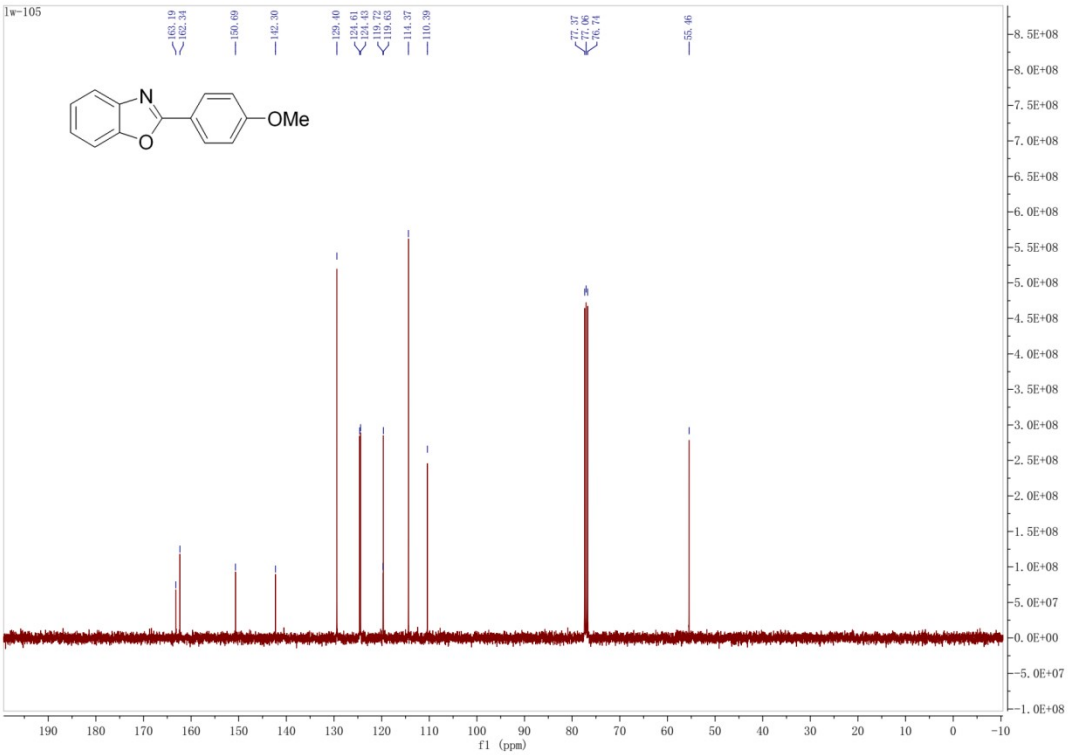

Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3a**

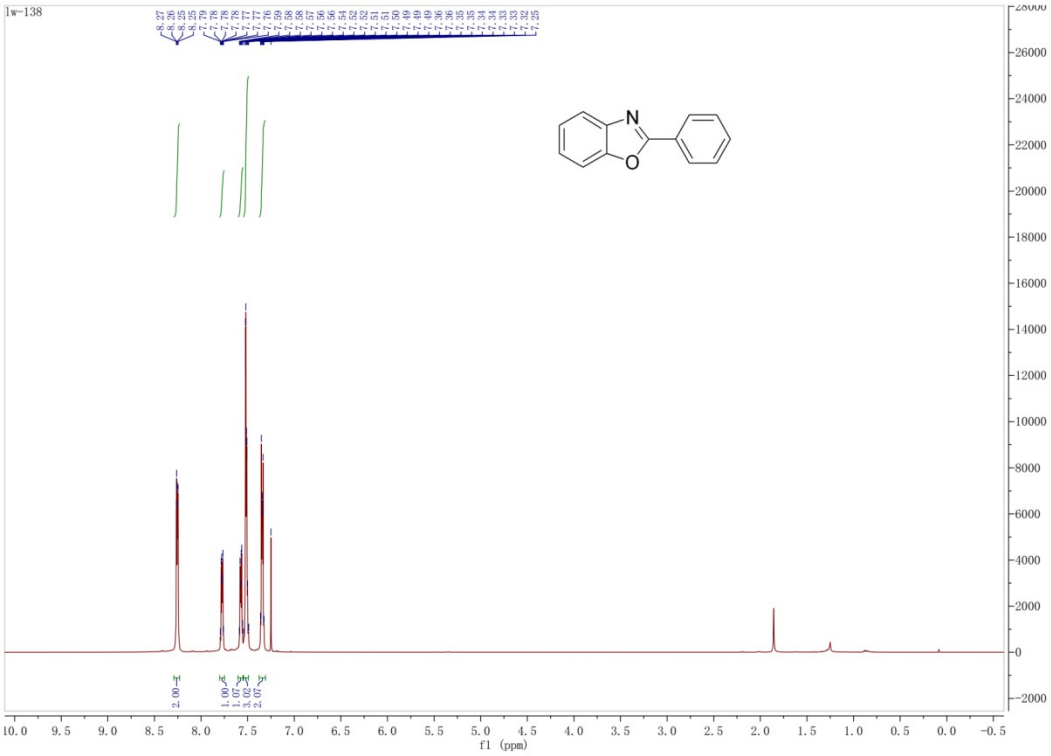

Figure S30. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3b**

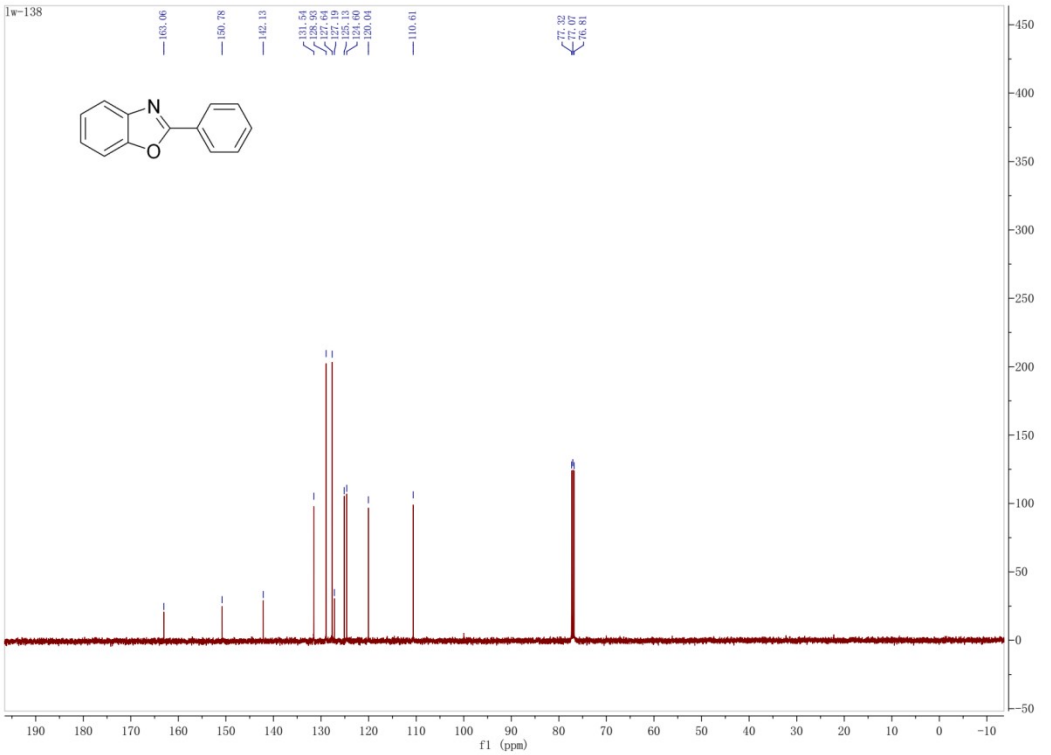

Figure S31. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3b**

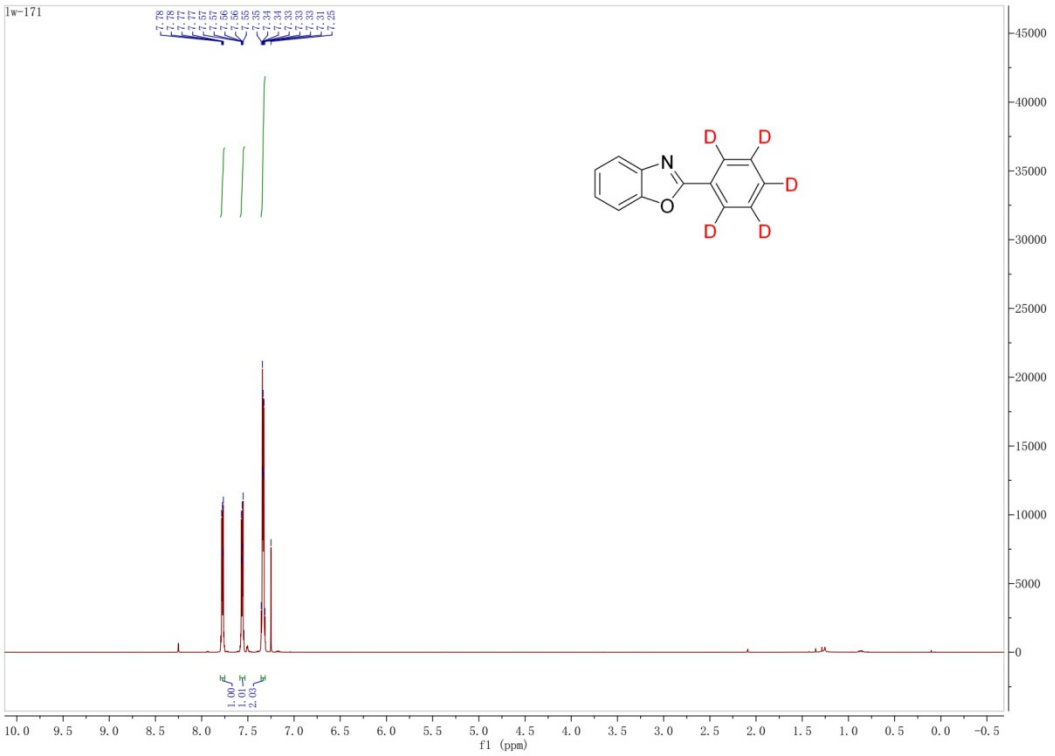

Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3b-D**

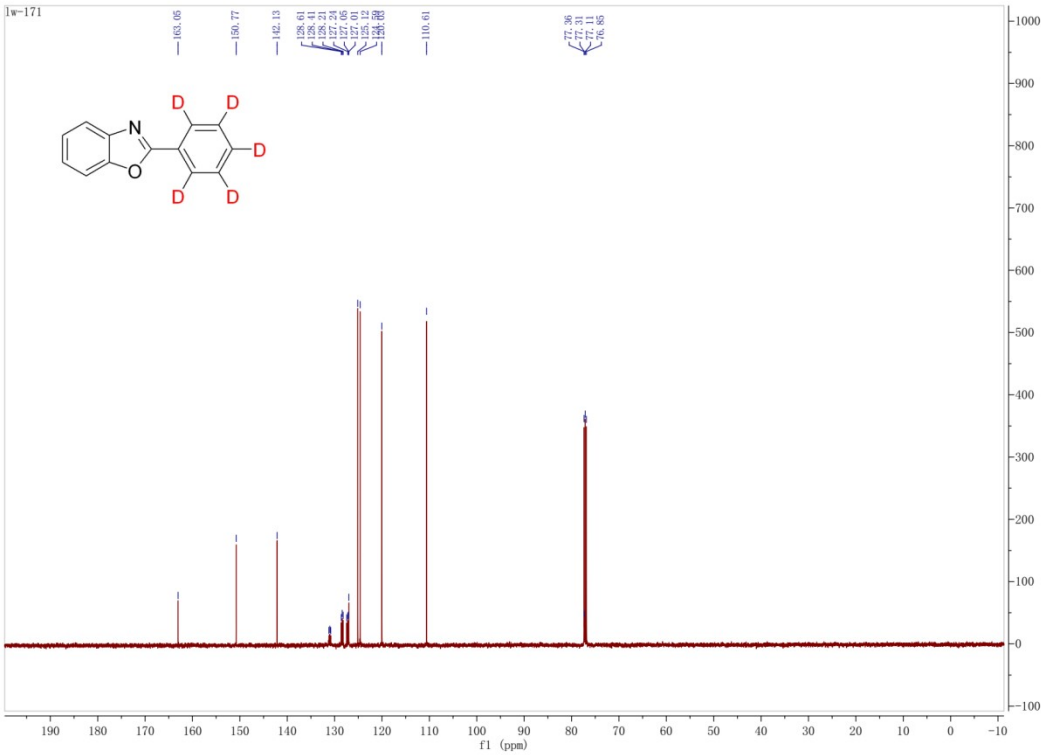

Figure S33. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3b-D**

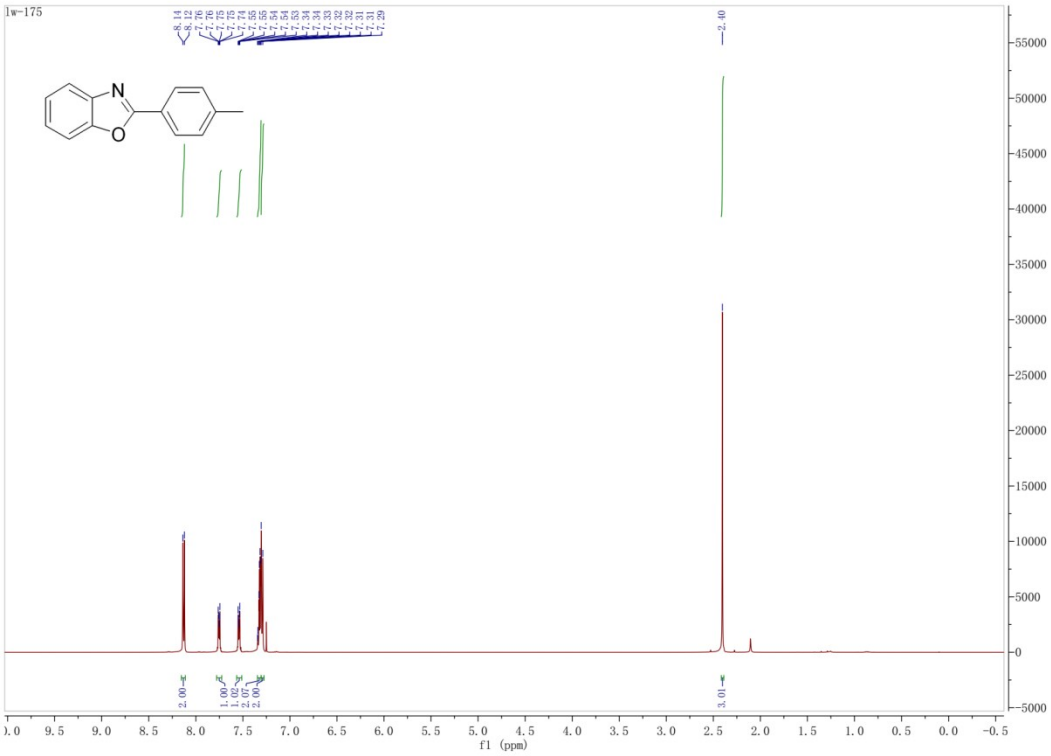

Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3c**

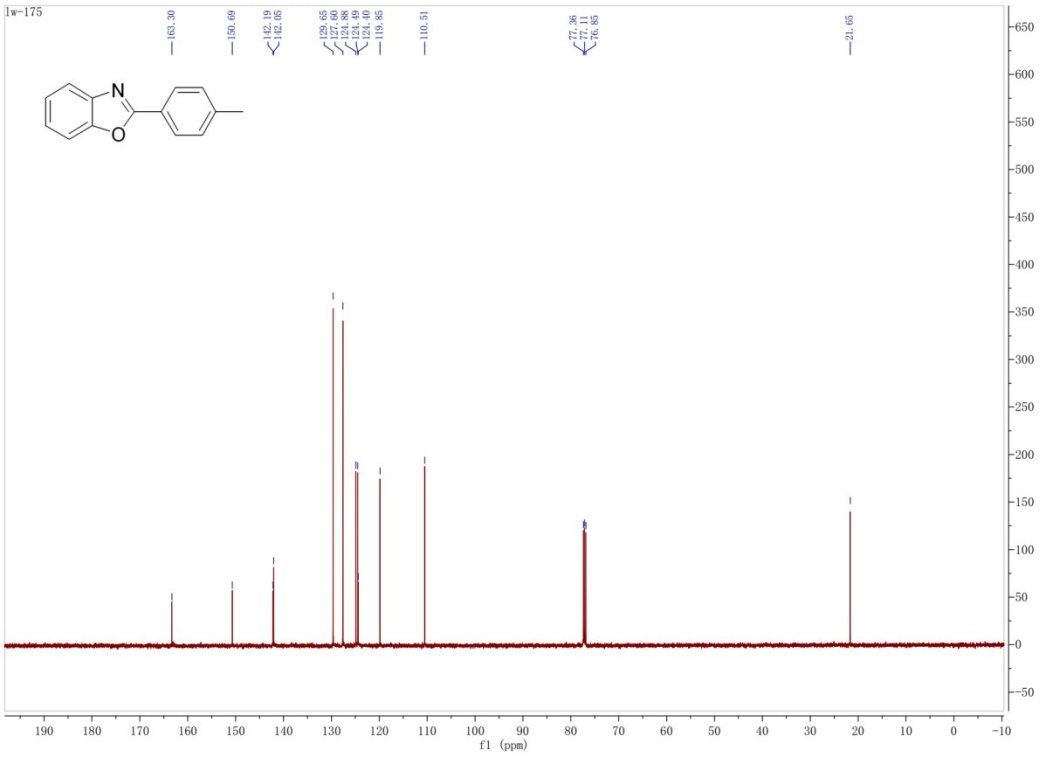

Figure S35. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3c**

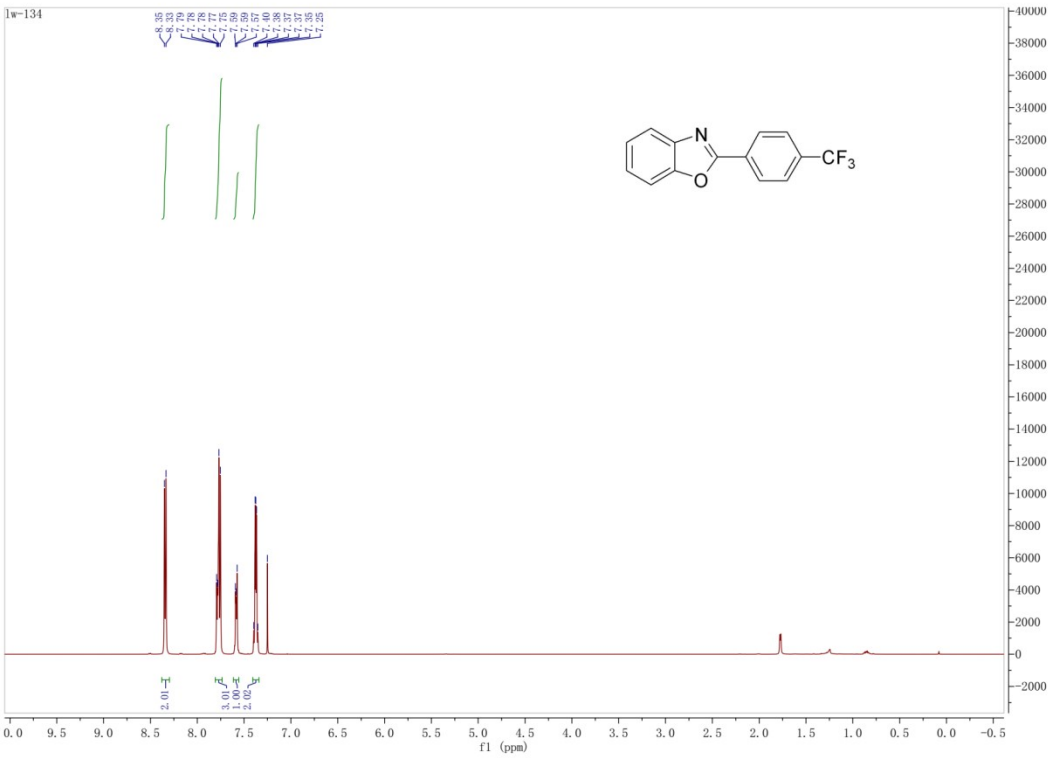

Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3d**

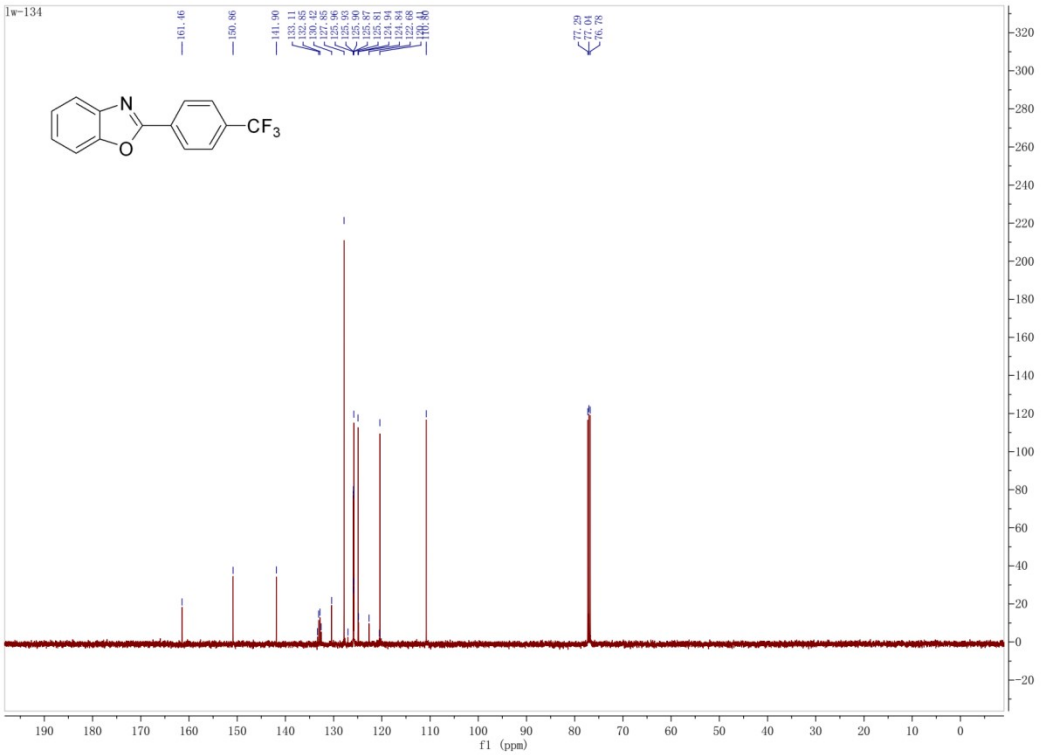

Figure S37. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3d**

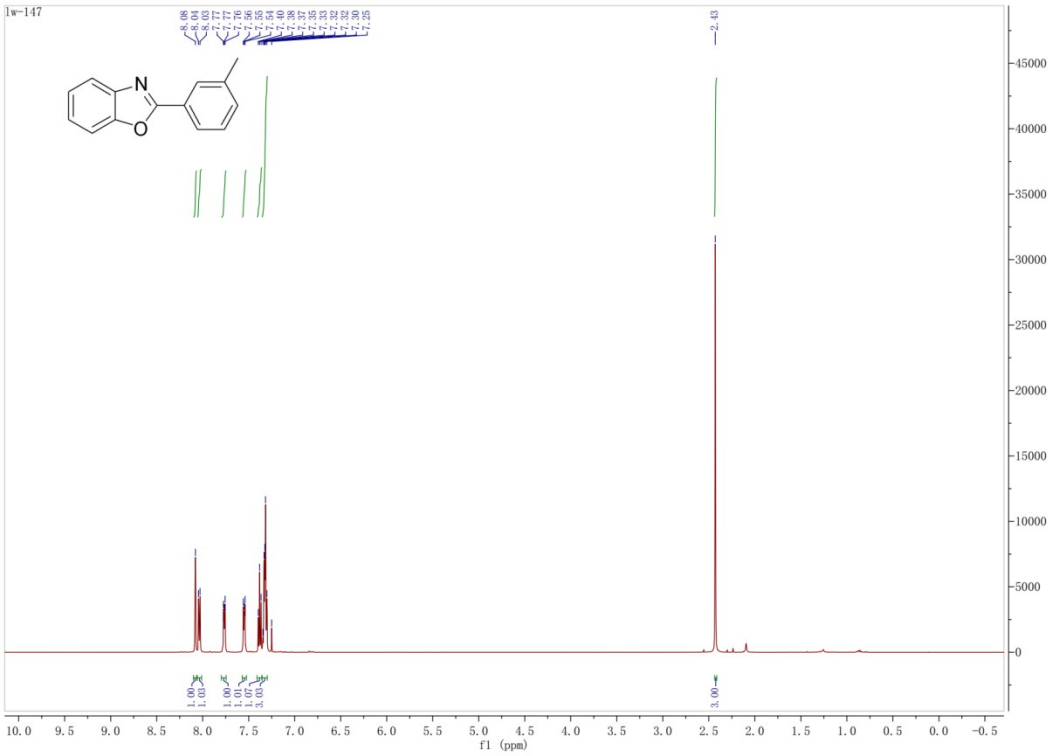

Figure S38. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3e**

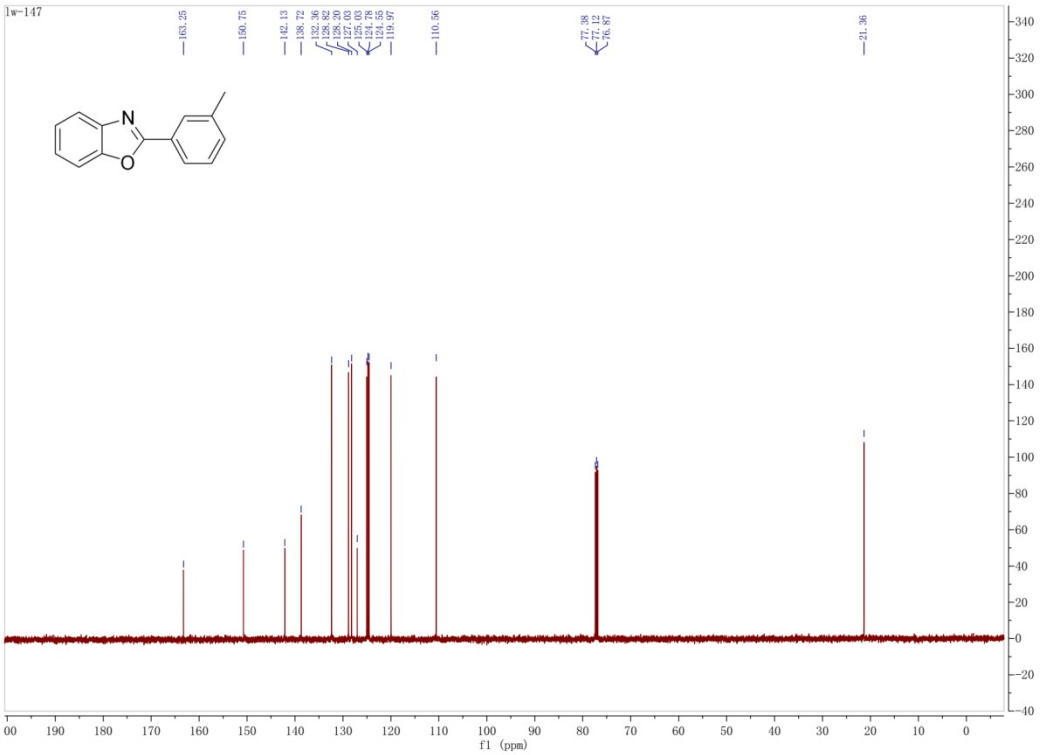

Figure S39. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3e**

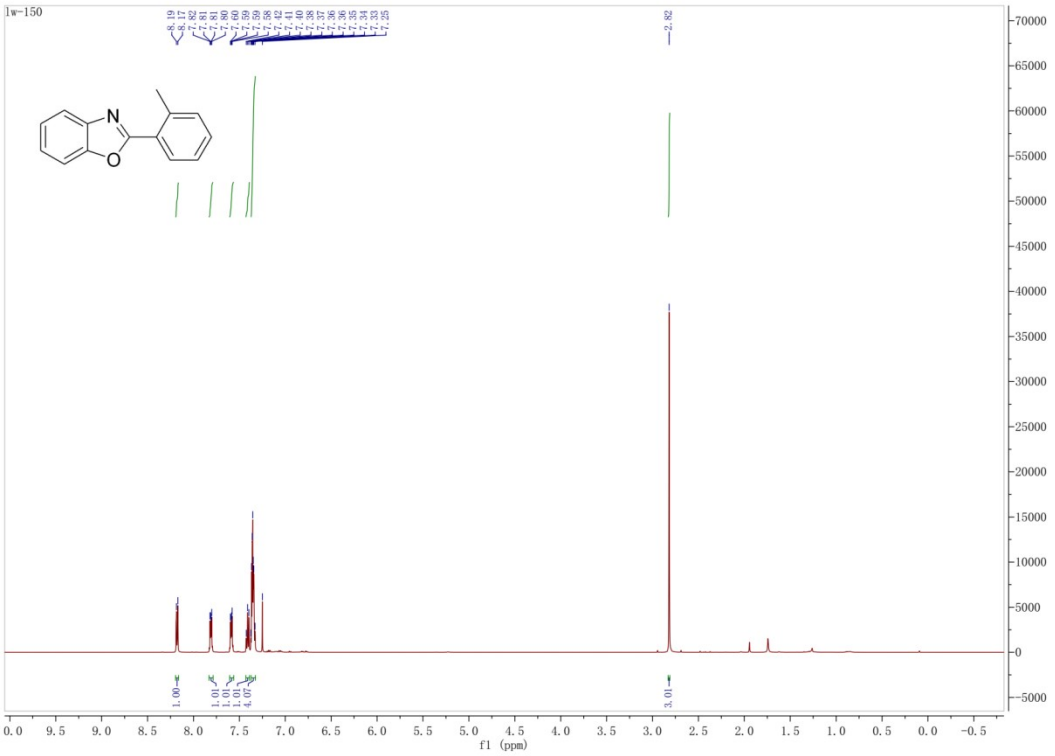

Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3f**

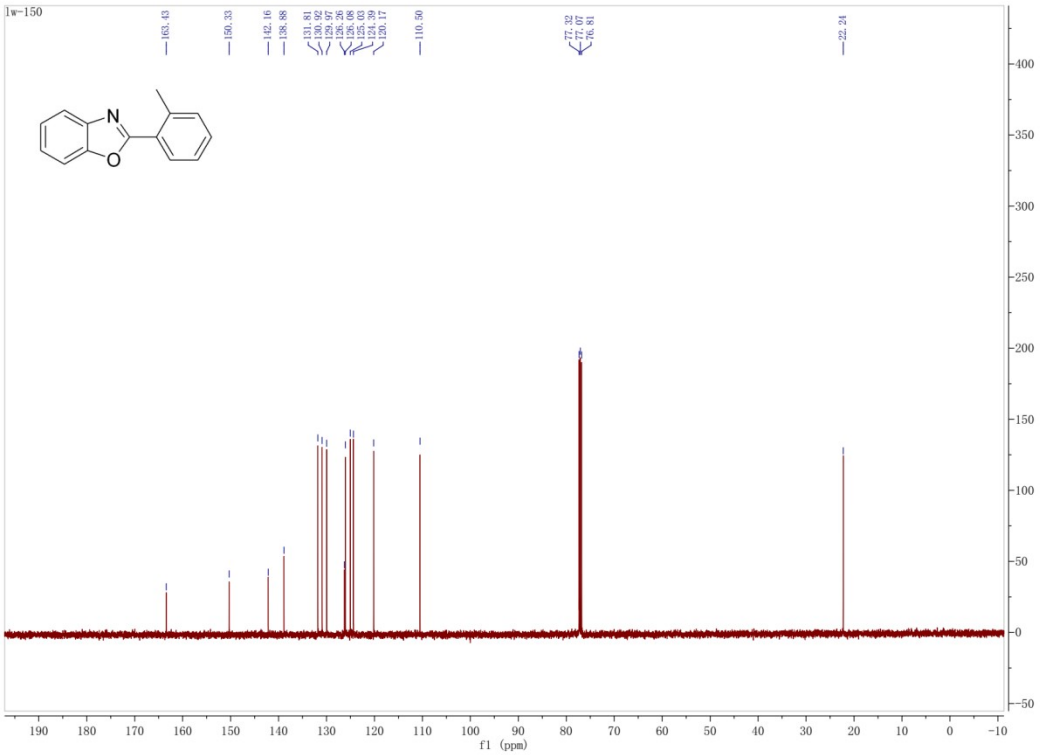

Figure S41. ^{13}C NMR (15025 MHz, $CDCl_3$) of Compound **3f**

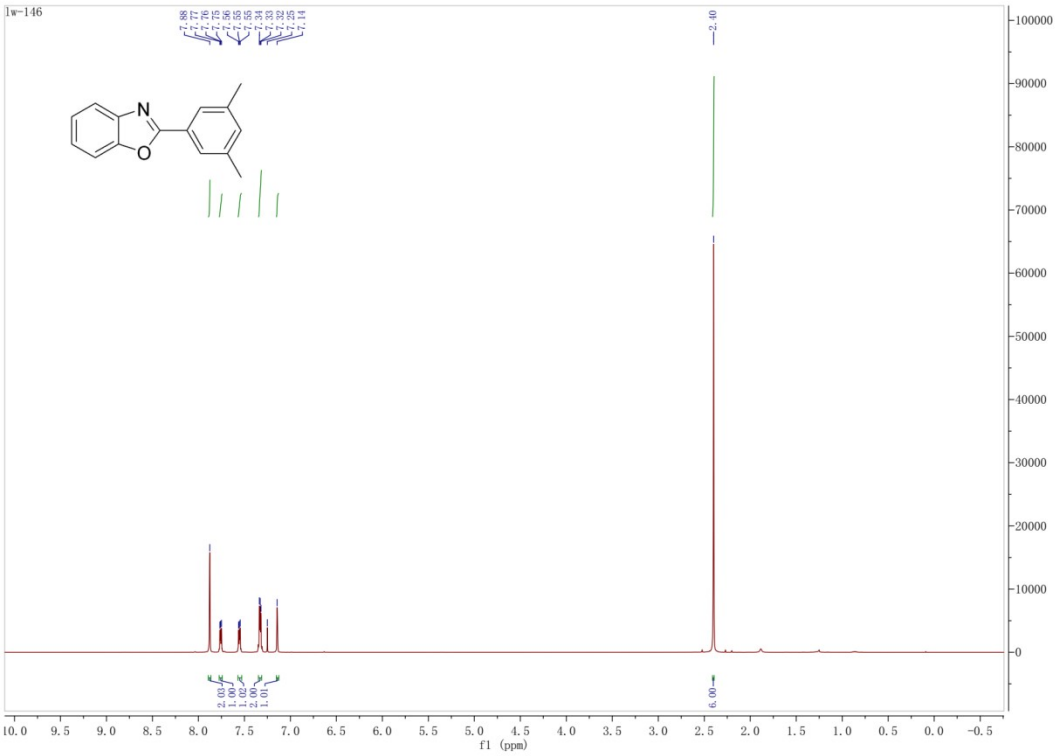

Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3g**

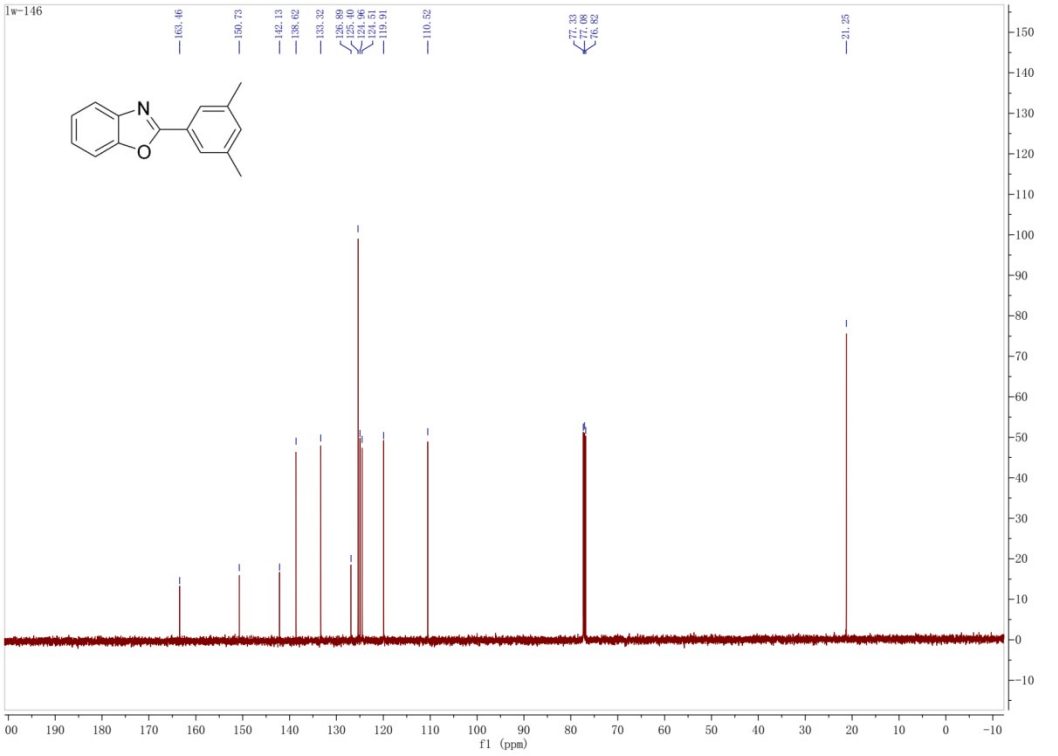

Figure S43. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3g**

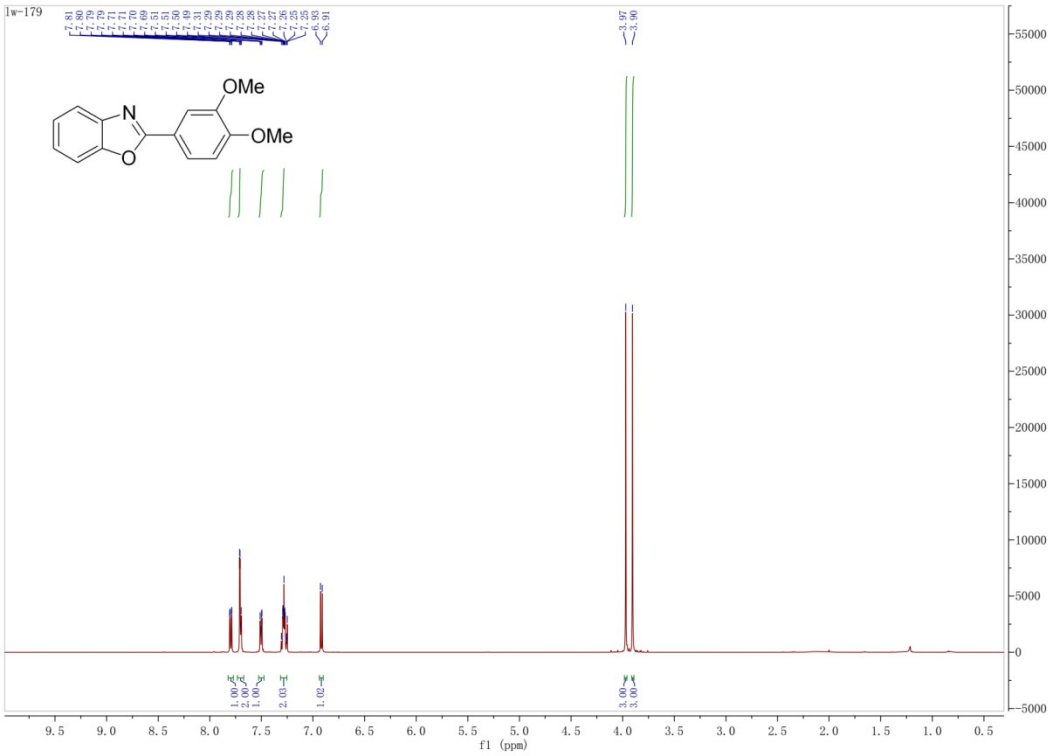

Figure S44. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3h**

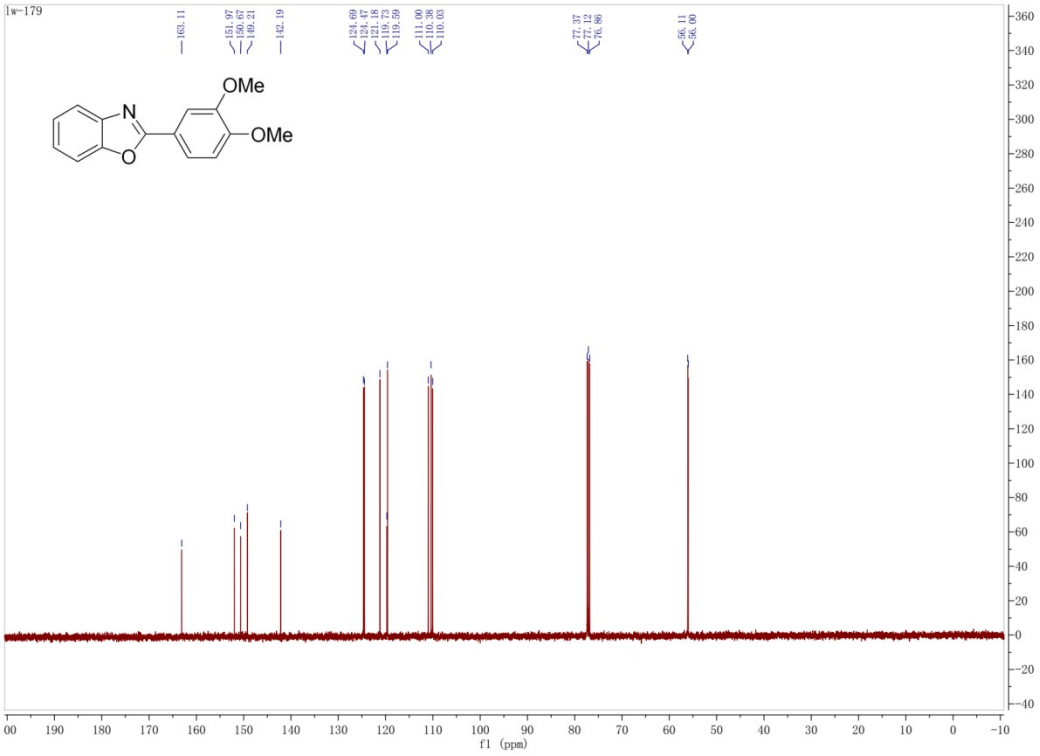

Figure S45. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3h**

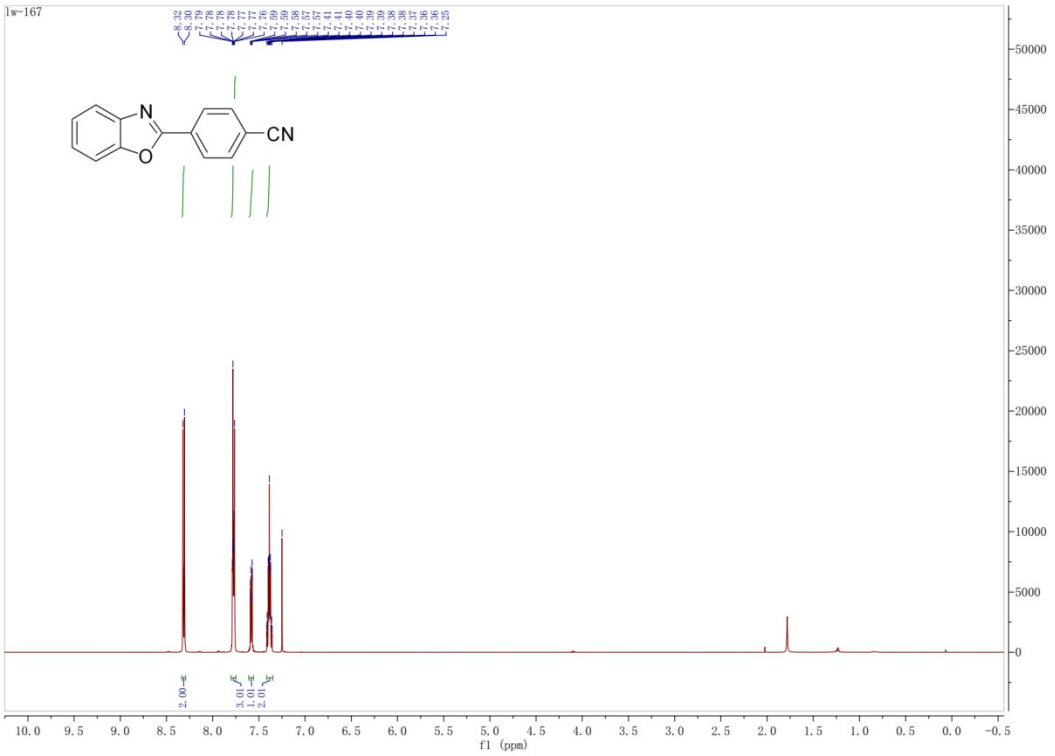

Figure S46. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3i**

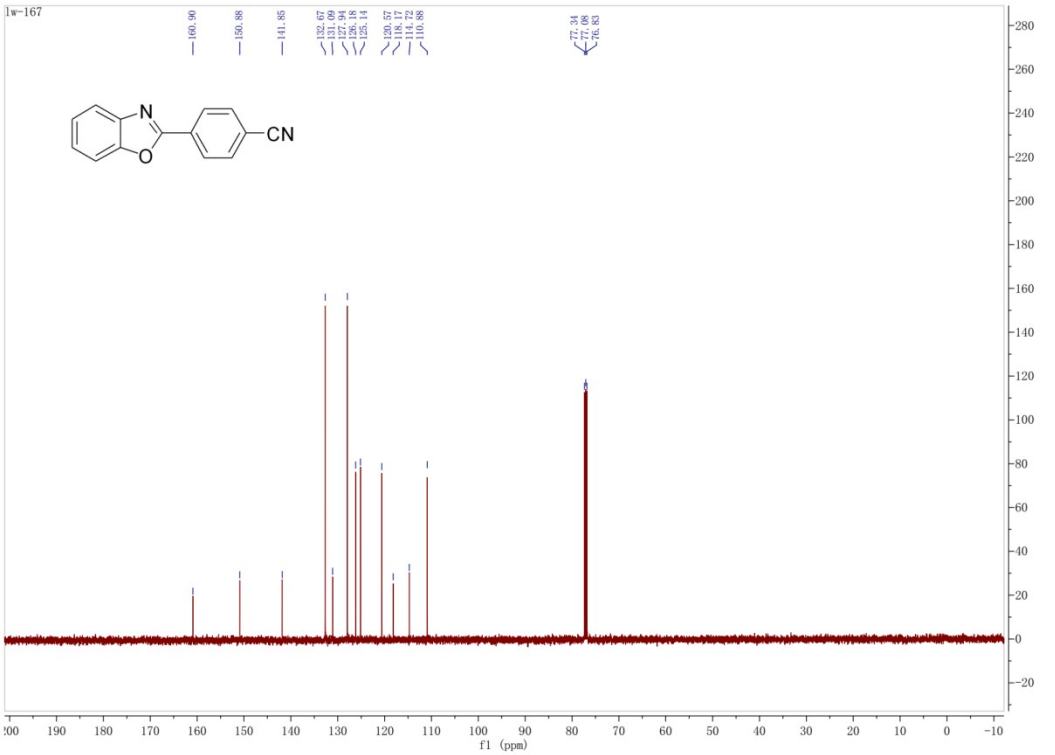

Figure S47. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3i**

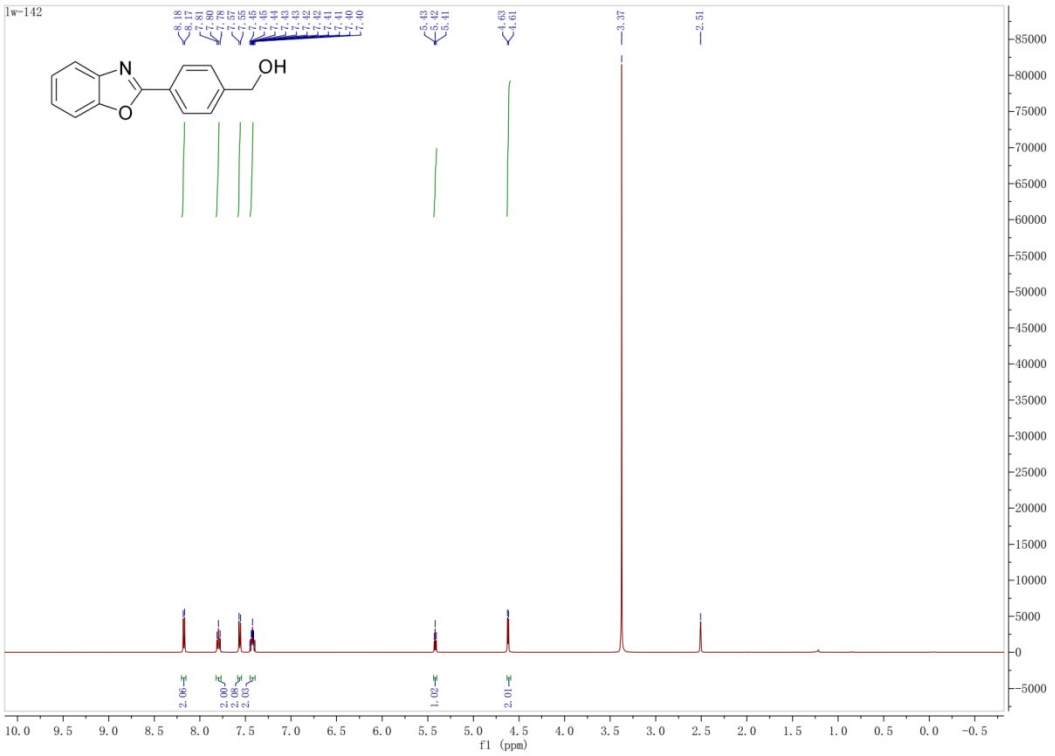

Figure S48. ^{1}H NMR (500 MHz, DMSO-d_6) of Compound **3j**

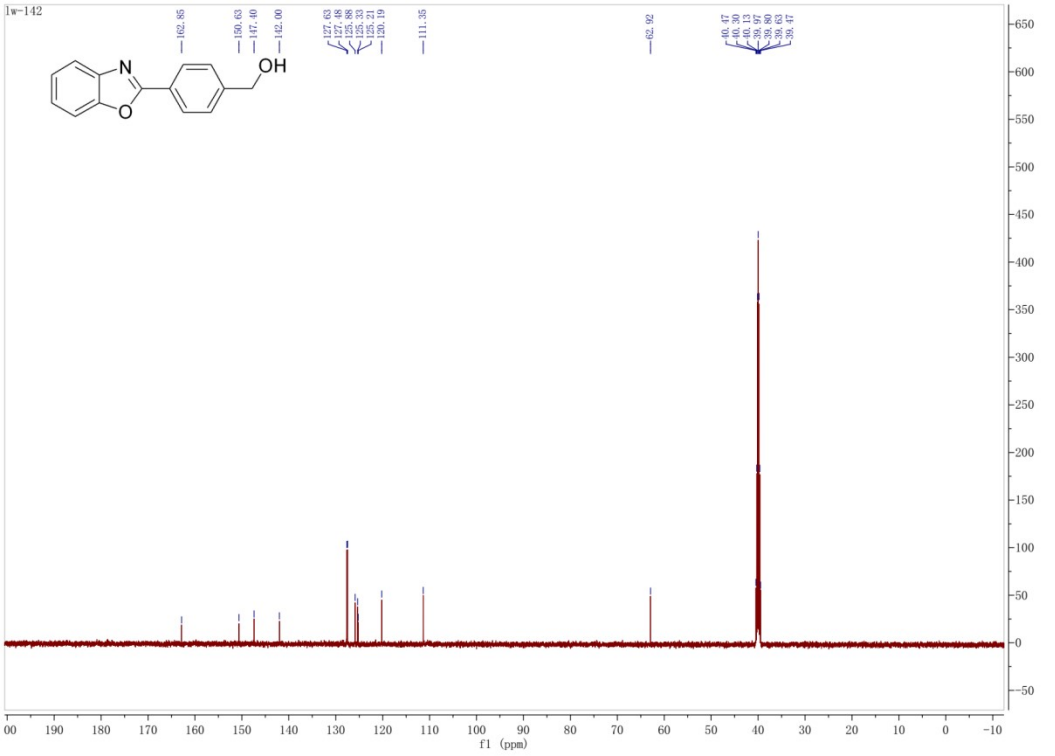

Figure S49. ^{13}C NMR (125 MHz, DMSO-d_6) of Compound **3j**

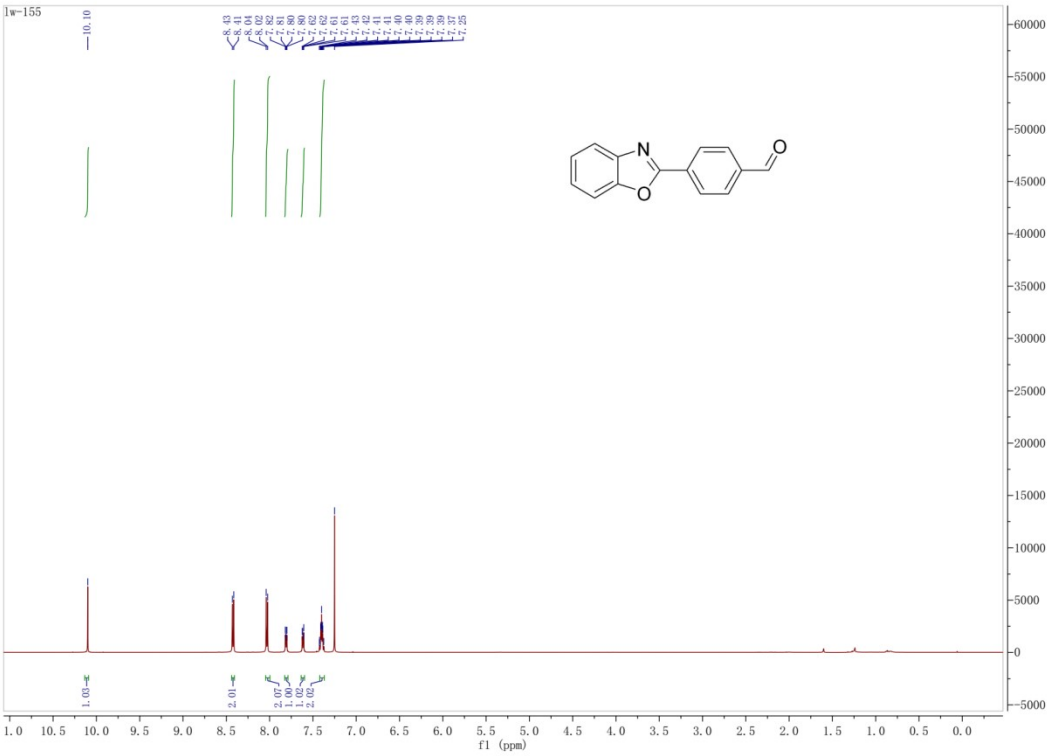

Figure S50. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3k**

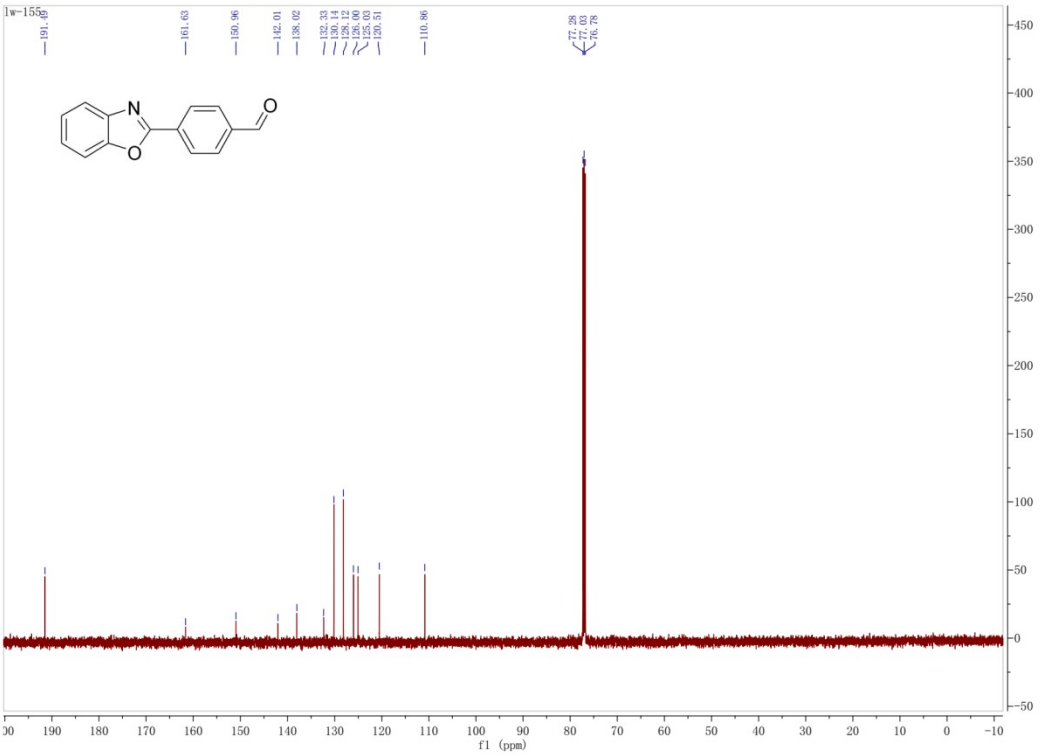

Figure S51. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3k**

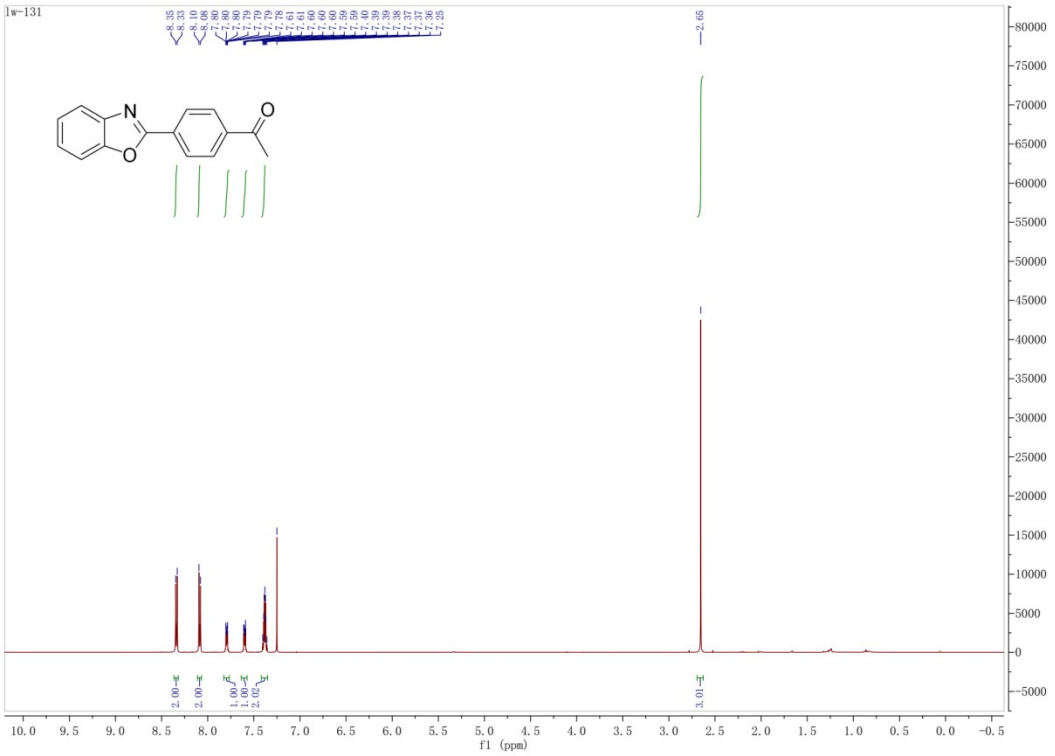

Figure S52. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3l**

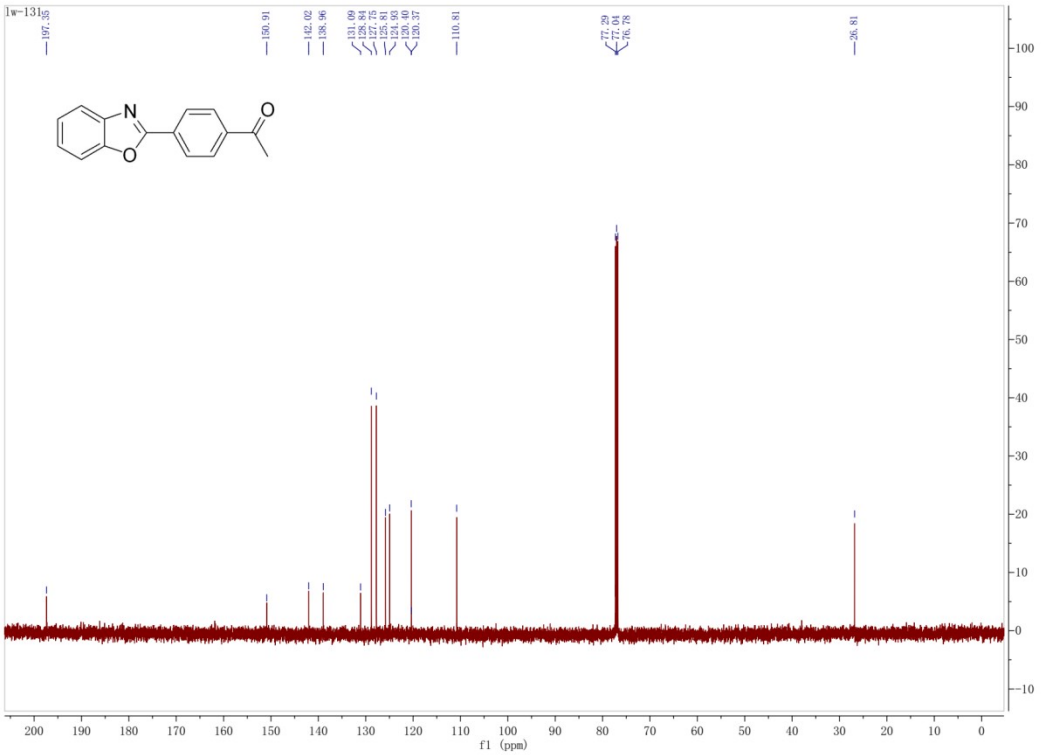

Figure S53. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3l**

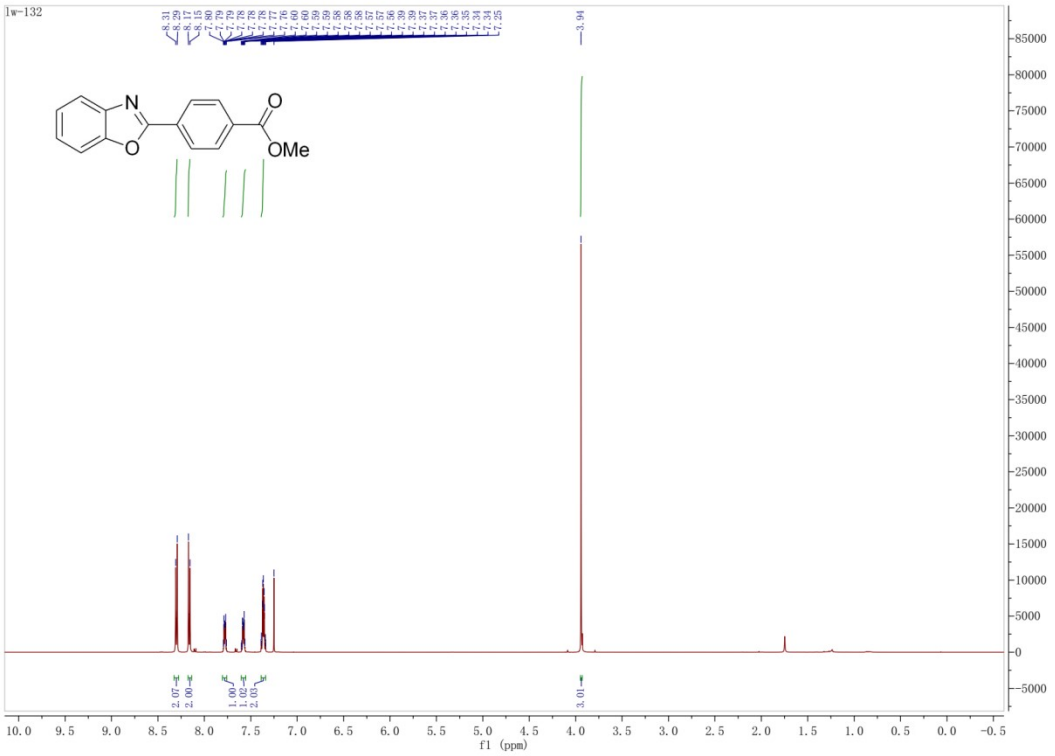

Figure S54. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3m**

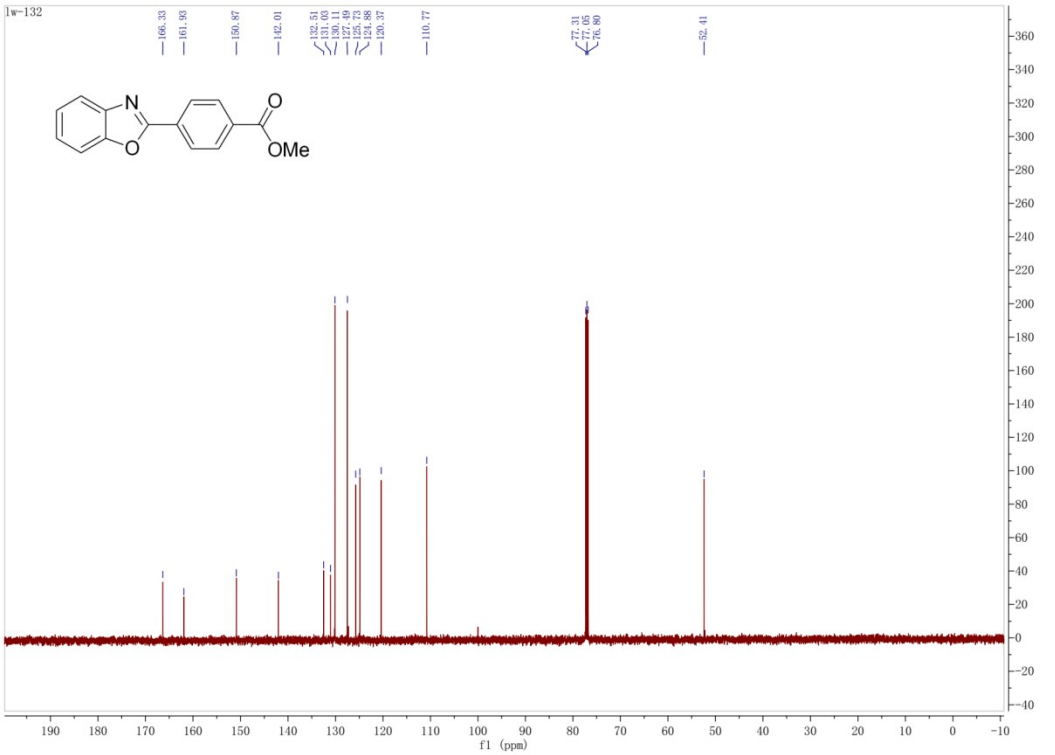

Figure S55. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3m**

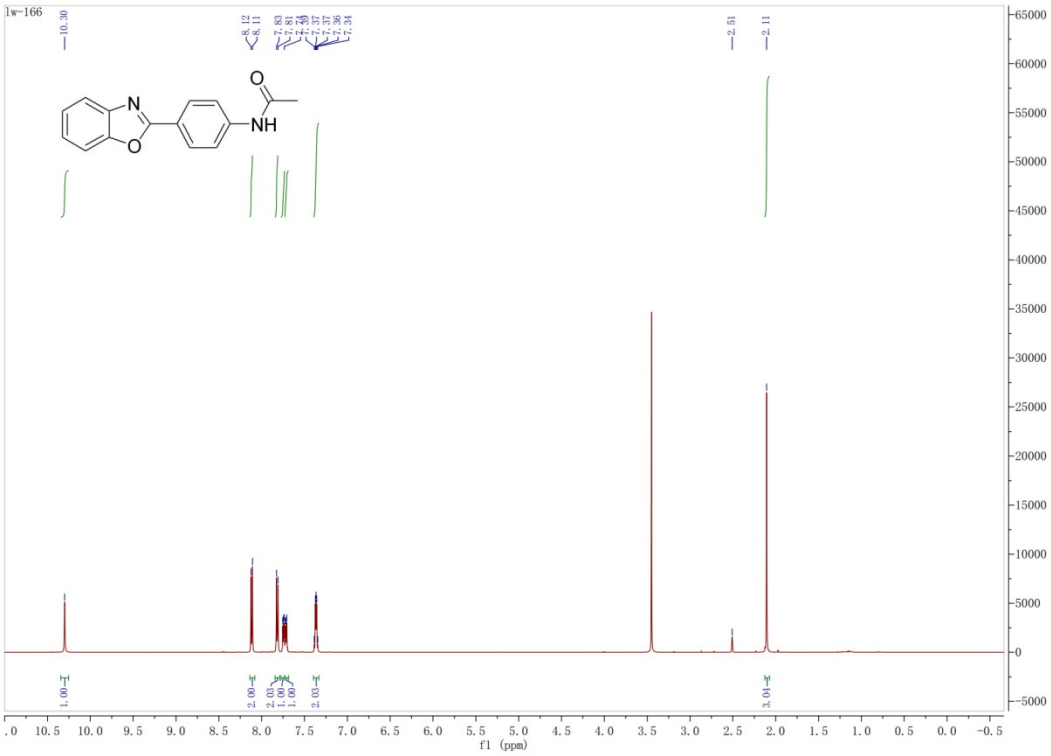

Figure S56. ^{1}H NMR (500 MHz, DMSO-d_6) of Compound **3n**

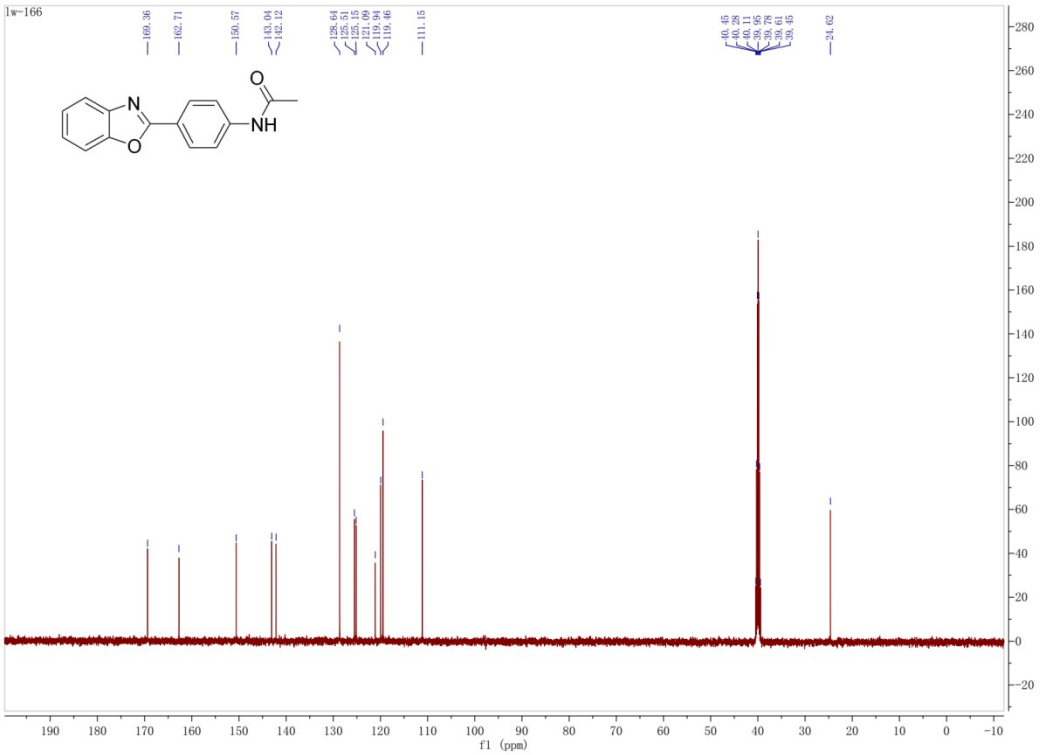

Figure S57. ^{13}C NMR (125 MHz, DMSO-d_6) of Compound **3n**

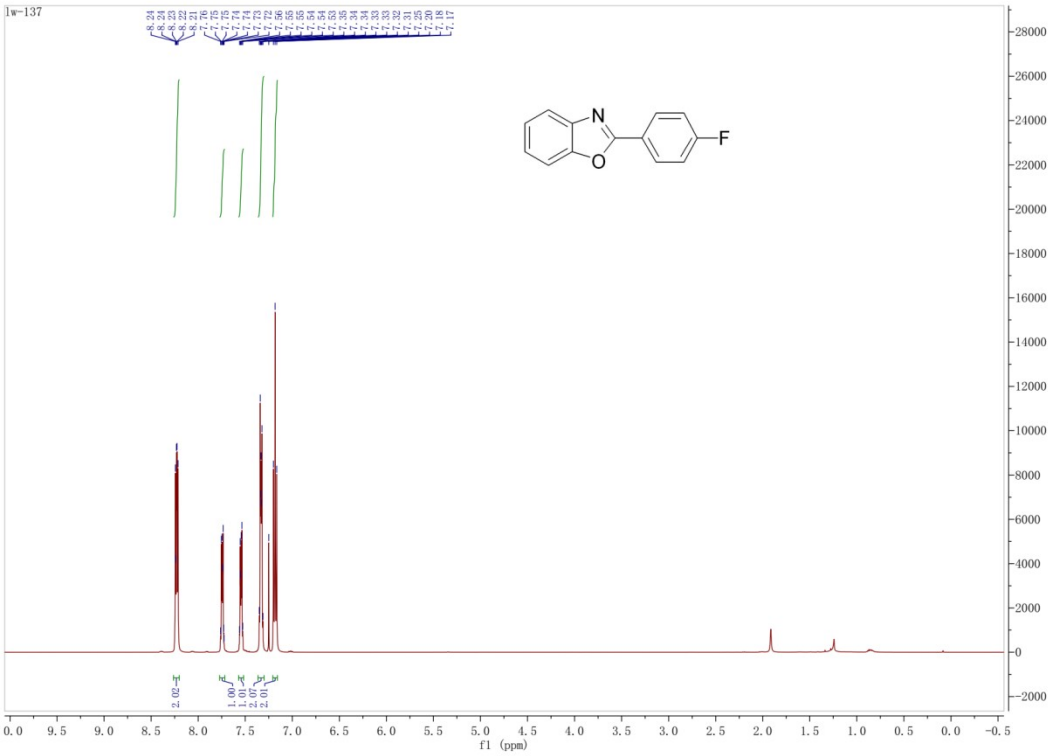

Figure S58. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3o**

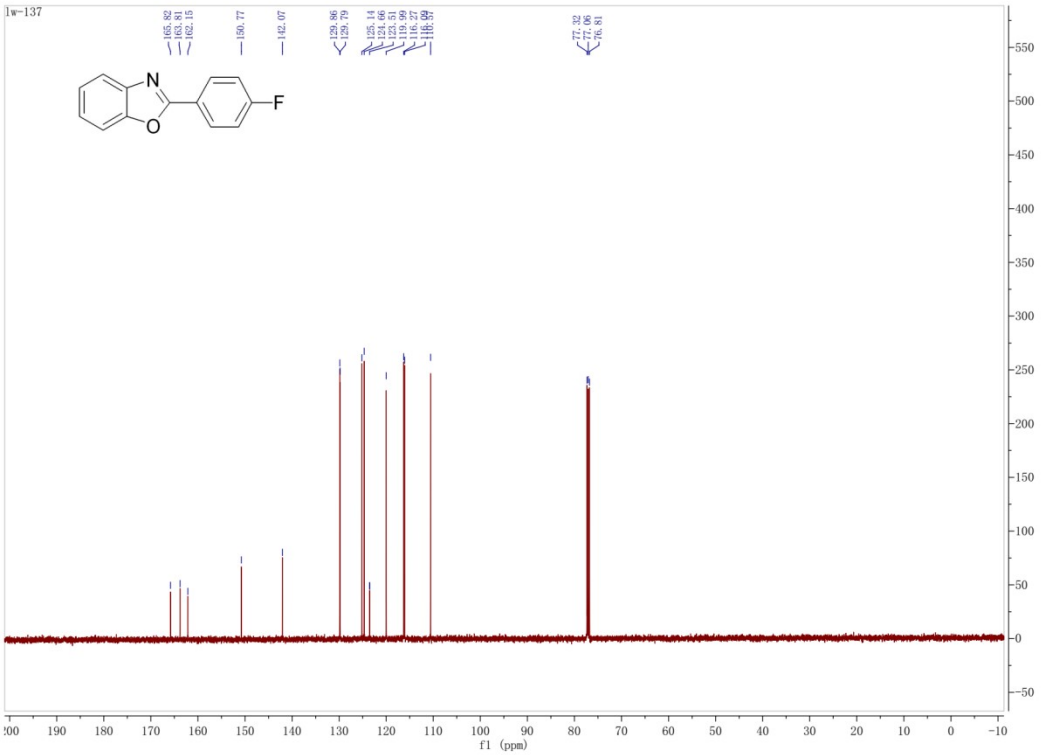

Figure S59. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3o**

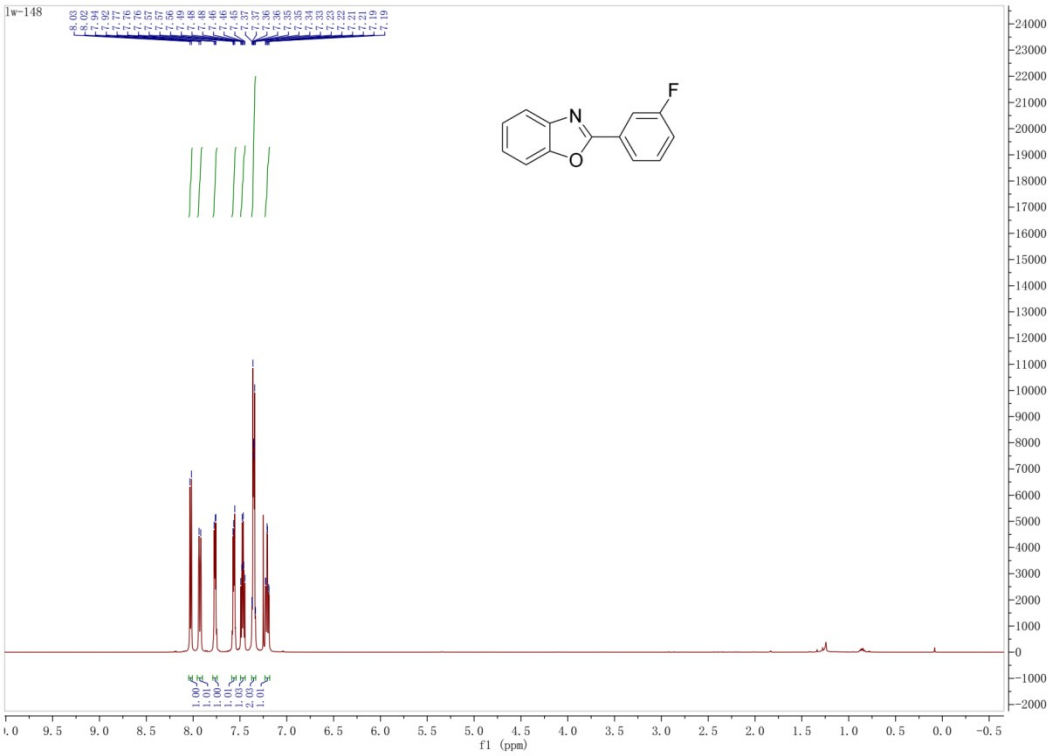

Figure S60. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3p**

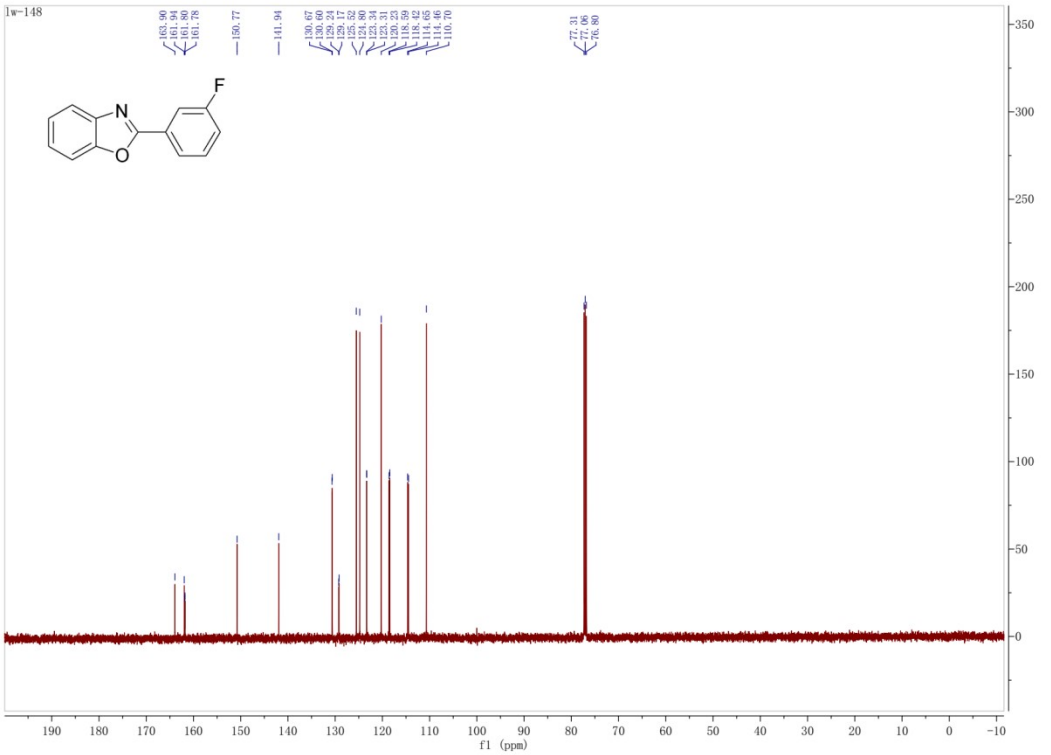

Figure S61. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3p**

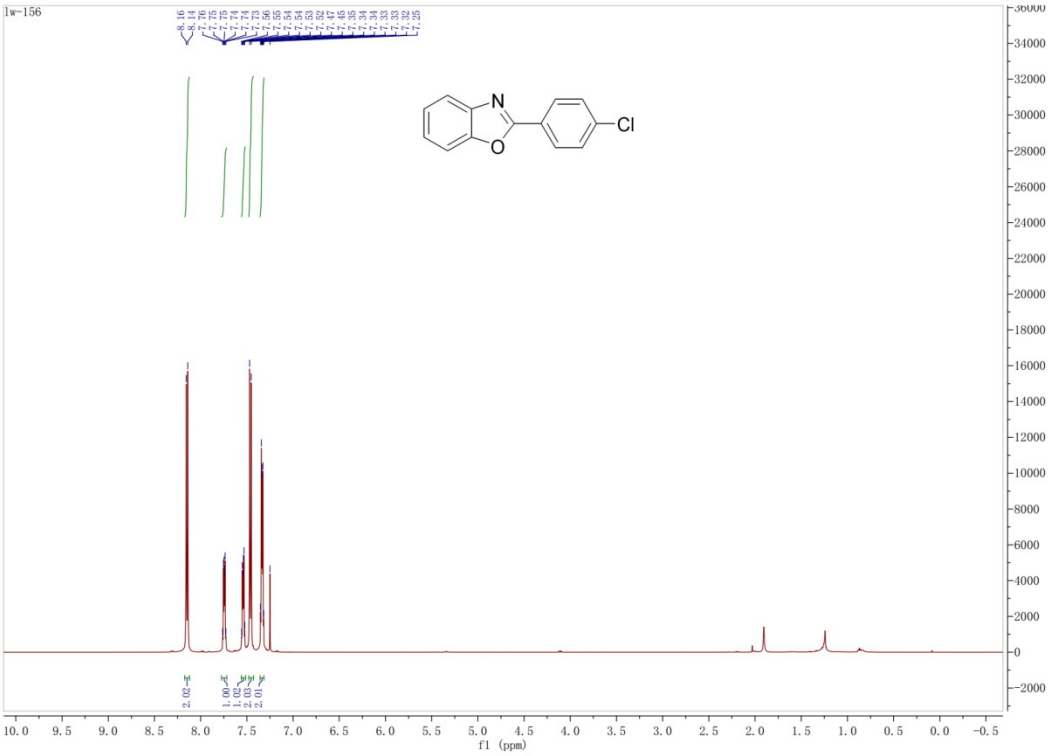

Figure S62. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3q**

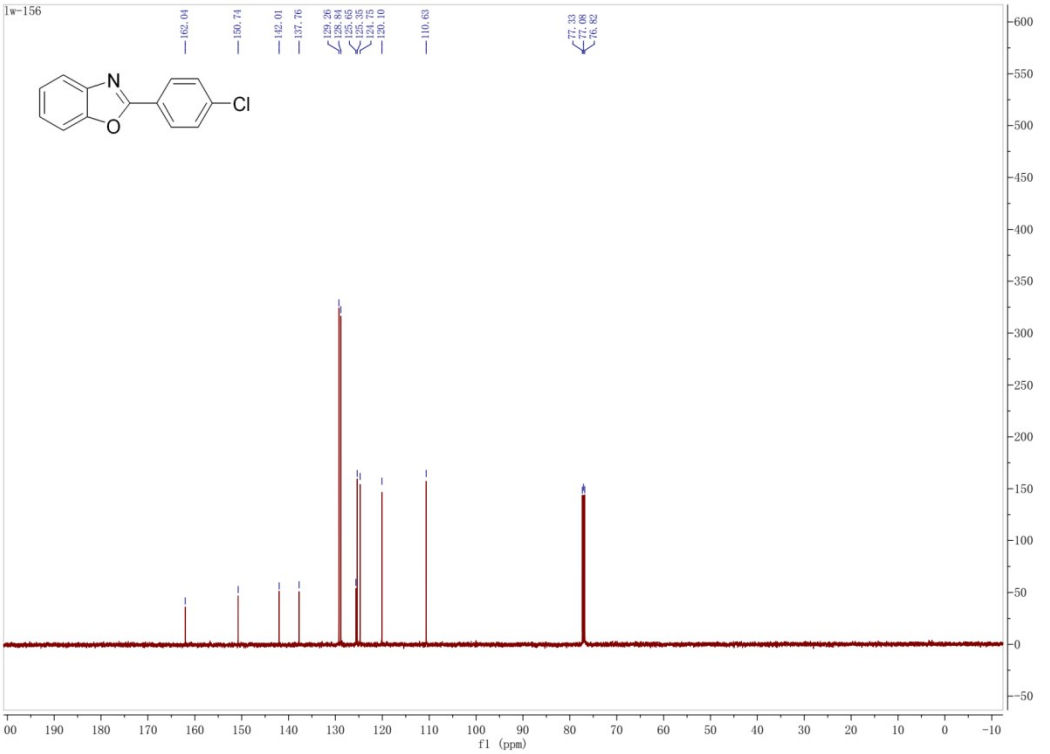

Figure S63. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3q**

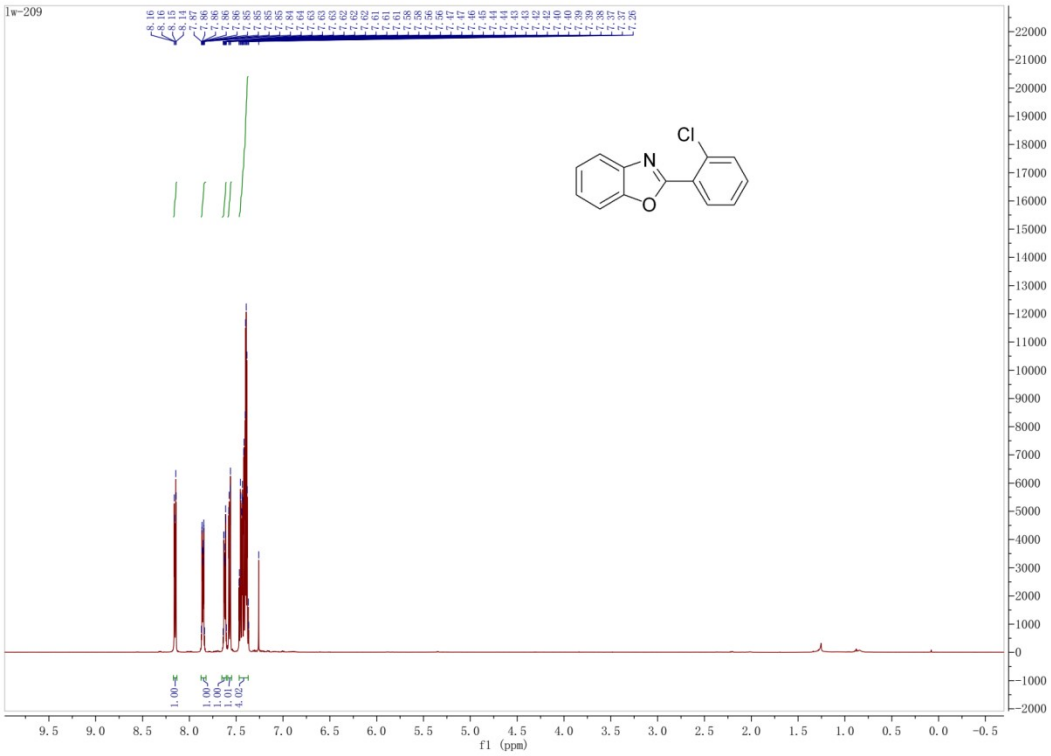

Figure S64. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3r**

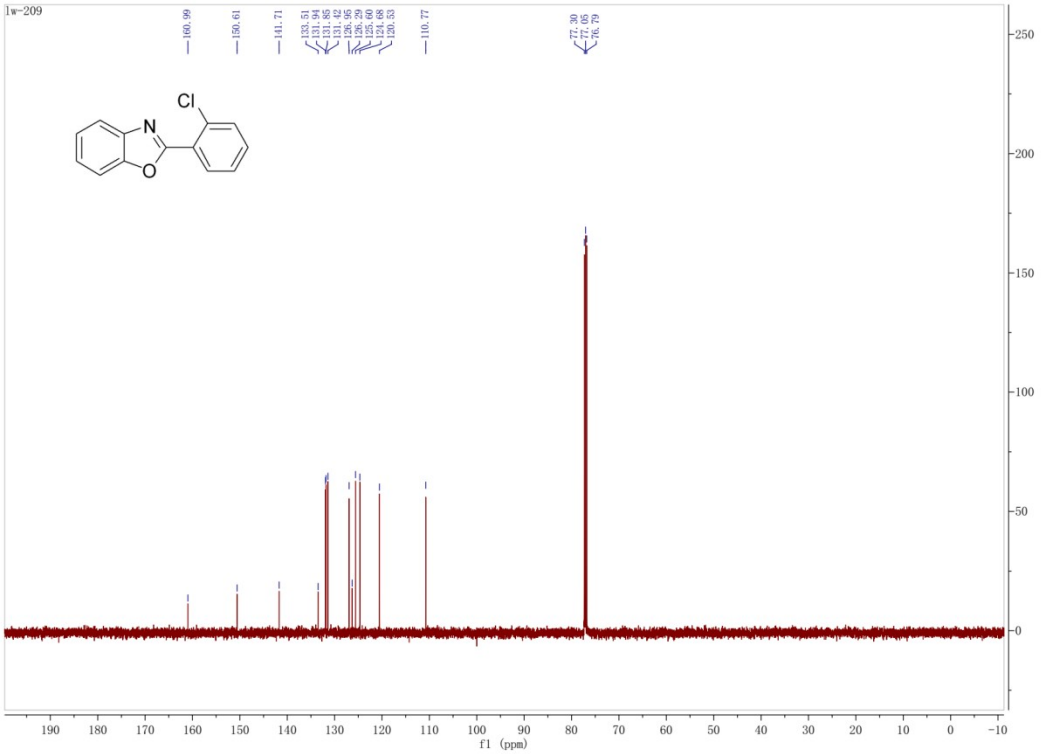

Figure S65. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3r**

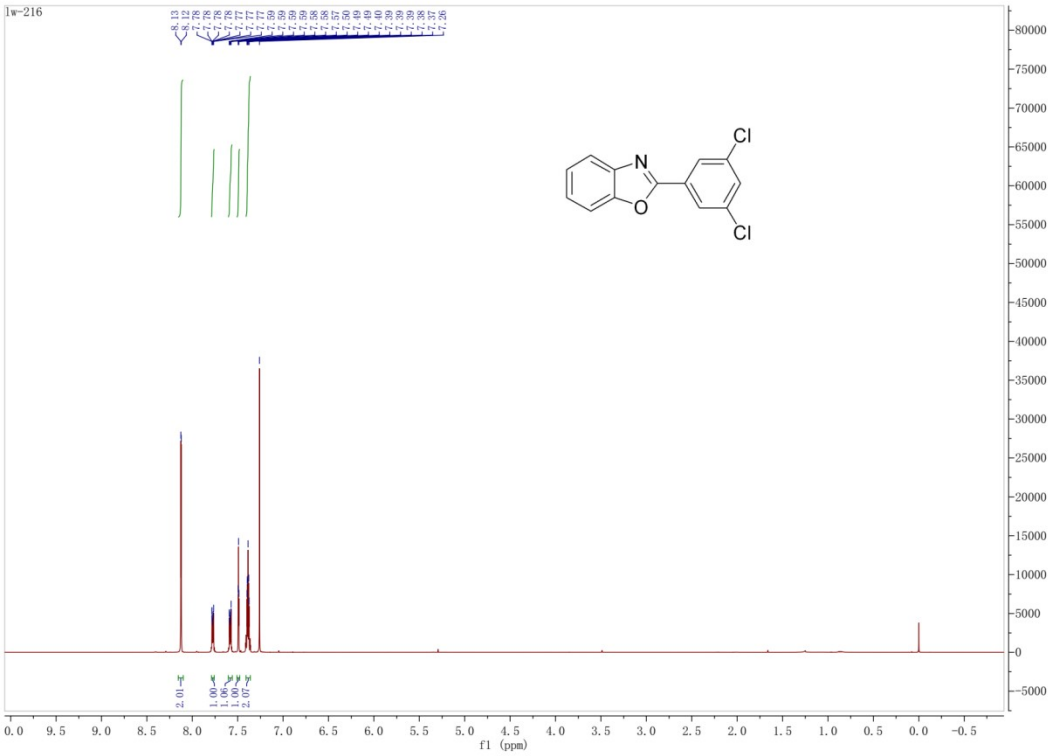

Figure S66. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3s**

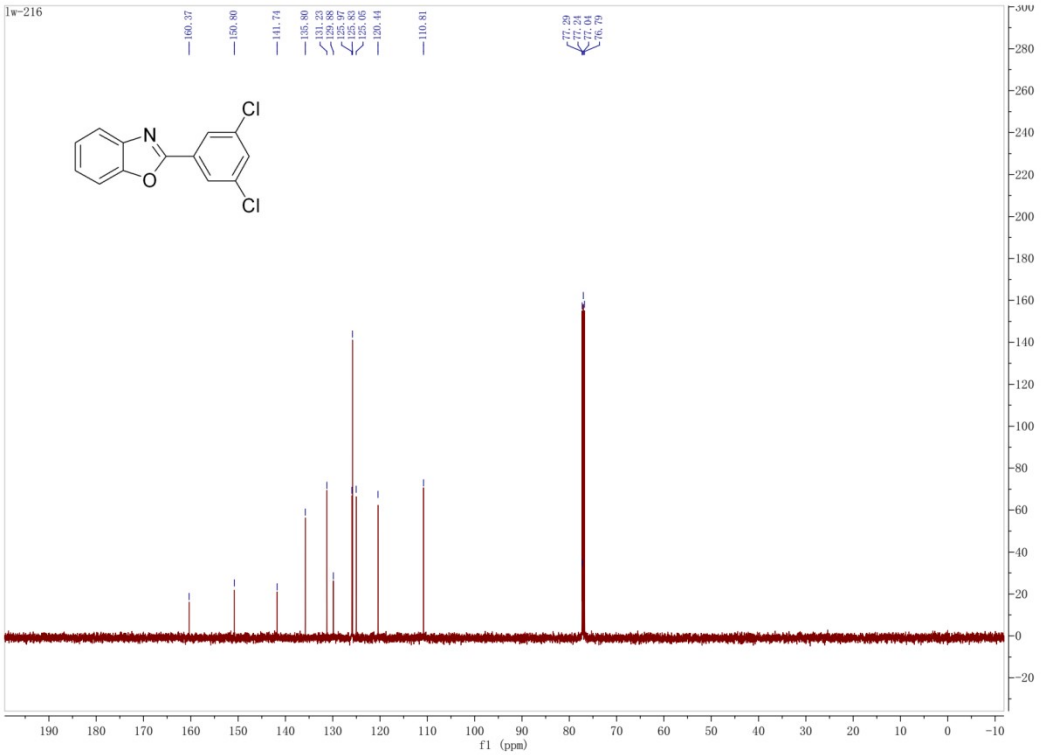

Figure S67. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3s**

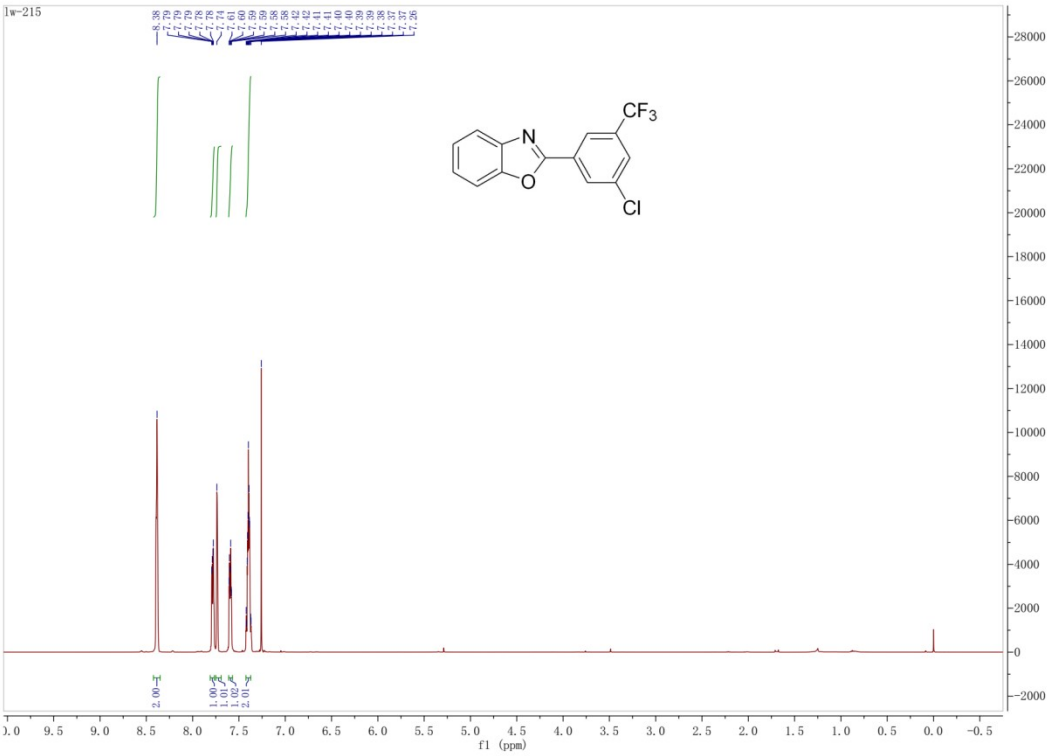

Figure S68. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3t**

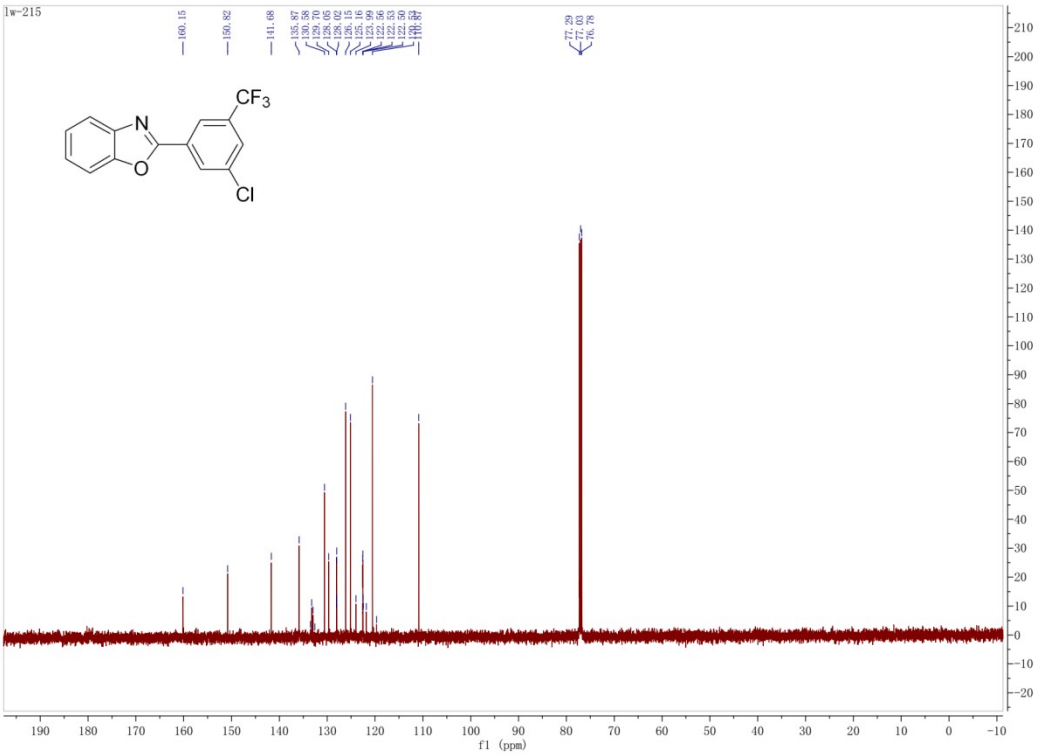

Figure S69. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3t**

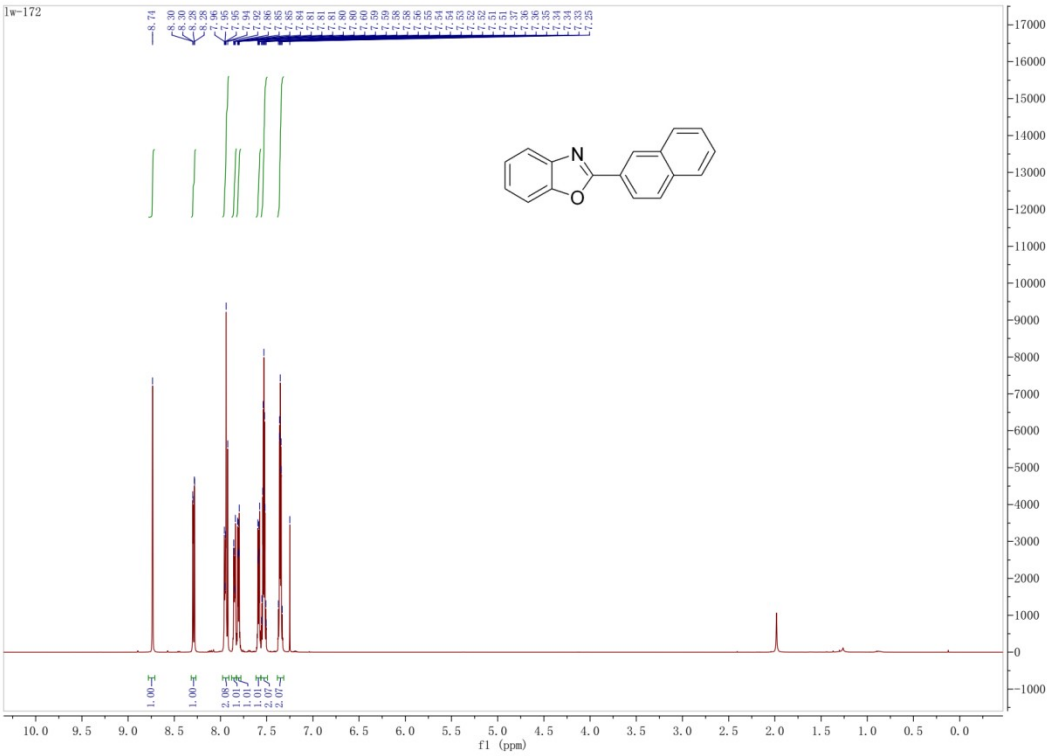

Figure S70. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3u**

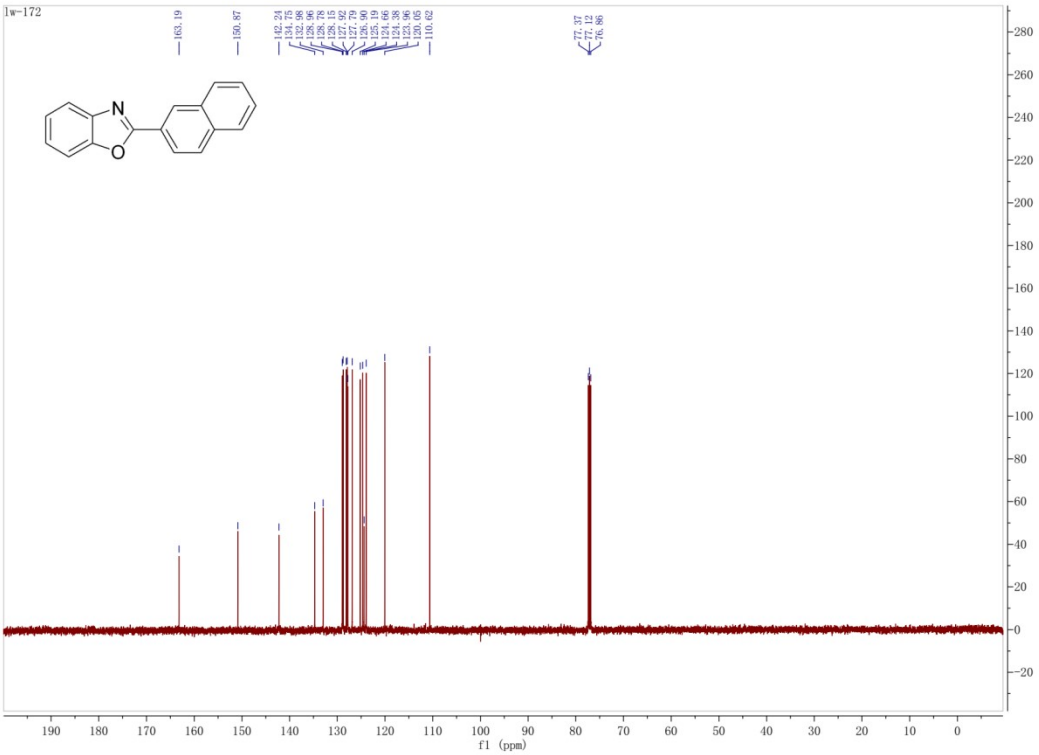

Figure S71. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3u**

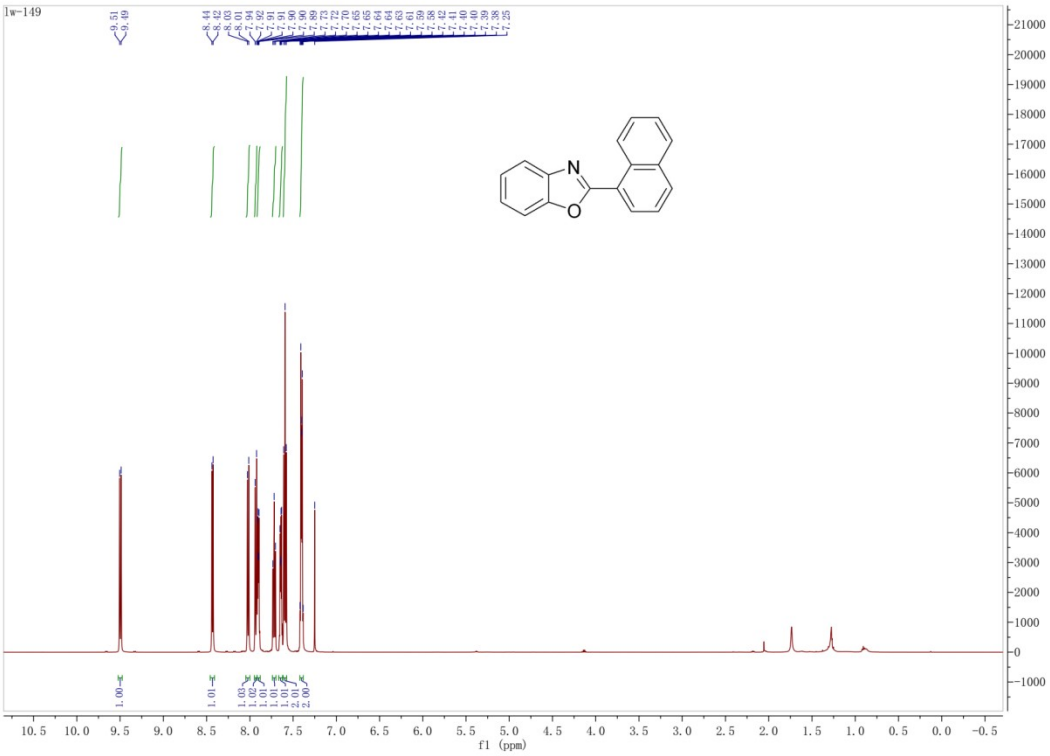

Figure S72. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3v**

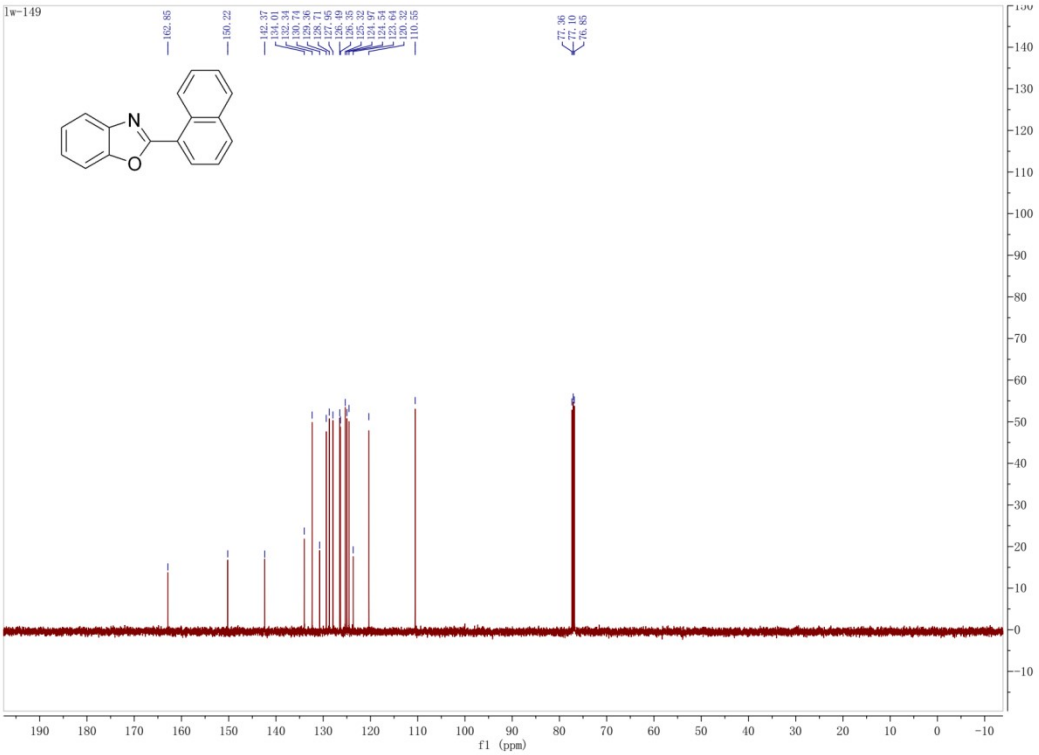

Figure S73. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3v**

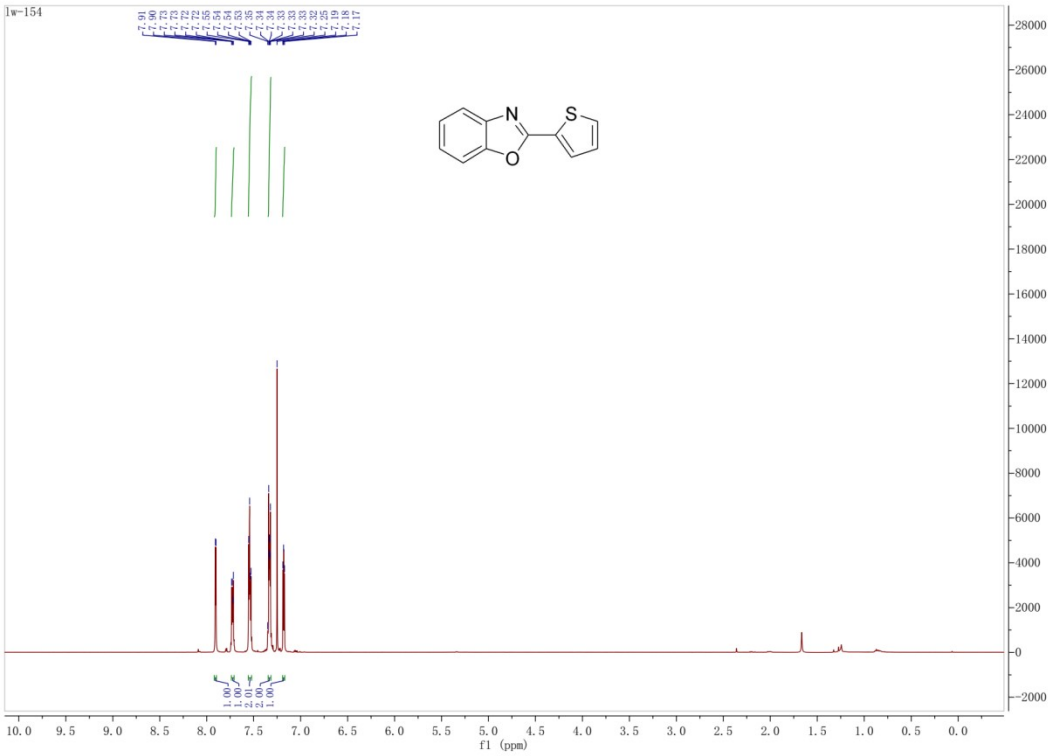

Figure S74. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3w**

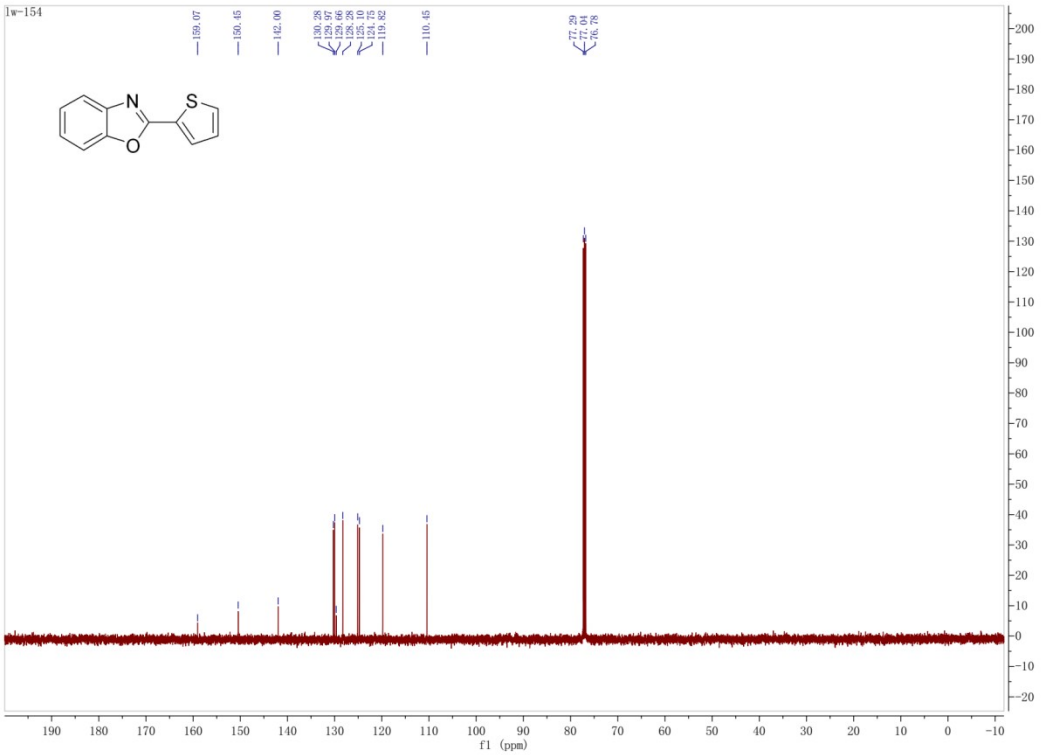

Figure S75. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3w**

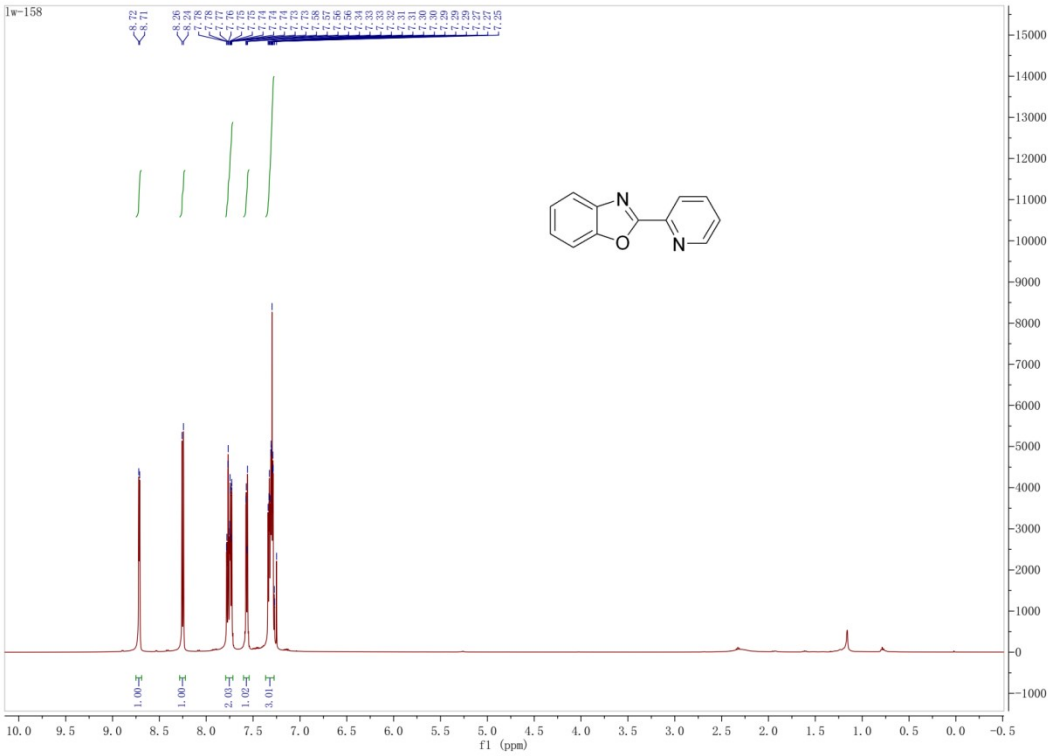

Figure S76. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3x**

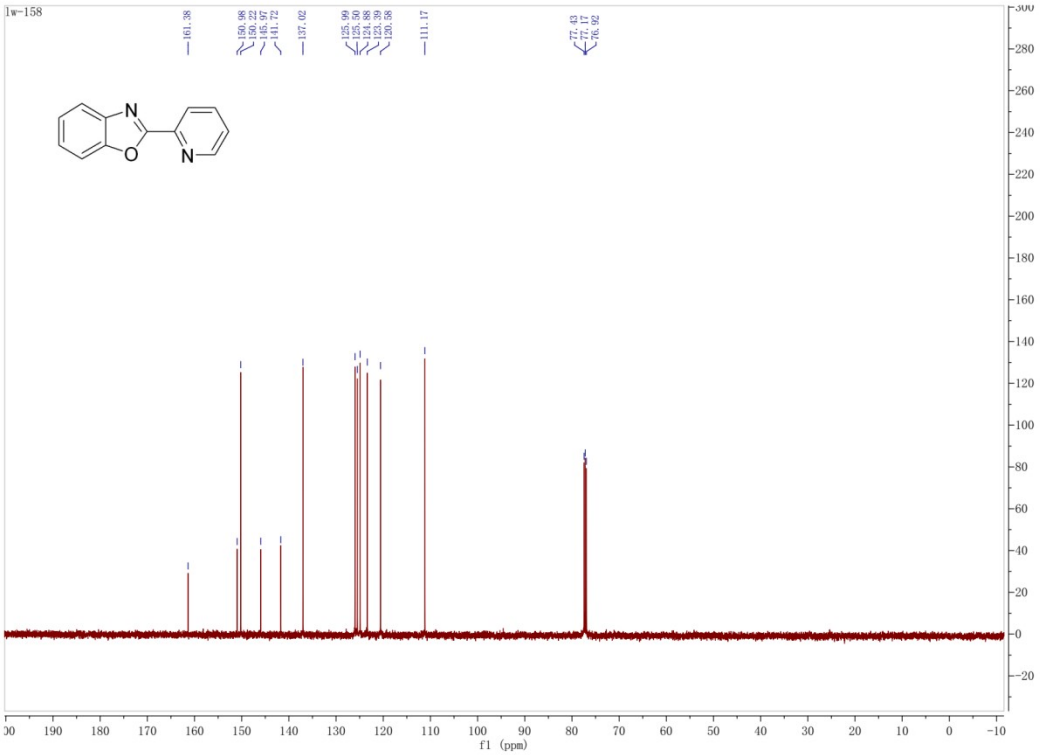

Figure S77. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3x**

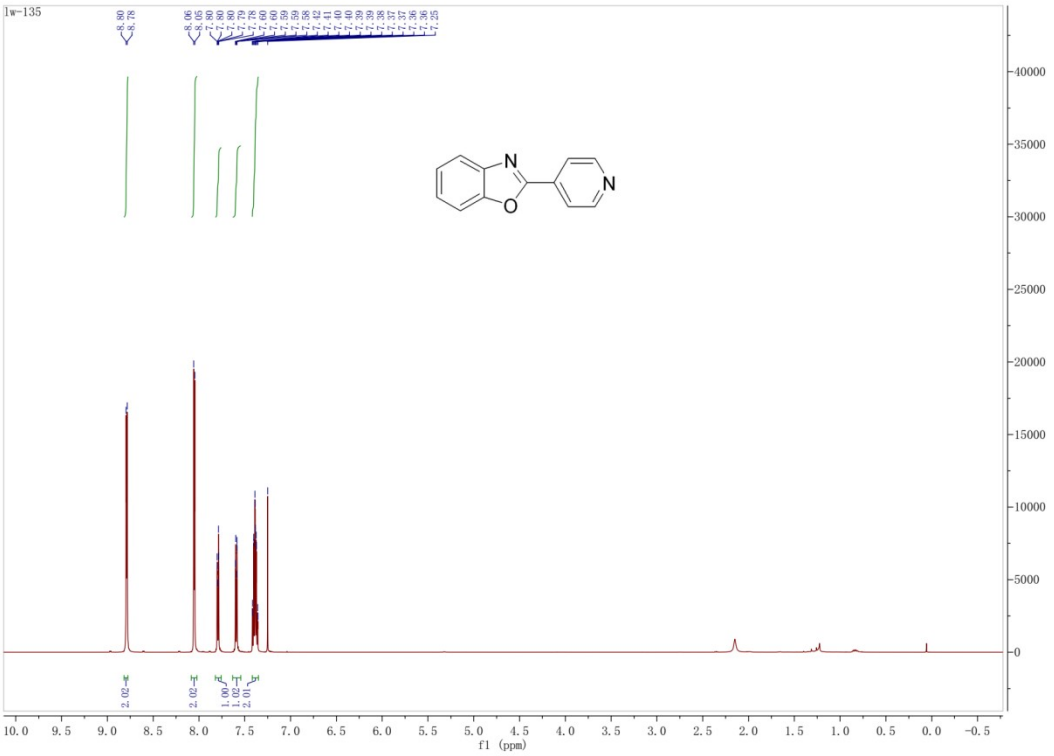

Figure S78. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3y**

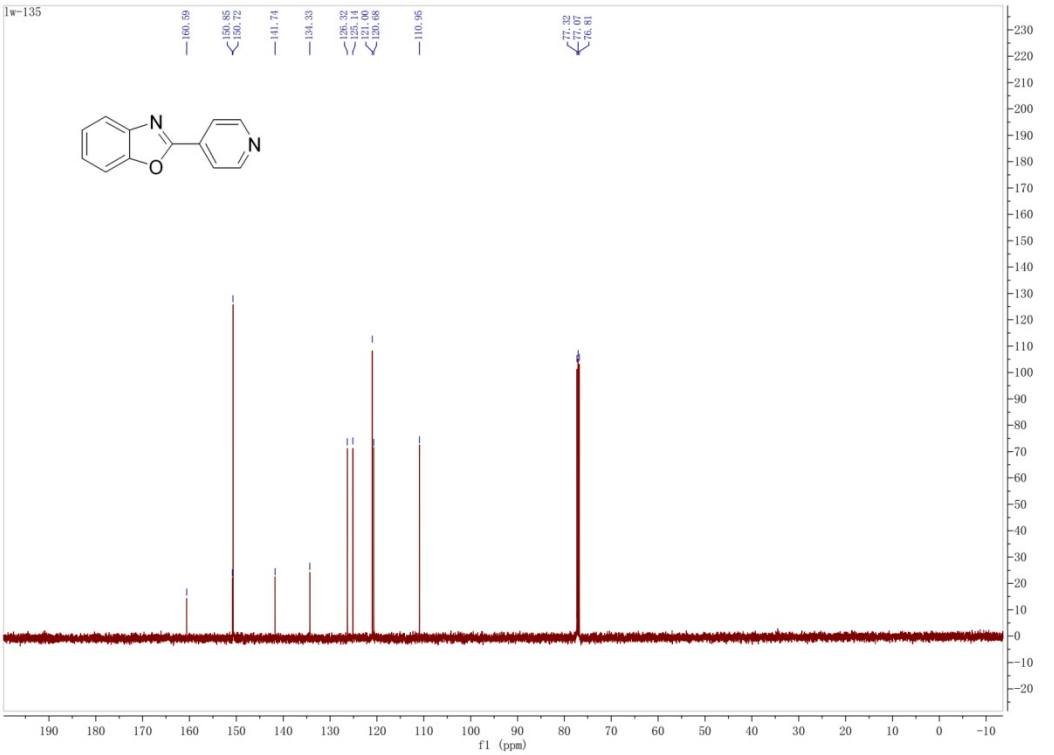

Figure S79. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3y**

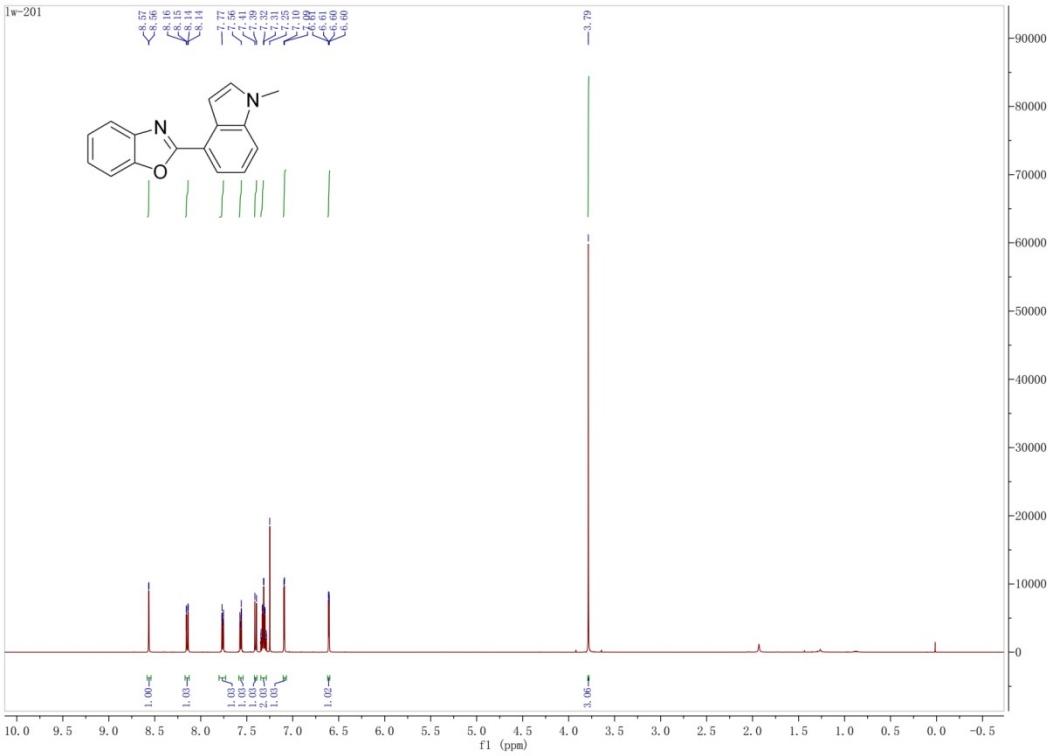

Figure S780. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3z**

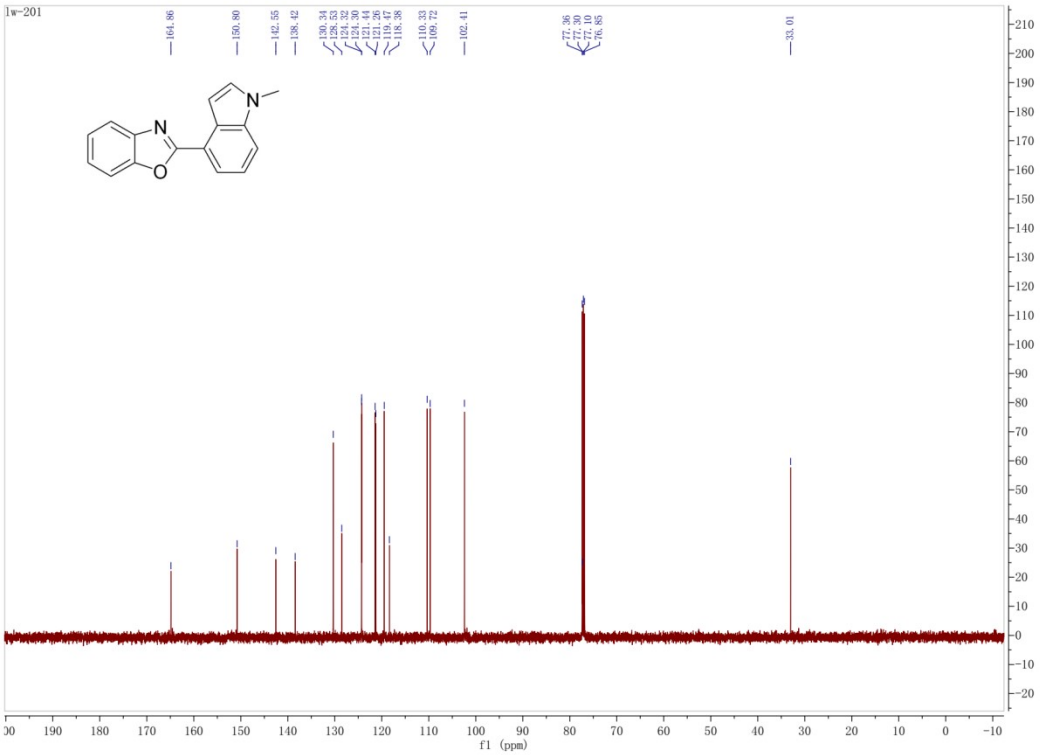

Figure S81. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3z**

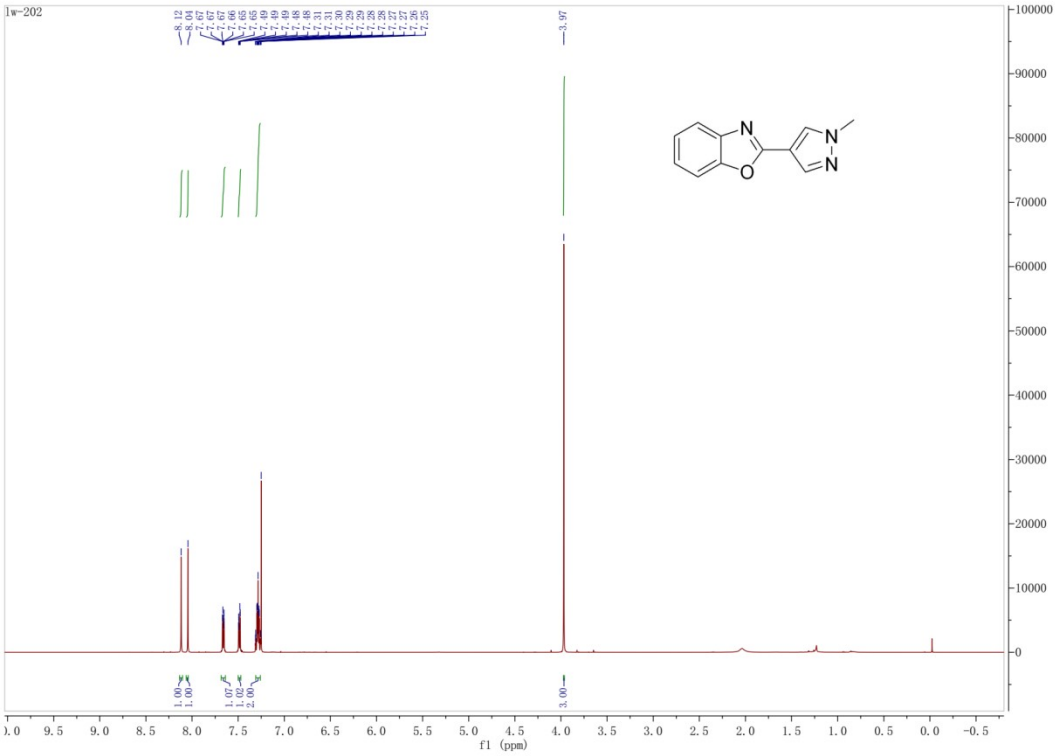

Figure S82. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3aa**

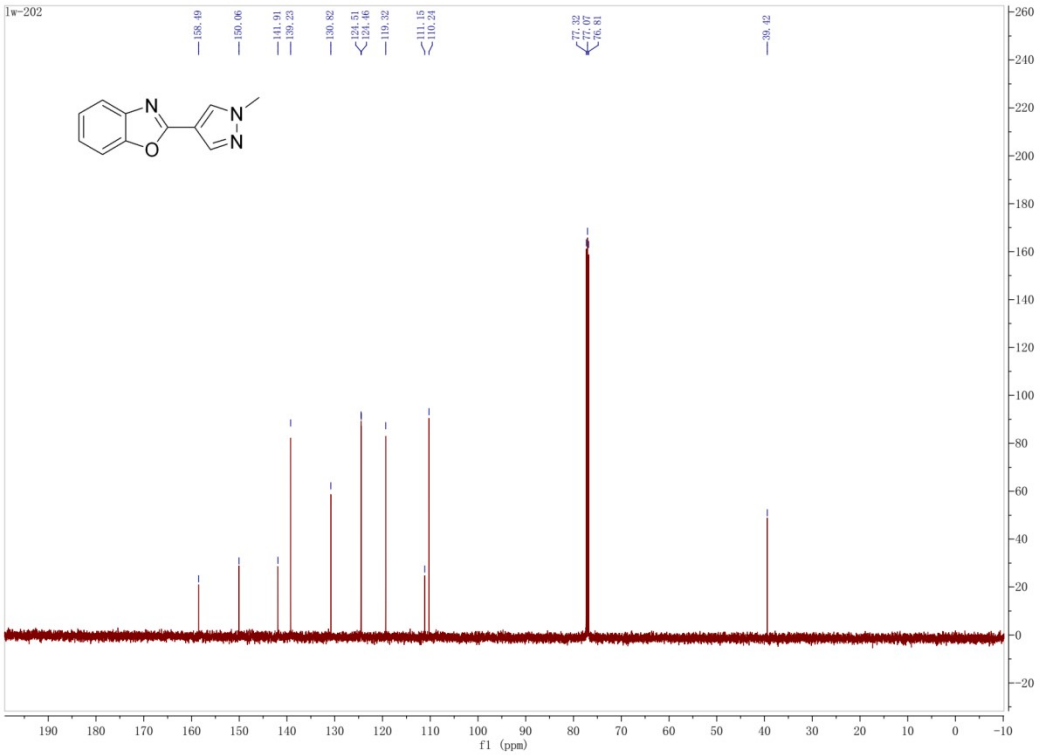

Figure S83. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3aa**

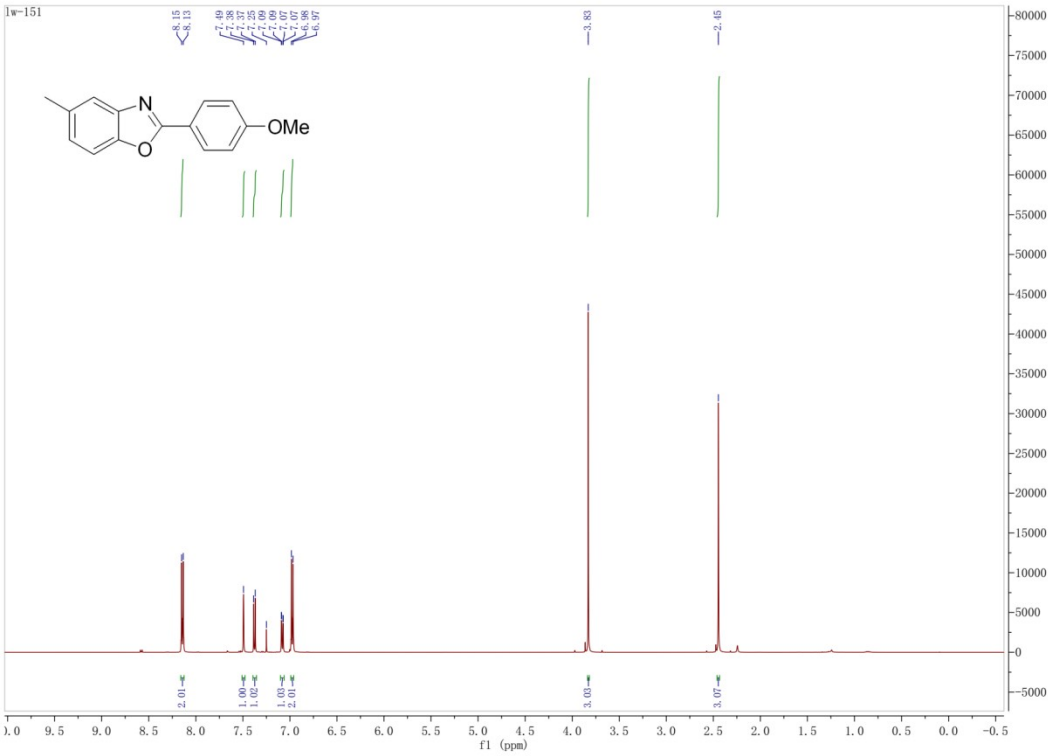

Figure S84. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3ab**

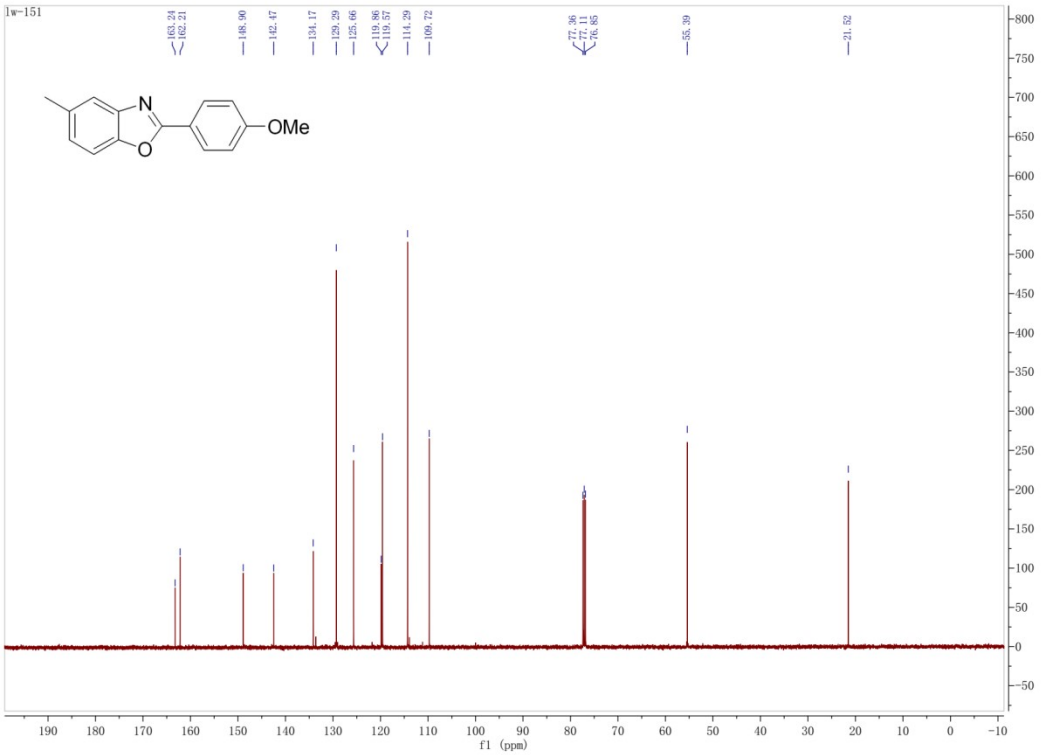

Figure S85. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3ab**

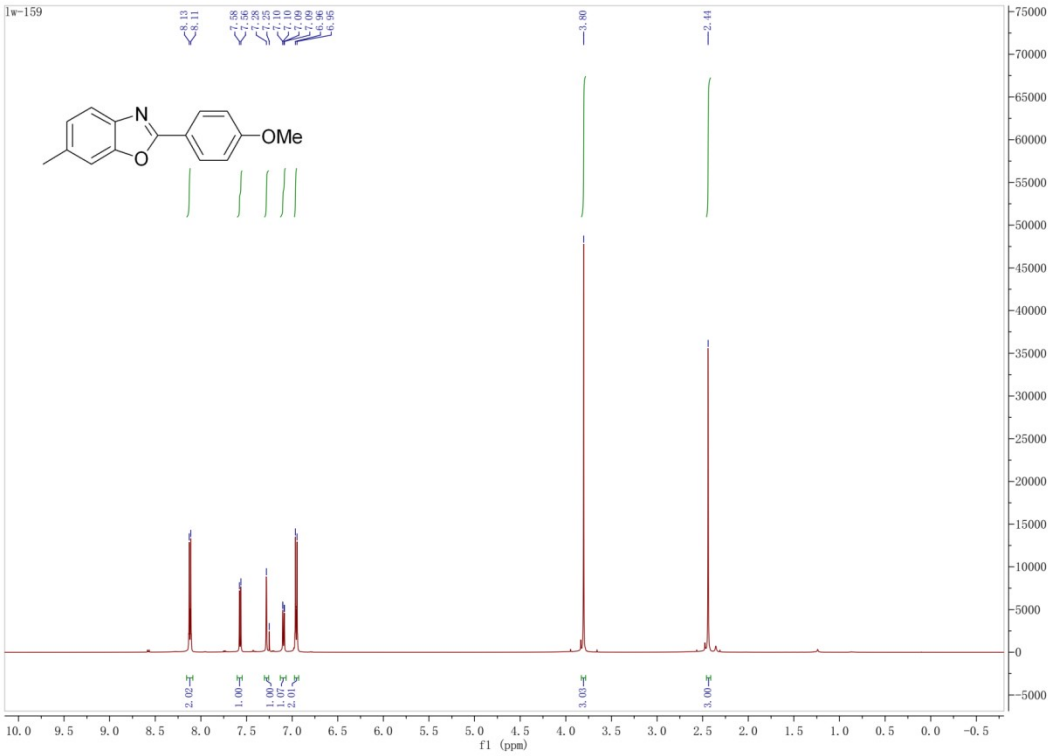

Figure S86. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3ac**

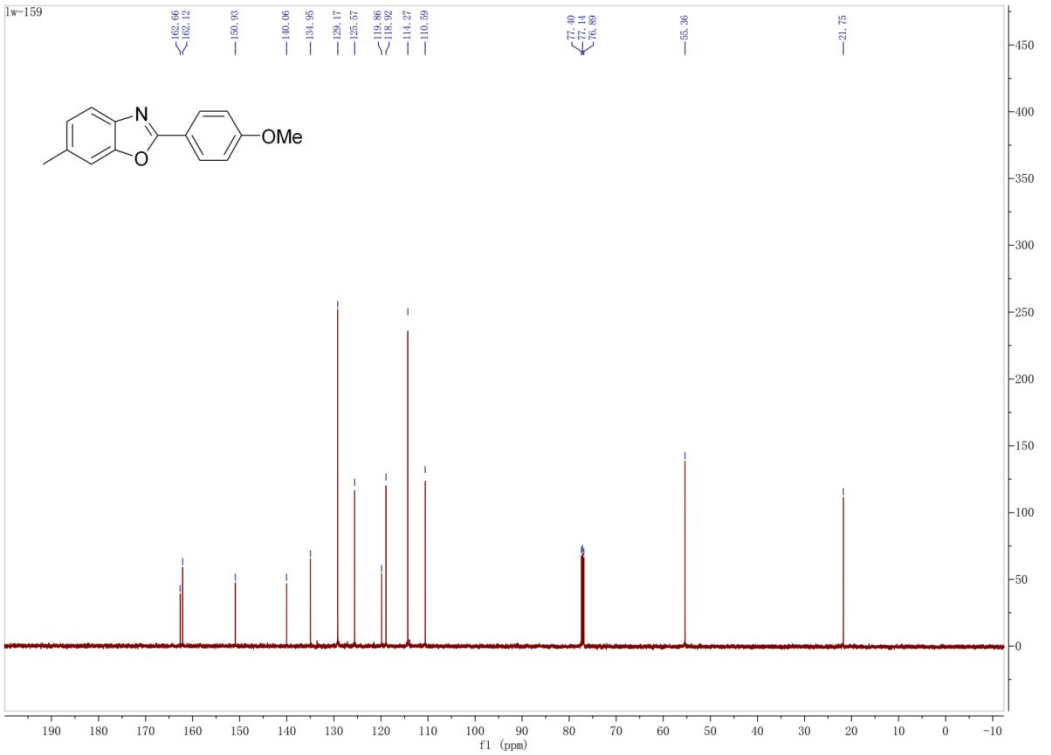

Figure S87. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3ac**

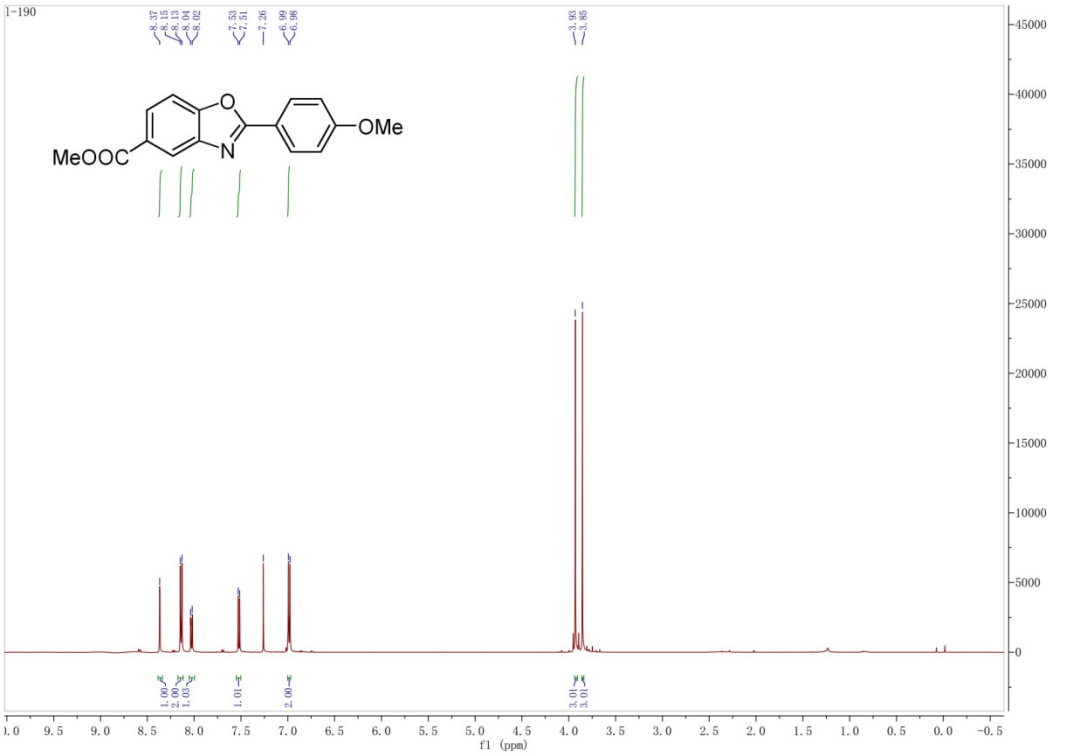

Figure S88. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3ad**

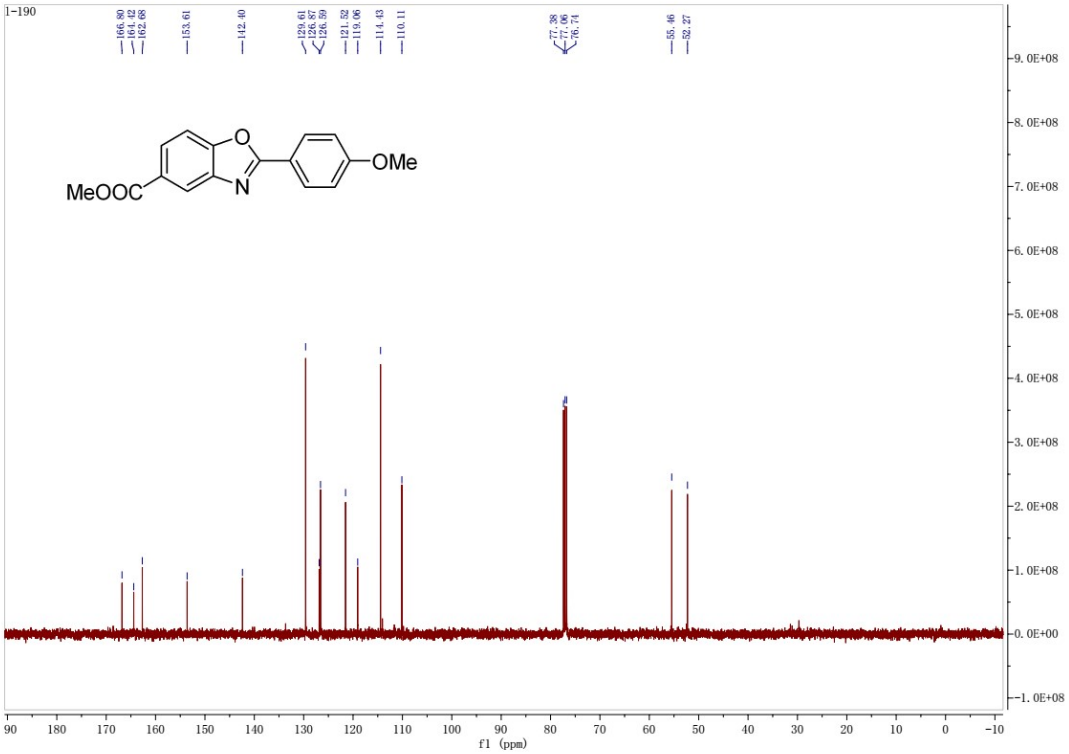

Figure S89. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3ad**

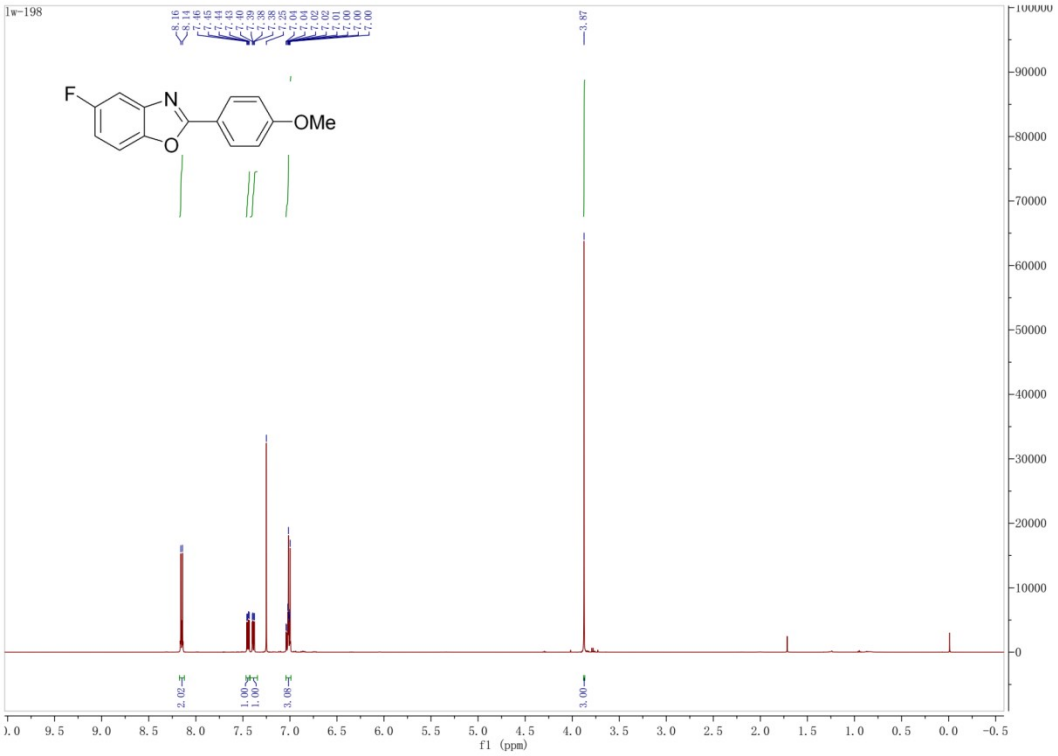

Figure S90. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3ae**

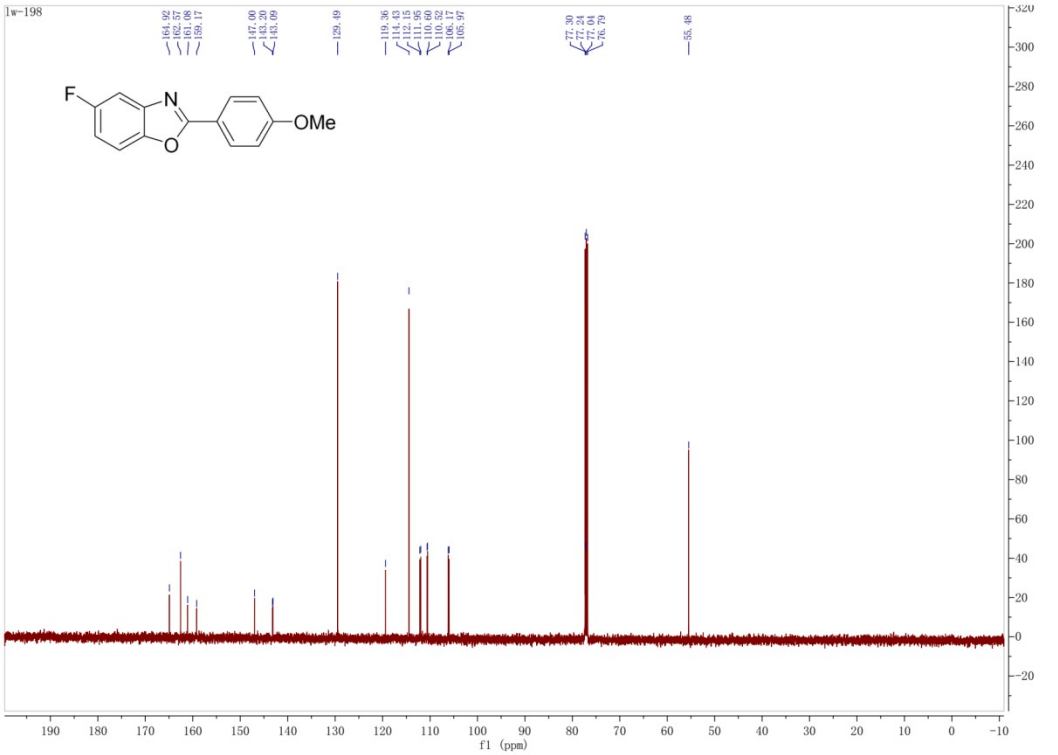

Figure S91. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3ae**

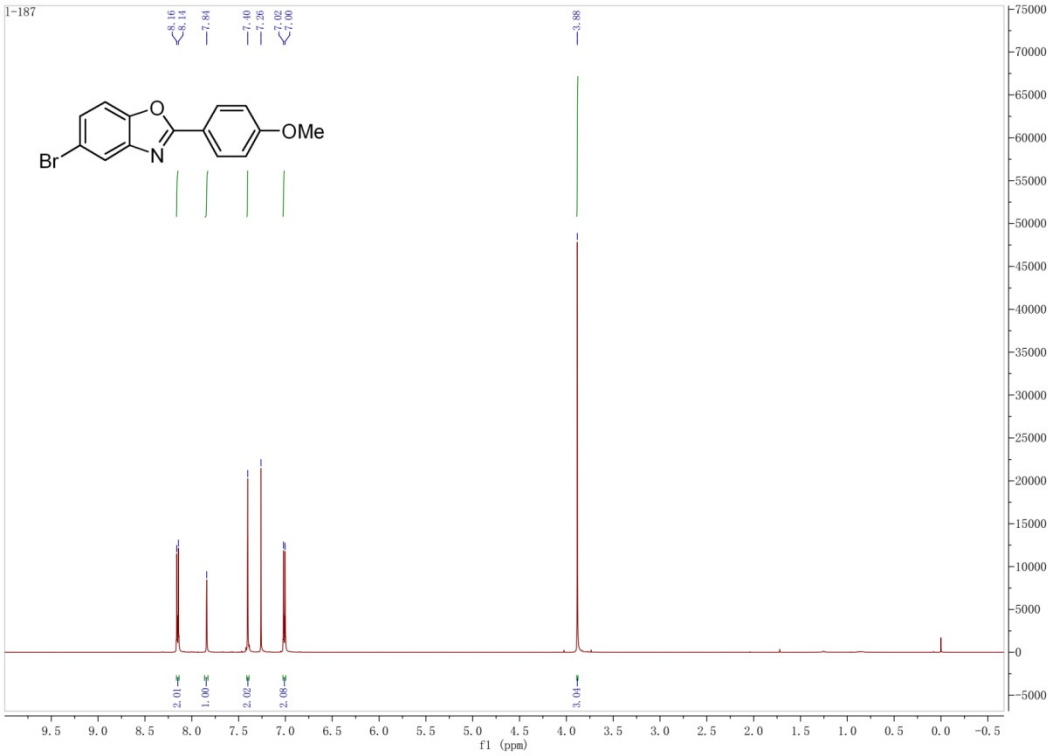

Figure S92. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3af**

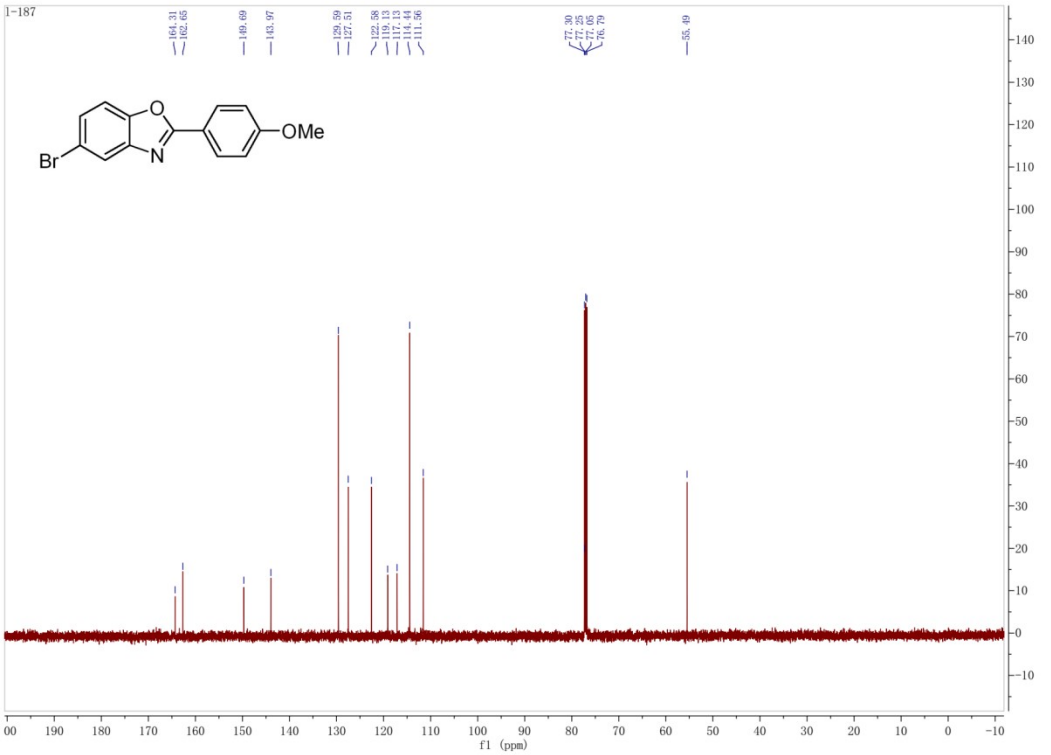

Figure S93. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3af**

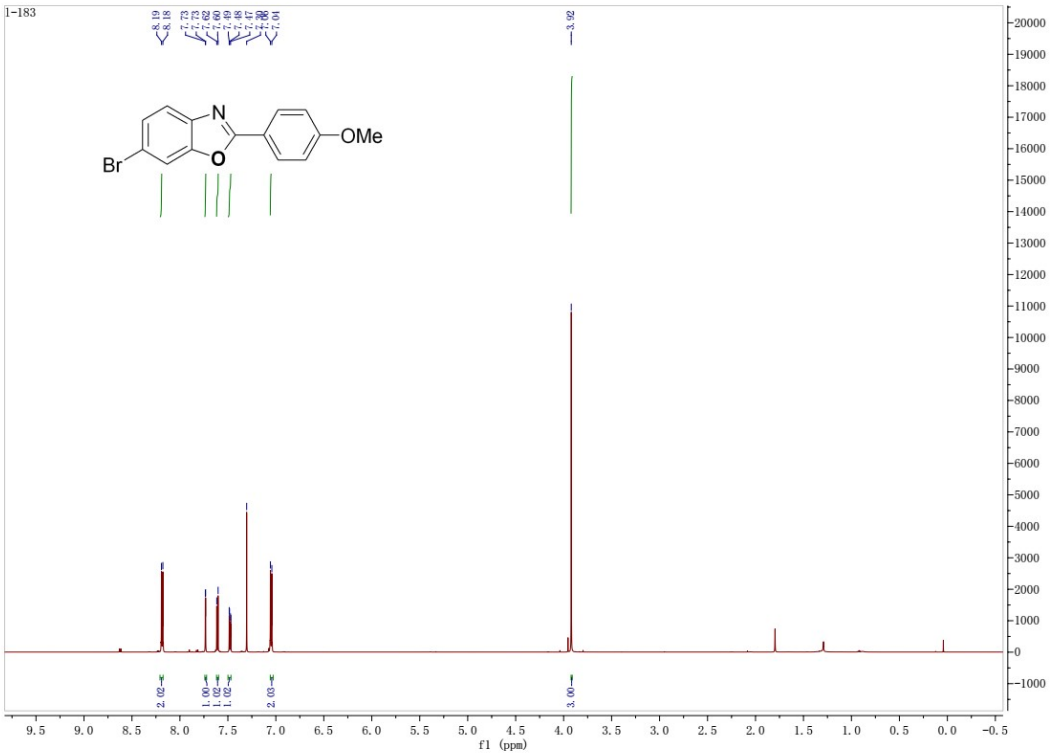

Figure S94. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3ag**

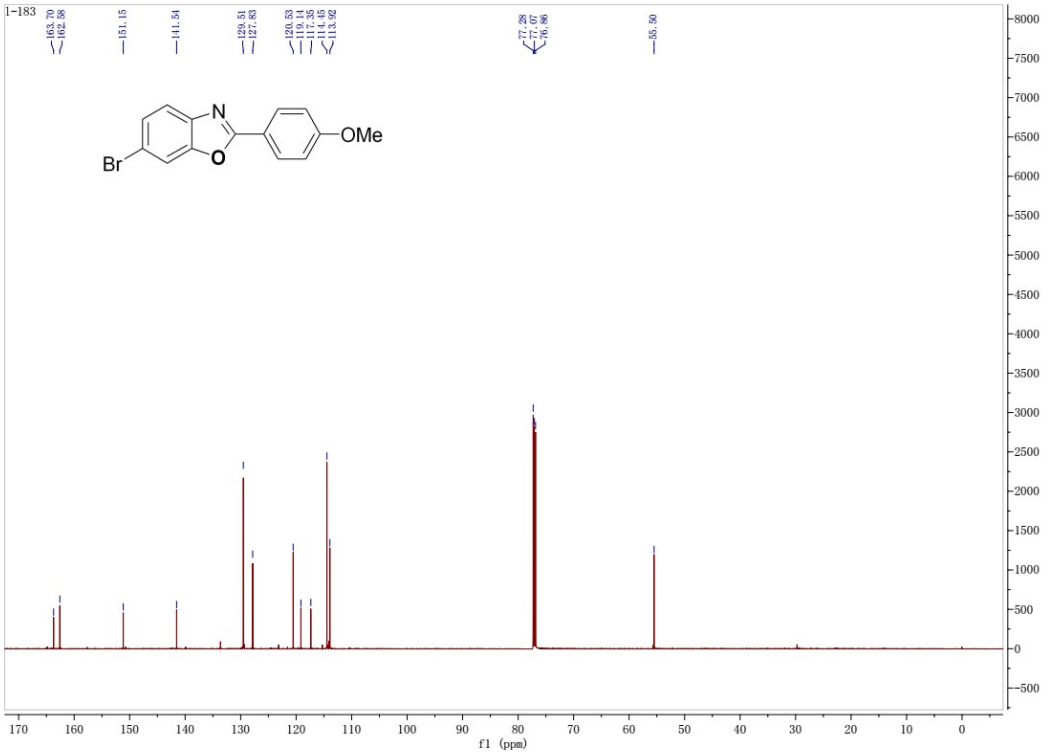

Figure S95. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3ag**

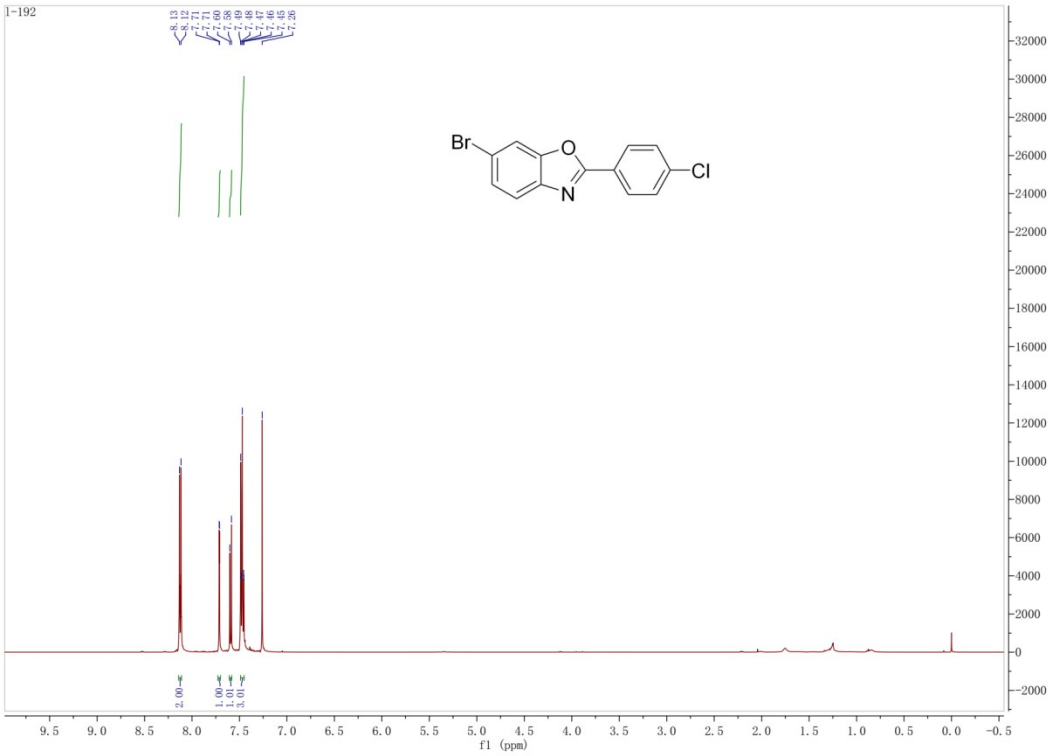

Figure S96. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3ah**

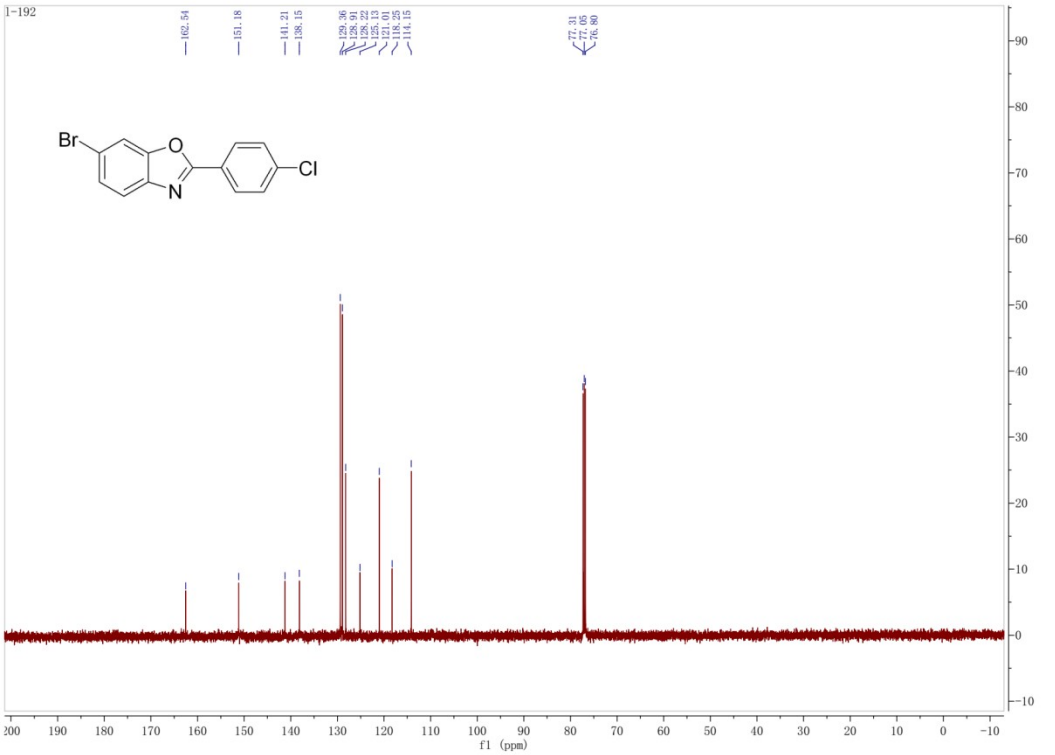

Figure S97. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3ah**

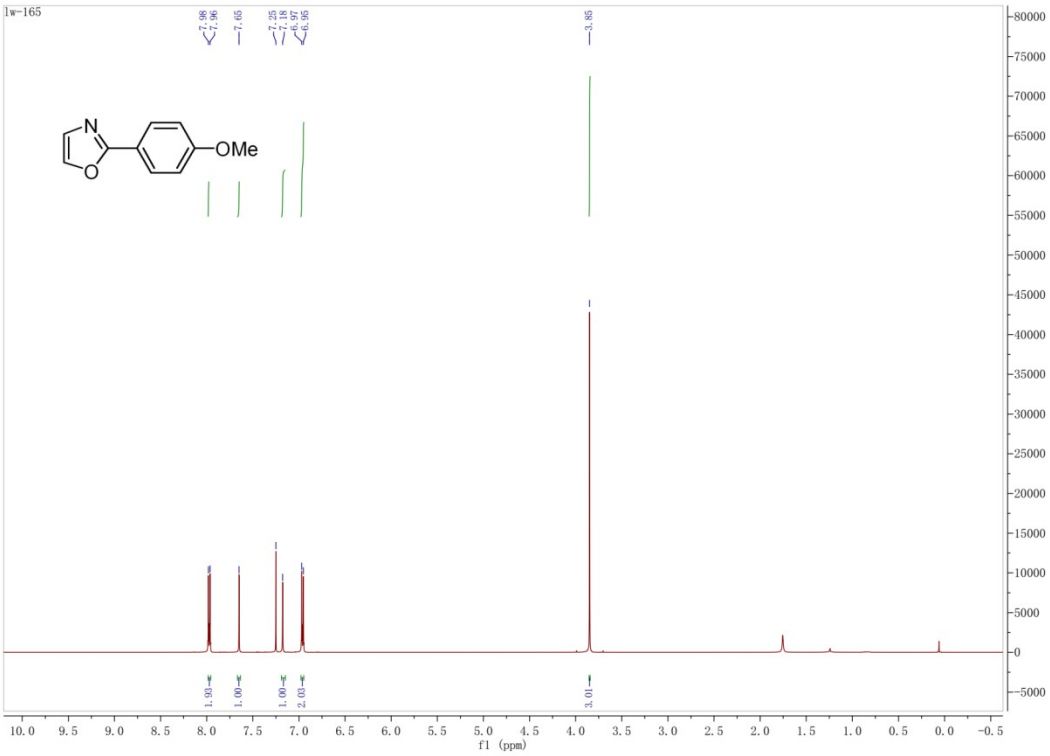

Figure S98. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3ai**

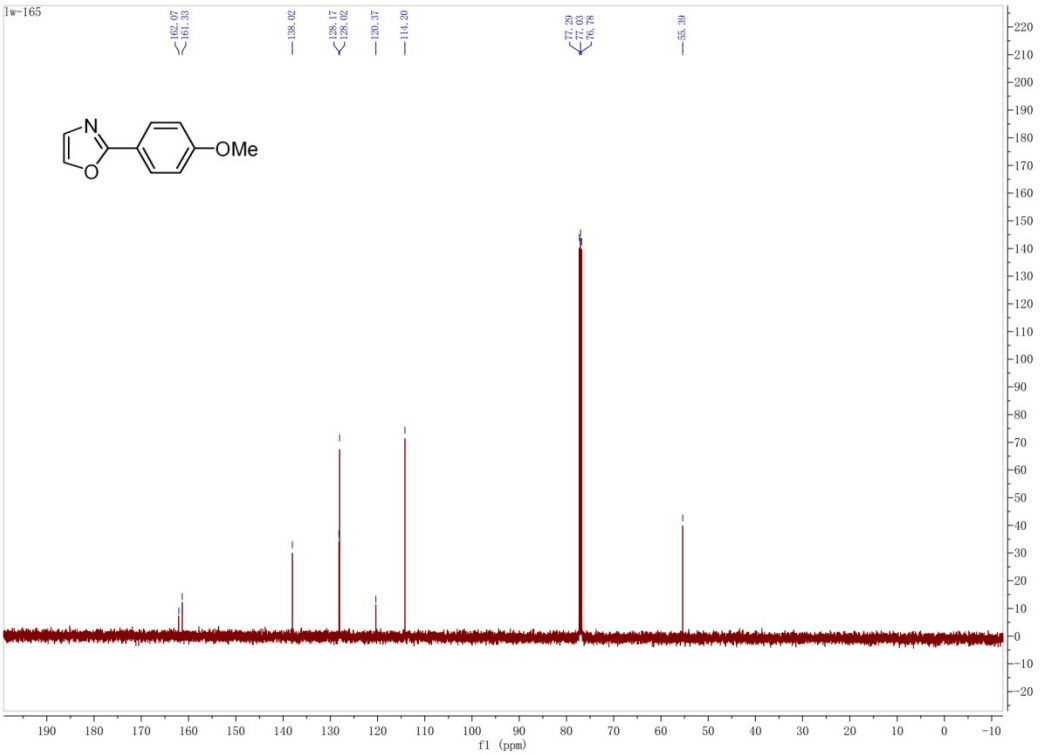

Figure S99. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3ai**

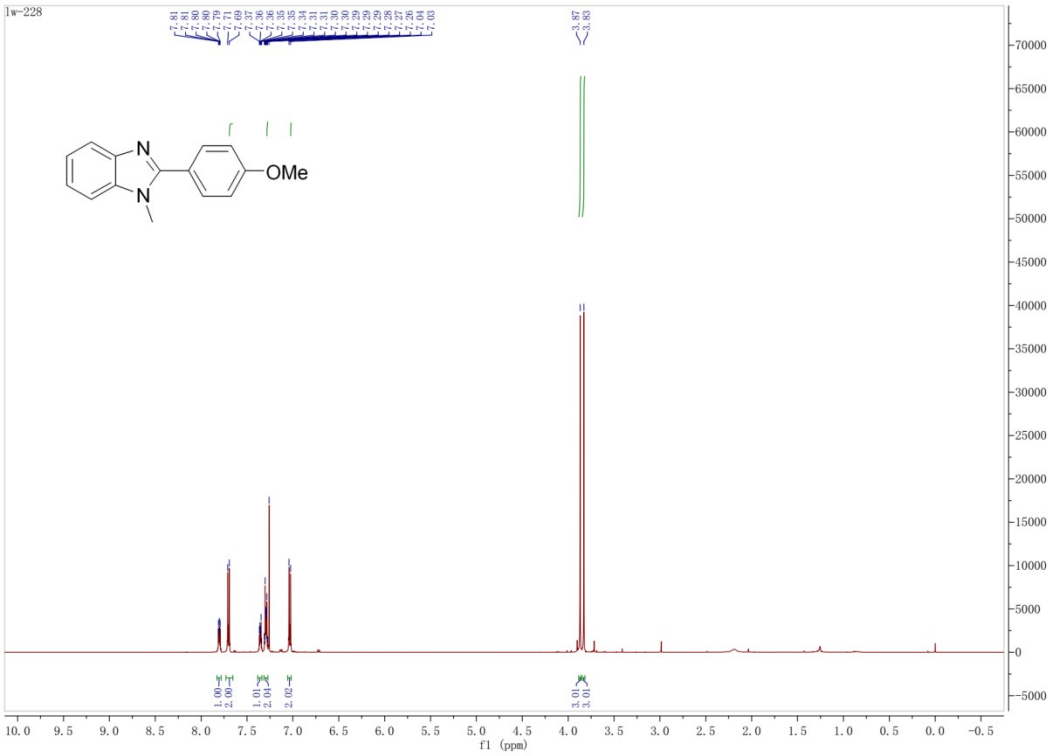

Figure S100. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3aj**

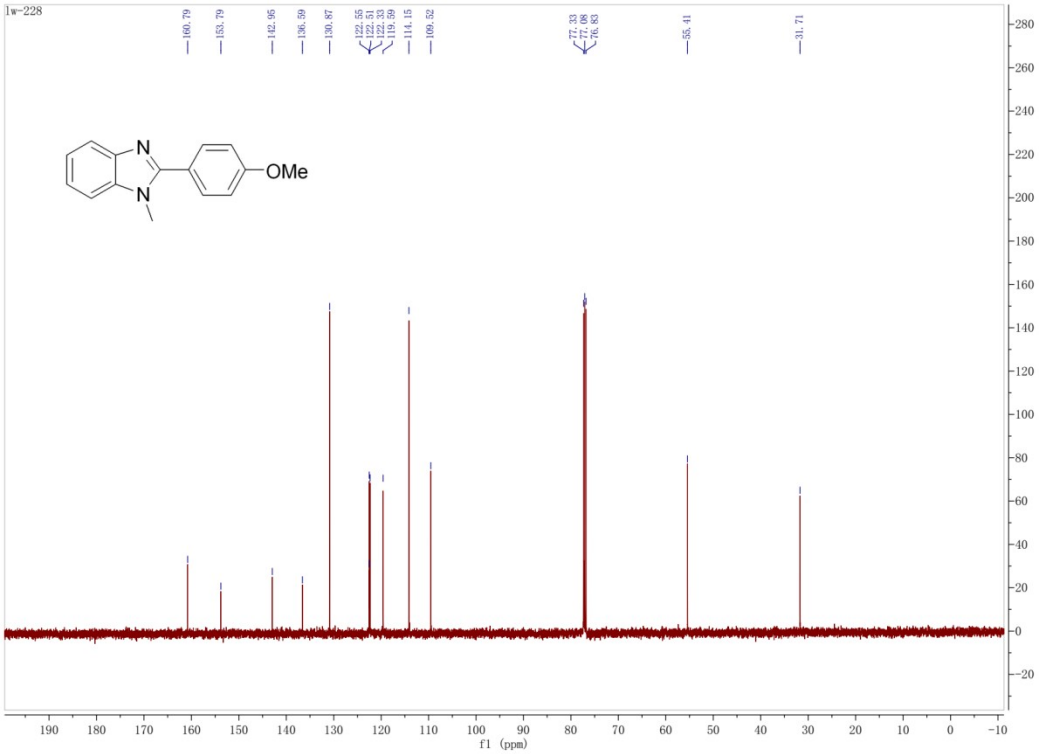

Figure S101. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3aj**

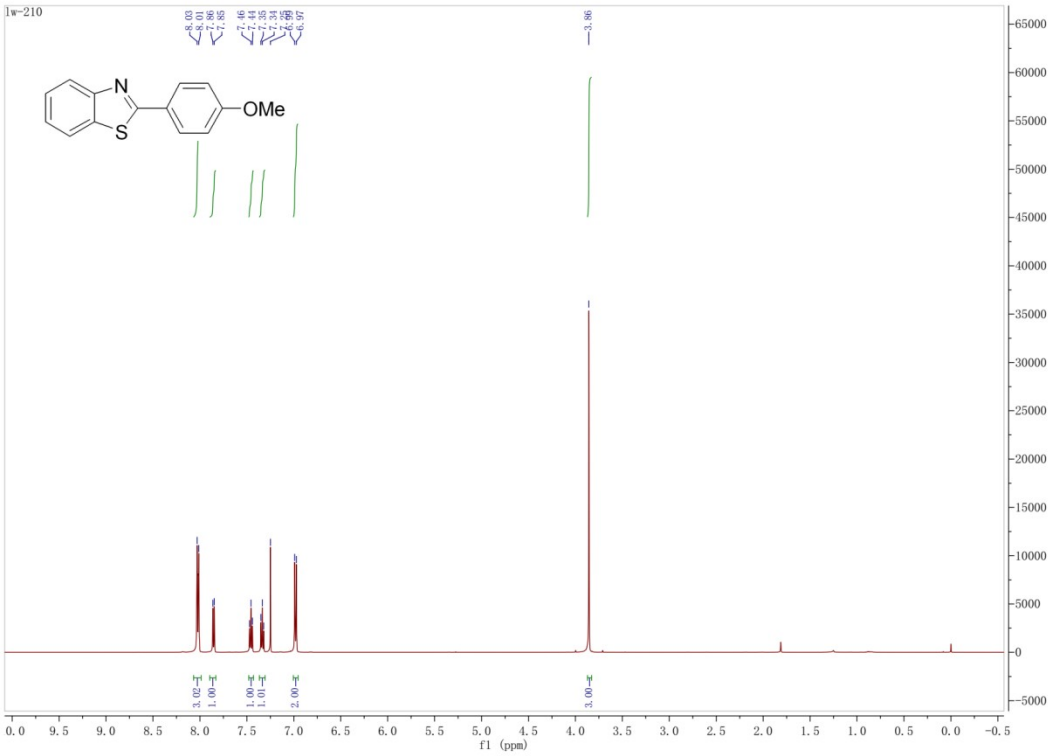

Figure S102. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3ak**

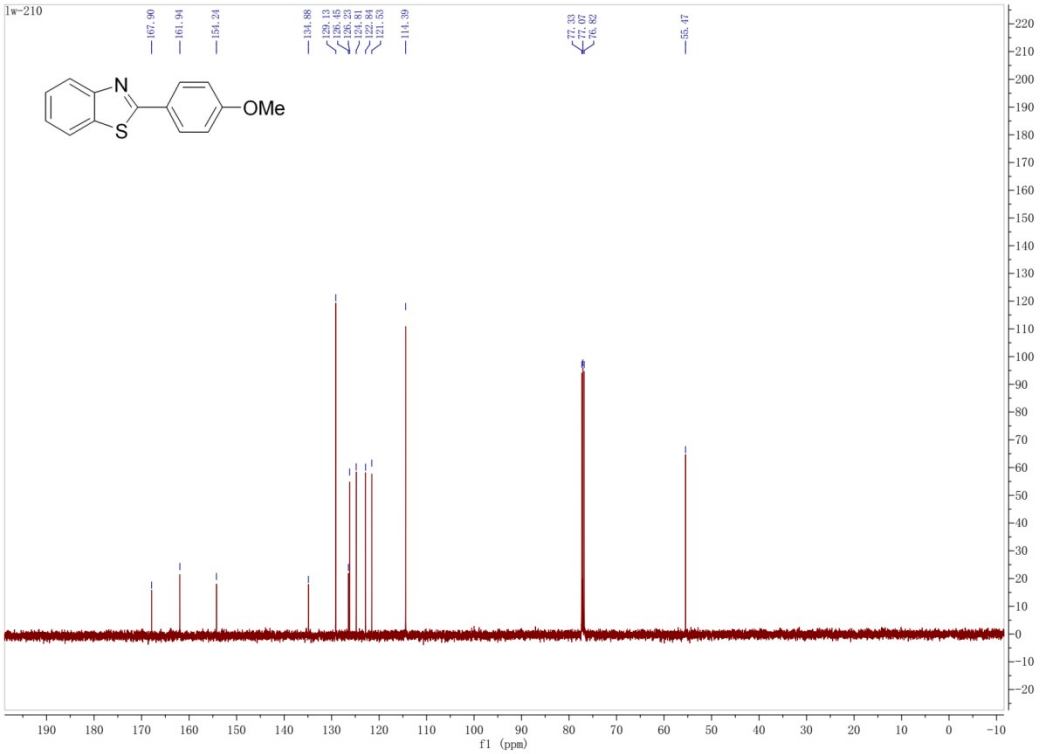

Figure S103. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3ak**

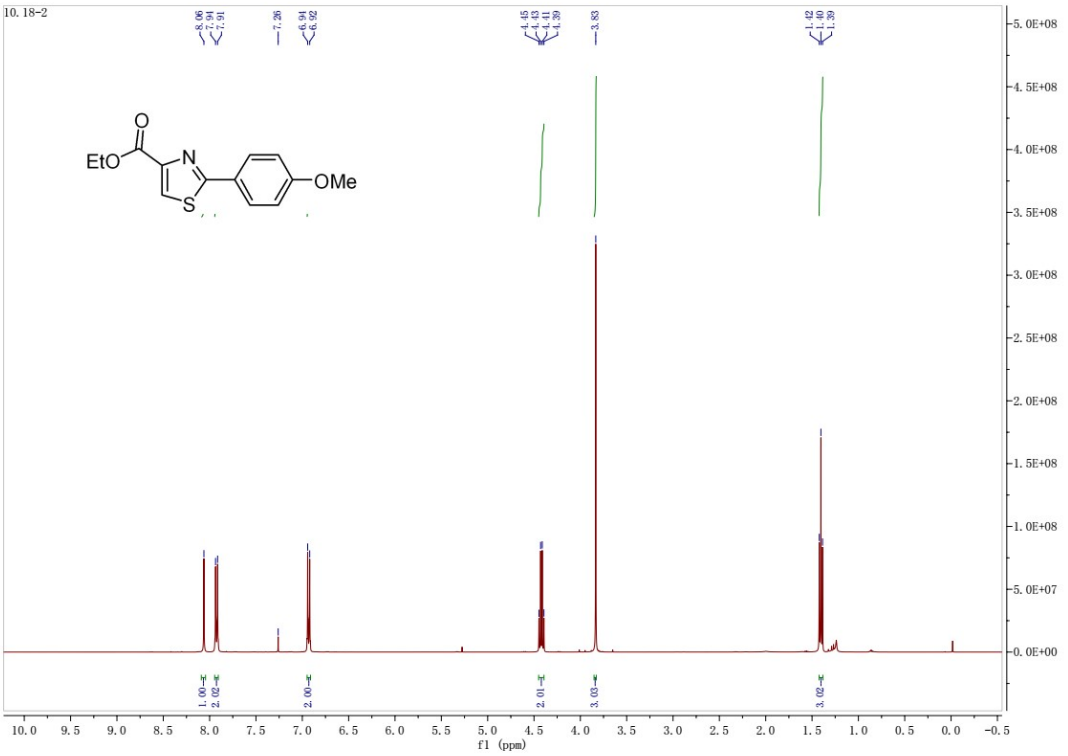

Figure S104. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3al**

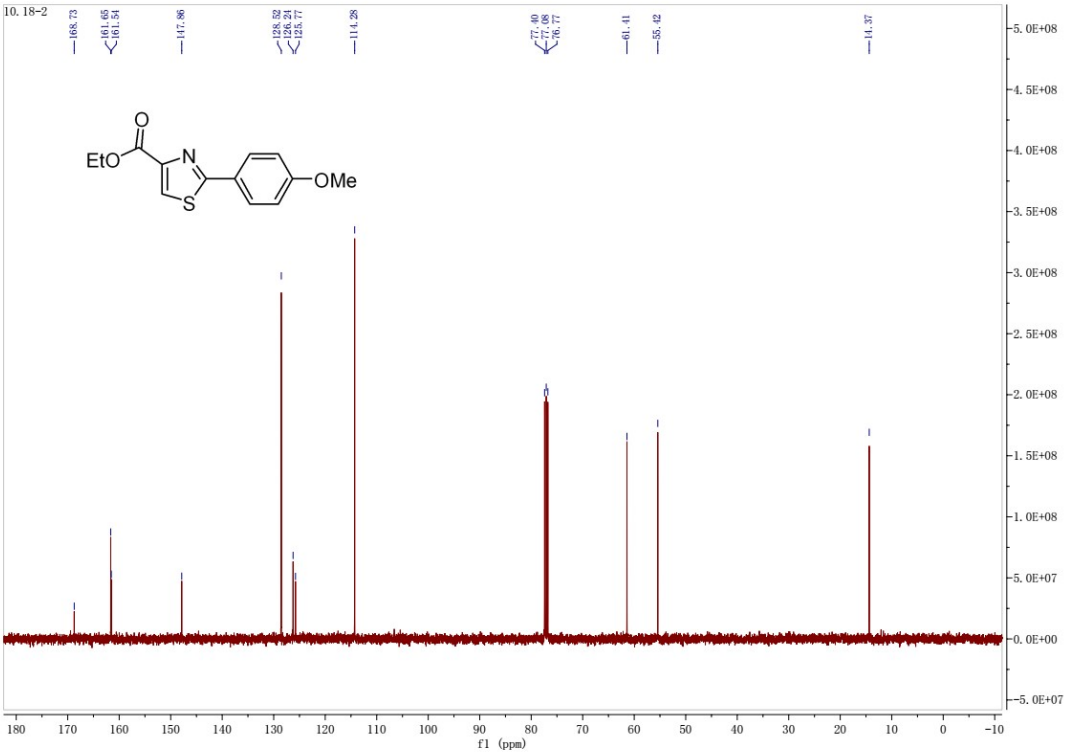

Figure S105. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3al**

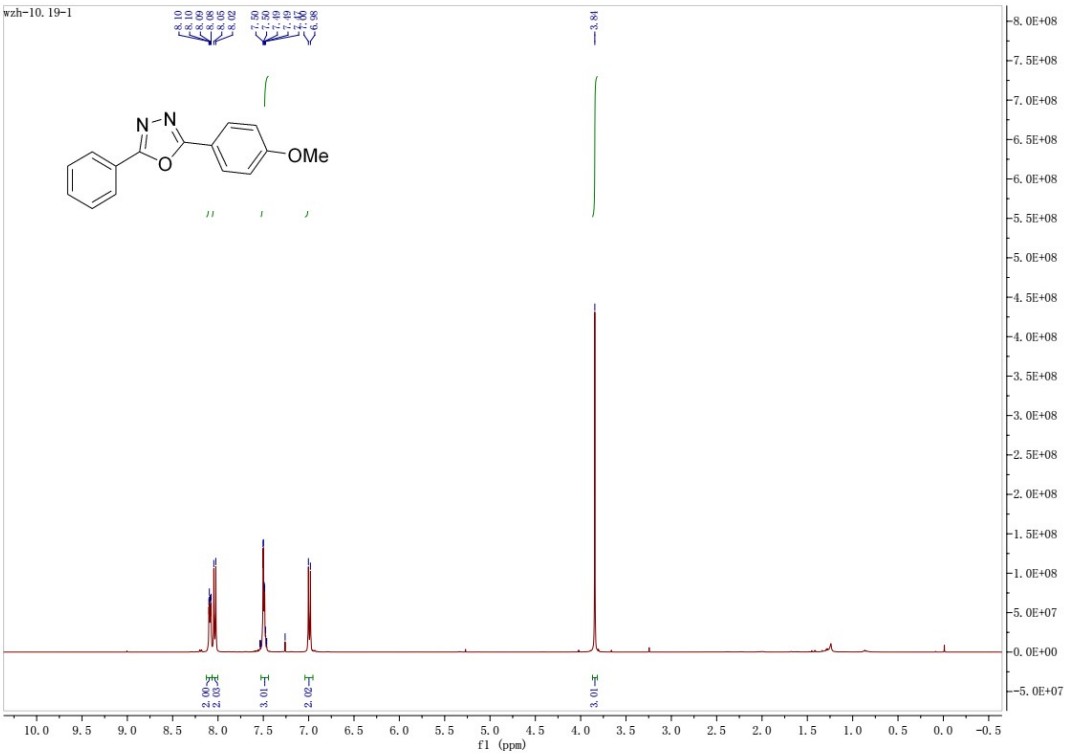

Figure S106. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3am**

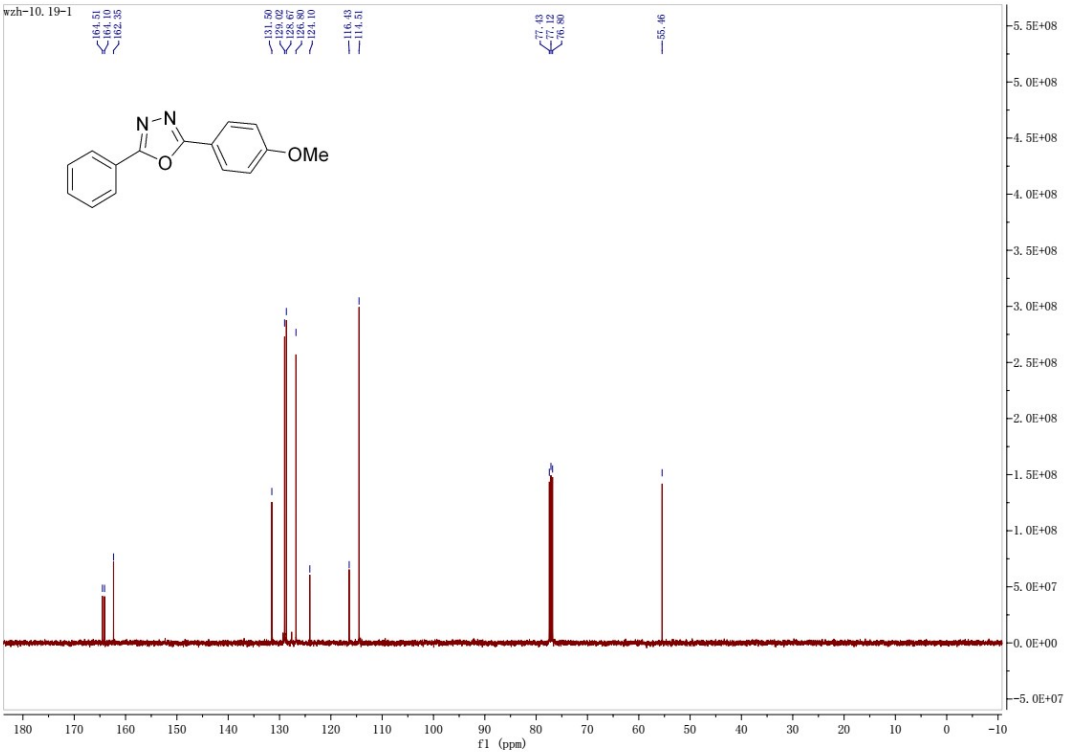

Figure S107. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3am**

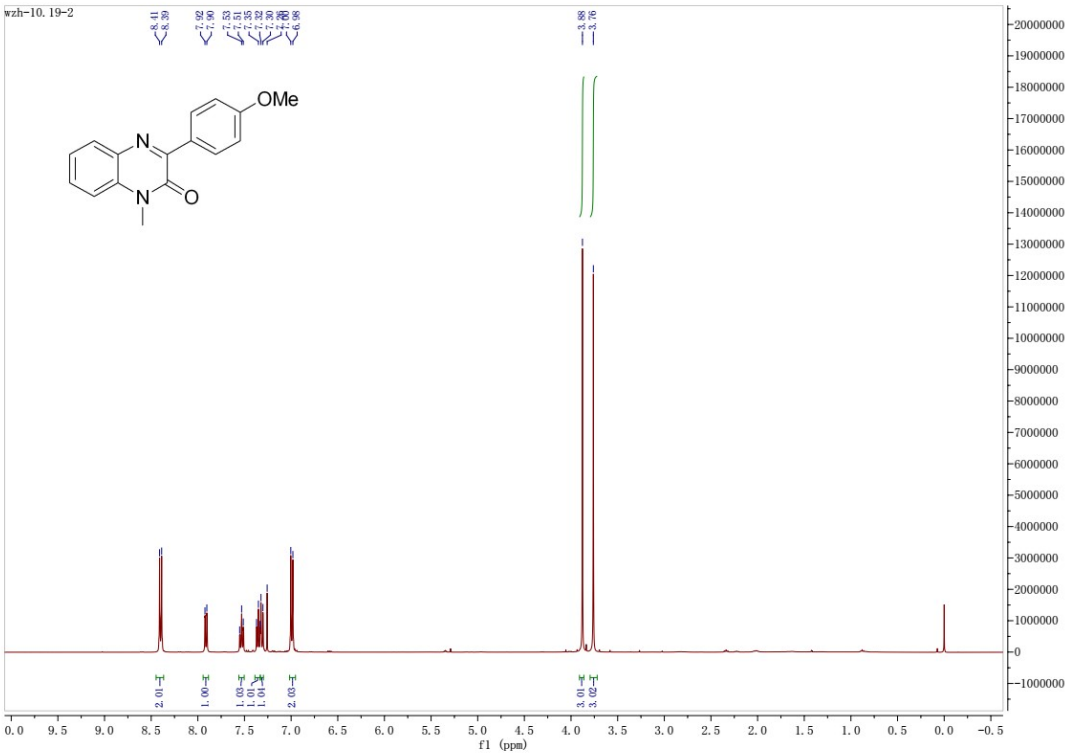

Figure S108. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3an**

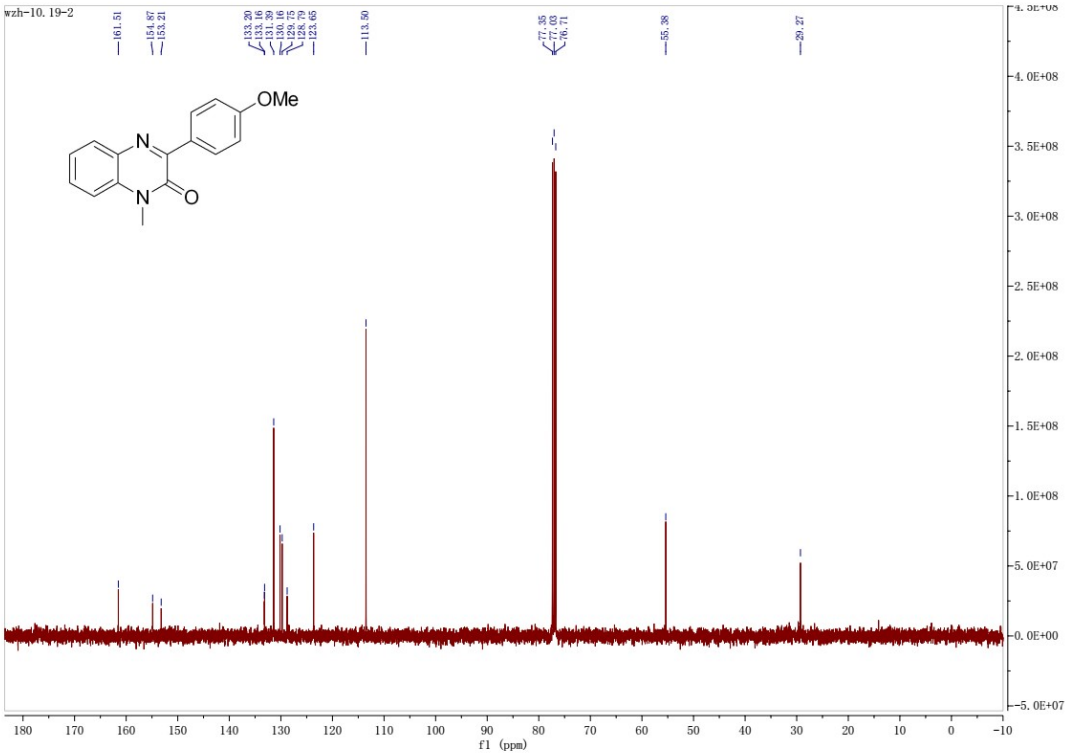

Figure S109. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3an**

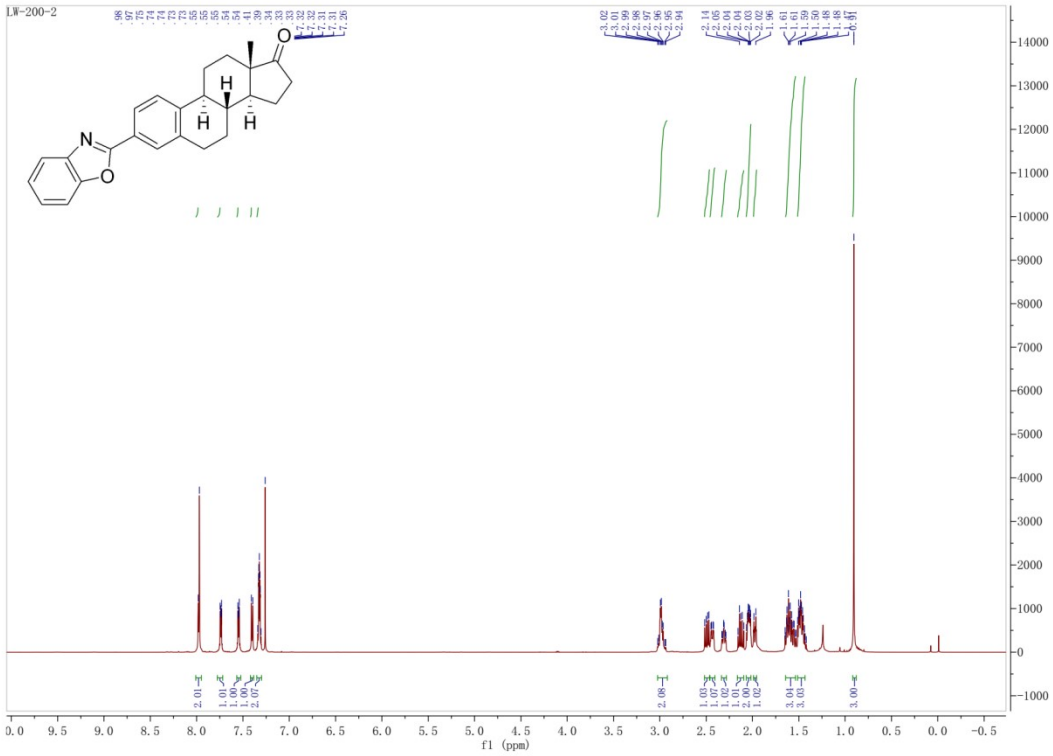

Figure S110. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3ao**

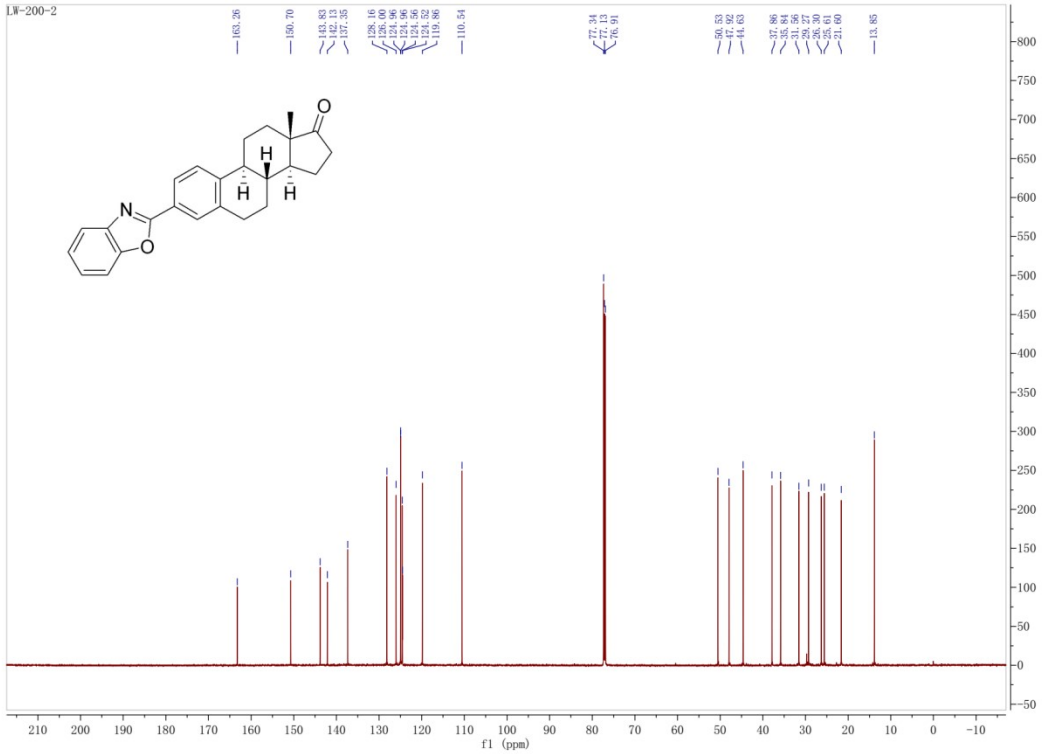

Figure S111. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3ao**

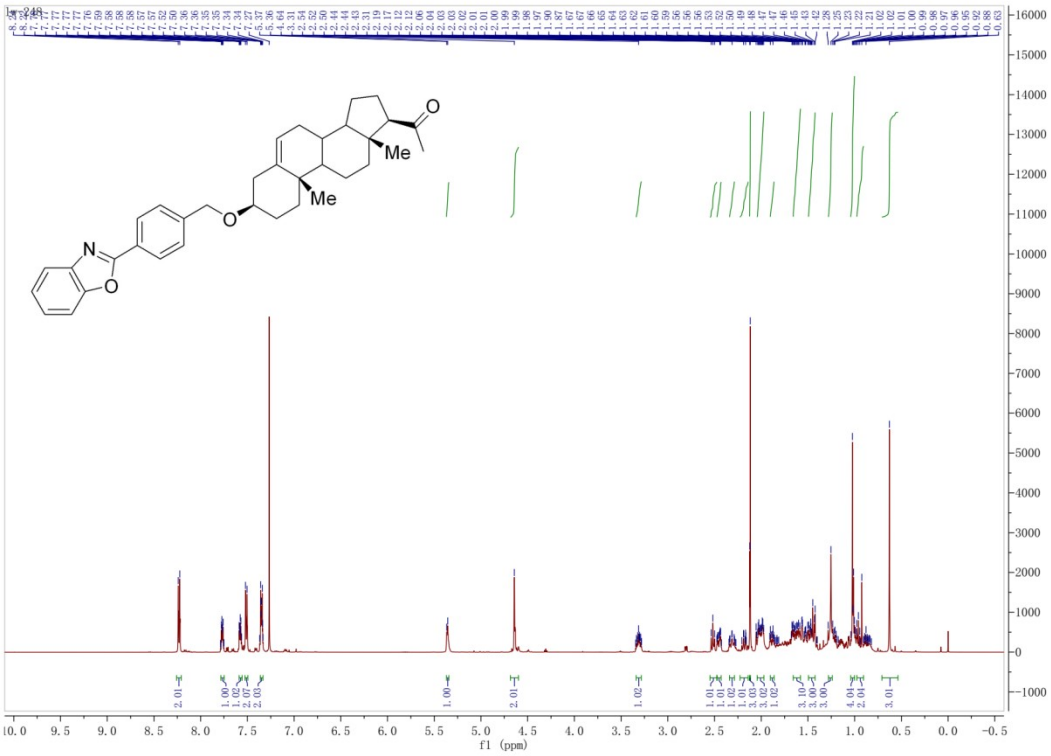

Figure S112. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3ap**

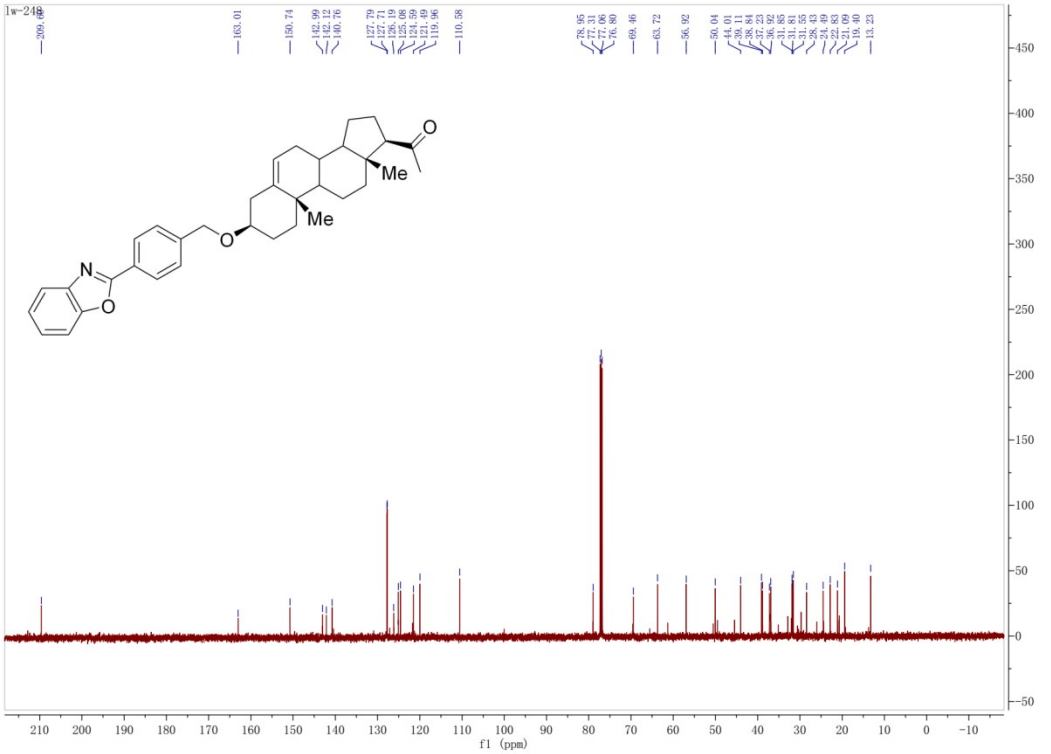

Figure S113. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3ap**

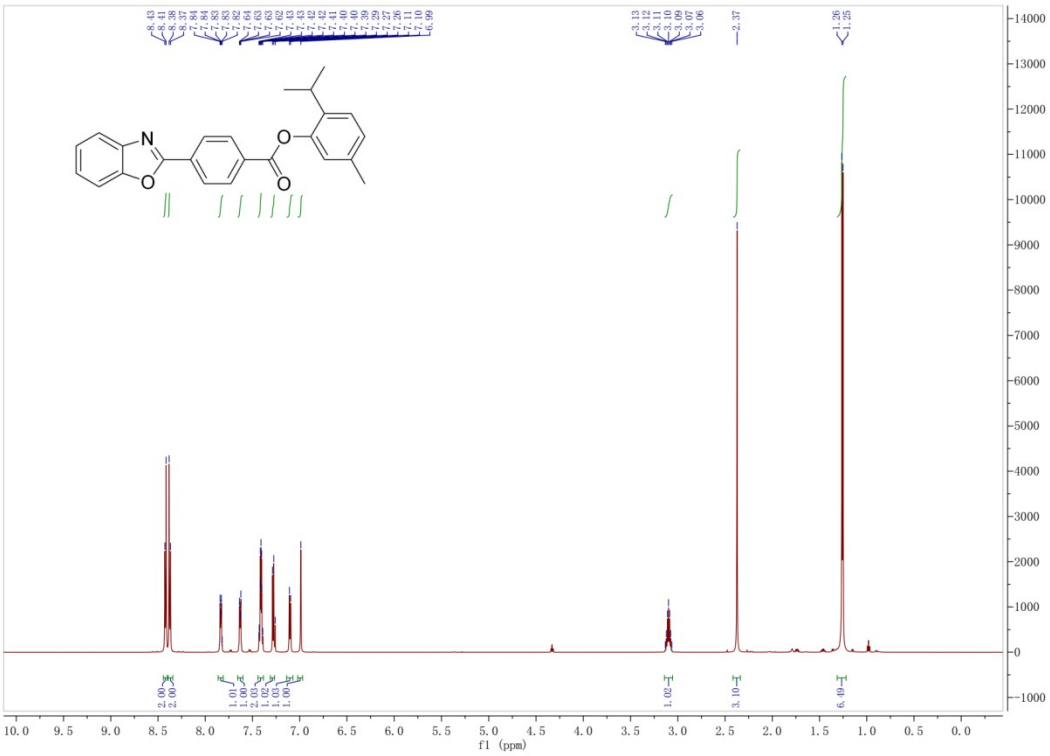

Figure S114. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3aq**

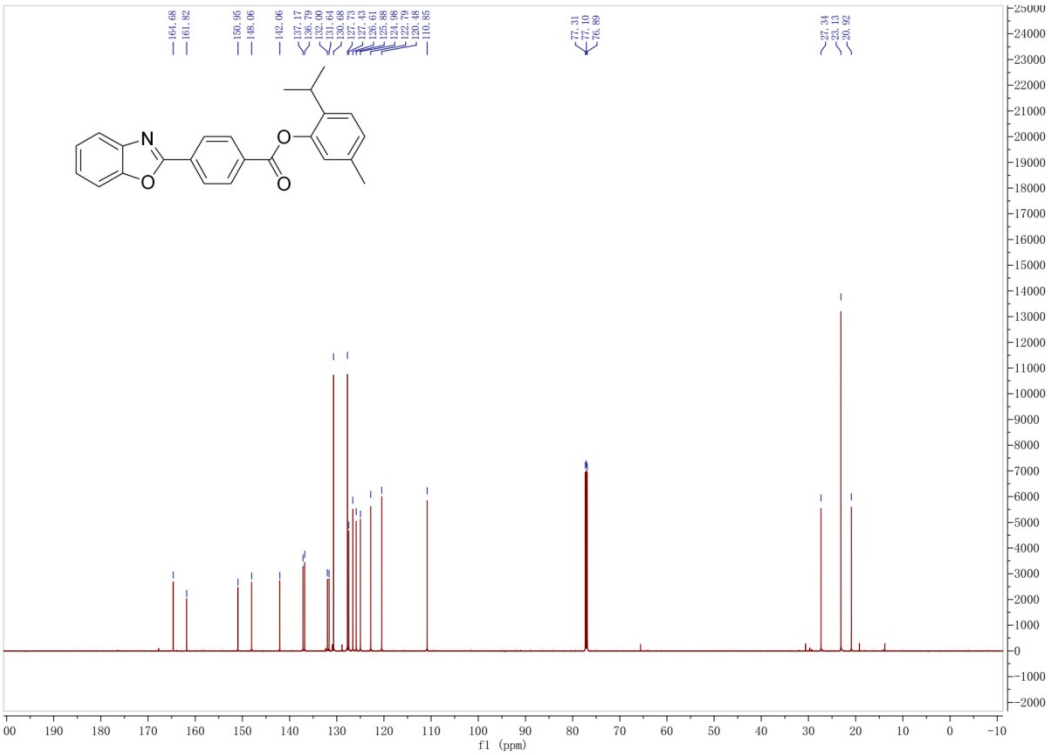

Figure S115. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3aq**

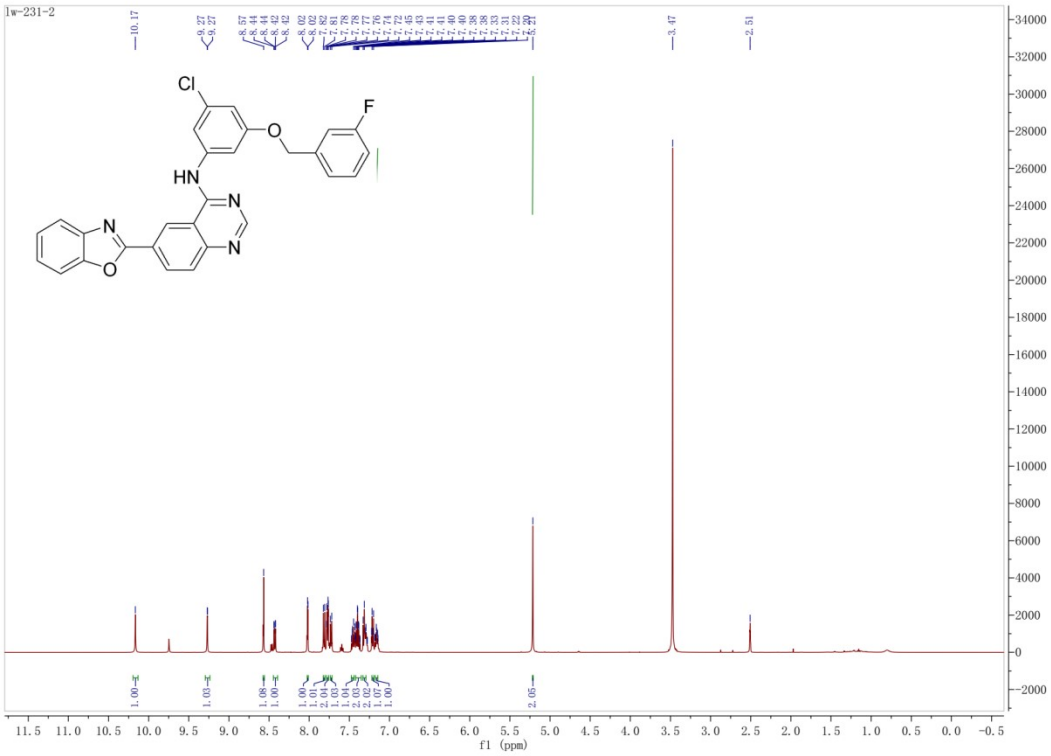

Figure S116. ^{1}H NMR (500 MHz, DMSO-d_6) of Compound **3ar**

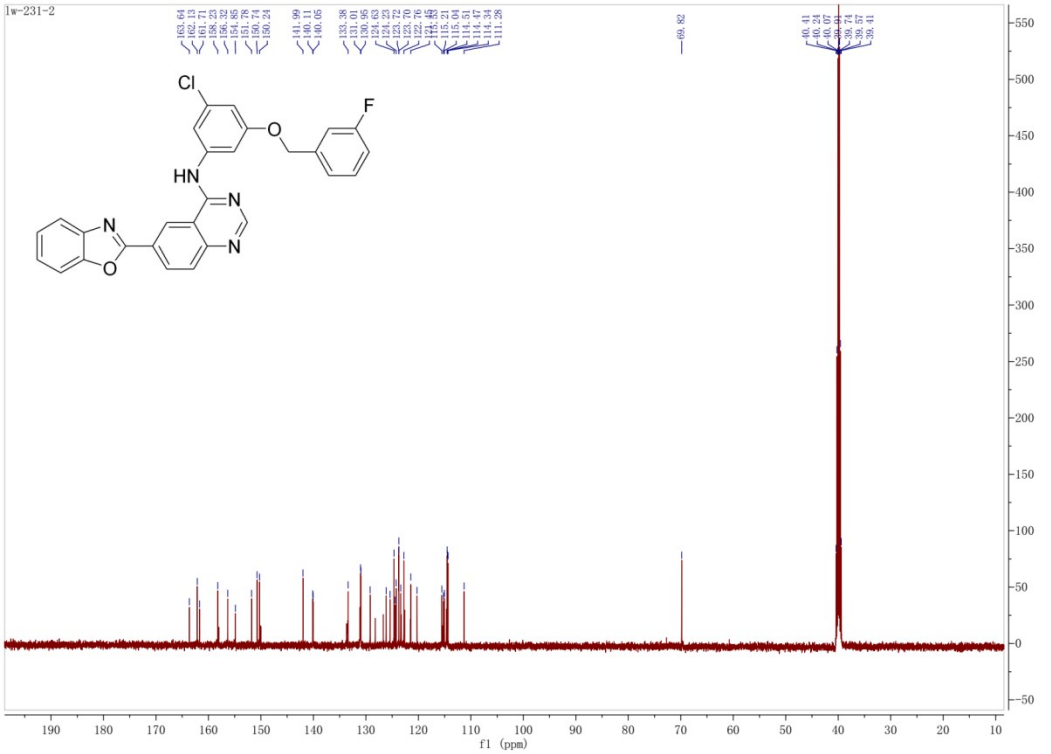

Figure S117. ^{13}C NMR (125 MHz, DMSO-d_6) of Compound **3ar**

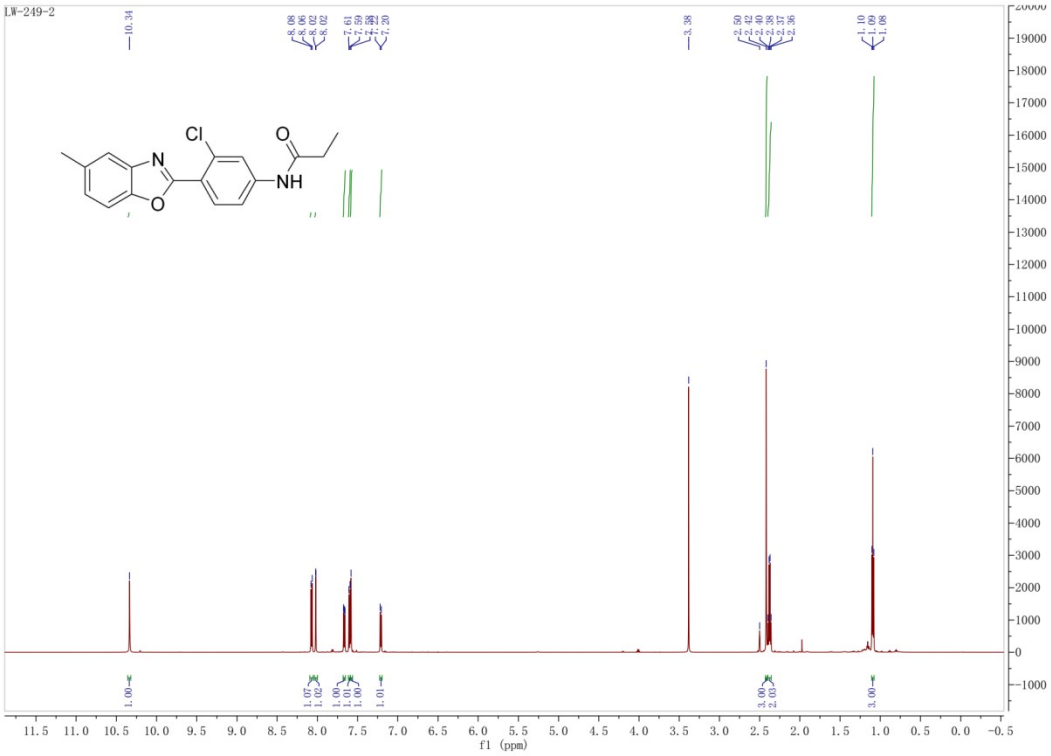

Figure S118. ^{1}H NMR (600 MHz, DMSO-d_6) of Compound **3as**

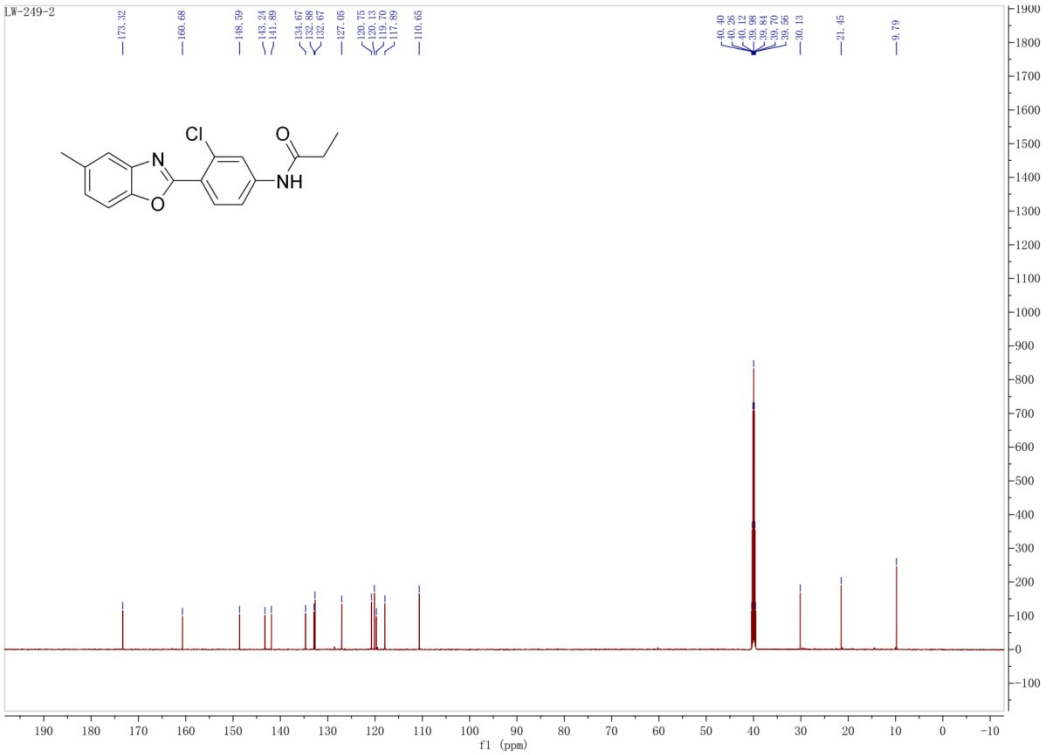

Figure S119. ^{13}C NMR (150 MHz, DMSO-d_6) of Compound **3as**

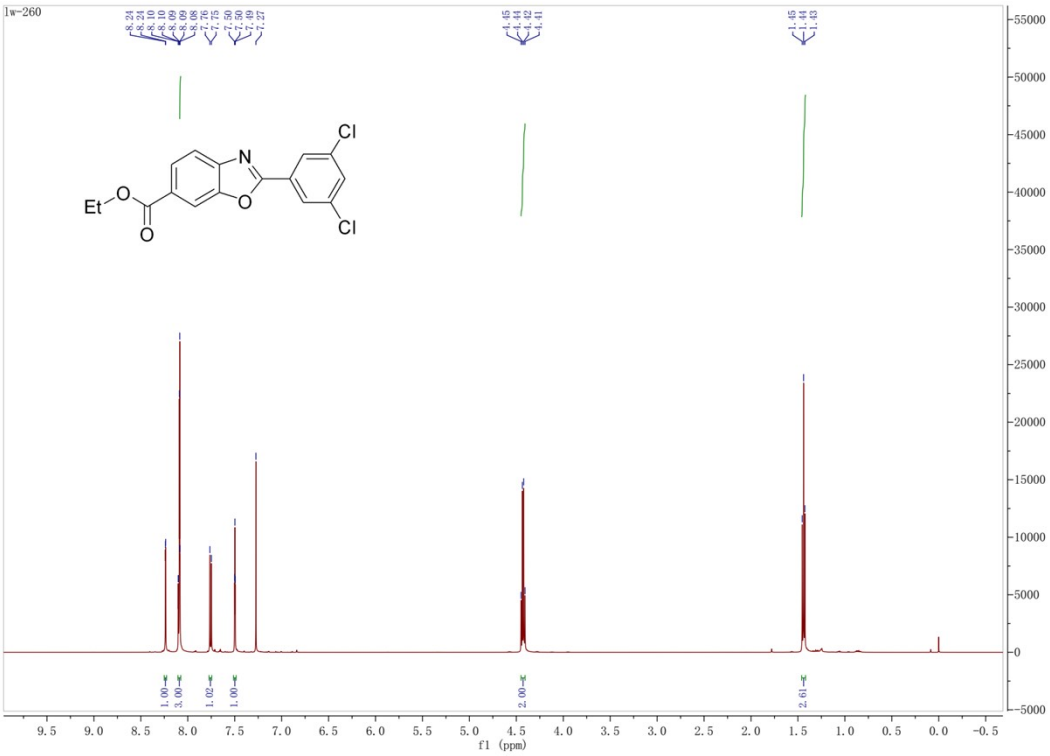

Figure S120. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3at**

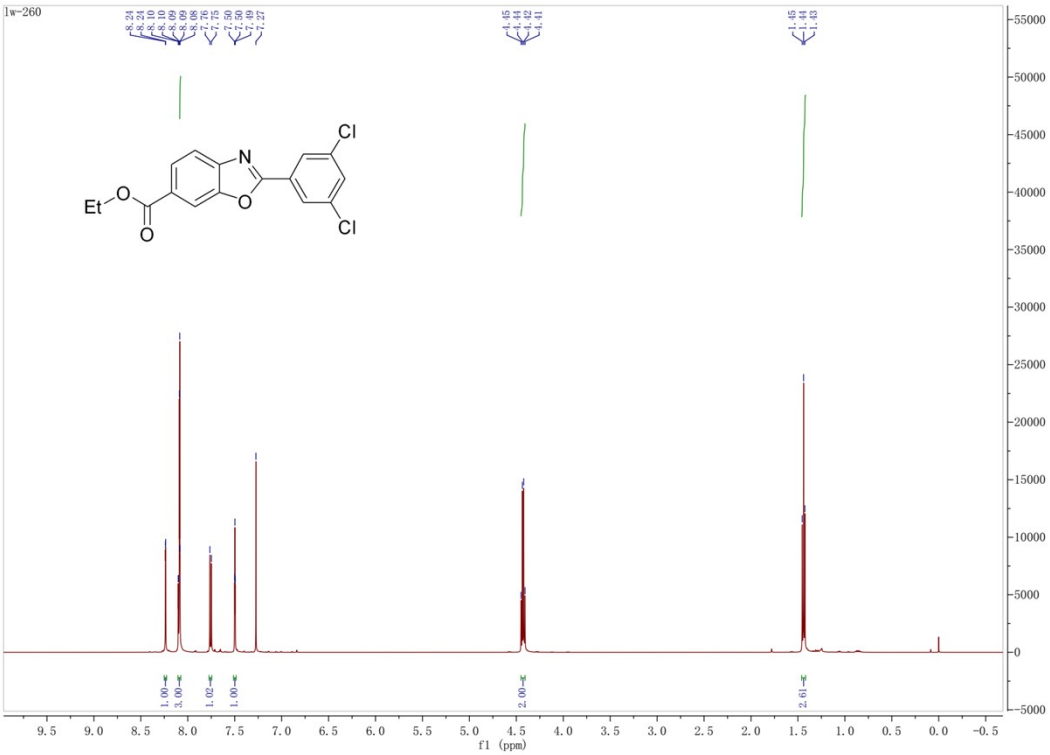

Figure S121. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3at**

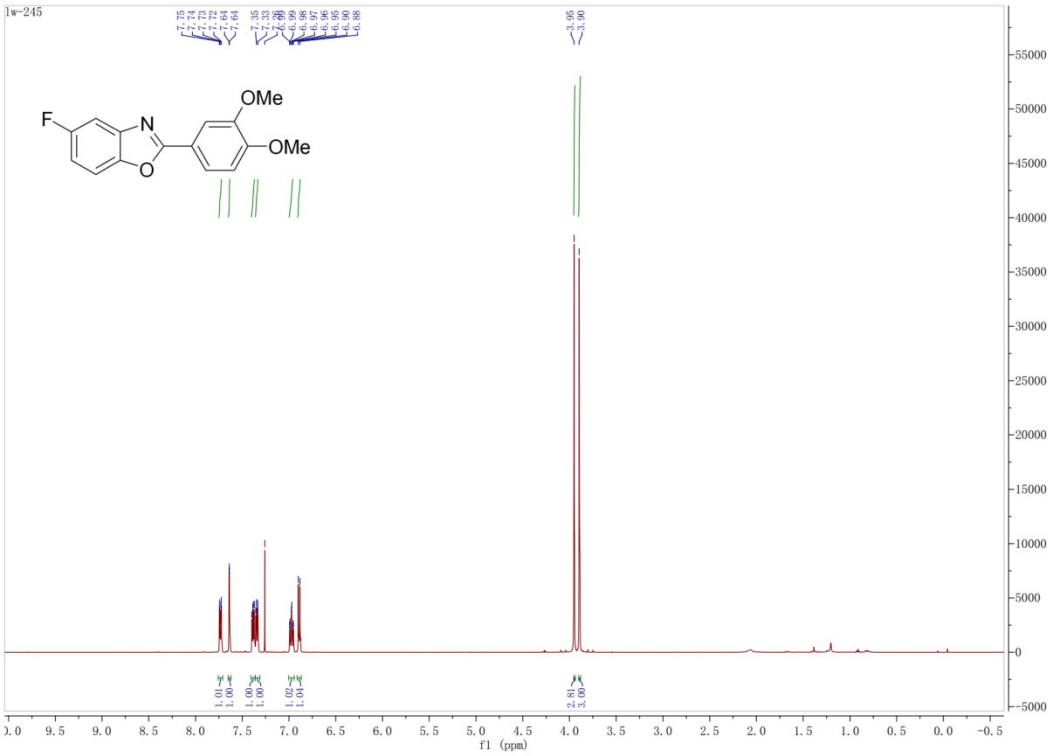

Figure S122. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3au**

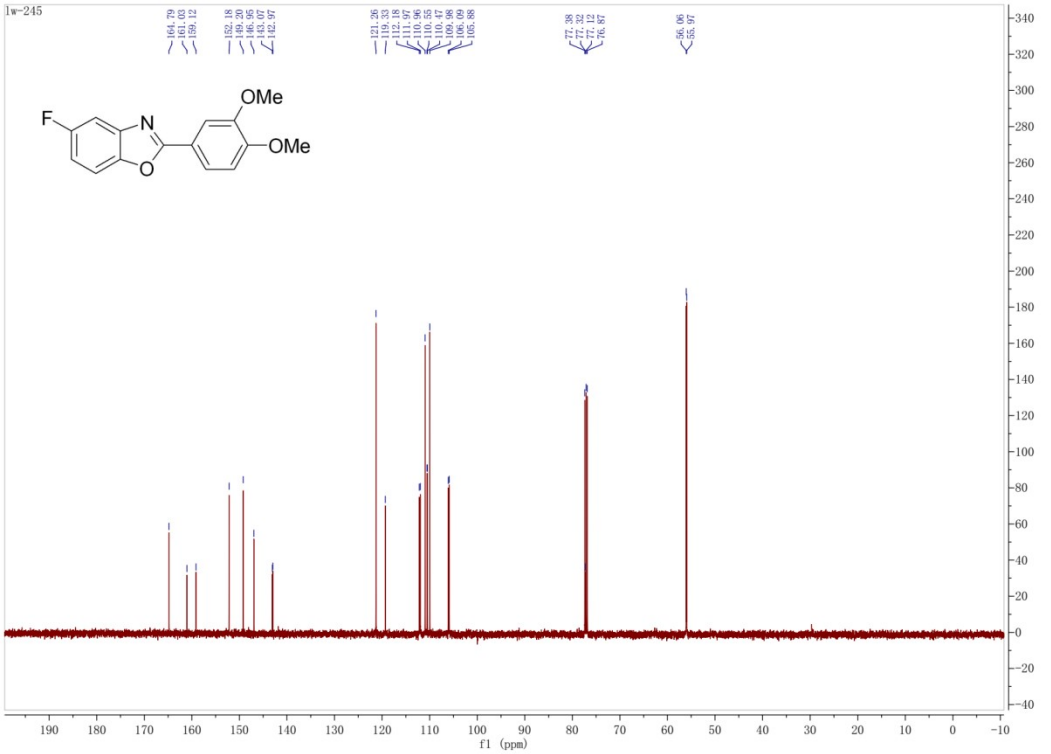

Figure S123. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3au**

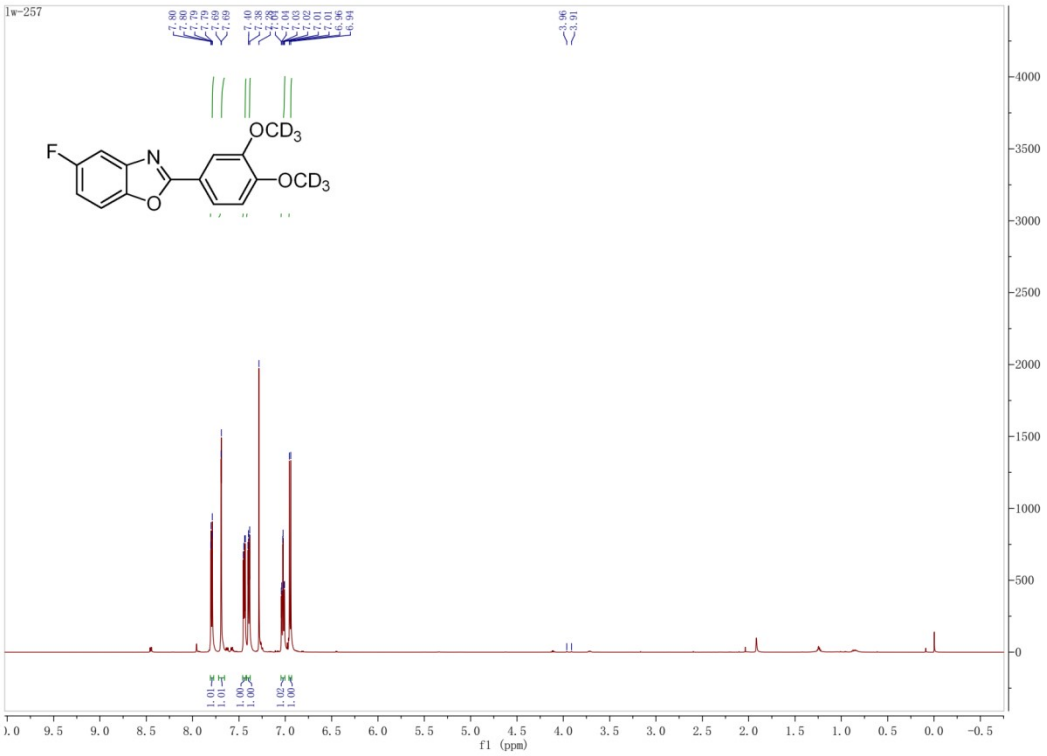

Figure S124. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3av**

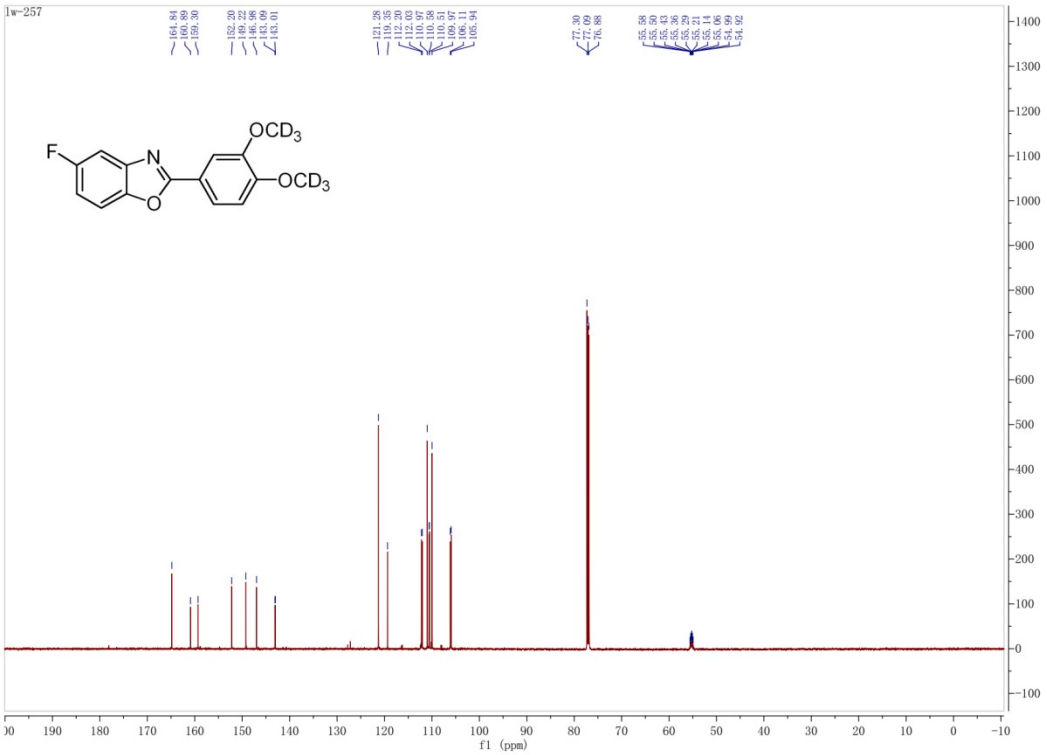

Figure S125. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3av**