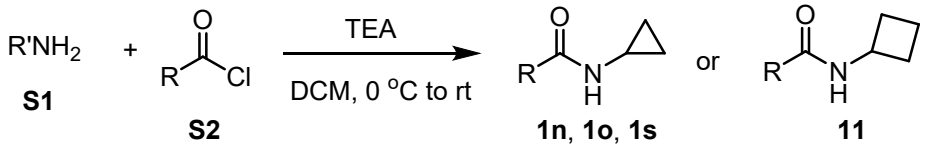
Content

I. General Information

^{1}H and ^{13}C spectra were recorded (as indicated) either on a Bruker 400 MHz spectrometer. ^{1}H NMR chemical shifts (δ) are reported in ppm relative to residual signals of the solvents ($CDCl_3$: 7.26 ppm; $SO(CD_3)_2$: 2.50 ppm). ^{13}C NMR chemical shifts were reported in ppm relative to the solvent ($CDCl_3$: 77.16 ppm; $SO(CD_3)_2$: 39.92 ppm). Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t) and quartet (q), with coupling constants (*J*) given in Hz, or multiplet (m). High resolution mass spectrometry (HRMS) was obtained on a Q-TOF micro spectrometer. Melting points were determined with an auto melting point system. TLC plates were visualized under ultraviolet light and colored with potassium permanganate ($KMnO_4$) solution and Iodine (I_2).

Unless otherwise noted, reagents and solvents were purchased as reagent grade and were used without further purification. Dichloromethane, 1,2-dichloroethane, chloroform and carbon tetrachloride were dried with activated molecular sieves. Flash column chromatography was performed over silica gel (200-300 m) using a mixture of ethyl acetate and petroleum ether.

II. Preparation of Compounds 1, 4, 6, 8, 9 and 11



General procedure a:[S1] To the solution of amine **S1** (10.0 mmol) and triethylamine (20.0 mmol) in DCM (50 mL) was added acyl chloride **S2** (10.0 mmol) dropwise or gradually in ca. 0.5-2 h at 0 °C. The reaction mixture was then warmed to room temperature and stired overnight. The resulting mixture was quenched with saturated NH_4Cl aqueous solution (50 mL) and extracted with DCM (3 x 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The given residue was purified by flash chromatography on silica gel using a mixture of EtOAc and PE (25-40%, V/V) as eluent to provide the amide substrates **1** and **11**.

Compound **1a** was synthesized as described in ref. S2.

Compound **1b** was synthesized as described in ref. S2.

Compound **1c** was synthesized as described in ref. S3.

Compound **1d** was synthesized as described in ref. S4.

Compound **1e** was synthesized as described in ref. S5.

Compound **1f** was synthesized as described in ref. S6.

Compound **1g** was synthesized as described in ref. S7.

Compound **1h** was synthesized as described in ref. S8.

Compound **1i** was synthesized as described in ref. S9.

Compound **1j** was synthesized as described in ref. S7.

Compound **1k** was synthesized as described in ref. S10.

Compound **1l** was synthesized as described in ref. S2.

Compound **1m** was synthesized as described in ref. S11.

Compound **1m** was synthesized as described in ref. S12.

Compound **1q** was synthesized as described in ref. S13.

Compound **1r** was synthesized as described in ref. S14.

Compound **1t** was synthesized as described in ref. S15.

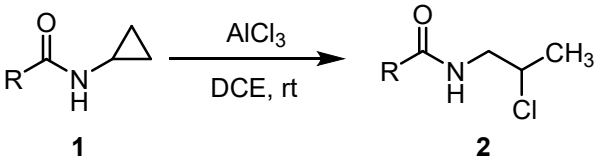
Compound **4** was synthesized as described in ref. S16.

Compound **6** was synthesized as described in ref. S17.

Compound **8** was synthesized as described in ref. S18.

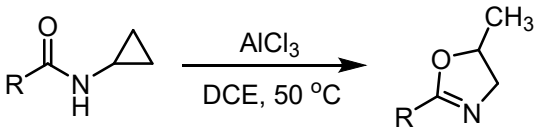
Compound **9** was synthesized as described in ref. S19.

III. Synthesis of Products 2 and 3



1 **2**

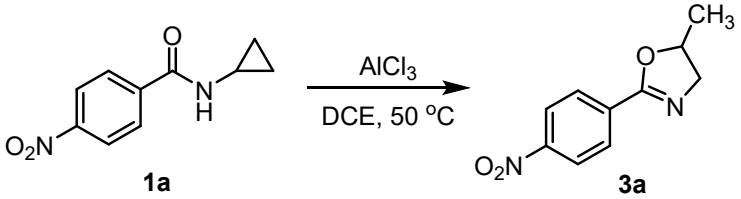
General procedure b: To an oven dried round bottom flask equipped with a glass stopper was added amide substrates (0.3 mmol), $AlCl_3$ (0.6-0.9 mmol), and 4 mL of freshly-dried solvent (DCE) at rt. The mixture was stirred at rt for 4 to 48 h. The resulting mixture was directly purified by flash chromatography on silica gel using a mixture of EtOAc and PE (25-60%, V/V) as eluent to provide the chlorinated intermediates **2**.



1 **3**

General procedure c: To an oven dried round bottom flask equipped with a glass stopper was added amide substrates **1** (0.3 mmol), $AlCl_3$ (1.5 mmol), and 4 mL of freshly-dried solvent (DCE) at rt. The mixture was stirred at 50 °C within 4-6 h. TLC was utilized for detecting the reaction till the total consumption of the starting materials. The resulting mixture was directly purified by flash chromatography on silica gel using a mixture of EtOAc and PE (15-50%, V/V) as eluent to provide products **3**.

IV. Gram-Scale Reaction of 1a

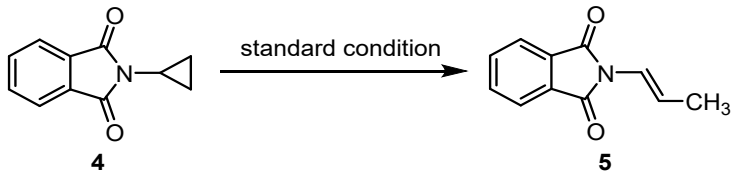


1a **3a**

General procedure d: To an oven dried round bottom flask equipped with a glass stopper was added substrate **1a** (2.12 g, 10.0 mmol), $AlCl_3$ (6.68 g, 45.0 mmol), and

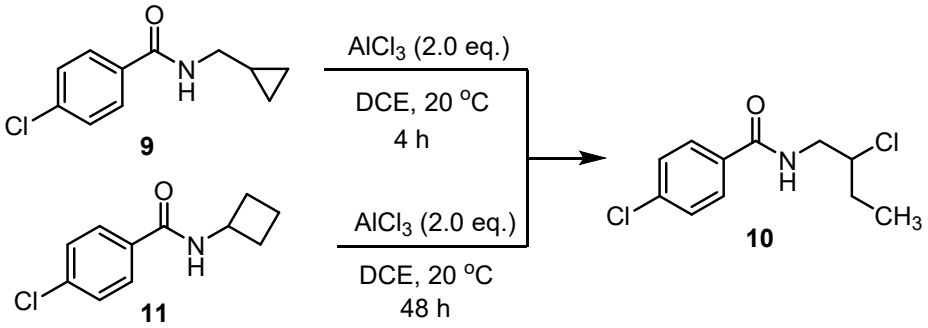
freshly-dried DCE (40 mL) at rt. The suspension was stirred at 50 °C for 8 h till the total consumption of the starting material. The resulting mixture was quenched in time with water (50 mL) and then extracted with DCM (3 x 100 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to remove the solvent. The given residue was purified by flash chromatography on silica gel using a mixture of EtOAc and PE (25%, V/V) as eluent to provide 1.67 g (81% yield) of the oxazoline product **3a**.

V. Synthesis of Compound 5



General procedure e: To an oven dried round bottom flask equipped with a glass stopper was added substrate **4** (150 mg, 0.802 mmol), $AlCl_3$ (537 mg, 4.0 mmol), and freshly-dried DCE (4 mL) at rt. The suspension was stirred at 50 °C for 4 h till the total consumption of the starting material. The resulting mixture was quenched in time with water (50 mL) and then extracted with DCM (3 x 100 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to remove the solvent. The given residue was purified by flash chromatography on silica gel using a mixture of EtOAc and PE (10%, V/V) as eluent to provide compound **5** in 77% yield.

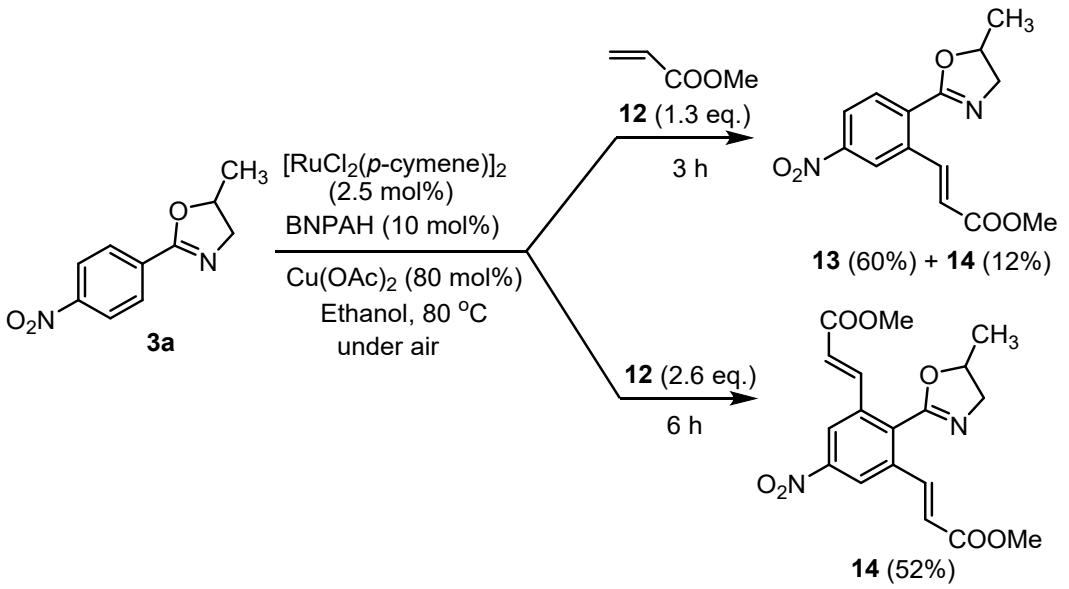
VI. Synthesis of Compound 10



General procedure f: To an oven dried round bottom flask equipped with a glass stopper was added amide substrates **9** or **11** (0.3 mmol), $AlCl_3$ (0.6 mmol), and 4 mL

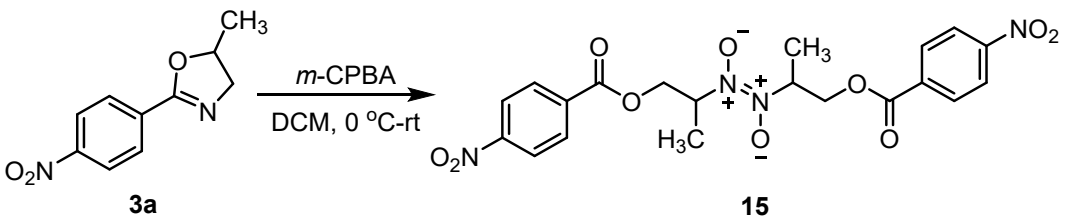
of freshly-dried solvent (DCE) at rt. The mixture was stirred at 20 °C for 4 h (for **9**) or 48 h (for **11**). The resulting mixture was directly purified by flash chromatography on silica gel using a mixture of EtOAc and PE (15%, V/V) as eluent to give compound **10**.

VII. Synthesis of 13 and 14



General procedure g:[20] $[RuCl_2(p\text{-cymene})]_2$ (0.025 mmol, 15.3 mg), alkene **12** (0.65 or 1.3 mmol), oxazoline **3a** (0.5 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol, 80 mg), 1,1'-binaphthyl-2,2' -diyl hydrogenphosphate (0.05 mmol, 17.4 mg) and ethanol (2 mL) were introduced in a tube sealing, equipped with a magnetic stirring bar and stirred at 80 °C. TLC was utilized for detecting the reaction till the total consumption of the starting materials. The solvent was then evaporated under vacuum and the desired product **13** or **14** was purified by silica gel column chromatography using a mixture of EtOAc and PE (25%, V/V) as the eluent.

VIII. Synthesis of Compound 15

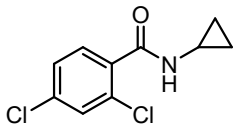


General procedure h:[21] A solution of *m*-CPBA (540 mg, 2.2 mmol, 70%) in CH_2Cl_2 (10 mL), previously cooled in an ice bath, was added dropwise to an ice cooled solution of the product **3a** (1.0 mmol) in CH_2Cl_2 (10 mL) The mixture was allowed to gradually

warm to room temperature (with stirring) over a 12 h period. After further dilution with CH_2Cl_2 (10 mL), the solution was stirred with excess powdered anhydrous sodium carbonate until carbon dioxide evolution ceased. After filtration, the solvent was evaporated in *vacuo* and purified by silica gel column chromatography using a mixture of EtOAc and PE (25%, V/V) as the eluent to give the dimer product **15** as a colorless solid.

IX. Spectral Data of Substrates and Products

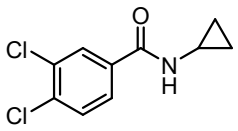
1. Spectral data of substrates **1**



1n

2,4-Dichloro-*N*-cyclopropylbenzamide (1n)

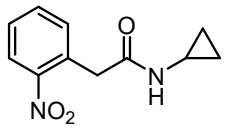
Following the general procedure **a**, **1n** was purified by silica gel chromatography (30% EtOAc/PE). Yield: 77%, colorless solid, mp. 144–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 1H), 7.39 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 6.36 (brs, 1H), 2.90 (tq, J = 7.4, 3.7 Hz, 1H), 0.88 (q, J = 6.3 Hz, 2H), 0.67 – 0.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.79, 136.77, 133.23, 131.46, 131.29, 129.98, 127.53, 23.19, 6.84. HRMS (ESI) calcd for $C_{10}H_{10}Cl_2NO$ $[M + H]^+$ 230.0134, found 230.0132.



1o

2,4-Dichloro-*N*-cyclopropylbenzamide (1o)

Following the general procedure **a**, **1o** was purified by silica gel chromatography (30% EtOAc/PE). Yield: 78%, colorless solid, mp. 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 2.0 Hz, 1H), 7.56 (dd, J = 8.3, 2.1 Hz, 1H), 7.49 (d, J = 8.3 Hz, 1H), 6.28 (brs, 1H), 2.88 (tq, J = 7.1, 3.7 Hz, 1H), 0.95 – 0.83 (m, 2H), 0.67 – 0.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 135.94, 134.19, 133.06, 130.63, 129.08, 126.06, 23.30, 6.81. HRMS (ESI) calcd for $C_{10}H_{10}Cl_2NO$ $[M + H]^+$ 230.0134, found 230.0135.

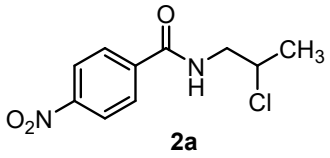


1s

***N*-Cyclopropyl-2-(2-nitrophenyl)acetamide (1s)**

Following the general procedure **a**, **1s** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 65%, colorless solid, mp. 153–156 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (d, J = 4.1 Hz, 1H), 7.99 (dd, J = 8.1, 1.4 Hz, 1H), 7.66 (td, J = 7.5, 1.4 Hz, 1H), 7.52 (td, J = 7.7, 1.5 Hz, 1H), 7.46 (dd, J = 7.6, 1.5 Hz, 1H), 3.80 (s, 2H), 2.57 (tq, J = 7.6, 3.9 Hz, 1H), 0.60 (td, J = 6.9, 4.7 Hz, 2H), 0.45 – 0.32 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.00, 149.66, 133.84, 133.77, 131.38, 128.61, 124.89, 39.76, 22.83, 6.15. HRMS (ESI) calcd for $C_{11}H_{13}N_2O_3$ $[M + H]^+$ 221.0921, found 221.0925.

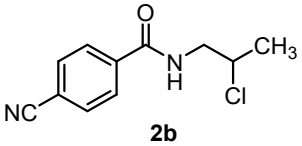
2. Spectral data of intermediates **2**



2a

***N*-(2-chloropropyl)-4-nitrobenzamide (2a)**

Following the general procedure **b**, **2a** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 45%, colorless solid. mp. >240 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 9.1 Hz, 2H), 7.96 (d, J = 8.9 Hz, 2H), 6.60 (brs, 1H), 4.35 – 4.24 (m, 1H), 4.01 (ddd, J = 14.3, 7.1, 3.3 Hz, 1H), 3.45 (ddd, J = 14.0, 8.4, 5.1 Hz, 1H), 1.59 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.55, 139.67, 128.23, 123.96, 57.72, 47.59, 22.55. HRMS (ESI) calcd for $C_{10}H_{11}ClN_2O_3$ $[M + H]^+$ 242.0458, found 242.0458.

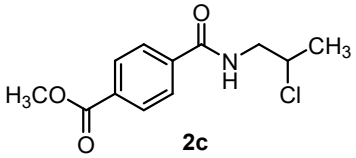


2b

***N*-(2-Chloropropyl)-4-cyanobenzamide (2b)**

Following the general procedure **b**, **2b** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 36%, colorless solid. mp. >240 °C. ^{1}H NMR (400 MHz,

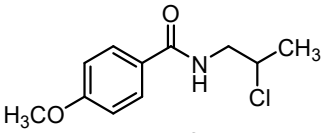
$CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 6.60 (brs, 1H), 4.28 (ddt, *J* = 10.7, 7.1, 5.1 Hz, 1H), 3.99 (ddd, *J* = 14.3, 6.9, 3.4 Hz, 1H), 3.43 (ddd, *J* = 13.9, 8.4, 5.1 Hz, 1H), 1.58 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.81, 138.02, 132.57, 127.75, 117.96, 115.39, 57.75, 47.54, 22.55. HRMS (ESI) calcd for $C_{11}H_{12}ClN_2O$ $[M + H]^+$ 223.0633, found 223.0629.



2c

Methyl 4-((2-chloropropyl)carbamoyl)benzoate (2c)

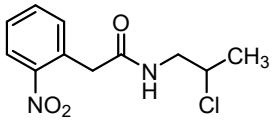
Following the general procedure **b**, **2c** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 20%, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 6.68 (brs, 1H), 4.34 – 4.23 (m, 1H), 4.02 – 3.94 (m, 1H), 3.95 (s, 3H), 3.45 (ddd, *J* = 13.9, 8.4, 5.1 Hz, 1H), 1.58 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.72, 166.25, 138.01, 132.97, 129.95, 127.07, 57.88, 52.47, 47.48, 22.57. HRMS (ESI) calcd for $C_{12}H_{15}ClNO_3$ $[M + H]^+$ 256.0735, found 256.0737.



2f

***N*-(2-Chloropropyl)-4-methoxybenzamide (2f)**

Following the general procedure **b**, **2f** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 21%, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.48 (brs, 1H), 4.27 (dtd, *J* = 13.2, 6.6, 3.5 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.86 (s, 3H), 3.42 (ddd, *J* = 13.8, 8.2, 5.1 Hz, 1H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.05, 162.38, 128.82, 126.38, 113.85, 58.27, 55.45, 47.34, 22.56. HRMS (ESI) calcd for $C_{11}H_{15}ClNO_2$ $[M + H]^+$ 228.0786, found 228.0788.

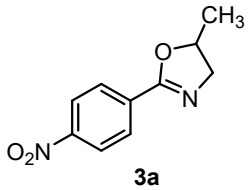


2s

***N*-(2-Chloropropyl)-2-(2-nitrophenyl)acetamide (2s)**

Following the general procedure **b**, **2s** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 34%, pale-yellow solid, mp. 89–91 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 (brs, 1H), 8.00 (dd, J = 8.1, 1.2 Hz, 1H), 7.67 (td, J = 7.5, 1.3 Hz, 1H), 7.55 – 7.49 (m, 2H), 4.16 – 4.09 (m, 1H), 3.91 (s, 2H), 3.31 (td, J = 6.1, 2.9 Hz, 2H), 1.41 (d, J = 6.5 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.20, 148.81, 133.71, 133.45, 130.15, 128.62, 125.27, 57.61, 47.16, 41.02, 22.39. HRMS (ESI) calcd for $C_{11}H_{14}ClN_2O_3$ $[M + H]^+$ 257.0687, found 257.0686.

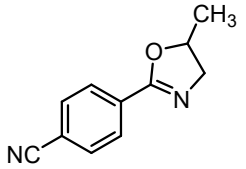
3. Spectral data of products **3**



3a

5-Methyl-2-(4-nitrophenyl)-4,5-dihydrooxazole (3a)

Following the general procedure **c**, **3a** was purified by silica gel chromatography (33% EtOAc/PE). Yield: 94%, light-brown solid, mp. 125–127 °C.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 4.92 (ddq, J = 9.4, 7.4, 6.2 Hz, 1H), 4.20 (dd, J = 15.0, 9.5 Hz, 1H), 3.66 (dd, J = 15.0, 7.6 Hz, 1H), 1.45 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.18, 149.45, 133.82, 129.16, 123.53, 77.17, 61.81, 21.11. HRMS (ESI) calcd for $C_{10}H_{10}N_2NaO_3^+$ $[M + Na]^+$ 229.0584, found 229.0581.

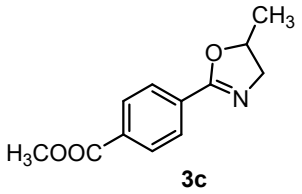


3b

5-Methyl-2-(4-cynaophenyl)-4,5-dihydrooxazole (3b)

Following the general procedure **c**, **3b** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 90%, light-yellow solid, mp. 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 4.94 – 4.85 (m, 1H), 4.18 (dd, J = 14.9, 9.4 Hz, 1H), 3.64 (dd, J = 14.9, 7.5 Hz, 1H), 1.43 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.36, 132.19, 132.11, 128.68, 118.31, 114.64, 76.94,

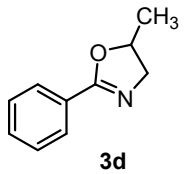
61.77, 21.10. HRMS (ESI) calcd for $C_{11}H_{10}N_2NaO$ $[M + Na]^+$ 209.0685, found 209.0689.



3c

Methyl 4-(5-methyl-4,5-dihydrooxazol-2-yl)benzoate (3c)

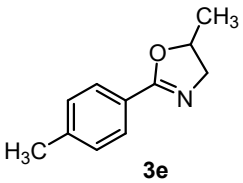
Following the general procedure **c**, **3c** was purified by silica gel chromatography (33% EtOAc/PE). Yield: 72%, light-yellow solid, mp. 110–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 4.94 – 4.81 (m, 1H), 4.17 (dd, *J* = 14.7, 9.4 Hz, 1H), 3.93 (s, 3H), 3.63 (dd, *J* = 14.7, 7.5 Hz, 1H), 1.44 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.53, 163.16, 132.36, 132.08, 129.53, 128.10, 76.64, 61.73, 52.33, 21.13. HRMS (ESI) calcd for $C_{12}H_{13}NNaO_3$ $[M + Na]^+$ 242.0788, found 242.0791.



3d

5-Methyl-2-phenyl-4,5-dihydrooxazole (3d)

Following the general procedure **c**, **3d** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 39%, light-yellow oil.[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 7.1 Hz, 2H), 4.92 – 4.76 (m, 1H), 4.12 (dd, *J* = 14.5, 9.4 Hz, 1H), 3.59 (dd, *J* = 14.4, 7.4 Hz, 1H), 1.41 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.92, 131.22, 128.30, 128.10, 128.03, 76.27, 61.54, 21.13. HRMS (ESI) calcd for $C_{10}H_{11}NNaO$ $[M + Na]^+$ 184.0733, found 184.0730.

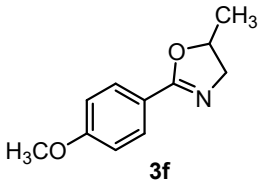


3e

5-Methyl-2-(*p*-tolyl)-4,5-dihydrooxazole (3e)

Following the general procedure **c**, **3e** was purified by silica gel chromatography

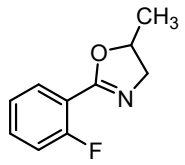
(20% EtOAc/PE). Yield: 36%, light-yellow oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.83 (ddd, *J* = 9.3, 7.2, 6.1 Hz, 1H), 4.13 (dd, *J* = 14.3, 9.4 Hz, 1H), 3.59 (dd, *J* = 14.4, 7.4 Hz, 1H), 2.38 (s, 3H), 1.42 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.11, 141.64, 129.04, 128.10, 125.15, 76.23, 61.39, 21.56, 21.13. HRMS (ESI) calcd for $C_{11}H_{13}NNaO$ $[M + Na]^+$ 198.0889, found 198.0885.



3f

2-(4-Methoxyphenyl)-5-methyl-4,5-dihydrooxazole (3f)

Following the general procedure **c**, **3f** was purified by silica gel chromatography (33% EtOAc/PE). Yield: 30%, light-yellow oil.[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.87 – 4.79 (m, 1H), 4.12 (dd, *J* = 14.2, 9.3 Hz, 1H), 3.85 (s, 3H), 3.59 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.42 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.12, 162.04, 128.62, 127.13, 113.71, 77.25, 55.40, 41.72, 22.99, 11.46. HRMS (ESI) calcd for $C_{11}H_{13}NNaO_2$ $[M + Na]^+$ 214.0838, found 214.0837.

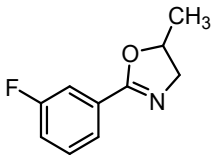


3g

2-(2-Fluorophenyl)-5-methyl-4,5-dihydrooxazole (3g)

Following the general procedure **c**, **3g** was purified by silica gel chromatography (20% EtOAc/PE). Yield: 40%, light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (td, *J* = 7.6, 1.8 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.20 – 7.16 (m, 1H), 7.13 (dd, *J* = 9.5, 6.7 Hz, 1H), 4.89 – 4.77 (m, 1H), 4.18 (dd, *J* = 14.6, 9.4 Hz, 1H), 3.66 (dd, *J* = 14.6, 7.4 Hz, 1H), 1.42 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.23 (d, *J* = 257.9 Hz), 160.70, 132.84 (d, *J* = 8.8 Hz), 131.00 (d, *J* = 1.8 Hz), 123.95 (d, *J* = 3.9 Hz), 116.68 (d, *J* = 22.2 Hz), 116.42 (d, *J* = 29.7 Hz), 75.90, 61.75, 21.08. ^{19}F NMR (376

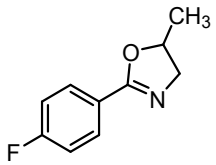
Hz, $CDCl_3$) δ -112.56. HRMS (ESI) calcd for $C_{10}H_{10}FNNaO$ $[M + Na]^+$ 202.0639, found 202.0642.



3h

2-(3-fluorophenyl)-5-methyl-4,5-dihydrooxazole (3h)

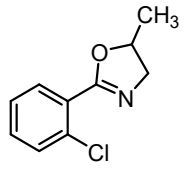
Following the general procedure **c**, **3h** was purified by silica gel chromatography (20% EtOAc/PE). Yield: 59%, light-yellow oil.[25] ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 9.7 Hz, 1H), 7.37 (td, *J* = 8.0, 5.6 Hz, 1H), 7.16 (td, *J* = 8.4, 2.7 Hz, 1H), 4.92 – 4.81 (m, 1H), 4.15 (dd, *J* = 14.6, 9.4 Hz, 1H), 3.61 (dd, *J* = 14.6, 7.5 Hz, 1H), 1.43 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.87 (d, *J* = 3.2 Hz), 162.87 (d, *J* = 244.0 Hz), 130.17 (d, *J* = 8.3 Hz), 129.93 (d, *J* = 8.0 Hz), 123.82 (d, *J* = 3.0 Hz), 118.16 (d, *J* = 21.3 Hz), 115.11 (d, *J* = 23.5 Hz). 76.57, 61.58, 21.08. ^{19}F NMR (376 Hz, $CDCl_3$) δ -111.79. HRMS (ESI) calcd for $C_{10}H_{10}FNNaO$ $[M + Na]^+$ 202.0639, found 202.0641.



3i

2-(4-Fluorophenyl)-5-methyl-4,5-dihydrooxazole (3i)

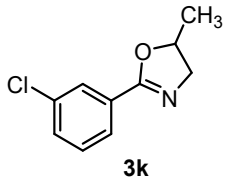
Following the general procedure **c**, **3i** was purified by silica gel chromatography (20% EtOAc/PE). Yield: 50%, light-yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 4.90 – 4.81 (m, 1H), 4.13 (dd, *J* = 14.4, 9.4 Hz, 1H), 3.60 (dd, *J* = 14.4, 7.4 Hz, 1H), 1.42 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.44 (d, *J* = 286.8 Hz), 163.01, 130.33 (d, *J* = 8.9 Hz), 124.29 (d, *J* = 3.4 Hz), 115.40 (d, *J* = 22.0 Hz), 76.47, 61.56, 21.09. ^{19}F NMR (376 Hz, $CDCl_3$) δ -108.00. HRMS (ESI) calcd for $C_{10}H_{10}FNNaO$ $[M + Na]^+$ 202.0639, found 202.0636.



3j

2-(2-Chlorophenyl)-5-methyl-4,5-dihydrooxazole (3j)

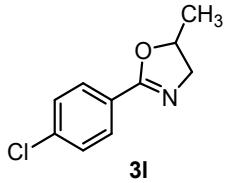
Following the general procedure **c**, **3j** was purified by silica gel chromatography (20% EtOAc/PE). Yield: 49%, light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 5.01 – 4.72 (m, 1H), 4.19 (dd, *J* = 14.5, 9.5 Hz, 1H), 3.67 (dd, *J* = 14.5, 7.2 Hz, 1H), 1.44 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.42, 133.39, 131.46, 131.24, 130.68, 127.68, 126.52, 76.29, 61.92, 21.06. HRMS (ESI) calcd for $C_{10}H_{10}ClNNaO$ $[M + Na]^+$ 218.0343, found 218.0341.



3k

2-(3-Chlorophenyl)-5-methyl-4,5-dihydrooxazole (3k)

Following the general procedure **c**, **3k** was purified by silica gel chromatography (20% EtOAc/PE). Yield: 56%, light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 4.92 – 4.79 (m, 1H), 4.14 (dd, *J* = 14.6, 9.4 Hz, 1H), 3.61 (dd, *J* = 14.6, 7.4 Hz, 1H), 1.44 – 1.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.42, 133.39, 131.46, 131.24, 130.68, 127.68, 126.52, 76.29, 61.92, 21.06. HRMS (ESI) calcd for $C_{10}H_{10}ClNNaO$ $[M + Na]^+$ 218.0343, found 218.0342.

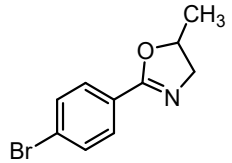


3l

2-(4-Chlorophenyl)-5-methyl-4,5-dihydrooxazole (3l)

Following the general procedure **c**, **3l** was purified by silica gel chromatography (33% EtOAc/PE). Yield: 55%, light-yellow oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 4.85 (ddt, *J* = 13.7, 9.5, 6.2 Hz, 1H), 4.14

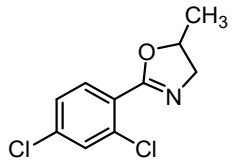
(dd, J = 14.6, 9.4 Hz, 1H), 3.60 (dd, J = 14.6, 7.4 Hz, 1H), 1.42 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.07, 137.38, 129.47, 128.61, 126.55, 76.55, 61.61, 21.11. HRMS (ESI) calcd for $C_{10}H_{10}ClNNaO$ $[M + Na]^+$ 218.0343, found 218.0345.



3m

2-(4-Bromophenyl)-5-methyl-4,5-dihydrooxazole (3m)

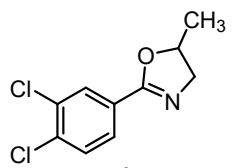
Following the general procedure **c**, **3m** was purified by silica gel chromatography (15% EtOAc/PE). Yield: 52%, light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 4.90 – 4.81 (m, 1H), 4.13 (dd, J = 14.6, 9.4 Hz, 1H), 3.59 (dd, J = 14.6, 7.5 Hz, 1H), 1.42 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.14, 131.58, 129.67, 127.01, 125.86, 76.56, 61.64, 21.12. HRMS (ESI) calcd for $C_{10}H_{10}BrNNaO$ $[M + Na]^+$ 261.9838, found 261.9836.



3n

2-(2,4-Dichlorophenyl)-5-methyl-4,5-dihydrooxazole (3n)

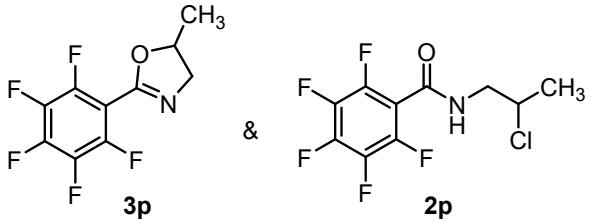
Following the general procedure **c**, **3n** was purified by silica gel chromatography (20% EtOAc/PE). Yield: 85%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.28 (dd, J = 8.5, 2.2 Hz, 1H), 4.91 – 4.80 (m, 1H), 4.18 (dd, J = 14.6, 9.4 Hz, 1H), 3.66 (dd, J = 14.6, 7.3 Hz, 1H), 1.43 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.58, 136.94, 134.36, 132.17, 130.63, 126.94, 126.09, 76.38, 61.97, 21.04. HRMS (ESI) calcd for $C_{10}H_9Cl_2NNaO$ $[M + Na]^+$ 251.9953, found 251.9956.



3o

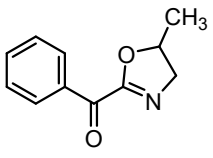
2-(3,4-Dichlorophenyl)-5-methyl-4,5-dihydrooxazole (3o)

Following the general procedure **c**, **3o** was purified by silica gel chromatography (20% EtOAc/PE). Yield: 60%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 4.92 – 4.81 (m, 1H), 4.14 (dd, *J* = 14.7, 9.4 Hz, 1H), 3.60 (dd, *J* = 14.7, 7.5 Hz, 1H), 1.42 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.06, 135.50, 132.70, 130.41, 130.06, 128.01, 127.25, 76.85, 61.66, 21.08. HRMS (ESI) calcd for $C_{10}H_9Cl_2NNaO$ $[M + Na]^+$ 251.9953, found 251.9954.



5-Methyl-2-(perfluorophenyl)-4,5-dihydrooxazole (3p) and *N*-(2-chloropropyl)-2,3,4,5,6-pentafluorobenzamide (2p)

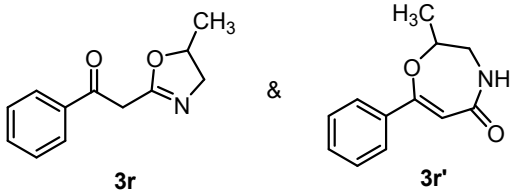
Following the general procedure **c**, **3p** and **3p'** were isolated as inseparable mixture by silica gel chromatography (20% EtOAc/PE). Yield: 84% (**3p**/**2p**=5/1), yellow oil.[26] ^{1}H NMR (400 MHz, $CDCl_3$) of **3p**: δ 4.97 – 4.80 (m, 1H), 4.19 (dd, *J* = 14.8, 9.5 Hz, 1H), 3.67 (dd, *J* = 14.8, 7.3 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 1H), 1.44 (d, *J* = 6.0 Hz, 3H). ^{1}H NMR (400 MHz, $CDCl_3$) of **2p**: δ 6.46 (s, 1H), 4.28 (qd, *J* = 7.0, 3.4 Hz, 1H), 3.92 (ddd, *J* = 14.3, 6.7, 3.5 Hz, 1H), 3.51 (ddd, *J* = 13.8, 7.9, 5.4 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) of **3p** and **2p** δ 166.81 (m), 154.53(m), 146.93(m), 145.04(m), 143.98(m), 141.41(m), 138.65(m), 137.09(m), 105.26(m), 61.81, 57.06, 47.62, 23.44, 22.48, 21.04, 6.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.88 – -136.93 (m), -137.24 – -137.32 (m), -140.21 – -140.58 (m), -149.98 – -150.12 (m), -150.28 – -150.75 (m), -159.76 – 160.14 (m), -160.89–161.03 (m). HRMS (ESI) calcd for $C_{10}H_6F_5NNaO$ [M(**3p**) + Na]$^+$ 274.0262, found 274.0260. HRMS (ESI) calcd for $C_{10}H_8ClF_5NO$ [M(**2p**) + H]$^+$ 288.0209, found 288.0211.



3q

(5-Methyl-4,5-dihydrooxazol-2-yl)(phenyl)methanone (3q)

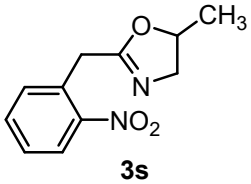
Following the general procedure **c**, **3q** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 67%, yellow solid, mp. 137–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.2 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 4.21 (dddd, *J* = 10.6, 7.8, 6.7, 3.8 Hz, 1H), 3.82 (ddd, *J* = 14.1, 6.9, 3.9 Hz, 1H), 3.47 (ddd, *J* = 13.9, 7.9, 5.7 Hz, 1H), 1.56 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.24, 161.86, 134.56, 133.19, 131.20, 128.57, 56.63, 46.87, 22.53. HRMS (ESI) calcd for $C_{11}H_{11}NNaO_2$ $[M + Na]^+$ 212.0682, found 212.0685.



3r **3r'**

2-(5-methyl-4,5-dihydrooxazol-2-yl)-1-phenylethan-1-one (3r) & 2-methyl-7-phenyl-3,4-dihydro-1,4-oxazepin-5(2*H*)-one (3r')

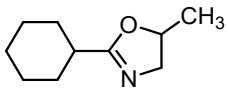
Following the general procedure **c**, **3r** and **3r'** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 63% (**3r**/**3r'**=6/1), yellow solid, mp. 134–136 °C. **3r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 4.23 – 4.12 (m, 1H), 4.00 (s, 2H), 3.80 – 3.71 (m, 1H), 3.36 (ddd, *J* = 13.8, 8.0, 5.3 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.78, 166.13, 136.11, 134.16, 128.91, 128.58, 57.08, 47.14, 45.13, 22.47. HRMS (ESI) calcd for $C_{12}H_{13}NNaO_2$ $[M + Na]^+$ 226.0838, found 226.0837. **3r'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.02 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.52 – (m, 1H), 7.42 (d, *J* = 7.4 Hz, 2H), 5.54 (s, 1H), 4.21 – 4.13 (m, 1H), 3.85 (ddd, *J* = 14.3, 7.0, 3.6 Hz, 1H), 3.40 – 3.33 (m, 1H), 1.55 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.82, 134.12, 130.80, 128.49, 125.81, 88.34, 57.89, 46.56, 29.70 (One carbon signal was missing due to peak overlapped). HRMS (ESI) calcd for $C_{12}H_{13}NNaO_2$ $[M + Na]^+$ 226.0838, found 226.0837.



3s

5-Methyl-2-(2-nitrobenzyl)-4,5-dihydrooxazole (3s)

Following the general procedure **c**, **3s** was purified by silica gel chromatography (40% EtOAc/PE). Yield: 50%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.59 (td, *J* = 7.6, 1.4 Hz, 1H), 7.48 – 7.40 (m, 2H), 4.70 (ddq, *J* = 9.3, 7.1, 6.2 Hz, 1H), 3.97 (d, *J* = 2.0 Hz, 2H), 3.88 (ddt, *J* = 13.9, 9.4, 1.6 Hz, 1H), 3.40 – 3.31 (m, 1H), 1.32 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.42, 148.85, 133.74, 133.51, 130.08, 128.65, 125.27, 57.57, 47.25, 41.04, 22.41. HRMS (ESI) calcd for $C_{11}H_{12}N_2NaO_3$ $[M + H]^+$ 243.0740, found 243.0741.

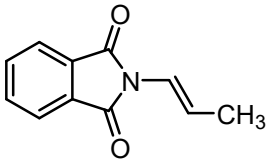


3t

2-Cyclohexyl-5-methyl-4,5-dihydrooxazole (3t)

Following the general procedure **c**, **3t** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 41%, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (dt, *J* = 9.6, 6.4 Hz, 1H), 3.89 (dd, *J* = 13.8, 9.3 Hz, 1H), 3.36 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.25 (t, *J* = 11.5 Hz, 1H), 1.92 (d, *J* = 11.3 Hz, 2H), 1.76 (d, *J* = 9.1 Hz, 2H), 1.45 – 1.35 (m, 2H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.32 – 1.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.14, 75.42, 60.86, 37.46, 29.79, 25.89, 25.68, 21.11. HRMS (ESI) calcd for $C_{10}H_{17}NNaO$ $[M + H]^+$ 190.1202, found 190.1201.

4. Spectral data of compound **5**

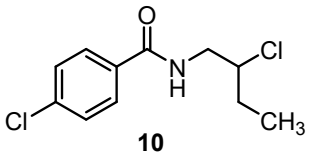


5

(*E*)-2-(Prop-1-en-1-yl)isoindoline-1,3-dione (5)

Following the general procedure **e**, **5** was purified by silica gel chromatography (10% EtOAc/PE). Yield: 77%, brown solid, mp. 144–146 °C.[27] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 – 7.80 (m, 4H), 6.52 (dq, *J* = 14.6, 1.5 Hz, 1H), 6.40 (dq, *J* = 14.6, 6.6 Hz, 1H), 1.78 (dd, *J* = 6.6, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.77, 135.19, 131.67, 123.74, 119.09, 117.35, 16.35. HRMS (ESI) calcd for $C_{11}H_{10}NO_2$ $[M + H]^+$ 188.0706, found 188.0707.

5. Spectral data of compound **10**

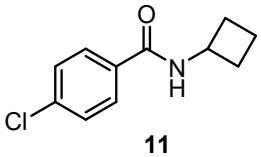


10

4-Chloro-*N*-(2-chlorobutyl)benzamide (10)

Following the general procedure **f**, **10** was purified by silica gel chromatography (15% EtOAc/PE). Yield: 25%, colorless solid, mp. 114–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.51 (brs, 1H), 4.04 (dddt, *J* = 24.2, 14.2, 6.9, 3.3 Hz, 2H), 3.46 (ddd, *J* = 14.2, 8.3, 5.0 Hz, 1H), 1.89 (ddd, *J* = 14.5, 7.3, 4.7 Hz, 2H), 1.09 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.47, 138.02, 132.53, 128.96, 128.43, 64.83, 45.92, 29.11, 10.94. HRMS (ESI) calcd for $C_{11}H_{13}ClNO$ $[M + H]^+$ 210.0680, found 210.0685.

6. Spectral data of compound **11**

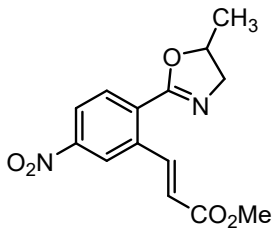


11

4-Chloro-*N*-cyclobutylbenzamide (11)

Following the general procedure **a**, **11** was purified by silica gel chromatography (20% EtOAc/PE). Yield: 84%, colorless solid, mp. 153-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 6.25 (s, 1H), 4.57 (h, *J* = 8.1 Hz, 1H), 2.48 – 2.37 (m, 2H), 1.96 (tt, *J* = 12.0, 9.2 Hz, 2H), 1.76 (ddt, *J* = 13.9, 8.8, 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.49, 137.61, 132.96, 128.79, 128.34, 45.28, 31.32, 15.20. HRMS (ESI) calcd for $C_{11}H_{13}ClNO$ $[M + H]^+$ 210.0680, found 210.0677.

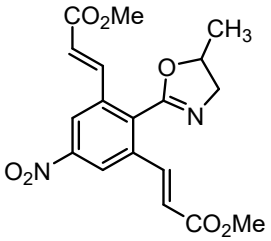
7. Spectral data of compounds **13** and **14**



13

Methyl (*E*)-3-(2-(5-methyl-4,5-dihydrooxazol-2-yl)-5-nitrophenyl)acrylate (13)

Following the general procedure **g**, **13** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 60% with 10% of **14**, light purple solid, mp. 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 16.0 Hz, 1H), 8.45 (d, *J* = 2.3 Hz, 1H), 8.22 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.07 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.91 (ddt, *J* = 9.5, 7.7, 6.1 Hz, 1H), 4.26 (dd, *J* = 15.1, 9.5 Hz, 1H), 3.83 (s, 3H), 3.74 (dd, *J* = 15.1, 7.5 Hz, 1H), 1.47 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.60, 161.65, 148.99, 141.96, 136.88, 132.91, 131.51, 123.59, 122.31, 122.24, 76.82, 62.36, 52.02, 21.09. HRMS (ESI) calcd for $C_{14}H_{14}N_2NaO_5$ $[M + H]^+$ 313.0795, found 313.0796.

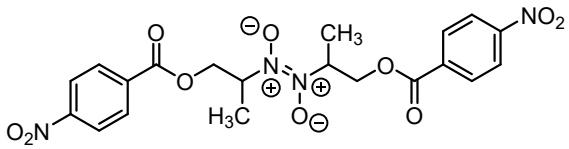


14

Dimethyl 3,3'-(2-(5-methyl-4,5-dihydrooxazol-2-yl)-5-nitro-1,3-phenylene)(2*E*,2'*E*)-diacrylate (14)

Following the general procedure **g**, **14** was purified by silica gel chromatography (25% EtOAc/PE). Yield: 52%, light purple solid, mp. 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 2H), 7.84 (d, *J* = 15.9 Hz, 2H), 6.55 (d, *J* = 15.9 Hz, 2H), 5.11 – 4.97 (m, 1H), 4.33 (t, *J* = 12.2 Hz, 1H), 3.83 (s, 6H), 1.56 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.17, 159.91, 148.82, 139.50, 137.02, 134.95, 123.36, 121.68, 77.77, 62.26, 52.15, 21.28. HRMS (ESI) calcd for $C_{18}H_{18}N_2NaO_7$ $[M + H]^+$ 397.1006, found 397.1005.

8. Spectral data of compound **15**



15

(*E*)-1,2-Bis(1-((4-nitrobenzoyl)oxy)propan-2-yl)diazene 1,2-dioxide (15)

Following the general procedure **h**, **15** was purified by silica gel chromatography

(25% EtOAc/PE). Yield: 50%, colorless solid, mp. 149–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 8.7 Hz, 2H), 5.78–5.68 (m, 1H), 4.54 (d, *J* = 5.9 Hz, 2H), 1.47 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.89, 150.61, 135.15, 130.86, 123.56, 67.36, 62.80, 17.86. HRMS (ESI) calcd for $C_{20}H_{21}N_4O_{10}$ $[M + H]^+$ 477.1252, found 477.1250.

X. References

[S1] M.-M. Wang, T. V. T. Nguyen, and J. Waser, *J. Am. Chem. Soc*., 2021, **143**, 11969.

[S2] M.-M. Wang and J. Waser, *Angew. Chem. Int. Ed*., 2019, **58**, 13880.

[S3] M. Takeshi, K. Tomoaki, S. Ryota, I. Hirofumi, Y. Seiji, O. Takehiko, H. Mitsuru, F. Hiroki and I. Yutaka, EP1790641, 2007.

[S4] P. Sureshbabu, A. Sadaf, P. Chaudhary and J. Kandasamy, *Org. Biomol. Chem*., 2019, **17**, 845.

[S5] Y. Zhang, B. Liu, Z. Gou, Y. Li, X. Zhang, Y. Wang, S. Yu, Y. Li, and D. Sun, *Bioorg. Med. Chem. Lett*., 2015, **25**, 791.

[S6] P. Baburajan, and K. P. Elango, *Tetrahedron Lett.*, 2014, **55**, 1006.

[S7] V. C. Agwada, *J. Chem. Eng. Data* 1984, **29**, 231.

[S8] P. P. Onys'ko, D. V. Klyukovskii and A. V. Bezdudnyi, *Russ. J. Gen. Chem.*, 2015, **85**, 418.

[S9] H. Kondo, K. Itami and J. Yamaguchi, *Chem. Sci*., 2017, **8**, 3799.

[S10] S. Mkrtchyan, M. Jakubczyk, S. Lanka, M. Pittelkow and V. O. Iaroshenko, *Molecules*, 2021, **26**, 2957.

[S11] F. Muth, M. Gunther, S. M. Bauer, E. Doring, S. Fischer, J. Maier, P. Druckes, J. Koppler, J. Trappe, U. Rothbauer, P. Koch, and S. A. Laufer, *J. Med. Chem.*, 2015, **58**, 443.

[S12] J.-Q. Zhang, D. Hu, J. Wang, B. Ni and H. Ren, Bimetallic Metal–Organic Coordination Polymers Facilitated the Selective C–F Cleavage of Polyfluoroarenes. *Org. Lett*., 2022, **24**, 7905.

[S13] S. Singh, S. Popuri, Q. M. Junaid, S. Sabiah and J. J. Kandasamy, *Org. Biomol. Chem.*, 2021, **19**, 7134.

[S14] J. K. Vandavasi, C.-T. Hsiao, W.-P. Hu, S. S. K. Boominathan, and J.-J. Wang, *Eur. J. Org. Chem*., 2015, **14**, 3171.

[S15] S. Miyamura, M. Araki, T. Suzuki, J. Yamaguchi and K. Itami. *Angew. Chem. Int. Ed.*, 2015, **54**, 846.

[S16] S. Benard, L. Neuville and J. Zhu, *J. Org. Chem*., 2008, **73**, 6441.

[S17] R. Shen, C. T. Lin, E. J. Bowman, B. J. Bowman and J. A. Porco Jr., *J. Am. Chem. Soc.*, 2003, **125**, 7889.

[S18] B. Wu, J. R. Parquette and T. V. RajanBabu, *Science*, 2009, **326**, 1662.

[S19] F. W. Gubitz, Aromatic substituted amidines. US3850909, 1974.

[S20] B. Li, K. Devaraj, C. Darcel and P. H. Dixneuf, *Green Chem.*, 2012, **14**, 2706.

[21] S. Perrone, T. Pilati, F. Rosato, A. Salomone, V. Videtta and L. Troisi, *Tetrahedron*, 2011, **67**, 2090.

[22] G. S. Kumar, M. Venkateshwar and U. Maheswari. *RSC Adv.* 2014, **4**, 39897.

[23] R. Kuwano, N. Kameyama, and R. Ikeda, *J. Am. Chem. Soc.*, 2011, **133**, 19, 7312.

[24] G.-Q. Liu, C.-H. Yang, and Y.-M. Li, *J. Org. Chem.*, 2015, **80**, 11339.

[25] R. Zhao, M. Yan, R. Zhang, Y. Ma, and J. Chen, *ChemistrySelect*, 2019, **4**, 10907.

[26] A. Martin, K. Casto, W. Morris and J. B. Morgan, *Org. Lett.*, 2011, **13**, 5444.

[27] D. P. Ojha, K. Gadde and K. R. Prabhu, *J. Org. Chem.*, 2017, **82**, 4859.

XI. 1D and 2D NMR Spectra

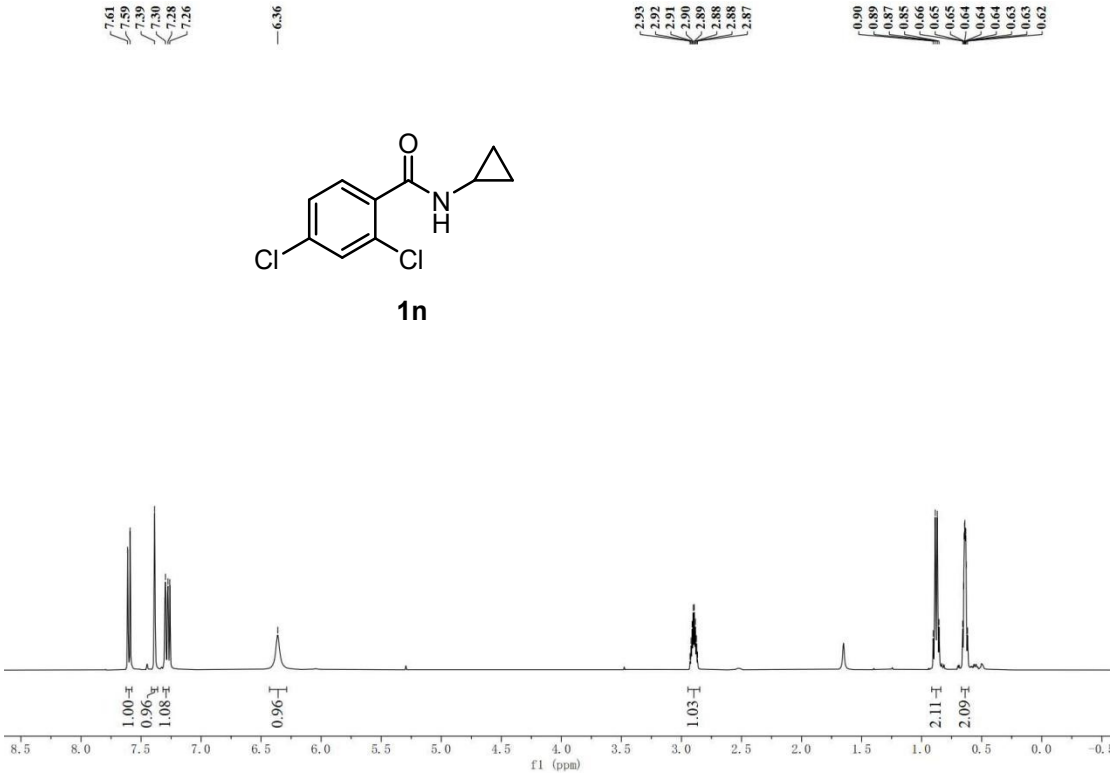


Figure S1. ^{1}H NMR spectrum of **1n** in $CDCl_3$ (400 MHz).

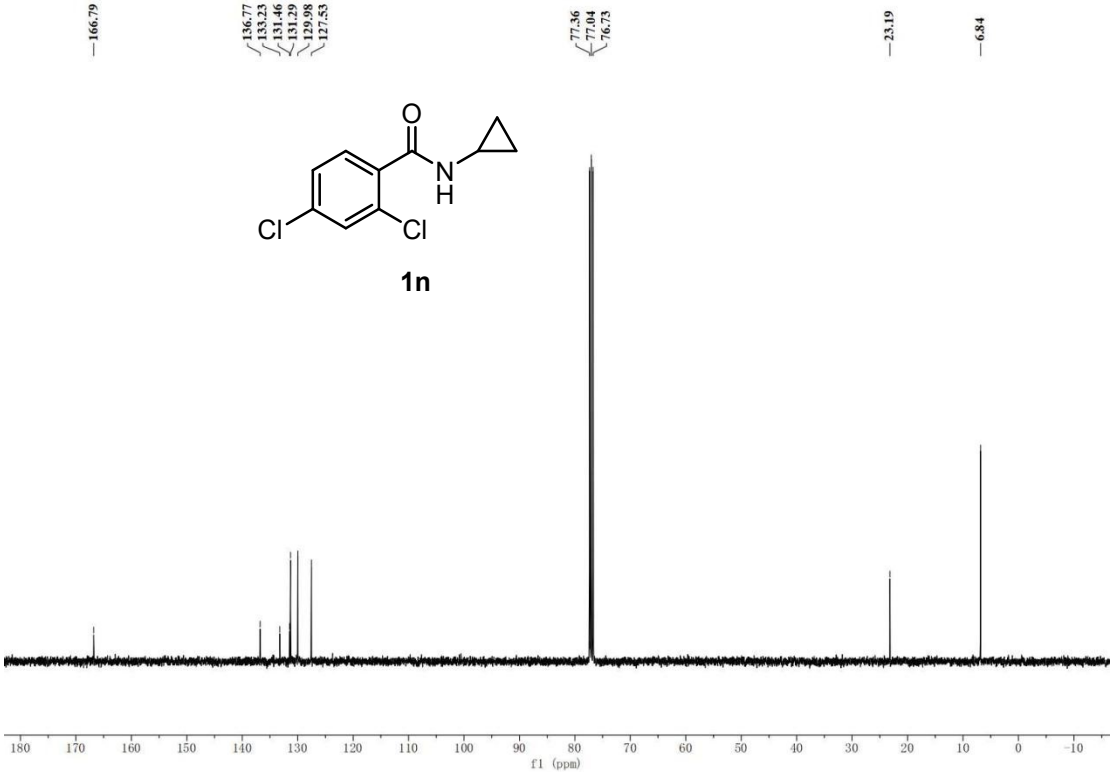


Figure S2. ^{13}C NMR spectrum of **1n** in $CDCl_3$ (100 MHz).

Figure S3. ^{1}H NMR spectrum of **1o** in $CDCl_3$ (400 MHz).

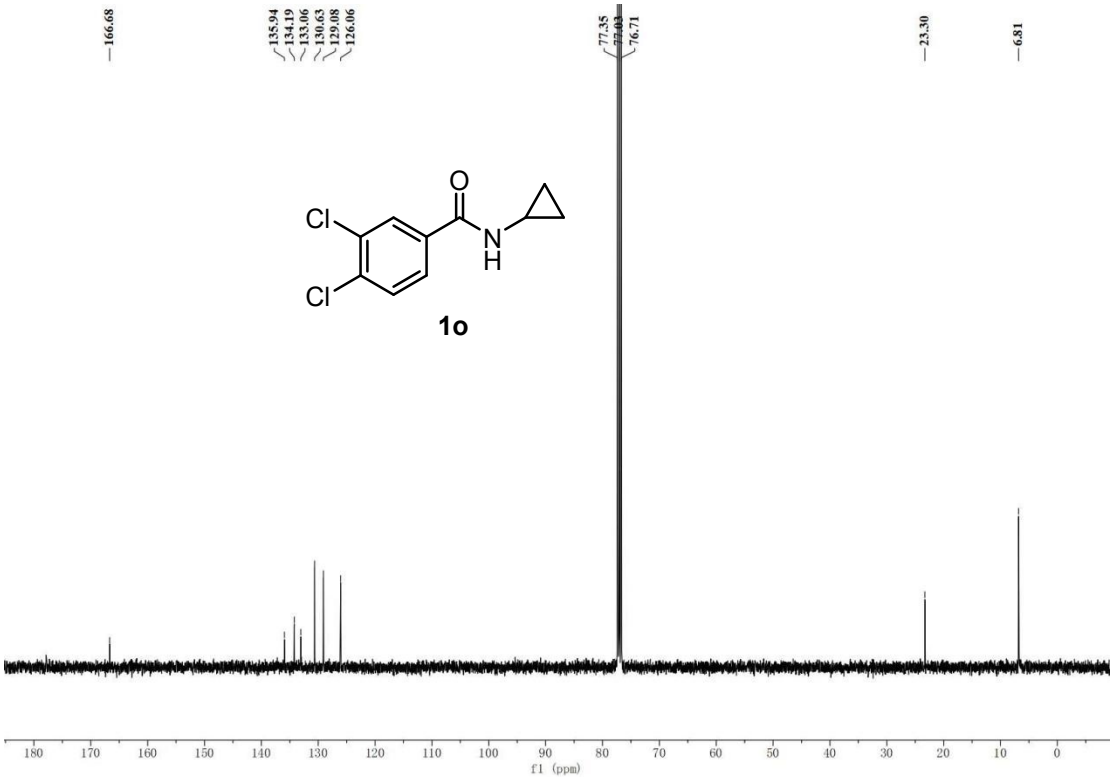


Figure S4. ^{13}C NMR spectrum of **1o** in $CDCl_3$ (100 MHz).

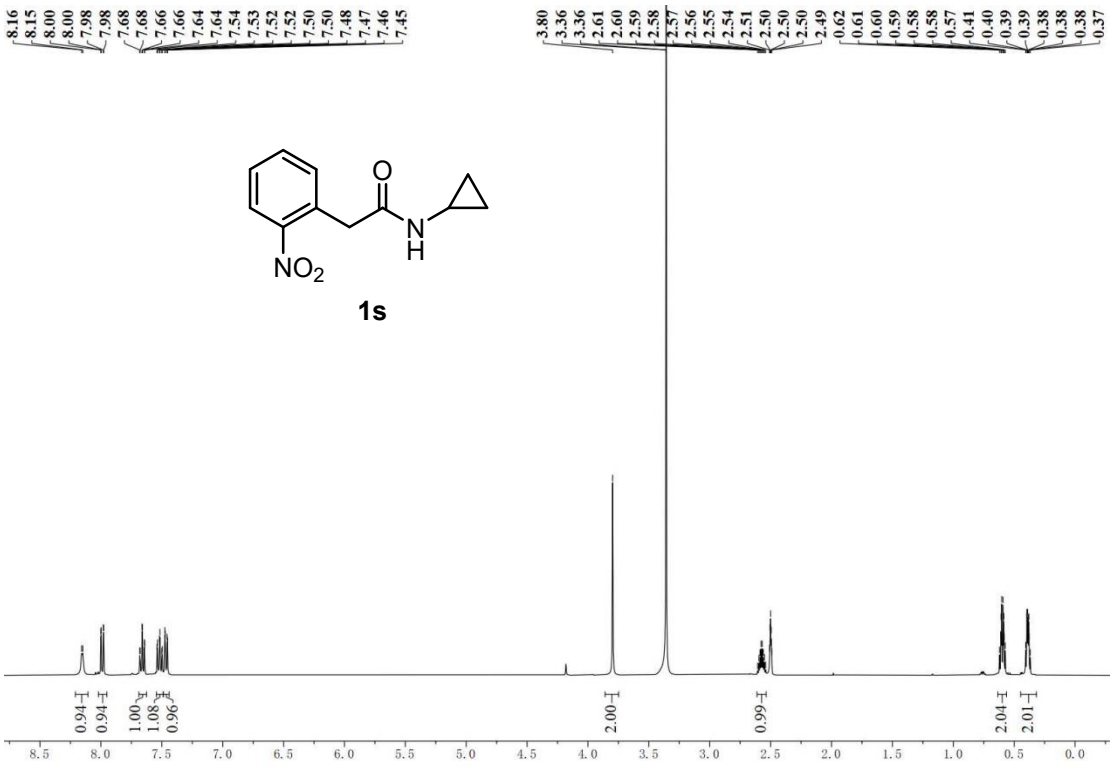


Figure S5. [1]H NMR spectrum of **1s** in DMSO-d_6 (400 MHz).

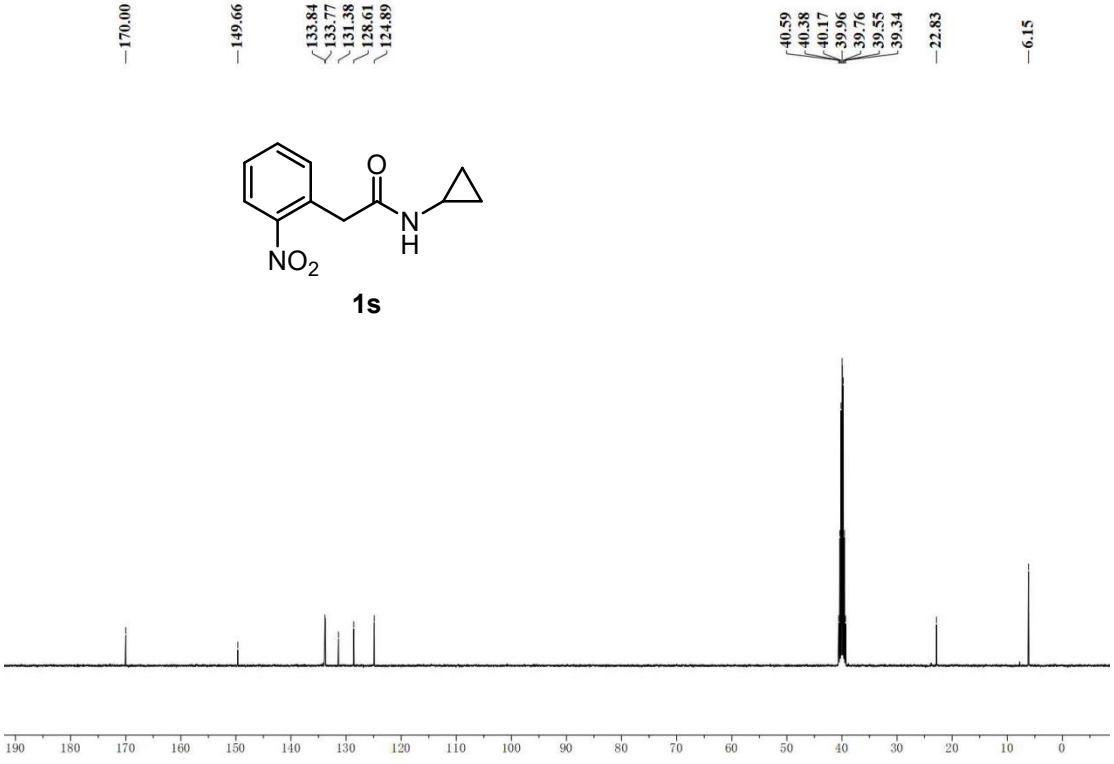


Figure S6. [13]C NMR spectrum of **1s** in DMSO-d_6 (100 MHz).

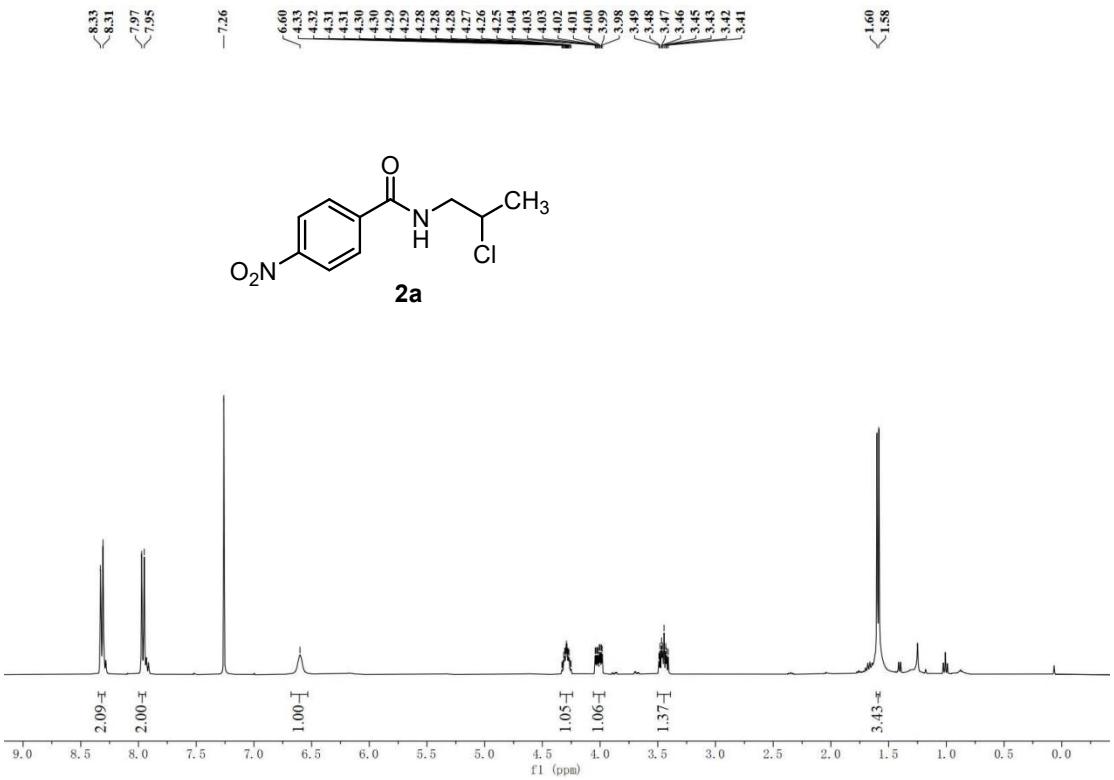


Figure S7. ^{1}H NMR spectrum of **2a** in $CDCl_3$ (400 MHz).

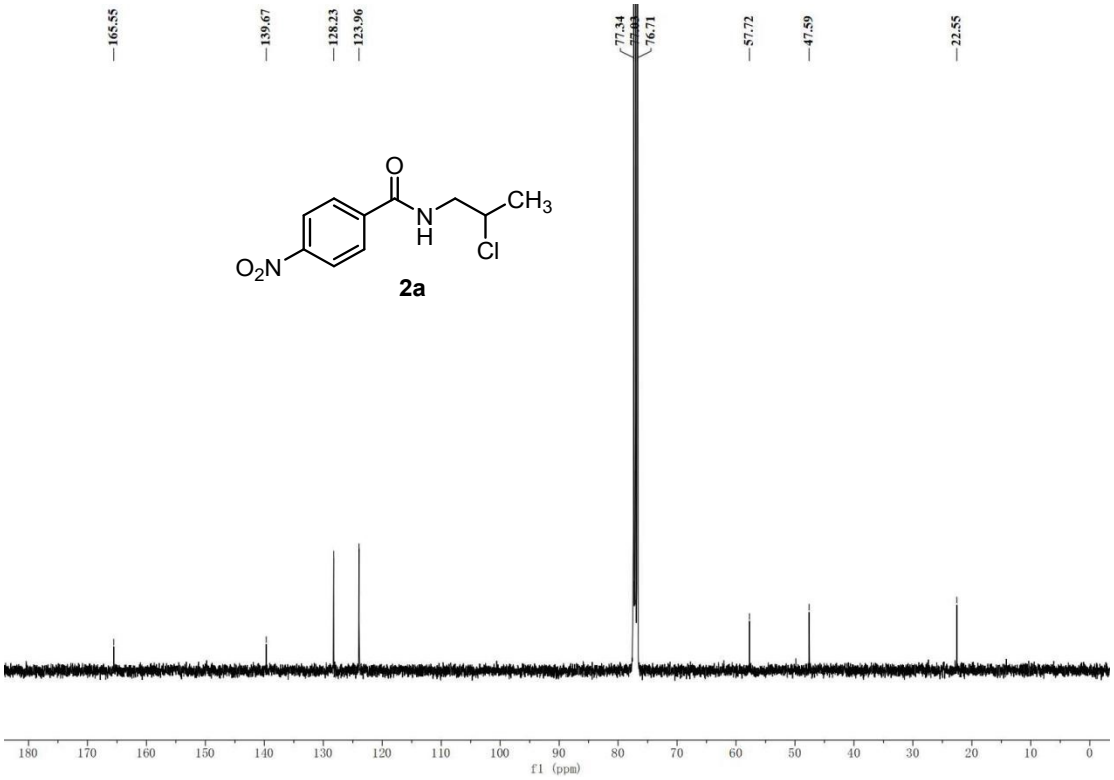


Figure S8. ^{13}C NMR spectrum of **2a** in $CDCl_3$ (100 MHz).

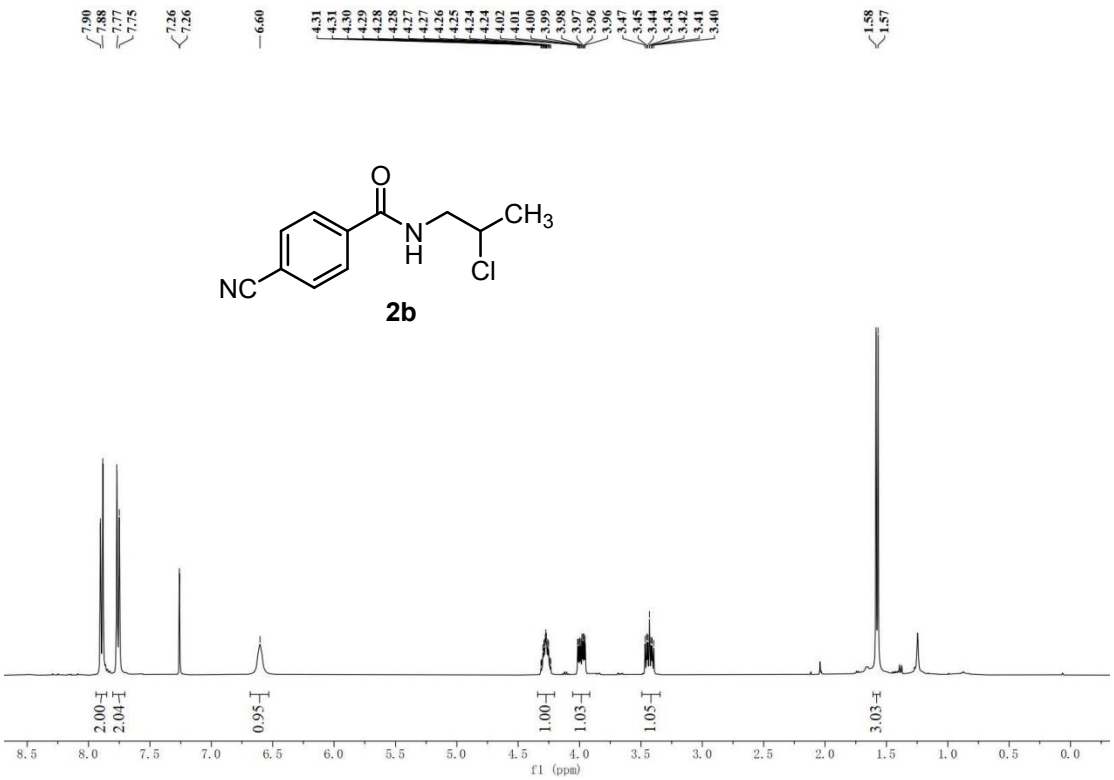


Figure S9. ^{1}H NMR spectrum of **2b** in $CDCl_3$ (400 MHz).

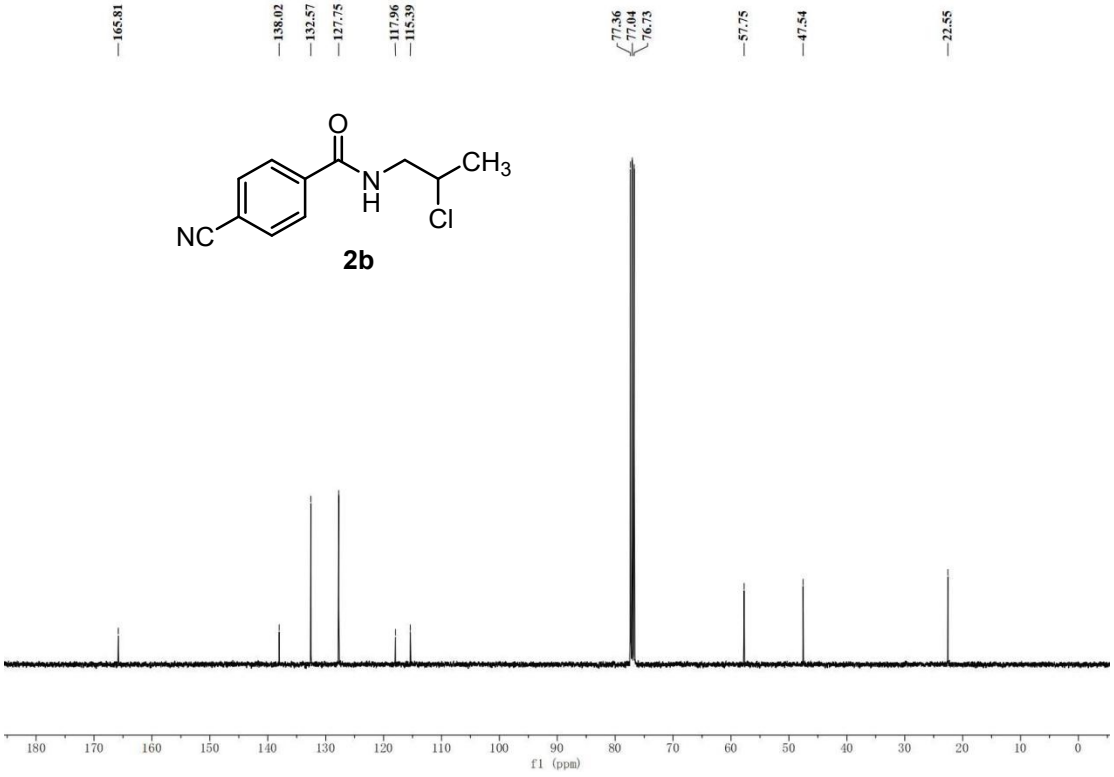


Figure S10. ^{13}C NMR spectrum of **2b** in $CDCl_3$ (100 MHz).

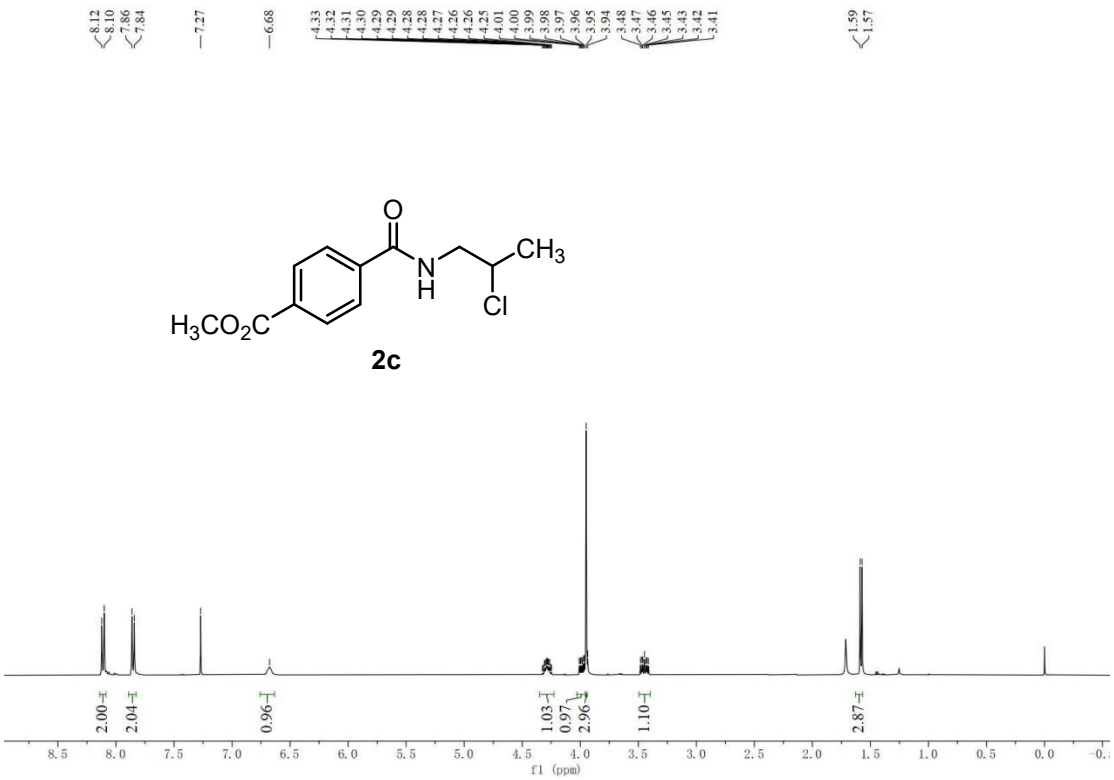


Figure S11. ^{1}H NMR spectrum of **2c** in $CDCl_3$ (400 MHz).

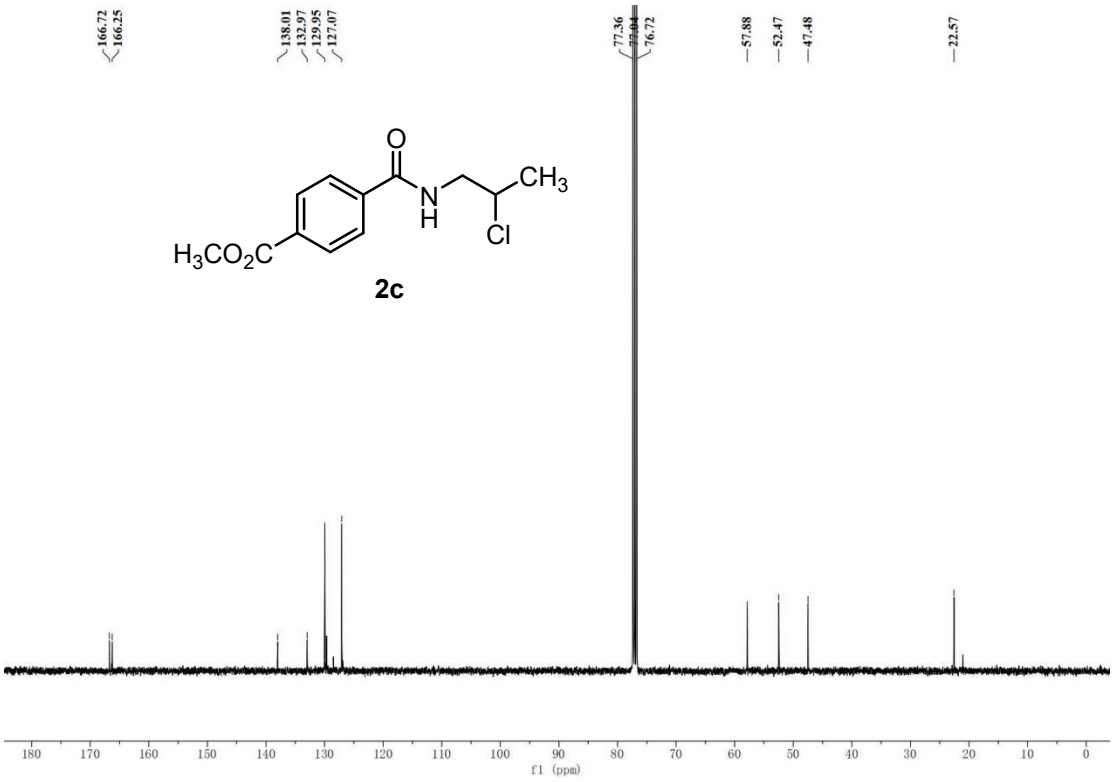


Figure S12. ^{13}C NMR spectrum of **2c** in $CDCl_3$ (100 MHz).

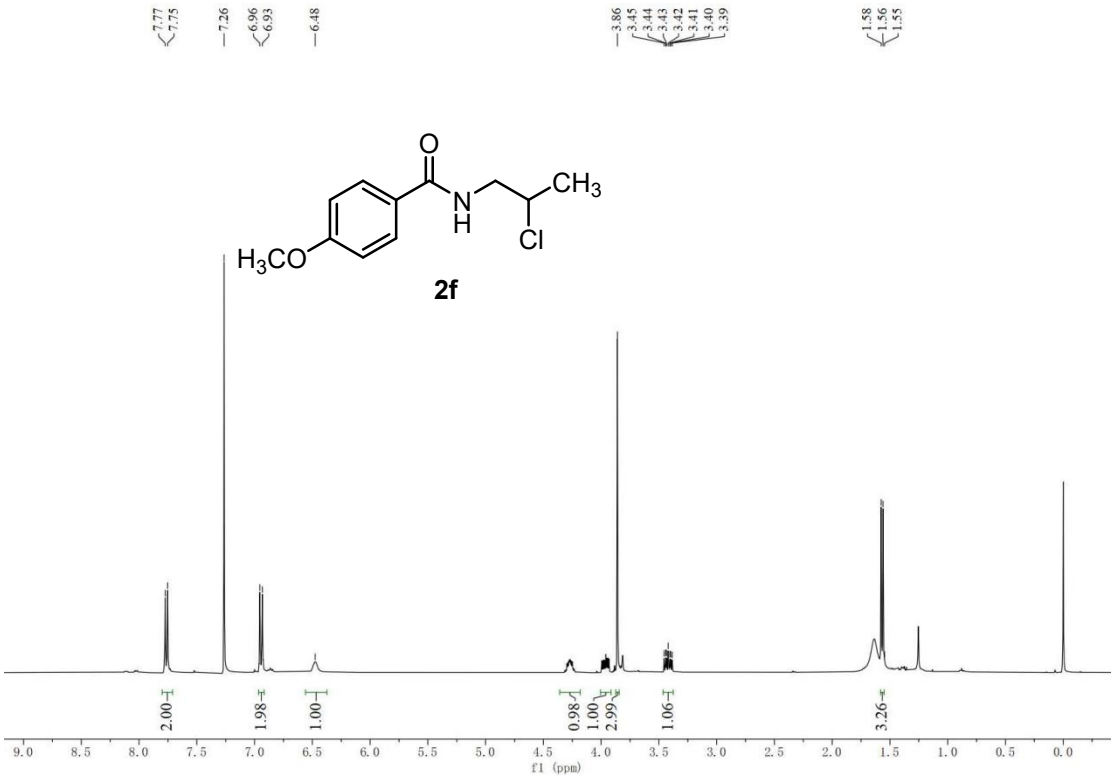


Figure S13. ^{1}H NMR spectrum of **2f** in $CDCl_3$ (400 MHz).

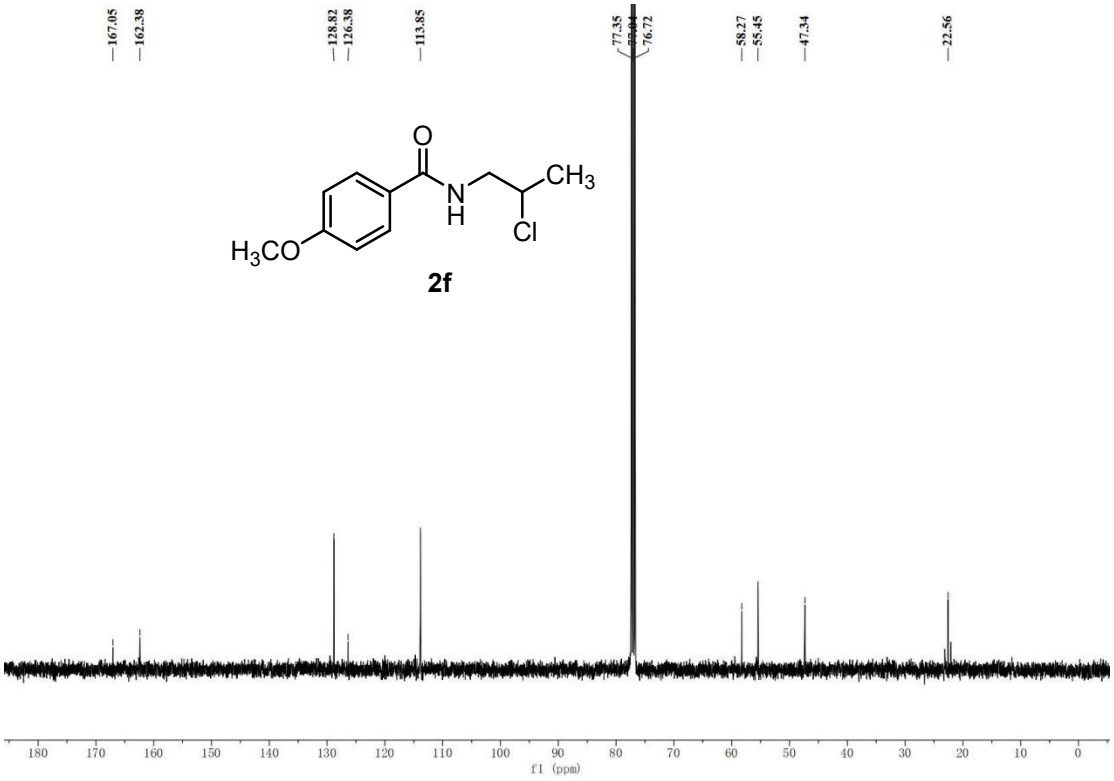


Figure S14. ^{13}C NMR spectrum of **2f** in $CDCl_3$ (100 MHz).

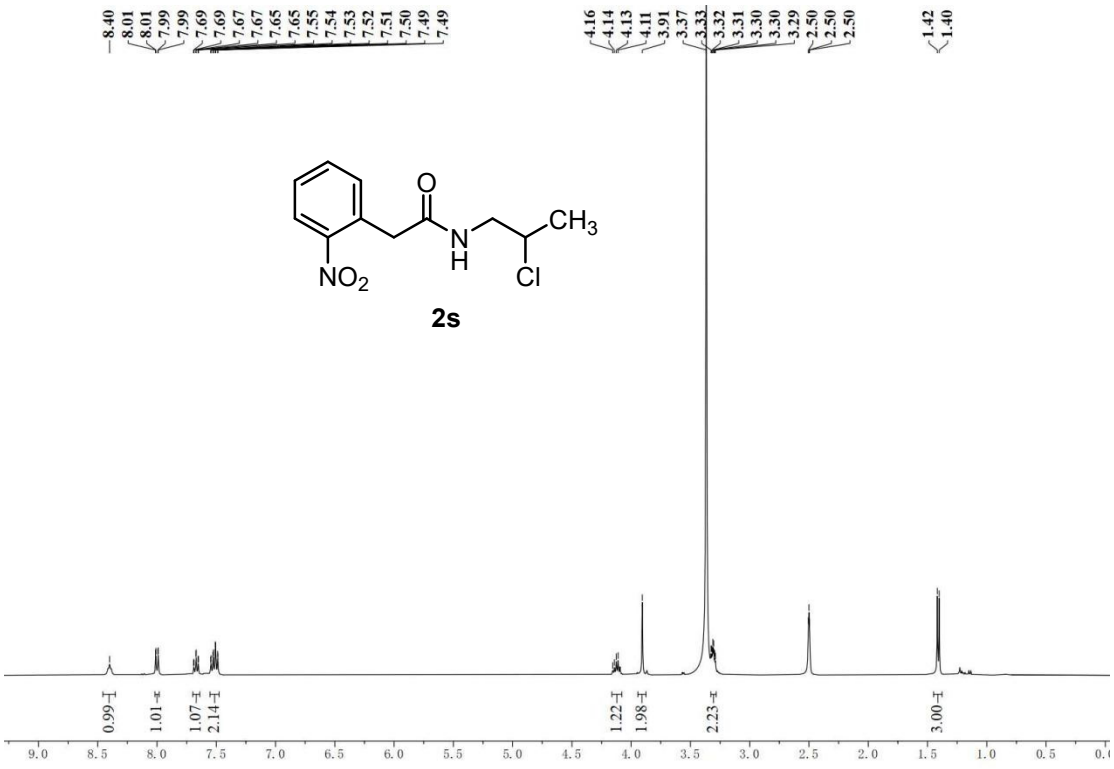


Figure S15. ^{1}H NMR spectrum of **2s** in DMSO-d_6 (400 MHz).

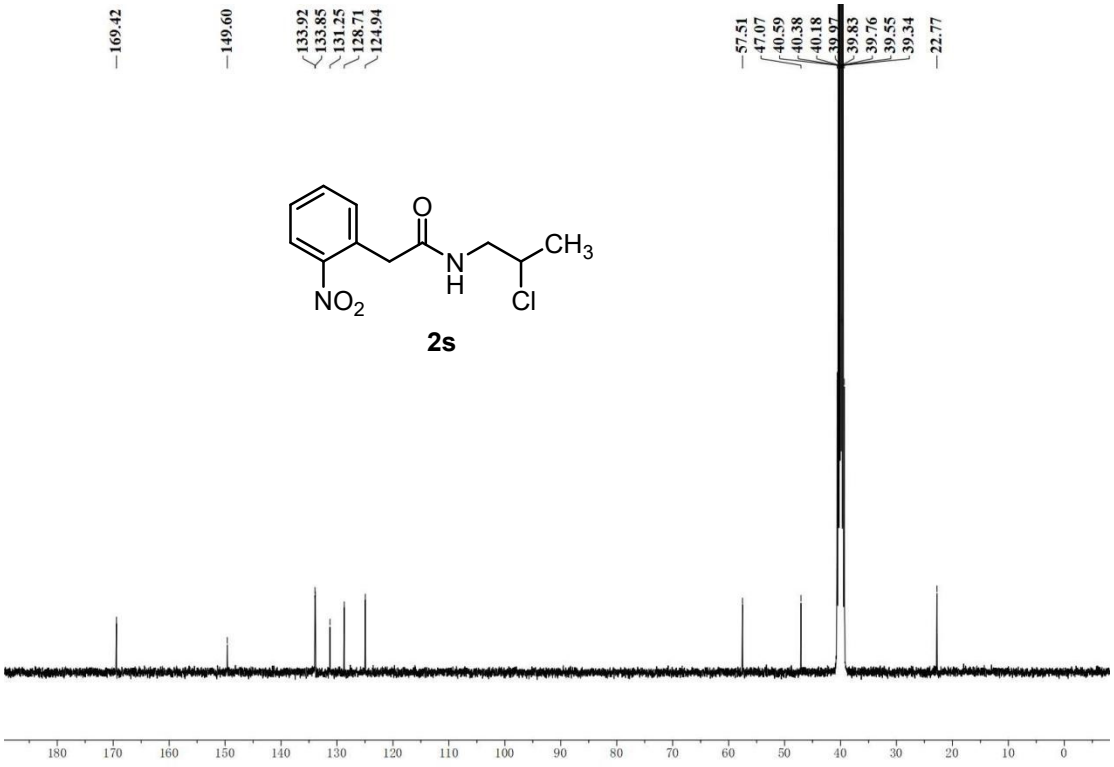


Figure S16. ^{13}C NMR spectrum of **2s** in DMSO-d_6 (100 MHz).

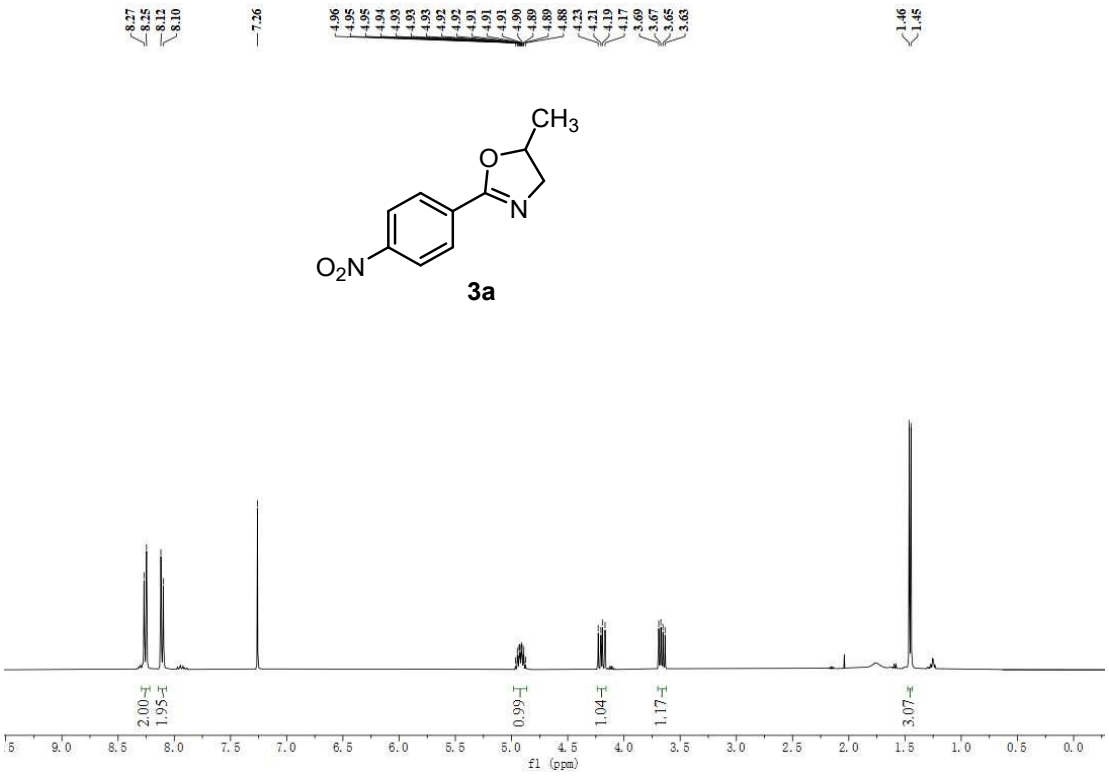


Figure S17. ^{1}H NMR spectrum of **3a** in $CDCl_3$ (400 MHz).

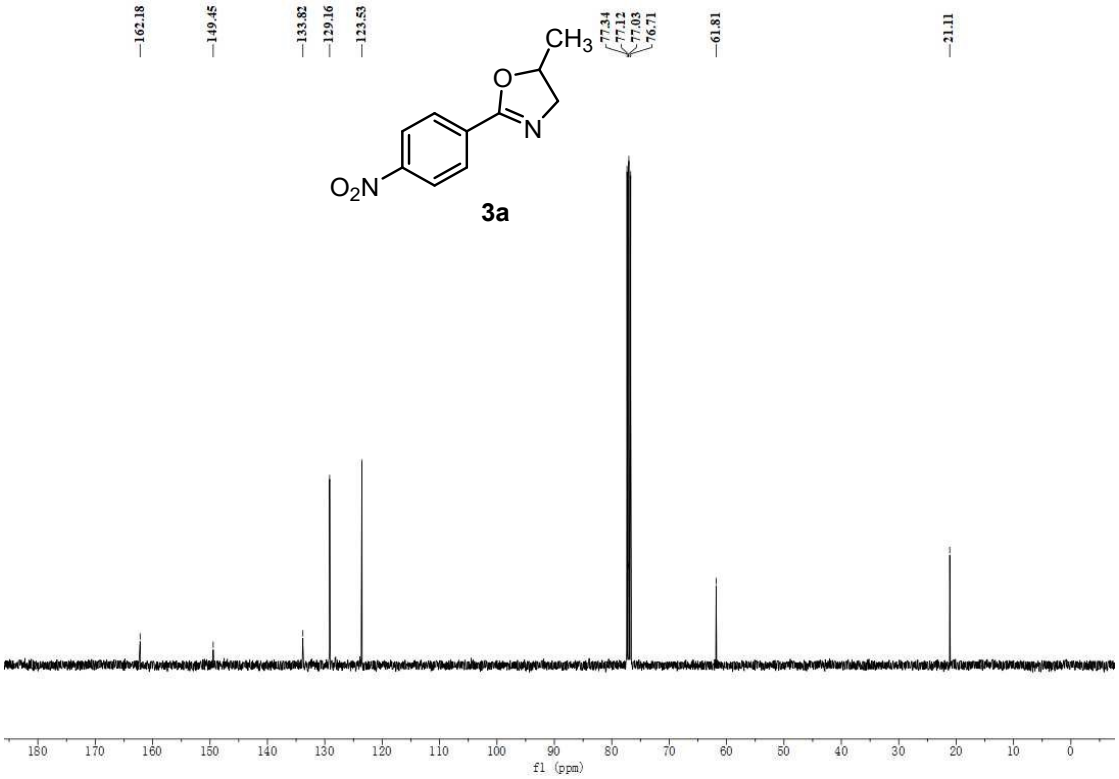


Figure S18. ^{13}C NMR spectrum of **3a** in $CDCl_3$ (100 MHz).

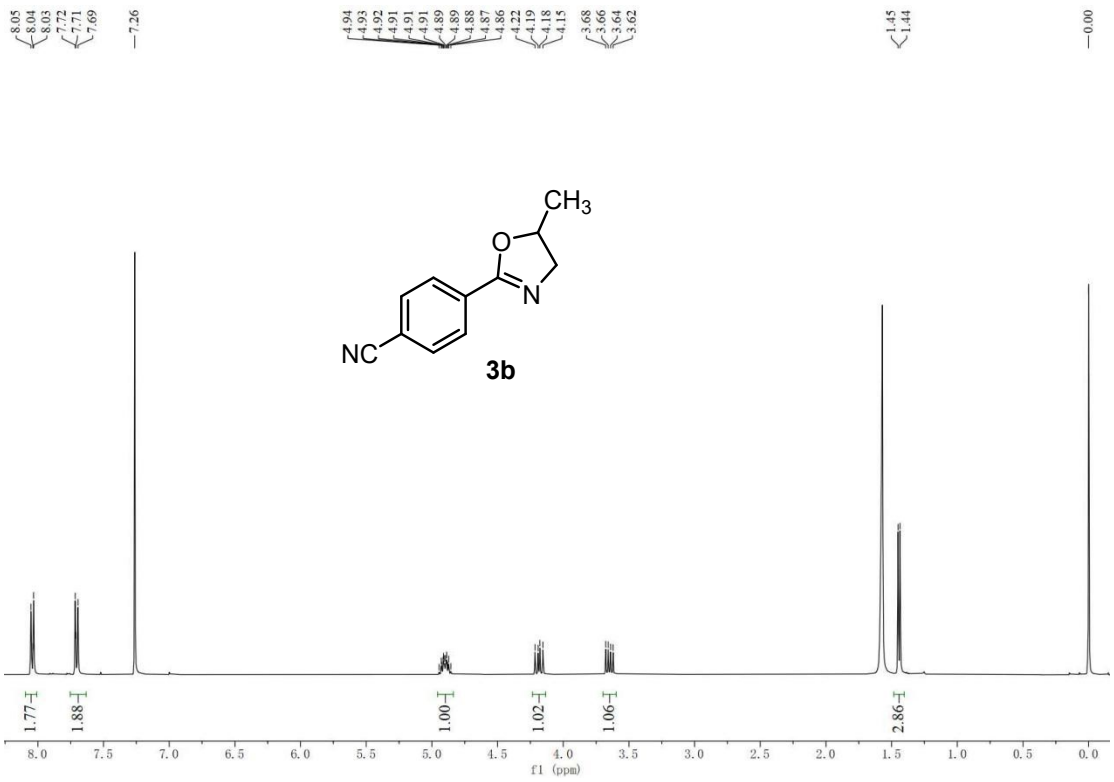


Figure S19. ^{1}H NMR spectrum of **3b** in $CDCl_3$ (400 MHz).

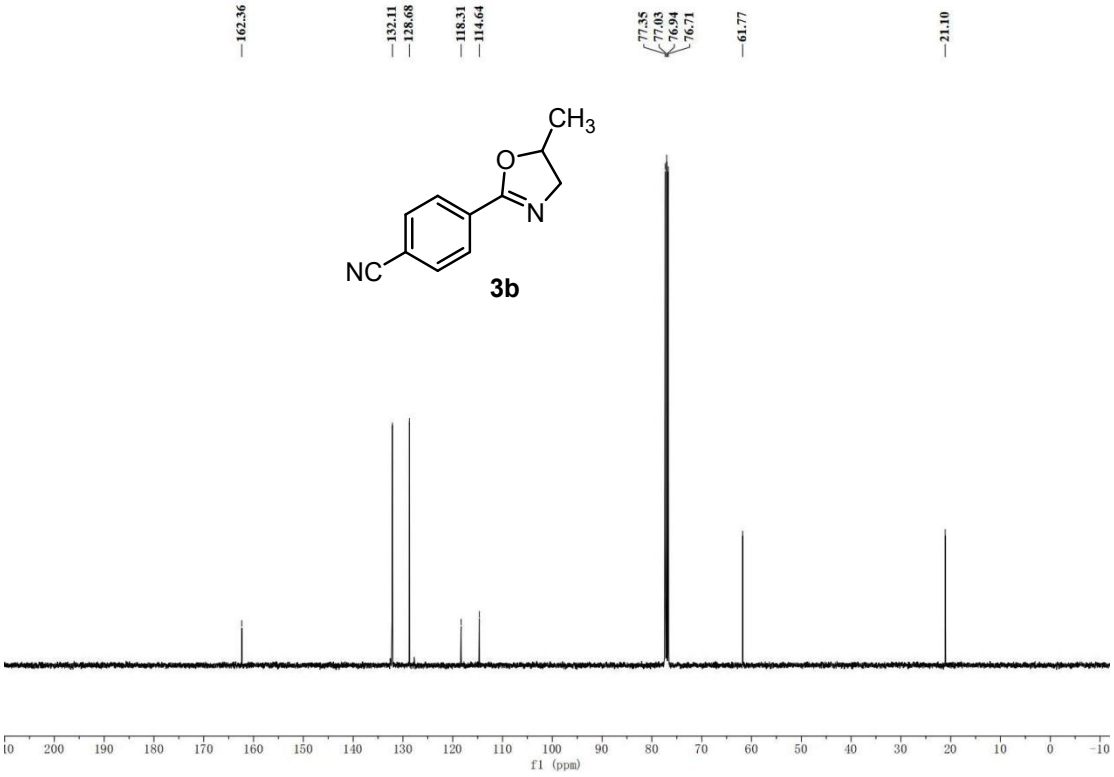


Figure S20. ^{13}C NMR spectrum of **3b** in $CDCl_3$ (100 MHz).

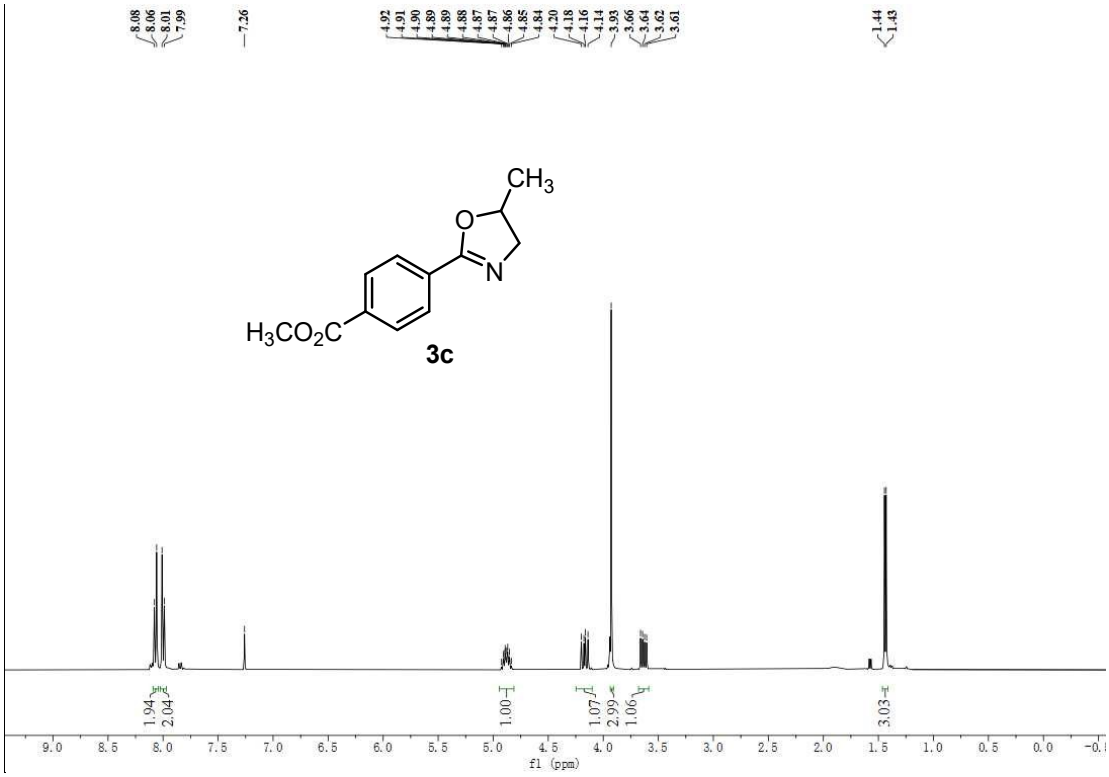


Figure S21. ^{1}H NMR spectrum of **3c** in $CDCl_3$ (400 MHz).

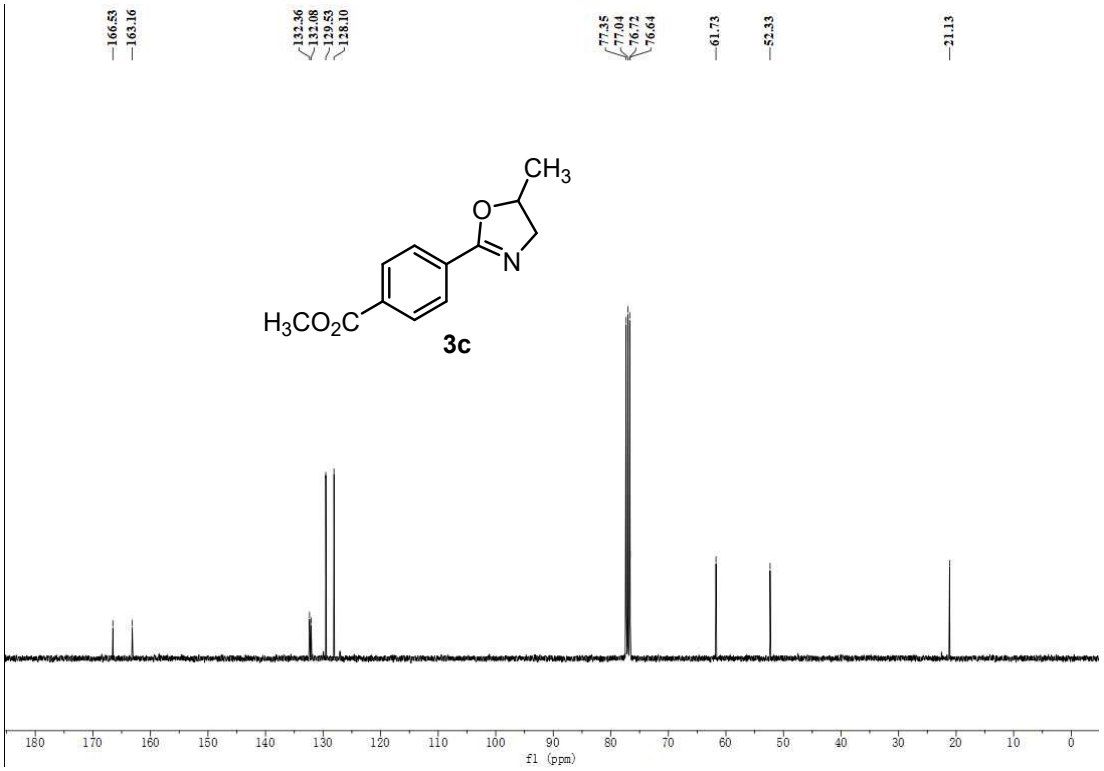


Figure S22. ^{13}C NMR spectrum of **3c** in $CDCl_3$ (100 MHz).

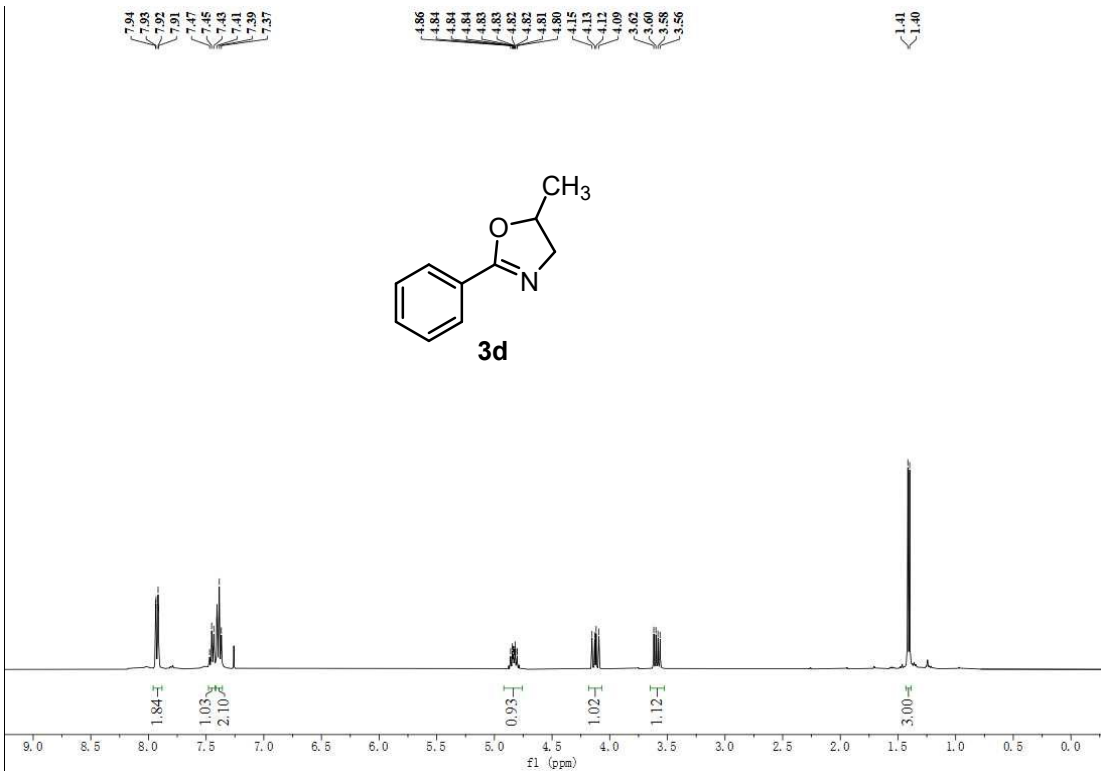


Figure S23. ^{1}H NMR spectrum of **3d** in $CDCl_3$ (400 MHz).

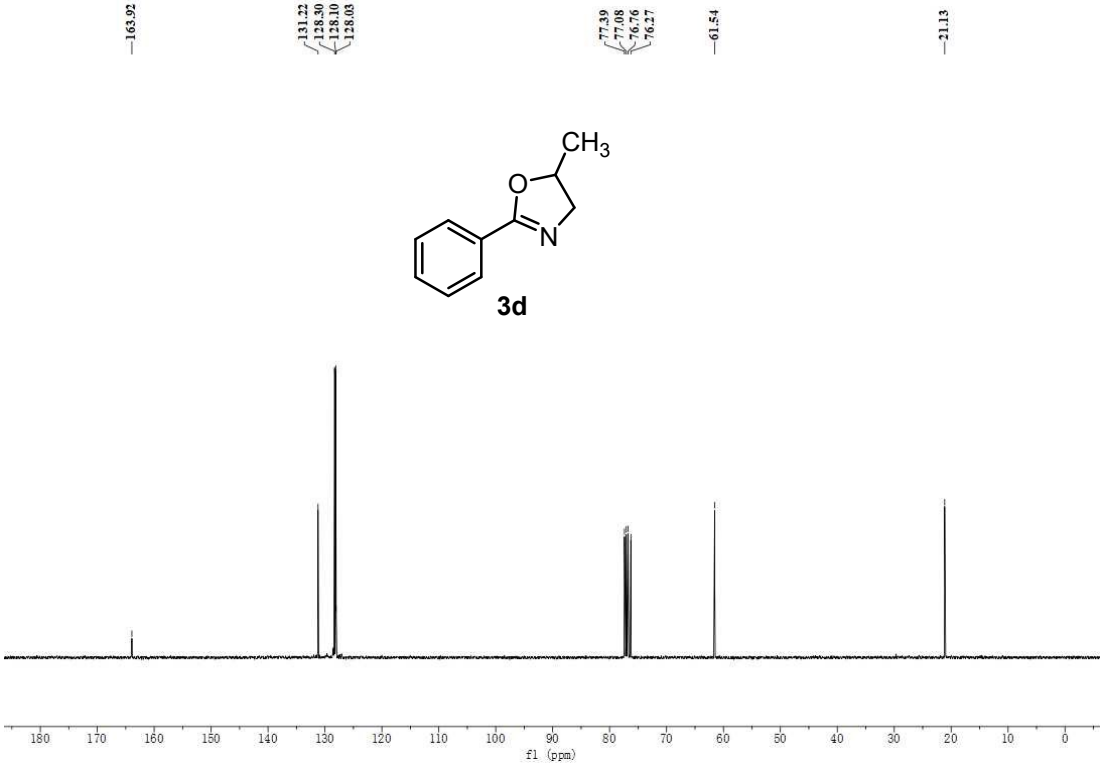


Figure S24. ^{13}C NMR spectrum of **3d** in $CDCl_3$ (100 MHz).

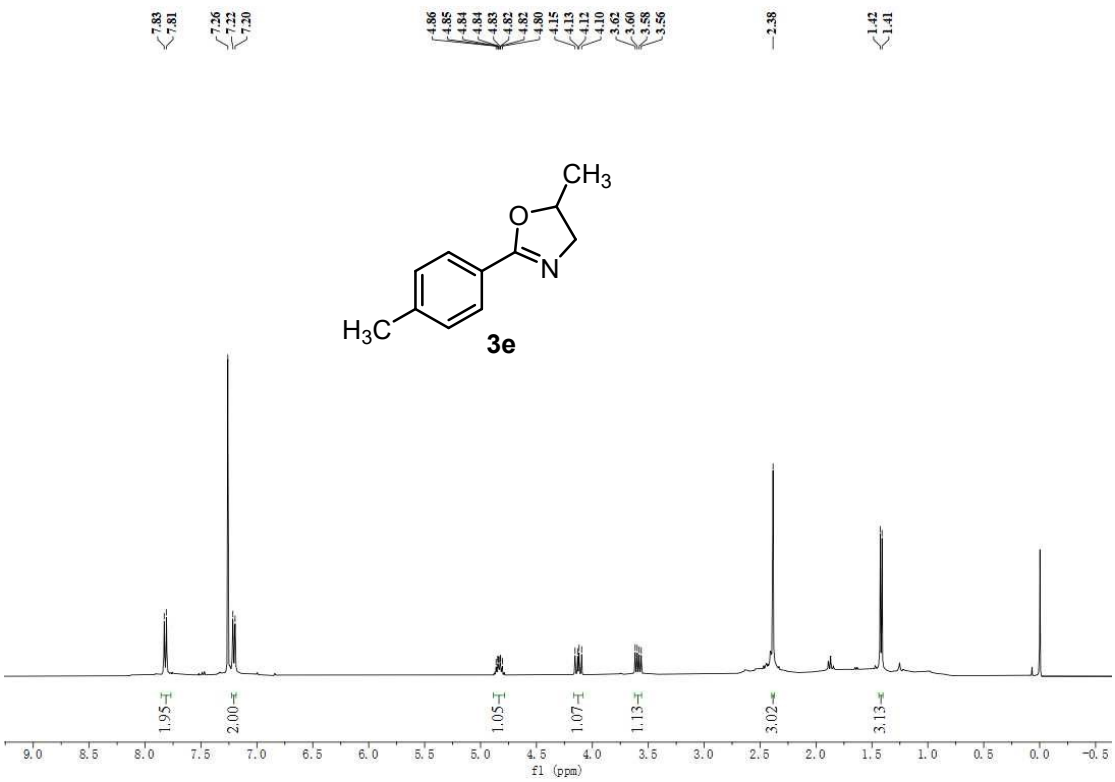


Figure S25. ^{1}H NMR spectrum of **3e** in $CDCl_3$ (400 MHz).

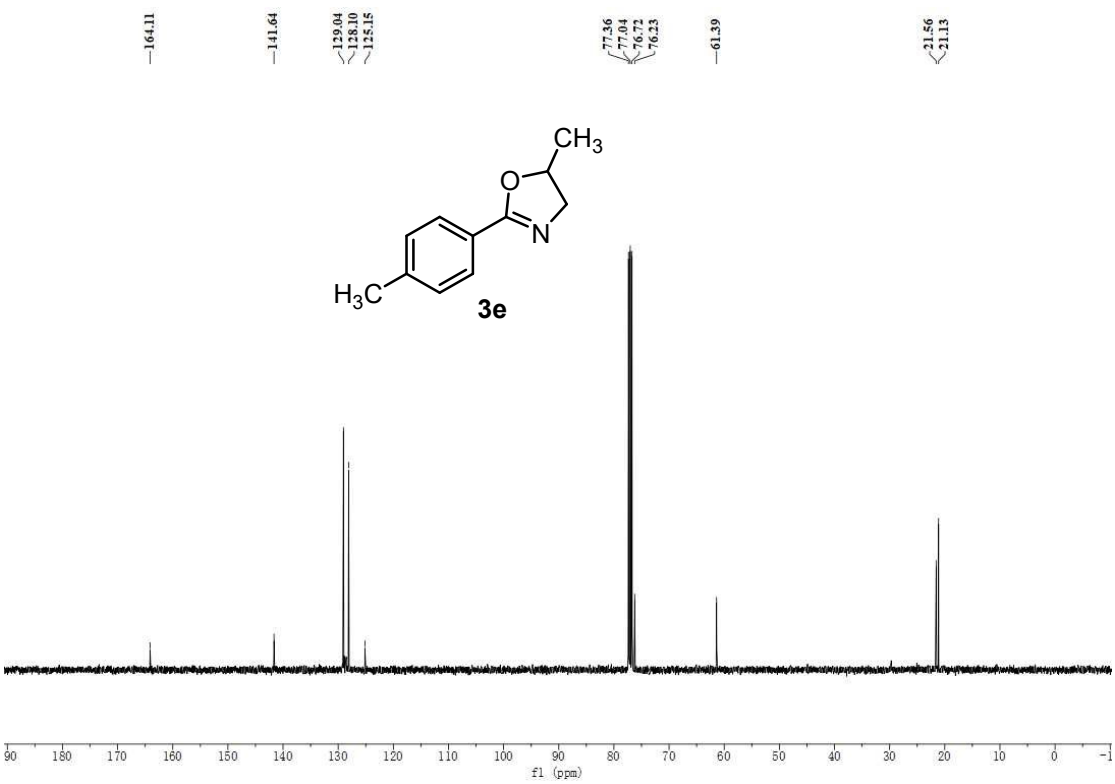


Figure S26. ^{13}C NMR spectrum of **3e** in $CDCl_3$ (100 MHz).

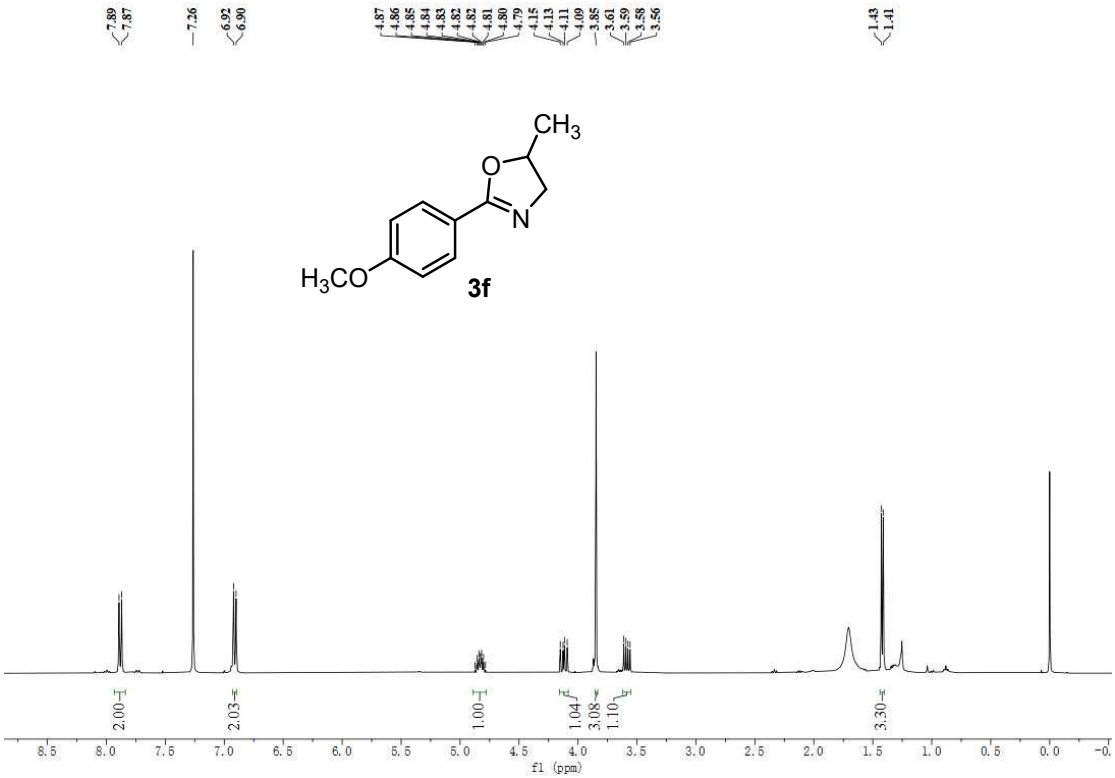


Figure S27. ^{1}H NMR spectrum of **3f** in $CDCl_3$ (400 MHz).

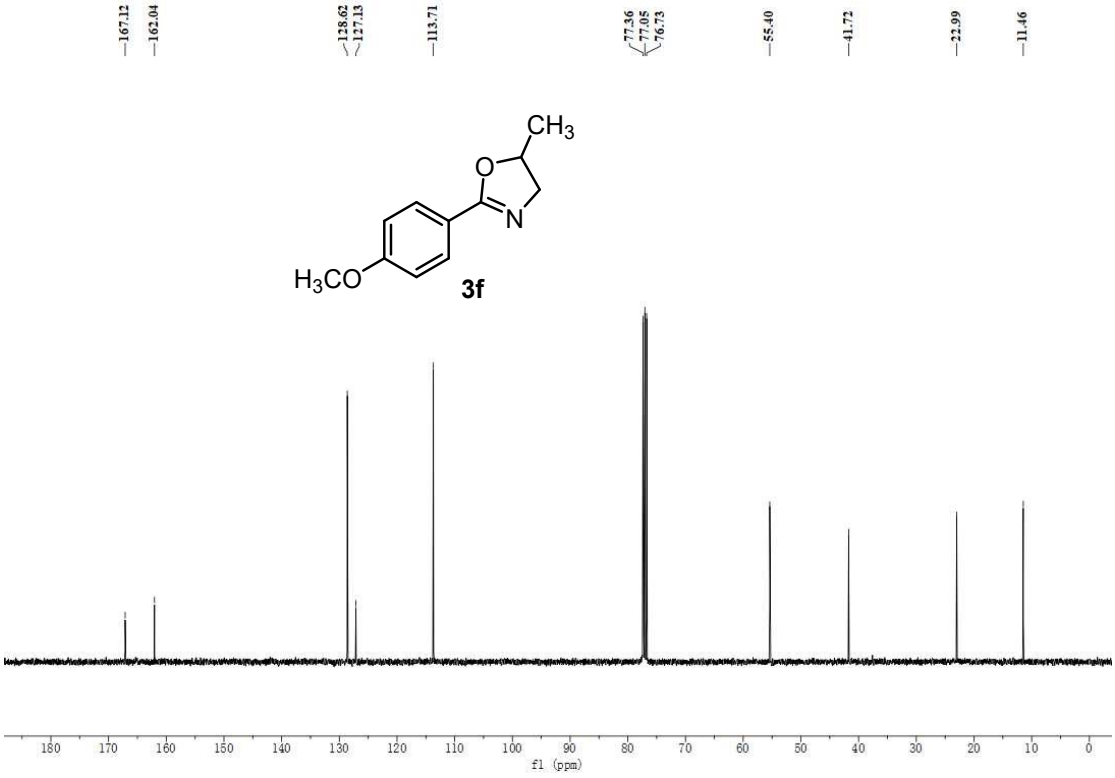


Figure S28. ^{13}C NMR spectrum of **3f** in $CDCl_3$ (100 MHz).

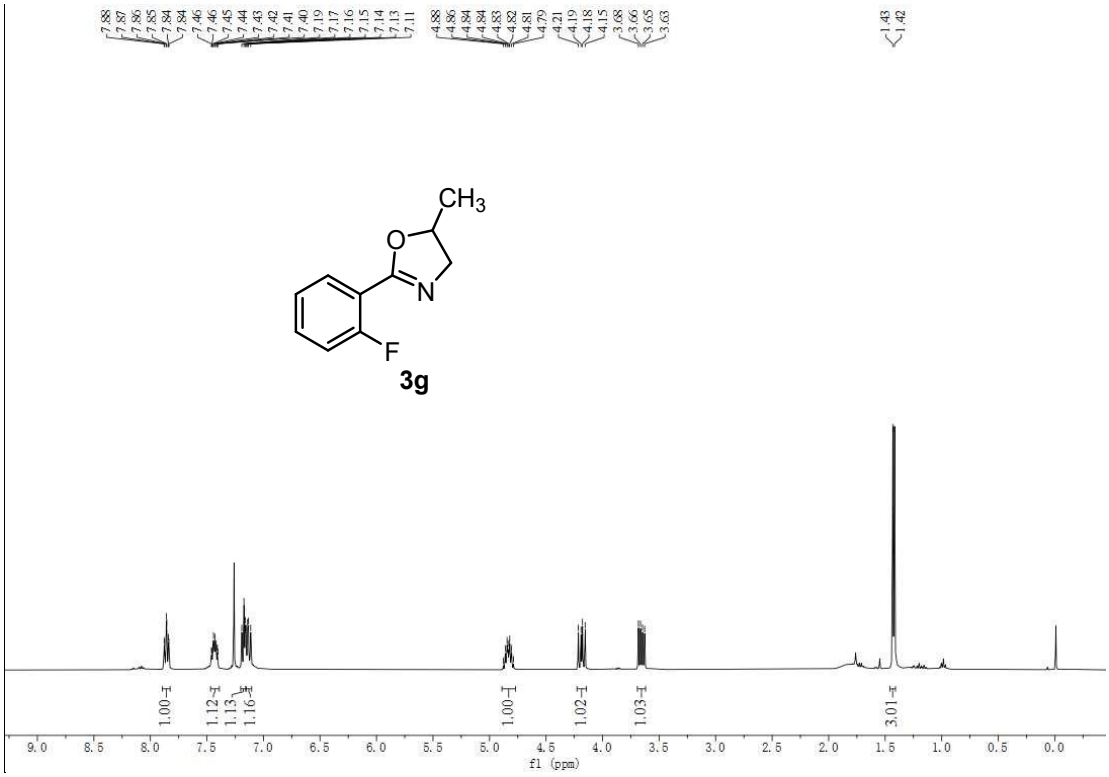


Figure S29. ^{1}H NMR spectrum of **3g** in $CDCl_3$ (400 MHz).

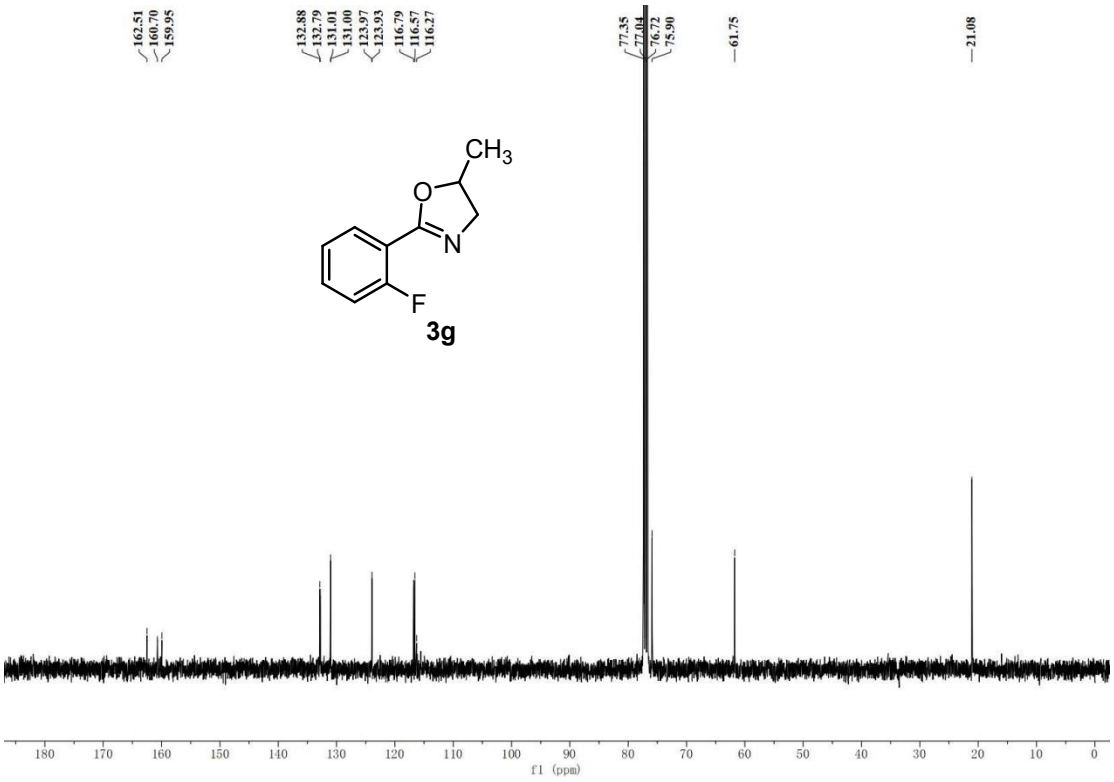


Figure S30. ^{13}C NMR spectrum of **3g** in $CDCl_3$ (100 MHz).

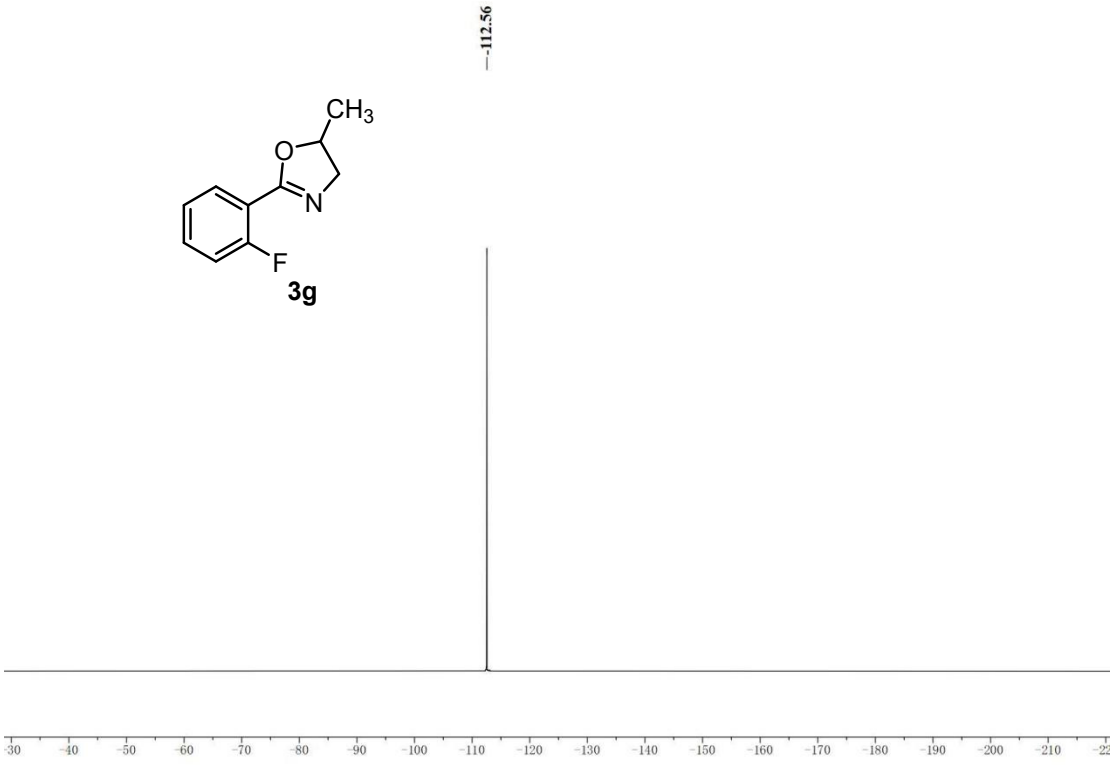


Figure S31. ^{19}F NMR spectrum of **3g** in $CDCl_3$ (376 MHz).

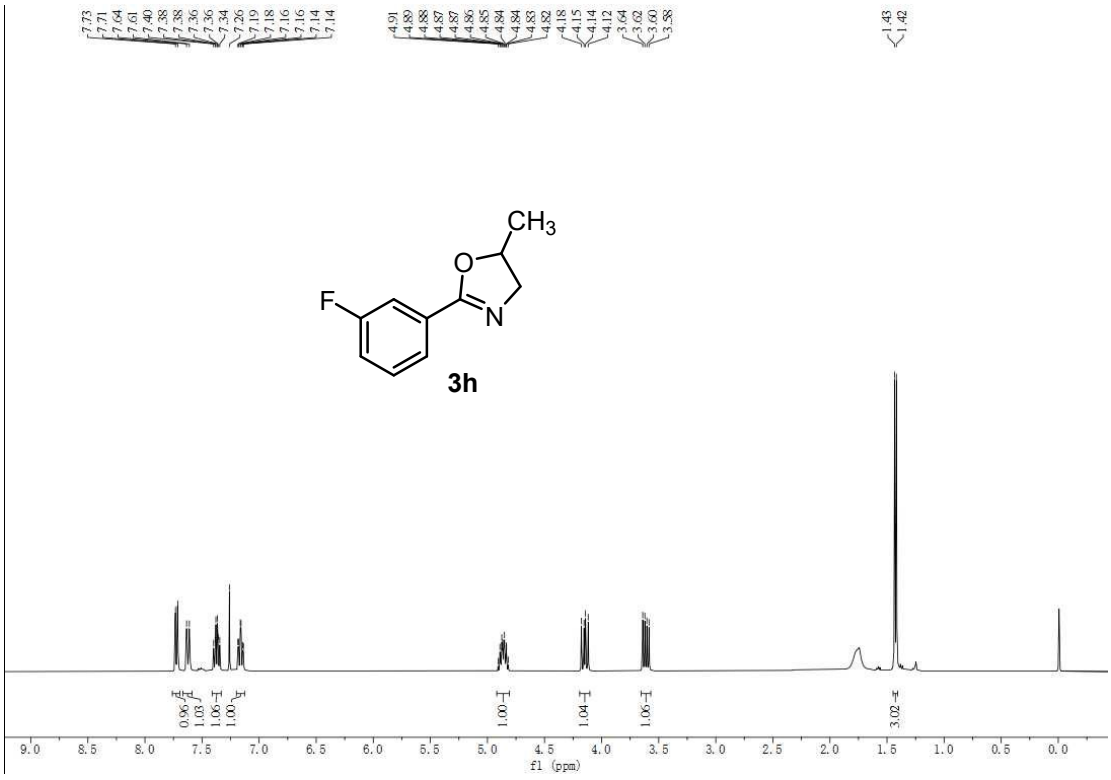


Figure S32. ^{1}H NMR spectrum of **3h** in $CDCl_3$ (400 MHz).

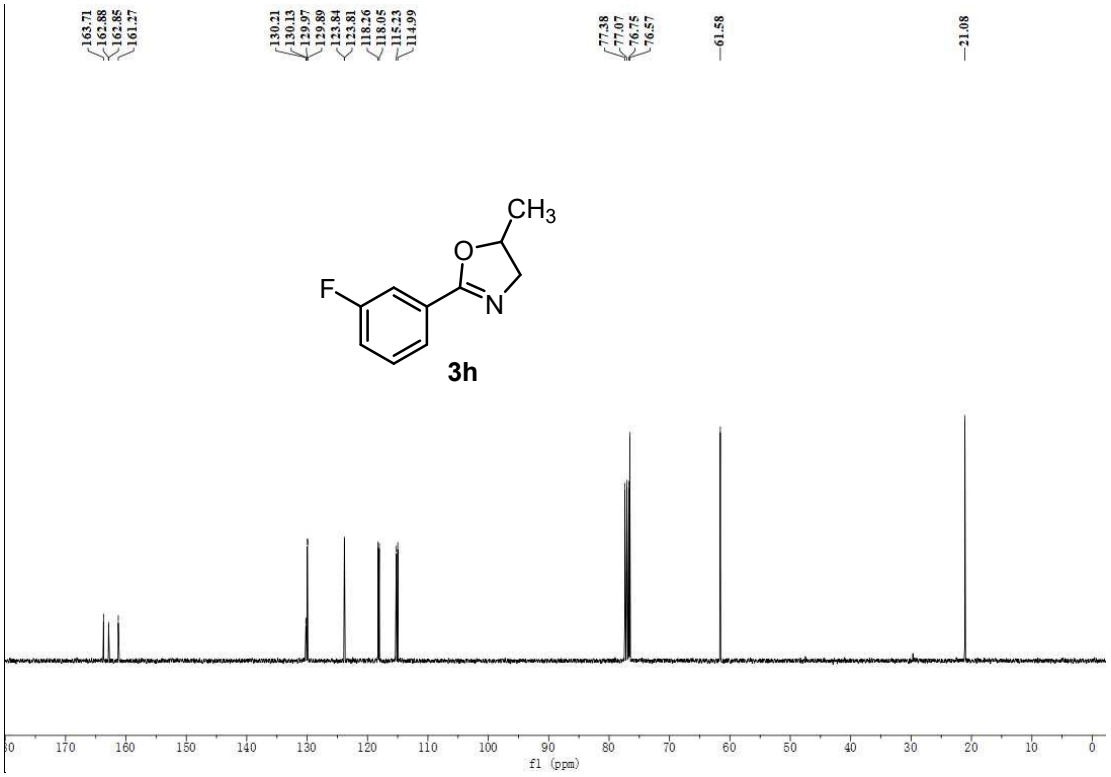


Figure S33. ^{13}C NMR spectrum of **3h** in $CDCl_3$ (100 MHz).

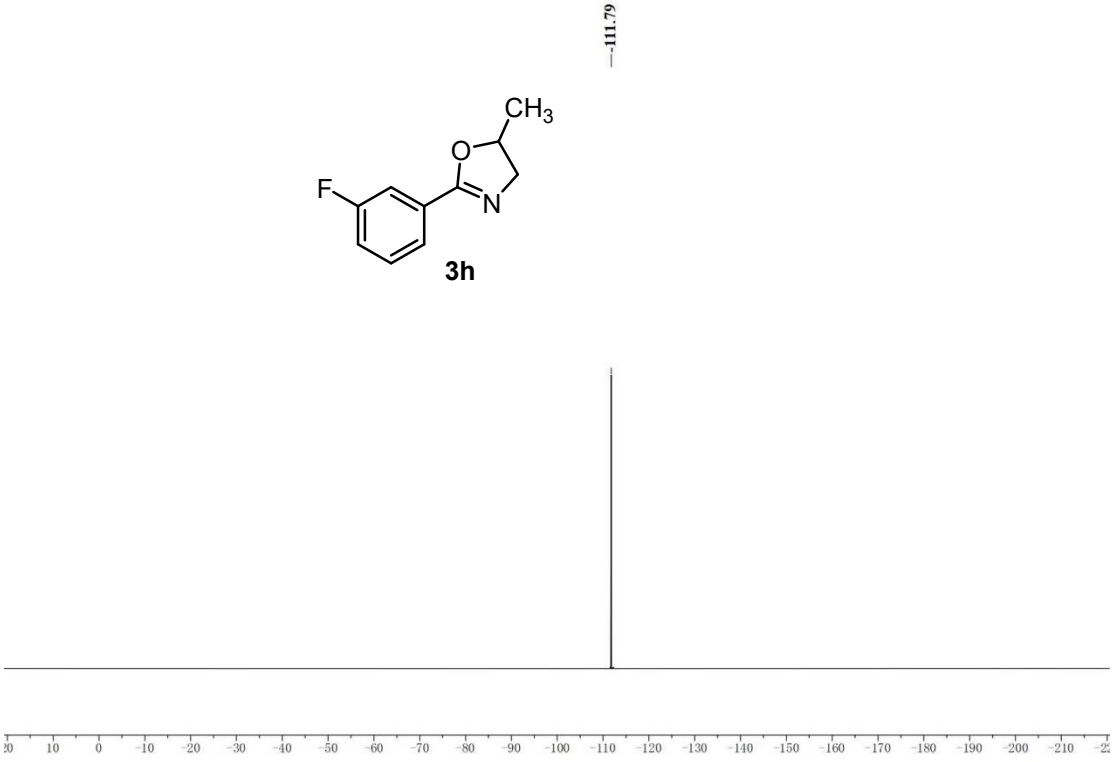


Figure S34. ^{19}F NMR spectrum of **3h** in $CDCl_3$ (376 MHz)

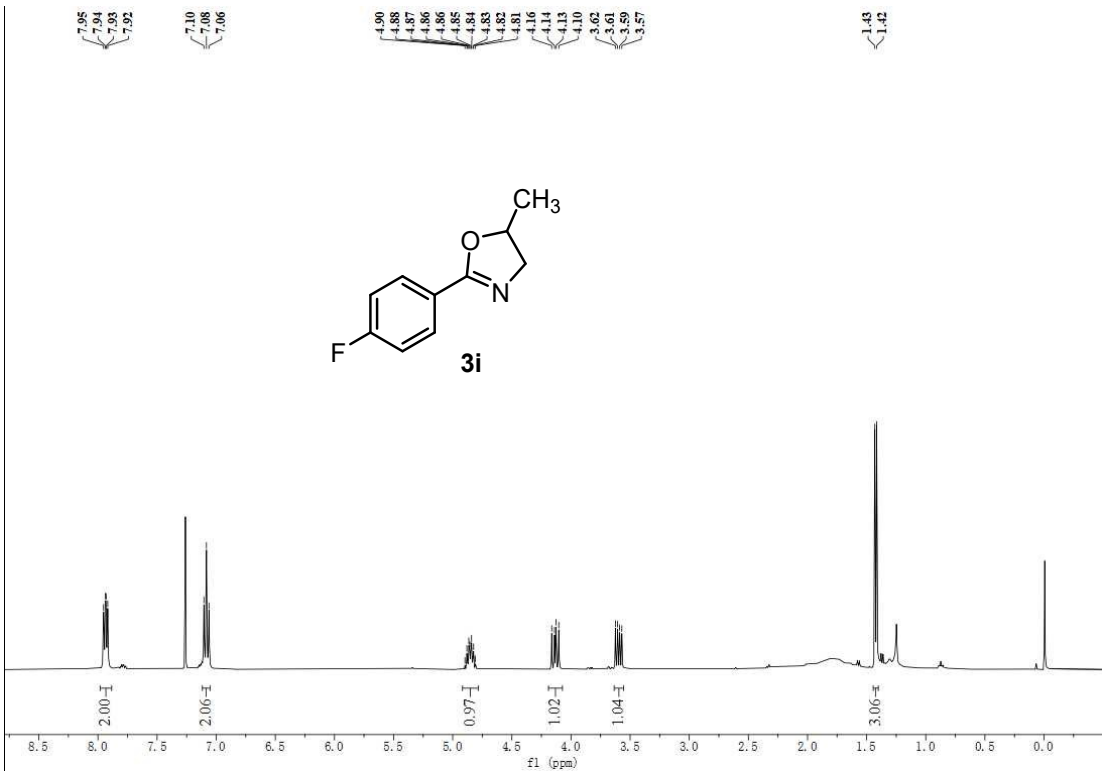


Figure S35. ^{1}H NMR spectrum of **3i** in $CDCl_3$ (400 MHz).

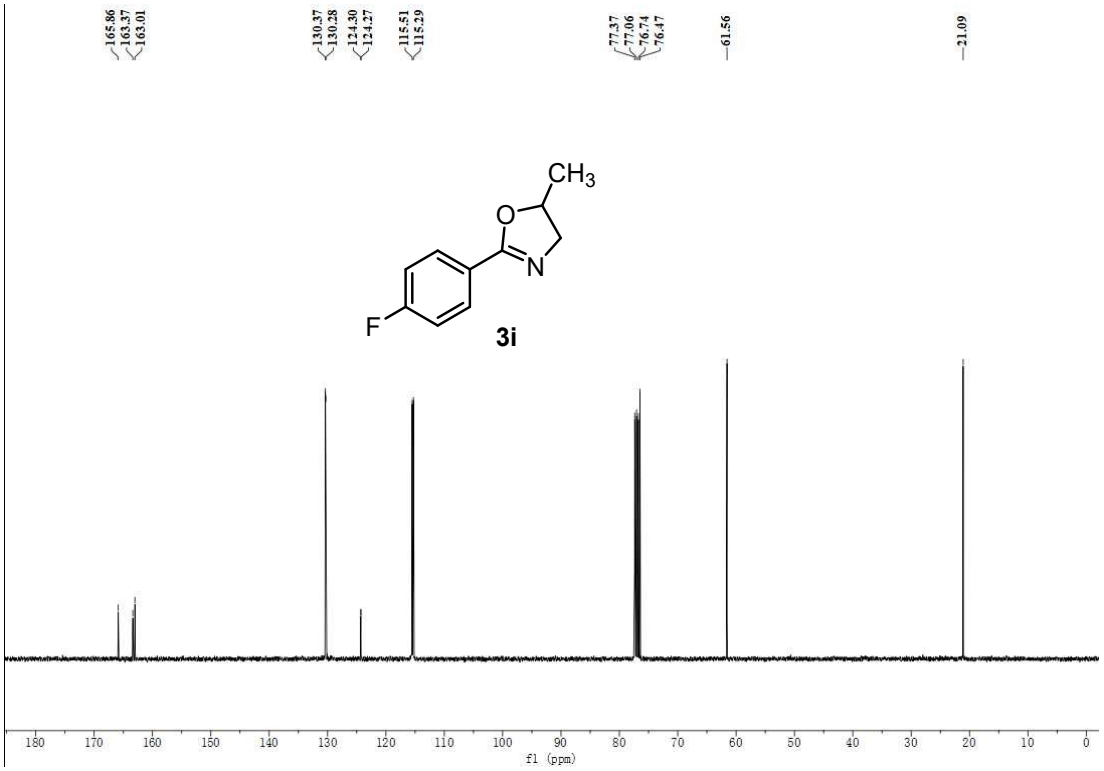


Figure S36. ^{13}C NMR spectrum of **3i** in $CDCl_3$ (100 MHz).

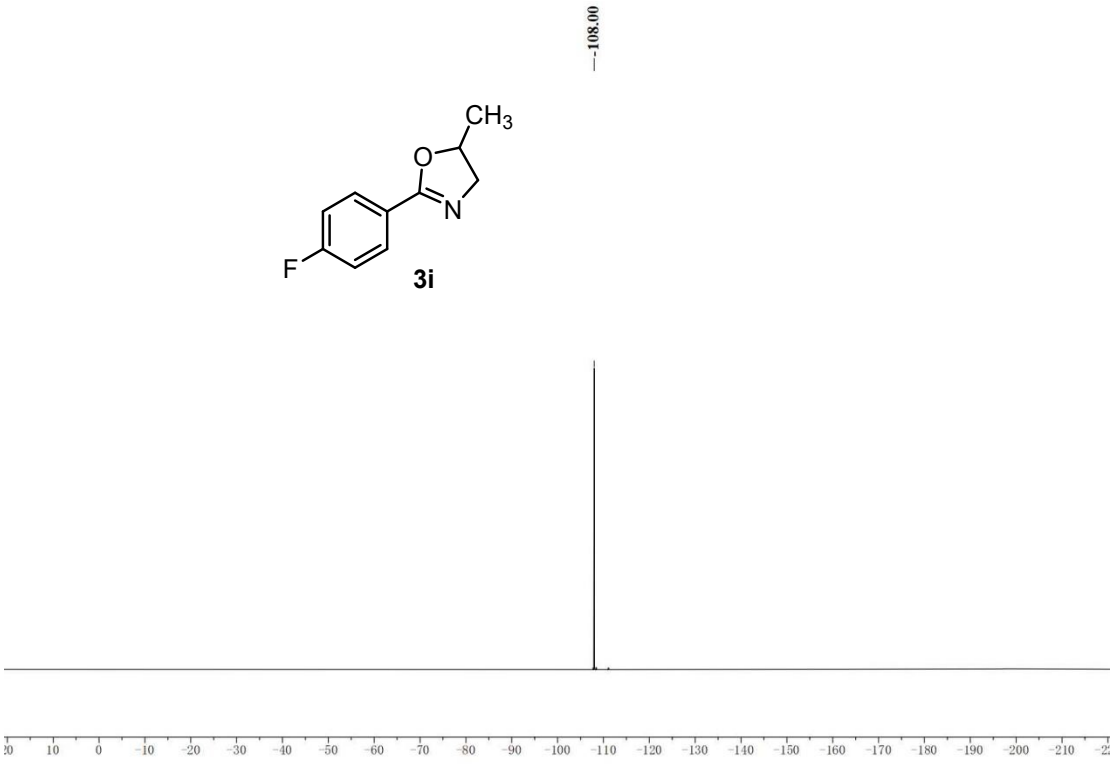


Figure S37. ^{19}F NMR spectrum of **3i** in $CDCl_3$ (376 MHz).

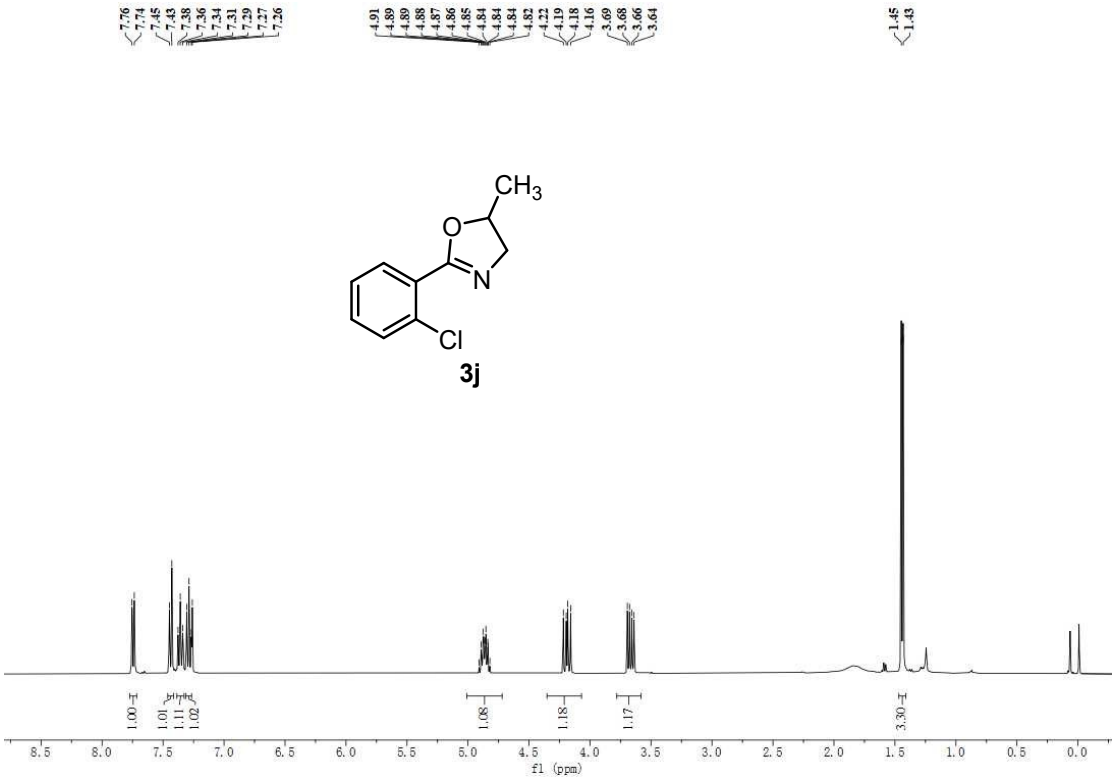


Figure S38. ^{1}H NMR spectrum of **3j** in $CDCl_3$ (400 MHz).

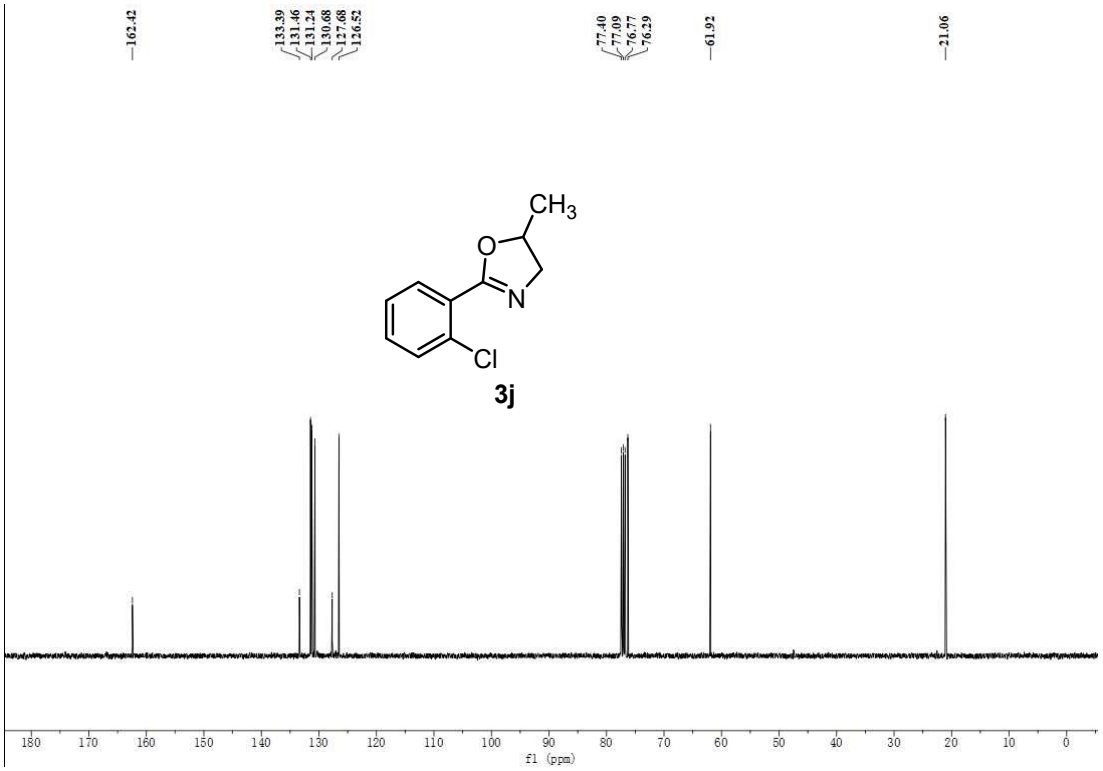


Figure S39. ^{13}C NMR spectrum of **3j** in $CDCl_3$ (100 MHz).

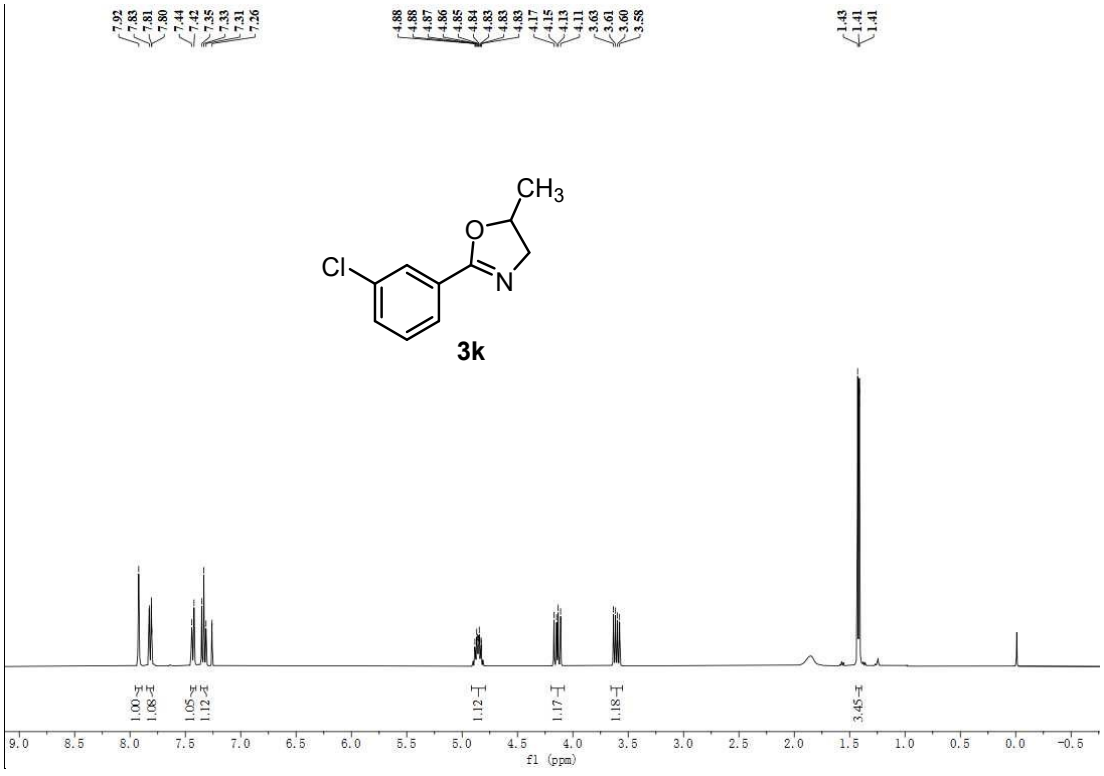


Figure S40. ^{1}H NMR spectrum of **3k** in $CDCl_3$ (400 MHz).

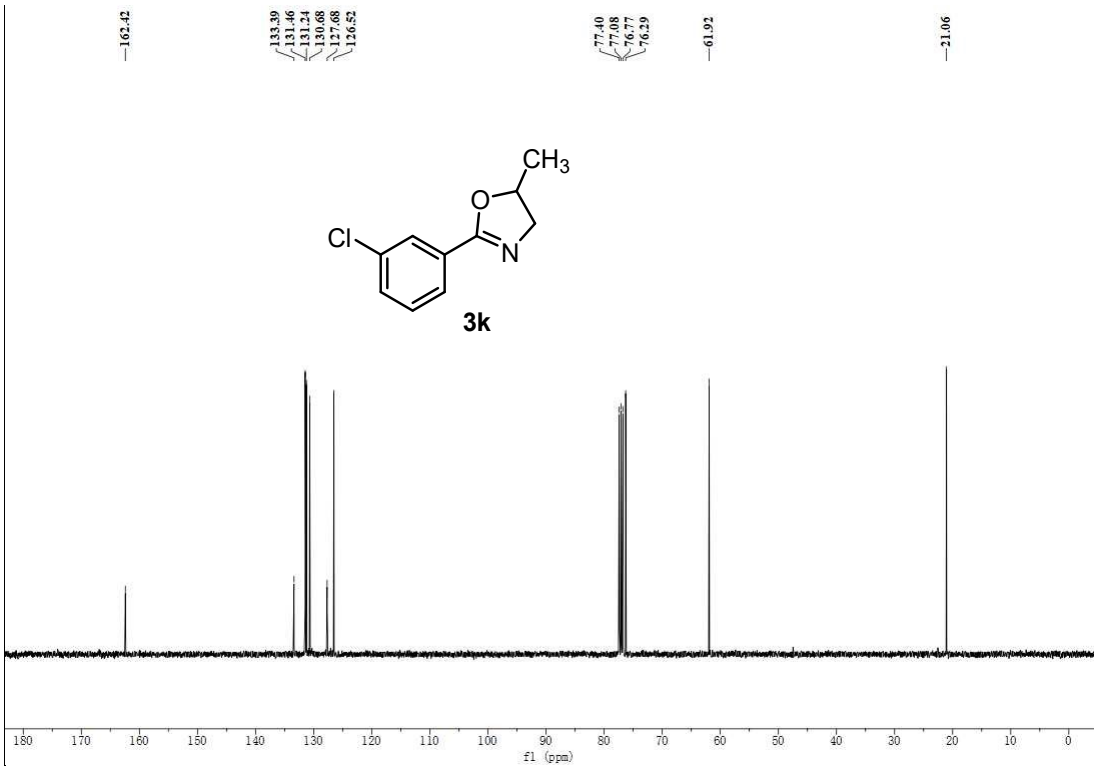


Figure S41. ^{13}C NMR spectrum of **3k** in $CDCl_3$ (100 MHz).

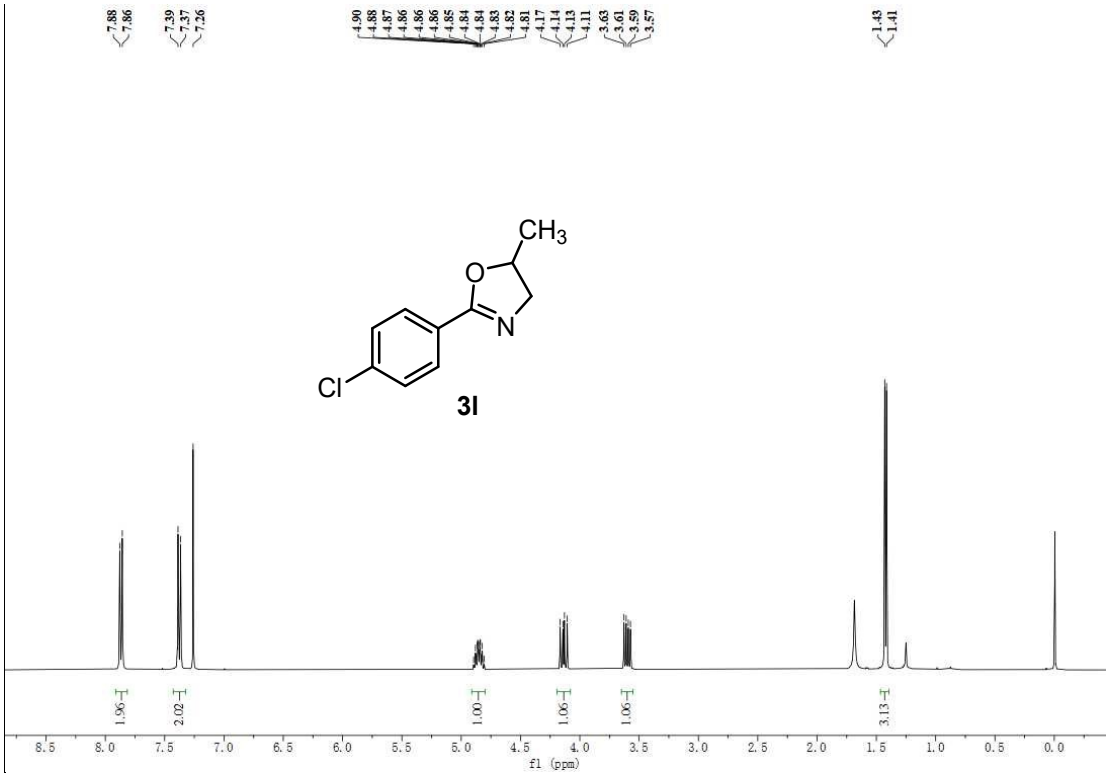


Figure S42. ^{1}H NMR spectrum of **3l** in $CDCl_3$ (400 MHz).

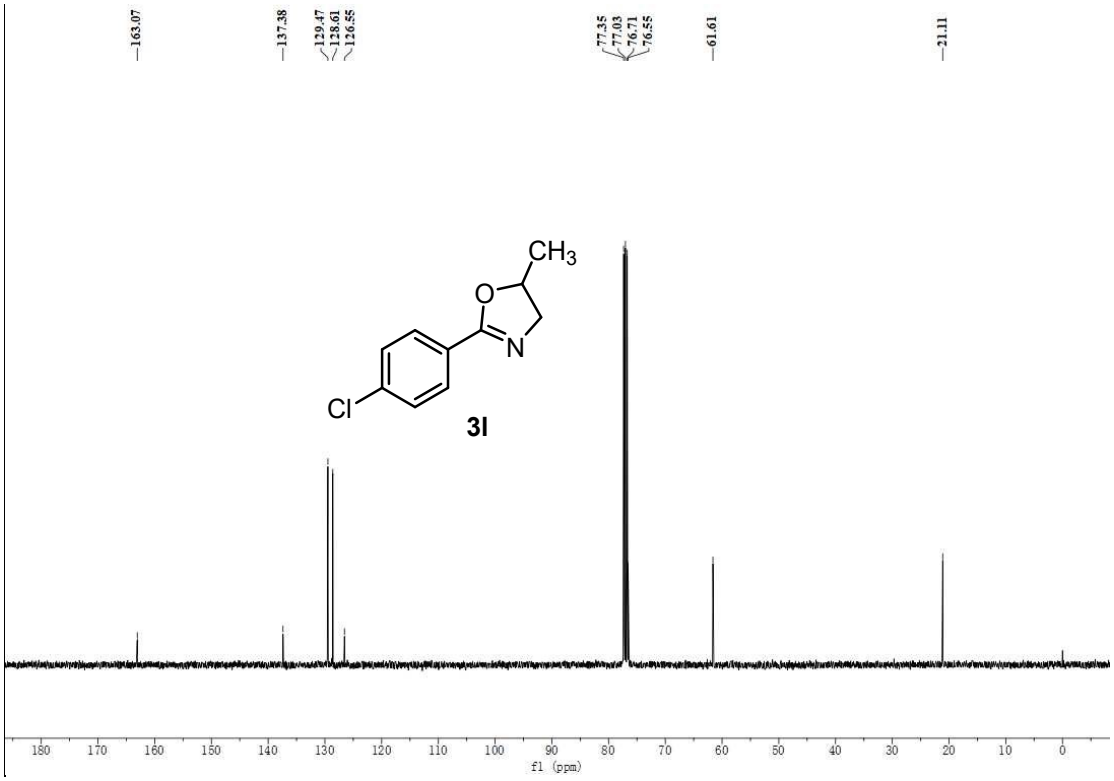


Figure S43. ^{13}C NMR spectrum of **3l** in $CDCl_3$ (100 MHz).

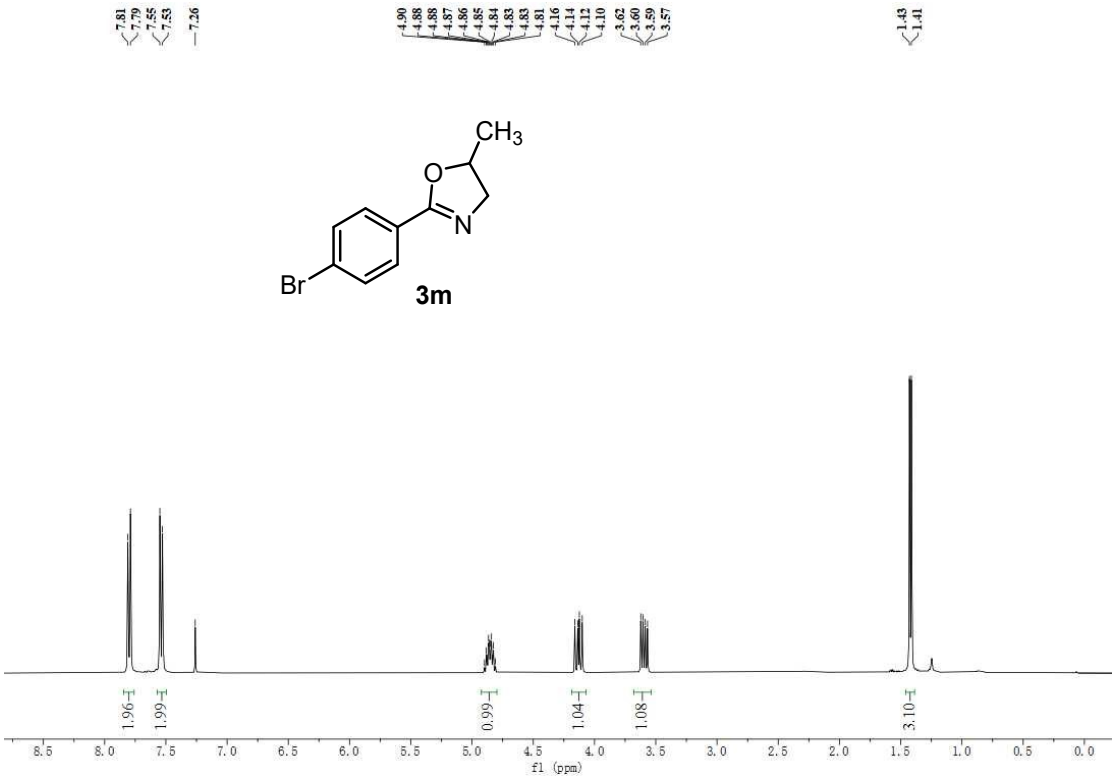


Figure S44. ^{1}H NMR spectrum of **3m** in $CDCl_3$ (400 MHz).

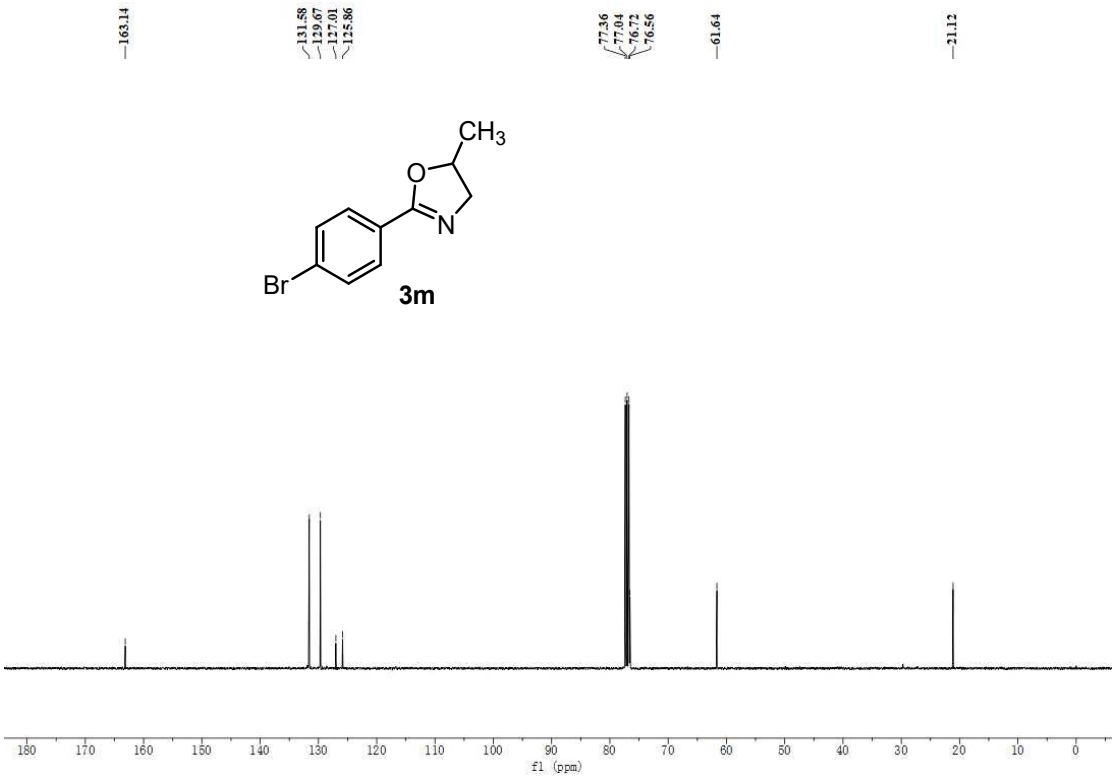


Figure S45. ^{13}C NMR spectrum of **3m** in $CDCl_3$ (100 MHz).

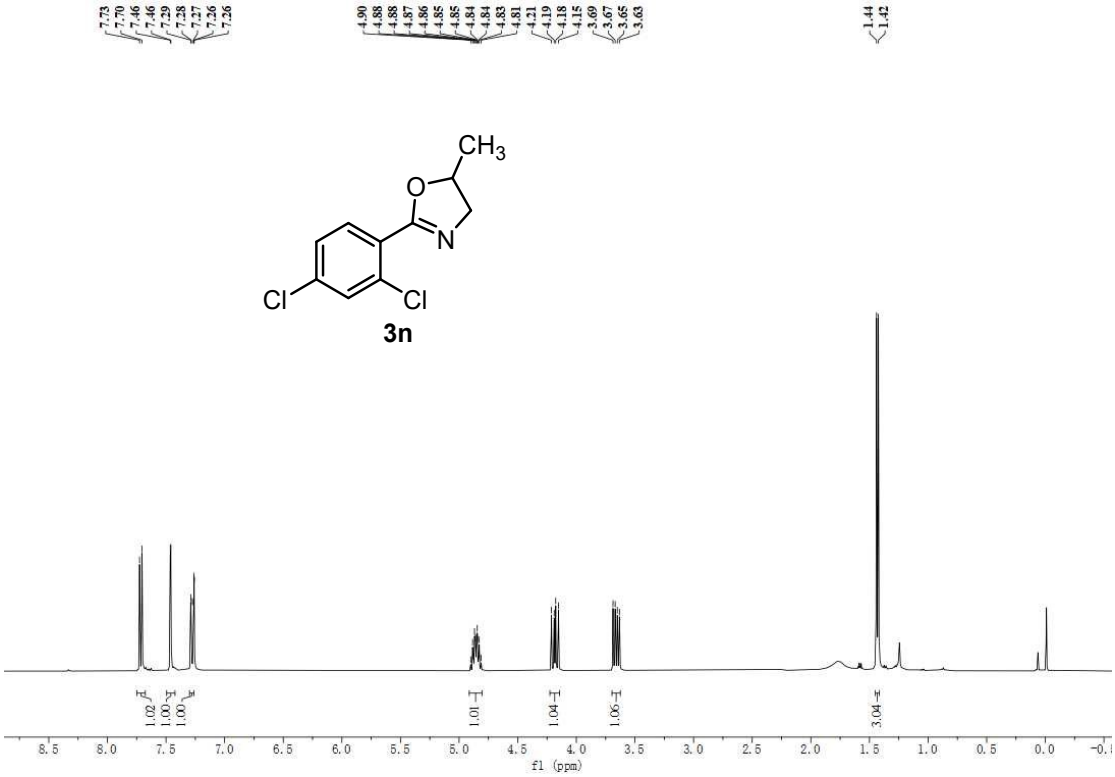


Figure S46. ^{1}H NMR spectrum of **3n** in $CDCl_3$ (400 MHz).

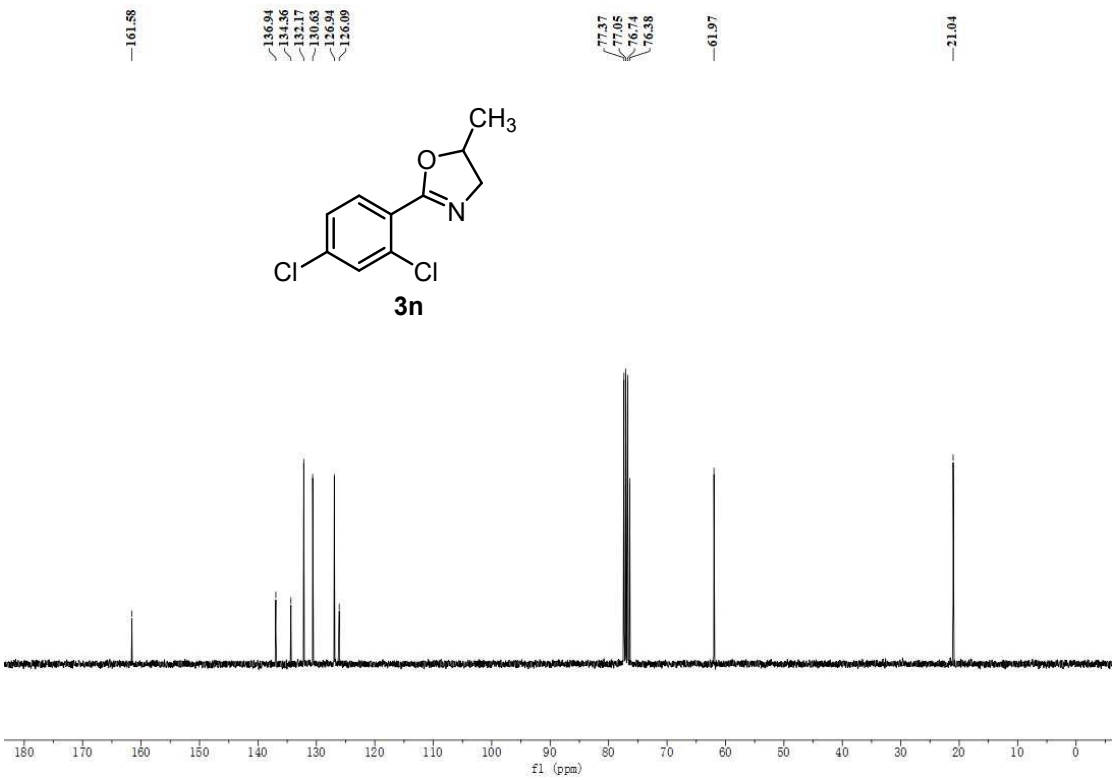


Figure S47. ^{13}C NMR spectrum of **3n** in $CDCl_3$ (100 MHz).

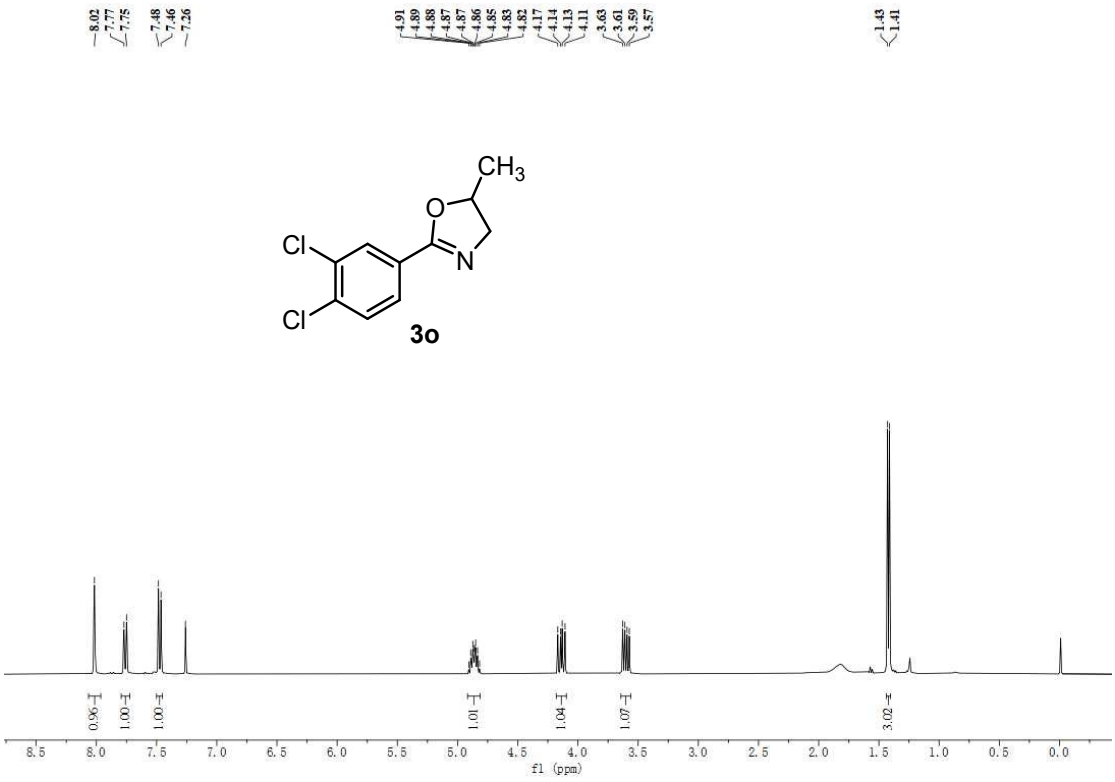


Figure S48. ^{1}H NMR spectrum of **3o** in $CDCl_3$ (400 MHz).

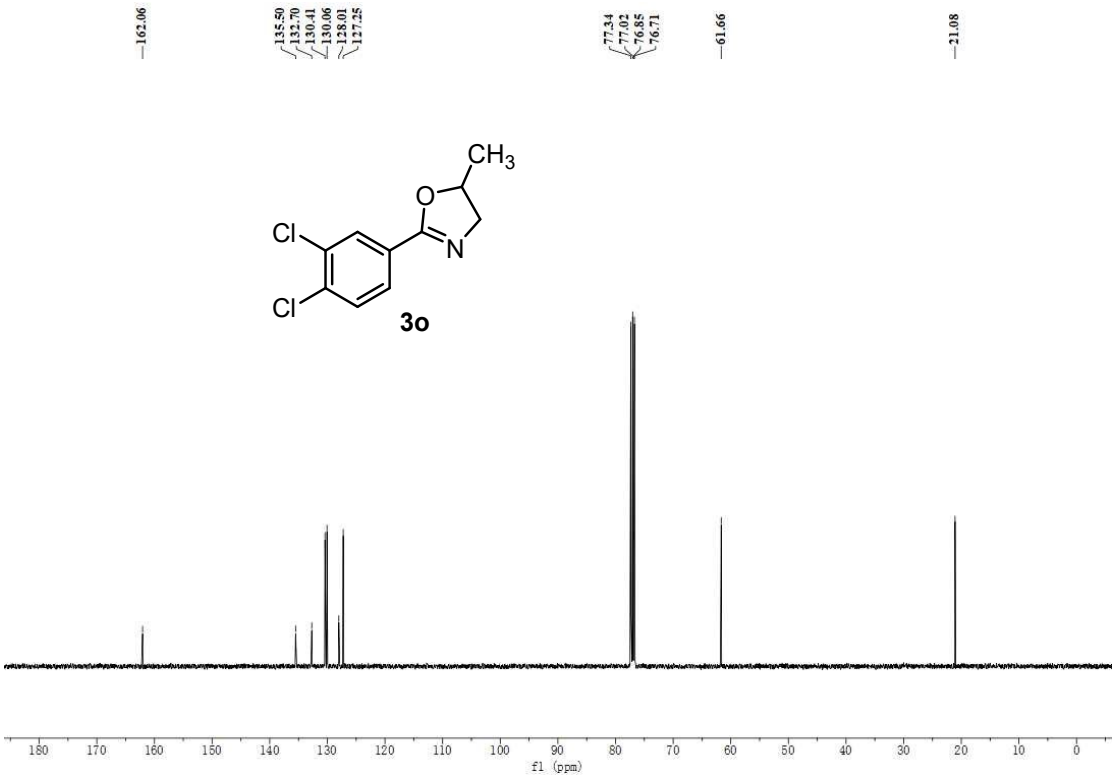


Figure S49. ^{13}C NMR spectrum of **3o** in $CDCl_3$ (100 MHz).

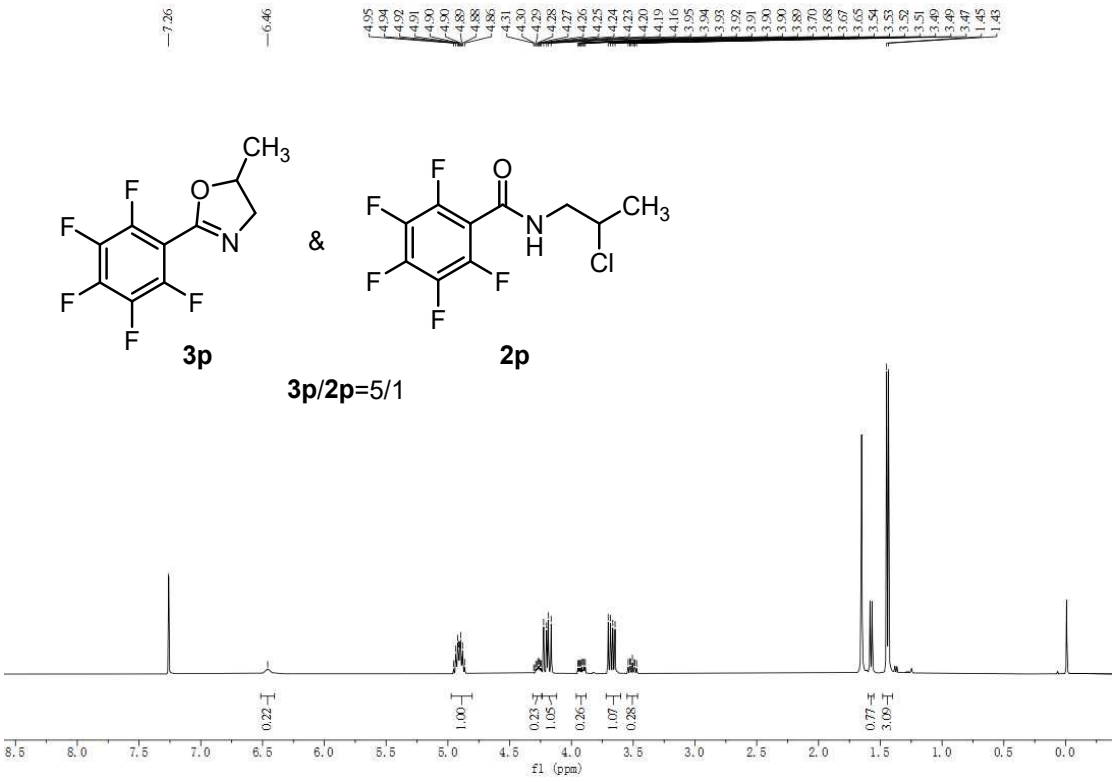


Figure S50. ^{1}H NMR spectrum of **3p** & **2p** in $CDCl_3$ (400 MHz).

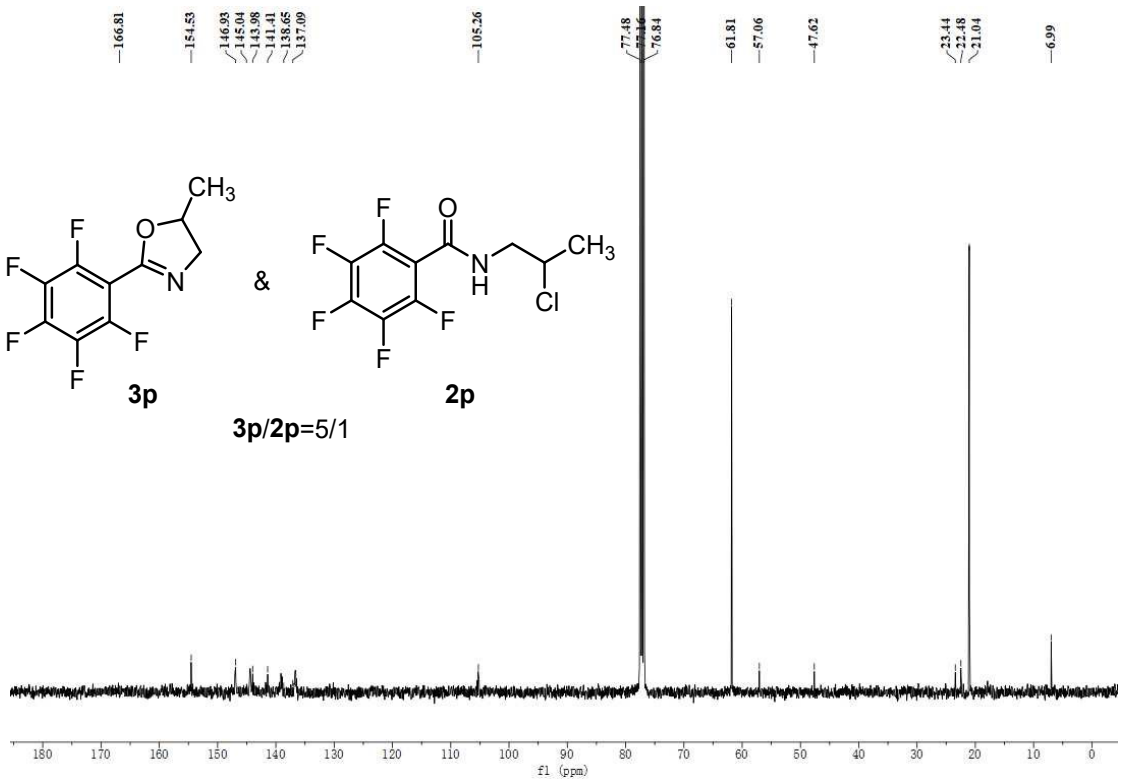


Figure S51. ^{13}C NMR spectrum of **3p** & **2p** in $CDCl_3$ (100 MHz).

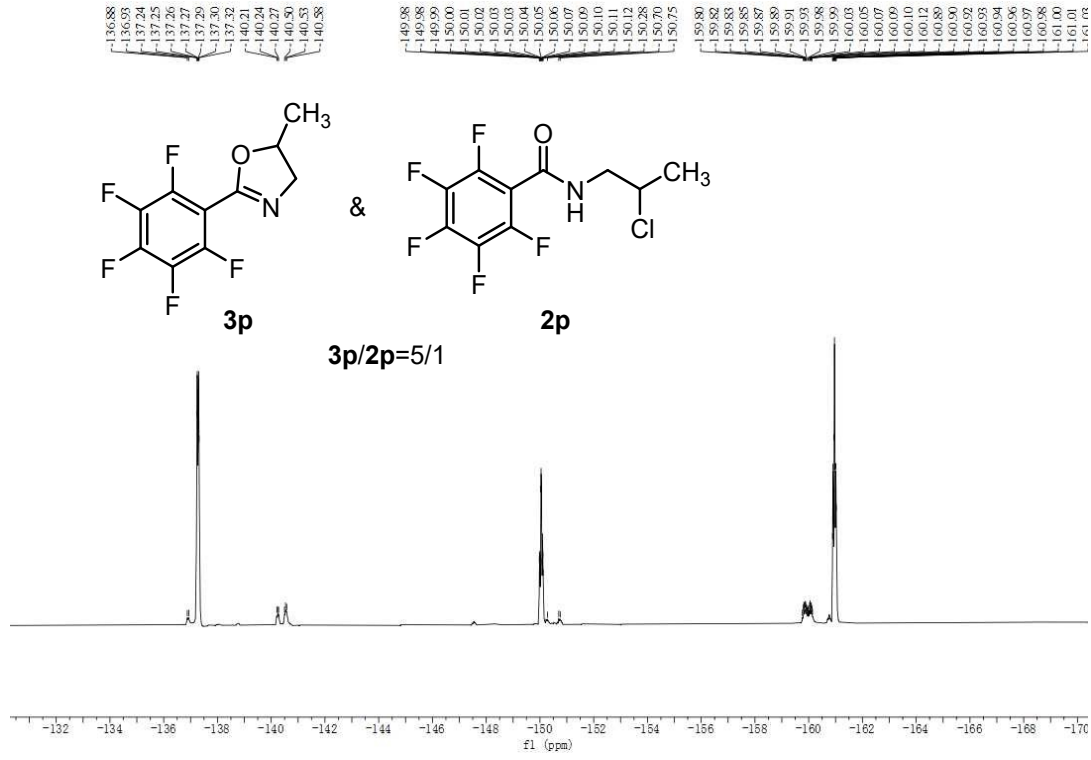


Figure S51. ^{19}F NMR spectrum of **3p** and **2p** in $CDCl_3$ (376 MHz).

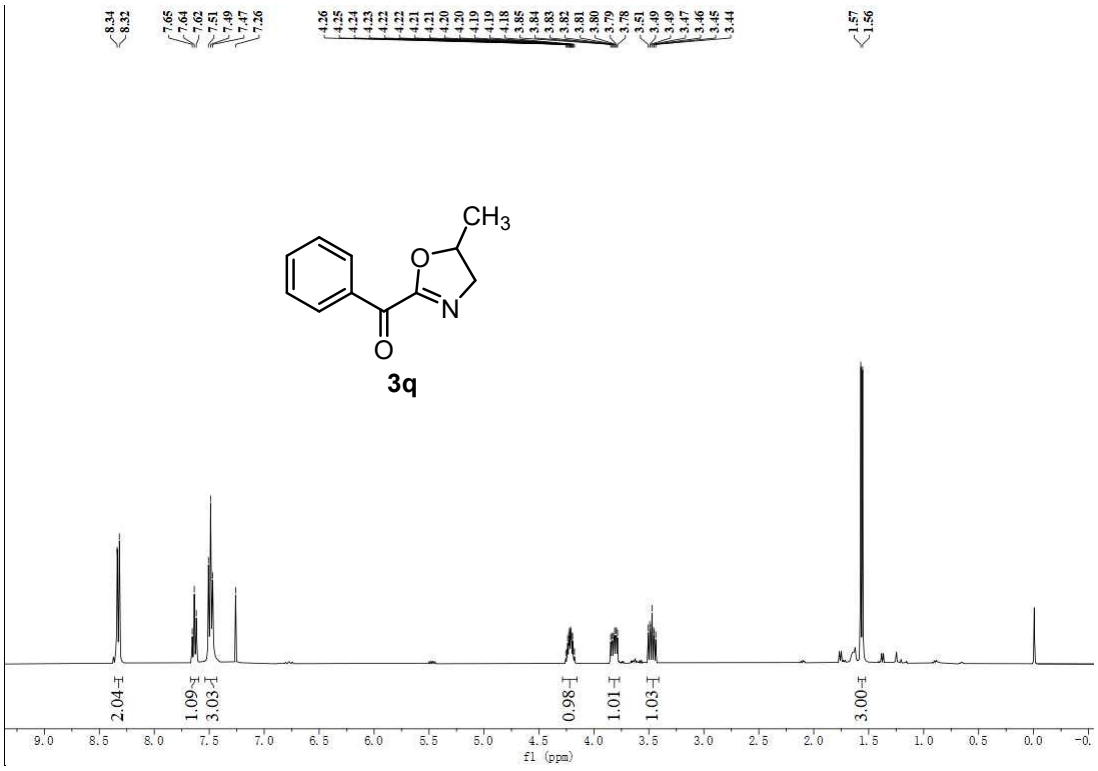


Figure S53. ^{1}H NMR spectrum of **3q** in $CDCl_3$ (400 MHz).

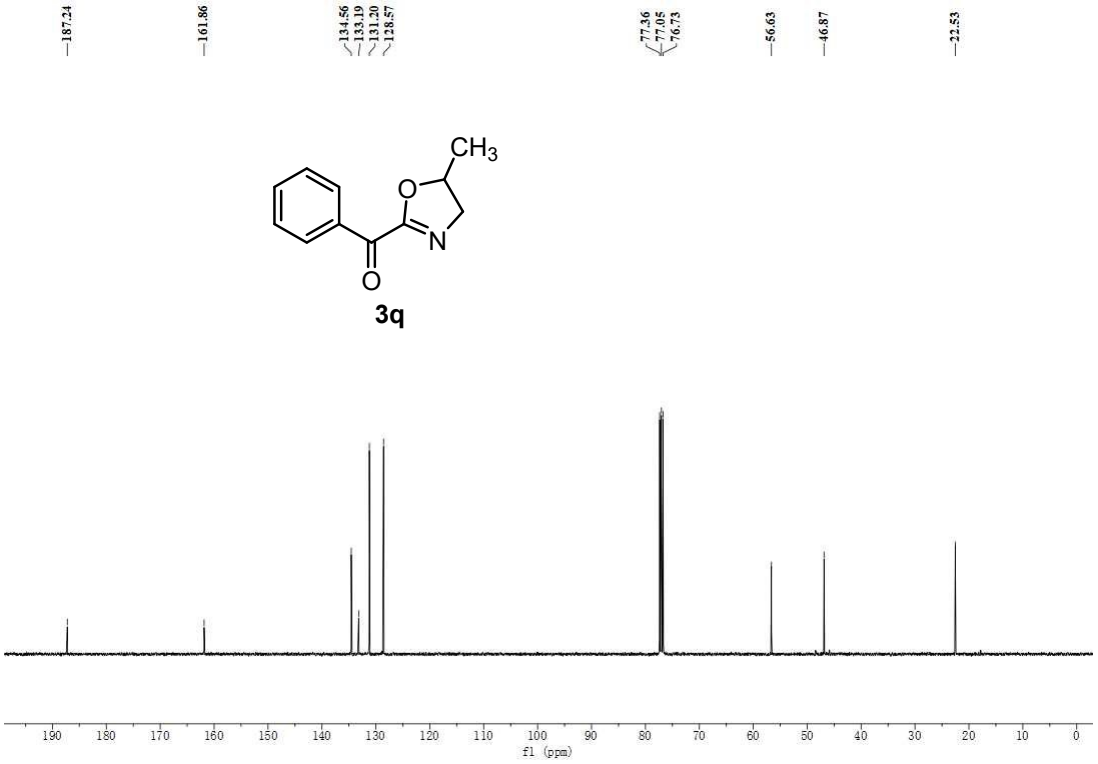


Figure S54. ^{13}C NMR spectrum of **3q** in $CDCl_3$ (100 MHz).

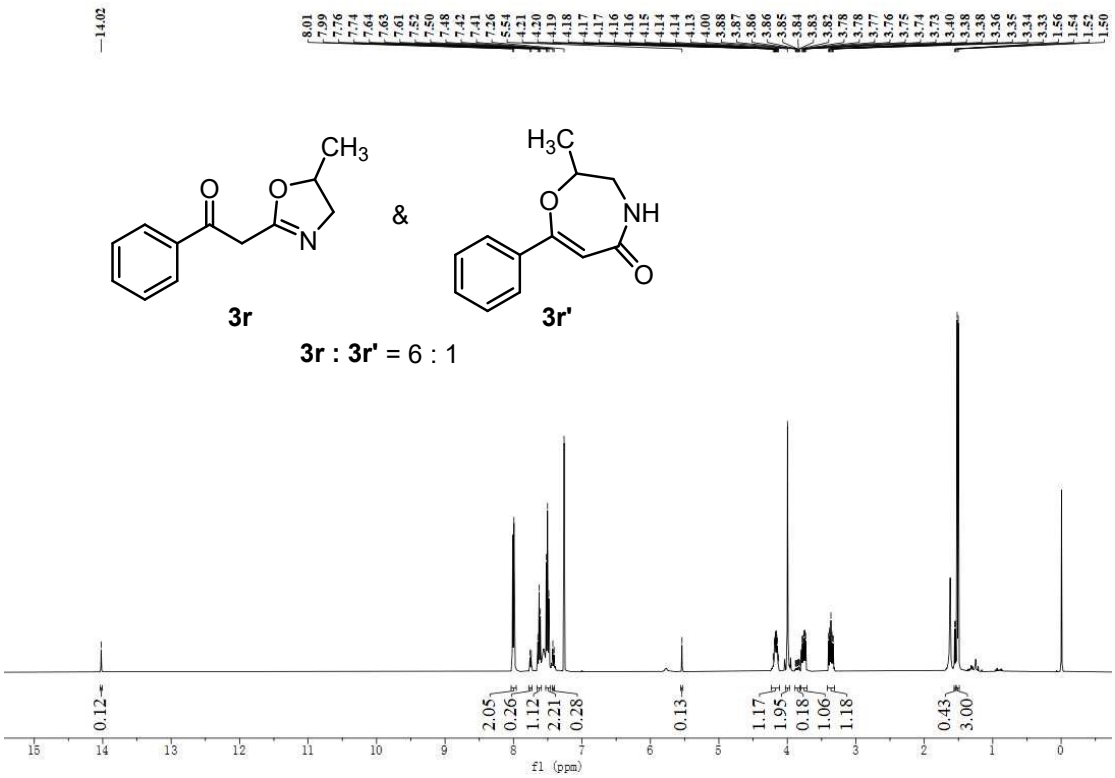


Figure S55. ^{1}H NMR spectrum of **3r** & **3r'** in $CDCl_3$ (400 MHz).

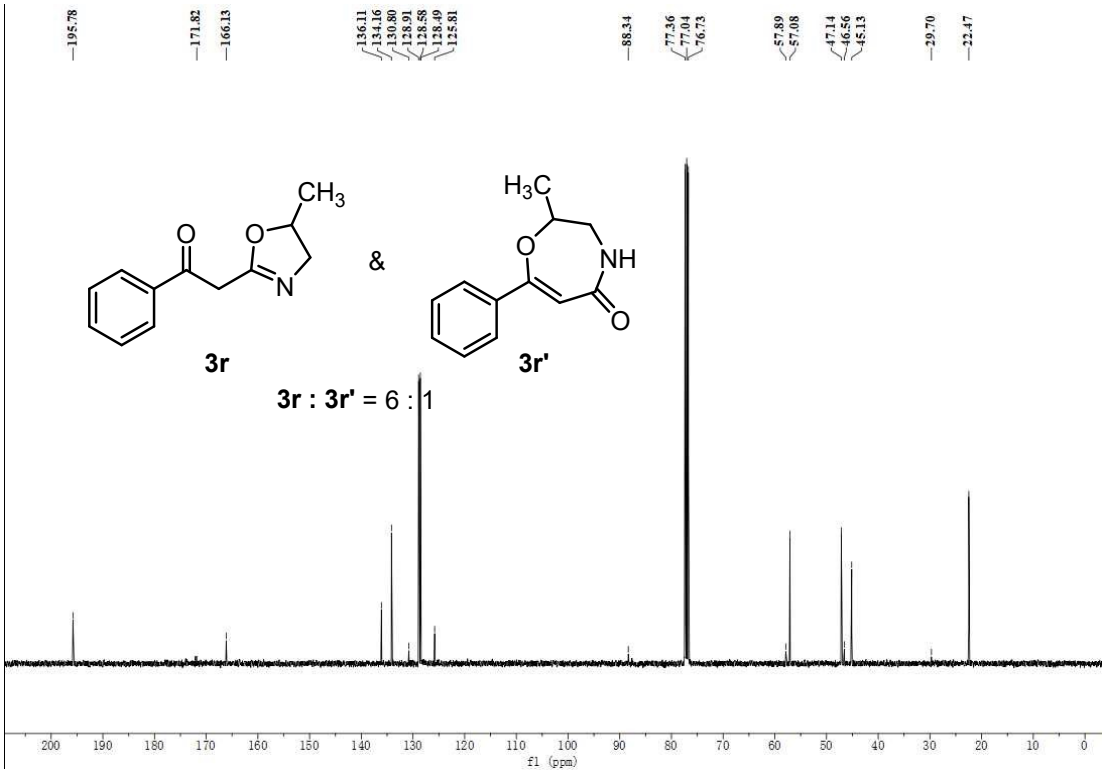


Figure S56. ^{13}C NMR spectrum of **3r** & **3r'** in $CDCl_3$ (100 MHz).

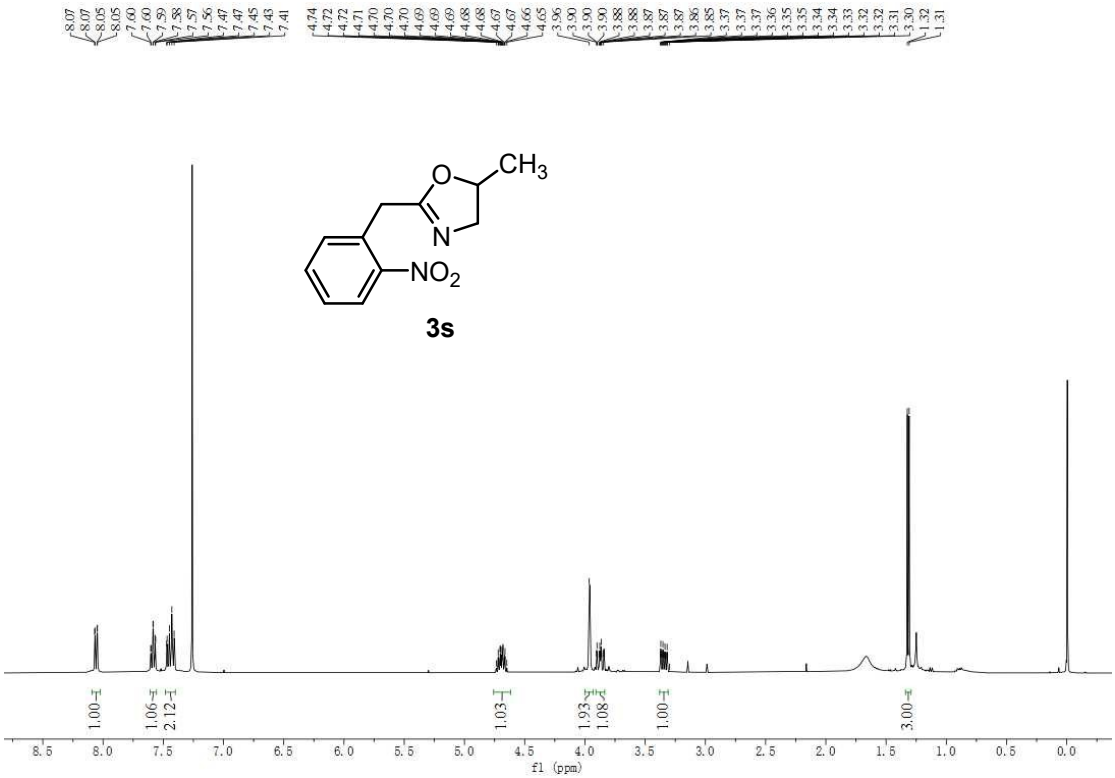


Figure S57. ^{1}H NMR spectrum of **3s** in $CDCl_3$ (400 MHz).

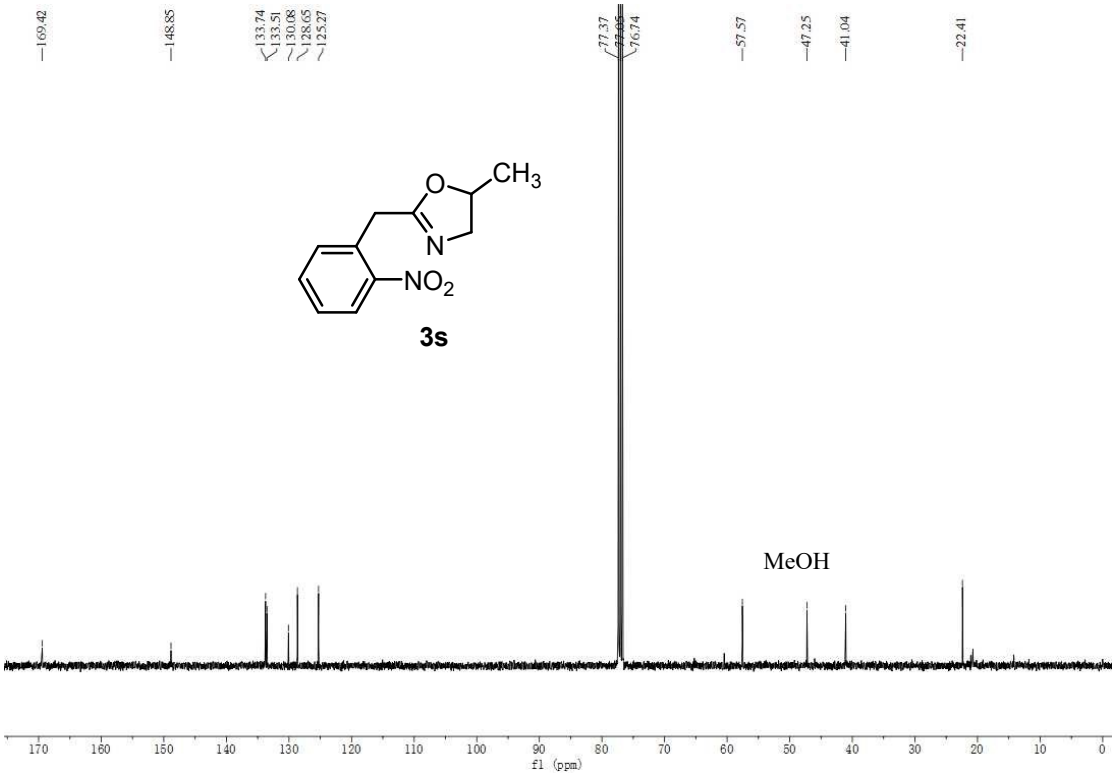


Figure S58. ^{13}C NMR spectrum of **3s** in $CDCl_3$ (100 MHz).

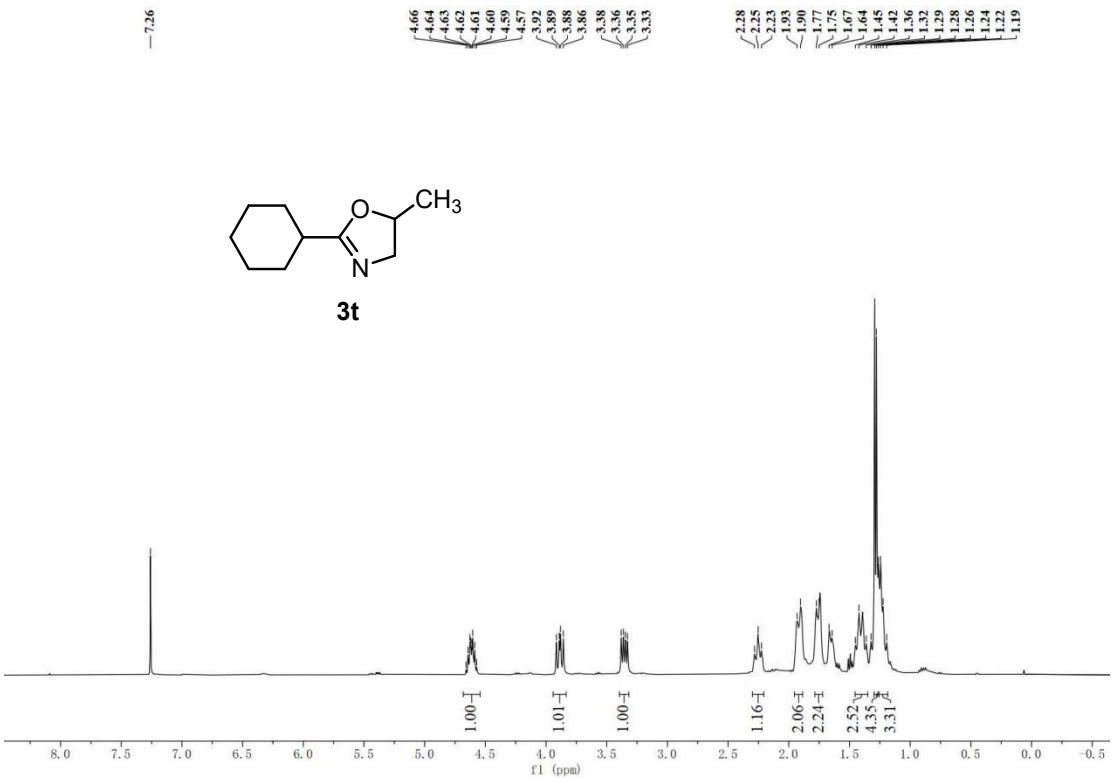


Figure S59. ^{1}H NMR spectrum of **3t** in $CDCl_3$ (400 MHz).

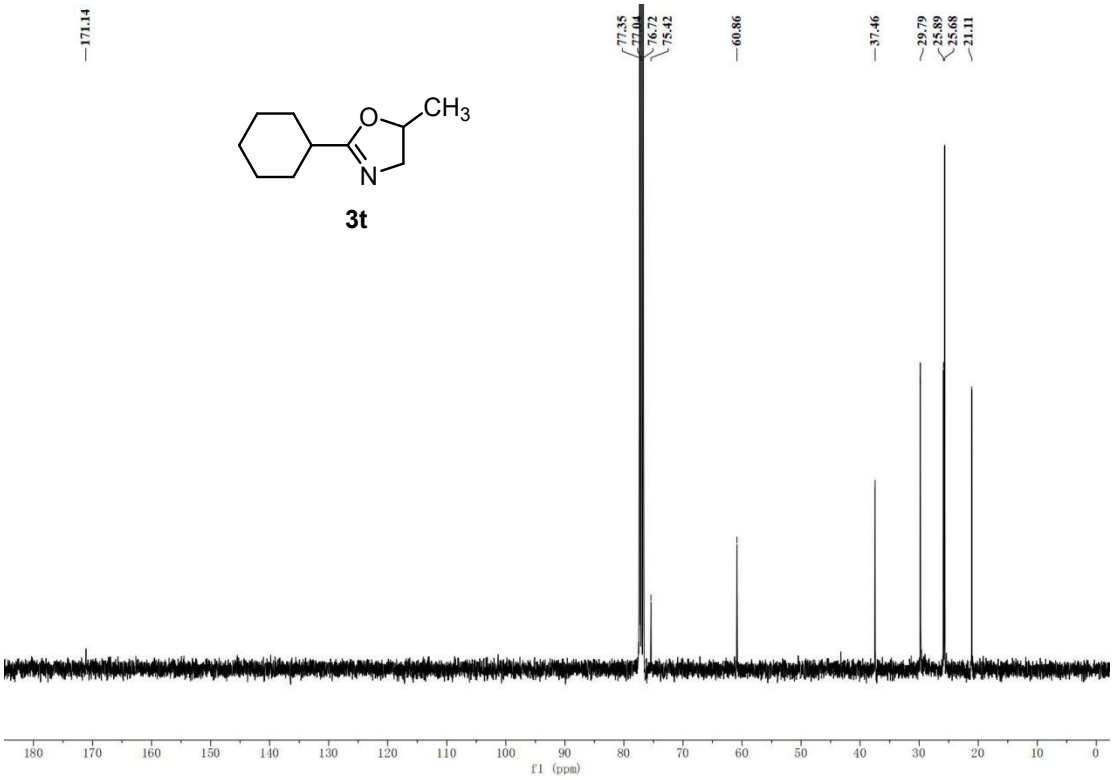


Figure S60. ^{13}C NMR spectrum of **3t** in $CDCl_3$ (100 MHz).

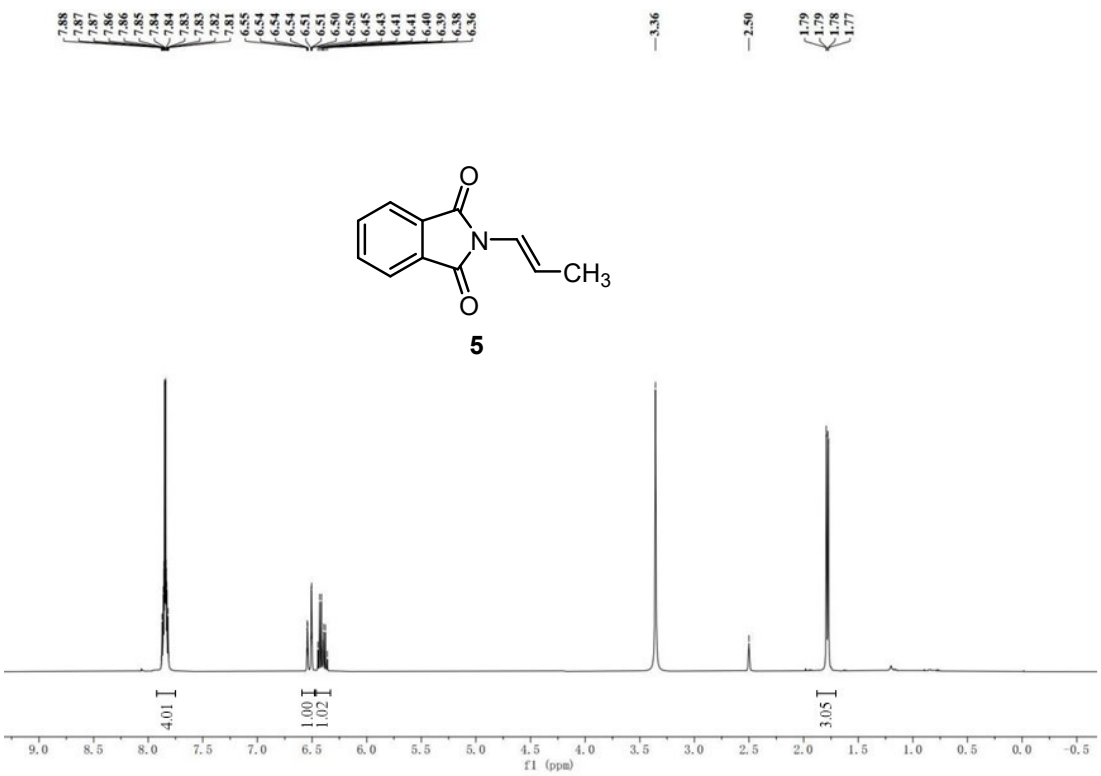


Figure S61. ^{1}H NMR spectrum of **5** in DMSO-d_6 (400 MHz).

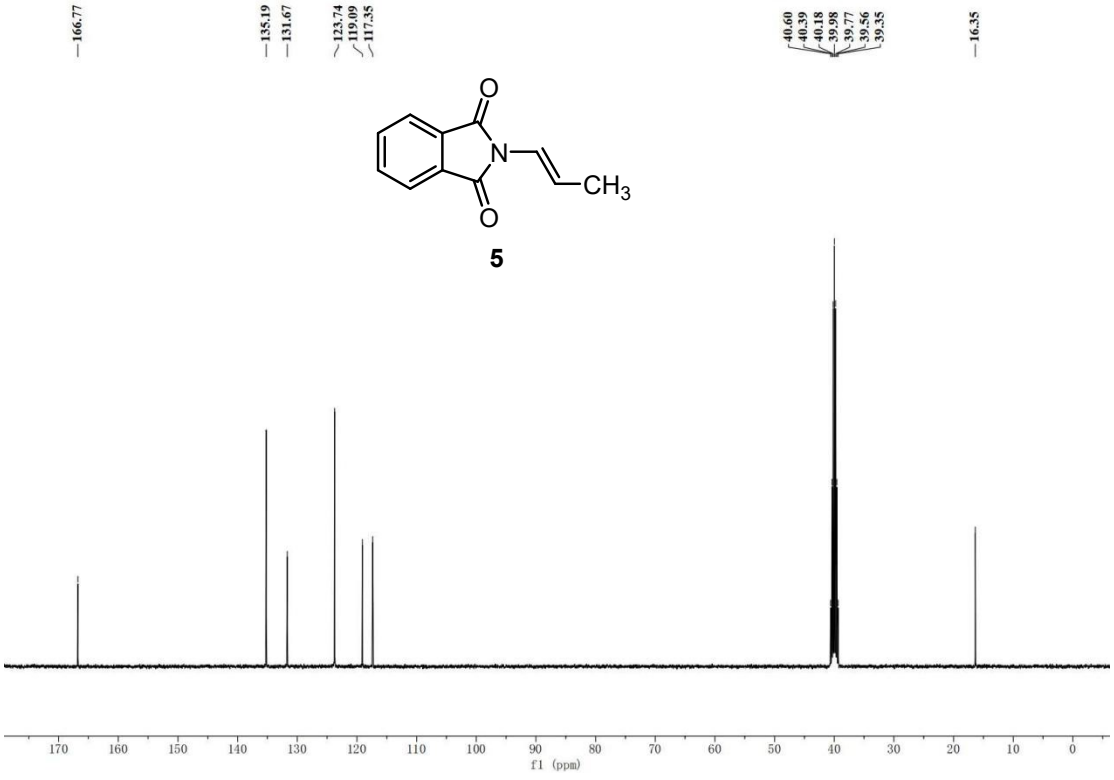


Figure S62. ^{13}C NMR spectrum of **5** in DMSO-d_6 (100 MHz).

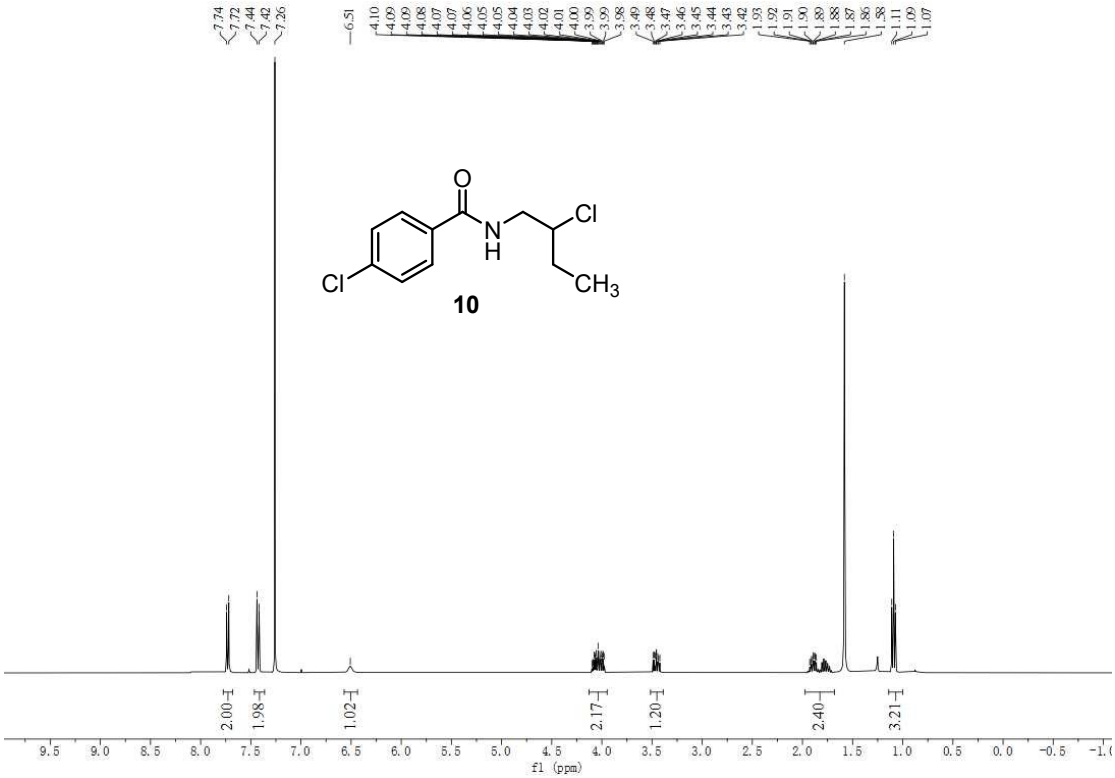


Figure S63. ^{1}H NMR spectrum of **10** in $CDCl_3$ (400 MHz).

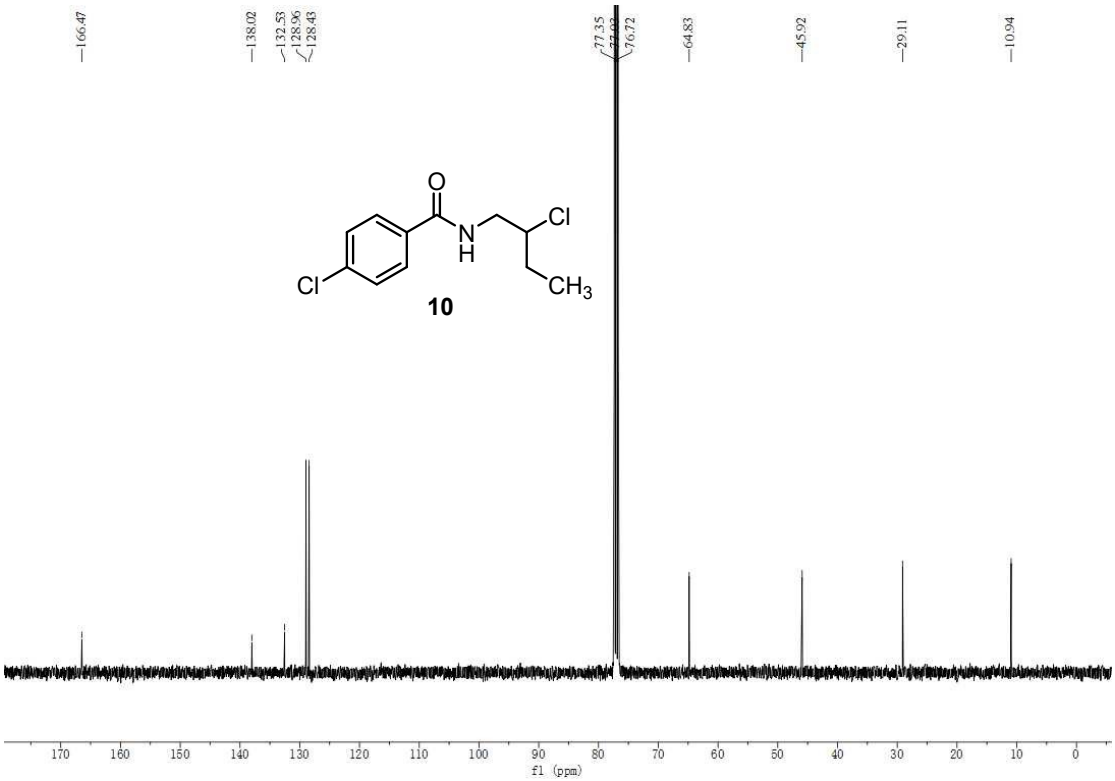


Figure S64. ^{13}C NMR spectrum of **10** in $CDCl_3$ (100 MHz).

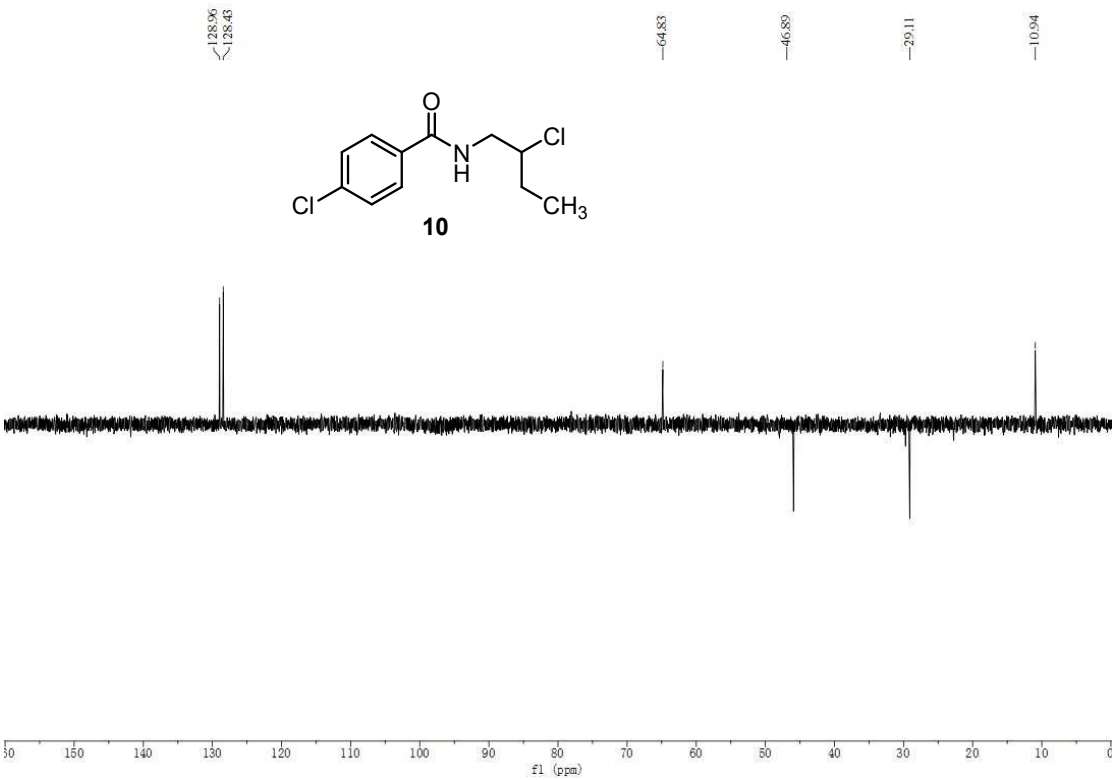


Figure S65. DEPT135 spectrum of **10** in $CDCl_3$ (100 MHz).

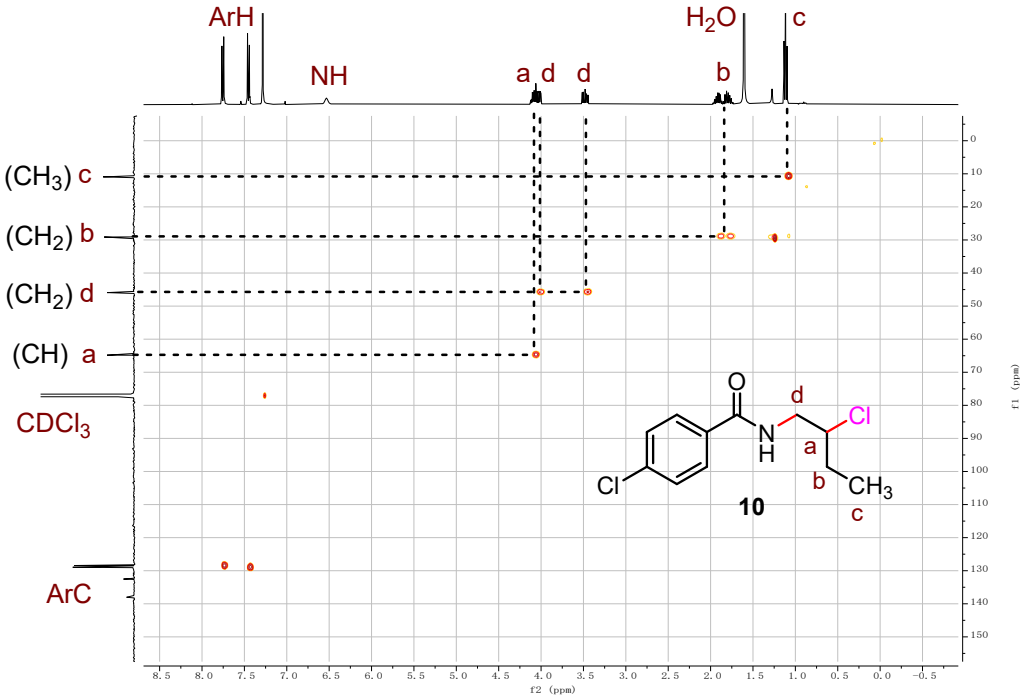


Figure S66. HMQC spectrum of **10** in $CDCl_3$ (400 MHz).

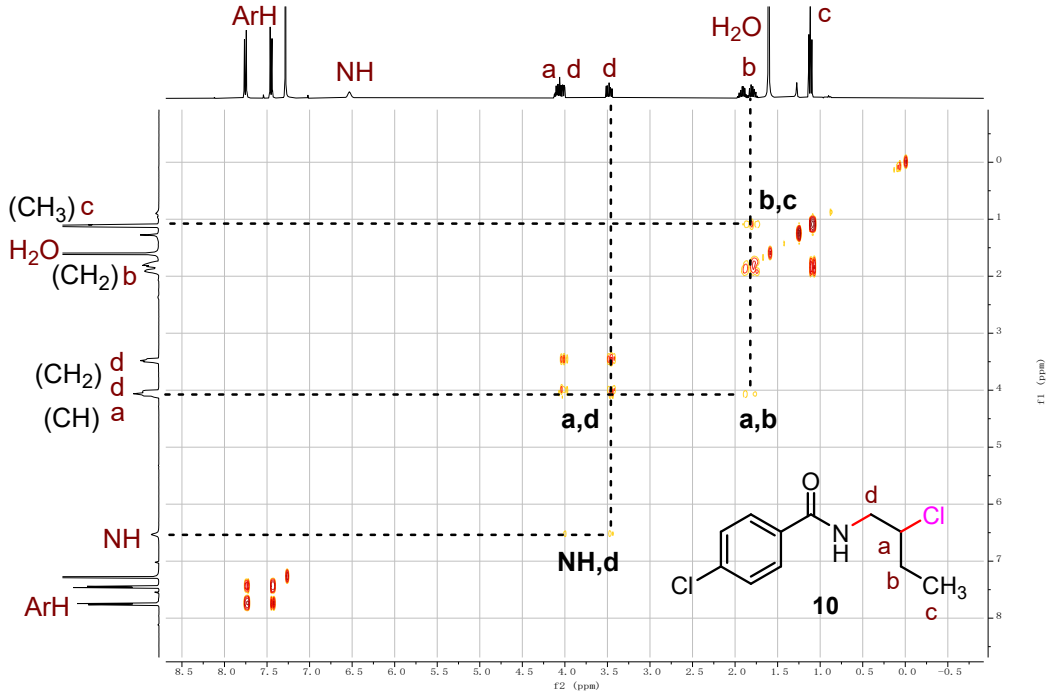


Figure S67. ^{1}H-^{1}H COSY spectrum of **10** in $CDCl_3$ (400 MHz).

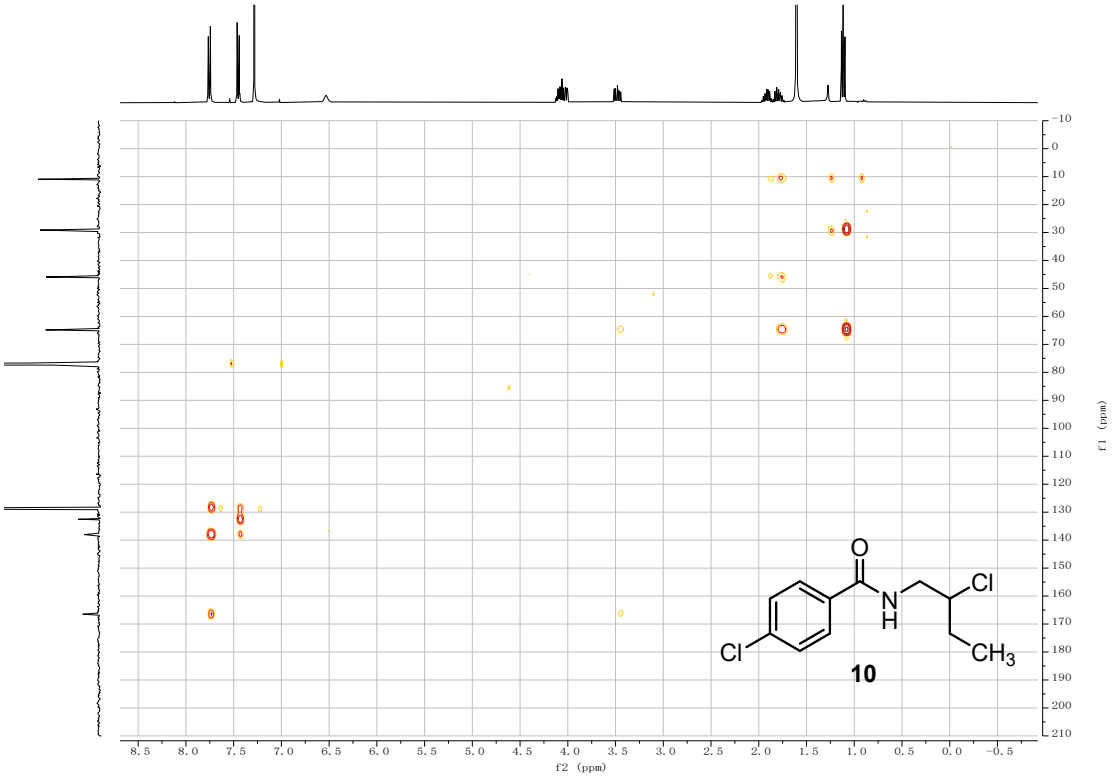


Figure S68. HMBC spectrum of **10** in $CDCl_3$ (400 MHz).

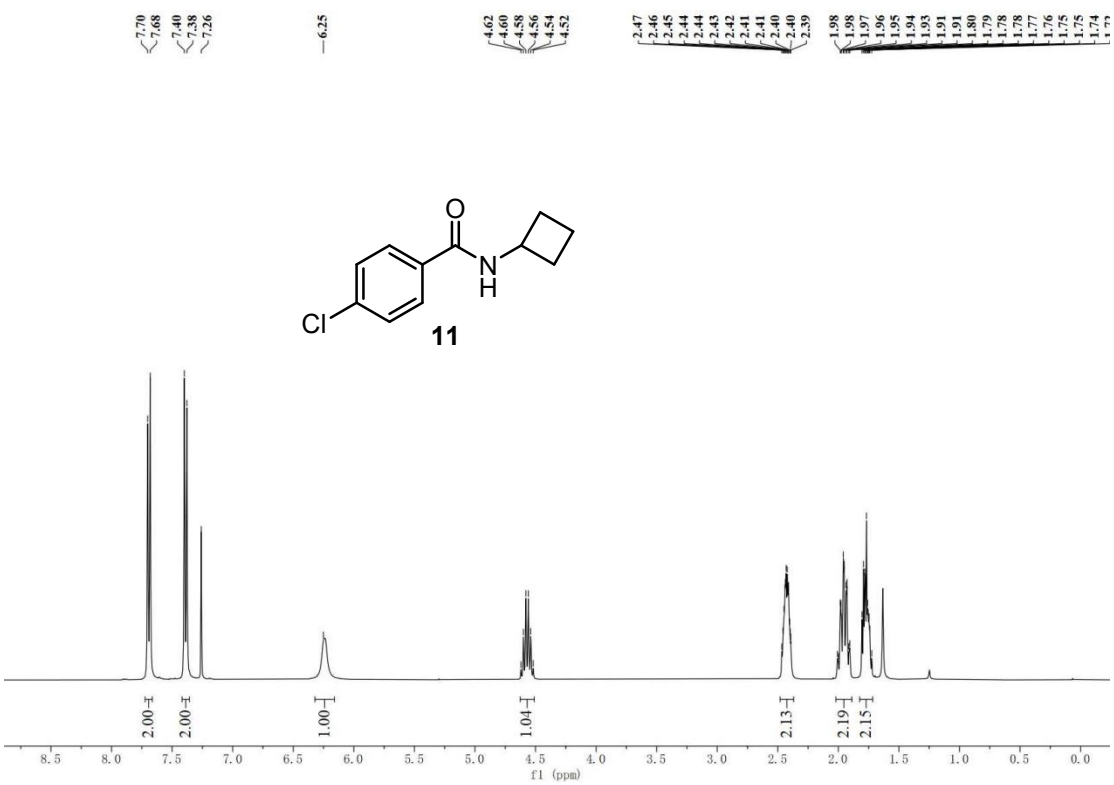


Figure S69. ^{1}H NMR spectrum of **11** in $CDCl_3$ (400 MHz).

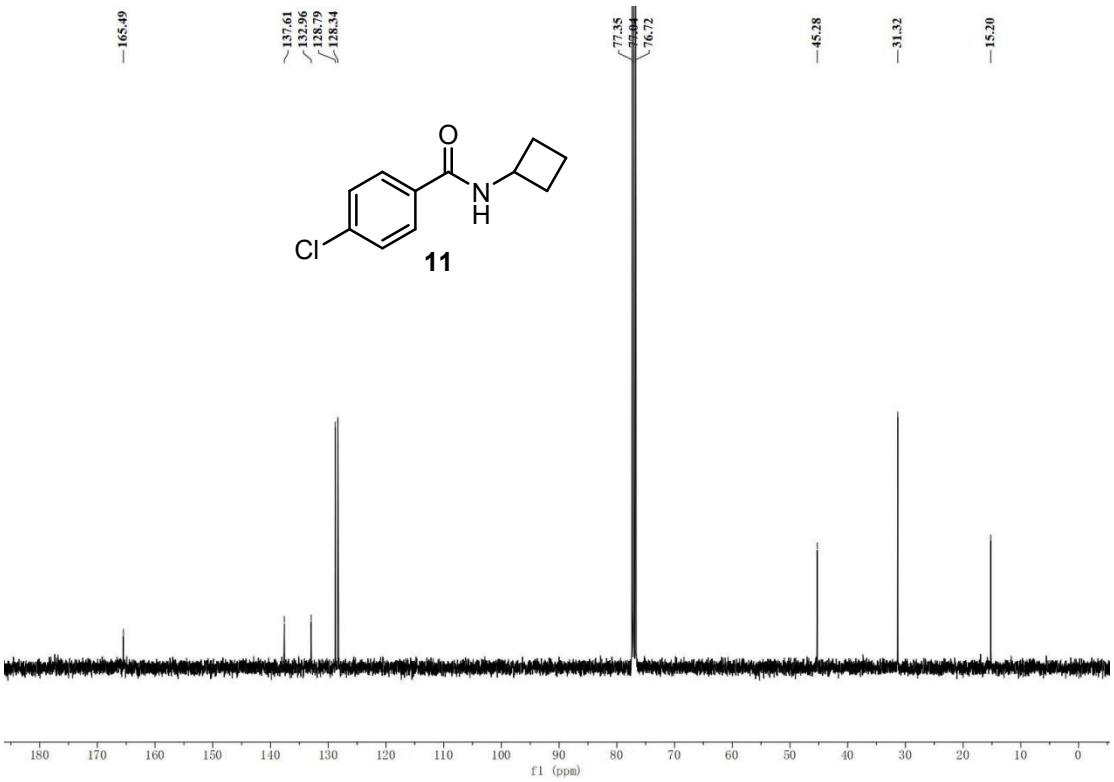


Figure S70. ^{13}C NMR spectrum of **11** in $CDCl_3$ (100 MHz).

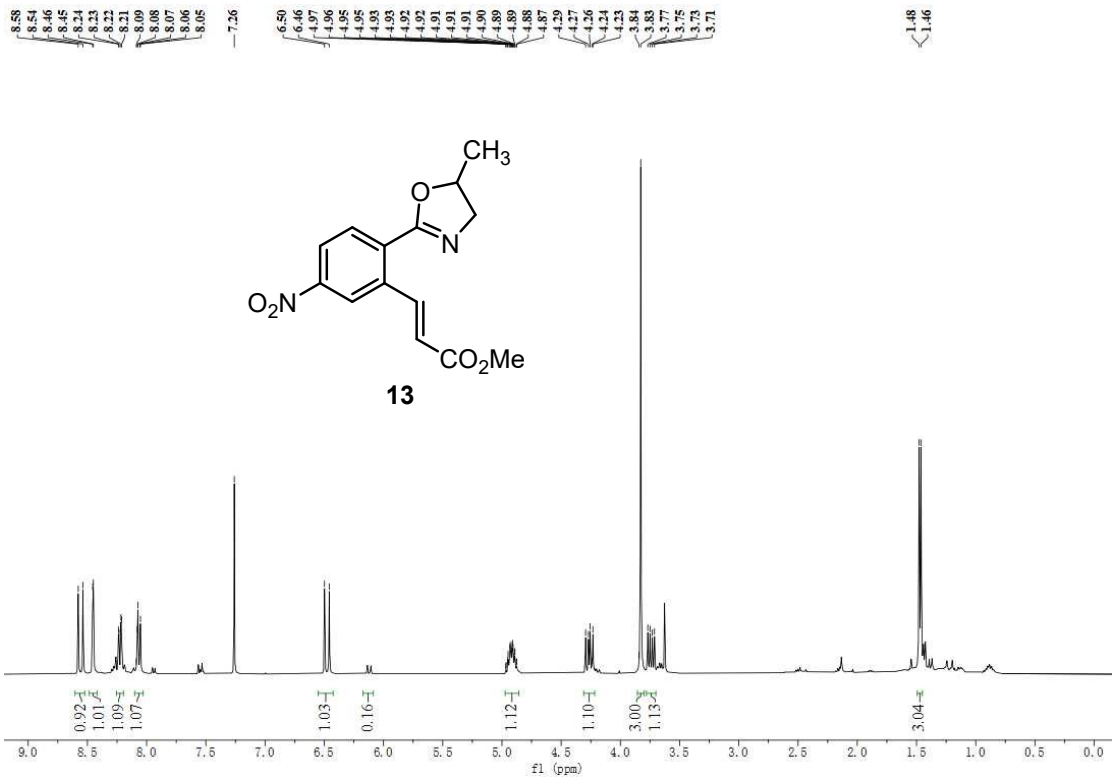


Figure S71. ^{1}H NMR spectrum of **13** in $CDCl_3$ (400 MHz).

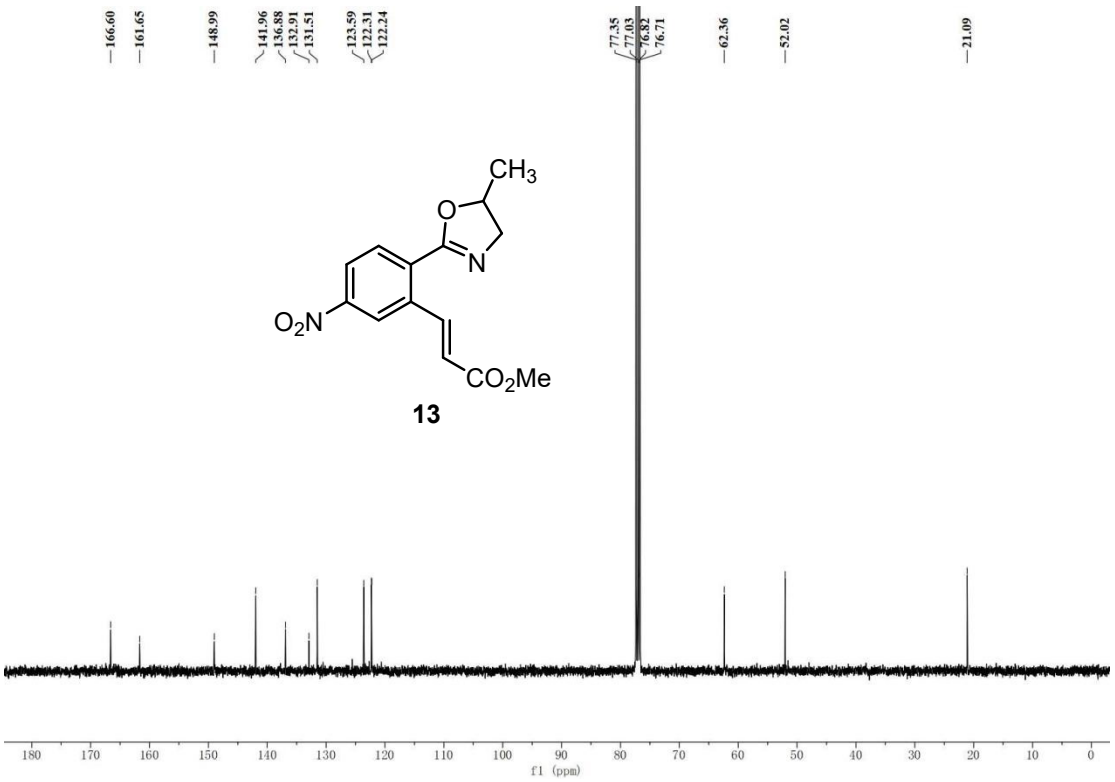


Figure S72. ^{13}C NMR spectrum of **13** in $CDCl_3$ (100 MHz).

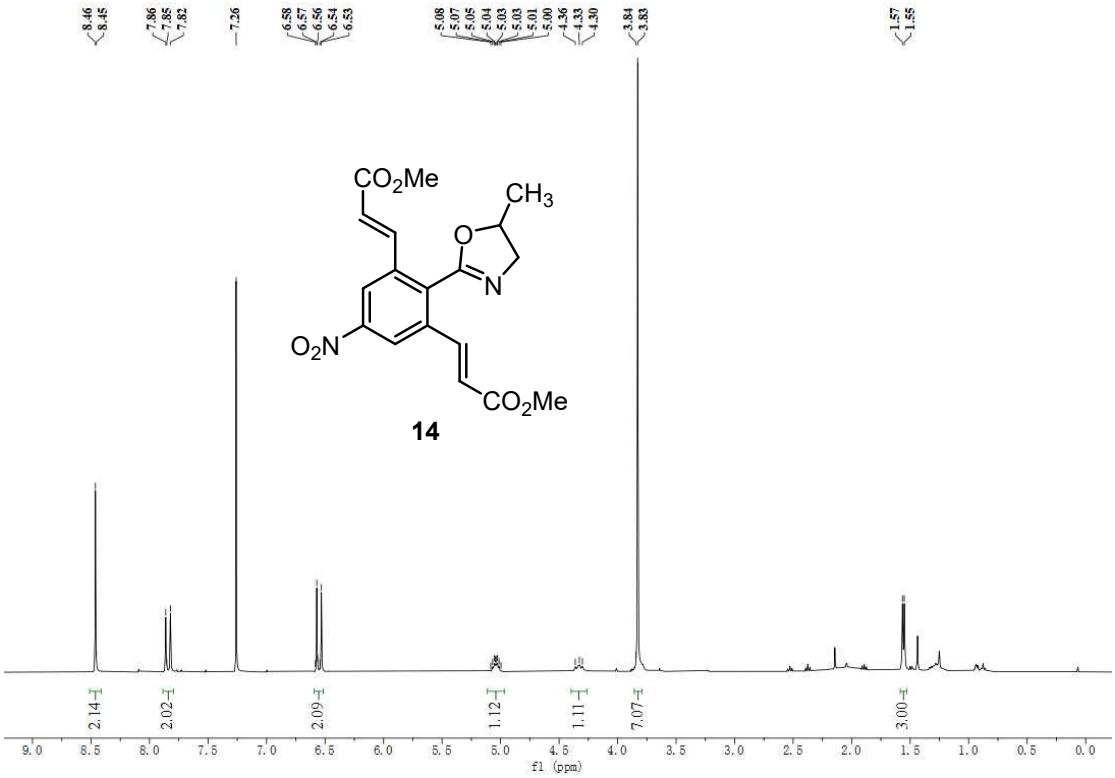


Figure S73. ^{1}H NMR spectrum of **14** in $CDCl_3$ (400 MHz).

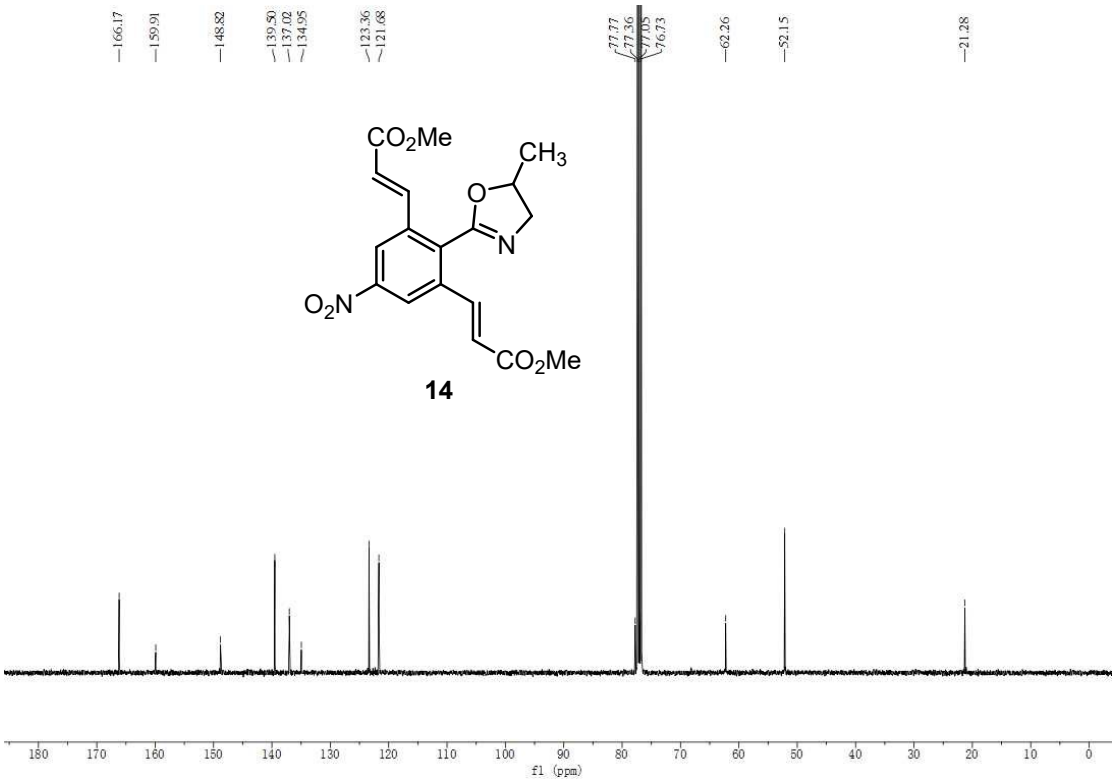


Figure S74. ^{13}C NMR spectrum of **14** in $CDCl_3$ (100 MHz).

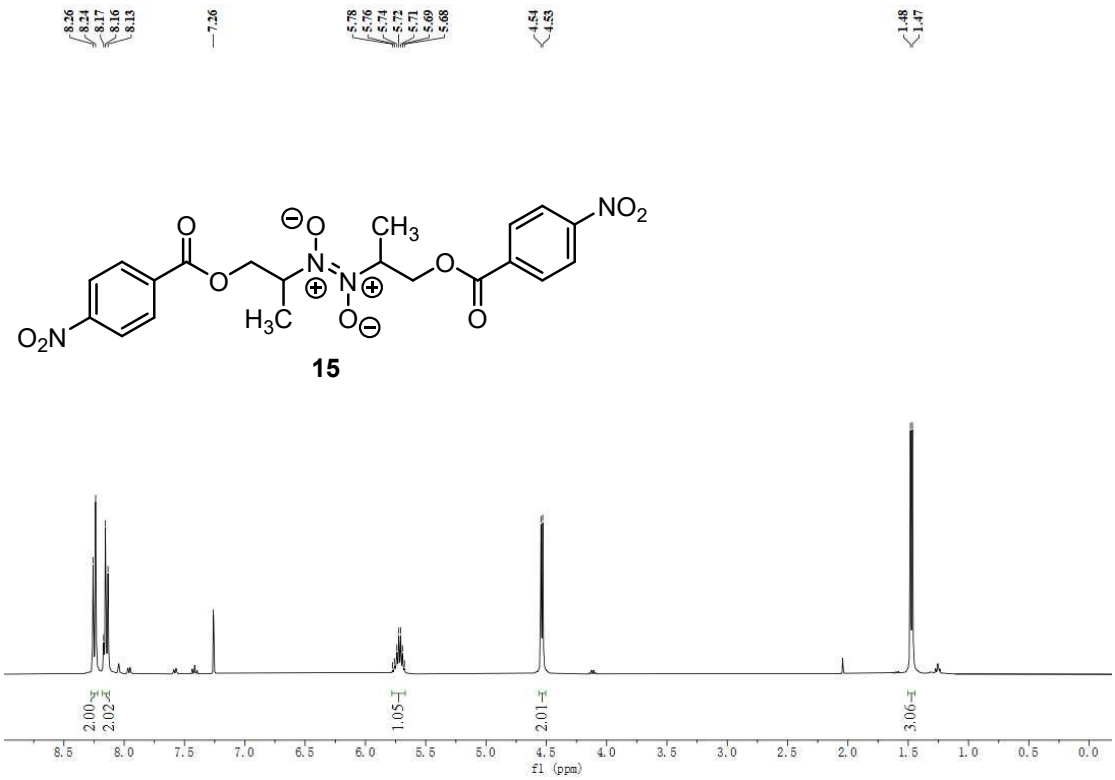


Figure S75. ^{1}H NMR spectrum of **15** in $CDCl_3$ (400 MHz).

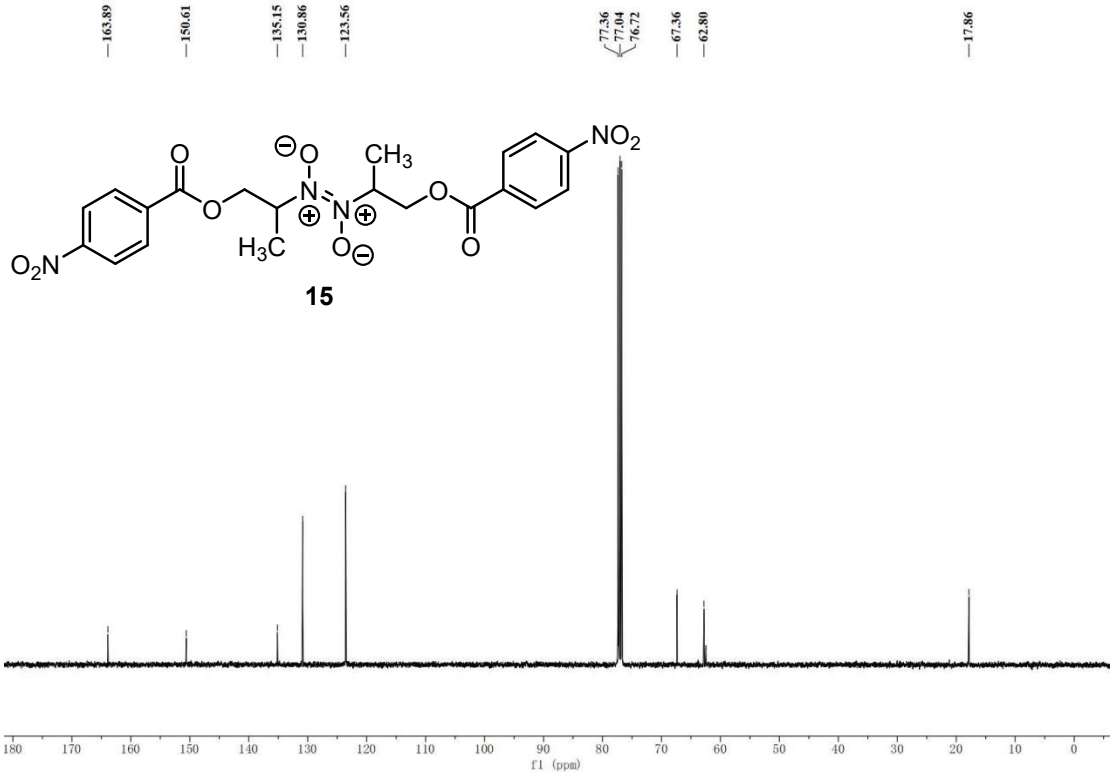


Figure S76. ^{13}C NMR spectrum of **15** in $CDCl_3$ (100 MHz).