

**ISCI, Volume 22**

**Supplemental Information**

**Nickel/Brønsted Acid-Catalyzed**

**Chemo- and Enantioselective Intermolecular**

**Hydroamination of Conjugated Dienes**

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Supplemental figures for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ -NMR spectra of substrate 1a-1j.

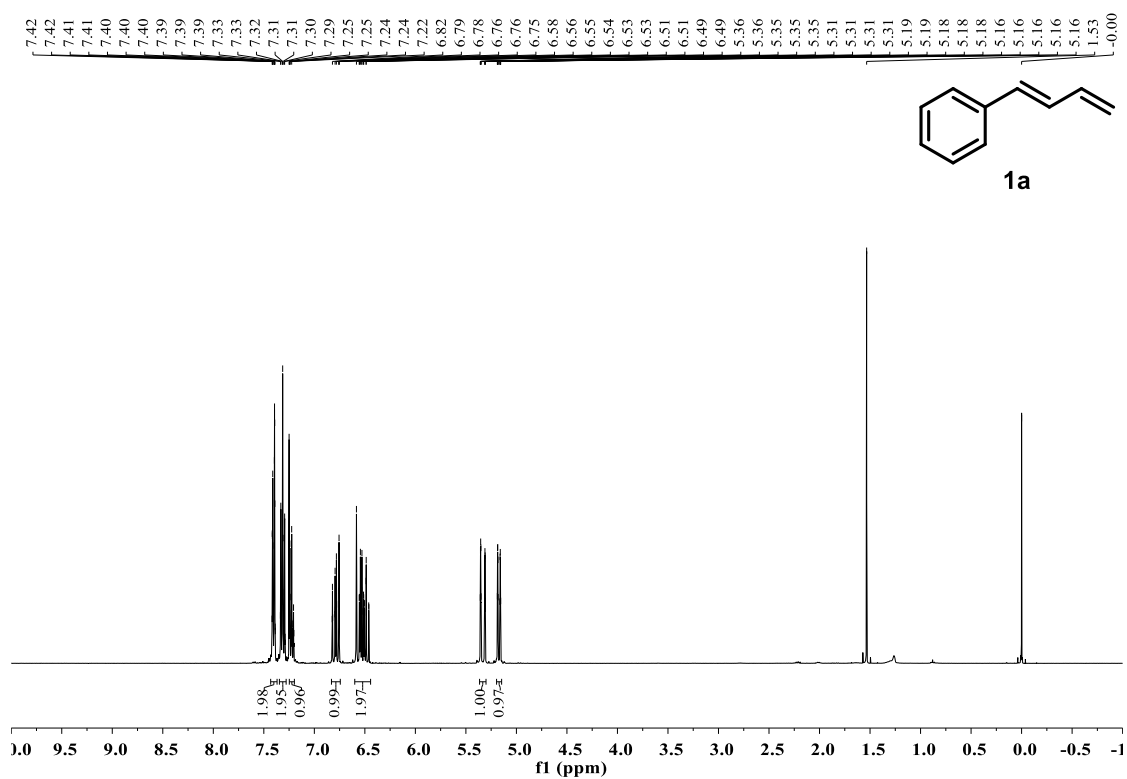


Figure S1.  $^1\text{H}$  NMR spectra of substrate **1a**, related to Figure 2.

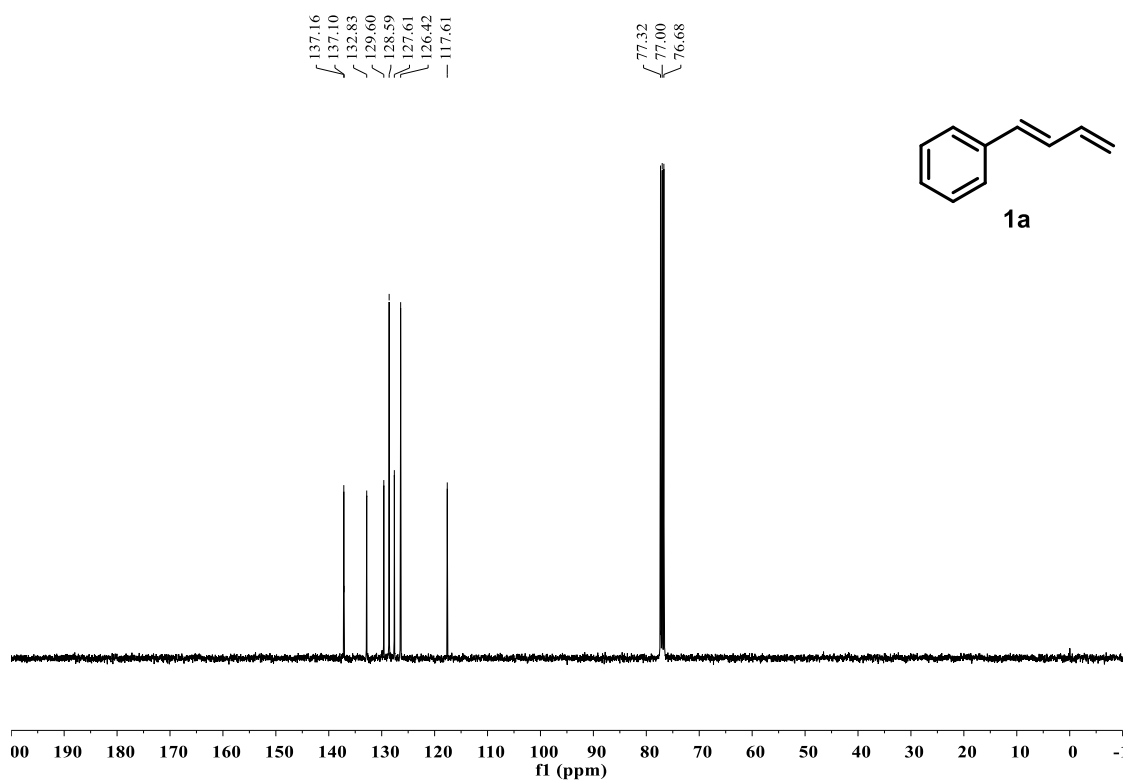
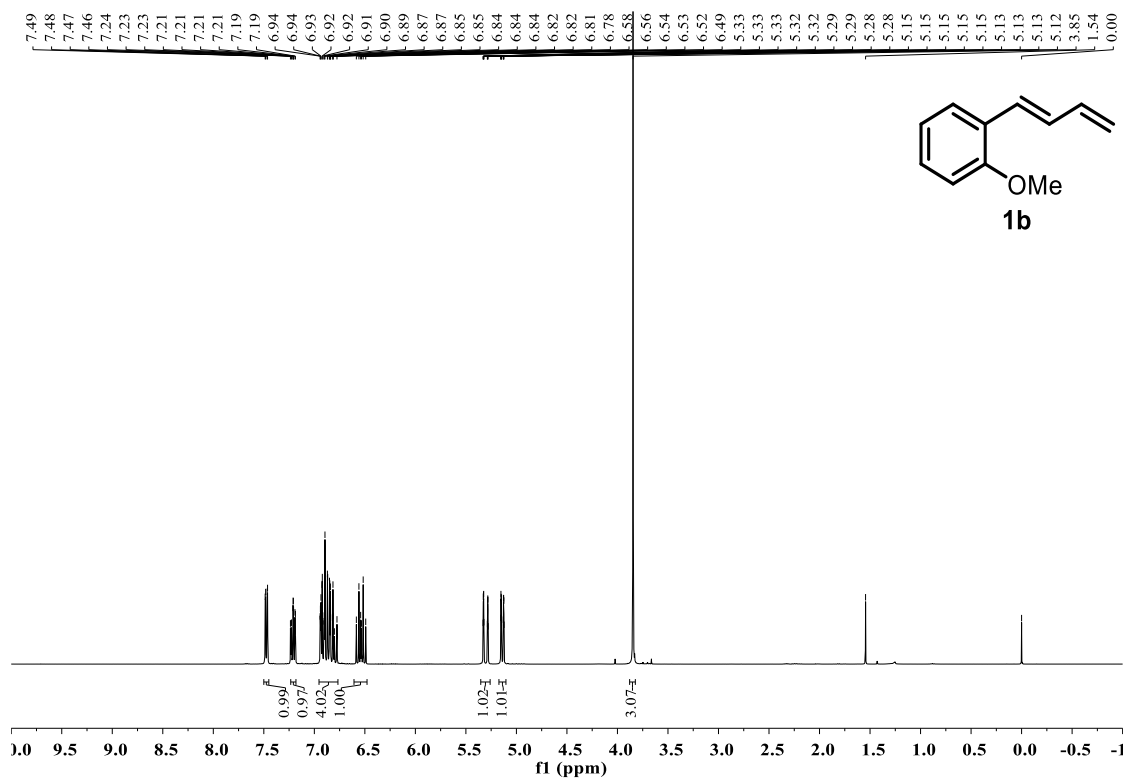
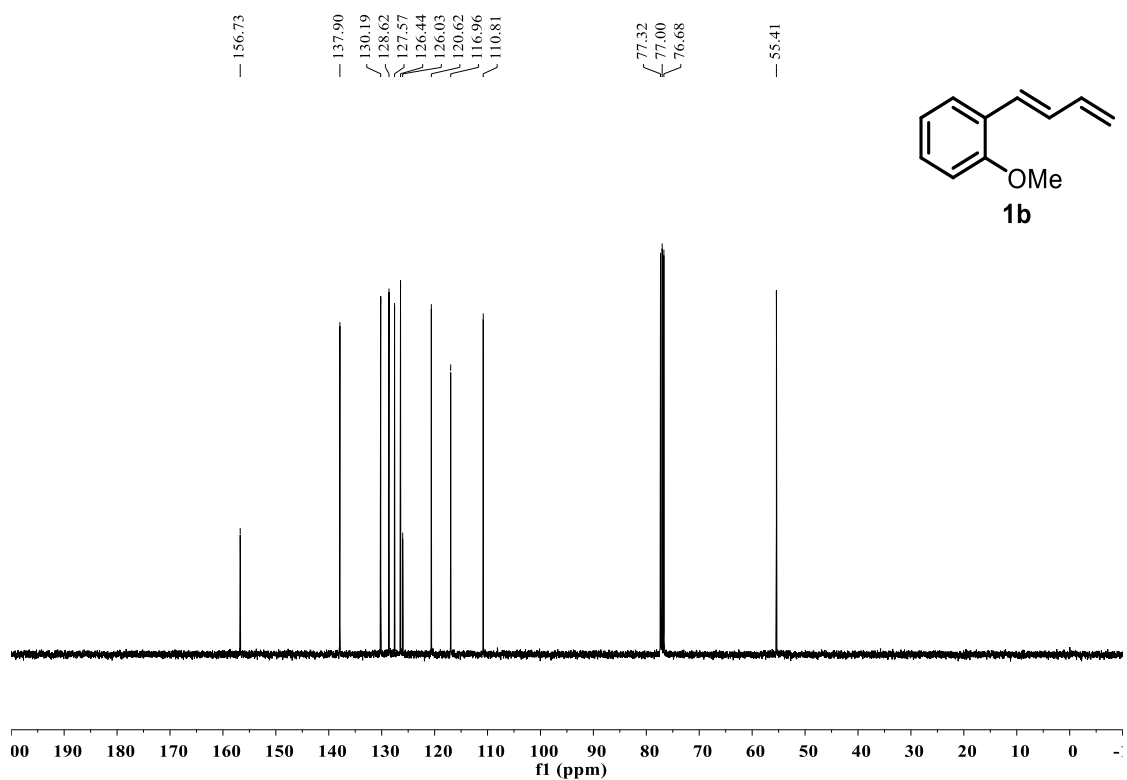


Figure S2.  $^{13}\text{C}$  NMR spectra of substrate **1a**, related to Figure 2.



**Figure S3.** <sup>1</sup>H NMR spectra of substrate **1b**, related to **Figure 4**.



**Figure S4.** <sup>13</sup>C NMR spectra of substrate **1b**, related to **Figure 4**.

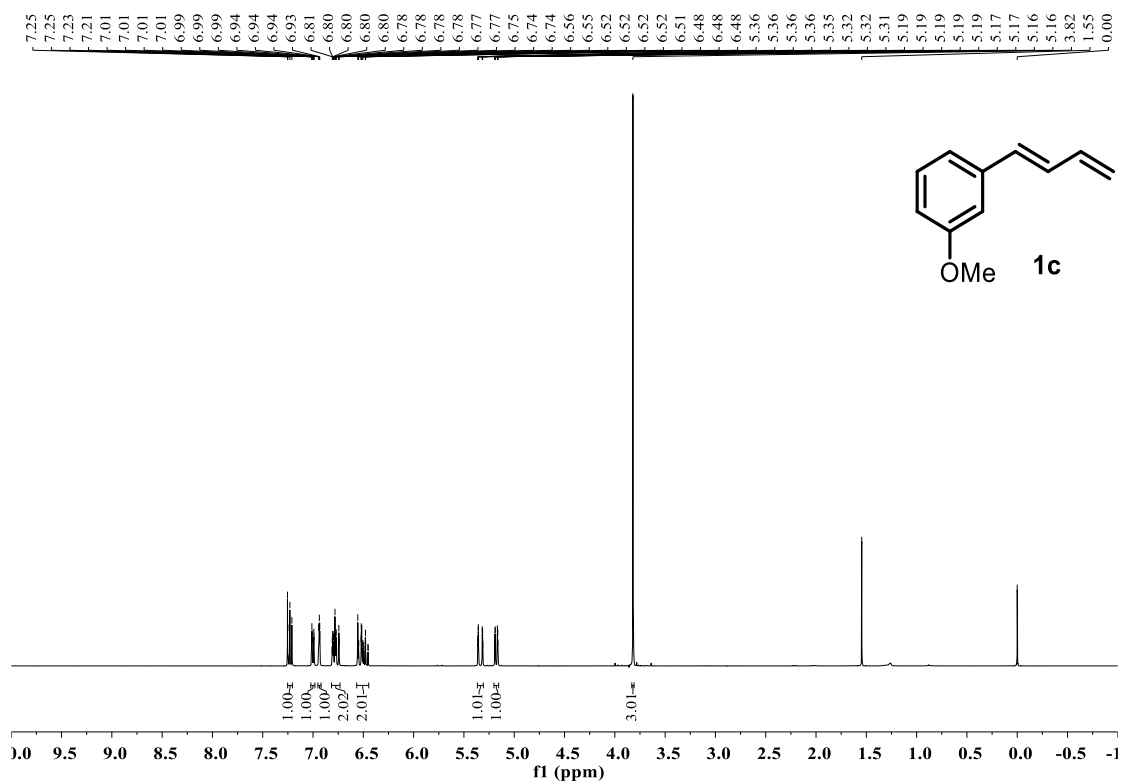


Figure S5. <sup>1</sup>H NMR spectra of substrate **1c**, related to Figure 4.

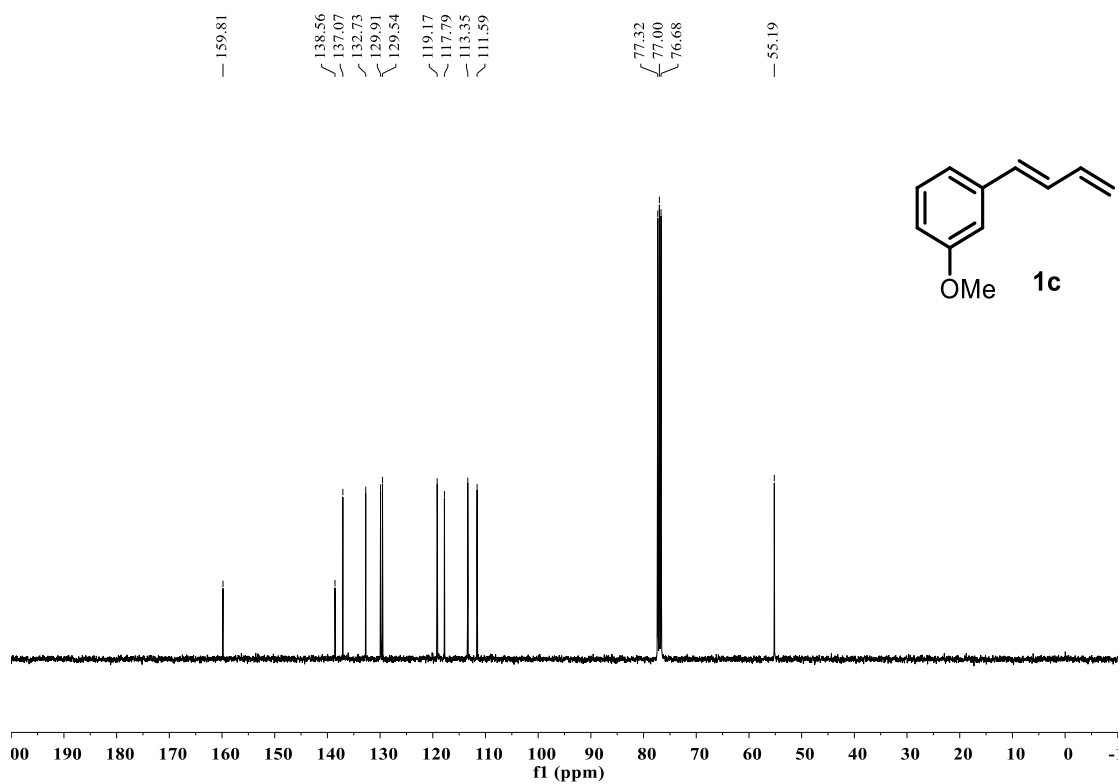
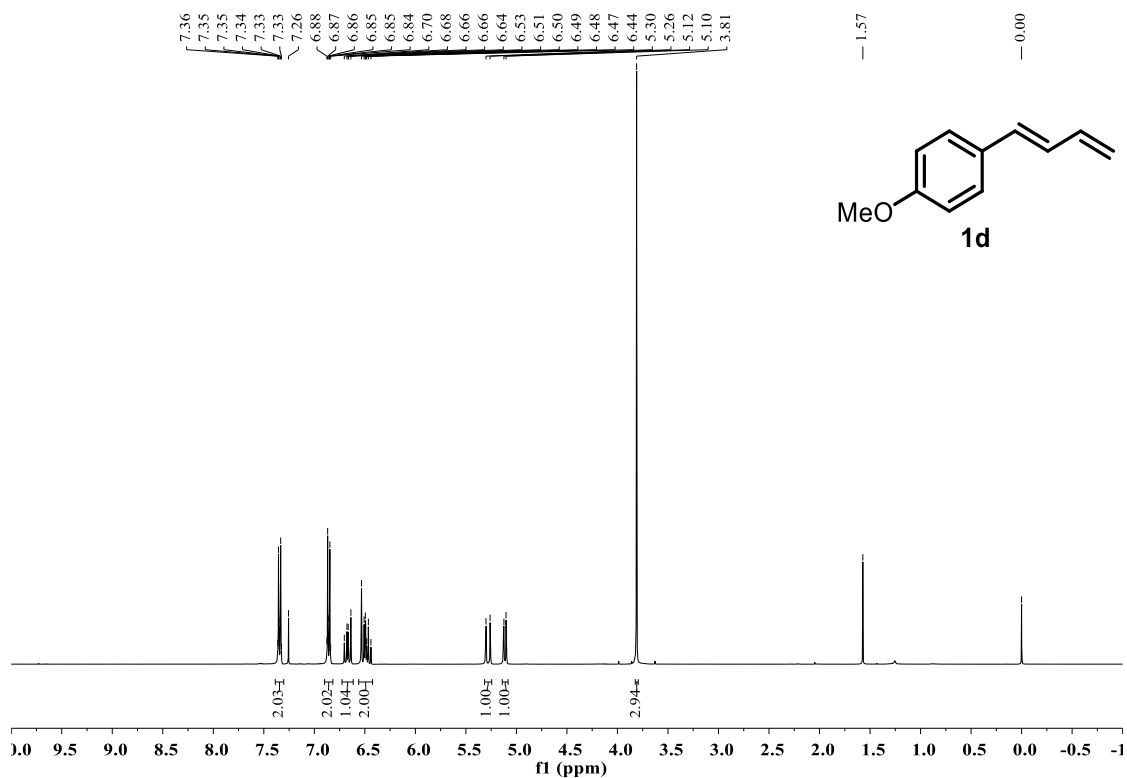
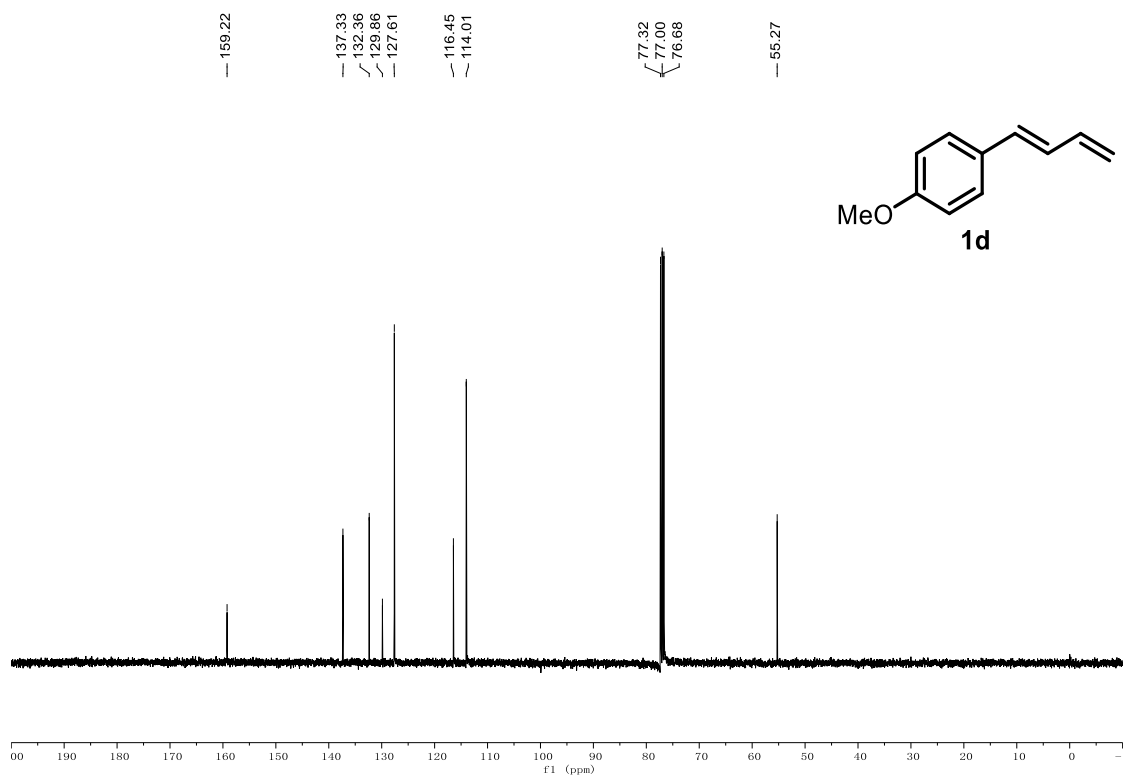


Figure S6. <sup>13</sup>C NMR spectra of substrate **1c**, related to Figure 4.



**Figure S7.** <sup>1</sup>H NMR spectra of substrate **1d**, related to **Figure 4**.



**Figure S8.** <sup>13</sup>C NMR spectra of substrate **1d**, related to **Figure 4**.

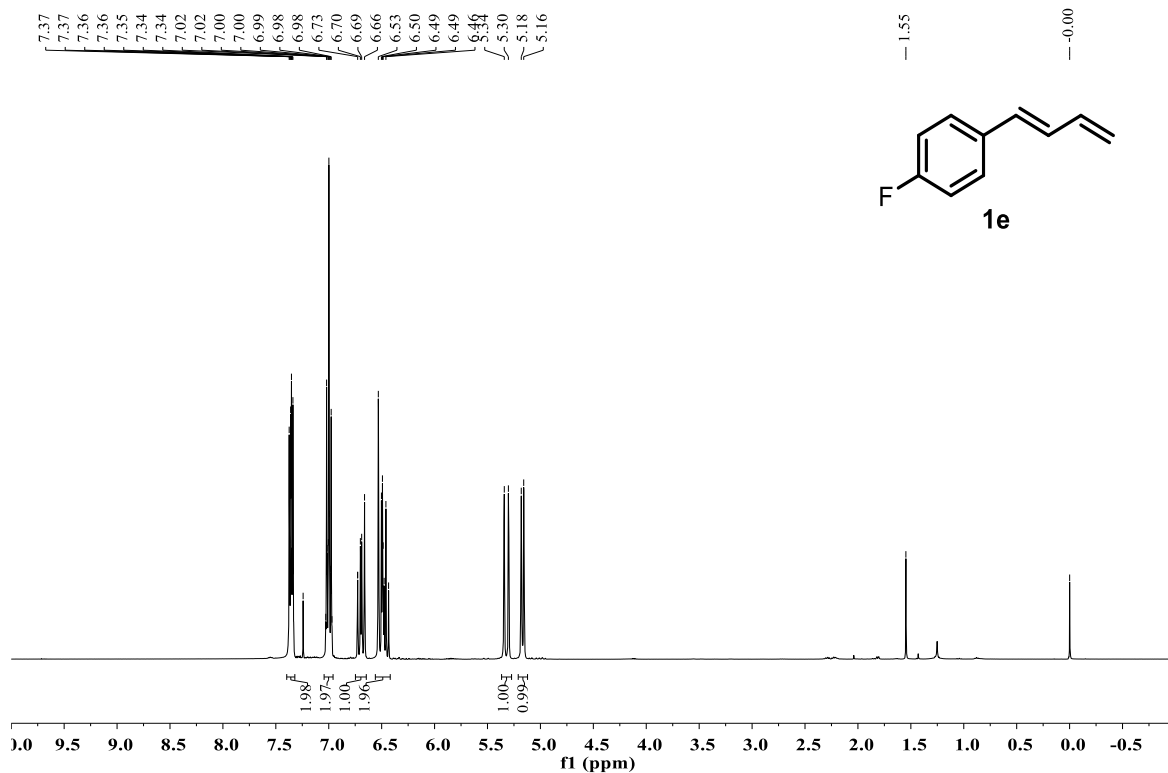


Figure S9. <sup>1</sup>H NMR spectra of substrate **1e**, related to Figure 4.

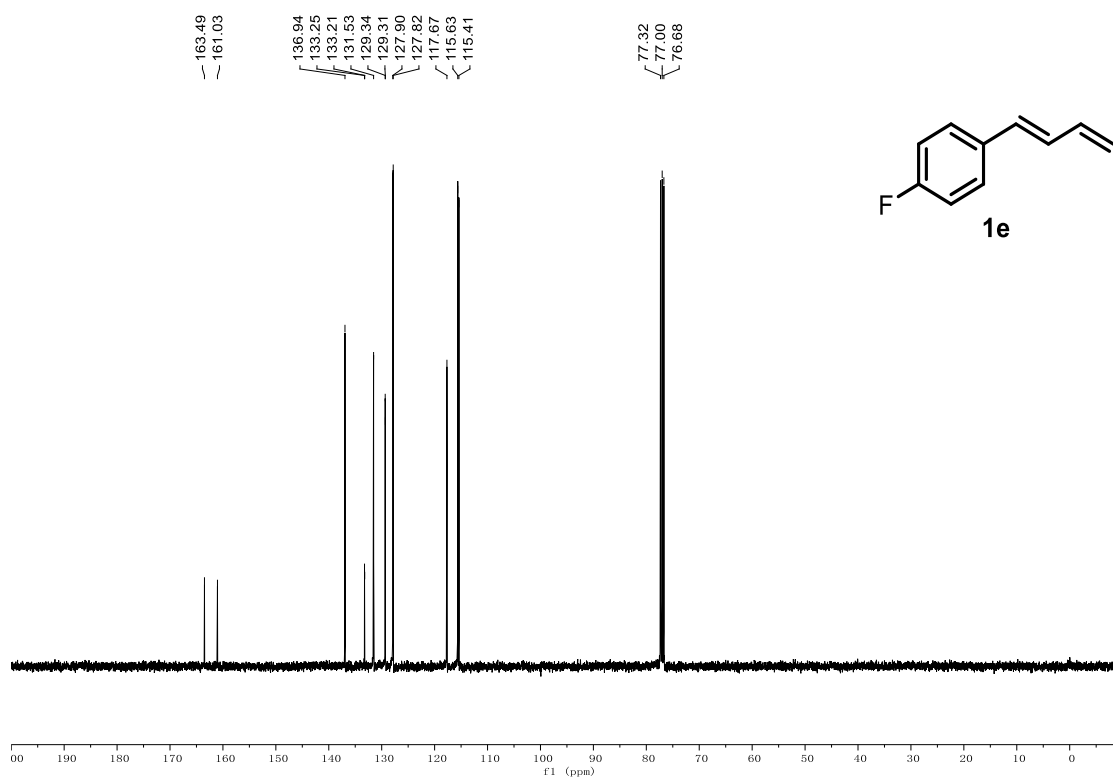
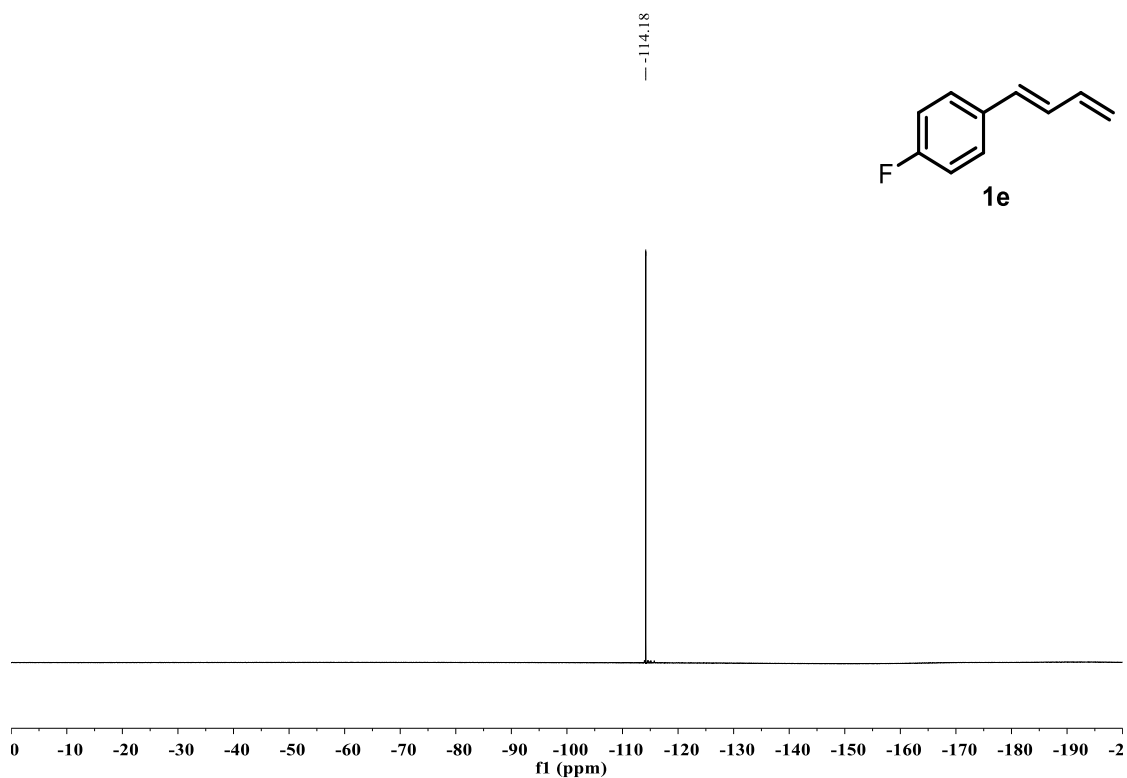
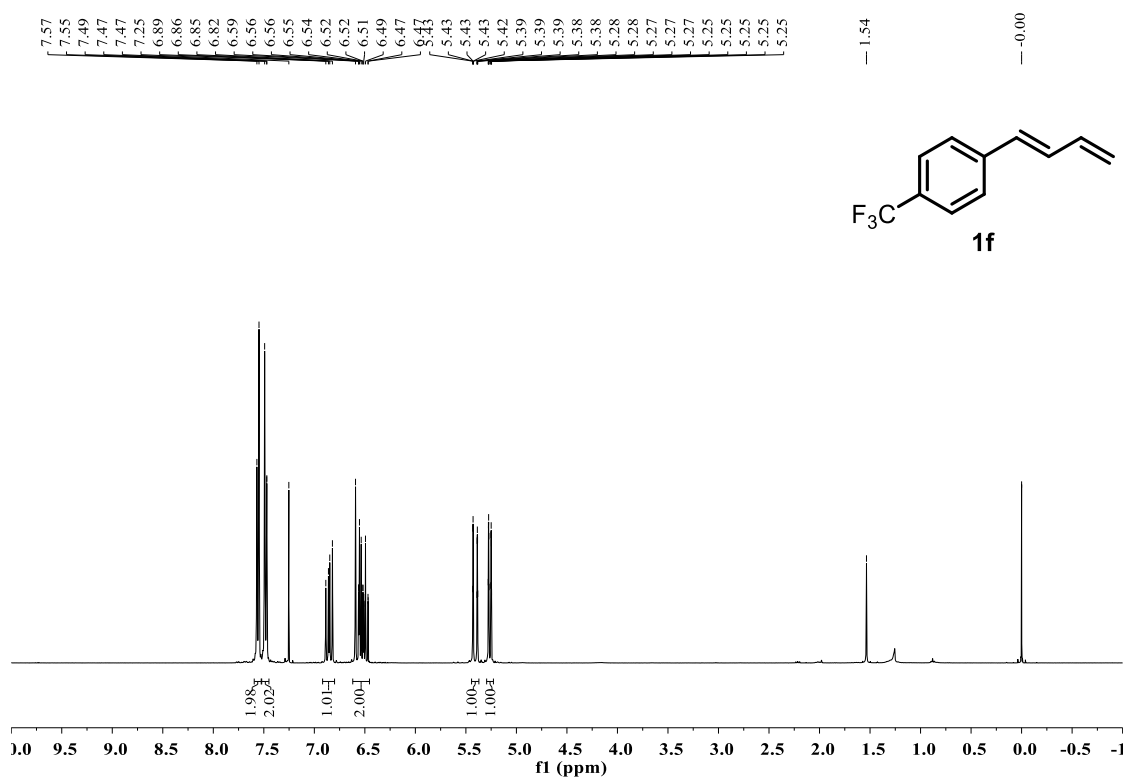


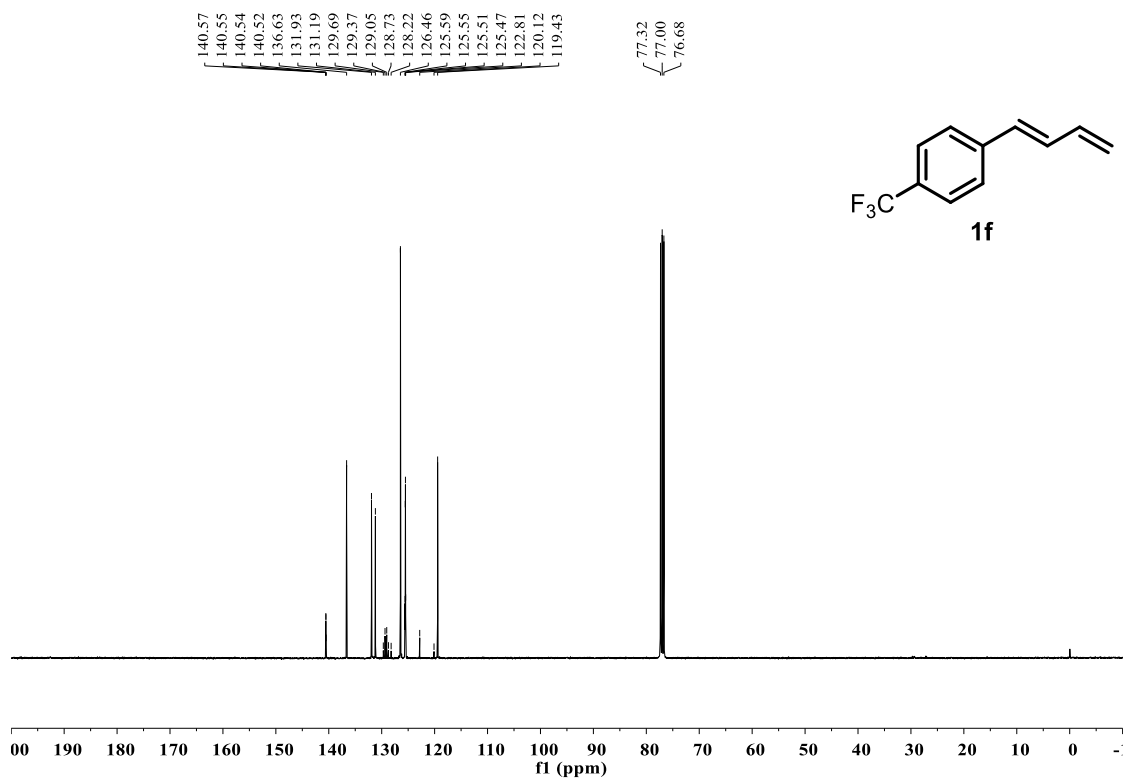
Figure S10. <sup>13</sup>C NMR spectra of substrate **1e**, related to Figure 4.



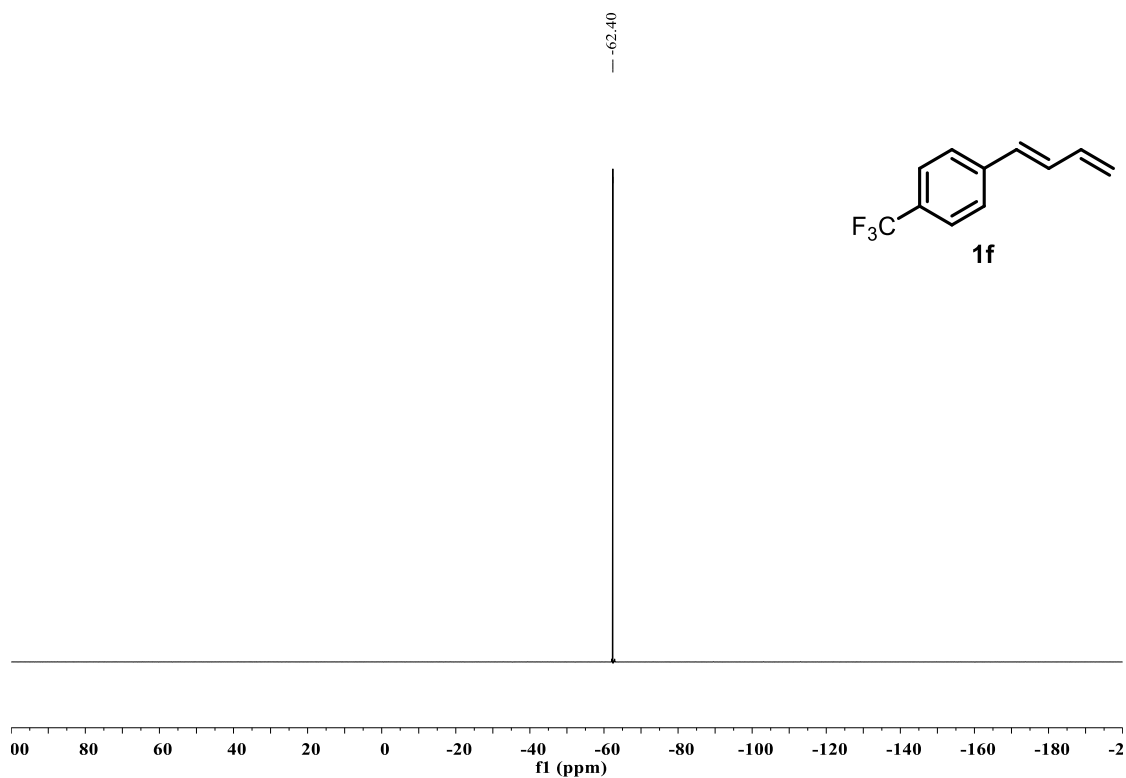
**Figure S11.**  $^{19}\text{F}$  NMR spectra of substrate **1e**, related to **Figure 4**.



**Figure S12.**  $^1\text{H}$  NMR spectra of substrate **1f**, related to **Figure 4**.

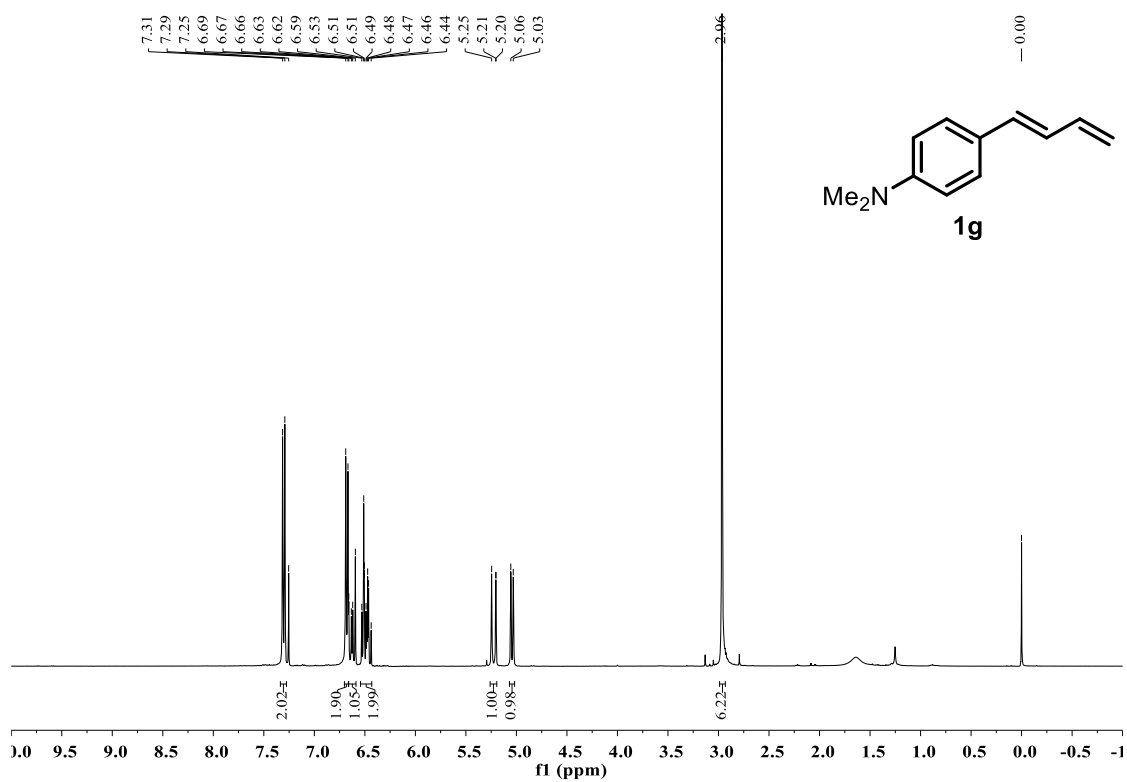


**Figure S13.** <sup>13</sup>C NMR spectra of substrate **1f**, related to **Figure 4**.

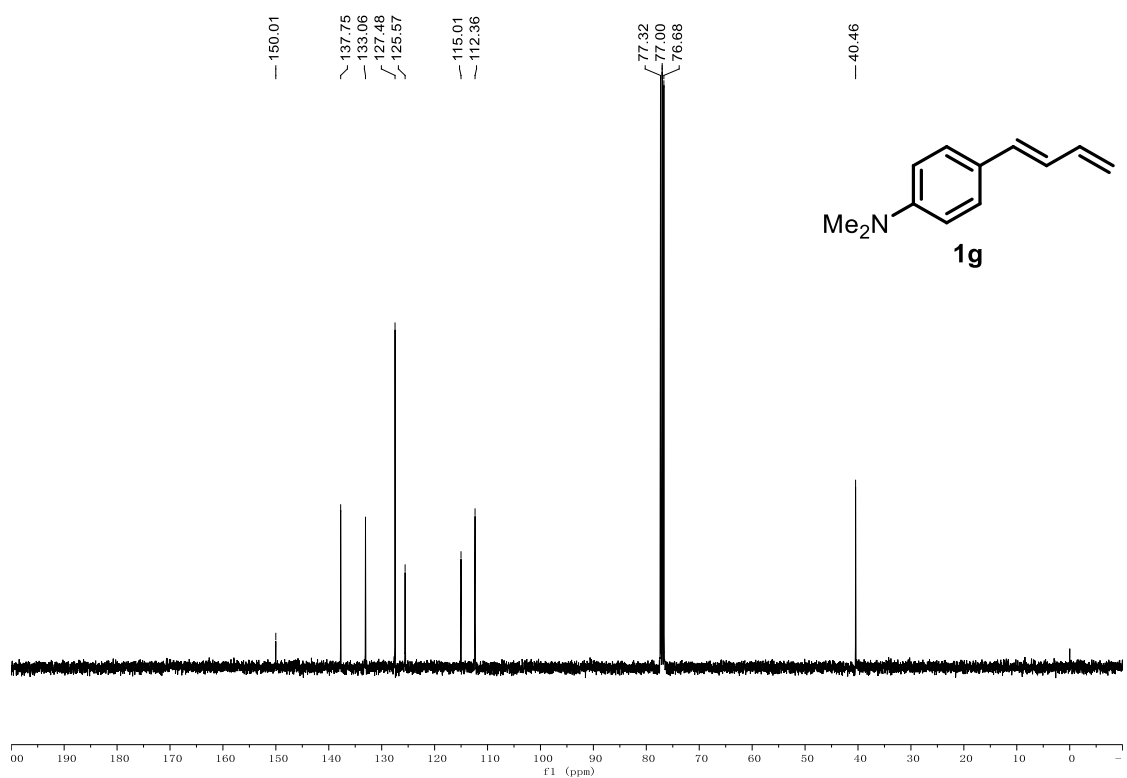


**Figure S14.** <sup>19</sup>F NMR spectra of substrate **1f**, related to **Figure 4**.

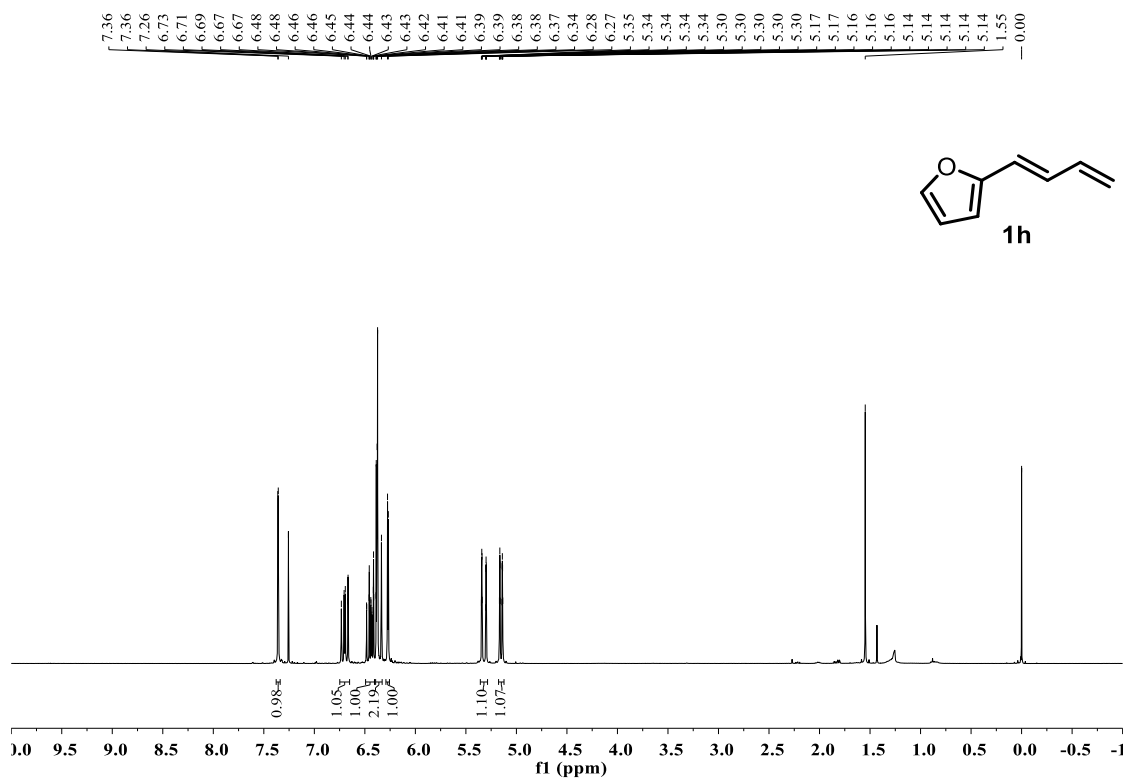




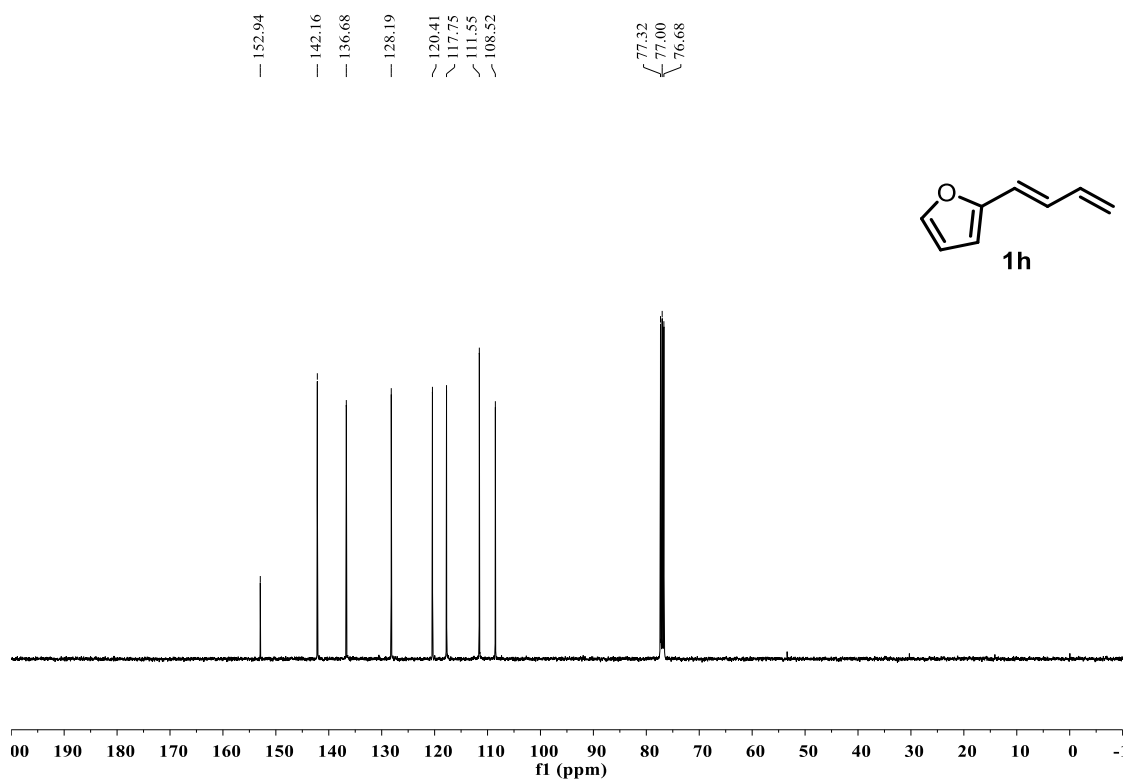
**Figure S15.** <sup>1</sup>H NMR spectra of substrate **1g**, related to **Figure 4**.



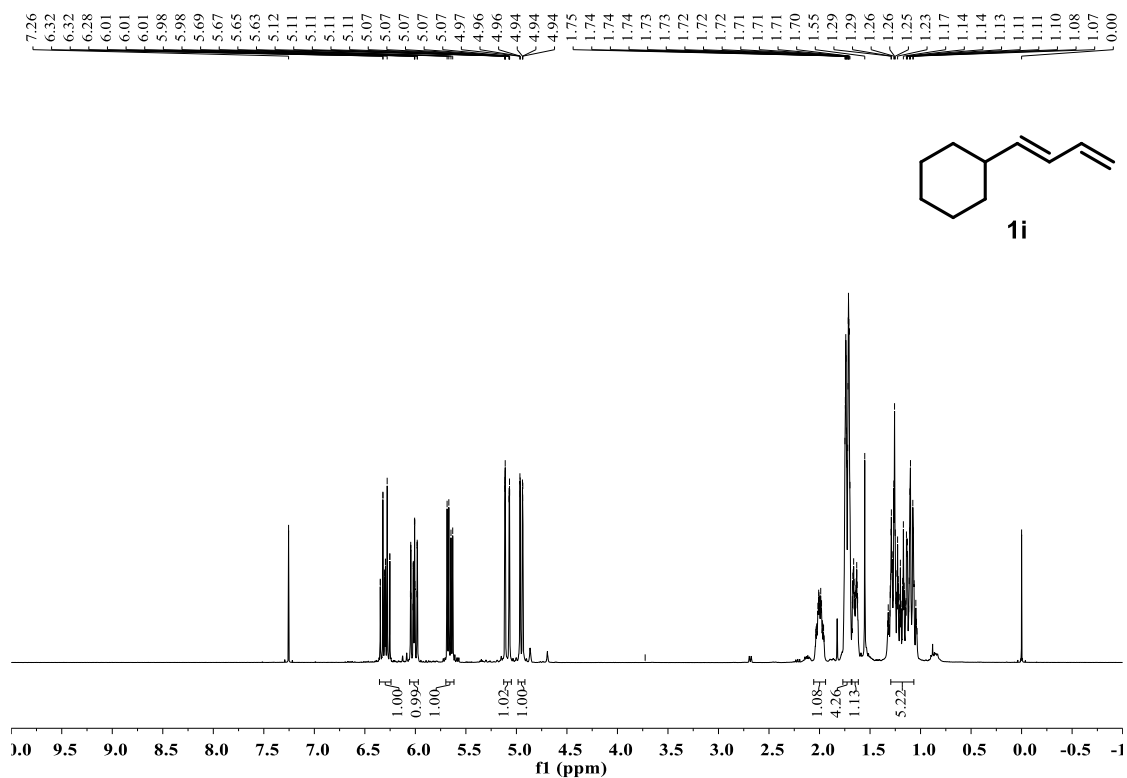
**Figure S16.** <sup>13</sup>C NMR spectra of substrate **1g**, related to **Figure 4**.



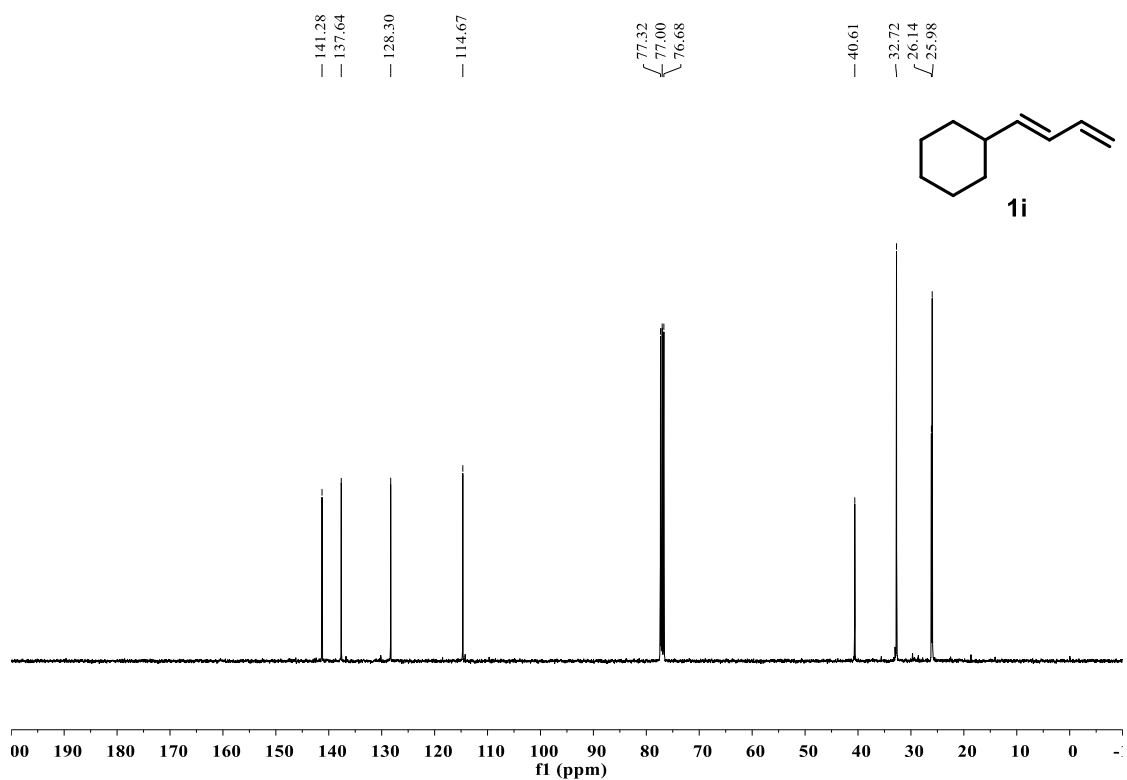
**Figure S17.** <sup>1</sup>H NMR spectra of substrate **1h**, related to **Figure 4**.



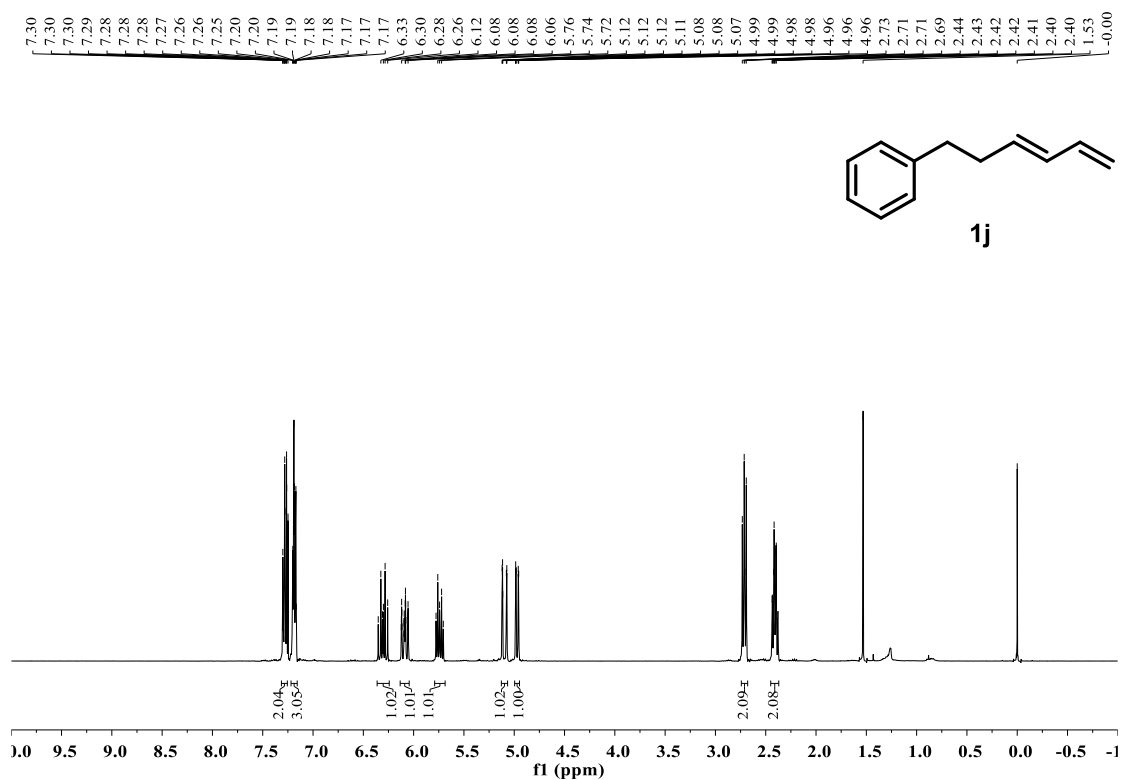
**Figure S18.** <sup>13</sup>C NMR spectra of substrate **1h**, related to **Figure 4**.



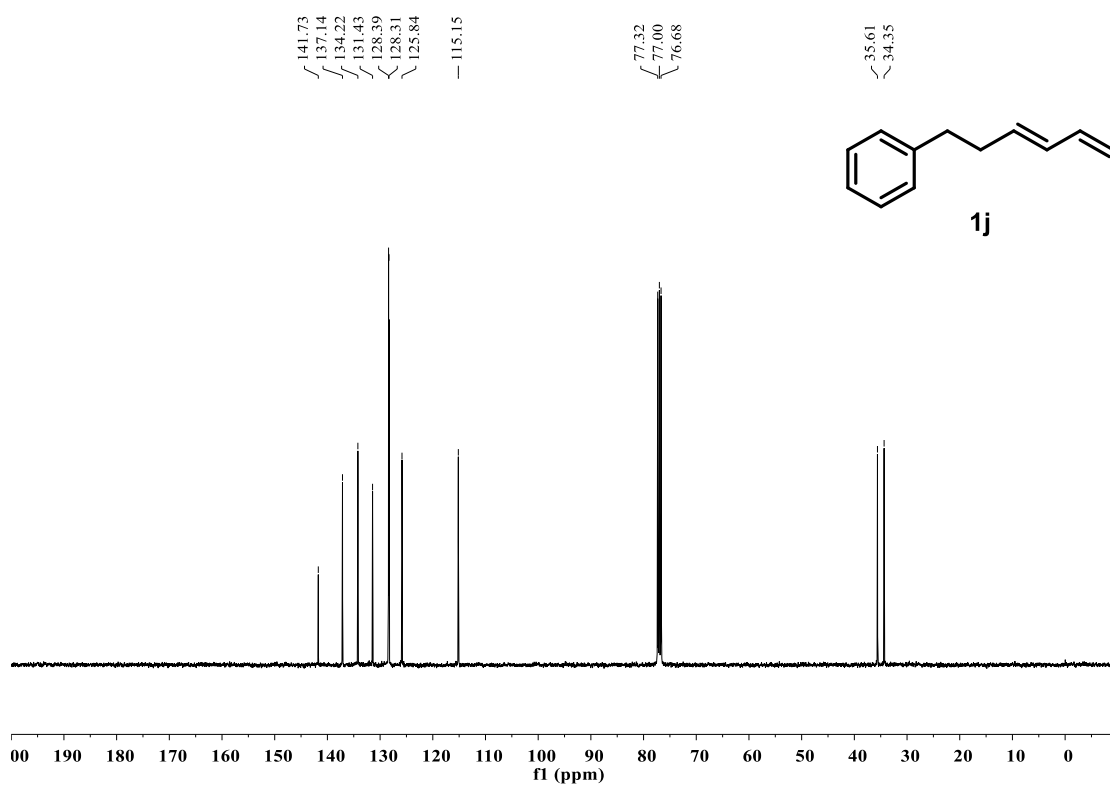
**Figure S19.** <sup>1</sup>H NMR spectra of substrate **1i**, related to **Figure 4**.



**Figure S20.** <sup>13</sup>C NMR spectra of substrate **1i**, related to **Figure 4**.



**Figure S21.**  $^1\text{H}$  NMR spectra of substrate **1j**, related to **Figure 4**.



**Figure S22.**  $^{13}\text{C}$  NMR spectra of substrate **1j**, related to **Figure 4**.

Supplemental figures for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ -NMR spectra of products 3a-3bd.

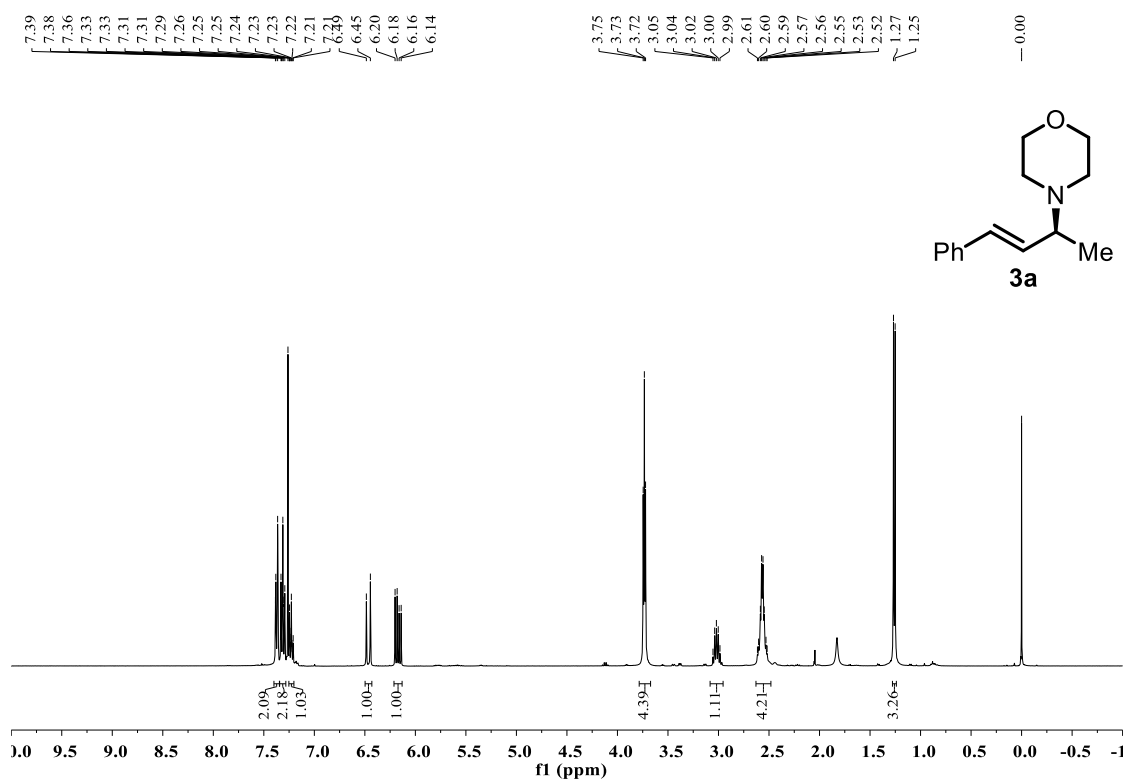


Figure S23.  $^1\text{H}$  NMR spectra of **3a**, related to Figure 3.

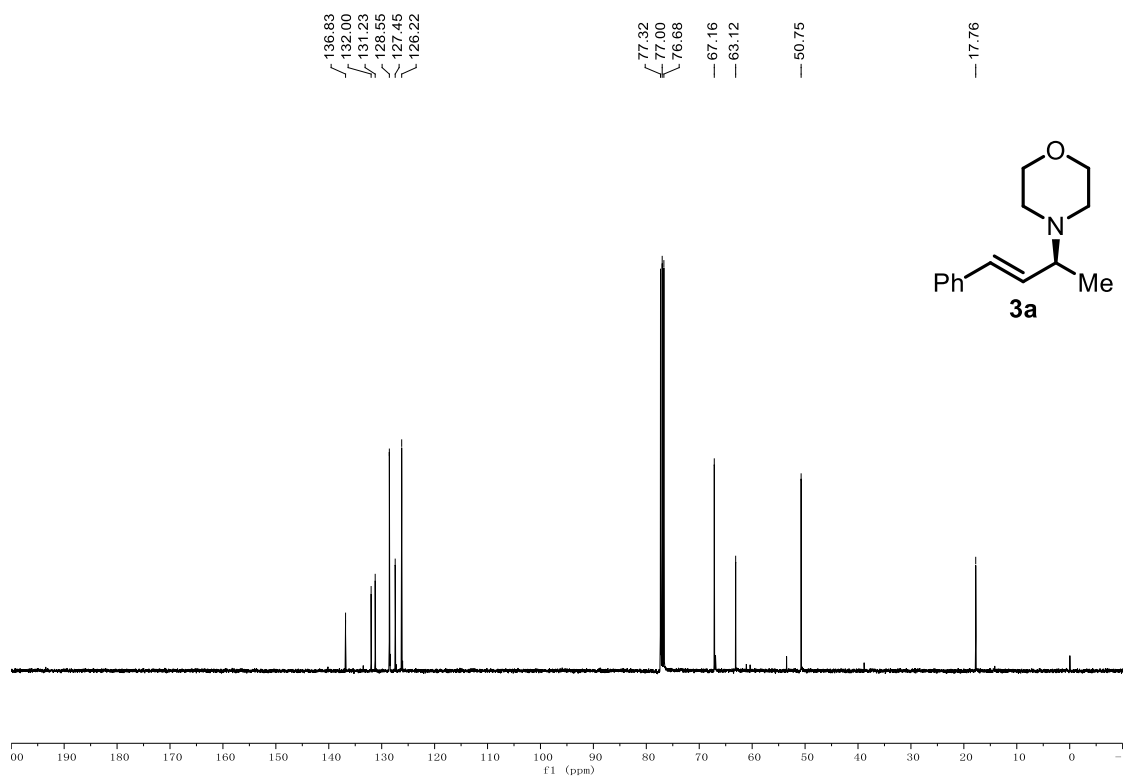
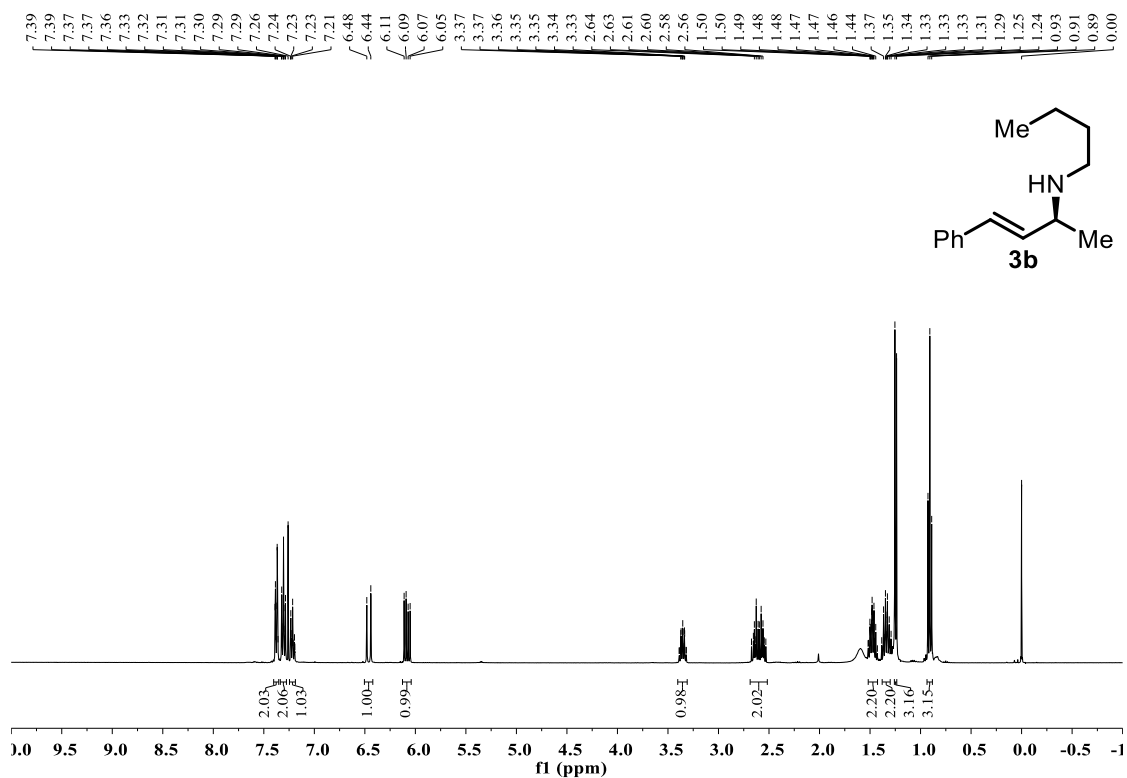
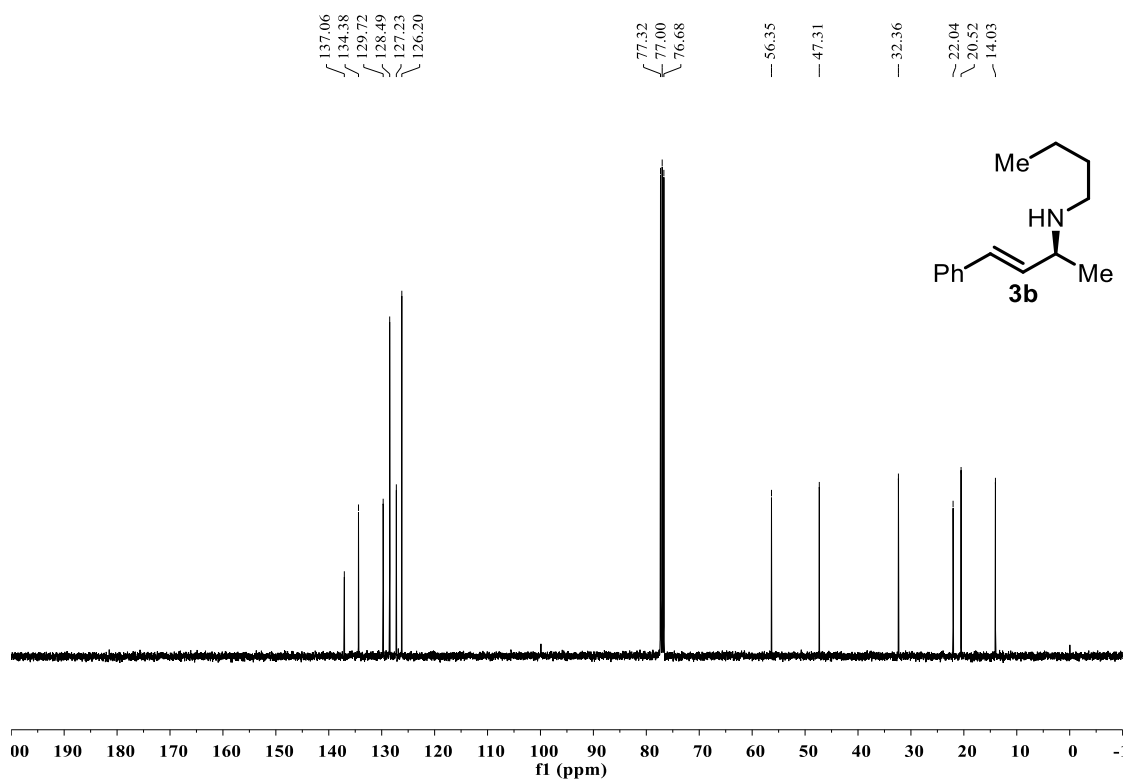


Figure S24.  $^{13}\text{C}$  NMR spectra of **3a**, related to Figure 3.



**Figure S25.** <sup>1</sup>H NMR spectra of **3b**, related to **Figure 3**.



**Figure S26.** <sup>13</sup>C NMR spectra of **3b**, related to **Figure 3**.

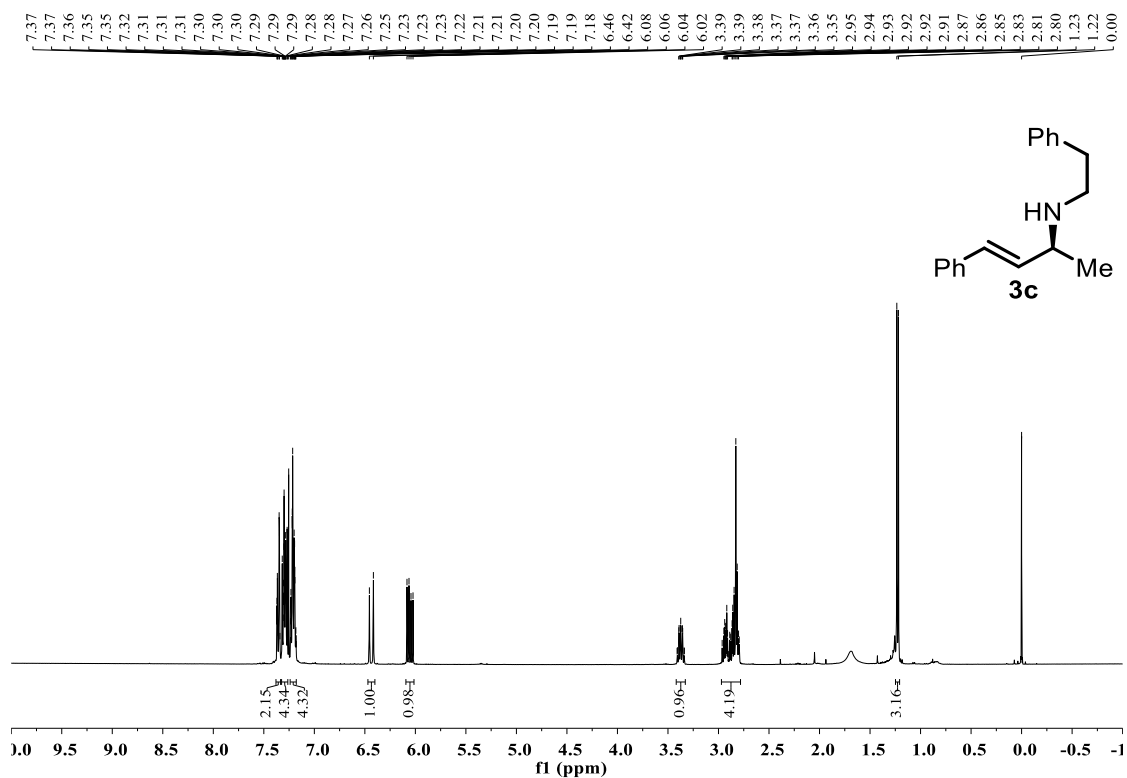


Figure S27. <sup>1</sup>H NMR spectra of **3c**, related to Figure 3.

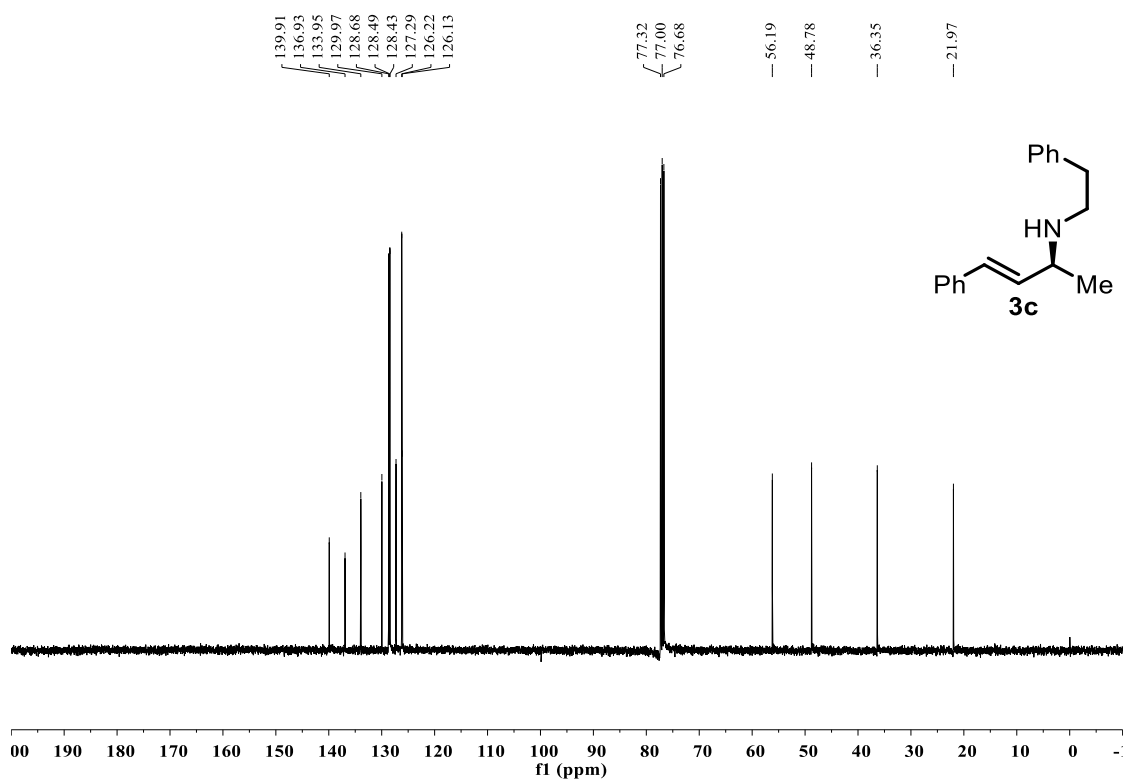
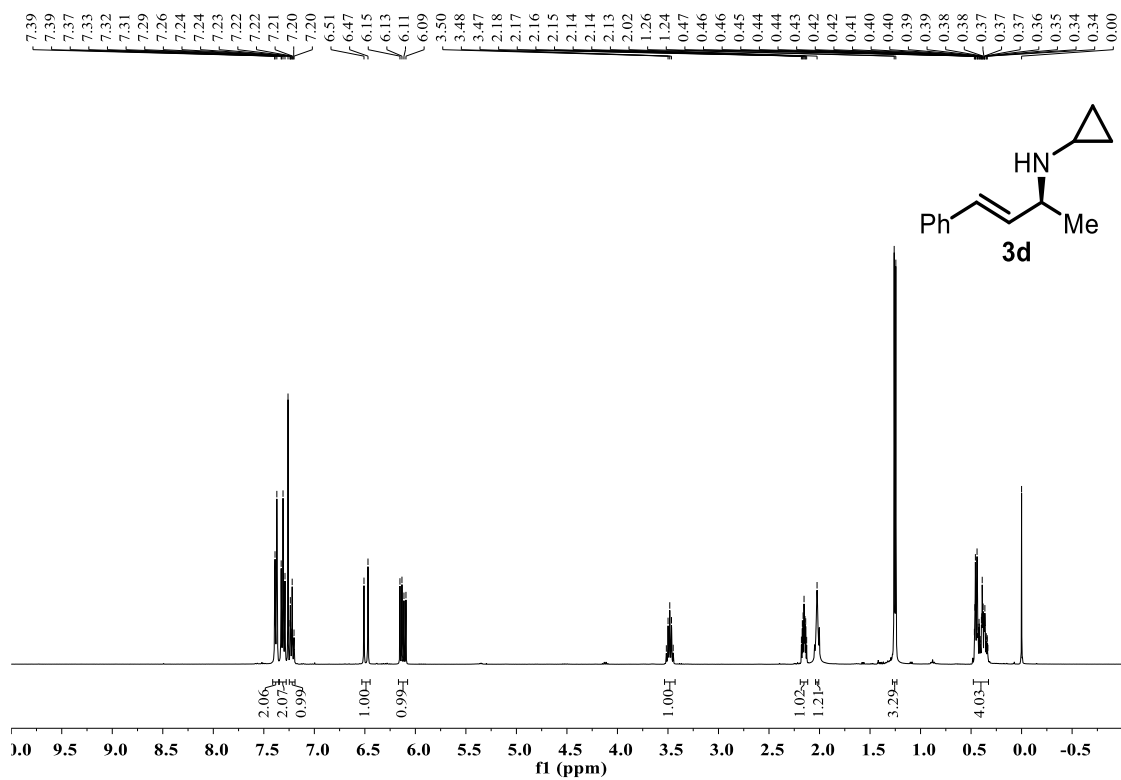
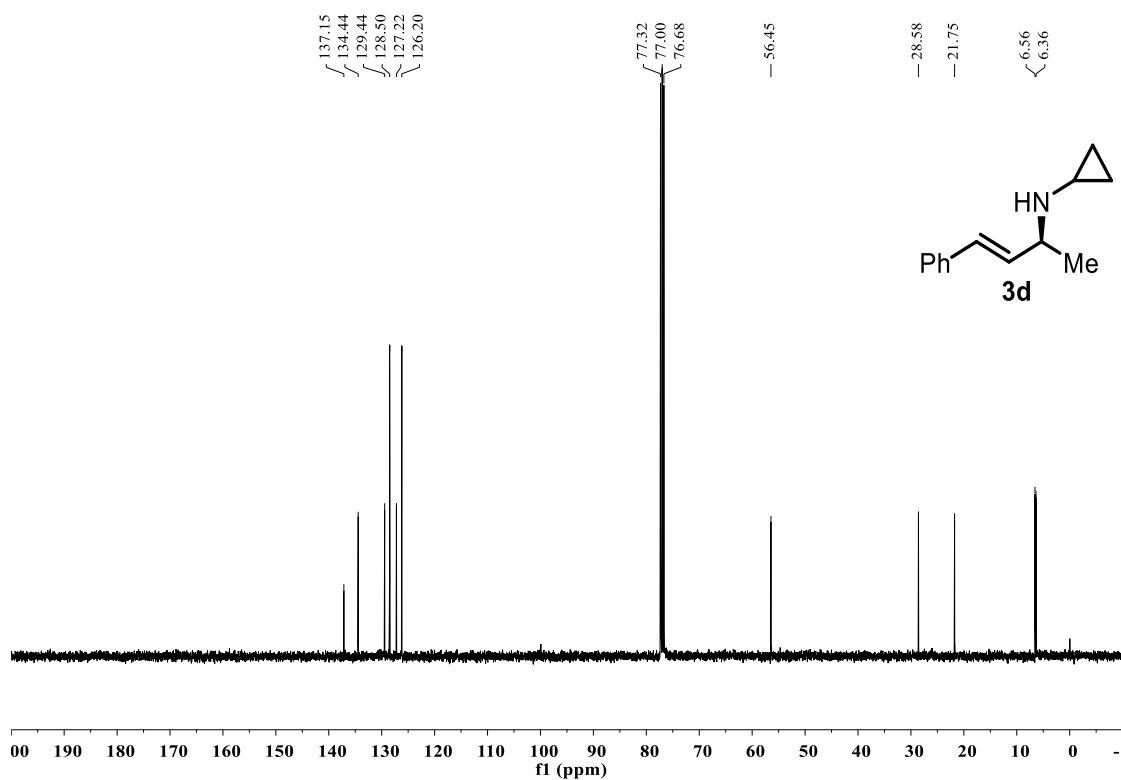


Figure S28. <sup>13</sup>C NMR spectra of **3c**, related to Figure 3.

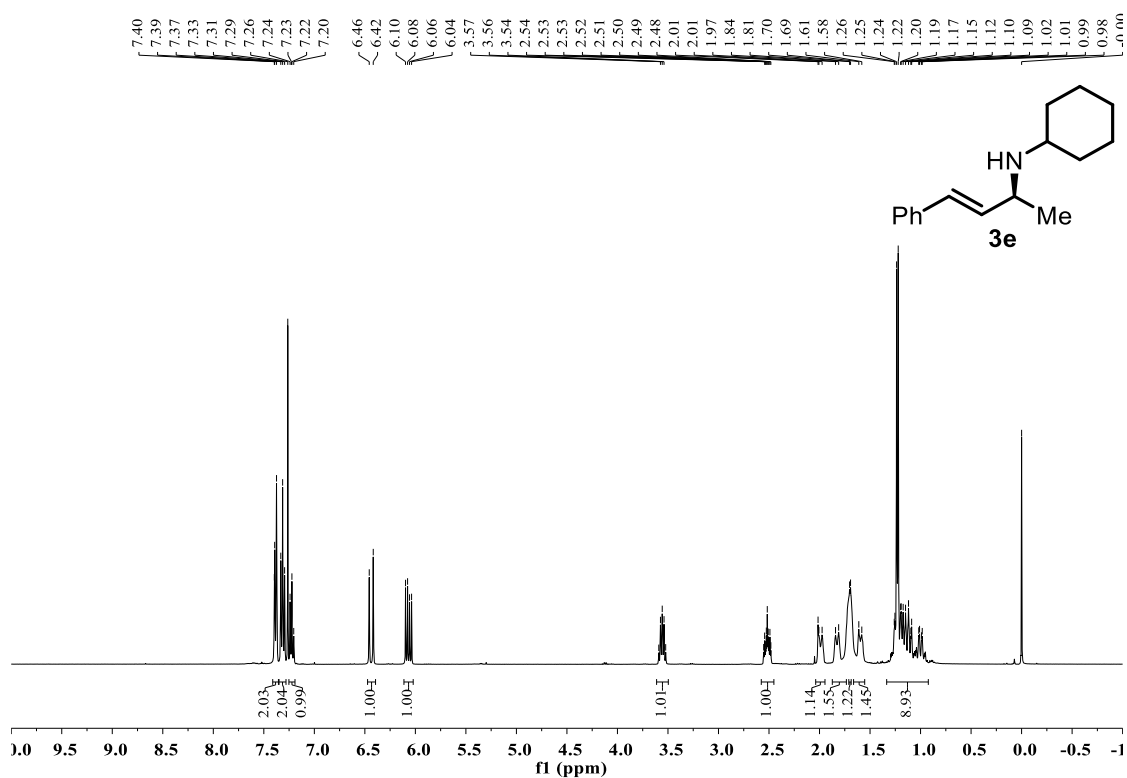


**Figure S29.** <sup>1</sup>H NMR spectra of **3d**, related to **Figure 3**.

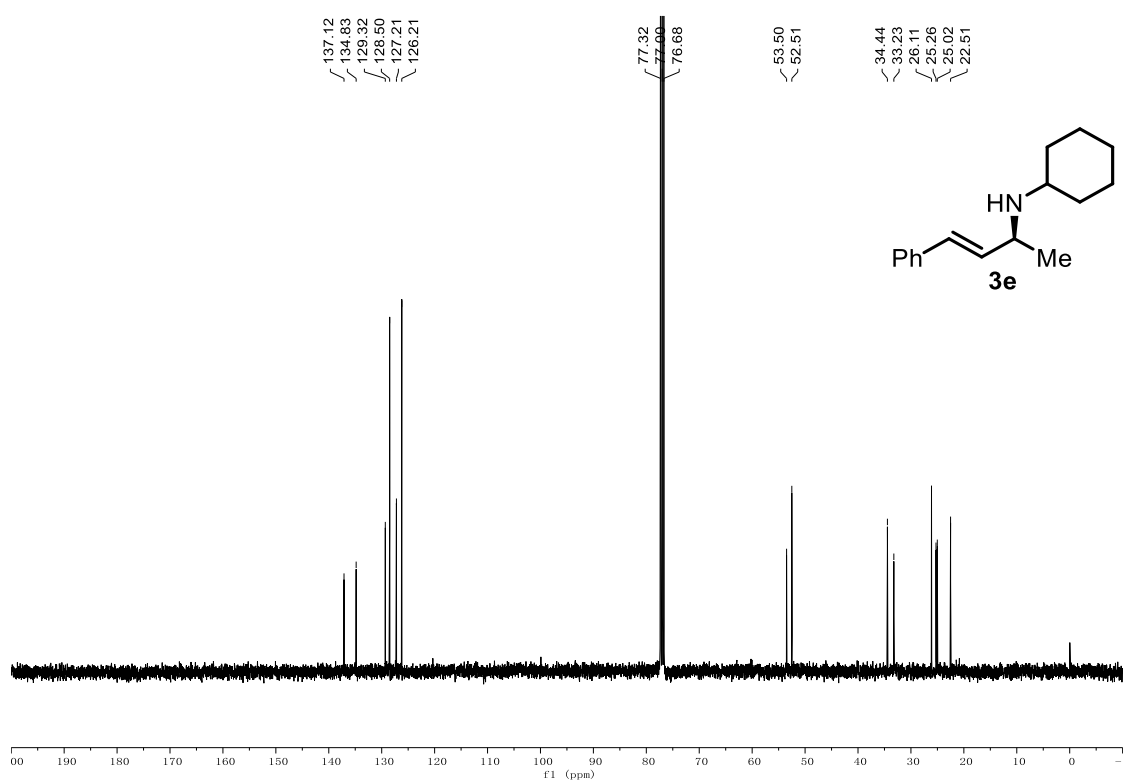


**Figure S30.** <sup>13</sup>C NMR spectra of **3d**, related to **Figure 3**.

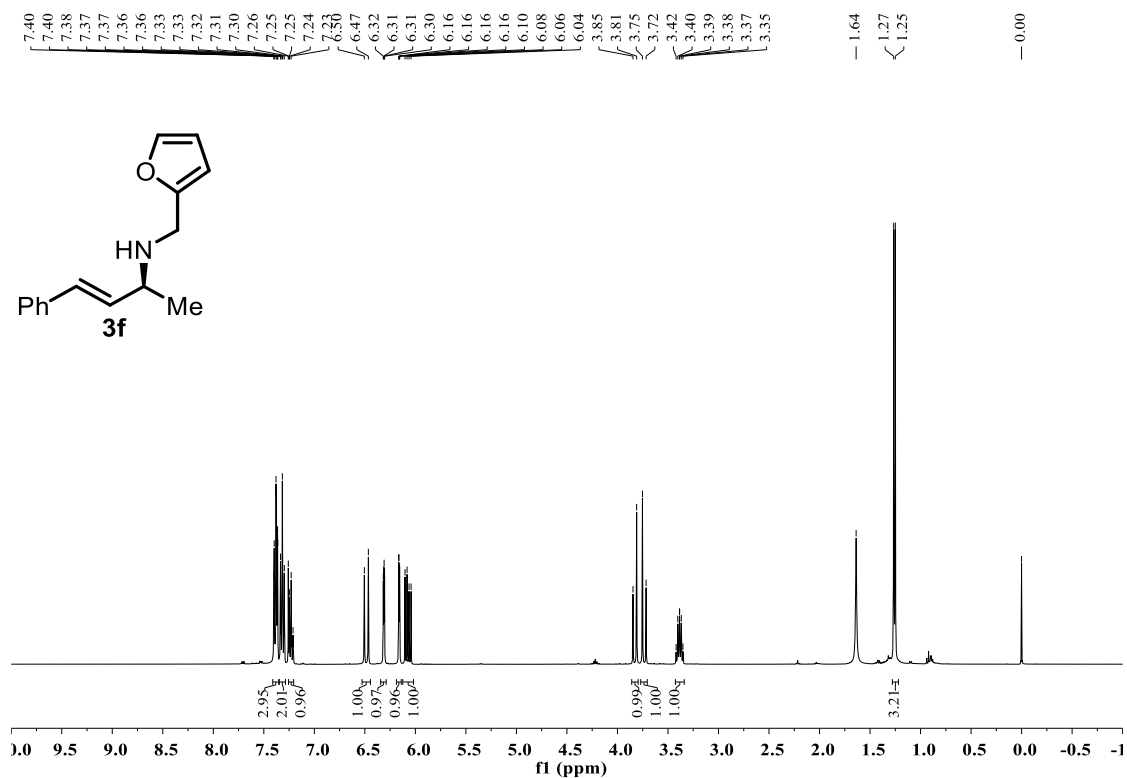




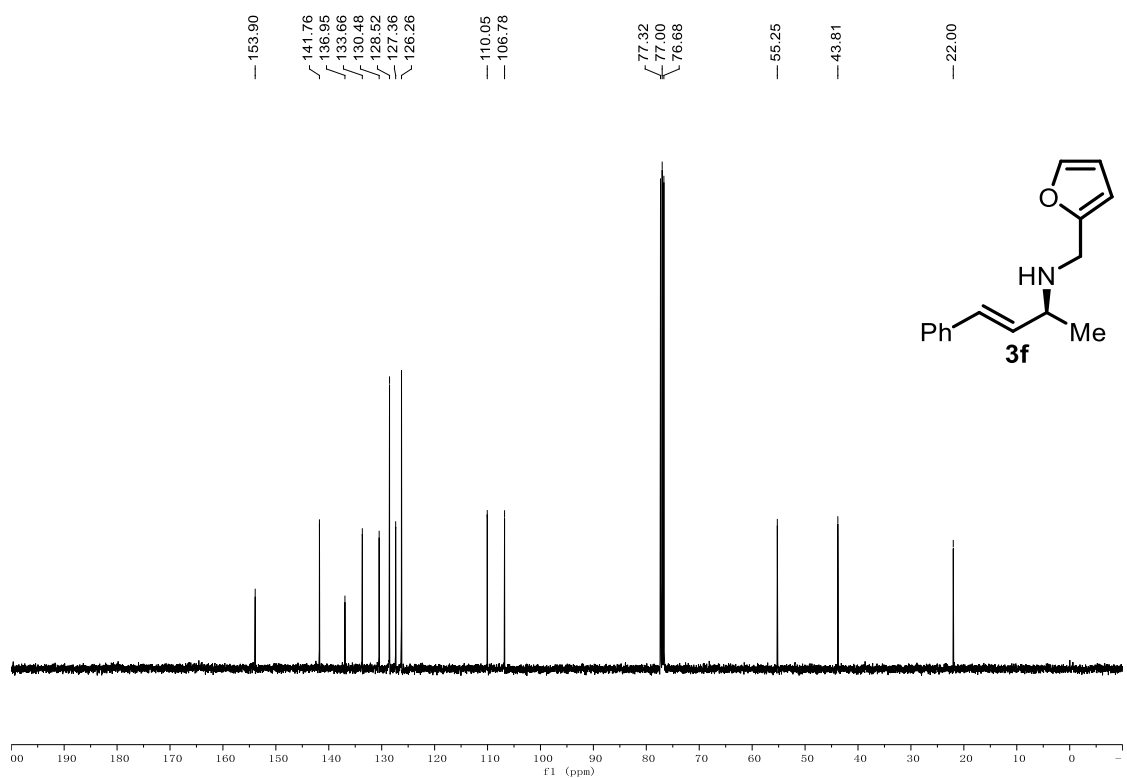
**Figure S31.** <sup>1</sup>H NMR spectra of **3e**, related to **Figure 3**.



**Figure S32.** <sup>13</sup>C NMR spectra of **3e**, related to **Figure 3**.



**Figure S33.** <sup>1</sup>H NMR spectra of **3f**, related to **Figure 3**.



**Figure S34.** <sup>13</sup>C NMR spectra of **3f**, related to **Figure 3**.

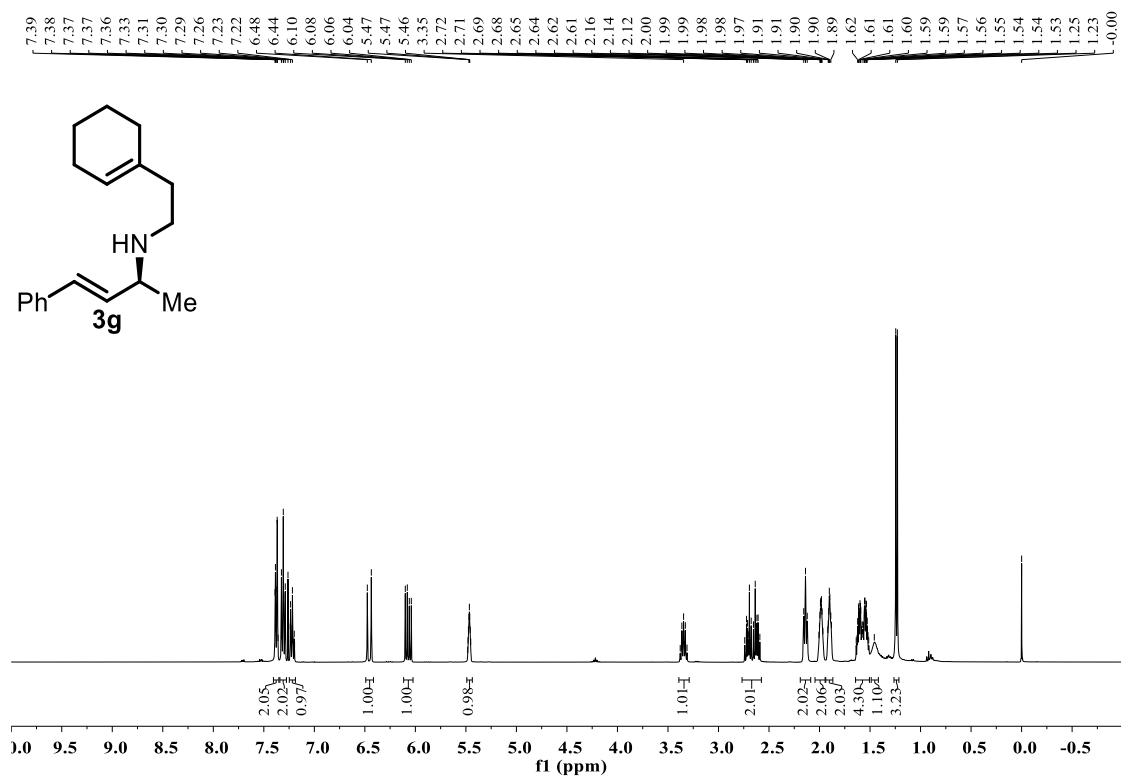


Figure S35.  $^1\text{H}$  NMR spectra of **3g**, related to Figure 3.

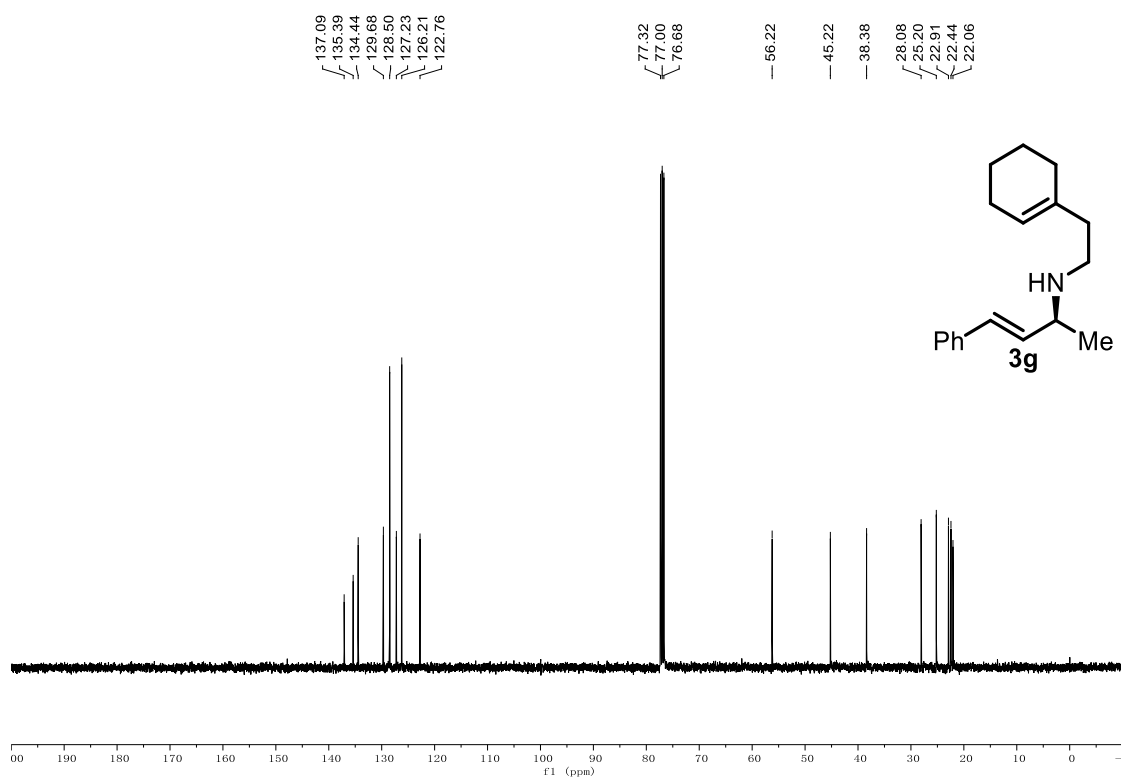


Figure S36.  $^{13}\text{C}$  NMR spectra of **3g**, related to Figure 3.

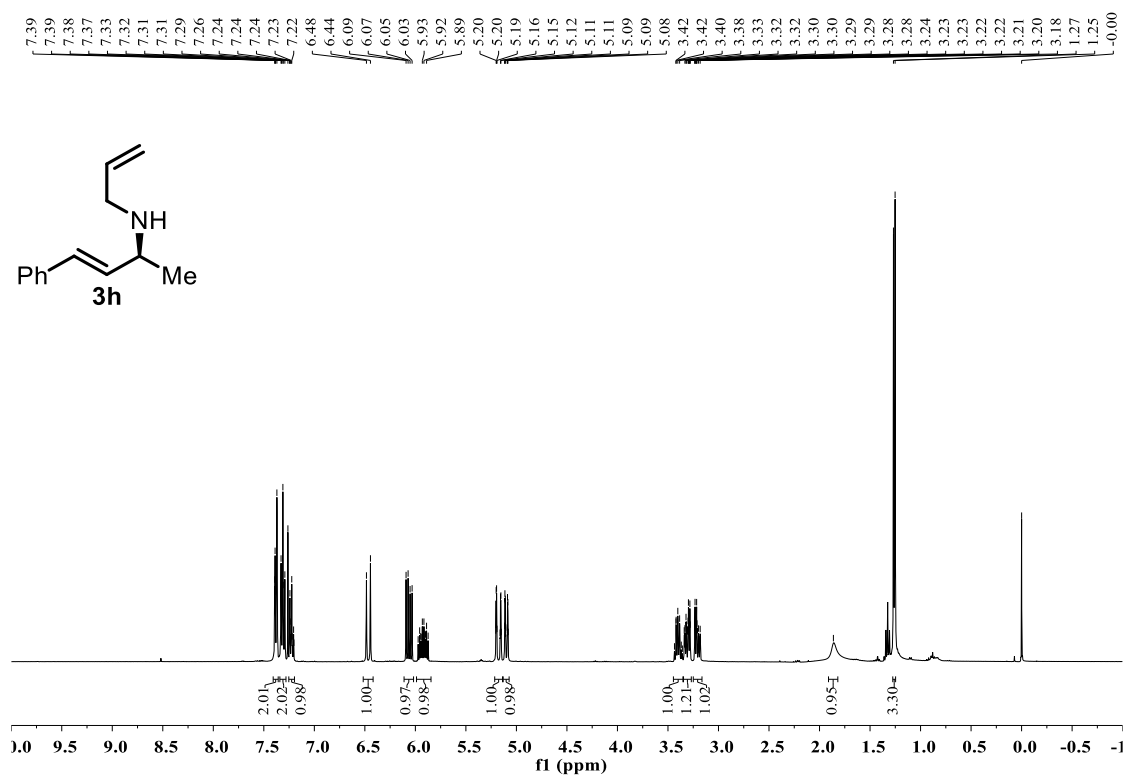


Figure S37. <sup>1</sup>H NMR spectra of **3h**, related to Figure 3.

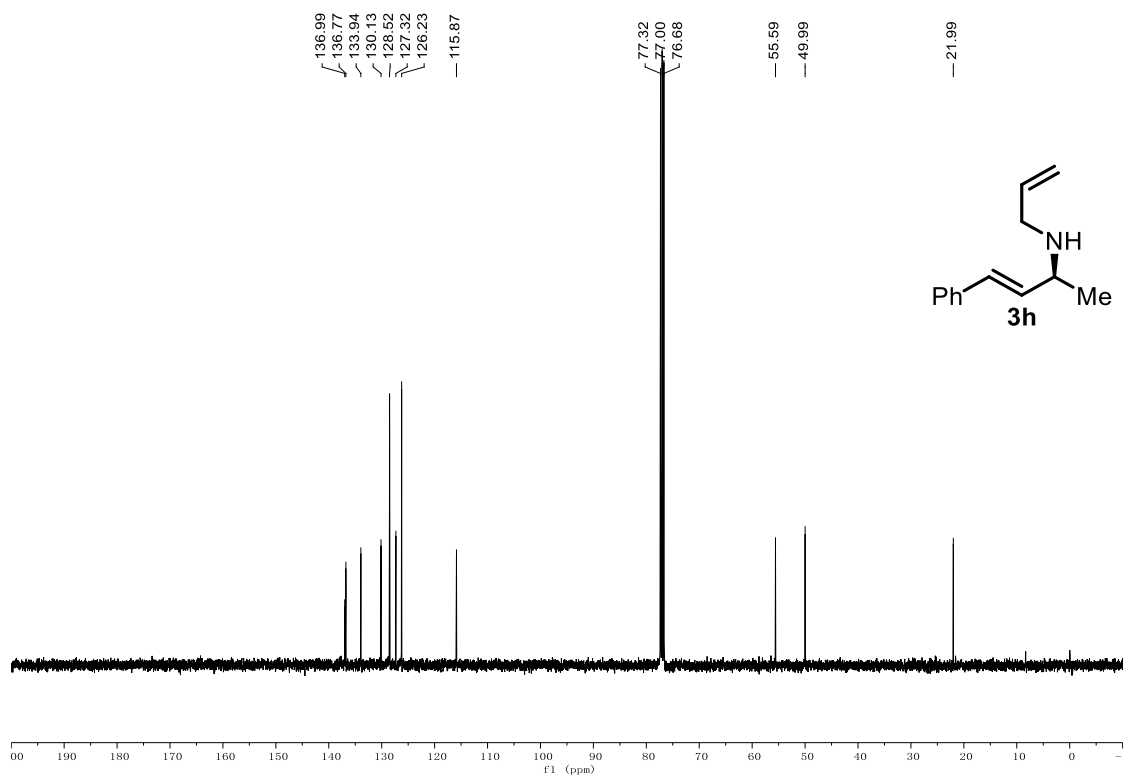


Figure S38. <sup>13</sup>C NMR spectra of **3h**, related to Figure 3.

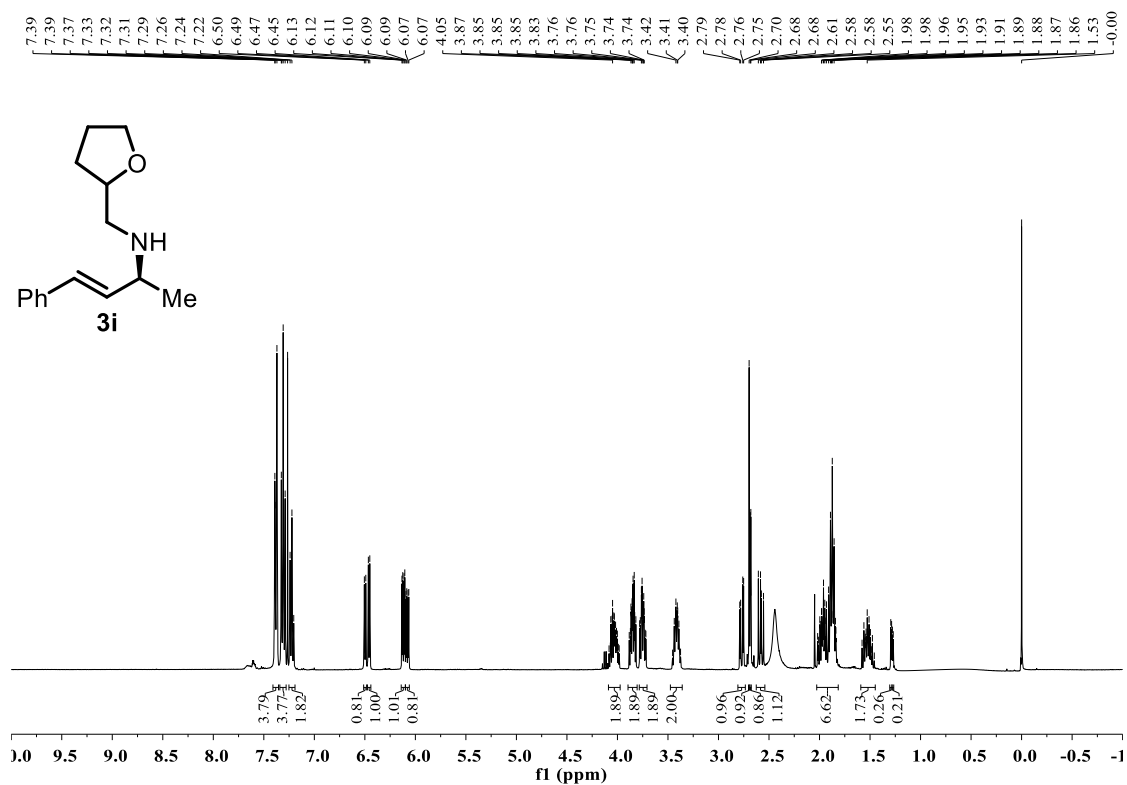


Figure S39. <sup>1</sup>H NMR spectra of **3i**, related to Figure 3.

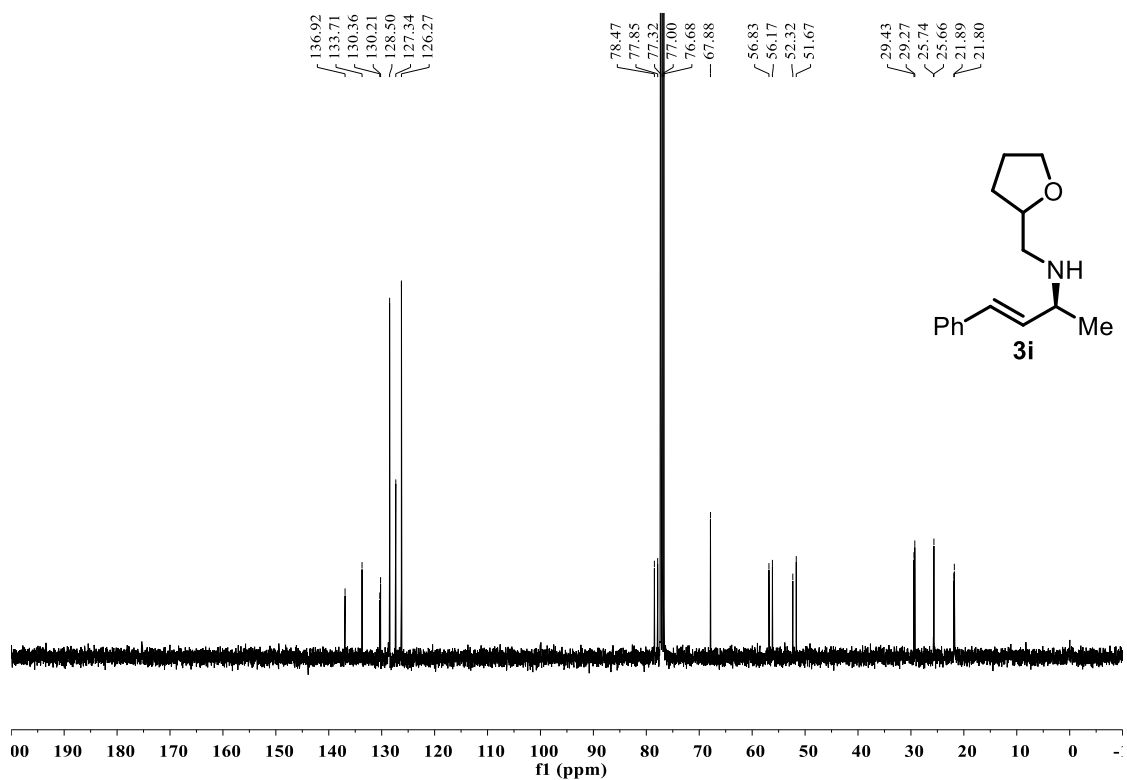


Figure S40. <sup>13</sup>C NMR spectra of **3i**, related to Figure 3.

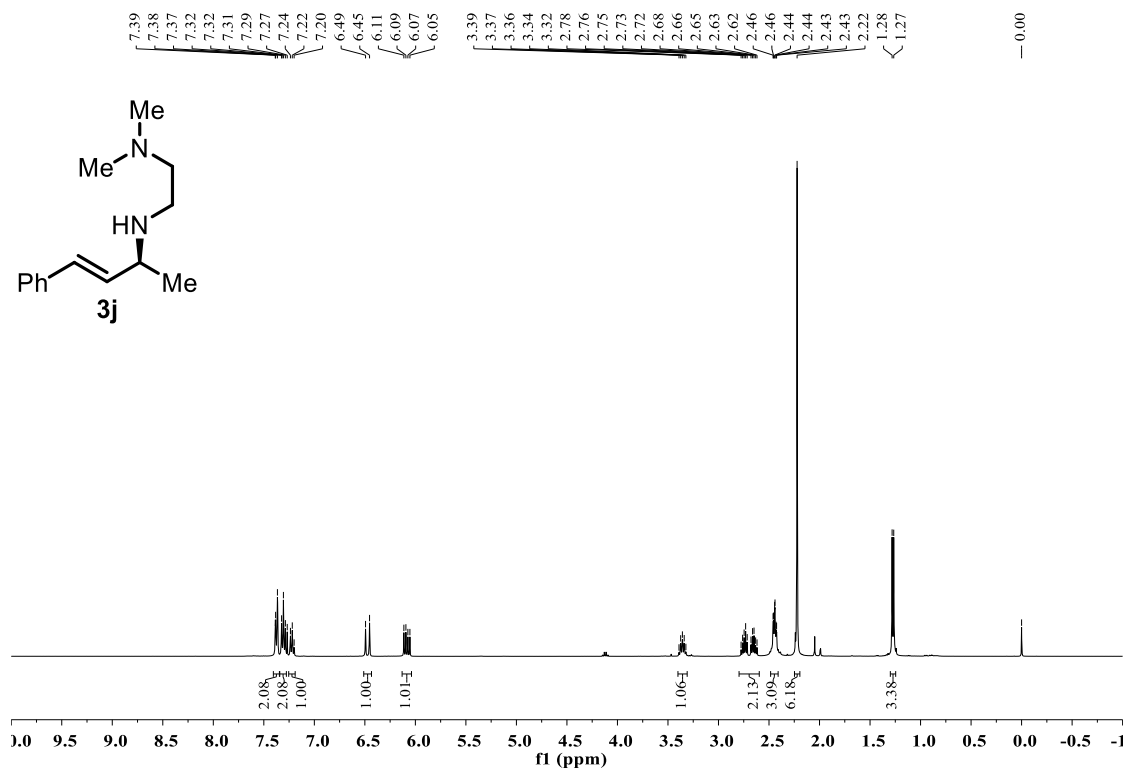


Figure S41. <sup>1</sup>H NMR spectra of **3j**, related to Figure 3.

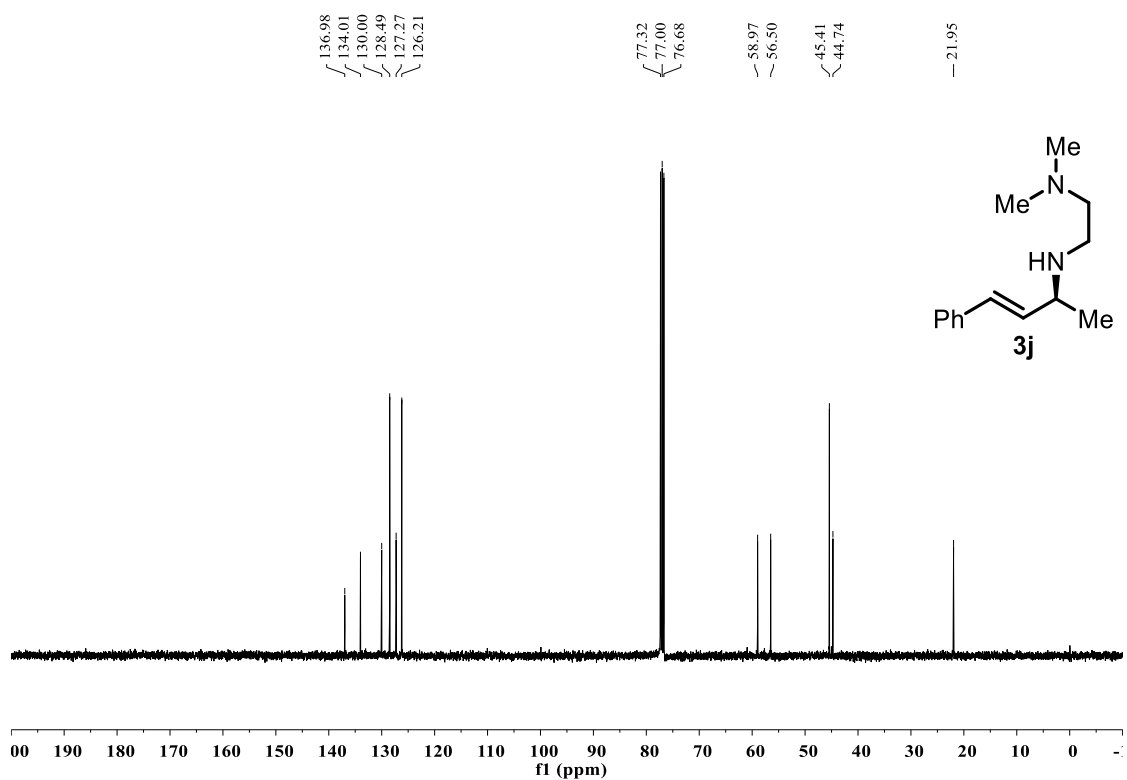


Figure S42. <sup>13</sup>C NMR spectra of **3j**, related to Figure 3.

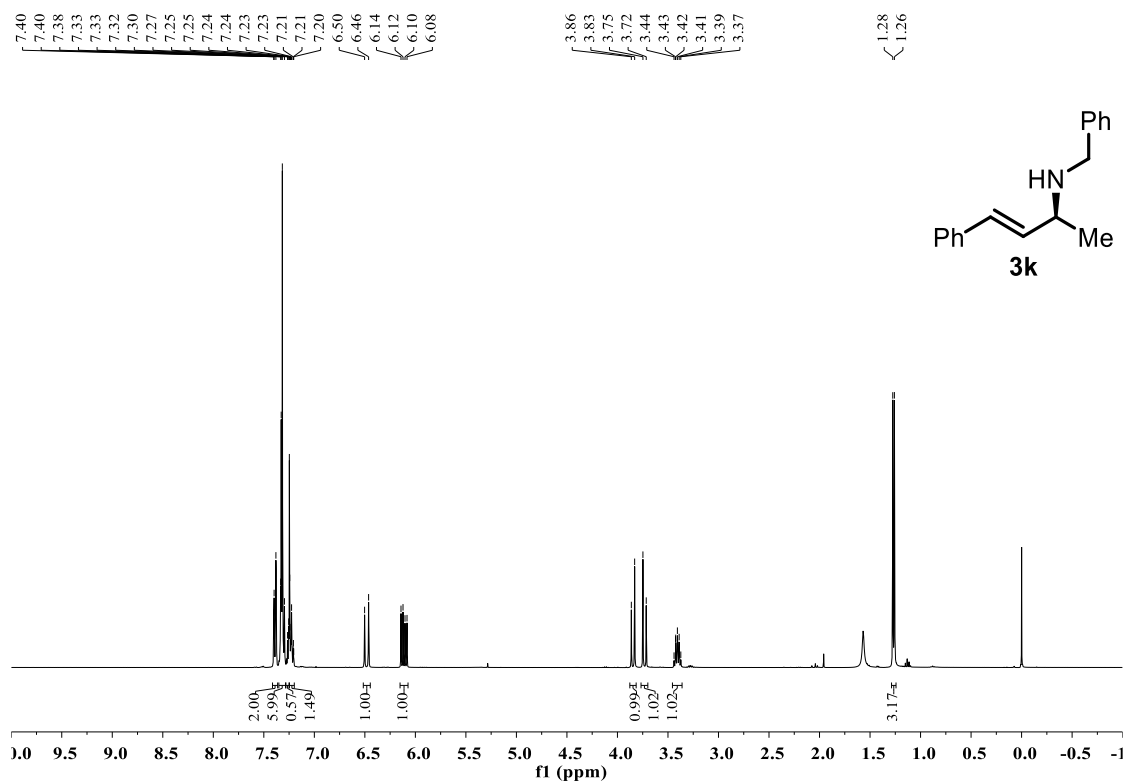


Figure S43. <sup>1</sup>H NMR spectra of **3k**, related to Figure 3.

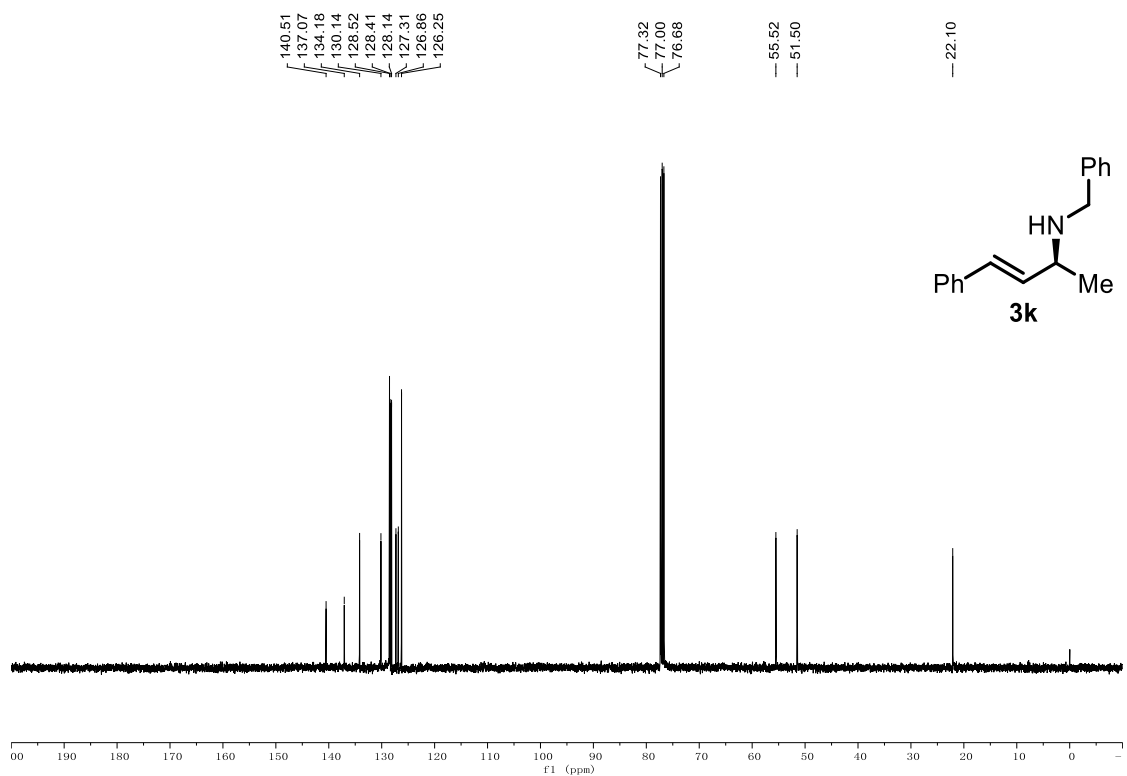
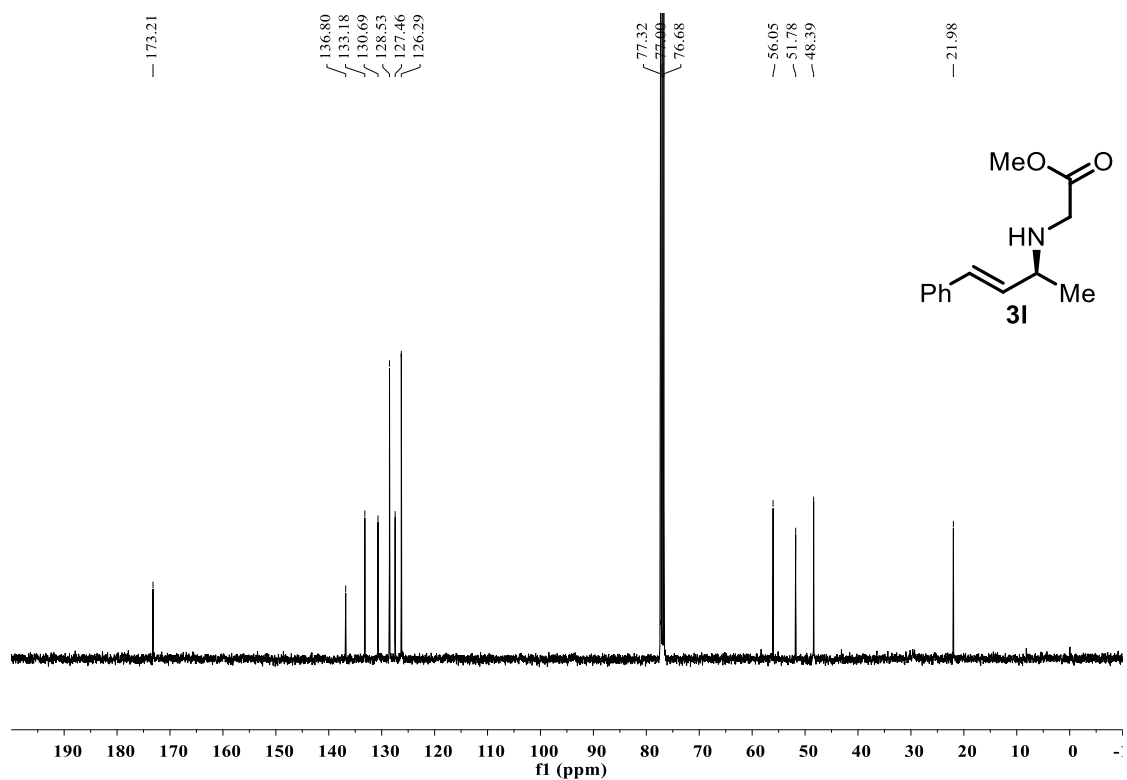
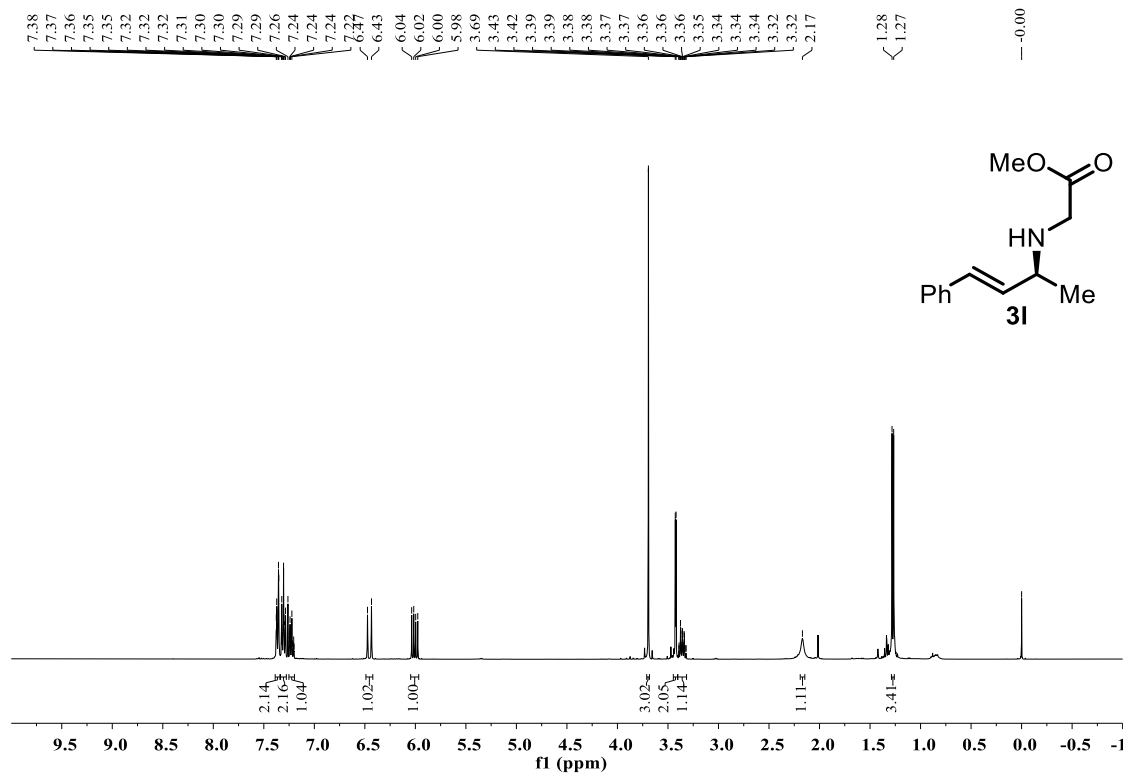


Figure S44. <sup>13</sup>C NMR spectra of **3k**, related to Figure 3.





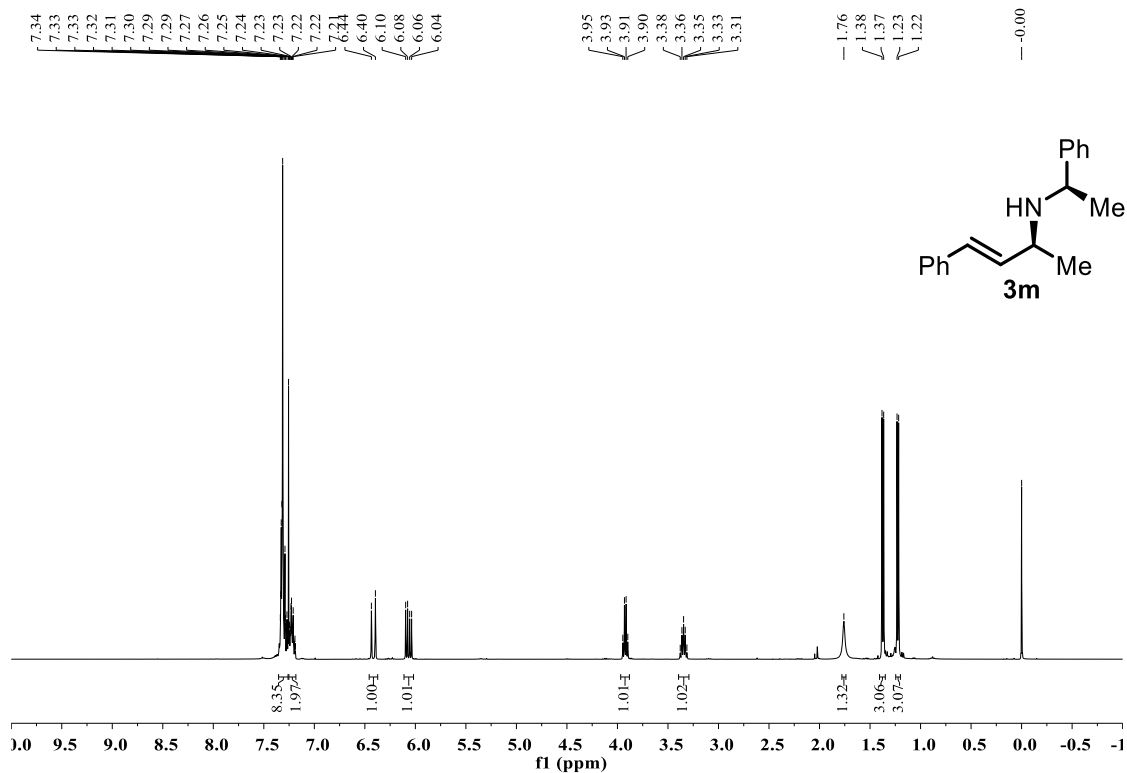


Figure S47. <sup>1</sup>H NMR spectra of **3m**, related to Figure 3.

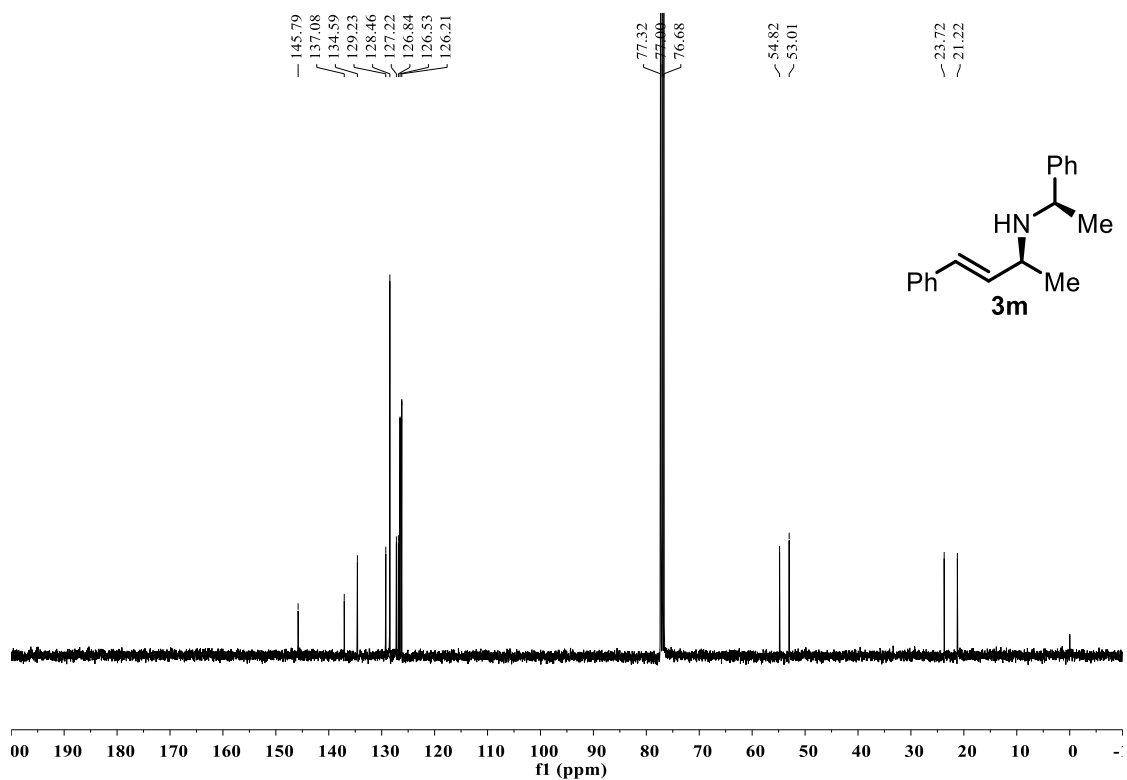
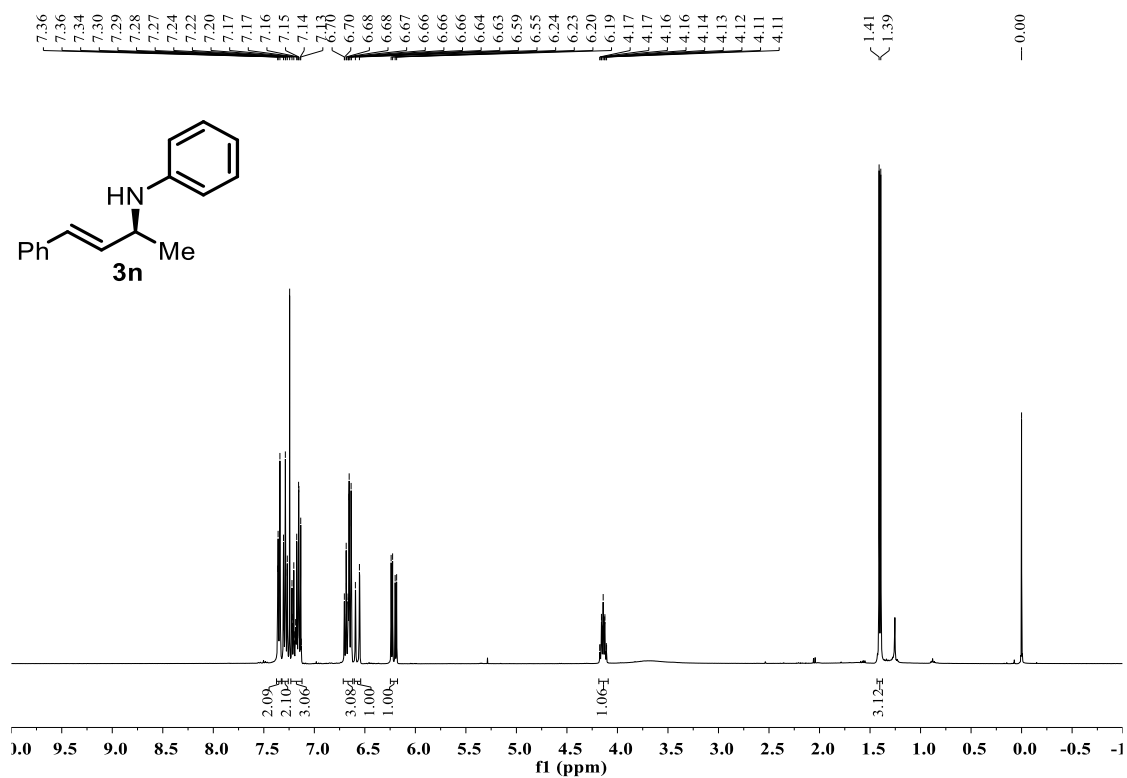
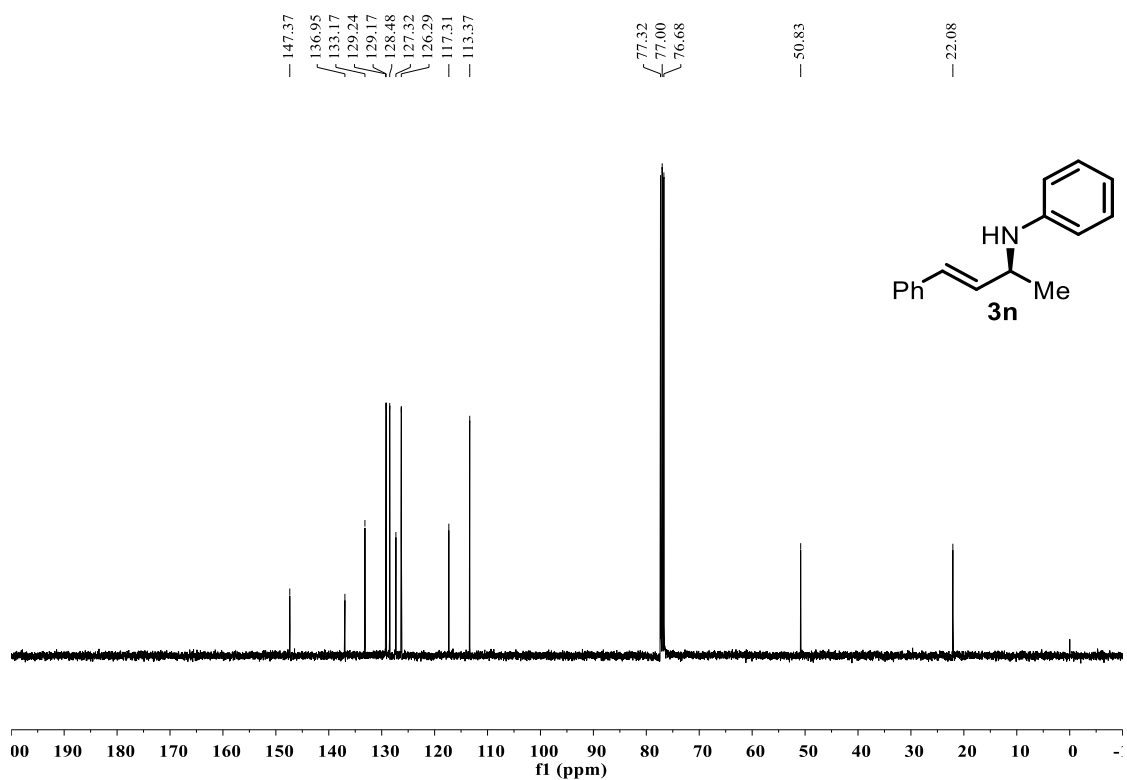


Figure S48. <sup>13</sup>C NMR spectra of **3m**, related to Figure 3.



**Figure S49.** <sup>1</sup>H NMR spectra of **3n**, related to **Figure 3**.



**Figure S50.** <sup>13</sup>C NMR spectra of **3n**, related to **Figure 3**.

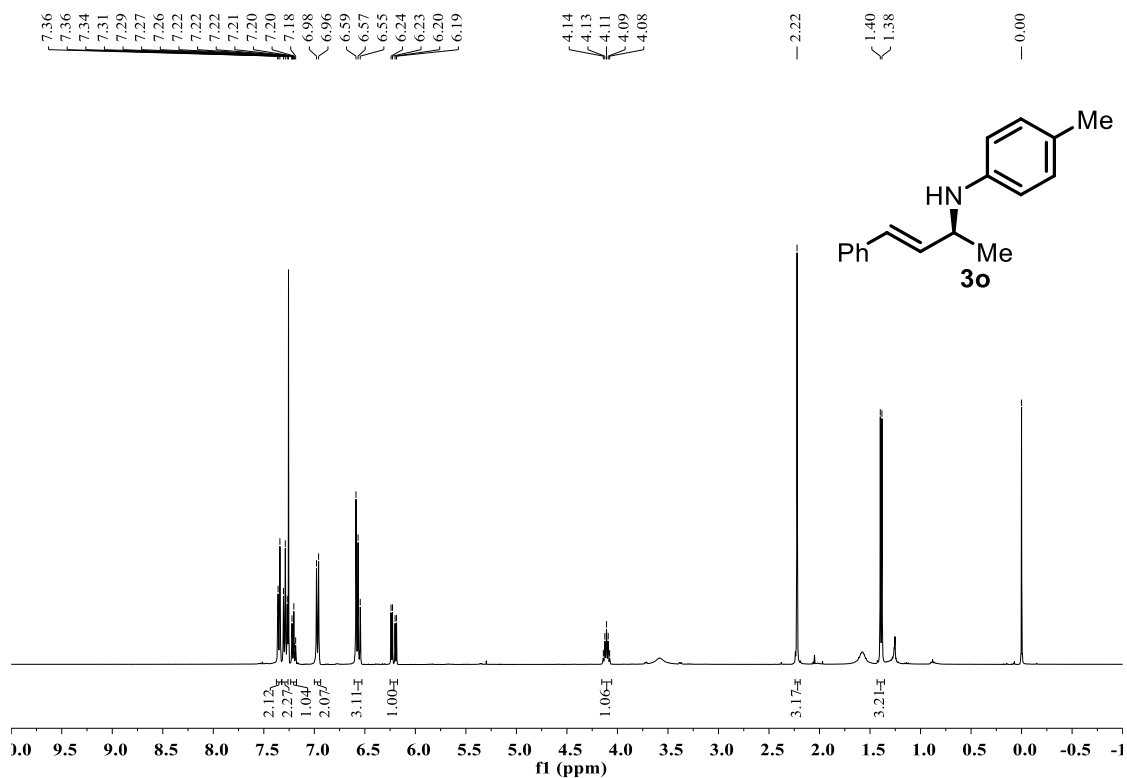


Figure S51. <sup>1</sup>H NMR spectra of **3o**, related to Figure 3.

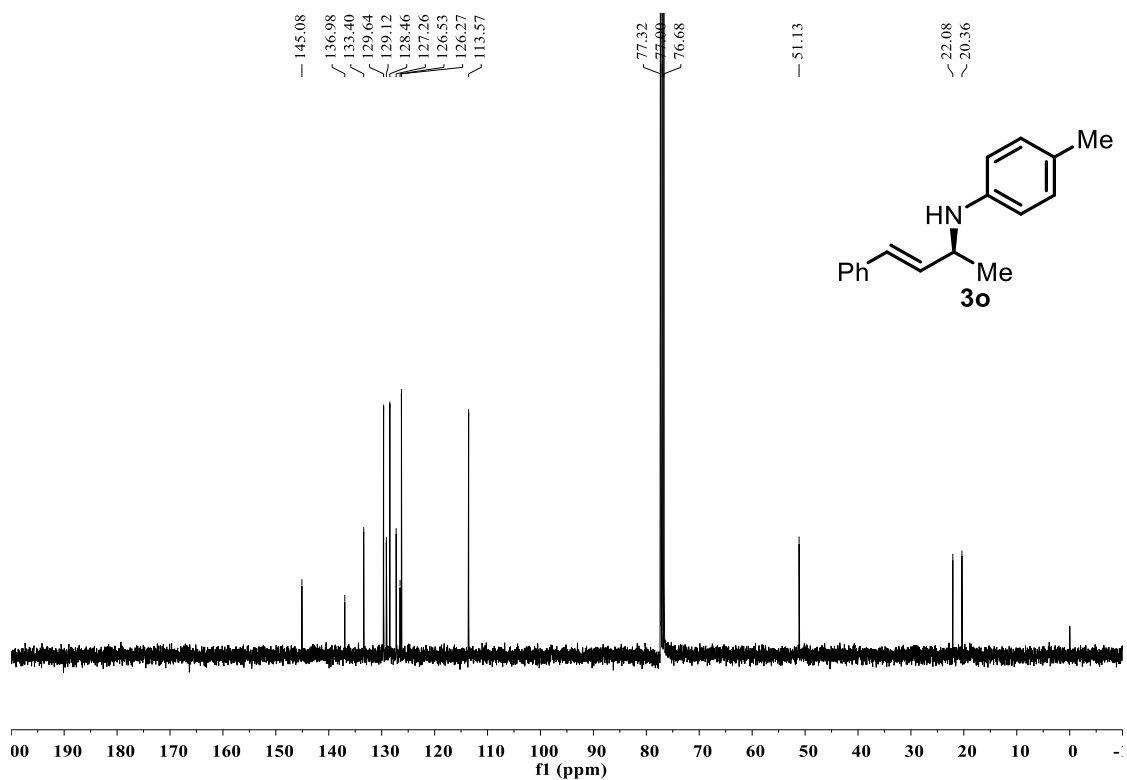
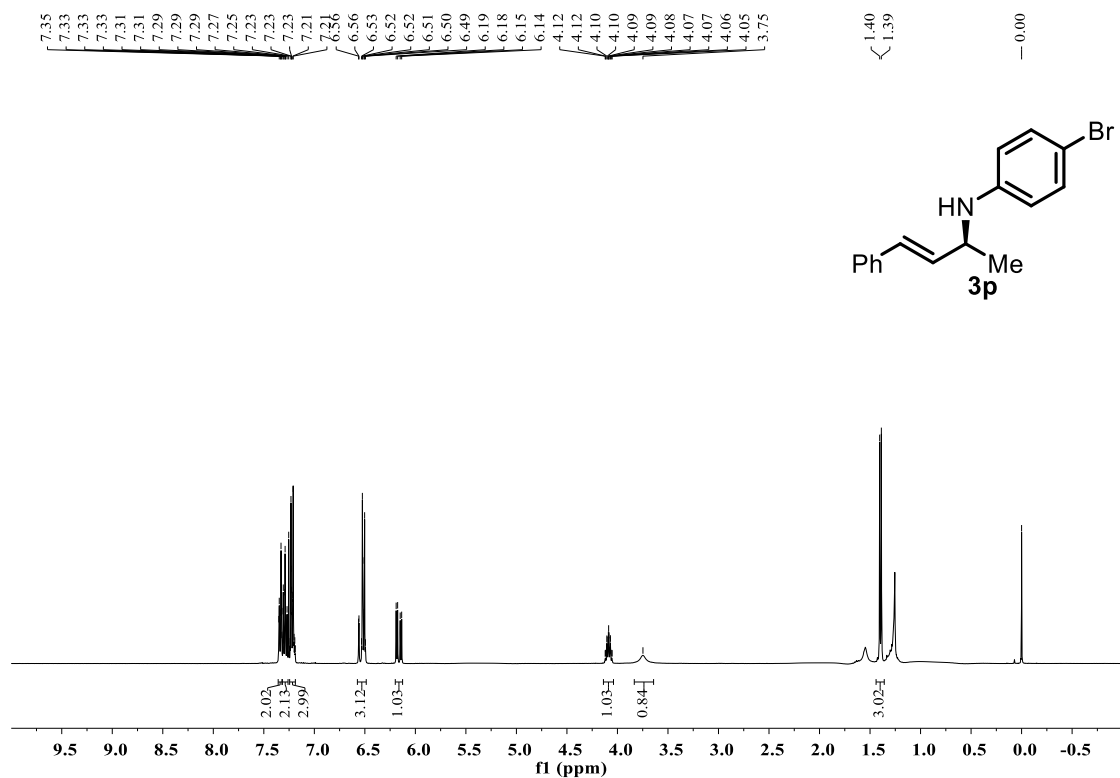
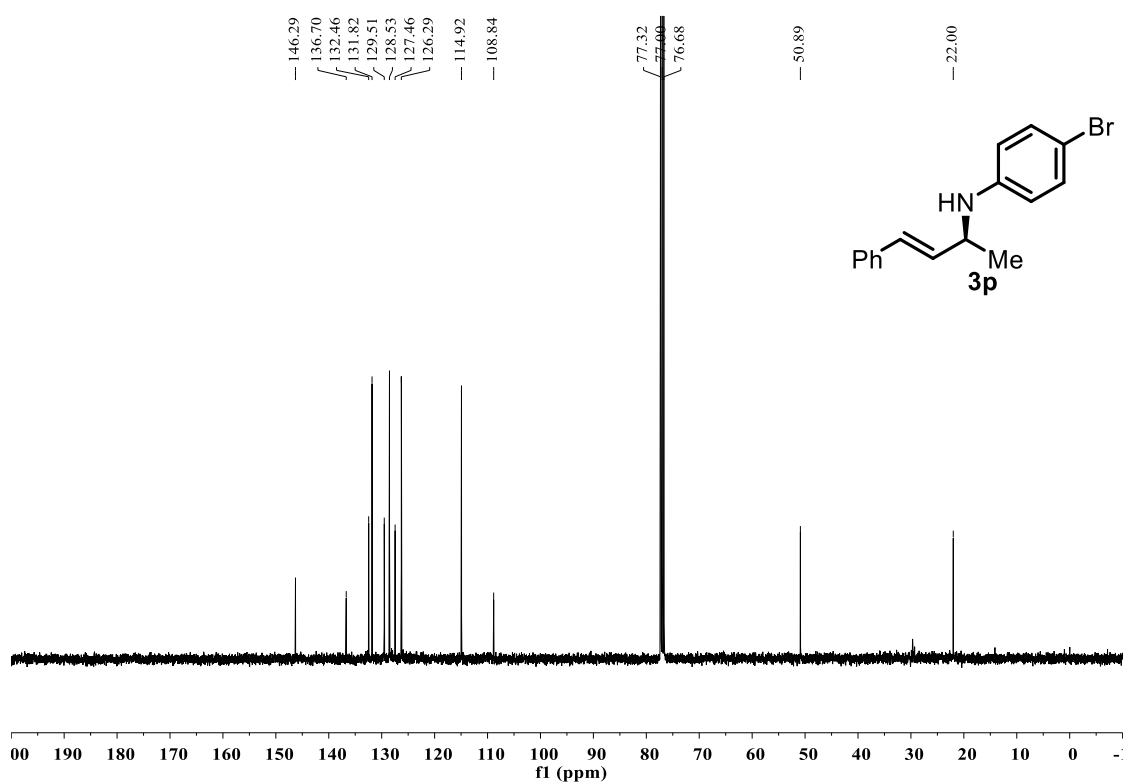


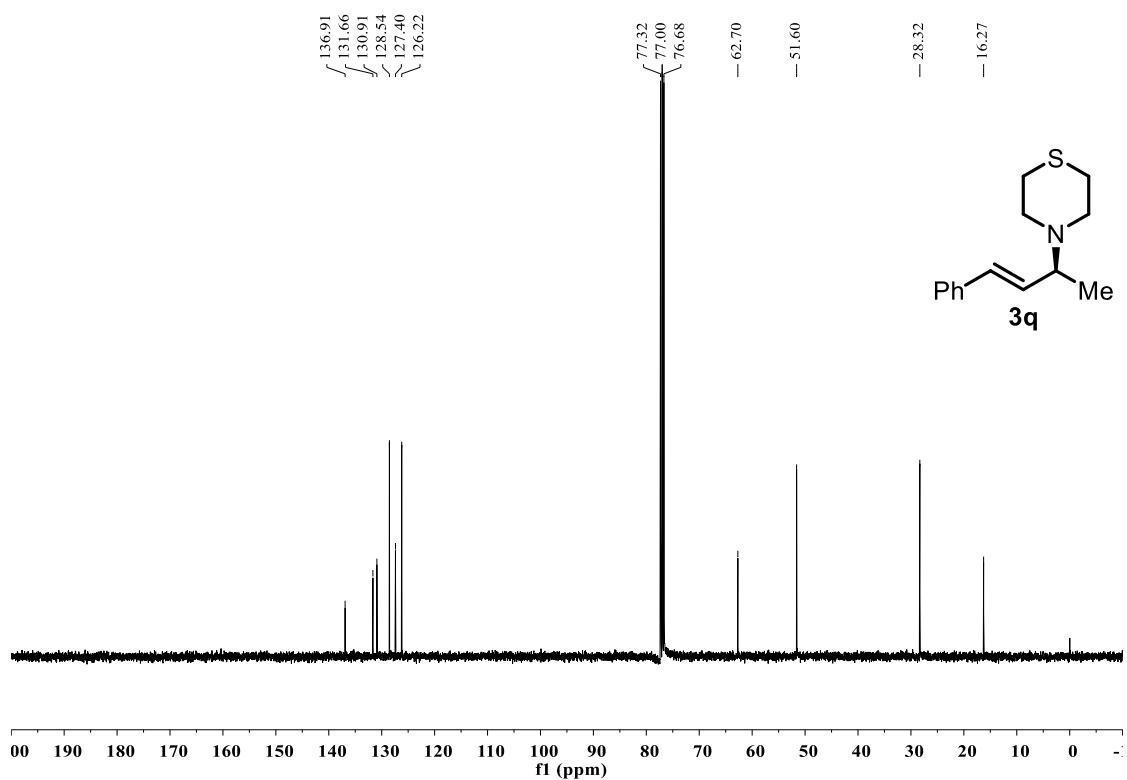
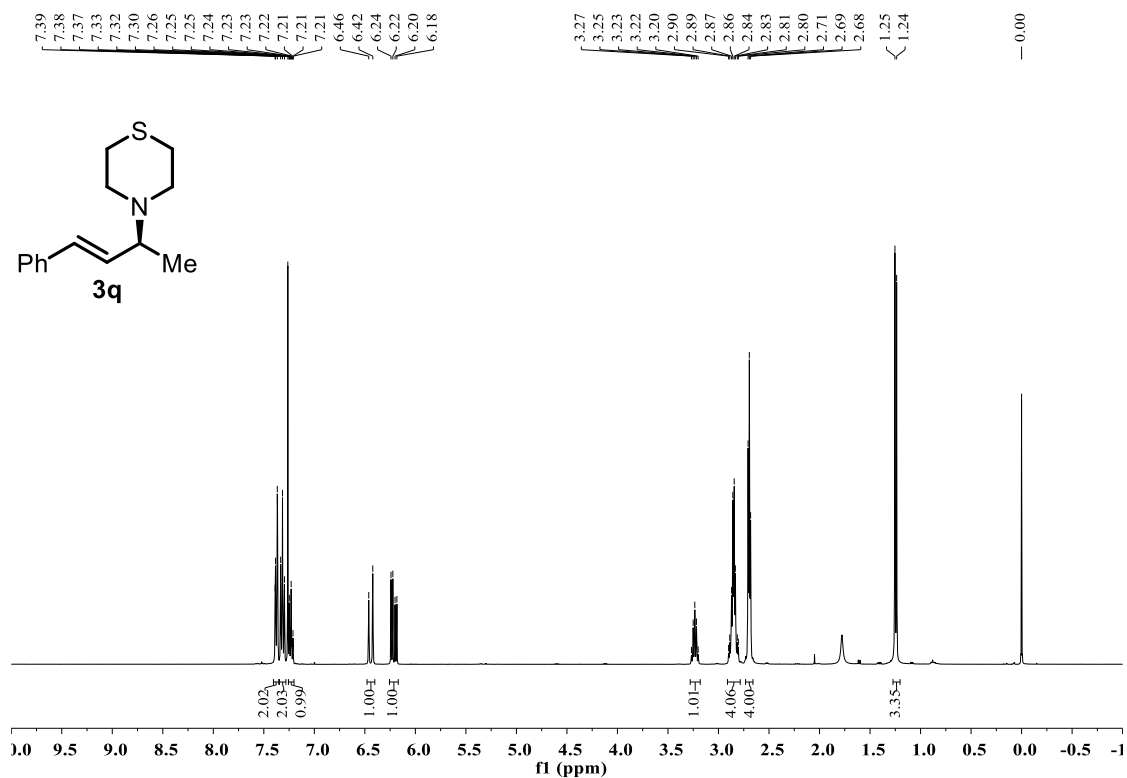
Figure S52. <sup>13</sup>C NMR spectra of **3o**, related to Figure 3.



**Figure S53.** <sup>1</sup>H NMR spectra of **3p**, related to **Figure 3**.



**Figure S54.** <sup>13</sup>C NMR spectra of **3p**, related to **Figure 3**.



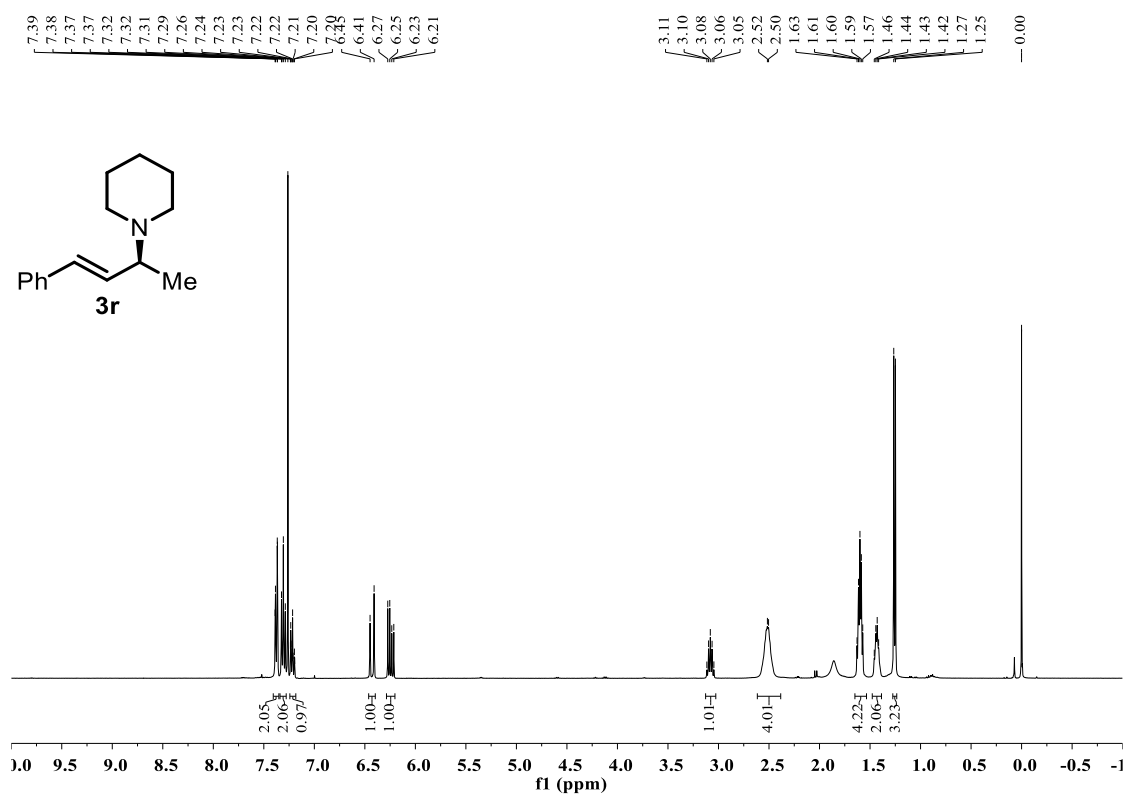


Figure S57. <sup>1</sup>H NMR spectra of **3r**, related to Figure 3.

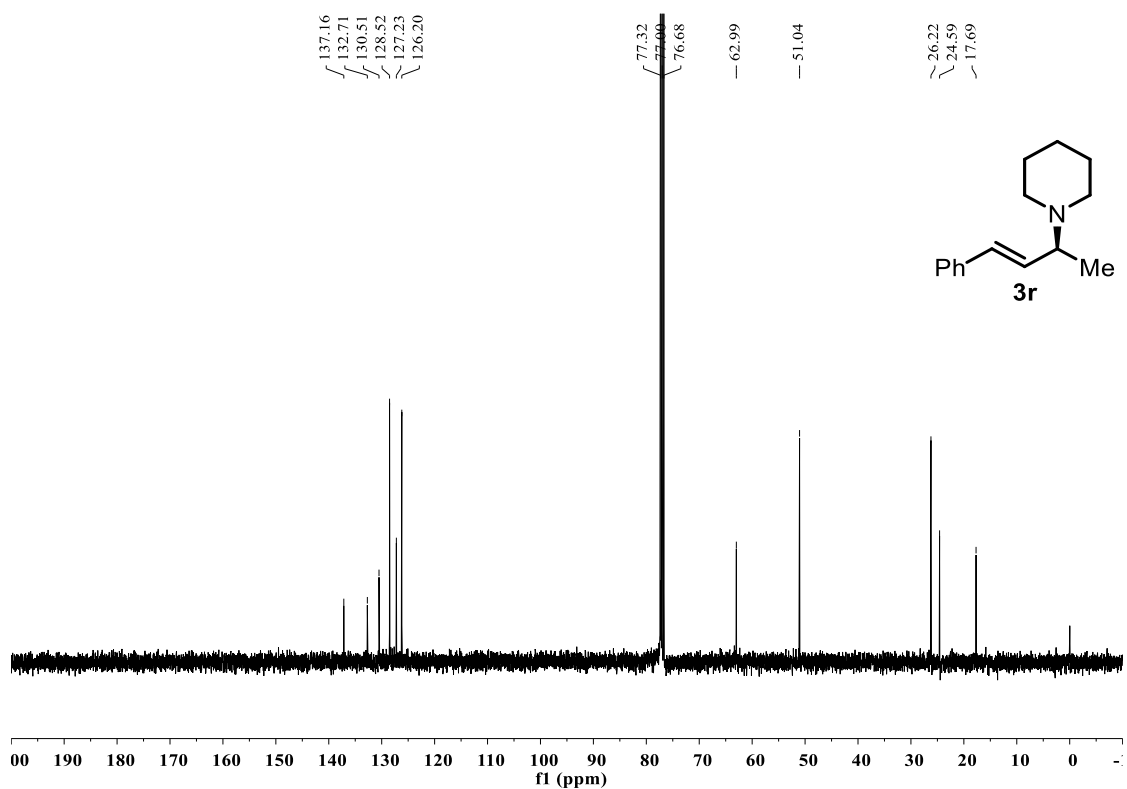


Figure S58. <sup>13</sup>C NMR spectra of **3r**, related to Figure 3.

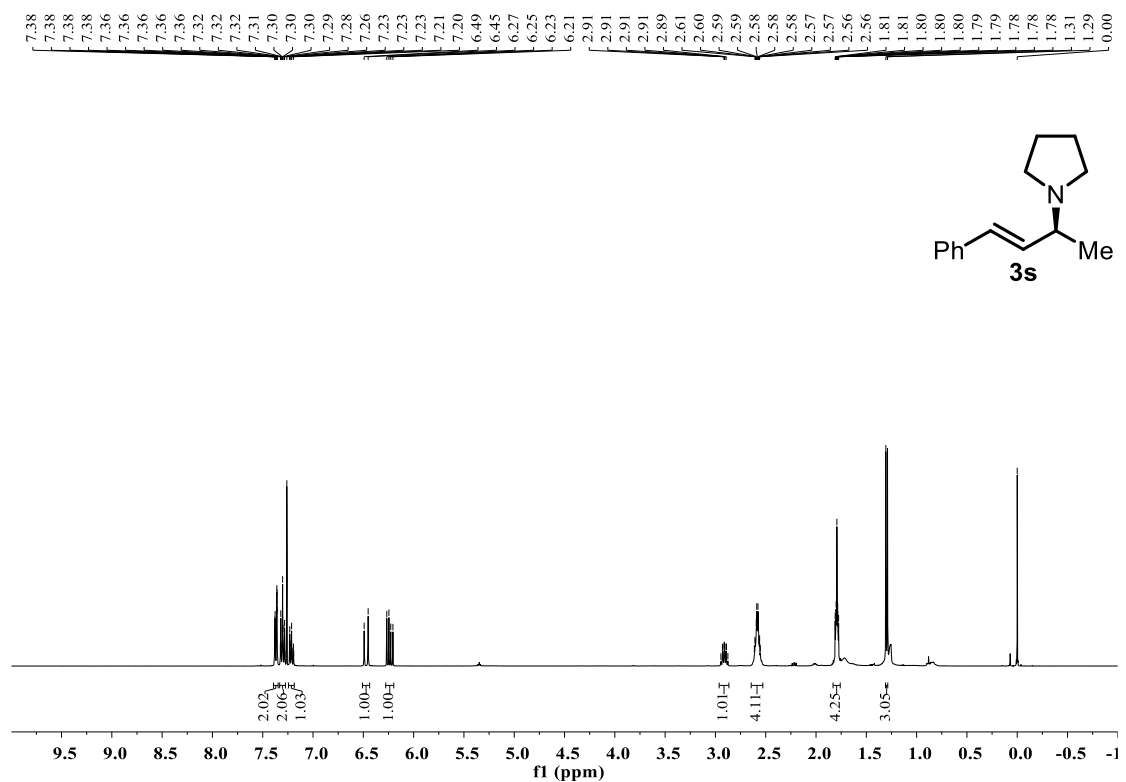


Figure S59. <sup>1</sup>H NMR spectra of **3s**, related to Figure 3.

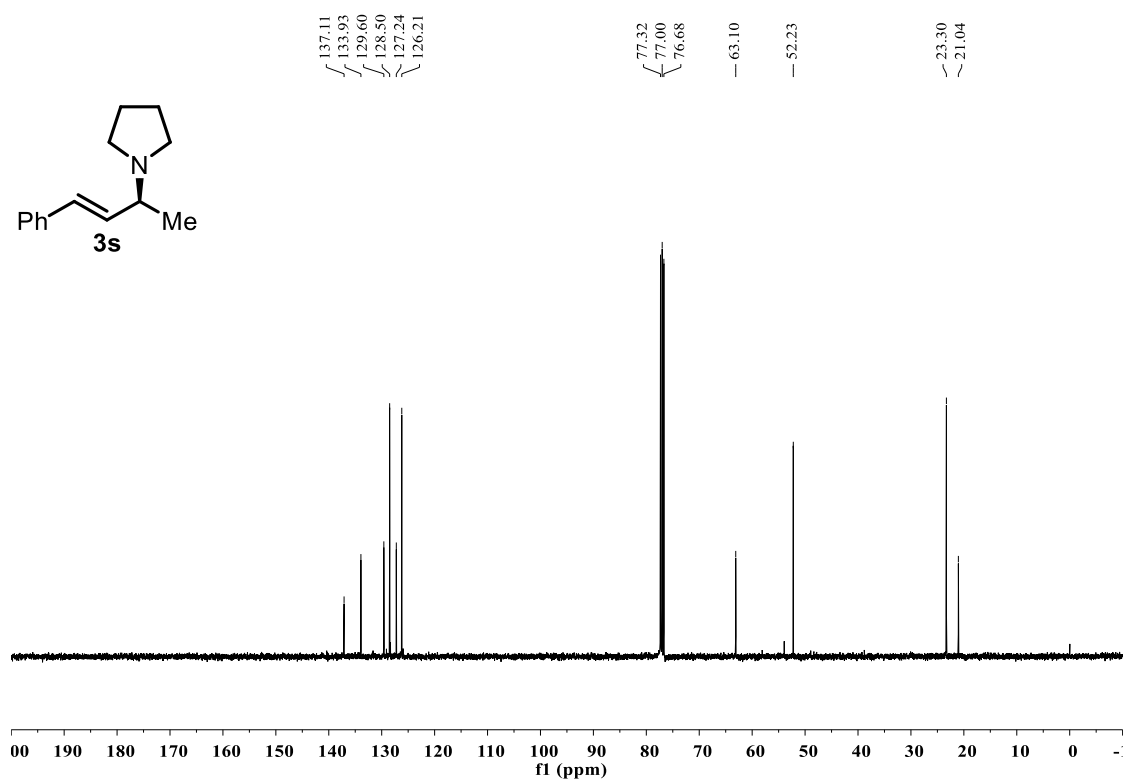


Figure S60. <sup>13</sup>C NMR spectra of **3s**, related to Figure 3.

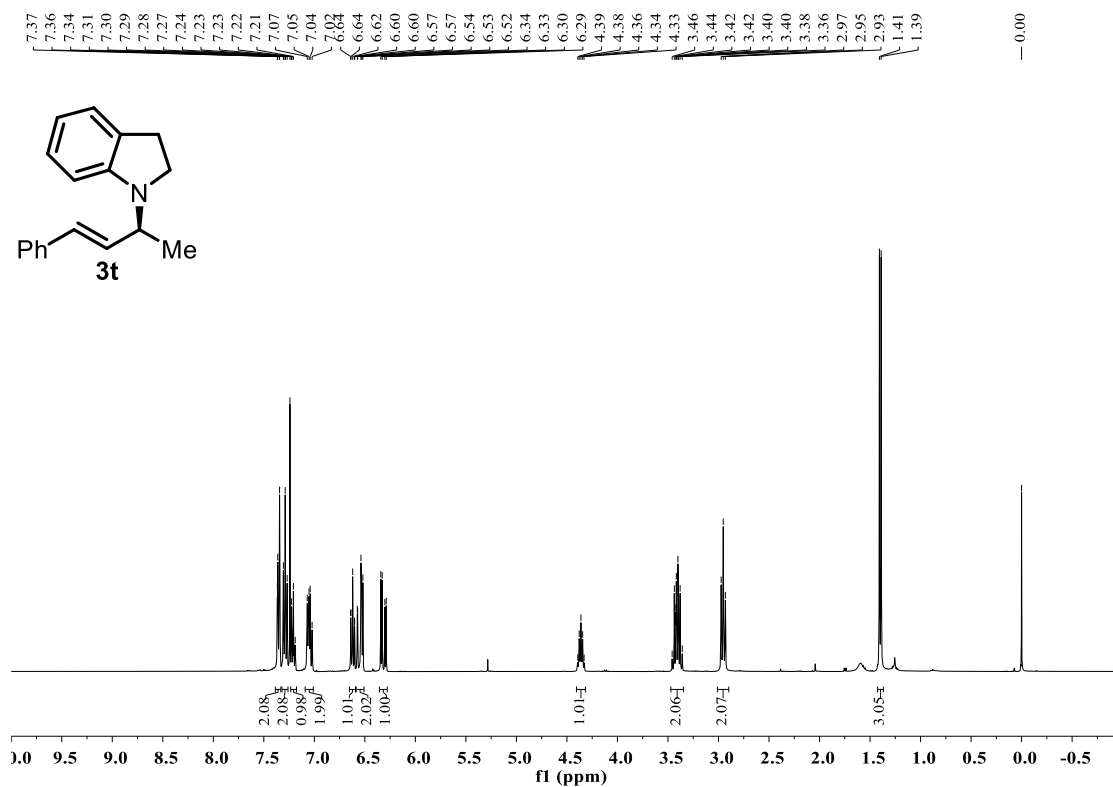


Figure S61. <sup>1</sup>H NMR spectra of **3t**, related to Figure 3.

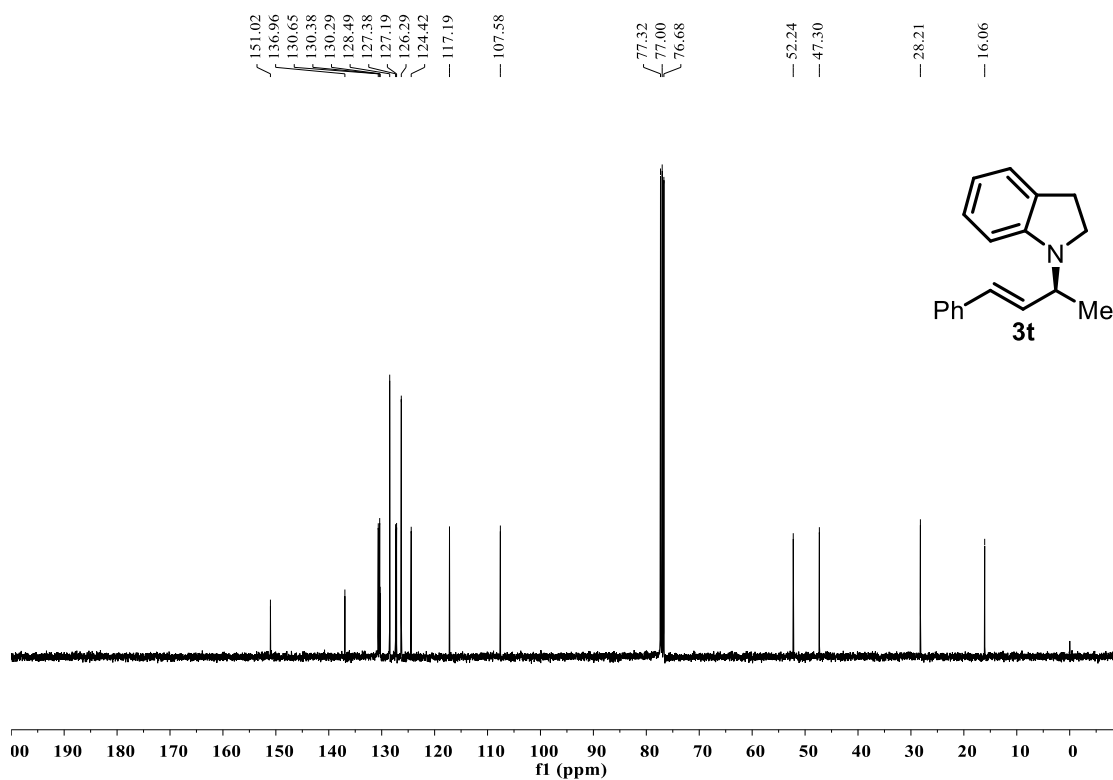
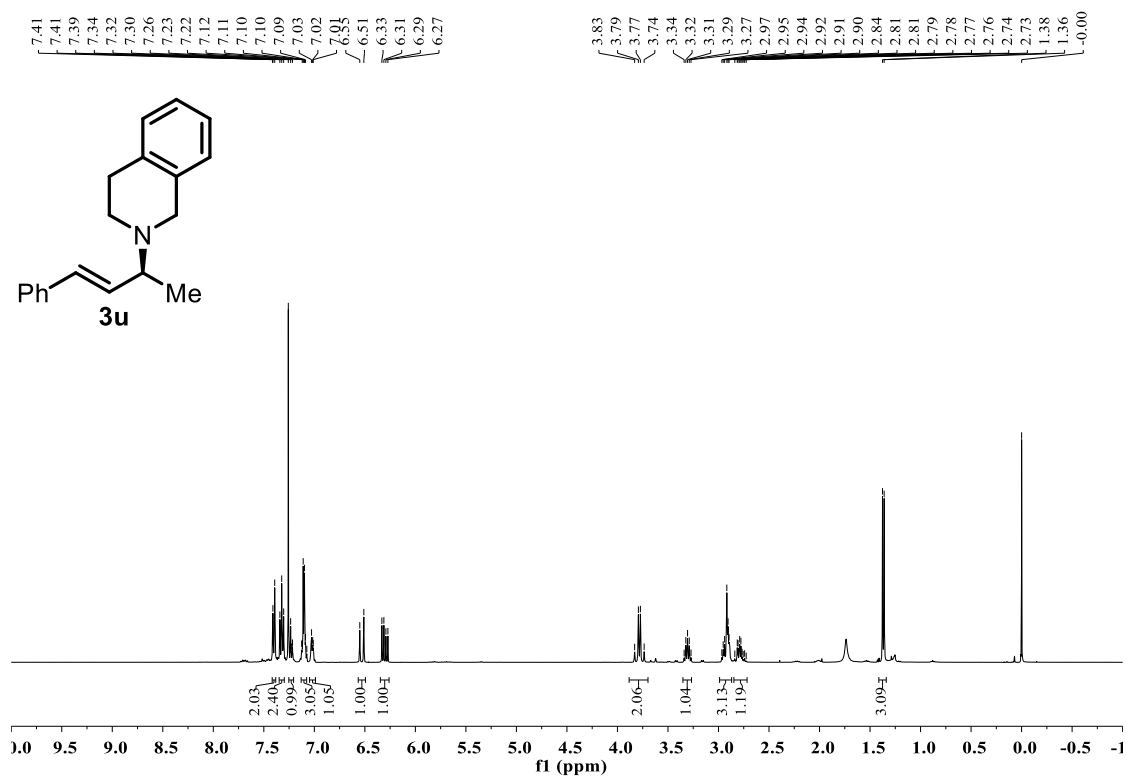
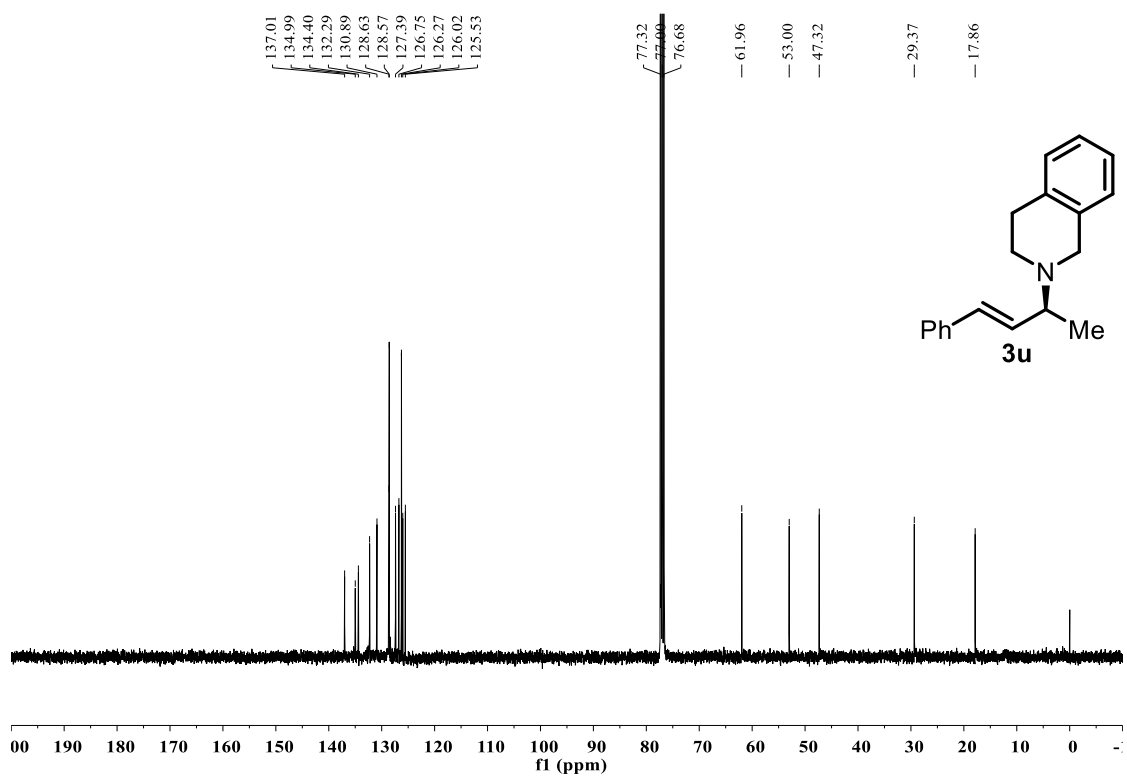


Figure S62. <sup>13</sup>C NMR spectra of **3t**, related to Figure 3.





**Figure S63.** <sup>1</sup>H NMR spectra of **3u**, related to **Figure 3**.



**Figure S64.** <sup>13</sup>C NMR spectra of **3u**, related to **Figure 3**.

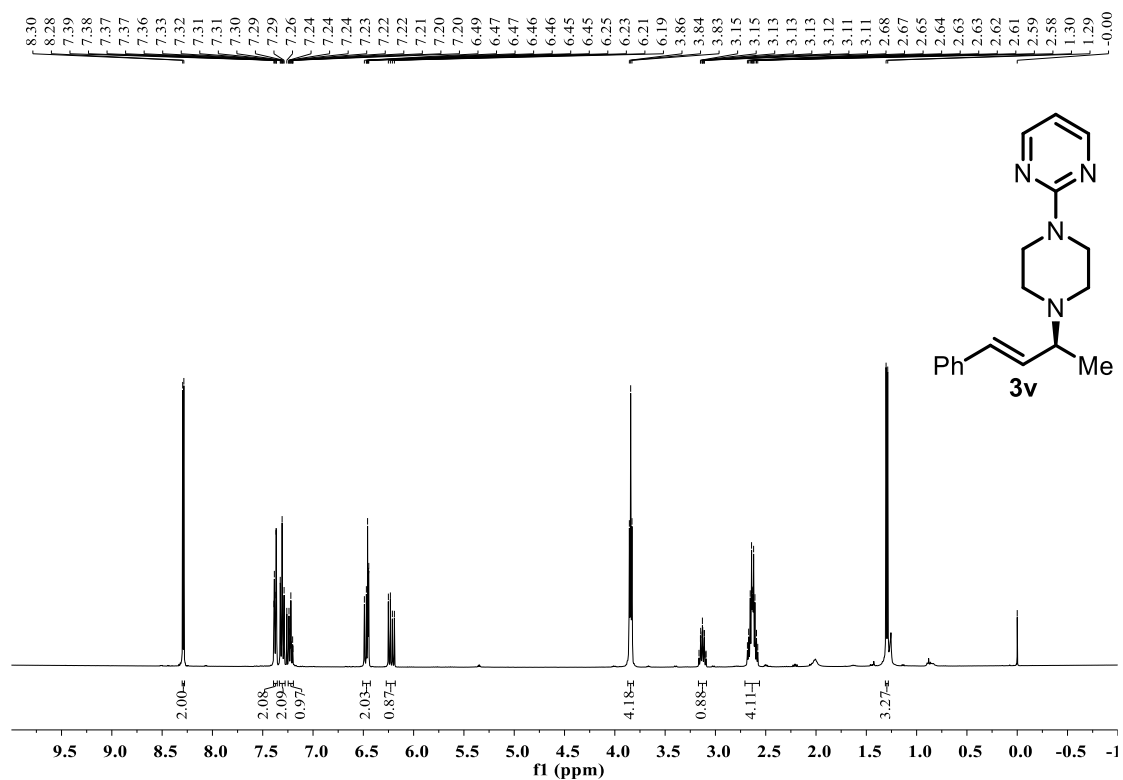


Figure S65. <sup>1</sup>H NMR spectra of **3v**, related to Figure 3.

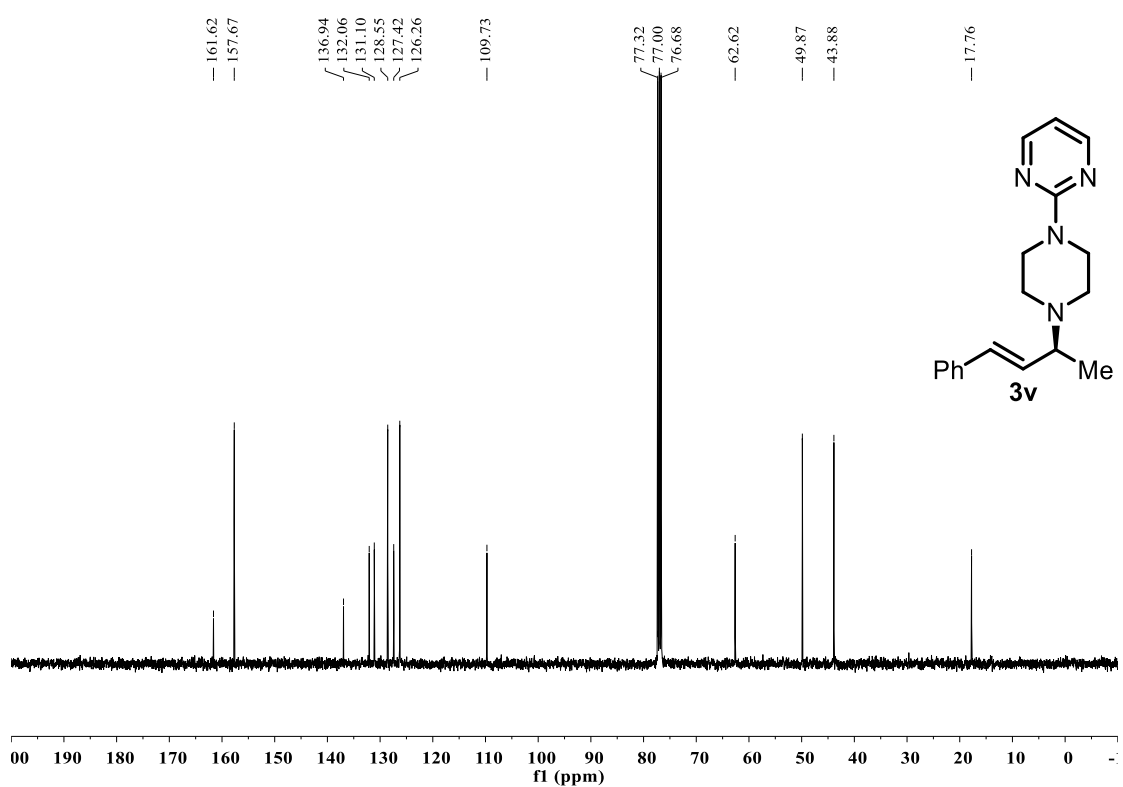
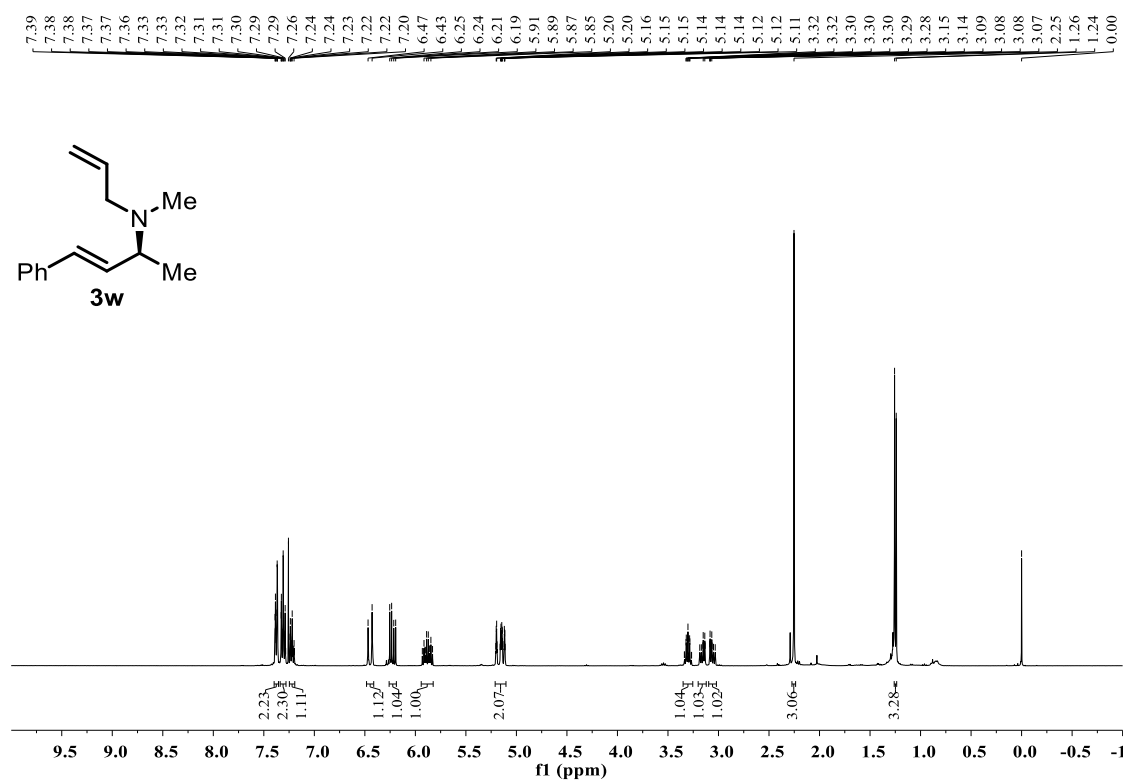
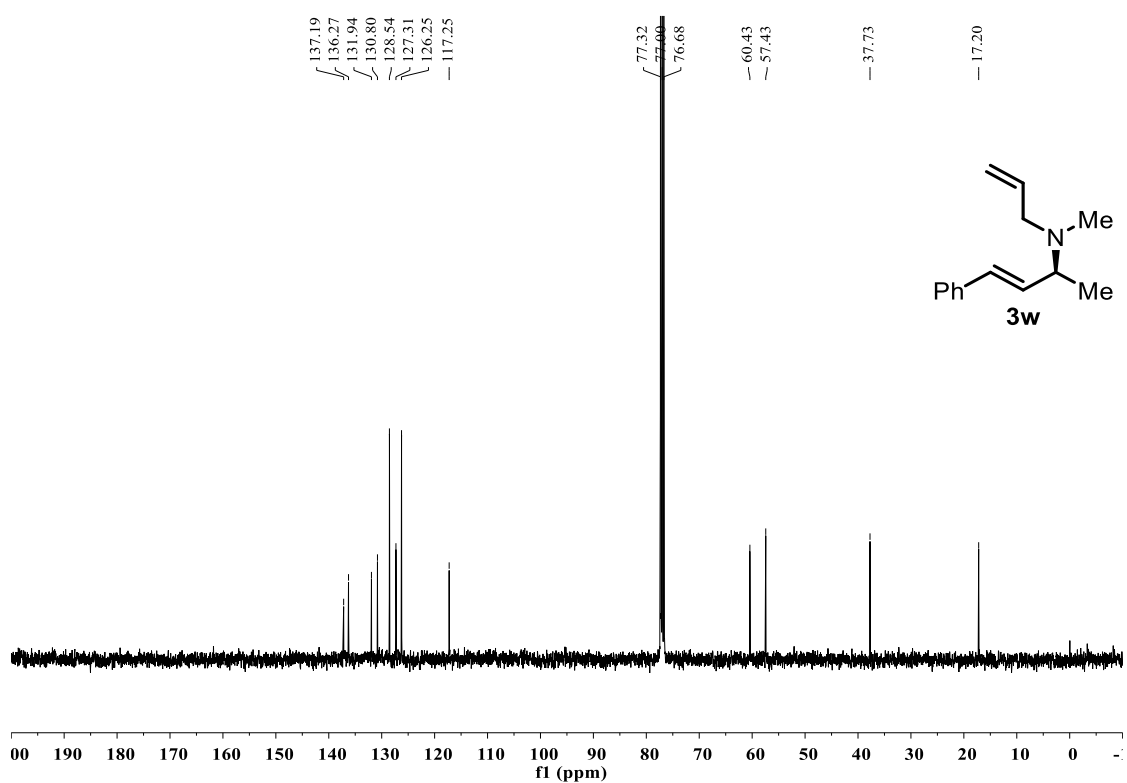


Figure S66. <sup>13</sup>C NMR spectra of **3v**, related to Figure 3.



**Figure S67.** <sup>1</sup>H NMR spectra of **3w**, related to **Figure 3**.



**Figure S68.** <sup>13</sup>C NMR spectra of **3w**, related to **Figure 3**.

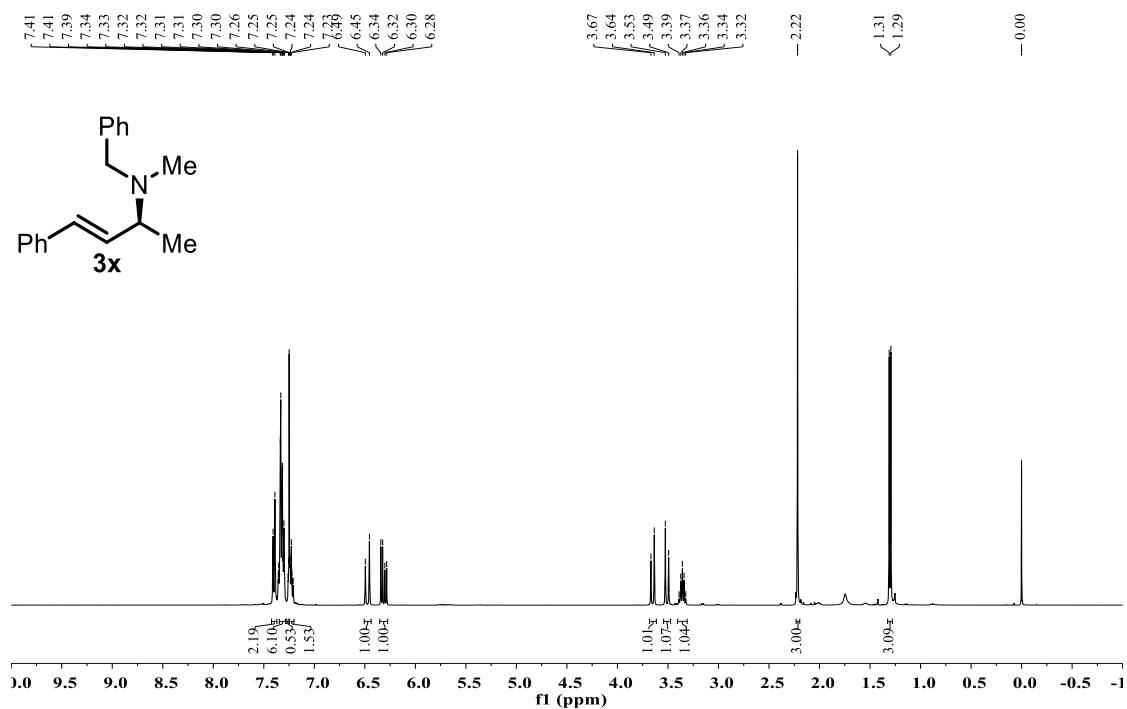


Figure S69. <sup>1</sup>H NMR spectra of **3x**, related to Figure 3.

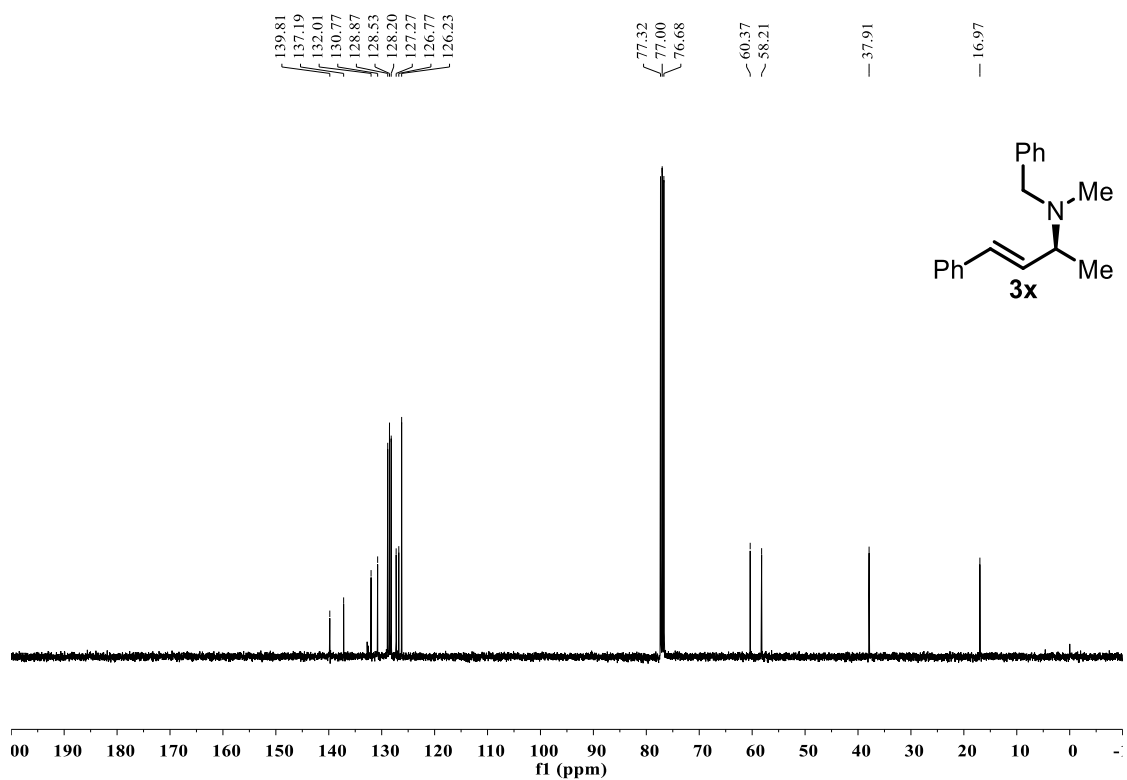


Figure S70. <sup>13</sup>C NMR spectra of **3x**, related to Figure 3.

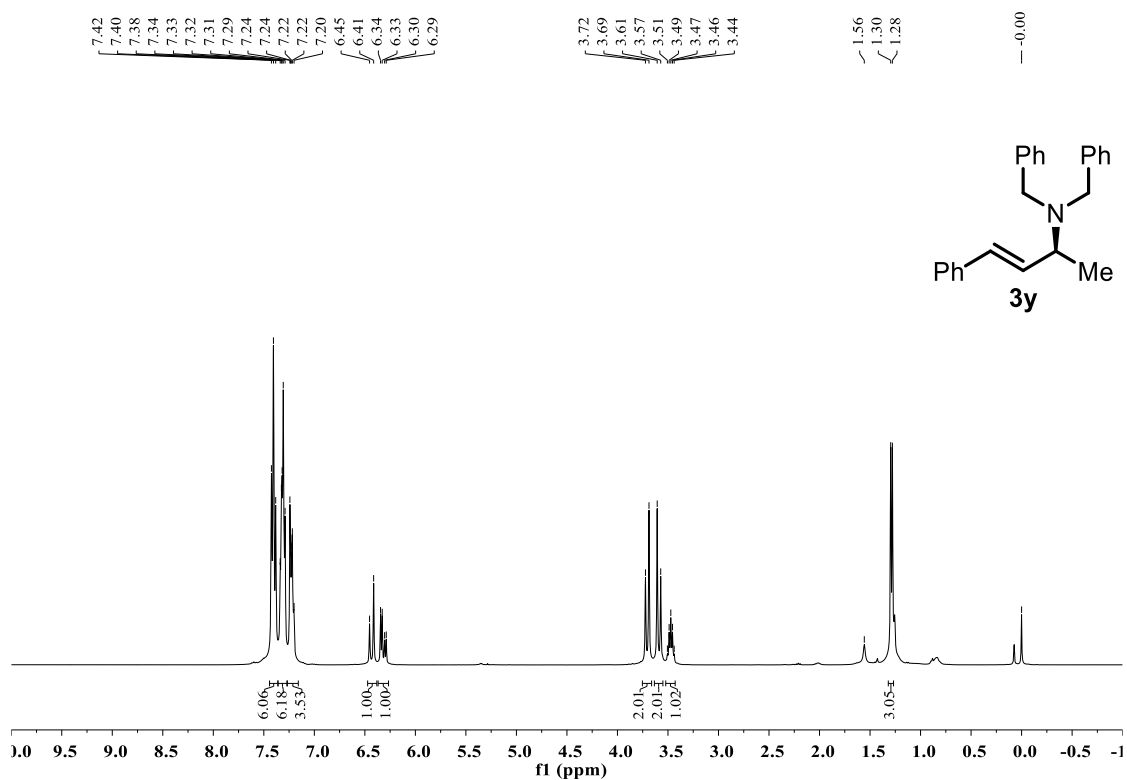


Figure S71. <sup>1</sup>H NMR spectra of **3y**, related to Figure 3.

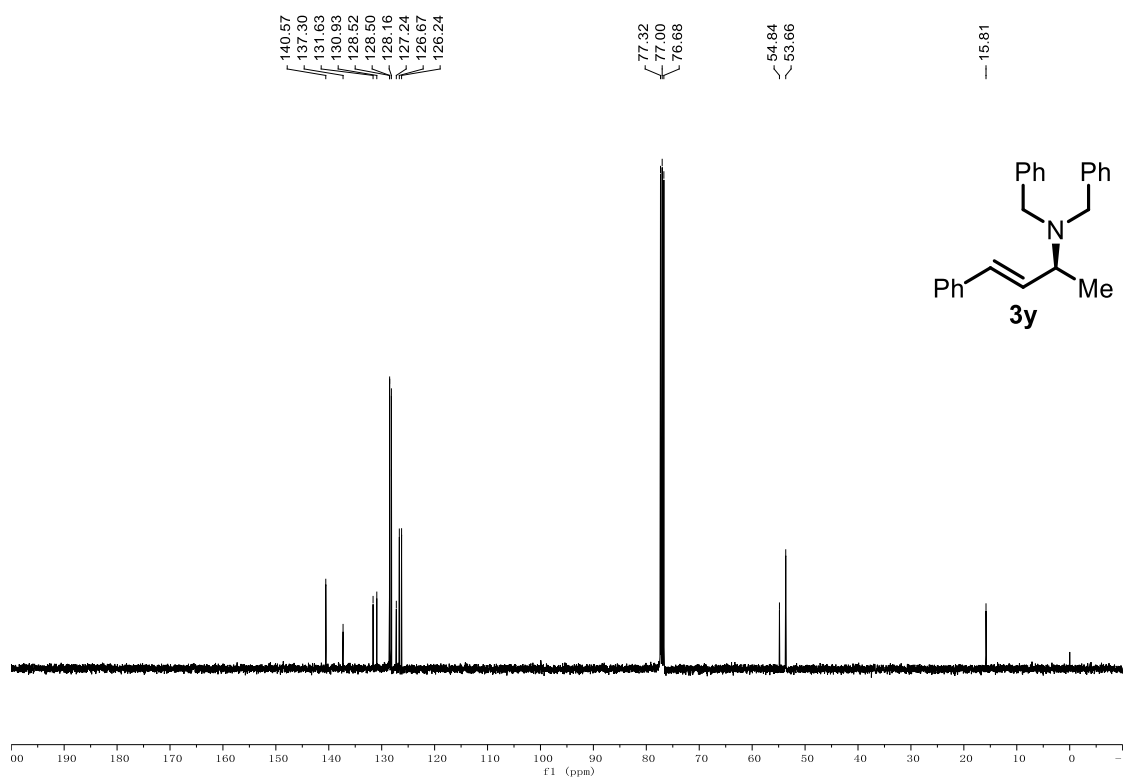
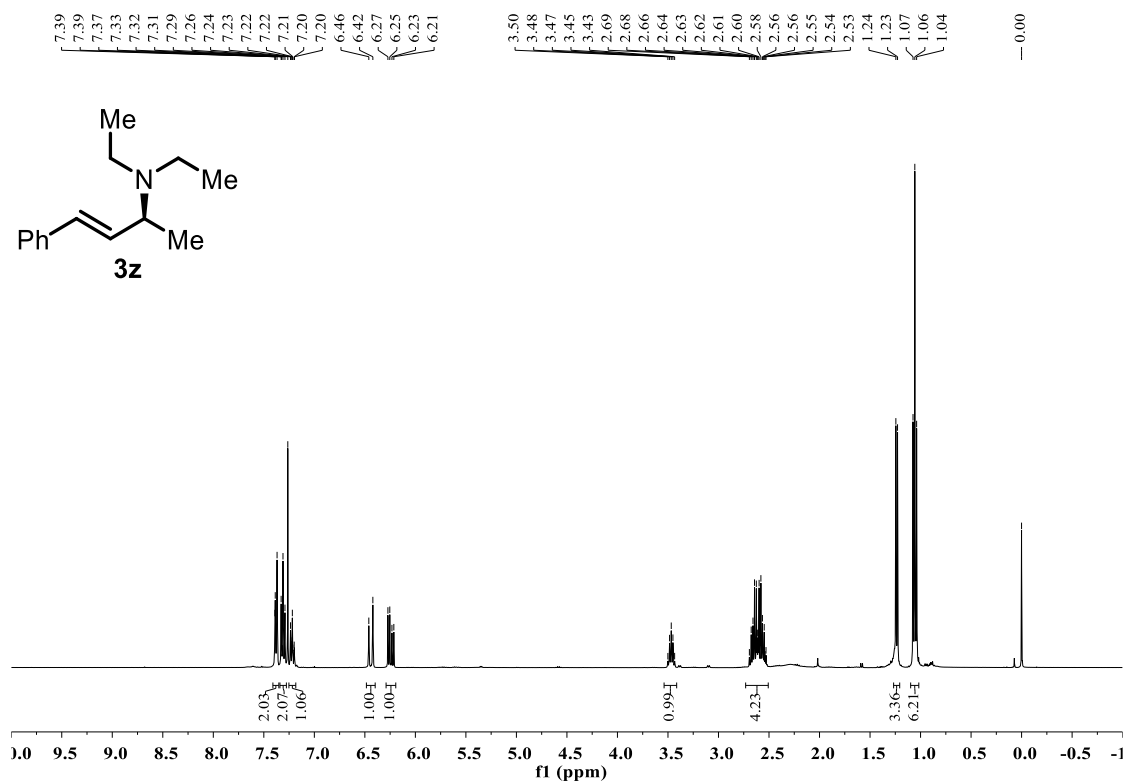
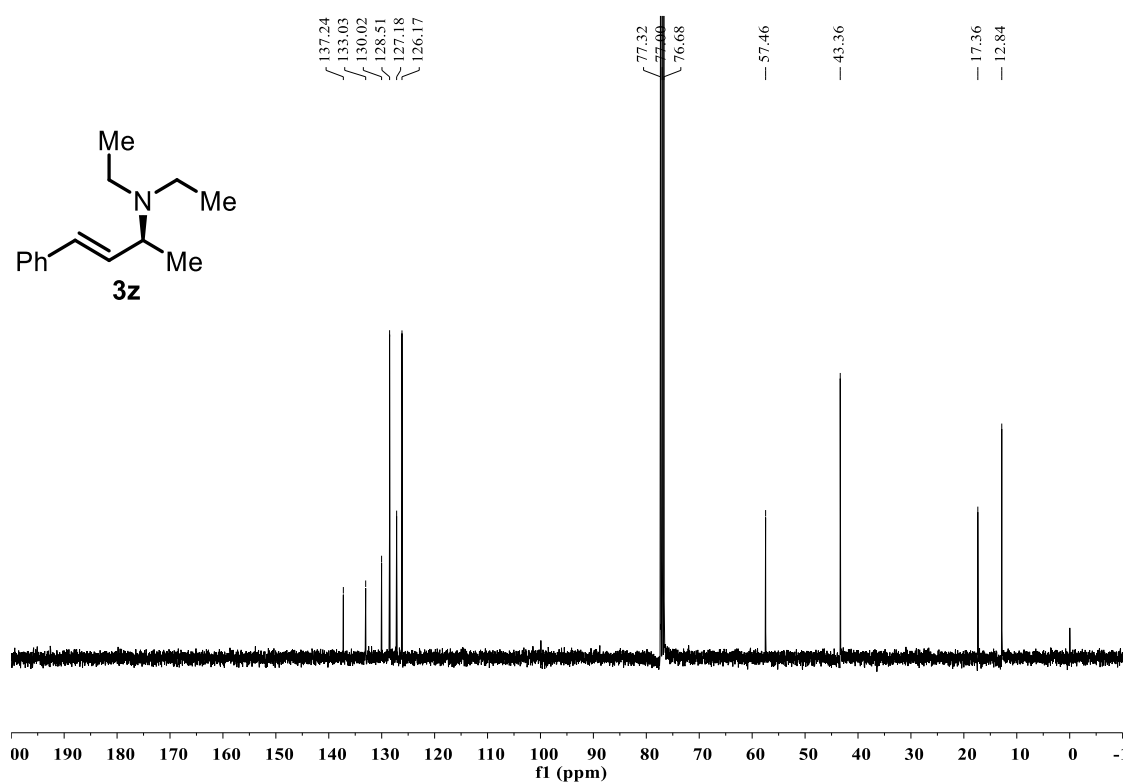


Figure S72. <sup>13</sup>C NMR spectra of **3y**, related to Figure 3.



**Figure S73.** <sup>1</sup>H NMR spectra of **3z**, related to **Figure 3**.



**Figure S74.** <sup>13</sup>C NMR spectra of **3z**, related to **Figure 3**.



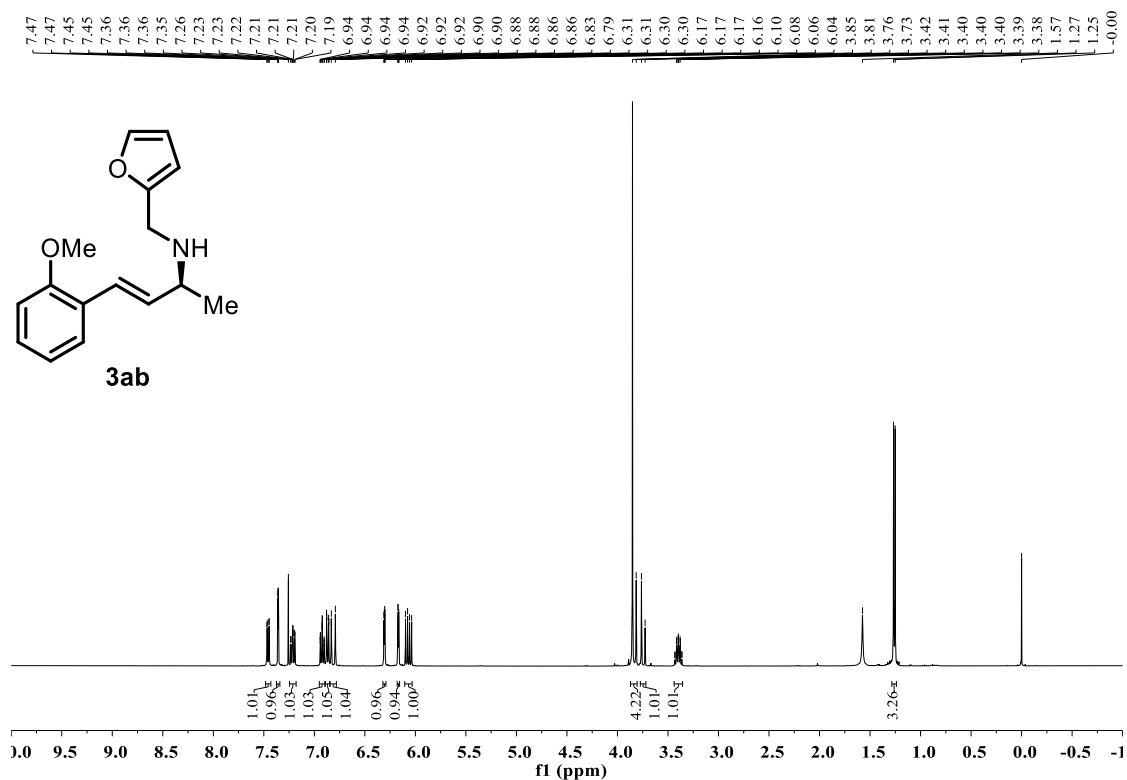


Figure S77. <sup>1</sup>H NMR spectra of **3ab**, related to Figure 4.

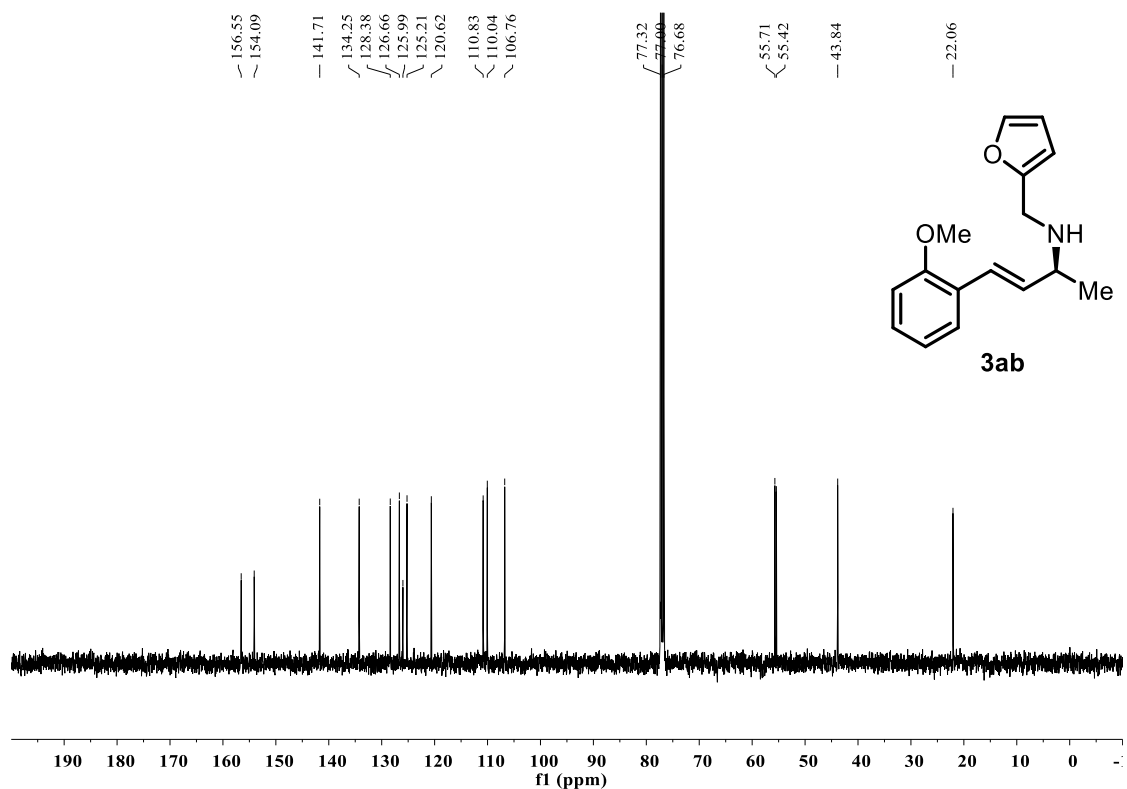


Figure S78. <sup>13</sup>C NMR spectra of **3ab**, related to Figure 4.



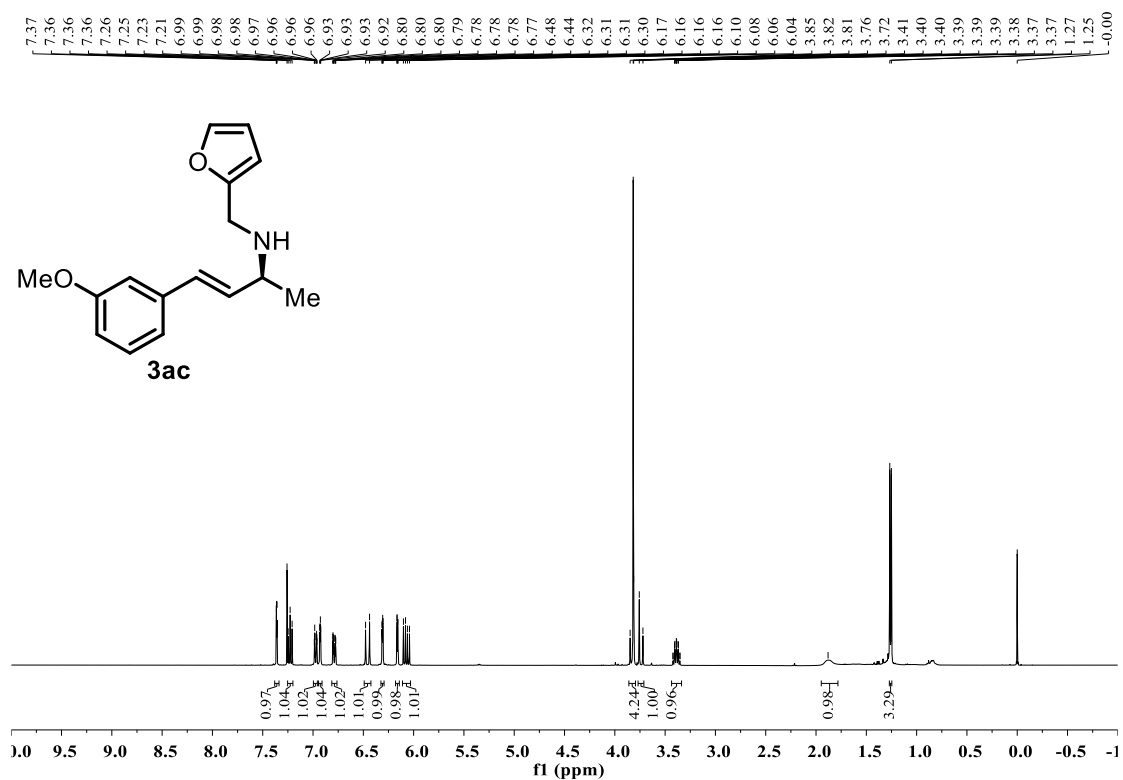


Figure S79. <sup>1</sup>H NMR spectra of **3ac**, related to Figure 4.

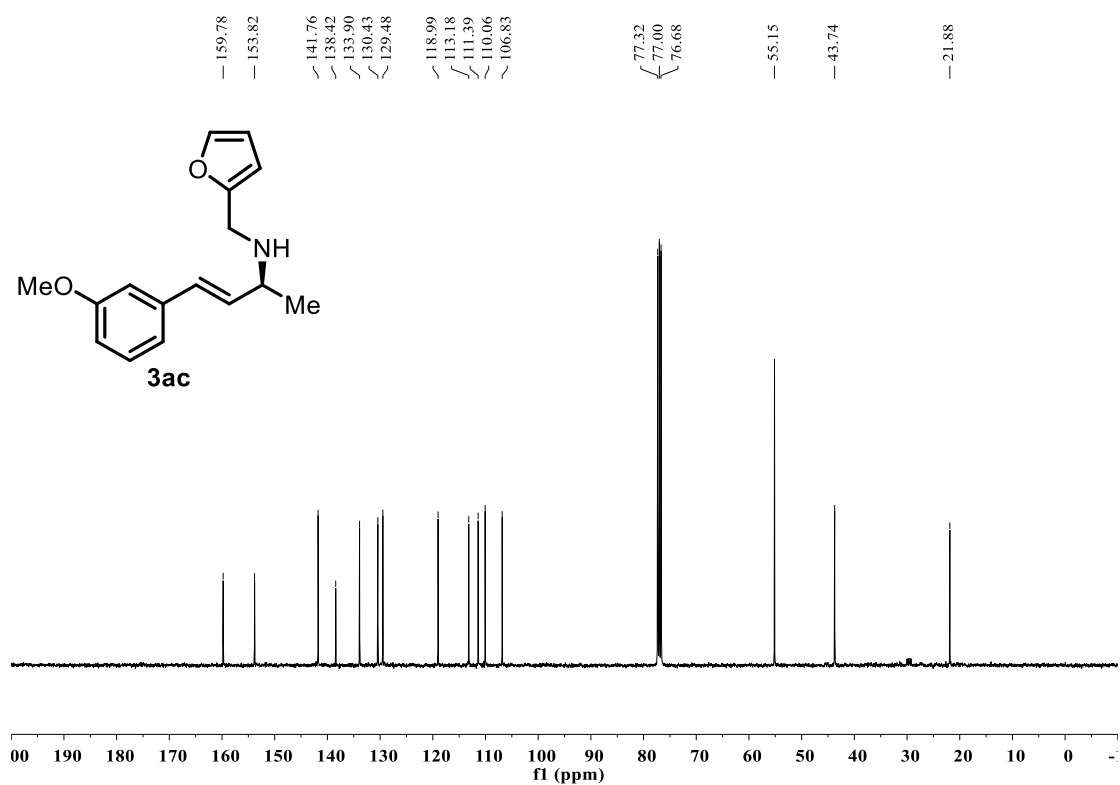
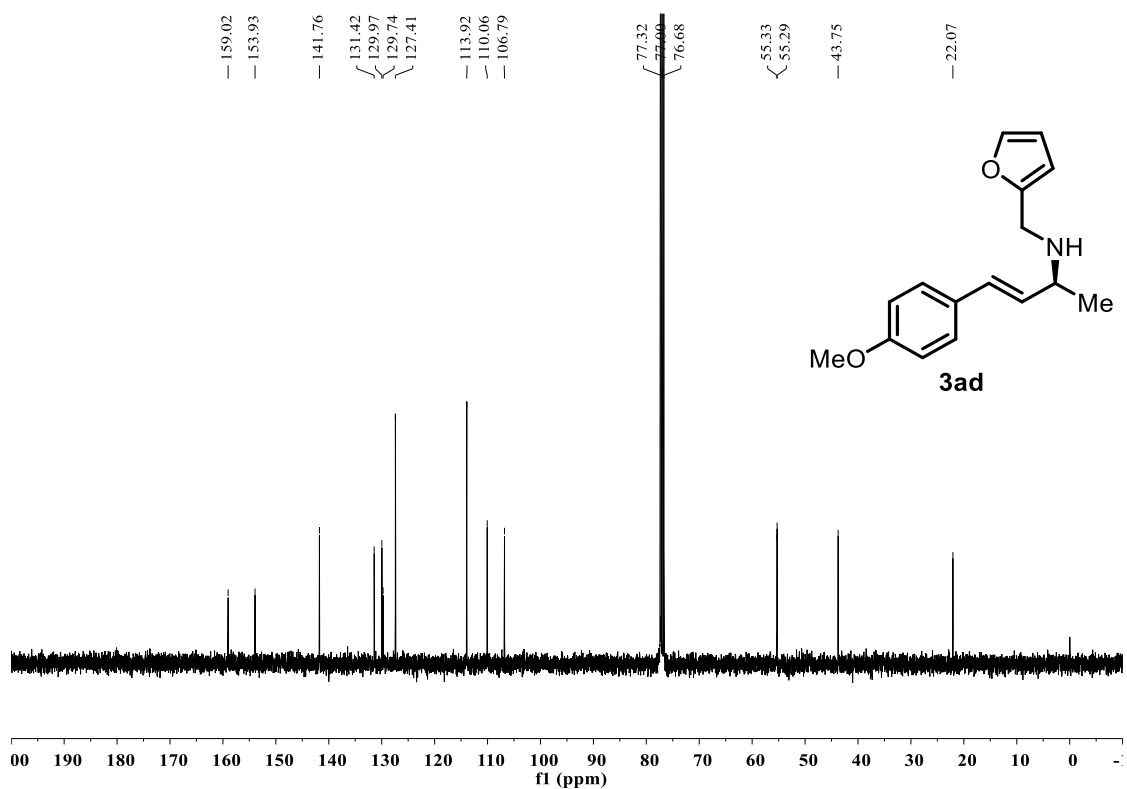
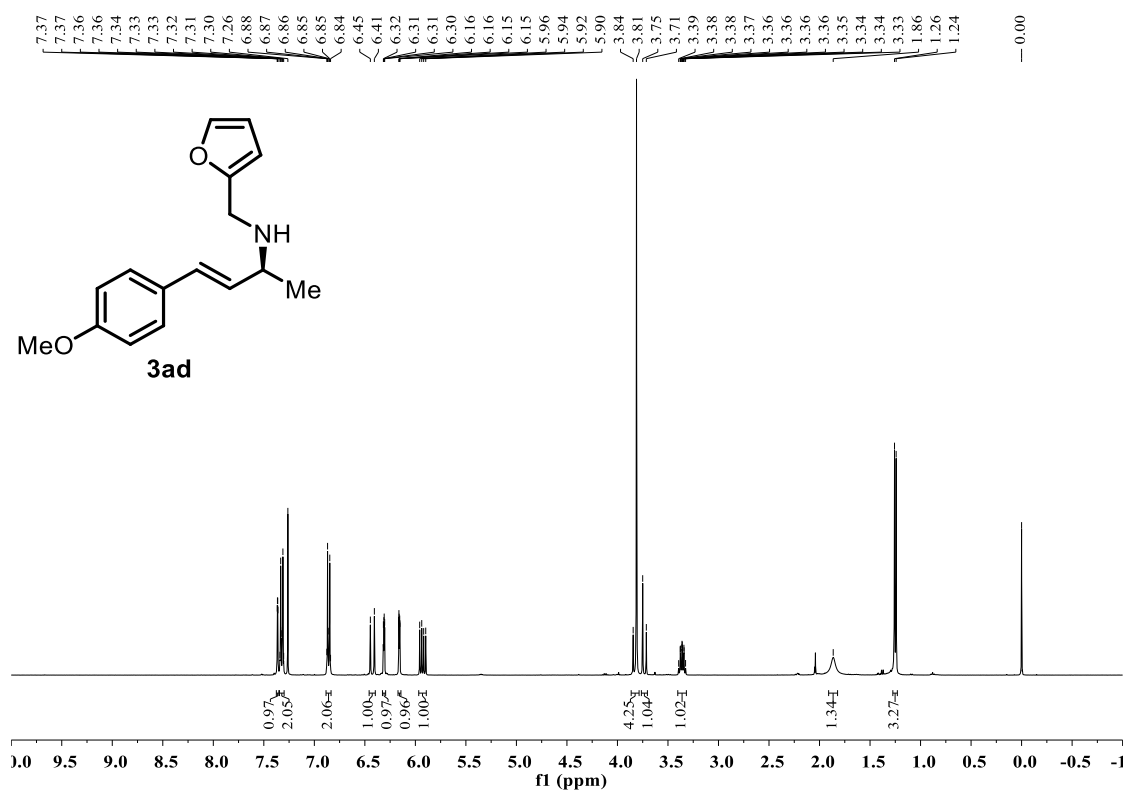
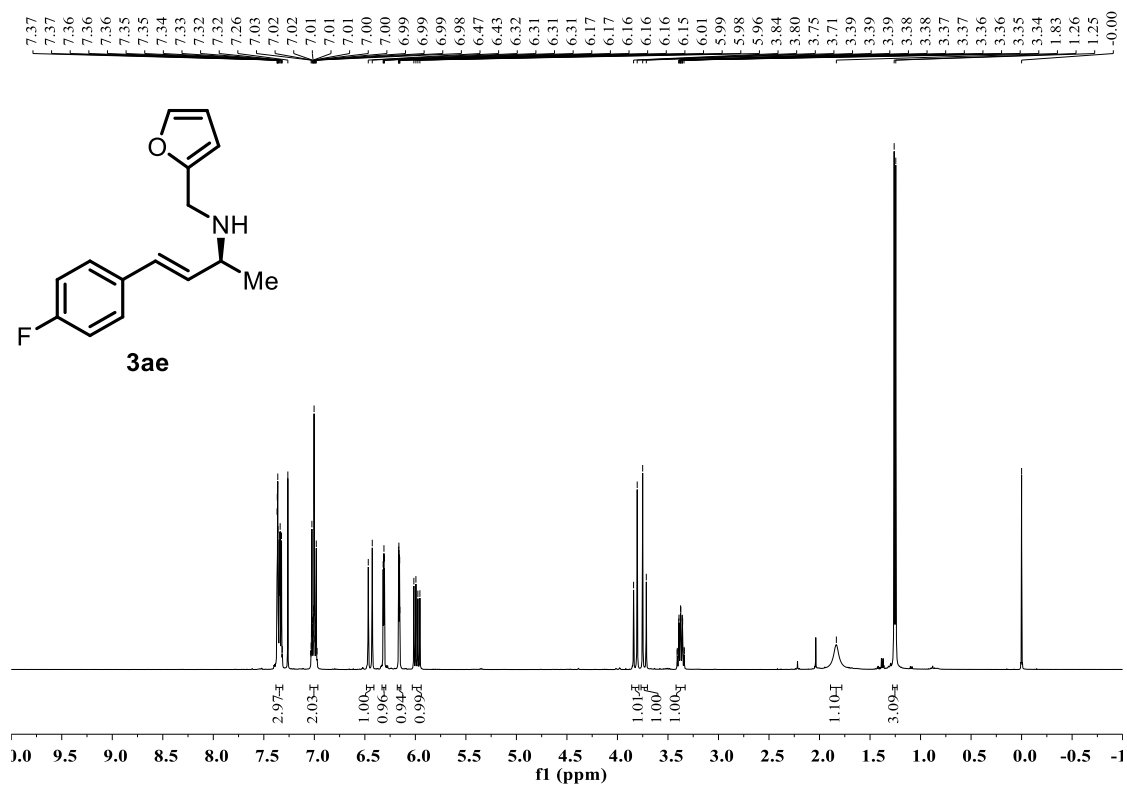
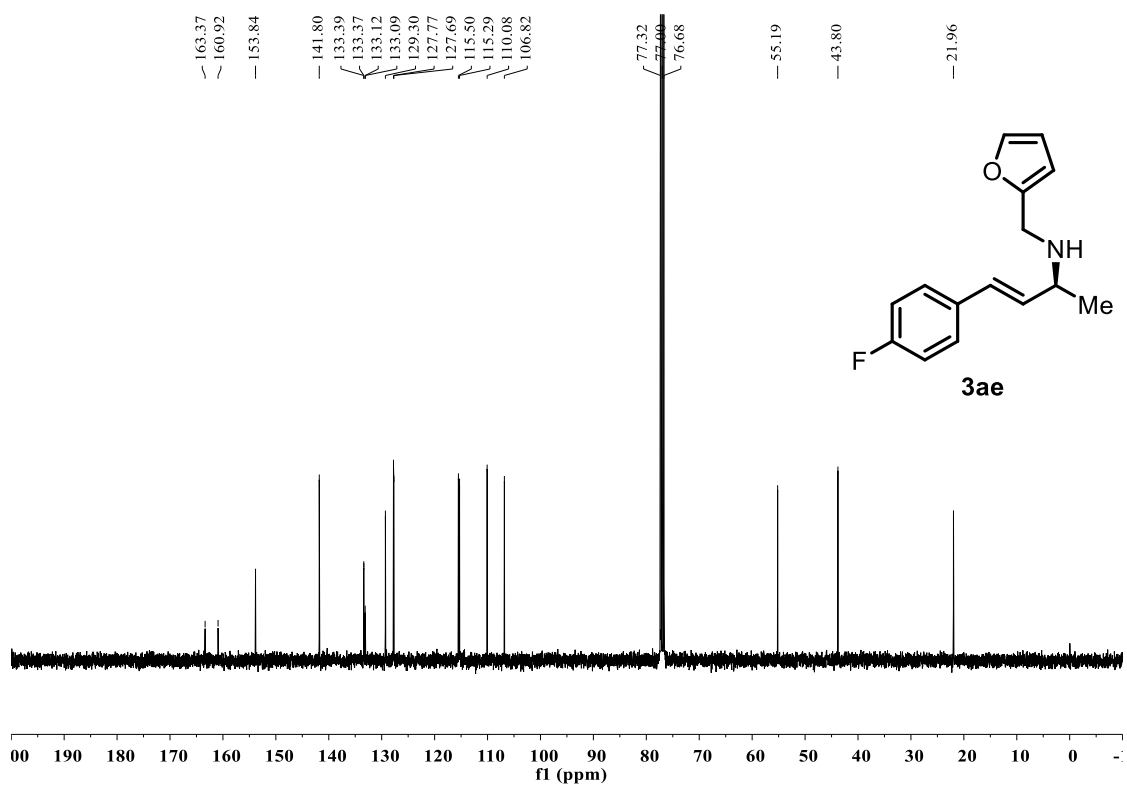


Figure S80. <sup>13</sup>C NMR spectra of **3ac**, related to Figure 4.

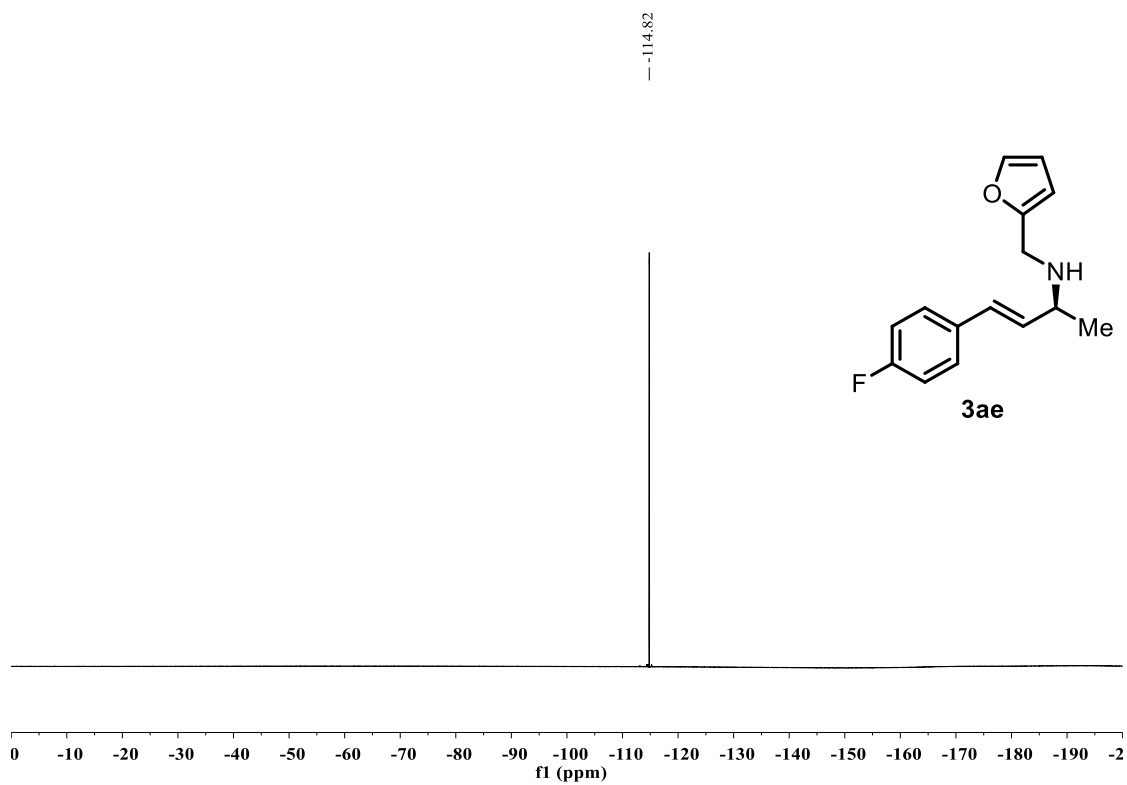




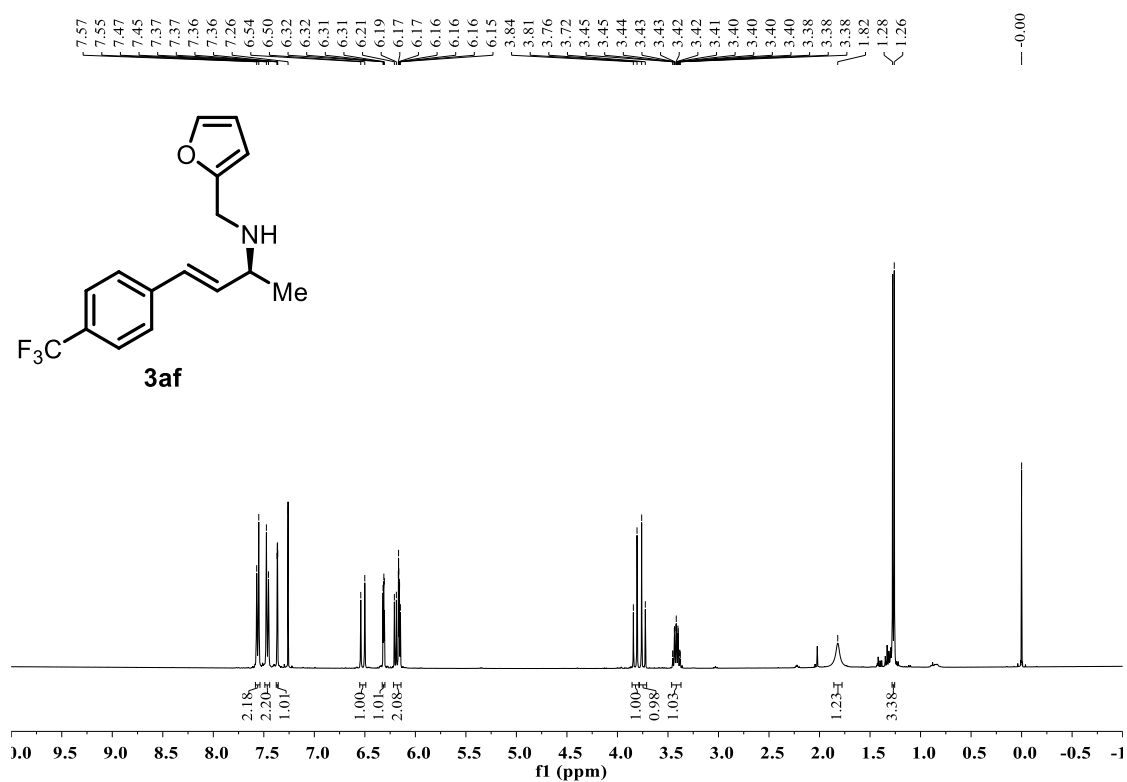
**Figure S83.** <sup>1</sup>H NMR spectra of **3ae**, related to **Figure 4**.



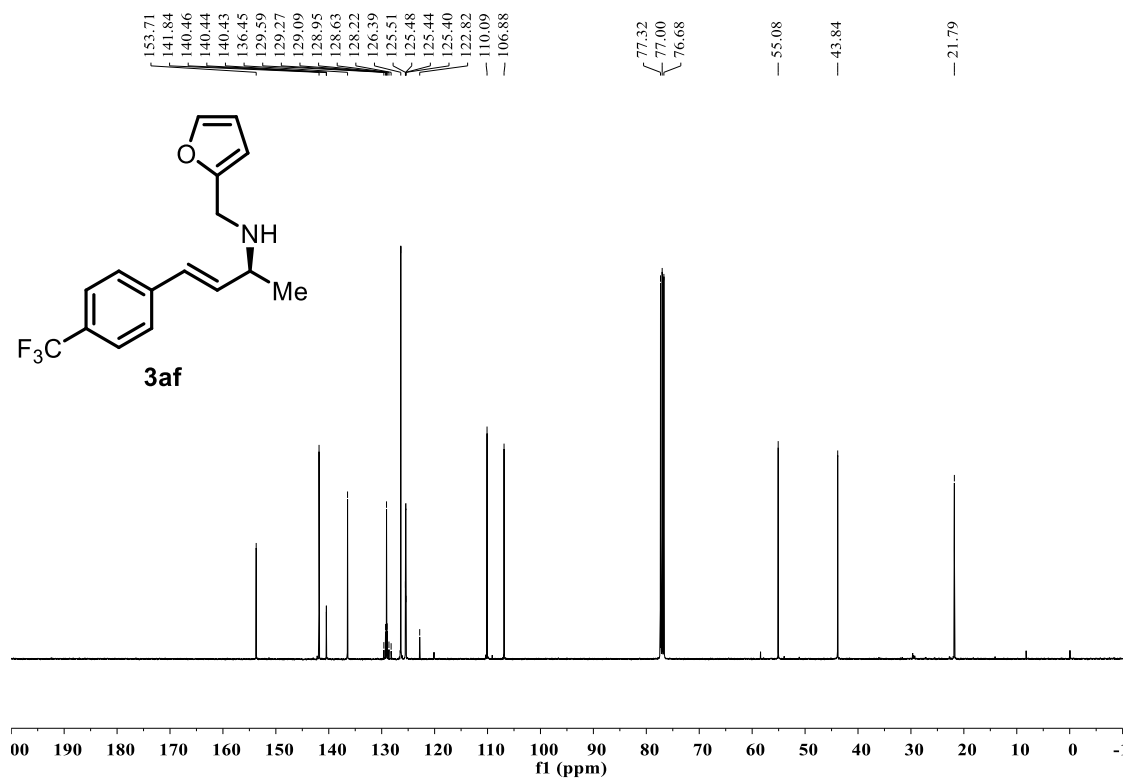
**Figure S84.** <sup>13</sup>C NMR spectra of **3ae**, related to **Figure 4**.



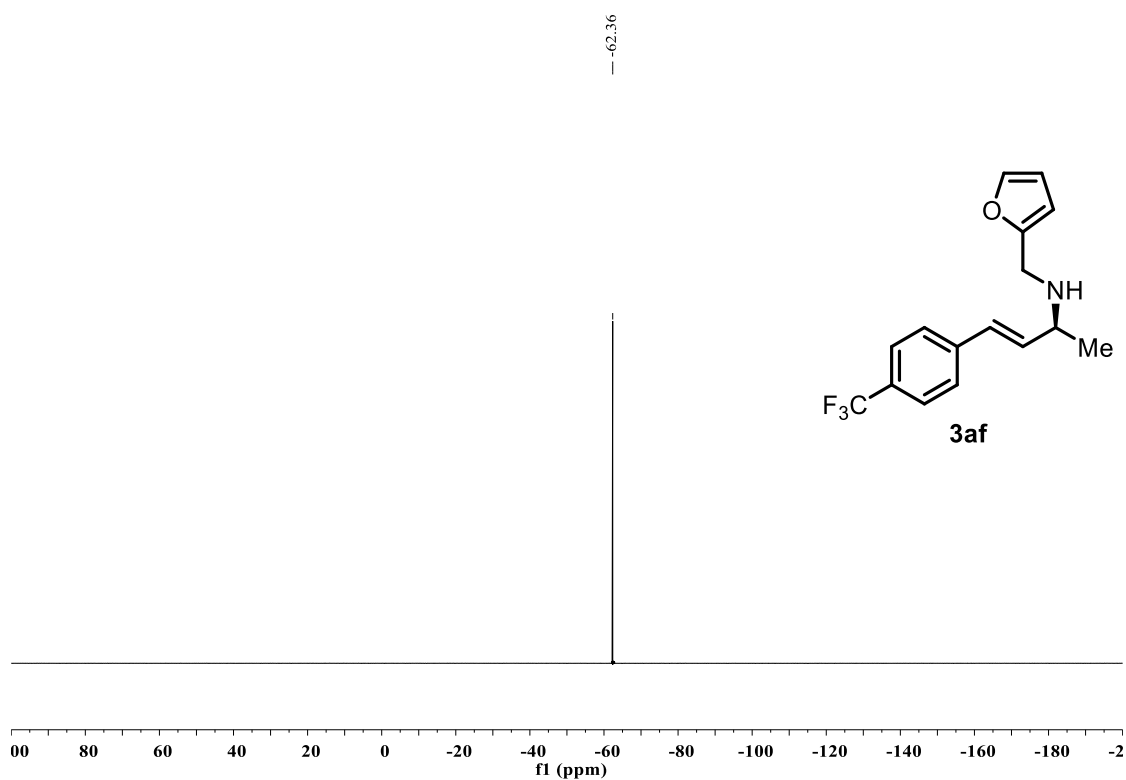
**Figure S85.**  $^{19}\text{F}$  NMR spectra of **3ae**, related to **Figure 4**.



**Figure S86.**  $^1\text{H}$  NMR spectra of **3af**, related to **Figure 4**.



**Figure S87.**  $^{13}\text{C}$  NMR spectra of **3af**, related to **Figure 4**.



**Figure S88.**  $^{19}\text{F}$  NMR spectra of **3af**, related to **Figure 4**.

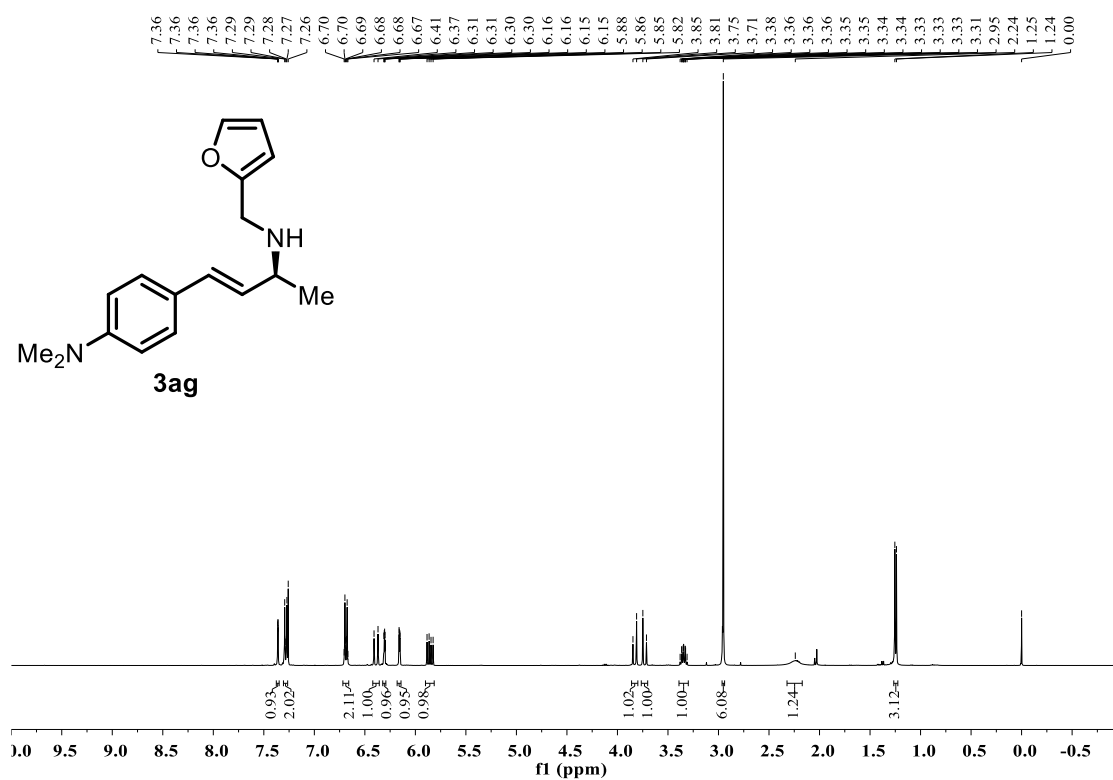


Figure S89. <sup>1</sup>H NMR spectra of **3ag**, related to Figure 4.

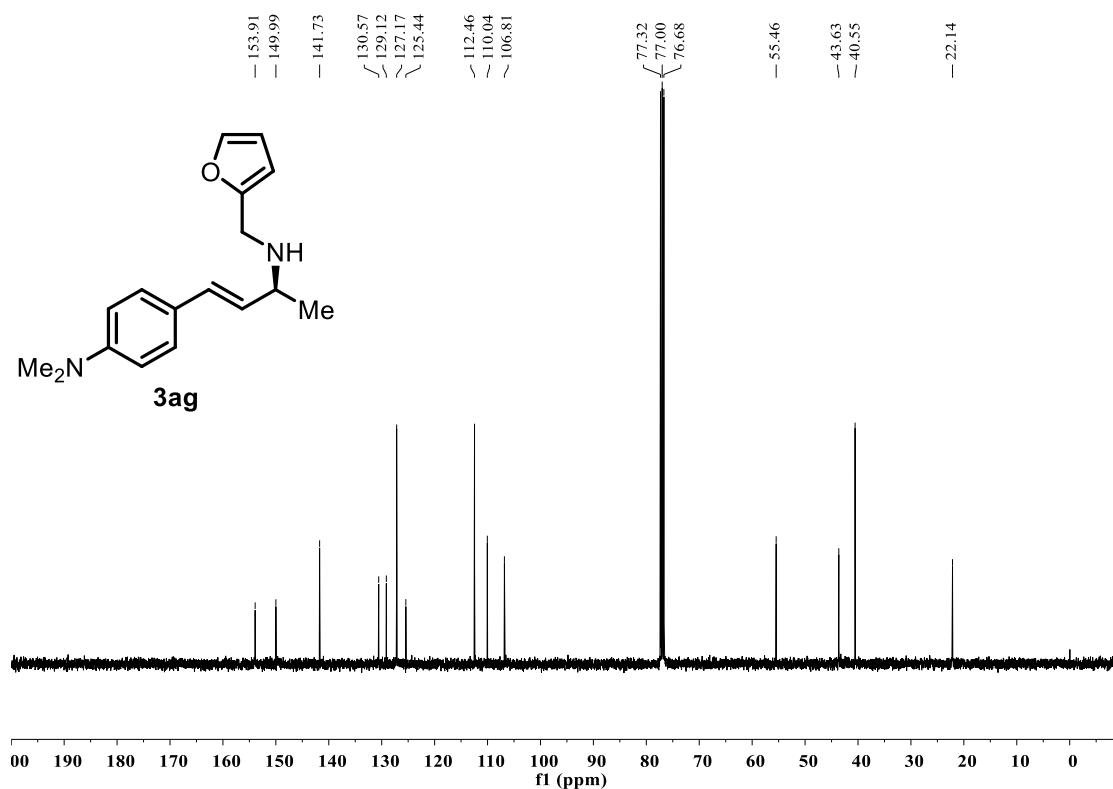
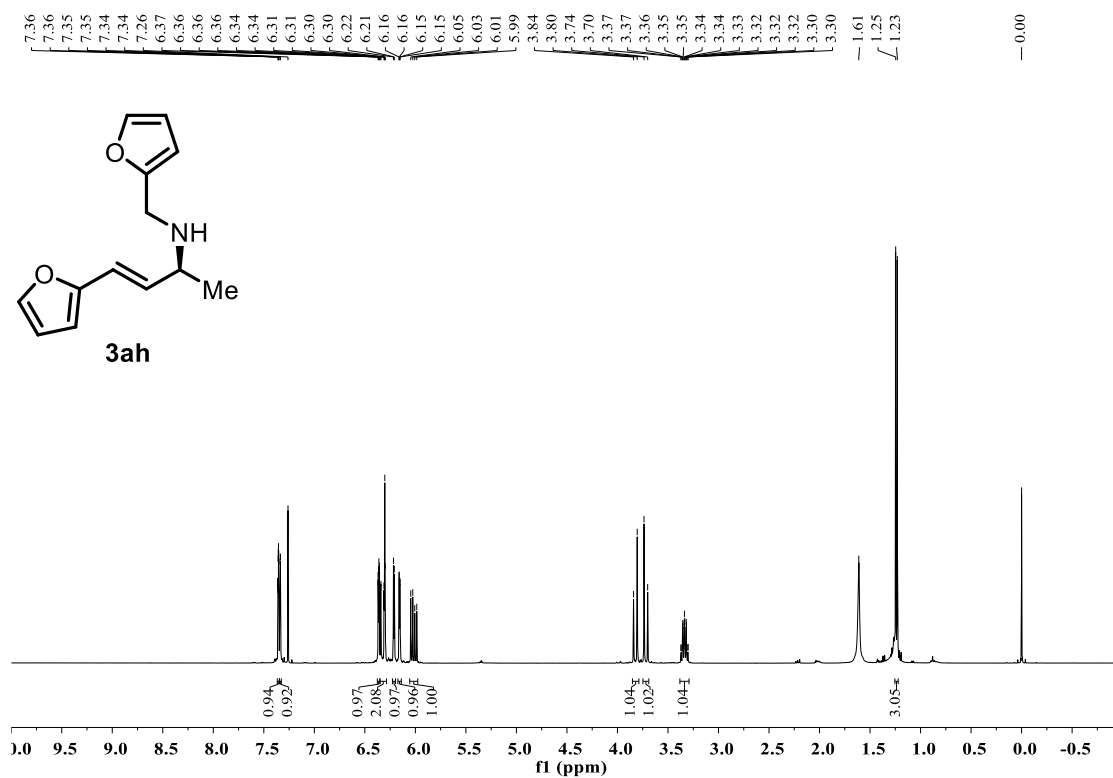
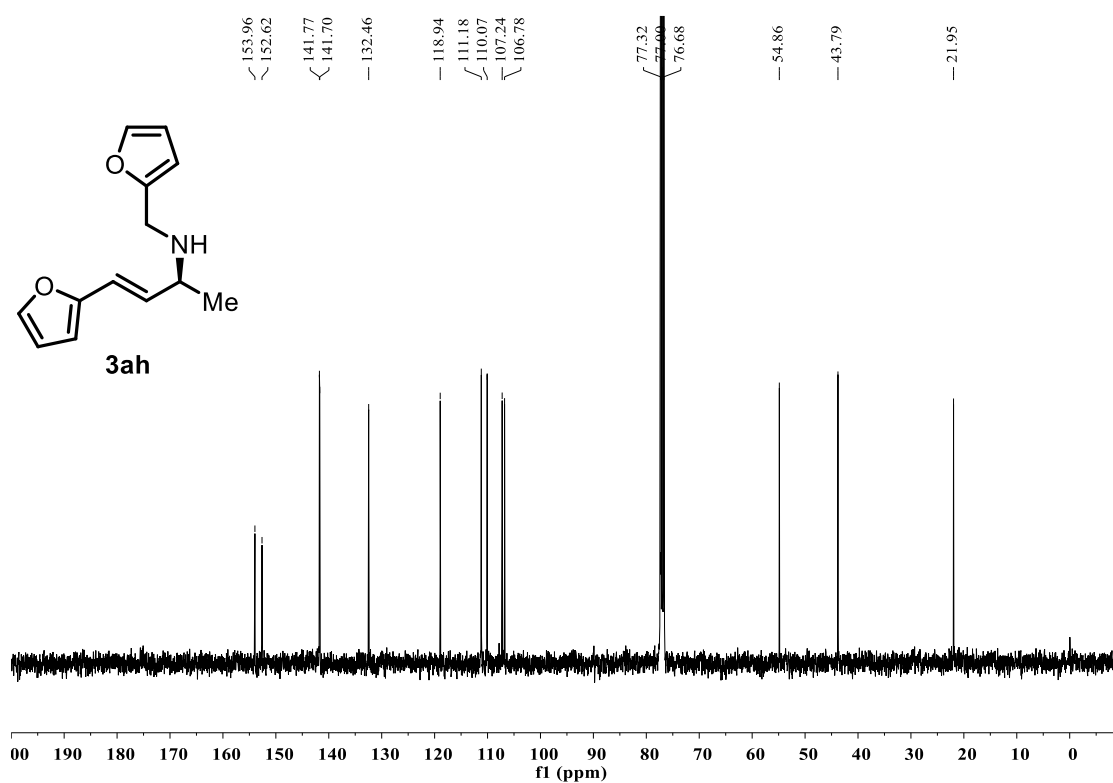


Figure S90. <sup>13</sup>C NMR spectra of **3ag**, related to Figure 4.



**Figure S91.** <sup>1</sup>H NMR spectra of **3ah**, related to **Figure 4**.



**Figure S92.** <sup>13</sup>C NMR spectra of **3ah**, related to **Figure 4**.

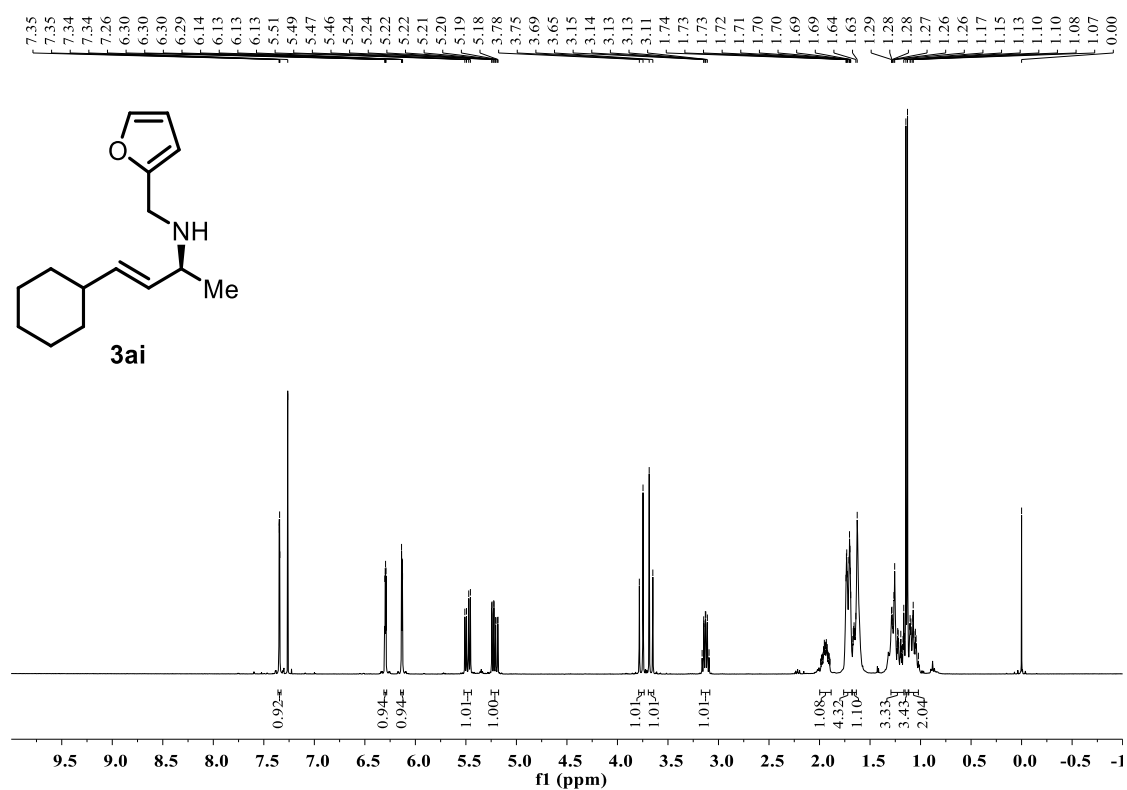


Figure S93.  $^1\text{H}$  NMR spectra of **3ai**, related to Figure 4.

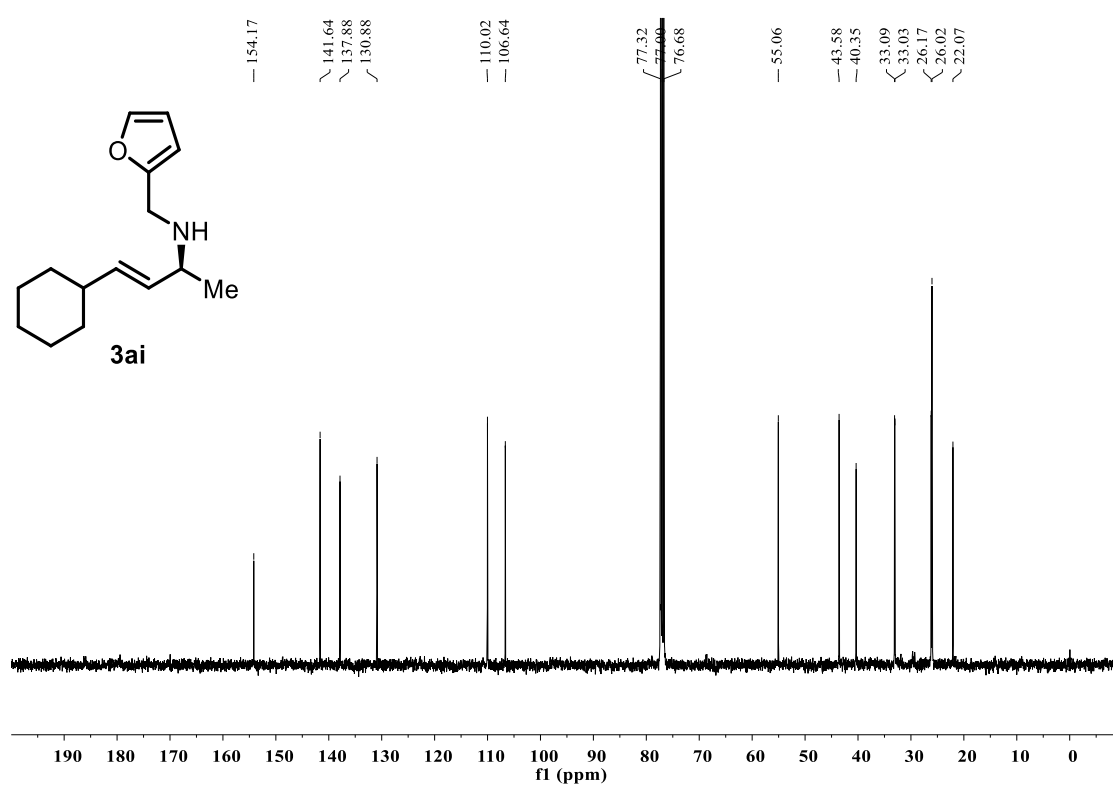


Figure S94.  $^{13}\text{C}$  NMR spectra of **3ai**, related to Figure 4.



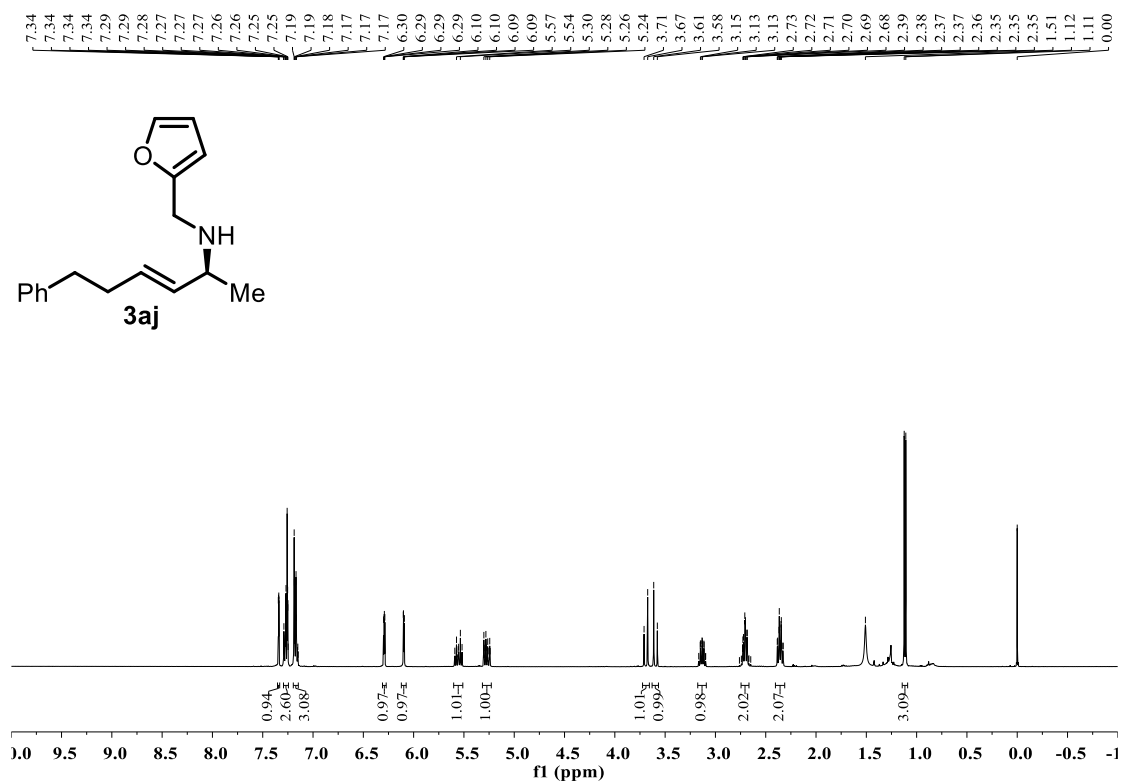


Figure S95. <sup>1</sup>H NMR spectra of **3aj**, related to Figure 4.

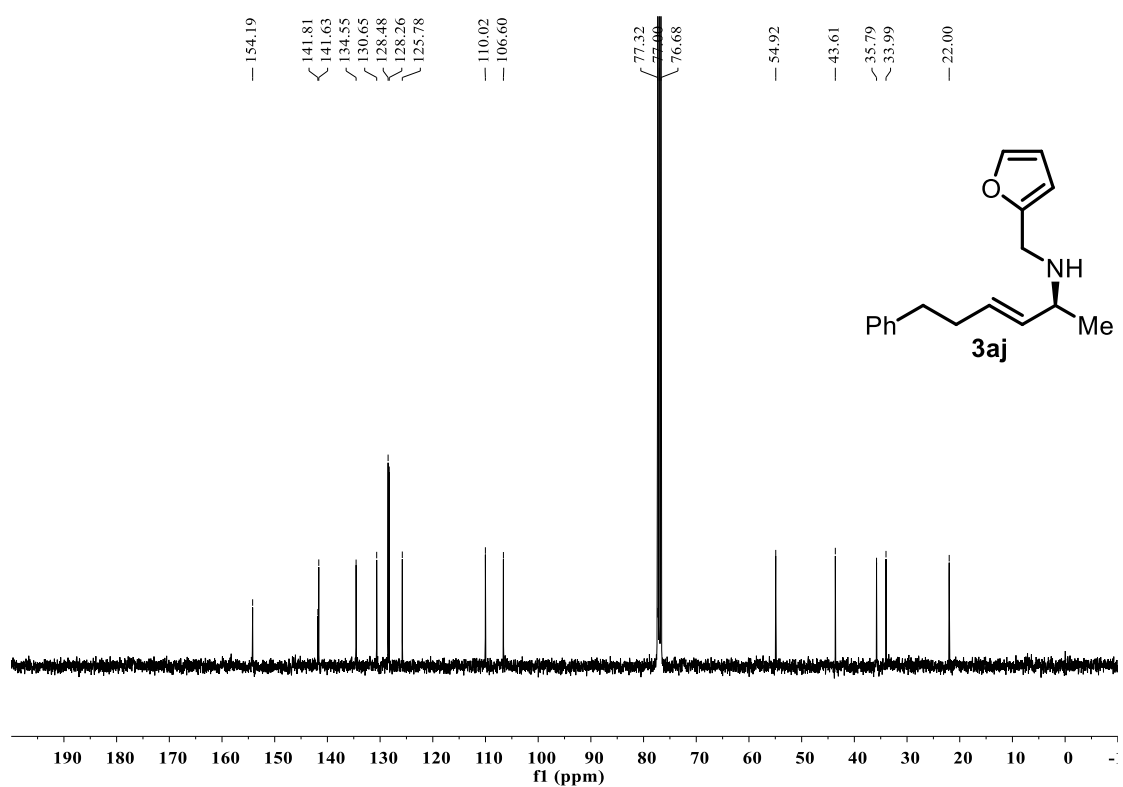


Figure S96. <sup>13</sup>C NMR spectra of **3aj**, related to Figure 4.

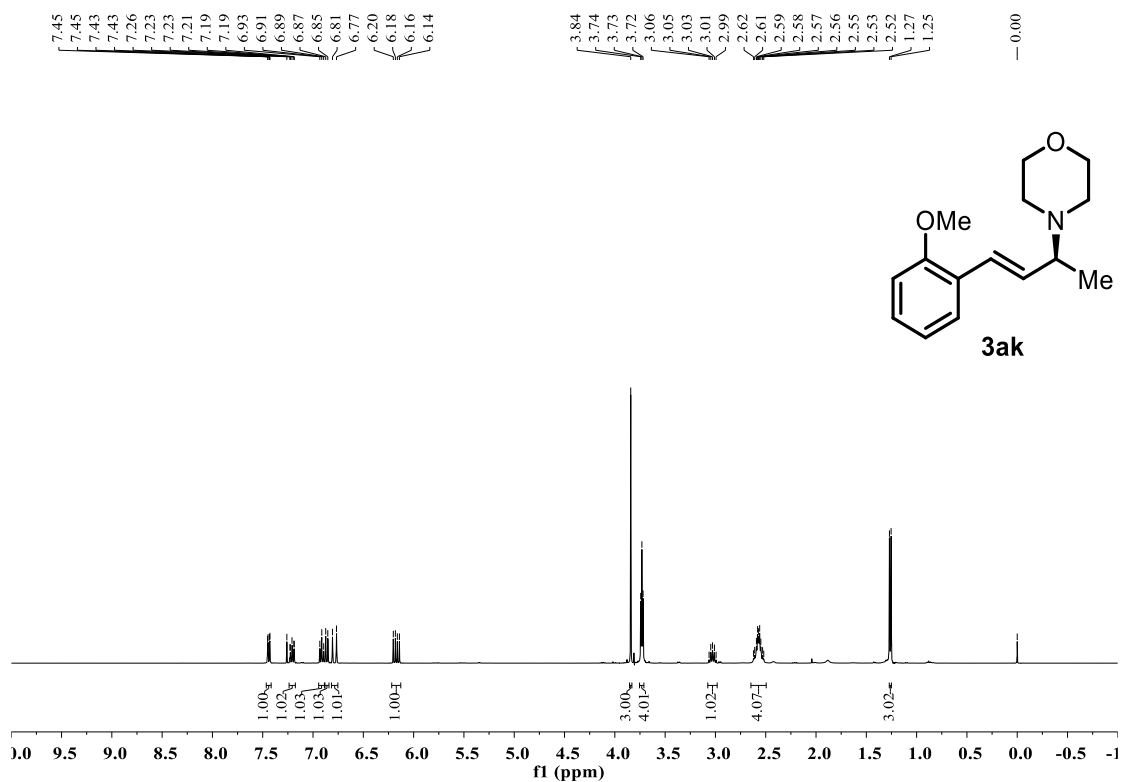


Figure S97. <sup>1</sup>H NMR spectra of **3ak**, related to Figure 4.

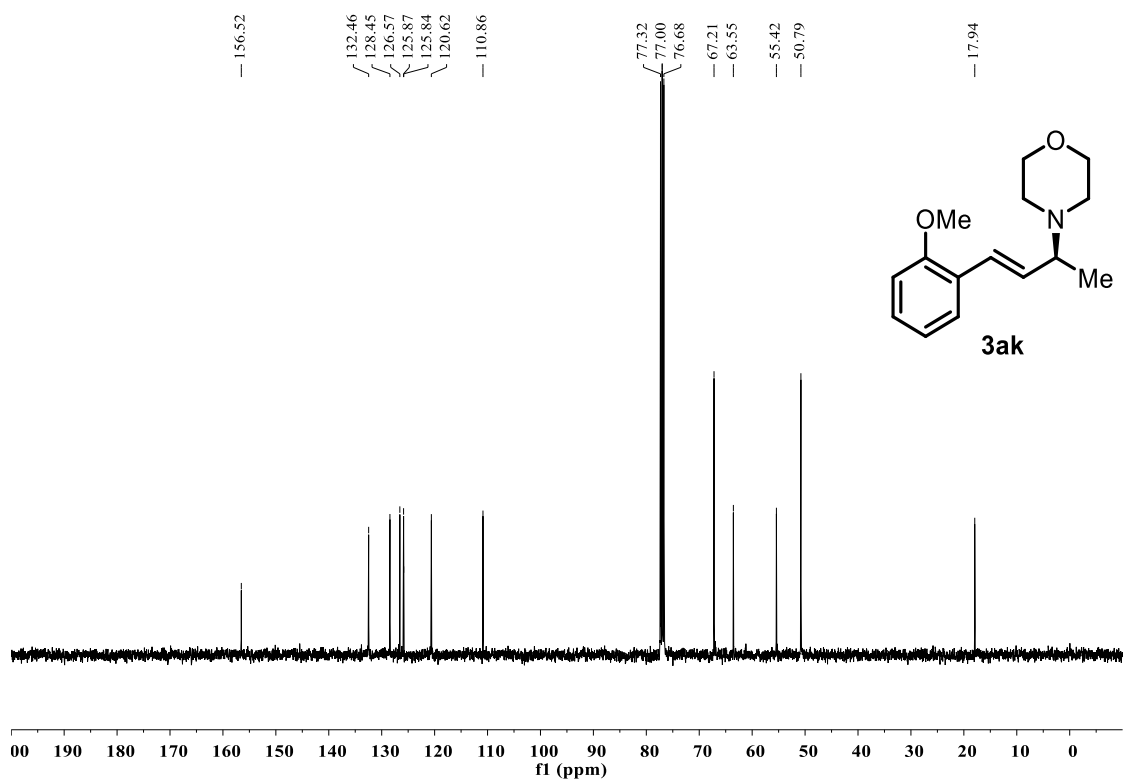
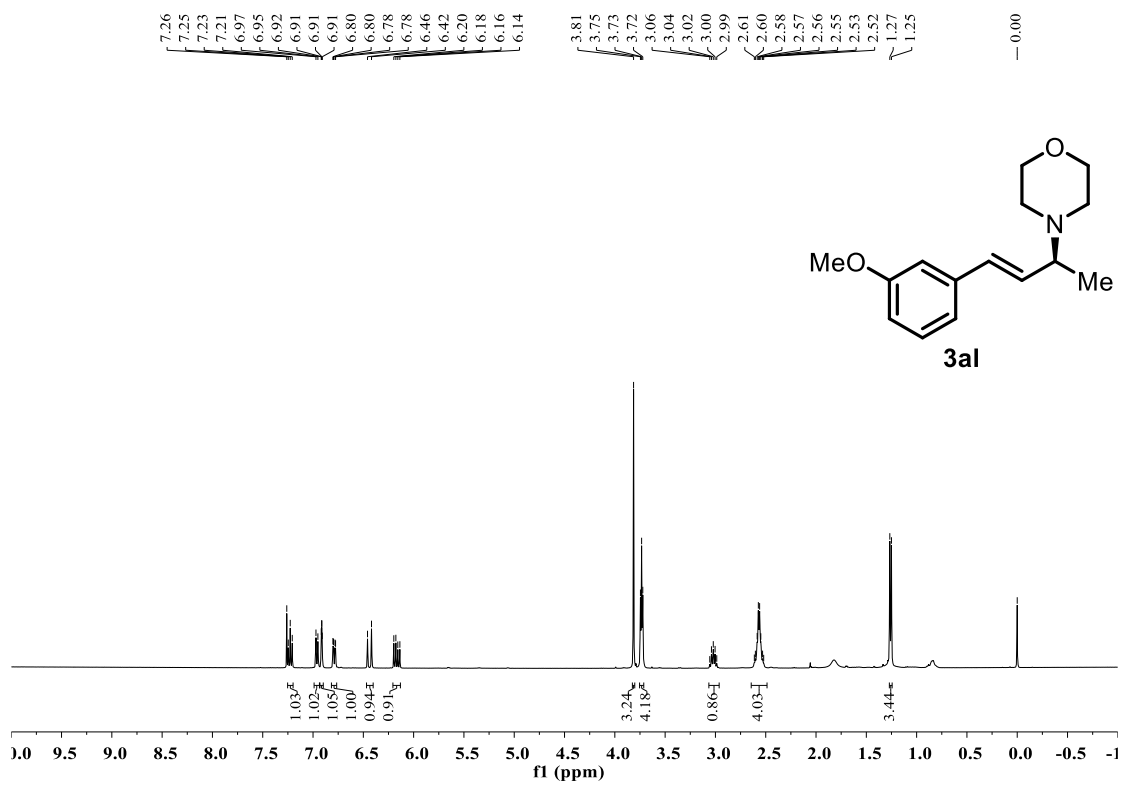
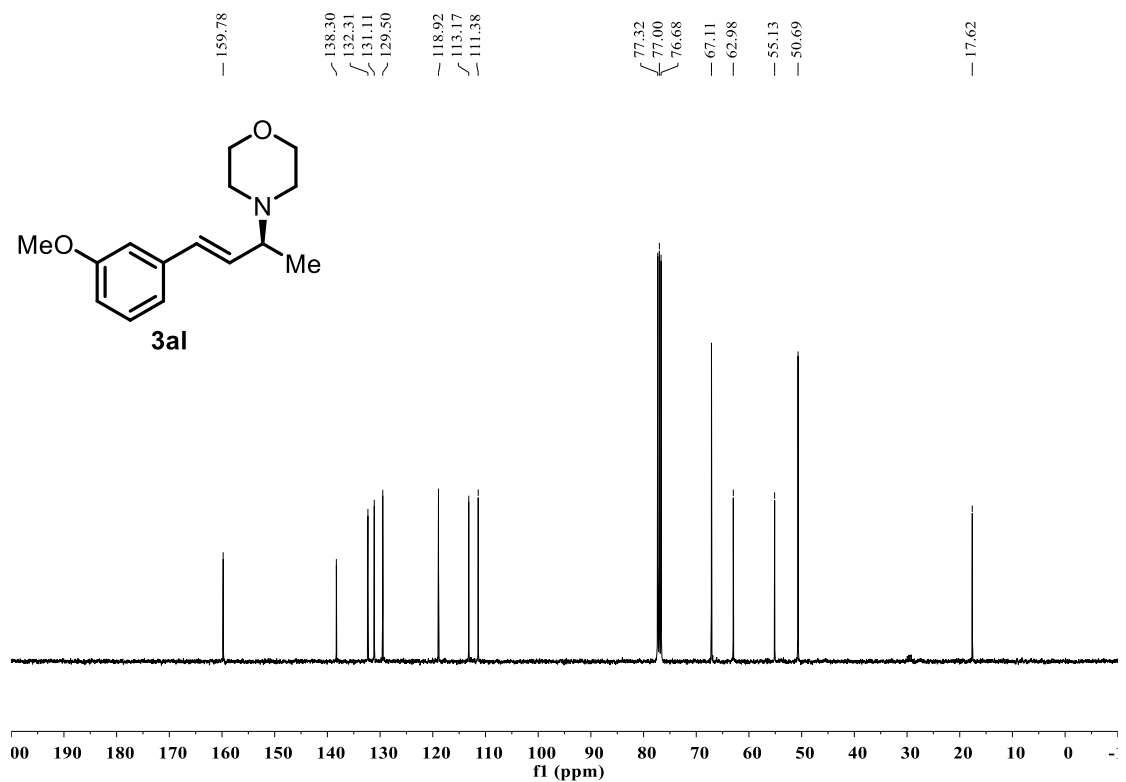


Figure S98. <sup>13</sup>C NMR spectra of **3ak**, related to Figure 4.



**Figure S99.** <sup>1</sup>H NMR spectra of **3al**, related to **Figure 4**.



**Figure S100.** <sup>13</sup>C NMR spectra of **3al**, related to **Figure 4**.

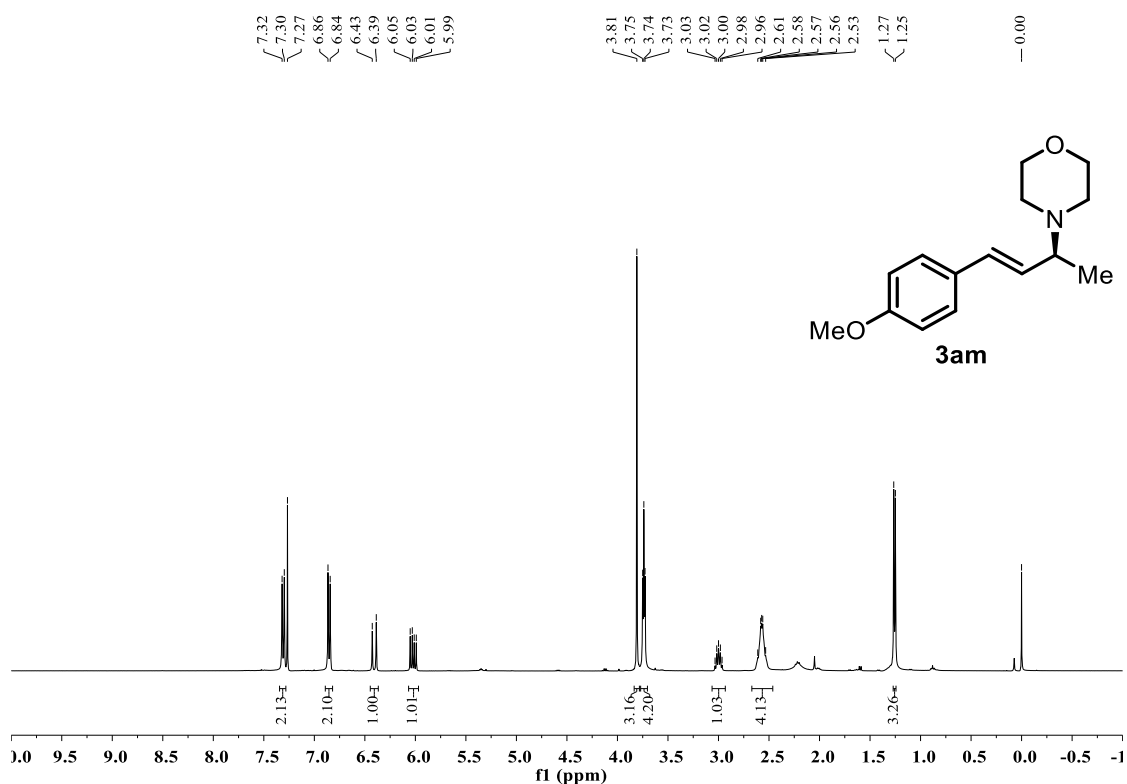


Figure S101. <sup>1</sup>H NMR spectra of **3am**, related to Figure 4.

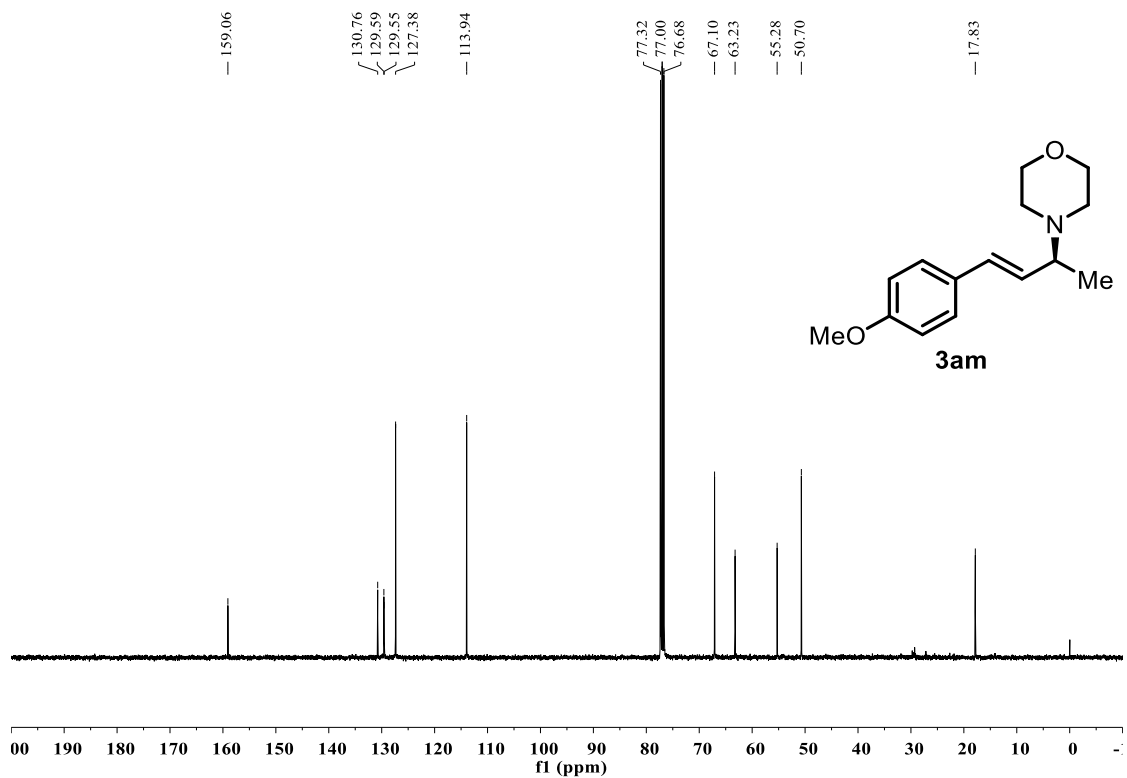


Figure S102. <sup>13</sup>C NMR spectra of **3am**, related to Figure 4.

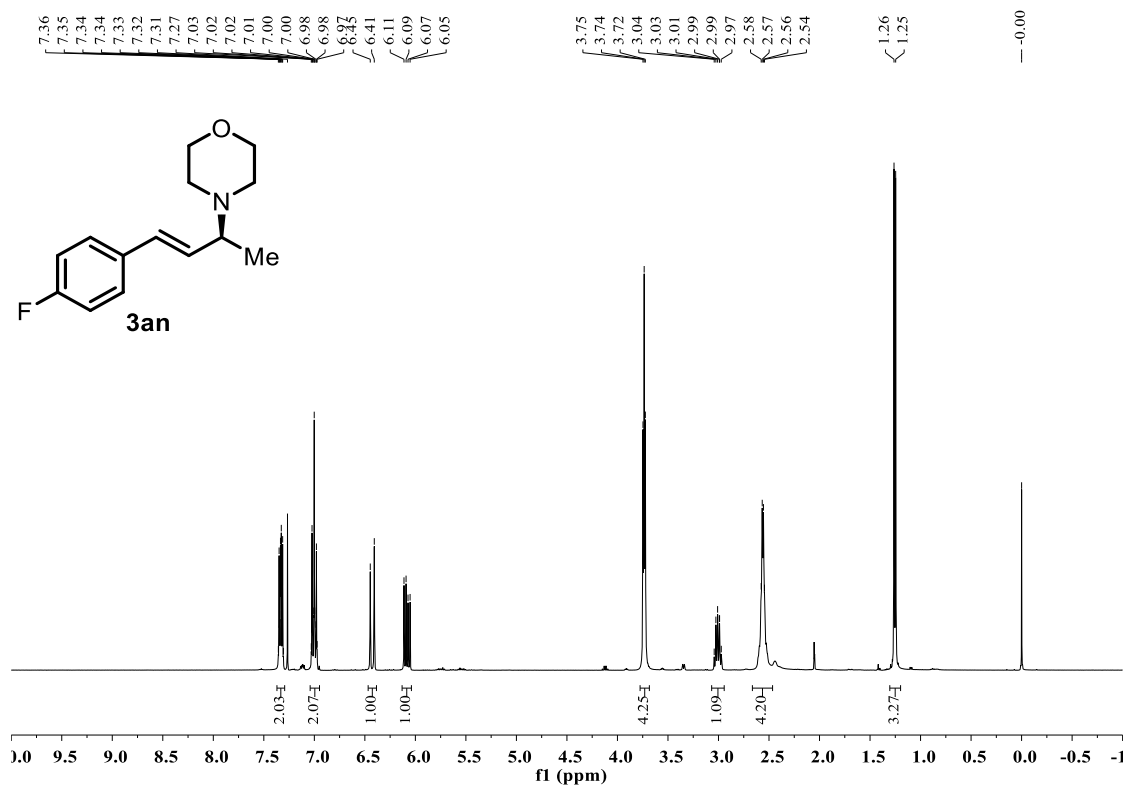


Figure S103. <sup>1</sup>H NMR spectra of **3an**, related to Figure 4.

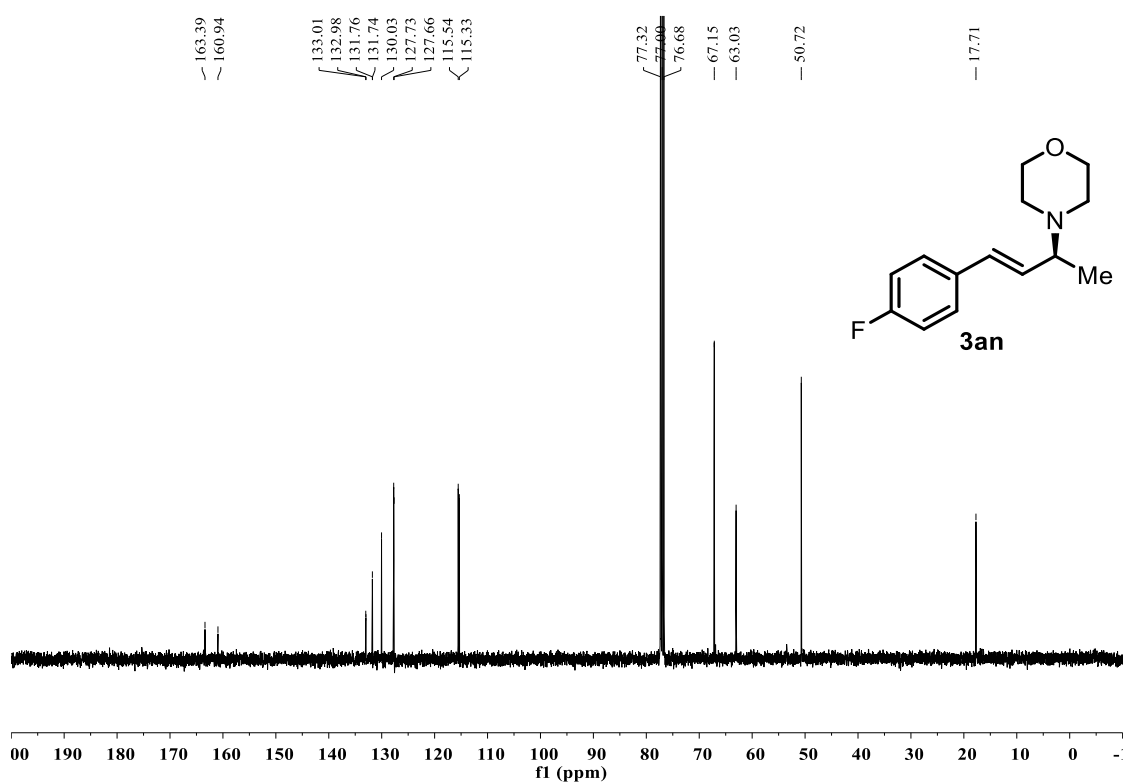


Figure S104. <sup>13</sup>C NMR spectra of **3an**, related to Figure 4.

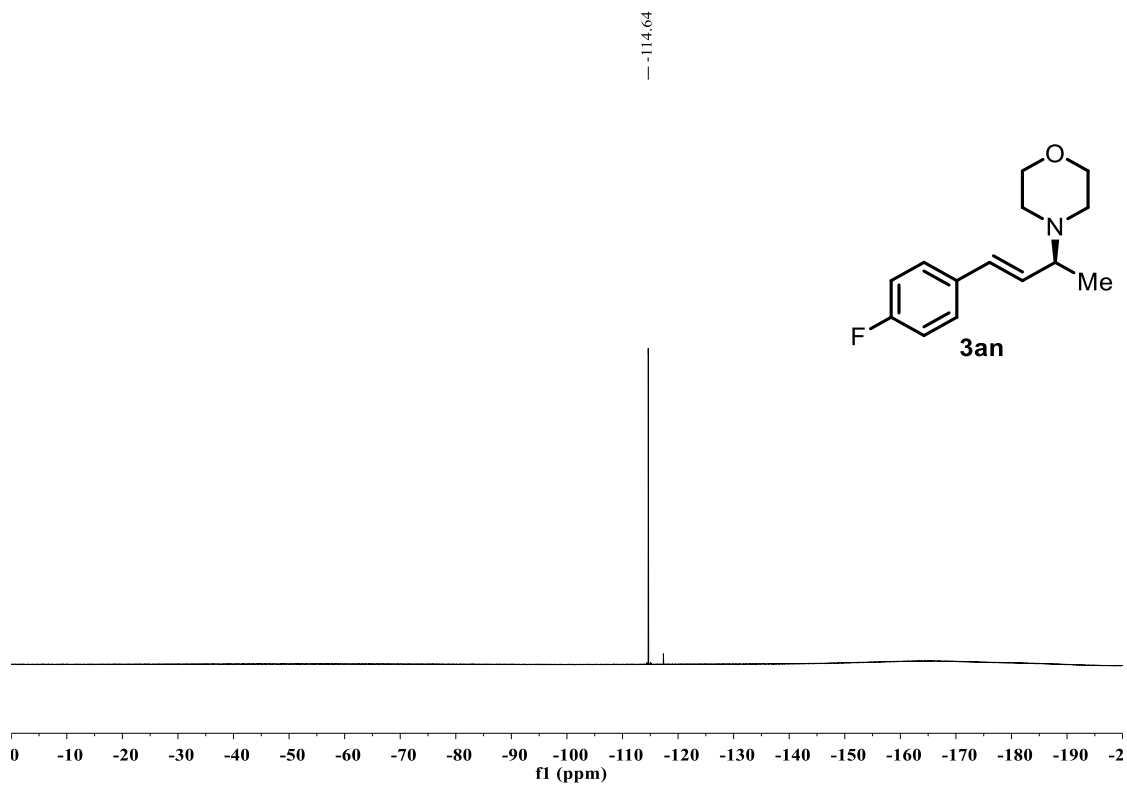


Figure S105.  $^{19}\text{F}$  NMR spectra of **3an**, related to Figure 4.

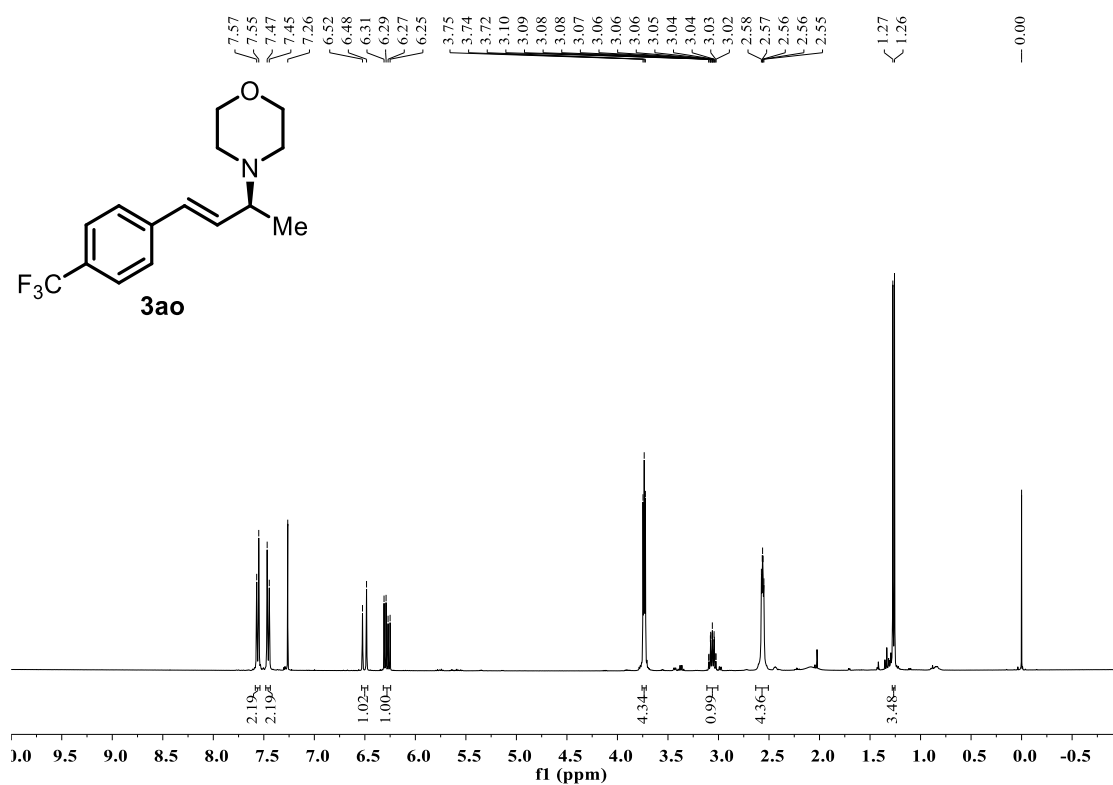
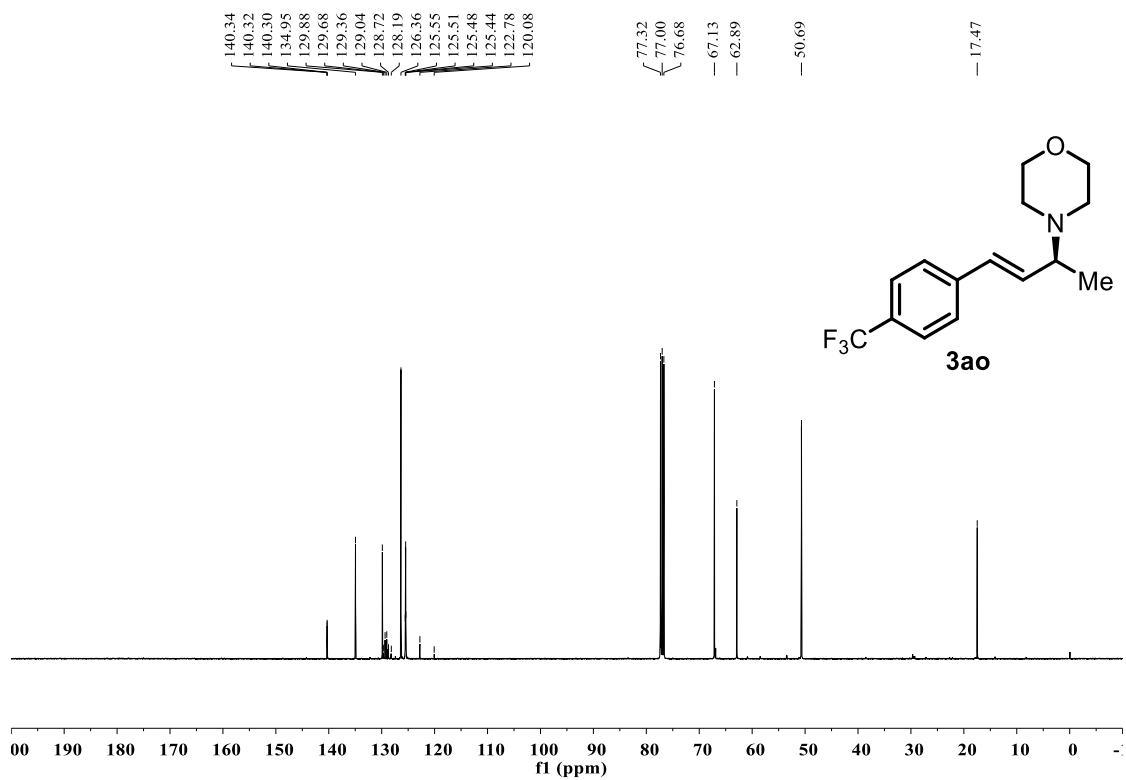
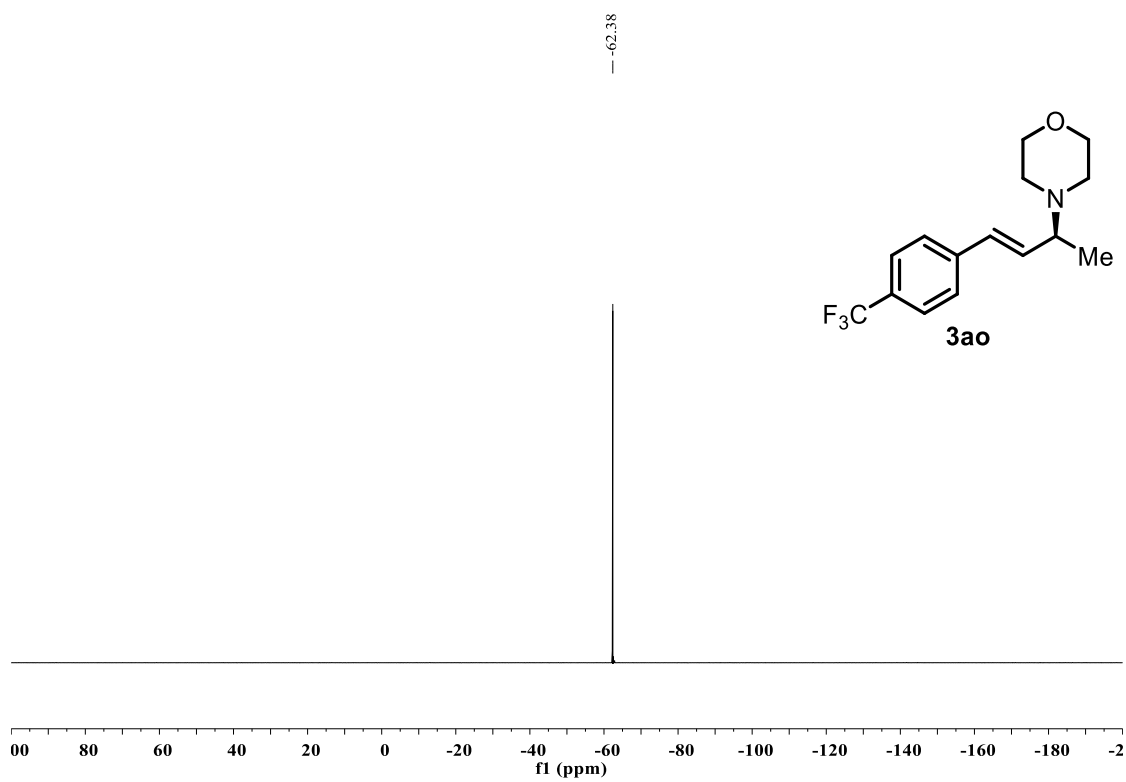


Figure S106.  $^1\text{H}$  NMR spectra of **3ao**, related to Figure 4.



**Figure S107.** <sup>13</sup>C NMR spectra of **3ao**, related to **Figure 4**.



**Figure S108.** <sup>19</sup>F NMR spectra of **3ao**, related to **Figure 4**.

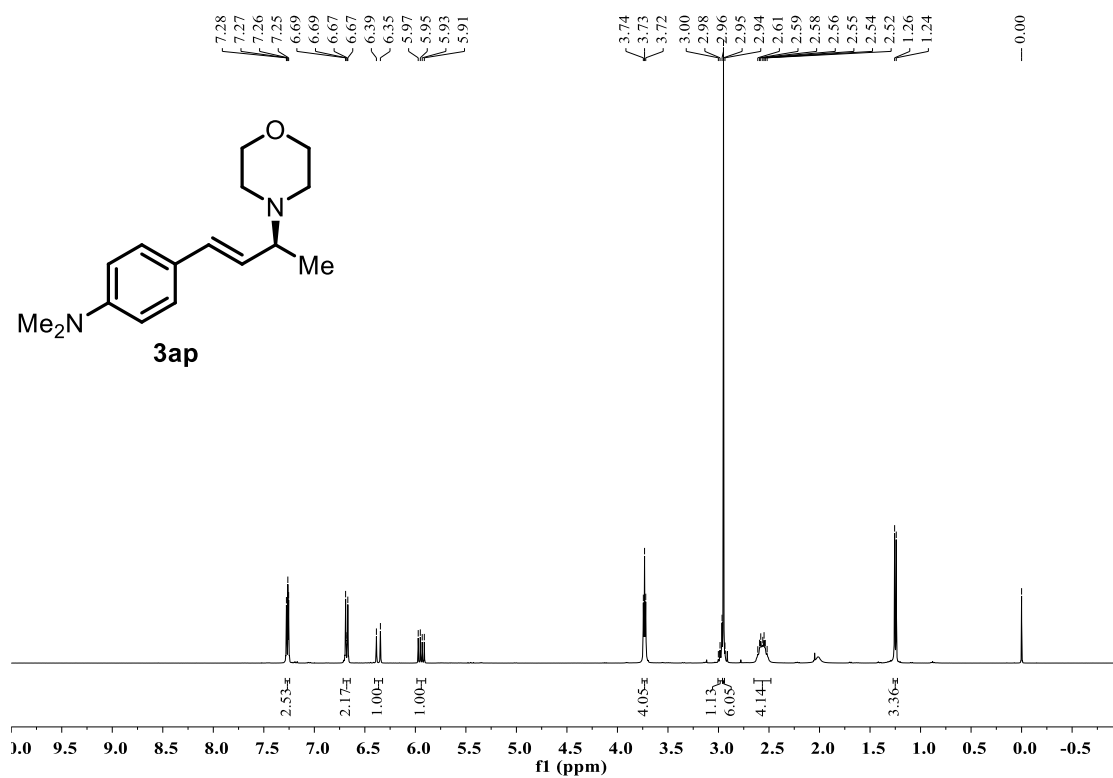


Figure S109. <sup>1</sup>H NMR spectra of **3ap**, related to Figure 4.

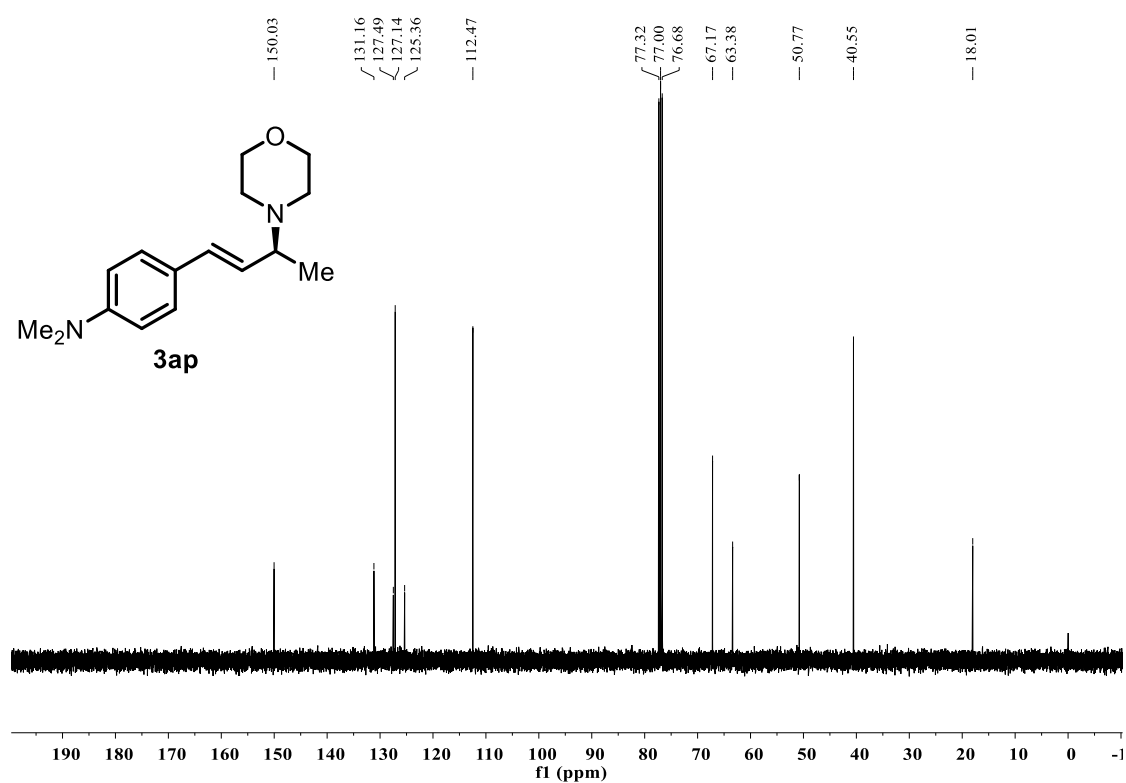
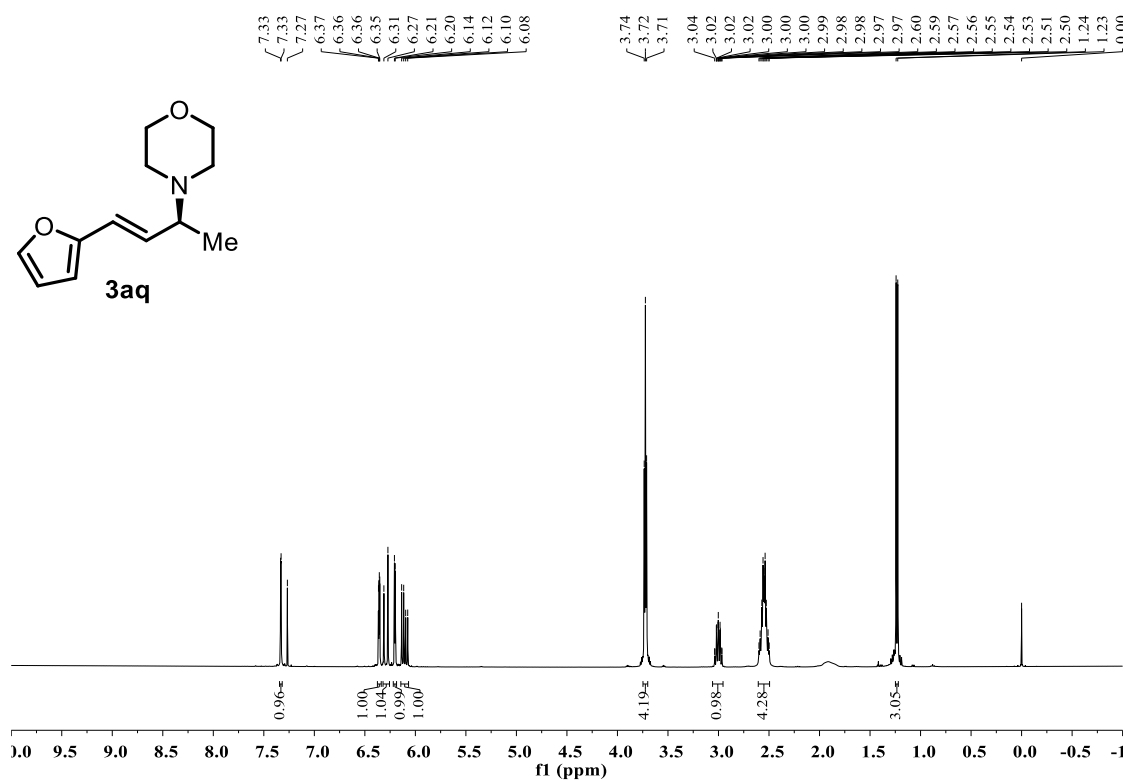
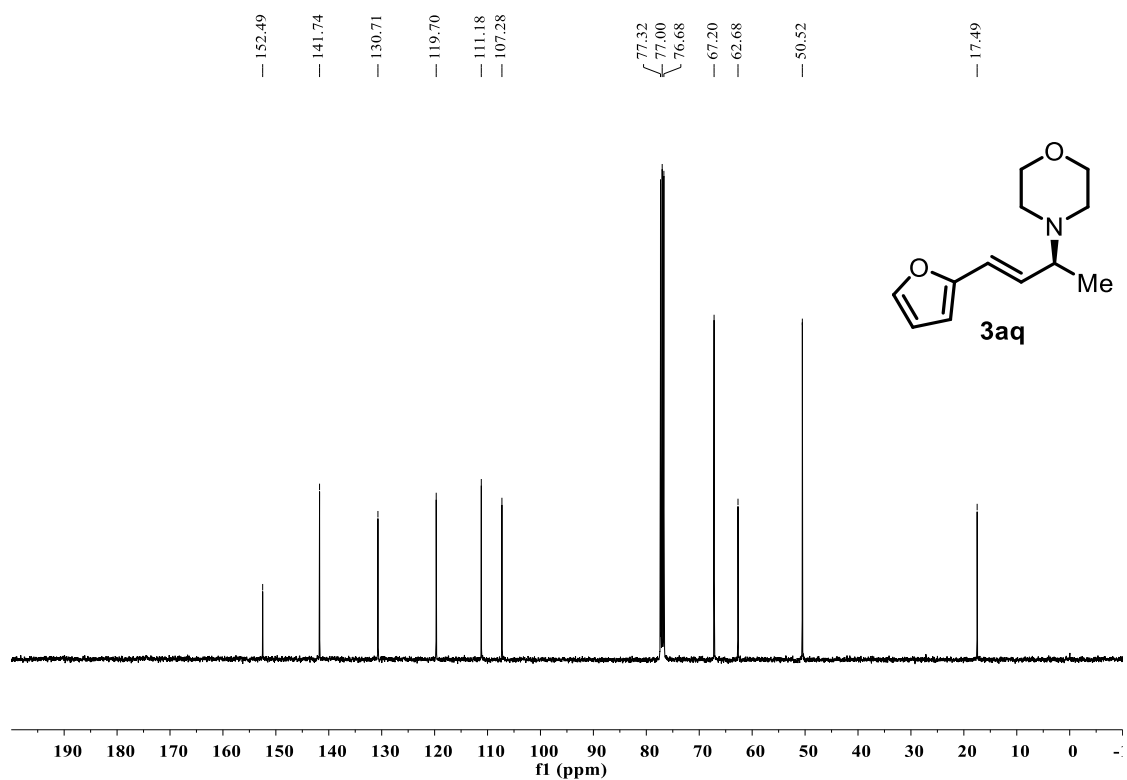


Figure S110. <sup>13</sup>C NMR spectra of **3ap**, related to Figure 4.





**Figure S111.**  $^1\text{H}$  NMR spectra of **3aq**, related to **Figure 4**.



**Figure S112.**  $^{13}\text{C}$  NMR spectra of **3aq**, related to **Figure 4**.

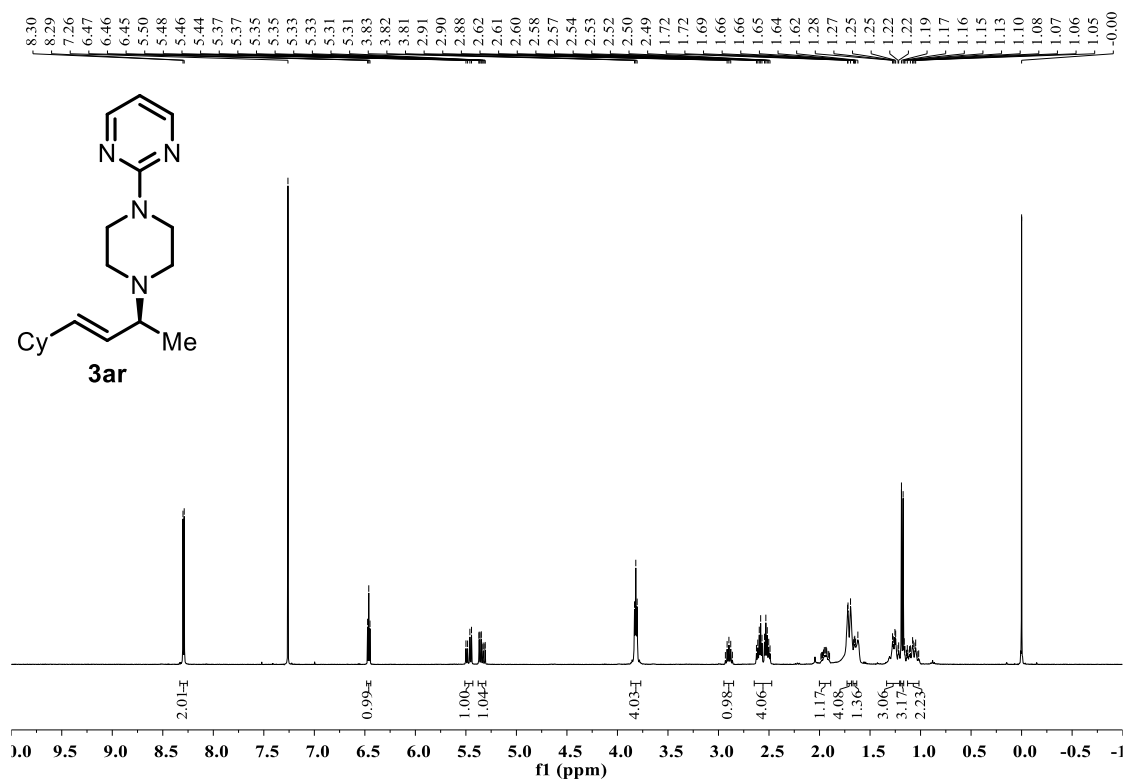


Figure S113. <sup>1</sup>H NMR spectra of **3ar**, related to Figure 4.

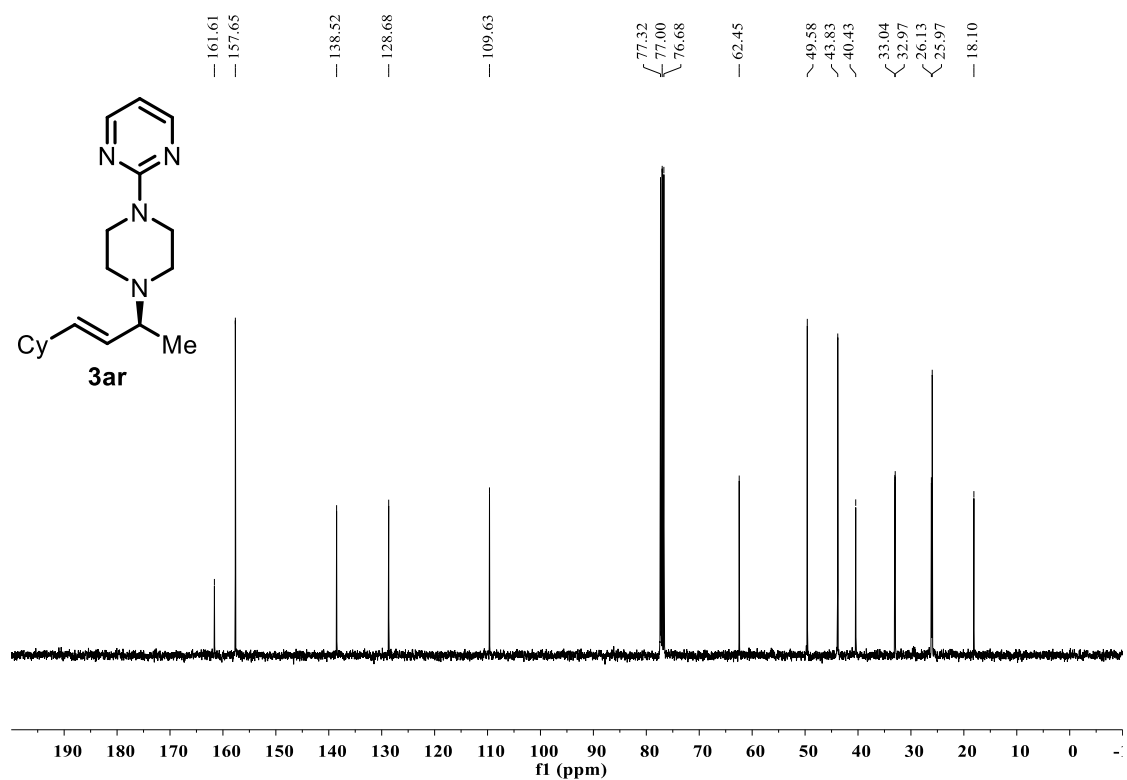


Figure S114. <sup>13</sup>C NMR spectra of **3ar**, related to Figure 4.

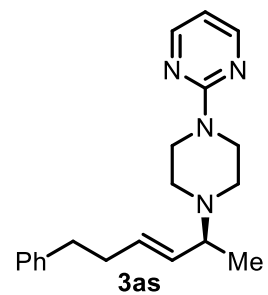
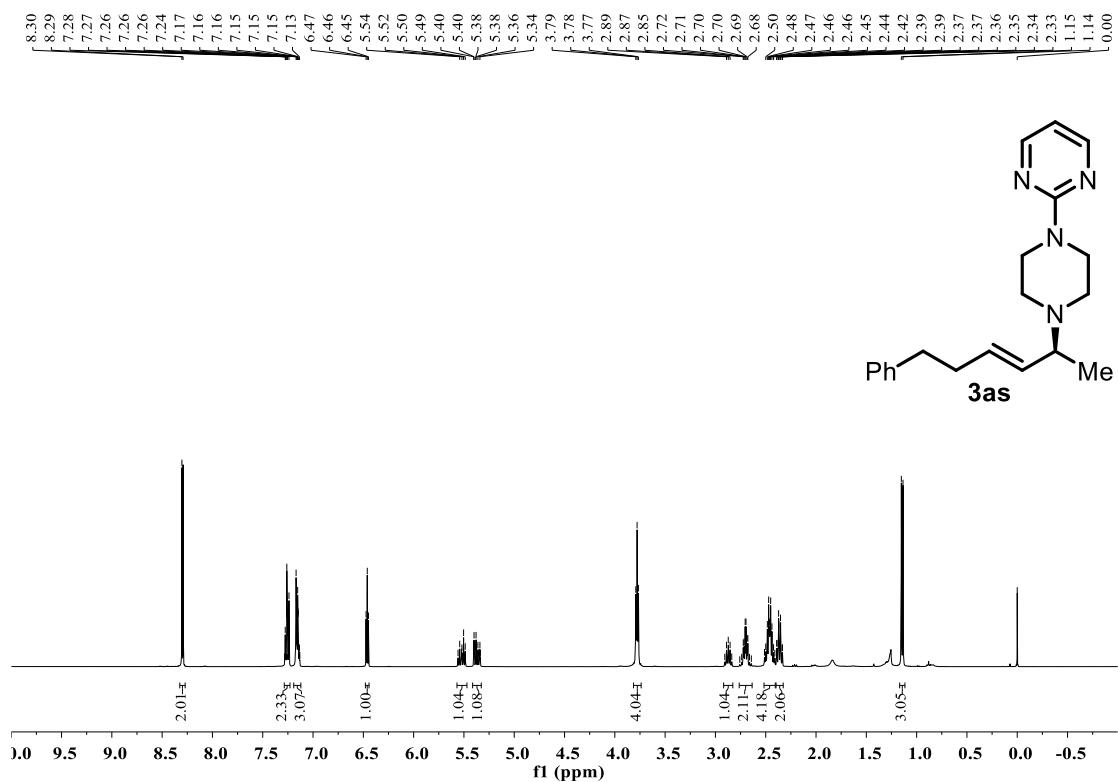


Figure S115. <sup>1</sup>H NMR spectra of **3as**, related to Figure 4.

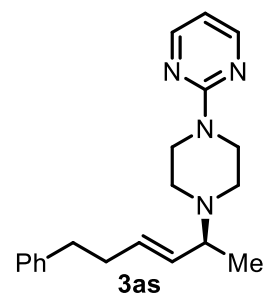
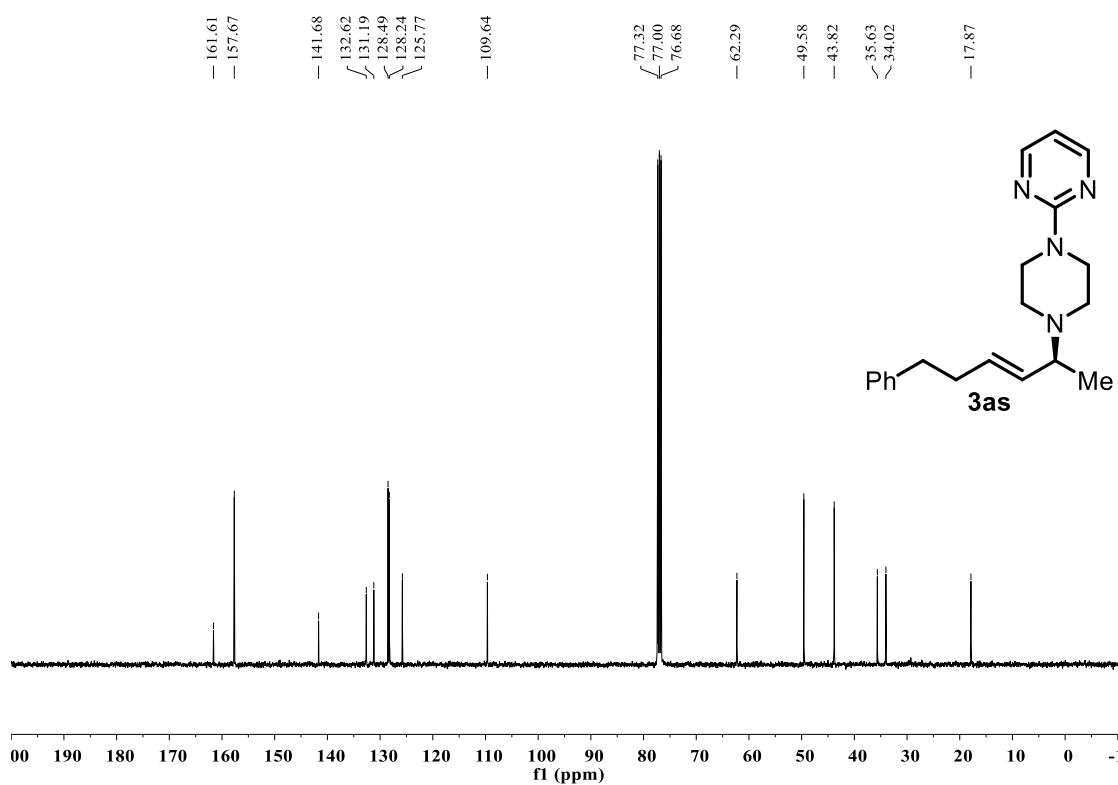


Figure S116. <sup>13</sup>C NMR spectra of **3as**, related to Figure 4.

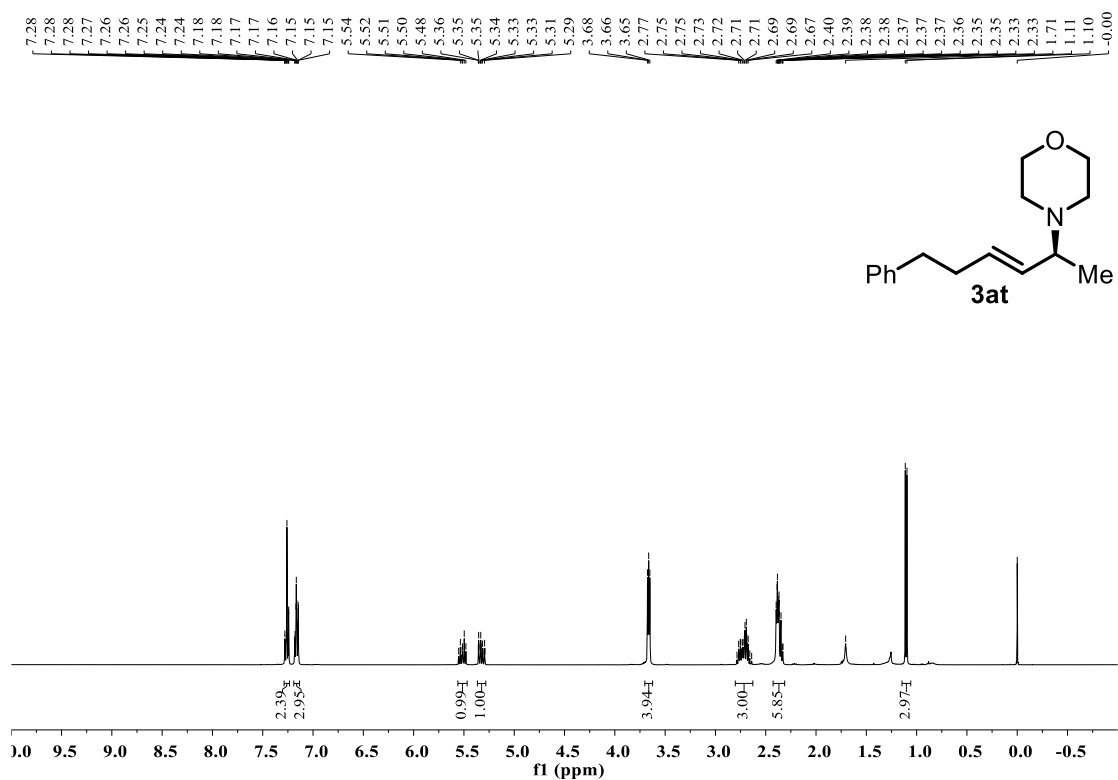


Figure S117. <sup>1</sup>H NMR spectra of **3at**, related to Figure 4.

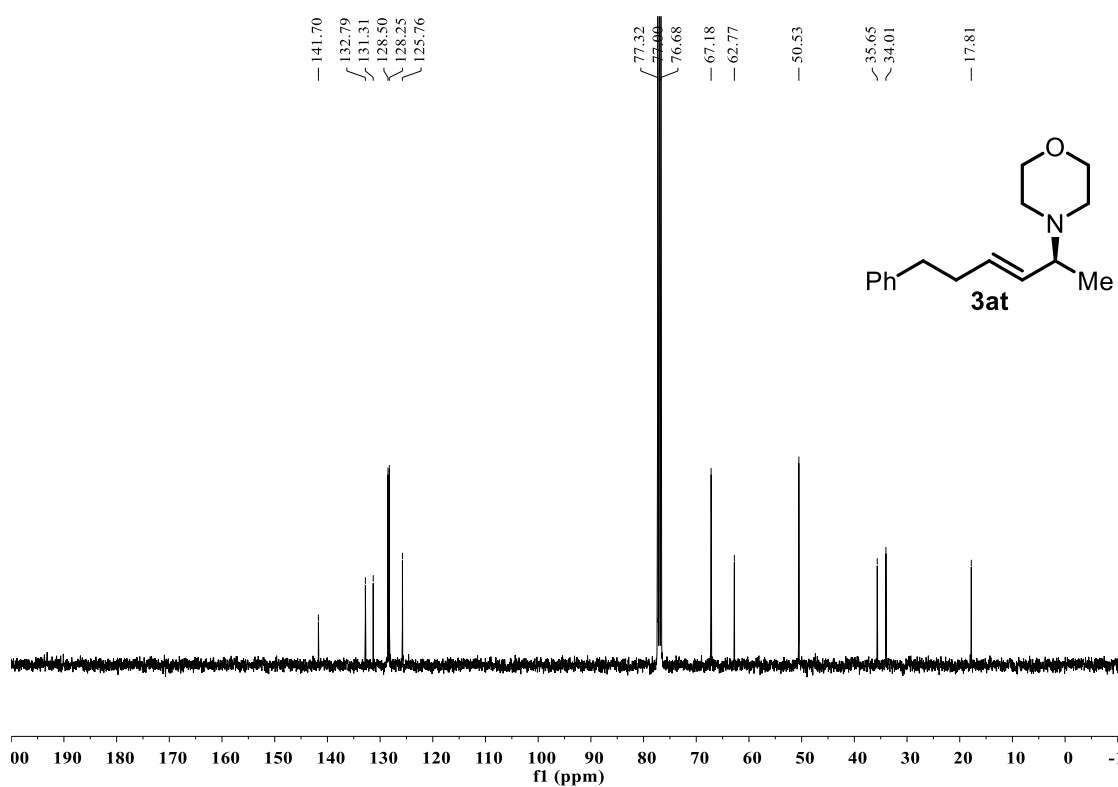


Figure S118. <sup>13</sup>C NMR spectra of **3at**, related to Figure 4.

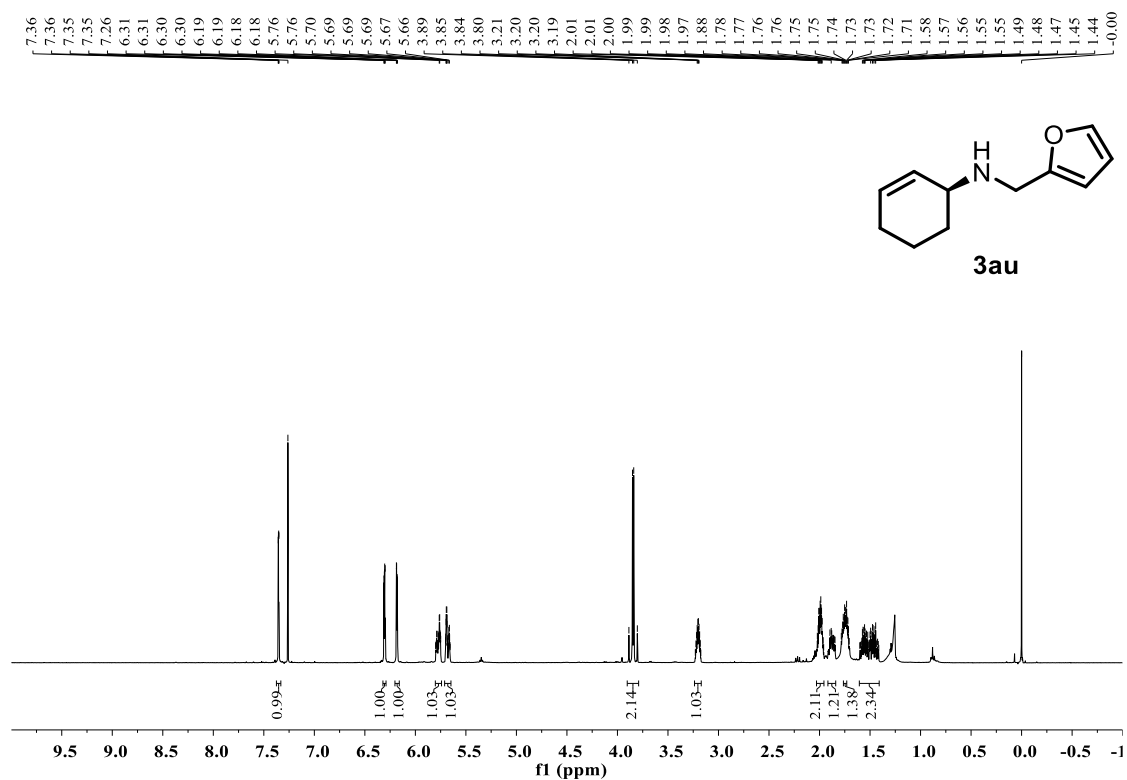


Figure S119. <sup>1</sup>H NMR spectra of **3au**, related to Figure 4.

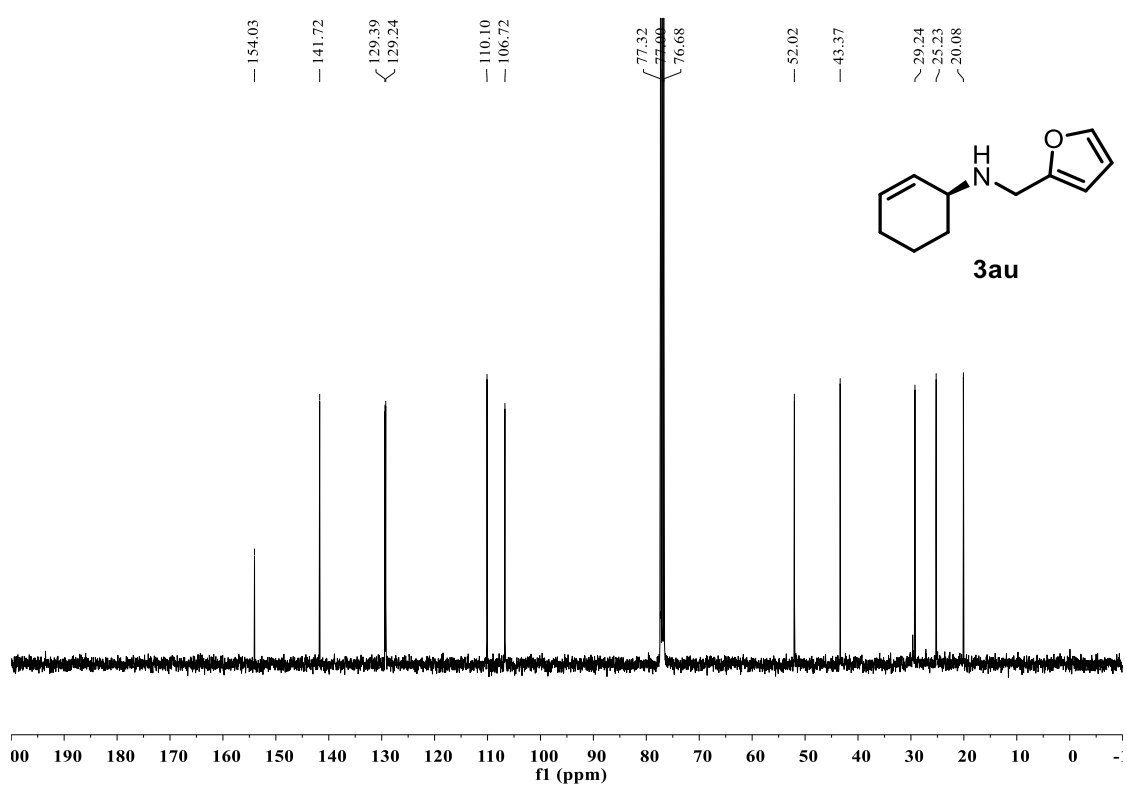


Figure S120. <sup>13</sup>C NMR spectra of **3au**, related to Figure 4.

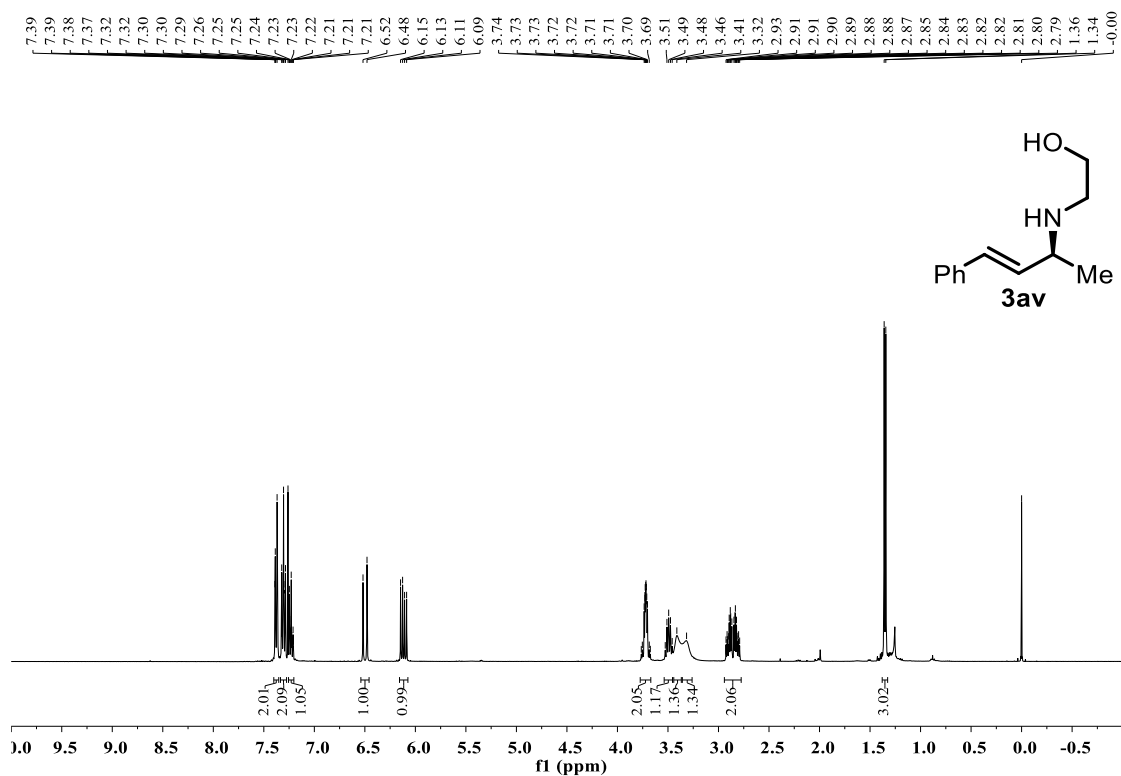


Figure S121. <sup>1</sup>H NMR spectra of **3av**, related to Figure 5.

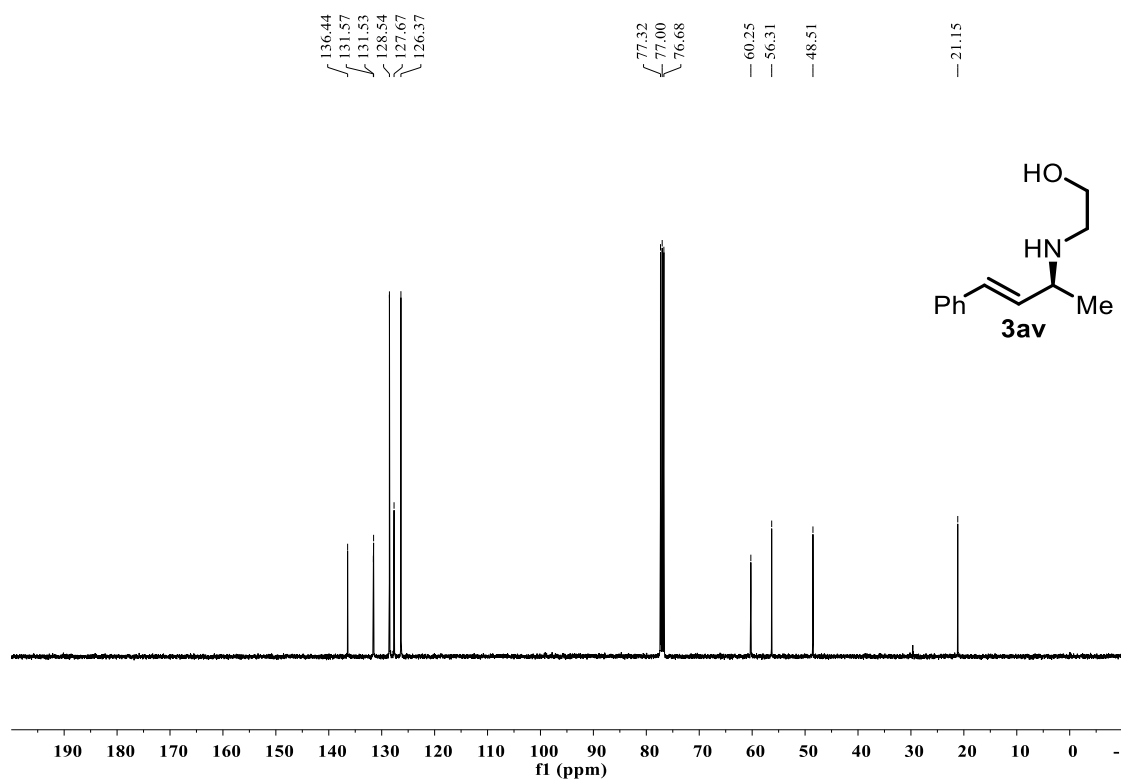


Figure S122. <sup>13</sup>C NMR spectra of **3av**, related to Figure 5.

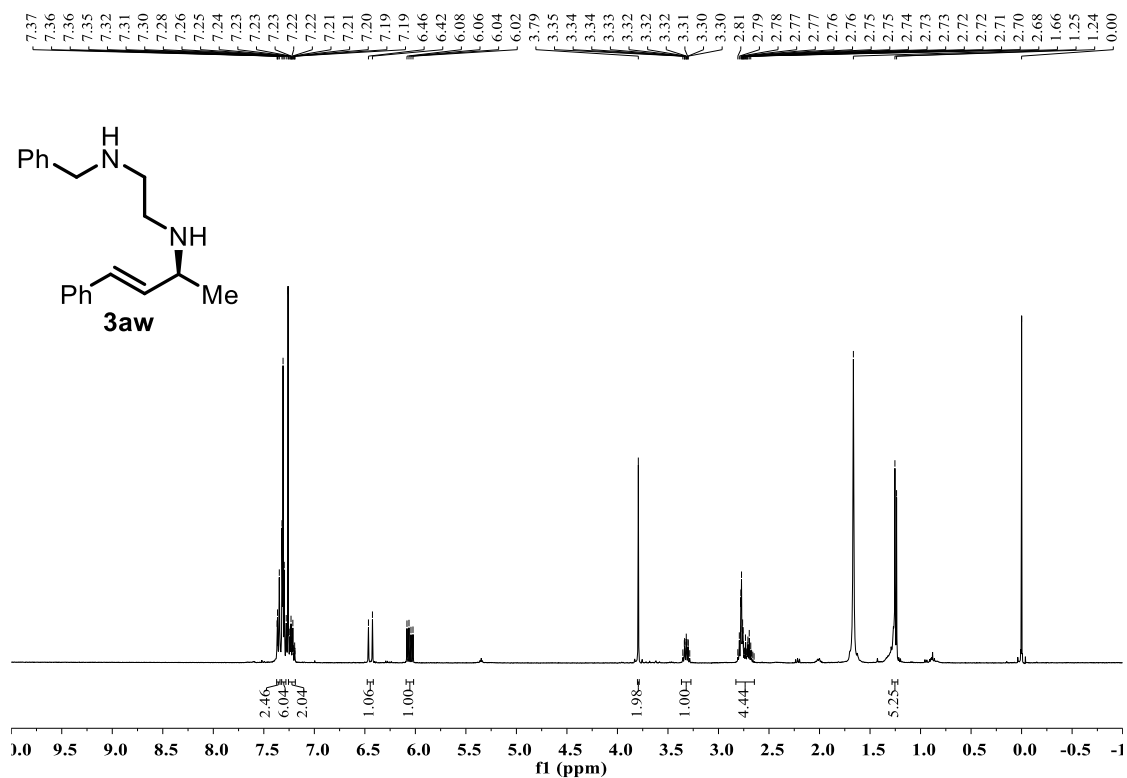


Figure S123. <sup>1</sup>H NMR spectra of **3aw**, related to Figure 5.

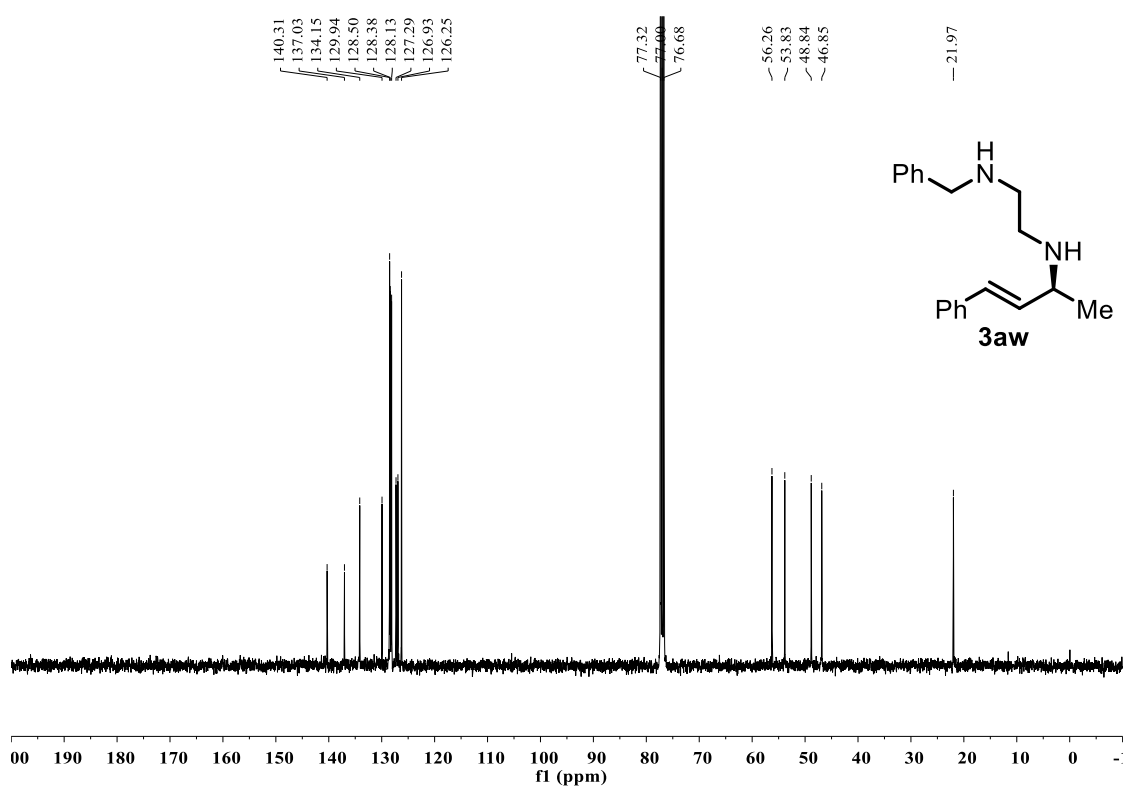


Figure S124. <sup>13</sup>C NMR spectra of **3aw**, related to Figure 5.

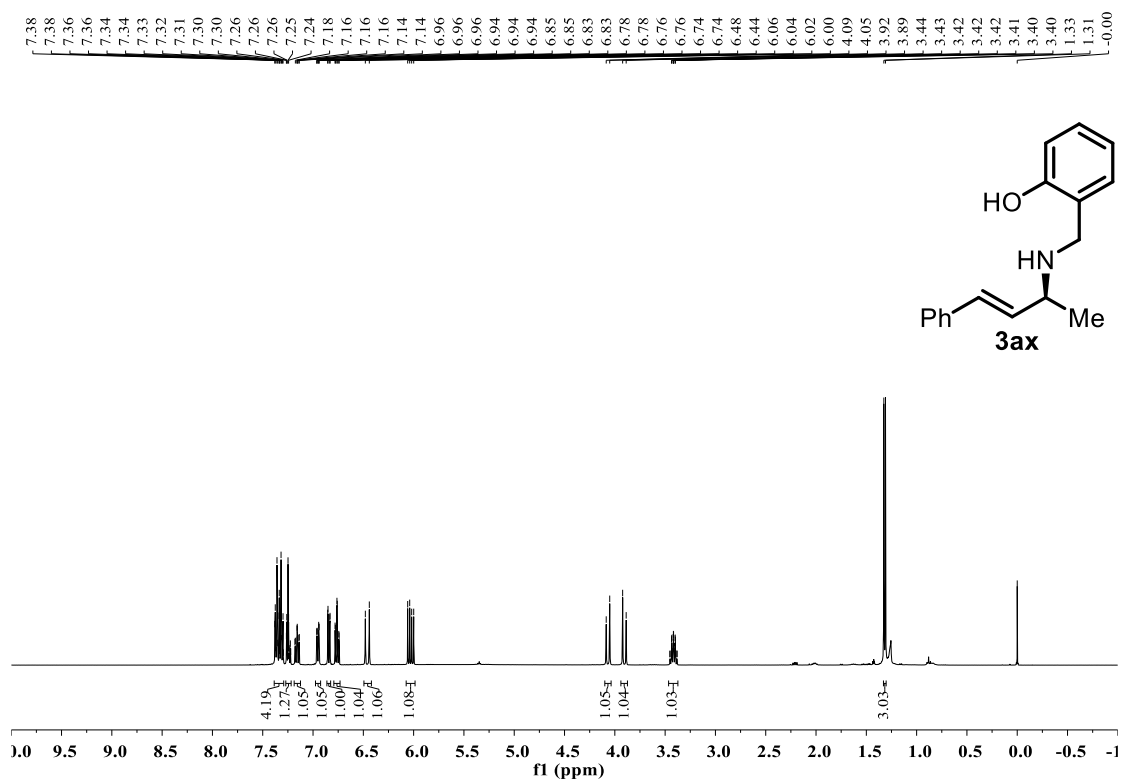


Figure S125. <sup>1</sup>H NMR spectra of **3ax**, related to Figure 5.

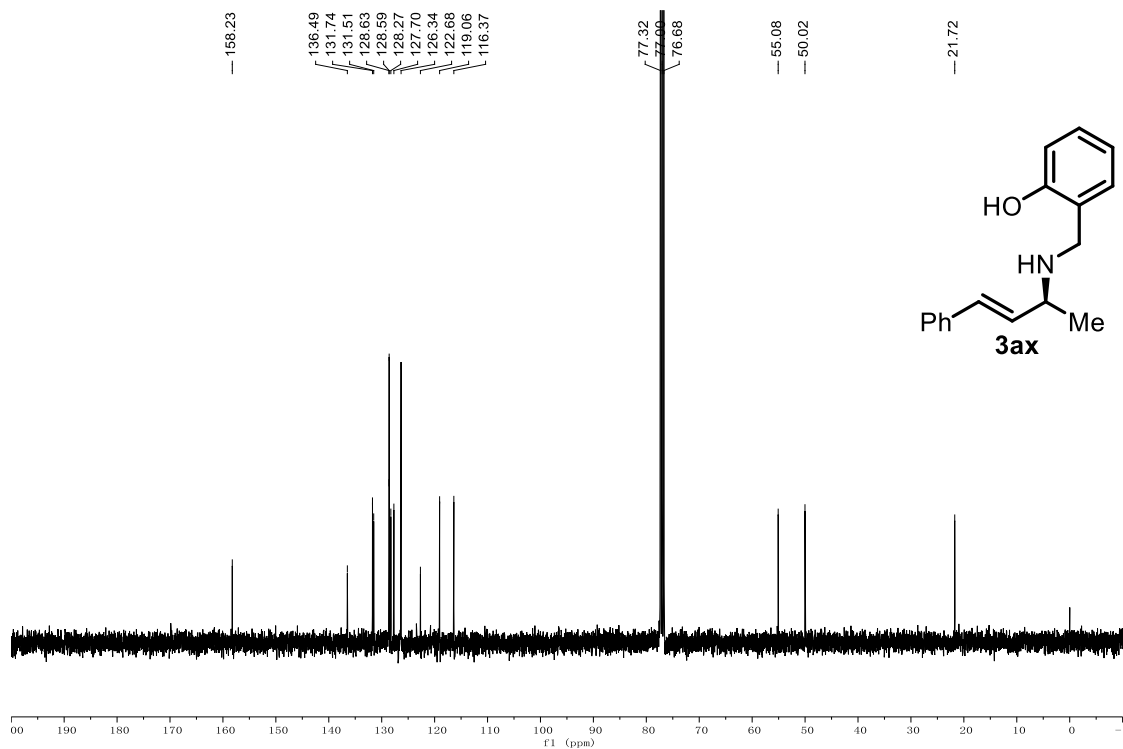


Figure S126. <sup>13</sup>C NMR spectra of **3ax**, related to Figure 5.



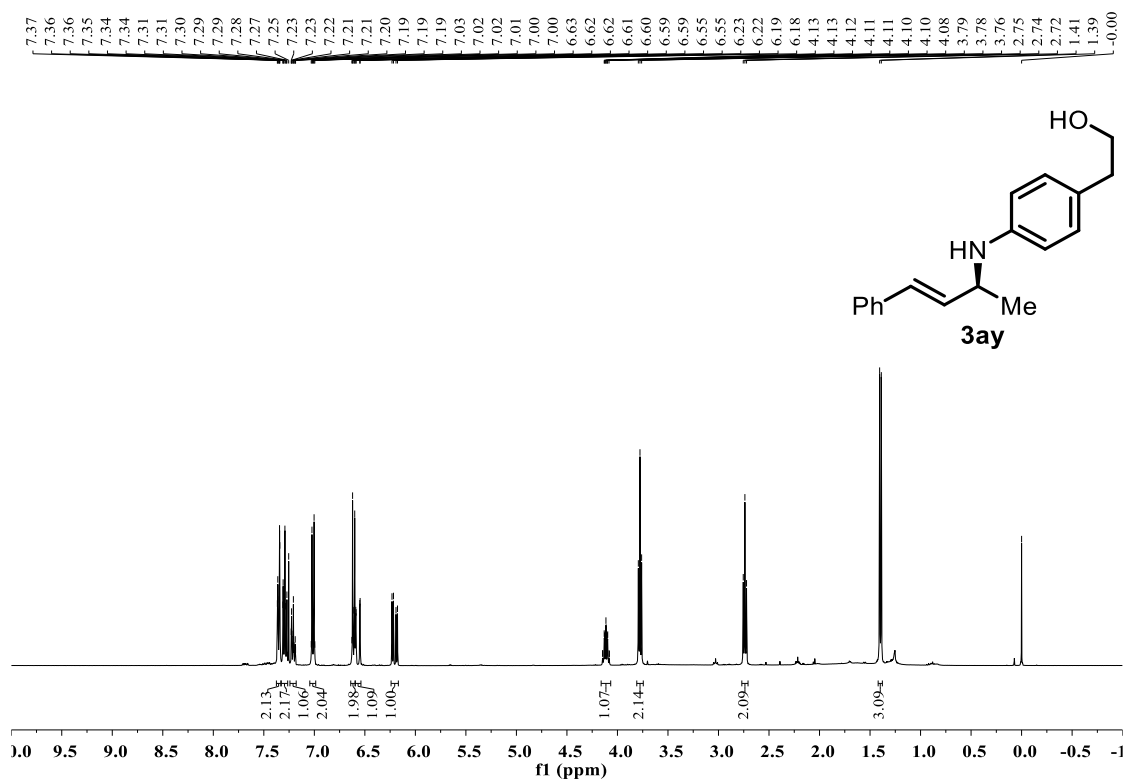


Figure S127. <sup>1</sup>H NMR spectra of **3ay**, related to Figure 5.

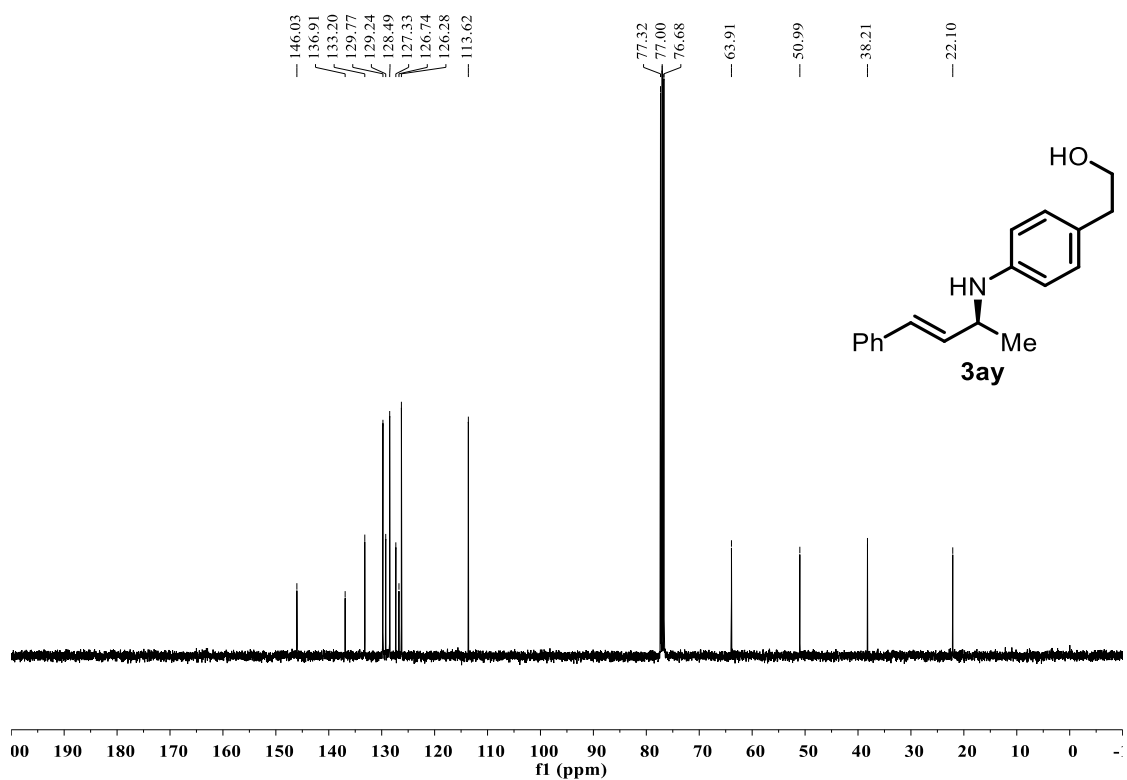


Figure S128. <sup>13</sup>C NMR spectra of **3ay**, related to Figure 5.

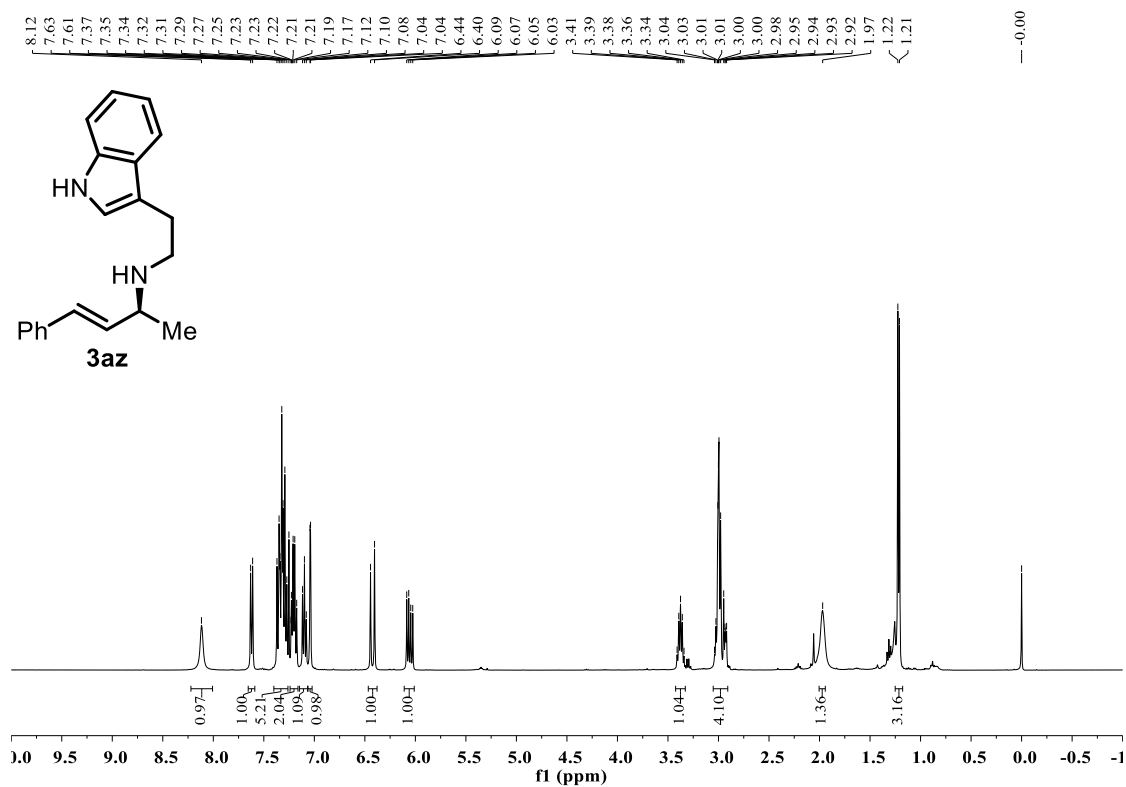


Figure S129. <sup>1</sup>H NMR spectra of **3az**, related to Figure 5.

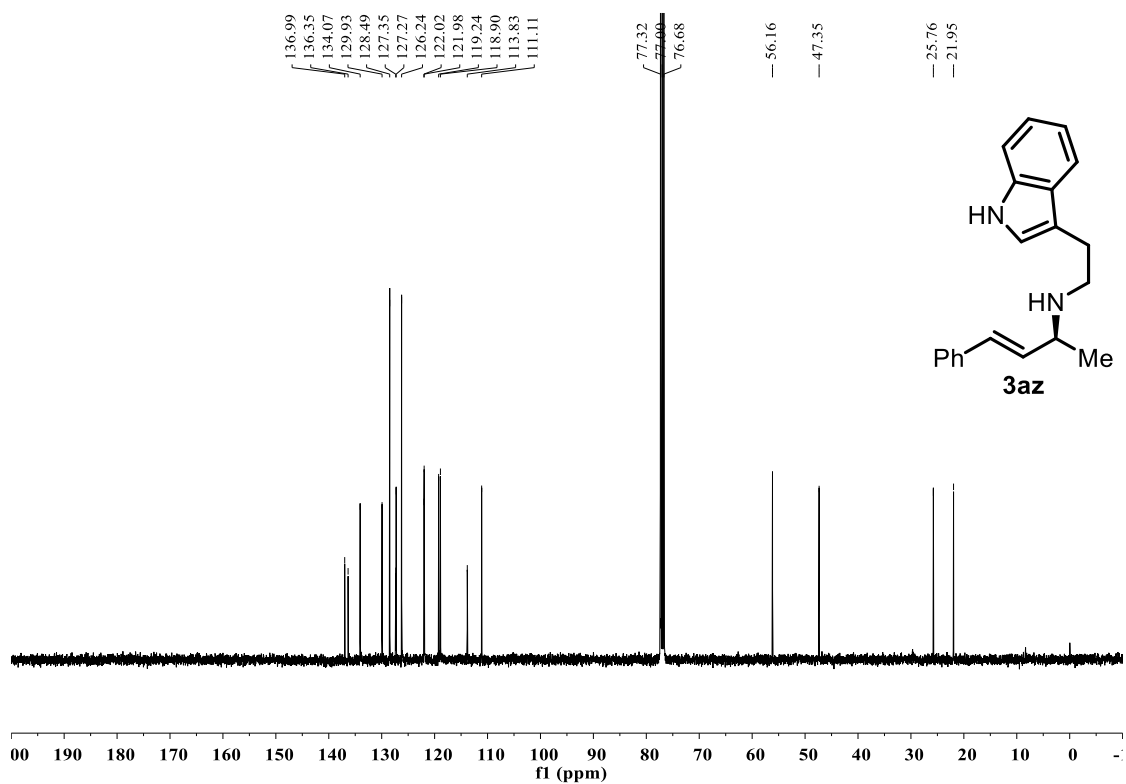


Figure S130. <sup>13</sup>C NMR spectra of **3az**, related to Figure 5.

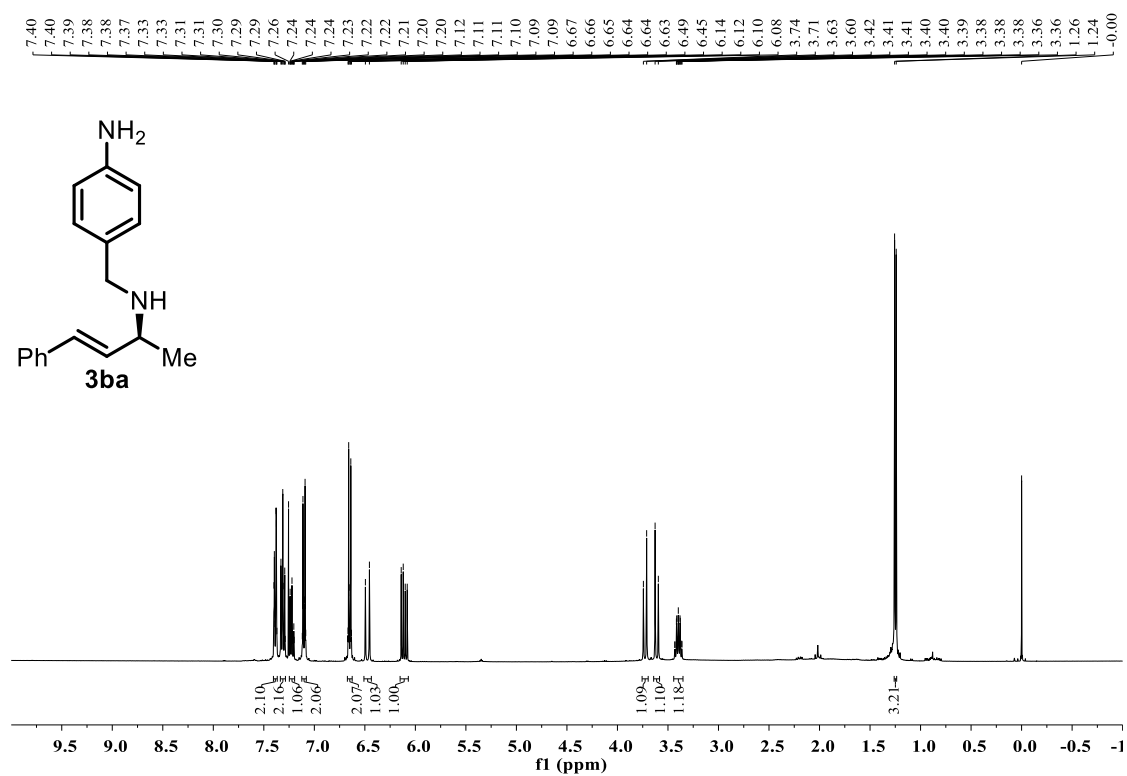


Figure S131. <sup>1</sup>H NMR spectra of **3ba**, related to Figure 5.

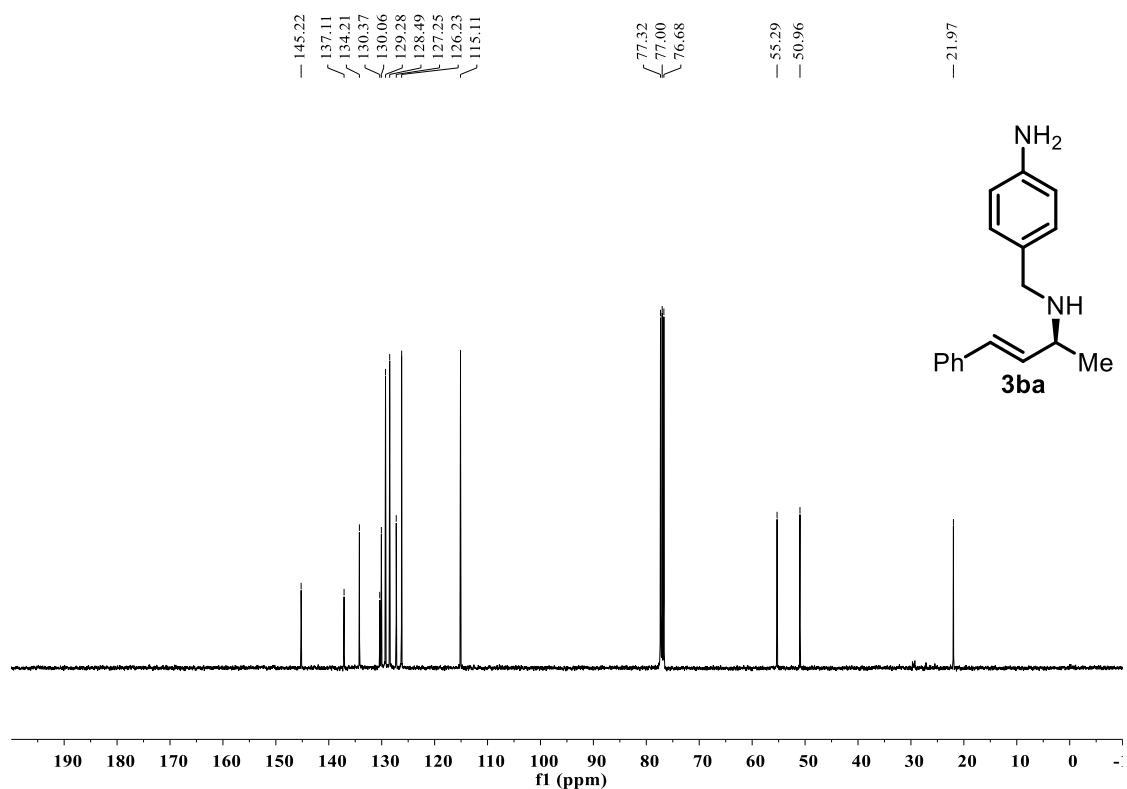


Figure S132. <sup>13</sup>C NMR spectra of **3ba**, related to Figure 5.

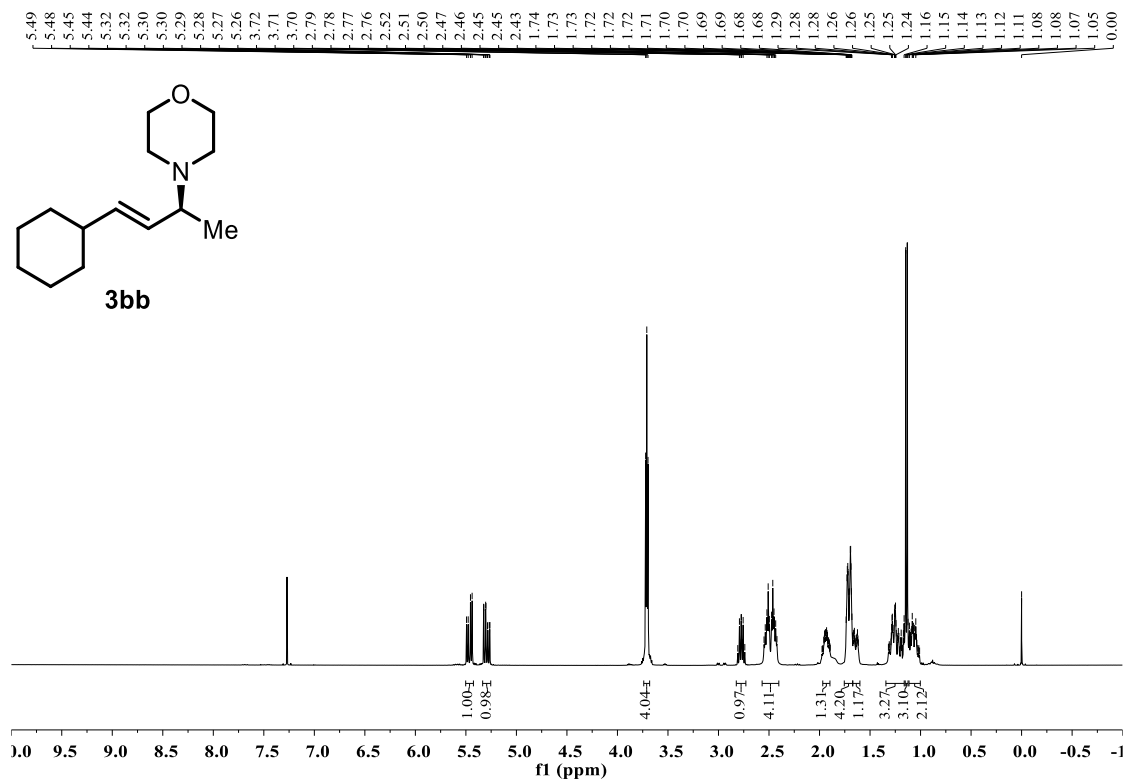


Figure S133. <sup>1</sup>H NMR spectra of **3ba**.

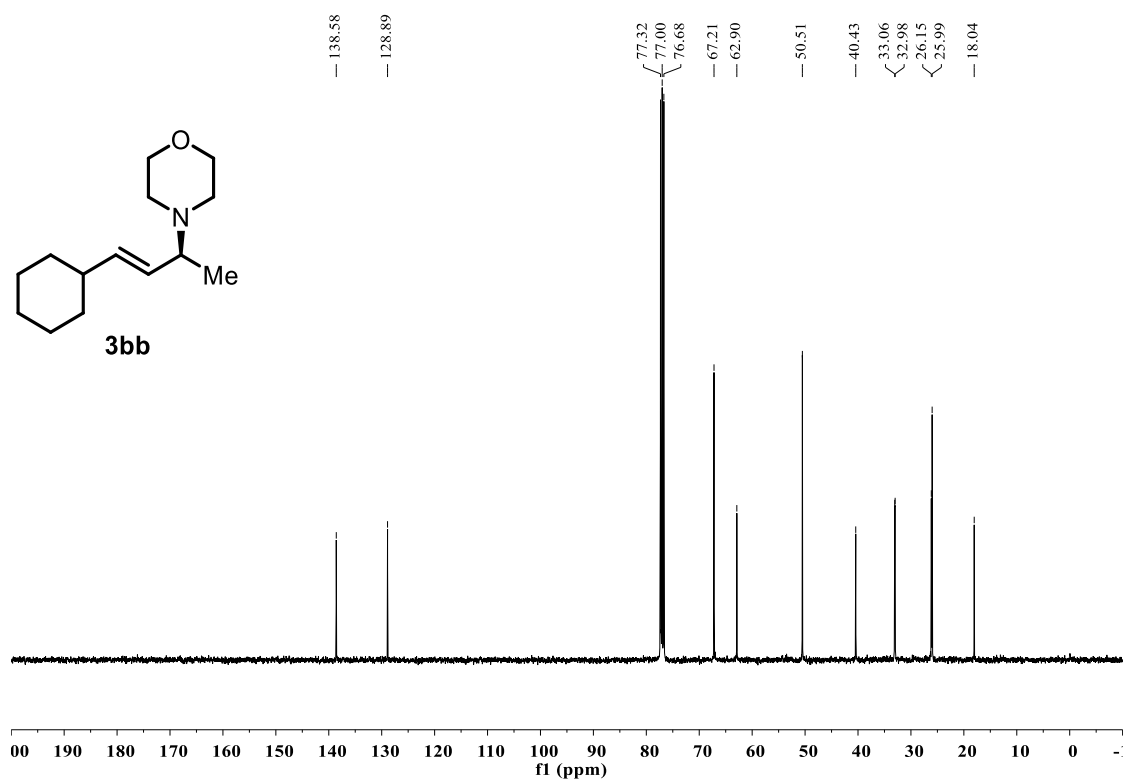


Figure S134. <sup>13</sup>C NMR spectra of **3ba**.

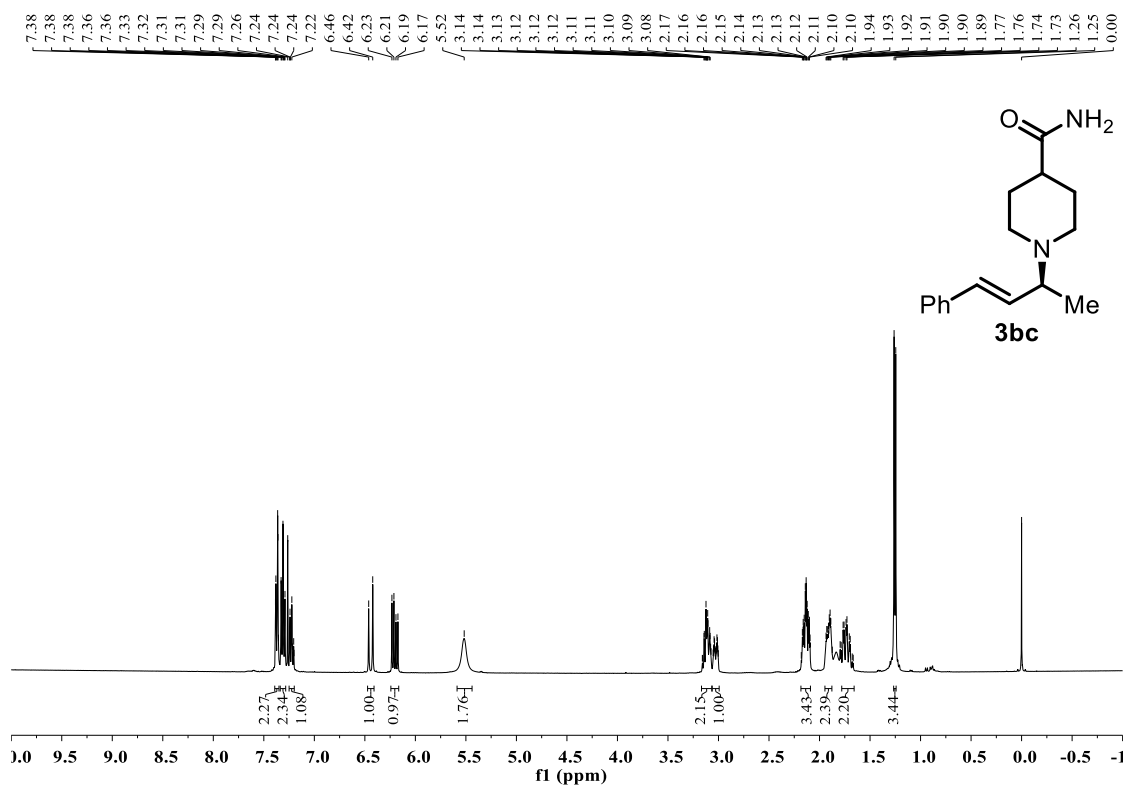


Figure S135. <sup>1</sup>H NMR spectra of **3bc**.

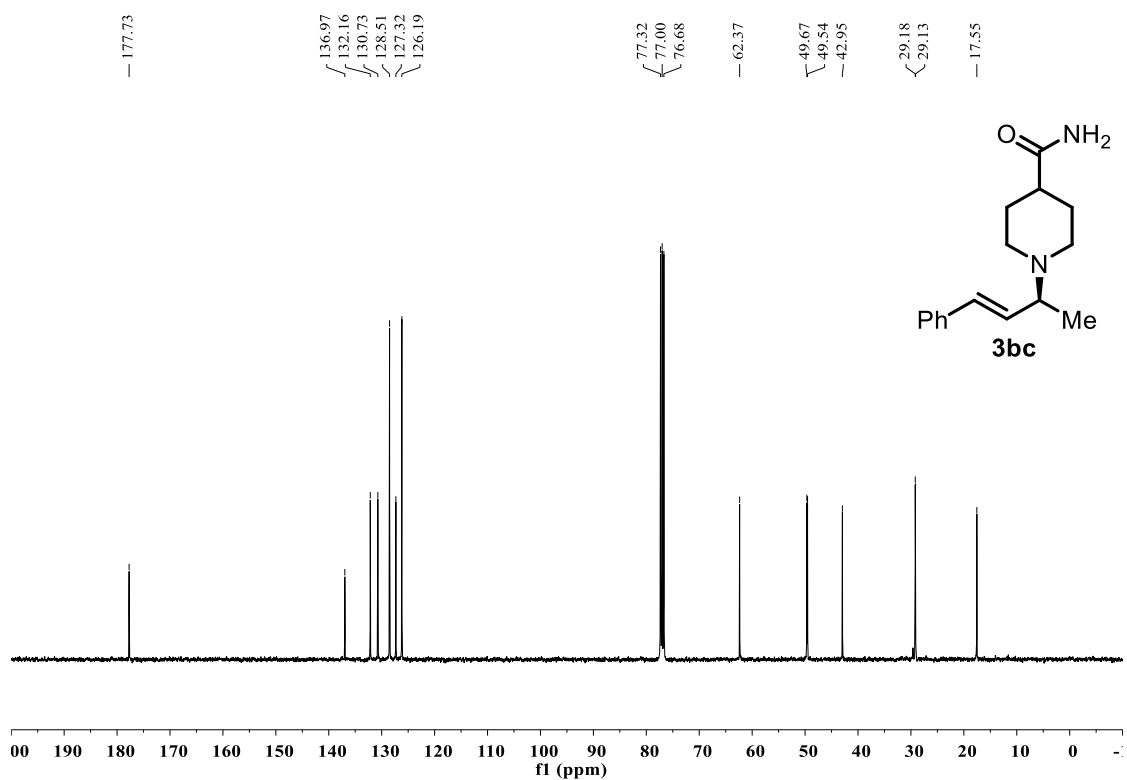
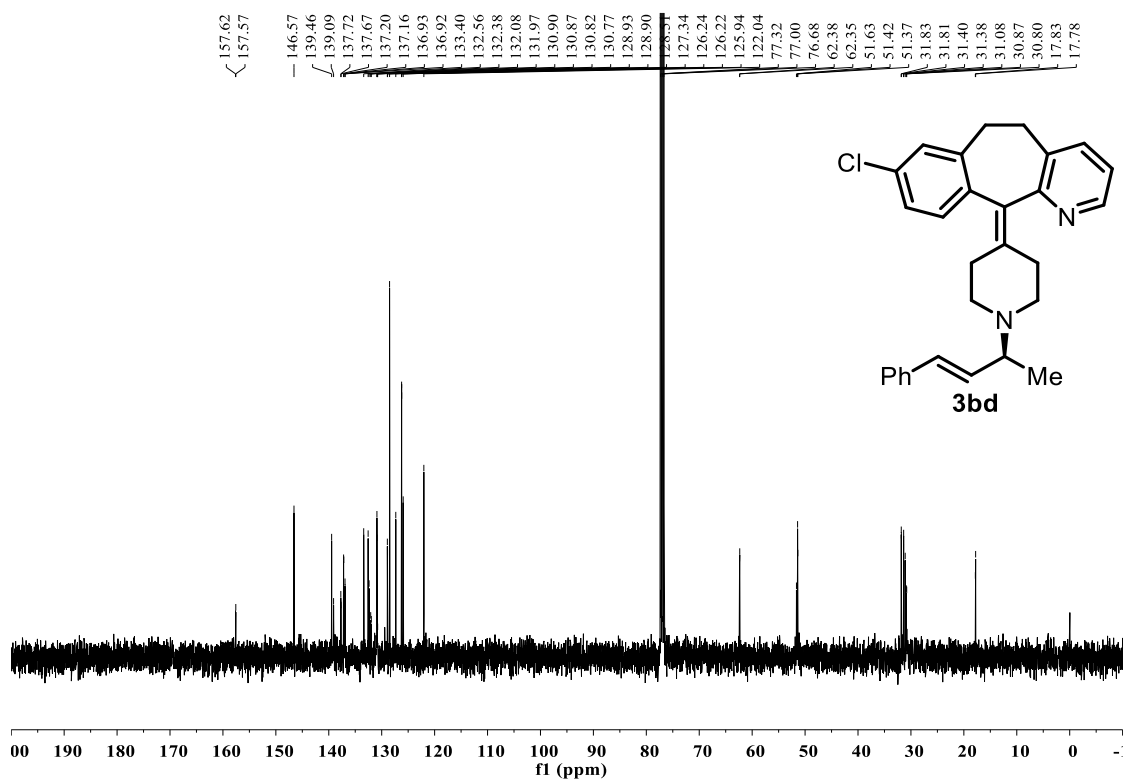
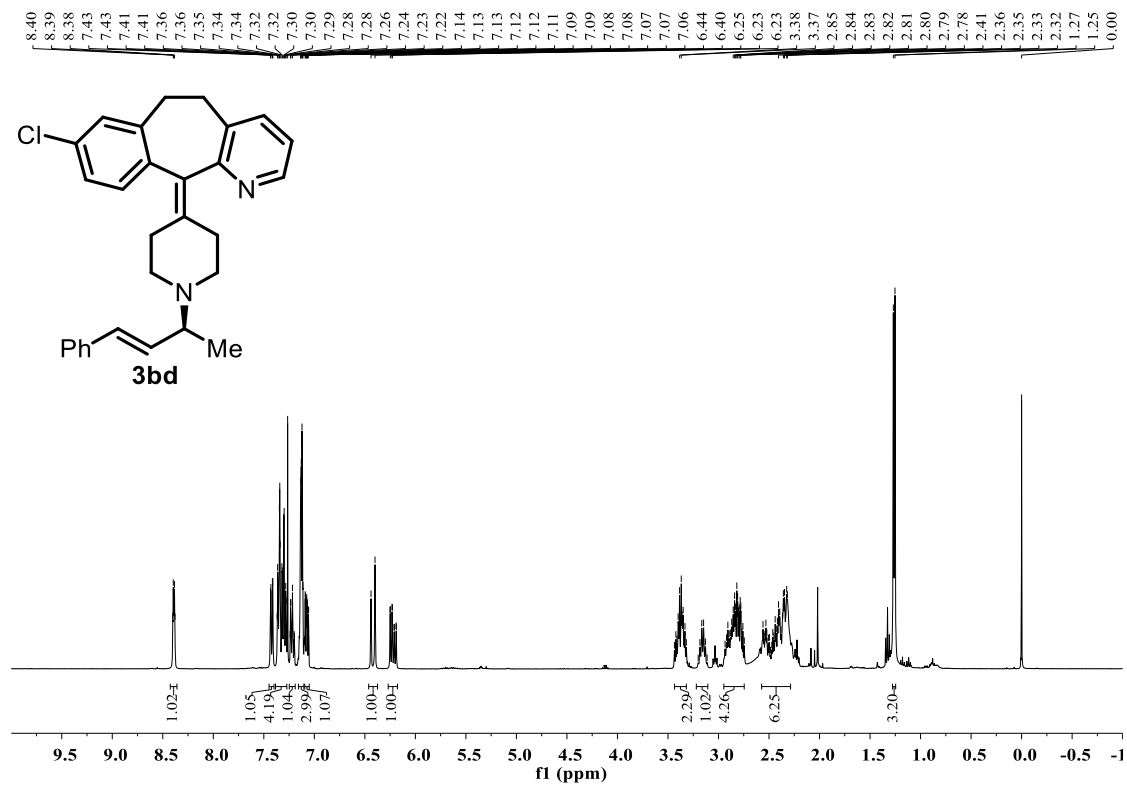


Figure S136. <sup>13</sup>C NMR spectra of **3bc**.



Supplemental figures for  $^1\text{H}$  and  $^2\text{H}$ -NMR spectra of deuterium labeling studies

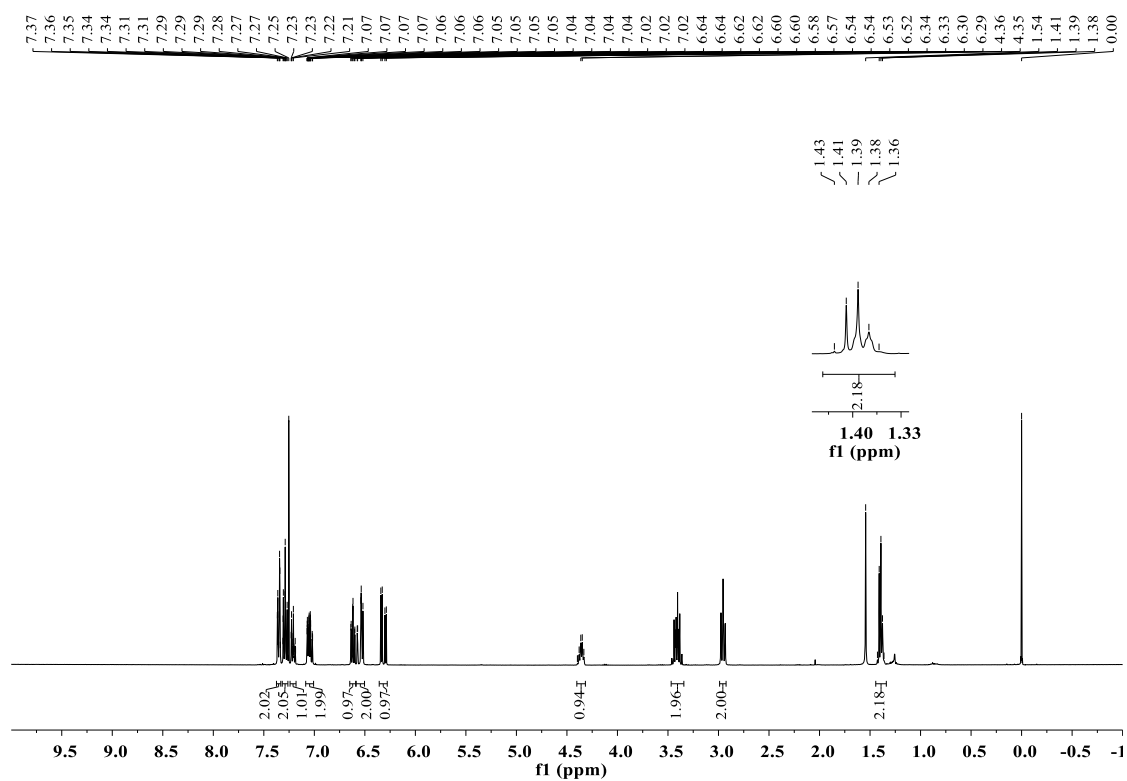


Figure S139.  $^1\text{H}$  NMR spectra of  $d\text{-3t}$ , related to Scheme S7.

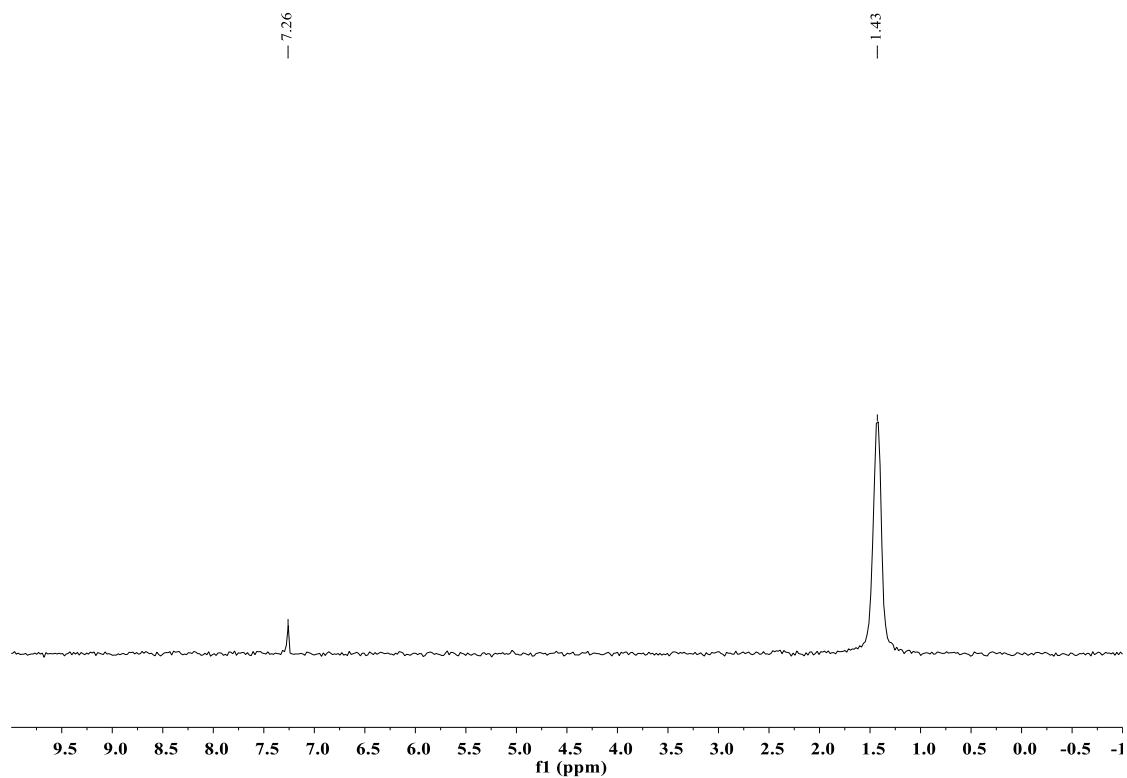
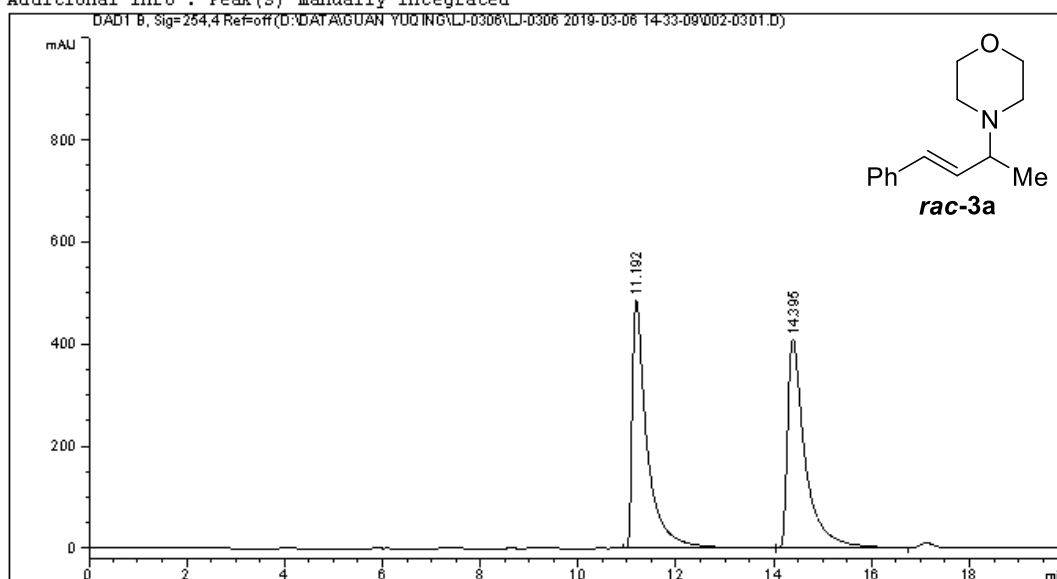


Figure S140.  $^2\text{H}$  NMR spectra of  $d\text{-3t}$ , related to Scheme S7.

## Supplemental Figures for HPLC spectra

Data File D:\DATA\GUAN YUQING\LJ-0306\LJ-0306 2019-03-06 14-33-09\002-0301.D  
Sample Name: LJ-100-7-RAC

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Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 2                   Location  : Vial 2
Injection Date  : 3/6/2019 3:06:17 PM           Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-0306\LJ-0306 2019-03-06 14-33-09\DAD-OD(1-2)-90-10-0
                  .SML-SUL-ALL-20MIN.M
Last changed    : 1/20/2019 9:58:06 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-OD(1-2)-95-5-1ML-SUL-ALL-20MIN.M
Last changed    : 3/6/2019 3:50:27 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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### Area Percent Report

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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
=====
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Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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2	14.395	BB	0.3613	1.01898e4	408.17218	49.7649

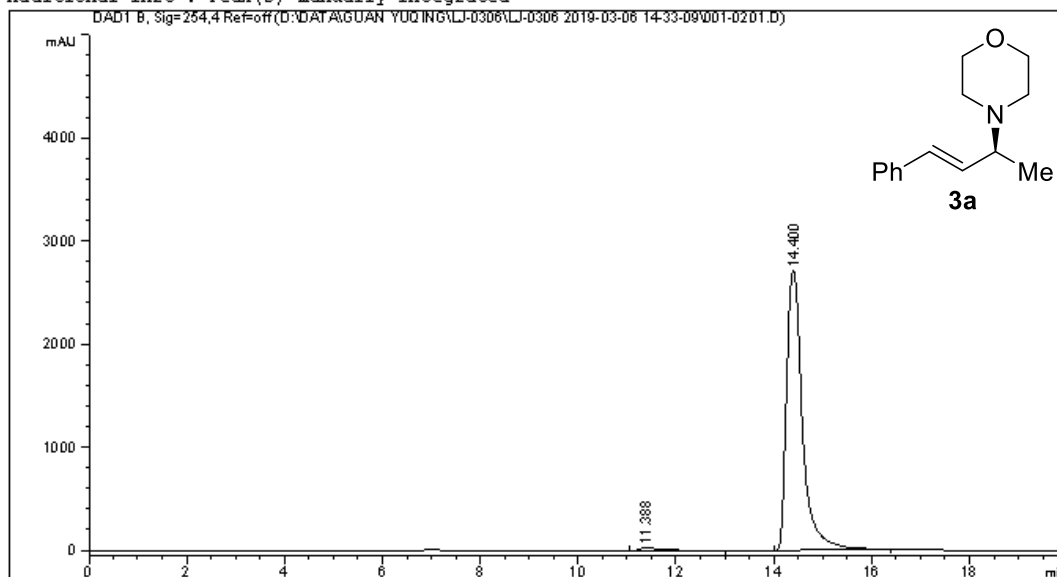
Totals :                                    2.04759e4    894.41354

Figure S141. HPLC spectra of *rac-3a*, related to Figure 3.



Data File D:\DATA\GUAN YUQING\LJ-0306\LJ-0306 2019-03-06 14-33-09\001-0201.D  
Sample Name: LJ-100-7

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 2                   Location  : Vial 1
Injection Date  : 3/6/2019 2:45:19 PM           Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-0306\2019-03-06 14-33-09\DAD-OD(1-2)-90-10-0
                  .SML-SUL-ALL-20MIN.M
Last changed    : 1/20/2019 9:58:06 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-OD(1-2)-95-5-1ML-SUL-ALL-20MIN.M
Last changed    : 3/6/2019 3:56:51 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.388	BB	0.4032	650.96808	23.07139	1.0541
2	14.400	BB	0.3453	6.11045e4	2707.21484	98.9459

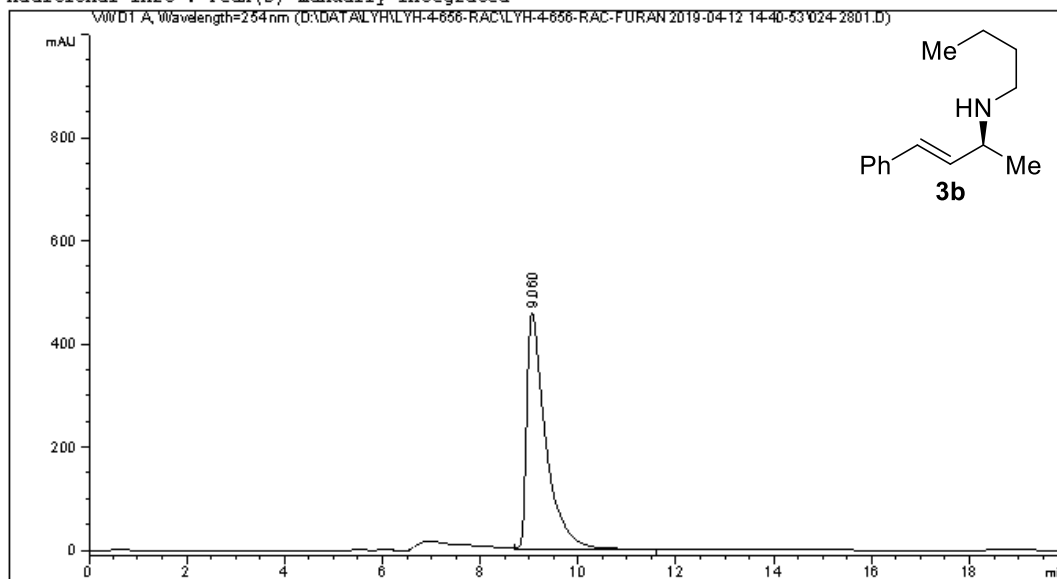
Totals :                                   6.17554e4  2730.28624

Figure S142. HPLC spectra of 3a, related to Figure 3.



Data File D:\DATA\LYH\LYH-4-656-RAC\LYH-4-656-RAC-FURAN 2019-04-12 14-40-53\024-2801.D  
Sample Name: LJ-108-7

```
=====
Acq. Operator   :                               Seq. Line :   28
Acq. Instrument : Instrument 1                   Location  : Vial 24
Injection Date  : 4/13/2019 6:39:44 AM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LYH\LYH-4-656-RAC\LYH-4-656-RAC-FURAN 2019-04-12 14-40-53\WVD-AD(1-
                2)-99-1-0.6ML-5UL-254NM-40MIN.M
Last changed    : 3/5/2019 3:34:42 PM
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-5UL-ALL-60MIN.M
Last changed    : 4/14/2019 8:49:14 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

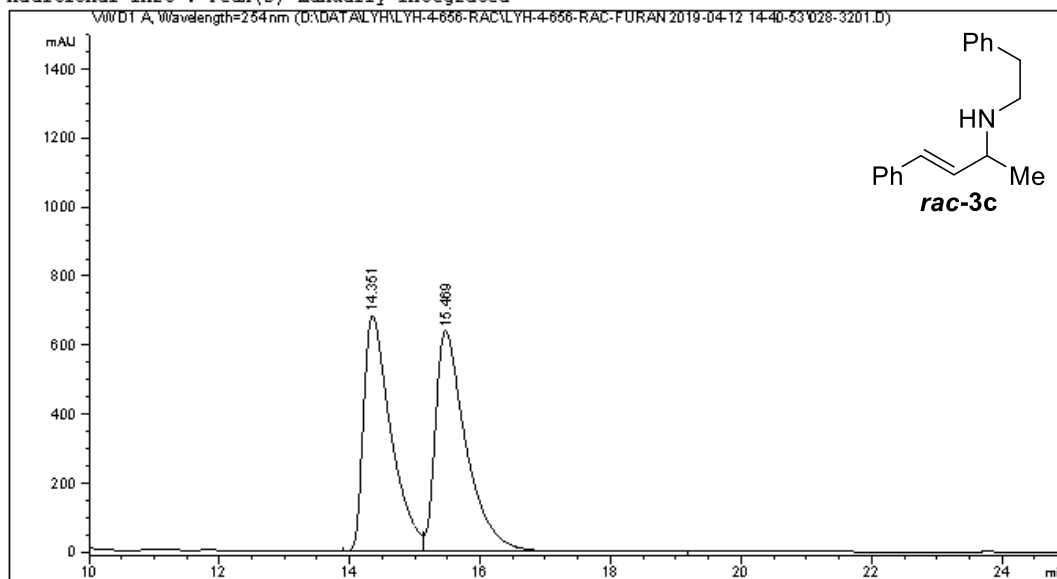
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.060	VB	0.3911	1.24684e4	460.12094	100.0000

Totals :                    1.24684e4   460.12094

**Figure S144.** HPLC spectra of **3b**, related to **Figure 3**.

Data File D:\DATA\LYH\LYH-4-656-RAC\LYH-4-656-RAC-FURAN 2019-04-12 14-40-53\028-3201.D  
Sample Name: LJ-130-3

```
=====
Acq. Operator   :                               Seq. Line :   32
Acq. Instrument : Instrument 1                   Location  : Vial 28
Injection Date  : 4/13/2019 9:23:12 AM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LYH\LYH-4-656-RAC\LYH-4-656-RAC-FURAN 2019-04-12 14-40-53\WVD-AD(1-
                2)-99-1-0.6ML-5UL-254NM-40MIN.M
Last changed    : 3/5/2019 3:34:42 PM
Analysis Method : D:\METHOD\LG\DAD-0D(1-2)-95-5-1ML-2UL-ALL-50MIN.M
Last changed    : 4/15/2019 11:29:25 AM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

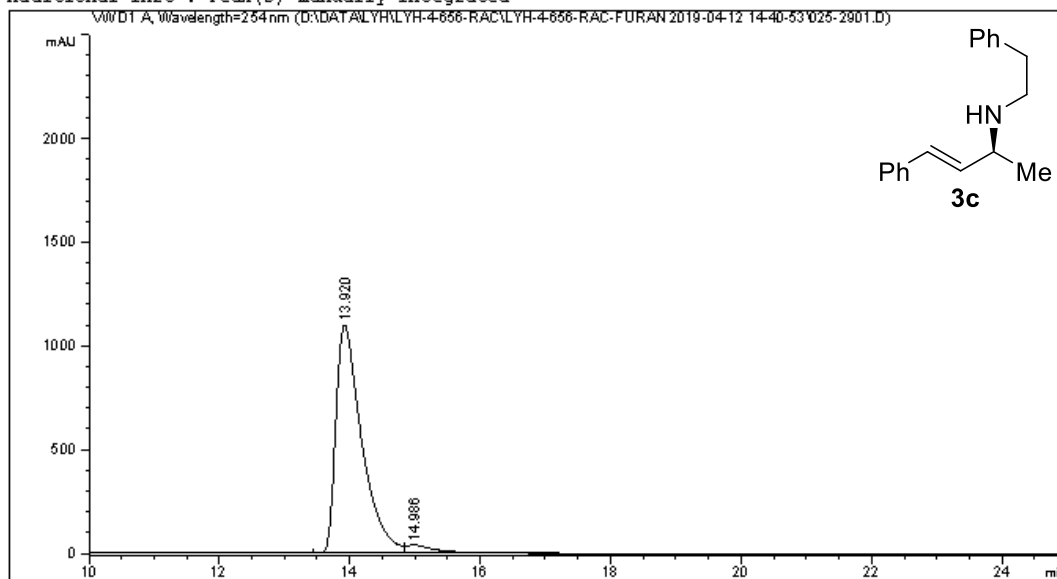
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.351	BV	0.4302	1.98917e4	684.26312	48.7101
2	15.469	VB	0.4812	2.09452e4	639.34631	51.2899

Totals :                                   4.08368e4 1323.60944

**Figure S145.** HPLC spectra of *rac-3c*, related to **Figure 3**.

Data File D:\DATA\LYH\LYH-4-656-RAC\LYH-4-656-RAC-FURAN 2019-04-12 14-40-53\025-2901.D  
Sample Name: LJ-108-9

```
=====
Acq. Operator   :                               Seq. Line :   29
Acq. Instrument : Instrument 1                   Location  : Vial 25
Injection Date  : 4/13/2019 7:20:36 AM          Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LYH\LYH-4-656-RAC\LYH-4-656-RAC-FURAN 2019-04-12 14-40-53\WVD-AD(1-
                2)-99-1-0.6ML-5UL-254NM-40MIN.M
Last changed    : 3/5/2019 3:34:42 PM
Analysis Method : D:\METHOD\LG\DAD-0D(1-2)-95-5-1ML-2UL-ALL-50MIN.M
Last changed    : 4/15/2019 11:31:56 AM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.920	VV	0.4096	3.02696e4	1097.99194	96.0947
2	14.986	VB	0.4442	1230.14990	38.24589	3.9053

Totals :                                    3.14997e4  1136.23783

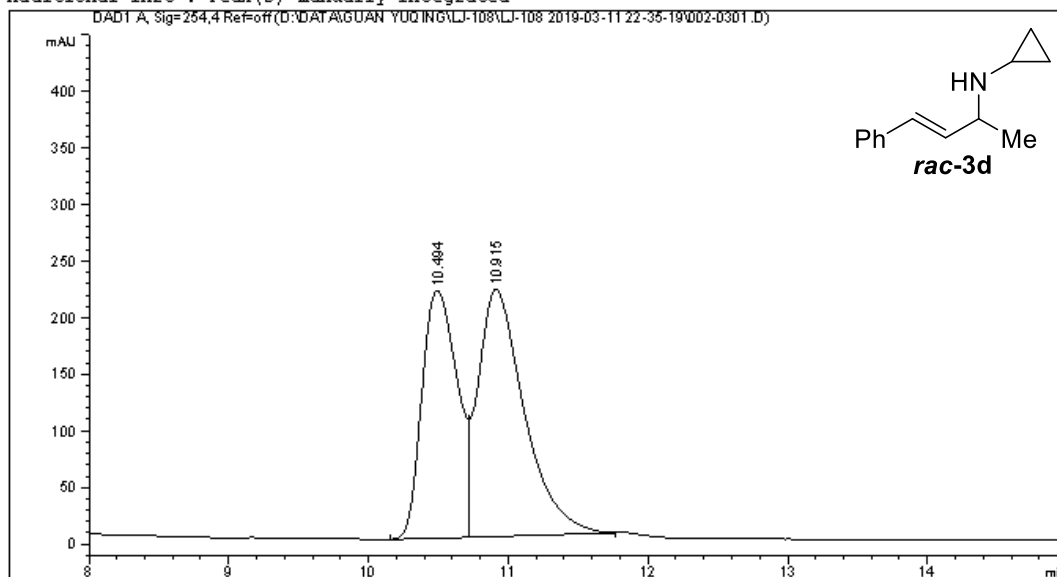
Instrument 2 4/15/2019 11:32:03 AM

Page 1 of 2

**Figure S146.** HPLC spectra of **3c**, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LJ-108\LJ-108 2019-03-11 22-35-19\002-0301.D  
Sample Name: LJ-108-5-RAC

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 2                   Location  : Vial 2
Injection Date  : 3/11/2019 11:48:25 PM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-108\LJ-108 2019-03-11 22-35-19\DAD-0J(1-6)-95-5-0.
                  SML-SUL-ALL-60MIN.M
Last changed    : 3/7/2019 10:25:35 PM
Analysis Method : D:\METHOD\YANG JIAXIN\VWD-IA-(1-2)-85-15-1.0ML-SUL-210NM-60MIN.M
Last changed    : 5/31/2019 8:36:13 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

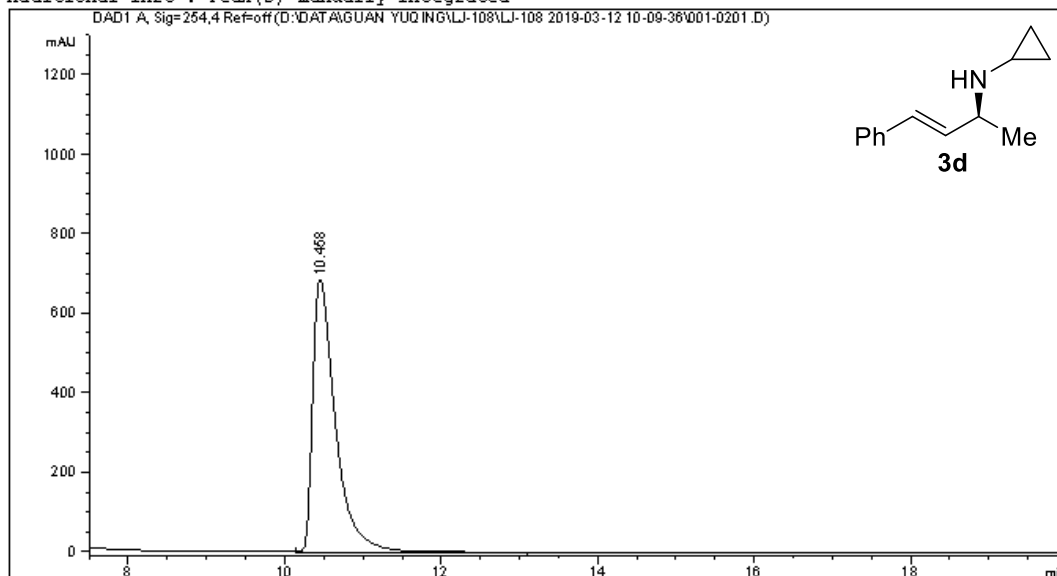
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.494	BV	0.2743	3832.56519	218.90829	43.3094
2	10.915	VB	0.3402	5016.70459	218.20282	56.6906

Totals : 8849.26978 437.11111

Figure S147. HPLC spectra of *rac-3d*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-108\LJ-108 2019-03-12 10-09-36\001-0201.D  
Sample Name: LJ-108-5

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 2                   Location  : Vial 1
Injection Date  : 3/12/2019 10:23:31 AM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-108\LJ-108 2019-03-12 10-09-36\DAD-0J(1-6)-95-5-0.
                  SML-5UL-ALL-60MIN.M
Last changed    : 3/12/2019 10:32:53 AM
                  (modified after loading)
Analysis Method : D:\METHOD\LWD\VWD-AD(1-2)-95-5-1ML-3UL-210NM-10MIN.M
Last changed    : 3/21/2019 8:42:39 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

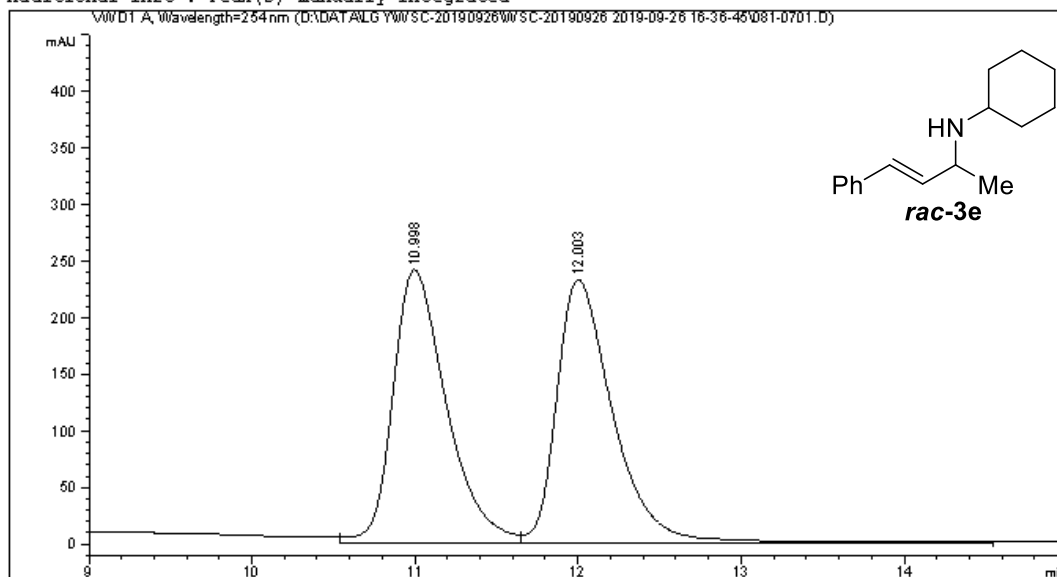
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.458	VB	0.3057	1.38817e4	687.03412	100.0000

Totals : 1.38817e4 687.03412

**Figure S148.** HPLC spectra of **3d**, related to **Figure 3**.

Data File D:\DATA\LGY\WSC-20190926\WSC-20190926 2019-09-26 16-36-45\081-0701.D  
Sample Name: LJ-108-3-RAC

```
=====
Acq. Operator   :                               Seq. Line :    7
Acq. Instrument : Instrument 1                  Location  : Vial 81
Injection Date  : 9/26/2019 7:23:06 PM         Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LGY\WSC-20190926\WSC-20190926 2019-09-26 16-36-45\VWD-AD(1-2)-99-1-
0.5ML-SUL-254NM-25MIN.M
Last changed    : 9/26/2019 6:06:23 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AD(1-2)-99-1-0.5ML-SUL-254NM-25MIN.M
Last changed    : 9/26/2019 8:26:00 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.998	VV	0.3455	5517.50684	241.51408	49.7795
2	12.003	VB	0.3631	5566.38281	232.71924	50.2205

Totals :                                   1.10839e4   474.23332

Figure S149. HPLC spectra of *rac-3e*, related to Figure 3.

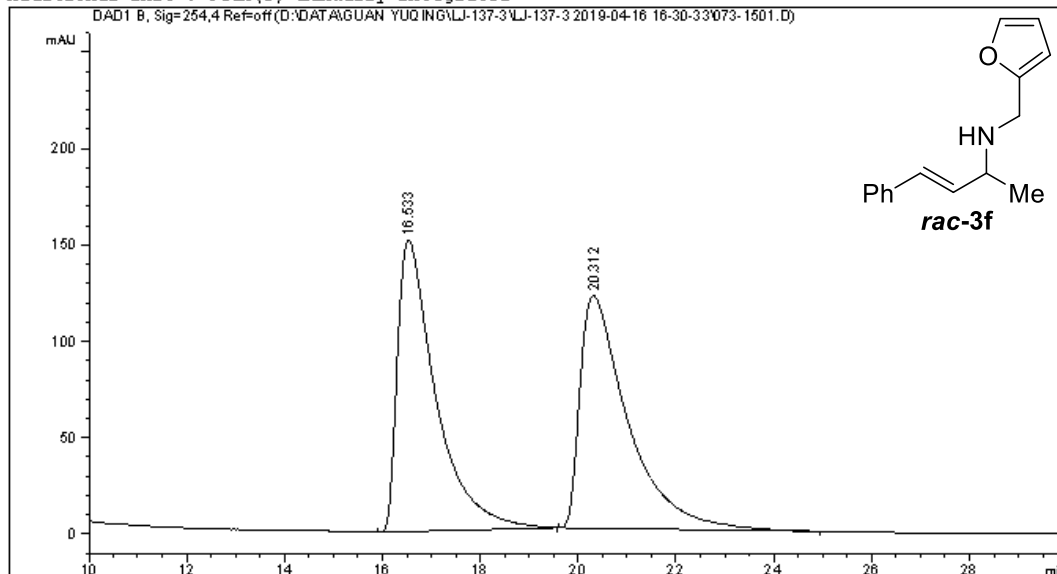




Data File D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\073-1501.D  
Sample Name: LJ-137-5-RAC

```
=====
Acq. Operator   :                               Seq. Line :   15
Acq. Instrument : Instrument 2                   Location  : Vial 73
Injection Date  : 4/16/2019 8:30:00 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0D(1-2)-99-1-
0.5ML-SUL-ALL-60MIN.M
Last changed    : 4/16/2019 8:04:43 PM
Analysis Method : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0D(1-2)-99-1-
0.5ML-SUL-ALL-60MIN.M (Sequence Method)
Last changed    : 4/17/2019 8:22:42 PM
                (modified after loading)
```

Additional Info : Peak(s) manually integrated



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.533	BB	0.7913	8224.38672	151.04292	49.9715
2	20.312	BB	0.9384	8233.77539	120.61980	50.0285

Totals : 1.64582e4 271.66273

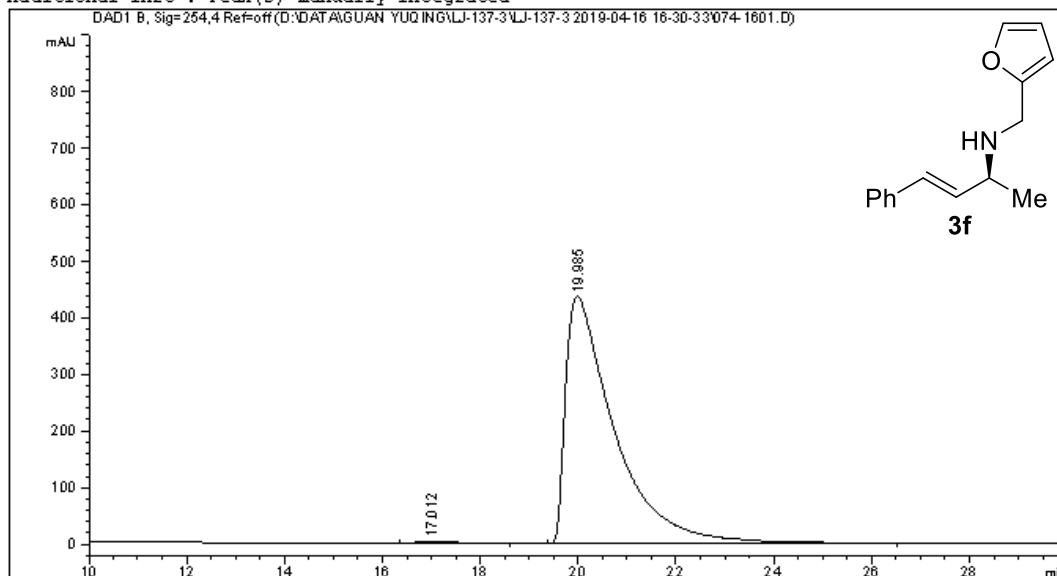
Instrument 2 4/17/2019 8:22:47 PM

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Figure S151. HPLC spectra of *rac-3f*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\074-1601.D  
Sample Name: LJ-137-5

```
=====
Acq. Operator   :                               Seq. Line :   16
Acq. Instrument : Instrument 2                   Location  : Vial 74
Injection Date  : 4/16/2019 9:31:03 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0D(1-2)-99-1-
                  0.5ML-SUL-ALL-60MIN.M
Last changed    : 4/16/2019 8:04:43 PM
Analysis Method : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0D(1-2)-99-1-
                  0.5ML-SUL-ALL-60MIN.M (Sequence Method)
Last changed    : 4/17/2019 8:24:00 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.012	BB	0.6427	203.91769	3.79637	0.6686
2	19.985	BB	0.9646	3.02947e4	436.01385	99.3314

Totals : 3.04986e4 439.81022

Instrument 2 4/17/2019 8:24:05 PM

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Figure S152. HPLC spectra of 3f, related to Figure 3.

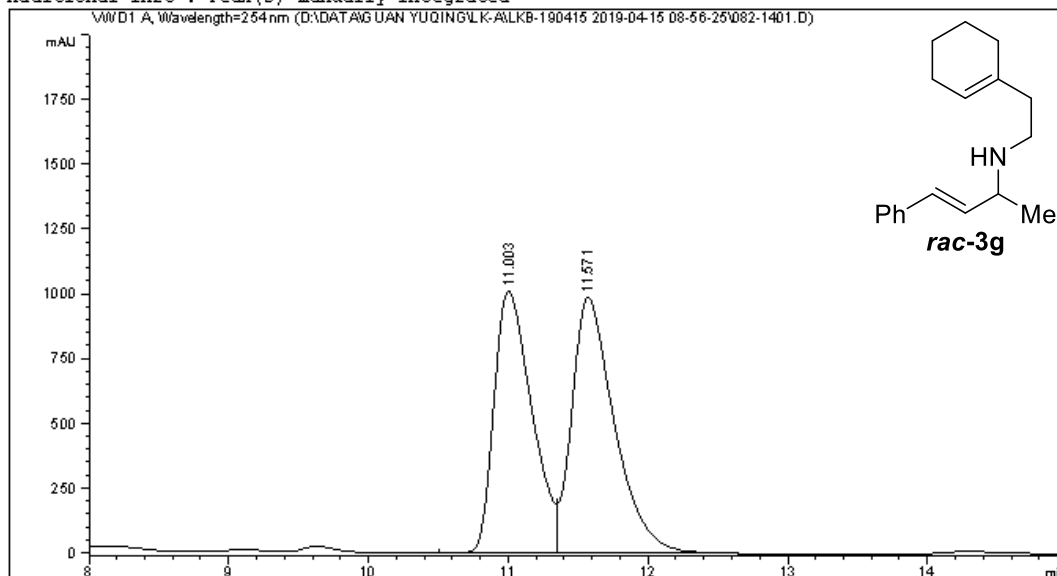
Data File D:\DATA\GUAN YUQING\LK-A\LKB-190415 2019-04-15 08-56-25\082-1401.D  
 Sample Name: LJ-137-2-RAC

```

=====
Acq. Operator   :                               Seq. Line :   14
Acq. Instrument : Instrument 1                   Location  : Vial 82
Injection Date  : 4/15/2019 4:32:13 PM          Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LK-A\LKB-190415 2019-04-15 08-56-25\WVD-AD(1-2)-95-5-0.
                  SML-5UL-254NM-20MIN.M
Last changed    : 3/6/2019 6:07:05 PM
Analysis Method : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0J(1-6)-99-1-
                  1ML-5UL-ALL-40MIN.M
Last changed    : 4/16/2019 5:10:13 PM
                  (modified after loading)
  
```

Additional Info : Peak(s) manually integrated



Area Percent Report

```

=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.003	BV	0.2840	1.88847e4	1010.75867	47.4026
2	11.571	VB	0.3170	2.09543e4	985.94733	52.5974

Totals : 3.98390e4 1996.70599

Instrument 2 4/16/2019 5:10:22 PM

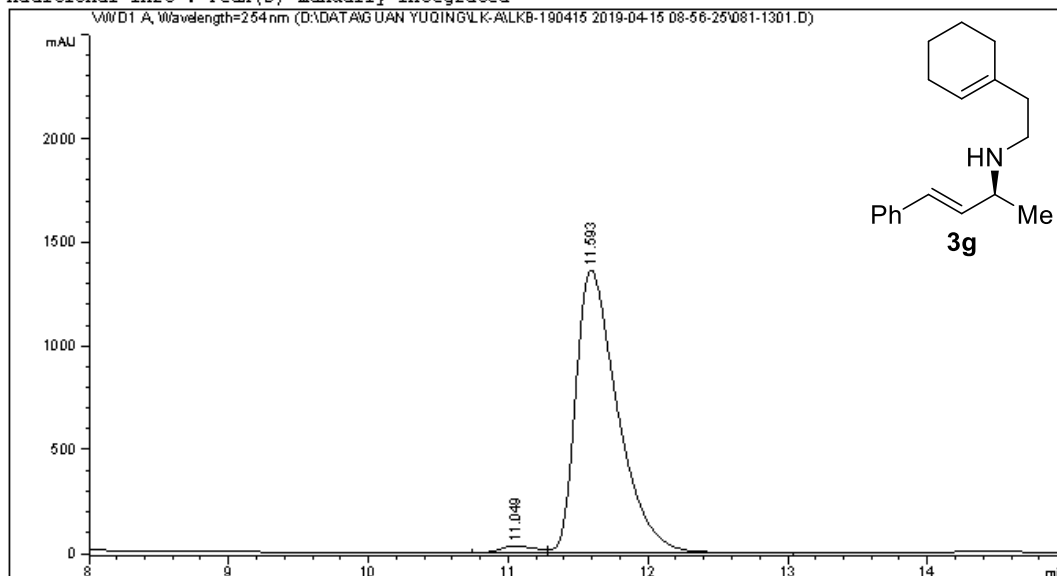
Page 1 of 2

Figure S153. HPLC spectra of *rac-3g*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LK-A\LKB-190415 2019-04-15 08-56-25\081-1301.D  
Sample Name: LJ-137-2

```
=====
Acq. Operator   :                               Seq. Line :   13
Acq. Instrument : Instrument 1                   Location  : Vial 81
Injection Date  : 4/15/2019 4:11:23 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LK-A\LKB-190415 2019-04-15 08-56-25\WVD-AD(1-2)-95-5-0.
                  SML-5UL-254NM-20MIN.M
Last changed    : 3/6/2019 6:07:05 PM
Analysis Method : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0J(1-6)-99-1-
                  1ML-5UL-ALL-40MIN.M
Last changed    : 4/16/2019 5:13:01 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.049	BV	0.2695	572.29053	32.96646	1.9854
2	11.593	VB	0.3129	2.82527e4	1362.80029	98.0146

Totals : 2.88250e4 1395.76675

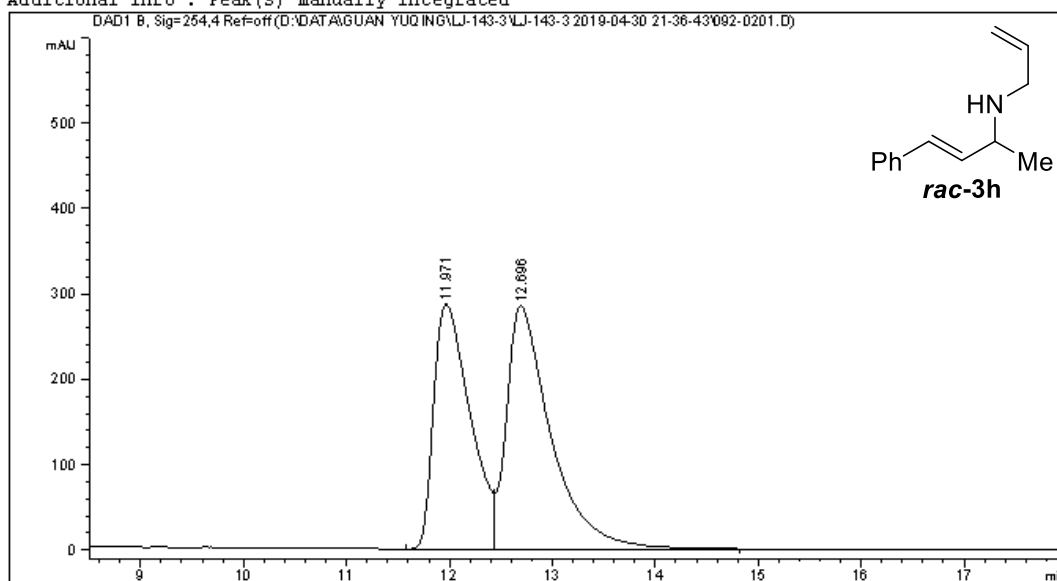
Instrument 2 4/16/2019 5:13:10 PM

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Figure S154. HPLC spectra of 3g, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-143-3\LJ-143-3 2019-04-30 21-36-43\092-0201.D  
Sample Name: LJ-143-3

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 2                  Location  : Vial 92
Injection Date  : 4/30/2019 9:48:50 PM         Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-143-3\LJ-143-3 2019-04-30 21-36-43\DAD-0J(1-6)-99-1-
0.5ML-SUL-ALL-60MIN.M
Last changed    : 4/30/2019 10:09:25 PM
                (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-143-3\LJ-143-3 2019-04-30 21-36-43\DAD-0J(1-6)-99-1-
0.5ML-SUL-ALL-60MIN.M (Sequence Method)
Last changed    : 5/15/2019 6:54:22 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.971	BV	0.3726	7039.42920	286.54825	45.4016
2	12.696	VB	0.4370	8465.38184	284.63971	54.5984

Totals :                    1.55048e4    571.18796

Instrument 2 5/15/2019 6:55:28 PM

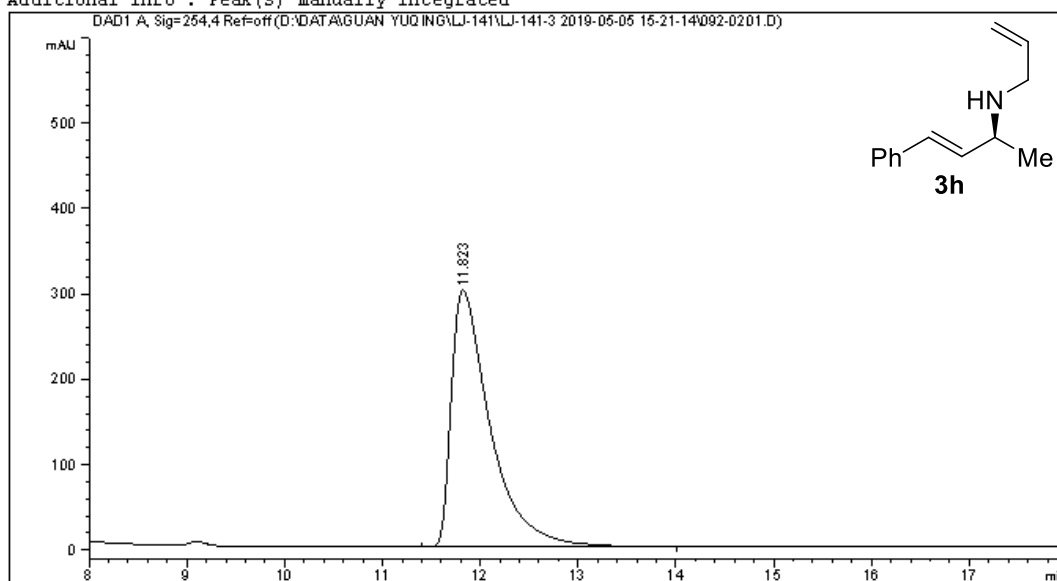
Page 1 of 2

Figure S155. HPLC spectra of *rac-3h*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-141\LJ-141-3 2019-05-05 15-21-14\092-0201.D  
Sample Name: LJ-141-3

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 2                   Location  : Vial 92
Injection Date  : 5/5/2019 3:33:20 PM           Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-141\LJ-141-3 2019-05-05 15-21-14\DAD-0J(1-6)-99-1-0.
                  SML-5UL-ALL-40MIN.M
Last changed    : 5/5/2019 3:47:20 PM
                  (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-141\LJ-141-3 2019-05-05 15-21-14\DAD-0J(1-6)-99-1-0.
                  SML-5UL-ALL-40MIN.M (Sequence Method)
Last changed    : 5/15/2019 6:58:10 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

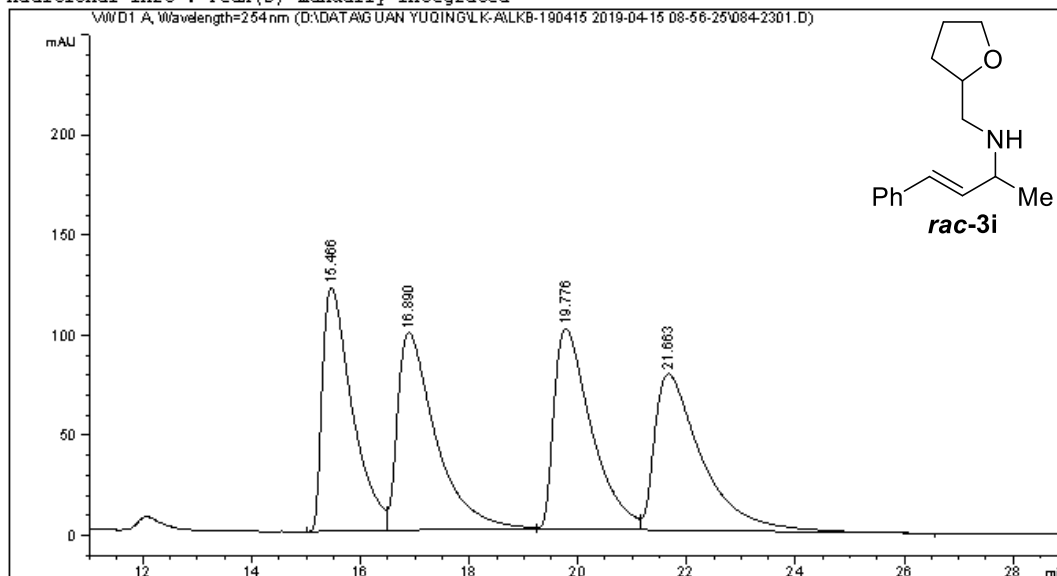
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.823	BB	0.4130	8336.08691	301.08655	100.0000

Totals : 8336.08691 301.08655

**Figure S156.** HPLC spectra of **3h**, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LK-A\LKB-190415 2019-04-15 08-56-25\084-2301.D  
Sample Name: LJ-137-4-RAC

```
=====
Acq. Operator   :                               Seq. Line :   23
Acq. Instrument : Instrument 1                   Location  : Vial 84
Injection Date  : 4/15/2019 8:20:08 PM         Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LK-A\LKB-190415 2019-04-15 08-56-25\WVD-AD(1-2)-99-1-0.
                                                6ML-5UL-254NM-40MIN.M
Last changed    : 3/5/2019 3:34:42 PM
Analysis Method : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\WVD-AD(1-6)-99-1-
                                                1ML-5UL-ALL-40MIN.M
Last changed    : 4/16/2019 5:15:44 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
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Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.466	BV	0.5692	4599.29883	121.60919	24.3744
2	16.890	VB	0.7248	4798.18164	98.42130	25.4284
3	19.776	BV	0.7116	4753.76123	100.00168	25.1929
4	21.663	VB	0.8876	4718.16992	77.89811	25.0043

Instrument 2 4/16/2019 5:15:54 PM

Page 1 of 2

Figure S157. HPLC spectra of *rac-3i*, related to Figure 3.

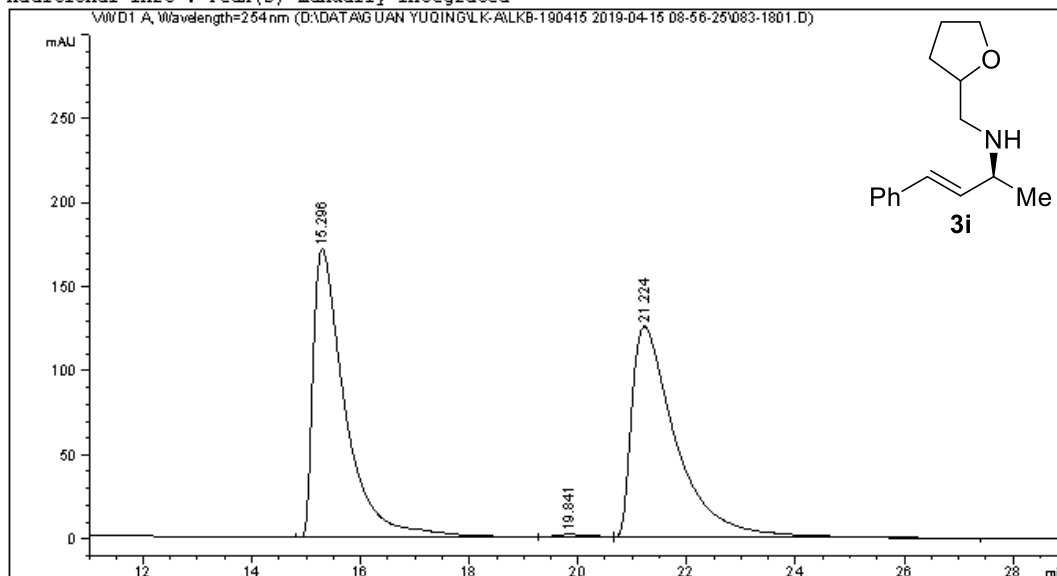


Data File D:\DATA\GUAN YUQING\LK-A\LKB-190415 2019-04-15 08-56-25\083-1801.D  
 Sample Name: LJ-137-4

```

=====
Acq. Operator   :                               Seq. Line :   18
Acq. Instrument : Instrument 1                   Location  : Vial 83
Injection Date  : 4/15/2019 6:25:42 PM         Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LK-A\LKB-190415 2019-04-15 08-56-25\WVD-AD(1-2)-99-1-0.
                  6ML-5UL-254NM-40MIN.M
Last changed    : 3/5/2019 3:34:42 PM
Analysis Method : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0J(1-6)-99-1-
                  1ML-5UL-ALL-40MIN.M
Last changed    : 4/16/2019 5:17:35 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



Area Percent Report

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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.296	BB	0.6059	7013.24561	171.57776	49.3191
2	19.841	BV	0.5918	75.46820	1.71367	0.5307
3	21.224	VB	0.8378	7131.41895	125.51943	50.1502

Totals : 1.42201e4 298.81086

Instrument 2 4/16/2019 5:19:31 PM

Page 1 of 2

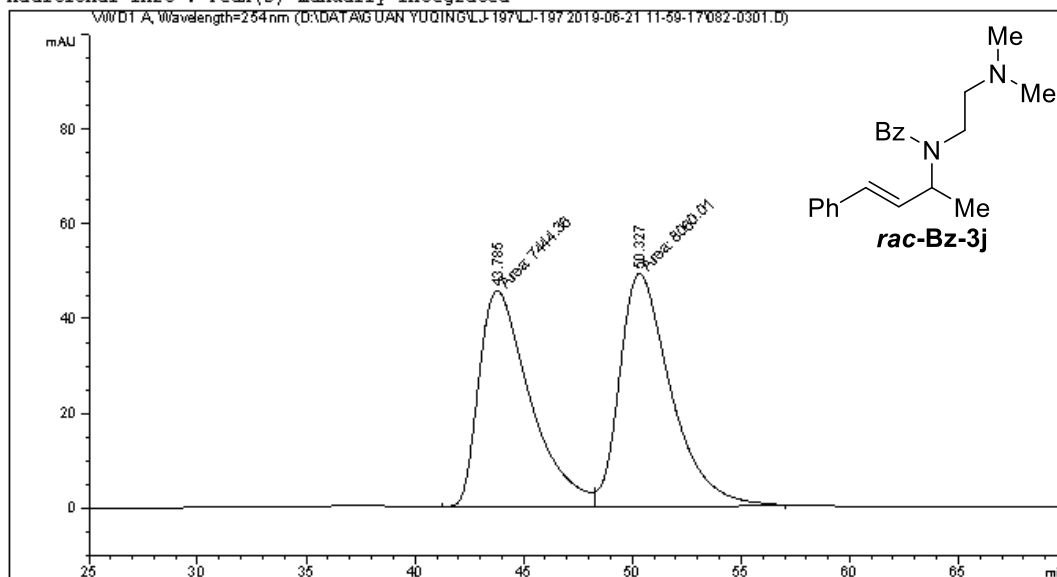
Figure S158. HPLC spectra of 3i, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-197\LJ-197 2019-06-21 11-59-17\082-0301.D  
 Sample Name: LJ-197-1

```

=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                  Location  : Vial 82
Injection Date  : 6/21/2019 1:33:44 PM        Inj       :    1
                                                Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-197\LJ-197 2019-06-21 11-59-17\VWD-AS(1-6)-90-10-0.
                  SML-5UL-254NM-80MIN.M
Last changed    : 6/21/2019 11:56:20 AM
Analysis Method : D:\METHOD\LG\VWD-AS(1-6)-85-15-1ML-2UL-210NM-30MIN.M
Last changed    : 6/26/2019 3:41:31 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.785	MF	2.7221	7444.35938	45.58009	48.0146
2	50.327	FM	2.7315	8060.00781	49.17983	51.9854

Totals :                      1.55044e4    94.75991

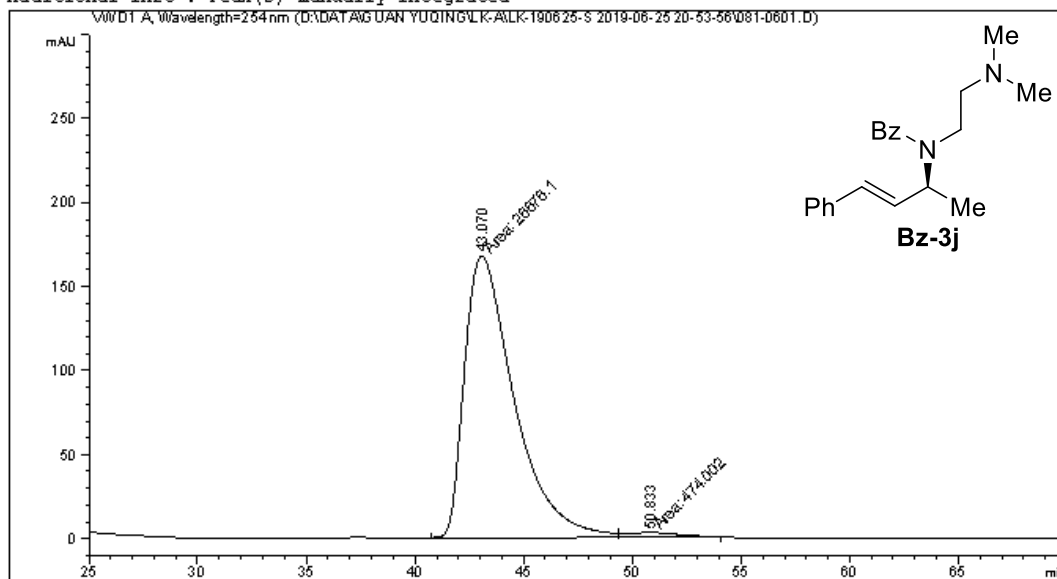
**Figure S159.** HPLC spectra of *rac-Bz-3j*, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LK-A\LK-190625-S 2019-06-25 20-53-56\081-0601.D  
 Sample Name: LJ-201-2

```

=====
Acq. Operator   :                               Seq. Line :    6
Acq. Instrument : Instrument 1                  Location  : Vial 81
Injection Date  : 6/26/2019 1:24:20 AM         Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LK-A\LK-190625-S 2019-06-25 20-53-56\VWD-AS(1-6)-90-10-
                  0.5ML-5UL-254NM-80MIN.M
Last changed    : 6/21/2019 11:56:20 AM
Analysis Method : D:\METHOD\LG\VWD-AS(1-6)-85-15-1ML-2UL-210NM-30MIN.M
Last changed    : 6/26/2019 3:39:40 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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 Area Percent Report  
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```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=254 nm

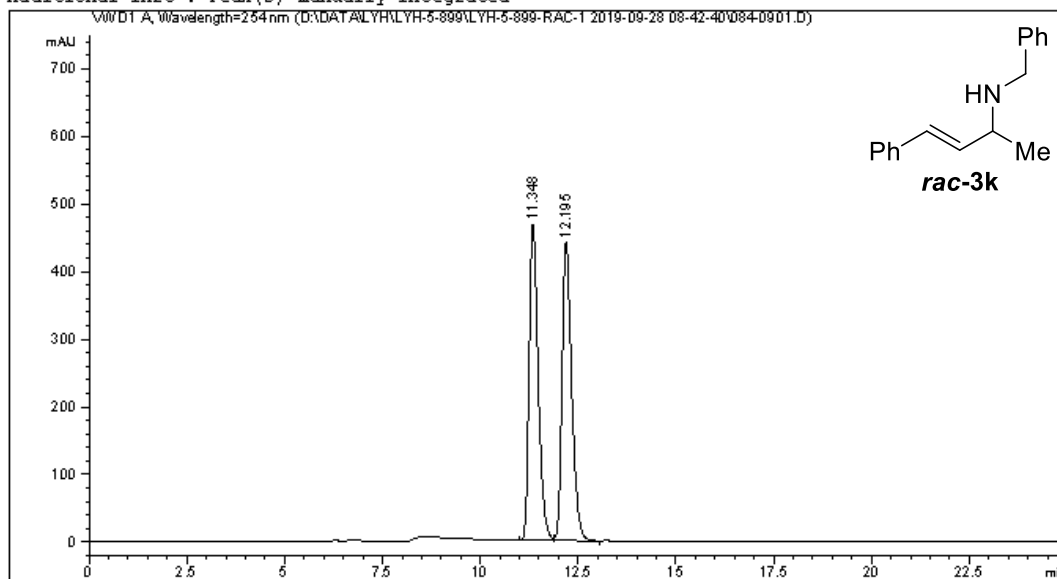
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.070	MF	2.6495	2.66761e4	167.80351	98.2541
2	50.833	FM	2.8864	474.00171	2.73700	1.7459

Totals :                            2.71501e4    170.54051

Figure S160. HPLC spectra of Bz-3j, related to Figure 3.

Data File D:\DATA\LYH\LYH-5-899\LYH-5-899-RAC-1 2019-09-28 08-42-40\084-0901.D  
Sample Name: LJ-2-48-RAC

```
=====
Acq. Operator   :                               Seq. Line :    9
Acq. Instrument : Instrument 1                   Location  : Vial 84
Injection Date  : 9/28/2019 12:30:11 PM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LYH\LYH-5-899\LYH-5-899-RAC-1 2019-09-28 08-42-40\VWD-AD(1-2)-95-5-
                  0.5ML-5UL-254NM-30MIN.M
Last changed    : 4/9/2019 4:22:03 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AD(1-2)-99-1-0.5ML-5UL-254NM-25MIN.M
Last changed    : 9/28/2019 10:40:08 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.348	BV	0.2453	7554.13770	468.01944	49.9302
2	12.195	VB	0.2624	7575.27100	441.02200	50.0698

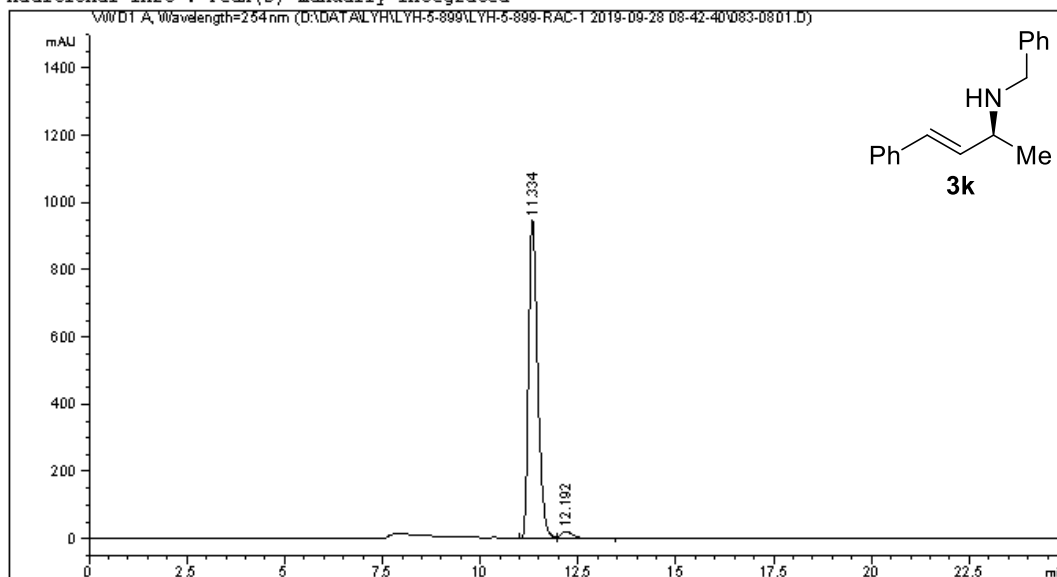
Totals :                                    1.51294e4    909.04144

Figure S161. HPLC spectra of *rac-3k*, related to Figure 3.

Data File D:\DATA\LYH\LYH-5-899\LYH-5-899-RAC-1 2019-09-28 08-42-40\083-0801.D  
Sample Name: LJ-2-48

```
=====
Acq. Operator   :                               Seq. Line :    8
Acq. Instrument : Instrument 1                   Location  : Vial 83
Injection Date  : 9/28/2019 11:59:20 AM         Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\LYH\LYH-5-899\LYH-5-899-RAC-1 2019-09-28 08-42-40\VWD-AD(1-2)-95-5-
                  0.5ML-5UL-254NM-30MIN.M
Last changed    : 4/9/2019 4:22:03 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AD(1-2)-99-1-0.5ML-5UL-254NM-25MIN.M
Last changed    : 9/28/2019 10:43:16 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.334	BV	0.2461	1.52293e4	944.59326	97.5071
2	12.192	VB	0.2853	389.35504	20.52347	2.4929

Totals :                           1.56187e4   965.11673

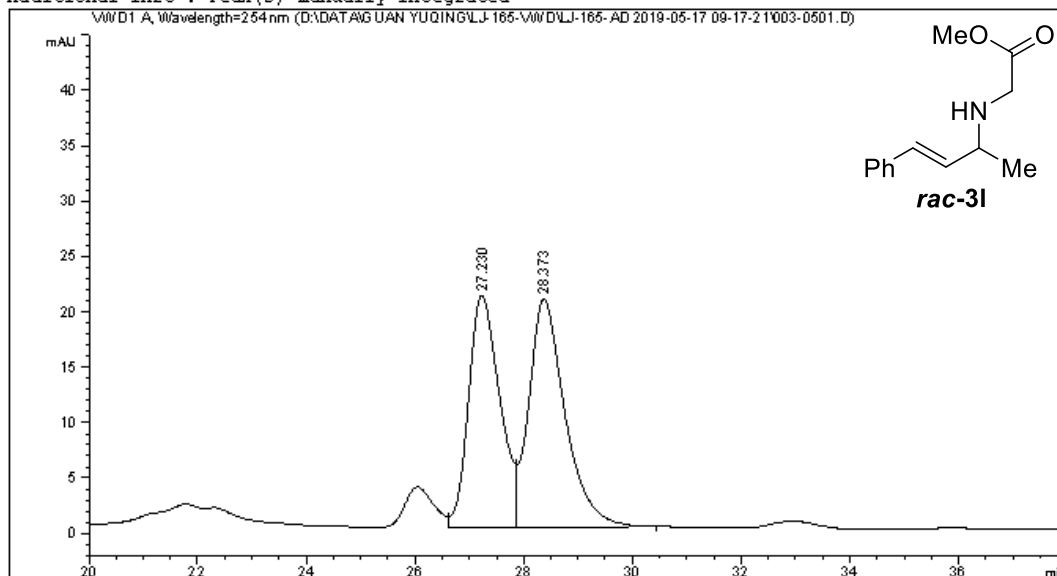
**Figure S162.** HPLC spectra of **3k**, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LJ-165-VWD\LJ-165-AD 2019-05-17 09-17-21\003-0501.D  
 Sample Name: LJ-165-RAC

```

=====
Acq. Operator   :                               Seq. Line :    5
Acq. Instrument : Instrument 1                   Location  : Vial 3
Injection Date  : 5/17/2019 11:13:20 AM         Inj       :    1
                                                    Inj Volume: 8.000 µl
Acq. Method    : D:\DATA\GUAN YUQING\LJ-165-VWD\LJ-165-AD 2019-05-17 09-17-21\VWD-AD(1-2)-99
                : -1-0.5ML-5UL-254NM-60MIN.M
Last changed   : 5/17/2019 9:43:47 AM
                : (modified after loading)
Analysis Method: D:\METHOD\LWD\DAD-OD(1-2)-95-5-0.5ML-3UL-ALL-60MIN-517.M
Last changed   : 5/18/2019 9:15:28 AM
                : (modified after loading)
  
```

Additional Info : Peak(s) manually integrated



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 Area Percent Report  
 =====

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WWD1 A, Wavelength=254 nm

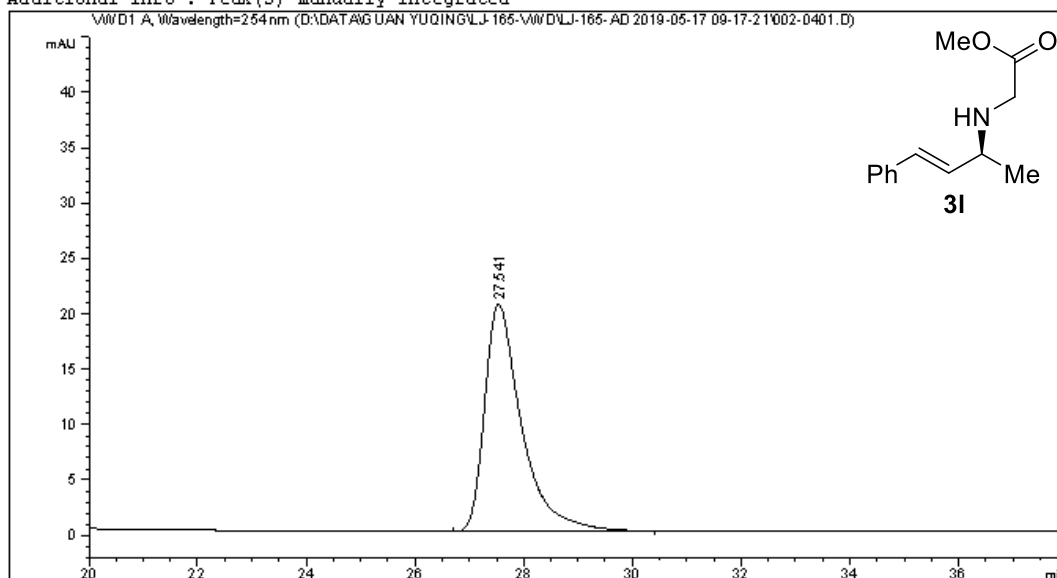
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.230	VV	0.5995	832.64209	20.91406	46.7610
2	28.373	VB	0.6807	947.98993	20.56817	53.2390

Totals :                    1780.63202    41.48223

Figure S163. HPLC spectra of *rac-3I*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-165-VWD\LJ-165-AD 2019-05-17 09-17-21\002-0401.D  
Sample Name: LJ-165-2

```
=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 1                  Location  : Vial 2
Injection Date  : 5/17/2019 10:27:26 AM        Inj       :    1
                                                Inj Volume: 8.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-165-VWD\LJ-165-AD 2019-05-17 09-17-21\VWD-AD(1-2)-99
                  -1-0.5ML-5UL-254NM-60MIN.M
Last changed    : 5/17/2019 9:43:47 AM
                  (modified after loading)
Analysis Method : D:\METHOD\LWD\DAD-OD(1-2)-95-5-0.5ML-3UL-ALL-60MIN-517.M
Last changed    : 5/18/2019 9:15:28 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WWD1 A, Wavelength=254 nm

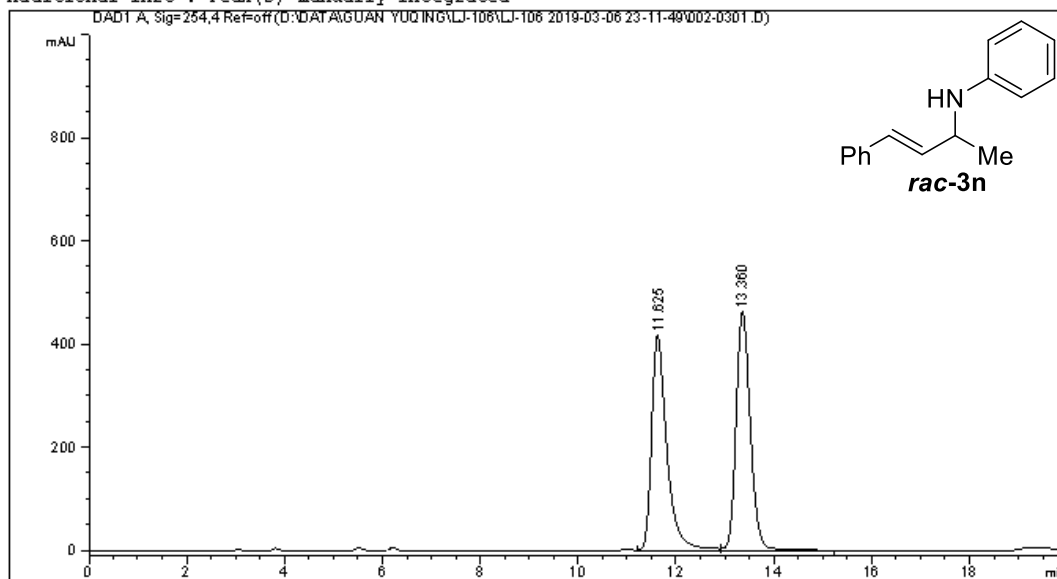
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.541	BB	0.6917	967.04639	20.52325	100.0000

Totals : 967.04639 20.52325

Figure S164. HPLC spectra of 3I, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-106\LJ-106 2019-03-06 23-11-49\002-0301.D  
Sample Name: LJ-103-1-RAC

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 2                   Location  : Vial 2
Injection Date  : 3/6/2019 11:49:55 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-106\LJ-106 2019-03-06 23-11-49\DAD-OD(1-2)-95-5-1ML-
                  SUL-ALL-20MIN.M
Last changed    : 3/5/2019 8:56:43 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-IA(1-6)-95-5-0.SML-SUL-ALL-40MIN.M
Last changed    : 3/19/2019 9:55:54 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.625	VV	0.3233	9037.16797	416.16431	49.3755
2	13.360	VB	0.3097	9265.78516	462.59473	50.6245

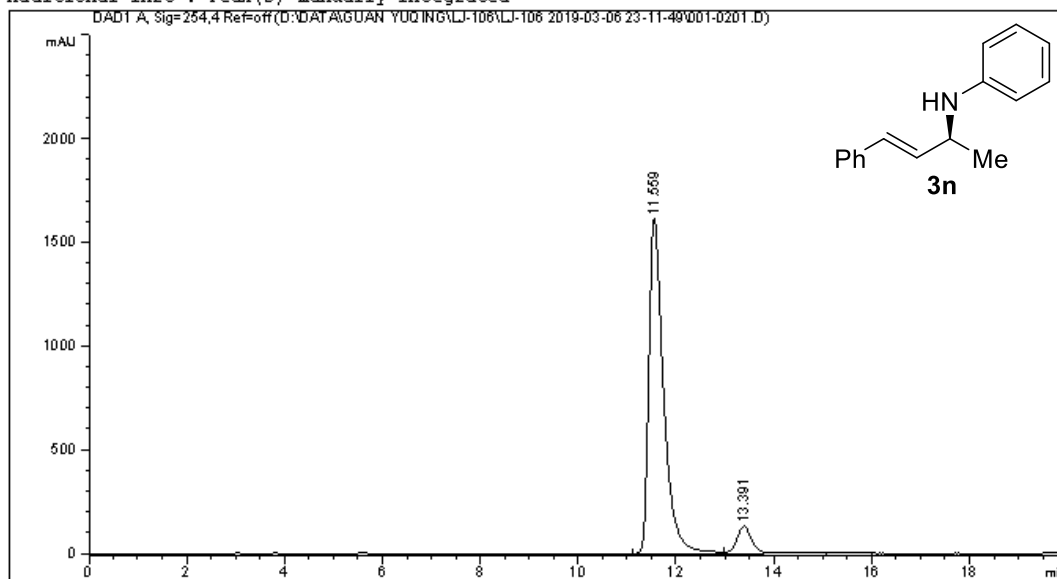
Totals : 1.83030e4 878.75903

Figure S165. HPLC spectra of *rac-3n*, related to Figure 3.



Data File D:\DATA\GUAN YUQING\LJ-106\LJ-106 2019-03-06 23-11-49\001-0201.D  
Sample Name: LJ-103-1

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 2                   Location  : Vial 1
Injection Date  : 3/6/2019 11:28:57 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-106\LJ-106 2019-03-06 23-11-49\DAD-OD(1-2)-95-5-1ML-
                  SUL-ALL-20MIN.M
Last changed    : 3/5/2019 8:56:43 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-IA(1-6)-95-5-0.SML-SUL-ALL-40MIN.M
Last changed    : 3/19/2019 9:58:51 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

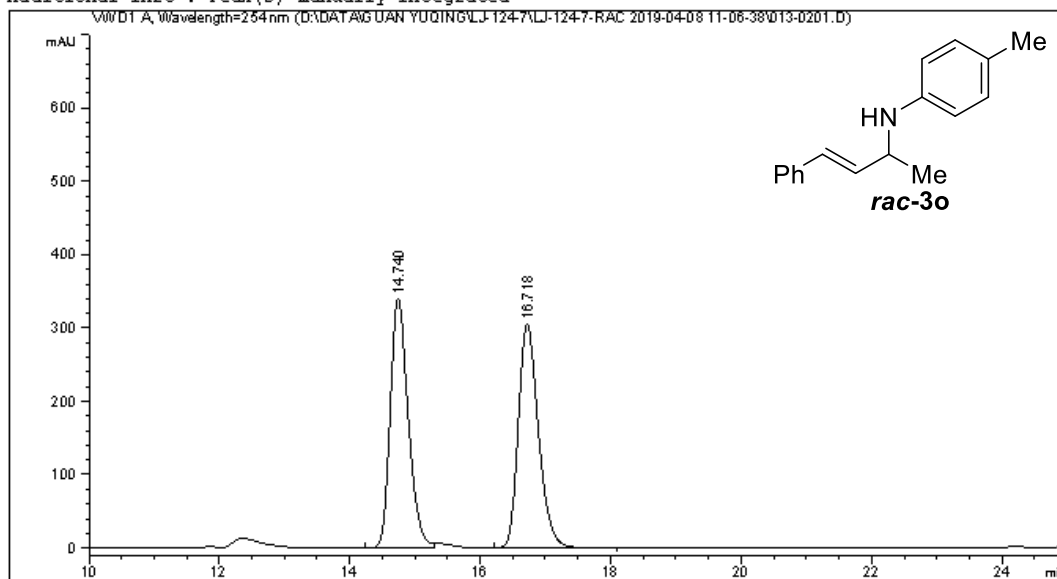
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.559	BV	0.3120	3.36730e4	1609.93042	92.6141
2	13.391	VB	0.3181	2685.40967	129.39296	7.3859

Totals :                           3.63584e4 1739.32338

**Figure S166.** HPLC spectra of **3n**, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LJ-124-7\LJ-124-7-RAC 2019-04-08 11-06-38\013-0201.D  
Sample Name: LJ-124-7-RAC

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 1                   Location  : Vial 13
Injection Date  : 4/8/2019 11:20:11 AM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-124-7\LJ-124-7-RAC 2019-04-08 11-06-38\VWD-AD (1-2)-
                  95-5-0.5ML-SUL-254NM-60MIN.M
Last changed    : 3/11/2019 10:31:45 PM
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-SUL-ALL-60MIN.M
Last changed    : 4/14/2019 9:50:19 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

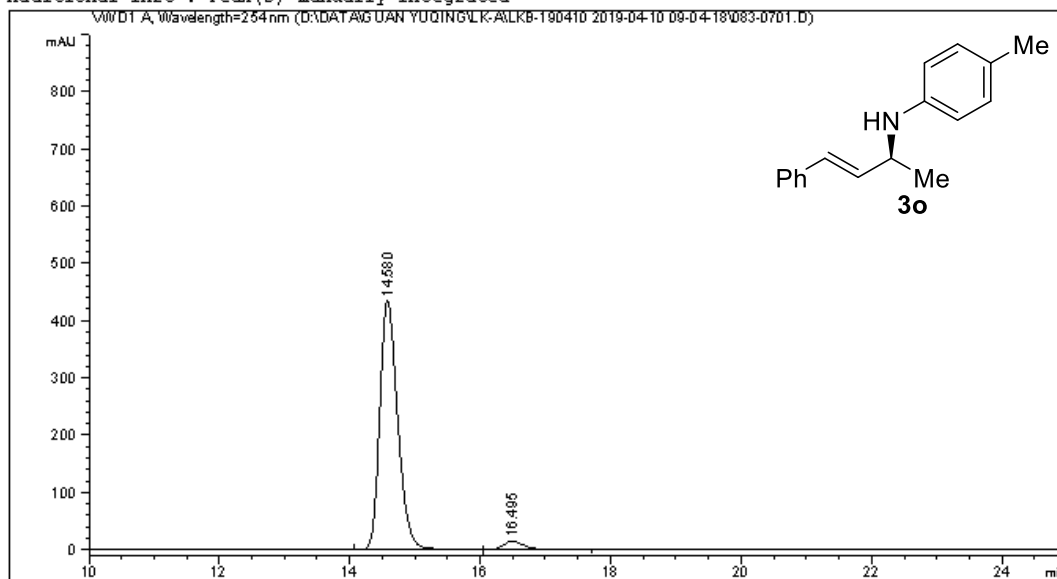
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.740	BV	0.2928	6485.12012	339.57712	50.0335
2	16.718	BB	0.3248	6476.43945	304.93433	49.9665

Totals :                                   1.29616e4   644.51144

Figure S167. HPLC spectra of *rac-3o*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LK-A\LKB-190410 2019-04-10 09-04-18\083-0701.D  
Sample Name: LJ-124-7

```
=====
Acq. Operator   :                               Seq. Line :    7
Acq. Instrument : Instrument 1                  Location  : Vial 83
Injection Date  : 4/10/2019 11:42:55 AM        Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LK-A\LKB-190410 2019-04-10 09-04-18\WVD-AD(1-2)-95-5-0.
                                           SML-SUL-254NM-30MIN.M
Last changed    : 4/9/2019 4:22:03 PM
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-SUL-ALL-60MIN.M
Last changed    : 4/14/2019 9:48:13 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

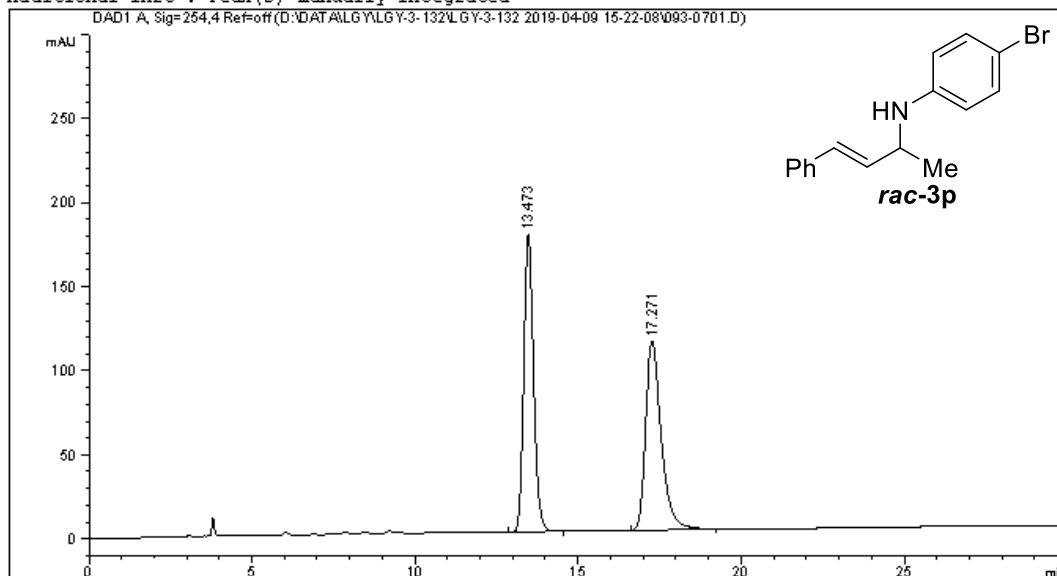
Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.580	BB	0.2905	8222.70313	435.13837	96.3629
2	16.495	BB	0.3246	310.35309	14.56537	3.6371

Totals :                                   8533.05621   449.70374

Figure S168. HPLC spectra of 3o, related to Figure 3.

```
=====
Acq. Operator   :                               Seq. Line :    7
Acq. Instrument : Instrument 2                   Location  : Vial 93
Injection Date  : 4/9/2019 6:24:24 PM           Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LG\GY-3-132\GY-3-132 2019-04-09 15-22-08\DAD-0D(1-2)-95-5-1ML-
                : SUL-ALL-60MIN.M
Last changed    : 4/9/2019 6:21:57 PM
                : (modified after loading)
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-5UL-ALL-60MIN.M
Last changed    : 4/14/2019 9:53:27 PM
                : (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

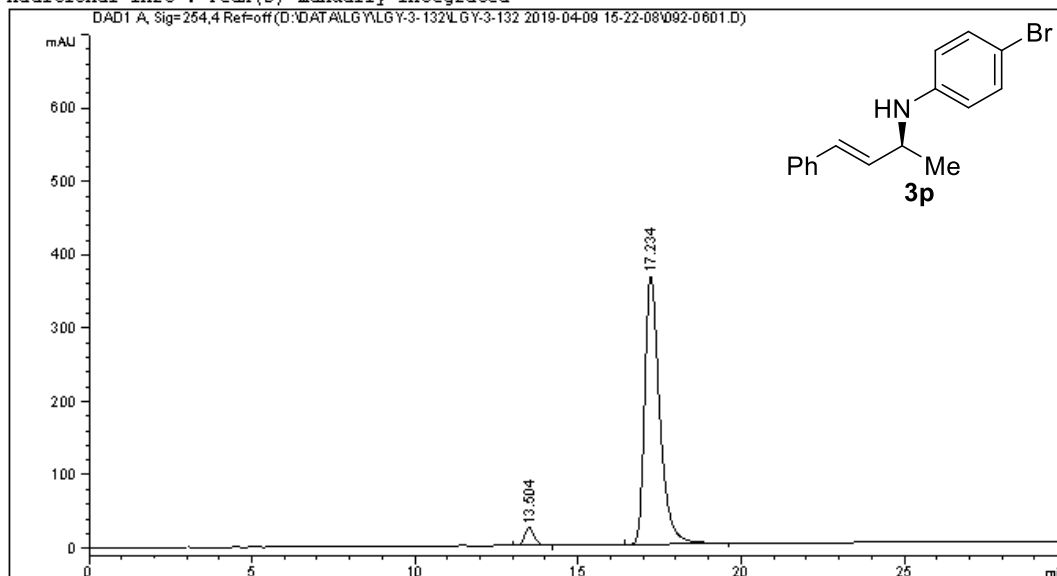
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.473	BB	0.3213	3693.51050	177.09816	49.7634
2	17.271	BB	0.4958	3728.63354	112.74161	50.2366

Totals : 7422.14404 289.83977

Figure S169. HPLC spectra of *rac-3p*, related to Figure 3.

Data File D:\DATA\LG\GY-3-132\GY-3-132 2019-04-09 15-22-08\092-0601.D  
Sample Name: LJ-129-10

```
=====
Acq. Operator   :                               Seq. Line :    6
Acq. Instrument : Instrument 2                  Location  : Vial 92
Injection Date  : 4/9/2019 5:43:24 PM          Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LG\GY-3-132\GY-3-132 2019-04-09 15-22-08\DAD-0D(1-2)-95-5-1ML-
SUL-ALL-60MIN.M
Last changed    : 4/9/2019 6:21:57 PM
                (modified after loading)
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-5UL-ALL-60MIN.M
Last changed    : 4/14/2019 9:54:40 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

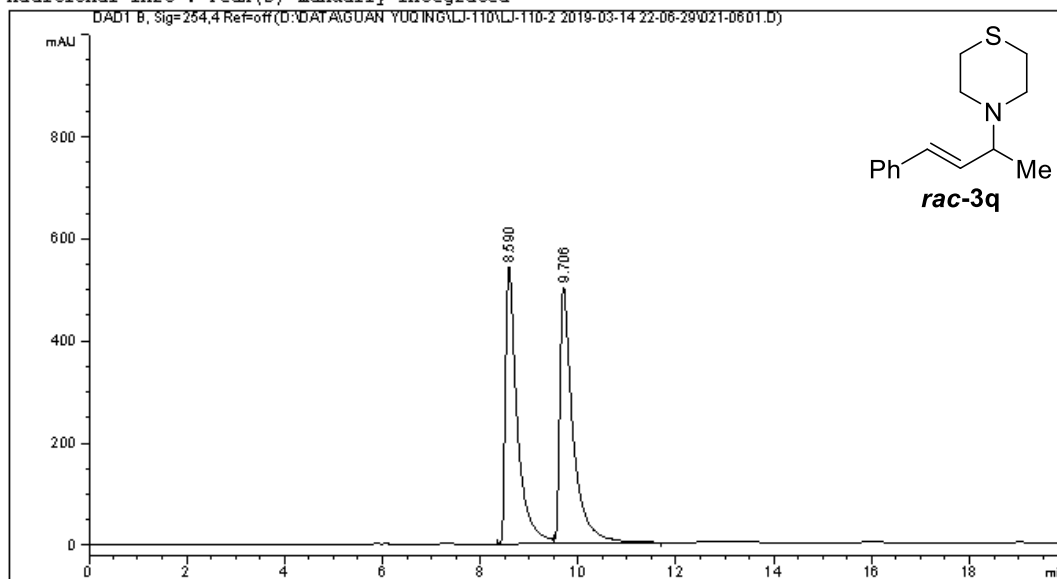
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.504	BB	0.3190	496.94272	23.86341	4.0801
2	17.234	BB	0.4827	1.16826e4	365.71744	95.9199

Totals : 1.21796e4 389.58085

Figure S170. HPLC spectra of 3p, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-110\LJ-110-2 2019-03-14 22-06-29\021-0601.D  
Sample Name: LJ-109-5

```
=====
Acq. Operator   :                               Seq. Line :    6
Acq. Instrument : Instrument 2                   Location  : Vial 21
Injection Date  : 3/14/2019 11:32:48 PM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-110\LJ-110-2 2019-03-14 22-06-29\DAD-OD(1-2)-90-10-0
                  .SML-SUL-ALL-30MIN.M
Last changed    : 10/30/2018 11:03:07 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-IA(1-6)-95-5-0.SML-SUL-ALL-40MIN.M
Last changed    : 3/19/2019 10:31:02 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.590	BV	0.2446	9138.08984	542.15143	49.1392
2	9.706	VB	0.2699	9458.22656	501.71347	50.8608

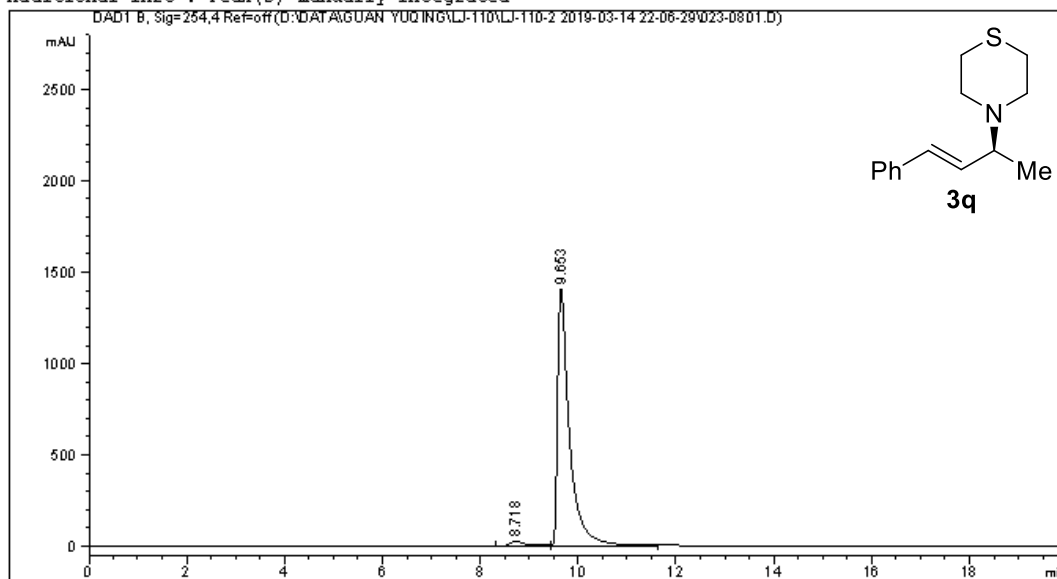
Totals :                                    1.85963e4  1043.86490

Figure S171. HPLC spectra of *rac-3q*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-110\LJ-110-2 2019-03-14 22-06-29\023-0801.D  
Sample Name: LJ-110-5

```
=====
Acq. Operator   :                               Seq. Line :    8
Acq. Instrument : Instrument 2                   Location  : Vial 23
Injection Date  : 3/15/2019 12:34:45 AM         Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-110\LJ-110-2 2019-03-14 22-06-29\DAD-OD(1-2)-90-10-0
                  .SML-SUL-ALL-30MIN.M
Last changed    : 10/30/2018 11:03:07 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-IA(1-6)-95-5-0.SML-SUL-ALL-40MIN.M
Last changed    : 3/19/2019 10:29:50 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.718	BV	0.3143	527.30475	24.37941	2.1601
2	9.653	VB	0.2483	2.38843e4	1404.88000	97.8399

Totals :                                   2.44116e4 1429.25941

Figure S172. HPLC spectra of 3q, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-105-11-OD\LJ-106-6 2019-03-08 19-55-22\001-0201.D  
 Sample Name: LJ-106-6-RAC

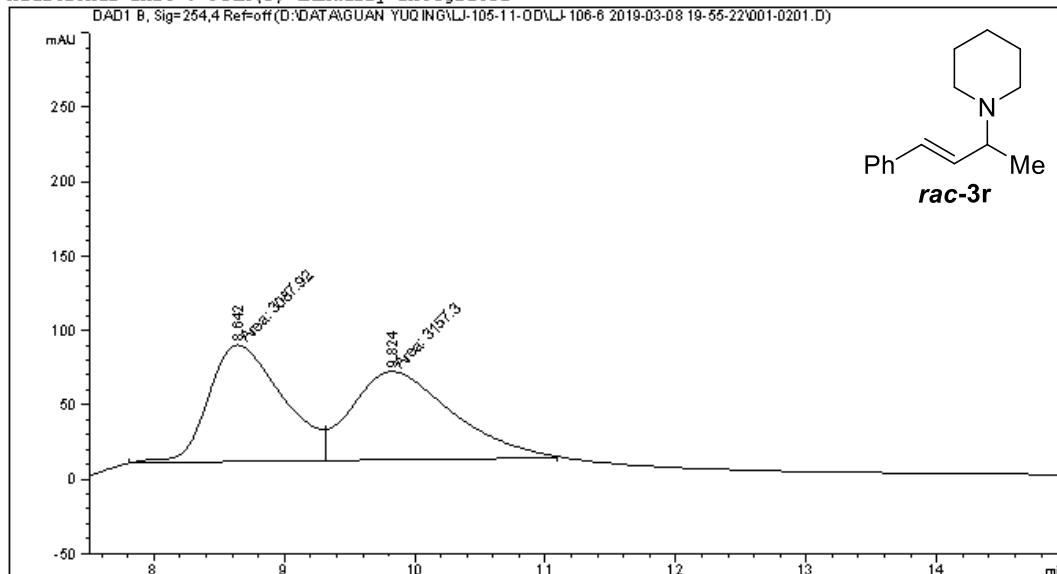
```

=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 2                 Location  : Vial 1
Injection Date  : 3/8/2019 8:07:24 PM        Inj       :    1
                                           Inj Volume: 2.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-105-11-OD\LJ-106-6 2019-03-08 19-55-22\DAD-OD (1-2)-
99-1-0.5ML-2UL-ALL-40MIN.M
Last changed    : 3/8/2019 8:20:08 PM
                 (modified after loading)

Analysis Method : D:\METHOD\YANG JIAXIN\DAD-0J(1-6)-90-10-1ML-3UL-ALL-40MIN.M
Last changed    : 3/8/2019 9:25:14 PM
                 (modified after loading)

Additional Info : Peak(s) manually integrated
  
```



Area Percent Report

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 E, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.642	MF	0.6583	3087.92310	78.17834	49.4446
2	9.824	FM	0.8897	3157.29639	59.14474	50.5554

Totals : 6245.21948 137.32309

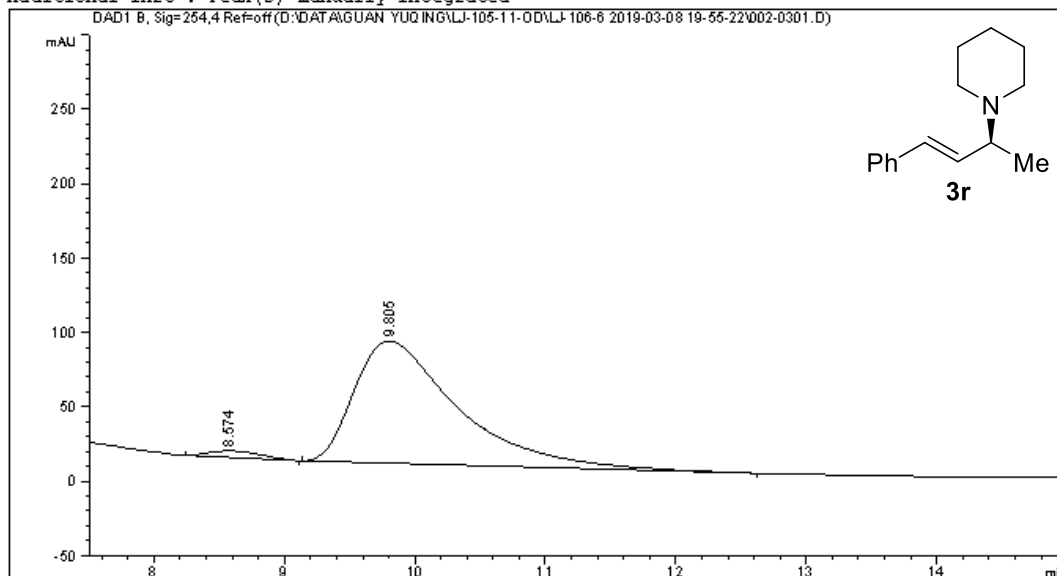
Figure S173. HPLC spectra of rac-3r, related to Figure 3.



Data File D:\DATA\GUAN YUQING\LJ-105-11-OD\LJ-106-6 2019-03-08 19-55-22\002-0301.D  
Sample Name: LJ-106-6

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 2                   Location  : Vial 2
Injection Date  : 3/8/2019 8:28:20 PM           Inj       :    1
                                                    Inj Volume: 2.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-105-11-OD\LJ-106-6 2019-03-08 19-55-22\DAD-OD (1-2)-
                  99-1-0.5ML-2UL-ALL-40MIN.M
Last changed    : 3/8/2019 8:20:08 PM
                  (modified after loading)
Analysis Method : D:\METHOD\YANG JIAXIN\DAD-0J(1-6)-90-10-1ML-3UL-ALL-40MIN.M
Last changed    : 3/8/2019 9:25:14 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
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```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.574	BB	0.3580	118.74886	4.30188	2.5651
2	9.805	BB	0.7912	4510.67627	82.06714	97.4349

Totals :                    4629.42513    86.36902

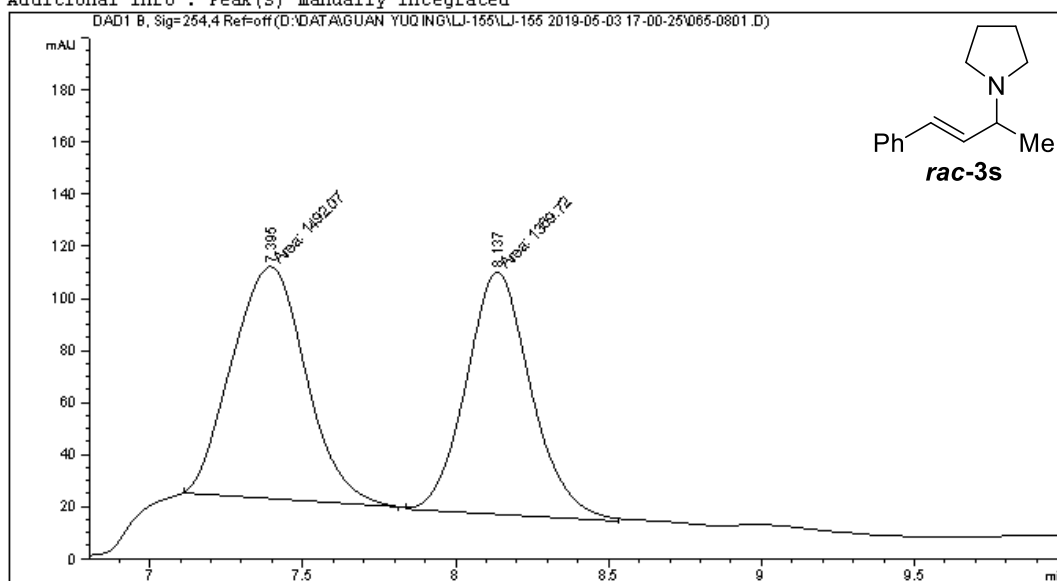
Instrument 2 3/8/2019 9:26:43 PM

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**Figure S174.** HPLC spectra of **3r**, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LJ-155\LJ-155 2019-05-03 17-00-25\065-0801.D  
Sample Name: LJ-108-4-RAC

```
=====
Acq. Operator   :                               Seq. Line :    8
Acq. Instrument : Instrument 2                   Location  : Vial 65
Injection Date  : 5/3/2019 9:52:17 PM           Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-155\LJ-155 2019-05-03 17-00-25\DAD-OD(1-2)-95-5-0.
                  SML-5UL-ALL-40MIN.M
Last changed    : 5/3/2019 10:02:26 PM
                  (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-155\LJ-155 2019-05-03 17-00-25\DAD-OD(1-2)-95-5-0.
                  SML-5UL-ALL-40MIN.M (Sequence Method)
Last changed    : 5/4/2019 9:40:19 AM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.395	MM	0.2795	1492.07043	88.97803	52.1377
2	8.137	MM	0.2450	1369.72009	93.17516	47.8623

Totals : 2861.79053 182.15319

Instrument 2 5/4/2019 9:40:34 AM

Page 1 of 2

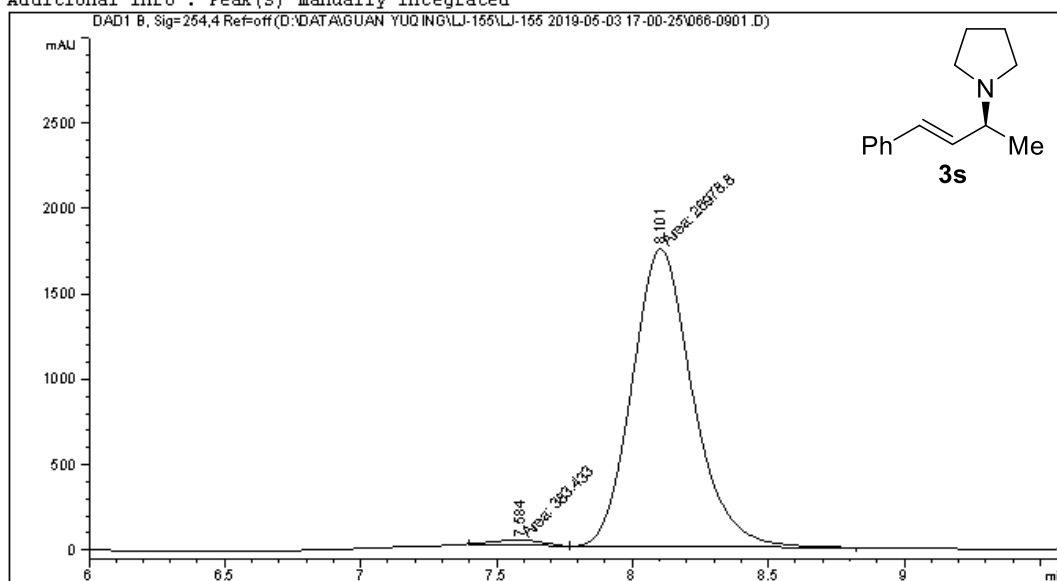
Figure S175. HPLC spectra of *rac-3s*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-155\LJ-155 2019-05-03 17-00-25\066-0901.D  
 Sample Name: LJ-108-4

```

=====
Acq. Operator   :                               Seq. Line :    9
Acq. Instrument : Instrument 2                 Location  : Vial 66
Injection Date  : 5/3/2019 10:13:18 PM        Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-155\LJ-155 2019-05-03 17-00-25\DAD-OD(1-2)-95-5-0.
                  SML-5UL-ALL-40MIN.M
Last changed    : 5/3/2019 10:02:26 PM
                  (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-155\LJ-155 2019-05-03 17-00-25\DAD-OD(1-2)-95-5-0.
                  SML-5UL-ALL-40MIN.M (Sequence Method)
Last changed    : 5/4/2019 9:54:17 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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 Area Percent Report  
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```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=254,4 Ref=off

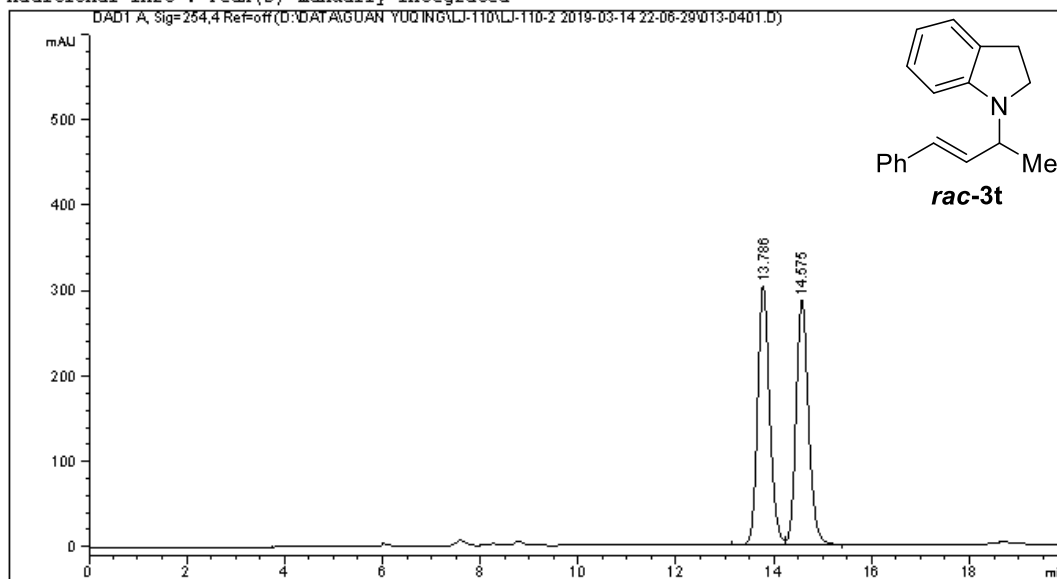
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.584	MF	0.2171	383.43253	29.43110	1.4013
2	8.101	FM	0.2581	2.69788e4	1742.11572	98.5987

Totals :                    2.73622e4  1771.54683

**Figure S176.** HPLC spectra of **3s**, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LJ-110\LJ-110-2 2019-03-14 22-06-29\013-0401.D  
Sample Name: LJ-110-2-RAC

```
=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 2                   Location  : Vial 13
Injection Date  : 3/14/2019 11:00:40 PM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-110\LJ-110-2 2019-03-14 22-06-29\DAD-OD(1-2)-95-5-0.
                  SML-5UL-ALL-20MIN.M
Last changed    : 3/4/2019 3:12:24 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-IA(1-6)-95-5-0.SML-5UL-ALL-40MIN.M
Last changed    : 3/19/2019 10:24:44 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

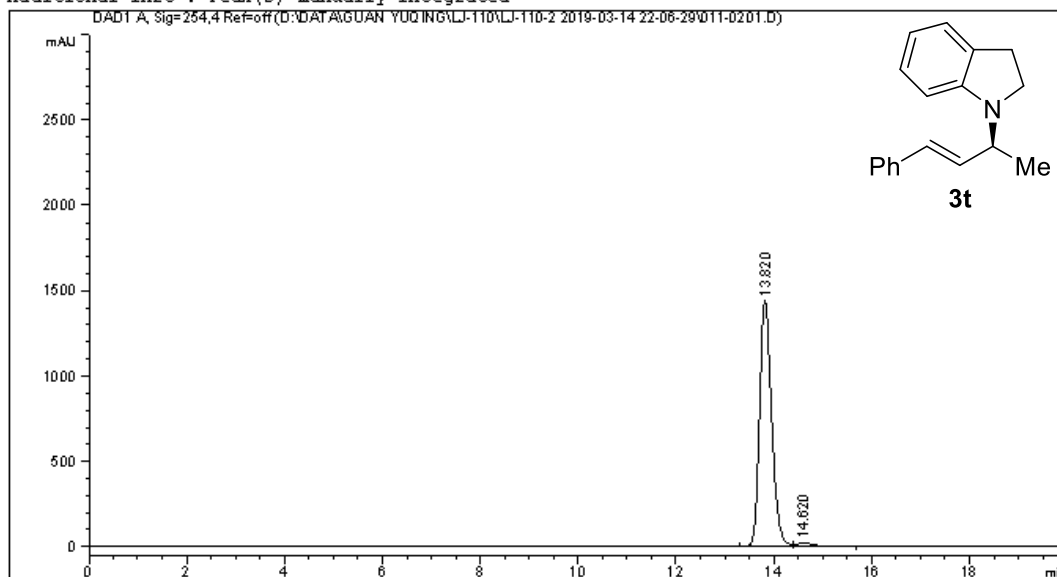
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.786	BV	0.2600	5142.11768	303.06146	50.4431
2	14.575	VB	0.2721	5051.77002	285.98007	49.5569

Totals :                                    1.01939e4    589.04153

Figure S177. HPLC spectra of *rac-3t*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-110\LJ-110-2 2019-03-14 22-06-29\011-0201.D  
Sample Name: LJ-110-2

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 2                  Location  : Vial 11
Injection Date  : 3/14/2019 10:18:39 PM       Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-110\LJ-110-2 2019-03-14 22-06-29\DAD-OD(1-2)-95-5-0.
                                                SML-5UL-ALL-20MIN.M
Last changed    : 3/4/2019 3:12:24 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-IA(1-6)-95-5-0.SML-5UL-ALL-40MIN.M
Last changed    : 3/19/2019 10:26:50 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

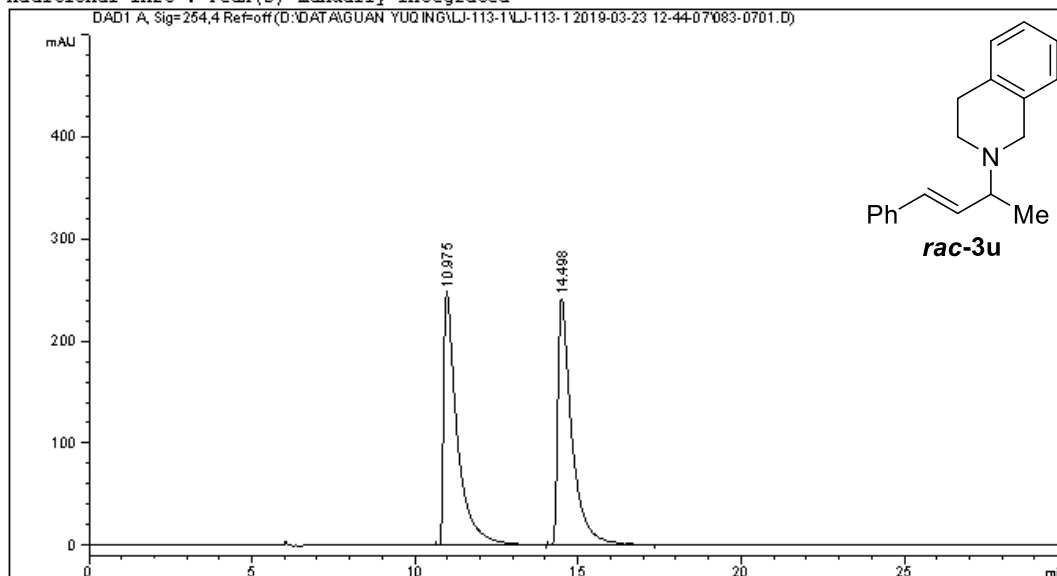
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.820	BV	0.2600	2.43711e4	1436.18689	98.4123
2	14.620	VB	0.2869	393.19205	20.21956	1.5877

Totals :                                    2.47643e4  1456.40645

Figure S178. HPLC spectra of 3t, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-113-1\LJ-113-1 2019-03-23 12-44-07\083-0701.D  
Sample Name: LJ-113-2-RAC

```
=====
Acq. Operator   :                               Seq. Line :    7
Acq. Instrument : Instrument 2                   Location  : Vial 83
Injection Date  : 3/23/2019 2:54:08 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-113-1\LJ-113-1 2019-03-23 12-44-07\DAD-OD(1-2)-95-5-
                  0.5ML-SUL-ALL-60MIN.M
Last changed    : 3/23/2019 3:10:35 PM
                  (modified after loading)
Analysis Method : D:\METHOD\XZC\DAD-OD(1-2)-95-5-1ML-SUL-ALL-50MIN.M
Last changed    : 3/23/2019 4:04:01 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.975	BB	0.4104	7225.67285	249.14714	50.1755
2	14.498	BB	0.4295	7175.11523	240.88791	49.8245

Totals : 1.44008e4 490.03505

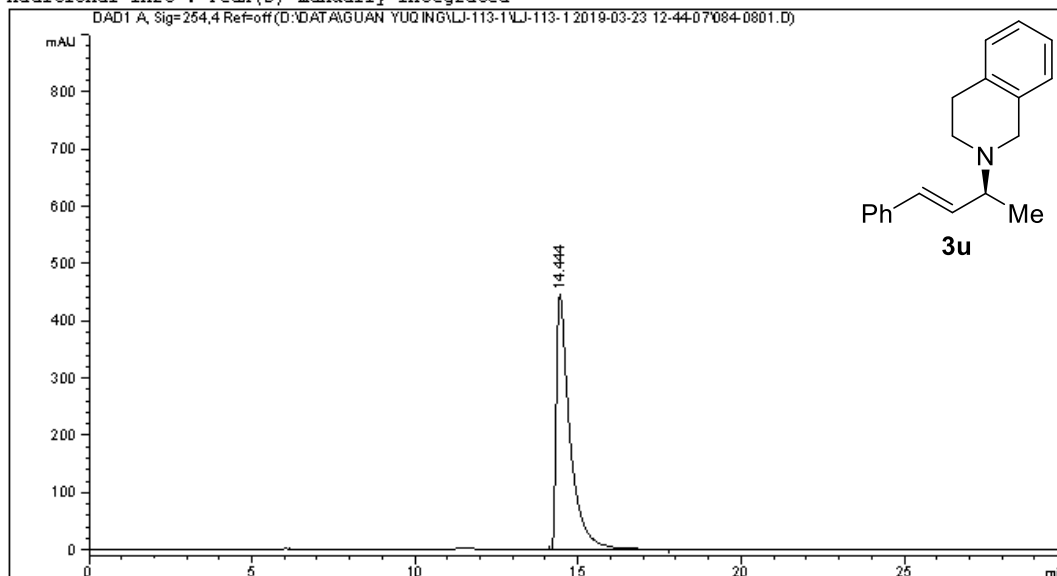
Instrument 2 3/23/2019 4:04:14 PM

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Figure S179. HPLC spectra of *rac-3u*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-113-1\LJ-113-1 2019-03-23 12-44-07\084-0801.D  
Sample Name: LJ-113-2

```
=====
Acq. Operator   :                               Seq. Line :    8
Acq. Instrument : Instrument 2                   Location  : Vial 84
Injection Date  : 3/23/2019 3:25:10 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-113-1\LJ-113-1 2019-03-23 12-44-07\DAD-OD(1-2)-95-5-
                  0.5ML-SUL-ALL-60MIN.M
Last changed    : 3/23/2019 3:10:35 PM
                  (modified after loading)
Analysis Method : D:\METHOD\XZC\DAD-OD(1-2)-95-5-1ML-SUL-ALL-50MIN.M
Last changed    : 3/23/2019 4:06:28 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

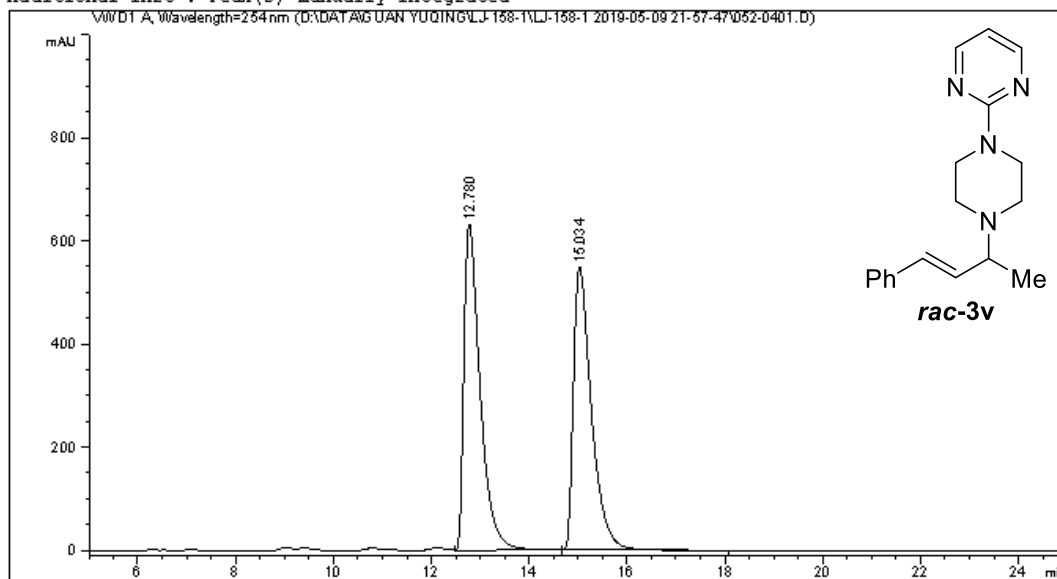
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.444	BB	0.4151	1.30190e4	447.92014	100.0000

Totals : 1.30190e4 447.92014

**Figure S180.** HPLC spectra of *rac*-3u, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LJ-158-1\LJ-158-1 2019-05-09 21-57-47\052-0401.D  
Sample Name: LJ-158-1-RAC

```
=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 1                   Location  : Vial 52
Injection Date  : 5/9/2019 11:02:38 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-158-1\LJ-158-1 2019-05-09 21-57-47\VWD-AD(1-2)-95-5-
                  0.5ML-5UL-254NM-30MIN.M
Last changed    : 4/9/2019 4:22:03 PM
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-100-0-0.2ML-1UL-220NM-100MIN.M
Last changed    : 5/10/2019 2:56:18 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.780	VB	0.3437	1.44385e4	631.57111	50.8506
2	15.034	BB	0.3822	1.39554e4	547.74023	49.1494

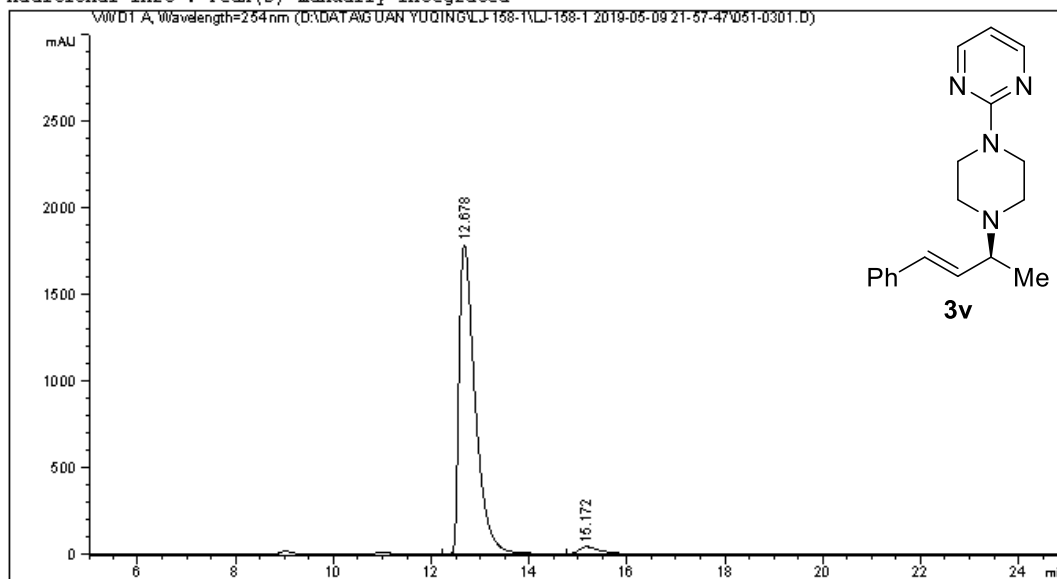
Totals :                                    2.83939e4 1179.31134

Figure S181. HPLC spectra of *rac-3v*, related to Figure 3.



Data File D:\DATA\GUAN YUQING\LJ-158-1\LJ-158-1 2019-05-09 21-57-47\051-0301.D  
Sample Name: LJ-158-1

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                  Location  : Vial 51
Injection Date  : 5/9/2019 10:31:48 PM         Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-158-1\LJ-158-1 2019-05-09 21-57-47\VWD-AD(1-2)-95-5-
                  0.5ML-SUL-254NM-30MIN.M
Last changed    : 4/9/2019 4:22:03 PM
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-100-0-0.2ML-1UL-220NM-100MIN.M
Last changed    : 5/10/2019 2:57:58 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.678	BV	0.3434	4.06017e4	1785.04187	97.2820
2	15.172	VB	0.4279	1134.37378	39.75301	2.7180

Totals :                                   4.17361e4 1824.79488

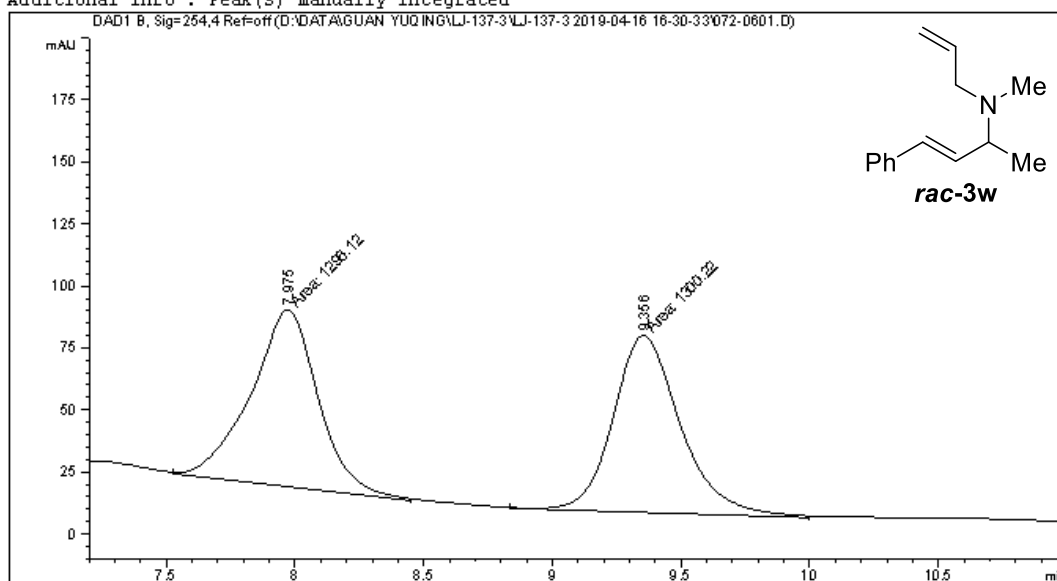
Figure S182. HPLC spectra of 3v, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\072-0601.D  
 Sample Name: LJ-137-3-RAC

```

=====
Acq. Operator   :                               Seq. Line :    6
Acq. Instrument : Instrument 2                  Location  : Vial 72
Injection Date  : 4/16/2019 5:30:41 PM        Inj       :    1
                                                Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0D(1-2)-99-1-
                  0.5ML-SUL-ALL-40MIN.M
Last changed    : 4/16/2019 5:44:26 PM
                  (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-0D(1-2)-99-1-
                  0.5ML-SUL-ALL-40MIN.M (Sequence Method)
Last changed    : 4/17/2019 8:15:04 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



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 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=254,4 Ref=off

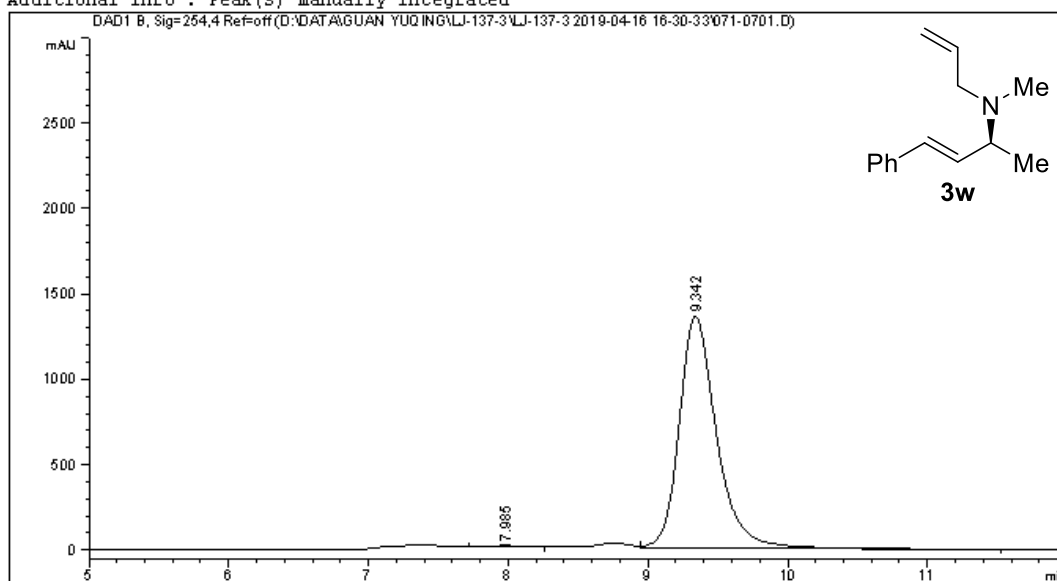
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.975	MM	0.3028	1296.12183	71.34225	49.9210
2	9.356	MM	0.3030	1300.22363	71.51093	50.0790

Totals :                    2596.34546   142.85318

**Figure S183.** HPLC spectra of *rac-3w*, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\071-0701.D  
Sample Name: LJ-137-3

```
=====
Acq. Operator   :                               Seq. Line :    7
Acq. Instrument : Instrument 2                   Location  : Vial 71
Injection Date  : 4/16/2019 5:51:42 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-OD(1-2)-99-1-
                  0.5ML-SUL-ALL-40MIN.M
Last changed    : 4/16/2019 5:44:26 PM
                  (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-137-3\LJ-137-3 2019-04-16 16-30-33\DAD-OD(1-2)-99-1-
                  0.5ML-SUL-ALL-40MIN.M (Sequence Method)
Last changed    : 4/17/2019 8:20:23 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.985	BB	0.2119	103.08399	7.24746	0.4068
2	9.342	VB	0.2788	2.52373e4	1357.84119	99.5932

Totals : 2.53404e4 1365.08865

Instrument 2 4/17/2019 8:20:29 PM

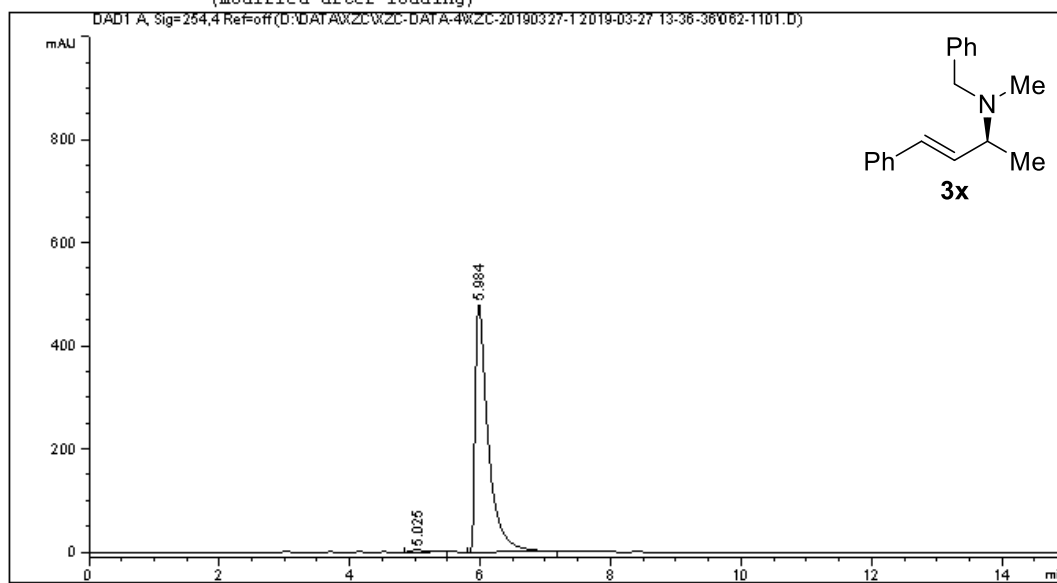
Page 1 of 2

**Figure S184.** HPLC spectra of **3w**, related to **Figure 3**.



Data File D:\DATA\XZC\XZC-DATA-4\XZC-20190327-1 2019-03-27 13-36-36\062-1101.D  
Sample Name: LJ-113-1

```
=====
Acq. Operator   :                               Seq. Line :   11
Acq. Instrument : Instrument 2                  Location  : Vial 62
Injection Date  : 3/27/2019 11:58:01 PM        Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\XZC\XZC-DATA-4\XZC-20190327-1 2019-03-27 13-36-36\DAD-0D(1-2)-90-10
                  -1ML-5UL-ALL-20MIN.M
Last changed    : 12/25/2018 5:41:36 PM
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-5UL-ALL-60MIN.M
Last changed    : 4/14/2019 9:24:48 PM
                  (modified after loading)
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.025	BB	0.2364	70.61983	4.46831	1.0636
2	5.984	BB	0.1998	6568.77344	479.64868	98.9364

Totals :                    6639.39326   484.11699

Instrument 2 4/14/2019 9:24:53 PM

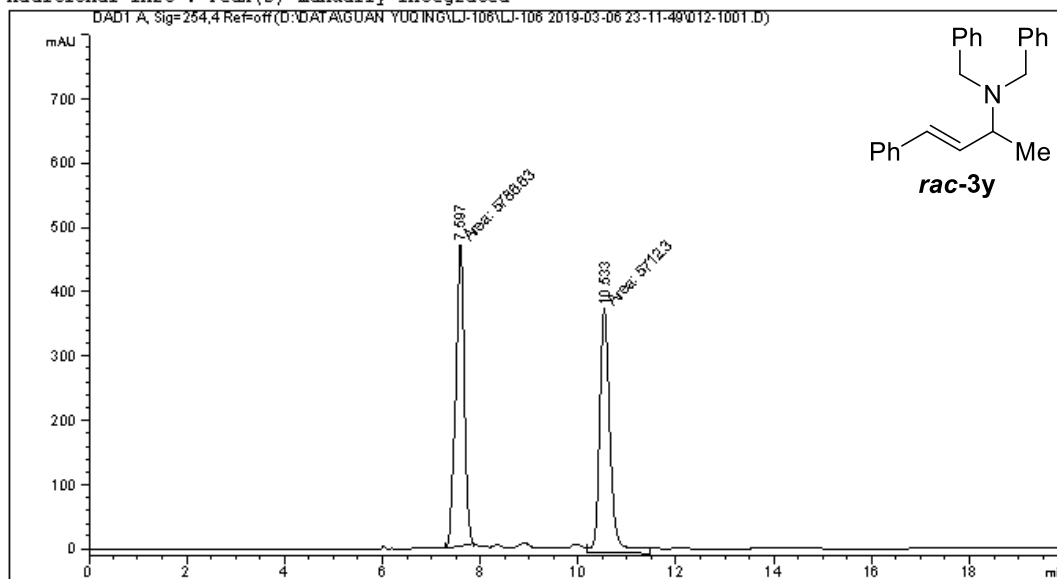
Page 1 of 1

Figure S186. HPLC spectra of 3x, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-106\LJ-106 2019-03-06 23-11-49\012-1001.D  
 Sample Name: LJ-103-4-RAC

```

=====
Acq. Operator   :                               Seq. Line :   10
Acq. Instrument : Instrument 2                 Location  : Vial 12
Injection Date  : 3/7/2019 2:17:08 AM        Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-106\LJ-106 2019-03-06 23-11-49\DAD-OD(1-2)-95-5-0.
                                                SML-5UL-ALL-20MIN.M
Last changed    : 3/4/2019 3:12:24 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-IA(1-6)-95-5-0.SML-5UL-ALL-40MIN.M
Last changed    : 3/19/2019 10:07:49 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



Area Percent Report

```

=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

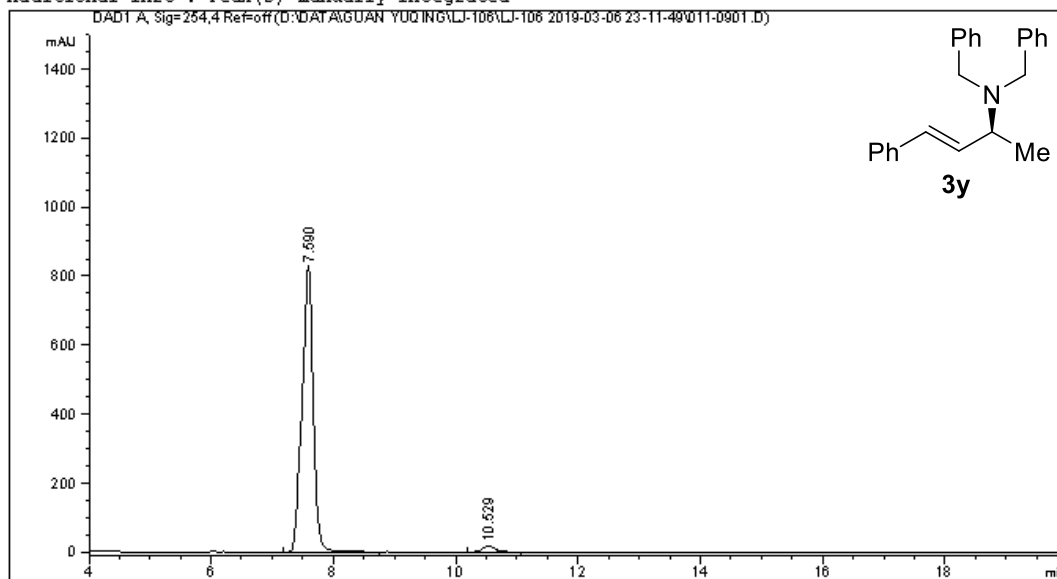
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.597	MM	0.2056	5786.62988	469.13281	50.3232
2	10.533	MM	0.2510	5712.29883	379.24442	49.6768

Totals : 1.14989e4 848.37723

Figure S187. HPLC spectra of *rac-3y*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-106\LJ-106 2019-03-06 23-11-49\011-0901.D  
Sample Name: LJ-103-4

```
=====
Acq. Operator   :                               Seq. Line :    9
Acq. Instrument : Instrument 2                   Location  : Vial 11
Injection Date  : 3/7/2019 1:56:04 AM           Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-106\LJ-106 2019-03-06 23-11-49\DAD-OD(1-2)-95-5-0.
                  SML-SUL-ALL-20MIN.M
Last changed    : 3/4/2019 3:12:24 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-IA(1-6)-95-5-0.SML-SUL-ALL-40MIN.M
Last changed    : 3/19/2019 10:11:39 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.590	BB	0.1842	1.05131e4	827.54132	97.6746
2	10.529	BB	0.2115	250.29330	18.30650	2.3254

Totals :                                   1.07634e4   845.84782

**Figure S188.** HPLC spectra of **3y**, related to **Figure 3**.

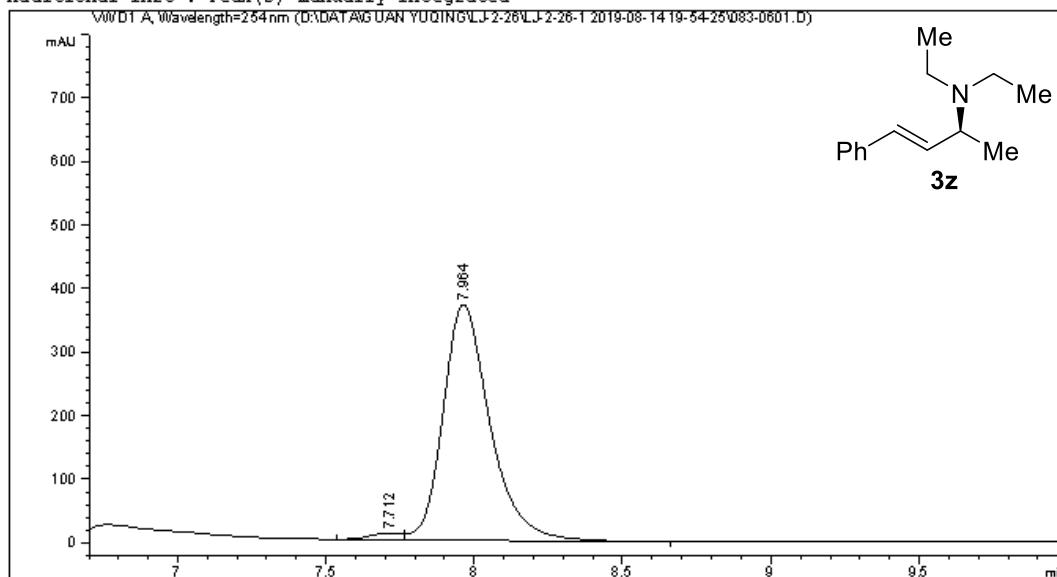




Data File D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26-1 2019-08-14 19-54-25\083-0601.D  
Sample Name: LJ-2-26-3

```
=====
Acq. Operator   :                               Seq. Line :    6
Acq. Instrument : Instrument 1                   Location  : Vial 83
Injection Date  : 8/14/2019 9:41:26 PM          Inj       :    1
                                                    Inj Volume: 1.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26-1 2019-08-14 19-54-25\VWD-0J(1-2)-95-5-
                  0.5ML-1UL-254NM-20MIN.M
Last changed    : 8/14/2019 7:57:29 PM
Analysis Method : D:\METHOD\LWD\DAD-AD(1-6)-95-5-1ML-3UL-ALL-30MIN-0813.M
Last changed    : 8/15/2019 6:36:03 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.712	BV	0.1156	78.80071	10.49263	1.8927
2	7.964	VB	0.1663	4084.59766	371.36200	98.1073

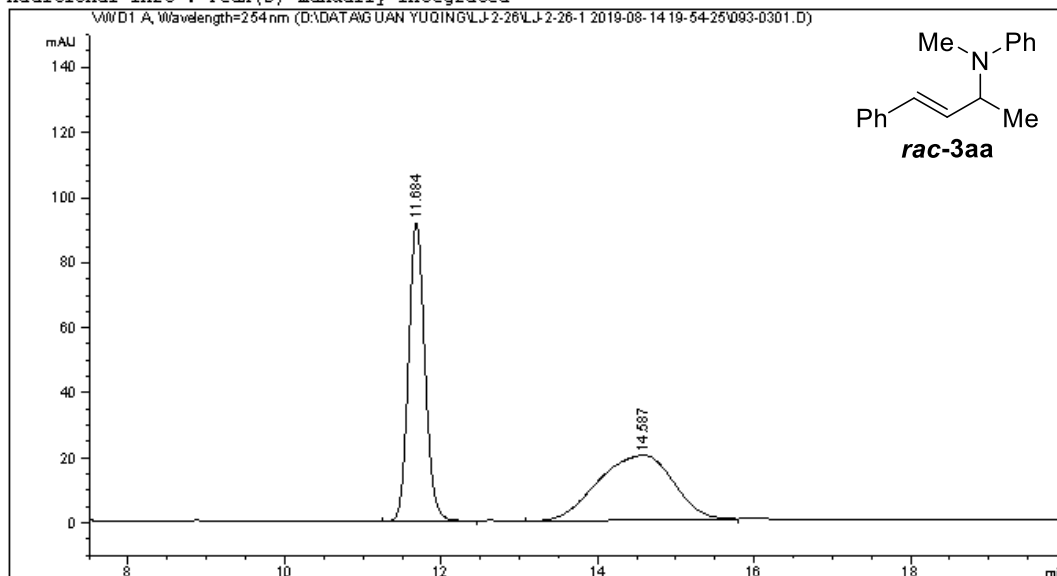
Totals :                                   4163.39837   381.85463

**Figure S190.** HPLC spectra of **3z**, related to **Figure 3**.

Data File D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26-1 2019-08-14 19-54-25\093-0301.D  
Sample Name: LJ-2-26-1-RAC

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                   Location  : Vial 93
Injection Date  : 8/14/2019 8:34:03 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26-1 2019-08-14 19-54-25\VWD-0J(1-2)-95-5-
                  1.0ML-5UL-254NM-30MIN.M
Last changed    : 8/14/2019 8:31:07 PM
                  (modified after loading)
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-0J(1-2)-95-5-0.5ML-1UL-254NM-20MIN.M
Last changed    : 8/14/2019 9:00:54 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.684	BB	0.2247	1341.73059	91.71468	50.3192
2	14.587	BB	1.0837	1324.70544	19.82213	49.6808

Totals : 2666.43604 111.53681

Instrument 1 8/14/2019 9:01:15 PM

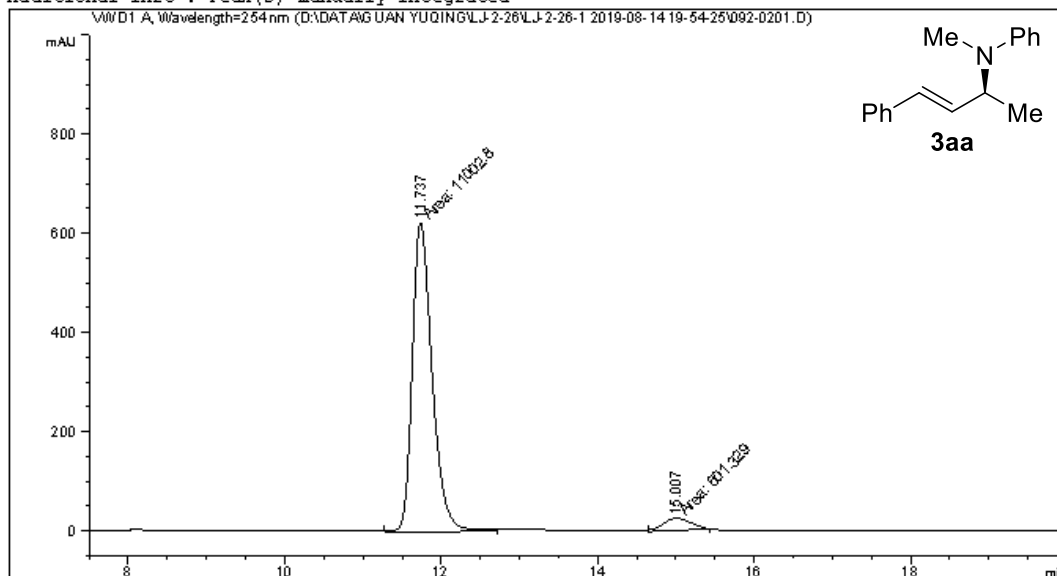
Page 1 of 2

Figure S191. HPLC spectra of *rac-3aa*, related to Figure 3.

Data File D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26-1 2019-08-14 19-54-25\092-0201.D  
Sample Name: LJ-2-26-1

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 1                  Location  : Vial 92
Injection Date  : 8/14/2019 8:08:13 PM        Inj       :    1
                                                Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26-1 2019-08-14 19-54-25\VWD-0J(1-2)-95-5-
                  1.0ML-5UL-254NM-30MIN.M
Last changed    : 8/14/2019 8:31:07 PM
                  (modified after loading)
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-0J(1-2)-95-5-0.5ML-1UL-254NM-20MIN.M
Last changed    : 8/14/2019 9:03:25 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.737	MM	0.2944	1.10028e4	622.86169	94.8180
2	15.007	MM	0.4183	601.32904	23.95970	5.1820

Totals : 1.16041e4 646.82139

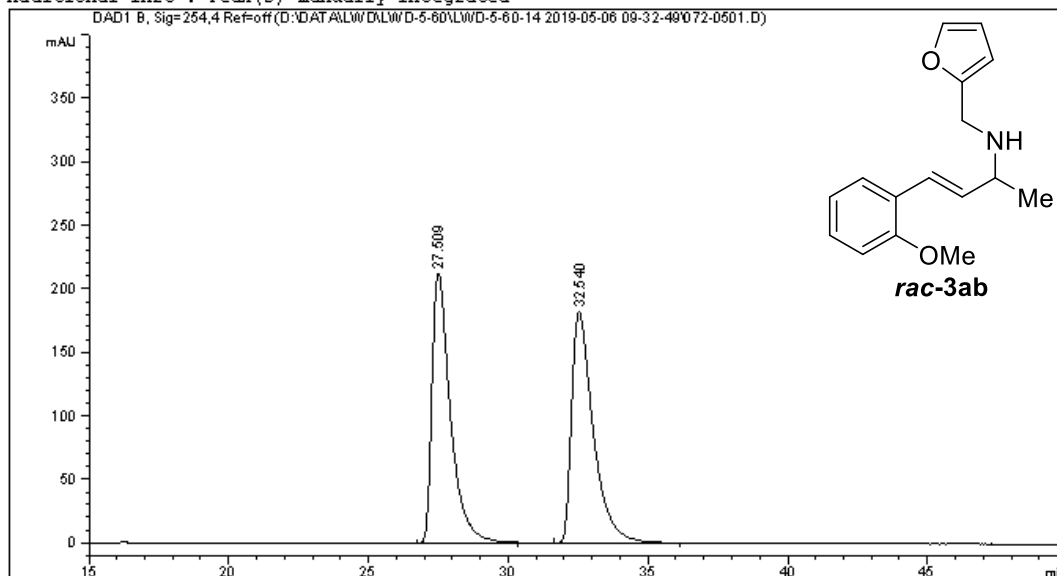
Instrument 1 8/14/2019 9:03:32 PM

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**Figure S192.** HPLC spectra of **3aa**, related to **Figure 3**.

Data File D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\072-0501.D  
Sample Name: LJ-157-8-RAC

```
=====
Acq. Operator   :                               Seq. Line :    5
Acq. Instrument : Instrument 2                  Location  : Vial 72
Injection Date  : 5/6/2019 11:23:57 AM         Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\DAD-0J(1-6)-99-1-0.5ML
                  -SUL-ALL-60MIN.M
Last changed    : 3/10/2019 2:55:21 PM
Analysis Method : D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\DAD-0J(1-6)-99-1-0.5ML
                  -SUL-ALL-60MIN.M (Sequence Method)
Last changed    : 5/16/2019 9:39:12 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.509	BB	0.6781	9748.92676	212.96362	49.7788
2	32.540	BB	0.7825	9835.56641	182.56171	50.2212

Totals : 1.95845e4 395.52533

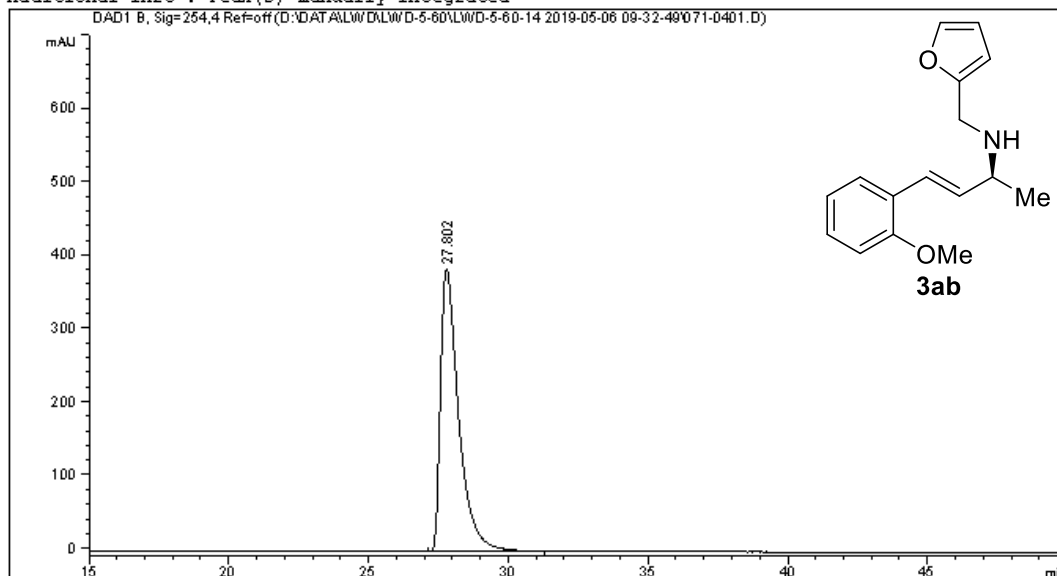
Instrument 2 5/16/2019 9:39:15 PM

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Figure S193. HPLC spectra of *rac-3ab*, related to Figure 4.

Data File D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\071-0401.D  
Sample Name: LJ-157-8

```
=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 2                   Location  : Vial 71
Injection Date  : 5/6/2019 10:22:58 AM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\DAD-0J(1-6)-99-1-0.5ML
                  -SUL-ALL-60MIN.M
Last changed    : 3/10/2019 2:55:21 PM
Analysis Method : D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\DAD-0J(1-6)-99-1-0.5ML
                  -SUL-ALL-60MIN.M (Sequence Method)
Last changed    : 5/16/2019 9:40:28 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

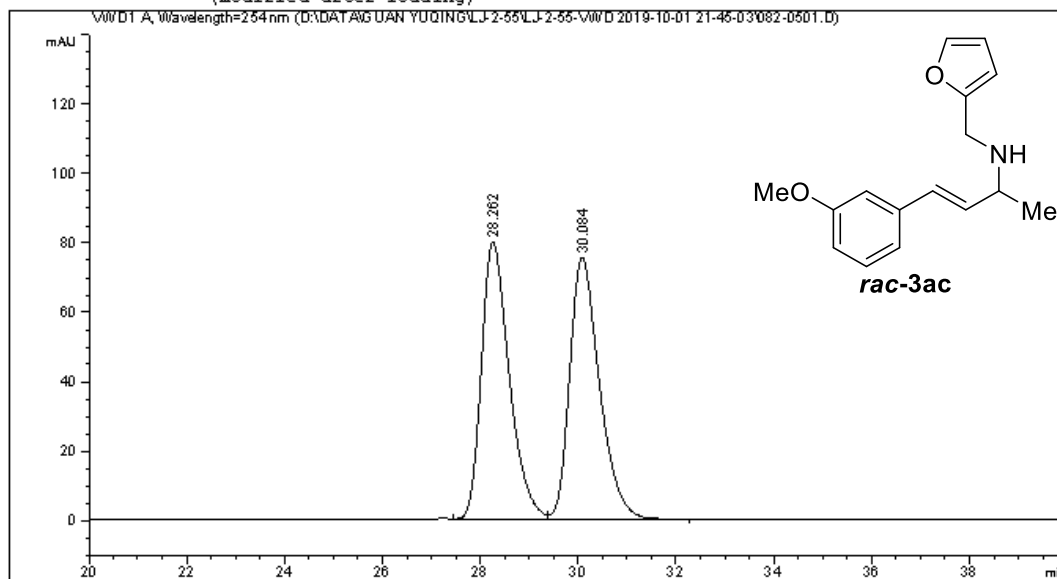
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.802	BB	0.6682	1.73284e4	385.65326	100.0000

Totals : 1.73284e4 385.65326

**Figure S194.** HPLC spectra of **3ab**, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-2-55\LJ-2-55-VWD 2019-10-01 21-45-03\082-0501.D  
Sample Name: LJ-2-55-2

```
=====
Acq. Operator   :                               Seq. Line :    5
Acq. Instrument : Instrument 1                   Location  : Vial 82
Injection Date  : 10/1/2019 11:21:53 PM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-55\LJ-2-55-VWD 2019-10-01 21-45-03\VWD-AD(1-2)-99-
                  1-0.5ML-5UL-254NM-40MIN.M
Last changed    : 10/1/2019 10:33:36 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\Y\VWD-AS(1-6)-99-1-1ML-5UL-254NM-35MIN.M
Last changed    : 10/2/2019 9:54:14 AM
                  (modified after loading)
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

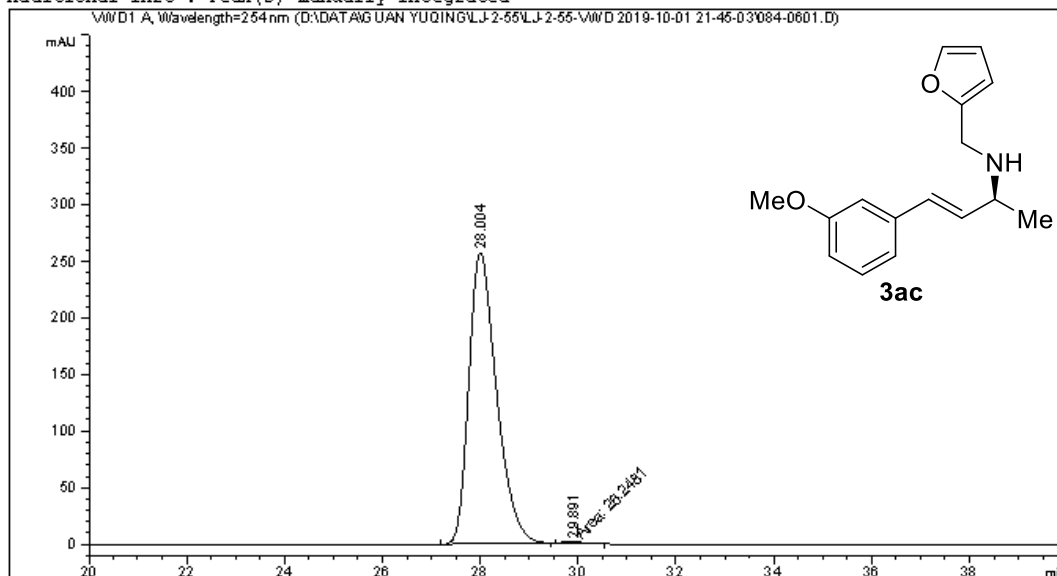
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.262	BV	0.6025	3147.13306	79.73415	49.7559
2	30.084	VB	0.6431	3178.01807	75.34550	50.2441

Totals :                                   6325.15112 155.07965

Figure S195. HPLC spectra of *rac-3ac*, related to Figure 4.

Data File D:\DATA\GUAN YUQING\LJ-2-55\LJ-2-55-VWD 2019-10-01 21-45-03\084-0601.D  
Sample Name: LJ-2-56-2

```
=====
Acq. Operator   :                               Seq. Line :    6
Acq. Instrument : Instrument 1                   Location  : Vial 84
Injection Date  : 10/2/2019 12:02:43 AM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-55\LJ-2-55-VWD 2019-10-01 21-45-03\VWD-AD(1-2)-99-
                  1-0.5ML-5UL-254NM-40MIN.M
Last changed    : 10/1/2019 10:33:36 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\Y\VWD-AS(1-6)-99-1-1ML-5UL-254NM-35MIN.M
Last changed    : 10/2/2019 9:57:02 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.004	BB	0.5997	1.01024e4	256.95374	99.7409
2	29.891	MM	0.4877	26.24809	8.96930e-1	0.2591

Totals : 1.01286e4 257.85067

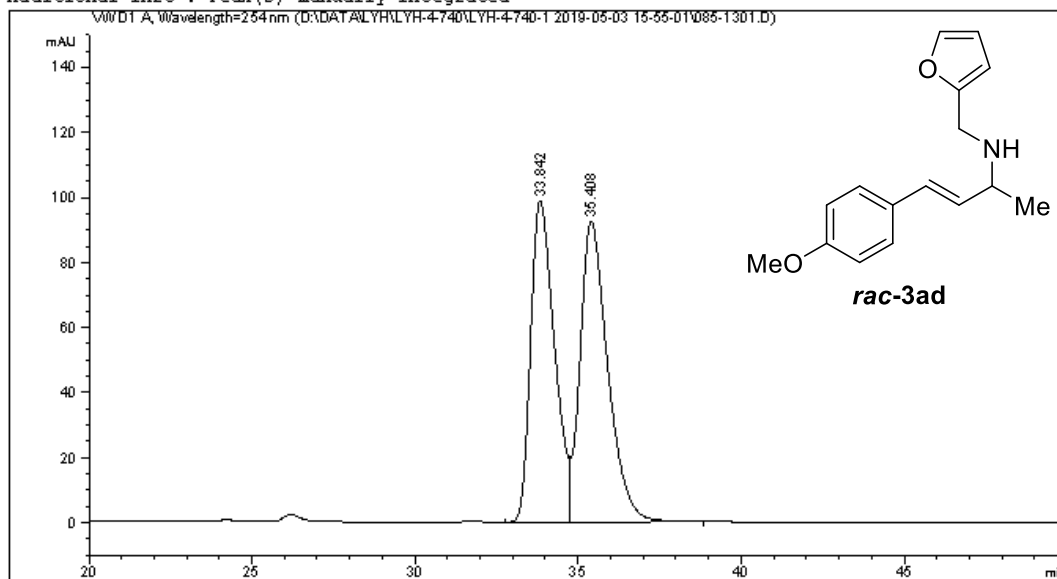
Instrument 1 10/2/2019 9:58:48 AM

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**Figure S196.** HPLC spectra of **3ac**, related to **Figure 4**.

Data File D:\DATA\LYH\LYH-4-740\LYH-4-740-1 2019-05-03 15-55-01\085-1301.D  
Sample Name: LJ-150-1-RAC

```
=====
Acq. Operator   :                               Seq. Line :   13
Acq. Instrument : Instrument 1                   Location  : Vial 85
Injection Date  : 5/3/2019 11:26:13 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LYH\LYH-4-740\LYH-4-740-1 2019-05-03 15-55-01\VWD-AD(1-2)-99-1-0.
                  SML-5UL-254NM-60MIN.M
Last changed    : 4/16/2019 4:38:17 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AD(1-2)-70-30-0.SML-5UL-254NM-40MIN.M
Last changed    : 5/4/2019 10:06:22 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.842	BV	0.7749	5006.37842	98.67974	47.8643
2	35.408	VB	0.8798	5453.14893	92.50365	52.1357

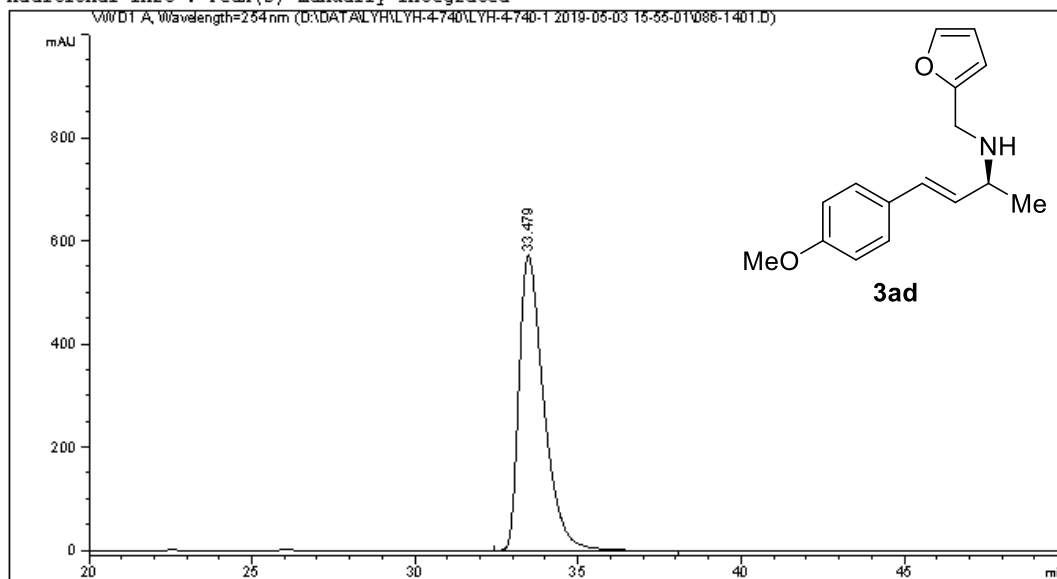
Totals :                                    1.04595e4    191.18340

**Figure S197.** HPLC spectra of *rac*-3ad, related to **Figure 4**.



Data File D:\DATA\LYH\LYH-4-740\LYH-4-740-1 2019-05-03 15-55-01\086-1401.D  
Sample Name: LJ-150-1

```
=====
Acq. Operator   :                               Seq. Line :   14
Acq. Instrument : Instrument 1                   Location  : Vial 86
Injection Date  : 5/4/2019 12:27:04 AM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LYH\LYH-4-740\LYH-4-740-1 2019-05-03 15-55-01\VWD-AD(1-2)-99-1-0.
                  SML-5UL-254NM-60MIN.M
Last changed    : 4/16/2019 4:38:17 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AD(1-2)-70-30-0.SML-5UL-254NM-40MIN.M
Last changed    : 5/4/2019 10:07:46 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

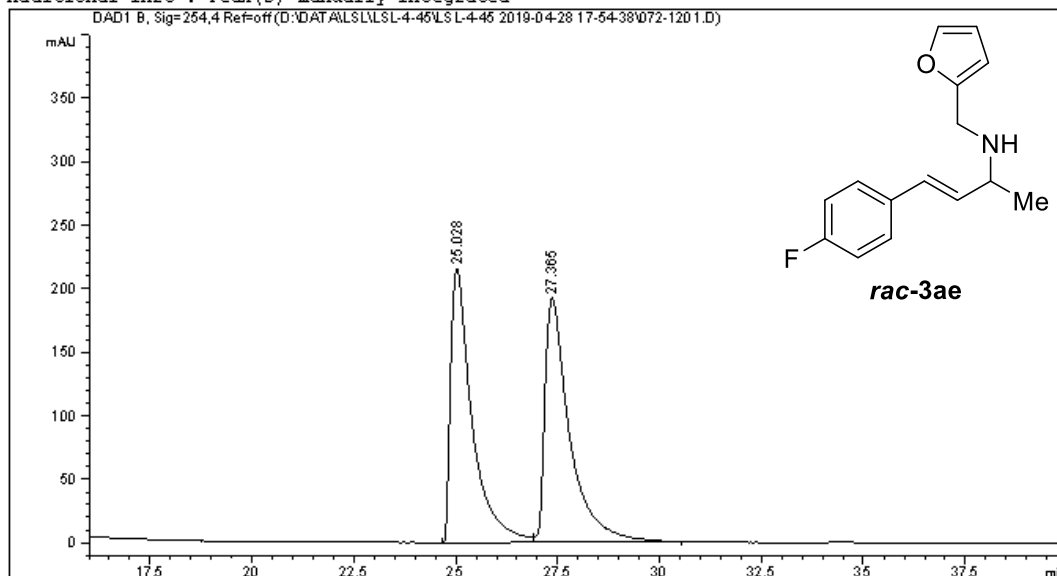
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.479	BB	0.7929	3.00404e4	571.85364	100.0000

Totals :                    3.00404e4   571.85364

**Figure S198.** HPLC spectra of **3ad**, related to **Figure 4**.

Data File D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\072-1201.D  
Sample Name: LJ-151-2

```
=====
Acq. Operator   :                               Seq. Line :   12
Acq. Instrument : Instrument 2                   Location  : Vial 72
Injection Date  : 4/28/2019 11:25:07 PM        Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\DAD-0J(1-6)-99-1-0.5ML-
SUL-ALL-60MIN.M
Last changed    : 3/10/2019 2:55:21 PM
Analysis Method : D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\DAD-0J(1-6)-99-1-0.5ML-
SUL-ALL-60MIN.M (Sequence Method)
Last changed    : 5/3/2019 5:50:12 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.028	BV	0.5388	7893.84473	215.79332	49.4747
2	27.365	VB	0.6179	8061.46973	191.99297	50.5253

Totals : 1.59553e4 407.78629

Instrument 2 5/3/2019 5:50:23 PM

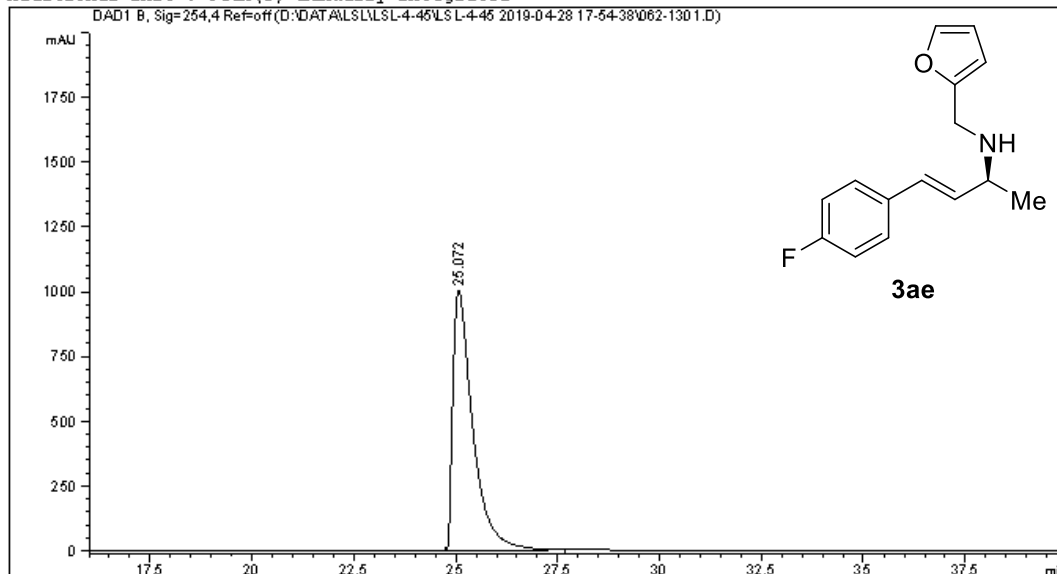
Page 1 of 2

Figure S199. HPLC spectra of *rac-3ae*, related to Figure 4.

Data File D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\062-1301.D  
Sample Name: LJ-150-2

```
=====
Acq. Operator   :                               Seq. Line :   13
Acq. Instrument : Instrument 2                   Location  : Vial 62
Injection Date  : 4/29/2019 12:26:10 AM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\DAD-0J(1-6)-99-1-0.5ML-
SUL-ALL-60MIN.M
Last changed    : 3/10/2019 2:55:21 PM
Analysis Method : D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\DAD-0J(1-6)-99-1-0.5ML-
SUL-ALL-60MIN.M (Sequence Method)
Last changed    : 5/3/2019 5:51:46 PM
                (modified after loading)
```

Additional Info : Peak(s) manually integrated



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.072	BB	0.5086	3.41880e4	1005.60474	100.0000

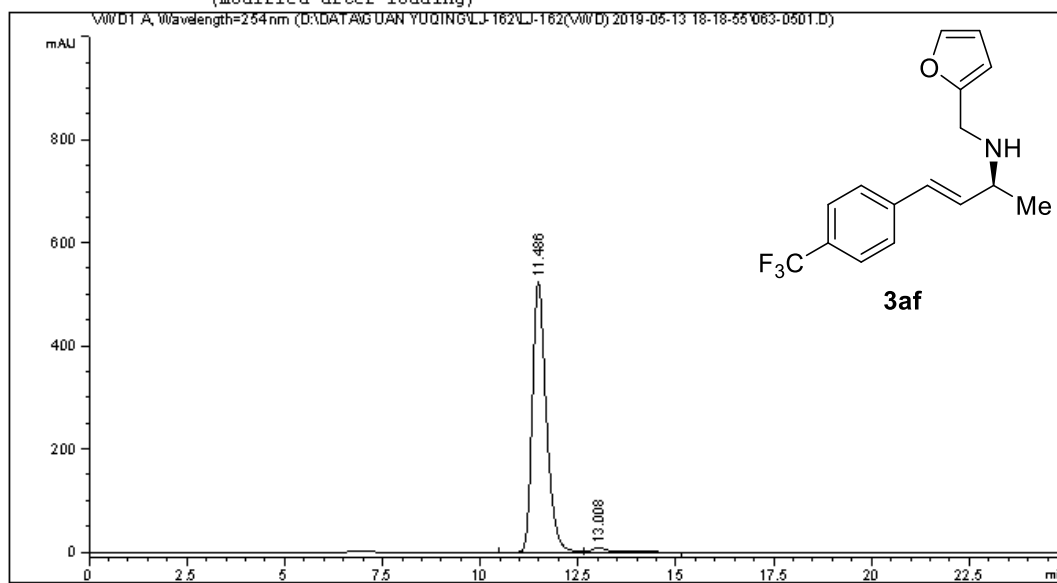
Totals : 3.41880e4 1005.60474

Figure S200. HPLC spectra of 3ae, related to Figure 4.



Data File D:\DATA\GUAN YUQING\LJ-162\LJ-162(VWD) 2019-05-13 18-18-55\063-0501.D  
Sample Name: LJ-162-2

```
=====
Acq. Operator   :                               Seq. Line :    5
Acq. Instrument : Instrument 1                  Location  : Vial 63
Injection Date  : 5/13/2019 8:03:30 PM         Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-162\LJ-162(VWD) 2019-05-13 18-18-55\VWD-AS(1-6)-99-1
                  -0.5ML-5UL-254NM-40MIN.M
Last changed    : 3/12/2019 10:38:44 AM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AD(1-2)-99-1-0.5ML-5UL-254NM-40MIN.M
Last changed    : 5/13/2019 9:40:43 PM
                  (modified after loading)
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.486	BV	0.3762	1.30095e4	524.87543	98.0807
2	13.008	VB	0.4413	254.57536	8.31177	1.9193

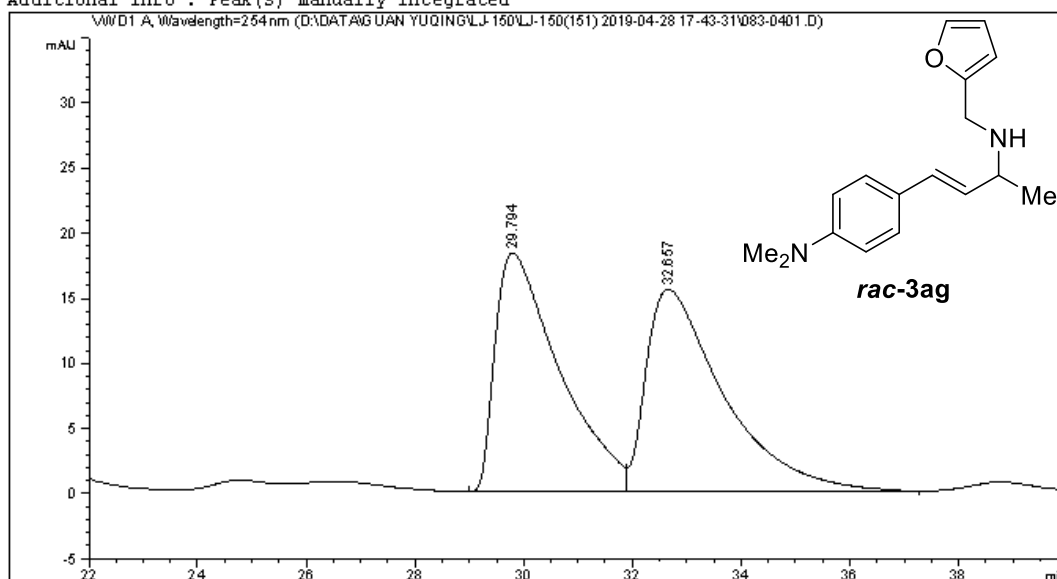
Totals : 1.32641e4 533.18720

**Figure S202.** HPLC spectra of **3af**, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-150\LJ-150(151) 2019-04-28 17-43-31\083-0401.D  
 Sample Name: LJ-151-3

```

=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 1                   Location  : Vial 83
Injection Date  : 4/28/2019 7:07:00 PM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-150\LJ-150(151) 2019-04-28 17-43-31\VWD-AD(1-2)-99-1
                  -0.6ML-5UL-254NM-40MIN.M
Last changed    : 4/28/2019 7:44:37 PM
                  (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-150\LJ-150(151) 2019-04-28 17-43-31\VWD-AD(1-2)-99-1
                  -0.6ML-5UL-254NM-40MIN.M (Sequence Method)
Last changed    : 5/3/2019 5:58:38 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



Area Percent Report

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.794	BV	1.1567	1494.45447	18.30020	49.4599
2	32.657	VB	1.3695	1527.09534	15.49839	50.5401

Totals : 3021.54980 33.79859

Instrument 2 5/3/2019 5:58:51 PM

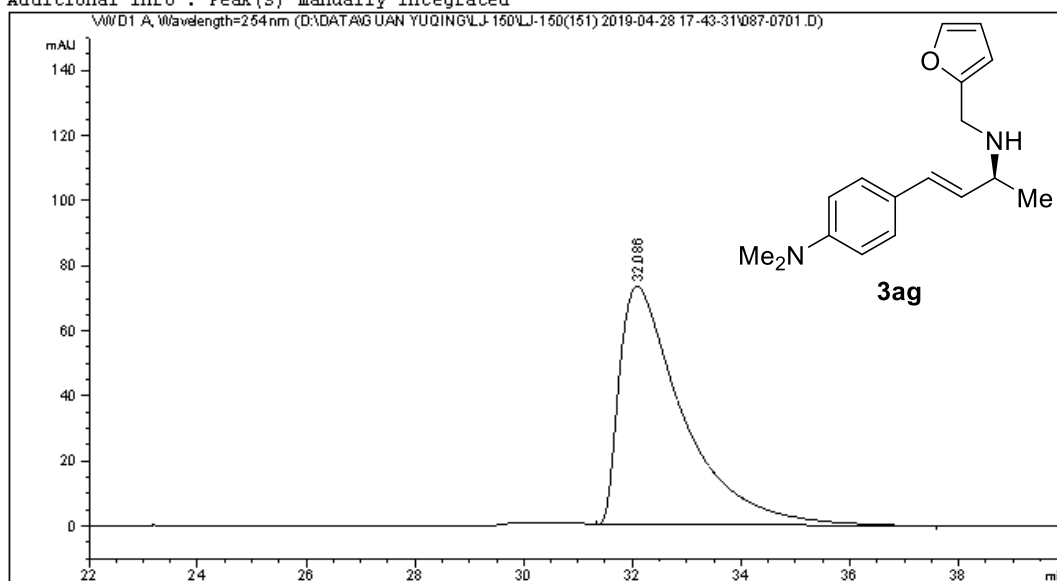
Page 1 of 2

Figure S203. HPLC spectra of *rac-3ag*, related to Figure 4.

Data File D:\DATA\GUAN YUQING\LJ-150\LJ-150(151) 2019-04-28 17-43-31\087-0701.D  
 Sample Name: LJ-150-3

```

=====
Acq. Operator   :                               Seq. Line :    7
Acq. Instrument : Instrument 1                  Location  : Vial 87
Injection Date  : 4/28/2019 9:09:34 PM         Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-150\LJ-150(151) 2019-04-28 17-43-31\VWD-AD(1-2)-99-1
                  -0.6ML-5UL-254NM-40MIN.M
Last changed    : 4/28/2019 7:44:37 PM
                  (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-150\LJ-150(151) 2019-04-28 17-43-31\VWD-AD(1-2)-99-1
                  -0.6ML-5UL-254NM-40MIN.M (Sequence Method)
Last changed    : 5/3/2019 6:00:17 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



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 Area Percent Report  
 =====

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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=254 nm

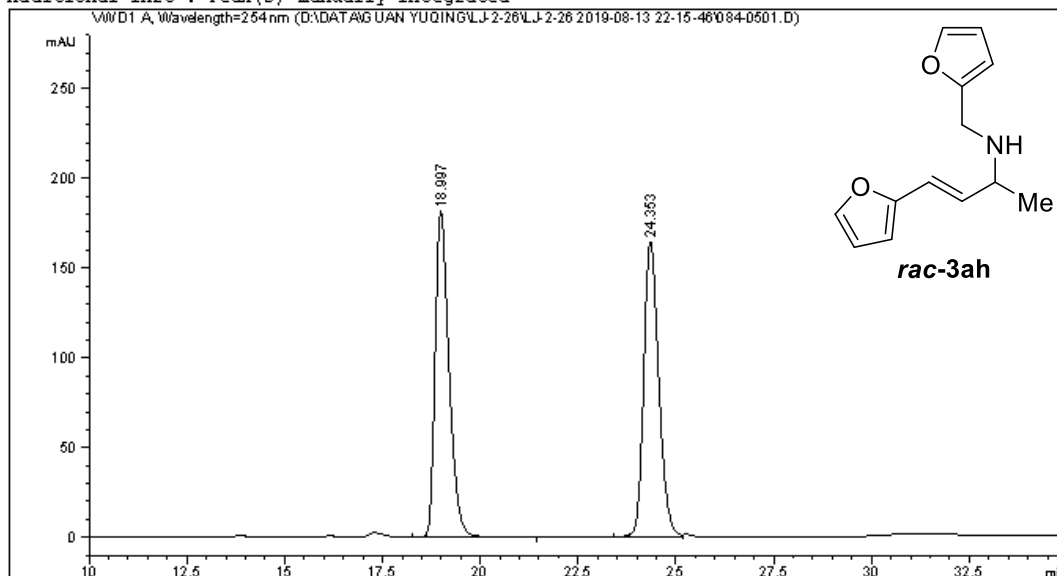
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.086	BB	1.1885	5973.43457	73.23915	100.0000

Totals :                                    5973.43457    73.23915

**Figure S204.** HPLC spectra of **3ag**, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26 2019-08-13 22-15-46\084-0501.D  
Sample Name: LJ-2-26-7-RAC

```
=====
Acq. Operator   :                               Seq. Line :    5
Acq. Instrument : Instrument 1                   Location  : Vial 84
Injection Date  : 8/14/2019 12:19:21 AM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26 2019-08-13 22-15-46\WVD1-0J(1-2)-95-5-0.
                  SML-5UL-254NM-40MIN.M
Last changed    : 8/13/2019 10:44:25 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\WVD-AD(1-2)-80-20-1ML-3UL-210NM-60MIN.M
Last changed    : 8/14/2019 10:07:13 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.997	BB	0.3724	4454.71484	181.45822	50.2576
2	24.353	BV	0.4114	4409.04004	164.66374	49.7424

Totals : 8863.75488 346.12196

Instrument 1 8/14/2019 10:07:21 AM

Page 1 of 2

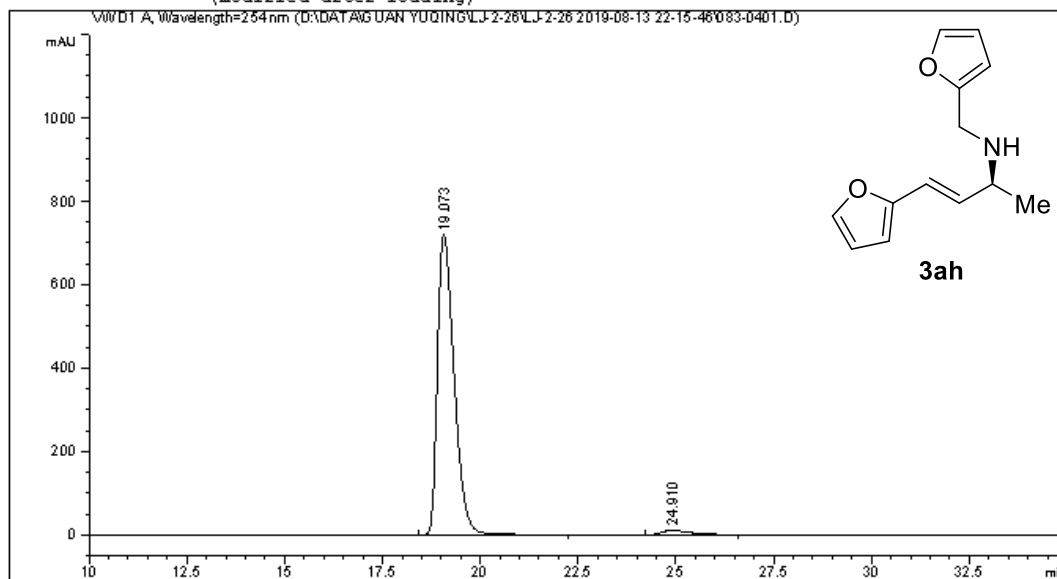
Figure S205. HPLC spectra of *rac*-3ah, related to Figure 4.



Data File D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26 2019-08-13 22-15-46\083-0401.D  
 Sample Name: LJ-2-26-7

```

=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 1                   Location  : Vial 83
Injection Date  : 8/13/2019 11:43:31 PM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-26\2019-08-13 22-15-46\WVD-0J(1-2)-95-5-0.
                  SML-5UL-254NM-40MIN.M
Last changed    : 8/13/2019 10:44:25 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\WVD-AD(1-2)-80-20-1ML-3UL-210NM-60MIN.M
Last changed    : 8/14/2019 10:05:00 AM
                  (modified after loading)
=====
  
```



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 Area Percent Report  
 =====

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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.073	BB	0.4558	2.10885e4	719.88995	97.8563
2	24.910	BB	0.6432	461.96768	10.62533	2.1437

Totals :                                    2.15505e4    730.51528

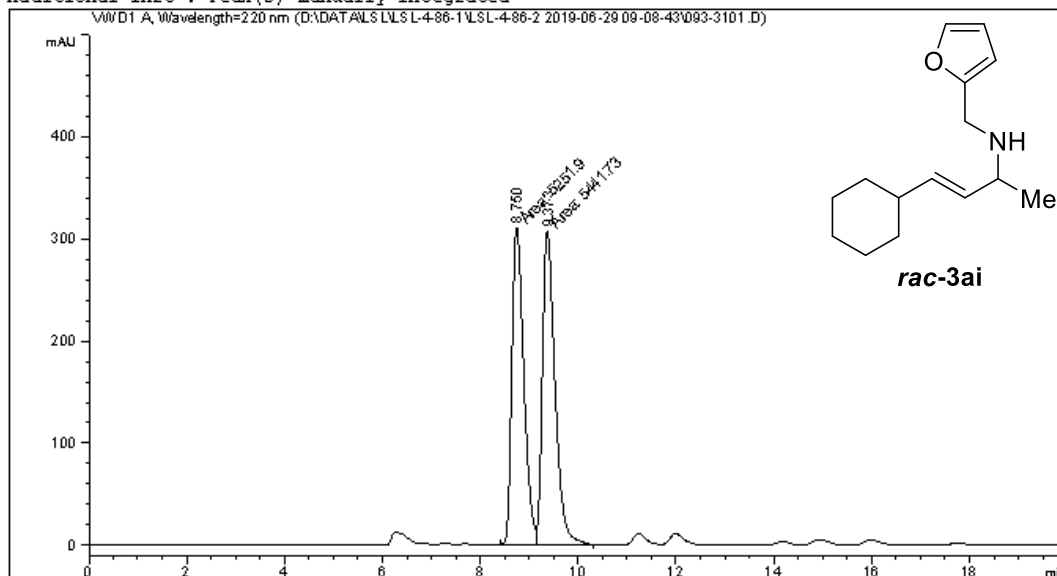
**Figure S206.** HPLC spectra of **3ah**, related to **Figure 4**.

Data File D:\DATA\LSL\LSL-4-86-1\LSL-4-86-2 2019-06-29 09-08-43\093-3101.D  
 Sample Name: LJ-2-1-2

```

=====
Acq. Operator   :                               Seq. Line :   31
Acq. Instrument : Instrument 1                   Location  : Vial 93
Injection Date  : 6/29/2019 9:16:35 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\LSL\LSL-4-86-1\LSL-4-86-2 2019-06-29 09-08-43\VWD-AD(1-2)-95-5-0.
                  SML-5UL-220NM-40MIN.M
Last changed    : 6/29/2019 9:54:18 PM
                  (modified after loading)
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AS(1-6)-80-20-1.OML-5UL-220NM-45MIN.M
Last changed    : 6/29/2019 10:12:37 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.750	MF	0.2815	5251.89600	310.98474	49.1124
2	9.373	FM	0.2955	5441.73340	306.92697	50.8876

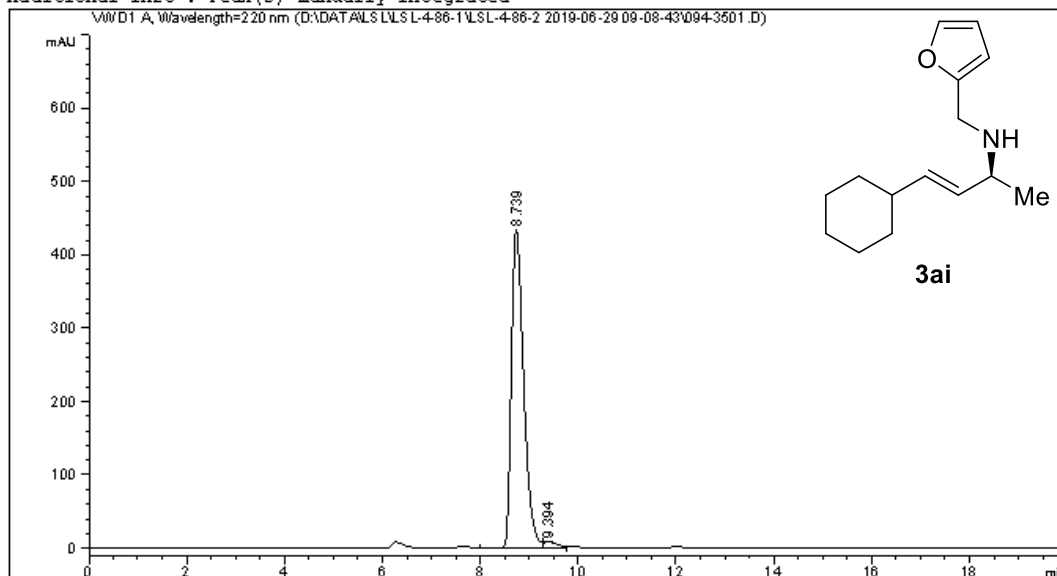
Totals :                    1.06936e4    617.91171

**Figure S207.** HPLC spectra of *rac-3ai*, related to **Figure 4**.

Data File D:\DATA\LSL\LSL-4-86-1\LSL-4-86-2 2019-06-29 09-08-43\094-3501.D  
Sample Name: LJ-2-2-2

```
=====
Acq. Operator   :                               Seq. Line :   35
Acq. Instrument : Instrument 1                  Location  : Vial 94
Injection Date  : 6/29/2019 10:30:10 PM        Inj       :    1
                                                Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\LSL\LSL-4-86-1\LSL-4-86-2 2019-06-29 09-08-43\VWD-AD(1-2)-95-5-0.
                  SML-5UL-220NM-40MIN.M
Last changed    : 6/29/2019 10:39:27 PM
                  (modified after loading)
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AS(1-6)-80-20-1.OML-5UL-220NM-45MIN.M
Last changed    : 6/29/2019 10:51:26 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.739	BV	0.2663	7521.54541	433.75995	97.8275
2	9.394	VV	0.2780	167.03423	8.62418	2.1725

Totals : 7688.57964 442.38413

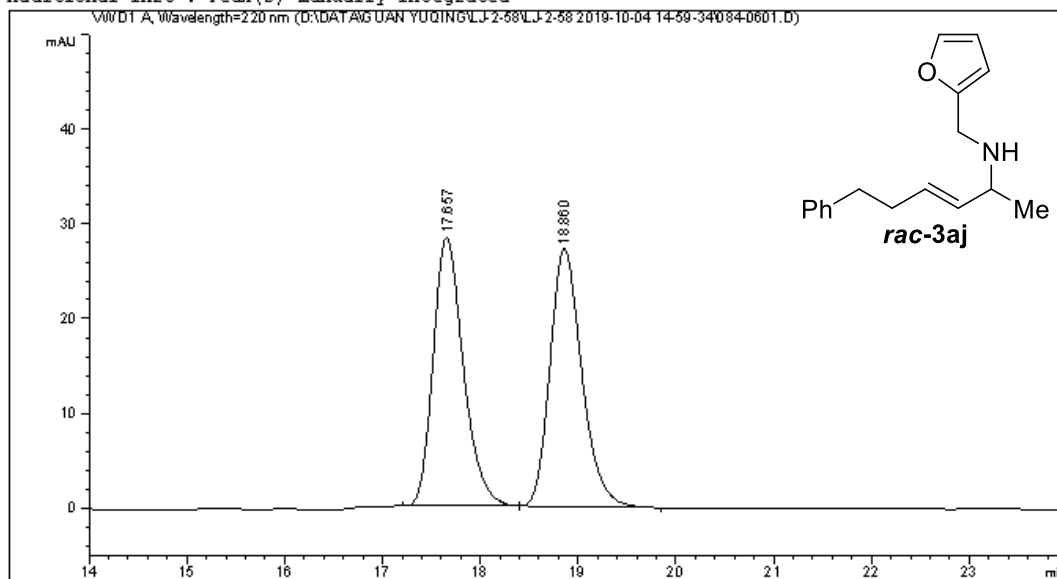
Instrument 1 6/29/2019 10:51:50 PM

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**Figure S208.** HPLC spectra of **3ai**, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\084-0601.D  
Sample Name: LJ-2-58-2-RAC

```
=====
Acq. Operator   :                               Seq. Line :    6
Acq. Instrument : Instrument 1                   Location  : Vial 84
Injection Date  : 10/4/2019 4:49:52 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\WVD-0J(1-6)-95-5-0.
                  SML-5UL-220NM-25MIN.M
Last changed    : 10/4/2019 2:55:51 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\WVD-OD(1-2)-95-5-0.SML-5UL-254NM-10MIN.M
Last changed    : 10/4/2019 7:02:46 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: WVD1 A, Wavelength=220 nm

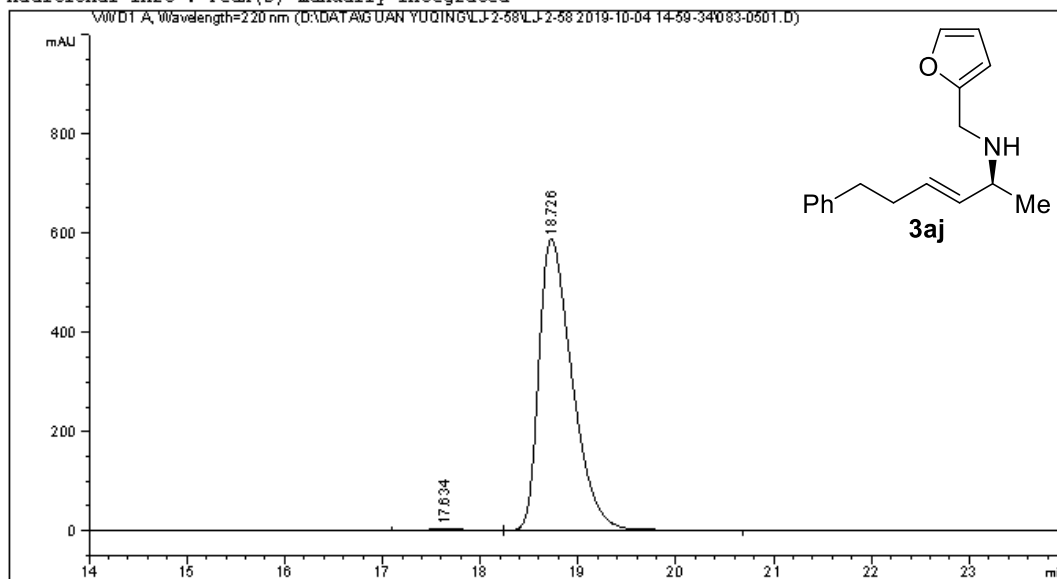
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.657	BB	0.3280	608.07892	28.37230	49.7003
2	18.860	BB	0.3465	615.41345	27.25274	50.2997

Totals :                                   1223.49237   55.62503

Figure S209. HPLC spectra of *rac-3aj*, related to Figure 4.

Data File D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\083-0501.D  
Sample Name: LJ-2-58-2

```
=====
Acq. Operator   :                               Seq. Line :    5
Acq. Instrument : Instrument 1                   Location  : Vial 83
Injection Date  : 10/4/2019 4:24:02 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\WVD-0J(1-6)-95-5-0.
                  SML-5UL-220NM-25MIN.M
Last changed    : 10/4/2019 2:55:51 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\WVD-OD(1-2)-95-5-0.SML-5UL-254NM-10MIN.M
Last changed    : 10/4/2019 7:04:34 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=220 nm

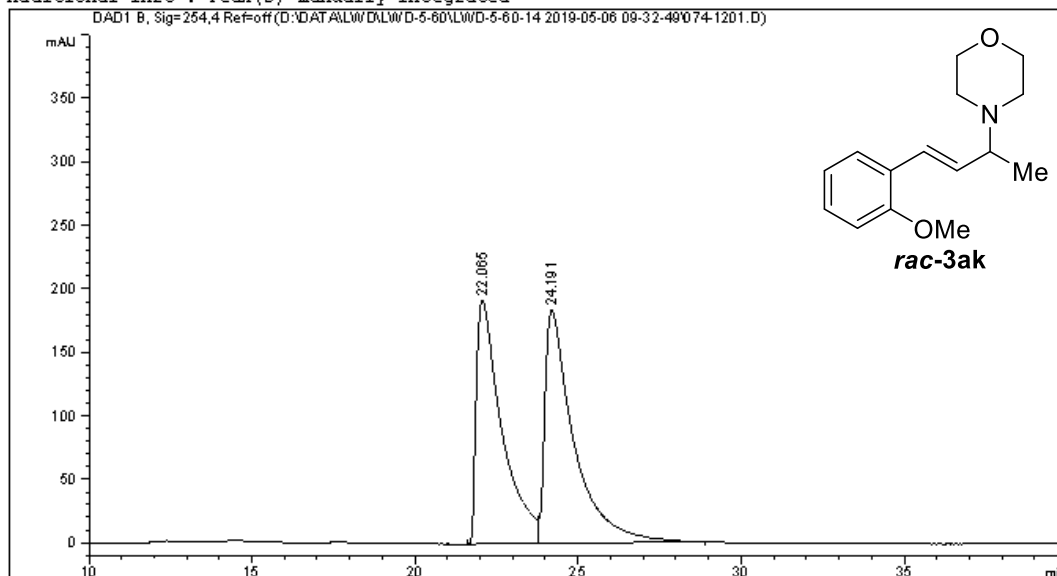
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.634	BB	0.3316	67.67126	3.10049	0.4848
2	18.726	BB	0.3628	1.38897e4	587.63940	99.5152

Totals : 1.39574e4 590.73990

Figure S210. HPLC spectra of 3aj, related to Figure 4.

Data File D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\074-1201.D  
Sample Name: LJ-157-7-RAC

```
=====
Acq. Operator   :                               Seq. Line :   12
Acq. Instrument : Instrument 2                   Location  : Vial 74
Injection Date  : 5/6/2019 3:51:09 PM           Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\DAD-OD(1-2)-99-1-0.5ML
                  -SUL-ALL-40MIN.M
Last changed    : 3/8/2019 11:06:52 AM
Analysis Method : D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\DAD-OD(1-2)-99-1-0.5ML
                  -SUL-ALL-40MIN.M (Sequence Method)
Last changed    : 5/16/2019 9:35:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.065	BV	0.7619	1.03696e4	192.05229	47.7532
2	24.191	VB	0.8610	1.13454e4	183.57259	52.2468

Totals : 2.17150e4 375.62488

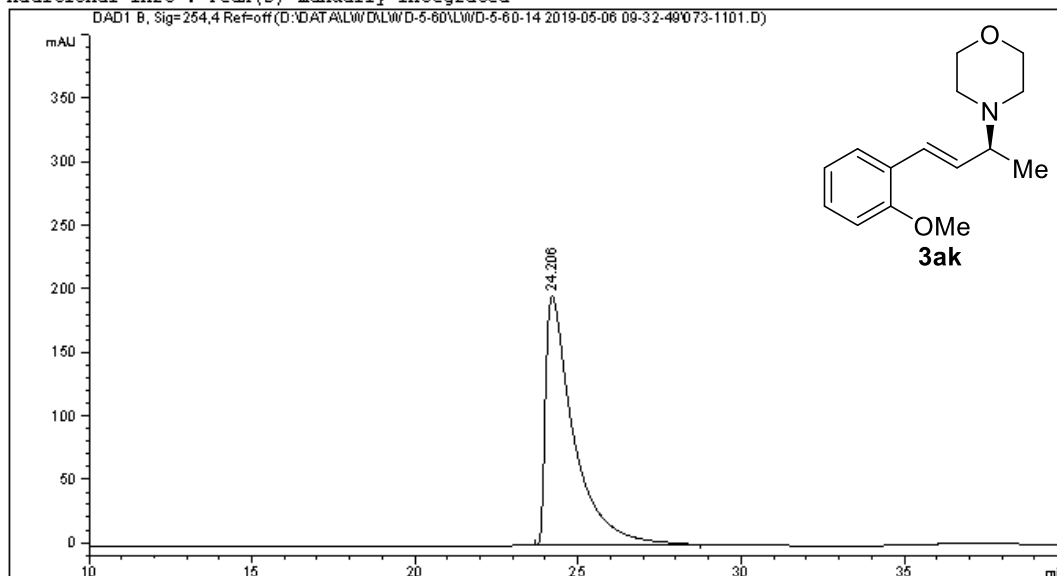
Instrument 2 5/16/2019 9:37:33 PM

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Figure S211. HPLC spectra of *rac-3ak*, related to Figure 4.

Data File D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\073-1101.D  
Sample Name: LJ-157-7

```
=====
Acq. Operator   :                               Seq. Line :   11
Acq. Instrument : Instrument 2                   Location  : Vial 73
Injection Date  : 5/6/2019 3:10:06 PM           Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\DAD-OD(1-2)-99-1-0.5ML
                  -SUL-ALL-40MIN.M
Last changed    : 3/8/2019 11:06:52 AM
Analysis Method : D:\DATA\LWD\LWD-5-60\LWD-5-60-14 2019-05-06 09-32-49\DAD-OD(1-2)-99-1-0.5ML
                  -SUL-ALL-40MIN.M (Sequence Method)
Last changed    : 5/16/2019 9:35:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.206	BB	0.8172	1.16287e4	196.28775	100.0000

Totals : 1.16287e4 196.28775

Figure S212. HPLC spectra of 3ak, related to Figure 4.

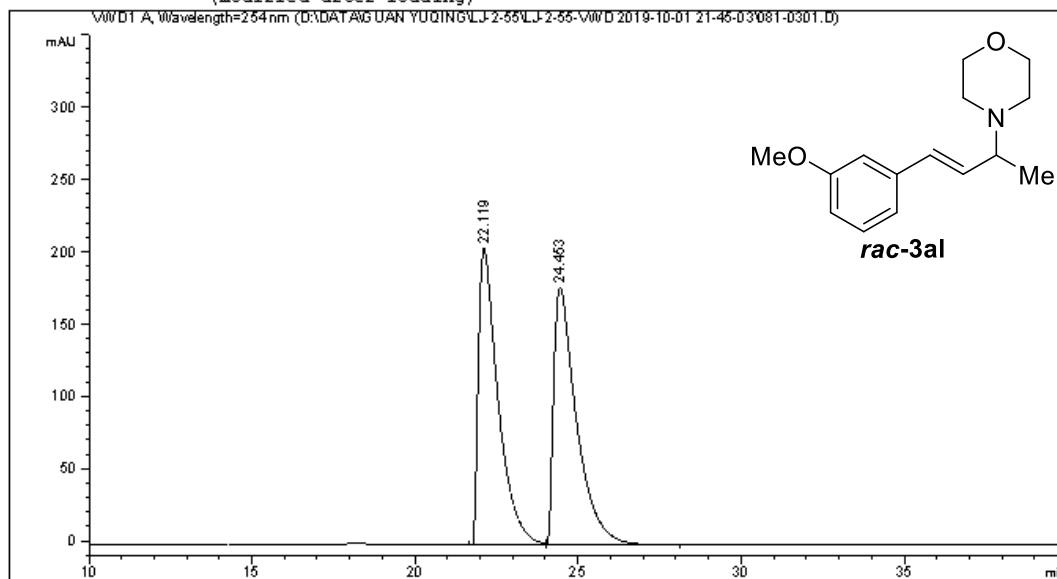
Data File D:\DATA\GUAN YUQING\LJ-2-55\LJ-2-55-VWD 2019-10-01 21-45-03\081-0301.D  
 Sample Name: LJ-2-55-1

```

=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                  Location  : Vial 81
Injection Date  : 10/1/2019 10:00:10 PM       Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-55\LJ-2-55-VWD 2019-10-01 21-45-03\VWD-AD(1-2)-99-
                  1-0.5ML-5UL-254NM-40MIN.M
Last changed    : 10/1/2019 10:33:36 PM
                  (modified after loading)

Analysis Method : D:\METHOD\LG\Y\VWD-AS(1-6)-99-1-1ML-5UL-254NM-35MIN.M
Last changed    : 10/2/2019 9:50:35 AM
                  (modified after loading)
=====
  
```



=====  
 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.119	BV	0.6259	8631.62793	205.12622	49.9469
2	24.453	VB	0.7208	8649.99707	178.04210	50.0531

Totals :                                    1.72816e4    383.16832

**Figure S213.** HPLC spectra of *rac-3al*, related to **Figure 4**.

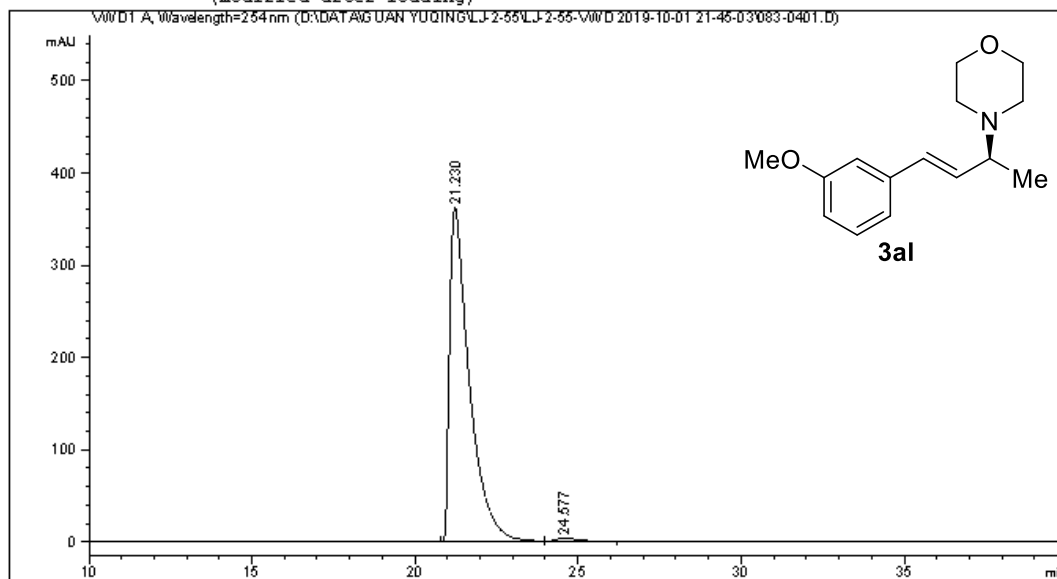


Data File D:\DATA\GUAN YUQING\LJ-2-55\LJ-2-55-VWD 2019-10-01 21-45-03\083-0401.D  
 Sample Name: LJ-2-56-1

```

=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 1                   Location  : Vial 83
Injection Date  : 10/1/2019 10:41:00 PM         Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-55\LJ-2-55-VWD 2019-10-01 21-45-03\VWD-AD(1-2)-99-
                  1-0.5ML-5UL-254NM-40MIN.M
Last changed    : 10/1/2019 10:33:36 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\Y\VWD-AS(1-6)-99-1-1ML-5UL-254NM-35MIN.M
Last changed    : 10/2/2019 9:52:43 AM
                  (modified after loading)
=====
  
```



Area Percent Report

```

=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
=====
  
```

Signal 1: VWD1 A, Wavelength=254 nm

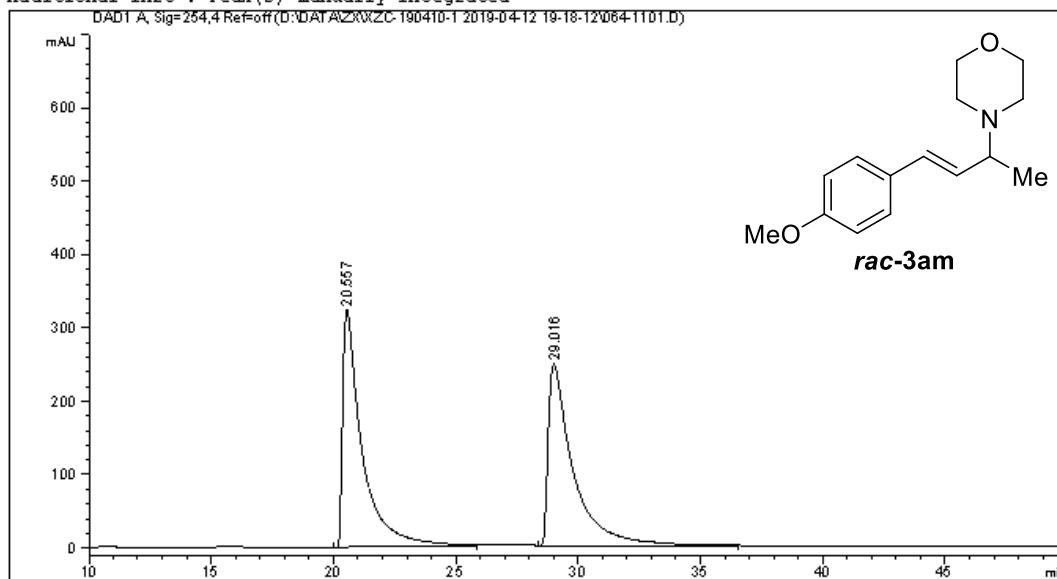
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.230	BB	0.6171	1.52116e4	361.37299	99.2011
2	24.577	BB	0.6320	122.49827	2.78591	0.7989

Totals :                                    1.53341e4    364.15890

Figure S214. HPLC spectra of 3al, related to Figure 4.

Data File D:\DATA\ZX\XZC-190410-1 2019-04-12 19-18-12\064-1101.D  
Sample Name: LJ-133-1

```
=====
Acq. Operator   :                               Seq. Line :   11
Acq. Instrument : Instrument 2                   Location  : Vial 64
Injection Date  : 4/13/2019 1:19:47 AM         Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\ZX\XZC-190410-1 2019-04-12 19-18-12\DAD-0J(1-6)-95-5-1ML-5UL-ALL-60MIN.M
Last changed    : 7/6/2018 10:36:38 PM
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-5UL-ALL-60MIN.M
Last changed    : 4/14/2019 9:57:24 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

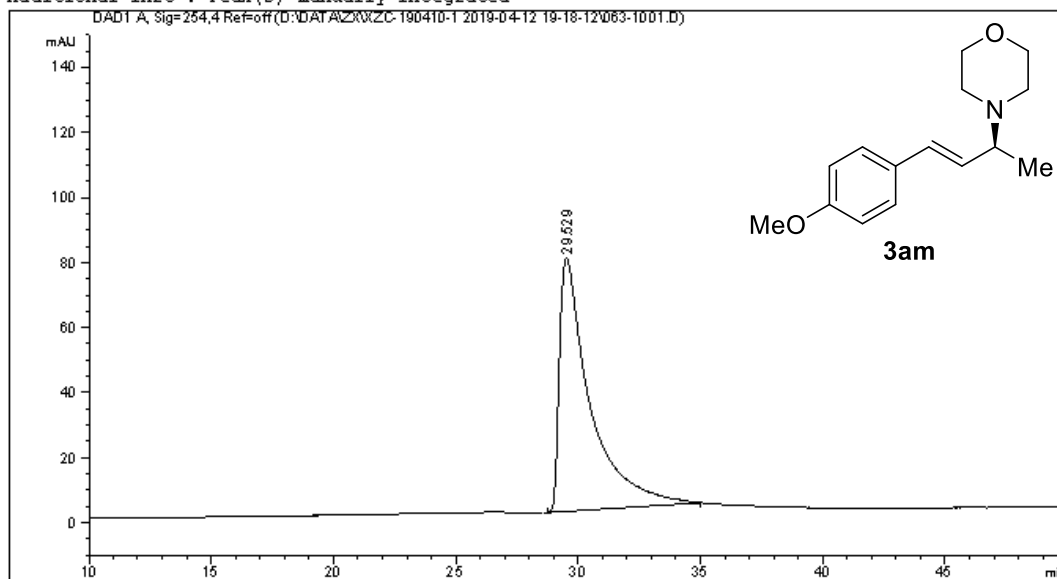
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.557	BB	0.7647	1.77001e4	323.29202	50.1433
2	29.016	BB	0.9701	1.75989e4	247.34940	49.8567

Totals :                                    3.52990e4    570.64142

Figure S215. HPLC spectra of *rac*-3am, related to Figure 4.

Data File D:\DATA\ZX\XZC-190410-1 2019-04-12 19-18-12\063-1001.D  
Sample Name: LJ-132-1

```
=====
Acq. Operator   :                               Seq. Line :   10
Acq. Instrument : Instrument 2                  Location  : Vial 63
Injection Date  : 4/13/2019 12:18:46 AM        Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\ZX\XZC-190410-1 2019-04-12 19-18-12\DAD-0J(1-6)-95-5-1ML-5UL-ALL-60MIN.M
Last changed    : 7/6/2018 10:36:38 PM
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-5UL-ALL-60MIN.M
Last changed    : 4/14/2019 9:58:32 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.529	BB	1.1823	6790.98779	77.80267	100.0000

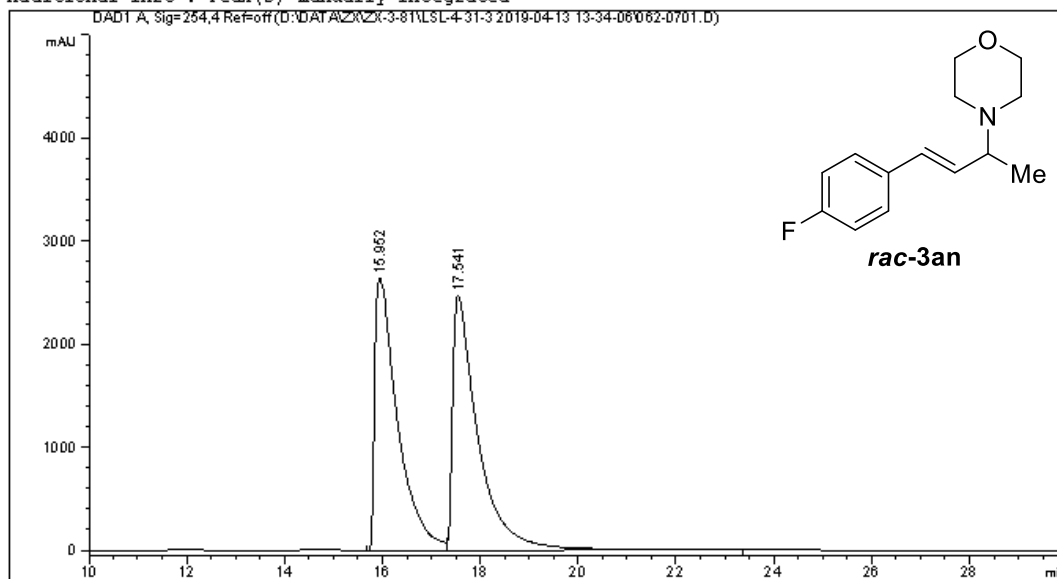
Totals :                    6790.98779    77.80267

Figure S216. HPLC spectra of 3am, related to Figure 4.

Data File D:\DATA\ZX\ZX-3-81\LSL-4-31-3 2019-04-13 13-34-06\062-0701.D  
 Sample Name: LJ-133-2

```

=====
Acq. Operator   :                               Seq. Line :    7
Acq. Instrument : Instrument 2                  Location  : Vial 62
Injection Date  : 4/13/2019 5:51:17 PM        Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\ZX\ZX-3-81\LSL-4-31-3 2019-04-13 13-34-06\DAD-0J(1-6)-95-5-0.5ML-
SUL-ALL-30MIN.M
Last changed    : 4/13/2019 3:13:40 PM
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-SUL-ALL-60MIN.M
Last changed    : 4/14/2019 10:00:29 PM
                (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

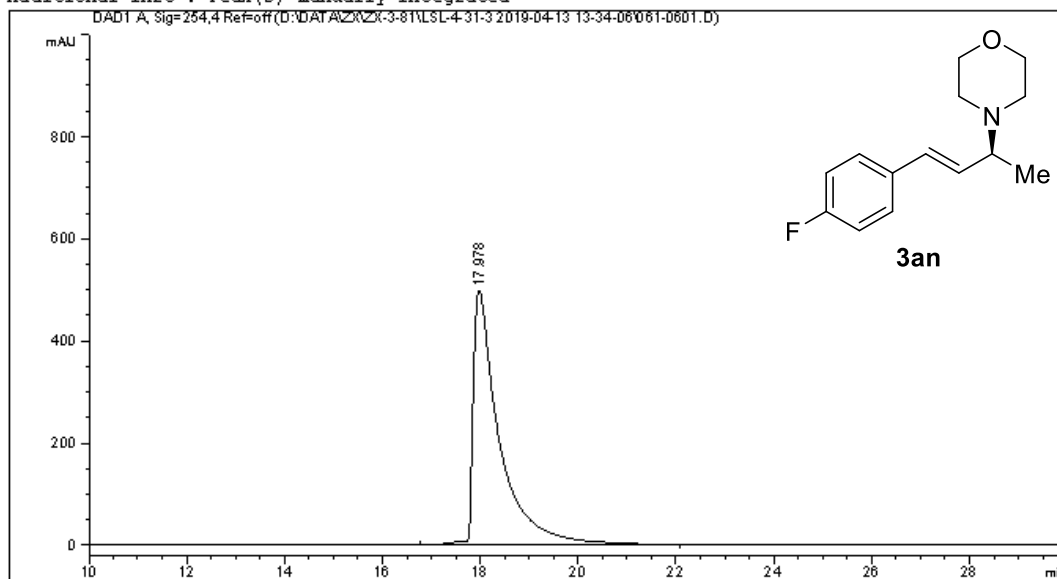
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.952	BV	0.4176	8.50486e4	2641.95483	48.8532
2	17.541	VB	0.4580	8.90417e4	2473.26196	51.1468

Totals :                            1.74090e5   5115.21680

**Figure S217.** HPLC spectra of *rac-3an*, related to **Figure 4**.

Data File D:\DATA\ZX\ZX-3-81\LSL-4-31-3 2019-04-13 13-34-06\061-0601.D  
Sample Name: LJ-132-2

```
=====
Acq. Operator   :                               Seq. Line :    6
Acq. Instrument : Instrument 2                   Location  : Vial 61
Injection Date  : 4/13/2019 5:20:17 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\ZX\ZX-3-81\LSL-4-31-3 2019-04-13 13-34-06\DAD-0J(1-6)-95-5-0.5ML-
                  SUL-ALL-30MIN.M
Last changed    : 4/13/2019 3:13:40 PM
Analysis Method : D:\METHOD\LG\DAD-0J(1-6)-80-20-1ML-SUL-ALL-60MIN.M
Last changed    : 4/14/2019 10:01:44 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

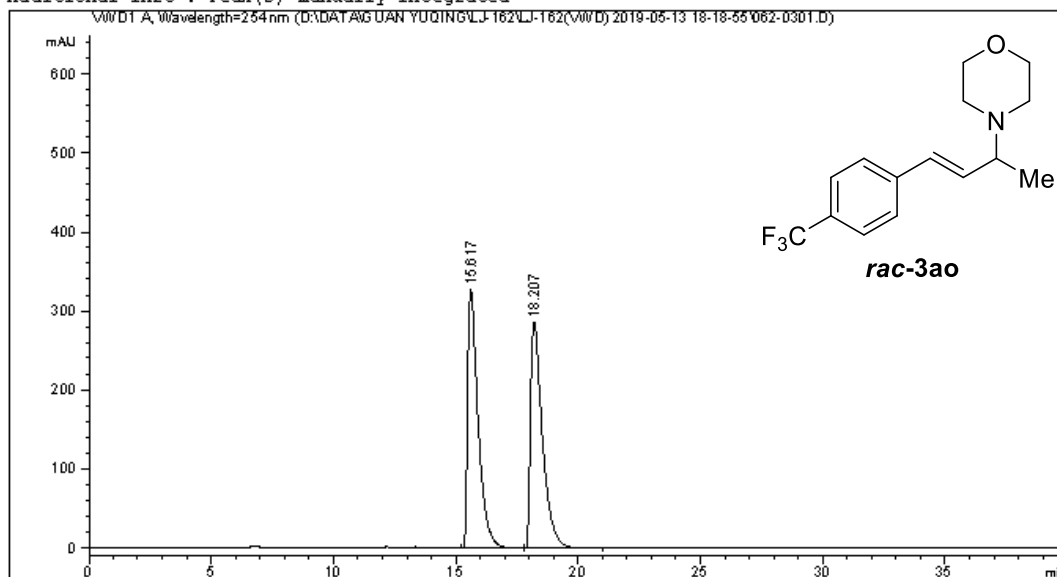
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.978	BB	0.5250	1.86330e4	499.70447	100.0000

Totals :                    1.86330e4   499.70447

**Figure S218.** HPLC spectra of **3an**, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-162\LJ-162(VWD) 2019-05-13 18-18-55\062-0301.D  
Sample Name: LJ-162-1-RAC

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                   Location  : Vial 62
Injection Date  : 5/13/2019 7:11:38 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-162\LJ-162(VWD) 2019-05-13 18-18-55\VWD-AD(1-2)-99-1
                  -0.5ML-5UL-254NM-40MIN.M
Last changed    : 5/13/2019 8:56:49 AM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AD(1-2)-99-1-0.5ML-5UL-254NM-40MIN.M
Last changed    : 5/13/2019 9:42:11 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

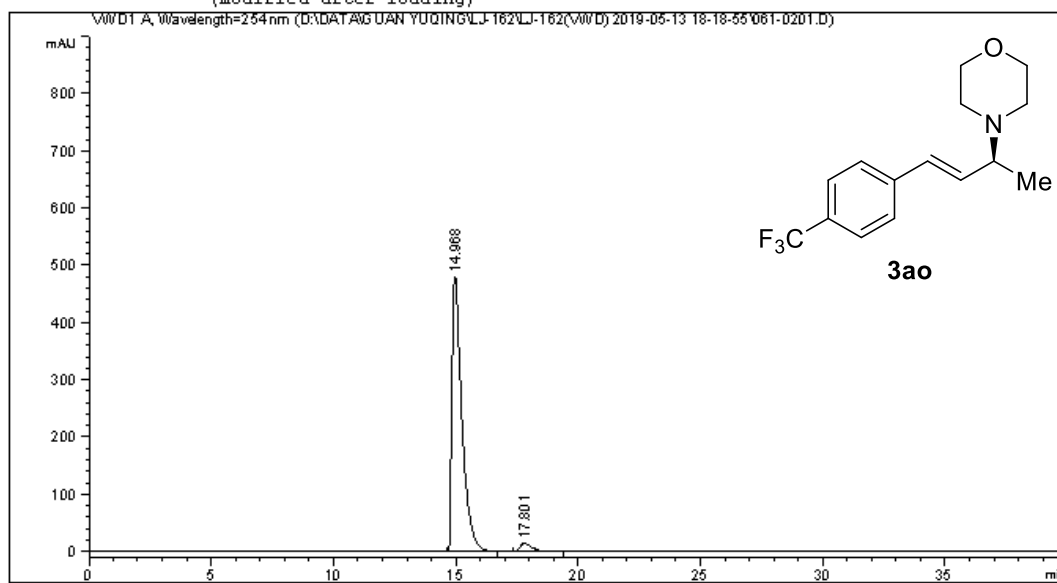
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.617	BB	0.4432	9690.17578	327.45148	49.9852
2	18.207	BB	0.5098	9695.92480	285.80896	50.0148

Totals : 1.93861e4 613.26044

Figure S219. HPLC spectra of *rac-3ao*, related to Figure 4.

Data File D:\DATA\GUAN YUQING\LJ-162\LJ-162(VWD) 2019-05-13 18-18-55\061-0201.D  
Sample Name: LJ-162-1

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 1                  Location  : Vial 61
Injection Date  : 5/13/2019 6:30:45 PM         Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-162\LJ-162(VWD) 2019-05-13 18-18-55\VWD-AD(1-2)-99-1
                  -0.5ML-5UL-254NM-40MIN.M
Last changed    : 5/13/2019 8:56:49 AM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-AD(1-2)-99-1-0.5ML-5UL-254NM-40MIN.M
Last changed    : 5/13/2019 9:43:18 PM
                  (modified after loading)
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.968	BB	0.4240	1.36424e4	480.86911	96.6598
2	17.801	BB	0.5077	471.42413	13.93580	3.3402

Totals :                    1.41138e4   494.80491

Instrument 1 5/13/2019 9:43:23 PM

Page 1 of 1

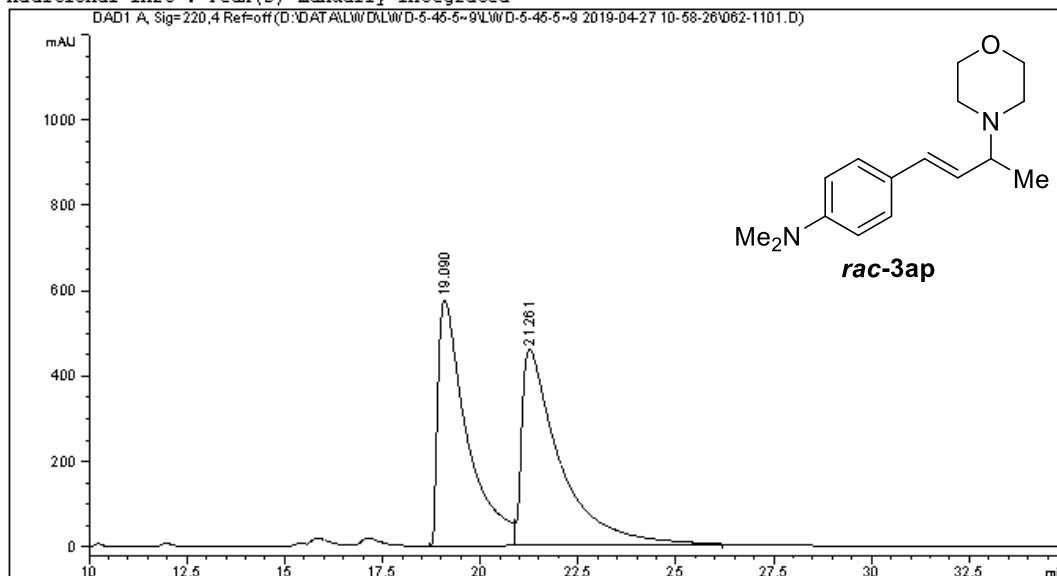
**Figure S220.** HPLC spectra of **3ao**, related to **Figure 4**.

Data File D:\DATA\LWD\LWD-5-45-5~9\LWD-5-45-5~9 2019-04-27 10-58-26\062-1101.D  
 Sample Name: LJ-150-5-RAC

```

=====
Acq. Operator   :                               Seq. Line :   11
Acq. Instrument : Instrument 2                  Location  : Vial 62
Injection Date  : 4/27/2019 3:24:38 PM         Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LWD\LWD-5-45-5~9\LWD-5-45-5~9 2019-04-27 10-58-26\DAD-OD(1-2)-99-1-
0.5ML-SUL-ALL-40MIN.M
Last changed    : 3/8/2019 11:06:52 AM
Analysis Method : D:\DATA\LWD\LWD-5-45-5~9\LWD-5-45-5~9 2019-04-27 10-58-26\DAD-OD(1-2)-99-1-
0.5ML-SUL-ALL-40MIN.M (Sequence Method)
Last changed    : 4/28/2019 6:43:34 PM
                 (modified after loading)
  
```

Additional Info : Peak(s) manually integrated



=====  
 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.090	BV	0.7033	2.94362e4	576.84332	48.6728
2	21.261	VB	0.8915	3.10416e4	458.71768	51.3272

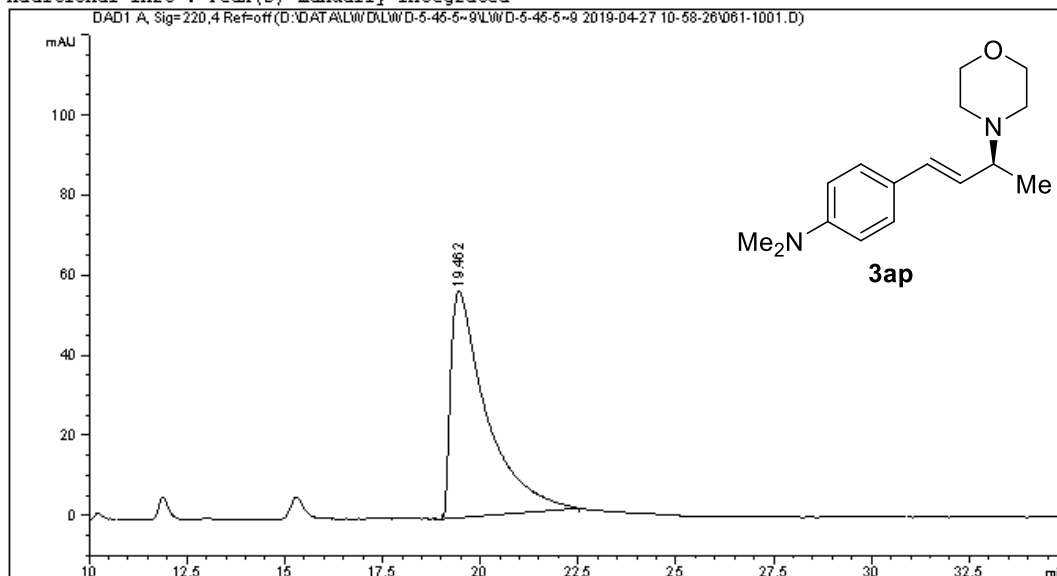
Totals :                    6.04778e4  1035.56100

**Figure S221.** HPLC spectra of *rac-3ap*, related to **Figure 4**.



Data File D:\DATA\LWD\LWD-5-45-5~9\LWD-5-45-5~9 2019-04-27 10-58-26\061-1001.D  
Sample Name: LJ-150-5

```
=====
Acq. Operator   :                               Seq. Line :   10
Acq. Instrument : Instrument 2                   Location  : Vial 61
Injection Date  : 4/27/2019 2:43:37 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\LWD\LWD-5-45-5~9\LWD-5-45-5~9 2019-04-27 10-58-26\DAD-OD(1-2)-99-1-
                  0.5ML-SUL-ALL-40MIN.M
Last changed    : 3/8/2019 11:06:52 AM
Analysis Method : D:\DATA\LWD\LWD-5-45-5~9\LWD-5-45-5~9 2019-04-27 10-58-26\DAD-OD(1-2)-99-1-
                  0.5ML-SUL-ALL-40MIN.M (Sequence Method)
Last changed    : 4/28/2019 6:45:59 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.462	BB	0.7553	3590.59058	56.51189	100.0000

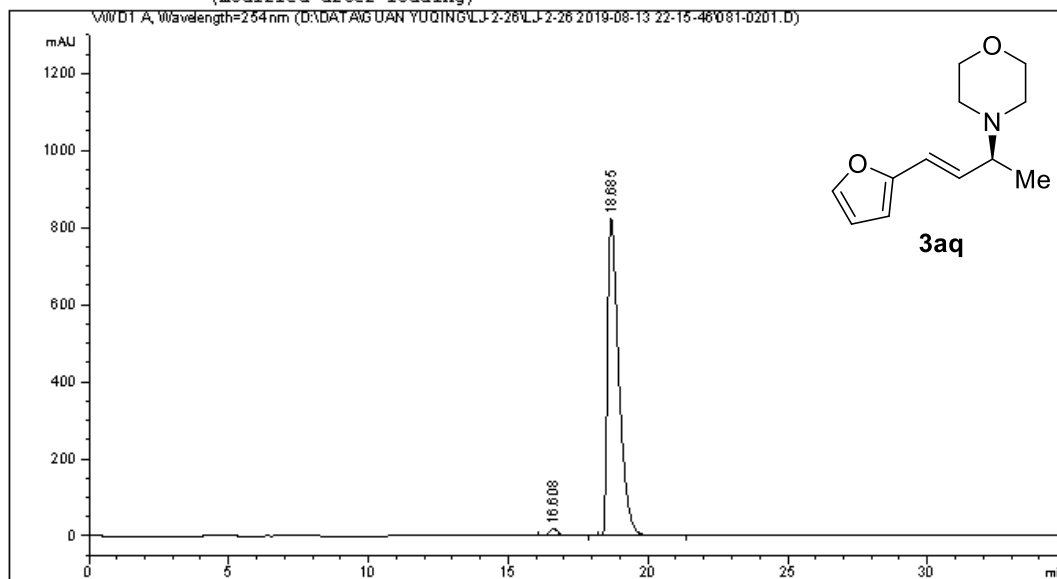
Totals : 3590.59058 56.51189

**Figure S222.** HPLC spectra of **3ap**, related to **Figure 4**.



Data File D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26 2019-08-13 22-15-46\081-0201.D  
Sample Name: LJ-2-26-8

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 1                  Location  : Vial 81
Injection Date  : 8/13/2019 10:31:48 PM       Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-26\LJ-2-26 2019-08-13 22-15-46\WVD-0J(1-2)-95-5-0.
                                                SML-5UL-254NM-40MIN.M
Last changed    : 8/13/2019 10:44:25 PM
                                                (modified after loading)
Analysis Method : D:\METHOD\LG\WVD-AD(1-2)-80-20-1ML-3UL-210NM-60MIN.M
Last changed    : 8/14/2019 10:13:25 AM
                                                (modified after loading)
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.608	BB	0.3357	430.80255	19.50537	1.8249
2	18.685	BB	0.4228	2.31767e4	822.39478	98.1751

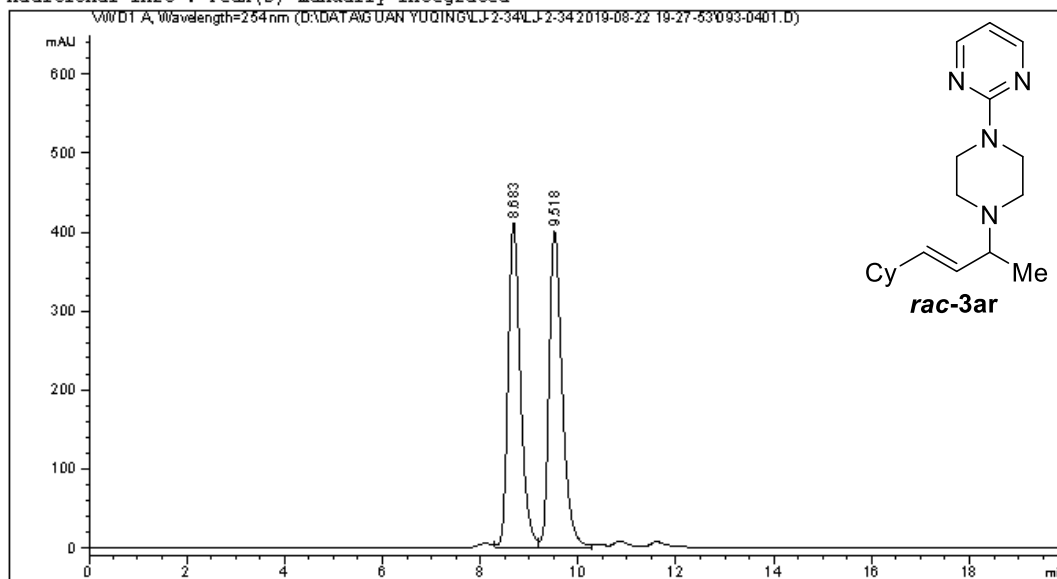
Totals : 2.36075e4 841.90014

**Figure S224.** HPLC spectra of **3aq**, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-2-34\LJ-2-34 2019-08-22 19-27-53\093-0401.D  
 Sample Name: LJ-2-34-RAC

```

=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 1                   Location  : Vial 93
Injection Date  : 8/22/2019 8:06:29 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-34\2019-08-22 19-27-53\WVD-0J(1-2)-95-5-0.
                  SML-5UL-254NM-20MIN.M
Last changed    : 8/22/2019 7:29:22 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\WVD-0J(1-2)-95-5-0.SML-5UL-254NM-20MIN.M
Last changed    : 8/22/2019 8:24:04 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=254 nm

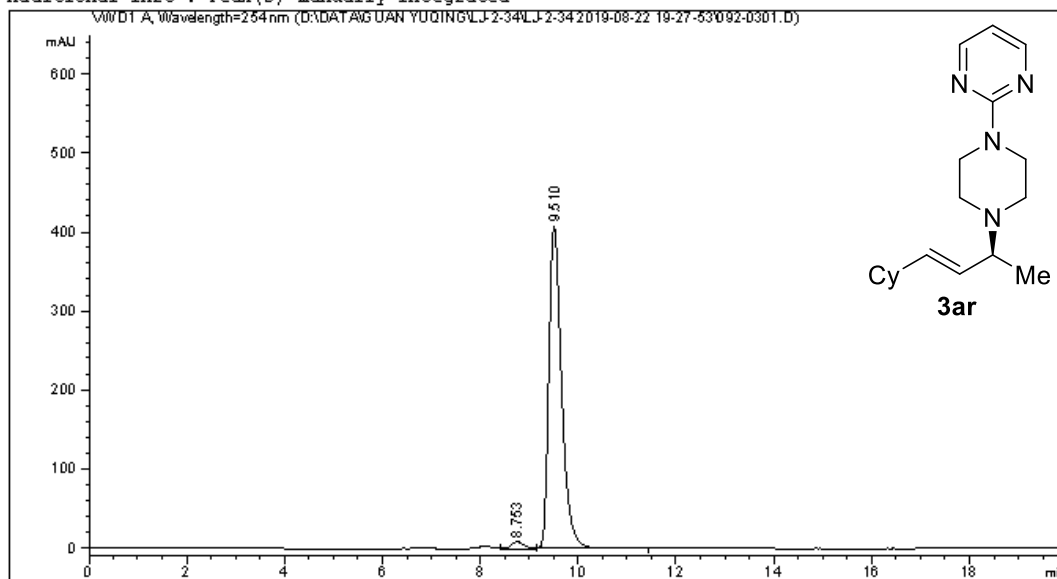
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.683	VV	0.2682	7229.00488	410.94553	49.3700
2	9.518	VV	0.2810	7413.50635	400.48196	50.6300

Totals :                      1.46425e4    811.42749

**Figure S225.** HPLC spectra of *rac-3ar*, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-2-34\LJ-2-34 2019-08-22 19-27-53\092-0301.D  
Sample Name: LJ-2-34

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                   Location  : Vial 92
Injection Date  : 8/22/2019 7:45:39 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-34\2019-08-22 19-27-53\WVD-0J(1-2)-95-5-0.
                  SML-5UL-254NM-20MIN.M
Last changed    : 8/22/2019 7:29:22 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\WVD-0J(1-2)-95-5-0.SML-5UL-254NM-20MIN.M
Last changed    : 8/22/2019 8:24:04 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

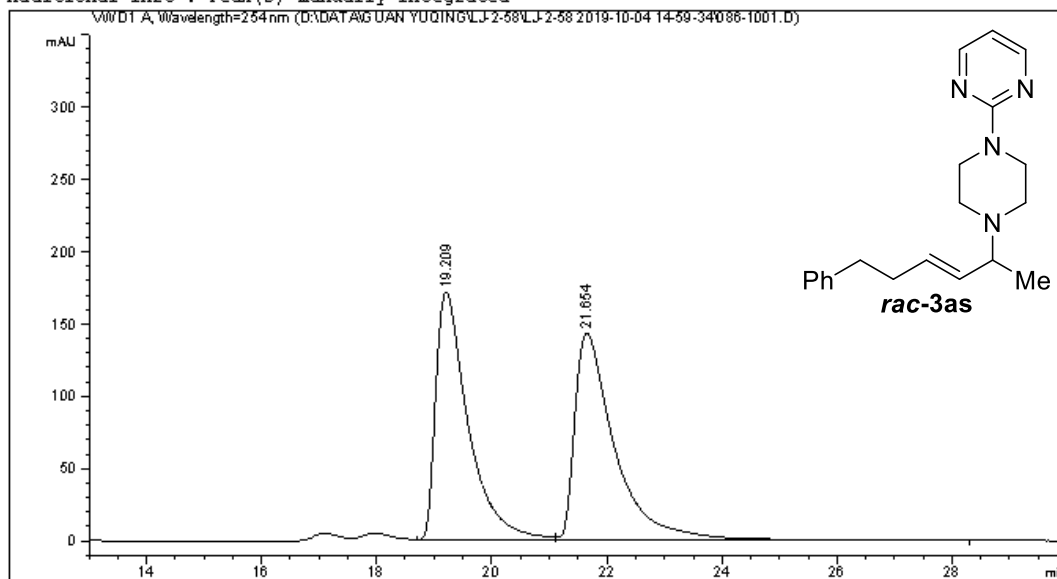
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.753	VV	0.2816	161.11761	8.63663	2.1291
2	9.510	VB	0.2766	7406.44824	408.39880	97.8709

Totals : 7567.56586 417.03543

Figure S226. HPLC spectra of 3ar, related to Figure 4.

Data File D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\086-1001.D  
Sample Name: LJ-2-58-3-RAC

```
=====
Acq. Operator   :                               Seq. Line :   10
Acq. Instrument : Instrument 1                   Location  : Vial 86
Injection Date  : 10/4/2019 6:18:32 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\WVD-OD(1-2)-95-5-0.
                  SML-5UL-254NM-30MIN.M
Last changed    : 10/4/2019 3:08:34 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\WVD-OD(1-2)-95-5-0.SML-5UL-254NM-10MIN.M
Last changed    : 10/4/2019 7:06:32 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.209	BV	0.5768	6710.61328	171.37782	49.2813
2	21.654	VB	0.7120	6906.34668	143.11708	50.7187

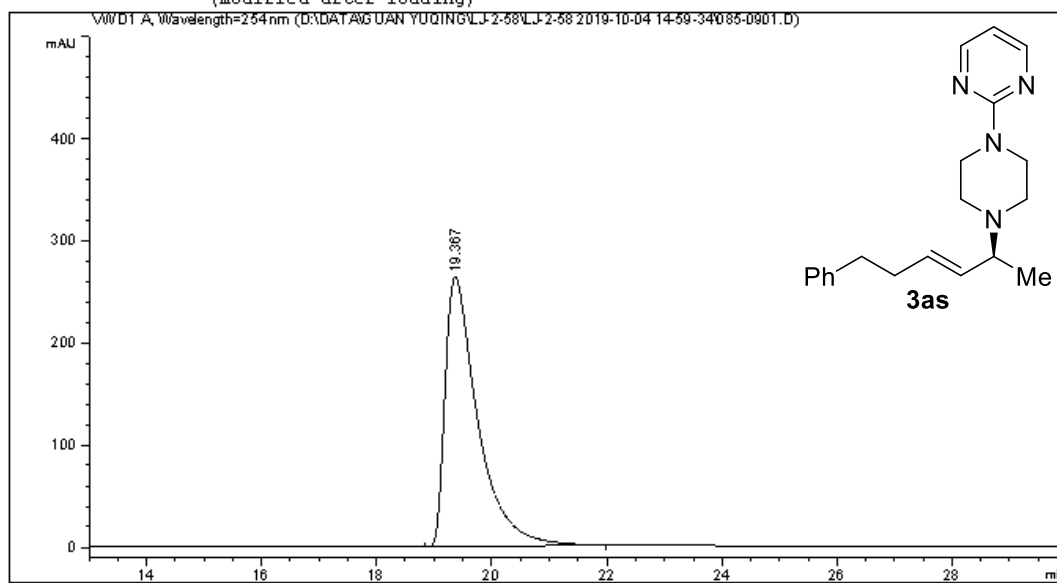
Totals : 1.36170e4 314.49490

Figure S227. HPLC spectra of *rac-3as*, related to Figure 4.

Data File D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\085-0901.D  
Sample Name: LJ-2-58-3

```
=====
Acq. Operator   :                               Seq. Line :    9
Acq. Instrument : Instrument 1                   Location  : Vial 85
Injection Date  : 10/4/2019 5:47:42 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\WVD1-OD(1-2)-95-5-0.
                  SML-5UL-254NM-30MIN.M
Last changed    : 10/4/2019 3:08:34 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\WVD1-OD(1-2)-95-5-0.SML-5UL-254NM-10MIN.M
Last changed    : 10/4/2019 7:07:41 PM
                  (modified after loading)
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```



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Area Percent Report  
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Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.367	BB	0.5810	1.04212e4	264.28088	100.0000

Totals : 1.04212e4 264.28088

=====  
\*\*\* End of Report \*\*\*

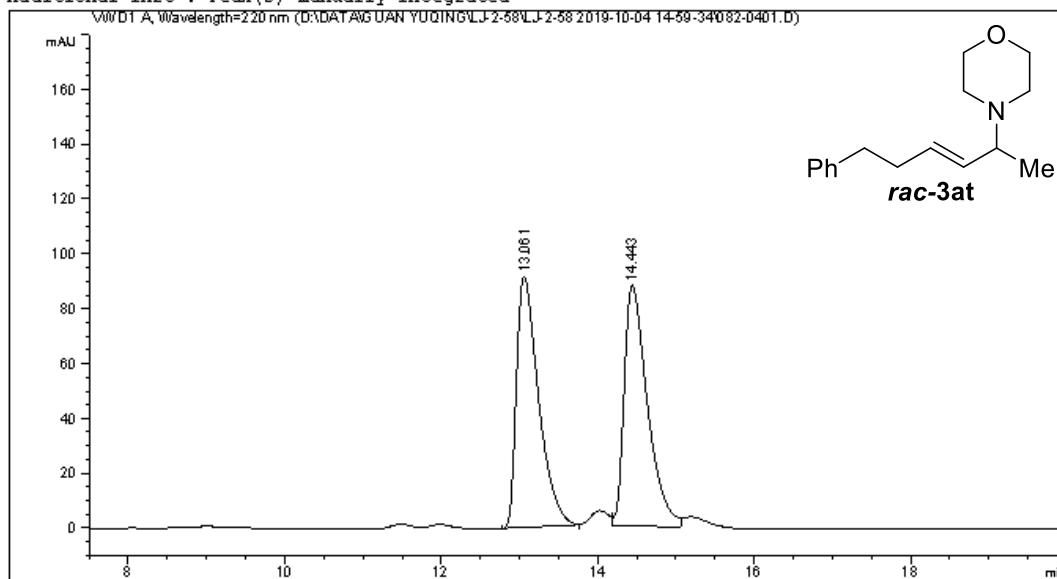
Instrument 1 10/4/2019 7:07:57 PM

Page 1 of 1

**Figure S228.** HPLC spectra of **3as**, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\082-0401.D  
Sample Name: LJ-2-58-1-RAC

```
=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 1                   Location  : Vial 82
Injection Date  : 10/4/2019 3:58:10 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-58\LJ-2-58 2019-10-04 14-59-34\WVD-OJ(1-6)-95-5-0.
                  SML-5UL-220NM-25MIN.M
Last changed    : 10/4/2019 2:55:51 PM
Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\WVD-OD(1-2)-95-5-0.SML-5UL-254NM-10MIN.M
Last changed    : 10/4/2019 6:56:30 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.061	BB	0.2980	1793.32349	91.35478	49.7739
2	14.443	VV	0.3104	1809.61426	87.80449	50.2261

Totals : 3602.93774 179.15927

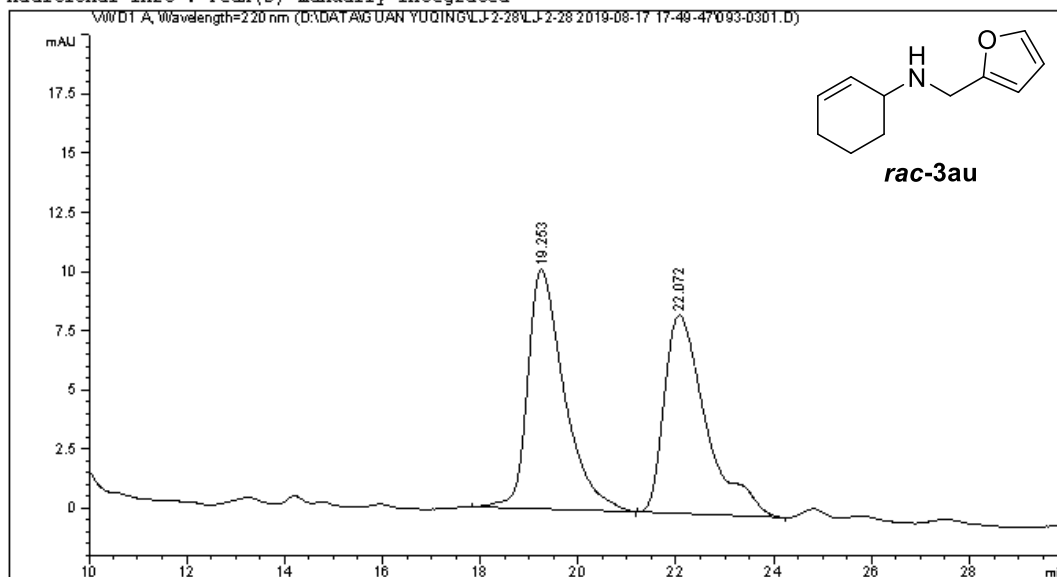
Figure S229. HPLC spectra of *rac-3at*, related to Figure 4.





Data File D:\DATA\GUAN YUQING\LJ-2-28\LJ-2-28 2019-08-17 17-49-47\093-0301.D  
Sample Name: LJ-2-28-RAC

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                   Location  : Vial 93
Injection Date  : 8/17/2019 7:08:37 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-28\2019-08-17 17-49-47\WVD-AS(1-6)-99-1-0.
                  SML-5UL-220NM-60MIN.M
Last changed    : 4/29/2019 8:58:31 AM
Analysis Method : D:\METHOD\LWD\DAD-OD (1-2)-90-10-LML-3ULALL-25MIN.M
Last changed    : 8/19/2019 9:39:21 AM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: WVD1 A, Wavelength=220 nm

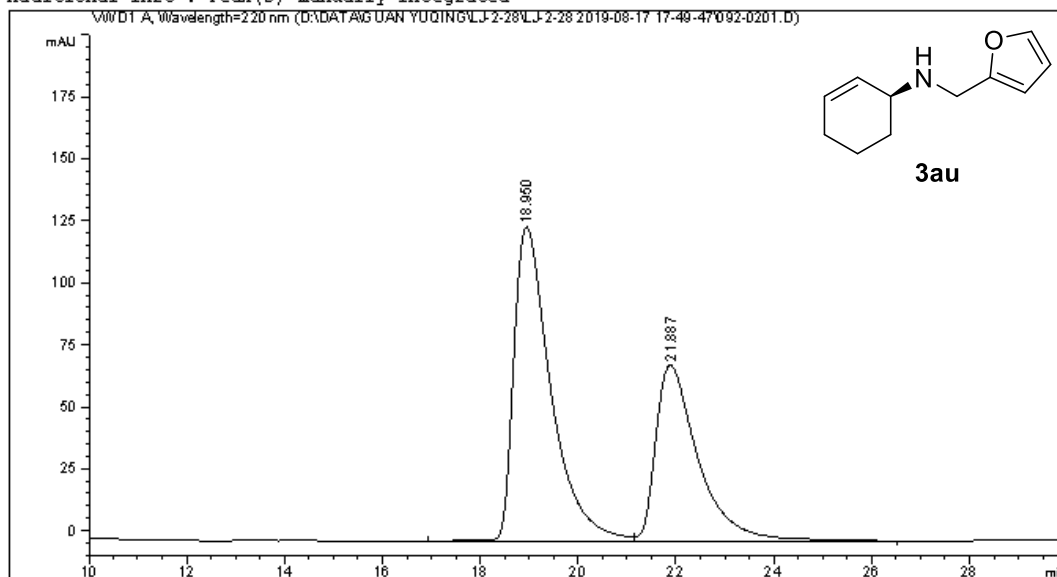
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.253	BB	0.7624	523.16156	10.09827	51.2498
2	22.072	BB	0.8799	497.64478	8.36683	48.7502

Totals :                                   1020.80634   18.46510

**Figure S231.** HPLC spectra of *rac-3au*, related to **Figure 4**.

Data File D:\DATA\GUAN YUQING\LJ-2-28\LJ-2-28 2019-08-17 17-49-47\092-0201.D  
Sample Name: LJ-2-28

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 1                   Location  : Vial 92
Injection Date  : 8/17/2019 6:07:48 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-28 2019-08-17 17-49-47\WVD-AS(1-6)-99-1-0.
                  SML-5UL-220NM-60MIN.M
Last changed    : 4/29/2019 8:58:31 AM
Analysis Method : D:\METHOD\LWD\DAD-OD (1-2)-90-10-1ML-3ULALL-25MIN.M
Last changed    : 8/19/2019 9:41:54 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.950	BV	0.7841	6617.87891	126.55463	60.8880
2	21.887	VB	0.8940	4251.05322	70.85488	39.1120

Totals :                                    1.08689e4    197.40951

Figure S232. HPLC spectra of 3au, related to Figure 4.



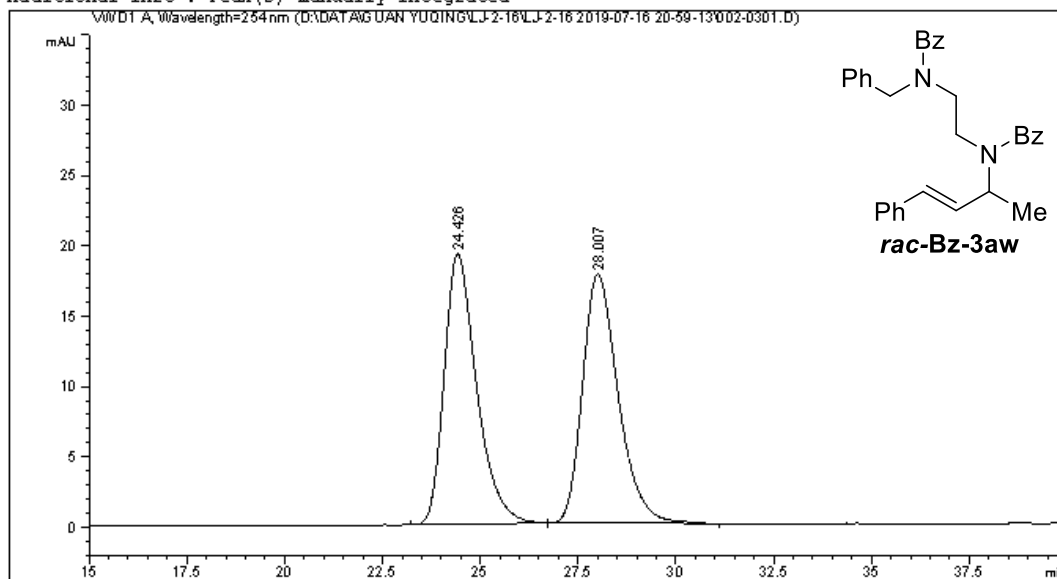


Data File D:\DATA\GUAN YUQING\LJ-2-16\LJ-2-16 2019-07-16 20-59-13\002-0301.D  
 Sample Name: LJ-2-16-RAC

```

=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                   Location  : Vial 2
Injection Date  : 7/16/2019 9:56:06 PM          Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-16\LJ-2-16 2019-07-16 20-59-13\WVD-AD(1-2)-85-15-
                  1ML-5UL-254NM-40MIN.M
Last changed    : 4/17/2019 5:00:46 PM
Analysis Method : D:\METHOD\LSL\DAD-OD(1-2)-97-3-1ML-5UL-ALL-60MIN.M
Last changed    : 7/19/2019 8:11:26 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



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 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.426	BB	0.8642	1106.68665	19.20644	49.6651
2	28.007	BB	0.9601	1121.61011	17.67954	50.3349

Totals :                                    2228.29675    36.88599

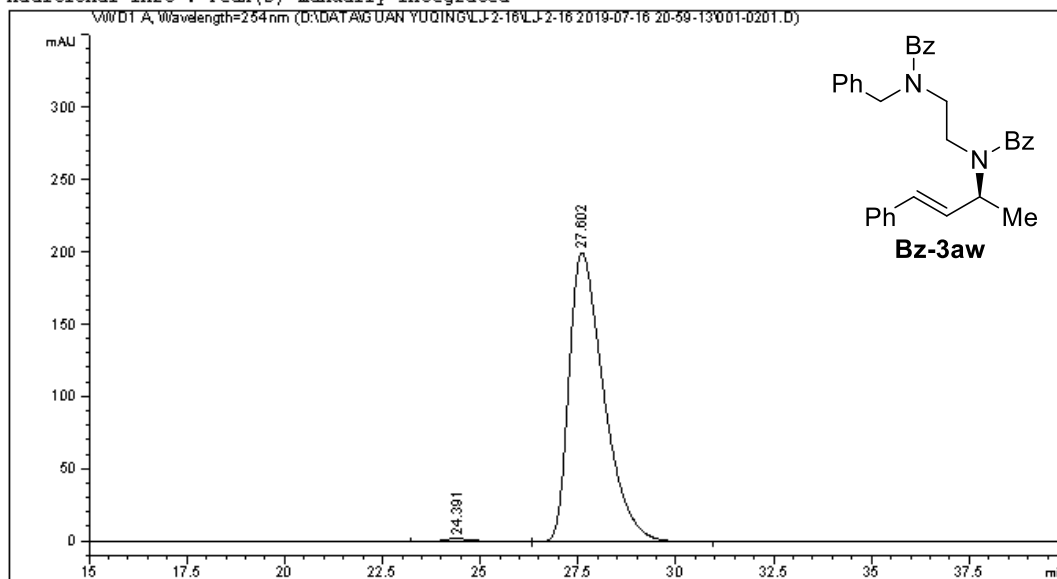
Figure S235. HPLC spectra of *rac-Bz-3aw*, related to Figure 5.

Data File D:\DATA\GUAN YUQING\LJ-2-16\LJ-2-16 2019-07-16 20-59-13\001-0201.D  
 Sample Name: LJ-2-16

```

=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 1                   Location  : Vial 1
Injection Date  : 7/16/2019 9:15:17 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-16\LJ-2-16 2019-07-16 20-59-13\WVD-AD(1-2)-85-15-
                  1ML-5UL-254NM-40MIN.M
Last changed    : 4/17/2019 5:00:46 PM
Analysis Method : D:\METHOD\LSL\DAD-OD(1-2)-97-3-1ML-5UL-ALL-60MIN.M
Last changed    : 7/19/2019 8:13:02 PM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



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 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.391	BB	0.8115	127.46741	2.11982	1.0228
2	27.602	BB	0.9399	1.23356e4	199.90909	98.9772

Totals :                            1.24631e4    202.02891

**Figure S236.** HPLC spectra of **Bz-3aw**, related to **Figure 5**.

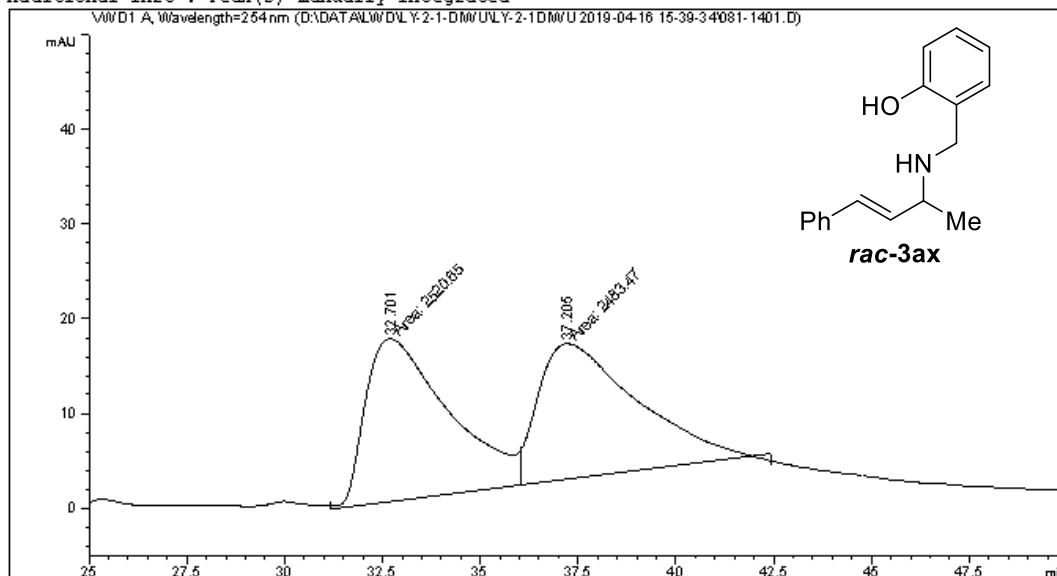
Data File D:\DATA\LWD\LY-2-1-DIWU\LY-2-1DIWU 2019-04-16 15-39-34\081-1401.D  
 Sample Name: LJ-137-6-RAC

```

=====
Acq. Operator   :                               Seq. Line :   14
Acq. Instrument : Instrument 1                   Location  : Vial 81
Injection Date  : 4/16/2019 8:39:31 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\LWD\LY-2-1-DIWU\LY-2-1DIWU 2019-04-16 15-39-34\VWD-AD(1-2)-99-1-0.
                  SML-5UL-254NM-60MIN.M
Last changed    : 4/16/2019 4:38:17 PM
Analysis Method : D:\DATA\LWD\LY-2-1-DIWU\LY-2-1DIWU 2019-04-16 15-39-34\VWD-AD(1-2)-99-1-0.
                  SML-5UL-254NM-60MIN.M (Sequence Method)
Last changed    : 4/17/2019 8:04:38 PM
                  (modified after loading)
  
```

Additional Info : Peak(s) manually integrated



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 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.701	MF	2.4469	2520.65356	17.16935	50.3716
2	37.205	FM	2.8903	2483.46680	14.32087	49.6284

Totals :                    5004.12036    31.49022

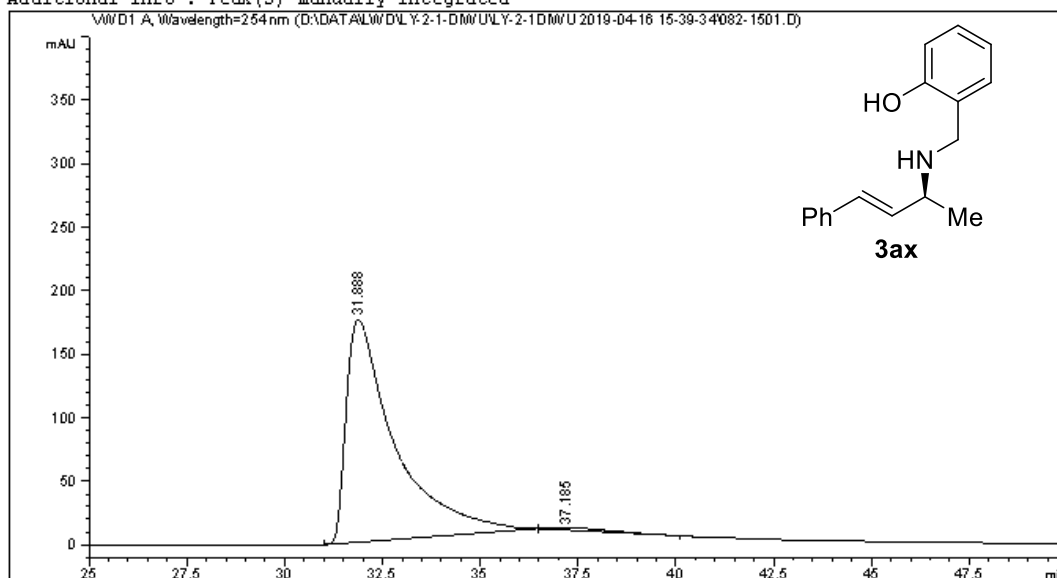
**Figure S237.** HPLC spectra of *rac-3ax*, related to **Figure 5**.



Data File D:\DATA\LWD\LY-2-1-DIWU\LY-2-1DIWU 2019-04-16 15-39-34\082-1501.D  
Sample Name: LJ-137-6

```
=====
Acq. Operator   :                               Seq. Line :   15
Acq. Instrument : Instrument 1                   Location  : Vial 82
Injection Date  : 4/16/2019 9:40:22 PM          Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\LWD\LY-2-1-DIWU\LY-2-1DIWU 2019-04-16 15-39-34\VWD-AD(1-2)-99-1-0.
                  SML-5UL-254NM-60MIN.M
Last changed    : 4/16/2019 4:38:17 PM
Analysis Method : D:\DATA\LWD\LY-2-1-DIWU\LY-2-1DIWU 2019-04-16 15-39-34\VWD-AD(1-2)-99-1-0.
                  SML-5UL-254NM-60MIN.M (Sequence Method)
Last changed    : 4/17/2019 8:07:01 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WVD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.888	BB	1.2270	1.51677e4	175.21049	98.5994
2	37.185	BB	1.4597	215.46088	1.73517	1.4006

Totals : 1.53832e4 176.94567

**Figure S238.** HPLC spectra of **3ax**, related to **Figure 5**.

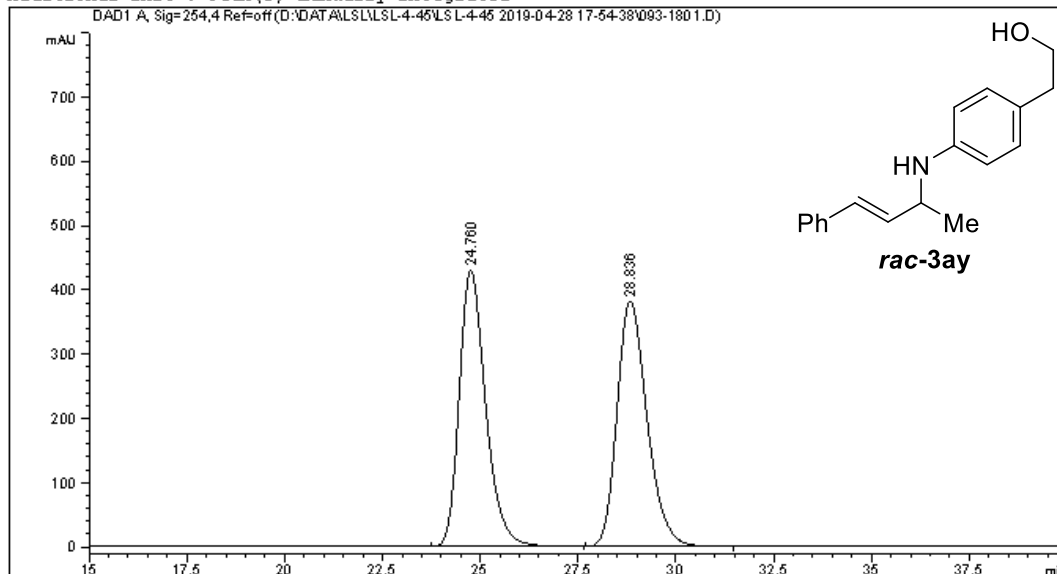
Data File D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\093-1801.D  
 Sample Name: LJ-148-4-RAC

```

=====
Acq. Operator   :                               Seq. Line :   18
Acq. Instrument : Instrument 2                   Location  : Vial 93
Injection Date  : 4/29/2019 4:26:23 AM          Inj       :    1
                                                    Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\DAD-OD(1-2)-80-20-0.5ML-
                  SUL-ALL-45MIN.M
Last changed    : 4/28/2019 10:10:52 PM
Analysis Method : D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\DAD-OD(1-2)-80-20-0.5ML-
                  SUL-ALL-45MIN.M (Sequence Method)
Last changed    : 5/3/2019 5:44:15 PM
                  (modified after loading)
  
```

Additional Info : Peak(s) manually integrated



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 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.760	BB	0.7097	2.01640e4	429.50250	49.8858
2	28.836	BB	0.8000	2.02563e4	381.19202	50.1142

Totals :                    4.04203e4    810.69452

**Figure S239.** HPLC spectra of *rac-3ay*, related to **Figure 5**.

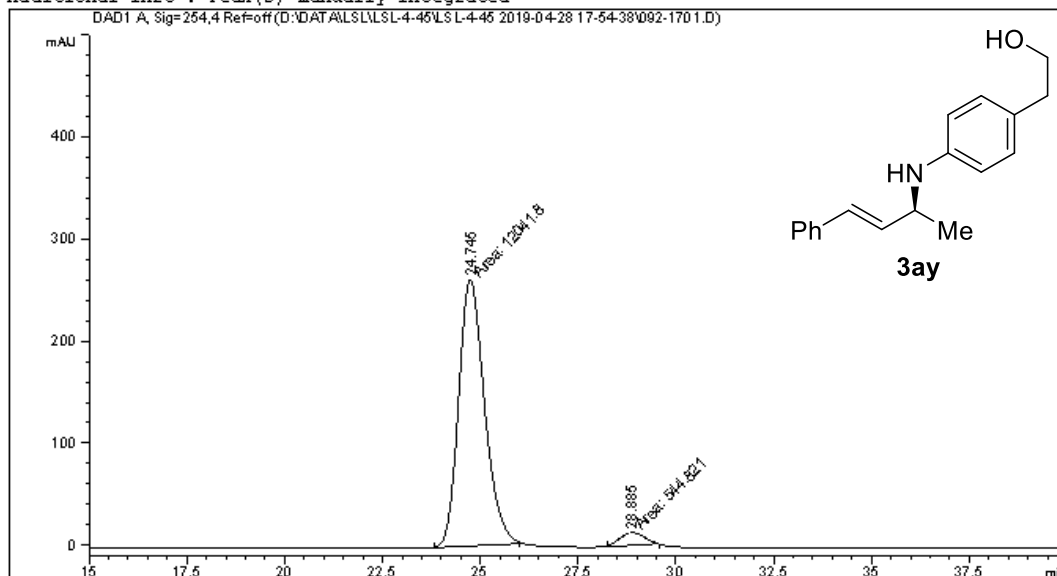
Data File D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\092-1701.D  
 Sample Name: LJ-148-4

```

=====
Acq. Operator   :                               Seq. Line :   17
Acq. Instrument : Instrument 2                 Location  : Vial 92
Injection Date  : 4/29/2019 3:40:21 AM        Inj       :    1
                                                Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\DAD-OD(1-2)-80-20-0.5ML-
SUL-ALL-45MIN.M
Last changed    : 4/28/2019 10:10:52 PM
Analysis Method : D:\DATA\LSL\LSL-4-45\LSL-4-45 2019-04-28 17-54-38\DAD-OD(1-2)-80-20-0.5ML-
SUL-ALL-45MIN.M (Sequence Method)
Last changed    : 5/3/2019 5:46:15 PM
                  (modified after loading)
  
```

Additional Info : Peak(s) manually integrated



Area Percent Report

```

=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.745	MM	0.7688	1.20418e4	261.04971	95.6714
2	28.885	MM	0.7354	544.82092	12.34704	4.3286

Totals : 1.25866e4 273.39676

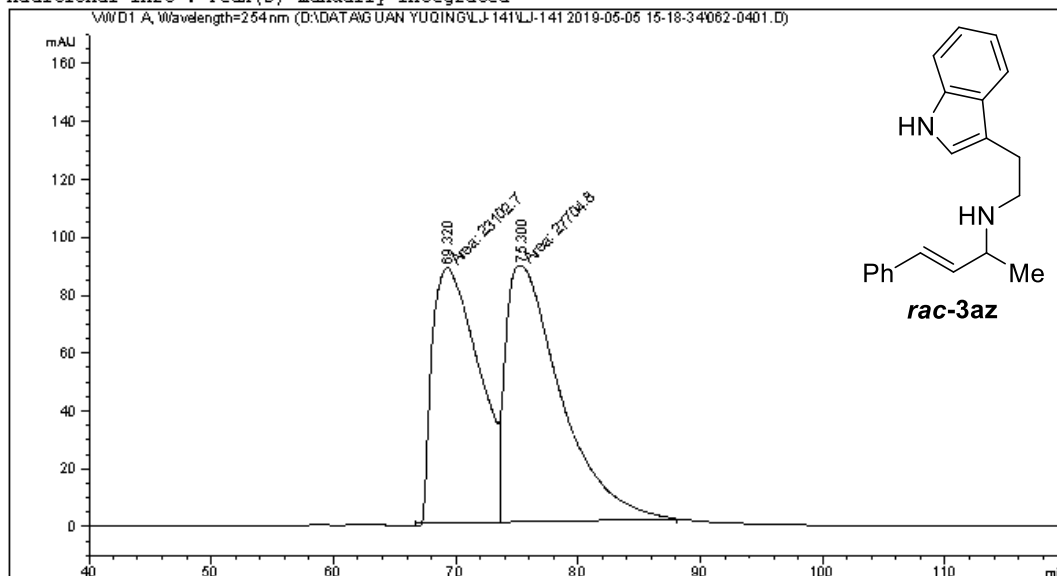
Figure S240. HPLC spectra of 3ay, related to Figure 5.

Data File D:\DATA\GUAN YUQING\LJ-141\LJ-141 2019-05-05 15-18-34\062-0401.D  
 Sample Name: LJ-143-2

```

=====
Acq. Operator   :                               Seq. Line :    4
Acq. Instrument : Instrument 1                   Location  : Vial 62
Injection Date  : 5/5/2019 5:42:09 PM           Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-141\LJ-141 2019-05-05 15-18-34\VWD-AS(1-6)-99-1-0.
                  SML-5UL-254NM-80MIN.M
Last changed    : 5/5/2019 3:41:41 PM
                  (modified after loading)
Analysis Method : D:\METHOD\YANG JIAXIN\VWD-IA-(1-2)-85-15-1.0ML-5UL-210NM-60MIN.M
Last changed    : 5/31/2019 8:42:20 PM
                  (modified after loading)
  
```

Additional Info : Peak(s) manually integrated



Area Percent Report

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: WVD1 A, Wavelength=254 nm

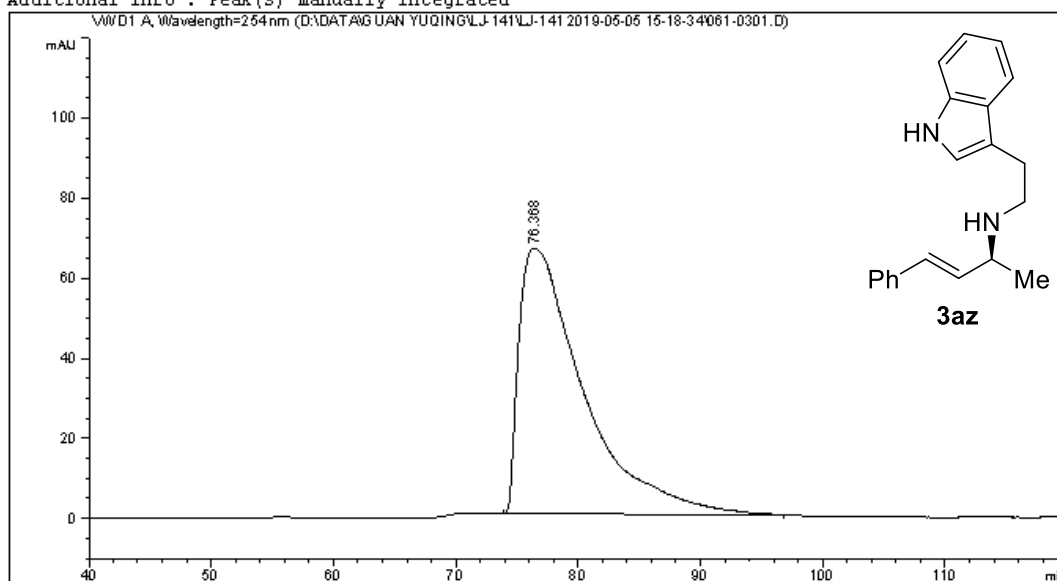
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	69.320	MF	4.3691	2.31027e4	88.12956	45.4710
2	75.300	FM	5.2276	2.77048e4	88.32815	54.5290

Totals :                    5.08076e4    176.45771

Figure S241. HPLC spectra of *rac-3az*, related to Figure 5.

Data File D:\DATA\GUAN YUQING\LJ-141\LJ-141 2019-05-05 15-18-34\061-0301.D  
Sample Name: LJ-141-2

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                  Location  : Vial 61
Injection Date  : 5/5/2019 3:41:19 PM          Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-141\LJ-141 2019-05-05 15-18-34\VWD-AS(1-6)-99-1-0.
                                                SML-5UL-254NM-80MIN.M
Last changed    : 5/5/2019 3:41:41 PM
                                                (modified after loading)
Analysis Method : D:\DATA\GUAN YUQING\LJ-141\LJ-141 2019-05-05 15-18-34\VWD-AS(1-6)-99-1-0.
                                                SML-5UL-254NM-80MIN.M (Sequence Method)
Last changed    : 5/6/2019 10:41:26 AM
                                                (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
```



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Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	76.368	BB	4.3045	2.42250e4	66.24274	100.0000
Totals :				2.42250e4	66.24274	

Instrument 2 5/6/2019 10:41:37 AM

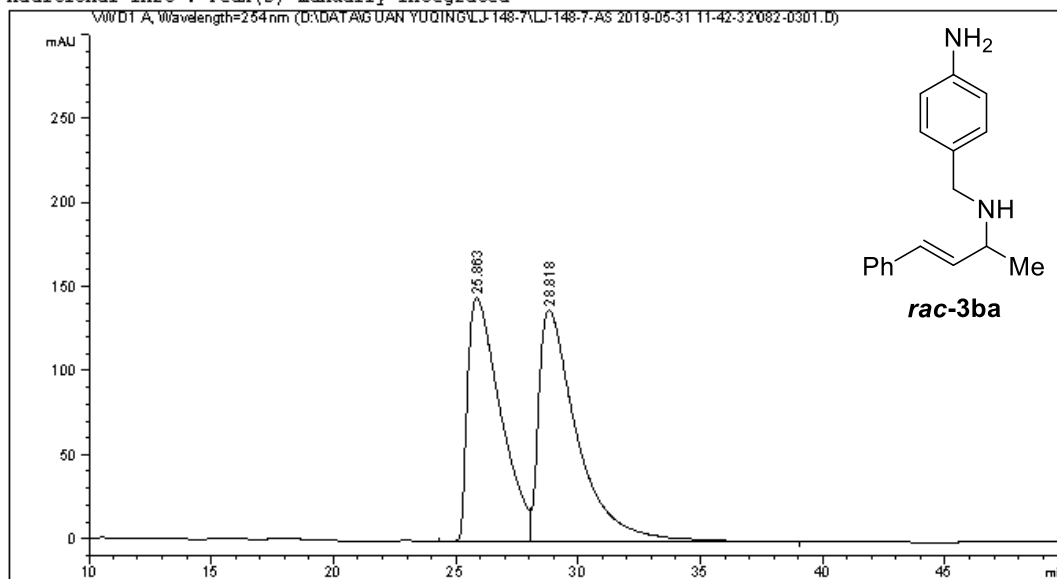
Page 1 of 2

Figure S242. HPLC spectra of 3az, related to Figure 5.

Data File D:\DATA\GUAN YUQING\LJ-148-7\LJ-148-7-AS 2019-05-31 11-42-32\082-0301.D  
Sample Name: LJ-148-7-RAC

```
=====
Acq. Operator   :                               Seq. Line :    3
Acq. Instrument : Instrument 1                  Location  : Vial 82
Injection Date  : 5/31/2019 12:55:10 PM        Inj       :    1
                                           Inj Volume: 5.000 µl

Acq. Method     : D:\DATA\GUAN YUQING\LJ-148-7\LJ-148-7-AS 2019-05-31 11-42-32\VWD-AS(1-6)-90
                  -10-0.5ML-SUL-254NM-60MIN.M
Last changed    : 5/30/2019 9:54:14 PM
Analysis Method : D:\METHOD\YANG JIAXIN\VWD-IA-(1-2)-85-15-1.0ML-SUL-210NM-60MIN.M
Last changed    : 5/31/2019 8:06:48 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

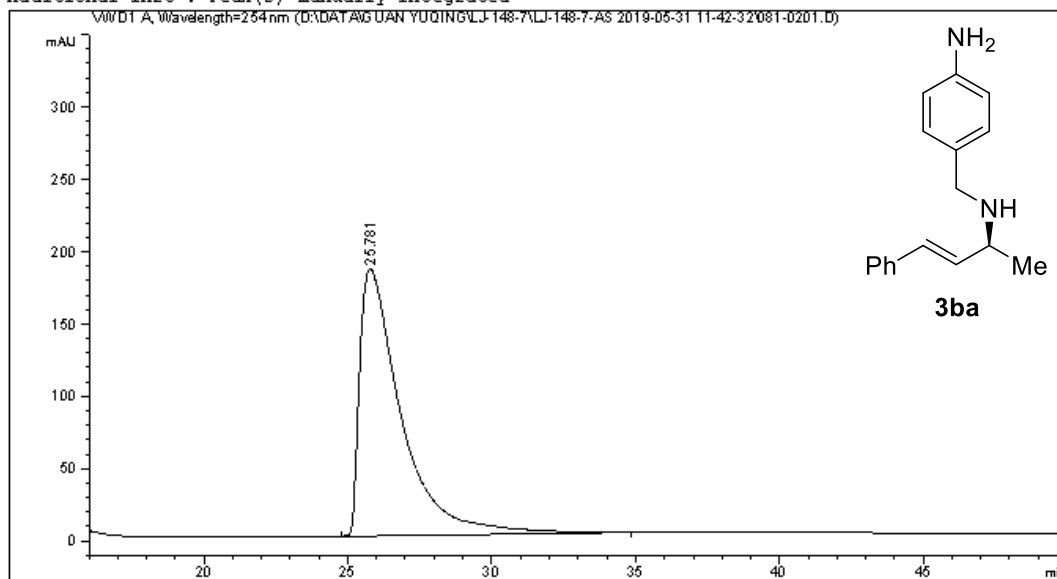
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.863	BV	1.3984	1.34952e4	145.05293	47.2055
2	28.818	VB	1.5954	1.50930e4	137.95860	52.7945

Totals :                                    2.85882e4    283.01154

Figure S243. HPLC spectra of *rac-3ba*, related to Figure 5.

Data File D:\DATA\GUAN YUQING\LJ-148-7\LJ-148-7-AS 2019-05-31 11-42-32\081-0201.D  
Sample Name: LJ-148-7

```
=====
Acq. Operator   :                               Seq. Line :    2
Acq. Instrument : Instrument 1                   Location  : Vial 81
Injection Date  : 5/31/2019 11:54:19 AM         Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-148-7\LJ-148-7-AS 2019-05-31 11-42-32\VWD-AS(1-6)-90
                  -10-0.5ML-5UL-254NM-60MIN.M
Last changed    : 5/30/2019 9:54:14 PM
Analysis Method : D:\METHOD\YANG JIAXIN\VWD-IA-(1-2)-85-15-1.0ML-5UL-210NM-60MIN.M
Last changed    : 5/31/2019 8:09:16 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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Totals :                    1.84618e4   184.20869

Figure S244. HPLC spectra of 3ba, related to Figure 5.

## Transparent Methods

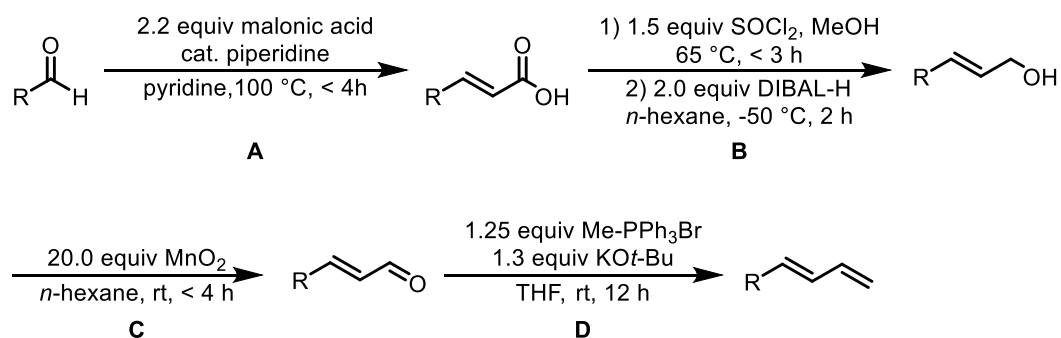
### General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers (Energy Chemical, Adamas-beta®, J&K and so on) and used without further purification. All reactions were performed under a dry argon atmosphere fitted on a glass tube or vial unless otherwise specified. All new compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{19}\text{F}$  NMR and HRMS. The known compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR data were recorded with Bruker 400 MHz with TMS as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, br = broad), coupling constants and integration. All chemical shifts ( $\delta$ ) were reported in ppm and coupling constants ( $J$ ) in Hz. All chemical shifts were reported relative to TMS (0.00 ppm) for  $^1\text{H}$  NMR,  $\text{CDCl}_3$  (77.00 ppm) for  $^{13}\text{C}$  NMR, respectively. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. GC-MS spectra were recorded on a Varian GC-MS 3900 - 2100 T. GC analysis was performed on an Agilent 7890B gas chromatograph with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.). Optical rotation was determined using a Perkin Elmer 343 polarimeter. HPLC analysis was conducted on an Agilent 1260 Series instrument. Column Chromatography was performed with silica gel Merck 60 (300-400 mesh). Purification of the product amine were performed on deactivated silica gel. The deactivated silica gel was prepared by washing the silica gel with petroleum ether/triethylamine (20:1 v/v) prior to purification.

### General Procedures for the Synthesis of Conjugated Dienes

Dienes **1a-1i** were prepared from commercially available cinnamic acids or cinnamaldehydes, the following scheme shows general procedures (Preuß et al, 2013; Sardini & Brown, 2017):

**Scheme S1** (related to **Figure 4**):



**Step A:** A mixture of aldehyde (125 mmol, 1.0 equiv) and malonic acid (28.7 g, 275 mmol, 2.2 equiv) was suspended in 65 mL pyridine. Piperidine (2.0 mL) was added and the mixture was



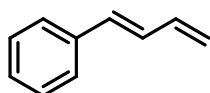
heated to 100 °C until no more gas formation was observed through a gas-washing bottle. The reaction mixture was then poured into ice-cold aqueous HCl solution (2 M, 500 mL) under continuous stirring. The pH-value was checked and adjusted with additional aqueous HCl solution to be strong acidic. The resulting suspension was filtered and the solid cinnamic acid was washed with aqueous HCl (2 M) until no basic reaction of the filtrate was observed. The cinnamic acid was obtained as a white solid which was dried under reduced pressure.

**Step B:** The cinnamic acid (50 mmol, 1.0 equiv) was suspended in 100 mL MeOH (2 mL *per* mmol acid) and SOCl<sub>2</sub> (5.4 mL, 75 mmol, 1.5 equiv) was added. The reaction mixture was heated to 65 °C for 2 h. Subsequently, the MeOH was removed under reduced pressure and the resulting solid was dissolved in dry *n*-hexane under an atmosphere of N<sub>2</sub>. The solution was cooled to -50 °C and a solution of DIBAL-H in *n*-hexane (1 M, 100 mL, 100 mmol, 2.0 equiv) was added slowly. After complete addition, the reaction mixture was stirred for 2.5 h at -50 °C. Then 10 mL MeOH and 50 mL aqueous NaHCO<sub>3</sub> solution were added slowly and the mixture was allowed to reach room temperature. The resulting slurry was carefully acidified with aqueous HCl (1 M) until all solid was dissolved. The layers were separated and the aqueous layer was extracted with *n*-hexane (3×100 mL). The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and the solvents were removed under reduced pressure.

**Step C:** The resulting crude allylic alcohol was dissolved in 400 mL *n*-hexane. Then manganese dioxide (65.2 g, 750 mmol, 20.0 equiv) was added and the reaction mixture was stirred under an atmosphere of N<sub>2</sub>. The progress of the reaction was monitored by thin layer chromatography and after complete conversion, the reaction mixture was filtered through silica gel. The solid residue was washed with EtOAc and the solvent was removed under reduced pressure. Finally, the crude product was purified by flash column chromatography to give the corresponding cinnamaldehyde.

**Step D:** To a flame-dried round bottom flask was added phosphonium (1.25 equiv) and KO<sup>t</sup>Bu (1.3 equiv). The flask was evacuated and backfilled with N<sub>2</sub> three times. THF (0.25 M) was then added via syringe. The solution was allowed to stir at ambient temperature for 30 min before adding aldehyde (1.0 equiv) dropwise over 10 minutes. The reaction was then allowed to stir at room temperature for 12 h. The reaction was then quenched with 100 mL saturated NH<sub>4</sub>Cl solution, and the aqueous layer was extracted with diethyl ether (3×100 mL). The combined organic extracts were washed with brine (1×100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and gravity filtered. The solvent was removed under reduced pressure, and the crude product was purified via silica gel column chromatography to give the desired diene.

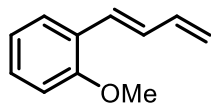
**(E)-buta-1,3-dien-1-ylbenzene (1a)** (Preuß et al, 2013): colorless liquid, 88% yield, step D. <sup>1</sup>H



NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.39 (m, 2H), 7.34-7.29 (m, 2H), 7.25-7.20 (m, 1H), 6.82-6.75 (m, 1H), 6.58-6.46 (m, 2H), 5.36-5.31 (m, 1H), 5.19-5.16

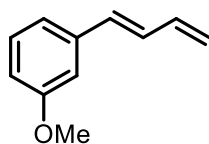
(m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.2, 137.1, 132.8, 129.6, 128.6, 127.6, 126.4, 117.6 ppm.

**(E)-1-(buta-1,3-dien-1-yl)-2-methoxybenzene (1b)** (Davenport & Fernandez, 2018): colorless



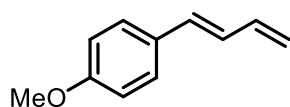
liquid, 80% yield, step D.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (dd,  $J = 7.7$ , 1.7 Hz, 1H), 7.24-7.19 (m, 1H), 6.94-6.77 (m, 4H), 6.54 (dt,  $J = 16.9$ , 10.1 Hz, 1H), 5.33-5.28 (m, 1H), 5.15-5.12 (m, 1H), 3.85 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 137.9, 130.2, 128.6, 127.6, 126.4, 126.0, 120.6, 117.0, 110.8, 55.4 ppm.

**(E)-1-(buta-1,3-dien-1-yl)-3-methoxybenzene (1c)** (Preuß et al, 2013): colorless solid, 41%



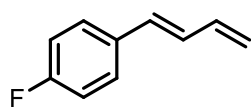
yield, steps A-D.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.21 (m, 1H), 7.01-6.99 (m, 1H), 6.94 (dd,  $J = 2.6$ , 1.6 Hz, 1H), 6.81-6.74 (m, 2H), 6.56-6.45 (m, 2H), 5.36-5.31 (m, 1H), 5.19-5.16 (m, 1H), 3.82 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 138.6, 137.1, 132.7, 129.9, 129.5, 119.2, 117.8, 113.4, 111.6, 55.19 ppm.

**(E)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (1d)** (Preuß et al, 2013): colorless solid, 85%



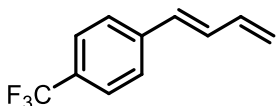
yield, step D.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.33 (m, 2H), 6.88-6.84 (m, 2H), 6.70-6.64 (m, 1H), 6.53-6.44 (m, 2H), 5.28 (d,  $J = 16.0$  Hz, 1H), 5.11 (d,  $J = 8.5$  Hz, 1H), 3.81 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 137.3, 132.4, 129.9, 127.6, 116.5, 114.0, 55.3 ppm.

**(E)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (1e)** (Hu et al, 2018): colorless liquid, 90% yield,



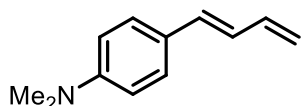
step D.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.34 (m, 2H), 7.03-6.97 (m, 2H), 6.73-6.66 (m, 1H), 6.53-6.43 (m, 2H), 5.32 (d,  $J = 15.6$  Hz, 1H), 5.17 (d,  $J = 9.2$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3 (d,  $J = 247.2$  Hz), 136.9, 133.2 (d,  $J = 3.4$  Hz), 131.5, 129.3 (d,  $J = 2.4$  Hz), 127.9 (d,  $J = 8.0$  Hz), 117.7, 115.5 (d,  $J = 21.7$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.18 ppm.

**(E)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (1f)** (Adamson & Malcolmson, 2017):

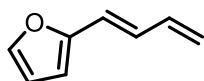


colorless liquid, 28% overall yield, steps B-D.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.55 (m, 2H), 7.49-7.47 (m, 2H), 6.85 (dd,  $J = 15.7$ , 10.5 Hz, 1H), 6.59-6.47 (m, 2H), 5.43-5.38 (m, 1H), 5.28-5.25 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.5 (q,  $J = 1.4$  Hz), 136.6, 131.9, 131.2, 129.2 (q,  $J = 32.4$  Hz), 126.5, 125.5 (q,  $J = 3.9$  Hz), 124.2 (q,  $J = 271.5$  Hz), 119.4 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.40 ppm.

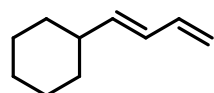
**(E)-4-(buta-1,3-dien-1-yl)-N,N-dimethylaniline (1g)** (Davenport & Fernandez, 2018): yellow solid, 37% yield, step D. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31-7.29 (m, 2H), 6.69-6.67 (m, 2H), 6.63 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.53-6.44 (m, 2H), 5.25-5.20 (m, 1H), 5.04 (d, *J* = 9.8 Hz, 1H), 2.96 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.0, 137.8, 133.1, 127.5, 125.6, 115.0, 112.4, 40.5 ppm.



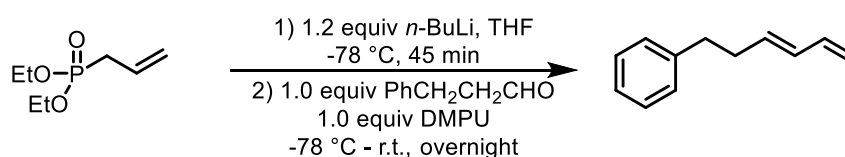
**(E)-2-(buta-1,3-dien-1-yl)furan (1h)** (Preuß et al, 2013): slight yellow liquid, 75% yield, step D. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (d, *J* = 1.9 Hz, 1H), 6.73-6.67 (m, 1H), 6.48-6.41 (m, 1H), 6.39-6.34 (m, 2H), 6.27 (d, *J* = 3.2 Hz, 1H), 5.35-5.30 (m, 1H), 5.17-5.14 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.9, 142.2, 136.7, 128.2, 120.4, 117.8, 111.6, 108.5 ppm.



**(E)-buta-1,3-dien-1-ylcyclohexane (1i)** (Preuß et al, 2013): colorless liquid, 32% overall yield, steps A-D. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.35-6.25 (m, 1H), 6.05-5.98 (m, 1H), 5.66 (dd, *J* = 15.3, 6.9 Hz, 1H), 5.12-5.07 (m, 1H), 4.97-4.94 (m, 1H), 2.04-1.95 (m, 1H), 1.75-1.70 (m, 4H), 1.67-1.62 (m, 1H), 1.33-1.03 (m, 5H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.3, 137.6, 128.3, 114.7, 40.6, 32.7, 26.1, 26.0 ppm.



**Scheme S2** (related to **Figure 4**):



**Synthesis of (E)-hexa-3,5-dien-1-ylbenzene (1j)** (Adamson & Malcolmson, 2017): To a solution of diethyl allylphosphonate (4.28 g, 24 mmol, 1.2 equiv) in anhydrous THF (45 mL) was added dropwise *n*BuLi (2.5 M in hexanes, 9.6 mL, 24 mmol, 1.2 equiv) at -78 °C. After stirring for 45 min, a solution of phenylpropyl aldehyde (2.6 mL, 20 mmol, 1.0 equiv) in DMPU (2.4 mL, 20 mmol, 1.0 equiv) was added dropwise via cannula. The resulting solution was stirred for 2 h at -78 °C, and then allowed to warm to room temperature. Stirring was continued overnight at room temperature before quenching with saturated aqueous NH<sub>4</sub>Cl solution. The mixture was extracted with diethyl ether (3×45 mL). The combined organic phases were washed with brine (100 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to afford the crude product. Purification by flash chromatography (PE as eluent) gave the desired diene **1j** (1.23 g, 39% yield) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.26 (m, 2H), 7.20-7.17 (m, 3H), 6.35-6.26 (m, 1H), 6.12-6.05 (m, 1H), 5.78-5.71 (m, 1H), 5.12-5.07 (m, 1H), 4.99-4.96 (m, 1H), 2.73-2.69 (m, 2H), 2.44-2.38 (m, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.7, 137.1, 134.2, 131.4, 128.4, 128.3, 125.8, 115.2, 35.6, 34.4 ppm.

**Reaction Optimization**

A reaction vial was charged with Ni(COD)<sub>2</sub> (2.8 mg, 0.01 mmol, 0.05 equiv vs amine), ligand (0.01 mmol, 0.05 equiv vs amine), morpholine (17  $\mu$ L, 0.2 mmol, 1.0 equiv), 1-phenylbutadiene (40  $\mu$ L, 0.3 mmol, 1.5 equiv), and 1.0 mL of solvent (toluene, THF, MTBE, EA, *n*-hexane, *i*-PrOH, CH<sub>3</sub>CN or PhCN) in an argon-filled glovebox, then acid (0.00-0.20 equiv vs amine) was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 25 °C for 24 h. Yields were determined by gas chromatogram analysis, using naphthalene as the internal standard. The ee values were determined by HPLC on a chiral stationary phase.

**Table S1.** Solvent screening for the Ni-catalyzed asymmetric hydroamination of **1a**, related to **Figure 2**.<sup>[a]</sup>

Entry	Solvent	Yield [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1	<i>i</i> -PrOH	trace	ND <sup>[d]</sup>
2	PhMe	90	23
3	THF	42	9
4	MTBE	trace	ND
5	EtOAc	trace	ND
6	CH <sub>3</sub> CN	trace	ND
7	PhCN	53	14
8	<i>n</i> -hexane	NP <sup>[e]</sup>	ND

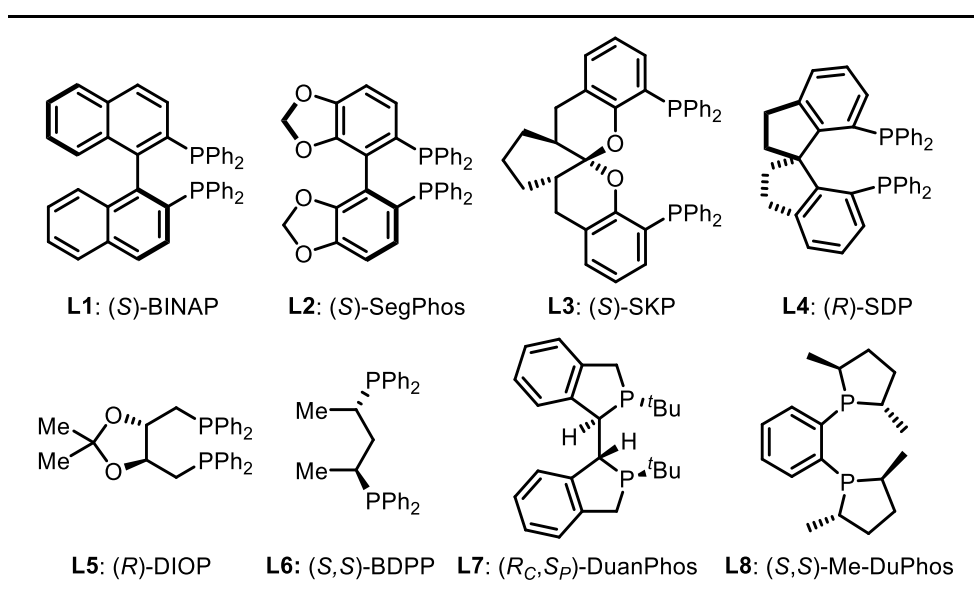
[a] Unless otherwise noted, all reactions were carried out with 0.10 mmol amine, 0.15 mmol diene, 5.0 mol % Ni(COD)<sub>2</sub>, 5.0 mol % (S,S)-BDPP, 5.0 mol % TsOH·H<sub>2</sub>O in 1 mL solvent at 25 °C for 24 h. [b] Yield was determined by gas chromatogram analysis, using naphthalene as the internal standard. [c] Determined by HPLC analysis using a chiral stationary phase. [d] Not determined. [e] No product.

**Table S2.** Ligand screening for Ni-catalyzed asymmetric hydroamination of **1a**, related to **Figure 2**.<sup>[a]</sup>

Entry	Ligand	Yield [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1	<b>L1</b>	65	30
2	<b>L2</b>	42	21

3	<b>L3</b>	trace	ND <sup>[d]</sup>
4	<b>L4</b>	trace	ND
5	<b>L5</b>	24	12
6	<b>L6</b>	90	23
7	<b>L7</b>	86	84
8	<b>L8</b>	30	98
9 <sup>[e]</sup>	<b>L8</b>	69 <sup>[f]</sup>	98

[a] Unless otherwise noted, all reactions were carried out with 0.10 mmol amine, 0.15 mmol diene, 5.0 mol % Ni(COD)<sub>2</sub>, 5.0 mol % ligand, 5.0 mol % TsOH·H<sub>2</sub>O in 1 mL toluene at 25 °C for 24 h. [b] Yield was determined by gas chromatogram analysis, using naphthalene as the internal standard. [c] Determined by HPLC analysis using a chiral stationary phase. [d] Not determined. [e] The catalyst was stirred at room temperature one hour in advance. [f] Isolated yield.



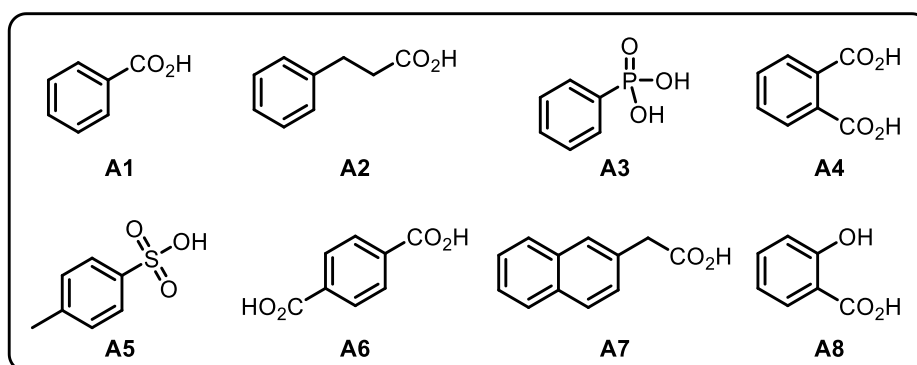
**Table S3.** Acid additives screening for Ni-catalyzed asymmetric hydroamination of **1a**, related to **Figure 2**.<sup>[a]</sup>



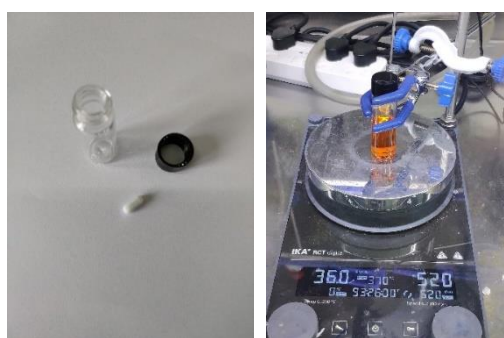
Entry	Acid	Yield[%] <sup>[b]</sup>	ee[%] <sup>[c]</sup>
1	<b>A1</b>	86	86
2	<b>A2</b>	86	98
3	<b>A3</b>	98	98
4	<b>A4</b>	94 <sup>[d]</sup>	96

5	<b>A5</b>	85	95
6	<b>A6</b>	89	96
7	<b>A7</b>	72	90
8	<b>A8</b>	83	93
9 <sup>[e]</sup>	<b>A3</b>	99	98
10 <sup>[e]</sup>	<b>A4</b>	99	96

[a] Unless otherwise noted, all reactions were carried out with 0.20 mmol diene, 0.40 mmol amine, 5.0 mol % Ni(COD)<sub>2</sub>/(S,S)-Me-DuPhos, 5.0 mol % acid in 1 mL toluene at 25 °C for 24 h; The catalyst was stirred at room temperature one hour in advance. [b] Yield was determined by gas chromatogram analysis, using naphthalene as the internal standard. [c] Determined by HPLC analysis using a chiral stationary phase. [d] Isolated yield. [e] With 0.30 mmol amine.



### General Procedure for Ni-catalyzed Asymmetric Hydroamination of Conjugated Dienes



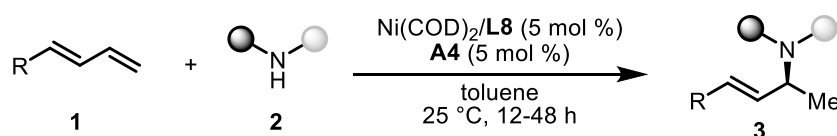
**catalyst solution**



**before reaction**

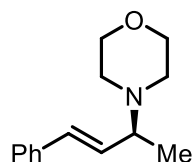
**after reaction**

**Scheme S3** (related to **Figure 3**, **Figure 4** and **Figure 5**):



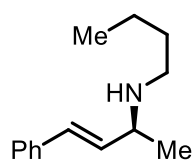
A stock solution was made by mixing  $\text{Ni}(\text{COD})_2$  with **L8** in a 1:1 molar ratio in toluene (0.01 M) at room temperature for 1 h in a argon-filled glovebox. An aliquot of the catalyst solution (1.0 mL, 0.01 mmol) was transferred by syringe into the vials charged with different 1,3-dienes (0.2 mmol for each) and amines (0.3 mmol for each), and then 0.01 mmol **A4** was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 25 °C for 12-48 h. The product was purified by column chromatography on deactivated silica gel using PE/EtOAc. The ee values of all compounds **3** were determined by HPLC on a chiral stationary phase.

**(S,E)-4-(4-phenylbut-3-en-2-yl)morpholine (3a)**: with **A3**, 12 h, obtained pale yellow oil 43.4



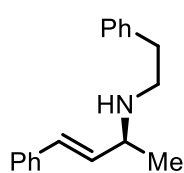
mg; Isolated yield: 99%; 98% ee;  $[\alpha]_D^{25} = -72.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 11.4$  min (minor), 14.4 min (major);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.47 (d,  $J = 15.9$  Hz, 1H), 6.17 (dd,  $J = 15.9, 8.2$  Hz, 1H), 3.73 (t,  $J = 4.7$  Hz, 4H), 3.05-2.99 (m, 1H), 2.61-2.52 (m, 4H), 1.26 (d,  $J = 6.6$  Hz, 3H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 132.0, 131.2, 128.6, 127.5, 126.2, 67.2, 63.1, 50.8, 17.8 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{14}\text{H}_{19}\text{NNaO} = 240.1359$ , found: 240.1359.

**(S,E)-N-butyl-4-phenylbut-3-en-2-amine (3b)**: with **A4**, 24 h, obtained colorless oil 37.7 mg;



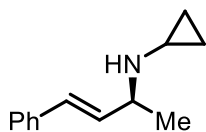
Isolated yield: 93%; > 99% ee;  $[\alpha]_D^{25} = -60.3$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.6 mL/min, UV detection at 254 nm,  $t_R = 9.2$  min (major), 9.7 min (minor);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.19 (m, 1H), 6.46 (d,  $J = 15.9$  Hz, 1H), 6.08 (dd,  $J = 15.9, 8.0$  Hz, 1H), 3.39-3.32 (m, 1H), 2.67-2.53 (m, 2H), 1.52-1.43 (m, 2H), 1.38-1.29 (m, 2H), 1.25 (d,  $J = 6.5$  Hz, 3H), 0.91 (t,  $J = 7.3$  Hz, 3H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 134.4, 129.7, 128.5, 127.2, 126.2, 56.4, 47.3, 32.4, 22.0, 20.5, 14.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{14}\text{H}_{21}\text{NNa} = 226.1566$ , found: 226.1565.

**(S,E)-N-phenethyl-4-phenylbut-3-en-2-amine (3c):** with **A4**, 24 h, obtained pale yellow oil



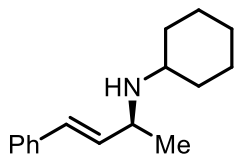
50.3 mg; Isolated yield: 99%; 92% ee;  $[\alpha]_D^{25} = -76.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.6 mL/min, UV detection at 254 nm,  $t_R = 13.9$  min (major), 15.0 min (minor);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.34 (m, 2H), 7.32-7.26 (m, 4H), 7.23-7.18 (m, 4H), 6.44 (d,  $J = 15.9$  Hz, 1H), 6.05 (dd,  $J = 15.9$ , 8.0 Hz, 1H), 3.41-3.34 (m, 1H), 2.96-2.79 (m, 4H), 1.23 (d,  $J = 6.5$  Hz, 3H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 136.9, 133.9, 129.9, 128.7, 128.5, 128.4, 127.3, 126.2, 126.1, 56.2, 48.8, 36.4, 21.9 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{18}\text{H}_{21}\text{NNa} = 274.1566$ , found: 274.1563.

**(S,E)-N-(4-phenylbut-3-en-2-yl)cyclopropanamine (3d):** with **A4**, 24 h, obtained colorless oil



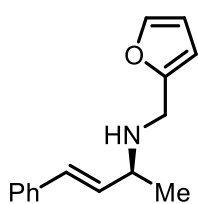
22.9 mg; Isolated yield: 61%; > 99% ee;  $[\alpha]_D^{25} = -91.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 10.5$  min (major), 10.9 min (minor);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.49 (d,  $J = 15.9$  Hz, 1H), 6.12 (dd,  $J = 15.9$ , 7.9 Hz, 1H), 3.52-3.45 (m,  $J = 6.7$  Hz, 1H), 2.18-2.13 (m, 1H), 2.02 (br, s 1H), 1.25 (d,  $J = 6.5$  Hz, 3H), 0.47-0.33 (m, 4H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.2, 134.4, 129.4, 128.5, 127.2, 126.2, 56.5, 28.6, 21.8, 6.6, 6.4 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{13}\text{H}_{17}\text{NNa} = 210.1253$ , found: 210.1254.

**(S,E)-N-(4-phenylbut-3-en-2-yl)cyclohexanamine (3e):** with **A4**, 24 h, obtained pale yellow



oil 34.9 mg; Isolated yield: 76%; 92% ee;  $[\alpha]_D^{25} = -66.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 11.0$  min (major), 12.1 min (minor);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.44 (d,  $J = 15.9$  Hz, 1H), 6.07 (dd,  $J = 15.9$ , 8.1 Hz, 1H), 3.59-3.52 (m, 1H), 2.55-2.48 (m, 1H), 2.01-1.97 (m, 1H), 1.84-1.58 (m, 3H), 1.69 (br, s, 1H), 1.26-0.98 (m, 9H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 134.8, 129.3, 128.5, 127.2, 126.2, 53.5, 52.5, 34.4, 33.2, 26.1, 25.3, 25.0, 22.5 ppm. **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{16}\text{H}_{23}\text{NNa} = 252.1723$ , found: 252.1722.

**(S,E)-N-(furan-2-ylmethyl)-4-phenylbut-3-en-2-amine (3f):** with **A4**, 24 h, obtained pale

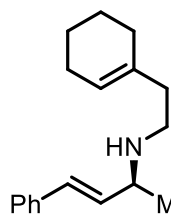


yellow oil 45.5 mg; Isolated yield: 99%; 99% ee;  $[\alpha]_D^{25} = -49.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 17.0$  min (minor), 20.0 min (major);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.36 (m, 3H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 1H), 6.49 (d,  $J = 15.9$  Hz, 1H), 6.31 (dd,  $J = 3.1$ , 1.9 Hz, 1H), 6.16 (dd,  $J = 3.1$ , 0.5 Hz, 1H), 6.07 (dd,  $J = 15.9$ , 8.1 Hz, 1H), 3.83 (d,  $J = 14.4$  Hz, 1H), 3.73 (d,  $J = 14.4$  Hz, 1H), 3.42-3.35 (m, 1H),



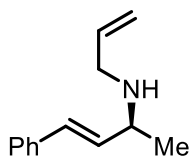
1.26 (d,  $J = 6.4$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 141.8, 137.0, 133.7, 130.5, 128.5, 127.4, 126.3, 110.1, 106.8, 55.3, 43.8, 22.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{18}\text{NO} = 228.1383$ , found: 228.1380.

**(S,E)-N-(2-(cyclohex-1-en-1-yl)ethyl)-4-phenylbut-3-en-2-amine (3g)**: with **A4**, 24 h,



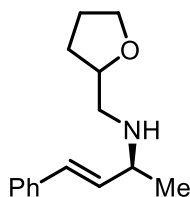
obtained pale yellow oil 50.9 mg; Isolated yield: 99%; 96% ee;  $[\alpha]_{\text{D}}^{25} = -66.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 11.0$  min (minor), 11.6 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.46 (d,  $J = 15.9$  Hz, 1H), 6.07 (dd,  $J = 15.9, 8.0$  Hz, 1H), 5.48-5.45 (m, 1H), 3.38-3.31 (m, 1H), 2.74-2.59 (m, 2H), 2.14 (t,  $J = 6.9$  Hz, 2H), 2.01-1.97 (m, 2H), 1.92-1.88 (m, 2H), 1.64-1.51 (m, 4H), 1.46 (br, s, 1H), 1.24 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 135.4, 134.4, 129.7, 128.5, 127.2, 126.2, 122.8, 56.2, 45.2, 38.4, 28.1, 25.2, 22.9, 22.4, 22.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{18}\text{H}_{26}\text{N} = 256.2060$ , found: 256.2057.

**(S,E)-N-allyl-4-phenylbut-3-en-2-amine (3h)**: with **A4**, 24 h, obtained pale yellow oil 29.1 mg;



Isolated yield: 78%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -60.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 11.9$  min (major), 12.7 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.46 (d,  $J = 15.9$  Hz, 1H), 6.06 (dd,  $J = 15.9, 8.1$  Hz, 1H), 5.97-5.87 (m, 1H), 5.20-5.15 (m, 1H), 5.12-5.08 (m, 1H), 3.44-3.36 (m, 1H), 3.34-3.28 (m, 1H), 3.24-3.18 (m, 1H), 1.86 (br, s, 1H), 1.26 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0, 136.8, 133.9, 130.1, 128.5, 127.3, 126.2, 115.9, 55.6, 50.0, 22.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{13}\text{H}_{17}\text{NNa} = 210.1253$ , found: 210.1258.

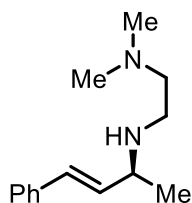
**(2S,E)-4-phenyl-N-((tetrahydrofuran-2-yl)methyl)but-3-en-2-amine (3i)**: with **A4**, 24 h,



obtained pale yellow oil 46.4 mg; Isolated yield: 99%; 99% ee; dr = 1:1;  $[\alpha]_{\text{D}}^{25} = -53.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.6 mL/min, UV detection at 254 nm,  $t_{\text{R}1} = 15.3$  min (major), 16.9 min (minor),  $t_{\text{R}2} = 19.8$  min (minor), 21.2 min (major); **3i**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.50 (d,  $J = 5.7$  Hz, 1H), 6.08 (dd,  $J = 8.1, 3.2$  Hz, 1H), 4.08-3.98 (m, 1H), 3.88-3.82 (m, 1H), 3.78-3.72 (m, 1H), 3.45-3.38 (m, 1H), 2.77 (dd,  $J = 11.9, 3.4$  Hz, 1H), 2.68 (d,  $J = 1.9$  Hz, 1H), 2.02-1.84 (m, 3H), 1.58-1.46 (m, 1H), 1.29 (d,  $J = 3.3$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.9, 133.7, 130.4, 128.5, 127.3, 126.3, 78.5, 67.9, 56.8, 52.3, 29.4, 25.7, 21.9 ppm; **3i'**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.46 (d,  $J = 5.7$  Hz, 1H), 6.12 (dd,  $J = 8.1, 3.2$  Hz, 1H), 4.08-3.98 (m, 1H), 3.88-3.82 (m, 1H), 3.78-3.72 (m, 1H), 3.45-3.38 (m, 1H),

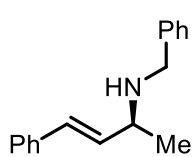
2.70 (s, 1H), 2.58 (dd,  $J = 11.9, 8.5$  Hz, 1H), 2.02-1.84 (m, 3H), 1.58-1.46 (m, 1H), 1.27 (d,  $J = 3.3$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.9, 133.7, 130.2, 128.5, 127.3, 126.3, 77.9, 67.9, 56.2, 51.7, 29.3, 25.7, 21.8 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{22}\text{NO} = 232.1696$ , found: 232.1693.

**(S,E)-N<sup>1</sup>,N<sup>1</sup>-dimethyl-N<sup>2</sup>-(4-phenylbut-3-en-2-yl)ethane-1,2-diamine (3j)**: with **A4**, 24 h,



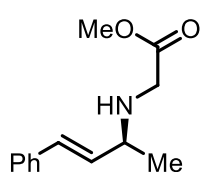
obtained pale yellow oil 42.0 mg; Isolated yield: 96%; 97% ee;  $[\alpha]_{\text{D}}^{25} = -71.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by (converting it to compound **Bz-3j**) HPLC on Chiralpak AS-H column, hexane: isopropanol = 90:10, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 43.1$  min (major), 50.8 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.47 (d,  $J = 15.9$  Hz, 1H), 6.08 (dd,  $J = 15.9, 8.0$  Hz, 1H), 3.39-3.32 (m, 1H), 2.78-2.62 (m, 2H), 2.46-2.43 (m, 3H), 2.22 (s, 6H), 1.27 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0, 134.0, 130.0, 128.5, 127.3, 126.2, 59.0, 56.5, 45.4, 44.7, 22.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{14}\text{H}_{23}\text{N}_2 = 219.1856$ , found: 219.1856.

**(S,E)-N-benzyl-4-phenylbut-3-en-2-amine (3k)**: with **A4**, 24 h, obtained pale yellow oil 43.3



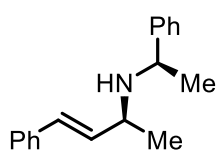
mg; Isolated yield: 91%; 95% ee;  $[\alpha]_{\text{D}}^{25} = -99.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 11.3$  min (major), 12.2 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.38 (m, 2H), 7.33-7.30 (m, 6H), 7.27-7.20 (m, 2H), 6.48 (d,  $J = 15.9$  Hz, 1H), 6.11 (dd,  $J = 15.9, 8.0$  Hz, 1H), 3.85 (d,  $J = 13.1$  Hz, 1H), 3.73 (d,  $J = 13.1$  Hz, 1H), 3.44-3.37 (m, 1H), 1.27 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.5, 137.1, 134.2, 130.1, 128.5, 128.4, 128.1, 127.3, 126.9, 126.3, 55.5, 51.5, 22.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{17}\text{H}_{19}\text{NNa} = 260.1410$ , found: 260.1405.

**methyl (S,E)-(4-phenylbut-3-en-2-yl)glycinate (3l)**: with **A3**, 48 h, obtained pale yellow oil



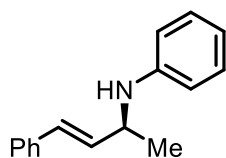
35.1 mg; Isolated yield: 80%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -154.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 27.2$  min (major), 28.4 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.35 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.45 (d,  $J = 15.8$  Hz, 1H), 6.01 (dd,  $J = 15.8, 8.2$  Hz, 1H), 3.69 (s, 3H), 3.42 (d,  $J = 3.1$  Hz, 2H), 3.39-3.32 (m, 1H), 2.17 (br, s, 1H), 1.27 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.2, 136.8, 133.2, 130.7, 128.5, 127.5, 126.3, 56.2, 51.8, 48.4, 22.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{13}\text{H}_{18}\text{NO}_2 = 220.1332$ , found: 220.1331.

**(S,E)-4-phenyl-N-((R)-1-phenylethyl)but-3-en-2-amine (3m):** with **A4**, 48 h, obtained pale yellow oil 28.2 mg; Isolated yield: 56%; > 20:1 dr;  $[\alpha]_{\text{D}}^{25} = -55.3$  (c = 1.0, CHCl<sub>3</sub>); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34-7.27 (m, 8H), 7.25-7.19 (m, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.07 (dd, *J* = 15.9, 7.7 Hz, 1H), 3.95-3.90 (m, 1H), 3.38-3.31 (m, 1H), 1.76 (br, s, 1H), 1.37 (d, *J* = 6.6 Hz, 3H), 1.22



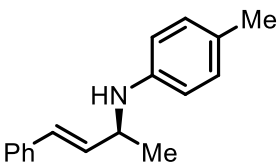
(d, *J* = 6.4 Hz, 3H) ppm; **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.8, 137.1, 134.6, 129.2, 128.5, 127.2, 126.8, 126.5, 126.2, 54.8, 53.0, 23.7, 21.2 ppm; **HRMS (ESI)** calculated  $[M+Na]^+$  for C<sub>18</sub>H<sub>21</sub>NNa = 274.1566, found: 274.1566.

**(S,E)-N-(4-phenylbut-3-en-2-yl)aniline (3n):** with **A3**, 24 h, obtained colorless oil 34.7 mg;



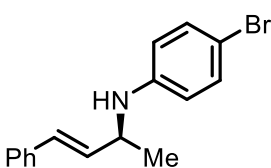
Isolated yield: 78%; 86% ee;  $[\alpha]_{\text{D}}^{25} = -80.6$  (c = 1.0, CHCl<sub>3</sub>); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm, *t<sub>R</sub>* = 11.6 min (major), 13.4 min (minor); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.34 (m, 2H), 7.30-7.27 (m, 2H), 7.22-7.13 (m, 3H), 6.70-6.63 (m, 3H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 5.8 Hz, 1H), 4.17-4.11 (m, 1H), 1.40 (d, *J* = 6.6 Hz, 3H) ppm; **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.4, 136.9, 133.2, 129.2, 129.1, 128.5, 127.3, 126.3, 117.3, 113.4, 50.8, 22.1 ppm; **HRMS (ESI)** calculated  $[M+Na]^+$  for C<sub>16</sub>H<sub>17</sub>NNa = 246.1253, found: 246.1253.

**(S,E)-4-methyl-N-(4-phenylbut-3-en-2-yl)aniline (3o):** with **A4**, 48 h, obtained reddish orange oil 10.8 mg (or with **A3**, 36 h, obtained reddish orange oil 43.9 mg);



Isolated yield: 23% (or 93%); 93% (or 73%) ee;  $[\alpha]_{\text{D}}^{25} = -99.5$  (c = 1.0, CHCl<sub>3</sub>); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, *t<sub>R</sub>* = 14.6 min (major), 16.5 min (minor); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.18 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.59-6.55 (m, 3H), 6.21 (dd, *J* = 16.0, 5.9 Hz, 1H), 4.14-4.08 (m, 1H), 2.22 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H) ppm; **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.1, 136.9, 133.4, 129.6, 129.1, 128.5, 127.3, 126.5, 126.3, 113.6, 51.1, 22.1, 20.4 ppm; **HRMS (ESI)** calculated  $[M+Na]^+$  for C<sub>17</sub>H<sub>19</sub>NNa = 260.1410, found: 260.1405.

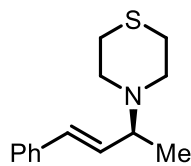
**(S,E)-4-bromo-N-(4-phenylbut-3-en-2-yl)aniline (3p):** with **A3**, 36 h, obtained reddish orange



oil 29.2 mg; Isolated yield: 48%; 92% ee;  $[\alpha]_{\text{D}}^{25} = -111.6$  (c = 1.0, CHCl<sub>3</sub>); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm, *t<sub>R</sub>* = 13.5 min (minor), 17.2 min (major); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35-7.32 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.19 (m, 3H), 6.56-6.49 (m, 3H), 6.16 (dd, *J* = 16.0, 5.8 Hz, 1H), 4.12-4.05 (m, 1H), 3.75 (br, s, 1H), 1.40 (d, *J* = 6.7 Hz, 3H) ppm; **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.3, 136.7, 132.5, 131.8, 129.5, 128.5,

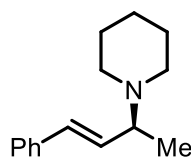
127.5, 126.3, 114.9, 108.8, 50.9, 22.0 ppm; **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{16}H_{17}BrN$  = 302.0539, found: 302.0524.

**(S,E)-4-(4-phenylbut-3-en-2-yl)thiomorpholine (3q)**: with **A4**, 24 h, obtained colorless oil 42.9



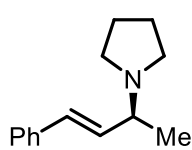
mg; Isolated yield: 92%; 96% ee;  $[\alpha]_D^{25} = -59.0$  ( $c = 1.0$ ,  $CHCl_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 8.7$  min (minor), 9.7 min (major);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 1H), 6.44 (d,  $J = 16.0$  Hz, 1H), 6.21 (dd,  $J = 16.0$ , 7.2 Hz, 1H), 3.27-3.20 (m, 1H), 2.90-2.80 (m, 4H), 2.69 (t,  $J = 5.0$  Hz, 4H), 1.25 (d,  $J = 6.7$  Hz, 3H) ppm;  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  136.9, 131.7, 130.9, 128.5, 127.4, 126.2, 62.7, 51.6, 28.3, 16.3 ppm; **HRMS (ESI)** calculated  $[M+Na]^+$  for  $C_{14}H_{19}NNS$  = 256.1130, found: 256.1130.

**(S,E)-1-(4-phenylbut-3-en-2-yl)piperidine (3r)**: with **A4**, 24 h, obtained pale yellow oil 40.8 mg;



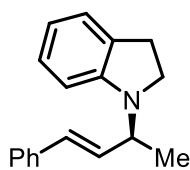
Isolated yield: 95%; 95% ee;  $[\alpha]_D^{25} = -55.7$  ( $c = 1.0$ ,  $CHCl_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 8.6$  min (minor), 9.8 min (major);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.19 (m, 1H), 6.43 (d,  $J = 16.0$  Hz, 1H), 6.24 (dd,  $J = 15.9$ , 8.0 Hz, 1H), 3.11-3.05 (m, 1H), 2.52-2.50 (m, 4H), 1.63-1.57 (m, 4H), 1.46-1.42 (m, 2H), 1.26 (d,  $J = 6.6$  Hz, 3H) ppm;  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  137.2, 132.7, 130.5, 128.5, 127.2, 126.2, 63.0, 51.0, 26.2, 24.6, 17.7 ppm; **HRMS (ESI)** calculated  $[M+Na]^+$  for  $C_{15}H_{21}NNA$  = 238.1566, found: 238.1568.

**(S,E)-1-(4-phenylbut-3-en-2-yl)pyrrolidine (3s)**: with **A4**, 24 h, obtained pale yellow oil 36.7



mg; Isolated yield: 91%; 97% ee;  $[\alpha]_D^{25} = -92.4$  ( $c = 1.0$ ,  $CHCl_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 7.6$  min (minor), 8.1 min (major);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.38-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.19 (m, 1H), 6.47 (d,  $J = 15.9$  Hz, 1H), 6.24 (dd,  $J = 15.8$ , 8.6 Hz, 1H), 2.95-2.88 (m, 1H), 2.61-2.55 (m, 4H), 1.81-1.78 (m, 4H), 1.30 (d,  $J = 6.5$  Hz, 3H) ppm;  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  137.1, 133.9, 129.6, 128.5, 127.2, 126.2, 63.1, 52.2, 23.3, 21.0 ppm; **HRMS (ESI)** calculated  $[M+Na]^+$  for  $C_{14}H_{19}NNA$  = 224.1410, found: 224.1410.

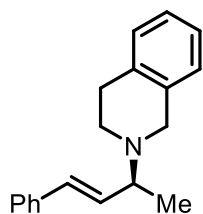
**(S,E)-1-(4-phenylbut-3-en-2-yl)indoline (3t)**: with **A3**, 24 h, obtained pale yellow oil 43.6 mg;



Isolated yield: 87%; 97% ee;  $[\alpha]_D^{25} = -109.4$  ( $c = 1.0$ ,  $CHCl_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min; UV detection at 254 nm,  $t_R = 13.8$  min (major), 14.6 min (minor);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.37-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 7.07-7.02 (m, 2H), 6.64-6.60 (m, 1H),

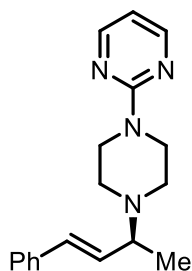
6.57-6.52 (m, 2H), 6.32 (dd,  $J = 16.1, 5.6$  Hz, 1H), 4.39-4.33 (m, 1H), 3.46-3.36 (m, 2H), 2.95 (t,  $J = 8.4$  Hz, 2H), 1.40 (d,  $J = 6.9$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.0, 136.9, 130.7, 130.4, 130.3, 128.5, 127.4, 127.2, 126.3, 124.4, 117.2, 107.6, 52.2, 47.3, 28.2, 16.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{18}\text{H}_{19}\text{NNa} = 272.1410$ , found: 272.1412.

**(S,E)-2-(4-phenylbut-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (3u)**: with **A4**, 24 h, obtained



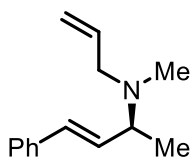
pale yellow oil 52.6 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -51.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 11.0$  min (minor), 14.5 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.24-7.22 (m, 1H), 7.12-7.07 (m, 3H), 7.03-7.01 (m, 1H), 6.53 (d,  $J = 16.0$  Hz, 1H), 6.30 (dd,  $J = 16.0, 7.9$  Hz, 1H), 3.83-3.74 (m, 2H), 3.34-3.27 (m, 1H), 2.97-2.90 (m, 3H), 2.84-2.73 (m, 1H), 1.37 (d,  $J = 6.6$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0, 134.9, 134.4, 132.3, 130.9, 128.6, 128.5, 127.4, 126.8, 126.3, 126.0, 125.5, 61.9, 53.0, 47.3, 29.4, 17.9 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{19}\text{H}_{21}\text{NNa} = 286.1566$ , found: 286.1563.

**(S,E)-2-(4-(4-phenylbut-3-en-2-yl)piperazin-1-yl)pyrimidine (3v)**: with **A4**, 48 h, obtained



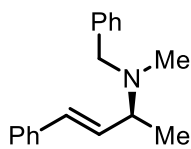
pale yellow oil 58.9 mg; Isolated yield: 99%; 95% ee;  $[\alpha]_{\text{D}}^{25} = -68.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 12.7$  min (major), 15.2 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 4.7$  Hz, 2H), 7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.49-6.45 (m, 2H), 6.22 (dd,  $J = 15.9, 8.0$  Hz, 1H), 3.84 (t,  $J = 5.2$  Hz, 4H), 3.16-3.09 (m, 1H), 2.68-2.58 (m, 4H), 1.30 (d,  $J = 6.6$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 157.7, 136.9, 132.1, 131.1, 128.6, 127.4, 126.3, 109.7, 62.6, 49.9, 43.9, 17.8 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{18}\text{H}_{22}\text{N}_4\text{Na} = 317.1737$ , found: 317.1730.

**(S,E)-N-allyl-N-methyl-4-phenylbut-3-en-2-amine (3w)**: with **A4**, 24 h, obtained pale yellow



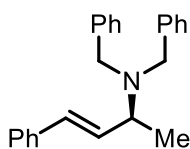
oil 33.2 mg; Isolated yield: 82%; 99% ee;  $[\alpha]_{\text{D}}^{25} = -49.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 8.0$  min (minor), 9.3 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.36 (m, 2H), 7.33-7.28 (m, 2H), 7.24-7.20 (m, 1H), 6.45 (d,  $J = 16.0$  Hz, 1H), 6.22 (dd,  $J = 16.0, 7.6$  Hz, 1H), 5.93-5.83 (m, 1H), 5.20-5.11 (m, 2H), 3.34-3.27 (m, 1H), 3.19-3.13 (m, 1H), 3.09-3.03 (m, 1H), 2.25 (s, 3H), 1.25 (d,  $J = 6.7$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.2, 136.3, 131.9, 130.8, 128.5, 127.3, 126.3, 117.3, 60.4, 57.4, 37.7, 17.2 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{14}\text{H}_{19}\text{NNa} = 224.1410$ , found: 224.1412.

**(S,E)-N-benzyl-N-methyl-4-phenylbut-3-en-2-amine (3x):** with **A3**, 24 h, obtained pale yellow



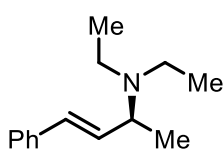
oil 44.2 mg; Isolated yield: 88%; 98% ee;  $[\alpha]_D^{25} = -91.9$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm,  $t_R = 5.0$  min (minor), 6.0 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.39 (m, 2H), 7.36-7.30 (m, 6H), 7.26-7.21 (m, 2H), 6.47 (d,  $J = 16.1$  Hz, 1H), 6.31 (dd,  $J = 16.0$ , 7.3 Hz, 1H), 3.65 (d,  $J = 13.2$  Hz, 1H), 3.51 (d,  $J = 13.2$  Hz, 1H), 3.39-3.32 (m, 1H), 2.22 (s, 3H), 1.30 (d,  $J = 6.7$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 137.2, 132.0, 130.8, 128.9, 128.5, 128.2, 127.3, 126.8, 126.2, 60.4, 58.2, 37.9, 16.9 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{18}\text{H}_{21}\text{NNa} = 274.1566$ , found: 274.1563.

**(S,E)-N,N-dibenzyl-4-phenylbut-3-en-2-amine (3y):** with **A3**, 24 h, obtained pale yellow oil



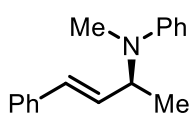
34.6 mg; Isolated yield: 53%; 96% ee;  $[\alpha]_D^{25} = -193.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 7.6$  min (major), 10.5 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.38 (m, 6H), 7.34-7.29 (m, 6H), 7.24-7.20 (m, 3H), 6.43 (d,  $J = 16.2$  Hz, 1H), 6.32 (dd,  $J = 16.1$ , 6.6 Hz, 1H), 3.71 (d,  $J = 13.9$  Hz, 2H), 3.59 (d,  $J = 13.9$  Hz, 2H), 3.51-3.44 (m, 1H), 1.29 (d,  $J = 6.8$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6, 137.3, 131.6, 130.9, 128.52, 128.50, 128.2, 127.2, 126.7, 126.2, 54.8, 53.7, 15.8 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{24}\text{H}_{25}\text{NNa} = 350.1879$ , found: 350.1873.

**(S,E)-N,N-diethyl-4-phenylbut-3-en-2-amine (3z):** with **A3**, 36 h, obtained pale yellow oil 11.0



mg; Isolated yield: 27%; 96% ee;  $[\alpha]_D^{25} = -26.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 7.7$  min (minor), 8.0 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.44 (d,  $J = 16.0$  Hz, 1H), 6.24 (dd,  $J = 16.0$ , 7.5 Hz, 1H), 3.50-3.43 (m, 1H), 2.69-2.53 (m, 4H), 1.24 (d,  $J = 6.6$  Hz, 3H), 1.06 (t,  $J = 7.2$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.2, 133.0, 130.0, 128.5, 127.2, 126.2, 57.5, 43.4, 17.4, 12.8 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{14}\text{H}_{21}\text{NNa} = 226.1566$ , found: 226.1568.

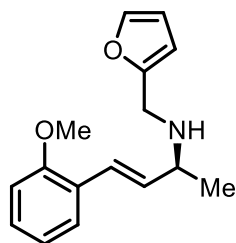
**(S,E)-N-methyl-N-(4-phenylbut-3-en-2-yl)aniline (3aa):** with **A3**, 36 h, obtained pale yellow



oil 10.4 mg; Isolated yield: 22%; 90% ee;  $[\alpha]_D^{25} = -169.9$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm,  $t_R = 11.7$  min (major), 15.0 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.35 (m, 2H), 7.32-7.20 (m, 5H), 6.86-6.83 (m, 2H), 6.75-6.71 (m, 1H), 6.48 (dd,  $J = 16.2$ , 1.9 Hz, 1H), 6.30 (dd,  $J = 16.2$ , 4.4 Hz, 1H), 4.69-4.62 (m, 1H), 2.79 (s, 3H), 1.37 (d,  $J = 6.8$  Hz, 3H) ppm;

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.0, 137.1, 131.3, 130.0, 129.2, 128.6, 127.4, 126.3, 116.8, 113.4, 54.9, 31.7, 16.2 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{17}\text{H}_{19}\text{NNa}$  = 260.1410, found: 260.1411.

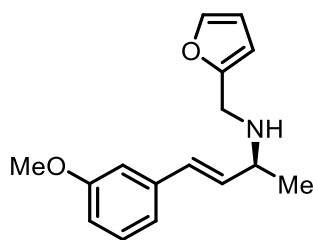
**(S,E)-N-(furan-2-ylmethyl)-4-(2-methoxyphenyl)but-3-en-2-amine (3ab)**: with **A4**, 24 h,



obtained pale yellow oil 51.5 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25}$  = -114.1 ( $c$  = 1.0,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}}$  = 27.5 min (major), 32.5 min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (dd,  $J$  = 7.6, 1.8 Hz, 1H), 7.36 (dd,  $J$  = 1.9, 0.9 Hz, 1H), 7.23-7.19 (m, 1H), 6.94-6.90 (m, 1H),

6.87 (dd,  $J$  = 8.2, 1.1 Hz, 1H), 6.81 (d,  $J$  = 16.0 Hz, 1H), 6.31 (dd,  $J$  = 3.2, 1.8 Hz, 1H), 6.17 (dd,  $J$  = 3.2, 0.8 Hz, 1H), 6.07 (dd,  $J$  = 16.0, 8.2 Hz, 1H), 3.85 (s, 3H), 3.83 (d,  $J$  = 14.7 Hz, 1H), 3.74 (d,  $J$  = 14.4 Hz, 1H), 3.43-3.36 (m, 1H), 1.26 (d,  $J$  = 6.4 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 154.1, 141.7, 134.3, 128.4, 126.7, 126.0, 125.2, 120.6, 110.8, 110.0, 106.8, 55.7, 55.4, 43.8, 22.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{16}\text{H}_{20}\text{NO}_2$  = 258.1489, found: 258.1484.

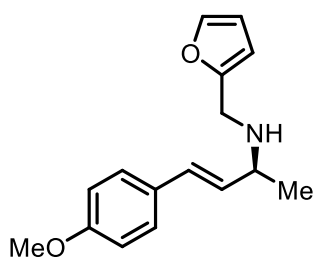
**(S,E)-N-(furan-2-ylmethyl)-4-(3-methoxyphenyl)but-3-en-2-amine (3ac)**: with **A4**, 24 h,



obtained pale yellow oil 51.0 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25}$  = -104.0 ( $c$  = 1.0,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}}$  = 28.0 min (major), 29.9 min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd,  $J$  = 1.9, 0.9 Hz, 1H), 7.23 (t,  $J$  = 7.9 Hz, 1H),

6.99-6.96 (m, 1H), 6.93-6.92 (m, 1H), 6.79 (ddd,  $J$  = 8.2, 2.6, 0.9 Hz, 1H), 6.46 (d,  $J$  = 15.9 Hz, 1H), 6.31 (dd,  $J$  = 3.1, 1.9 Hz, 1H), 6.16 (dd,  $J$  = 3.2, 0.8 Hz, 1H), 6.07 (dd,  $J$  = 15.9, 8.1 Hz, 1H), 3.83 (d,  $J$  = 14.4 Hz, 1H), 3.82 (s, 3H), 3.74 (d,  $J$  = 14.4 Hz, 1H), 3.42-3.35 (m, 1H), 1.88 (br, s, 1H), 1.26 (d,  $J$  = 6.4 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 153.8, 141.8, 138.4, 133.9, 130.4, 129.5, 119.0, 113.2, 111.4, 110.1, 106.8, 55.2, 43.7, 21.9 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{16}\text{H}_{20}\text{NO}_2$  = 258.1489, found: 258.1481.

**(S,E)-N-(furan-2-ylmethyl)-4-(4-methoxyphenyl)but-3-en-2-amine (3ad)**: with **A4**, 24 h,

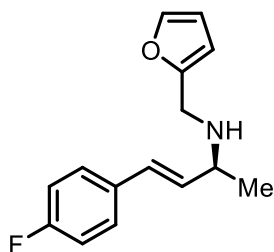


obtained pale yellow oil 51.5 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25}$  = -159.0 ( $c$  = 1.0,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}}$  = 33.8 min (major), 35.4 min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd,  $J$  = 2.0, 0.8 Hz, 1H), 7.34-7.30 (m, 2H), 6.88-

6.84 (m, 2H), 6.43 (d,  $J$  = 15.9 Hz, 1H), 6.31 (dd,  $J$  = 3.2, 1.8 Hz, 1H), 6.16 (dd,  $J$  = 3.1, 0.8 Hz,

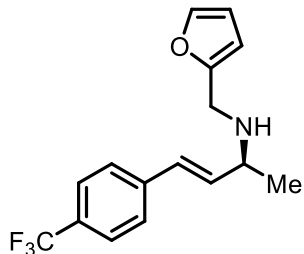
1H), 5.93 (dd,  $J = 15.8, 8.2$  Hz, 1H), 3.83 (d,  $J = 13.2$  Hz, 1H), 3.81 (s, 3H), 3.73 (d,  $J = 14.4$  Hz, 1H), 3.39-3.33 (m, 1H), 1.86 (br, s, 1H), 1.25 (d,  $J = 6.4$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 153.9, 141.8, 131.4, 130.0, 129.7, 127.4, 113.9, 110.1, 106.8, 55.33, 55.29, 43.8, 22.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{16}\text{H}_{19}\text{NNaO}_2 = 280.1308$ , found: 280.1310.

**(S,E)-4-(4-fluorophenyl)-N-(furan-2-ylmethyl)but-3-en-2-amine (3ae):** with **A4**, 24 h,



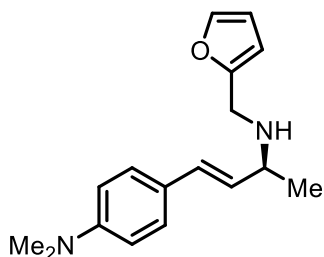
obtained pale yellow oil 49.1 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -137.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 25.0$  min (major), 27.4 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.32 (m, 3H), 7.03-6.97 (m, 2H), 6.45 (d,  $J = 15.8$  Hz, 1H), 6.31 (dd,  $J = 3.1, 1.9$  Hz, 1H), 6.16 (dd,  $J = 3.2, 0.8$  Hz, 1H), 5.99 (dd,  $J = 15.8, 8.1$  Hz, 1H), 3.82 (d,  $J = 14.4$  Hz, 1H), 3.73 (d,  $J = 14.4$  Hz, 1H), 3.41-3.34 (m, 1H), 1.83 (br, s, 1H), 1.25 (d,  $J = 6.4$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1 (d,  $J = 246.5$  Hz), 153.8, 141.8, 133.4 (d,  $J = 2.2$  Hz), 133.1 (d,  $J = 3.2$  Hz), 129.3, 127.7 (d,  $J = 7.9$  Hz), 115.4 (d,  $J = 21.4$  Hz), 110.1, 106.8, 55.2, 43.8, 22.0 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.82 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{15}\text{H}_{16}\text{FNNaO} = 268.1108$ , found: 268.1103.

**(S,E)-N-(furan-2-ylmethyl)-4-(4-(trifluoromethyl)phenyl)but-3-en-2-amine (3af):** with **A4**,



24 h, obtained pale yellow oil 59.2 mg; Isolated yield: 99%; 96% ee;  $[\alpha]_{\text{D}}^{25} = -99.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 11.5$  min (major), 13.0 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 8.2$  Hz, 2H), 7.46 (d,  $J = 8.2$  Hz, 2H), 7.37 (dd,  $J = 1.9, 0.8$  Hz, 1H), 6.52 (d,  $J = 15.9$  Hz, 1H), 6.31 (dd,  $J = 3.2, 1.8$  Hz, 1H), 6.21-6.15 (m, 2H), 3.82 (d,  $J = 14.5$  Hz, 1H), 3.74 (d,  $J = 14.5$  Hz, 1H), 3.45-3.38 (m, 1H), 1.82 (br, s, 1H), 1.27 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7, 141.8, 140.5 (q,  $J = 1.6$  Hz), 136.5, 129.11 (q,  $J = 32.2$  Hz), 129.09, 126.4, 125.5 (q,  $J = 3.9$  Hz), 124.2 (q,  $J = 270.5$  Hz), 110.1, 106.9, 55.1, 43.8, 21.8 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.36 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{16}\text{H}_{17}\text{F}_3\text{NO} = 296.1257$ , found: 296.1250.

**(S,E)-4-(3-((furan-2-ylmethyl)amino)but-1-en-1-yl)-N,N-dimethylaniline (3ag):** with **A4**, 24 h,

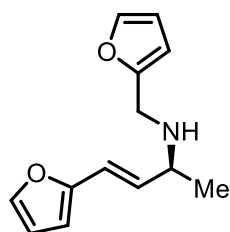


obtained pale yellow oil 49.8 mg; Isolated yield: 92%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -167.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.6 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 29.8$  min (minor), 32.1 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd,  $J = 1.9, 0.8$  Hz, 1H), 7.29-7.27 (m, 2H), 6.70-



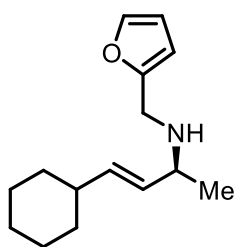
6.67 (m, 2H), 6.39 (d,  $J = 15.8$  Hz, 1H), 6.31 (dd,  $J = 3.2, 1.9$  Hz, 1H), 6.16 (dd,  $J = 3.1, 0.8$  Hz, 1H), 5.85 (dd,  $J = 15.8, 8.2$  Hz, 1H), 3.83 (d,  $J = 14.4$  Hz, 1H), 3.73 (d,  $J = 14.4$  Hz, 1H), 3.38-3.31 (m, 1H), 2.95 (s, 6H), 2.24 (br, s, 1H), 1.25 (d,  $J = 6.4$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 150.0, 141.7, 130.6, 129.1, 127.2, 125.4, 112.5, 110.0, 106.8, 55.5, 43.6, 40.6, 22.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O} = 271.1805$ , found: 271.1805.

**(S,E)-4-(furan-2-yl)-N-(furan-2-ylmethyl)but-3-en-2-amine (3ah):** with **A4**, 36 h, obtained



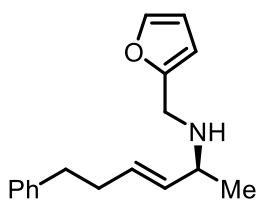
pale yellow oil 37.0 mg; Isolated yield: 85%; 96% ee;  $[\alpha]_{\text{D}}^{25} = -124.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 19.1$  min (major), 24.9 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd,  $J = 1.9, 0.9$  Hz, 1H), 7.34 (d,  $J = 1.8$  Hz, 1H), 6.36 (dd,  $J = 3.3, 1.8$  Hz, 1H), 6.34-6.30 (m, 2H), 6.21 (d,  $J = 3.2$  Hz, 1H), 6.16 (dd,  $J = 3.2, 0.8$  Hz, 1H), 6.02 (dd,  $J = 15.8, 8.0$  Hz, 1H), 3.82 (d,  $J = 14.5$  Hz, 1H), 3.72 (d,  $J = 14.4$  Hz, 1H), 3.37-3.30 (m, 1H), 1.24 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.0, 152.6, 141.8, 141.7, 132.5, 118.9, 111.2, 110.1, 107.2, 106.8, 54.9, 43.8, 22.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{13}\text{H}_{16}\text{NO}_2 = 218.1176$ , found: 218.1177.

**(S,E)-4-cyclohexyl-N-(furan-2-ylmethyl)but-3-en-2-amine (3ai):** with **A4**, 24 h, obtained



pale yellow oil 45.4 mg; Isolated yield: 97%; 96% ee;  $[\alpha]_{\text{D}}^{25} = -51.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 220 nm,  $t_{\text{R}} = 8.7$  min (major), 9.4 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (dd,  $J = 1.9, 0.9$  Hz, 1H), 6.30 (dd,  $J = 3.2, 1.8$  Hz, 1H), 6.13 (dd,  $J = 3.1, 0.9$  Hz, 1H), 5.48 (dd,  $J = 15.4, 6.6$  Hz, 1H), 5.24-5.18 m, 1H), 3.77 (d,  $J = 14.5$  Hz, 1H), 3.67 (d,  $J = 14.4$  Hz, 1H), 3.16-3.09 (m, 1H), 1.99-1.90 (m, 1H), 1.74-1.69 (m, 4H), 1.67-1.64 (m, 1H), 1.29-1.16 (m, 3H), 1.14 (d,  $J = 6.4$  Hz, 3H), 1.11-1.02 (m, 2H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 141.6, 137.9, 130.9, 110.0, 106.6, 55.1, 43.6, 40.4, 33.1, 33.0, 26.2, 26.0, 22.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{24}\text{NO} = 234.1852$ , found: 234.1853.

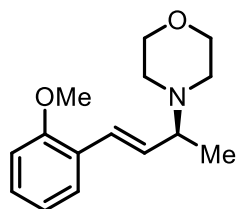
**(S,E)-N-(furan-2-ylmethyl)-6-phenylhex-3-en-2-amine (3aj):** with **A4**, 24 h, obtained



pale yellow oil 51.0 mg; Isolated yield: 99%; 99% ee;  $[\alpha]_{\text{D}}^{25} = -41.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 220 nm,  $t_{\text{R}} = 17.6$  min (minor), 18.7 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (dd,  $J = 1.9, 0.9$  Hz, 1H), 7.29-7.25 (m, 2H), 7.19-7.15 (m, 3H), 6.29 (dd,  $J = 3.1, 1.9$  Hz, 1H), 6.10 (dd,  $J = 3.2, 0.7$  Hz, 1H), 5.55 (dt,  $J = 15.2, 6.6$  Hz, 1H), 5.27 (ddt,  $J = 15.4, 8.1, 1.4$  Hz, 1H), 3.69 (d,  $J = 14.4$  Hz, 1H), 3.60 (d,  $J = 14.4$  Hz, 1H), 3.17-3.10 (m, 1H), 2.76-2.65 (m, 2H), 2.39-2.33 (m, 2H), 1.12

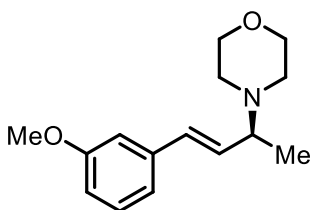
(d,  $J = 6.4$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 141.8, 141.6, 134.6, 130.7, 128.5, 128.3, 125.8, 110.0, 106.6, 54.9, 43.6, 35.8, 34.0, 22.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{17}\text{H}_{22}\text{NO}$  = 256.1696, found: 256.1691.

**(S,E)-4-(4-(2-methoxyphenyl)but-3-en-2-yl)morpholine (3ak)**: with **A4**, 24 h, obtained pale



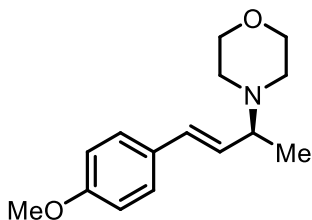
yellow oil 49.5 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -61.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 22.1$  min (minor), 24.2 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.23-7.19 (m, 1H), 6.93-6.89 (m, 1H), 6.86 (dd,  $J = 8.2, 1.2$  Hz, 1H), 6.79 (d,  $J = 16.0$  Hz, 1H), 6.17 (dd,  $J = 16.0, 8.3$  Hz, 1H), 3.84 (s, 3H), 3.73 (t,  $J = 4.7$  Hz, 4H), 3.06-2.99 (m, 1H), 2.62-2.52 (m, 4H), 1.26 (d,  $J = 6.6$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 132.5, 128.5, 126.6, 125.9, 125.8, 120.6, 110.9, 67.2, 63.6, 55.4, 50.8, 17.9 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{22}\text{NO}_2$  = 248.1645, found: 248.1641.

**(S,E)-4-(4-(3-methoxyphenyl)but-3-en-2-yl)morpholine (3al)**: with **A4**, 24 h, obtained pale



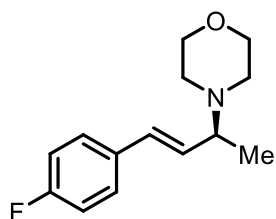
yellow oil 49.5 mg; Isolated yield: 99%; 98% ee;  $[\alpha]_{\text{D}}^{25} = -58.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 21.2$  min (major), 24.6 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (t,  $J = 7.9$  Hz, 1H), 6.96 (d,  $J = 7.7$  Hz, 1H), 6.92-6.91 (m, 1H), 6.79 (dd,  $J = 8.2, 2.4$  Hz, 1H), 6.44 (d,  $J = 15.9$  Hz, 1H), 6.17 (dd,  $J = 15.9, 8.2$  Hz, 1H), 3.81 (s, 3H), 3.73 (t,  $J = 4.7$  Hz, 4H), 3.06-2.99 (m, 1H), 2.61-2.52 (m, 4H), 1.26 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 138.3, 132.3, 131.1, 129.5, 118.9, 113.2, 111.4, 67.1, 63.0, 55.1, 50.7, 17.6 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{22}\text{NO}_2$  = 248.1645, found: 248.1637.

**(S,E)-4-(4-(4-methoxyphenyl)but-3-en-2-yl)morpholine (3am)**: with **A4**, 24 h, obtained pale



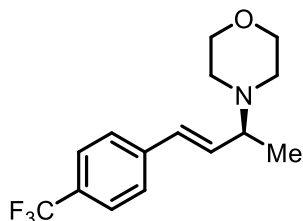
yellow oil 49.3 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -80.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 20.6$  min (minor), 29.0 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.7$  Hz, 2H), 6.85 (d,  $J = 8.7$  Hz, 2H), 6.41 (d,  $J = 15.9$  Hz, 1H), 6.02 (dd,  $J = 15.9, 8.3$  Hz, 1H), 3.81 (s, 3H), 3.74 (t,  $J = 4.7$  Hz, 4H), 3.03-2.96 (m, 1H), 2.61-2.53 (m, 4H), 1.26 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 130.8, 129.6, 129.5, 127.4, 113.9, 67.10, 63.2, 55.3, 50.7, 17.8 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{15}\text{H}_{21}\text{NNaO}_2$  = 270.1465, found: 270.1464.

**(S,E)-4-(4-(4-fluorophenyl)but-3-en-2-yl)morpholine (3an):** with **A4**, 24 h, obtained pale



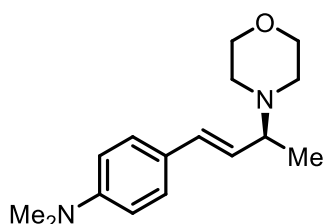
yellow oil 47.2 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -70.3$  (c = 1.0,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 16.0$  min (minor), 17.5 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.31 (m, 2H), 7.03-6.97 (m, 2H), 6.43 (d,  $J = 15.9$  Hz, 1H), 6.08 (dd,  $J = 15.9, 8.2$  Hz, 1H), 3.74 (t,  $J = 4.7$  Hz, 4H), 3.04-2.97 (m, 1H), 2.58-2.54 (m, 4H), 1.25 (d,  $J = 6.6$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2 (d,  $J = 246.6$  Hz), 133.0 (d,  $J = 3.3$  Hz), 131.8 (d,  $J = 2.1$  Hz), 130.0, 127.7 (d,  $J = 7.9$  Hz), 115.4 (d,  $J = 21.6$  Hz), 67.2, 63.0, 50.7, 17.7 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.64 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{14}\text{H}_{19}\text{FNO} = 236.1445$ , found: 236.1442.

**(S,E)-4-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)morpholine (3ao):** with **A4**, 24 h,



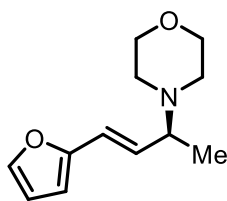
obtained pale yellow oil 57.1 mg; Isolated yield: 99%; 93% ee;  $[\alpha]_{\text{D}}^{25} = -48.3$  (c = 1.0,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 15.0$  min (major), 17.8 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 8.2$  Hz, 2H), 7.46 (d,  $J = 8.4$  Hz, 2H), 6.50 (d,  $J = 16.0$  Hz, 1H), 6.28 (dd,  $J = 16.0, 8.0$  Hz, 1H), 3.75-3.72 (m, 4H), 3.10-3.02 (m, 1H), 2.58-2.55 (m, 4H), 1.27 (d,  $J = 6.6$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.3 (q,  $J = 1.9$  Hz), 135.0, 129.9, 129.2 (q,  $J = 32.4$  Hz), 126.4, 125.5 (q,  $J = 3.8$  Hz), 124.1 (q,  $J = 270.9$  Hz), 67.1, 62.9, 50.7, 17.5 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.38 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{19}\text{F}_3\text{NO} = 286.1413$ , found: 286.1418.

**(S,E)-N,N-dimethyl-4-(3-morpholinobut-1-en-1-yl)aniline (3ap):** with **A4**, 24 h, obtained pale



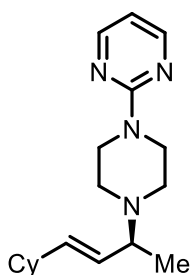
yellow oil 38.8 mg; Isolated yield: 74%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -98.5$  (c = 1.0,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 19.5$  min (major), 21.3 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.25 (m, 2H), 6.69-6.67 (m, 2H), 6.37 (d,  $J = 15.8$  Hz, 1H), 5.94 (dd,  $J = 15.9, 8.3$  Hz, 1H), 3.73 (t,  $J = 4.7$  Hz, 4H), 3.00-2.97 (m, 1H), 2.95 (s, 6H), 2.61-2.52 (m, 4H), 1.25 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.0, 131.2, 127.5, 127.1, 125.4, 112.5, 67.2, 63.4, 50.8, 40.6, 18.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O} = 261.1961$ , found: 261.1960.

**(S,E)-4-(4-(furan-2-yl)but-3-en-2-yl)morpholine (3aq):** with **A4**, 36 h, obtained pale yellow oil



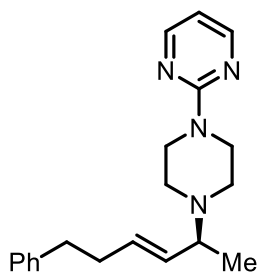
41.4 mg; Isolated yield: 99%; 96% ee;  $[\alpha]_D^{25} = -73.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 16.6$  min (minor), 18.7 min (major);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 1.8$  Hz, 1H), 6.36 (dd,  $J = 3.3, 1.8$  Hz, 1H), 6.31-6.27 (m, 1H), 6.20 (d,  $J = 3.3$  Hz, 1H), 6.11 (dd,  $J = 15.9, 8.1$  Hz, 1H), 3.72 (t,  $J = 4.7$  Hz, 4H), 3.04-2.97 (m, 1H), 2.60-2.50 (m, 4H), 1.23 (d,  $J = 6.6$  Hz, 3H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 141.7, 130.7, 119.7, 111.2, 107.3, 67.2, 62.7, 50.5, 17.5 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{12}\text{H}_{18}\text{NO}_2 = 208.1332$ , found: 208.1333.

**(S,E)-2-(4-(4-cyclohexylbut-3-en-2-yl)piperazin-1-yl)pyrimidine (3ar):** with **A4**, 24 h,



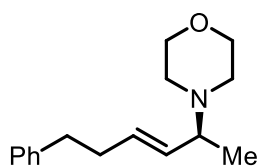
obtained colourless oil 34.7 mg; Isolated yield: 58%; 96% ee;  $[\alpha]_D^{25} = -17.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 8.8$  min (minor), 9.5 min (major);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 4.7$  Hz, 2H), 6.46 (t,  $J = 4.7$  Hz, 1H), 5.47 (dd,  $J = 15.6, 6.4$  Hz, 1H), 5.37-5.31 (m, 1H), 3.83-3.81 (m, 4H), 2.93-2.86 (m, 1H), 2.62-2.49 (m, 4H), 1.99-1.90 (m, 1H), 1.72-1.69 (m, 4H), 1.66-1.62 (m, 1H), 1.28-1.22 (m, 3H), 1.18 (d,  $J = 6.6$  Hz, 3H), 1.14-1.02 (m, 2H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 157.7, 138.5, 128.7, 109.6, 62.5, 49.6, 43.8, 40.4, 33.04, 32.97, 26.1, 26.0, 18.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{18}\text{H}_{29}\text{N}_4 = 301.2387$ , found: 301.2380.

**(S,E)-2-(4-(6-phenylhex-3-en-2-yl)piperazin-1-yl)pyrimidine (3as):** with **A4**, 24 h, obtained



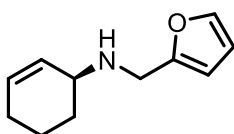
colorless oil 63.5 mg; Isolated yield: 98%; > 99% ee;  $[\alpha]_D^{25} = -14.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R = 19.2$  min (major), 21.7 min (minor);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (d,  $J = 4.7$  Hz, 2H), 7.28-7.24 (m, 2H), 7.17-7.13 (m, 3H), 6.46 (t,  $J = 4.7$  Hz, 1H), 5.52 (dt,  $J = 15.3, 6.5$  Hz, 1H), 5.37 (ddt,  $J = 15.4, 8.0, 1.2$  Hz, 1H), 3.78 (t,  $J = 5.2$  Hz, 4H), 2.91-2.84 (m, 1H), 2.76-2.64 (m, 2H), 2.51-2.41 (m, 4H), 2.39-2.33 (m, 2H), 1.14 (d,  $J = 6.6$  Hz, 3H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 157.7, 141.7, 132.6, 131.2, 128.5, 128.2, 125.8, 109.6, 62.3, 49.6, 43.8, 35.6, 34.0, 17.9 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{20}\text{H}_{27}\text{N}_4 = 323.2230$ , found: 323.2224.

**(S,E)-4-(6-phenylhex-3-en-2-yl)morpholine (3at):** with **A4**, 24 h, obtained colorless oil 43.1



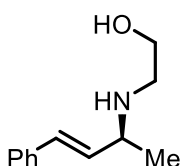
mg; Isolated yield: 88%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -21.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 220 nm,  $t_{\text{R}} = 13.1$  min (minor), 14.4 min (major);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.24 (m, 2H), 7.18-7.15 (m, 3H), 5.52 (dt,  $J = 15.2, 6.6$  Hz, 1H), 5.32 (ddt,  $J = 15.3, 8.1, 1.4$  Hz, 1H), 3.66 (t,  $J = 5.2$  Hz, 4H), 2.79-2.64 (m, 3H), 2.40-2.33 (m, 6H), 1.10 (d,  $J = 6.5$  Hz, 3H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.7, 132.8, 131.3, 128.5, 128.3, 125.8, 67.2, 62.8, 50.5, 35.7, 34.0, 17.8 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{16}\text{H}_{24}\text{NO} = 246.1852$ , found: 246.1847.

**(S)-N-(furan-2-ylmethyl)cyclohex-2-en-1-amine (3au):** with **A4**, 24 h, obtained pale yellow oil



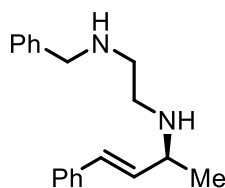
17.4 mg; Isolated yield: 28%; 22% ee;  $[\alpha]_{\text{D}}^{25} = -13.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 220 nm;  $t_{\text{R}} = 19.0$  min (major), 21.9 min (minor);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (dd,  $J = 1.9, 0.9$  Hz, 1H), 6.31 (dd,  $J = 3.1, 1.9$  Hz, 1H), 6.18 (dd,  $J = 3.1, 0.8$  Hz, 1H), 5.80-5.75 (m, 1H), 5.70-5.66 (m, 1H), 3.89-3.80 (m, 2H), 3.23-3.17 (m, 1H), 2.02-1.96 (m, 2H), 1.90-1.85 (m, 1H), 1.78-1.71 (m, 1H), 1.60-1.41 (m, 2H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.0, 141.7, 129.4, 129.2, 110.1, 106.7, 52.0, 43.4, 29.2, 25.2, 20.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{11}\text{H}_{16}\text{NO} = 178.1226$ , found: 178.1221.

**(S,E)-2-((4-phenylbut-3-en-2-yl)amino)ethan-1-ol (3av):** with **A4**, 24 h, obtained pale yellow



oil 34.8 mg; Isolated yield: 91%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -54.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by (converting it to compound **Bz-3av**) HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15; flow rate = 1.0 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 20.0$  min (major), 24.7 min (minor);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.50 (d,  $J = 15.9$  Hz, 1H), 6.12 (dd,  $J = 15.9, 8.1$  Hz, 1H), 3.76-3.67 (m, 2H), 3.53-3.41 (m, 1H), 3.41 (br, s, 1H), 3.32 (br, s, 1H), 2.93-2.79 (m, 2H), 1.35 (d,  $J = 6.5$  Hz, 3H) ppm;  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.4, 131.6, 131.5, 128.5, 127.7, 126.4, 60.3, 56.3, 48.5, 21.2 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{12}\text{H}_{18}\text{NO} = 192.1383$ , found: 192.1381.

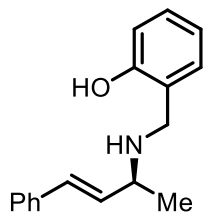
**(S,E)-N1-benzyl-N1-(4-phenylbut-3-en-2-yl)ethane-1,2-diamine (3aw):** with **A4**, 24 h,



obtained pale yellow oil 46.5 mg; Isolated yield: 83%; 98% ee;  $[\alpha]_{\text{D}}^{25} = -56.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by (converting it to compound **Bz-3aw**) HPLC on Chiralpak AD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 24.4$  min (minor), 27.6 min (major);  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.35 (m, 2H), 7.32-7.28 (m, 6H), 7.25-7.19 (m, 2H), 6.44 (d,  $J = 15.9$  Hz, 1H),

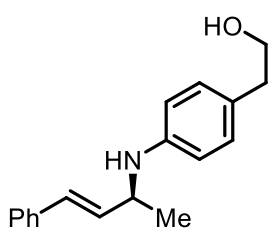
6.05 (dd,  $J = 15.9, 7.9$  Hz, 1H), 3.79 (s, 2H), 3.35-3.28 (m, 1H), 2.81-2.65 (m, 4H), 1.25 (br, s, 2H), 1.25 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.3, 137.0, 134.2, 129.9, 128.5, 128.4, 128.1, 127.3, 126.9, 126.3, 56.3, 53.8, 48.8, 46.9, 22.0 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{19}\text{H}_{25}\text{N}_2 = 281.2012$ , found: 282.2011.

**(S,E)-2-(((4-phenylbut-3-en-2-yl)amino)methyl)phenol (3ax)**: with **A4**, 24 h, obtained pale yellow oil 47.6 mg; Isolated yield: 94%; 97% ee;  $[\alpha]_{\text{D}}^{25} = -110.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_{\text{R}} = 31.9$  min (major), 37.2 min (minor);  $^1\text{H NMR}$  (400



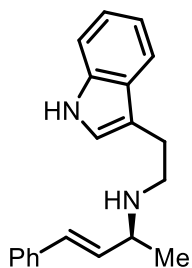
MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.30 (m, 4H), 7.26-7.22 (m, 1H), 7.18-7.14 (m, 1H), 6.96-6.94 (m, 1H), 6.84 (dd,  $J = 8.1, 1.2$  Hz, 1H), 6.78-6.74 (m, 1H), 6.46 (d,  $J = 15.9$  Hz, 1H), 6.03 (dd,  $J = 15.9, 8.2$  Hz, 1H), 4.07 (d,  $J = 14.0$  Hz, 1H), 3.91 (d,  $J = 13.9$  Hz, 1H), 3.45-3.38 (m, 1H), 1.32 (d,  $J = 6.5$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 136.5, 131.7, 131.5, 128.6, 128.6, 128.3, 127.7, 126.3, 122.7, 119.1, 116.4, 55.1, 50.0, 21.7 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{17}\text{H}_{19}\text{NO} = 276.1359$ , found: 276.1361.

**(S,E)-2-(2-(((4-phenylbut-3-en-2-yl)amino)phenyl)ethan-1-ol (3ay)**: with **A3**, 24 h, obtained white solid 31.4 mg; Isolated yield: 59%; 91% ee;  $[\alpha]_{\text{D}}^{25} = -114.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 80:20, flow rate = 0.5



mL/min, UV detection at 254 nm,  $t_{\text{R}} = 24.7$  min (major), 28.9 min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.23- 7.19 (m, 1H), 7.03-7.00 (m, 2H), 6.63-6.60 (m, 2H), 6.57 (dd,  $J = 15.9, 1.3$  Hz, 1H), 6.20 (dd,  $J = 15.9, 5.9$  Hz, 1H), 4.15-4.08 (m, 1H), 3.78 (t,  $J = 6.5$  Hz, 2H), 2.74 (t,  $J = 6.5$  Hz, 2H), 1.40 (d,  $J = 6.6$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.0, 136.9, 133.2, 129.8, 129.2, 128.5, 127.3, 126.7, 126.3, 113.6, 63.9, 51.0, 38.2, 22.1 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{18}\text{H}_{21}\text{NNO} = 290.1532$ , found: 290.1531.

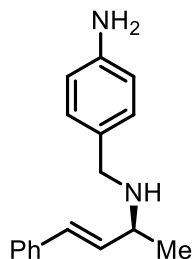
**(S,E)-N-(2-(1H-indol-3-yl)ethyl)-4-phenylbut-3-en-2-amine (3az)**: with **A4**, 24 h, obtained pale yellow oil 58.2 mg; Isolated yield: 99%; > 99% ee;  $[\alpha]_{\text{D}}^{25} = -76.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 99:1, flow rate = 0.5



mL/min, UV detection at 254 nm;  $t_{\text{R}} = 69.3$  min (minor), 75.3 min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (s, 1H), 7.62 (d,  $J = 7.9$  Hz, 1H), 7.37-7.27 (m, 5H), 7.23-7.17 (m, 2H), 7.10 (t,  $J = 7.5$  Hz, 1H), 7.04 (d,  $J = 2.3$  Hz, 1H), 6.42 (d,  $J = 15.9$  Hz, 1H), 6.06 (dd,  $J = 15.9, 8.0$  Hz, 1H), 3.41-3.34 (m, 1H), 3.04-2.92 (m, 4H), 1.97 (br, s, 1H), 1.22 (d,  $J = 6.4$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0, 136.4, 134.1, 129.9, 128.5, 127.4, 127.3, 126.2, 122.02, 121.98, 119.2, 118.9, 113.8, 111.1,

56.2, 47.4, 25.8, 22.0 ppm; **HRMS (ESI)** calculated  $[M+Na]^+$  for  $C_{20}H_{22}N_2Na$  = 313.1675, found: 313.1675.

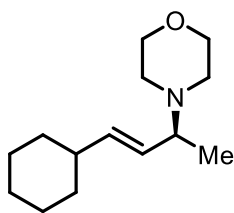
**(S,E)-4-(((4-phenylbut-3-en-2-yl)amino)methyl)aniline (3ba)**: with **A3**, 24 h, obtained pale yellow oil 20.4 mg; Isolated yield: 40%; > 99% ee;  $[\alpha]_D^{25} = -148.5$  (c = 1.0,  $CHCl_3$ );



The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 90:10, flow rate = 0.5 mL/min, UV detection at 254 nm,  $t_R$  = 25.8 min (major), 28.8 min (minor);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.40-7.37(m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 7.12-7.09 (m, 2H), 6.67-6.63 (m, 2H), 6.47 (d,  $J$  = 15.9 Hz, 1H), 6.11 (dd,  $J$  = 15.9, 8.0 Hz, 1H), 3.73 (d,  $J$  = 12.8 Hz, 1H), 3.61 (d,  $J$  = 12.9 Hz, 1H),

3.43-3.36 (m, 1H), 1.25 (d,  $J$  = 6.5 Hz, 3H) ppm;  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  145.2, 137.1, 134.2, 130.4, 130.1, 129.3, 128.5, 127.3, 126.2, 115.1, 55.3, 51.0, 22.0 ppm; **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{17}H_{21}N_2$  = 253.1699, found: 253.1670.

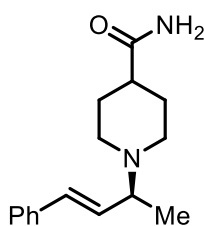
**(S,E)-4-(4-cyclohexylbut-3-en-2-yl)morpholine (3bb)**: with **A4**, 24 h, obtained pale yellow oil



29.8 mg; Isolated yield: 67%; The enantiomeric excess couldn't be determined;  $[\alpha]_D^{25} = -25.2$  (c = 1.0,  $CHCl_3$ );  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  5.47 (dd,  $J$  = 15.5, 6.5 Hz, 1H), 5.32-5.26 (m, 1H), 3.71 (t,  $J$  = 4.7 Hz, 4H), 2.81-2.74 (m, 1H), 2.55-2.42 (m, 4H), 1.97-1.89 (m, 1H), 1.74-1.67 (m, 4H), 1.67-1.62 (m, 1H), 1.32-1.16 (m, 3H), 1.14 (d,  $J$  = 6.5 Hz, 3H),

1.12-1.01 (m, 2H) ppm;  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  138.6, 128.9, 67.2, 62.9, 50.5, 40.4, 33.1, 33.0, 26.2, 26.0, 18.0 ppm; **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{14}H_{26}NO$  = 224.2009, found: 224.2011.

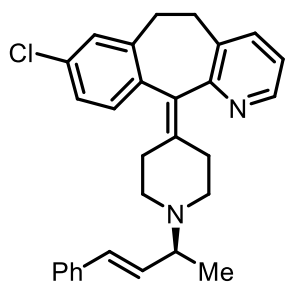
**(S,E)-1-(4-phenylbut-3-en-2-yl)piperidine-4-carboxamide (3bc)**: white solid 44.9 mg;



Isolated yield: 87%; The enantiomeric excess couldn't be determined;  $[\alpha]_D^{25} = -35.4$  (c = 1.0,  $CHCl_3$ );  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.38-3.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.44 (d,  $J$  = 15.9 Hz, 1H), 6.20 (dd,  $J$  = 15.9, 7.9 Hz, 1H), 5.52 (br, s, 2H), 3.16-3.07 (m, 2H), 3.05-3.00 (m, 1H), 2.18-2.09 (m, 3H), 1.94-1.87 (m, 2H), 1.80-1.67 (m, 2H), 1.25 (d,  $J$  =

6.6 Hz, 3H) ppm;  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  177.7, 137.0, 132.2, 130.7, 128.5, 127.3, 126.2, 62.4, 49.7, 49.5, 43.0, 29.2, 29.1, 17.6 ppm; **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{16}H_{23}N_2O$  = 218.1176, found: 218.1177.

**(S,E)-8-chloro-11-(1-(4-phenylbut-3-en-2-yl)piperidin-4-ylidene)-6,11-dihydro-5H-**

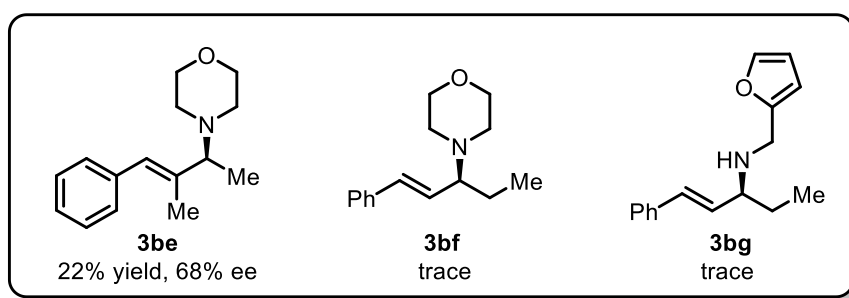


**benzo[5,6]cyclohepta[1,2-b]pyridine (3bd):** with **A4**, 48 h, obtained reddish orange oil 88.1 mg; Isolated yield: 99%; The enantiomeric excess couldn't be determined;  $[\alpha]_D^{25} = -64.3$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); **3ay:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40-8.38 (m, 1H), 7.42 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.37-7.28 (m, 4H), 7.24-7.20 (m, 1H), 7.14-7.11 (m, 3H), 7.09-7.06 (m, 1H), 6.42 (d,  $J = 15.9$  Hz, 1H), 6.25-6.19 (m, 1H), 3.44-3.32 (m, 2H), 3.20-3.11 (m, 1H), 2.93-2.74 (m, 4H),

2.56-2.32 (m, 6H), 1.26 (d,  $J = 6.6$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.62, 146.57, 139.46, 139.09, 137.72, 137.20, 136.93, 133.40, 132.56, 132.38, 132.08, 130.90, 130.82, 128.93, 128.51, 127.34, 126.24, 125.94, 122.04, 62.38, 51.63, 51.42, 31.83, 31.40, 31.08, 30.87, 17.83 ppm; **3ay':**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40-8.38 (m, 1H), 7.42 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.37-7.28 (m, 4H), 7.24-7.20 (m, 1H), 7.14-7.11 (m, 3H), 7.09-7.06 (m, 1H), 6.42 (d,  $J = 15.9$  Hz, 1H), 6.25-6.19 (m, 1H), 3.44-3.32 (m, 2H), 3.20-3.11 (m, 1H), 2.93-2.74 (m, 4H), 2.56-2.32 (m, 6H), 1.26 (d,  $J = 6.6$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.57, 146.57, 139.46, 139.09, 137.67, 137.16, 136.92, 133.40, 132.56, 132.38, 131.97, 130.87, 130.77, 128.90, 128.51, 127.34, 126.22, 125.94, 122.04, 62.35, 51.63, 51.37, 31.81, 31.38, 31.08, 30.80, 17.78 ppm; **HRMS (ESI)** calculated  $[\text{M}+\text{Na}]^+$  for  $\text{C}_{29}\text{H}_{29}\text{ClN}_2\text{Na} = 463.1911$ , found: 463.1907.

**Non-reactive and inefficient substrates**

we also have prepared two disubstituted dienes **1k** and **1l**, and examined them in the hydroamination reaction. It was found that substrate **1k** could participate in the reaction to afford the corresponding product **3be** in 22% yield and 68% ee. However, substrate **1l** failed to provide the desired product (**3bf** and **3bg**) under standard reaction condition.

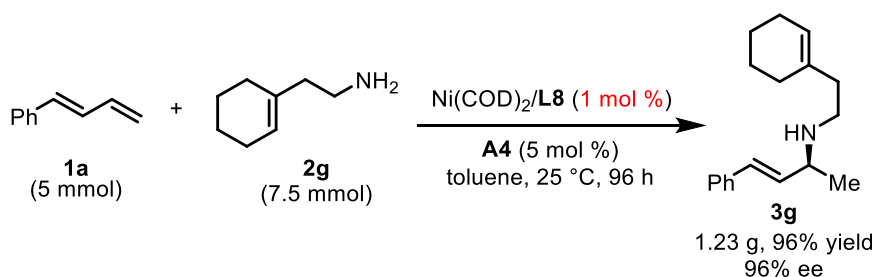


**Figure S245.** Non-reactive and inefficient dienes, related to **Figure 4**.

**Scalability of Asymmetric Hydroamination**

**Scheme S4** (related to **Figure 3**):



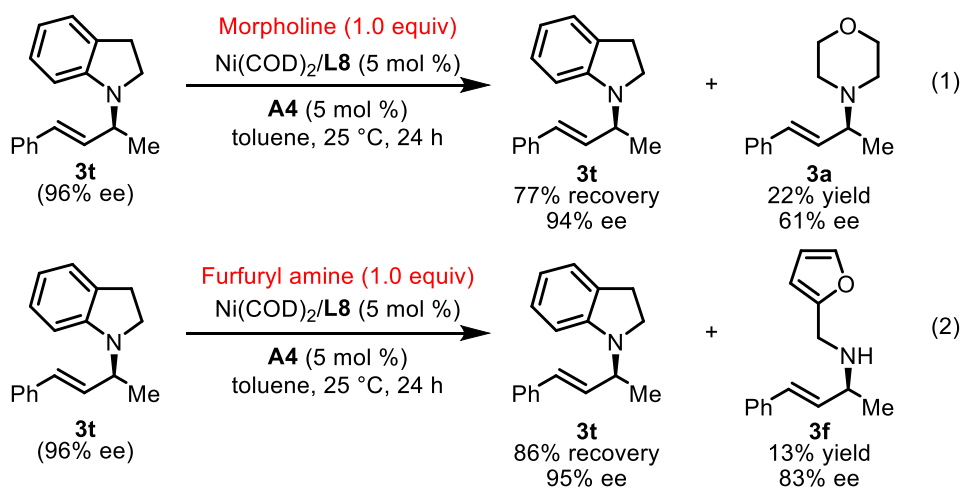


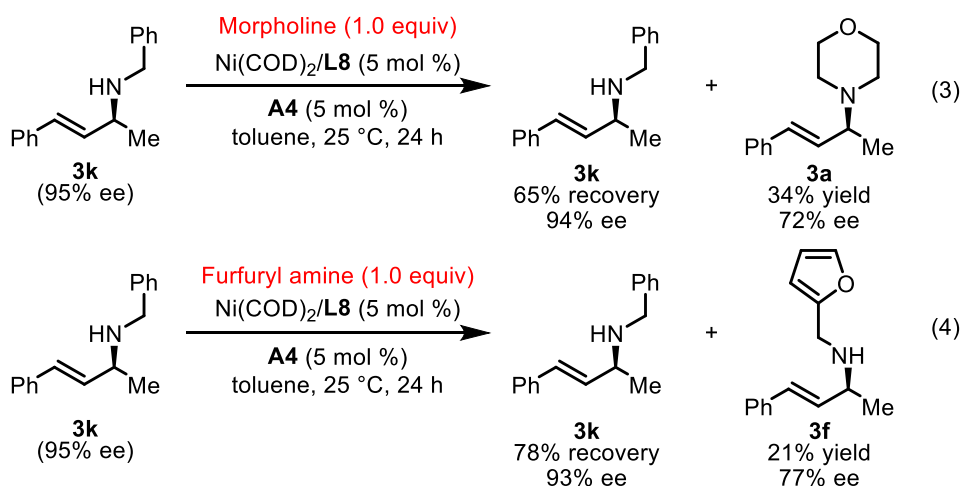
To a 20 mL vial was added the catalyst precursor  $\text{Ni(COD)}_2$  (13.8 mg, 0.05 mmol), **L8** (15.3 mg, 0.05 mmol) and toluene (5 mL) in an argon-filled glovebox. The mixture was stirred for 1 h at room temperature to give a clear orange solution. Then 1-phenylbutadiene (651.0 mg, 5.0 mmol, 1.0 equiv), amine (939.1 mg, 7.5 mmol, 1.5 equiv), **A4** (41.5 mg, 0.25 mmol) and another 5 mL toluene was added in the catalyst solution. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 25 °C for 96 h. The product was purified by column chromatography on deactivated silica gel with PE/EtOAc=1:1 to yield 1.23 g of **3g** (96% yield, 96% ee), the enantiomeric excess was determined by HPLC on Chiralpak AD-H column.



## Transamination Experiments

Scheme S5 (related to Scheme 1):

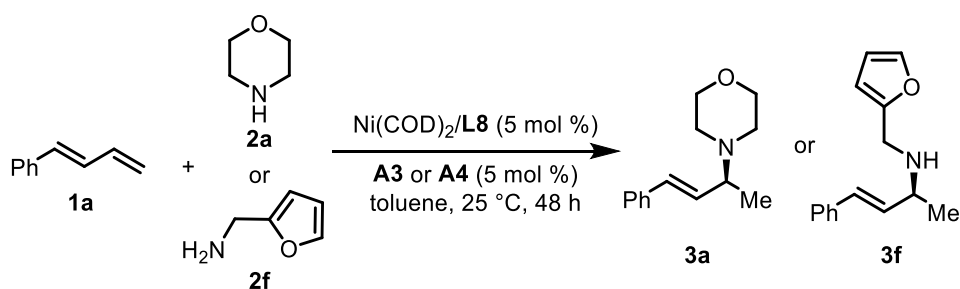




A stock solution was made by mixing  $\text{Ni}(\text{COD})_2$  with **L8** in a 1:1 molar ratio in toluene (0.01 M) at room temperature for 1 h in a argon-filled glovebox. An aliquot of the catalyst solution (0.5 mL, 0.005 mmol) was transferred by syringe into the vials charged with **3t** or **3k** (0.1 mmol, 1.0 equiv), amines (**2a** or **2f**, 0.1 mmol, 1.0 equiv) and naphthalene (3.2 mg, 0.025 mmol, 0.25 equiv), then 0.005 mmol **A4** and another 0.5 mL toluene were added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 25 °C for 24 h. Yields were determined by gas chromatogram analysis, using naphthalene as the internal standard. The ee values were determined by HPLC on a chiral stationary phase.

## Reaction Profiles

**Scheme S6** (related to **Figure 6**)<sup>[a]</sup>:



A stock solution was made by mixing  $\text{Ni}(\text{COD})_2$  with **L8** in a 1:1 molar ratio in toluene (0.01 M) at room temperature for 1 h in a argon-filled glovebox. An aliquot of the catalyst solution (1.0 mL, 0.01 mmol) was transferred by syringe into the vials charged with **1a** (0.4 mmol), amines (0.6 mmol for each) and naphthalene (12.8 mg, 0.1 mmol, 0.25 equiv), then **A3** (3.2 mg, 0.02 mmol) or **A4** (3.3 mg, 0.02 mmol) and another 1.0 mL toluene were added. The reaction vessel was sealed using a PTFE septum and stirred at 25 °C in the glovebox. The reaction progress was monitored by GC with naphthalene as the internal standard. The ee values were determined by HPLC on a chiral stationary phase.

Time [h]	Yield [%]	ee [%]	Yield [%] <sup>[b]</sup>	ee [%] <sup>[b]</sup>	Yield [%] <sup>[c]</sup>	ee [%] <sup>[c]</sup>	Yield [%] <sup>[d]</sup>	ee [%] <sup>[d]</sup>
6 h	84	98	86	97	12	98	91	98
12 h	99	97	94	96	19	98	95	98
24 h	99	94	99	93	30	97	99	98
36 h	99	91	99	92	38	97	98	98
48 h	99	88	99	90	39	97	98	98

Reaction conditions: [a] 0.40 mmol **1a**, 0.60 mmol **2a**, 5.0 mol % Ni(COD)<sub>2</sub>/L8, 5.0 mol % **A3**, 1 mL toluene, 25 °C, 48 h. [b] **A4** instead of **A3**. [c] **2f** instead of **2a**. [d] **2f** instead of **2a**, **A4** instead of **A3**.

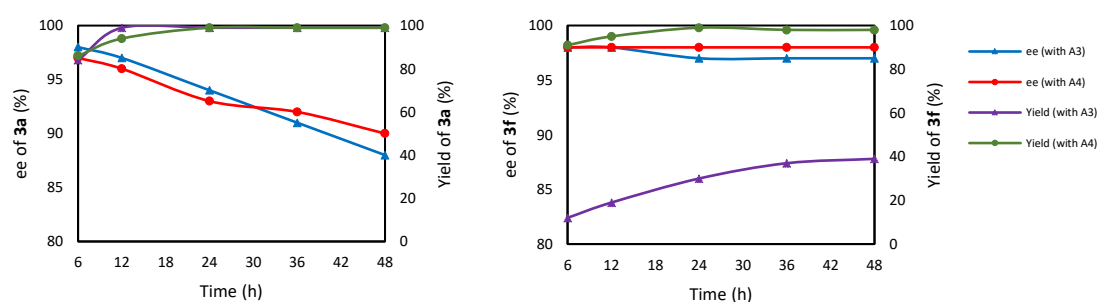
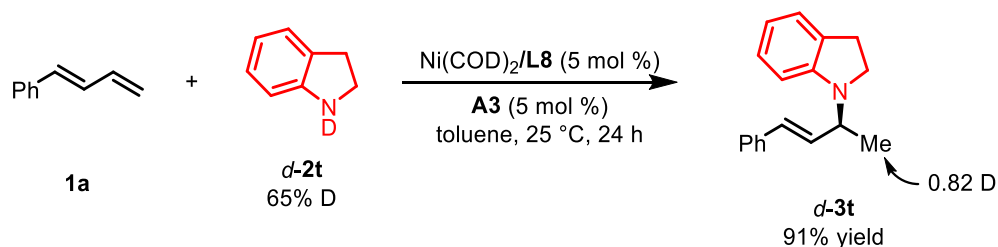


Figure S246. Time Course of Scheme S6.

## Deuterium Labeling Experiments

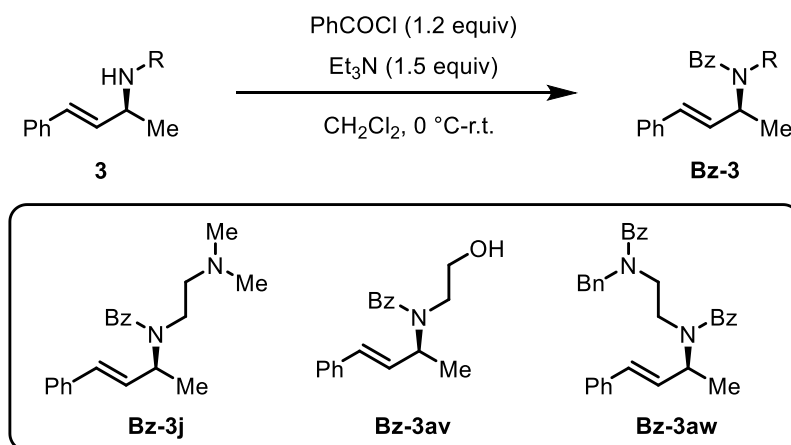
### Scheme S7:



Reaction was carried as described in General Procedure for Ni-catalyzed Asymmetric Hydroamination of Conjugated Dienes. *d*-indoline was prepared by a known previously established method (Yi & Lee, 2009). The *d-3t* was determined by <sup>1</sup>H NMR and <sup>2</sup>H NMR analysis.

## Amines Benzoylation for ee Determination (Wang et al, 2014)

### Scheme S8 (related to Figure 3 and Figure 5):



To a solution of chiral amine **3** (0.20 mmol, 1.0 equiv) and triethylamine (42  $\mu\text{L}$ , 0.30 mmol, 1.5 equiv) in DCM (0.8 mL) at 0  $^\circ\text{C}$  was added dropwise a solution of benzoyl chloride (28  $\mu\text{L}$ , 0.24 mmol, 1.2 equiv) in DCM (0.2 mL). The mixture was warmed to room temperature and stirred overnight. The mixture was quenched with water (1.0 mL) and extracted with DCM (5.0 mL), and the aqueous layer was extracted with DCM (3.0 mL). The organic layers were combined, dried over sodium sulfate, and concentrated. The residue was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether, to give amide **Bz-3**.

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