Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Simple pyrazoles as efficient organocatalysts for alkyne-CO_2 carboxylation and one-pot construction of heterocycles

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S1 General information

^{1}H and ^{13}C spectra were collected on 300 MHz, 400 MHz or 500 MHz NMR spectrometers (Bruker AVANCE) using $CDCl_3$, DMSO-*d6* solution. For mechanism studies, NMR spectra were recorded in anhydrous DMSO, with positioning of a glass capillary filled with D_2O inside the NMR tube for magnetic field locking. ^{1}H chemical shifts (δ_H) are expressed in parts per million (ppm) and reported relative to the internal standard $CDCl_3$ (δ_H = 7.26 ppm) or DMSO-*d6* (δ_H = 2.50 ppm), or relative to the external standard DMSO (δ_H = 2.50 ppm) in a D_2O capillary. ^{13}C chemical shifts (δ_C) are expressed in ppm and reported relative to the internal standard DMSO-*d6* (δ_C = 39.6 ppm), or relative to the external standard DMSO (δ_C = 39.4 ppm) in a D_2O capillary. Silica gel (300 - 400 mesh) was used for flash column chromatograph, eluting with ethyl acetate/petroleum ether (60 - 90 °C) mixture. Unless otherwise noted, the chemicals and reagents were purchased in analytical purity from commercial sources and used directly without further purification. Anhydrous DMSO was further dried over molecular sieve.

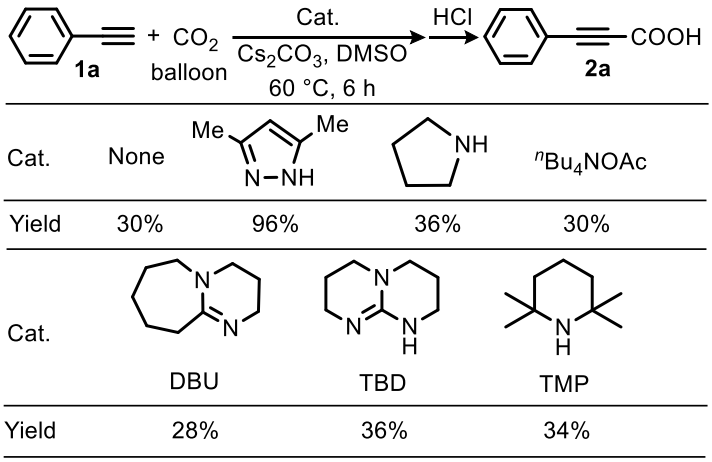
S2 Experimental section

General procedure for catalytic carboxylation. The catalyst and base were added to a Schlenk tube. After three times of atmosphere exchange with CO_2, the reactor was equipped with a CO_2 balloon and heated in an oil bath. Then 1.0 mmol terminal alkyne dissolved in 3 mL solution was injected under stirring to start the reaction. After stirring at required temperature for specified time, the reaction was quenched with water (15 mL). The resultant solution was washed with CH_2Cl_2 to separate the catalyst and any unreacted alkyne. The aqueous phase was acidified with 1 M HCl to pH = 1 and then extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to obtain the product, which was weighed for yield calculations.

Catalyst recovery. A scale-up catalytic reaction was performed in a 250 mL flask by following the typical procedure with 10 mmol **1a**, 1.0 mmol Me_2Pz and 15 mmol Cs_2CO_3 in 20 mL DMSO. The reaction was performed at 80 °C until the alkyne was completely consumed as indicated by TLC. After addition of 100 mL water, the solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were washed with aqueous $NaHCO_3$, dried over $MgSO_4$ and evaporated in vacuo. The solid thus obtained was confirmed by NMR to be Me_2Pz with satisfactory purity. The recovery rate is 95%. The aqueous phase after above extraction was treated by typical procedures to give **2a** in a yield of about 99%.

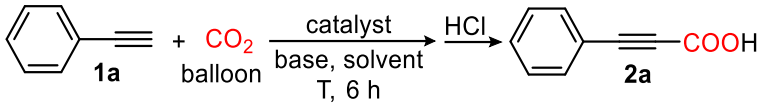
S3 Catalytic carboxylation of phenylacetylene (1a) with CO_2

Table S1. Additional control tests with potential catalysts [a]



[a] Reaction conditions: **1a** (1.0 mmol), catalyst (0.1 mmol, 10 mol%), Cs_2CO_3 (1.5 mmol, 1.5 eq.), CO_2 (balloon), DMSO (3 mL), 60 ℃, 6 h; isolated yield.

Table S2. Optimization of carboxylation of **1a** with CO_2 [a]



Entry	Catalyst (mol%)	Base	Solvent	T/°C	Yield/%
1	Me_2Pz (10)	Cs_2CO_3	DMSO	60	96
2	Me_2Pz (10)	Cs_2CO_3	DMSO	40	13
3	Me_2Pz (10)	Cs_2CO_3	DMSO	55	68
4	Me_2Pz (10)	Cs_2CO_3	DMSO	70	>99
5	Me_2Pz (10)	Cs_2CO_3	DMSO	80	>99
6	-	K_2CO_3	DMSO	60	-
7	Me_2Pz (10)	K_2CO_3	DMSO	60	24
8	-	CsF	DMSO	60	-
9	Me_2Pz (10)	CsF	DMSO	60	42
10	Me_2Pz (10)	KOH	DMSO	60	-
11	Me_2Pz (10)	*t*-KOBu	DMSO	60	5
12	Me_2Pz (10)	DBU	DMSO	60	24
13	-	DBU	DMSO	60	25
14	Me_2Pz (10)	TBD	DMSO	60	30
15	-	TBD	DMSO	60	28
16	Me_2Pz (10)	TMP	DMSO	60	-
17	-	Cs_2CO_3	DMF	60	-
18	Me_2Pz (10)	Cs_2CO_3	DMF	60	63
19	Me_2Pz (10)	Cs_2CO_3	CH_3CN	60	8
20	Me_2Pz (10)	Cs_2CO_3	PC [b]	60	-
21	Me_2Pz (5)	Cs_2CO_3	DMSO	60	78
22	Me_2Pz (20)	Cs_2CO_3	DMSO	60	>99

[a] Reaction conditions: **1a** (1.0 mmol), catalyst, base (1.5 mmol, 1.5 eq.), CO_2 (balloon), solvent (3 mL), 6 h; isolated yield. [b] PC: propylene carbonate.

S4 Comparison of Me_2Pz with the reported catalysts

Table S3. Carboxylation of **1a** using various metal and organic catalysts at ambient CO_2 pressure. [a]

Entry	Catalyst	Base	T/°C	t/h	Yield/%	Ref.
Homogeneous metal catalysts						
1	$Cu(BPhen)(4\text{-}F\text{-}PPh_3)_2(NO_3)$ [c]	Cs_2CO_3	35	16	98 [b]	1
2	CuCl-TMEDA	K_2CO_3	25	16	90 [b]	2
3	CuI(dtbpf)	Cs_2CO_3	25	24	94 [b]	3
4	CuCl-*n*-Bu_4NOAc [d]	K_2CO_3	rt	16	90	4
5	$(NHC)_2$-Ag complex	Cs_2CO_3	rt	16	85	5
6	$AgBF_4$	Cs_2CO_3	50	16	98	6
7	Nd-bis(amidate)	Cs_2CO_3	40	24	94	7
8	NHC-Mo	Cs_2CO_3	70	18	94 [b]	8
9	CuI [e]	Cs_2CO_3	80	18	96	9
Heterogeneous metal catalysts						
10	Ag/Schiff-SiO_2	Cs_2CO_3	60	24	98 [b]	10
11	Fe_3O_4@Ag-40B	Cs_2CO_3	50	15	97 [b]	11
12	CeO_2-Ag	Cs_2CO_3	80	12	98 [b]	12
13	Ag/PCNF-700	Cs_2CO_3	25	18	90	13
14	Cu-CN-8.0	Cs_2CO_3	80	10	97 [b]	14
15	Ag@MIL-101(Cr)	Cs_2CO_3	50	15	96.5 [b]	15
16	Ag/Co-MOF	Cs_2CO_3	80	14	96 [b]	16
17	UiO-66@UiO-67-BPY-Ag	Cs_2CO_3	50	24	96 [b]	17
18	$Au_{12}Ag_{32}(SR)_{30}$@ZIF-8	K_2CO_3	50	24	100	18
19	Poly-NHC-Ag	Cs_2CO_3	rt	20	98 [b]	19
20	Ag-HMP-2	Cs_2CO_3	80	12	98 [b]	20
21	AgNPs/MCC	Cs_2CO_3	50	16	99	21
22	Ag@FeNT	Cs_2CO_3	60	15	70	22
23	CTF-DCE-Ag	Cs_2CO_3	50	20	90.2 [b]	23
25	Ag@CTFN	Cs_2CO_3	60	24	97	24
26	TpBpy-Cu-14	Cs_2CO_3	60	24	95	25
27	NHC-AuCl-COF	Cs_2CO_3	50	16	96	26
Organocatalysts						
28	PAPBI	Cs_2CO_3	60	24	94	27
29	TpBpy	Cs_2CO_3	60	6	67	28
30	TG-DMPZ	Cs_2CO_3	80	10	95	29
31	$TG(PZ)_3$	Cs_2CO_3	80	10	90	29
32	Pz	Cs_2CO_3	60	6	85	*This work*
33	Me_2Pz	Cs_2CO_3	60	6	96	*This work*

[a] The solvent is DMSO unless otherwise specified. For a more complete collection, see ref. 30. [b] The solvent is DMF. [c] The CO_2 pressure is 5 atm. [d] *n*-Bu_4NOAc (1.5 mmol, 1.5 eq.), the solvent is MeCN. [e] The reaction performs ethylene carbonate (EC) as the solvent in the presence of *n*-butyl iodide.

S5 Mechanism exploration

S5.1 Interactions between azoles and Cs_2CO_3

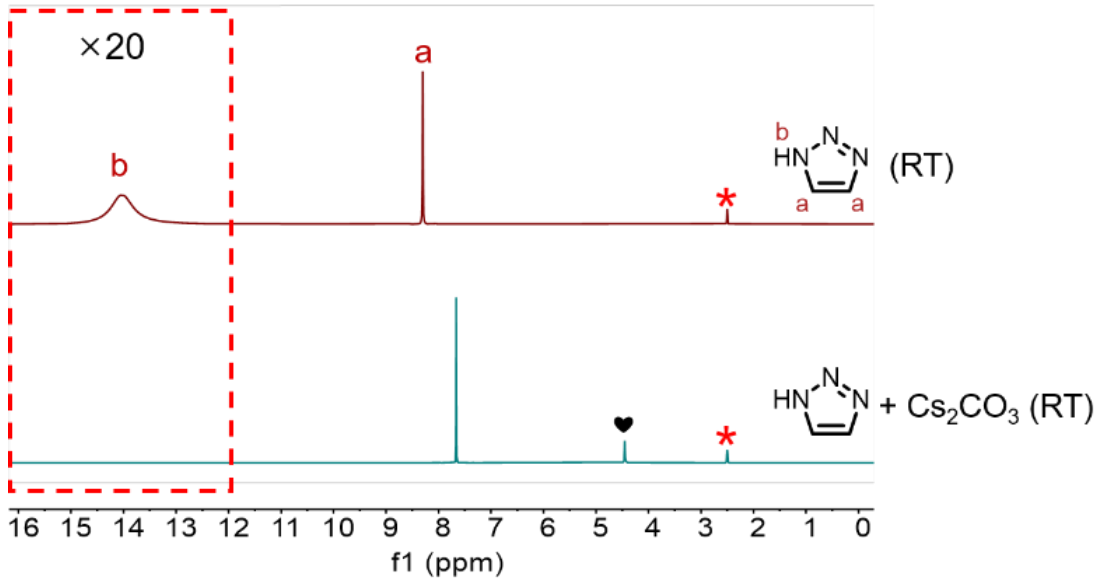


Fig. S1. ^{1}H NMR spectra of 1,2,3-triazole with/without Cs_2CO_3 in DMSO-d_6 at room temperature (*: DMSO-d_6; ❤: H_2O). The red dashed box shows the magnification in the 16 - 12 ppm range.

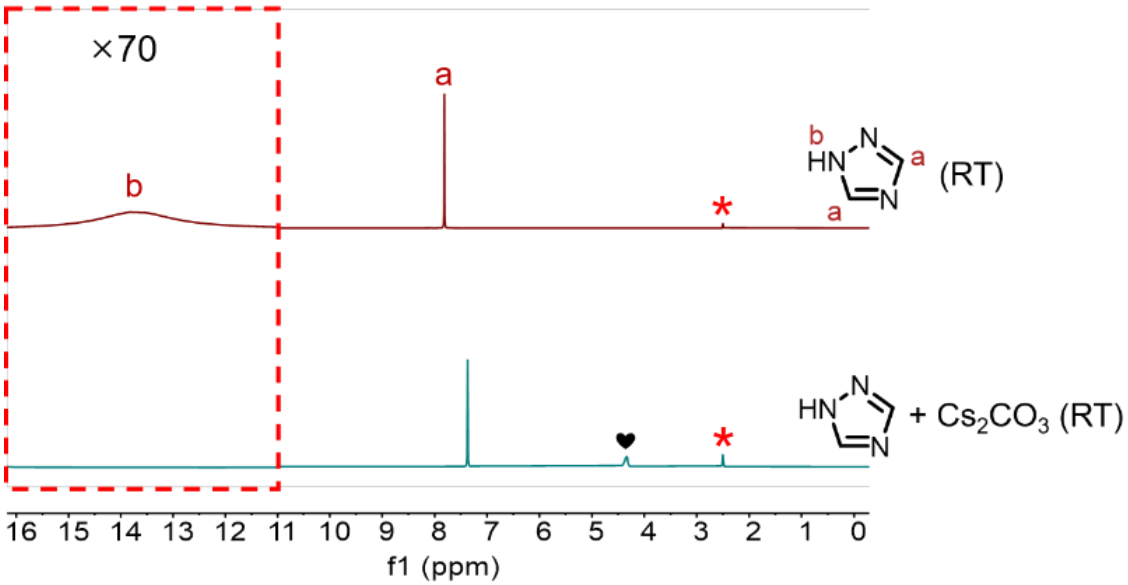


Fig. S2. ^{1}H NMR spectra of 1,2,4-triazole with/without Cs_2CO_3 in DMSO-d_6 at room temperature (*: DMSO-d_6; ❤: H_2O). The red dashed box shows the magnification in the 16 - 11 ppm range.

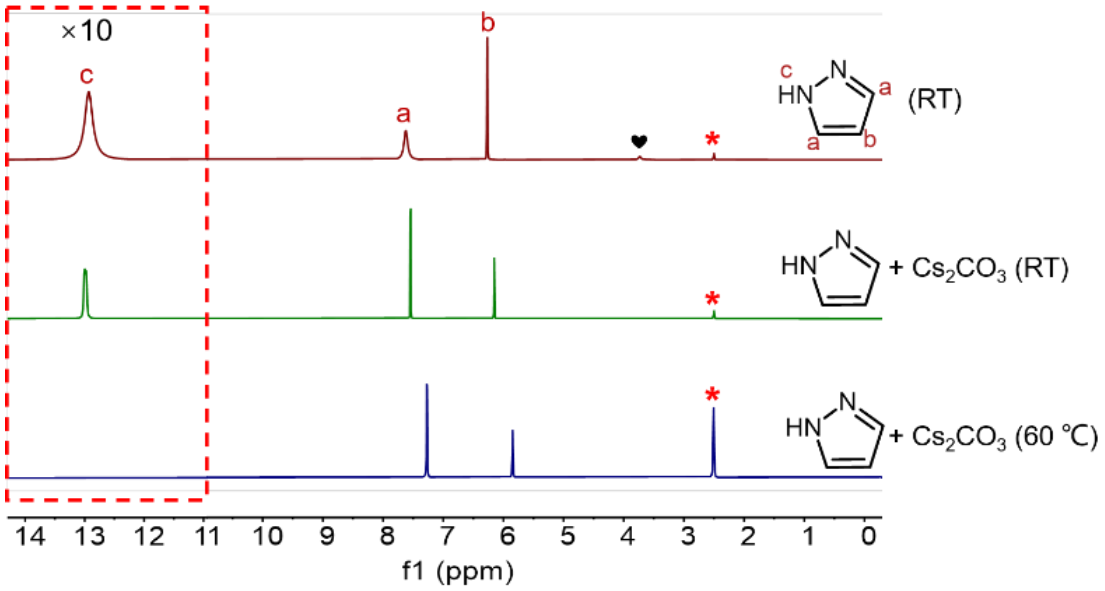


Fig. S3. ^{1}H NMR spectra of pyrazole (Pz) with/without Cs_2CO_3 in DMSO-d_6 at RT or 60 °C (*: DMSO-d_6; ❤: H_2O). The red dashed box shows the magnification in the 14 - 11 ppm range.

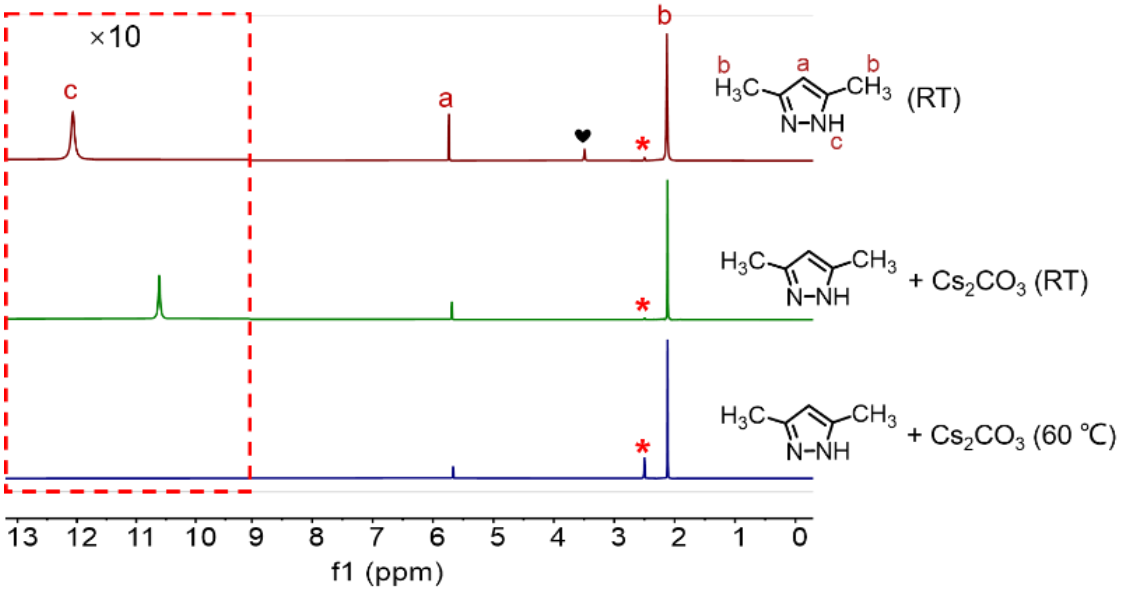


Fig. S4. ^{1}H NMR spectra of 3,5-dimethylpyrazole (Me_2Pz) with/without Cs_2CO_3 in DMSO-d_6 at RT or 60 °C (*: DMSO-d_6; ❤: H_2O). The red dashed box shows the magnification in the 13 - 9 ppm range.

S5.2 Formation of the Pz-CO_2 adduct

Cs(PzCO_2). A mixture of Pz (10 mmol) and Cs_2CO_3 (1.5 eq.) in anhydrous DMSO was placed in a sealed round bottom flask. The resulting mixture was stirred for 2 h at 60 °C and then filtered. The filtrate, which contains CsPz, was stirred under CO_2 or $^{13}CO_2$ (balloon) for another 2 h. The solutions before and after reacting with CO_2 were tested by ^{1}H NMR and ^{13}C NMR.

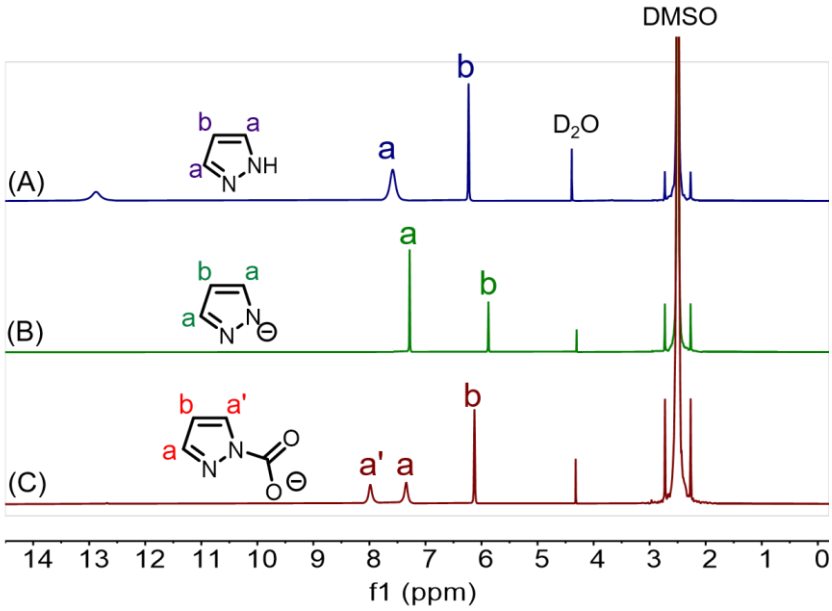


Fig. S5. ^{1}H NMR spectra (300 MHz, DMSO, 298 K, locked to a D_2O capillary) of Pz (A), CsPz (B) and Cs(PzCO_2) (C).

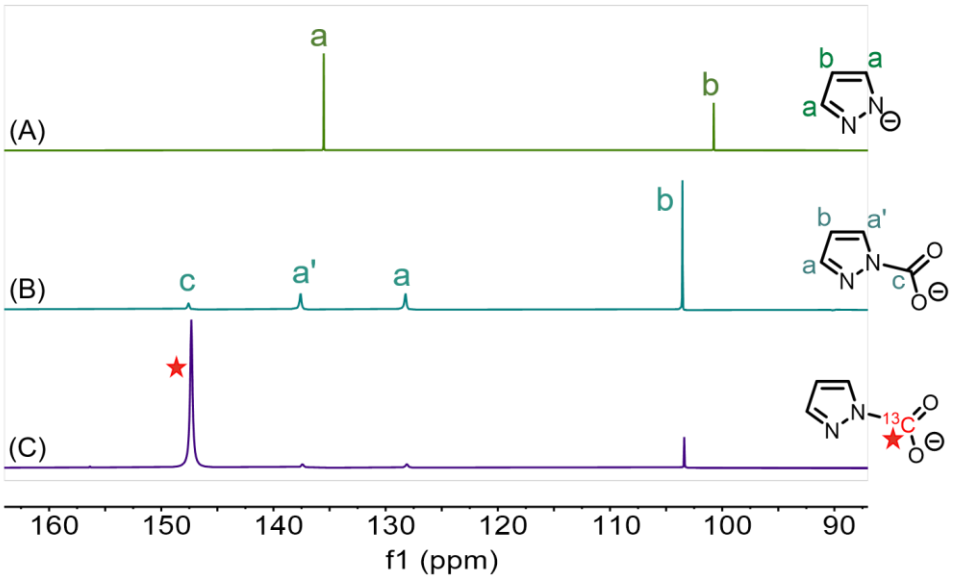


Fig. S6. ^{13}C NMR spectra (400 MHz, DMSO, 298 K, locked to a D_2O capillary) of CsPz (A, 1024 scans), Cs(PzCO_2) (B, 1024 scans) and Cs(Pz$^{13}CO_2$) (C, 8 scans).

S5.3 Carboxylation of 1a with Cs(Pz$^{13}CO_2$)

Synthetic procedure: The reactor with or without Cs_2CO_3 was equipped with a N_2/CO_2 balloon and heated in an oil bath. Then **1a** (1.0 mmol) and Cs(Pz$^{13}CO_2$) (1 mmol in 3 mL DMSO) were injected under stirring to start the reaction. After stirring at 60 °C for 6 h, the reaction was quenched with water (15 mL). The resultant solution was washed with CH_2Cl_2, acidified with 1 M HCl to pH = 1 and then extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to obtain product, which was weighed for yield calculations.

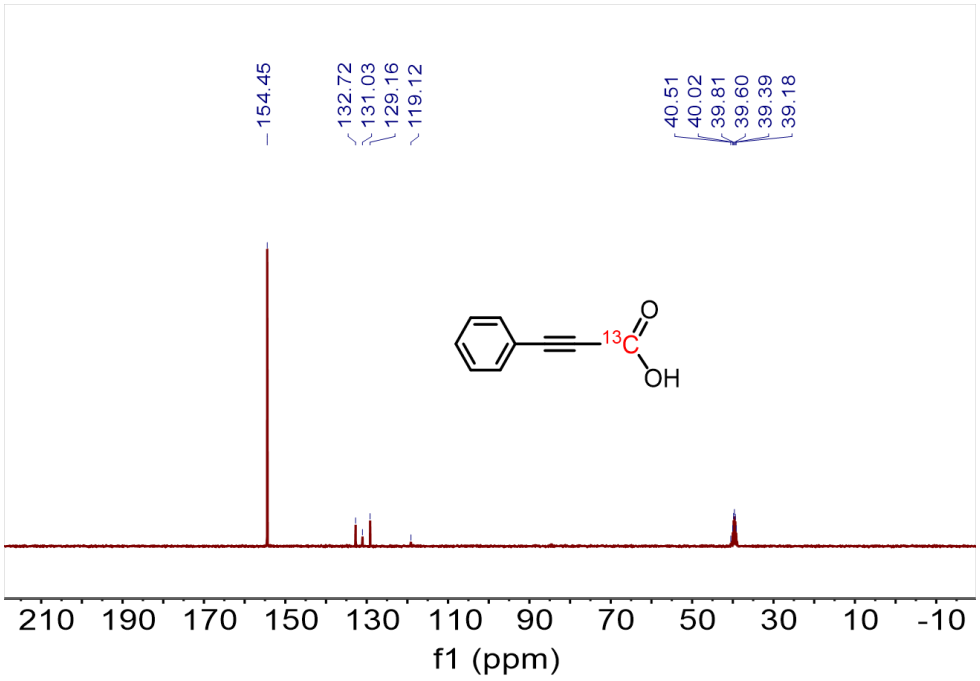


Fig. S7. ^{13}C NMR spectra (400 MHz, DMSO-d_6) of $^{13}C_{carboxyl}$-labeled **2a** with 8 scans.

S5.4 Interaction between 1a and Cs_2CO_3

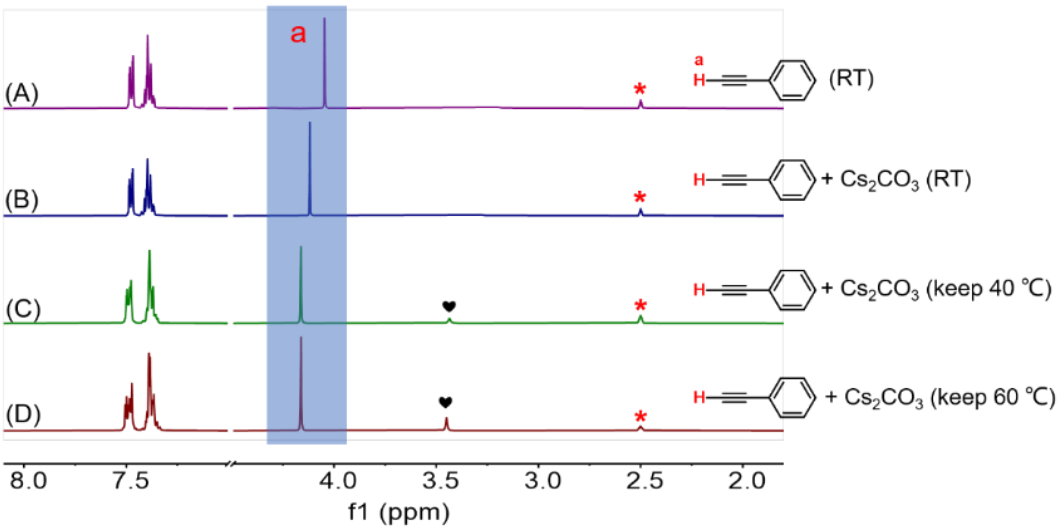


Fig. S8. ^{1}H NMR spectra of **1a** (A), **1a** with Cs_2CO_3 (B) and variable-temperature NMR spectra of **1a** with Cs_2CO_3 at 40 °C (C) and at 60 °C (D) in DMSO-d$_6$ (***:** DMSO-*d*$_6$; ❤: H_2O).

S5.5 Interaction between 1a and $Cs(PzCO_2)$

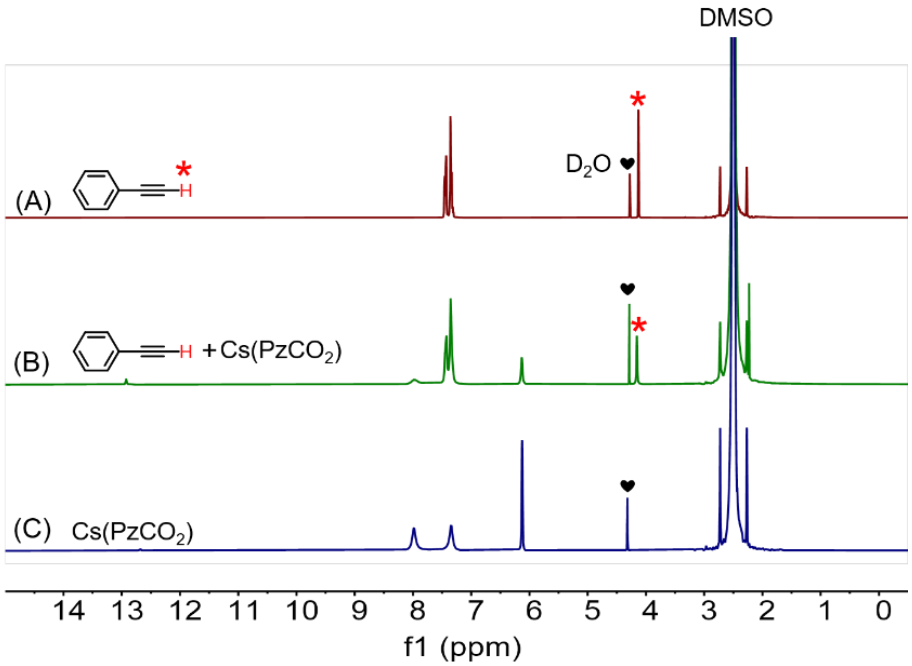


Fig. S9. ^{1}H NMR spectra (300 MHz, DMSO, 298 K, locked to a D_2O capillary) of **1a** (A), **1a** with $Cs(PzCO_2)$ (B) and $Cs(PzCO_2)$ (C).

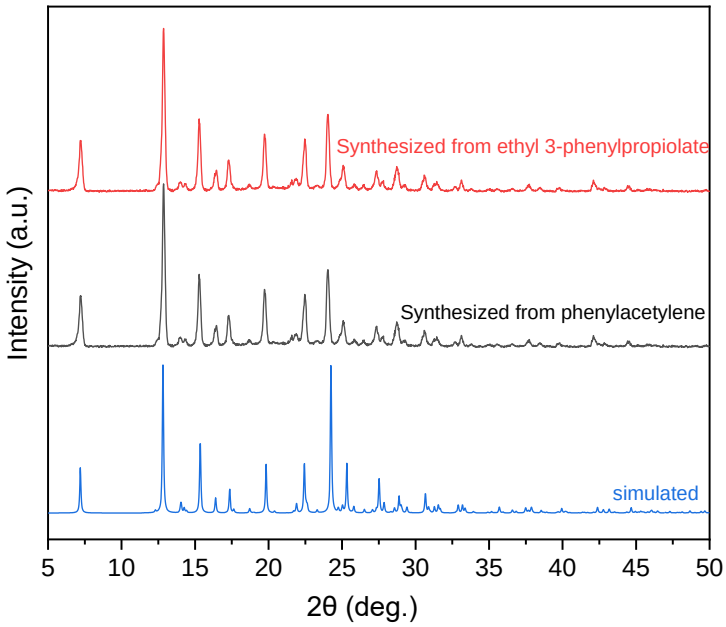


Fig S10. Experimental and simulated XRD patterns of **4d**.

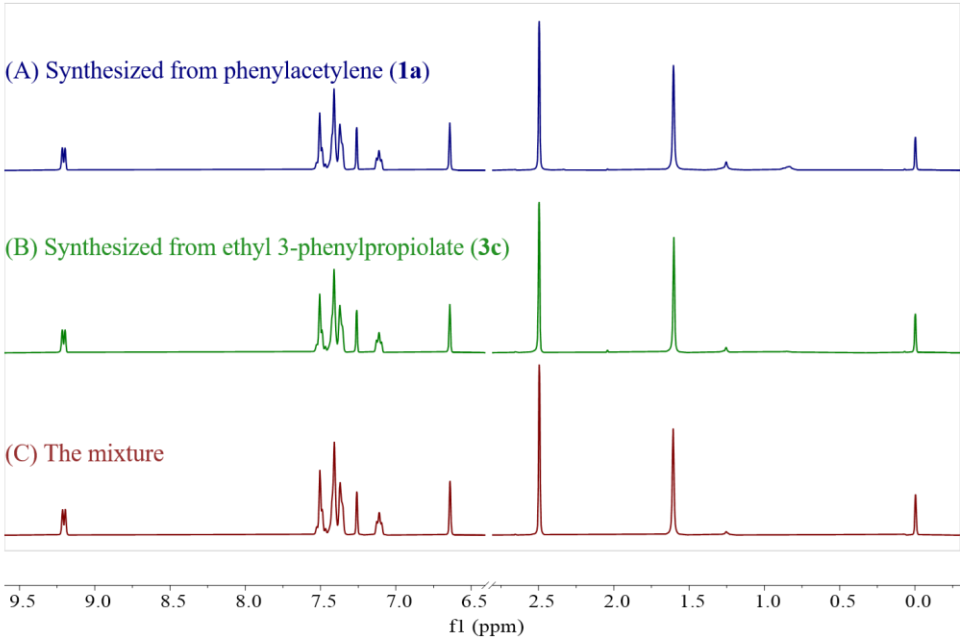
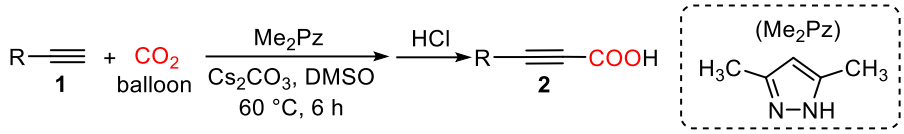


Fig S11. ^{1}H NMR spectrum of **4d** synthesized from **1a** (A) or **3c** (B), the products obtained by these two methods are mixed for (C).

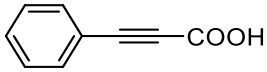
S6 Synthesis and characterization for propiolic acids (2)



General synthetic procedure: The catalyst (Me_2Pz, 10 mol%) and Cs_2CO_3 (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO_2, the reactor was equipped with a CO_2 balloon and heated to 60 °C in an oil bath. Then 1.0 mmol terminal alkyne dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h, the reaction was quenched with water (15 mL). The resultant solution was washed with CH_2Cl_2, acidified with 1 M HCl to pH = 1 and then extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to obtain the propiolic acid, which was weighed for yield calculations.

Characterization data

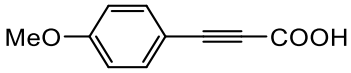
3-Phenylpropiolic acid (**2a**)



White solid; 140.3 mg, yield: 96%

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.58 (s, 1H), 7.64 - 7.61 (m, 2H), 7.57 - 7.52 (m, 1H), 7.49 - 7.45 (m, 2H).

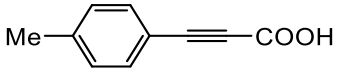
4-Methoxylphenylpropiolic acid (**2b**)



Yellow solid; 134 mg, yield: 76%

^{1}H NMR (500 MHz, DMSO-d_6) δ 13.59 (s, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 3.80 (s, 3H).

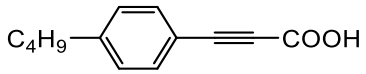
4-Methylphenylpropiolic acid (**2c**)



White solid; 128.4 mg, yield: 80%

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.49 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 2.33 (s, 3H).

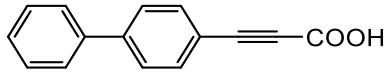
4-Pentylphenylpropiolic acid (**2d**)



White solid; 121.4 mg, yield: 60%

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.55 (d, J = 7.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 1.28 (s, 9H).

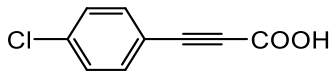
3-(Biphenyl-4-yl)propiolic acid (**2e**)



Yellow solid; 210.5 mg, yield: 95%

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.77 (d, J = 8.0 Hz, 2H), 7.72 - 7.69 (m, 4H), 7.49 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H).

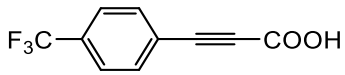
4-Chlorophenylpropiolic acid (**2f**)



Yellow solid; 173 mg, yield: 96%

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H).

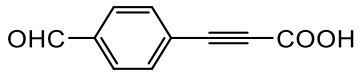
4-Trifluoromethylphenylpropiolic acid (**2g**)



White solid; 211.5 mg, yield: 99%

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.85 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H).

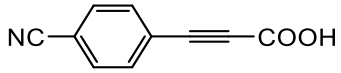
4-Formylphenylpropiolic acid (**2h**)



White solid; 169 mg, yield: 97%

^{1}H NMR (300 MHz, DMSO-d_6) δ 13.36 (br), 10.06 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H).

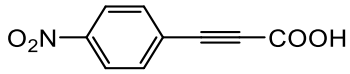
4-Cyanophenylpropiolic acid (**2i**)



White solid; 167.8 mg, yield: 98%

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H).

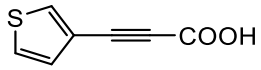
4-Nitrophenylpropiolic acid (**2j**)



Yellow solid; 189 mg, yield: 99%

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.29 (d, J = 7.7 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H).

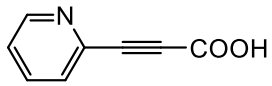
3-(Thiophen-3-yl)propiolic acid (**2k**)



White solid; 150 mg, yield: 99%

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.89 (dd, J = 5.1, 1.2 Hz, 1H), 7.67 (dd, J = 3.7, 1.2 Hz, 1H), 7.20 (dd, J = 5.1, 3.7 Hz, 1H).

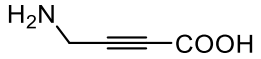
(Pyridin-2-yl)propynoic acid (**2l**)



Dark red solid; 73 mg, yield: 50%

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.65 (dt, J = 4.8, 1.4 Hz, 1H), 7.90 (td, J = 7.7, 1.8 Hz, 1H), 7.73 (dt, J = 7.9, 1.2 Hz, 1H), 7.52 (ddd, J = 7.7, 1.2 Hz, 1H).

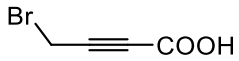
4-Amino-2-butynoic acid (**2m**)



Colorless oil; 66 mg, yield: 67%

^{1}H NMR (300 MHz, DMSO-d_6) δ 3.79 (s, 2H).

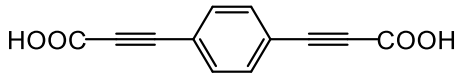
4-Bromo-2-butynoic acid (**2n**)



Brown oil; 113 mg, yield: 70%

^{1}H NMR (300 MHz, DMSO-d_6) δ 4.23 (s, 2H).

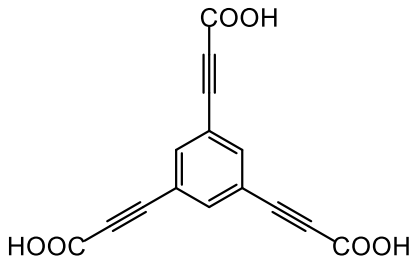
3,3′-(1,4-Phenylene)dipropiolic acid (**2q**)



White solid; 197 mg, yield: 92%

^{1}H NMR (300 MHz, DMSO-d_6) δ 13.85 (br), 7.70 (s, 4H).

3,3′,3″-(1,3,5-Phenylene)tripropiolic acid (**2r**)



Yellow solid; 279 mg, yield: 99%

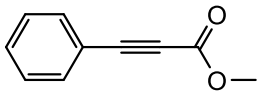
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.96 (s, 3H).

S7 Synthesis and characterization for propiolic acid esters (3)

General synthetic procedure: The catalyst (Me_2Pz, 10 mol%) and Cs_2CO_3 (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO_2, the reactor was equipped with a CO_2 balloon and heated to 60 °C in an oil bath. Then **1a** (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, RX (1.2 eq.) was added and stirred for another 4 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

Characterization data

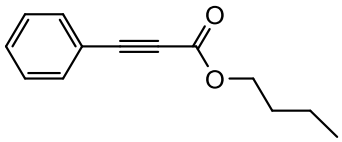
Methyl 3-phenylpropiolate (**3a**)



Colorless oil; 155.4 mg, yield: 97%

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.69 - 7.66 (m, 2H), 7.62 - 7.56 (m, 1H), 7.53 - 7.47 (m, 2H), 3.79 (s, 3H).

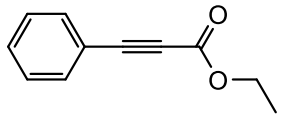
Butyl 3-phenyl-2-propynoate (**3b**)



Colorless oil; 186 mg, yield: 92%

^{1}H NMR (300 MHz, Chloroform-d) δ 7.57 - 7.54 (m, 2H), 7.44 - 7.38 (m, 1H), 7.36 - 7.31 (m, 2H), 4.21 (t, J = 6.7 Hz, 2H), 1.70 - 1.60 (m, 2H), 1.45 - 1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H).

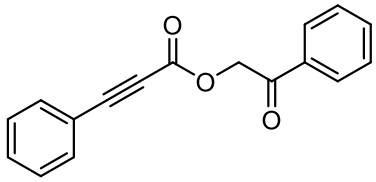
Ethyl 3-phenylpropiolate (**3c**)



Colorless oil; 163.5 mg, yield: 94%

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 - 7.57 (m, 2H), 7.48 - 7.42 (m, 1H), 7.40 – 7.34 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H).

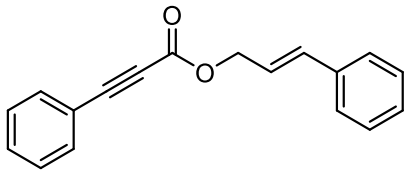
2-Oxo-2-phenylethyl 3-phenylpropiolate (**3d**)



Pale yellow solid; 250 mg, yield: 95%

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.63 (dd, *J* = 6.9, 1.8 Hz, 3H), 7.54 - 7.45 (m, 3H), 7.39 (t, *J* = 7.3 Hz, 2H), 5.50 (s, 2H).

Cinnamyl 3-phenylpropiolate (**3e**)



Colourless oil; 207 mg, yield: 79%

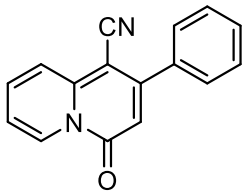
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.62 - 7.59 (m, 2H), 7.49 - 7.28 (m, 8H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.90 (dd, *J* = 6.6, 1.3 Hz, 2H).

S8 Synthesis and characterization for 4H-quinazin-4-ones (4)

General synthetic procedure: The catalyst (Me_2Pz, 10 mol%) and Cs_2CO_3 (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO_2, the reactor was equipped with a CO_2 balloon and heated to 60 °C in an oil bath. Then **1a** (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, EtBr (1.2 eq.) and pyridine derivatives (2.0 eq.) were added and heated at 100 °C for another 8 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

Characterization data

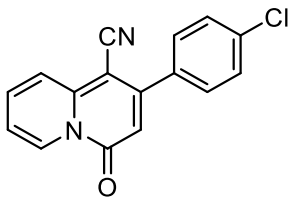
4-Oxo-2-phenyl-4H-quinolizine-1-carbonitrile (**4a**)



Yellow solid; 218 mg, yield: 89%

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.28 (d, *J* = 7.0 Hz, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 7.81 - 7.75 (m, 1H), 7.66 - 7.63 (m, 2H), 7.53 (dd, *J* = 4.3, 2.4 Hz, 3H), 7.29 - 7.24 (m, 1H), 6.63 (s, 1H).

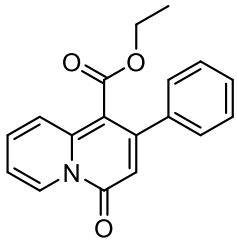
2-(3-Chlorophenyl)-4-oxo-4H-quinolizine-1-carbonitrile (**4b**)



Yellow solid; 257 mg, yield: 92%

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.28 (d, *J* = 7.2 Hz, 1H), 8.13 (d, *J* = 8.9 Hz, 1H), 7.83 - 7.77 (m, 1H), 7.61 - 7.56 (m, 2H), 7.53 - 7.48 (m, 2H), 7.31 - 7.28 (m, 1H), 6.58 (s, 1H).

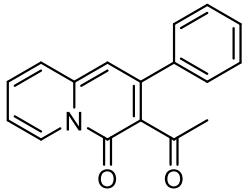
Ethyl 4-oxo-2-phenyl-4H-quinolizine-1-carboxylate (**4c**)



Yellow solid; 220 mg, yield: 75%

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.25 (d, *J* = 7.4 Hz, 1H), 8.22 (d, *J* = 9.2 Hz, 1H), 7.58 - 7.52 (m, 1H), 7.45 - 7.36 (m, 5H), 7.15 - 7.10 (m, 1H), 6.59 (s, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 0.79 (t, *J* = 7.1 Hz, 3H).

3-Acetyl-2-phenyl-4H-quinolizin-4-one (**4d**)



Yellow solid; 238 mg, yield: 90%

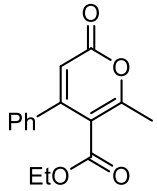
^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.21 (d, *J* = 8.4 Hz, 1H), 7.54 - 7.49 (m, 2H), 7.43 - 7.35 (m, 5H), 7.12 (ddd, *J* = 7.4, 5.5, 2.5 Hz, 1H), 6.64 (s, 1H), 2.50 (s, 3H).

S9 Synthesis and characterization for 2H-pyran-2-one (5)

General synthetic procedure: The catalyst (Me_2Pz, 10 mol%) and Cs_2CO_3 (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO_2, the reactor was equipped with a CO_2 balloon and heated to 60 °C in an oil bath. Then **1a** (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, EtBr (1.2 eq.) was added and stirred at RT for 4 h. Then, 1,3-dicarbonyl compound (1.0 eq.) was added at 100 °C and allowed to react for 4 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

Characterization date

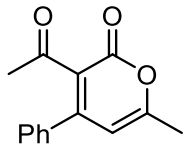
Ethyl 6-methyl-2-oxo-4-phenyl-2H-pyran-5-carboxylate (**5a**)



Pale yellow solid; 116 mg, yield: 45%

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 - 7.40 (m, 3H), 7.28 (dt, *J* = 7.6, 1.9 Hz, 2H), 6.15 (s, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 0.86 (t, *J* = 6.4 Hz, 3H).

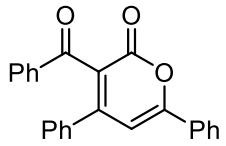
5-Acetyl-6-methyl-4-phenyl-2H-pyran-2-one (**5b**)



White solid; 86.8 mg, yield: 38%

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 6.3 Hz, 3H), 7.32 - 7.29 (m, 2H), 6.12 (s, 1H), 2.33 (s, 3H), 2.31 (s, 3H).

5-Benzoyl-4,6-diphenyl-2H-pyran-2-one (**5c**)



Yellow solid; 263 mg, yield: 75%

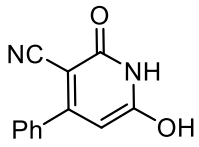
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 - 7.91 (m, 2H), 7.88 - 7.85 (m, 2H), 7.53 - 7.46 (m, 4H), 7.41 - 7.35 (m, 4H), 7.34 - 7.30 (m, 3H), 6.89 (s, 1H).

S10 Synthesis and characterization for 3-cyano-6-hydroxy-2-pyridones (6)

General synthetic procedure: The catalyst (Me_2Pz, 10 mol%) and Cs_2CO_3 (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO_2, the reactor was equipped with a CO_2 balloon and heated to 60 °C in an oil bath. Then **1a** (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, CH_3I (1.2 eq.) was added and stirred at RT for 4 h. Then, cyanoacetamide or 2-cyano-*N*-methyl-acetamide (1.02 eq.) was added and heated to 100 °C for 12 h. The reaction was quenched with water (15 mL) and the resultant solution was acidified with 1M HCl to produce solid. The solid was filtered and dried in vacuum.

Characterization data

6-Hydroxy-2-oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (**6a**)

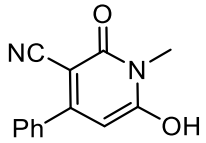


White solid; 159.7 mg, yield: 75%

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.51 (s, 5H), 5.65 (s, 1H).

MS: $[M+H]^+$; 213.21 , found: 213.2

6-Hydroxy-1-methyl-2-oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (**6b**)



White solid; 162.5 mg, yield: 72%

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.51 - 7.50 (m, 5H), 5.63 (s, 1H), 3.31 (s, 3H).

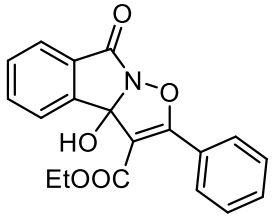
MS: $[M+H]^+$; 227.24 , found: 227.2

S11 Synthesis and characterization for 3a-hydroxyisoxazolo[3,2-a]isoindol-8(3aH)-ones (7)

General synthetic procedure: The catalyst (Me_2Pz, 10 mol%) and Cs_2CO_3 (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO_2, the reactor was equipped with a CO_2 balloon and heated to 60 °C in an oil bath. Then **1a** or **1o** (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, EtBr (1.2 eq.), NHPI (1.0 eq.) and PPh_3 (0.1 eq.) were added. The reaction system soon became reddish brown and was stirred at RT for 6 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

Characterization data

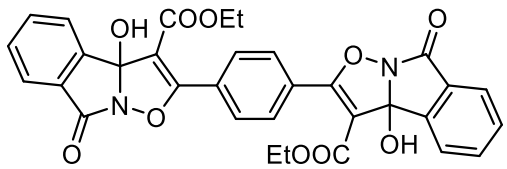
Ethyl 3a-hydroxy-8-oxo-2-phenyl-3a,8-dihydroisoxazolo[3,2-a]-isoindole-3-carboxylate (**7a**)



White solid; 327 mg, yield: 97%

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.01 (d, J = 7.7 Hz, 1H), 7.98 (s, 1H), 7.90 - 7.83 (m, 2H), 7.72 - 7.63 (m, 3H), 7.61 - 7.48 (m, 3H), 4.11 - 4.00 (m, 2H), 1.10 (t, J = 7.1 Hz, 3H).

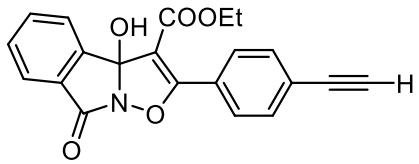
Diethyl 2,2′-(1,4-phenylene)bis(3a-hydroxy-8-oxo-3a,8-dihydroisoxazolo[3,2-a]isoindole-3-carboxylate) (**7b**)



Pale yellow solid; 378 mg, yield: 69%

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.00 (d, J = 6.8 Hz, 4H), 7.92 - 7.83 (m, 8H), 7.68 (t, J = 8.0 Hz, 2H), 4.13 - 4.08 (m, 4H), 1.15 - 1.10 (m, 6H).

Ethyl 2-(4-ethynylphenyl)-3a-hydroxy-8-oxo-3a,8-dihydro-isoxazolo[3,2-a]isoindole-3-carboxylate (**7b'**)



White solid; 72 mg, yield: 22%

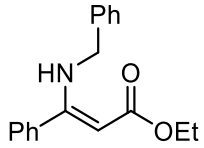
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.01 - 7.96 (m, 2H), 7.90 - 7.83 (m, 2H), 7.73 - 7.61 (m, 5H), 4.43 (s, 1H), 4.12 - 4.07 (m, 2H), 1.13 (t, J = 7.1 Hz, 3H).

S12 Synthesis and characterization for imidazole-4-carboxylic derivatives (9)

General synthetic procedure: The catalyst (Me_2Pz, 10 mol%) and Cs_2CO_3 (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO_2, the reactor was equipped with a CO_2 balloon and heated to 60 °C in an oil bath. Then **1a** (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, EtBr (1.2 eq.) was added and stirred for 4 h. Benzylamine (1.2 eq.) and Cs_2CO_3 (1.0 mmol) were addition to form intermediate products (**8**). KI (0.3 eq.) and ^{t}BuONO (2.0 eq.) were added and the reaction mixture was stirred at 80 °C for 18 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

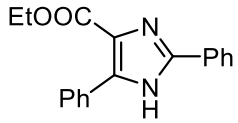
Characterization data

Ethyl-3-(benzylamino)-3-phenylacrylate (**8**)



^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.02 (t, *J* = 6.4 Hz, 1H), 7.40 - 7.37 (m, 5H), 7.34 - 7.31 (m, 2H), 7.29 - 7.21 (m, 3H), 4.76 (s, 1H), 4.31 (d, *J* = 6.5 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

Ethyl 2,5-diphenyl-1H-imidazole-4-carboxylate (**9**)



Yellow solid; 175 mg, yield: 60%

^{1}H NMR (300 MHz, Chloroform-*d*) δ 10.13 (br), 7.97 - 7.95 (m, 4H), 7.48 - 7.38 (m, 6H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

MS: $[M+H]^+$; 293.34 , found: 293.3

S13 X-ray crystallographic study

Crystal structure determination. The diffraction intensity data of **4b - d**, **5a - c** were collected at 173 K on a Rigaku XtaLAB PRO MM003-DS dual System with a Cu micro-focus source (Cu-K_α, λ = 1.54184 Å). The structure was refined by Olex2 program. The nonhydrogen atoms were refined anisotropically. The H atoms attached to carbons were added geometrically and refined isotropically with the riding model. The crystal data were collected in Table S4.

Table S4. Summary of single crystal X-ray diffraction analysis

	4b	**4c**	**4d**	**5a**	**5b**	**5c**
CCDC No.	2306337	2306336	2306341	2306338	2306339	2306340
Description	prism	prism	block	block	prism	block
Color	yellow	colorless	yellow	colourless	colourless	colourless
From solution	DCM/Hexane	DCM/Hexane	DCM/Hexane	DCM/Hexane	DCM/Hexane	DCM/Hexane
Empirical formula	$C_{16}H_9ClN_2O$	$C_{18}H_{15}NO_3$	$C_{17}H_{13}NO_2$	$C_{15}H_{14}O_4$	$C_{14}H_{12}O_3$	$C_{24}H_{16}O_3$
Formula weight	280.715	293.325	263.298	258.26	228.249	352.393
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*Pccn*	$P2_1/c$	*Pbca*	$P2_1/c$	$P2_1/n$	$P2_1$
a, Å	14.1800(2)	13.9261(3)	7.3350(2)	9.3720(2)	9.7106(2)	10.0411(2)
b, Å	19.7617(3)	7.8917(2)	14.3799(3)	19.4732(4)	7.7880(1)	16.9542(3)
c, Å	18.2437(2)	13.2129(3)	24.5438(7)	7.2389(1)	15.1238(3)	10.2605(2)
α, deg	90	90	90	90	90	90
β, deg	90	98.325(2)	90	95.595(2)	102.369(2)	90.799(2)
γ, deg	90	90	90	90	90	90
V, Å^3	5112.27(12)	1436.80(6)	2588.80(12)	1314.83(4)	1117.21(4)	1746.57(6)
Z	16	4	8	4	4	4
ρ calcd, g cm^{-3}	1.459	1.356	1.351	1.305	1.357	1.340
R_1 [$I > 2\sigma(I)$]	0.0445	0.0405	0.0490	0.0436	0.0380	0.0371
wR_2 (all data)	0.1446	0.1049	0.1517	0.1305	0.1386	0.0826

S14 References

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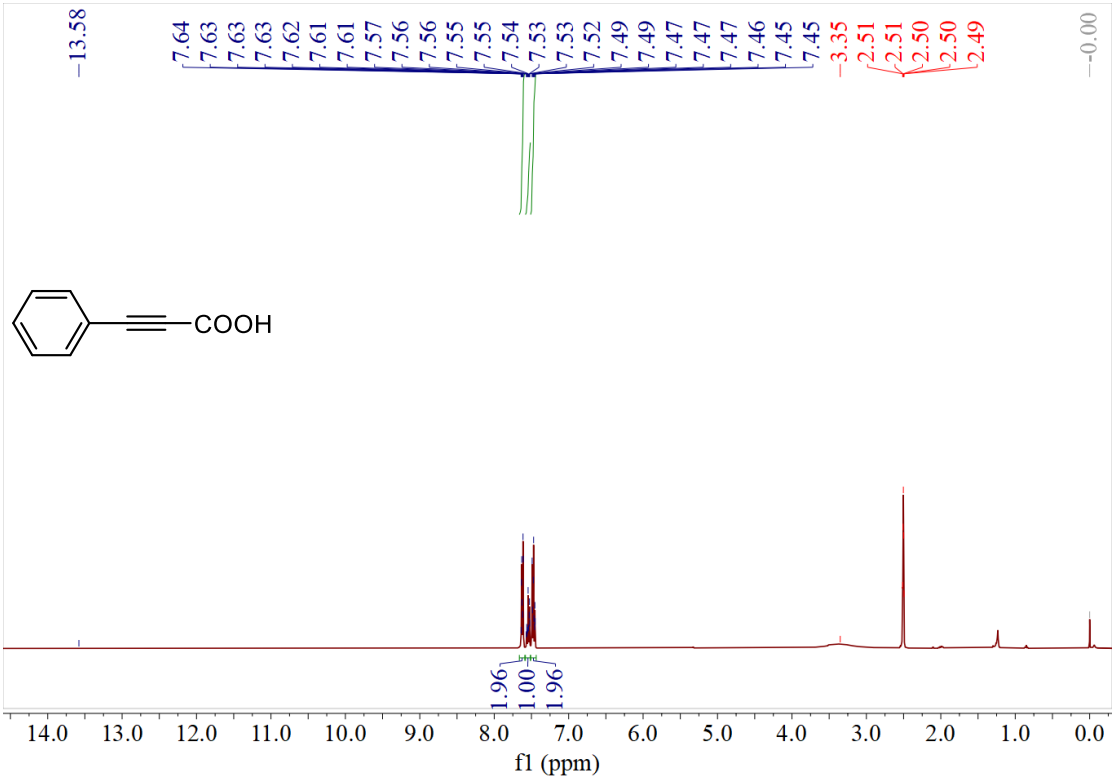
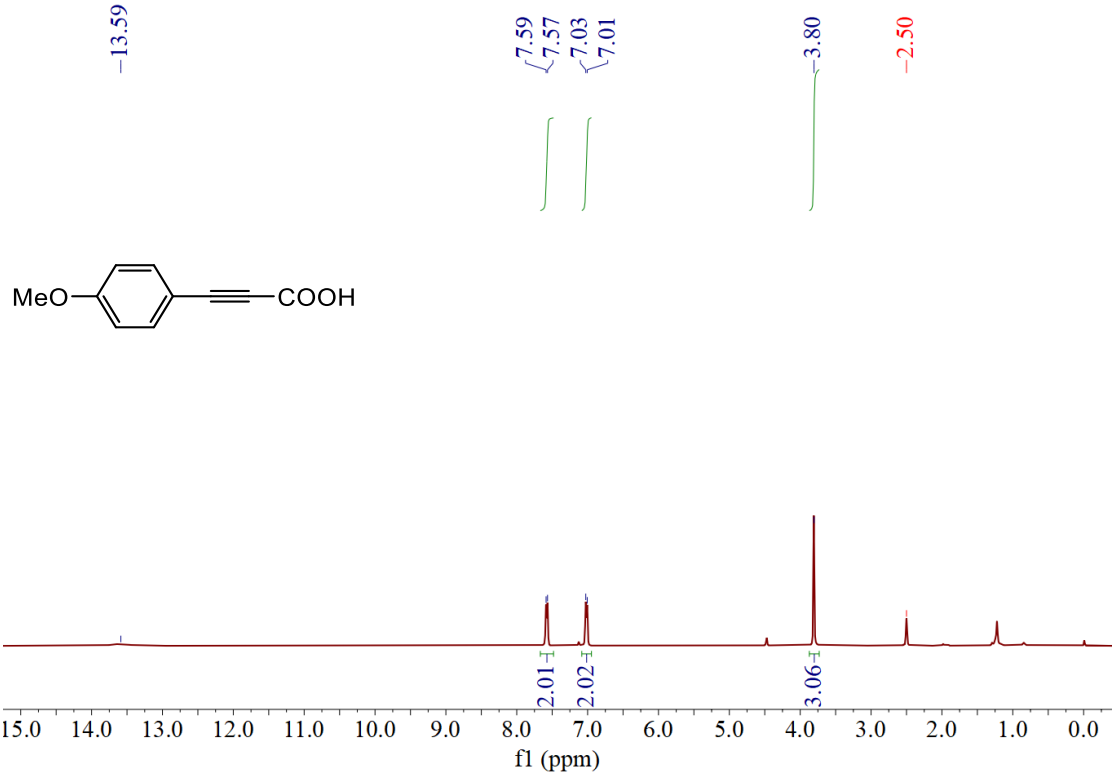
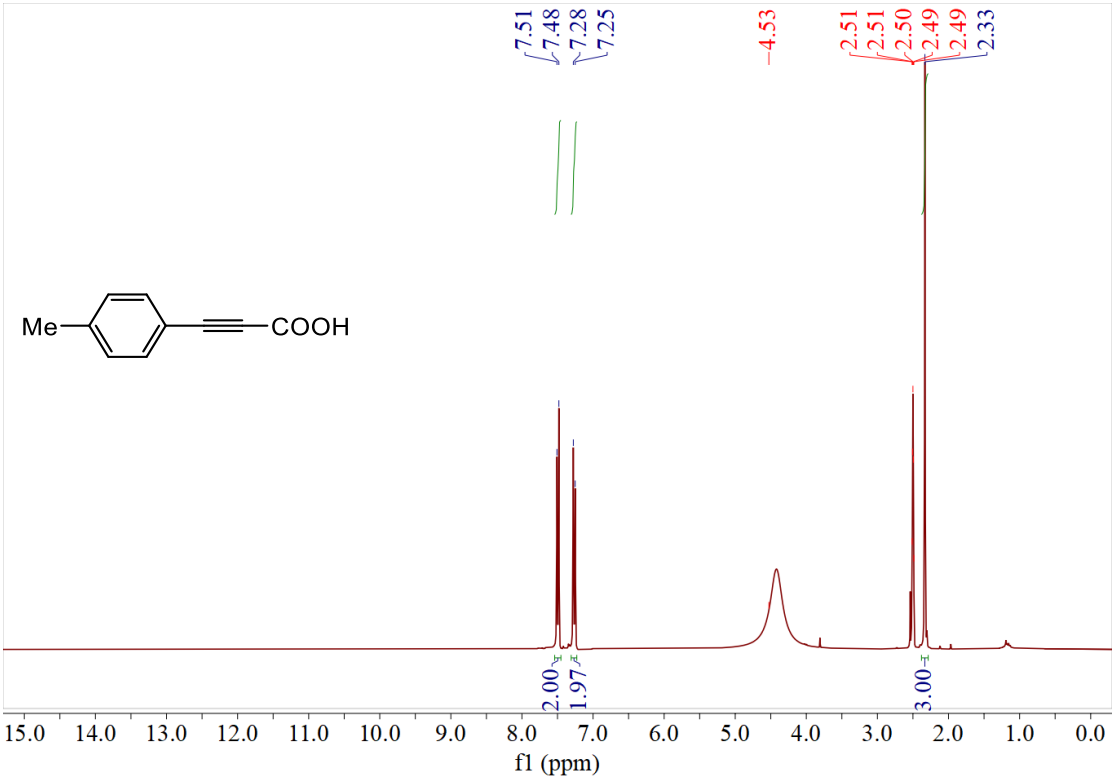
S15 Copies of ^{1}H NMR spectra of products



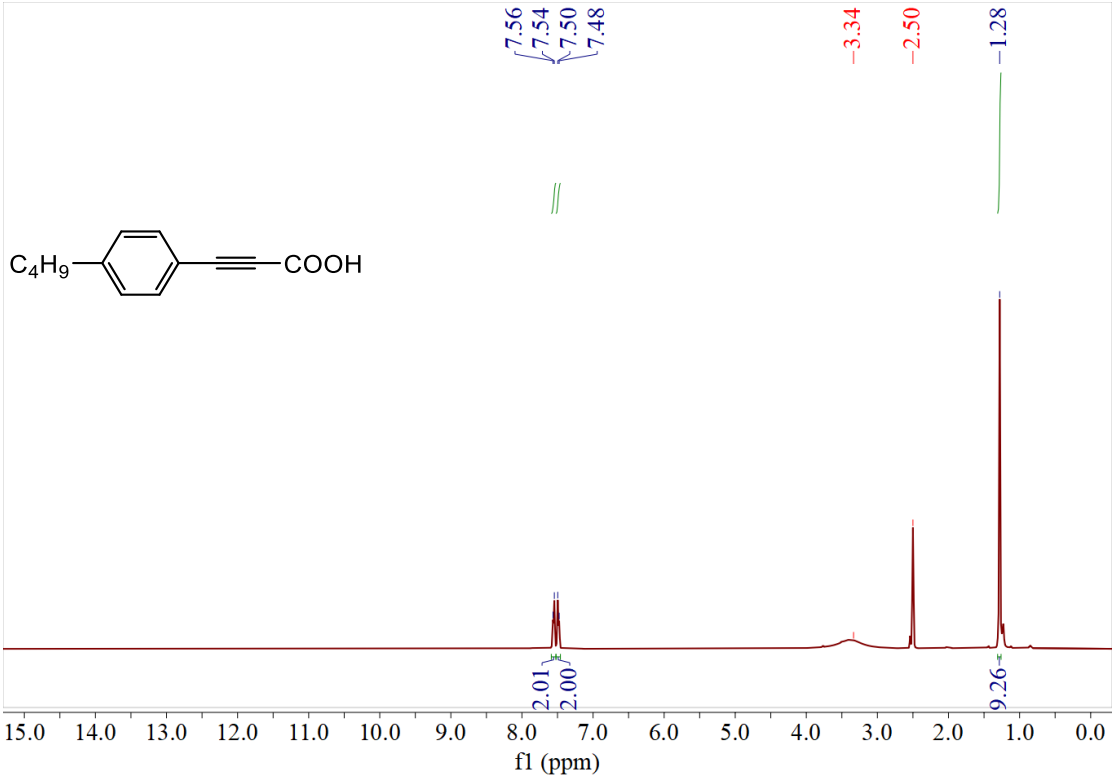
^{1}H NMR (400 MHz) spectrum of **2a** in DMSO-d_6



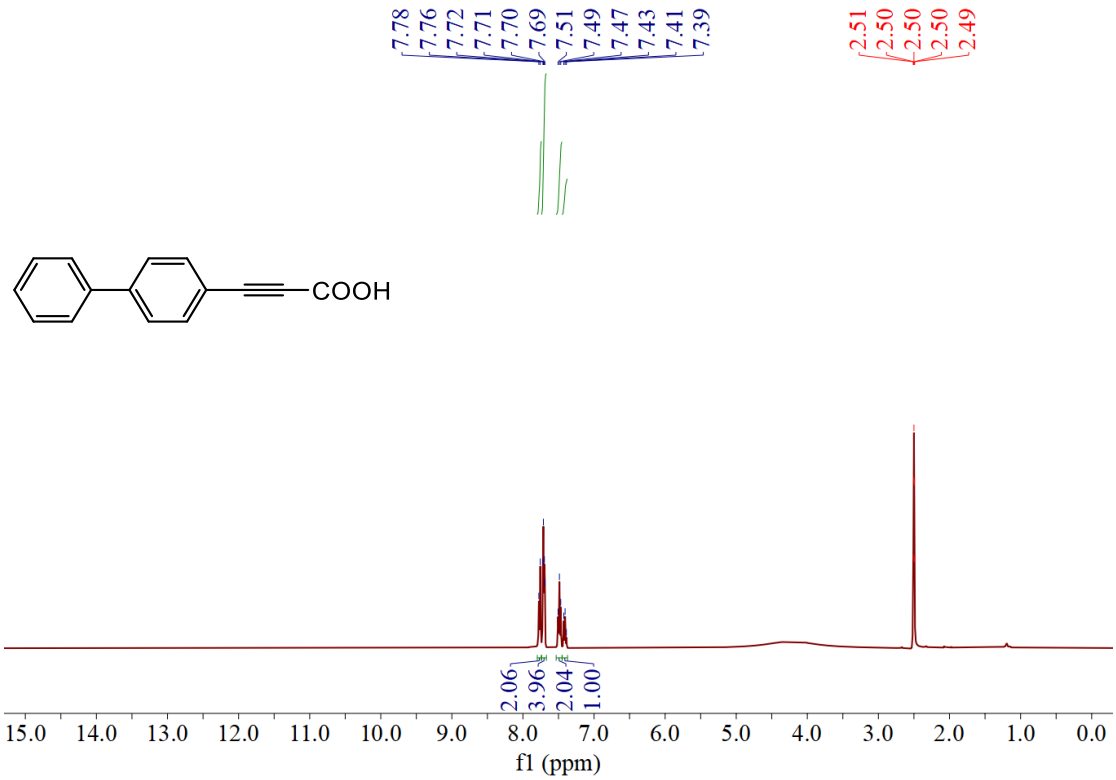
^{1}H NMR (500 MHz) spectrum of **2b** in DMSO-d_6



^{1}H NMR (400 MHz) spectrum of **2c** in DMSO-d_6



^{1}H NMR (300 MHz) spectrum of **2d** in DMSO-d_6



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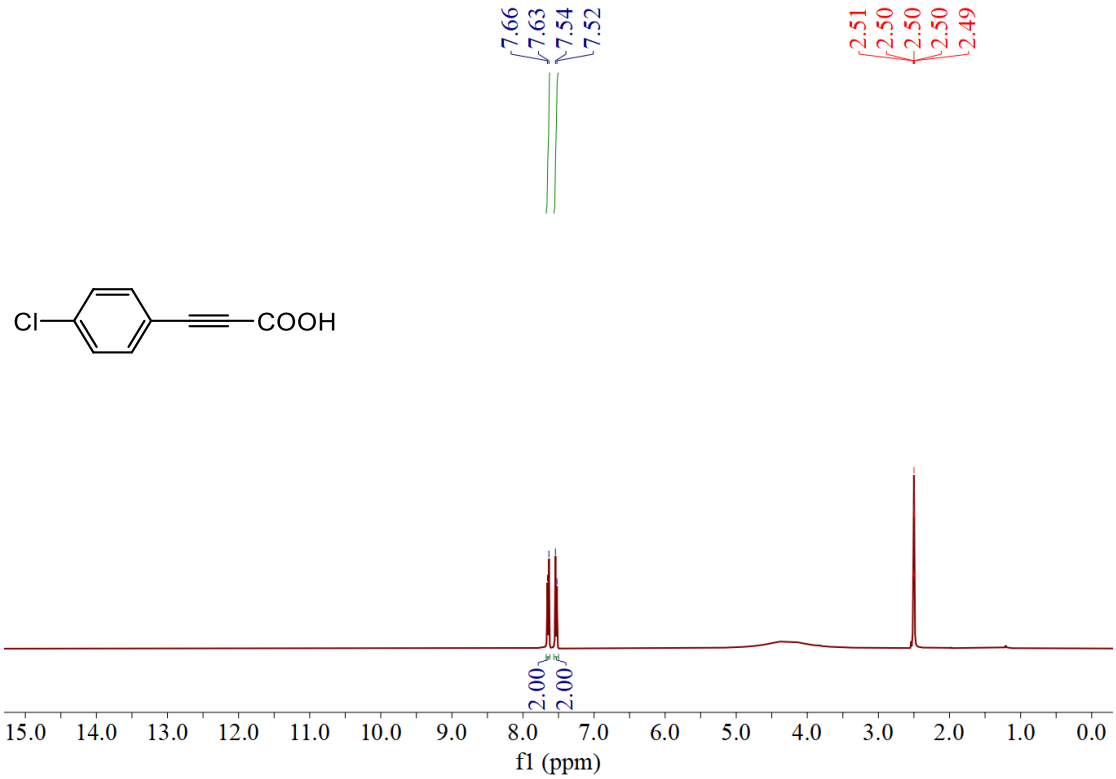
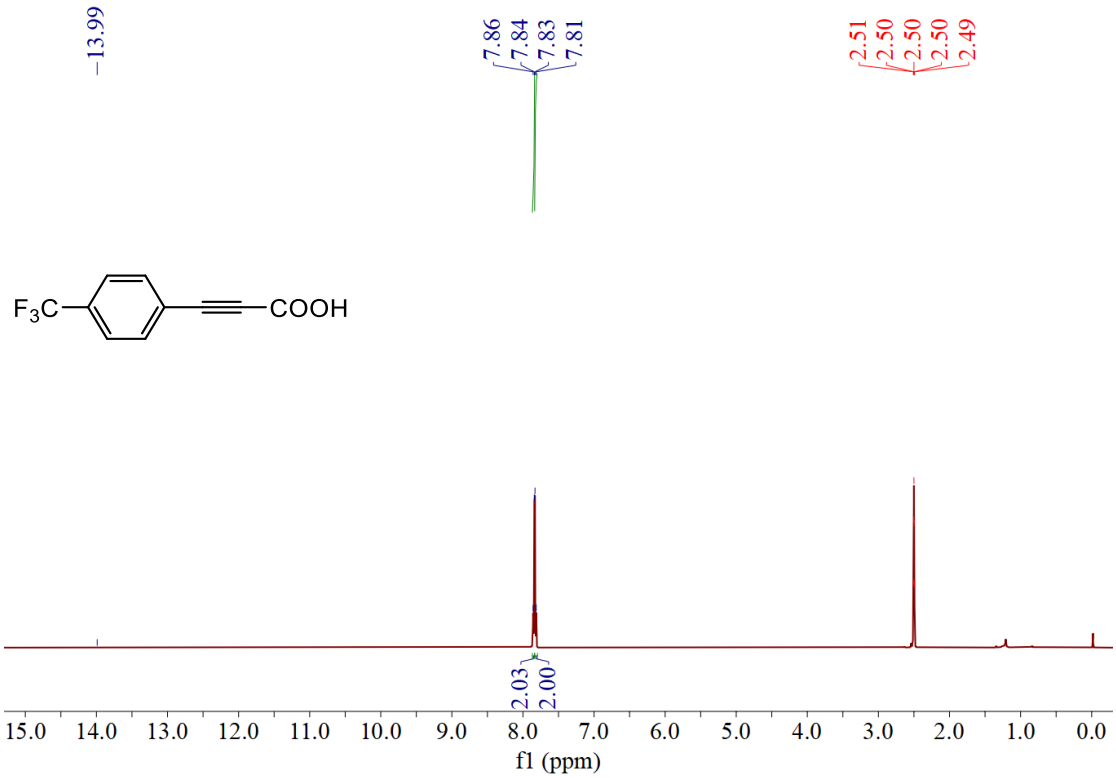
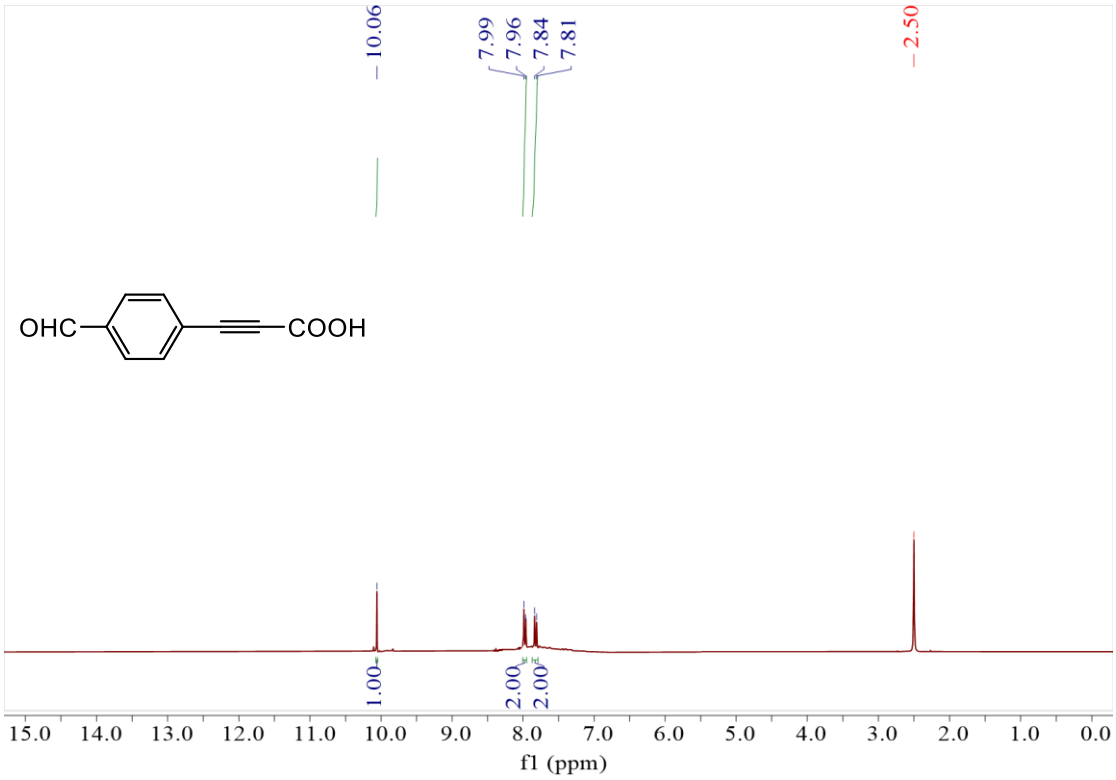


^{1}H NMR (500 MHz) spectrum of **2f** in DMSO-d_6



^{1}H NMR (500 MHz) spectrum of **2g** in DMSO-d_6



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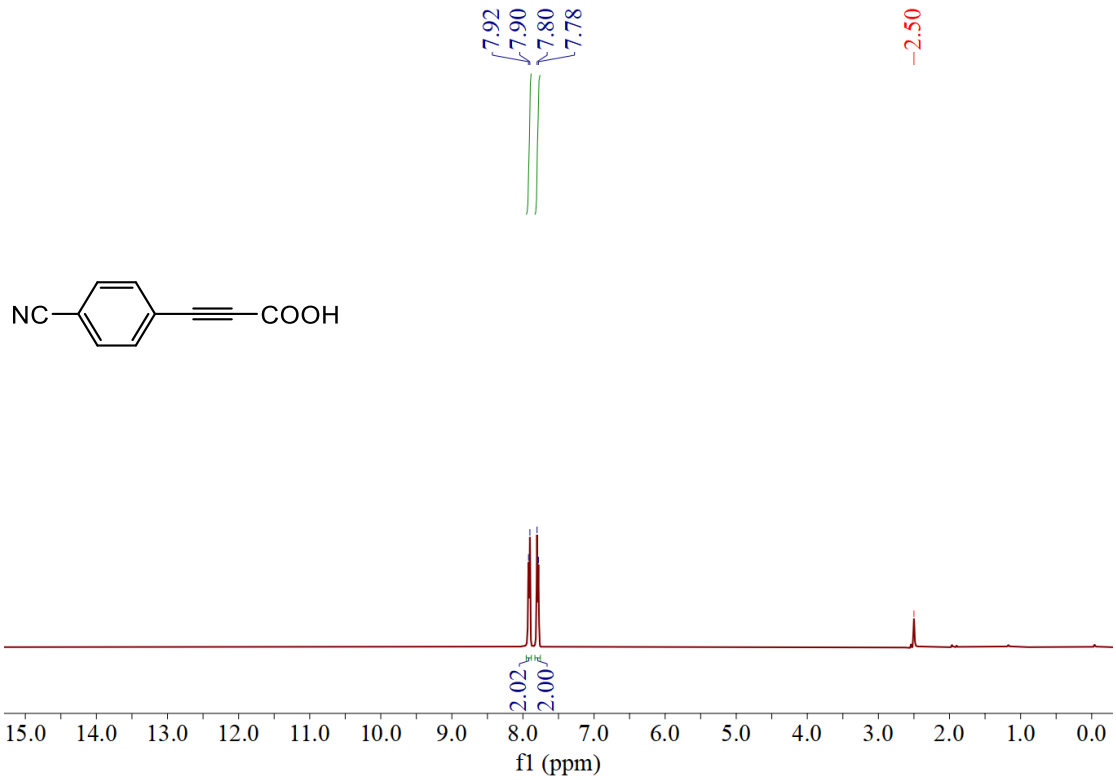
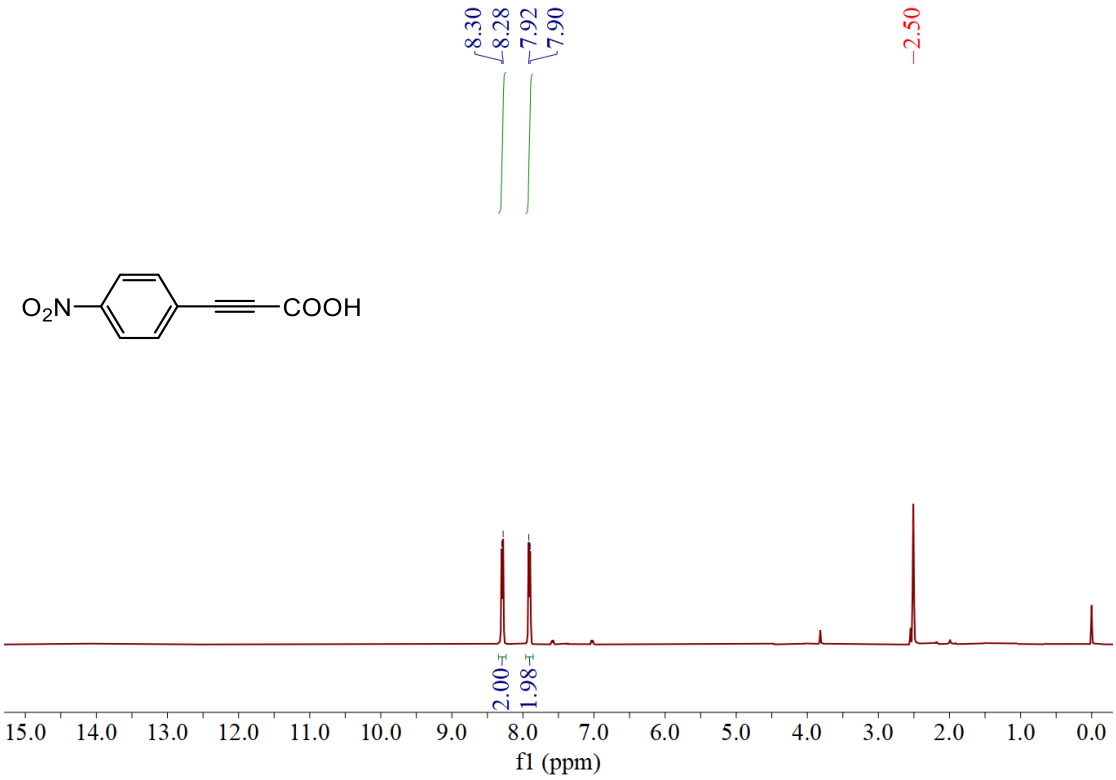
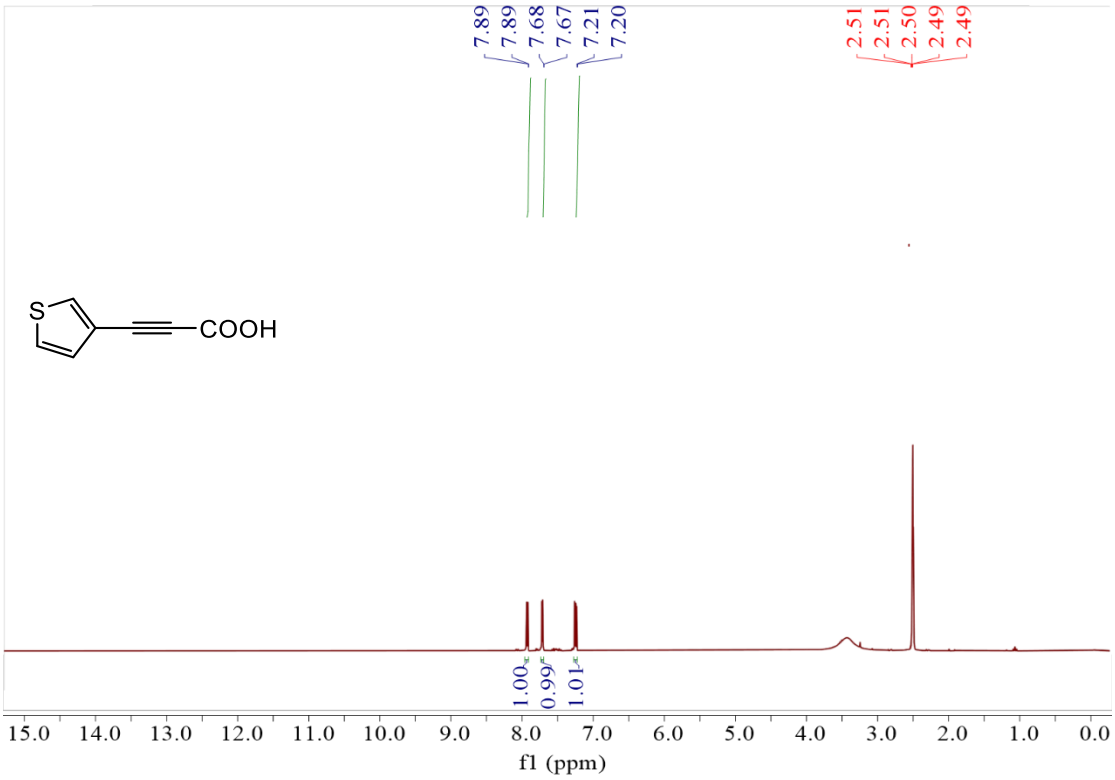


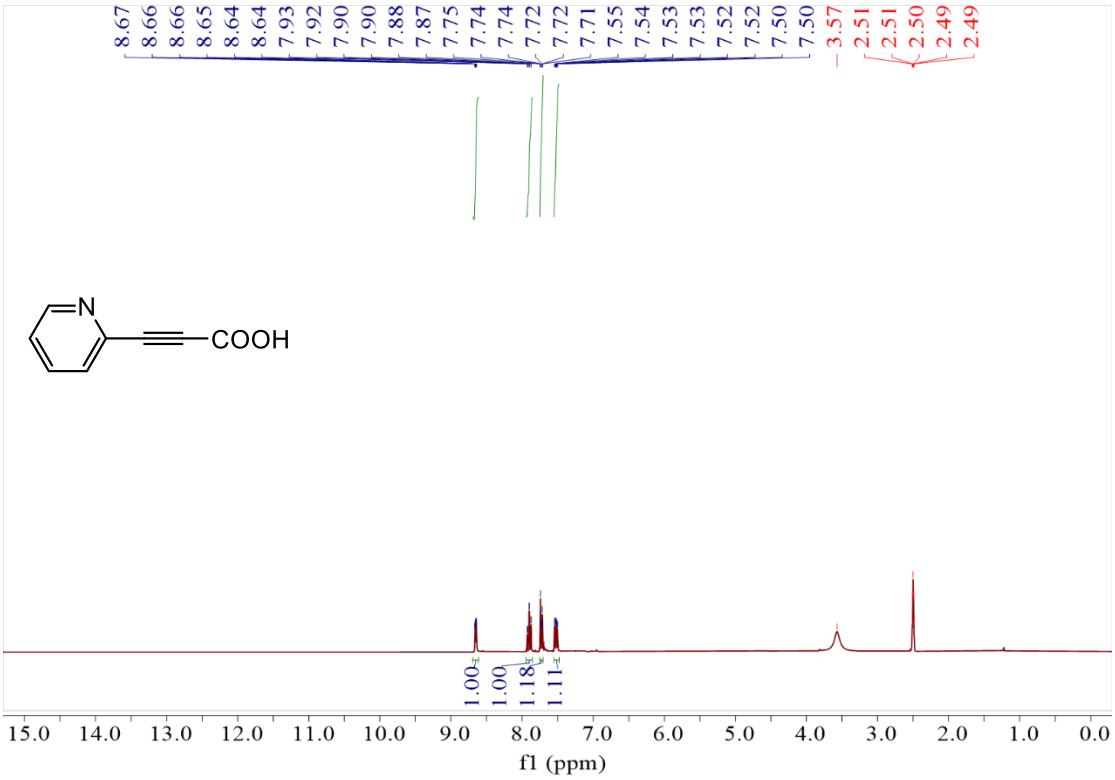
^{1}H NMR (400 MHz) spectrum of **2i** in DMSO-d_6



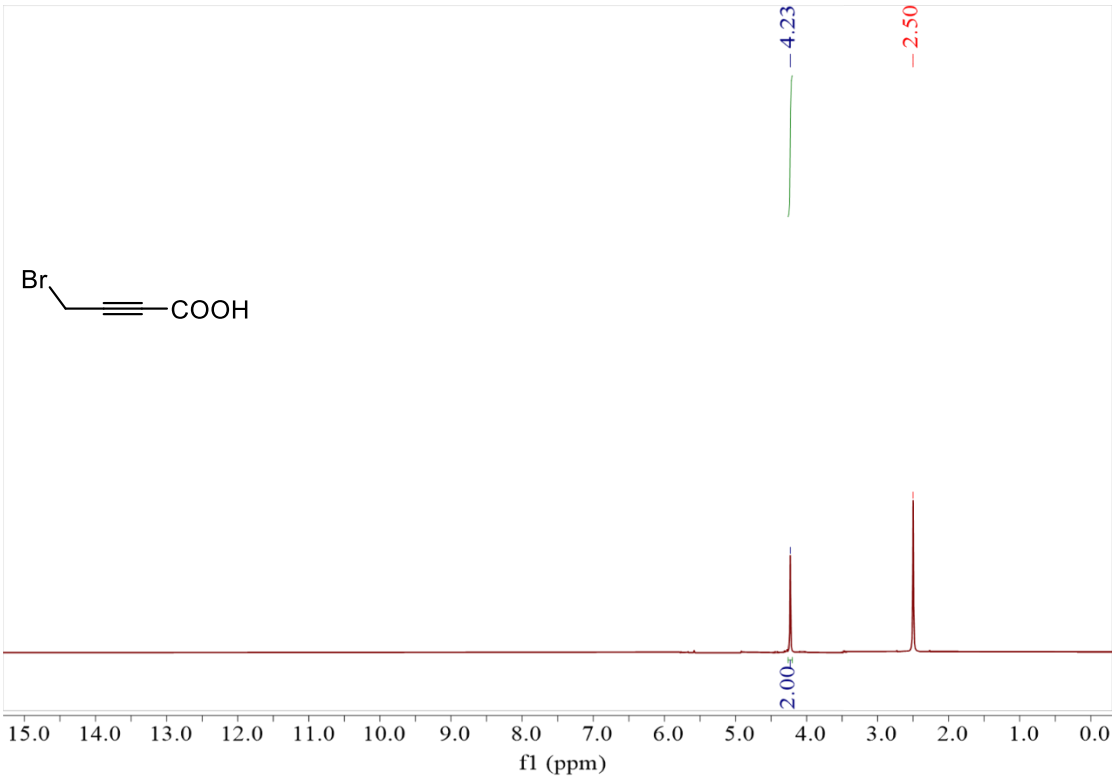
^{1}H NMR (500 MHz) spectrum of **2j** in DMSO-d_6



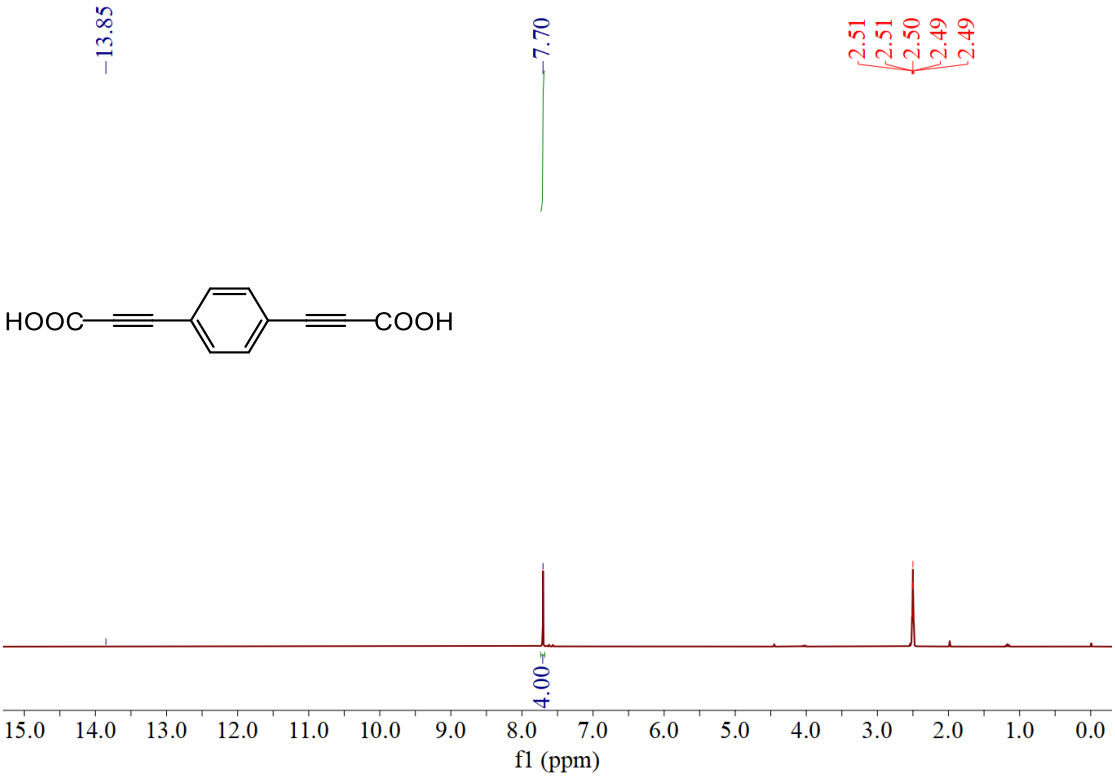
^{1}H NMR (500 MHz) spectrum of **2k** in DMSO-d_6



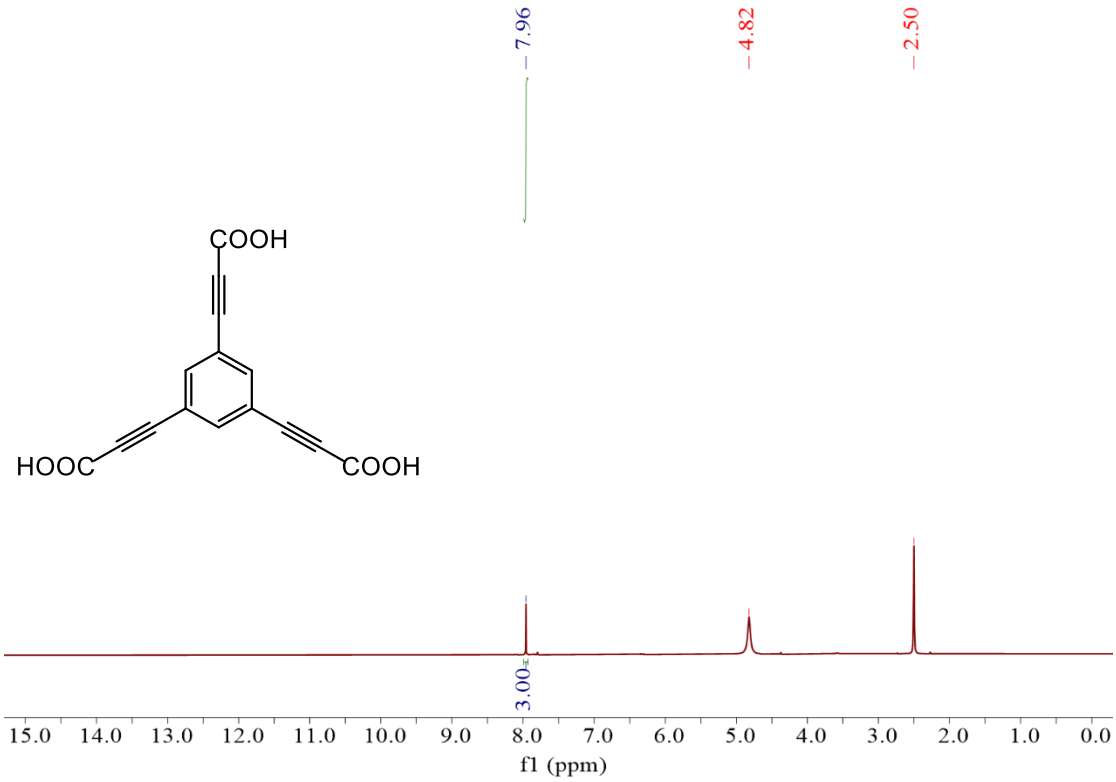
^{1}H NMR (500 MHz) spectrum of **2l** in DMSO-d_6



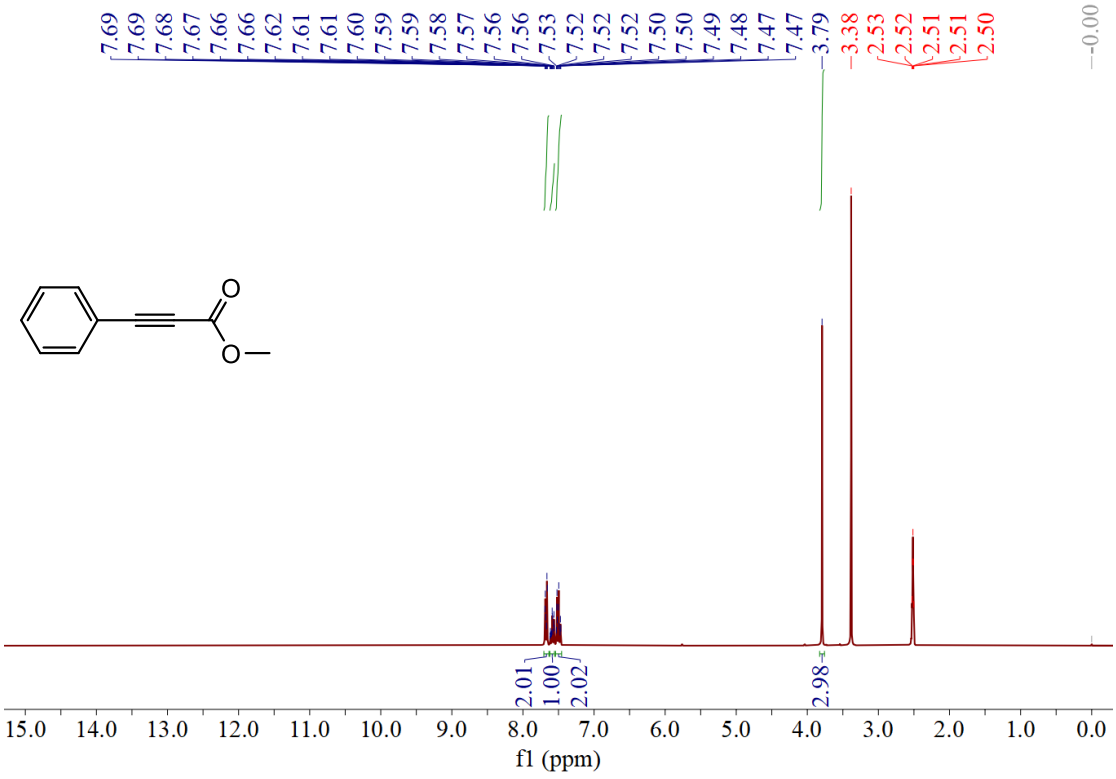
^{1}H NMR (300 MHz) spectrum of **2n** in DMSO-d_6



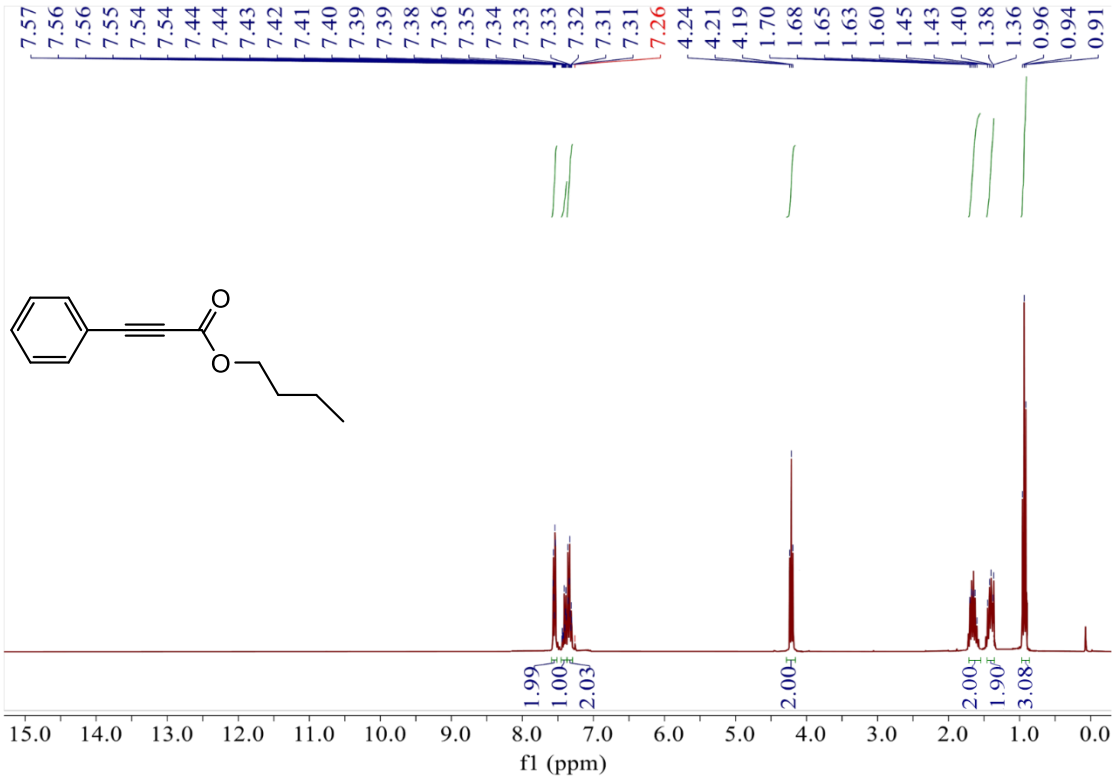
^{1}H NMR (300 MHz) spectrum of **2q** in DMSO-d_6



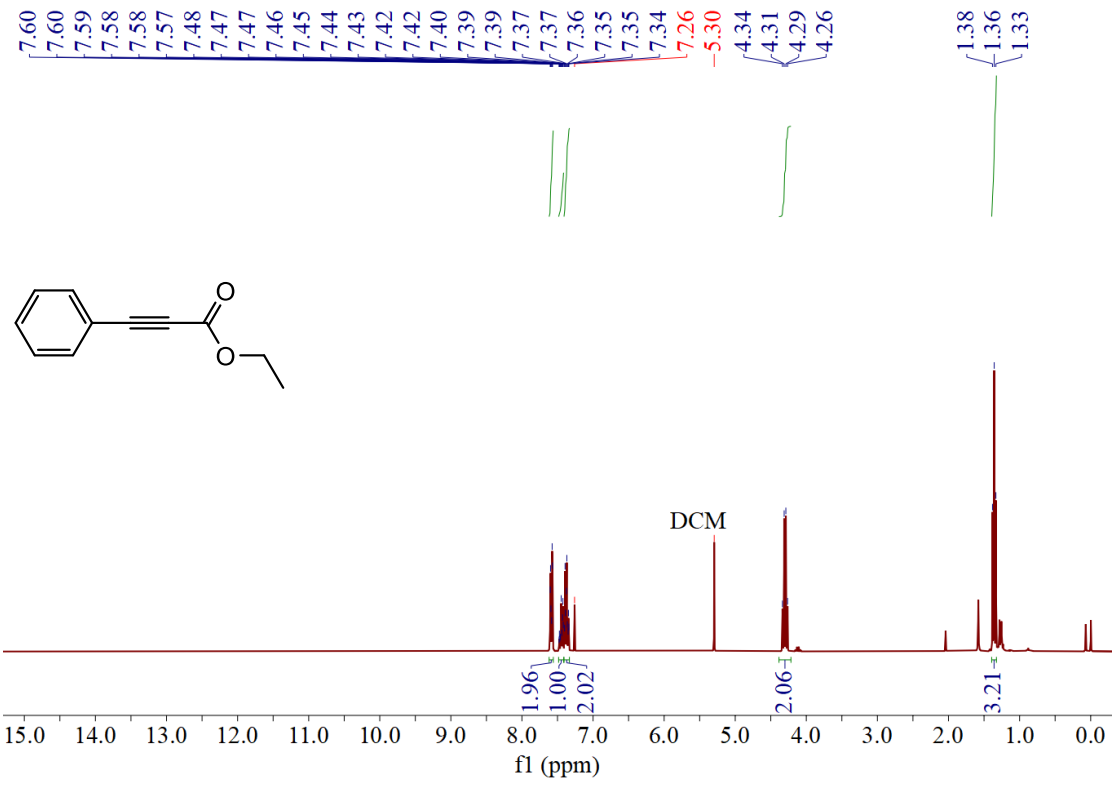
^{1}H NMR (300 MHz) spectrum of **2r** in DMSO-d_6



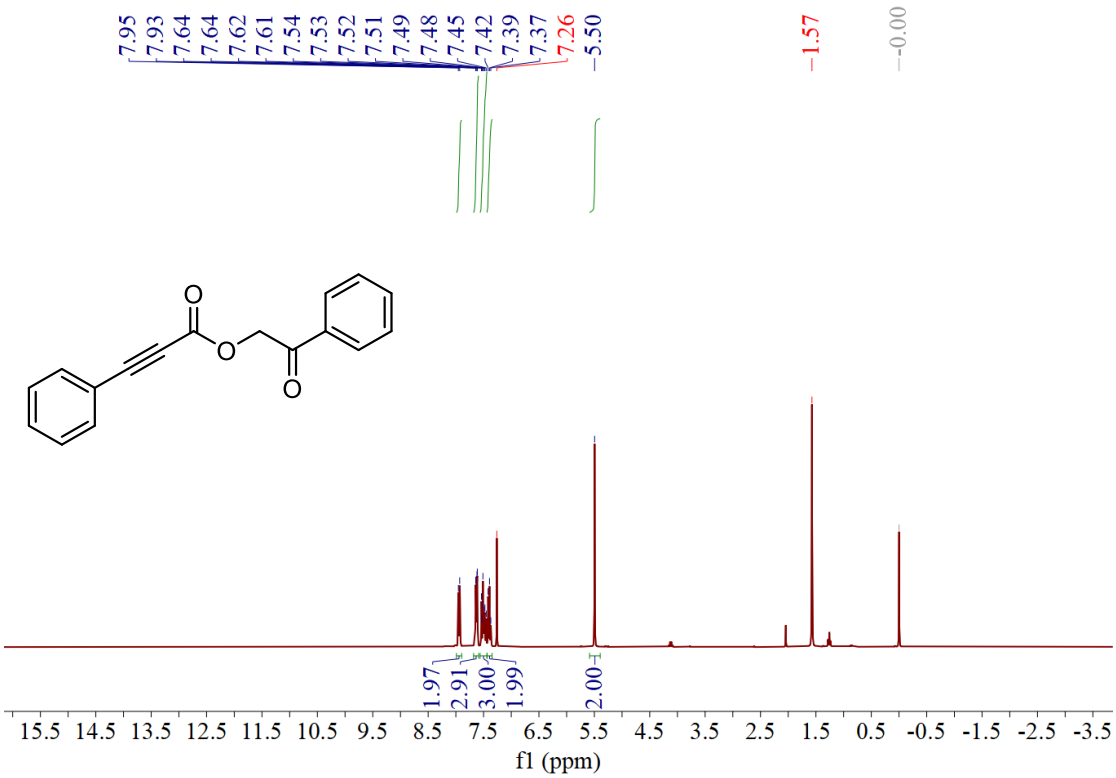
^{1}H NMR (300 MHz) spectrum of **3a** in DMSO-d_6



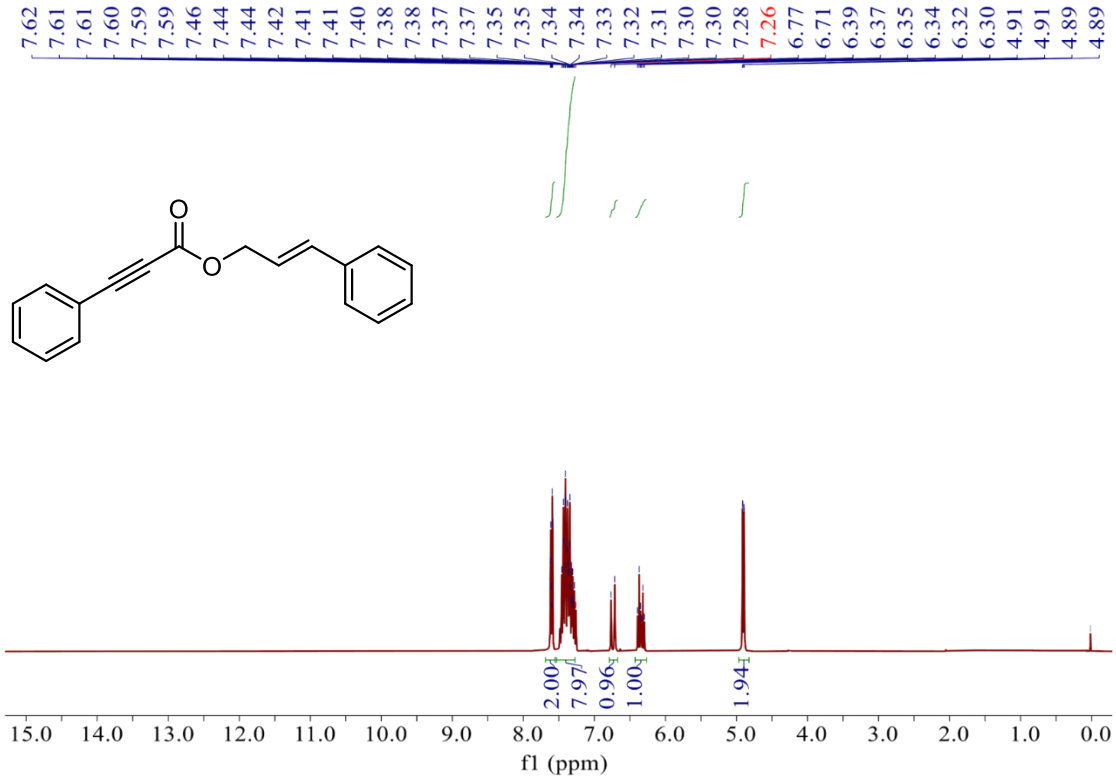
^{1}H NMR (300 MHz) spectrum of **3b** in DMSO-d_6



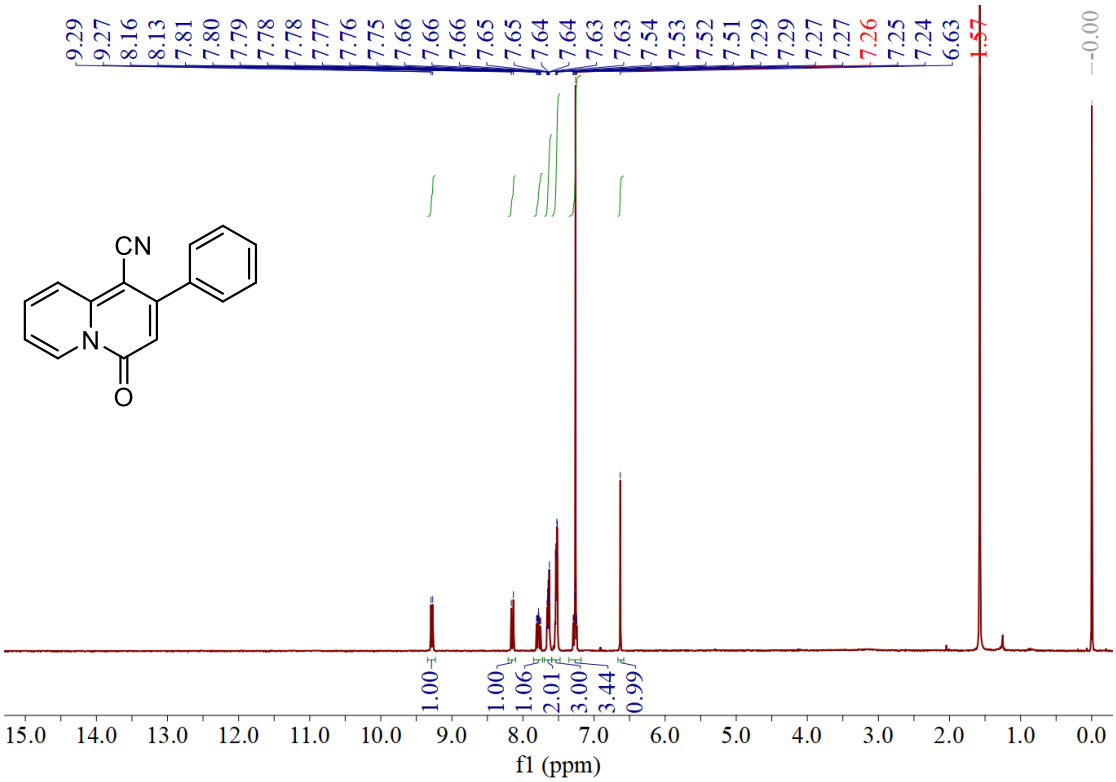
^{1}H NMR (300 MHz) spectrum of **3c** in Chloroform-*d*



^{1}H NMR (300 MHz) spectrum of **3d** in Chloroform-*d*



^{1}H NMR (300 MHz) spectrum of **3e** in Chloroform-*d*



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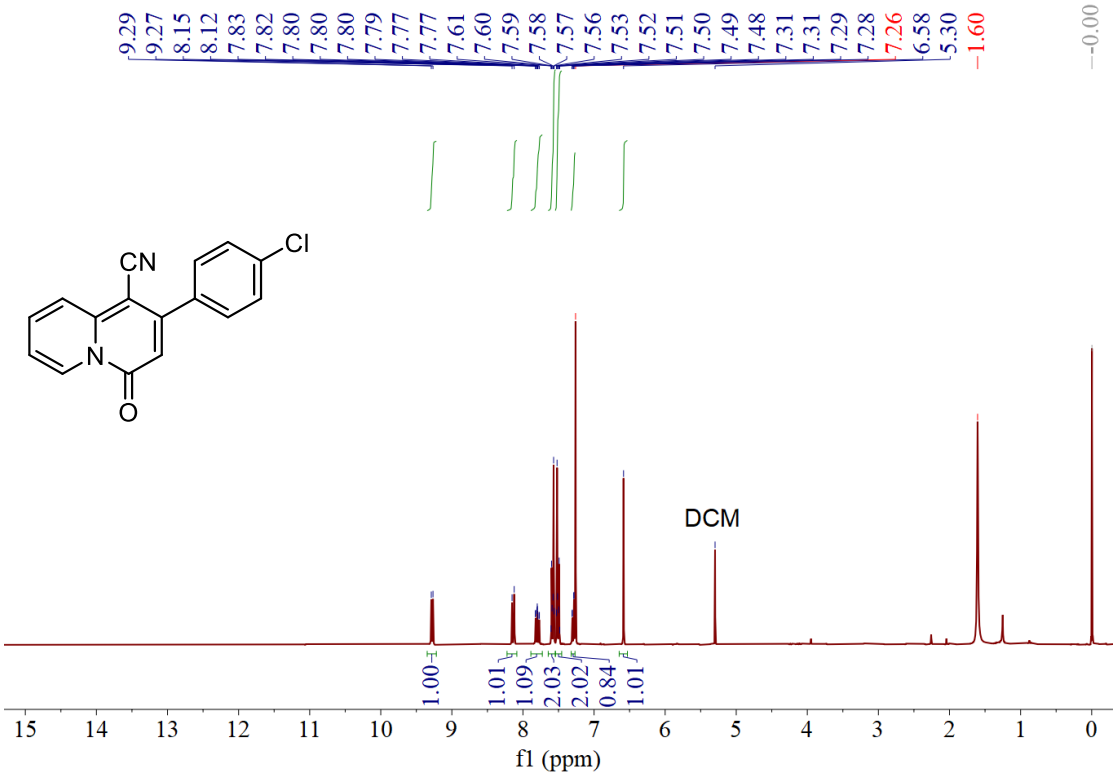

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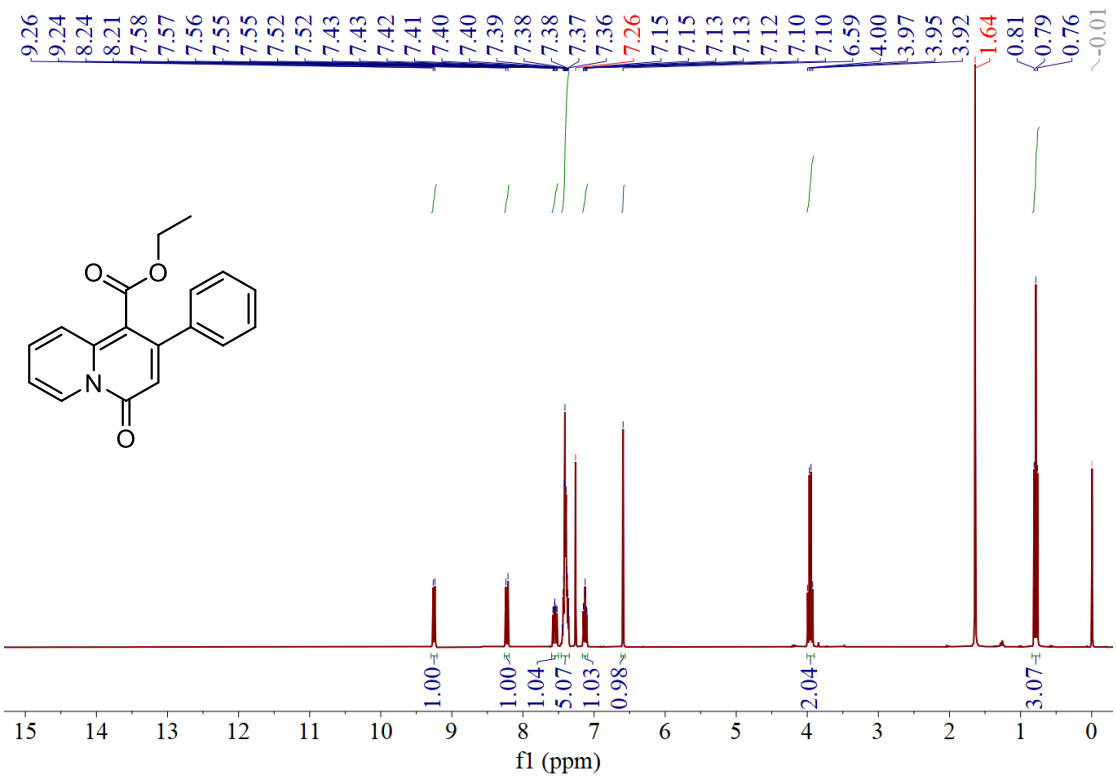
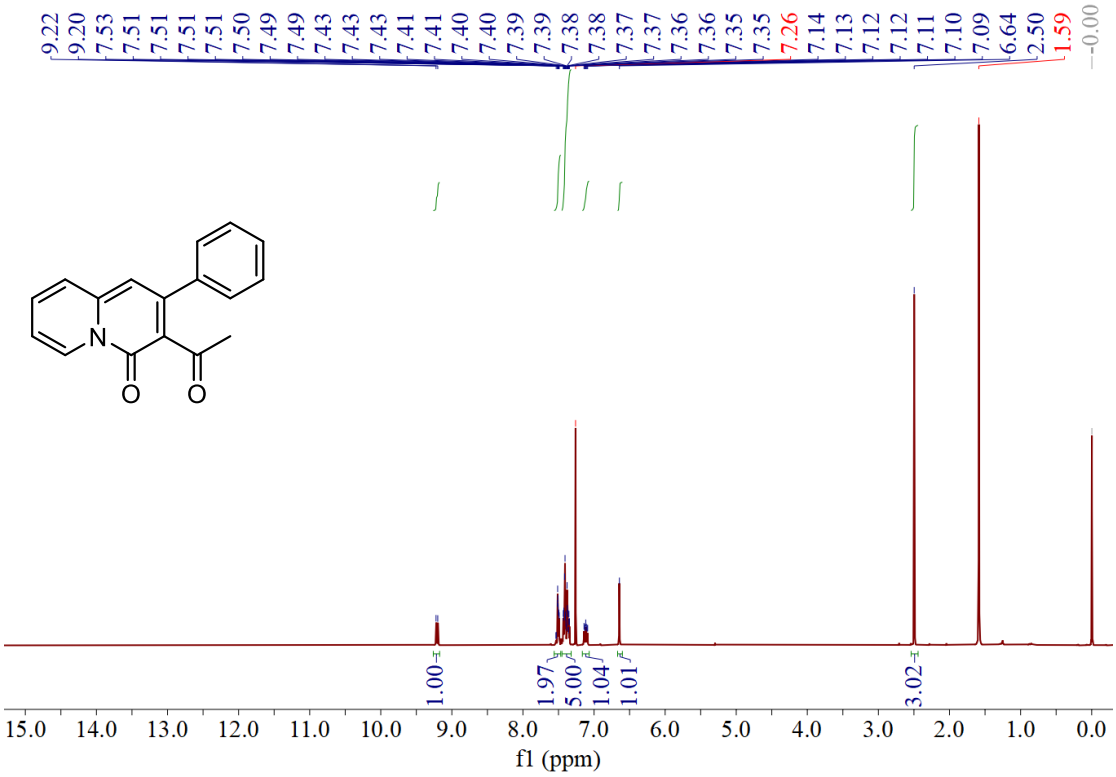


^{1}H NMR (400 MHz) spectrum of **4c** in Chloroform-*d*



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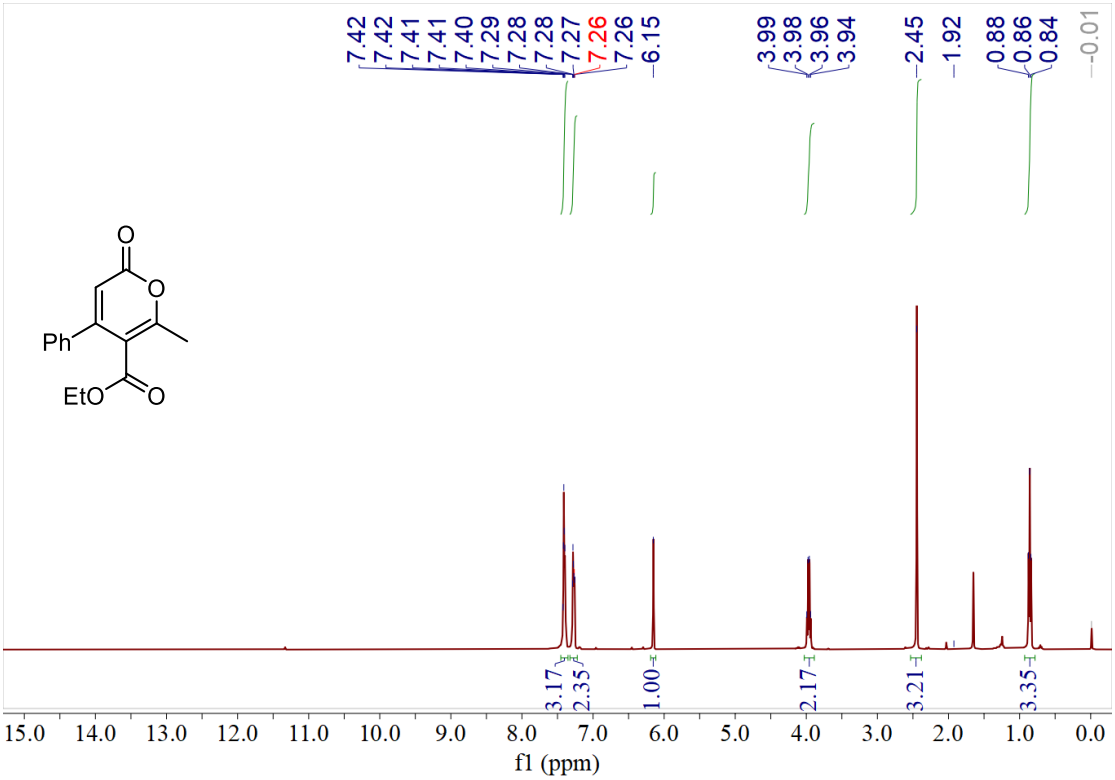
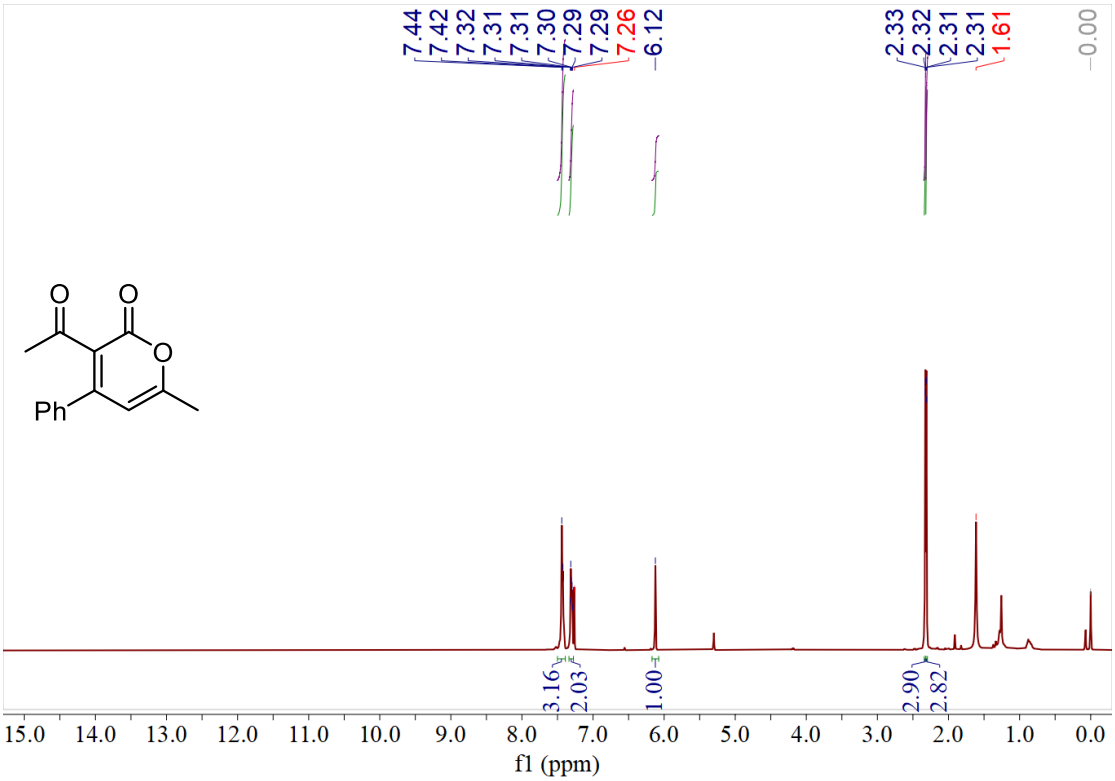


^{1}H NMR (400 MHz) spectrum of **5a** in Chloroform-*d*



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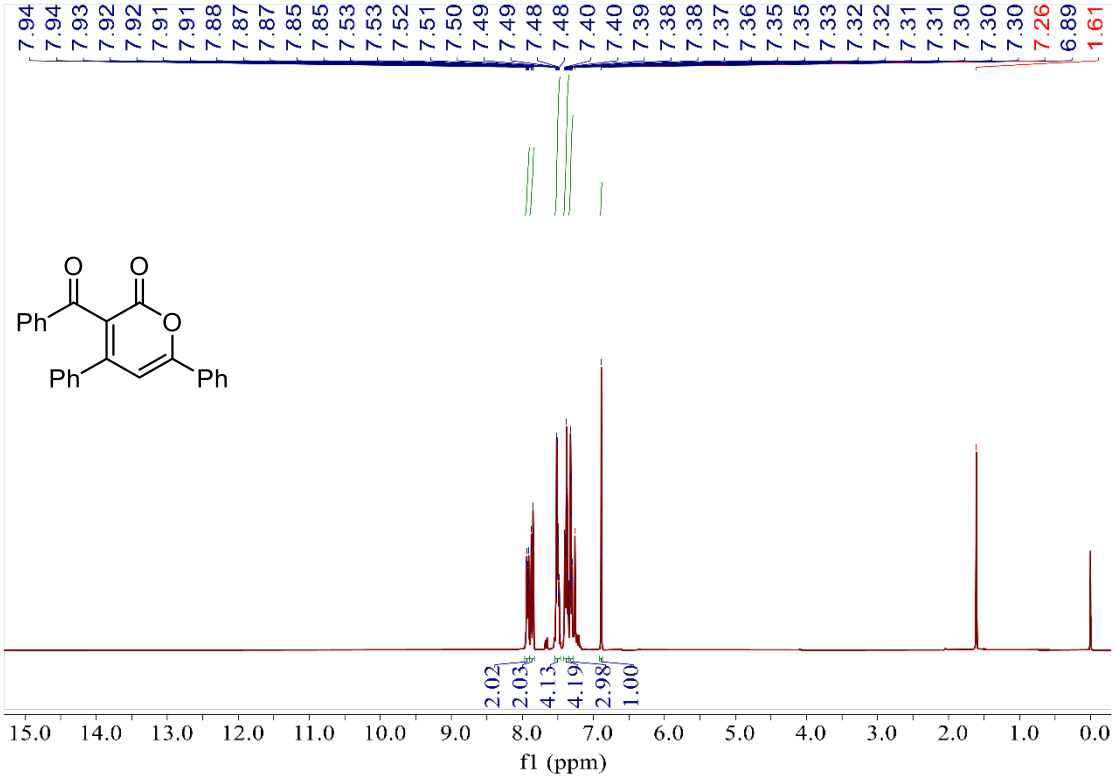

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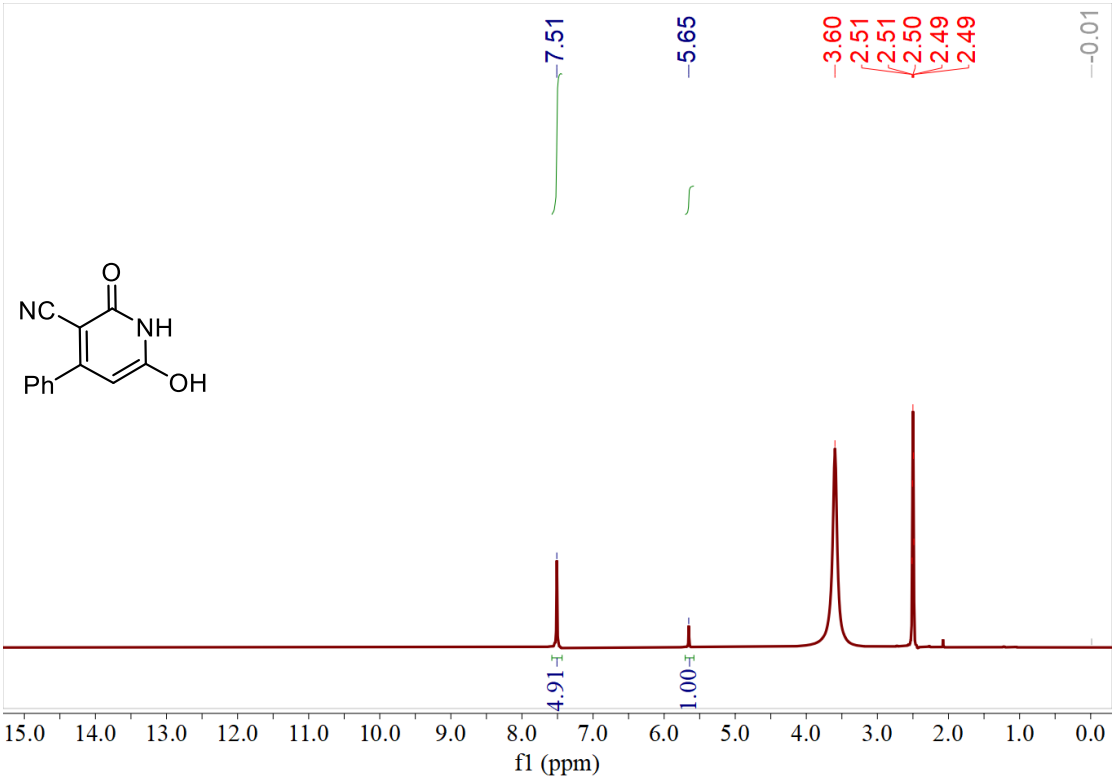

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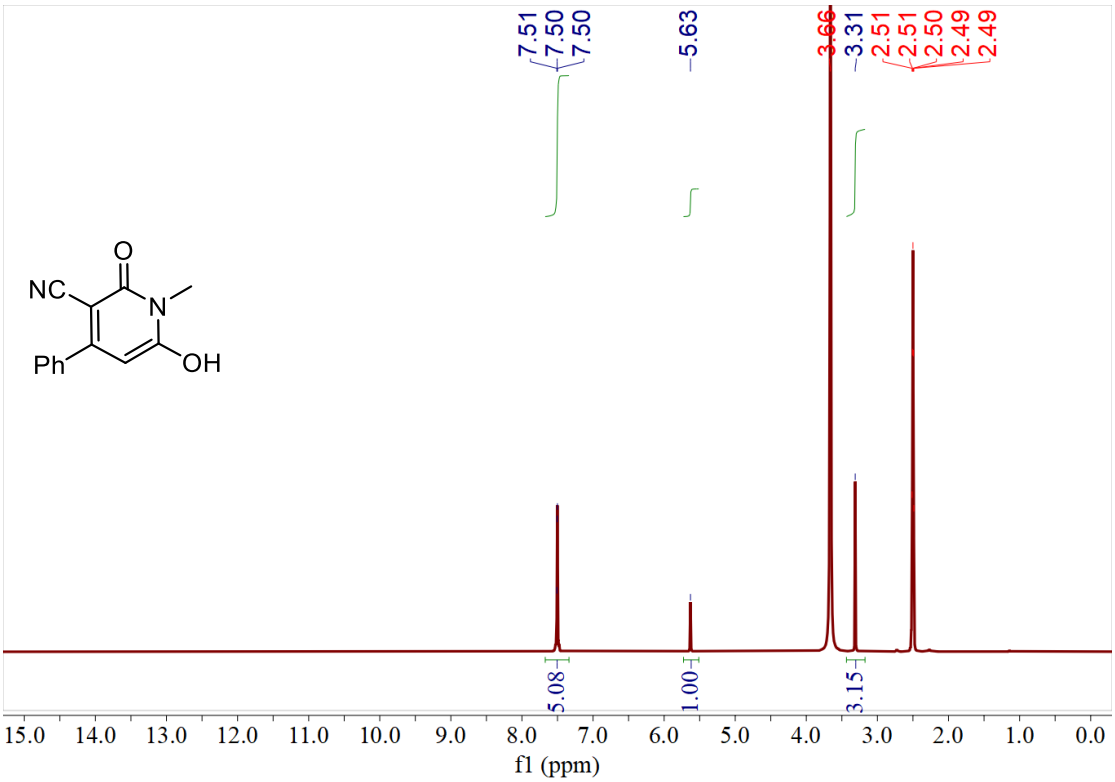

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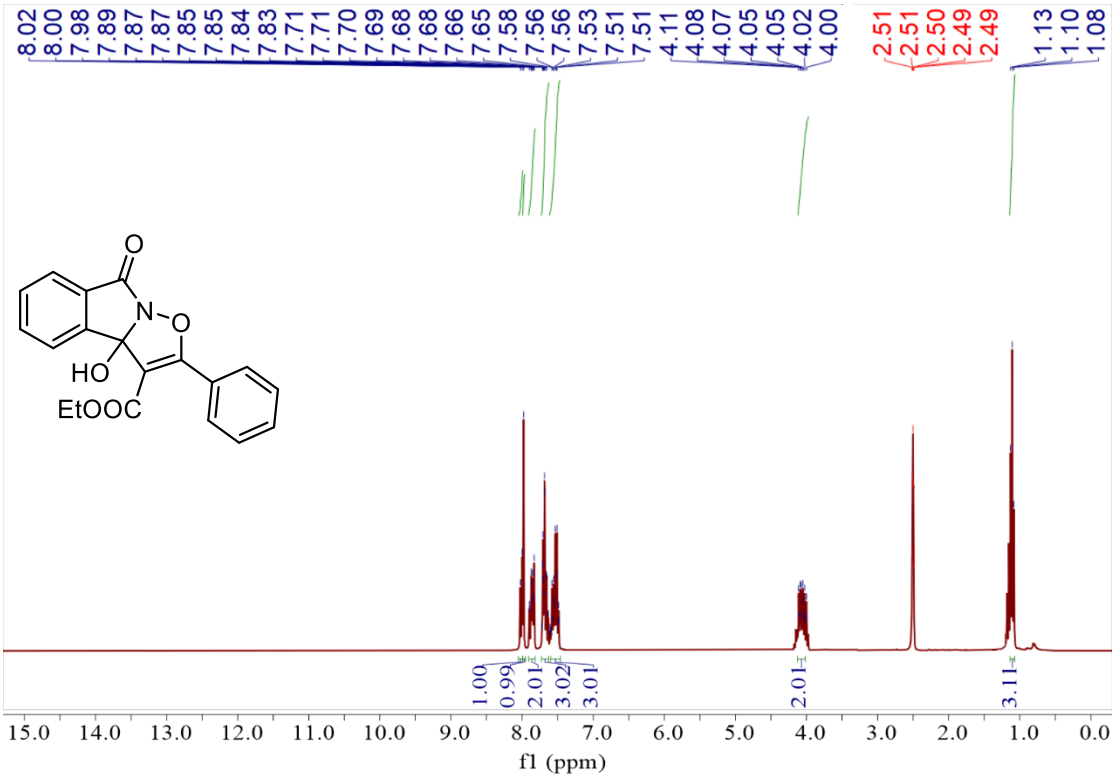

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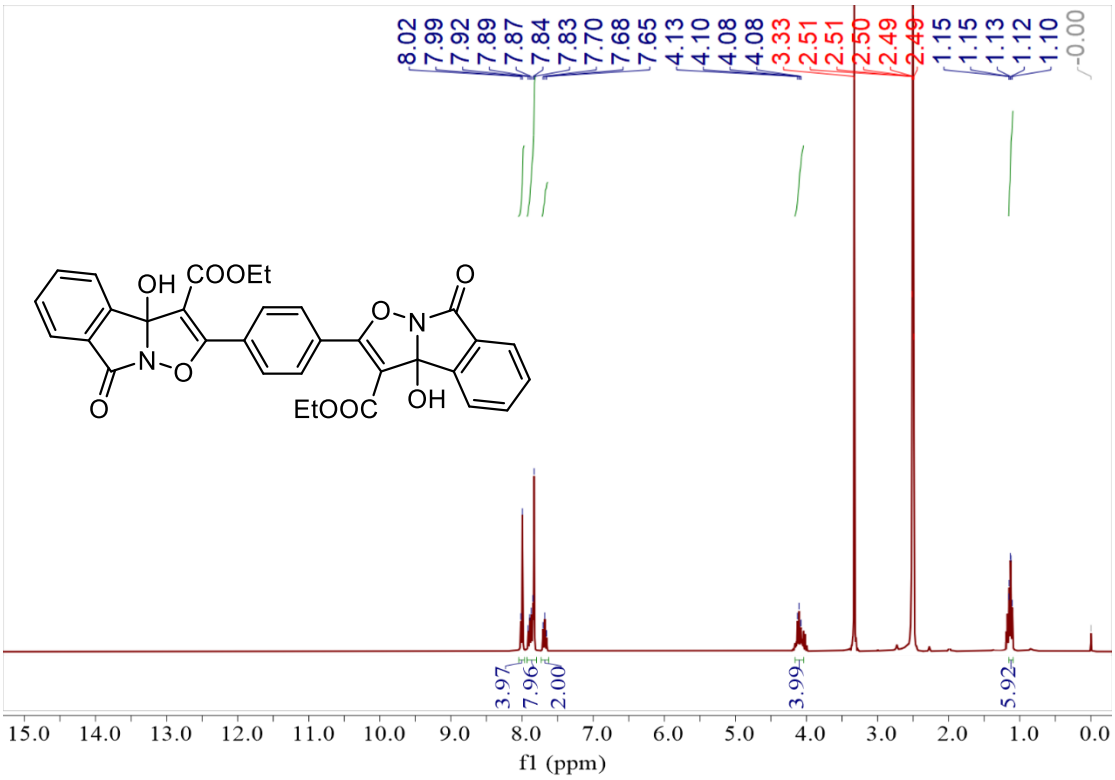

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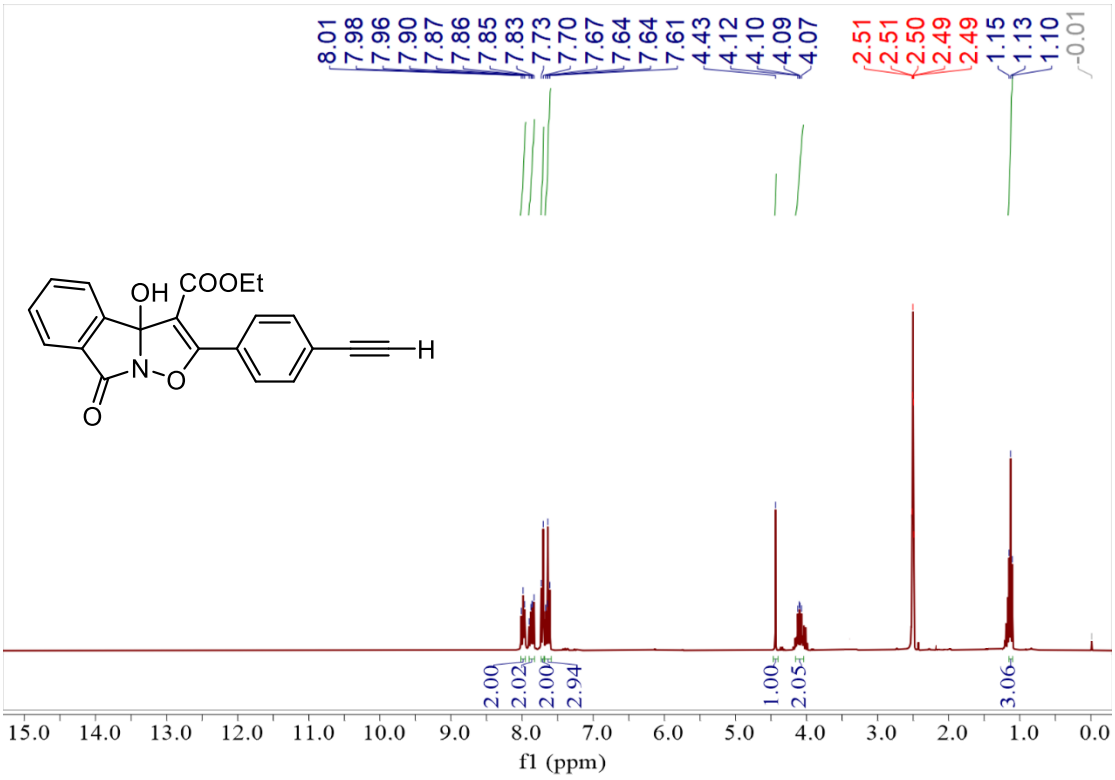
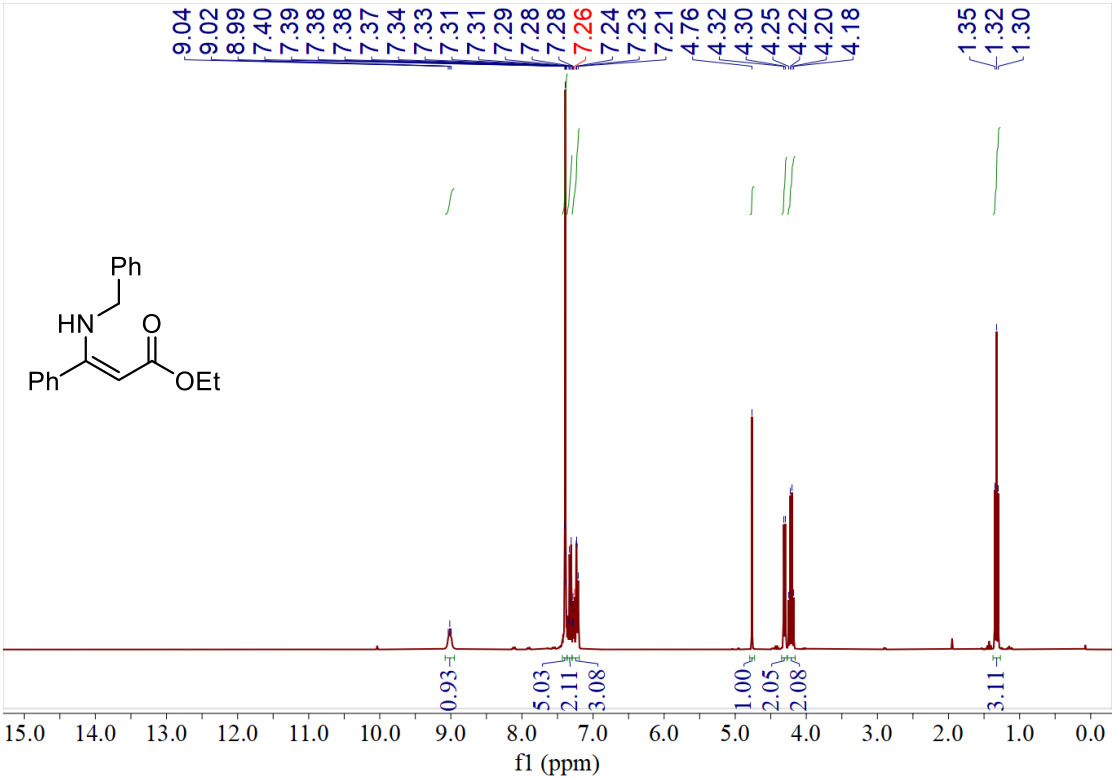
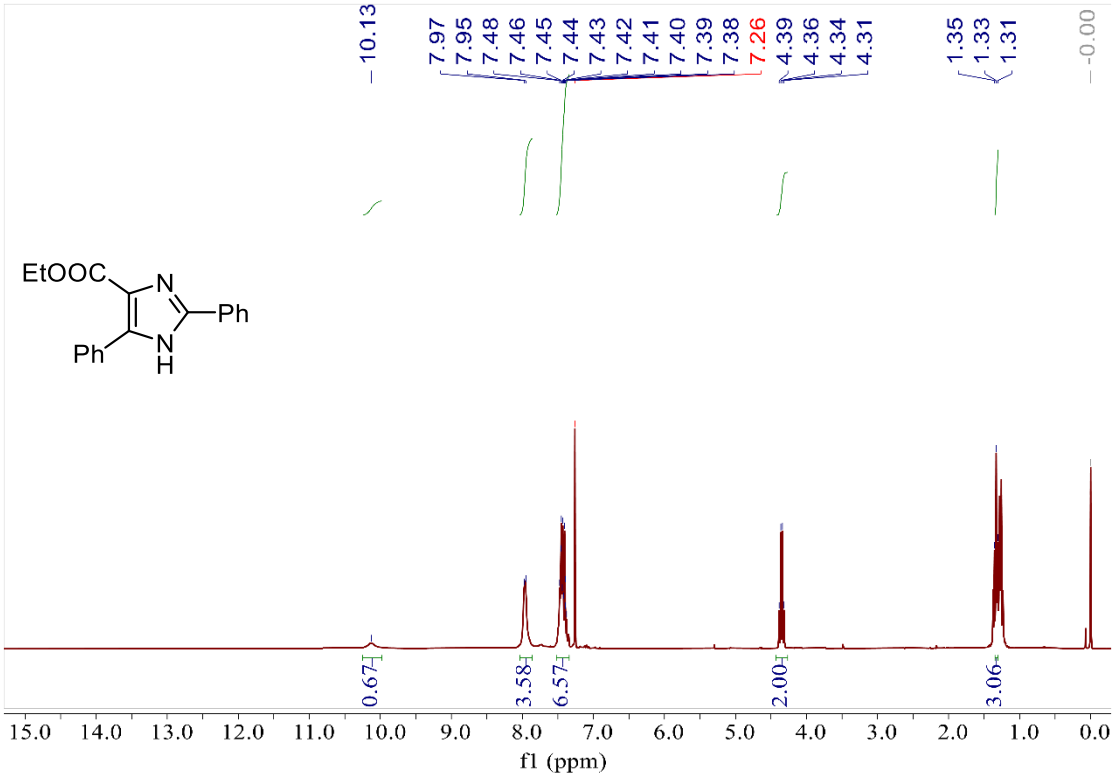


^{1}H NMR (300 MHz) spectrum of **7b'** in DMSO-d_6



^{1}H NMR (300 MHz) spectrum of **8** in Chloroform-*d*



^{1}H NMR (300 MHz) spectrum of **9** in Chloroform-*d*