Electronic Supplementary Material (ESI) for ChemComm.

A Cascade Approach to 3D Cyclic Carbamates via an Ionic Decarboxylative Functionalization of Olefinic Oxamic Acids

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[§] These two authors contributed equally to this paper

CONTENTS

Figure S1 Selected bioactive compounds containing 3D cyclic carbamate scaffolds.

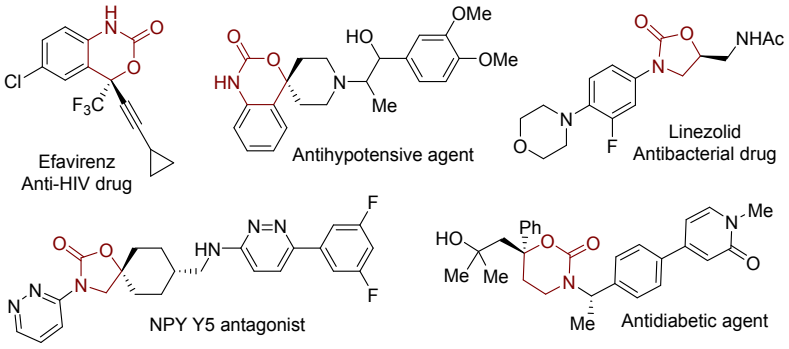
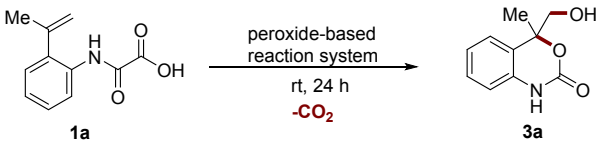


Table S1 The control reactions employing various peroxides. [a]



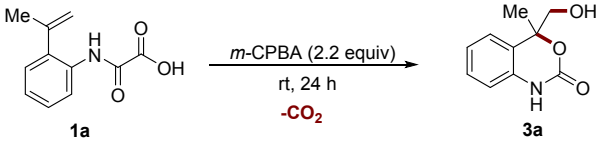
1a 3a

Entry	Reaction conditions	2a [b] (%)
1	*m*-CPBA (2.2 equiv), $CHCl_3$	88
2	BPO (2.2 equiv), $CHCl_3$	n.d [c]
3	TBHP (2.2 equiv), $CHCl_3$	n.d [c]
4	$Na_2S_2O_8$ (2.2 equiv), DMSO	n.d [c]
5	H_2O_2 (30%) (2.2 equiv), MeOH	n.d [c]
6 [1]	H_2O_2 (30%) (2.2 equiv), Na_2WO_4 (10 mol%), H_3PO_4 (1 drop), MeOH	23
7 [2]	H_2O_2 (2.2 equiv), $MnSO_4$ (1 mol %), $NaHCO_3$ (0.25 equiv), DMF	17
8 [3]	H_2O_2 (2.2 equiv), MTO (0.2 mol %), Pyridine (10 mol %), ^{t}BuOH	21
9	Oxone (2.2 equiv), dioxane : H_2O = 1 : 1	28

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), oxidant (0.33 mmol, 2.2 equiv), solvent (3.0 mL), rt, 24h, otherwise noted; [b] Yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard; [c] not detected.

Notes: Only the reaction system, which is able to mediate the epoxidation reaction, was proved to be effective in this transformation. *m*-CPBA-based reaction system displayed the most superior reactivity.

Table S2 The screening of solvents. [a]

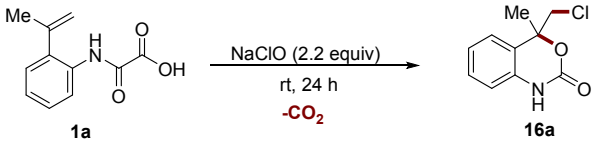


1a 3a

Entry	Solvent	Time	Yield [b]
1	$CHCl_3$	24h	88%
2	MeCN	24h	76%
3	DCE	24h	65%
4	THF	24h	35%
5	DMF	24h	trace
6	Toluene	24h	72%
7	MeOH	24h	59%

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), *m*-CPBA (0.33 mmol, 2.2 equiv), solvent (3.0 mL), otherwise noted; [b] Yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard; [c] Performed at 50 °C.

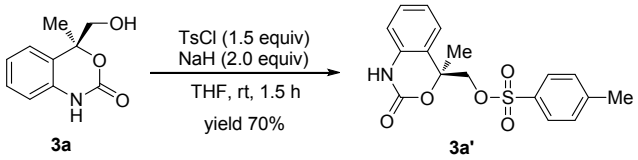
Table S3 The screening of solvents of NaClO-promoted decarboxylative alkoxylation cascade reaction. [a]



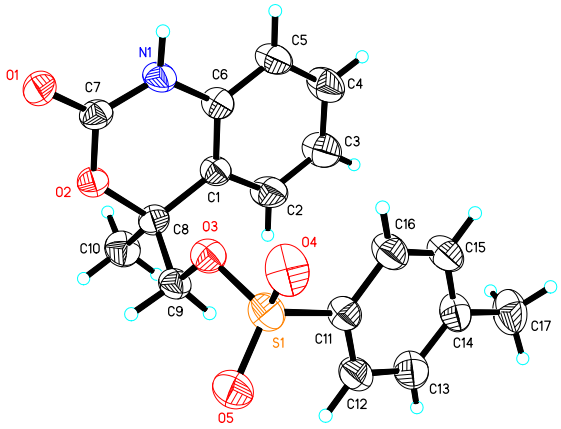
Entry	Solvent	Yield [b]
1	$CHCl_3$	34%
2	DMF	12%
3	MeOH	38%
4	MeCN	56%
5	1,4-dioxane	63% (57%) [c]
6	1,4-dioxane/H_2O (1 : 1)	35%

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), NaClO (5%) (0.33 mmol, 2.2 equiv), solvent (3.0 mL), otherwise noted; [b] Yields were determined by ^1H NMR using CH_2Br_2 as an internal standard; [c] Isolated yield was reported.

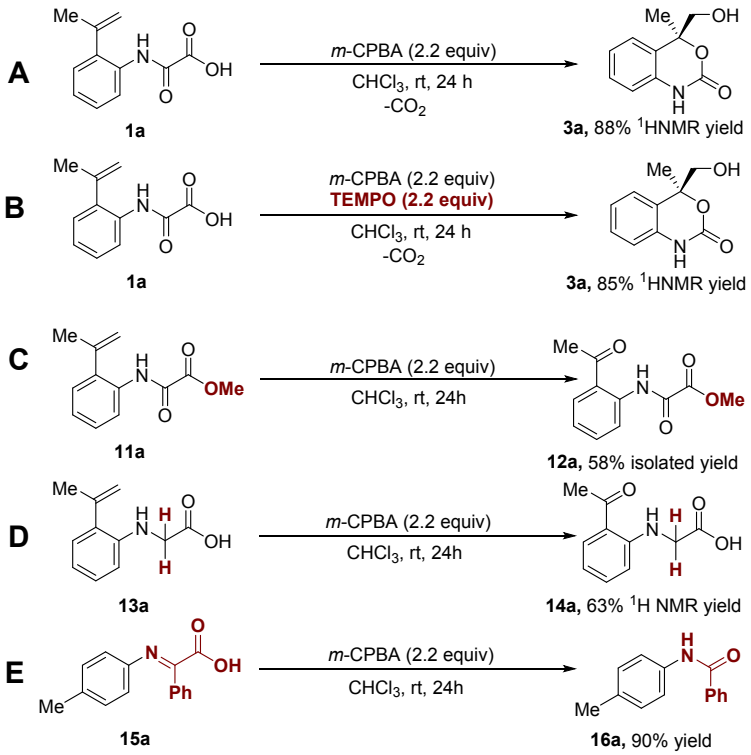
Scheme S1 The confirmation of the structure of **3a** via single x-ray analysis.



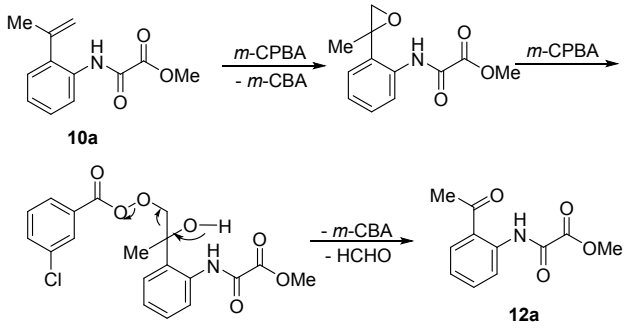
X-ray Crystallography data of **3a'**.



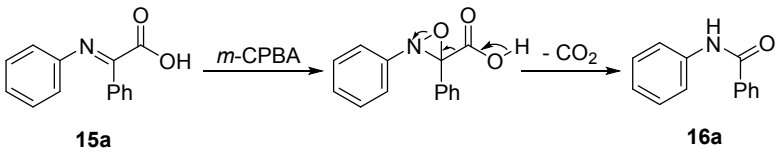
Scheme S2 The control reactions.



Scheme S3 The proposed mechanism for the synthesis of **12a**.



Scheme S4 The proposed mechanism for the synthesis of **16a**.

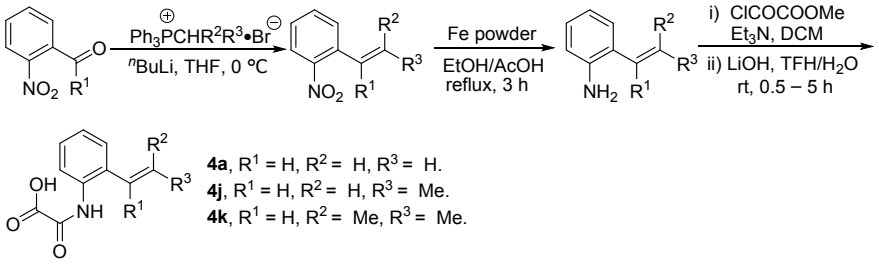


General Information

Commercial reagents and solvents were used as received and without further purification, unless otherwise stated. Organic solution was concentrated under reduced pressure on a Büchi rotary evaporator using an isopropyl alcohol-dry ice bath. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized with a UV lamp at 254 nm. Flash chromatography was performed on silica gel 200–300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Adamas-beta®). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 Spectrometer (400 and 100 MHz for ^{1}H and ^{13}C NMR, respectively) and are internally referenced to residual solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.16 ppm in ^{1}H and ^{13}C NMR, respectively; DMSO-d_6 referenced at 2.50 and 39.52 ppm in ^{1}H and ^{13}C NMR, respectively). Data from the ^{1}H-NMR spectroscopy are reported as chemical shift (δ ppm) with the corresponding integration values. Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (double of doublet), and m (multiplets). Coupling constants were reported in Hertz (Hz). Data for ^{13}C NMR are reported in terms of chemical shift. High-resolution mass spectrometry (HRMS) was recorded on Waters LCT Premier XE spectrometer.

Synthesis and Characterization of the Substrates

General procedure A [4-5]



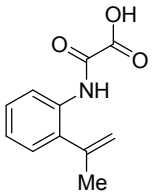
To a suspension of alkyltriphenylphosphonium bromide (1.8 equiv) in dry THF (20 mL) under an argon atmosphere at 0 °C is added n-butyllithium (2.3 equiv, 2.5 M in hexanes). The resulting mixture is stirred at 0 °C for 2 h. A solution of 2-nitrobenzaldehyde (1.0 equiv) in dry THF (10 mL) is added dropwise and the mixture is stirred at 0 °C for 2 h. After that, it is allowed to warm to room temperature and stirred for another 16 h. Then, the reaction was quenched with NH_4Cl (aq) and extracted with EtOAc (30 mL × 3). The combined organic phase was washed with brine (20 mL × 3), dried over sodium sulfate, filtered, and concentrated under vacuum. The resulting residue was purified through chromatography on silica gel (petroleum ether/ethyl acetate = 60/1 - 20/1) to yield the desired alkene structures.

To a solution of the above product (1.0 equiv) in a solvent mixture (EtOH/AcOH = 1:1, 20 mL) is added iron powder (4.0 equiv). The resulting suspension is stirred at 100 °C for 3 h. Then, the mixture was cooled to room temperature, diluted with EtOAc (20 mL). The organic phase was washed with $NaHCO_3$ (aq) (20 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to give the

crude product. The crude product is purified through chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the title compound as a yellow oil.

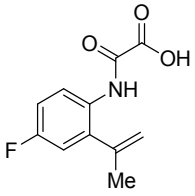
To a stirred solution of the above product (1.0 equiv) and Et_3N (1.1 equiv) in CH_2Cl_2 (25 mL) at 0 °C was added the solution of methyl chlorooxoacetate (1.2 equiv) in 10 mL of CH_2Cl_2 dropwise over 10 minutes. After that, the reaction mixture was stirred at room temperature for 2 - 6 h. Then it is diluted with water (50 mL) followed by extraction with CH_2Cl_2 (30 mL × 3). The combined organic layers were washed with brine (20 mL × 3), and then dried over $MgSO_4$, filtrated and concentrated under vacuum to give the crude product. This crude product was used directly in next step without further purification.

To a stirred solution of the above crude product (1.0 equiv) in a solvent mixture (20 mL, THF/H_2O = 2 : 1) was added LiOH (5.0 equiv). The resulting mixture was stirred at room temperature for 0.5 - 5 h, then acidified by HCl (1 M) (pH = 3) and extracted with EtOAc (20 mL x 3). The combined organic phase was dried over Na_2SO_4, filtrated and concentrated under vacuum to give the target compound.



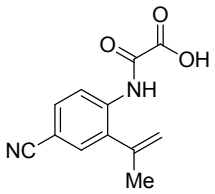
2-oxo-2-((2-(prop-1-en-2-yl)phenyl)amino)acetic acid (1a)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.96 (s, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.39 (t, J = 4.6 Hz, 1H), 7.35 (d, J = 5.9 Hz, 1H), 7.27 (t, J = 7.0 Hz, 1H), 5.39 (s, 1H), 5.05 (s, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.0, 156.2, 141.9, 136.3, 132.8, 128.0, 127.6, 125.5, 122.9, 116.4, 23.7; HRMS (ESI): m/z Calcd. for $C_{11}H_{11}NO_3$ [(M-H)$^-$] 204.0661, found 204.0664.



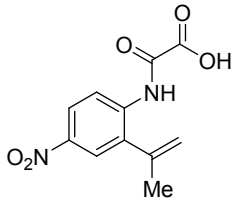
2-((4-fluoro-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1b)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.98 (s, 1H), 7.74 (dd, J = 9.5, 5.4 Hz, 1H), 7.30 - 7.02 (m, 2H), 5.32 (s, 1H), 5.02 (s, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.9, 160.7 (d, J_{CF} = 251.7 Hz), 156.7, 141.0, 139.3 (d, J_{CF} = 7.9 Hz), 129.3, 125.9 (d, J_{CF} = 8.6 Hz), 116.9, 114.8 (d, J_{CF} = 22.6 Hz), 114.3 (d, J_{CF} = 22.1 Hz), 23.3; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -116.32; HRMS (ESI): m/z Calcd. for $C_{11}H_{10}FNO_3$ [(M-H)$^-$] 222.0566, found 222.0558.



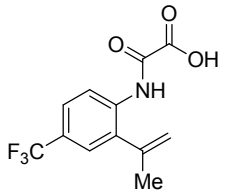
2-((4-cyano-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1c)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.02 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.79 (d, J = 1.9 Hz, 1H), 5.68 - 5.35 (m, 1H), 5.13 (s, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.5, 156.2, 140.2, 137.2, 135.9, 131.9, 131.85, 122.0, 118.5, 118.1, 107.4, 23.4; HRMS (ESI): m/z Calcd. for $C_{12}H_{10}N_2O_3$ [(M-H)$^-$] 229.0613, found 229.0614.



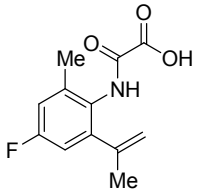
2-((4-nitro-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1d)

This compound was prepared according to the reported procedure [4].^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.02 (s, 1H),7.97(d, J = 8.5Hz, 2H), 6.65(d, J = 8.5Hz, 2H), 5.35 (s, 1H), 5.08 (s, 1H), 2.08 (s ,3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 157.4, 143.8, 141.7, 136.5, 130.8, 125.8, 117.1, 108.32, 85.26, 68.50, 23.51; HRMS (ESI) Calcd. for $C_{11}H_{10}N_2O_5$ [(M+Na)$^+$] 250.0482, found 250.0487



2-oxo-2-((2-(prop-1-en-2-yl)-4-(trifluoromethyl)phenyl)amino)acetic acid (1e)

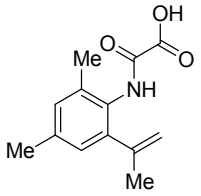
This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.04 (s, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.63 (s, 1H), 5.45 (s, 1H), 5.11 (s, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.7, 156.4, 140.8, 136.7, 136.3, 125.5 (q, J_{CF} = 25.2 Hz), 124.9 (q, J_{CF} = 3.7 Hz), 124.7 (q, J_{CF} = 3.7 Hz), 124.1 (q, J_{CF} =270.0 Hz), 122.7, 117.9, 23.4; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -60.70; HRMS (ESI): m/z Calcd. for $C_{12}H_{10}F_3NO_3$ [(M-H)$^-$] 272.0535, found 272.0533.



2-((4-fluoro-2-methyl-6-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1f)

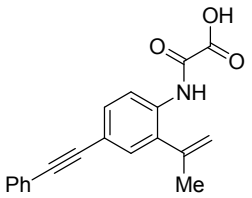
This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.15 (s, 1H), 7.08 (dd, J = 9.2, 2.5 Hz, 1H), 6.95 (dd, J =

9.3, 2.6 Hz, 1H), 5.12 (s, 1H), 4.88 (s, 1H), 2.15 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.5, 160.9 (d, J_{CF} = 242.2 Hz), 158.1, 144.3 (d, J_{CF} = 8.5 Hz), 142.4, 139.2 (d, J_{CF} = 8.9 Hz), 128.7 (d, J_{CF} = 2.6 Hz), 116.1, 115.8 (d, J_{CF} = 21.9 Hz), 112.7 (d, J_{CF} = 22.1 Hz), 23.6, 18.5; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -115.68; HRMS (ESI): m/z Calcd. for $C_{12}H_{12}FNO_3$ [(M-H)$^-$] 236.0723, found 236.0719.



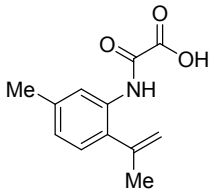
2-((2,4-dimethyl-6-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1g)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.11 (s, 1H), 7.05 (s, 1H), 6.95 (s, 1H), 5.11 (s, 1H), 4.87 (s, 1H), 2.31 (s, 3H), 2.15 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.7, 158.0, 143.4, 142.0, 136.8, 136.0, 130.0, 129.7, 126.8, 115.2, 24.0, 21.0, 18.4; HRMS (ESI): m/z Calcd. for $C_{13}H_{15}NO_3$ [(M-H)$^-$] 232.0974, found 232.0971.



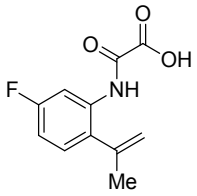
2-oxo-2-((4-(phenylethynyl)-2-(prop-1-en-2-yl)phenyl)amino)acetic acid (1h)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.93 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.56 (dd, J = 6.5, 3.0 Hz, 2H), 7.51 (dd, J = 8.4, 1.8 Hz, 1H), 7.49 - 7.46 (m, 1H), 7.45 - 7.42 (m, 3H), 5.42 (s, 1H), 5.08 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.8, 156.5, 141.0, 135.7, 133.4, 131.3, 130.9, 130.7, 128.7 (2C, overlap), 122.2, 122.0, 118.8, 117.3, 89.4, 88.9, 23.6; HRMS (ESI): m/z Calcd. for $C_{19}H_{15}NO_3$ [(M-H)$^-$] 304.0974, found 304.0970.



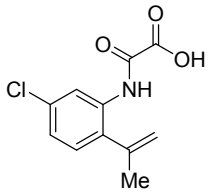
2-((5-methyl-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1i)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.91 (s, 1H), 7.71 (s, 1H), 7.22 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.8, 1H), 5.35 (d, J = 0.7 Hz, 1H), 5.01 (d, J = 0.7 Hz, 1H), 2.35 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.6, 156.6, 142.30, 137.5, 133.9, 133.2, 128.3, 126.6, 123.8, 116.7, 24.3, 21.3; HRMS (ESI): m/z Calcd. for $C_{12}H_{13}NO_3$ [(M-H)$^-$] 218.0817, found 218.0824.



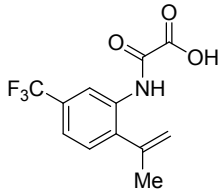
2-((5-fluoro-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1j)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.91 (s, 1H), 7.81 (dd, J = 11.0, 2.7 Hz, 1H), 7.34 (dd, J = 8.6, 6.5 Hz, 1H), 7.09 (dd, J = 8.5, 2.7 Hz, 1H), 5.39 (s, 1H), 5.02 (s, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.44 (d, J_{CF} = 241.2 Hz), 162.2, 156.7, 141.5, 134.9, (d, J_{CF} = 11.1 Hz), 132.1, (d, J_{CF} = 3.2 Hz), 130.2, (d, J_{CF} = 9.2 Hz), 117.6, 112.4, (d, J_{CF} = 21.0 Hz), 109.4, (d, J_{CF} = 25.9 Hz), 24.3; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -113.42; HRMS (ESI): m/z Calcd. for $C_{11}H_{10}FNO_3$ [(M-H)$^-$] 222.0566, found 222.0563.



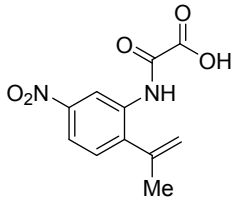
2-((5-chloro-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1k)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.96 (s, 1H), 7.99 (s, 1H), 7.33 (d, J = 8.3 Hz, 1H), 7.28 (d, J = 8.3, 1H), 5.39 (s, 1H), 5.04 (s, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.2, 156.9, 141.4, 135.1, 134.8, 132.1, 130.1, 125.6, 122.4, 117.7, 24.0; HRMS (ESI): m/z Calcd. for $C_{11}H_{10}ClNO_3$ [(M-H)$^-$] 238.0271, found 238.0269.



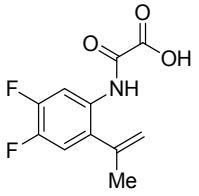
2-oxo-2-((2-(prop-1-en-2-yl)-5-(trifluoromethyl)phenyl)amino)acetic acid (1l)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.07 (s, 1H), 8.24 (s, 1H), 7.58 (d, J = 8.1, 1H), 7.53 (d, J = 8.1 Hz, 1H), 5.52 - 5.33 (m, 1H), 5.10 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.6, 156.7, 140.8, 140.1, 133.7, 129.2, 128.0 (q, J_{CF} = 31.9 Hz), 123.7 (q, J_{CF} = 270.6 Hz), 121.9 (q, J_{CF} = 3.7 Hz), 119.2 (q, J_{CF} = 4.0 Hz), 117.6, 23.2; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -61.29; HRMS (ESI): m/z Calcd. for $C_{12}H_{10}F_3NO_3$ [(M-H)$^-$] 272.0535, found 272.0537.



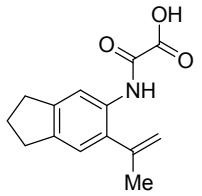
2-((5-nitro-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1m)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.12 (s, 1H), 8.26 (s, 1H), 7.54 (d, J = 8.1, 1H), 7.52 (d, J = 8.1 Hz, 1H), 5.42 (s, 1H), 5.08 (s, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.6, 156.7, 140.8, 140.1, 133.7, 129.2, 128.0, 123.7 , 121.9, 119.2, 23.2; HRMS (ESI): m/z Calcd. for $C_{11}H_{10}N_2O_5$ [(M-H)$^-$] 250.0482, found 250.0487



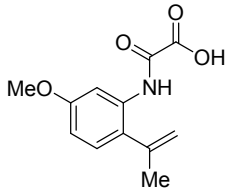
2-((4,5-difluoro-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1n)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.00 (s, 1H), 7.88 (dd, J = 12.4, 7.9 Hz, 1H), 7.44 (dd, J = 11.5, 8.9 Hz, 1H), 5.38 (s, 1H), 5.05 (s, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.1, 156.9, 148.1 (dd, J_{CF} =243.3, 13.1 Hz), 147.1 (dd, J_{CF} = 243.5, 13.2 Hz), 140.7, 134.2 (dd, J_{CF} = 5.7, 3.7 Hz), 130.3 (dd, J_{CF} = 8.7, 2.8 Hz), 117.9, 117.3 (d, J_{CF} = 18.0 Hz), 112.8 (d, J_{CF} =20.6 Hz), 23.9; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -138.53 (d, J_{FF} = 23.7 Hz), -141.54 (d, J_{FF} = 23.7 Hz); HRMS (ESI): m/z Calcd. for $C_{11}H_9F_2NO_3$ [(M-H)$^-$] 240.0472, found 240.0473.



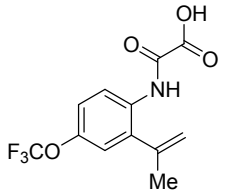
2-oxo-2-((6-(prop-1-en-2-yl)-2,3-dihydro-1H-inden-5-yl)amino)acetic acid (1o)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.81 (s, 1H), 7.68 (s, 1H), 7.12 (s, 1H), 5.29 (s, 1H), 4.94 (s, 1H), 2.87 - 2.81 (m, 4H), 2.19 - 1.81 (m, 5H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.6, 156.5, 143.7, 142.9, 141.5, 134.9, 131.4, 124.0, 119.2, 116.5, 32.7, 32.4, 25.7, 24.4; HRMS (ESI): m/z Calcd. for $C_{14}H_{15}NO_3$ [(M-H)$^-$] 244.0974, found 244.0968.



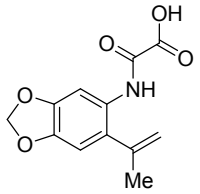
2-((5-methoxy-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1p)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.85 (s, 1H), 7.59 (s, 1H), 7.22 (d, J = 8.5 Hz, 1H), 6.80 (d, J = 8.5, 1H), 5.33 (s, 1H), 4.98 (s, 1H), 3.76 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.9, 158.4, 156.0, 141.5, 133.9, 128.8, 127.8, 116.2, 110.5, 107.7, 55.2, 24.0; HRMS (ESI): m/z Calcd. for $C_{12}H_{13}NO_4$ [(M-H)$^-$] 234.0766, found 234.0758.



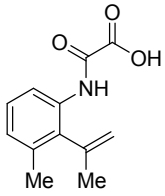
2-oxo-2-((2-(prop-1-en-2-yl)-4-(trifluoromthoxy)phenyl)amino)acetic acid (1q)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.15 (s, 1H), 7.95 (s, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.29 (s, 1H), 5.37 (s, 1H), 5.04 (s, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.8, 156.5, 145.4, 140.7, 138.7, 132.2, 125.2, 120.7, 120.2, 120.0 (q, J_{CF} = 254.6 Hz), 117.33, 23.25; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -56.96; HRMS (ESI): m/z Calcd. for $C_{12}H_{10}F_3NO_4$ [(M-H)$^-$] 288.0484, found 288.0486.



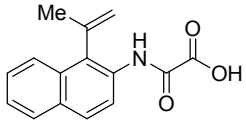
2-oxo-2-((6-(prop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)amino)acetic acid (1r)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.85 (s, 1H), 7.33 (s, 1H), 6.88 (s, 1H), 6.04 (s, 2H), 5.27 (d, J = 0.9 Hz, 1H), 4.94 (d, J = 0.9 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.0, 156.2, 146.1, 144.9, 141.7, 130.2, 126.6, 116.3, 107.6, 104.4, 101.5, 23.7; HRMS (ESI): m/z Calcd. for $C_{12}H_{11}NO_5$ [(M-H)$^-$] 248.0559, found 248.0558.



2-((3-methyl-2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1s)

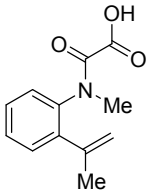
This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.54 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 7.9 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 5.49 (s, 1H), 4.92 (s, 1H), 2.23 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.4, 156.2, 141.8, 135.7, 135.6, 133.4, 127.7, 127.2, 119.2, 118.0, 23.5, 19.6; HRMS (ESI): m/z Calcd. for $C_{12}H_{13}NO_3$ [(M-H)$^-$] 218.0817, found 218.0825.



2-oxo-2-((1-(prop-1-en-2-yl)naphthalen-2-yl)amino)acetic acid (1t)

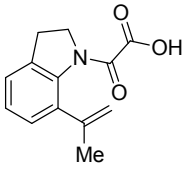
This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.64 (s, 1H), 8.47 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 7.8 Hz, 3H), 7.64 - 7.39 (m, 2H), 5.82 (s, 1H), 5.21 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.5, 155.1, 140.3, 131.5, 130.8, 130.8, 128.9, 128.4, 128.3, 126.9,

125.9, 125.5, 120.2, 118.5, 24.2; HRMS (ESI): m/z Calcd. for $C_{15}H_{13}NO_3$ [(M-H)$^-$] 254.0817, found 254.0808.



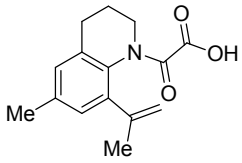
2-(methyl(2-(prop-1-en-2-yl)phenyl)amino)-2-oxoacetic acid (1u)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 7.34 - 7.14 (m, 3H), 7.09 (d, J = 7.6 Hz, 1H), 5.11 (s, 1H), 5.02 (s, 1H), 2.93 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 164.6, 163.1, 142.4, 140.8, 138.7, 129.8, 129.1, 129.0, 128.6, 117.2, 35.5, 23.4; HRMS (ESI): m/z Calcd. for $C_{12}H_{13}NO_3$ [(M-H)$^-$] 218.0817, found 254.0802.



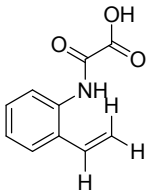
2-oxo-2-(7-(prop-1-en-2-yl)indolin-1-yl)acetic acid (1v)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (500 MHz, DMSO - d_6) δ (ppm) 7.23 (d, J = 6.3 Hz, 1H), 7.20 - 7.13 (m, 2H), 4.97 (s, 1H), 4.88 (s, 1H), 4.08 (t, J = 7.3 Hz, 2H), 3.04 (t, J = 7.7 Hz, 2H), 1.99 (s, 3H); ^{13}C NMR (126 MHz, DMSO - d_6) δ (ppm) 164.2, 159.6, 144.3, 137.7, 136.1, 134.3, 126.8, 125.9, 123.9, 112.6, 50.4, 29.8, 22.2; HRMS (ESI): m/z Calcd. for $C_{13}H_{13}NO_3$ [(M-H)$^-$] 230.0817, found 230.0813.



2-oxo-2-(8-(prop-1-en-2-yl)-3,4-dihydroquinolin-1(2H)-yl)acetic acid (1w)

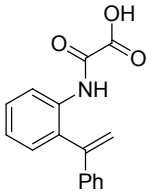
This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.96 (s, 1H), 6.92 (s, 1H), 5.24 (s, 1H), 4.93 (s, 1H), 4.45 - 4.38 (m, 1H), 3.22- 3.15 (m, 1H), 2.75 - 2.52 (m, 2H), 2.33 (s, 3H), 1.95 (s, 3H), 1.79 - 1.63 (m, 2H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 165.4, 163.0, 142.8, 139.8, 137.6, 135.818, 133.4, 127.6, 127.0, 117.7, 45.2, 26.5, 24.4, 22.6, 21.1; HRMS (ESI): m/z Calcd. for $C_{15}H_{17}NO_3$ [(M+Na)$^+$] 282.1106, found 282.1096



2-oxo-2-((2-vinylphenyl)amino)acetic acid (4a)

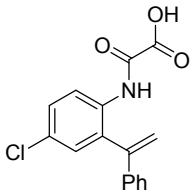
This compound was obtained as a light yellow solid by following the general procedure **A**. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.12 (s, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 6.6 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.27(t, J = 7.8 Hz, 1H), 6.83 (d,

J = 17.4, 11.1 Hz, 1H), 5.74 (d, *J* = 17.4 Hz, 1H), 5.57 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.2, 155.1, 132.1, 131.1, 130.4, 128.7, 127.6, 126.8, 122.0, 120.0; HRMS (ESI): m/z Calcd. for $C_{10}H_9NO_3$ [(M-H)$^-$] 190.0504, found 190.0507.



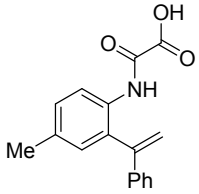
2-oxo-2-((2-(1-phenylvinyl)phenyl)amino)acetic acid (4b)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.53 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.45 - 7.41 (m, 1H), 7.36 - 7.30 (m, 3H), 7.29 - 7.22 (m, 4H), 5.93 (d, *J* = 0.6 Hz, 1H), 5.37 (d, *J* = 0.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.0, 156.3, 145.6, 139.7, 134.7, 134.5, 130.7, 129.0, 128.9, 128.6, 127.0, 126.1, 123.2, 117.8; HRMS (ESI): m/z Calcd. for $C_{16}H_{13}NO_3$ [(M-H)$^-$] 266.0817, found 266.0804.



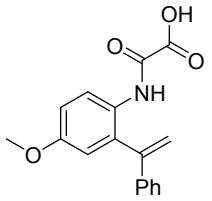
2-((4-chloro-2-(1-phenylvinyl)phenyl)amino)-2-oxoacetic acid (4c)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.58 (s, 1H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 8.7, 1H), 7.34 - 7.33 (m, 3H), 7.30 - 7.21 (m, 3H), 5.95 (s, 1H), 5.42 (s, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.8, 156.4, 144.5, 139.1, 136.8, 133.7, 130.1, 130.0, 129.0, 128.8, 128.8, 127.0, 125.2, 118.7; HRMS (ESI): m/z Calcd. for $C_{16}H_{12}ClNO_3$ [(M-H)$^-$] 300.0427, found 300.0421.



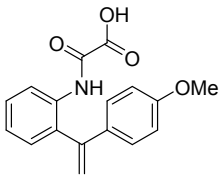
2-((4-methyl-2-(1-phenylvinyl)phenyl)amino)-2-oxoacetic acid (4d)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.91 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.29 - 7.19 (m, 5H), 7.16 (d, *J* = 8.2 Hz 1H), 7.07 (s, 1H), 5.86 (d, *J* = 0.8 Hz, 1H), 5.30 (d, *J* = 0.8 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.8, 154.5, 145.5, 139.0, 136.1, 133.1, 131.2, 130.5, 129.5, 128.8, 128.7, 126.7, 120.8, 117.8, 21.0; HRMS (ESI): m/z Calcd. for $C_{17}H_{15}NO_3$ [(M-H)$^-$] 280.0974, found 280.0990.



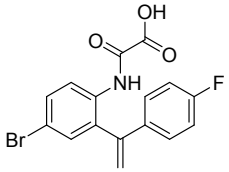
2-((4-methoxy-2-(1-phenylvinyl)phenyl)amino)-2-oxoacetic acid (4e)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.47 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.52 - 7.34 (m, 1H), 7.35 - 7.14 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.86 (s, 1H), 5.23 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.5, 159.3, 155.7, 144.4, 134.0, 133.9, 131.4, 130.1, 128.3, 127.8, 125.4, 121.9, 115.3, 113.9, 55.1; HRMS (ESI): m/z Calcd. for $C_{17}H_{15}NO_4$ [(M-H)$^-$] 296.0923, found 296.0923.



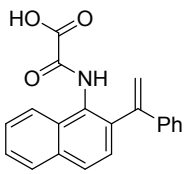
2-((2-(1-(4-methoxyphenyl)vinyl)phenyl)amino)-2-oxoacetic acid (4f)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.47 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.52 - 7.34 (m, 1H), 7.35 - 7.14 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.86 (s, 1H), 5.23 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.5, 159.3, 155.7, 144.4, 134.0, 133.9, 131.4, 130.1, 128.3, 127.8, 125.4, 121.9, 115.3, 113.9, 55.1; HRMS (ESI): m/z Calcd. for $C_{17}H_{15}NO_4$ [(M-H)$^-$] 296.0923, found 296.0923.



2-((4-bromo-2-(1-(4-fluorophenyl)vinyl)phenyl)amino)-2-oxoacetic acid (4g)

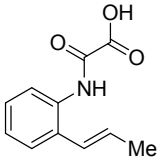
This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.96 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.42 (s, 1H), 7.36 - 7.23 (m, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 5.90 (s, 1H), 5.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.8, 156.4, 143.5, 137.2, 135.7, 134.0, 132.9, 131.8, 129.1 125.9, 118.7, 118.5, 115.8; ^{9}F NMR (376 MHz, DMSO - *d*$_6$) δ (ppm) -113.87 HRMS (ESI): m/z Calcd. for $C_{16}H_{11}BrFNO_3$ [(M-H)$^-$] 361.9828, found 361.9820.



2-oxo-2-((2-(1-phenylvinyl)naphthalen-1-yl)amino)acetic acid (4h)

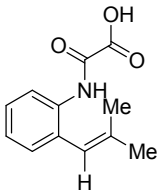
This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400

MHz, DMSO - d_6) δ (ppm) 10.47 (s, 1H), 7.96 - 7.88 (m, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.82 - 7.76 (m, 1H), 7.57 - 7.47 (m, 2H), 7.28 - 7.14 (m, 6H), 5.74 (s, 1H), 5.31 (s, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.3, 158.4, 146.4, 140.7, 137.7, 133.5, 130.8, 130.6, 128.6, 128.4, 128.2, 128.1, 127.9, 127.6, 127.3, 126.8, 124.2, 117.1; HRMS (ESI): m/z Calcd. for $C_{20}H_{15}NO_3$ [(M-H)$^-$] 316.0974, found 316.0966.



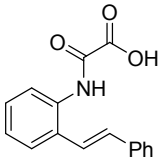
2-oxo-2-((2-(prop-1-en-1-yl)phenyl)amino)acetic acid (4j)

This compound was obtained as a light yellow solid by following the general procedure **A** (E/Z = 3.2:1). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.81 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.28 - 7.21 (m, 3H), 6.46 (d, J = 12 Hz, 1H), 5.91 - 5.97 (m, 1H), 1.67 (dd, J = 7.0, 1.7 Hz, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.1, 156.4, 134.2, 130.2, 129.5, 129.3, 127.4, 125.5, 125.3, 123.1, 14.3; HRMS (ESI): m/z Calcd. for $C_{11}H_{11}NO_3$ [(M-H)$^-$] 204.0661, found 204.0667.



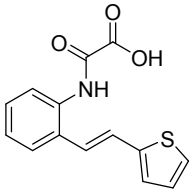
2-((2-(2-methylprop-1-en-1-yl)phenyl)amino)-2-oxoacetic acid (4k)

This compound was obtained as a light yellow solid by following the general procedure **A**. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.21 (s, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.36 - 7.29 (m, 1H), 7.23 - 7.19 (m, 2H), 6.17 (s, 1H), 2.00 (d, J = 1.3 Hz, 3H), 1.64 (d, J = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.5, 154.6, 141.7, 133.2, 130.1, 129.5, 127.7, 125.7, 119.8, 118.9, 25.7, 19.5; HRMS (ESI): m/z Calcd. for $C_{12}H_{13}NO_3$ [(M-H)$^-$] 218.0817, found 218.0822.



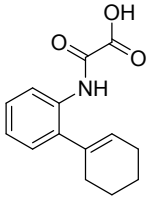
(*E*)-2-oxo-2-((2-styrylphenyl)amino)acetic acid (4l)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.15 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.40 (t, J = 7.5 Hz, 3H), 7.36 - 7.28 (m, 2H), 7.15 (d, J = 16.1 Hz, 1H), 7.07 (d, J = 16.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.4, 155.5, 136.4, 134.1, 132.3, 130.3, 128.9, 128.5, 128.5, 127.4, 127.0, 126.8, 122.5, 121.8; HRMS (ESI): m/z Calcd. for $C_{16}H_{13}NO_3$ [(M-H)$^-$] 266.0817, found 266.0805.



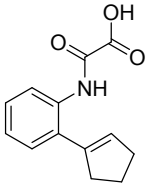
(E)-2-oxo-2-((2-(2-(thiophen-2-yl)vinyl)phenyl)amino)acetic acid (4m)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.79 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.36 - 7.28 (m, 4H), 7.25 (d, *J* = 15.4Hz, 1H), 7.02 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.4, 155.5, 136.4, 134.1, 132.3, 130.3, 128.9, 128.5, 128.5, 127.4, 126.8, 125.4, 122.5, 121.8; HRMS (ESI): m/z Calcd. for $C_{14}H_{11}NO_3S$ [(M-H)$^-$] 272.0623, found 272.0589.



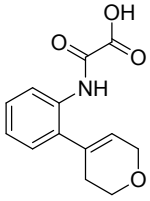
2-oxo-2-((2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-yl)amino)acetic acid (4n)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.77 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.34 - 7.25 (m, 1H), 7.25 - 7.13 (m, 2H), 5.72 (m, 1H), 2.19 - 2.14 (m, 4H), 1.79 - 1.68 (m, 2H), 1.68 - 1.57 (m, 2H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.5, 156.6, 136.9, 135.4, 133.7, 128.8, 128.4, 127.7, 125.6, 122.1, 29.6, 25.5, 23.0, 21.9; HRMS (ESI): m/z Calcd. for $C_{14}H_{15}NO_3$ [(M-H)$^-$] 244.0974, found 244.0973.\



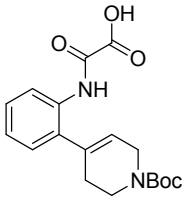
2-((2-(cyclopent-1-en-1-yl)phenyl)amino)-2-oxoacetic acid (4o)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.95 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.35 - 7.30 (m, 1H), 7.28 (d, *J* = 7.8, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.17 - 5.93 (m, 1H), 2.66 - 2.59 (m, 2H), 2.52 - 2.43 (m, 2H), 2.03 - 1.86 (m, 2H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.6, 156.8, 140.2, 133.8, 131.5, 130.6, 128.6, 127.8, 126.1, 124.0, 36.1, 33.9, 23.4; HRMS (ESI): m/z Calcd. for $C_{13}H_{13}NO_3$ [(M-H)$^-$] 230.0817, found 230.0822.



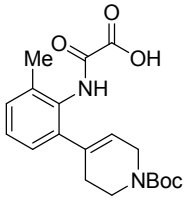
2-((2-(3,6-dihydro-2H-pyran-4-yl)phenyl)amino)-2-oxoacetic acid (4p)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.93 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.28 - 7.19 (m, 2H), 5.85 - 5.79 (m, 1H), 4.17 (d, *J* = 2.3 Hz, 2H), 3.80 (t, *J* = 5.3 Hz, 2H), 2.36 - 2.28 (m, 2H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.1, 156.4, 135.6, 133.1, 132.4, 128.2, 127.5, 126.4, 125.7, 123.4, 64.7, 63.6, 28.7; HRMS (ESI): m/z Calcd. for $C_{13}H_{14}NO_4$ [(M-H)$^-$] 246.0767, found 246.0774.



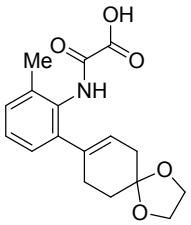
2-((2-(1-(tert-butoxycarbonyl)-1,2,3,6-tetrahydropyridin-4-yl)phenyl)amino)-2-oxoacetic acid (4q)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.94 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.35 - 7.28 (m, 1H), 7.28 - 7.19 (m, 2H), 5.67 (d, J = 52.0 Hz, 1H), 3.94 (s, 2H), 3.52 (t, J = 5.3 Hz, 2H), 2.33 (s, 2H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.6, 157.0, 154.4, 136.5, 134.0, 133.6, 128.8, 128.0, 126.2, 124.8, 124.2, 79.4, 60.2, 29.3, 28.6; HRMS (ESI): m/z Calcd. for $C_{18}H_{22}N_2O_5$ [(M-H)$^-$] 345.1451, found 345.1449.



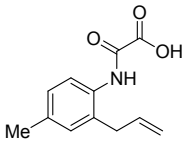
2-((2-(1-(tert-butoxycarbonyl)-1,2,3,6-tetrahydropyridin-4-yl)-6-methylphenyl)amino)-2-oxoacetic acid (4r)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.17 (s, 1H), 7.35 - 7.14 (m, 2H), 7.16 - 7.00 (m, 1H), 5.59 (s, 1H), 3.89 (s, 2H), 3.45 (d, J = 4.7 Hz, 2H), 2.28 (s, 2H), 2.16 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.8, 158.2, 154.4, 141.3, 136.3, 135.2, 132.6, 129.4, 127.7, 126.5, 123.1, 79.2, 60.2, 29.2, 28.5, 18.4; HRMS (ESI): m/z Calcd. for $C_{19}H_{24}N_2O_5$ [(M-H)$^-$] 359.1607, found 359.1602.



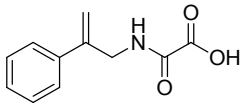
2-((2-methyl-6-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)phenyl)amino)-2-oxoacetic acid (4s)

This compound was prepared according to the reported procedure [4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.76 (s, 1H), 7.26 - 7.16 (m, 2H), 7.08 (d, J = 7.0 Hz, 1H), 5.53 - 5.45 (m, 1H), 4.21 - 3.95 (m, 4H), 2.38 (d J = 6.7 Hz, 2H), 2.22 (s, 3H), 1.84 (t, J = 5.8 Hz, 2H), 1.26 (t, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.1, 157.4, 141.8, 135.7, 135.4, 132.3, 128.6, 127.1, 125.9, 123.2, 106.7, 63.7, 35.6, 31.14, 28.2, 17.9; HRMS (ESI): m/z Calcd. for $C_{17}H_{19}NO_5$ [(M+Na)$^+$] 340.1161, found 340.1166.



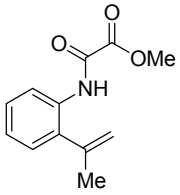
2-((2-allyl-4-methylphenyl)amino)-2-oxoacetic acid (6a)

This compound was prepared according to the reported procedure [4, 7]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.02 (s, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.06 - 7.05 (m, 2H), 5.91 - 5.81 (m, 1H), 5.07 - 5.03 (m, 2H), 3.32 (d, J = 6.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.7, 157.6, 136.7, 136.2, 134.4, 132.6, 130.6, 127.7, 126.0, 116.7, 35.9, 21.0; HRMS (ESI): m/z Calcd. for $C_{12}H_{13}NO_3$ [(M-H)$^-$] 218.0817, found 218.0816.



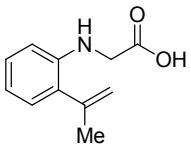
2-oxo-2-((2-phenylallyl)amino)acetic acid (8a)

This compound was prepared according to the reported procedures as a pale yellow solid [4, 8]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.10 (t, J = 6.0 Hz, 1H), 7.54 - 7.45 (m, 2H), 7.42 - 7.27 (m, 3H), 5.48 (s, 1H), 5.14 (s, 1H), 4.17 (d, J = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 162.6, 159.0, 143.7, 138.8, 128.9, 128.4, 126.2, 112.9, 42.5; HRMS (ESI): m/z Calcd. for $C_{11}H_{11}NO_3$ [(M-H)$^-$] 204.0661, found 204.0659.



Methyl 2-oxo-2-((2-(prop-1-en-2-yl)phenyl)amino)acetate (11a)

This compound was obtained as a light yellow solid according to the reported procedure [4]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.03 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.35 - 7.27 (m, 2H), 7.24 (t, J = 7.4 Hz, 1H), 5.29 (s, 1H), 4.98 (s, 1H), 3.84 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.65, 155.54, 142.42, 137.56, 133.10, 128.59, 128.10, 126.40, 124.40, 116.75, 53.74, 24.08; HRMS (ESI): m/z Calcd. for $C_{12}H_{13}NO_3$ [(M+Na)$^+$] 242.0793, found 242.0790.



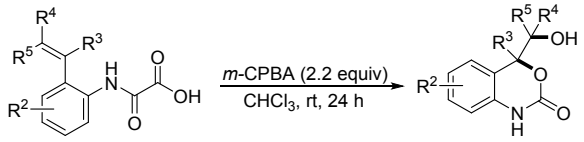
2-((2-(prop-1-en-2-yl)phenyl)amino)acetic acid (13a)

This compound was obtained as a light yellow solid according to the reported procedure [4, 9]. ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 7.06 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 7.4 Hz, 1H), 6.60 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 8.1 Hz, 1H), 5.30 (d, J = 1.5 Hz, 1H), 4.99 (d, J = 1.2 Hz, 1H), 3.83 (s, 2H), 2.01 (s, 3H);^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 172.9, 144.2, 143.5, 129.1, 128.4, 128.1, 116.7, 116.0, 110.7, 45.5, 24.2; HRMS (ESI): m/z Calcd. for $C_{11}H_{13}NO_2$ [(M-H)$^-$] 190.0868, found

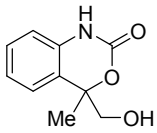
190.0871.

Synthesis and Characterization of the 3D Cyclic Carbamates

General Procedure B

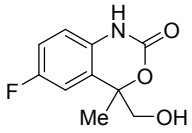


To a 10 mL sealed tube equipped with a magnetic stir bar was added *m*-CPBA (0.33 mmol, 2.2 equiv), olefinic oxamic acid (0.15 mmol, 1.0 equiv), and $CHCl_3$ (3.0 mL). The resulting mixture was stirred at room temperature for the indicated time. Then the solvent was removed under reduced pressure. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.



4-(hydroxymethyl)-4-methyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3a)

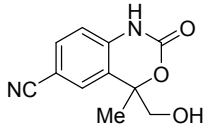
According to the general procedure **B**, the solution of **1a** (31.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (23.0 mg, 79% yield). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.02 (s, 1H), 7.24 - 7.20 (m, 1H), 7.20 (d, J = 4.6 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.20 (t, J = 5.4 Hz, 1H), 3.62 (dd, J = 11.5, 5.2 Hz, 1H), 3.55 (dd, J = 11.5, 5.3 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.4, 135.7, 128.5, 124.6, 122.9, 122.1, 113.6, 84.4, 67.6, 23.3; HRMS (ESI): m/z Calcd. for $C_{10}H_{11}NO_3$ [(M+Na)$^+$] 216.0637, found 216.0630.



6-fluoro-4-(hydroxymethyl)-4-methyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3b)

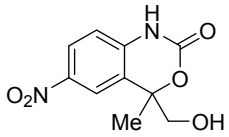
According to the general procedure **B**, the solution of **1b** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (26.0 mg, 82%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.14 (s, 1H), 7.20 (dd, J = 9.4, 2.8 Hz, 1H), 7.13 (td, J = 8.7, 2.8 Hz, 1H), 6.88 (dd, J = 8.7, 4.9 Hz, 1H), 5.31 (t, J = 5.7 Hz, 1H), 3.69 (dd, J = 11.6, 5.7 Hz, 1H), 3.61 (dd, J = 11.6, 5.8 Hz,

1H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 157.6 (d, J_{CF} = 235.8 Hz), 150.1, 132.2 (d, J_{CF} = 1.9 Hz), 124.7 (d, J_{CF} = 7.3 Hz), 115.2 (d, J_{CF} = 22.8 Hz), 114.9 (d, J_{CF} = 8.1 Hz), 111.8 (d, J_{CF} = 24.4 Hz), 84.3 (d, J_{CF} = 1.8 Hz), 67.6, 23.2; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -121.27; HRMS (ESI) Calcd. for $C_{10}H_{10}FNO_3$ [(M+Na)$^+$] 234.0542, found 234.0549.

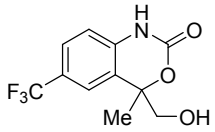


4-(hydroxymethyl)-4-methyl-2-oxo-2,4-dihydro-1H-benzo[d][1,3]oxazine-6-carbonitrile (3c)

According to the general procedure B, the solution of **1c** (34.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (28.0 mg, 86%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.54 (s, 1H), 7.77 (s, 1H), 7.69 -7.67 (m, 1H), 6.95 (d, J = 8.3 Hz, 1H), 5.30 (t, J = 5.7 Hz, 1H), 3.66 (dd, J = 11.7, 5.6 Hz, 1H), 3.59 (dd, J = 11.7, 5.7 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 149.6, 140.2, 133.0, 129.3, 123.8, 119.0, 114.4, 104.1, 84.8, 68.3, 23.2; HRMS (ESI) Calcd. for $C_{11}H_{10}N_2O_3$ [(M-H)$^+$] 217.0613, found 217.0608.

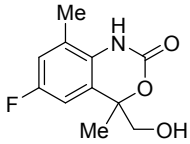


4-(hydroxymethyl)-4-methyl-6-nitro-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (3d) According to the general procedure **B**, the solution of **1d** (45.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (34.0 mg, 78%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.48 (s, 1H), 7.97(d, J = 8.5Hz, 2H), 6.65 (d, J = 8.5Hz, 2H), 5.35 (s, 1H), 3.65 (q, J = 11.6 Hz,2H), 1.58 (s ,3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 143.8, 141.7, 136.5, 130.8, 125.8, 117.1, 108.3, 85.3, 68.5, 23.5; HRMS (ESI) Calcd. for $C_{10}H_{10}N_2O_5$ [(M+Na)$^+$] 261.0486, found 261.0492



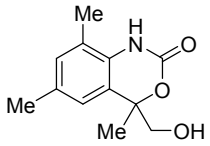
4-(hydroxymethyl)-4-methyl-6-(trifluoromethyl)-1H-benzo[d][1,3]oxazin-2(4H)-one (3e)

According to the general procedure **B**, the solution of **1e** (41.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (32.0 mg, 82%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.38 (s, 1H), 7.53 - 7.52 (m, 2H), 6.92 (d, J = 8.7 Hz, 1H), 5.24 (t, J = 5.4 Hz, 1H), 3.62 (dd, J = 11.6, 5.1 Hz, 1H), 3.53 (dd, J = 11.6, 5.2 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 149.9, 139.5, 125.9 (q, J_{CF} = 3.6 Hz), 124.4 (q, J_{CF} = 269.7 Hz), 123.5 (q, J_{CF} = 31.9 Hz), 122.4, 122.0 (q, J_{CF} = 3.6 Hz), 114.1, 84.8, 68.1, 23.3; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -59.86; HRMS (ESI) Calcd. for $C_{11}H_{10}F_3NO_3$ [(M+Na)$^+$] 284.0510, found 284.0498.



6-fluoro-4-(hydroxymethyl)-4,8-dimethyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3f)

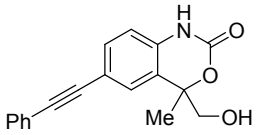
According to the general procedure **B**, the solution of **1f** (35.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (28.0 mg, 84%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.50 (s, 1H), 7.03 (d, J = 5.9 Hz, 1H), 7.01 (d, J = 6.2 Hz, 1H), 5.30 (t, J = 5.7 Hz, 1H), 3.69 (dd, J = 11.6, 5.7 Hz, 1H), 3.61 (dd, J = 11.6, 5.8 Hz, 1H), 2.27 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 157.3 (d, J_{CF} = 235.9 Hz), 150.5, 130.4 (d, J_{CF} = 2.0 Hz), 125.1 (d, J_{CF} = 7.7 Hz), 124.7 (d, J_{CF} = 7.9 Hz), 116.3 (d, J_{CF} = 22.3 Hz), 109.1 (d, J_{CF} = 24.1 Hz), 83.8 (d, J_{CF} = 2.0 Hz), 67.5, 23.1, 17.0; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -121.86; HRMS (ESI) Calcd. for $C_{11}H_{12}FNO_3$ [(M+Na)$^+$] 248.0699, found 248.0691.



4-(hydroxymethyl)-4,6,8-trimethyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3g)

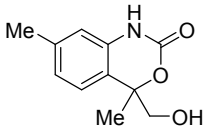
According to the general procedure **B**, the solution of **1g** (35.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (30.0 mg, 91%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.31 (s, 1H), 6.87 (s, 2H), 5.18 (t, J = 5.7 Hz, 1H), 3.61 (dd, J = 11.5, 5.7 Hz, 1H), 3.53 (dd, J = 11.5, 5.8 Hz, 1H), 2.20 (s, 3H), 2.17 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ

(ppm) 150.8, 131.4, 130.7, 130.6, 123.4, 122.5, 122.1, 84.0, 67.5, 23.2, 20.3, 16.9; HRMS (ESI) Calcd. for $C_{12}H_{15}NO_3$ [(M+K)$^+$] 260.0689, found 260.0686.



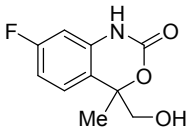
4-(hydroxymethyl)-4-methyl-6-(phenylethynyl)-1H-benzo[d][1,3]oxazin-2(4H)-one (3h)

According to the general procedure **B**, the solution of **1h** (46.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (30.0 mg, 68%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.29 (s, 1H), 7.58 - 7.49 (m, 2H), 7.49 - 7.35 (m, 5H), 6.87 (d, J = 8.2 Hz, 1H), 5.27 (t, J = 5.6 Hz, 1H), 3.68 (dd, J = 11.6, 5.7 Hz, 1H), 3.59 (dd, J = 11.6, 5.7 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.0, 136.3, 131.9, 131.1, 128.7, 128.5, 128.0, 123.4, 122.5, 115.7, 114.0, 89.5, 88.3, 84.7, 67.9, 23.3; HRMS (ESI) Calcd. for $C_{18}H_{15}NO_3$ [(M+K)$^+$] 332.0689, found 332.0673.



4-(hydroxymethyl)-4,7-dimethyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3i)

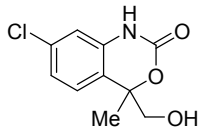
According to the general procedure **B**, the solution of **1i** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (21.0 mg, 74% yield). ^{1}H NMR (400 MHz, DMSO - d_6)) δ (ppm) 10.02 (s, 1H), 7.13 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.68 (s, 1H), 5.22 (t, J = 5.7 Hz, 1H), 3.64 (dd, J = 11.5, 5.7 Hz, 1H), 3.56 (dd, J = 11.5, 5.8 Hz, 1H), 2.29 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.5, 137.9, 135.7, 124.5, 122.9, 120.1, 113.9, 84.4, 67.7; HRMS (ESI): m/z Calcd. for $C_{11}H_{13}NO_3$ [(M+Na)$^+$] 230.0793, found 230.0787.



7-fluoro-4-(hydroxymethyl)-4-methyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3j)

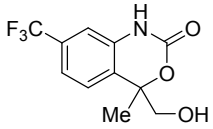
According to the general procedure **B**, the solution of **1j** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography

(petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (20.0 mg, 70%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.23 (s, 1H), 7.30 (dd, J = 8.5, 6.0 Hz, 1H), 6.86 (td, J = 8.7, 2.6 Hz, 1H), 6.65 (dd, J = 10.0, 2.6 Hz, 1H), 5.28 (t, J = 5.7 Hz, 1H), 3.64 (dd, J = 11.6, 5.6 Hz, 1H), 3.59 (dd, J = 11.6, 5.8 Hz, 1H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.9 (d, J_{CF} = 241.1 Hz), 150.1, 137.61 (d, J_{CF} = 11.3 Hz), 126.7 (d, J_{CF} = 9.8 Hz), 119.1 (d, J_{CF} = 2.8 Hz), 108.6 (d, J_{CF} = 21.5 Hz), 100.5 (d, J_{CF} = 25.6 Hz), 84.5, 67.9, 23.3; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -113.67; HRMS (ESI) Calcd. for $C_{10}H_{10}FNO_3$ [(M+Na)$^+$] 234.0542, found 234.0546.



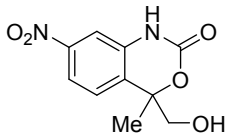
7-chloro-4-(hydroxymethyl)-4-methyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3k)

According to the general procedure **B**, the solution of **1k** (36.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (24.0 mg, 70%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.24 (s, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.10 - 7.07 (m, 1H), 6.90 (s, 1H), 5.29 (t, J = 5.6 Hz, 1H), 3.65 (dd, J = 11.6, 5.5 Hz, 1H), 3.60 (dd, J = 11.6, 5.7 Hz, 1H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 149.9, 137.4, 132.7, 126.6, 121.8, 121.8, 113.0, 84.6, 67.9, 23.2; HRMS (ESI) Calcd. for $C_{10}H_{10}ClNO_3$ [(M+Na)$^+$] 250.0247, found 250.0240.

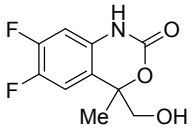


4-(hydroxymethyl)-4-methyl-7-(trifluoromethyl)-1H-benzo[d][1,3]oxazin-2(4H)-one (3l)

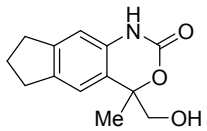
According to the general procedure **B**, the solution of **1l** (41.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (28.0 mg, 71%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.39 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 7.4 Hz, 1H), 7.15 (s, 1H), 5.36 (t, J = 5.7 Hz, 1H), 3.71 (dd, J = 11.6, 5.6 Hz, 1H), 3.65 (dd, J = 11.6, 5.7 Hz, 1H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 149.8, 136.8, 129.1 (q, J_{CF} = 32.0 Hz), 127.1, 126.1, 123.8 (q, J_{CF} = 270.5 Hz), 118.6 (q, J_{CF} = 3.8 Hz), 109.8 (q, J_{CF} = 3.9 Hz), 84.8, 68.1, 23.2; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -61.45; HRMS (ESI) Calcd. for $C_{11}H_{10}F_3NO_3$ [(M+Na)$^+$] 284.0510, found 284.0498.



4-(hydroxymethyl)-4-methyl-7-nitro-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (3m) According to the general procedure **B**, the solution of **1m** (45.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (34.0 mg, 78%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.48 (s, 1H),7.84 (d, J = 8.5Hz, 1H), 7.64 (s, 1H), 7.54 (d, J = 8.4 Hz, 1H), 5.35 (s, 1H), 3.65 (q, J = 11.6 Hz, 2H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.1, 148.0, 137.8, 130.3, 126.9, 117.3, 108.5, 85.4, 68.6, 23.6; HRMS (ESI) Calcd. for $C_{10}H_{10}N_2O_5$ [(M+Na)$^+$] 261.0486, found 261.0492



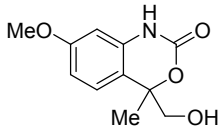
6,7-difluoro-4-(hydroxymethyl)-4-methyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3n) According to the general procedure **B**, the solution of **1n** (36.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (24.0 mg, 70%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.22 (s, 1H), 7.47 (dd, J = 11.2, 8.4 Hz, 1H), 6.83 (dd, J = 11.4, 7.1 Hz, 1H), 5.31 (t, J = 5.7 Hz, 1H), 3.66 (dd, J = 11.7, 5.7 Hz, 1H), 3.60 (dd, J = 11.7, 5.8 Hz, 1H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 149.9, 148.9 (dd, J_{CF} = 244.8, 13.6 Hz), 144.8 (dd, J_{CF} = 239.0, 12.8 Hz), 132.9 (d, J_{CF} = 9.4 Hz), 119.5 (dd, J_{CF} = 5.5, 3.6 Hz), 114.3 (d, J_{CF} = 19.6 Hz), 102.4 (d, J_{CF} = 21.2 Hz), 84.3, 67.8, 23.2; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -138.46 (d, J_{FF} = 23.0 Hz), -146.92 (d, J_{FF} = 23.1 Hz); HRMS (ESI) Calcd. for $C_{10}H_9F_2NO_3$ [(M+Na)$^+$] 252.0448, found 252.0446.



4-(hydroxymethyl)-4-methyl-4,6,7,8-tetrahydroindeno[5,6-d][1,3]oxazin-2(1H)-one (3o)

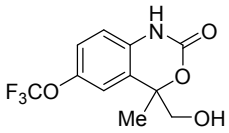
According to the general procedure **B**, the solution of **1o** (37.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white

solid (28.0 mg, 80%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.83 (s, 1H), 6.98 (s, 1H), 6.62 (s, 1H), 5.09 (t, J = 5.7 Hz, 1H), 3.52 (dd, J = 11.6, 5.7 Hz, 1H), 3.44 (dd, J = 11.5, 5.8 Hz, 1H), 2.71 (t, J = 7.5 Hz, 4H), 1.87 - 1.94 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 151.1, 144.6, 137.9, 134.6, 121.5, 120.7, 110.0, 84.9, 68.1, 32.6, 32.2, 25.6, 23.8; HRMS (ESI) Calcd. for $C_{13}H_{15}NO_3$ [(M+Na)$^+$] 256.0950, found 256.0931.



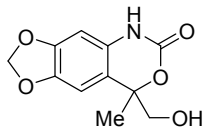
4-(hydroxymethyl)-7-methoxy-4-methyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3p)

According to the general procedure **B**, the solution of **1p** (35.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (20.0 mg, 60%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.00 (s, 1H), 7.17 (d, J = 8.5 Hz, 1H), 6.63 - 6.60 (m, 1H), 6.45 (s, 1H), 5.21 (t, J = 5.7 Hz, 1H), 3.77 (s, 3H), 3.62 (dd, J = 11.5, 5.6 Hz, 1H), 3.55 (dd, J = 11.5, 5.8 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 159.4, 150.5, 136.9, 125.7, 115.3, 107.6, 84.3, 67.7, 55.1, 23.3; HRMS (ESI) Calcd. for $C_{11}H_{13}NO_4$ [(M+Na)$^+$] 246.0742, found 246.0745.



4-(hydroxymethyl)-4-methyl-6-(trifluoromethoxy)-1H-benzo[d][1,3]oxazin-2(4H)-one (3q)

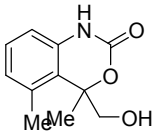
According to the general procedure **B**, the solution of **1q** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (27.0 mg, 65%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.30 (s, 1H), 7.33 (s, 1H), 7.30 (d, J = 8.6 Hz, 1H), 6.96 (d, J = 8.6 Hz, 1H), 5.34 (t, J = 5.6 Hz, 1H), 3.70 (dd, J = 11.6, 5.6 Hz, 1H), 3.62 (dd, J = 11.6, 5.6 Hz, 1H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 149.9, 143.0, 135.1, 124.6, 121.6, 120.1 (q, J_{CF} = 255.6 Hz), 118.3, 114.8, 84.4, 67.8, 23.2; ^{19}F NMR (376 MHz, DMSO - d_6) δ (ppm) -57.14; HRMS (ESI) Calcd. for $C_{11}H_{10}F_3NO_4$ [(M-H)$^+$] 276.0484, found 276.0478.



8-(hydroxymethyl)-8-methyl-5H-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]oxazin-

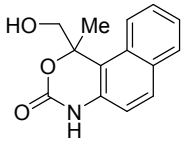
6(8H)-one (3r)

According to the general procedure **B**, the solution of **1r** (37.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (17.0 mg, 48%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.88 (s, 1H), 6.91 (s, 1H), 6.47 (s, 1H), 6.02 (s, 2H), 3.63 (d, J = 11.6 Hz, 1H), 3.54 (d, J = 11.6 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.9, 147.5, 143.0, 130.7, 115.6, 105.6, 101.6, 95.9, 84.8, 67.9, 23.7; HRMS (ESI) Calcd. for $C_{11}H_{11}NO_5$ [(M+Na)$^+$] 260.0535, found 260.0551.



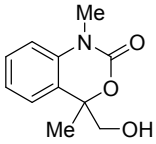
4-(hydroxymethyl)-4,5-dimethyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3s)

According to the general procedure **B**, the solution of **1s** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (20.0 mg, 64%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.89 (s, 1H), 7.01 (t, J = 7.7 Hz, 1H), 6.72 (d, J = 7.5 Hz, 1H), 6.64 (d, J = 7.4 Hz, 1H), 5.16 (t, J = 5.7 Hz, 1H), 3.77 (dd, J = 12.1, 6.1 Hz, 1H), 3.53 (dd, J = 12.1, 5.4 Hz, 1H), 2.29 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.3, 136.6, 134.1, 128.0, 126.0, 121.3, 112.4, 86.3, 66.8, 23.6, 21.6; HRMS (ESI) Calcd. for $C_{11}H_{13}NO_3$ [(M+Na)$^+$] 230.0793, found 230.0796.



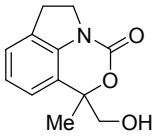
1-(hydroxymethyl)-1-methyl-1H-naphtho[2,1-d][1,3]oxazin-3(4H)-one (3t)

According to the general procedure **B**, the solution of **1t** (38.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (22.0 mg, 60%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.08 (s, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.79 (t, J = 8.3 Hz, 2H), 7.44 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 8.7 Hz, 1H), 5.23 (t, J = 5.7 Hz, 1H), 4.13 (dd, J = 12.0, 5.6 Hz, 1H), 3.69 (dd, J = 12.0, 5.7 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 154.9, 139.5, 135.6, 135.2, 134.5, 134.2, 132.1, 128.8, 128.6, 120.9, 119.1, 92.9, 73.2, 30.6; HRMS (ESI) Calcd. for $C_{14}H_{13}NO_3$ [(M+Na)$^+$] 266.0793, found 266.0787.



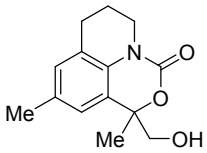
4-(hydroxymethyl)-1,4-dimethyl-1H-benzo[d][1,3]oxazin-2(4H)-one (3u)

According to the general procedure **B**, the solution of **1u** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (27.0 mg, 82%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 7.32 (td, J = 8.2, 1.4 Hz, 1H), 7.25 (dd, J = 7.6, 1.3 Hz, 1H), 7.06 (td, J = 7.5, 0.9 Hz, 1H), 7.02 (d, J = 8.2 Hz, 1H), 5.21 (t, J = 5.7 Hz, 1H), 3.61 (dd, J = 11.6, 5.6 Hz, 1H), 3.53 (dd, J = 11.6, 5.8 Hz, 1H), 3.24 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.9, 137.2, 128.7, 125.1, 124.5, 122.5, 113.2, 83.0, 67.2, 30.9, 22.9; HRMS (ESI) Calcd. for $C_{11}H_{13}NO_3$ [(M+Na)$^+$] 230.0793, found 239.0780.



1-(hydroxymethyl)-1-methyl-5,6-dihydro-[1,3]oxazino[5,4,3-hi]indol-3(1H)-one (3v)

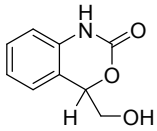
According to the general procedure **B**, the solution of **1v** (35.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a green solid (20.0 mg, 61%).^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 7.14 (d, J = 7.4 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 5.20 (t, J = 5.7 Hz, 1H), 3.91 (t, J = 8.7 Hz, 2H), 3.59 (dd, J = 11.7, 5.7 Hz, 1H), 3.54 (dd, J = 11.8, 5.9 Hz, 1H), 3.16 (t, J = 8.6 Hz, 2H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 149.5, 138.9, 127.6, 124.4, 123.0, 122.0, 120.2, 87.1, 67.8, 46.3, 27.4, 23.2; HRMS (ESI) Calcd. for $C_{12}H_{13}NO_3$ [(M+Na)$^+$] 242.0793, found 242.0786.



1-(hydroxymethyl)-1-methyl-6,7-dihydro-1H-[1,3]oxazino[5,4,3-ij]quinolin-3(5H)-one (3w)

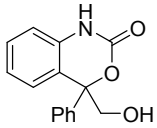
According to the general procedure **B**, the solution of **1w** (39.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white

solid (21.0 mg, 56%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 6.88 (s, 2H), 5.16 (t, J = 5.8 Hz, 1H), 3.78 - 3.69 (m, 1H), 3.64 - 3.55 (m, 2H), 3.49 (dd, J = 11.6, 5.8 Hz, 1H), 2.67 (t, J = 6.1 Hz, 2H), 2.20 (s, 3H), 1.89 - 1.77 (m, 2H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.3, 130.9, 130.4, 129.1, 124.3, 123.4, 122.8, 82.8, 67.2, 42.6, 26.0, 22.9, 20.6, 20.3; HRMS (ESI) Calcd. for $C_{14}H_{17}NO_3$ [(M+Na)$^+$] 270.1106, found 270.1098.



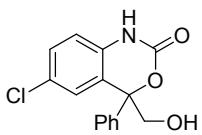
4-(hydroxymethyl)-1H-benzo[d][1,3]oxazin-2(4H)-one (5a)

According to the general procedure **B**, the solution of **4a** (28.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (18.0 mg, 67%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.01 (s, 1H), 7.21 - 7.14 (m, 2H), 6.95 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 5.31 (t, J = 4.3 Hz, 1H), 5.15 (t, J = 5.5 Hz, 1H), 3.72 - 3.63 (m, 2H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.7, 136.2, 128.6, 125.0, 122.0, 118.8, 113.5, 79.6, 63.7; HRMS (ESI) Calcd. for $C_9H_9NO_3$ [(M-H)$^+$] 178.0504, found 178.0497.



4-(hydroxymethyl)-4-phenyl-1H-benzo[d][1,3]oxazin-2(4H)-one (5b)

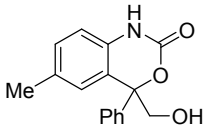
According to the general procedure **B**, the solution of **4b** (40.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (27.0 mg, 71%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.23 (s, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.43 - 7.25 (m, 6H), 7.14 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 5.49 (t, J = 5.9 Hz, 1H), 4.17 (dd, J = 12.4, 6.7 Hz, 1H), 3.95 (dd, J = 12.4, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 151.1, 140.5, 136.3, 128.8, 128.3, 128.1, 126.2, 125.6, 122.1, 121.9, 114.2, 87.2, 66.1; HRMS (ESI) Calcd. for $C_{15}H_{13}NO_3$ [(M+Na)$^+$] 278.0793, found 278.0783.



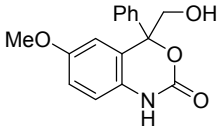
6-chloro-4-(hydroxymethyl)-4-phenyl-1H-benzo[d][1,3]oxazin-2(4H)-one (5c)

According to the general procedure **B**, the solution of **4c** (45.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred

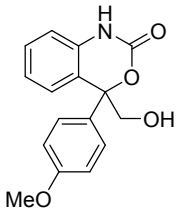
for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (34.0 mg, 78%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.31 (s, 1H), 7.54 (d, J = 2.3 Hz, 1H), 7.36 - 7.27 (m, 4H), 7.23 (d, J = 1.6 Hz, 1H), 7.21 (d, J = 1.6 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 5.48 (t, J = 5.7 Hz, 1H), 4.14 (dd, J = 12.4, 6.9 Hz, 1H), 3.86 (dd, J = 12.4, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.6, 139.8, 135.3, 128.8, 128.4, 128.3, 126.1, 126.1, 125.6, 123.8, 115.9, 87.0, 65.9; HRMS (ESI) Calcd. for $C_{15}H_{12}NO_3$ [(M+Na)$^+$] 312.0403, found 312.0398.



4-(hydroxymethyl)-6-methyl-4-phenyl-1H-benzo[d][1,3]oxazin-2(4H)-one (5d)
According to the general procedure **B**, the solution of **4d** (42.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (31.0 mg, 77%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.03 (s, 1H), 7.32 - 7.23 (m, 4H), 7.21 (d, J = 1.6 Hz, 1H), 7.19 (d, J = 1.5 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 5.37 (t, J = 5.2 Hz, 1H), 4.06 (dd, J = 12.4, 6.9 Hz, 1H), 3.84 (dd, J = 12.4, 5.3 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 151.1, 140.6, 133.9, 131.0, 129.3, 128.2, 128.0, 126.4, 125.7, 121.8, 114.0, 87.2, 66.1, 20.6; HRMS (ESI) Calcd. for $C_{16}H_{15}NO_3$ [(M+Na)$^+$] 292.0950, found 292.0940.

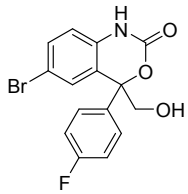


4-(hydroxymethyl)-6-methoxy-4-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (5e) According to the general procedure **B**, the solution of **4e** (45.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (34.0 mg, 78%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.99 (s, 1H), 7.30-7.25 (m, 5H), 7.08 (d, J = 1.6 Hz, 1H), 6.89 (d, J = 1.6 Hz, 1H), 6.80 (d, J = 1.6 Hz, 1H), 5.40 (t, J = 5.7 Hz, 1H), 4.13 (dd, J = 12.4, 6.9 Hz, 1H), 3.89 (dd, J = 12.4, 5.1 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 155.1, 151.5, 140.9, 130.2, 128.7, 128.5, 126.2, 123.6, 115.5, 114.5, 112.6, 87.5, 67.5, 66.5, 56.0, 25.6; HRMS (ESI) Calcd. for $C_{16}H_{15}NO_4$ [(M+Na)$^+$] 308.0899, found 308.0894.



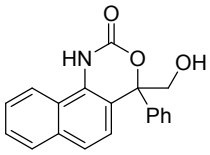
4-(hydroxymethyl)-4-(4-methoxyphenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (5f)

According to the general procedure **B**, the solution of **4f** (45.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (34.0 mg, 78%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.18 (s, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.32 (td, J = 7.8, 1.2 Hz, 1H), 7.20 - 7.09 (m, 3H), 6.94 (dq, J = 4.9, 2.9 Hz, 3H), 5.42 (dd, J = 6.6, 5.3 Hz, 1H), 4.12 (dd, J = 12.4, 6.8 Hz, 1H), 3.94 (dd, J = 12.4, 5.1 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 159.0, 151.1, 136.3, 132.4, 128.7, 127.0, 126.1, 122.0, 114.1, 113.6, 87.0, 66.1, 55.1; HRMS (ESI) Calcd. for $C_{16}H_{15}NO_4$ [(M+Na)$^+$] 308.0899, found 308.0894.



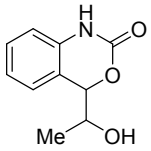
6-bromo-4-(4-fluorophenyl)-4-(hydroxymethyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (5g)

According to the general procedure **B**, the solution of **4g** (45.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (34.0 mg, 78%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.44 (s, 1H), 7.73 (d, J = 2.1 Hz, 1H), 7.55 (dd, J = 8.5, 2.1 Hz, 1H), 7.36 - 7.32 (m, 2H), 7.27 (dt, J = 8.9, 2.4 Hz, 2H), 6.91 (d, J = 8.5 Hz, 1H), 5.59 (t, J = 5.3 Hz, 1H), 4.21 (dd, J = 12.3, 6.0 Hz, 1H), 3.96 (dd, J = 12.3, 3.9 Hz, 1H).; ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 161.8, 150.5, 136.0, 135.7, 131.9, 128.7, 128.0, 127.9, 124.0, 116.4, 115.4, 115.2, 114.0, 86.5, 65.8; HRMS (ESI) Calcd. for $C_{16}H_{15}NO_4$ [(M+Na)$^+$] 373.9804, found 373.9800



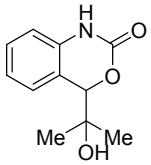
4-(hydroxymethyl)-4-phenyl-1H-naphtho[1,2-d][1,3]oxazin-2(4H)-one (5h)

According to the general procedure **B**, the solution of **4h** (48.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (38.0 mg, 83%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.45 (s, 1H), 8.31 (d, J = 9.4 Hz, 1H), 7.90 (d, J = 9.4 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.54 - 7.46 (m, 2H), 7.33 - 7.27 (m, 2H), 7.27 - 7.22 (m, 3H), 5.48 (t, J = 6.0 Hz, 1H), 4.22 (dd, J = 12.4, 6.9 Hz, 1H), 3.97 (dd, J = 12.4, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 156.7, 146.0, 138.3, 136.9, 133.6, 133.4, 131.8, 131.4, 131.0, 129.0, 127.3, 126.6, 126.5 (2C, overlap), 123.0, 92.6, 71.4; HRMS (ESI) Calcd. for $C_{19}H_{15}NO_3$ [$(M+Na)^+$] 328.0950, found 328.0957.



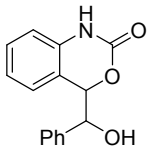
4-(1-hydroxyethyl)-1H-benzo[d][1,3]oxazin-2(4H)-one (5j)

According to the general procedure **B**, the solution of **4j** (31.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (25.0 mg, 86%). ^{1}H NMR (400 MHz, DMSO - d_6) (dr = 3.7 : 1), δ (ppm) 9.93 (s, 1H), 7.17 - 7.12 (m, 2H), 6.96 - 6.89 (m, 1H), 6.76 (d, J = 7.8 Hz, 1H), 5.13 (d, J = 3.1 Hz, 1H), 4.96 (d, J = 4.9 Hz, 1H), 3.86 - 3.83 (m, 1H), 1.08 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.7, 136.3, 128.4, 125.4, 121.8, 119.0, 113.4, 82.3, 69.0, 18.9; HRMS (ESI) Calcd. for $C_{10}H_{11}NO_3$ [$(M+K)^+$] 232.0376, found 232.0369.



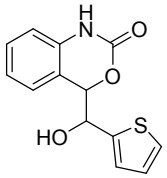
4-(2-hydroxypropan-2-yl)-1H-benzo[d][1,3]oxazin-2(4H)-one (5k)

According to the general procedure **B**, the solution of **4k** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (26.0 mg, 84%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.95 (s, 1H), 7.18 (td, J = 7.8, 1.3 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 6.92 (td, J = 7.5, 1.0 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 4.97 (s, 1H), 4.73 (s, 1H), 1.12 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.8, 136.4, 128.5, 127.5, 121.2, 117.5, 113.5, 84.9, 72.5, 26.2, 24.5; HRMS (ESI) Calcd. for $C_{11}H_{13}NO_3$ [$(M+Na)^+$] 230.0793, found 232.03787.

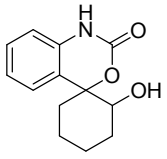


4-(hydroxy(phenyl)methyl)-1H-benzo[d][1,3]oxazin-2(4H)-one (5l)

According to the general procedure **B**, the solution of **4l** (40.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (18.0 mg, 47%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.98 (s, 1H), 7.37 - 7.30 (m, 3H), 7.28 - 7.23 (m, 2H), 7.21 (d, J = 7.5 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 7.9 Hz, 1H), 6.63 (d, J = 7.4 Hz, 1H), 5.92 (d, J = 4.6 Hz, 1H), 5.51 (d, J = 4.7 Hz, 1H), 4.93 (t, J = 4.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.4, 140.3, 136.3, 128.6, 127.7, 127.4, 126.9, 126.4, 121.0, 117.1, 113.4, 82.3, 75.1; HRMS (ESI) Calcd. for $C_{15}H_{13}NO_3$ [$(M+H)^+$] 256.0974, found 256.0969



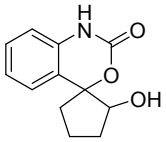
4-(hydroxy(thiophen-2-yl)methyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (5m) According to the general procedure **B**, the solution of **4m** (45.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (34.0 mg, 78%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.97 (s, 1H), 7.80-7.48 (m, 4H), 7.44-7.12 (m, 3H), 6.69 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 8.4 Hz, 1H), 5.41 (s,1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 154.6, 143.4, 139.8, 134.0, 133.8, 131.2, 129.8, 129.0, 125.7, 121.4, 117.5, 82.3,77.5; HRMS (ESI) Calcd. for $C_{13}H_{11}NO_3S$ [$(M+Na)^+$] 284.7023, found 284.7018



2'-hydroxyspiro[benzo[d][1,3]oxazine-4,1'-cyclohexan]-2(1H)-one (5n)

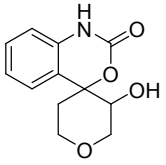
According to the general procedure **B**, the solution of **4n** (37.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (28.0 mg, 80%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.17 (s, 1H), 7.30 - 7.25 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 4.99 (d, J = 5.1 Hz,

1H), 3.83 - 3.78 m, 1H), 2.43 (t, J = 12.7 Hz, 1H), 1.91 (t, J = 12.1 Hz, 1H), 1.81 - 1.57 (m, 5H), 1.50 - 1.43 (m, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.5, 135.1, 128.4, 126.6, 124.1, 121.9, 113.6, 82.8, 66.1, 29.0, 28.2, 20.0, 18.1; HRMS (ESI) Calcd. for $C_{13}H_{15}NO_3$ [(M+Na)$^+$] 256.0950, found 256.0955.



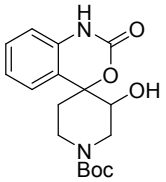
2'-hydroxyspiro[benzo[d][1,3]oxazine-4,1'-cyclopentan]-2(1H)-one (5o)

According to the general procedure **B**, the solution of **4o** (35.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (17.0 mg, 52%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.19 (s, 1H), 7.31 - 7.27 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 7.4 Hz, 1H), 5.00 (d, J = 5.2 Hz, 1H), 4.07 - 4.04 (m, 1H), 2.54 - 2.45 (m, 1H), 2.23 - 2.09 (m, 1H), 2.02 - 1.78 (m, 3H), 1.76 - 1.65 (m, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.7, 136.0, 128.6, 126.5, 121.7, 120.7, 113.5, 92.8, 74.6, 33.2, 32.1, 19.6; HRMS (ESI) Calcd. for $C_{12}H_{13}NO_3$ [(M-H)$^+$] 218.0817, found 218.0811.



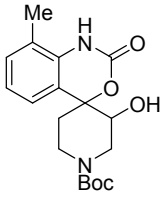
3'-hydroxy-2',3',5',6'-tetrahydrospiro[benzo[d][1,3]oxazine-4,4'-pyran]-2(1H)-one (5p)

According to the general procedure **B**, the solution of **4p** (37.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (29.0 mg, 82%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.21 (s, 1H), 7.23 - 7.21 (m, 2H), 6.99 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 7.4 Hz, 1H), 5.23 (d, J = 6.4 Hz, 1H), 3.83 - 3.74 (m, 3H), 3.66 - 3.59 (m, 1H), 3.50 (d, J = 5.9 Hz, 1H), 2.74 - 2.66 (m, 1H), 1.58 (d, J = 13.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.0, 135.1, 128.8, 126.7, 122.6, 122.0, 113.8, 80.5, 67.5, 65.6, 61.7, 29.3; HRMS (ESI) Calcd. for $C_{12}H_{13}NO_4$ [(M+Na)$^+$] 258.0742, found 258.0746.



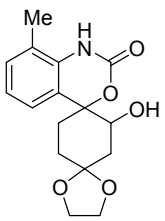
Tert-butyl 3'-hydroxy-2-oxo-1,2-dihydrospiro[benzo[d][1,3]oxazine-4,4'-piperidine]-1'-carboxylate (5q)

According to the general procedure **B**, the solution of **4q** (52.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction was quenched with $NaHCO_3$ (aq) and extracted with DCM (20 mL x 3). The combined organic phase was washed with brine (20 mL x 3), dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. Then it was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (31.0 mg, 62%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.31 (s, 1H), 7.32 - 7.29 (m, 2H), 7.06 (t, J = 7.3 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 5.33 (s, 1H), 4.11-3.81 (m, 2H), 3.76- 3.68 (m, 1H), 3.34 - 3.11 (m, 2H), 2.69 - 2.58 (m, 1H), 1.71 (d, J = 13.6 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.5, 135.5, 129.3, 127.2, 123.1, 122.6, 114.3, 81.5, 79.1, 65.6, 28.6; HRMS (ESI) Calcd. for $C_{17}H_{22}N_2O_5$ [(M+Na)$^+$] 357.1426, found 357.1428.



Tert-butyl 3'-hydroxy-8-methyl-2-oxo-1,2-dihydrospiro[benzo[d][1,3]oxazine-4, 4'-piperidine]-1'-carboxylate (5r)

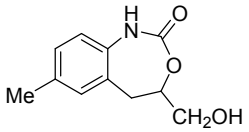
According to the general procedure **B**, the solution of **4r** (54.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction was quenched with $NaHCO_3$ (aq) and extracted with DCM (20 mL x 3). The combined organic phase was washed with brine (20 mL x 3), dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. Then it was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (35.0 mg, 67%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.73 (s, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 7.7 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 5.30 (s, 1H), 4.05 - 3.85 (m, 2H), 3.76 - 3.66 (m, 1H), 3.35 - 3.11 (m, 2H), 2.67 - 2.58 (m, 1H), 2.29 (s, 3H), 1.69 (d, J = 13.6 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 150.3, 133.1, 130.3, 124.3, 123.3, 122.5, 121.9, 80.6, 78.5, 78.2, 65.0, 28.1, 17.0; HRMS (ESI) Calcd. for $C_{18}H_{24}N_2O_5$ [(M-H)$^-$] 347.1607, found 347.1607.



2'-hydroxy-4'-(1,4-dioxa-spiro[4.5]decan-8-yl)-8-methylspiro[benzo[d][1,3]oxazine-4,1'-cyclohexan]-2(1H)-one (5s)

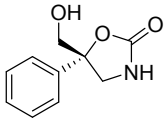
According to the general procedure **B**, the solution of **4s** (48.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction was quenched with $NaHCO_3$ (aq) and

extracted with DCM (20 mL x 3). The combined organic phase was washed with brine (20 mL x 3), dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. Then it was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (34.0 mg, 74%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.59 (s, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 4.64 (d, J = 6.3 Hz, 1H), 3.99 - 3.83 (m, 5H), 2.22 (s, 3H), 2.05 (dd, J = 14.0, 3.7 Hz, 1H), 1.98 - 1.64 (m, 4H), 1.25 (d, J = 9.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 151.1, 133.9, 130.6, 124.5, 123.8, 123.0, 122.3, 107.4, 82.6, 68.6, 64.5, 63.9, 37.1, 30.3, 28.3, 17.5; HRMS (ESI) Calcd. for $C_{16}H_{19}NO_5$ [(M+Na)$^+$] 328.1161, found 328.1153.



4-(hydroxymethyl)-7-methyl-4,5-dihydrobenzo[d][1,3]oxazepin-2(1H)-one (7a)

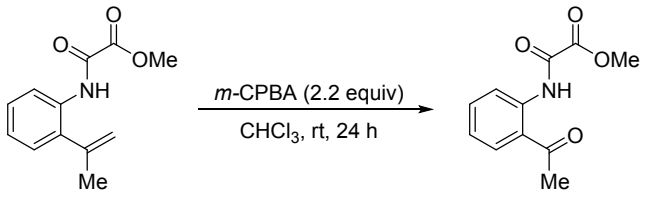
According to the general procedure **B**, the solution of **6a** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (13.0 mg, 41%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.42 (s, 1H), 7.00 - 6.89 (m, 3H), 5.05 (t, J = 5.8 Hz, 1H), 4.44 - 4.35 (m, 1H), 3.62 - 3.44 (m, 2H), 3.02 - 2.91 (m, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 153.8, 134.5, 131.5, 130.7, 127.7, 126.1, 119.1, 80.0, 63.0, 35.0, 20.0; HRMS (ESI) Calcd. for $C_{11}H_{13}NO_3$ [(M+Na)$^+$] 230.0793, found 230.0791.



5-(hydroxymethyl)-5-phenyloxazolidin-2-one (9a)

According to the general procedure **B**, the solution of **8a** (31.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (11.0 mg, 32%).^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 7.56 (s, 1H), 7.43 - 7.29 (m, 5H), 5.44 (t, J = 6.0 Hz, 1H), 3.87 (d, J = 8.8 Hz, 1H), 3.56 (d, J = 6.0 Hz, 2H), 3.44 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 158.5, 142.3, 128.8, 128.2, 125.3, 85.1, 67.1, 48.4; HRMS (ESI) Calcd. for $C_{10}H_{11}NO_3$ [(M+Na)$^+$] 216.0637, found 216.0638.

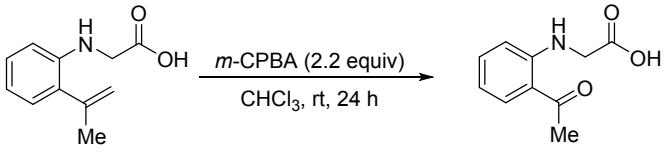
The synthesis of methyl 2-((2-acetylphenyl)amino)-2-oxoacetate (12a)



11a **12a**

According to the general procedure **B**, the solution of **11a** (33.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 50/1) to provide the title compound **12a** as a yellow solid (19.0 mg, 58%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 12.77 (s, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 3.89 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 203.4, 160.9, 155.0, 138.4, 135.3, 133.0, 124.6, 123.6, 120.4, 54.1, 29.2.

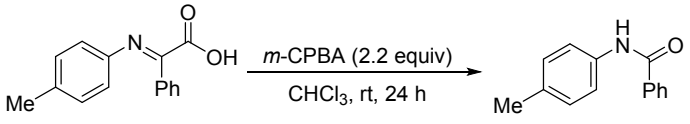
The synthesis of 2-((2-acetylphenyl)amino)acetic acid (14a)



13a **14a**

According to the general procedure B, **13a** (29.0 mg, 0.15 mmol, 1.0 equiv), *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv), and $CHCl_3$ (3.0 mL). After stirring 24h at room temperature. Then the solvent was removed under reduced pressure (63%, yield was determined by ^{1}H NMR using CH_2Br_2 as an internal standard). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 9.01 (t, J = 4.6 Hz, 1H), 7.85 (d, J = 7.1 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 6.68 - 6.59 (m, 2H), 4.01 (d, J = 5.0 Hz, 2H), 2.55 (s, 3H).

The synthesis of N-(p-tolyl)benzamide (16a) [11]



15a **16a**

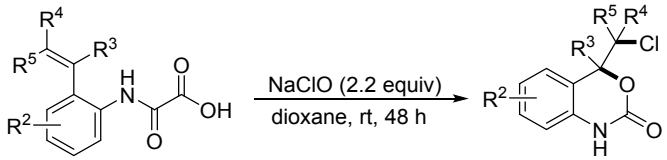
The compound **15a** was prepared according to the reported procedure [10] as a light yellow solid (1.10 g, 82% yield). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 7.85 (d, J = 6.7 Hz, 2H), 7.63 - 7.50 (m, 3H), 7.17 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 166.85, 161.56, 147.73, 134.36, 134.13, 132.25, 129.83, 129.41, 128.03, 120.22, 20.96.

According to the general procedure **B**, the solution of **15a** (36.0 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (57.0 mg, 0.33 mmol, 2.2 equiv) in $CHCl_3$ (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **B** and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1) to provide the title compound **16a** as a white

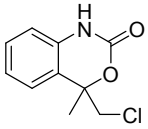
solid (28.5 mg, 90%). ^{1}H NMR (400 MHz, DMSO - d_6) δ (ppm) 10.18 (s, 1H), 7.96 (d, J = 7.1 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ (ppm) 165.8, 137.1, 135.5, 133.0, 131.9, 129.4, 128.8, 128.1, 120.8, 21.0.

The synthesis of chloro-substituted 3D cyclic carbamates

General Procedure C

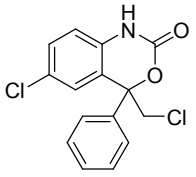


To a 10 mL sealed tube equipped with a magnetic stir bar was added *NaClO* (0.33 mmol, 2.2 equiv), olefinic oxamic acid (0.15 mmol, 1.0 equiv), and 1,4-dioxane(3.0 mL). The resulting mixture was stirred at room temperature for the indicated time. Then the solvent was removed under reduced pressure. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.



4-(chloromethyl)-4-methyl-1H-benzo[d][1,3]oxazin-2(4H)-one (10a)

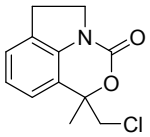
According to the general procedure **C**, the solution of **1a** (31 mg, 0.15 mmol, 1.0 equiv) and *NaClO* (57.0 mg, 0.33 mmol, 2.2 equiv) in dioxane (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **C** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (28.0 mg, 71%). ^{1}H NMR (400 MHz, DMSO - d_6) δ 10.20 (s, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.20 (td, J = 7.9, 1.3 Hz, 1H), 6.96 (td, J = 7.6, 1.1 Hz, 1H), 6.81 (dd, J = 7.9, 0.7 Hz, 1H), 4.05 (d, J = 12.0 Hz, 1H), 3.91 (d, J = 12.0 Hz, 1H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ 149.90, 135.86, 129.76, 125.12, 123.02, 121.89, 114.52, 83.44, 51.79, 25.78; HRMS (ESI) Calcd. for $C_{10}H_{10}ClNO_2$ [(M+Na)$^+$] 234.0298, found 234.0299.



6-chloro-4-(chloromethyl)-4-phenyl-1H-benzo[d][1,3]oxazin-2(4H)-one(10b)

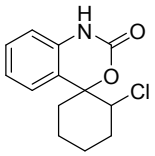
According to the general procedure **C**, the solution of **4c** (35.0 mg, 0.15 mmol, 1.0

equiv) and *NaClO* (57.0 mg, 0.33 mmol, 2.2 equiv) in dioxane (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **C** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (28.0 mg, 71%). ^{1}H NMR (400 MHz, DMSO - d_6) δ 10.53 (s, 1H), 7.80 (d, J = 2.2 Hz, 1H), 7.45 – 7.35 (m, 4H), 7.31 (dt, J = 8.4, 2.8 Hz, 2H), 6.92 (d, J = 8.5 Hz, 1H), 4.77 (d, J = 12.5 Hz, 1H), 4.31 (d, J = 12.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO - d_6) δ 150.25, 139.69, 135.44, 130.07, 129.45, 129.22, 127.01, 126.31, 126.08, 123.08, 116.77, 86.03, 49.07; HRMS (ESI) Calcd. for $C_{15}H_{11}Cl_2NO_2$ [(M+Na)$^+$] 330.0065, found 330.0070.



1-(chloromethyl)-1-methyl-5,6-dihydro-[1,3]oxazino[5,4,3-hi]indol-3(1H)-one (10c)

According to the general procedure **C**, the solution of **1v** (35.0 mg, 0.15 mmol, 1.0 equiv) and *NaClO* (57.0 mg, 0.33 mmol, 2.2 equiv) in dioxane (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **C** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (28.0 mg, 71%). ^{1}H NMR (400 MHz, DMSO - d_6) δ 7.21 (dd, J = 7.4, 0.8 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.00 (t, J = 7.6 Hz, 1H), 4.13 (dd, J = 21.4, 12.0 Hz, 1H), 4.05 – 3.93 (m, 3H), 3.20 (t, J = 8.5 Hz, 2H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, DMSO - d_6) δ 148.92, 138.97, 128.68, 125.67, 123.84, 122.41, 119.28, 85.76, 51.93, 46.88, 27.91, 25.70; HRMS (ESI) Calcd. for $C_{12}H_{12}ClNO_2$ [(M+Na)$^+$] 260.0454, found 260.0453.



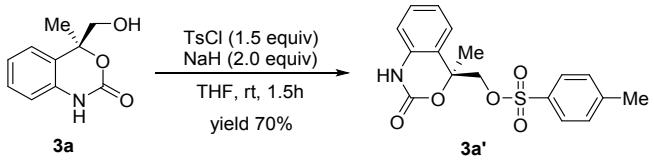
2'-chlorospiro[benzo[d][1,3]oxazine-4,1'-cyclohexan]-2(1H)-one (10d)

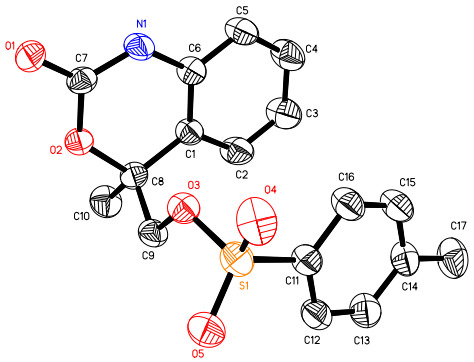
According to the general procedure **C**, the solution of **4n** (37.0 mg, 0.15 mmol, 1.0 equiv) and *NaClO* (57.0 mg, 0.33 mmol, 2.2 equiv) in dioxane (3.0 mL) was stirred for 24h at room temperature. The reaction mixture was subjected to the workup protocol outlined in the general procedure **C** and purified by flash chromatography (petroleum ether/ethyl acetate = 5/1 - 1/2) to provide the title compound as a white solid (28.0 mg, 71%). ^{1}H NMR (400 MHz, DMSO - d_6) δ 10.37 (s, 1H), 7.30 (dd, J = 12.1, 4.4 Hz, 2H), 7.07 – 7.01 (m, 1H), 6.93 (d, J = 7.8 Hz, 1H), 4.49 (s, 1H), 2.65 – 2.52 (m, 1H), 2.25 (tt, J = 11.7, 3.7 Hz, 1H), 1.93 – 1.52 (m, 6H); ^{13}C NMR (100 MHz, DMSO - d_6) δ 150.26, 135.63, 129.76, 127.25, 122.87, 122.54, 114.67, 82.56, 59.79, 29.31, 29.13, 20.14, 18.76; HRMS (ESI) Calcd. for $C_{13}H_{14}ClNO_2$ [(M+Na)$^+$]

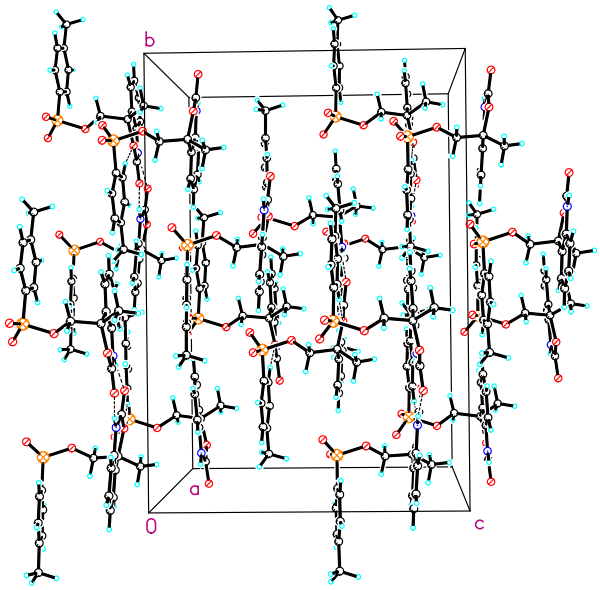
274.0611, found 274.0613.

X-ray Crystallography data

X-ray crystal structure analysis of 3a'







Crystal data and structure refinement for compound **3a'**

Table 1 Crystal data and structure refinement for cd16437.

Identification code	cd16437
Empirical formula	C17 H17 N O5 S
Formula weight	347.37
Temperature	293(2) K

Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	F d d 2	
Unit cell dimensions	a = 20.250(3) Å	α= 90°.
	b = 21.622(3) Å	β= 90°.
	c = 15.041(2) Å	γ= 90°.
Volume	6585.5(15) $Å^3$	
Z	16	
Density (calculated)	1.401 Mg/m^3	
Absorption coefficient	0.224 mm^{-1}	
F(000)	2912	
Crystal size	0.200 x 0.160 x 0.110 mm^3	
Theta range for data collection	1.932 to 25.500°.	
Index ranges	-24<=h<=21, -26<=k<=26, -18<=l<=17	
Reflections collected	9205	
Independent reflections	3023 [R(int) = 0.0524]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6600	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3023 / 1 / 223	
Goodness-of-fit on F^2	0.990	
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.0937	
R indices (all data)	R1 = 0.0697, wR2 = 0.1023	
Absolute structure parameter	-0.01(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.156 and -0.120 e.$Å^{-3}$	

Table 2 Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for cd16437. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U (eq)
S(1)	1276(1)	9108(1)	774(1)	68(1)
N(1)	2296(2)	8337(2)	3478(3)	65(1)
O(1)	1625(2)	7522(1)	3644(3)	72(1)
O(2)	1178(1)	8443(1)	3526(2)	69(1)
O(3)	1324(2)	8888(1)	1767(2)	61(1)
O(4)	1706(2)	8701(2)	317(3)	88(1)
O(5)	600(2)	9144(2)	528(2)	85(1)
C(1)	1879(2)	9363(2)	3351(3)	56(1)
C(2)	1994(3)	9990(2)	3298(4)	81(2)
C(3)	2621(3)	10221(2)	3318(5)	93(2)
C(4)	3145(3)	9829(2)	3382(5)	86(2)
C(5)	3041(2)	9203(2)	3447(4)	72(1)
C(6)	2406(2)	8972(2)	3420(3)	56(1)
C(7)	1704(2)	8073(2)	3546(3)	56(1)
C(8)	1187(2)	9104(2)	3320(3)	57(1)
C(9)	885(2)	9170(2)	2407(3)	61(1)
C(10)	720(3)	9393(3)	3986(4)	79(2)
C(11)	1605(2)	9857(2)	792(3)	63(1)
C(12)	1201(3)	10363(2)	723(4)	74(1)

C(13)	1482(3)	10945(3)	755(4)	85(2)
C(14)	2149(3)	11026(2)	830(4)	76(1)
C(15)	2539(2)	10512(2)	901(4)	79(1)
C(16)	2273(2)	9927(2)	884(4)	77(2)
C(17)	2442(3)	11670(2)	864(5)	104(2)

Table 3. Bond lengths [Å] and angles [°] for cd16437.

S(1)-O(4)	1.415(4)
S(1)-O(5)	1.419(4)
S(1)-O(3)	1.572(3)
S(1)-C(11)	1.751(5)
N(1)-C(7)	1.333(6)
N(1)-C(6)	1.394(5)
N(1)-H(1)	0.87(5)
O(1)-C(7)	1.211(5)
O(2)-C(7)	1.332(5)
O(2)-C(8)	1.464(4)
O(3)-C(9)	1.446(5)
C(1)-C(6)	1.365(6)
C(1)-C(2)	1.379(6)
C(1)-C(8)	1.509(6)
C(2)-C(3)	1.364(7)
C(2)-H(2)	0.9300
C(3)-C(4)	1.361(7)
C(3)-H(3)	0.9300
C(4)-C(5)	1.372(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.380(6)
C(5)-H(5)	0.9300
C(8)-C(9)	1.510(7)
C(8)-C(10)	1.514(6)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(16)	1.368(7)
C(11)-C(12)	1.371(6)
C(12)-C(13)	1.382(7)
C(12)-H(12)	0.9300
C(13)-C(14)	1.367(8)
C(13)-H(13)	0.9300
C(14)-C(15)	1.366(7)
C(14)-C(17)	1.515(7)
C(15)-C(16)	1.375(7)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
O(4)-S(1)-O(5)	120.1(2)
O(4)-S(1)-O(3)	103.6(2)
O(5)-S(1)-O(3)	108.9(2)

O(4)-S(1)-C(11)	110.4(2)
O(5)-S(1)-C(11)	108.7(2)
O(3)-S(1)-C(11)	104.0(2)
C(7)-N(1)-C(6)	124.8(4)
C(7)-N(1)-H(1)	118(3)
C(6)-N(1)-H(1)	117(3)
C(7)-O(2)-C(8)	125.5(3)
C(9)-O(3)-S(1)	117.8(3)
C(6)-C(1)-C(2)	118.8(4)
C(6)-C(1)-C(8)	119.9(4)
C(2)-C(1)-C(8)	121.3(4)
C(3)-C(2)-C(1)	121.0(5)
C(3)-C(2)-H(2)	119.5
C(1)-C(2)-H(2)	119.5
C(4)-C(3)-C(2)	119.9(5)
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
C(3)-C(4)-C(5)	120.0(5)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	119.8(4)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(1)-C(6)-C(5)	120.4(4)
C(1)-C(6)-N(1)	119.3(4)
C(5)-C(6)-N(1)	120.3(4)
O(1)-C(7)-O(2)	119.1(4)
O(1)-C(7)-N(1)	123.4(4)
O(2)-C(7)-N(1)	117.5(4)
O(2)-C(8)-C(1)	111.6(3)
O(2)-C(8)-C(9)	106.2(3)
C(1)-C(8)-C(9)	111.7(4)
O(2)-C(8)-C(10)	104.8(4)
C(1)-C(8)-C(10)	114.0(4)
C(9)-C(8)-C(10)	108.0(4)
O(3)-C(9)-C(8)	108.4(3)
O(3)-C(9)-H(9A)	110.0
C(8)-C(9)-H(9A)	110.0
O(3)-C(9)-H(9B)	110.0
C(8)-C(9)-H(9B)	110.0
H(9A)-C(9)-H(9B)	108.4
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(16)-C(11)-C(12)	120.7(4)
C(16)-C(11)-S(1)	118.7(4)
C(12)-C(11)-S(1)	120.6(4)
C(11)-C(12)-C(13)	118.6(5)
C(11)-C(12)-H(12)	120.7
C(13)-C(12)-H(12)	120.7
C(14)-C(13)-C(12)	121.7(5)
C(14)-C(13)-H(13)	119.1
C(12)-C(13)-H(13)	119.1

C(15)-C(14)-C(13)	118.3(5)
C(15)-C(14)-C(17)	121.2(5)
C(13)-C(14)-C(17)	120.5(5)
C(14)-C(15)-C(16)	121.4(5)
C(14)-C(15)-H(15)	119.3
C(16)-C(15)-H(15)	119.3
C(11)-C(16)-C(15)	119.4(5)
C(11)-C(16)-H(16)	120.3
C(15)-C(16)-H(16)	120.3
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4 Anisotropic displacement parameters ($Å^2x10^3$) for cd16437. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+ ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	66(1)	66(1)	71(1)	-11(1)	-4(1)	-9(1)
N(1)	47(2)	48(2)	99(4)	-2(2)	6(2)	11(2)
O(1)	64(2)	44(2)	109(3)	9(2)	9(2)	7(2)
O(2)	51(2)	50(2)	105(3)	15(2)	5(2)	10(2)
O(3)	60(2)	53(2)	70(2)	-7(2)	2(2)	6(2)
O(4)	102(3)	74(2)	88(3)	-30(2)	20(2)	-9(2)
O(5)	75(3)	95(3)	84(3)	-2(2)	-20(2)	-20(2)
C(1)	53(3)	48(2)	67(3)	-6(2)	0(2)	4(2)
C(2)	69(3)	52(3)	122(5)	-6(3)	-16(4)	6(3)
C(3)	78(4)	54(3)	147(6)	-12(4)	-18(4)	-6(3)
C(4)	64(3)	65(3)	127(5)	-16(4)	-11(3)	-11(3)
C(5)	53(3)	62(3)	101(4)	-13(3)	-9(3)	3(2)
C(6)	57(3)	47(2)	64(3)	-14(2)	-1(2)	1(2)
C(7)	57(3)	52(3)	59(3)	0(2)	3(2)	12(2)
C(8)	57(3)	43(2)	72(3)	0(3)	5(2)	9(2)
C(9)	49(3)	55(3)	79(3)	1(2)	1(2)	6(2)
C(10)	74(4)	79(4)	85(4)	-9(3)	17(3)	12(3)
C(11)	57(3)	65(3)	68(3)	-3(2)	3(3)	0(2)
C(12)	54(3)	75(4)	95(4)	8(3)	4(3)	2(3)
C(13)	74(4)	65(3)	117(5)	12(3)	21(4)	16(3)
C(14)	71(3)	68(3)	89(4)	-1(3)	17(3)	-7(3)
C(15)	54(3)	75(3)	109(4)	-6(3)	5(3)	-1(3)
C(16)	56(3)	64(3)	110(4)	-3(3)	6(3)	1(2)
C(17)	106(5)	72(3)	134(6)	4(4)	24(4)	-18(3)

Table 5 Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for cd16437.

	x	y	z	U(eq)
H(2)	1639	10260	3249	97
H(3)	2690	10645	3288	112
H(4)	3573	9985	3383	103
H(5)	3398	8936	3509	86
H(9A)	457	8968	2391	73
H(9B)	823	9604	2267	73
H(10A)	888	9332	4577	119
H(10B)	293	9203	3936	119
H(10C)	682	9828	3869	119
H(12)	747	10316	655	89
H(13)	1210	11291	724	102
H(15)	2993	10559	963	95
H(16)	2545	9582	934	92
H(17A)	2867	11669	582	156
H(17B)	2489	11796	1473	156
H(17C)	2155	11953	560	156
H(1)	2640(20)	8100(20)	3490(30)	76(16)

Table 6. Torsion angles [°] for cd16437.

O(4)-S(1)-O(3)-C(9)	-173.6(3)
O(5)-S(1)-O(3)-C(9)	-44.8(3)
C(11)-S(1)-O(3)-C(9)	71.0(3)
C(6)-C(1)-C(2)-C(3)	-0.3(9)
C(8)-C(1)-C(2)-C(3)	-179.4(6)
C(1)-C(2)-C(3)-C(4)	0.6(10)
C(2)-C(3)-C(4)-C(5)	-1.4(11)
C(3)-C(4)-C(5)-C(6)	1.9(10)
C(2)-C(1)-C(6)-C(5)	0.8(8)
C(8)-C(1)-C(6)-C(5)	179.8(5)
C(2)-C(1)-C(6)-N(1)	179.7(5)
C(8)-C(1)-C(6)-N(1)	-1.2(7)
C(4)-C(5)-C(6)-C(1)	-1.6(8)
C(4)-C(5)-C(6)-N(1)	179.4(5)
C(7)-N(1)-C(6)-C(1)	-6.0(8)
C(7)-N(1)-C(6)-C(5)	173.0(5)
C(8)-O(2)-C(7)-O(1)	-173.2(4)
C(8)-O(2)-C(7)-N(1)	8.4(6)
C(6)-N(1)-C(7)-O(1)	-175.8(5)
C(6)-N(1)-C(7)-O(2)	2.6(7)
C(7)-O(2)-C(8)-C(1)	-14.0(6)
C(7)-O(2)-C(8)-C(9)	107.9(5)
C(7)-O(2)-C(8)-C(10)	-137.9(4)
C(6)-C(1)-C(8)-O(2)	9.9(6)
C(2)-C(1)-C(8)-O(2)	-171.1(5)
C(6)-C(1)-C(8)-C(9)	-108.9(5)
C(2)-C(1)-C(8)-C(9)	70.2(6)
C(6)-C(1)-C(8)-C(10)	128.3(5)
C(2)-C(1)-C(8)-C(10)	-52.6(7)
S(1)-O(3)-C(9)-C(8)	-156.8(3)
O(2)-C(8)-C(9)-O(3)	-67.3(4)
C(1)-C(8)-C(9)-O(3)	54.6(4)
C(10)-C(8)-C(9)-O(3)	-179.2(4)
O(4)-S(1)-C(11)-C(16)	-36.9(5)
O(5)-S(1)-C(11)-C(16)	-170.5(4)
O(3)-S(1)-C(11)-C(16)	73.6(5)
O(4)-S(1)-C(11)-C(12)	143.6(4)
O(5)-S(1)-C(11)-C(12)	10.0(5)
O(3)-S(1)-C(11)-C(12)	-105.9(4)
C(16)-C(11)-C(12)-C(13)	-0.5(8)
S(1)-C(11)-C(12)-C(13)	179.0(5)
C(11)-C(12)-C(13)-C(14)	1.7(9)
C(12)-C(13)-C(14)-C(15)	-2.0(10)
C(12)-C(13)-C(14)-C(17)	-179.9(6)
C(13)-C(14)-C(15)-C(16)	1.1(9)
C(17)-C(14)-C(15)-C(16)	179.0(6)
C(12)-C(11)-C(16)-C(15)	-0.3(8)
S(1)-C(11)-C(16)-C(15)	-179.9(5)
C(14)-C(15)-C(16)-C(11)	0.1(9)

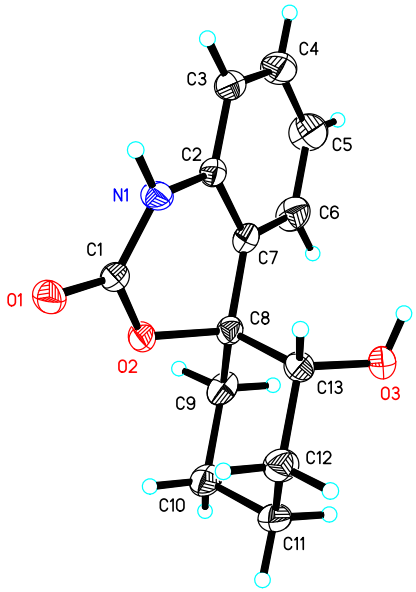
Symmetry transformations used to generate equivalent atoms:

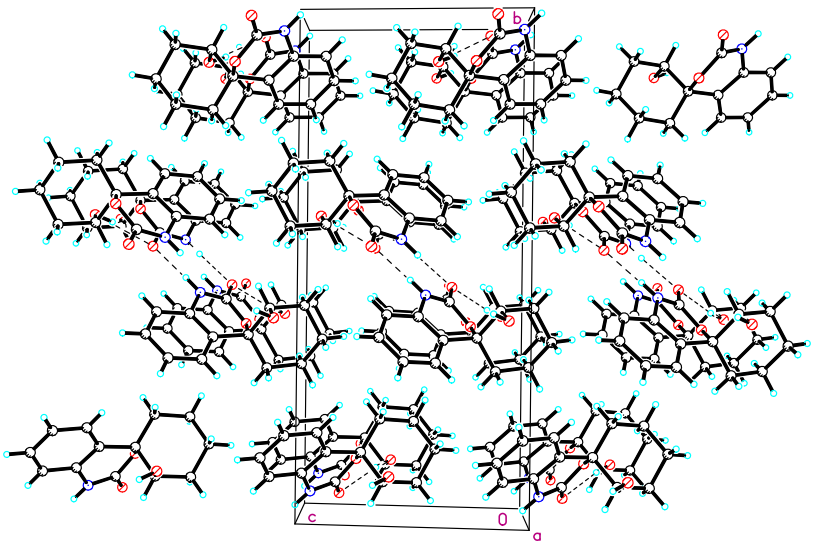
Table 7 Hydrogen bonds for cd16437 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.87(5)	2.02(5)	2.879(5)	172(5)
C(16)-H(16)...O(2)#2	0.93	2.56	3.416(6)	152.8
C(9)-H(9A)...O(4)#3	0.97	2.64	3.548(6)	156.0

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,z #2 x+1/4,-y+7/4,z-1/4 #3 x-1/4,-y+7/4,z+1/4

X-ray crystal structure analysis of 5j





Crystal data and structure refinement for compound **5j**

Table 1. Crystal data and structure refinement for mo_d8v17224_0m.

Identification code	mo_d8v17224_0m	
Empirical formula	C13 H15 N O3	
Formula weight	233.26	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 6.3499(4) Å	α= 90°.
	b = 20.1527(14) Å	β= 96.921(2)°.
	c = 9.1657(7) Å	γ= 90°.
Volume	1164.37(14) $Å^3$	
Z	4	
Density (calculated)	1.331 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	496	
Crystal size	0.200 x 0.160 x 0.130 mm^3	
Theta range for data collection	3.232 to 24.991°.	
Index ranges	-7<=h<=7, -23<=k<=23, -10<=l<=10	
Reflections collected	14539	
Independent reflections	2026 [R(int) = 0.0485]	
Completeness to theta = 25.242°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2026 / 0 / 160	
Goodness-of-fit on F^2	1.162	
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1137	
R indices (all data)	R1 = 0.0696, wR2 = 0.1190	
Extinction coefficient	0.032(7)	
Largest diff. peak and hole	0.168 and -0.150 e.$Å^{-3}$	

Table 2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for mo_d8v17224_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2909(3)	5536(1)	5528(2)	39(1)
O(1)	6201(2)	5386(1)	6723(2)	46(1)
O(2)	4174(2)	6160(1)	7522(2)	39(1)
O(3)	-916(2)	5991(1)	9026(2)	51(1)
C(1)	4489(3)	5672(1)	6589(2)	34(1)
C(2)	1136(3)	5950(1)	5214(2)	34(1)
C(3)	-83(4)	5912(1)	3863(3)	45(1)
C(4)	-1786(4)	6329(2)	3558(3)	58(1)
C(5)	-2271(5)	6778(2)	4595(3)	64(1)
C(6)	-1058(4)	6813(1)	5948(3)	51(1)
C(7)	669(3)	6396(1)	6290(2)	35(1)
C(8)	1993(3)	6358(1)	7761(2)	33(1)
C(9)	2294(4)	7015(1)	8583(3)	43(1)
C(10)	3656(4)	6945(1)	10057(3)	47(1)
C(11)	2721(4)	6432(1)	11004(3)	47(1)
C(12)	2533(4)	5768(1)	10215(3)	46(1)
C(13)	1157(3)	5821(1)	8748(2)	36(1)

Table 3. Bond lengths [Å] and angles [°] for mo_d8v17224_0m.

N(1)-C(1)	1.338(3)
N(1)-C(2)	1.403(3)
N(1)-H(1)	0.88(3)
O(1)-C(1)	1.224(3)
O(2)-C(1)	1.334(2)
O(2)-C(8)	1.483(2)
O(3)-C(13)	1.413(3)
O(3)-H(3)	0.8200
C(2)-C(3)	1.381(3)
C(2)-C(7)	1.392(3)
C(3)-C(4)	1.371(4)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.374(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.381(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.387(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.503(3)
C(8)-C(9)	1.523(3)
C(8)-C(13)	1.546(3)
C(9)-C(10)	1.520(3)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.516(3)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.520(3)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.516(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13)	0.9800
C(1)-N(1)-C(2)	122.70(19)
C(1)-N(1)-H(1)	118.0(15)
C(2)-N(1)-H(1)	117.1(15)
C(1)-O(2)-C(8)	120.54(16)
C(13)-O(3)-H(3)	109.5
O(1)-C(1)-O(2)	118.88(19)
O(1)-C(1)-N(1)	123.7(2)
O(2)-C(1)-N(1)	117.35(19)
C(3)-C(2)-C(7)	121.8(2)
C(3)-C(2)-N(1)	120.0(2)
C(7)-C(2)-N(1)	118.20(19)
C(4)-C(3)-C(2)	119.5(2)
C(4)-C(3)-H(3A)	120.3
C(2)-C(3)-H(3A)	120.3
C(3)-C(4)-C(5)	119.9(2)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	120.6(2)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7

C(5)-C(6)-C(7)	120.8(2)
C(5)-C(6)-H(6)	119.6
C(7)-C(6)-H(6)	119.6
C(6)-C(7)-C(2)	117.5(2)
C(6)-C(7)-C(8)	125.1(2)
C(2)-C(7)-C(8)	117.32(19)
O(2)-C(8)-C(7)	108.24(16)
O(2)-C(8)-C(9)	104.10(17)
C(7)-C(8)-C(9)	115.03(19)
O(2)-C(8)-C(13)	106.83(17)
C(7)-C(8)-C(13)	111.47(18)
C(9)-C(8)-C(13)	110.55(17)
C(10)-C(9)-C(8)	112.52(19)
C(10)-C(9)-H(9A)	109.1
C(8)-C(9)-H(9A)	109.1
C(10)-C(9)-H(9B)	109.1
C(8)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.8
C(11)-C(10)-C(9)	110.6(2)
C(11)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
C(10)-C(11)-C(12)	109.95(19)
C(10)-C(11)-H(11A)	109.7
C(12)-C(11)-H(11A)	109.7
C(10)-C(11)-H(11B)	109.7
C(12)-C(11)-H(11B)	109.7
H(11A)-C(11)-H(11B)	108.2
C(13)-C(12)-C(11)	111.4(2)
C(13)-C(12)-H(12A)	109.3
C(11)-C(12)-H(12A)	109.3
C(13)-C(12)-H(12B)	109.3
C(11)-C(12)-H(12B)	109.3
H(12A)-C(12)-H(12B)	108.0
O(3)-C(13)-C(12)	107.84(19)
O(3)-C(13)-C(8)	109.15(18)
C(12)-C(13)-C(8)	111.47(18)
O(3)-C(13)-H(13)	109.4
C(12)-C(13)-H(13)	109.4
C(8)-C(13)-H(13)	109.4

Symmetry transformations used to generate equivalent atoms

Table 4. Anisotropic displacement parameters ($Å^2x10^3$) for mo_d8v17224_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	34(1)	45(1)	36(1)	-14(1)	1(1)	7(1)
O(1)	33(1)	58(1)	45(1)	-12(1)	0(1)	12(1)
O(2)	30(1)	48(1)	40(1)	-15(1)	7(1)	-2(1)
O(3)	36(1)	75(1)	44(1)	-7(1)	10(1)	-13(1)
C(1)	33(1)	38(1)	32(1)	-5(1)	6(1)	1(1)
C(2)	29(1)	41(1)	32(1)	0(1)	6(1)	2(1)
C(3)	39(1)	60(2)	35(1)	-4(1)	4(1)	3(1)
C(4)	48(2)	80(2)	42(2)	7(1)	-4(1)	10(1)
C(5)	54(2)	76(2)	59(2)	9(2)	-1(1)	29(2)
C(6)	51(2)	53(2)	50(2)	-1(1)	11(1)	18(1)
C(7)	35(1)	38(1)	34(1)	2(1)	12(1)	2(1)
C(8)	32(1)	34(1)	34(1)	-4(1)	8(1)	1(1)
C(9)	57(2)	30(1)	44(1)	-4(1)	20(1)	-4(1)
C(10)	56(2)	47(2)	42(1)	-16(1)	14(1)	-15(1)
C(11)	51(2)	58(2)	33(1)	-5(1)	3(1)	-10(1)
C(12)	52(2)	46(2)	40(1)	6(1)	4(1)	-5(1)
C(13)	38(1)	33(1)	37(1)	-4(1)	4(1)	-6(1)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for mo_d8v17224_0m.

	x	y	z	U(eq)
H(3)	-1776	5856	8353	77
H(3A)	249	5607	3165	54
H(4)	-2613	6308	2649	69
H(5)	-3427	7060	4385	76
H(6)	-1402	7121	6639	61
H(9A)	2954	7331	7982	51
H(9B)	916	7189	8741	51
H(10A)	5080	6813	9900	57
H(10B)	3745	7370	10559	57
H(11A)	1331	6577	11212	57
H(11B)	3623	6386	11931	57
H(12A)	3935	5615	10057	56
H(12B)	1923	5445	10826	56
H(13)	1125	5391	8245	43
H(1)	3150(40)	5243(12)	4850(30)	43(7)

Table 6. Torsion angles [°] for mo_d8v17224_0m.

C(8)-O(2)-C(1)-O(1)	-158.4(2)
C(8)-O(2)-C(1)-N(1)	23.3(3)
C(2)-N(1)-C(1)-O(1)	-167.1(2)
C(2)-N(1)-C(1)-O(2)	11.2(3)
C(1)-N(1)-C(2)-C(3)	159.5(2)
C(1)-N(1)-C(2)-C(7)	-20.0(3)
C(7)-C(2)-C(3)-C(4)	0.8(4)
N(1)-C(2)-C(3)-C(4)	-178.7(2)
C(2)-C(3)-C(4)-C(5)	-0.2(4)
C(3)-C(4)-C(5)-C(6)	-0.1(5)
C(4)-C(5)-C(6)-C(7)	-0.2(4)
C(5)-C(6)-C(7)-C(2)	0.8(4)
C(5)-C(6)-C(7)-C(8)	-175.2(2)
C(3)-C(2)-C(7)-C(6)	-1.1(3)
N(1)-C(2)-C(7)-C(6)	178.4(2)
C(3)-C(2)-C(7)-C(8)	175.3(2)
N(1)-C(2)-C(7)-C(8)	-5.3(3)
C(1)-O(2)-C(8)-C(7)	-44.2(2)
C(1)-O(2)-C(8)-C(9)	-167.01(18)
C(1)-O(2)-C(8)-C(13)	76.0(2)
C(6)-C(7)-C(8)-O(2)	-150.6(2)
C(2)-C(7)-C(8)-O(2)	33.4(3)
C(6)-C(7)-C(8)-C(9)	-34.7(3)
C(2)-C(7)-C(8)-C(9)	149.3(2)
C(6)-C(7)-C(8)-C(13)	92.2(3)
C(2)-C(7)-C(8)-C(13)	-83.9(2)
O(2)-C(8)-C(9)-C(10)	-61.4(2)
C(7)-C(8)-C(9)-C(10)	-179.69(19)
C(13)-C(8)-C(9)-C(10)	53.0(3)
C(8)-C(9)-C(10)-C(11)	-56.4(3)
C(9)-C(10)-C(11)-C(12)	58.1(3)
C(10)-C(11)-C(12)-C(13)	-58.6(3)
C(11)-C(12)-C(13)-O(3)	-63.8(2)
C(11)-C(12)-C(13)-C(8)	56.0(3)
O(2)-C(8)-C(13)-O(3)	179.22(16)
C(7)-C(8)-C(13)-O(3)	-62.7(2)
C(9)-C(8)-C(13)-O(3)	66.6(2)
O(2)-C(8)-C(13)-C(12)	60.2(2)
C(7)-C(8)-C(13)-C(12)	178.27(18)
C(9)-C(8)-C(13)-C(12)	-52.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_d8v17224_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.88(3)	2.00(3)	2.882(2)	177(2)
O(3)-H(3)...O(1)#2	0.82	2.08	2.893(2)	172.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 x-1,y,z

References

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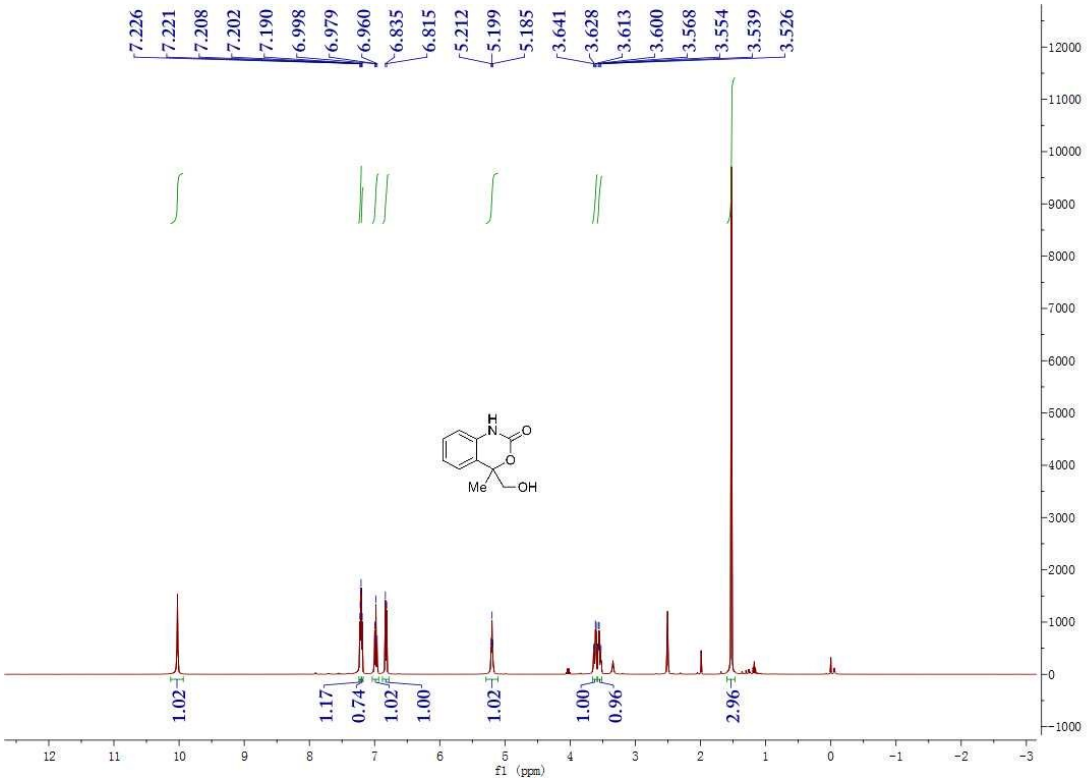
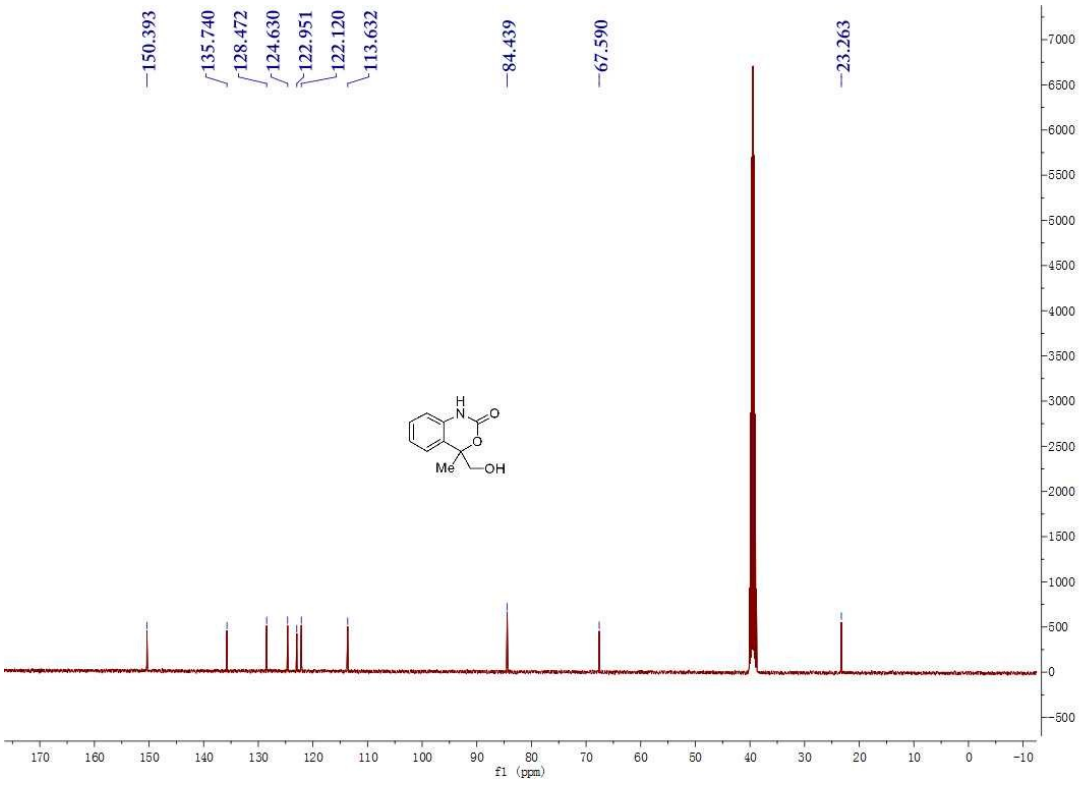
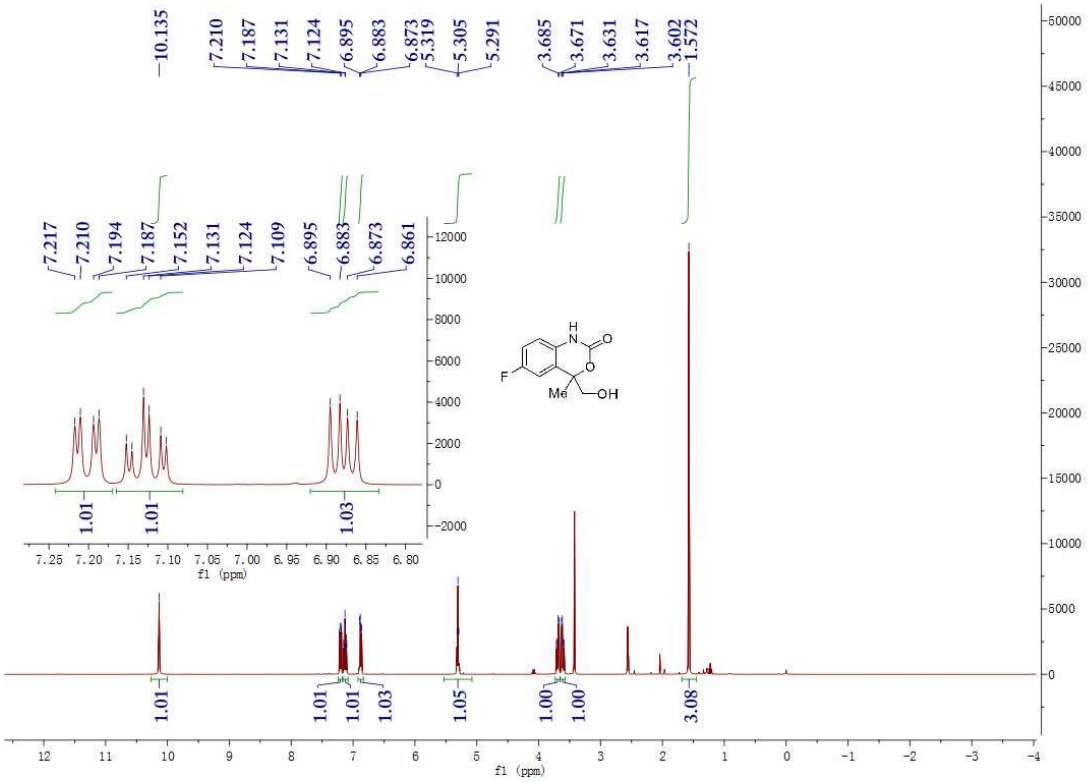
Spectral Data for the Products

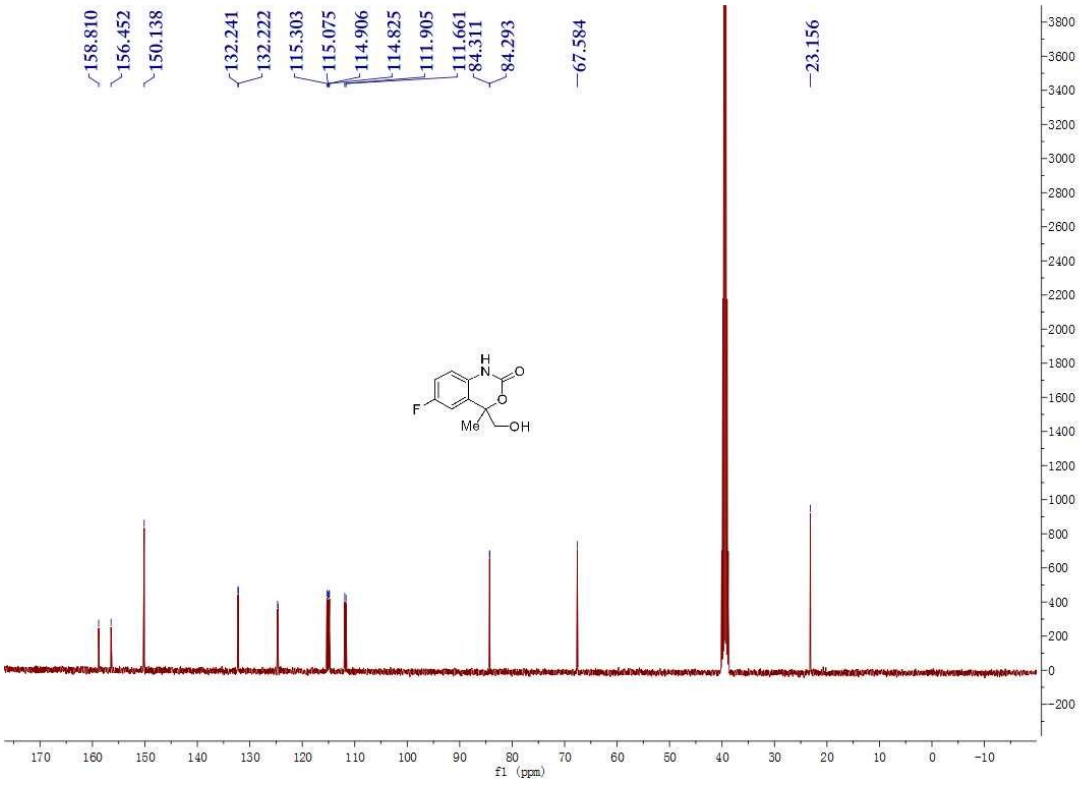
NMR spectra of 3a

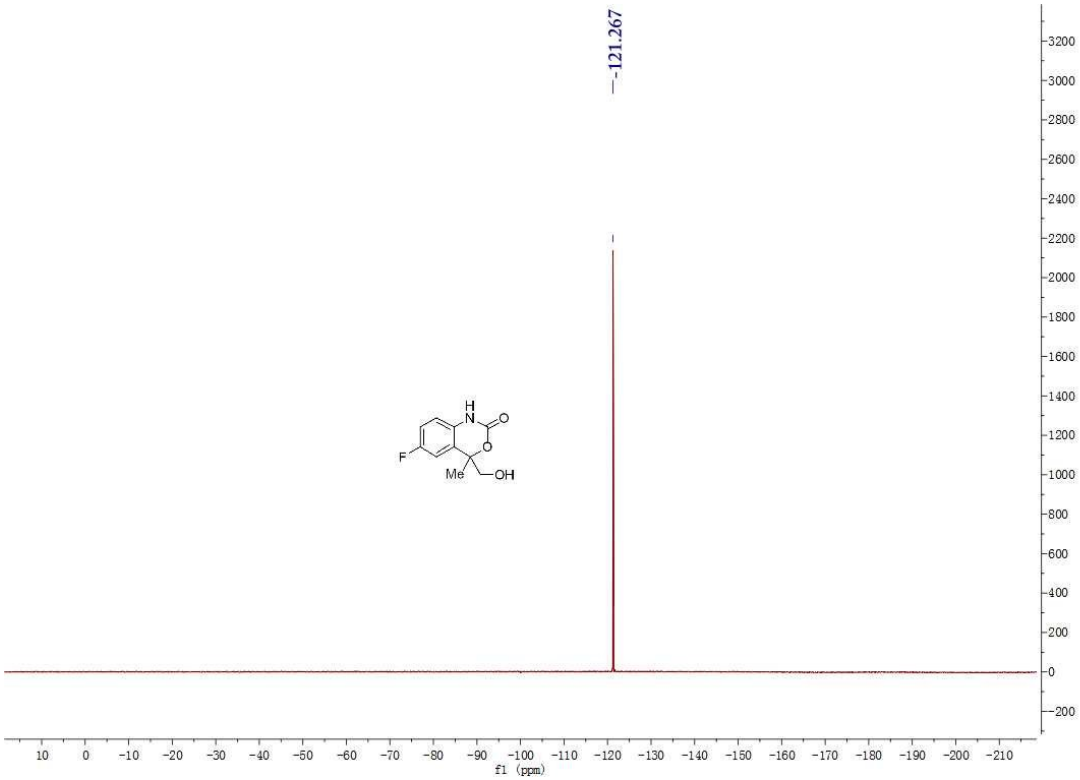




NMR spectra of 3b



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F
Me
OH
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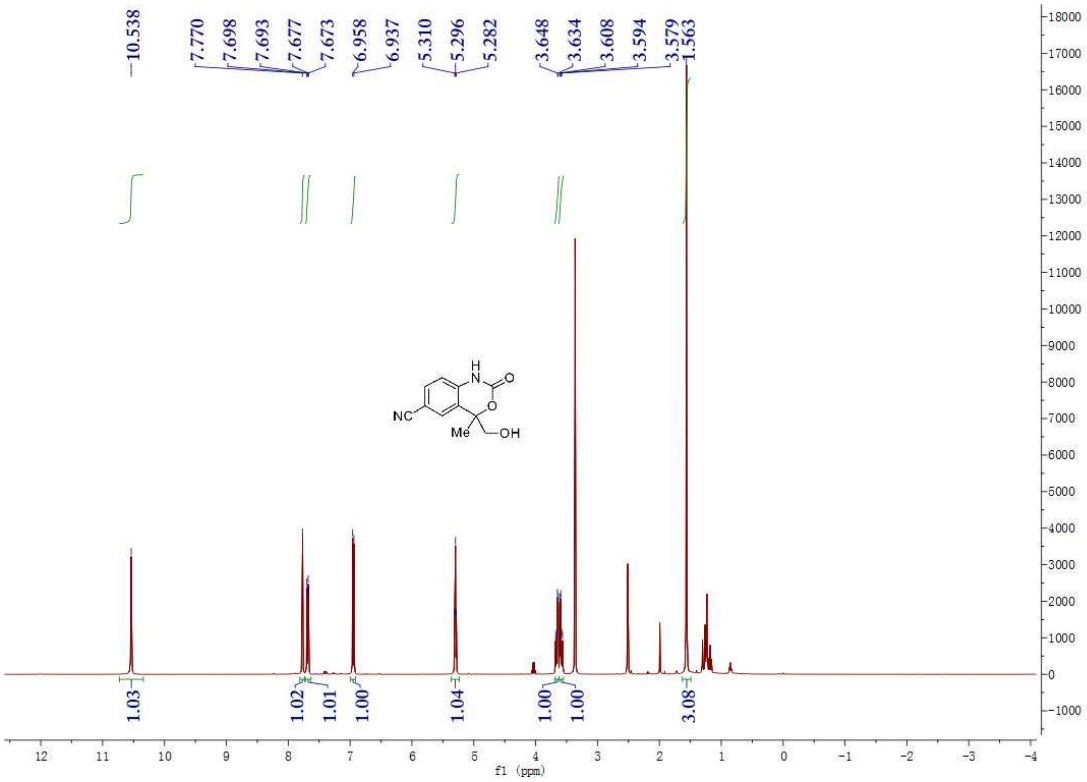
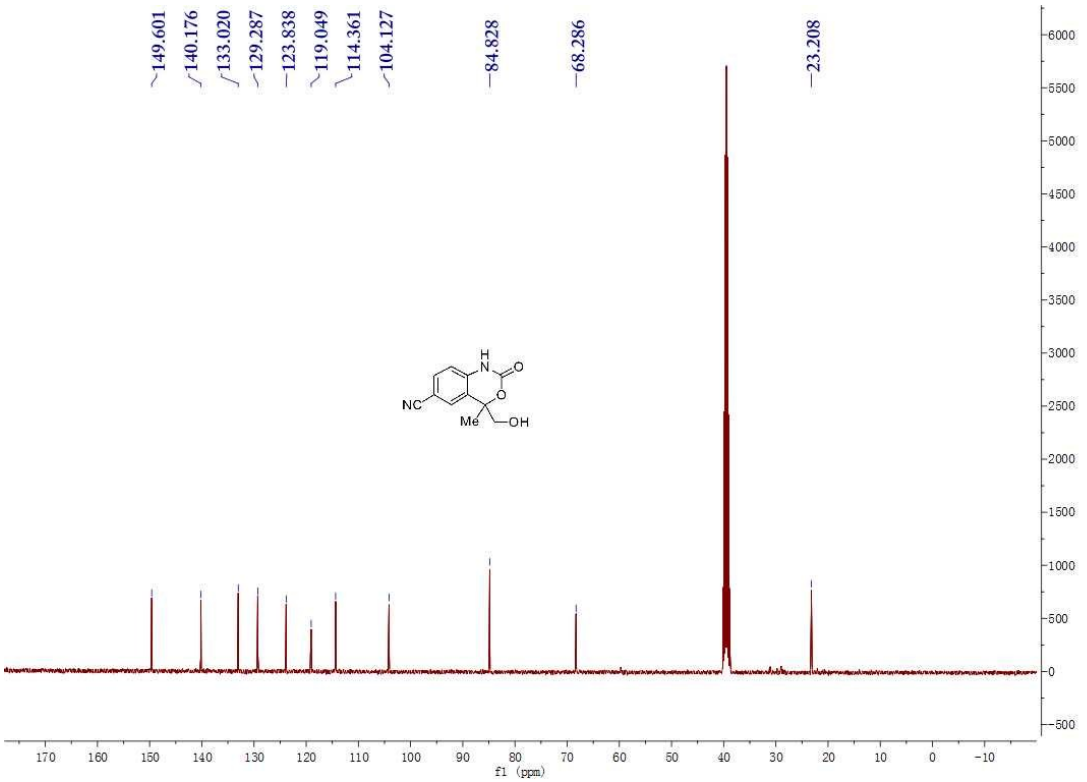
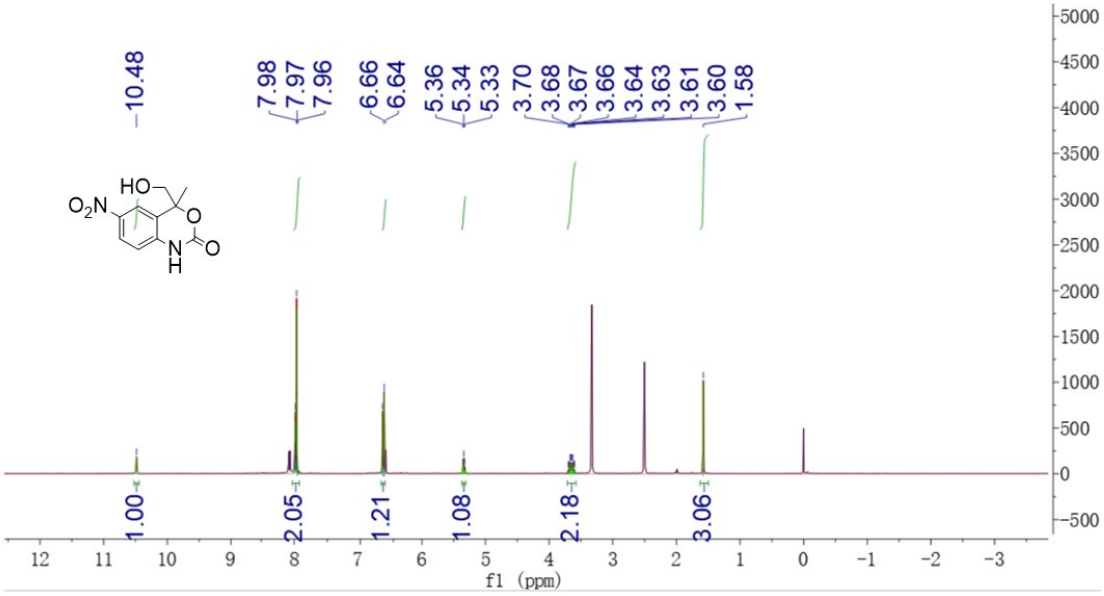
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

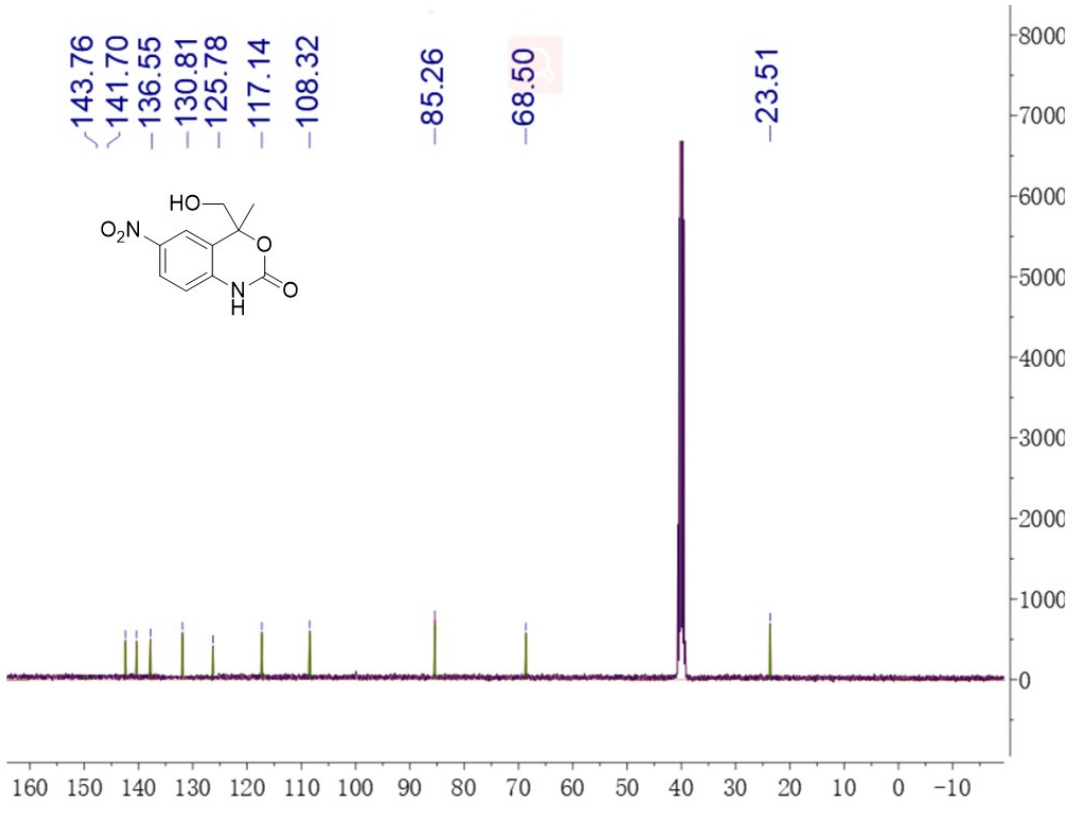
NMR spectra of 3c



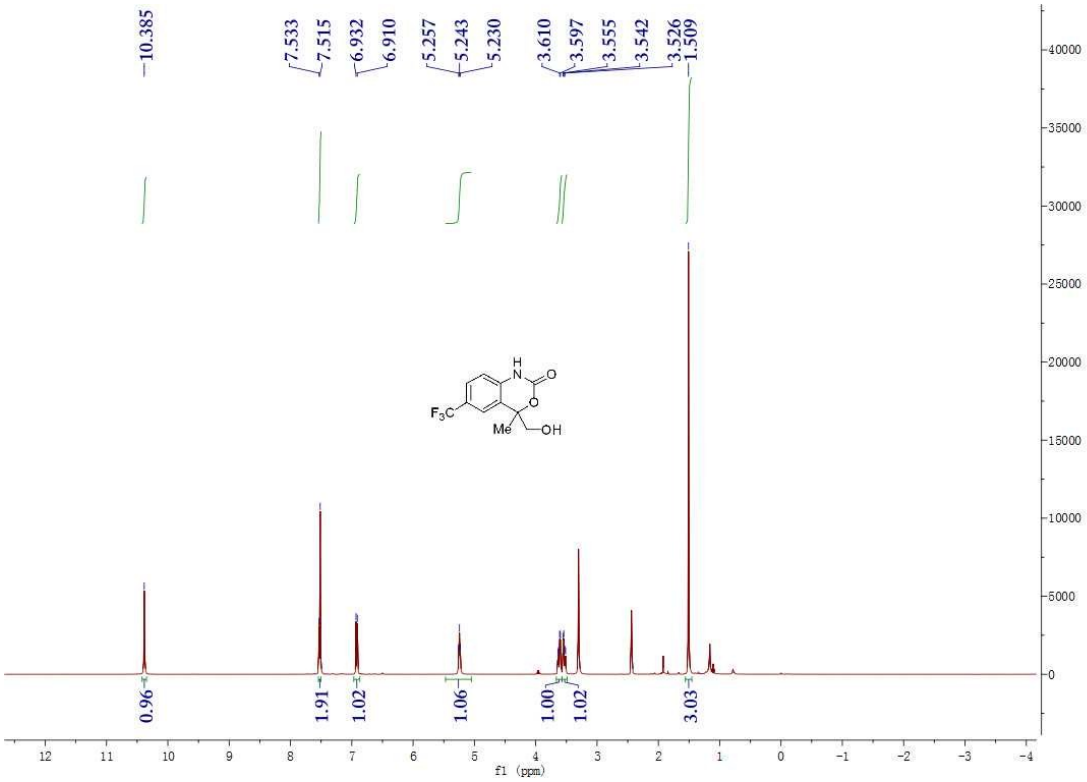


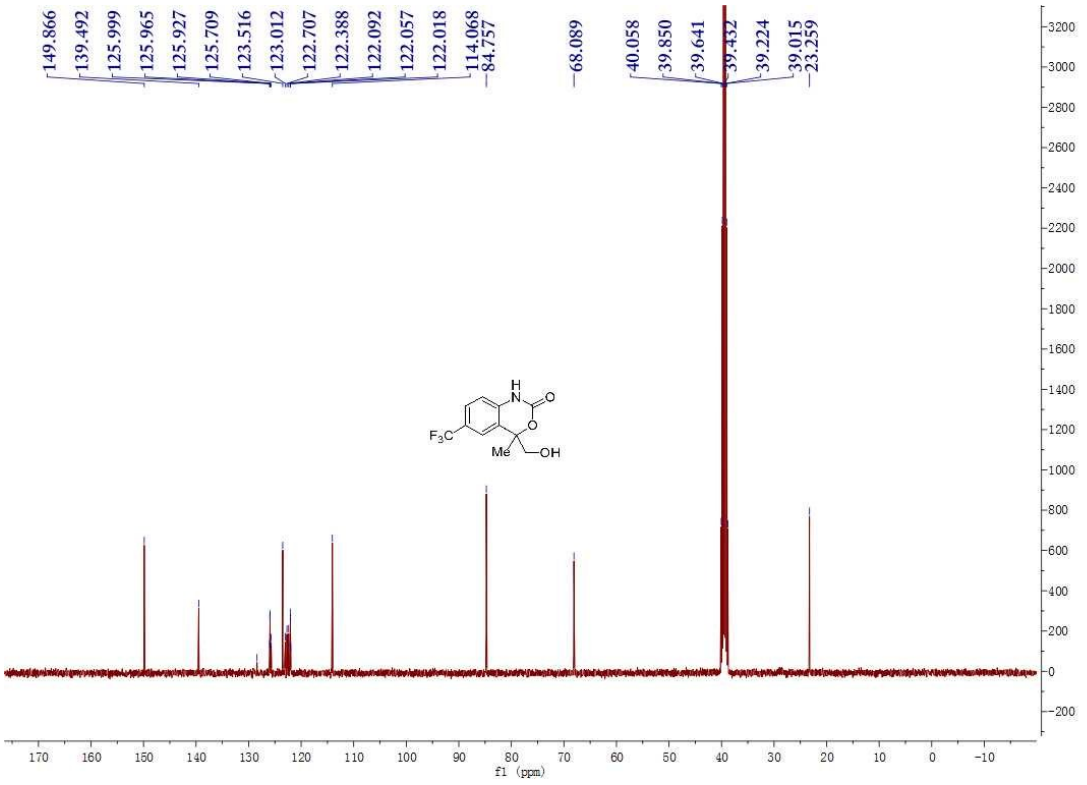
NMR spectra of 3d

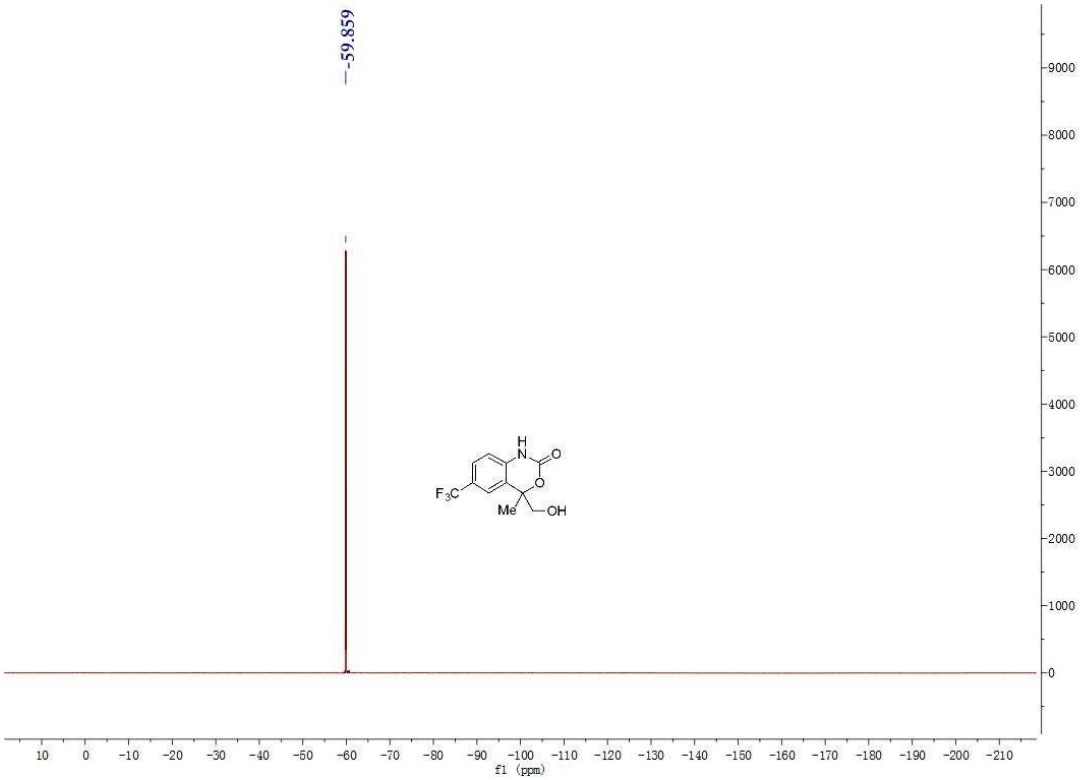




NMR spectra of 3e



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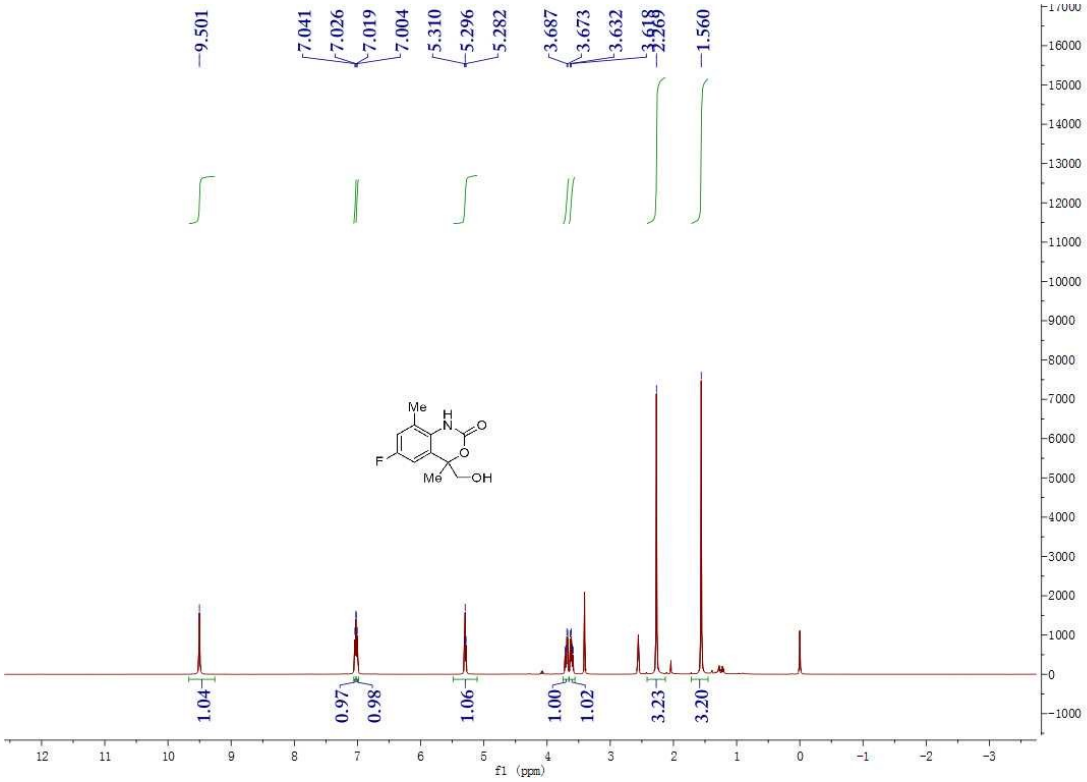
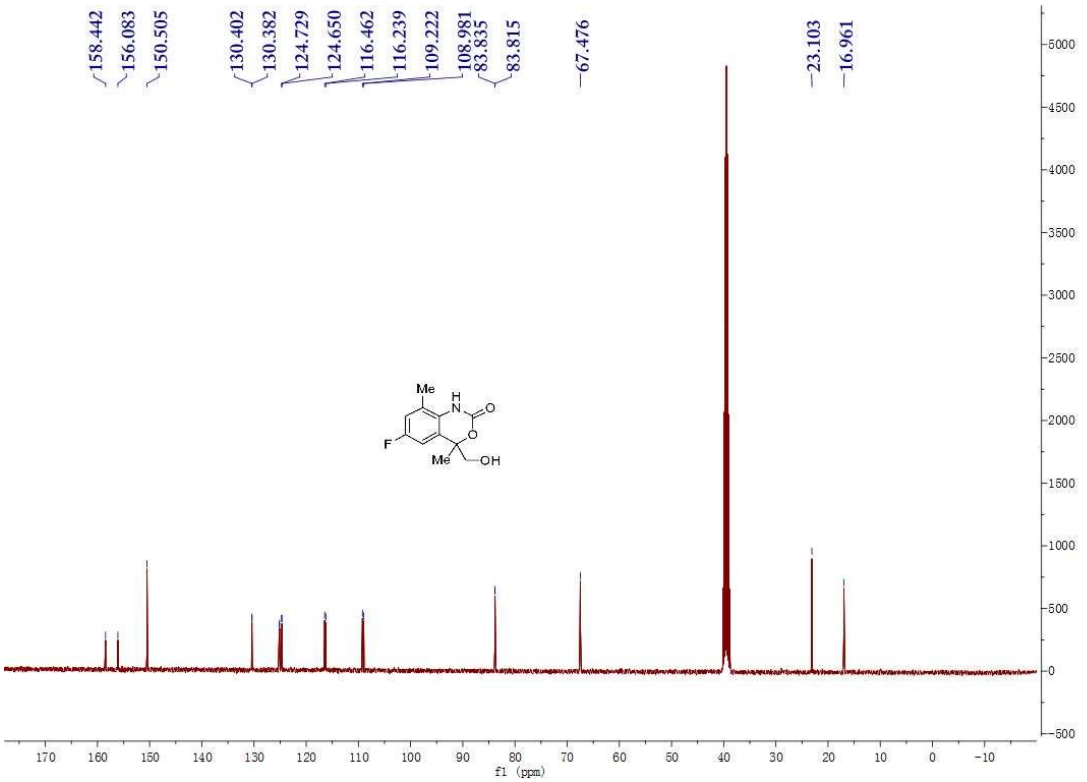
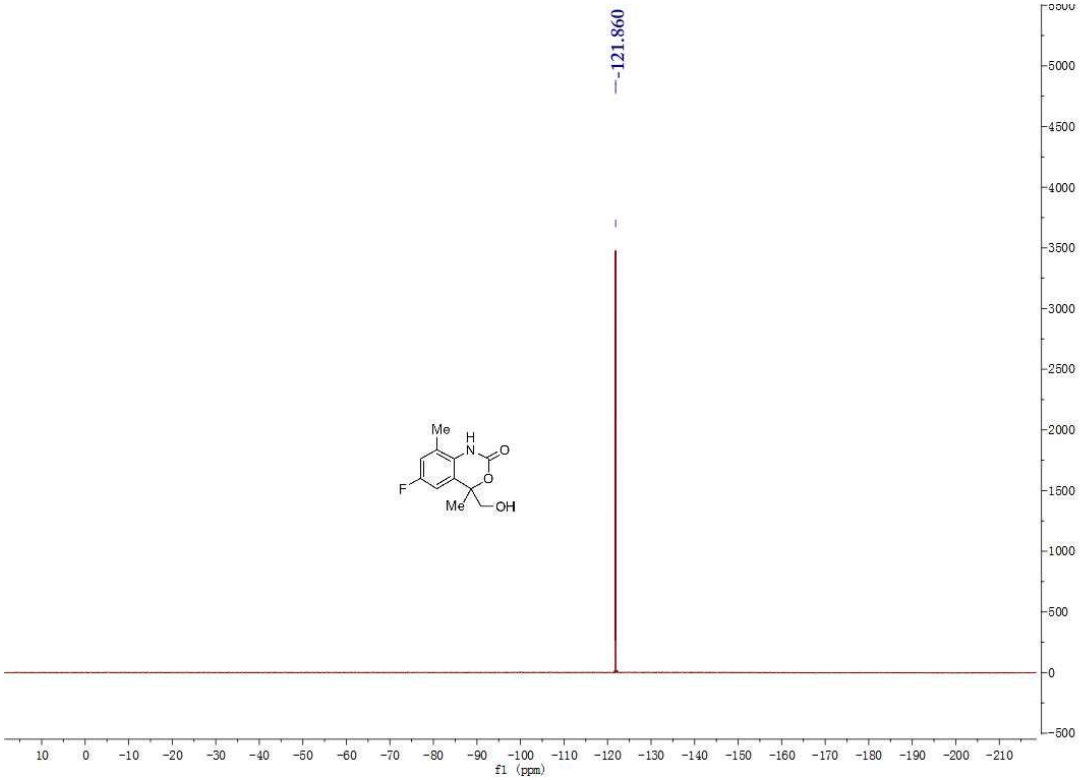
5000
4000
3000
2000
1000
0
H
N
O
O
F3C
Me
OH
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

NMR spectra of 3f



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2000
1500
1000
500
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-500
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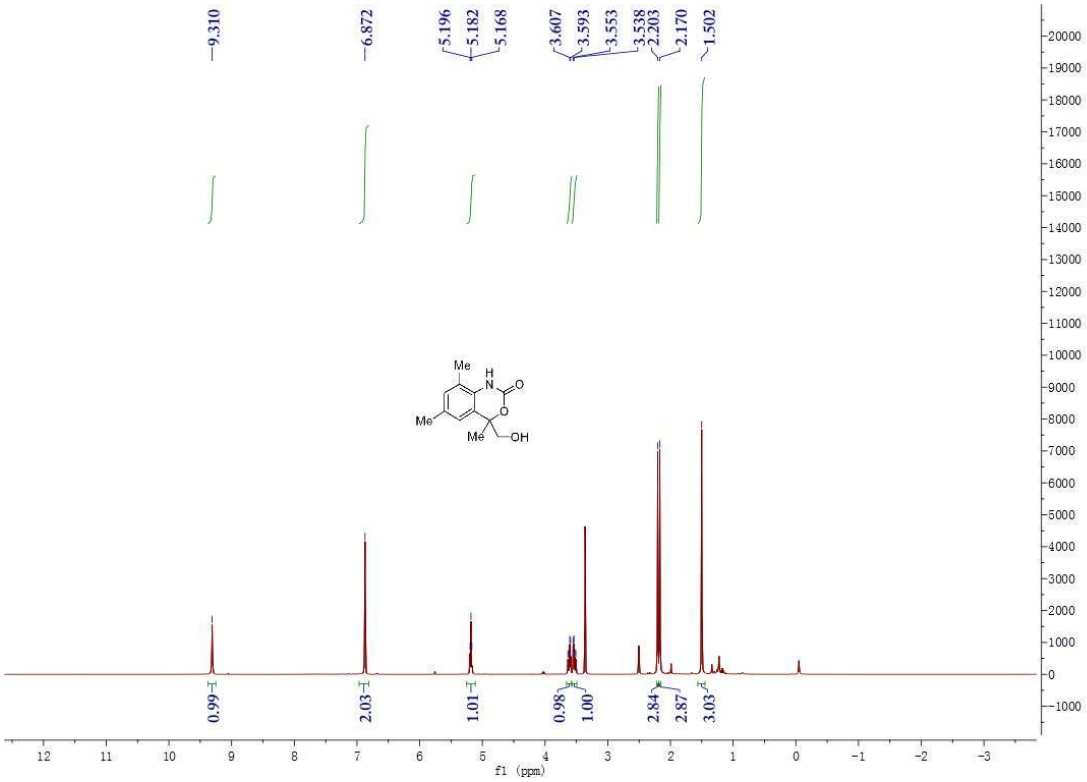
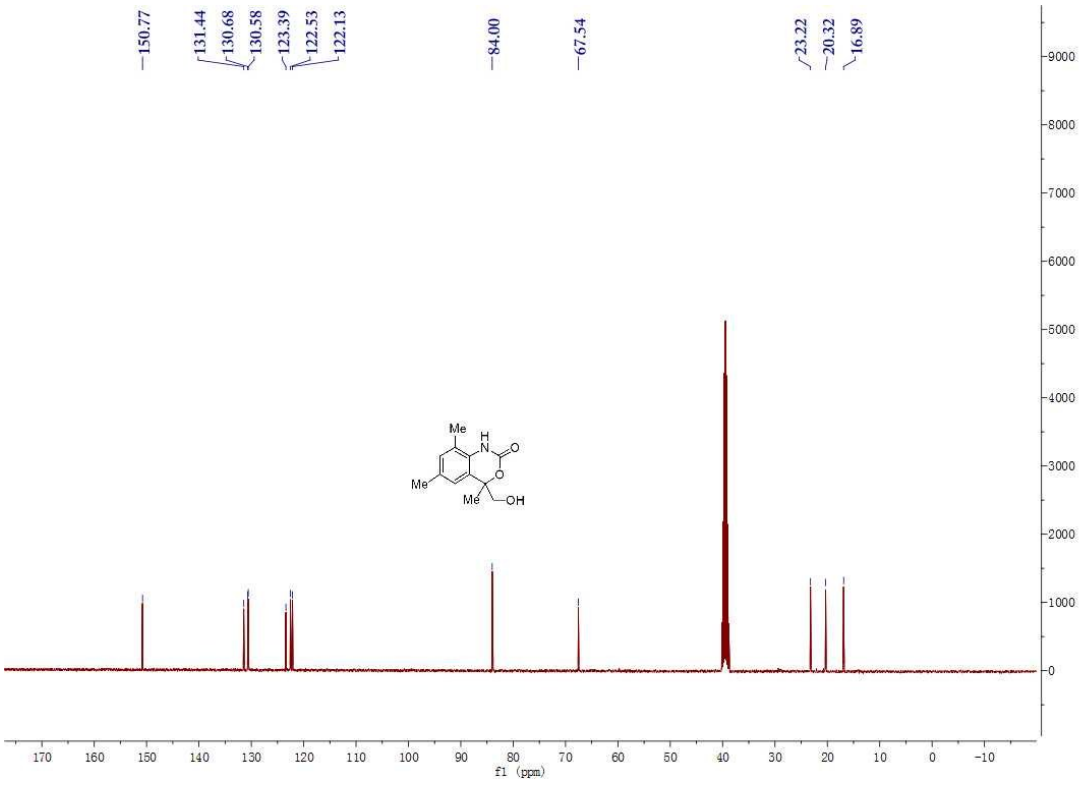
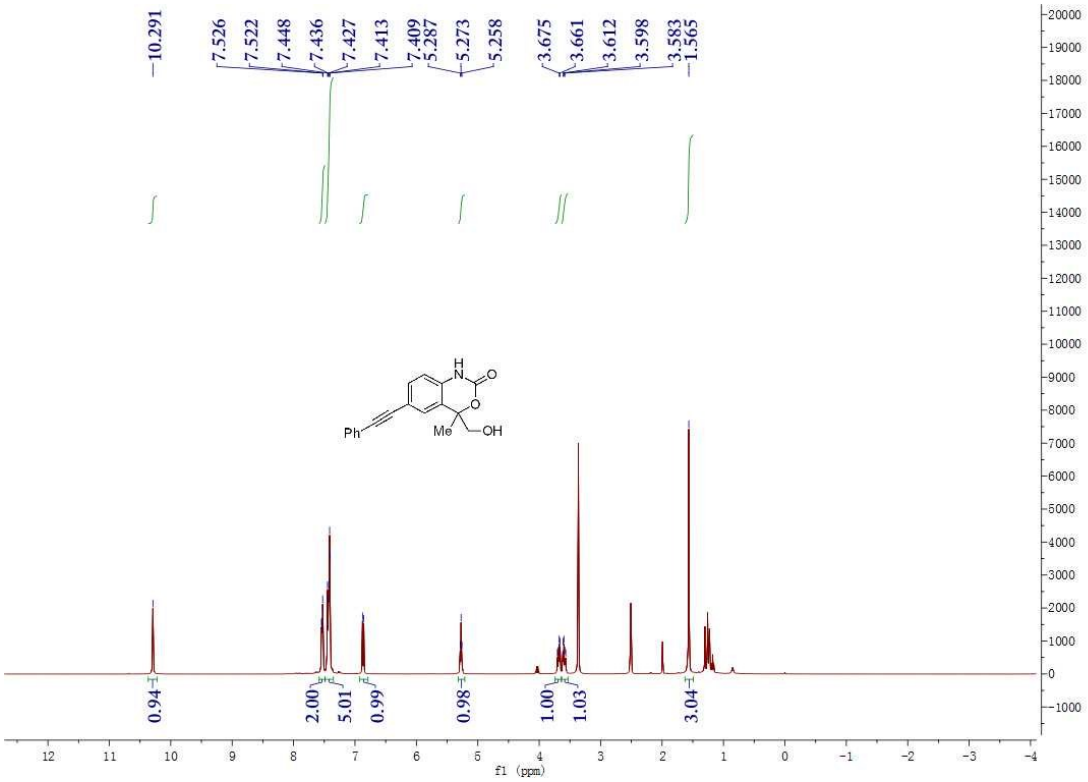
f1 (ppm)

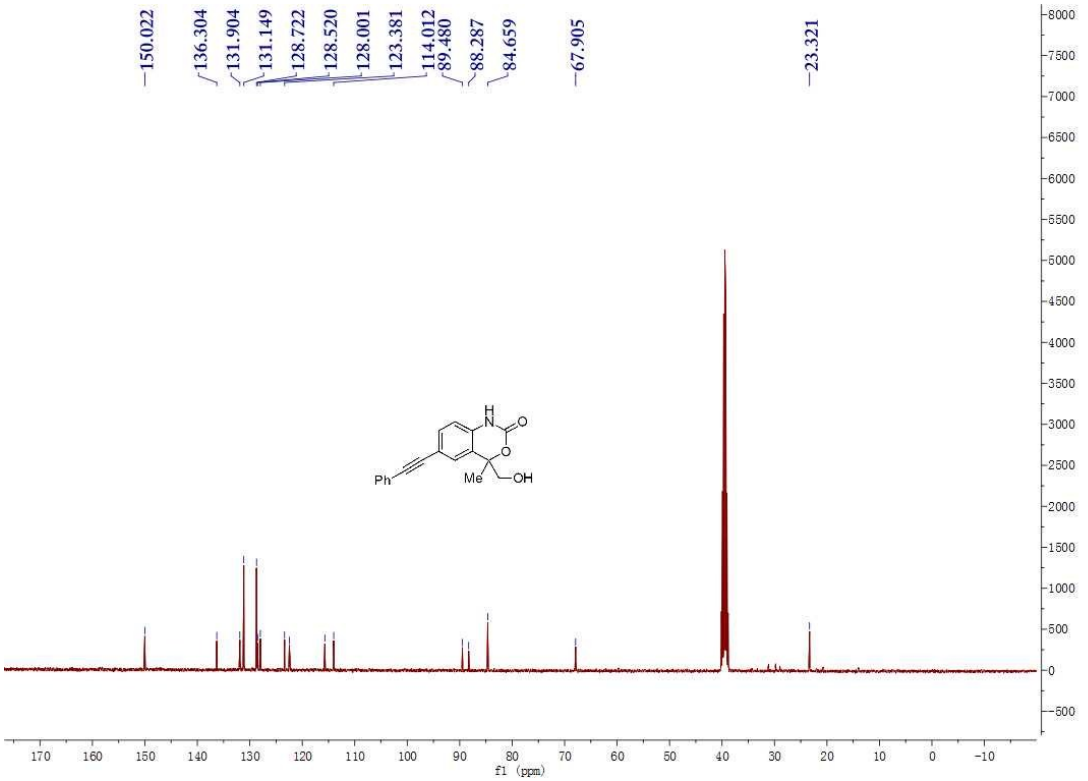
NMR spectra of 3g



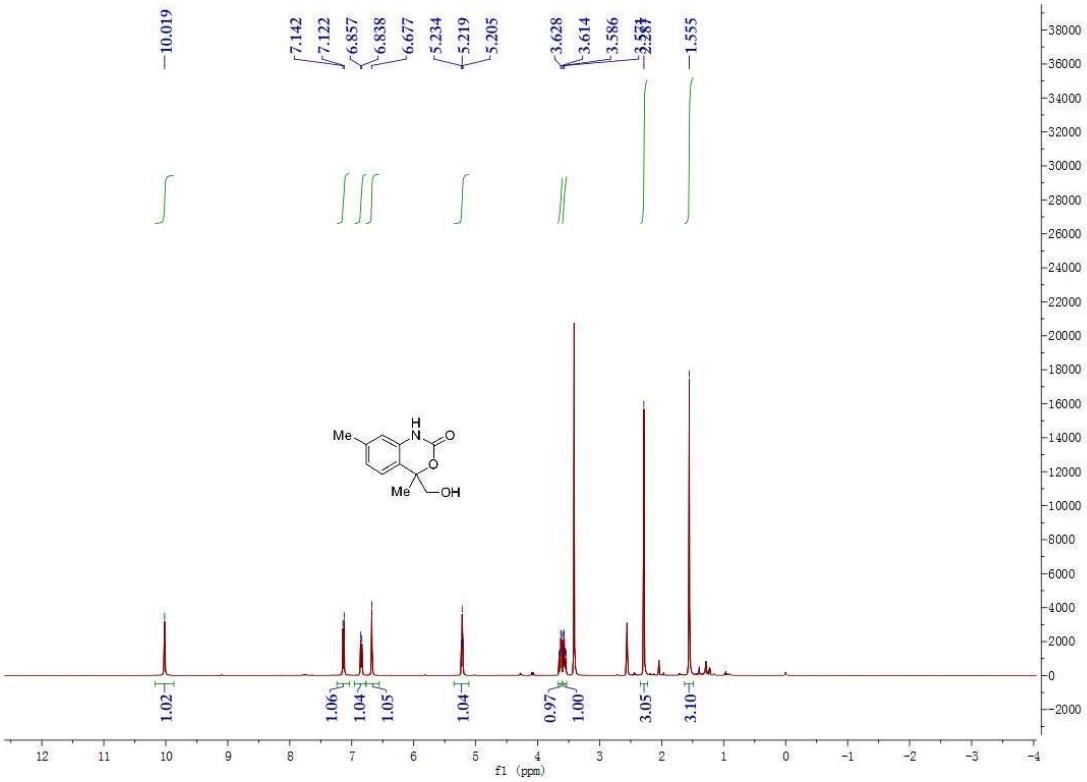


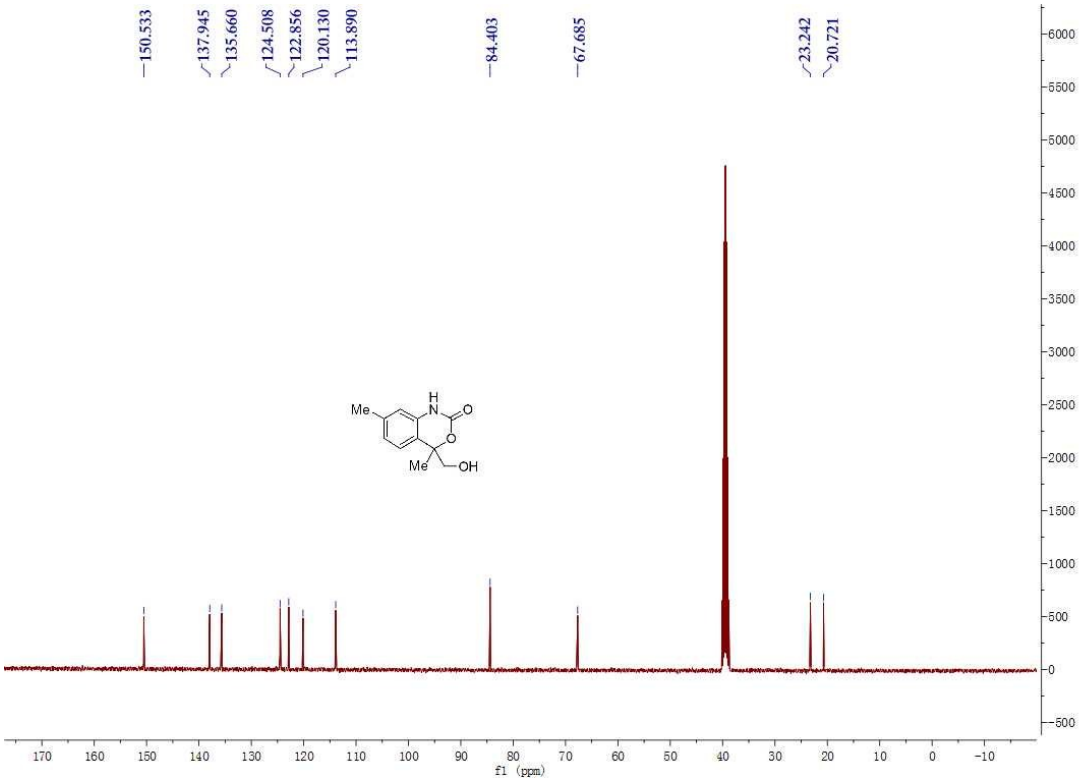
NMR spectra of 3h



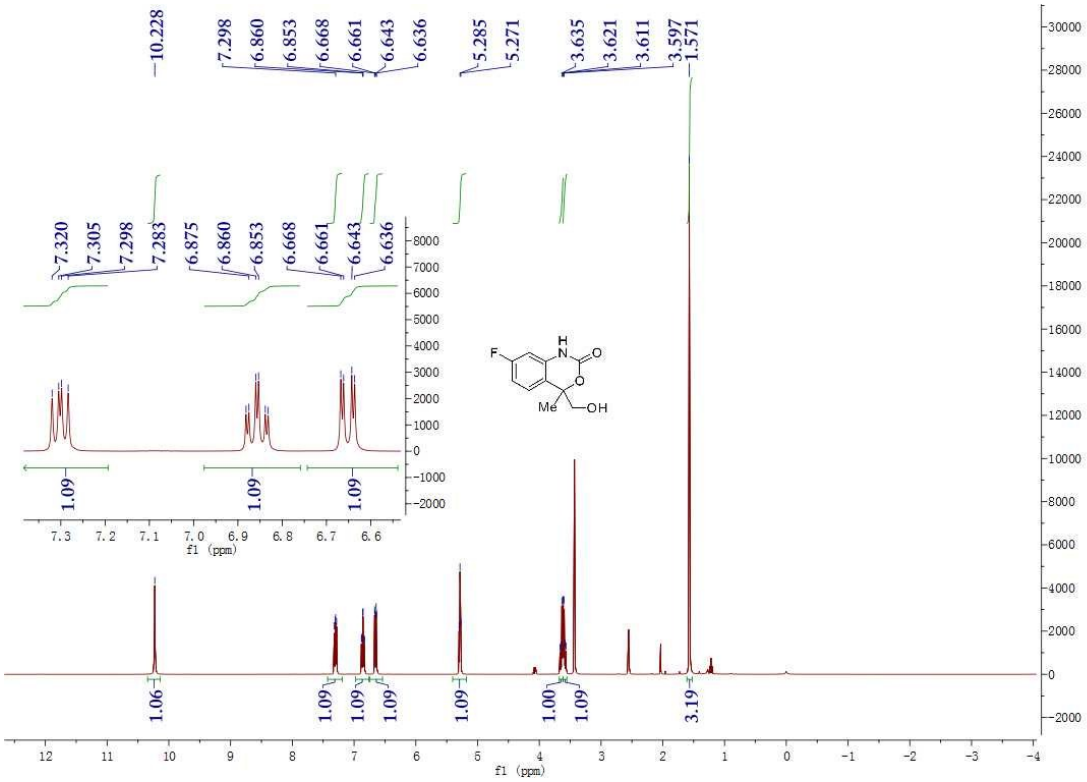


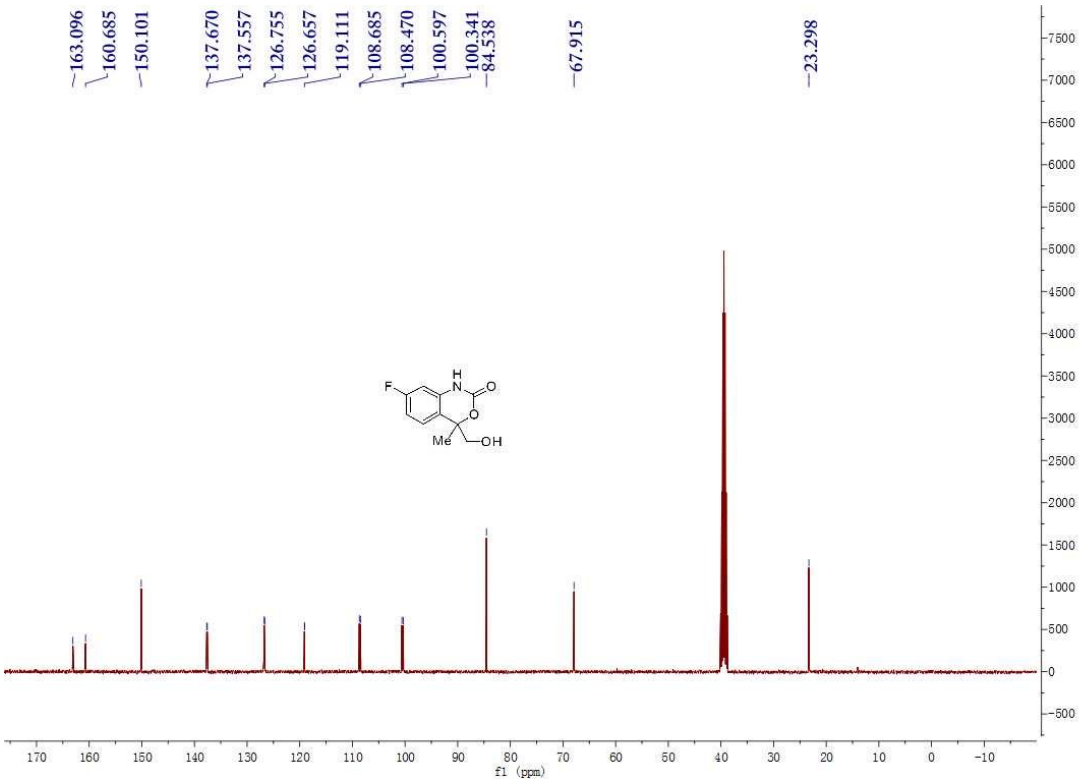
NMR spectra of 3i

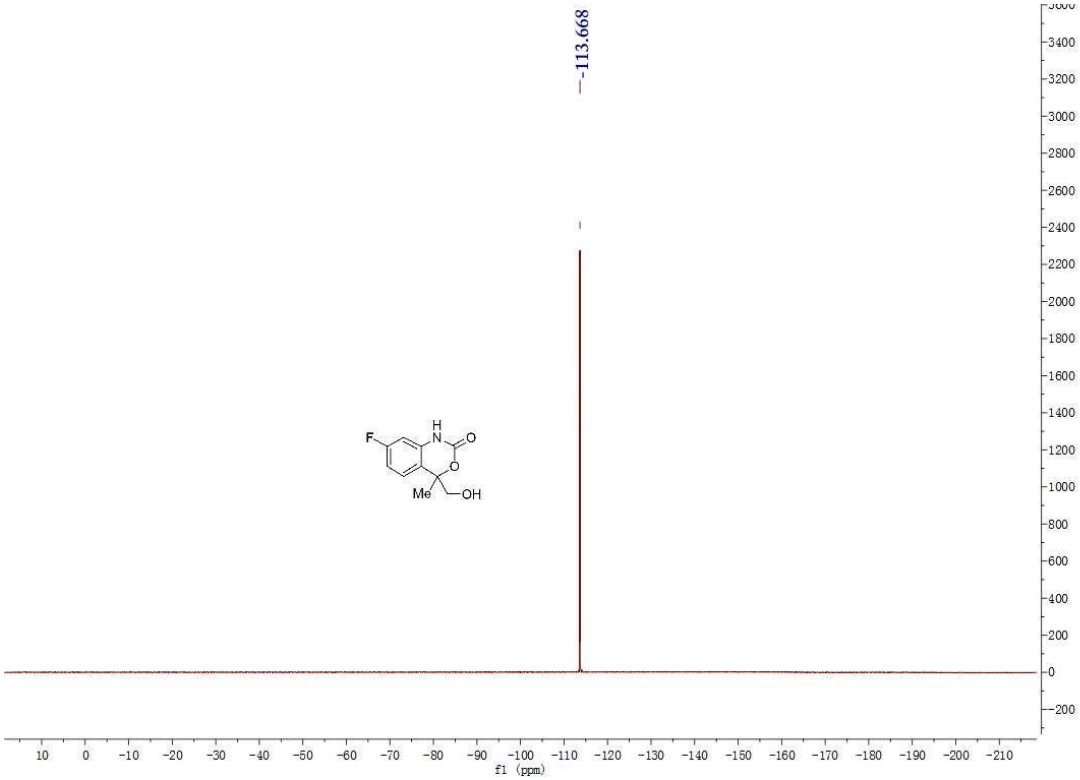




NMR spectra of 3j



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1600
1400
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1000
800
600
400
200
0
-200
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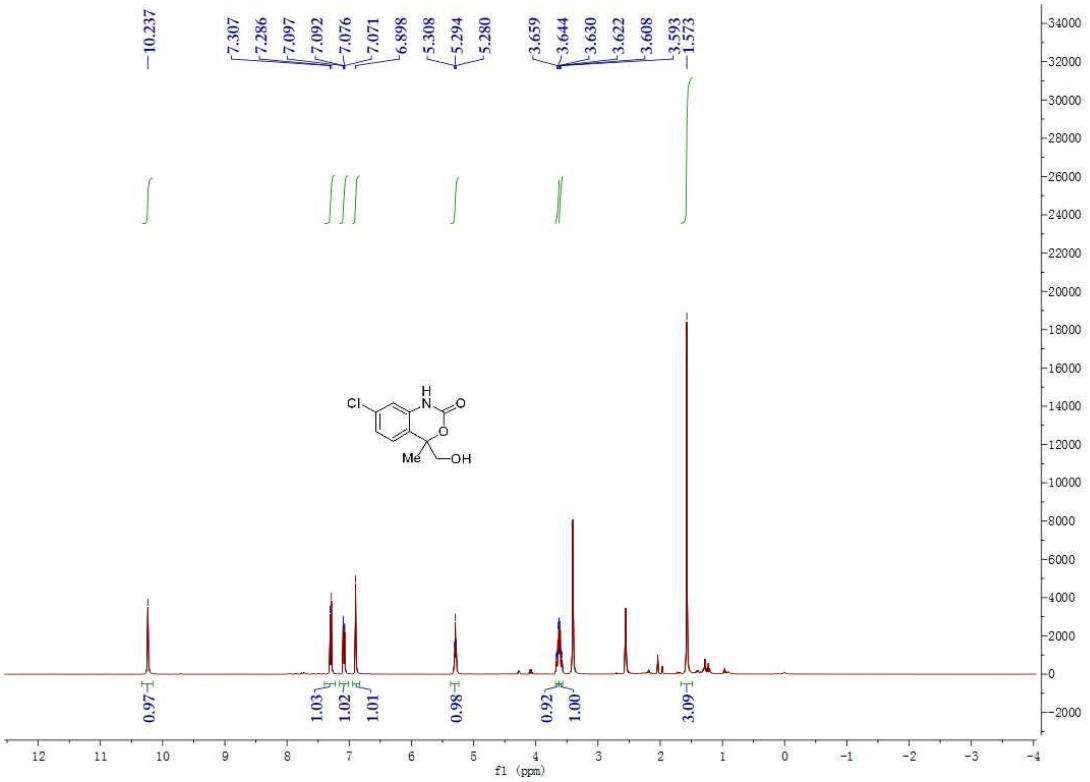
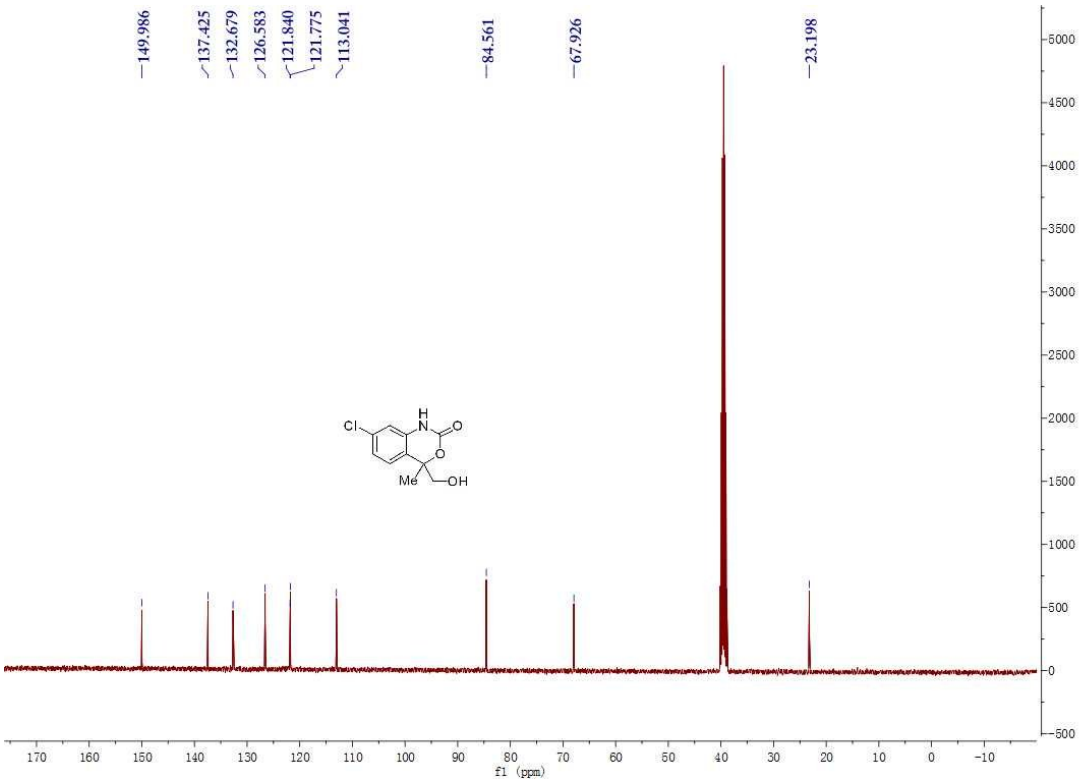
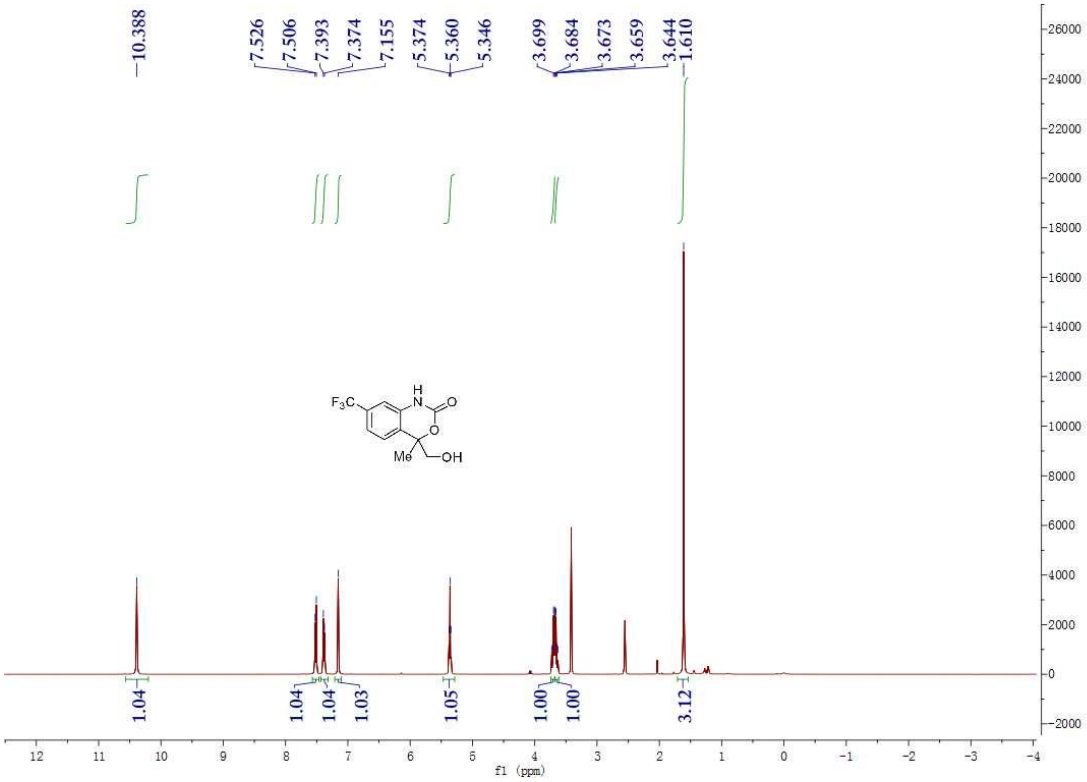
f1 (ppm)

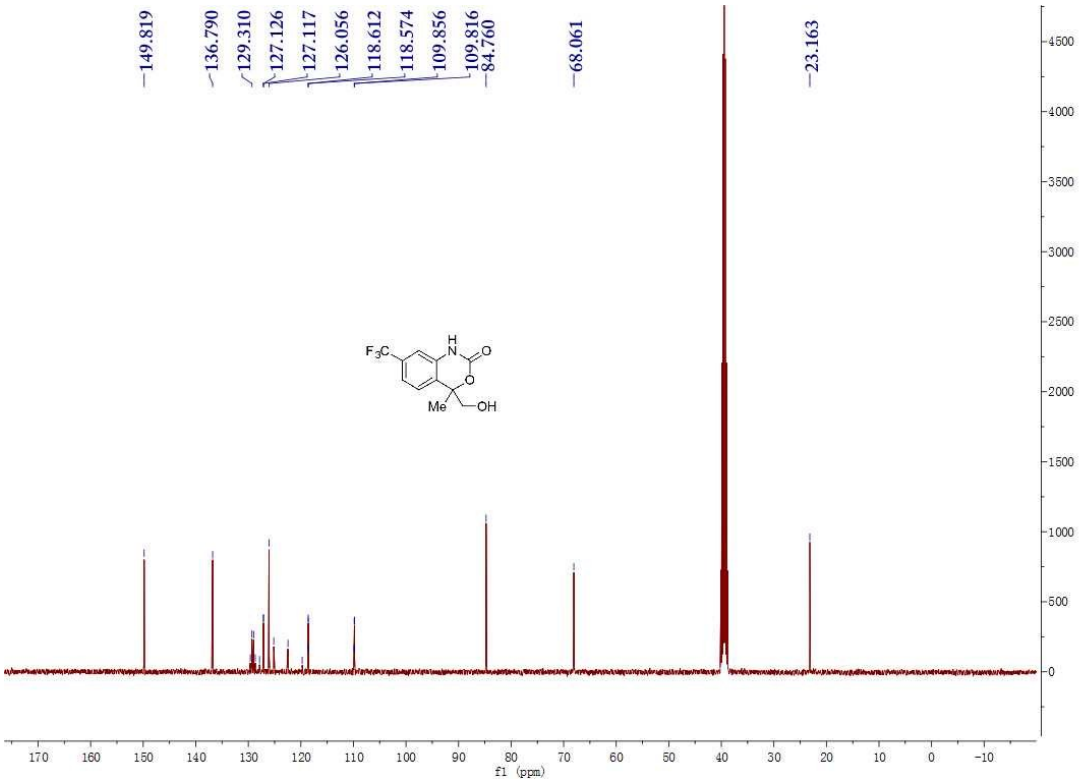
NMR spectra of 3k

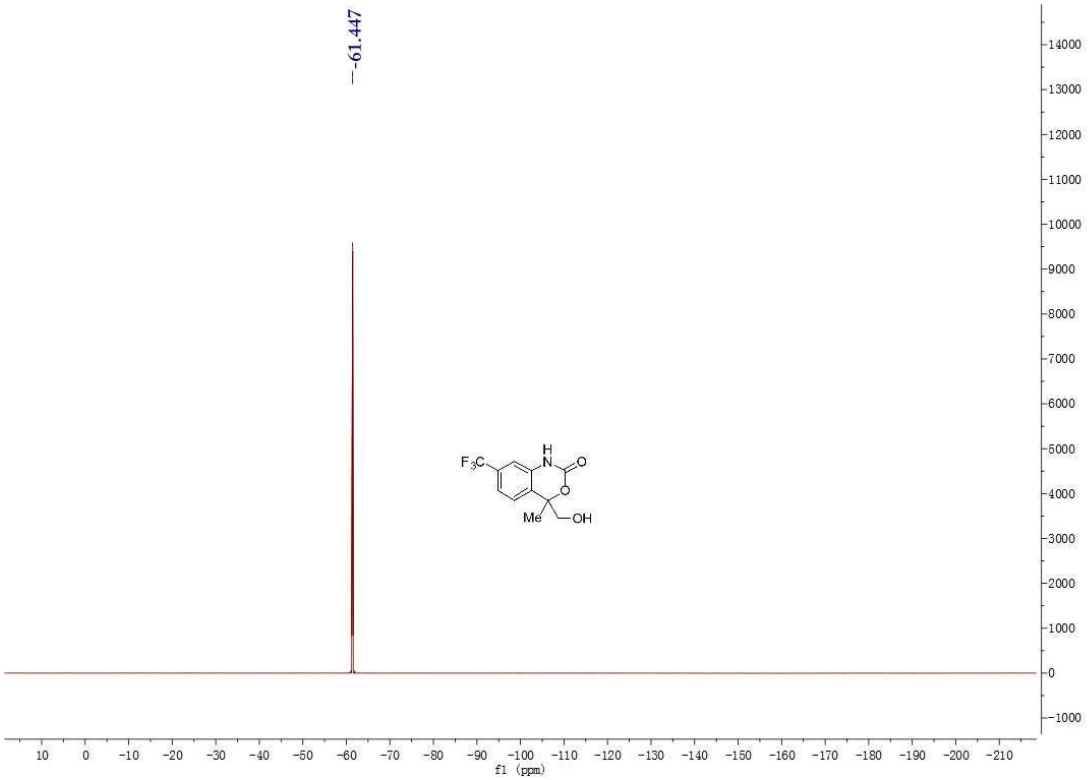




NMR spectra of 3l



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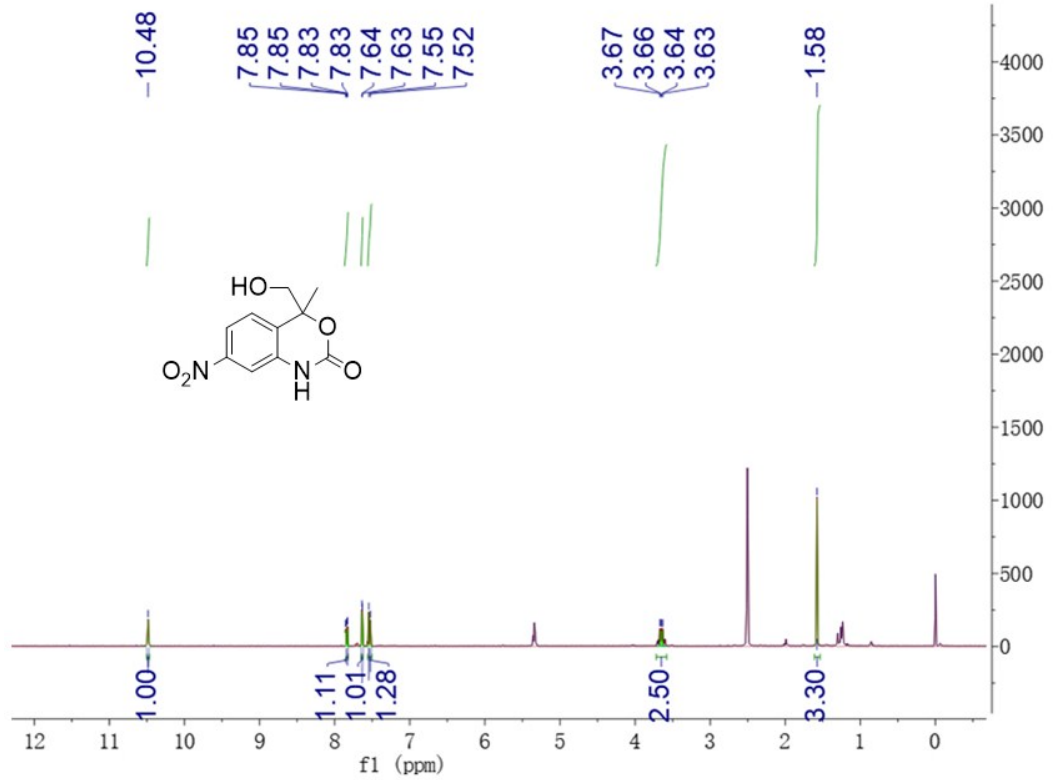
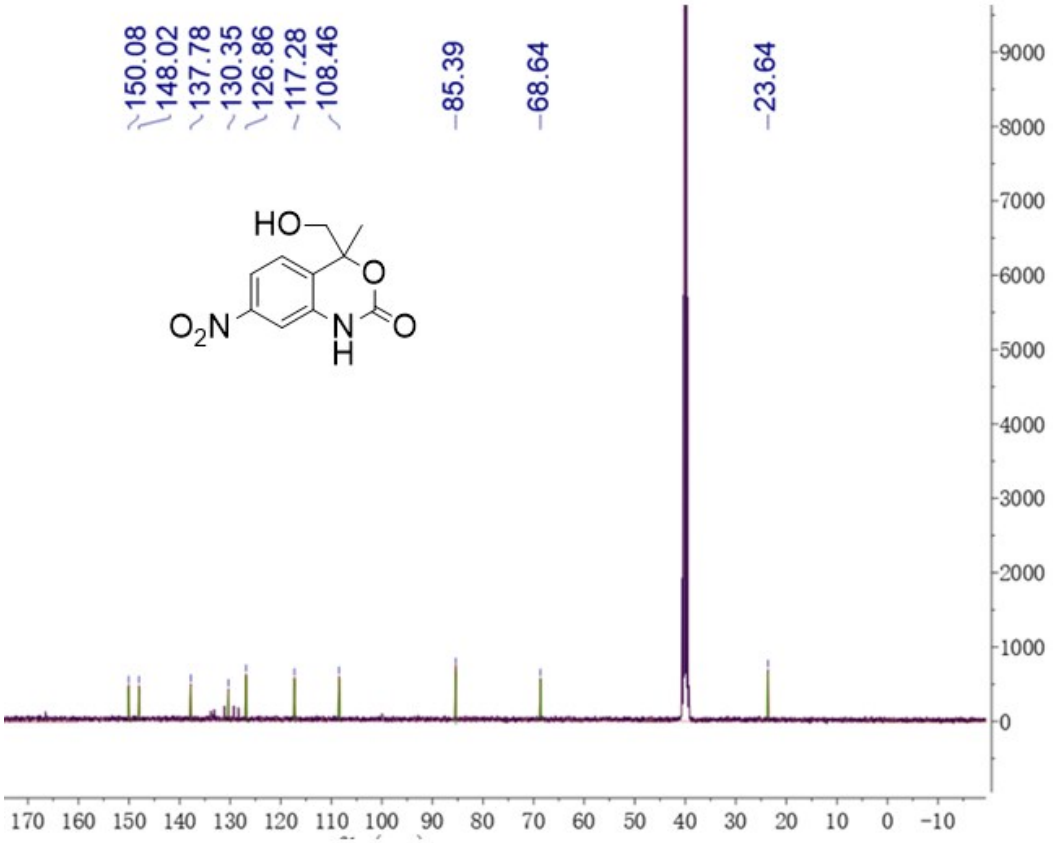
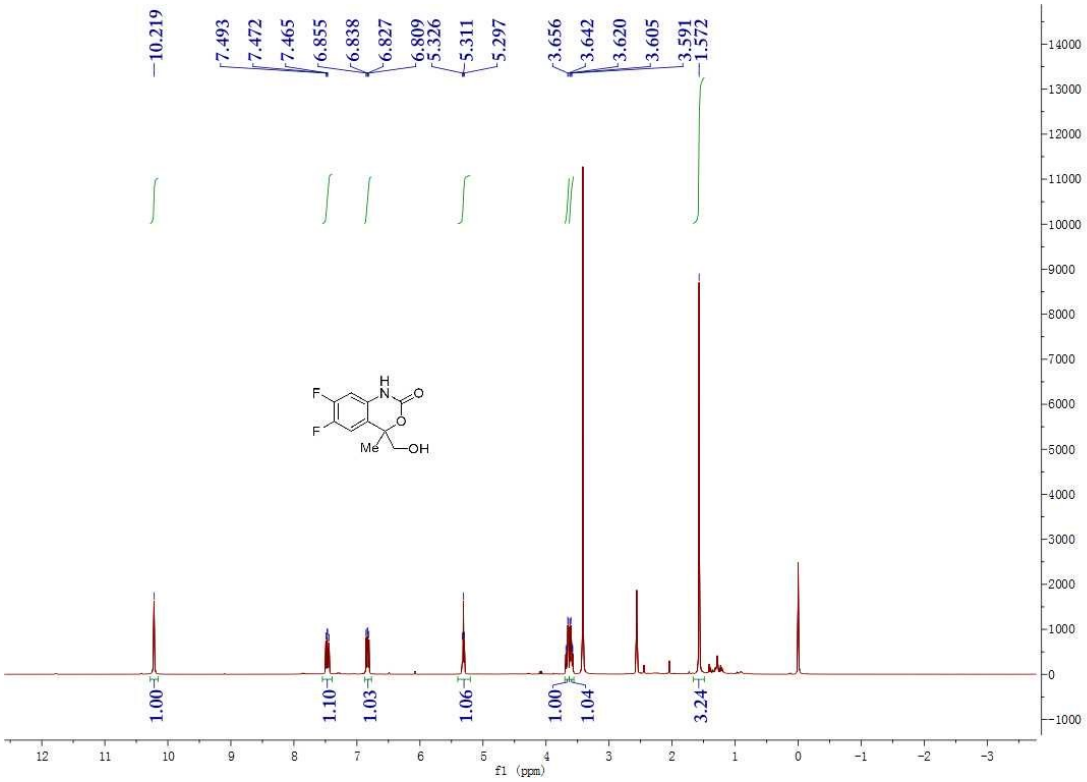
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

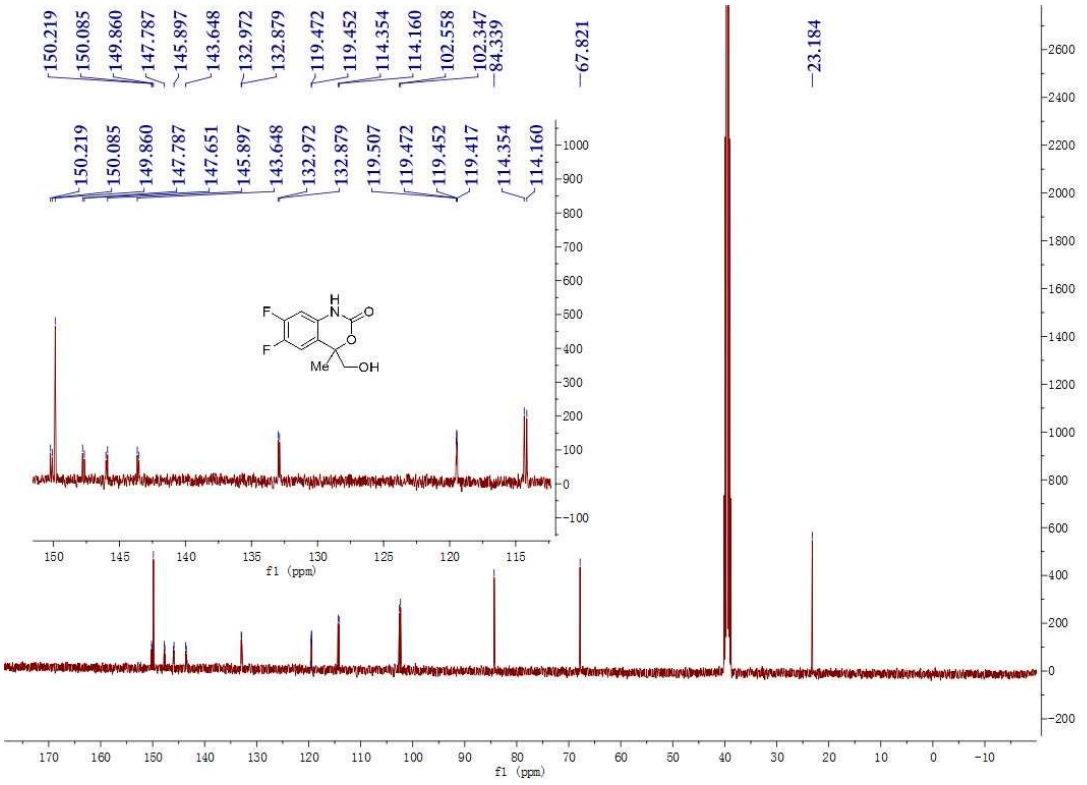
NMR spectra of 3m

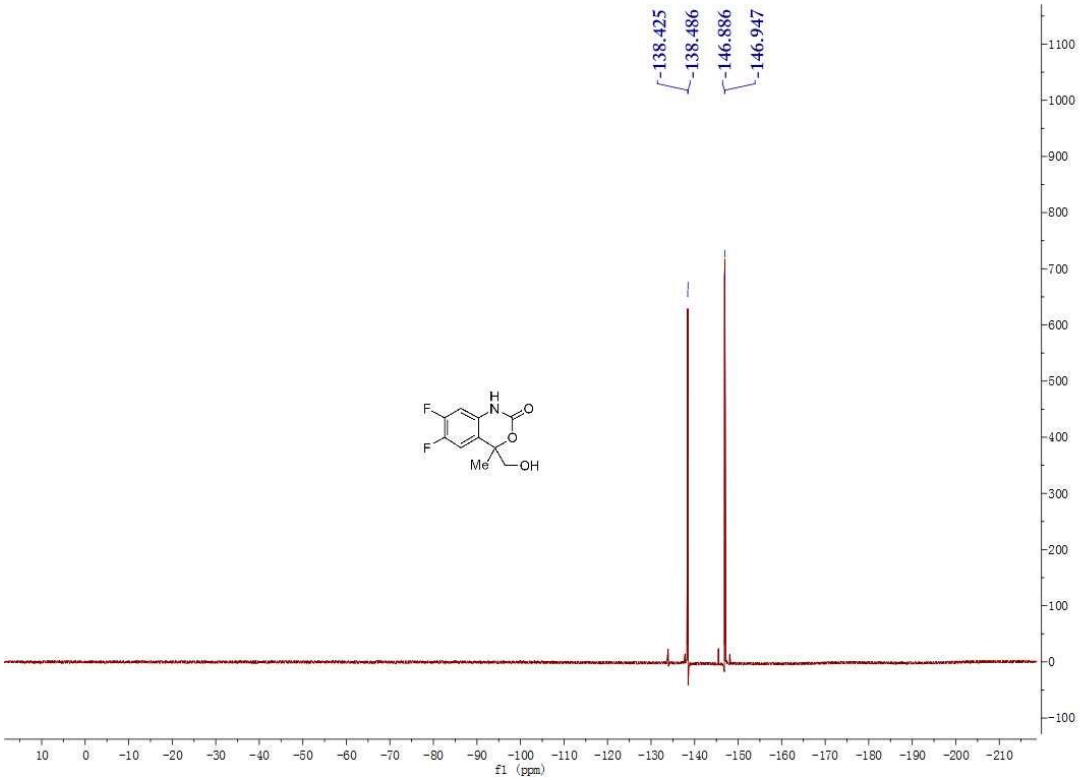




NMR spectra of 3n



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800
700
600
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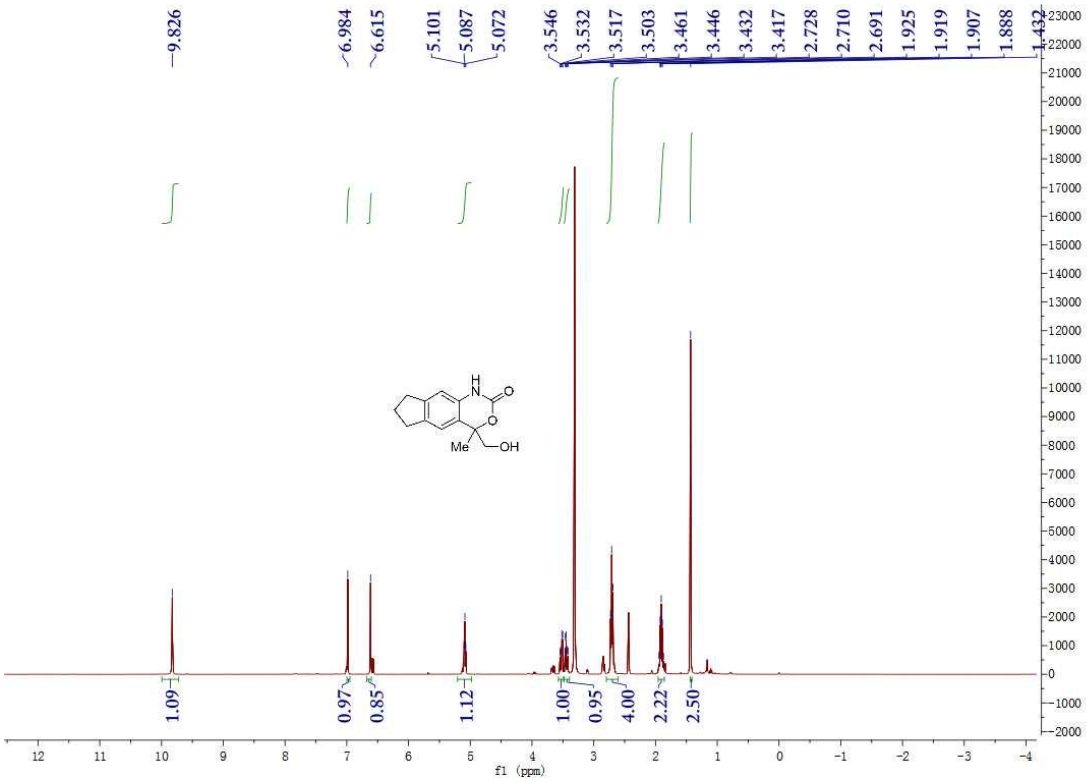
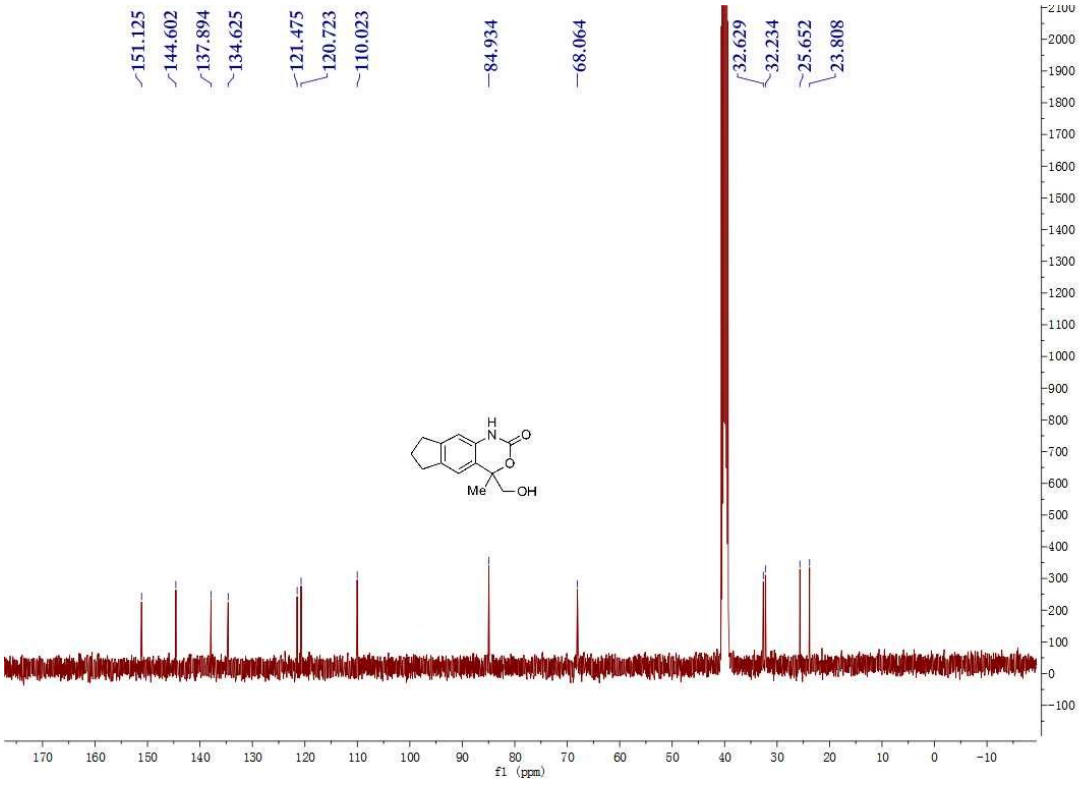
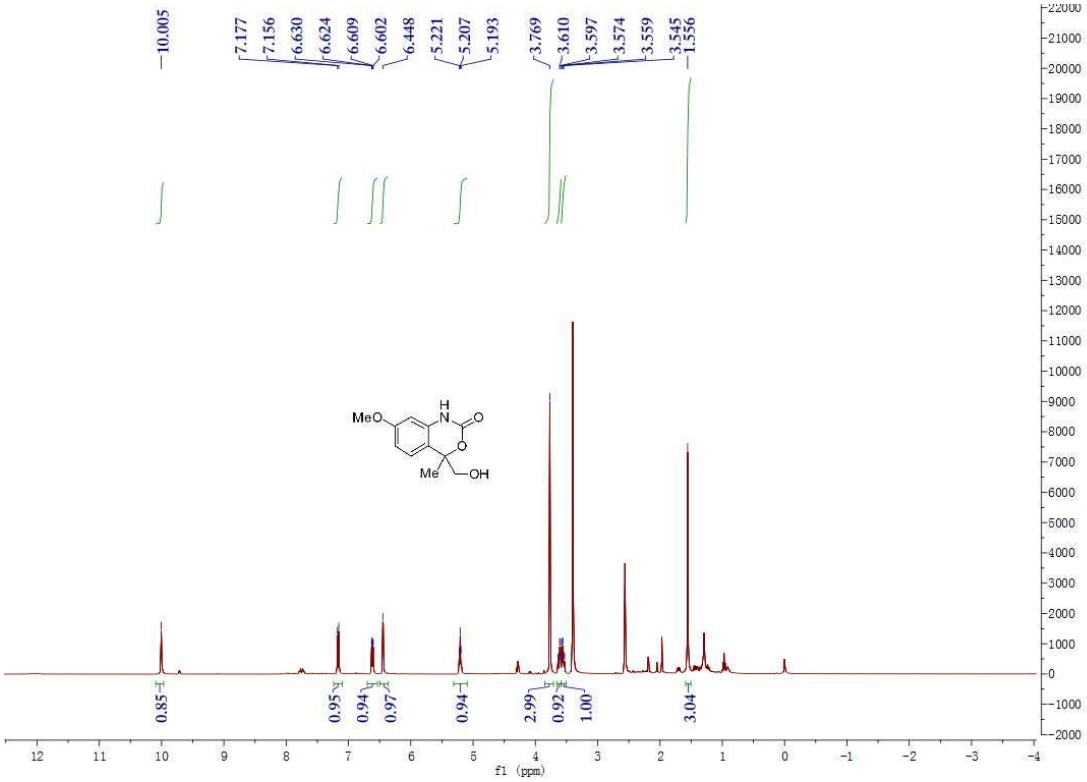
400
300
200
100
0
-100
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

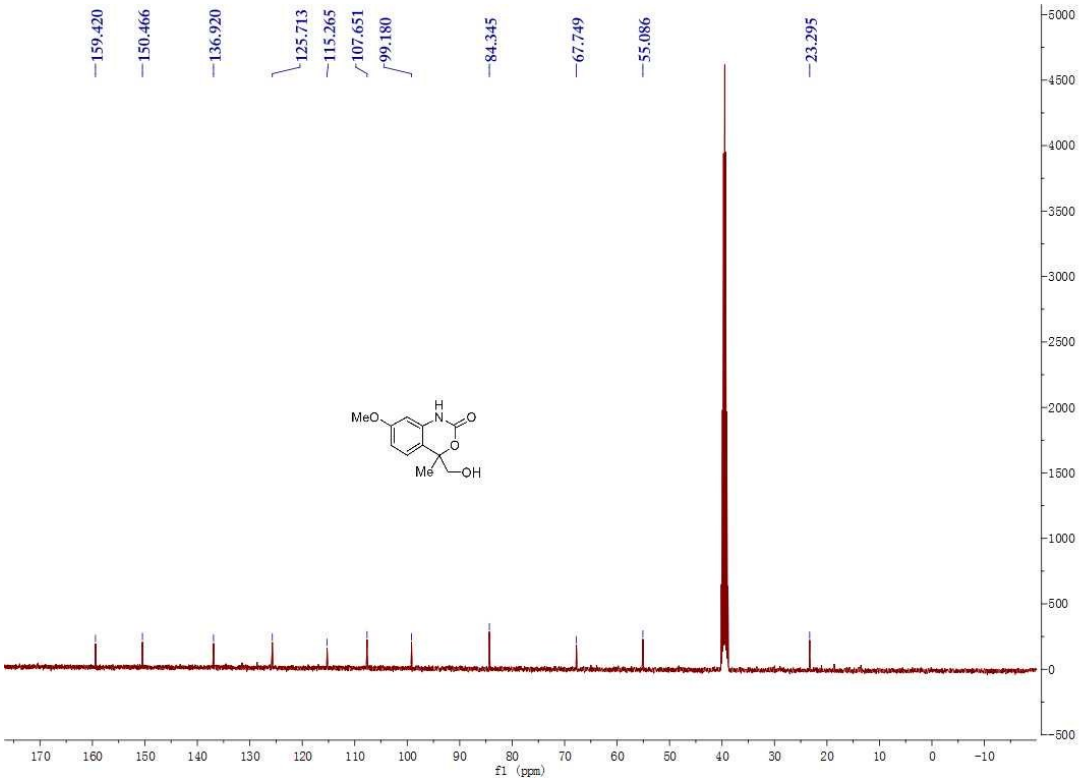
NMR spectra of 3o



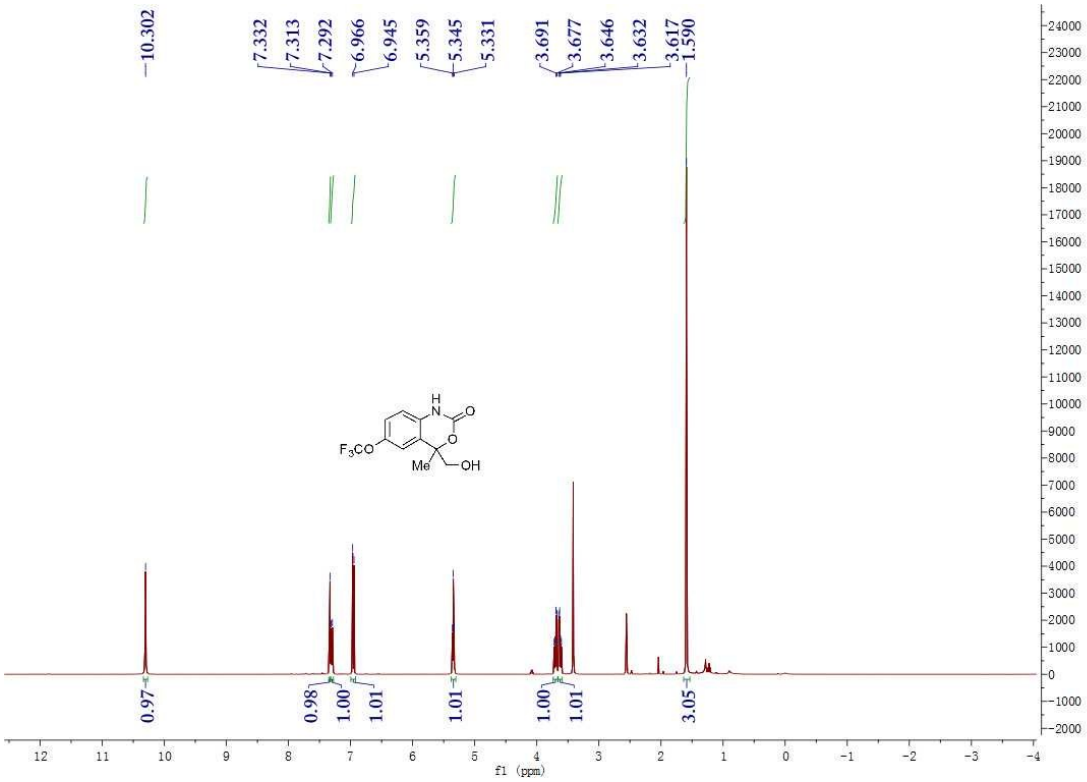


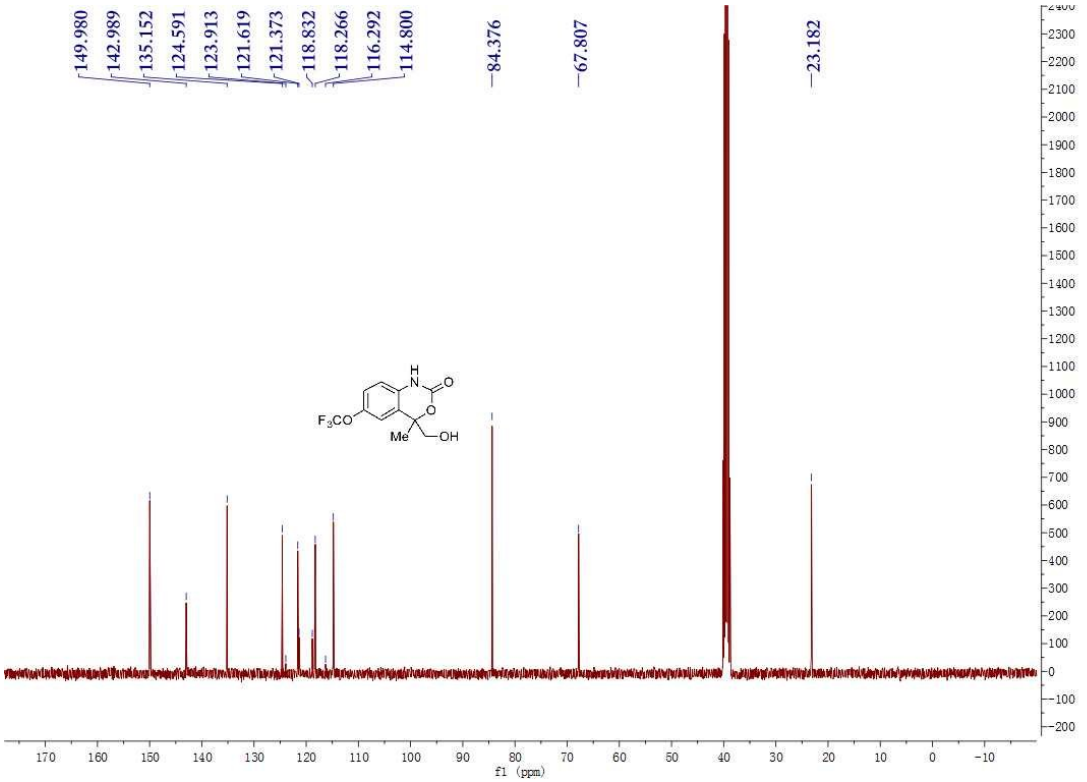
NMR spectra of 3p

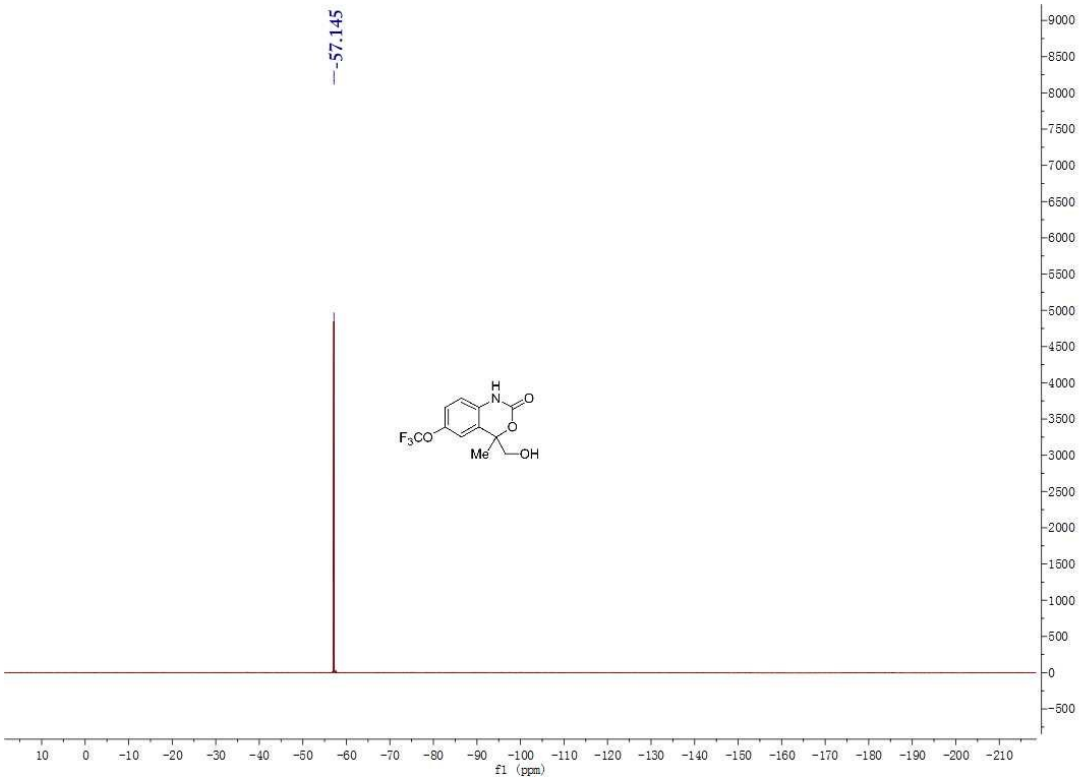




NMR spectra of 3q



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4500
4000
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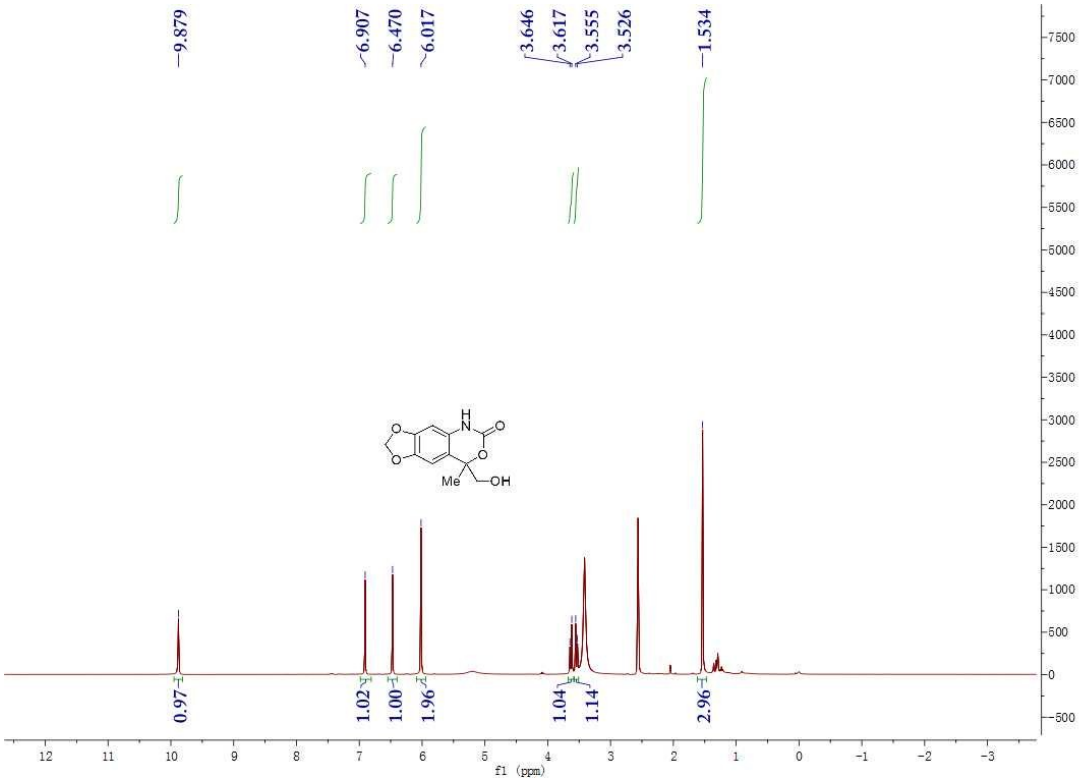
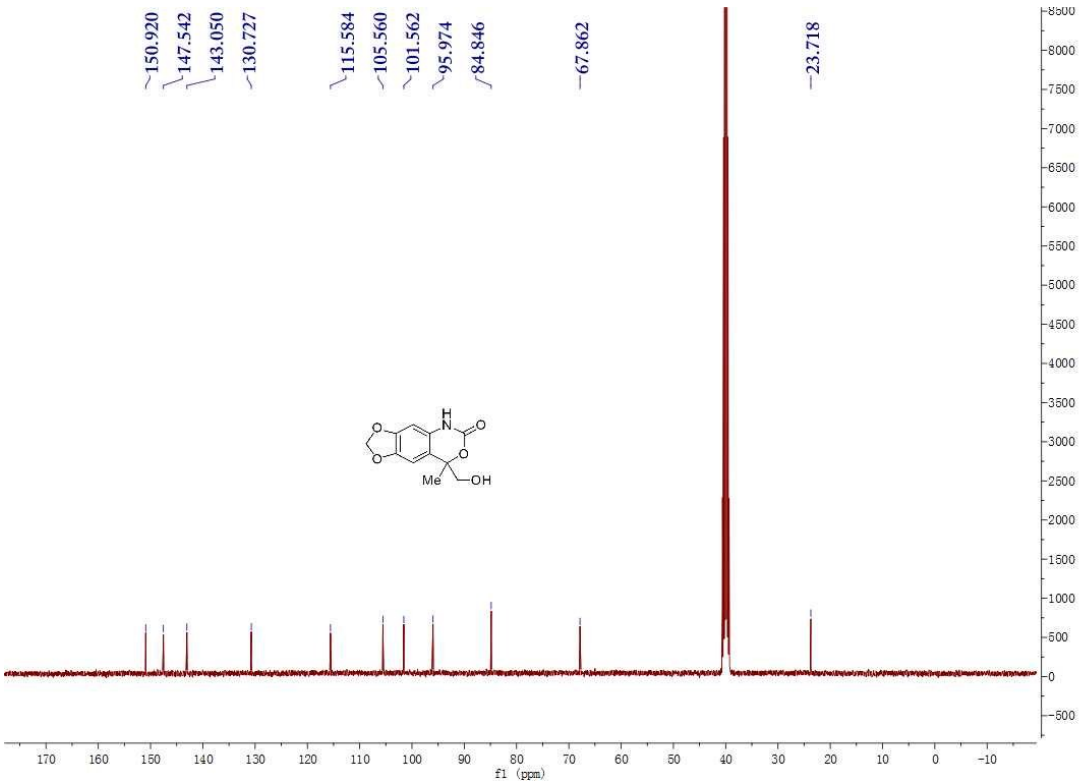
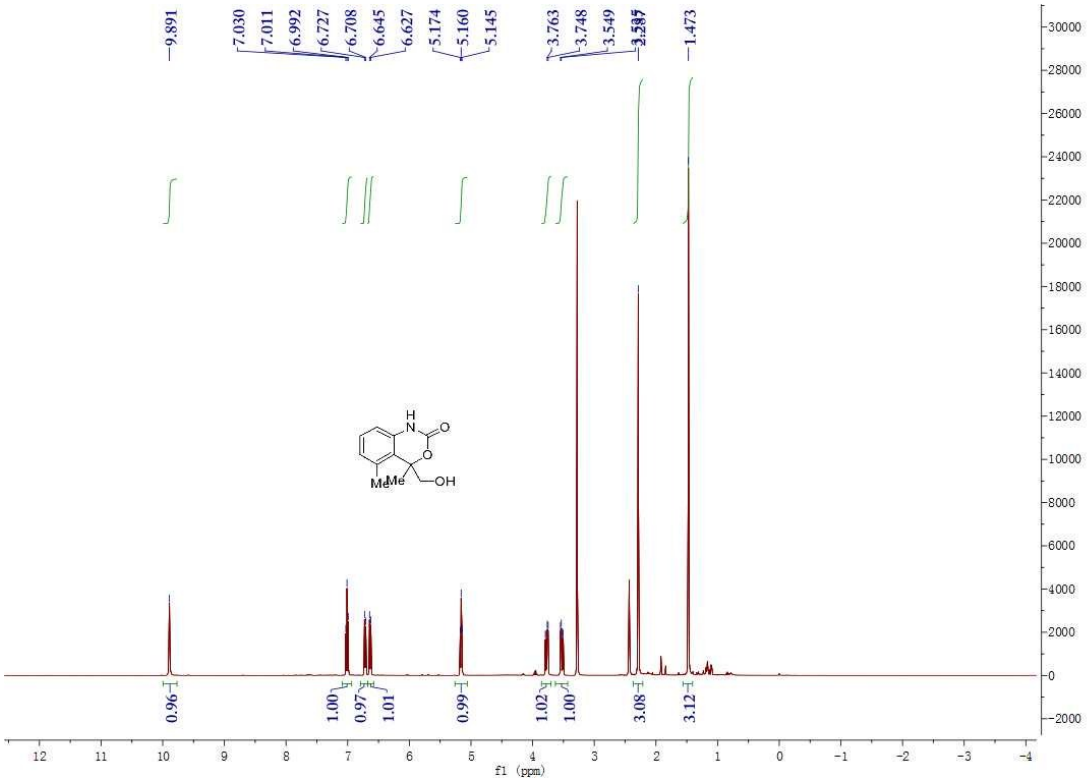
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

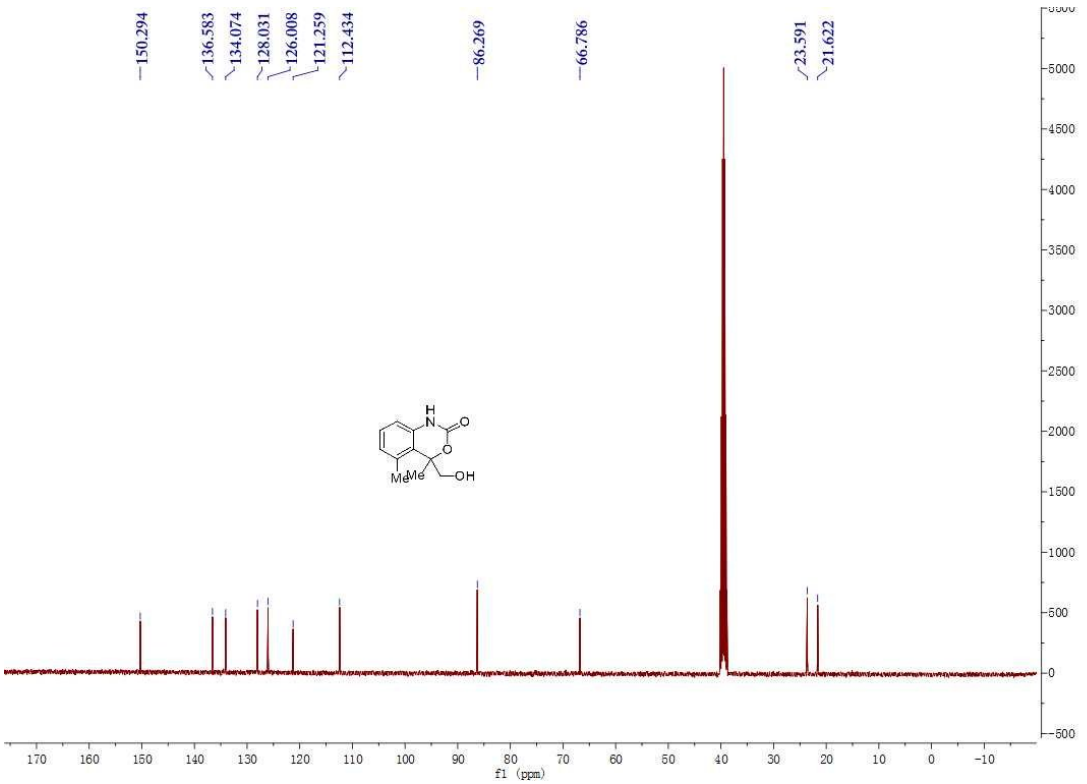
NMR spectra of 3r



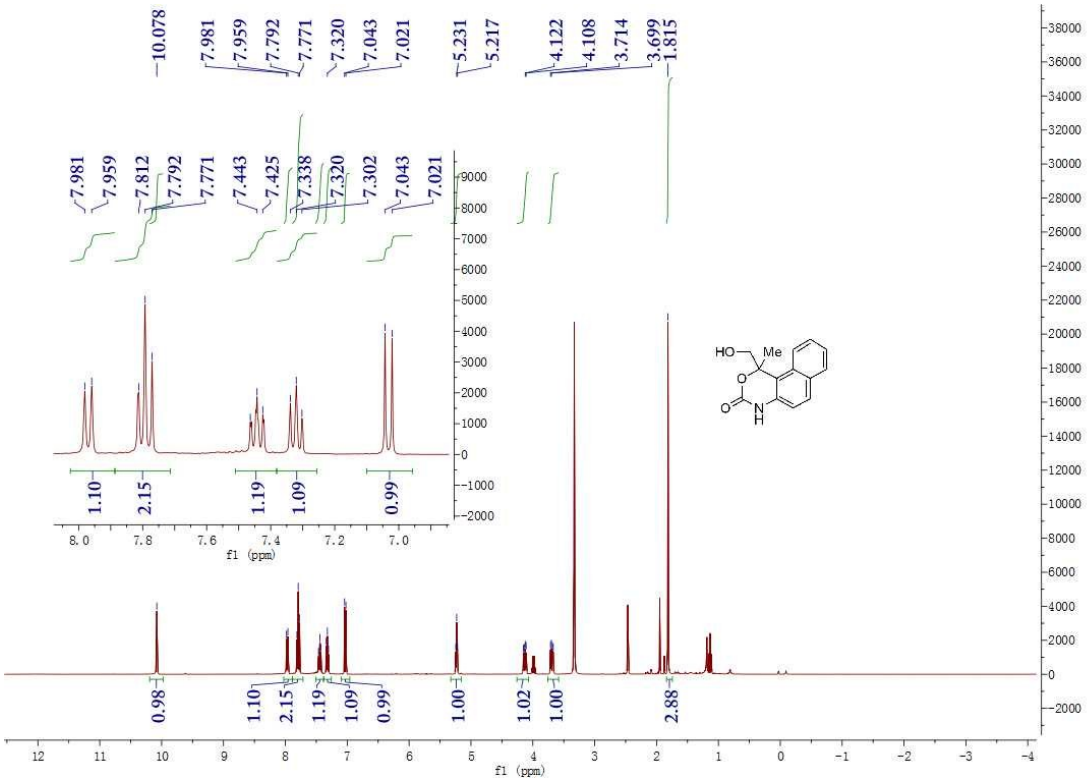


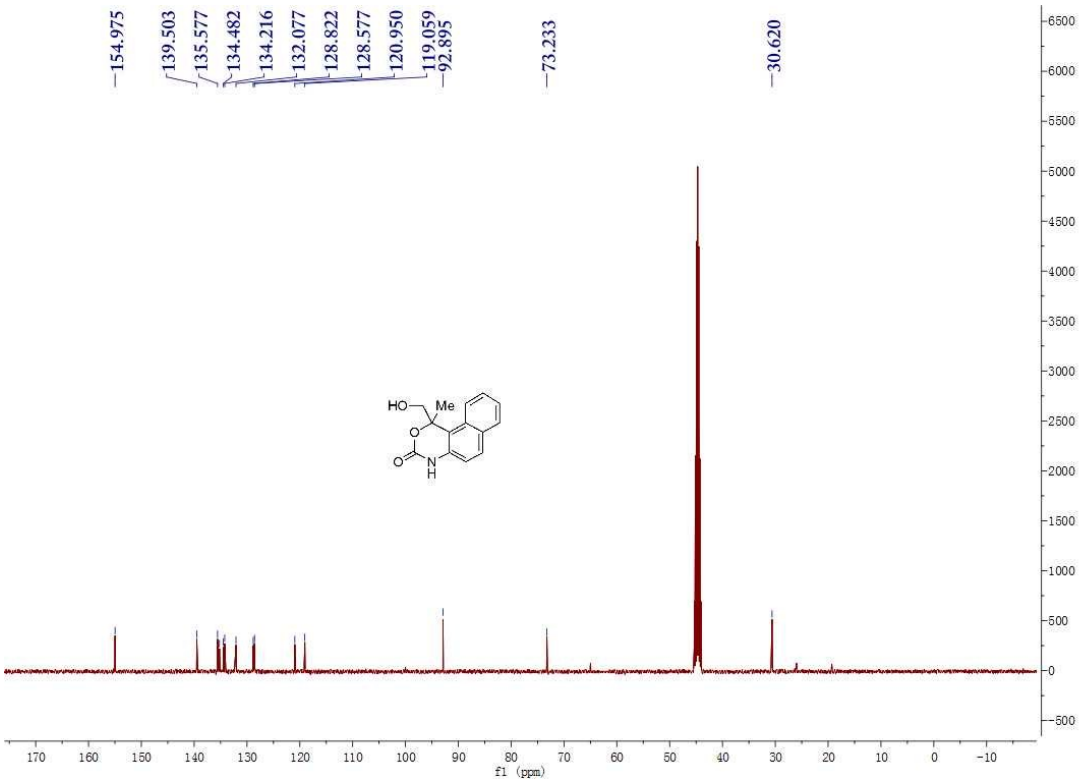
NMR spectra of 3s



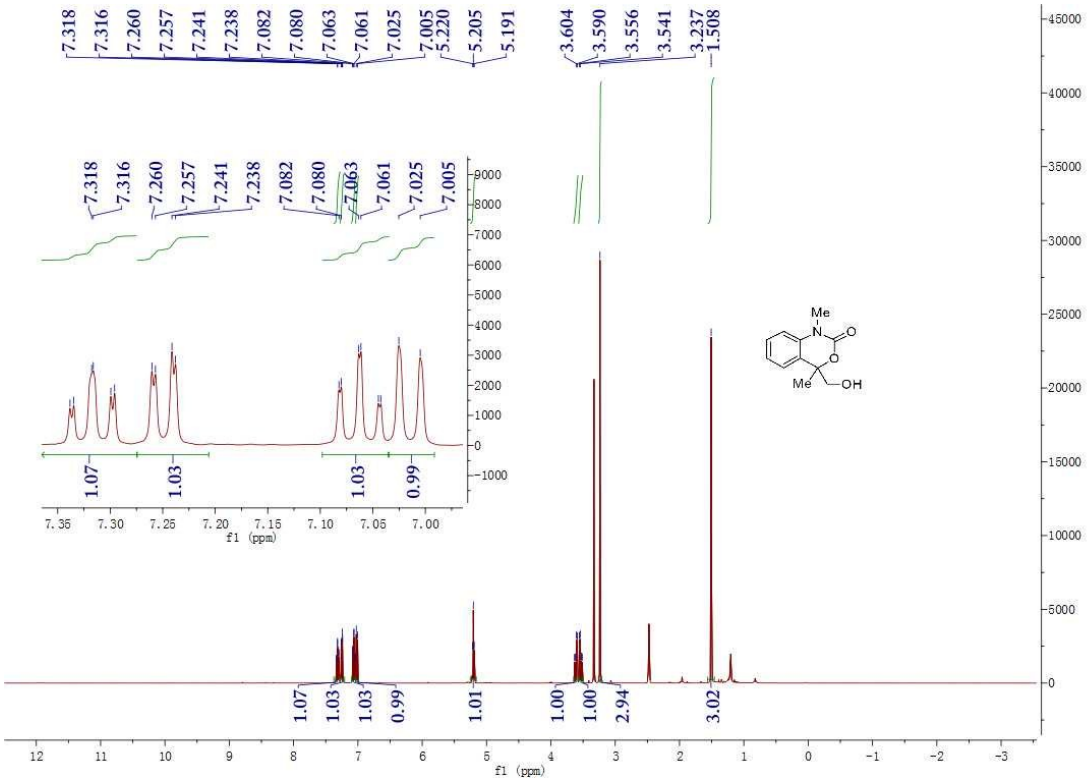


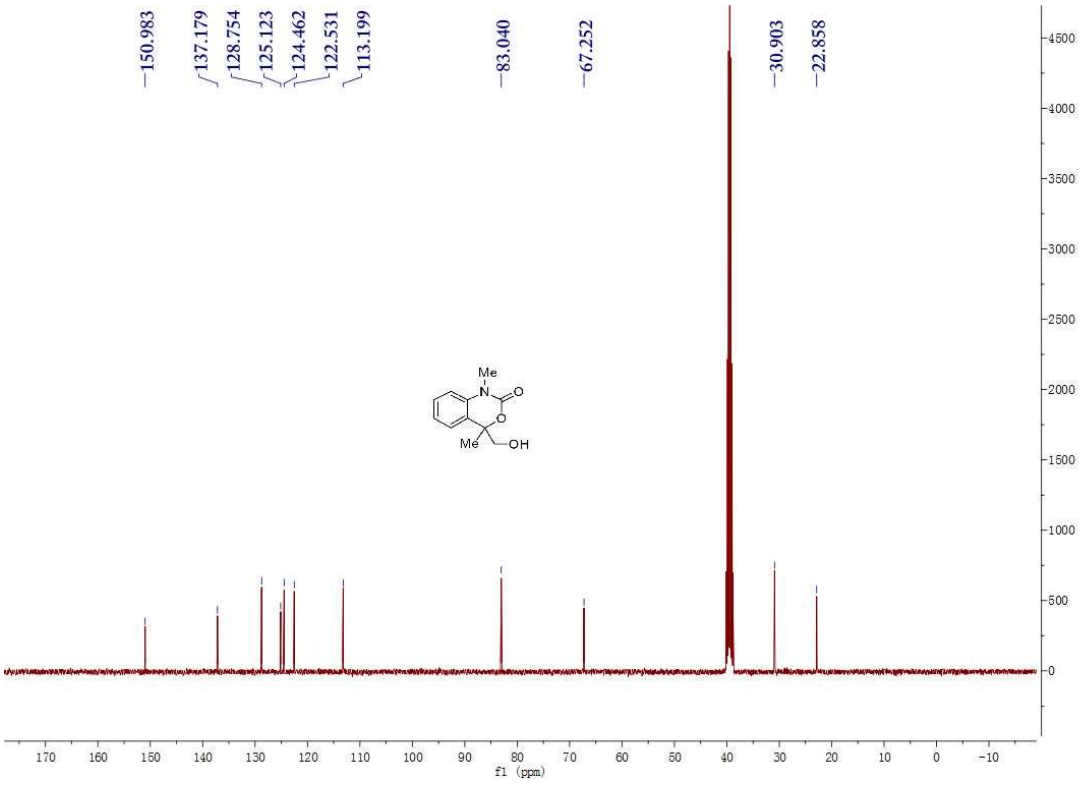
NMR spectra of 3t



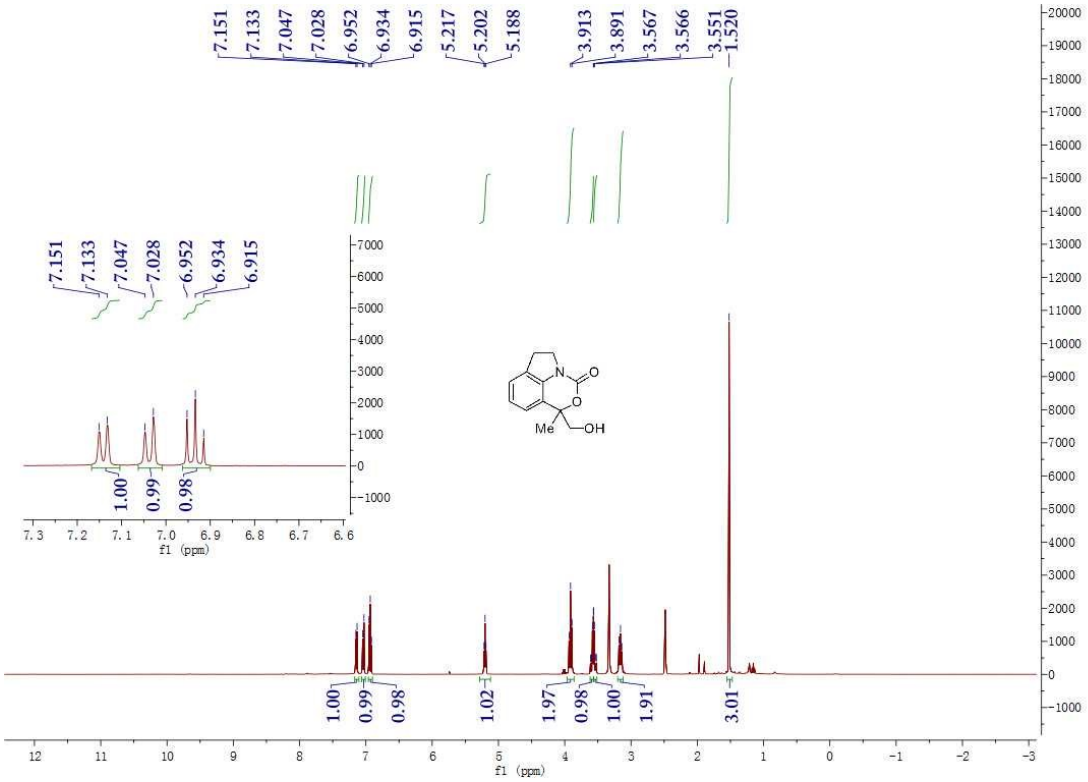


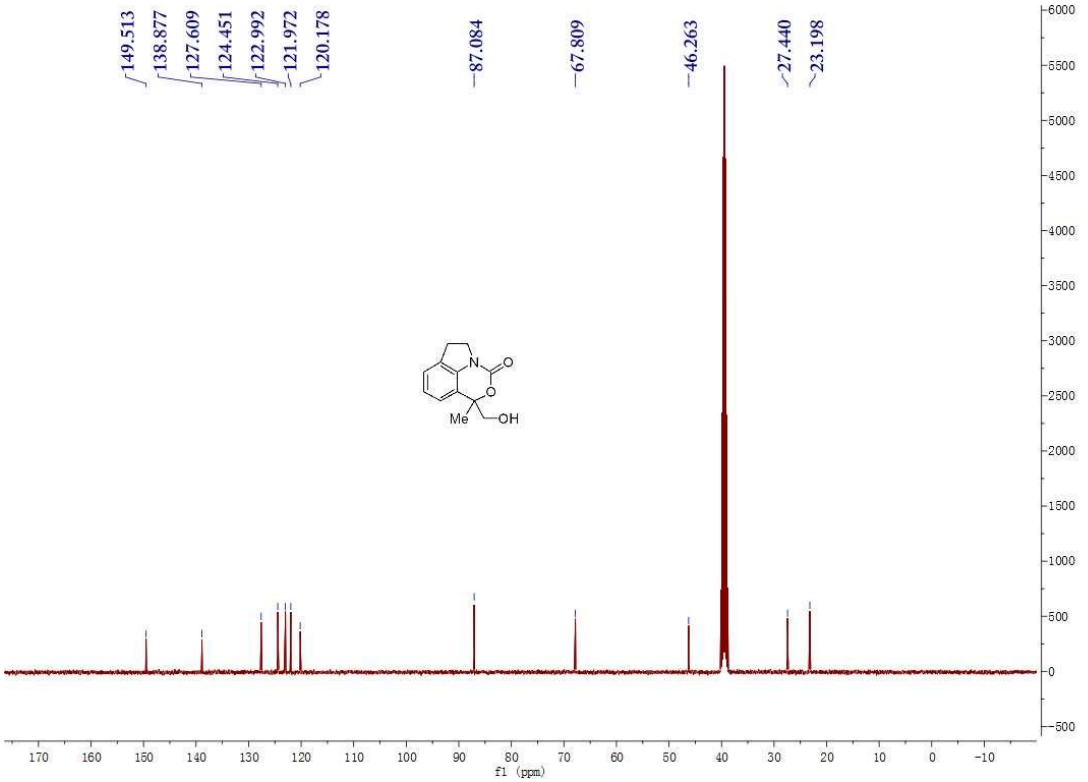
NMR spectra of 3u



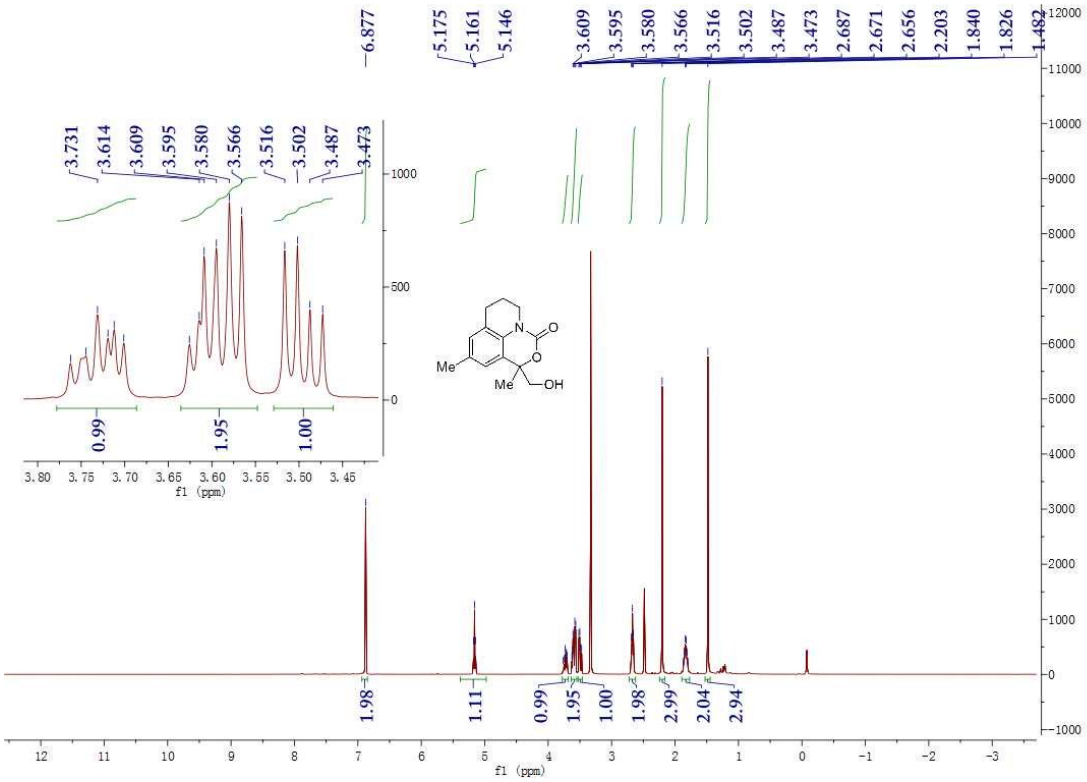


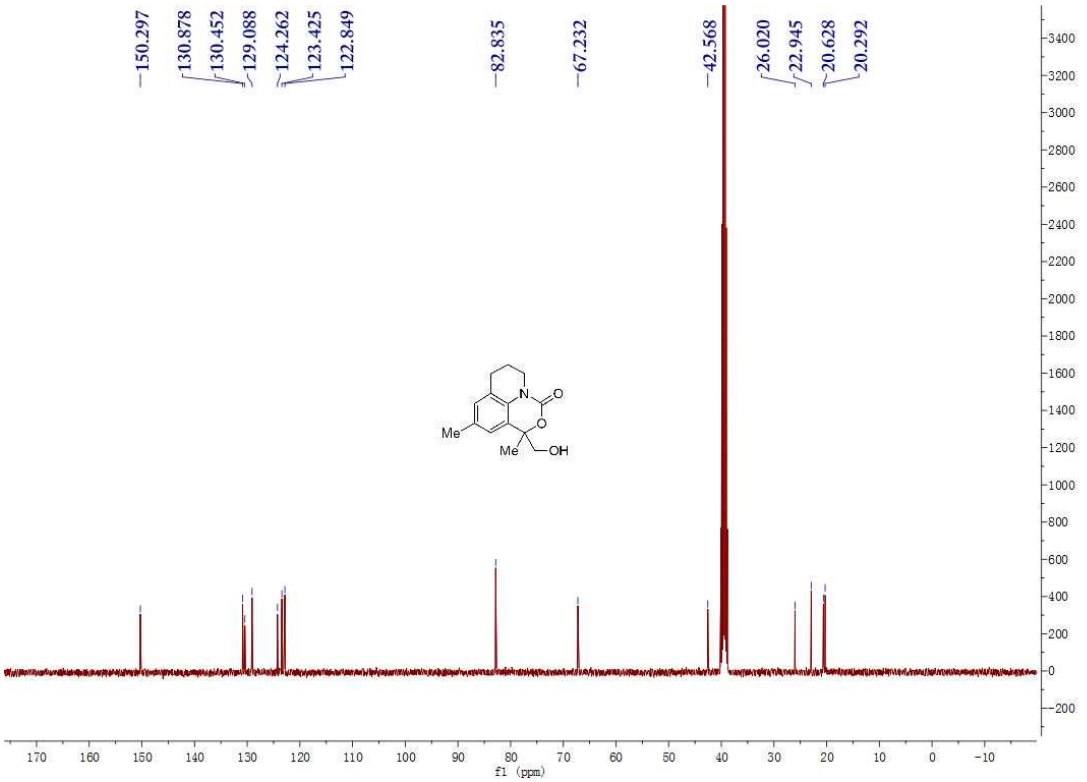
NMR spectra of 3v



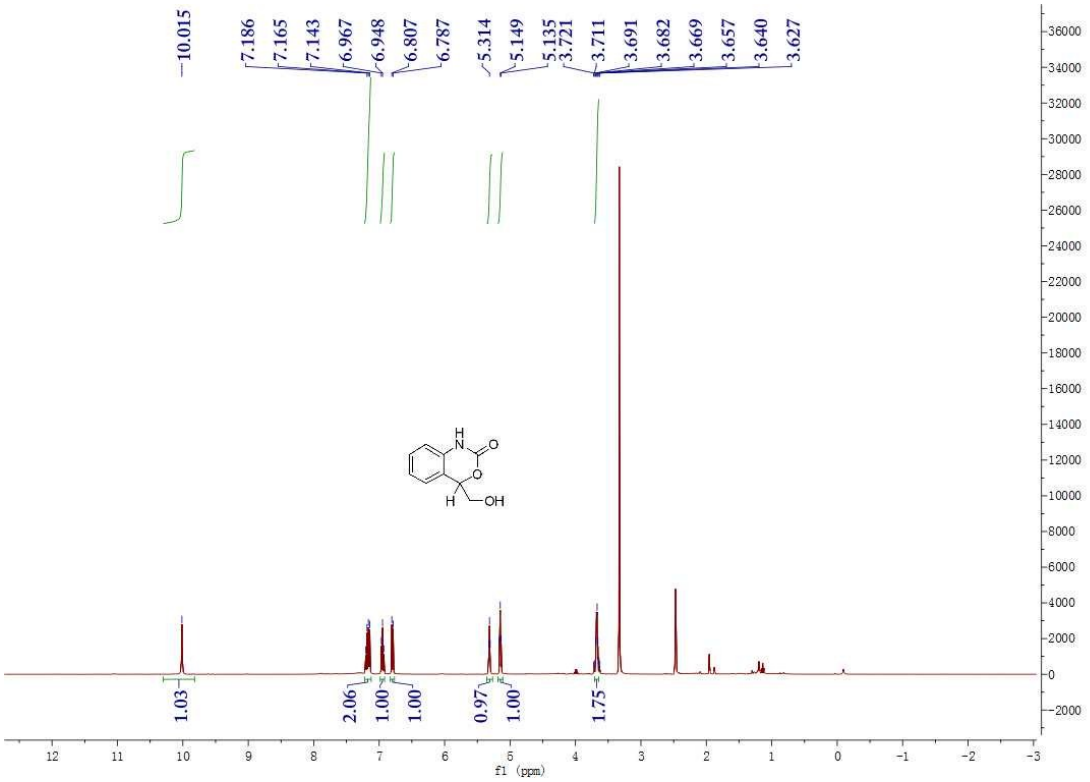


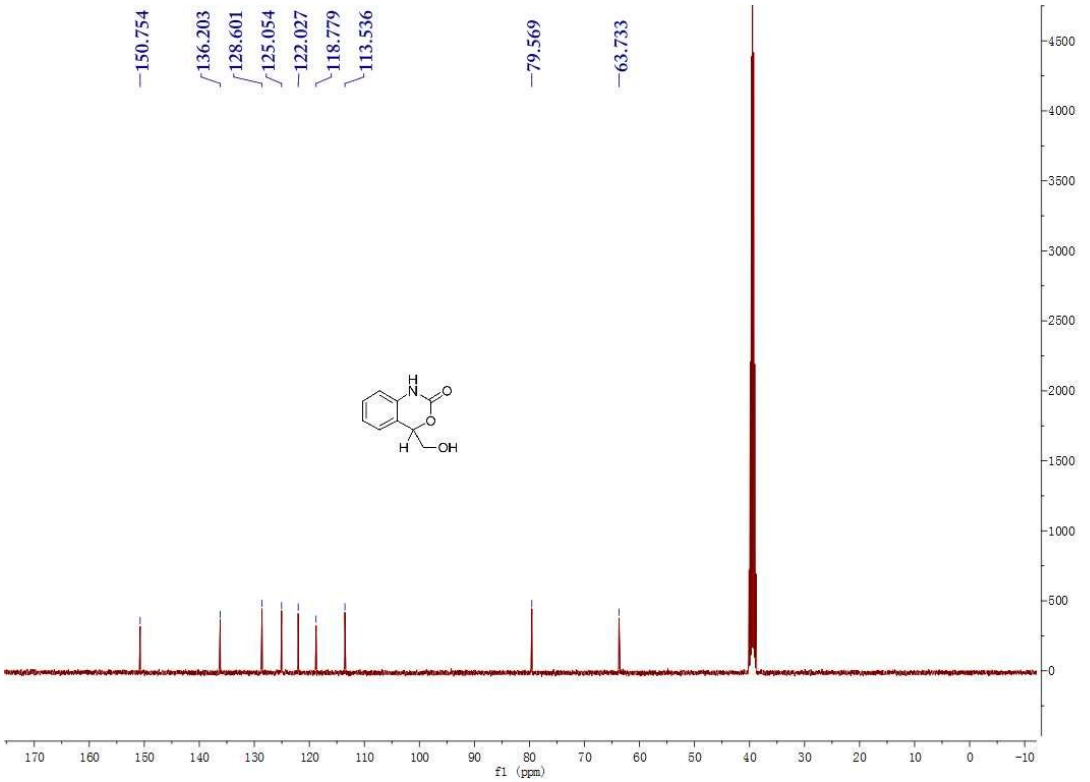
NMR spectra of 3w



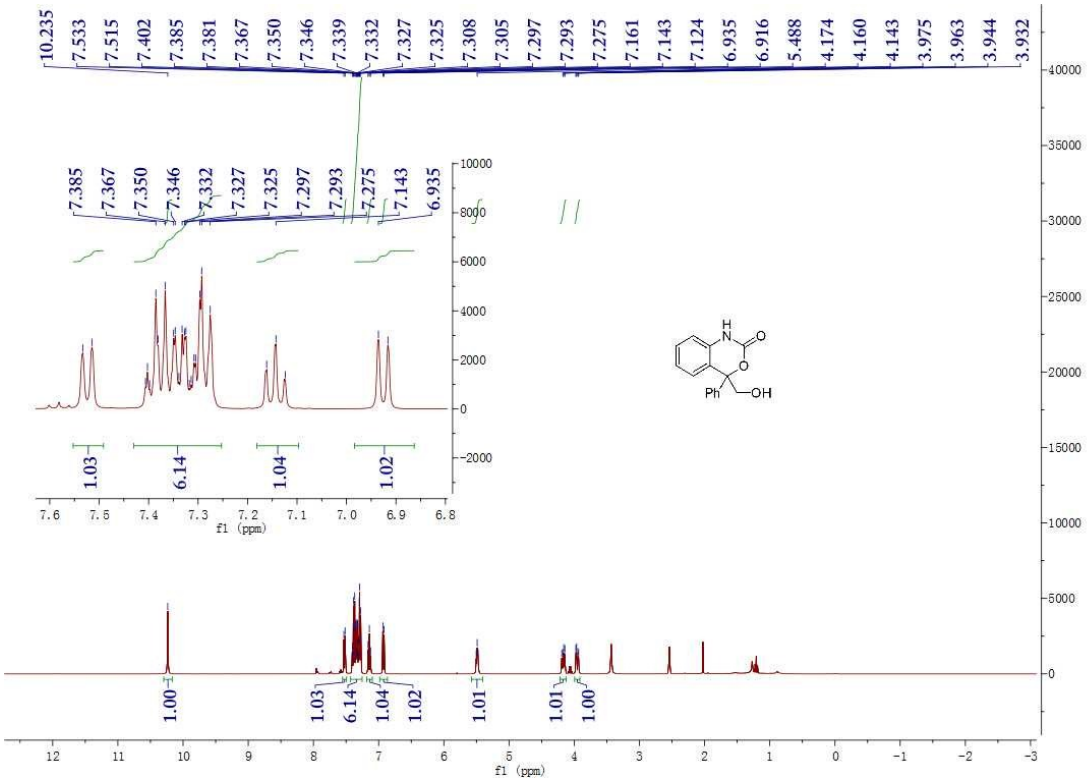


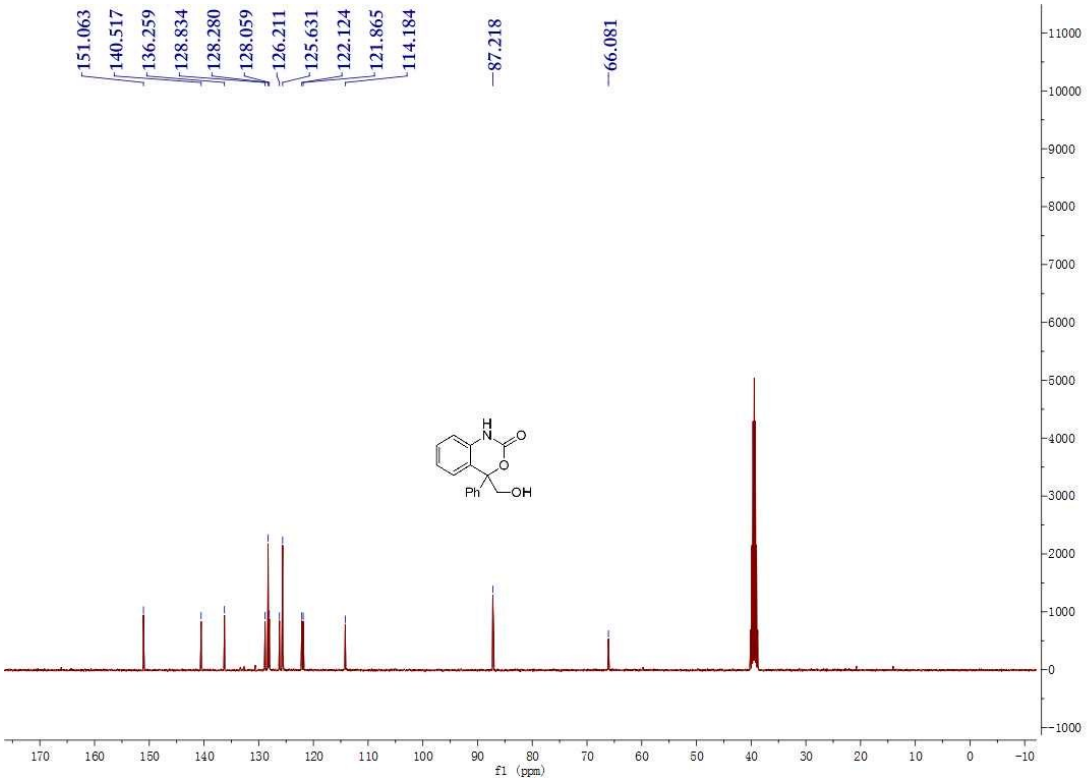
NMR spectra of 5a



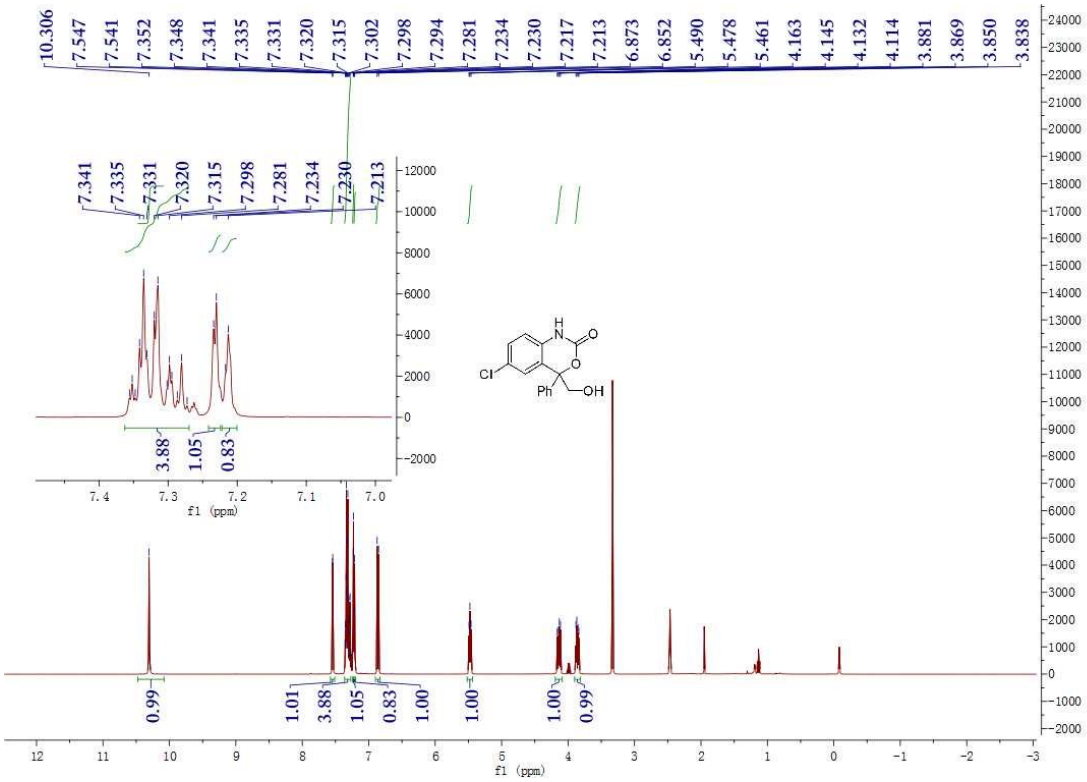


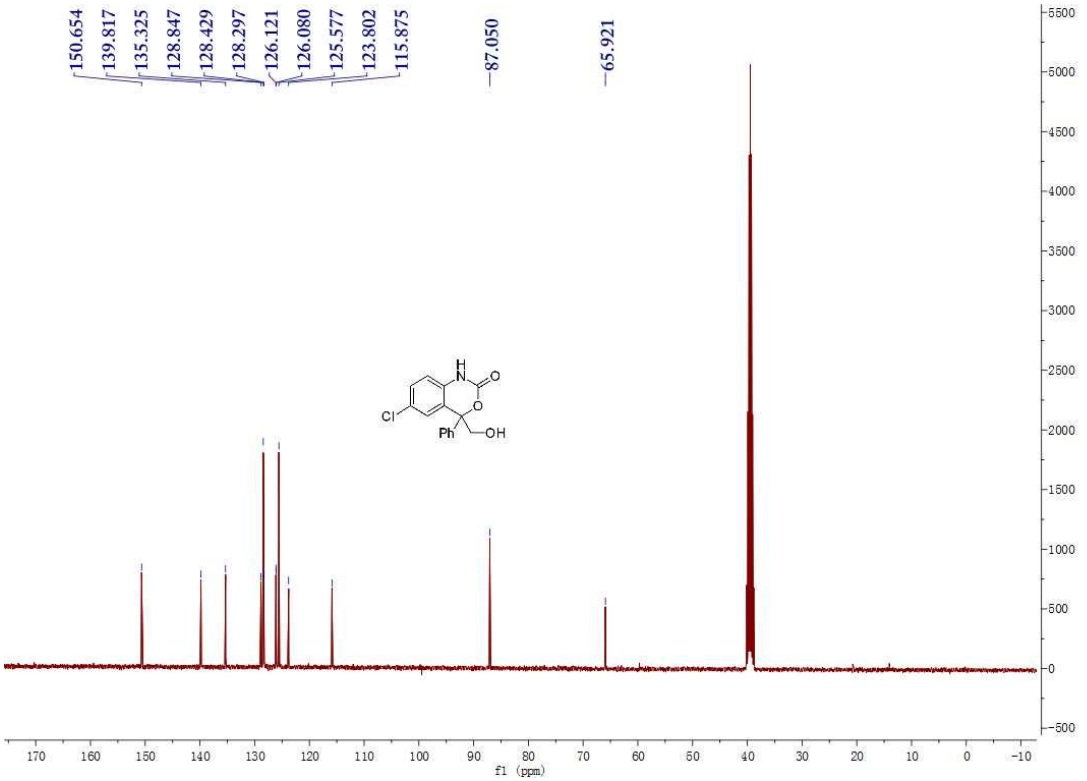
NMR spectra of 5b



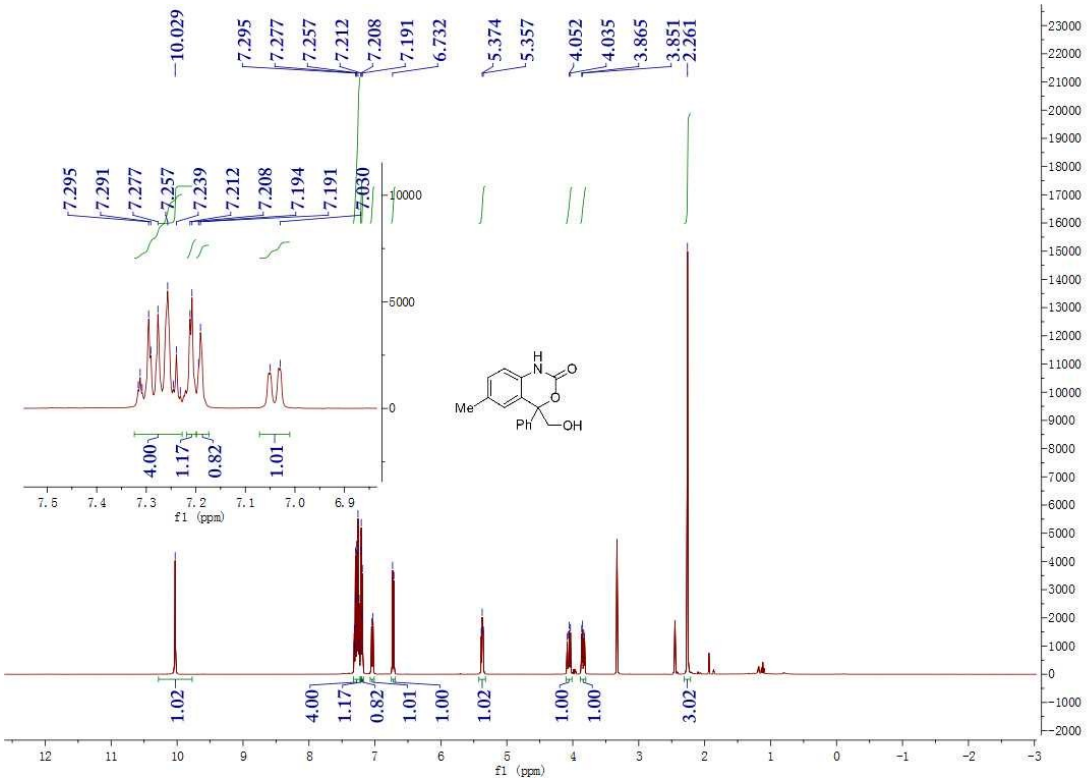


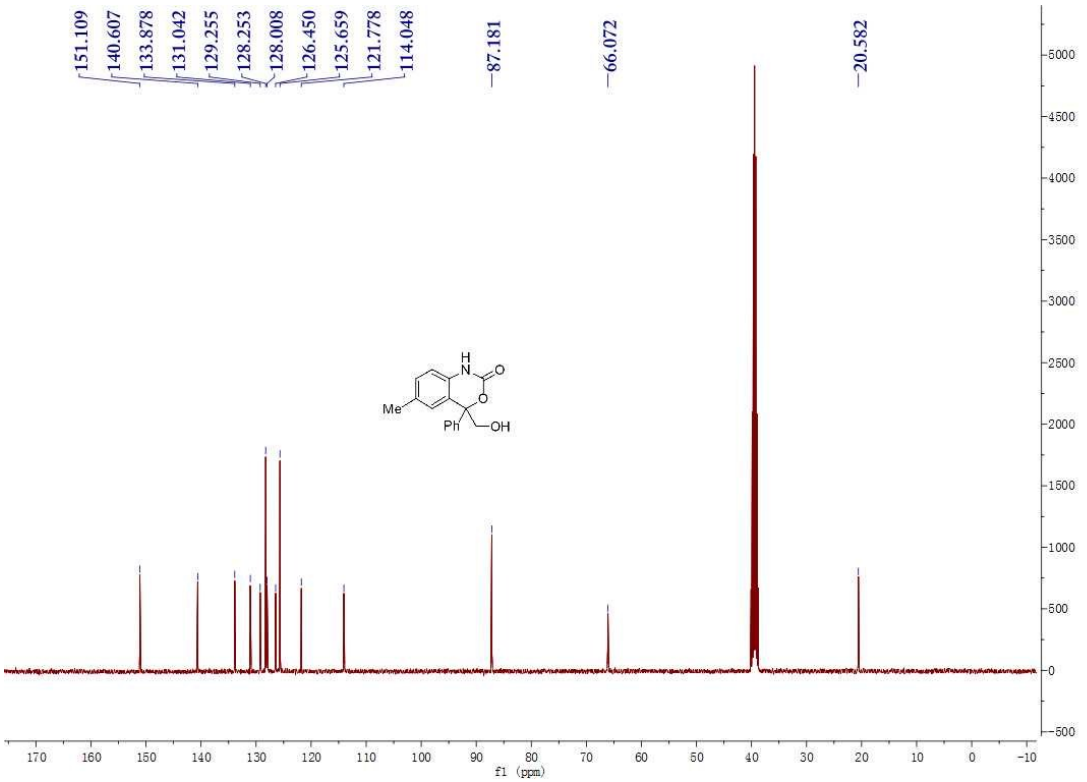
NMR spectra of 5c



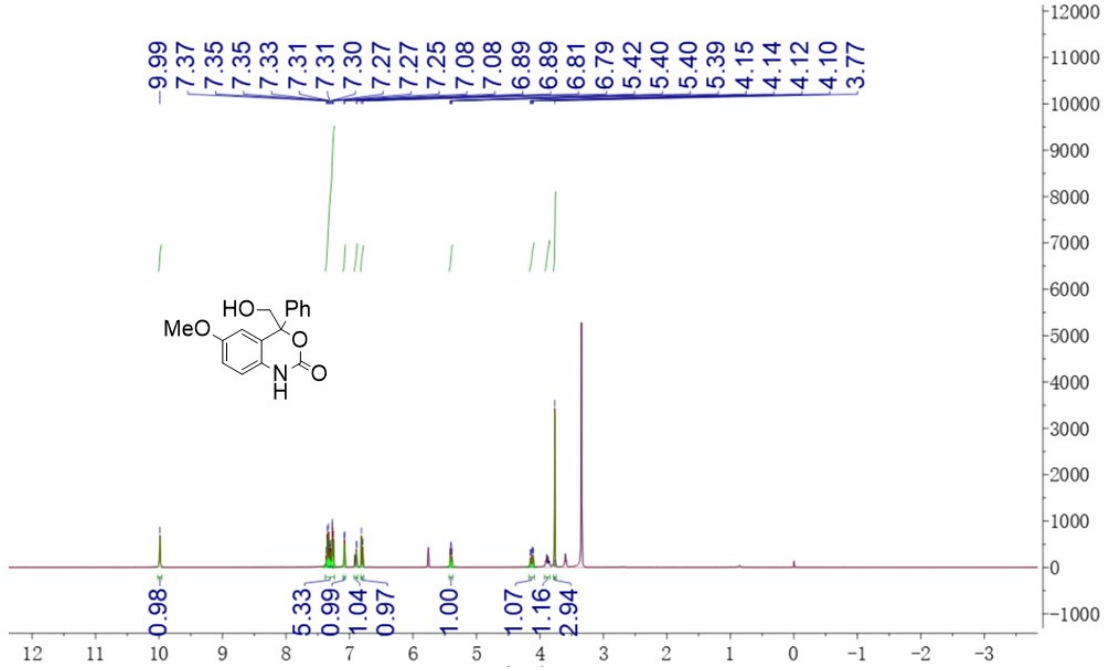


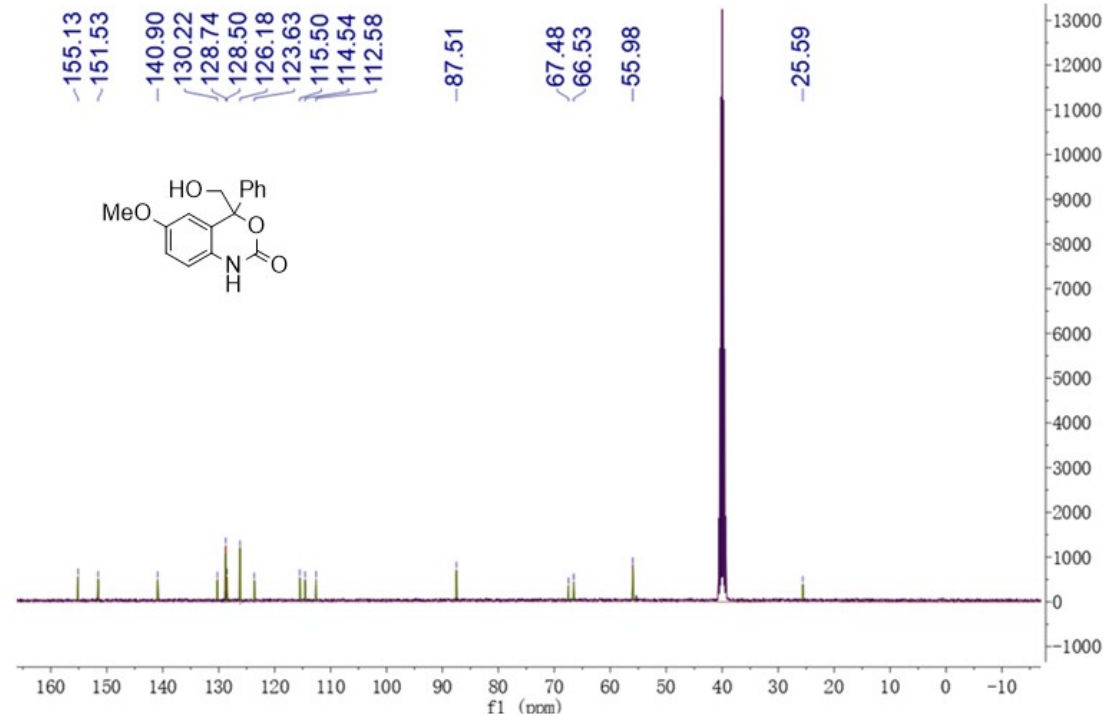
NMR spectra of 5d



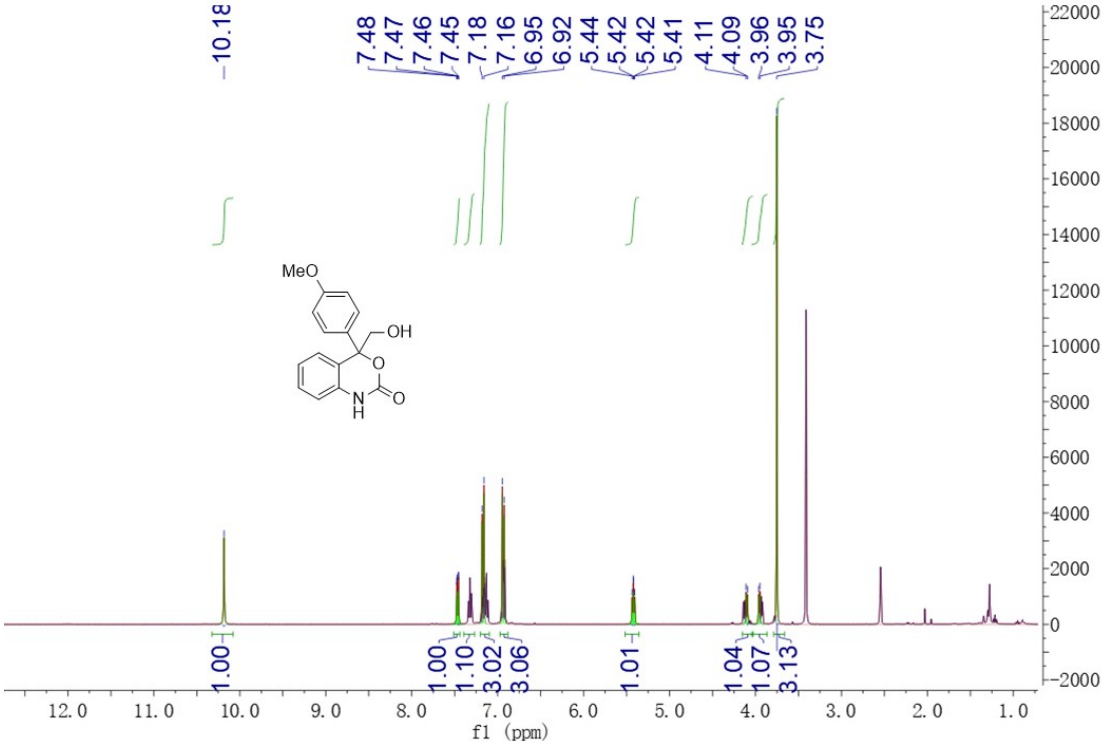


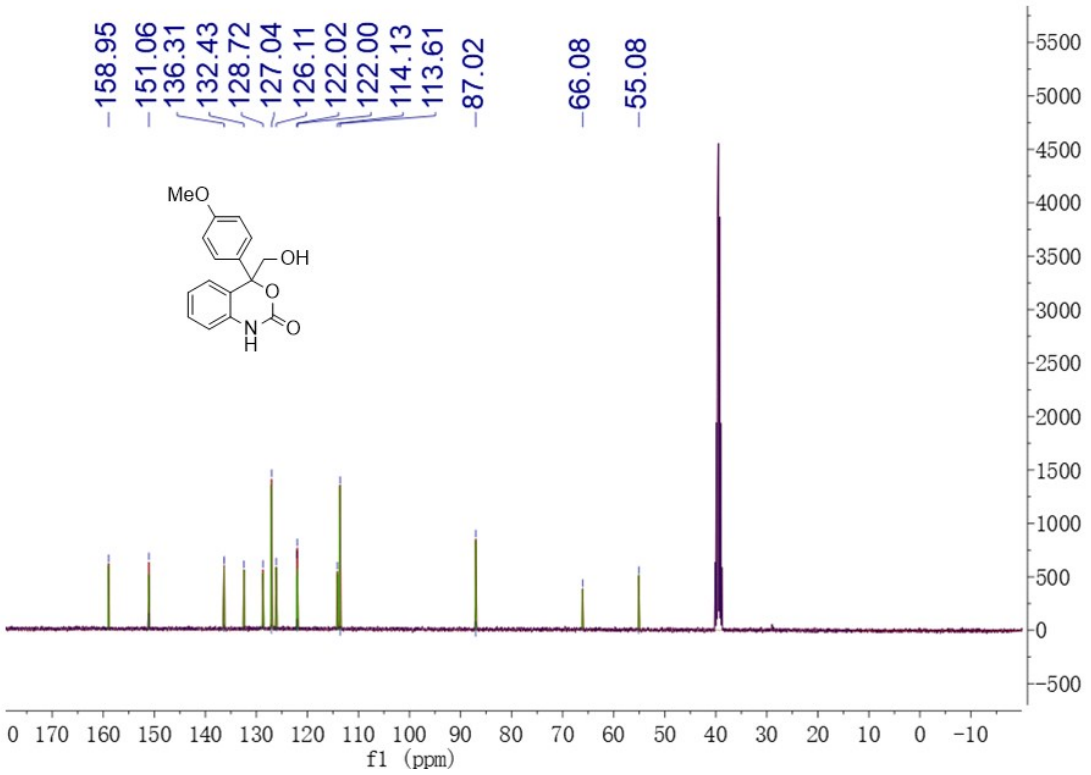
NMR spectra of 5e



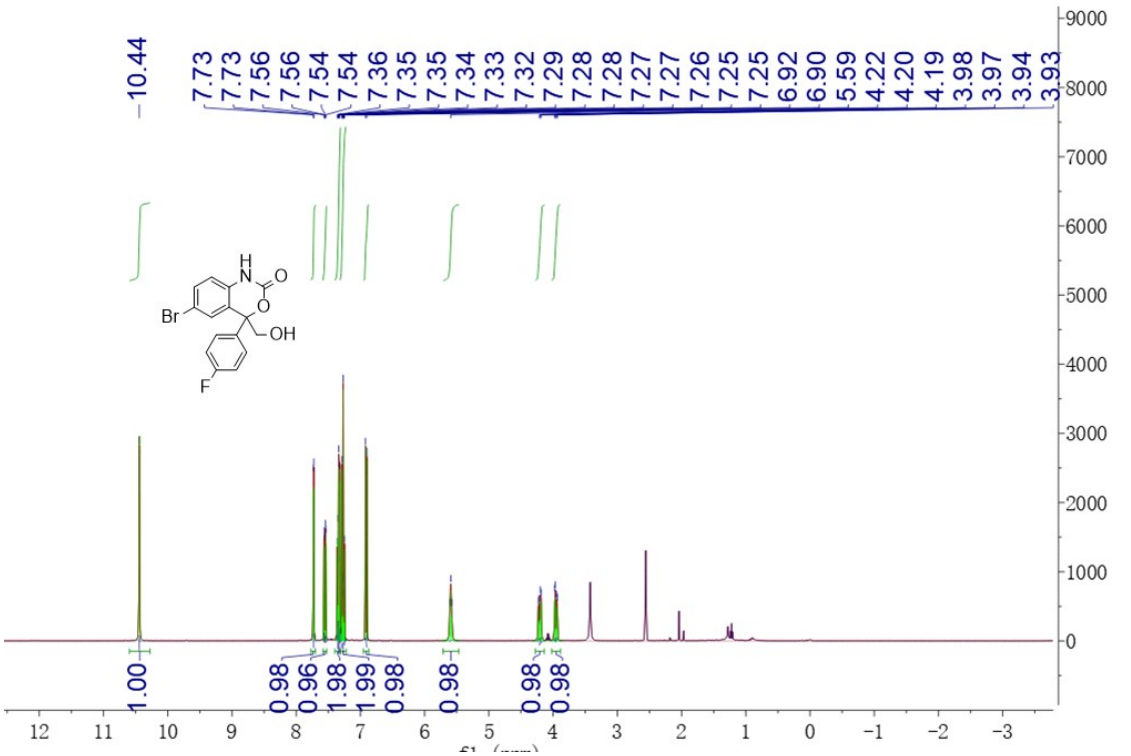


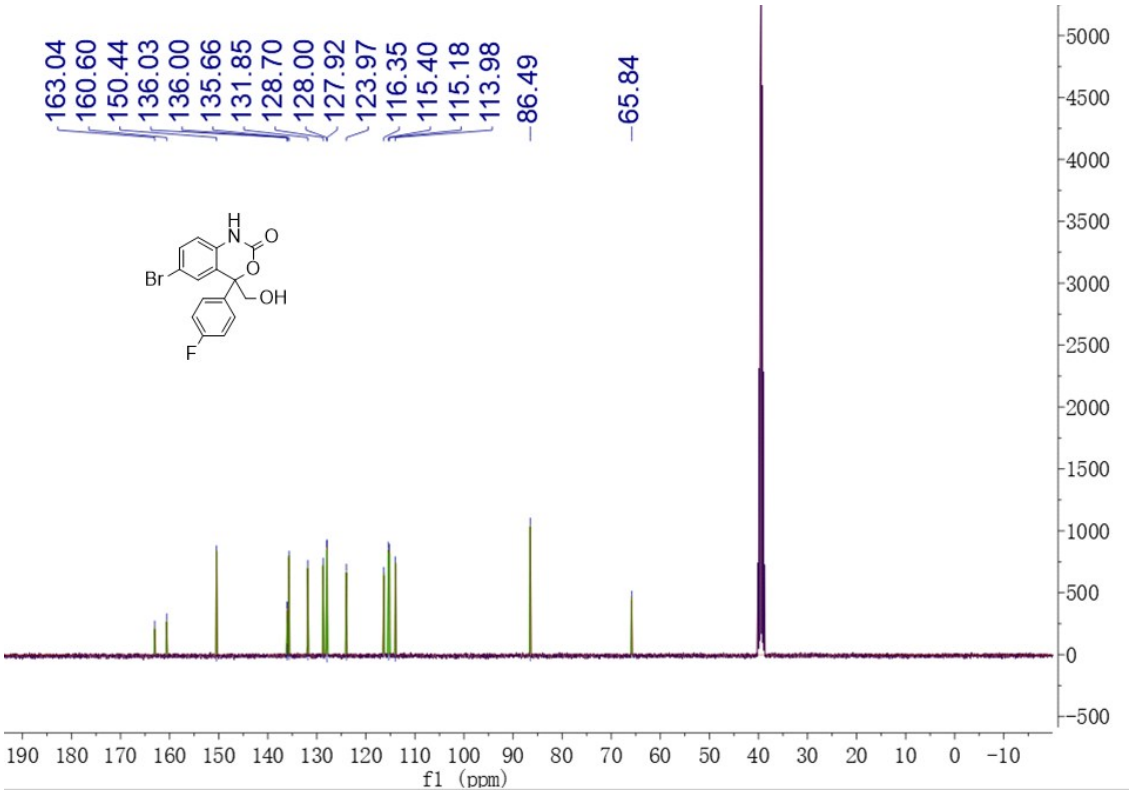
NMR spectra of 5f



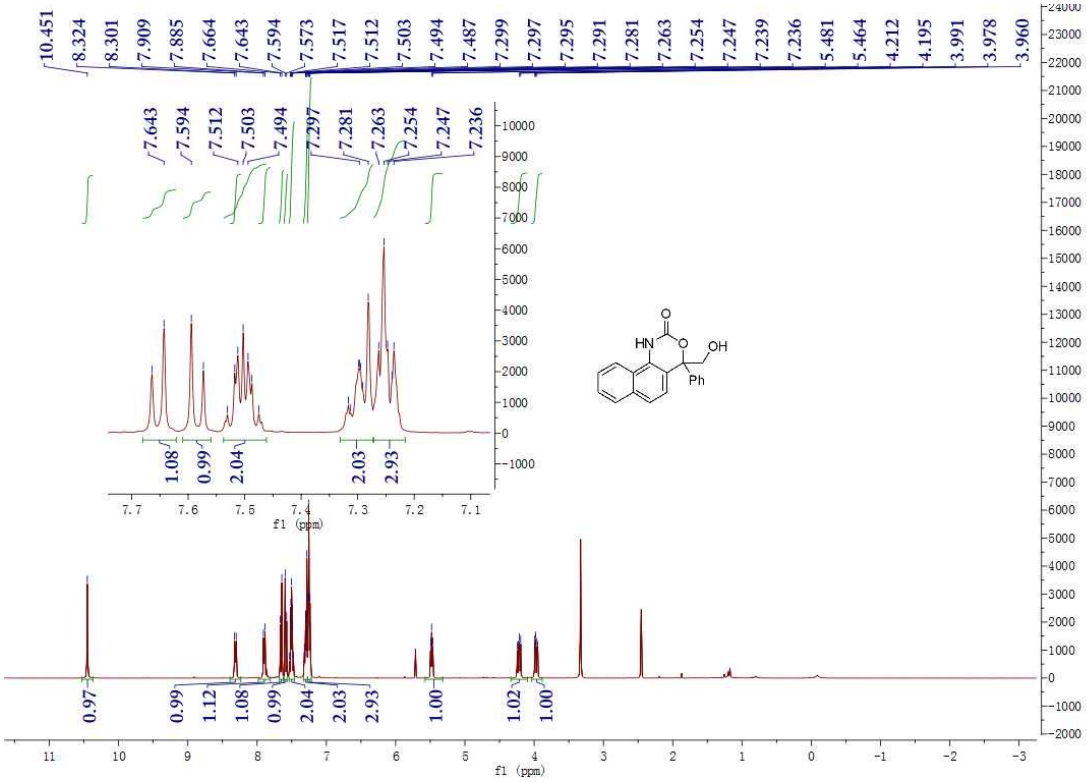


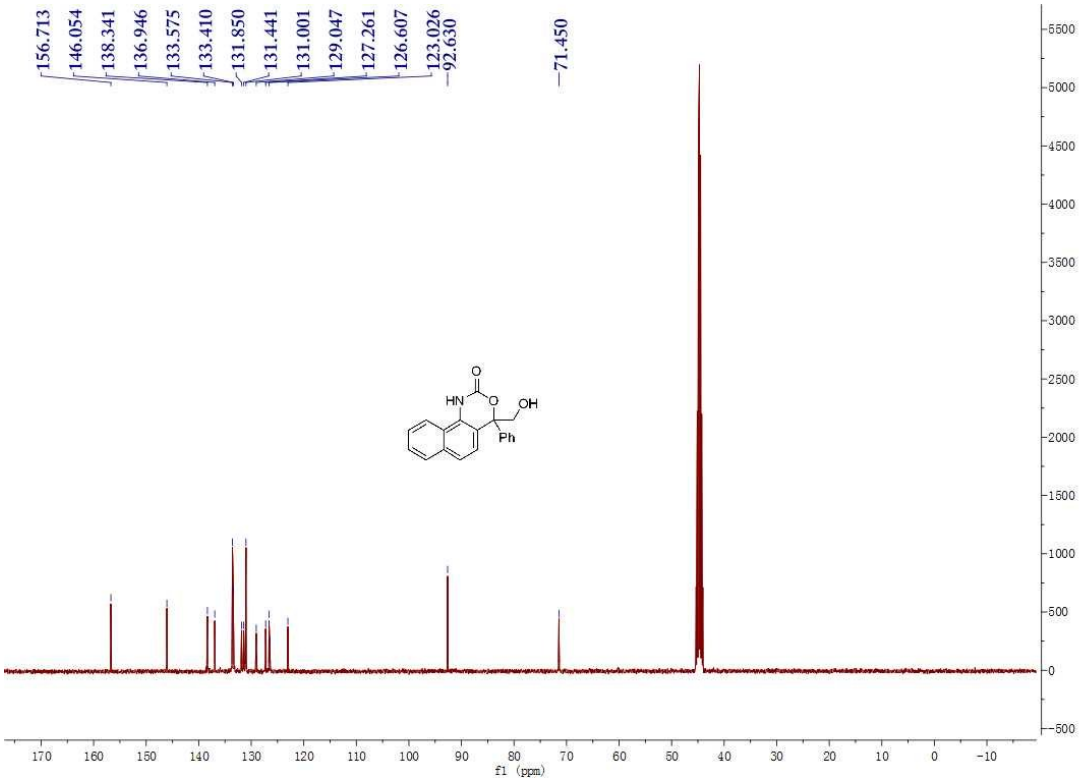
NMR spectra of 5g



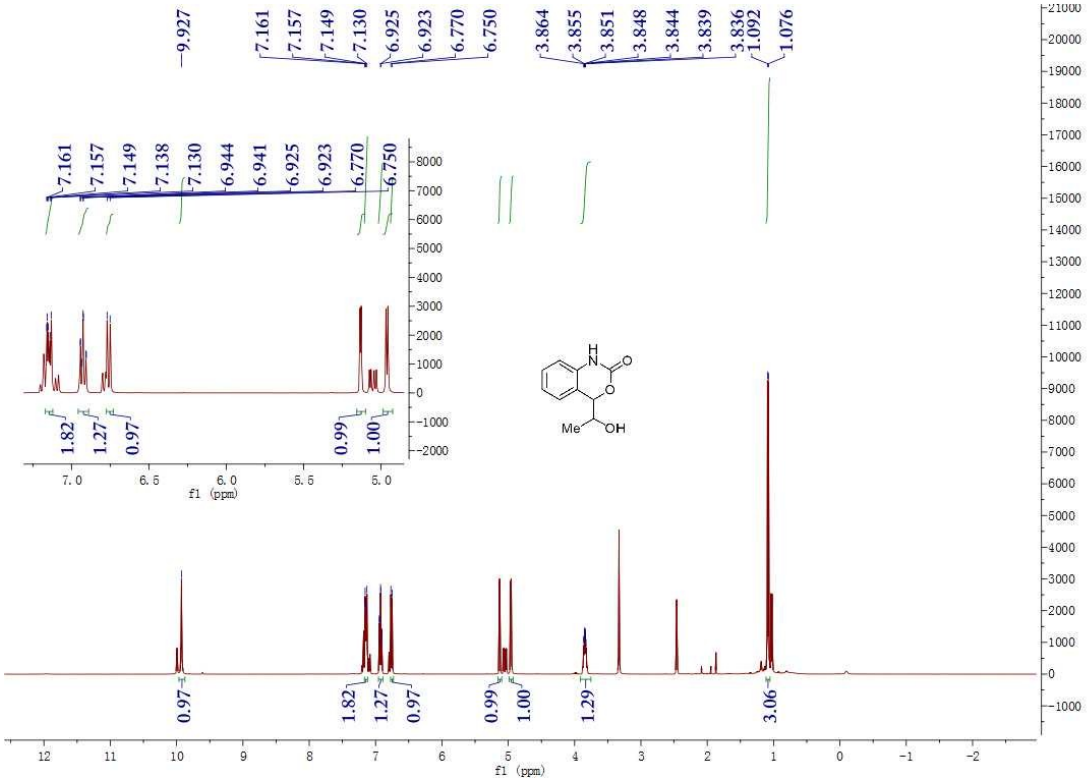


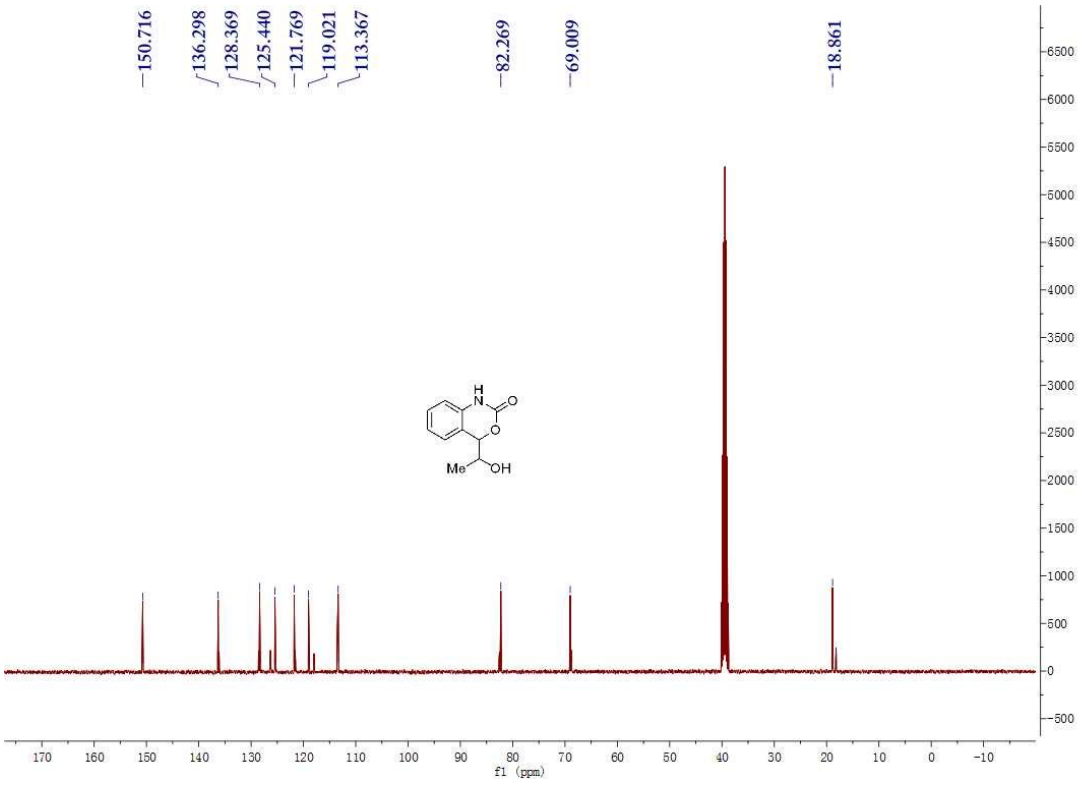
NMR spectra of 5h



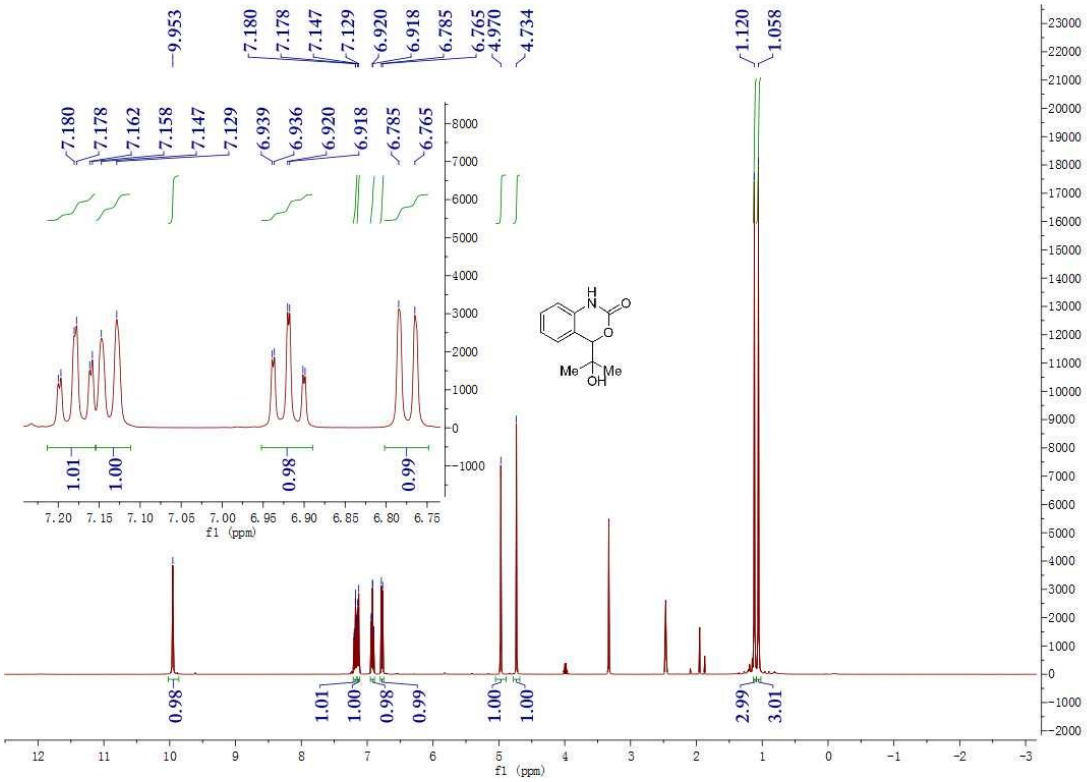


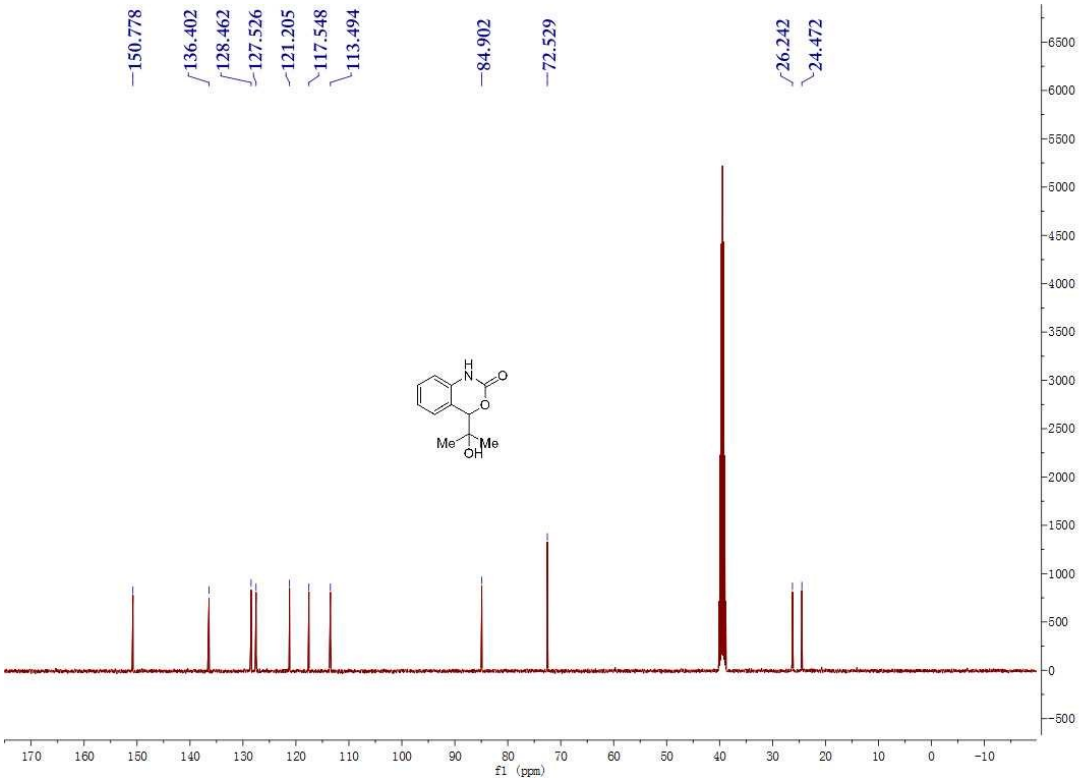
NMR spectra of 5j



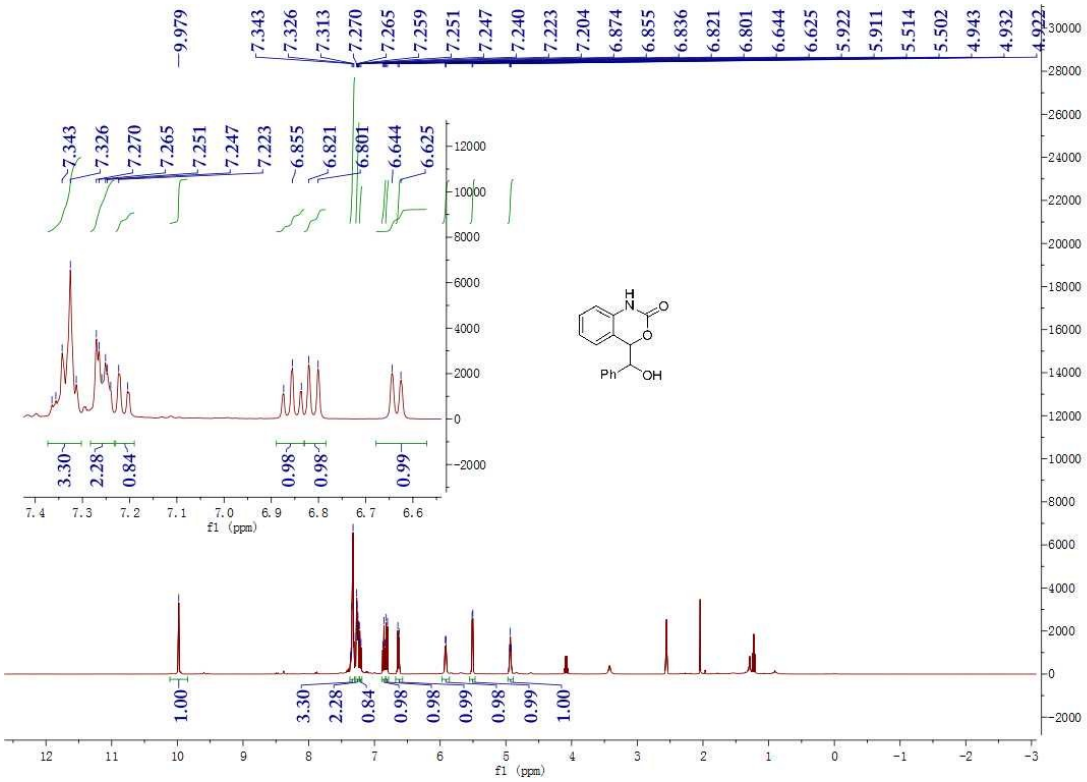


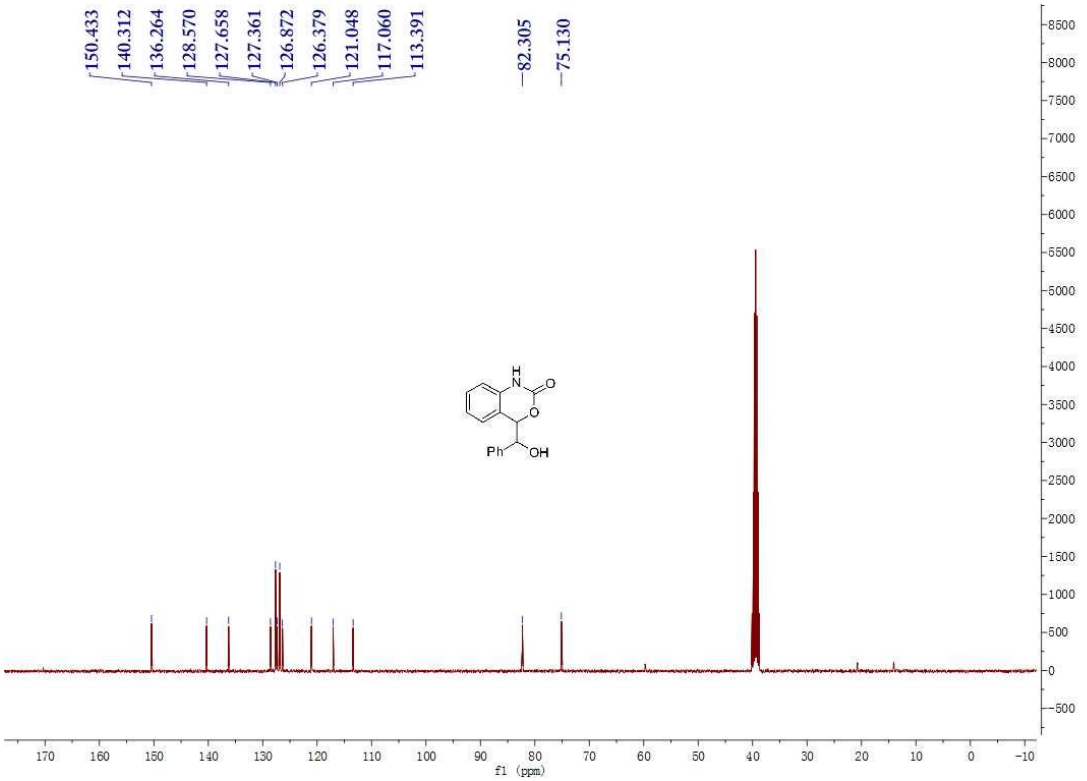
NMR spectra of 5k



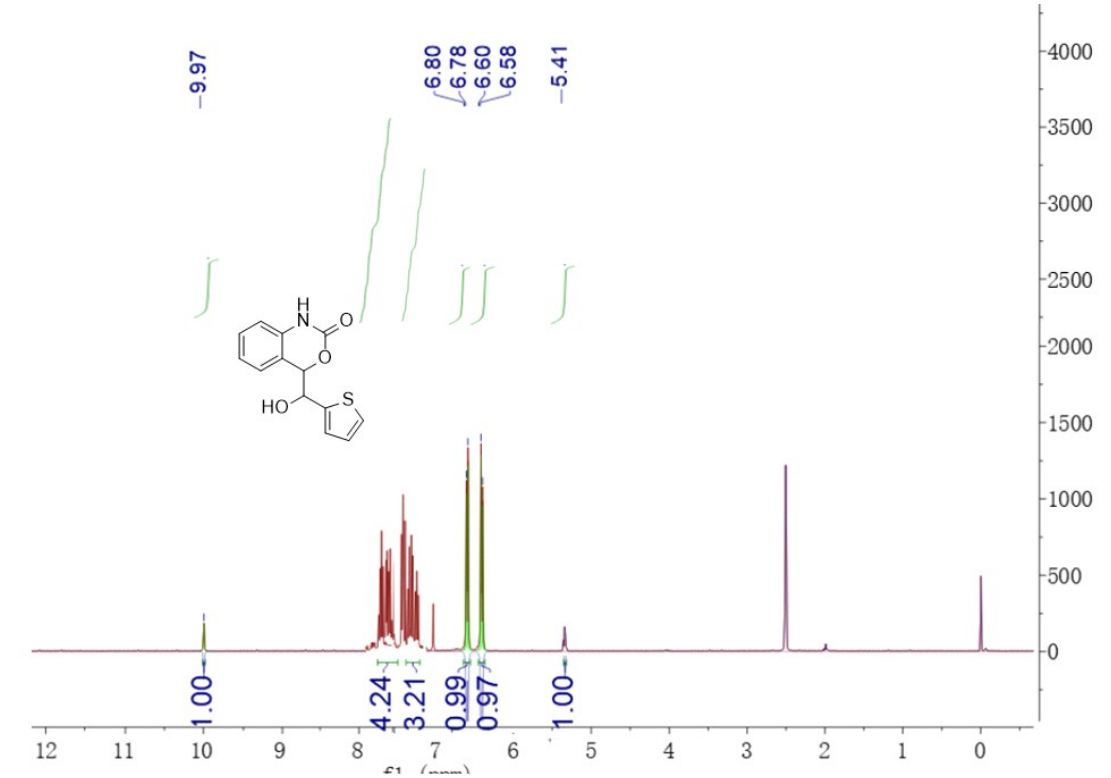


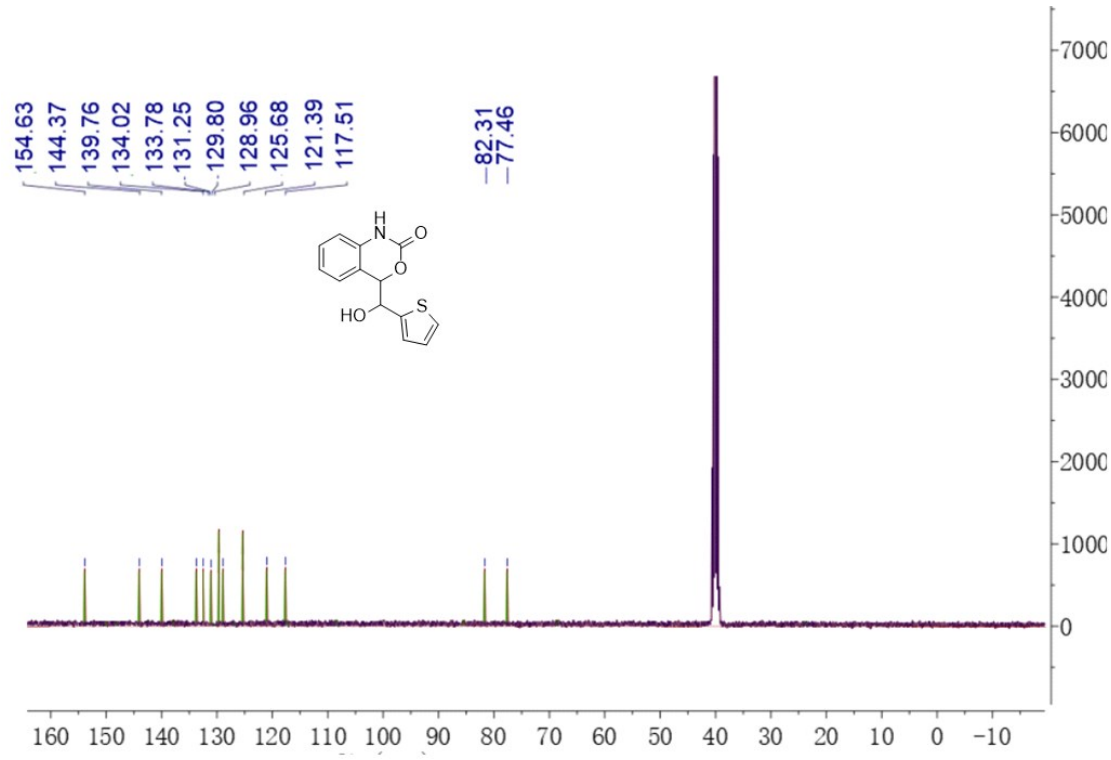
NMR spectra of 5l



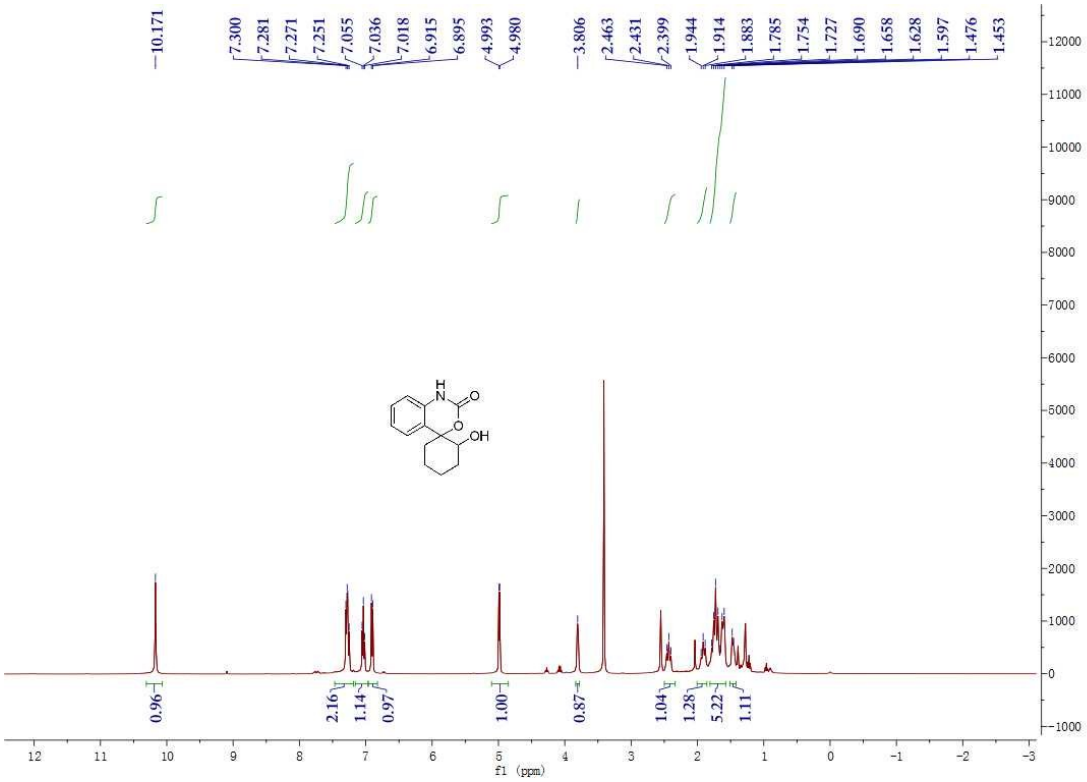


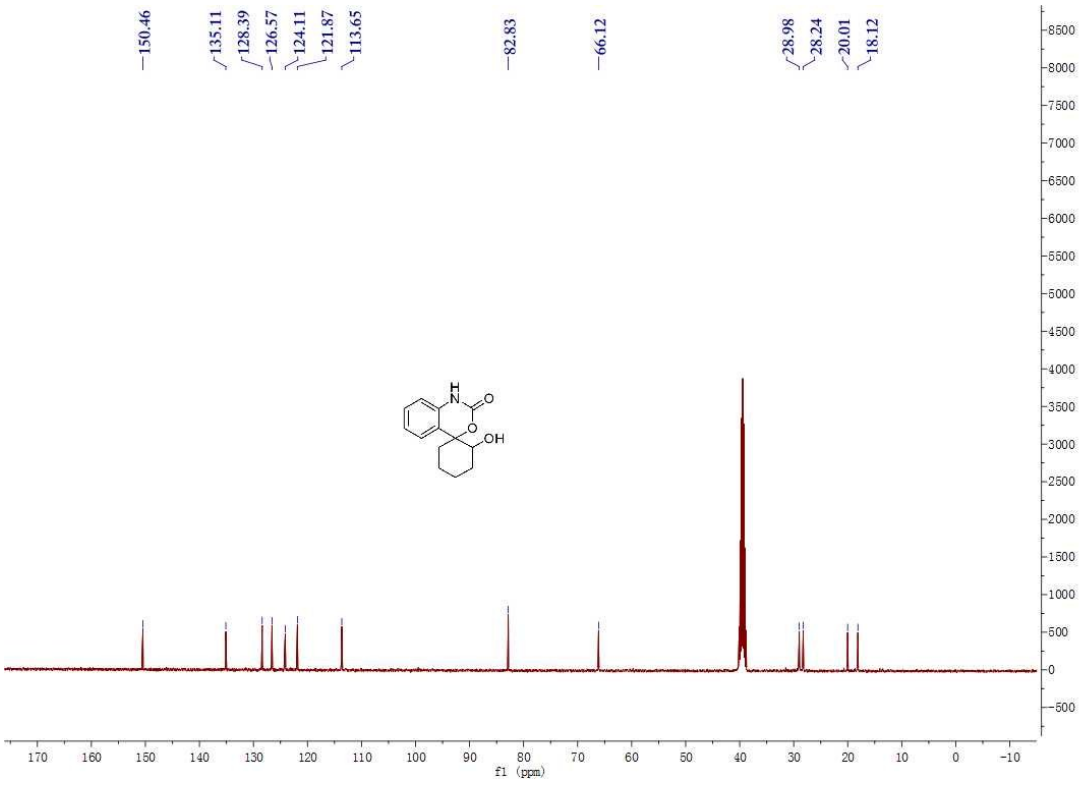
NMR spectra of 5m



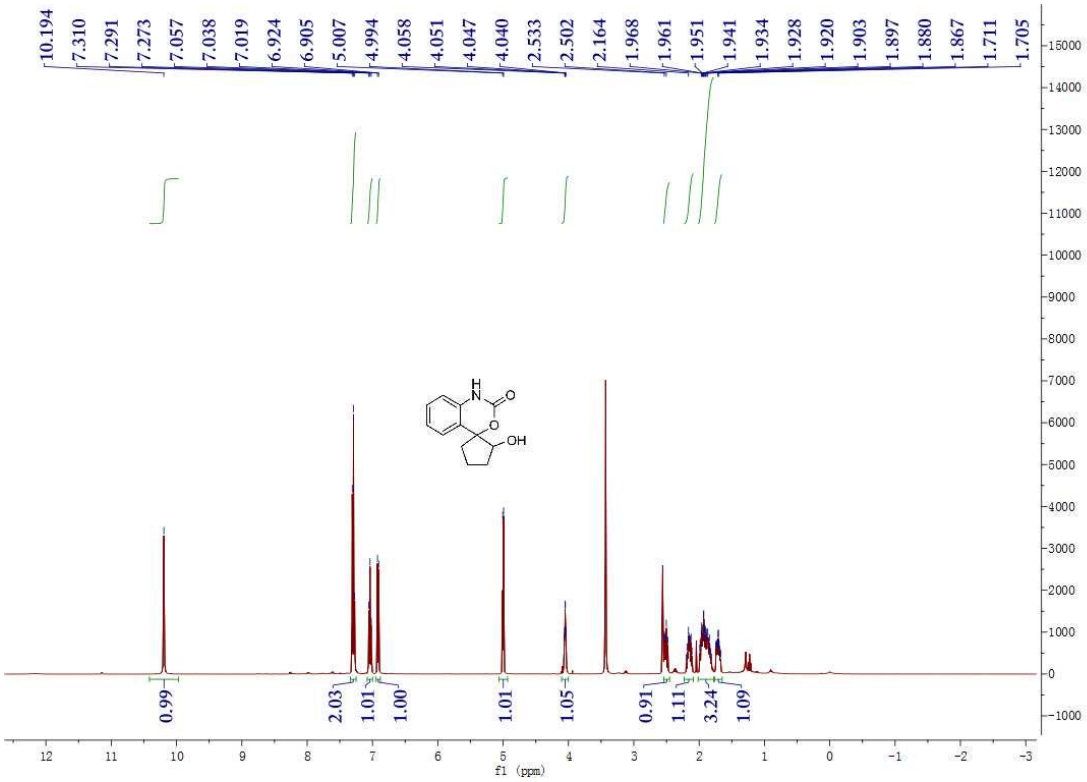


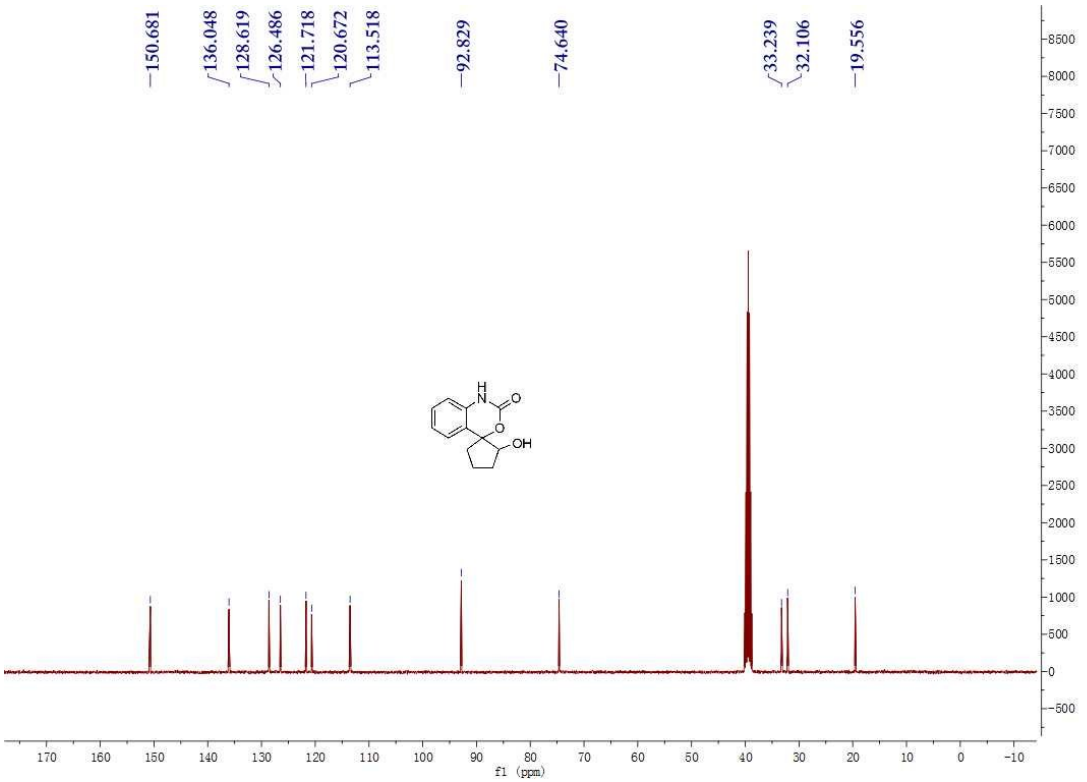
NMR spectra of 5n



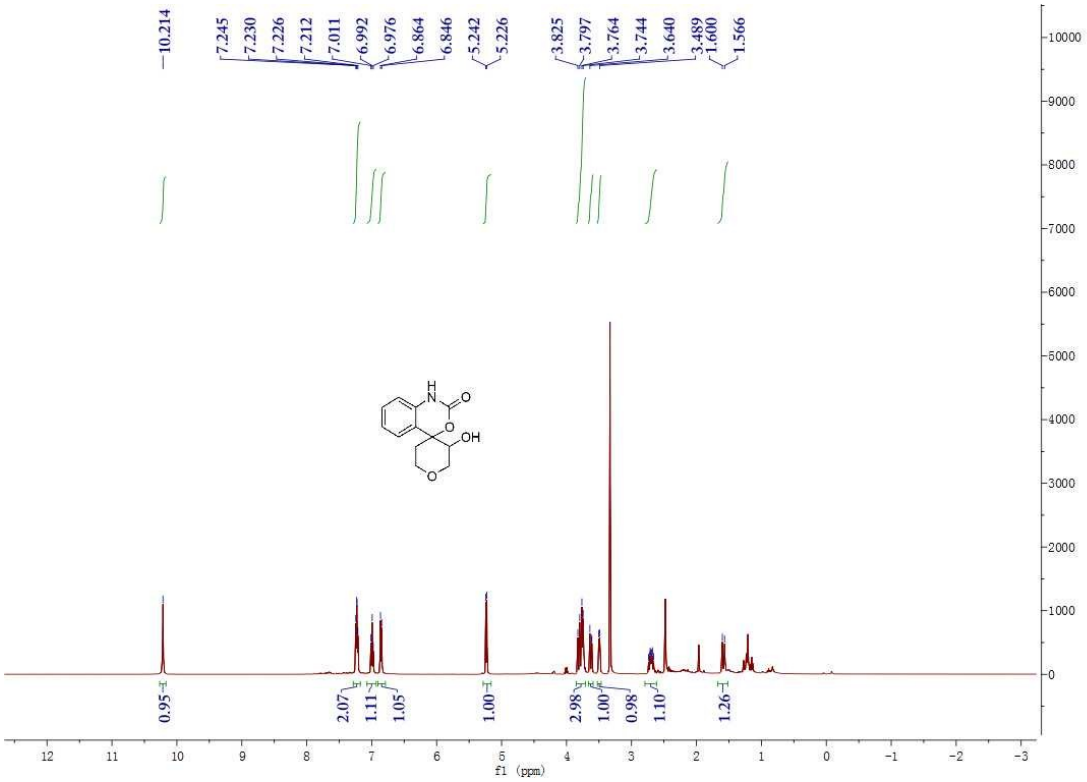


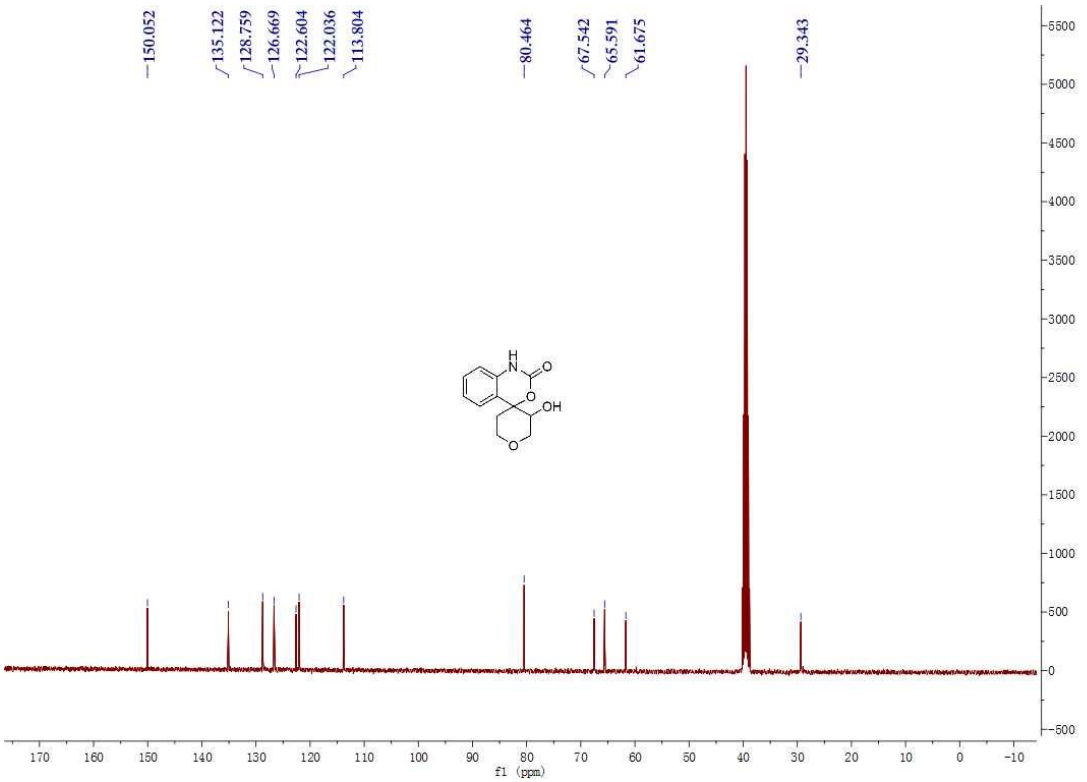
NMR spectra of 5o



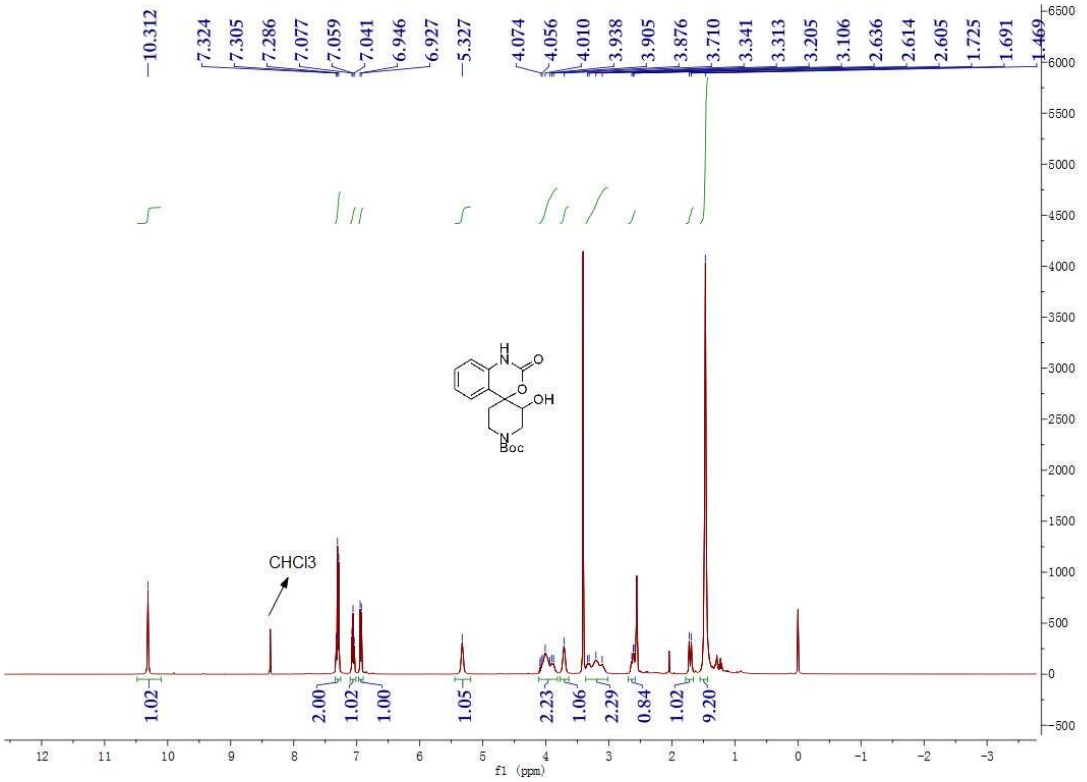


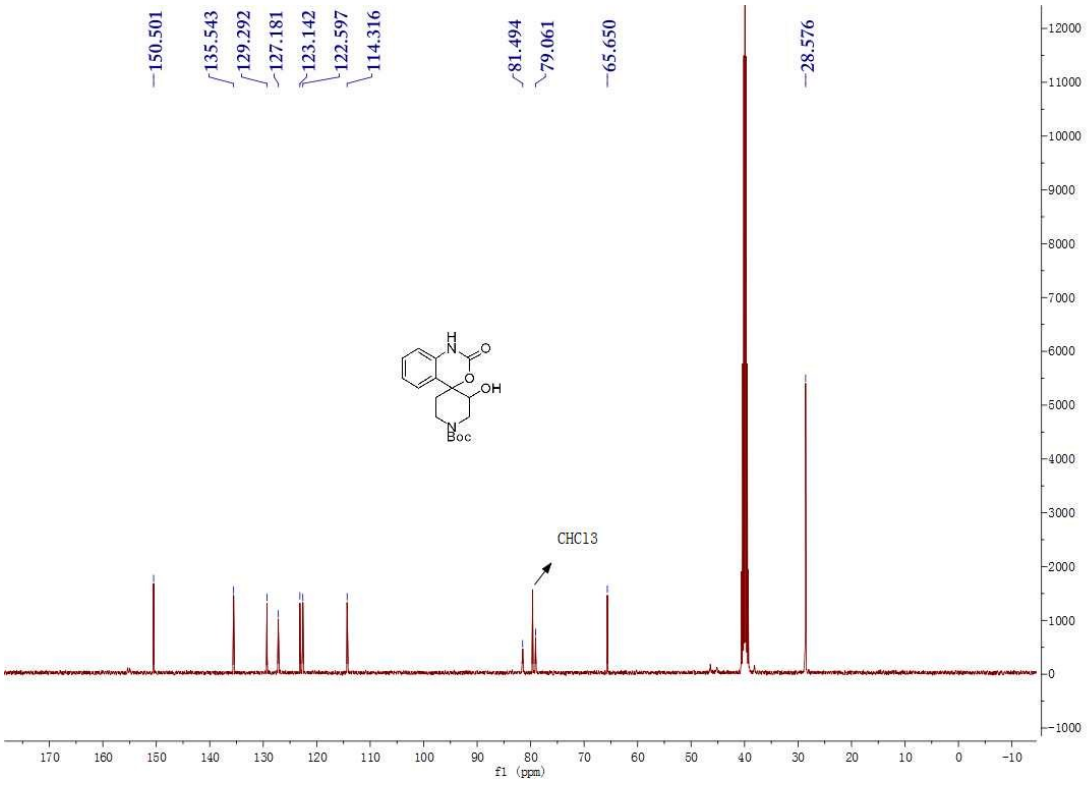
NMR spectra of 5p



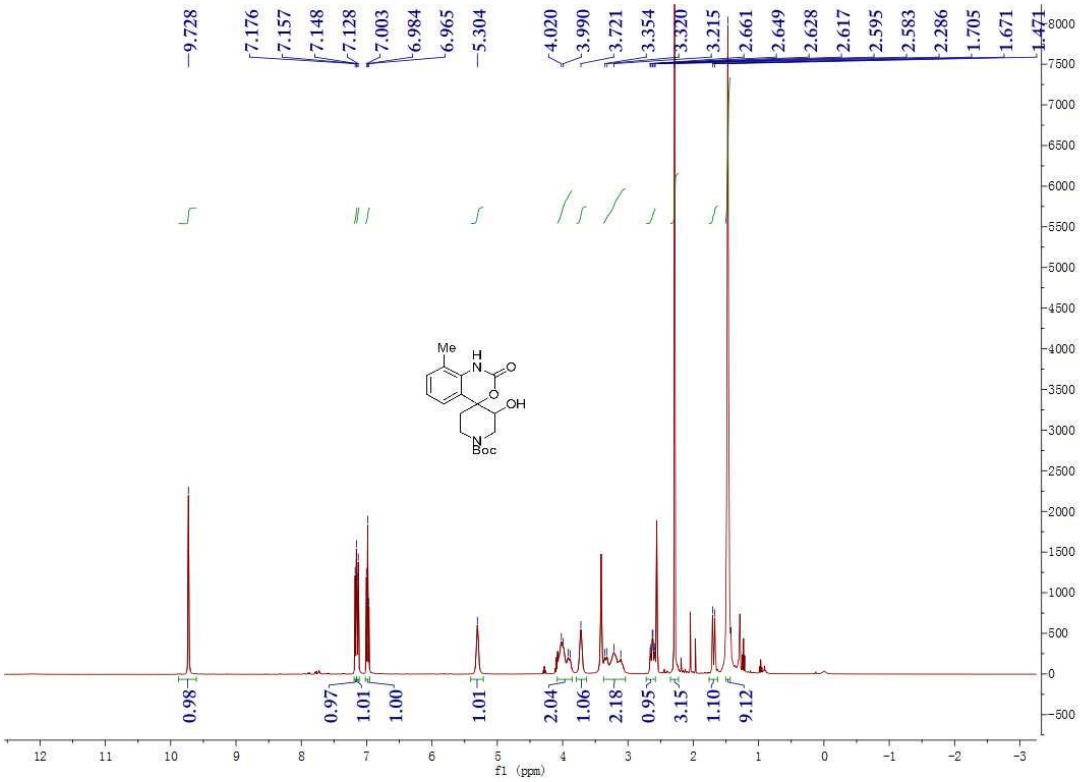


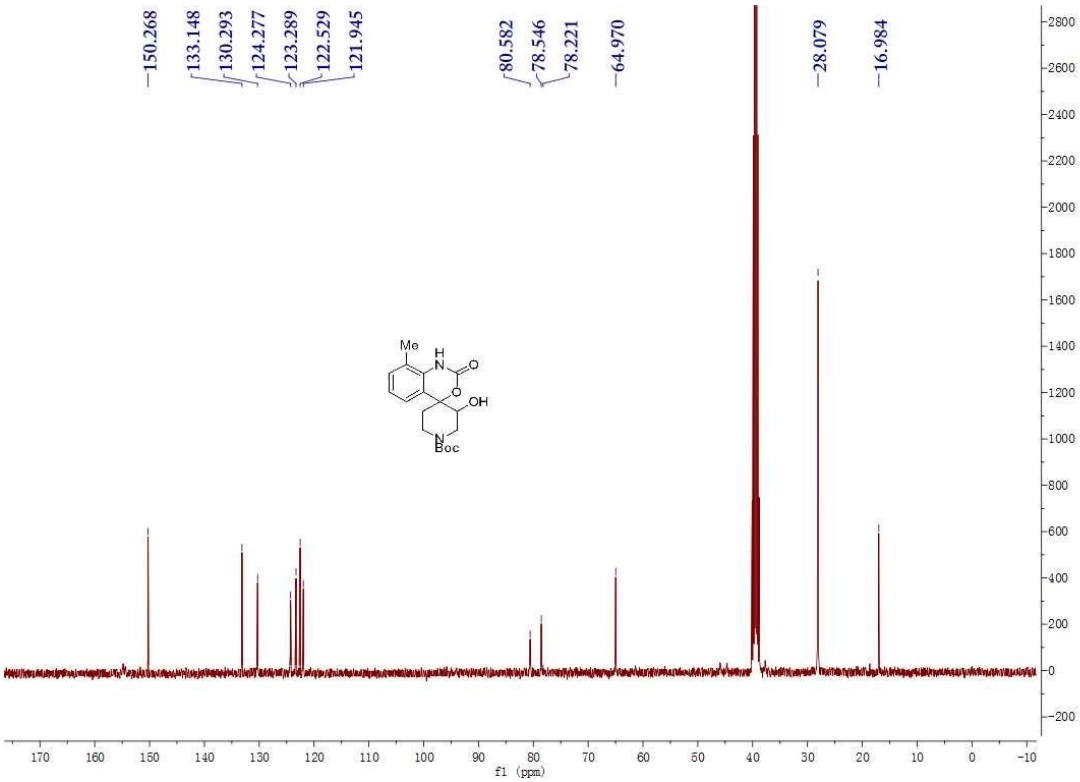
NMR spectra of 5q



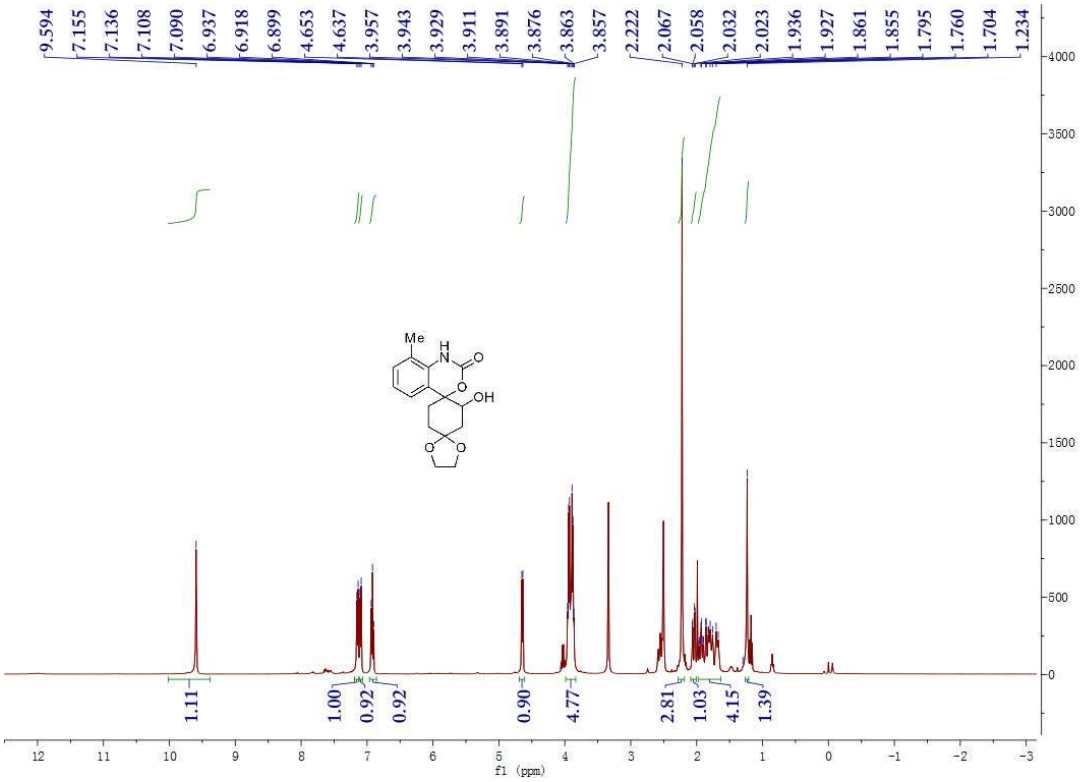


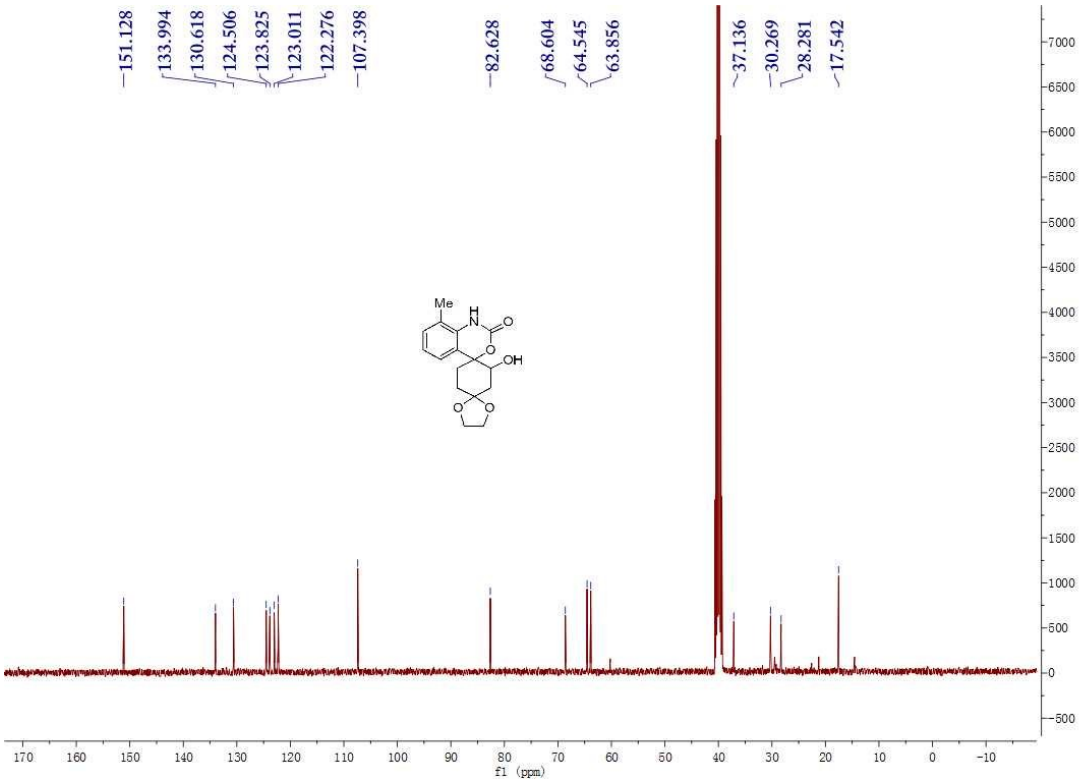
NMR spectra of 5r



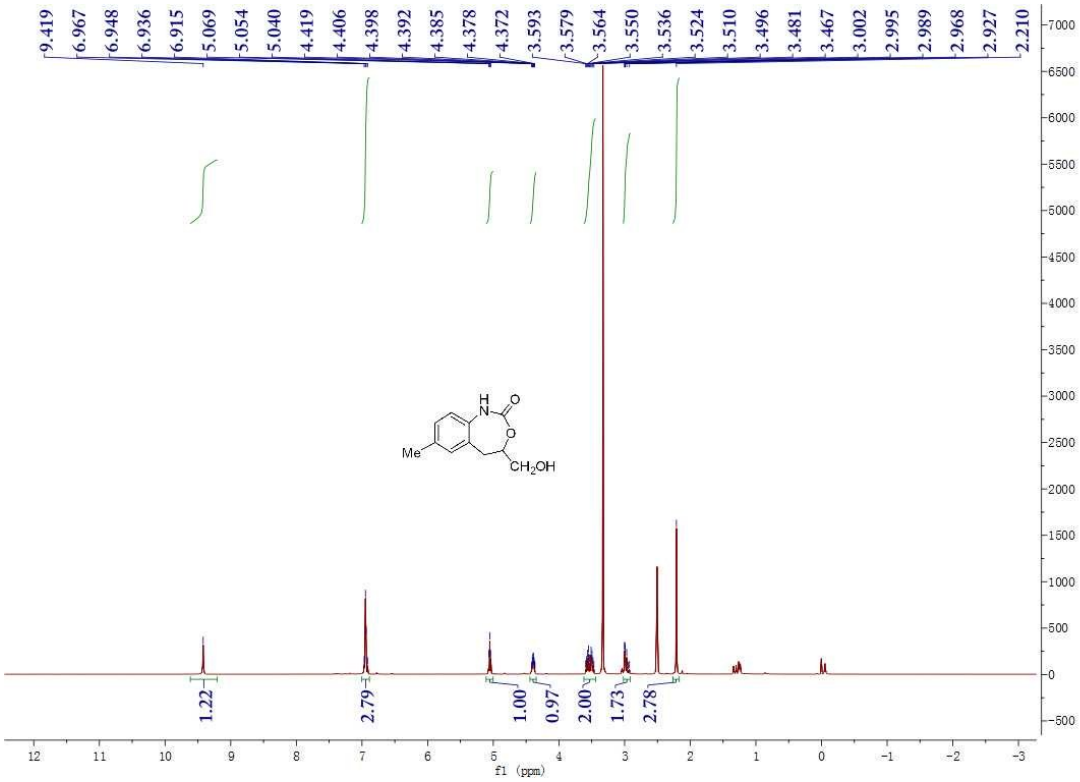


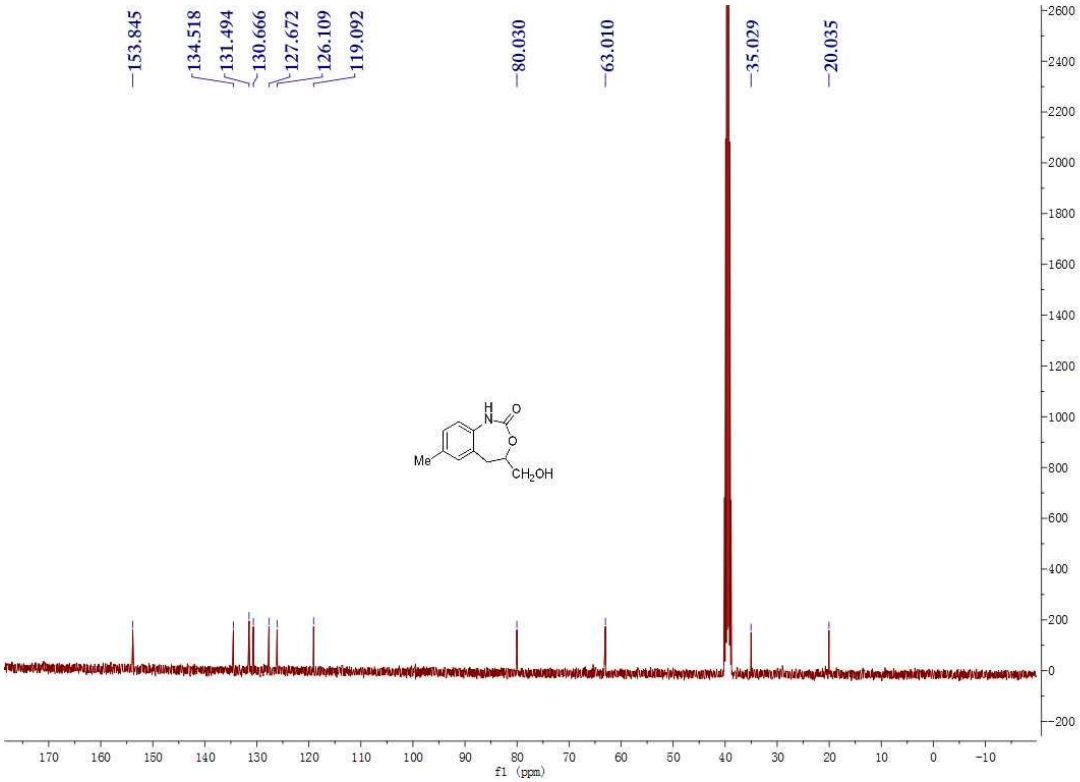
NMR spectra of 5s



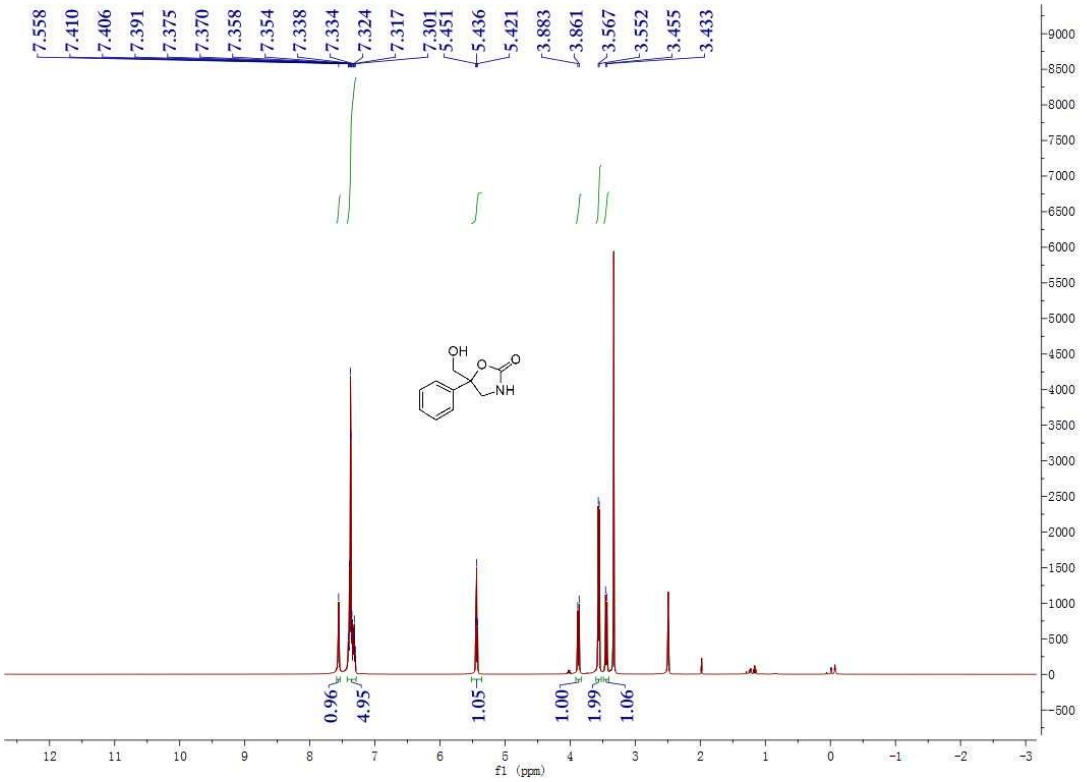


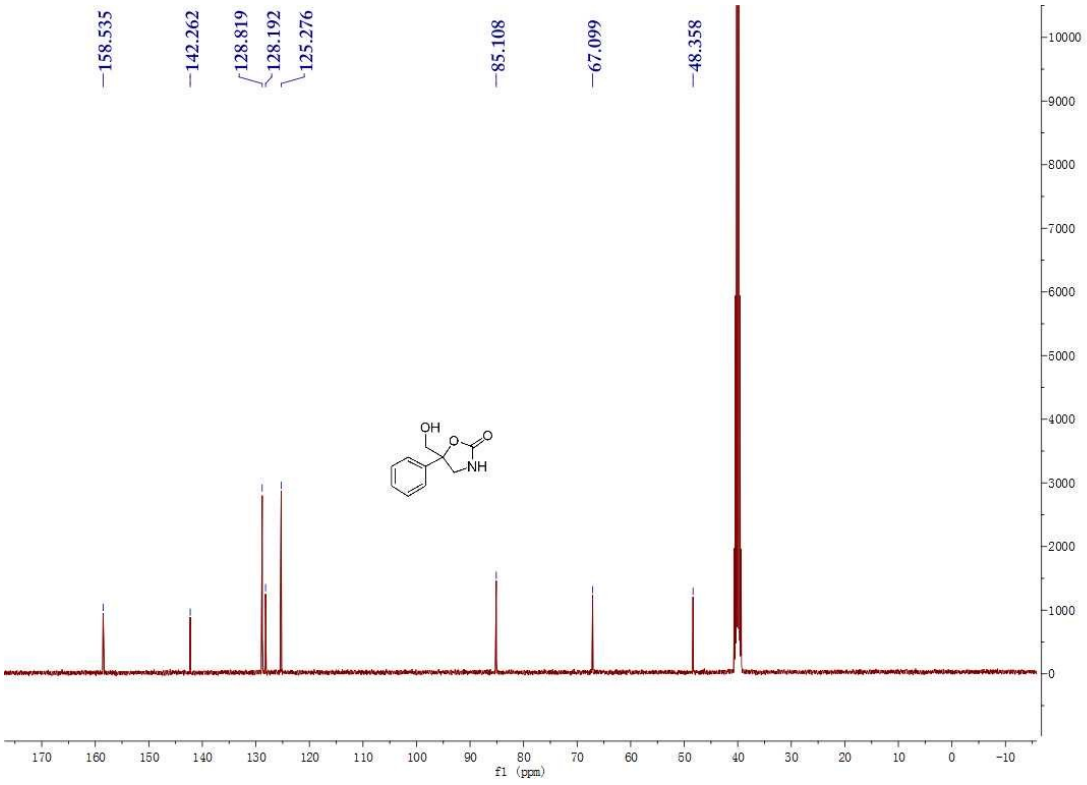
NMR spectra of 7a



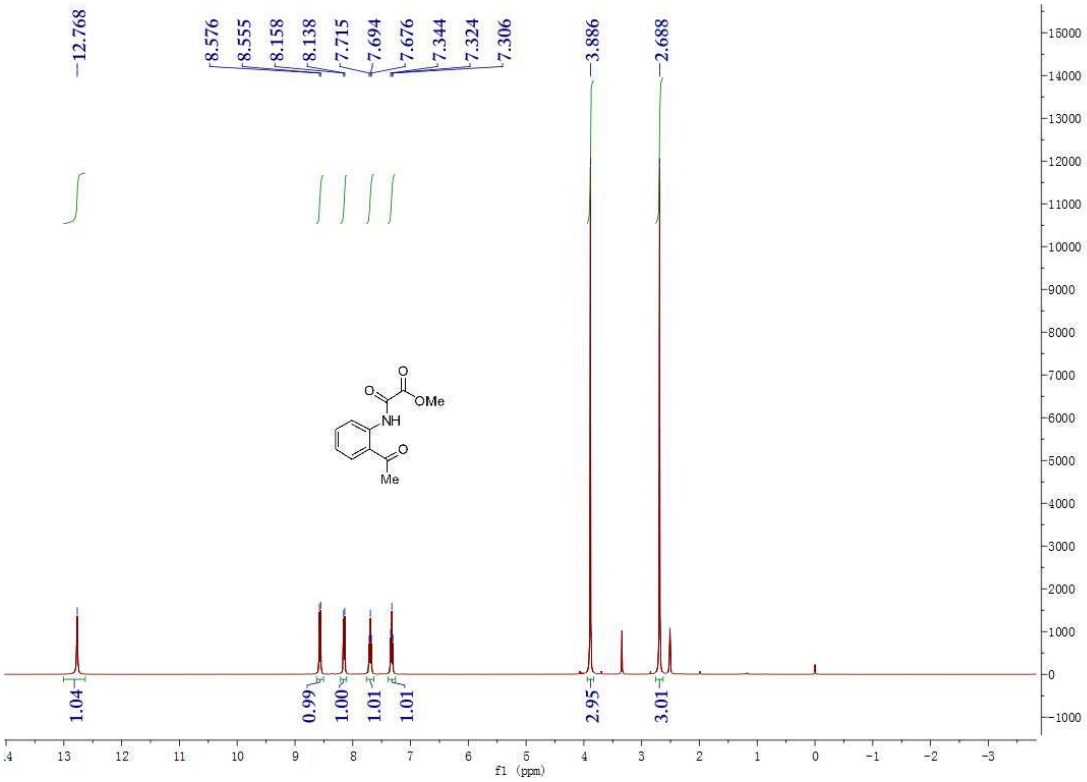


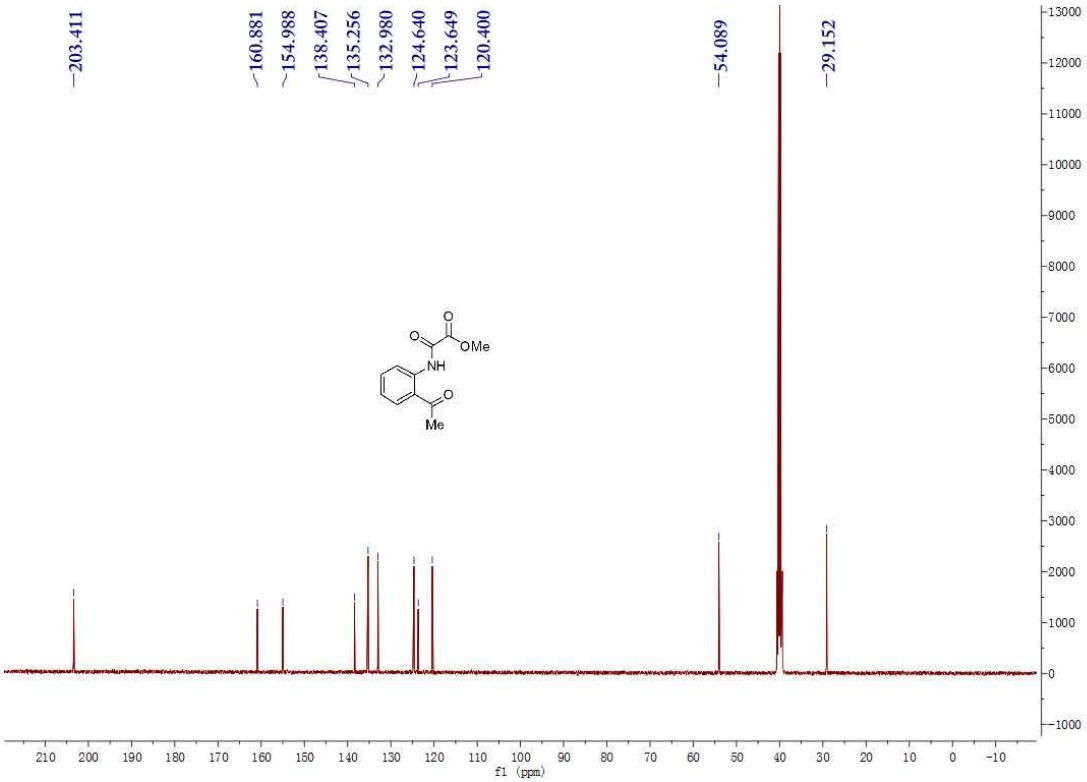
NMR spectra of 9a



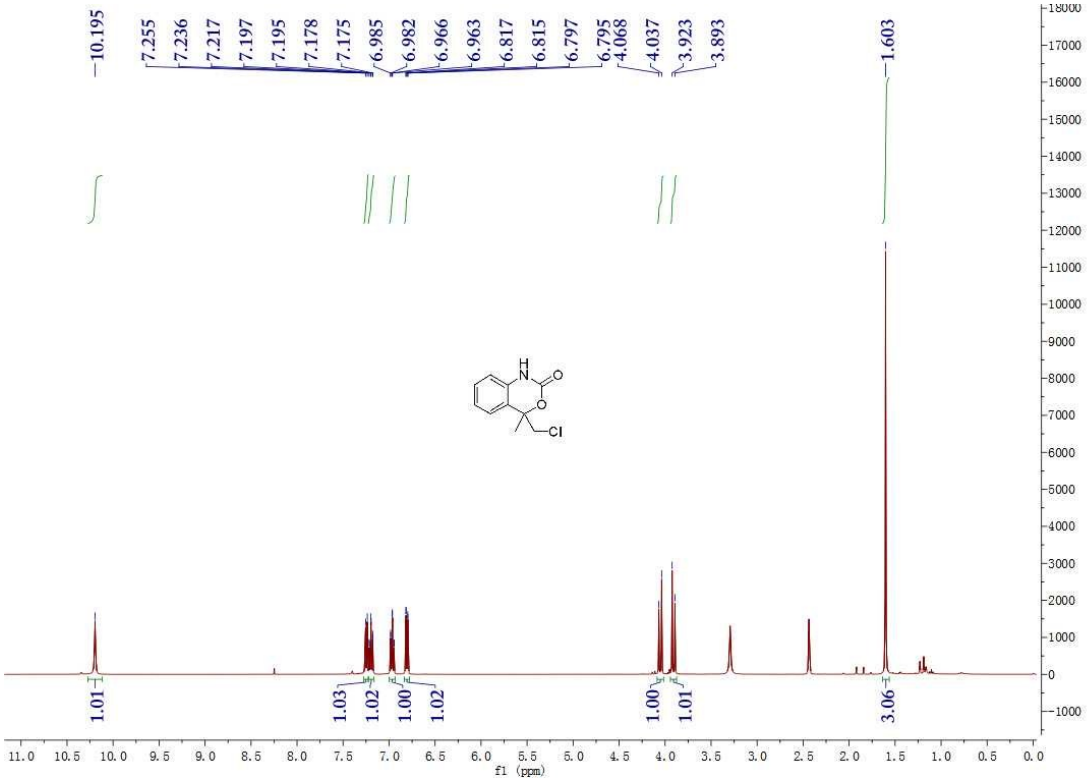


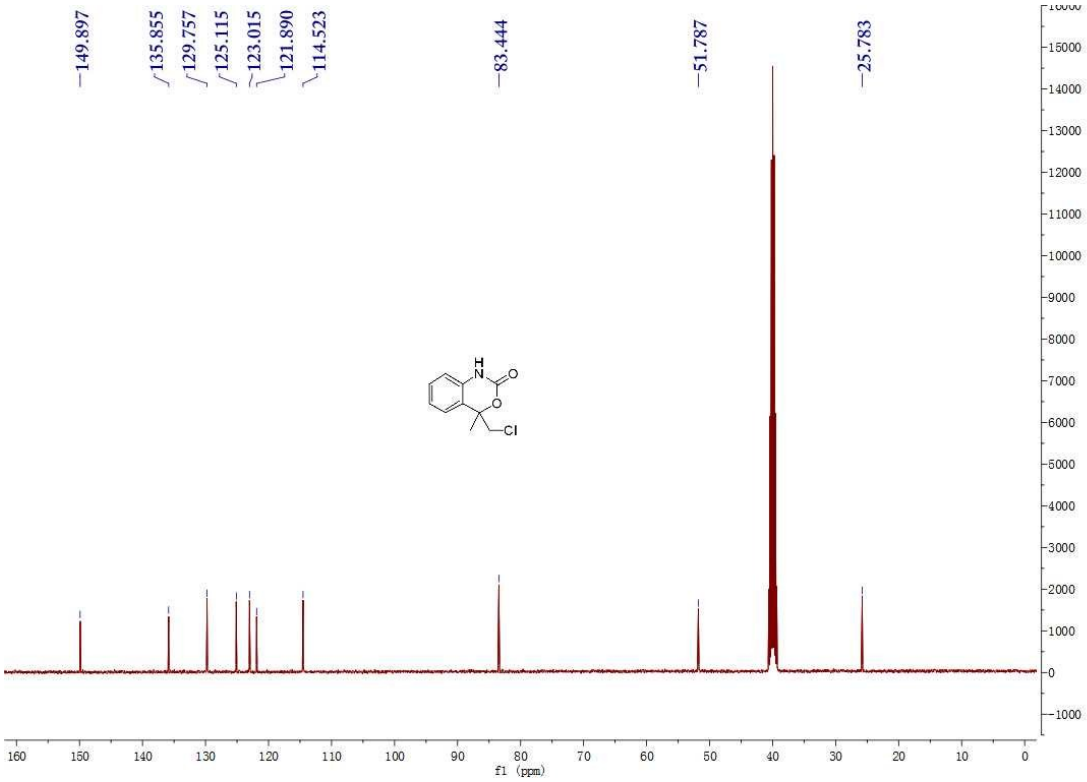
NMR spectra of 12a



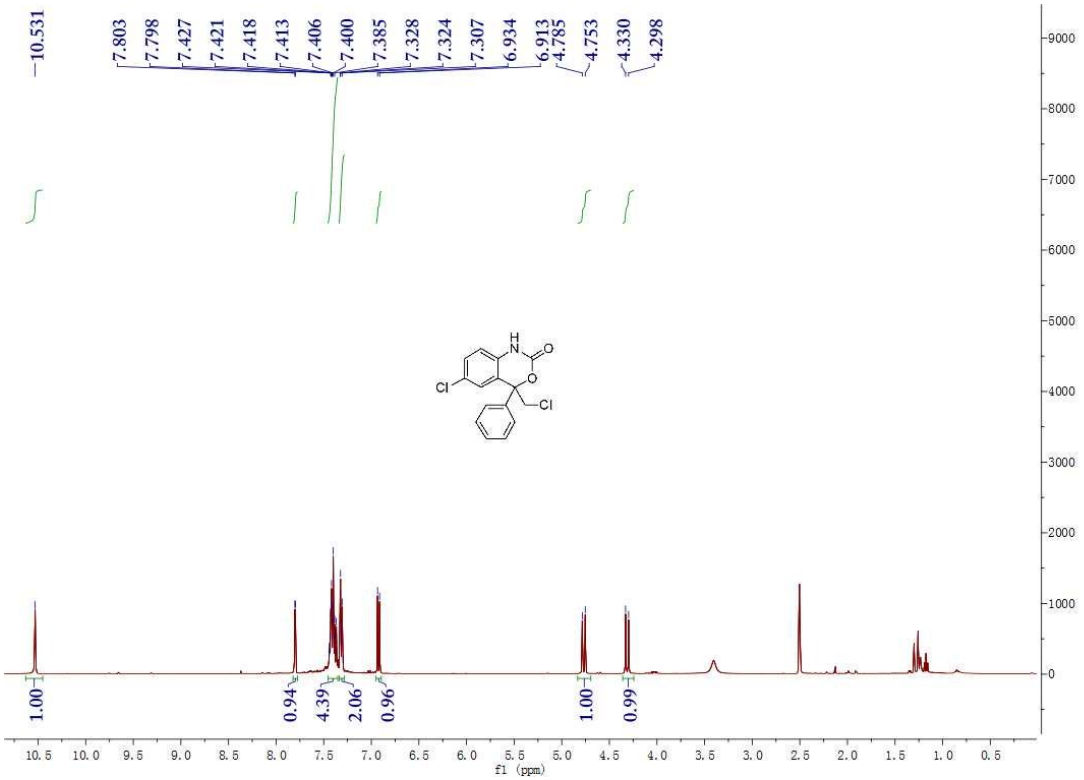


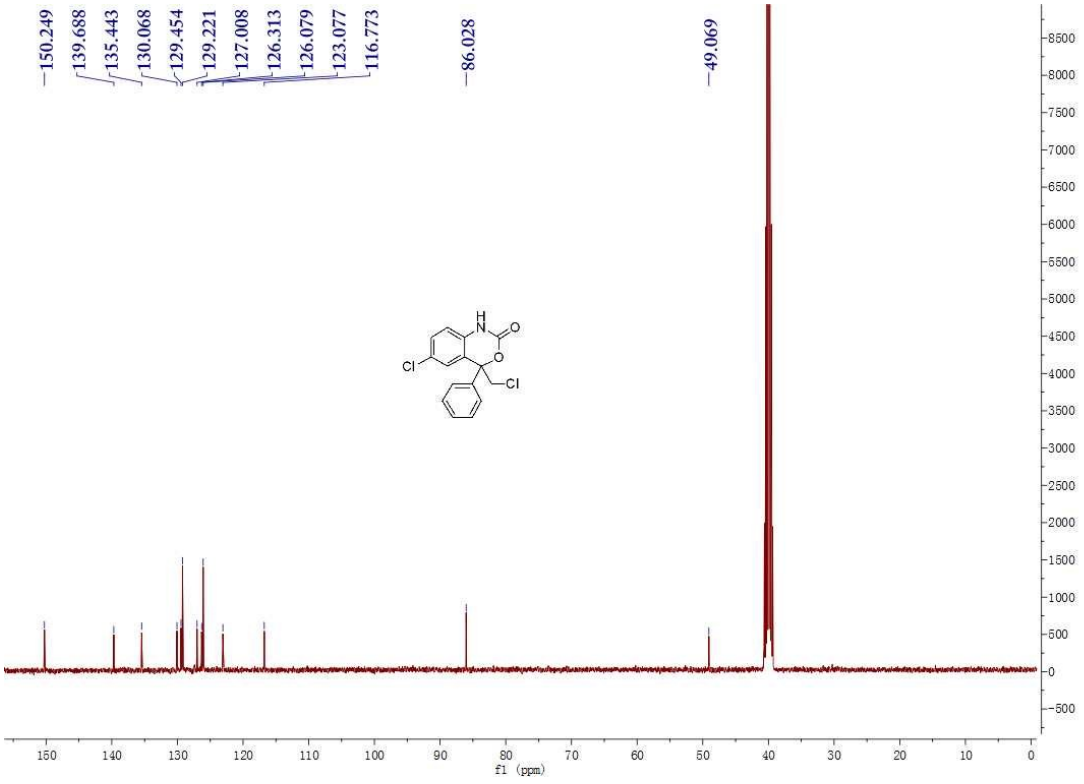
NMR spectra of 10a



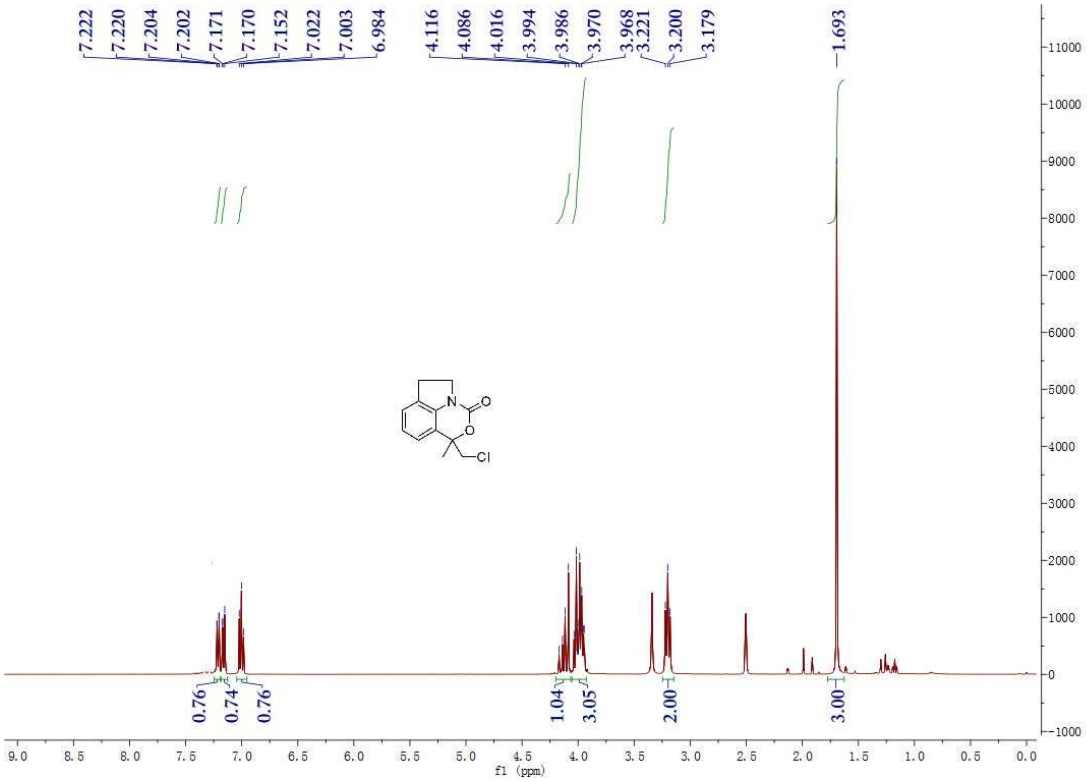


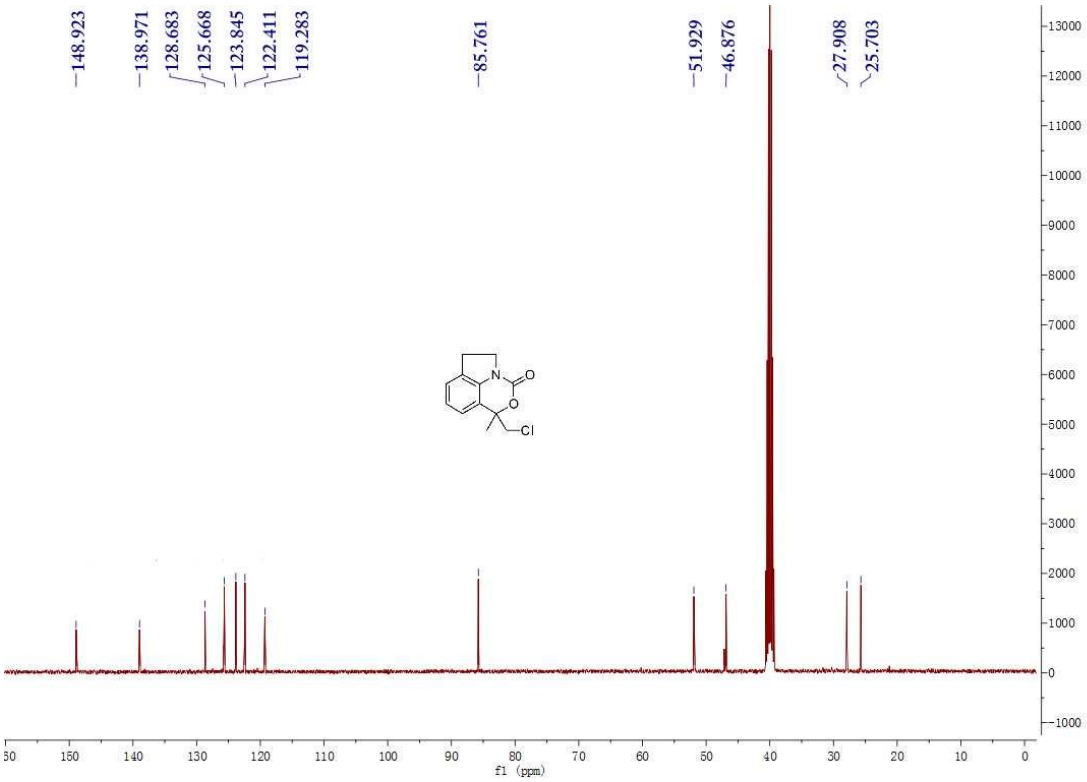
NMR spectra of 10b



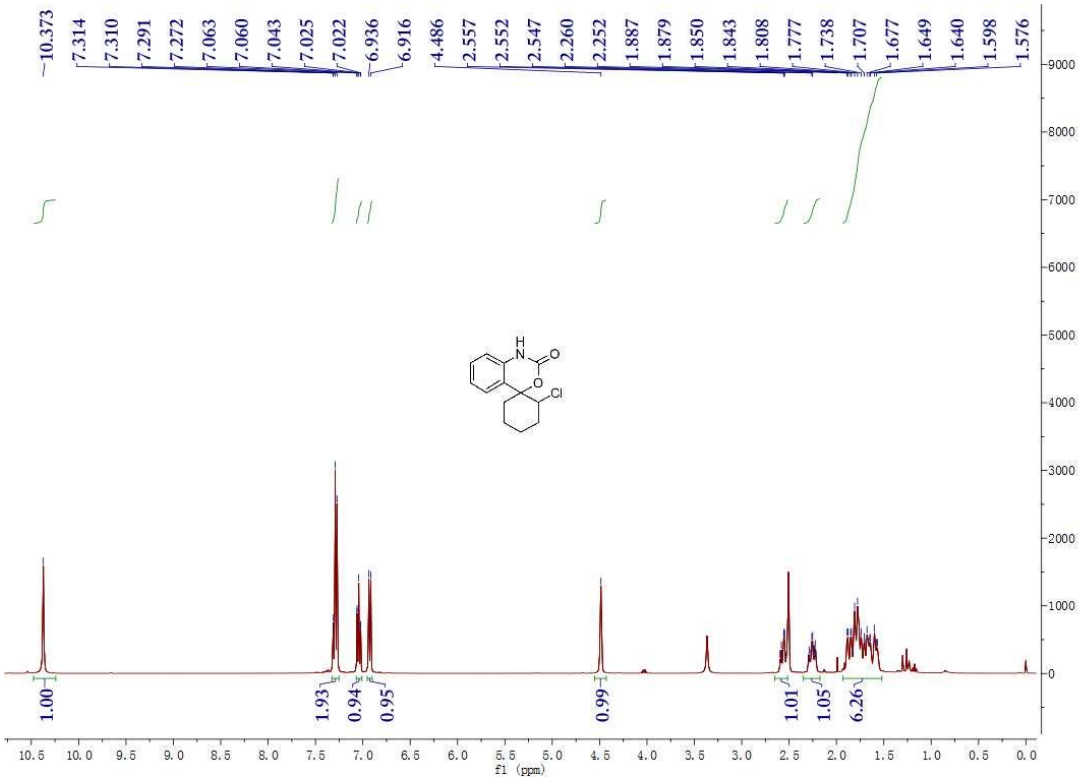


NMR spectra of 10c





NMR spectra of 10d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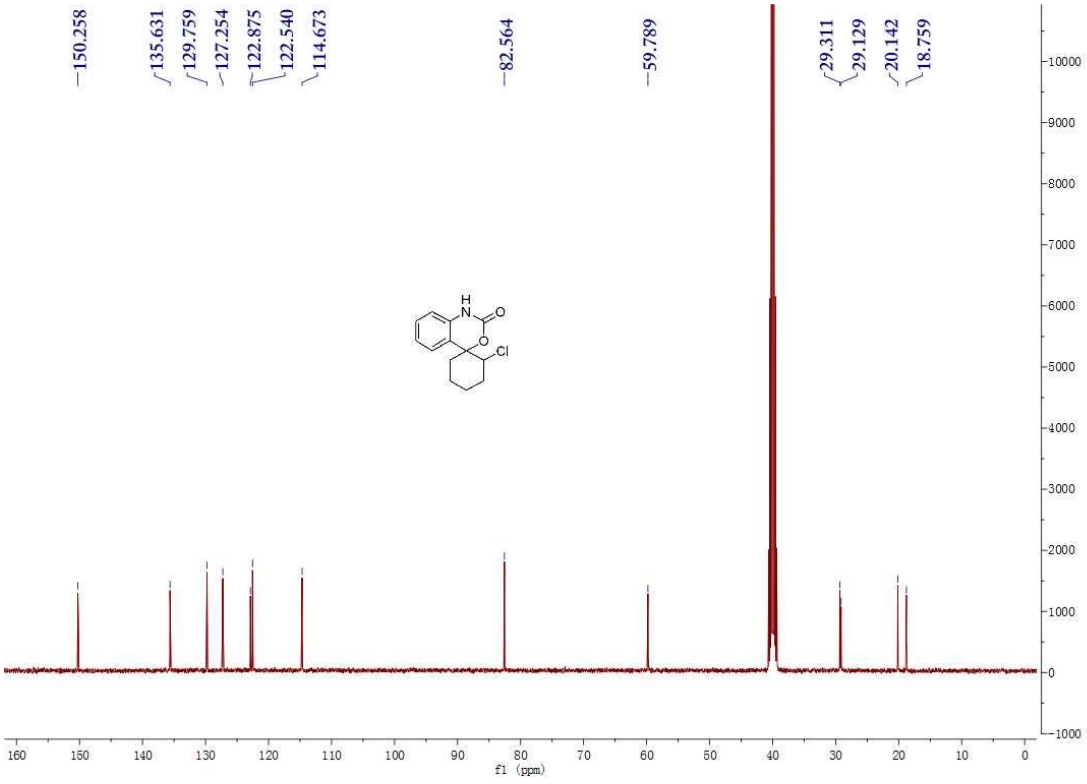
1.05
6.26
f1 (ppm)


150.258
135.631
129.759
127.254
122.875
122.540
114.673
82.564
59.789
29.311
29.129
20.142
18.759
f1 (ppm)