Supporting Information

Palladium-Catalyzed Carboxylative Cyclization of Propargylic Amine with Aryl Iodides, CO_2 and CO at Ambient Pressure

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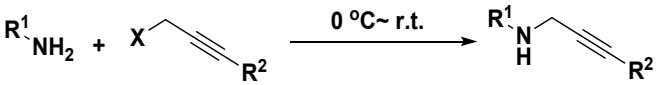
1. General Information

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under a carbon dioxide and carbon monoxide atmosphere. All reagents were purchased from Aldrich, Macklin, DB, Across, Alfa Aesar, Heowns and TCI without further purification.

NMR spectra were recorded on ^{1}H NMR, 400 MHz, ^{13}C NMR, 101 MHz, spectrometer in $CDCl_3$ at ambient temperature and chemical shifts are expressed in parts per million (δ, ppm). Proton chemical shifts are referenced to 7.26 ppm ($CDCl_3$) and carbon chemical shifts are referenced to 77.0 ppm ($CDCl_3$). Data reporting uses the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; hept, heptet, and J, coupling constant in Hz. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry equipped with Z-spray ionization source. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. X-ray single crystal diffraction was detected with Rigaku 007 Saturn 70. The moles of CO_2 and CO in the balloon were analyzed by gas chromatography (GC, FuLi 9790II) with a TCD detector and capillary column to determine.

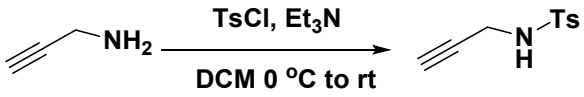
2. Synthesis and Characterization of Substrates

General Procedure for the Synthesis of Propargylamines (1a-1l, 5a-5i)[1]



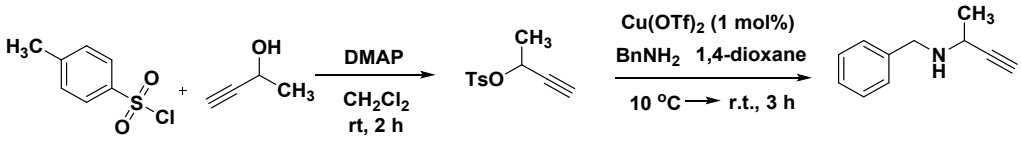
For the preparation of propargyl amines, the propargyl halide (1 equiv.) was added dropwise to the correspondding amine (6 equiv.) at 0 °C. Upon complete addition, the reaction was allowed to warm to room temperature and stirred for 16 h. Then, aqueous 1 M NaOH (4 mL/mmol) and EtOAc (4 mL/mmol) were added and the layers were separated. After extraction of the aqueous layer with EtOAc (2 x 4 mL/mmol), the combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography (silica gel, Petrolether/EtOAc).

Procedure for the Synthesis of 1m [2]



Prop-2-yn-1-amine (1.3 mL, 21 mmol) was dissolved in DCM (50 mL) and the solution was cooled to 0 °C. To this solution triethylamine (7 mL, 50 mmol) and p-toluenesulfonyl chloride (3.8 g, 20 mmol) were added sequentially. Then the mixture was allowed to warm to room temperature and stirred overnight. After that, the reaction mixture was dissolved in Et_2O (200 mL), first washed with a solution of HCl (1M) and then with a satured solution of NH_4Cl. The organic layer was dried over Na_2SO_4, filtered and the solvent was evaporated, leading to 4-methyl-N-(prop-2-yn-1-yl) benzene-1-sulfonamide as a white powder.

Procedure for the Synthesis of 1n [3,4]

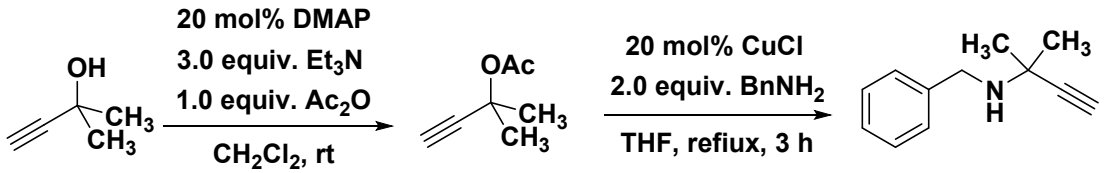


To a solution of 4-Dimethylaminopyridine (DMAP) (37 mg, 0.3 mmol) in CH_2Cl_2 (3 mL), aqueous 3-butyn-2-ol (7.5 M, 1.5 mL, 11.3 mmol), aqueous NaOH (25%, 2 mL) and tosyl chloride (1.90 g, 10 mmol) were successively added at 0 °C, and then the mixture was stirred at rt for 2 h. After addition of H_2O (30 mL), the reaction mixture was extracted with CH_2Cl_2 (30 mL×3). Combined organic layer was washed with H_2O (50 mL×3) and then dried over anhydrous $MgSO_4$. Evaporation of

the solvent gave the corresponding 3-butyn-2-yl tosylate (1.97 g, 88%), which was used for next step without further purification.

A solution of Cu $(OTf)_2$ (0.0794 mmol) in 6.0 mL of 1,4-dioxane was cooled to 10 °C and treated with 1.2 mL of benzylamine (11 mmol). After 15 min, a solution of the tosyl alcohol (5 mmol) in 1,4-dioxane (6.0 mL) was slowly added. The reaction mixture was warmed to room temperature, stirred for 3 h, and extracted with 1 N HCl. The aqueous layer was neutralized with NaOH and then extracted with EtOAc. The organic extracts were dried (Na_2SO_4) and concentrated. The resulting greenish oil was purified by column chromatography on SiO_2 (hexanes/EtOAc 8:2) to afford the desired secondary amine as a yellow oil.

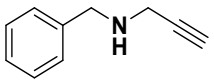
Procedure for the Synthesis of 1o [5]



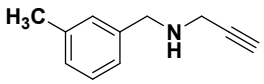
To the solution of DMAP (20 mol%, 4 mmol) and 2-methyl-3-butyn-2-ol (1.0 equiv., 20 mmol) in CH_2Cl_2 (40 mL), Et_3N (3.0 equiv., 60 mmol) and Ac_2O (1.0 equiv., 20 mmol) were added, and the mixture was stirred at room temperature for 12 h. Upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, eluent: $CHCl_3$) to give 2-methylbut-3-yn-2-yl acetate as a colorless oil.

N-benzyl-2-methylbut-3-yn-2-amine was synthesized according to the procedure of the literature. To the solution of CuCl (20 mol%, 2 mmol) in THF (20 mL), propargyl acetate (1.0 eq., 10 mmol) and benzylamine (2.0 eq., 20 mmol) were added, and the mixture was refluxed for 3 h. After cooling to room temperature, the mixture was diluted with EtOAc and acidified with 2 N HCl. The aqueous layer was then neutralized with 1 N NaOH and extracted three times with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (SiO_2, eluent: EtOAc/ petroleum ether) to give *N*-benzyl-2-methylbut-3-yn-2- amine as a colorless solid.

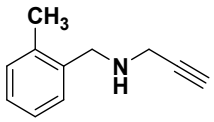
The characterization data of substrates are in good agreement with literature value [1,2,3,4,5,6,7,8,9,10].



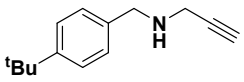
N-benzylprop-2-yn-1-amine (1a), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.24 (m, 5H), 3.87 (s, 2H), 3.41 (s, 2H), 2.25 (s, 1H), 1.49 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$): 139.4, 128.4, 127.1, 82.0, 71.5, 52.2, 37.3.



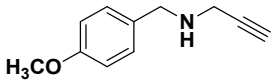
N-(3-methylbenzyl) prop-2-yn-1-amine (1b), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.05 (m, 4H), 3.84 (s, 2H), 3.43 (d, *J* = 2.4 Hz, 2H), 2.34 (s, 3H), 2.26 (t, *J* = 2.4 Hz, 1H), 1.60 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): 139.3, 138.1, 129.1, 128.3, 127.9, 125.4, 82.1, 71.5, 52.3, 37.3, 21.3.



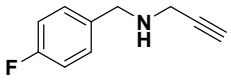
N-(2-methylbenzyl) prop-2-yn-1-amine (1c), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 51.7, 3.3 Hz, 4H), 3.86 (s, 2H), 3.45 (d, J = 2.5 Hz, 2H), 2.37 (s, 3H), 2.26 (t, J = 2.5 Hz, 1H), 1.53 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 137.3, 136.6, 130.1, 128.7, 127.2, 82.2, 71.5, 49.9, 37.6, 18.9.



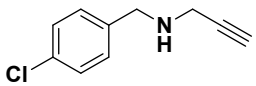
N-(4-(tert-butyl) benzyl) prop-2-yn-1-amine (1d), yellow solid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 4H), 3.85 (s, 2H), 3.43 (s, 2H), 2.26 (s, 1H), 1.80 (s, 1H), 1.29 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 150.1, 136.2, 128.1, 125.3, 82.0, 71.5, 51.8, 37.3, 34.4, 31.4, 31.3.



N-(4-methoxybenzyl) prop-2-yn-1-amine (1e), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d,*J* = 8.1, 2H), 6.86 (d, *J* = 8.3, 2.0 Hz, 2H), 3.81 (d, *J* = 8.9 Hz, 5H), 3.40 (s, 2H), 2.26 (t, 1H), 1.49 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 158.7, 131.4, 129.5, 113.78, 82.0, 71.4, 55.2, 51.5, 37.1.

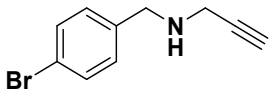


N-(4-fluorobenzyl) prop-2-yn-1-amine (1f), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 3.85 (s, 2H), 3.41 (d, *J* = 2.4 Hz, 2H), 2.26 (t, *J* = 2.4 Hz, 1H), 1.66 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 163.2, 160.8, 135.0, 130.0, 129.9, 115.3, 115.1, 81.9, 71.6, 51.4, 37.2.

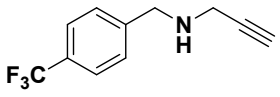


N-(4-chlorobenzyl) prop-2-yn-1-amine (1g), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (s, 4H), 3.83 (s, 2H), 3.39 (s, 2H), 2.26 (s, 1H), 1.49

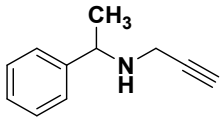
(s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 132.7, 129.6, 128.4, 81.8, 71.7, 51.3, 37.1.



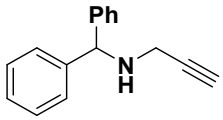
N-(4-bromobenzyl) prop-2-yn-1-amine (1h), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 3.84 (s, 2H), 3.41 (d, J = 2.4 Hz, 2H), 2.26 (t, J = 2.4 Hz, 1H), 1.54 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 131.5, 130.1, 120.9, 81.8, 71.7, 51.5, 37.2.



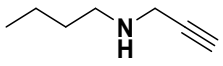
N-(4-(trifluoromethyl) benzyl) prop-2-yn-1-amine (1i), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.44 (m, 4H), 3.95 (s, 2H), 3.42 (dd, *J* = 5.9, 2.4 Hz, 2H), 2.28 (q, *J* = 2.8 Hz, 1H), 1.85 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 129.3, 128.6, 125.4, 125.3, 81.6, 78.4, 73.4, 71.9, 56.5, 51.6, 42.0, 37.3.



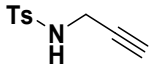
N-(1-phenylethyl) prop-2-yn-1-amine (1j), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 5H), 4.01 (q, *J* = 6.6 Hz, 1H), 3.26 (ddd, *J* = 77.5, 17.1, 2.3 Hz, 2H), 2.21 (t, *J* = 2.4 Hz, 1H), 1.65 (s, 1H), 1.36 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 128.5, 127.3, 127.2, 126.9, 82.2, 71.2, 56.3, 35.9, 23.9.



N-benzhydrylprop-2-yn-1-amine (1k), white solid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.24 (m, 10H), 5.17 (s, 1H), 3.43 (s, 2H), 2.32 (s, 1H), 1.95 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 143.0, 128.5, 127.4, 127.2, 82.0, 71.6, 65.2, 36.1.

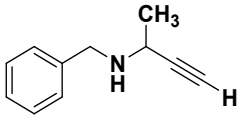


N-(prop-2-yn-1-yl) butan-1-amine (1l), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.38 (d, *J* = 2.4 Hz, 2H), 2.67 – 2.61 (m, 2H), 2.17 (t, *J* = 2.4 Hz, 1H), 1.43 (dt, *J* = 14.1, 6.9 Hz, 2H), 1.31 (dd, *J* = 15.1, 7.2 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 82.2, 71.0, 48.3, 38.1, 31.8, 20.3, 13.9.

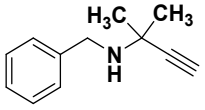


4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (1m), white power, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 1H), 3.82 (d, *J* = 3.1 Hz, 2H), 2.43 (s, 2H), 2.10 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 82.2, 71.0, 48.3, 38.1, 31.8, 20.3, 13.9. **^{13}C NMR** (101 MHz, $CDCl_3$)

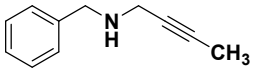
δ 143.7, 136.4, 129.6, 127.3, 77.9, 72.9, 32.7, 21.5.



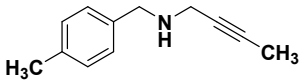
N-benzylbut-3-yn-2-amine (1n), yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 5H), 4.02 (d, *J* = 12.8 Hz, 1H), 3.81 (d, *J* = 12.8 Hz, 1H), 3.49 (qd, *J* = 6.8, 1.9 Hz, 1H), 2.32 (s, 1H), 1.38 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 128.4, 127.0, 86.2, 70.8, 51.3, 44.2, 22.3.



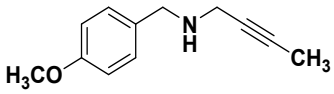
***N*-benzyl-2-methylbut-3-yn-2-amine (1o),** white solid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.29 (m, 5H), 3.91(s, 2H), 2.41 (s, 1H), 1.47 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 104.5, 128.4, 127.0, 88.9, 69.9, 50.0, 48.9, 29.5.



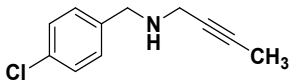
N-benzylbut-2-yn-1-amine (5a), colourless oil,**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25-7.16 (m, 5H), 3.76 (s, 2H), 3.28 (s, 2H), 1.75 (s, 3H), 1.43 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$): 139.7, 128.4, 127.0, 79.2, 76.1, 52.5, 37.9, 3.5.



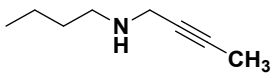
N-(4-methylbenzyl) but-2-yn-1-amine (5b), yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 40.1, 8.1 Hz, 4H), 3.78 (s, 2H), 3.33 (s, 2H), 2.31 (s, 3H), 1.82 (s, 3H), 1.68 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): 136.4, 128.9, 128.1, 78.9, 52.0, 37.6, 20.9, 3.3.



N-(4-methoxybenzyl) but-2-yn-1-amine (5c), yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 5H), 3.35 (s, 2H), 1.83 (s, 3H), 1.70 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): 158.6, 131.7, 129.5, 113.7, 79.0, 55.1, 51.8, 37.6, 3.4.

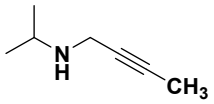


N-(4-chlorobenzyl) but-2-yn-1-amine (5d), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (s, 4H), 3.82 (s, 2H), 3.35 (q, *J* = 2.4 Hz, 2H), 1.84 (t, *J* = 2.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0, 132.6, 129.6, 128.4, 79.3, 51.6, 37.6.

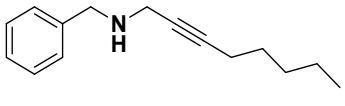


N-butylbut-2-yn-1-amine (5e), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.31 (s, 2H), 2.60 (t, *J* = 6.9 Hz, 2H), 1.77 (s, 3H), 1.52 – 1.37 (m, 2H), 1.36 – 1.24 (m, 2H), 0.87 (t, *J* = 7.1 Hz, 3H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ

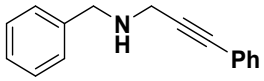
78.5, 77.3, 48.4, 38.5, 31.9, 20.3, 13.8, 2.3.



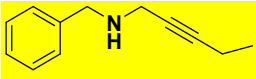
N-isopropylbut-2-yn-1-amine (5f), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.37 (s, 2H), 2.98(s, 1H), 1.81 (s, 1H), 1.51 (s, 1H), 1.05 (s, 6H).; **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 78.6, 47.0, 36.0, 22.5, 3.5.



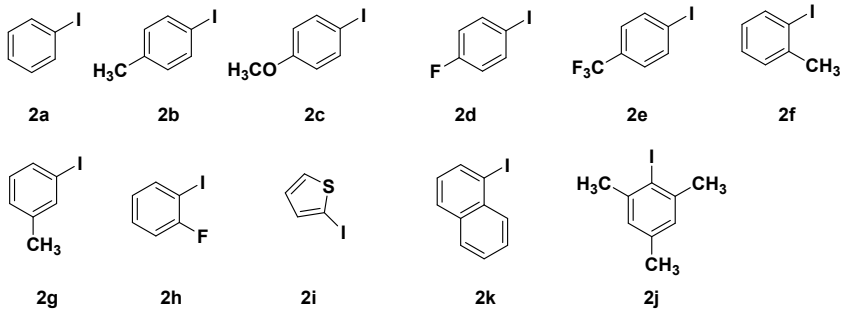
N-benzyloct-2-yn-1-amine (5g), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 5H), 3.86 (s, 2H), 3.40 (s, 2H), 2.20 (t, *J* = 7.0 Hz, 2H), 1.70 (s, 1H), 1.52 (p, *J* = 7.0 Hz, 2H), 1.36 (ddt, *J* = 20.4, 14.2, 7.1 Hz, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6, 128.4, 127.0, 84.0, 77.8, 52.4, 37.8, 35.4, 31.1, 28.6, 22.2, 18.7, 14.1, 14.0.



N-benzyl-3-phenylprop-2-yn-1-amine (5h), yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.23 (m, 10H), 3.94 (s, 2H), 3.64 (s, 2H), 1.64(s, H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.5, 131.6, 128.4, 128.2, 128.0, 127.1, 123.2, 87.5, 83.7, 52.5, 38.2.



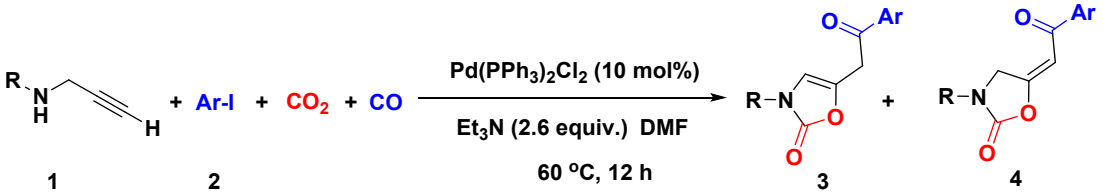
N-benzylpent-2-yn-1-amine (5i), yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 5H), 3.85 (s, 2H), 3.39 (s, 2H), 2.22 (q, *J* = 7.6, 6.9 Hz, 2H), 1.15 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6, 128.3, 127.0, 85.3, 52.4, 37.8, 14.1 12.4.



Aryl iodides were commercially available.

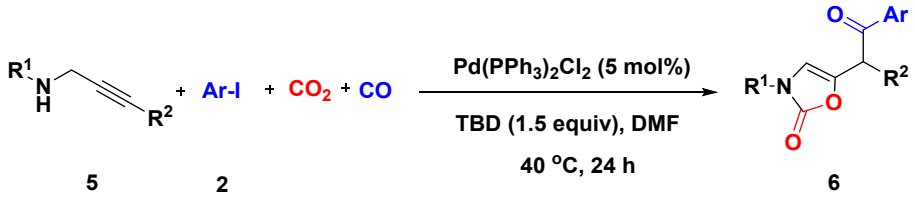
3. General Procedures and Optimization of the Reaction Conditions

General procedures



For the reactions incorporating terminal propargylic amines, an oven-dried Schlenk tube with a stir bar was charged with 1 (0.25 mmol), 2 (3.0 equiv.), Et_3N (2.6 equiv.), $Pd(PPh_3)_2Cl_2$ (10 mol%) and 2.5 mL *N,N*-dimethylformamide (DMF). Then freeze-thaw was performed three times to expel the air in the system and the Schlenk tube was then connected with a balloon containing mixture of CO_2 and CO with a molar ratio 1:2. (the molar ratio of CO_2 to CO was determined by GC). Afterward, the reaction mixture was stirred at 60 °C for 12 h. After that, the solvent was evaporated under reduced pressure and the resulting crude product was purified by flash column chromatography (silica gel, Petrolether/EtOAc).

For the reactions that were performed under pressured CO_2 and CO mixture, a 25 mL glass lined autoclave with a stirring bar was used. Firstly, 1 (0.25 mmol), 2 (3.0 equiv.), Et_3N (2.6 equiv.), $Pd(PPh_3)_2Cl_2$ (10 mol%) and 2.5 mL DMF were added into the autoclave and air in the system is evacuated. Then, CO_2 and CO were filled into the autoclave sequentially and the molar ratio of CO_2 to CO was calculated by the partial pressure of these two gases. Afterwards, the autoclave was heated to 60 °C and this temperature was kept for 12 h. Then the reaction was terminated by cooling to room temperature and releasing the pressure. Subsequently, the solvent was evaporated under reduced pressure and the resulting crude product was purified by flash column chromatography (silica gel, Petrolether/EtOAc).

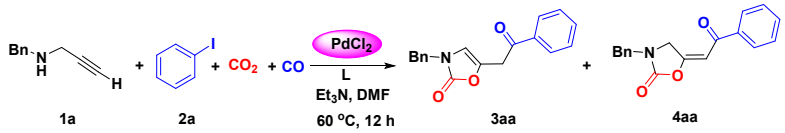


For the reactions incorporating internal propargylic amines, an oven-dried Schlenk tube with a stir bar was charged with 4 (0.25 mmol), 5 (1.5 equiv.), 1,5,7-triazabicyclo [4,4,0] dec-5-ene (TBD) (1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (5 mol%), and 2.5 mL DMF. Then freeze-thaw was performed three times to expel the air in the system and the Schlenk tube was connected with a balloon containing CO_2 and CO mixture

with a molar ratio 1:2. (the molar ratio of CO_2 to CO was determined by GC). The reaction mixture was stirred at 40 °C for 24 h and the solvent was then evaporated under reduced pressure. The resulting crude product was purified by flash column chromatography (silica gel, Petrolether/EtOAc).

Optimization of the Reaction Conditions

Table S1 Screening of Ligand for Terminal Propargylic Amine [a]



Entry	[L] (20 mol %)	Yield of 3aa (%) [b]
1	dppf	n.d.
2	DPPP	trace
3	XantPhos	n.d.
4	DPE phos	n.d.
5	P(*o*-tol)$_3$	37
6	(*n*-Bu)$_3$P	28
7	TFP	33
8	P(*p*-anis)$_3$	62
9	P(*o*-anis)$_3$	68
10	PPh_3	75

[a]Reaction conditions: **1a** (36.3 mg, 0.25 mmol), **2a** (84 μL, 3.0 equiv.), $PdCl_2$ (4.4 mg, 10 mol%), Et_3N (90 μL, 2.6 equiv), DMF (2.5 mL), CO_2/CO balloon, 60 °C, 12 h. [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard. n.d.= not detected.

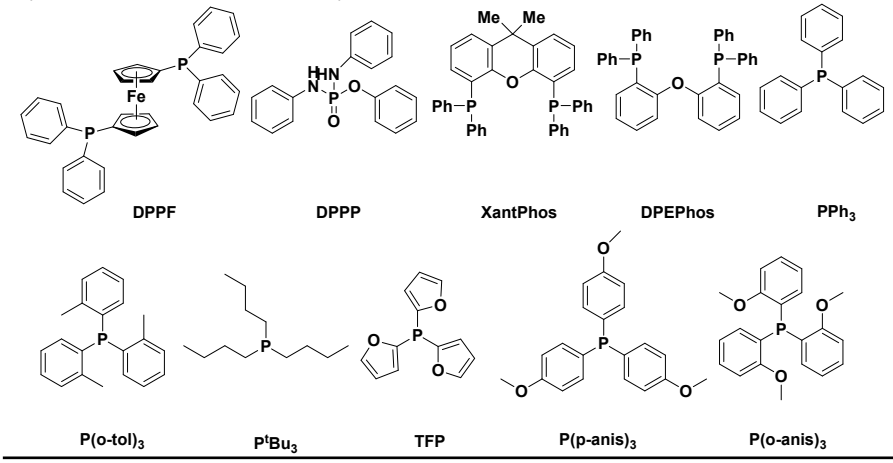
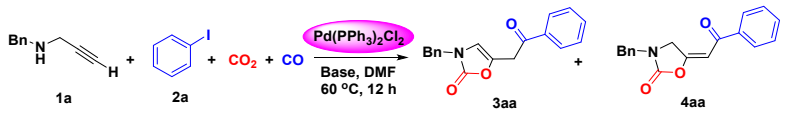


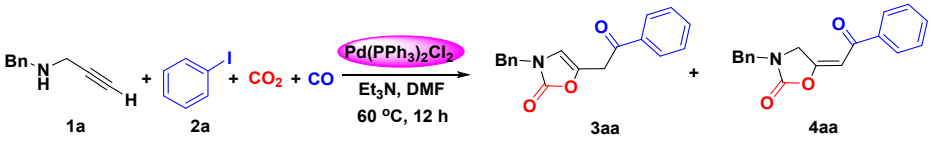
Table S2 Screening of Bases for Terminal Propargylic Amine [a]



Entry	Base (equiv.)	Yield of 3aa (%) [b]
1	DABCO (2.6)	50
2	Et_3N (2.6)	75
3	Cs_2CO_3 (2.6)	n.d.
4	K_2CO_3 (2.6)	n.d.
5	DBU (2.6)	n.d.
6	Et_2NH (2.6)	n.d.
7	TBD (2.6)	33
8	NaO^{t}Bu (2.6)	29
9	Et_3N (1)	34
10	Et_3N (1.5)	48
11	Et_3N (3)	60
12	----	n.d

[a]Reaction conditions: **1a** (36.3 mg, 0.25 mmol), **2a** (84 μL, 3.0 equiv.), $Pd(PPh_3)_2Cl_2$ (17.6 mg, 10 mol%), DMF (2.5 mL), CO_2/CO balloon, 60 °C, 12 h. [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard. n.d.= not detected. DBU=1,8-Diazabicyclo [5.4.0] undec-7-ene, DABCO=Triethylenediamine.

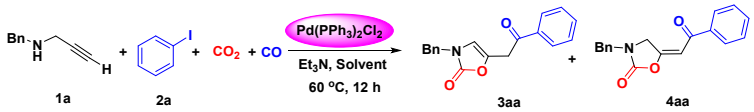
Table S3 Screen the amount of Iodobenzene for Terminal Propargylic Amine [a]



Entry	2a (equiv)	Yield of 3aa (%) [b]
1	1.5	53
2	3	75

[a] Reaction conditions: **1a** (36.3 mg, 0.25 mmol), $Pd(PPh_3)_2Cl_2$ (17.6 mg, 10 mol%), Et_3N (90 μL, 2.6 equiv), DMF (2.5 mL), CO_2/CO balloon, 60 °C, 12 h. [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S4 Screening of Solvent for Terminal Propargylic Amine [a]

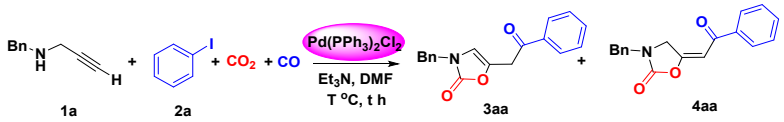


1a 2a 3aa 4aa

Entry	Solvent	Yield of 3aa (%) [b]
1	MeCN	46
2	Toluene	28
3	DMSO	40
4	DMF	75
5	DMAC	53

[a]Reaction conditions: **1a** (36.3 mg, 0.25 mmol), **2a** (84 μL, 3.0 equiv.), $Pd(PPh_3)_2Cl_2$ (17.6 mg, 10 mol%), Et_3N (90 μL, 2.6 equiv.), Solvent (2.5 mL), CO_2/CO balloon, 60 °C, 12 h. [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S5 Screening of Time and Temperature for Terminal Propargylic Amine [a]

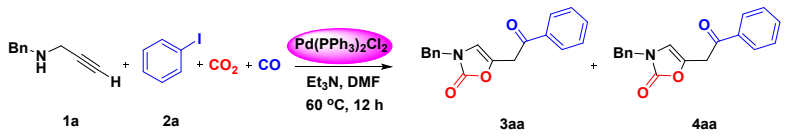


1a 2a 3aa 4aa

Entry	Time (h)	Temperature (°C)	Yield of 3aa (%) [b]
1	8	60	63
2	12	60	75
3	16	60	76
4	12	25	60
5	12	40	64
6	12	80	42

[a]Reaction conditions: **1a** (36.3 mg, 0.25 mmol), **2a** (84 μL, 3.0 equiv.), $Pd(PPh_3)_2Cl_2$ (17.6 mg, 10 mol%), Et_3N (90 μL, 2.6 equiv.), DMF (2.5 mL), CO_2/CO balloon, [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S6 Screening of Total Pressure and Molar ratio of CO_2 and CO for Terminal Propargylic Amine [a]



Entry	Total pressure/bar	CO_2/CO[b]	Yield of 3aa (%)[c]
1	1	1 1	48
2	10	1 1	53
3	30	1 1	54
4	1	1 2	75
5	6	2 1	50
6	6	1 5	68
7	1	0 1	n.d
8	1	1 0	n.d

[a]Reaction conditions: **1a** (36.3 mg, 0.25 mmol), **2a** (84 μL, 3.0 equiv.), $Pd(PPh_3)_2Cl_2$ (17.6 mg, 10 mol%), Et_3N (90 μL, 2.6 equiv.), DMF (2.5 mL), 60 °C, 12 h. [b]When the total pressure is higher than 1 bar, the reaction was performed in an autoclave and the molar ratio of CO_2 to CO was determined by their partial pressure. When CO_2/CO balloon was used, the molar ratio of CO_2 to CO was determined by GC. [c]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard. n.d.= not detected.

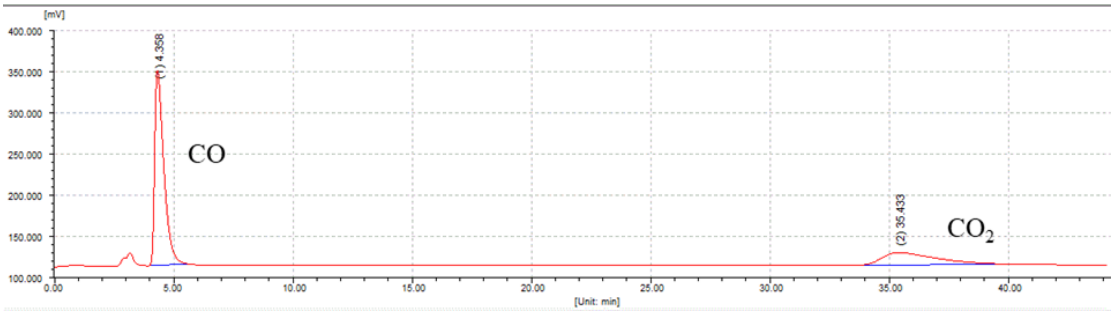


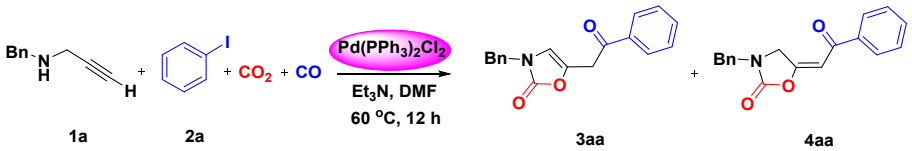
Figure S1 Typical gas chromatogram of the CO_2 and CO mixture.

Before the reaction, the gas (1 mL) in the balloon containing mixture of CO_2 and CO were taken using a syringe, and then analyzed by gas chromatography (GC, FuLi 9790II) with a TCD detector and capillary column to determine the moles of CO_2 and CO.

$$\frac{n_{CO_2}}{n_{co}} = \frac{S_{CO_2} / S_{CO_2\,(1\,mL)}}{S_{CO} / S_{CO\,(1mL)}}$$

wherein S_{CO2} and S_{CO} are the peak areas of CO_2 and CO in the gas chromatogram for gaseous mixture. S_{CO2}(1mL) and S_{CO}(1mL) are the peak areas of 1 mL pure CO_2 and pure CO in the gas chromatogram respectively.

Table S7 Effect of Additive on the Reaction [a]

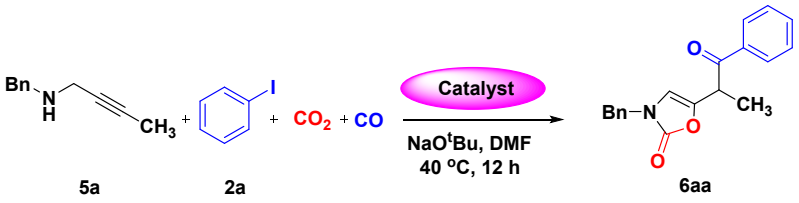


1a 2a 3aa 4aa

Entry	Additive (equiv.)	Yield of 3aa (%) [b]
1	O_2	n.d
2	H_2O (4)	65

[a] Reaction conditions: **1a** (36.3 mg, 0.25 mmol), **2a** (84 μL, 3.0 equiv.), $Pd(PPh_3)_2Cl_2$ (17.6 mg, 10 mol%), Et_3N (90 μL, 2.6 equiv.), DMF (2.5 mL), CO_2/CO balloon, 60 °C, 12 h. [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S8 Screening of Catalyst for Internal Propargylic Amine [a]

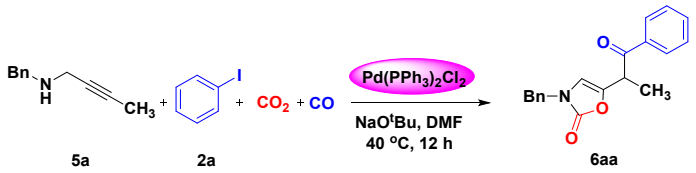


5a 2a 6aa

Entry	Catalyst (mol%)	Yield of 6aa (%) [b]
1[c]	$Pd(PPh_3)_2Cl_2$ (5)	n.d.
2	$Pd(PPh_3)_2Cl_2$ (5)	35
3	$Pd(PPh_3)_4$ (5)	trace
4	$Pd(OAc)_2/PPh_3$ (5/10)	23
5	$Pd/C/PPh_3$ (5/10)	n.d.
6	$Pd(PPh_3)_2Cl_2$ (10)	39

[a] Reaction conditions: **5a** (39.8 mg, 0.25 mmol), **2a** (42 μL, 1.5 equiv.), NaO^{t}Bu (1.5 equiv.), DMF (2.5 mL), CO_2/ CO balloon, 40 °C, 12 h. [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard. n.d.= not detected. [c]Et_3N (1.5 equiv.).

Table S9 Screening of the Amount of Iodobenzene for Internal Propargylic Amine [a]

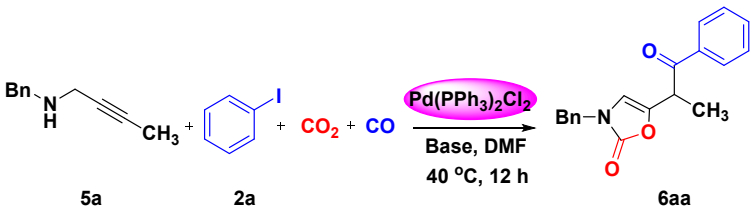


5a 2a 6aa

Entry	2a (equiv.)	Yield of 6aa (%) [b]
1	1	39
2	1.5	30
3	3	36

[a]Reaction conditions: **5a** (39.8 mg, 0.25 mmol), $Pd(PPh_3)_2Cl_2$ (8.8 mg, 5 mol%), NaO^{t}Bu (36 mg, 1.5 equiv.), DMF (2.5 mL), CO_2/ CO balloon, 40 °C, 12 h. [b]Determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S10 Screening of Bases for Internal Propargylic Amine [a]

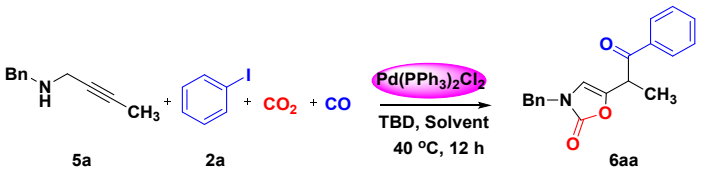


5a 2a 6aa

Entry	Base (equiv.)	Yield of 6aa (%) [b]
1	Et_3N（1.5）	n.d.
2	NaO^{t}Bu (1.5)	35
3	Cs_2CO_3 (1.5)	n.d.
4	DBU（1.5）	11
5	Et_2NH (1.5)	n.d.
6	K_2CO_3 (1.5)	n.d.
7	TBD (1.5)	52
8	KO^{t}Bu (1.5)	30
9	DABCO (1.5)	22
10	TBD (1)	50
11	TBD (3)	n.d.

[a] Reaction conditions: **5a** (39.8 mg, 0.25 mmol), **2a** (42 μL, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (8.8 mg, 5 mol%), DMF (2.5 mL), CO_2/ CO balloon, 40 °C, 12 h. [b]Determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard. n.d.= not detected.

Table S11 Screening of Solvent for Internal Propargylic Amine [a]

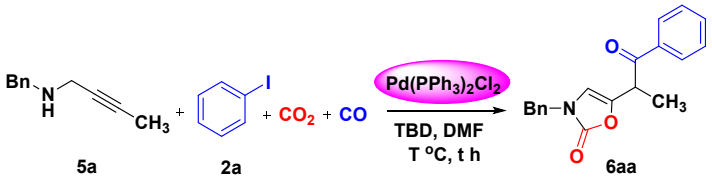


5a 2a 6aa

Entry	Solvent	Yield of 6aa (%) [b]
1	MeCN	46
2	Toluene	24
3	THF	trace
4	DMF	52
5	DMAC	45

[a]Reaction conditions: **5a** (39.8 mg, 0.25 mmol), **2a** (42 μL, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (8.8 mg, 5 mol%), TBD (52.2 mg, 1.5 equiv.), Solvent (2.5 mL), CO_2/CO balloon, 40 °C, 12 h. [b] Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S12 Screening of Time and Temperature for Internal Propargylic Amine [a]



5a 2a 6aa

Entry	Time (h)	Temperature (°C)	Yield of 6aa (%) [b]
1	12	40	52
2	16	40	59
3	24	25	44
4	24	40	66 (57[c])
5	24	60	21

[a]Reaction conditions: **5a** (39.8 mg, 0.25 mmol), **2a** (42 μL, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (8.8 mg, 5 mol%), TBD (52.2 mg, 1.5 equiv.), DMF (2.5 mL), CO_2/CO balloon, [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard. [c]Isolated yield.

4. Control Experiments

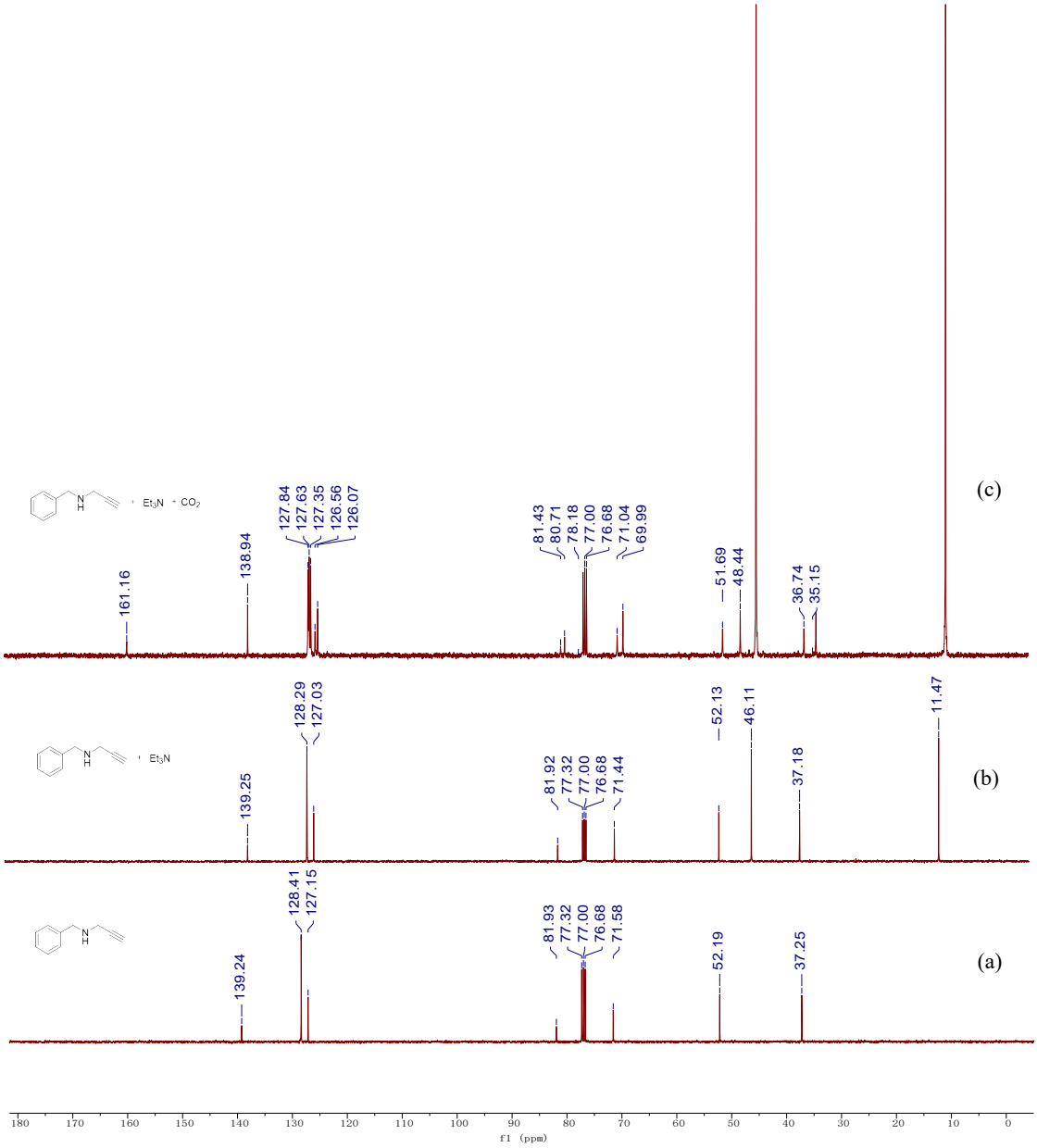
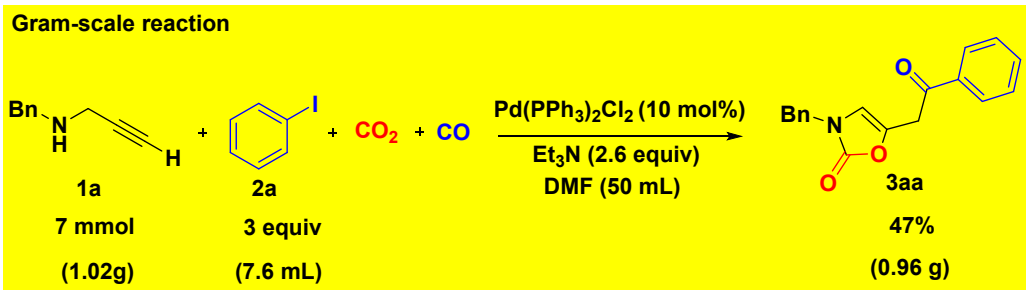


Figure S2 ^{13}C NMR investigation for interaction among 1a (36.3mg, 0.25 mmol), Et_3N (90 µL, 3 equiv), and bubbled CO_2 in $CDCl_3$ (0.5 mL).

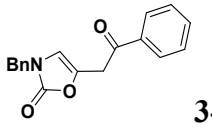
5. Gram-Scale Experiment

For the gram-scale experiment, an oven-dried Schlenk bottle with a stir bar was charged with **1a** (1.02 g, 7 mmol), 2 (7.6 mL, 3.0 equiv.), Et_3N (2.5 mL, 2.6 equiv.), $Pd(PPh_3)_2Cl_2$ (0.49 g, 10 mol%) and 50 mL DMF. Then freeze-thaw was performed three times to expel the air in the system and the Schlenk bottle was then connected with a balloon containing mixture of CO_2 and CO with a molar ratio 1:2. (the molar ratio of CO_2 to CO was determined by GC). Afterward, the reaction mixture was stirred at 60 °C for 12 h. After that, the solvent was evaporated under reduced pressure and the resulting crude product was purified by flash column chromatography (silica gel, Petrolether/EtOAc).

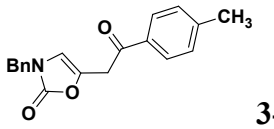
Scheme S1. Gram-Scale Experiment



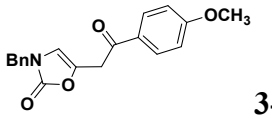
6. Characterization of Products



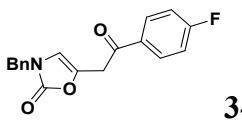
3-benzyl-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3aa), pale yellow solid, m.p. 140~142 °C. R_f = 0.4 (EtOAc/ petroleum ether = 1:2).**^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 15.4, 8.2 Hz, 3H), 7.28 (d, *J* = 7.3 Hz, 2H), 6.48 (s, 1H), 4,70 (s, 1H), 4.09 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.4, 155.3, 135.8, 135.3, 133.8, 133.7, 129.0, 128.8, 128.3, 128.2, 128.0, 113.0, 47.7, 35.7. **IR:** 3732, 3651, 3632, 3301, 2920, 2849, 1750, 1689, 1595, 1447, 1396, 1384, 1265, 1214, 1068, 750, 701, 688, 571, 550 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{18}H_{13}NO_3Na^+$ [M+Na^+] 316.0944, found: 316.0948.



3-benzyl-5-(2-oxo-2-(p-tolyl) ethyl) oxazol-2(3H)-one (3ab), yellow solid, m.p. 134-136 °C. R_f=0.4 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.36-7.29(m, 7H), 6.46 (s, 1H), 4,70 (s, 1H), 4.06 (s, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.1, 155.3, 144.8, 135.3, 133.9, 133.3, 129.5, 129.0, 128.3, 128.2, 128.0, 113.0, 47.6, 35.5, 21.6. **IR:** 2953, 2924, 2851, 1751,1686, 1607, 1363, 1183, 1082, 1012, 962, 810, 741, 704, 687 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_3^+$ [M+H^+] 308.1281, found: 308.1284.

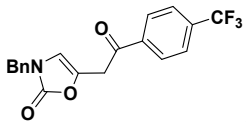


3-benzyl-5-(2-(4-methoxyphenyl)-2-oxoethyl) oxazol-2(3H)-one (3ac), pale yellow solid, m.p.146-147 °C. R_f=0.4 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.40 – 7.25 (m, 5H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.46 (s, 1H), 4.70 (s, 2H), 4.04 (s, 2H), 3.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 191.9, 164.0, 155.3, 135.4, 134.0, 130.7, 129.0, 128.8, 128.2, 128.0, 114.0, 112.8, 55.5, 47.7, 35.4. **IR:** 2934, 2837, 1751, 1689, 1611, 1514, 1448, 1407, 1249, 1178, 1030, 1001, 759, 689 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_4^+$ [M+H^+] 324.1230, found:324.1230.

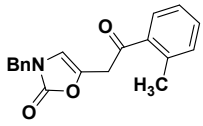


3-benzyl-5-(2-(4-fluorophenyl)-2-oxoethyl) oxazol-2(3H)-one (3ad), white solid, m.p.123-124 °C. R_f=0.4 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.87 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.23 (d, *J* = 9.6 Hz, 2H), 7.20 –

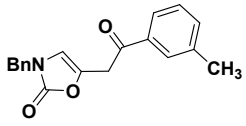
7.14 (m, 3H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.35 (s, 1H), 4.60 (s, 2H), 3.95 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): 191.9, 167.4, 164.8, 155.2, 135.3, 133.4, 131.1, 131.0, 129.0, 128.3, 128.0, 116.2, 115.9, 113.1, 47.7, 35.7. **IR:** 3067, 3033, 2925, 1801, 1752, 1688, 1958, 1507, 1410, 1234, 1157, 1071, 1012, 962, 810, 741, 704, 687 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}FNO_3^+$ [M+H$^+$] 312.1030, found: 312.1028.



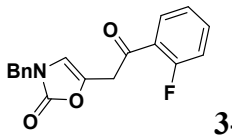
3-benzyl-5-(2-oxo-2-(4-(trifluoromethyl) phenyl) ethyl) oxazol-2(3H)-one (3ae), pale yellow solid, m.p.131-133 ^oC. R_f =0.4 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.41 – 7.25 (m, 5H), 6.49 (s, 1H), 4.71 (s, 2H), 4.12 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): 192.5, 155.1, 138.4, 135.3, 132.9, 129.0, 128.6, 128.3, 128.0, 113.3, 47.7, 36.1. **IR:** 3136, 3067, 3034, 2936, 1753, 1698, 1607, 1581, 1512, 1497, 1455, 1441, 1410, 1325, 1169, 1129, 1066, 1011, 960, 833, 747, 704, 604 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{15}F_3NO_3^+$ [M+H$^+$] 362.0999, found: 362.0993.



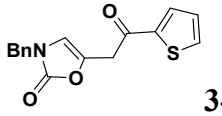
3-benzyl-5-(2-oxo-2-(o-tolyl) ethyl) oxazol-2(3H)-one (3af), yellow oil. R_f =0.4 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.65 (d, *J* = 7.7 Hz, 1H),7.42-7.28 (m, 8H), 6.44 (s, 1H), 4.70 (s, 2H), 4.01 (s, 2H), 2.49 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 196.7, 155.2, 138.9, 135.3, 133.9, 132.2, 132.1, 128.9, 128.7, 128.2, 127.9, 125.8, 112.9, 47.6, 38.2, 21.4. **IR:** 2959, 2925, 1799, 1752, 1675, 1606, 1455, 1409, 1363, 1009, 889, 739, 703 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_3^+$ [M+H$^+$] 308.1281, found: 308.1279.



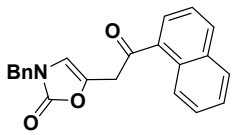
3-benzyl-5-(2-oxo-2-(m-tolyl) ethyl) oxazol-2(3H)-one(3ag), pale yellow solid, m.p.124-126 ^oC. R_f =0.4 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.44 – 7.24 (m, 7H), 6.48 (s, 1H), 4.69 (s, 2H), 4.06 (s, 2H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.5, 155.1, 138.5, 135.6, 135.3, 134.4, 133.6, 128.8, 128.6, 128.6, 128.5, 128.1, 127.8, 125.4, 125.3, 113.0, 47.5, 35.6, 21.2. **IR:** 3136, 3062, 2923, 1750, 1689, 1604, 1585, 1497, 1454, 1441, 1397, 1365, 1262, 1245, 1161, 1083, 1070, 1029, 1014, 961, 745, 704, 688, 637, 613 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_3^+$ [M+H$^+$] 308.1281, found: 308.1276.



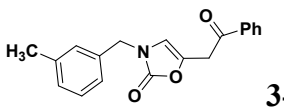
3-benzyl-5-(2-(2-fluorophenyl)-2-oxoethyl) oxazol-2(3H)-one (3ah), pale yellow solid, m.p.108-109 °C. R_f =0.4 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (t, *J* = 8.5 Hz, 1H), 7.56 (q, *J* = 6.5, 5.4 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.27 (dd, *J* = 8.6, 5.1 Hz, 3H), 7.15 (dd, *J* = 11.4, 8.3 Hz, 1H), 6.47 (s, 1H), 4.72 (s, 2H), 4.09 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 162.2, 160.6, 155.3, 135.40, 133.5, 130.9, 129.0, 128.3, 127.9, 124.8, 124.7, 116.8, 116.6, 113.1, 47.6, 40.4, 40.3. **IR:** 3135, 3070, 3035, 1751, 1692, 1609, 1497, 1480, 1453, 1406, 1366, 1342, 1278, 1200, 1154, 1102, 1084, 1069, 995, 961, 764, 744, 704 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}FNO_3^+$ [M+H$^+$] 312.1030, found: 312.1026.



3-benzyl-5-(2-oxo-2-(thiophen-2-yl) ethyl) oxazol-2(3H)-one (3ai), pale yellow solid, m.p.102-103 °C. R_f =0.4 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.77 (d, *J* = 3.7 Hz, 2H), 7.70 (d, *J* = 4.9 Hz, 2H), 7.41-7.32(m, 3H),7.31-7.25(m, 2H), 7.16(t, *J* = 4.4 Hz, 1H), 6.45 (s, 1H), 4.71 (s, 2H), 4.01 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): 186.2, 155.2, 142.8, 135.0, 133.2, 133.0, 129.0, 128.4, 128.3, 128.0, 113.0, 112.8, 47.7, 36.4. **IR:** 2955, 2923, 2851, 1751, 1665, 1509, 1458, 1407, 1074, 737, 703 cm^{-1}. **HRMS(ESI)** m/z calcd for $C_{16}H_{14}NO_3S^+$ [M+H$^+$] 300.0689, found: 300.0687.

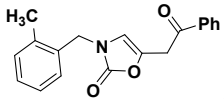


3-benzyl-5-(2-(naphthalen-1-yl)-2-oxoethyl) oxazol-2(3H)-one (3aj), yellow solid. R_f =0.5 (EtOAc/petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 8.61 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.88 (t, *J* = 7.2 Hz, 2H), 7.53 (ddd, *J* = 26.0, 15.2, 6.6 Hz, 3H), 7.30 (dd, *J* = 30.4, 6.7 Hz, 5H), 6.47 (s, 1H), 4.69 (s, 2H), 4.14 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): 196.9, 155.2, 135.3, 133.9, 133.8, 133.6, 130.1, 128.9, 128.5, 128.3, 128.2, 127.9, 126.6, 125.5, 124.2, 113.0, 47.6, 38.7. **IR:** 3138, 3082, 2929, 1752, 1685, 1593, 1572, 1507, 1455, 1439, 1399, 1363, 1233, 1175, 968, 942, 803, 775, 739, 703 cm^{-1}. **HRMS(ESI)** m/z calcd for $C_{22}H_{18}NO_3^+$ [M+H$^+$] 344.1281, found: 344.1280.

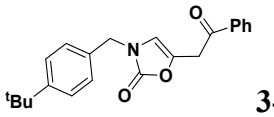


3-(3-methylbenzyl)-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3ba), pale yellow solid, m.p.100-102 °C. R_f =0.5 (EtOAc/petroleum ether = 1:2).**^{1}H**

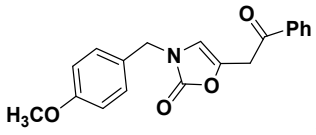
NMR (400 MHz, $CDCl_3$)：δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.01 (dd, *J* = 13.6, 6.1 Hz, 1H), 6.87 (dd, *J* = 18.2, 8.9 Hz, 3H), 6.25 (s, 1H), 4.42 (s, 2H), 3.85 (s, 2H), 2.10 (3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.4, 155.2, 138.7, 135.7, 135.2, 133.7, 133.5, 128.9, 128.7, 128.6, 124.9, 113.0, 47.5, 35.6, 21.2. **IR:** 3139, 3058, 2920, 1798, 1751, 1691, 1608, 1448, 1408, 1214, 1185, 1077, 1014, 959, 687, 754, 709, 689 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_3^+$[M+H$^+$] 308.1281, found: 308.1280.



3-(2-methylbenzyl)-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3ca), pale yellow solid, m.p.106-107 °C. R_f =0.5 (EtOAc/petroleum ether = 1:2).**^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.21 (m, 4H), 6.41 (s, 1H), 4.76 (s, 2H), 4.13 (s, 2H), 2.36 (3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.4, 155.0, 136.7, 133.8, 133.7, 133.1, 130.1, 129.0, 128.8, 128.6, 128.3, 126.4, 112.7, 45.7, 35.6, 19.0. **IR:** 3062, 3027, 2933, 1802, 1757, 1682, 1622, 1448, 1409, 1362, 1267, 1215, 1181, 1067, 1011, 896, 748, 696 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_3^+$ [M+H$^+$] 308.1281, found: 308.1278.

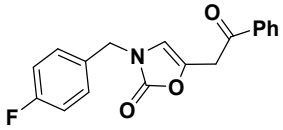


3-(4-(tert-butyl) benzyl)-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3da), white solid, m.p.173-175 °C. R_f =0.5 (EtOAc/petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.49 (s, 1H),4.68(s, 2H), 4.09 (s, 2H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.5, 155.2, 151.3, 135.7, 133.8, 133.4, 132.3, 128.8, 128.2, 127.7, 125.8, 113.1, 47.3, 35.7, 34.5, 31.2. **IR:** 2959, 1786, 1742, 1689, 1680, 1594, 1446, 1392, 1362, 1266, 1244, 1142, 1073, 1003, 956, 908, 886, 744, 731, 684 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{22}H_{24}NO_3^+$ [M+H$^+$] 350.1751, found: 350.1749.

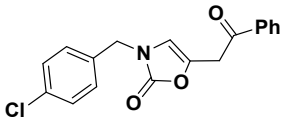


3-(4-methoxybenzyl)-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3ea), white solid, m.p.107-108 °C. R_f =0.5 (EtOAc/petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.95(d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 2H), 7.49(t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.46 (s, 1H), 4.08 (s, 2H), 3.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.5, 159.6, 155.2, 135.8, 133.8, 133.5, 129.5, 128.8, 128.3, 127.4, 114.3, 112.9, 55.3, 47.2, 35.7. **IR:** 2955, 2922,

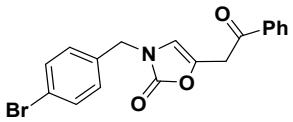
2850, 1744, 1689, 1514, 1448, 1247, 1212, 1177, 1080, 1030, 818, 754, 687, 669 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_4^+$ [M+H$^+$] 324.1231, found: 324.1228.



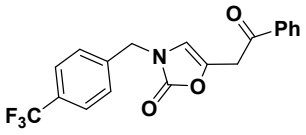
3-(4-fluorobenzyl)-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3fa), white solid, m.p.116-118 °C. R_f =0.4 (EtOAc/petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.27 (m, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.51 (s, 1H),4.68(s, 2H), 4.10 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.4, 163.8, 161.3, 155.1, 135.7, 133.8, 133.7, 131.2, 129.8, 129.7, 127.7, 128.8, 128.2, 116.0, 115.8, 112.9, 46.9, 35.6. **IR:** 3139, 3067, 2936, 1797, 1751, 1691, 1605, 1511, 1448, 1408, 1364, 1221, 1157, 1076, 1013, 1001, 958, 888, 824, 754, 689 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}FNO_3^+$ [M+H$^+$]312.1030, found: 312.1030.



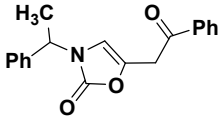
3-(4-chlorobenzyl)-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3ga), white solid, m.p.117-118 °C. R_f =0.4 (EtOAc/petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 6.8 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.38-7.20 (m, 4H), 6.50 (s, 1H), 4.68 (s, 2H), 4.11 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.3, 155.1, 141.6, 135.7, 134.3, 133.9, 129.3, 129.2, 128.8, 128.2, 112.9, 47.0, 35.6. **IR:** 3137, 3063, 2914, 1750, 1691, 1605, 1597, 1492, 1448, 1397, 1216, 1078, 1015, 959, 889, 802, 754, 688, 624 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}ClNO_3^+$ [M+H$^+$] 328.0735, found: 328.0733.



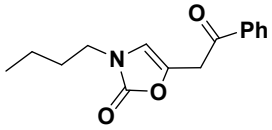
3-(4-bromobenzyl)-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3ha), yellow solid, m.p.134-135 °C. R_f =0.3 (EtOAc/petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.50 (d, *J* = 5.4 Hz, 4H), 7.19 (d, *J* = 7.0 Hz, 2H), 6.52 (s, 1H), 4.68 (s, 2H), 4.12 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.3, 155.1, 135.7, 134.4, 133.8, 132.1, 129.6, 128.8, 128.2, 122.4, 112.9, 47.0, 35.6. **IR:** 3138, 3062, 2936, 1797, 1751, 1690, 1605, 1596, 1579, 1489, 1448, 1398, 1215, 1070, 1012, 958, 888, 842, 798, 753, 688 cm^{-1}.**HRMS (ESI)** m/z calcd for $C_{18}H_{15}BrNO_3^+$ [M+H$^+$] 372.0230, found: 372.0229.



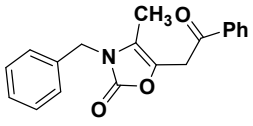
5-(2-oxo-2-phenylethyl)-3-(4-(trifluoromethyl) benzyl) oxazol-2(3H)-one (3ia), pale yellow solid, m.p. 116-117 °C. R_f =0.4 (EtOAc/petroleum ether = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 3H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 6.54 (s, 1H), 4.77 (s, 2H), 4.12 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.3, 155.1, 139.4, 135.7, 134.1, 133.9, 128.9, 128.2, 128.1, 126.0, 125.9, 113.0, 47.2, 36.1. **IR:** 3136, 3061, 2915, 1752, 1692, 1597, 1581, 1449, 1409, 1366, 1325, 1275, 1261, 1216, 1164, 1124, 1112, 1066, 1018, 1001, 954, 907, 845, 819, 750, 687 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{15}F_3NO_3^+$ [M+H$^+$] 362.0999, found: 362.0995.



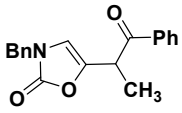
5-(2-oxo-2-phenylethyl)-3-(1-phenylethyl) oxazol-2(3H)-one(3ja), yellow oil, R_f =0.5 (EtOAc/petroleum ether = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.0 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.34 (dt, J = 13.9, 7.0 Hz, 5H), 6.55 (s, 1H), 5.30 (q, J = 7.1 Hz, 1H), 4.09 (d, J = 6.5 Hz, 2H), 1.69 (d, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.5, 154.7, 139.7, 135.7, 133.7, 133.5, 128.8, 128.2, 128.0, 126.5, 110.7, 52.5, 35.7, 19.2. **IR:** 3135, 3062, 3032, 2981, 2937, 1749, 1692, 1597, 1580, 1495, 1449, 1385, 1341, 1275, 1261, 1214, 1173, 1159, 1103, 1080, 1025, 1000, 954, 915, 887, 750, 699, 660 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_3^+$ [M+H$^+$] 308.1281, found: 308.1276.



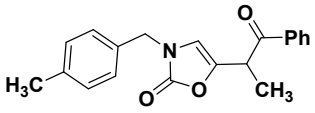
3-butyl-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3ja), yellow oil, R_f =0.5 (EtOAc/petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 6.57(s, 1H), 4.13 (s, 2H), 3.54 (t, *J* = 7.1 Hz, 2H), 1.65 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.36 (td, *J* = 14.6, 7.2 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 193.6, 155.2, 135.8, 133.8, 133.3, 128.8, 128.3, 113.3, 43.7, 35.7, 30.8, 19.6, 13.5. **IR:** 2959, 2930, 2873, 1748, 1692, 1448, 1408, 1214, 1075, 1000, 957, 742, 689 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{15}H_{18}NO_3^+$ [M+H$^+$] 260.1281, found: 260.1280.



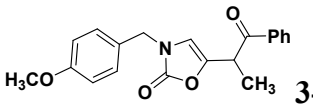
3-benzyl-4-methyl-5-(2-oxo-2-phenylethyl) oxazol-2(3H)-one (3oa), yellow solid, m.p.85-87 °C. R_f =0.3 (EtOAc/petroleum ether = 1:2).**^{1}H NMR** (400 MHz, $CDCl_3$)：δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.31 (ddd, *J* = 20.4, 13.9, 7.1 Hz, 5H), 4.77 (s, 2H), 4.05 (s, 2H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 194.0, 155.7, 136.1, 135.8, 133.7, 128.9, 128.8, 128.5, 127.9, 127.0, 121.2, 45.4, 35.0, 8.3. **IR:** 3060, 3033, 2926, 1751, 1691, 1596, 1579, 1496, 1448, 1403, 1384, 1352, 1213, 1179, 1112, 1079, 1044, 755, 719, 692, 626 cm-^{1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_3^+$ [M+H$^+$] 308.1281, found:308.1279.



3-benzyl-5-(1-oxo-1-phenylpropan-2-yl) oxazol-2(3H)-one (6aa), pale yellow oil, R_f = 0.4 (EtOAc/petroleum ether = 1:4). **^{1}H NMR** (400 MHz, $CDCl_3$)： δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 6.8 Hz, 2H), 7.33 (s, 2H), 7.24 (s, 2H), 6.26 (s, 1H), 4.66 (dd, *J* = 32.9, 15.0 Hz, 1H), 4.56 (d, *J* = 6.9 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$):197.3, 155.1, 139.2, 135.2, 133.5, 129.0, 128.8, 128.6, 128.4, 127.7, 111.4, 47.5, 38.7, 15.3. **IR:** 2956, 2923, 1749, 1677, 1595, 1615, 1451, 1378, 1264, 1184, 1078, 1011, 895, 739, 703 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{18}NO_3^+$ [M+H$^+$] 308.1281, found: 308.1280.

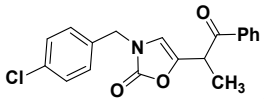


3-(4-methylbenzyl)-5-(1-oxo-1-phenylpropan-2-yl)oxazol-2(3H)-one (6ab), yellow oil; R_f = 0.5 (EtOAc/petroleum ether = 1:3).**^{1}H NMR** (400z MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.13 (s, 4H), 6.25 (s, 1H), 4.68 – 4.58 (m, 2H), 4.54 (d, *J* = 6.6 Hz, 1H), 2.33 (s, 3H), 1.43 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$):197.3, 155.1, 139.1, 138.0, 135.2, 133.5, 132.1, 129.5, 128.7, 128.5, 127.8, 111.3, 47.3, 38.7, 21.0, 15.4. **IR:** 3135, 3058, 2937, 2873, 1755, 1688, 1596, 1516, 1448, 1400, 1363, 1275, 1214, 1173, 1056, 1001, 968, 756, 723, 689, 655, 472 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{20}H_{20}NO_3^+$ [M+H$^+$] 322.1438, found: 322.1434.

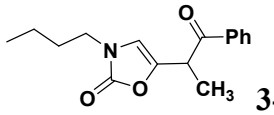


3-(4-methoxybenzyl)-5-(1-oxo-1-phenylpropan-2-yl)oxazol-2(3H)-one(6ac), yellow oil; R_f = 0.5 (EtOAc/petroleum ether = 1:3).**^{1}H NMR** (400z

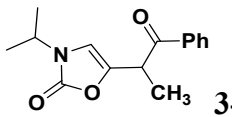
MHz, $CDCl_3$) δ 7.94 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.7 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.22 (s, 1H), 4.65-4.55 (m, 2H), 4.53 (d, J = 6.7 Hz, 1H), 3.78 (s, 3H), 1.42 (d, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$):197.4, 159.5, 155.1, 139.2, 135.3, 129.4, 128.8, 128.6, 128.5, 127.2, 114.2, 111.3, 111.1, 55.2, 47.1, 38.9, 15.6. **IR:** 2929, 2850, 1750, 1687, 1612, 1514, 1448, 1402, 1249, 1177, 1032, 969, 820, 726, 689 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{20}H_{20}NO_4^+$ [M+H$^+$] 338.1387, found: 338.1383.



3-(4-chlorobenzyl)-5-(1-oxo-1-phenylpropan-2-yl) oxazol-2(3H)-one (6ad), yellow oil; R_f = 0.4 (EtOAc/petroleum ether = 1:3). **^{1}H NMR** (400z MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 1H), 4.68-4.54 (m, 2H), 4.52-4.44 (m, 1H), 1.39 (d, *J* = 7.1 Hz,3H). **^{13}C NMR** (101 MHz, $CDCl_3$):197.3, 155.1, 139.6, 135.3, 134.2, 133.8, 133.7, 129.2, 129.1, 128.8, 128.5, 111.2, 47.0, 38.8, 15.6. **IR:** 3136, 3059, 2986, 2937, 1749, 1688, 1596, 1493, 1448, 1401, 1213, 1172, 1077, 1060, 1015, 1001, 968, 841, 803, 748, 687, 642, 599 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{19}H_{17}ClNO_3^+$ [M+H$^+$] 342.0891, found: 342.0889.

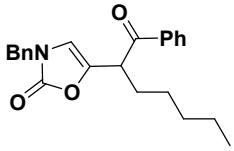


3-butyl-5-(1-oxo-1-phenylpropan-2-yl) oxazol-2(3H)-one (6ae), yellow oil; R_f = 0.5 (EtOAc/petroleum ether = 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 6.33 (s, 1H), 4.58 (q, *J* = 7.1 Hz, 1H), 3.50 (h, *J* = 6.7 Hz, 2H), 1.61 (p, *J* = 7.3 Hz, 2H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.32 (q, *J* = 7.5 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$):197.4, 155.1, 139.0, 135.3, 133.6, 128.8, 128.5, 111.6, 43.6, 38.8, 30.7, 19.6, 15.6, 13.5. **IR:** 2960, 2936, 2874, 1749, 1688, 1596, 1578, 1449, 1403, 1375, 1216, 1177, 1075, 968, 746, 690 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{16}H_{20}NO_3^+$ [M+H$^+$] 274.1438, found: 274.1434.

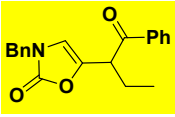


3-isopropyl-5-(1-oxo-1-phenylpropan-2-yl) oxazol-2(3H)-one (6af), yellow oil; R_f = 0.5 (EtOAc/petroleum ether = 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 6.32 (s, 1H), 4.51 (q, *J* = 7.1 Hz, 1H), 4.12 (p, *J* = 6.7 Hz, 1H), 1.40 (d, *J* = 7.1 Hz, 3H), 1.19 (dd, *J* = 9.5, 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$):197.5, 154.4, 139.1, 135.3, 133.5, 129.8, 128.7, 128.5, 108.2, 45.7, 38.7, 21.3, 15.6. **IR:** 3133, 2980, 2937, 2879, 1736,

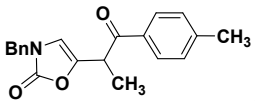
1680, 1649, 1449, 1390, 1373, 1275, 1215, 1175, 1133, 1097, 1034, 1001, 967, 932, 886, 749, 725, 689, 656 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{15}H_{18}NO_3^+$ [M+H$^+$] 260.1281, found: 260.1278.



3-benzyl-5-(1-oxo-1-phenylheptan-2-yl) oxazol-2(3H)-one (6ag), yellow oil; R_f = 0.5 (EtOAc/petroleum ether = 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 3H), 7.19 – 7.11 (m, 2H), 6.19 (s, 1H), 4.65 – 4.52 (m, 2H), 4.38 (t, *J* = 7.0 Hz, 1H), 1.88 (dt, *J* = 14.5, 7.1 Hz, 1H), 1.72 (dt, *J* = 14.2, 7.0 Hz, 1H), 1.18 (s, 6H), 0.79 – 0.71 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.2, 155.2, 138.5, 136.0, 135, 133.6, 128.9, 128.8, 128.5, 128.2, 127.8, 111.7, 47.6, 44.3, 31.5, 30.9, 26.7, 22.3, 13.9. **IR:** 2955, 2928, 2858, 1753, 1686, 1595, 1580, 1497, 1447, 1401, 1364, 1224, 1158, 1067, 1029, 1001, 965, 908, 737, 702 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{23}H_{26}NO_3^+$ [M+H$^+$] 364.1907, found: 364.1903.

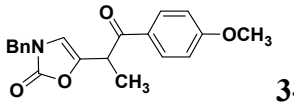


3-benzyl-5-(1-oxo-1-phenylbutan-2-yl) oxazol-2(3H)-one (6ah), pale yellow solid, m.p.104-105 °C. R_f =0.4 (EtOAc/petroleum ether = 1:3).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.19 (m, 5H), 6.31 (s, 1H), 4.72 – 4.60 (m, 2H), 4.41 (t, *J* = 6.9 Hz, 1H), 1.94 (ddq, *J* = 55.0, 14.0, 7.1 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.1, 155.2, 138.2, 135.9, 135.2, 133.5, 128.9, 128.7, 128.4, 128.2, 127.8, 111.9, 47.6, 45.7, 24.1, 11.5. **IR:** 2968, 2934, 2877, 1750, 1684, 1596, 1580, 1559, 1497, 1401, 1363, 1261, 1211, 1179, 1065, 965, 748, 703 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{20}H_{20}NO_3^+$ [M+H$^+$] 322.1438, found:322.1439.

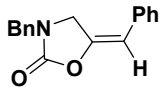


3-benzyl-5-(1-oxo-1-(p-tolyl) propan-2-yl) oxazol-2(3H)-one (6ai), yellow oil; R_f = 0.5 (EtOAc/petroleum ether = 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.2 Hz, 2H), 7.29 (dt, J = 15.7, 7.4 Hz, 7H), 6.28 (s, 1H), 4.66 (dd, J = 33.4, 15.1 Hz, 2H), 4.54 (q, J = 7.1 Hz, 1H), 2.41 (s, 3H), 1.44 (d, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$):196.9, 155.1, 144.5,139.4, 135.2, 132.7, 129.3, 128.8, 128.6, 128.5, 128.1, 127.8, 111.3, 111.2, 47.5, 38.6, 21.5, 15.5. **IR:** 3035, 2982,

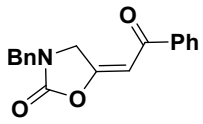
2935, 1752, 1682, 1606, 1454,, 1401, 1366, 1276, 1226, 1206, 1180, 1057, 966, 749, 703 cm^{-1}.**HRMS (ESI)** m/z calcd for $C_{20}H_{20}NO_3^+$ [M+H$^+$] 322.1438, found: 322.1434.



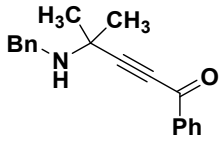
3-benzyl-5-(1-(4-methoxyphenyl)-1-oxopropan-2-yl) oxazol-2(3H)-one (6aj), yellow oil; R_f = 0.5 (EtOAc/petroleum ether = 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.25 (d, *J* = 7.1 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.27 (s, 1H), 4.67 (dd, *J* = 34.8, 15.1 Hz, 2H), 4.52 (q, *J* = 6.9 Hz, 1H), 3.87 (s, 3H), 1.43 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$):195.8, 163.8, 155.1, 139.6, 135.2, 130.9, 128.8, 128.2, 127.8, 113.9, 111.2, 55.4, 47.5, 38.3, 15.5. **IR:** 3137, 2952, 2936, 2842, 1750, 1678, 1599, 1573, 1510, 1455, 1401, 1260, 1170, 1028, 967, 844, 750, 703 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{20}H_{20}NO_4^+$ [M+H$^+$] 338.1387, found: 338.1383.



(E)-3-benzyl-5-benzylideneoxazolidin-2-one (3'aa), white solid; m.p. 156-158 ^{o}C. R_f = 0.5 (EtOAc/petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.43-7.31 (m, 8H), 7.24 (t, *J* = 7.4 Hz,1H), 5.48 (s, 1H), 4.55 (s, 2H), 4.19 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$):155.5, 141.7, 134.8, 133.3, 128.9, 128.4, 128.2, 128.1, 126.8, 103.1, 48.1, 47.8. **IR:** 3085, 3061, 3027, 1770, 1695, 1546,1494, 1471, 1450, 1440, 1427, 1390, 1350, 1329, 1266, 1047, 937, 921, 908, 818, 747, 704, 664, 566 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{17}H_{16}NO_2^+$ [M+H$^+$] 266.1176, found: 266.1173.

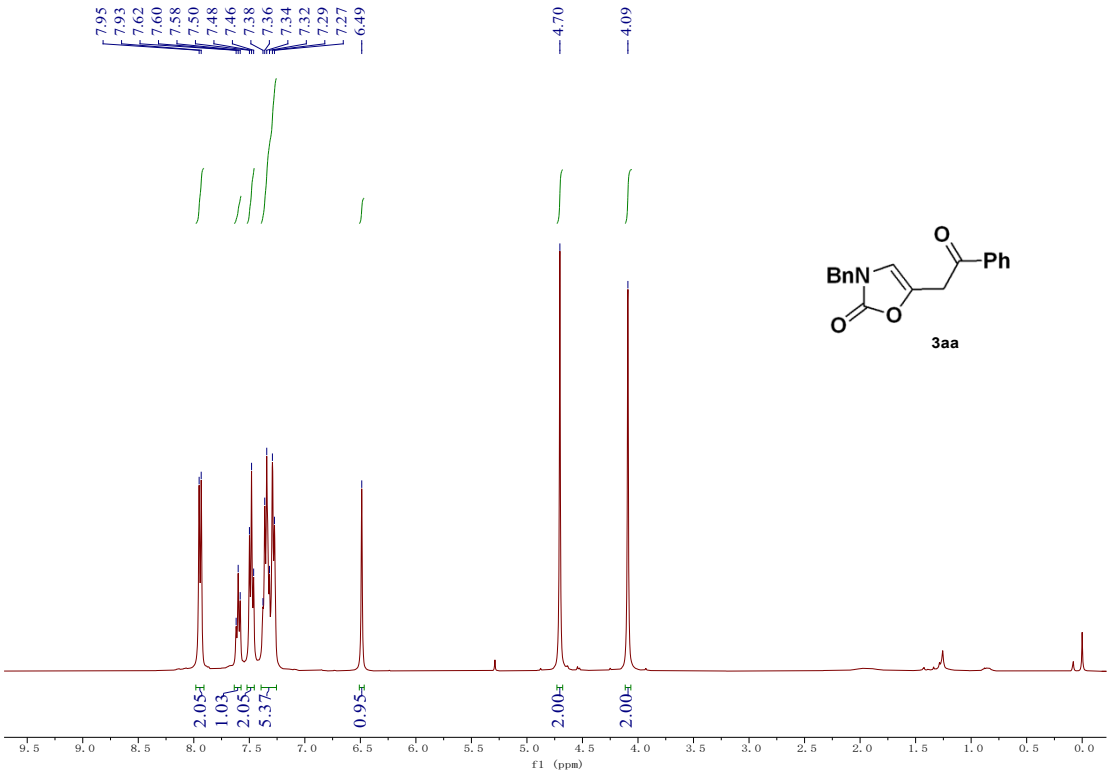


(E)-3-benzyl-5-(2-oxo-2-phenylethylidene) oxazolidin-2-one (4aa), white solid, m.p. 145-147 ^{o}C, R_f = 0.6 (EtOAc/petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.41 – 7.30 (m, 5H), 6.86 (t, J = 2.5 Hz, 1H), 4.64 (d, J = 2.4 Hz, 2H), 4.55 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$):190.0, 163.1, 153.6, 137.8, 134.4, 133.0, 129.1, 128.7, 128.5, 128.4, 127.8, 98.5, 50.8, 48.0. **IR:** 1781, 1742, 1677, 1605, 1573, 1494, 1447, 1416, 1388, 1364, 1332, 1301, 1273, 1226, 1205, 1190, 1149, 1081, 1059, 1012, 887, 831, 758, 748, 698, 677, 633, 591, 544 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{18}H_{16}NO_3^+$ [M+H$^+$] 294.1125, found: 294.1120.

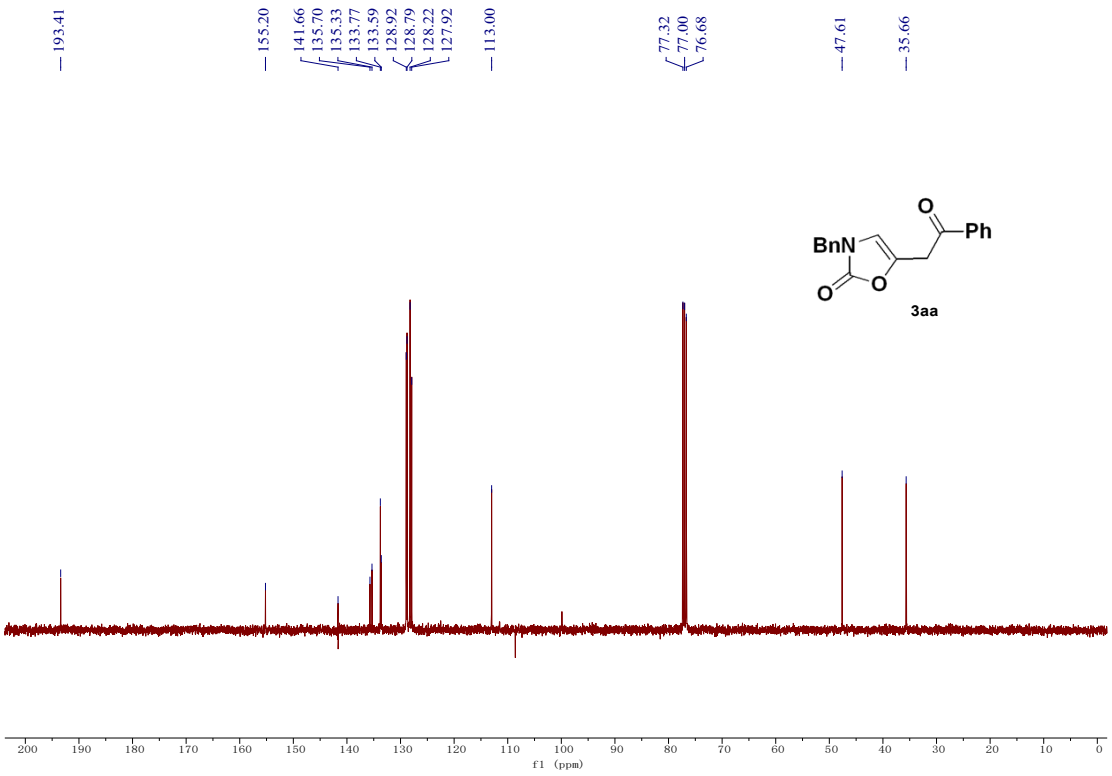


4-(benzylamino)-4-methyl-1-phenylpent-2-yn-1-one (3na'), yellow oil, R_f = 0.6 (EtOAc/petroleum ether = 1:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.1 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.52 – 7.47 (m, 2H), 7.41 – 7.23 (m, 6H), 3.98 (s, 2H), 1.57 (s, 6H). **^{3}C NMR** (101 MHz, $CDCl_3$):178.0, 140.0, 136.9, 134.0, 129.5, 128.6, 128.5, 128.3, 127.2, 99.6, 80.6, 50.6, 49.2, 29.0.

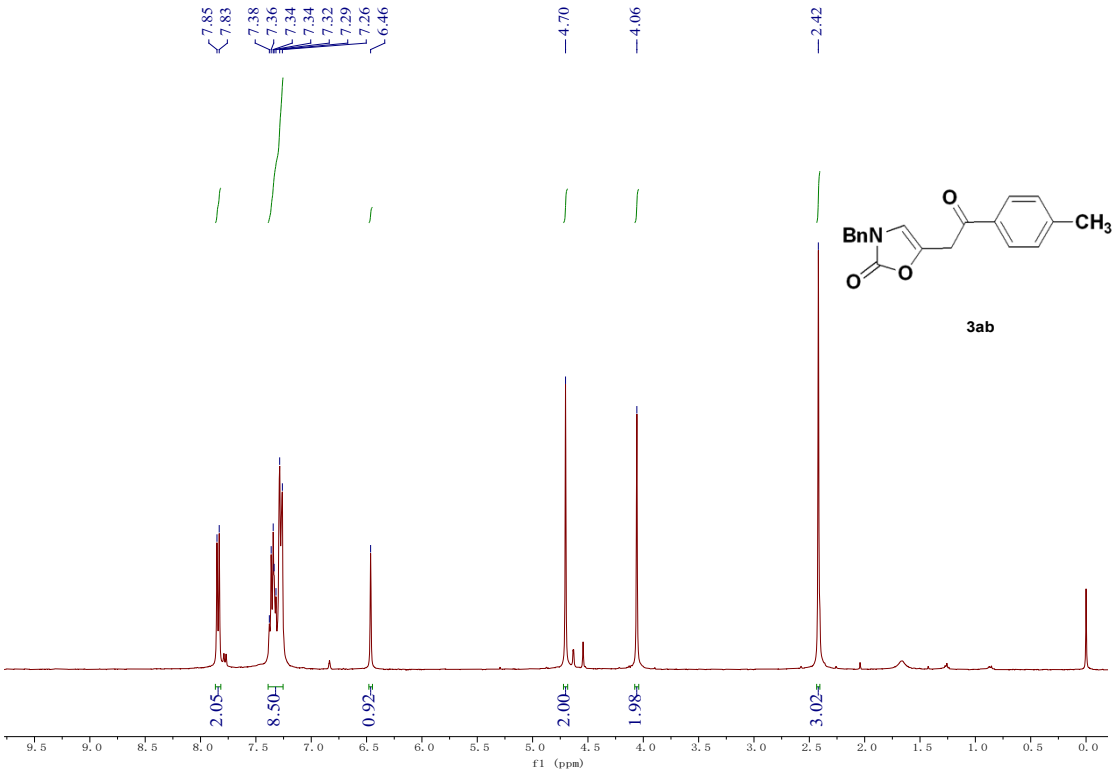
7. ^{1}H and ^{13}C Spectra of all Products



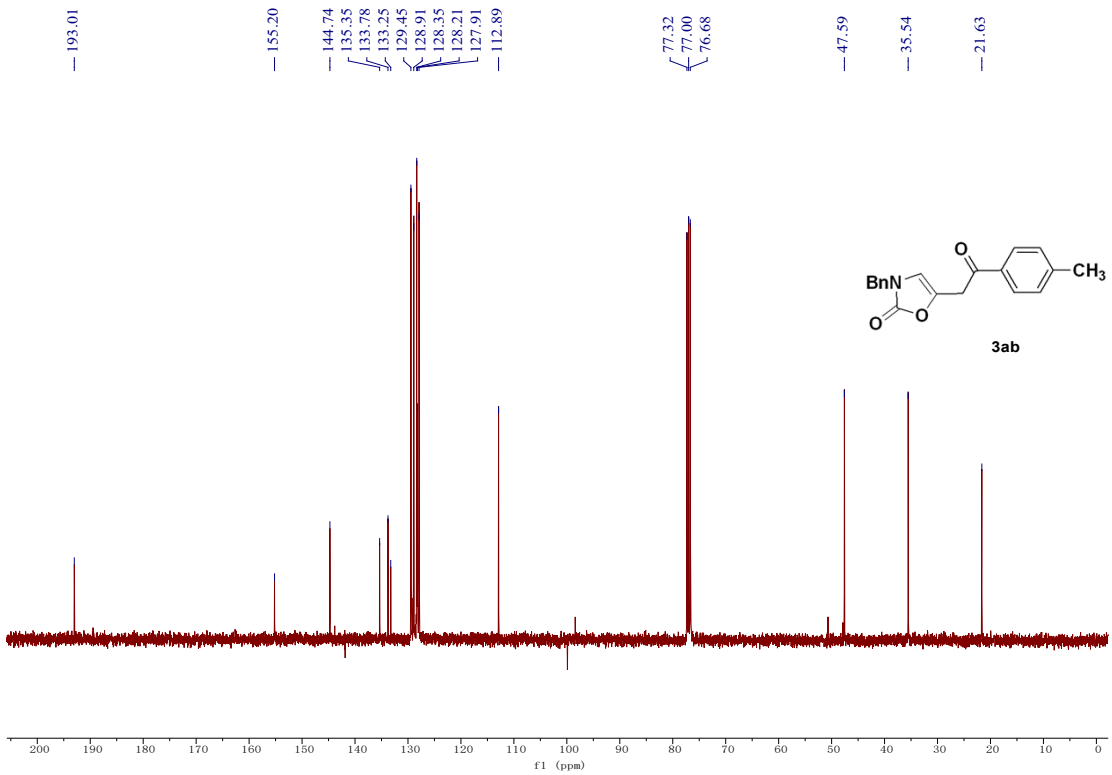
^{1}H NMR (400 MHz, $CDCl_3$)



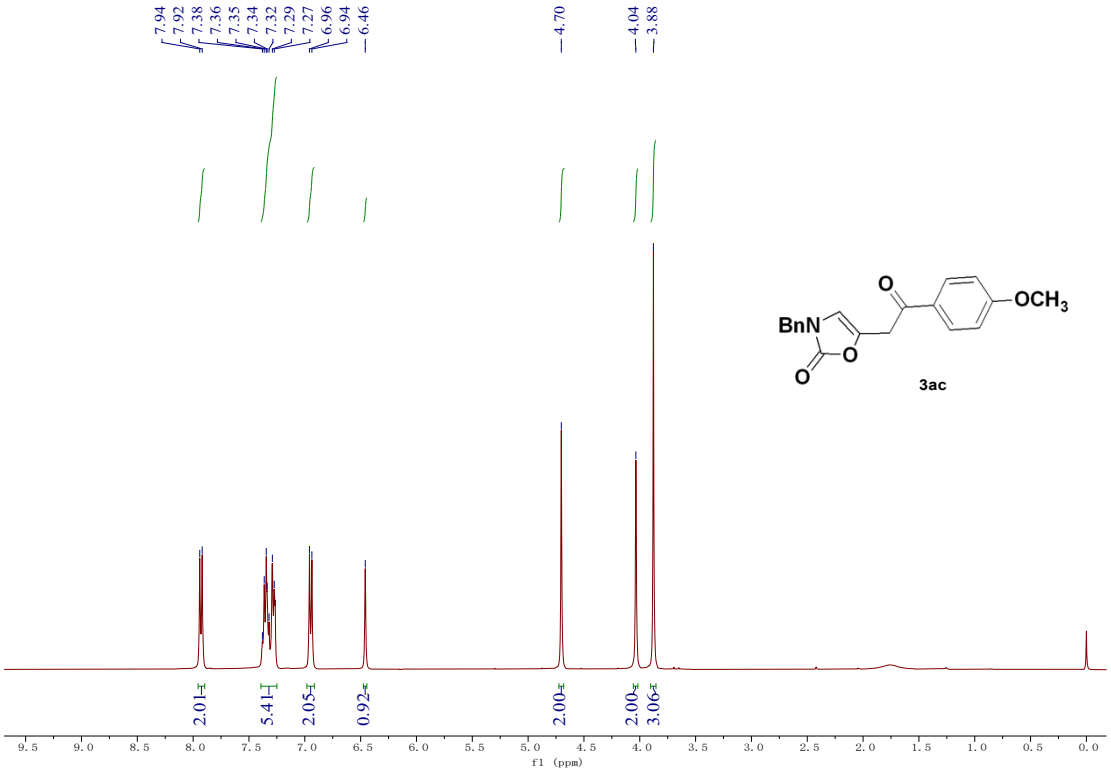
^{13}C NMR (101 MHz, $CDCl_3$)



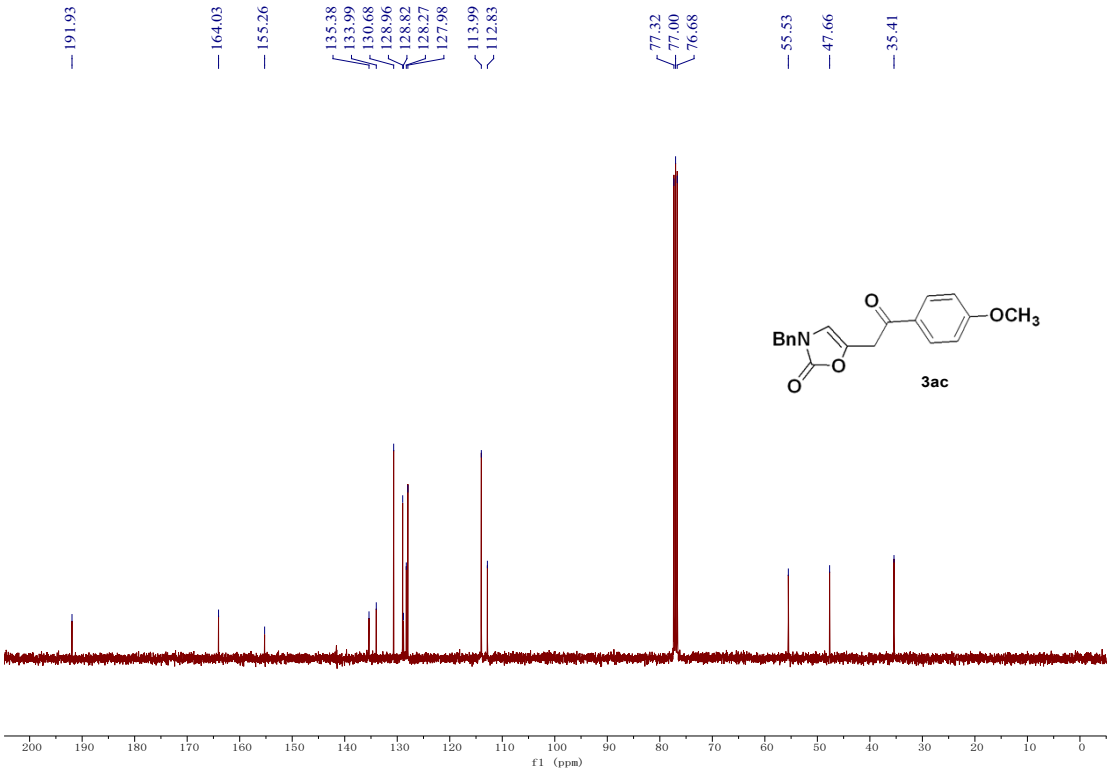
^{1}H NMR (400 MHz, $CDCl_3$)



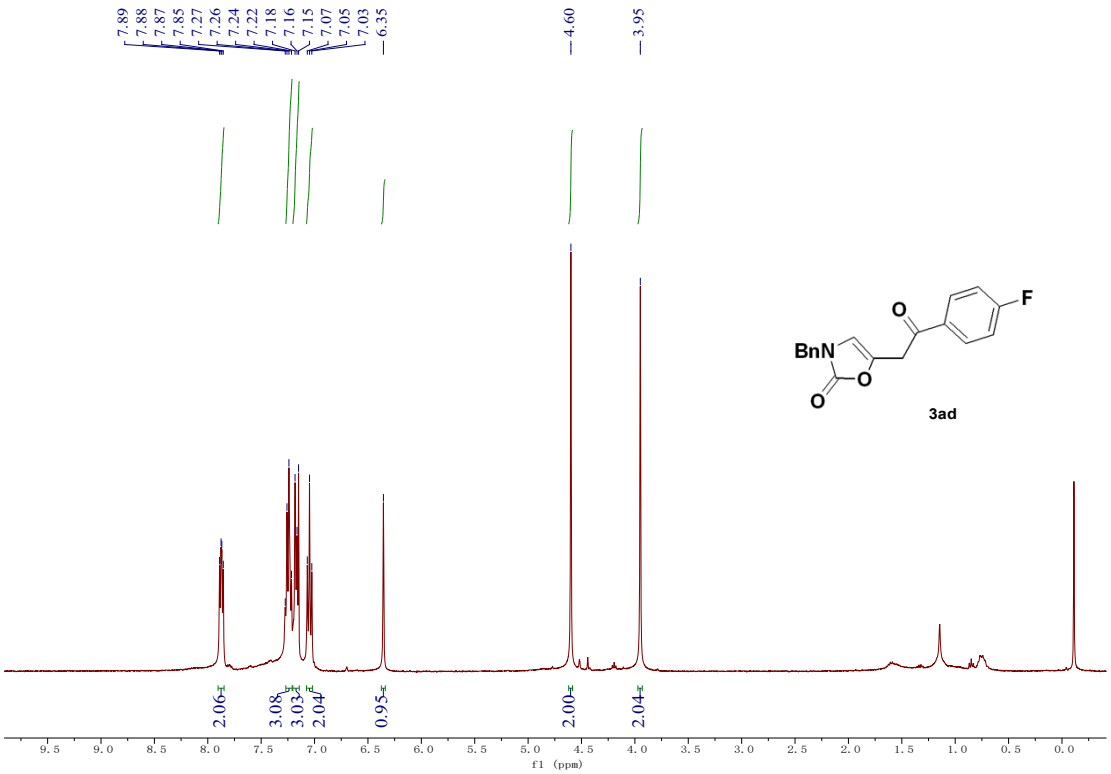
^{13}C NMR (101 MHz, $CDCl_3$)



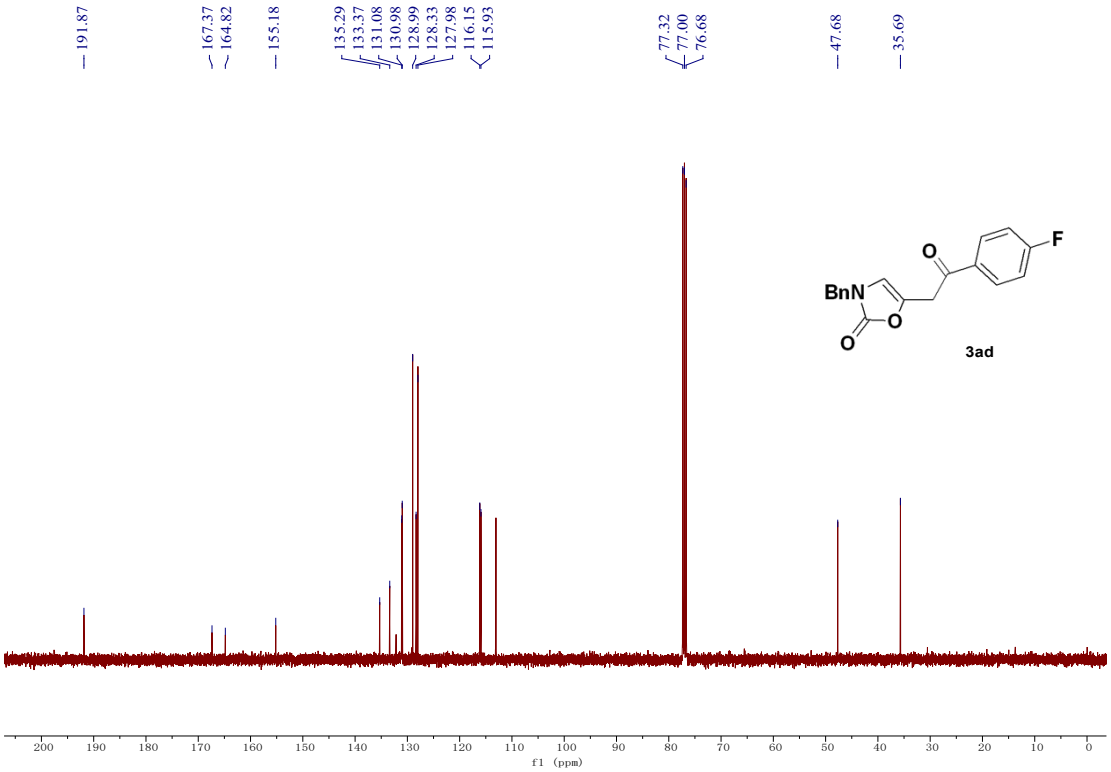
^{1}H NMR (400 MHz, $CDCl_3$)



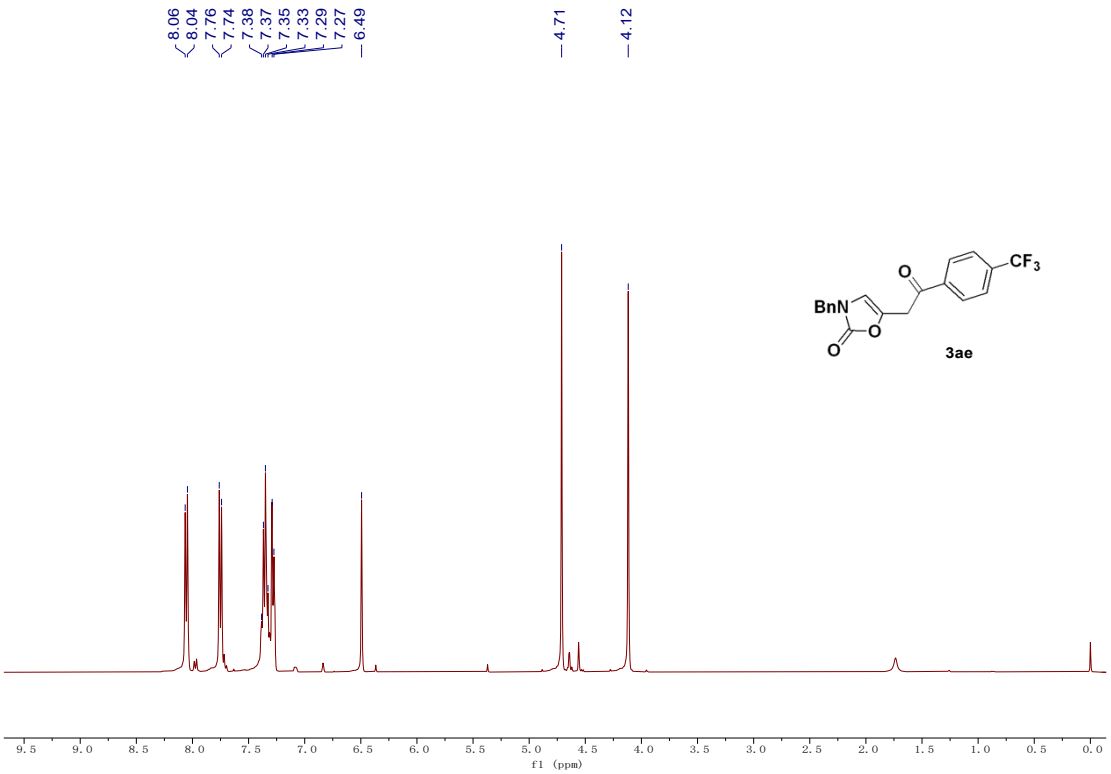
^{13}C NMR (101 MHz, $CDCl_3$)



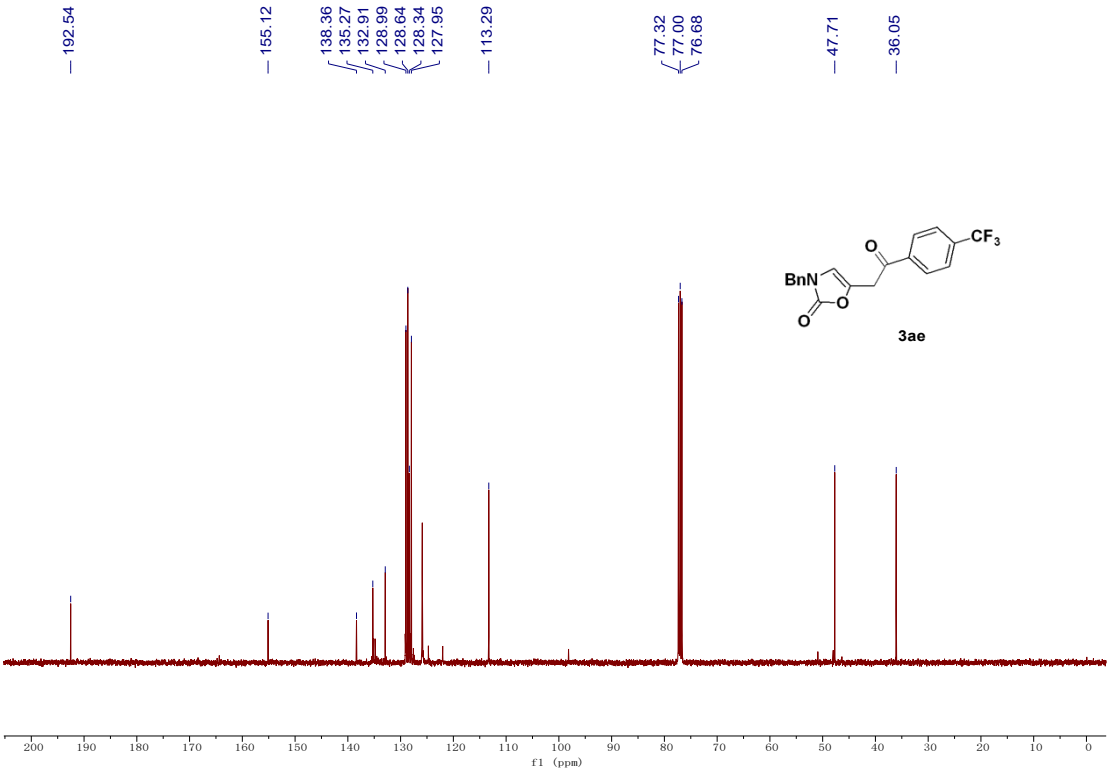
^{1}H NMR (400 MHz, $CDCl_3$)



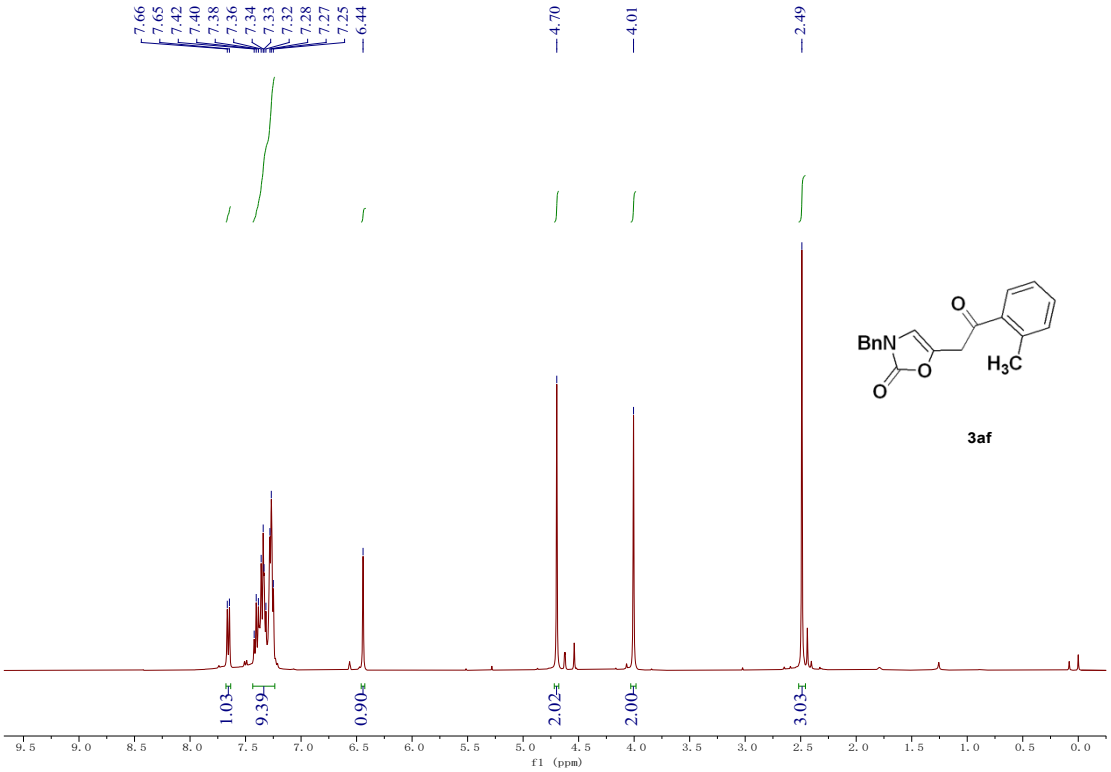
^{13}C NMR (101 MHz, $CDCl_3$)



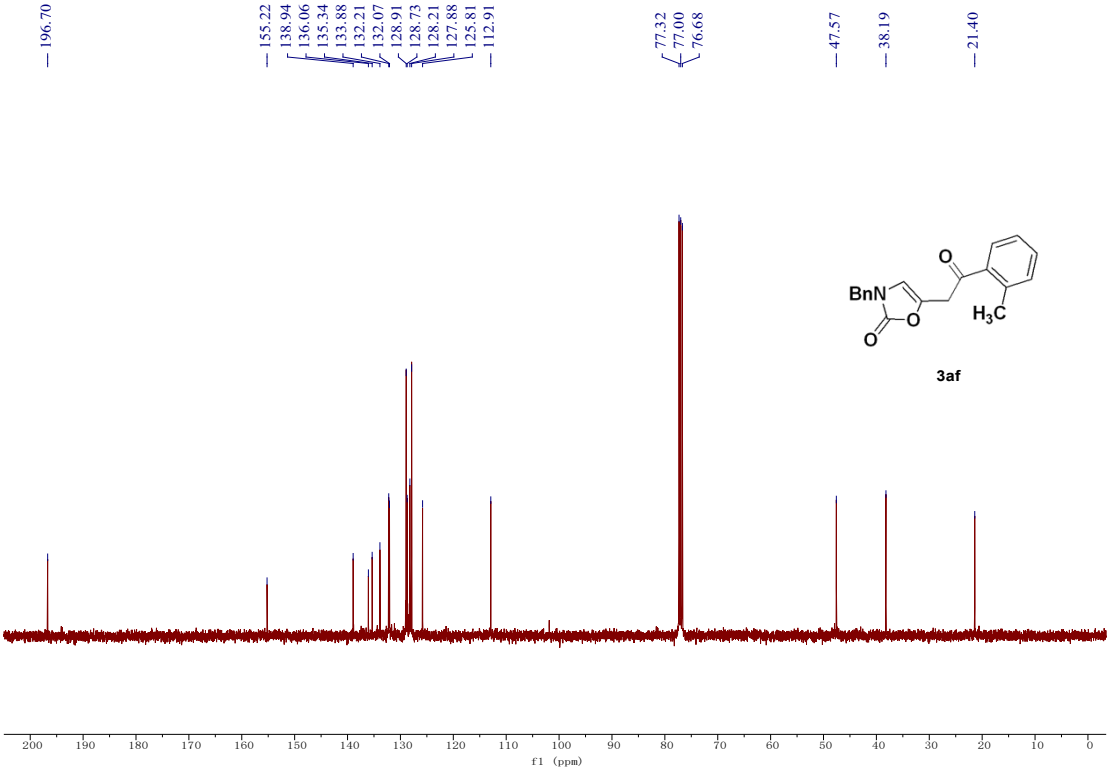
^{1}H NMR (400 MHz, $CDCl_3$)



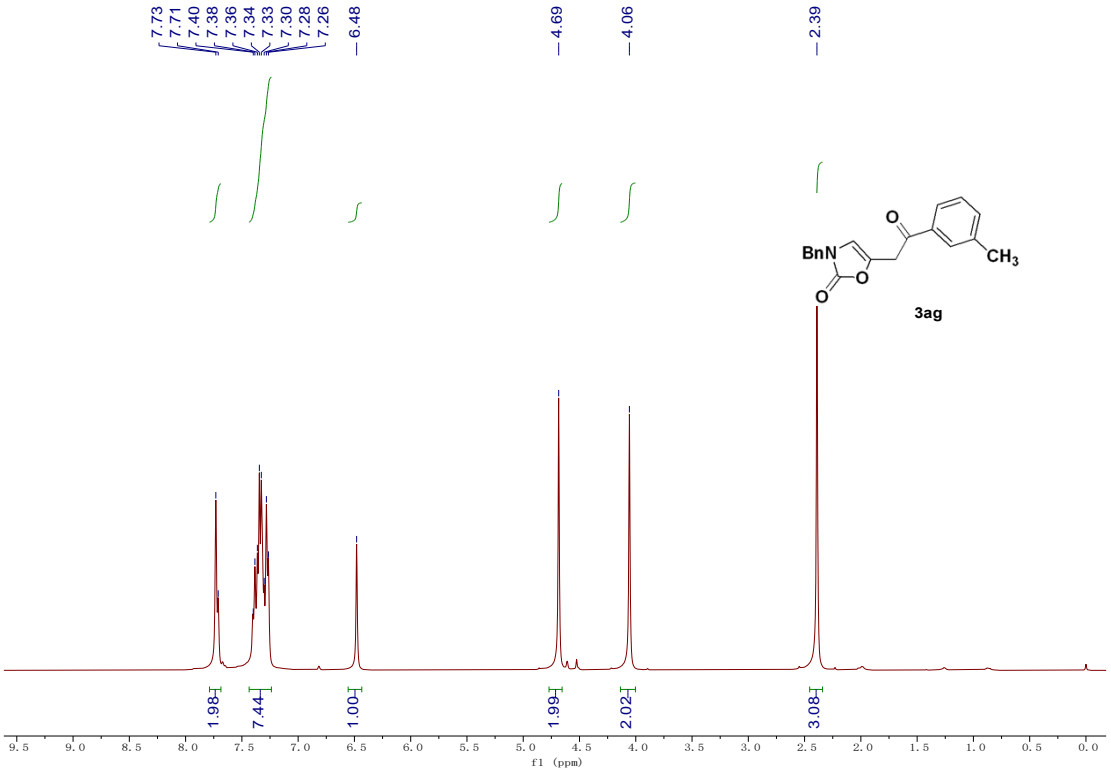
^{13}C NMR (101 MHz, $CDCl_3$)



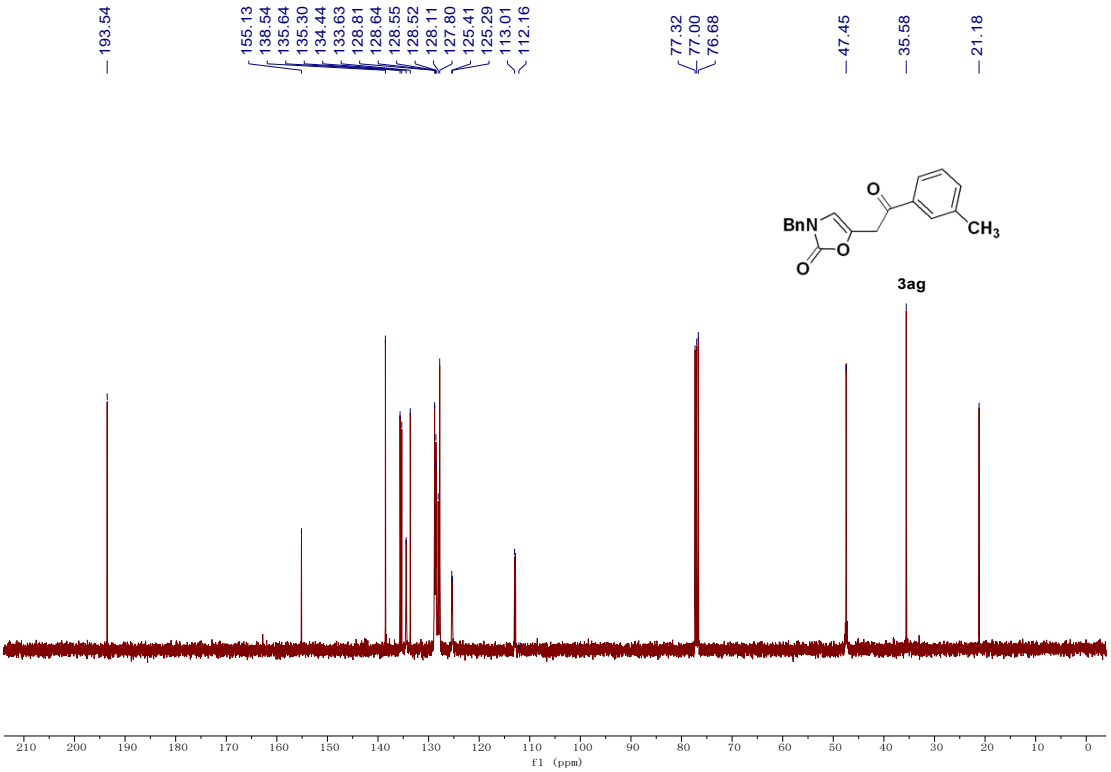
^{1}H NMR (400 MHz, $CDCl_3$)



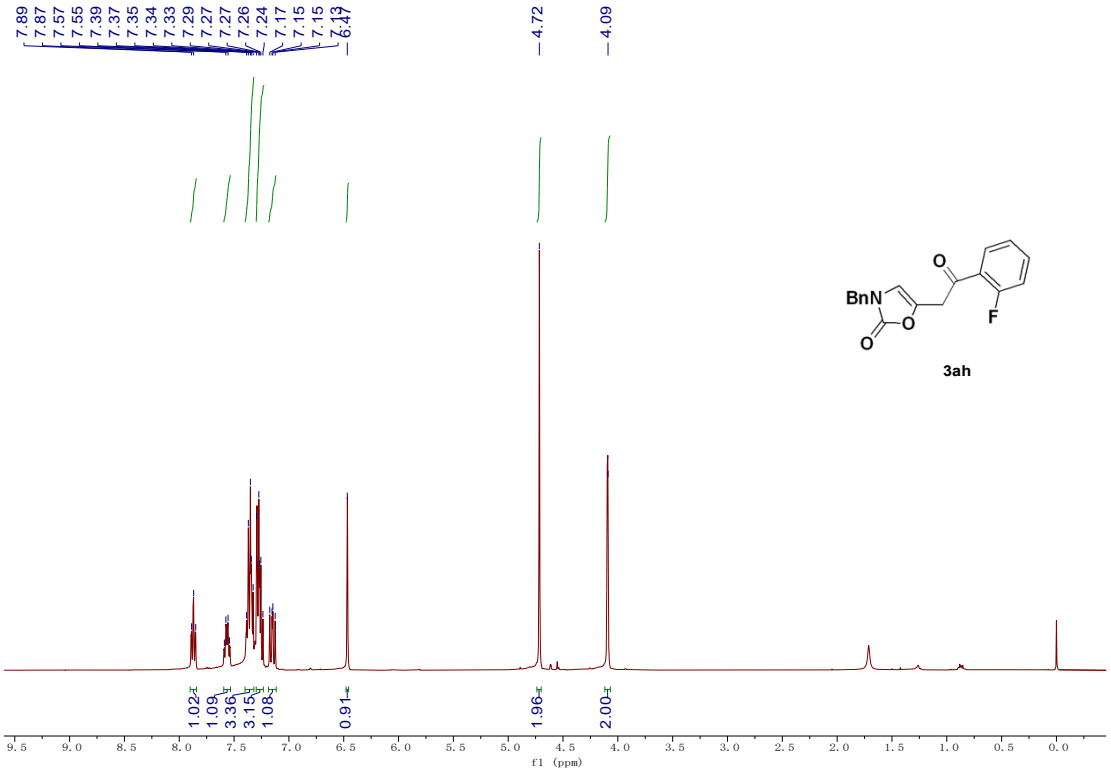
^{13}C NMR (101 MHz, $CDCl_3$)



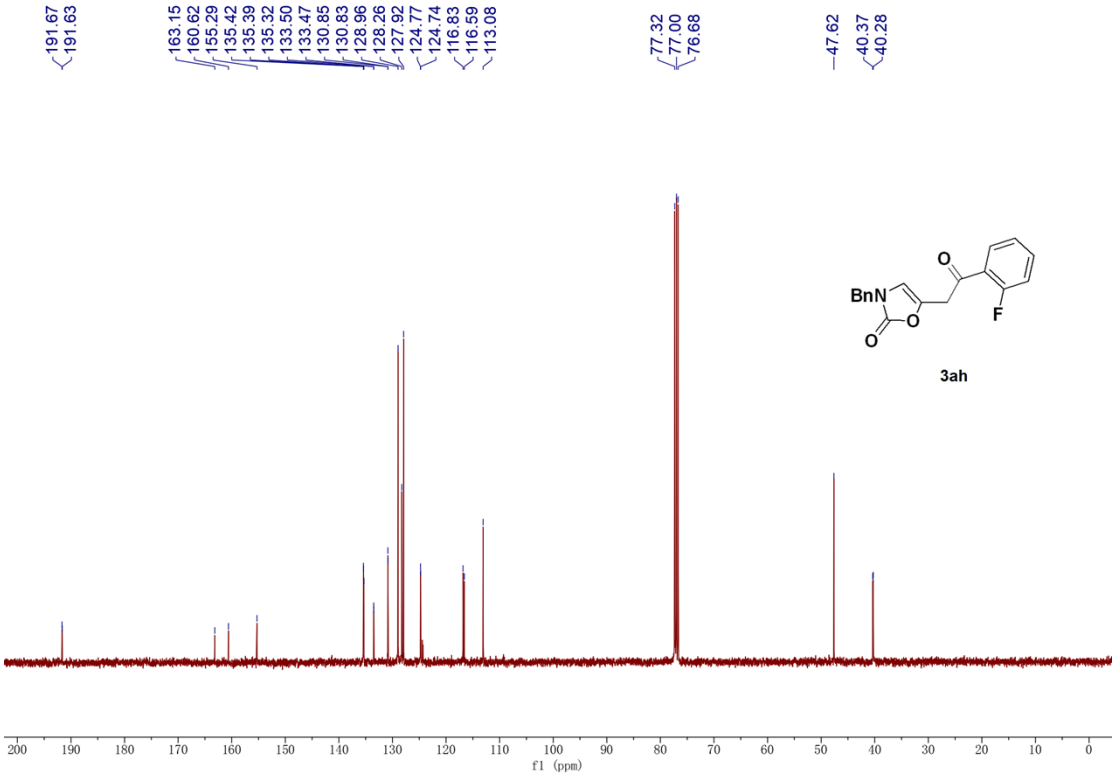
^{1}H NMR (400 MHz, $CDCl_3$)



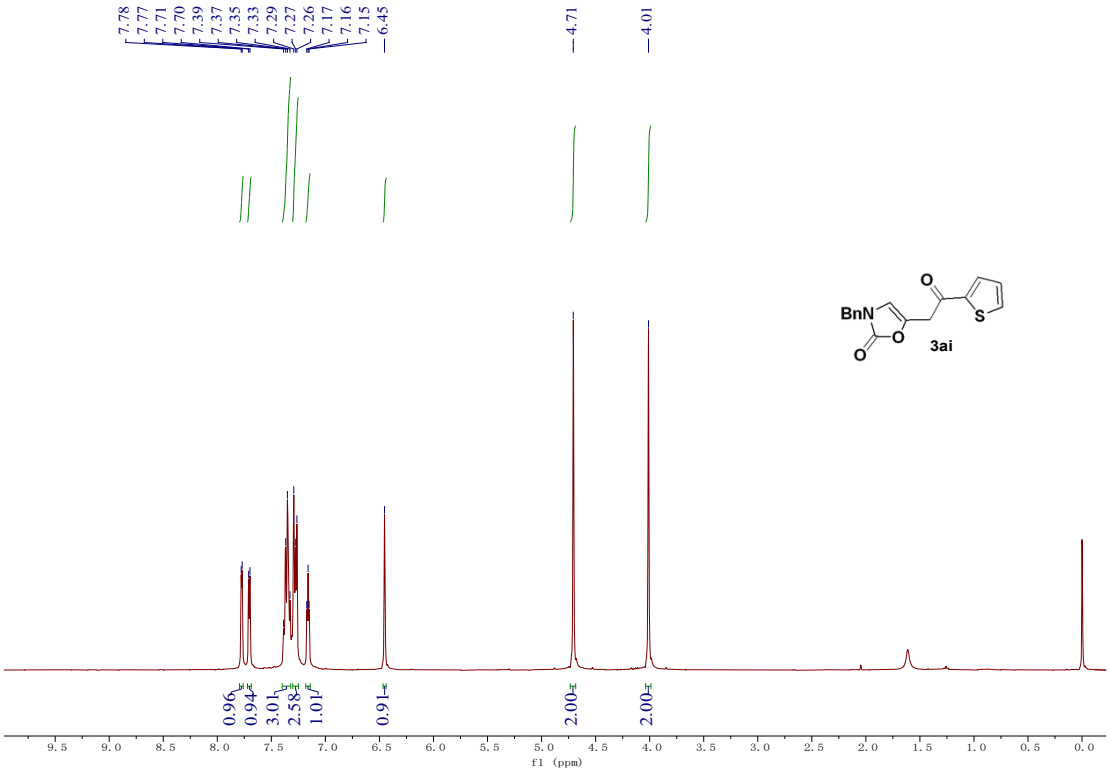
^{13}C NMR (101 MHz, $CDCl_3$)



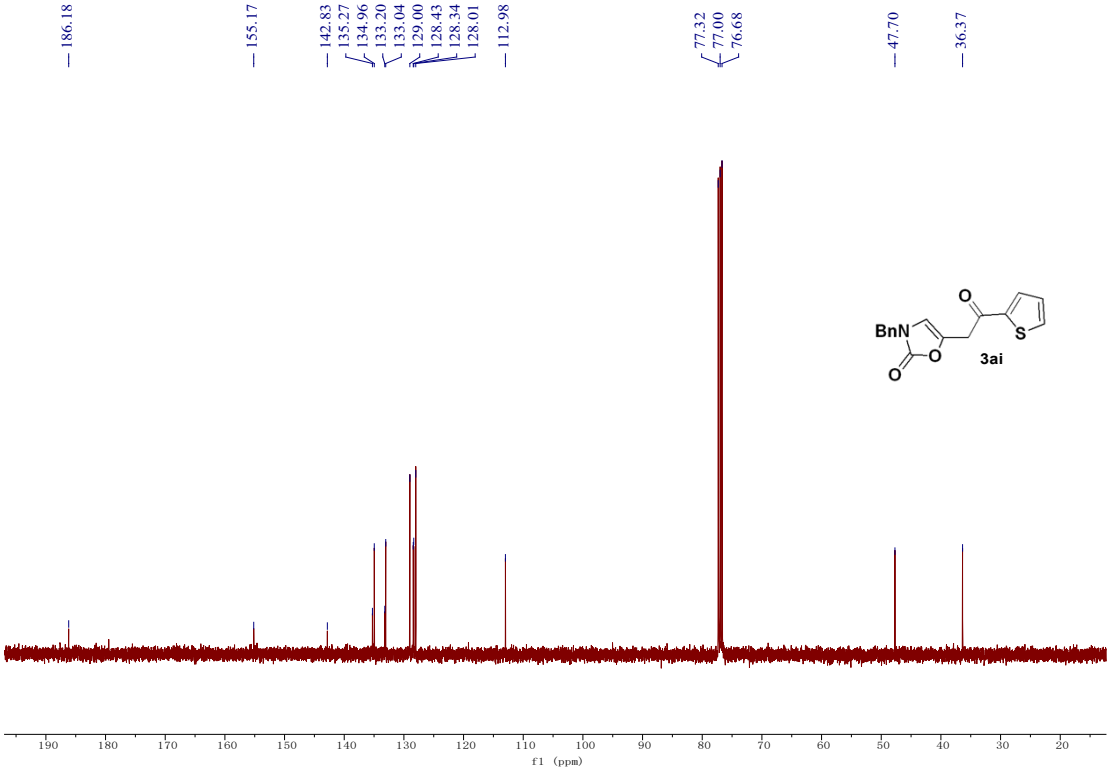
^{1}H NMR (400 MHz, $CDCl_3$)



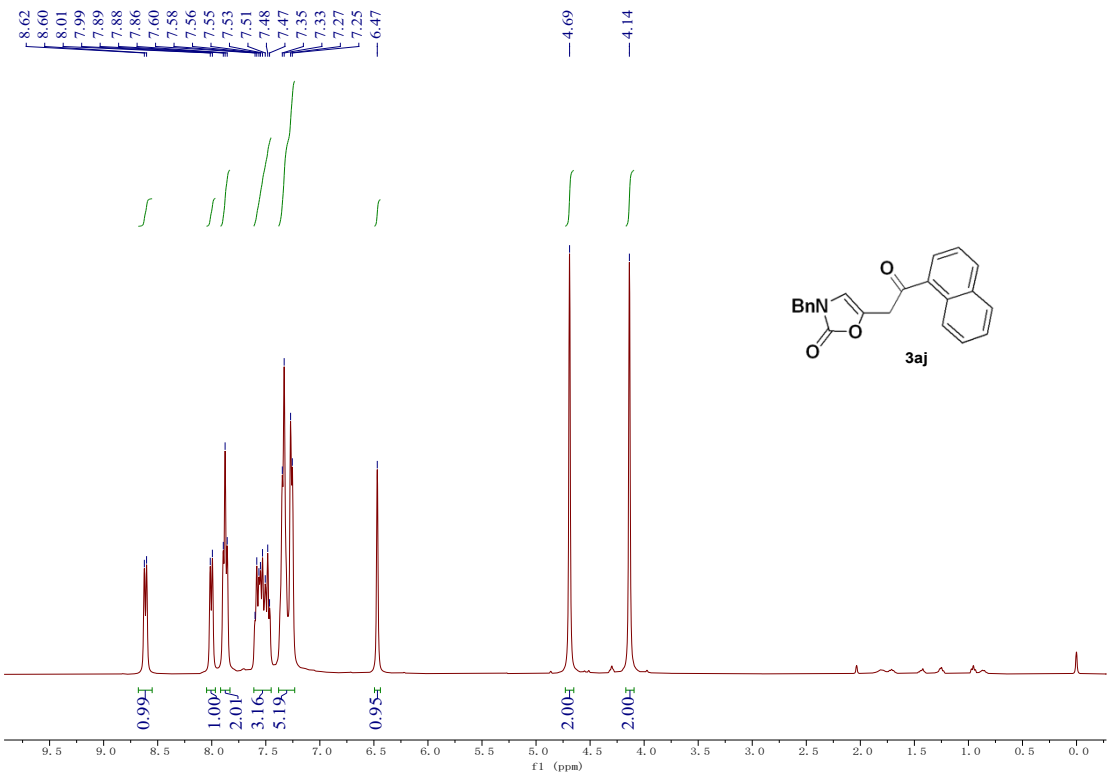
^{13}C NMR (101 MHz, $CDCl_3$)



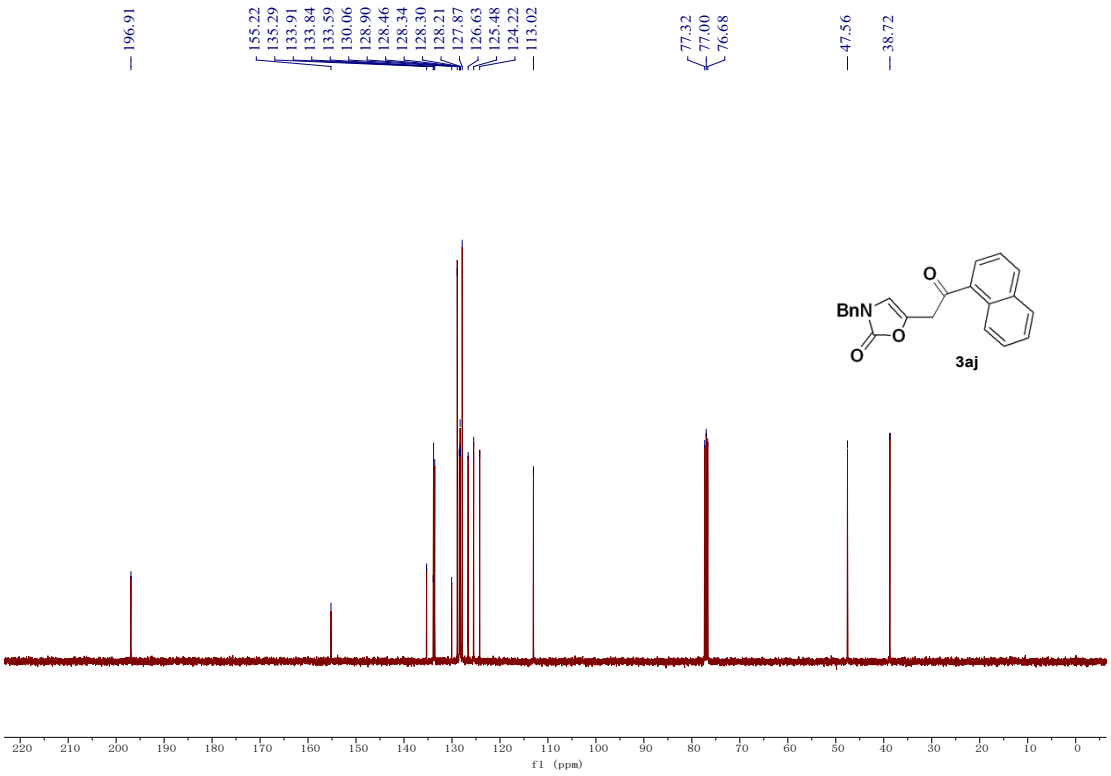
^{1}H NMR (400 MHz, $CDCl_3$)



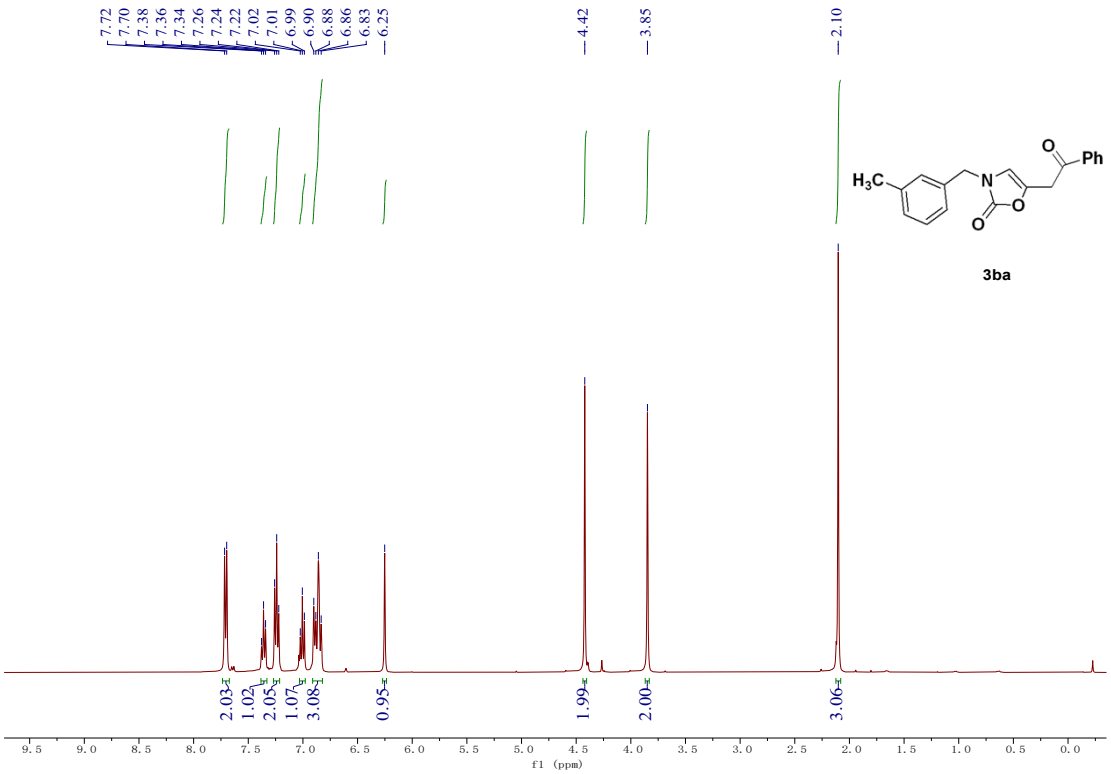
^{13}C NMR (101 MHz, $CDCl_3$)



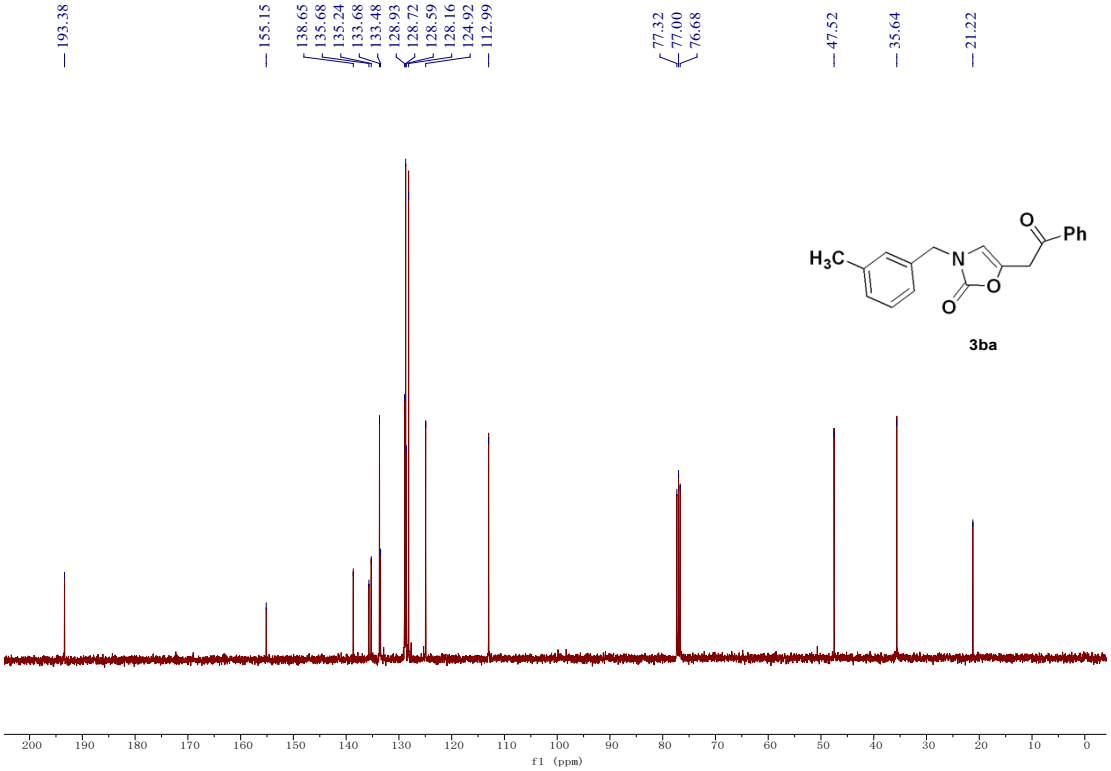
^{1}H NMR (400 MHz, $CDCl_3$)



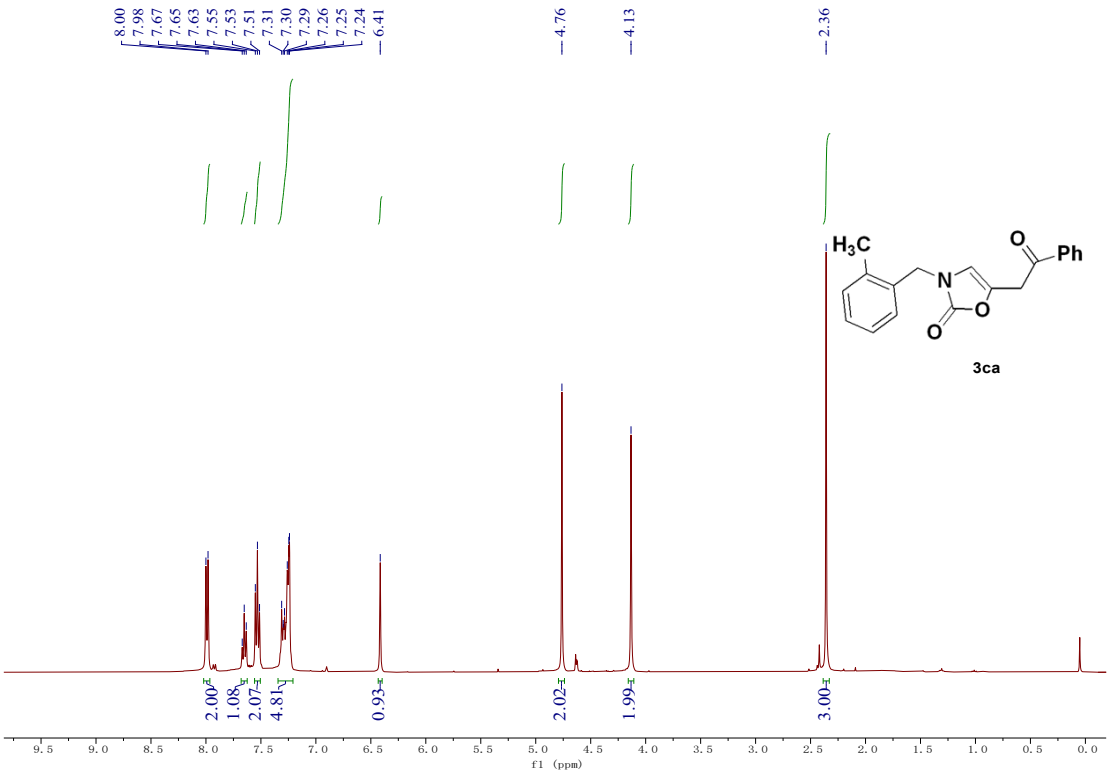
^{13}C NMR (101 MHz, $CDCl_3$)



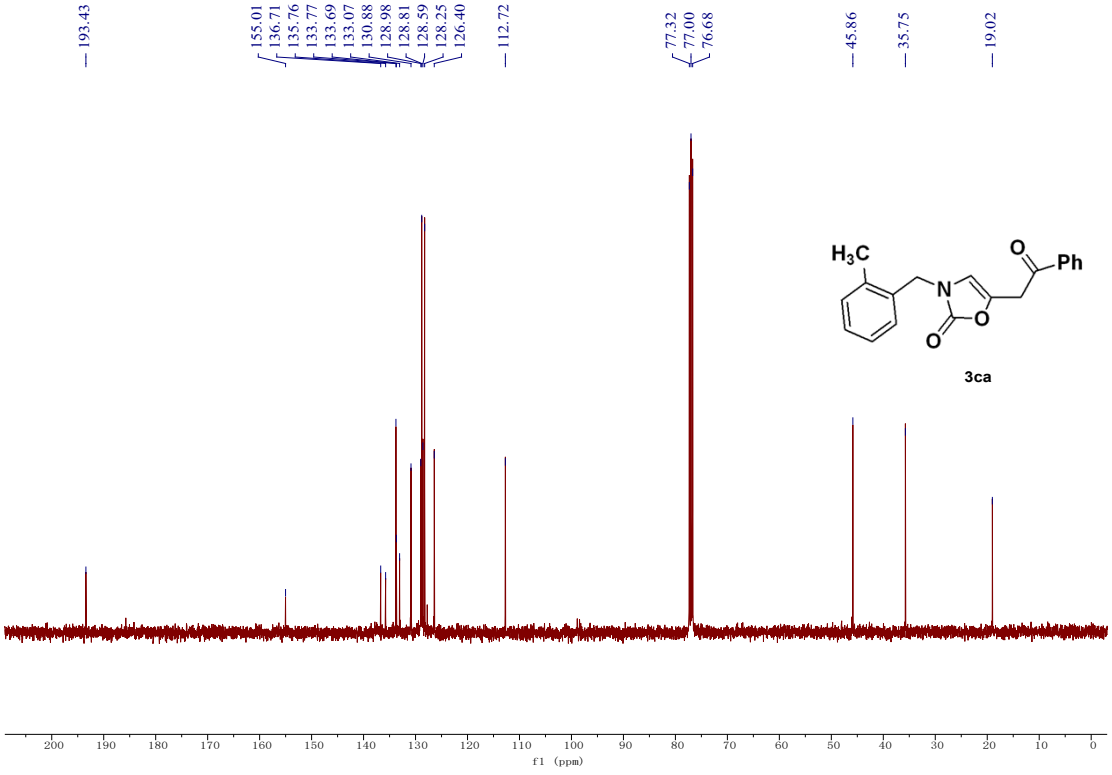
^{1}H NMR (400 MHz, $CDCl_3$)



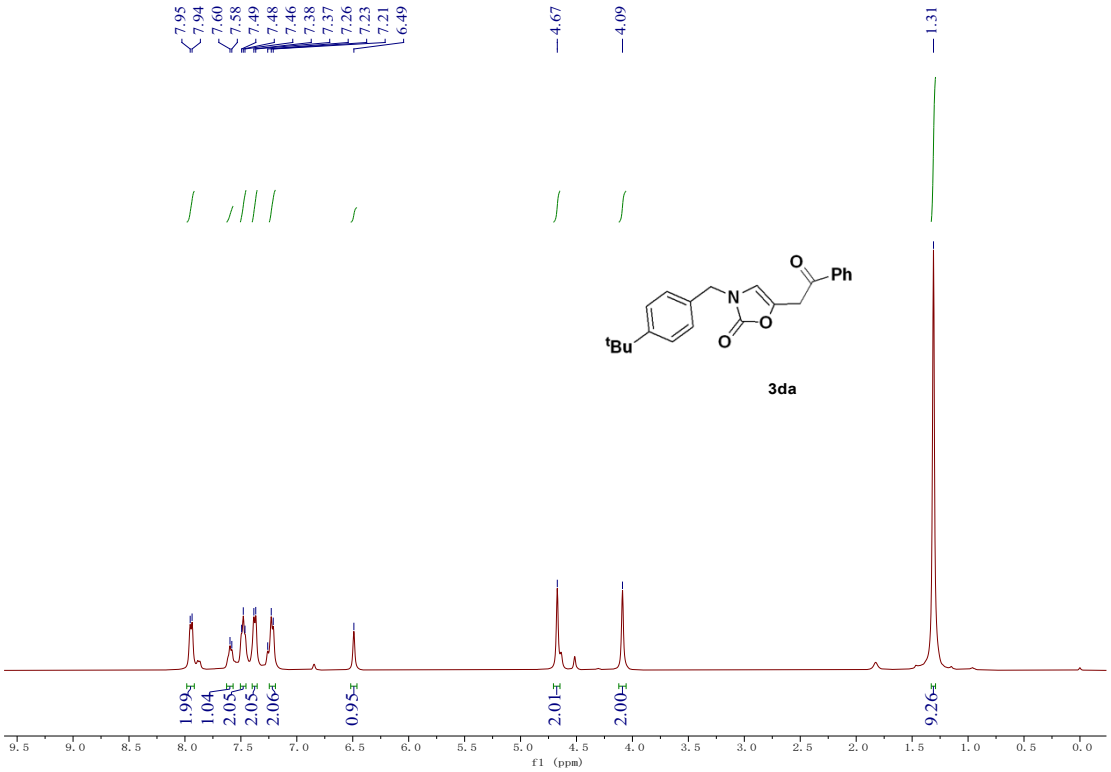
^{13}C NMR (101 MHz, $CDCl_3$)



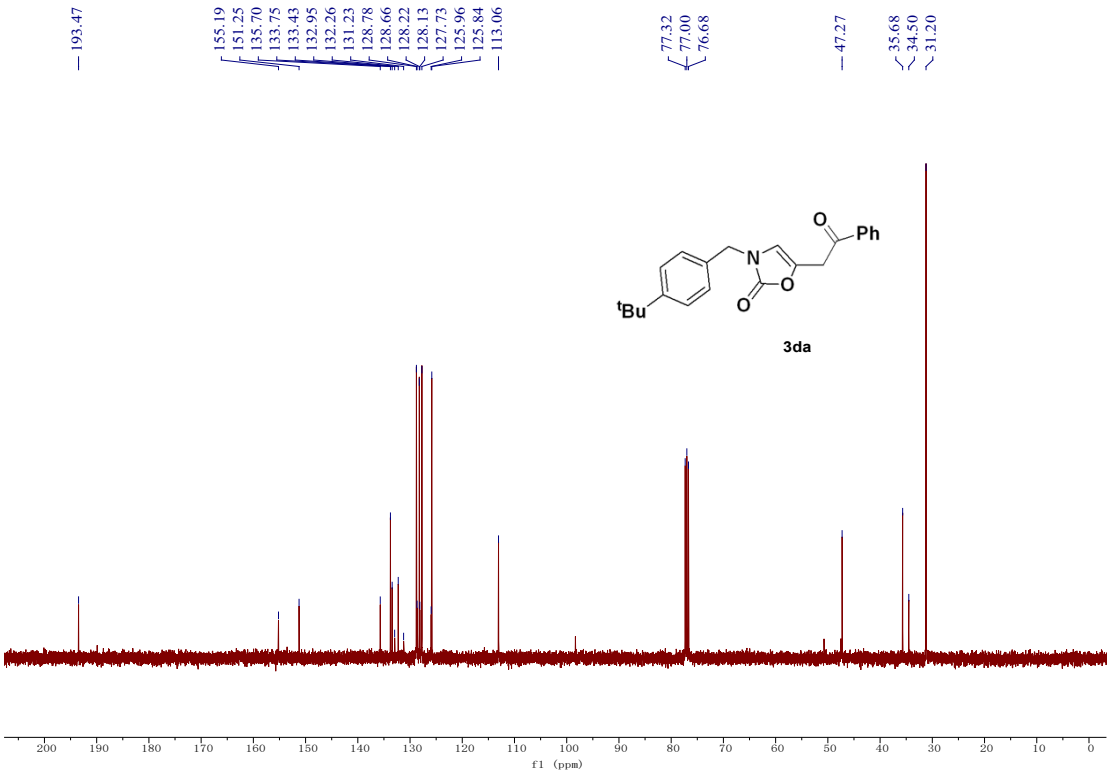
^{1}H NMR (400 MHz, $CDCl_3$)



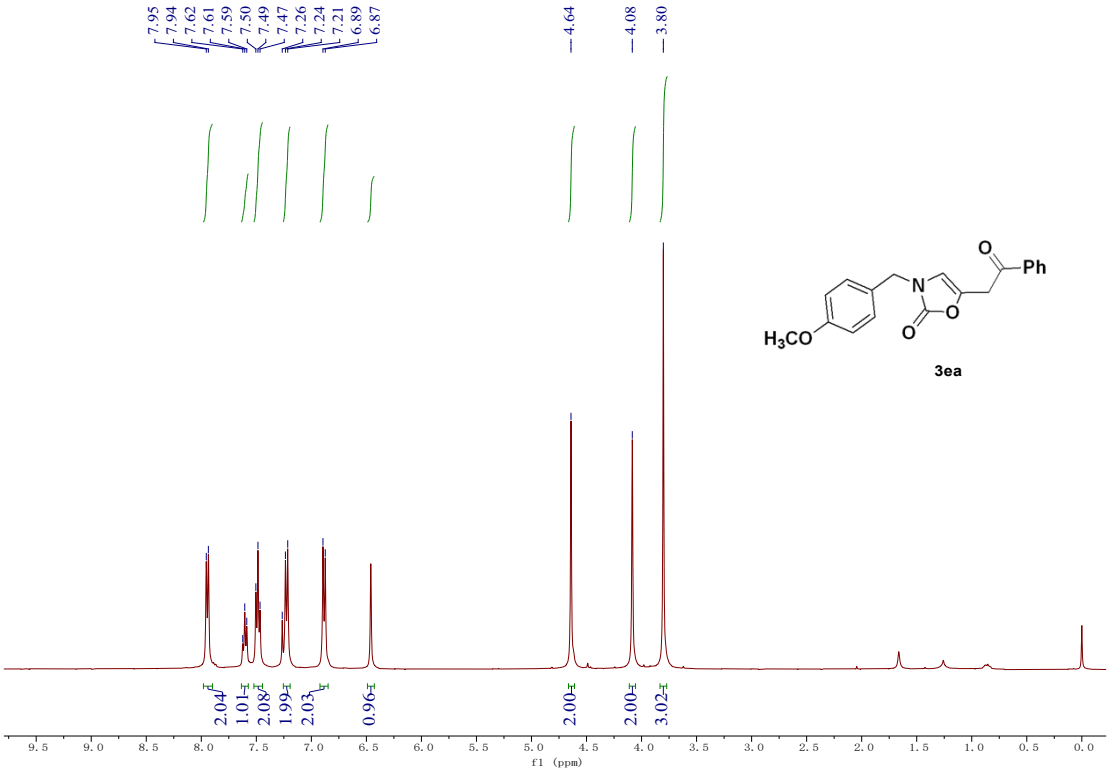
^{13}C NMR (101 MHz, $CDCl_3$)



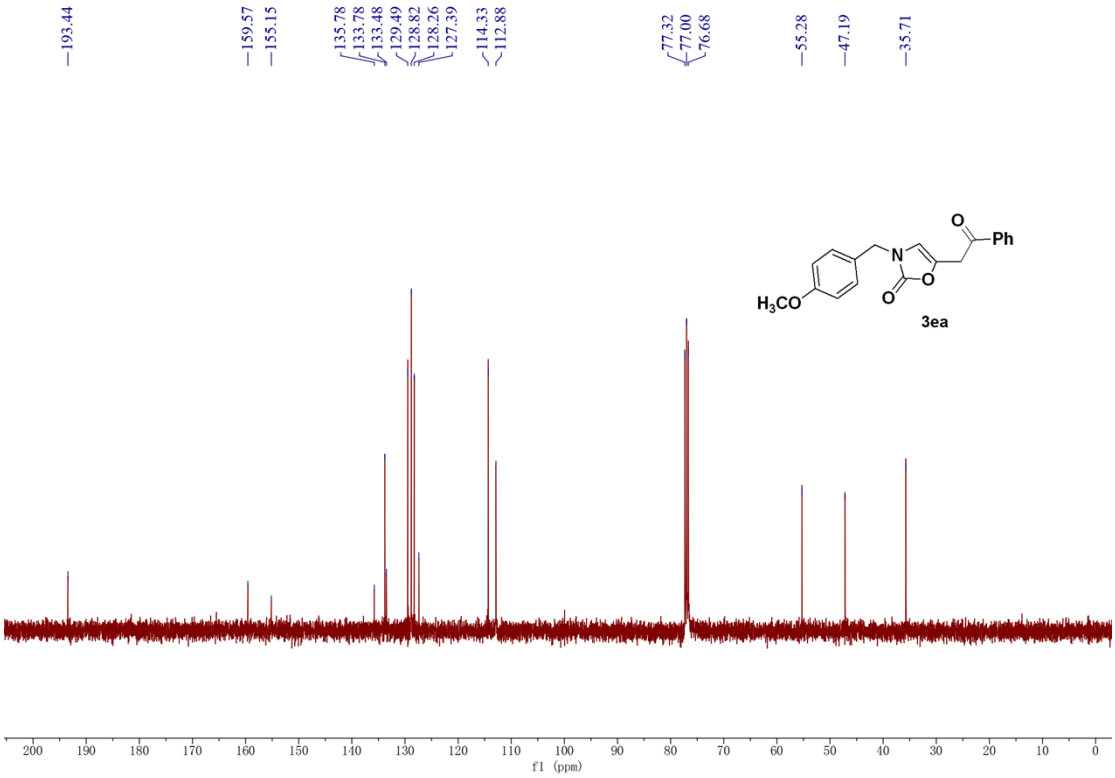
^{1}H NMR (400 MHz, $CDCl_3$)



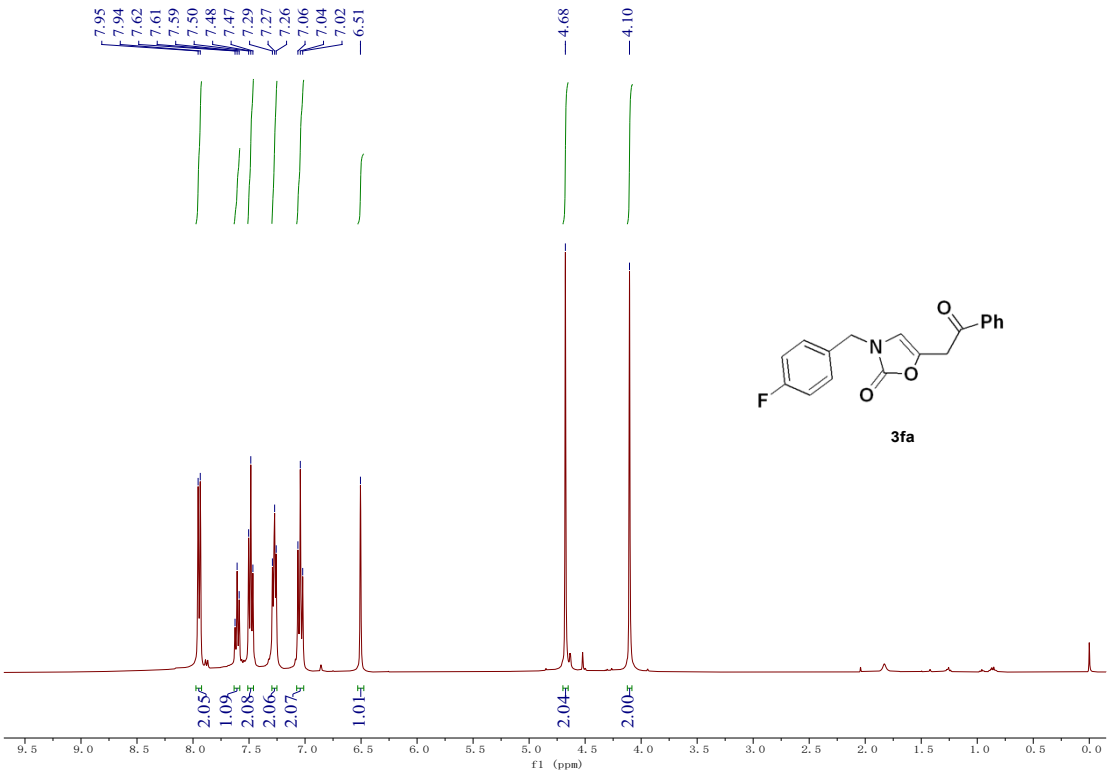
^{13}C NMR (101 MHz, $CDCl_3$)



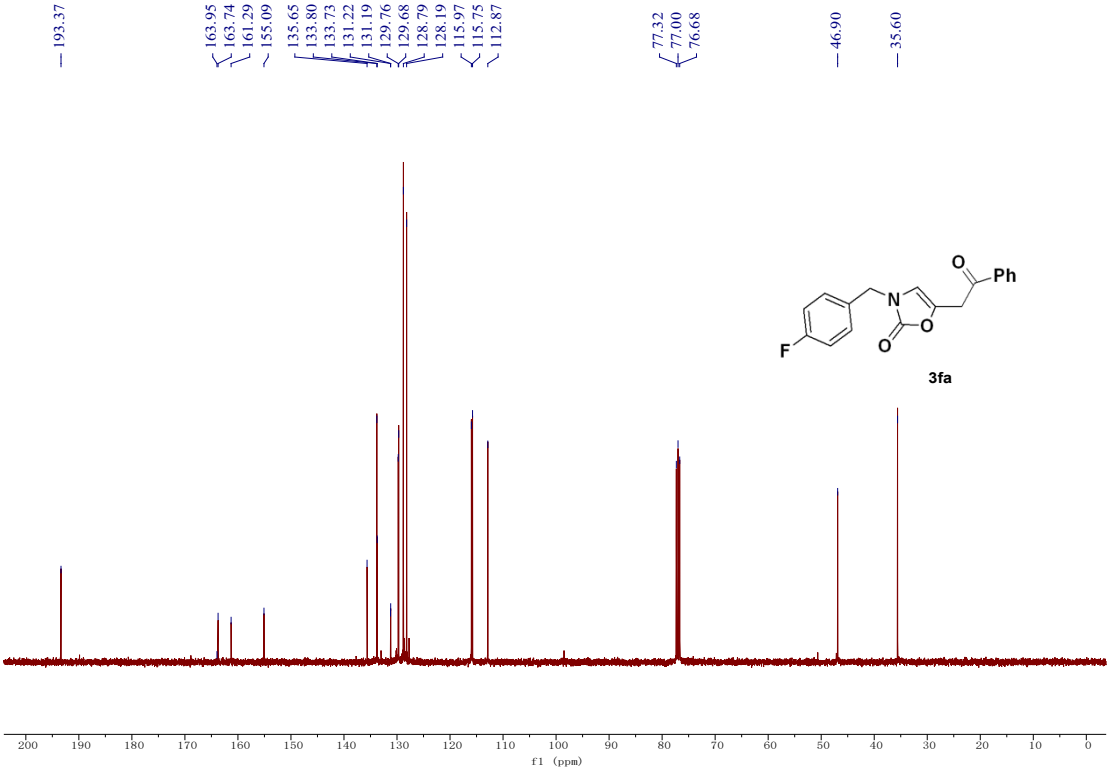
^{1}H NMR (400 MHz, $CDCl_3$)



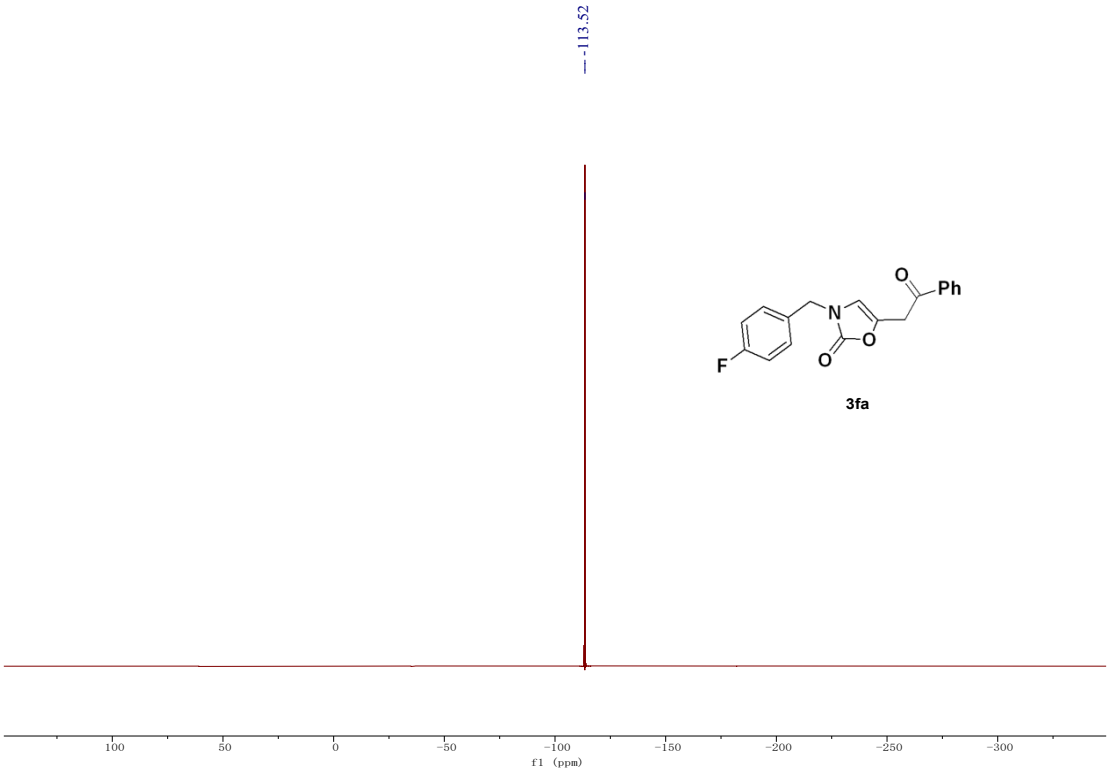
^{13}C NMR (101 MHz, $CDCl_3$)



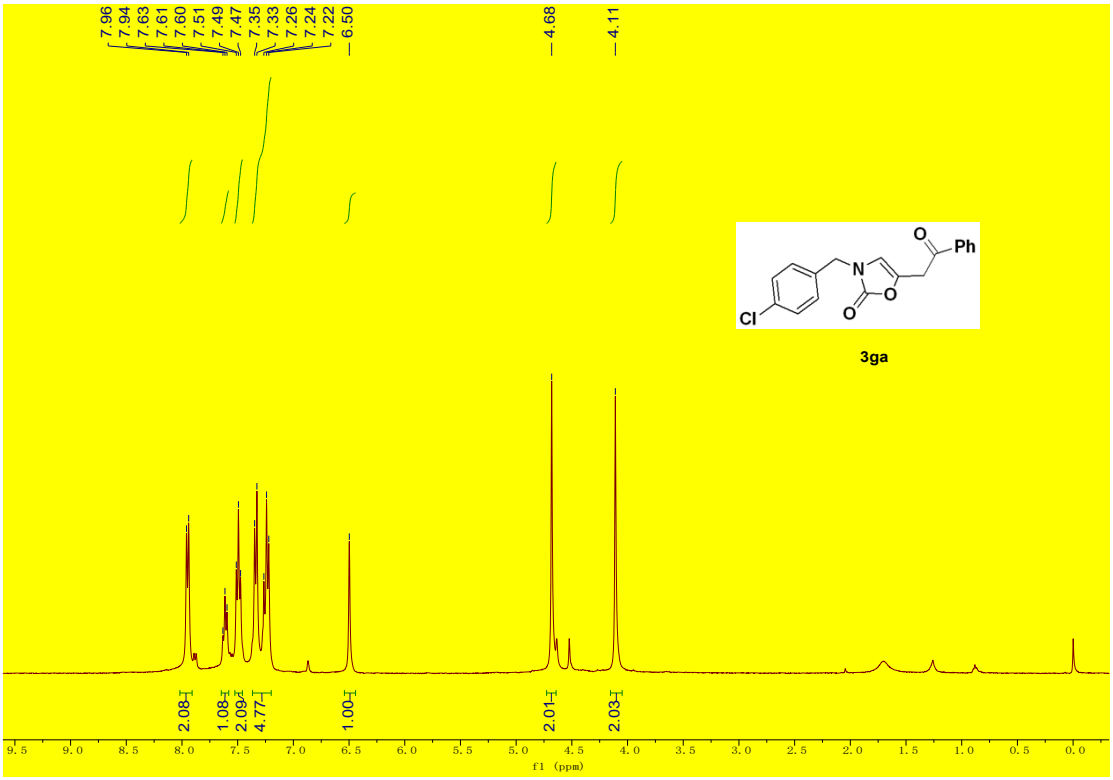
^{1}H NMR (400 MHz, $CDCl_3$)



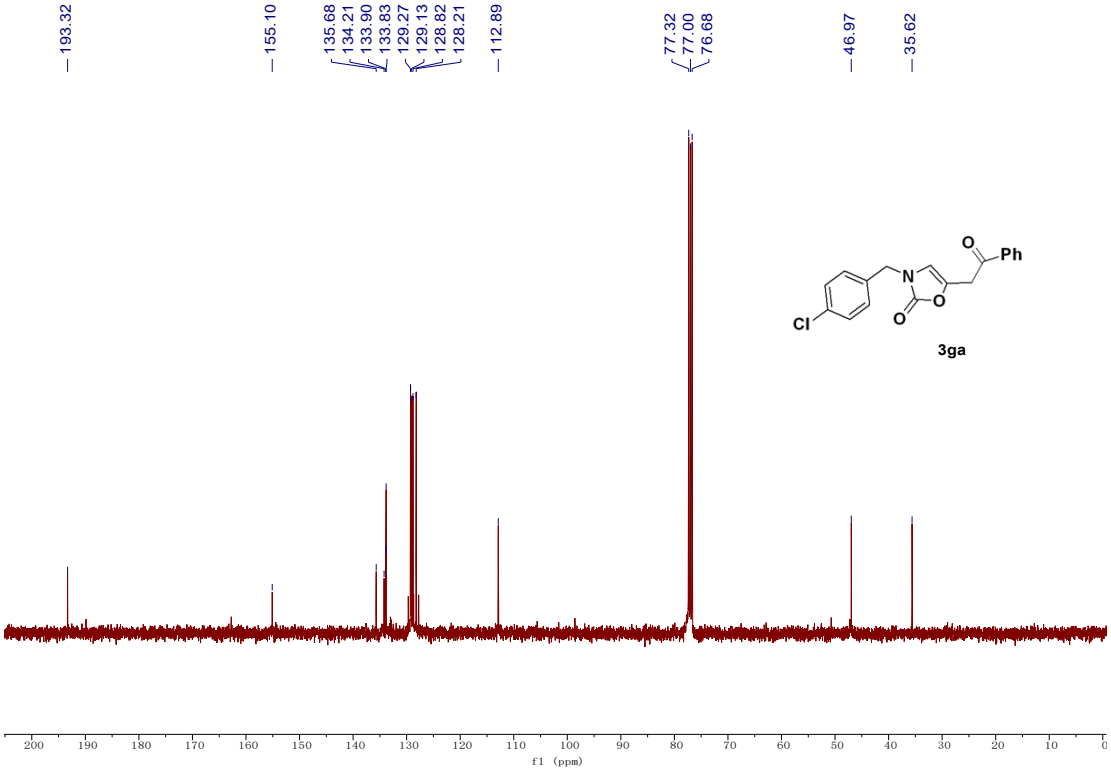
^{13}C NMR (101 MHz, $CDCl_3$)



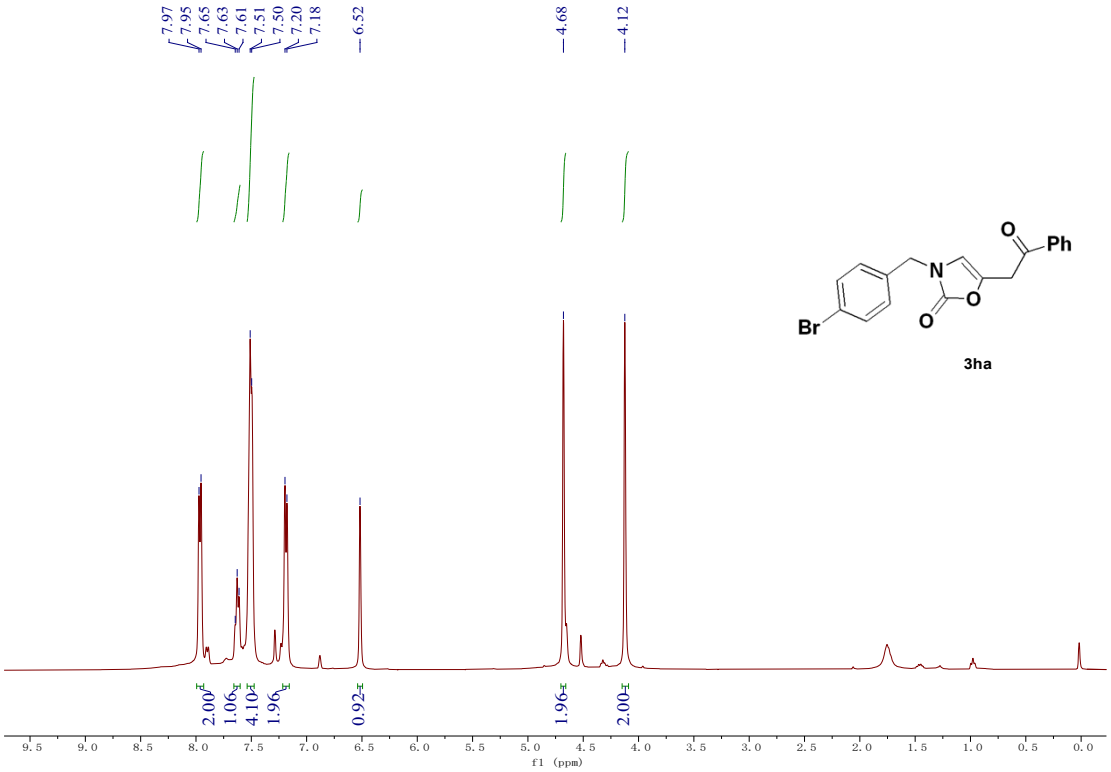
^{18}F NMR (162 MHz, $CDCl_3$)



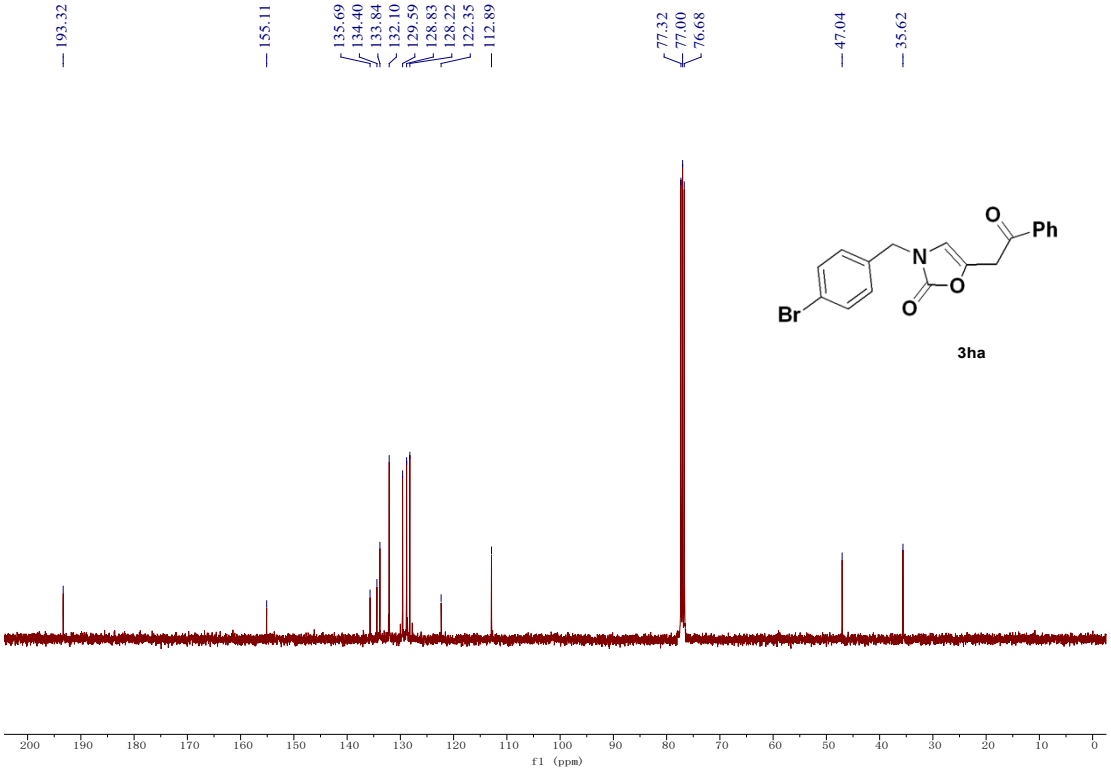
^{1}H NMR (400 MHz, $CDCl_3$)



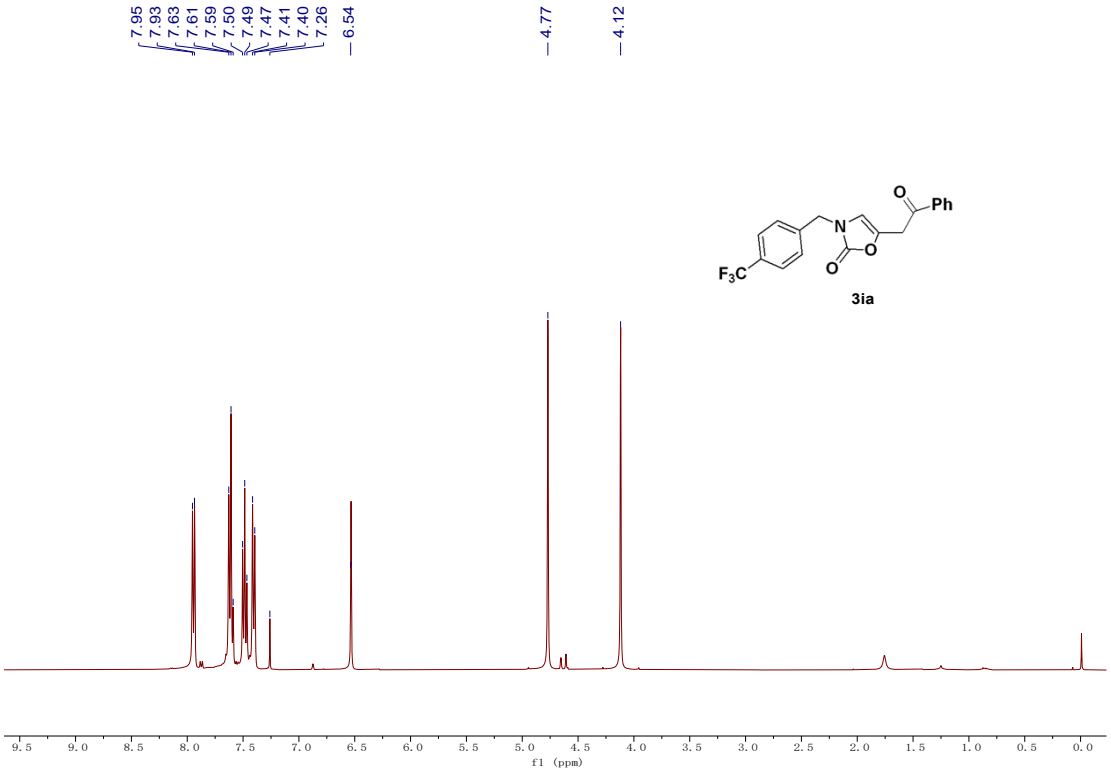
^{13}C NMR (101 MHz, $CDCl_3$)



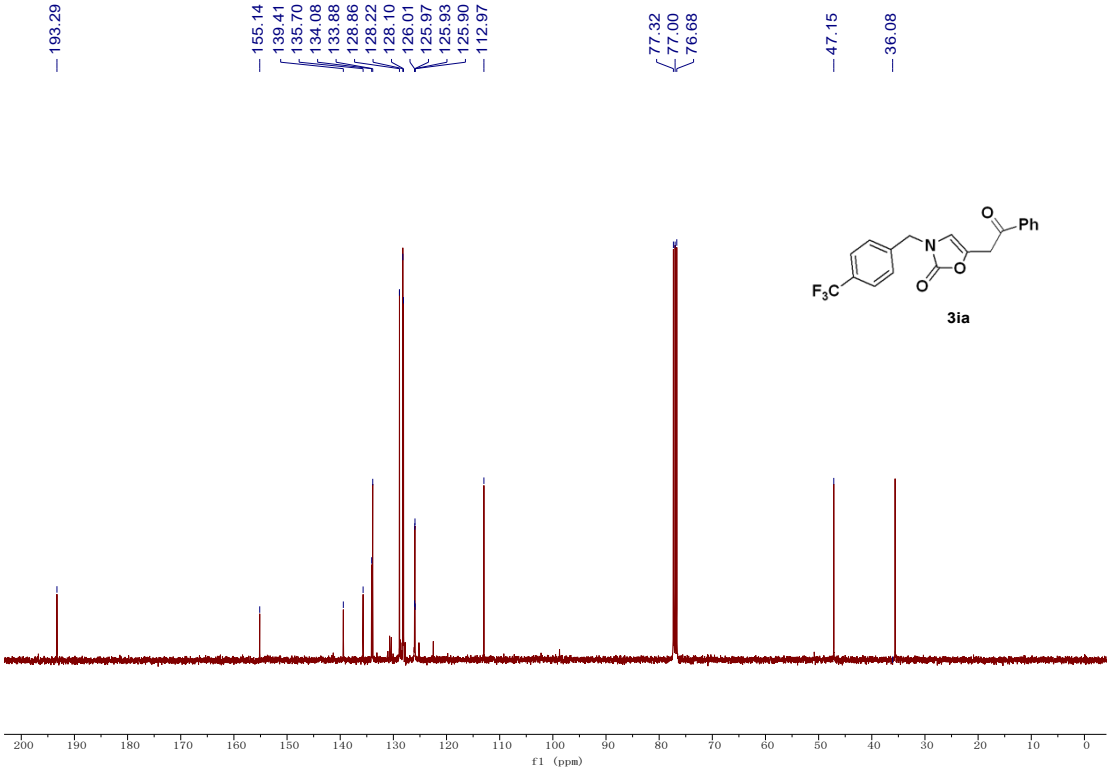
^{1}H NMR (400 MHz, $CDCl_3$)



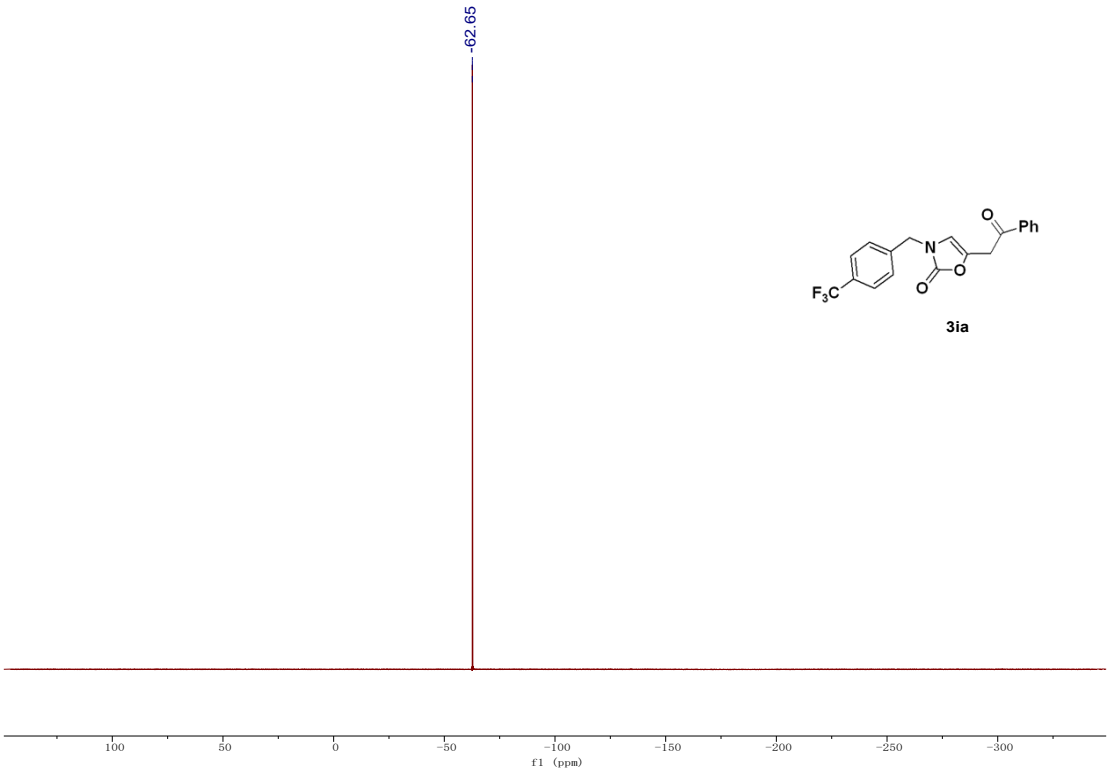
^{13}C NMR (101 MHz, $CDCl_3$)



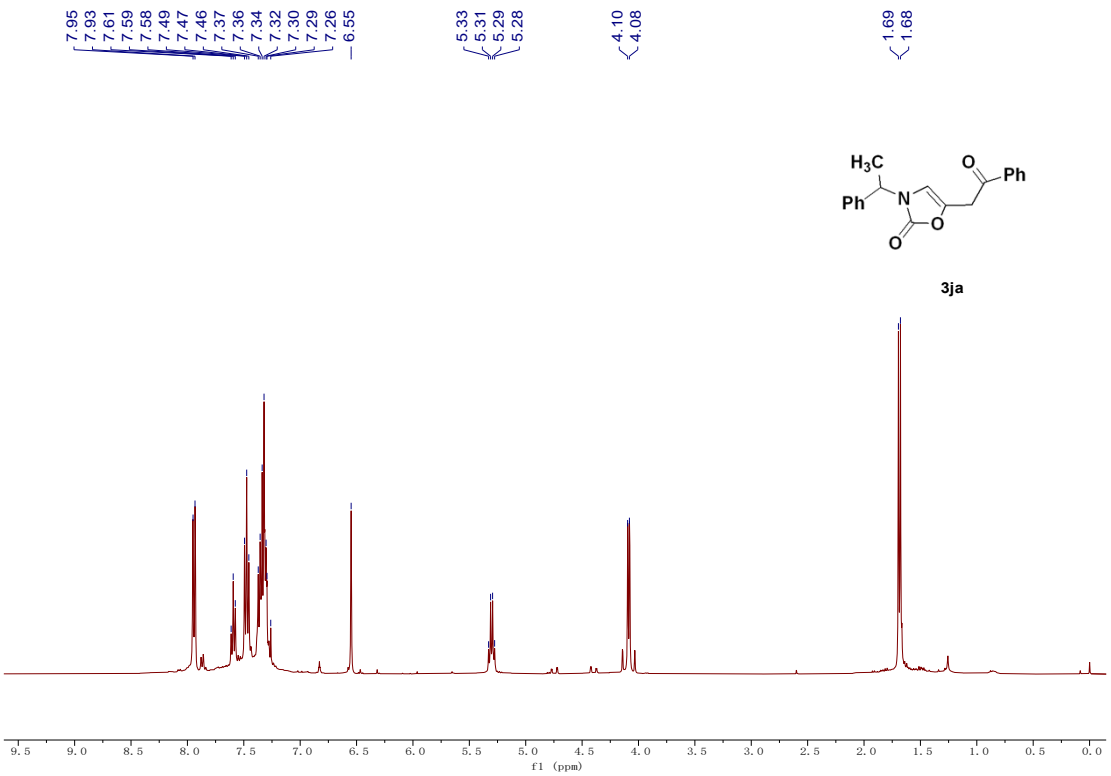
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{18}F NMR (162 MHz, $CDCl_3$)



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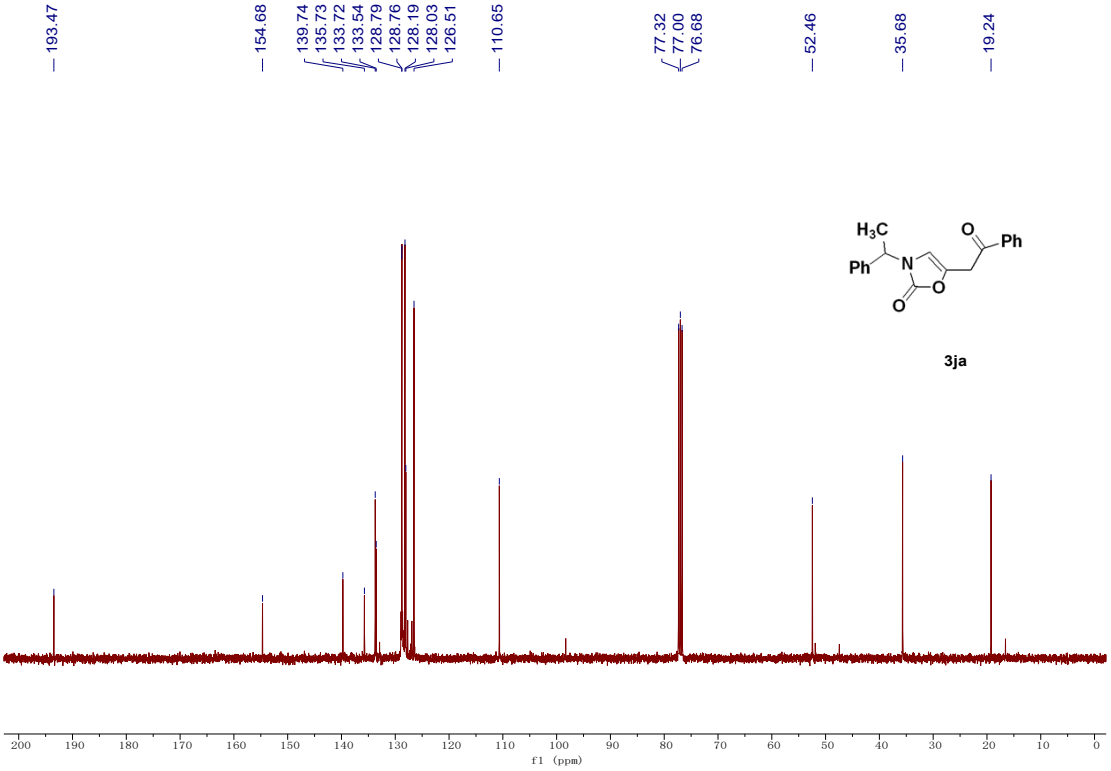
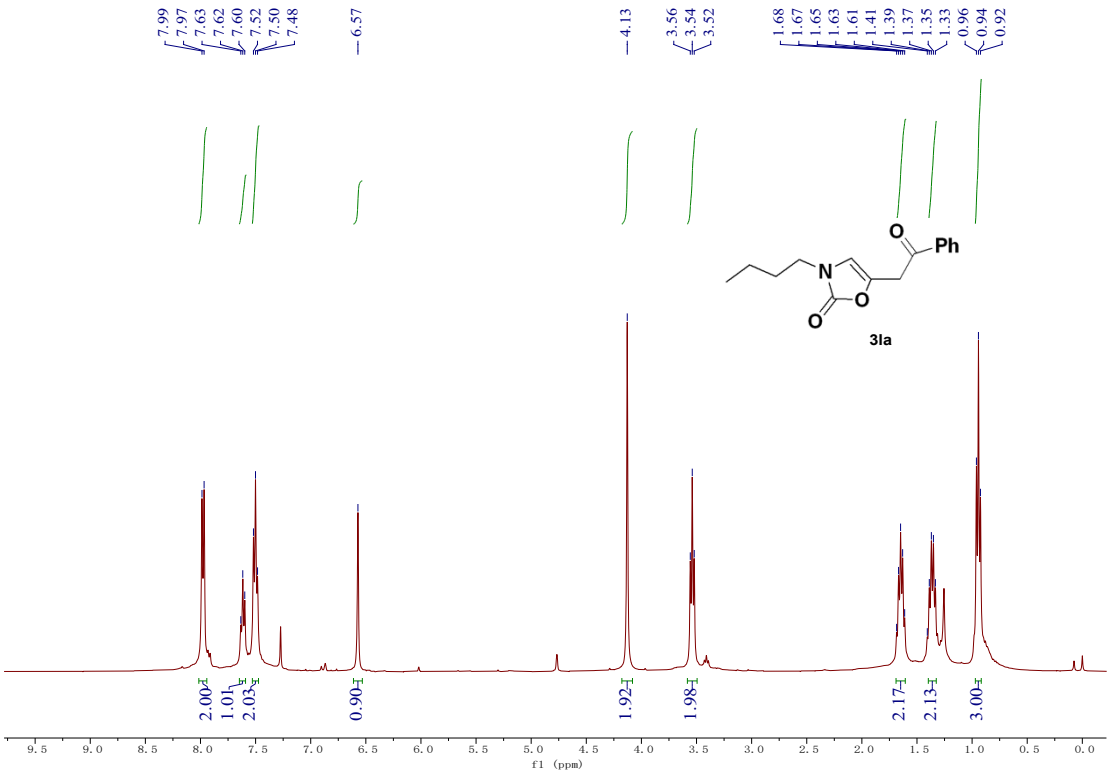


^{13}C NMR (101 MHz, $CDCl_3$)



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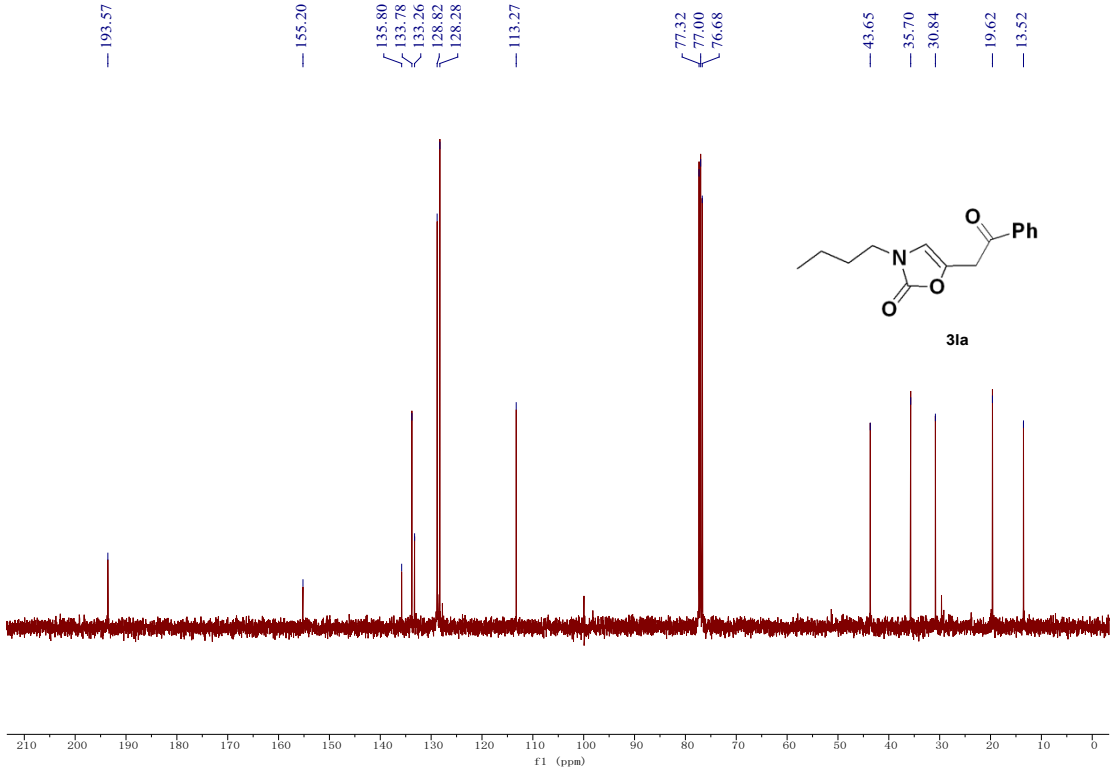
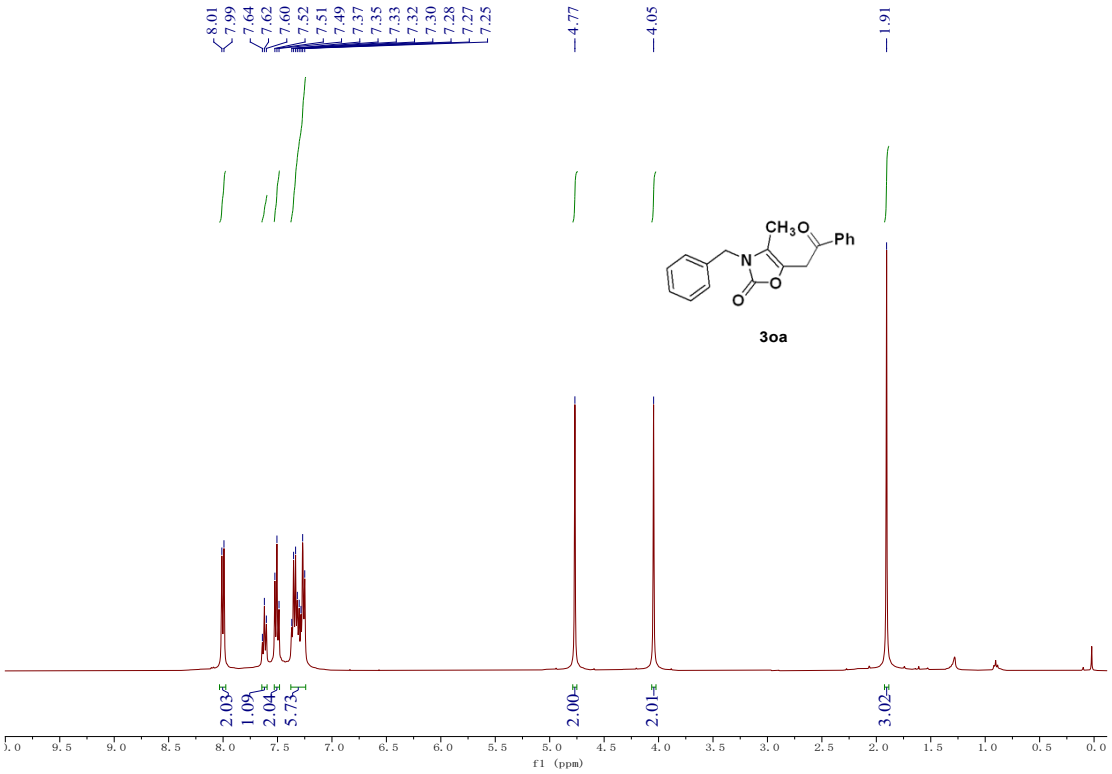
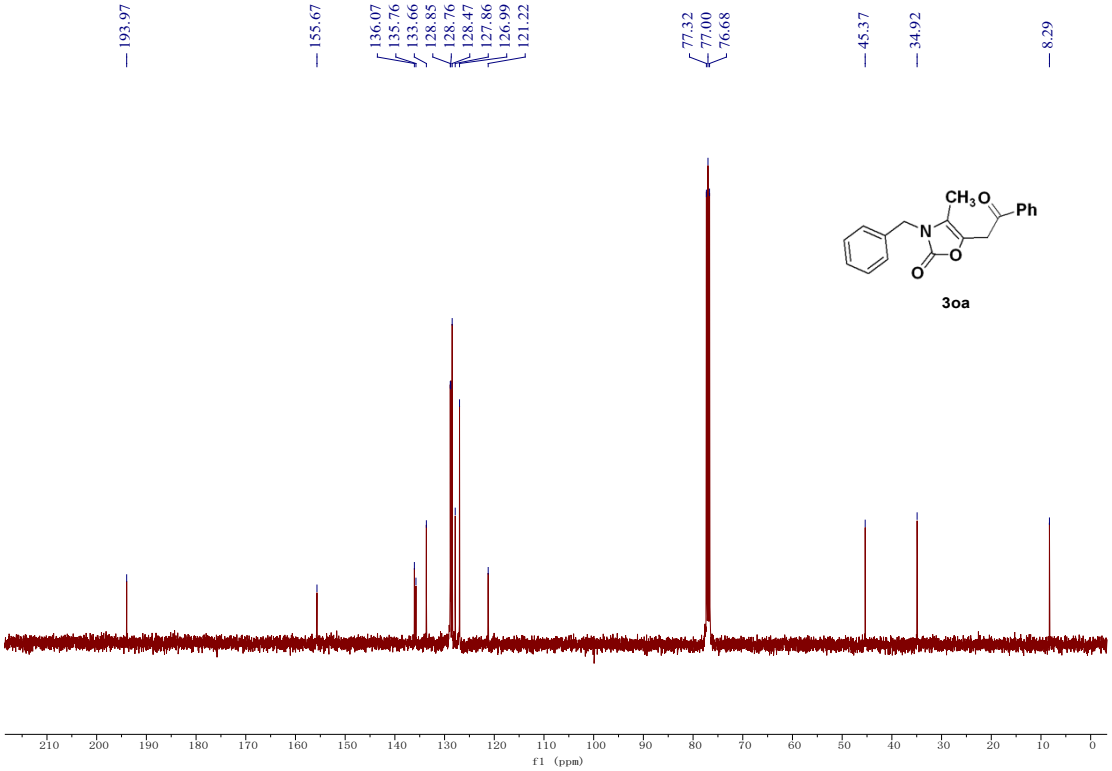


^{13}C NMR (101 MHz, $CDCl_3$)



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



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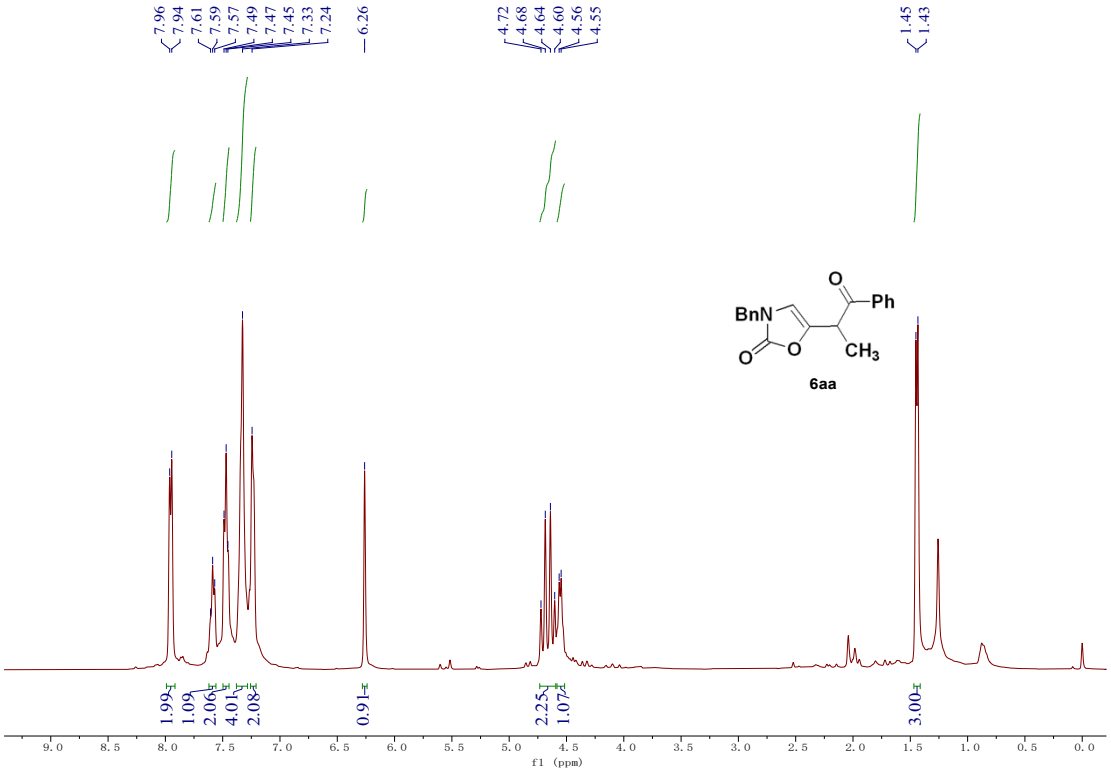

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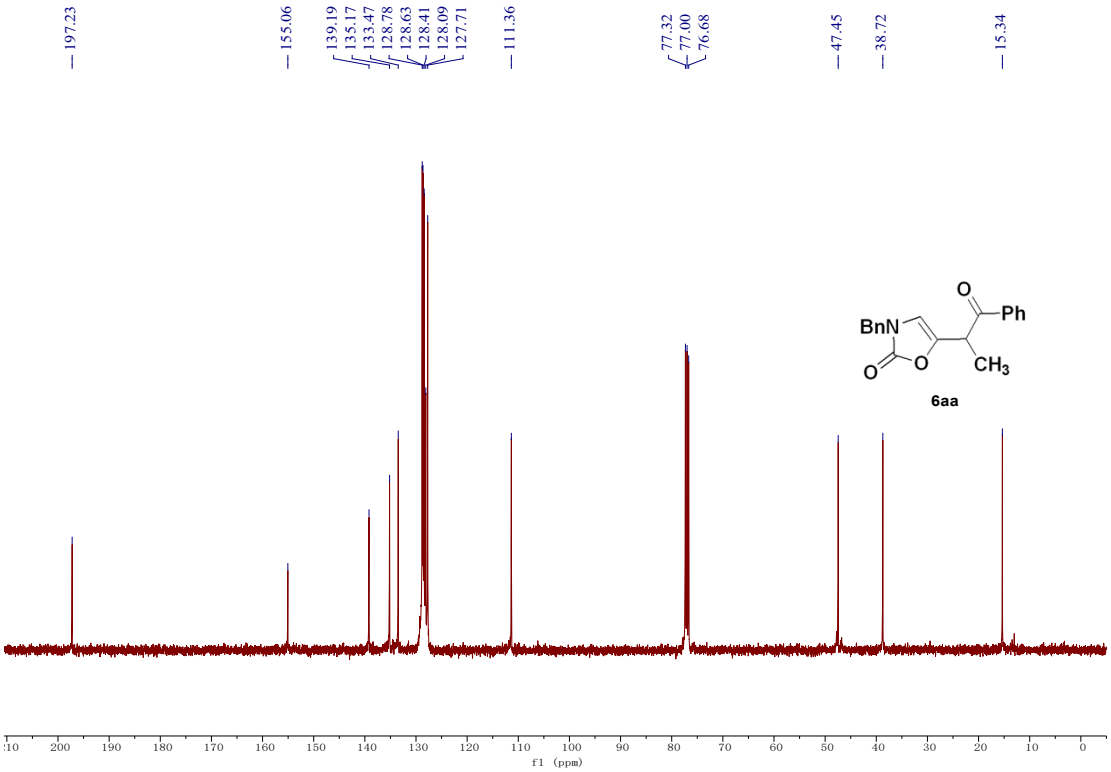

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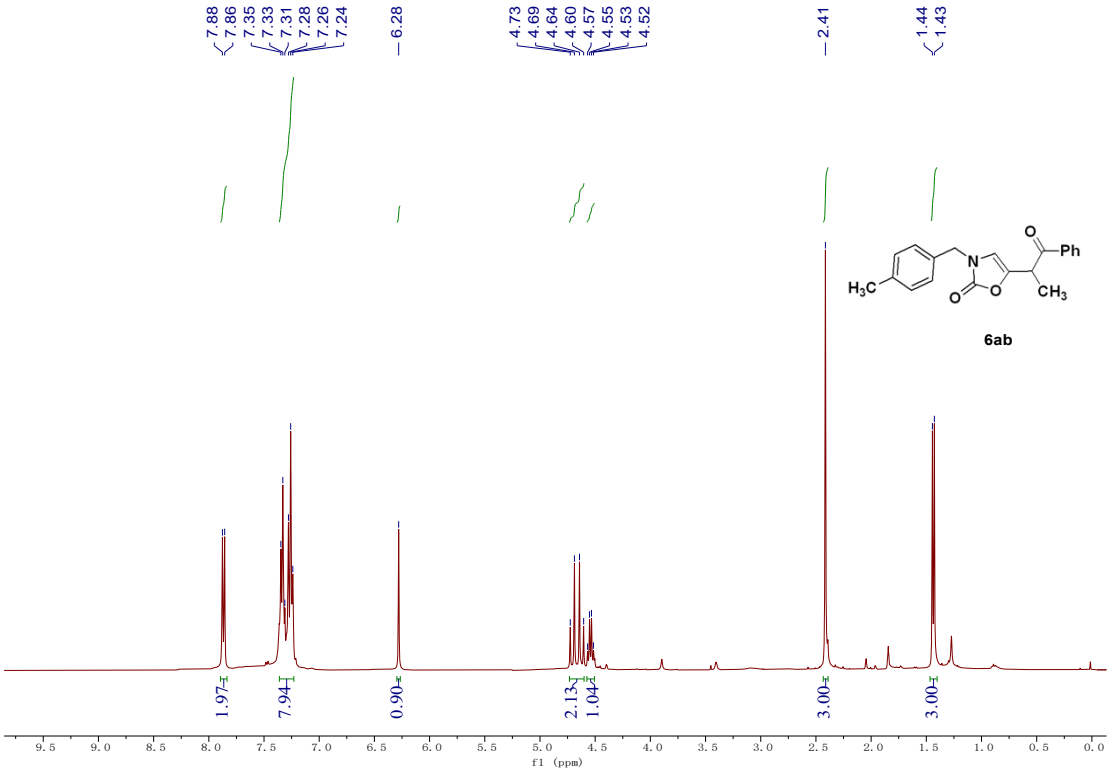

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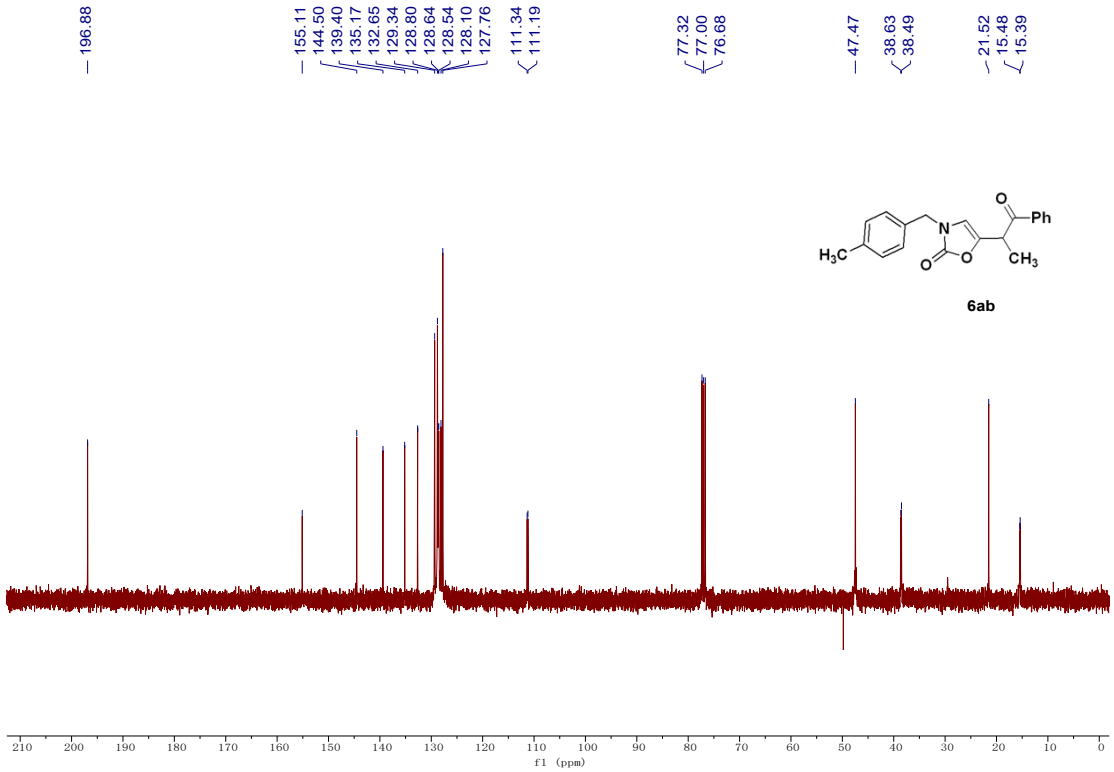

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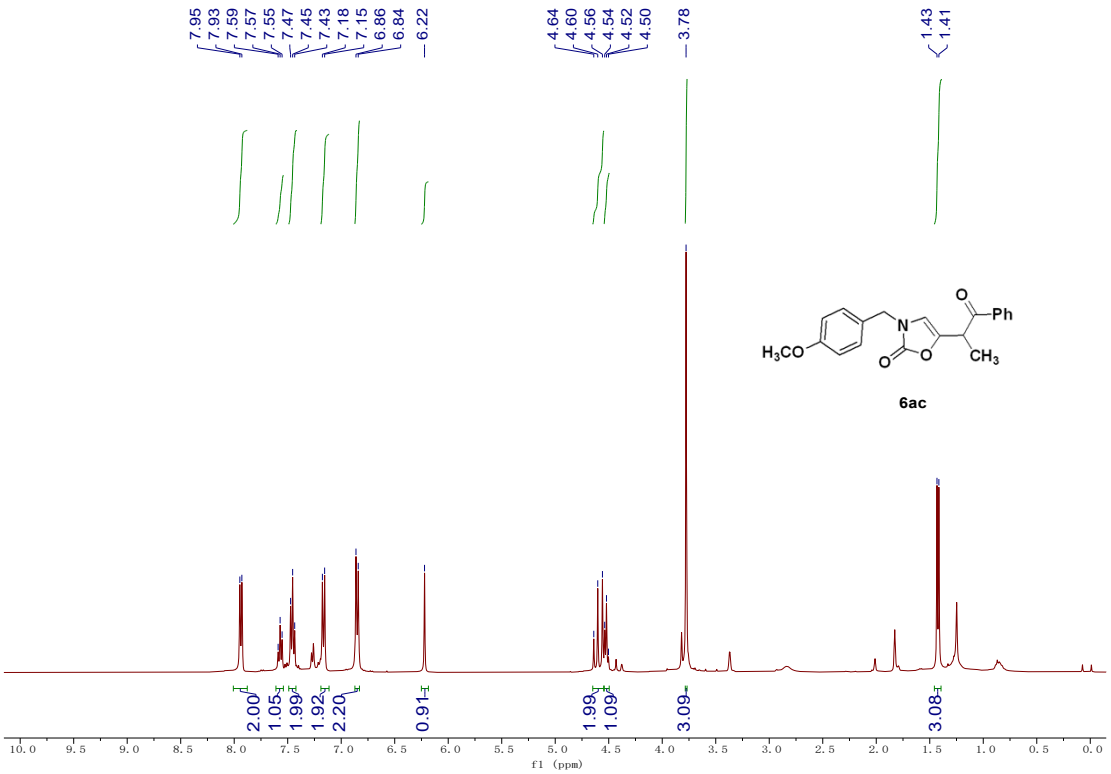

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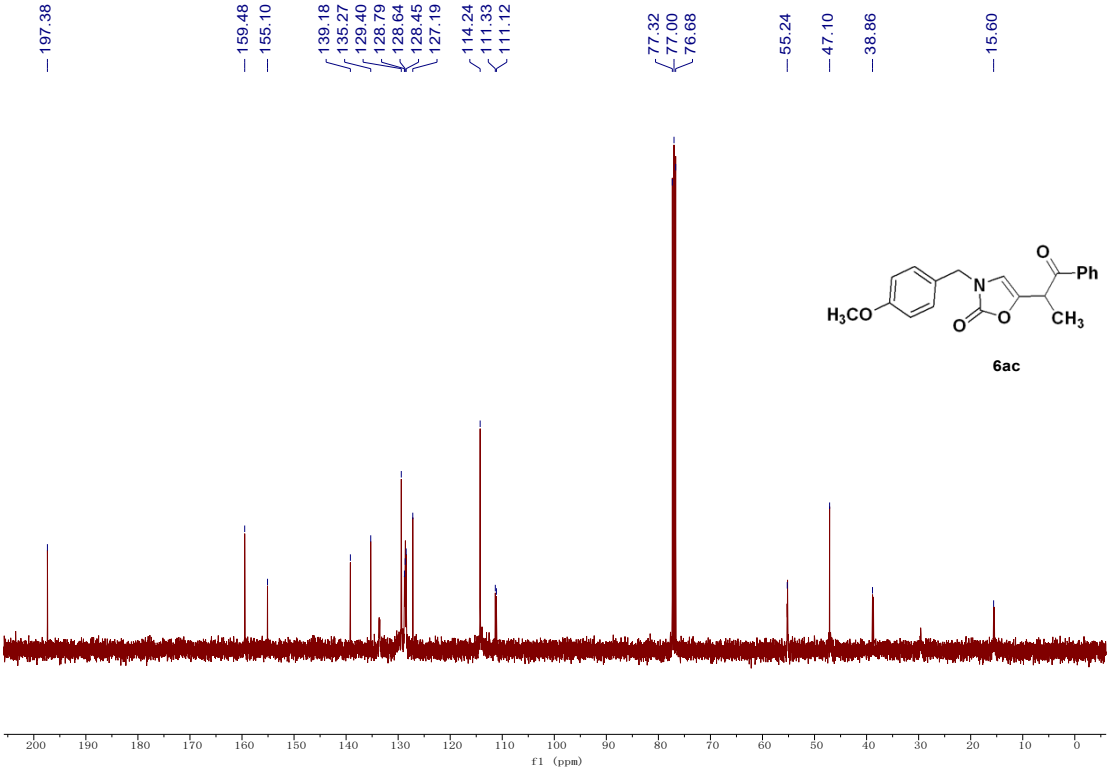

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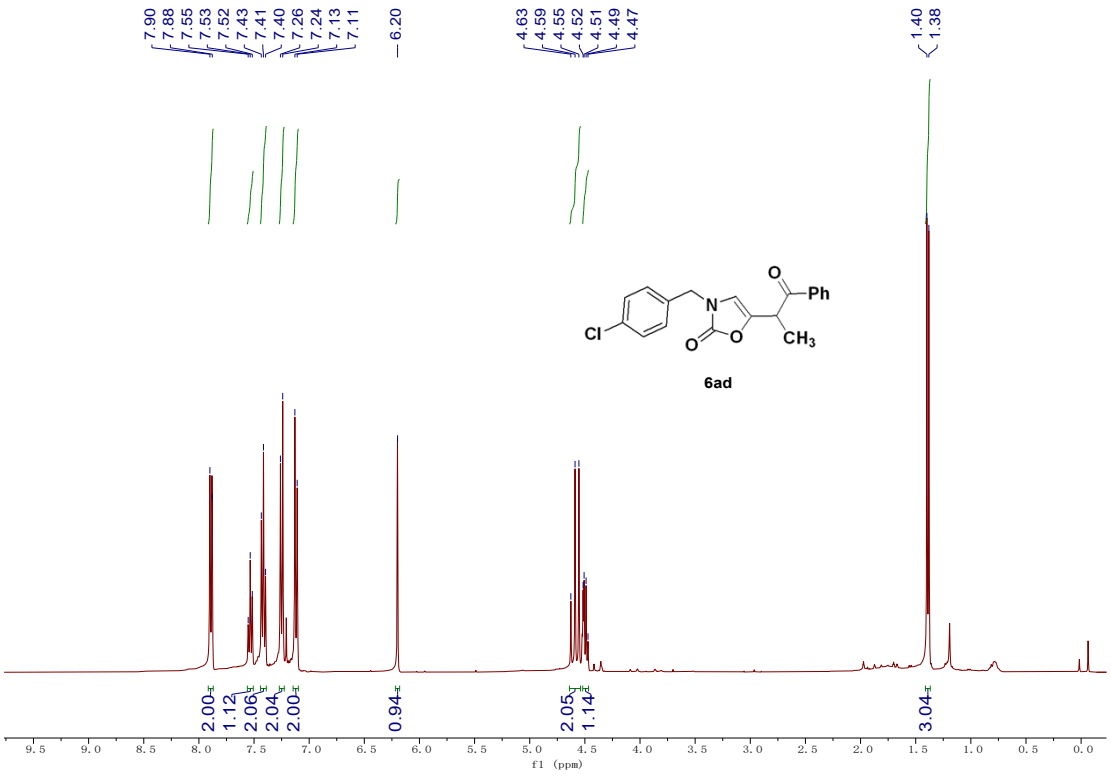

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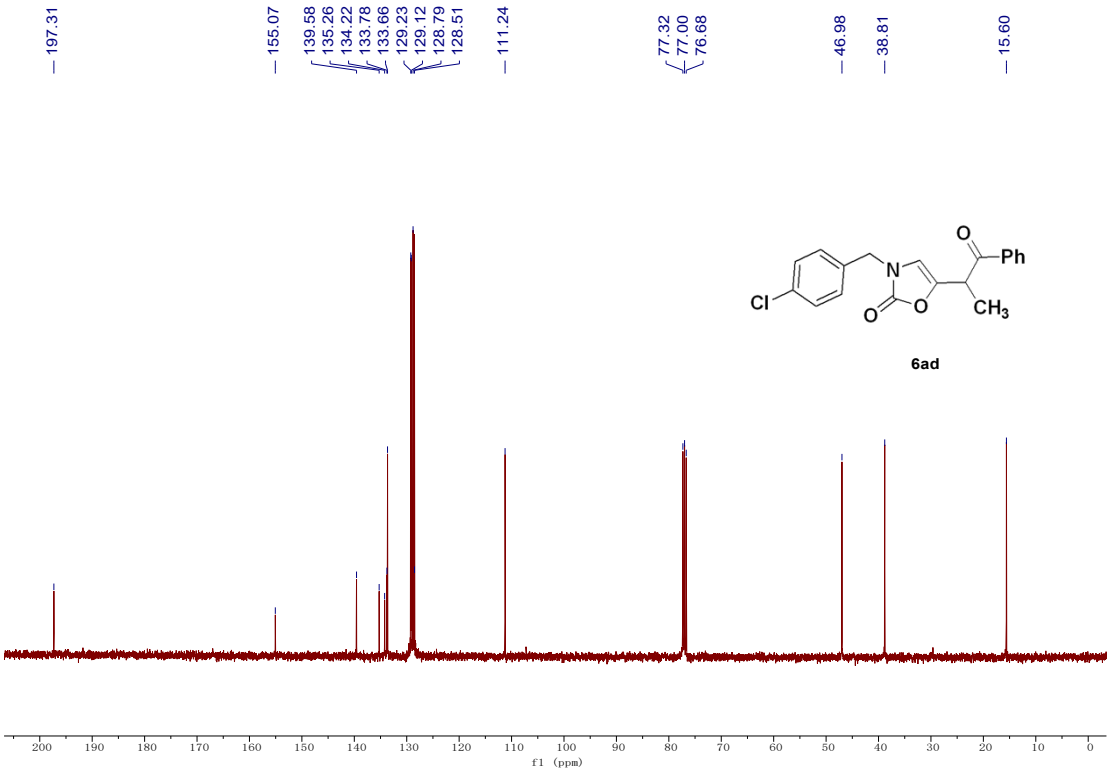
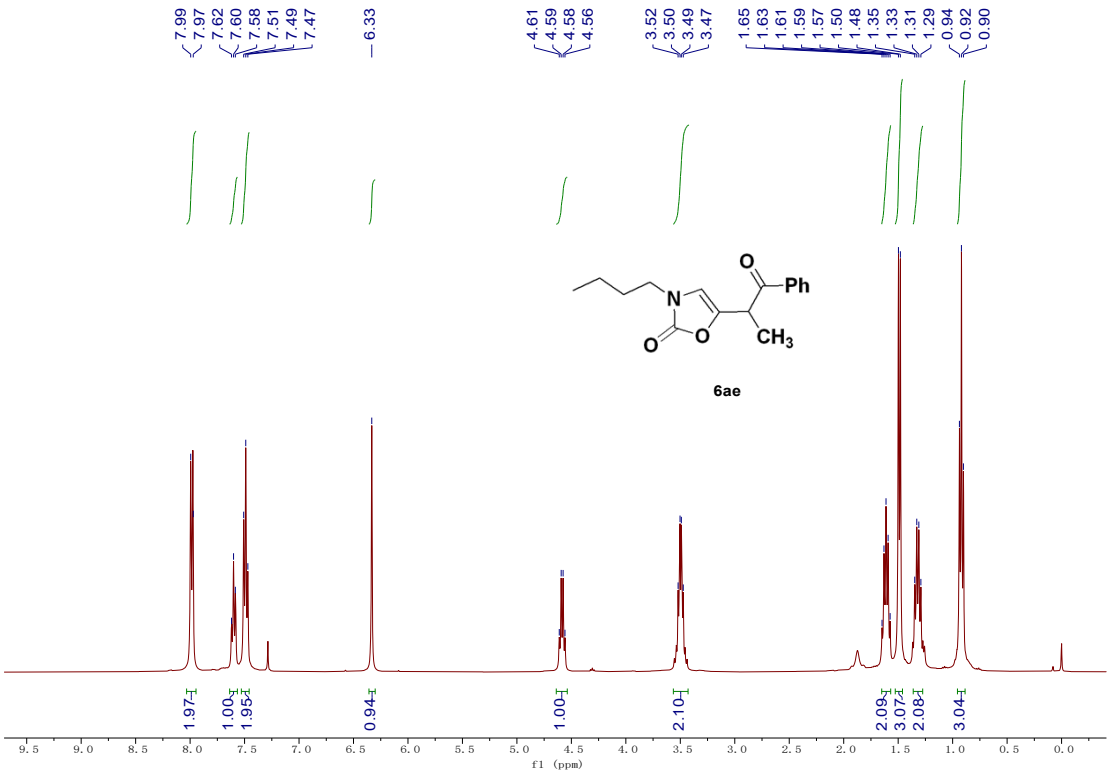


^{13}C NMR (101 MHz, $CDCl_3$)



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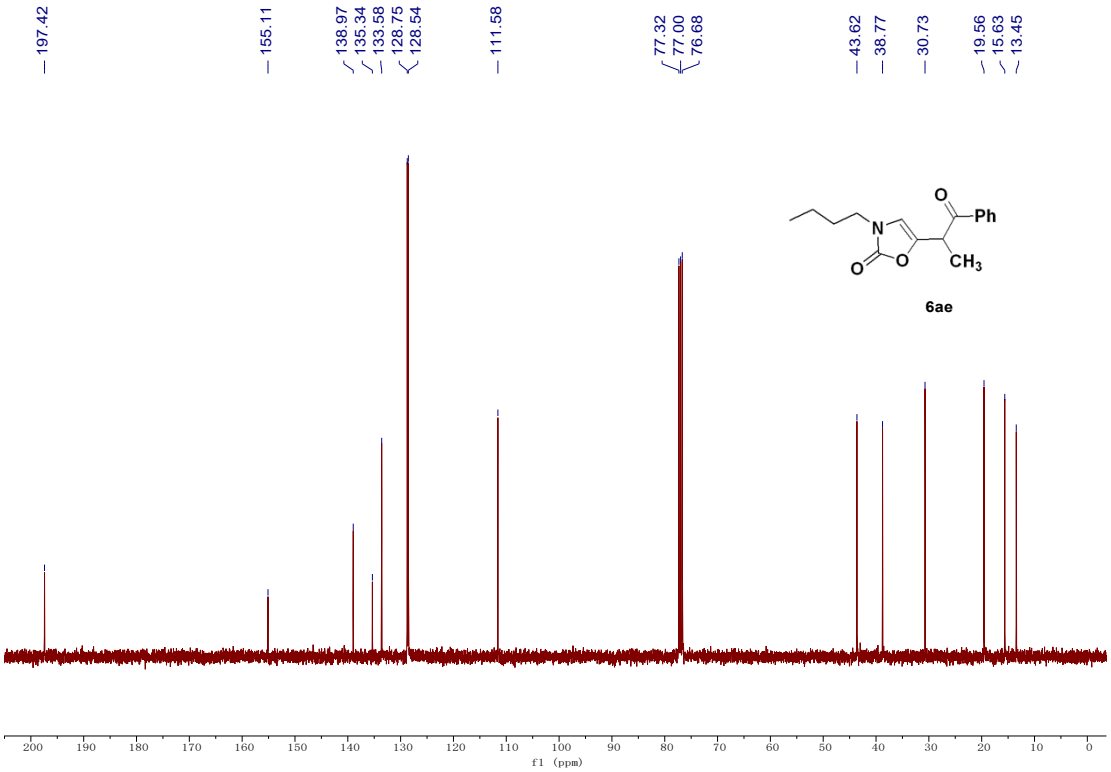

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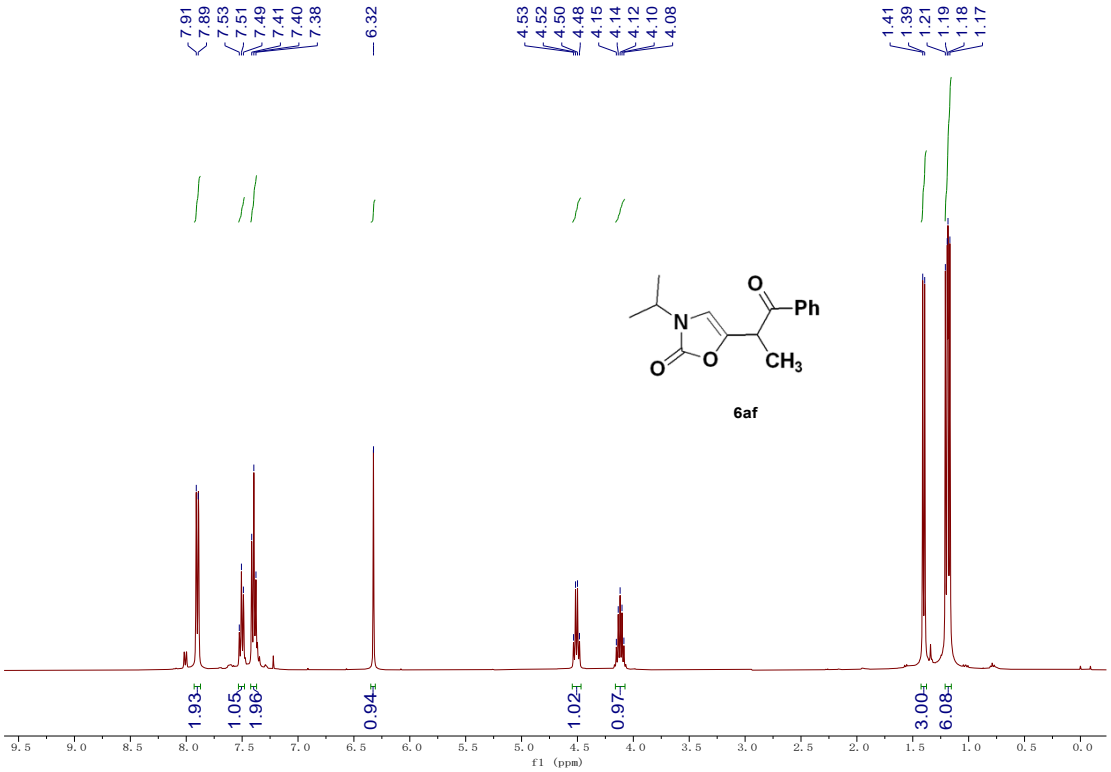
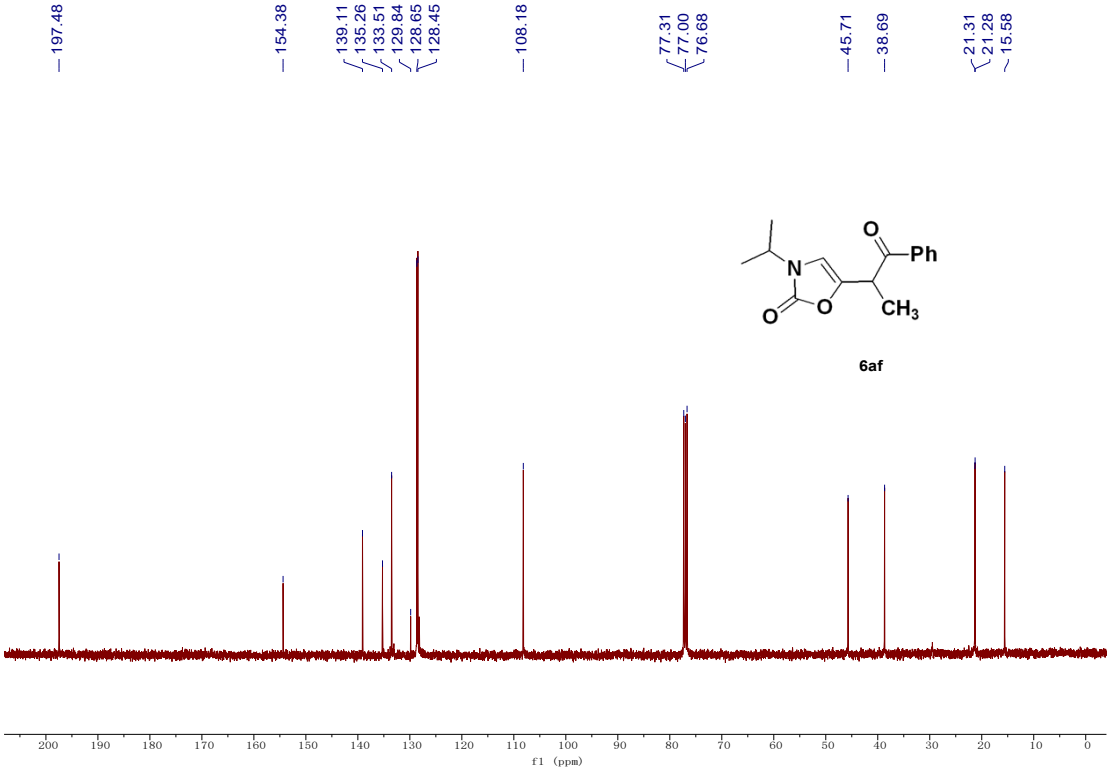


^{1}H NMR (400 MHz, $CDCl_3$)



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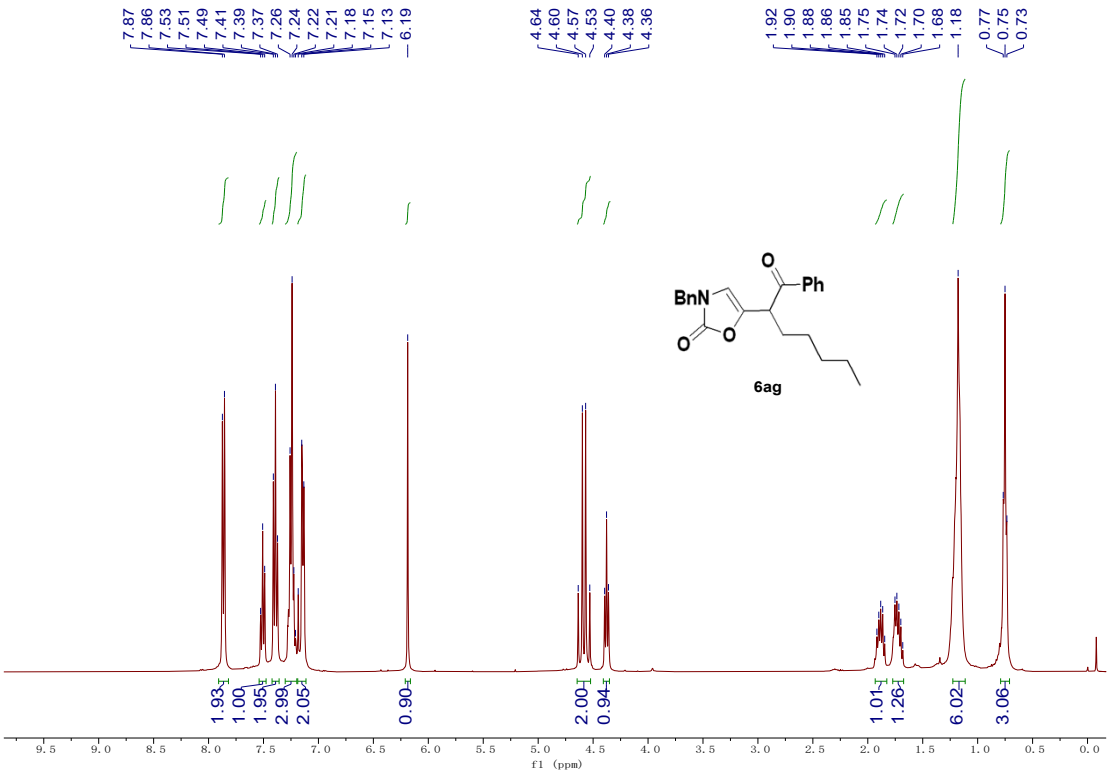

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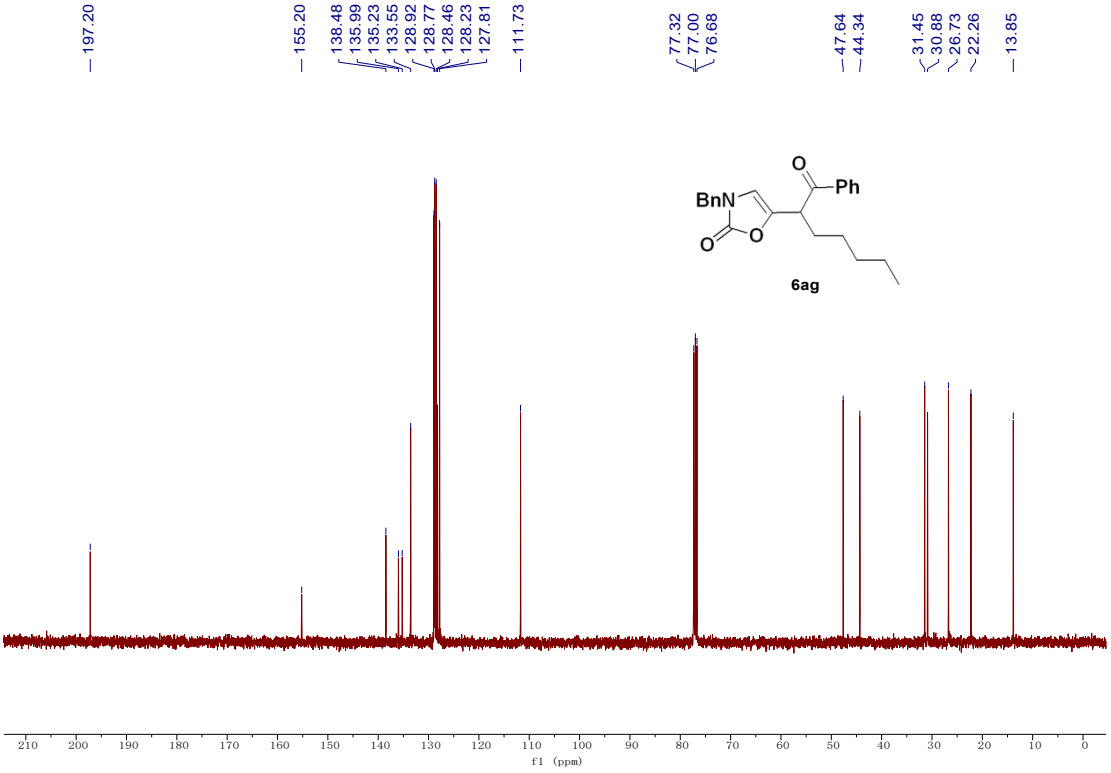

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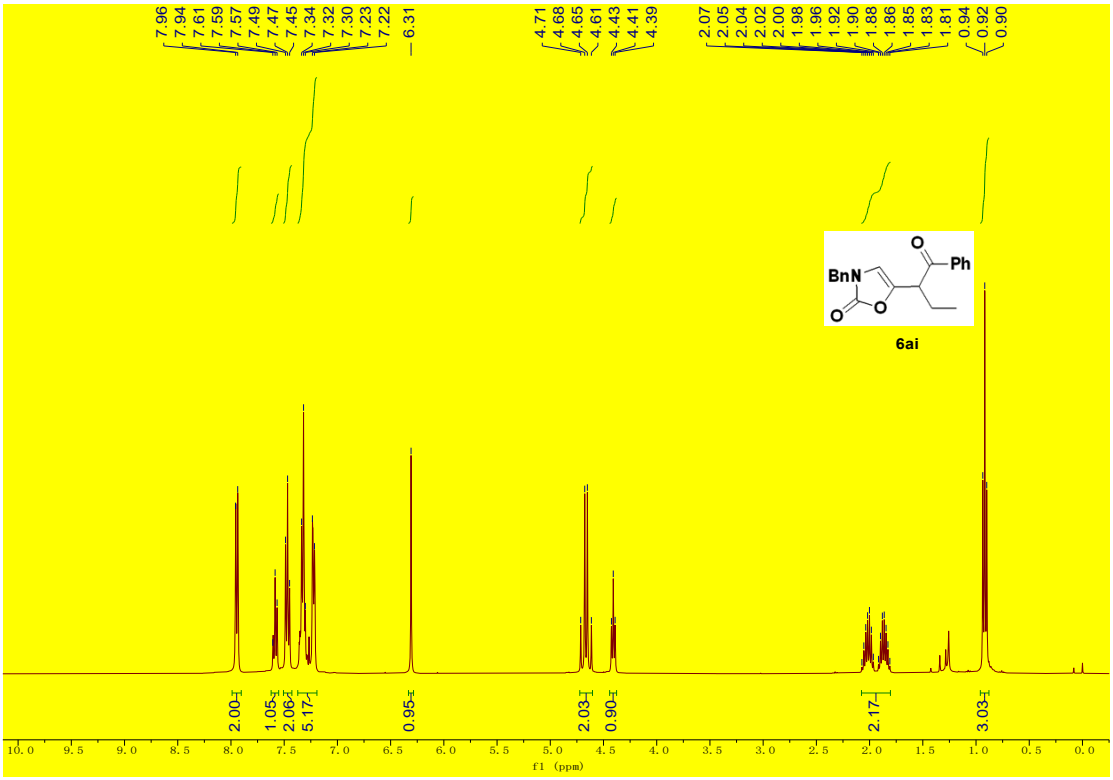

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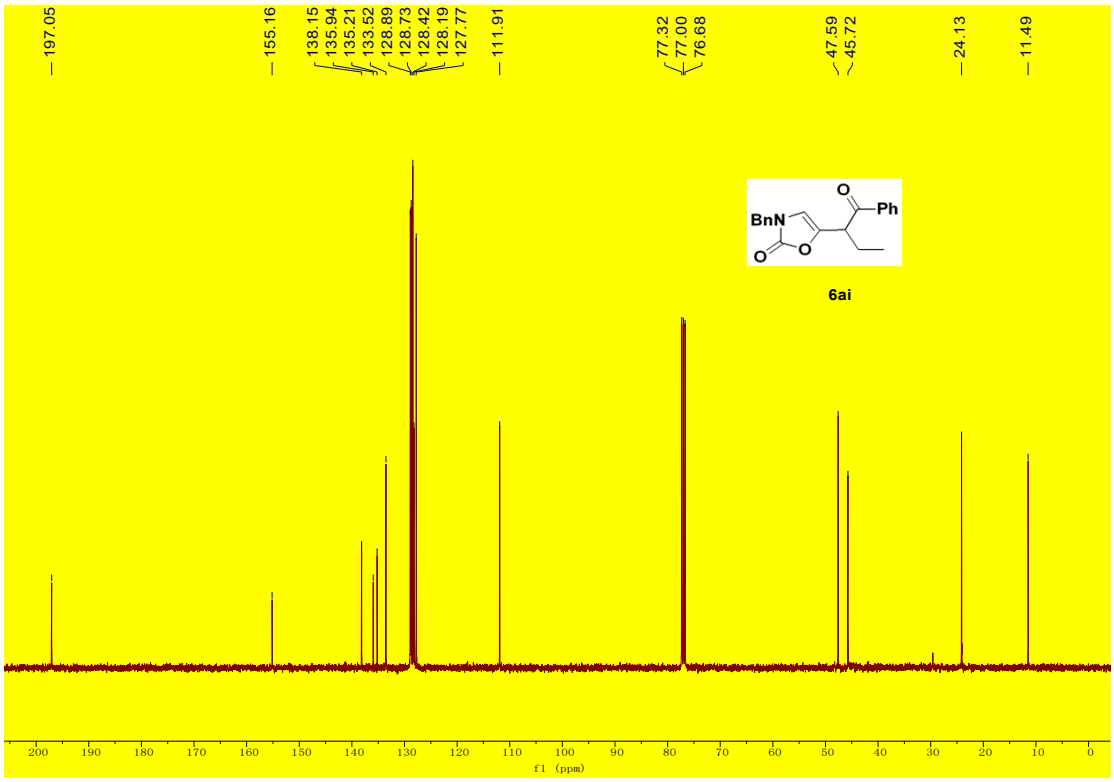

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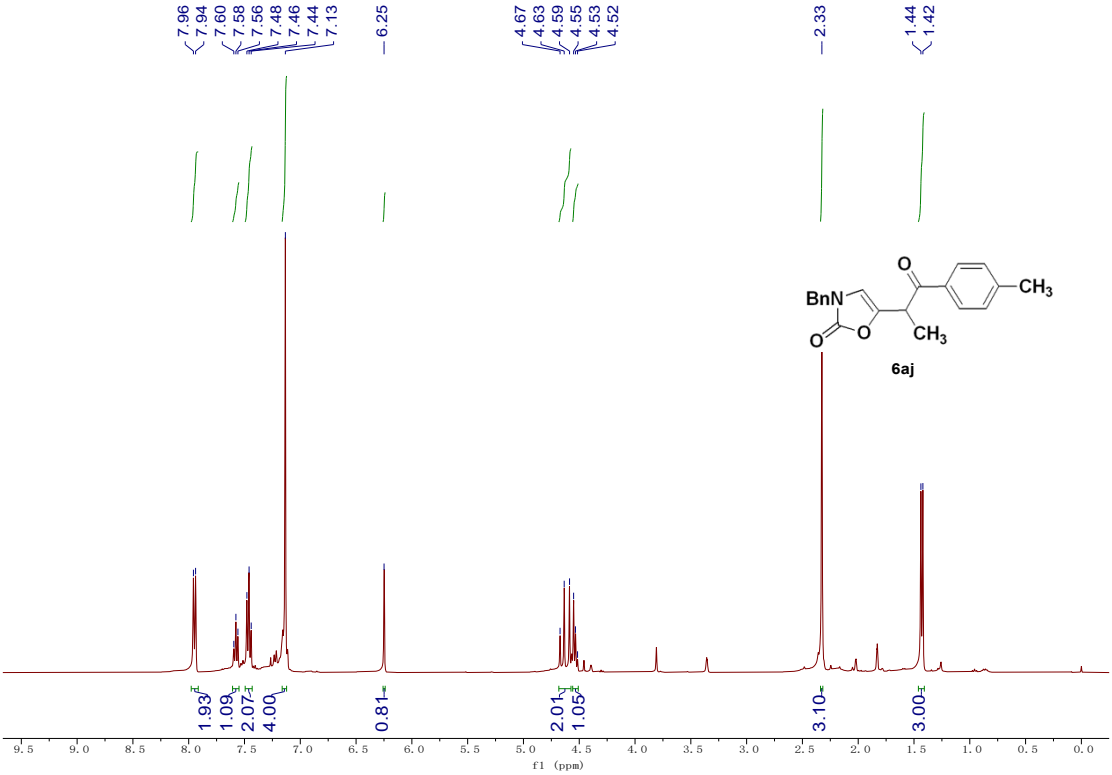

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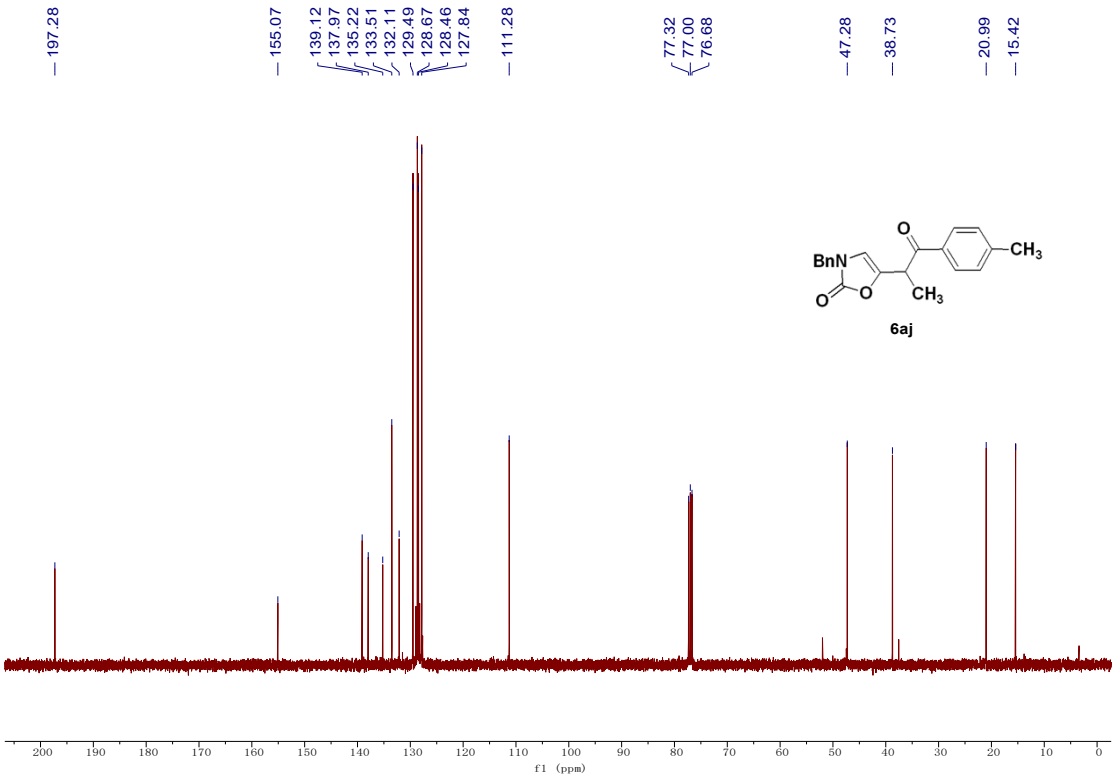

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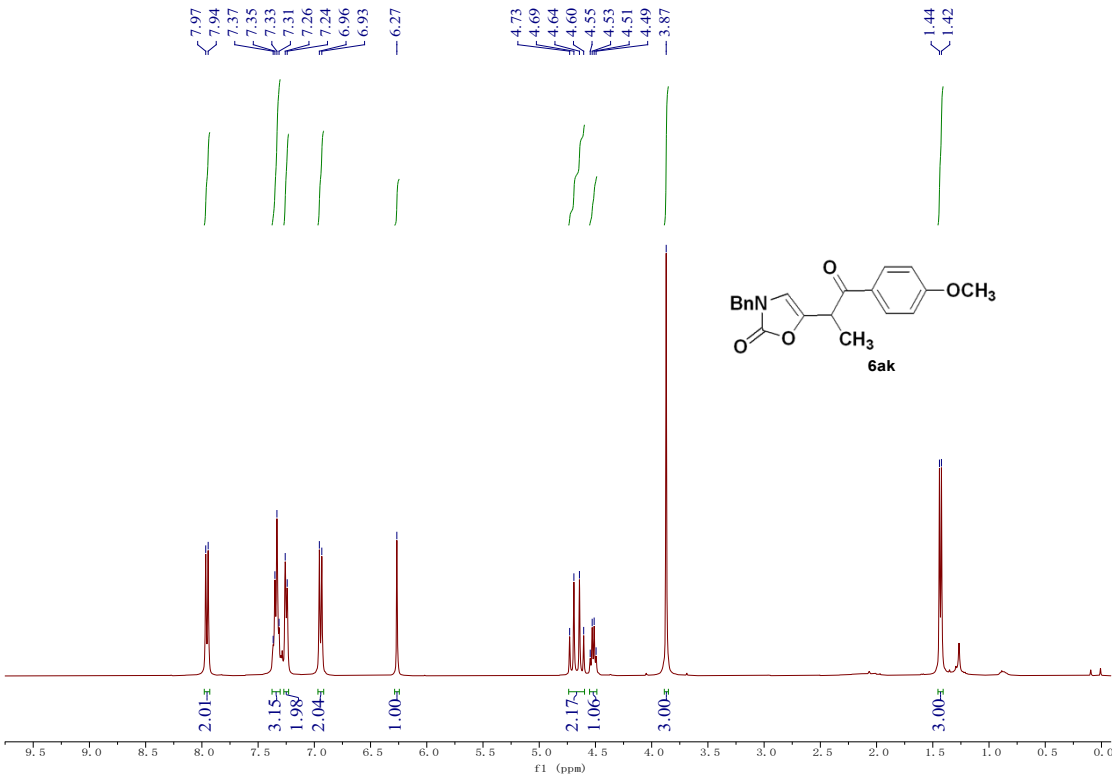

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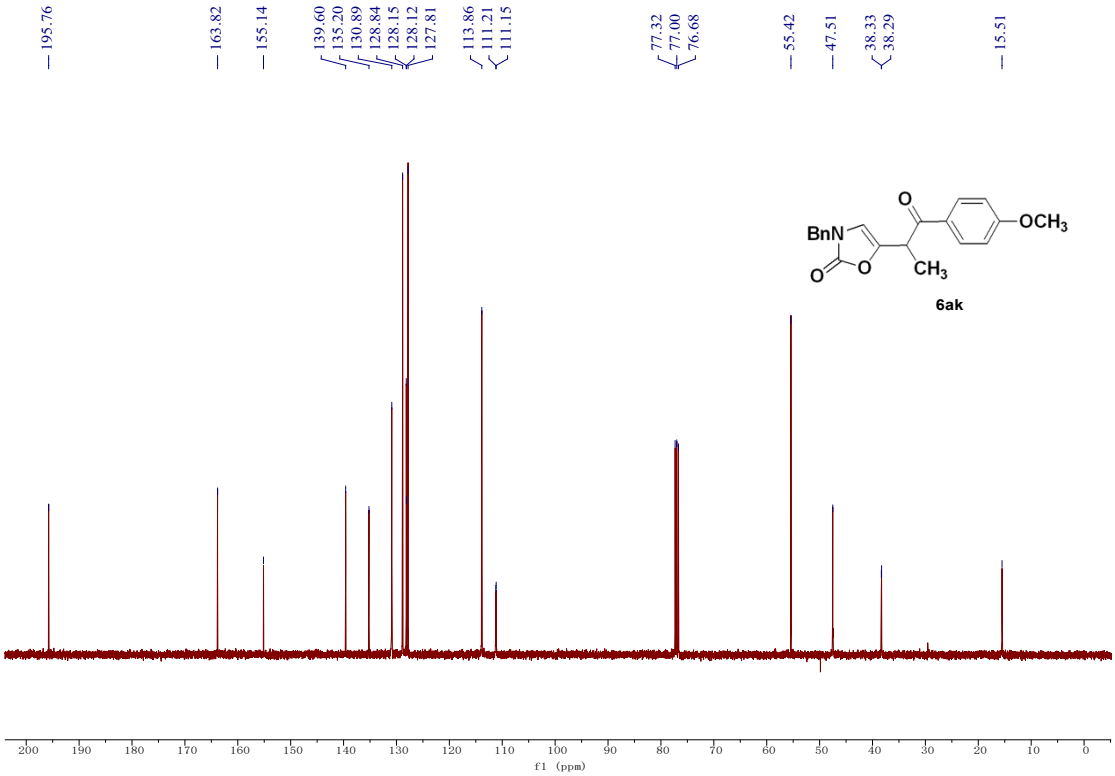

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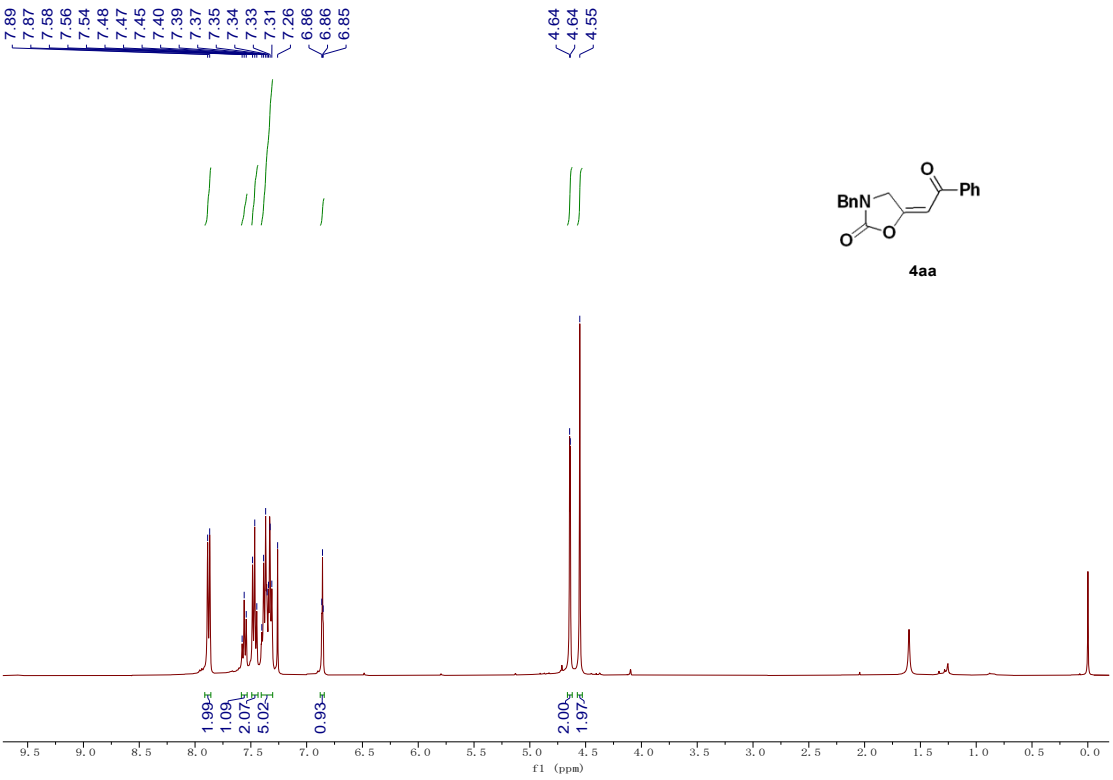

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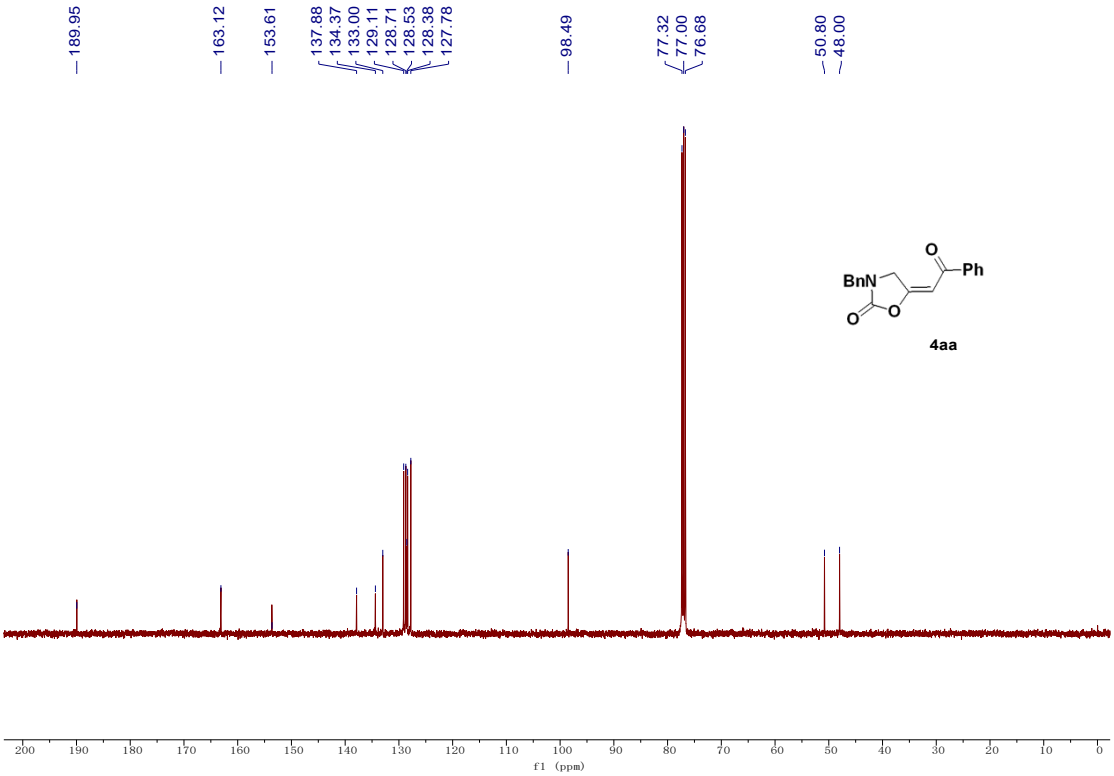

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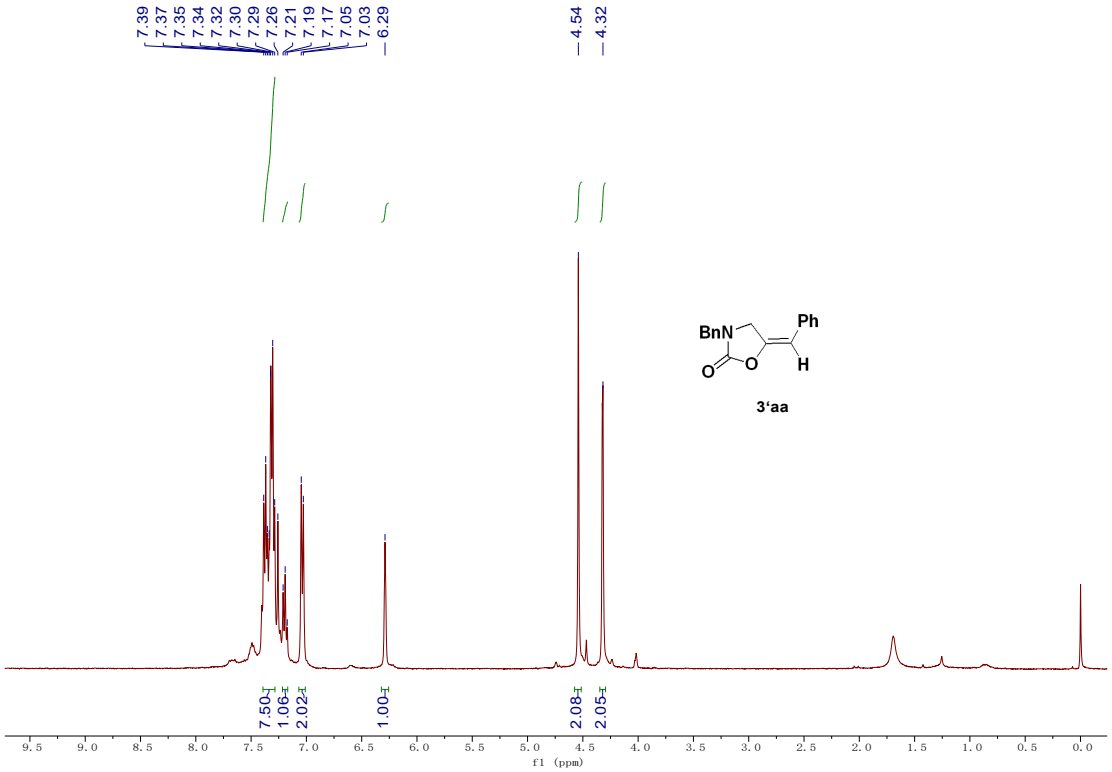

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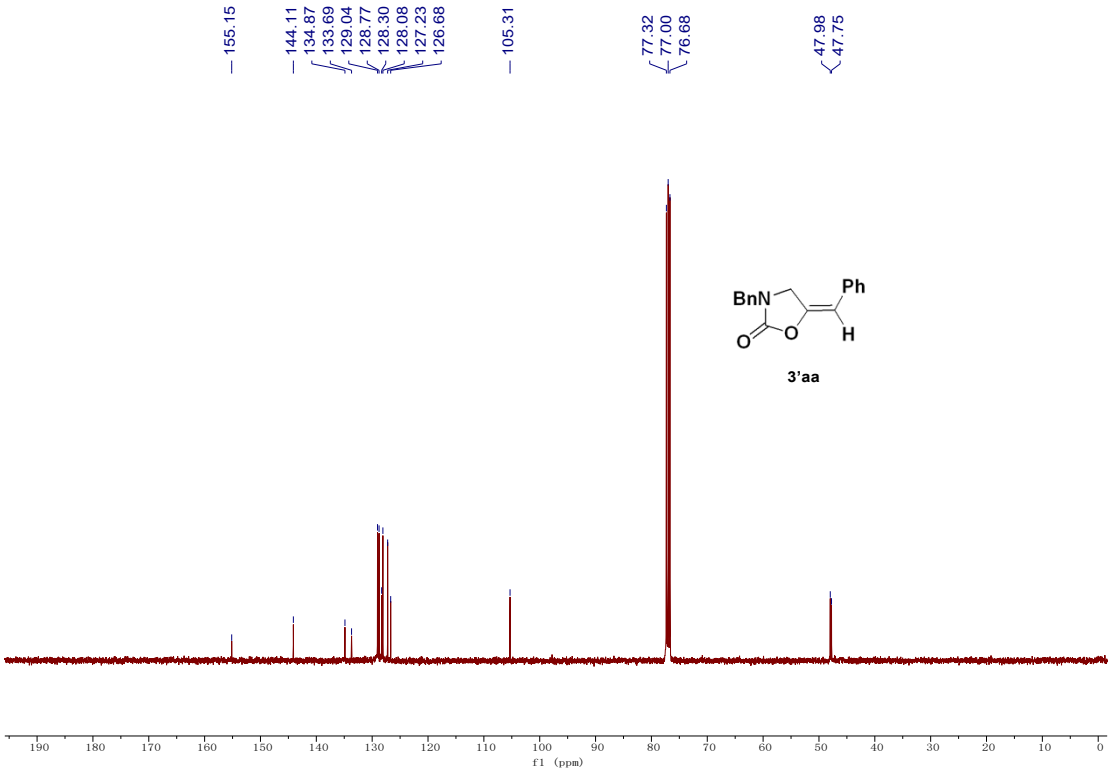

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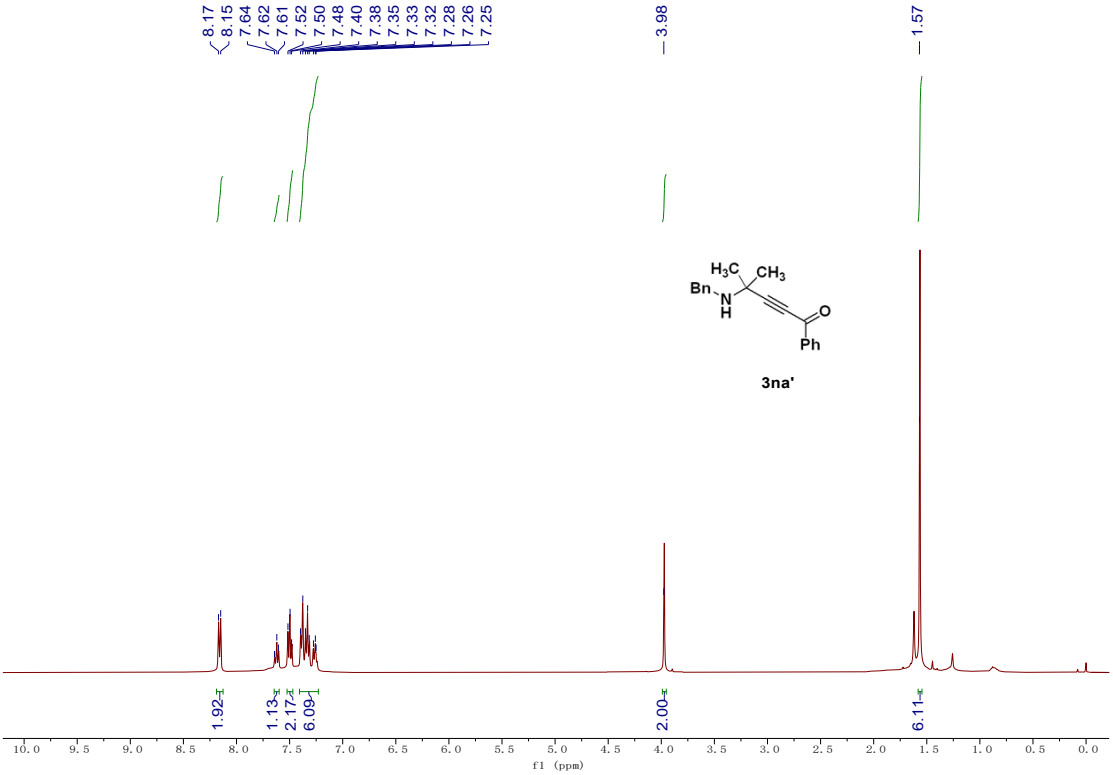
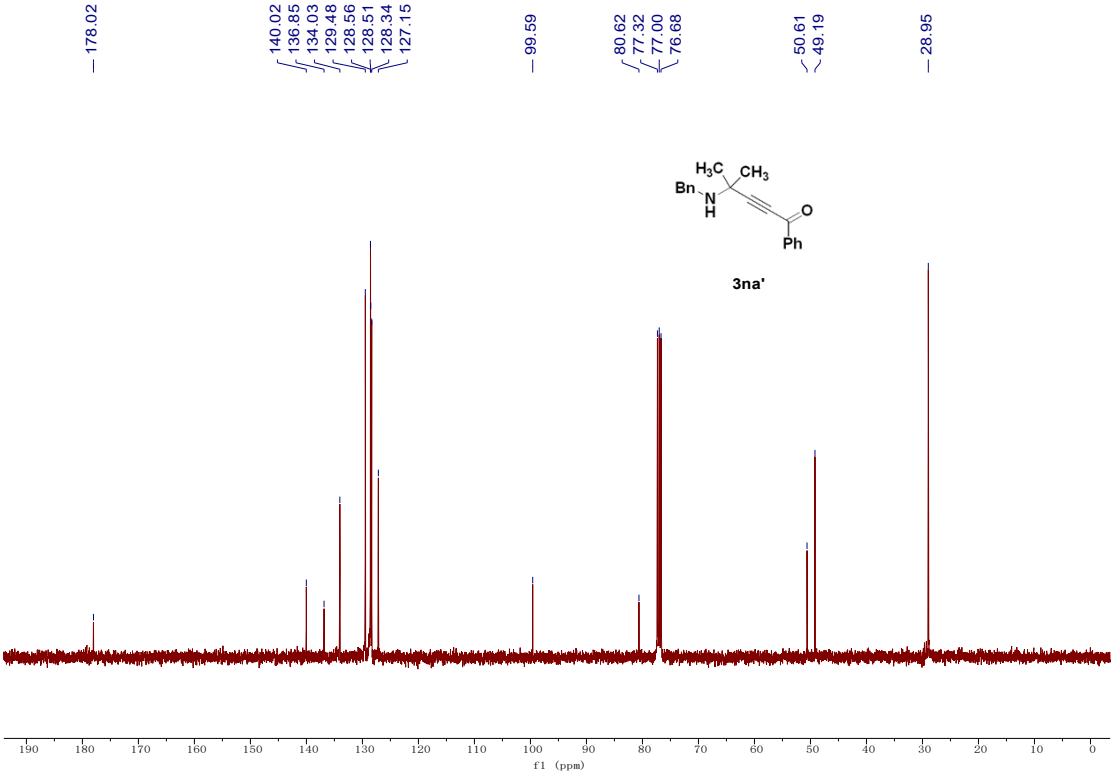


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

8. X-Ray crystal Structure of 3aa

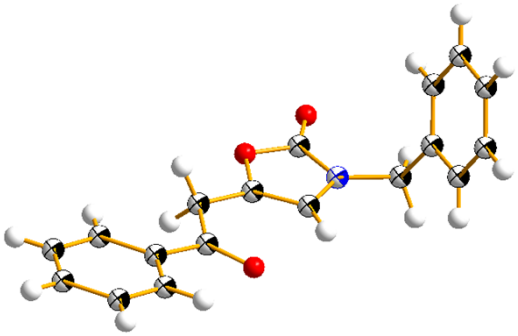


Figure S3 X-ray crystal structure of 3aa

Table S13 Crystal Data and Structure Refinement for 3aa

Identification code	3aa
Empirical formula	$C_{18}H_{15}NO_3$
Formula weight	293.31
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.7848(3)
b/Å	11.3961(5)
c/Å	21.8769(9)
α/°	90
β/°	91.520(4)
γ/°	90
Volume/Å^3	1441.71(11)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	0.093
F(000)	616.0
Crystal size/mm^3	0.42 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.03 to 56.556
Index ranges	$-7 \le h \le 7$, $-15 \le k \le 15$, $-29 \le l \le 29$
Reflections collected	17338
Independent reflections	3567 [R_{int} = 0.0774, R_{sigma} = 0.0435]
Data/restraints/parameters	3567/0/200
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.1109
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1212
Largest diff. peak/hole / e Å^{-3}	0.25/-0.21

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