Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Enantioselective and Regiodivergent Allylation of Pyrimidines with Terminal Allenes: An Approach to Pyrimidine Acyclic Nucleosides

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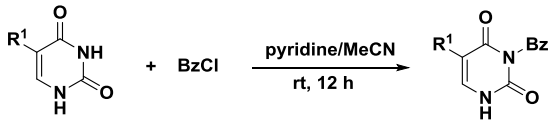
1. General information:

^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quaternary, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IA/IE/ID/ODH in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). All regents and solvents were purchased from commercial sources and purified commonly before used.

2. Synthesis of starting materials

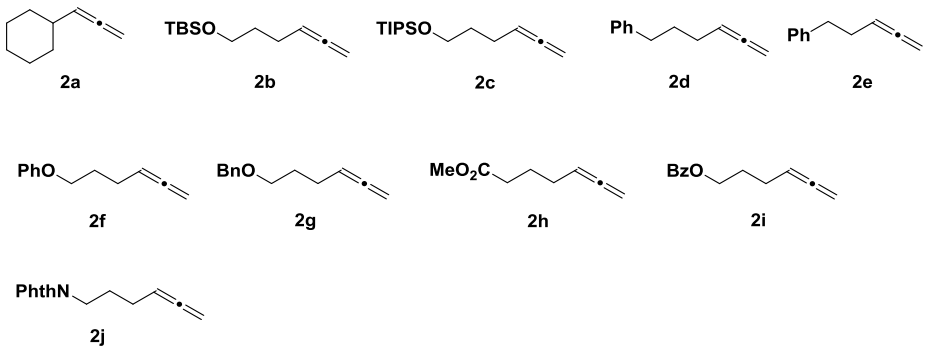
Synthesis of N^3-Bz-protected-pyrimidines (1a-1h):



R_1 = H, CH_3, Et, F, Cl, Br, I, CF_3 1a-1h

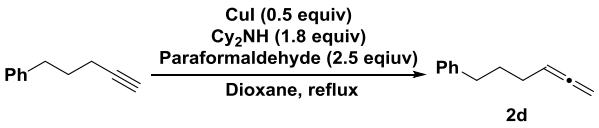
To a flask were added thymine (10 mmol), pyridine (6 mL) and MeCN (4 mL) at rt. Then, benzoyl chloride (2.6 mL, 22.7 mmol, 2.27 equiv) was added dropwise. The resulting solution was stirred at room temperature overnight. Then the reaction was partitioned between DCM (50 mL) and water (50 mL). The aqueous layer was extracted three times with DCM and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in dioxane (20 mL) and K_2CO_3 (0.75 g, 0.5 equiv), 10 mL water were added. The reaction mixture was stirred for 2 h. AcOH was added to reach pH 5. The crude residue was concentrated under vacuo and suspended in 40 mL of a saturated solution of $NaHCO_3$ for 1 h and filtered with cold water. The pure product was obtained after recrystallization in acetone (20 mL) as a solid.

Synthesis of allenes (2a-2j):



Allenes: **2a** was purchased from commercial sources. **2b-2j** were prepared via Crabbé homologation from terminal alkynes.[1]

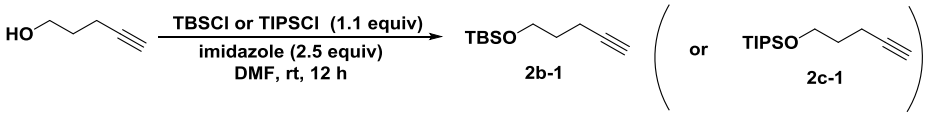
Crabbé homologation



Pent-4-yn-1-ylbenzene (1.4 g, 11.6 mmol), dicyclohexylamine (4.2 mL, 21 mmol, 1.8 equiv), CuI (1.1 g, 5.8 mmol, 0.5 equiv) and paraformaldehyde (0.9 g, 29 mmol, 2.5 equiv) were added sequentially in dioxane (80 mL). This mixture was stirred at 100 ℃ during 16 h. After cooling to room temperature the mixture was filtered through a silica pad and washed with CH_2Cl_2. The solvent was removed under reduced pressure and the remaining residue was purified by flash chromatography (eluting with PE). Purified by flash chromatography afforded the pure product **2d** as a colourless oil (1.2 g, 7.5 mmol, 66% yield).

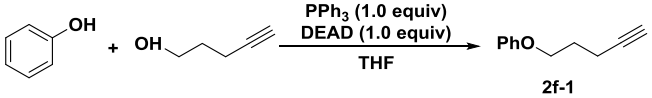
2b-2j were prepared via Crabbé homologation from corresponding terminal alkynes as described above. The corresponding terminal alkynes for the synthesis of **2d**, **2e**, **2h** and **2j** were purchased from commercial sources. Other terminal alkynes (**2b-1**, **2c-1**, **2f-1**, **2g-1**, **2h-1 and 2i-1**) for the synthesis of **2b**, **2c**, **2f**, **2g**, **2h** and **2i** were synthesized as follows:

General procedure A for the synthesis of **2d-1** and **2e-1** from 4-Pentyn-1-ol, tert-Butyldimethylsilyl chloride (TBSCl) or Triisoprpylchlorosilane chloride (TIPSCl):



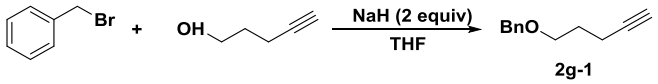
4-Pentyn-1-ol (841 mg, 10 mmol), imidazole (1.7 g, 25 mmol, 2.5 equiv) and dry DMF (15 mL) were added to a flask at 0 ^{o}C. Then a solution of tert-Butyldimethylsilyl (1.6 g, 11 mmol, 1.1 equiv) in dry DMF (10 mL) was added. The resulting mixture was stirred overnight at room temperature. The mixture was poured into water and extracted with diethyl ether (100 mL×3). The organic layer was dried over Na_2SO_4. The solvent was removed in *vacuo* and **2b-1** was obtained by silica gel column chromatography (PE/EA = 40/1) in 75% yield (colorless oil, 1.7 g). (**2c-1** was synthesized in the same reaction condition)

General procedure B for the synthesis of **2f-1**



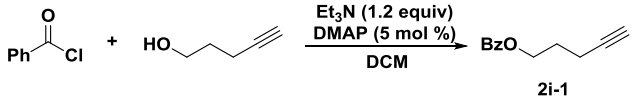
To a mixture of Phenol (0.94 g, 10 mmol), PPh_3 (2.62 g, 10 mmol, 1.0 equiv), and 4-Pentyn-1-ol (1.0 g, 12 mmol, 1.2 equiv) in THF (25 mL) was added DEAD (10 mmol, 1.0 equiv) at 0 ^oC. The mixture was stirred for 6 h and cooled to room temperature. After THF was removed under reduced pressure, the residue was chromatographed on silica gel to afford the desired alkynes **2f-1** in 68% yield (0.99 g, 6.8 mmol).

General procedure C for the synthesis of **2g-1**



To a flame-dried 250 mL RBF was added NaH (60% dispersion in mineral oil, 0.4 g, 9 mmol, 2 equiv). The solid was washed with hexanes (10 mL). Then THF (95 mL) was added to the flask and the suspension was cooled to 0 ℃. Pentynol (0.4 g, 4.6 mmol, 1 equiv) in THF (5 mL) was added dropwise. BnBr (0.52 mL, 4.6 mmol, 1 equiv) was added dropwise. The reaction was then warmed to room temperature over 15 h and then quenched with a saturated aqueous solution of NH_4Cl (25 mL). The mixture was diluted with H_2O (10 mL), and the resulting solution was extracted with EtOAc (60 mL). The combined organic layers were washed with brine (40 mL), dried with Na_2SO_4, and concentrated in vacuo. Purification by flash chromatography (PE/EA = 30:1) afforded the benzyl ether (0.72 g, 4.2 mmol, 91% yield) as a colorless oil.

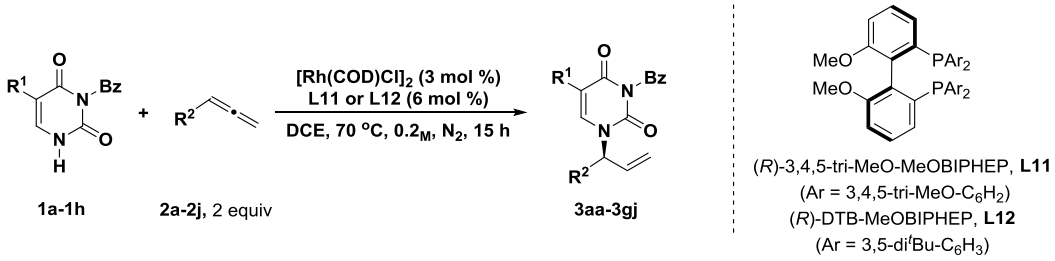
General procedure D for the synthesis of **2i-1**



To a solution of 4-Pentyn-1-ol (1.0 mL, 10 mmol) in DCM (25 mL) were added DMAP (90 mg, 0.75 mmol, 5 mol %) and Et_3N (1.7 mL, 12 mmol). The solution was cooled down to 0 ^oC and Benzoyl chloride (1.4 mL, 12 mmol, 1.2 equiv) was added dropwise. The resulting solution was stirred at room temperature during 1 h. The resulting mixture was filtrated through a short pad of silica and evaporated *in vacuo*. The residue was purified by flash chromatography (PE/EA = 30:1) afforded the product **2h-1** (1.5 g, 0.8 mmol, 80% yield) as a colorless oil.

3. Synthetic Procedures for the *N*–Allylation of Pyridazinones

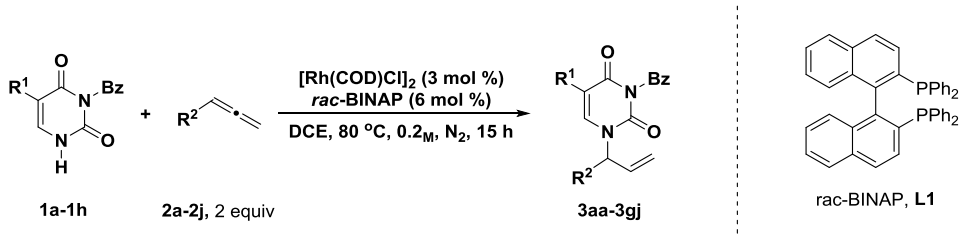
1) Procedure A: Synthesis of Chiral *N*-Allylated Pyrimidines (3aa-3gj)



The synthesis of **3aa**-**3ha**: A 10 mL screw-cap Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The tube was charged with all solid substances like substituted pyrimidines **1a**-**1d** (0.2 mmol), [Rh(COD)Cl_2] (2.9 mg, 0.006 mmol, 3 mol %) and **L11** (11.3 mg, 0.012 mmol, 6 mol %). The reaction tube was placed under vacuum and backfilled with argon three times. Freshly distilled DCE (1.0 mL, 0.2 M) followed by cyclohexylallene **2a** (48.8 mg, 0.4 mmol, 2 equiv) were added via syringe under argon. The reaction tube was sealed by a screw cap. The resulting mixture was stirred at 70 ℃ for 15 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel (V_{PE}/V_{EA} = 5:1-3:1 as eluent) to give the corresponding chiral products. **1e**-**1h** 80 ^{o}C.

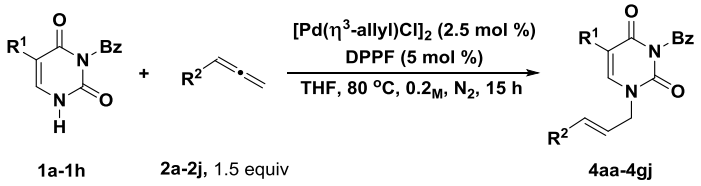
The synthesis of **3ab**-**3gj**: A 10 mL screw-cap Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The tube was charged with all solid substances like **1a** (50 mg, 0.2 mmol), [Rh(COD)Cl_2] (2.9 mg, 0.006 mmol, 3 mol %) and **L12** (12.4 mg, 0.012 mmol, 6 mol %). The reaction tube was placed under vacuum and backfilled with argon three times. Freshly distilled DCE (1.0 mL, 0.2 M) followed by allenes **2a**-**2j** (0.4 mmol, 2 equiv) were added via syringe under argon. The reaction tube was sealed by a screw cap. The resulting mixture was stirred at 70 ℃ for 15 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel (V_{PE}/V_{EA} = 5:1-3:1 as eluent) to give the corresponding chiral products.

2) Procedure B: Synthesis of Racemic *N*-Allylated Pyrimidines using [Rh(COD)Cl]$_2$/ *rac*-BINAP Catalyst System



The procedure B was utilized for the synthesis of racemic samples of compounds **3aa**-**3gj**. A 10 mL screw-cap Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The tube was charged with all solid substances like substituted pyrimidines **1a**-**1h** (0.2 mmol), [Rh(COD)Cl$_2$] (2.9 mg, 0.006 mmol, 3 mol %) and *rac*-BINAP (7.5 mg, 0.012 mmol, 6 mol %). The reaction tube was placed under vacuum and backfilled with argon three times. Freshly distilled DCE (1.0 mL, 0.2 M) followed by allenes **2a**-**2j** (0.4 mmol, 2 equiv) were added via syringe under argon. The reaction tube was sealed by a screw cap. The resulting mixture was stirred at 80 ℃ for 12 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel (V_{PE}/V_{EA} = 5:1-3:1 as eluent) to give the corresponding racemic products.

3) Procedure C: Synthesis of Linear *N*-Allylation Pyrimidine Derivatives Using [Pd(η^3-allyl)Cl]$_2$/DPPF Catalyst System

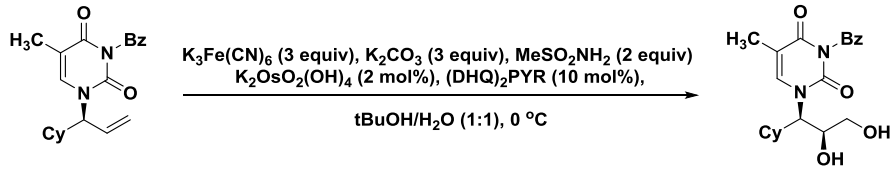


The procedure C was utilized for the synthesis of linear samples of compounds **4aa**-**3gj** and In a 10 mL sealed tube was charged with all solid substances like substituted pyrimidines **1a**-**1h** (0.2 mmol), [Pd(η^3-allyl)Cl]$_2$ (1.8 mg, 0.005 mmol, 2.5 mol %) and DPPF (5.5 mg, 0.01 mmol, 5 mol %). Freshly distilled THF (1.0 mL, 0.2 M) followed by allenes **2a**-**2j** (0.3 mmol) were added. The reaction tube was sealed by a screw cap. The resulting mixture was stirred at 80 ℃ for 15 h.

After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel (V_{PE}/V_{EA} = 2:1-3:1 as eluent) to give the corresponding linear products.

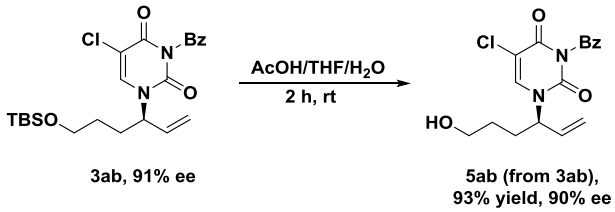
4. The Synthesis of Chiral Acyclic Nucleoside Analogues

Path a: Sharpless asymmetric dihydroxylation



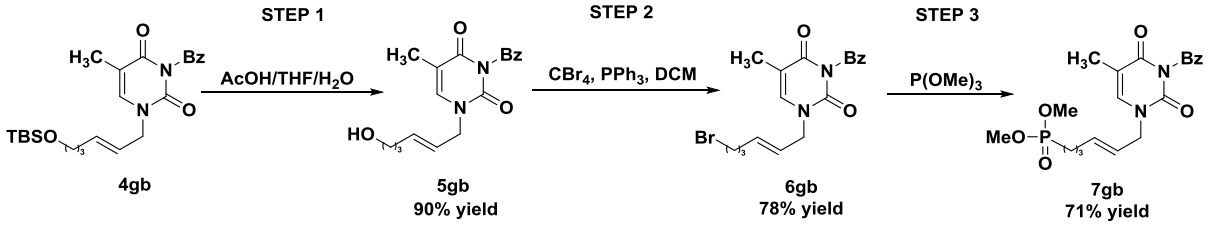
$(DHQ)_2PYR$ (17.6 mg, 0.02 mmol, 10 mol %), $K_3Fe(CN)_6$ (196 mg, 0.6 mmol, 3 equiv), K_2CO_3 (84 mg, 0.6 mmol, 3 equiv), $K_2OsO_2(OH)_4$ (1.2 mg, 0.004 mmol, 2 mol %) were suspended in a mixture of water and *tert*-butyl alcohol (1:1, 8 mL). Methanesulfonamide (38 mg, 0.4 mmol, 2 equiv) was added and the mixture stirred at room temperature for 1 hour. The reaction mixture was then added to the alkene **(*S*)-3aa** (74.4 mg, 0.2 mmol), and the heterogeneous slurry was stirred at 0 ^{o}C for 12 hours (t.l.c. control). The reaction was quenched at 0 ℃ by addition of $Na_2S_2O_3$ (6.97 g) and the mixture stirred at room temperature for *ca.* 2 hours. The reaction mixture was then partitioned between ethyl acetate and water. The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash column chromatography (V_{DCM}/V_{MeOH} = 25:1 as eluent) furnished the diol **5aa** (67.4 mg, 83% yield) as a colorless oil.

Path b: Deprotection of **3ab**



To a 25 mL flask charged with **3ab** (92.4 mg, 0.2 mmol) and AcOH /THF/H_2O (1.5 mL/0.5 mL/0.5 mL). The mixture stirred at room temperature for 3 hours. The reaction mixture was partitioned between ethyl acetate and water. The combined organic phases were dried (Na_2SO_4), filtered and concentrated in vacuo to afford a crude oil. Purification by flash column chromatography (V_{PE}/V_{EA} = 2:1 as eluent) furnished desired product **5ab** (64.7 mg, 93% yield) as a colorless oil.

Path c: The synthesis acyclic nucleoside phosphonate analogues



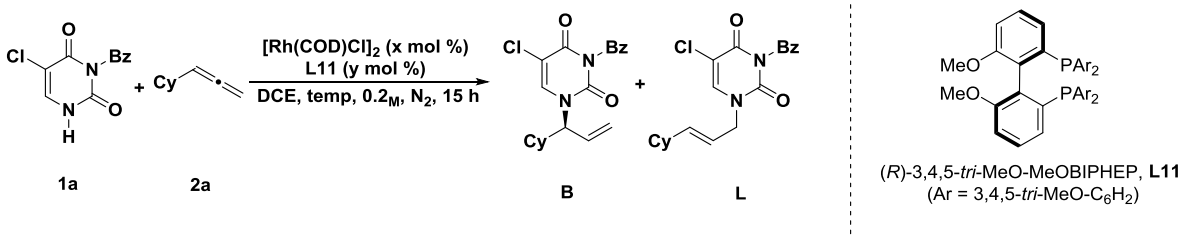
STEP 1: To a 25 mL flask charged with **4gb** (176.8 mg, 0.4 mmol) and AcOH /THF/H_2O (1.5 mL/0.5 mL/0.5 mL). The mixture stirred at room temperature for 3 hours. The reaction mixture was partitioned between ethyl acetate and water. The combined organic phases were dried (Na_2SO_4), filtered and concentrated in vacuo to afford a colorless oil (118 mg, 90% yield). **5gb** was pure enough for the next step.

STEP 2: To a 25 mL flask charged with **5gb** (65.6 mg, 0.2 mmol), CBr_4 (132 mg, 0.4 mmol, 2 equiv) and DCM (10 mL), the mixture cooled to 0 ^oC. PPh_3 (105 mg, 0.4 mmol, 2 equiv) was added via powder funnel in portions over 30 min with vigorous stirring. Upon addition of the phosphine, the colorless solution turned a pale brown color and was stirred for an additional 2 h at room temperature. The reaction mixture was partitioned between DCM and water. The combined organic phases were dried (Na_2SO_4), filtered and concentrated in vacuo to afford a crude oil. Purification by flash column chromatography (V_{PE}/V_{EA} = 4:1 as eluent) furnished desired product **5gb** (60.8 mg, 78% yield) as a light brown oil.

STEP 3: To a 10 mL flask charged with **6gb** (60.8 mg, 0.156 mmol) and $P(MeO)_3$ (3 mL). The resulting mixture was stirred at 130 ℃ for 3 h. The reaction mixture was partitioned between ethyl acetate and water. The combined organic phases were dried (Na_2SO_4), filtered and concentrated in vacuo to afford a crude oil. Purification by flash column chromatography (V_{EA}/V_{PE} = 3:1 as eluent) furnished desired product **7gb** (46.5 mg, 71% yield) as a colorless oil.

5. **Condition optimization**

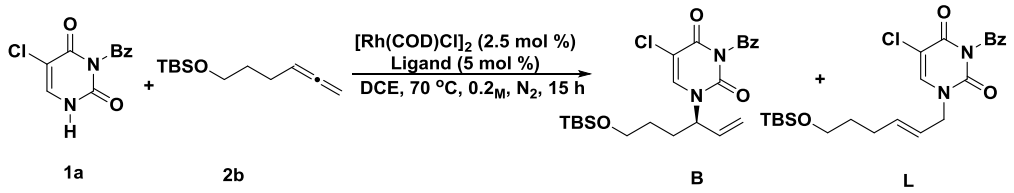
Table S1: Condition optimizations[a]

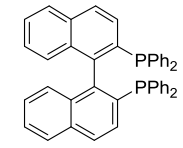


entry	solvent	x	y	temp (^{o}C)	yield[b] (%)	B:L[c]	ee[d] (%)
1	DCE	1	2	70	28		90
2	DCE	2	4	70	68	15:1	92
3	DCE	3	6	70	86	18:1	94
4	DCE	4	8	70	85	17:1	91
5	DCE	3	6	80	85	15:1	87
6	DCE	3	6	60	51	16:1	92
7	DCE	3	6	50	41	8:1	90
8	THF	3	6	70	65	10:1	56
9	toluene	3	6	70	53	9:1	72
10	DCM	3	6	70	45	11:1	63
[e]11	DCE	3	6	70	83	13:1	82
[f]12	DCE	3	6	70	71	15:1	92

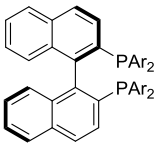
[a] **1a** (0.2 mmol), cyclohexylallene **2a** (0.4 mmol), $[Rh(COD)Cl]_2$ (x mol %) and **L11** (y mol %), in 1.0 mL of DCE, temp., N_2, 15 h. [b] Yields of isolated product. [c] The B/L ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d] Determined by chiral HPLC analysis. [e] in 0.66 mL of DCE (0.3_M). [f] in 2.0 mL of DCE (0.1_M).

Table S2: Optimization of the Reaction Conditions for allene 2b[a]

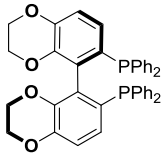




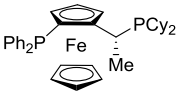
rac-BINAP, **L1**



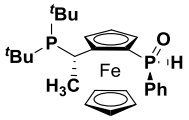
(*R*)-BINAP (Ar = Ph), **L2**
(*R*)-DTBM-BINAP, **L3**
(Ar = 3,5-di*t*Bu-4-MeOC$_6$H$_2$)



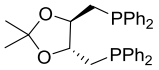
(*R*)-Synphos, **L4**



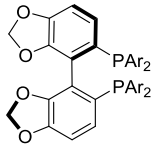
Josiphos SL-J001-1, **L5**



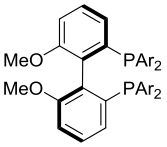
JosPOphos SL-J688-2, **L6**



(*R*,*R*)-DIOP, **L7**



(*R*)-DTBM-Segphos, **L8**
(Ar = 3,5-di*t*Bu-4-MeOC$_6$H$_2$)

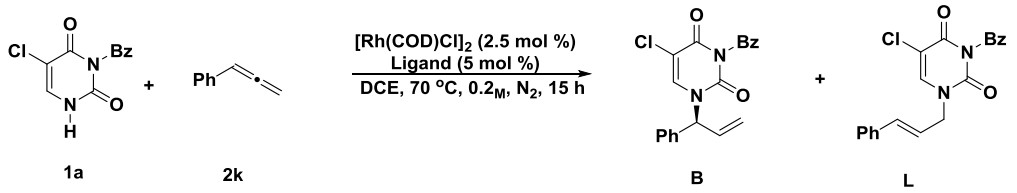


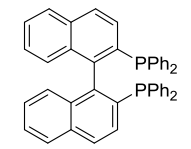
(*R*)-MeOBIPHEP (Ar = Ph), **L9**
(*R*)-DTBM-MeOBIPHEP, **L10**
(Ar = 3,5-di*t*Bu-4-MeOC$_6$H$_2$)
(R)-3,4,5-MeO-MeOBIPHEP, **L11**
(R)-3,5-^{t}Bu-MeOBIPHEP, **L12**
(R)-3,5-^{i}Pr-4-NMe$_2$-MeOBIPHEP, **L13**

entry	ligand	yield[b] (%)	B/L[c]	ee[d] (%)
1	**L3**	86	>20:1	76
2	**L8**	81	>20:1	80
3	**L10**	85	>20:1	75
4	**L11**	83	>20:1	79
5	**L12**	85	>20:1	91

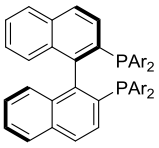
[a] **1a** (0.2 mmol), **2b** (0.4 mmol), [Rh(COD)Cl]$_2$ (3 mol %) and **Ligand** (6 mol %), in 1.0 mL of DCE, 70 °C, N_2, 15 h. [b] Yields of isolated product. [c] The B/L ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d] Determined by chiral HPLC analysis.

Table S3: Optimization of the Reaction Conditions for allene 2k[a]

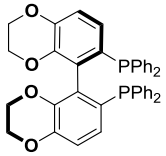




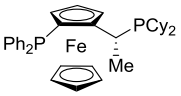
rac-BINAP, **L1**



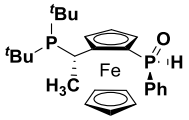
(*R*)-BINAP (Ar = Ph), **L2**
(*R*)-DTBM-BINAP, **L3**
(Ar = 3,5-di*t*Bu-4-MeOC$_6$H$_2$)



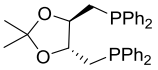
(*R*)-Synphos, **L4**



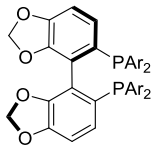
Josiphos SL-J001-1, **L5**



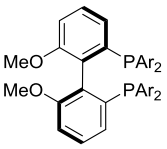
JosPOphos SL-J688-2, **L6**



(*R*,*R*)-DIOP, **L7**



(*R*)-DTBM-Segphos, **L8**
(Ar = 3,5-di*t*Bu-4-MeOC$_6$H$_2$)

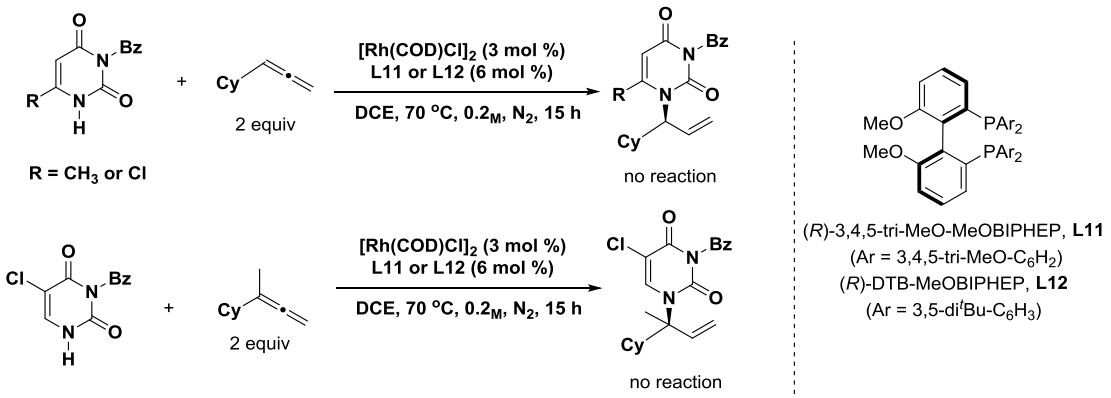


(*R*)-MeOBIPHEP (Ar = Ph), **L9**
(*R*)-DTBM-MeOBIPHEP, **L10**
(Ar = 3,5-di*t*Bu-4-MeOC$_6$H$_2$)
(R)-3,4,5-MeO-MeOBIPHEP, **L11**
(R)-3,5-^{t}Bu-MeOBIPHEP, **L12**
(R)-3,5-^{i}Pr-4-NMe$_2$-MeOBIPHEP, **L13**

entry	ligand	yield[b] (%)	B/L[c]	ee[d] (%)
1	**L3**	53	>20:1	11
2	**L8**	38	>20:1	12
3	**L10**	41	>20:1	31
4	**L11**	32	>20:1	60
5	**L12**	51	>20:1	25
[e]6	**L11**	62	>20:1	55
[f]7	**L11**	trace		

[a]**1a** (0.2 mmol), **2b** (0.4 mmol), [Rh(COD)Cl]$_2$ (3 mol %) and **Ligand** (6 mol %), in 1.0 mL of DCE, 70 °C, N_2, 15 h. [b]Yields of isolated product. [c]The B/L ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d]Determined by chiral HPLC analysis. [e](PhO)$_2$PCO$_2$H (10 mol %) was used as additive. [f]Cs_2CO_3 (10 mol %) was used as additive.

6. Some special substrates

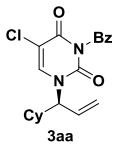


Inorder to extend this study towards ortho-substituted and 1,1-disubstituted allene pyrimidines to broaden the reaction scope. We selected 6-Cl-3-Bz pyrimidine, 6-CH_3-3-Bz pyrimidine and buta-2,3-dien-2-ylcyclohexane as the substrates to test allylation reaction. Unfortunately, we did not get the target product.

A 10 mL screw-cap Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The tube was charged with all solid substances like substituted pyrimidines (0.2 mmol), [Rh(COD)Cl_2] (2.9 mg, 0.006 mmol, 3 mol %) and **L11** or **L12** (0.012 mmol, 6 mol %). The reaction tube was placed under vacuum and backfilled with argon three times. Freshly distilled DCE (1.0 mL, 0.2 M) followed by cyclohexylallene (0.4 mmol, 2 equiv) were added via syringe under argon. The reaction tube was sealed by a screw cap. The resulting mixture was stirred at 70 ℃ for 15 h.

7. The analytical and spectral characterization data for the *N*-allylated pyrimidine analogues

(*S*)-3-Benzoyl-5-chloro-1-(1-cyclohexylallyl)pyrimidine-2,4(1*H*,3*H*)-dione (3aa)



3aa

Colorless oil, 64.0 mg, 86% yield, 18:1 B/L, 94% ee.

$[\alpha]_D^{25}$ = -49.3° (*c* = 0.50, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 15.923 min (major), 17.875 min (minor).

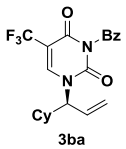
TLC: R_f = 0.32 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.43 (s, 1H), 5.94-5.88 (m, 1H), 5.41 (d, *J* = 10.2 Hz, 1H), 5.35 (d, *J* = 16.8 Hz, 1H), 4.76 (t, *J* = 8.7 Hz, 1H), 1.84-1.82 (m, 1H), 1.80-1.77 (m, 2H), 1.74-1.68 (m, 2H), 1.63-1.61 (m, 1H), 1.29-1.21 (m, 2H), 1.20-1.15 (m, 1H), 1.07-0.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 157.9, 149.4, 138.6, 135.4, 133.4, 131.2, 130.6, 129.4, 121.7, 108.9, 77.5, 77.2, 76.8, 64.2, 40.1, 30.2, 29.2, 26.0, 25.7.

HRMS (ESI): m/z calcd. For $C_{20}H_{21}ClN_2NaO_3$ $[M+Na]^+$ 395.1133, found m/z 395.1137.

(*S*)-3-Benzoyl-1-(1-cyclohexylallyl)-5-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione (3ba)



3ba

Colorless oil, 64.2 mg, 79% yield, 9:1 B/L, 91% ee.

$[\alpha]_D^{25}$ = -41.4° (*c* = 1.40, CH_2Cl_2).

HPLC CHIRALCEL OJLH, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 13.888 min (minor), 18.190 min (major).

TLC: R_f = 0.36 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.69-7.67 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 5.96-5.90 (m, 1H), 5.45 (d, *J* = 10.2 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 4.78 (t, *J* = 8.7 Hz,

1H), 1.84-1.75 (m, 4H), 1.71-1.69 (m, 1H), 1.61-1.59 (m, 1H), 1.30-1.23 (m, 2H), 1.21-1.15 (m, 1H), 1.07-0.99 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.5, 157.3, 149.4, 142.4 (d, J = 6.0 Hz), 135.5, 133.0, 131.1, 130.5, 129.4, 122.7, 122.2, 120.9, 105.3 (d, $J_{C\text{-}F}$ = 34.5 Hz), 77.4, 77.2, 77.0, 65.0, 40.1, 30.1, 29.2, 26.0, 25.6.

HRMS (ESI): m/z calcd. For $C_{21}H_{21}F_3N_2NaO_3$ $[M+Na]^+$ 429.1396, found m/z 429.1402.

(*S*)-3-Benzoyl-1-(1-cyclohexylallyl)-5-fluoropyrimidine-2,4(1*H*,3*H*)-dione (3ca)

Light yellow oil, 59.1 mg, 83% yield, 13:1 B/L, 93% ee.

$[\alpha]_D^{25}$ = -32.5° (*c* = 0.35, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 34.724 min (major), 40.742 min (minor).

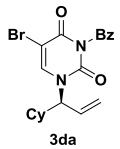
TLC: R_f = 0.3 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 6.0 Hz, 1H), 5.91-5.85 (m, 1H), 5.42 (d, J = 10.8 Hz, 1H), 5.35 (d, J = 16.8 Hz, 1H), 4.77 (t, J = 8.7 Hz, 1H), 1.84-1.81 (m, 1H), 1.81-1.77 (m, 2H), 1.72-1.66 (m, 2H), 1.65-1.60 (m, 1H), 1.28-1.21 (m, 2H), 1.20-1.14 (m, 1H), 1.09-0.98 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 155.8 (d, $J_{C\text{-}F}$ = 40.5 Hz), 148.9, 141.4, 139.0, 135.5, 133.3, 131.3, 130.6, 129.4, 125.9 (d, $J_{C\text{-}F}$ = 48.0 Hz), 121.6, 77.5, 77.2, 76.8, 63.7, 40.0, 30.2, 29.2, 26.0, 25.7.

HRMS (ESI): m/z calcd. For $C_{20}H_{21}FN_2NaO_3$ $[M+Na]^+$ 379.1428, found m/z 379.1428.

(*S*)-3-Benzoyl-5-bromo-1-(1-cyclohexylallyl)pyrimidine-2,4(1*H*,3*H*)-dione (3da)



3da

Colorless oil, 70.7 mg, 85% yield, 12:1 B/L, 93% ee.

$[\alpha]_D^{25}$ = -28.0° (*c* = 1.25, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 17.145 min (major), 18.810 min (minor).

TLC: R_f = 0.3 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (s, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 5.95-5.87 (m, 1H), 5.41 (d, *J* = 10.4 Hz, 1H), 5.35 (d, *J* = 17.2 Hz, 1H), 4.75 (t, *J* = 8.8 Hz, 1H), 1.84-1.77 (m, 3H), 1.74-1.68 (m, 2H), 1.64-1.60 (m, 1H), 1.27-1.14 (m, 3H), 1.08-0.95 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 157.9, 149.6, 141.2, 135.4, 133.4, 131.2, 130.6, 129.4, 121.8, 96.5, 77.5, 77.2, 76.8, 64.3, 40.1, 30.2, 29.2, 26.0, 25.7.

HRMS (ESI): m/z calcd. For $C_{20}H_{21}BrN_2NaO_3$ $[M+Na]^+$ 439.0628, found m/z 439.0633.

(*S*)-3-Benzoyl-1-(1-cyclohexylallyl)-5-iodopyrimidine-2,4(1*H*,3*H*)-dione (3ea)

3ea

Brown oil, 60.3 mg, 65% yield, 8:1 B/L, 87% ee.

$[\alpha]_D^{25}$ = -35.8° (*c* = 0.60, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 17.892 min (major), 19.622 min (minor).

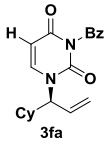
TLC: R_f = 0.28 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.68-7.63 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 5.96-5.87 (m, 1H), 5.41 (d, *J* = 10.0 Hz, 1H), 5.35 (d, *J* = 16.8 Hz, 1H), 4.73 (t, *J* = 9.0 Hz, 1H), 1.84-1.68 (m, 5H), 1.63-1.57 (m, 1H), 1.30-1.24 (m, 2H), 1.20-1.14 (m, 1H), 1.07-0.97 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 158.8, 150.0, 146.3, 135.3, 133.6, 131.2, 130.6, 129.4, 121.7, 77.4, 77.2, 77.0, 67.8, 64.4, 40.2, 30.2, 29.2, 26.0, 25.7.

HRMS (ESI): m/z calcd. For $C_{20}H_{21}IN_2NaO_3$ $[M+Na]^+$ 487.0489, found m/z 487.0486.

(*S*)-3-Benzoyl-1-(1-cyclohexylallyl)pyrimidine-2,4(1*H*,3*H*)-dione (3fa)



3fa

Light yellow oil, 41.2 mg, 61% yield, 6:1 B/L, 85% ee.

$[\alpha]_D^{25}$ = -28.1° (*c* = 0.85, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 19.765 min (minor), 22.315 min (major).

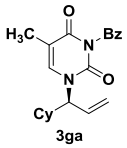
TLC: R_f = 0.25 (petroleum ether:ethyl acetate =2:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 5.94-5.88 (m, 1H), 5.83 (d, *J* = 7.8 Hz, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 4.75 (t, *J* = 8.7 Hz, 1H), 1.85-1.82 (m, 1H), 1.80-1.76 (m, 2H), 1.73-1.66 (m, 2H), 1.64-1.59 (m, 1H), 1.26-1.20 (m, 2H), 1.20-1.15 (m, 1H), 1.07-0.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 162.0, 150.3, 141.7, 135.1, 133.8, 131.7, 130.5, 129.3, 121.0, 102.4, 77.5, 77.2, 76.8, 63.6, 40.1, 30.2, 29.2, 26.1, 25.8.

HRMS (ESI): m/z calcd. For $C_{20}H_{22}N_2NaO_3$ $[M+Na]^+$ 361.1523, found m/z 361.1530.

(*S*)-3-Benzoyl-1-(1-cyclohexylallyl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (3ga)



3ga

Colorless oil, 43.3 mg, 62% yield, 10:1 B/L, 93% ee.

$[\alpha]_D^{25}$ = -71.3° (*c* = 1.21 CH_2Cl_2). ; $[\alpha]_D^{27}$ = -93.7° (*c* = 1.95 CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 18.983 min (major), 24.112 min (minor).

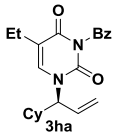
TLC: R_f = 0.34 (petroleum ether:ethyl acetate = 3:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.05 (s, 1H), 5.95-5.89 (m, 1H), 5.36 (d, *J* = 10.8 Hz, 1H), 5.31 (d, *J* = 17.4 Hz, 1H), 4.73 (t, *J* = 8.4 Hz, 1H), 1.97 (s, 3H), 1.84-1.82 (m, 1H), 1.79-1.76 (m, 2H), 1.74-1.72 (m, 1H), 1.70-1.67 (m, 1H), 1.63-1.61 (m, 1H), 1.26-1.15 (m, 4H), 1.06-0.98 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 162.7, 150.3, 137.5, 135.0, 134.0, 131.9, 130.5, 129.2, 120.8, 110.9, 77.2, 63.3, 40.0, 30.3, 29.2, 26.1, 25.8, 12.8.

HRMS (ESI): m/z calcd. For $C_{21}H_{24}N_2NaO_3$ $[M+Na]^+$ 375.1679, found m/z 375.1673.

(*S*)-3-Benzoyl-1-(1-cyclohexylallyl)-5-ethylpyrimidine-2,4(1*H*,3*H*)-dione (3ha)



Light yellow oil, 57.1 mg, 78% yield, 13:1 B/L, 92% ee.

$[\alpha]_D^{25}$ = -33.5° (*c* = 0.65, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 59.427 min (major), 66.705 min (minor).

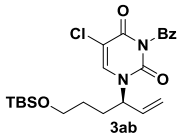
TLC: R_f = 0.35 (petroleum ether:ethyl acetate = 3:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 6.98 (s, 1H), 5.96-5.90 (m, 1H), 5.36 (d, *J* = 10.2 Hz, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 4.74 (t, *J* = 9 Hz, 1H), 2.43-2.39 (m, 2H), 1.85-1.83 (m, 1H), 1.79-1.77 (m, 2H), 1.75-1.73 (m, 1H), 1.69-1.67 (m, 1H), 1.63-1.61 (m, 1H), 1.27-1.24 (m, 2H), 1.23-1.20 (m, 1H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.07-0.98 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 162.3, 150.3, 136.7, 135.0, 134.1, 131.9, 130.5, 129.2, 120.7, 116.7, 77.5, 77.2, 76.8, 63.4, 40.0, 30.3, 29.3, 26.1, 25.8, 20.4, 13.1.

HRMS (ESI): m/z calcd. For $C_{22}H_{26}N_2NaO_3$ $[M+Na]^+$ 389.1836, found m/z 389.1843.

(*R*)-3-Benzoyl-1-(6-((*tert*-butyldimethylsilyl)oxy)hex-1-en-3-yl)-5-chloropyrimidine-2,4(1*H*,3*H*)-dione (3ab)



Colorless oil, 78.5 mg, 85% yield, >20:1 B/L, 91% ee.

$[\alpha]_D^{25}$ = -2.4^o (*c* = 0.60, CH_2Cl_2).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 254 nm, retention time: 12.578 min (minor), 14.075 min (major).

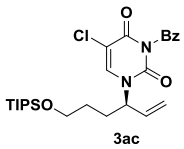
TLC: R_f = 0.37 (petroleum ether:ethyl acetate = 3:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.43 (s, 1H), 5.94-5.85 (m, 1H), 5.43 (d, *J* = 9.6 Hz, 1H), 5.37 (d, *J* = 16.0 Hz, 1H), 5.16 (q, *J* = 8.4 Hz, 1H), 3.65 (t, *J* = 5.8 Hz, 2H), 2.03-1.94 (m, 1H), 1.86-1.76 (m, 1H), 1.63-1.47 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 158.0, 149.4, 137.9, 135.4, 134.9, 131.2, 130.6, 129.4, 120.0, 109.2, 77.4, 77.2, 77.0, 62.0, 57.7, 29.1, 29.0, 26.1, 18.4, -5.2.

HRMS (ESI): m/z calcd. For $C_{23}H_{31}ClN_2NaO_4Si$ $[M+Na]^+$ 485.1634, found m/z 485.1642.

(*R*)-3-Benzoyl-5-chloro-1-(6-((triisopropylsilyl)oxy)hex-1-en-3-yl)pyrimidine-2,4(1*H*,3*H*)-dione (3ac)



3ac

Colorless oil, 81.7 mg, 81% yield, 19:1 B/L, 89% ee.

$[\alpha]_D^{25}$ = -10.3^o (*c* = 0.83, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 254 nm, retention time: 19.942 min (major), 21.785 min (minor).

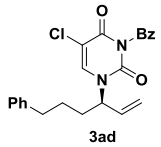
TLC: R_f = 0.40 (petroleum ether:ethyl acetate = 3:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.44 (s, 1H), 5.94-5.85 (m, 1H), 5.42 (d, *J* = 10.4 Hz, 1H), 5.37 (d, *J* = 17.6 Hz, 1H), 5.16 (q, *J* = 7.2 Hz, 1H), 3.73 (t, *J* = 6.0 Hz, 2H), 2.07-1.97 (m, 1H), 1.90-1.80. (m, 1H), 1.64-1.50 (m, 2H), 1.13-1.05 (m, 21H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 157.9, 149.4, 137.9, 135.4, 135.0, 131.2, 130.6, 129.4, 119.9, 109.1, 77.4, 77.2, 77.0, 62.2, 57.7, 29.2, 29.0, 18.1, 12.0.

HRMS (ESI): m/z calcd. For $C_{26}H_{37}ClN_2NaO_4Si$ $[M+Na]^+$ 527.2103, found m/z 527.2108.

(*R*)-3-Benzoyl-5-chloro-1-(6-phenylhex-1-en-3-yl)pyrimidine-2,4(1*H*,3*H*)-dione (3ad)



3ad

Light yellow oil, 67.7 mg, 83% yield, >20:1 B/L, 89% ee.

$[\alpha]_D^{25}$ = -0.9° (*c* = 0.90, CH_2Cl_2).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 21.382 min (major), 25.283 min (minor).

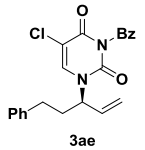
TLC: R_f = 0.28 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 6.0 Hz, 2H), 7.36 (s, 1H), 7.30-7.25 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.90-5.81 (m, 1H), 5.40 (d, *J* = 11.6 Hz, 1H), 5.32 (d, *J* = 16.0 Hz, 1H), 5.17 (q, *J* = 7.2 Hz, 1H), 2.73-2.60 (m, 2H), 1.93-1.83 (m, 1H), 1.80-1.61 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 157.9, 149.4, 141.2, 137.8, 135.4, 134.7, 131.1, 130.6, 129.4, 128.7, 128.5, 126.3, 120.1, 109.2, 77.4, 77.2, 77.0, 57.6, 35.2, 32.0, 27.6.

HRMS (ESI): m/z calcd. For $C_{23}H_{21}ClN_2NaO_3$ $[M+Na]^+$ 431.1133, found m/z 431.1140.

(*R*)-3-Benzoyl-5-chloro-1-(5-phenylpent-1-en-3-yl)pyrimidine-2,4(1*H*,3*H*)-dione (3ae)



3ae

Colorless oil, 67.8 mg, 86% yield, >20:1 B/L, 88% ee.

$[\alpha]_D^{25}$ = -35.8° (*c* = 0.88, CH_2Cl_2).

HPLC CHIRALCEL ID, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 23.637 min (major), 28.008 min (minor).

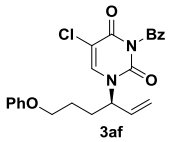
TLC: R_f = 0.31 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.35 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 5.94-5.88 (m, 1H), 5.43 (d, *J* = 11.4 Hz, 1H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.18 (q, *J* = 7.8 Hz, 1H), 2.79-2.74 (m, 1H), 2.66-2.61 (m, 1H), 2.24-2.18 (m, 1H), 2.15-2.10 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 157.9, 149.3, 140.1, 137.9, 135.4, 134.6, 131.2, 130.6, 129.4, 128.9, 128.3, 126.6, 120.1, 109.0, 77.4, 77.2, 77.0, 58.1, 34.1, 32.3.

HRMS (ESI): m/z calcd. For $C_{22}H_{19}ClN_2NaO_3$ $[M+Na]^+$ 417.0976, found m/z 417.0972.

(*R*)-3-Benzoyl-5-chloro-1-(6-phenoxyhex-1-en-3-yl)pyrimidine-2,4(1*H*,3*H*)-dione (3af)



3af

Light brown oil, 72.1 mg, 85% yield, >20:1 B/L, 89% ee.

$[\alpha]_D^{25}$ = -21.4° (*c* = 1.40, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 19.418 min (major), 27.092 min (minor).

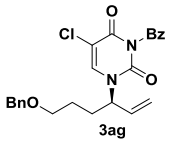
TLC: R_f = 0.33 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.49 (m, 3H), 7.30-7.25 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 5.95-5.87 (m, 1H), 5.45 (d, *J* = 10.0 Hz, 1H), 5.40 (d, *J* = 16.0 Hz, 1H), 5.20 (q, *J* = 7.2 Hz, 1H), 3.99 (t, *J* = 5.0 Hz, 2H), 2.16-2.07 (m, 1H), 2.00-1.89 (m, 1H), 1.88-1.79 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 158.7, 157.9, 149.4, 137.9, 135.5, 134.6, 131.1, 130.6, 129.6, 129.4, 121.1, 120.4, 114.6, 109.3, 77.4, 77.2, 77.0, 66.7, 57.8, 29.4, 25.8.

HRMS (ESI): m/z calcd. For $C_{23}H_{21}ClN_2NaO_4$ $[M+Na]^+$ 447.1082, found m/z 447.1092.

(*R*)-3-Benzoyl-1-(6-(benzyloxy)hex-1-en-3-yl)-5-chloropyrimidine-2,4(1*H*,3*H*)-dione (3ag)



3ag

Light yellow oil, 72.7 mg, 83% yield, 14:1 B/L, 88% ee.

$[\alpha]_D^{25}$ = -6.1° (*c* = 0.70, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 19.890 min (major), 21.807 min (minor).

TLC: R_f = 0.29 (petroleum ether:ethyl acetate = 4:1) [UV].

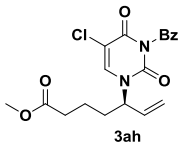
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.43 (s, 1H), 7.37-7.28 (m, 5H), 5.93-5.84 (m, 1H), 5.42 (d, *J* = 10.0 Hz, 1H), 5.36 (d, *J*

= 16.4 Hz, 1H), 5.13 (q, *J* = 7.6 Hz, 1H), 4.50 (s, 2H), 3.51 (t, *J* = 5.2 Hz, 2H), 2.04-1.96 (m, 1H), 1.90-1.81 (m, 1H), 1.73-1.60 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 158.0, 149.3, 138.3, 138.1, 135.4, 134.7, 131.2, 130.6, 129.4, 128.6, 127.9, 127.8, 120.1, 109.1, 77.4, 77.2, 77.0, 73.2, 69.2, 58.0, 29.5, 26.2.

HRMS (ESI): m/z calcd. For $C_{24}H_{23}ClN_2NaO_4$ $[M+Na]^+$ 461.1239, found m/z 461.1245.

Methyl (*R*)-5-(3-Benzoyl-5-chloro-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)hept-6-enoate (3ah)



3ah

Colorless oil, 56.2 mg, 72% yield, 11:1 B/L, 87% ee.

$[\alpha]_D^{25}$ = -5.3^o (*c* = 0.55, CH_2Cl_2).

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 254 nm, retention time: 32.918 min (minor), 34.833 min (major).

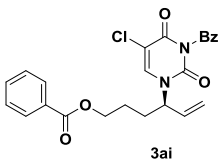
TLC: R_f = 0.32 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.44 (s, 1H), 5.92-5.84 (m, 1H), 5.44 (d, *J* = 11.2 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.13 (q, *J* = 7.6 Hz, 1H), 3.67 (s, 3H), 2.38 (t, *J* = 7.0 Hz, 2H), 1.97-1.88 (m, 1H), 1.84-1.73 (m, 1H), 1.72-1.62 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3, 167.6, 157.9, 149.3, 137.8, 135.5, 134.4, 131.1, 130.7, 129.4, 120.4, 109.3, 77.4, 77.2, 77.0, 57.6, 51.9, 33.1, 31.9, 21.1.

HRMS (ESI): m/z calcd. For $C_{19}H_{19}ClN_2NaO_5$ $[M+Na]^+$ 413.0875, found m/z 413.0881.

(*R*)-4-(3-Benzoyl-5-chloro-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)hex-5-en-1-yl benzoate (3ai)



3ai

Light yellow oil, 63.3 mg, 70% yield, 9:1 B/L, 85% ee.

$[\alpha]_D^{25}$ = -16.1^o (*c* = 0.70, CH_2Cl_2).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 254 nm, retention time: 18.153 min (major), 23.453 min (minor).

TLC: R_f = 0.33 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.52-7.43 (m, 5H), 5.96-5.87 (m, 1H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.20 (q, *J* = 6.4 Hz, 1H), 4.37 (t, *J* = 6.0 Hz, 2H), 2.08-1.99 (m, 1H), 1.95-1.76 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 166.6, 157.9, 149.3, 137.7, 135.5, 134.3, 133.3, 131.1, 130.6, 130.1, 129.7, 129.4, 128.6, 120.7, 109.4, 77.4, 77.2, 77.0, 63.9, 57.7, 29.4, 25.5.

HRMS (ESI): m/z calcd. For $C_{24}H_{21}ClN_2NaO_5$ $[M+Na]^+$ 475.1031, found m/z 475.1037.

(*S*)-3-benzoyl-5-chloro-1-(1-phenylallyl)pyrimidine-2,4(1*H*,3*H*)-dione (3ak)

3ak

Light yellow oil, 23.4 mg, 32% yield, >20:1 B/L, 60% ee.

$[\alpha]_D^{25}$ = -49^{o} (*c* = 0.43, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 254 nm, retention time: 22.209 min (major), 23.591 min (minor).

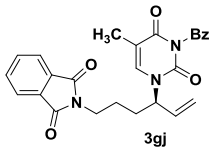
TLC: R_f = 0.31 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.42 (m, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 6.38 (d, *J* = 5.3 Hz, 1H), 6.19 (m, 1H), 5.60 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 17.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 157.9, 149.2, 138.6, 135.9, 135.5, 133.5, 131.1, 130.7, 129.6, 129.4, 129.4, 128.2, 121.3, 109.0, 77.4, 77.2, 76.9, 61.2.

HRMS (ESI): m/z calcd. For $C_{20}H_{15}ClN_2NaO_3$ $[M+Na]^+$ 389.0663, found m/z 389.0670.

(*R*)-2-(4-(3-Benzoyl-5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)hex-5-en-1-yl)isoindoline-1,3-dione (3gj)



3gj

Light yellow oil, 51.2 mg, 56% yield, 7:1 B/L, 91% ee.

$[\alpha]_D^{25}$ = -17.6^{o} (*c* = 0.43, CH_2Cl_2).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 254 nm, retention time: 29.740 min (major), 38.777 min (minor).

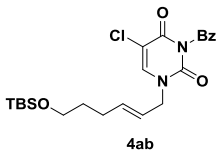
TLC: R_f = 0.33 (petroleum ether:ethyl acetate = 4:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.90-7.83 (m, 2H), 7.34-7.72 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.01 (s, 1H), 5.92-5.84 (m, 1H), 5.38 (d, *J* = 10.8 Hz, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.16 (q, *J* = 6.4 Hz, 1H), 3.77-3.69(m, 2H), 1.94 (s, 3H), 1.90-1.68 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.5, 162.7, 150.2, 136.5, 135.1, 134.2, 132.1, 131.7, 130.6, 129.3, 123.5, 119.7, 111.5, 77.5, 77.2, 76.8, 56.7, 37.4, 29.9, 25.3, 12.8.

HRMS (ESI): m/z calcd. For $C_{26}H_{23}N_3NaO_5$ $[M+Na]^+$ 480.1530, found m/z 480.1539.

(*E*)-3-Benzoyl-1-(6-((*tert*-butyldimethylsilyl)oxy)hex-2-en-1-yl)-5-chloropyrimidine-2,4(1*H*,3*H*)-dione (4ab)



4ab

Light brown oil, 78.5 mg, 85% yield, 12:1 E/Z.

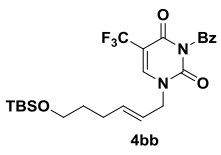
TLC: R_f = 0.25 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.52-7.48 (m, 3H), 5.86 (dt, *J* = 6.8 Hz, 15.2 Hz, 1H), 5.52 (dt, *J* = 6.8 Hz, 15.2 Hz, 1H), 4.32 (d, *J* = 6.8 Hz, 2H), 3.62 (t, *J* = 6.2 Hz, 2H), 2.18 (q, *J* = 7.2 Hz, 2H), 1.66-1.59 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 158.4, 149.0, 140.3, 138.8, 135.5, 131.1, 130.7, 129.4, 122.4, 108.7, 77.5, 77.2, 76.8, 62.4, 50.4, 31.9, 28.8, 26.1, 18.4, -5.2.

HRMS (ESI): m/z calcd. For $C_{23}H_{31}ClN_2NaO_4Si$ $[M+Na]^+$ 485.1634, found m/z 485.1635.

(*E*)-3-Benzoyl-1-(6-((*tert*-butyldimethylsilyl)oxy)hex-2-en-1-yl)-5-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione (4bb)



4bb

Brown oil, 79.4 mg, 80% yield, 13:1 E/Z.

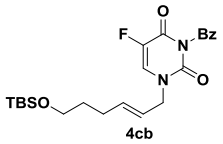
TLC: R_f = 0.30 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.76 (s, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 5.94-5.87 (m, 1H), 5.57-5.50 (m, 1H), 4.37 (d, *J* = 6.8 Hz, 2H), 3.62 (t, *J* = 6.0 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 2H), 1.66-1.59 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 157.9, 149.0, 144.1 (d, J_{C-F} = 5.0 Hz), 139.5, 135.6, 131.1, 130.6, 129.4, 122.0, 105.2 (d, J_{C-F} = 33.0 Hz), 77.5, 77.2, 76.8, 62.3, 50.9, 31.9, 28.8, 26.1, 18.4, -5.2.

HRMS (ESI): m/z calcd. For $C_{24}H_{31}F_3N_2NaO_4Si$ $[M+Na]^+$ 519.1897, found m/z 519.1895.

(*E*)-3-Benzoyl-1-(6-((*tert*-butyldimethylsilyl)oxy)hex-2-en-1-yl)-5-fluoropyrimidine-2,4(1*H*,3*H*)-dione (4cb)



4cb

Brown oil, 72.3 mg, 81% yield, 16:1 E/Z.

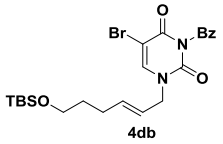
TLC: R_f = 0.31 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 5.2 Hz, 1H), 5.90-5.83 (m, 1H), 5.55-5.48 (m, 1H), 4.30 (d, *J* = 6.8 Hz, 2H), 3.62 (t, *J* = 6.2 Hz, 2H), 2.18 (q, *J* = 7.6 Hz, 2H), 1.66-1.60 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 156.3 (d, J_{C-F} = 27.0 Hz), 148.4, 141.3, 138.9, 135.6, 131.1, 130.7, 129.4, 127.5 (d, J_{C-F} = 33.0 Hz), 122.4, 77.5, 77.2, 76.8, 62.4, 50.2, 31.9, 28.8, 26.1, 18.5, -5.2.

HRMS (ESI): m/z calcd. For $C_{23}H_{31}FN_2NaO_4Si$ $[M+Na]^+$ 469.1929, found m/z 469.1922.

(*E*)-3-Benzoyl-5-bromo-1-(6-((*tert*-butyldimethylsilyl)oxy)hex-2-en-1-yl)pyrimidine-2,4(1*H*,3*H*)-dione (4db)



4db

Brown oil, 84.0 mg, 83% yield, 14:1 E/Z.

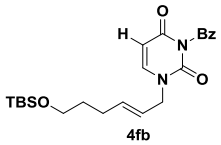
TLC: R_f = 0.26 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.60 (s, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 5.87 (dt, *J* = 6.4 Hz, 14.8 Hz, 1H), 5.52 (dt, *J* = 6.8 Hz, 15.2 Hz, 1H), 4.33 (d, *J* = 6.8 Hz, 2H), 3.62 (t, *J* = 6.2 Hz, 2H), 2.18 (q, *J* = 7.2 Hz, 2H), 1.66-1.59 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 158.3, 149.1, 142.8, 138.7, 135.4, 131.0, 130.6, 129.3, 122.4, 96.3, 77.4, 77.1, 76.7, 62.3, 50.4, 31.8, 28.7, 26.0, 18.4, -5.3.

HRMS (ESI): m/z calcd. For $C_{23}H_{31}BrN_2NaO_4Si$ $[M+Na]^+$ 529.1129, found m/z 529.1131.

(*E*)-3-Benzoyl-1-(6-((*tert*-butyldimethylsilyl)oxy)hex-2-en-1-yl)pyrimidine-2,4(1*H*,3*H*)-dione (4fb)



4fb

Brown oil, 59.9 mg, 70% yield, 13:1 E/Z.

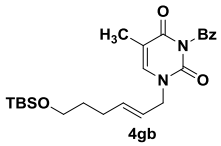
TLC: R_f = 0.22 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.24 (s, 1H), 5.84-5.75 (m, 2H), 5.54-5.47 (m, 1H), 4.30 (d, *J* = 6.4 Hz, 2H), 3.60 (t, *J* = 6.2 Hz, 2H), 2.14 (q, *J* = 7.2 Hz, 2H), 1.63-1.56 (m, 2H), 0.87 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 162.6, 149.9, 143.4, 137.9, 135.2, 131.6, 130.6, 129.3, 122.9, 102.4, 77.5, 77.2, 76.8, 62.4, 50.1, 32.0, 28.8, 26.1, 18.5, -5.2.

HRMS (ESI): m/z calcd. For $C_{23}H_{32}N_2NaO_4Si$ $[M+Na]^+$ 451.2024, found m/z 451.2019.

(*E*)-3-Benzoyl-1-(6-((*tert*-butyldimethylsilyl)oxy)hex-2-en-1-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (4gb)



4gb

Light brown oil, 78.2 mg, 88% yield, 17:1 E/Z.

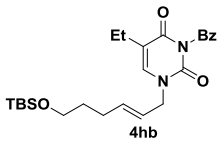
TLC: R_f = 0.30 (petroleum ether:ethyl acetate = 3:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.04 (s, 1H), 5.80-5.73 (m, 1H), 5.51-5.44 (m, 1H), 4.24 (d, *J* = 6.4 Hz, 2H), 3.57 (t, *J* = 6.2 Hz, 2H), 2.11 (q, *J* = 7.2 Hz, 2H), 1.91 (s, 3H), 1.61-1.54 (m, 2H), 0.85 (s, 9H), 0.00 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 163.2, 149.9, 139.4, 137.3, 135.1, 131.8, 130.5, 129.2, 123.3, 110.9, 77.5, 77.2, 76.8, 62.4, 49.8, 32.0, 28.7, 26.1, 18.5, 12.6, -5.2.

HRMS (ESI): m/z calcd. For $C_{24}H_{34}N_2NaO_4Si$ $[M+Na]^+$ 465.2180, found m/z 465.2177.

(*E*)-3-Benzoyl-1-(6-((tert-butyldimethylsilyl)oxy)hex-2-en-1-yl)-5-ethylpyrimidine-2,4 (1*H*,3*H*)-dione (4hb)



Brown oil, 59.3 mg, 65% yield, 15:1 E/Z.

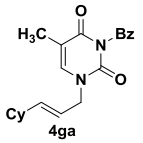
TLC: R_f = 0.31 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 8.6 Hz, 2H), 7.02 (s, 1H), 5.84-5.77 (m, 1H), 5.56-5.49 (m, 1H), 4.30 (d, *J* = 6.4 Hz, 2H), 3.61 (t, *J* = 6.2 Hz, 2H), 2.38 (q, *J* = 7.2 Hz, 2H), 2.16 (q, *J* = 7.6 Hz, 2H), 1.65-1.58 (m, 2H), 1.14 (t, *J* = 7.4 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 162.9, 149.8, 138.7, 137.2, 135.0, 131.8, 130.5, 129.2, 123.4, 116.7, 77.5, 77.2, 76.8, 62.4, 49.9, 32.0, 28.7, 26.1, 20.2, 18.4, 12.9, -5.2.

HRMS (ESI): m/z calcd. For $C_{25}H_{36}N_2NaO_4Si$ $[M+Na]^+$ 479.2337, found m/z 479.2335.

(*E*)-3-Benzoyl-1-(3-cyclohexylallyl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (4ga)



Colorless oil, 60.5 mg, 86% yield, 14:1 E/Z.

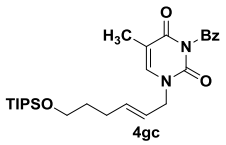
TLC: R_f = 0.23 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.08 (s, 1H), 5.74 (dd, *J* = 6.4, *J* = 6.8 Hz, 15.6 Hz, 1H), 5.49-5.42 (m, 1H), 4.29 (d, *J* = 6.4 Hz, 2H), 2.05-2.01 (m, 1H), 1.96 (s, 3H), 1.75-1.60 (m, 5H), 1.33-1.24 (m, 2H), 1.20-1.05 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 163.3, 149.9, 143.5, 139.4, 135.1, 131.8, 130.6, 129.2, 120.6, 110.9, 77.5, 77.2, 76.8, 49.9, 40.5, 32.7, 26.1, 26.0, 12.6.

HRMS (ESI): m/z calcd. For $C_{21}H_{24}N_2NaO_3$ $[M+Na]^+$ 375.1679, found m/z 375.1684.

(*E*)-3-Benzoyl-5-methyl-1-(6-((triisopropylsilyl)oxy)hex-2-en-1-yl)pyrimidine-2,4(1*H*,3*H*)-dione (4gc)



Light brown oil, 69.7 mg, 72% yield, 13:1 E/Z.

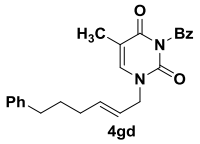
TLC: R_f = 0.33 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.09 (s, 1H), 5.84 (dt, *J* = 6.4 Hz, 14.8 Hz, 1H), 5.52 (dt, *J* = 6.4 Hz, 15.2 Hz, 1H), 4.28 (d, *J* = 6.4 Hz, 2H), 3.69 (t, *J* = 6.2 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 2H), 1.95 (s, 3H), 1.67-1.61 (m, 2H), 1.11-1.03 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 163.2, 149.9, 139.4, 137.4, 135.1, 131.7, 130.5, 129.2, 123.2, 110.9, 77.5, 77.2, 76.8, 62.6, 49.8, 32.2, 28.7, 18.1, 12.6, 12.0.

HRMS (ESI): m/z calcd. For $C_{27}H_{40}N_2NaO_4Si$ $[M+Na]^+$ 507.2650, found m/z 507.2645.

(*E*)-3-Benzoyl-5-methyl-1-(6-phenylhex-2-en-1-yl)pyrimidine-2,4(1*H*,3*H*)-dione (4gd)



Colorless oil, 58.2 mg, 75% yield, 8:1 E/Z.

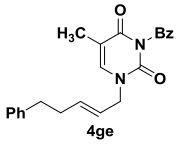
TLC: R_f = 0.33 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 6.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22-7.16 (m, 3H), 7.08 (s, 1H), 5.80 (dt, *J* = 6.8 Hz, 15.2 Hz, 1H), 5.32 (dt, *J* = 6.4 Hz, 15.2 Hz, 1H), 4.29 (d, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.14 (q, *J* = 7.2 Hz, 2H), 1.95 (s, 3H), 1.78-1.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 163.2, 149.9, 142.1, 139.5, 137.1, 135.0, 131.8, 130.5, 129.2, 128.5, 128.4, 125.9, 123.5, 110.9, 77.5, 77.2, 76.8, 49.8, 35.4, 31.8, 30.6, 12.5.

HRMS (ESI): m/z calcd. For $C_{24}H_{24}N_2NaO_3$ $[M+Na]^+$ 411.1679, found m/z 411.1682.

(*E*)-3-Benzoyl-5-methyl-1-(5-phenylpent-2-en-1-yl)pyrimidine-2,4(1*H*,3*H*)-dione (4ge)



Colorless oil, 62.1 mg, 83% yield, 10:1 E/Z.

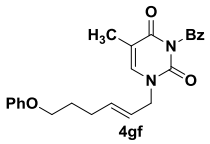
TLC: R_f = 0.31 (petroleum ether:ethyl acetate = 3:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.31-7.26 (m, 2H), 7.22-7.16 (m, 3H), 6.96 (s, 1H), 5.80 (dt, *J* = 6.8 Hz, 14.8 Hz, 1H), 5.49 (dt, *J* = 6.8 Hz, 15.2 Hz, 1H), 4.26 (d, *J* = 6.4 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.43 (q, *J* = 7.2 Hz, 2H), 1.94 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 163.2, 149.9, 141.2, 139.3, 136.5, 135.0, 131.8, 130.5, 129.2, 128.6, 128.5, 126.2, 124.0, 110.9, 77.4, 77.2, 77.0, 49.6, 35.2, 33.9, 12.6.

HRMS (ESI): m/z calcd. For $C_{23}H_{22}N_2NaO_3$ $[M+Na]^+$ 397.1523, found m/z 397.1513.

(*E*)-3-Benzoyl-5-methyl-1-(6-phenoxyhex-2-en-1-yl)pyrimidine-2,4(1*H*,3*H*)-dione (4gf)



4gf

Colorless oil, 60.6 mg, 75% yield, 8:1 E/Z.

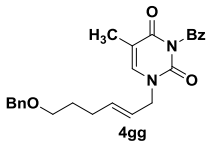
TLC: R_f = 0.31 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.83 (t, *J* = 7.4 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.08-6.01 (m, 1H), 5.80-5.73 (m, 1H), 4.50 (d, *J* = 6.8 Hz, 2H), 4.17 (t, *J* = 6.0 Hz, 2H), 2.50 (q, *J* = 7.6 Hz, 2H), 2.13 (s, 3H), 2.12-2.07 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 163.2, 159.0, 149.9, 139.4, 136.5, 135.1, 131.7, 130.6, 129.6, 129.2, 123.9, 120.8, 114.5, 111.0, 77.5, 77.2, 76.8, 66.9, 49.8, 28.9, 28.5, 12.6.

HRMS (ESI): m/z calcd. For $C_{24}H_{24}N_2NaO_4$ $[M+Na]^+$ 427.1628, found m/z 427.1633.

(*E*)-3-Benzoyl-1-(6-(benzyloxy)hex-2-en-1-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (4gg)



4gg

Light brown oil, 64.4 mg, 77% yield, 10:1 E/Z.

TLC: R_f = 0.21 (petroleum ether:ethyl acetate = 3:1) [UV].

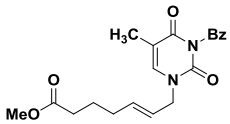
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.37-7.27 (m, 5H), 7.05 (s, 1H), 5.79 (dt, *J* = 6.8 Hz, 15.2 Hz, 1H), 5.50 (dt, *J* = 6.4 Hz,

15.6 Hz, 1H), 4.50 (s, 2H), 4.28 (d, *J* = 6.8 Hz, 2H), 3.48 (t, *J* = 6.4 Hz, 2H), 2.21 (q, *J* = 7.2 Hz, 2H), 1.94 (s, 3H), 1.76-1.69 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 163.3, 149.9, 139.4, 138.6, 137.0, 135.1, 131.8, 130.6, 129.2, 128.5, 127.8, 127.8, 123.6, 111.0, 77.4, 77.2, 77.0, 73.1, 69.5, 49.8, 29.1, 12.6.

HRMS (ESI): m/z calcd. For $C_{25}H_{26}N_2NaO_4$ $[M+Na]^+$ 441.1785 found m/z 441.1790.

Methyl (*E*)-7-(3-benzoyl-5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)hept-5-enoate (4gh)



4gh

Brown oil, 54.0 mg, 73% yield, 13:1 E/Z.

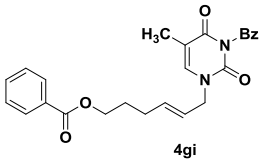
TLC: R_f = 0.31 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.07 (s, 1H), 5.75 (dt, *J* = 7.2 Hz, 15.0 Hz, 1H), 5.53 (dt, *J* = 6.6 Hz, 15.6 Hz, 1H), 4.28 (d, *J* = 6.6 Hz, 2H), 3.67 (s, 3H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.95 (s, 3H), 1.77-1.72 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 169.2, 163.2, 149.9, 139.4, 136.2, 135.1, 131.7, 130.5, 129.2, 124.1, 111.0, 77.5, 77.2, 76.8, 51.7, 49.7, 33.4, 31.6, 24.0, 12.6.

HRMS (ESI): m/z calcd. For $C_{20}H_{22}N_2NaO_5$ $[M+Na]^+$ 393.1421, found m/z 393.1422.

(*E*)-6-(3-Benzoyl-5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)hex-4-en-1-yl benzoate (4gi)



4gi

Colorless oil, 58.7 mg, 68% yield, 15:1 E/Z.

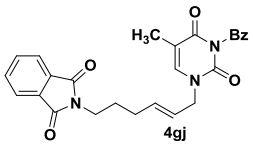
TLC: R_f = 0.32 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.50-7.43 (m, 4H), 7.07 (s, 1H), 5.87-5.80 (m, 1H), 5.62-5.55 (m, 1H), 4.35 (t, *J* = 6.4 Hz, 2H), 4.30 (d, *J* = 6.4 Hz, 2H), 2.27 (q, *J* = 7.2 Hz, 2H), 1.96 (s, 3H), 1.94-1.87 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 166.7, 163.2, 149.9, 139.4, 136.0, 135.1, 133.2, 131.8, 130.6, 130.4, 129.7, 129.2, 128.6, 124.3, 111.1, 77.4, 77.2, 77.0, 64.1, 49.8, 28.8, 28.1, 12.6.

HRMS (ESI): m/z calcd. For $C_{25}H_{24}N_2NaO_5$ $[M+Na]^+$ 455.1577, found m/z 455.1581.

(*E*)-2-(6-(3-Benzoyl-5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)hex-4-en-1-yl)isoindoline-1,3-dione (4gj)



Light yellow oil, 56.7 mg, 62% yield, 9:1 E/Z.

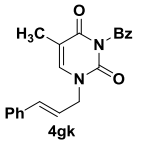
TLC: R_f = 0.26 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.86-7.84 (m, 2H), 7.74-7.72 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.13 (s, 1H), 5.85-5.77 (m, 1H), 5.60-5.53 (m, 1H), 4.29 (d, *J* = 6.4 Hz, 2H), 3.71 (t, *J* = 7.0 Hz, 2H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.97 (s, 3H), 1.86-1.78 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 168.5, 163.3, 149.9, 139.4, 135.9, 135.1, 134.2, 132.1, 131.8, 130.6, 129.2, 124.3, 123.4, 111.0, 77.5, 77.2, 76.8, 49.6, 37.3, 29.4, 27.7, 12.6.

HRMS (ESI): m/z calcd. For $C_{26}H_{23}N_3NaO_5$ $[M+Na]^+$ 480.1530, found m/z 480.1531.

3-benzoyl-1-cinnamyl-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (4gk)



Light yellow oil, 29.8 mg, 43% yield, 6:1 E/Z.

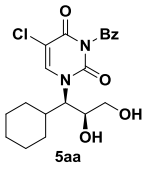
TLC: R_f = 0.21 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.14 (s, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.6, 6.7 Hz, 1H), 4.52 (d, *J* = 6.6 Hz, 2H), 1.96 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 163.2, 149.9, 139.4, 135.7, 135.6, 135.1, 131.8, 130.6, 129.3, 128.9, 128.7, 126.8, 122.3, 111.3, 77.4, 77.2, 76.9, 50.1, 12.6.

HRMS (ESI): m/z calcd. For $C_{21}H_{18}N_2NaO_3$ $[M+Na]^+$ 369.1210, found m/z 369.1215.

3-Benzoyl-5-chloro-1-((1*S*,2*S*)-1-cyclohexyl-2,3-dihydroxypropyl)pyrimidine-2,4(1*H*,3*H*)-dione (5aa)



5aa

Colorless oil, 67.4 mg, 83% yield, *ds* > 20:1.

$[\alpha]_D^{25}$ = -55.7° (*c* = 0.60, CH_2Cl_2).

TLC: R_f = 0.25 (DCM:MeOH = 15:1) [UV].

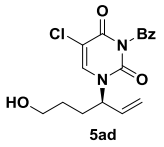
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 250 nm, retention time: 18.497 min (major), 23.047 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 4.37 (d, *J* = 10.8 Hz, 1H), 4.16 (s, 1H), 3.56-3.53 (m, 1H), 3.45-3.41 (m, 1H), 2.85 (d, *J* = 2.4 Hz, 1H), 2.51 (s, 1H), 2.04-1.95 (m, 2H), 1.81-1.76 (m, 2H), 1.70 (d, *J* = 13.2 Hz, 1H), 1.58 (d, *J* = 12.6 Hz, 1H), 1.35-1.25 (m, 2H), 1.21-1.14 (m, 1H), 1.10-1.03 (m, 1H), 1.02-0.95 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 158.1, 150.7, 140.8, 135.5, 131.1, 130.6, 129.5, 108.4, 77.4, 77.2, 77.0, 69.4, 64.1, 60.9, 36.8, 30.1, 29.4, 26.0, 25.7.

HRMS (ESI): m/z calcd. For $C_{20}H_{23}ClN_2NaO_5$ $[M+Na]^+$ 429.1188, found m/z 429.1191.

(*R*)-3-Benzoyl-5-chloro-1-(6-hydroxyhex-1-en-3-yl)pyrimidine-2,4(1*H*,3*H*)-dione (5ad)



5ad

Colorless oil, 64.7 mg, 93% yield, 90% ee.

$[\alpha]_D^{25}$ = 4.0° (*c* = 1.15, CH_2Cl_2). HPLC CHIRALCEL IA, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 250 nm, retention time: 17.950 min (major), 21.747 min (minor).

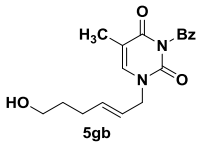
TLC: R_f = 0.3 (petroleum ether:ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.45 (s, 1H), 5.95-5.86 (m, 1H), 5.46 (d, *J* = 10.4 Hz, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.18 (q, *J* = 7.2 Hz, 1H), 3.70 (t, *J* = 5.6 Hz, 2H), 2.07-1.98 (m, 1H), 1.90-1.81 (m, 1H), 1.68-1.56 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 158.0, 149.4, 138.1, 135.5, 134.6, 131.1, 130.6, 129.4, 120.3, 109.1, 77.4, 77.2, 77.0, 61.8, 57.9, 29.1, 28.7.

HRMS (ESI): m/z calcd. For $C_{17}H_{17}ClN_2NaO_4$ $[M+Na]^+$ 371.0769, found m/z 371.0766.

(*E*)-3-benzoyl-1-(6-hydroxyhex-2-en-1-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (5gb)



5gb

Colorless oil, 122.0 mg, 90% yield.

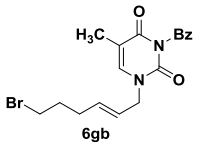
TLC: R_f = 0.25 (petroleum ether:ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.10 (s, 1H), 5.76 (dt, *J* = 6.4 Hz, 14.8 Hz, 1H), 5.49 (dt, *J* = 6.4 Hz, 15.2 Hz, 1H), 4.25 (d, *J* = 6.4 Hz, 2H), 3.57 (t, *J* = 6.3 Hz, 2H), 2.13 (q, *J* = 7.2 Hz, 2H), 2.08 (s, 1H), 1.91 (s, 3H), 1.63-1.58 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 163.2, 149.8, 139.7, 136.8, 135.1, 131.7, 130.5, 129.2, 123.4, 110.8, 77.4, 77.2, 76.9, 62.0, 49.8, 31.7, 28.6, 12.5.

HRMS (ESI): m/z calcd. For $C_{18}H_{20}N_2NaO_4$ $[M+Na]^+$ 351.1315, found m/z 351.1321.

(*E*)-3-benzoyl-1-(6-bromohex-2-en-1-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (6gb)



6gb

Light brown oil, 60.8 mg, 78% yield.

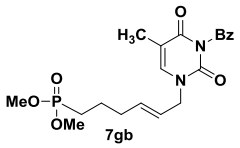
TLC: R_f = 0.35 (petroleum ether:ethyl acetate =3:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.07 (s, 1H), 5.75 (dt, *J* = 6.6 Hz, 15.6 Hz, 1H), 5.59 (m, 1H), 4.29 (d, *J* = 6.6 Hz, 2H), 3.40 (t, *J* = 6.6 Hz, 2H), 2.27 (q, *J* = 7.2 Hz, 2H), 1.95 (s, 3H), 1.99-1.94 (m, 5H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 163.2, 149.9, 139.4, 135.2, 135.1, 131.8, 130.6, 129.3, 124.7, 111.1, 77.4, 77.2, 76.9, 49.8, 32.9, 31.6, 30.6, 12.6.

HRMS (ESI): m/z calcd. For $C_{18}H_{19}BrN_2NaO_3$ $[M+Na]^+$ 413.0471, found m/z 413.0465.

Dimethyl (*E*)-(6-(3-benzoyl-5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)hex-4-en-1-yl)phosphonate (7gb)



7gb

Light brown oil, 46.5 mg, 71% yield.

TLC: R_f = 0.31 (petroleum ether:ethyl acetate =3:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.06 (s, 1H), 5.74 (dt, *J* = 6.6 Hz, 15.0 Hz, 1H), 5.57-5.52 (m, 1H), 4.28 (d, *J* = 6.0 Hz, 2H), 3.74 (s, 3H), 3.72 (s, 3H), 2.18 (q, *J* = 6.6 Hz, 2H), 1.95 (s, 3H), 1.75-1.70 (m, 4H).

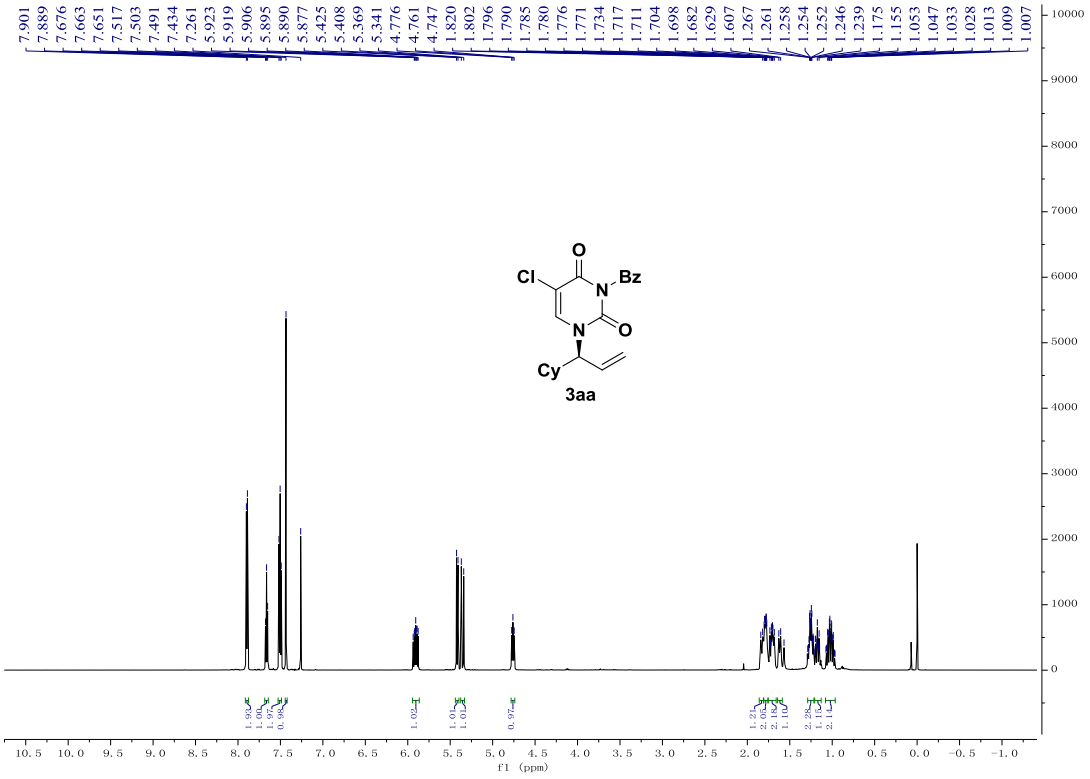
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 163.2, 149.9, 139.4, 135.7, 135.1, 131.8, 130.6, 129.2, 124.5, 111.1, 77.4, 77.2, 76.9, 52.5, 49.8, 32.9, 24.6, 23.7, 21.7, 12.6.

^{31}P NMR (243 MHz, $CDCl_3$) δ 34.4.

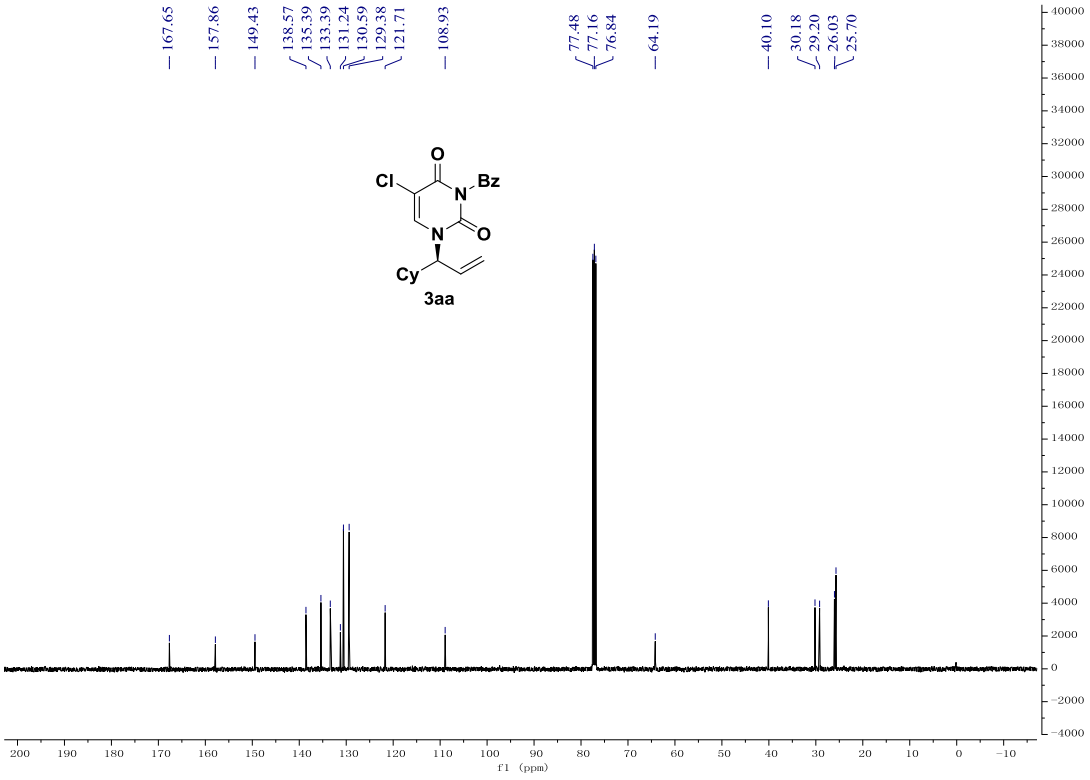
HRMS (ESI): m/z calcd. For $C_{20}H_{25}N_2NaO_6P$ $[M+Na]^+$ 443.1342, found m/z 413.1340.

8. Copies of ^{1}H and ^{13}C NMR spectra

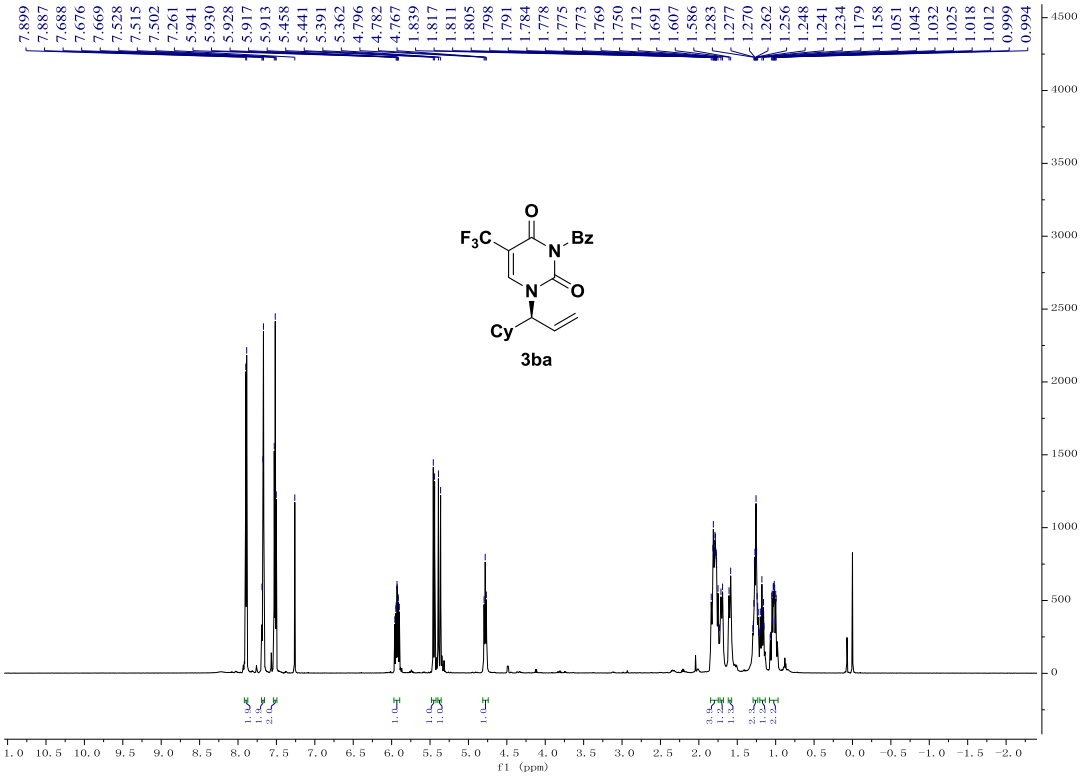
^{1}H NMR of 3aa



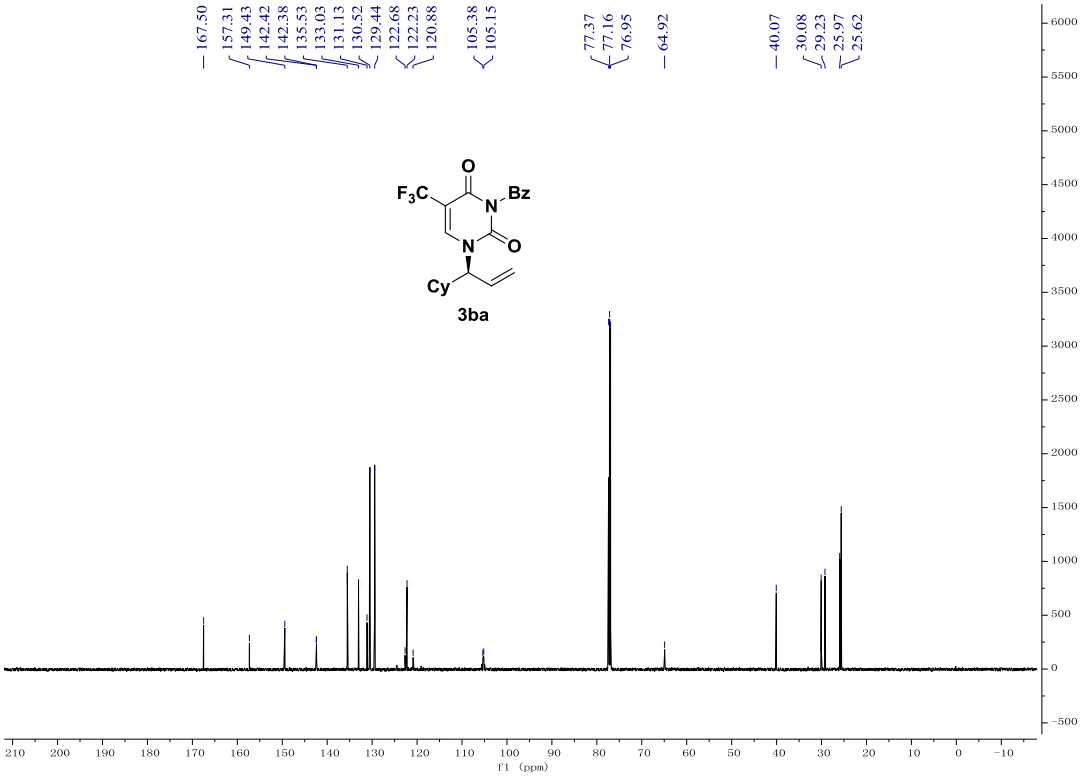
^{13}C NMR of 3aa



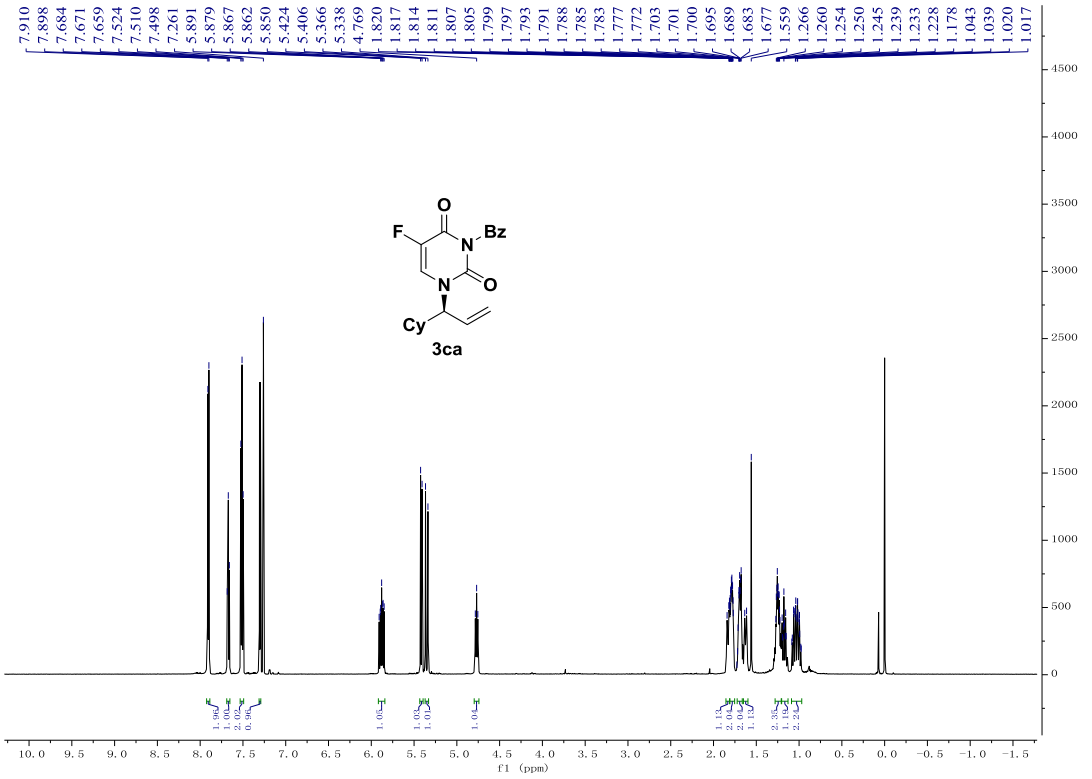
^{1}H NMR of 3ba



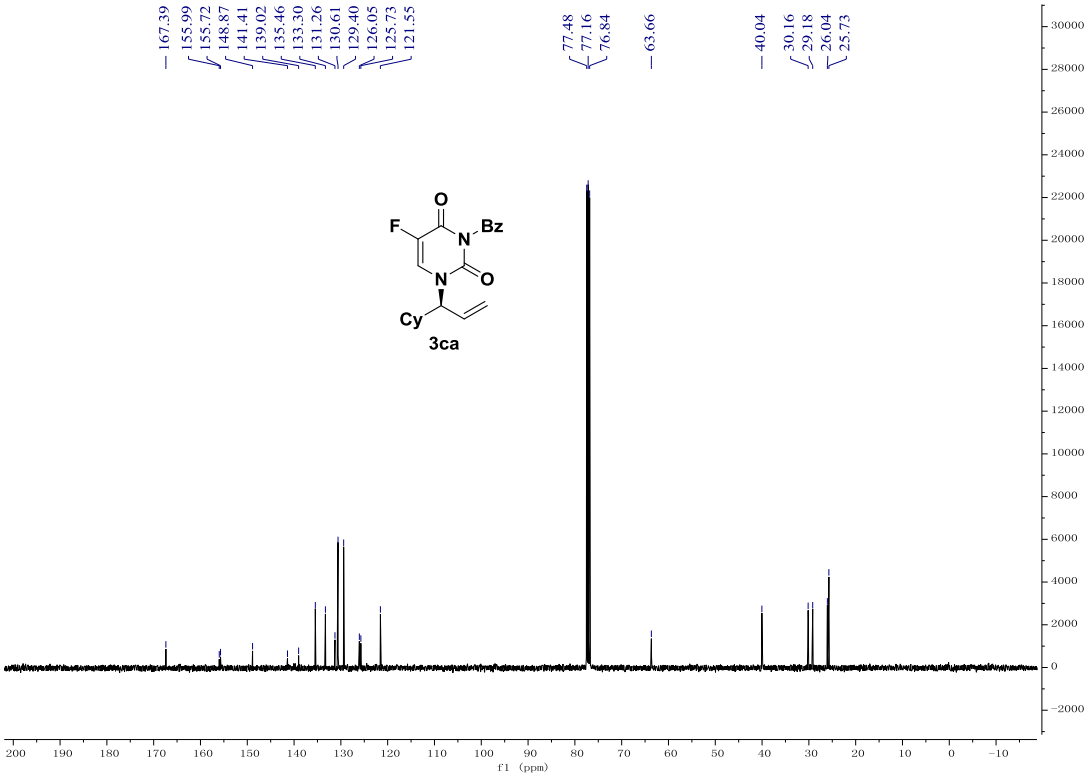
^{13}C NMR of 3ba



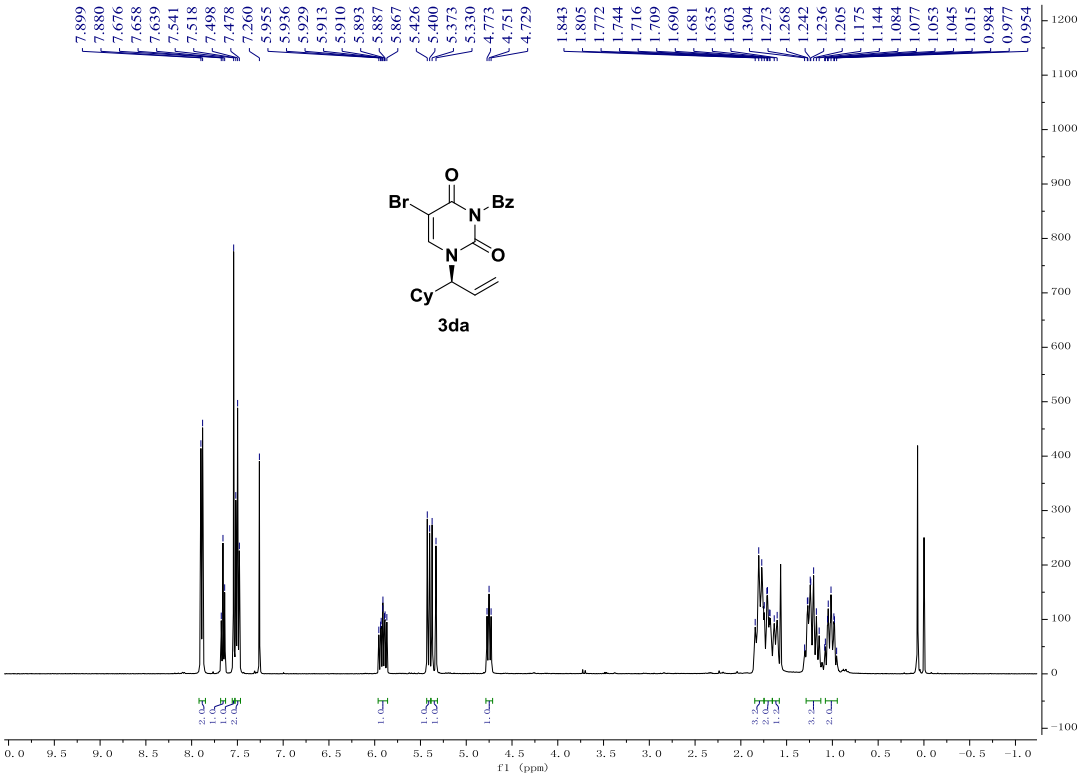
^{1}H NMR of 3ca



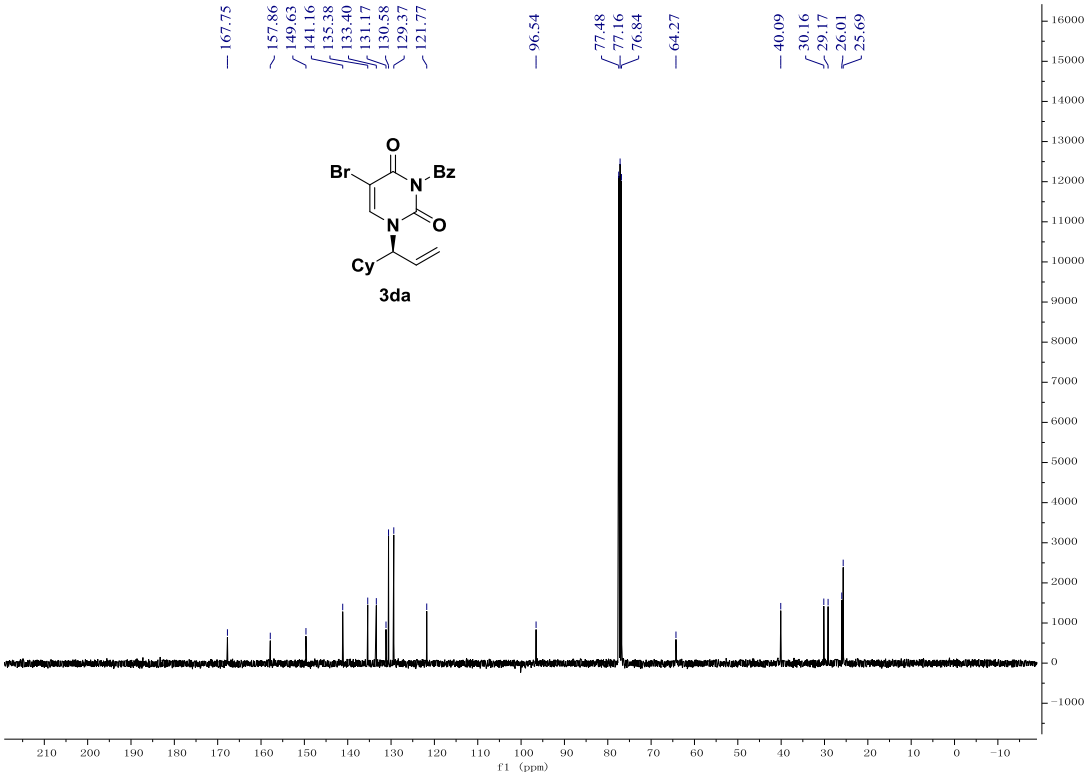
^{13}C NMR of 3ca



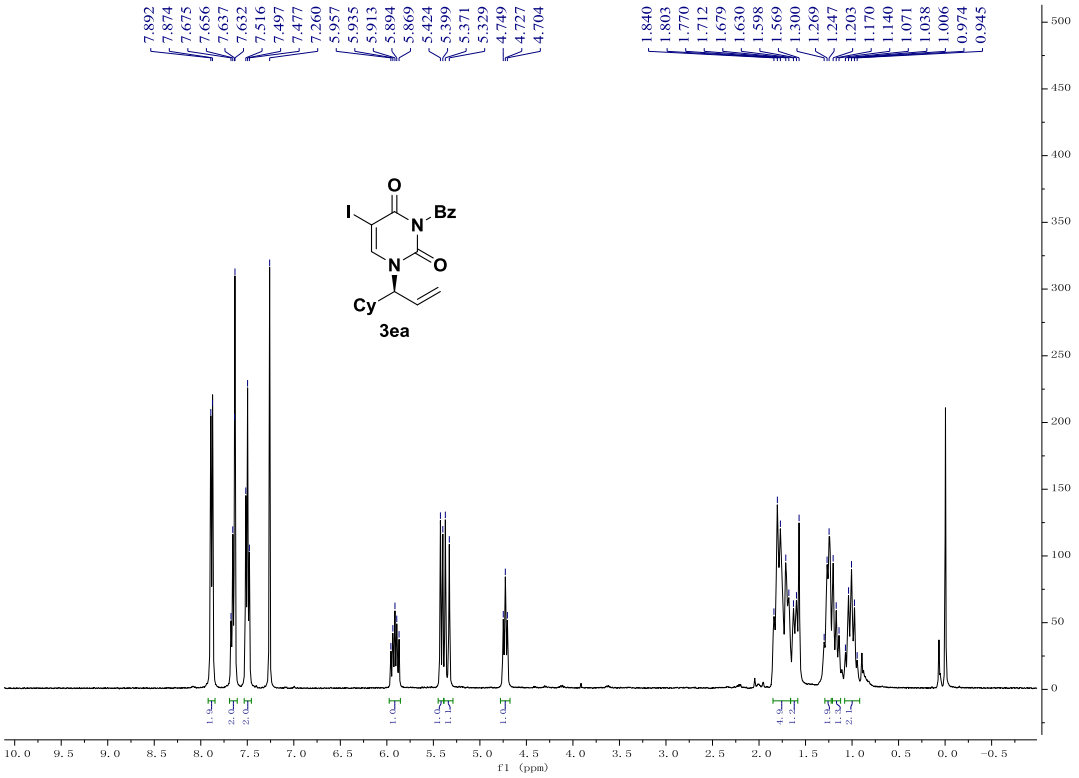
^{1}H NMR of 3da



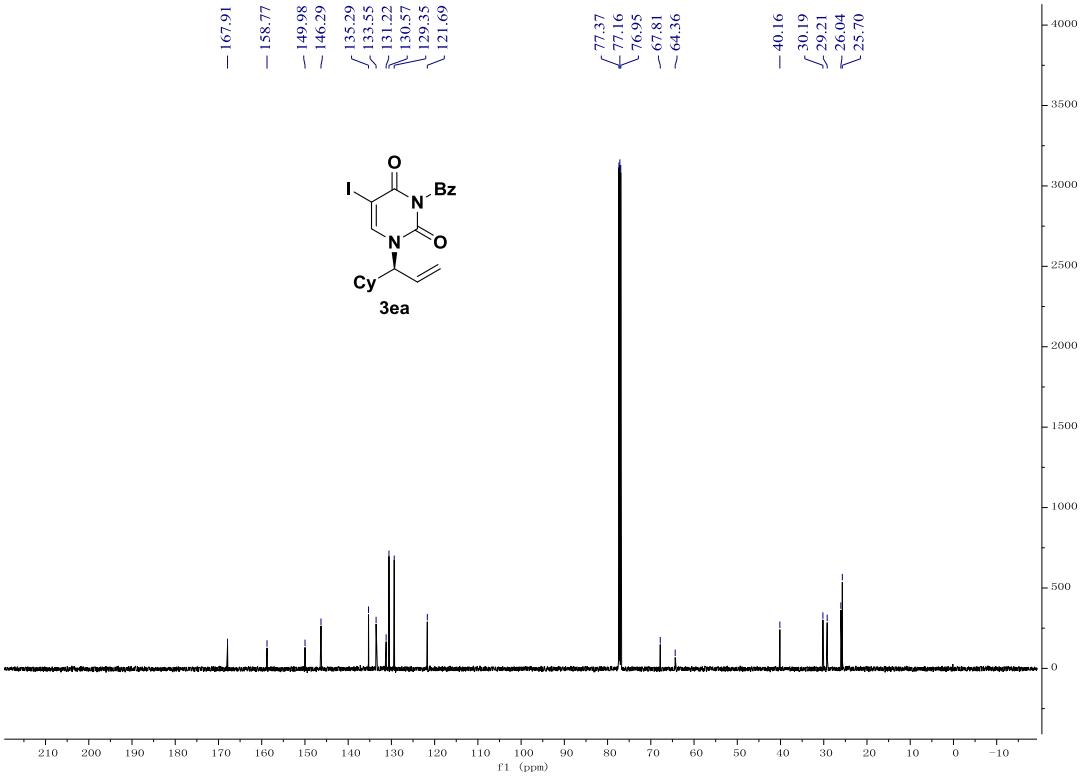
^{13}C NMR of 3da



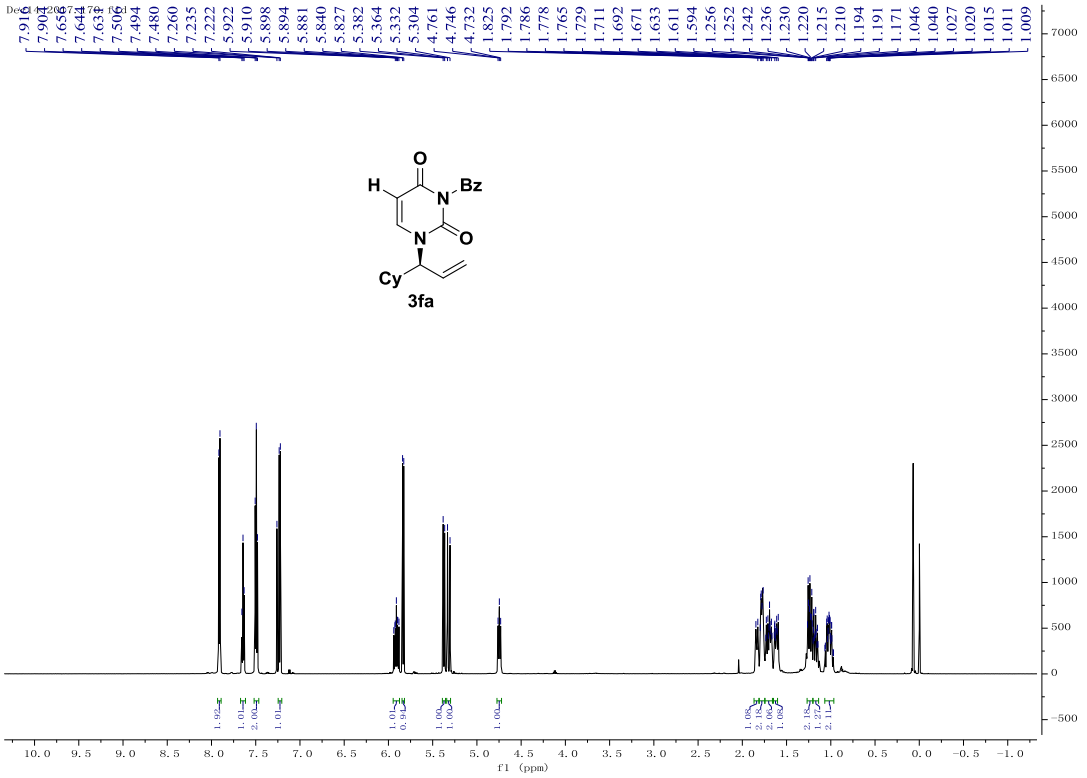
^{1}H NMR of 3ea



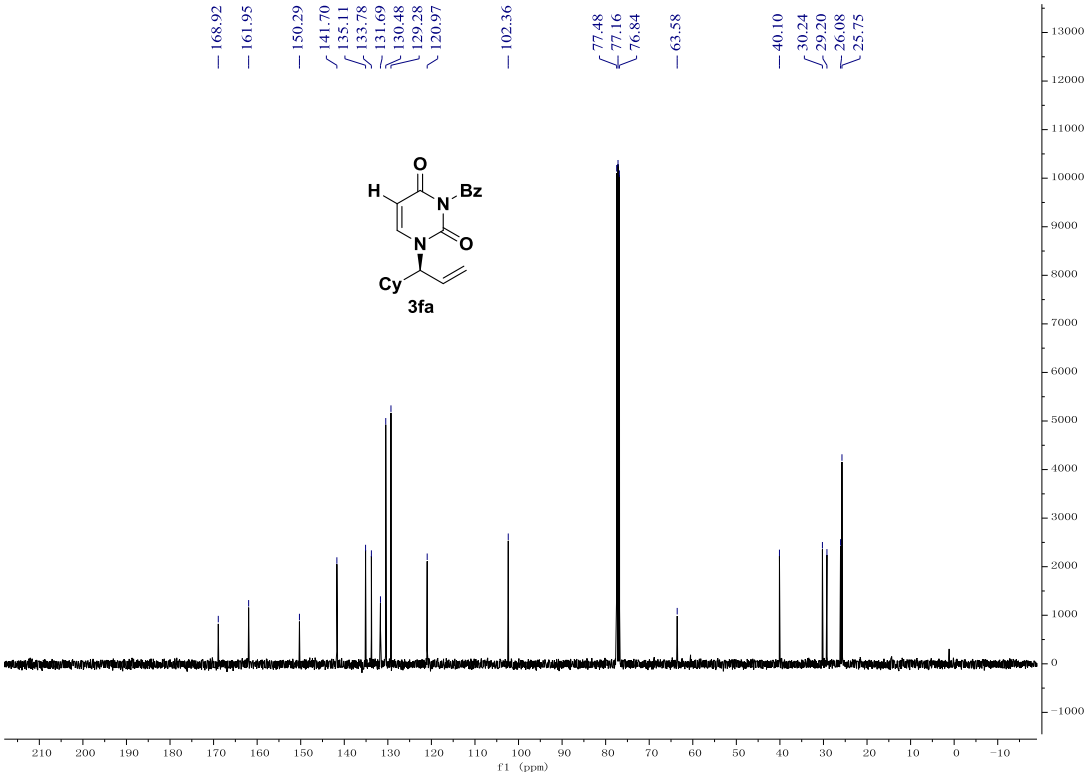
^{13}C NMR of 3ea



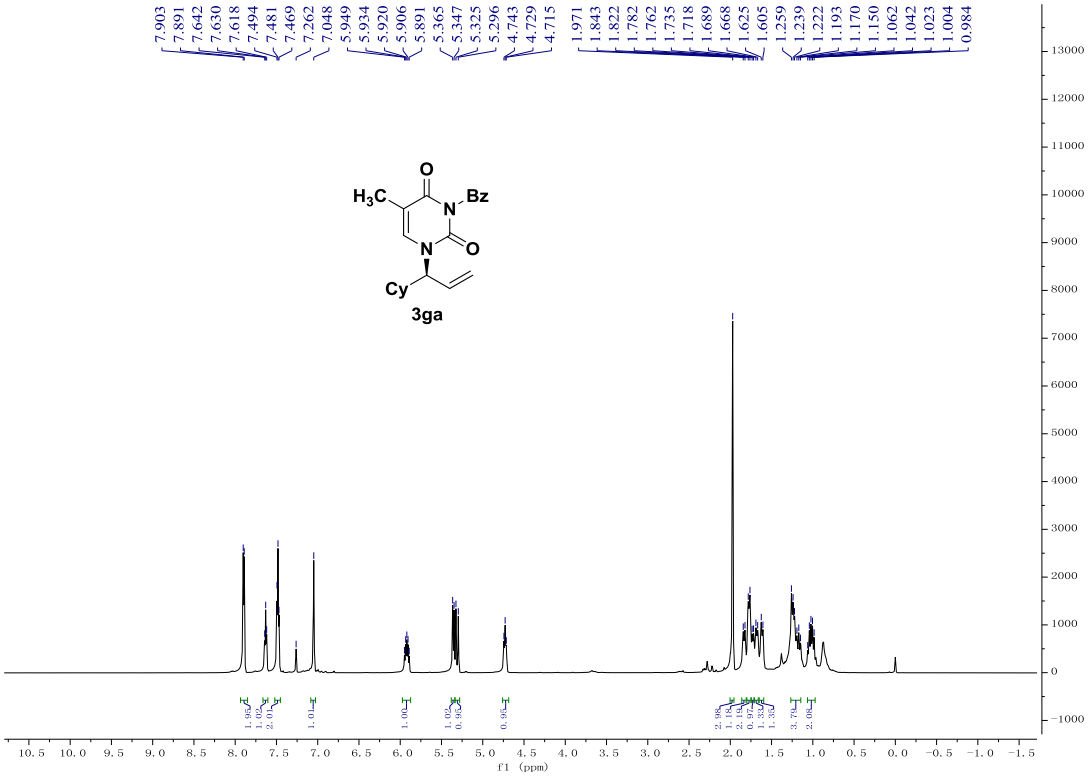
^{1}H NMR of 3fa



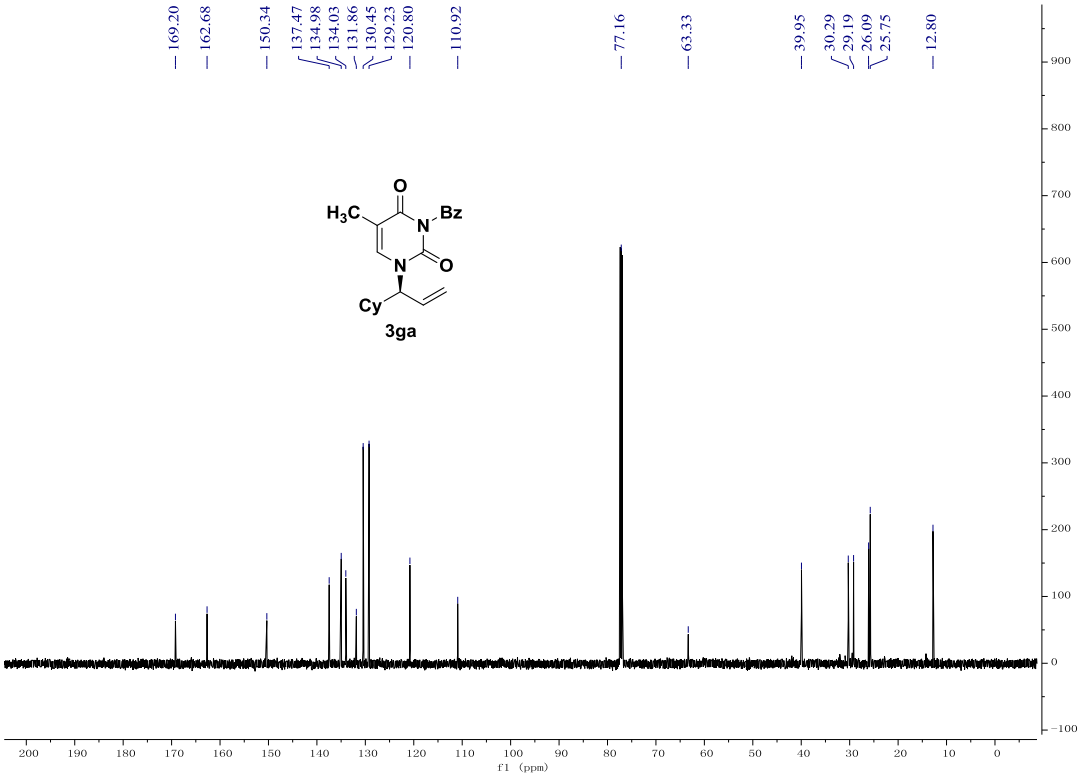
^{13}C NMR of 3fa



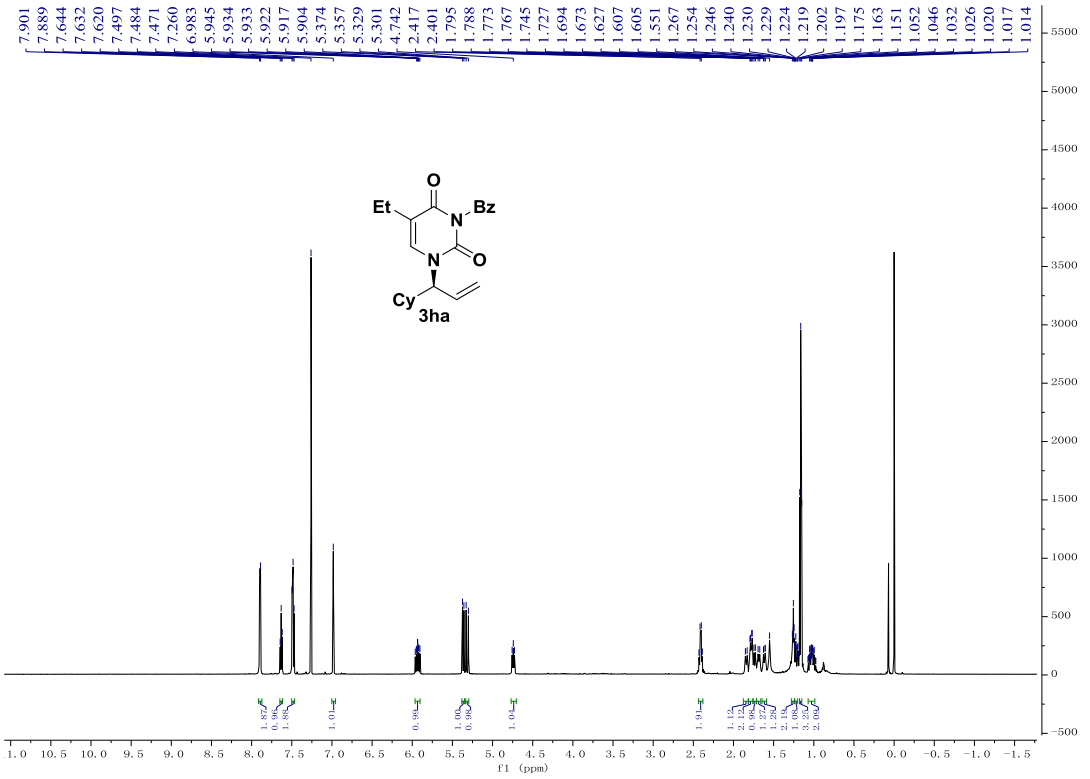
^{1}H NMR of 3ga



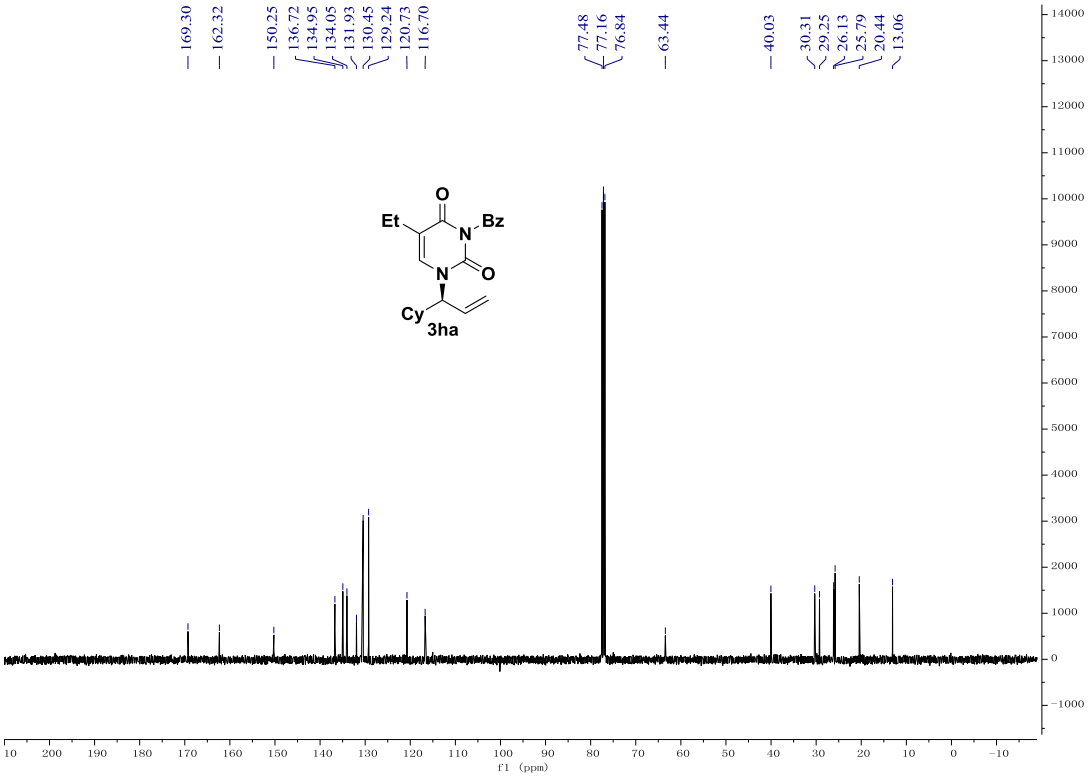
^{13}C NMR of 3ga



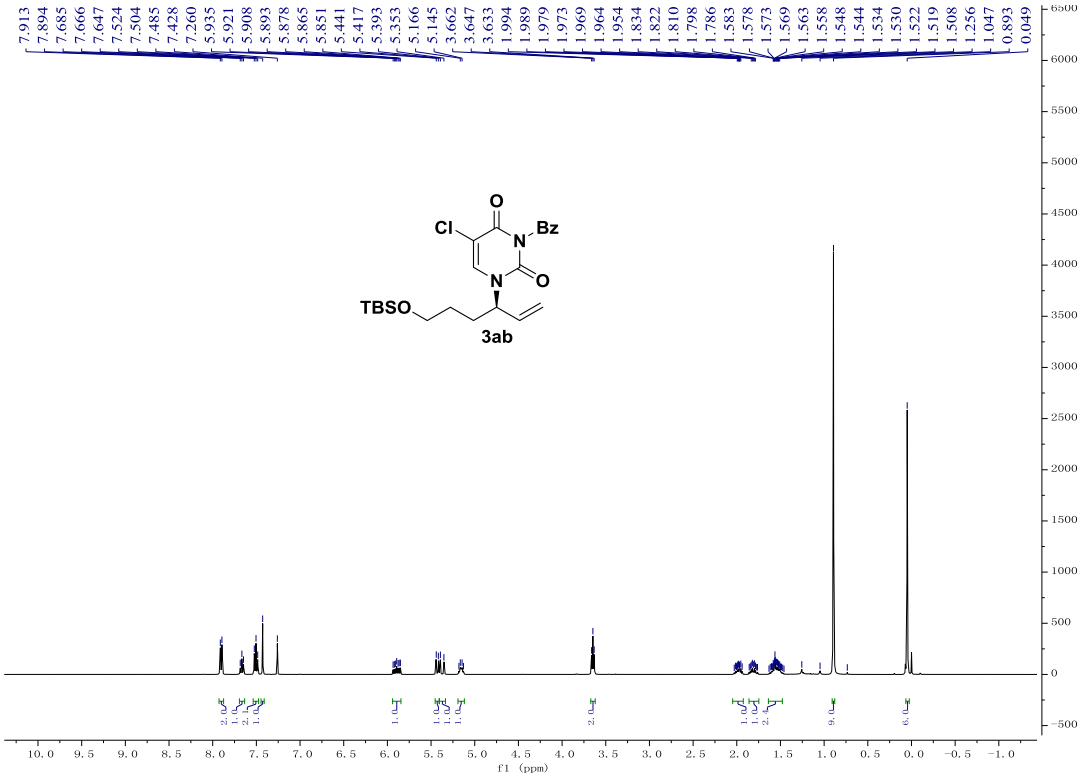
^{1}H NMR of 3ha



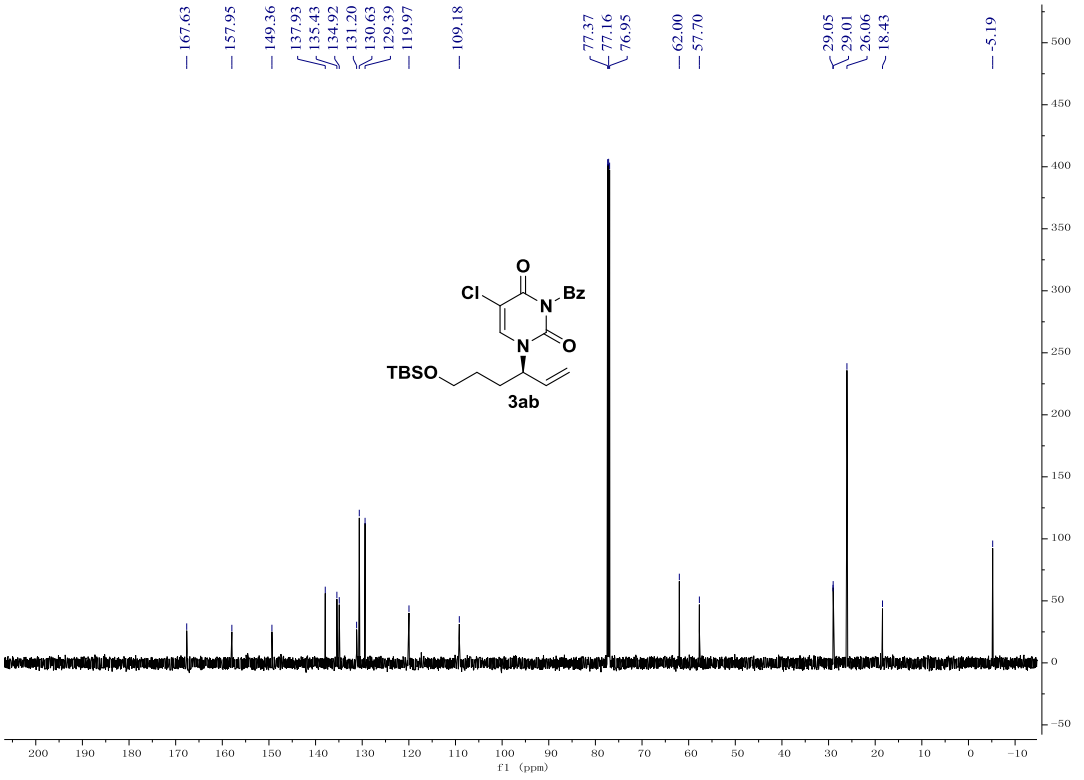
^{13}C NMR of 3ha



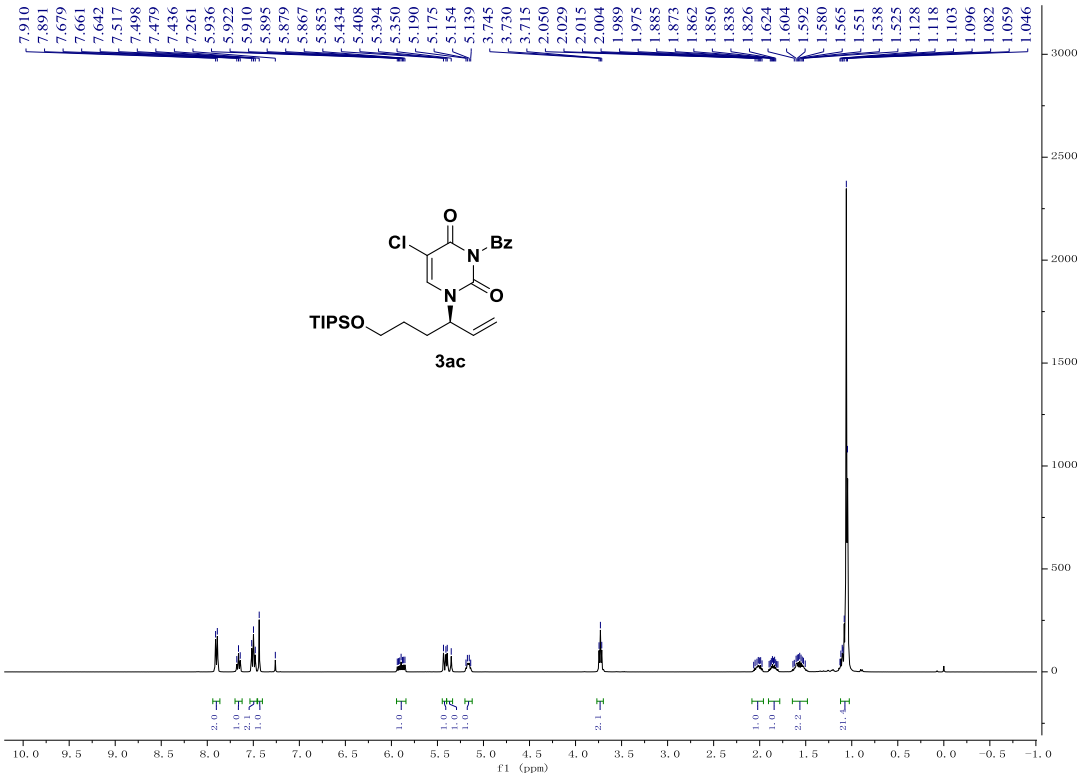
^{1}H NMR of 3ab



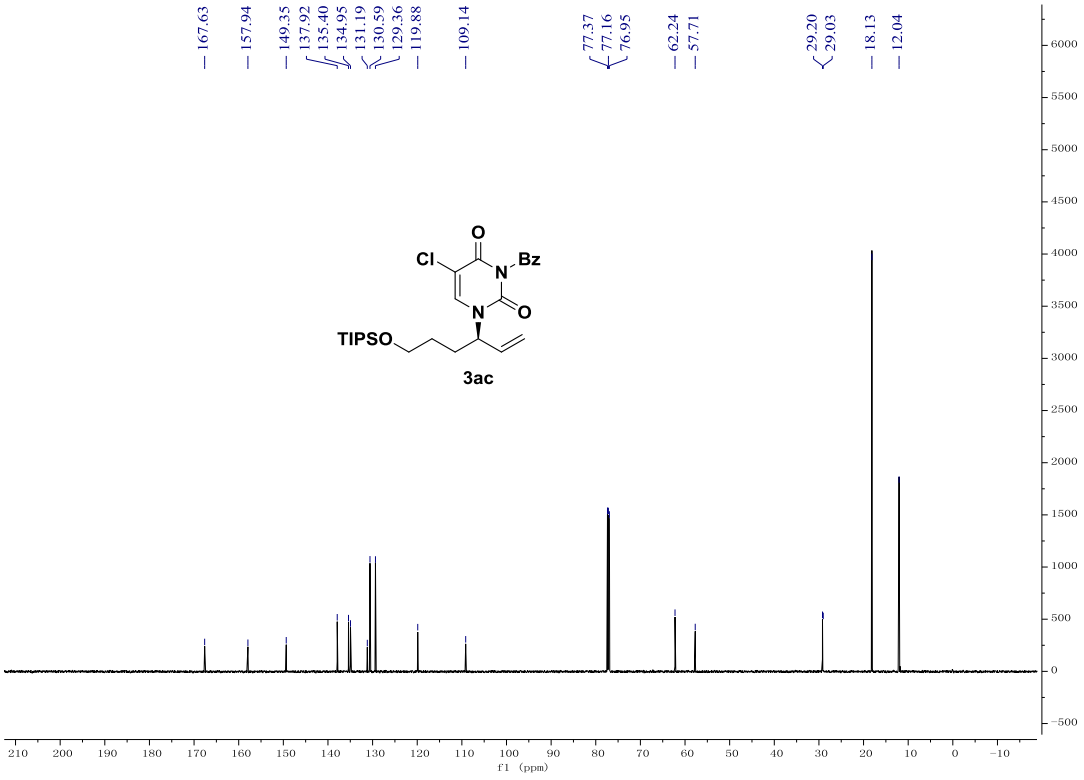
^{13}C NMR of 3ab



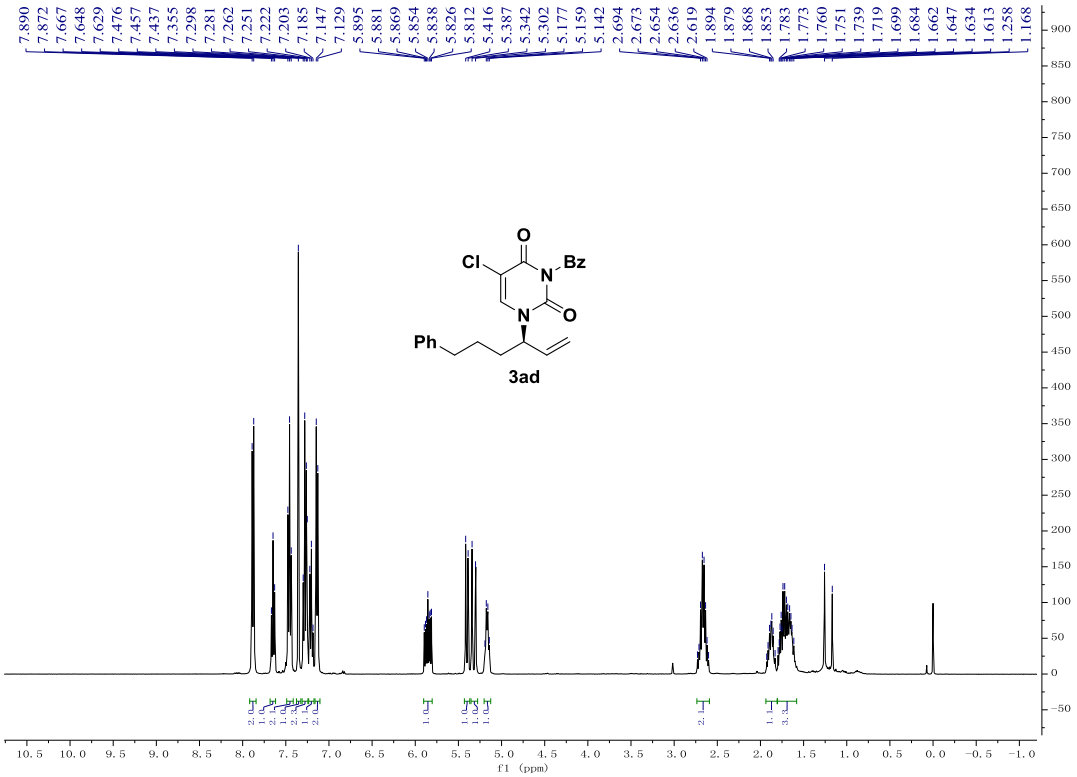
^{1}H NMR of 3ac



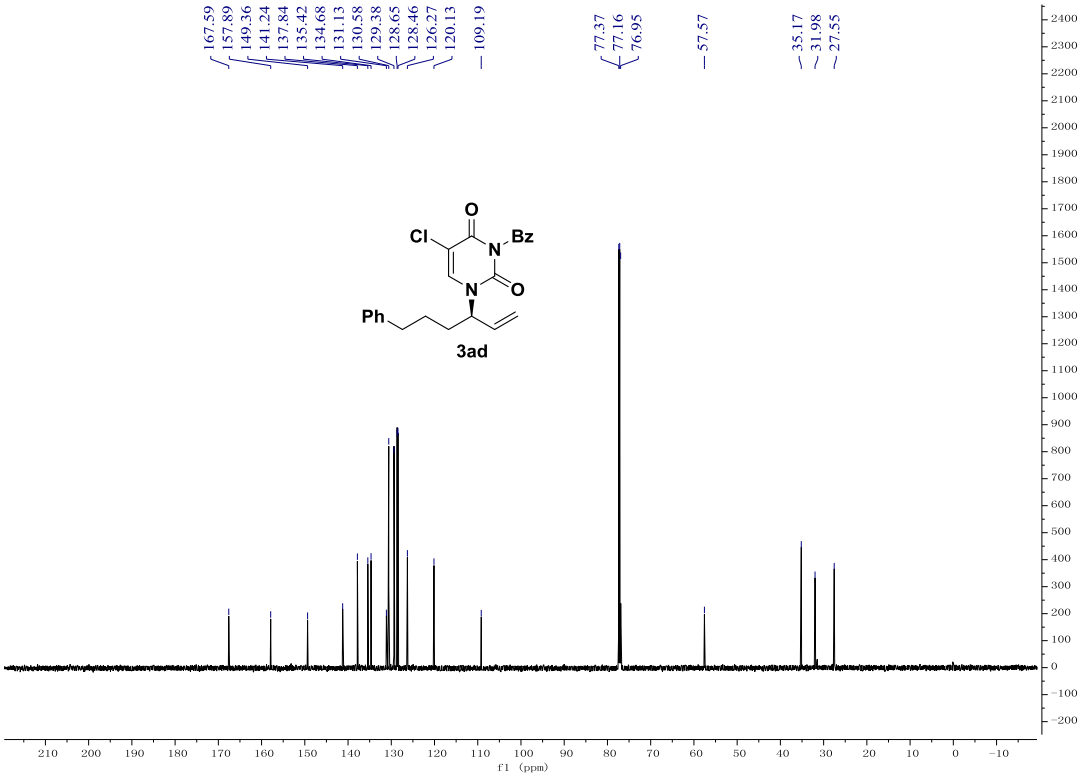
^{13}C NMR of 3ac



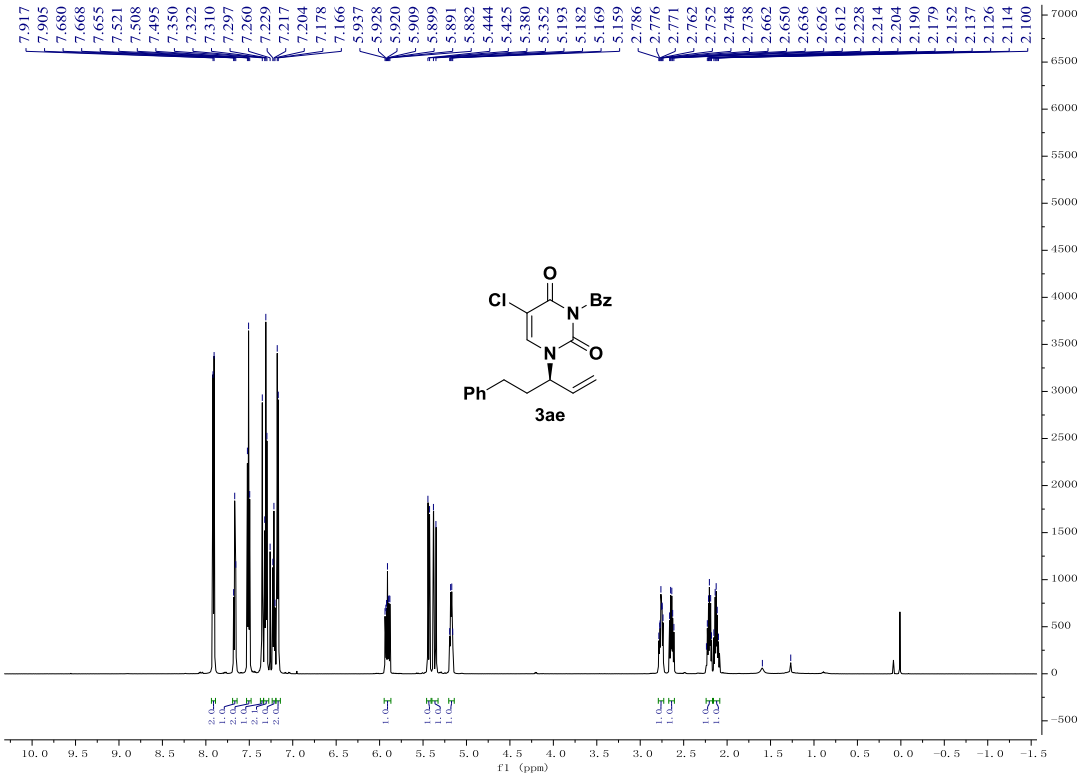
^{1}H NMR of 3ad



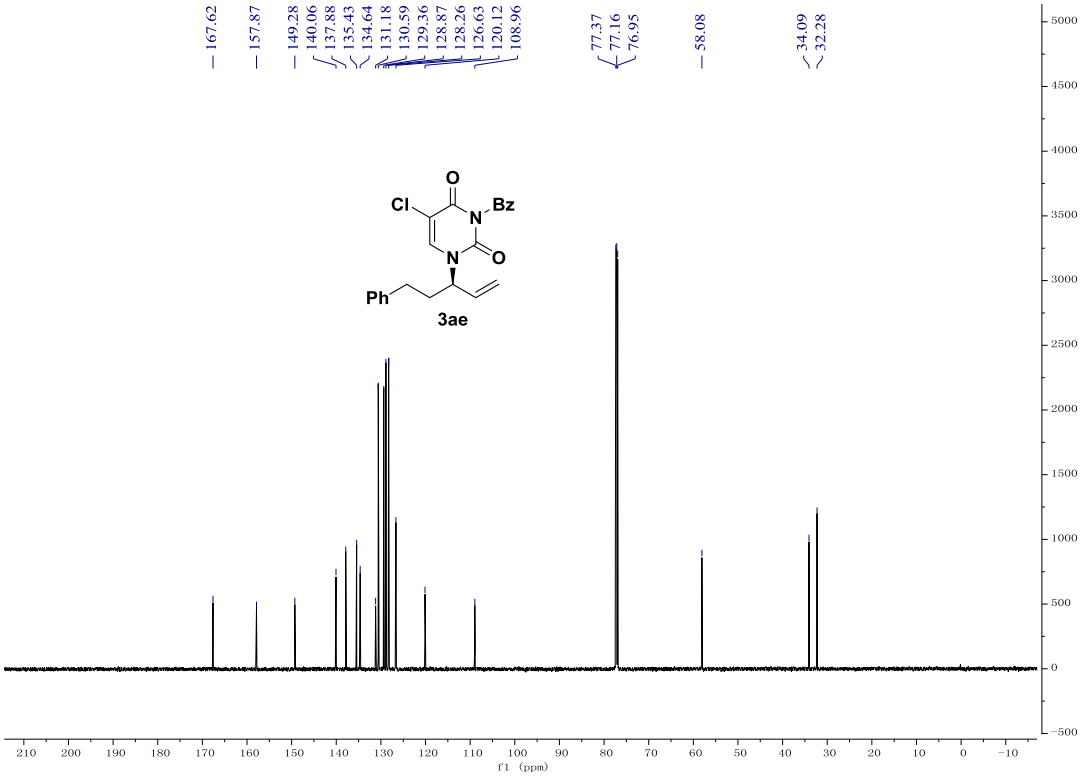
^{13}C NMR of 3ad



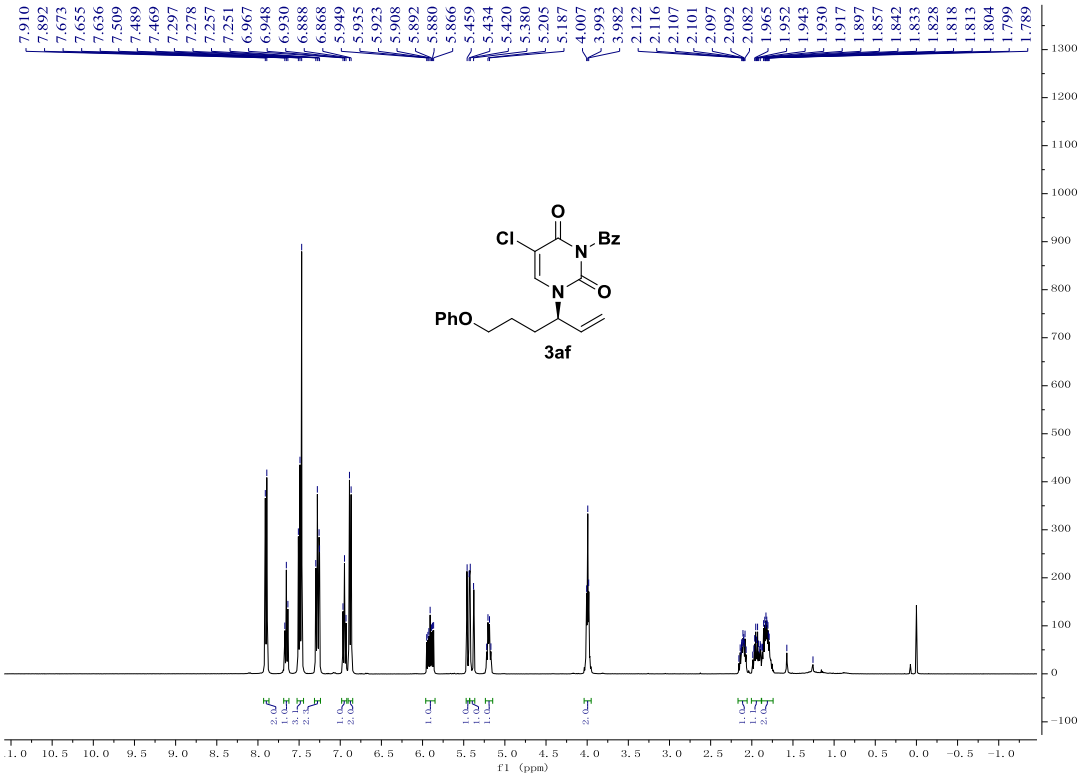
^{1}H NMR of 3ae



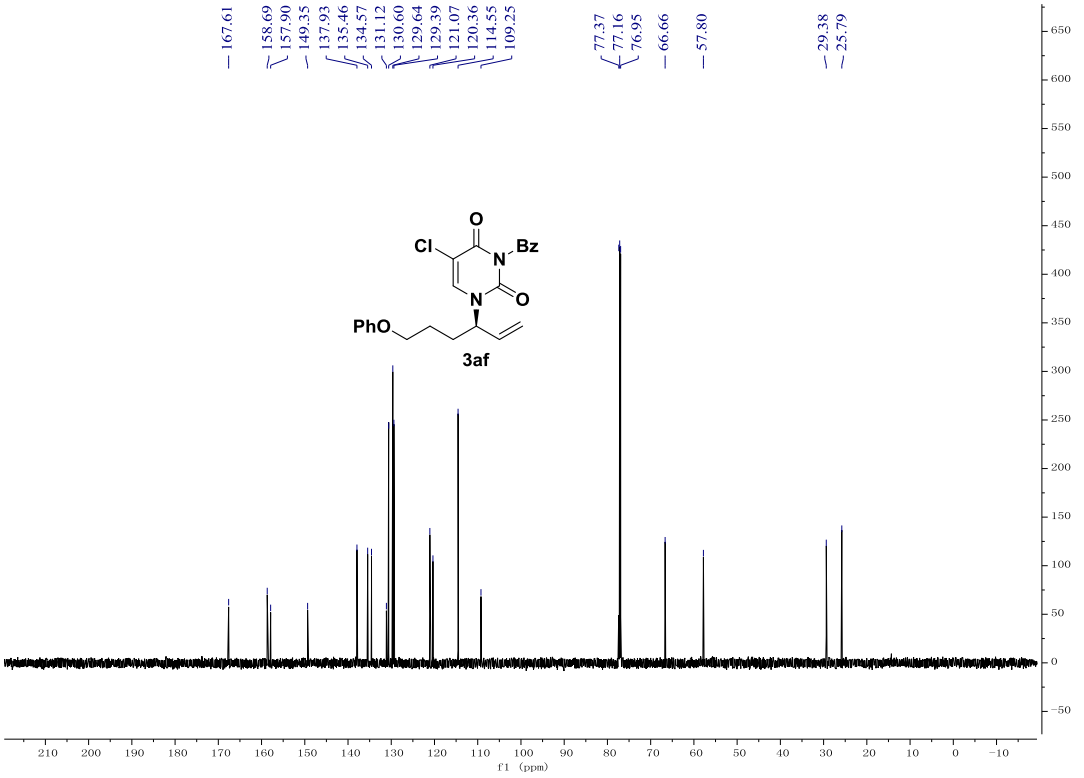
^{13}C NMR of 3ae



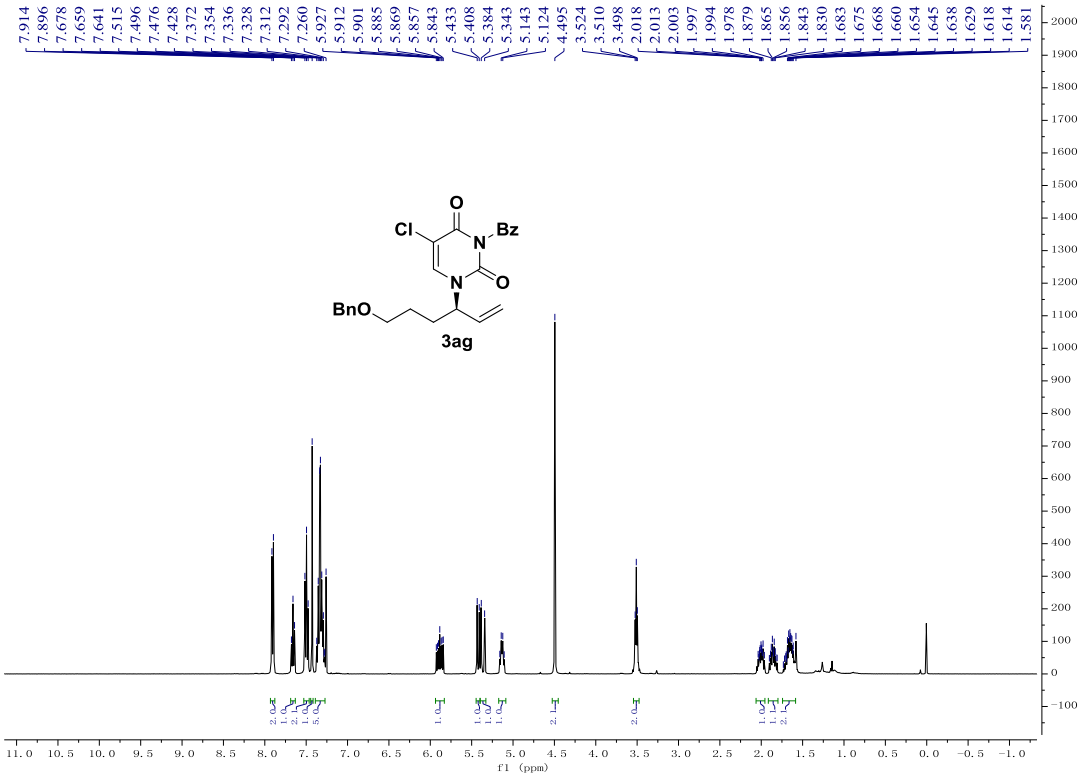
^{1}H NMR of 3af



^{13}C NMR of 3af



^{1}H NMR of 3ag



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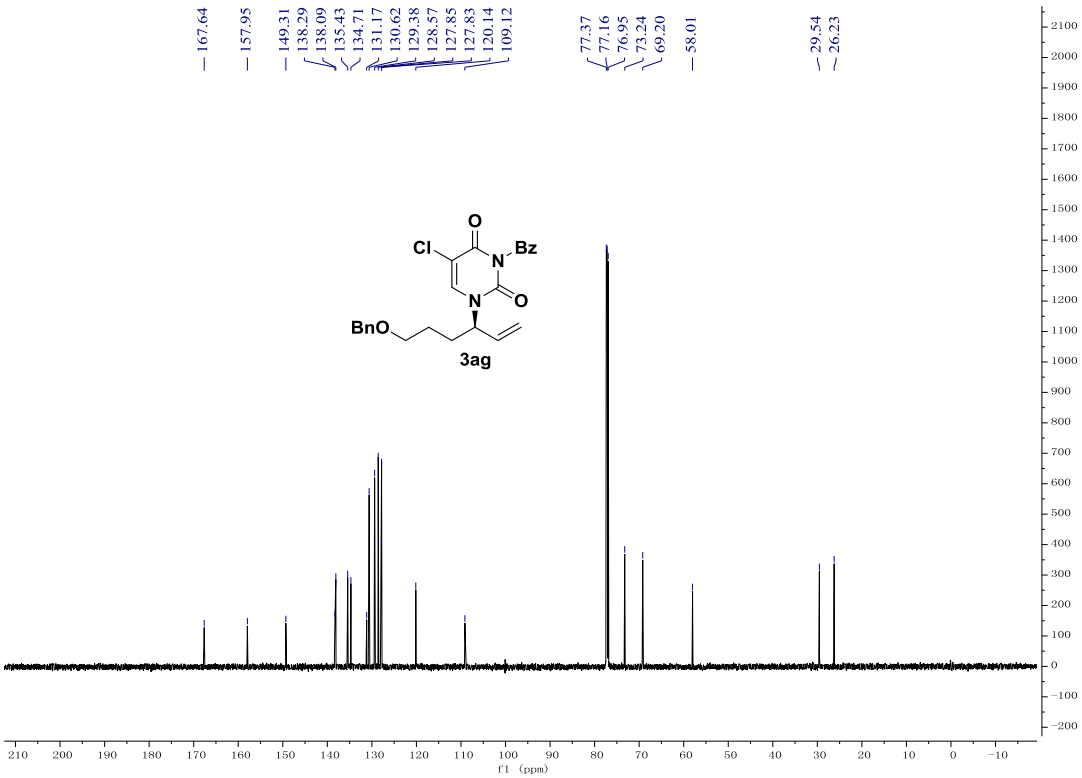
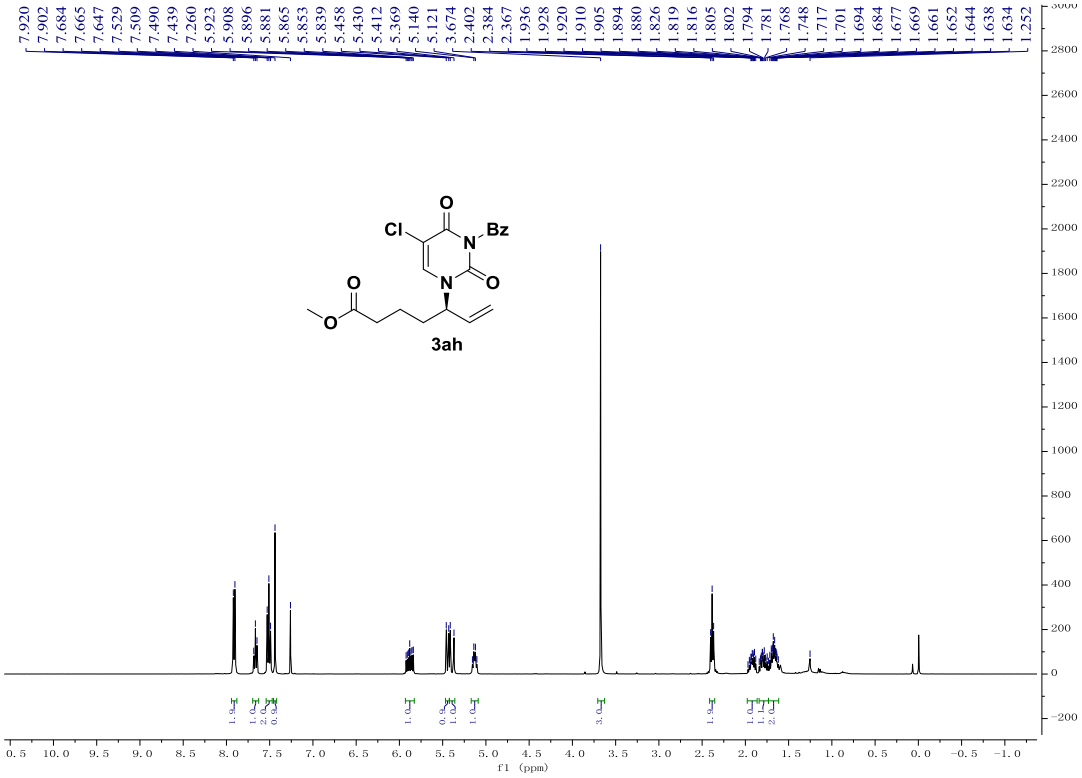
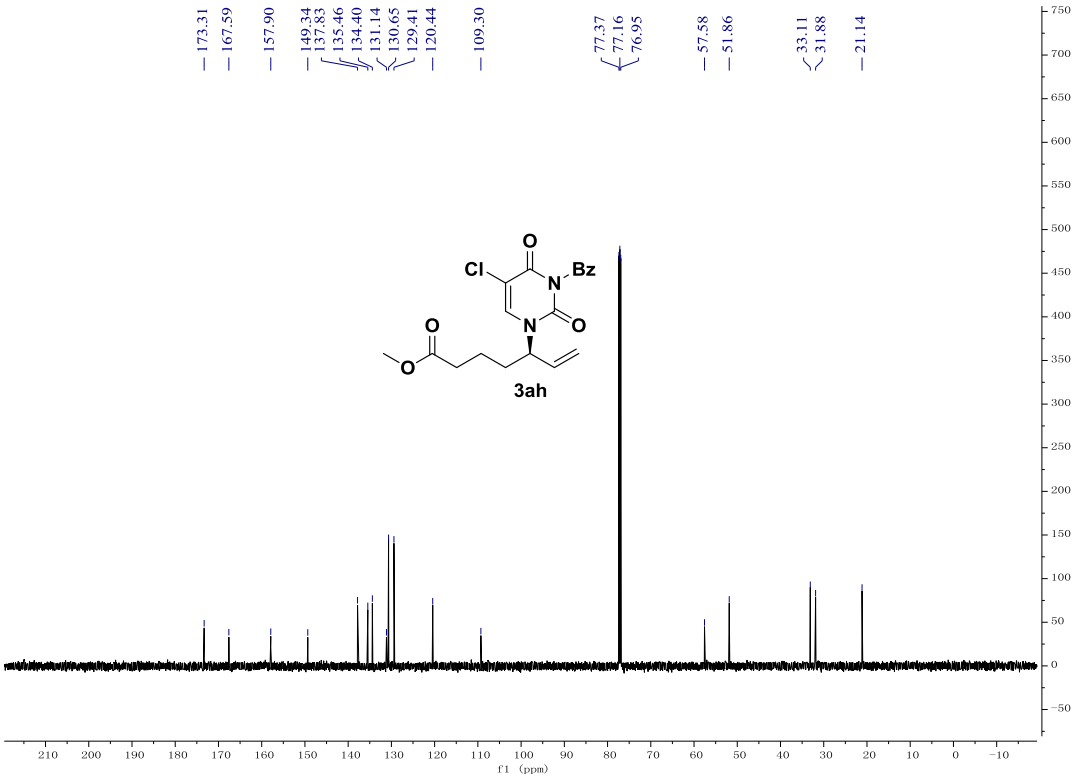


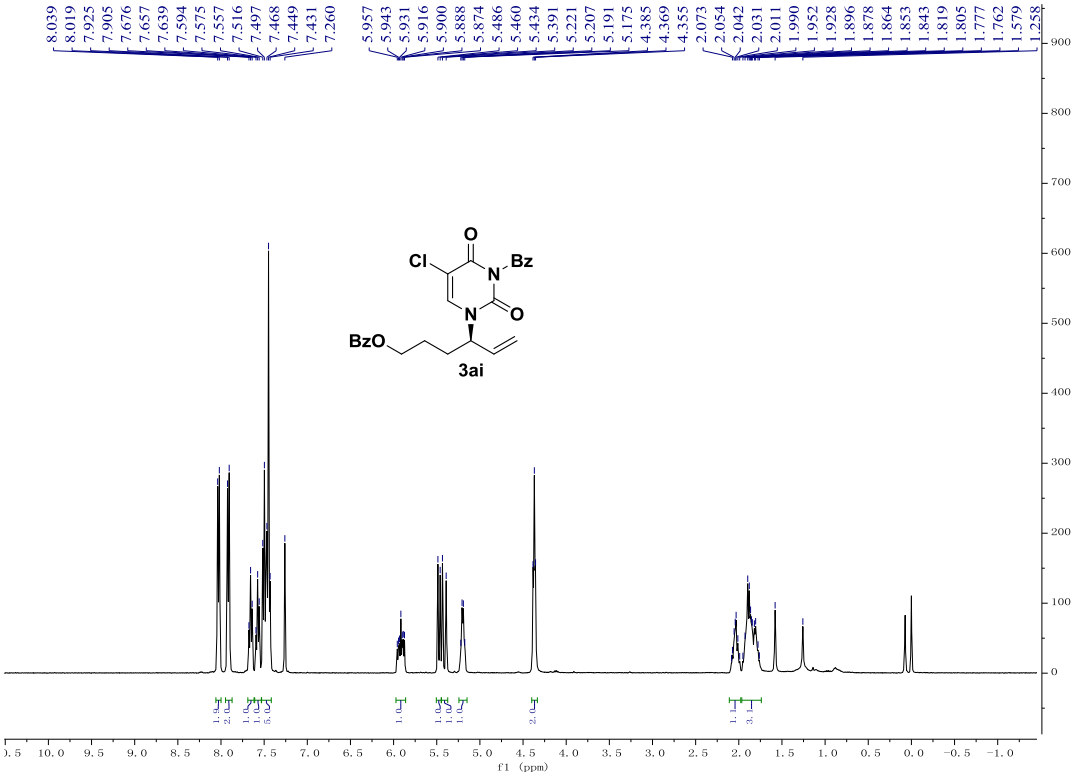
^{1}H NMR of 3ah



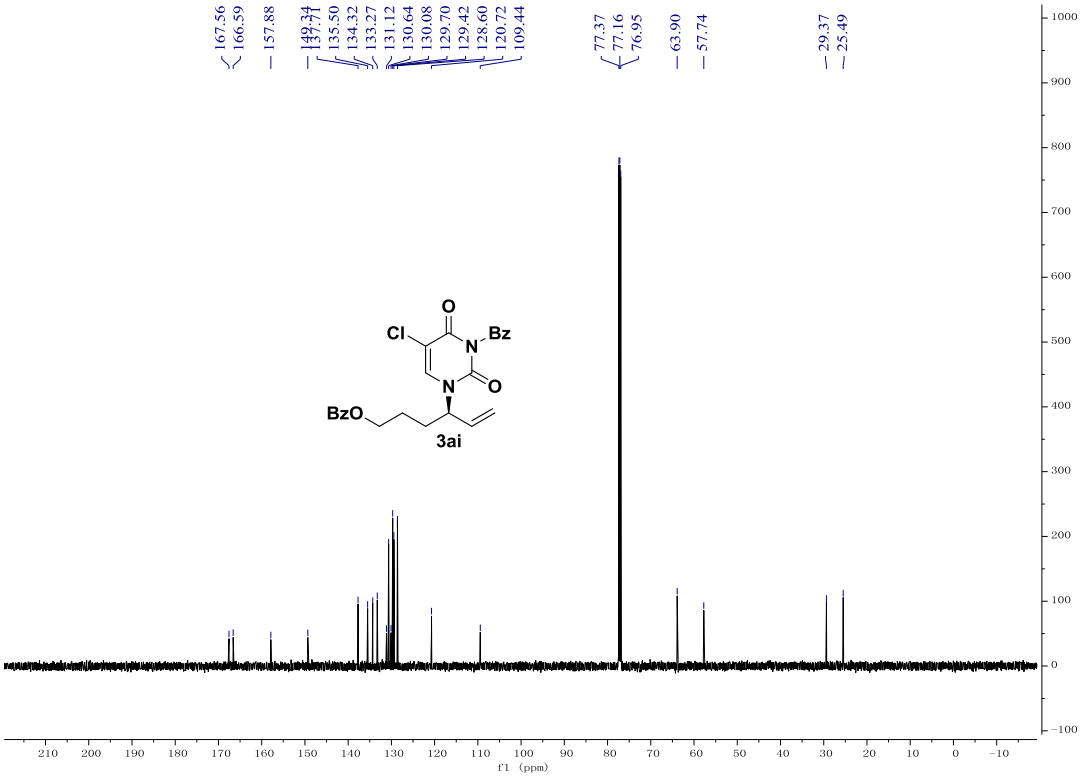
^{13}C NMR of 3ah



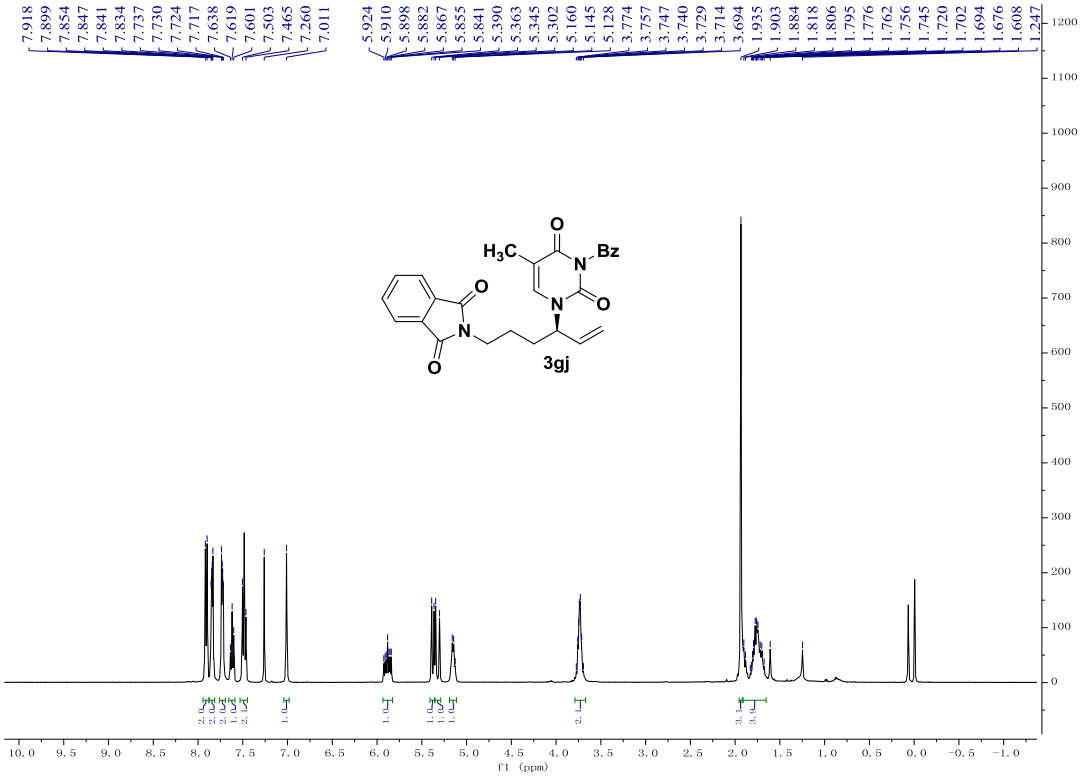
^{1}H NMR of 3ai



^{13}C NMR of 3ai



^{1}H NMR of 3gj



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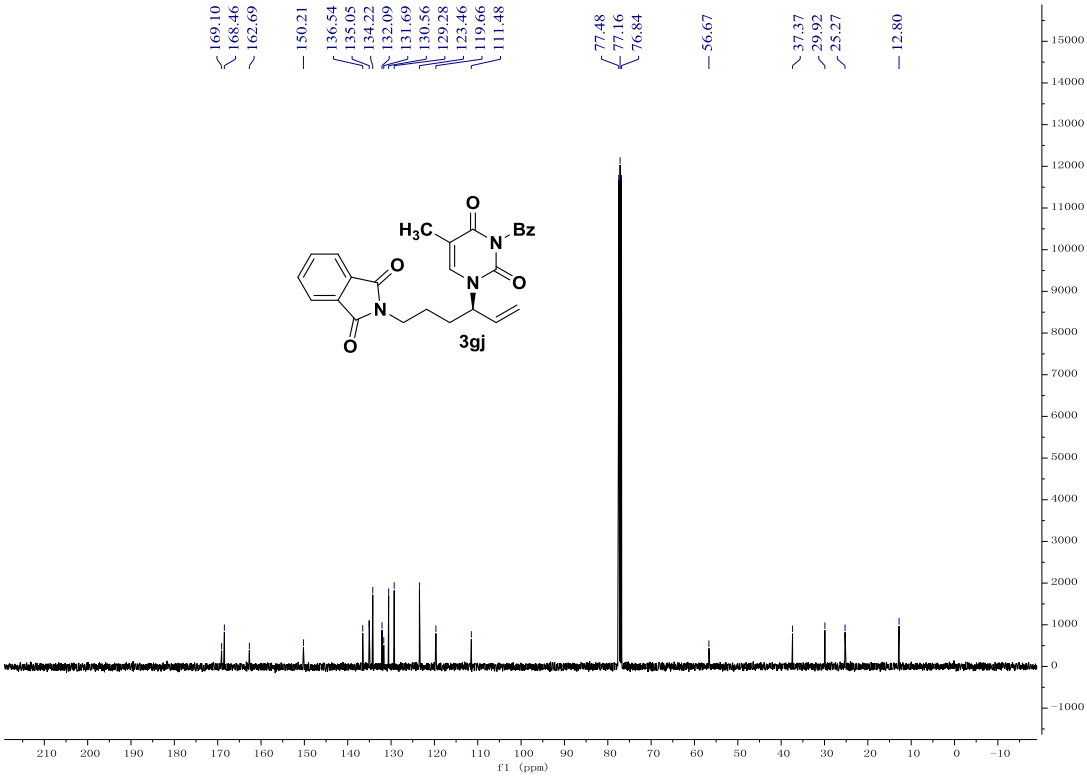
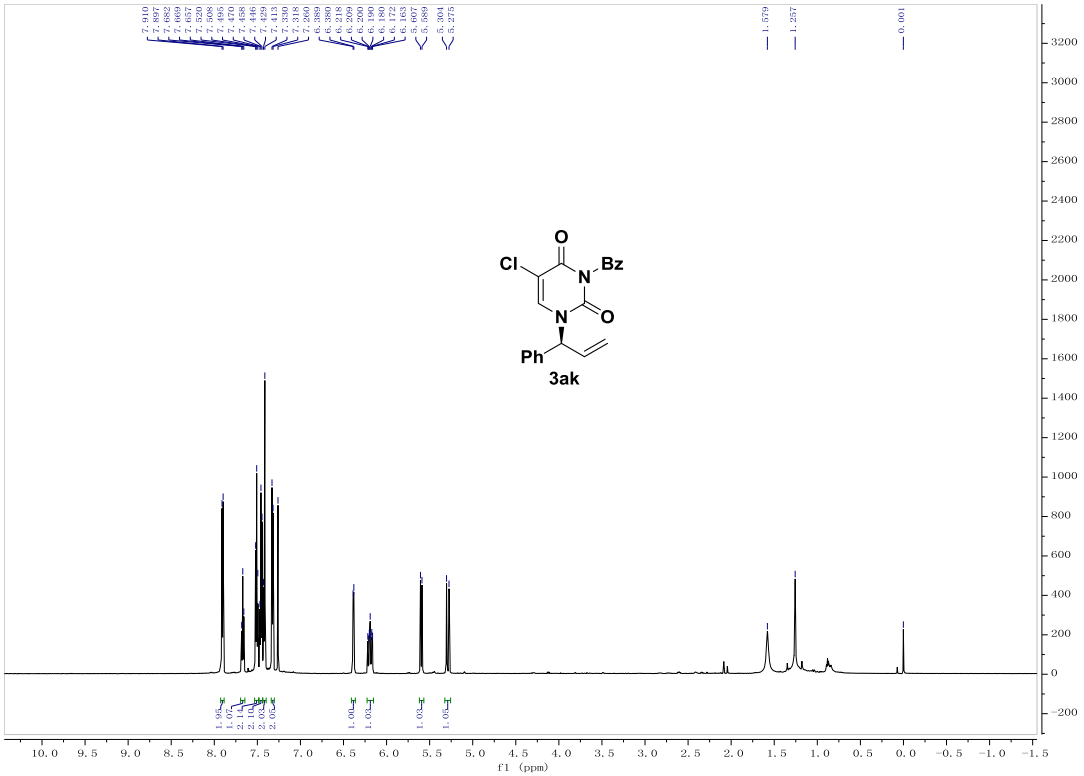


^{1}H NMR of 3ak



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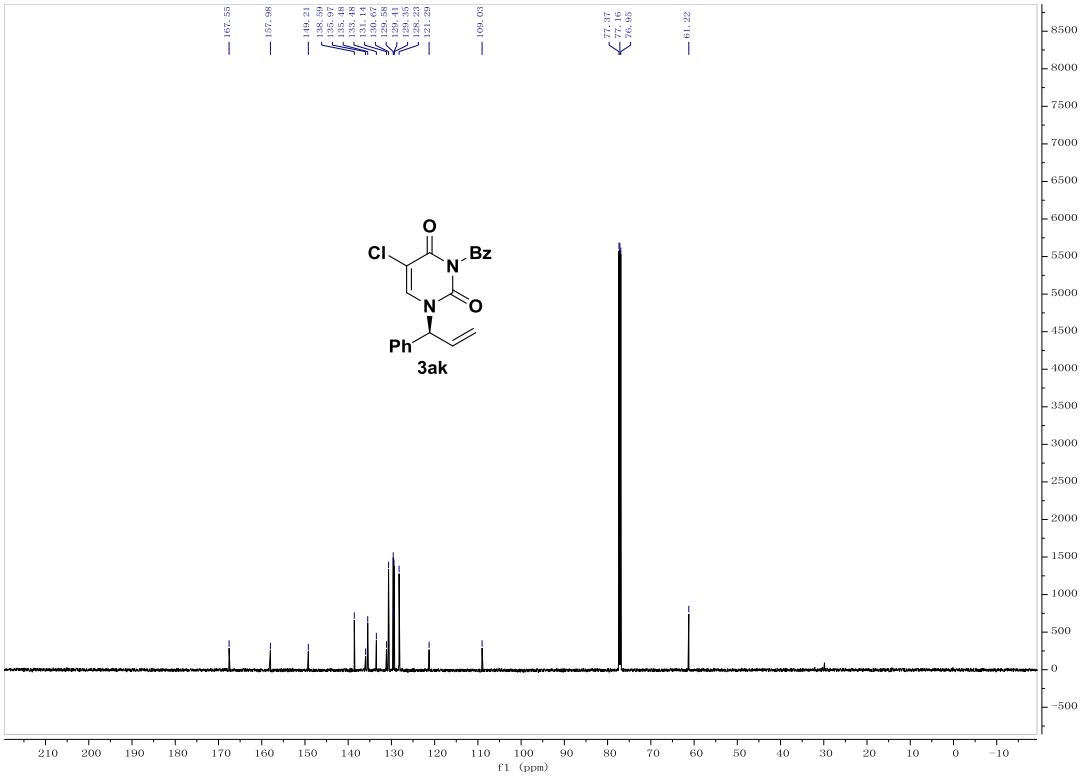
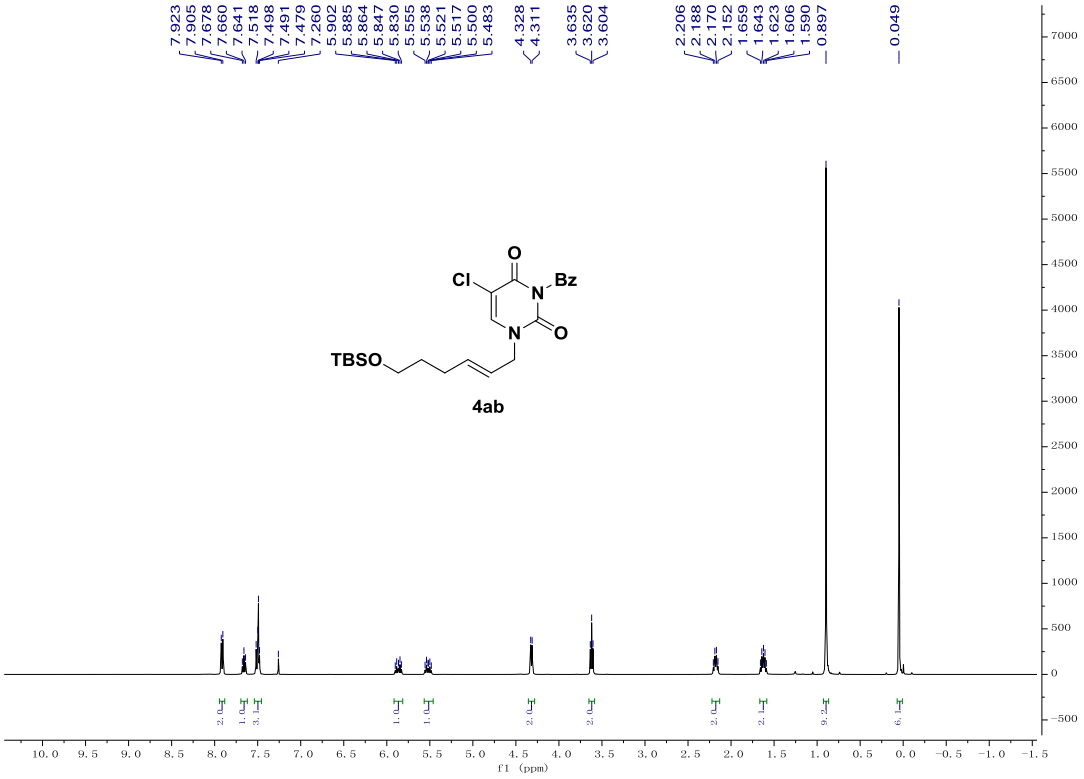
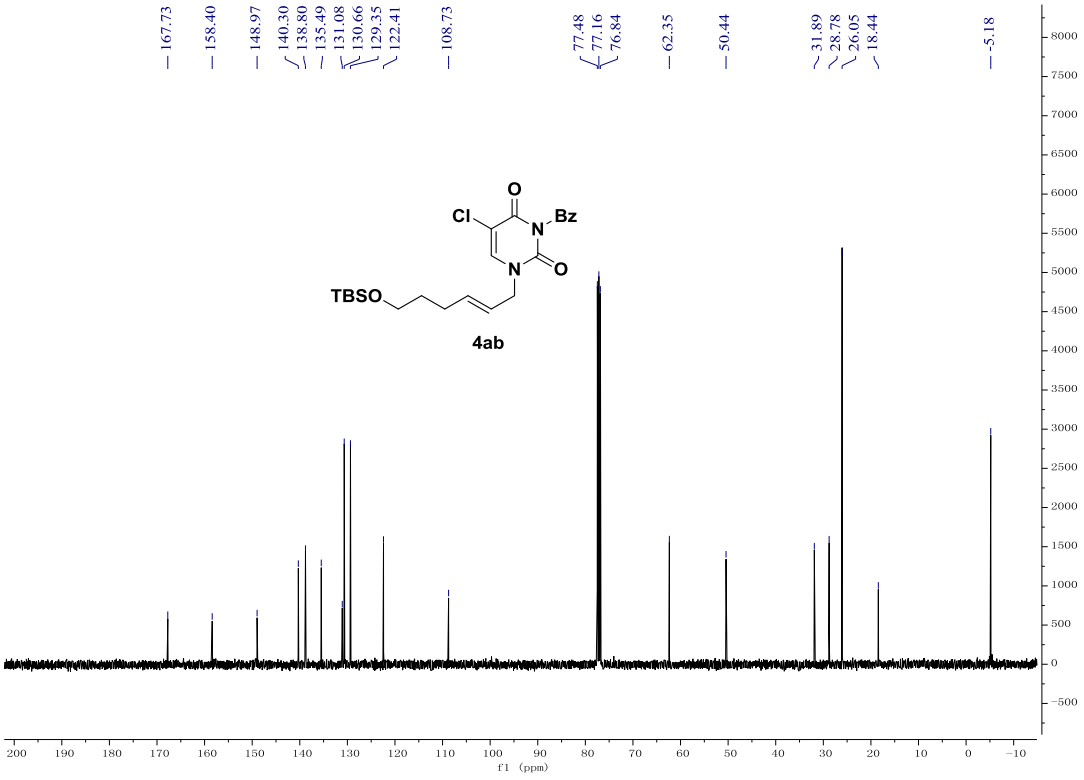


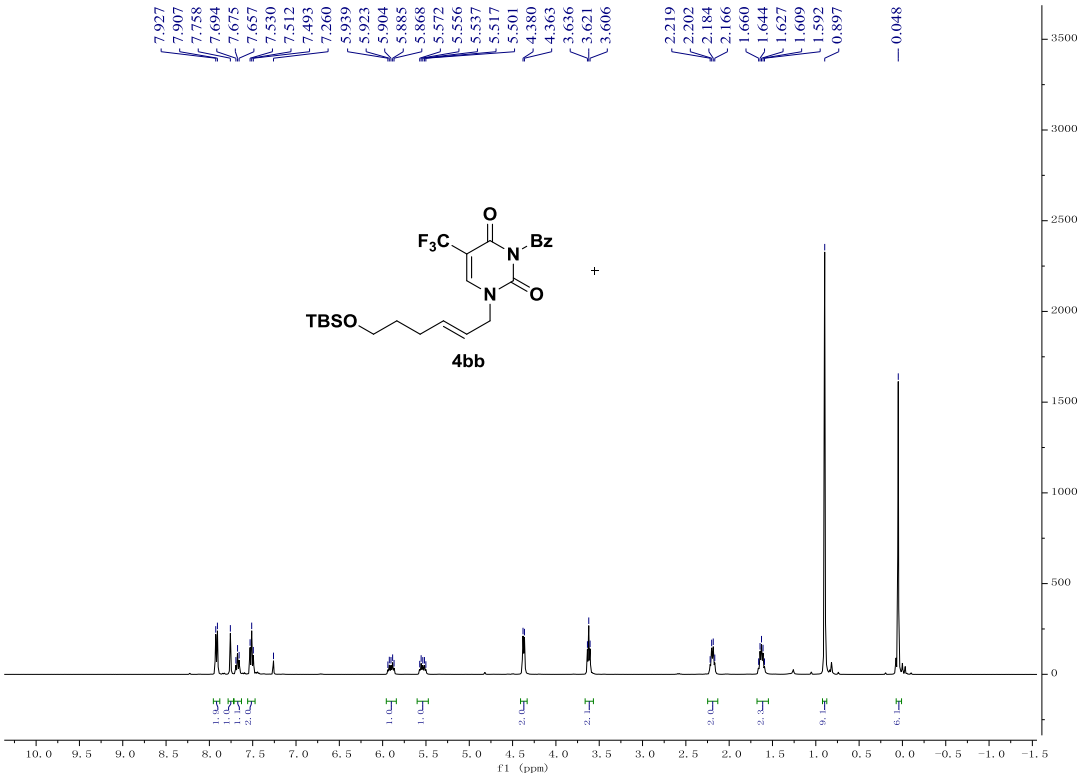
^{1}H NMR of 4ab



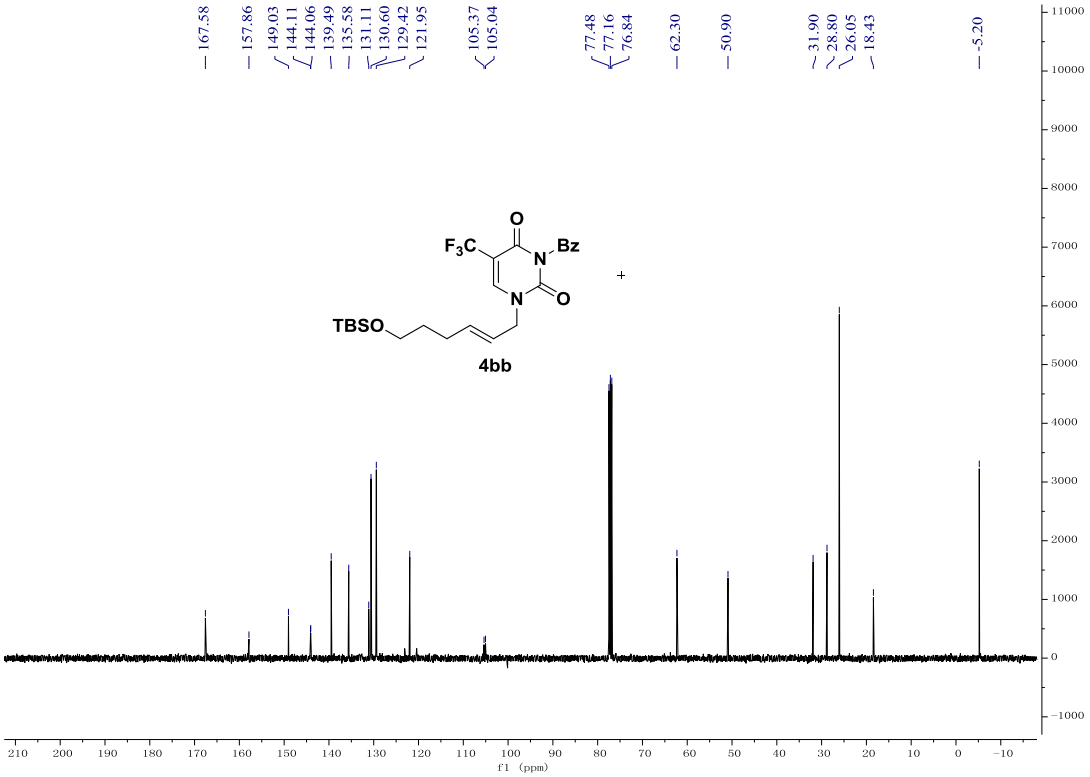
^{13}C NMR of 4ab



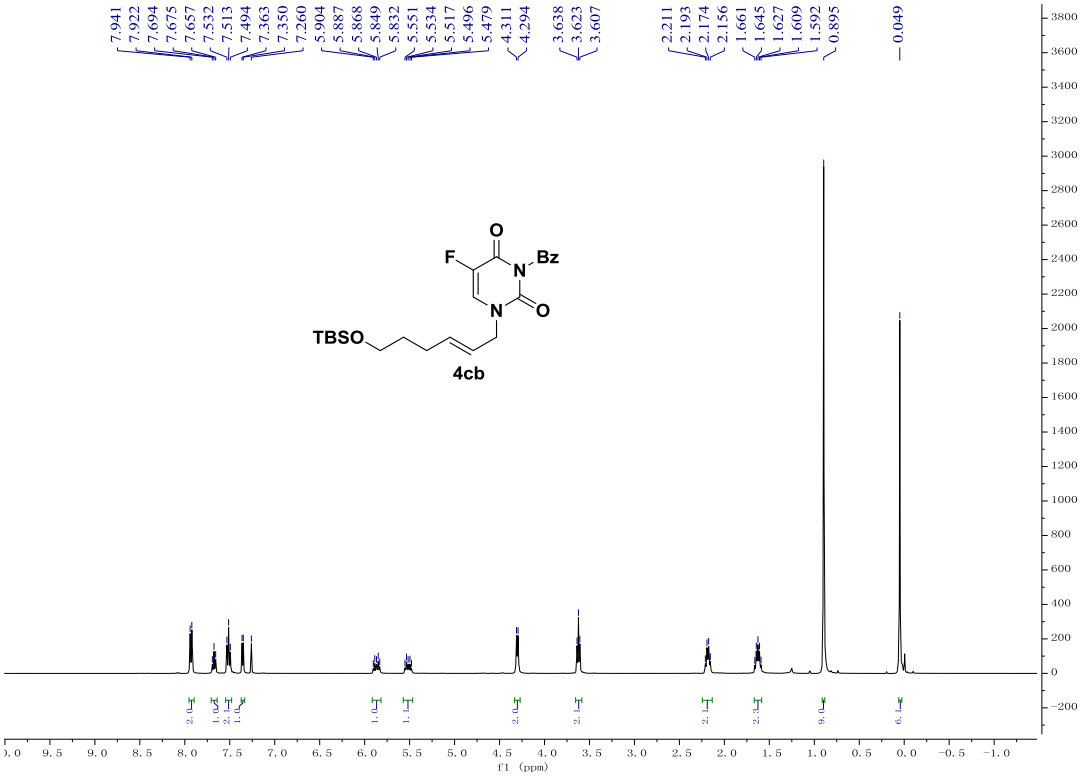
^{1}H NMR of 4bb



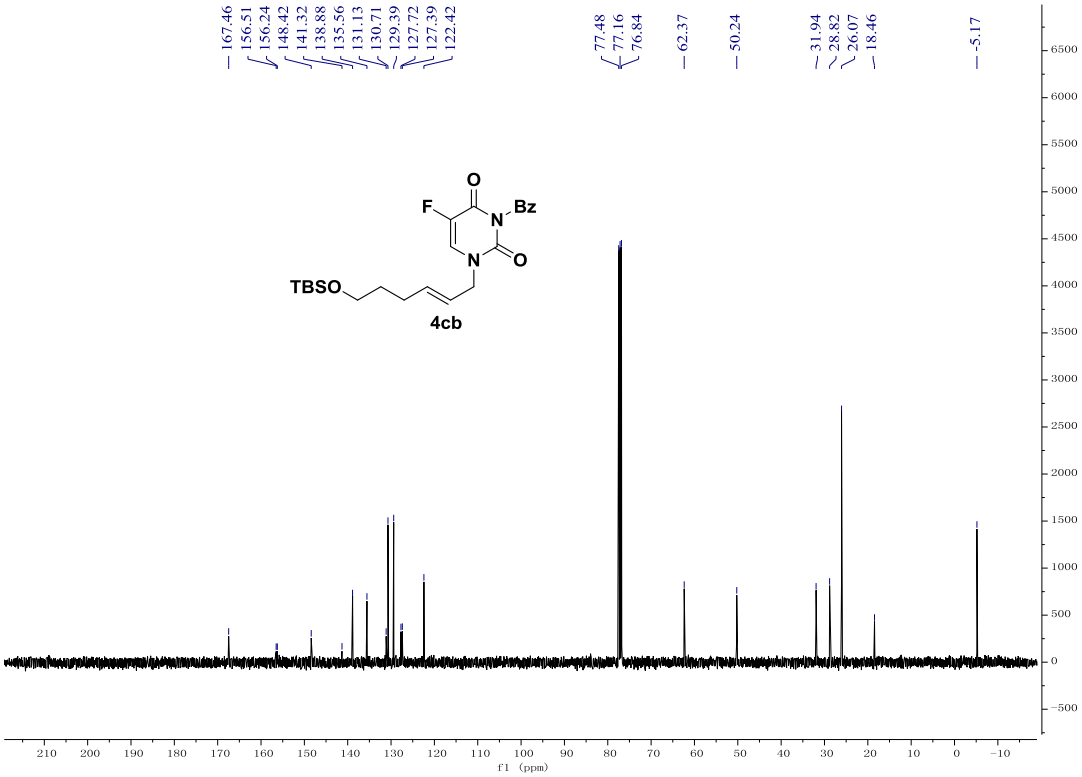
^{13}C NMR of 4bb



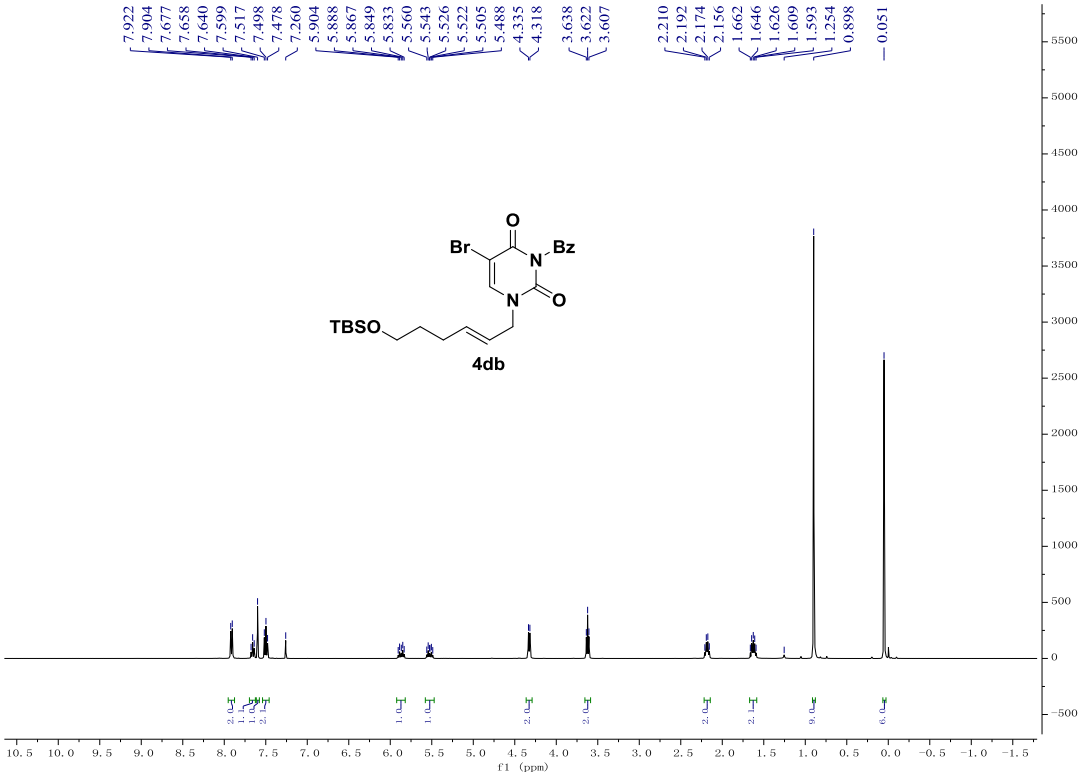
^{1}H NMR of 4cb



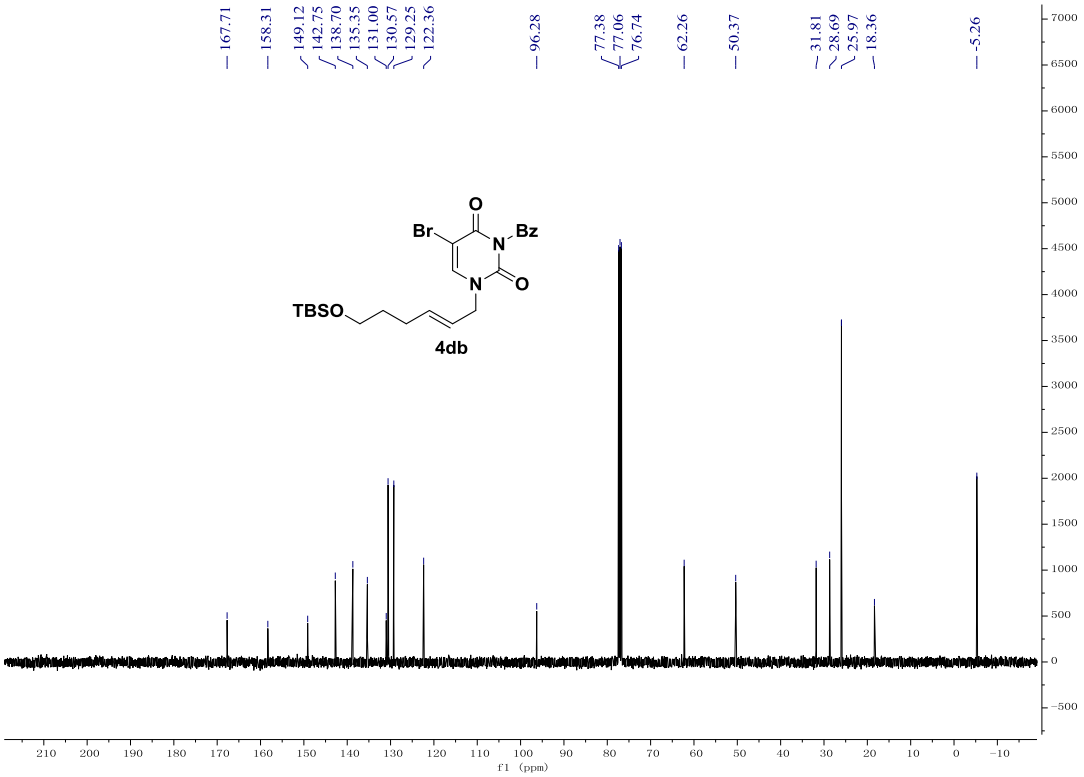
^{13}C NMR of 4cb



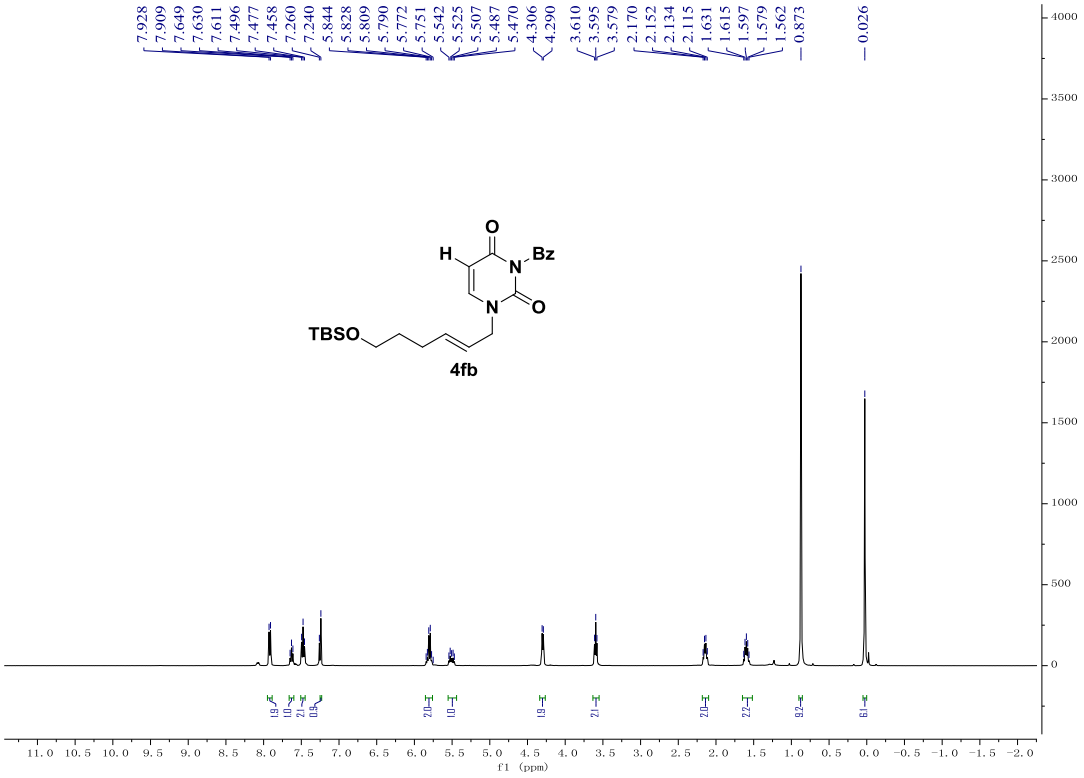
^{1}H NMR of 4db



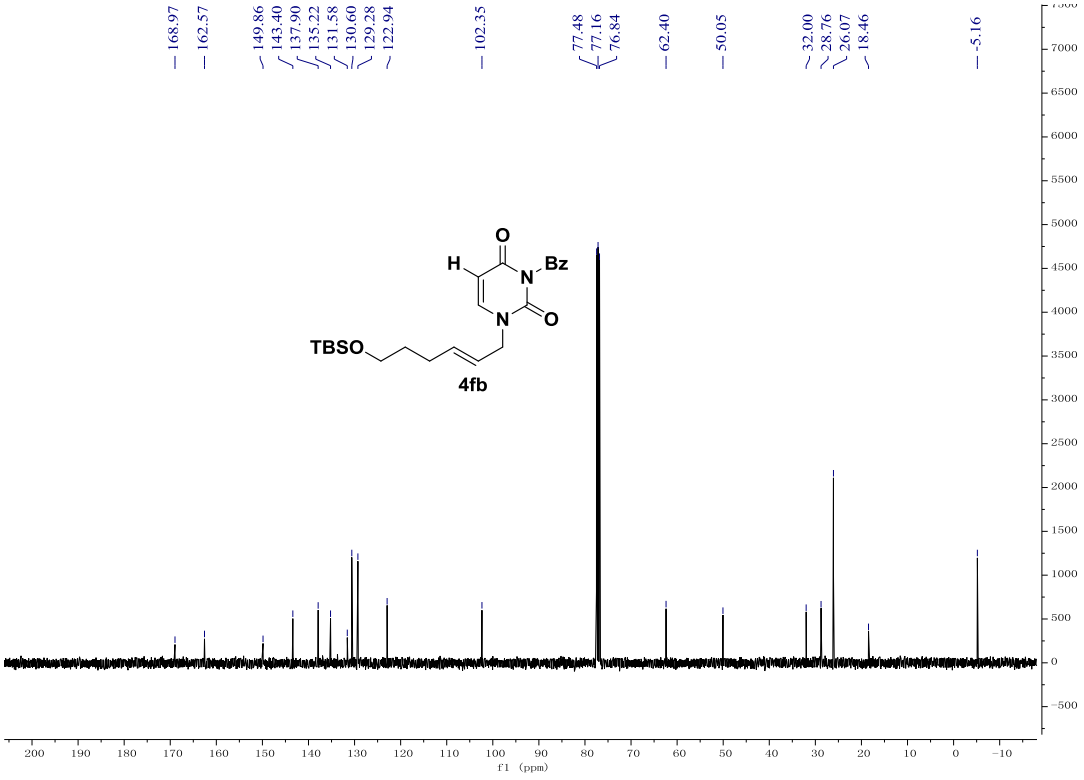
^{13}C NMR of 4db



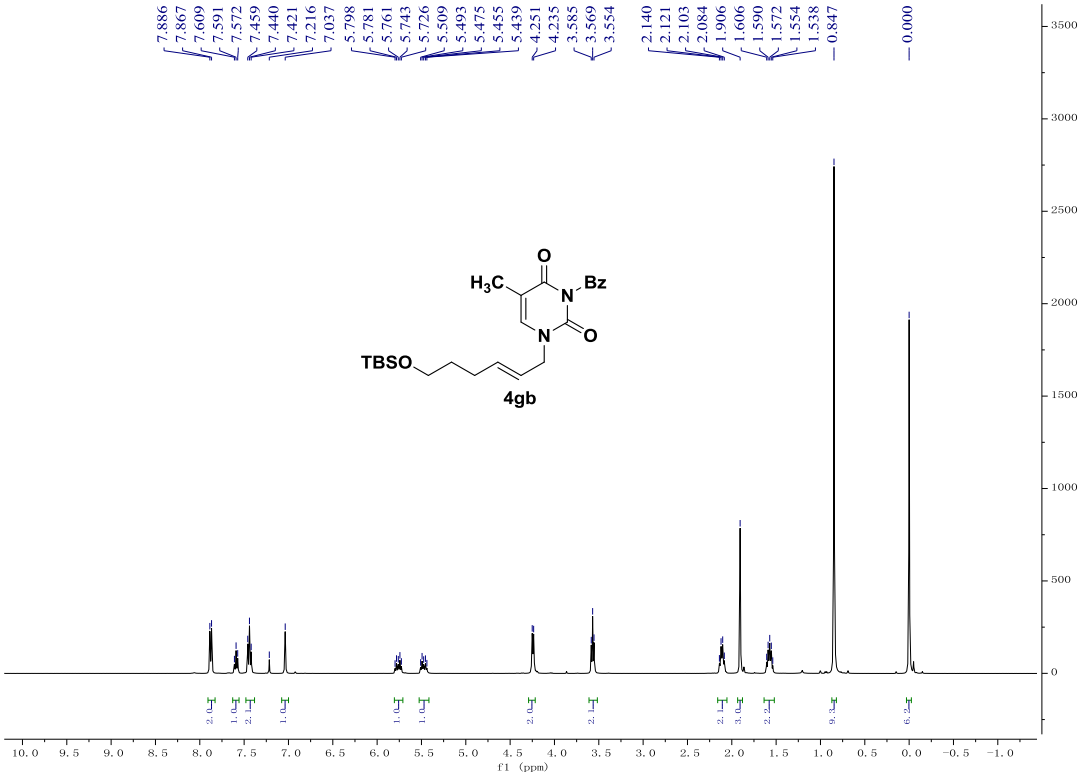
^{1}H NMR of 4fb



^{13}C NMR of 4fb



^{1}H NMR of 4gb



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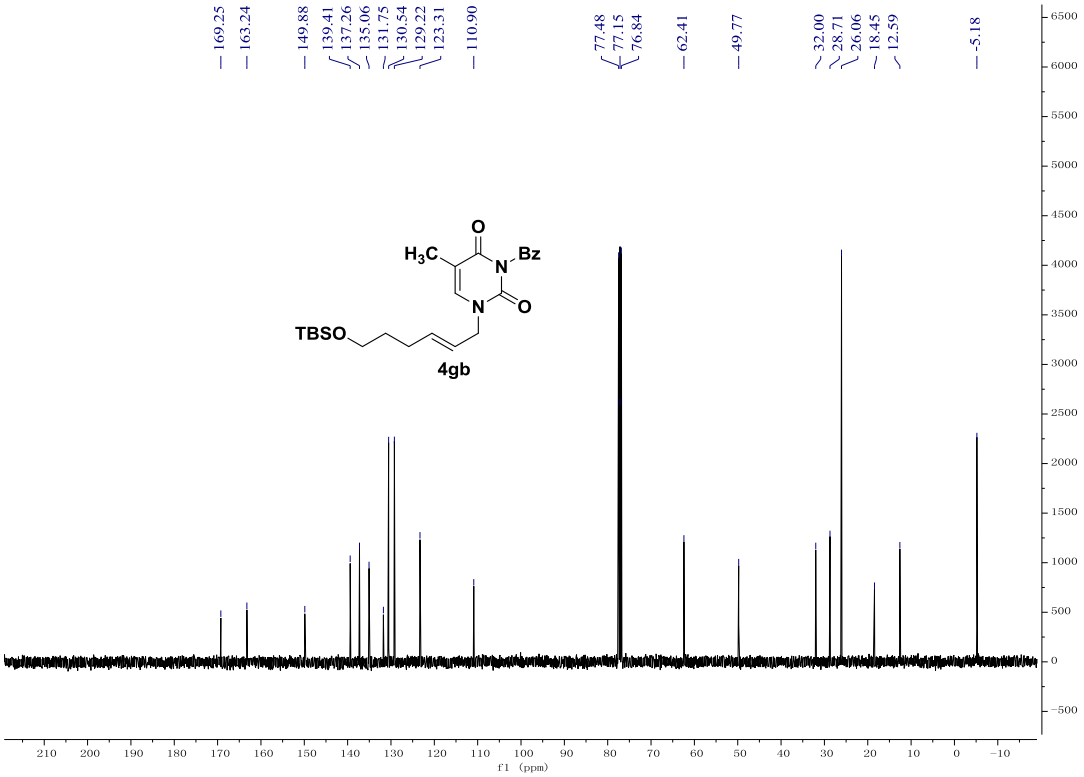
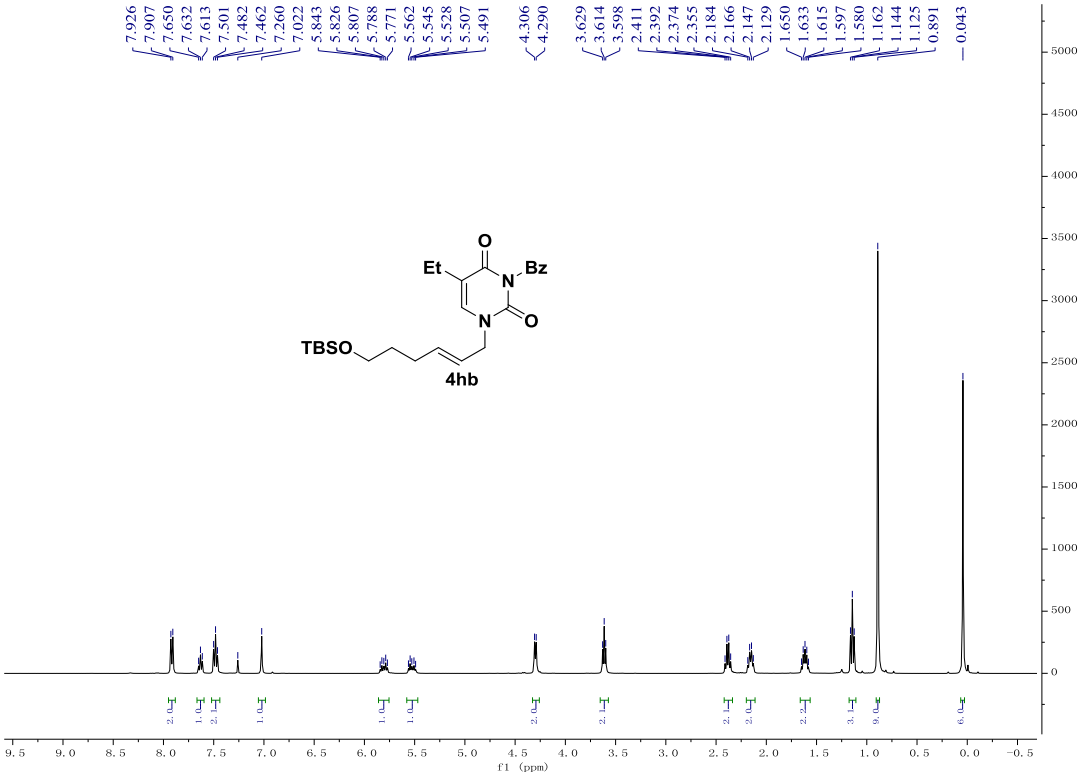


^{1}H NMR of 4hb



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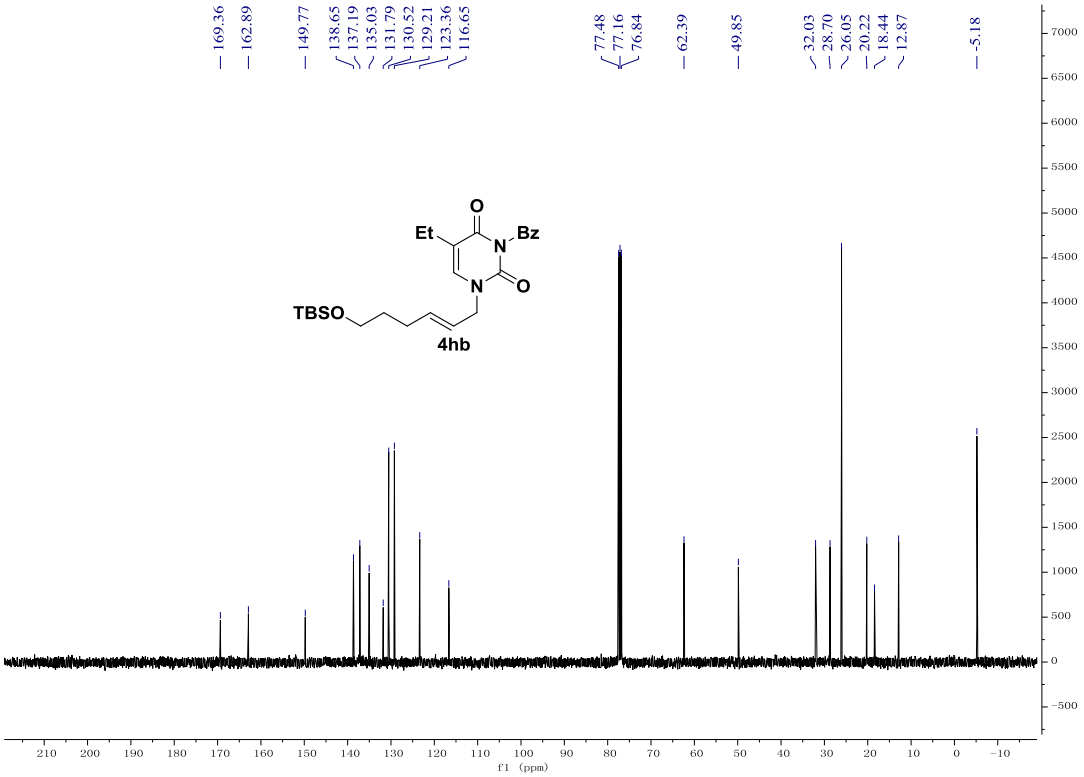
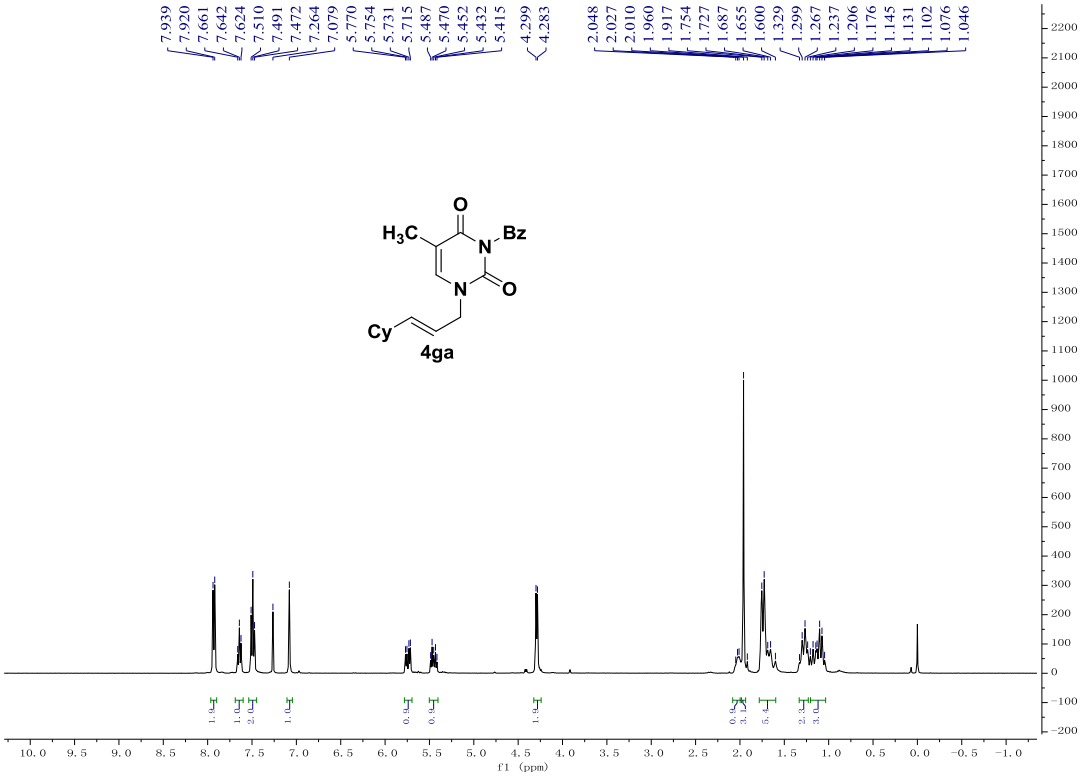
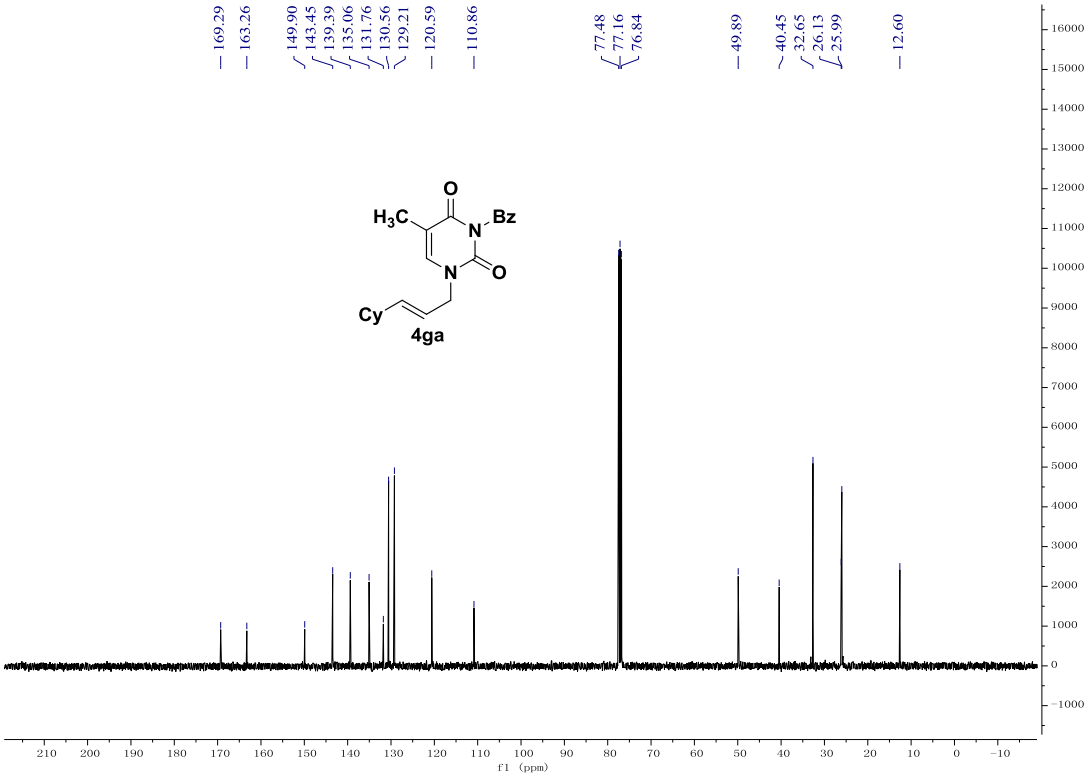


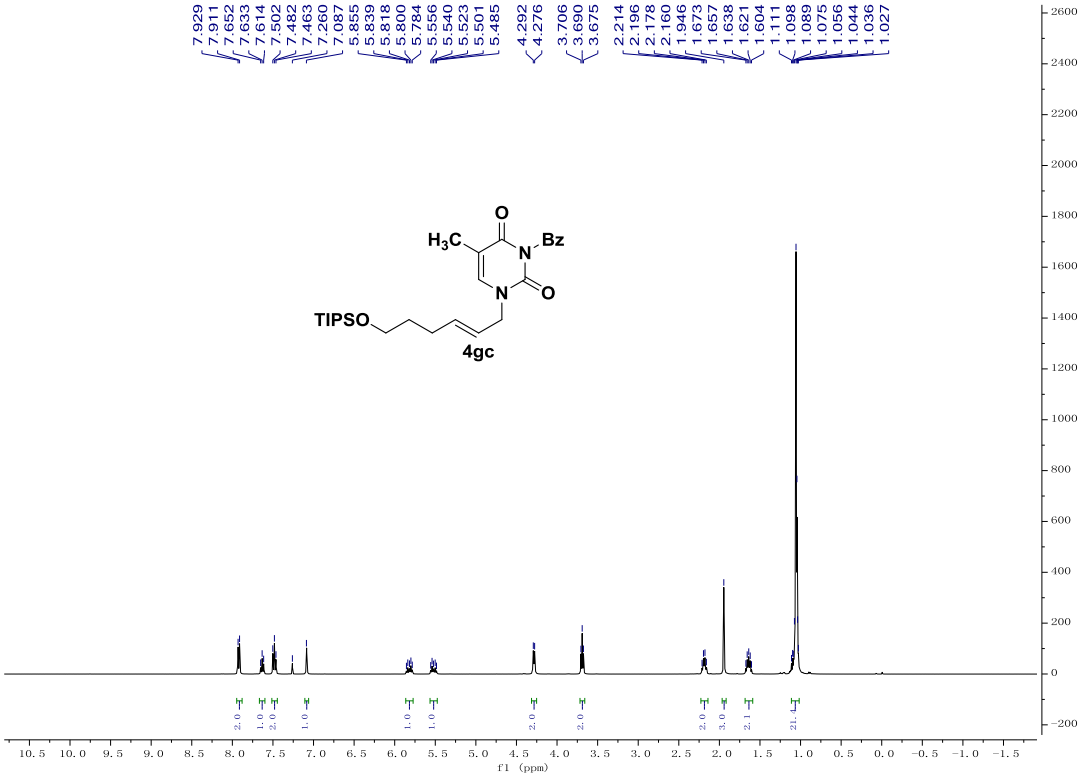
^{1}H NMR of 4ga



^{13}C NMR of 4ga



^{1}H NMR of 4gc



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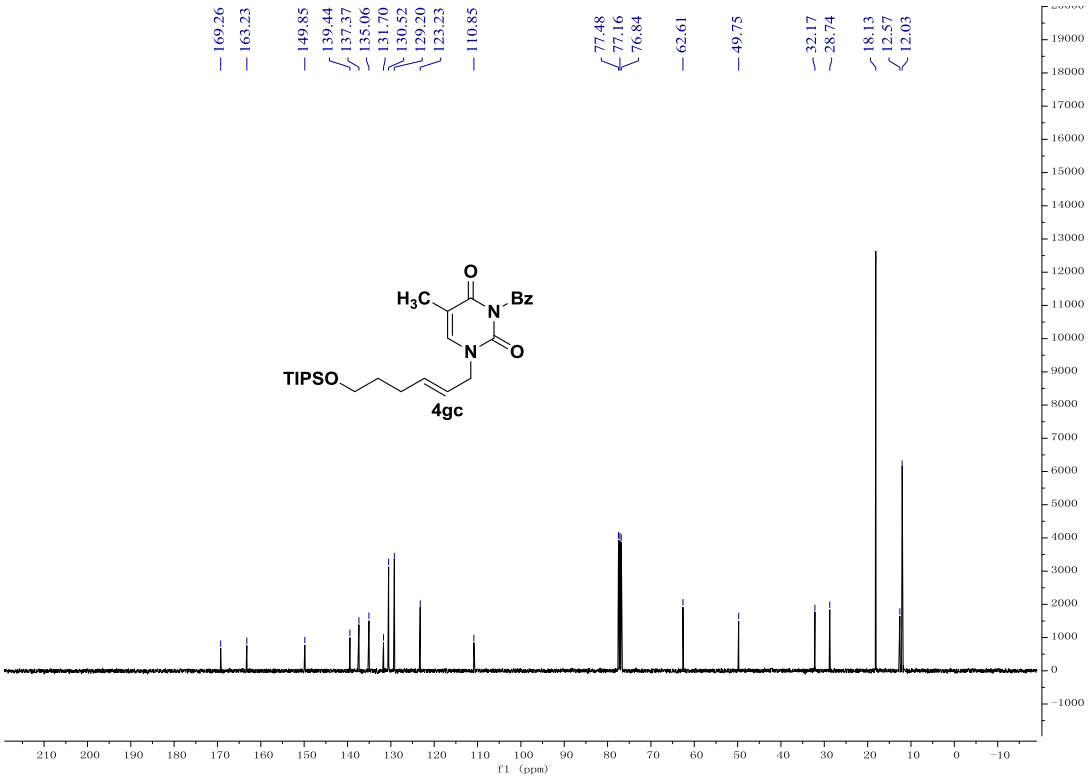
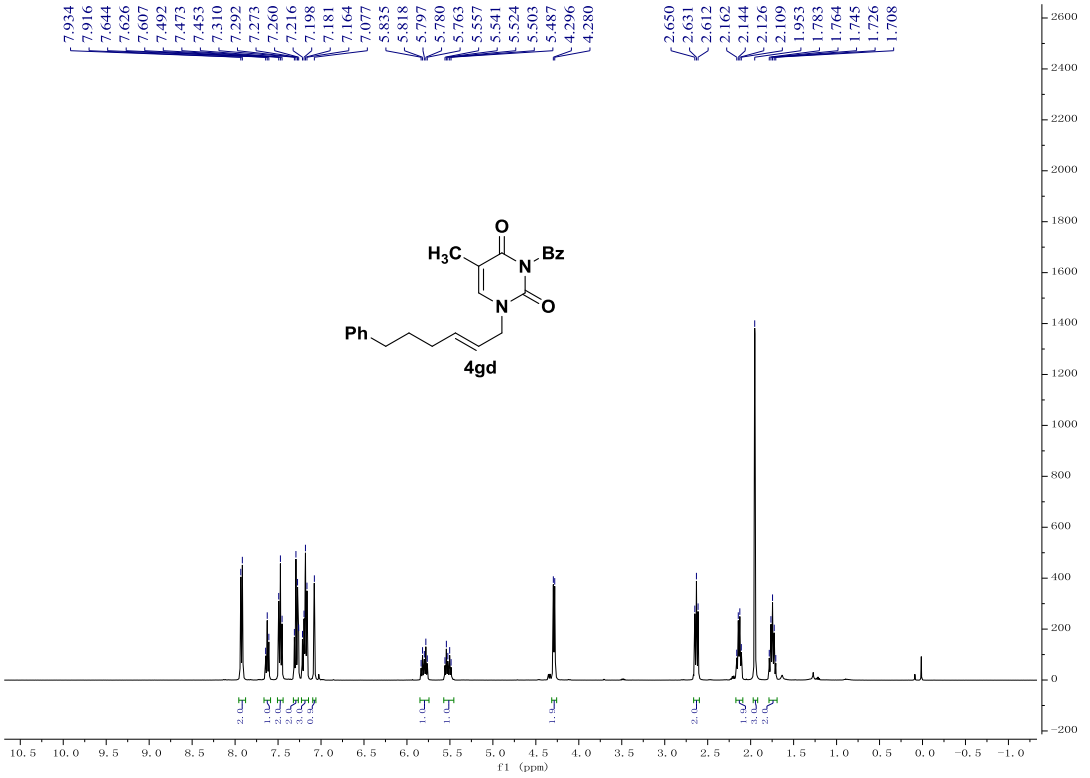


^{1}H NMR of 4gd



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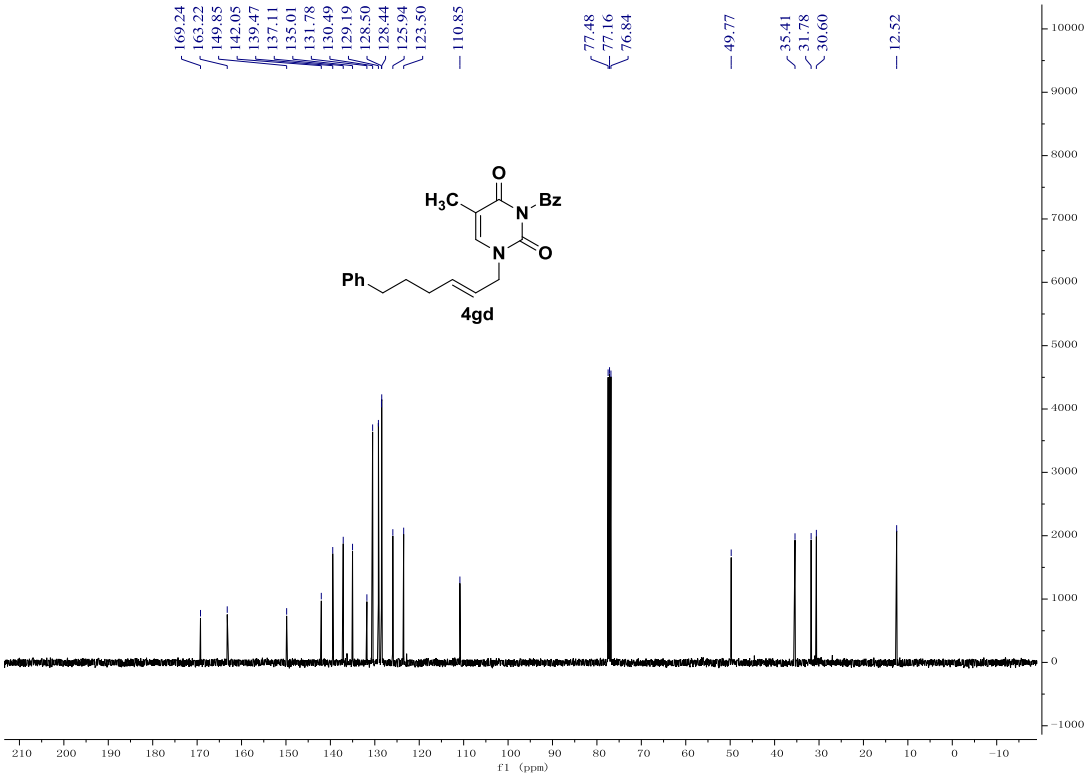

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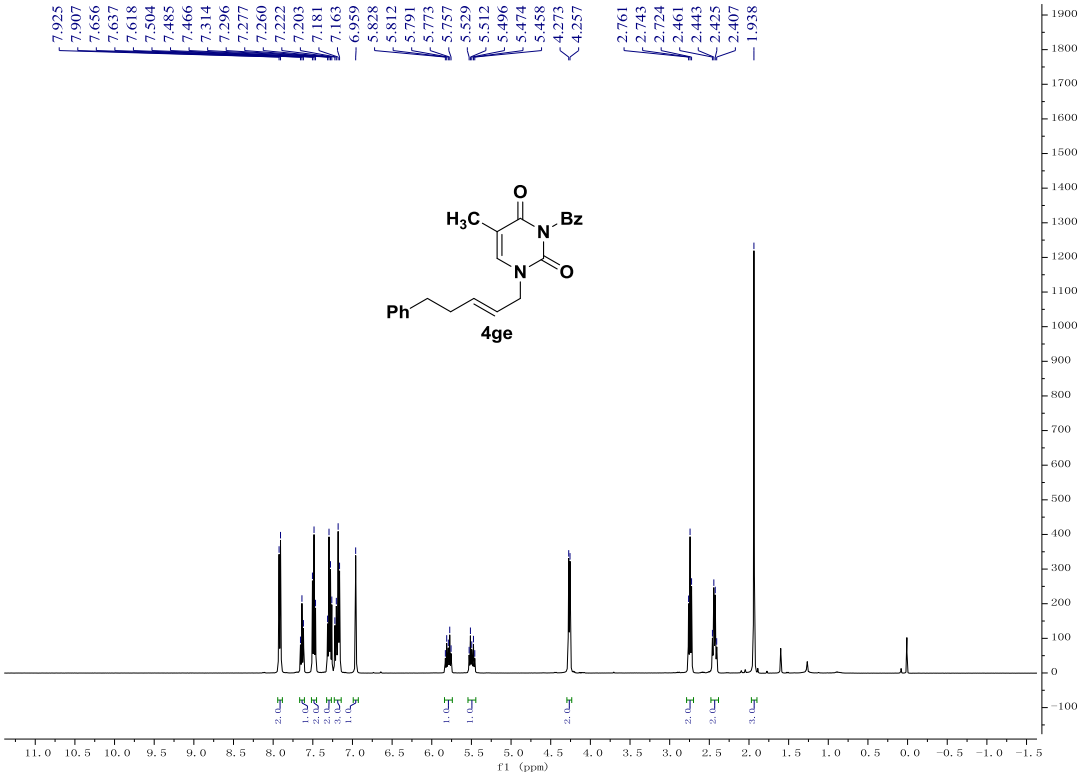

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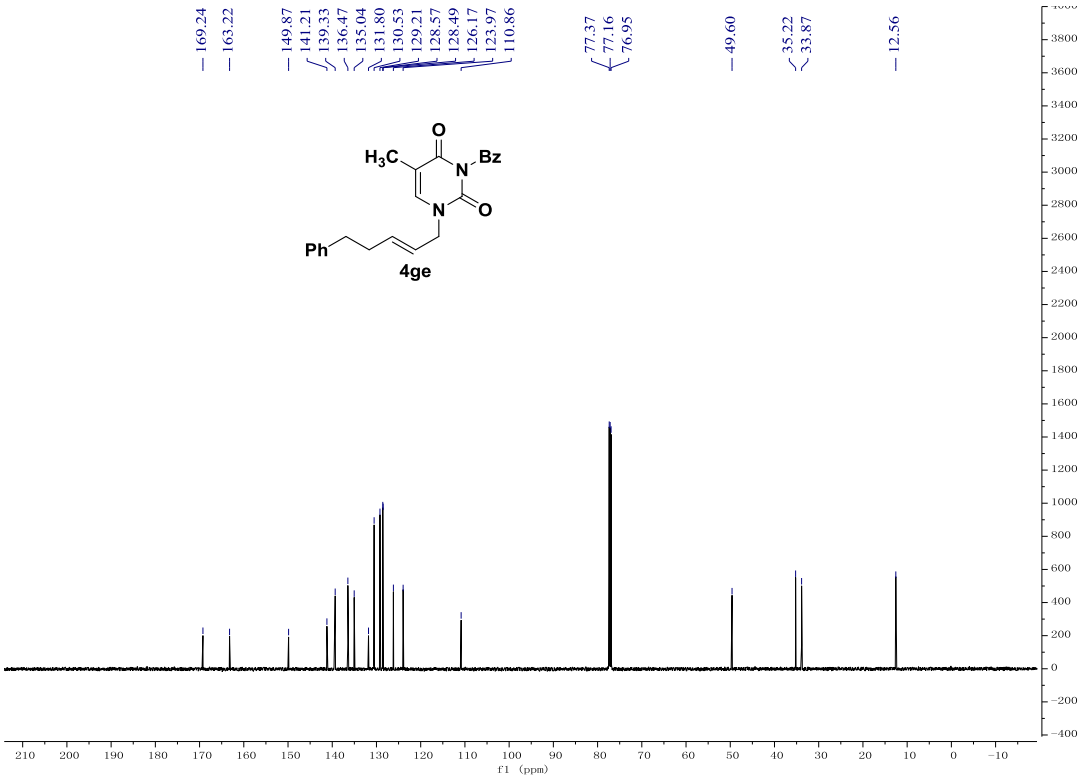
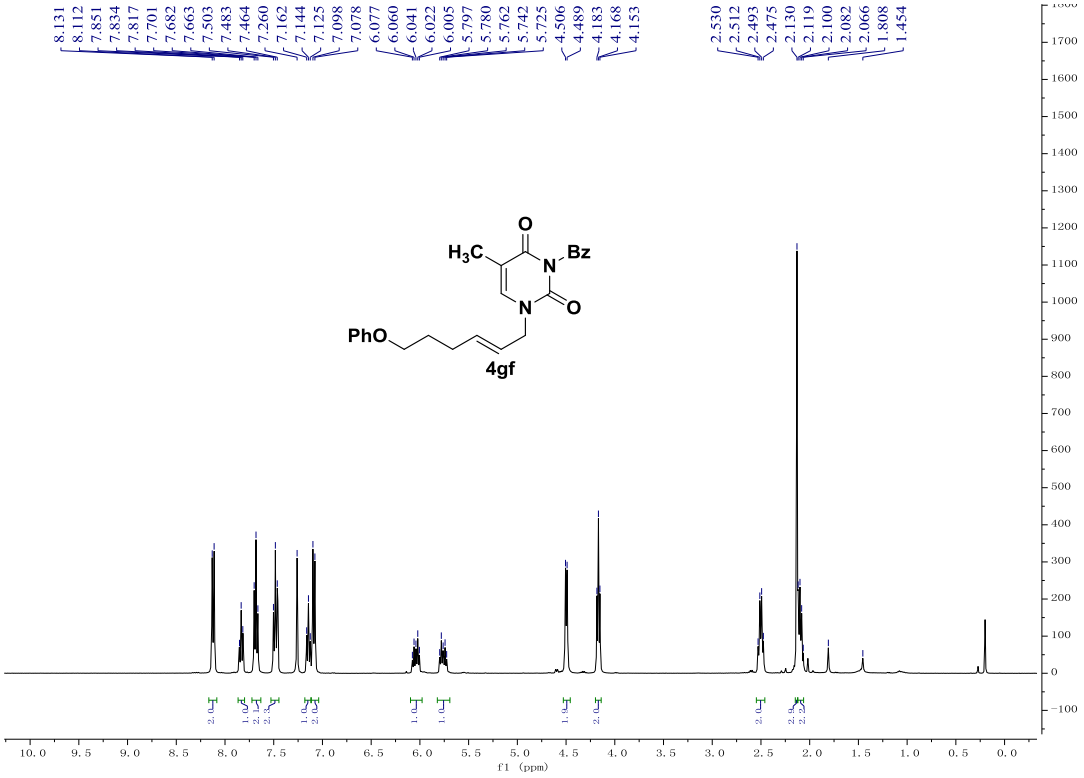
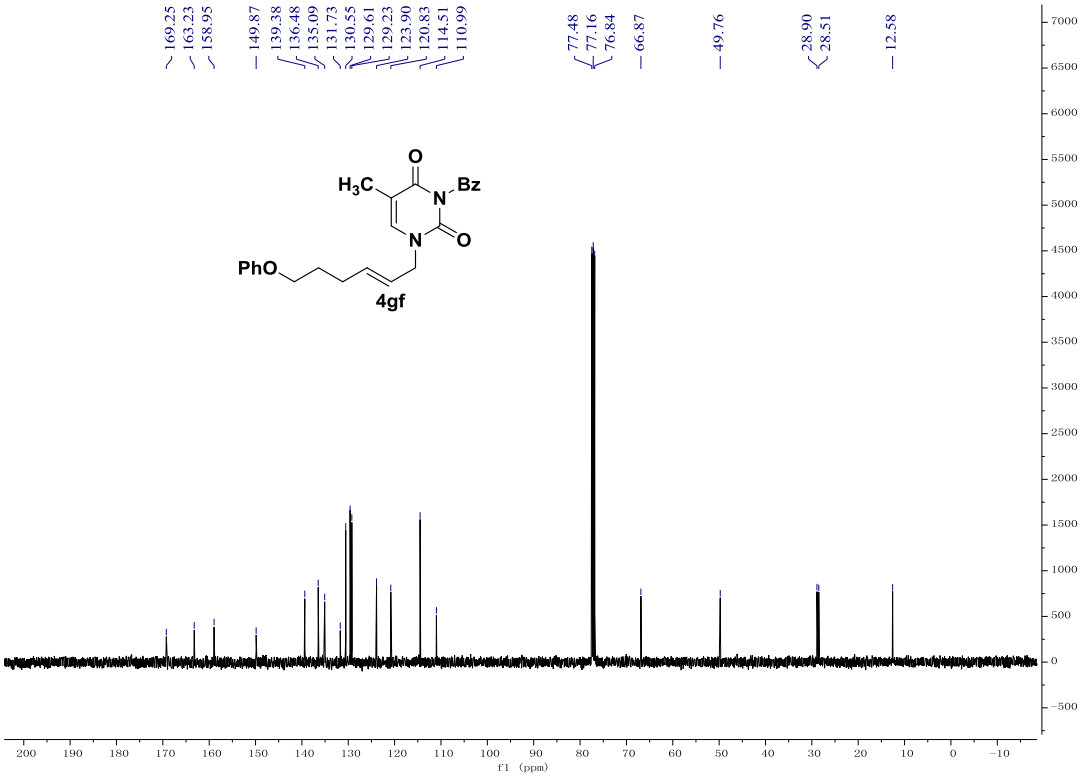


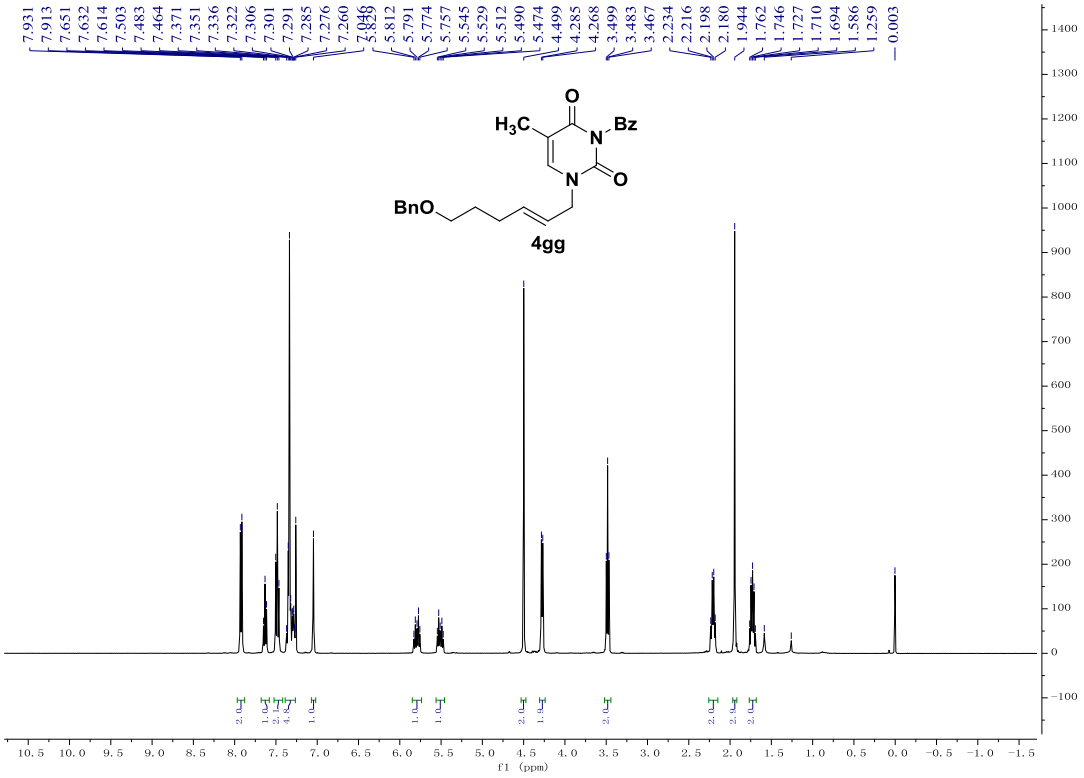
^{1}H NMR of 4gf



^{13}C NMR of 4gf



^{1}H NMR of 4gg



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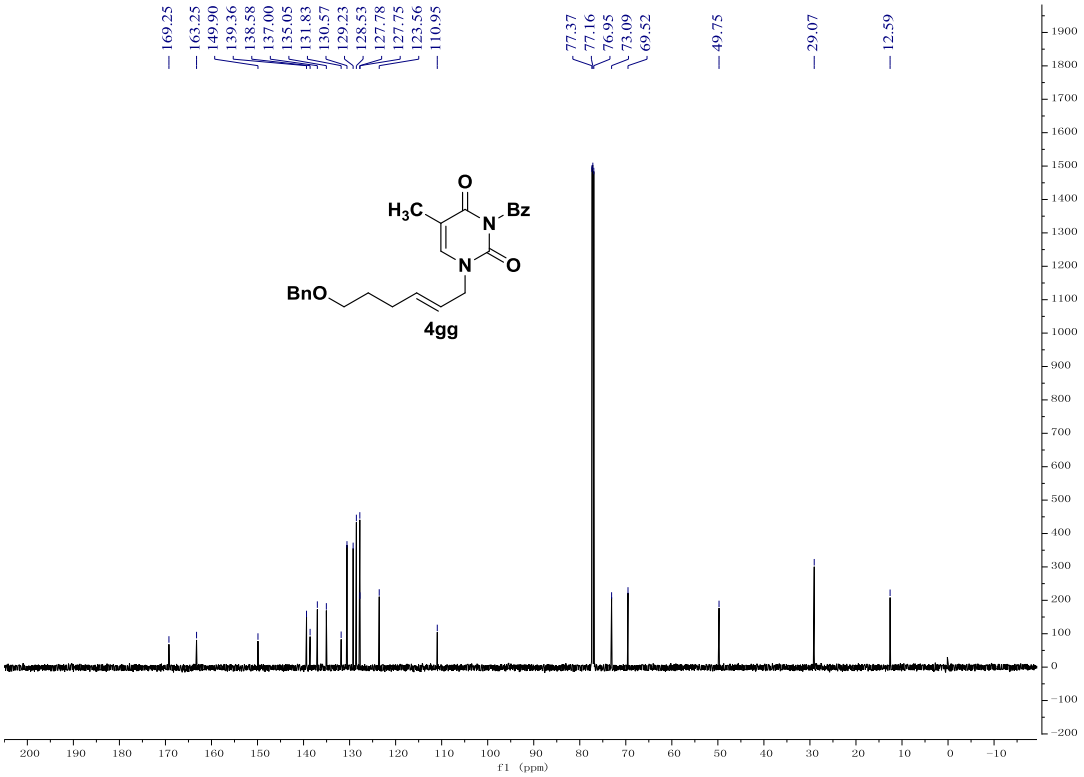

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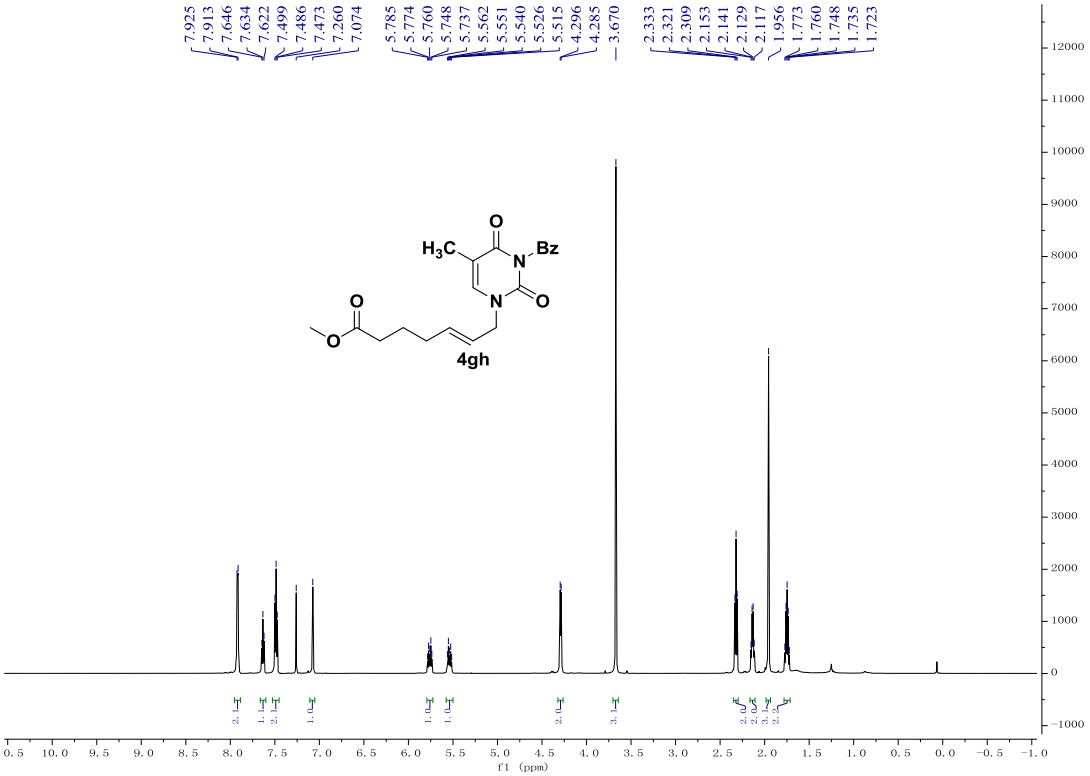

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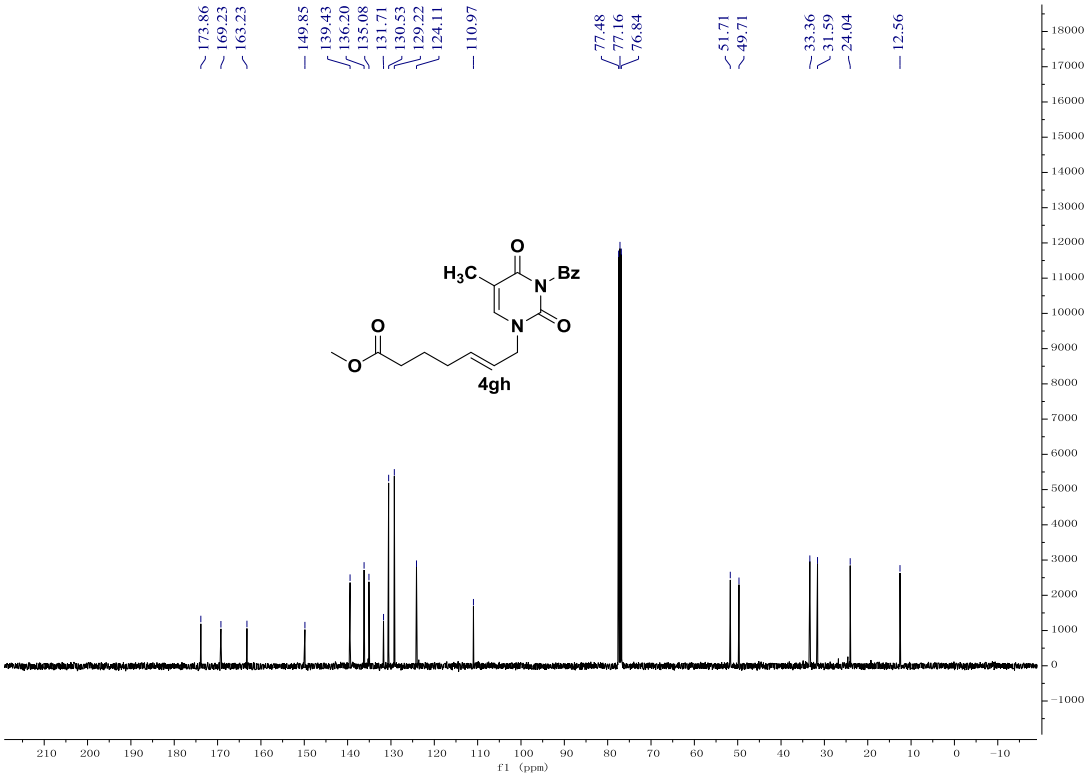
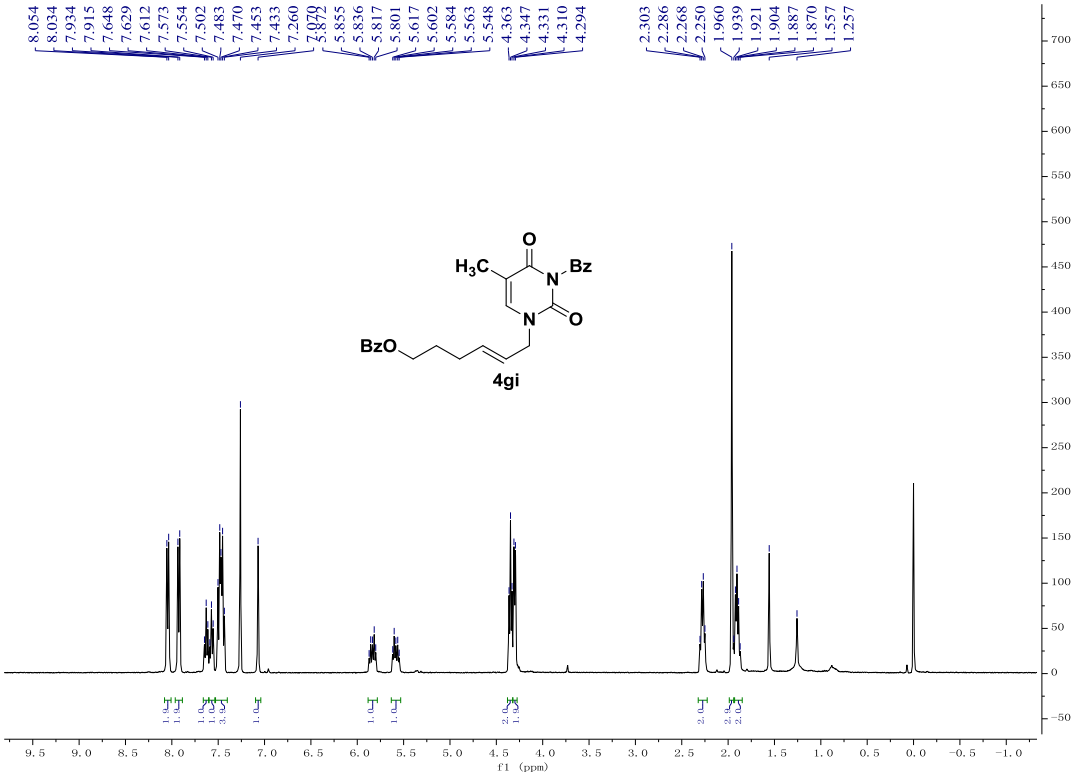
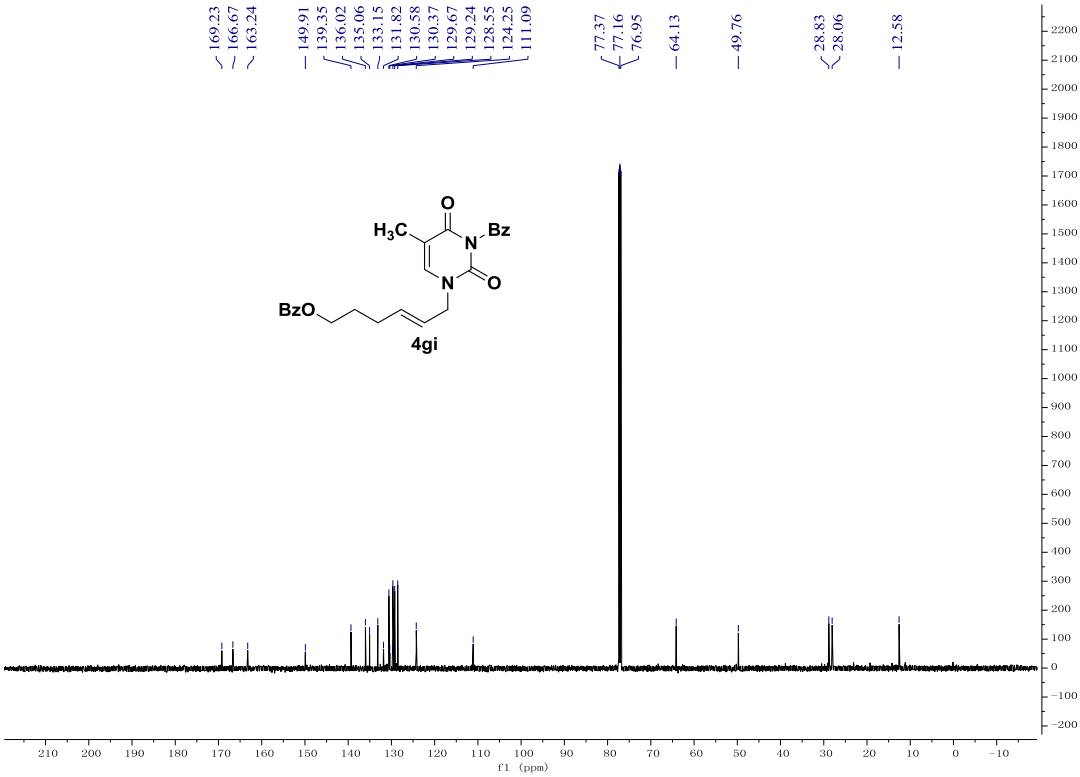


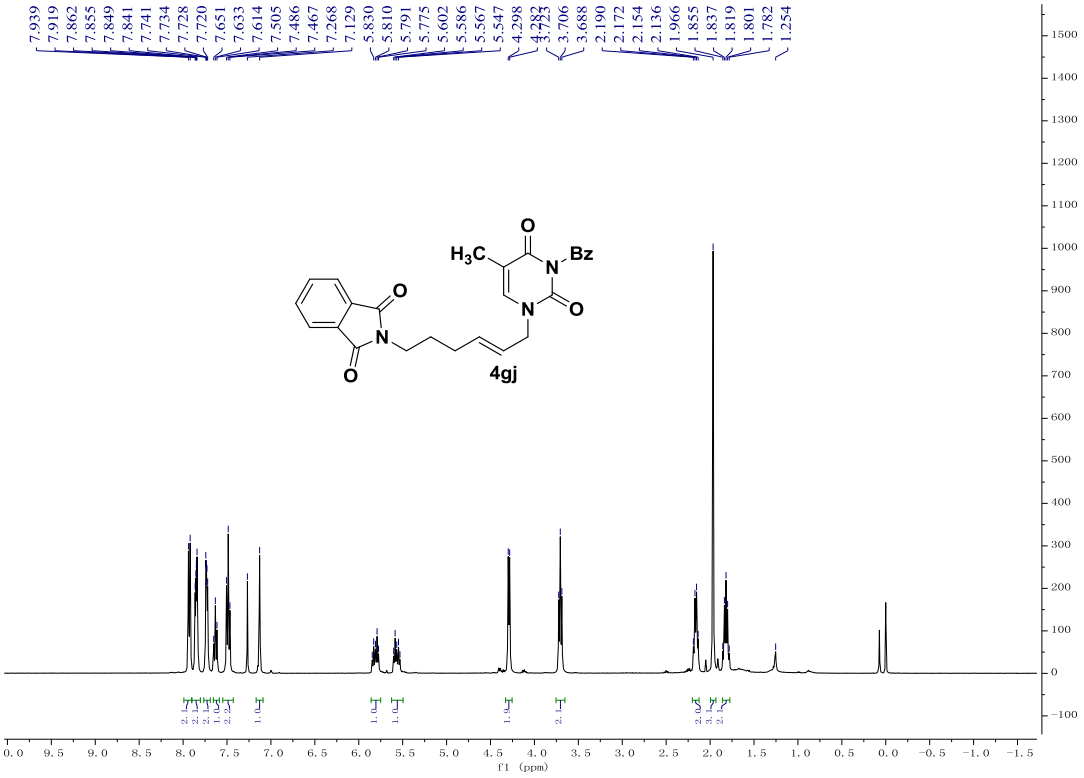
^{1}H NMR of 4gi



^{13}C NMR of 4gi



^{1}H NMR of 4gj



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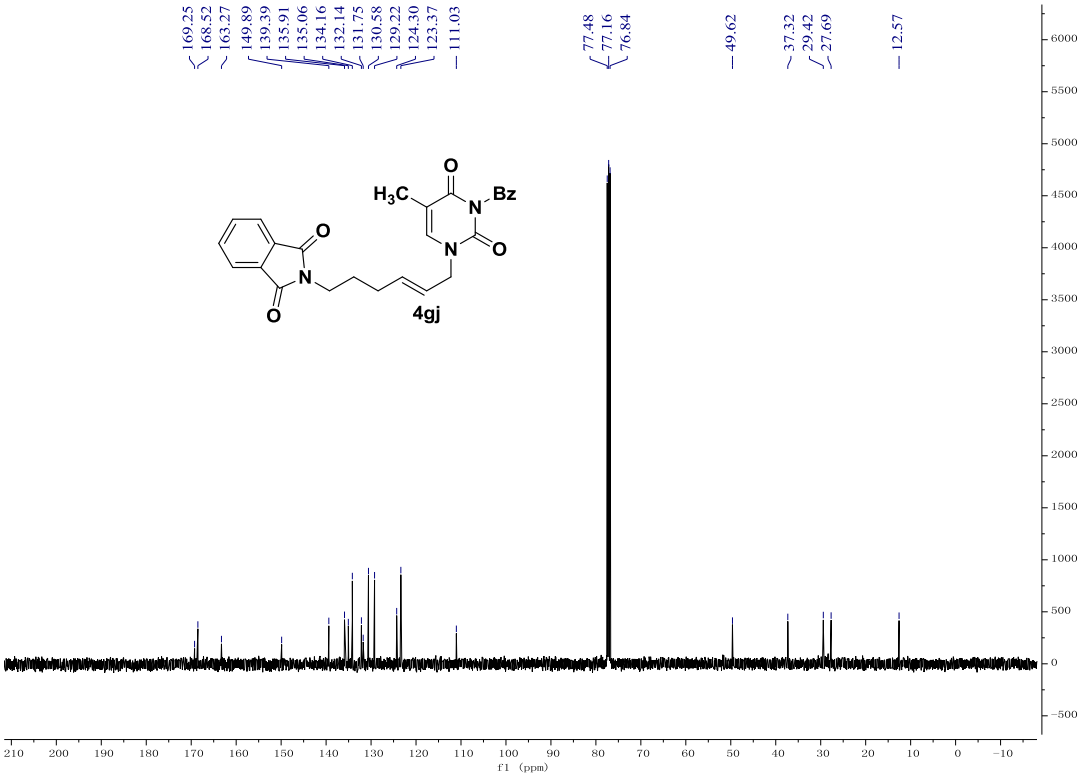
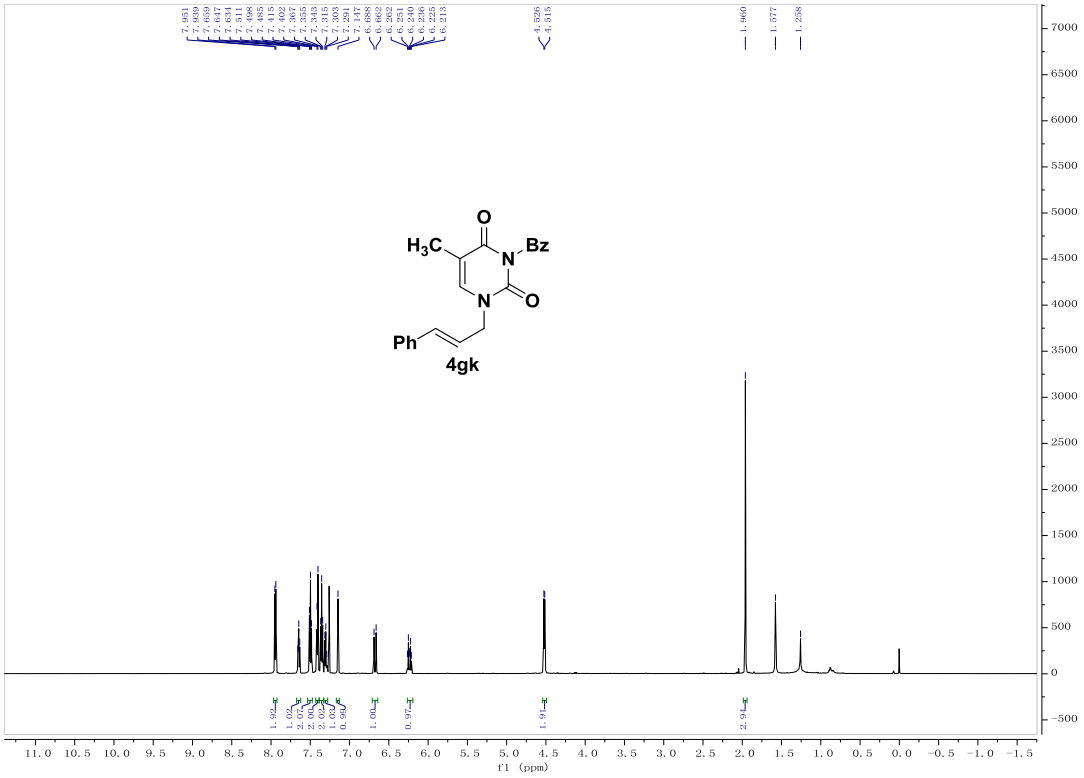


^{1}H NMR of 4gk



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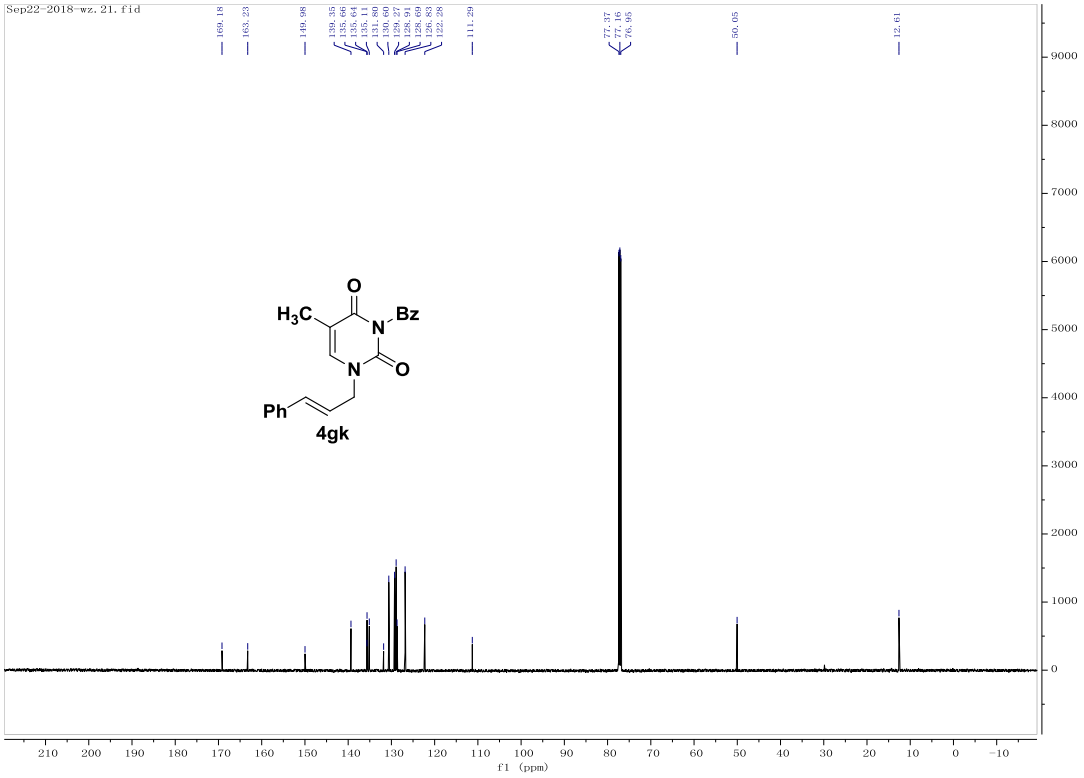
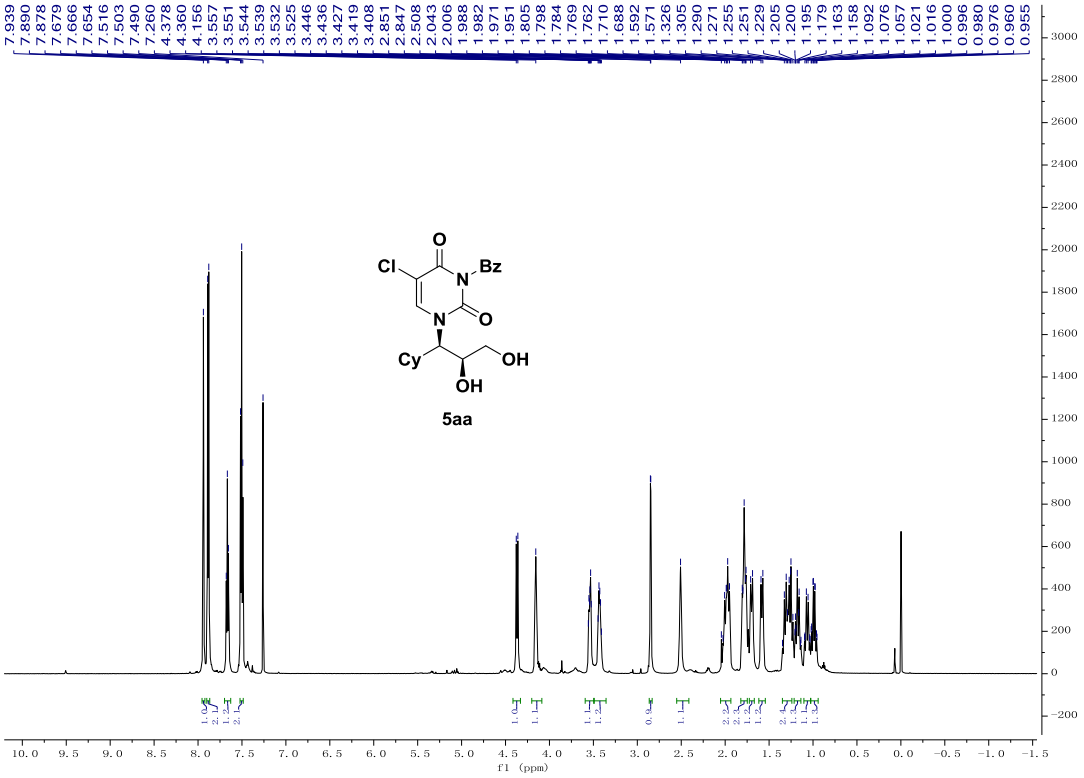


^{1}H NMR of 5aa



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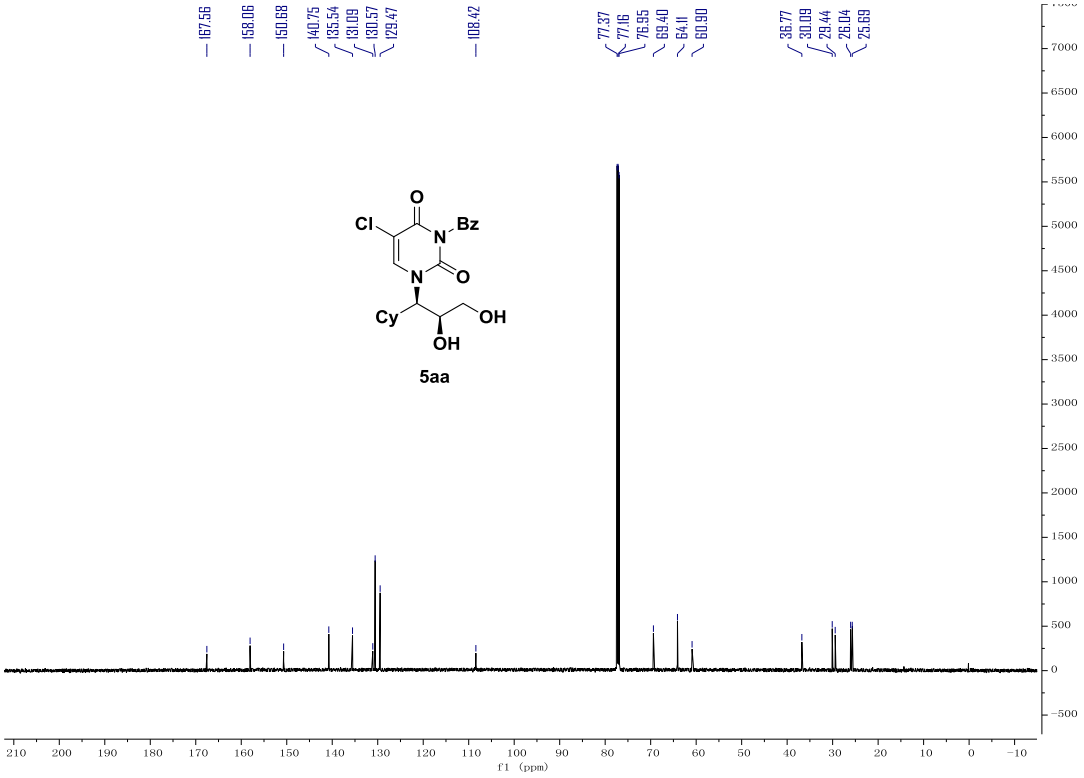
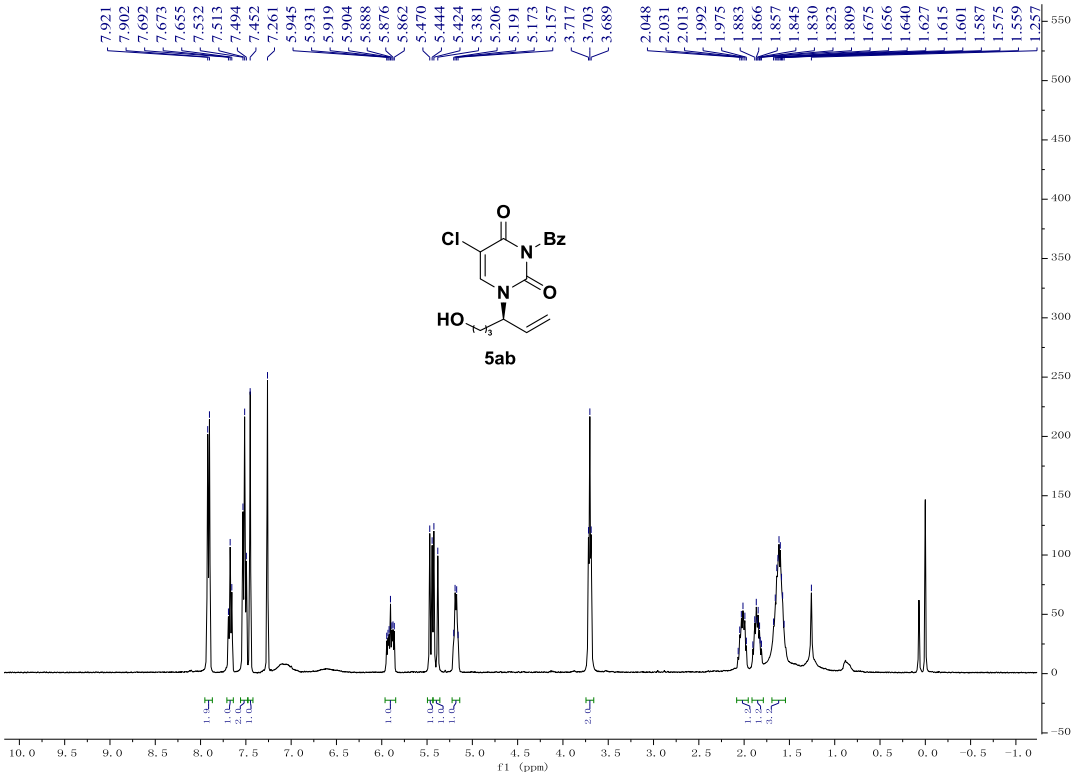


^{1}H NMR of 5ab



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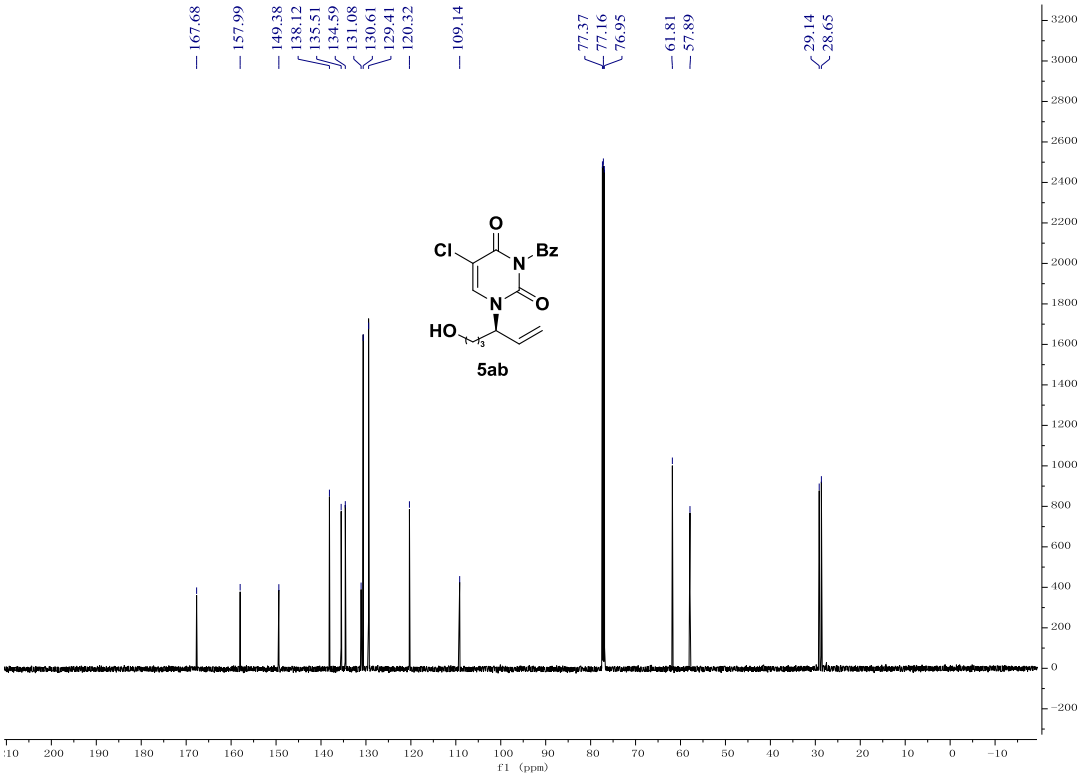

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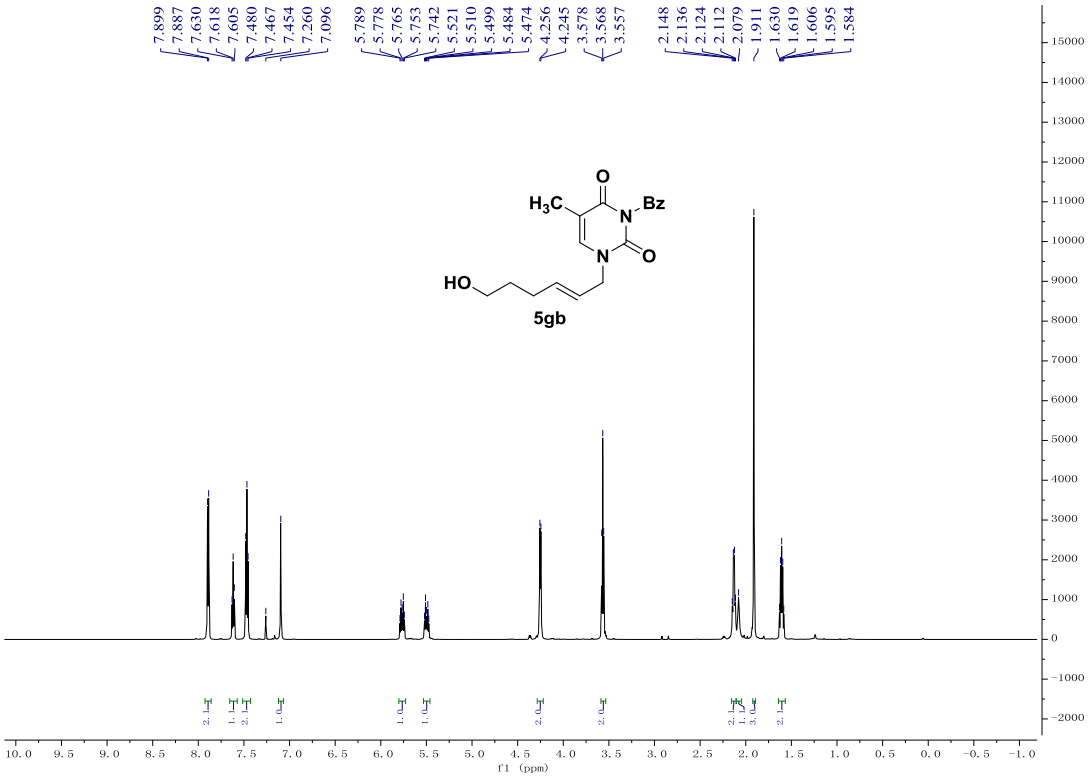

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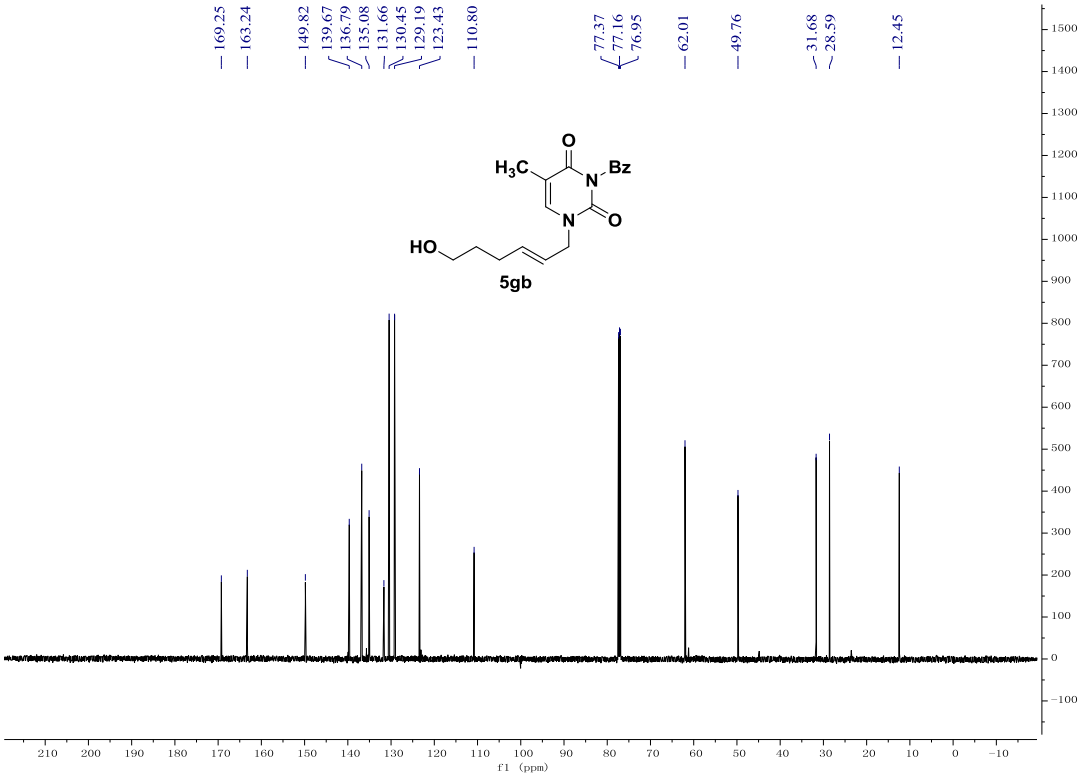

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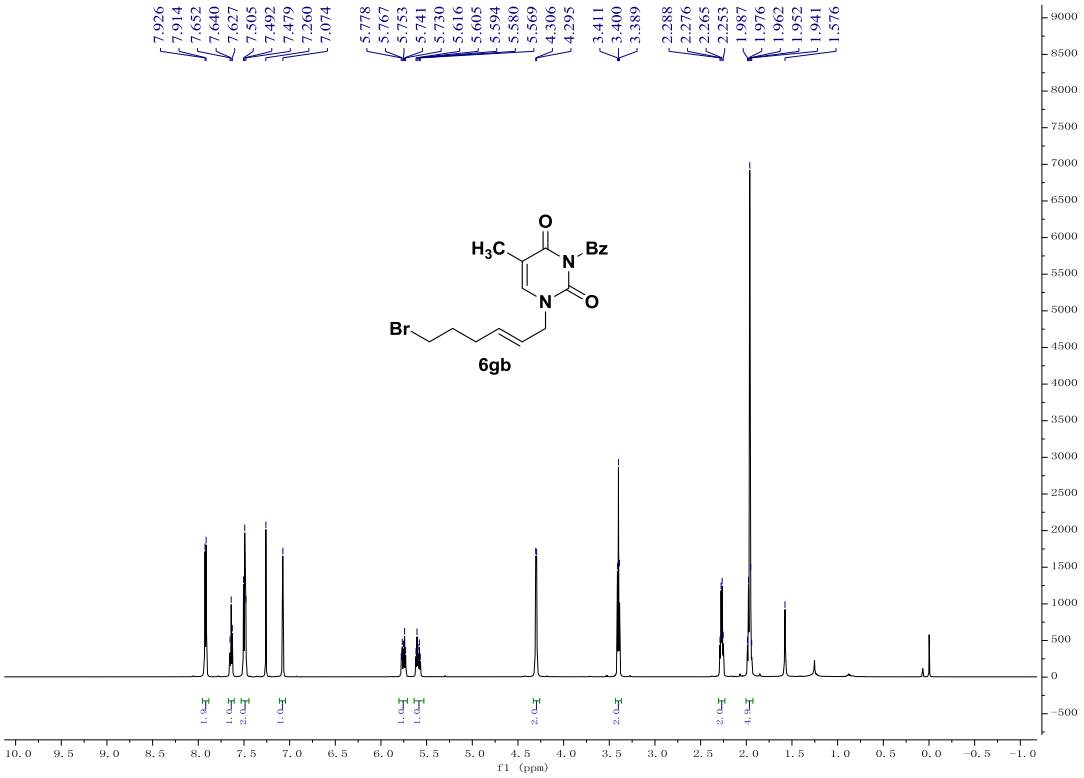

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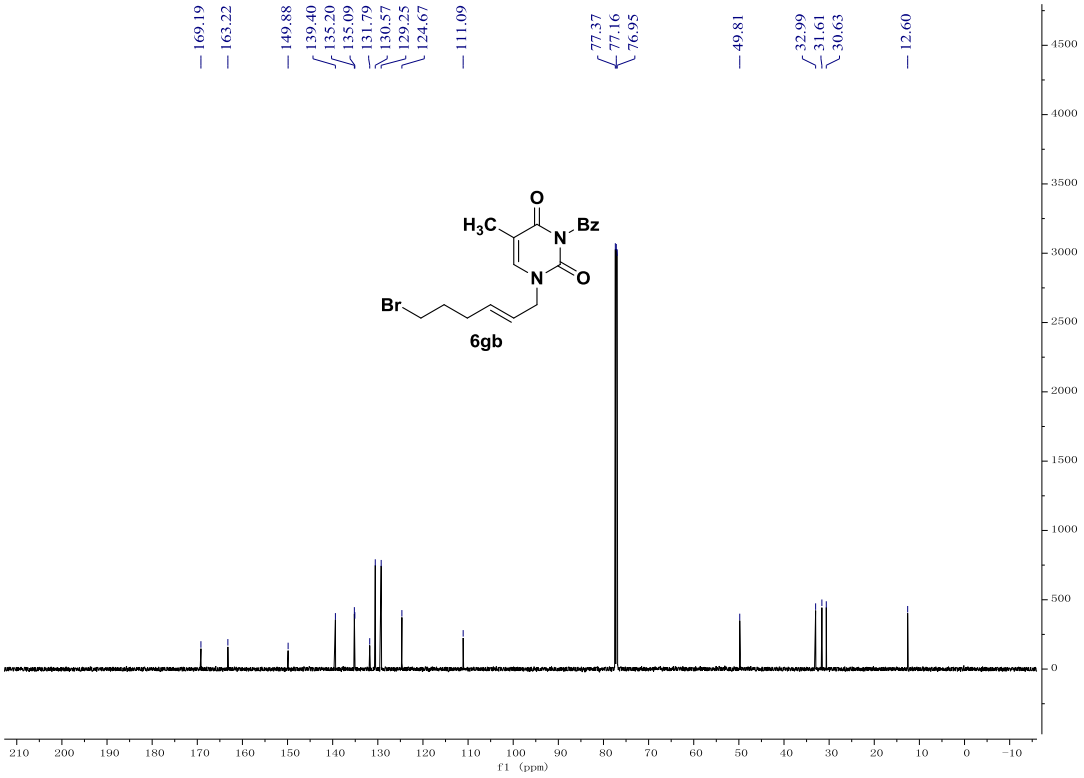
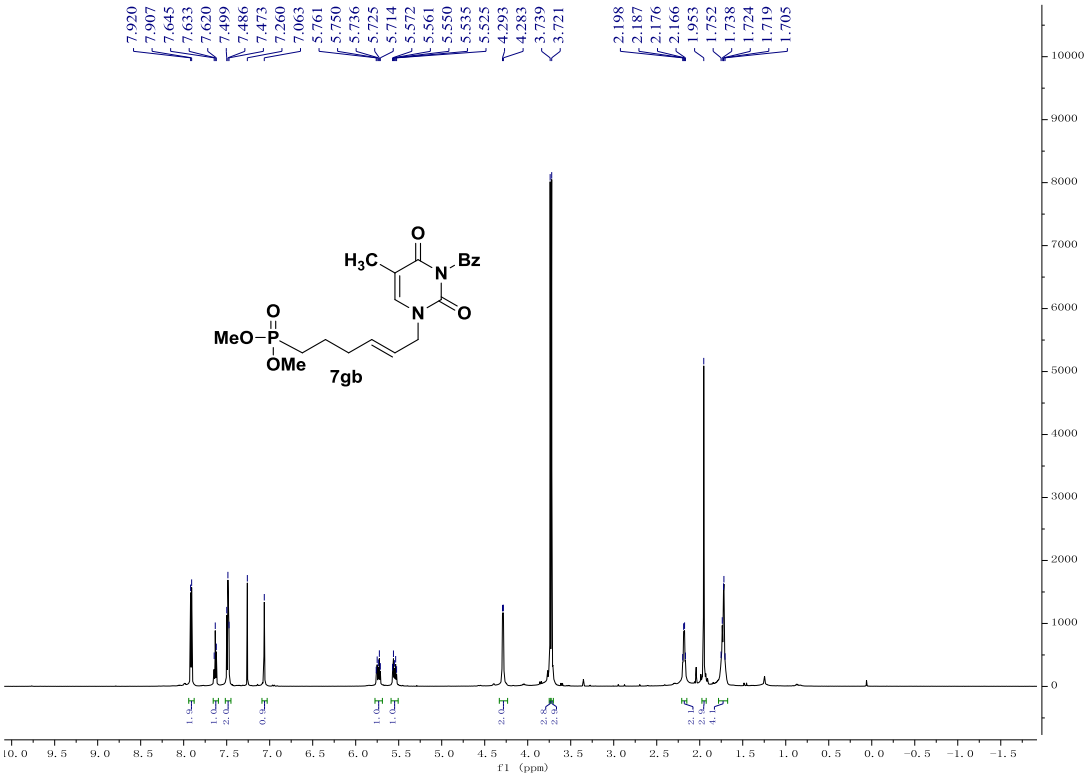


^{1}H NMR of 7gb



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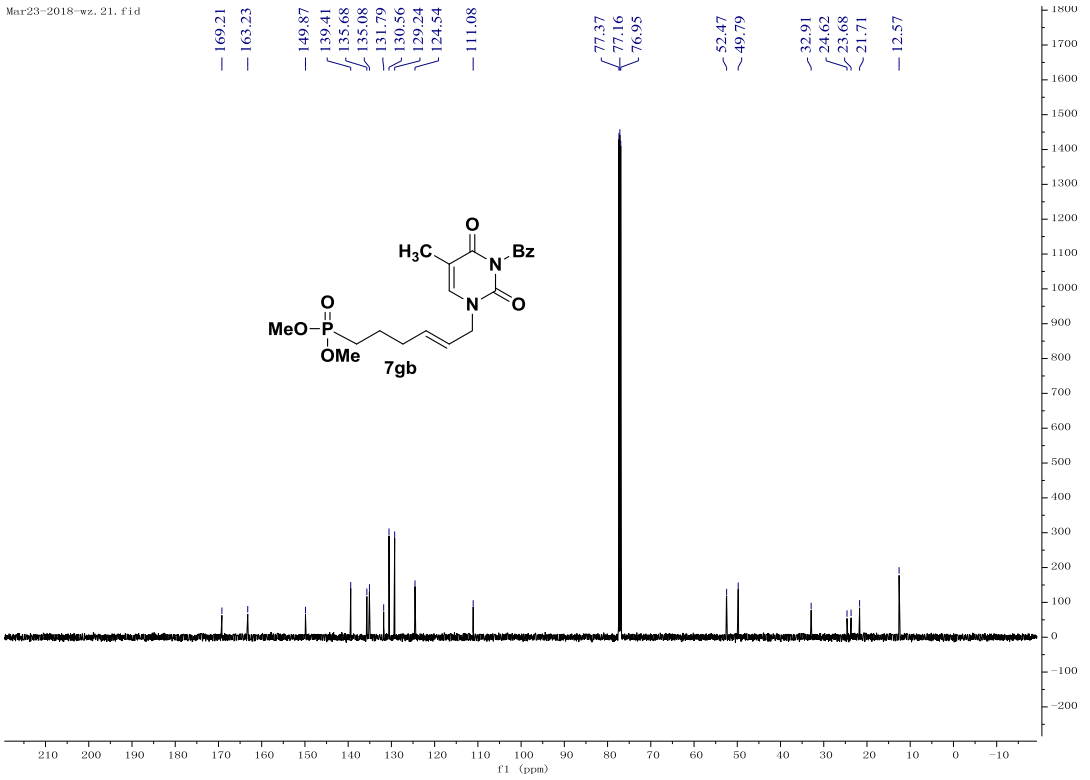

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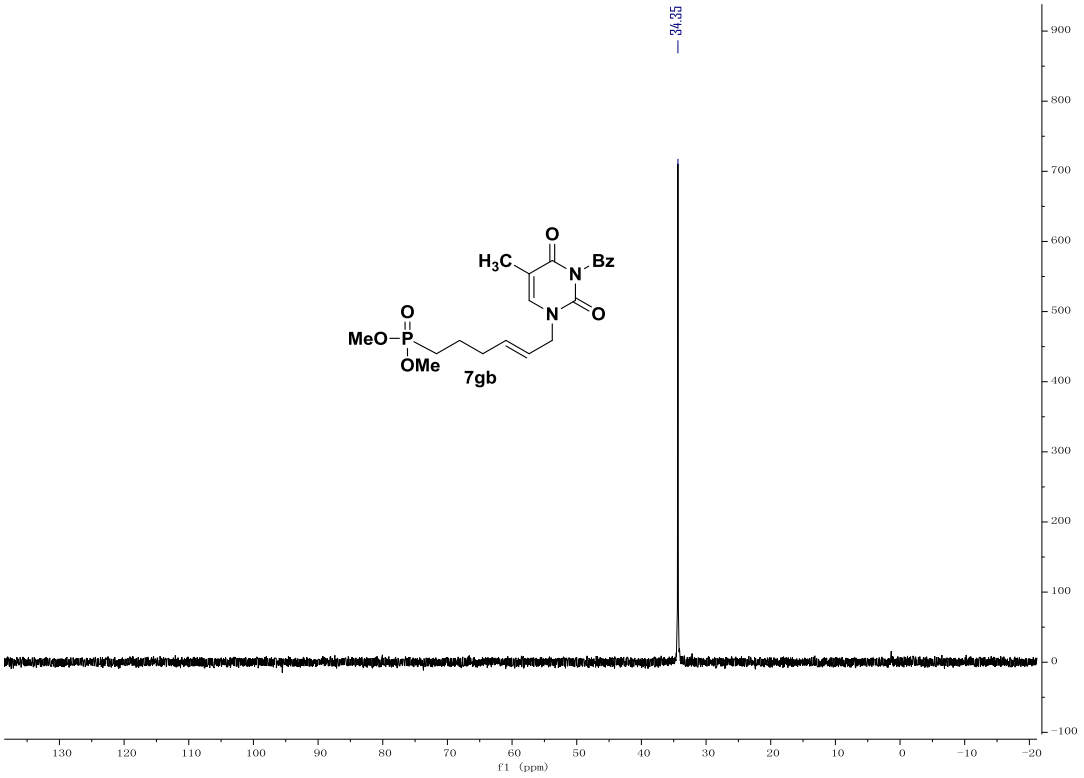
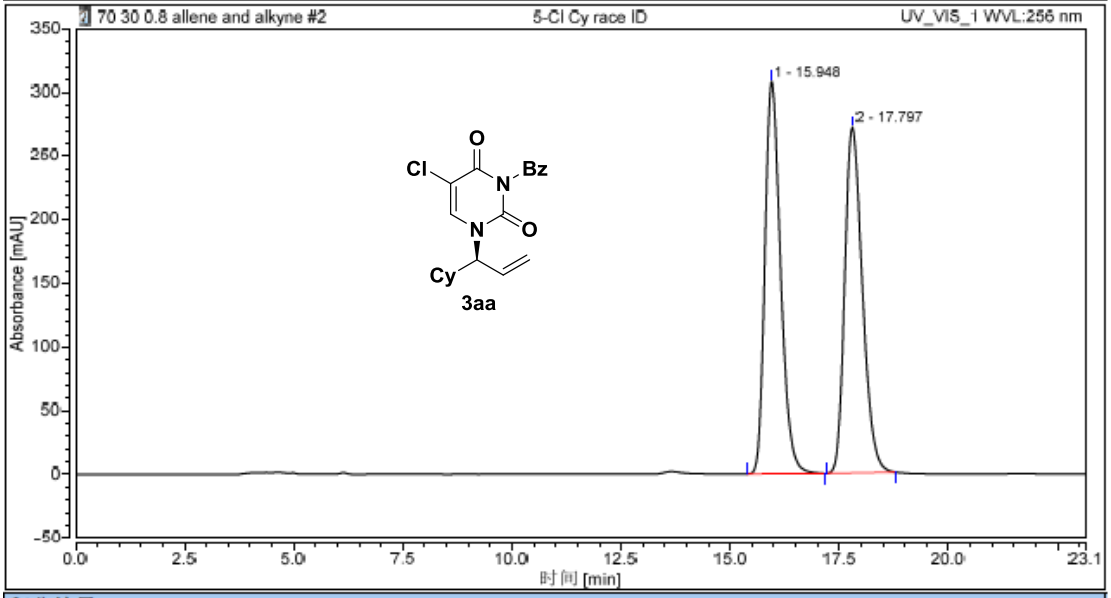


9. Copies of HPLC spectra for racemic and chiral compounds

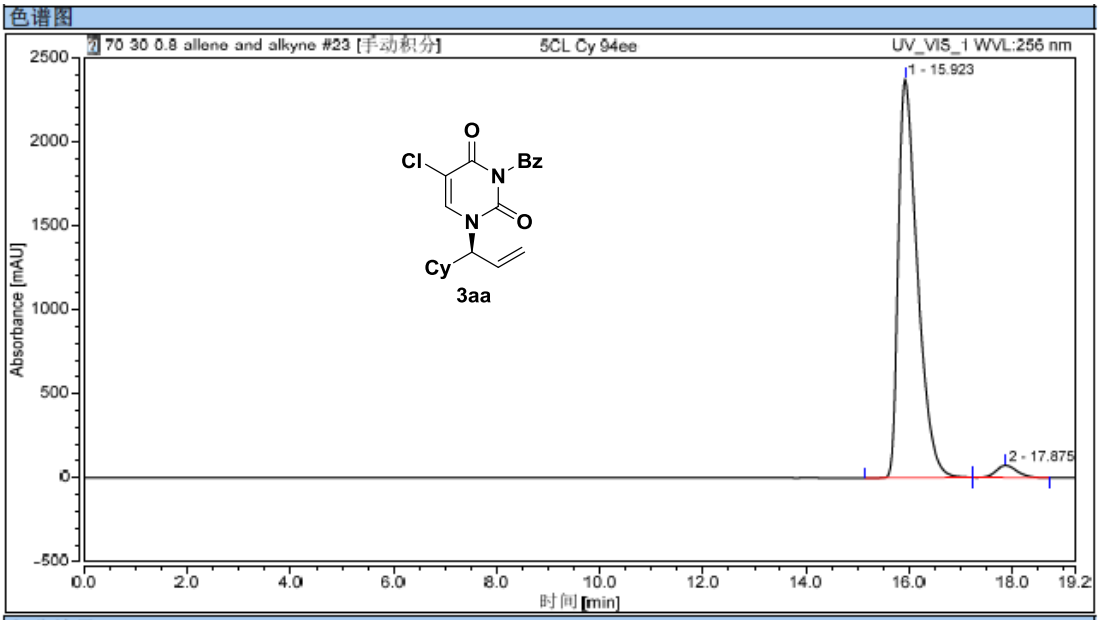
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		15.948	128.346	308.120	50.20	53.14	n.a.
2		17.797	127.342	271.741	49.80	46.86	n.a.
总和:			**255.688**	**579.861**	**100.00**	**100.00**	

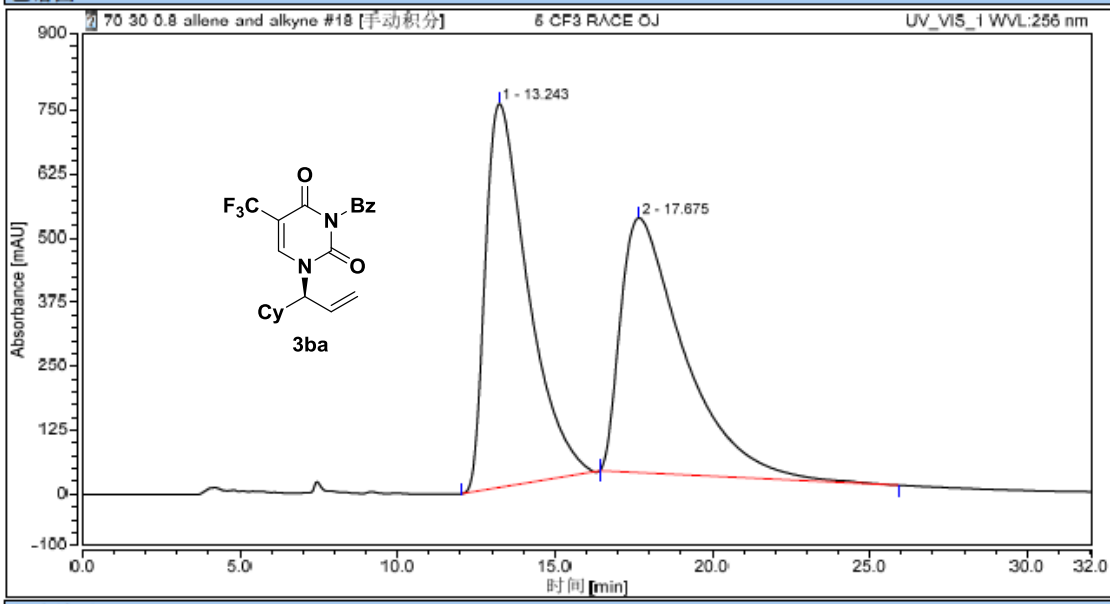
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		15.923	1019.501	2373.064	96.82	97.06	n.a.
2		17.875	33.523	71.976	3.18	2.94	n.a.
总和:			**1053.024**	**2445.039**	**100.00**	**100.00**	

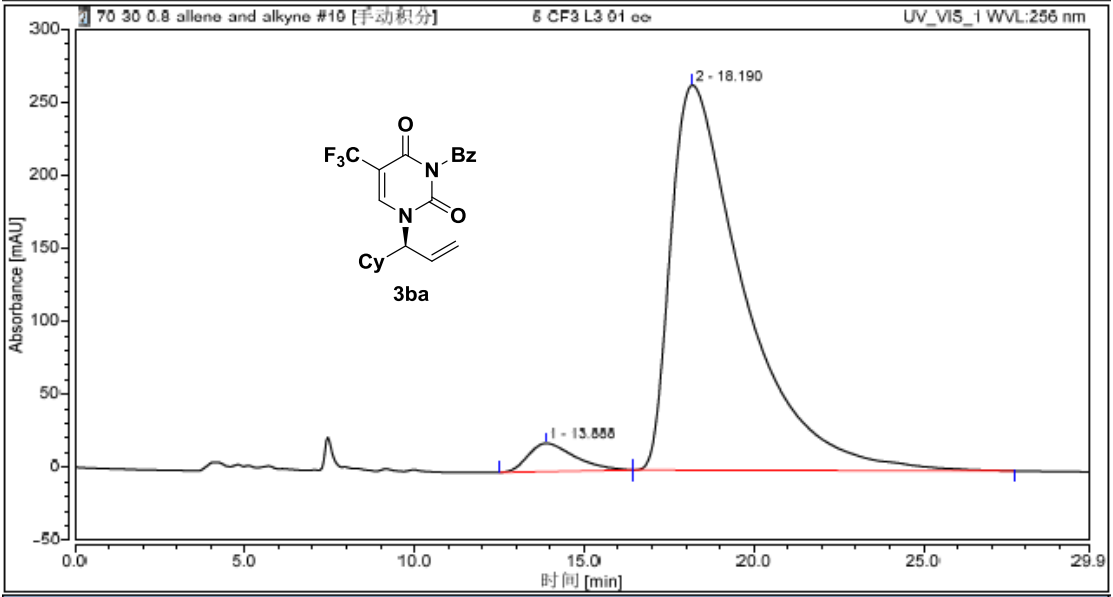
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		13.243	1169.189	748.960	50.15	60.12	n.a.
2		17.675	1162.224	496.884	49.85	39.88	n.a.
总和:			**2331.413**	**1245.843**	**100.00**	**100.00**	

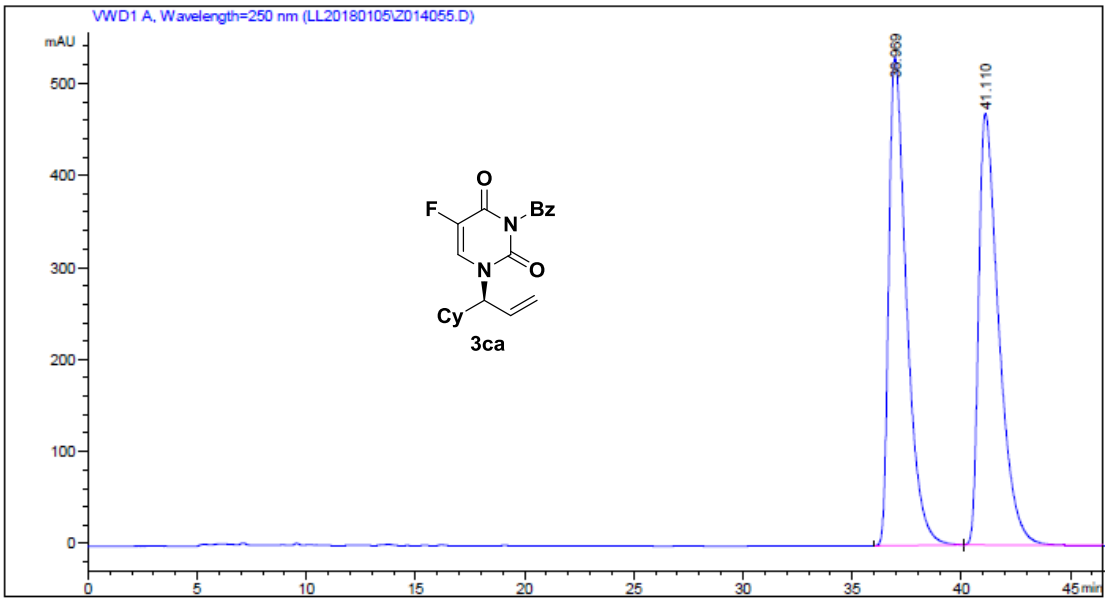
色谱图



积分结果

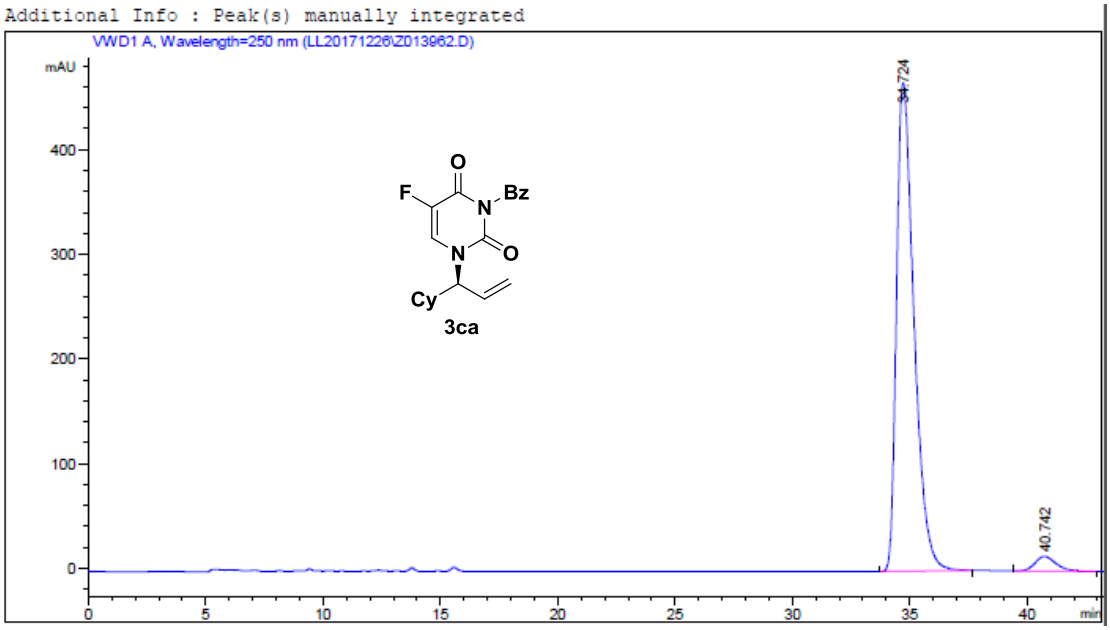
Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		13.888	30.522	19.321	4.43	6.83	n.a.
2		18.190	658.293	263.721	95.57	93.17	n.a.
总和:			**688.815**	**283.041**	**100.00**	**100.00**	

Additional Info : Peak(s) manually integrated



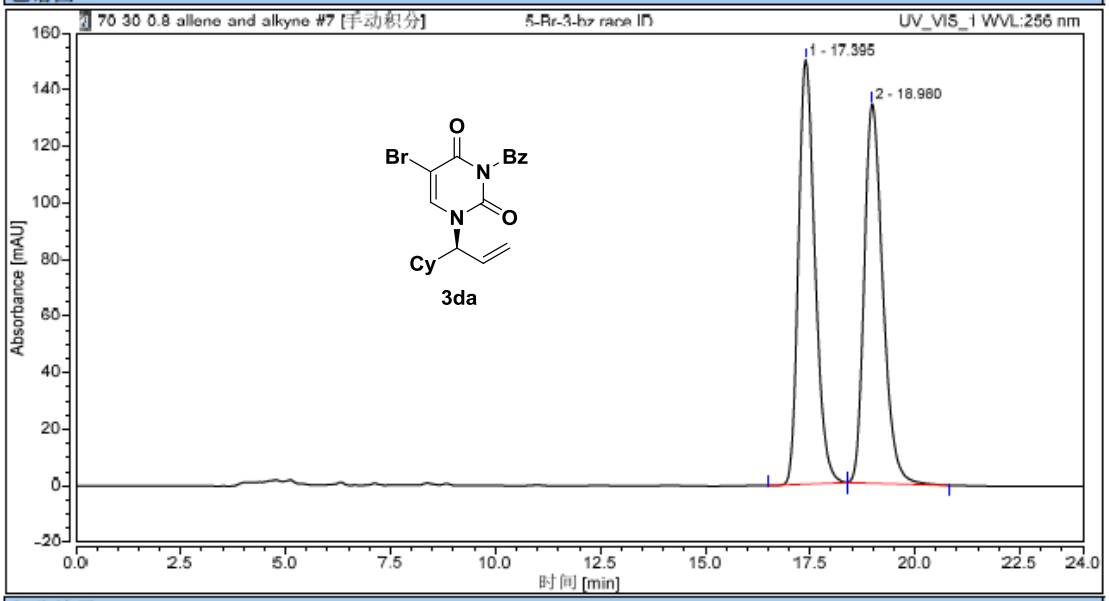
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.969	BB	0.8429	2.98614e4	530.60913	49.9262
2	41.110	BBA	0.9436	2.99497e4	468.63690	50.0738

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.724	BB	0.7891	2.40720e4	467.05893	96.5144
2	40.742	BB	0.9198	869.34460	13.93976	3.4856

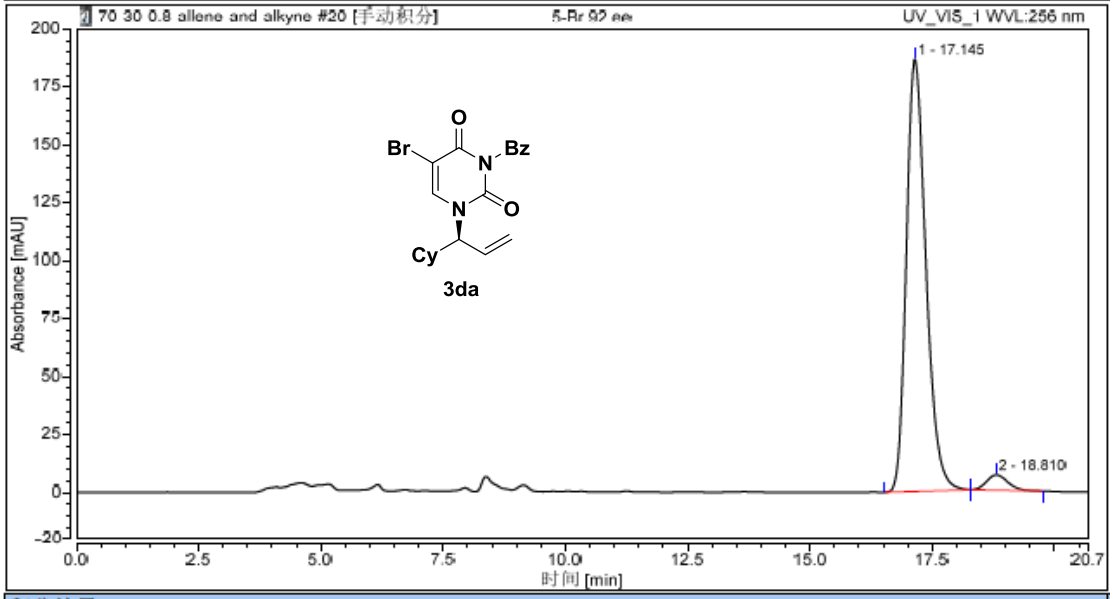
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		17.395	68.354	150.234	49.80	52.77	n.a.
2		18.980	68.899	134.437	50.20	47.23	n.a.
总和:			**137.253**	**284.671**	**100.00**	**100.00**	

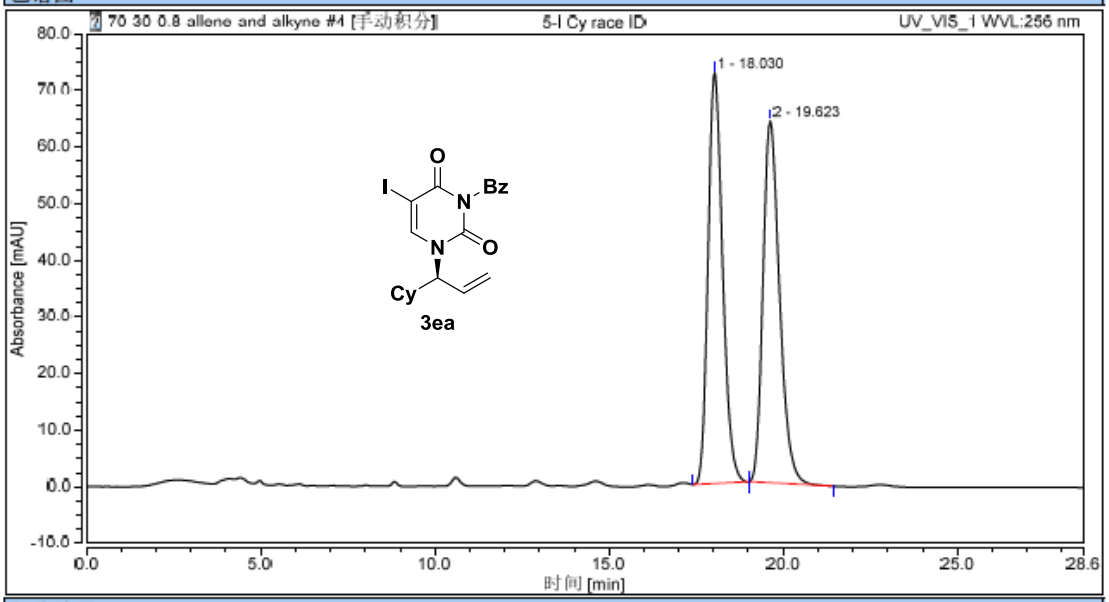
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		17.145	86.411	186.441	96.30	96.57	n.a.
2		18.810	3.317	6.618	3.70	3.43	n.a.
总和:			**89.728**	**193.059**	**100.00**	**100.00**	

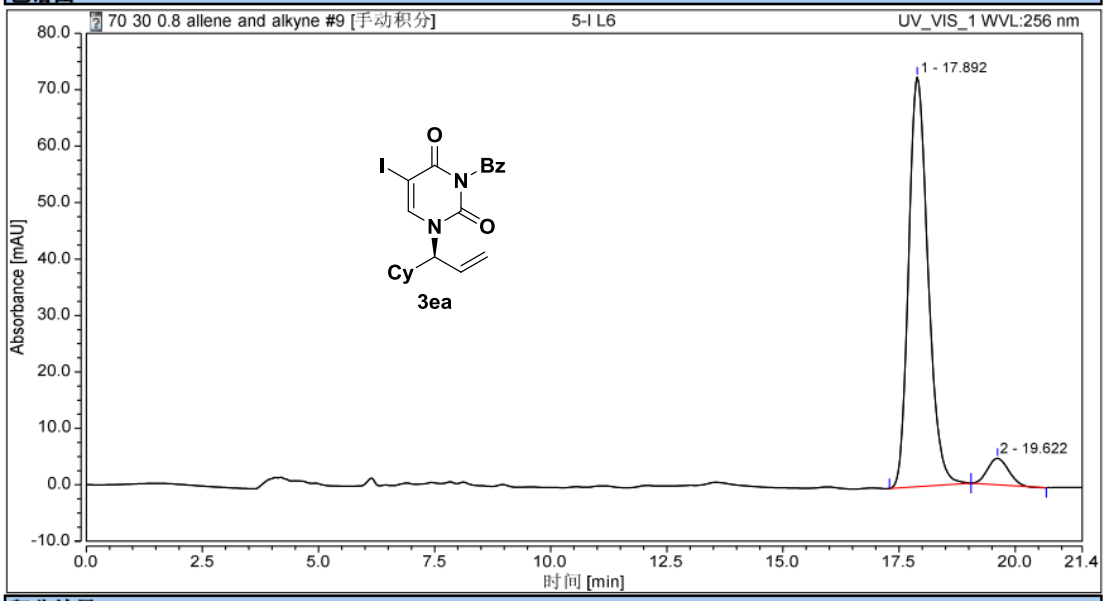
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.030	34.946	72.629	49.80	53.17	n.a.
2		19.623	35.227	63.959	50.20	46.83	n.a.
总和:			**70.174**	**136.588**	**100.00**	**100.00**	

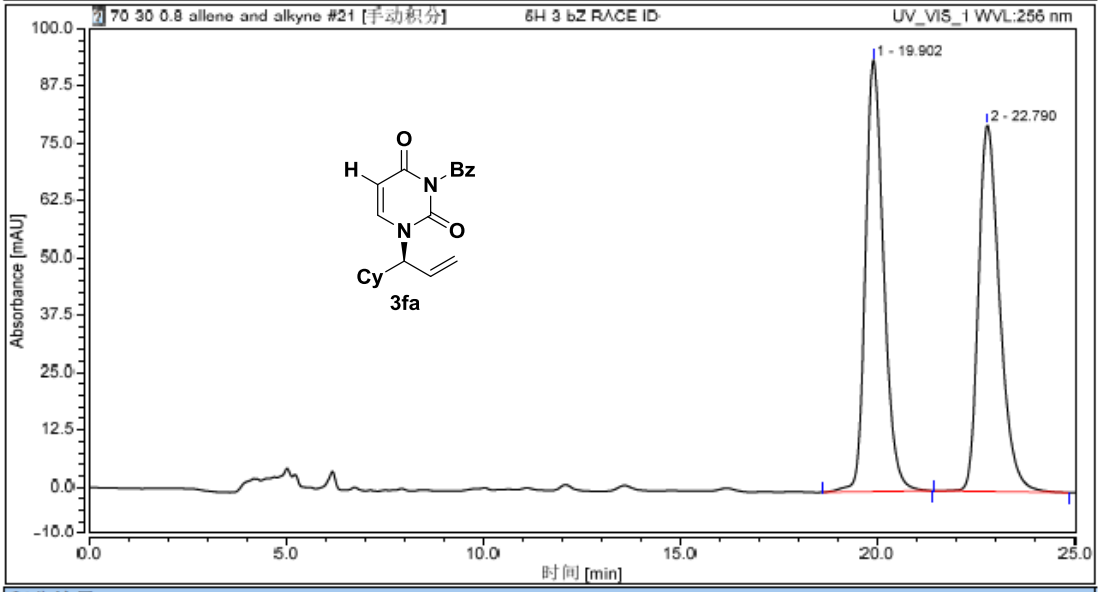
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		17.892	35.140	72.600	93.57	93.95	n.a.
2		19.622	2.415	4.672	6.43	6.05	n.a.
总和:			**37.555**	**77.273**	**100.00**	**100.00**	

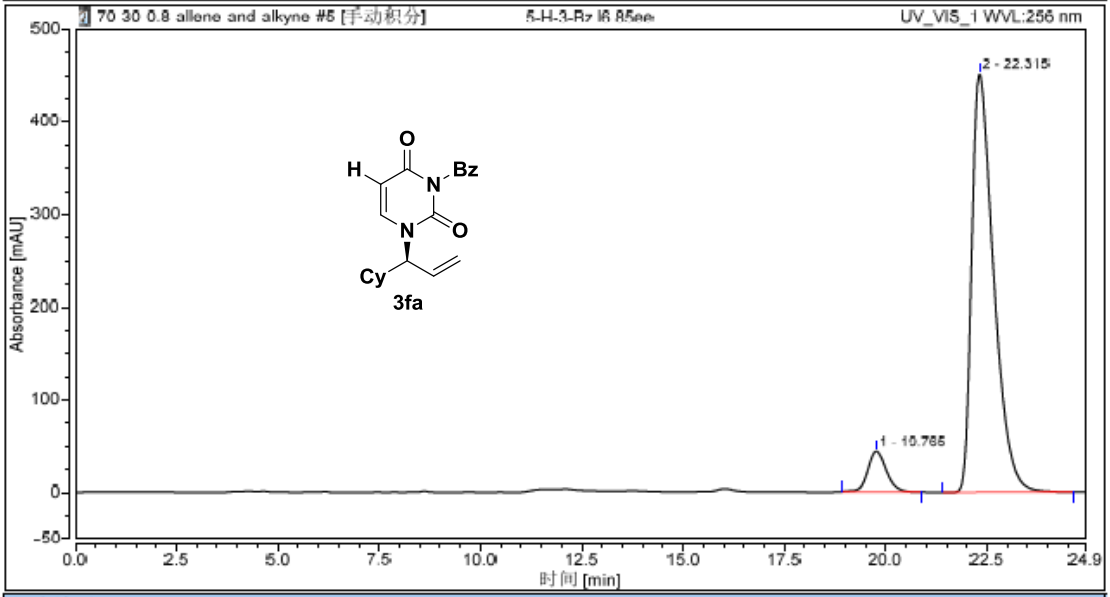
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		19.902	50.503	94.124	50.24	54.07	n.a.
2		22.790	50.022	79.952	49.76	45.93	n.a.
总和:			**100.525**	**174.076**	**100.00**	**100.00**	

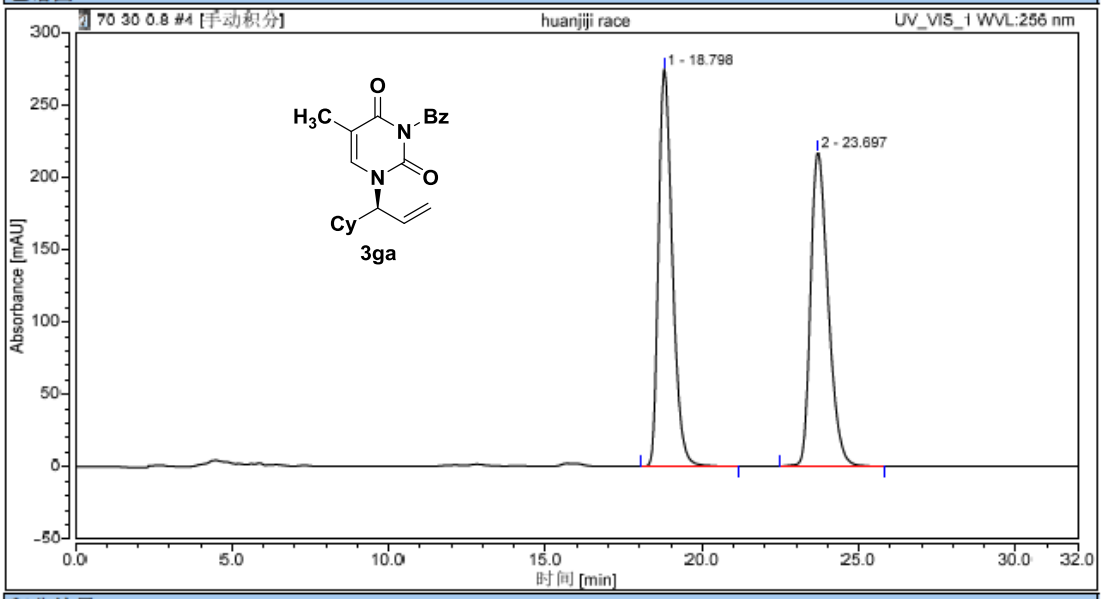
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		19.765	23.353	43.870	7.63	8.86	n.a.
2		22.315	282.812	451.494	92.37	91.14	n.a.
总和:			**306.165**	**495.364**	**100.00**	**100.00**	

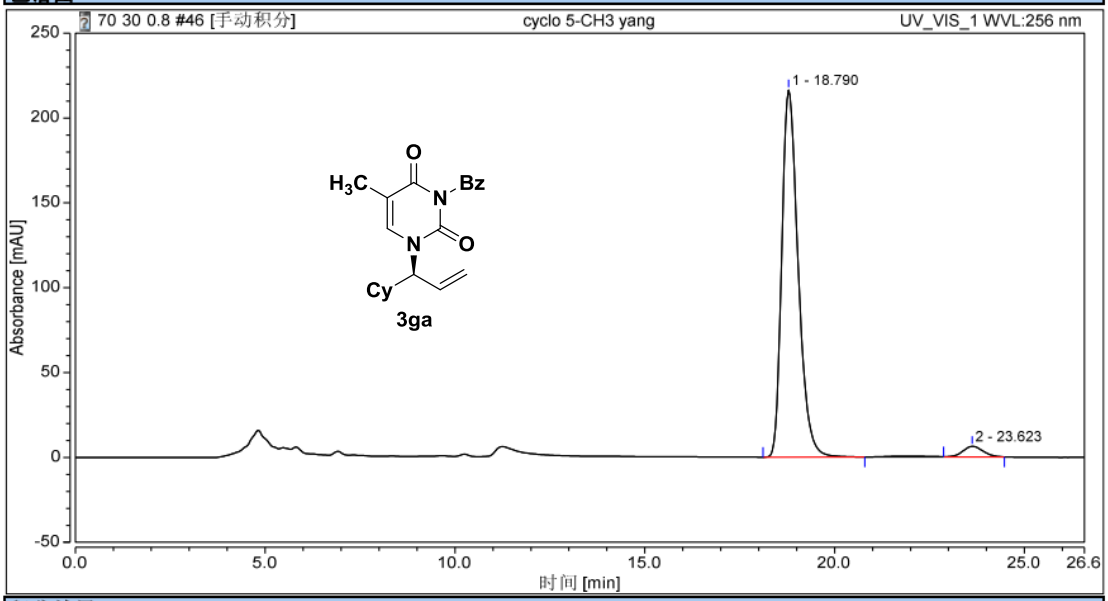
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.798	140.220	274.322	49.96	55.83	n.a.
2		23.697	140.469	216.991	50.04	44.17	n.a.
总和:			**280.689**	**491.312**	**100.00**	**100.00**	

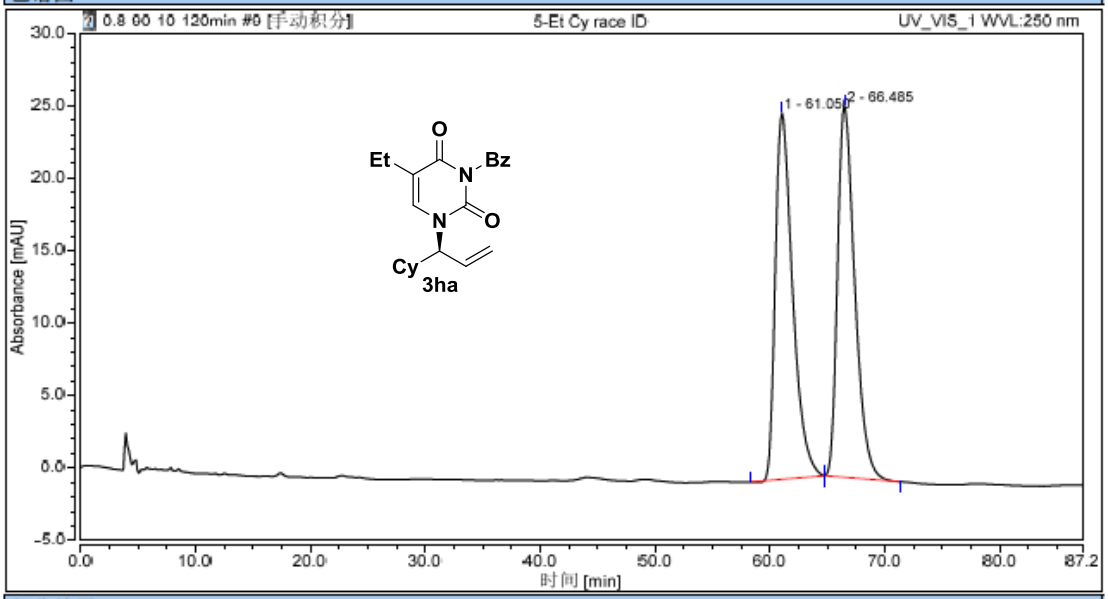
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.790	108.026	216.488	96.56	97.20	n.a.
2		23.623	3.852	6.226	3.44	2.80	n.a.
总和:			**111.878**	**222.714**	**100.00**	**100.00**	

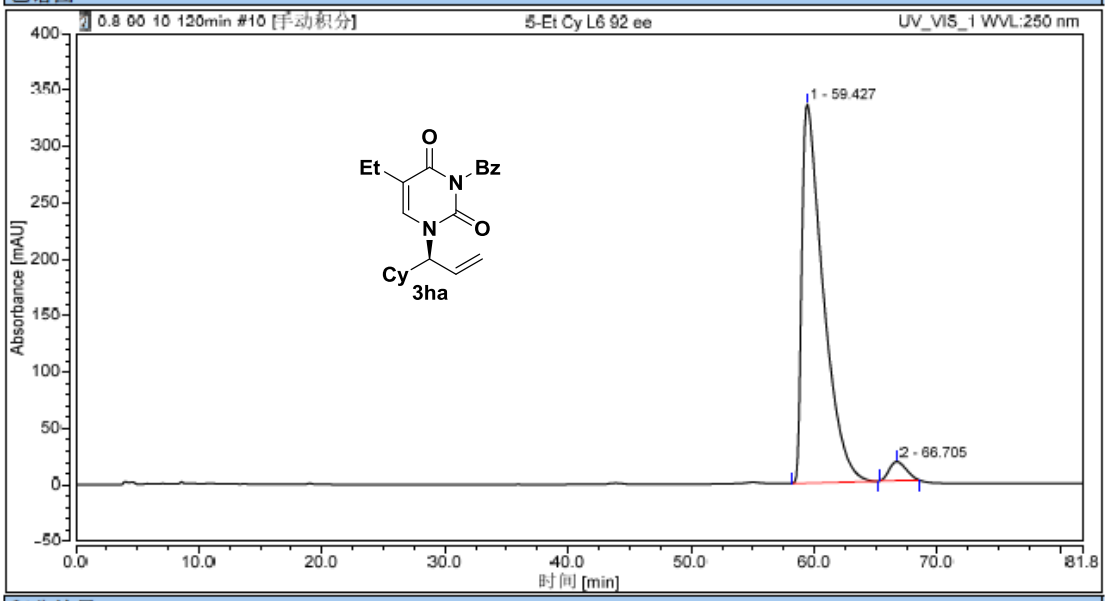
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		61.050	44.073	25.281	49.78	49.67	n.a.
2		66.485	44.467	25.622	50.22	50.33	n.a.
总和:			**88.540**	**50.903**	**100.00**	**100.00**	

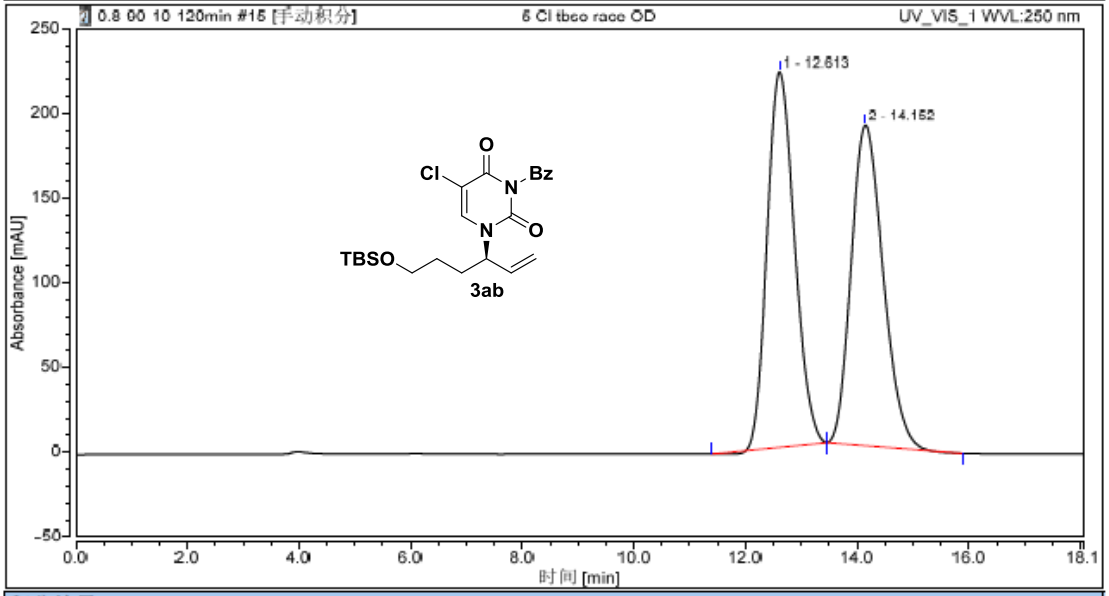
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		59.427	672.778	336.399	96.14	95.23	n.a.
2		66.705	27.040	16.832	3.86	4.77	n.a.
总和:			**699.818**	**353.231**	**100.00**	**100.00**	

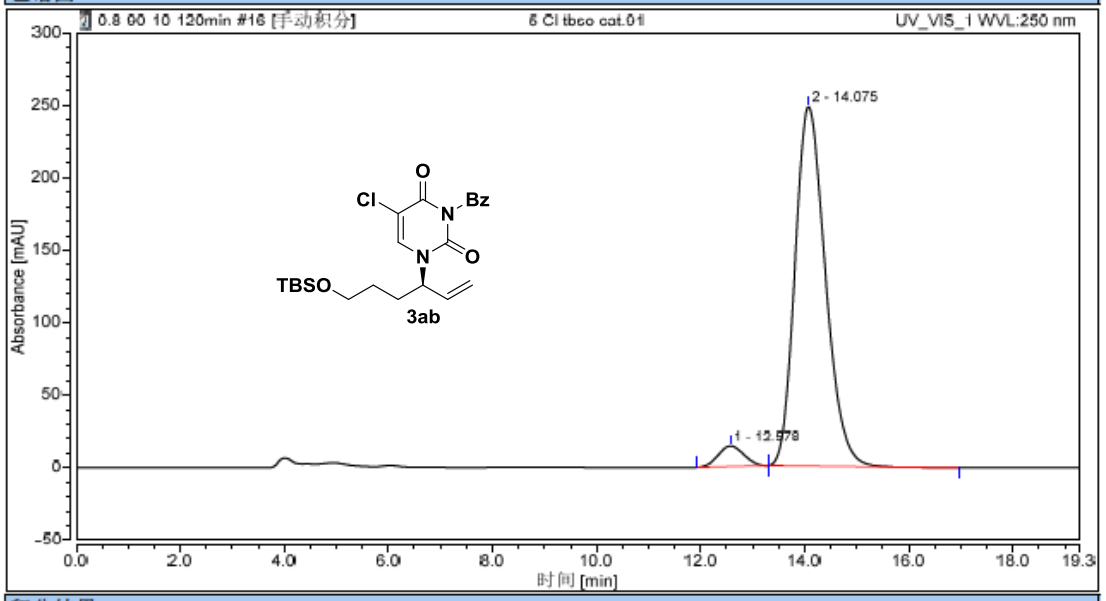
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		12.613	125.352	221.684	50.01	53.95	n.a.
2		14.152	125.279	189.226	49.99	46.05	n.a.
总和:			**250.632**	**410.910**	**100.00**	**100.00**	

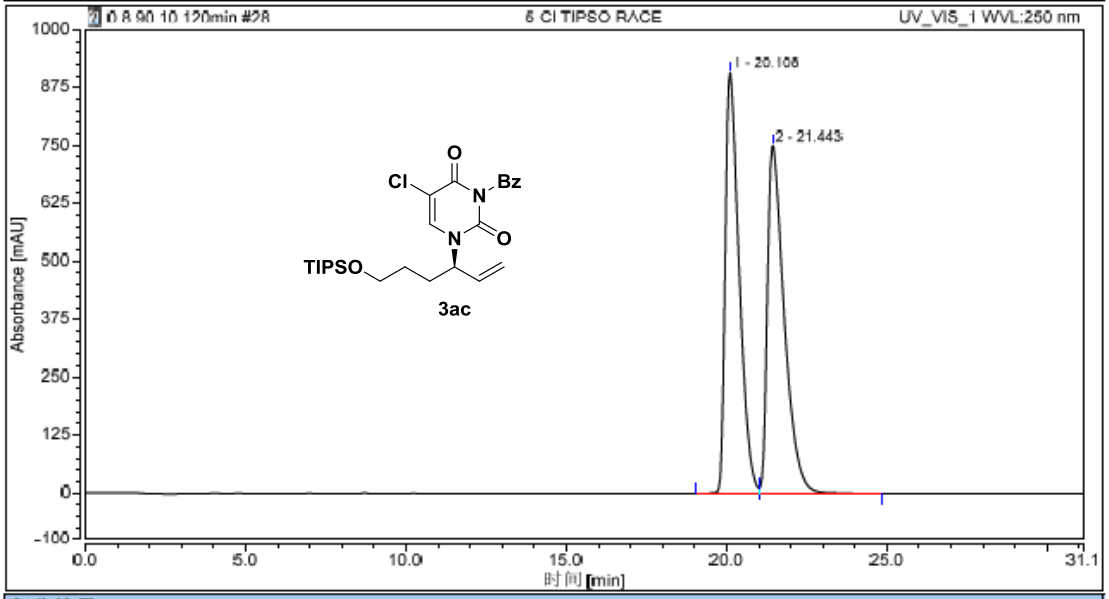
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		12.578	8.045	14.186	4.58	5.41	n.a.
2		14.075	167.741	248.133	95.42	94.59	n.a.
总和:			**175.787**	**262.319**	**100.00**	**100.00**	

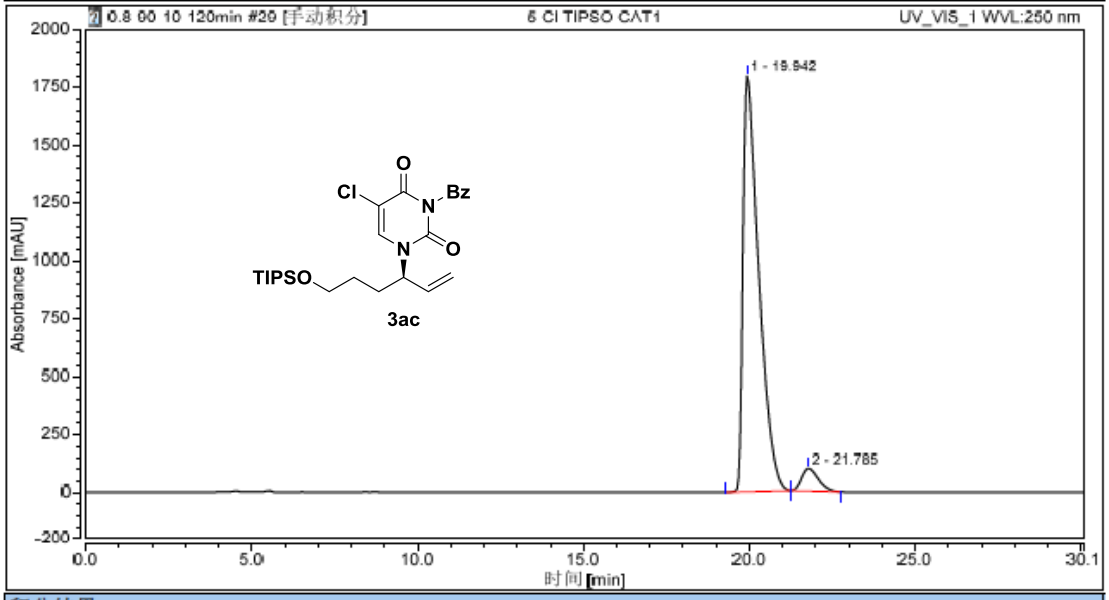
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		20.108	456.873	908.865	49.93	54.75	n.a.
2		21.443	458.135	751.059	50.07	45.25	n.a.
总和:			**915.008**	**1659.924**	**100.00**	**100.00**	

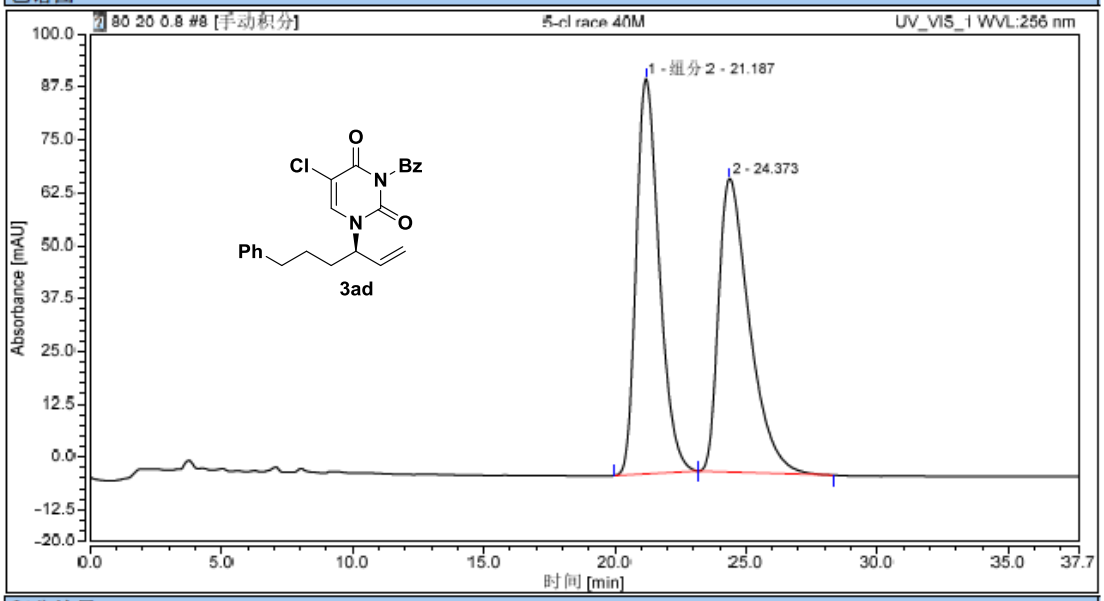
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		19.942	994.617	1796.683	94.58	94.86	n.a.
2		21.785	56.987	97.319	5.42	5.14	n.a.
总和:			**1051.604**	**1894.001**	**100.00**	**100.00**	

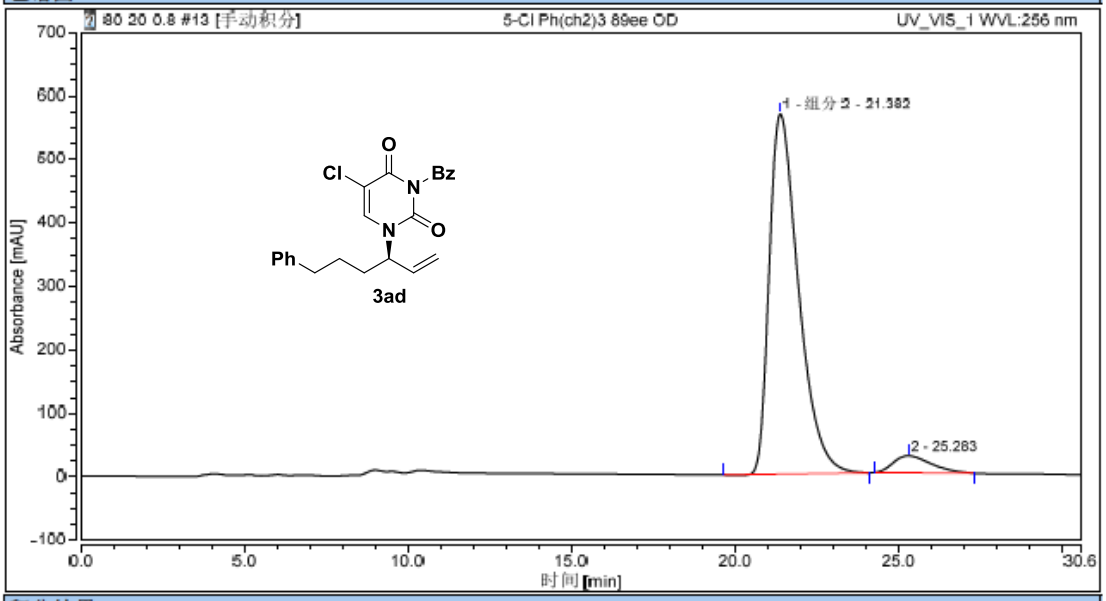
色谱图



积分结果

序号	Name	Rettime min	Area mAU*min	Height mAU	Area %	Height %	样品量
n.a.	组分 1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	组分 2	21.187	94.943	93.531	50.12	57.39	n.a.
2		24.373	94.503	69.453	49.88	42.61	n.a.
总和:			**189.447**	**162.985**	**100.00**	**100.00**	

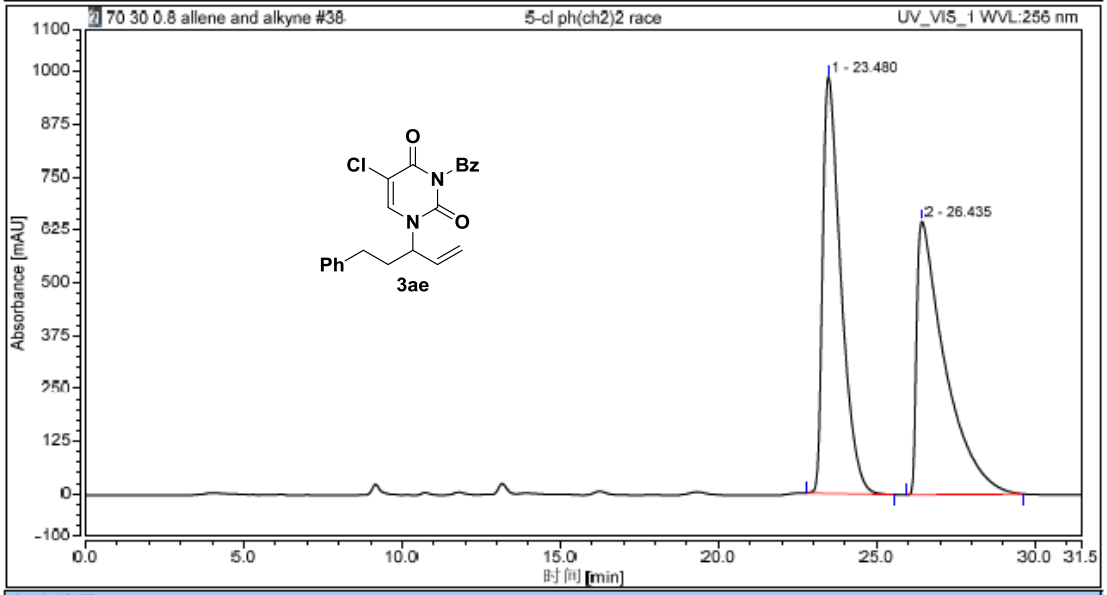
色谱图



积分结果

序号	Name	Rettime min	Area mAU*min	Height mAU	Area %	Height %	样品量
n.a.	组分 1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	组分 2	21.382	587.446	567.722	94.29	95.51	n.a.
2		25.283	35.578	26.709	5.71	4.49	n.a.
总和:			**623.024**	**594.431**	**100.00**	**100.00**	

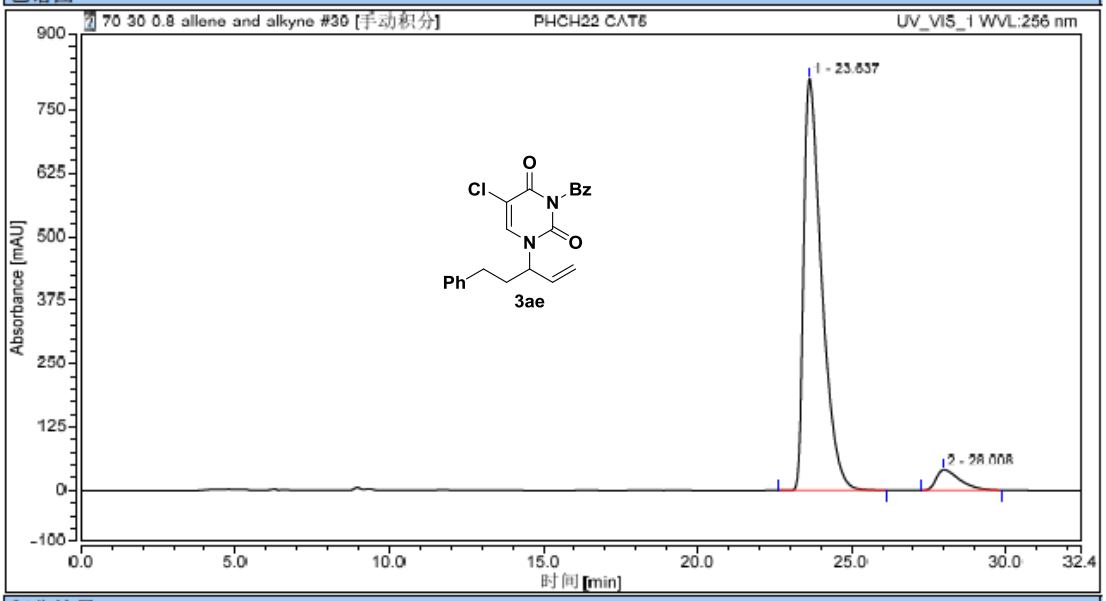
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		23.480	659.407	987.221	49.61	60.36	n.a.
2		26.435	669.673	648.269	50.39	39.64	n.a.
总和:			**1329.080**	**1635.490**	**100.00**	**100.00**	

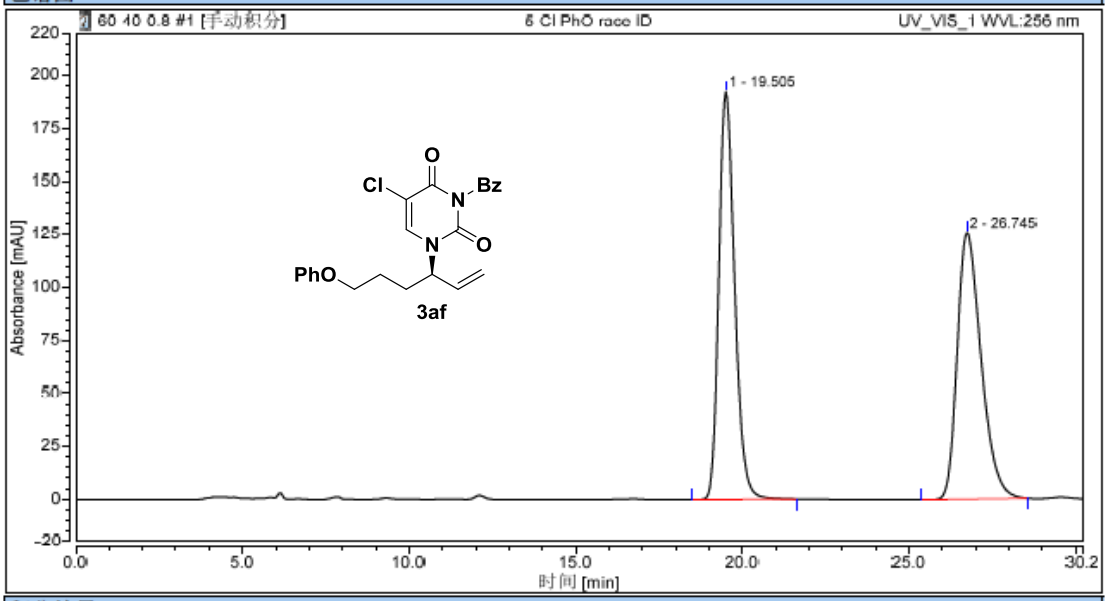
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		23.637	548.819	812.180	93.81	95.23	n.a.
2		28.008	36.210	40.703	6.19	4.77	n.a.
总和:			**585.029**	**852.883**	**100.00**	**100.00**	

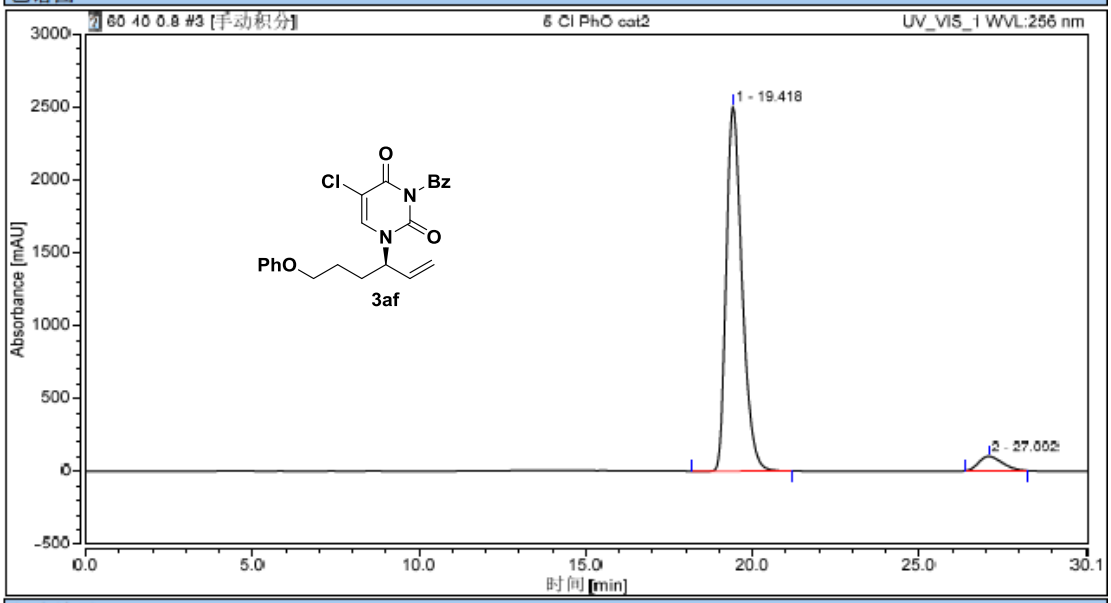
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		19.505	105.812	192.632	50.34	60.49	n.a.
2		26.745	104.366	125.812	49.66	39.51	n.a.
总和:			**210.178**	**318.444**	**100.00**	**100.00**	

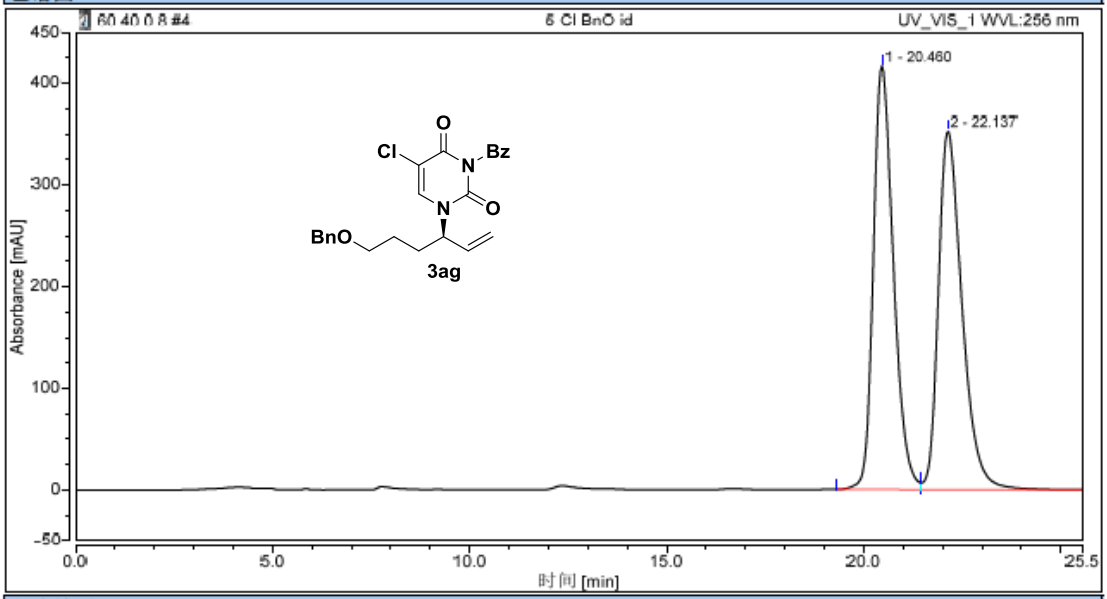
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		19.418	1374.523	2504.292	94.43	96.19	n.a.
2		27.092	81.061	99.218	5.57	3.81	n.a.
总和:			**1455.584**	**2603.510**	**100.00**	**100.00**	

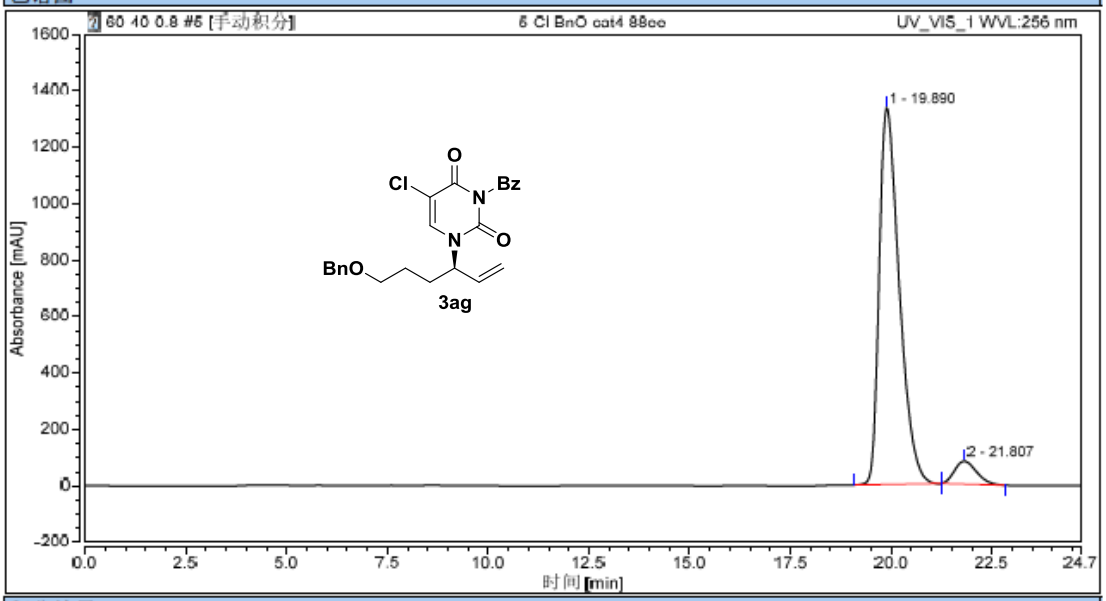
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		20.460	246.051	416.820	50.07	54.16	n.a.
2		22.137	245.352	352.729	49.93	45.84	n.a.
总和:			**491.403**	**769.548**	**100.00**	**100.00**	

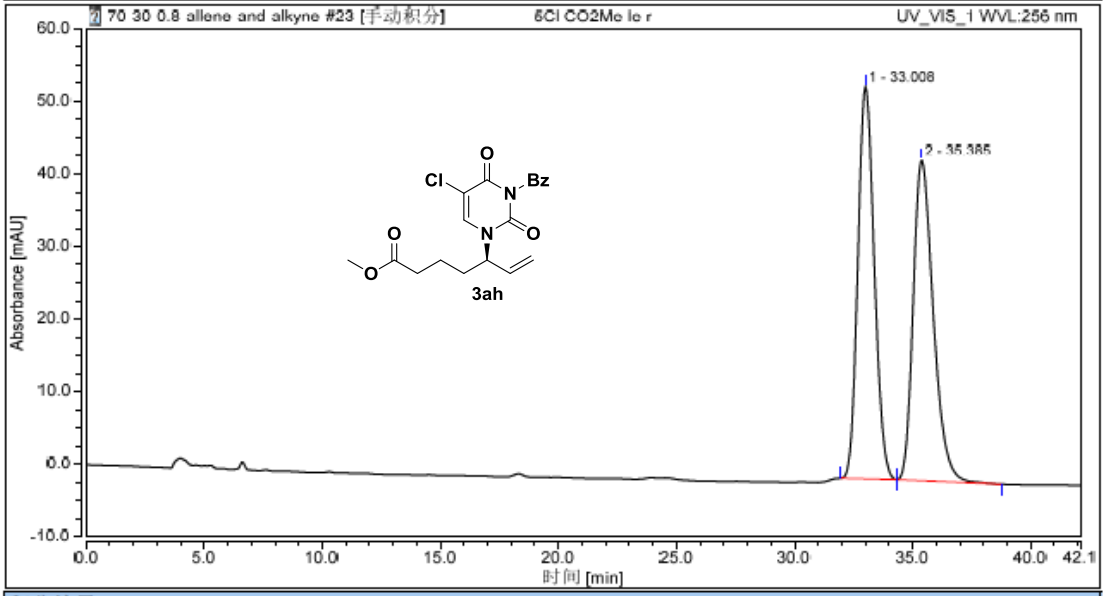
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		19.890	769.401	1336.778	93.75	94.28	n.a.
2		21.807	51.333	81.142	6.25	5.72	n.a.
总和:			**820.734**	**1417.920**	**100.00**	**100.00**	

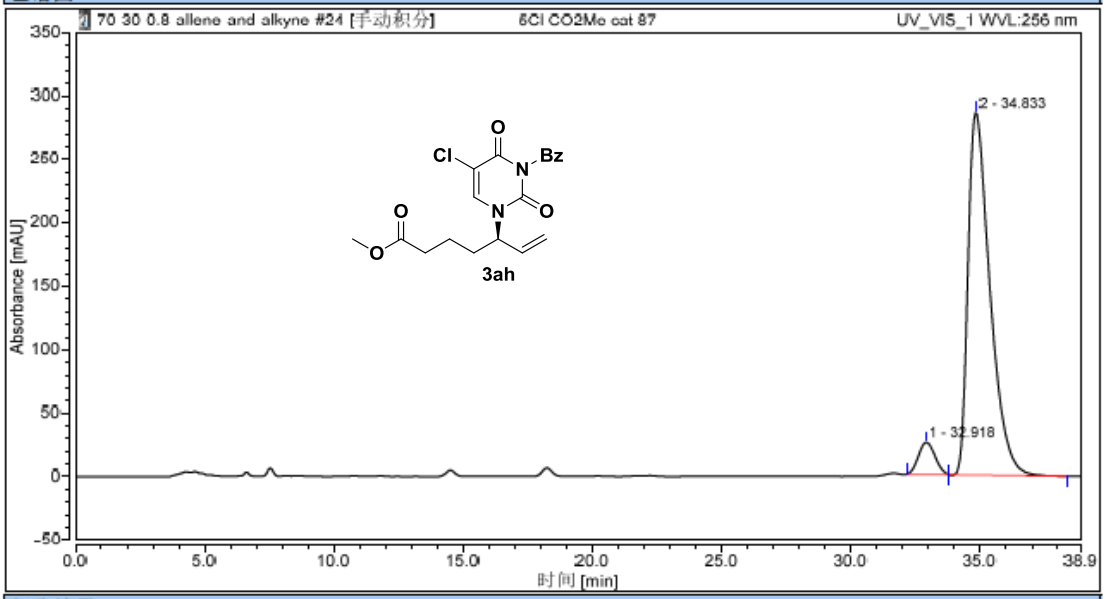
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		33.008	43.456	54.101	49.95	55.03	n.a.
2		35.385	43.538	44.205	50.05	44.97	n.a.
总和:			**86.994**	**98.306**	**100.00**	**100.00**	

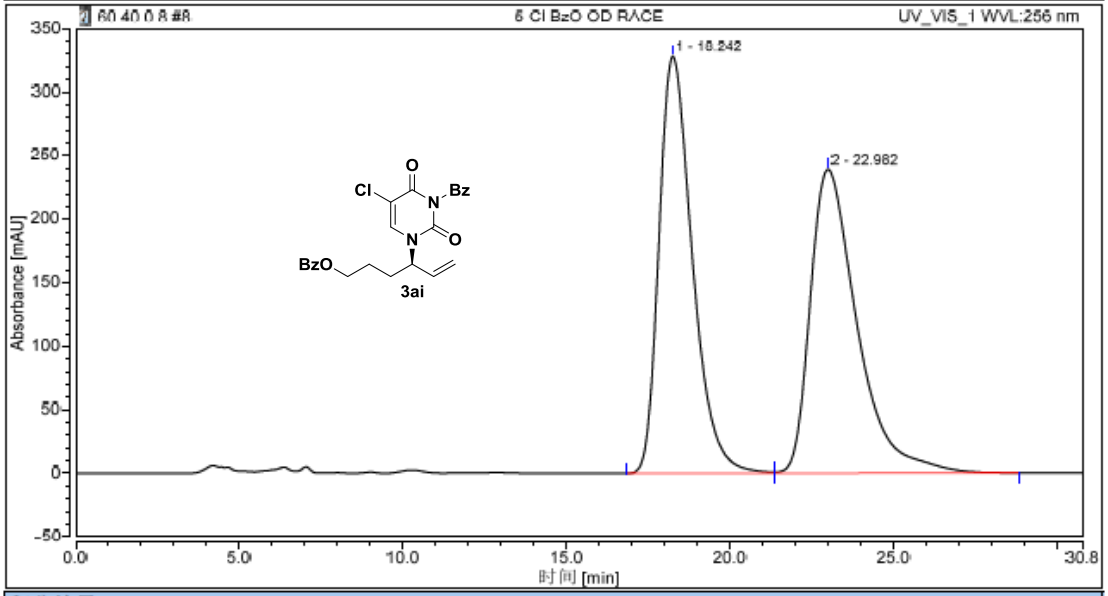
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		32.918	18.850	25.393	6.30	8.16	n.a.
2		34.833	280.554	285.896	93.70	91.84	n.a.
总和:			**299.404**	**311.289**	**100.00**	**100.00**	

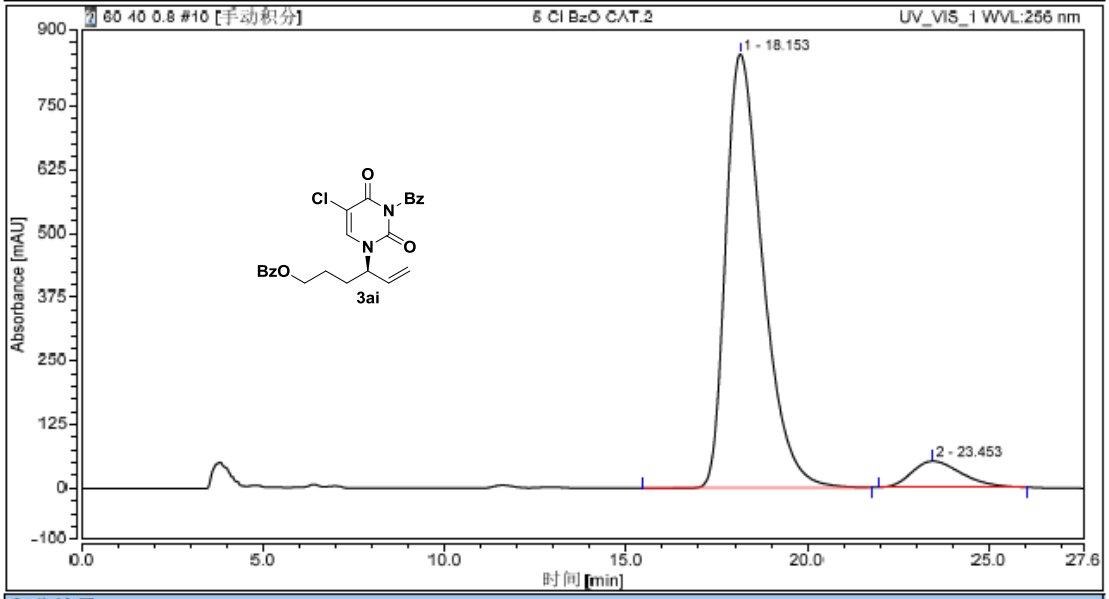
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.242	388.410	328.576	49.52	57.87	n.a.
2		22.982	395.964	239.159	50.48	42.13	n.a.
总和:			**784.373**	**567.734**	**100.00**	**100.00**	

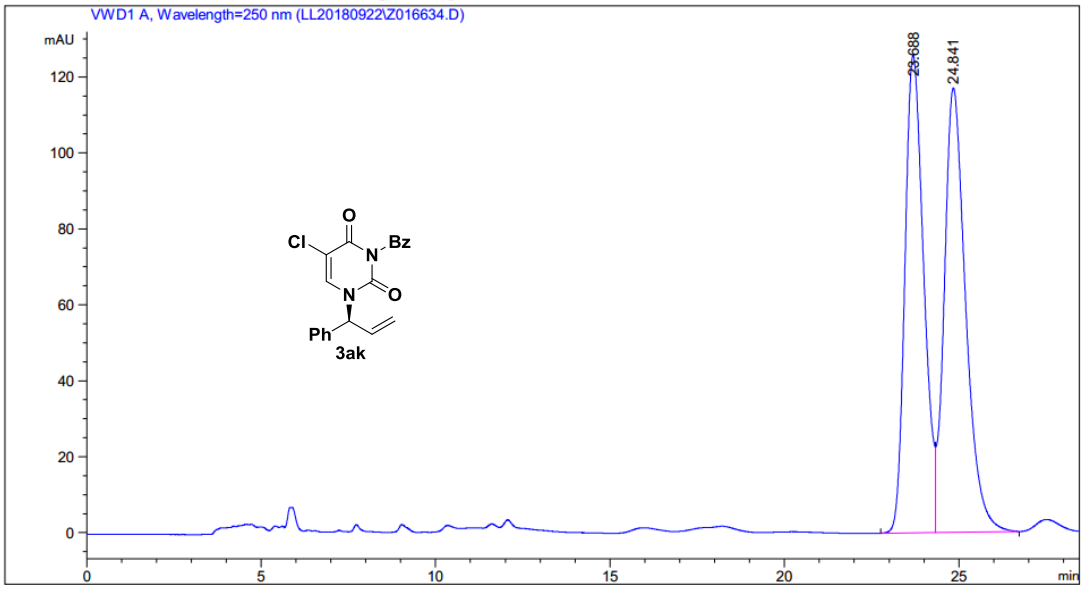
色谱图



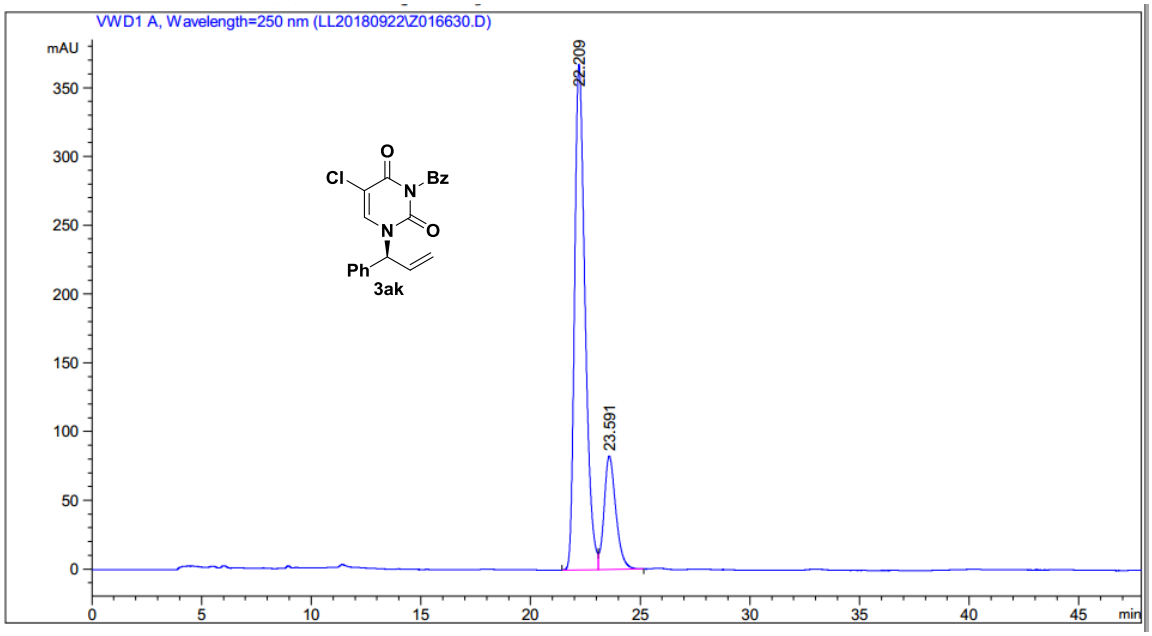
积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.153	1001.567	850.892	92.47	94.30	n.a.
2		23.453	81.587	51.420	7.53	5.70	n.a.
总和:			**1083.154**	**902.313**	**100.00**	**100.00**	

Additional Info : Peak(s) manually integrated

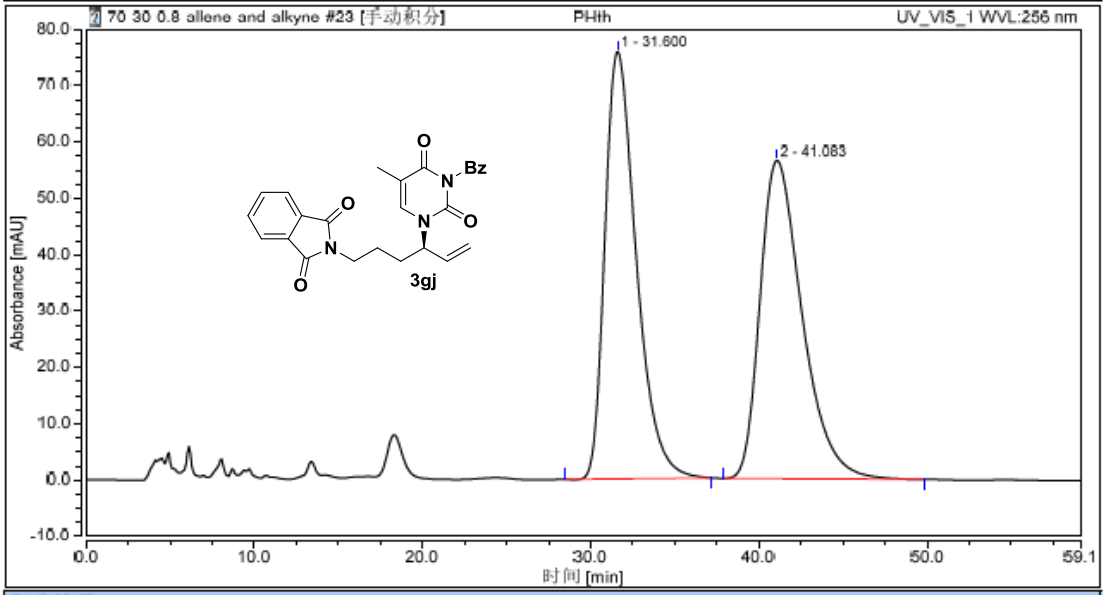


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.333	BV	0.5831	6117.58398	161.52724	49.7677
2	25.976	VB	0.6344	6174.68457	147.38928	50.2323



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.209	BV	0.5087	1.22111e4	367.32230	79.8664
2	23.591	VB	0.5634	3078.30762	82.51152	20.1336

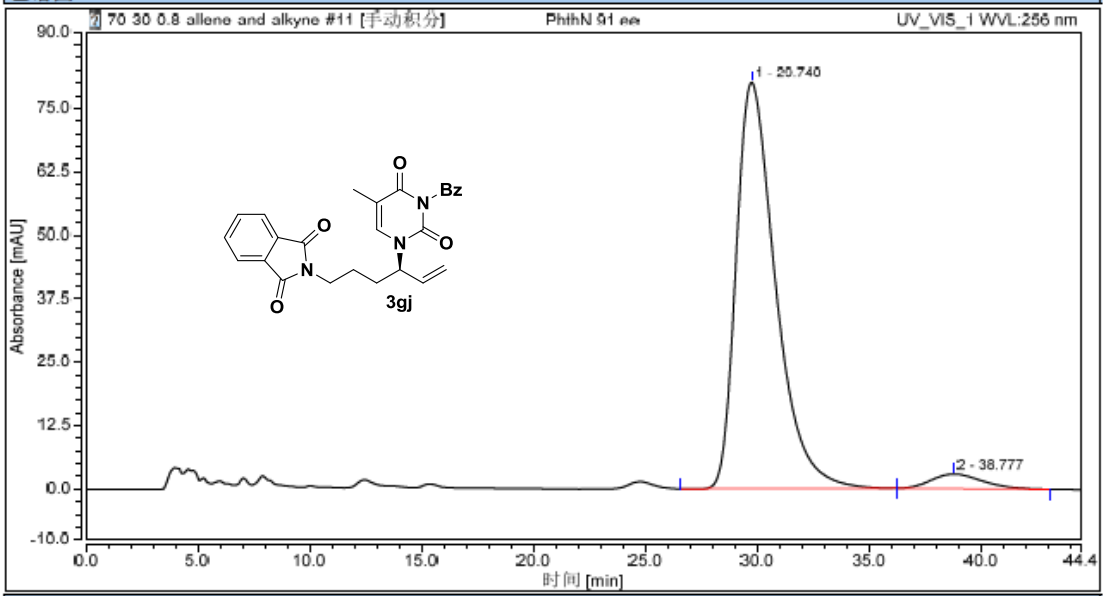
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		31.600	163.921	75.903	50.03	57.32	n.a.
2		41.083	163.742	56.526	49.97	42.68	n.a.
总和:			**327.663**	**132.428**	**100.00**	**100.00**	

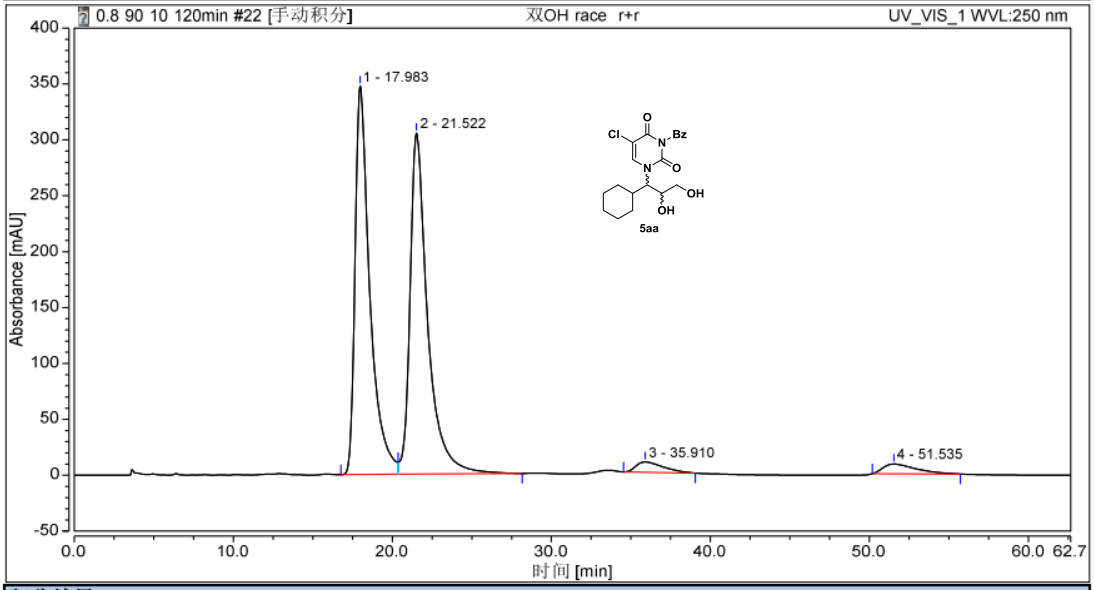
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		29.740	163.100	80.088	95.56	96.53	n.a.
2		38.777	7.587	2.876	4.44	3.47	n.a.
总和:			**170.687**	**82.964**	**100.00**	**100.00**	

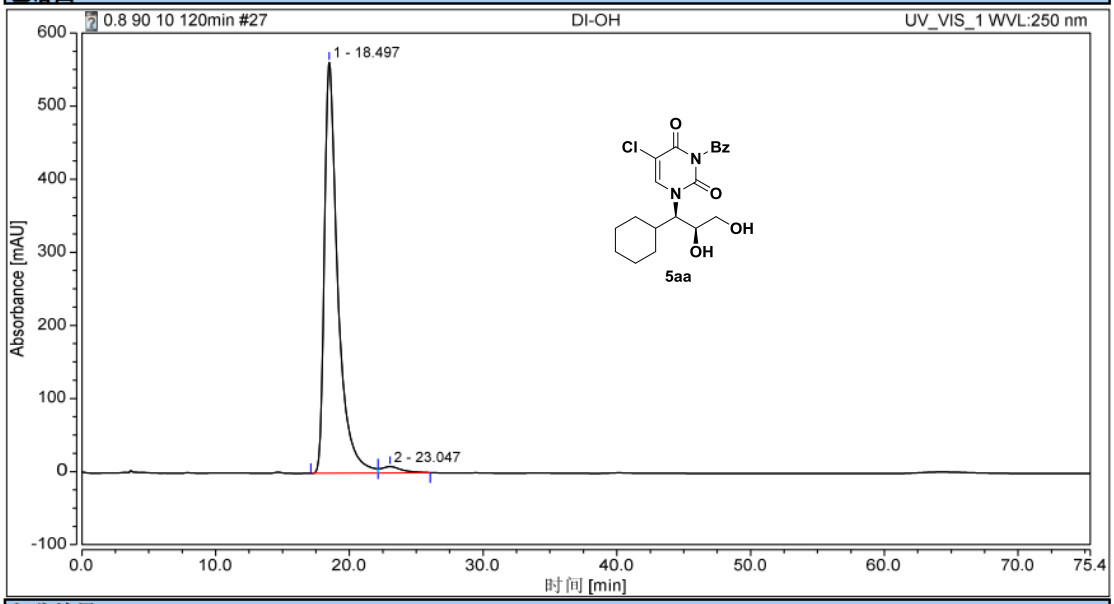
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		17.983	374.393	347.515	46.54	51.81	n.a.
2		21.522	390.453	305.175	48.54	45.50	n.a.
3		35.910	18.414	9.262	2.29	1.38	n.a.
4		51.535	21.158	8.808	2.63	1.31	n.a.
总和:			**804.418**	**670.759**	**100.00**	**100.00**	

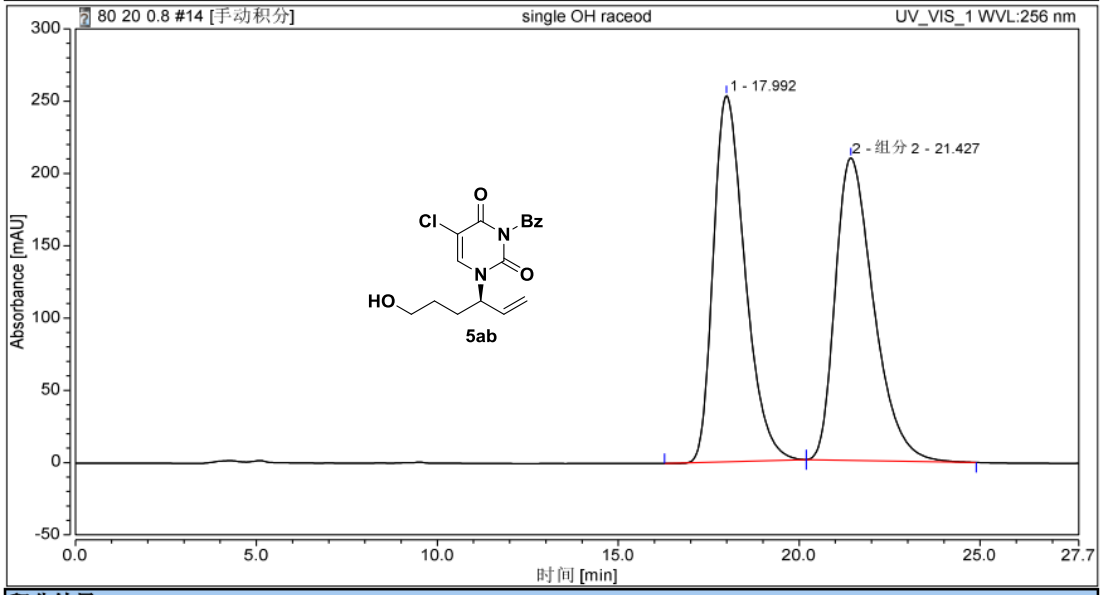
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.497	651.964	562.179	97.71	98.47	n.a.
2		23.047	15.307	8.744	2.29	1.53	n.a.
总和:			**667.270**	**570.922**	**100.00**	**100.00**	

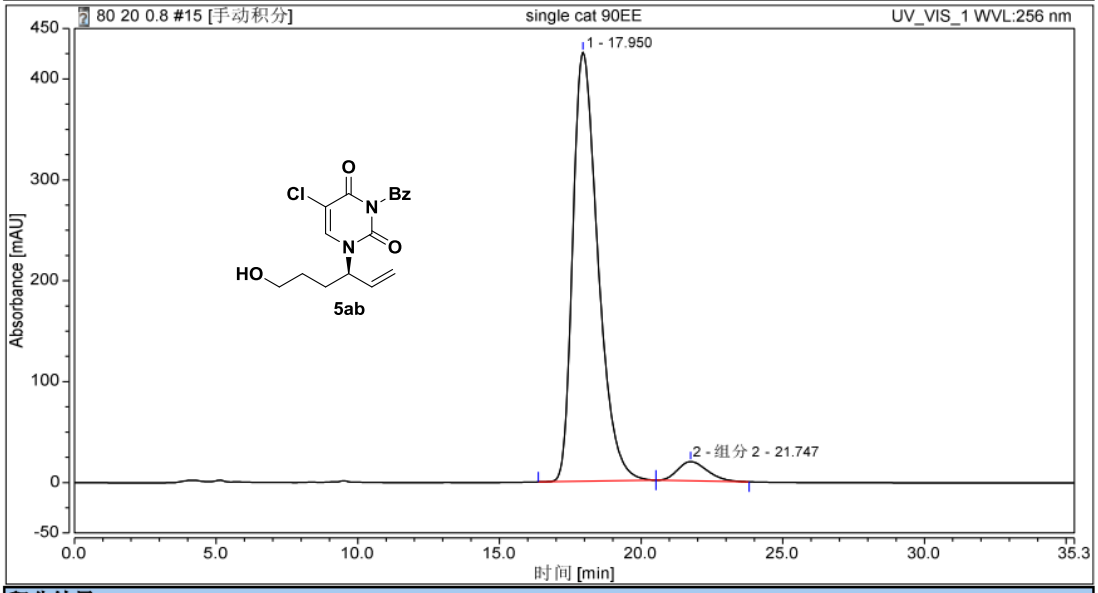
色谱图



积分结果

序号	Name	Rettime min	Area mAU*min	Height mAU	Area %	Height %	样品量
1		17.992	256.429	253.285	49.96	54.76	n.a.
n.a.	组分 1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	组分 2	21.427	256.841	209.216	50.04	45.24	n.a.
总和:			**513.270**	**462.501**	**100.00**	**100.00**	

色谱图



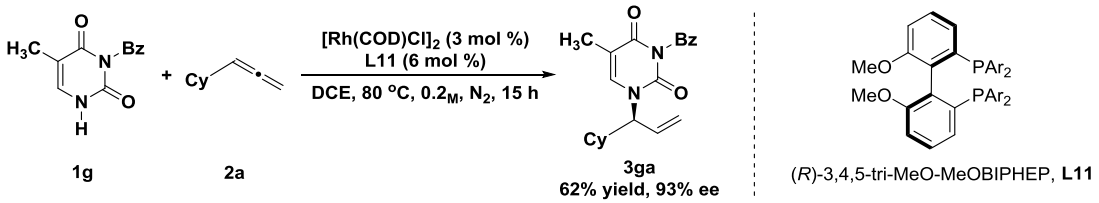
积分结果

序号	Name	Rettime min	Area mAU*min	Height mAU	Area %	Height %	样品量
1		17.950	437.704	425.271	94.98	95.73	n.a.
n.a.	组分 1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	组分 2	21.747	23.137	18.985	5.02	4.27	n.a.
总和:			**460.841**	**444.256**	**100.00**	**100.00**	

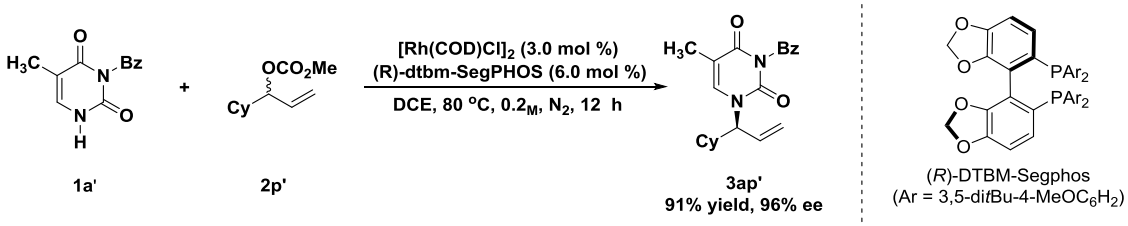
10. Determination of the absolute configuration of compound 3ga

The absolute configuration of **3ga** was assigned as ***S*** by comparison with our previous literture[2] data.

This work:



Previous report: (Lei Liang, Ming-Sheng Xie, Tao Qin, Man Zhu, Gui-Rong Qu, and Hai-Ming Guo, *Org. Lett.* **2017**, *19*, 5212) (In order to distinguish the compound numbers, **1a'**, **2p'** and **3ap'** were used)



1) By comparison the specific optical [α] values, the absolute configuration of **3ga** was determined to be (***S***) by comparison with literature data.

This work: 93% ee. $[\alpha]_D^{27}$ = -93.7° (*c* = 1.95 CH_2Cl_2). (this work, **3ga**)

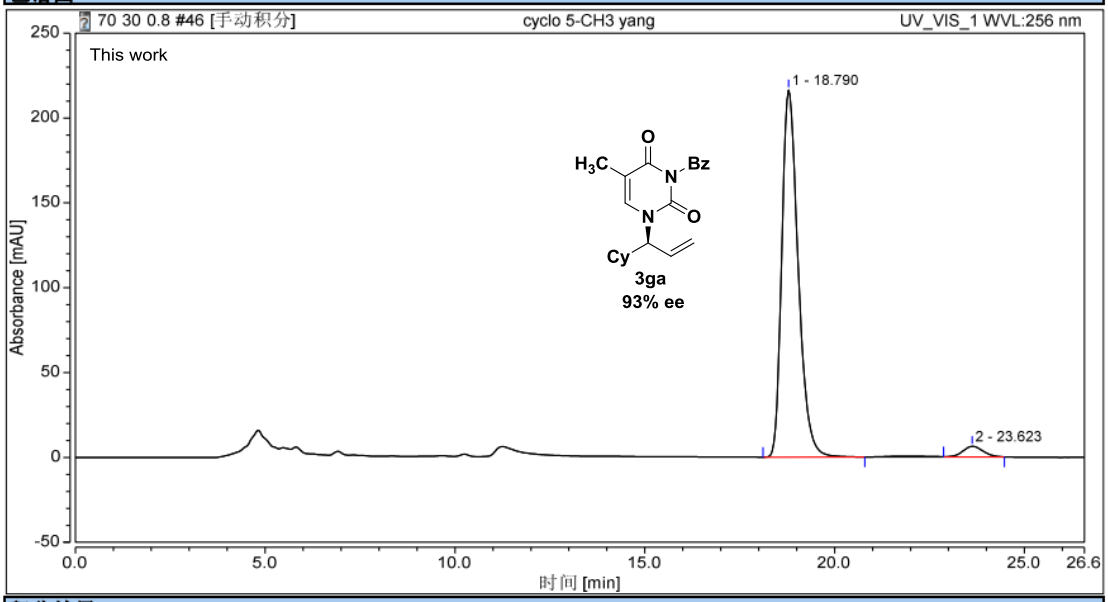
Ref: 96% ee $[\alpha]_D^{27}$ = -110.5° (*c* = 1.95, CH_2Cl_2). (previous work, **3ap'**)

2) By comparison the chiral HPLC spectra of **3ga** and **3ap'**, the same absolute configuration of the two same chiral *N*-allyl pyrimidines were further confirmed.

In the HPLC spectra for **3ga** HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 256 nm, retention time: 18.790 min (major), 23.623 min (minor). (this work, **3ga**)

In the HPLC spectra for **3ap'** HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 256 nm, retention time: 18.247 min (major), 23.438 min (minor). (previous work, **3ap'**)

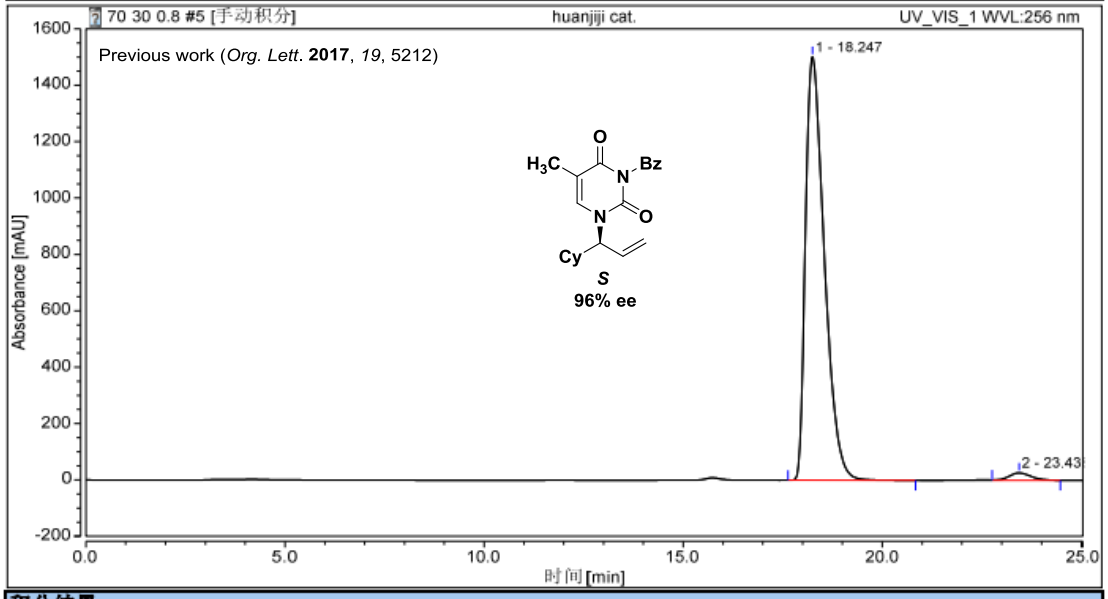
色谱图



积分结果

Peak	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.790	108.026	216.488	96.56	97.20	n.a.
2		23.623	3.852	6.226	3.44	2.80	n.a.
总和:			**111.878**	**222.714**	**100.00**	**100.00**	

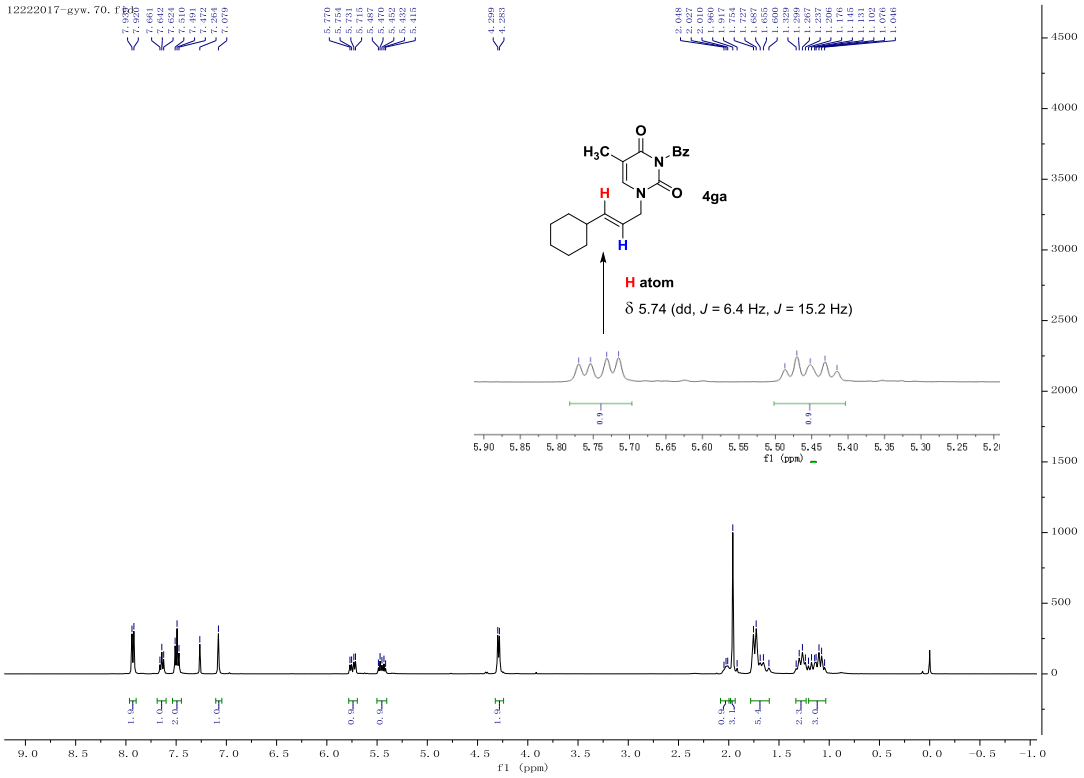
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.247	824.584	1502.824	98.01	98.29	n.a.
2		23.438	16.776	26.208	1.99	1.71	n.a.
总和:			**841.361**	**1529.032**	**100.00**	**100.00**	

11. Determination of the *E/Z* configuration of 4ga



The determination of the *E/Z* configuration of **4ga** was determined by ^{1}H-NMR analysis.

The red H atom: (600 MHz, $CDCl_3$) δ 5.74 (dd, *J* = 6.4, *J* = 6.8 Hz, 15.6 Hz, 1H). Due to the *J* value of red H atom, the configuration of the C=C bond in the side chain of the product was mainly found to be *E*-form.

12. Reference

[1] Kuang, J.; Ma, S.; *J. Org. Chem.* **2009**, *74*, 1763.
[2] Liang, L.; Xie, M.-S.; Qin, T.; Zhu, M.; Qu, G.-R.; Guo, H.-M. *Org. Lett.* **2017**, *19*, 5212.