Rhodium(III)-Catalyzed C–H Activation/[4+3] Annulation of *N*-Phenoxyacetamides and α,β-Unsaturated Aldehydes: an Efficient Route to 1,2-Oxazepines at Room Temperature

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Supporting Information

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1. General Information

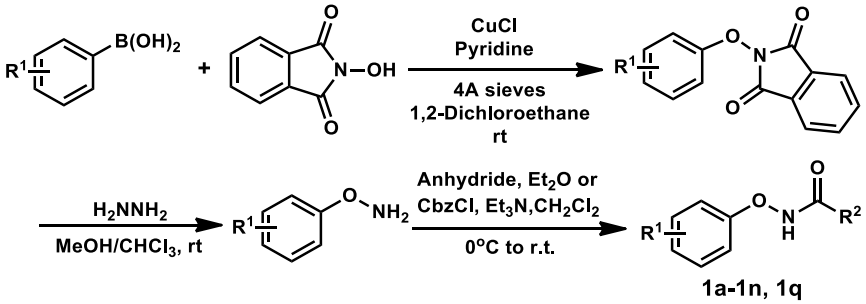
All reactions were carried out under an atmosphere of nitrogen unless otherwise noted. The dry solvents used were purified by distillation and were transferred under nitrogen.

Commercially available reagents were purchased from Adamas-beta, Sigma-Aldrich, Alfa Aesar, TCI, Accela, J&K and Aladdin and used as received unless otherwise stated. Dichloro(pentamethylcyclopentadienyl)rhodium(III) dimer, 99% purchased from Sino compound Technology Co.,Ltd.

Reactions were monitored with analytical thin-layer chromatography (TLC) on silica. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker nuclear resonance (300MHZ, 400 MHz and 500MHz) spectrometers, respectively. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H=7.26 ppm, δ_C=77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm; MeOD-d_4: δ_H=3.31 ppm, δ_C=49.00 ppm; Acetone-d_6: δ_H = 2.05ppm, δ_C = 29.84 ppm, 206.26 ppm; CD_2Cl_2: δ_H=5.32 ppm, δ_C=54.0 ppm). HRMS (ESI) analysis were performed by the Analytical Instrumentation Center at Peking University, Shenzhen Graduate School and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units. All melting points were uncorrected.

2. Synthesis and Characterization of Starting Materials

General procedure for preparation of substrates 1a-1n, 1q.



Following a literature report,[1] in a 50ml round-bottom flask, *N*-hydroxyphthalimide (1.0 eq), cooper (I) chloride (1.0 eq), freshly activated 4 Å molecular sieves (250mg/mmol), and phenylboronic acid (2.0 eq) were combined in 1,2-dichloroethane (0.2 M). The pyridine (1.1 eq) was then added to the suspension. The reaction mixture was open to the atmosphere and stirred at room temperature over 24-48h. Upon completion, silica gel was added to the flask and the solvent was removed under vacuum. The desired *N*-aryloxyphthalimides were obtained by flash column chromatography on silica gel.

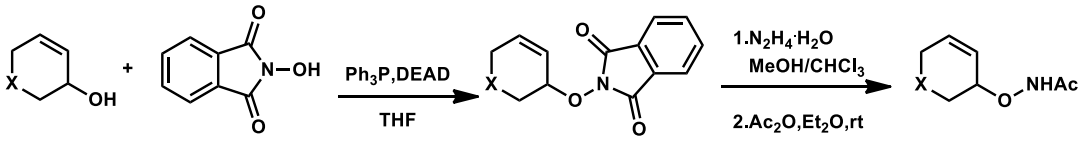
Hydrazine monohydrate (3.0 eq) was added to the solution of *N*-aryloxyphthalimide (1.0 eq) in 10% MeOH in $CHCl_3$ (0.1 M). The reaction was allowed to stir at room temperature overnight. Upon completion, the reaction mixture was filtered off and washed with CH_2Cl_2.The filtrate was concentrated under reduced

pressure, and purified by flash silica gel column chromatography to give the corresponding N-aryloxyamine.

For the synthesis of 1a-1b, 1d-1n, 1q: In a 20 ml round-bottom flask, *N*-aryloxyamine (1.0 eq) was dissolved in ether (0.2 M).The flask was cooled in an ice bath, to which anhydride (2.0 eq) was slowly added. The ice bath was allowed to warm to room temperature and the mixture was stirred for 3 h at room temperature. The reaction mixture was concentrated under reduced pressure and purified by flash silica gel column chromatography to give the corresponding *N*-aryloxyacetamide.

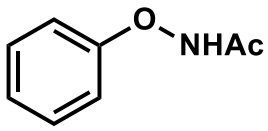
For the synthesis of 1c: In a 20 mL round-bottom flask, *N*-aryloxyamine (1.0 eq) was dissolved in CH_2Cl_2 (0.2 M).The flask was cooled in an ice bath, to which CbzCl (1.2 eq) and Et_3N (1.5 eq) was slowly added. The ice bath was allowed to warm to room temperature and the mixture was stirred for 3 h at room temperature. The reaction mixture was concentrated under reduced pressure and purified by flash silica gel column chromatography to give the corresponding *N*-aryloxyacetamide.

General procedure for preparation of substrates 1o-1p.

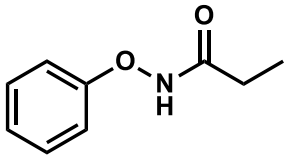


2-Cyclohexen-1-ol or its derivative (1 eq) was added to a solution of 2-hydroxyisoindoline -1,3-dione (1.1 eq) and triphenylphosphine (1.5 eq) in dry THF, then the reaction solution was cooled to 0℃ and DEAD (Diethyl azodicarboxylate) (1.5 eq) was added dropwise. The reaction mixture was warmed to room temperature. After stirring overnight, the reaction solution was concentrated and the residue was purified by column chromatography on silica gel to provide the desired products.
The last two steps are the same as above described.

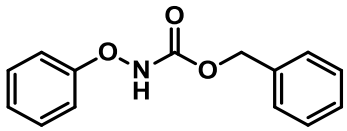
Characterization of Substrates 1



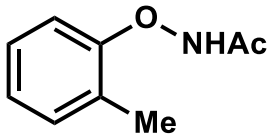
***N*-phenoxyacetamide (1a):** 60% yield, white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.67 (s, 1H), 7.32 (t, J = 7.9 Hz, 2H), 7.01 (t, J = 7.6 Hz, 3H), 1.92 (s, 3H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 167.22, 159.55, 129.45, 122.25, 112.86, 19.43. **IR (cm^{-1})** 3107, 2907, 1645, 1539, 1506, 743, 689. **HRMS (ESI)** calculated for $C_8H_9NO_2Na(+)$: 174.0633; Found: 174.0527. **Melting Point:** 154-156 °C.



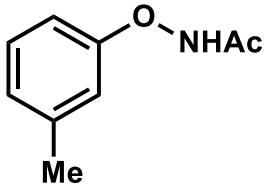
***N*-phenoxypropionamide (1b):** 55% yield, white solid. **^{1}H NMR (500 MHz, DMSO)** δ 11.62 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 6.99 (dd, *J* = 15.1, 7.6 Hz, 3H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, DMSO) δ 171.40, 160.08, 129.88, 122.65, 113.33, 25.85, 9.93. **HRMS (ESI)** calculated for $C_9H_{12}NO_2$(+): 166.0869; Found: 166.0863. **Melting Point:** 139-140 °C.



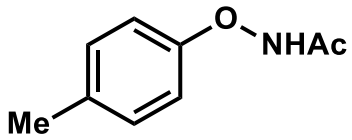
benzyl phenoxycarbamate (1c): 46% yield, colorless oil. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.20 (s, 1H), 7.55 – 7.17 (m, 7H), 7.02 (d, *J* = 8.4 Hz, 3H), 5.16 (s, 2H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 160.22, 157.16, 136.57, 129.91, 128.90, 128.60, 128.37, 122.77, 113.34, 66.90. **HRMS (ESI)** calculated for $C_{14}H_{14}NO_3$(+):244.0793; Found: 244.0793.



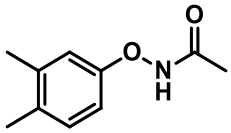
***N*-(*o*-tolyloxy)acetamide (1d):** 56% yield, white solid. **1H NMR (400 MHz, DMSO-d_6)** δ 11.62 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 2.21 (s, 3H), 1.92 (s, 3H); **^{13}C NMR (101MHz, DMSO-d_6)** δ 167.09, 157.46, 130.69, 126.87, 123.50, 121.99, 111.54, 19.44, 15.48.**IR (cm^{-1}):**3177，2984，2808，1653, 1506, 1456, 1119, 991, 750. **HRMS (ESI)** calculated for $C_9H_{11}NO_2Na$ (+): 188.0790; Found: 188.0682. **Melting Point:** 122-125 °C.



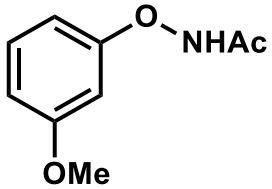
***N*-(*m*-tolyloxy)acetamide (1e):** 50% yield, white solid. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 10.75 (s, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.85 (d, *J* = 14.0 Hz, 3H), 2.29 (s, 3H), 1.97 (s, 3H); **^{13}C NMR (101 MHz, Acetone-d_6)** δ 167.75, 160.08, 139.21, 129.01, 122.99, 113.51, 109.98, 20.54, 18.75. **HRMS (ESI)** calculated for $C_9H_{11}NO_2Na$ (+): 188.0790; Found: 188.0682. **Melting Point:** 119-120 °C.



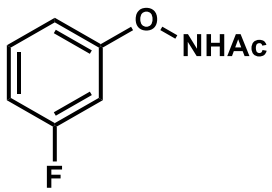
***N*-(*p*-tolyloxy)acetamide (1f):** 45% yield, white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.61 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 2.24 (s, 3H), 1.90 (s, 3H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 167.58, 158.00, 131.51, 130.14, 113.28, 20.52, 19.84. **HRMS (ESI)** calculated for $C_9H_{11}NO_2Na(+)$: 188.0790; Found: 188.0682. **Melting Point:** 141-143 °C.



***N*-(3,4-dimethylphenoxy)acetamide (1g):** 45% yield, white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.57 (s, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.78 (s, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 2.19 (s, 3H), 2.14 (s, 3H), 1.89 (s, 3H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 167.41, 158.08, 137.70, 130.43, 130.15, 114.38, 110.36, 19.99, 19.85, 18.87. **HRMS (ESI)** calculated for$C_{10}H_{14}NO_2(+)$: 180.1020; Found:180.1019. **Melting Point:** 140-142 °C.

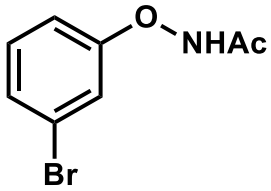


***N*-(3-methoxyphenoxy)acetamide (1h):** 50% yield, brick-red solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.62 (s, 1H), 7.20 (t, *J* = 8.1 Hz, 1H), 6.75 – 6.48 (m, 3H), 3.73 (s, 3H), 1.90 (s, 3H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 167.61, 161.30, 160.88, 130.47, 108.23, 105.50, 99.59, 55.68, 19.83. **IR (cm^{-1}):** 3177, 2957, 1684, 1607, 1489, 1134, 685. **HRMS (ESI)** calculated for $C_9H_{11}NO_3Na(+)$:204.0739 ; Found: 204.0631. **Melting Point:** 98-100 °C.

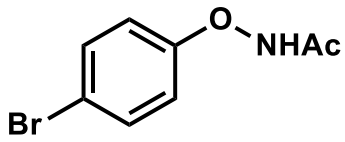


***N*-(3-fluorophenoxy)acetamide(1i):** 35% yield, white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.76 (s, 1H), 7.34 (dd, *J* = 15.4, 8.0 Hz, 1H), 6.85 (dd, *J* = 15.3, 9.9 Hz, 3H), 1.92 (s, 3H); **^{13}C NMR (101MHz,DMSO-d_6)** δ 167.92, 163.27 (J_{1F} = 244.5), 161.52 (J_{3F} = 10.6), 131.28 (J_{3F} = 10.2),109.56, 109.34 (J_{2F} = 21.4), 101.12 (J_{2F} = 26.7), 19.85. **HRMS (ESI)** calculated for $C_8H_8NO_2FNa(+)$: 192.0539; Found:

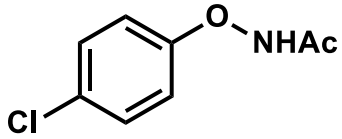
192.0430. **Melting Point:** 149-151 °C.



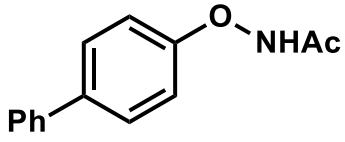
***N*-(3-bromophenoxy)acetamide (1j):** 30% yield, white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.76 (s, 1H), 7.27 (t, J = 8.2 Hz, 1H), 7.21 (d, J = 5.4 Hz, 2H), 7.03 (d, J = 8.1 Hz, 1H), 1.92 (s, 3H); **^{13}C NMR (101 MHz, DMSO-d_6)**:δ167.91, 160.93, 131.72, 125.63, 122.43, 116.24, 112.84, 19.84. **IR (cm^{-1})**: 3102, 2911, 1653, 1506, 991, 779. **HRMS (ESI)** calculated for $C_8H_8NO_2NaBr(+)$: 251.9738; Found: 251.9631. **Melting Point:** 129-131 °C.



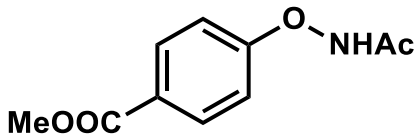
***N*-(4-bromophenoxy)acetamide (1k):** 35% yield, white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.74 (s, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 1.91 (s, 3H); **^{13}CNMR (101 MHz, DMSO-d_6)** δ 167.88, 159.37, 132.58, 115.71, 114.05, 19.86. **HRMS (ESI)** calculated for $C_8H_8NO_2NaBr(+)$: 251.9738; Found: 251.9630. **Melting Point:** 163-165 °C.



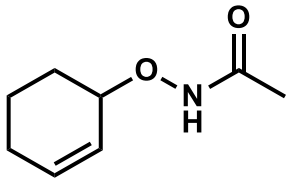
***N*-(4-chlorophenoxy)acetamide (1l):**45% yield, white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.74 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 1.91 (s, 3H); **^{13}C NMR (101MHz, DMSO-d_6)** δ 167.88, 158.89, 129.68, 126.34, 115.22, 19.87. **IR (cm^{-1}):**3109, 2911, 1663, 1506, 989, 824. **HRMS (ESI)** calculated for $C_8H_8NO_2NaCl(+)$: 208.0244; Found: 208.0137. **Melting Point:** 151-153 °C.



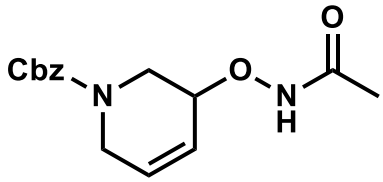
***N*-([1,1'-biphenyl]-4-yloxy)acetamide (1m):** 37% yield, white solid. **^{1}H NMR (400 MHz, DMSO)** δ 11.76 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 1.91 (s, 3H); **^{13}C NMR (101 MHz, DMSO)** δ 167.55, 159.76, 140.12, 134.65, 129.36, 128.17, 127.41, 126.80, 113.89,19.92. **HRMS (ESI)** calculated for $C_{14}H_{13}NO_2Na(+)$: 250.0844; Found: 250.0839. **Melting Point:** 182-183 °C.



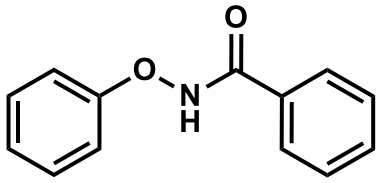
methyl 4-(acetamidooxy)benzoate (1n): 25% yield, white solid. **^{1}H NMR (400 MHz, DMSO)** δ 11.83 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 1.93 (s, 3H); **^{13}C NMR (101 MHz, DMSO)** δ 167.93, 166.12, 163.73, 131.66, 124.10, 113.42, 52.41, 19.82. **HRMS (ESI)** calculated for $C_{10}H_{12}NO_4$(+): 210.0767; Found: 210.0759. **Melting Point:** 163-165 °C.



***N*-(cyclohex-2-en-1-yloxy)acetamide (1o):** 76% yield, white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.58 (s, 1H), 5.98 (d, J=17.8, 1H), 5.80 (s, 1H), 4.31 (d, J=81.4, 1H), 2.18 – 1.96 (m, 3H), 1.84 (m, 4H), 1.79 – 1.48 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.33, 133.57, 125.02, 78.58, 26.89, 25.19, 19.74, 18.63. **HRMS (ESI)** calculated for $C_8H_{13}NO_2Na$(+):178.0844; Found: 178.0838. **Melting Point:** 50-52 °C.



benzyl 5-(acetamidooxy)-5,6-dihydropyridine-1(2H)-carboxylate (1p): 80% yield, colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.39 (s, 1H), 7.29 (d, *J* = 28.5 Hz, 5H), 5.97 (d, *J* = 24.0 Hz, 2H), 5.20 (dd, *J* = 40.2, 12.8 Hz, 1H), 5.08 (d, *J* = 12.3 Hz,1H), 4.53 – 3.94 (m, 3H), 3.74 (d, *J* = 18.9 Hz, 1H), 3.24 (dd, *J* = 96.4, 13.3 Hz, 1H), 2.18 – 1.53 (m, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.12, 156.31, 136.32, 131.01, 128.59, 128.21, 127.86, 123.19, 74.47, 67.60, 44.02, 43.03, 19.74. **HRMS (ESI)** calculated for $C_{15}H_{18}N_2O_4Na$(+):313.1165; Found: 313.1158.



***N*-phenoxybenzamide (1q):** 48% yield, white solid. **^{1}H NMR (500 MHz, DMSO)** δ 12.49 (s, 1H), 7.95 – 7.85 (m, 2H), 7.60 (t, *J*=7.0, 1H), 7.53 (t, *J*=7.5, 2H), 7.35 (t, *J*=8.0, 2H), 7.11 (d, *J*=7.2, 2H), 7.04 (t, *J*=7.3, 1H). **^{13}C NMR (126 MHz, DMSO)** δ 165.53, 160.16, 132.49, 132.07, 129.95, 129.08, 127.77, 122.83, 113.57. **HRMS (ESI)** calculated for $C_{13}H_{12}NO_2$(+): 214.0869; Found: 214.0862. **Melting Point:** 150-152

^{o}C.

3. Condition Screening

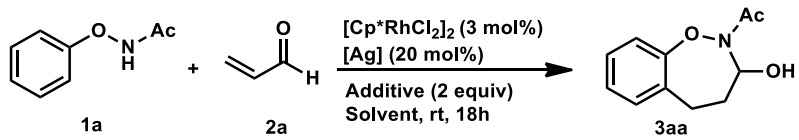
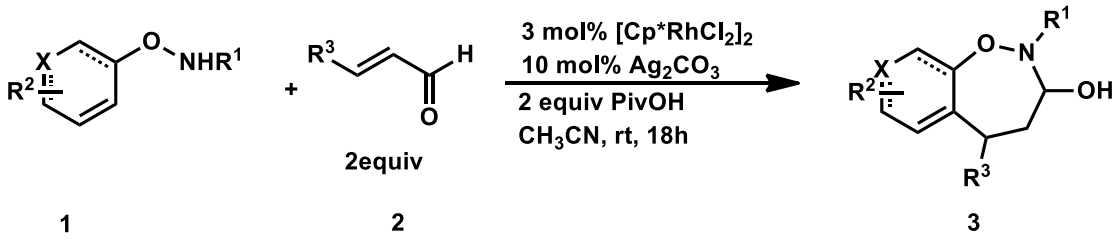


Table S1. Optimization of reaction conditions

Entry	[Ag]	Acid	Solvent	Yield[%][b]
1	Ag_2CO_3	AcOH	CH_3CN	71
2	-	AcOH	CH_3CN	NR
3	Ag_2CO_3	PivOH	CH_3CN	98(93)[c]
4	AgOAc	PivOH	CH_3CN	89[c]
5	$AgSbF_6$	PivOH	CH_3CN	NR
6	$AgBF_4$	PivOH	CH_3CN	NR
7	Ag_2CO_3	PivOH	DCE	95
8	Ag_2CO_3	PivOH	DCM	97
9	Ag_2CO_3	PivOH	THF	96
10	Ag_2CO_3	PivOH	MeOH	87
11	Ag_2CO_3	PivOH	*t*-AmOH	94
12	Ag_2CO_3	PivOH	Dioxane	96
13[d]	Ag_2CO_3	PivOH	CH_3CN	NR
14[e]	-	AcOH	CH_3CN	40%
15[e]	-	PivOH	CH_3CN	57%
16[e]	-	-	CH_3CN	33%

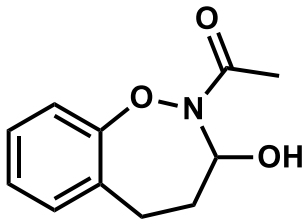
[a]Conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (3 mol%), [Ag] (20 mol%), solvent (1 mL), rt, under N_2. [b]Yield determined by NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard. [c]isolated yield. [d]Without $[Cp^*RhCl_2]_2$ catalyst. [e]$Cp^*Rh(OAc)_2$ was used as the catalyst.

4. Experimental Procedure and Characterization of Products

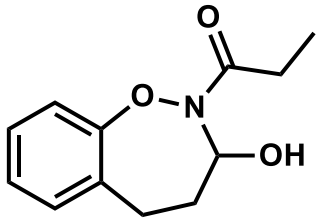


N-Phenoxyacetamides substrates (1) (0.4 mmol), $[Cp^*RhCl_2]_2$ (3 mol%), Ag_2CO_3 (10 mol%) and PivOH (2 equiv) were weighed into a 15ml pressure tube, to which was added unsaturated aldehyde (2 equiv) in CH_3CN (2 mL) in a glove box. The reaction vessel was stirred at room temperature for 18h. Then the reaction mixture was filtered, the solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc=1:1) to give the desired product.

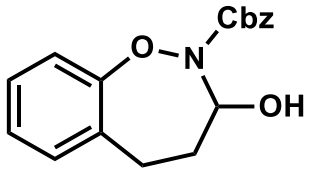
Characterization Data



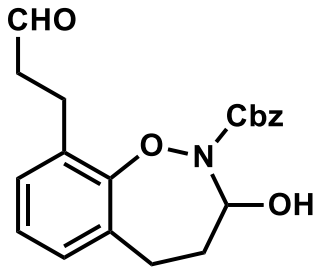
1-(3-hydroxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone (3aa): 93% yield, yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (dd, *J* = 7.1, 5.5 Hz, 2H), 7.07 (dt, *J* = 14.0, 4.6 Hz, 2H), 6.01 (t, *J* = 7.5 Hz, 1H), 3.90 (m, 1H), 2.94 – 2.85 (m, 2H), 2.36 (dd, *J* = 7.8, 4.3 Hz, 2H), 2.24 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.98, 158.21, 131.52, 129.82, 126.92, 124.79, 117.92, 80.11, 30.08, 27.78, 21.77. **IR (cm^{-1}):**3334, 2940, 2359, 1653, 1386, 760. **HRMS (ESI)** calculated for $C_{11}H_{13}NO_3Na(+)$: 230.0793; Found: 230.0787. **Melting Point:** 86-88 °C.



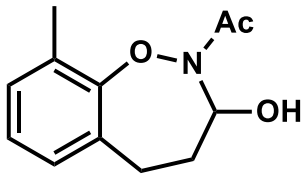
1-(3-hydroxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)propan-1-one (3ba): 86% yield, white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.22 – 7.11 (m, 2H), 7.10 – 7.03 (m, 2H), 6.00 (t, *J*=7.5, 1H), 3.68 – 3.51 (m, 1H), 3.00 – 2.81 (m, 2H), 2.79 – 2.67 (m, 1H), 2.48 – 2.40 (m, 1H), 2.41 – 2.29 (m, 2H), 1.12 (t, *J*=7.4, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 178.47, 158.29, 131.45, 129.76, 126.84, 124.67, 117.88, 80.39, 29.96, 27.78, 26.97, 7.95. **HRMS (ESI)** calculated for $C_{12}H_{15}NO_3Na(+)$: 244.0950; Found: 244.0945. **Melting Point:** 93-95 °C.



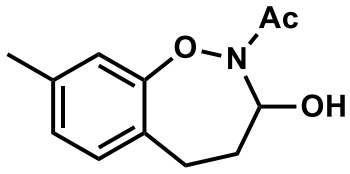
Benzyl 3-hydroxy-4,5-dihydrobenzo[*f*][1,2]oxazepine-2(3*H*)-carboxylate(3ca): 40% yield, brick-red solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.32 (m, 5H), 7.17 – 7.09 (m, 3H), 7.09 – 7.02 (m, 1H), 5.81 (t, *J* = 7.2 Hz, 1H), 5.22 (q, *J* = 12.4 Hz, 2H), 3.62(m, 1H), 2.92 (dd, *J* = 9.1, 4.0 Hz, 2H), 2.41 – 2.29 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.95, 156.28, 135.53, 130.86, 130.24, 128.56, 128.29, 127.83, 126.85, 124.77, 118.86, 82.79, 68.15, 30.97, 27.82. **IR (cm^{-1}):**3429, 2941, 1701, 1485, 1319, 760. **HRMS (ESI)** calculated for $C_{17}H_{17}NO_4Na(+)$: 322.1056; Found: 322.1047. **Melting Point:** 106-108 °C.



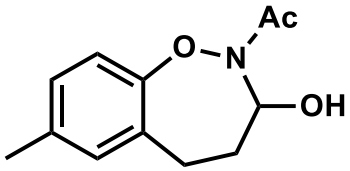
Benzyl 3-hydroxy-9-(3-oxopropyl)-4,5-dihydrobenzo[*f*][1,2]oxazepine-2(3*H*)-Carboxylate (3ca'): 46% yield, yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.59 (s, 1H), 7.41 – 7.29 (m,5H), 6.96 (s, 3H), 5.80 (dd, *J* = 8.6, 6.4 Hz, 1H), 5.24 (d, *J* = 11.9 Hz, 1H), 5.15 (d, *J* = 11.9 Hz, 1H),3.69 (m, 1H), 3.28 – 3.13 (m, 1H), 3.00 – 2.75 (m, 3H), 2.63 (m, 2H), 2.41 – 2.25 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.39, 156.81, 156.37, 135.06, 130.65, 130.11, 129.36, 128.68(2C), 128.66, 127.65, 124.39, 83.35, 68.66, 44.34, 30.71, 28.21, 22.44. **IR (cm^{-1}):**3383, 2359, 1717, 1456, 1308, 754. **HRMS (ESI)** calculated for $C_{20}H_{21}NO_5Na(+)$:378.1318; Found: 378.1312. **Melting Point:** 105-108 °C.



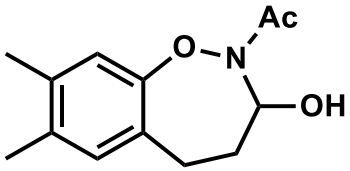
1-(3-hydroxy-9-methyl-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone (3da): 90% yield, yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.05 – 6.95 (m, 1H), 6.91 (d, *J* = 6.7 Hz, 2H), 6.07 (t, 1H),4.77(m,1H), 2.94 – 2.82 (m, 1H), 2.73 (dd, *J* = 16.6, 5.8 Hz, 1H), 2.39 – 2.30 (m, 4H), 2.24 (dd, *J* = 23.1, 12.6 Hz, 1H), 2.20 (d, *J* = 10.0 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.27, 156.56, 129.38, 129.04, 128.97, 126.41, 123.77, 79.98, 30.30, 28.22, 21.89, 16.11. **HRMS (ESI)** calculated for $C_{12}H_{15}NO_3Na(+)$:244.0950;Found: 244.0944.



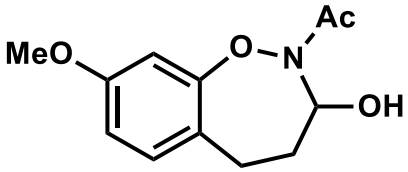
1-(3-hydroxy-8-methyl-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ea): 89% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.99 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.80 (m, 2H), 6.02 (t, *J* = 7.4 Hz, 1H), 4.71 (s, 1H), 2.92 – 2.73 (m, 2H), 2.38 – 2.25 (m, 5H), 2.22 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.83, 158.07, 136.98, 131.24, 126.60, 125.43, 118.30, 79.90, 30.32, 27.39, 21.78, 20.80. **HRMS (ESI)** calculated for $C_{12}H_{15}NO_3Na(+)$: 244.0950; Found: 244.0943. **Melting Point:** 108-110 °C.



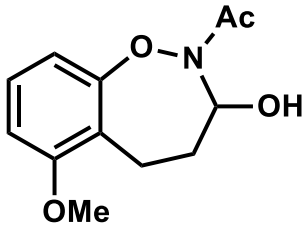
1-(3-hydroxy-7-methyl-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3fa): 70% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.99 – 6.87 (m, 3H), 6.01 (t, *J* = 7.3 Hz, 1H), 4.61 (s, 1H), 2.91 – 2.77 (m, 2H), 2.36 – 2.29 (m, 2H), 2.28 (s, 3H), 2.21 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.83, 156.18, 134.32, 131.99, 129.55, 127.29, 117.72, 79.90, 30.19, 27.67, 21.70, 20.60. **IR (cm^{-1}):** 3360, 2920, 1663, 1493, 1387, 1198, 822. **HRMS (ESI)** calculated for $C_{12}H_{15}NO_3Na(+)$:244.0950; Found: 244.0945. **Melting Point:** 110-112 ^{o}C.



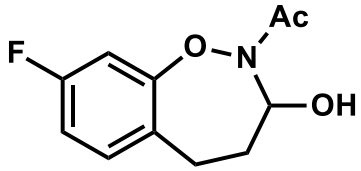
1-(3-hydroxy-7,8-dimethyl-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ga): 83% yield, brown solid. **^{1}H NMR (500 MHz, CD_2Cl_2)** δ 6.91 (d, *J* = 5.3 Hz, 1H), 6.86 (s, 1H), 5.98 (d, *J* = 6.1 Hz, 1H), 4.23(m,1H), 2.87 – 2.74 (m, 2H), 2.31 – 2.26 (m, 2H), 2.26 – 2.20 (m, 9H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.80, 156.21, 135.18, 132.86, 132.35, 126.67, 118.78, 80.12, 30.35, 27.21, 21.66, 19.23, 18.82. **IR (cm^{-1}):**3375, 2934, 1674, 1504, 1260, 1028, 800. **HRMS (ESI)** calculated for $C_{13}H_{17}NO_3Na(+)$:258.1106; Found: 258.1100. **Melting Point:** 93-97 ^{o}C.



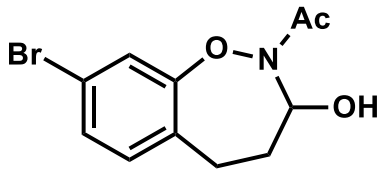
1-(3-hydroxy-8-methoxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3h a): 40% yield, brown oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.02 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 6.60 (d, *J* = 2.1 Hz, 1H), 6.05 – 5.92 (m, 1H), 3.79 (s, 3H), 2.81 (dd, *J* = 8.8, 3.6 Hz, 2H), 2.35 – 2.26 (m, 2H), 2.23 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.85, 158.79, 158.43, 131.87, 121.55, 110.04, 103.93, 80.20, 55.54, 30.35, 27.00, 21.72. **IR (cm^{-1}):**3235, 2951, 1684, 1506, 1260, 1134, 1034. **HRMS (ESI)** calculated for $C_{12}H_{15}NO_4Na(+)$:260.0899; Found: 260.0894.



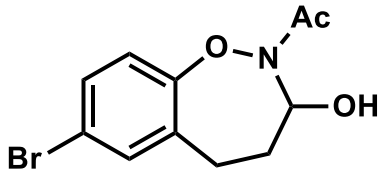
1-(3-hydroxy-6-methoxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ha'): 20% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.12 (t, *J* = 8.2 Hz, 1H), 6.68 (dd, *J* = 11.8, 8.2 Hz, 2H), 5.97 (t, *J* = 7.5 Hz, 1H), 4.10(m,1H), 3.82 (s, 3H), 3.23 – 3.08 (m, 1H), 2.57 – 2.40 (m, 1H), 2.37 – 2.27 (m, 2H), 2.21 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.92, 159.39, 158.60, 126.73, 118.59, 110.59, 106.83, 80.65, 55.81, 29.38, 21.73, 20.93. **IR (cm^{-1}):**2920, 1659, 1466, 1267, 1080, 750. **HRMS (ESI)** calculated for $C_{12}H_{15}NO_4Na(+)$:260.0899; Found: 260.0894. **Melting Point:** 160-162 °C.



1-(8-fluoro-3-hydroxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ia): 92% yield, white solid. **^{1}H NMR (400 MHz, CD_2Cl_2)** δ 7.17 (dd, *J* = 14.6, 7.9 Hz, 1H), 6.99 – 6.80 (m, 2H), 5.97 (s, 1H), 4.00 (d, *J* = 4.2 Hz, 1H), 3.11 (dd, *J* = 17.5, 6.3 Hz, 1H), 2.70 – 2.55 (m, 1H), 2.45 – 2.21 (m, 2H), 2.26 – 2.15 (s, 3H). **^{13}C NMR (101 MHz, CD_2Cl_2)** δ 174.77, 161.42 (J = 246.2), 159.63(J= 6.1), 127.11(J= 10.4), 118.30(J= 18.9), 113.55, 111.54(J= 23.4), 80.37, 29.32, 21.55, 19.98(J= 5.7). **IR (cm^{-1}):**3374, 2359, 1684, 1462, 1024. **HRMS (ESI)** calculated for $C_{11}H_{12}NO_3FNa(+)$: 248.0699; Found: 248.0693. **Melting Point:** 116-117 °C.

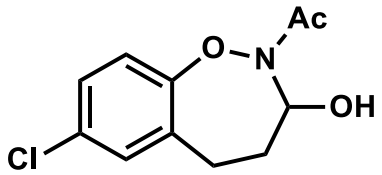


1-(8-bromo-3-hydroxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ja): 89% yield, colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.18 (t, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.98 (s, 1H), 2.80 (dd, *J* = 8.8, 3.5 Hz, 2H), 2.39 – 2.25 (m, 2H), 2.26 – 2.14 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.97, 158.69, 132.67, 128.99, 127.84, 121.05, 119.39, 80.22, 29.93, 27.44, 21.75. **HRMS (ESI)** calculated for $C_{11}H_{12}NO_3NaBr(+)$:307.9899; Found: 307.9894.

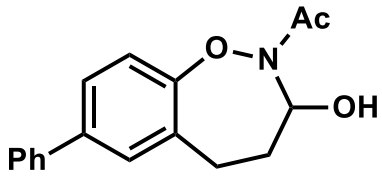


1-(7-bromo-3-hydroxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ka): 88% yield, yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (dd, *J* = 9.3, 2.2 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 1H), 5.98 (t, *J* = 6.6 Hz, 1H), 4.63 (m, 1H), 2.91 – 2.74 (m, 2H), 2.42 – 2.22 (m, 2H), 2.18 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.92,

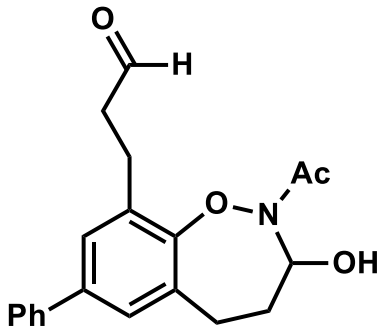
157.34, 134.20, 132.16, 129.82, 119.54, 117.43, 79.90, 29.85, 27.59, 21.76. **HRMS (ESI)** calculated for $C_{11}H_{12}NO_3NaBr(+)$: 307.9899; Found: 307.9893. **Melting Point:** 105-107 °C.



1-(7-chloro-3-hydroxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3la): 90% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ7.10 (d, J=2.2, 2H), 6.96 (d, J=8.7, 1H), 5.98 (s, 1H), 4.70 (m, 1H), 2.82 (d, J=7.7, 2H), 2.30 (t, J=6.8, 2H), 2.18 (s, 3H). **13C NMR (101 MHz, CDCl3)** δ 174.87, 156.83, 131.77, 131.23, 129.78, 126.81, 119.16, 79.89, 29.86, 27.64, 21.72.**IR (cm^{-1}):**3435, 2359, 1663, 1481, 1379, 1028, 822. **HRMS (ESI)** calculated for $C_{11}H_{12}NO_3NaCl(+)$:264.0404; Found: 264.0397. **Melting Point:** 113-114 °C.

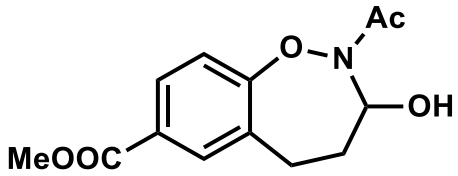


1-(3-hydroxy-7-phenyl-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ma): 66% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (dd, *J*=5.2, 3.4, 2H), 7.44 (dd, *J*=10.3, 4.8, 2H), 7.41 – 7.31 (m, 3H), 7.12 (d, *J*=8.2, 1H), 6.06 (d, *J*=4.2, 1H), 4.38 (d, *J*=4.6, 1H), 3.02 – 2.90 (m, 2H), 2.39 (td, *J*=7.5, 3.0, 2H), 2.27 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.01, 157.73, 140.15, 138.01, 130.28, 130.12, 128.83, 127.36, 127.00, 125.61, 118.30, 80.13, 30.11, 27.97, 21.81. **IR (cm^{-1}):**2922, 2359, 1337, 1109, 669. **HRMS (ESI)** calculated for $C_{17}H_{17}NO_3Na(+)$:306.1106; Found: 306.1103. **Melting Point:**85-86 °C.

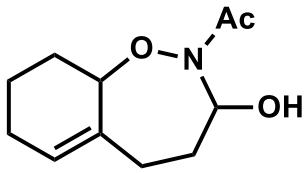


3-(2-acetyl-3-hydroxy-7-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxazepin-9-yl)propanal(3ma'): 33% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.86 (s, 1H), 7.57 – 7.47 (m, 2H), 7.43 (dd, *J*=10.3, 4.8, 2H), 7.35 (dd, *J*=5.7, 1.5, 1H), 7.24 (d, *J*=1.9, 1H), 7.20 (s, 1H), 6.07 (s, 1H), 4.00 (d, *J*=2.9, 1H), 3.42 – 3.25 (m, 1H), 3.11 –

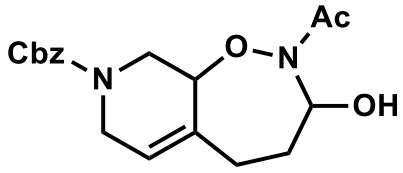
2.74 (m, 5H), 2.50 – 2.37 (m, 1H), 2.34 – 2.18 (m, 4H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 201.32, 173.71, 155.76, 140.06, 137.31, 132.13, 132.05, 129.78, 128.76, 127.30, 126.90, 126.50, 80.43, 44.37, 30.54, 28.50, 22.72, 21.88. **HRMS (ESI)** calculated for $C_{20}H_{21}NO_4Na(+)$:362.1369; Found: 362.1366. **Melting Point:** 88-89 °C.



Methyl2-acetyl-3-hydroxy-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxazepine-7-carboxylate(3na): 70% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.81 (dd, *J*=4.3, 2.4, 2H), 7.04 (d, *J*=8.9, 1H), 6.01 (s, 1H), 4.71 (m, 1H), 3.86 (s, 3H), 2.87 (t, *J*=5.0, 2H), 2.51 – 2.31 (m, 1H), 2.31 – 2.20 (m, 1H), 2.16 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.79, 166.27, 161.62, 133.38, 129.83, 128.75, 126.54, 117.78, 79.85, 52.19, 29.98, 27.82, 21.73. **IR (cm^{-1}):**3374, 2357, 1715, 1285, 1115, 1032. **HRMS (ESI)** calculated for $C_{13}H_{15}NO_5Na(+)$: 288.0848; Found: 288.0840. **Melting Point:** 140-142°C.

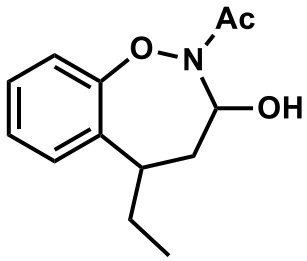


1-(3-hydroxy-4,5,7,8,9,9a-hexahydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3oa): 81% yield, yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.75 (dd, *J* = 9.5, 5.8 Hz, 1H), 5.53 (s, 1H), 4.24 – 4.14 (m, 1H), 4.03 (s, 1H), 2.27 (dd, *J* = 14.1, 7.9 Hz, 1H), 2.18 (s, 3H), 2.13 – 1.88 (m, 5H), 1.85 – 1.73 (m, 2H), 1.64 (m, 1H), 1.56 – 1.46 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.88, 137.48, 126.36, 85.88, 80.54, 31.47, 30.85, 28.07, 24.99, 21.16, 20.79. **IR (cm^{-1}):**3445, 2930, 2359, 1639, 1393, 1076, 1024. **HRMS (ESI)** calculated for $C_{11}H_{17}NO_3Na(+)$:234.1106; Found: 234.1100. **Melting Point:** 150-151 °C.

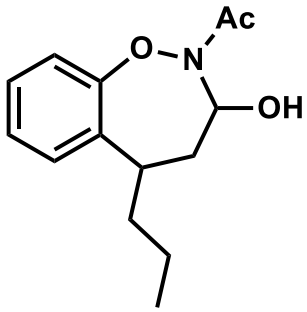


Benzyl 2-acetyl-3-hydroxy-2,3,4,5,9,9a-hexahydropyrido[4,3-*f*][1,2]oxazepine-8(7*H*)-carboxylate (3pa): 65% yield, colorless oil. **^{1}H NMR (500 MHz, MeOD)** δ 7.62 – 7.13 (m, 5H), 5.75 (m, 1H), 5.58 (m, 1H), 5.15 (d, J=8.9, 2H), 4.30 (d, J=32.8, 2H), 4.11 (d, J=18.5, 1H), 3.92 (d, J=15.9, 1H), 3.72 (m, 1H), 3.09 (m, 1H), 2.41 (dd, J=14.5, 7.9, 1H), 2.34 – 2.03 (m, 5H), 1.88 – 1.69 (m, 1H). **13C NMR (101 MHz, $CDCl_3$)** δ 175.28, 155.24, 136.32, 128.56, 128.23, 128.08, 128.00, 121.75, 80.71,

80.66, 67.51, 43.16, 30.85, 29.94, 28.07, 21.18. **HRMS (ESI)** calculated for $C_{18}H_{22}N_2O_5Na(+)$:369.1427; Found: 369.1420.

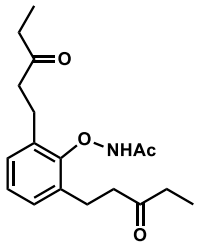


1-(5-ethyl-3-hydroxy-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ab): 96% yield, pale yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (ddd, *J* = 6.9, 5.1, 2.4 Hz, 2H), 7.08 (ddd, *J* = 15.7, 10.6, 4.5 Hz, 2H), 6.08 (dd, *J* = 9.6, 5.9 Hz, 1H), 4.56 – 4.08 (m, 1H), 2.88 (d, *J* = 7.1 Hz, 1H), 2.57 – 2.31 (m, 2H), 2.23 (d, *J* = 2.7 Hz, 3H), 1.70 – 1.56 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.28, 157.86, 134.14, 132.34, 126.81, 124.75, 118.10, 79.94, 41.42, 31.74, 28.23, 21.79, 12.51. **HRMS (ESI)** calculated for $C_{13}H_{17}NO_3Na(+)$:258.1106; Found: 258.1098.



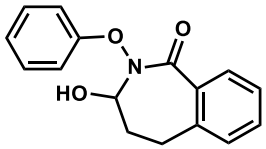
1-(3-hydroxy-5-propyl-4,5-dihydrobenzo[*f*][1,2]oxazepin-2(3*H*)-yl)ethanone(3ac): 88% yield, pale yellow solid. **^{1}H NMR (500 MHz, CD_2Cl_2)** δ = 7.18 (dd, *J*=11.3, 4.3, 2H), 7.11 (ddd, *J*=16.9, 11.0, 4.5, 2H), 6.08 (dd, *J*=8.8, 6.0, 1H), 4.50 (m, 1H), 3.14 – 2.98 (m, 1H), 2.51 – 2.32 (m, 2H), 2.23 (s, 3H), 1.74 – 1.52 (m, 3H), 1.50 – 1.42 (m, 1H), 0.99 (t, *J*=6.9, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 173.83, 158.04, 134.53, 132.17, 126.65, 124.64, 118.03, 76.72, 39.33, 37.43, 32.45, 21.48, 20.74, 13.77. **IR (cm^{-1}):** 3381, 2955, 2357, 1645, 1485, 1379, 1192, 766. **HRMS (ESI)** calculated for $C_{14}H_{19}NO_3Na(+)$:272.1263; Found: 272.1254. **Melting Point:** 112-114 °C.

5. Characterization of Products 4 and 5



***N*-(2,6-bis(3-oxopentyl)phenoxy)acetamide (4):** 48% yield, white solid. **^{1}H NMR**

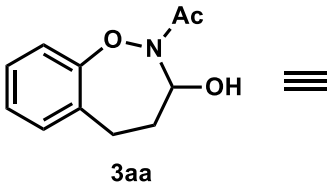
(400 MHz, MeOD) δ 7.08 (m, 3H), 2.96 (t, J=7.6, 4H), 2.80 (t, J=7.6, 4H), 2.47 (q, J=7.3, 4H), 1.92 (s, 3H), 1.01 (t, J=7.3, 6H). **^{13}C NMR (126 MHz, MeOD)** δ 212.26, 167.64, 153.88, 134.94, 128.20, 126.09, 42.49, 35.18, 24.05, 17.94, 6.64. **IR (cm^{-1}):**3215, 2359, 1709, 1454, 669. **HRMS (ESI)** calculated for $C_{18}H_{25}NO_4Na(+)$: 342.1682; Found: 342.1677. **Melting Point:** 87-89 °C.



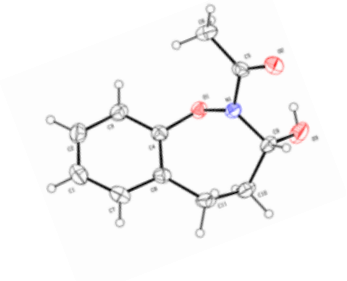
3-hydroxy-2-phenoxy-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-1-one (5): 80% yield, white solid. **^{1}H NMR (400 MHz, CD_2Cl_2)** δ 8.07 (dd, *J*=7.7, 1.0, 1H), 7.57 (td, *J*=7.5, 1.2, 1H), 7.42 (dd, *J*=11.0, 4.1, 1H), 7.38 (d, *J*=7.5, 1H), 7.32 (dd, *J*=8.5, 7.5, 2H), 7.09 (t, *J*=7.3, 1H), 7.01 (d, *J*=7.9, 2H), 5.58 (dd, *J*=7.5, 2.3, 1H), 5.43 (s, 1H), 3.38 – 3.16 (m, 1H), 2.97 (dt, *J*=14.1, 4.4, 1H), 2.70 (ddt, *J*=9.6, 7.6, 4.9, 1H), 2.19 (m, 1H). **^{13}C NMR (101 MHz, CD_2Cl_2)** δ 170.75, 158.90, 141.04, 132.61, 132.52, 130.82, 129.55, 129.15, 126.90, 122.90, 113.56, 86.54, 36.96, 30.86. **IR (cm^{-1}):**3391, 2940, 2359, 1647, 1487, 1202, 752. **HRMS (ESI)** calculated for $C_{16}H_{15}NO_3Na(+)$: 292.0950; Found: 292.0945. **Melting Point:** 107-108 °C.

6. X-ray Crystallographic Data

Figure S1.



3aa



CCDC 1003334

Table S2. Crystal data and structure refinement for b4.

Identification code	shelx	
Empirical formula	C11 H13 N O3	
Formula weight	207.22	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 13.1081(9) Å	α= 90 °.
	b = 9.6334(3) Å	β= 90 °.
	c = 8.0059(3) Å	γ = 90 °.

Volume	1010.95(9) $Å^3$
Z	4
Density (calculated)	1.362 Mg/m^3
Absorption coefficient	0.824 mm^{-1}
F(000)	440
Crystal size	0.40 x 0.20 x 0.10 mm^3
Theta range for data collection	6.755 to 68.143 °.
Index ranges	-14<=h<=15, -11<=k<=10, -9<=l<=8
Reflections collected	5343
Independent reflections	1608 [R(int) = 0.0352]
Completeness to theta = 67.687 °	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.921 and 0.775
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1608 / 2 / 140
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0708
R indices (all data)	R1 = 0.0386, wR2 = 0.0788
Absolute structure parameter	0.01(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.115 and -0.129 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for b4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1762(1)	2641(2)	8567(2)	39(1)
O(2)	2564(2)	37(2)	11280(3)	56(1)
O(3)	674(2)	-103(2)	8445(3)	63(1)
N(1)	1679(2)	1617(2)	9820(3)	39(1)
C(1)	1214(2)	6648(3)	10234(5)	57(1)
C(2)	2013(2)	6359(3)	9174(5)	54(1)
C(3)	2186(2)	5009(3)	8661(4)	46(1)
C(4)	1544(2)	3972(2)	9202(3)	37(1)
C(5)	2580(2)	1060(3)	10371(4)	41(1)
C(6)	3533(2)	1782(3)	9841(4)	52(1)
C(7)	577(2)	5592(3)	10740(4)	51(1)

C(8)	707(2)	4215(3)	10233(3)	40(1)
C(9)	719(2)	852(3)	9771(4)	41(1)
C(10)	-152(2)	1874(3)	9627(4)	47(1)
C(11)	-41(2)	3117(3)	10793(4)	50(1)

Table S4. Bond lengths [Å] and angles [°] for b4.

O(1)-C(4)	1.409(3)
O(1)-N(1)	1.411(3)
O(2)-C(5)	1.225(3)
O(3)-C(9)	1.405(4)
O(3)-H(3O)	0.81(2)
N(1)-C(5)	1.370(3)
N(1)-C(9)	1.458(3)
C(1)-C(2)	1.375(5)
C(1)-C(7)	1.378(4)
C(1)-H(1)	0.9300
C(2)-C(3)	1.382(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.376(4)
C(3)-H(3)	0.9300
C(4)-C(8)	1.393(3)
C(5)-C(6)	1.491(4)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-C(8)	1.397(4)
C(7)-H(7)	0.9300
C(8)-C(11)	1.511(4)
C(9)-C(10)	1.512(3)
C(9)-H(9)	0.9800
C(10)-C(11)	1.525(4)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(4)-O(1)-N(1)	111.35(19)
C(9)-O(3)-H(3O)	110(3)

C(5)-N(1)-O(1)	115.8(2)
C(5)-N(1)-C(9)	123.7(2)
O(1)-N(1)-C(9)	113.6(2)
C(2)-C(1)-C(7)	119.6(3)
C(2)-C(1)-H(1)	120.2
C(7)-C(1)-H(1)	120.2
C(1)-C(2)-C(3)	119.9(3)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
C(4)-C(3)-C(2)	119.3(3)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(3)-C(4)-C(8)	123.1(2)
C(3)-C(4)-O(1)	115.1(2)
C(8)-C(4)-O(1)	121.8(2)
O(2)-C(5)-N(1)	119.4(2)
O(2)-C(5)-C(6)	123.9(3)
N(1)-C(5)-C(6)	116.6(2)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(1)-C(7)-C(8)	122.7(3)
C(1)-C(7)-H(7)	118.6
C(8)-C(7)-H(7)	118.6
C(4)-C(8)-C(7)	115.4(2)
C(4)-C(8)-C(11)	124.7(2)
C(7)-C(8)-C(11)	119.9(3)
O(3)-C(9)-N(1)	112.8(2)
O(3)-C(9)-C(10)	109.7(2)
N(1)-C(9)-C(10)	108.91(19)
O(3)-C(9)-H(9)	108.5
N(1)-C(9)-H(9)	108.5
C(10)-C(9)-H(9)	108.5
C(9)-C(10)-C(11)	113.1(2)
C(9)-C(10)-H(10A)	109.0

C(11)-C(10)-H(10A)	109.0
C(9)-C(10)-H(10B)	109.0
C(11)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
C(8)-C(11)-C(10)	115.5(2)
C(8)-C(11)-H(11A)	108.4
C(10)-C(11)-H(11A)	108.4
C(8)-C(11)-H(11B)	108.4
C(10)-C(11)-H(11B)	108.4
H(11A)-C(11)-H(11B)	107.5

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for b4. 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}
O(1)	40(1)	39(1)	38(1)	0(1)	6(1)	-5(1)
O(2)	48(1)	49(1)	71(2)	3(1)	-5(1)	8(1)
O(3)	56(1)	65(1)	66(2)	-17(1)	10(1)	-26(1)
N(1)	31(1)	39(1)	45(1)	4(1)	0(1)	-2(1)
C(1)	66(2)	42(2)	64(2)	-1(2)	-6(2)	10(2)
C(2)	55(2)	43(1)	64(2)	8(2)	-6(2)	-6(1)
C(3)	40(1)	50(1)	47(2)	5(1)	3(1)	-4(1)
C(4)	36(1)	39(1)	36(1)	-1(1)	-4(1)	1(1)
C(5)	35(1)	41(1)	45(2)	-11(1)	-1(1)	5(1)
C(6)	33(1)	72(2)	51(2)	-6(2)	3(1)	-2(1)
C(7)	51(2)	54(2)	50(2)	-1(2)	3(2)	16(1)
C(8)	35(1)	46(1)	39(2)	4(1)	-2(1)	5(1)
C(9)	34(1)	45(1)	44(2)	6(1)	3(1)	-10(1)
C(10)	31(1)	55(2)	56(2)	13(2)	-2(1)	-6(1)
C(11)	34(1)	59(2)	55(2)	7(2)	10(1)	7(1)

Table S6. Hydrogen bonds for b4 [Å and °].

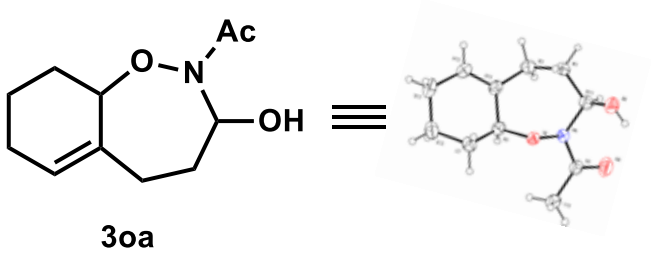
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

O(3)-H(3O)...O(2)#1	0.81(2)	2.10(2)	2.891(3)	165(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y,z-1/2

Figure S2.



3oa

CCDC 1003335

Table S7. Crystal data and structure refinement for b15.

Identification code	shelx	
Empirical formula	C11 H17 N O3	
Formula weight	211.25	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.9758(10) Å	α= 90 °.
	b = 6.7000(5) Å	β= 110.070(8) °.
	c = 14.3713(11) Å	γ = 90 °.
Volume	1083.10(16) $Å^3$	
Z	4	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.770 mm^{-1}	
F(000)	456	
Crystal size	0.320 x 0.140 x 0.100 mm^3	
Theta range for data collection	6.559 to 59.966 °.	
Index ranges	-13<=h<=11, -7<=k<=7, -15<=l<=16	
Reflections collected	5306	
Independent reflections	1519 [R(int) = 0.0676]	
Completeness to theta = 67.687 °	77.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.926 and 0.626	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1519 / 0 / 138
Goodness-of-fit on F^2	1.105
Final R indices [I>2sigma(I)]	R1 = 0.0996, wR2 = 0.2607
R indices (all data)	R1 = 0.1146, wR2 = 0.2680
Extinction coefficient	0.029(4)
Largest diff. peak and hole	0.611 and -0.379 e.$Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for b15. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2344(3)	2120(5)	798(2)	40(1)
O(2)	3116(4)	3328(6)	-972(3)	60(1)
O(3)	5169(4)	3992(7)	1154(3)	70(1)
N(4)	3471(4)	2293(7)	694(3)	41(1)
C(5)	4262(5)	3564(8)	1320(4)	46(1)
C(6)	2257(4)	286(8)	1323(4)	42(1)
C(7)	1221(5)	629(9)	1666(4)	51(2)
C(8)	2777(6)	-51(8)	-693(4)	53(2)
C(9)	2918(6)	-1726(8)	68(5)	55(2)
C(10)	3519(5)	1769(8)	-278(4)	47(1)
C(11)	4002(6)	4304(9)	2200(4)	56(2)
C(12)	2120(5)	-1520(8)	673(4)	44(1)
C(13)	923(6)	-1323(10)	2077(5)	65(2)
C(14)	1339(5)	-2935(9)	673(4)	54(2)
C(15)	559(6)	-2933(10)	1275(5)	67(2)

Table S9. Bond lengths [Å] and angles [°] for b15.

O(1)-N(4)	1.412(5)
O(1)-C(6)	1.464(6)
O(2)-C(10)	1.411(7)
O(2)-H(2)	0.8200
O(3)-C(5)	1.223(7)
N(4)-C(5)	1.359(7)
N(4)-C(10)	1.461(7)
C(5)-C(11)	1.487(8)

C(6)-C(12)	1.502(7)
C(6)-C(7)	1.502(7)
C(6)-H(6)	0.9800
C(7)-C(13)	1.527(8)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(10)	1.506(8)
C(8)-C(9)	1.536(8)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(12)	1.503(8)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10)	0.9800
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(14)	1.332(8)
C(13)-C(15)	1.529(10)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-C(15)	1.474(9)
C(14)-H(14)	0.9300
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700

N(4)-O(1)-C(6)	111.3(3)
C(10)-O(2)-H(2)	109.5
C(5)-N(4)-O(1)	117.1(4)
C(5)-N(4)-C(10)	122.4(4)
O(1)-N(4)-C(10)	115.7(4)
O(3)-C(5)-N(4)	118.8(5)
O(3)-C(5)-C(11)	123.1(5)
N(4)-C(5)-C(11)	118.0(5)
O(1)-C(6)-C(12)	111.6(4)
O(1)-C(6)-C(7)	104.7(4)
C(12)-C(6)-C(7)	113.6(4)
O(1)-C(6)-H(6)	108.9

C(12)-C(6)-H(6)	108.9
C(7)-C(6)-H(6)	108.9
C(6)-C(7)-C(13)	109.0(5)
C(6)-C(7)-H(7A)	109.9
C(13)-C(7)-H(7A)	109.9
C(6)-C(7)-H(7B)	109.9
C(13)-C(7)-H(7B)	109.9
H(7A)-C(7)-H(7B)	108.3
C(10)-C(8)-C(9)	113.8(5)
C(10)-C(8)-H(8A)	108.8
C(9)-C(8)-H(8A)	108.8
C(10)-C(8)-H(8B)	108.8
C(9)-C(8)-H(8B)	108.8
H(8A)-C(8)-H(8B)	107.7
C(12)-C(9)-C(8)	114.1(5)
C(12)-C(9)-H(9A)	108.7
C(8)-C(9)-H(9A)	108.7
C(12)-C(9)-H(9B)	108.7
C(8)-C(9)-H(9B)	108.7
H(9A)-C(9)-H(9B)	107.6
O(2)-C(10)-N(4)	112.5(4)
O(2)-C(10)-C(8)	107.9(4)
N(4)-C(10)-C(8)	111.2(4)
O(2)-C(10)-H(10)	108.4
N(4)-C(10)-H(10)	108.4
C(8)-C(10)-H(10)	108.4
C(5)-C(11)-H(11A)	109.5
C(5)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(5)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(14)-C(12)-C(6)	120.0(5)
C(14)-C(12)-C(9)	121.4(5)
C(6)-C(12)-C(9)	118.5(5)
C(7)-C(13)-C(15)	110.9(5)
C(7)-C(13)-H(13A)	109.5
C(15)-C(13)-H(13A)	109.5

C(7)-C(13)-H(13B)	109.5
C(15)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	108.1
C(12)-C(14)-C(15)	125.9(6)
C(12)-C(14)-H(14)	117.1
C(15)-C(14)-H(14)	117.1
C(14)-C(15)-C(13)	111.7(5)
C(14)-C(15)-H(15A)	109.3
C(13)-C(15)-H(15A)	109.3
C(14)-C(15)-H(15B)	109.3
C(13)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for b15. 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}
O(1)	45(2)	31(2)	46(2)	0(2)	20(2)	-1(2)
O(2)	77(3)	47(2)	55(2)	6(2)	22(2)	-10(2)
O(3)	64(3)	74(3)	74(3)	5(2)	27(2)	-22(2)
N(4)	49(2)	41(3)	40(2)	-5(2)	22(2)	-8(2)
C(5)	50(3)	39(3)	47(3)	7(2)	15(2)	-5(3)
C(6)	43(3)	35(3)	46(3)	3(2)	14(2)	2(2)
C(7)	54(3)	51(3)	59(3)	-1(3)	31(3)	0(3)
C(8)	76(4)	43(3)	52(3)	-11(3)	38(3)	-7(3)
C(9)	70(4)	38(3)	67(4)	-6(3)	36(3)	4(3)
C(10)	51(3)	45(3)	52(3)	-1(3)	26(3)	3(3)
C(11)	67(4)	50(3)	47(3)	-7(3)	14(3)	-15(3)
C(12)	49(3)	30(3)	52(3)	7(2)	19(2)	5(2)
C(13)	66(4)	72(4)	65(4)	9(3)	35(3)	-8(3)
C(14)	63(4)	37(3)	63(4)	-3(3)	22(3)	-6(3)
C(15)	68(4)	53(4)	86(5)	14(4)	33(4)	-14(3)

Table S11. Hydrogen bonds for b15 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(3)#1	0.82	2.16	2.807(6)	135.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z

Figure S3.

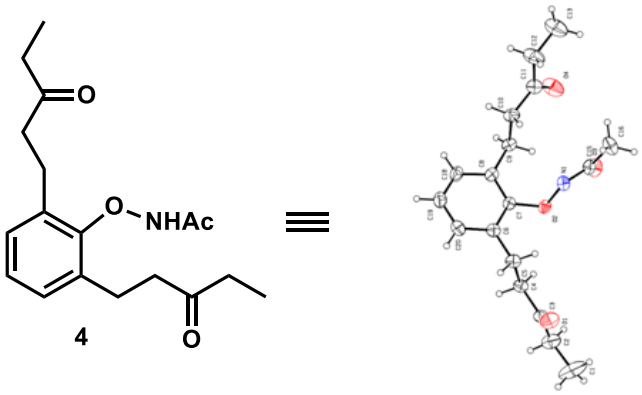


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Table S12. Crystal data and structure refinement for c1.

Identification code	shelx	
Empirical formula	C18 H24 N O4	
Formula weight	318.38	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P c	
Unit cell dimensions	a = 12.7071(2) Å	α= 90 °.
	b = 4.847 Å	β= 98.347(7) °.
	c = 14.6978(10) Å	γ = 90 °.
Volume	895.67(6) $Å^3$	
Z	2	
Density (calculated)	1.180 Mg/m^3	
Absorption coefficient	0.675 mm^{-1}	
F(000)	342	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	6.576 to 68.144 °.	
Index ranges	-15<=h<=15, -5<=k<=5, -17<=l<=17	

Reflections collected	10812
Independent reflections	3101 [R(int) = 0.0314]
Completeness to theta = 67.687 °	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.859 and 0.737
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3101 / 2 / 211
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1179
R indices (all data)	R1 = 0.0509, wR2 = 0.1291
Absolute structure parameter	0.52(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.260 and -0.261 e.$Å^{-3}$

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for c1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6709(2)	9315(5)	658(2)	72(1)
O(2)	4096(2)	3333(4)	1713(1)	45(1)
O(3)	2708(2)	-195(5)	773(2)	63(1)
O(4)	1036(3)	-1810(6)	2439(3)	90(1)
N(1)	3046(2)	4102(5)	1353(2)	44(1)
C(1)	8249(7)	6705(16)	-189(6)	138(3)
C(2)	7819(4)	5417(9)	599(3)	74(1)
C(3)	6984(2)	7087(6)	970(2)	51(1)
C(4)	6490(2)	5816(6)	1746(2)	47(1)
C(5)	5612(2)	7571(7)	2049(2)	50(1)
C(6)	5112(2)	6227(6)	2815(2)	44(1)
C(7)	4350(2)	4184(6)	2637(2)	40(1)
C(8)	3871(2)	2893(6)	3326(2)	42(1)
C(9)	3016(2)	741(6)	3131(2)	46(1)
C(10)	1937(3)	1986(7)	3220(2)	55(1)
C(11)	985(3)	321(7)	2866(2)	54(1)
C(12)	-62(3)	1461(12)	3041(5)	92(2)
C(13)	-1023(4)	-148(13)	2695(5)	103(2)
C(15)	2455(2)	2212(6)	846(2)	47(1)

C(16)	1401(3)	3342(9)	398(3)	71(1)
C(18)	4198(3)	3790(7)	4224(2)	53(1)
C(19)	4943(3)	5819(8)	4421(2)	58(1)
C(20)	5404(3)	7027(7)	3727(2)	55(1)

Table S14. Bond lengths [Å] and angles [°] for c1.

O(1)-C(3)	1.205(4)
O(2)-N(1)	1.412(3)
O(2)-C(7)	1.411(3)
O(3)-C(15)	1.219(4)
O(4)-C(11)	1.215(5)
N(1)-C(15)	1.340(4)
C(1)-C(2)	1.488(7)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-C(3)	1.498(5)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.512(4)
C(4)-C(5)	1.519(4)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.517(4)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.383(4)
C(6)-C(20)	1.394(4)
C(7)-C(8)	1.402(4)
C(8)-C(18)	1.395(4)
C(8)-C(9)	1.503(4)
C(9)-C(10)	1.521(4)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.484(5)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700

C(11)-C(12)	1.496(5)
C(12)-C(13)	1.476(7)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(15)-C(16)	1.507(5)
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(18)-C(19)	1.366(5)
C(18)-H(18)	0.9300
C(19)-C(20)	1.378(5)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300

N(1)-O(2)-C(7)	110.87(18)
C(15)-N(1)-O(2)	116.8(2)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(1)-C(2)-C(3)	114.6(4)
C(1)-C(2)-H(2A)	108.6
C(3)-C(2)-H(2A)	108.6
C(1)-C(2)-H(2B)	108.6
C(3)-C(2)-H(2B)	108.6
H(2A)-C(2)-H(2B)	107.6
O(1)-C(3)-C(2)	121.9(3)
O(1)-C(3)-C(4)	121.5(3)
C(2)-C(3)-C(4)	116.6(3)
C(3)-C(4)-C(5)	113.3(2)
C(3)-C(4)-H(4A)	108.9
C(5)-C(4)-H(4A)	108.9
C(3)-C(4)-H(4B)	108.9

C(5)-C(4)-H(4B)	108.9
H(4A)-C(4)-H(4B)	107.7
C(4)-C(5)-C(6)	112.4(2)
C(4)-C(5)-H(5A)	109.1
C(6)-C(5)-H(5A)	109.1
C(4)-C(5)-H(5B)	109.1
C(6)-C(5)-H(5B)	109.1
H(5A)-C(5)-H(5B)	107.9
C(7)-C(6)-C(20)	117.5(3)
C(7)-C(6)-C(5)	121.7(2)
C(20)-C(6)-C(5)	120.8(3)
C(6)-C(7)-C(8)	123.3(2)
C(6)-C(7)-O(2)	116.5(2)
C(8)-C(7)-O(2)	120.1(2)
C(18)-C(8)-C(7)	116.3(3)
C(18)-C(8)-C(9)	120.3(2)
C(7)-C(8)-C(9)	123.4(2)
C(8)-C(9)-C(10)	110.1(2)
C(8)-C(9)-H(9A)	109.6
C(10)-C(9)-H(9A)	109.6
C(8)-C(9)-H(9B)	109.6
C(10)-C(9)-H(9B)	109.6
H(9A)-C(9)-H(9B)	108.1
C(11)-C(10)-C(9)	116.9(3)
C(11)-C(10)-H(10A)	108.1
C(9)-C(10)-H(10A)	108.1
C(11)-C(10)-H(10B)	108.1
C(9)-C(10)-H(10B)	108.1
H(10A)-C(10)-H(10B)	107.3
O(4)-C(11)-C(10)	122.8(3)
O(4)-C(11)-C(12)	121.2(3)
C(10)-C(11)-C(12)	116.0(3)
C(13)-C(12)-C(11)	117.2(4)
C(13)-C(12)-H(12A)	108.0
C(11)-C(12)-H(12A)	108.0
C(13)-C(12)-H(12B)	108.0
C(11)-C(12)-H(12B)	108.0
H(12A)-C(12)-H(12B)	107.2

C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(3)-C(15)-N(1)	124.7(3)
O(3)-C(15)-C(16)	122.6(3)
N(1)-C(15)-C(16)	112.6(3)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(19)-C(18)-C(8)	121.8(3)
C(19)-C(18)-H(18)	119.1
C(8)-C(18)-H(18)	119.1
C(18)-C(19)-C(20)	120.4(3)
C(18)-C(19)-H(19)	119.8
C(20)-C(19)-H(19)	119.8
C(19)-C(20)-C(6)	120.7(3)
C(19)-C(20)-H(20)	119.6
C(6)-C(20)-H(20)	119.6

Symmetry transformations used to generate equivalent atoms:

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for c1. 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}
O(1)	86(2)	51(1)	82(2)	19(1)	24(1)	-2(1)
O(2)	47(1)	47(1)	42(1)	-4(1)	10(1)	8(1)
O(3)	97(2)	32(1)	59(1)	-5(1)	9(1)	1(1)
O(4)	70(2)	59(2)	140(3)	-30(2)	11(2)	-2(1)
N(1)	53(1)	35(1)	43(1)	-1(1)	1(1)	3(1)
C(1)	162(7)	118(5)	160(6)	18(4)	117(6)	0(5)

C(2)	77(2)	62(2)	89(3)	-3(2)	36(2)	-6(2)
C(3)	51(2)	42(2)	62(2)	0(1)	12(1)	-10(1)
C(4)	45(1)	40(2)	56(2)	5(1)	6(1)	-1(1)
C(5)	50(2)	38(1)	63(2)	6(1)	13(1)	1(1)
C(6)	41(1)	39(1)	51(2)	3(1)	6(1)	10(1)
C(7)	41(1)	36(1)	42(1)	0(1)	7(1)	7(1)
C(8)	46(1)	37(1)	45(1)	5(1)	9(1)	10(1)
C(9)	51(2)	37(1)	51(2)	6(1)	15(1)	5(1)
C(10)	51(2)	50(2)	67(2)	-6(1)	18(1)	2(1)
C(11)	54(2)	43(2)	64(2)	4(1)	11(1)	3(1)
C(12)	51(2)	83(3)	142(4)	-31(3)	18(2)	0(2)
C(13)	61(3)	93(3)	153(5)	-14(3)	5(3)	0(2)
C(15)	65(2)	35(1)	40(1)	3(1)	6(1)	-1(1)
C(16)	70(2)	64(2)	72(2)	1(2)	-16(2)	-4(2)
C(18)	57(2)	62(2)	39(1)	6(1)	7(1)	10(1)
C(19)	58(2)	68(2)	46(2)	-5(1)	-1(1)	7(2)
C(20)	49(2)	53(2)	60(2)	-4(1)	-2(1)	2(1)

Table S16. Hydrogen bonds for c1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2B)...O(1)#1	0.97	2.39	3.283(5)	153.7
C(10)-H(10B)...O(4)#2	0.97	2.46	3.360(5)	154.4

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 x,y+1,z

Figure S4.

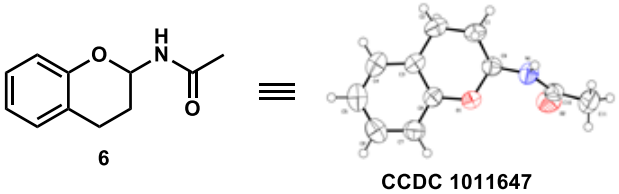


Table S17. Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	C11 H13 N O2
Formula weight	191.22

Temperature	273(2) K
Wavelength	0.71073 A
Crystal system, space group	"monoclinic", " P 21/c "
Unit cell dimensions	a = 20.667(3) A alpha = 90 deg.
	b = 5.2935(8) A beta = 94.551(4) deg.
	c = 9.2989(12) A gamma = 90 deg.
Volume	1014.1(2) A^3
Z, Calculated density	4, 1.252 Mg/m^3
Absorption coefficient	0.086 mm^-1
F(000)	408
Crystal size	0.16 x 0.12 x 0.12 mm
Theta range for data collection	2.97 to 25.04 deg.
Limiting indices	-24<=h<=22, -6<=k<=6, -11<=l<=10
Reflections collected / unique	8734 / 1792 [R(int) = 0.0518]
Completeness to theta = 25.04	99.8 %
Max. and min. transmission	0.9897 and 0.9863
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1792 / 0 / 128
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0825
R indices (all data)	R1 = 0.1038, wR2 = 0.0994
Largest diff. peak and hole	0.129 and -0.126 e.A^-3

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	2532(1)	3311(2)	6674(1)	55(1)
N(1)	3611(1)	3346(3)	7428(2)	53(1)
O(2)	3914(1)	4128(3)	5200(1)	69(1)
C(8)	1900(1)	4104(4)	6793(2)	45(1)
C(3)	1746(1)	6091(3)	7656(2)	47(1)
C(9)	3043(1)	4894(4)	7305(2)	47(1)
C(2)	2268(1)	7484(4)	8534(2)	63(1)
C(1)	2881(1)	5921(4)	8732(2)	54(1)
C(7)	1428(1)	2745(4)	6001(2)	61(1)
C(10)	3989(1)	2969(4)	6343(2)	53(1)
C(4)	1092(1)	6674(4)	7687(2)	68(1)
C(6)	788(1)	3370(5)	6060(3)	72(1)
C(11)	4504(1)	1008(4)	6619(2)	80(1)
C(5)	620(1)	5347(5)	6899(3)	77(1)

Table S19. Bond lengths [A] and angles [deg] for 1.

O(1)-C(8)	1.385(2)
O(1)-C(9)	1.436(2)
N(1)-C(10)	1.339(2)
N(1)-C(9)	1.428(2)
N(1)-H(1)	0.8600
O(2)-C(10)	1.226(2)
C(8)-C(3)	1.375(2)
C(8)-C(7)	1.377(3)
C(3)-C(4)	1.390(3)
C(3)-C(2)	1.494(3)
C(9)-C(1)	1.497(2)
C(9)-H(9)	0.9800
C(2)-C(1)	1.513(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(7)-C(6)	1.369(3)
C(7)-H(7)	0.9300
C(10)-C(11)	1.494(3)
C(4)-C(5)	1.367(3)
C(4)-H(4)	0.9300
C(6)-C(5)	1.367(3)
C(6)-H(6)	0.9300
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(5)-H(5)	0.9300

C(8)-O(1)-C(9)	117.27(14)
C(10)-N(1)-C(9)	123.32(15)
C(10)-N(1)-H(1)	118.3
C(9)-N(1)-H(1)	118.3
C(3)-C(8)-C(7)	121.67(18)
C(3)-C(8)-O(1)	122.78(17)
C(7)-C(8)-O(1)	115.54(17)
C(8)-C(3)-C(4)	116.87(19)
C(8)-C(3)-C(2)	120.42(17)
C(4)-C(3)-C(2)	122.70(19)
N(1)-C(9)-O(1)	105.72(14)

N(1)-C(9)-C(1)	112.17(14)
O(1)-C(9)-C(1)	111.42(14)
N(1)-C(9)-H(9)	109.1
O(1)-C(9)-H(9)	109.1
C(1)-C(9)-H(9)	109.1
C(3)-C(2)-C(1)	110.97(16)
C(3)-C(2)-H(2A)	109.4
C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2B)	109.4
C(1)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
C(9)-C(1)-C(2)	109.58(15)
C(9)-C(1)-H(1A)	109.8
C(2)-C(1)-H(1A)	109.8
C(9)-C(1)-H(1B)	109.8
C(2)-C(1)-H(1B)	109.8
H(1A)-C(1)-H(1B)	108.2
C(6)-C(7)-C(8)	119.9(2)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
O(2)-C(10)-N(1)	122.55(19)
O(2)-C(10)-C(11)	122.34(18)
N(1)-C(10)-C(11)	115.10(18)
C(5)-C(4)-C(3)	122.0(2)
C(5)-C(4)-H(4)	119.0
C(3)-C(4)-H(4)	119.0
C(5)-C(6)-C(7)	119.9(2)
C(5)-C(6)-H(6)	120.1
C(7)-C(6)-H(6)	120.1
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(4)-C(5)-C(6)	119.8(2)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1

Symmetry transformations used to generate equivalent atoms:

Table S20. Anisotropic displacement parameters (A^2 x 10^3) for 1. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	52(1)	61(1)	52(1)	-17(1)	6(1)	1(1)
N(1)	56(1)	71(1)	33(1)	6(1)	7(1)	12(1)
O(2)	82(1)	91(1)	36(1)	-1(1)	14(1)	-4(1)
C(8)	50(1)	46(1)	40(1)	5(1)	9(1)	0(1)
C(3)	60(1)	41(1)	42(1)	3(1)	10(1)	5(1)
C(9)	53(1)	51(1)	37(1)	2(1)	4(1)	-2(1)
C(2)	76(2)	51(1)	60(1)	-14(1)	9(1)	5(1)
C(1)	65(1)	57(1)	41(1)	-8(1)	5(1)	-1(1)
C(7)	63(1)	60(1)	59(1)	-6(1)	5(1)	-5(1)
C(10)	51(1)	67(1)	41(1)	-13(1)	5(1)	-6(1)
C(4)	70(2)	63(2)	73(2)	1(1)	17(1)	17(1)
C(6)	57(2)	78(2)	80(2)	5(1)	0(1)	-11(1)
C(11)	68(1)	99(2)	74(2)	-17(1)	10(1)	18(1)
C(5)	55(2)	88(2)	88(2)	10(2)	10(1)	7(1)

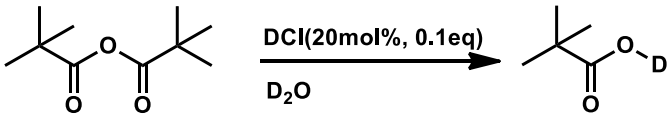
Table S21. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(1)	3715	2618	8241	63
H(9)	3112	6302	6650	56
H(2A)	2119	7886	9471	75
H(2B)	2360	9058	8057	75
H(1A)	3236	6960	9141	65
H(1B)	2819	4540	9393	65
H(7)	1544	1406	5427	73
H(4)	971	8007	8260	82
H(6)	468	2451	5529	86
H(11A)	4362	-550	6169	120
H(11B)	4585	753	7639	120
H(11C)	4895	1560	6225	120
H(5)	185	5788	6934	92

7. Mechanistic Studies

7.1 Reversibility of C-H activation

7.1.1 Synthesis of ^{t}BuCOOD[2]

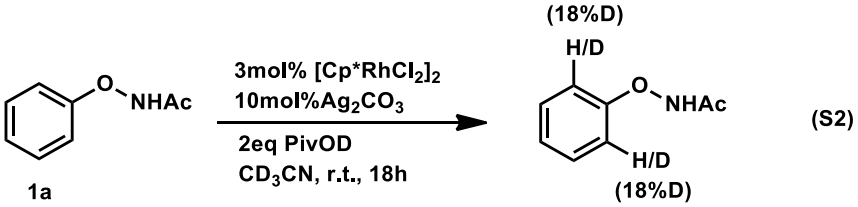


(S1)

To a thoroughly dried round-bottom flask equipped with magnetic stir bar were added (^{t}BuCO)$_2$O (9.3 g, 0.05 mol, 1 equiv), D_2O (5 ml), and DCl (20%, 0.005 mol, 0.1 equiv, 0.8mL; 80% D_2O). The reaction was allowed to proceed at rt for 3 days. (If the starting material was not consumed completely, you can allow the reaction to stirred at 90 ^{o}C and the progress was monitored by TLC.) Upon complete consumption of starting material, the reaction was cooled to room temperature and underwent an extraction process with CD_2Cl_2. The CD_2Cl_2 solution was dried over $MgSO_4$ and filtered. Purification by distillation at reduced pressure (collection of 163-164^{o}C component) affords the desired product ^{t}BuCOOD (6.07 g, 59% yield).

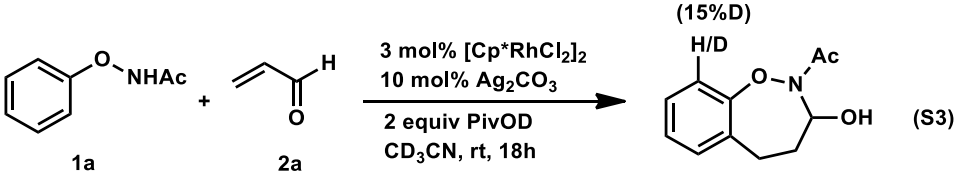
7.1.2 General procedure for the catalytic deuterium labeling experiments.

N-Phenoxyacetamides substrates (1) (0.2 mmol), $[Cp^*RhCl_2]_2$ (3 mol%), Ag_2CO_3 (10 mol%) and PivOD (2 eq) were weighed into a 15ml pressure tube, to which was added CD_3CN (1ml) in a glove box. The reaction vessel was stirred at room temperature for 18h. After reaction, 1,4-dimethoxybenzene (0.2 mmol) was added as an internal standard. Then the mixture was subjected to ^{1}HNMR.

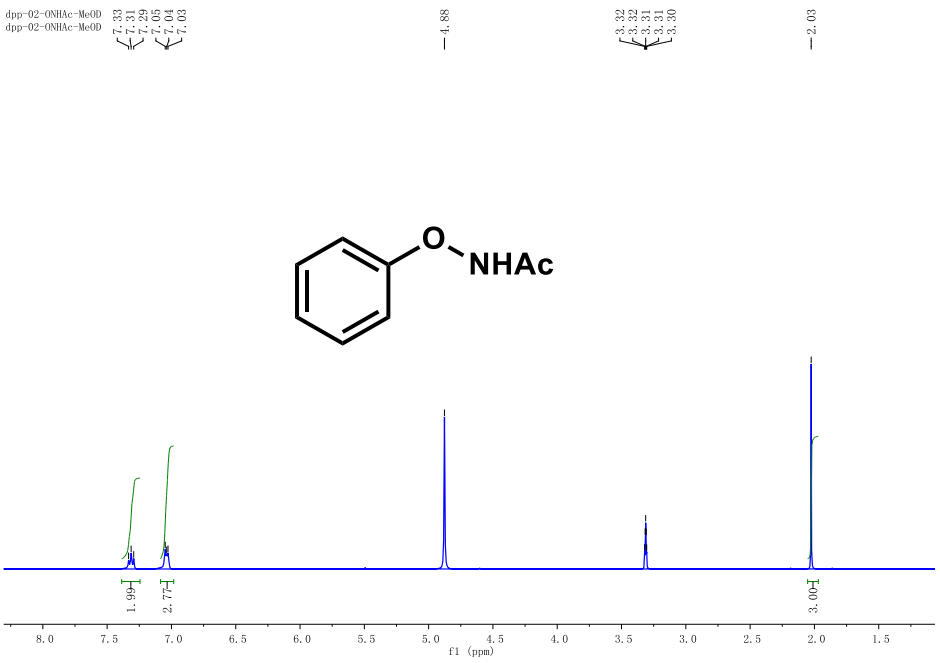


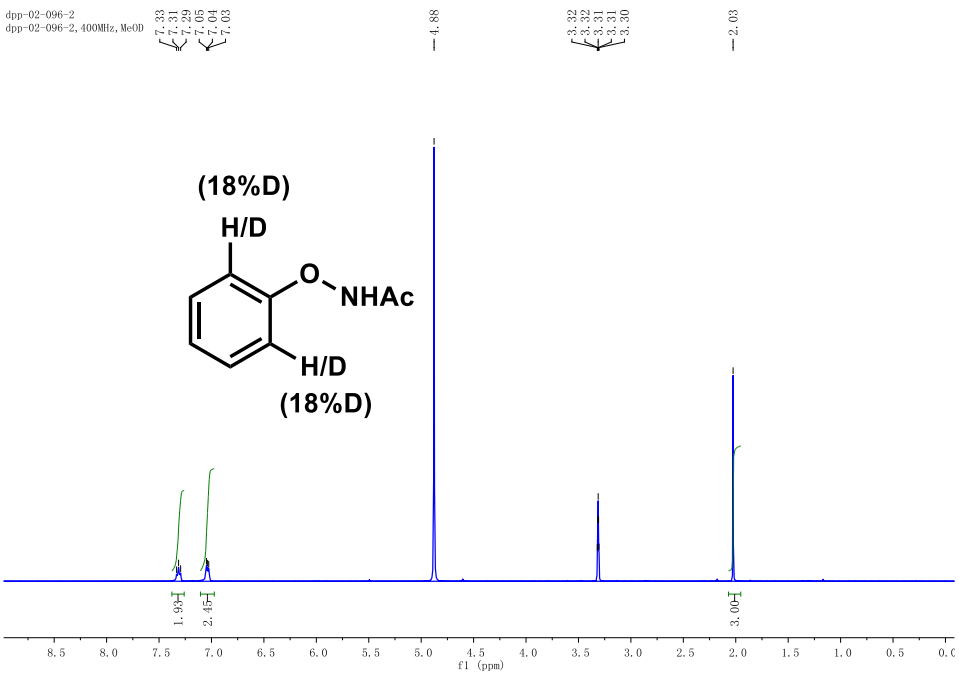
(S2)

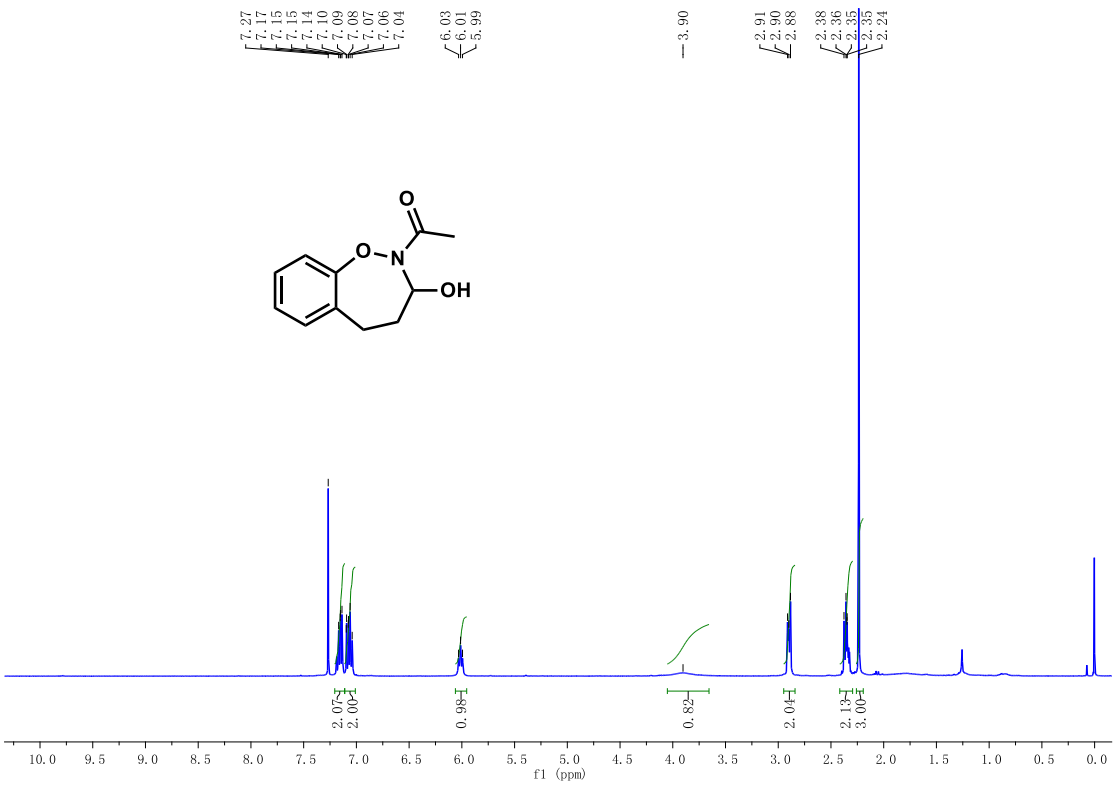
N-Phenoxyacetamides substrates (1) (0.2 mmol), $[Cp^*RhCl_2]_2$ (3 mol%), Ag_2CO_3 (10 mol%) and PivOD (2 equiv) were weighed into a 15ml pressure tube, to which was added unsaturated aldehyde (2 equiv) in CD_3CN (2 mL) in a glove box. The reaction vessel was stirred at room temperature for 18h. After reaction, 1,4-dimethoxybenzene (0.2 mmol) was added as an internal standard. Then the mixture was subjected to ^{1}HNMR.

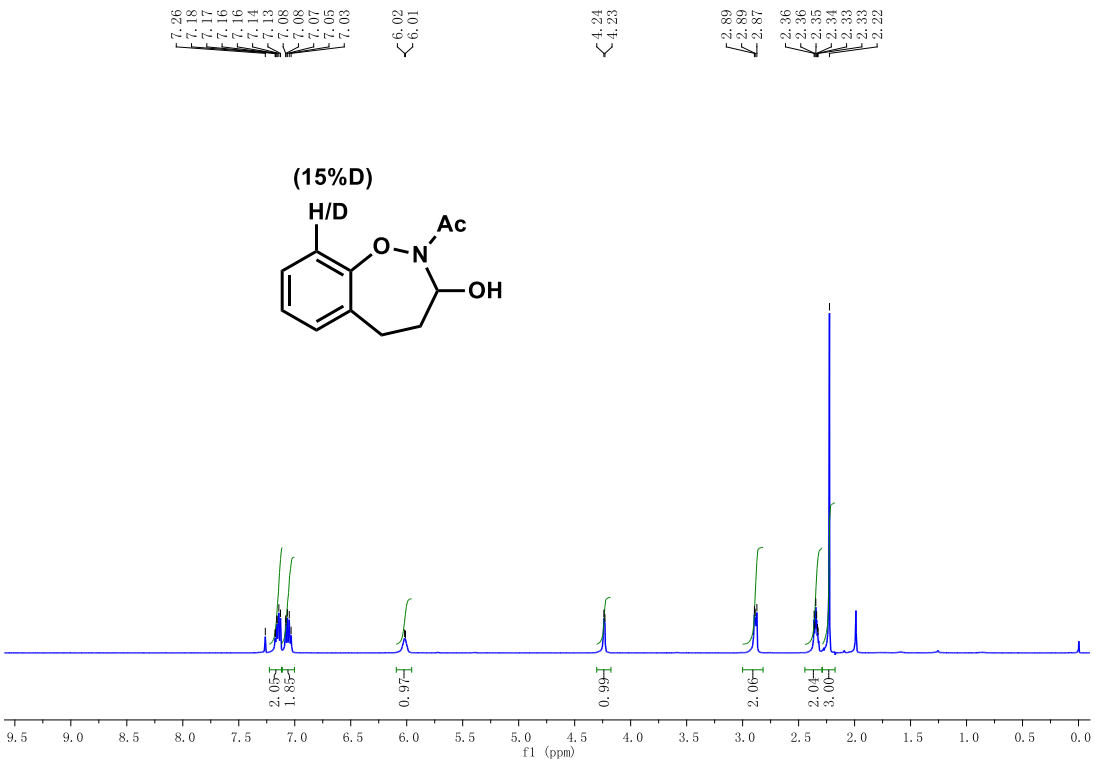


(S3)


dpp-02-ONHAc-MeOD
dpp-02-ONHAc-MeOD
7.33
7.31
7.29
7.05
7.04
7.03
4.88
3.32
3.32
3.31
3.31
3.30
2.03
O
NHAc
1.99
2.77
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

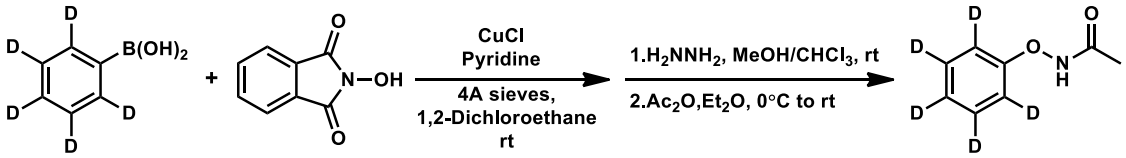

dpp-02-096-2
dpp-02-096-2, 400MHz, MeOD
7.33
7.31
7.29
7.05
7.04
7.03
4.88
3.32
3.32
3.31
3.31
3.30
2.03
(18%D)
H/D
O
NHAc
H/D
(18%D)
1.93
2.45
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)





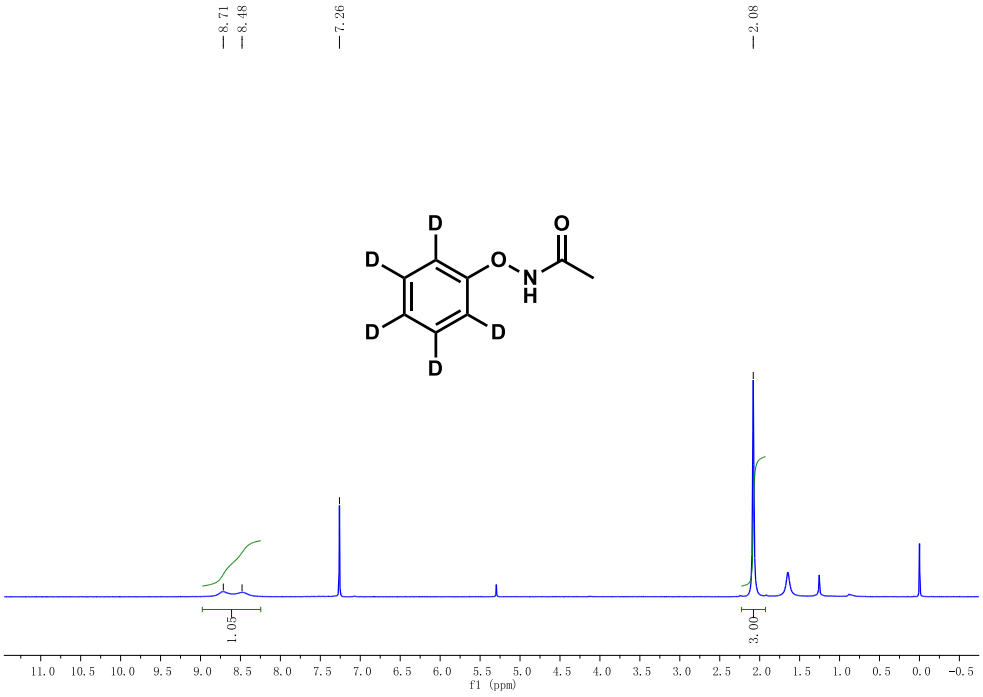
7.2 KIE Experiment

7.2.1 Synthesis of deuterated substrate 1a-d_5



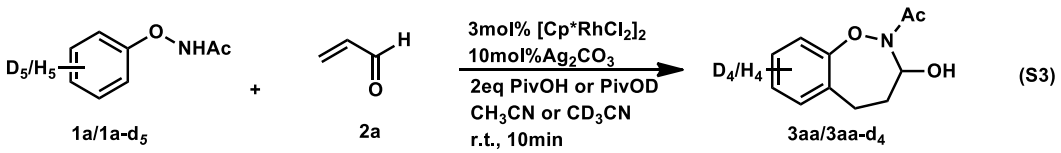
1a-d$_5$

Following the general procedure for the synthesis of substrate **1**[1], deuterated substrate **1a-d$_5$**was obtained from (d$_5$-phenyl)boronic acid.



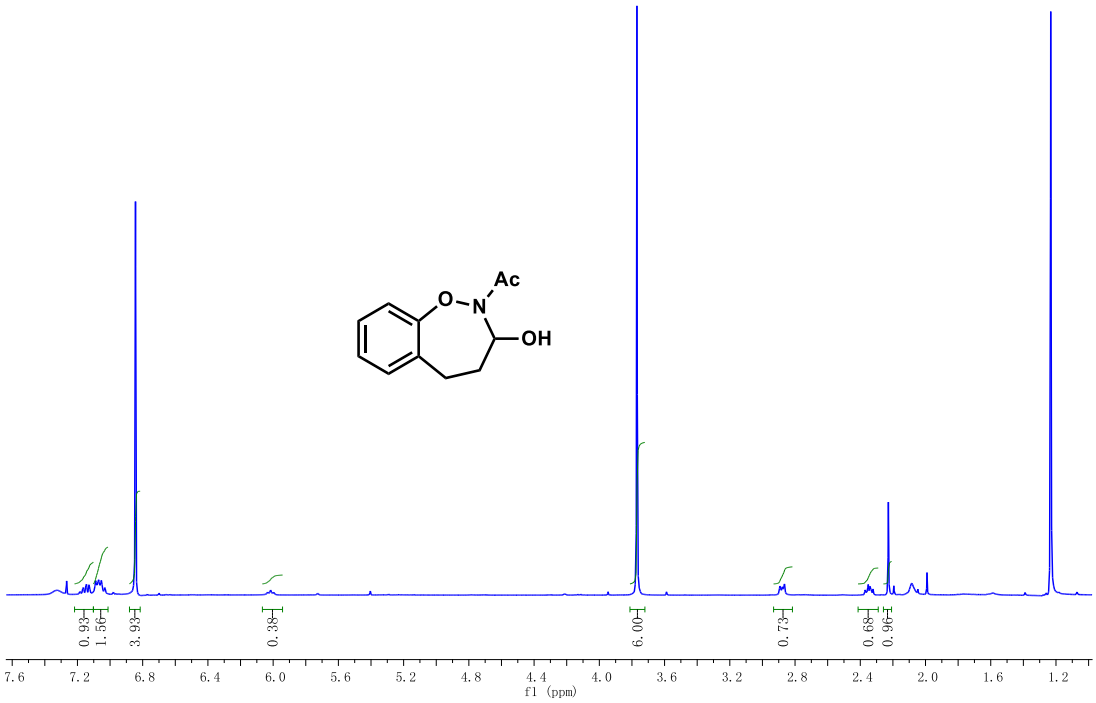
7.2.2 Determination of kinetic isotope effect from two parallel reactions.

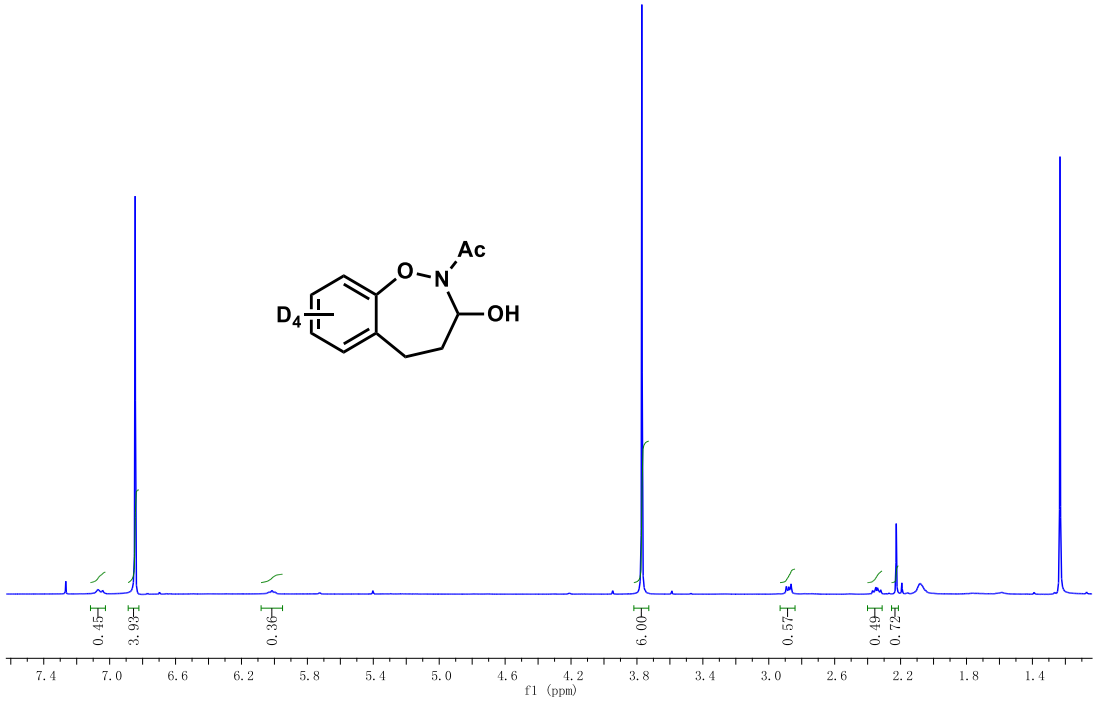
N-Phenoxyacetamides substrates (1) or (d$_5$-phenyl)boronic acid (0.1 mmol), [Cp*RhCl$_2$]$_2$ (3 mol%), Ag$_2$CO$_3$ (10 mol%) and PivOH or PivOD (2 eq) were weighed into a 15ml pressure tube, to which respectively was added acrolein (2 eq) in CH$_3$CN or CD$_3$CN (1 ml) in a glove box. The reaction vessel was stirred at room temperature for 10min. After reaction, 1,4-dimethoxybenzene (0.1 mmol) was added as an internal standard. Then the mixture was subjected to ^{1}HNMR.



1a/1a-d$_5$ + 2a → 3aa/3aa-d$_4$ (S3)

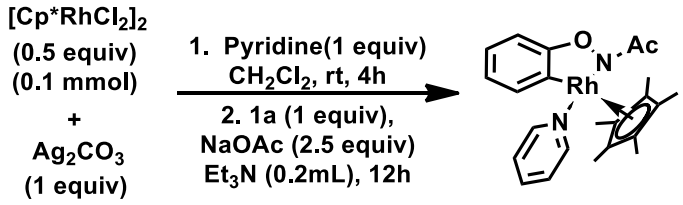
Parallel reaction: K_H/K_D=1.3





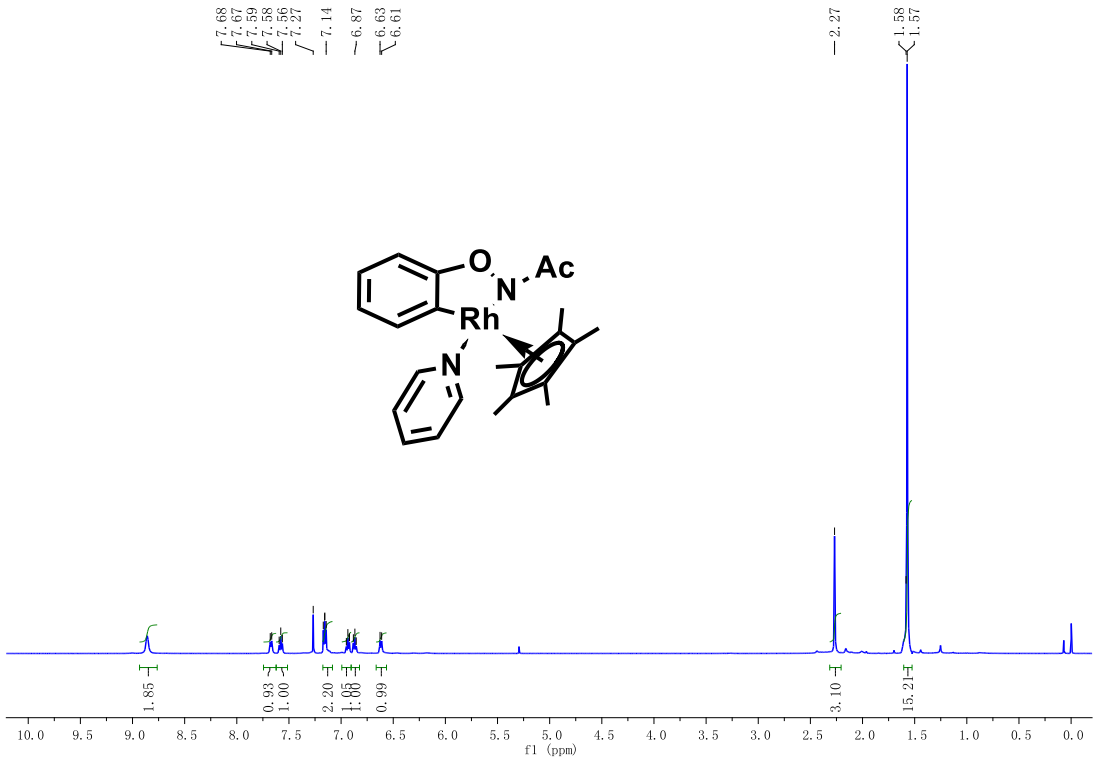
7.3 Synthesis and analysis of the possible intermediate

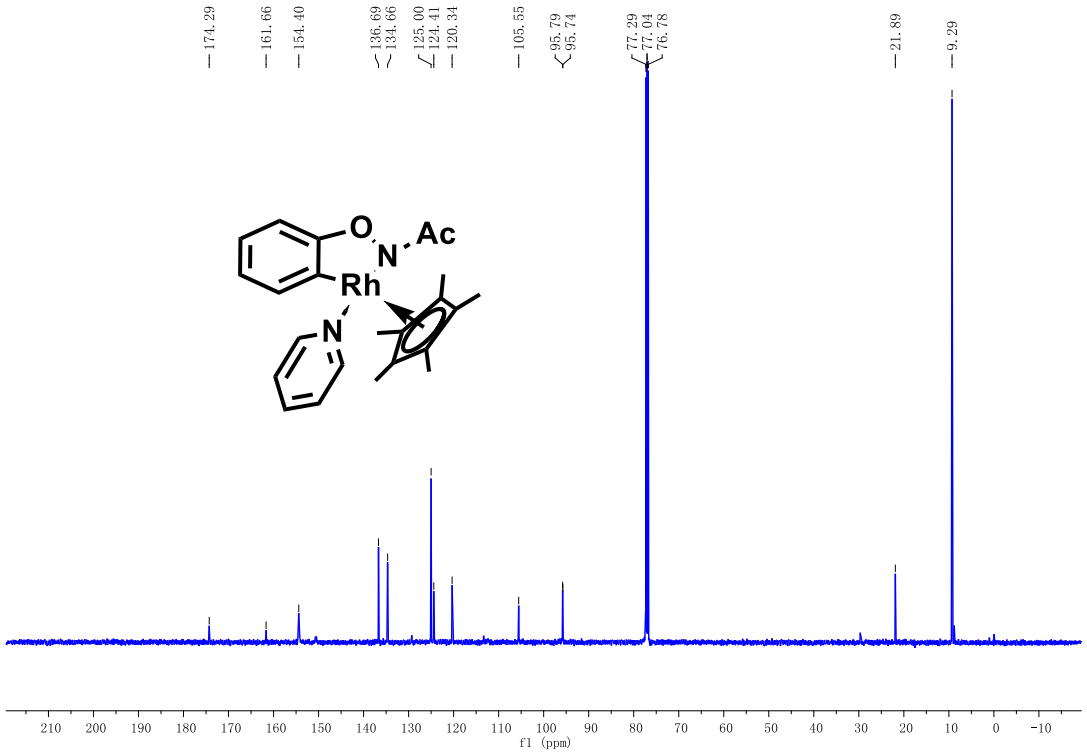
First, we synthesized the catalyst Cp*Rh(OAc)$_2$.[3] Then we attempted to synthesize the cyclometalated intermediates.

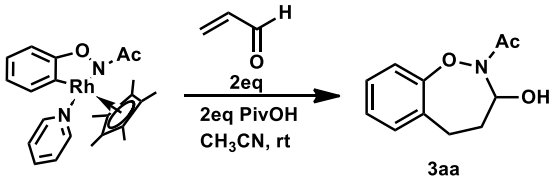


intermediate A'

By following the relate method[4], to a solution of $[Cp^*RhCl_2]_2$ (0.10 mmol) and Ag_2CO_3 (0.2mmol) in CH_2Cl_2 (2 ml) was added pyridine (0.20 mmol) at room temperature. After vigorous stirring for 4 h, NaOAc (0.50 mmol) and *N*-Phenoxyacetamide(1a) (0.2 mmol) were added to the solution with TEA (0.2 ml), and vigorous stirring was continued for 12 h. After the reaction was complete, the solvent was filtered and evaporated under reduced pressure. The crude product was obtained with 90% yield. The structure was identified by NMR. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.86 (s, 1H), 7.67 (d, J=7.0, 1H), 7.58 (t, J=7.6, 1H), 7.16 (dd, J=7.4, 6.5, 2H), 6.93 (dd, J=10.8, 4.1, 1H), 6.87 (t, J=6.8, 1H), 6.62 (d, J=7.7, 1H), 2.27 (s, 3H), 1.58 (s, 15H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.29, 161.66, 154.40, 136.69, 134.66, 125.00 (2C), 124.41, 120.34, 105.55, 95.77 (d, J=6.3 HZ), 21.89, 9.29.





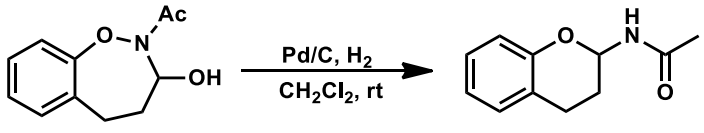


3aa

Yield=30%

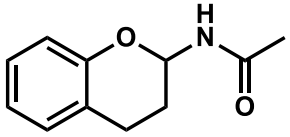
The complex 1(1eq), acrolein(2eq) and PivOH(2eq) were added to the solution of CH_3CN.The mixture was stirred at rt. When the reaction was complete, the solvent was filtered and evaporated. The crude product was purified by column chromatography on silica gel to afford the desired product.

8. Synthetic transformations



3aa 6

The compound 3aa was dissolved in CH_2Cl_2, then added Pd/C with H_2 balloon. The mixture was stirred at rt for overnight. Then the mixture was filtered and evaporated.



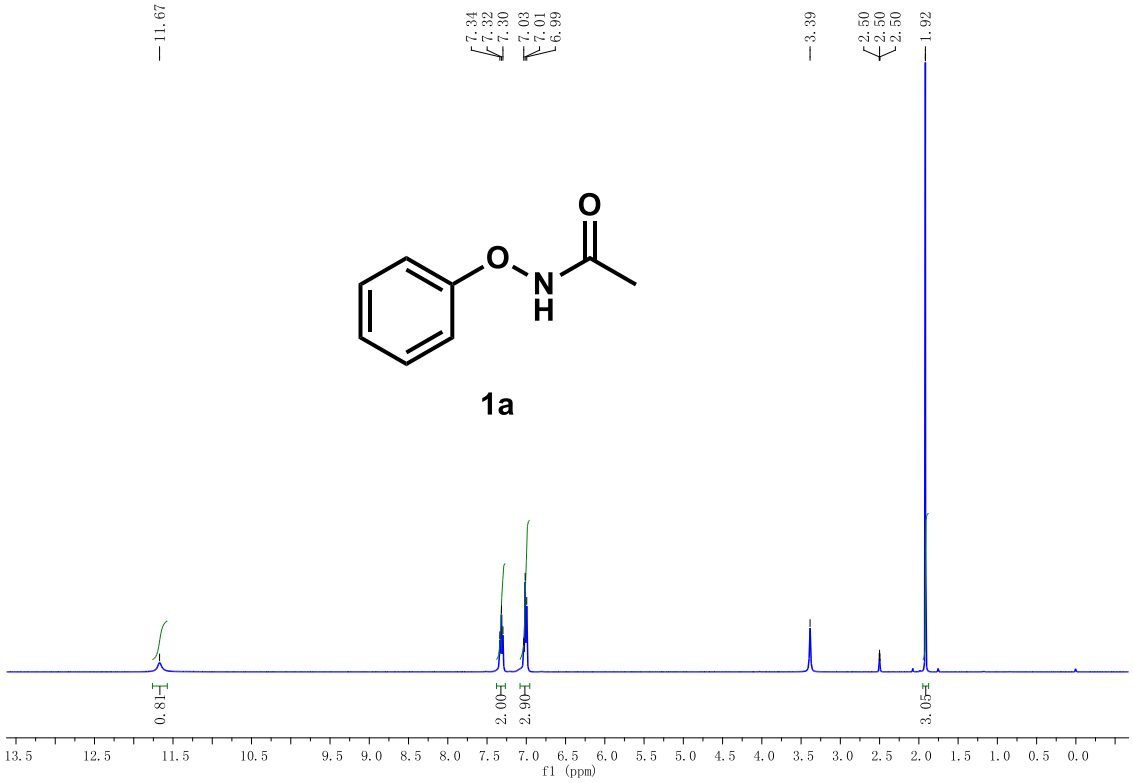
***N*-(chroman-2-yl)acetamide (6):** 80% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.19 – 6.98 (m, 2H), 6.86 (ddd, J = 18.1, 12.2, 4.6 Hz, 2H), 6.27 (d, J = 8.0

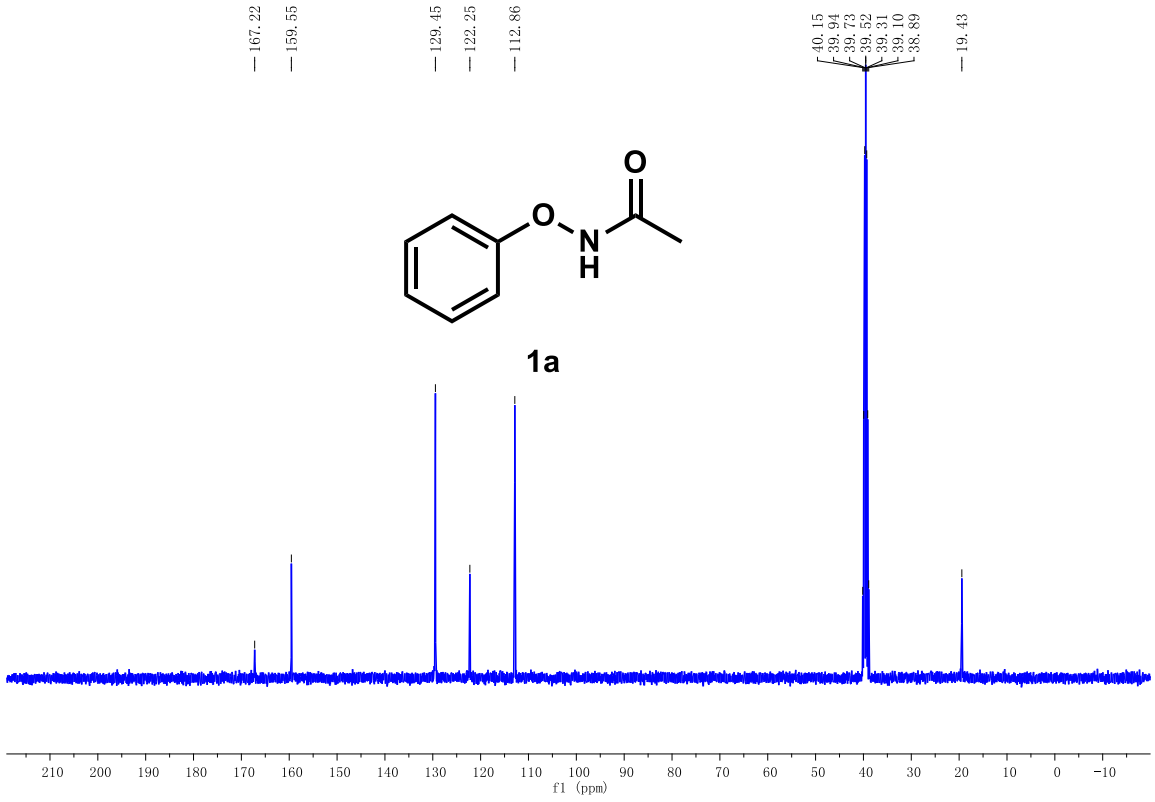
Hz, 1H), 5.89 (ddd, J = 9.2, 8.5, 2.7 Hz, 1H), 2.96 (ddd, J = 15.8, 9.5, 6.0 Hz, 1H), 2.81 (dt, J = 16.8, 5.6 Hz, 1H), 2.15 (dtd, J = 14.2, 5.8, 2.7 Hz, 1H), 2.05 (s, 3H), 1.92 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.87, 153.37, 129.22, 127.63, 120.84, 120.70, 117.15, 75.84, 26.97, 23.52, 23.31. HRMS **(ESI)** calculated for $C_{11}H_{14}NO_3$ (+):192.0954; Found:192.1000. **Melting Point:** 144-146 °C.

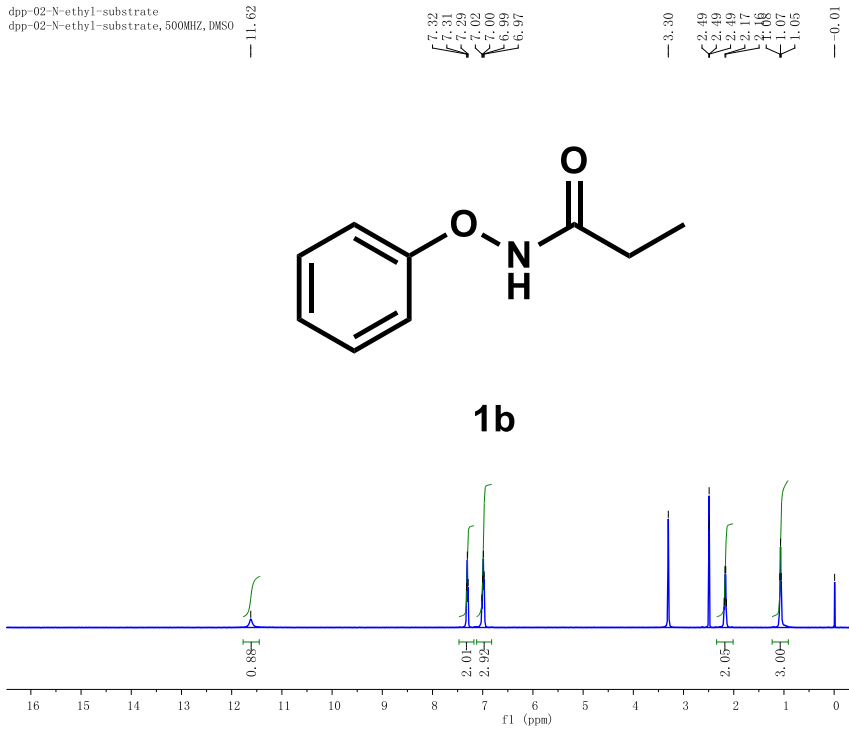
References

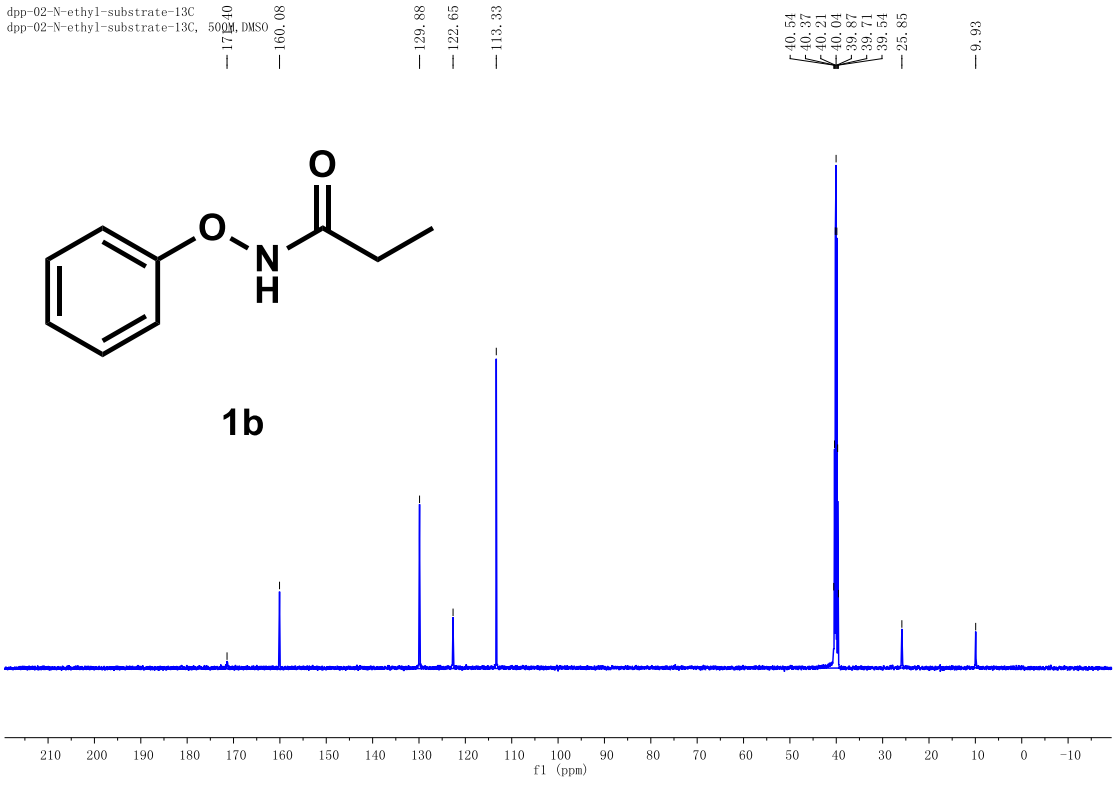
1. H. M. Petrassi, K. B. Sharpless and J. W. Kelly, *Org. Lett.*, 2001, **3**, 139.
2. B. Liu, C. Song, C. Sun, S. Zhou and J. Zhu, *J. Am. Chem. Soc.*, 2013, **135**, 16625.
3. C. Wang and Y. Huang, *Org. Lett.*, 2013, **15**, 5294.
4. N. Wang, B. Li, H. Song, S. Xu and B. Wang, *Chem. Eur. J.*, 2013, **19**, 358.

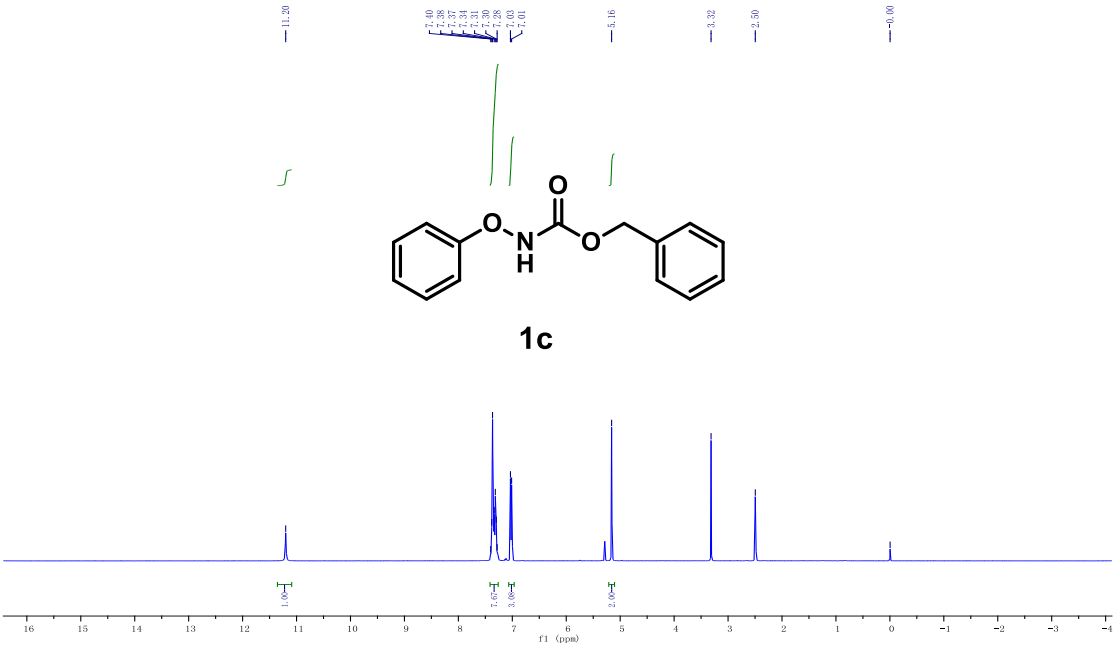
^{1}H and ^{13}C NMR Spectra of Substrates and Products

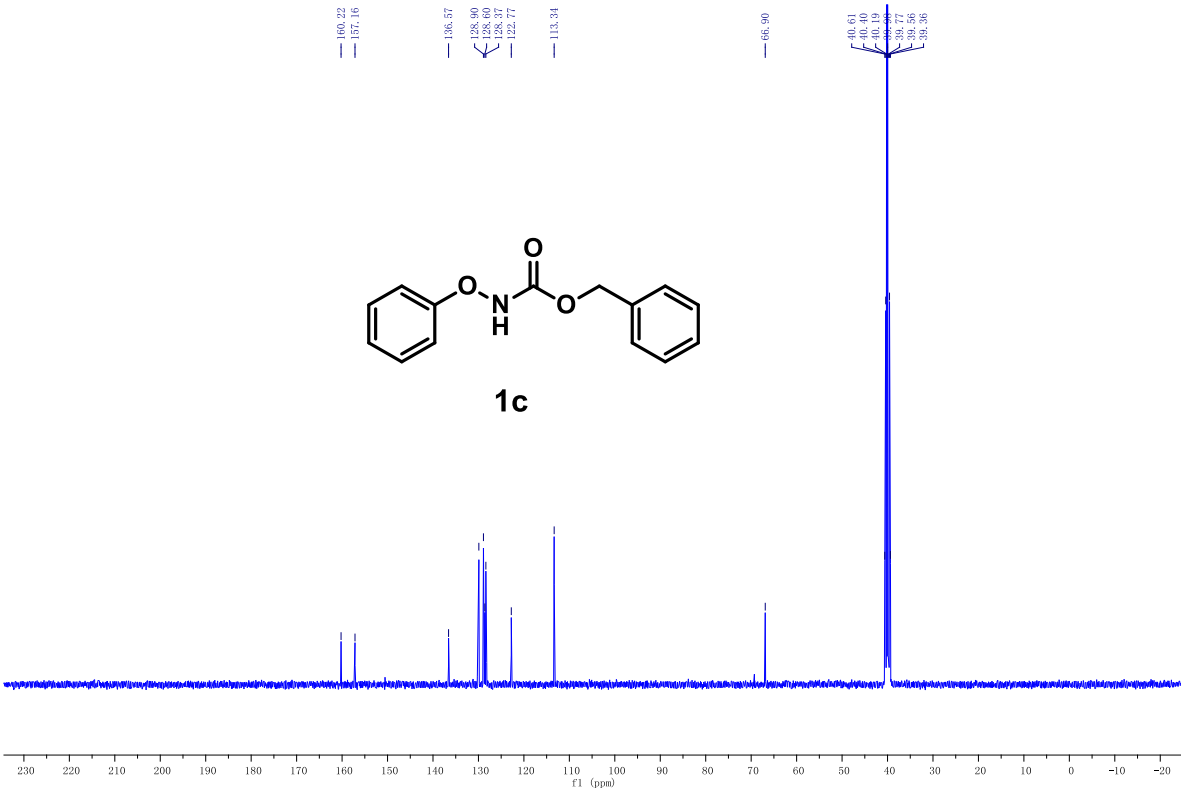


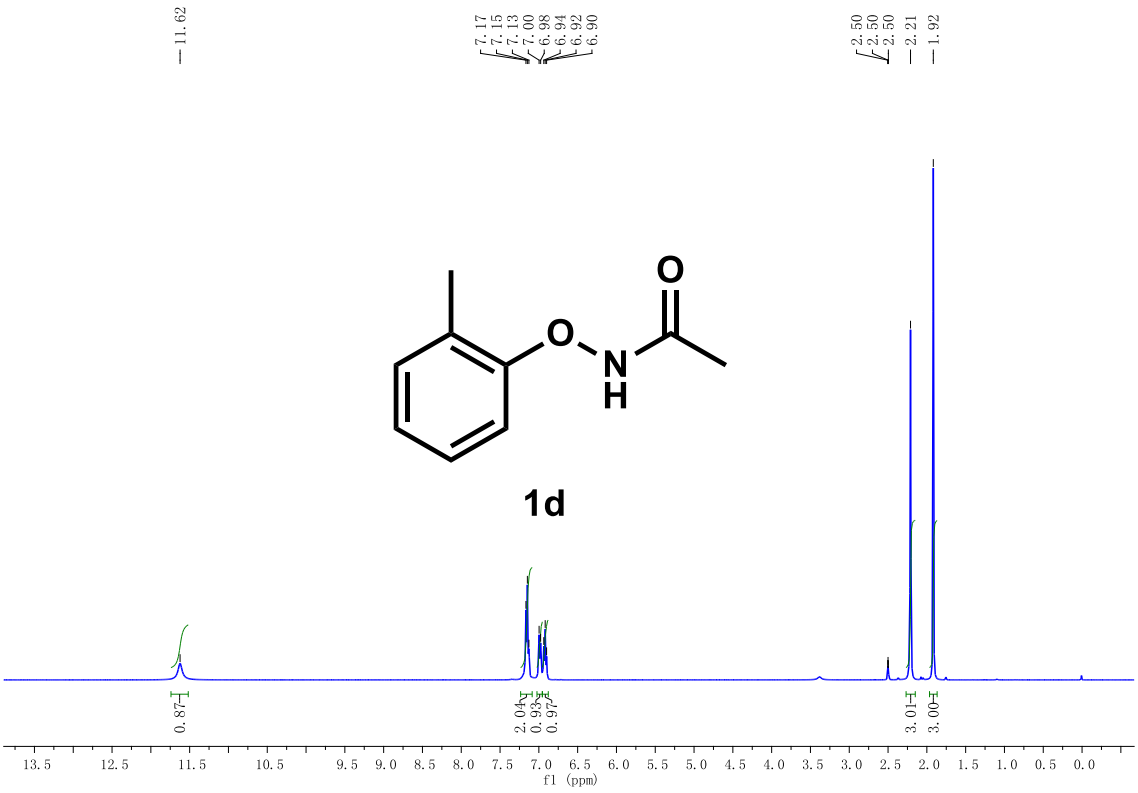


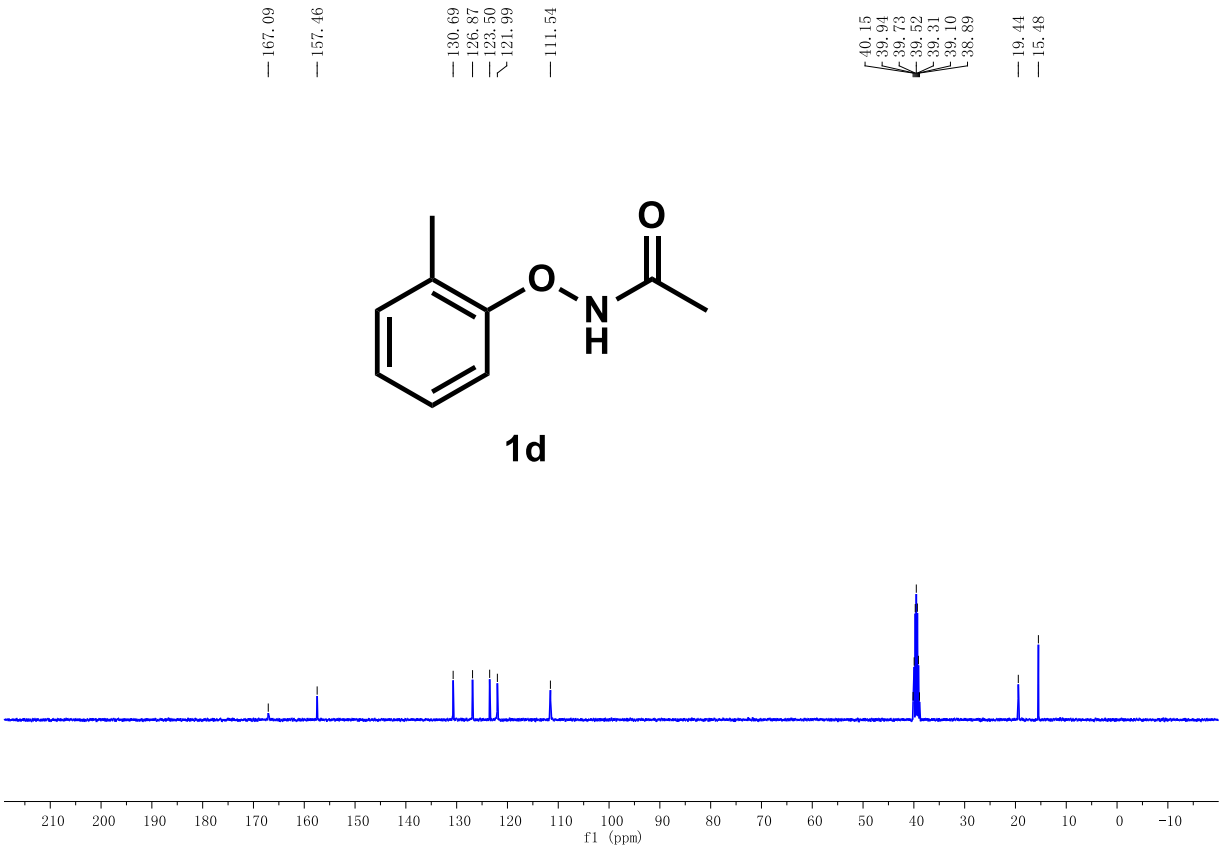

dpp-02-N-ethyl-substrate
dpp-02-N-ethyl-substrate,500MHZ,DMSO
11.62
7.32
7.31
7.29
7.02
7.00
6.99
6.97
3.30
2.49
2.49
2.49
2.17
1.08
1.07
1.05
-0.01
O
O
N
H
1b
0.88
2.01
2.92
2.05
3.00
f1 (ppm)

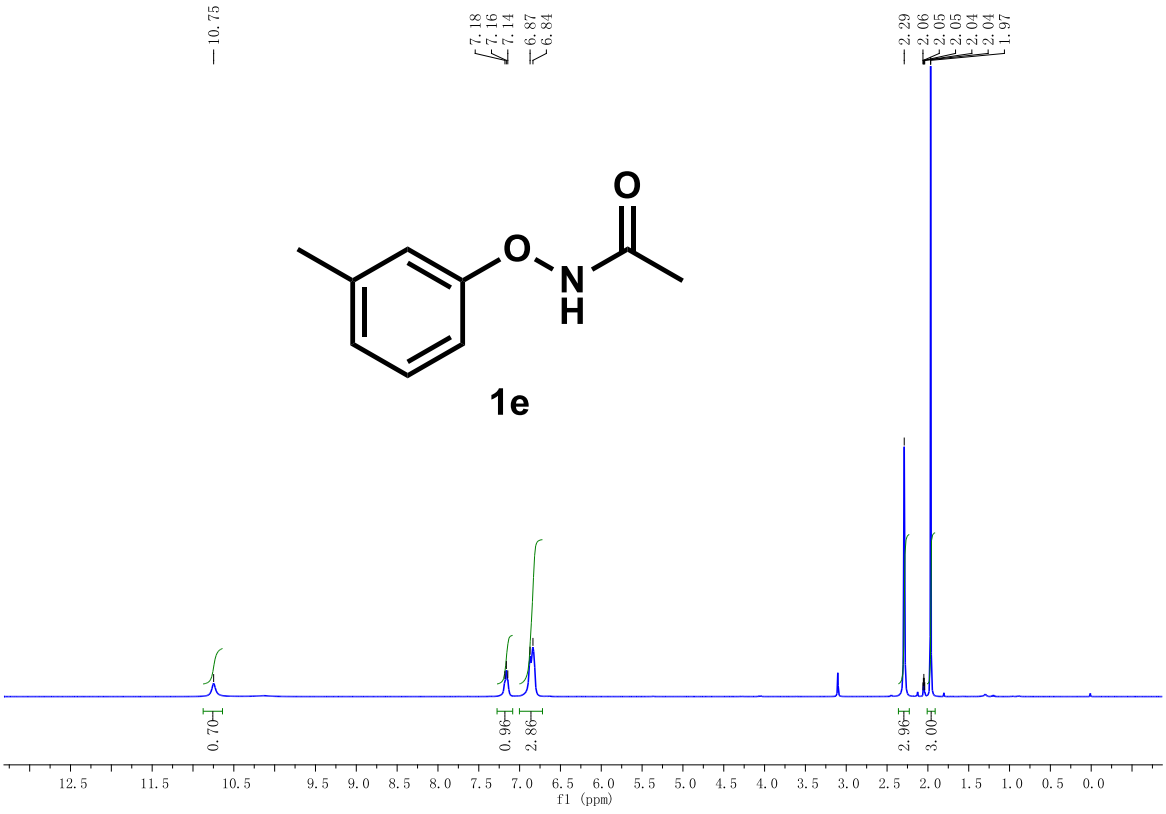

dpp-02-N-ethyl-substrate-13C
dpp-02-N-ethyl-substrate-13C, 500M,DMSO
171.40
160.08
129.88
122.65
113.33
40.54
40.37
40.21
40.04
39.87
39.71
39.54
25.85
9.93
O
O
N
H
1b
f1 (ppm)

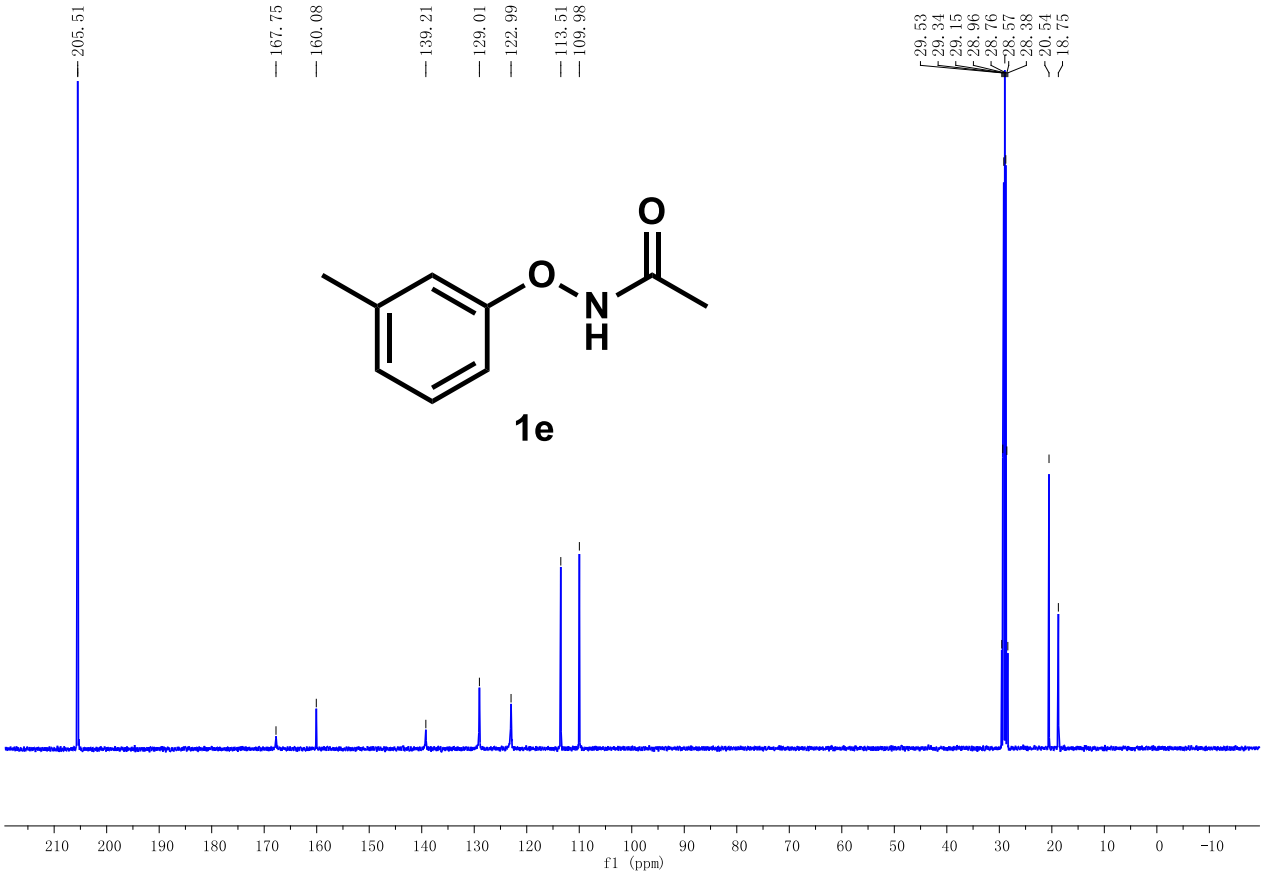

11.20
7.40
7.38
7.37
7.34
7.31
7.30
7.28
7.03
7.01
5.16
3.32
2.50
0.00
O
O
N
H
O
1c
1.00
7.67
3.08
2.00
f1 (ppm)

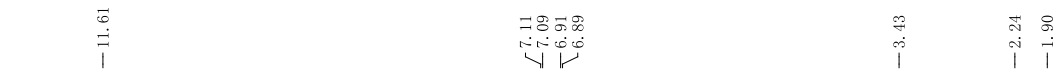

160.22
157.16
136.57
128.90
128.60
128.37
122.77
113.34
66.90
40.61
40.40
40.19
39.77
39.56
39.36
O
O
N
H
O
1c
f1 (ppm)

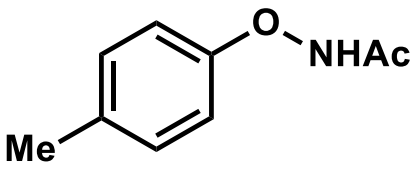

11.62
7.17
7.15
7.13
7.00
6.98
6.94
6.92
6.90
2.50
2.50
2.50
2.21
1.92
O
O
N
H
1d
0.87
2.04
0.93
0.97
3.01
3.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.09
157.46
130.69
126.87
123.50
121.99
111.54
40.15
39.94
39.73
39.52
39.31
39.10
38.89
19.44
15.48
O
O
N
H
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

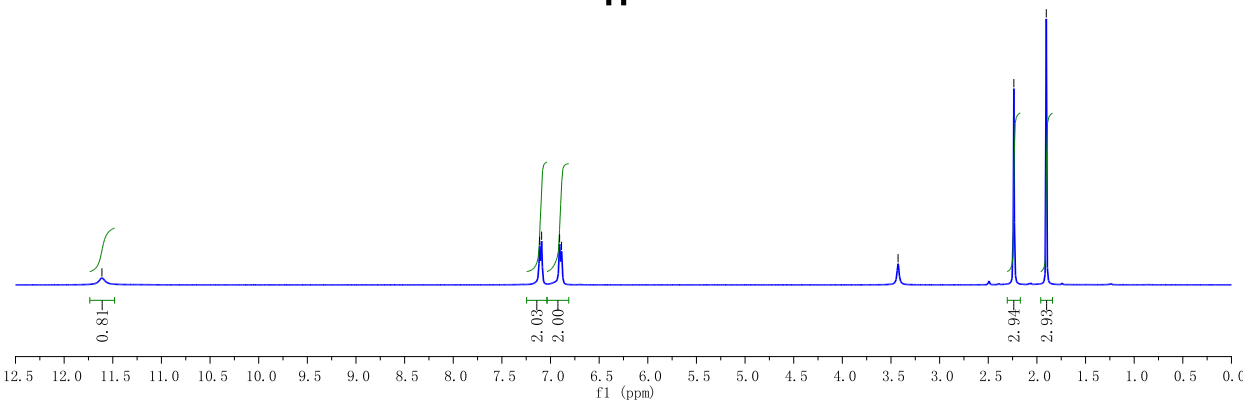

10.75
7.18
7.16
7.14
6.87
6.84
2.29
2.06
2.05
2.05
2.04
2.04
1.97
O
O
N
H
1e
0.70
0.96
2.86
2.96
3.00
f1 (ppm)


205.51
167.75
160.08
139.21
129.01
122.99
113.51
109.98
29.53
29.34
29.15
28.96
28.76
28.57
28.38
20.54
18.75
O
O
N
H
1e
f1 (ppm)

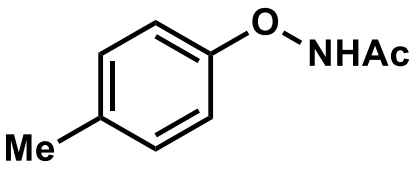

11.61
7.11
7.09
6.91
6.89
3.43
2.24
1.90


O
NHAc
Me

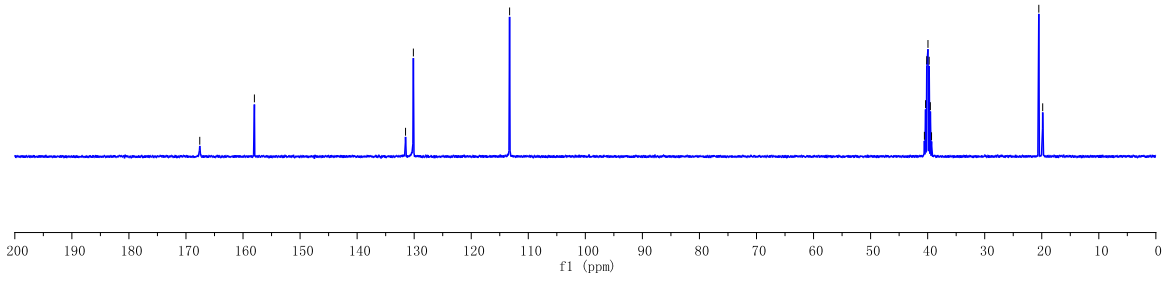
1f

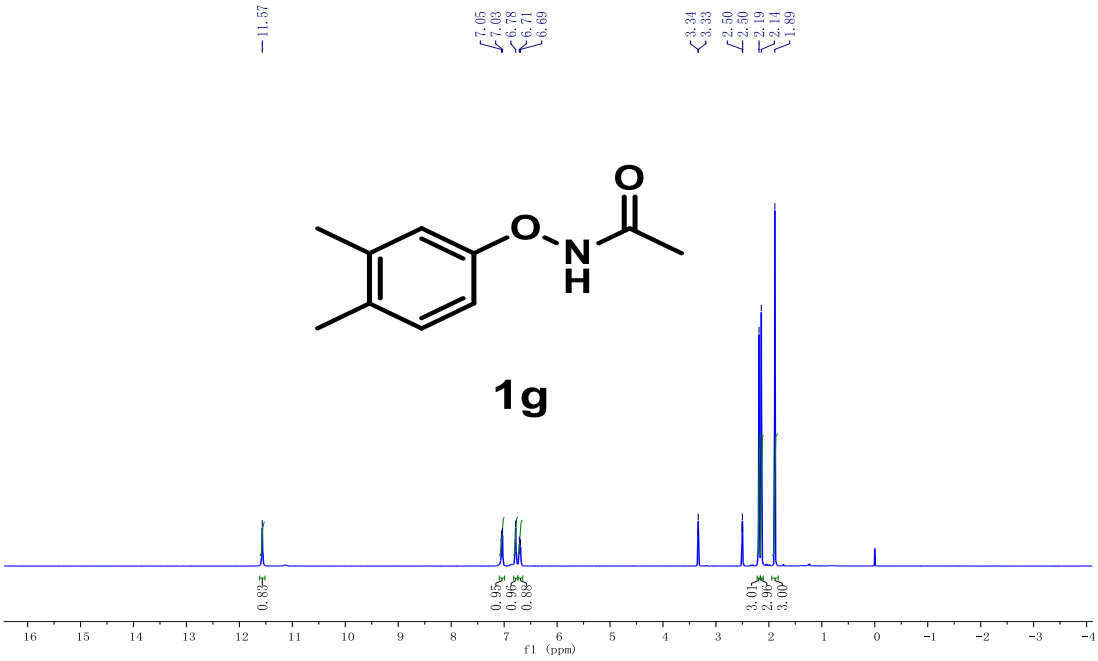

0.81
2.03
2.00
2.94
2.93
f1 (ppm)

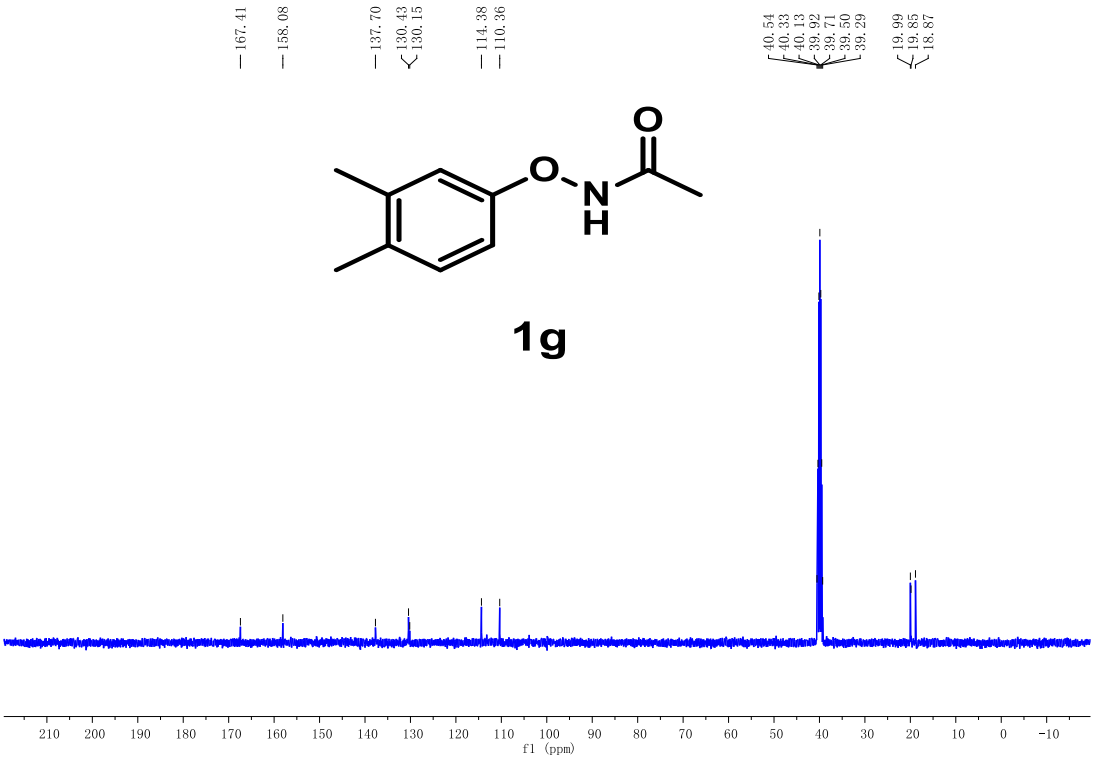

167.58
158.00
131.51
130.14
113.28
40.57
40.36
40.15
39.94
39.74
39.53
39.32
20.52
19.84

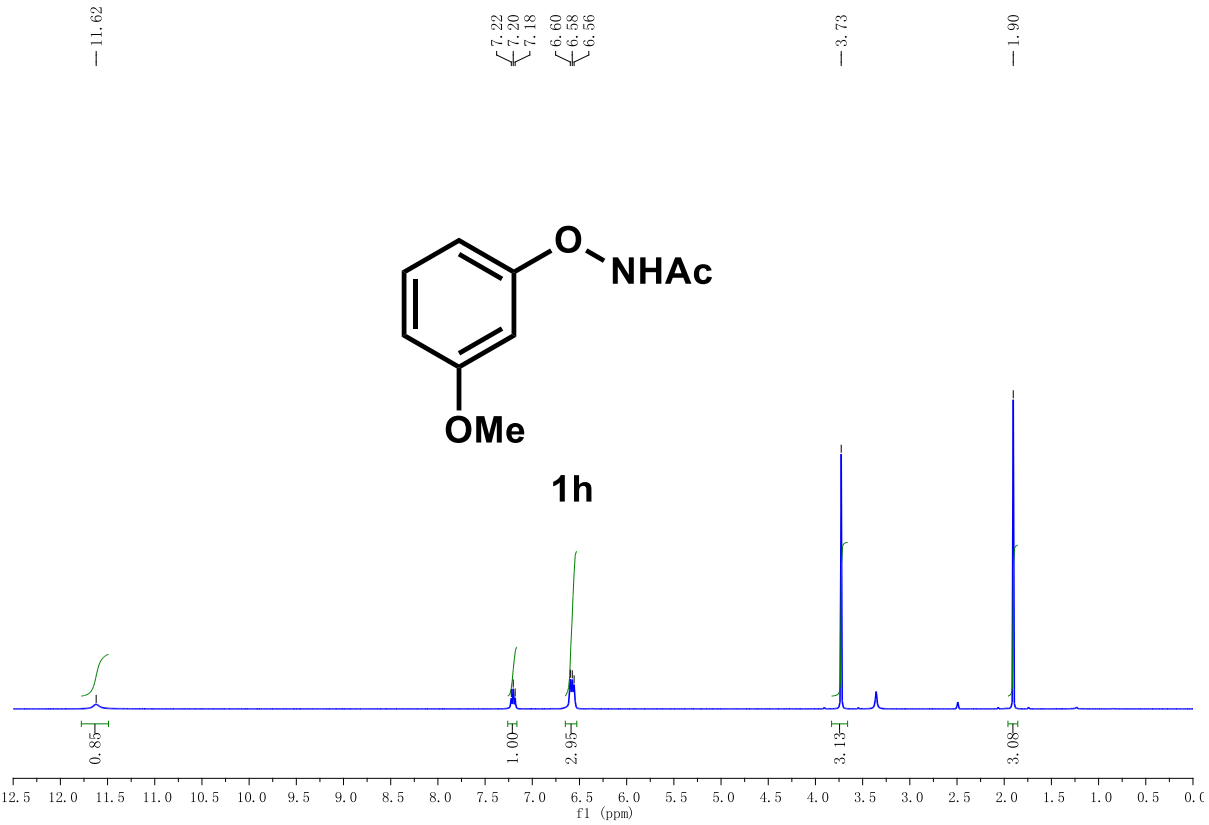

O
NHAc
Me

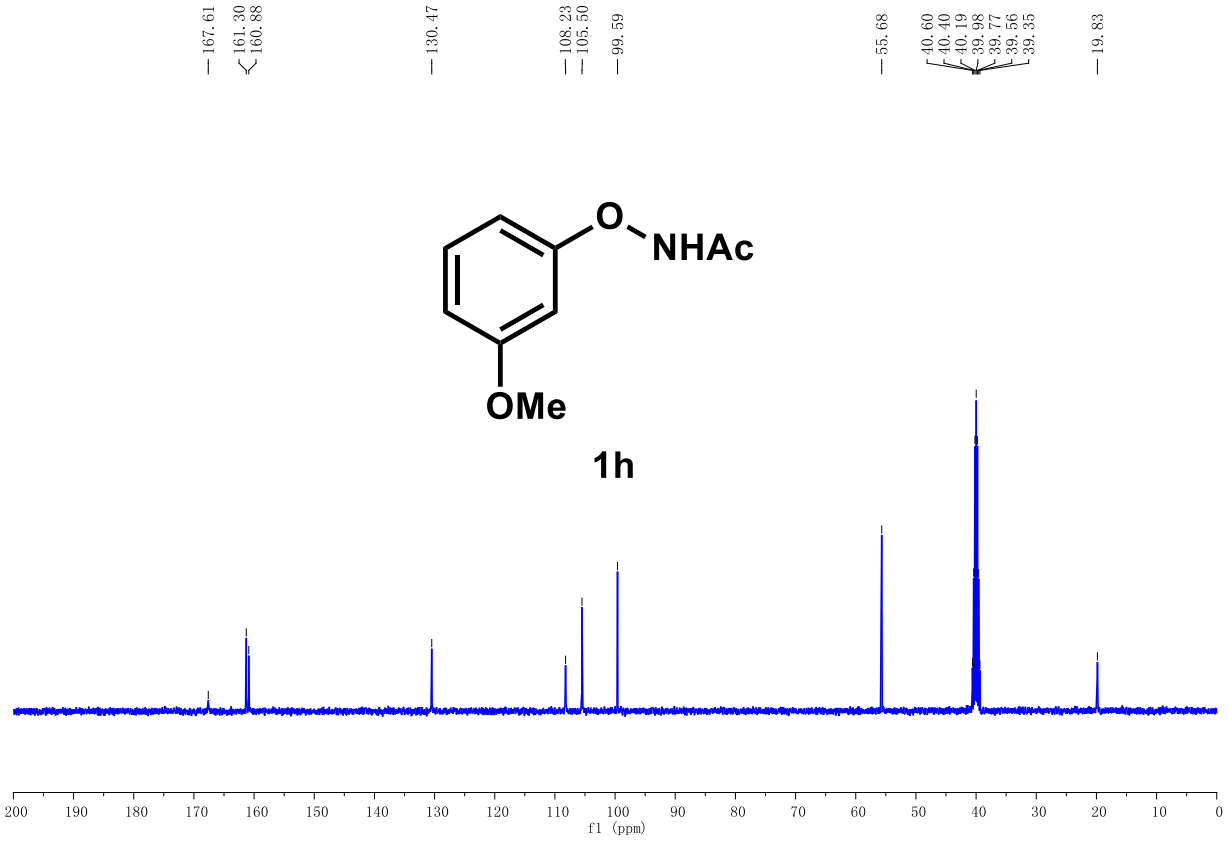
1f

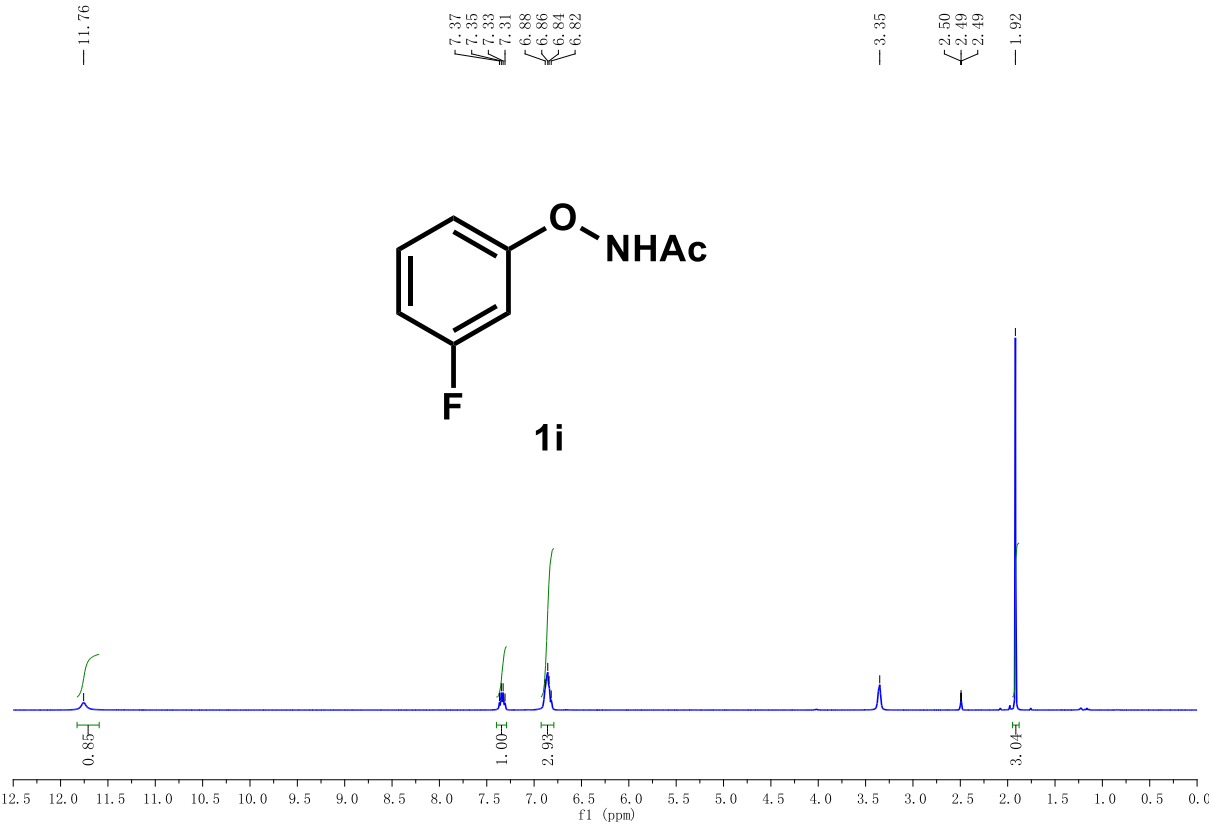

f1 (ppm)

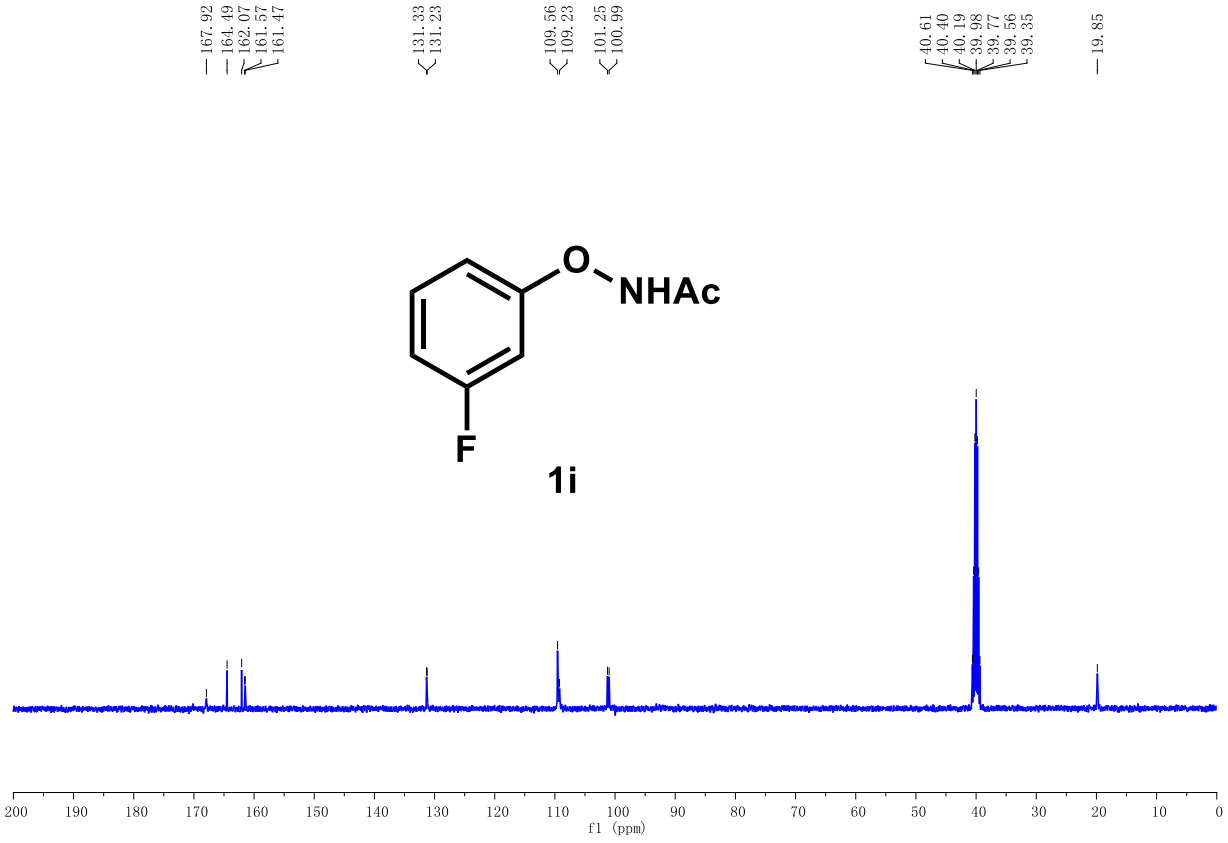

11.57
7.05
7.03
6.78
6.71
6.69
3.34
3.33
2.50
2.50
2.19
2.14
1.89
O
O
N
H
1g
0.83
0.95
0.96
0.88
3.01
2.96
3.00
f1 (ppm)

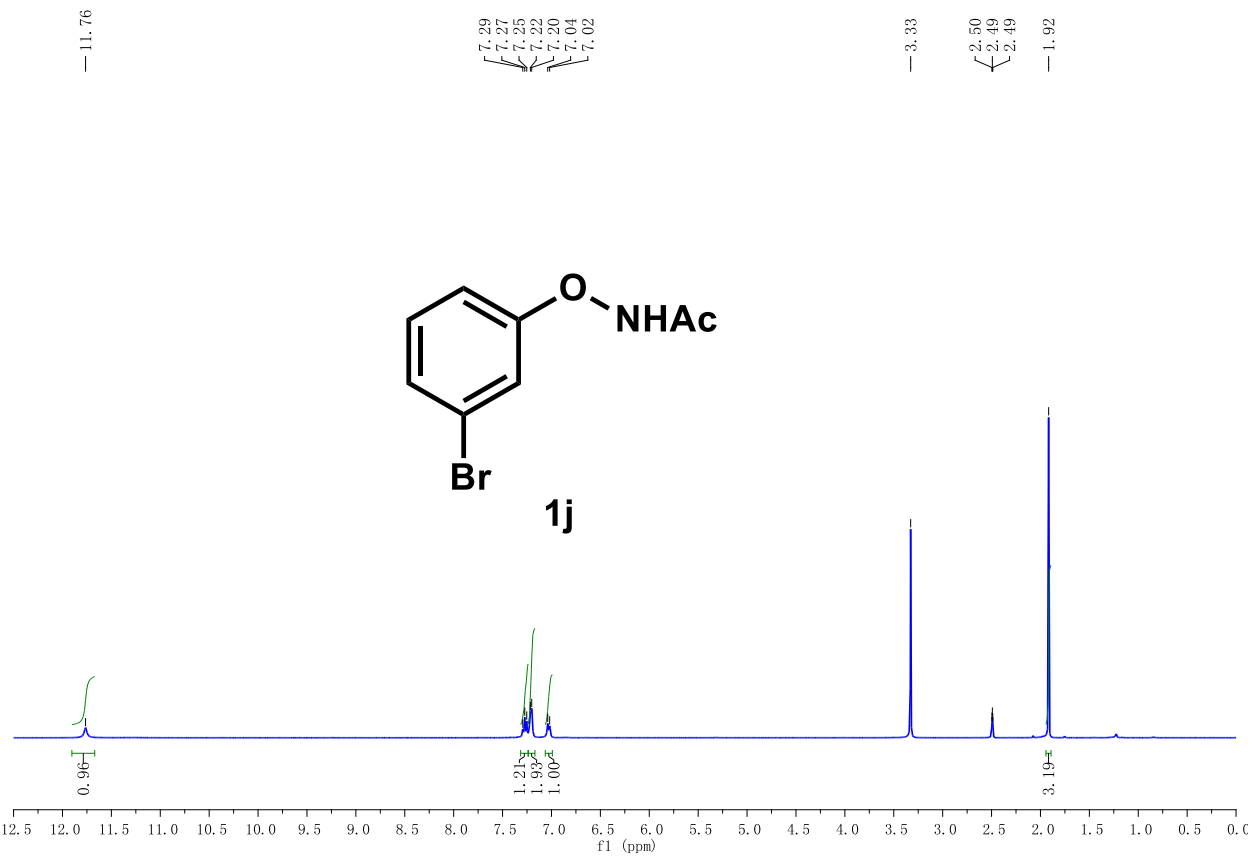

167.41
158.08
137.70
130.43
130.15
114.38
110.36
40.54
40.33
40.13
39.92
39.71
39.50
39.29
19.99
19.85
18.87
O
O
N
H
1g
f1 (ppm)

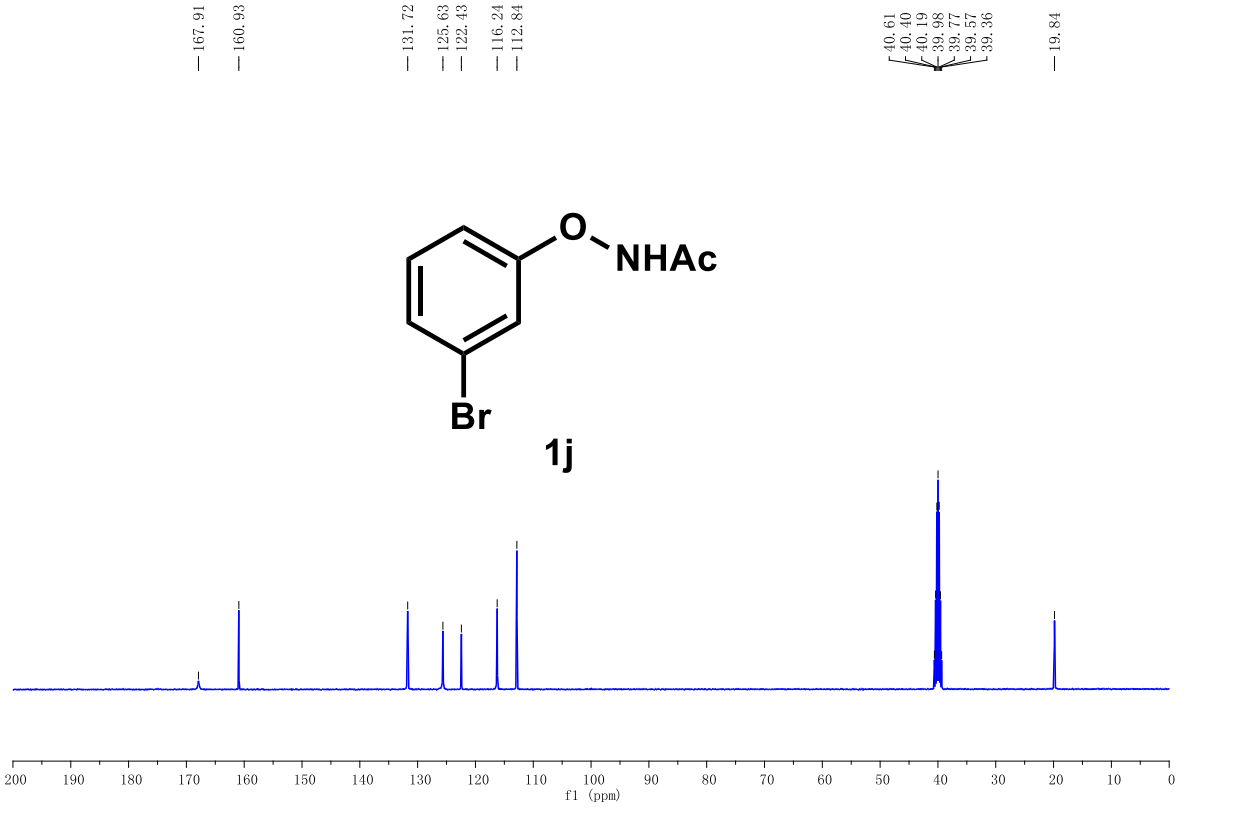

11.62
7.22
7.20
7.18
6.60
6.58
6.56
3.73
1.90
O
NHAc
OMe
1h
0.85
1.00
2.95
3.13
3.08
f1 (ppm)

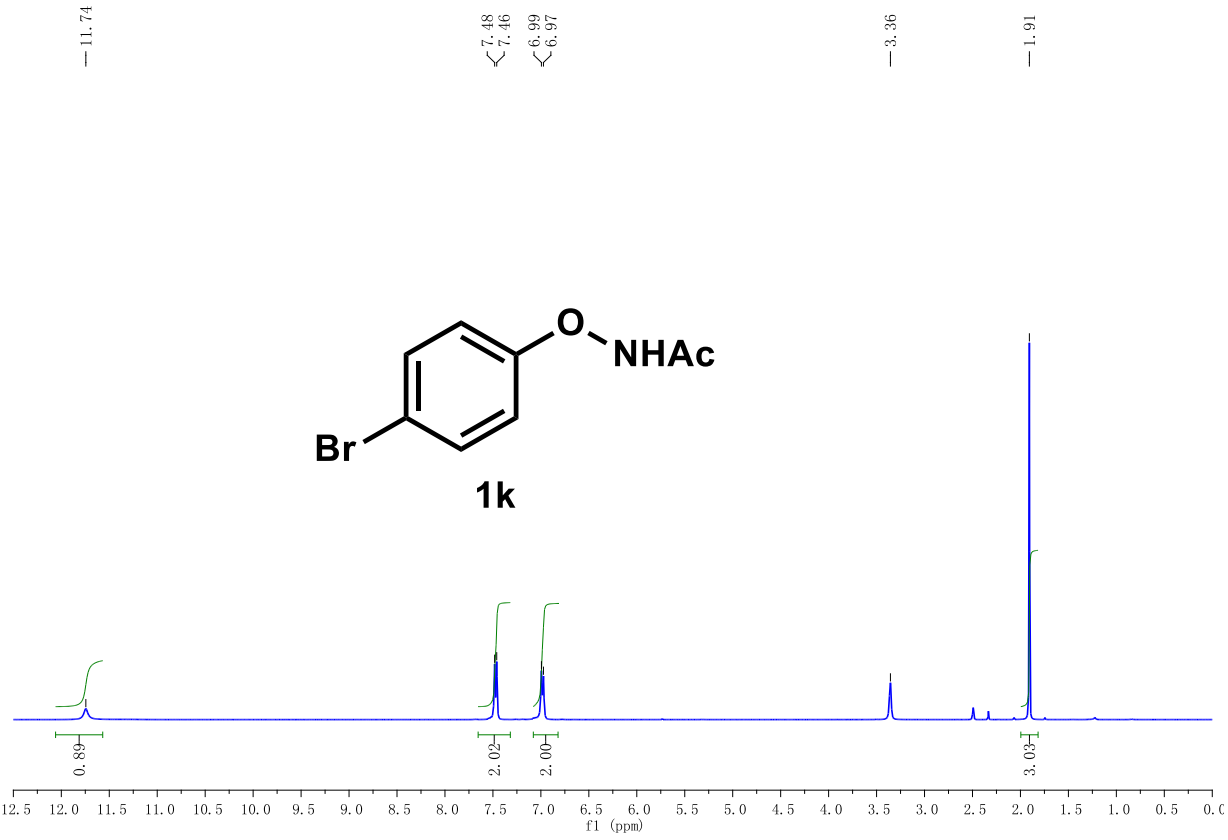

167.61
161.30
160.88
130.47
108.23
105.50
99.59
55.68
40.60
40.40
40.19
39.98
39.77
39.56
39.35
19.83
O
NHAc
OMe
1h
f1 (ppm)

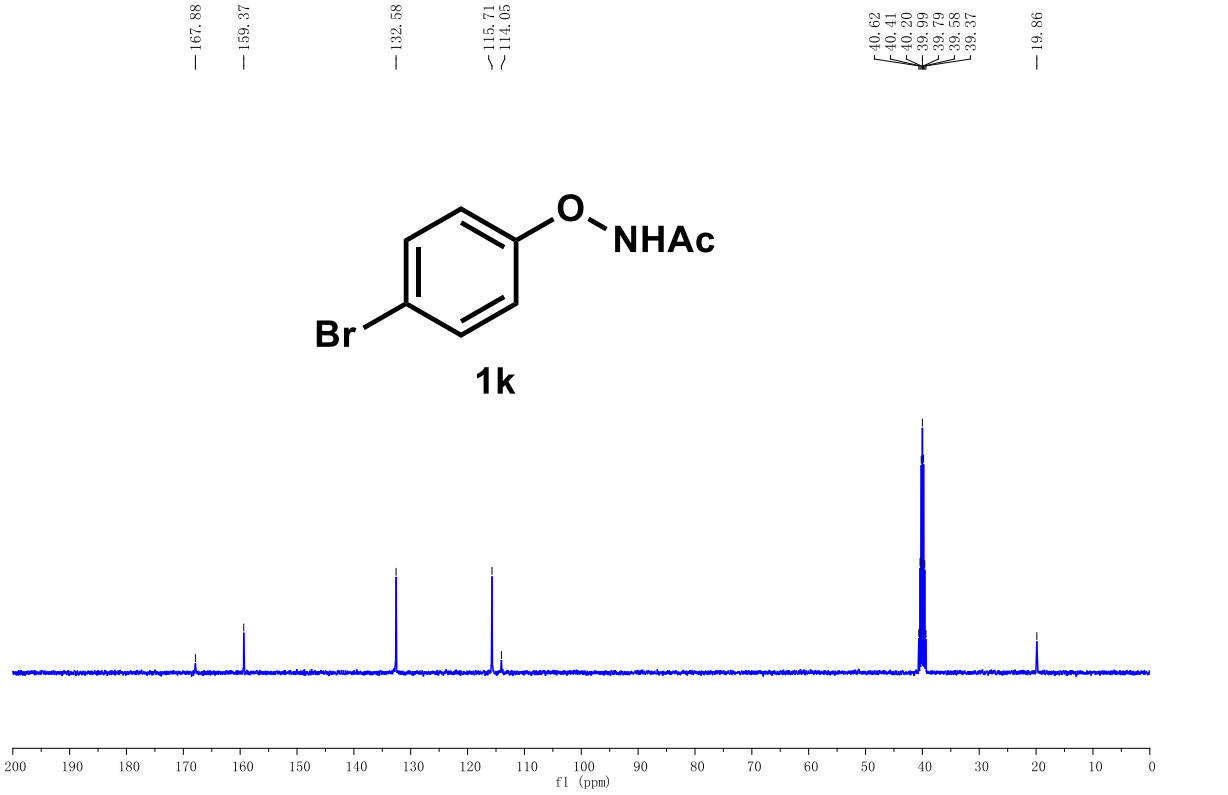

11.76
7.37
7.35
7.33
7.31
6.88
6.86
6.84
6.82
3.35
2.50
2.49
2.49
1.92
O
NHAc
F
1i
0.85
1.00
2.93
3.04
f1 (ppm)

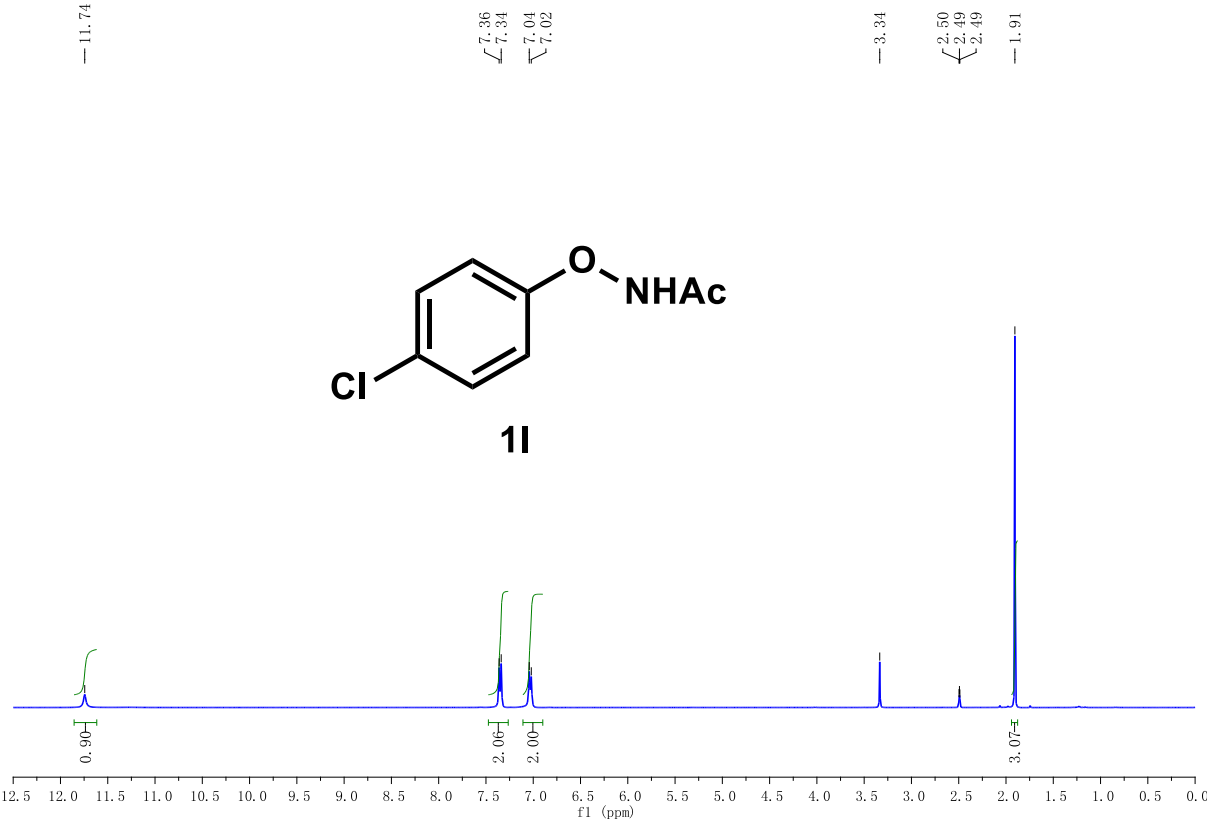

167.92
164.49
162.07
161.57
161.47
131.33
131.23
109.56
109.23
101.25
100.99
40.61
40.40
40.19
39.98
39.77
39.56
39.35
19.85
O
NHAc
F
1i
f1 (ppm)

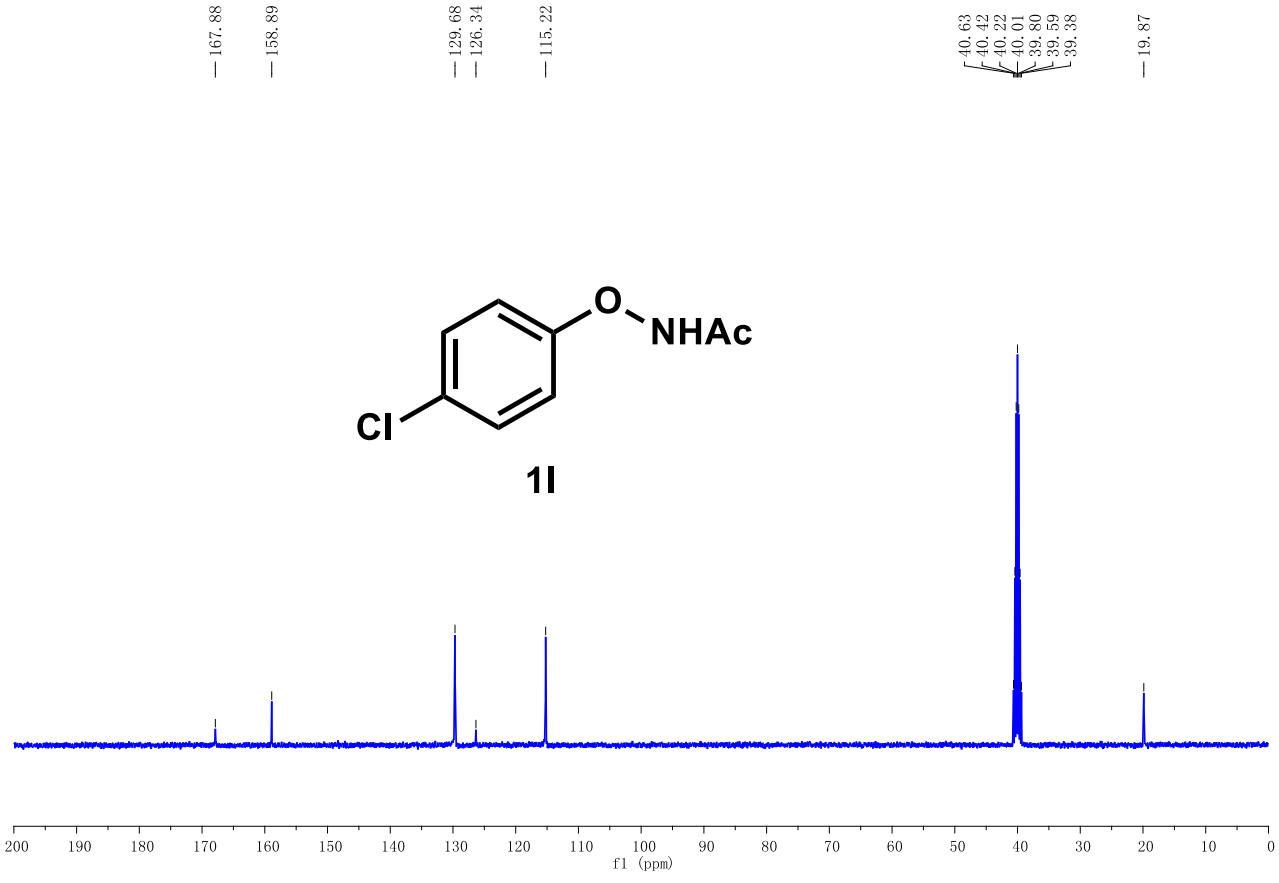

11.76
7.29
7.27
7.25
7.22
7.20
7.04
7.02
3.33
2.50
2.49
2.49
1.92
O
NHAc
Br
1j
0.96
1.21
1.93
1.00
3.19
f1 (ppm)

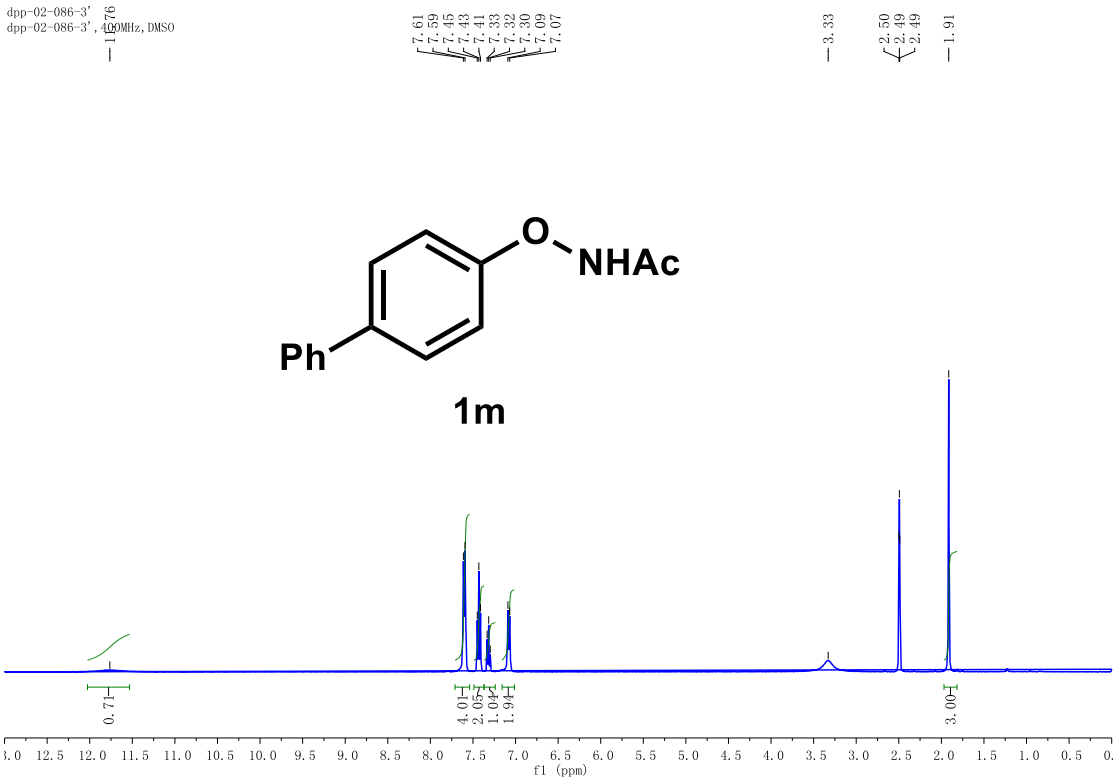

167.91
160.93
131.72
125.63
122.43
116.24
112.84
40.61
40.40
40.19
39.98
39.77
39.57
39.36
19.84
O
NHAc
Br
1j
f1 (ppm)

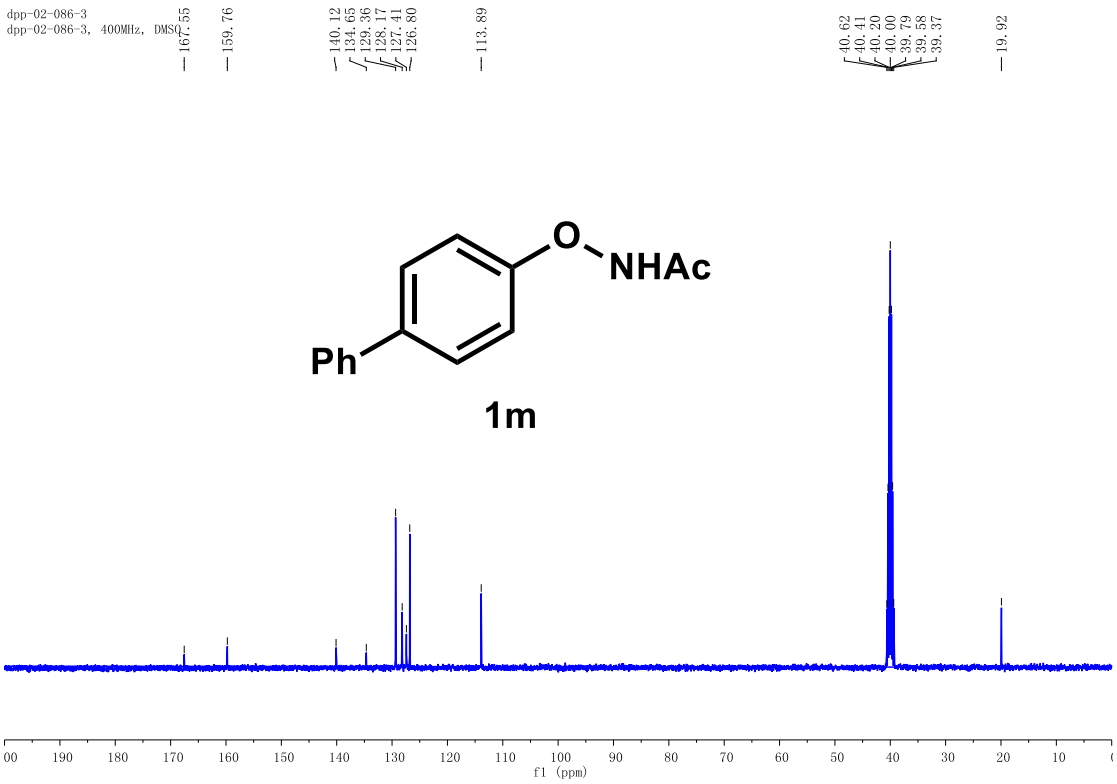

11.74
7.48
7.46
6.99
6.97
3.36
1.91
O
NHAc
Br
1k
0.89
2.02
2.00
3.03
f1 (ppm)

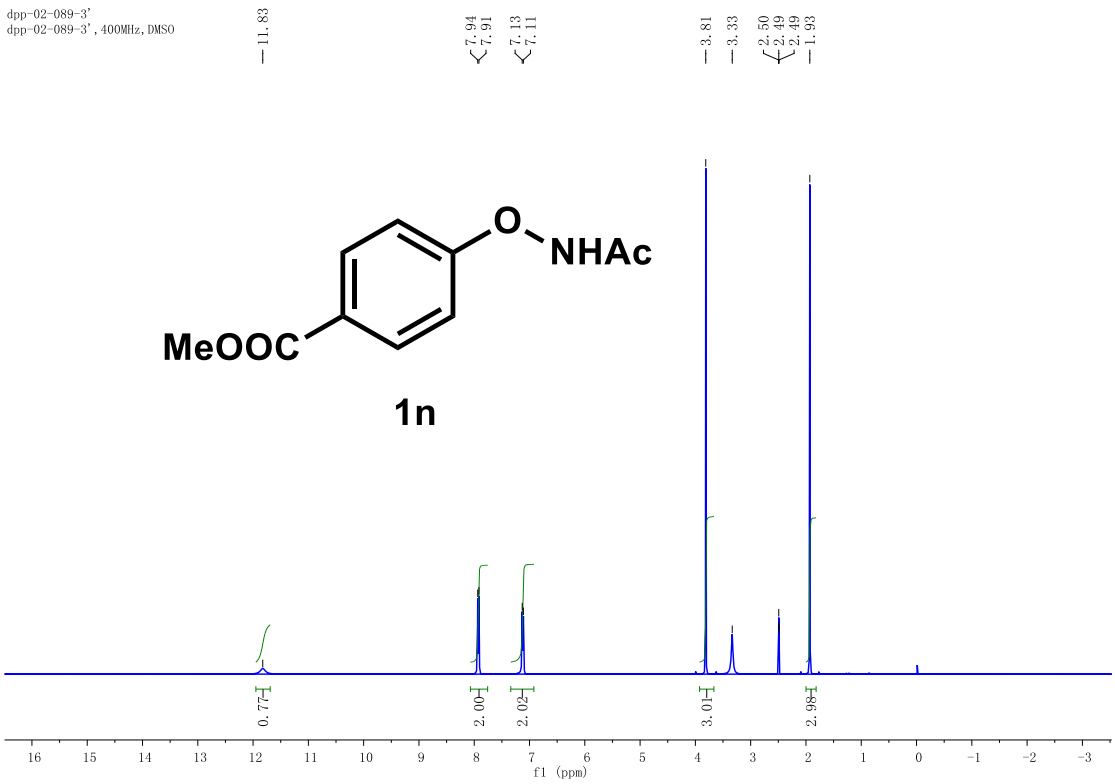

167.88
159.37
132.58
115.71
114.05
40.62
40.41
40.20
39.99
39.79
39.58
39.37
19.86
O
NHAc
Br
1k
f1 (ppm)

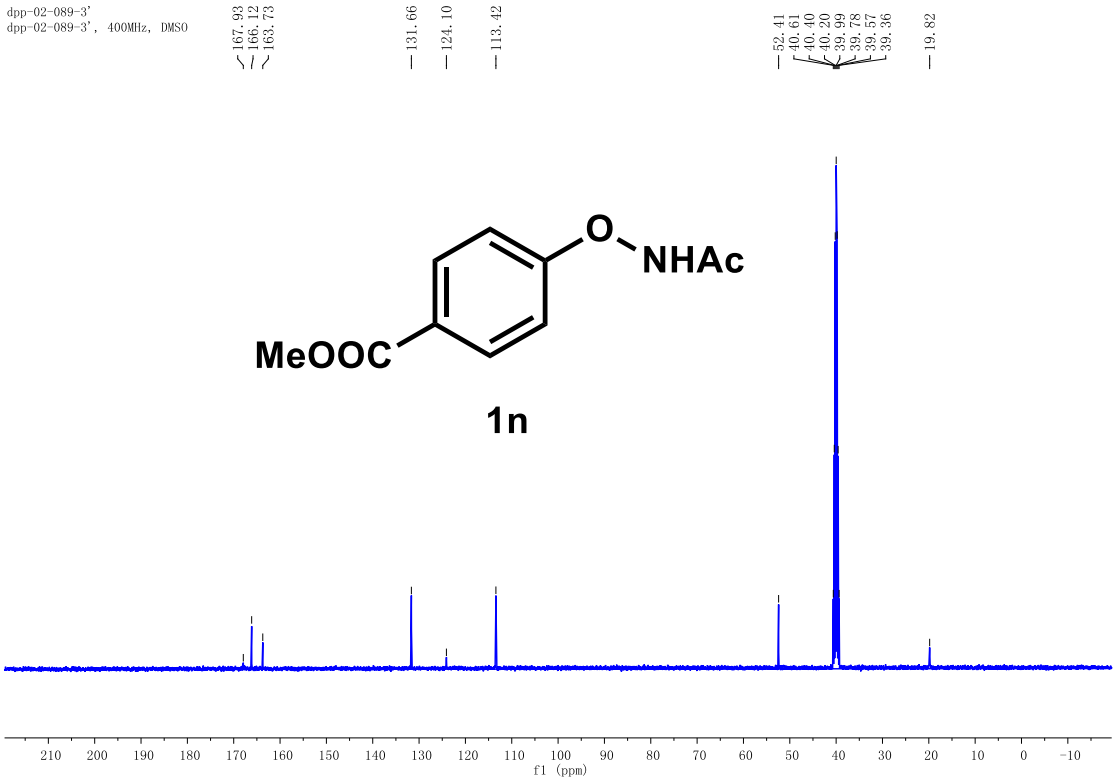

11.74
7.36
7.34
7.04
7.02
3.34
2.50
2.49
2.49
1.91
O
NHAc
Cl
1l
0.90
2.06
2.00
3.07
f1 (ppm)

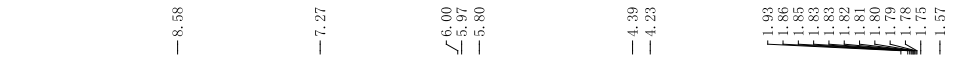

167.88
158.89
129.68
126.34
115.22
40.63
40.42
40.22
40.01
39.80
39.59
39.38
19.87
O
NHAc
Cl
1l
f1 (ppm)

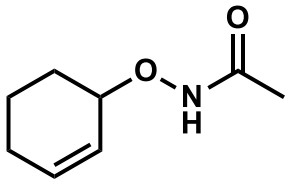

dpp-02-086-3'
dpp-02-086-3', 400MHz, DMSO
11.76
7.61
7.59
7.45
7.43
7.41
7.33
7.32
7.30
7.09
7.07
3.33
2.50
2.49
2.49
1.91
O
NHAc
Ph
1m
0.71
4.01
2.05
1.04
1.94
3.00
f1 (ppm)


dpp-02-086-3
dpp-02-086-3, 400MHz, DMSO
167.55
159.76
140.12
134.65
129.36
128.17
127.41
126.80
113.89
40.62
40.41
40.20
40.00
39.79
39.58
39.37
19.92
O
NHAc
Ph
1m
f1 (ppm)

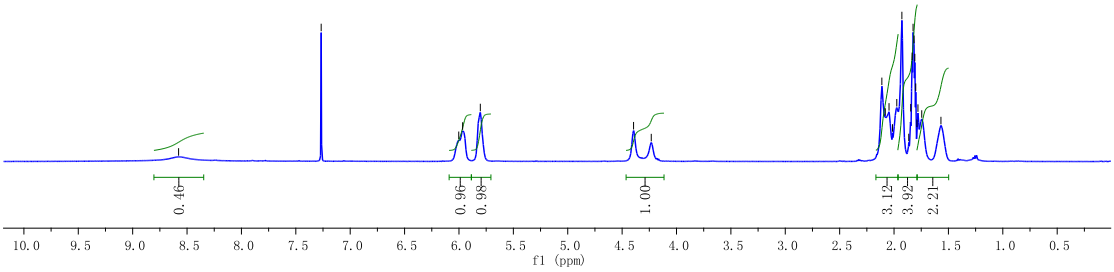

dpp-02-089-3'
dpp-02-089-3', 400MHz, DMSO
11.83
7.94
7.91
7.13
7.11
3.81
3.33
2.50
2.49
2.49
1.93
O
NHAc
MeOOC
1n
0.77
2.00
2.02
3.01
2.98
f1 (ppm)


dpp-02-089-3'
dpp-02-089-3', 400MHz, DMSO
167.93
166.12
163.73
131.66
124.10
113.42
52.41
40.61
40.40
40.20
39.99
39.78
39.57
39.36
19.82
O
NHAc
MeOOC
1n
f1 (ppm)

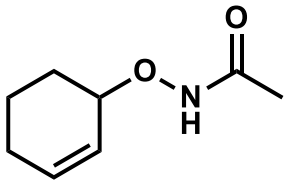

8.58
7.27
6.00
5.97
5.80
4.39
4.23
1.93
1.86
1.85
1.83
1.83
1.82
1.81
1.80
1.79
1.78
1.75
1.57


O
O
N
H

1o

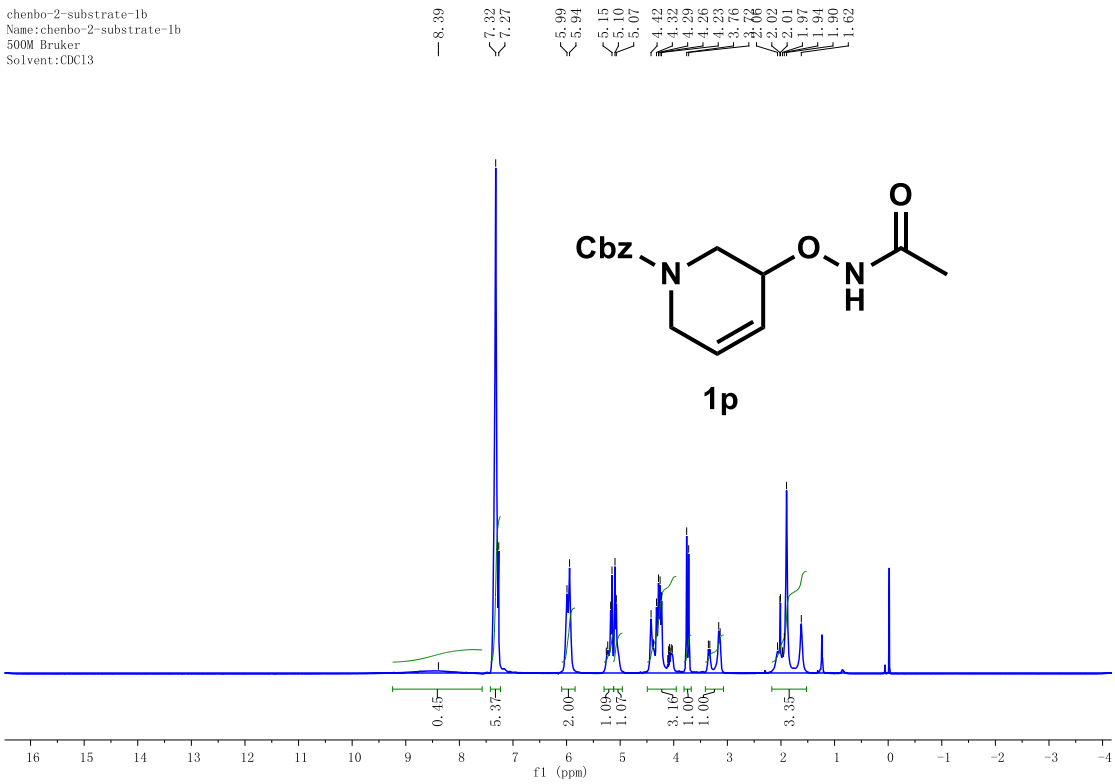

0.46
0.96
0.98
1.00
3.12
3.92
2.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

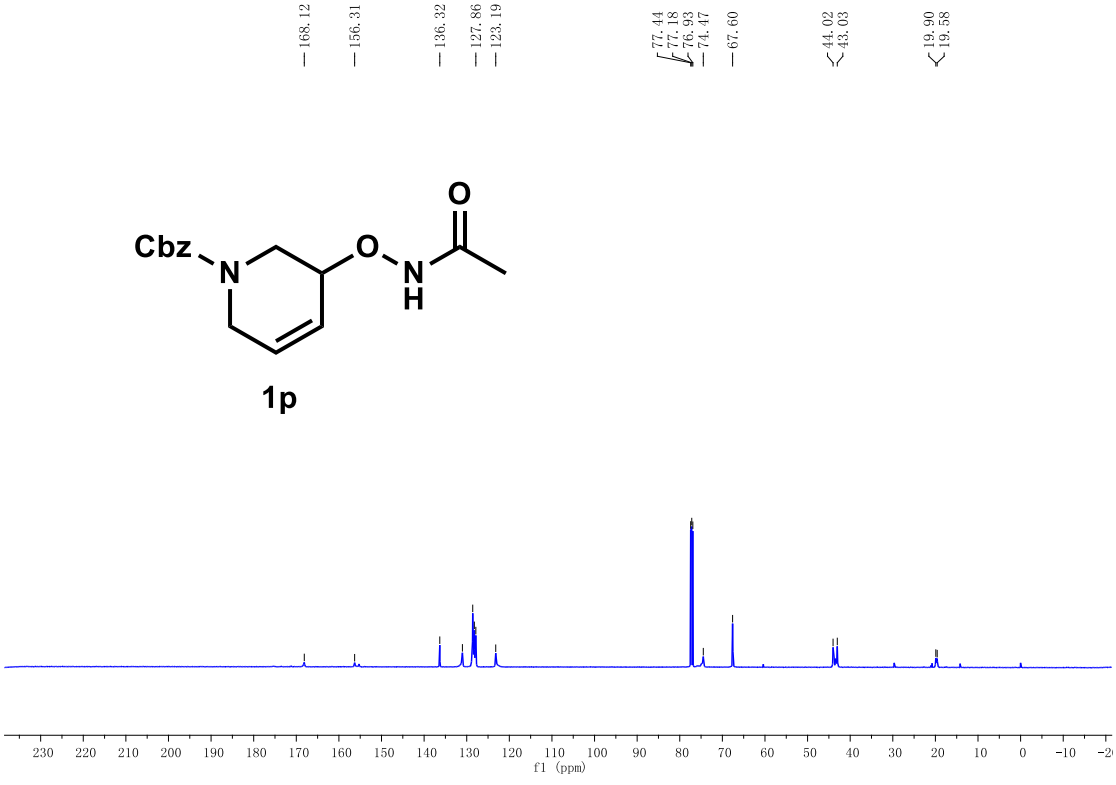

chenbo-2-substrate-1a
Avance 500, Bruker, SZPKU
chenbo-2-substrate-1a
CDCl3
168.33
133.57
125.02
78.58
77.32
77.06
76.81
26.89
25.19
19.74
18.63

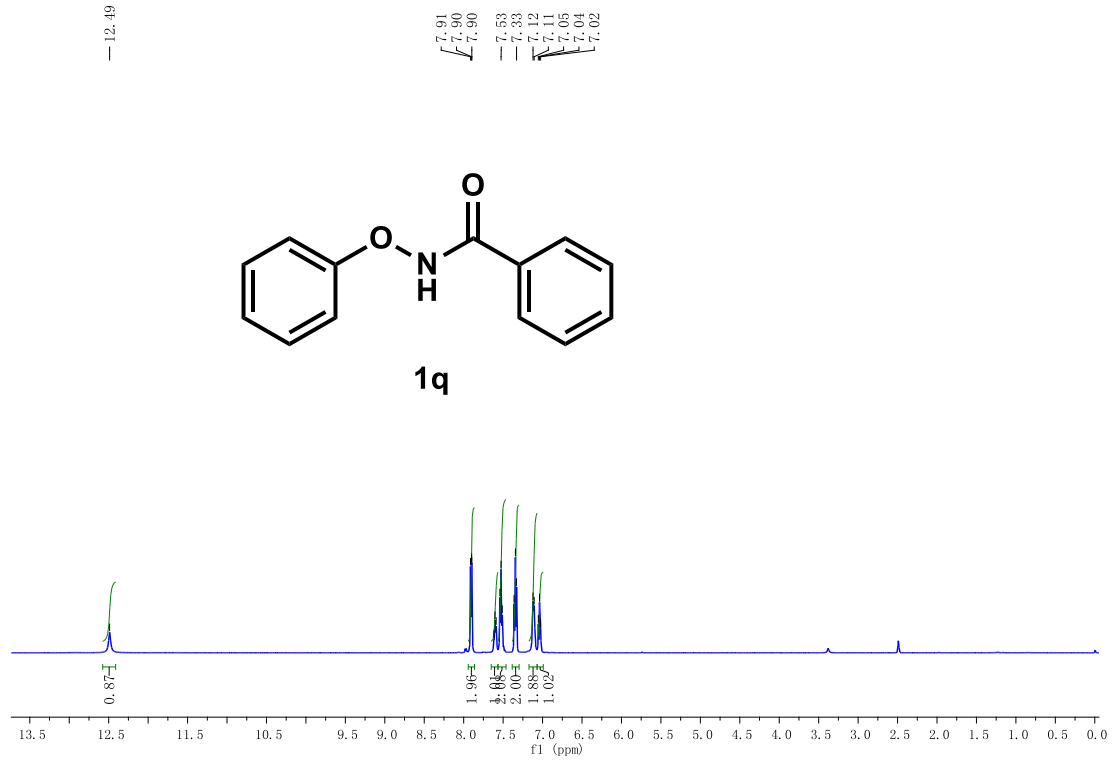

O
O
N
H

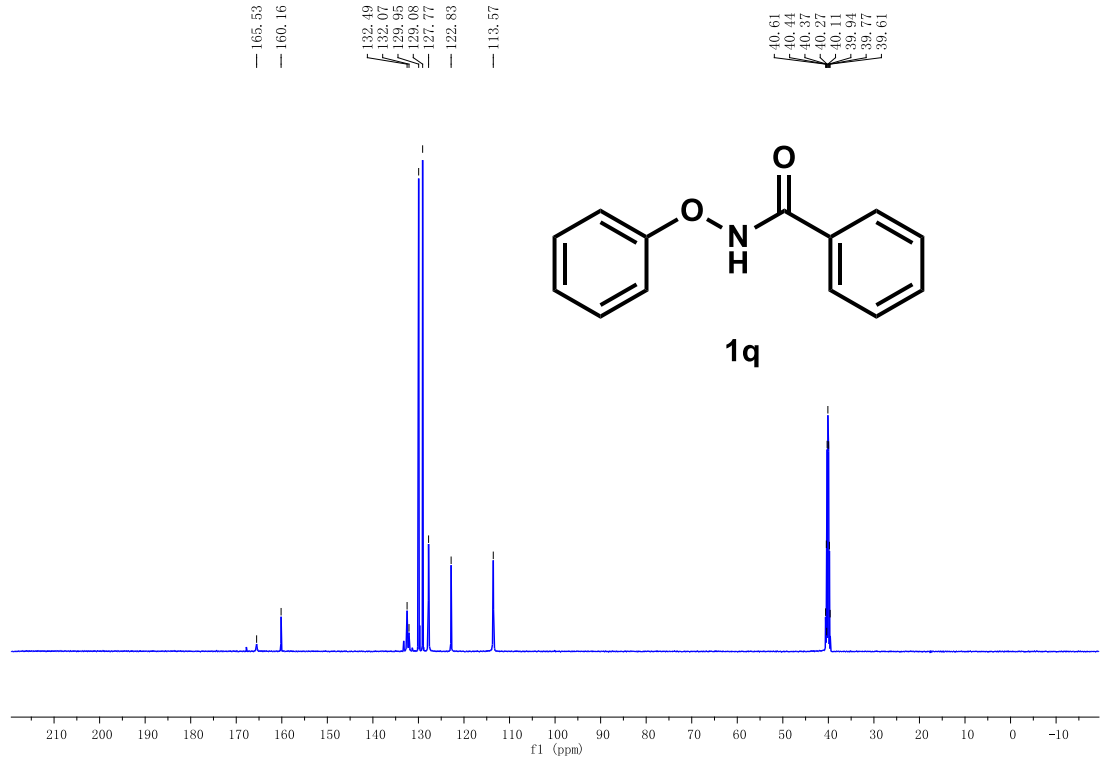
1o

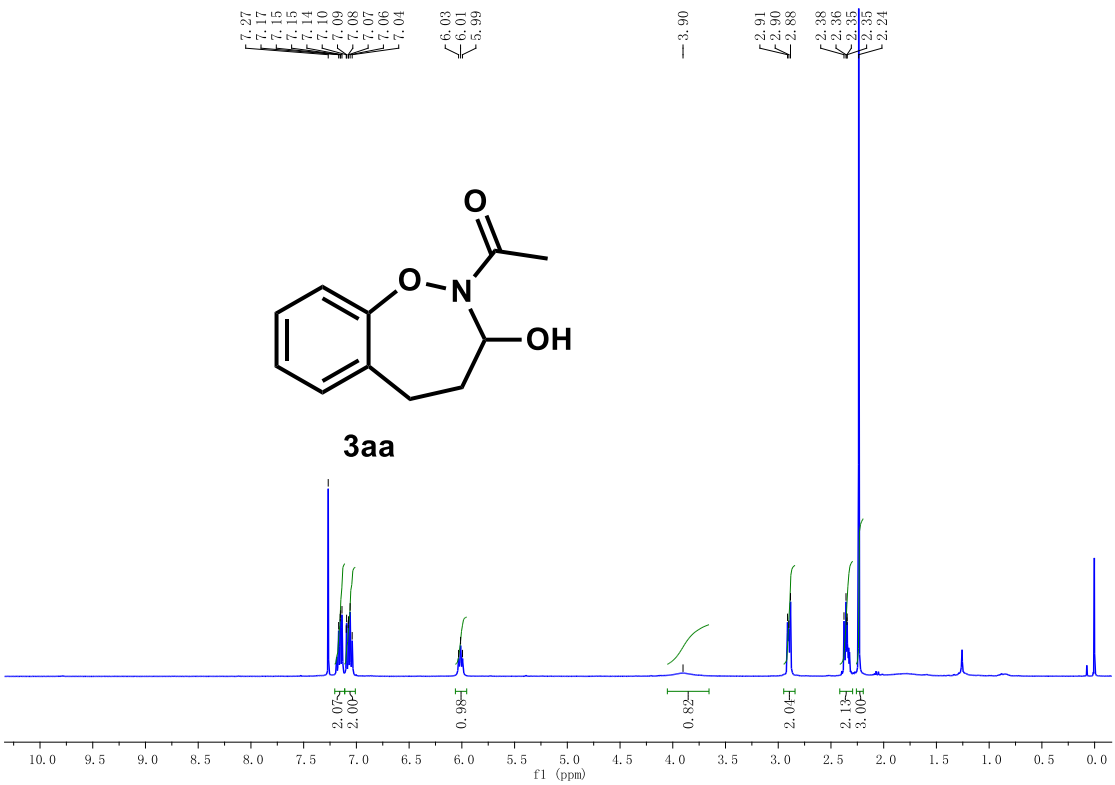
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


chenbo-2-substrate-1b
Name:chenbo-2-substrate-1b
500M Bruker
Solvent:CDCl3
8.39
7.32
7.27
5.99
5.94
5.15
5.10
5.07
4.42
4.32
4.29
4.26
4.23
3.76
2.02
2.01
1.97
1.94
1.90
1.62
Cbz
N
O
O
N
H
1p
0.45
5.37
2.00
1.09
1.07
3.16
1.00
1.00
3.35
f1 (ppm)

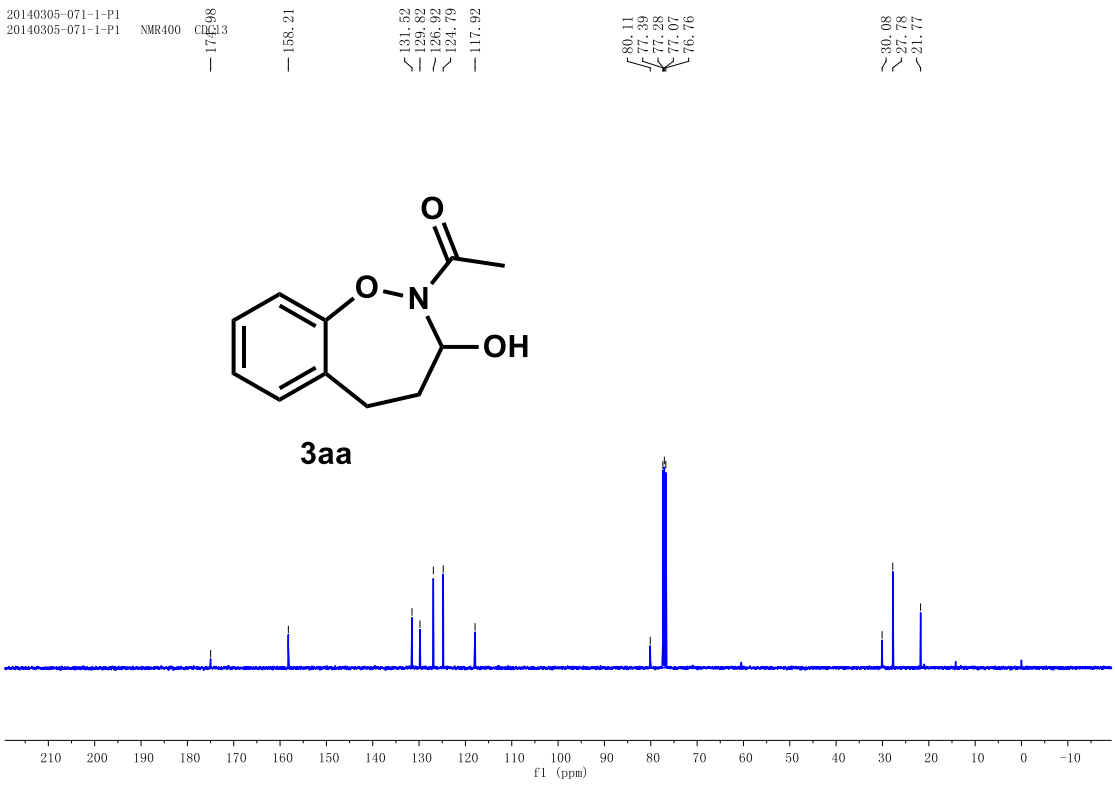

168.12
156.31
136.32
127.86
123.19
77.44
77.18
76.93
74.47
67.60
44.02
43.03
19.90
19.58
Cbz
N
O
O
N
H
1p
f1 (ppm)


12.49
7.91
7.90
7.90
7.53
7.33
7.12
7.11
7.05
7.04
7.02
O
O
N
H
1q
0.87
1.96
2.00
1.88
1.02
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.53
160.16
132.49
132.07
129.95
129.08
127.77
122.83
113.57
40.61
40.44
40.37
40.27
40.11
39.94
39.77
39.61
O
O
N
H
1q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

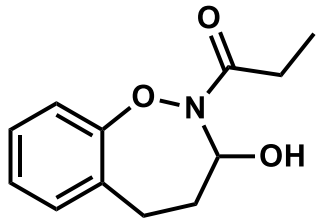

7.27
7.17
7.15
7.15
7.14
7.10
7.09
7.08
7.07
7.06
7.04
6.03
6.01
5.99
3.90
2.91
2.90
2.88
2.38
2.36
2.35
2.35
2.24
O
O
N
OH
2.07
2.00
0.98
0.82
2.04
2.13
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3aa

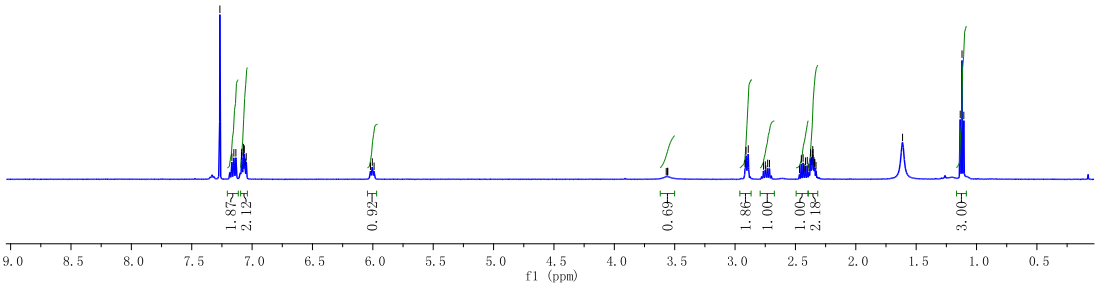

20140305-071-1-P1
20140305-071-1-P1 NMR400 CDCl3
174.98
158.21
131.52
129.82
126.92
124.79
117.92
80.11
77.39
77.28
77.07
76.76
30.08
27.78
21.77
O
O
N
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

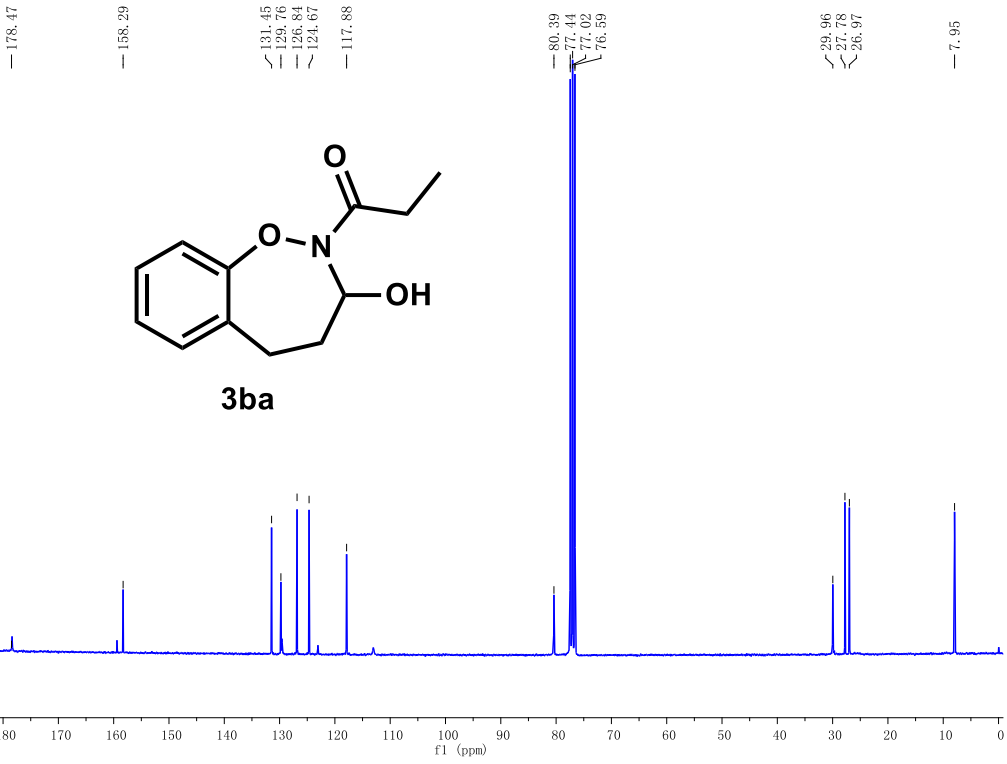
3aa


7.27
7.17
7.15
7.13
7.09
7.09
7.07
7.07
7.06
7.06
7.05
6.02
6.00
5.99
3.57
3.56
3.55
3.55
2.89
2.75
2.75
2.73
2.72
2.45
2.37
2.35
2.33
1.61
1.14
1.12
1.11

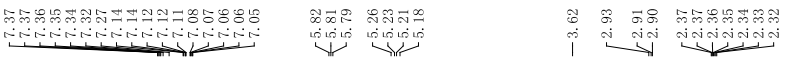

O
O
N
OH

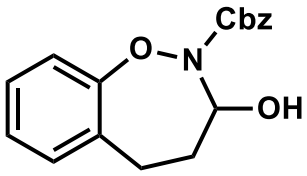
3ba


1.87
2.12
0.92
0.69
1.86
1.00
1.00
2.18
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

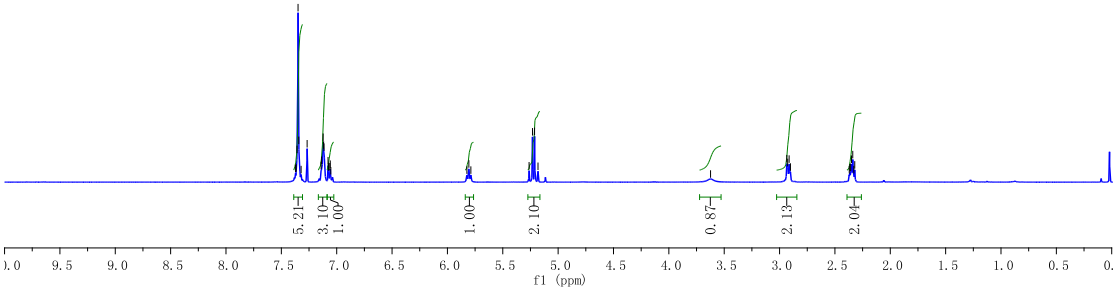

178.47
158.29
131.45
129.76
126.84
124.67
117.88
80.39
77.44
77.02
76.59
29.96
27.78
26.97
7.95
O
O
N
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ba

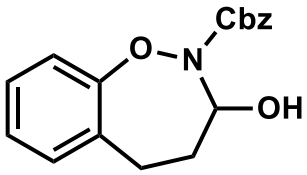

7.37
7.37
7.36
7.35
7.34
7.32
7.27
7.14
7.14
7.12
7.12
7.11
7.08
7.07
7.06
7.06
7.05
5.82
5.81
5.79
5.26
5.23
5.21
5.18
3.62
2.93
2.91
2.90
2.37
2.37
2.36
2.35
2.34
2.33
2.32


Cbz
O
N
OH

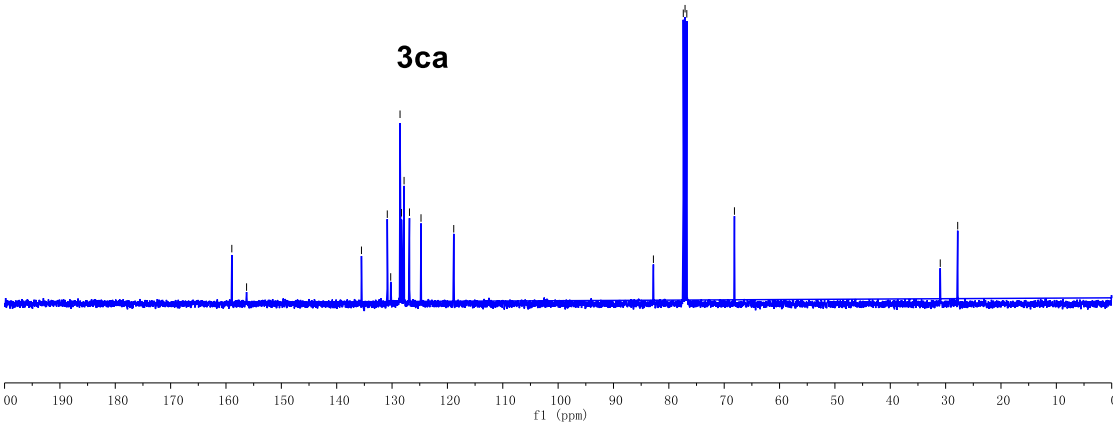
3ca

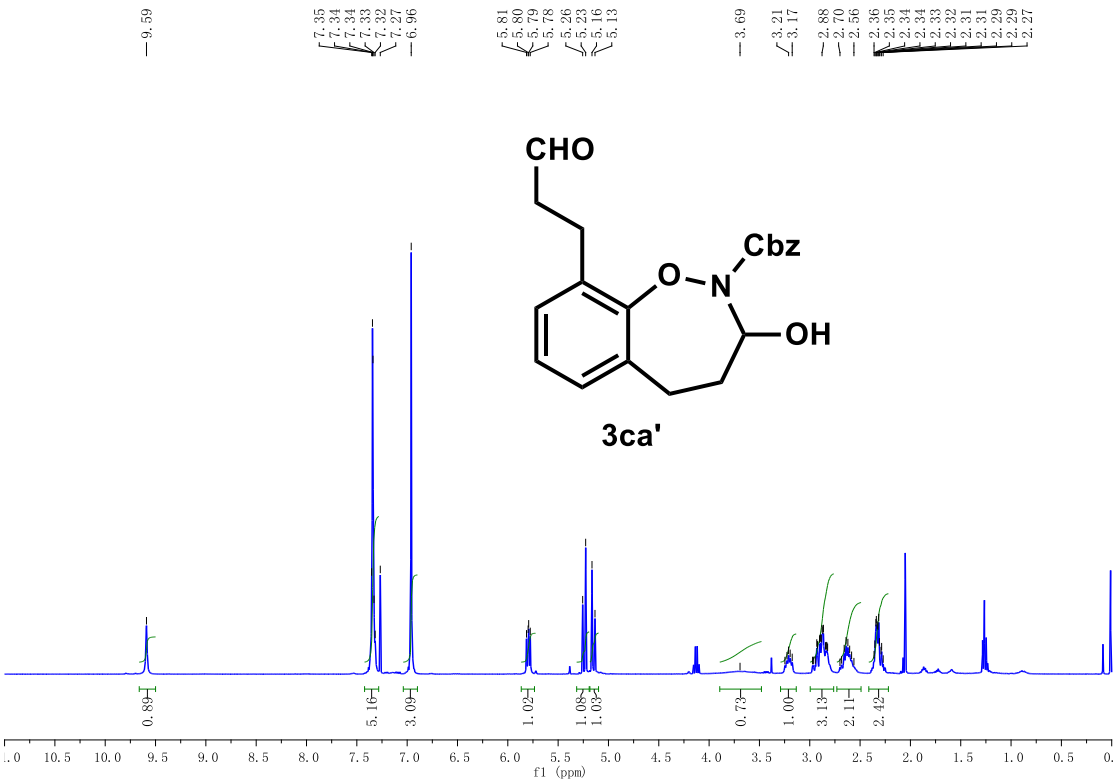

5.21
3.10
1.00
1.00
2.10
0.87
2.13
2.04
f1 (ppm)

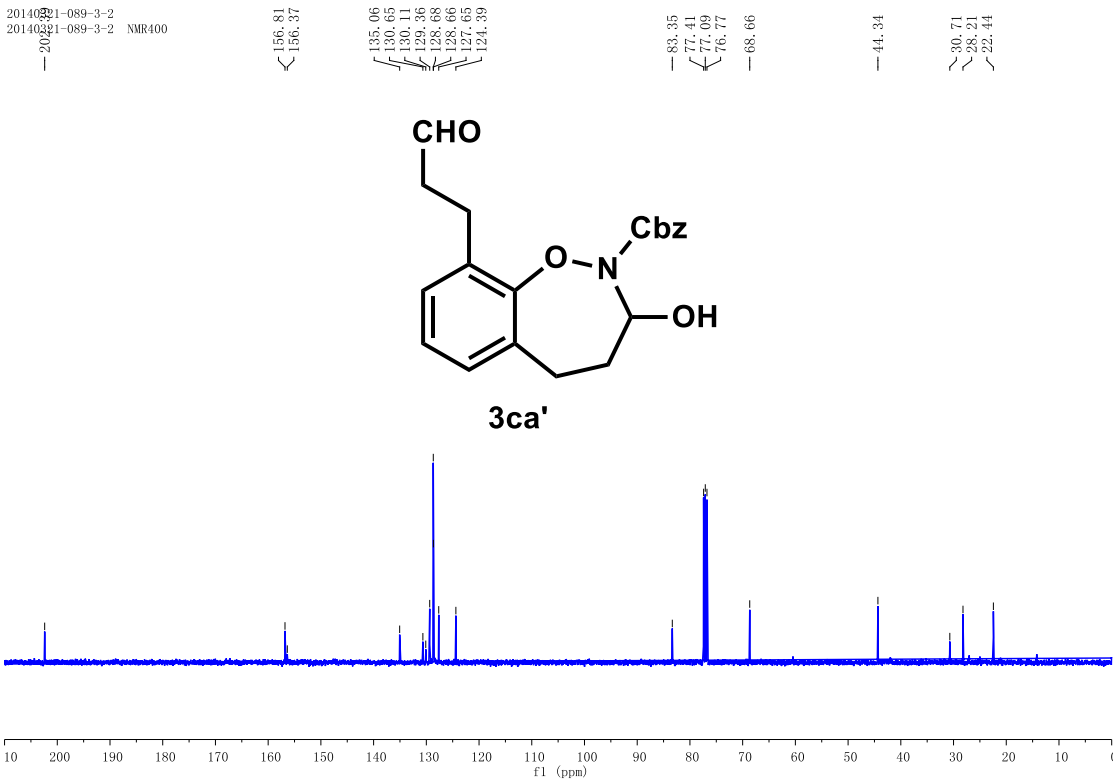

20140321-089-3-1
20140321-089-3-1 NMR400
158.95
156.28
135.53
130.86
130.24
128.56
128.29
127.83
126.85
124.77
118.86
82.79
77.39
77.07
76.75
68.15
30.97
27.82

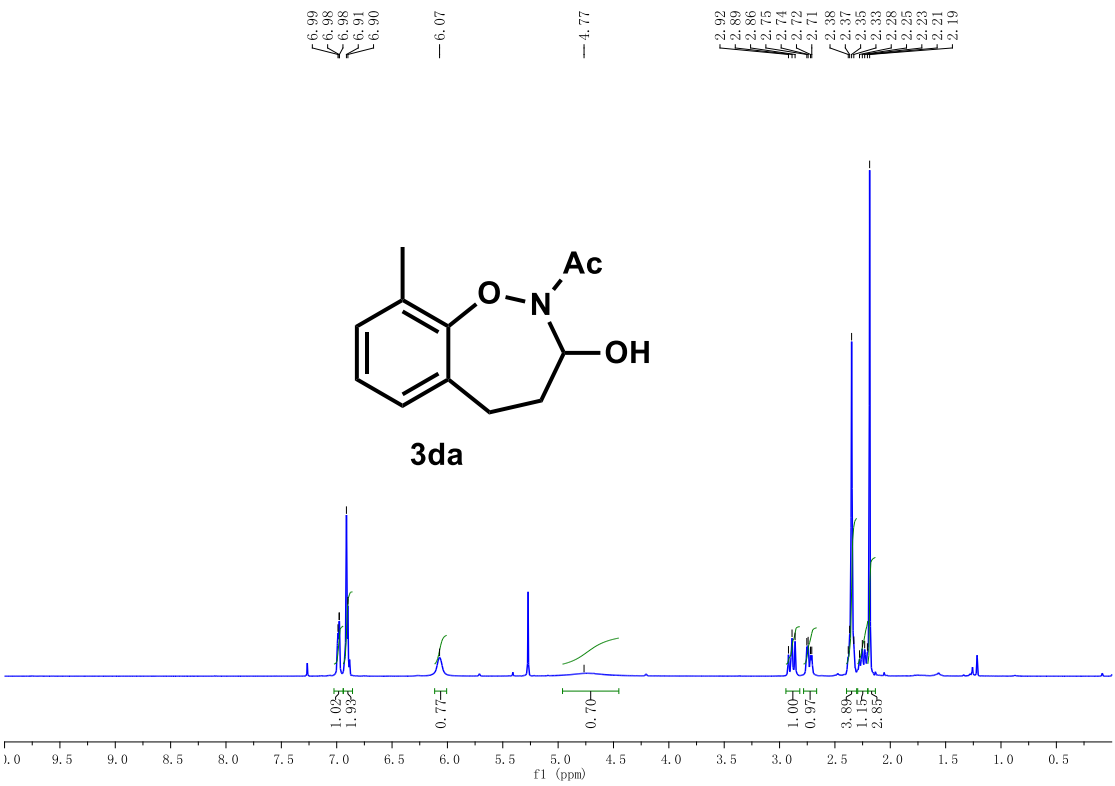

Cbz
O
N
OH

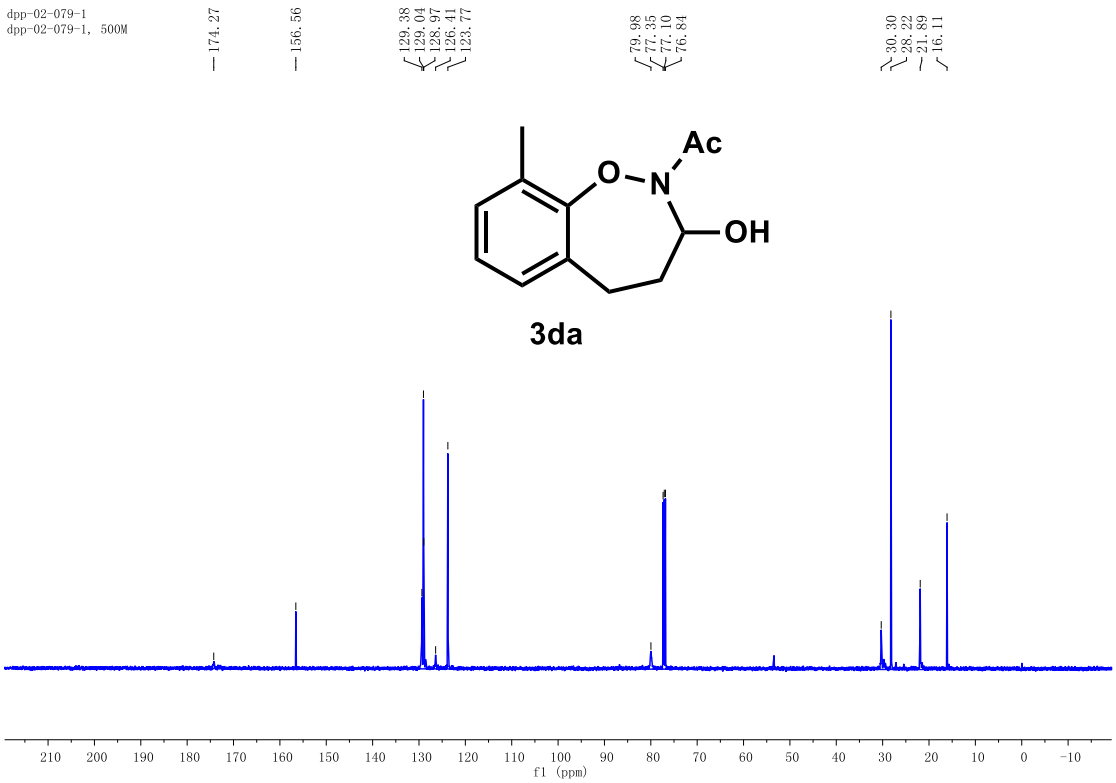
3ca


f1 (ppm)


9.59
7.35
7.34
7.34
7.33
7.32
7.27
6.96
5.81
5.80
5.79
5.78
5.26
5.23
5.16
5.13
3.69
3.21
3.17
2.88
2.70
2.56
2.36
2.35
2.34
2.34
2.33
2.32
2.31
2.31
2.29
2.29
2.27
CHO
Cbz
O
N
OH
3ca'
0.89
5.16
3.09
1.02
1.08
1.03
0.79
1.00
3.13
2.11
2.42
f1 (ppm)

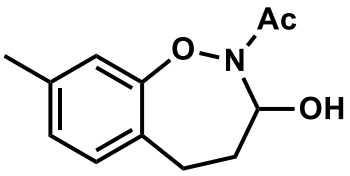

20140321-089-3-2
20140321-089-3-2 NMR400
156.81
156.37
135.06
130.65
130.11
129.36
128.68
128.66
127.65
124.39
83.35
77.41
77.09
76.77
68.66
44.34
30.71
28.21
22.44
CHO
Cbz
O
N
OH
3ca'
f1 (ppm)


6.99
6.98
6.98
6.91
6.90
6.07
4.77
2.92
2.89
2.86
2.75
2.74
2.72
2.71
2.38
2.37
2.35
2.33
2.28
2.25
2.23
2.21
2.19
Ac
O
N
OH
3da
1.02
1.93
0.77
0.70
1.00
0.97
3.89
1.15
2.85
f1 (ppm)

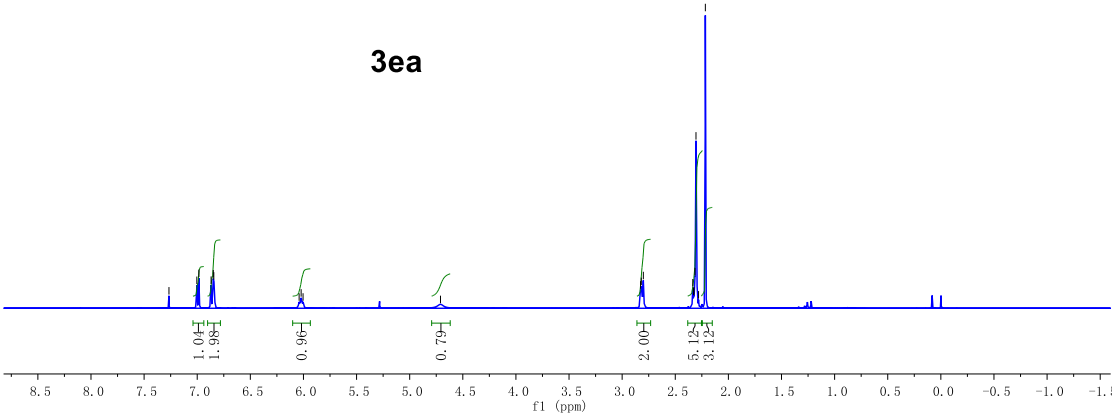

dpp-02-079-1
dpp-02-079-1, 500M
174.27
156.56
129.38
129.04
128.97
126.41
123.77
79.98
77.35
77.10
76.84
30.30
28.22
21.89
16.11
Ac
O
N
OH
3da
f1 (ppm)

dpp-02-079-2
dpp-02-079-2

7.27
7.00
6.98
6.87
6.85
6.84
6.04
6.02
6.00
4.71
2.83
2.82
2.80
2.34
2.33
2.32
2.31
2.30
2.28
2.22

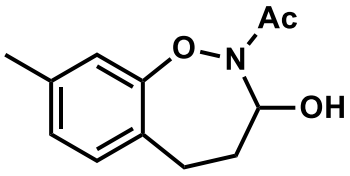


3ea

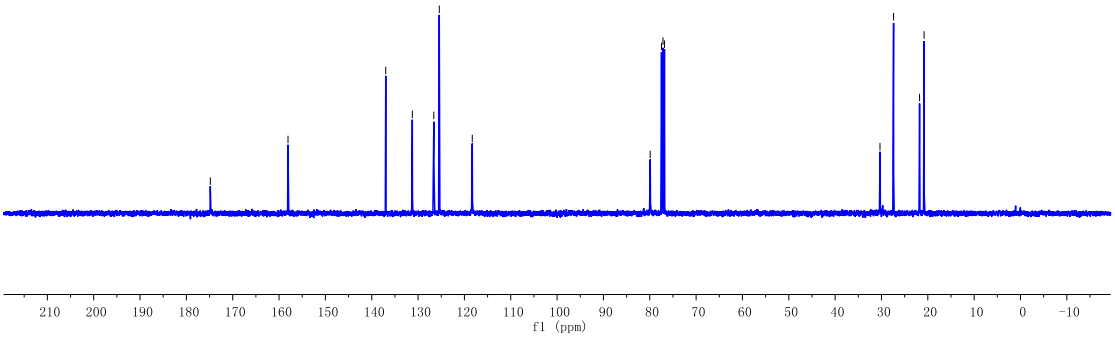


dpp-02-079-2
dpp-02-079-2

174.83
158.07
136.98
131.24
126.60
125.43
118.30
79.90
77.47
77.15
76.83
30.32
27.39
21.78
20.80

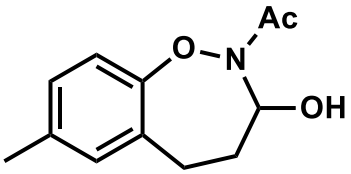


3ea

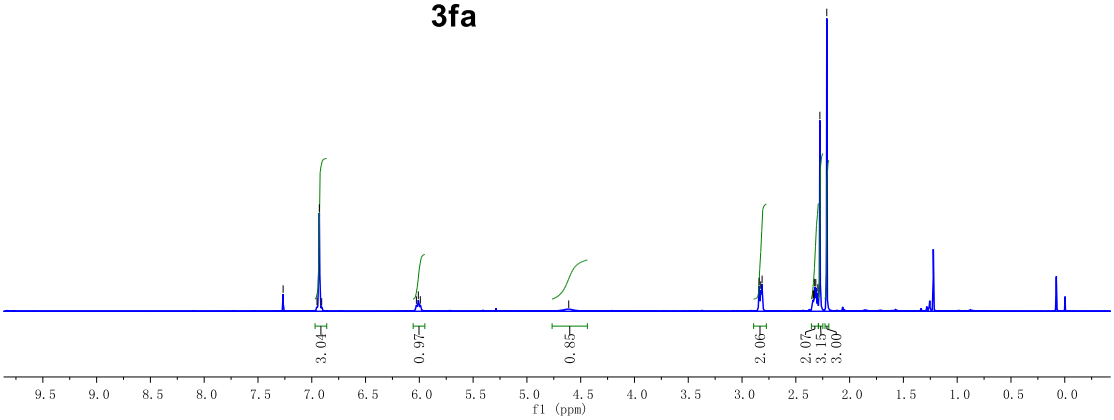


dpp-02-079-3-1
dpp-02-079-3-1

7.27
6.95
6.93
6.91
6.03
6.01
5.99
4.61
2.84
2.83
2.81
2.34
2.33
2.33
2.32
2.31
2.30
2.28
2.21

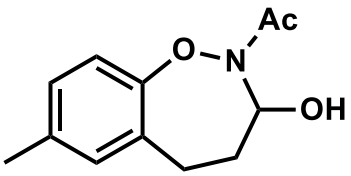


3fa

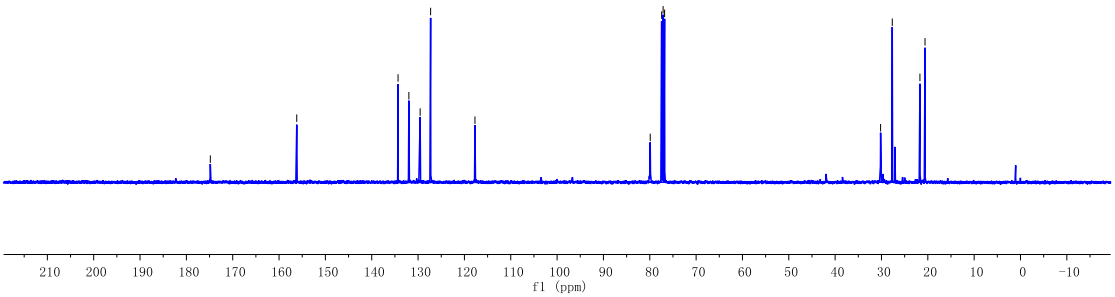


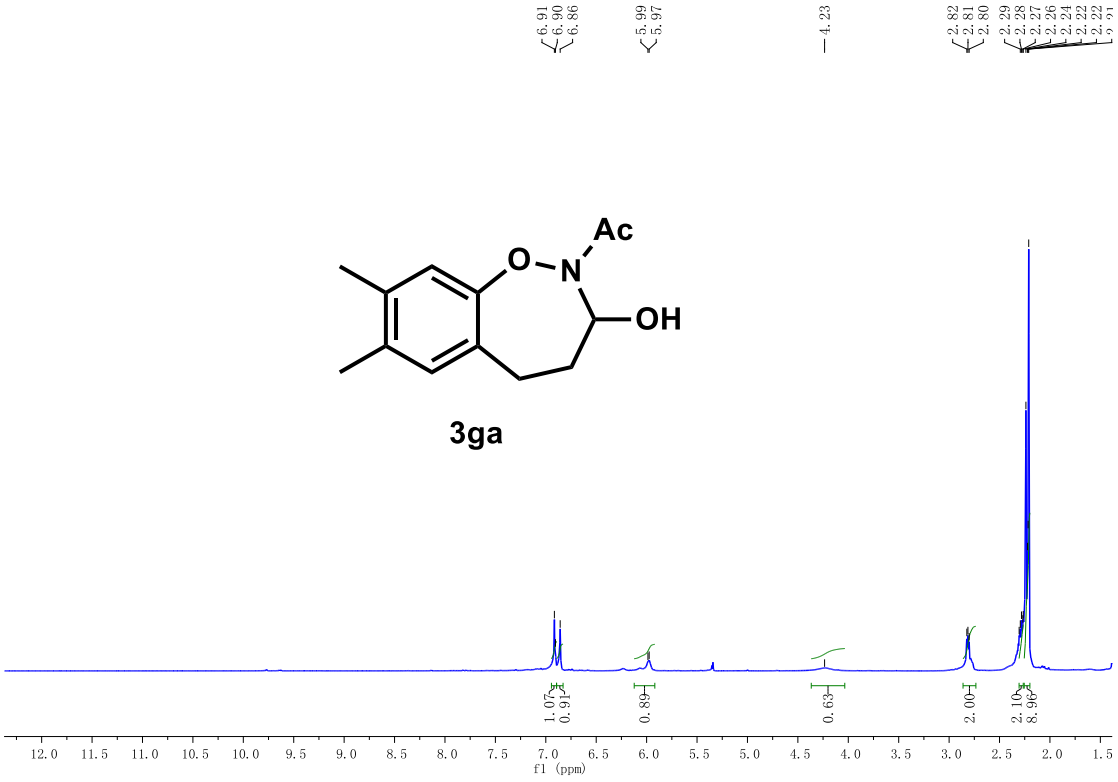
dpp-02-079-3-1
dpp-02-079-3-1

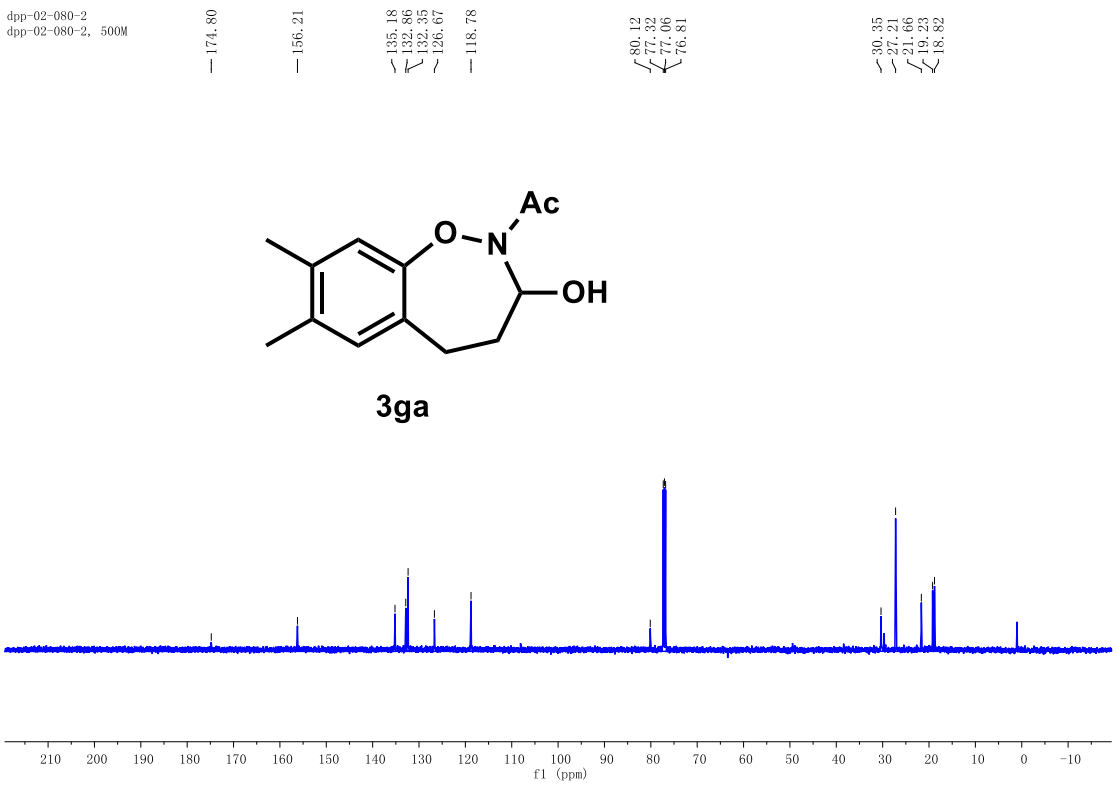
174.83
156.18
134.32
131.99
129.55
127.29
117.72
79.90
77.44
77.12
76.80
30.19
27.67
21.70
20.60



3fa

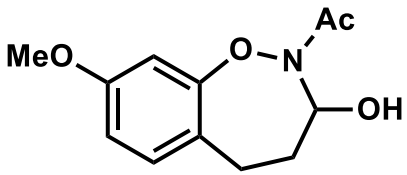



6.91
6.90
6.86
5.99
5.97
4.23
2.82
2.81
2.80
2.29
2.28
2.27
2.26
2.24
2.22
2.22
Ac
O
N
OH
3ga
1.07
0.91
0.89
0.63
2.00
2.10
8.96
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

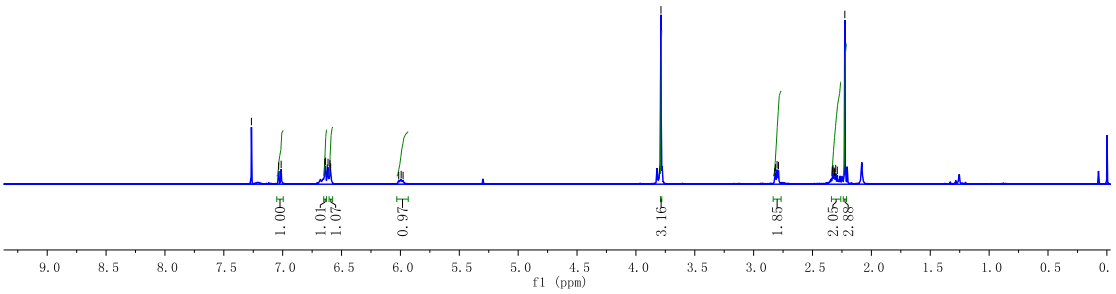

dpp-02-080-2
dpp-02-080-2, 500M
174.80
156.21
135.18
132.86
132.35
126.67
118.78
80.12
77.32
77.06
76.81
30.35
27.21
21.66
19.23
18.82
Ac
O
N
OH
3ga
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

dpp-02-080-1-2
dpp-02-080-1-2

7.27
7.03
7.01
6.64
6.64
6.61
6.60
6.59
6.01
5.99
5.98
3.79
2.82
2.81
2.80
2.79
2.33
2.33
2.32
2.31
2.31
2.30
2.29
2.23

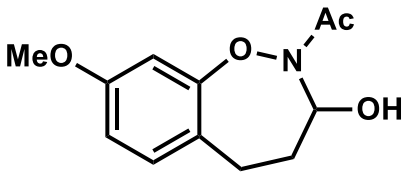


3ha

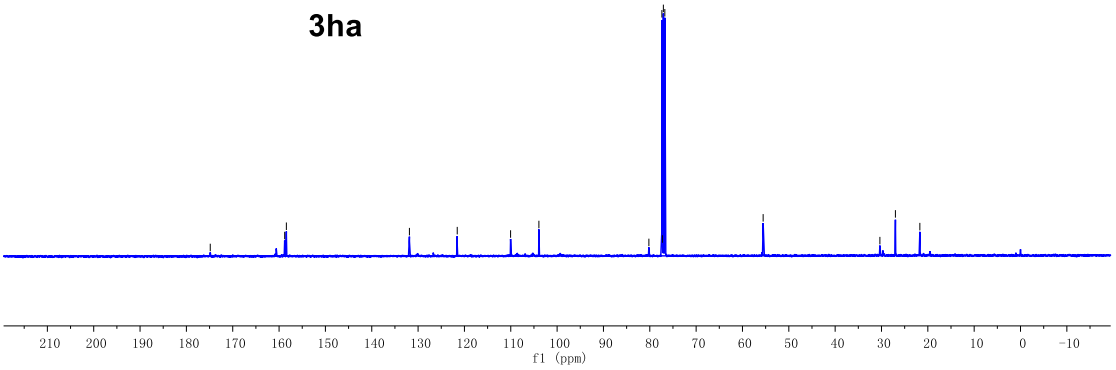


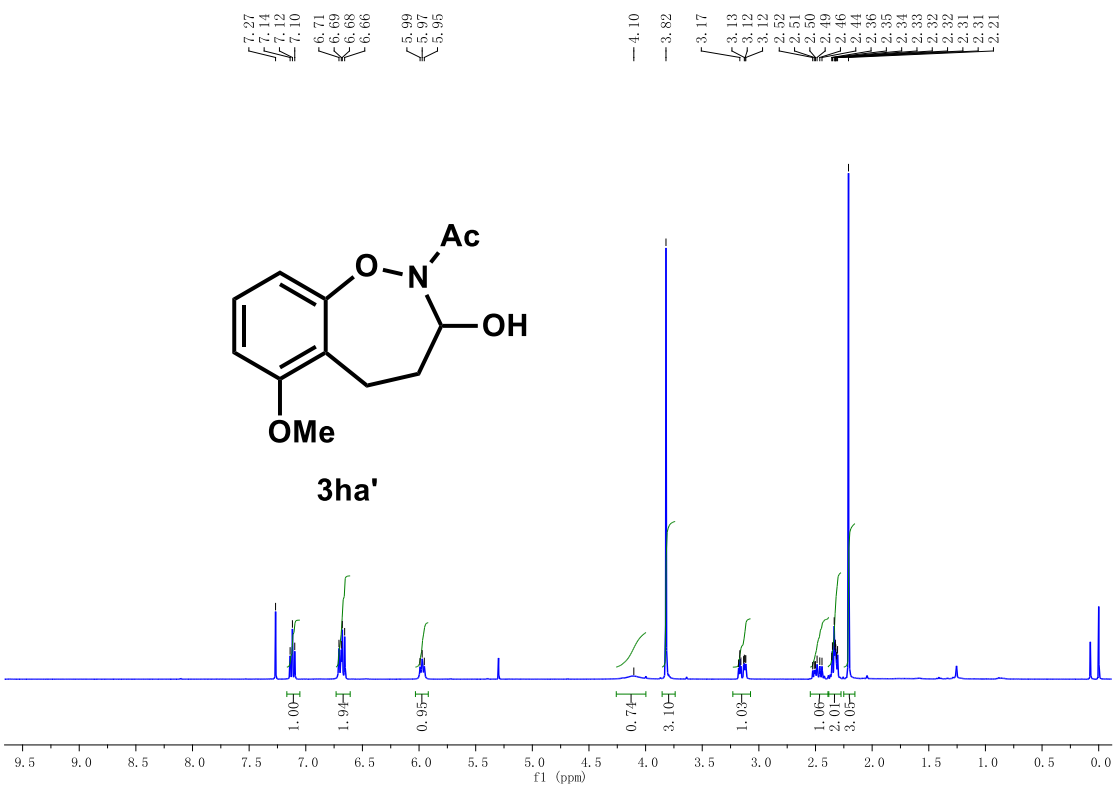
dpp-02-080-1-2'
dpp-02-080-1-2', 400MHz, CDCl3

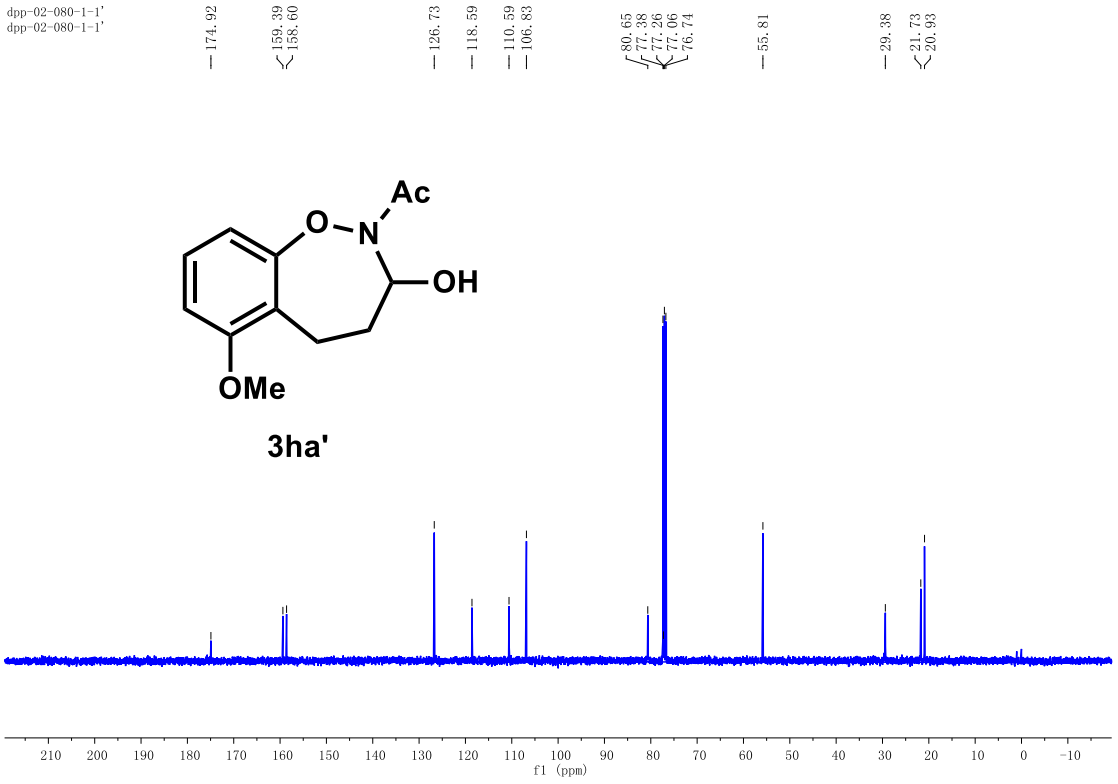
174.85
158.79
158.43
131.87
121.55
110.04
103.93
80.20
77.39
77.27
77.07
76.75
55.54
30.35
27.00
21.72

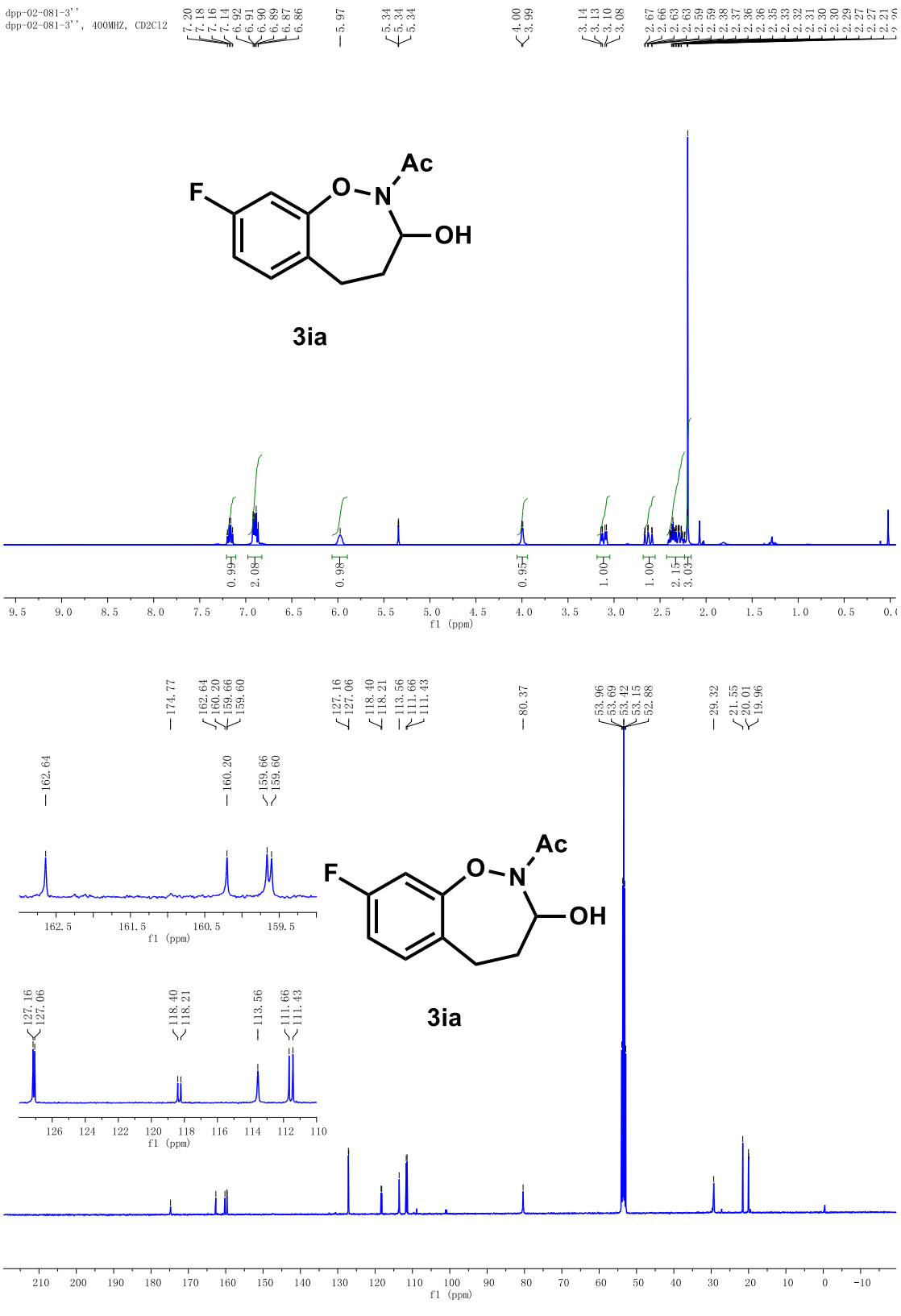


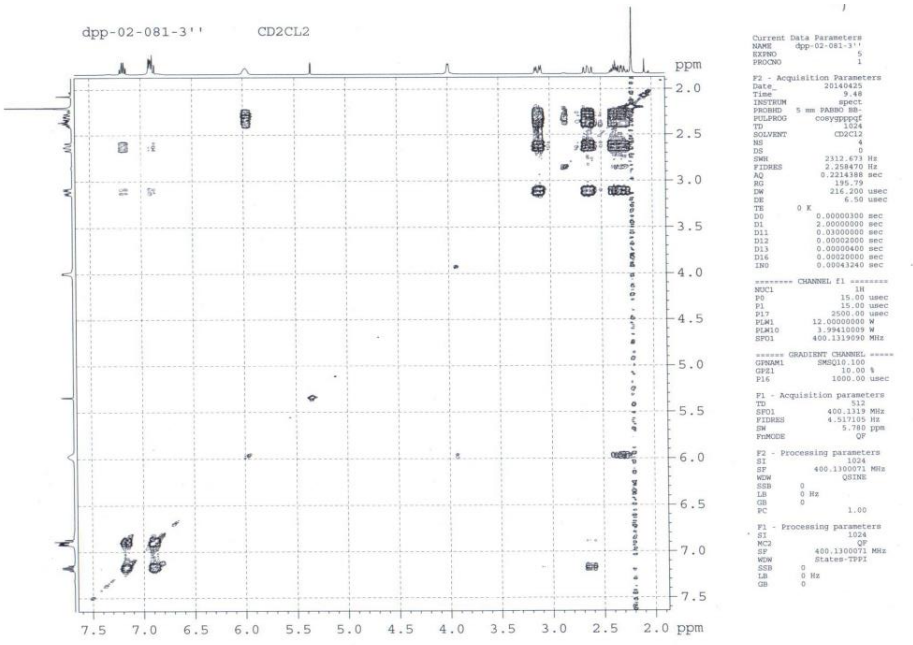
3ha

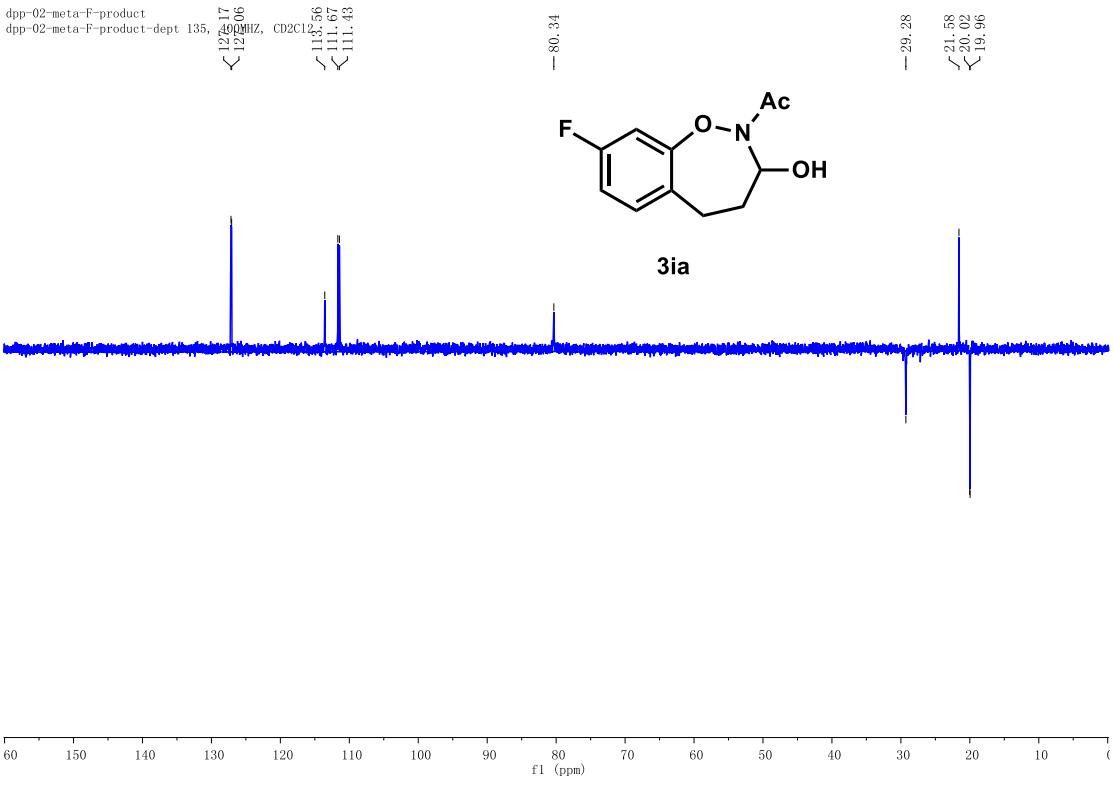



7.27
7.14
7.12
7.10
6.71
6.69
6.68
6.66
5.99
5.97
5.95
4.10
3.82
3.17
3.13
3.12
3.12
2.52
2.51
2.50
2.49
2.46
2.44
2.36
2.35
2.34
2.33
2.32
2.32
2.31
2.31
2.21
Ac
O
N
OH
OMe
3ha'
1.00
1.94
0.95
0.74
3.10
1.03
1.06
2.01
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

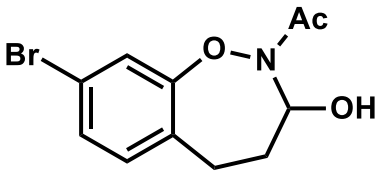

dpp-02-080-1-1'
dpp-02-080-1-1'
174.92
159.39
158.60
126.73
118.59
110.59
106.83
80.65
77.38
77.26
77.06
76.74
55.81
29.38
21.73
20.93
Ac
O
N
OH
OMe
3ha'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


dpp-02-081-3''
dpp-02-081-3'', 400MHZ, CD2Cl2
7.20
7.18
7.16
7.14
6.92
6.91
6.90
6.89
6.87
6.86
5.97
5.34
5.34
5.34
4.00
3.99
3.14
3.13
3.10
3.08
2.67
2.66
2.63
2.63
2.59
2.59
2.38
2.37
2.36
2.36
2.35
2.33
2.32
2.31
2.30
2.30
2.29
2.27
2.27
2.21
F
O
N
Ac
OH
3ia
0.99
2.08
0.98
0.95
1.00
1.00
2.15
3.03
f1 (ppm)
174.77
162.64
160.20
159.66
159.60
127.16
127.06
118.40
118.21
113.56
111.66
111.43
80.37
53.96
53.69
53.42
53.15
52.88
29.32
21.55
20.01
19.96
f1 (ppm)
f1 (ppm)
f1 (ppm)

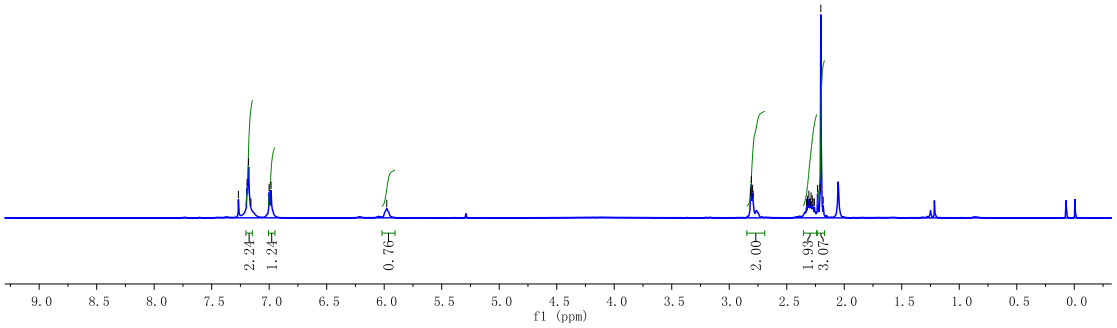

dpp-02-081-3''
CD2CL2
ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm


dpp-02-meta-F-product
dpp-02-meta-F-product-dept 135, 400MHZ, CD2Cl2
127.17
127.06
113.56
111.67
111.43
80.34
29.28
21.58
20.02
19.96
F
O
N
Ac
OH
3ia
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

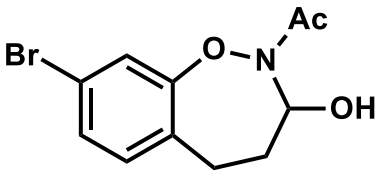

dpp-02-084-1
dpp-02-084-1
7.27
7.19
7.18
7.16
7.00
6.98
5.98
2.82
2.81
2.80
2.79
2.33
2.32
2.32
2.31
2.30
2.29
2.29
2.28
2.27
2.26
2.23
2.21
2.20
2.18


Br
O
N
Ac
OH

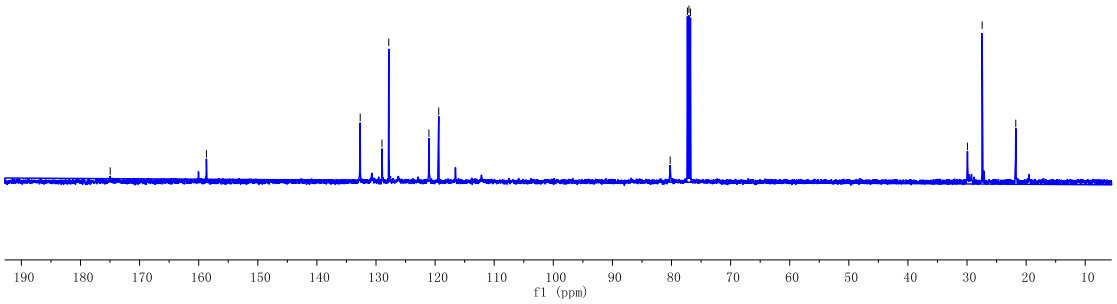
3ja

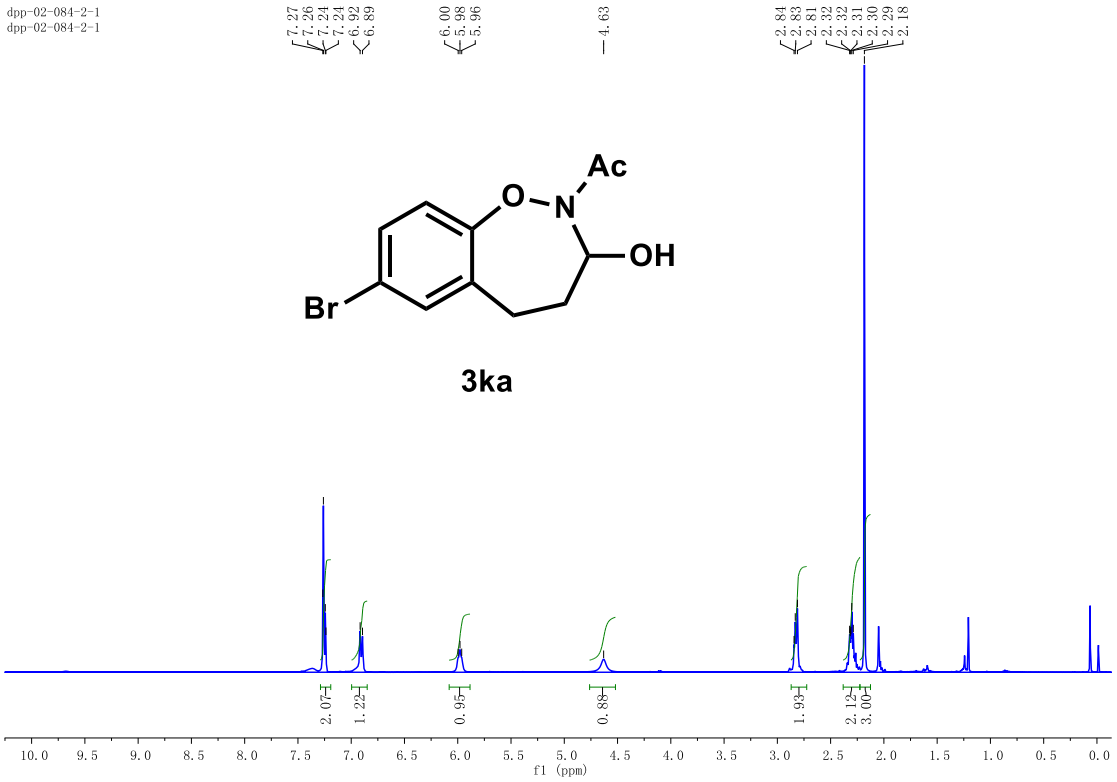

2.24
1.24
0.76
2.00
1.93
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

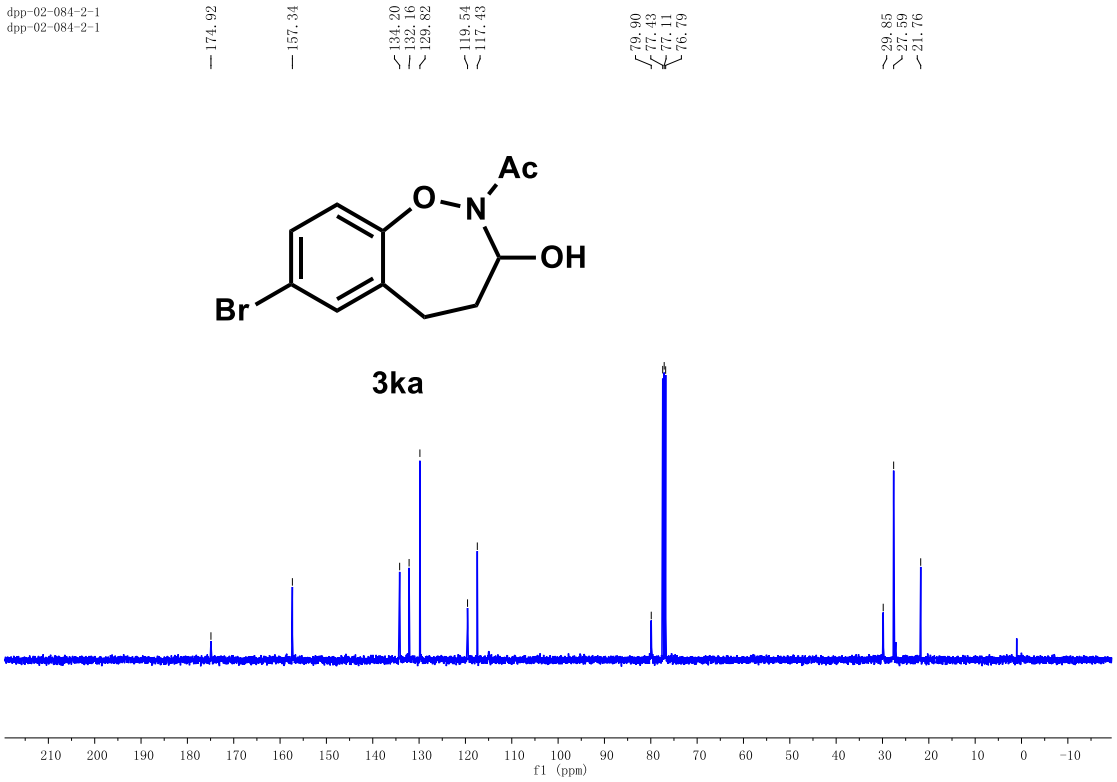

dpp-02-084-1
dpp-02-084-1, EOM
170.97
158.69
132.67
128.99
127.84
121.05
119.39
80.22
77.31
77.05
76.80
29.93
27.44
21.75

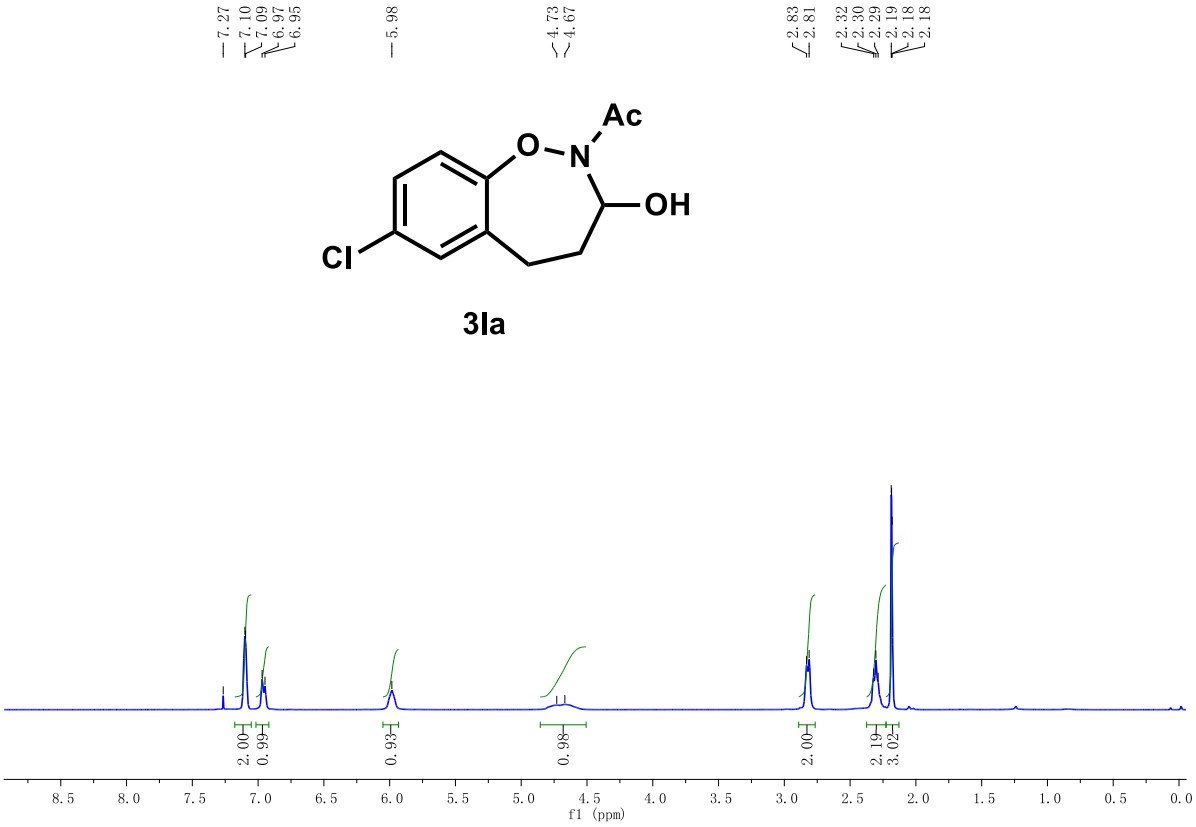

Br
O
N
Ac
OH

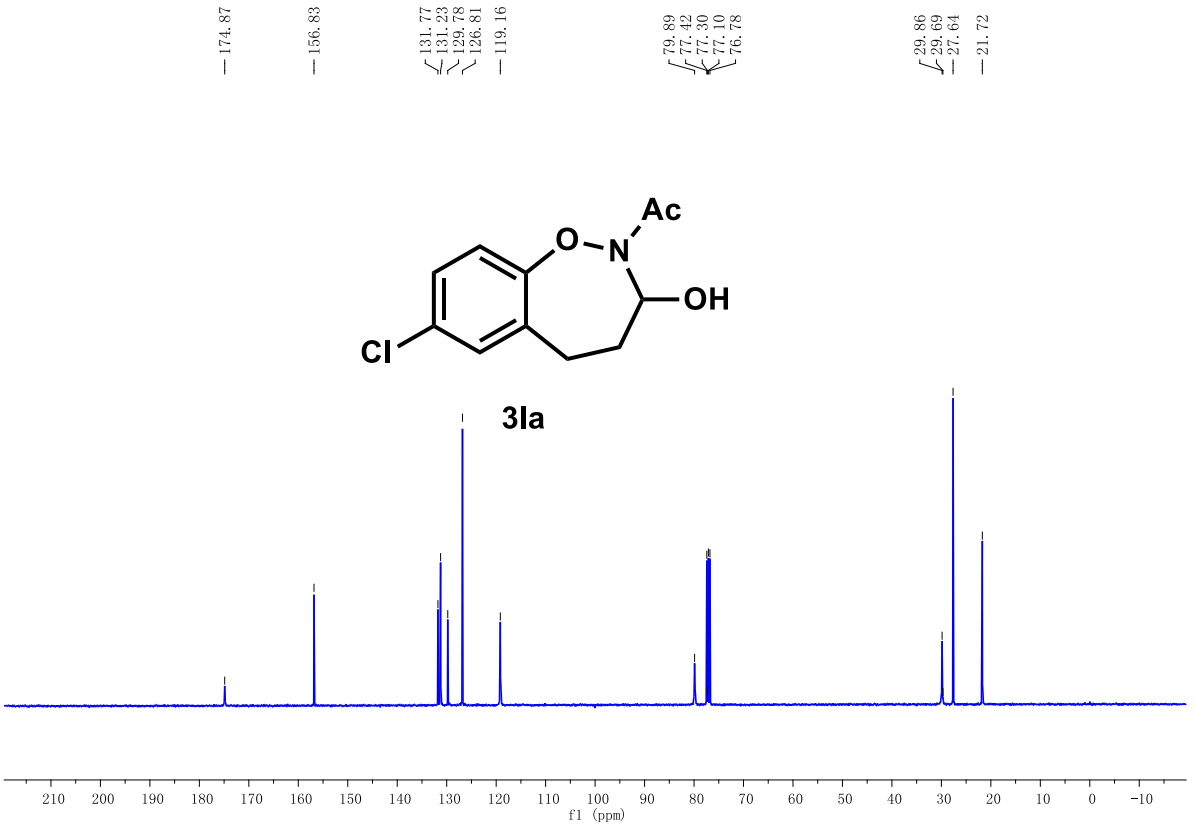
3ja


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

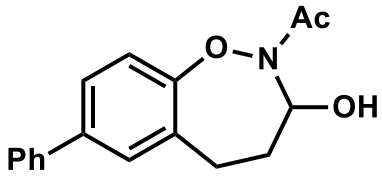

dpp-02-084-2-1
dpp-02-084-2-1
7.27
7.26
7.24
7.24
6.92
6.89
6.00
5.98
5.96
4.63
2.84
2.83
2.81
2.32
2.32
2.31
2.30
2.29
2.18
Ac
O
N
OH
Br
3ka
2.07
1.22
0.95
0.88
1.99
2.12
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


dpp-02-084-2-1
dpp-02-084-2-1
174.92
157.34
134.20
132.16
129.82
119.54
117.43
79.90
77.43
77.11
76.79
29.85
27.59
21.76
Ac
O
N
OH
Br
3ka
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

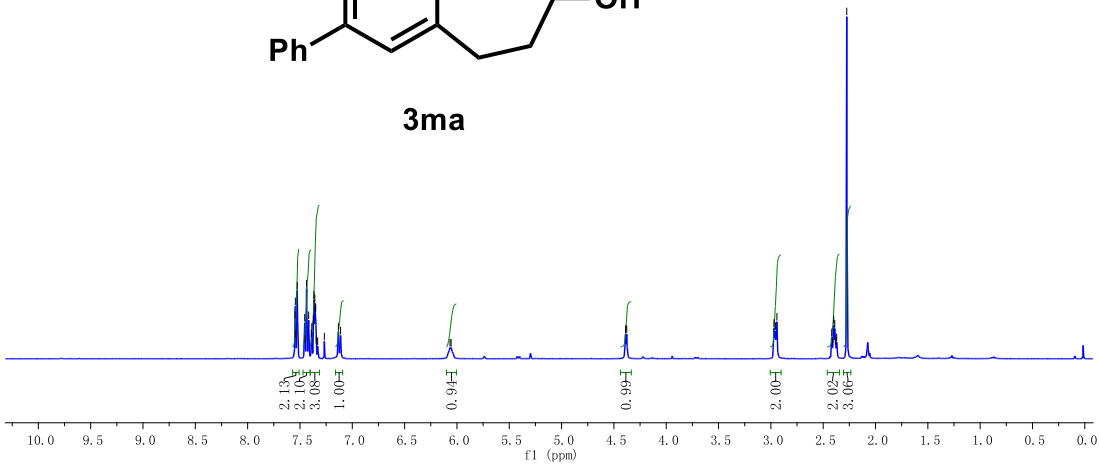

7.27
7.10
7.09
6.97
6.95
5.98
4.73
4.67
2.83
2.81
2.32
2.30
2.29
2.19
2.18
2.18
Ac
O
N
OH
Cl
3la
2.00
0.99
0.93
0.98
2.00
2.19
3.02
f1 (ppm)


174.87
156.83
131.77
131.23
129.78
126.81
119.16
79.89
77.42
77.30
77.10
76.78
29.86
29.69
27.64
21.72
Ac
O
N
OH
Cl
3la
f1 (ppm)

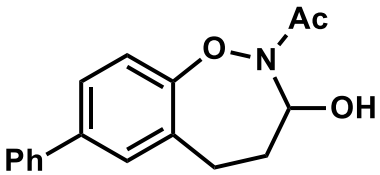

7.55
7.54
7.54
7.53
7.45
7.45
7.44
7.42
7.39
7.39
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.27
7.13
7.11
6.07
6.06
4.39
4.38
2.97
2.96
2.94
2.42
2.41
2.40
2.39
2.38
2.37
2.27


Ac
O
N
OH
Ph

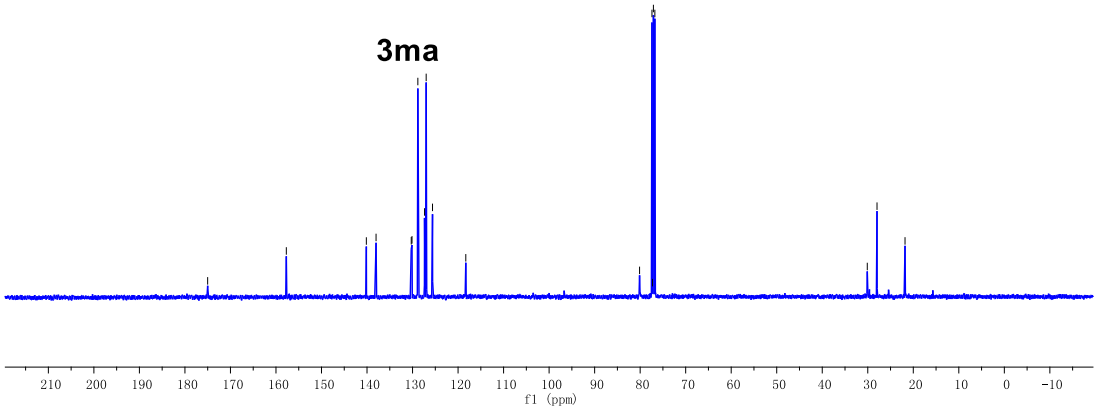
3ma

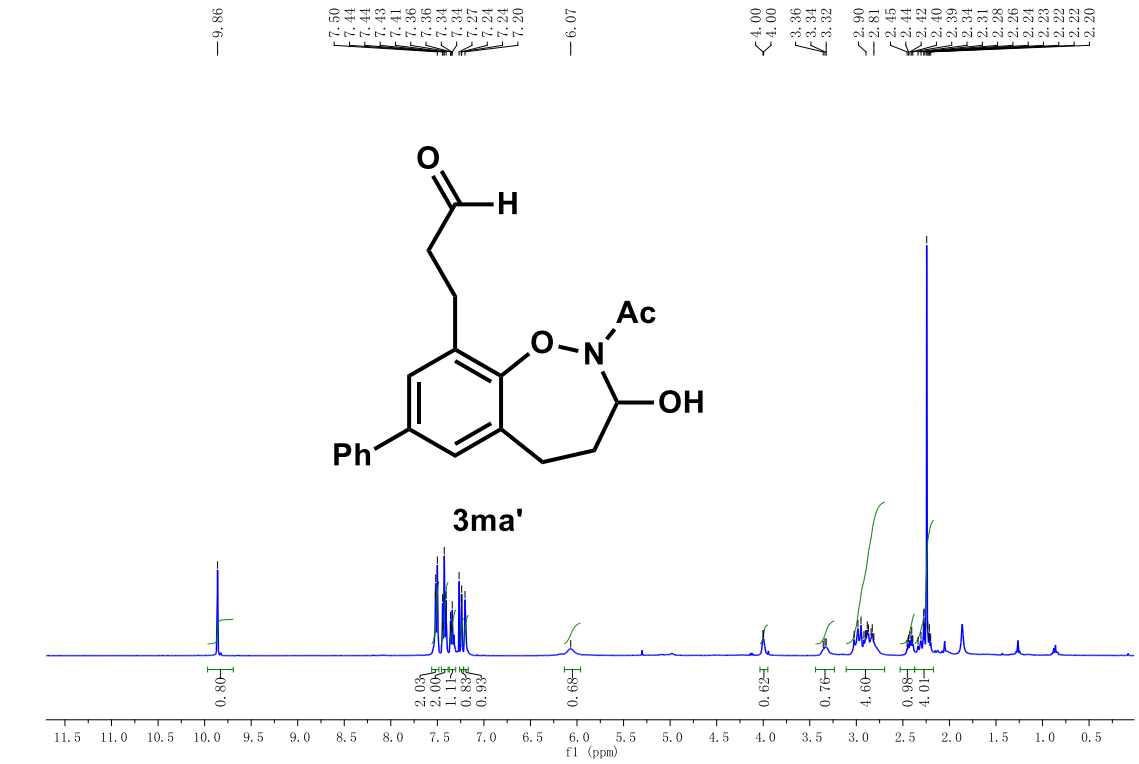

2.13
2.10
3.08
1.00
0.94
0.99
2.00
2.02
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

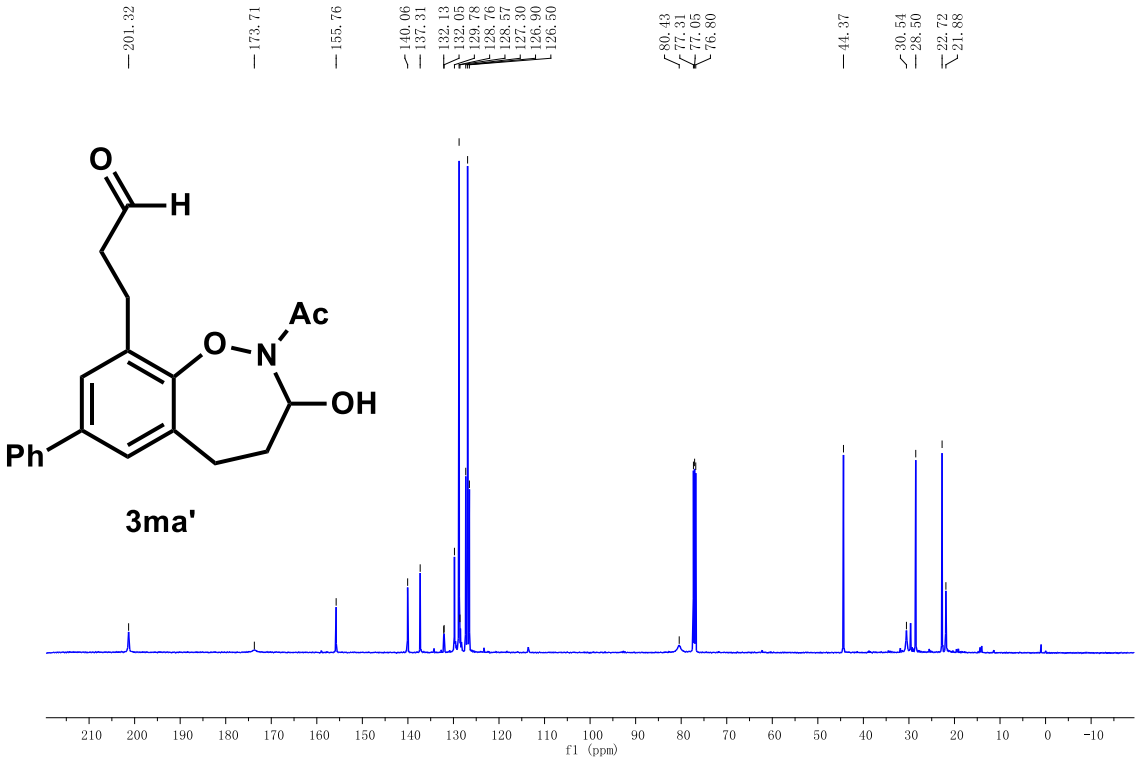

175.01
157.73
140.15
138.01
128.83
127.36
127.00
125.61
118.30
80.13
77.41
77.29
77.09
76.77
30.11
27.97
21.81

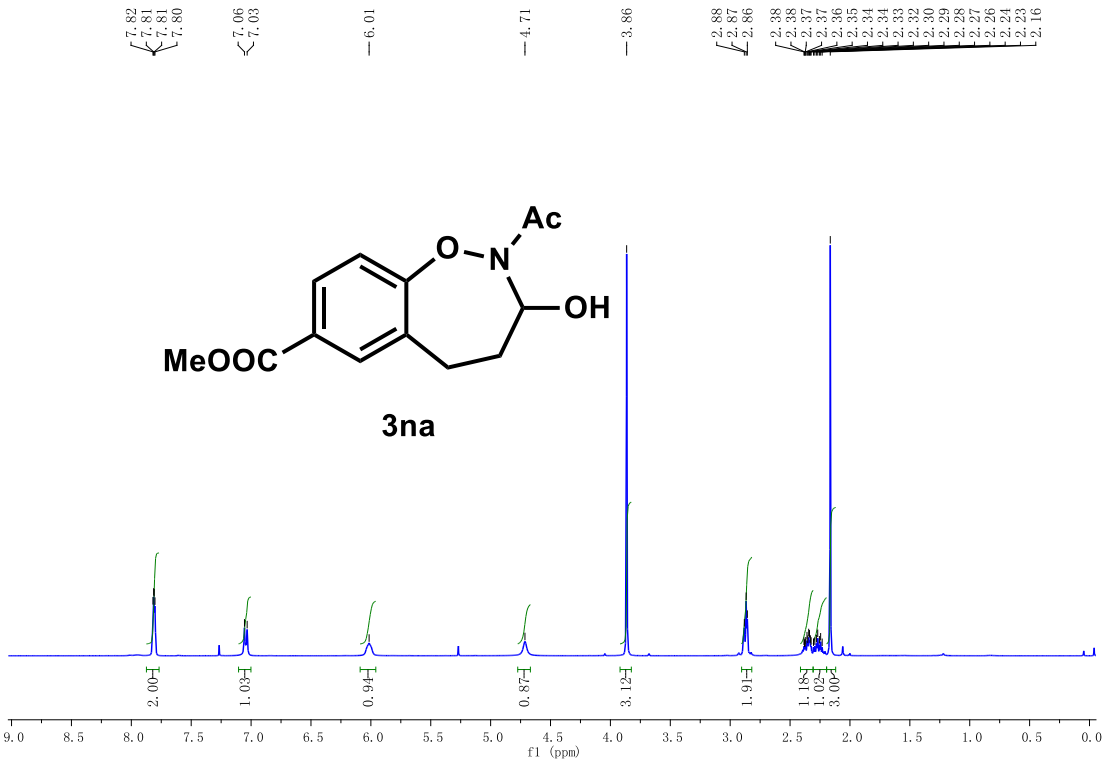

Ac
O
N
OH
Ph

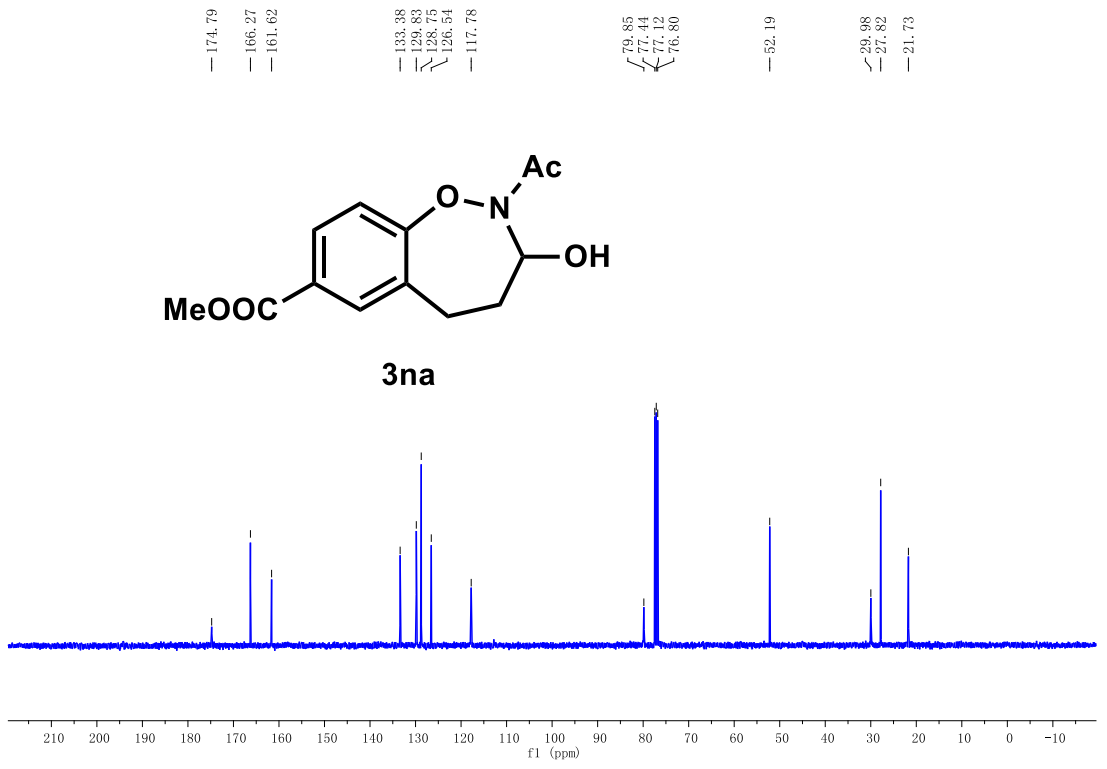
3ma


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

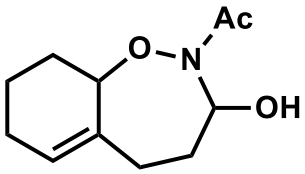

9.86
7.50
7.44
7.44
7.43
7.41
7.36
7.36
7.34
7.34
7.27
7.24
7.24
7.20
6.07
4.00
4.00
3.36
3.34
3.32
2.90
2.81
2.45
2.44
2.42
2.40
2.39
2.34
2.31
2.28
2.26
2.24
2.23
2.22
2.22
2.20
O
H
Ac
O
N
OH
Ph
3ma'
0.80
2.03
2.00
1.11
0.83
0.93
0.68
0.62
0.76
4.60
0.98
4.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


201.32
173.71
155.76
140.06
137.31
132.13
132.05
129.78
128.76
128.57
127.30
126.90
126.50
80.43
77.31
77.05
76.80
44.37
30.54
28.50
22.72
21.88
O
H
Ac
O
N
OH
Ph
3ma'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

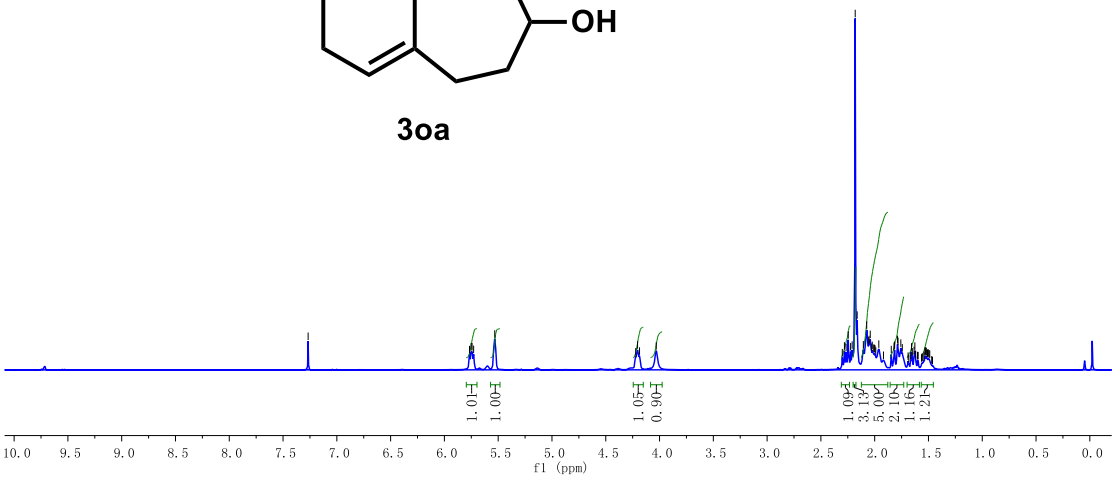

7.82
7.81
7.81
7.80
7.06
7.03
6.01
4.71
3.86
2.88
2.87
2.86
2.38
2.38
2.37
2.37
2.36
2.35
2.34
2.34
2.33
2.32
2.30
2.29
2.28
2.27
2.26
2.24
2.23
2.16
Ac
O
N
OH
MeOOC
3na
2.00
1.03
0.94
0.87
3.12
1.91
1.18
1.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.79
166.27
161.62
133.38
129.83
128.75
126.54
117.78
79.85
77.44
77.12
76.80
52.19
29.98
27.82
21.73
Ac
O
N
OH
MeOOC
3na
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

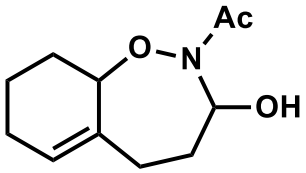

20140325-089-1
20140325-089-1
7.27
5.77
5.75
5.74
5.73
5.53
4.22
4.20
4.19
4.03
2.28
2.27
2.25
2.22
2.21
2.18
2.16
2.11
2.07
2.06
2.05
2.04
2.03
2.02
2.01
2.00
2.00
1.96
1.85
1.82
1.81
1.79
1.78
1.76
1.74
1.66
1.63


Ac
O
N
OH

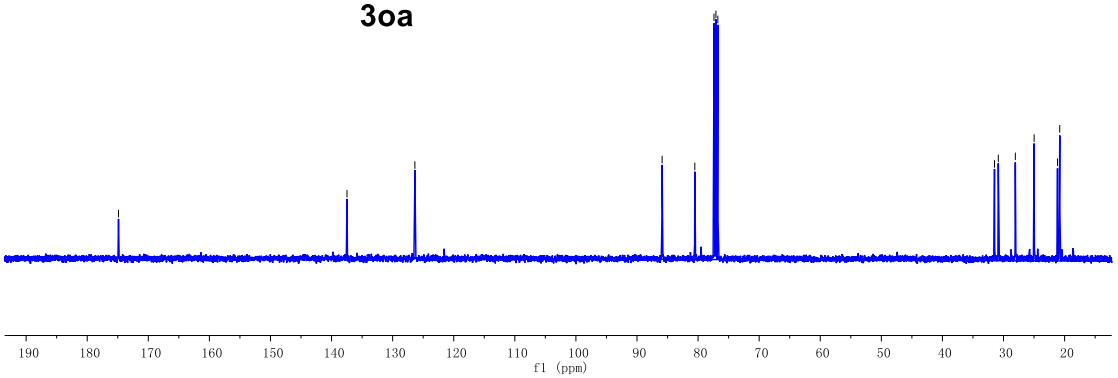
3oa

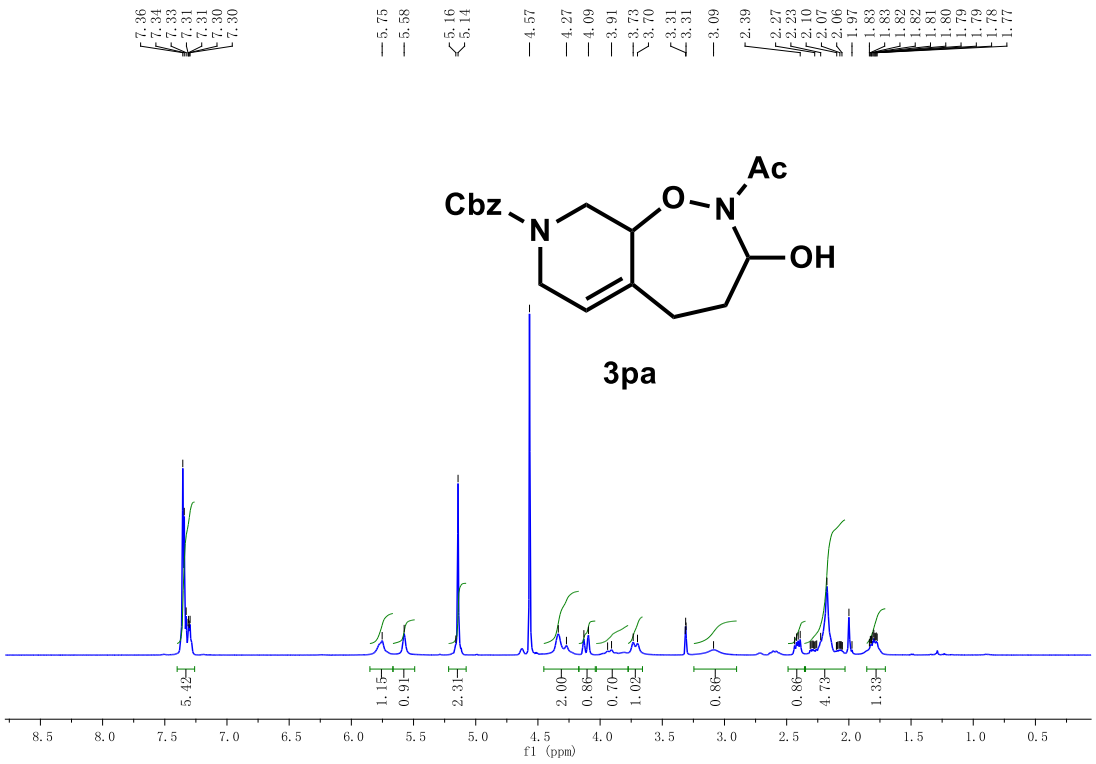

1.01
1.00
1.05
0.90
1.09
3.13
5.00
2.10
1.16
1.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

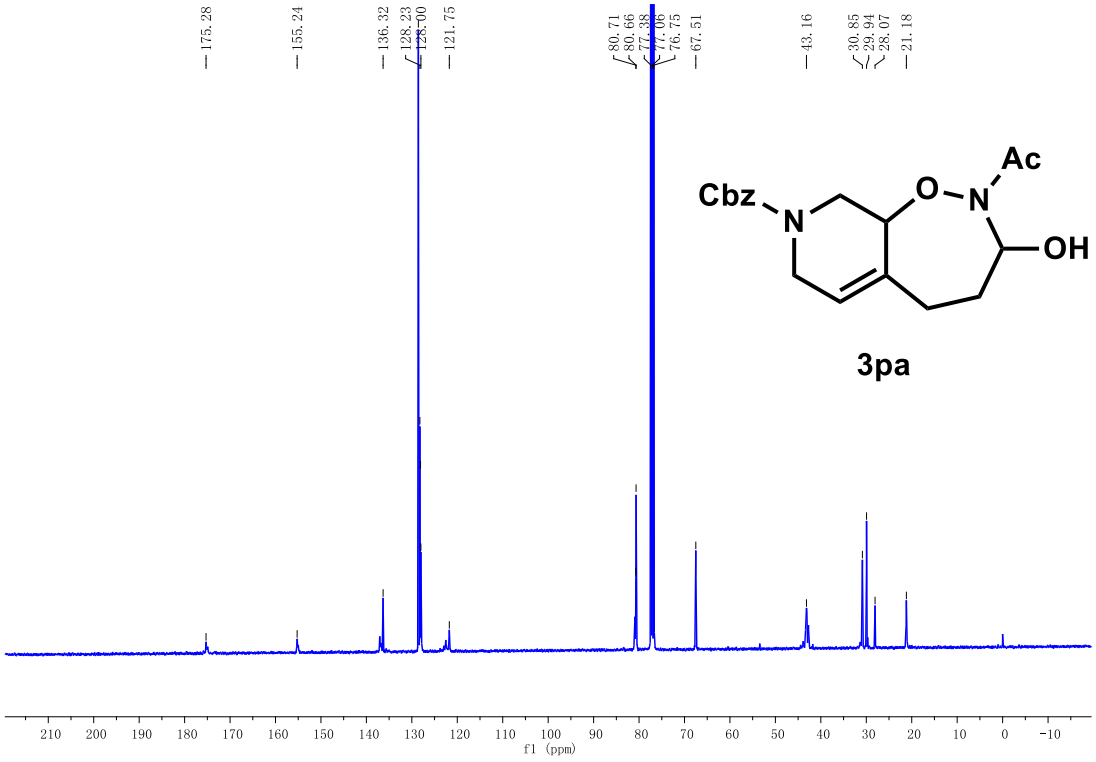

20140325-089-1
20140325-089-1 ZMR400
174.88
137.48
126.36
85.88
80.54
77.40
77.08
76.76
31.47
30.85
28.07
24.99
21.16
20.79


Ac
O
N
OH

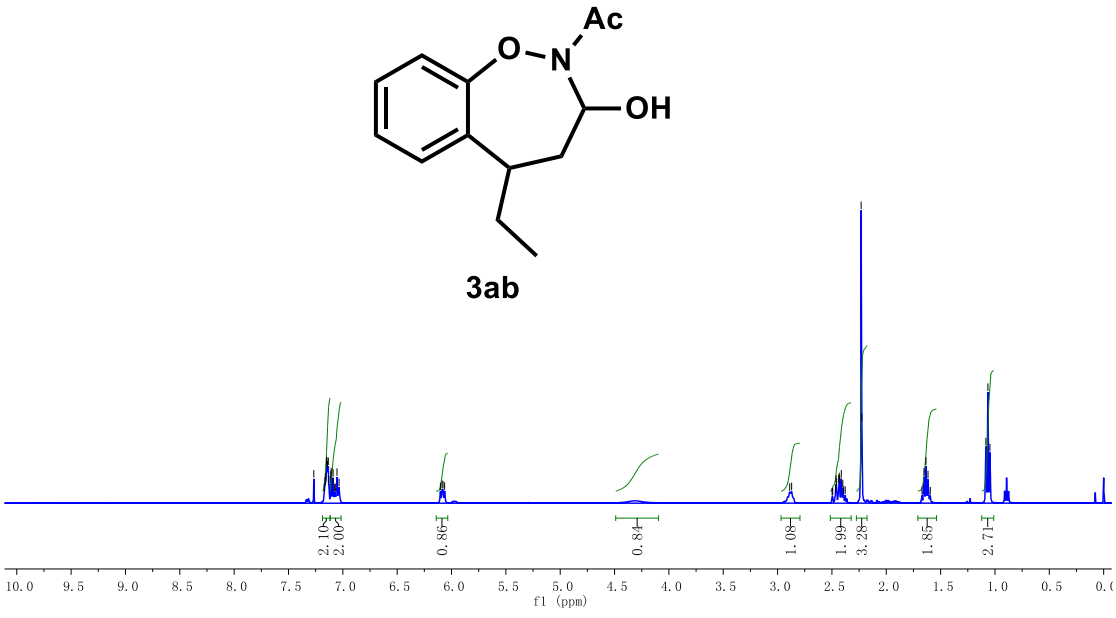
3oa


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

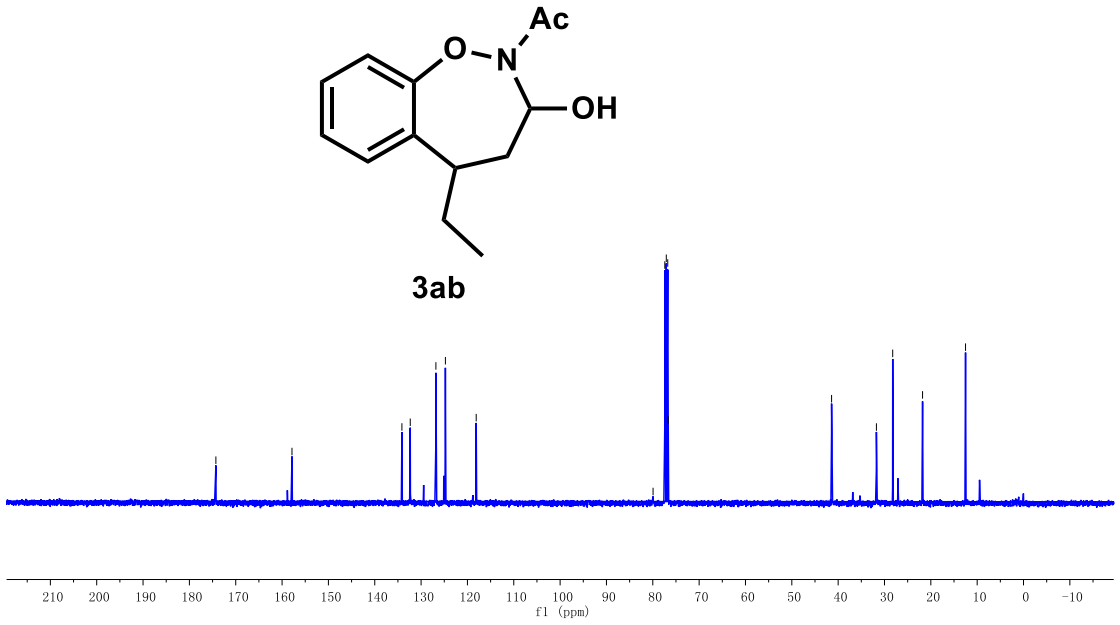

7.36
7.34
7.33
7.31
7.31
7.30
7.30
5.75
5.58
5.16
5.14
4.57
4.27
4.09
3.91
3.73
3.70
3.31
3.31
3.09
2.39
2.27
2.23
2.10
2.07
2.06
1.97
1.83
1.83
1.82
1.82
1.81
1.80
1.79
1.79
1.78
1.77
Cbz
N
O
N
Ac
OH
3pa
5.42
1.15
0.91
2.31
2.00
0.86
0.70
1.02
0.86
0.86
4.73
1.33
f1 (ppm)

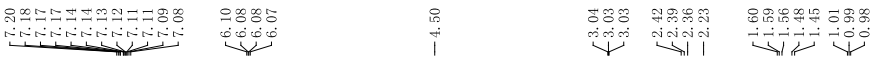

175.28
155.24
136.32
128.23
128.00
121.75
80.71
80.66
77.38
77.06
76.75
67.51
43.16
30.85
29.94
28.07
21.18
Cbz
N
O
N
Ac
OH
3pa
f1 (ppm)

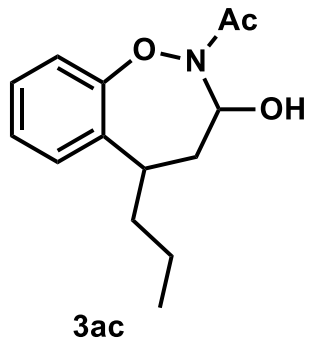

20140321-087-1
20140321-087-1
7.27
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.11
7.11
7.09
7.09
7.07
7.07
7.05
7.03
6.10
6.09
6.08
6.06
2.89
2.87
2.44
2.43
2.41
2.23
2.22
1.67
1.65
1.63
1.62
1.08
1.07
1.05


Ac
O
N
OH
3ab
2.10
2.00
0.86
0.84
1.08
1.99
3.28
1.85
2.71
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

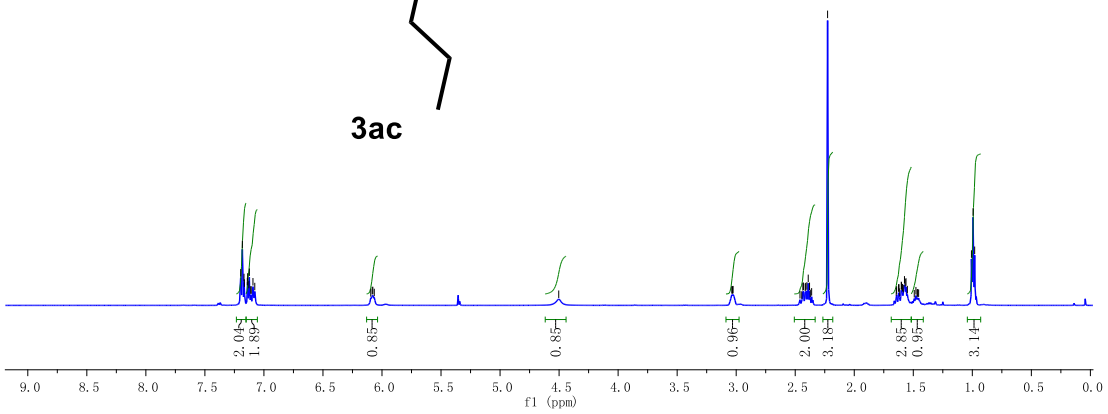

20140321-087-1
20140321-087-1 NMR400
174.28
157.86
134.14
132.34
126.81
124.75
118.10
79.94
77.41
77.09
76.77
76.68
41.42
31.74
28.23
21.79
12.51


Ac
O
N
OH
3ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

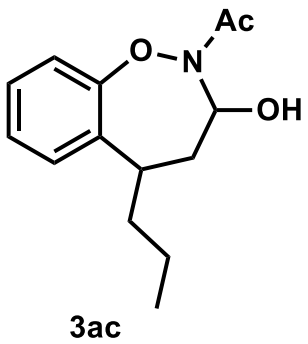

7.20
7.18
7.17
7.17
7.14
7.14
7.13
7.12
7.11
7.11
7.09
7.08
6.10
6.08
6.08
6.07
4.50
3.04
3.03
3.03
2.42
2.39
2.36
2.23
1.60
1.59
1.56
1.48
1.45
1.01
0.99
0.98


Ac
O
N
OH

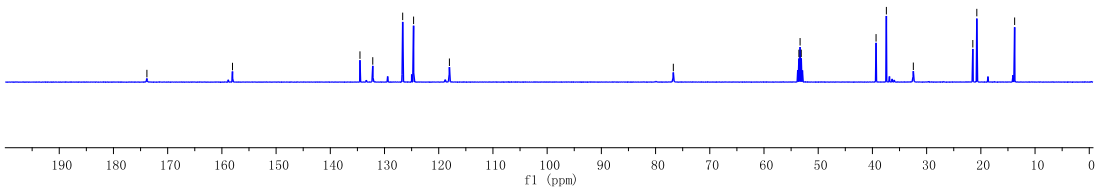
3ac

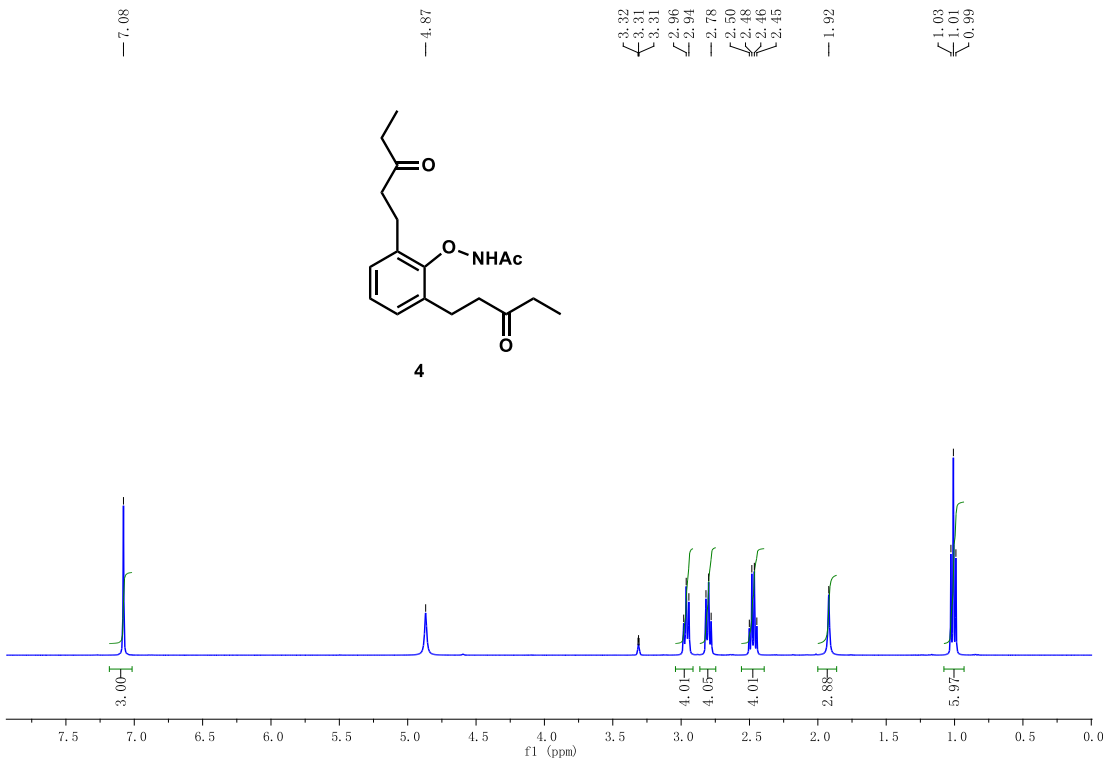

2.04
1.89
0.85
0.85
0.96
2.00
3.18
2.85
0.95
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

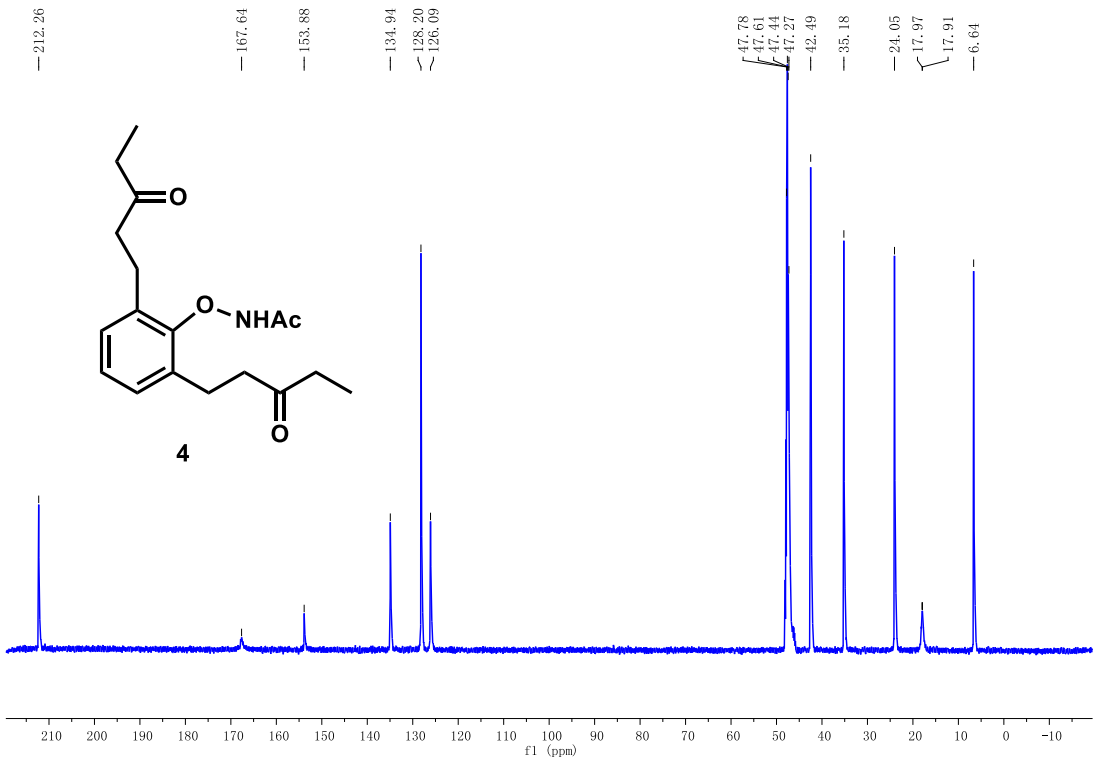

173.83
158.04
134.53
132.17
126.65
124.64
118.03
76.72
53.56
53.34
53.13
39.33
37.43
32.45
21.48
20.74
13.77


Ac
O
N
OH

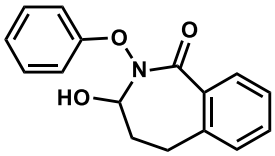
3ac


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

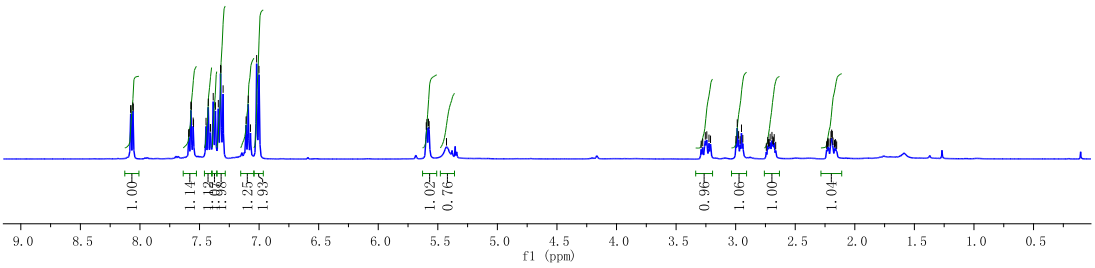

7.08
4.87
3.32
3.31
3.31
2.96
2.94
2.78
2.50
2.48
2.46
2.45
1.92
1.03
1.01
0.99
O
O
NHAc
O
4
3.00
4.01
4.05
4.01
2.88
5.97
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


212.26
167.64
153.88
134.94
128.20
126.09
47.78
47.61
47.44
47.27
42.49
35.18
24.05
17.97
17.91
6.64
O
O
NHAc
O
4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

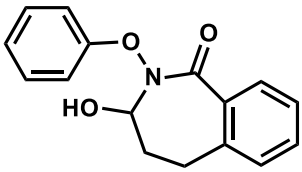

8.08
8.08
8.06
8.06
7.57
7.45
7.41
7.34
7.30
7.11
7.09
7.07
7.02
7.00
5.60
5.59
5.58
5.57
5.43
3.29
3.28
3.25
3.24
3.22
3.21
2.94
2.66
2.24
2.23
2.22
2.22
2.21
2.20
2.19
2.19
2.18
2.17
2.16
2.16
2.15


O
N
O
HO

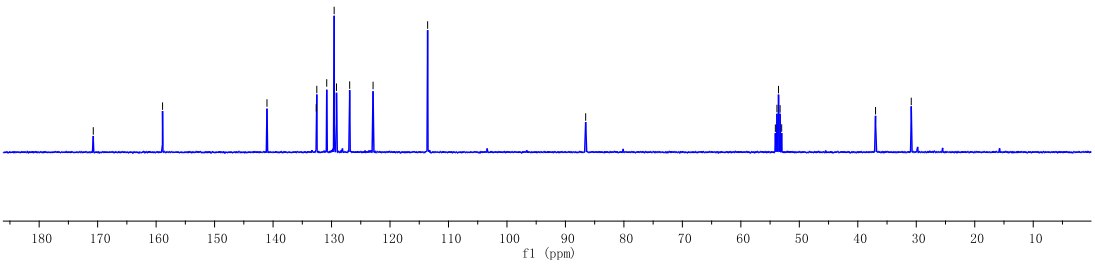
5

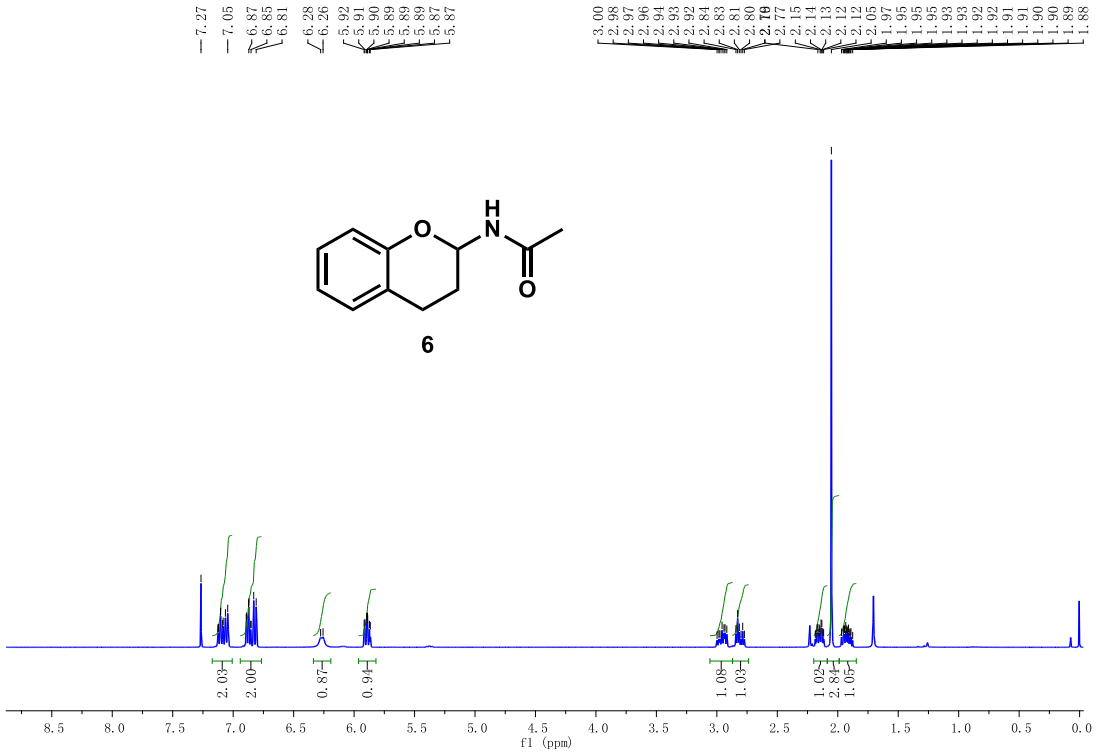

1.00
1.14
1.25
1.93
1.02
0.76
0.96
1.06
1.00
1.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

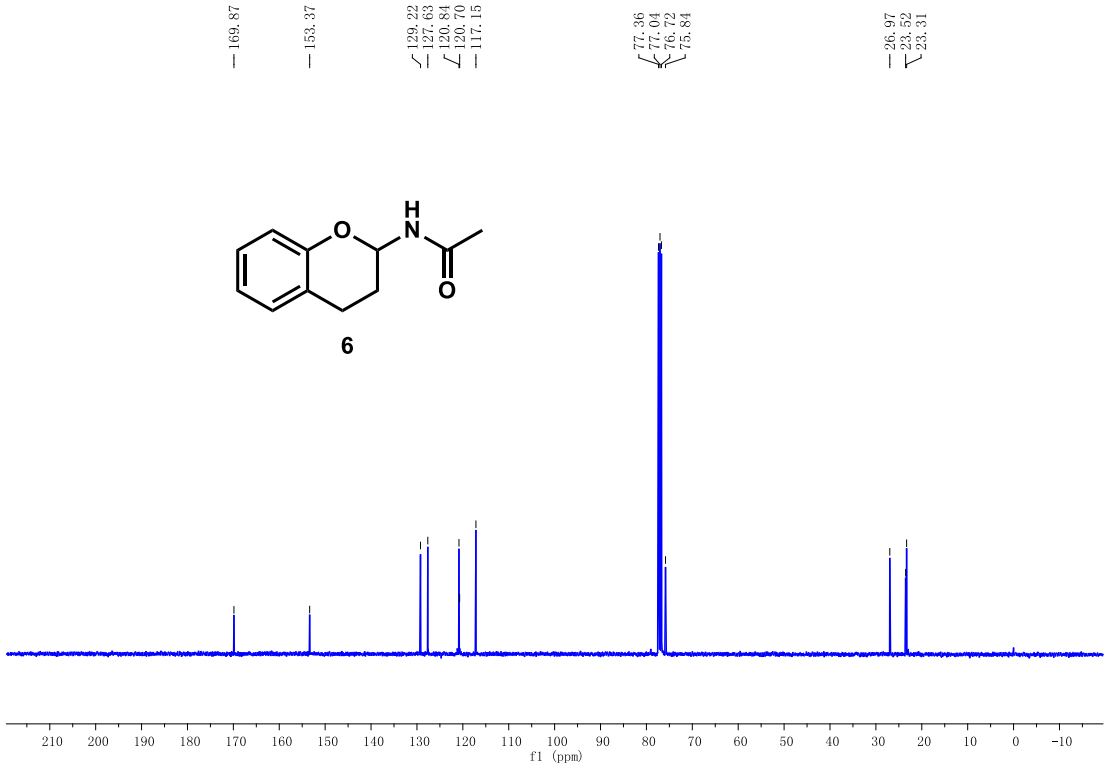

170.75
158.90
141.04
130.82
129.55
129.15
126.90
122.90
113.56
86.54
54.10
53.83
53.56
53.29
53.02
36.96
30.86


O
N
O
HO

5


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.27
7.05
6.87
6.85
6.81
6.28
6.26
5.92
5.91
5.90
5.89
5.89
5.87
5.87
3.00
2.98
2.97
2.96
2.94
2.93
2.92
2.84
2.83
2.81
2.80
2.77
2.15
2.14
2.13
2.12
2.12
2.05
1.97
1.95
1.95
1.93
1.93
1.92
1.92
1.91
1.91
1.90
1.90
1.89
1.88
O
H
N
O
6
2.03
2.00
0.87
0.94
1.08
1.03
1.02
2.84
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.87
153.37
129.22
127.63
120.84
120.70
117.15
77.36
77.04
76.72
75.84
26.97
23.52
23.31
O
H
N
O
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)