

# Supporting Information (SI)

## Catalytic Asymmetric Access to Noncanonical Chiral $\alpha$ -Amino Acids from Cyclic Iminoglyoxylates and Enamides

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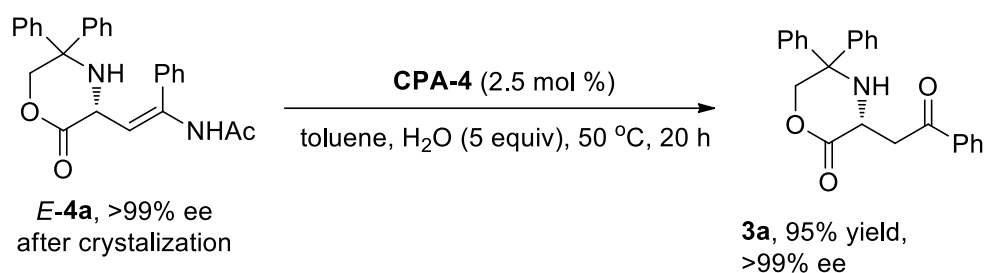
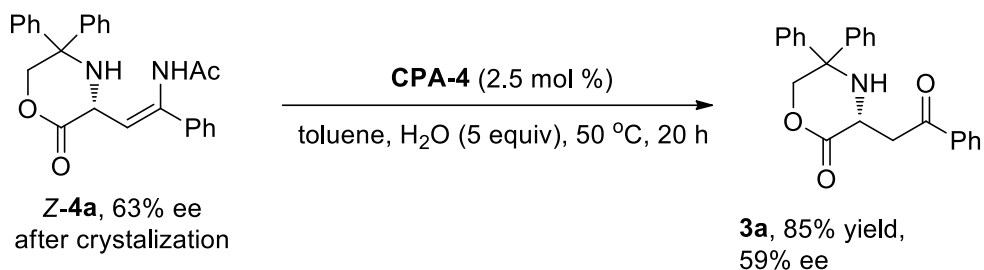
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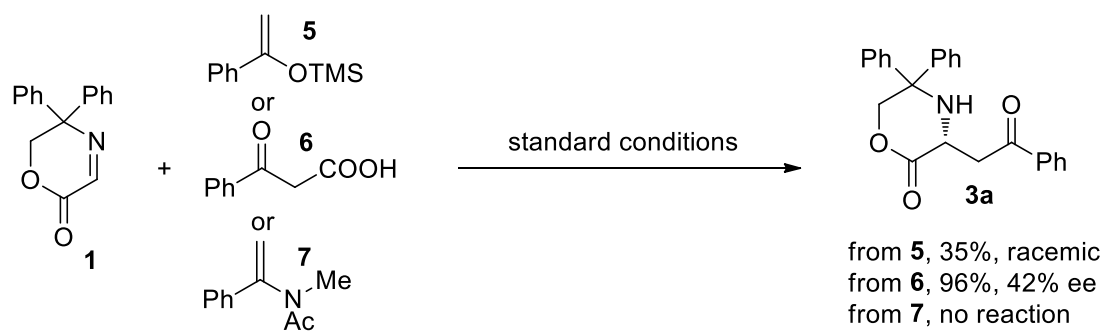
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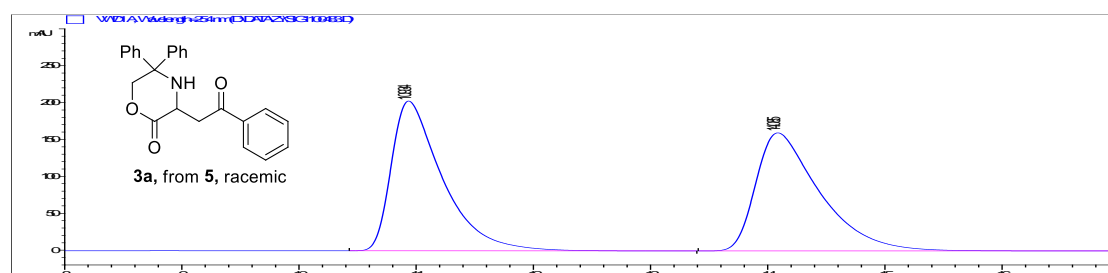
# 1. Control experiments



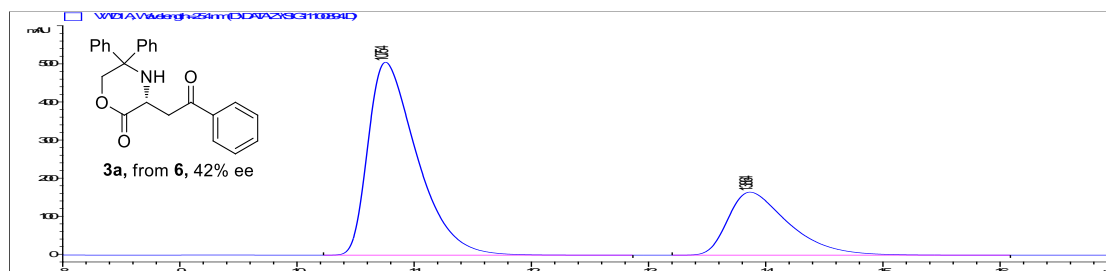
To a 25 mL Schlenk flask equipped with a stirring bar was added **Z-4a** or **E-4a** (82.4 mg, 0.2 mmol, 1.0 equiv), and chiral phosphoric acid **CPA-4** (2.9 mg, 2.5 mol %). Then toluene (3 mL) and H<sub>2</sub>O (18  $\mu$ L, 5.0 equiv) were added successively at 0 °C, the resulting mixture was stirred at 50 °C for 20 h until the disappearance of the starting material as monitored by thin layer chromatography (TLC). After that, they could transform to the final product **3a** in good yields with unchanged ee values.



Reaction performed on a 0.2 mmol scale utilizing the same procedure for the preparation of **3a**.



#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.934	6158.4	203.1	0.4441	0.475	50.330
2	14.085	6077.7	160.1	0.5595	0.491	49.670



#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.754	14677.6	506.4	0.44	0.521	71.137
2	13.864	5955.2	165.4	0.5423	0.532	28.863

## 2. NMR mechanistic experiments

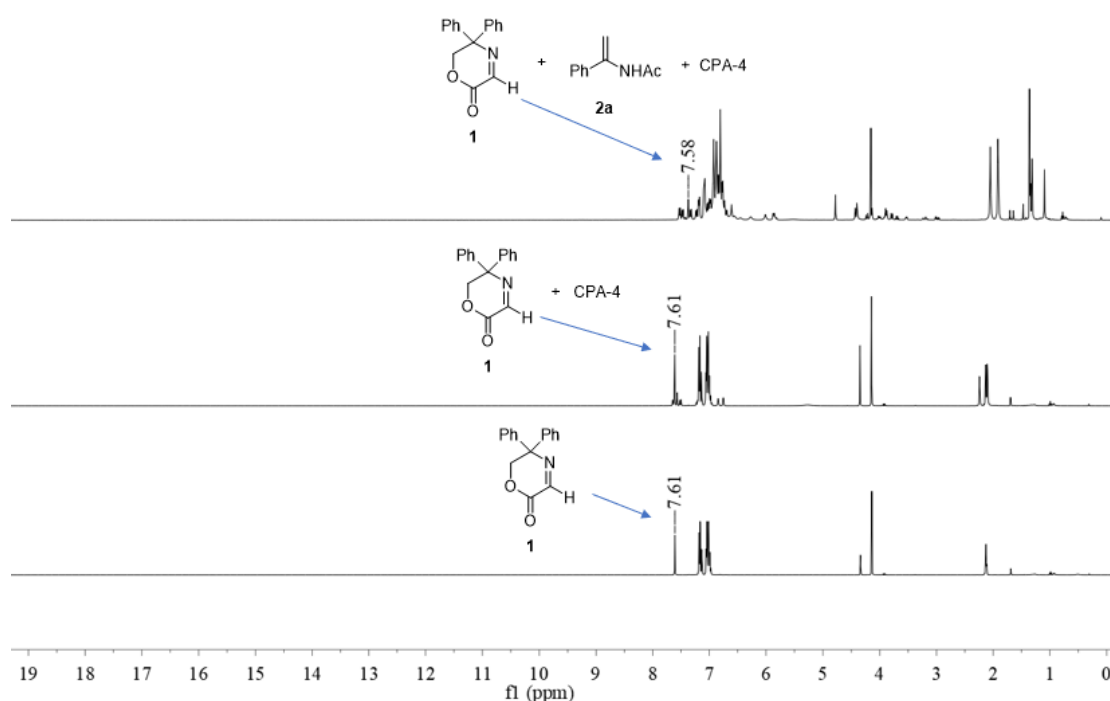
Table S1. NMR experiments about the chemical shifts of hydrogen atoms between **1**, **2a** and CPA-4

Entry	Step-1	Step-2
<b>Exp-1</b>	Cyclic iminoglyoxylate <b>1</b> (8.4 mg, 0.03 mmol) in Toluene-d <sub>8</sub> (0.5 mL) for 15 min; Detected by <sup>1</sup> H NMR	Addition of chiral phosphoric acid CPA-4 (5.0 mg, 25 mol %); Detected by <sup>1</sup> H NMR and <sup>31</sup> P NMR
<b>Exp-2</b>	Phenyl enamide <b>2a</b> (8.1 mg, 0.05 mmol) in Toluene-d <sub>8</sub> (0.5 mL) for 15 min; Detected by <sup>1</sup> H NMR	Addition of chiral phosphoric acid CPA-4 (5.0 mg, 25 mol %); Detected by <sup>1</sup> H NMR and <sup>31</sup> P NMR
<b>Exp-3</b>	Cyclic iminoglyoxylate <b>1</b> (8.4 mg, 0.03 mmol) and phenyl enamide <b>2a</b> (8.1 mg, 0.05 mmol) in Toluene-d <sub>8</sub> (0.5 mL) for 15 min; Detected by <sup>1</sup> H NMR	Addition of chiral phosphoric acid CPA-4 (5.0 mg, 25 mol %); Detected by <sup>1</sup> H NMR and <sup>31</sup> P NMR
<b>Exp-4</b>	Chiral phosphoric acid CPA-4 (5.0 mg, 25 mol %) in Toluene-d <sub>8</sub> (0.5 mL) for 15 min; Detected by <sup>1</sup> H NMR and <sup>31</sup> P NMR	

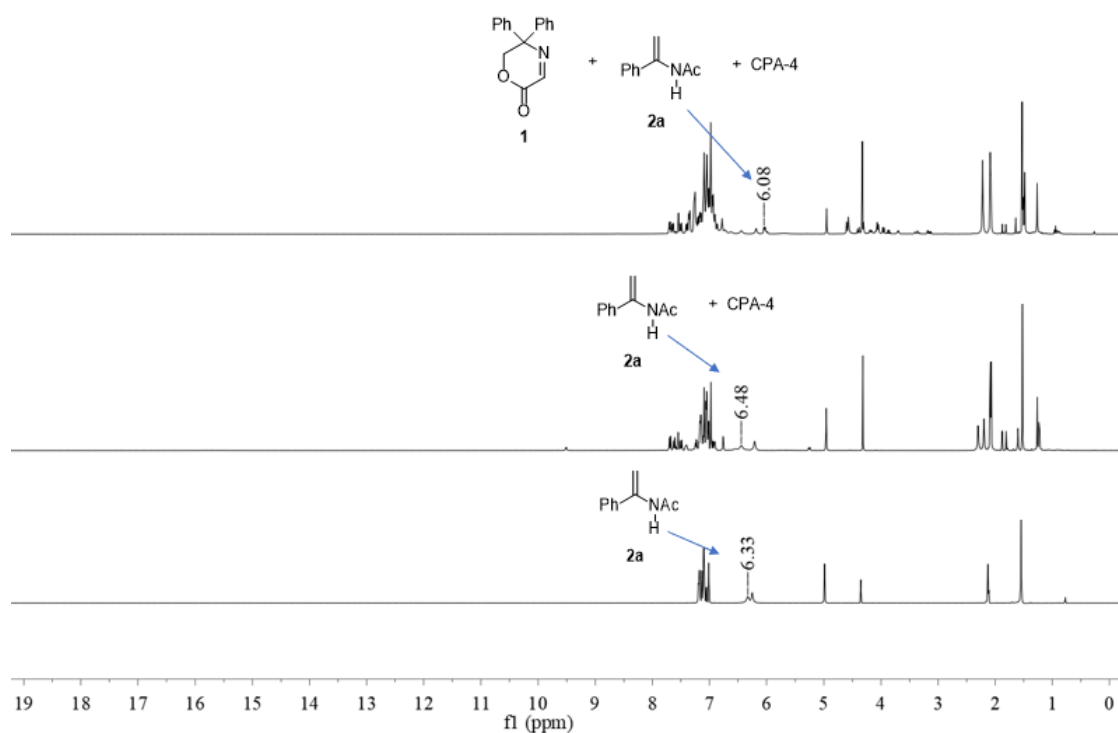
Table S2. NMR experiments about the chemical shift of hydrogen bonds between **1**, **2a** and CPA-4

δ substrates	<sup>1</sup> H NMR (ppm)			<sup>31</sup> P NMR (ppm)
	<b>1</b>	<b>2a</b>	CPA-4	CPA-4
Adding <b>1</b>	7.61	-	5.26	3.89
Adding <b>2a</b>	-	6.33	6.80	3.15
Adding CPA-4	7.61	6.48	6.13	4.03
Mixture of <b>1+2a+CPA</b>	7.58	6.08	Missing	3.31

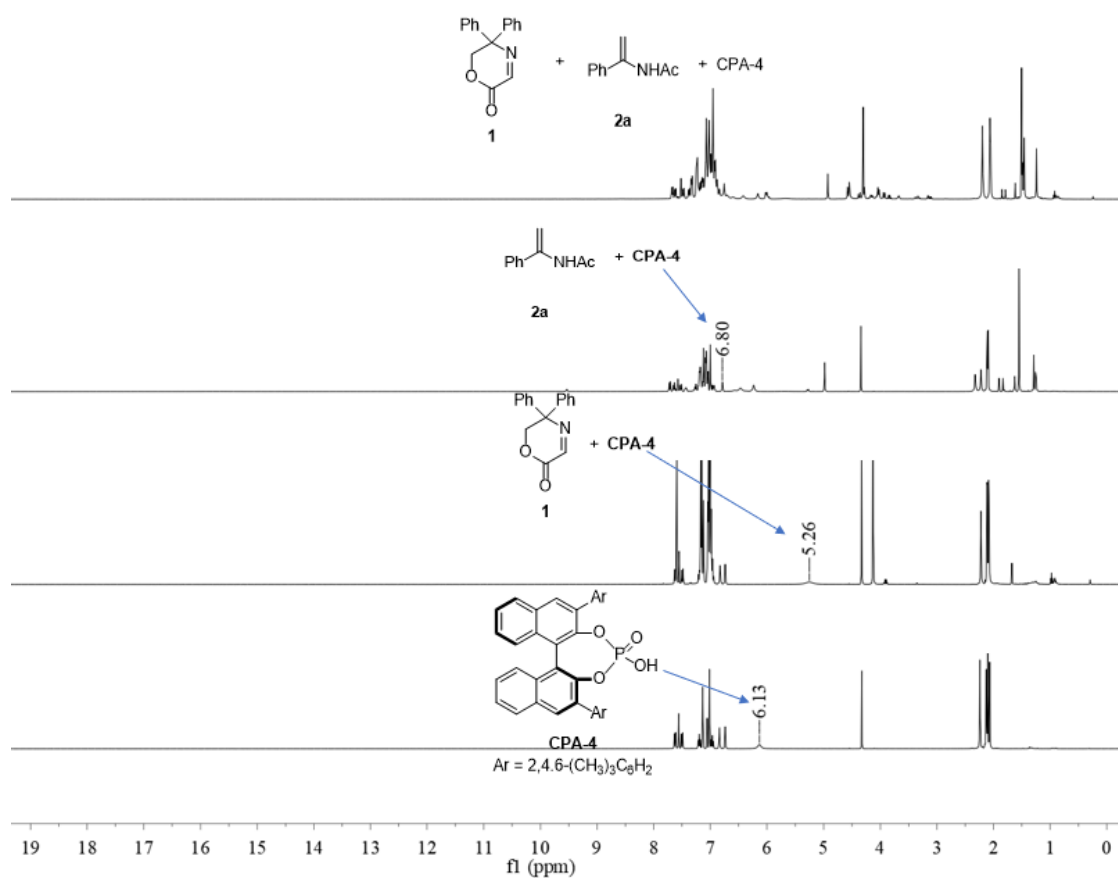
From the preliminary NMR experiments, we can conclude that: 1) The hydrogen atom (H-C=N) of imine **1** was not involved in obvious hydrogen bonding interactions (Figure S1); 2) The N-H proton chemical shift of enamide **2a** changed from 6.33 to 6.48 when mixing with CPA-4, indicating the potential hydrogen-bonding association (Figure S2); 3): The O-H proton chemical shift of CPA-4 changed largely when mixed with either imine **1** or enamide **2a** (Figure S3), and the P-chemical shift was also observed with corresponding variations (Figure S4). These results reveal that chiral phosphoric acid CPA-4 may interact with both substrates through multiple hydrogen bonding as suggested in Scheme 4c in the main text. Further studies via DFT calculations are currently underway in our lab and will be reported in due course.



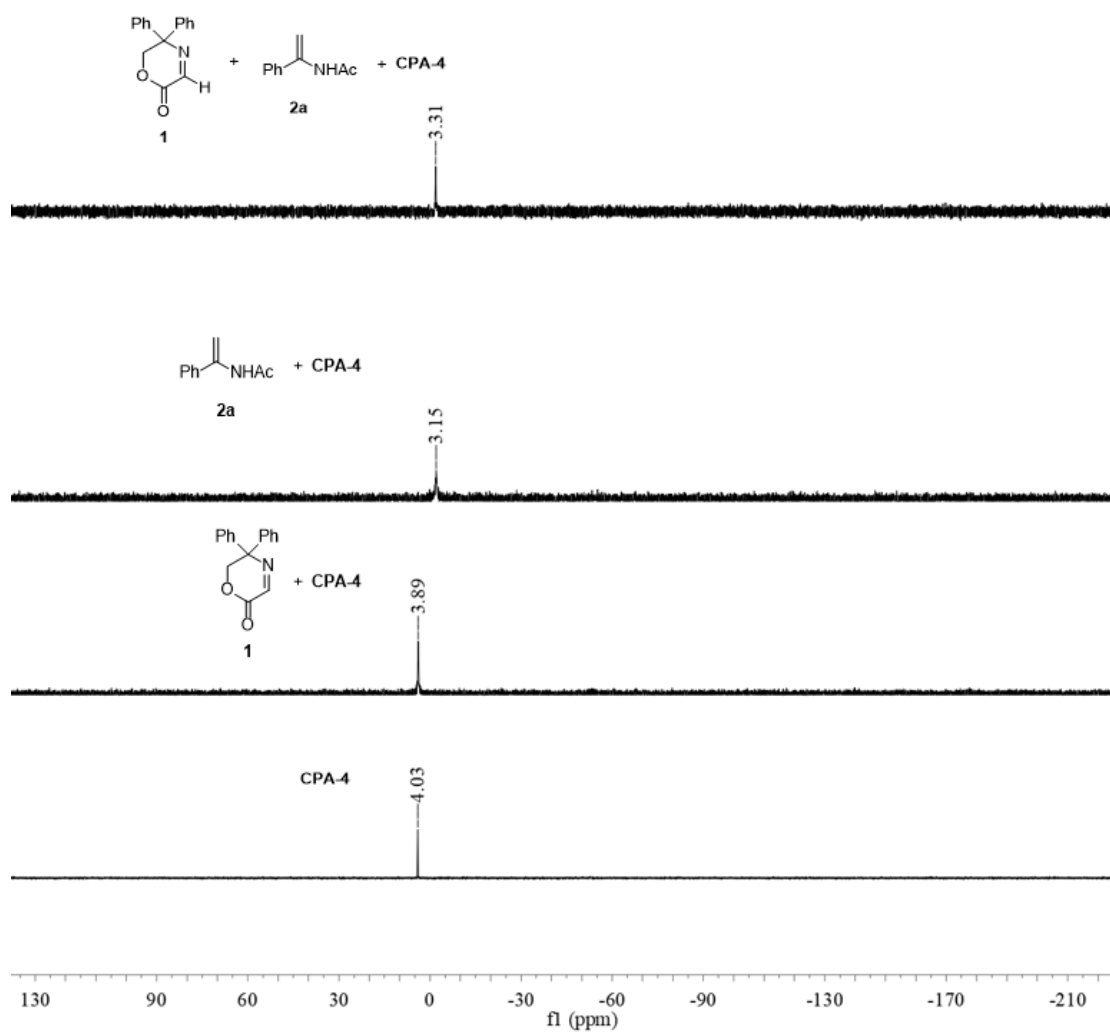
**Figure S1.** <sup>1</sup>H NMR spectra of the reaction mixture of **1** with **2a** and CPA-4



**Figure S2.**  $^1\text{H}$  NMR spectra of the reaction mixture of **2a** with **1** and CPA-4



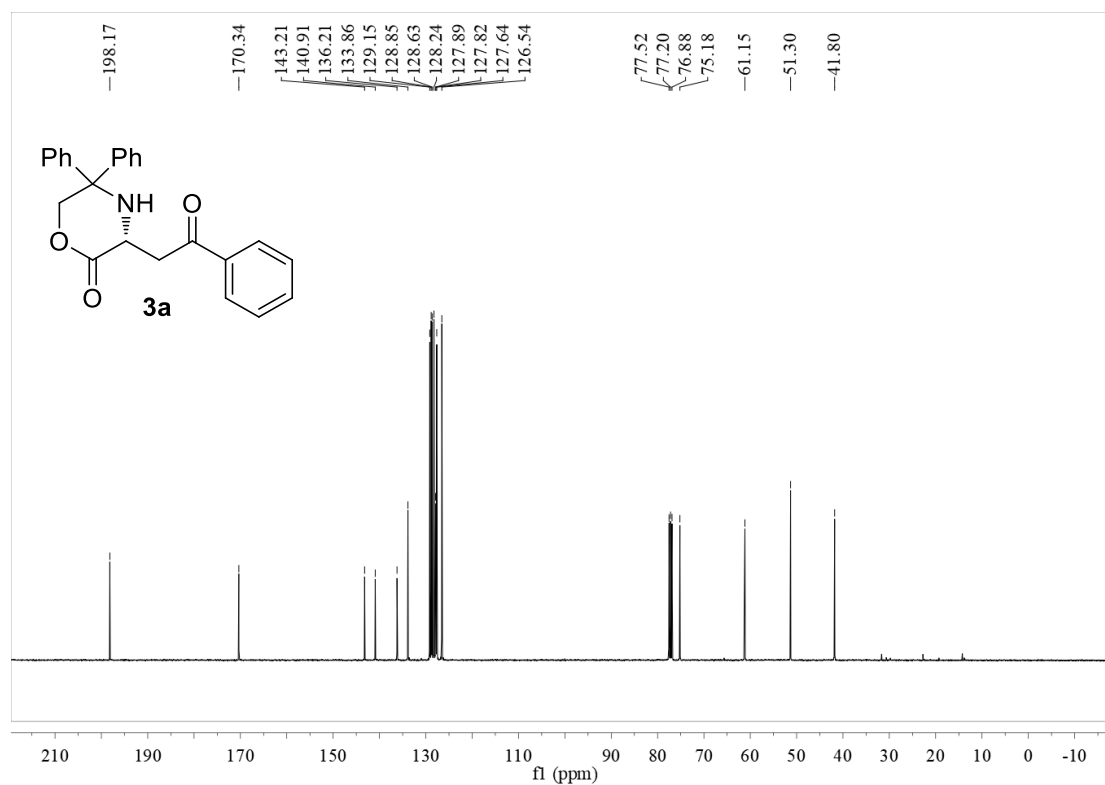
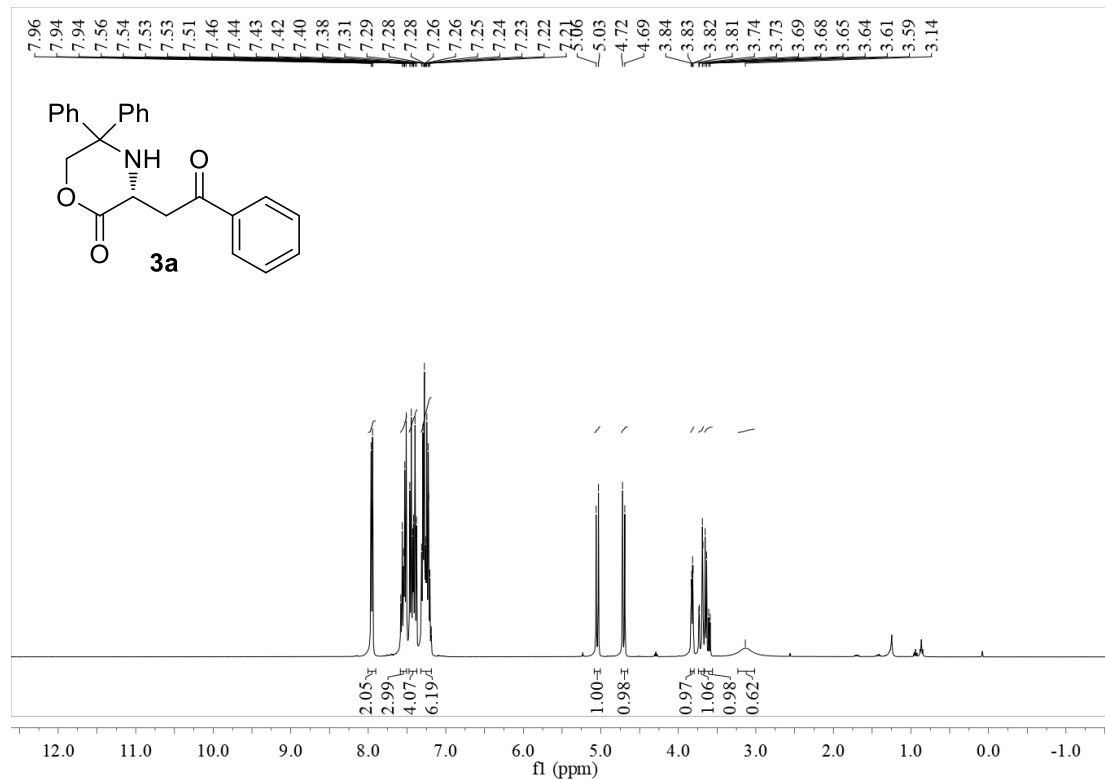
**Figure S3.**  $^1\text{H}$  NMR spectra of the reaction mixture of CPA-4 with **1** and **2a**



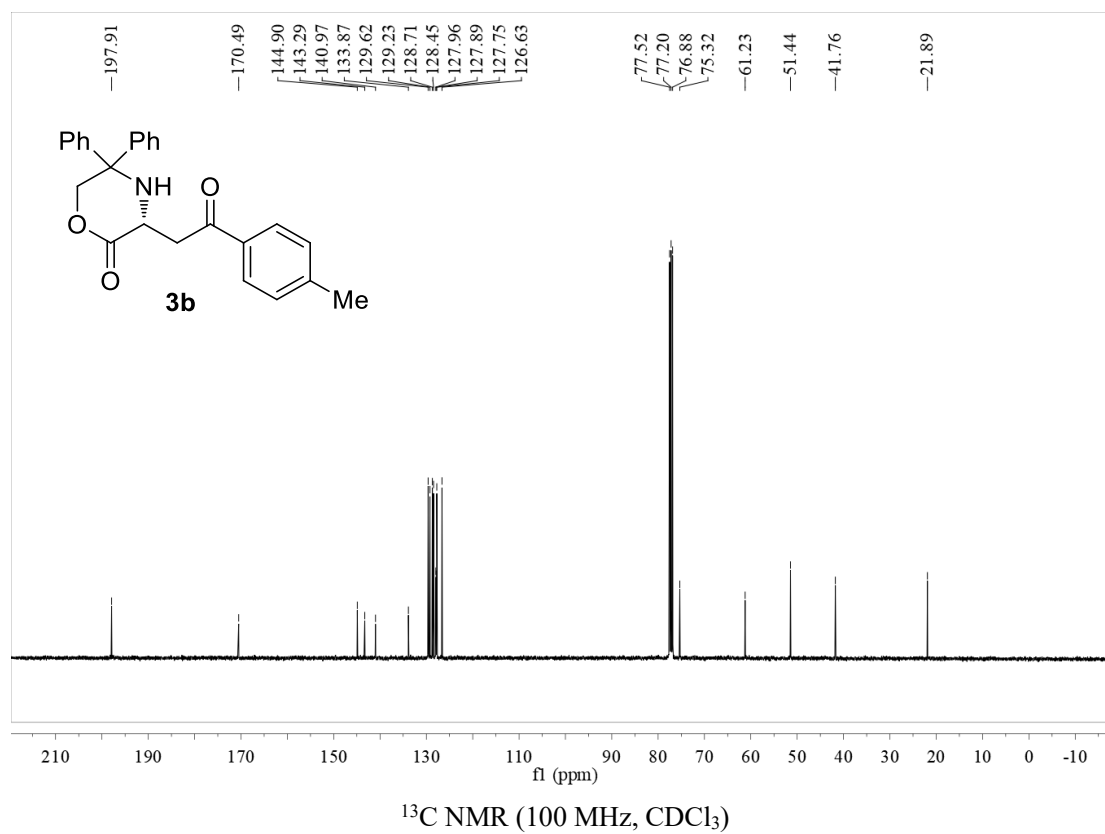
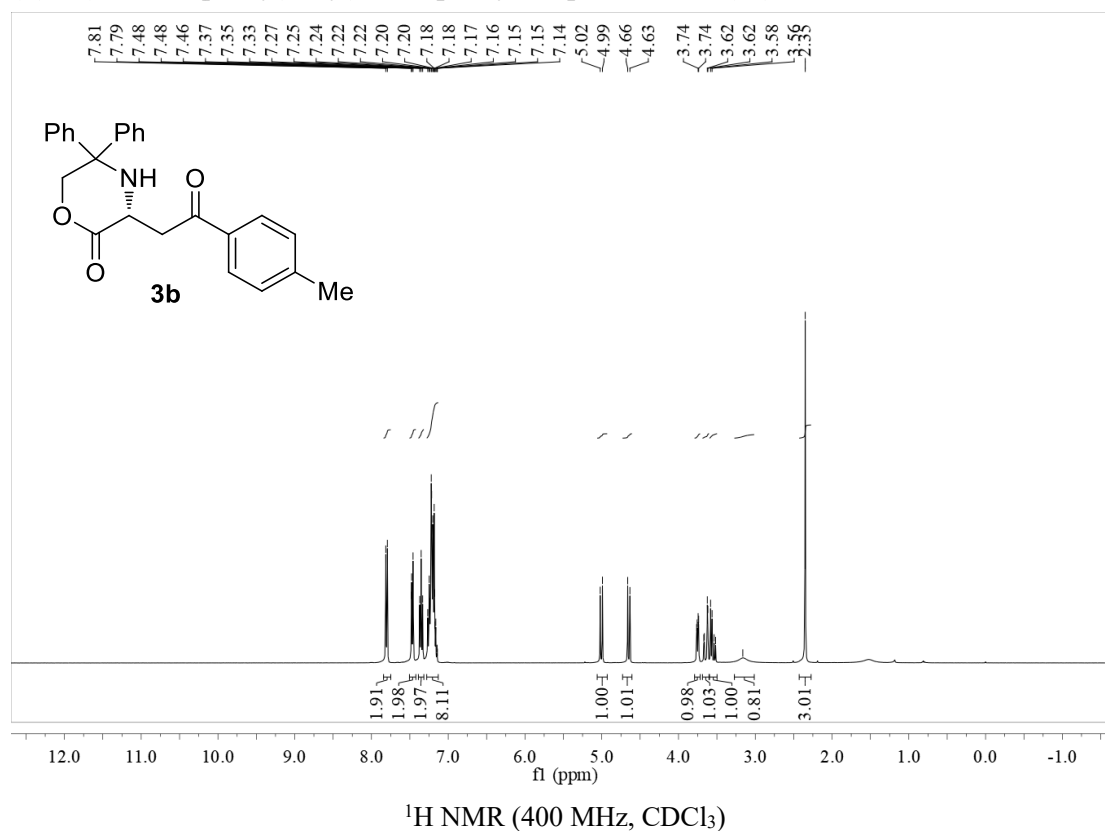
**Figure S4.**  $^{31}\text{P}$  NMR spectra of the reaction mixture of CPA-4 with 1 and 2a

### 3. NMR spectra of the related compounds

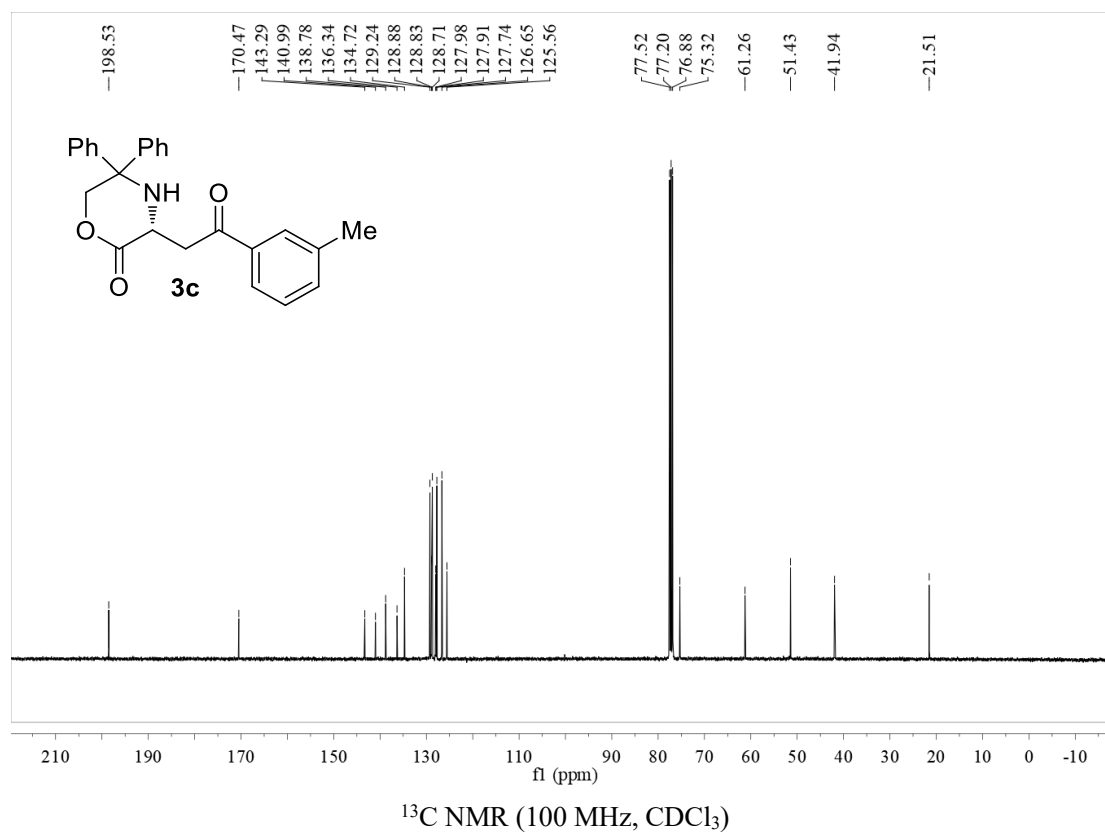
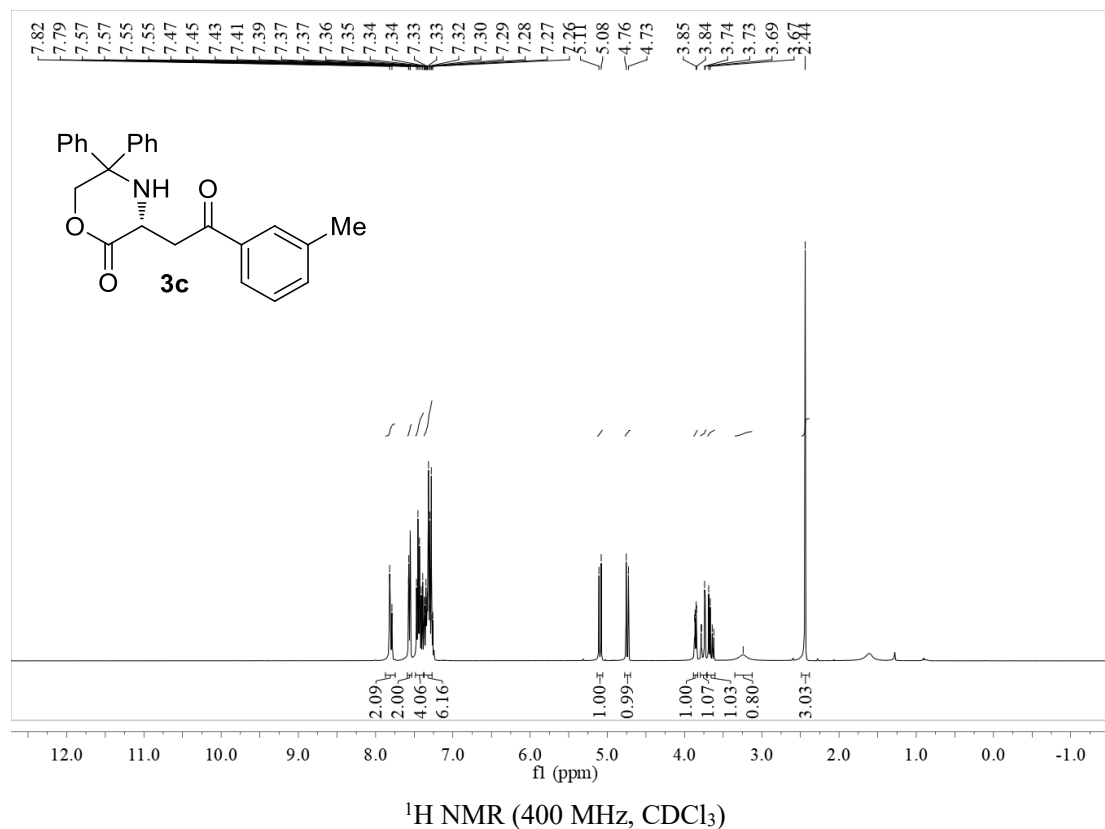
#### (*R*)-3-(2-Oxo-2-phenylethyl)-5,5-diphenylmorpholin-2-one (3a)



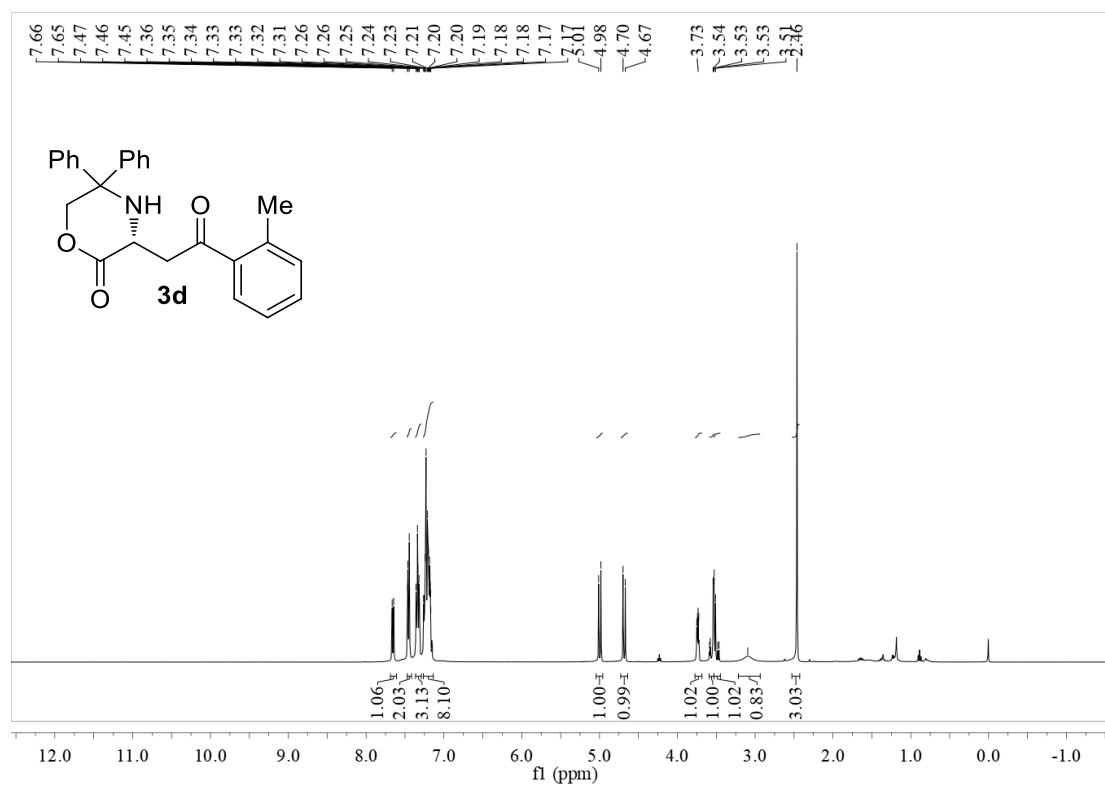
**(R)-3-(2-Oxo-2-(p-tolyl)ethyl)-5,5-diphenylmorpholin-2-one (3b)**



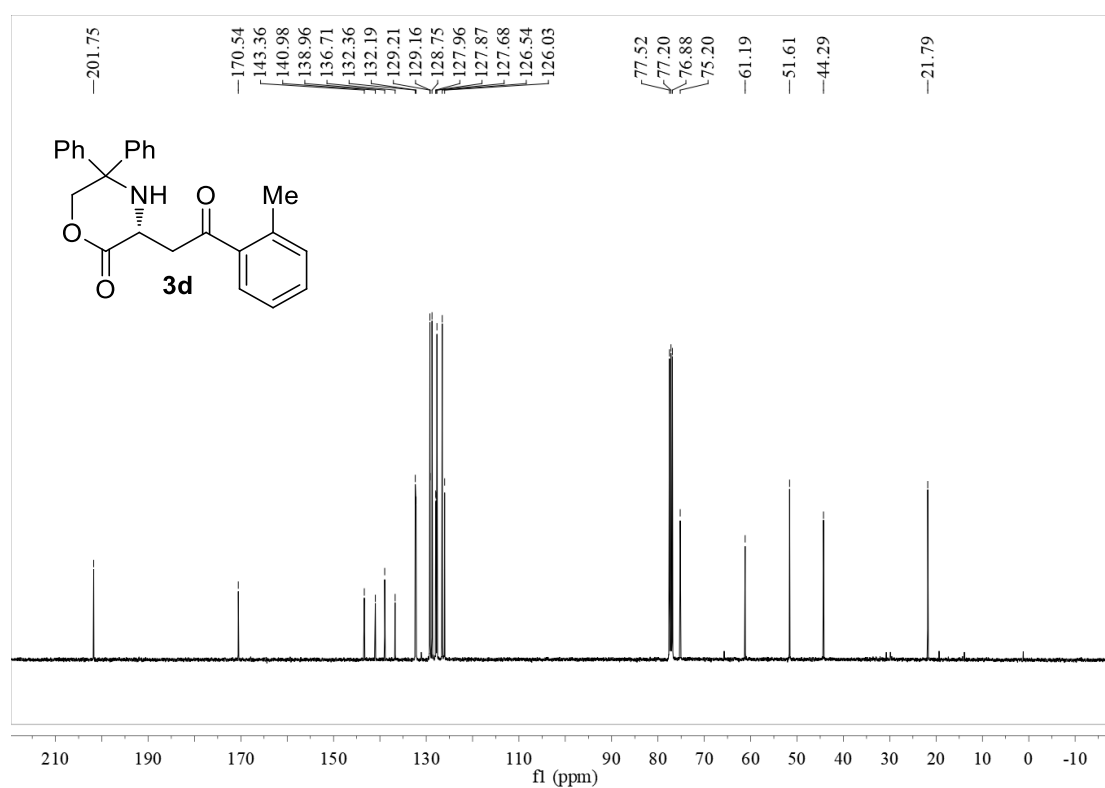
**(R)-3-(2-Oxo-2-(*m*-tolyl)ethyl)-5,5-diphenylmorpholin-2-one (3c)**



**(R)-3-(2-Oxo-2-(*o*-tolyl)ethyl)-5,5-diphenylmorpholin-2-one (3d)**

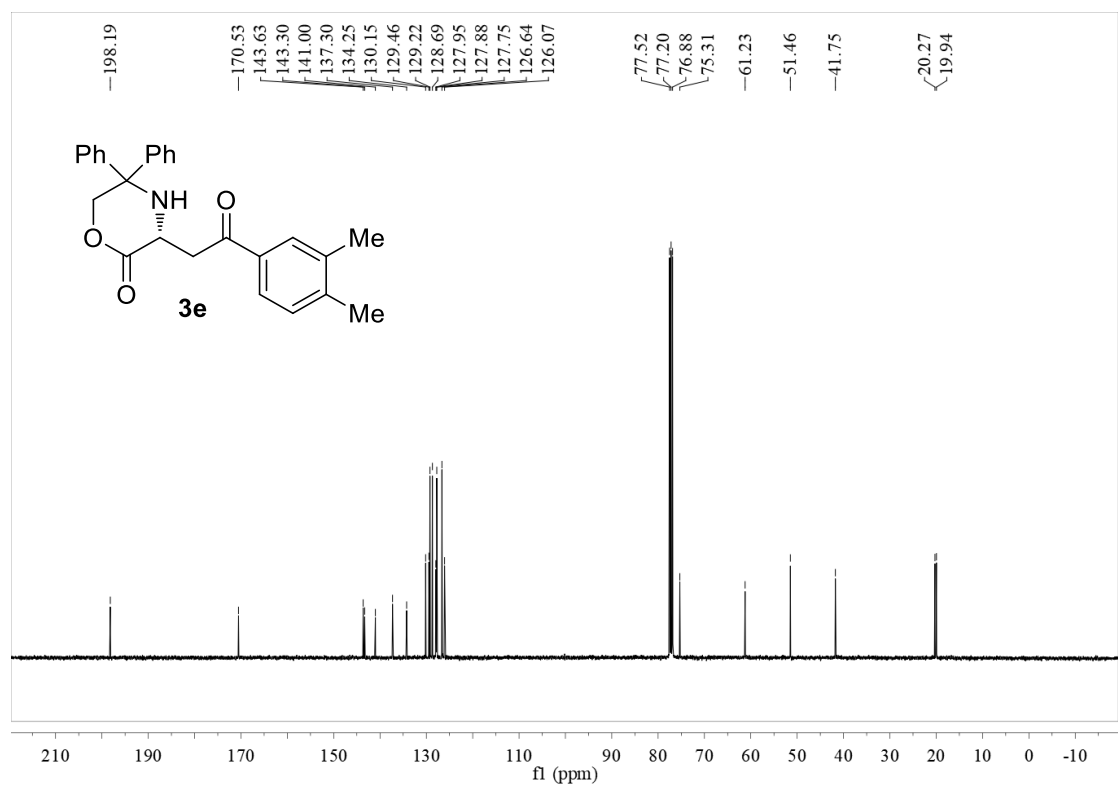
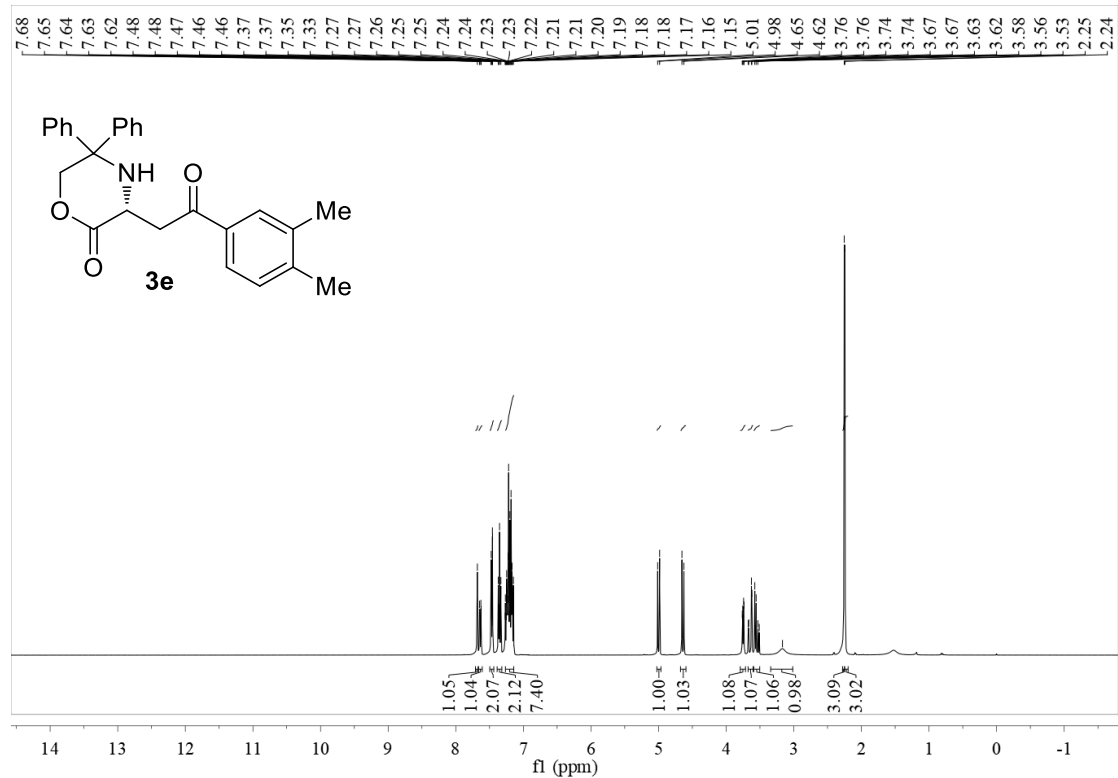


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

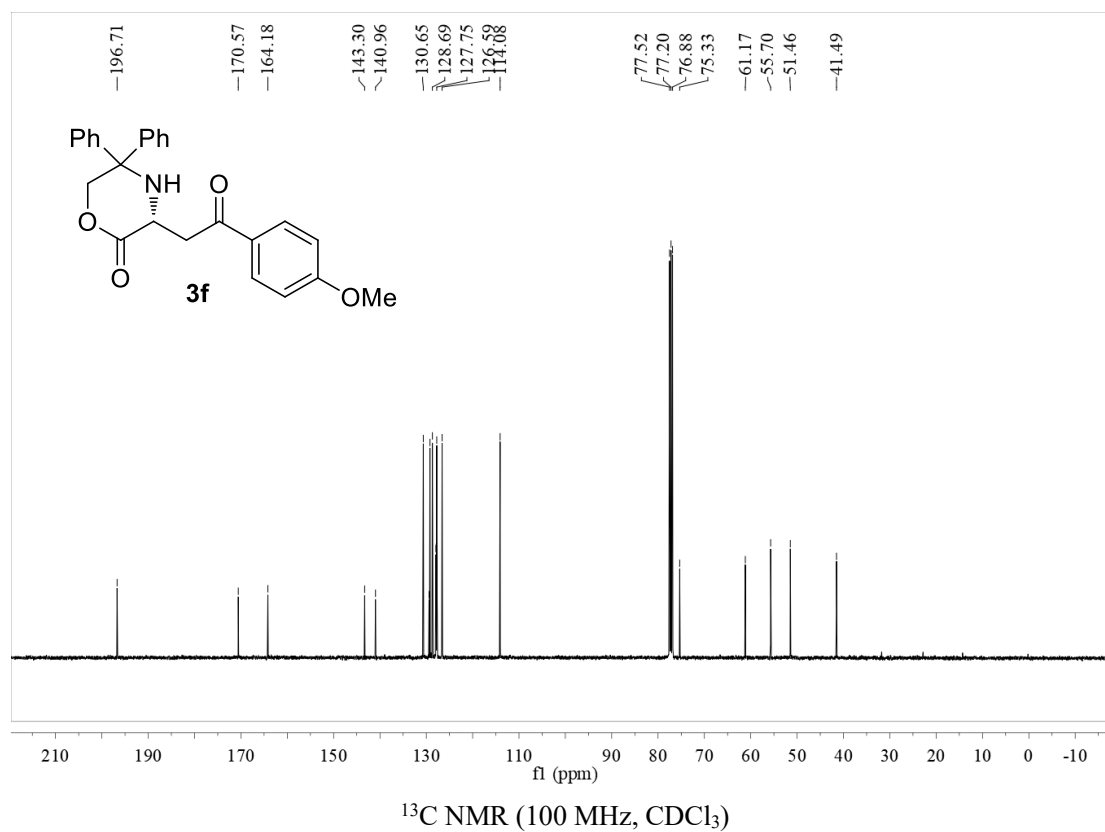
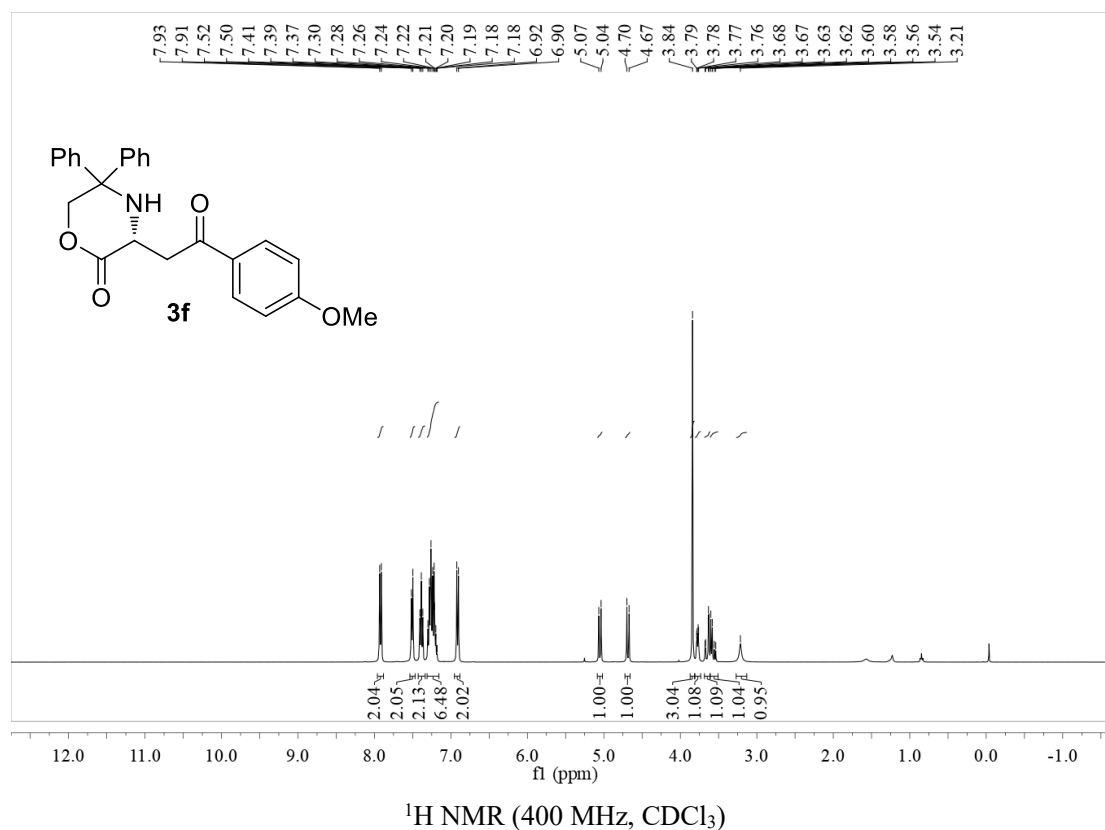


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

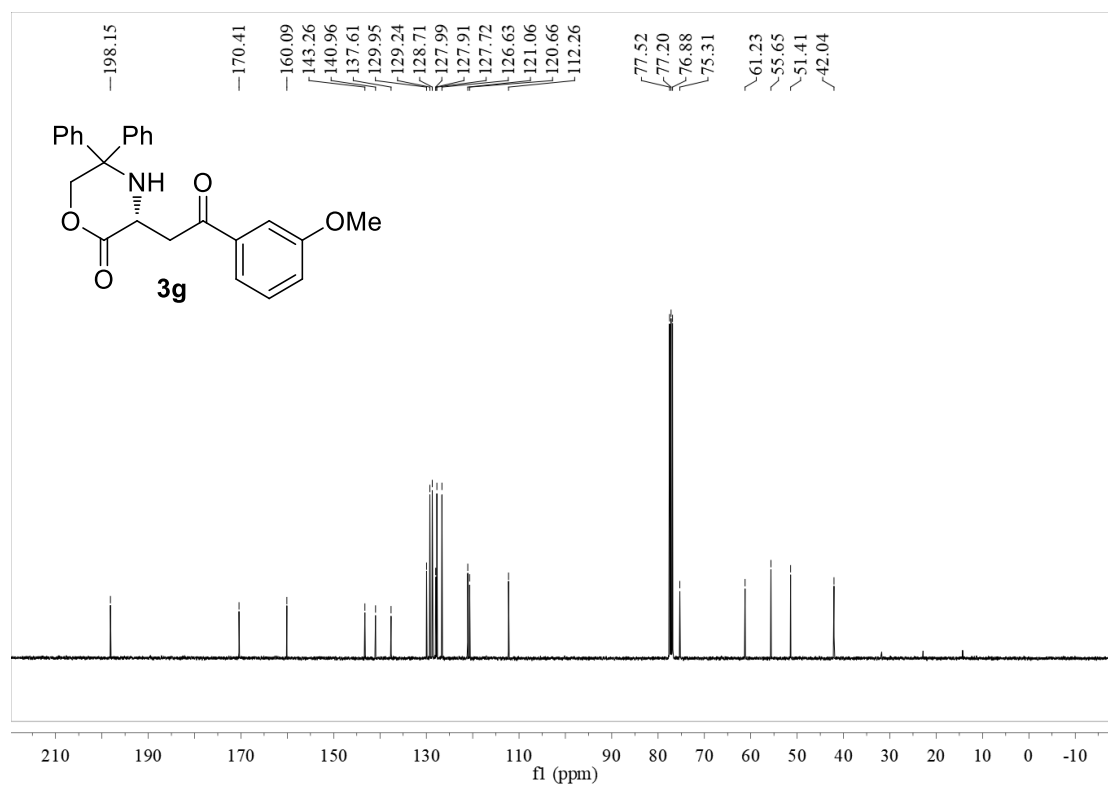
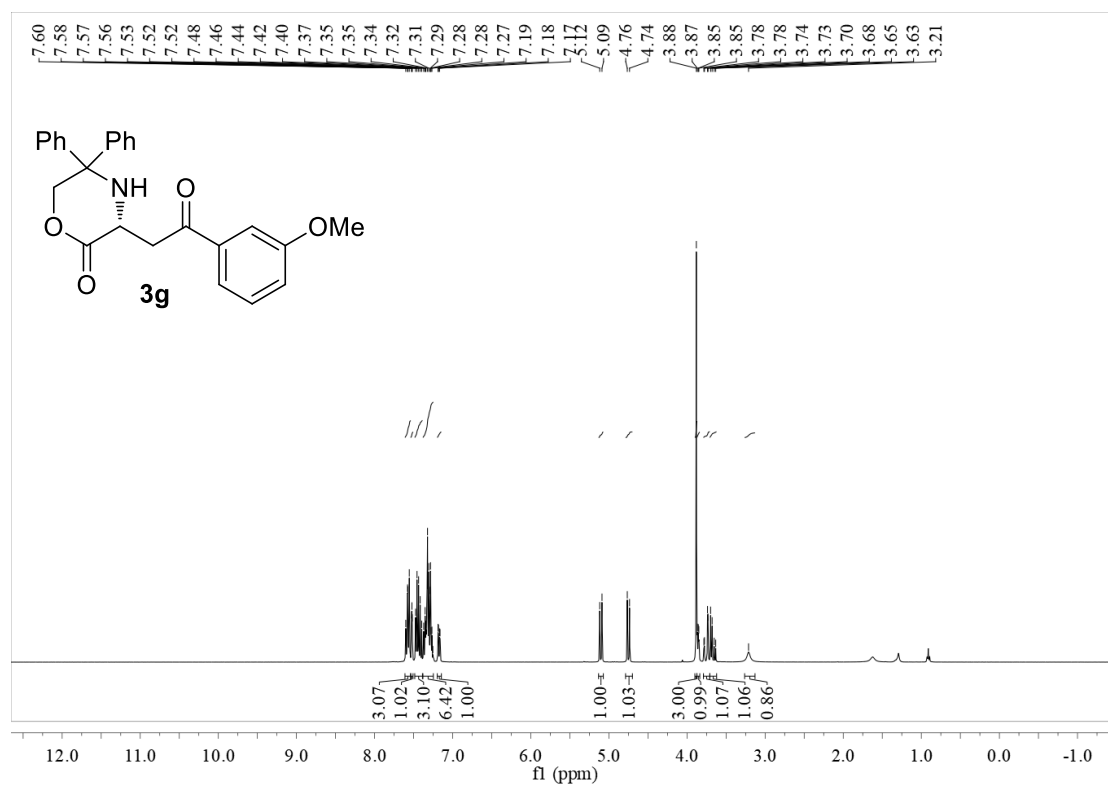
**(R)-3-(2-(3,4-Dimethylphenyl)-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3e)**



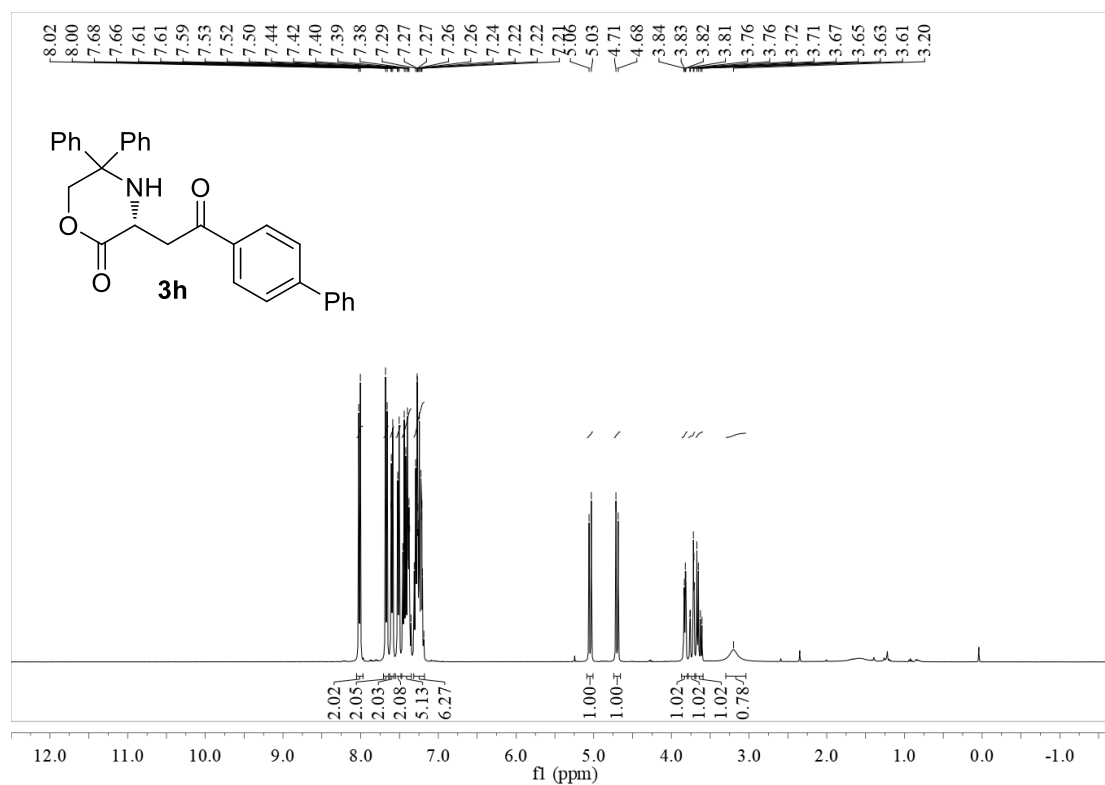
**(R)-3-(2-(4-Methoxyphenyl)-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3f)**



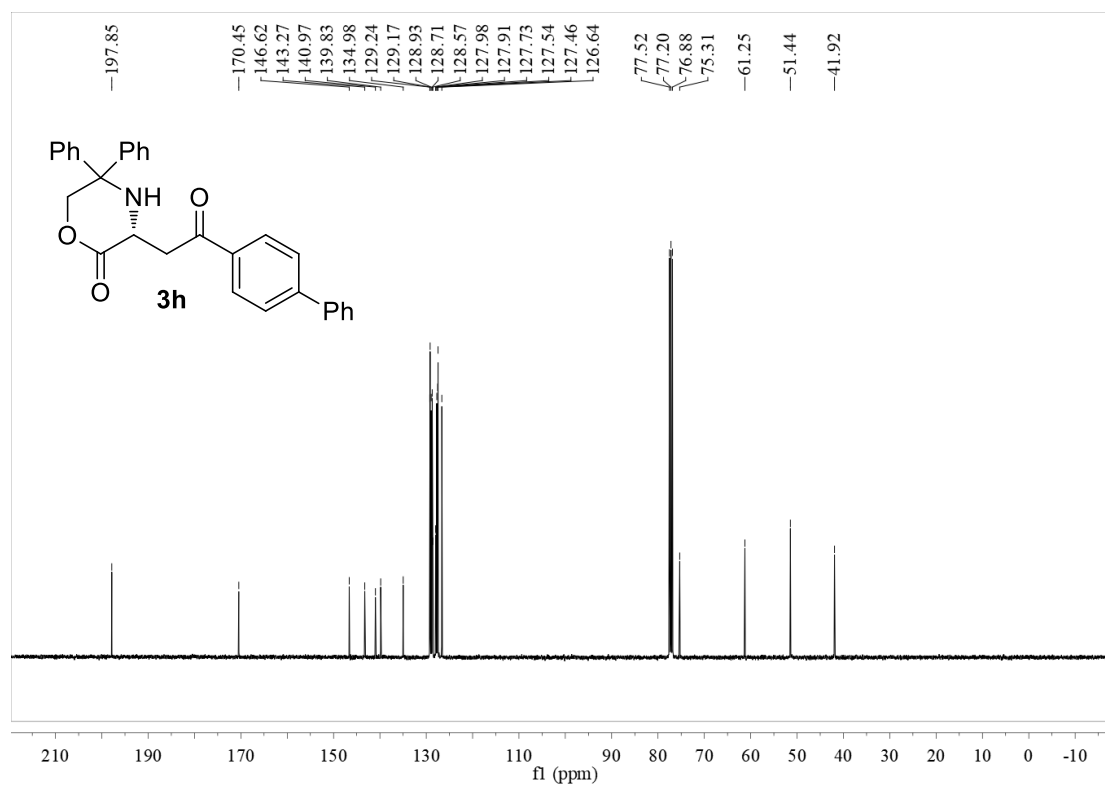
**(R)-3-(2-(3-Methoxyphenyl)-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3g)**



**(R)-3-(2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3h)**

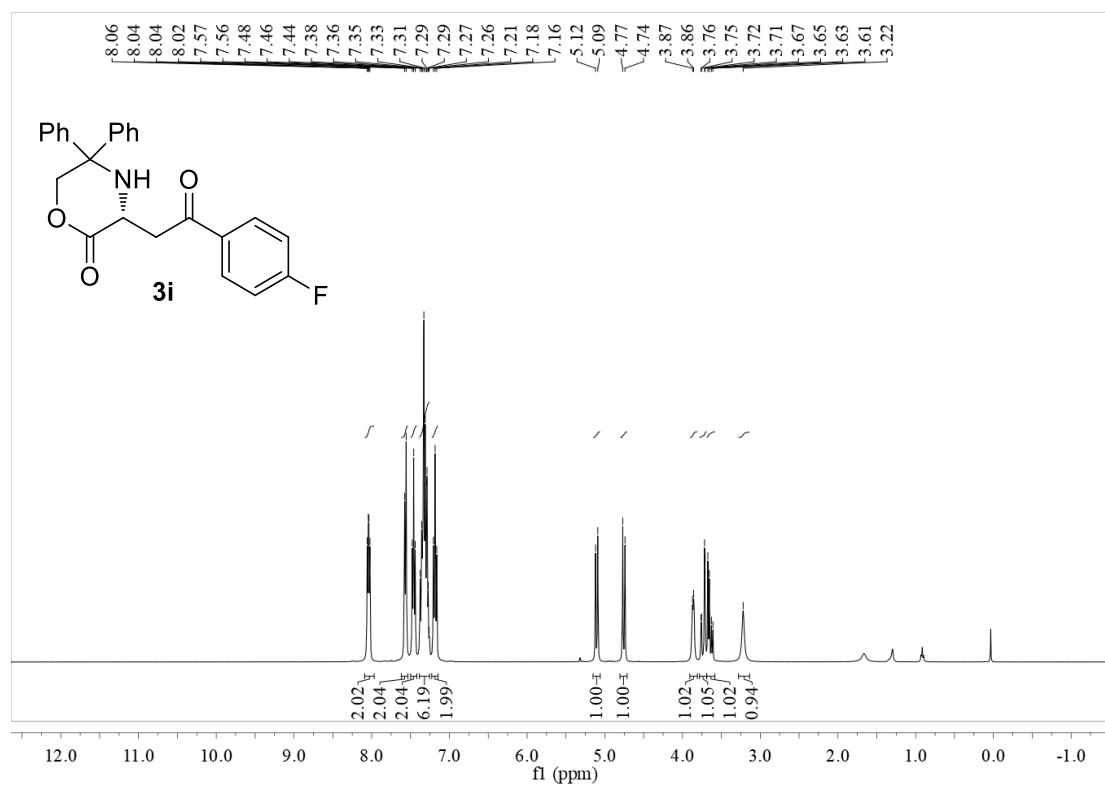


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

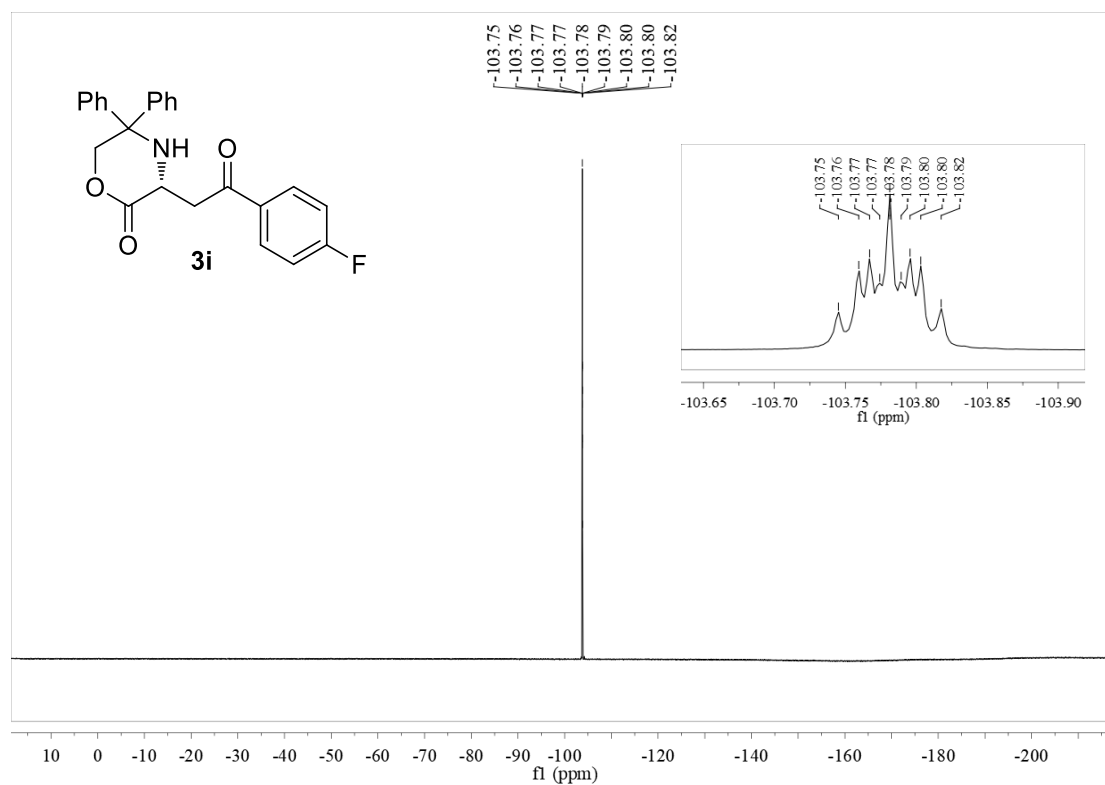


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

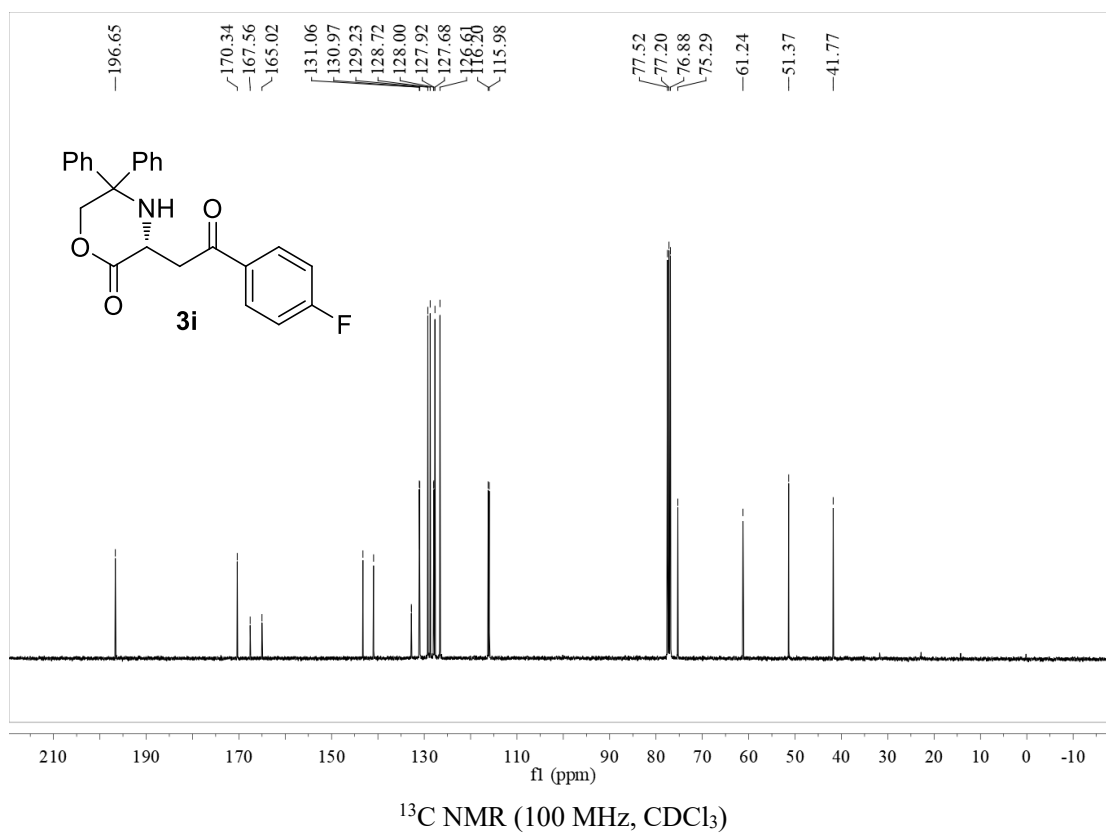
**(R)-3-(2-(4-Fluorophenyl)-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3i)**



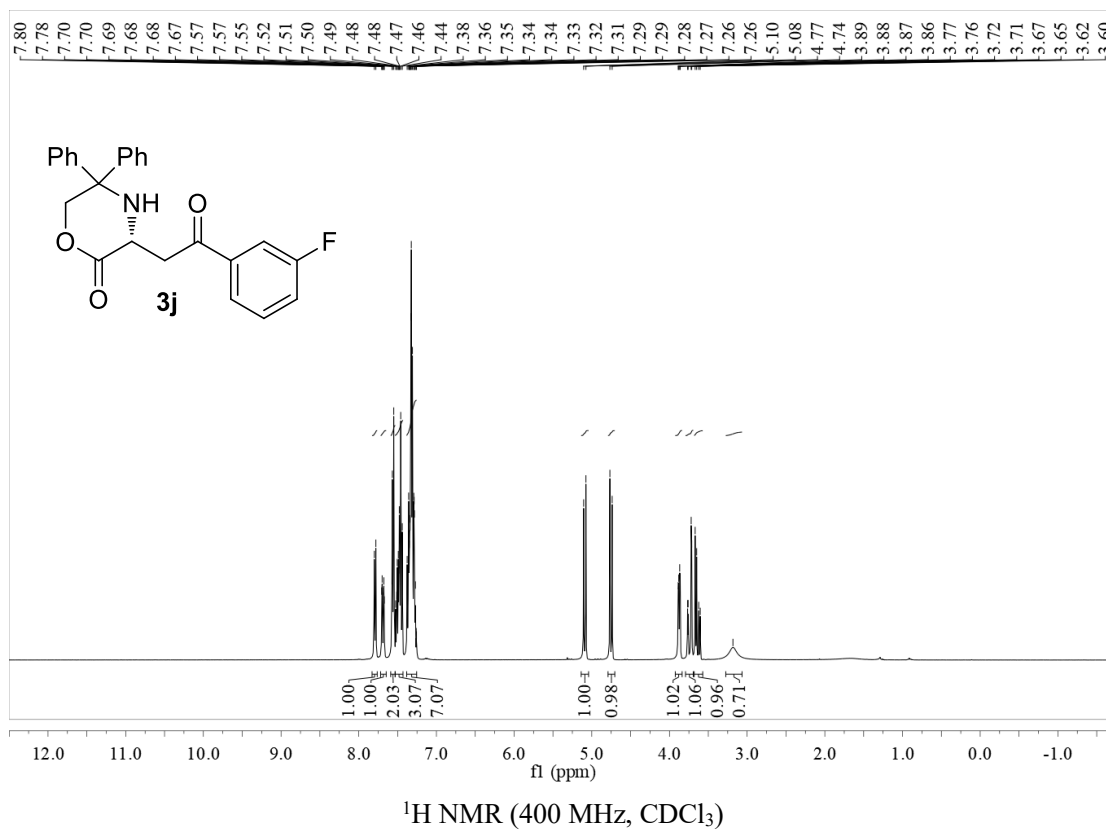
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

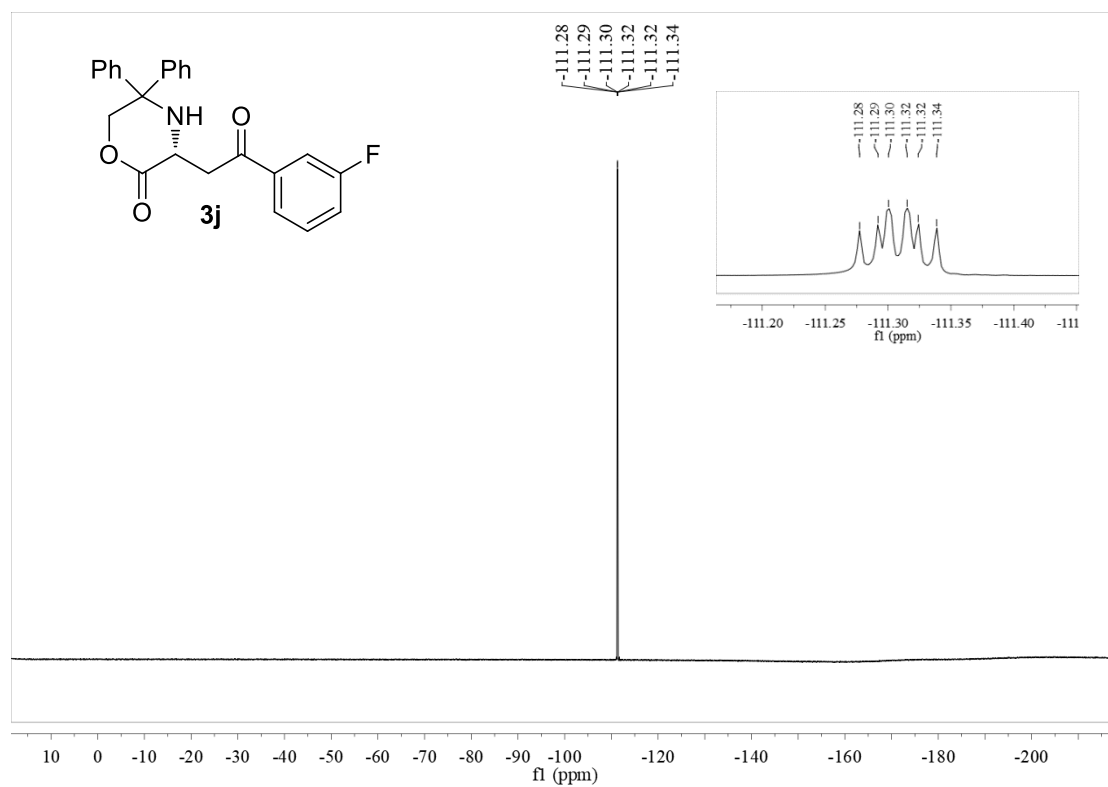


**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**

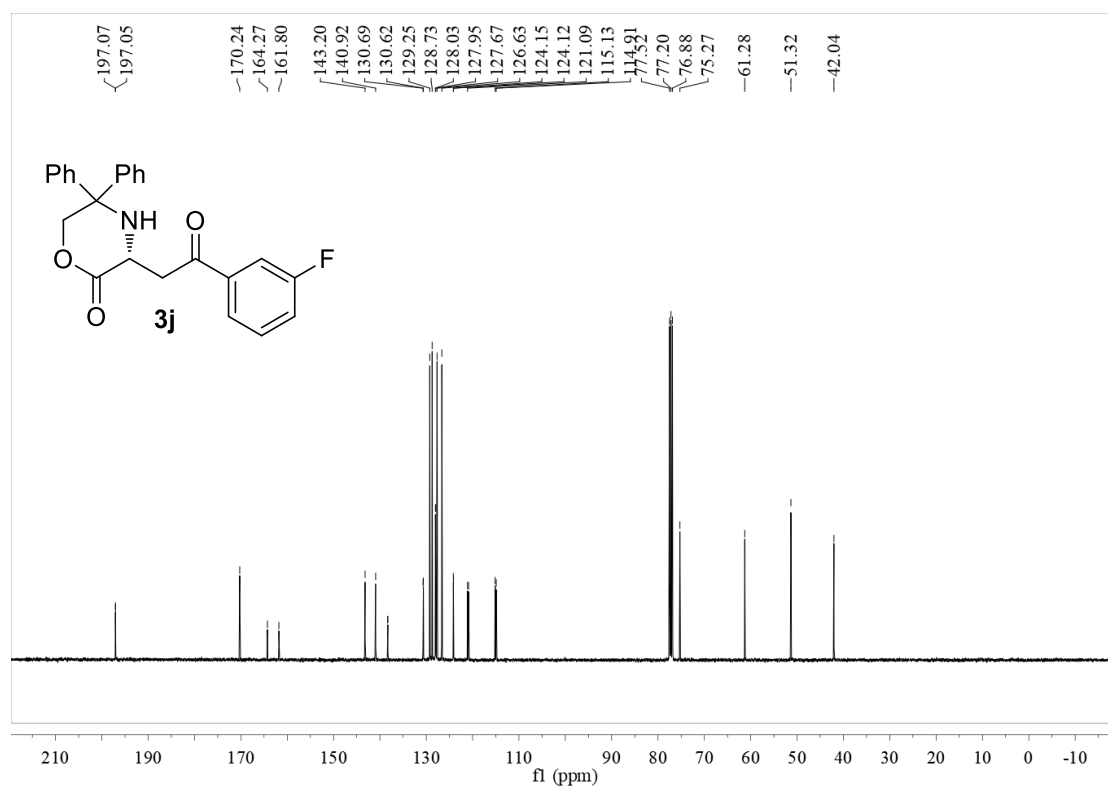


**(R)-3-(2-(3-Fluorophenyl)-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3j)**



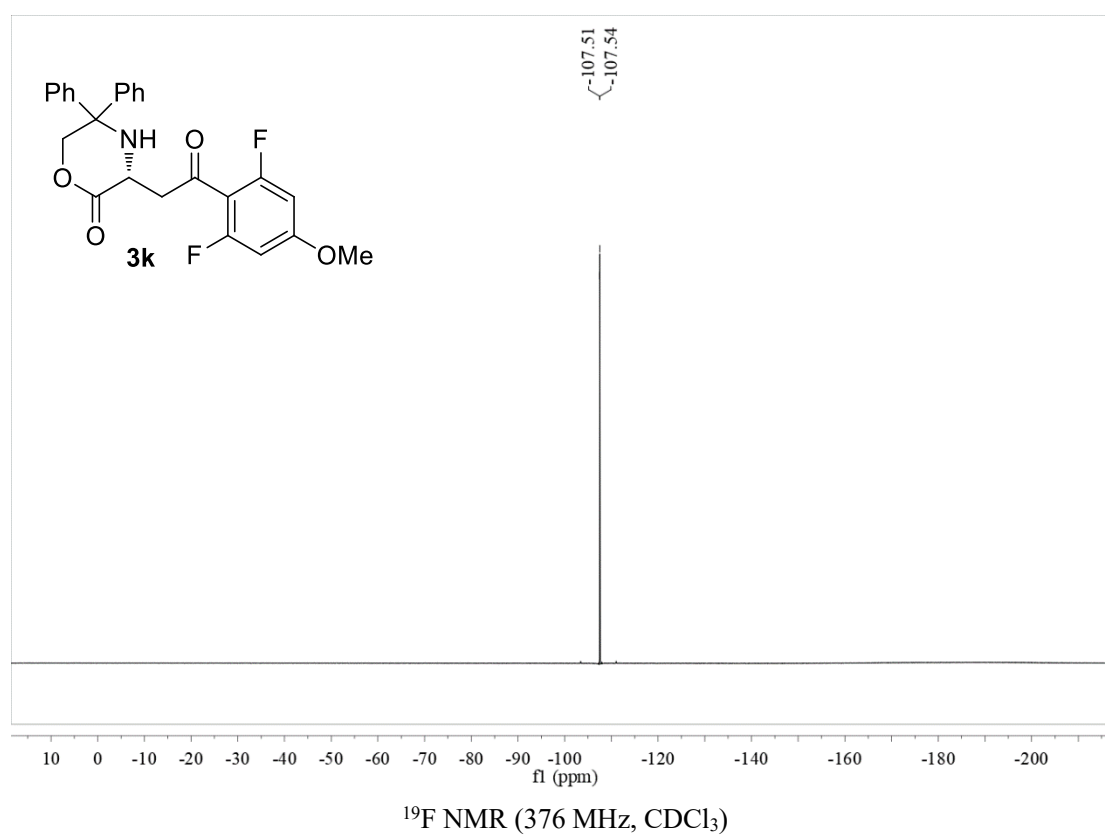
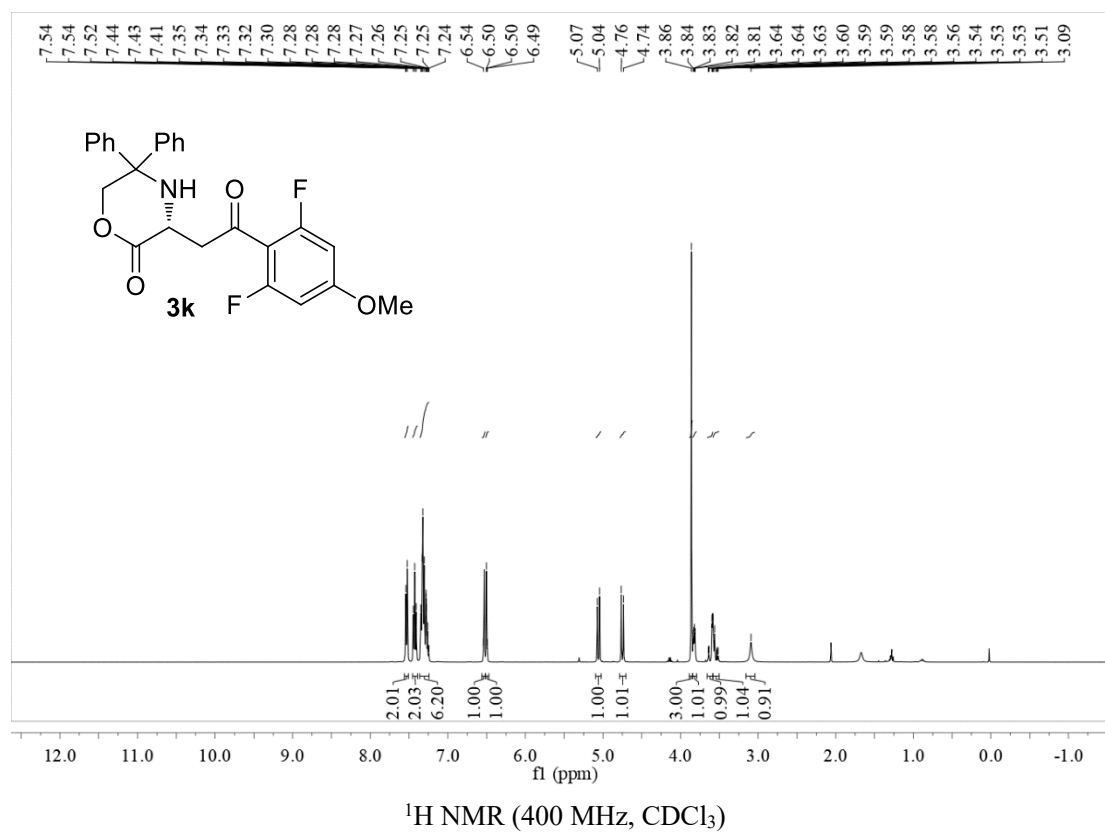


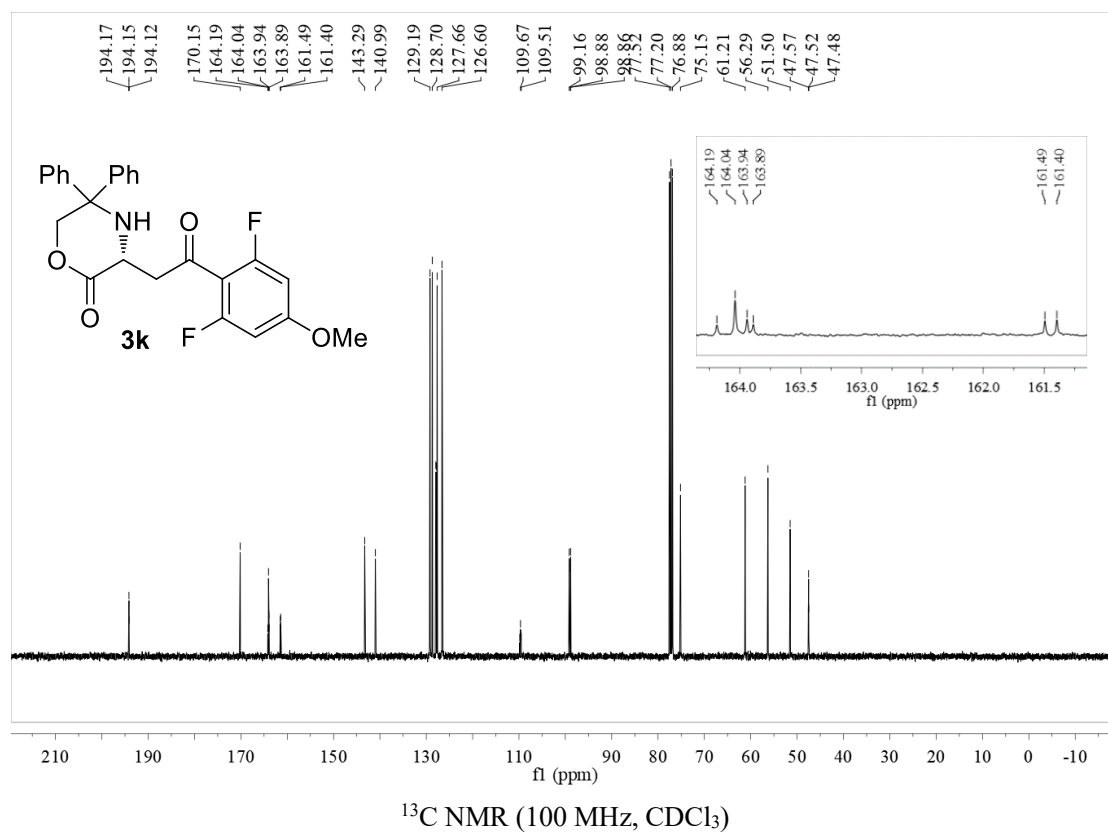
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



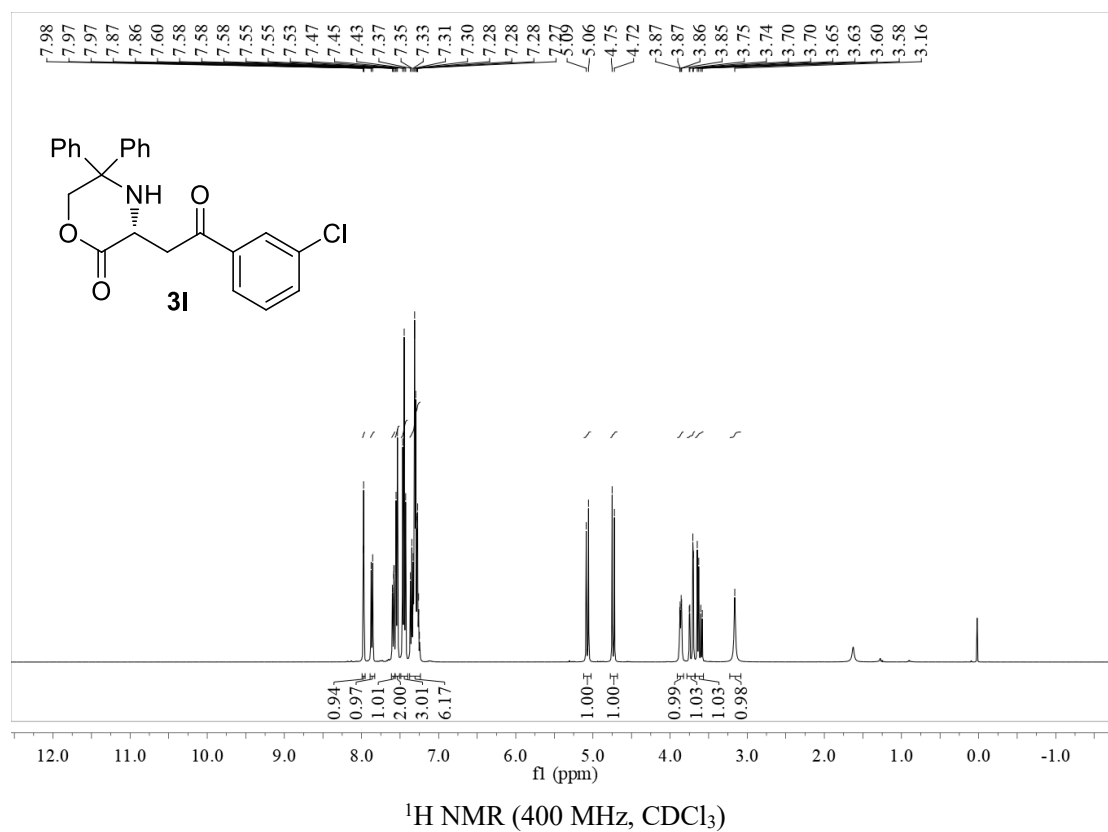
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

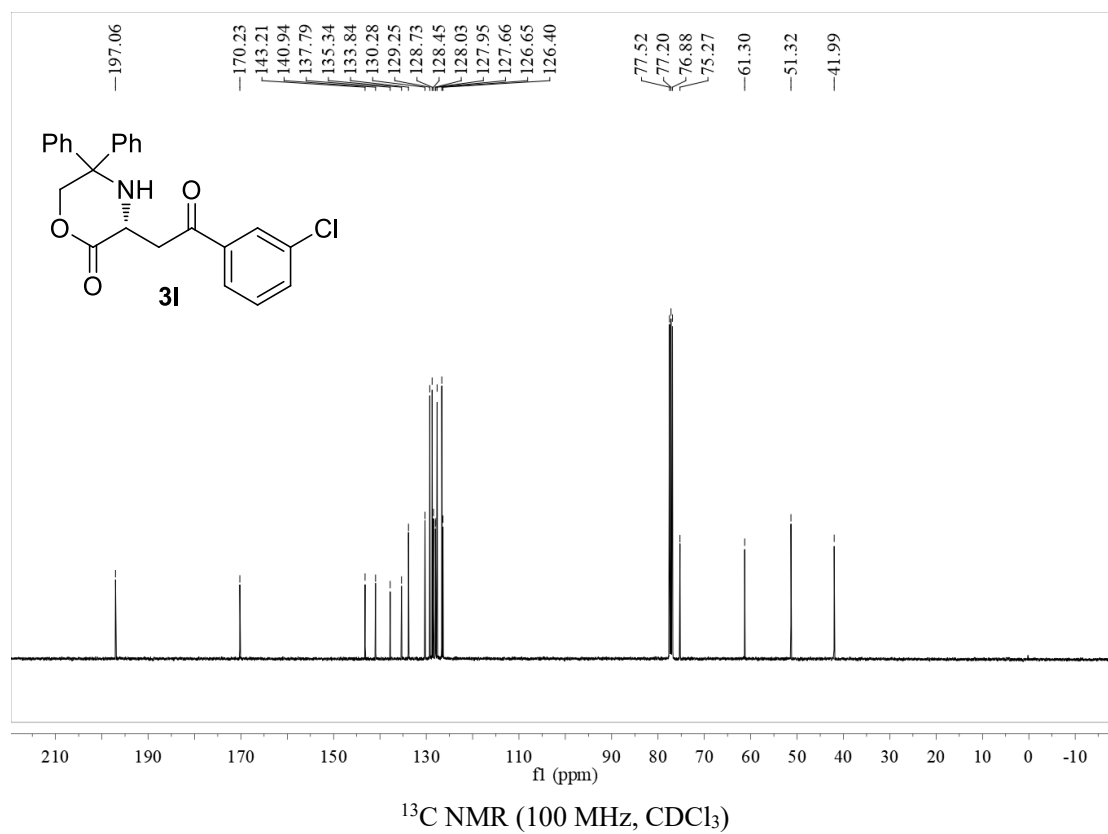
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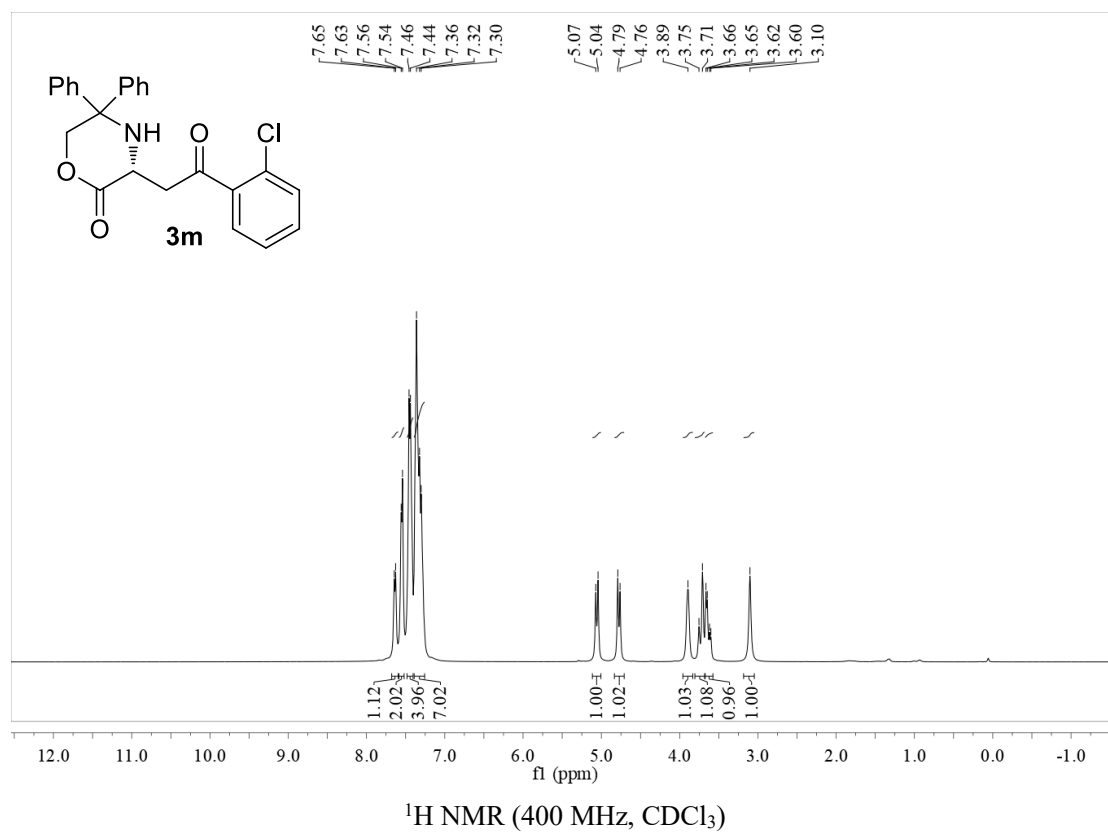


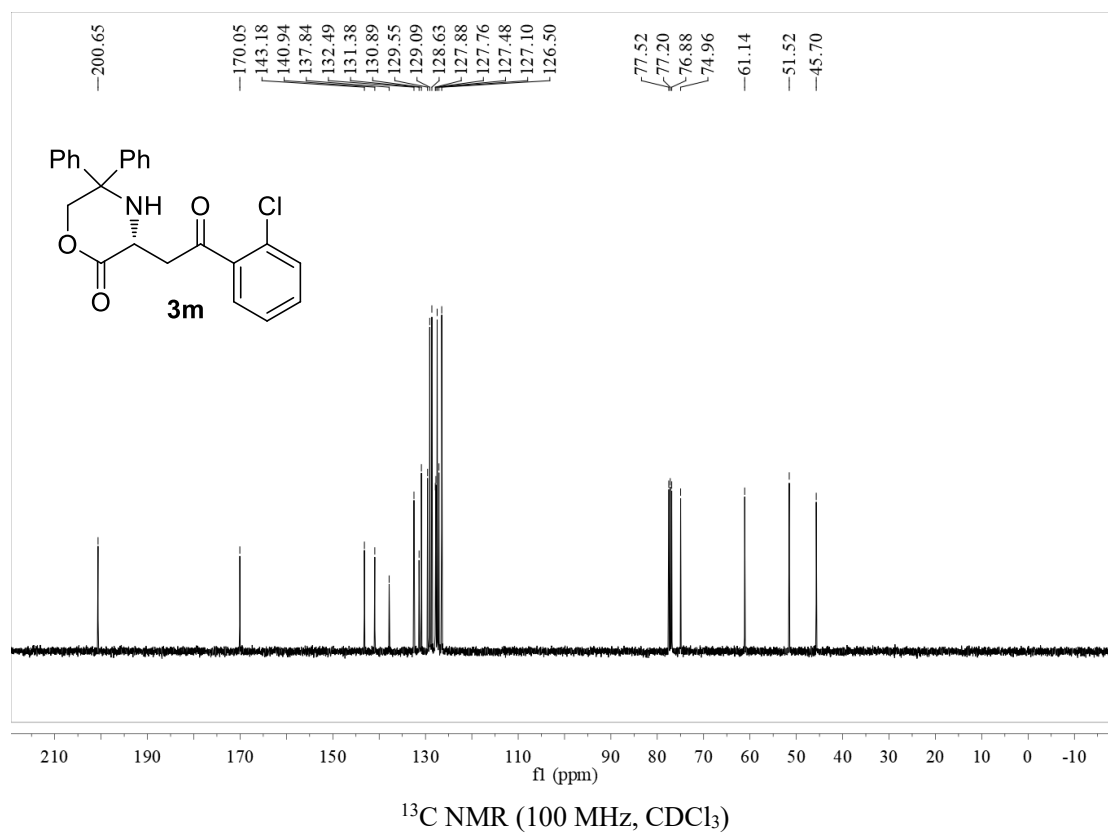
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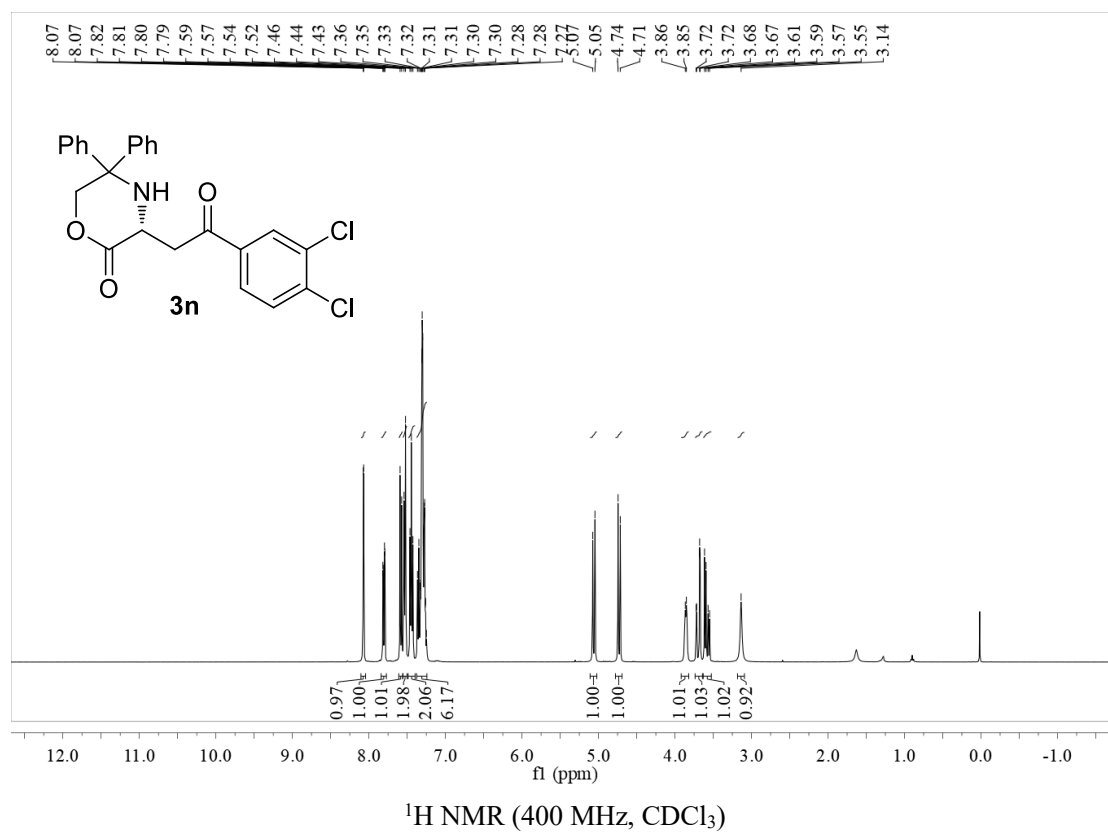


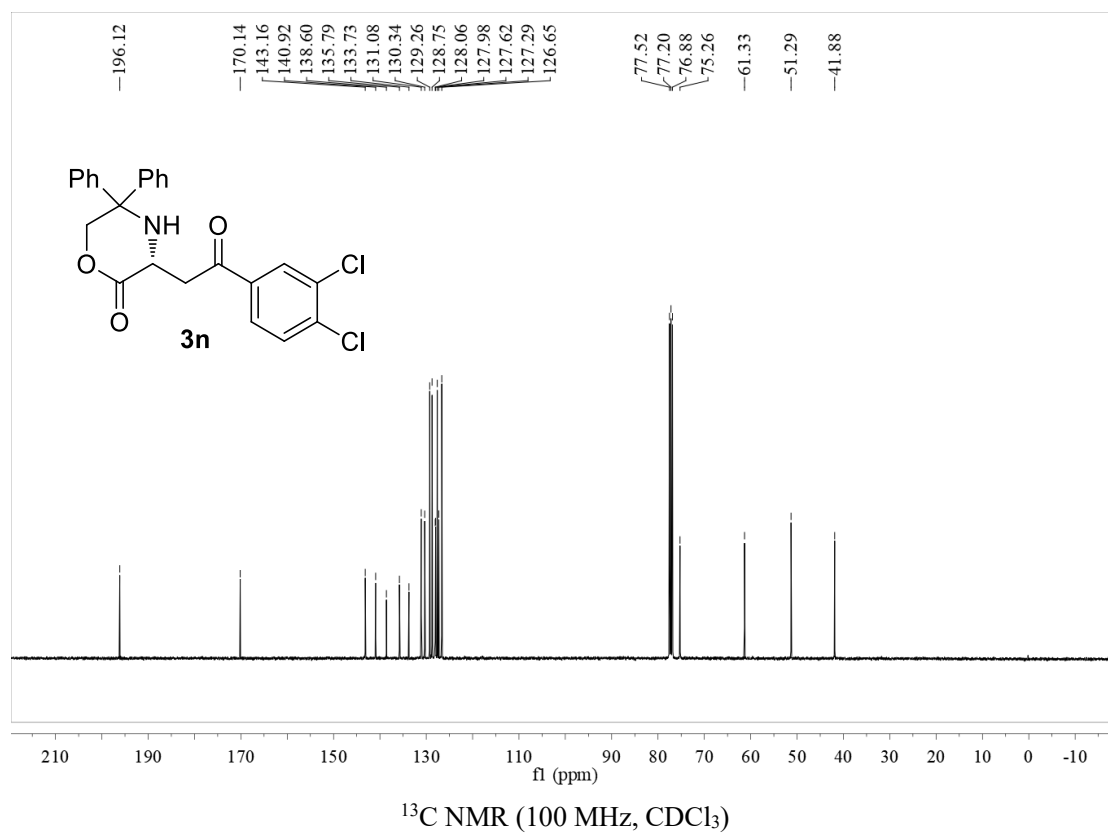
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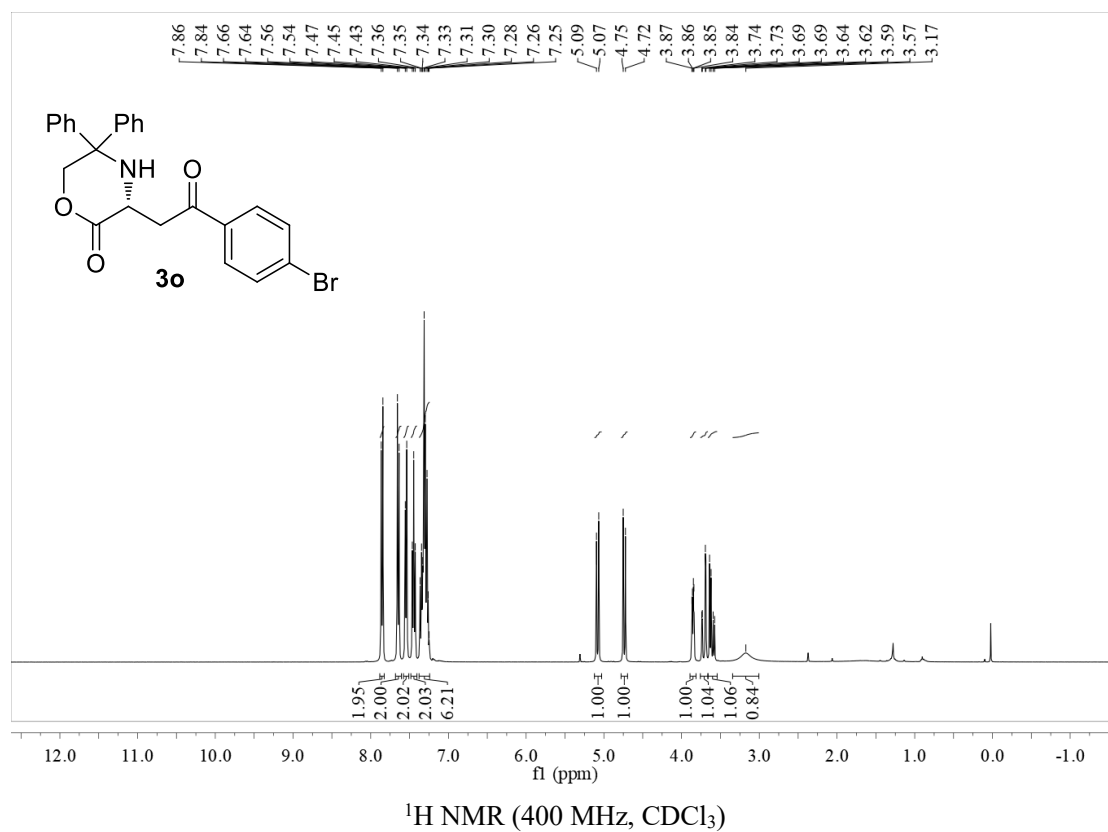


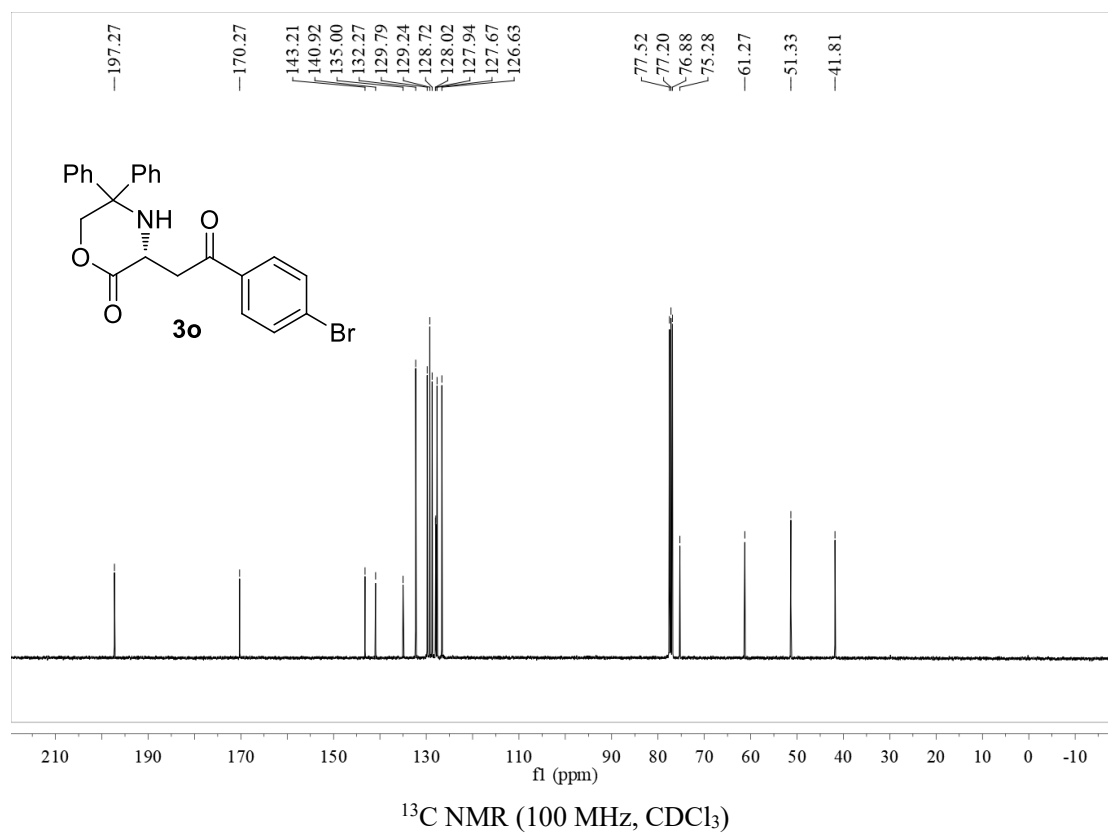
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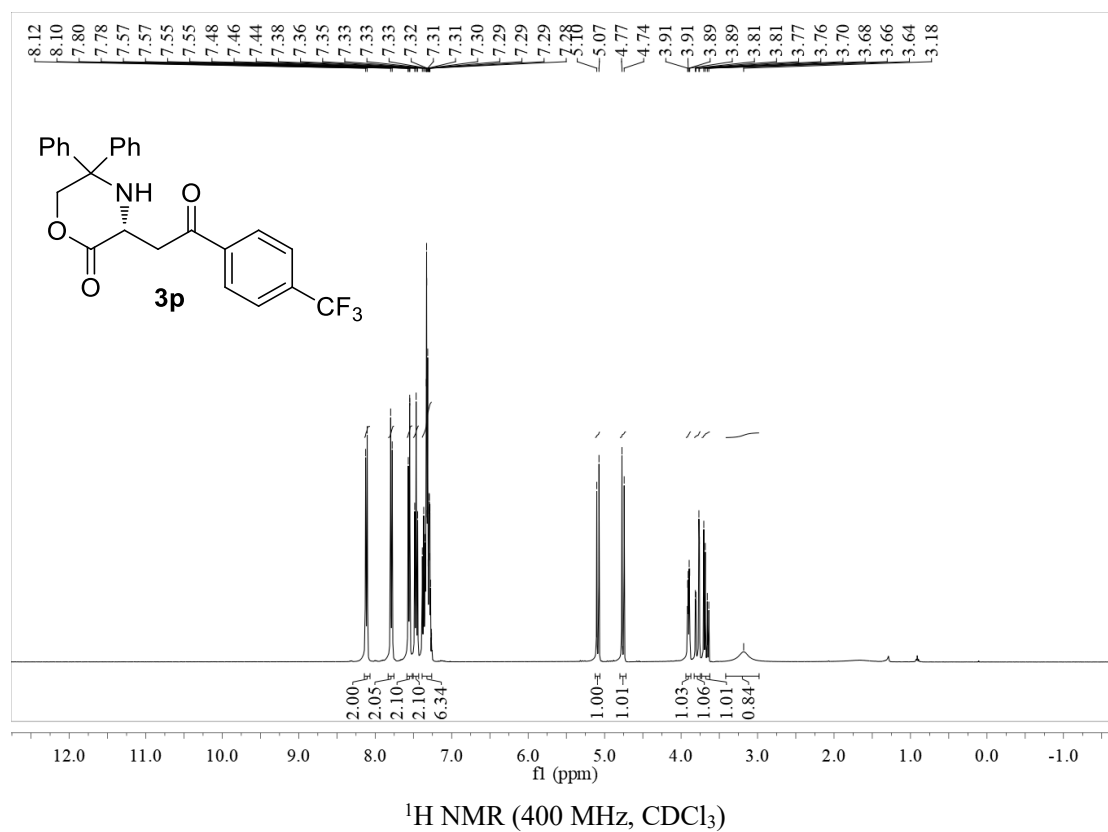


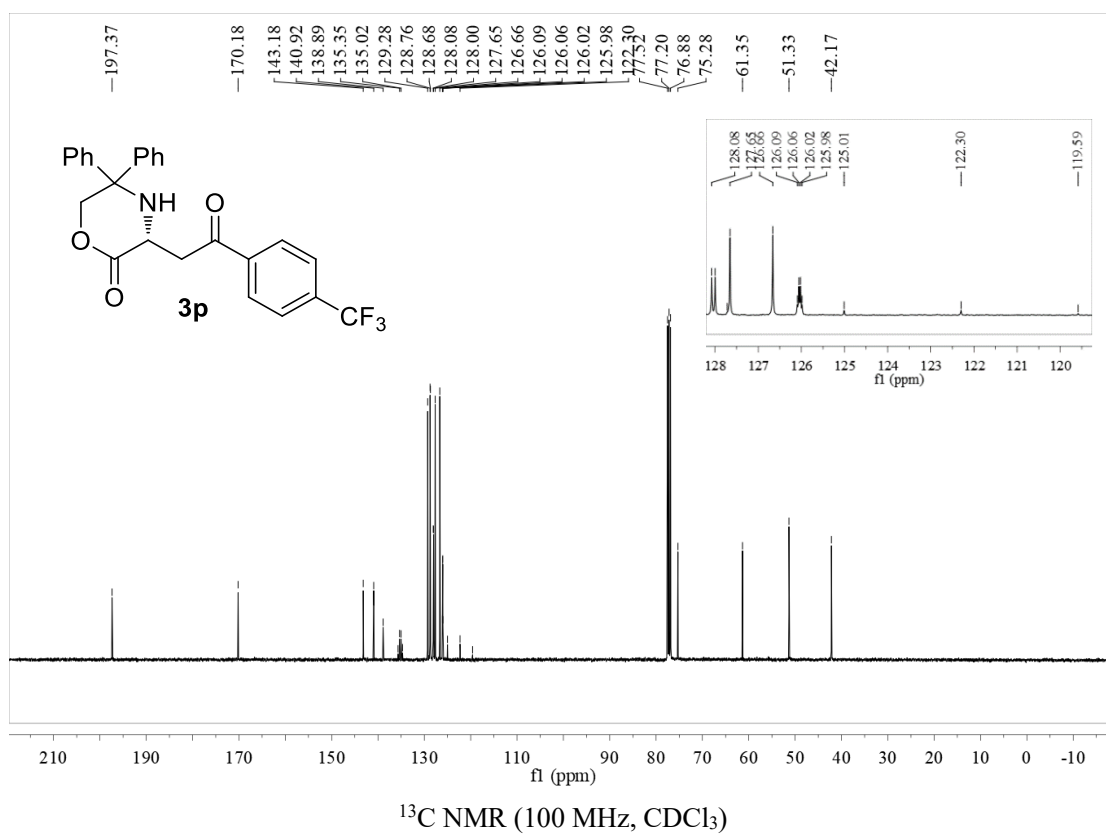
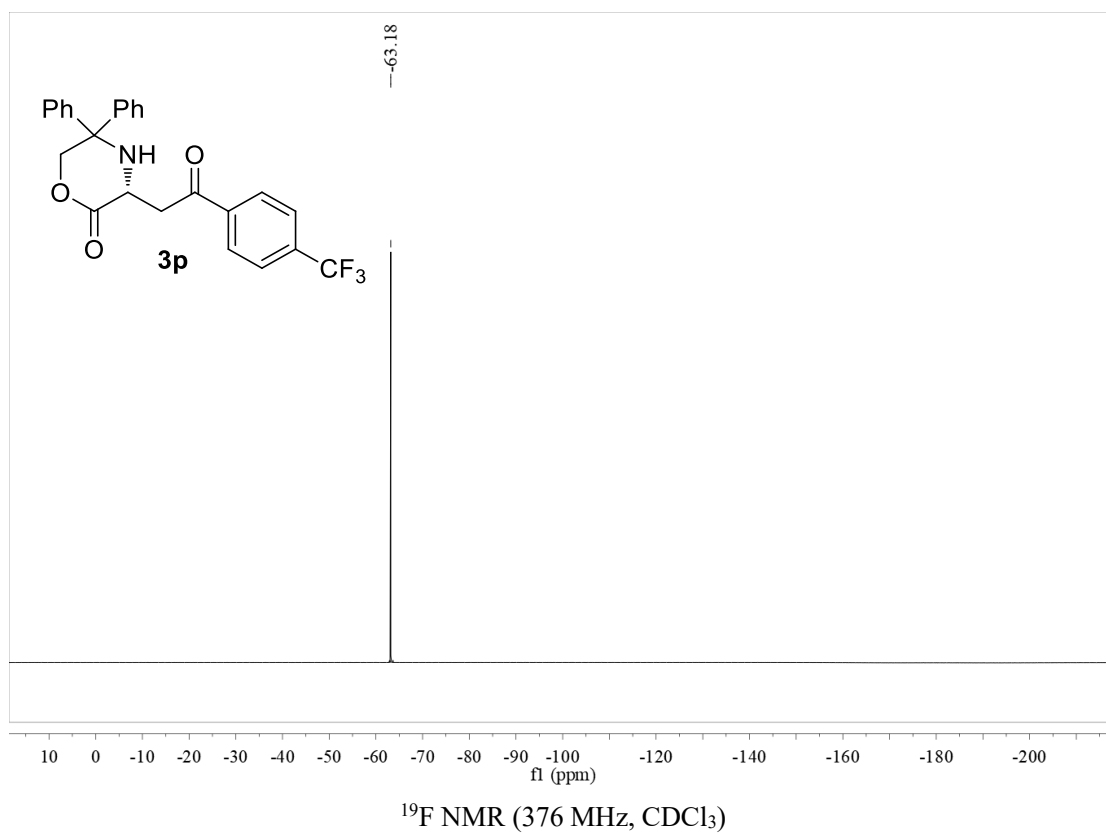
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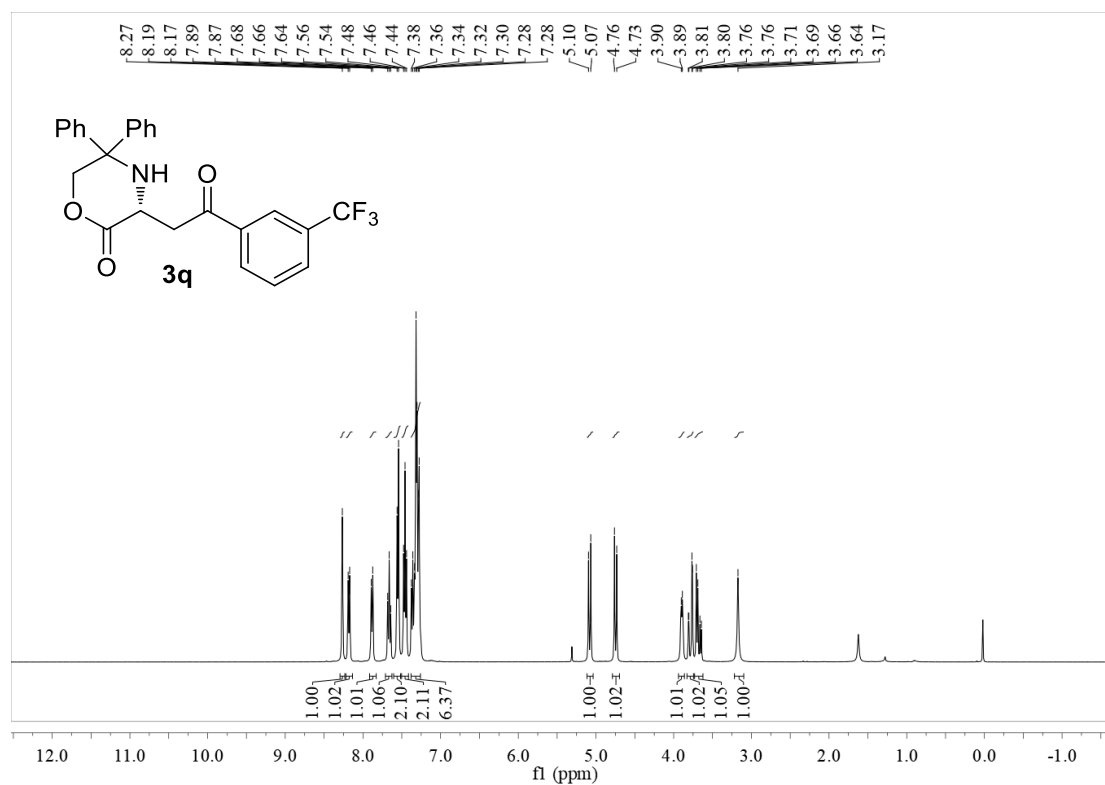


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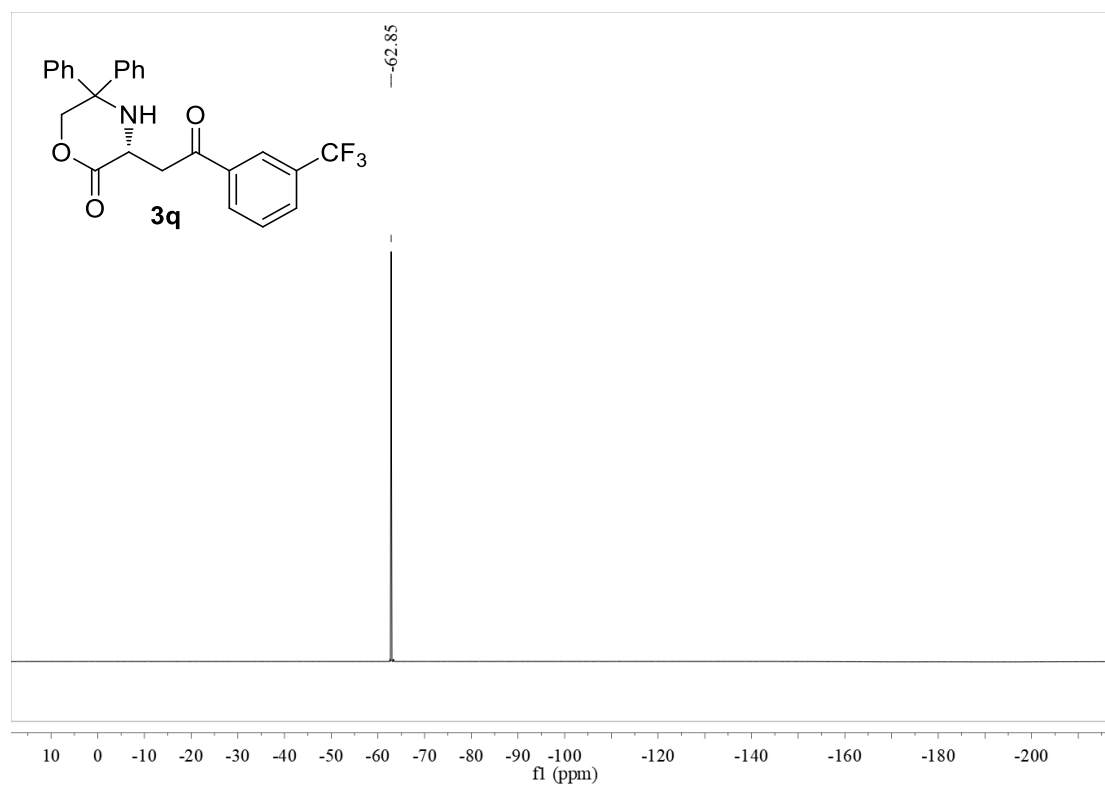




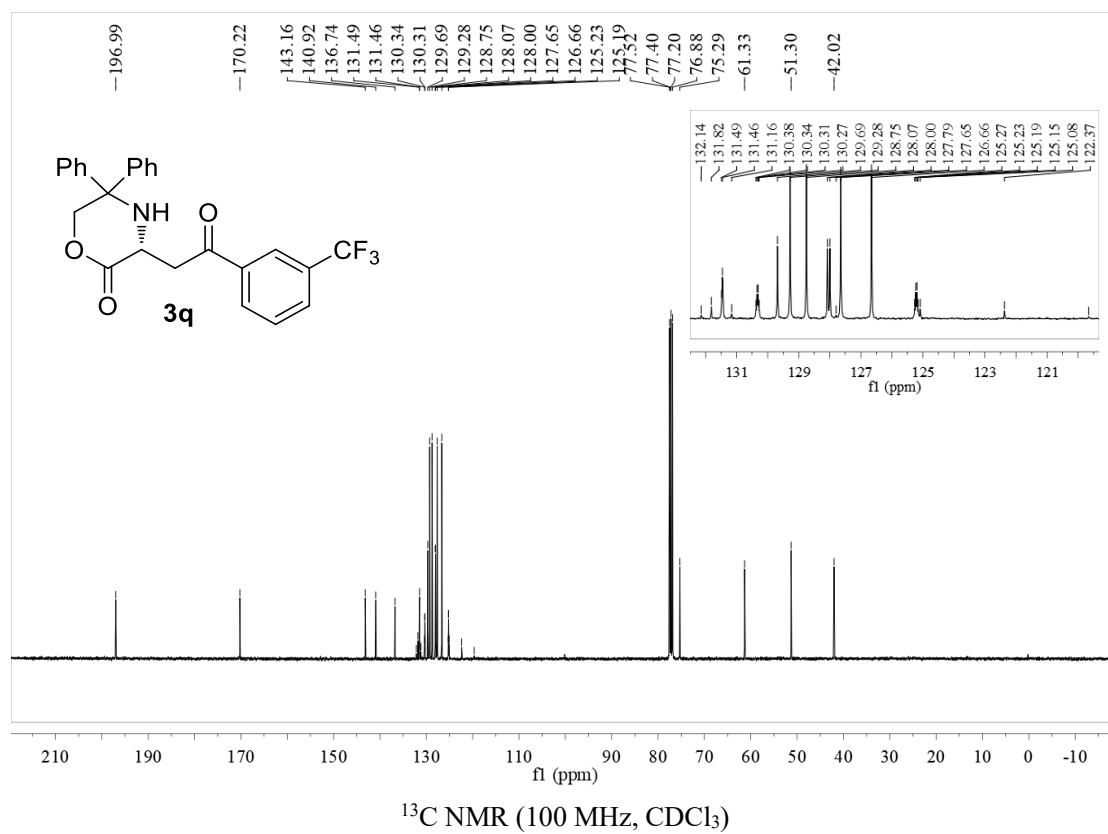
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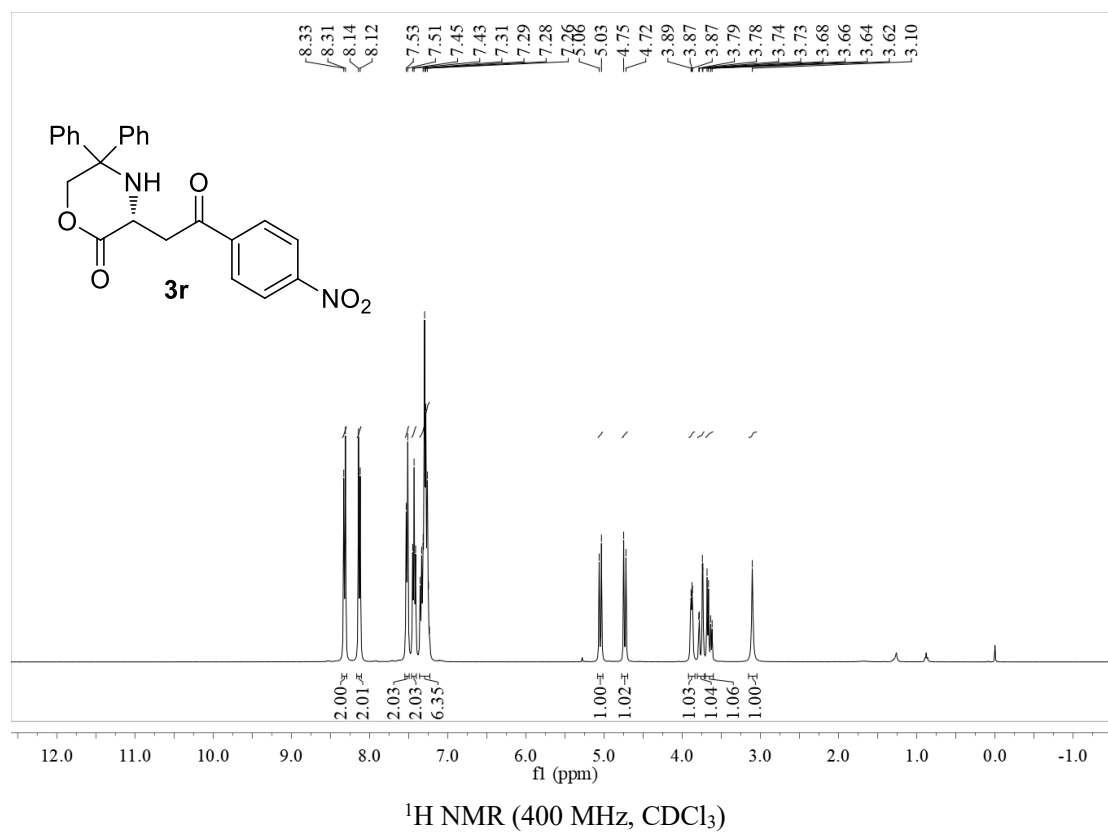
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

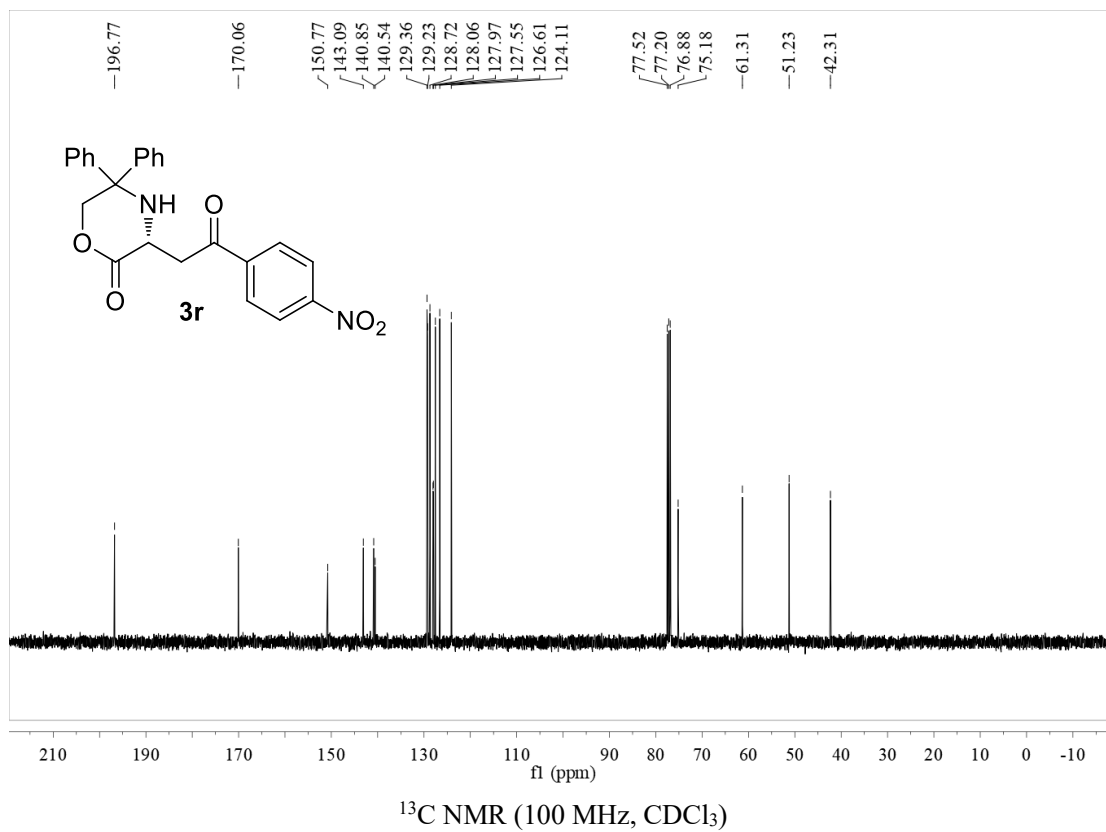


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

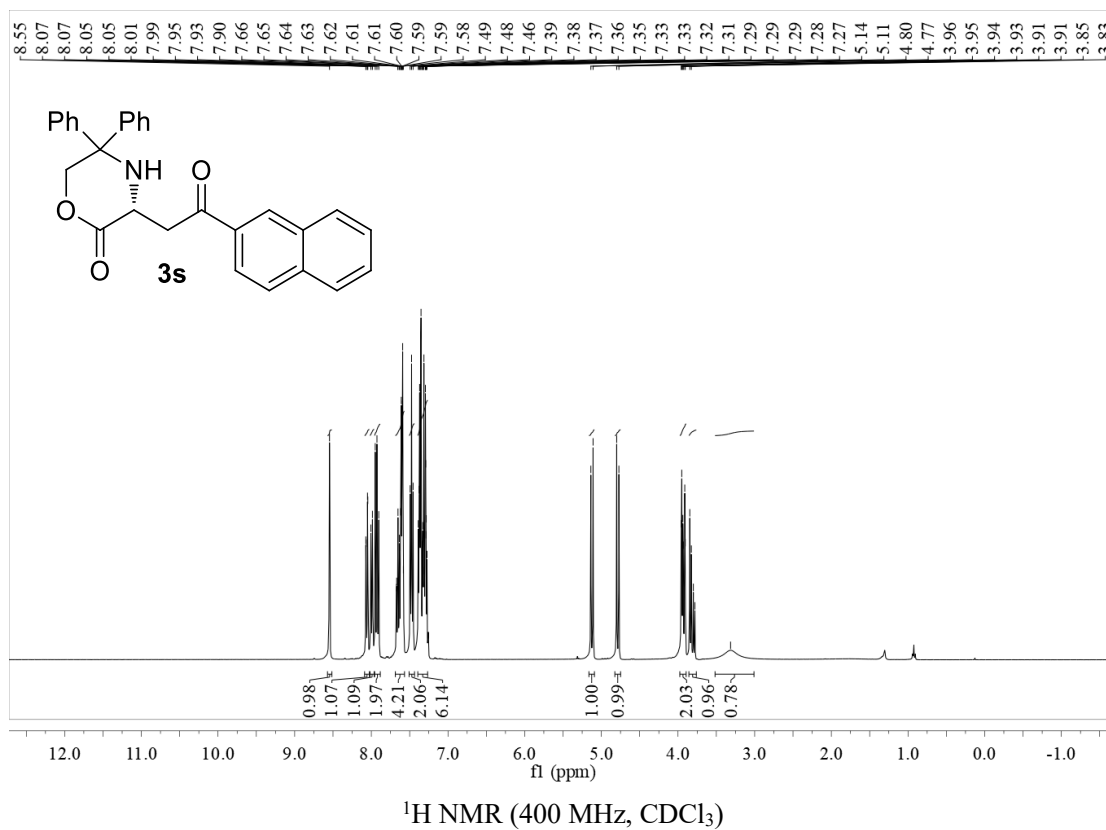


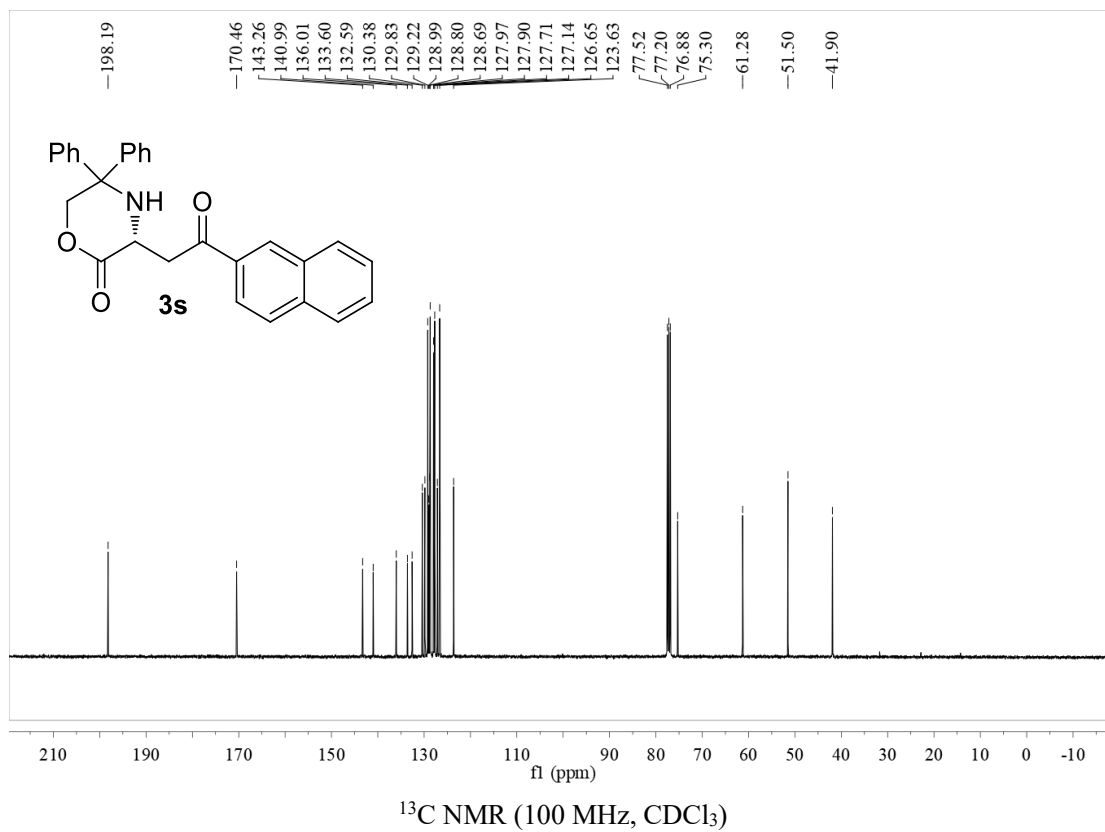
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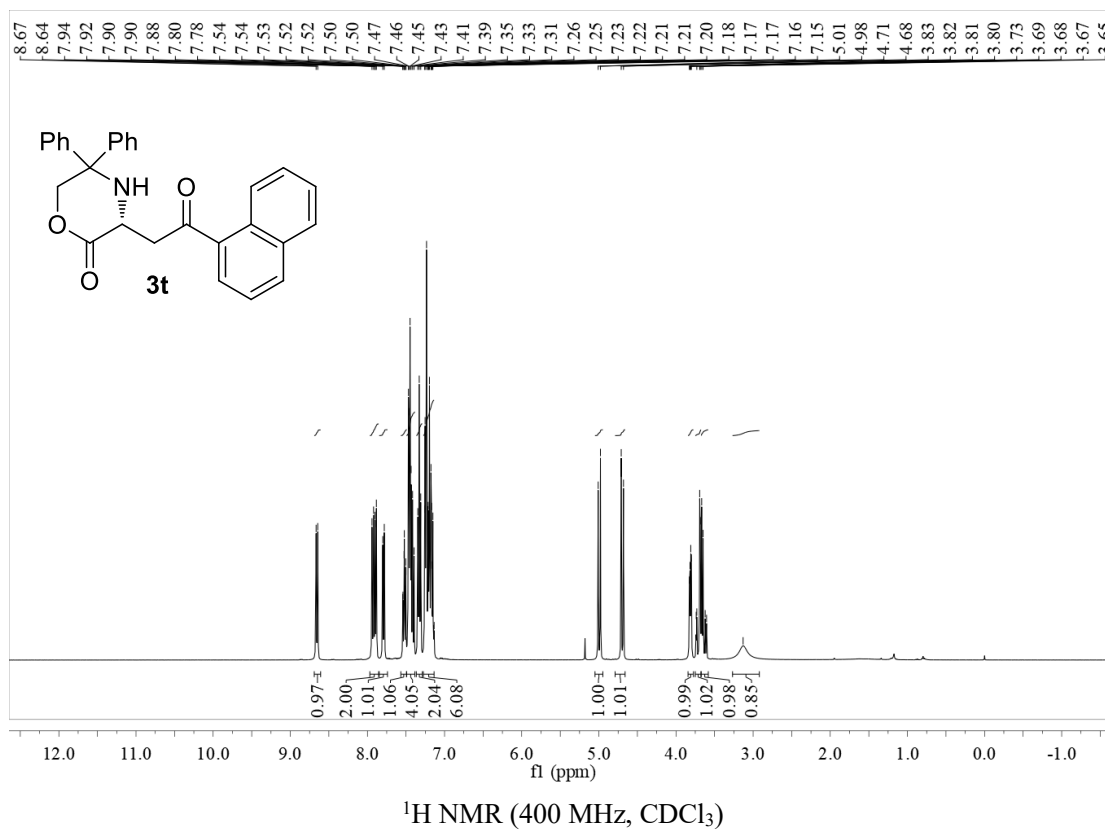


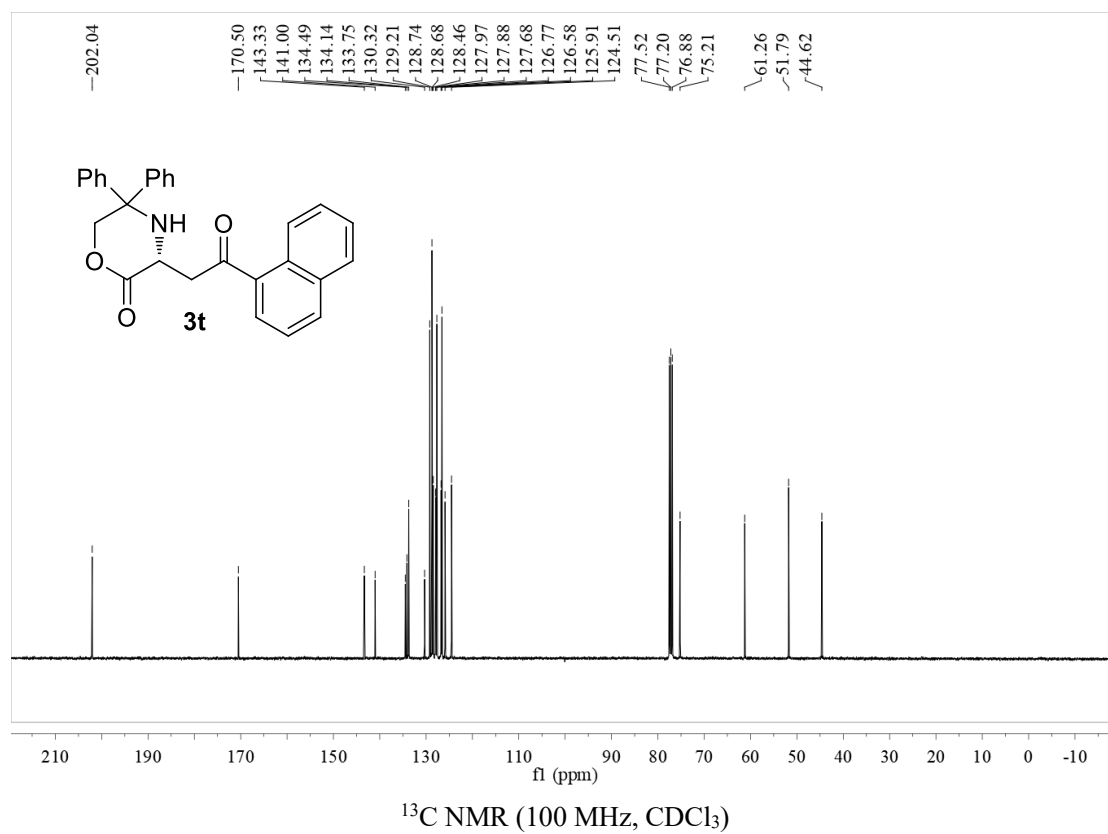
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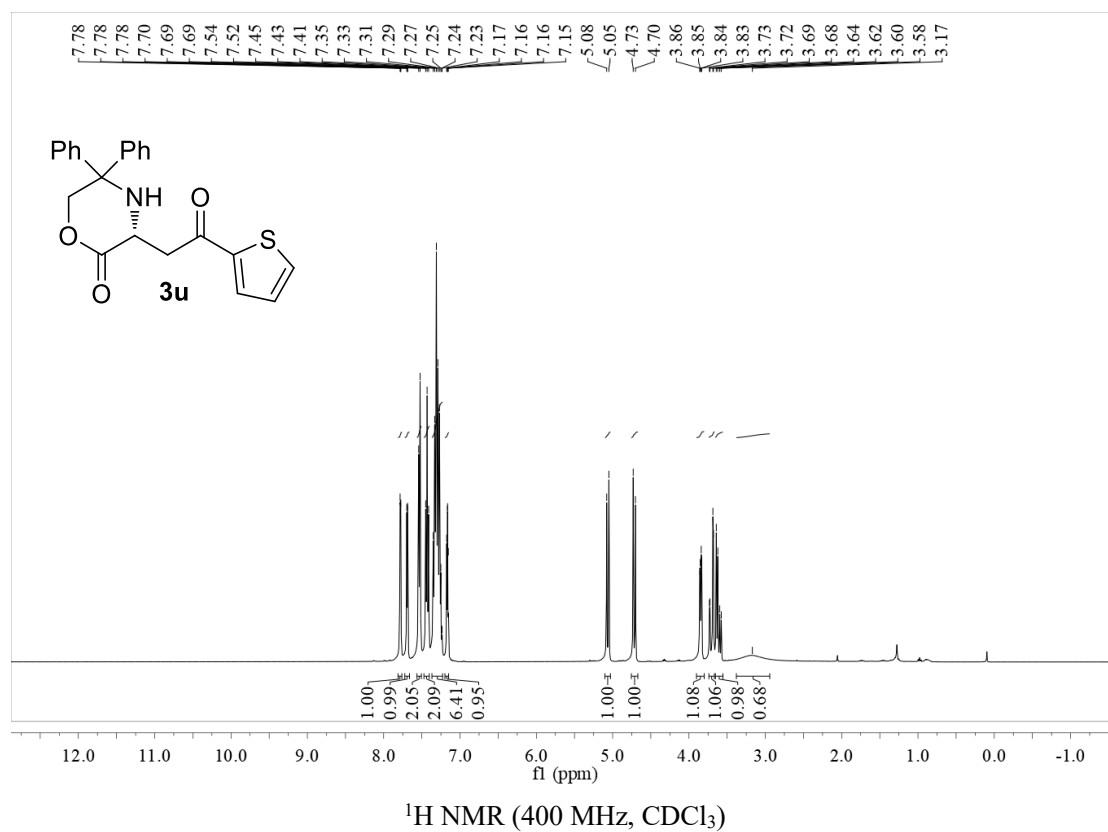


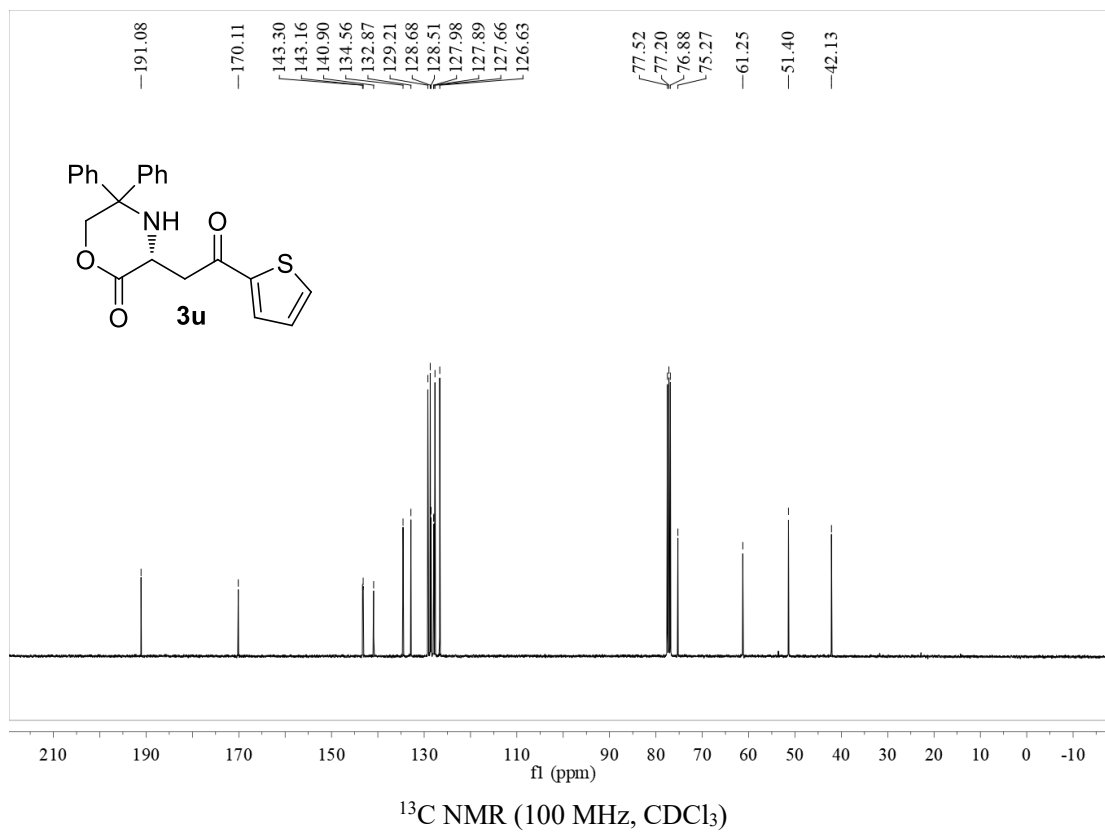
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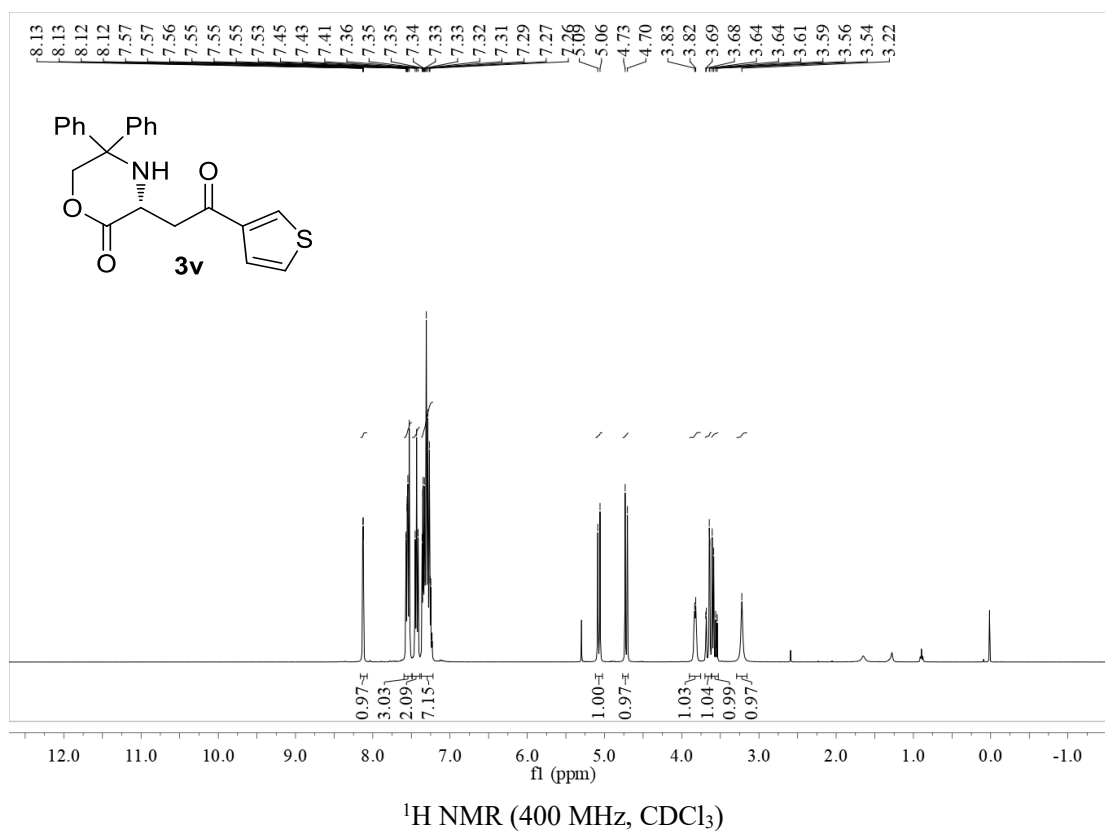


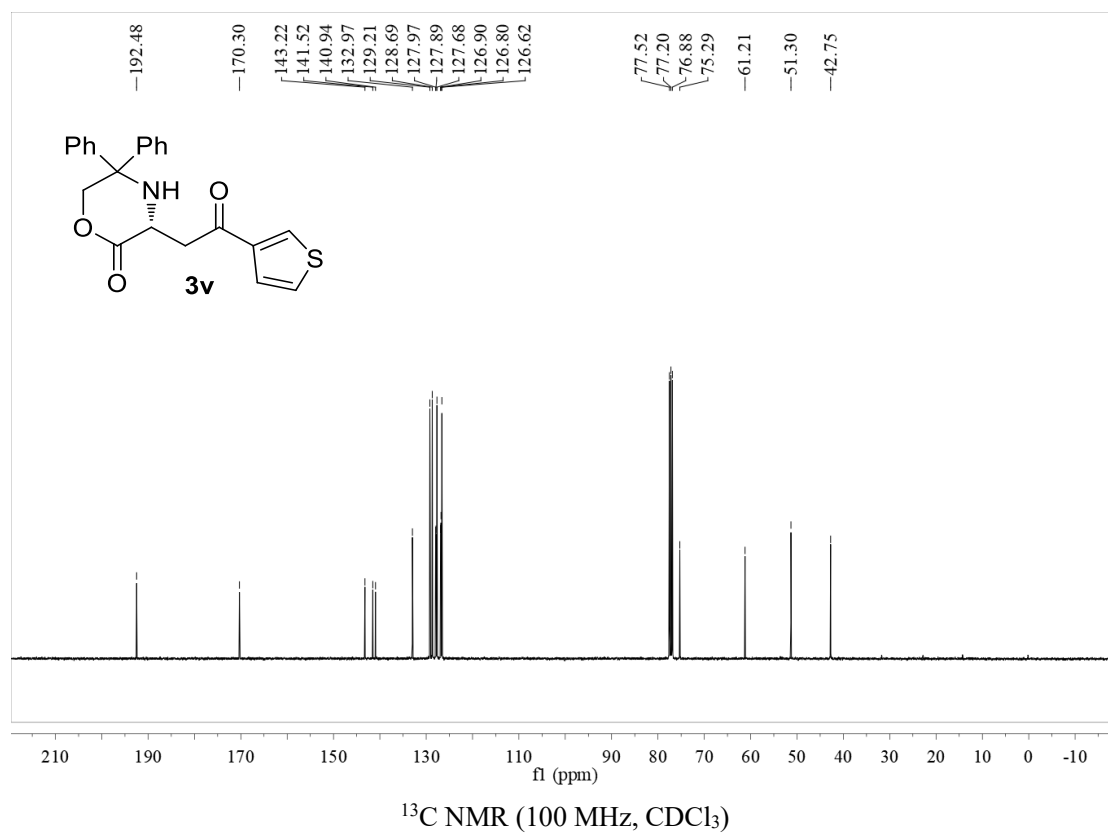
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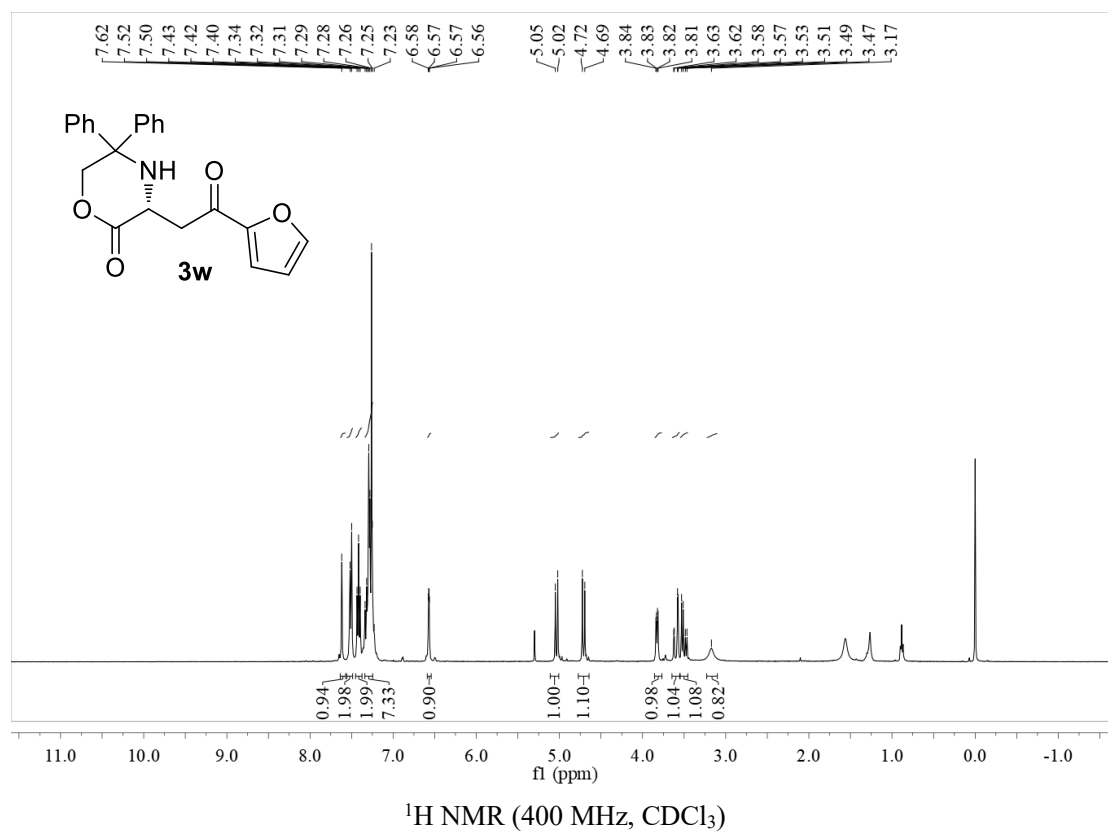


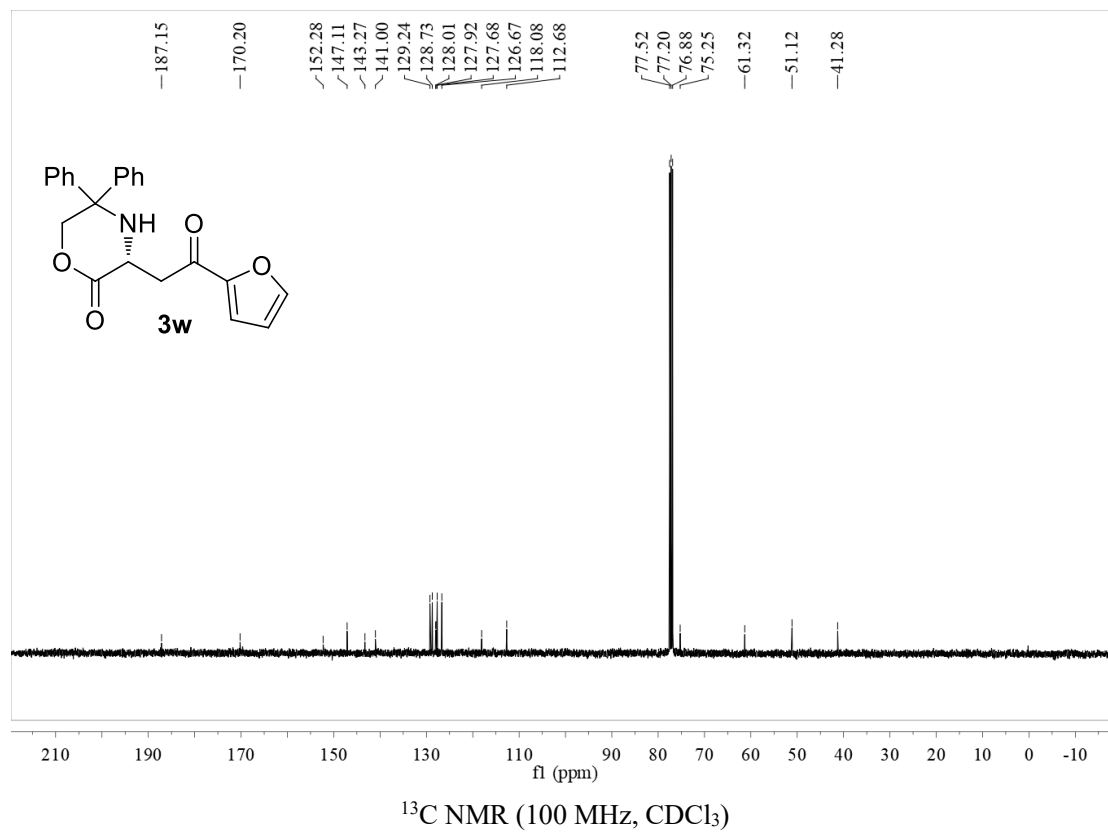
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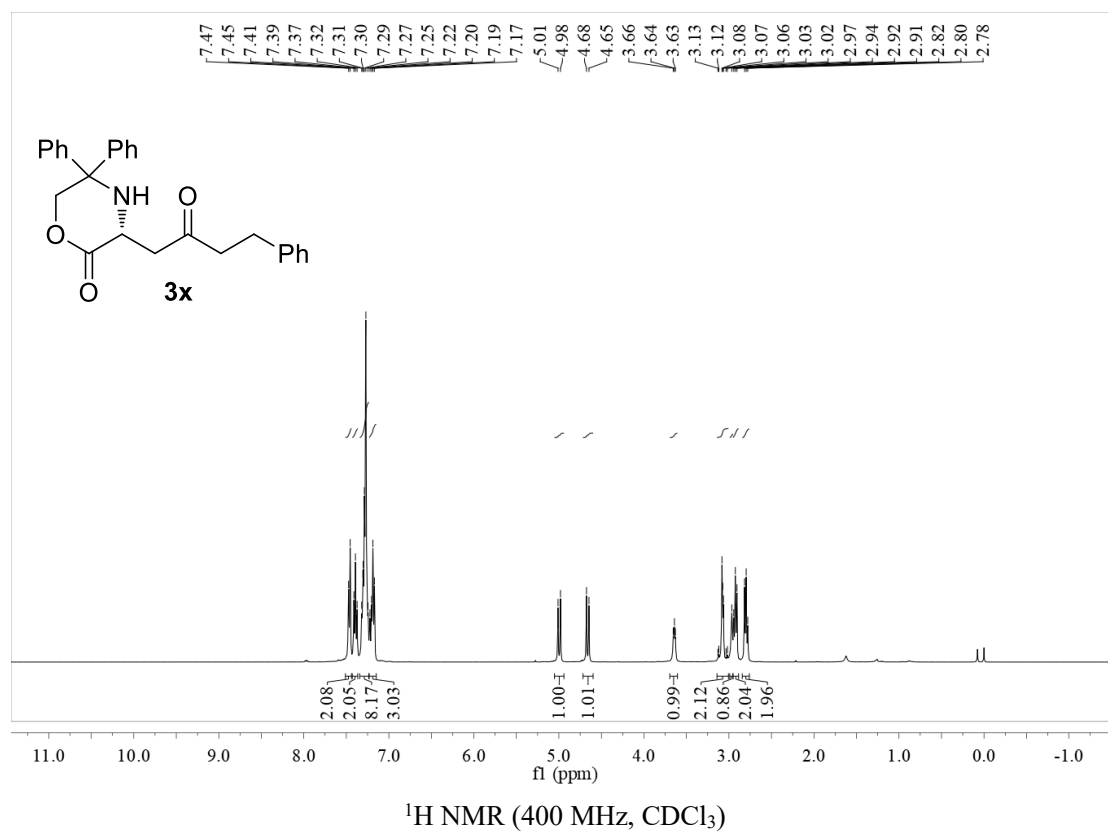


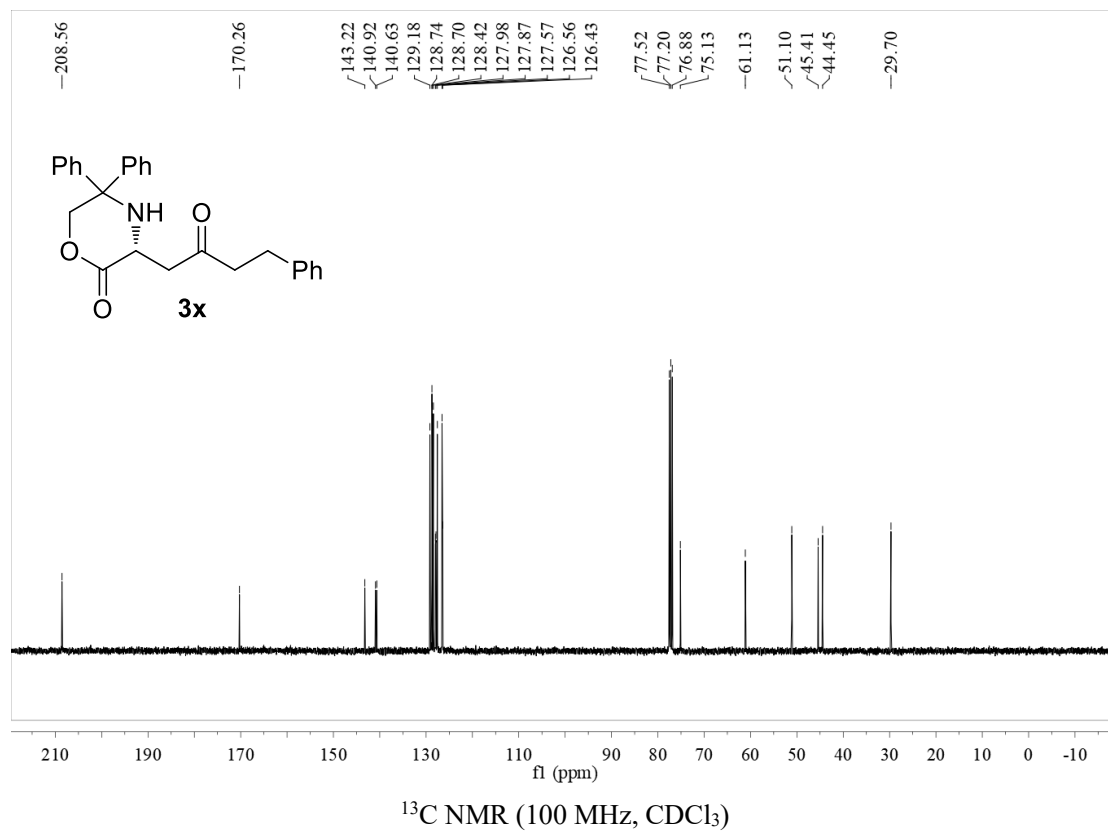
**(R)-3-(2-(Furan-2-yl)-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3w)**



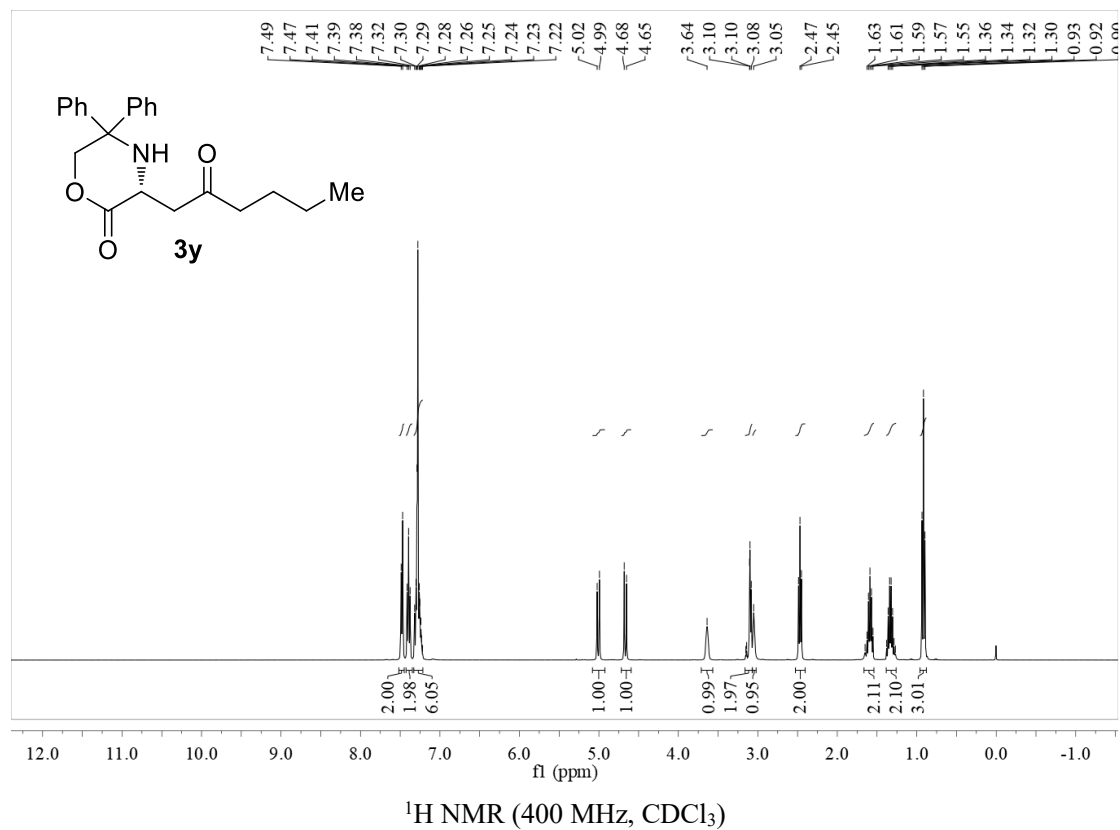


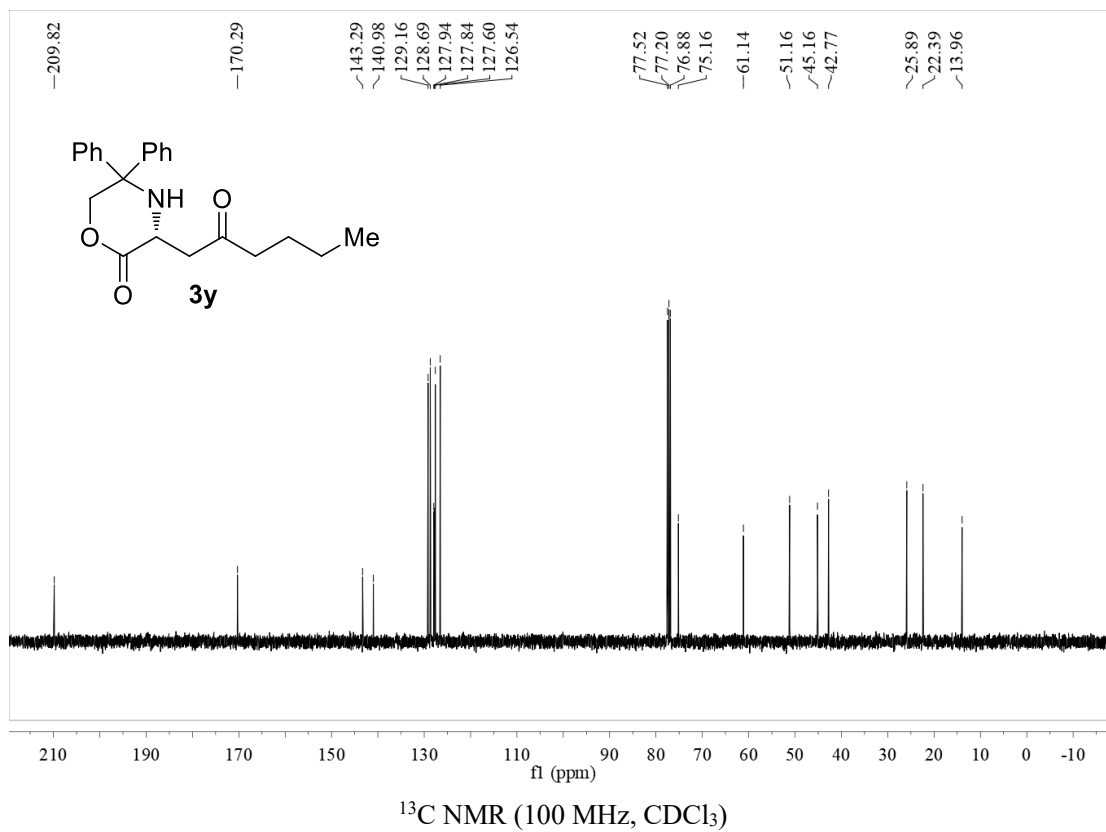
**(R)-3-(2-Oxo-4-phenylbutyl)-5,5-diphenylmorpholin-2-one (3x)**



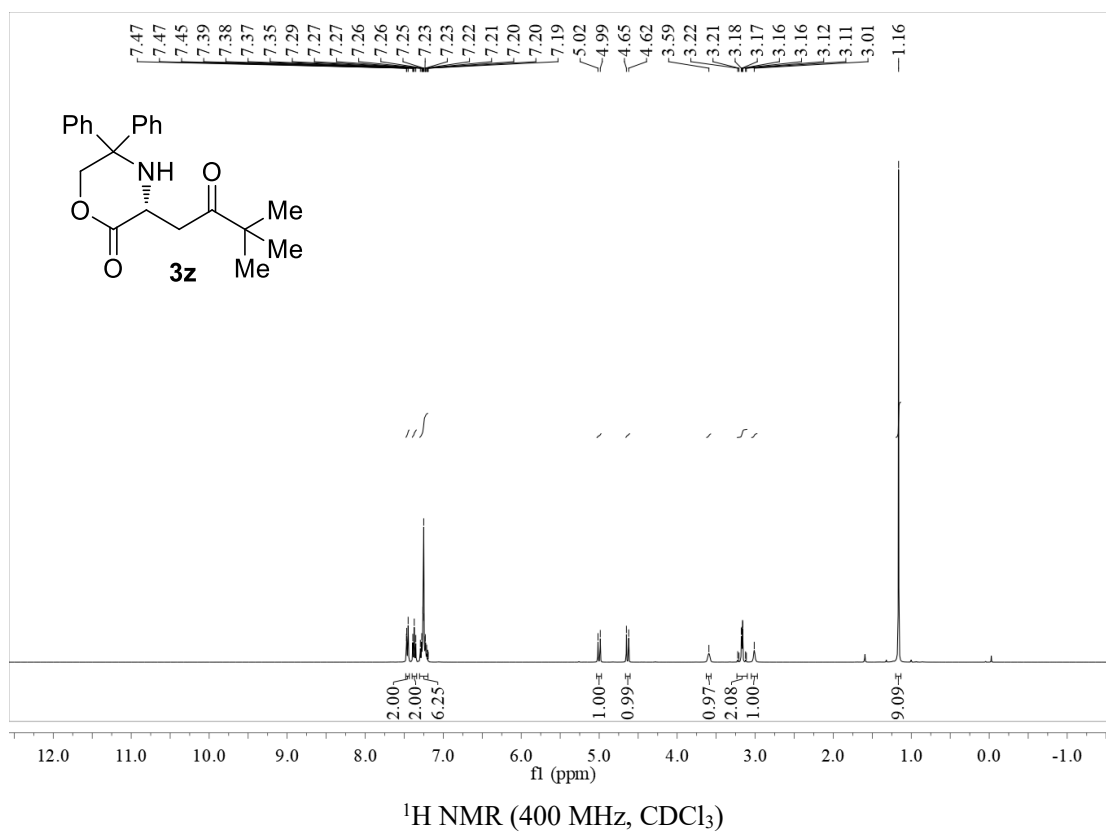


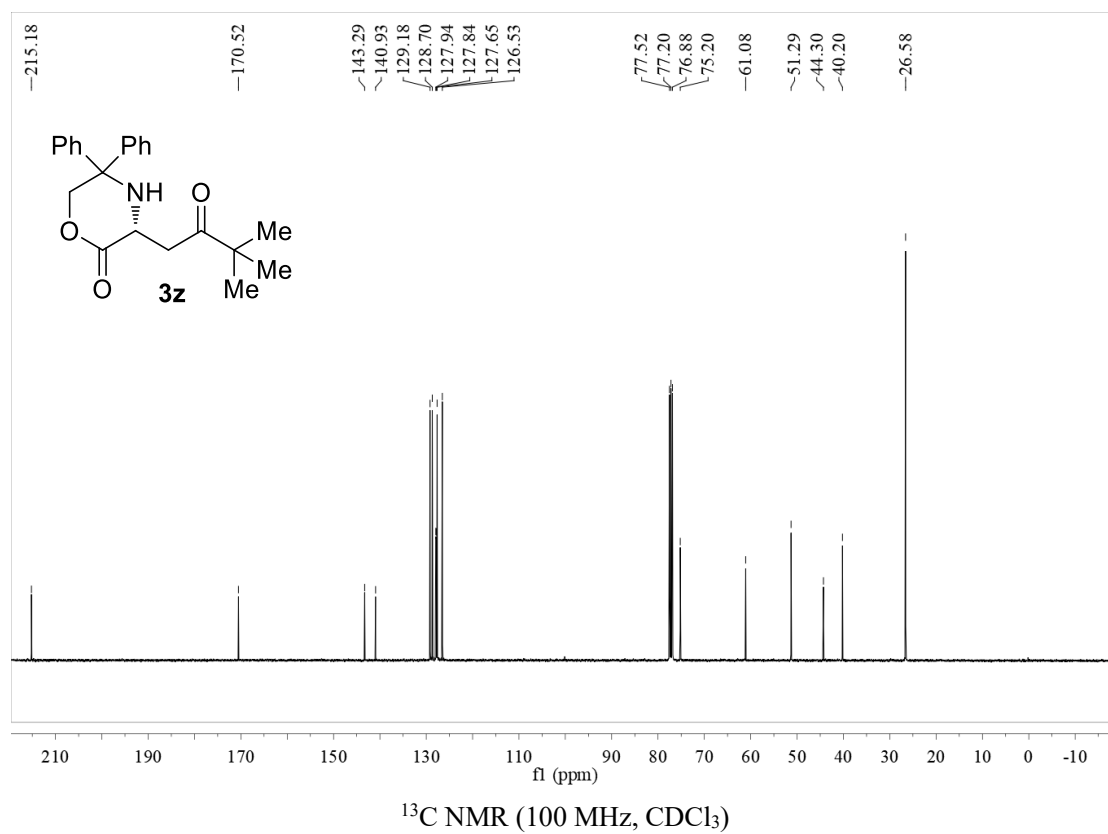
**(R)-3-(2-Oxohexyl)-5,5-diphenylmorpholin-2-one (3y)**



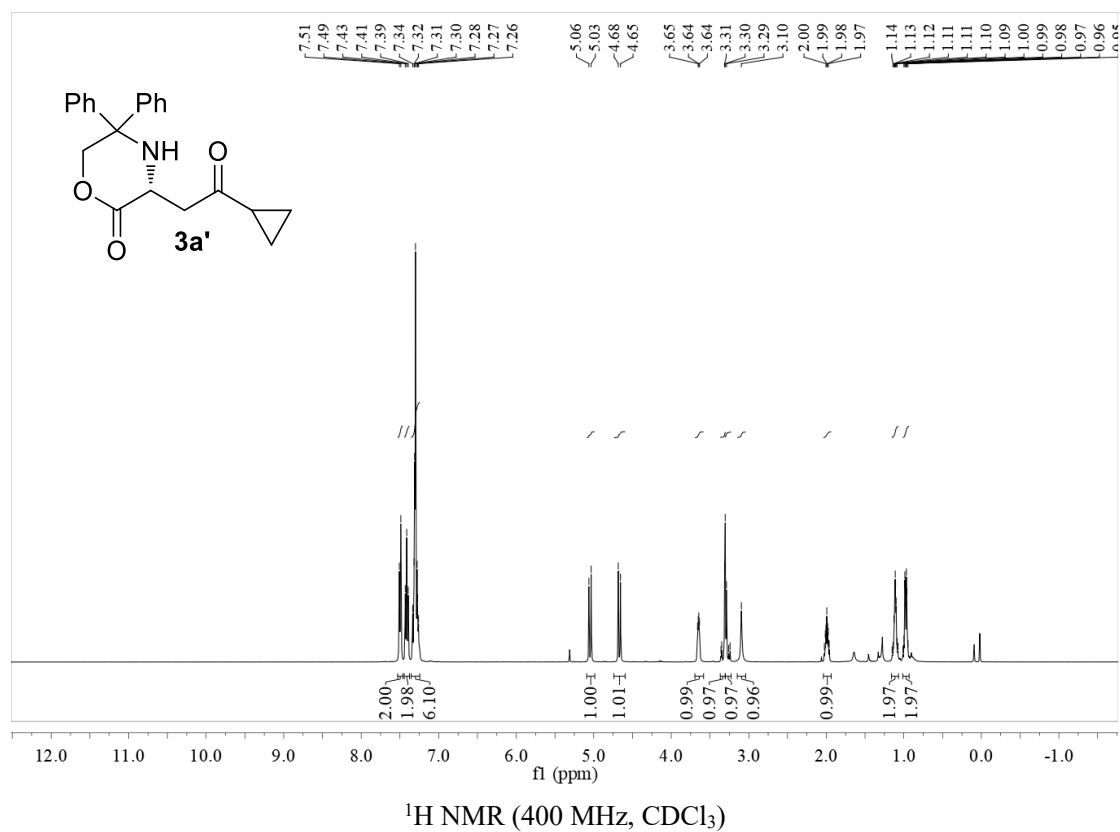


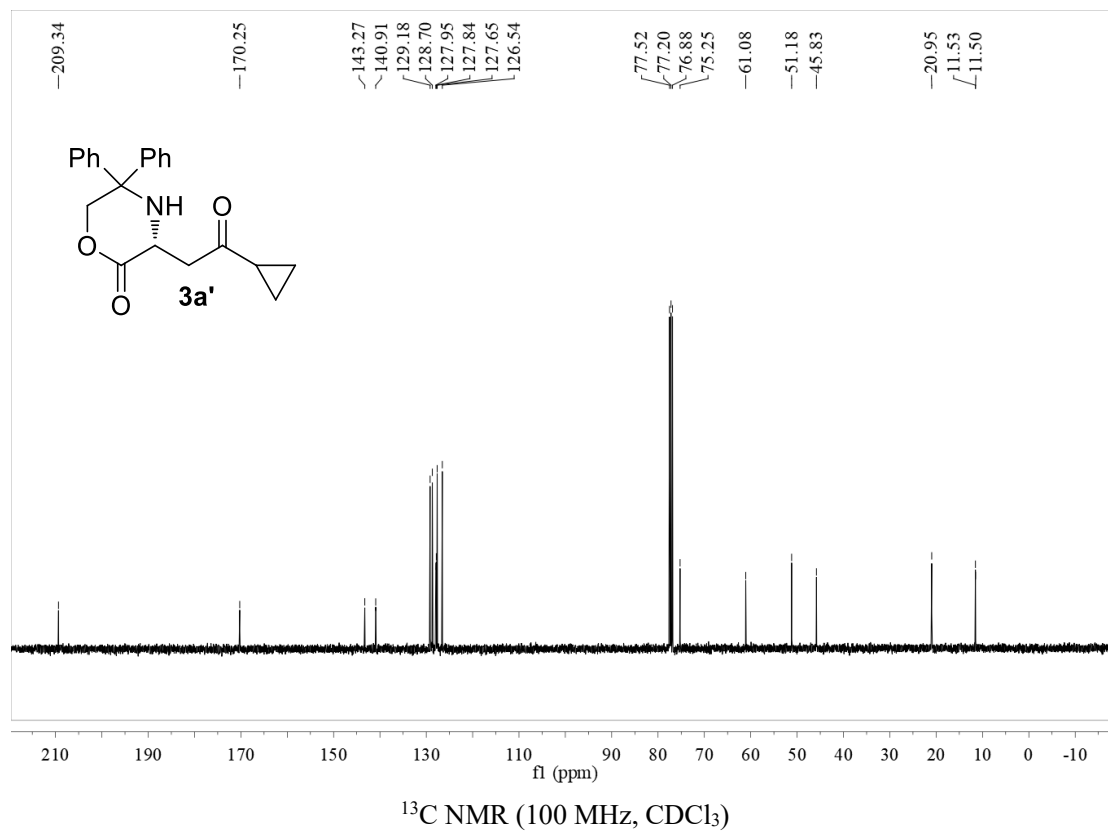
**(R)-3-(3,3-Dimethyl-2-oxobutyl)-5,5-diphenylmorpholin-2-one (3z)**



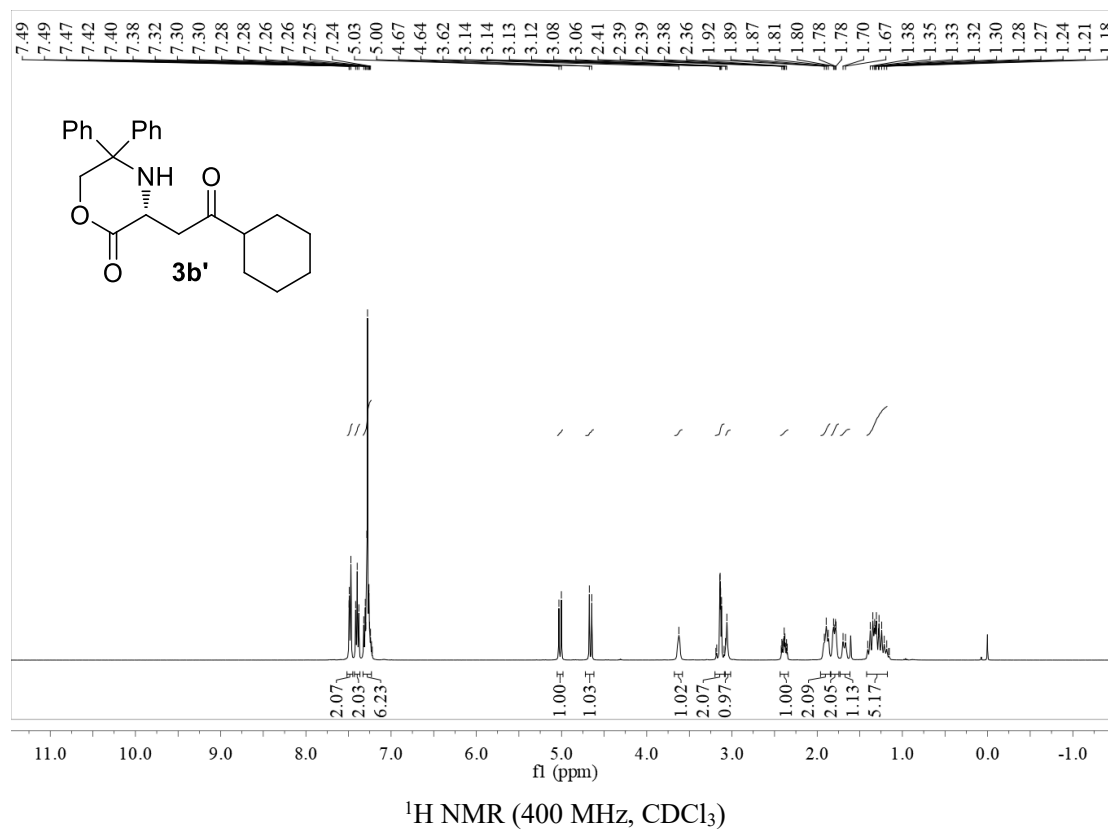


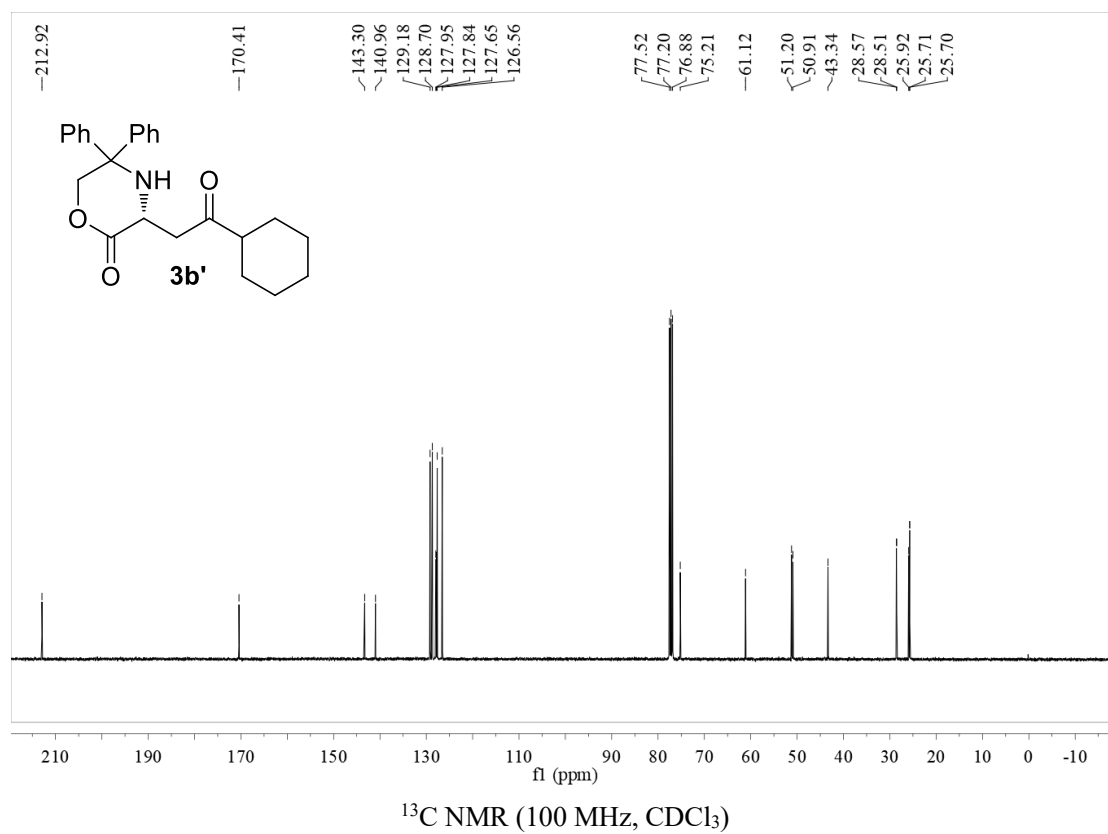
**(R)-3-(2-Cyclopropyl-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3a')**



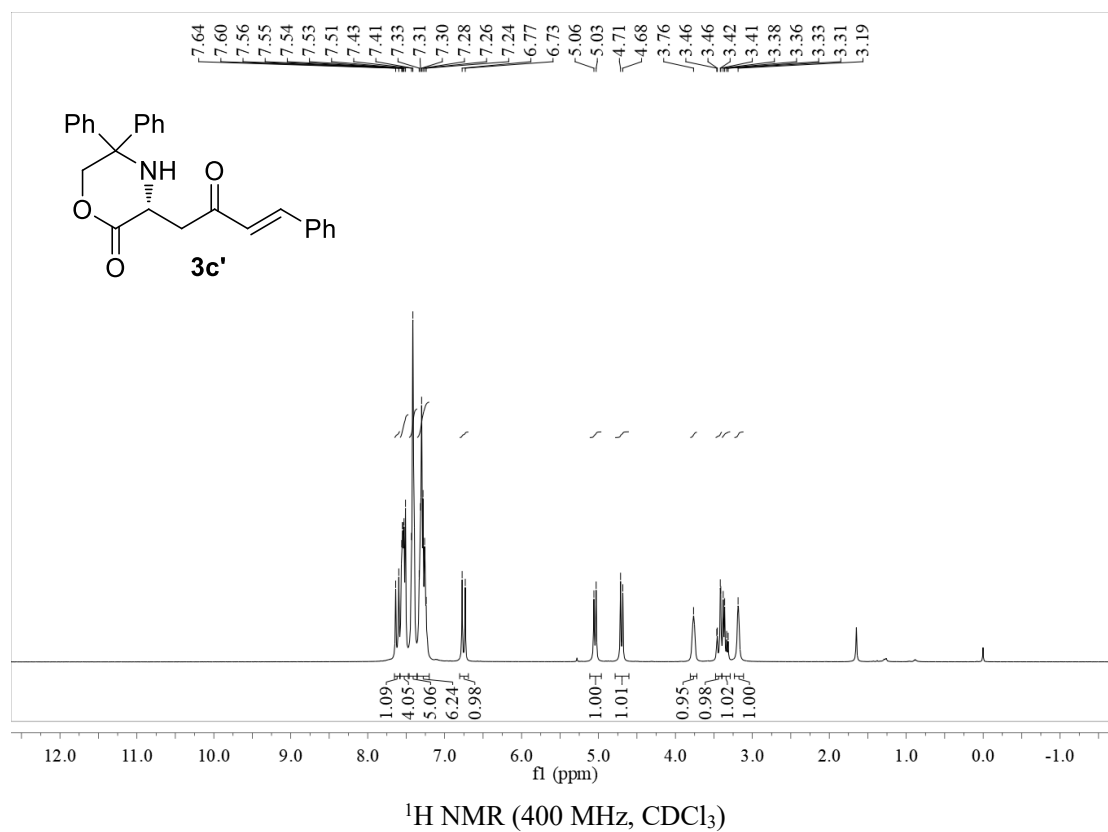


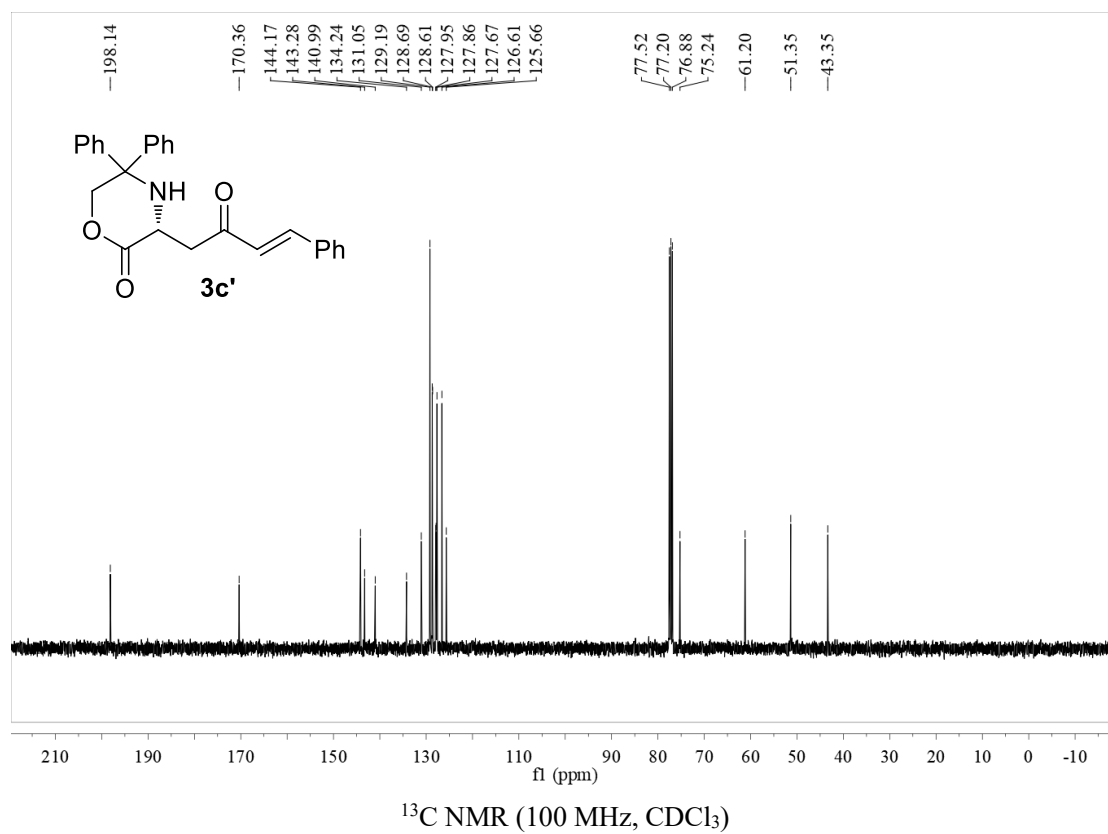
**(R)-3-(2-Cyclohexyl-2-oxoethyl)-5,5-diphenylmorpholin-2-one (3b')**



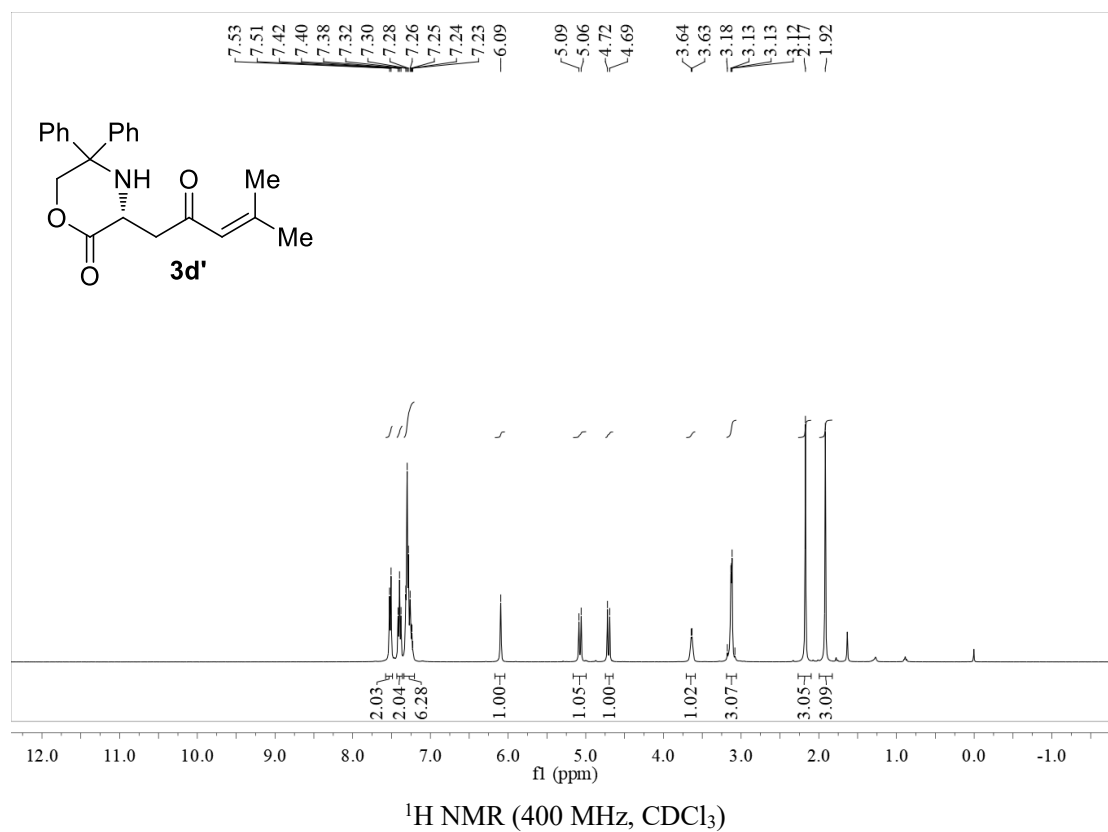


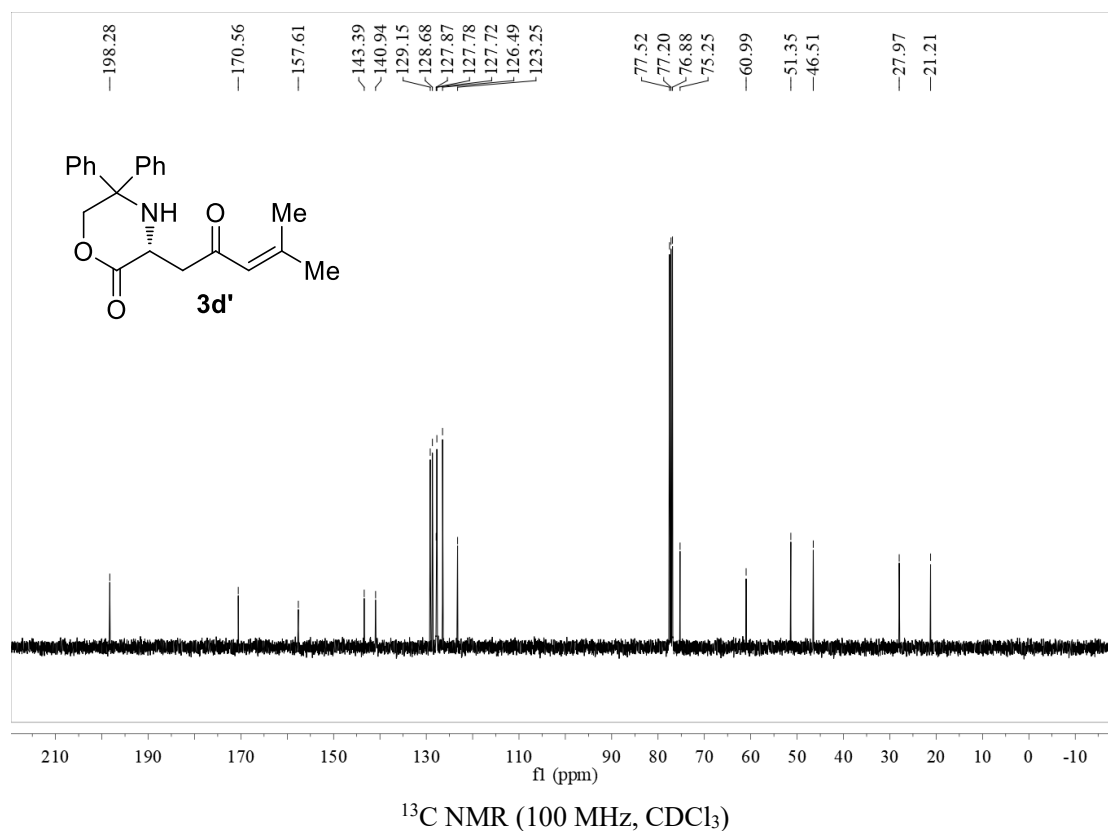
**(R,E)-3-(2-Oxo-4-phenylbut-3-en-1-yl)-5,5-diphenylmorpholin-2-one (3c')**



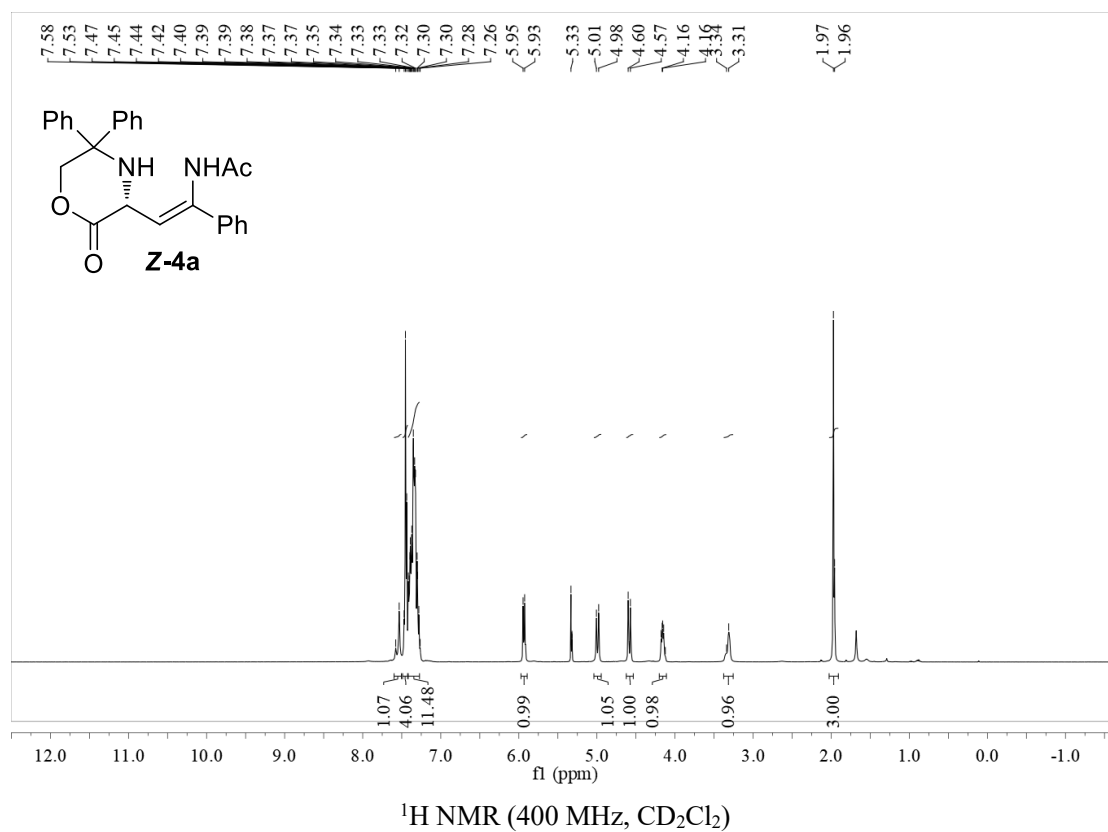


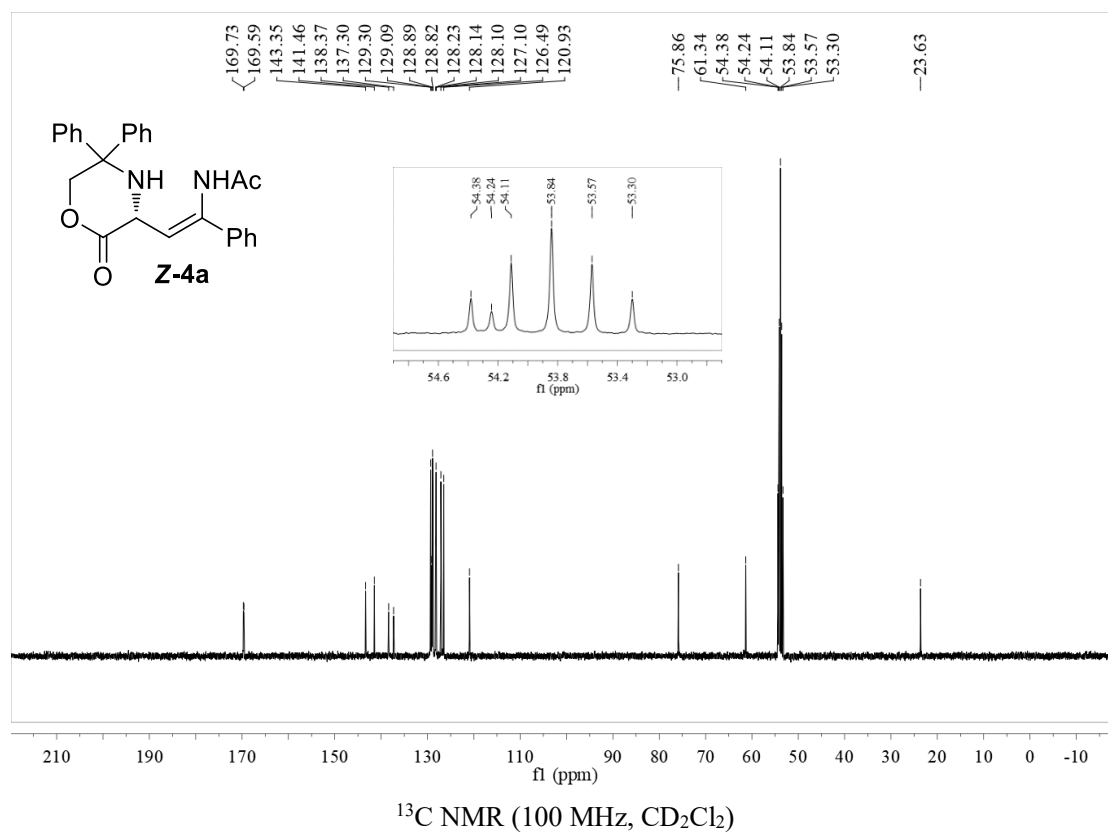
**(R)-3-(4-Methyl-2-oxopent-3-en-1-yl)-5,5-diphenylmorpholin-2-one (3d')**



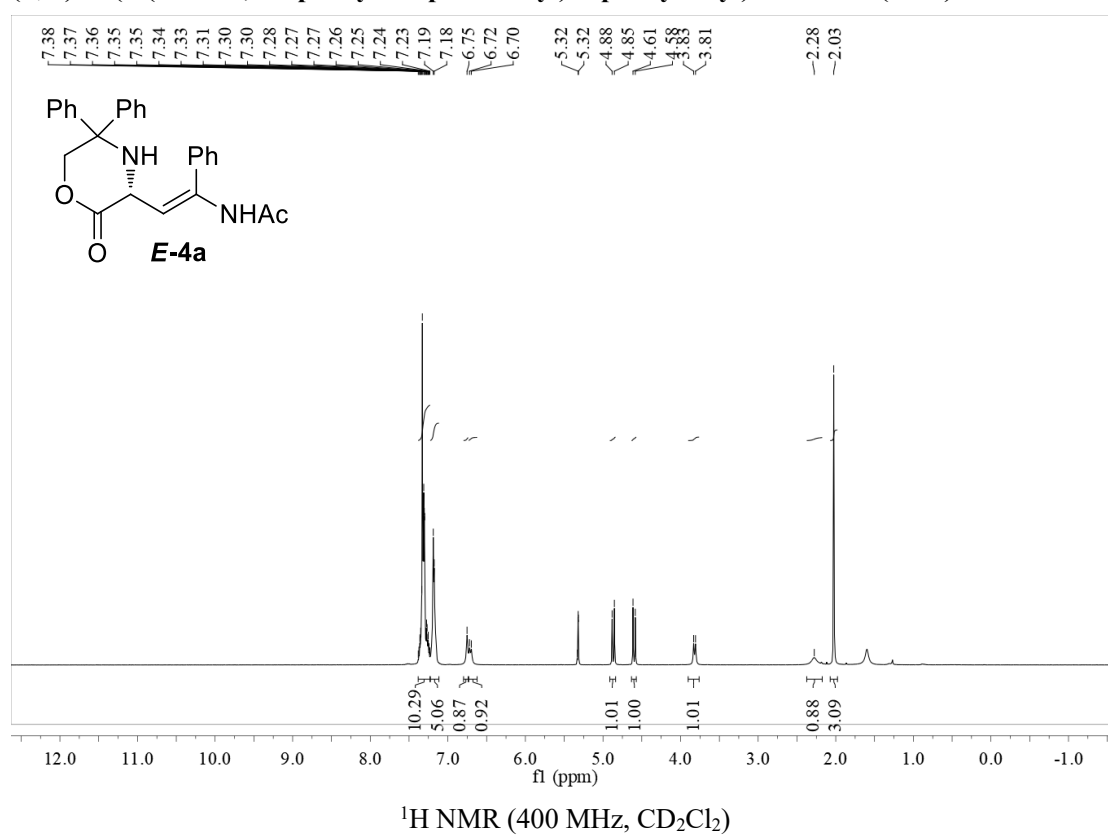


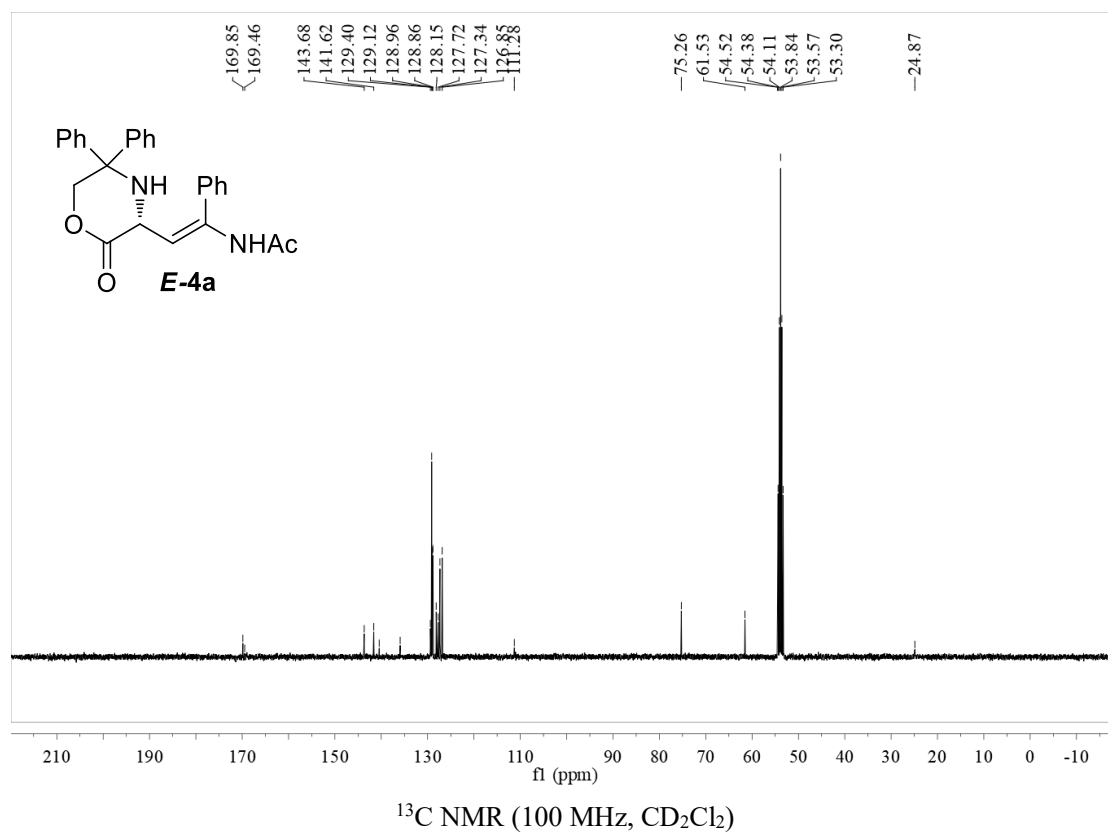
**(R,Z)-N-(2-(2-oxo-5,5-diphenylmorpholin-3-yl)-1-phenylvinyl)acetamide (Z-4a)**



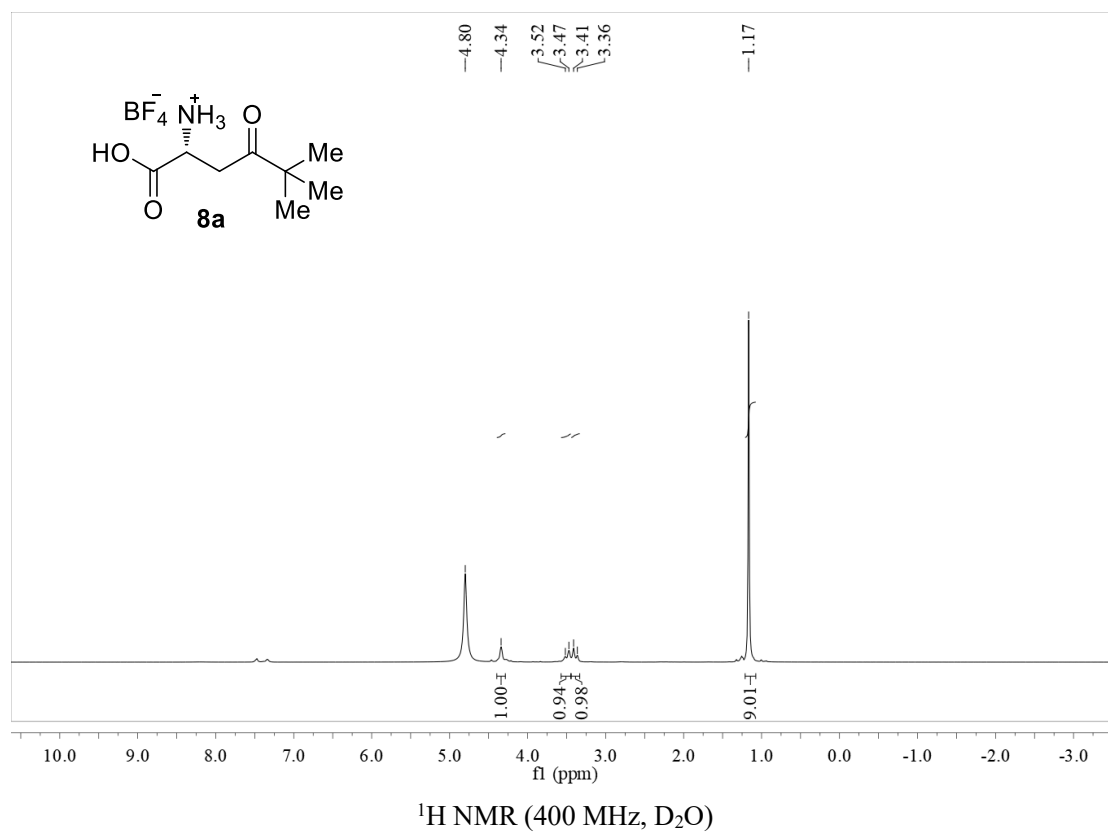


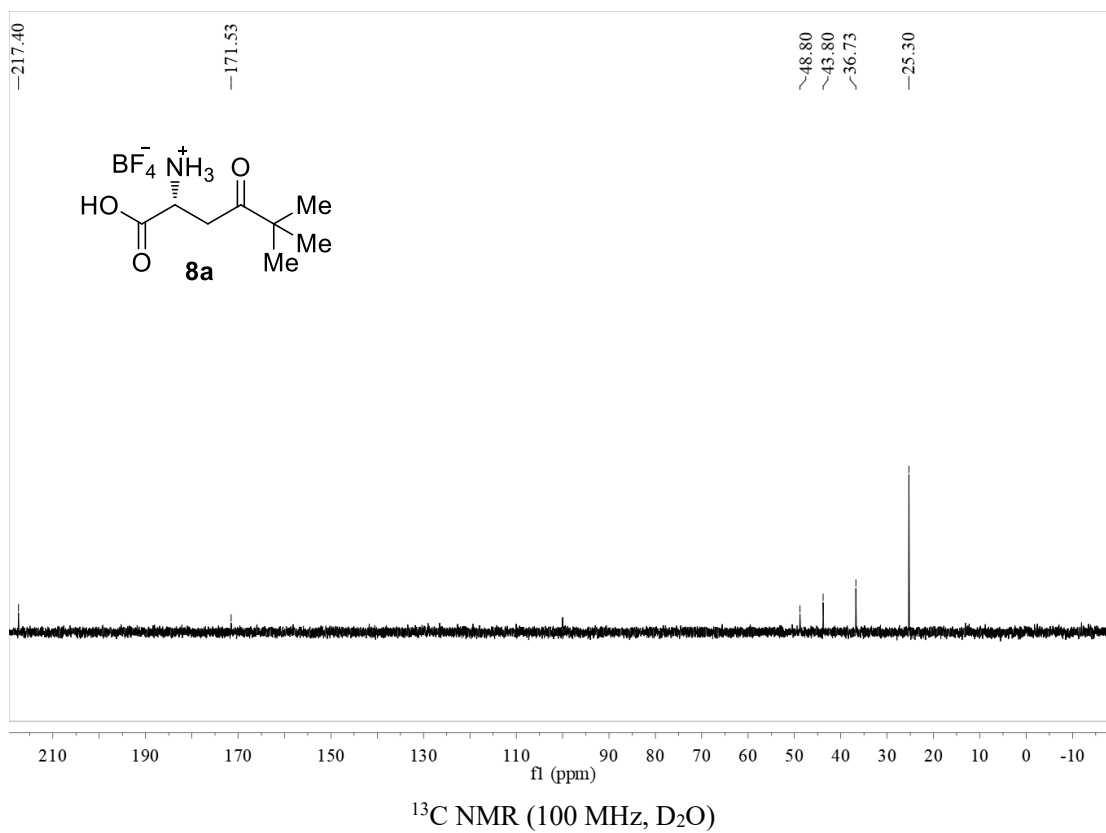
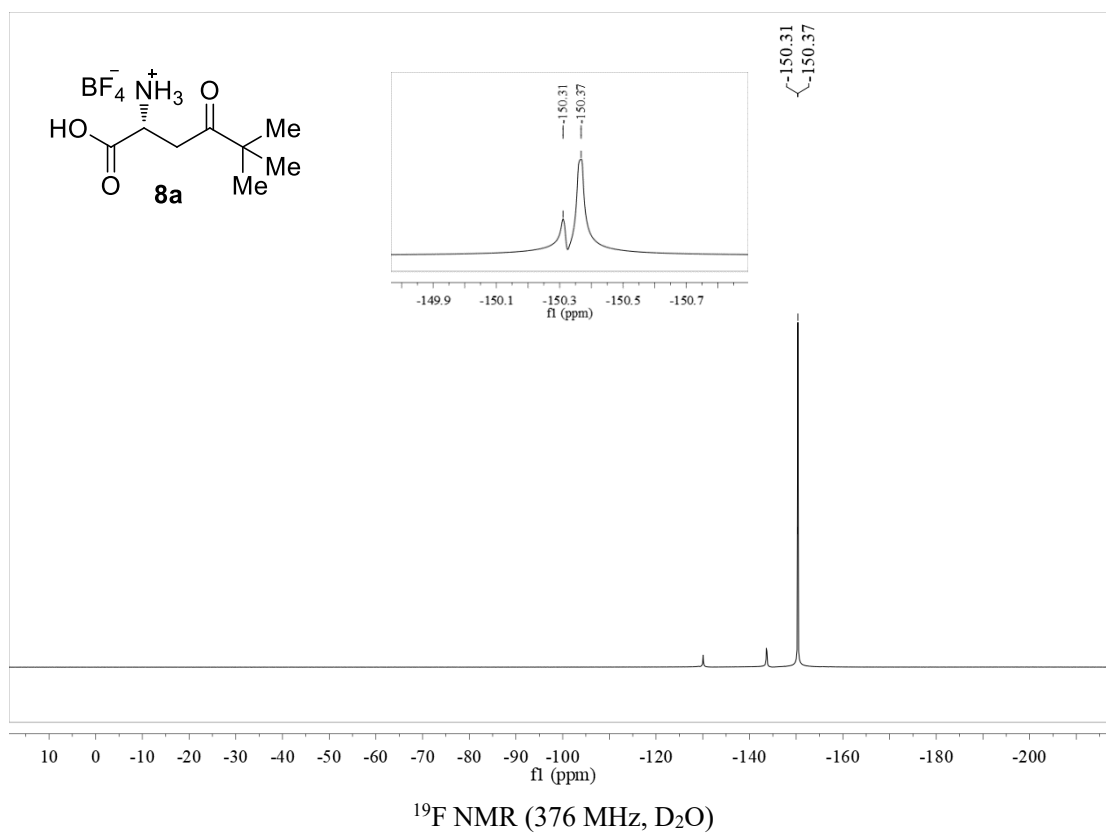
**(R,E)-N-(2-(2-oxo-5,5-diphenylmorpholin-3-yl)-1-phenylvinyl)acetamide (E-4a)**



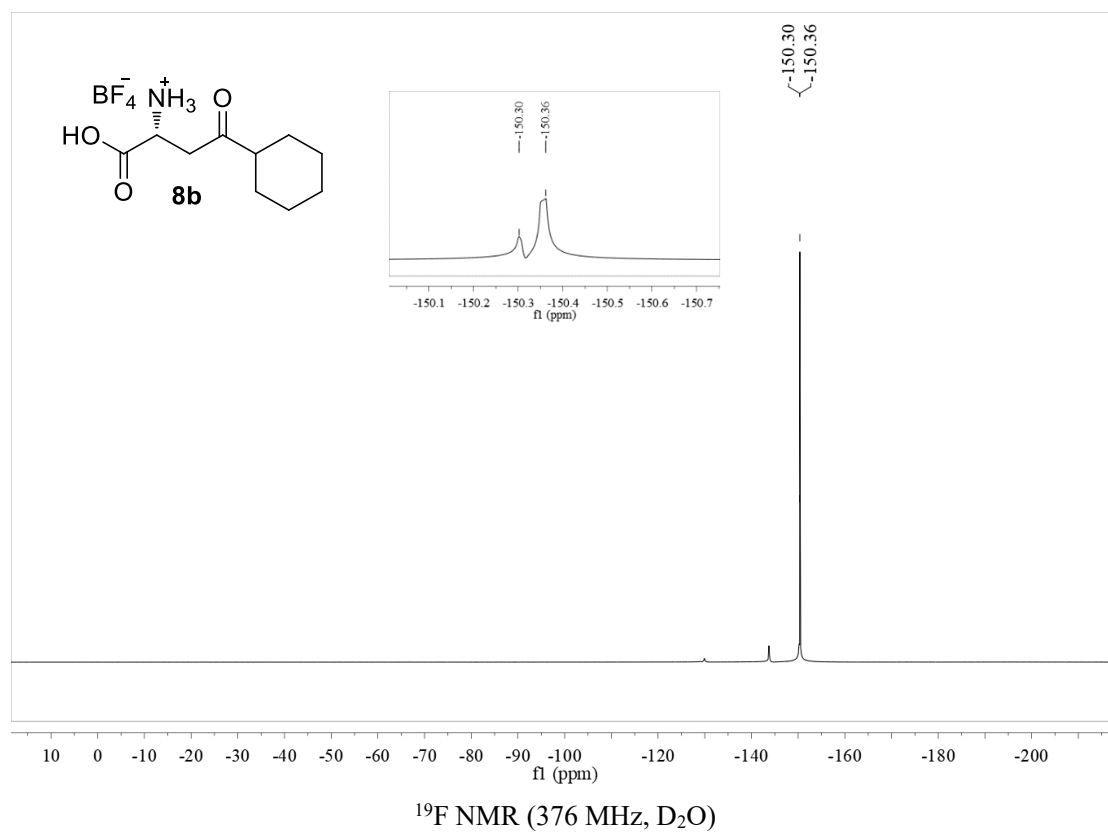
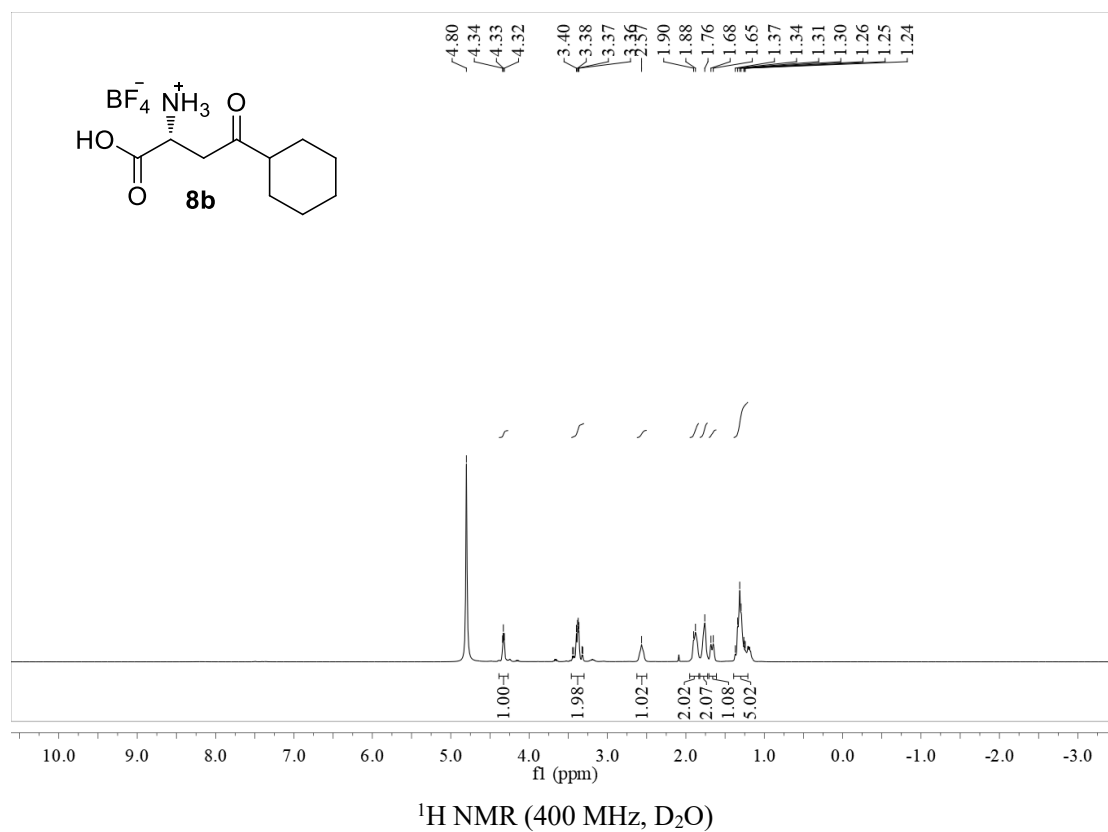


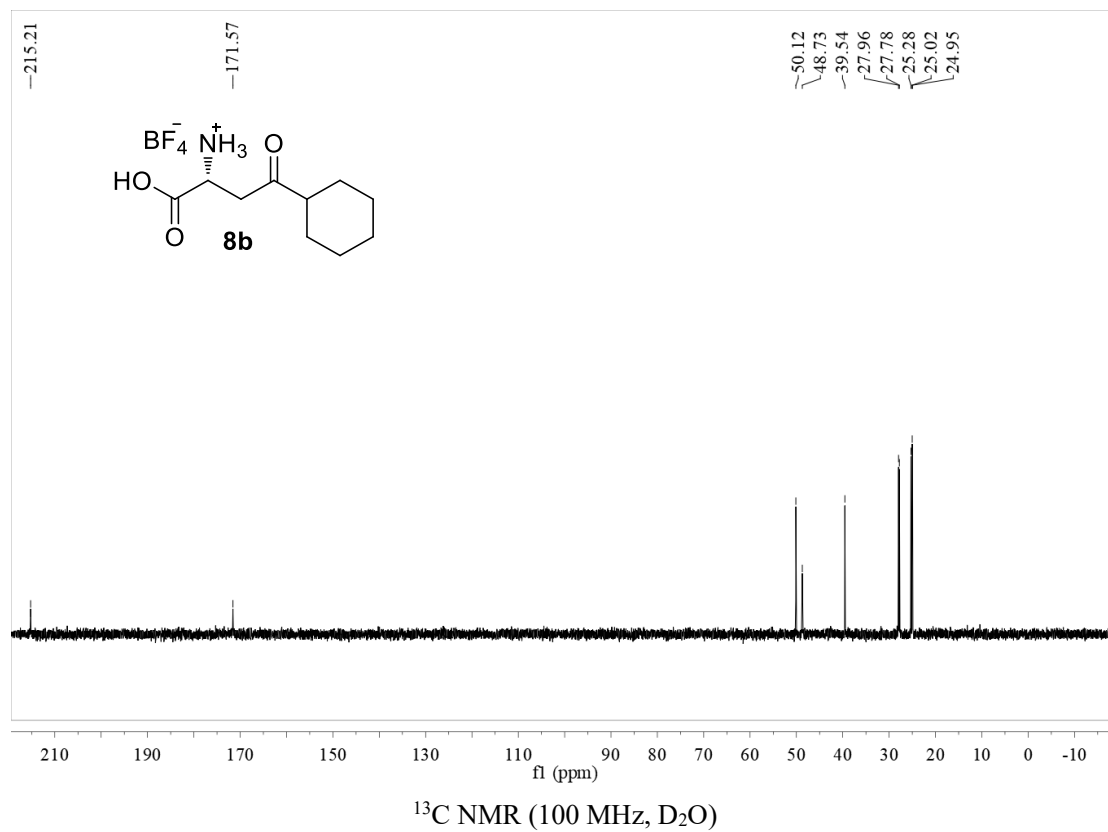
**(*R*)-2-Amino-5,5-dimethyl-4-oxohexanoic acid  $\text{HBF}_4$ -salt (**8a**)**



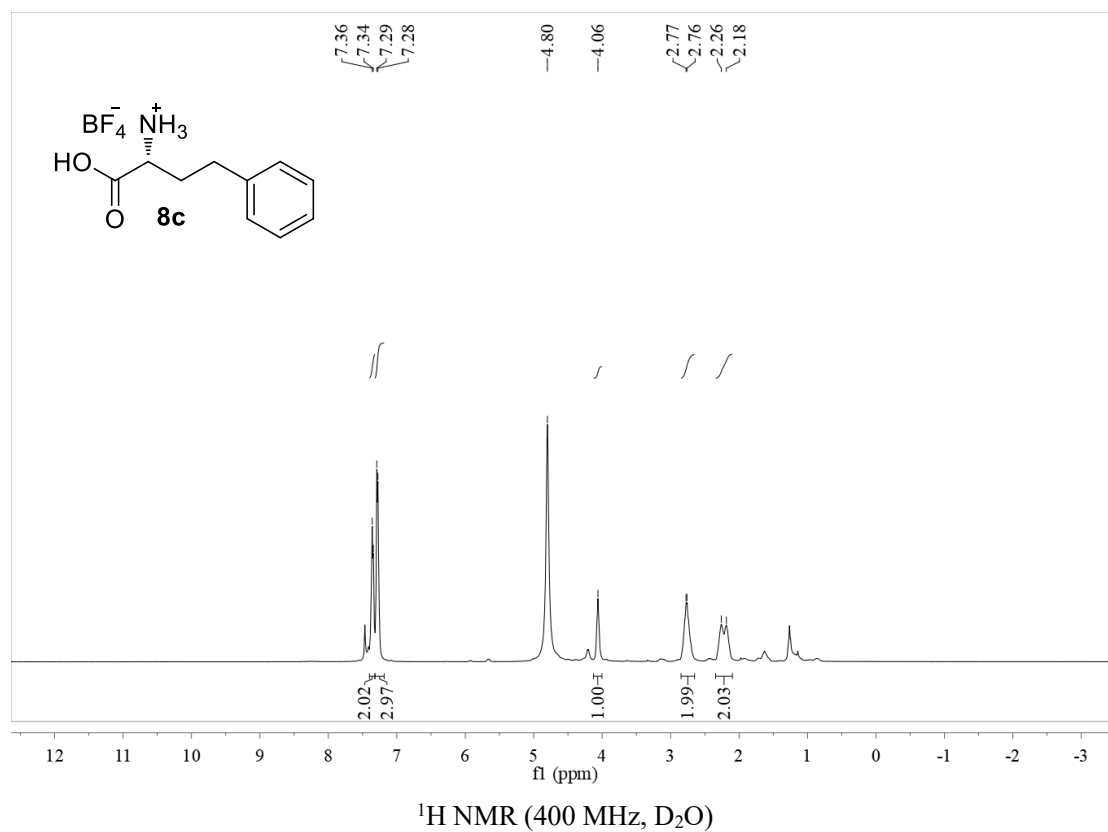


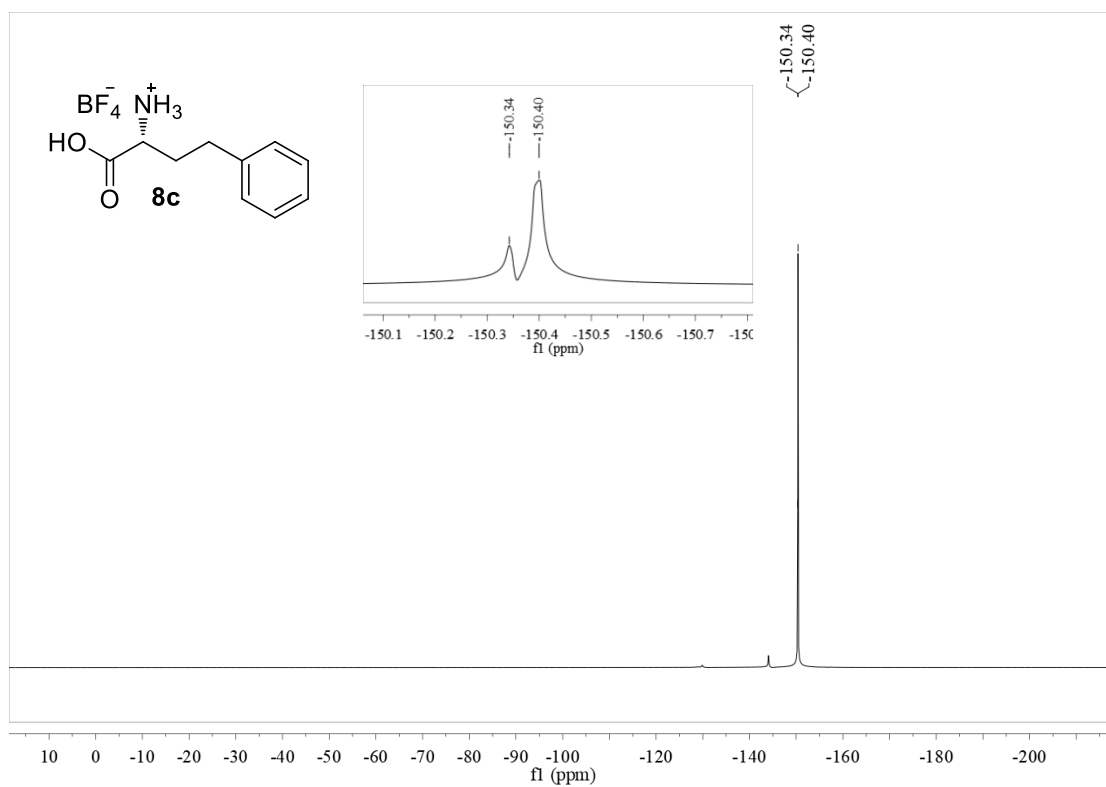
**(R)-2-Amino-4-cyclohexyl-4-oxobutanoic acid HBF<sub>4</sub>-salt (8b)**



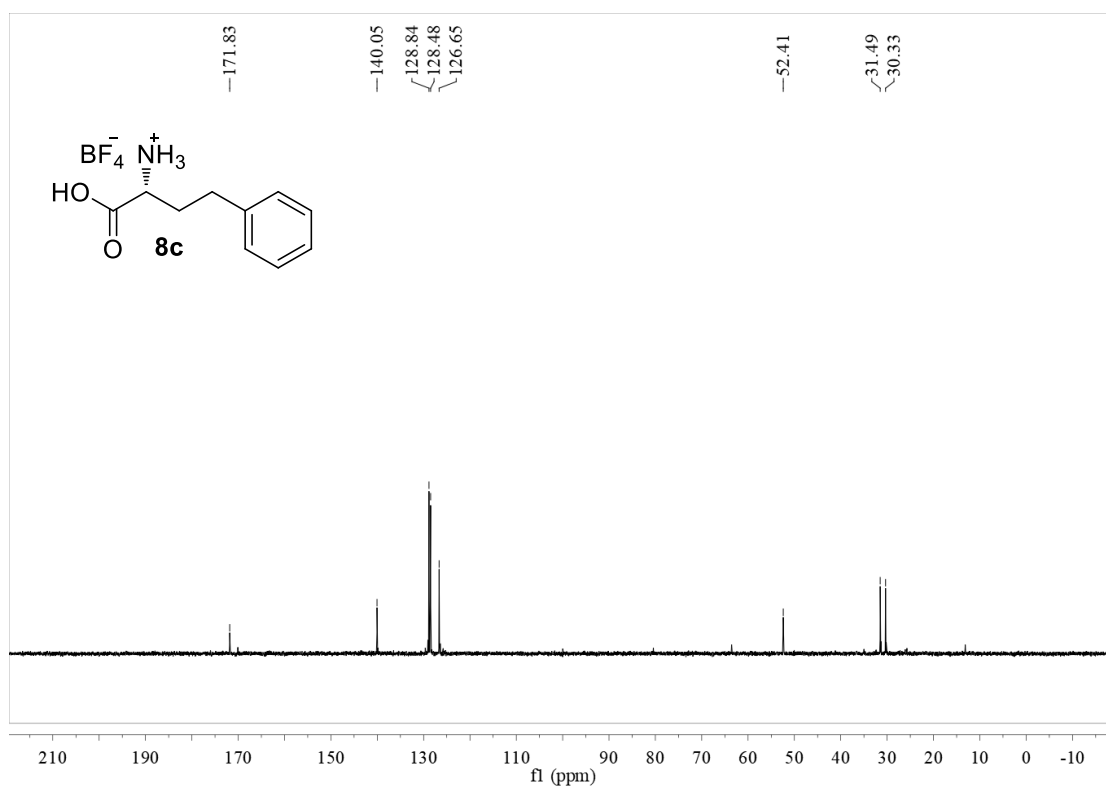


**(R)-2-Amino-4-phenylbutanoic acid HBF<sub>4</sub>-salt (8c)**



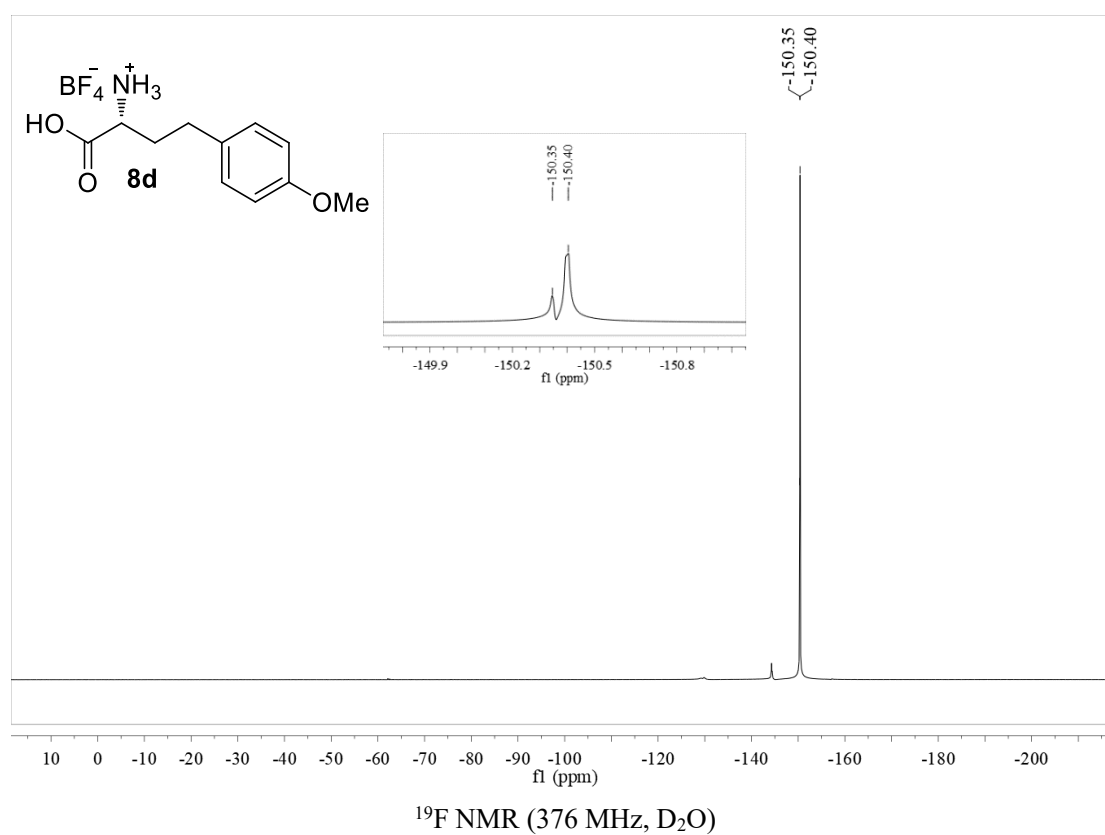
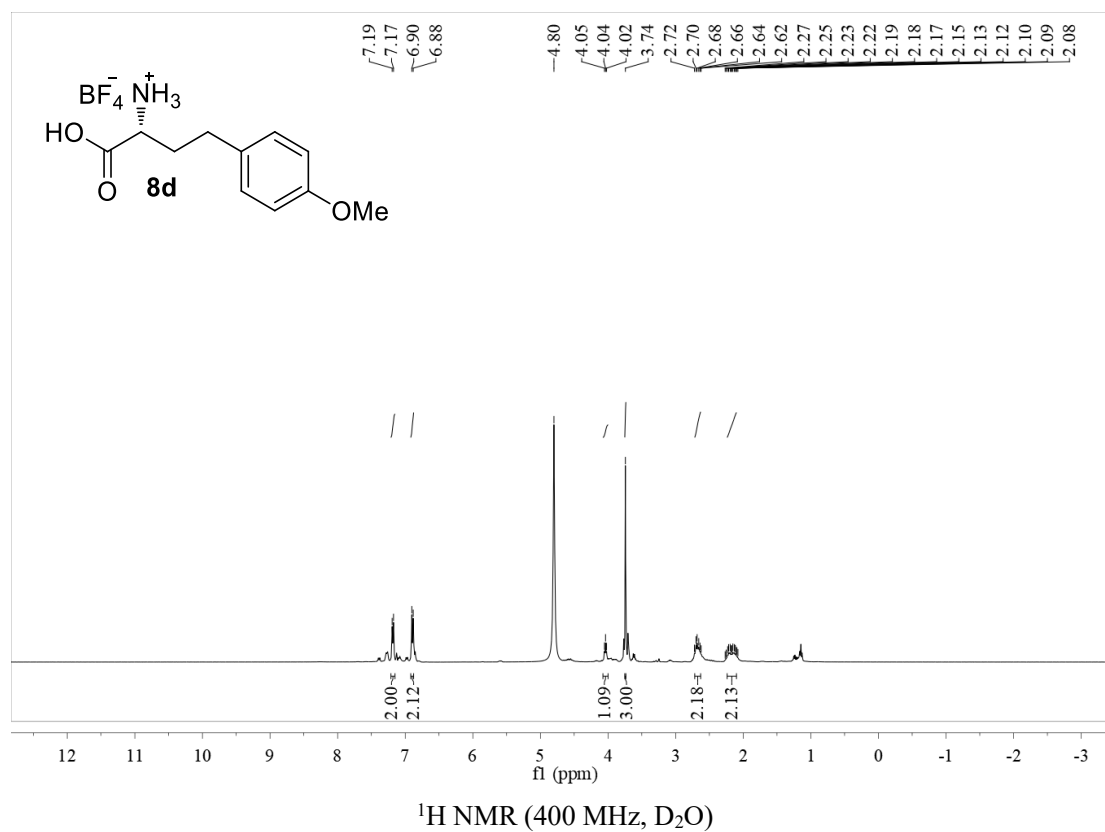


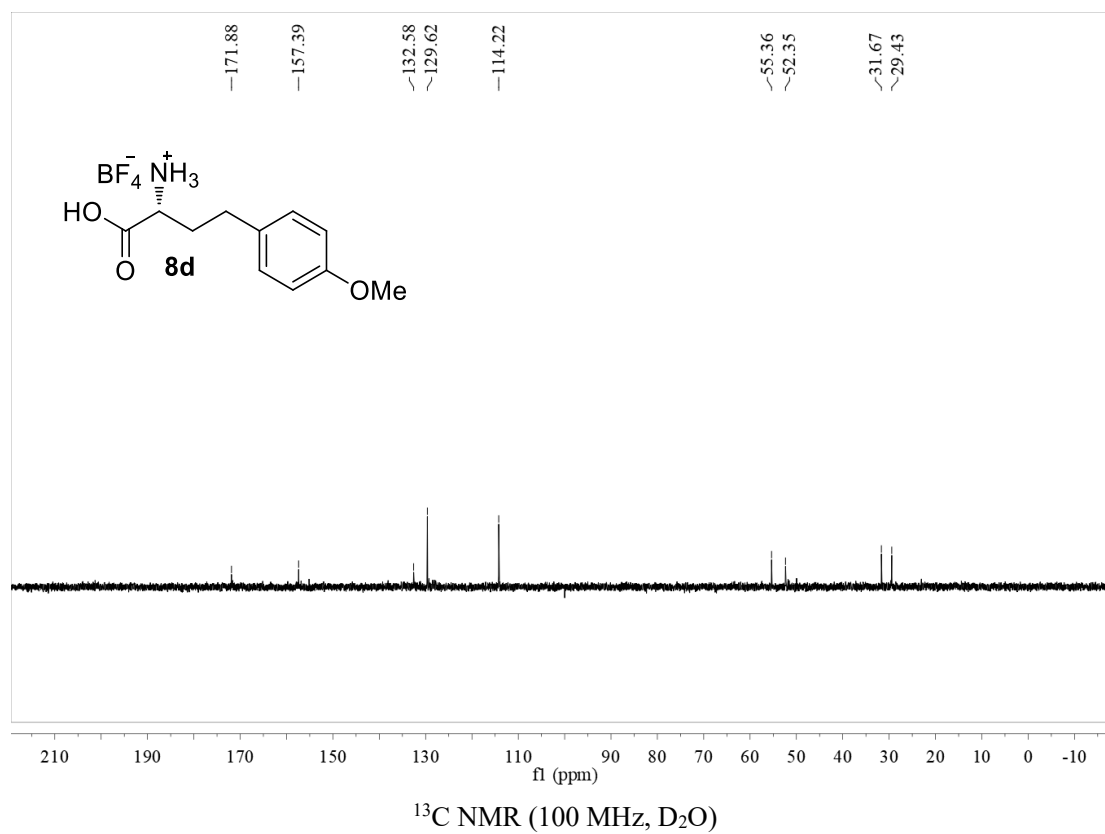
$^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )



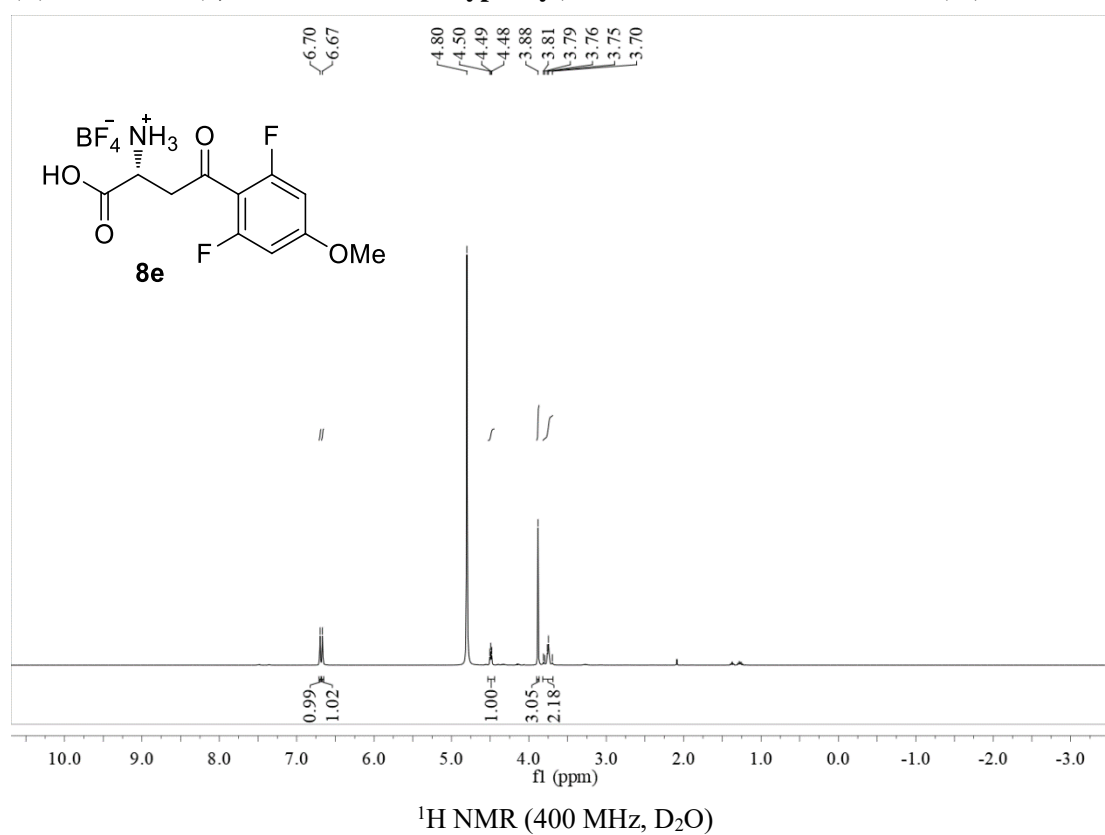
$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ )

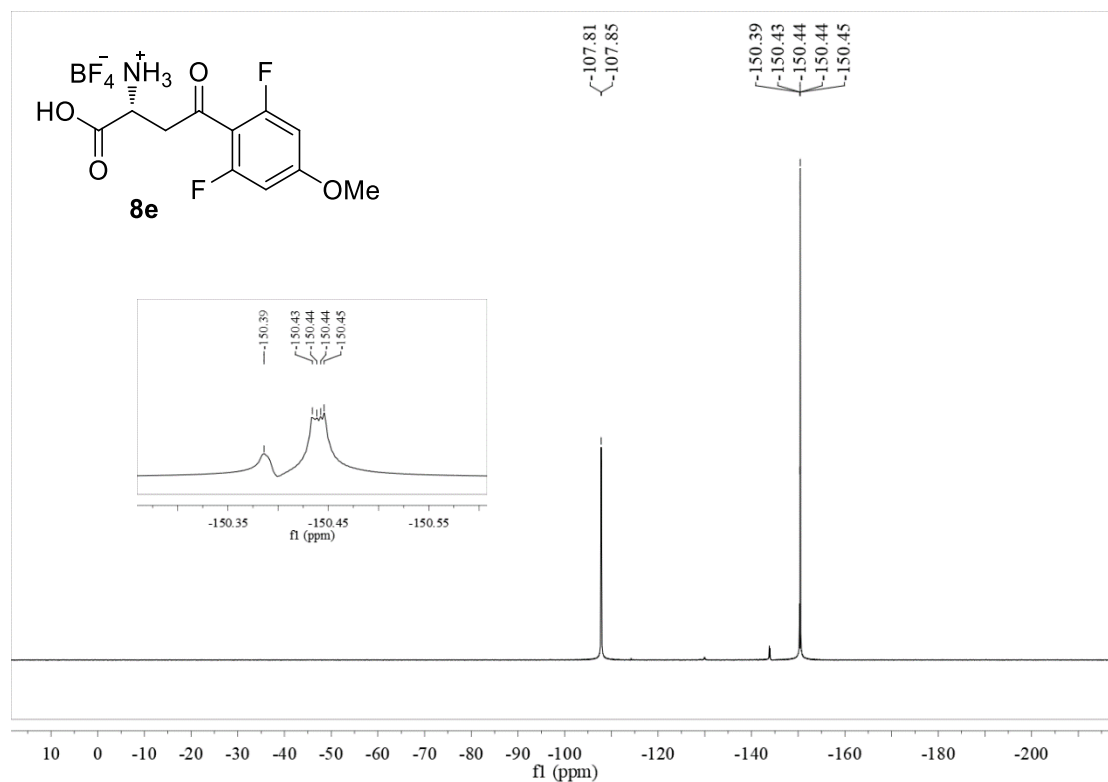
**(R)-2-Amino-4-(4-methoxyphenyl)butanoic acid HBF<sub>4</sub>-salt (8d)**



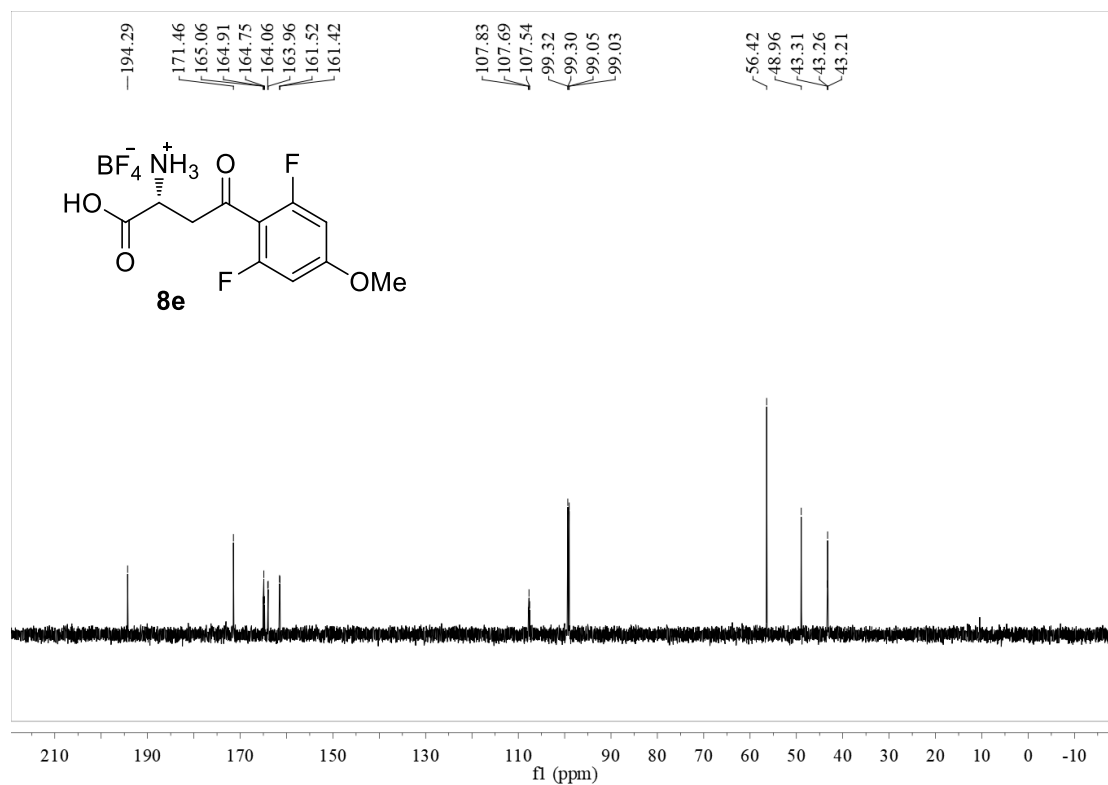


**(R)-2-Amino-4-(2,6-difluoro-4-methoxyphenyl)-4-oxobutanoic acid HBF<sub>4</sub>-salt (8e)**



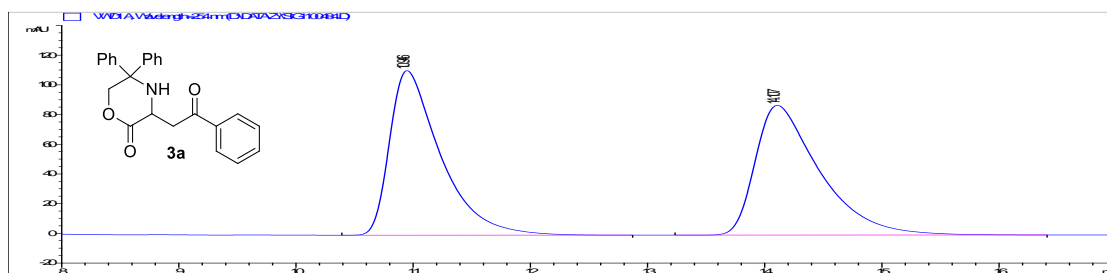


$^{19}\text{F}$  NMR (377 MHz,  $\text{D}_2\text{O}$ )

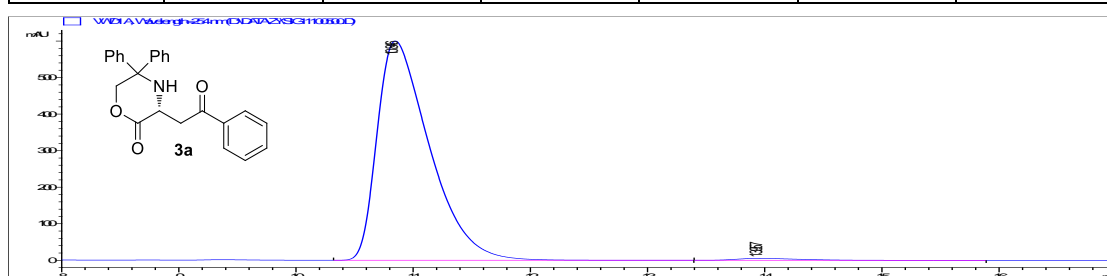


$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ )

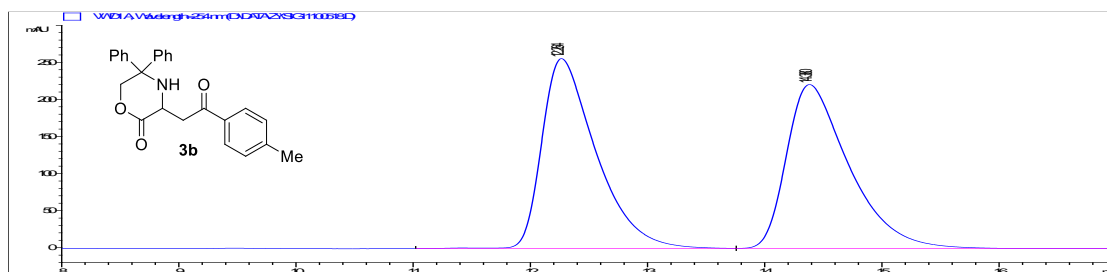
## 4. HPLC charts of the related compounds



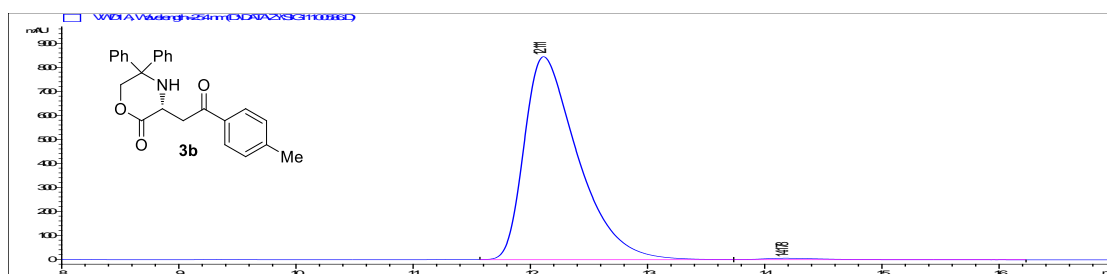
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.946	3350.8	110.8	0.4459	0.482	50.072
2	14.107	3341.2	87.4	0.5656	0.489	49.928



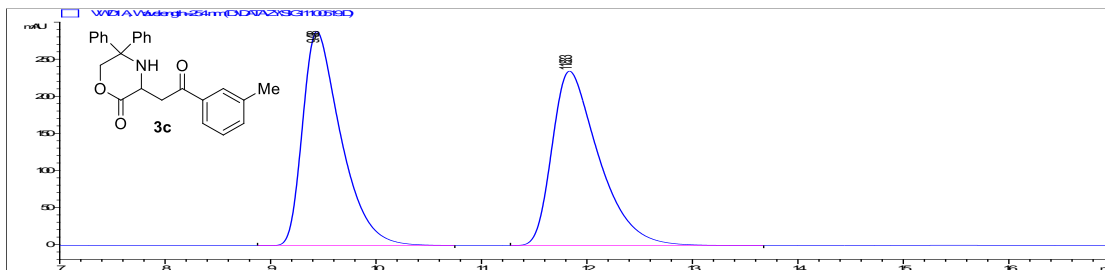
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.846	18570.5	600.1	0.4775	0.497	98.938
2	13.957	199.4	5.3	0.543	0.523	1.062



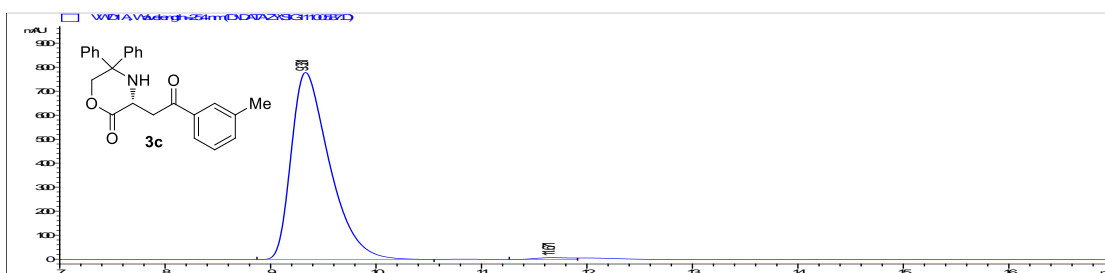
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	12.264	8270.7	256.3	0.4842	0.533	50.095
2	14.38	8239.4	221.3	0.5537	0.543	49.905



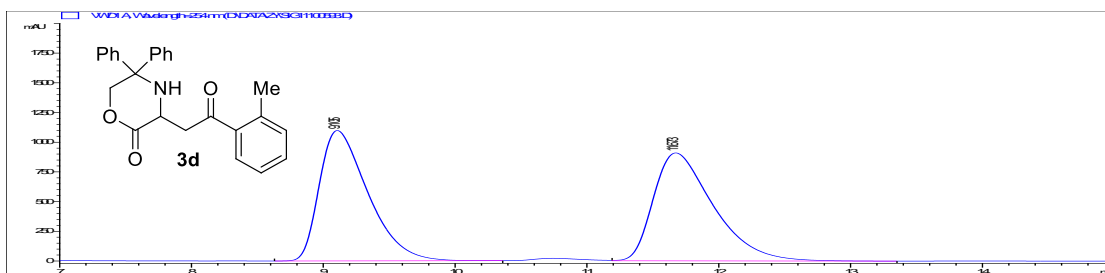
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	12.111	26974.4	846.2	0.4825	0.527	99.113
2	14.178	241.4	6.4	0.5533	0.58	0.887



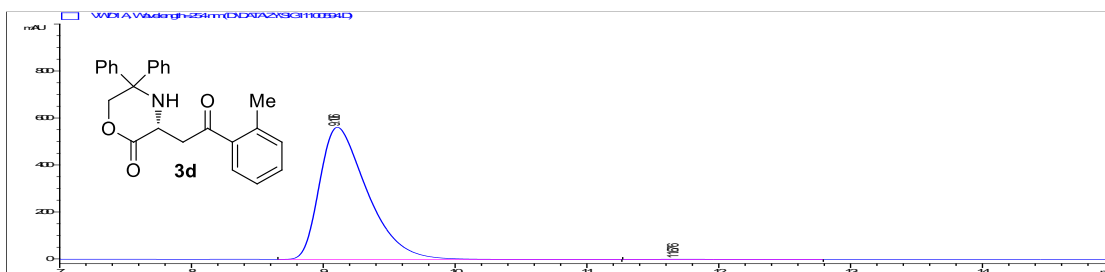
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	9.438	7261.5	288.6	0.378	0.553	50.075
2	11.833	7239.8	235.1	0.4612	0.556	49.925



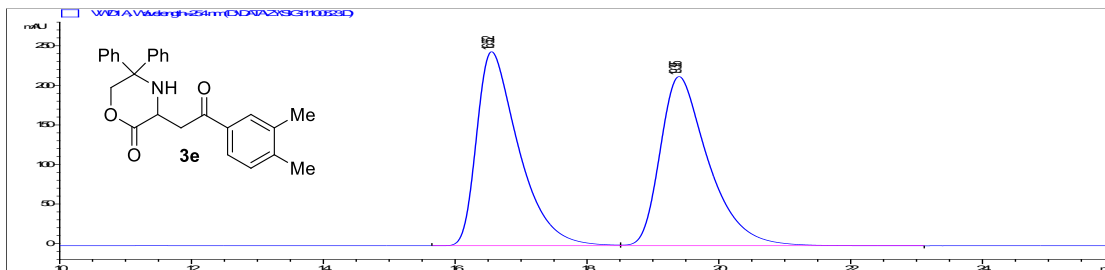
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	9.331	19634.5	779.5	0.3812	0.561	99.085
2	11.671	181.3	7.7	0.3559	0.874	0.915



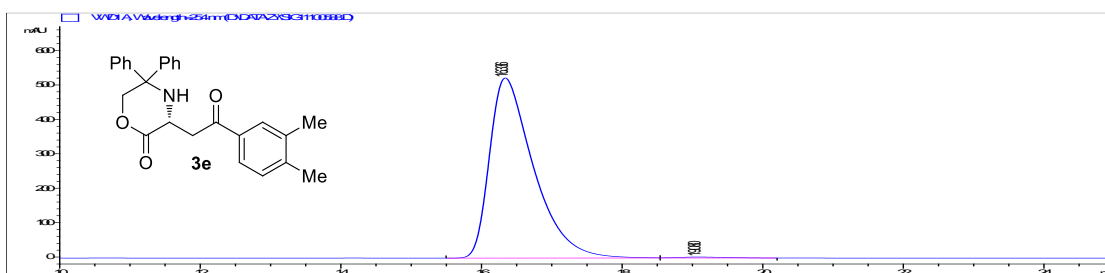
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	9.105	28137.8	1097.6	0.3952	0.55	49.566
2	11.673	28630.9	908.9	0.4782	0.56	50.434



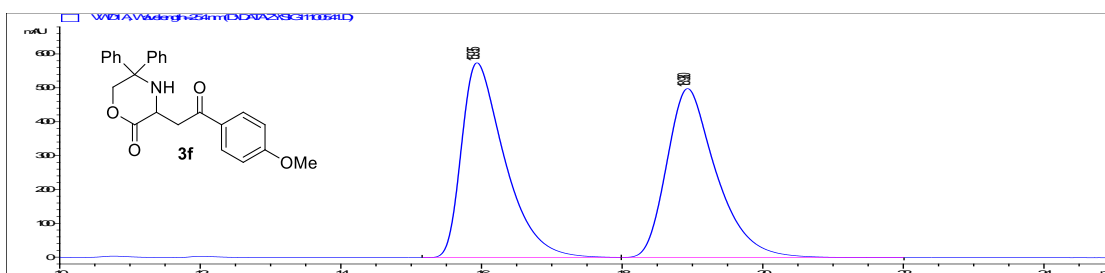
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	9.106	14088.4	561.9	0.3828	0.555	99.803
2	11.676	27.8	7.8E-1	0.4711	0.418	0.197



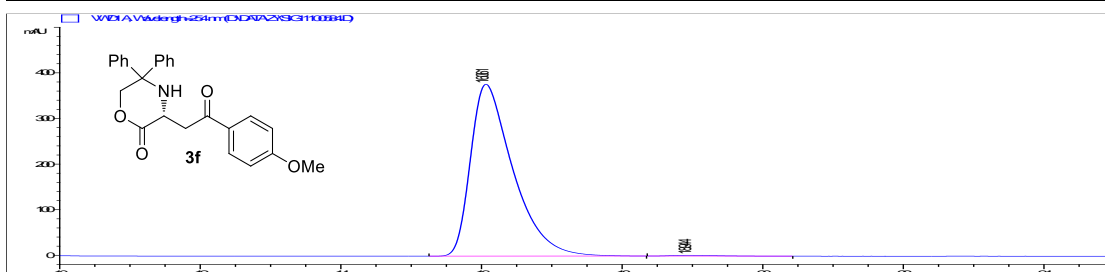
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	16.552	10877.8	245.3	0.6629	0.518	49.994
2	19.395	10880.3	214	0.7593	0.601	50.006



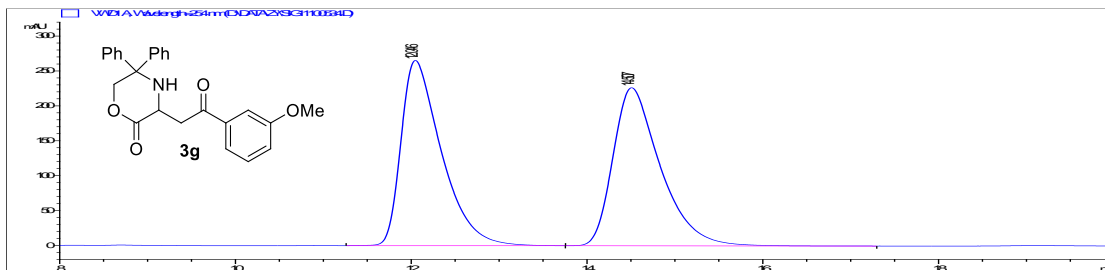
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	16.336	22755.3	523.1	0.6531	0.519	99.431
2	19.08	130.2	2.9	0.6629	0.695	0.569



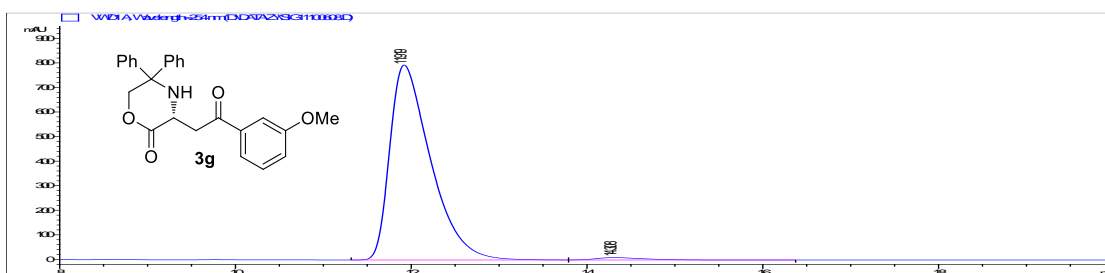
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	15.935	24477.2	575.1	0.6421	0.524	50.130
2	18.93	24350.6	498.4	0.7273	0.678	49.870



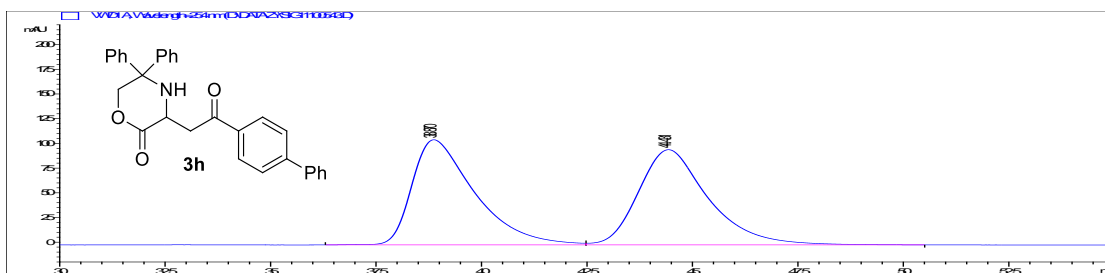
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	16.061	15775.5	376.6	0.6284	0.532	99.528
2	18.944	74.8	1.7	0.6056	0.554	0.472



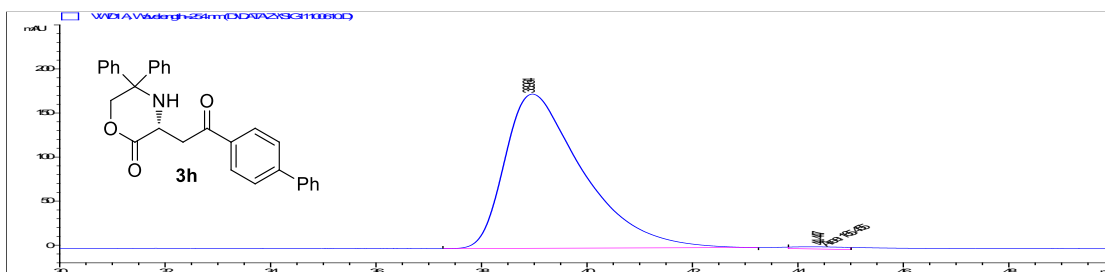
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	12.046	8477.6	265.5	0.4745	0.516	50.034
2	14.507	8466	226.5	0.5585	0.611	49.966



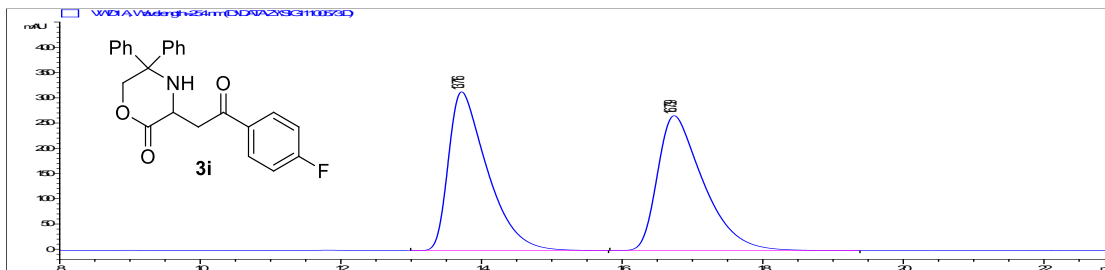
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	11.919	25592.6	793.8	0.4868	0.51	98.567
2	14.308	372.2	9.9	0.5522	0.553	1.433



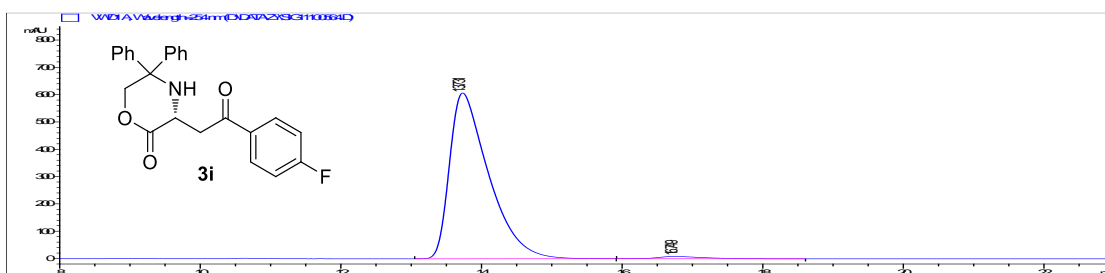
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	38.87	11003.4	106.4	1.5263	0.504	49.775
2	44.431	11102.7	96.4	1.7051	0.706	50.225



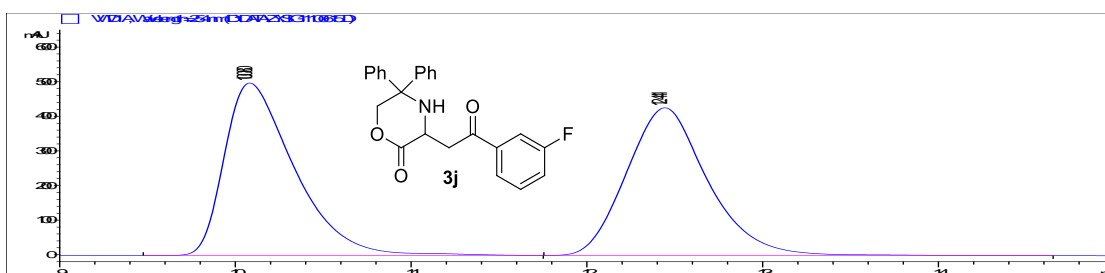
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	38.964	17969.4	175	1.4948	0.51	99.088
2	44.447	165.5	2.5	1.1065	0	0.912



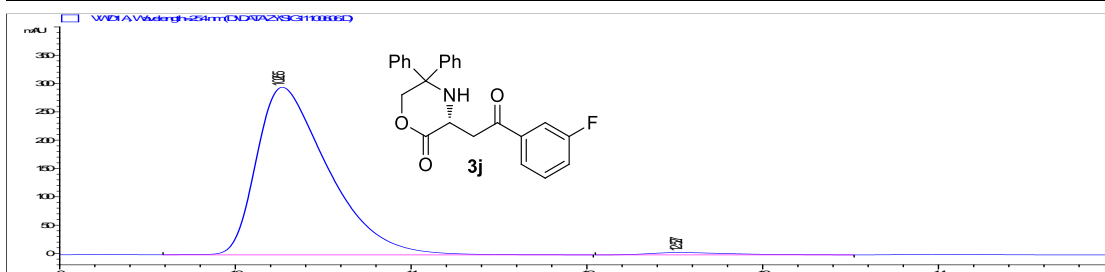
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	13.716	12049.9	314.3	0.5696	0.482	49.979
2	16.739	12059.9	266.9	0.6727	0.536	50.021



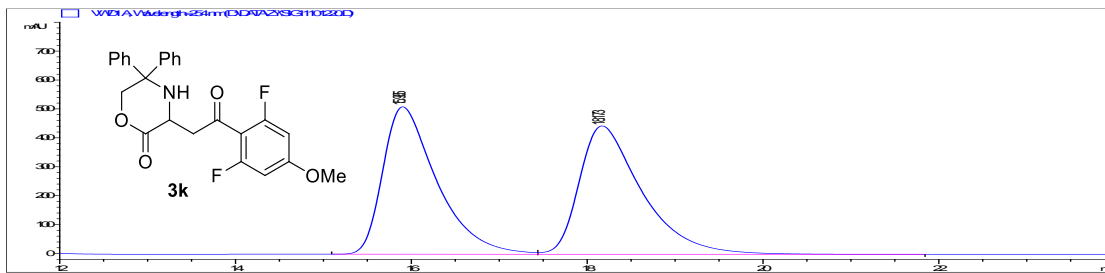
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	13.731	23440.3	607.1	0.5698	0.472	98.467
2	16.749	364.9	8.2	0.6426	0.545	1.533



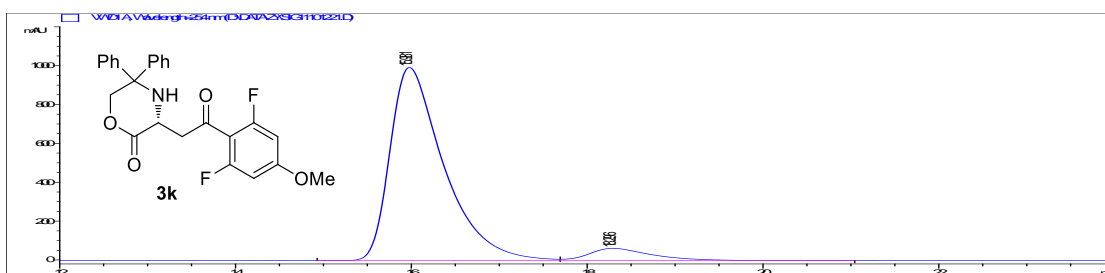
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.08	13772.8	498.3	0.4186	0.533	50.102
2	12.441	13716.9	426.7	0.4886	0.839	49.898



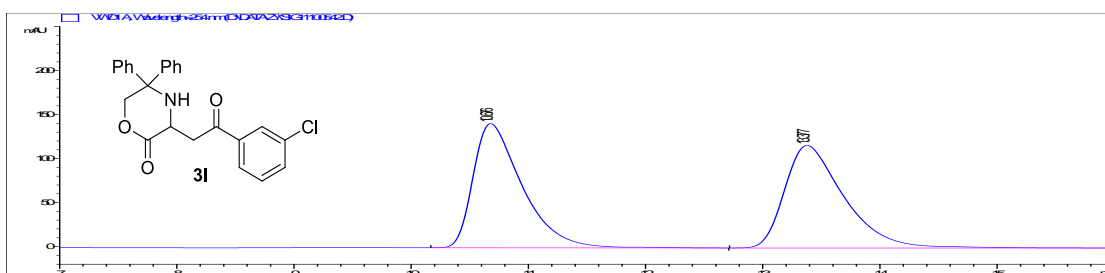
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.265	8378.9	295.9	0.4264	0.527	98.443
2	12.527	132.5	4.1	0.4963	0.531	1.557



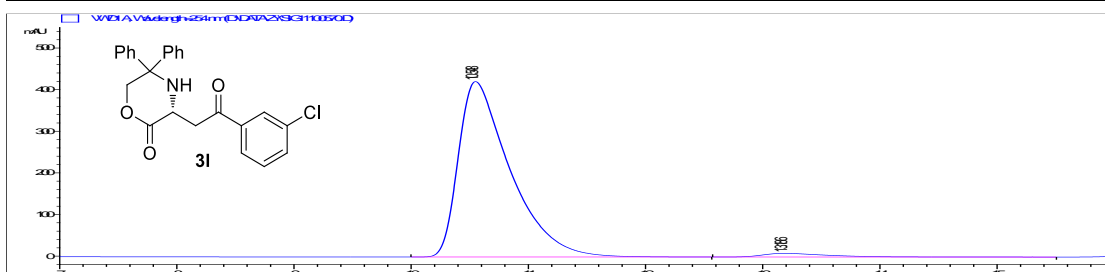
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	15.905	21780.3	509.7	0.6383	0.545	49.809
2	18.173	21947.6	443.7	0.7344	0.539	50.191



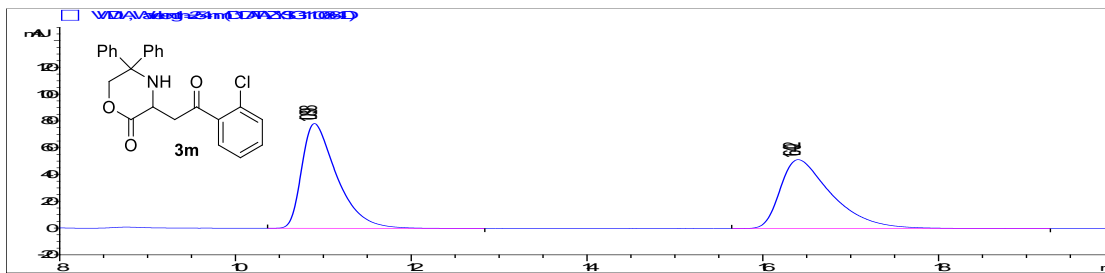
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	15.981	42297.2	993.7	0.6335	0.527	93.159
2	18.296	3106.1	63	0.7297	0.585	6.841



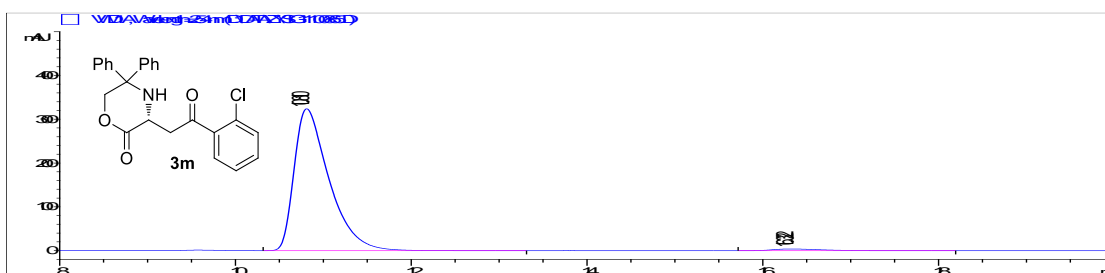
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.676	4100	141.2	0.4348	0.517	50.045
2	13.377	4092.6	116.4	0.5236	0.57	49.955



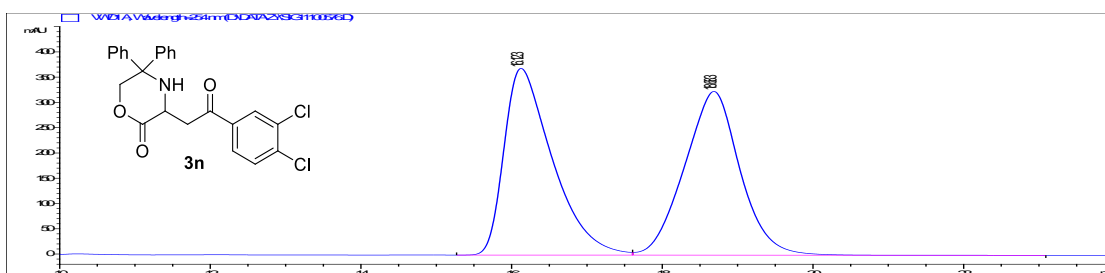
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.548	12919.6	421.4	0.4509	0.464	97.453
2	13.186	337.7	8.9	0.5419	0.469	2.547



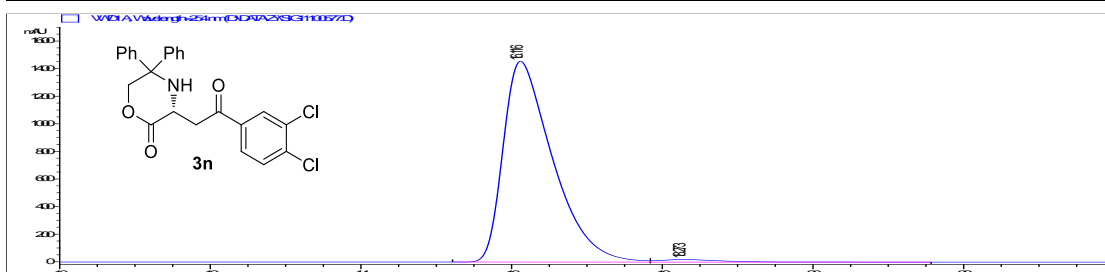
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.898	2168.6	78.3	0.4164	0.527	50.903
2	16.402	2091.6	51.5	0.6024	0.498	49.097



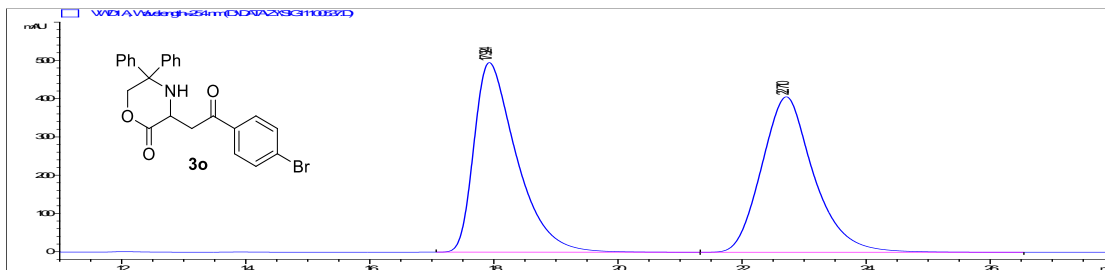
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.81	8945.4	324.1	0.4152	0.525	98.220
2	16.322	162.1	4.1	0.5798	0.549	1.780



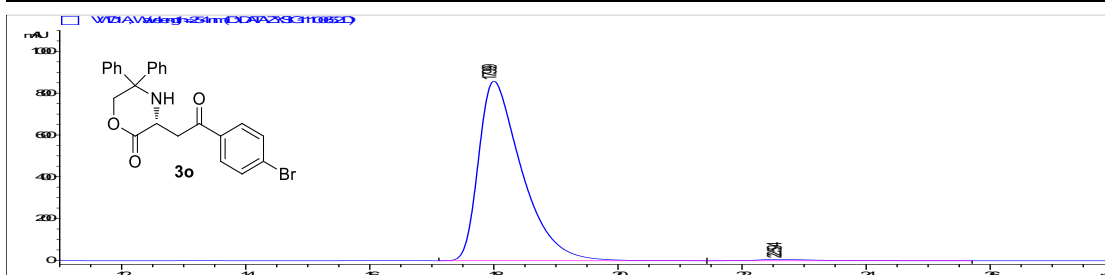
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	16.123	16498.7	369.4	0.6667	0.51	49.861
2	18.683	16590.4	324	0.7692	1.072	50.139



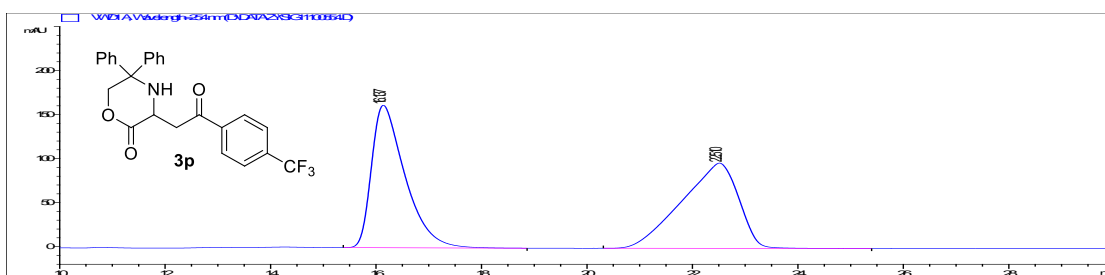
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	16.116	66366.3	1455.5	0.6834	0.507	98.547
2	18.273	978.6	18.6	0.7632	0.561	1.453



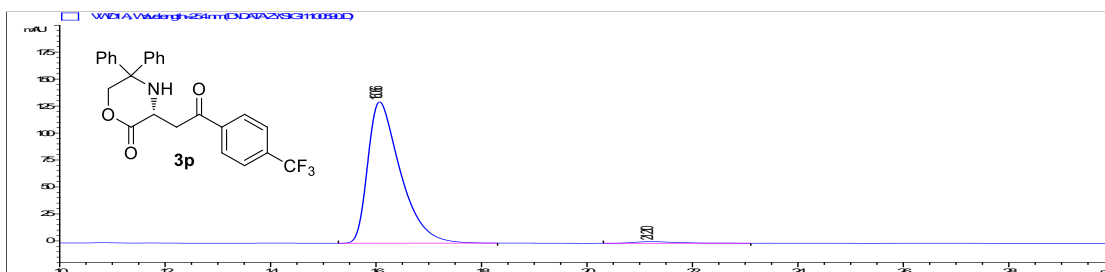
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	17.924	23636.9	495.3	0.714	0.525	49.980
2	22.71	23656.1	406.1	0.8719	0.836	50.020



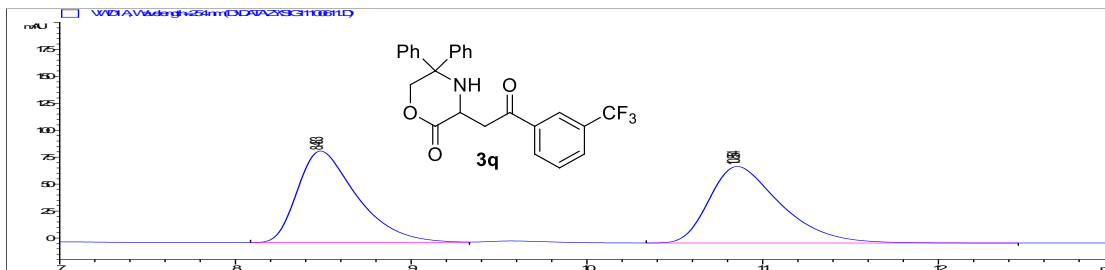
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	17.999	41508	859.5	0.7236	0.515	99.077
2	22.594	386.6	6.2	0.919	0.531	0.923



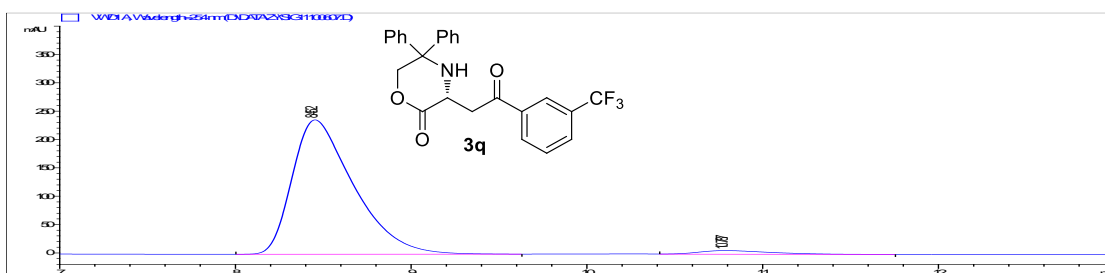
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	16.137	7141.7	161.8	0.6605	0.511	49.589
2	22.51	7260	96.9	1.0783	1.941	50.411



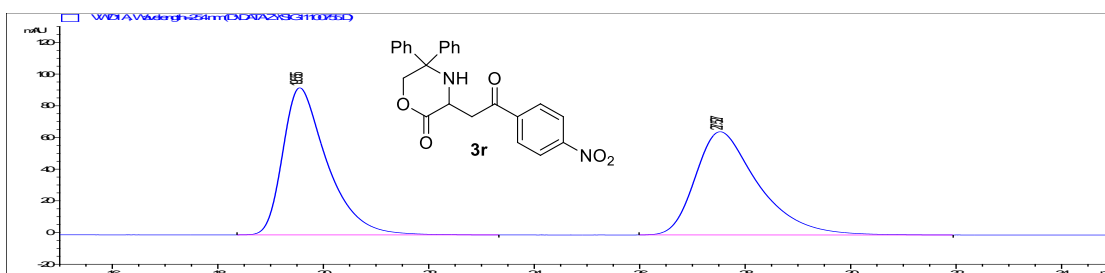
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	16.066	5626.5	131	0.6466	0.529	98.585
2	21.21	80.8	1.5	0.7199	0.628	1.415



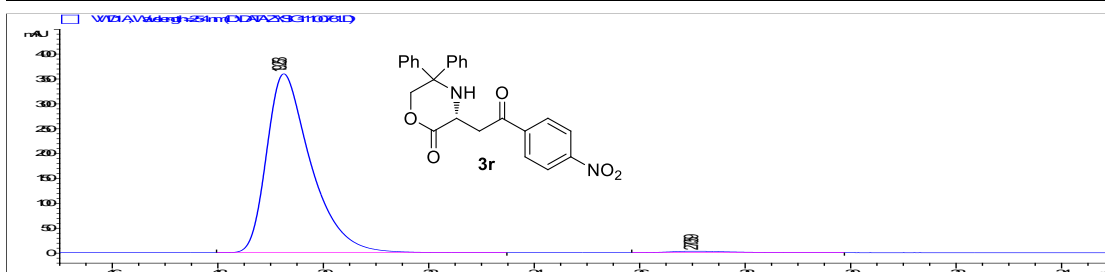
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	8.483	2005.4	84.9	0.3542	0.587	50.067
2	10.854	2000	70.9	0.4252	0.609	49.933



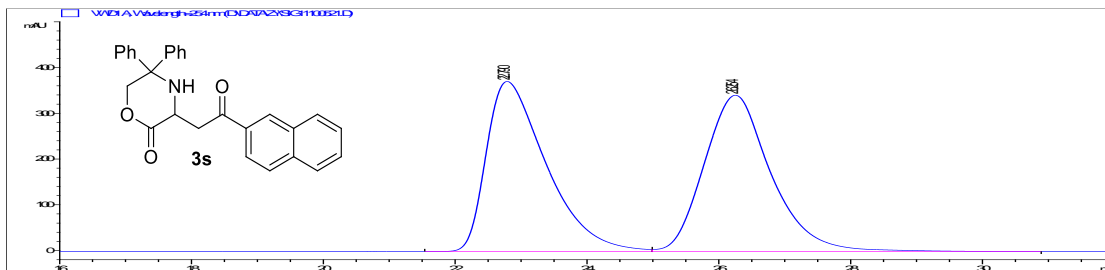
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	8.452	5739.9	236.8	0.3614	0.56	96.984
2	10.787	178.5	6.4	0.4248	0.567	3.016



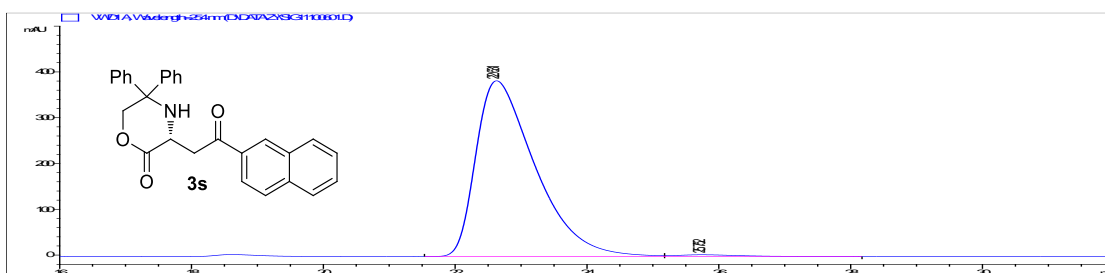
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	19.555	5429.4	92.8	0.8687	0.579	50.117
2	27.527	5404	65.2	1.2297	0.614	49.883



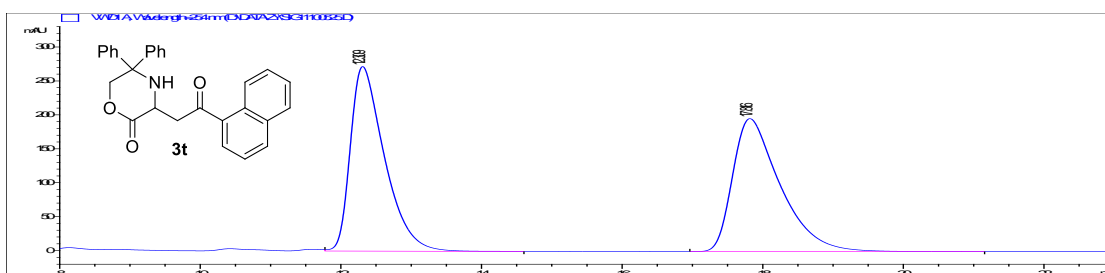
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	19.253	20943.6	359.5	0.869	0.59	98.846
2	27.059	244.6	3	0.9914	0.652	1.154



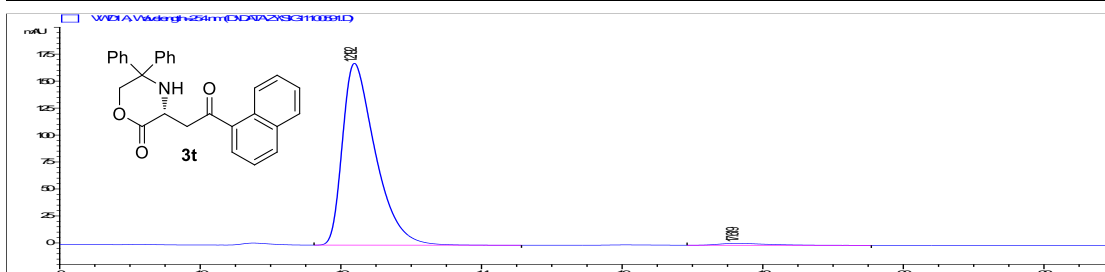
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	22.79	23452.7	371.5	0.9549	0.499	49.451
2	26.254	23973.8	341.4	1.0551	0.82	50.549



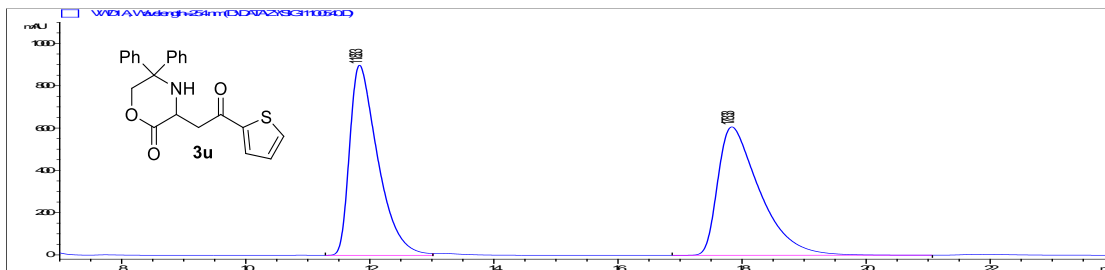
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	22.631	23986.2	383.7	0.939	0.5	98.911
2	25.752	264	3.9	0.8372	0.628	1.089



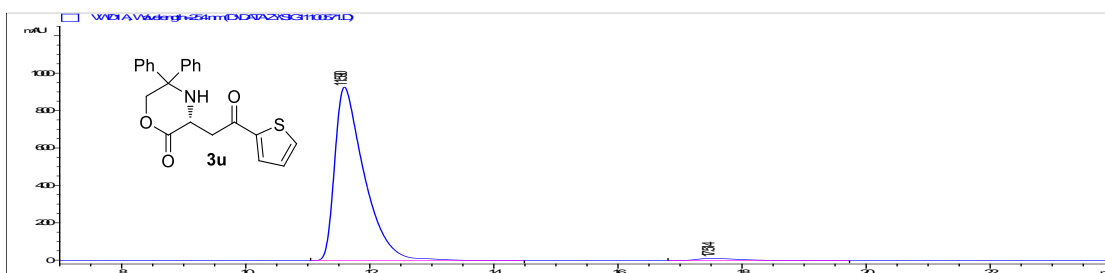
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	12.309	9148.3	271.8	0.5033	0.532	49.897
2	17.816	9186.2	195.8	0.6959	0.534	50.103



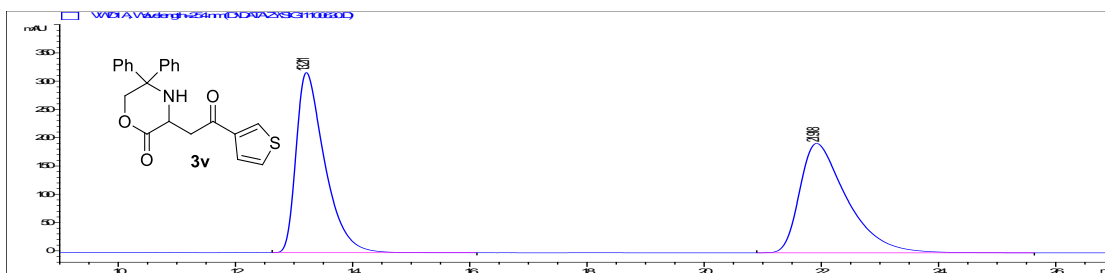
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	12.192	5470.8	168.6	0.4921	0.533	98.493
2	17.619	83.7	1.7	0.707	0.513	1.507



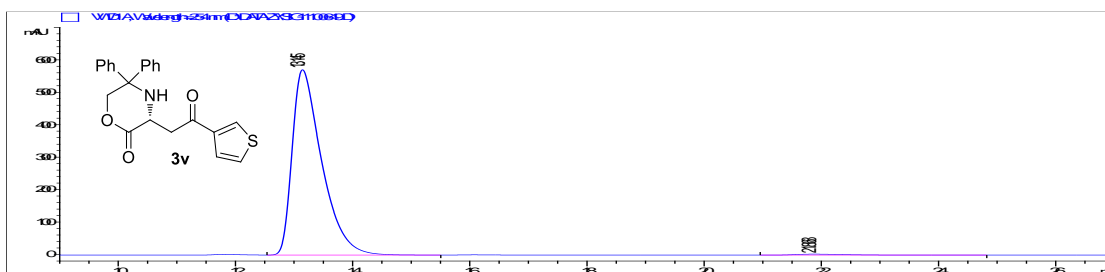
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	11.833	28320.6	898.8	0.4754	0.505	49.925
2	17.833	28405.9	606.9	0.7004	0.465	50.075



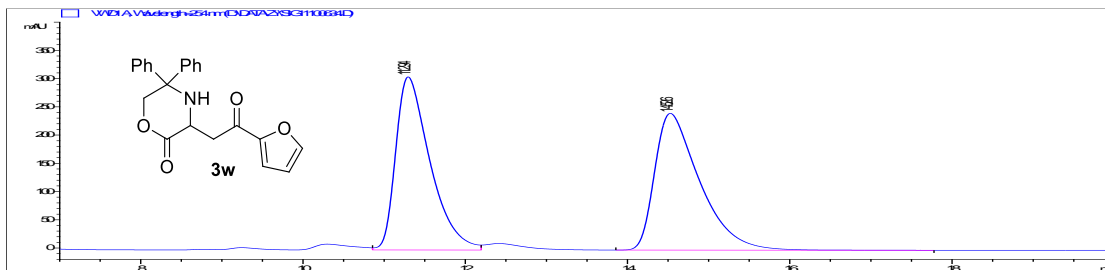
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	11.59	30580.5	927.3	0.4808	0.452	98.115
2	17.514	587.5	12.3	0.6963	0.487	1.885



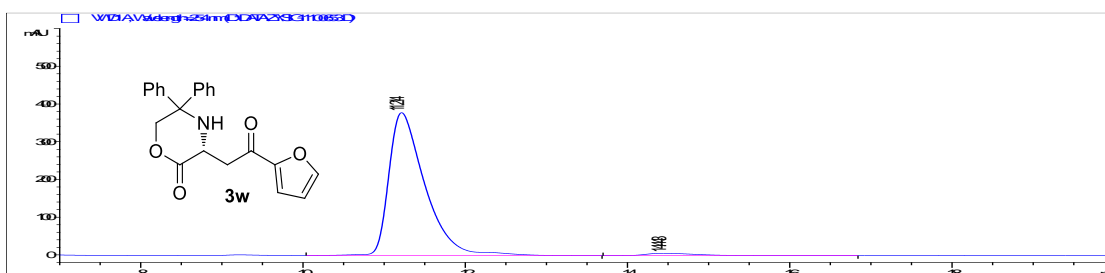
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	13.211	10803.2	318.6	0.5092	0.529	50.019
2	21.918	10795.1	193.4	0.8318	0.519	49.981



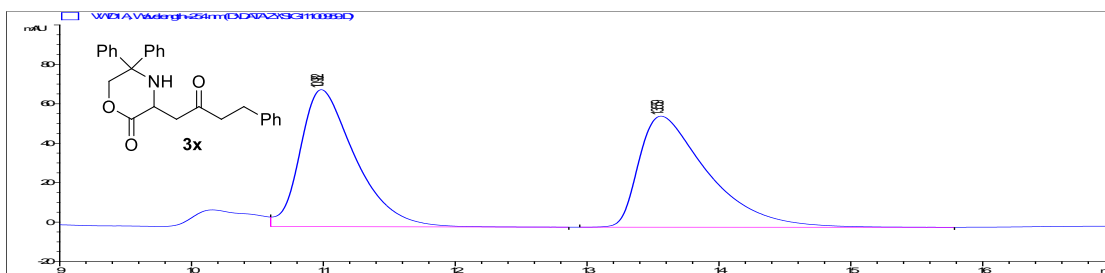
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	13.145	19962.3	571	0.5244	0.508	99.125
2	21.868	176.1	3	0.8253	0.53	0.875



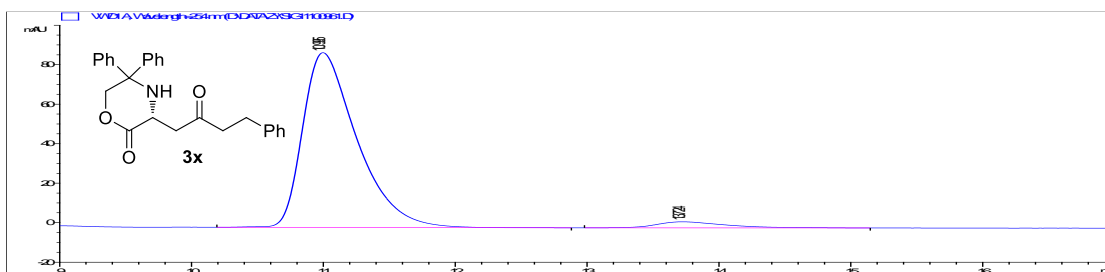
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	11.294	9019.5	306.4	0.4454	0.534	49.187
2	14.526	9317.5	242.1	0.5743	0.497	50.813



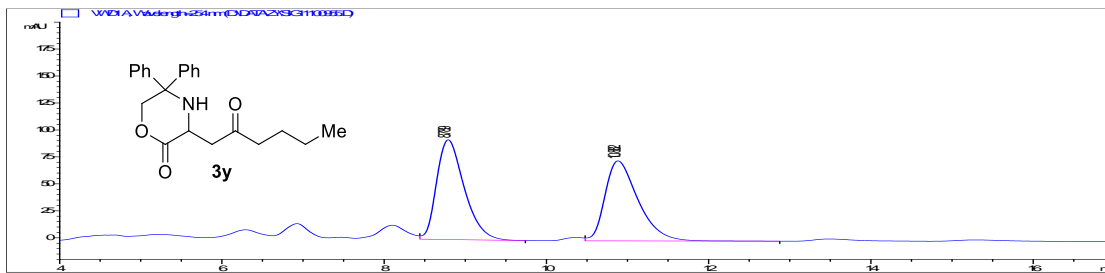
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	11.214	11723.6	378.7	0.4631	0.509	97.710
2	14.443	274.7	6.4	0.6741	0.495	2.290



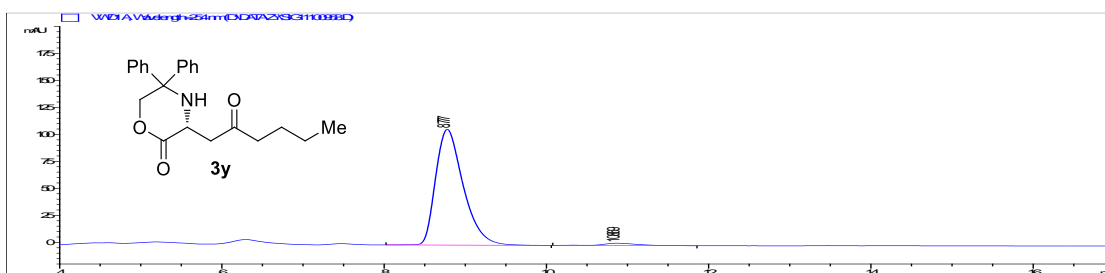
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.982	2020.3	69.5	0.4384	0.586	49.734
2	13.559	2042	56.3	0.5397	0.437	50.266



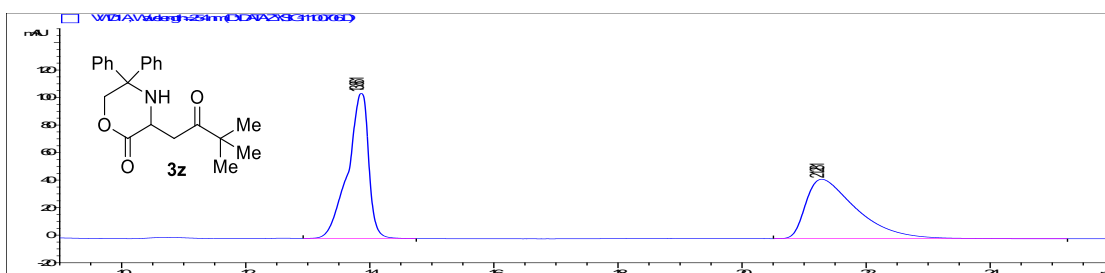
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	10.995	2531.1	88.5	0.4327	0.559	95.697
2	13.724	113.8	3.1	0.506	0.594	4.303



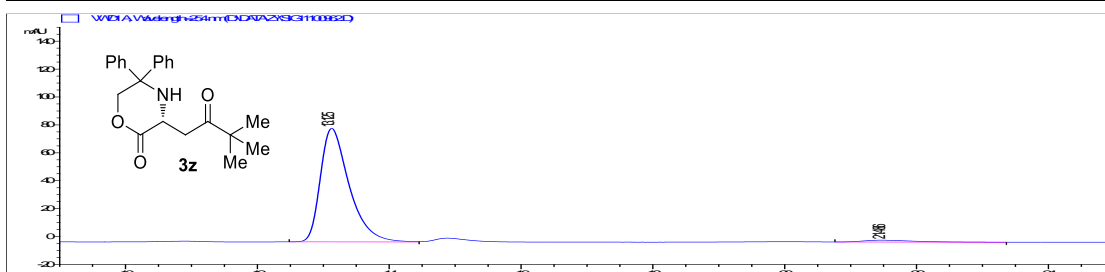
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	8.789	2191.1	92.5	0.3667	0.679	51.028
2	10.882	2102.7	74.2	0.4326	0.608	48.972



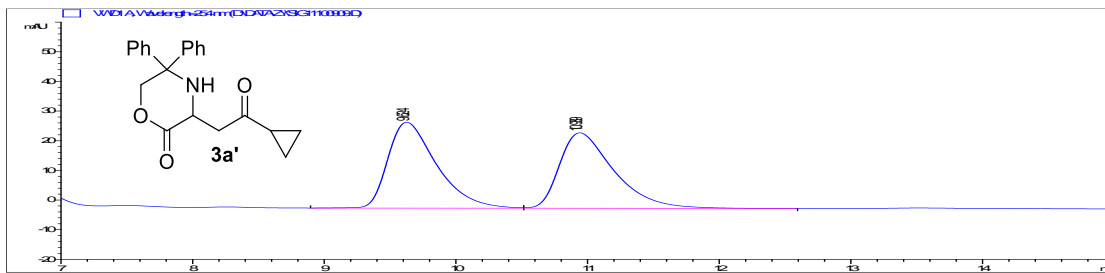
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	8.777	2536.7	107.2	0.3634	0.678	97.474
2	10.869	65.7	2.2	0.4447	0.748	2.526



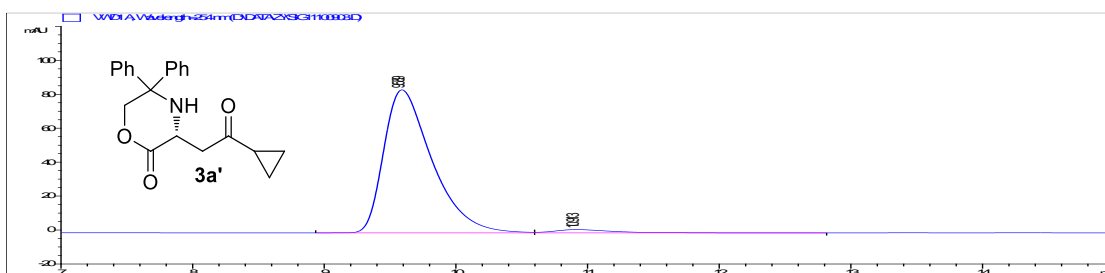
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	13.861	2452.5	105.4	0.3472	1.82	49.986
2	21.281	2453.8	43.2	0.8495	0.419	50.014



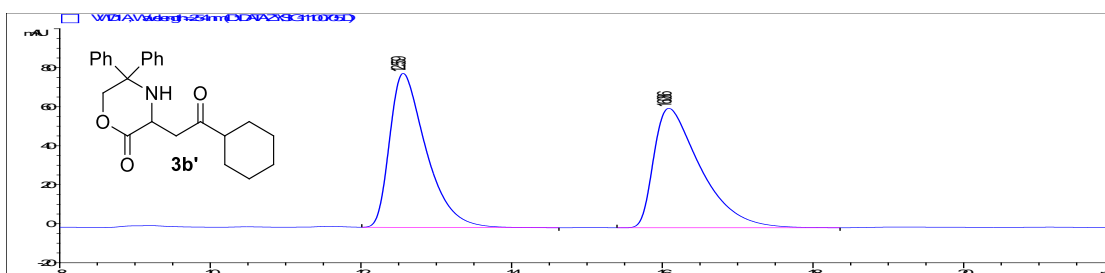
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	13.125	2471.2	81.3	0.4594	0.605	97.260
2	21.486	69.6	1.3	0.6324	0.613	2.740



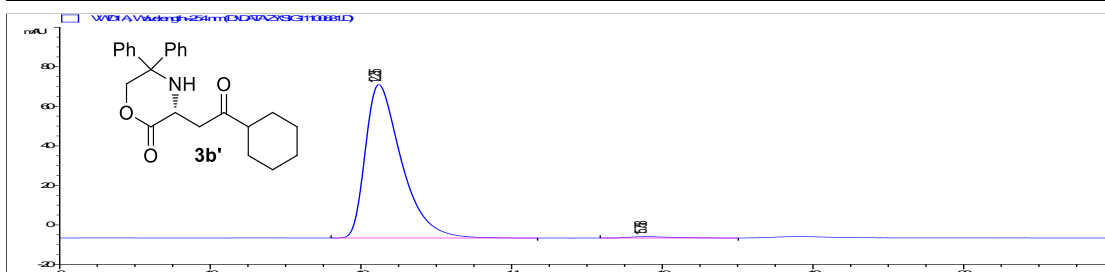
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	9.624	743	29	0.3896	0.587	50.547
2	10.939	726.9	25.4	0.4328	0.552	49.453



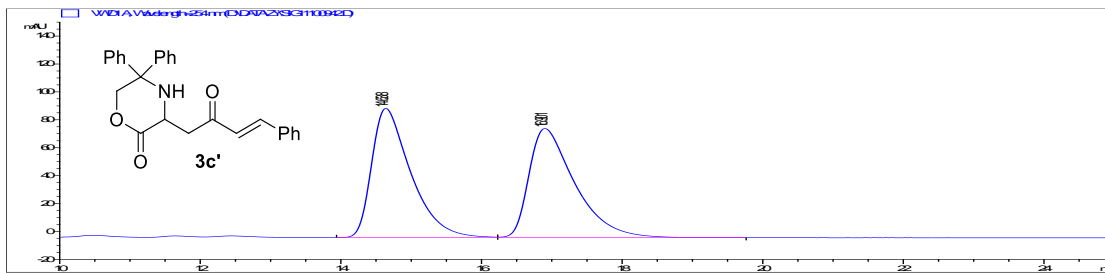
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	9.589	2150.8	84.3	0.3851	0.566	97.229
2	10.913	61.3	2	0.4598	0.52	2.771



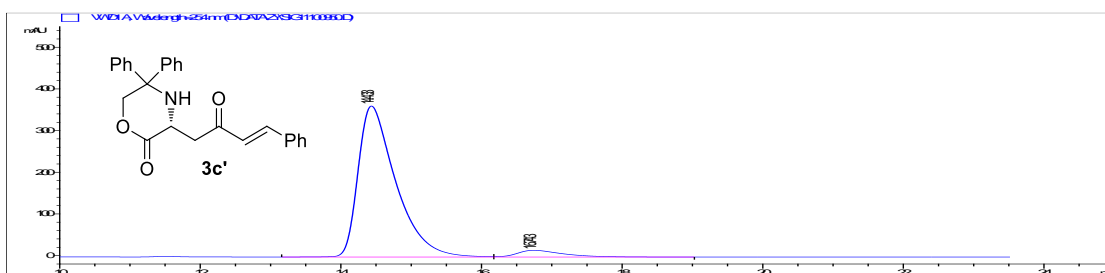
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	12.559	2653.9	79	0.5057	0.552	50.080
2	16.086	2645.5	61.3	0.6465	0.442	49.920



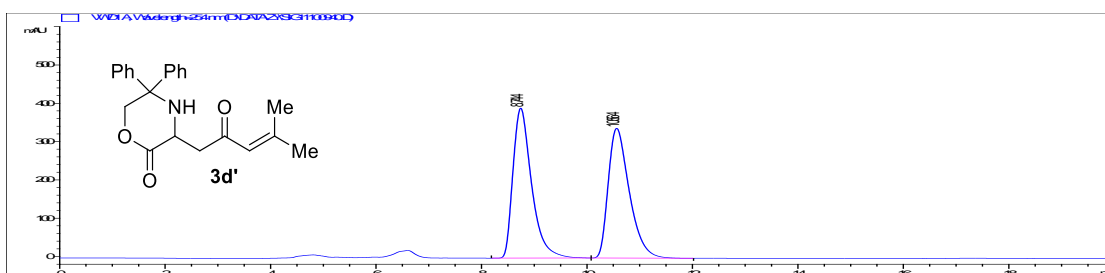
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	12.235	2583.4	77.6	0.5048	0.552	98.974
2	15.758	26.8	6.7E-1	0.4827	0.533	1.026



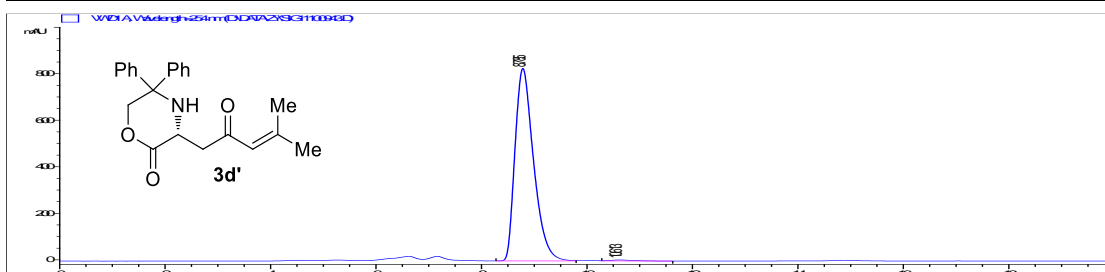
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	14.638	3573.5	92.5	0.573	0.533	50.227
2	16.901	3541.2	78.2	0.6801	0.498	49.773



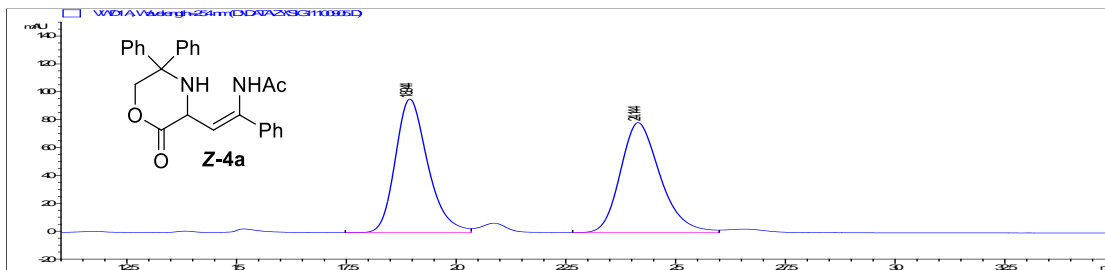
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	14.433	13495.3	362.4	0.5539	0.511	94.899
2	16.743	725.4	16.2	0.6476	0.539	5.101



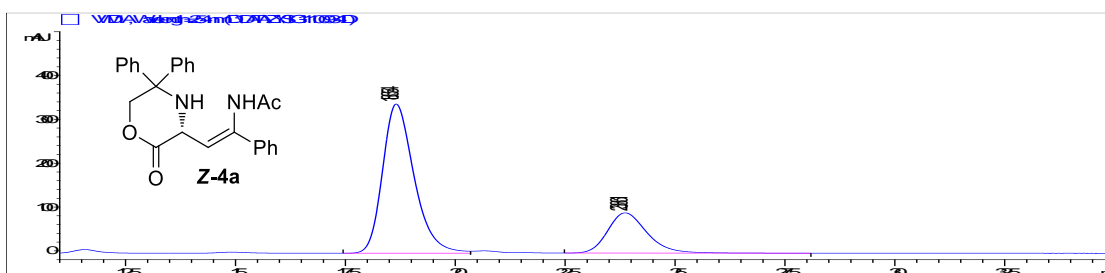
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	8.744	9612.8	391.4	0.3797	0.658	50.588
2	10.564	9389.4	338.8	0.4252	0.629	49.412



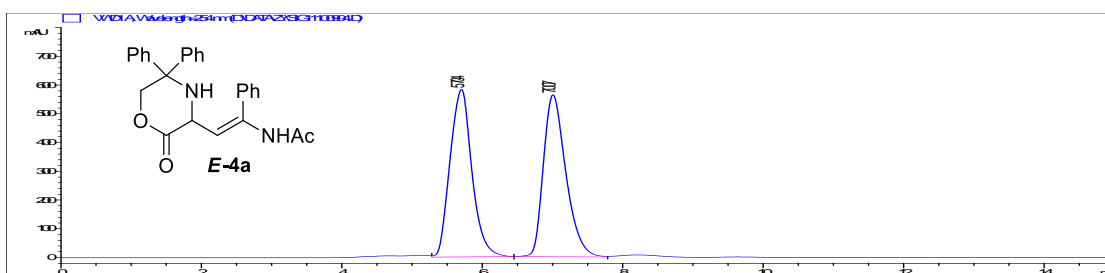
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	8.785	20236.6	827.4	0.3785	0.682	99.370
2	10.613	128.3	4.4	0.4337	0.661	0.630



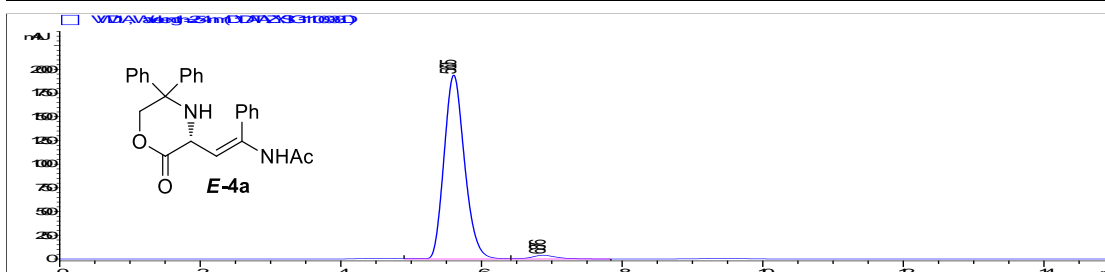
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	18.944	4934.5	95.8	0.7842	0.76	49.809
2	24.144	4972.4	78.9	0.9738	0.758	50.191



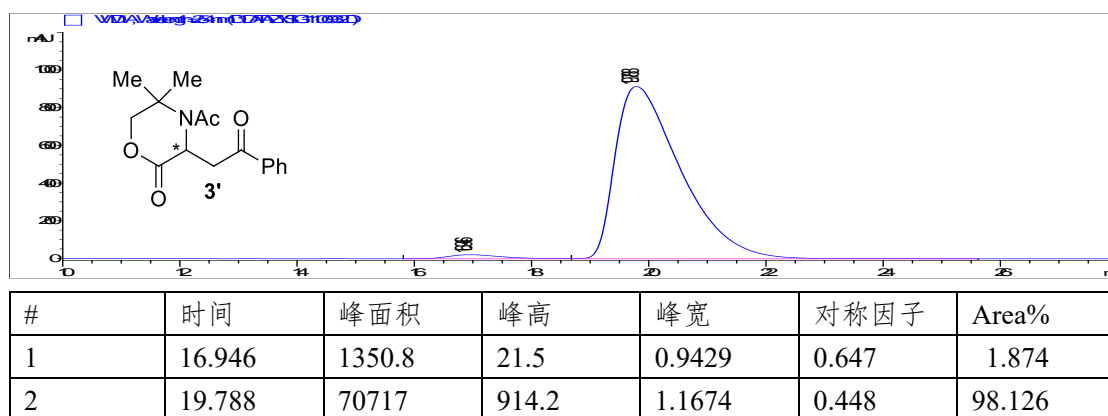
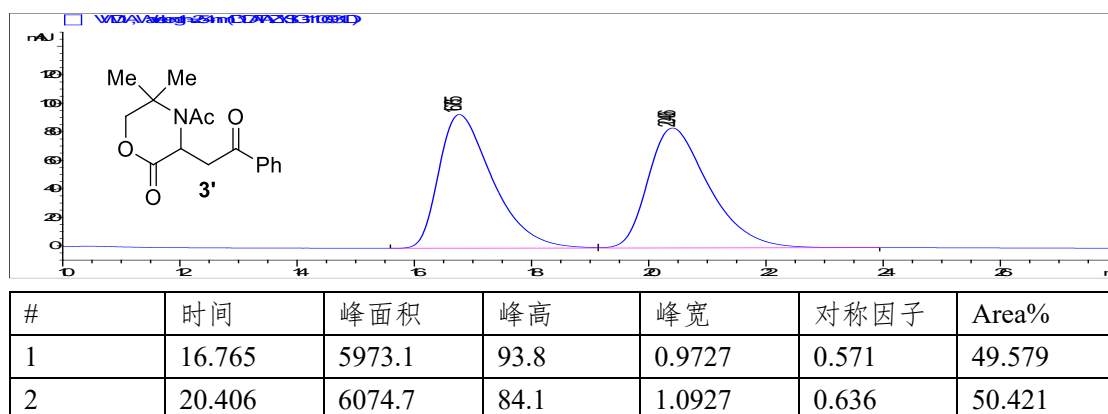
#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	18.654	16995	340.4	0.7689	0.716	74.886
2	23.861	5699.5	91.8	0.9572	0.753	25.114



#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	5.704	12597.1	582.5	0.3397	1.011	50.152
2	7.007	12520.9	563.6	0.3437	0.698	49.848

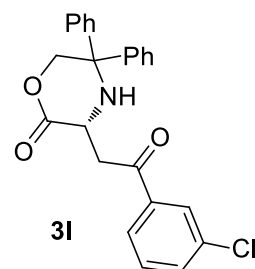
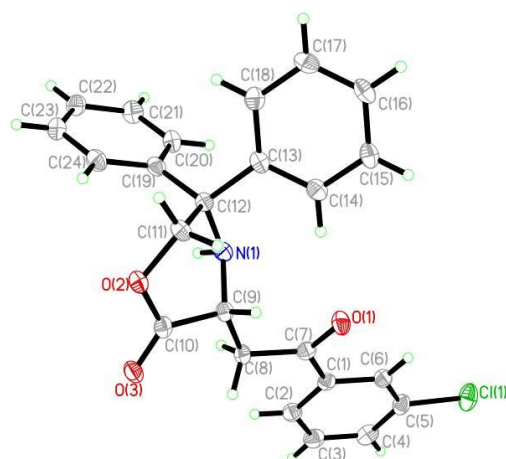


#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	5.605	39255.9	1940.1	0.3118	0.841	97.617
2	6.876	958.5	39.1	0.3675	0.855	2.383



## 5. X-Ray crystallographic data

The X-ray crystallographic structures for compound **31**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 1914728. The compound **31** (60 mg) was dissolved in DCM (1.5 mL), then n-hexane (15.0 mL) was added slowly, and the mixture was allowed to stand at room temperature to recrystallize to provided the single stereoisomer. The absolute configuration was determined to be *R* from the X-ray structural analysis.



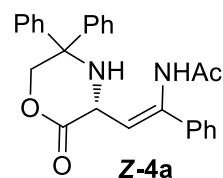
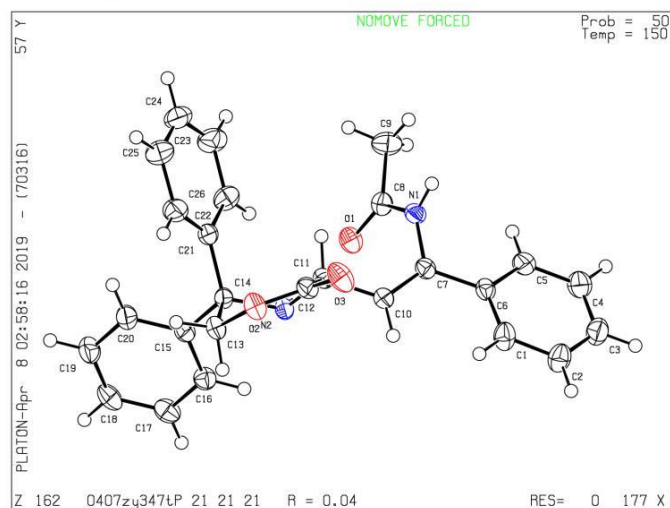
Crystal data and structure refinement for **3I**.

Empirical formula	C <sub>24</sub> H <sub>20</sub> Cl N O <sub>3</sub>
Identification code	3I
Formula weight	405.86
Temperature	100 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P1211
Unit cell dimensions	a = 9.2465 (3) Å    a = 90° b = 7.9689 (3) Å    b = 99.416 (4)° c = 13.2794 (6) Å    c = 90°
Volume	965.30 (7) Å <sup>3</sup>
Z, Calculated density	2, 1.396 g/cm <sup>3</sup>
Absorption coefficient	0.225 mm <sup>-1</sup>
F(000)	424.0
Crystal size	0.2 x 0.2 x 0.1 mm <sup>3</sup>
Theta range for data collection	4.466 to 61.588°
Limiting indices	-11 ≤ h ≤ 12, -11 ≤ k ≤ 10, -18 ≤ l ≤ 16
Reflections collected / unique	15330/4868 [R(int) = 0.0477, R(sigma) = 0.0555]
Data/restraints/parameters	4868 / 1 / 266
Goodness-of-fit on F <sup>2</sup>	1.057
Final R indices [I > 2σ(I)]	R1 = 0.0429, wR2 = 0.0877
R indices (all data)	R1 = 0.0565, wR2 = 0.0926
Largest diff. peak and hole	0.28 and -0.23 e.Å <sup>-3</sup>

The X-ray crystallographic structures for compound **Z-4a**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 1914731. The

compound **Z-4a** (10 mg) was dissolved in DCM (1.0 mL), then n-hexane (10.0 mL) was added slowly, and the mixture was allowed to stand at room temperature to recrystallize to provided the single stereoisomer.

Datablock 0407zq347tP\_0m - ellipsoid plot

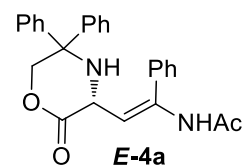
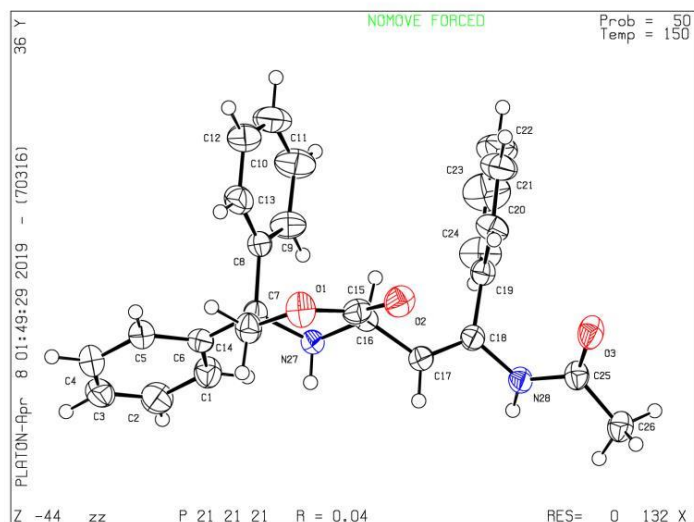


#### Crystal data and structure refinement for **Z-4a**.

Empirical formula	C <sub>26</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub>
Identification code	Z-4a
Formula weight	412.47
Temperature	150 K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, P212121
Unit cell dimensions	a = 8.6867 (2) Å a = 90° b = 15.1223 (3) Å b = 90° c = 16.0874 (3) Å g = 90°
Volume	2113.29 (8) Å <sup>3</sup>
Z, Calculated density	4, 1.296 g/cm <sup>3</sup>
Absorption coefficient	0.684 mm <sup>-1</sup>
F(000)	872.0
Crystal size	0.15 x 0.12 x 0.08 mm <sup>3</sup>
Theta range for data collection	8.024 to 149.206°
Limiting indices	-9<=h<=10, -18<=k<=18, -20<=l<=20
Reflections collected / unique	20597/4270 [R(int) = 0.0599, R(sigma) = 0.0386]
Data/restraints/parameters	4270/0/285
Goodness-of-fit on F <sup>2</sup>	1.125
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.0872
R indices (all data)	R1 = 0.0483, wR2 = 0.0907
Largest diff. peak and hole	0.18/-0.20 e.Å <sup>-3</sup>

The X-ray crystallographic structures for compound **E-4a**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 1914733. The compound **E-4a** (10 mg) was dissolved in DCM (1.0 mL), then n-hexane (10.0 mL) was added slowly, and the mixture was allowed to stand at room temperature to recrystallize to provided the single stereoisomer.

Datablock zz - ellipsoid plot



#### Crystal data and structure refinement for **E-4a**.

Empirical formula	C <sub>26</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub>
Identification code	<i>E-4a</i>
Formula weight	412.47
Temperature	150 K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, P212121
Unit cell dimensions	a = 9.4501(3) Å a = 90° b = 9.7777(3) Å b = 90° c = 23.5886(8) Å g = 90°
Volume	2179.59(12) Å <sup>3</sup>
Z, Calculated density	4, 1.257 g/cm <sup>3</sup>
Absorption coefficient	0.663 mm <sup>-1</sup>
F(000)	872.0
Crystal size	0.08 x 0.05 x 0.04 mm <sup>3</sup>
Theta range for data collection	9.792 to 148.972°
Limiting indices	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -28 ≤ l ≤ 29
Reflections collected / unique	23098/4337 [R(int) = 0.0510]
Data/restraints/parameters	4337/0/285
Goodness-of-fit on F <sup>2</sup>	1.009
Final R indices [I > 2σ(I)]	R1 = 0.0430, wR2 = 0.1172

R indices (all data)	R1 = 0.0460, wR2 = 0.1202
Largest diff. peak and hole	0.25/-0.16 e.Å <sup>-3</sup>