

Supporting Information

Preparation of α -Amino Acids via Ni-Catalyzed Reductive Vinylolation and Arylation of α -Pivaloyloxy Glycine

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I. Experimental Section

Part 1. General Information

A. Chemical and reagents

Unless otherwise mentioned, all reactions were performed under an atmosphere of nitrogen or nitrogen using anhydrous solvents in flame-dried tube. Extra dry 1, 4-Dioxane (99.9%, with molecular sieves, water \leq 30 ppm (by K.F.)) was purchased from Energy Chemical, China. Deuterated solvents were used as received (CDCl_3 from J&K Co., China). NiCl_2 (Alfa Aesar), NiBr_2 (Alfa Aesar), NiI_2 (Alfa Aesar), $\text{Ni}(\text{COD})_2$ (Strem), $\text{Ni}(\text{ClO}_4)_2$ (Alfa Aesar), TBAI (TCI), $\text{Ni}(\text{acac})_2$ (Maclin Co., China) were used as purchased. $\text{NiCl}_2(\text{Py})_4$ was prepared according to a literature procedure.¹ Zinc powder (Aladdin) was activated with hydrochloric acid before use. Anhydrous MgCl_2 (Alfa Aesar) was purchased, and used directly. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

B. Physical method

Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on JNM-ECZ400s/L or a Bruker Avance 600 MHz spectrometer at STP. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded at 151 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. NMR spectra are internally referenced to residual proton solvent signals (note: CDCl_3 referenced at 7.26 for ^1H NMR and 77.0 ppm for ^{13}C NMR). Coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); br (broad). High-resolution mass spectra (HRMS) were obtained using Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China)

Part 2. Optimization Experiments

A. Optimization for reductive coupling of α -pivaloyloxy glycine with vinyl bromides.

A typical procedure for optimization of the reaction conditions: To a flame-dried Schlenk tube equipped with a stir bar was added 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv), NiBr_2 (4.37 mg, 0.02 mmol, 0.1 equiv), dtBBPy (2.68 mg, 0.01 mmol, 0.05 equiv), Zn (26.0 mg, 0.4 mmol, 2.0 equiv), MgCl_2 (28.5 mg, 0.3 mmol, 1.5

equiv), and TBAI (147 mg, 0.4 mmol, 2.0 equiv) in a glovebox under N₂ atmosphere. The tube was capped with a rubber septum and was moved out of the glovebox. Following this, (*E/Z*)-(2-bromovinyl)benzene (54.9 mg, 0.30 mmol, 1.5 equiv) and 1 mL of 1,4-dioxane were added via syringes. The resulting mixture was allowed to stir at 60 °C for 12 h. After which point, the reaction mixture was directly loaded onto a short silica gel column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided a mixture containing the product. The yields were determined by ¹H NMR using 2,5-dimethylfuran as internal standard.

Table S1. Optimization for reductive coupling of α -pivaloxy glycine with vinyl bromides

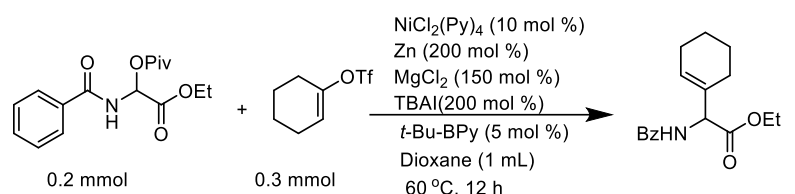
entry	variation from the above conditions	yield (%) ^a	entry	variation from the above conditions	yield (%) ^a
1	None	75%	15	100% Zn	10%
2	NiF ₂ instead of NiBr ₂	trace	16	250% Zn	50%
3	Ni(acac) ₂ instead of NiBr ₂	20%	17	5% NiBr ₂	30%
4	NiBr ₂ ·4H ₂ O instead of NiBr ₂	50%	18	15% NiBr ₂	25%
5	NiCl ₂ (dppe) instead of NiBr ₂	<5%	19	2.5% dtBBPy	15%
6	NiBr ₂ ·DME instead of NiBr ₂	40%	20	10% dtBBPy	50%
7	NiCl ₂	10%	21	100% MgCl ₂	30%
8	NiI ₂	40%	22	200% MgCl ₂	60%
9	Ni(COD) ₂	60%	23	150% TBAI	52%
10	PPh ₃ instead of dtBBPy	ND	24	100% vinyl bromide	50%
11	DMAP instead of dtBBPy	ND	25	DMAP instead of L1	not detected
12	DMA instead of 1, 4-dioxane	trace	26	25 °C instead of 60 °C	10%
13	DMSO instead of 1, 4-dioxane	trace	27	50 °C instead of 60 °C	53%
14	THF instead of 1, 4-dioxane	60%	28	70 °C instead of 60 °C	43%
			29	Mn instead of Zn	40%

^a NMR yield using 2,5-dimethylfuran as standard. ^b ND = not detected.

B. Optimization for reductive coupling of α -pivaloxy glycine with vinyl triflates.

A typical procedure for optimization of the reaction conditions: To a flame-dried Schlenk tube equipped with a stir bar was added 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv), NiCl₂(Py)₄ (8.9 mg, 0.02 mmol, 0.1 equiv), dtBBPy (2.68 mg, 0.01 mmol, 0.05 equiv), Zn (26.0 mg, 0.4 mmol, 2.0 equiv), MgCl₂ (38.5 mg, 0.3 mmol, 1.5 equiv), and TBAI (147 mg, 0.4 mmol, 2.0 equiv) in a glovebox under N₂ atmosphere. The tube was capped with a rubber septum and took out of glove-box. Following this, cyclohex-1-en-1-yl trifluoromethanesulfonate (69.0 mg, 0.30 mmol, 1.5 equiv) and 1 mL of 1,4-dioxane were added via syringes. The resulting mixture was allowed to stir at 60 °C for 12 h. After which point, the reaction mixture was directly loaded onto a silica gel column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided a mixture containing the product. The yields were determined by ¹H NMR using 2,5-dimethylfuran as internal standard.

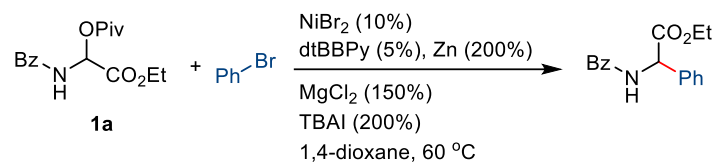
Table S2. Optimization for reductive coupling of α-pivaloyloxy glycine with vinyl triflates.

					
entry	variation from the above conditions	yield (%) ^a	entry	variation from the above conditions	yield (%) ^a
1	None	80%	7	NiBr ₂ ·DME instead of NiCl ₂ (Py) ₄	53%
2	NiBr ₂ instead of NiCl ₂ (Py) ₄	45%	8	200 mol % MgCl ₂	78%
3	Ni(acac) ₂ instead of NiCl ₂ (Py) ₄	35%	9	300 mol % Zn	70%
4	Ni(COD) ₂ instead of NiCl ₂ (Py) ₄	41%	10	150 mol % TBAI	55%
5	NiCl ₂ dppe instead of NiCl ₂ (Py) ₄	20%	11	10 mol % dtBBPy	62%
6	NiCl ₂ ·DME instead of NiCl ₂ (Py) ₄	41%	12	0.4 mmol vinyl triflates	56 %
			13	0.5 mmol vinyl triflates	68%

^aNMR yield using 2,5-dimethylfuran as internal standard.

Part 3. Mechanistic Investigation

(1) Tracking the product-forming progress for the coupling of **1a** with bromobenzene



To an oven-dried round bottom flask (5mL) was added 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv), Zn (26 mg, 0.4 mmol, 2.0 equiv), MgCl₂ (28.5 mg, 0.2 mmol, 1.5 equiv), TBAI (147.74 mg, 0.4 mmol, 2.0 equiv) and NiBr₂ (4.37 mg, 0.02 mmol, 0.1 equiv). After the flask was evacuated and refilled with N₂ for three times, bromobenzene (46.8 mg, 0.3 mmol, 1.5 equiv), dioxane (1 mL), *n*-dodecane (45 μL, 0.2 mmol, 1.0 equiv) were sequentially added to the reaction mixture. An aliquot (5 μL) was collected from the reaction mixture every 2 min via a syringe and was immediately injected into a vial containing aqueous NaHSO₄ (1 M). After the aqueous mixtures were partitioned with ethyl acetate (1.5 mL), the organic layers were collected, filtered through a short silica pad. The filtrates were analyzed by GC-MS (dodecane as internal standard).

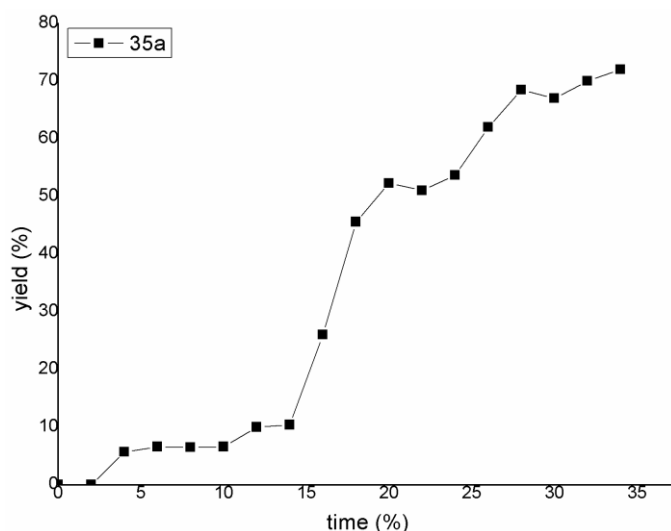
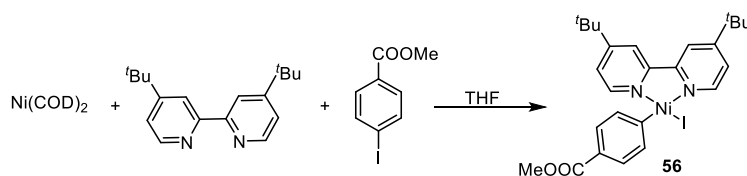


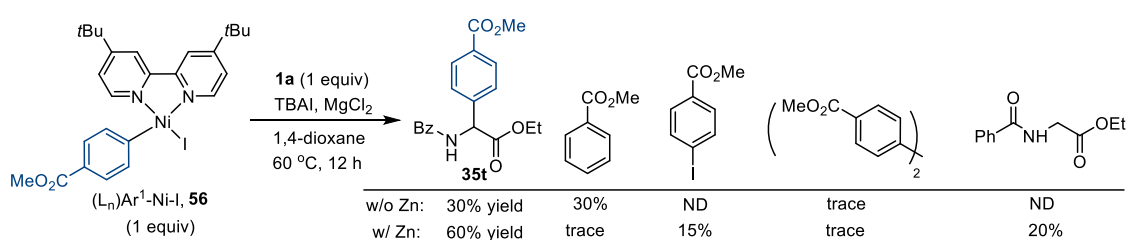
Figure S1. The profile of formation of **35a** over the course of coupling of α-pivaloyloxy glycine with bromobenzene

(2) Preparation of **56**.²



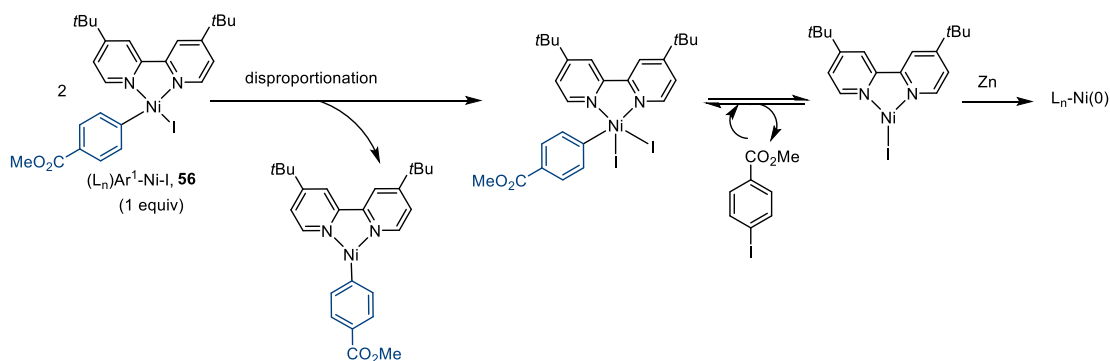
In a glove box, a suspension of $\text{Ni}(\text{cod})_2$ (330.4 mg, 1.20 mmol, 1.0 equiv) in dry THF (8 mL) was stirred for 1 minute in a 50 mL flame-dried Schlenk tube, at which point a solution of dtBBPy (322.1 mg, 1.20 mmol, 1.0 equiv) in 8 mL of dry THF was added dropwise. The resulting mixture was allowed to stir overnight at ambient temperature. A solution of methyl 4-iodobenzoate (314.4 mg, 1.20 mmol, 1.2 equiv) in 4 mL of dry THF was added via syringe. The resultant mixture was allowed to stir for 1 h. The solvent was removed under vacuum. The residue was filtrated with a fritted funnel, and washed with diethyl ether (6×3 mL). The brownish red solid was collected, and further stirred in ether (50 mL) to dissolve aryl dimer. After filtration, and dried in vacuum, the title compound was obtained in ~70% yield (94.7 mg, 0.84 mmol, with trace THF and diethyl ether), which was stored in the glove box at -30 °C. Spectral data matched those reported in the literature.²

(3) Reaction of **56** with **1a**.



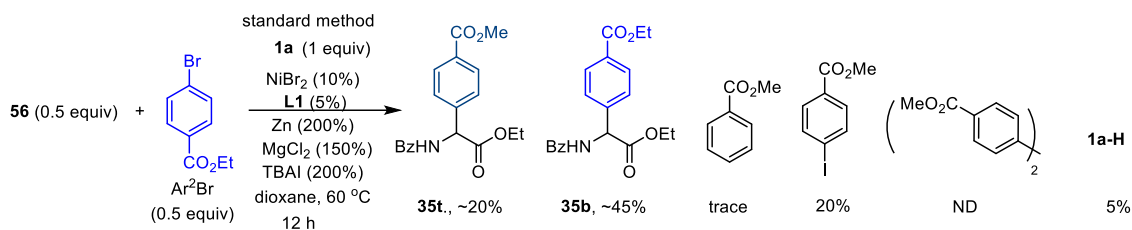
Scheme S1. Reaction of **56** with **1a**. The yields of the products were referred to NMR yields using 2,5-dimehtyl furan as internal standard.

Formation of Ar^{I} is tentatively explained as follows. Disproportionation of **56** leads to $(\text{L}_n)\text{Ar}^{\text{I}}-\text{NiI}_2$ and $(\text{L}_n)\text{Ar}^{\text{I}}-\text{Ni}^{\text{I}}$. Reductive elimination of $(\text{L}_n)\text{Ar}^{\text{I}}-\text{NiI}_2$ resulted in $\text{Ar}^{\text{I}}\text{I}$ and $\text{L}_n-\text{Ni}^{\text{I}}-\text{I}$. Such a reductive elimination process maybe reversible but disfavored as compared to the reverse oxidative addition of $\text{Ar}^{\text{I}}\text{I}$ to $\text{L}_n-\text{Ni}^{\text{I}}-\text{I}$. However, this reversible process can be pushed toward right by facile reduction of the $\text{L}_n-\text{Ni}^{\text{I}}-\text{I}$ intermediate to $\text{Ni}(0)$ by Zn.



Scheme S2. A hypothesis for the formation of Ar^{I} from **56** in the presence of Zn.

(4) Competition experiment.



Scheme S3. Reaction of **56** with **1a** and Ar^2Br . The yields of the products were referred to NMR yields using 2,5-dimethyl furan as internal standard.

To an oven-dried Schlenk tube was charged with 1-benzamido-2-ethoxy-2-oxoethyl pivalate **1** (30.7 mg, 0.1 mmol, 1.0 equiv), Zn (6.5 mg, 0.1 mmol, 1.0 equiv), NiBr_2 (1.09 mg, 0.005 mmol, 0.05 equiv), dtBBPy (0.67 mg, 0.0025 mmol, 0.025 equiv), MgCl_2 (7 mg, 0.075 mmol, 1.5 equiv), TBAI (36.7 mg, 0.1 mmol, 1 equiv) and Ar-Ni(II) complex (29.4 mg, 0.05 mmol, 0.5 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane was added via a syringe prior to the addition of ethyl 4-bromobenzoate (11.4 mg, 0.05 mmol, 0.5 equiv). The reaction mixture was allowed to stir at 60 °C for 12 h. Flash column chromatograph gave a mixture containing the coupling products. ^1H NMR spectral analysis of the mixture indicated that methyl 4-(1-benzamido-2-ethoxy-2-oxoethyl)benzoate **35i** and ethyl 4-(1-benzamido-2-ethoxy-2-oxoethyl)benzoate **35b** were obtained in 20% and 45% yields, respectively, using 2,5-dimethyl furan as internal reference.

(5) Tracking the progress for the crossover experiment

To an oven-dried round bottom flask was charged with 1-benzamido-2-ethoxy-2-oxoethyl pivalate **1a** (30.7 mg, 0.1 mmol, 1.0 equiv), Zn (6.5 mg, 0.1 mmol, 1.0 equiv), MgCl_2 (7 mg, 0.075 mmol, 1.5 equiv), TBAI (36.7 mg, 0.1 mmol, 1 equiv), Ar-Ni(II) complex (29.4 mg, 0.05 mmol, 0.5 equiv), NiBr_2 (1.09 mg, 0.005 mmol, 0.05 equiv), dtBBPy (0.67 mg, 0.0025 mmol, 0.025 equiv). The round bottom flask was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane was added via a syringe prior to the addition of ethyl 4-bromobenzoate (11.4 mg, 0.05 mmol, 0.5 equiv) or 4-iodobenzoate (13.8 mg, 0.05 mmol, 0.5 equiv) and n-dodecane (11 μL , 0.05 mmol, 0.5 equiv). An aliquot (5 μL) was collected from the reaction mixture every 2 min via a syringe and was immediately injected into a vial containing aqueous NaHSO_4 (1 M). The mixture in the GC vial was partitioned with ethyl acetate (1.5 mL), and was filtered through a short silica pad. The filtrate was analyzed by GC-MS.

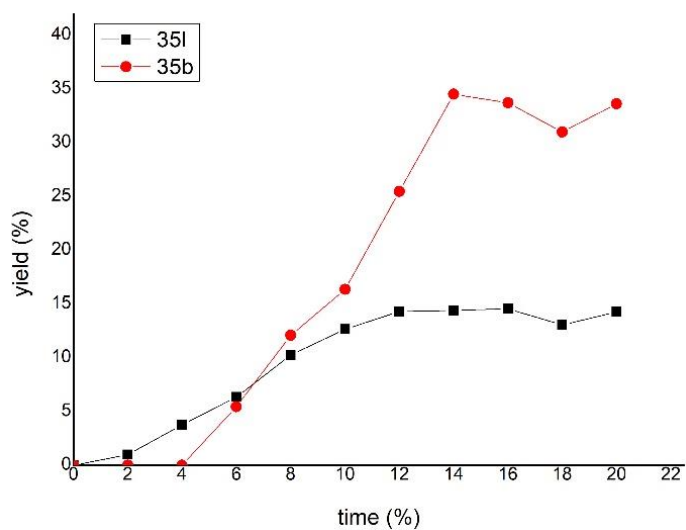
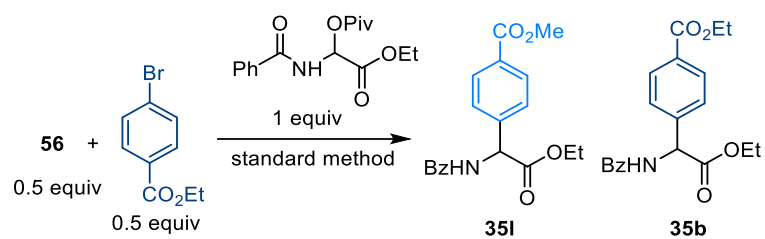


Figure S2. The reaction profile for the crossover experiment of **1a**, Ar²Br with **56**. Yield based on 1 equiv of **1a**.

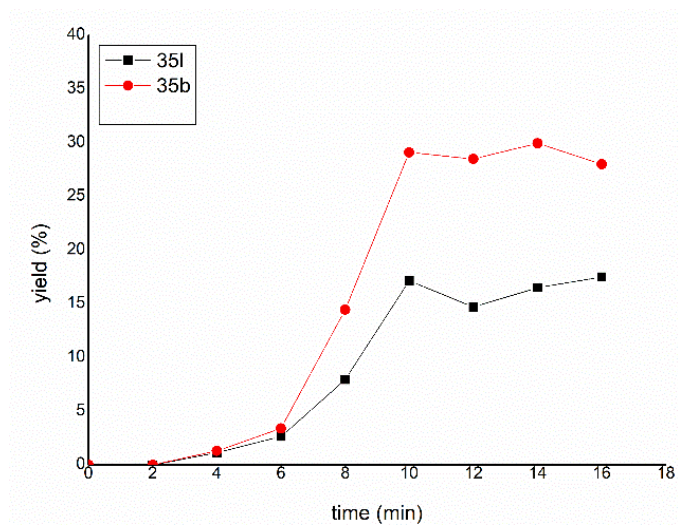
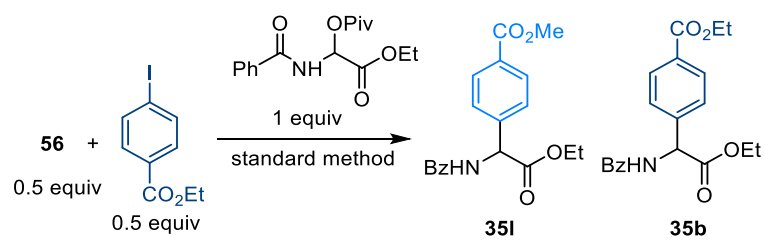
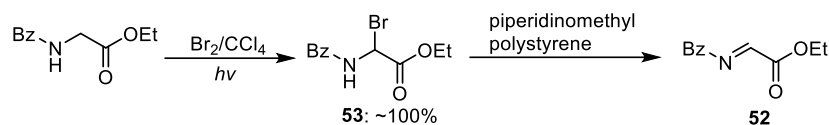


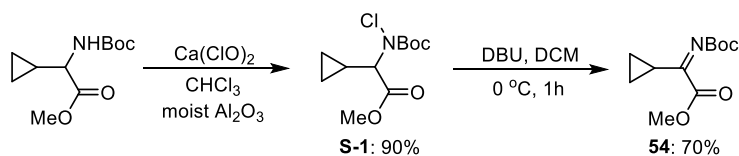
Figure S3. The reaction profile for the crossover experiment of **1a**, Ar²I with **56**. Yield based on 1 equiv of **1a**.

(6) Preparation of ethyl (*E*)-2-(benzoylimino)acetate **52**.³



This compound was prepared according to a literature procedure.² To a solution of *N*-benzoylglycine ethyl ester (2.0 g, 9.7 mmol) in DCM (20 mL) was added a solution of Br₂ (1.62 g, 10.1 mmol) in CCl₄ (8 mL). The reaction mixture was refluxed under UV irradiation for 60 min (220 V, 300W, light bulb) and cooled to rt. The solvent was removed *in vacuo* to afford almost pure *N*-benzoyl α-bromoglycine ethyl ester in a quantitative yield. Further purification was done by washing the white precipitate with petroleum ether under nitrogen atmosphere three times. To a mixture of this product (128 mg, 0.45 mmol) and 3.5 mmol/g piperidinomethyl polystyrene (257 mg, 0.90 mmol) was added DCM (4.5 mL). The reaction mixture was stirred for 10 min at rt. The polymer floated on the surface and the clear part of the solution (2.5 mL, 0.25 mmol of imine) was taken by gas-tight syringe, then the solvent was removed *in vacuo* to give the title compound. This product was used immediately for next step.

(7) Preparation of methyl 2-(*N*-tert-Butoxycarbonylimino)-2-cyclopropylacetate **54**.^{4,5}



This compound was prepared according to a literature procedure.^{4,5} A mixture of Ca(OCl)₂ (1.43 g, 10 mmol), moist alumina (10.0 g) in CHCl₃ (50 mL) was vigorously stirred at 40 °C for 10 min. A solution of methyl 2-((tert-butoxycarbonyl)amino)-2-cyclopropylacetate (1.10 g, 5.0 mmol) in CHCl₃ (10.0 mL) was then added, and the mixture was stirred for 24 h at 40 °C. The solid was removed by filtration, and the filtrate was concentrated under reduced pressure to give methyl 2-((tert-butoxycarbonyl)chloroamino)-2-cyclopropylacetate (**S-1**).

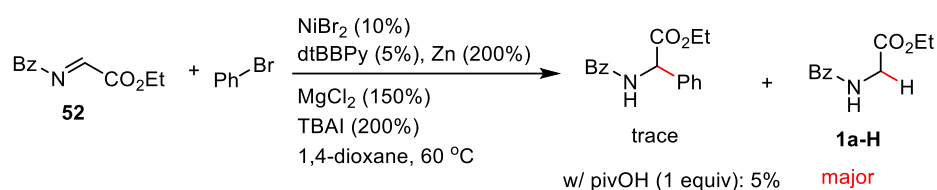
¹H NMR (400 MHz, CDCl₃) δ 3.93 (d, *J* = 9.6 Hz, 1H), 3.78 (s, 3 H), 1.49 (s, 9 H), 0.87 – 0.78 (m, 1H), 0.71 – 0.63 (m, 1H), 0.61 – 0.52 (m, 1H), 0.47 – 0.38 (m, 1H).

To a solution of methyl 2-((tert-butoxycarbonyl)chloroamino)-2-cyclopropylacetate (**S-1**) (1.0 g, 4 mmol) in DCM (30 mL) was added a solution of DBU (2.87 mmol, 0.44 g) in DCM (2 mL) dropwise within 20 min at 0 °C. The mixture was stirred at room temperature until the

starting material completely disappeared (ca. 1 h, TLC, hexane/Et₂O, 2:1). The solvent was then removed under reduced pressure at ca. 10-15 °C. To the residual oil was added hexane (10 mL), and the precipitate was filtered off and washed with hexane. The combined filtrates were concentrated under reduced pressure, and the residue was immediately loaded onto a neutral alumina column. Flash chromatography (hexane/Et₂O, 5:1) gave *N*-Boc-imino ester **54** as a colorless oil. The product was used immediately for next step.

¹H NMR (600 MHz, CDCl₃) δ 3.84 (s, 3H), 2.19 – 2.02 (m, 2H), 1.51 (s, 9H), 1.18 – 1.13 (m, 2H), 1.07 – 0.99 (m, 2H).

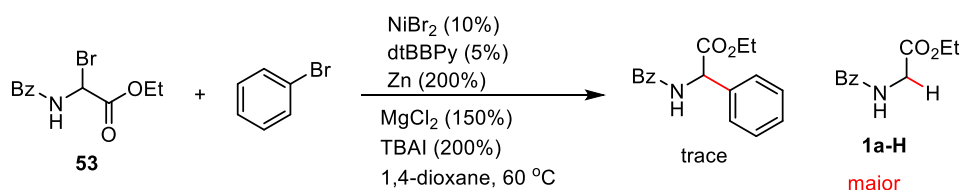
(8) Coupling of ethyl *N*-benzoyl-α-imino ester **52** with bromobenzene.



A Schlenk tube was charged with freshly prepared *N*-benzoyl-α-imino ester **52** (0.2 mmol, 1.0 equiv), NiBr₂ (4.37 mg, 0.02 mmol, 0.1 equiv), dtBBPy (2.68 mg, 0.01 mmol, 0.05 equiv), Zn (26 mg, 0.4 mmol, 2.0 equiv), MgCl₂ (28.5 mg, 0.3 mmol, 1.5 equiv) and TBAI (147 mg, 0.4 mmol, 2.0 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane (1 mL) was added via a syringe followed by the addition of bromobenzene (46.8 mg, 0.3 mmol, 1.5 equiv). The reaction mixture was allowed to stir at 60 °C for 12 h, after which point it was directly loaded onto a short silica gel column without work-up. Flash column chromatography provided a mixture containing trace amount of the desired product based on ¹H NMR spectral analysis of the mixture using 2,5-dimethyl furan as internal reference.

In a second reaction, pivalic acid (20.4 mg, 0.2 mmol, 1.0 equiv) was added following the same reaction procedure as above.

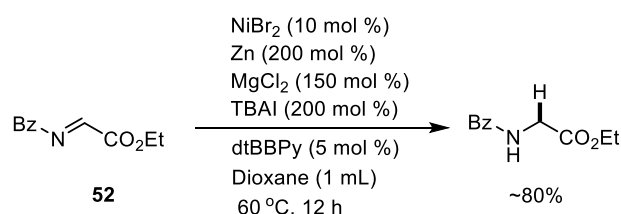
(9) Coupling of ethyl 2-benzamido-2-bromoacetate **53** with bromobenzene.



To an oven-dried Schlenk tube was charged with ethyl 2-benzamido-2-bromoacetate **53** (57.0 mg, 0.2 mmol, 1.0 equiv), NiBr₂ (4.37 mg, 0.02 mmol, 0.1 equiv), dtBBPy (2.68 mg, 0.01 mmol, 0.05 equiv), Zn (26 mg, 0.4 mmol, 2.0 equiv), MgCl₂ (28.5 mg, 0.3 mmol, 1.5

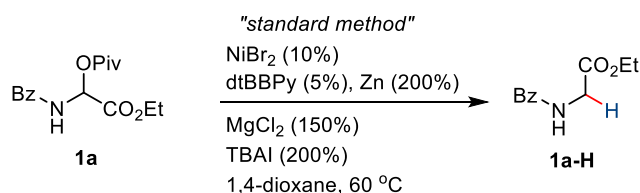
equiv) and TBAI (147 mg, 0.4 mmol, 2.0 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane (1 mL) was added via a syringe followed by the addition of bromobenzene (46.8 mg, 0.3 mmol, 1.5equiv). The reaction mixture was allowed to stir at 60 °C for 12 h, after which point it was directly loaded onto a silica gel column without work-up. Flash column chromatography provided a mixture containing trace amount of the desired product based on ¹H NMR spectral analysis of the mixture using 2,5-dimethyl furan as internal reference.

(10) Reduction of N-benzoyl- α -imino ester **52** under the standard method.



To an oven-dried Schlenk tube was charged with 1-benzamido-2-ethoxy-2-oxoethyl pivalate **52** (0.2 mmol, 0.2 equiv), NiBr₂ (4.37 mg, 0.02 mmol, 0.1 equiv), dtBBPy (2.68 mg, 0.01 mmol, 0.05 equiv), Zn (26 mg, 0.4 mmol, 2.0 equiv), MgCl₂ (28.5 mg, 0.3 mmol, 1.5 equiv) and TBAI (147 mg, 0.4 mmol, 2.0 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane (1 mL) was added via a syringe. The reaction mixture was allowed to stir at 60 °C for 12 h. After which point, the reaction mixture was directly loaded onto a silica gel column without work-up. Flash column chromatography gave a mixture containing ethyl benzoylglycinate **1a-H**. The yield was determined based on ¹H NMR spectral analysis of the mixture using 2,5-dimethylfuran as internal standard.

(11) Track of the progress of reduction of **1a** with Zn.



By variation of conditions from the standard method shown above, the consumption of **1a** and formation of **1a-H** were tracked as indicated in Figures S4 and S5. The results suggested TBAI was crucial to speed up the reduction rates of **1a**. The data were obtained by running parallel reactions, and quenching the reaction at specific point. After flash column, a mixture containing **1a** and **1a-H** was analyzed by ¹H NMR spectroscopic studies using 2,5-dimethyl furan as the internal standard.

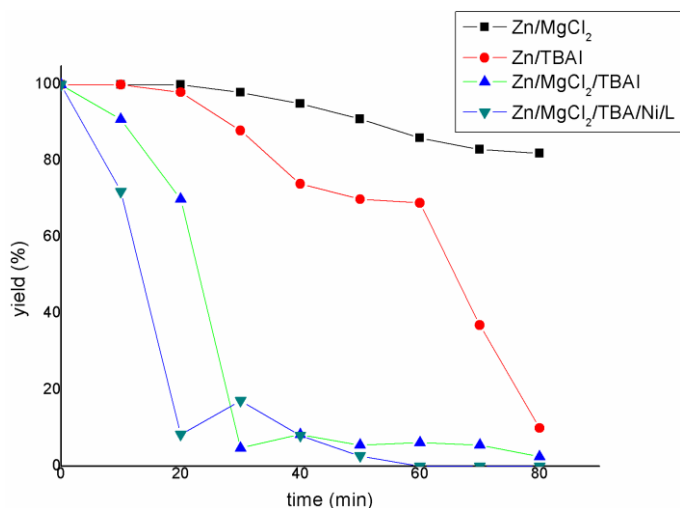


Figure S4. Track of the progress of consumption of **1a** under different conditions.

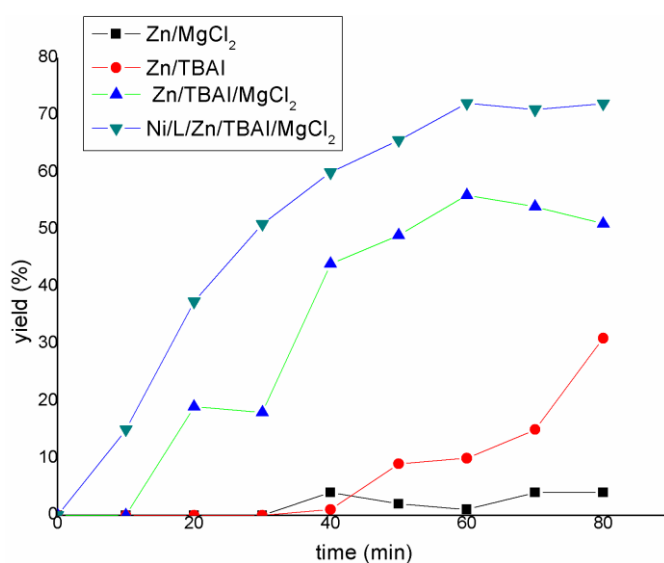
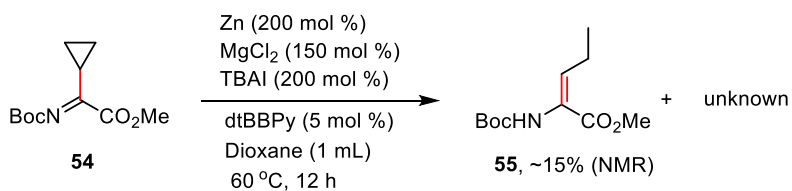


Figure S5. Track of the progress of formation of **1a-H** under different conditions.

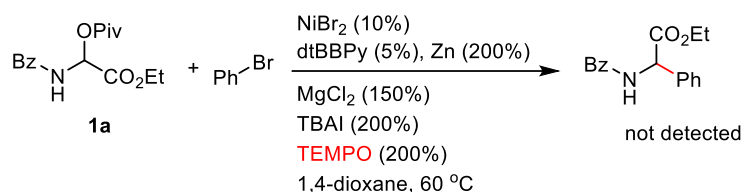
(12) Free radical ring opening reaction.



To an oven-dried Schlenk tube was charged with methyl 2-(*N*-tert-Butoxycarbonylimino)-2-cyclopropylacetate **54** (45.4 mg, 0.2 mmol, 1.0 equiv), Zn (26 mg, 0.4 mmol, 2.0 equiv), dtBBPy (2.68 mg, 0.01 mmol, 0.05 equiv), MgCl₂ (28.5 mg, 0.3 mmol, 1.5 equiv) and TBAI (147 mg, 0.4 mmol, 2.0 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane (1

mL) was added via a syringe. The reaction mixture was allowed to stir at 60 °C for 12 h, and was directly loaded onto a silica gel column without work-up. Flash column chromatography provided a mixture containing the desired product. ¹H NMR spectral analysis of the mixture using 2,5-dimethyl furan as internal reference indicated the formation of methyl (*E*)-2-((tert-butoxycarbonyl)amino)pent-2-enoate **55** in 15% yield.

(13) Free radical inhibition experiment.



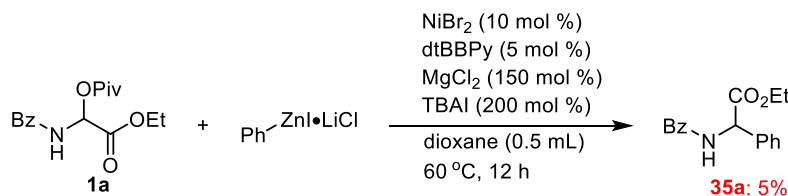
To an oven-dried Schlenk tube was charged with 1-benzamido-2-ethoxy-2-oxoethyl pivalate **1a** (30.7 mg, 0.1 mmol, 1.0 equiv), Zn (13mg, 0.4 mmol, 2.0 equiv), NiBr₂ (2.18 mg, 0.02 mmol, 0.1 equiv), dtBBPy (1.34 mg, 0.01 mmol, 0.05 equiv), MgCl₂ (14 mg, 0.3 mmol, 1.5 equiv) and TBAI (73.5 mg, 0.4 mmol, 2.0 equiv) and TEMPO (62.4 mg, 0.4 mmol, 2.0 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane (1mL) was added via a syringe followed by iodobenzene (30.6 mg, 0.15 mmol, 0.15equiv). The reaction mixture was allowed to stir at 60 °C for 12 h. The desired product was not detected by GC-MS.

(14) Coupling of **1a** with phenylzinc iodide.

a. Preparation of the phenylzinc reagent.⁶

Anhydrous LiCl (5 mmol) was placed in an N₂-flushed flask and dried for 20 min at 160 °C under high vacuum. Zinc powder (7 mmol, 1.4 equiv) was added under nitrogen atmosphere and the heterogeneous mixture of Zn and LiCl was dried again for 10 - 20 min at 150 -170 °C under high vacuum. The reaction flask was evacuated and refilled with nitrogen three times. THF (5 mL) was added and the Zn was activated with BrCH₂CH₂Br (5 mol%) and Me₃SiCl (1 mol%). Iodobenzene (5 mmol) was then added neat at room temperature. The insertion reaction was complete after 24 h. The solution was titrated with iodine following the Knochel method, which established that the phenylzinc reagent was formed in a concentration of 0.4 M.

b. Coupling with Ph-ZnI·LiCl:

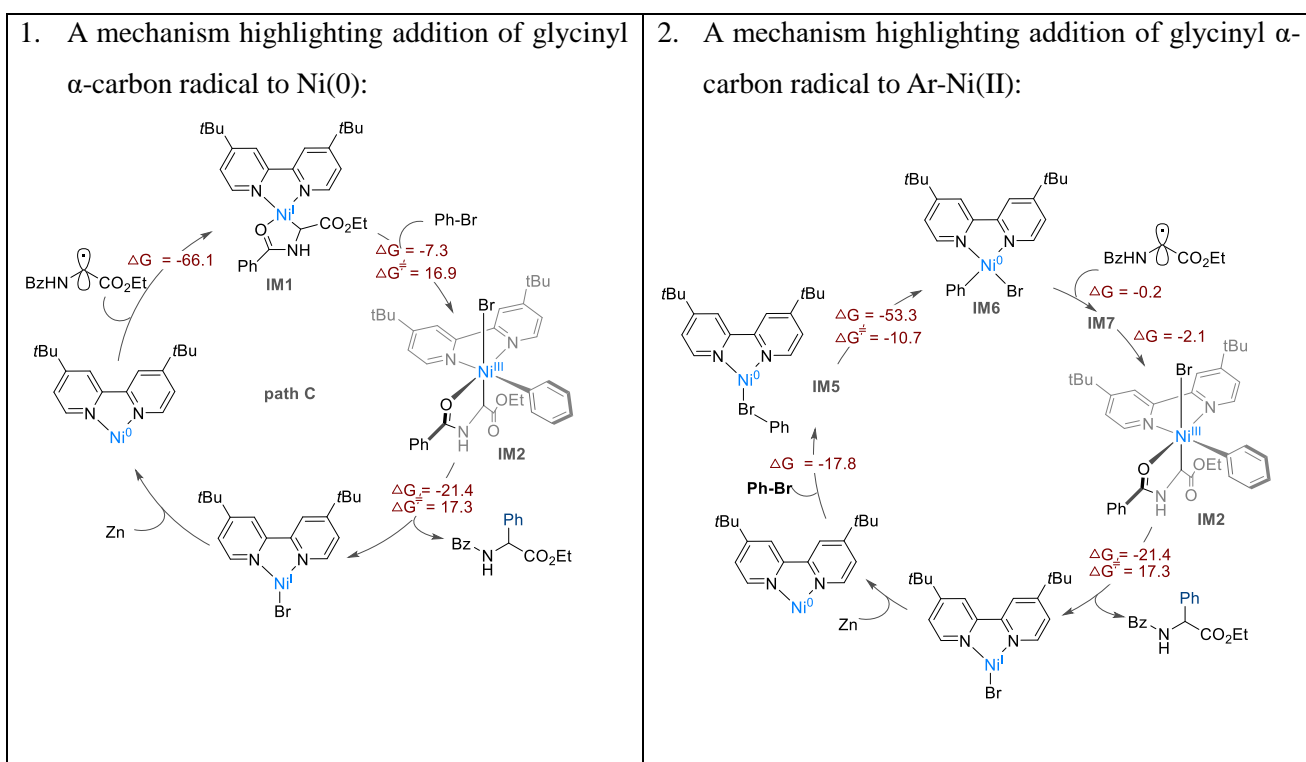


To an oven-dried Schlenk tube was charged with 1-benzamido-2-ethoxy-2-oxoethyl pivalate **1a** (30.7 mg, 0.2 mmol, 1.0 equiv), NiBr₂ (2.18 mg, 0.02 mmol, 0.1 equiv), dtBBPy (1.34 mg, 0.01 mmol, 0.05 equiv), MgCl₂ (14 mg, 0.3 mmol, 1.5 equiv) and TBAI (73.5 mg, 0.4 mmol, 2.0 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane (0.5 mL) was added via a syringe prior to the addition of the arylzinc solution (0.5 mL of a 0.4 M solution in THF, 0.2 mmol, 1.5 equiv). The reaction mixture was allowed to stir at 60 °C for 12 h. After that, it was directly loaded onto a silica gel column without work-up. Flash column chromatography provided a mixture containing the desired product in 5% yield based on ¹H NMR spectral analysis of the mixture using 2,5-dimethyl furan as internal reference. Note: for the model reaction of **1a** with **2**, the yield for **35a** was obtained in 60% using THF as solvent (Table S1, entry 14).

Part 4. DFT Studies

Computational Methods: The UltraFine integration grid was used to enhance computational accuracy, along with the keyword `acc2e=11`. Geometries were optimized and characterized by frequency calculations to be energy minima (zero imaginary frequencies) or transition states (only one imaginary frequency) at the M06-L/BS1 level in the gas phase,^{7a,b} BS1 designating a mixed basis set of SDD^{7c,d} for nickel and 6-31G(d,p) for other atoms. The energies were then refined by M06-L/BS2//M06-L/BS1 single-point energy calculations in 1,4-dioxane solution using the SMD solvation model,⁸ BS2 denoting a mixed basis set of SDD for nickel and 6-311++G(d,p) for other atoms. The refined energies were converted to zero-point energy-corrected free energies at 298.15 K and 1 atm, using the M06-L/BS1 harmonic frequencies. All calculations were performed with Gaussian 09.⁹

Mechanistic Proposals and Schematic Summary of DFT Data Based on Figure S6:



Scheme S4. Left: A mechanism highlighting addition of glycyl α -carbon radical to Ni(0); Right: A mechanism highlighting addition of glycyl α -carbon radical to Ar-Ni(II).

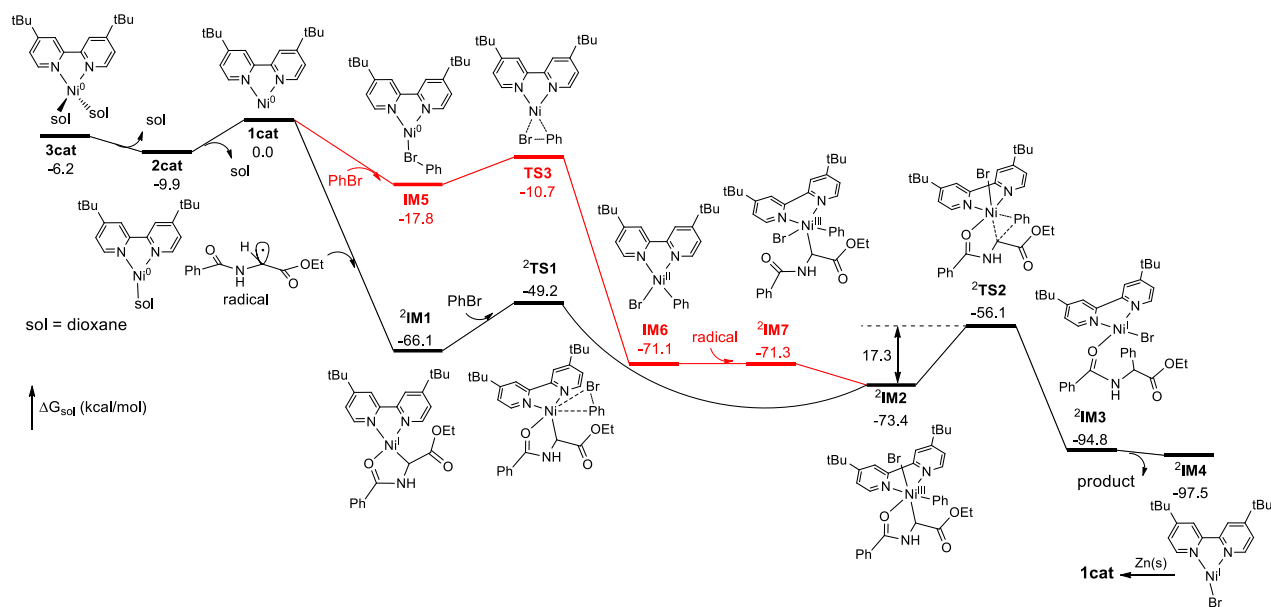


Figure S5. Free energy profile comparing the favored Ni^0 Ni^{I} Ni^{III} Ni^{I} pathway (black) and the Ni^0 Ni^{II} Ni^{III} Ni^{I} pathway (red).

Cartesian Coordinates, SCF Energies, and Free Energies of DFT-Computed Structures

1cat

E_{gas} optimization: -980.772610171 a.u.

E_{sol} single-point: -980.950042417 a.u.

G_{sol} thermo-corrected: -980.618526417 a.u.

Ni	0.050143	3.114312	0.100868
C	0.719673	0.572331	-0.157081
C	2.620756	1.814108	-0.653203
C	3.444503	0.722179	-0.444567
C	2.896904	-0.519788	-0.089399
C	1.506665	-0.552495	0.058001
C	-0.725026	0.579216	0.054075
C	-2.617788	1.875681	0.445484
C	-3.450694	0.781718	0.296390
C	-2.913234	-0.489539	0.039851
C	-1.524136	-0.549246	-0.093203
H	3.039101	2.767090	-0.967052
H	4.512960	0.843633	-0.591116
H	1.018711	-1.466212	0.391872
H	-3.023051	2.854603	0.683843
H	-4.519467	0.926686	0.413757
H	-1.043517	-1.488209	-0.360201
N	1.270154	1.783021	-0.542490
N	-1.267840	1.808473	0.372302
C	-3.757906	-1.746354	-0.125660
C	3.727256	-1.771736	0.161027
C	-3.307207	-2.800570	0.894587
H	-3.894879	-3.718485	0.782623

H	-2.253098	-3.065175	0.764290
H	-3.435093	-2.439746	1.920043
C	-5.244173	-1.466057	0.088359
H	-5.444165	-1.074254	1.091162
H	-5.632121	-0.746555	-0.640173
H	-5.818534	-2.390643	-0.025474
C	-3.564659	-2.305309	-1.542231
H	-4.157549	-3.216695	-1.678546
H	-3.878782	-1.580502	-2.299836
H	-2.518031	-2.558352	-1.738290
C	3.541262	-2.222047	1.616764
H	2.493234	-2.443995	1.840989
H	4.122524	-3.129699	1.814663
H	3.873547	-1.447900	2.315568
C	5.214746	-1.527724	-0.086297
H	5.410200	-1.216338	-1.117826
H	5.617982	-0.759511	0.581703
H	5.778972	-2.448222	0.092973
C	3.253953	-2.892870	-0.774220
H	2.197549	-3.132451	-0.616705
H	3.377860	-2.611070	-1.824635
H	3.830090	-3.808168	-0.598662

2cat

E_{gas} optimization: -1288.430522 a.u.

E_{sol} single-point: -1288.68965718a.u.

G_{sol} thermo-corrected: -1288.24350318 a.u.

Ni	1.348840	1.359352	0.117818
C	-0.456016	-0.673831	-0.269287
C	1.616069	-1.566280	-0.767177
C	1.184991	-2.852811	-0.504172
C	-0.143344	-3.082103	-0.101422
C	-0.943719	-1.945805	0.021506
C	-1.237320	0.535336	-0.081570
C	-1.155262	2.834368	0.255832
C	-2.532709	2.938829	0.186331
C	-3.321024	1.789705	0.002359

C	-2.628690	0.589164	-0.145064
H	2.643535	-1.393936	-1.088880
H	1.880425	-3.675335	-0.639613
H	-1.964481	-2.037525	0.389560
H	-0.535781	3.708526	0.432649
H	-2.983195	3.918667	0.301845
H	-3.170303	-0.332366	-0.349159
N	0.842614	-0.459201	-0.687888
N	-0.485767	1.663545	0.166367
C	-4.843217	1.815522	-0.068851
C	-0.700975	-4.460713	0.228529
C	-5.418781	0.902491	1.022027
H	-6.513790	0.896956	0.980017
H	-5.077435	-0.130871	0.905419
H	-5.119986	1.240514	2.019356
C	-5.400599	3.223591	0.131327
H	-5.121503	3.636835	1.106233
H	-5.049243	3.914286	-0.642276
H	-6.493814	3.202855	0.082023
C	-5.296275	1.301962	-1.442491
H	-6.390012	1.304309	-1.511018
H	-4.905085	1.930944	-2.248399
H	-4.954357	0.278424	-1.624526
C	-1.116054	-4.501361	1.705861
H	-1.879144	-3.749537	1.930400
H	-1.529587	-5.483356	1.963179
H	-0.260472	-4.311388	2.361702
C	0.325262	-5.565040	-0.018582
H	0.652501	-5.589381	-1.063429
H	1.213045	-5.443878	0.610920
H	-0.112148	-6.541178	0.213841
C	-1.933075	-4.736552	-0.643946
H	-2.717238	-3.989987	-0.483373
H	-1.675428	-4.724044	-1.707772
H	-2.358555	-5.718902	-0.409612
C	3.917352	1.293795	-1.118154
C	4.098310	1.879411	1.168177
C	5.330994	0.765502	-1.071822
H	3.903021	2.354129	-1.409256
H	3.271751	0.730822	-1.798858
C	5.511663	1.344693	1.165853
H	4.078118	2.950576	0.919493
H	3.592472	1.725245	2.123128
H	5.825140	0.893608	-2.038786
H	5.314707	-0.311012	-0.826527
H	6.139516	1.906176	1.863019
H	5.504650	0.285694	1.476018
O	3.321250	1.162050	0.189374
O	6.101467	1.473276	-0.116517

3cat

E_{gas} optimization: -1596.066047 a.u.

E_{sol} single-point: -1596.40792096 a.u.

G_{sol} thermo-corrected: -1595.84694596 a.u.

Ni	-1.129554	0.000006	-0.000025
C	1.534689	0.697730	-0.163510
C	0.217750	2.530660	-0.738397
C	1.294032	3.387981	-0.684034
C	2.579825	2.892517	-0.360950
C	2.653958	1.531654	-0.092217
C	1.534651	-0.697492	0.164263
C	0.217582	-2.530417	0.738904
C	1.293743	-3.387843	0.684115
C	2.579557	-2.892454	0.360979
C	2.653817	-1.531518	0.092627
H	-0.764649	2.903067	-1.028011
H	1.139811	4.433387	-0.931490
H	3.598477	1.091580	0.225305
H	-0.764802	-2.902758	1.028655
H	1.139437	-4.433317	0.931242
H	3.598356	-1.091465	-0.224869
N	0.281652	1.191589	-0.520391
N	0.281608	-1.191260	0.521244
C	3.820180	-3.772712	0.263507
C	3.820529	3.772687	-0.263679
C	4.906976	-3.237347	1.205357
H	5.814368	-3.848771	1.137011
H	5.182397	-2.207284	0.958251
H	4.567876	-3.248920	2.246166
C	3.522328	-5.222132	0.644423
H	3.146437	-5.303551	1.669871
H	2.781361	-5.674251	-0.023365
H	4.435398	-5.822594	0.577696
C	4.352916	-3.748803	-1.175989
H	5.251428	-4.370638	-1.267571
H	3.604818	-4.128828	-1.879277
H	4.616650	-2.733919	-1.489795
C	4.352791	3.749529	1.176010
H	4.616328	2.734782	1.490429
H	5.251316	4.371350	1.267567
H	3.604477	4.129979	1.878839
C	3.522955	5.221917	-0.645534
H	3.147182	5.302746	-1.671073
H	2.782002	5.674591	0.021890
H	4.436118	5.822268	-0.579082
C	4.907569	3.236684	-1.204872
H	5.182845	2.206743	-0.957110
H	4.568813	3.247711	-2.245798
H	5.814989	3.848070	-1.136567
C	-2.569387	-2.367024	-1.336023
C	-3.543209	-1.762300	0.731033
C	-3.917920	-2.864366	-1.800428
H	-1.989117	-3.178964	-0.872259
H	-1.978267	-1.931088	-2.146222
C	-4.874208	-2.270201	0.228281
H	-2.999380	-2.558882	1.262848
H	-3.646944	-0.895518	1.390478
H	-3.810985	-3.708631	-2.486906
H	-4.449010	-2.050978	-2.326875
H	-5.478435	-2.671717	1.046633
H	-5.430192	-1.437663	-0.240776
O	-2.755937	-1.313768	-0.379885
O	-4.693930	-3.320029	-0.704831
C	-2.570143	2.367275	1.335538
C	-3.544228	1.761958	-0.731142
C	-3.918667	2.864425	1.800138
H	-1.990177	3.179253	0.871456
H	-1.978702	1.931681	2.145685
C	-4.875228	2.269696	-0.228244
H	-3.000666	2.558542	-1.263233
H	-3.647952	0.895043	-1.390413

H	-3.811777	3.708812	2.486470
H	-4.449515	2.051015	2.326805
H	-5.479675	2.670921	-1.046575
H	-5.430952	1.437162	0.241117
O	-2.756659	1.313776	0.379682
O	-4.694993	3.319763	0.704613

radical

E_{gas} optimization: -706.753416188 a.u.

E_{sol} single-point: -706.933712745 a.u.

G_{sol} thermo-corrected: -706.762659745 a.u.

N	-0.093017	0.189861	0.029885
H	-0.045671	-0.817471	-0.083597
C	-1.352987	0.689221	0.068947
C	-2.415404	-0.272749	-0.028009
O	-2.223549	-1.481428	-0.143383
O	-3.636656	0.304066	0.022321
C	-4.735050	-0.620568	-0.071919
H	-4.644330	-1.182368	-1.008490
H	-4.653210	-1.350303	0.741657
C	-6.005927	0.180161	-0.001468
H	-6.062023	0.900840	-0.820882
H	-6.873014	-0.481231	-0.069508
H	-6.070975	0.731742	0.939533
C	1.050477	0.981088	0.074221
O	0.957039	2.200951	0.132931
C	2.346009	0.261134	0.033645
C	3.493604	1.043484	-0.146043
C	2.483835	-1.125752	0.177988
C	4.748490	0.453192	-0.196221
H	3.364707	2.116896	-0.243826
C	3.742255	-1.714508	0.132296
H	1.620370	-1.762644	0.354157
C	4.876059	-0.928120	-0.059093
H	5.630974	1.069539	-0.341192
H	3.837971	-2.789651	0.251359
H	5.857749	-1.391657	-0.096161
H	-1.474267	1.759058	0.166730

²IM1

E_{gas} optimization: -1687.66533241 a.u.

E_{sol} single-point: -1688.01532007 a.u.

G_{sol} thermo-corrected: -1687.48646607 a.u.

Ni	0.925682	-0.357384	-0.579203
C	-1.898976	-0.031727	-0.477146
C	-1.385509	-2.162743	-1.216789
C	-2.711377	-2.556478	-1.150169
C	-3.682444	-1.668124	-0.669213
C	-3.238918	-0.386852	-0.337557
C	-1.361627	1.298360	-0.205769
C	0.573990	2.556285	-0.021786
C	-0.146032	3.710738	0.234847
C	-1.547792	3.671151	0.274862
C	-2.137481	2.428259	0.041429
H	-0.610688	-2.858783	-1.524852
H	-2.970427	-3.566598	-1.448500
H	-3.943503	0.345542	0.049798
H	1.660172	2.556961	-0.061736
H	0.394175	4.636173	0.402884
H	-3.221187	2.337293	0.035755
N	-0.959767	-0.934669	-0.884591
N	0.000843	1.359782	-0.234866
C	-2.416246	4.894914	0.542222
C	-5.143094	-2.052946	-0.467874

C	-3.277369	4.642052	1.787131
H	-3.916212	5.508181	1.991053
H	-3.929945	3.772662	1.659794
H	-2.655749	4.465032	2.670393
C	-1.577764	6.150065	0.776269
H	-0.916098	6.042791	1.642005
H	-0.960685	6.396360	-0.093972
H	-2.233345	7.005113	0.967092
C	-3.333783	5.136694	-0.664088
H	-3.973023	6.008611	-0.487803
H	-2.753210	5.321445	-1.573334
H	-3.987746	4.280189	-0.855256
C	-5.479853	-1.943983	1.026023
H	-5.329562	-0.927175	1.402137
H	-6.527174	-2.212866	1.201969
H	-4.852976	-2.615377	1.622120
C	-5.424588	-3.482814	-0.925887
H	-5.206637	-3.621534	-1.989918
H	-4.836686	-4.213887	-0.360561
H	-6.481215	-3.721769	-0.771751
C	-6.042580	-1.096382	-1.261053
H	-5.910157	-0.056934	-0.945147
H	-5.829449	-1.148391	-2.333370
H	-7.096792	-1.354105	-1.113131
N	3.378827	-1.673378	-0.296391
H	4.031934	-2.242199	0.230210
C	1.988601	-2.082337	-0.319800
C	1.648073	-2.775485	0.913337
O	2.310508	-2.776640	1.942998
O	0.448092	-3.434342	0.802018
C	-0.076322	-3.994844	2.009349
H	0.188955	-5.059870	2.046908
H	0.405574	-3.511231	2.863841
C	-1.572134	-3.800030	2.010070
H	-2.040738	-4.291727	1.151544
H	-2.013988	-4.213687	2.921576
H	-1.820918	-2.734881	1.958264
C	3.686399	-0.376154	-0.465054
O	2.791230	0.469828	-0.727547
C	5.097423	0.043047	-0.343773
C	5.377244	1.396267	-0.120522
C	6.159334	-0.864410	-0.449400
C	6.689052	1.829392	0.017108
H	4.545156	2.090505	-0.055102
C	7.472344	-0.427559	-0.316184
H	5.959785	-1.909985	-0.669328
C	7.740297	0.918385	-0.078069
H	6.895412	2.880527	0.197984
H	8.289035	-1.137923	-0.407168
H	8.766950	1.258235	0.025470
H	1.750686	-2.669296	-1.216107

PhBr

E_{gas} optimization: -2802.85097382 a.u.

E_{sol} single-point: -2805.68987779 a.u.

G_{sol} thermo-corrected: -2805.63002279 a.u.

C	-2.170587	-1.204471	-0.000001
C	-0.778510	-1.212658	0.000022
C	-0.095571	-0.000035	-0.000013
C	-0.778489	1.212645	0.000001
C	-2.170531	1.204505	0.000019
C	-2.869244	0.000014	-0.000019
H	-2.707705	-2.148607	-0.000017
H	-0.226590	-2.146608	0.000022
H	-0.226469	2.146535	-0.000001
H	-2.707671	2.148629	0.000011

H	-3.954993	0.000062	-0.000025
Br	1.800029	0.000000	-0.000001

²TS1

E_{gas} optimization: -4490.51604383 a.u.

E_{sol} single-point: -4493.70127814 a.u.

G_{sol} thermo-corrected: -4493.08960114 a.u.

Ni	0.797736	-0.484005	-0.353754
C	-2.149529	-0.544456	-0.361752
C	-1.372981	-2.559691	0.429393
C	-2.657390	-3.034218	0.655581
C	-3.756491	-2.250268	0.288175
C	-3.466931	-0.987248	-0.222944
C	-1.804790	0.844556	-0.677855
C	-0.094194	2.354930	-1.033236
C	-0.974645	3.426293	-1.056919
C	-2.344723	3.203980	-0.871108
C	-2.740324	1.879215	-0.681997
H	-0.507119	-3.161911	0.693543
H	-2.783441	-4.013327	1.104212
H	-4.280004	-0.320382	-0.497312
H	0.978023	2.495816	-1.144917
H	-0.580998	4.425949	-1.204240
H	-3.787600	1.656125	-0.492856
N	-1.098413	-1.365224	-0.103433
N	-0.482537	1.086646	-0.855013
C	-3.380503	4.321276	-0.823656
C	-5.204217	-2.694971	0.457871
C	-4.050009	4.317932	0.558279
H	-4.799128	5.114751	0.620677
H	-4.557657	3.369044	0.761182
H	-3.315848	4.479889	1.354449
C	-2.752063	5.693350	-1.058543
H	-2.008256	5.937060	-0.293295
H	-2.265355	5.755885	-2.037348
H	-3.525051	6.467122	-1.024791
C	-4.444473	4.076281	-1.901464
H	-5.205171	4.863731	-1.871448
H	-4.001965	4.072417	-2.902525
H	-4.954741	3.118479	-1.759155
C	-5.910875	-1.733773	1.424166
H	-5.904902	-0.704278	1.051060
H	-6.956081	-2.031440	1.560374
H	-5.427501	-1.732740	2.406546
C	-5.303571	-4.112187	1.018847
H	-4.819047	-4.843937	0.364192
H	-4.848913	-4.191009	2.011656
H	-6.354412	-4.401111	1.115729
C	-5.909280	-2.654297	-0.903983
H	-5.901089	-1.649533	-1.337397
H	-5.430059	-3.329441	-1.619738
H	-6.955454	-2.960702	-0.798720
N	2.671395	0.056794	1.670531
H	3.143284	0.223211	2.550501
C	1.278467	-0.326677	1.666609
C	0.431538	0.778532	2.099568
O	0.748120	1.960887	2.145112
O	-0.848092	0.365174	2.396531
C	-1.728171	1.431499	2.764421
H	-1.364310	1.901068	3.687170
H	-1.703666	2.209645	1.990070
C	-3.108347	0.853258	2.934209
H	-3.108783	0.040132	3.666194
H	-3.806396	1.622751	3.277365
H	-3.483568	0.449578	1.988333

C	3.178191	0.681179	0.594313
O	2.537154	0.761484	-0.479934
C	4.556530	1.221427	0.676775
C	4.937027	2.215999	-0.229281
C	5.495154	0.735532	1.594629
C	6.223951	2.738393	-0.197878
H	4.203592	2.563822	-0.950144
C	6.785878	1.252159	1.617731
H	5.227562	-0.076613	2.266954
C	7.149922	2.259794	0.727119
H	6.508705	3.518143	-0.898518
H	7.511574	0.861946	2.325577
H	8.157819	2.664746	0.748224
H	1.103977	-1.277574	2.173313
C	3.438311	-4.124019	0.611895
C	4.088088	-2.969885	0.164605
C	3.453799	-2.076075	-0.684428
C	2.103423	-2.289412	-1.026856
C	1.498743	-3.519597	-0.702763
C	2.150547	-4.401639	0.148045
H	3.947060	-4.821404	1.270181
H	5.112270	-2.766901	0.470479
H	3.967318	-1.194840	-1.052111
H	0.520789	-3.755399	-1.108760
H	1.655467	-5.327267	0.433272
Br	1.412444	-1.396865	-2.698758

²IM2

E_{gas} optimization: -4490.55442911 a.u.

E_{sol} single-point: -4493.74259314 a.u.

G_{sol} thermo-corrected: -4493.12817614 a.u.

Ni	0.755955	-1.040717	-0.401231
C	-2.019098	-0.010936	-0.283832
C	-2.083293	-2.256787	0.206947
C	-3.470473	-2.247556	0.311052
C	-4.173904	-1.063760	0.085314
C	-3.406941	0.068337	-0.203295
C	-1.161061	1.157530	-0.540206
C	0.978073	1.909057	-0.966374
C	0.557696	3.230869	-1.021873
C	-0.782345	3.541073	-0.791880
C	-1.642484	2.462298	-0.579090
H	-1.513061	-3.167211	0.373577
H	-3.982749	-3.170340	0.560109
H	-3.901659	1.019361	-0.379696
H	2.014768	1.635728	-1.139007
H	1.291120	4.004094	-1.220701
H	-2.698830	2.646419	-0.406115
N	-1.367871	-1.178840	-0.106021
N	0.154226	0.895401	-0.700021
C	-1.317530	4.964376	-0.717591
C	-5.693680	-0.961032	0.140820
C	-1.871001	5.187102	0.698161
H	-2.227030	6.216644	0.809870
H	-2.712309	4.519954	0.912789
H	-1.102793	5.003600	1.456334
C	-0.227712	5.999028	-0.989111
H	0.583769	5.938069	-0.256992
H	0.204663	5.883565	-1.988379
H	-0.649710	7.006455	-0.928105
C	-2.442518	5.150273	-1.743166
H	-2.848533	6.165025	-1.678053
H	-2.080355	4.996477	-2.764307
H	-3.269755	4.453897	-1.574344
C	-6.096536	0.051309	1.221825

H	-5.642408	1.033787	1.054689
H	-7.183311	0.184633	1.227528
H	-5.794759	-0.289485	2.217203
C	-6.344271	-2.304150	0.464815
H	-6.114273	-3.061993	-0.290852
H	-6.024396	-2.686878	1.439684
H	-7.431929	-2.191560	0.497292
C	-6.207274	-0.478587	-1.222766
H	-5.810474	0.507565	-1.482561
H	-5.925440	-1.171138	-2.021584
H	-7.299509	-0.403074	-1.209186
N	2.526702	-0.078373	1.604389
H	2.773510	0.566855	2.344444
C	1.169595	-0.585379	1.604860
C	0.277229	0.436189	2.168860
O	0.536334	1.626779	2.284669
O	-0.913149	-0.091741	2.561683
C	-1.863059	0.861151	3.057156
H	-1.389905	1.476229	3.830139
H	-2.143404	1.544862	2.241338
C	-3.044398	0.086461	3.574684
H	-2.755348	-0.560749	4.406527
H	-3.825607	0.767135	3.924536
H	-3.467143	-0.545448	2.787369
C	3.264347	-0.025852	0.475715
O	2.840304	-0.491969	-0.601095
C	4.603181	0.607610	0.542445
C	5.209709	0.975571	-0.663657
C	5.274752	0.840587	1.748253
C	6.455790	1.589094	-0.661540
H	4.684876	0.760468	-1.589858
C	6.524126	1.450142	1.746940
H	4.840296	0.514675	2.690049
C	7.113361	1.830830	0.543312
H	6.918975	1.875028	-1.601370
H	7.043060	1.619872	2.685789
H	8.089998	2.306624	0.544470
H	1.082074	-1.542358	2.124320
C	1.901519	-5.630813	0.275003
C	2.638825	-4.630415	0.899394
C	2.309882	-3.286763	0.709663
C	1.241446	-2.918584	-0.111786
C	0.522069	-3.930555	-0.756134
C	0.842171	-5.274176	-0.553860
H	2.156234	-6.676846	0.424263
H	3.476806	-4.888638	1.543616
H	2.906090	-2.533868	1.218812
H	-0.269174	-3.671910	-1.454276
H	0.269027	-6.041256	-1.070629
Br	0.498439	-1.356494	-2.816832

²TS2

E_{gas} optimization: -4490.52635500 a.u.

E_{sol} single-point: -4493.71550325 a.u.

G_{sol} thermo-corrected: -4493.10068225 a.u.

Ni	0.765371	-0.491069	-0.100929
C	-2.183054	-0.396570	-0.204534
C	-1.457607	-2.575564	-0.064989
C	-2.745373	-3.067662	-0.229708
C	-3.816166	-2.182184	-0.372202
C	-3.499385	-0.822680	-0.372933
C	-1.777739	1.012474	-0.312352
C	-0.012947	2.461109	-0.622825
C	-0.860007	3.563240	-0.649183
C	-2.232362	3.388914	-0.461638

C	-2.678725	2.073483	-0.303729
H	-0.605047	-3.242793	0.023905
H	-2.893263	-4.141388	-0.257971
H	-4.280235	-0.086054	-0.541617
H	1.062315	2.565839	-0.728118
H	-0.431337	4.548720	-0.793107
H	-3.736007	1.876327	-0.145561
N	-1.174497	-1.271738	-0.009681
N	-0.447274	1.212253	-0.439590
C	-3.224984	4.542633	-0.388815
C	-5.261281	-2.630914	-0.552162
C	-3.862042	4.546468	1.008422
H	-4.582794	5.366305	1.096587
H	-4.394506	3.611996	1.214025
H	-3.104082	4.677854	1.788283
C	-2.551423	5.892777	-0.624840
H	-1.785861	6.104232	0.128469
H	-2.080637	5.945654	-1.611767
H	-3.295373	6.693205	-0.571122
C	-4.319374	4.346361	-1.445653
H	-5.045039	5.164852	-1.395295
H	-3.898111	4.330151	-2.455449
H	-4.867471	3.410735	-1.298120
C	-6.113617	-2.033089	0.575394
H	-6.082351	-0.938897	0.572415
H	-7.160107	-2.334494	0.460424
H	-5.770239	-2.374141	1.557294
C	-5.395637	-4.151795	-0.514852
H	-4.833069	-4.630695	-1.322463
H	-5.047443	-4.568846	0.435757
H	-6.445874	-4.434419	-0.633770
C	-5.781080	-2.123633	-1.904055
H	-5.751369	-1.031626	-1.968696
H	-5.187448	-2.521928	-2.732298
H	-6.820536	-2.435832	-2.050382
N	3.257343	0.299749	1.496203
H	4.054487	-0.070663	1.990800
C	1.963507	-0.140130	1.904566
C	1.021810	1.001633	2.099337
O	1.271475	2.173829	1.885823
O	-0.156241	0.564681	2.626985
C	-1.100557	1.610965	2.915004
H	-0.718197	2.208905	3.751503
H	-1.166474	2.282104	2.050459
C	-2.419440	0.963271	3.237931
H	-2.335078	0.297870	4.101007
H	-3.167263	1.727433	3.468516
H	-2.785132	0.373246	2.391561
C	3.436928	0.671980	0.201889
O	2.463990	0.731630	-0.569261
C	4.807087	0.951491	-0.263512
C	5.073325	0.785708	-1.628003
C	5.827751	1.359549	0.602659
C	6.354835	1.010901	-2.113685
H	4.262409	0.466140	-2.277597
C	7.105731	1.593708	0.108116
H	5.611548	1.531729	1.654720
C	7.370835	1.414998	-1.248305
H	6.563782	0.870735	-3.170138
H	7.893873	1.923477	0.778745
H	8.370889	1.596090	-1.632243
H	2.038203	-0.686277	2.839591
C	2.370796	-4.581279	1.474852
C	3.156939	-3.776349	0.649289
C	2.832843	-2.441538	0.437598
C	1.671765	-1.887514	1.007848
C	0.911557	-2.697307	1.875033

C	1.247077	-4.029735	2.089114
H	2.636524	-5.620783	1.643340
H	4.025207	-4.196627	0.147303
H	3.435934	-1.851295	-0.249083
H	0.050317	-2.263728	2.382063
H	0.633287	-4.636195	2.751951
Br	0.941670	-1.517779	-2.368551

²IM3

E_{gas} optimization: -4490.59050848 a.u.

E_{sol} single-point: -4493.77747703 a.u.

G_{sol} thermo-corrected: -4493.16228903 a.u.

Ni	0.794206	-0.270006	-1.133632
C	-2.041990	-0.368064	-0.821550
C	-1.208206	-2.495023	-1.193265
C	-2.442722	-3.072677	-0.935429
C	-3.531663	-2.266645	-0.582779
C	-3.306223	-0.887845	-0.559642
C	-1.701438	1.054295	-0.777331
C	0.036898	2.586601	-0.740187
C	-0.846135	3.653406	-0.693446
C	-2.230013	3.423117	-0.689899
C	-2.634390	2.086023	-0.727891
H	-0.336214	-3.084074	-1.471997
H	-2.537710	-4.151597	-0.996319
H	-4.117578	-0.210192	-0.302007
H	1.112468	2.736383	-0.719115
H	-0.443222	4.659322	-0.652031
H	-3.694209	1.840077	-0.727176
N	-0.989352	-1.177079	-1.110079
N	-0.359579	1.302729	-0.794063
C	-3.267548	4.536666	-0.616743
C	-4.897603	-2.821015	-0.197650
C	-4.070057	4.379098	0.682716
H	-4.828017	5.165703	0.764481
H	-4.586787	3.414226	0.724319
H	-3.416749	4.448148	1.559908
C	-2.621757	5.920837	-0.625925
H	-1.962796	6.069848	0.235580
H	-2.035143	6.089660	-1.534706
H	-3.395979	6.692952	-0.584604
C	-4.220160	4.431364	-1.814625
H	-4.979299	5.219519	-1.767651
H	-3.680278	4.538202	-2.760447
H	-4.743243	3.470419	-1.837056
C	-5.196467	-2.411641	1.252228
H	-5.236966	-1.323344	1.366244
H	-6.162952	-2.815544	1.572790
H	-4.426384	-2.787784	1.934370
C	-4.942938	-4.344584	-0.293545
H	-4.742459	-4.695005	-1.311197
H	-4.216224	-4.815760	0.376522
H	-5.935794	-4.706450	-0.009648
C	-5.973155	-2.237009	-1.122147
H	-6.008501	-1.144502	-1.066801
H	-5.791191	-2.511962	-2.165716
H	-6.962448	-2.613736	-0.841056
N	3.123842	0.113347	1.958670
H	3.925600	-0.209694	2.475902
C	1.817650	-0.162226	2.519750
C	0.898672	1.054814	2.327333
O	1.287992	2.194355	2.222337
O	-0.386651	0.694367	2.451927
C	-1.333109	1.780618	2.519153
H	-1.064698	2.422394	3.366641

H	-1.240351	2.387352	1.613330
C	-2.697972	1.165120	2.666616
H	-2.772229	0.576034	3.585009
H	-3.463546	1.945232	2.697283
H	-2.915398	0.502745	1.822820
C	3.329981	0.522912	0.676583
O	2.395736	0.735602	-0.106269
C	4.741636	0.689806	0.262100
C	5.056460	0.444970	-1.079584
C	5.745139	1.082560	1.155769
C	6.370872	0.574898	-1.511530
H	4.263834	0.115647	-1.749743
C	7.054426	1.227997	0.711656
H	5.493868	1.318663	2.187815
C	7.368525	0.968529	-0.621053
H	6.618032	0.366586	-2.548364
H	7.828304	1.550711	1.402250
H	8.393136	1.077317	-0.966049
H	1.964914	-0.165795	3.610777
C	0.191067	-4.049742	1.549900
C	1.236440	-3.527587	0.797727
C	1.760175	-2.270773	1.097763
C	1.240841	-1.519858	2.151093
C	0.193875	-2.056583	2.909699
C	-0.332408	-3.306938	2.608017
H	-0.218938	-5.028737	1.314045
H	1.647871	-4.073082	-0.047588
H	2.572800	-1.890682	0.487016
H	-0.216313	-1.484070	3.737645
H	-1.146147	-3.706970	3.207704
Br	2.203942	-1.743088	-2.367727

product

E_{gas} optimization: -938.409767239 a.u.

E_{sol} single-point: -938.641300973 a.u.

G_{sol} thermo-corrected: -938.382683973 a.u.

N	0.599384	0.267364	-1.028799
H	1.054081	0.977751	-1.578696
C	-0.837685	0.098381	-1.213081
C	-1.175045	-1.380068	-0.976037
O	-0.609919	-2.278627	-1.555441
O	-2.196447	-1.535450	-0.126530
C	-2.493217	-2.909106	0.197739
H	-2.756502	-3.440816	-0.723016
H	-1.577465	-3.368001	0.586197
C	-3.609856	-2.898166	1.204304
H	-4.506178	-2.426115	0.794339
H	-3.865249	-3.919632	1.496830
H	-3.318115	-2.347807	2.102138
C	1.271784	-0.302025	0.014196
O	0.700788	-0.996691	0.854045
C	2.736742	-0.032252	0.077264
C	3.371621	-0.233071	1.306543
C	3.494536	0.382650	-1.023220
C	4.733664	0.002441	1.441335
H	2.768535	-0.578133	2.140870
C	4.860261	0.610325	-0.889808
H	3.031541	0.488211	-2.001616
C	5.480174	0.428048	0.343942
H	5.217123	-0.148961	2.402217
H	5.443129	0.920616	-1.752238
H	6.546522	0.608244	0.447282
H	-1.015936	0.241003	-2.287241
C	-3.204576	3.045020	0.858223
C	-2.374986	2.187458	1.580805

C	-1.613670	1.226563	0.927124
C	-1.669723	1.114193	-0.467070
C	-2.501971	1.975603	-1.182406
C	-3.268954	2.936239	-0.526558
H	-3.798565	3.793786	1.374971
H	-2.326226	2.265800	2.663614
H	-0.980280	0.543672	1.485694
H	-2.550131	1.892254	-2.267298
H	-3.911924	3.599321	-1.098816

²IM4

E_{gas} optimization: -3552.14673820 a.u.

E_{sol} single-point: -3555.11214846 a.u.

G_{sol} thermo-corrected: -3554.78393346 a.u.

Ni	1.789906	-1.535983	-0.000114
C	0.077184	0.732459	-0.000218
C	2.292017	1.410895	0.000297
C	1.929910	2.749899	0.000463
C	0.576235	3.106858	0.000175
C	-0.346950	2.057929	-0.000234
C	-0.809108	-0.432661	-0.000293
C	-0.903924	-2.747240	-0.000295
C	-2.287635	-2.736160	-0.000140
C	-2.982487	-1.518948	-0.000057
C	-2.197561	-0.363541	-0.000175
H	3.333796	1.099397	0.000420
H	2.710233	3.502596	0.000834
H	-1.411437	2.278055	-0.000574
H	-0.351873	-3.683154	-0.000374
H	-2.814194	-3.684135	-0.000053
H	-2.676979	0.612243	-0.000114
N	1.398024	0.414471	-0.000012
N	-0.150931	-1.631002	-0.000342
C	-4.502437	-1.416560	0.000162
C	0.089941	4.551427	0.000008
C	-4.956761	-0.652142	-1.250877
H	-6.048008	-0.561286	-1.264570
H	-4.541043	0.359798	-1.283168
H	-4.649249	-1.168204	-2.165642
C	-5.166041	-2.792274	0.000391
H	-4.896656	-3.375775	-0.885981
H	-4.896332	-3.375631	0.886760
H	-6.254178	-2.679596	0.000581
C	-4.956397	-0.651914	1.251193
H	-6.047640	-0.561066	1.265193
H	-4.648610	-1.167802	2.165963
H	-4.540684	0.360037	1.283178
C	-0.763228	4.793967	-1.252573
H	-1.635700	4.134039	-1.285712
H	-1.128857	5.826026	-1.267428
H	-0.184333	4.627739	-2.166321
C	1.249833	5.545095	0.001992
H	1.881830	5.433617	0.888943
H	1.883866	5.434839	-0.883654
H	0.861578	6.567810	0.002207
C	-0.766861	4.793395	1.250202
H	-1.639629	4.133728	1.280469
H	-0.190701	4.626564	2.165566
H	-1.132304	5.825524	1.264533
Br	3.906163	-2.332144	0.000129

IM5

E_{gas} optimization: -3783.67571267 a.u.

E_{sol} single-point: -3786.68839173 a.u.

G_{sol} thermo-corrected: -3786.27693073 a.u.

Ni	0.933223	-1.199242	-0.391976
C	-1.011494	0.776377	-0.022252
C	1.074243	1.768544	0.057071
C	0.527353	3.034975	-0.064623
C	-0.861475	3.197278	-0.166997
C	-1.616541	2.022084	-0.151420
C	-1.737378	-0.487407	-0.050021
C	-1.557450	-2.776865	-0.342089
C	-2.903118	-2.961214	-0.075573
C	-3.724903	-1.861293	0.209603
C	-3.095162	-0.615254	0.222224
H	2.150897	1.635887	0.146054
H	1.194638	3.890424	-0.066116
H	-2.696779	2.069016	-0.274039
H	-0.916335	-3.618848	-0.585909
H	-3.304258	-3.968569	-0.109137
H	-3.662698	0.278068	0.474586
N	0.347314	0.632566	0.091301
N	-0.951731	-1.570488	-0.350103
C	-5.213929	-1.975286	0.511291
C	-1.545327	4.550937	-0.311325
C	-6.002235	-1.127597	-0.496290
H	-7.076164	-1.187191	-0.288415
H	-5.714946	-0.072428	-0.450828
H	-5.836374	-1.473757	-1.521317
C	-5.705014	-3.419020	0.423113
H	-5.551881	-3.841302	-0.575475
H	-5.198967	-4.066633	1.146539
H	-6.777186	-3.461482	0.637940
C	-5.484270	-1.451765	1.928575
H	-6.552704	-1.516472	2.162114
H	-4.938428	-2.034729	2.676993
H	-5.183904	-0.405074	2.038484
C	-2.311114	4.592089	-1.640886
H	-3.072868	3.808067	-1.694421
H	-2.818118	5.555995	-1.759866
H	-1.635470	4.457770	-2.491374
C	-0.541143	5.701819	-0.291381
H	0.025052	5.731974	0.645402
H	0.174096	5.632540	-1.117468
H	-1.066385	6.656764	-0.390065
C	-2.535744	4.744637	0.844863
H	-3.301804	3.962912	0.857313
H	-2.024452	4.725131	1.812494
H	-3.048045	5.708526	0.752146
C	4.333583	-0.846306	0.162246
C	3.894385	-0.105278	1.247019
C	5.658082	-0.853086	-0.244339
C	4.818810	0.667847	1.947256
H	2.838824	-0.140014	1.524231
C	6.574250	-0.074593	0.463302
H	5.973481	-1.449235	-1.096936
C	6.156596	0.683861	1.555048
H	4.493578	1.255078	2.802606
H	7.617525	-0.061075	0.157798
H	6.875233	1.287068	2.102351
Br	2.971117	-1.952203	-0.829007

TS3

E_{gas} optimization: -3783.66395085 a.u.

E_{sol} single-point: -3786.67639143 a.u.

G_{sol} thermo-corrected: -3786.26565243 a.u.

Ni	1.060167	-1.260426	-0.370058
C	-0.773085	0.829653	-0.198786
C	1.375795	1.691806	-0.125046
C	0.900639	2.992944	-0.113868
C	-0.479104	3.241181	-0.149770
C	-1.304223	2.115514	-0.204188
C	-1.576027	-0.387718	-0.268863
C	-1.580806	-2.651919	-0.734813
C	-2.920431	-2.767113	-0.400789
C	-3.638343	-1.641188	0.026348
C	-2.918858	-0.444614	0.088267
H	2.443767	1.485648	-0.089082
H	1.617148	3.806053	-0.064145
H	-2.383171	2.235730	-0.276653
H	-1.020874	-3.517132	-1.081668
H	-3.398567	-3.736900	-0.492753
H	-3.402485	0.460958	0.449439
N	0.576953	0.606097	-0.147341
N	-0.883931	-1.498122	-0.683744
C	-5.107916	-1.677357	0.426140
C	-1.085007	4.639319	-0.150684
C	-5.896550	-0.690474	-0.445404
H	-6.955329	-0.692549	-0.163859
H	-5.526928	0.333714	-0.333704
H	-5.827719	-0.955213	-1.505249
C	-5.712130	-3.069572	0.253389
H	-5.656818	-3.411283	-0.785473
H	-5.209887	-3.812497	0.881609
H	-6.768147	-3.056172	0.540420
C	-5.242295	-1.264675	1.898427
H	-6.294377	-1.276102	2.204419
H	-4.692007	-1.948127	2.552721
H	-4.856906	-0.255260	2.072877
C	-1.896004	4.839440	-1.438312
H	-2.705177	4.107777	-1.525844
H	-2.348024	5.837389	-1.454199
H	-1.261641	4.741066	-2.324818
C	-0.013775	5.725716	-0.076562
H	0.586053	5.644630	0.835919
H	0.666501	5.685607	-0.933564
H	-0.484164	6.713864	-0.075370
C	-2.018086	4.788566	1.058550
H	-2.828967	4.053659	1.037048
H	-1.473094	4.654912	1.998359
H	-2.473932	5.784750	1.070075
C	3.731432	-1.053458	0.247472
C	3.779358	-0.599438	1.569799
C	4.422486	-0.395741	-0.775668
C	4.485998	0.561698	1.850731
H	3.246533	-1.134255	2.349343
C	5.125197	0.765826	-0.466652
H	4.390767	-0.778070	-1.790600
C	5.163877	1.252307	0.839514
H	4.514646	0.926855	2.873892
H	5.654331	1.287987	-1.259648
H	5.717559	2.156534	1.071298
Br	2.807493	-2.703191	-0.167342

IM6

E_{gas} optimization: -3783.76060586 a.u.

E_{sol} single-point: -3786.77672801 a.u.

G_{sol} thermo-corrected: -3786.36184601 a.u.

Ni	1.399351	-0.958813	-0.000377
C	-0.673477	0.948995	-0.000227
C	1.392458	1.989772	-0.001156

C	0.804632	3.244905	-0.000779
C	-0.586105	3.377043	0.000034
C	-1.311324	2.183712	0.000264
C	-1.380199	-0.331483	-0.000210
C	-1.118021	-2.626315	-0.000692
C	-2.492031	-2.824986	-0.000658
C	-3.360323	-1.730638	-0.000328
C	-2.764716	-0.466664	-0.000109
H	2.471374	1.877271	-0.001726
H	1.453525	4.113610	-0.001097
H	-2.397338	2.213975	0.000863
H	-0.409042	-3.451710	-0.000820
H	-2.868619	-3.841803	-0.000887
H	-3.389281	0.422313	0.000086
N	0.688238	0.842720	-0.000844
N	-0.558749	-1.410455	-0.000456
C	-4.878534	-1.859659	-0.000200
C	-1.309013	4.717355	0.000576
C	-5.440147	-1.170879	-1.251505
H	-6.532378	-1.245937	-1.265917
H	-5.181912	-0.107720	-1.282782
H	-5.057937	-1.634369	-2.166218
C	-5.327426	-3.319483	-0.000513
H	-4.973414	-3.855475	-0.886932
H	-4.973224	-3.855909	0.885569
H	-6.420102	-3.371024	-0.000405
C	-5.439840	-1.171508	1.251593
H	-6.532069	-1.246560	1.266232
H	-5.057412	-1.635464	2.165977
H	-5.181573	-0.108369	1.283338
C	-2.193216	4.811567	-1.250453
H	-2.941916	4.013818	-1.281943
H	-2.728190	5.766806	-1.263987
H	-1.596534	4.745855	-2.165455
C	-0.331773	5.891158	0.000355
H	0.311142	5.887632	0.886416
H	0.310350	5.887965	-0.886281
H	-0.885635	6.834458	0.000772
C	-2.192158	4.811181	1.252377
H	-2.940861	4.013452	1.284256
H	-1.594707	4.745163	2.166855
H	-2.727094	5.766429	1.266662
C	3.188758	-0.383752	-0.000472
C	3.842165	-0.095868	1.202881
C	3.842353	-0.096083	-1.203766
C	5.103539	0.501492	1.202595
H	3.366056	-0.337540	2.151826
C	5.103746	0.501256	-1.203375
H	3.366381	-0.337868	-2.152754
C	5.735848	0.808487	-0.000371
H	5.595124	0.722919	2.147906
H	5.595502	0.722474	-2.148645
H	6.718771	1.272378	-0.000339
Br	2.166331	-3.126099	0.001255

³IM7

E_{gas} optimization: -4490.55064474 a.u.

E_{sol} single-point: -4493.73991712 a.u.

G_{sol} thermo-corrected: -4493.12480512 a.u.

Ni	0.360214	-1.214357	-0.552073
C	-1.923797	0.675254	-0.523793
C	-2.732154	-1.482280	-0.411039
C	-4.041114	-1.038059	-0.284341
C	-4.313202	0.331720	-0.264222
C	-3.213293	1.183735	-0.389233

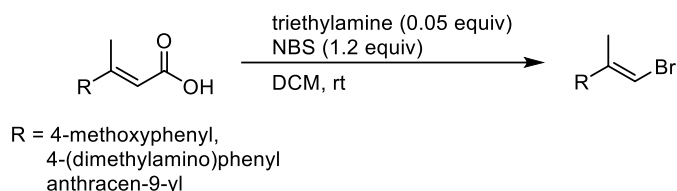
C	-0.725887	1.521747	-0.615297
C	1.581323	1.548385	-0.671682
C	1.612382	2.935959	-0.693336
C	0.417049	3.658566	-0.705699
C	-0.762928	2.911528	-0.677173
H	-2.492849	-2.542643	-0.401600
H	-4.832576	-1.772648	-0.184061
H	-3.360170	2.259225	-0.354682
H	2.492308	0.953815	-0.706746
H	2.576726	3.431957	-0.710182
H	-1.721417	3.421794	-0.696183
N	-1.687072	-0.658937	-0.546342
N	0.443771	0.848120	-0.619735
C	0.357148	5.180319	-0.752582
C	-5.710623	0.905743	-0.070089
C	-0.405041	5.690866	0.477807
H	-0.459821	6.784237	0.459988
H	-1.430196	5.309361	0.510763
H	0.090841	5.391669	1.406192
C	1.750628	5.805529	-0.760718
H	2.320586	5.543797	0.136708
H	2.332320	5.496644	-1.635063
H	1.667012	6.895807	-0.790308
C	-0.384772	5.612472	-2.024714
H	-0.442714	6.704703	-2.074605
H	0.128765	5.260034	-2.924473
H	-1.408379	5.226061	-2.051336
C	-5.723034	1.744041	1.216174
H	-5.006738	2.570264	1.173909
H	-6.716997	2.173574	1.378000
H	-5.474053	1.132779	2.090097
C	-6.764912	-0.192512	0.054055
H	-6.810180	-0.820518	-0.841502
H	-6.576967	-0.841576	0.916363
H	-7.753083	0.255941	0.191163
C	-6.062626	1.800681	-1.265306
H	-5.357596	2.630428	-1.375473
H	-6.060500	1.233901	-2.201403
H	-7.060608	2.231120	-1.133952
N	1.861817	-0.511491	1.657144

H	1.739103	0.491418	1.703696
C	0.664554	-1.246489	1.515415
C	-0.467161	-0.536498	2.110070
O	-0.519818	0.677335	2.277733
O	-1.491625	-1.368205	2.417147
C	-2.660528	-0.709069	2.930214
H	-2.387627	-0.150761	3.832778
H	-3.003649	0.030564	2.194631
C	-3.695825	-1.766035	3.202863
H	-3.336005	-2.489105	3.938720
H	-4.611235	-1.311121	3.592414
H	-3.947157	-2.313672	2.289999
C	3.102012	-1.059039	1.447160
O	3.266624	-2.268372	1.325894
C	4.220058	-0.080787	1.324535
C	5.361835	-0.509488	0.640313
C	4.172440	1.227977	1.820952
C	6.428797	0.357848	0.440726
H	5.373947	-1.528091	0.264511
C	5.245472	2.092116	1.628396
H	3.310852	1.574249	2.389029
C	6.373211	1.660491	0.932884
H	7.306133	0.019074	-0.102942
H	5.204810	3.101599	2.028945
H	7.208893	2.337798	0.779497
H	0.771923	-2.289412	1.795153
C	-0.364533	-5.842060	-1.143084
C	0.515542	-5.451234	-0.137760
C	0.776595	-4.100317	0.097506
C	0.134271	-3.123703	-0.662963
C	-0.708603	-3.519670	-1.706652
C	-0.968971	-4.871616	-1.936730
H	-0.560183	-6.895939	-1.322480
H	1.021260	-6.201937	0.465462
H	1.518805	-3.821164	0.841021
H	-1.160017	-2.773800	-2.360546
H	-1.632092	-5.160029	-2.749621
Br	2.216446	-1.414687	-2.021814

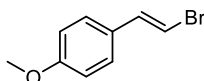
Part 5. Substrate Preparation

A. Preparation of vinyl bromides

(1) The following procedure was used to prepare (*E*)-1-(2-bromovinyl)-4-methoxybenzene, (*E*)-4-(2-bromovinyl)-*N,N*-dimethylaniline, and (*E*)-9-(2-bromovinyl)anthracene.^{10,11}



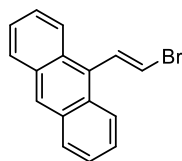
To a solution of acrylic acid (10 mmol, 1.0 equiv) in CH_2Cl_2 (80 mL, technical grade) was added NEt_3 (0.5 mmol, 0.05 equiv). The mixture was stirred for 5 min at room temperature, and NBS (12 mmol, 1.2 equiv) was added in separate portions. After 20 min, CO_2 evolution stopped, indicating the completion of the reaction. CH_2Cl_2 was evaporated under reduced pressure and the remaining slush was purified by flash column chromatography over silica gel.



(*E*)-1-(2-Bromovinyl)-4-methoxybenzene.^{10,11}

This compound was prepared from (*E*)-3-(4-methoxyphenyl)acrylic acid (1.78 g, 10.0 mmol). The crude residue was purified by silica gel chromatography (SiO_2 : 5% ethyl acetate in petroleum ether) to yield the vinyl bromide as a colorless solid (1.69 g, 8.0 mmol, 80% yield).

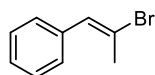
¹H NMR (600 MHz, CDCl_3) δ 7.26 (d, J = 8.9 Hz, 2H), 7.07 (d, J = 13.9 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 13.9 Hz, 1H), 3.83 (s, 3H).



(*E*)-9-(2-Bromovinyl)anthracene.¹²

This compound was prepared from (*E*)-3-(anthracen-9-yl)acrylic acid (2.48 g, 10.0 mmol). The crude residue was purified by silica gel chromatography to yield the vinyl bromide as a yellow solid (1.41 g, 5.0 mmol, 50% yield).

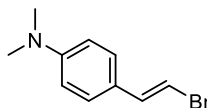
¹H NMR (600 MHz, CDCl₃) δ 8.43 (s, 1H), 8.23 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 14.2 Hz, 1H), 7.55 – 7.46 (m, 4H), 6.62 (d, *J* = 14.2 Hz, 1H).



(*E*)-(2-Bromoprop-1-en-1-yl)benzene.¹³

This compound was prepared from (*E*)-2-methyl-3-phenylacrylic acid (1.62 g, 10.0 mmol). The crude residue was purified by silica gel chromatography to yield the vinyl bromide as colorless oil (1.37 g, 7.0 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.41 – 7.37 (m, 2H), 7.32 – 7.29 (m, 1H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.01 (s, 1H), 2.50 (d, *J* = 1.4 Hz, 3H).



(*E*)-4-(2-Bromovinyl)-*N,N*-dimethylaniline.¹⁴

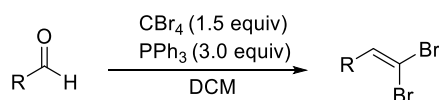
This compound was prepared from (*E*)-3-(4-(dimethylamino)phenyl)acrylic acid (1.9 g, 10.0 mmol). The crude residue was purified by silica gel chromatography to yield the vinyl bromide as colorless solid (1.1 g, 5.0 mmol, 50% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.18 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 13.9 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 2H), 6.50 (d, *J* = 13.2 Hz, 1H), 2.96 (s, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 150.3, 136.9, 130.3, 127.1, 112.3, 101.5, 40.4.

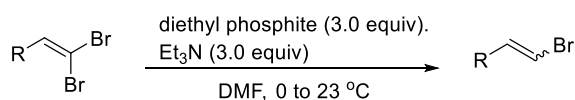
(2) The following procedure was used to prepare (*E*)-(2-bromovinyl)cyclohexane, (*E*)-(4-bromobut-3-en-1-yl)benzene, (*E*)-1-(2-bromovinyl)-2,3-dimethylbenzene, (*E*)-1-(2-bromovinyl)-2-methoxybenzene, (*E*)-1-(2-bromovinyl)-4-(trifluoromethyl)benzene, (*E*)-2-(2-bromovinyl)furan, (*E*)-2-(2-bromovinyl)naphthalene, (*E*)-2-(2-bromovinyl)thiophene, (*E*)-6-(2-bromovinyl)-2,3-dihydrobenzo[*b*][1,4]dioxine.

Step 1: The Ramirez protocol for the Wittig-type dibromoolefination.¹⁵



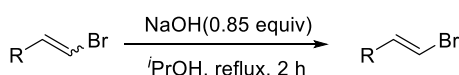
To a flame-dried flask was added aldehyde (20 mmol, 1.0 equiv), CBr₄ (30 mmol, 1.5 equiv), and DCM (80 mL). The flask was cooled to 0 °C, then a solution of PPh₃ (60 mmol, 3.0 equiv) in DCM (70 mL) was added dropwise via addition funnel over 30 min. The solution was stirred at 0 °C under N₂ for 1 h. About half of the volume of DCM was removed under reduced pressure. Pentane (100 mL) was added, and triphenylphosphine oxide (TPPO) precipitated out. After filtration and evaporation of the solvent, the residue was dissolved in pentane (50 mL) which led to further precipitation of TPPO. Filtration and evaporation of the solvent afforded the crude dibromide which was directly used for the next step.

Step 2: Hayes protocol of the Hiraio reaction.¹⁶

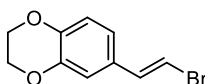


To a solution of the crude dibromide (~20.0 mmol, 1.0 equiv) and NEt₃ (60 mmol, 3.0 equiv) in DMF (20 mL) was added dimethyl phosphonate (60.0 mmol, 3.0 equiv). The solution was stirred over night at room temperature. Water was added to the mixture. The aqueous layer was extracted with DCM and the combined organic layers were washed with brine and dried (Na₂SO₄), filtered, and concentrated. The crude material was purified by flash chromatography.

Step 3: Selective destruction of the (Z)-isomer as reported by Dolby.¹⁷



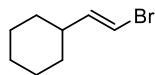
The crude product (~20.0 mmol, 1.0 equiv) from the previous step was dissolved in *i*-PrOH (30 mL). Solid NaOH (17.0 mmol, 0.85 equiv) was added and the mixture was heated to reflux for 2 hours. The reaction mixture was cooled to room temperature, diluted with pentane (100 mL), and partitioned with distilled H₂O. The organic phase was collected, and washed with an aqueous solution of HCl (1M, 75 mL), dried over Na₂SO₄. The solvent was removed under reduced pressure. The crude material was purified by flash chromatography.



(E)-6-(2-Bromovinyl)-2,3-dihydrobenzo[b][1,4]dioxine.²

This compound was prepared from 2,3-dihydrobenzo[b][1,4]dioxine-6-carbaldehyde (3.28 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: 5% ethyl acetate in petroleum ether) to yield the (*E*)-vinyl bromide as a white solid (3.1 g, 13.0 mmol, 65% yield).

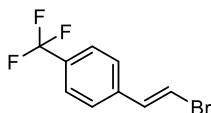
¹H NMR (600 MHz, CDCl₃) δ 6.89 (d, *J* = 13.9 Hz, 1H), 6.75 – 6.68 (m, 1H), 6.52 (d, *J* = 13.9 Hz, 1H), 4.17 (s, 4H).



(*E*)-1-(2-Bromovinyl)cyclohexane.¹⁸

This compound was prepared from cyclohexanecarboxaldehyde (2.2 g, 20.0 mmol) at 80 °C for 12 h. The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the vinyl bromide (*E/Z* = 10:1) as a colorless oil (1.8 g, 12.0 mmol, 60%).

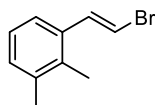
¹H NMR (600 MHz, CDCl₃) δ 6.16 (dd, *J*₁ = 13.6 Hz, *J*₂ = 7.3 Hz, 1H), 6.02 (dd, *J*₁ = 13.6 Hz, *J*₂ = 1.2 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.77 – 1.71 (m, 4H), 1.38 – 1.06 (m, 6H).



(*E*)-1-(2-Bromovinyl)-4-(trifluoromethyl)benzene.¹⁹

This compound was prepared from 4-(trifluoromethyl)benzaldehyde (3.48 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the (*E*)-vinyl bromide as a light yellow oil (3.75 g, 15.0 mmol, 75% yield).

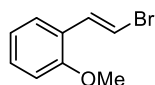
¹H NMR (600 MHz, CDCl₃) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 14.1 Hz, 1H), 6.91 (d, *J* = 14.1 Hz, 1H).



(*E*)-1-(2-Bromovinyl)-2,3-dimethylbenzene.¹⁹

This compound was prepared from 2,3-dimethylbenzaldehyde (2.68 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the (*E*)-vinyl bromide as a light yellow oil (2.94 g, 7.0 mmol, 70% yield).

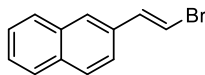
¹H NMR (600 MHz, CDCl₃) δ 7.39 (d, *J* = 13.7 Hz, 1H), 7.18 – 7.11 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 13.7 Hz, 1H), 2.30 (s, 3H), 2.24 (s, 3H).



(*E*)-1-(2-Bromovinyl)-2-methoxybenzene.²⁰

This compound was prepared from 3-methoxybenzaldehyde (2.72 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: 5% ethyl acetate in petroleum ether) to yield the (*E*)-vinyl bromide as a light yellow oil (3.0 g, 15.0 mmol, 75% yield).

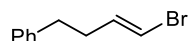
¹H NMR (600 MHz, CDCl₃) δ 7.36 (d, *J* = 14.0 Hz, 1H), 7.31 – 7.28 (m, 2H), 6.98 – 6.94 (m, 2H), 6.92 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H).



(*E*)-2-(2-Bromovinyl)naphthalene.²¹

This compound was prepared from 2-naphthaldehyde (3.12 g, 20.0 mmol) according to Standard method except NiCl₂(Py)₄ as the precatalyst. The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the (*E*)-vinyl bromide as a white solid (3.25 g, 14.0 mmol, 70% yield).

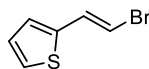
¹H NMR (600 MHz, CDCl₃) δ 7.83 – 7.76 (m, 4H), 7.67 (s, 1H), 7.48 – 7.43 (m, 3H), 7.24 (d, *J* = 4.9 Hz, 1H), 6.89 (d, *J* = 14.0 Hz, 1H).



(*E*)-(4-Bromobut-3-en-1-yl)benzene.²²

This compound was prepared from 3-phenylpropanal (2.6 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the vinyl bromide (*E/Z* = 1.8:1) as a colorless oil (1.89 g, 9.0 mmol, 45% yield).

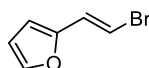
¹H NMR (600 MHz, CDCl₃) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 6.24 – 6.17 (m, 1H), 6.15 – 6.01 (m, 1H), 2.77 – 2.69 (m, 2H), 2.57 – 2.30 (m, 2H).



(*E*)-2-(2-Bromovinyl)thiophene.¹⁰

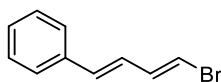
This compound was prepared from 3-phenylpropanal (2.24 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the (*E*)-vinyl bromide as a light yellow oil (1.50 g, 8.0 mmol, 40% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.41 – 7.38 (m, 1H), 7.30 – 7.27 (m, 1H), 7.07 – 7.03 (m, 2H), 6.71 (d, *J* = 13.9 Hz, 1H).



(*E*)-2-(2-Bromovinyl)furan.²³

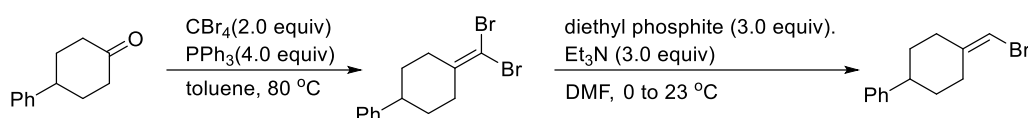
This compound was prepared from furan-2-carbaldehyde (1.92 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the (*E*)-vinyl bromide as a yellow oil (1.7 g, 10.8 mmol, 54% yield).



(1*E*,3*E*)-1-Bromo-4-phenyl-1,3-butadien.²⁴

This compound was prepared from cinnamaldehyde (2.64 g, 20.0 mmol) according to Standard method. The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the (*E*)-vinyl bromide (1.4 g, 7.0 mmol, 35% yield) as a yellow oil.

(3) Preparation of (4-(bromomethylene)cyclohexyl)benzene



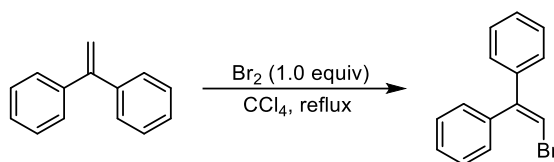
To a flame-dried Schlenk flask was charged with 4-phenylcyclohexan-1-one (1.74 g, 10 mmol, 1.0 equiv), CBr₄ (6.62 g, 20 mmol, 2.0 equiv) and PPh₃ (20.9 g, 80 mmol, 4.0 equiv). After degassed and fulfilled with N₂ thrice, toluene (70 mL) was added through a syringe. The flask was sealed and heated at 80 °C overnight. After cooled to room temperature, the mixture was filtrated through a pad of silica gel and washed with petroleum ether. Then solvent evaporated off in vacuum, the product was isolated by silica gel chromatography (2.62 g, 16.0 mmol, 80% yield).²⁵

To a solution of the (4-(dibromomethylene)cyclohexyl)benzene (2.6 g, 8 mmol, 1.0 equiv) and NEt₃ (2.4 g, 24 mmol, 3.0 equiv) in DMF (10 mL) was added dimethyl phosphonate (2.6 g, 24 mmol, 3.0 equiv). The solution was stirred over night at room temperature. Water was added to the mixture. The aqueous layer was extracted with DCM and the combined organic layers were washed with brine and dried (Na₂SO₄), filtered, and concentrated. The crude material was purified by flash chromatography (SiO₂: petroleum ether) gave the desired product as light yellow solid (1.5 g, 6.0 mmol, 75% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.41 – 7.33 (m, 2H), 7.30 – 7.23 (m, 3H), 6.02 – 5.98 (m, 1H), 3.15 – 3.07 (m, 1H), 2.81 – 2.73 (m, 1H), 2.59 – 2.49 (m, 1H), 2.33 – 2.24 (m, 1H), 2.13 – 1.99 (m, 3H), 1.67 – 1.55 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 146.09, 146.07, 143.82, 143.81, 128.41, 128.40, 128.39, 126.77, 126.76, 126.75, 126.17, 126.16, 98.38, 98.34, 44.07, 44.06, 35.25, 35.23, 35.02, 34.99, 33.83, 33.81, 33.80, 30.92, 30.91, 30.89.

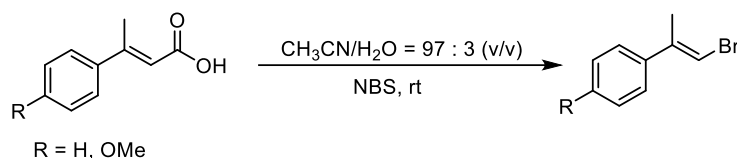
(4) Preparation of (2-bromoethene-1,1-diyl)dibenzene.²⁶



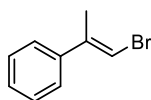
To a flame-dried flask was added 1,1-diphenylethene (3.6 g, 20 mmol, 1.0 equiv), Br_2 (3.2 g, 20 mmol, 1.0 equiv) and CCl_4 (30 mL). The mixture was heated to reflux. Spontaneous dehydrobromination occurred during workup. The solvent was removed under reduced pressure. Finally, the crude material was purified by flash chromatography (SiO_2 : petroleum ether), the title compound was obtained as light yellow solid (6.1 g, 14.0 mmol, 70%).

^1H NMR (600 MHz, CDCl_3) δ 7.45 – 7.28 (m, 10H), 6.79 (s, 1H).

(5) Preparation of (*E*)-1-(1-bromoprop-1-en-2-yl)-4-methoxybenzene, (*E*)-(1-bromoprop-1-en-2-yl)benzene.^{28,29}



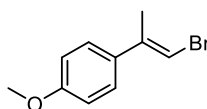
α,β -Unsaturated carboxylic acid (10.0 mmol, 1.0 equiv) was added to a solution of LiOAc (2 mmol, 0.2 equiv) in 50 mL of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (97:3 v/v). After the mixture was stirred for 5 min at room temperature, NBS (1.9 g, 2.2 mmol, 1.1 equiv) was added. After completion of the reaction monitored by TLC, the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, and dried Na_2SO_4 . After filtered, the mixture was concentrated under vacuum. The residue was purified by flash column chromatography.



(*E*)-(1-Bromoprop-1-en-2-yl)benzene.^{27,28}

This compound was prepared from (*E*)-3-phenylbut-2-enoic acid (1.62g, 10.0 mmol). The crude residue was purified by flash chromatography (SiO_2 : petroleum ether) to yield the vinyl bromide as a colorless liquid (1.47 g, 7.5 mmol, 75%).

^1H NMR (600 MHz, CDCl_3) δ 7.35 – 7.29 (m, 5H), 6.45 (d, $J = 1.3$ Hz, 1H), 2.23 (d, $J = 1.3$ Hz, 3H).

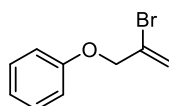


(E)-1-(1-Bromoprop-1-en-2-yl)-4-methoxybenzene.²⁸

This compound was prepared from (E)-3-(4-methoxyphenyl)but-2-enoic acid (1.92g, 10.0 mmol). The crude residue was purified by flash chromatography (SiO₂: 10% ethyl acetate in petroleum ether) to yield the vinyl bromide as a light yellow solid (1.58 g, 7.0 mmol, 70%).

¹H NMR (600 MHz, CDCl₃) δ 7.22 – 7.17 (m, 3H), 6.82 – 6.77 (m, 2H), 6.30 – 6.27 (m, 1H), 3.74 (s, 3H), 2.13 (d, *J* = 1.3 Hz, 3H).

(6) Preparation of ((2-bromoallyl)oxy)benzene.²⁹

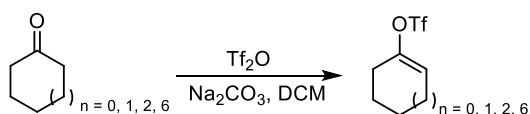


Phenol (0.94 g, 10 mmol, 1.0 equiv) was dissolved in anhydrous DMF (10 mL) in a dried three necked vessel. The mixture was cooled to 0 °C. NaH (440 mg, 22 mmol, 1.1 equiv, 60% in mineral oil) was added in portions. The mixture was stirred at for 30 min, then 2,3-dibromopropene was added to the resulting mixture at 0 °C. After that, the mixture was stirred overnight at room temperature and quenched with diluted NaOH (aq). Then the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, and dried Na₂SO₄. After filtered, the mixture was concentrated under vacuum. The residue was purified by flash column chromatography (SiO₂: petroleum ether) to give the desired product as light yellow oil (1.27 g, 6.6 mmol, 66% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.22 – 7.17 (m, 2H), 7.00 – 6.86 (m, 1H), 6.85 – 6.81 (m, 2H), 5.90 (s, 1H), 5.57 (s, 1H), 4.54 (s, 2H).

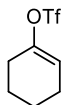
B. Synthesis of Vinyl Triflates.

(1) The Hanack's procedure as follows was used to prepare cyclohex-1-en-1-yl trifluoromethanesulfonate, cyclohept-1-en-1-yl trifluoromethanesulfonate, cyclooct-1-en-1-yl trifluoromethanesulfonate, cyclododec-1-en-1-yl trifluoromethanesulfonate.³⁰



To a solution of ketone (20 mmol, 1.0 equiv) in dichloromethane (30 mL) was added anhydrous sodium carbonate (3.4 g, 32.0 mmol, 1.6 equiv). A solution of

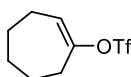
trifluoromethanesulfonic anhydride (11.2 g, 40 mmol, 2.0 equiv) in DCM (30 mL) was added over a period of 10 minutes. The reaction mixture was stirred for 24 h at room temperature. It was washed with sodium hydrogen carbonate, water and dried with Na₂SO₄, filtered, and the solvent was removed *in vacuo*. Flash column chromatography provided the vinyl triflate.



Cyclohex-1-en-1-yl trifluoromethanesulfonate.³¹

This compound was prepared from cycloheptanone (2.2 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the vinyl bromide as a colorless oil (1.79 g, 15.0 mmol, 75% yield).

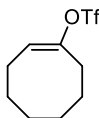
¹H NMR (600 MHz, CDCl₃) δ 5.79 – 5.75 (m, 1H), 2.35 – 2.30 (m, 2H), 2.16 – 2.12 (m, 2H), 1.84 – 1.77 (m, 2H), 1.65 – 1.59 (m, 2H).



Cyclohept-1-en-1-yl trifluoromethanesulfonate.³¹

This compound was prepared from cyclohexanone (1.96 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the vinyl bromide as a colorless oil (3.6 g, 15.0 mmol, 75% yield).

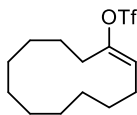
¹H NMR (600 MHz, CDCl₃) δ 5.90 (t, *J* = 6.4 Hz, 1H), 2.56 – 2.51 (m, 2H), 2.20 – 2.15 (m, 2H), 1.79 – 1.57 (m, 6H).



Cyclooct-1-en-1-yl trifluoromethanesulfonate.³¹

This compound was prepared from cyclooctanone (2.52 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the vinyl bromide as a colorless oil (3.1 g, 12.0 mmol, 60% yield).

¹H NMR (600 MHz, CDCl₃) δ 5.71 (t, *J* = 8.7 Hz, 1H), 2.51 – 2.47 (m, 2H), 2.22 – 2.16 (m, 2H), 1.77 – 1.71 (m, 2H), 1.67 – 1.55 (m, 6H).



Cyclododec-1-en-1-yl trifluoromethanesulfonate.³²

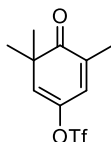
This compound was prepared from cyclododecanone (3.6 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the vinyl bromide as a colorless oil (3.5 g, 11.0 mmol, 55% yield).

¹H NMR (600 MHz, CDCl₃) δ 5.37 (t, J = 7.7 Hz, 1H), 2.40 (t, J = 6.0 Hz 2H), 2.27 – 2.20 (m, 2H), 1.62 – 1.22 (m, 16H).

¹H NMR data of the contaminated *E*-isomer (40%): 5.48 (t, J = 8.3 Hz, 1H), 2.45 (t, J = 6.7 Hz, 1H), 2.17 – 2.11 (m, 1H), 1.70 – 1.25 (m, 16H).

(2) The following compounds were synthesized using Ramamurthy-S procedure: (4R,7R)-2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoinden-5-yl trifluoromethanesulfonate, 3,3,5-trimethyl-4-oxocyclohexa-1,5-dien-1-yl trifluoromethanesulfonate.³³

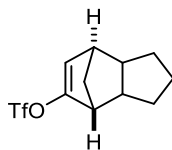
To a dry 3-necked round-bottomed flask (100 mL) loaded with 20 mL of LDA. The flask was cooled to -78 °C and stirred for 5 minutes under nitrogen. A solution of ketone (20 mmol, 1.0 equiv) in 10 mL of dry THF was added dropwise to the cooled LDA over a period of 5 minutes. The mixture was stirred for additional 2 h, enabling the complete formation of the enolate. At which point, *N*-phenyl triflimide (6.2 g, 17.5 mmol, 1.1 equiv) was added in one portion to the above enolate and the suspension was stirred continuously and warmed to room temperature. After additional stirring for 12 h, the reaction mixture was quenched with saturated ammonium chloride solution and extracted with ether. The ether extract was washed with water, 5% sodium bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude triflate was purified by column chromatography.



3,3,5-Trimethyl-4-oxocyclohexa-1,5-dien-1-yl trifluoromethanesulfonate.³³

This compound was prepared from 2,6,6-trimethylcyclohex-2-ene-1,4-dione (3.0 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the vinyl bromide as a light yellow oil (3.1 g, 11.0 mmol, 55% yield).

¹H NMR (600 MHz, CDCl₃) δ 6.76 (dq, *J* = 3.1, 1.6 Hz, 1H), 6.13 (d, *J* = 3.1 Hz, 1H), 1.97 (dd, *J* = 1.5, 0.8 Hz, 4H), 1.30 (s, 6H).

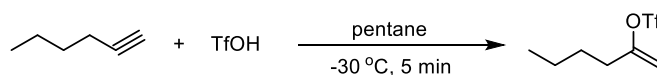


2,3,3a,4,7,7a-Hexahydro-1H-4,7-methanoinden-5-yl trifluoromethanesulfonate.

This compound was prepared from tricyclo[5.2.1.0(2,6)]decan-8-one (CAS No. 13380-94-4, 3.0 g, 20.0 mmol). The crude residue was purified by silica gel chromatography (SiO₂: petroleum ether) to yield the vinyl bromide as a light yellow oil (3.4 g, 12.0 mmol, 60% yield).

¹H NMR (600 MHz, CDCl₃) δ 5.77 (d, *J* = 3.4 Hz, 1H), 2.62 (brs, 2H), 2.44 – 2.37 (m, 1H), 2.26 – 2.20 (m, 1H), 1.99 – 1.93 (m, 1H), 1.93 – 1.83 (m, 2H), 1.73 – 1.63 (m, 3H), 1.07 – 0.98 (m, 2H).

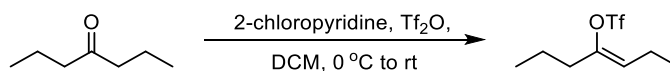
(3) Preparation of 1-hexen-2-yl-triflate.³²



A solution of 1-hexyne (3.4 mL, 18.0 mmol) in pentane (20 mL) was cooled to -30 °C. Trifluoromethanesulfonic acid (0.9 mL, 10.0 mmol) was added dropwise over 5 min. The cooling bath was removed and the reaction mixture was warmed to 0 °C. Saturated aqueous NaHCO₃ was added to the reaction mixture and the resulting mixture was stirred for another 5 min. The organic layer was separated, washed twice with saturated NaHCO₃ and dried over K₂CO₃. The solvent was evaporated and the residue was distilled to give 1-hexen-2-yl-triflate (2.5 g, 9.0 mmol, 50% yield).

¹H NMR (600 MHz, CDCl₃) δ 5.11 (d, *J* = 3.5 Hz, 1H), 4.95 (d, *J* = 3.5 Hz, 1H), 2.39 – 2.34 (m, 2H), 1.59 – 1.53 (m, 2H), 1.45 – 1.36 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

(4) Hept-3-en-4-yl trifluoromethanesulfonate.³⁴



To a solution of heptan-4-one (2.2 g, 20 mmol, 1.0 equiv) in anhydrous dichloromethane (5 mL) under nitrogen atmosphere was added 2-chloropyridine (0.22 mL, 2.4 mmol, 1.1 equiv) at 0 °C. After the mixture was stirred for 10 min at 0 °C, trifluoromethanesulfonic

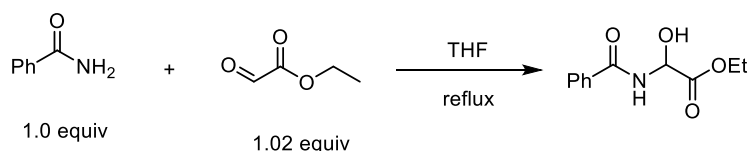
anhydride (0.21 mL, 2.6 mmol, 1.2 equiv) was added dropwise. The resulting solution was warmed to rt and stirred for 2 h. After the completion of the reaction (monitored by TLC), the solution was concentrated *in vacuo* and the resulting vinyl triflates were purified by column chromatography. A mixture of *Z* and *E* isomers in a ratio of 1:2.3 (*Z/E*) was obtained in 65% yield (3.2 g, 13.0 mmol).

E isomer ¹H NMR (600 MHz, CDCl₃) δ 5.24 (t, *J* = 7.4 Hz, 1H), 2.33 – 2.28 (m, 2H), 2.24 – 2.16 (m, 2H), 1.60 – 1.52 (m, 2H), 1.08 – 1.03 (m, 3H), 0.99 – 0.93 (m, 3H).

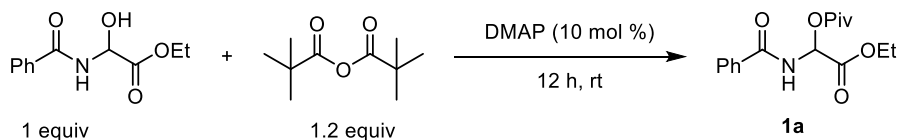
Z isomer ¹H NMR (600 MHz, CDCl₃) δ 5.56 (t, *J* = 7.9 Hz, 1H), 2.37 (t, *J* = 7.3 Hz, 2H), 2.14 – 2.09 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 149.7, 148.3, 123.6, 122.7, 121.6, 119.6, 119.5, 117.5, 117.4, 115.2, 35.4, 31.5, 20.1, 19.6, 19.6, 19.24, 13.8, 13.3, 13.2, 13.1.

C. Preparation α-pivaloyloxy glycine



A solution of benzamide (3.38 g, 28 mmol, 1 equiv) and ethyl glyoxylate (50% w/w in toluene, 2.96 g, 29.0 mmol, 1.02 eq) in THF (125 mL) was refluxed for 24 h. The reaction mixture was then concentrated at reduced pressure to obtain a thick white residue, which was triturated with 30% EtOAc/hexanes (100 mL) to obtain a white solid. The white solid was collected by filtration and dried *in vacuo* to give ethyl 2-benzamido-2-hydroxyacetate as a white powder (5.87 g, 90%) which was used without further purification.



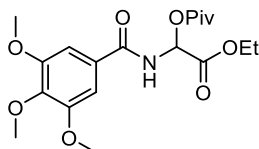
A general procedure: In a flame-dried round bottom flask, a mixture of ethyl 2-benzamido-2-hydroxyacetate (2.23 g, 10.0 mmol, 1.0 equiv) and DMAP (122 mg, 1.0 mmol, 0.10 equiv) in pivalic anhydride (10.0 mL) were stirred for 12 h under air at r.t. It was quenched with a saturated aqueous NaHCO₃ solution. The aqueous phase was extracted with ethyl acetate. The organic phases were collected, dried over MgSO₄, concentrated under reduced pressure. The crude material was purified by flash column chromatograph on silica gel to give the desired product (2.6 g, 8.5 mmol, 85%).

¹H NMR (600 MHz, CDCl₃) δ 7.85 – 7.81 (m, 2H), 7.58 – 7.44 (m, 4H), 6.56 (d, *J* = 9.0 Hz, 1H), 4.35 – 4.22 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 178.2, 167.0, 166.6, 132.6, 132.4, 128.7, 127.4, 72.9, 62.6, 38.70, 26.8, 14.00.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₆H₂₂NO₅: 308.1492. Found: 308.1494.

M.P. 82-83 °C.



2-Ethoxy-2-oxo-1-(3,4,5-trimethoxybenzamido)ethyl pivalate (1b).

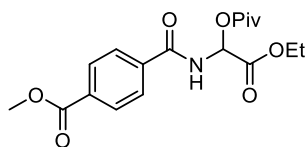
The compound was prepared according to the general procedure using ethyl 2-hydroxy-2-(3,4,5-trimethoxybenzamido)acetate (3.1 g, 10 mmol, 1.0 equiv). After purification by flash column chromatograph on silica gel (EA:PE = 2 : 3), the title compound was obtained in 65 % yield (2.5 g, 6.5 mmol) as a light brown solid.

¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.9 Hz, 1H), 7.05 (s, 2H), 6.54 (d, *J* = 8.9 Hz, 1H), 4.38 – 4.20 (m, 2H), 3.91 (s, 6H), 3.89 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 178.2, 167.1, 166.3, 153.3, 141.8, 128.1, 104.8, 73.0, 62.6, 60.9, 56.4, 38.7, 26.8, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₉H₂₈NO₈: 398.1809. Found: 398.1804.

M.P. 108-109 °C.



Methyl 4-((2-ethoxy-2-oxo-1-(pivaloyloxy)ethyl)carbamoyl)benzoate (1c).

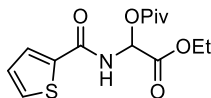
The compound was prepared according to the general procedure using methyl 4-((2-ethoxy-1-hydroxy-2-oxoethyl)carbamoyl)benzoate (2.8 g, 10 mmol, 1.0 equiv). After purification by flash column chromatograph on silica gel (EA : PE = 1 : 3), the title compound was obtained in 75 % yield (2.7 g, 7.5 mmol) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.07 (m, 2H), 7.91 – 7.85 (m, 2H), 7.70 – 7.55 (m, 1H), 6.55 (d, *J* = 8.9 Hz, 1H), 4.37 – 4.17 (m, 2H), 3.95 – 3.90 (m, 3H), 1.32 – 1.25 (m, 3H), 1.23 – 1.20 (m, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 178.1, 166.9, 166.1, 165.9, 136.6, 133.5, 129.9, 127.4, 72.7, 62.7, 52.4, 38.7, 26.7, 13.9.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₈H₂₄NO₇: 366.1547. Found: 366.1543

M.P. 138-139 °C.



2-Ethoxy-2-oxo-1-(thiophene-2-carboxamido)ethyl pivalate (1d).

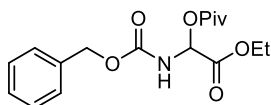
The compound was prepared according to the general procedure using ethyl 2-hydroxy-2-(thiophene-2-carboxamido)acetate (2.3 g, 10 mmol, 1.0 equiv). After purification by flash column chromatograph on silica gel (EA : PE = 1 : 3), the title compound was obtained in 80 % yield (2.5 g, 8.0 mmol) as a light brown solid.

¹H NMR (400 MHz, CDCl₃) δ NMR (400 MHz,) δ 7.60 (dd, *J*₁ = 3.8 Hz, *J*₂ = 1.1 Hz, 1H), 7.56 (dd, *J*₁ = 5.0 Hz, *J*₂ = 1.1 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.11 (dd, *J*₁ = 5.0, *J*₂ = 3.8 Hz, 1H), 6.52 (d, *J* = 9.1 Hz, 1H), 4.36 – 4.19 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 178.1, 166.9, 161.1, 137.2, 131.64, 129.4, 127.8, 72.73, 62.6, 38.7, 26.79, 26.8, 26.8, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₄H₂₀NO₅S: 314.1056. Found: 314.1058.

M.P. 92-93 °C.



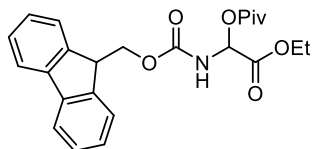
1-(((Benzyloxy)carbonyl)amino)-2-ethoxy-2-oxoethyl pivalate (1e).

The compound was prepared according to the general procedure using benzyl 2-((2-ethoxy-1-hydroxy-2-oxoethyl)amino)-2-oxoacetate (2.8 g, 10 mmol, 1.0 equiv). After purification by flash column chromatograph on silica gel (EA : PE = 1 : 3), the title compound was obtained in 70 % yield (2.5 g, 7.0 mmol) as a colorless liquid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 5H), 6.25 (d, *J* = 15.5 Hz, 2H), 5.15 (s, 2H), 4.32 – 4.16 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 177.8, 166.5, 154.9, 135.6, 128.5, 128.3, 128.1, 74.7, 67.6, 62.5, 38.60, 26.7, 13.9

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₇H₂₄NO₆: 338.16036. Found: 398.1804.



1-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-2-ethoxy-2-oxoethyl pivalate (1f).

The compound was prepared according to the general procedure using ethyl 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-2-hydroxyacetate (3.4 g, 10 mmol, 1.0 equiv). After purification by flash column chromatograph on silica gel (EA: PE = 1 : 3), the title compound was obtained in 70 % yield (2.9 g, 7.0 mmol) as a white solid.

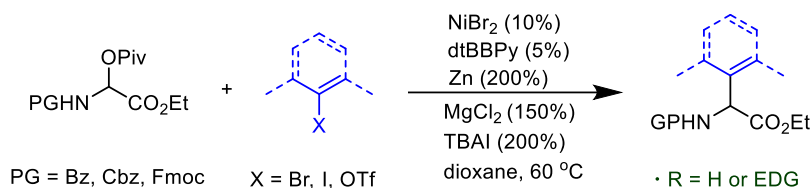
¹H NMR (600 MHz, CD₂Cl₂) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 6.35 – 6.22 (m, 2H), 4.45 (d, *J* = 7.1 Hz, 2H), 4.31 – 4.19 (m, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 9H).

¹³C NMR (151 MHz, CD₂Cl₂) δ 178.1, 167.0, 155.5, 144.3, 144.2, 141.9, 128.3, 127.3, 125.6, 120.6, 75.1, 68.0, 63.10, 47.6, 39.1, 27.2, 27.1, 14.4.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₄H₂₈NO₆: 426.1911. Found: 426.1915

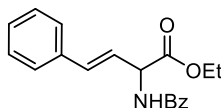
M.P. 95-96 °C.

Part 6. Reductive Coupling of α -Pivaloyloxy Glycine with Vinyl Bromides, Aryl Iodides, Aryl bromides and Vinyl Triflates



Standard method: To an oven-dried Schlenk tube was charged with 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv), Zn (26.0 mg, 0.4 mmol, 2.0 equiv), NiBr₂ (4.37 mg, 0.02 mmol, 0.1 equiv), dtBBPy (2.68 mg, 0.01 mmol, 0.05 equiv), MgCl₂ (28.5 mg, 0.3 mmol, 1.5 equiv) and TBAI (147 mg, 0.4 mmol, 2.0 equiv). The C(sp²)-halide (0.3 mmol, 1.5 equiv) was added at this time if it is a solid. The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point 1,4-dioxane (1 mL) was added via a syringe. If the C(sp²)-halide is a liquid, it was added following the addition of solvent via a syringe. The reaction mixture was allowed to stir at 60 °C for 12 h. 1,4-Dioxane was evaporated under reduced pressure. The residue was purified by flash chromatography and afforded the title compound.

Note: For vinyl triflates (0.3 mmol, 1.5 equiv), NiCl₂(Py)₄ (8.9 mg, 0.02 mmol, 0.1 equiv) was used as the precatalyst.



Ethyl (*E*)-2-benzamido-4-phenylbut-3-enoate (3a).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and 2-bromovinyl)benzene (54.9 mg, 0.3 mmol, 1.5 equiv, *E/Z* = 5:1). After purification by flash column chromatograph, the title compound was isolated as a white solid (46.4 mg, 0.15 mmol, 75% yield; an average of two runs).

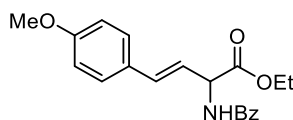
The reaction was also scaled-up using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (2.46 g, 8.0 mmol, 1.0 equiv), 2-bromovinyl)benzene (2.20 g, 12.0 mmol, 1.5 equiv, *E/Z* = 5:1), Zn (1.04 g, 16.0 mmol, 2.0 equiv), NiBr₂ (0.17 g, 0.8 mmol, 0.1 equiv), dtBBPy (0.11 g, 0.4 mmol, 0.05 equiv), MgCl₂ (1.14 g, 12.0 mmol, 1.5 equiv) and TBAI (5.88 g, 16.0 mmol, 2.0 equiv) in 1,4-dioxane (40 mL). The product was isolated as a white solid (1.53 g, 4.94 mmol, 63% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.51 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.44 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 6.94 (d, *J* = 6.8 Hz, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.29 (dd, *J*₁ = 15.9 Hz, *J*₂ = 6.4 Hz, 1H), 5.50 – 5.45 (m, 1H), 4.35 – 4.24 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.9, 166.7, 135.9, 133.8, 133.3, 131.9, 128.7, 128.6, 128.2, 127.1, 126.7, 123.5, 62.1, 54.6, 14.2.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₉H₂₀NO₃: 310.1443. Found 310.1439.

M.P. 91-92 °C.



Ethyl (*E*)-2-benzamido-4-(4-methoxyphenyl)but-3-enoate (3b).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and (*E*)-1-(2-bromovinyl)-4-methoxybenzene (63.6 mg, 0.3 mmol, 1.5 equiv). After purification by flash column

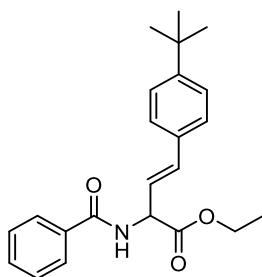
chromatograph, the title compound was isolated as a white solid (47.5 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.43 (m, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 7.3 Hz, 1H), 6.87 – 6.83 (m, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J*₁ = 15.8 Hz, *J*₂ = 6.5 Hz, 1H), 5.48 – 5.42 (m, 1H), 4.34 – 4.23 (m, 2H), 3.80 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.0, 166.6, 159.7, 133.8, 132.9, 131.8, 128.6, 128.0, 127.1, 121.1, 114.0, 62.0, 55.3, 54.7, 14.2.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₀H₂₂NO₄: 340.1543. Found: 340.1546.

M.P. 60-6 °C.



Ethyl (*E*)-2-benzamido-4-(4-(tert-butyl)phenyl)but-3-enoate (3c).

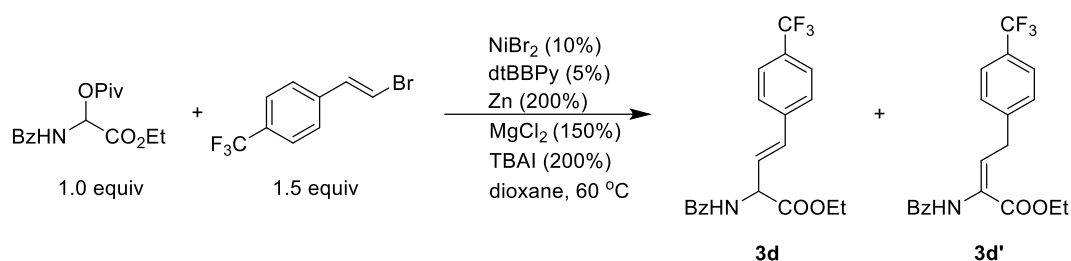
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and (*E*)-1-(2-bromovinyl)-4-(tert-butyl)benzene (142.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (58.4 mg, 0.16 mmol, 80% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.87 – 7.84 (m, 2H), 7.55 – 7.52 (m, 1H), 7.49 – 7.44 (m, 2H), 7.36 – 7.30 (m, 4H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.71 (dd, *J*₁ = 16.0 Hz, *J*₂ = 1.5 Hz, 1H), 6.24 (dd, *J*₁ = 15.9 Hz, *J*₂ = 6.5 Hz, 1H), 5.48 – 5.43 (m, 1H), 4.33 – 4.23 (m, 2H), 1.34 – 1.29 (m, 12H).

¹³C NMR (151 MHz, CDCl₃) δ 171.0, 166.7, 151.4, 133.8, 133.2, 133.1, 131.9, 128.6, 127.1, 126.4, 125.5, 122.6, 62.1, 54.7, 34.6, 31.2, 14.2.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₃H₂₈NO₃: 366.1594. Found: 336.1596.

M.P. 96-97 °C.



Ethyl (*E*)-2-benzamido-4-(4-(trifluoromethyl)phenyl)but-3-enoate (3d**).**

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and (*E*)-1-(2-bromovinyl)-4-(trifluoromethyl)benzene (75.0 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, a white solid was isolated which was contaminated with 20% of enamine tautomer based on ¹H NMR analysis of the mixture (60.3 mg, 0.16 mmol, 80% total yield). Further purification using preparative TLC gave **3d** in a pure form.

¹H NMR (600 MHz, CDCl₃) δ 7.89 – 7.85 (m, 2H), 7.56 – 7.51 (m, 3H), 7.47 – 7.43 (m, 4H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.39 (dd, *J*₁ = 15.9 Hz, *J*₂ = 6.2 Hz, 1H), 5.53 – 5.58 (m, 1H), 4.35 – 4.23 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

¹⁹F NMR (565 MHz, CDCl₃) δ -62.58.

¹³C NMR (151 MHz, CDCl₃) δ 170.4, 166.7, 139.3, 133.5, 132.0, 131.6, 128.6, 127.1, 126.8, 126.3, 125.51, 125.49, 125.46, 125.44, 62.27, 54.51, 14.08.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₀H₁₉F₃NO₃ : 378.1312. Found: 378.1312.

M.P. 82-83 °C.

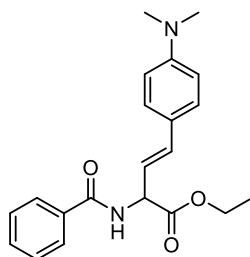
Ethyl (*E*)-2-benzamido-4-(4-(trifluoromethyl)phenyl)but-2-enoate (3d'**)**

¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.85 (m, 2H), 7.75 (brs, 1H), 7.60 – 7.54 (m, 3H), 7.51 – 7.45 (m, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 6.86 (t, *J* = 7.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.66 (d, *J* = 7.0 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 4H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.30.

¹³C NMR (101 MHz, CDCl₃) δ 165.6, 164.6, 143.0, 133.8, 132.3, 129.1, 129.0, 128.8, 128.7, 127.4, 125.62, 125.56, 125.52, 125.48, 61.97, 35.51, 14.17.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₀H₁₉F₃NO₃ : 378.1312. Found: 378.1312.



Ethyl (*E*)-2-benzamido-4-(4-(dimethylamino)phenyl)but-3-enoate (3e).

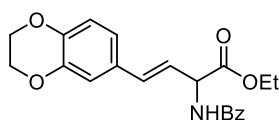
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-4-(2-bromovinyl)-*N,N*-dimethylaniline (67.5mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid. (28.1 mg, 0.08 mmol, 40% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.87 – 7.84 (m, 2H), 7.55 – 7.51 (m, 1H), 7.47 – 7.43 (m, 2H), 7.30 – 7.25 (m, 2H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.65 (dd, *J* = 15.8, 1.4 Hz, 3H), 5.41 (m, 1H), 4.33 – 4.22 (m, 2H), 2.96 (s, 6H), 1.32 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.3, 166.7, 133.9, 131.8, 133.6, 128.6, 127.7, 127.1, 118.7, 112.3, 77.2, 61.9, 54.9, 40.5, 14.2.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₁H₂₅N₂O₃: 353.1859. Found 353.1856.

M.P. 124-125 °C.



Ethyl (*E*)-2-benzamido-4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)but-3-enoate (3f).

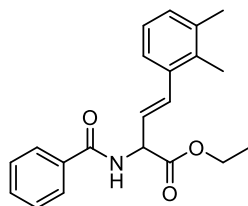
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and (*E*)-6-(2-bromovinyl)-2,3-dihydrobenzo[b][1,4]dioxine (72.0 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (47.7 mg, 0.13 mmol, 65% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.87 – 7.83 (m, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.42 (m 2H), 6.92 – 6.84 (m, 3H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.12 (dd, *J*₁ = 15.8 Hz, *J*₂ = 6.5 Hz, 1H), 5.46 – 5.42 (m, 1H), 4.33 – 4.22 (m, 6H), 1.32 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.0, 166.6, 143.8, 143.5, 133.8, 132.7, 131.8, 129.7, 128.6, 127.1, 121.8, 120.2, 117.3, 115.3, 64.4, 64.3, 62.0, 54.6, 14.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{22}NO_5$: 368.1492. Found 368.1491

M.P. 105-106 °C.



Ethyl (*E*)-2-benzamido-4-(3,4-dimethylphenyl)but-3-enoate (3g).

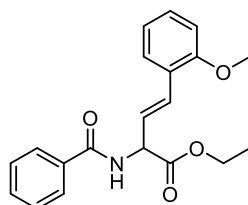
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-4-(2-bromovinyl)-1,2-dimethylbenzene (63.3 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (47.1 mg, 0.14 mmol, 70% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.55 – 7.52 (m, 1H), 7.48 – 7.44 (m, 2H), 7.26 – 7.22 (m, 1H), 7.10 – 6.99 (m, 3H), 6.93 (d, J = 7.4 Hz, 1H), 6.08 (dd, J_1 = 15.7, J_2 = 6.4 Hz, 1H), 5.51 – 5.46 (m, 1H), 4.32 – 4.26 (m, 2H), 2.28 (s, 3H), 2.23 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 166.7, 136.9, 135.5, 134.3, 133.9, 132.5, 131.8, 129.7, 128.64, 127.1, 125.6, 125.1, 124.2, 62.0, 54.9, 20.5, 15.4, 14.2

HRMS (ESI) m/z ($[M+H]^+$) calcd $C_{21}H_{24}NO_3$: 338.1750. Found: 338.1752.

M.P. 102-103 °C.



Ethyl (*E*)-2-benzamido-4-(2-methoxyphenyl)but-3-enoate (3h).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-1-(2-bromovinyl)-2-methoxybenzene (63.3 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (44.0 mg, 0.13 mmol, 65% yield).

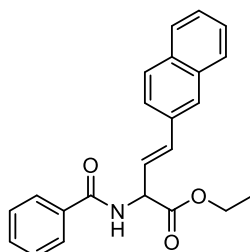
1H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 7.7 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.48 – 7.43 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.05 (d, J = 16.1 Hz, 1H), 6.93 – 6.88 (m, 2H), 6.86

(d, $J = 8.3$ Hz, 1H), 6.35 (dd, $J_1 = 16.1$, $J_2 = 6.4$ Hz, 1H), 5.47 (m 1H), 4.33 – 4.24 (m, 2H), 3.83 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.1, 166.8, 156.9, 133.9, 131.8, 129.3, 128.6, 128.5, 127.3, 127.2, 124.9, 123.9, 120.6, 110.9, 62.0, 55.4, 55.1, 14.1

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_4$: 340.1543. Found: 340.1543.

M.P. 116-117 °C.



Ethyl (*E*)-2-benzamido-4-(naphthalen-2-yl)but-3-enoate (4).

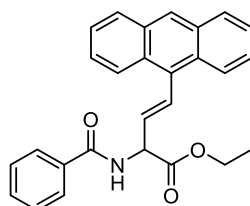
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-2-(2-bromovinyl)naphthalene (69 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (58.1 mg, 0.162 mmol, 81% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.89 (d, $J = 7.6$ Hz, 2H), 7.73 – 7.81 (m, 3H), 7.75 (br, 1H), 7.60 – 7.53 (m, 2H), 7.50 – 7.43 (m, 4H), 6.99 (d, $J = 7.2$ Hz, 1H), 6.89 (d, $J = 15.6$, 1H), 6.42 (dd, $J_1 = 15.9$ Hz, $J_2 = 6.3$ Hz, 1H), 5.56 – 5.52 (m, 1H), 4.37 – 4.26 (m, 2H), 1.35 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 170.9, 166.7, 133.8, 133.5, 133.3, 133.2, 131.9, 128.7, 128.3, 128.1, 127.7, 127.2, 127.2, 126.4, 126.2, 123.8, 123.5, 62.2, 54.7, 14.1.

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_3$: 360.1594. Found: 360.1599.

M.P. 95-96 °C.



Ethyl (*E*)-4-(anthracen-9-yl)-2-benzamidobut-3-enoate (5).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-9-(2-bromovinyl)anthracene (84.6

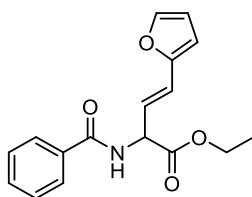
mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a light brown solid (57.2 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 8.39 (s, 1H), 8.26–8.22 (m, 2H), 8.01–7.97 (m, 2H), 7.96–7.92 (m, 2H), 7.58–7.43 (m, 8H), 7.17 (d, *J* = 6.7 Hz, 1H), 6.11 (dd, *J*₁ = 16.1 Hz, *J*₂ = 6.4 Hz, 1H), 5.76–5.29 (m, 1H), 4.47–4.33 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.9, 166.9, 134.0, 132.0, 131.9, 131.4, 131.3, 123.0, 123.0, 128.8, 128.7, 128.6, 127.2, 126.7, 125.8, 125.6, 125.2, 62.3, 55.3, 14.3.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₇H₂₄NO₃: 410.1750. Found: 410.1755.

M.P. 96–97 °C.



Ethyl (*E*)-2-benzamido-4-(furan-2-yl)but-3-enoate (6).

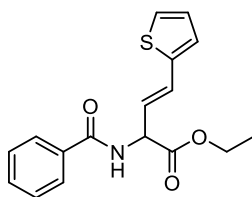
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-2-(2-bromovinyl)furan (51.9 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (40.7 mg, 0.136 mmol, 68% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.87–7.84 (m, 2H), 7.55–7.51 (m, 1H), 7.43–7.48 (m, 2H), 7.35 (br, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.54 (dd, *J*₁ = 15.8 Hz, *J*₂ = 1.5 Hz, 1H), 6.36 (dd, *J*₁ = 3.3 Hz, *J*₂ = 1.8 Hz, 1H), 6.28 (d, *J* = 3.3 Hz, 1H), 6.23 (dd, *J*₁ = 15.8 Hz, *J*₂ = 6.4 Hz, 1H), 4.34–4.22 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.7, 166.7, 151.6, 142.4, 133.7, 131.9, 128.6, 127.1, 121.9, 121.4, 111.4, 109.4, 62.2, 54.4, 14.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd C₁₇H₁₈NO₄: 300.1230. Found: 300.1231

M.P. 104–105 °C.



Ethyl (*E*)-2-benzamido-4-(thiophen-2-yl)but-3-enoate (7).

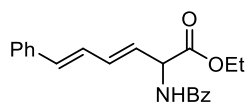
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-2-(2-bromovinyl)thiophene (56.1 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (47.2 mg, 0.15 mmol, 75% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.89 – 7.84 (m, 2H), 7.56 – 7.52 (m, 1H), 7.47 (dd, *J*₁ = 8.3, *J*₂ = 7.0 Hz, 2H), 7.18 (d, *J* = 5.0 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.90 (d, *J* = 7.3 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.11 (dd, *J*₁ = 15.6, *J*₂ = 6.5 Hz, 1H), 5.46 – 5.41 (m, 1H), 4.35 – 4.24 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.7, 166.6, 140.8, 133.78, 131.9, 128.6, 127.4, 127.1, 126.8, 126.5, 125.0, 122.9, 62.2, 54.4, 14.1

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₇H₁₈NO₃S: 316.1002. Found: 316.1007.

M.P. 79-80 °C.



Ethyl (3*E*,5*E*)-2-benzamido-6-phenylhexa-3,5-dienoate (8).

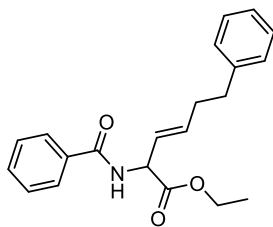
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and ((1*E*,3*E*)-4-bromobuta-1,3-dien-1-yl)benzene (62.4 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (50.3 mg, 0.15 mmol, 75% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.49 – 7.44 (m, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 6.88 (d, *J* = 7.1 Hz, 1H), 6.77 (dd, *J*₁ = 15.6 Hz, *J*₂ = 10.5 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.53 (dd, *J*₁ = 15.0 Hz, *J*₂ = 11.0 Hz, 1H), 5.90 (dd, *J*₁ = 15.2 Hz, *J*₂ = 6.4 Hz, 1H), 5.43 – 5.38 (m, 1H), 4.34 – 4.23 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.8, 166.6, 136.8, 134.2, 133.8, 133.5, 131.9, 128.6, 128.6, 127.9, 127.3, 127.1, 127.0, 126.5, 62.1, 54.4, 14.2.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₁H₂₂NO₃: 336.1594. Found: 336.1596.

M.P. 124-125 °C.



Ethyl (*E*)-2-benzamido-6-phenylhex-3-enoate (9).

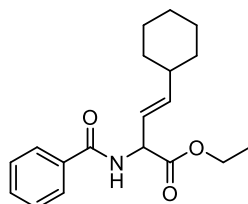
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-(4-bromobut-3-en-1-yl)benzene (63.0 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound containing a mixture of *E/Z* isomers in a ratio of >2:1 was isolated as a colorless liquid. (43.8 mg, 0.13 mmol, 65% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.76 – 7.70 (m, 2H), 7.47 – 7.42 (m, 1H), 7.40 – 7.33 (m, 2H), 7.21 – 7.14 (m, 3H), 7.11 – 7.05 (m, 3H), 6.67 (d, *J* = 7.5 Hz, 1H), 5.84 – 5.77 (m, 1H), 5.44 (s, 1H), 5.42 (s, 1H), 5.18 – 5.14 (m, 1H), 4.21 – 4.12 (m, 2H), 2.66 – 2.56 (m, 2H), 2.35 – 2.27 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H).

¹H NMR (600 MHz, CDCl₃) minor isomer δ 6.62 (d, *J* = 6.8 Hz, 1H), 5.74 – 5.68 (m, 1H), 5.42 – 5.36 (m, 1H), 5.33 – 5.28 (m, 1H), 2.73 – 2.68 (m, 2H), other peaks are overlapped with signals of the major isomer;

¹³C NMR (151 MHz, CDCl₃) δ 171.3, 171.1, 166.6, 166.6, 141.3, 141.3, 135.8, 133.4, 133.8, 133.8, 131.8, 131.7, 128.6, 128.3, 128.5, 128.3, 128.3, 127.1, 125.9, 125.9, 124.7, 124.2, 61.8, 54.4, 50.9, 35.4, 35.2, 33.9, 29.7, 14.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₁H₂₄NO₃:338.1750. Found: 338.1758.



Ethyl (*E*)-2-benzamido-4-cyclohexylbut-3-enoate (10).

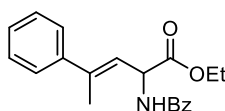
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-(2-bromovinyl)cyclohexane (56.4 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound containing a mixture of *E/Z* isomers in a ratio of >10:1 was isolated as a colorless liquid (38.4 mg, 0.122 mmol, 61% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.44 – 7.40 (m, 2H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.77 (dd, *J*₁ = 15.6 Hz, *J*₂ = 6.6 Hz, 1H), 5.46 – 5.53 (m, 1H), 5.25 – 5.20 (m, 1H), 4.26 – 4.18 (m, 2H), 2.01 – 1.93 (m, 1H), 1.74 – 1.67 (m, 4H), 1.65 – 1.61 (m, 1H), 1.32 – 1.01 (m, 9H).

¹H NMR (600 MHz, CDCl₃) minor isomer: δ 5.58 – 5.53 (m, 1H), 1.66 – 1.59 (m, 4H), other peaks are overlapped with signals of the major isomer;

¹³C NMR (151 MHz, CDCl₃) δ 171.3, 166.6, 140.6, 133.9, 131.7, 128.5, 127.1, 121.5, 61.6, 54.5, 40.2,

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₉H₂₆NO₃: C₁₈H₂₀NO₄: 316.1907. Found: 316.1907.



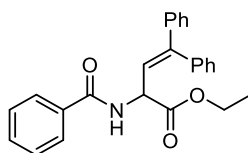
Ethyl (*E*)-2-benzamido-4-phenylpent-3-enoate (11).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and (*E*)-(1-bromoprop-1-en-2-yl)benzene (58.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (45.2 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.39 – 7.34 (m, 2H), 7.35 – 7.32 (m, 2H), 7.28 – 7.18 (m, 1H), 6.85 (d, *J* = 7.1 Hz, 1H), 5.64 – 5.59 (m, 1H), 5.56 (dd, *J*₁ = 9.1 Hz, *J*₂ = 7.1 Hz, 1H), 4.23 – 4.14 (m, 2H), 2.25 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.5, 166.7, 142.2, 142.1, 133.8, 131.7, 128.6, 128.3, 127.7, 127.1, 125.9, 121.6, 61.8, 52.1, 16.9, 14.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₀H₂₂NO₃: 324.1594. Found: 324.1598.



Ethyl 2-benzamido-4,4-diphenylbut-3-enoate (12).

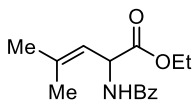
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (2-bromoethene-1,1-diyl)dibenzene (52 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (50.1 mg, 0.13 mmol, 65% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.37 (m, 7H), 7.32 – 7.25 (m, 6H), 6.82 (d, *J* = 6.7 Hz, 1H), 6.06 (d, *J* = 9.5 Hz, 1H), 5.35 (dd, *J*₁ = 9.5, *J*₂ = 6.7 Hz, 1H), 4.25 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.2, 166.4, 147.5, 141.3, 138.5, 133.8, 131.7, 129.8, 128.5, 128.4, 128.2, 128.1, 127.9, 127.6, 127.1, 122.0, 61.9, 53.2, 14.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₅H₂₄NO₃: 386.1750. Found 386.1753.

M.P. 170-171 °C.



Ethyl 2-benzamido-4-methylpent-3-enoate (13).

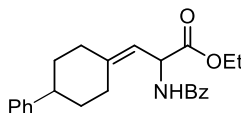
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 1-bromo-2-methylprop-1-ene (40.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (36.5 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.50 (m, 1H), 7.45 – 7.40 (m, 2H), 6.69 (d, *J* = 5.9 Hz, 1H), 5.39 (dd, *J*₁ = 8.9 Hz, *J*₂ = 7.2 Hz, 1H), 5.13 (d, *J* = 9.2 Hz, 1H), 4.27 – 4.17 (m, 2H), 1.88 (s, 3H), 1.78 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.9, 166.5, 140.2, 133.9, 131.7, 128.5, 127.1, 119.1, 61.6, 51.9, 25.8, 18.7, 14.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₅H₂₀NO₃: 262.1437. Found: 262.1438.

M.P. 101-102 °C.



Ethyl 2-benzamido-3-(4-phenylcyclohexylidene)propanoate (14).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (4-(bromomethylene)cyclohexyl)benzene (75 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (52.7 mg, 0.14 mmol, 70% yield).

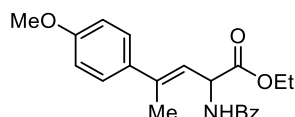
¹H NMR (600 MHz, CDCl₃) δ 7.84 – 7.80 (m, 2H), 7.54 – 7.49 (m, 1H), 7.47 – 7.42 (m, 2H), 7.33 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 6.73 (dd, *J*₁ = 12.1 Hz, *J*₂ = 7.2 Hz, 1H), 5.53 –

5.48 (m, 1H), 5.19 – 5.14 (m, 1H), 4.31 – 4.17 (m, 2H), 3.06 (d, $J = 13.3$ Hz, 1H), 2.78 – 2.70 (m, 1H), 2.38 – 2.23 (m, 2H), 2.15 – 1.96 (m, 3H), 1.64 – 1.52 (m, 2H), 1.31 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.8, 166.6, 146.4, 146.3, 134.0, 131.7, 128.58, 128.56, 128.40, 128.35, 127.1, 126.82, 126.77, 126.12, 126.07, 116.58, 116.55, 61.7, 51.15, 51.11, 44.30, 44.28, 36.7, 36.6, 35.6, 35.4, 34.9, 34.6, 29.5, 29.4, 14.21, 14.16.

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{24}\text{H}_{28}\text{NO}_3$: 378.2069. Found 378.2038.

M.P. 102-103 °C.



Ethyl (*E*)-2-benzamido-4-(4-methoxyphenyl)pent-3-enoate (15).

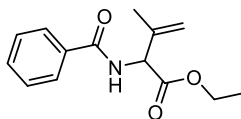
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-1-(1-bromoprop-1-en-2-yl)-4-methoxybenzene (67.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (48.0 mg, 0.136 mmol, 68% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 7.4$ Hz, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 7.35 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.82 (brs, 1H), 5.64 – 5.58 (m, 1H), 4.29 – 4.21 (m, 2H), 3.81 (s, 3H), 2.28 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.6, 166.6, 159.3, 141.4, 134.6, 133.8, 131.7, 128.6, 127.1, 127.1, 120.0, 113.6, 61.8, 55.3, 52.2, 16.9, 14.2.

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_4$: 354.1705. Found: 354.1769.

M.P. 94-95 °C.



Ethyl 2-benzamido-3-methylbut-3-enoate (16).

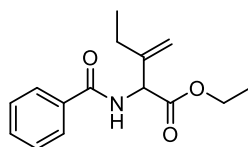
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 2-bromoprop-1-ene (36.0 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid. (35.6 mg, 0.144 mmol, 72% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.43 (m, 2H), 6.96 (d, *J* = 7.4 Hz, 1H), 5.21 (d, *J* = 7.3 Hz, 1H), 5.16 (br, 1H), 5.07 (br, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.86 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.8, 166.6, 140.2, 133.9, 131.8, 128.6, 127.1, 115.1, 61.9, 58.1, 19.7, 14.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₄H₁₈NO₃: 248.1281. Found: 248.1281.

M.P. 66-67 °C.



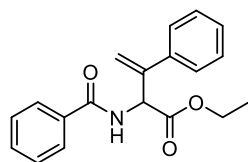
Ethyl 2-benzamido-3-methylenepentanoate (17).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 2-bromobut-1-ene (40.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (26.1 mg, 0.10 mmol, 50% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.84 – 7.79 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.41 (m, 2H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.22 (d, *J* = 7.5 Hz, 1H), 5.17 (br, 1H), 5.05 (br, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.26 – 2.14 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.1, 166.6, 146.4, 133.8, 131.8, 128.6, 127.1, 112.4, 61.8, 57.3, 26.3, 14.0, 11.9.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₅H₂₀NO₃: 262.14372. Found: 262.1439



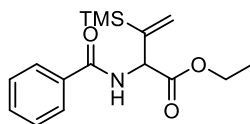
Ethyl 2-benzamido-3-phenylbut-3-enoate (18).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.20 mmol, 1.0 equiv), (1-bromovinyl)benzene (54.9 mg, 0.30 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (15.5 mg, 0.05 mmol, 25% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.48 (m, 3H), 7.40 – 7.46 (m, 2H), 7.38 – 7.30 (m, 4H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.73 (d, *J* = 7.5 Hz, 1H), 5.53 (s, 1H), 5.46 (s, 1H), 4.22 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.9, 166.7, 144.8, 138.8, 133.7, 131.8, 128.6, 128.5, 128.2, 127.1, 126.8, 116.5, 61.9, 56.5, 13.9.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₉H₂₀NO₃: 310.1437. Found 310.1439.



Ethyl 2-benzamido-3-(trimethylsilyl)but-3-enoate (19).

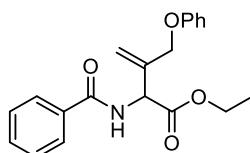
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (1-bromovinyl)trimethylsilane (53.4 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (39.6 mg, 0.13 mmol, 65% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.49 m, 1H), 7.46 – 7.42 (m, 2H), 6.78 (d, *J* = 7.3 Hz, 1H), 5.96 (s, 1H), 5.65 (s, 1H), 5.35 (d, *J* = 7.5 Hz, 1H), 4.30 – 4.16 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.18 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 171.4, 166.4, 147.7, 133.9, 131.7, 128.7, 128.6, 127.0, 77.2, 61.7, 56.4, 14.05, -1.20.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd C₁₆H₂₄NO₃Si: 306.1519. Found: 306.1516.

M.P. 35-36 °C.



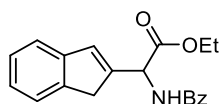
Ethyl 2-benzamido-3-(phenoxyethyl)but-3-enoate (20).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and ((2-bromoallyl)oxy)benzene (63.3 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (37.3 mg, 0.11 mmol, 55% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.42 (m, 1H), 7.37 – 7.33 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 (d, *J* = 7.1 Hz, 1H), 6.91 – 6.87 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.44 (s, 1H), 5.42 (s, 1H), 5.30 (d, *J* = 7.1 Hz, 1H), 4.59 (s, 2H), 4.21 – 4.06 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.3, 166.7, 158.2, 139.9, 133.7, 131.8, 129.5, 128.6, 127.1, 121.3, 118.5, 114.7, 68.9, 62.1, 55.9, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd C₂₀H₂₂NO₄: 340.1548. Found: 340.1543



Ethyl 2-benzamido-2-(1H-inden-2-yl)acetate (21).

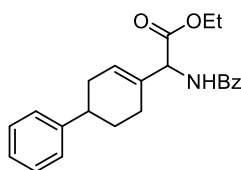
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 2-bromo-1H-indene (58.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (48.0 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.43 (m, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.21 – 7.19 (m, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.88 (s, 1H), 5.79 (t, *J* = 10.1 Hz, 1H), 4.35 – 4.24 (m, 2H), 3.53 (d, *J* = 4.5 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.5, 166.6, 143.8, 143.0, 142.9, 133.7, 131.9, 130.0, 128.6, 127.1, 126.6, 125.1, 123.7, 121.2, 62.2, 53.4, 39.4, 14.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₀H₂₀NO₃: 322.1443. Found: 322.1139.

M.P. 137-138 °C.



Ethyl 2-benzamido-2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)acetate (22).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 4-bromo-1,2,3,6-tetrahydro-1,1'-

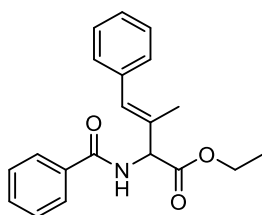
biphenyl (70.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (50.8 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.84 (d, J = 7.8 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.43 (m, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 6.95 (dd, J_1 = 27.2 Hz, J_2 = 7.3 Hz, 1H), 6.00 – 5.96 (m, 1H), 5.21 (dd, J_1 = 10.5 Hz, J_2 = 7.6 Hz, 1H), 4.31 – 4.25 (m, 2H), 2.85 – 2.75 (m, 1H), 2.45 – 2.12 (m, 5H), 2.02 – 1.96 (m, 1H), 1.84 – 1.75 (m, 2H), 1.33 (t, J = 7.0 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.2, 171.1, 166.61, 166.55, 146.4, 133.97, 133.95, 133.3, 133.0, 131.77, 131.76, 128.6, 128.4, 127.1, 126.8, 126.6, 126.3, 126.2, 61.83, 61.81, 58.1, 58.0, 39.6, 39.5, 33.2, 29.6, 26.1, 14.20, 14.19.

HRMS (ESI) m/z ($[M+H]^+$) calcd for C₂₃H₂₆NO₃: 364.1907. Found: 364.1908.

M.P. 107-108 °C.



Ethyl (*E*)-2-benzamido-3-methyl-4-phenylbut-3-enoate (23).

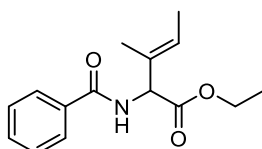
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-(2-bromoprop-1-en-1-yl)benzene (58.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (45.2 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.85 (d, J = 7.3 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.43 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.25 – 7.21 (m, 1H), 7.08 (d, J = 6.7 Hz, 1H), 6.70 (s, 1H), 5.34 (d, J = 7.2 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.97 (d, J = 1.1 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.1, 166.7, 136.8, 133.9, 132.9, 131.8, 129.8, 129.0, 128.6, 128.1, 127.1, 126.9, 62.0, 59.9, 15.2, 14.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for C₂₀H₂₂NO₃: 324.1594. Found 324.1595.

M.P. 67-68 °C.



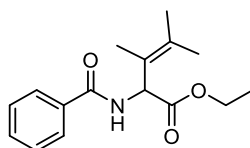
Ethyl (*E*)-2-benzamido-3-methylpent-3-enoate (24).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*Z/E*)-2-bromobut-2-ene (40.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (26.1 mg, 0.10 mmol, 50% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.41 (m, 3H), 6.93 (d, *J* = 7.3 Hz, 1H), 5.73 – 5.68 (m, 1H), 5.16 (d, *J* = 7.3 Hz, 1H), 4.27 – 4.20 (m, 2H), 1.69 (s, 3H), 1.65 (d, *J* = 6.9 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H)

¹³C NMR (151 MHz, CDCl₃) δ 171.3, 166.5, 134.0, 131.7, 130.7, 128.6, 127.1, 125.0, 61.7, 59.5, 14.1, 13.5, 13.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₅H₂₀NO₃: 262.1437. Found: 262.1438.



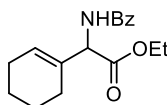
Ethyl 2-benzamido-3,4-dimethylpent-3-enoate (25).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 2-bromo-3-methylbut-2-ene (44.4 mg, 0.3 mmol, 1.5 equiv). NiCl₂(DME) (4.39 mg, 0.02 mmol, 10 mol %) was used to replace NiBr₂. After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (23.1 mg, 0.088 mmol, 44% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.52 – 7.47 (m, 2H), 6.97 (d, *J* = 6.7 Hz, 1H), 5.69 (d, *J* = 6.9 Hz, 1H), 4.27 – 4.16 (m, 2H), 2.00 (s, 3H), 1.73 (s, 3H), 1.60 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.8, 166.4, 134.1, 132.4, 131.6, 128.5, 127.1, 121.9, 61.6, 54.7, 21.3, 20.6, 14.1, 13.3.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₆H₂₂NO₃: 276.1594. Found 276.1595.



Ethyl 2-benzamido-2-(cyclohex-1-en-1-yl)acetate (26).

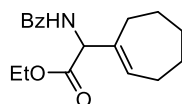
This compound was prepared according to standard method except $\text{NiCl}_2(\text{Py})_4$ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and cyclohex-1-en-1-yl trifluoromethanesulfonate (69.0 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (45.9 mg, 0.16 mmol, 80% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.82 (d, $J = 7.4$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 6.86 (d, $J = 7.0$ Hz, 1H), 5.86 (s, 1H), 5.14 (d, $J = 7.5$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.13 – 1.98 (m, 4H), 1.68 – 1.54 (m, 4H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.3, 166.6, 134.0, 133.1, 131.7, 128.6, 127.1, 126.9, 61.7, 58.3, 25.6, 25.1, 22.5, 21.9, 14.2.

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_3$: 288.1594. Found: 288.1595.

M.P. 92-93 °C.



Ethyl 2-benzamido-2-(cyclohept-1-en-1-yl)acetate (27).

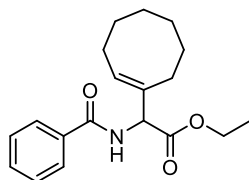
This compound was prepared according to standard method except $\text{NiCl}_2(\text{Py})_4$ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4mg, 0.2 mmol, 1.0 equiv) and cyclohept-1-en-1-yl trifluoromethanesulfonate (73.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (34.3 mg, 0.114 mmol, 57% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 7.5$ Hz, 2H), 7.53 – 7.49 (m, 1H), 7.46 – 7.42 (t, $J = 7.6$ Hz, 2H), 6.90 (d, $J = 6.5$ Hz, 1H), 6.03 (t, $J = 6.5$ Hz, 1H), 5.13 (d, $J = 7.2$ Hz, 1H), 4.29 – 4.21 (m, 2H), 2.25 – 2.15 (m, 4H), 1.77 – 1.69 (m, 2H), 1.52 – 1.44 (m, 4H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.4, 166.5, 138.8, 134.2, 132.4, 131.7, 128.6, 127.1, 61.7, 59.2, 32.3, 29.8, 28.3, 26.8, 26.4, 14.2.

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_3$: 302.1756. Found: 302.1752.

M.P. 87-88 °C.



Ethyl (*E*)-2-benzamido-2-(cyclooct-1-en-1-yl)acetate (28).

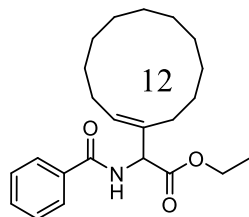
This compound was prepared according to standard method except $\text{NiCl}_2(\text{Py})_4$ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (*E*)-cyclooct-1-en-1-yl trifluoromethanesulfonate (77.4 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (31.5 mg, 0.10 mmol, 50% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 7.8$ Hz, 2H), 7.53 – 7.49 (m, 1H), 7.46 – 7.41 (m, 2H), 6.89 (d, $J = 7.4$ Hz, 1H), 5.85 – 5.80 (m, 1H), 5.18 (d, $J = 7.4$ Hz, 1H), 4.28 – 4.20 (m, 2H), 2.34 – 2.14 (m, 4H), 1.58 – 1.45 (m, 8H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.6, 166.5, 134.1, 131.7, 130.5, 128.6, 127.1, 61.7, 58.5, 29.3, 29.2, 26.9, 26.3, 26.1, 14.1

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_3$: 316.1907. Found 316.1909.

M.P. 105-106 °C.



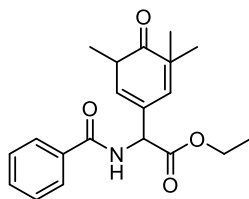
Ethyl (*E*)-2-benzamido-2-(cyclododec-1-en-1-yl)acetate (29).

This compound was prepared according to standard method except $\text{NiCl}_2(\text{Py})_4$ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and cyclododec-1-en-1-yl trifluoromethanesulfonate (94.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (14.8 mg, 0.04 mmol, 20% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.83 – 7.78 (m, 2H), 7.53 – 7.46 (m, 1H), 7.46 – 7.41 (m, 2H), 6.73 (d, $J = 7.8$ Hz, 1H), 5.55 – 5.41 (m, 1H), 5.21 (d, $J = 7.8$ Hz, 1H), 4.30 – 4.15 (m, 2H), 2.34 – 2.02 (m, 4H), 1.47 – 1.40 (m, 2H), 1.40 – 1.33 (m, 9H), 1.33 – 1.25 (m, 8H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.9, 166.8, 135.6, 134.1, 131.7, 131.1, 128.6, 127.1, 61.47, 56.36, 26.7, 25.7, 25.4, 25.0, 24.9, 24.7, 24.5, 24.0, 22.7, 22.2, 14.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{23}H_{33}NO_3$: 372.2533. Found 372.2534.

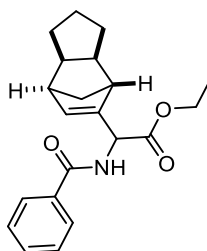


Ethyl 2-benzamido-2-(3,5,5-trimethyl-4-oxo-5H-cyclohexa-1,5-dien-1-yl)acetate (30).

This compound was prepared according to standard method except $NiCl_2(Py)_4$ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 5,5-trimethyl-4-oxo-5H-cyclohexa-1,5-dien-1-yl trifluoromethanesulfonate (85.5 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid. (34.2 mg, 0.10 mmol, 50% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.53 – 7.49 (m, 1H), 7.53 – 7.48 (m, 2H), 7.10 (d, J = 7.0 Hz, 1H), 6.88 (br, 1H), 6.20 (d, J = 2.4 Hz, 1H), 5.33 (d, J = 6.9 Hz, 1H), 4.31 – 4.20 (m, 2H), 1.87 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.18 (s, 3H), 1.16 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 205.05, 170.4, 166.6, 143.5, 137.0, 133.8, 133.4, 131.9, 128.6, 127.1, 127.0, 62.1, 55.9, 46.3, 25.7, 25.6, 15.6, 14.0.



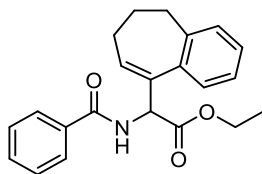
Ethyl 2-benzamido-2-2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoinden-5-yl)acetate (31).

This compound was prepared according to standard method except $NiCl_2(Py)_4$ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4mg, 0.2 mmol, 1.0 equiv) and 2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoinden-5-yl trifluoromethanesulfonate. (84.6 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (40.7 mg, 0.12 mmol, 60% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.4 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.41 (m, 2H), 6.79 (dd, J_1 = 75.7 Hz, J_2 = 7.9 Hz, 1H), 6.02 – 5.99 (m, 1H), 5.37 (dd, J_1 = 47.9 Hz, J_2 = 7.8 Hz, 1H), 4.30 – 4.18 (m, 2H), 2.64 – 2.48 (m, 2H), 2.13 – 1.95 (m, 2H), 1.91 – 1.75 (m, 3H), 1.61 – 1.40 (m, 3H), 1.30 (t, J = 7.1, 2.5 Hz, 3H), 1.01 – 0.92 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 170.63, 170.58, 166.7, 166.4, 146.3, 146.1, 134.5, 134.3, 134.00, 133.95, 131.71, 131.68, 128.6, 127.1, 127.0, 61.7, 61.6, 53.0, 52.8, 47.40, 47.37, 47.4, 47.2, 46.3, 46.2, 46.1, 42.7, 42.3, 30.9, 30.8, 30.7, 30.6, 30.5, 14.1.

HRMS (ESI) m/z ([M+H]⁺) calcd for C₂₁H₂₆NO₃: 340.1907. Found: 340.1909.



Ethyl 2-benzamido-2-(6,7-dihydro-5H-benzo[7]annulen-9-yl)acetate (32).

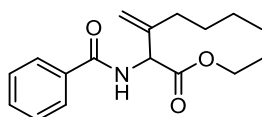
This compound was prepared according to standard method except NiCl₂(Py)₄ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4mg, 0.2 mmol, 1.0 equiv) and 6,7-dihydro-5H-benzo[7]annulen-9-yl trifluoromethanesulfonate (87.6 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (45.3 mg, 0.13 mmol, 65% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.80 – 7.77 (m, 2H), 7.55 – 7.49 (m, 2H), 7.46 – 7.42 (m, 2H), 7.31 – 7.26 (m, 1H), 7.22 – 7.19 (m, 2H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.40 – 6.35 (m, 1H), 5.61 (d, *J* = 7.2 Hz, 1H), 4.23 – 4.10 (m, 2H), 2.55 – 2.51 (m, 2H), 2.15 – 2.08 (m, 2H), 1.96 – 1.78 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.3, 166.6, 141.4, 138.2, 137.2, 133.9, 131.8, 130.5, 128.8, 128.6, 127.4, 127.1, 126.5, 126.3, 61.8, 57.2, 34.8, 32.0, 24.4, 13.9.

HRMS (ESI) m/z ([M+H]⁺) calcd for C₂₂H₂₄NO₃: 350.1750. Found: 350.1752.

M.P. 92-93 °C.



Ethyl 2-benzamido-3-methyleneheptanoate (33).

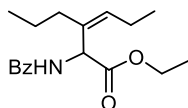
This compound was prepared according to standard method except NiCl₂(Py)₄ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and hex-1-en-2-yl trifluoromethanesulfonate (69.6 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (35.8 mg, 0.124 mmol, 62% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.83 – 7.80 (m, 2H), 7.53 – 7.49 (m, 1H), 7.46 – 7.42 (m, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 5.21 (d, *J* = 7.5 Hz, 1H), 5.17 (br, 1H), 5.05 (br, 1H), 4.25 (q, *J*

= 7.1 Hz, 2H), 2.17 (m, J = 7.9 Hz, 2H), 1.38 – 1.33 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.1, 166.6, 145.1, 133.9, 131.8, 128.6, 127.1, 113.3, 61.8, 57.1, 33.3, 29.6, 22.3, 14.1, 13.9.

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{23}\text{H}_{33}\text{NO}_3$: 290.1750. Found 290.1754



Ethyl (Z)-2-benzamido-3-propylhex-3-enoate (34).

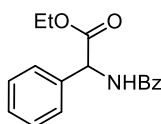
This compound was prepared according to standard method except $\text{NiCl}_2(\text{Py})_4$ as the precatalyst using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (Z/E)-hept-3-en-4-yl trifluoromethanesulfonate (73.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid containing a mixture of *cis/trans* isomers in a ratio of 1:5 (12.2 mg, 0.04 mmol, 20% yield). Note: the stereochemistry of the major isomer was not assigned.

^1H NMR (600 MHz, CDCl_3) δ 7.83 – 7.79 (m, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 6.78 (d, J = 7.7 Hz, 1H), 5.56 – 5.53 (m, 1H), 5.15 (d, J = 7.6 Hz, 1H), 4.26 – 4.19 (m, 2H), 2.21 – 2.02 (m, 4H), 1.53 – 1.53 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.5 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H).

^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 7.4 Hz, 1H), 5.53 – 5.10 (m, 1H), 5.17 (d, J = 7.6 Hz, 1H), 4.37 – 4.28 (m, 2H), 1.44 – 1.35 (m, 4H), 1.33 (t, J = 7.2 Hz, 3H), 1.10 – 1.03 (m, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 171.7, 166.7, 136.8, 134.6, 132.2, 131.7, 130.0, 127.1, 61.6, 61.5, 57.4, 57.3, 31.2, 29.6, 22.6, 22.1, 21.9, 21.2, 14.1, 14.0, 14.0, 13.7, 13.5.

HRMS (ESI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_3$: 304.19107. Found: 304.1908.



Ethyl 2-benzamido-2-phenylacetate (35a).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and bromobenzene (46.8 mg, 0.3 mmol, 1.5

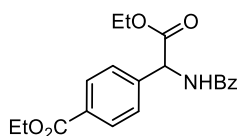
equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (48.1 mg, 0.17 mmol, 85% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.78 (m, 2H), 7.52 – 7.24 (m, 9H), 5.76 (d, *J* = 7.2 Hz, 1H), 4.30 – 4.11 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.9, 166.5, 136.6, 133.5, 131.7, 128.8, 128.5, 128.4, 127.2, 127.1, 61.9, 56.7, 13.9.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₇H₁₈NO₃: 284.1281. Found: 284.1286.

M.P. 83-84 °C.



Ethyl 4-(1-benzamido-2-ethoxy-2-oxoethyl)benzoate (35b).

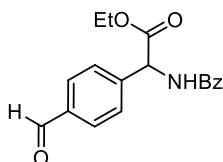
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and ethyl 4-bromobenzoate (68.7 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (55.4 mg, 0.156 mmol, 78% yield).

¹H NMR (600 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.84 – 7.82 (m, 2H), 7.55 – 7.51 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 6.7 Hz, 1H), 5.81 (d, *J* = 6.8 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.31 – 4.17 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.5, 166.5, 166.1, 141.6, 133.5, 132.0, 130.6, 130.2, 128.7, 127.2, 127.1, 62.4, 61.1, 56.6, 14.3, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₀H₂₂NO₅: 356.1492. Found: 356.1496.

M.P. 93-94 °C.



Ethyl 2-benzamido-2-(4-formylphenyl)acetate (35c).

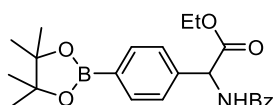
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 4-bromobenzaldehyde (55.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (43.5 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.01 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.85 – 7.83 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.48 – 7.43 (m, 2H), 7.35 (d, *J* = 6.4 Hz, 1H), 5.83 (d, *J* = 6.6 Hz, 1H), 4.36 – 4.17 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 191.6, 170.2, 166.5, 143.4, 136.3, 133.3, 132.1, 130.3, 128.7, 127.9, 127.1, 62.6, 56.7, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₈H₁₈NO₄: 312.1235. Found: 312.1230.

M.P. 95-96 °C.



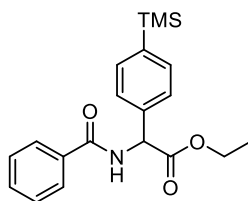
Ethyl 2-benzamido-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetate (35d).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (84.7 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (65.44 mg, 0.16 mmol, 80% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.83 – 7.80 (m, 4H), 7.53 – 7.49 (m, 1H), 7.47 – 7.41 (m, 4H), 7.17 (d, *J* = 6.9 Hz, 1H), 5.77 (d, *J* = 7.0 Hz, 1H), 4.30 – 4.12 (m, 2H), 1.33 (s, 12H), 1.23 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.9, 166.5, 139.6, 135.4, 133.7, 131.8, 128.6, 127.1, 126.6, 83.9, 62.1, 56.9, 24.8, 13.9.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₃H₂₉BNO₅: 410.2138. Found: 410.2137.



Ethyl 2-benzamido-2-(4-(trimethylsilyl)phenyl)acetate (35e).

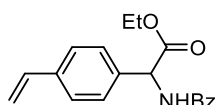
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and (4-bromophenyl)trimethylsilane (68.4 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (53.2 mg, 0.15 mmol, 75% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.82 (d, *J* = 7.3 Hz, 2H), 7.54 – 7.48 (m, 3H), 7.43 (m, 4H), 7.15 (d, *J* = 7.0 Hz, 1H), 5.76 (d, *J* = 7.0 Hz, 1H), 4.29 (m, 1H), 4.18 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.26 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 171.0, 166.5, 141.0, 137.1, 134.0, 133.7, 131.8, 128.6, 127.1, 126.5, 62.1, 56.8, 14., -1.21.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₀H₂₆NO₃Si: 356.1676. Found 356.1675.

M.P. 104-105 °C.



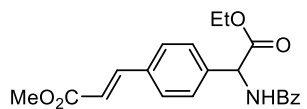
Ethyl 2-benzamido-2-(4-vinylphenyl)acetate (35f).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and 1-bromo-4-vinylbenzene (54.6 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (44.5 mg, 0.144 mmol, 72% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.80 (m, 2H), 7.54 – 7.49 (m, 1H), 7.47 – 7.38 (m, 6H), 7.18 (d, *J* = 6.8 Hz, 1H), 6.70 (dd, *J*₁ = 17.6 Hz, *J*₂ = 10.9 Hz, 1H), 5.75 (dd, *J*₁ = 12.3 Hz, *J*₂ = 5.3 Hz, 2H), 5.27 (d, *J* = 10.9 Hz, 1H), 4.33 – 4.13 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.0, 166.5, 137.8, 136.1, 133.62, 131.9, 128.6, 127.5, 127.1, 126.7, 114.6, 62.1, 56.6, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₉H₂₀NO: 310.1437. Found: 310.1439.



Methyl (*E*)-3-(4-(1-benzamido-2-ethoxy-2-oxoethyl)phenyl)acrylate (35g).

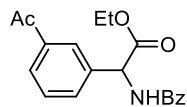
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and methyl (*E*)-3-(4-bromophenyl)acrylate (72.0 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (51.4 mg, 0.14 mmol, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.84 – 7.82 (m, 2H), 7.67 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.51 (m, 3H), 7.49 – 7.43 (m, 4H), 7.25 (s, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.77 (d, *J* = 6.8 Hz, 1H), 4.32 – 4.16 (m, 2H), 3.80 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.6, 167.3, 166.4, 144.0, 139.0, 134.6, 133.5, 132.0, 128.7, 128.6, 127.8, 127.1, 118.4, 62.3, 56.7, 51.8, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₁H₂₂NO₅: 368.1492. Found: 368.1498.

M.P. 119-120 °C.



Ethyl 2-(3-acetylphenyl)-2-benzamidoacetate (35h).

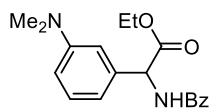
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and 1-(3-bromophenyl)ethan-1-one (59.4 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (48.8 mg, 0.15 mmol, 75% yield).

¹H NMR (600 MHz, CDCl₃) δ 8.04 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.50 – 7.43 (m, 3H), 7.33 (d, *J* = 6.4 Hz, 1H), 5.82 (d, *J* = 6.7 Hz, 1H), 4.31 – 4.17 (m, 2H), 2.61 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 197.5, 170.6, 166.5, 137.71, 137.68, 133.4, 132.00, 131.98, 129.2, 128.7, 128.4, 127.1, 126.9, 62.4, 56.6, 26.7, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₉H₂₀NO₄: 326.1386. Found: 326.1389.

M.P. 80-81 °C.



Ethyl 2-benzamido-2-(3-(dimethylamino)phenyl)acetate (35i).

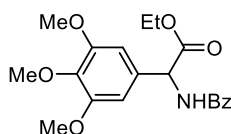
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and 3-bromo-*N,N*-dimethylaniline (59.7 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (44.3 mg, 0.136 mmol, 68% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.83 – 7.80 (m, 2H), 7.52 – 7.48 (m, 1H), 7.45 – 7.41 (m, 2H), 7.25 – 7.20 (m, 1H), 7.03 (br, 1H), 6.80 – 6.74 (m, 2H), 6.71 – 6.67 (m, 1H), 5.70 (d, *J* = 7.1 Hz, 1H), 4.32 – 4.14 (m, 2H), 2.96 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.2, 166.6, 150.9, 137.3, 133.9, 131.7, 129.7, 128.5, 127.1, 114.9, 112.5, 111.4, 61.8, 57.3, 40.5, 14.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{23}N_2O_3$: 327.1703. Found: 327.1705.

M.P. 75-76 °C.



Ethyl 2-benzamido-2-(3,4,5-trimethoxyphenyl)acetate (35j).

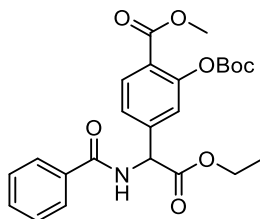
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and 5-iodo-1,2,3-trimethoxybenzene (88.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (60.0 mg, 0.15 mmol, 75% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 7.3 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.46 – 7.42 (m, 2H), 7.14 (d, J = 6.6 Hz, 1H), 6.65 (s, 2H), 5.67 (d, J = 6.9 Hz, 1H), 4.32 – 4.17 (m, 2H), 3.86 (s, 6H), 3.83 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 166.5, 153.6, 138.1, 133.6, 132.2, 131.9, 128.6, 127.1, 104.4, 62.1, 60.8, 57.0, 56.2, 14.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{24}NO_6$: 374.1598. Found: 374.1797.

M.P. 102-103 °C.



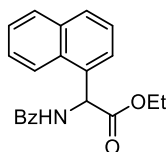
Ethyl 4-(1-benzamido-2-ethoxy-2-oxoethyl)-2-((tert-butoxycarbonyl)oxy)benzoate (35k)

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and methyl 4-bromo-2-((tert-butoxycarbonyl)oxy)benzoate (99.0 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (68.5 mg, 0.15 mmol, 75% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.1 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.53 – 7.48 (m, 1H), 7.45 – 7.37 (m, 3H), 7.27 – 7.23 (m, 1H), 5.80 (d, J = 6.9 Hz, 1H), 4.28 – 4.15 (m, 2H), 3.85 (s, 3H), 1.53 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0, 166.5, 164.7, 151.2, 150.8, 142.8, 133.2, 132.2, 132.0, 128.6, 127.2, 124.9, 123.5, 122.3, 83.9, 62.5, 56.0, 52.3, 27.6, 13.9.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{24}H_{28}NO_3$: 458.18094. Found: 458.1806.



Ethyl 2-benzamido-2-(naphthalen-1-yl)acetate (36).

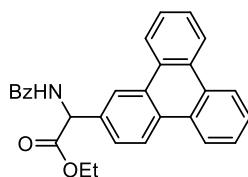
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and 1-bromonaphthalene (61.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (50.0 mg, 0.15 mmol, 75% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.87 – 7.82 (m, 5H), 7.55 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.7$ Hz, 1H), 7.53 – 7.47 (m, 3H), 7.46 – 7.43 (t, $J = 7.6$ Hz, 2H), 7.29 (d, $J = 6.6$ Hz, 1H), 5.94 (d, $J = 7.0$ Hz, 1H), 4.33 – 4.16 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 166.5, 134.1, 133.7, 133.3, 133.2, 131.9, 128.9, 128.6, 128.1, 127.7, 127.2, 126.7, 126.5, 124.8, 62.1, 57.0, 14.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{20}NO_3$: 334.1437. Found: 334.1439.

M.P. 100-101 °C.



Ethyl 2-benzamido-2-(triphenylen-2-yl)acetate (37).

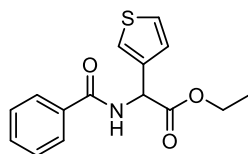
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and 2-bromotriphenylene (88.2 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (71.9 mg, 0.166 mmol, 83% yield).

1H NMR (600 MHz, $CDCl_3$) δ 8.76 – 8.58 (m, 6H), 7.88 (d, $J = 7.3$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 1H), 7.66 (d, $J = 3.0$ Hz, 4H), 7.55 – 7.35 (m, 4H), 6.04 (d, $J = 6.4$ Hz, 1H), 4.37 – 4.19 (m, 2H), 1.26 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 166.6, 135.5, 133.7, 131.9, 130.2, 130.0, 129.9, 129.33, 129.29, 128.6, 127.54, 127.49, 127.3, 127.2, 125.9, 124.2, 123.43, 123.37, 123.31, 122.5, 62.2, 57.1, 14.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{29}H_{24}NO_3$: 434.1750. Found: 434.1754.

M.P. 214-215 °C.



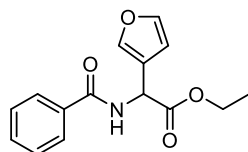
Ethyl 2-benzamido-2-(thiophen-3-yl)acetate (38).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv) and 3-bromothiophene (48.3 mg, 0.3 mmol, 1.5 equiv). $NiCl_2(DME)$ (4.39 mg, 0.02 mmol, 10 mol %) was used to replace $NiBr_2$. After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (23.1 mg, 0.08 mmol, 40% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.53 – 7.50 (m, 1H), 7.46 – 7.42 (m, 2H), 7.35 – 7.31 (m, 2H), 7.14 (dd, $J_1 = 5.0$ Hz, $J_2 = 1.4$ Hz, 1H), 7.08 (d, $J = 7.4$ Hz, 1H), 5.91 (d, $J = 7.4$ Hz, 1H), 4.33 – 4.20 (m, 2H), 1.28 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 166.6, 136.8, 133.6, 131.9, 128.6, 126.7, 126.3, 123.2, 62.1, 52.6, 14.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{15}H_{16}NO_3S$: 290.0845. Found: 290.0844.



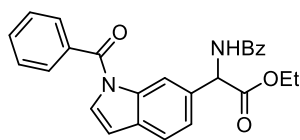
Ethyl 2-benzamido-2-(furan-3-yl)acetate (39).

This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (61.4 mg, 0.2 mmol, 1.0 equiv), 3-bromofuran (43.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (17.5 mg, 0.064 mmol, 32% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, $J = 7.7$ Hz, 2H), 7.54 – 7.50 (m, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.40 (s, 1H), 6.96 (d, $J = 6.8$ Hz, 1H), 6.45 (d, $J = 1.9$ Hz, 1H), 5.78 (d, $J = 7.4$ Hz, 1H), 4.32 – 4.23 (m, 2H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 166.7, 143.6, 140.6, 133.6, 131.9, 128.6, 127.1, 121.4, 109.2, 62.1, 49.1, 14.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd $C_{15}H_{16}NO_4$: 274.1074. Found 274.1073.



Ethyl 2-benzamido-2-(1-benzoyl-1H-indol-6-yl)acetate (40).

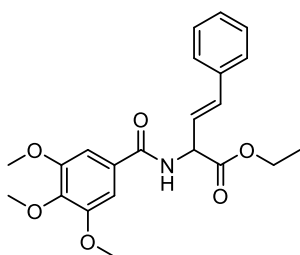
This compound was prepared according to standard method using 1-benzamido-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 61.4 mg, 1.0 equiv) and (6-iodo-1H-indol-1-yl)(phenyl)methanone (104.0 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (69.9 mg, 0.164 mmol, 82% yield).

¹H NMR (600 MHz, CDCl₃) δ 8.38 (d, *J* = 8.6 Hz, 1H), 7.85 – 7.83 (m, 2H), 7.73 – 7.70 (m, 3H), 7.63 – 7.59 (m, 1H), 7.55 – 7.50 (m, 3H), 7.47 – 7.42 (m, 3H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.25 (d, *J* = 6.5 Hz, 1H), 6.61 (dd, *J*₁ = 3.8 Hz, *J*₂ = 0.4 Hz, 1H), 5.87 (d, *J* = 6.9 Hz, 1H), 4.33 – 4.15 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.2, 168.6, 166.5, 135.9, 134.3, 133.7, 132.5, 132.1, 131.8, 131.2, 129.2, 128.6, 128.6, 128.4, 127.1, 123.9, 120.1, 116.9, 108.5, 62.1, 57.0, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₆H₂₃N₂O₄: 427.1652. Found: 427.1650.

M.P. 139-140 °C.



Ethyl (E)-4-phenyl-2-(3,4,5-trimethoxybenzamido)but-3-enoate (41).

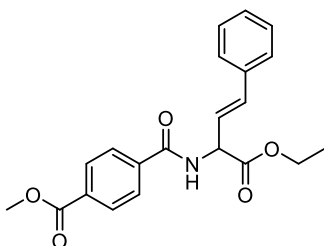
This compound was prepared according to standard method using 2-ethoxy-2-oxo-1-(3,4,5-trimethoxybenzamido)ethyl pivalate (0.2 mmol, 79.4 mg, 1.0 equiv) and (*E*)-(2-bromovinyl)benzene (054.9 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid. (51.9 mg, 0.13 mmol, 65% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.14 – 7.04 (m, 1H), 6.90 (d, *J* = 15.9 Hz, 1H), 5.64 - 5.59 (m, 1H), 4.51 – 4.41 (m, 2H), 4.08 (s, 6H), 4.06 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.0, 166.4, 153.2, 141.3, 135.8, 133.5, 129.0, 128.6, 128.2, 126.7, 123.3, 104.6, 62.1, 60.9, 56.2, 54.8, 14.1.

HRMS (ESI) m/z ($[M+Na]^+$) calcd $C_{22}H_{26}NO_6$: 400.1754. Found: 400.1751.

M.P. 115-116 °C.



Methyl (E)-4-((1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl)carbamoyl)benzoate (42).

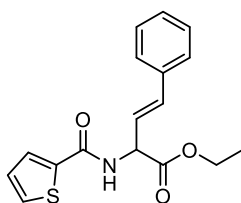
This compound was prepared according to standard method using methyl 4-((2-ethoxy-2-oxo-1-(pivaloyloxy)ethyl)carbamoyl)benzoate (73.0 mg, 0.2 mmol, 1.0 equiv) and (*E*)-(2-bromovinyl)benzene (54.9 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (55.0 mg, 0.15 mmol, 75% yield).

1H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 7.4 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 6.99 (d, J = 7.4 Hz, 1H), 6.74 (d, J = 15.8 Hz, 1H), 6.28 (dd, J_1 = 15.9, J_2 = 6.5 Hz, 1H), 5.49 – 5.44 (m, 1H), 4.36 – 4.24 (m, 2H), 3.95 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 166.2, 165.8, 137.6, 135.7, 133.7, 133.1, 129.9, 128.6, 128.3, 127.2, 126.7, 123.1, 62.3, 54.7, 52.4, 14.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{22}NO_5$: 368.1492. Found 368.1496.

M.P. 91-92 °C.



Ethyl (E)-4-phenyl-2-(thiophene-2-carboxamido)but-3-enoate (43).

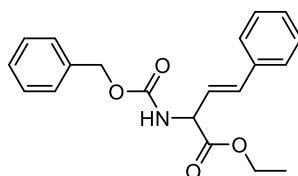
This compound was prepared according to standard method using 2-ethoxy-2-oxo-1-(thiophene-2-carboxamido)ethyl pivalate (0.2 mmol, 62.6 mg, 1.0 equiv) and (*E*)-(2-bromovinyl)benzene (54.9 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (50.5 mg, 0.16 mmol, 80% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.49 – 7.43 (m, 2H), 7.18 (d, *J* = 5.1 Hz, 1H), 7.00 – 6.93 (m, 3H), 6.85 (d, *J* = 15.7 Hz, 1H), 6.11 (dd, *J*₁ = 15.7, *J*₂ = 6.5 Hz, 1H), 5.43 (m, 1H), 4.35 – 4.22 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.7, 166.7, 140.8, 133.68, 131.9, 128.6, 127.4, 127.1, 126.8, 126.5, 125.0, 122.8, 62.27, 54.4, 14.1

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₁₇H₁₈NO₃S: 316.1002. Found 356.1007.

M.P. 96-97 °C.



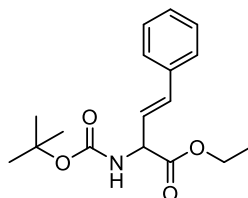
Ethyl (*E*)-2-(((benzyloxy)carbonyl)amino)-4-phenylbut-3-enoate (44).

This compound was prepared according to standard method using 1-(((benzyloxy)carbonyl)amino)-2-ethoxy-2-oxoethyl pivalate (67.0 mg, 0.2 mmol, 1.0 equiv) and (*E*)-(2-bromovinyl)benzene (54.9 mg, 0.3 mmol, 1.5 equiv. NiCl₂ (2.60 mg, 0.02 mmol, 10 mol %) was used to replace NiBr₂. After purification by flash column chromatograph, the title compound was obtained as a colorless liquid (41.3 mg, 0.122 mmol, 61% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.24 (m, 11H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J*₁ = 15.9, *J*₂ = 6.4 Hz, 1H), 5.59 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 2H), 5.08 – 5.04 (m, 1H), 4.32 – 4.16 (m, 2H), 1.32 – 1.28 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.6, 155.49, 136.15, 135.8, 132.9, 128.6, 128.6, 128.5, 128.2, 128.1, 126.64, 123.6, 67.1, 62.0, 55.9, 14.1.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₀H₂₂NO₄:340.1543. Found:340.1544.



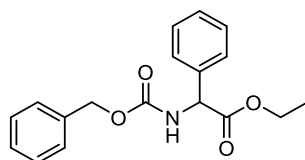
Ethyl (*E*)-2-((tert-butoxycarbonyl)amino)-4-phenylbut-3-enoate (45).

This compound was prepared according to standard method using 1-((tert-butoxycarbonyl)amino)-2-ethoxy-2-oxoethyl pivalate (60.6 mg, 0.2 mmol, 1.0 equiv) and (*E*)-(2-bromovinyl)benzene (54.9 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (36.6 mg, 0.10 mmol, 50% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.40 – 7.22 (m, 5H), 6.66 (d, J = 15.9 Hz, 1H), 6.19 (dd, J_1 = 16.4 Hz, J_2 = 6.2 Hz, 1H), 5.31 (br, 1H), 4.99 (br, 1H), 4.29 – 4.18 (m, 2H), 1.46 (s, 9H), 1.30 (t, J = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.9, 155.0, 136.0, 132.6, 128.6, 128.1, 126.6, 124.1, 80.1, 61.8, 55.5, 28.3, 14.1

HRMS (ESI) m/z ($[M+H]^+$) calcd C₁₇H₂₄NO₄: 306.1699. Found 306.1697.



Ethyl 2-(((benzyloxy)carbonyl)amino)-2-phenylacetate (46).

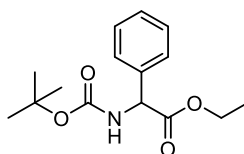
This compound was prepared according to standard method using 1-(((benzyloxy)carbonyl)amino)-2-ethoxy-2-oxoethyl pivalate (67.4 mg, 0.2 mmol, 1.0 equiv), bromobenzene (46.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (25.0 mg, 0.08 mmol, 40% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.40 – 7.30 (m, 10H), 7.14 (br, 1H), 5.87 (d, J = 7.5 Hz, 1H), 5.37 (d, J = 7.4 Hz, 1H), 5.16 – 5.05 (m, 2H), 4.26 – 4.06 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.8, 155.3, 136.8, 136.1, 128.9, 128.51, 128.48, 128.19, 128.15, 127.1, 67.1, 61.9, 58.0, 14.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for C₁₈H₂₀NO₄: 314.1586. Found: 314.1385.

M.P. 70-71 °C.



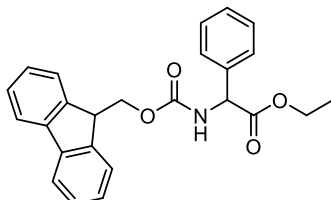
Ethyl 2-((tert-butoxycarbonyl)amino)-2-phenylacetate (47).

This compound was prepared according to standard method using 1-((tert-butoxycarbonyl)amino)-2-ethoxy-2-oxoethyl pivalate (60.6 mg, 0.2 mmol, 1.0 equiv) and bromobenzene (46.8 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a colorless liquid (16.7 mg, 0.06 mmol, 30% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.39 – 7.29 (m, 5H), 5.57 (d, *J* = 7.6 Hz, 1H), 5.30 (d, *J* = 7.6 Hz, 1H), 4.24 – 4.10 (m, 2H), 1.43 (s, 9H), 1.20 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.1, 154.8, 137.0, 128.8, 128.3, 127.1, 80.0, 61.7, 57.6, 28.3, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd C₁₅H₂₂NO₄: 280.1543. Found: 280.1541.



Ethyl 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-2-phenylacetate (48).

This compound was prepared according to standard method using 2-ethoxy-2-oxo-11-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-2-ethoxy-2-oxoethyl pivalate (0.2 mmol, 85.0 mg, 1.0 equiv) and (*E*)-(2-bromovinyl)benzene (54.9 mg, 0.3 mmol, 1.5 equiv). After purification by flash column chromatograph, the title compound was isolated as a white solid (48.1 mg, 0.12 mmol, 60% yield).

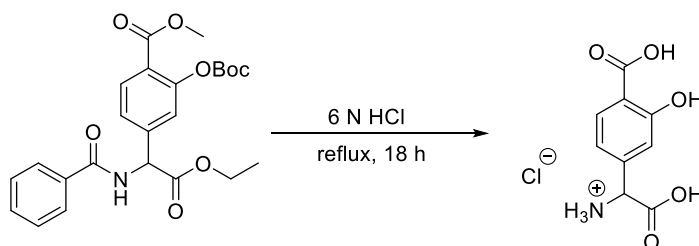
¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.28 (m, 10H), 5.90 (d, *J* = 7.5 Hz, 1H), 5.38 (d, *J* = 7.4 Hz, 1H), 4.40 (m, 2H), 4.29 – 4.13 (m, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.8 155.4, 143.8, 143.7, 141.3, 136.7, 128.9, 128.5, 127.7, 127.1, 127.0, 125.0 112.0, 67.1, 62.0, 58.0, 47.1, 14.0.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₂₅H₂₄NO₄: 402.1699. Found 402.1695.

M.P. 141-142 °C.

Deprotection of *N*-Bz Group and Cleavage of Ester.³⁵



4-(Amino(carboxy)methyl)-2-hydroxybenzoic acid hydrochloride (51).

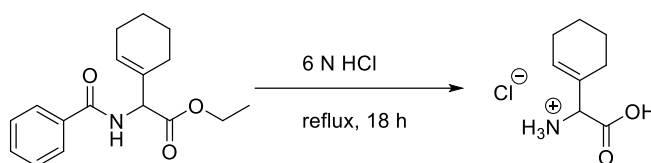
A 10 mL flask was charged with methyl 4-(1-benzamido-2-ethoxy-2-oxoethyl)-2-((tert-butoxycarbonyl)oxy)benzoate (45.7 mg, 0.1 mmol, 1.0 equiv.) and a 6 M of aqueous HCl solution (2.0 mL, 12.0 mmol, 60.0 equiv). The reaction mixture was heated at 120 °C for 18 h.

After concentration under reduced pressure, the crude product was washed with DCM to give 4-(amino(carboxy)methyl)-2-hydroxybenzoic acid hydrochloride as white solid. (22.2 mg, 0.18 mmol, 90% yield).

¹H NMR (600 MHz, CD₃OD) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.09 (s, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 5.10 (s, 1H).

¹³C NMR (151 MHz, CD₃OD) δ 172.8, 170.0, 163.4, 140.9, 132.7, 119.4, 117.9, 115.2, 57.2.

HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₉H₁₀NO₅: 212.0553. Found: 212.0555.



2-Amino-2-(cyclohex-1-en-1-yl)acetic acid hydrochloride (50).

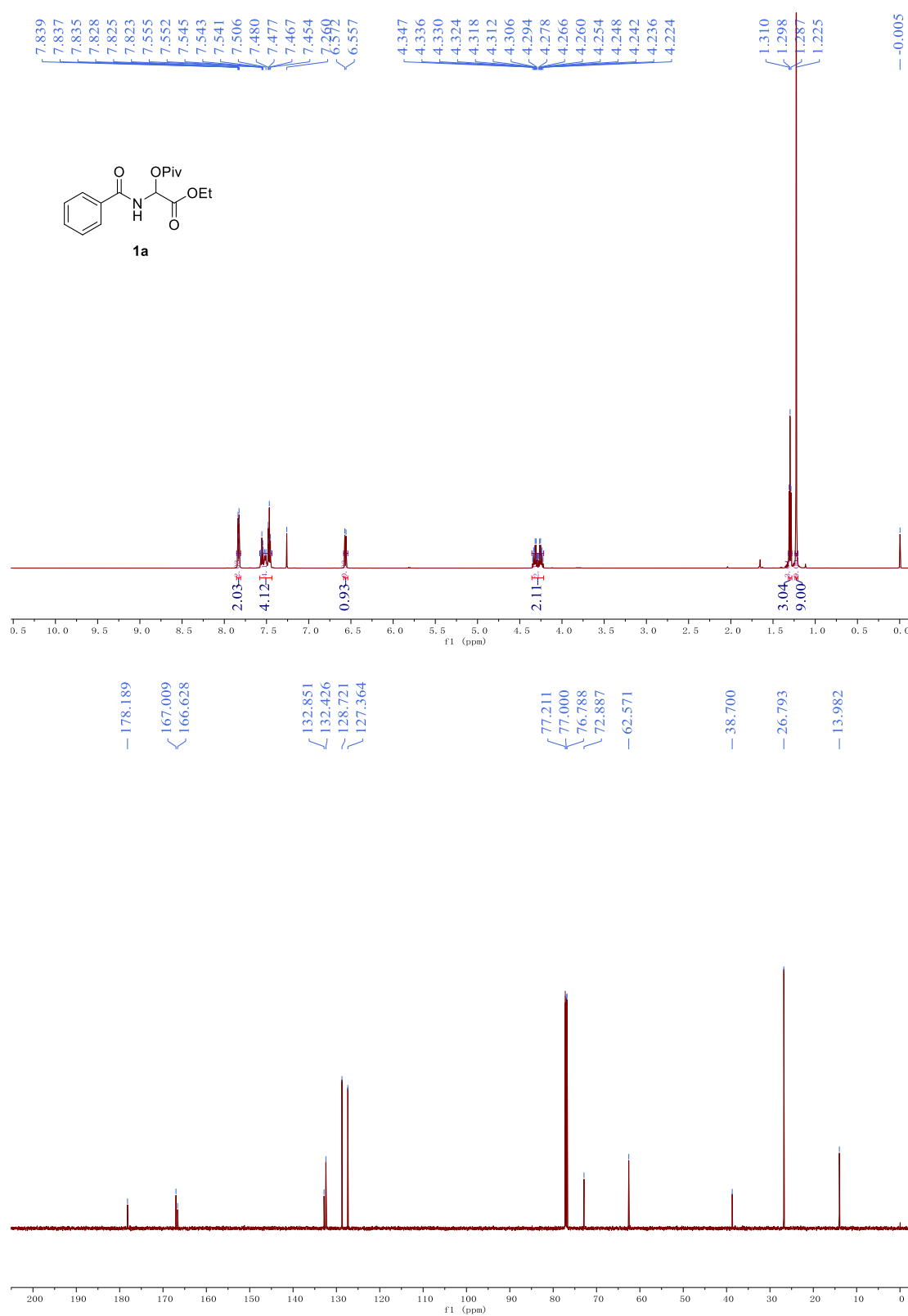
A 10 mL flask was charged with ethyl 2-benzamido-2-(cyclohex-1-en-1-yl)acetate (57.4 mg, 0.2 mmol, 1.0 equiv.) and a 6 M of aqueous HCl (4.0 mL, 24.0 mmol, 60.0 equiv). The reaction mixture was heated at 120 °C for 18 h. After concentration under reduced pressure, the crude product was washed with DCM to give 2-amino-2-(cyclohex-1-en-1-yl)acetic acid hydrochloride as white solid. (28.6 mg, 0.15 mmol, 75% yield).

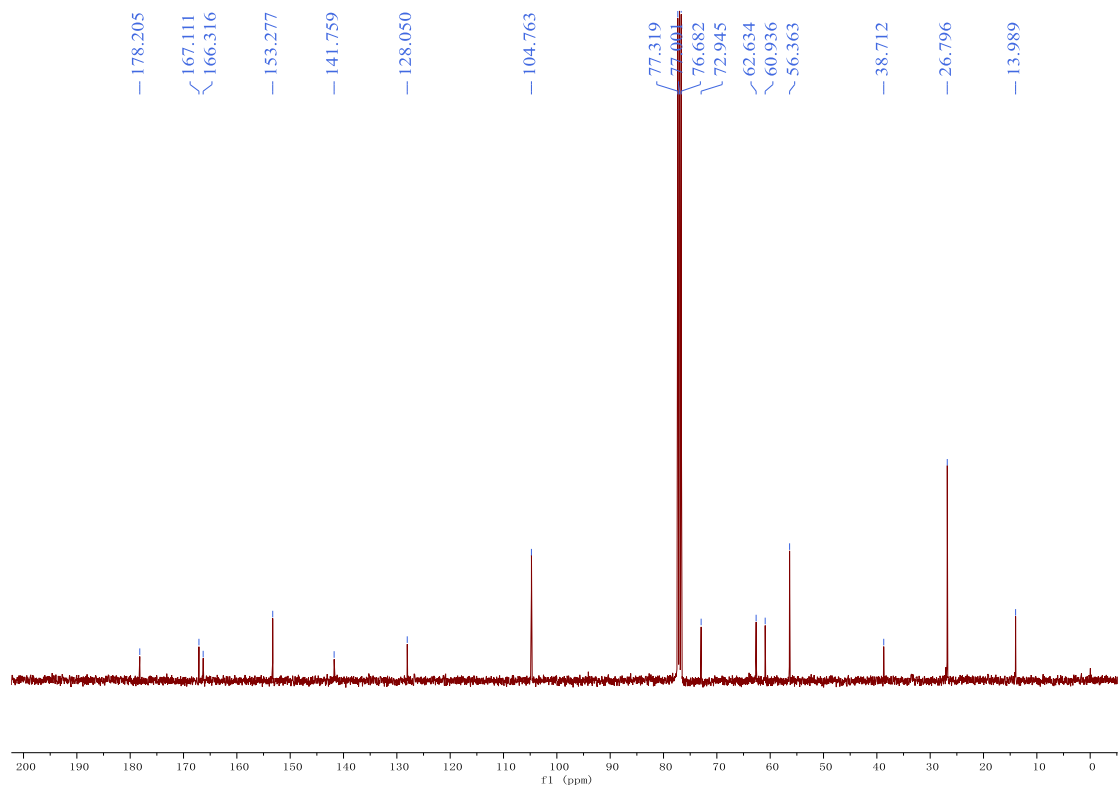
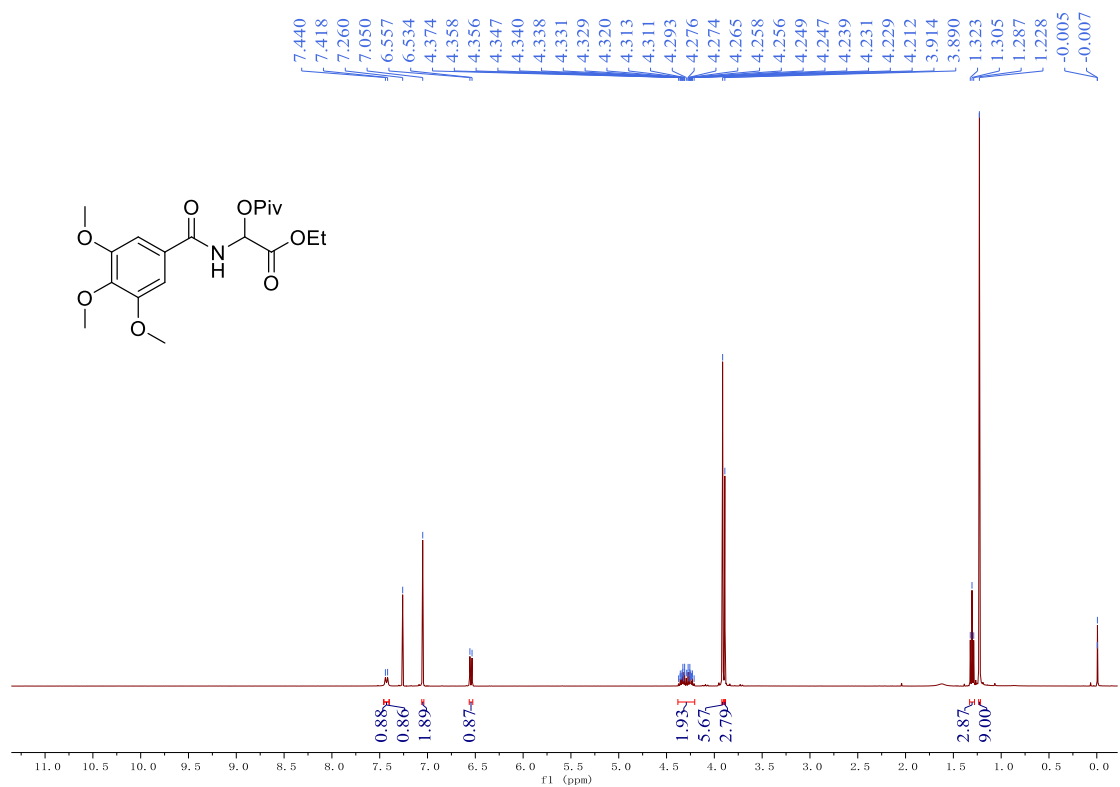
¹H NMR (600 MHz, CD₃OD) δ 6.03 – 5.99 (m, 1H), 4.34 (s, 1H), 2.17 – 2.09 (m, 3H), 2.01 – 1.93 (m, 1H), 1.74 – 1.58 (m, 4H).

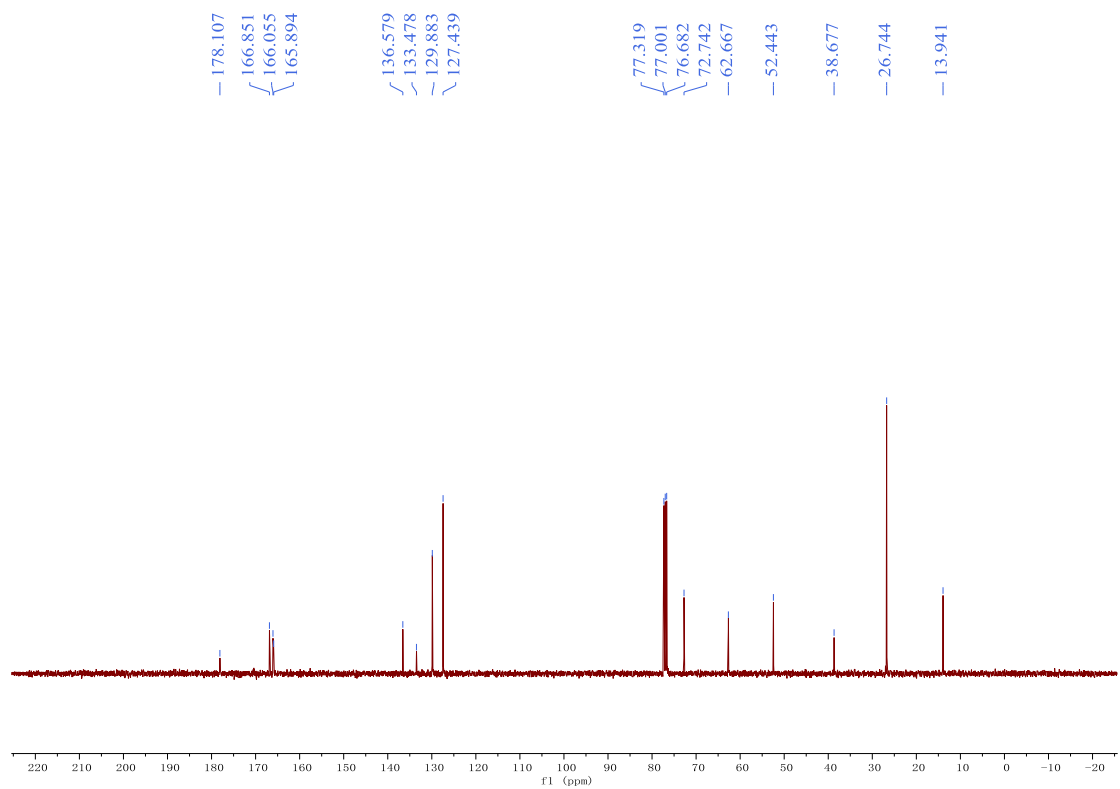
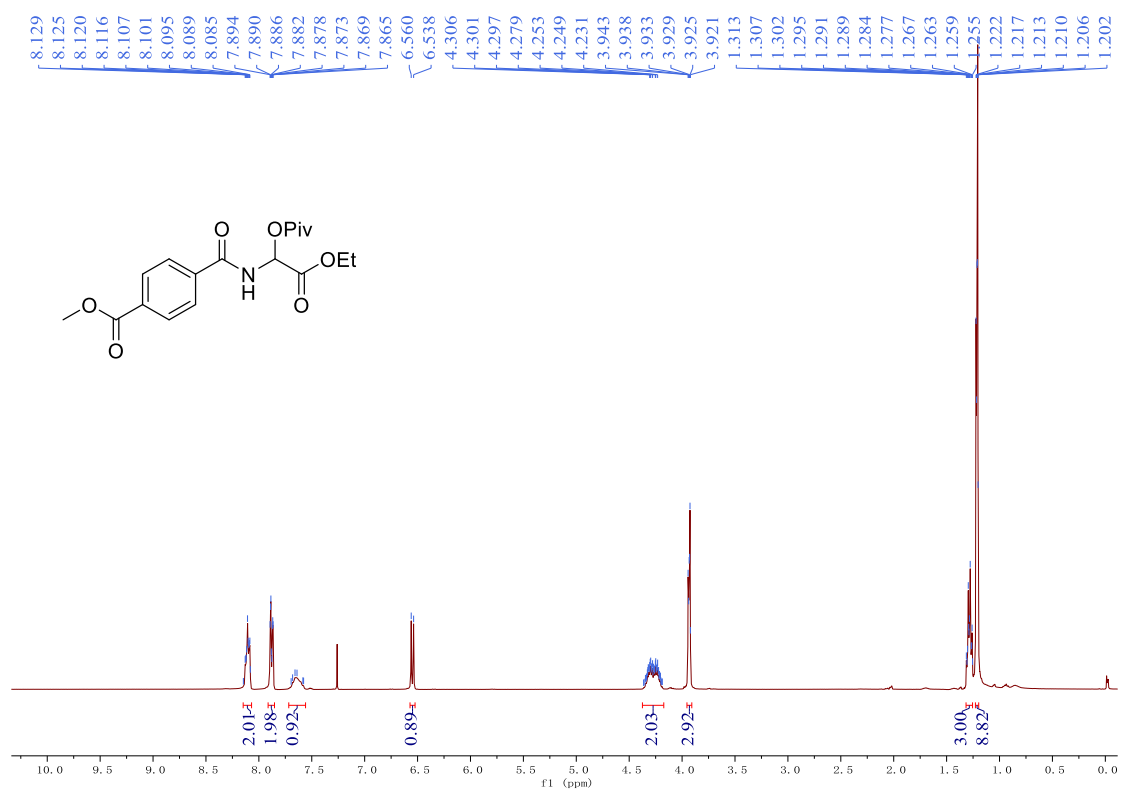
¹³C NMR (151 MHz, CD₃OD) δ 170.8, 132.6, 131.2, 59.7, 26.2, 25.7, 23.3, 22.6.

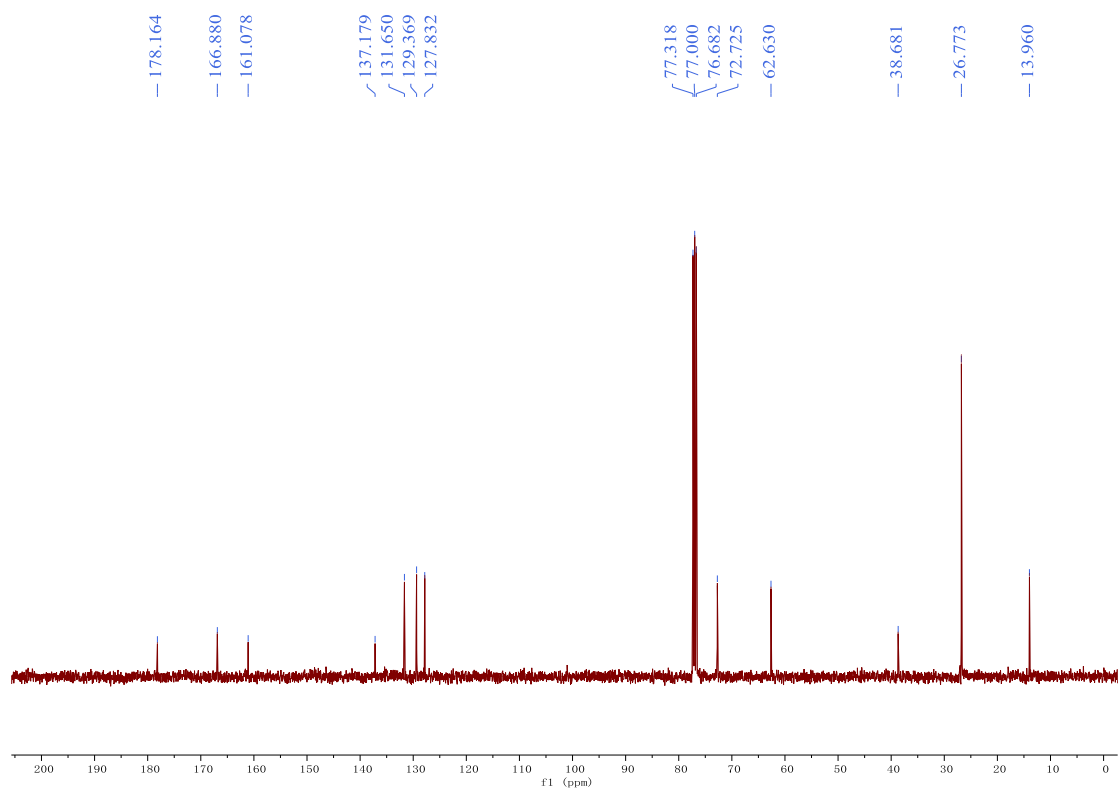
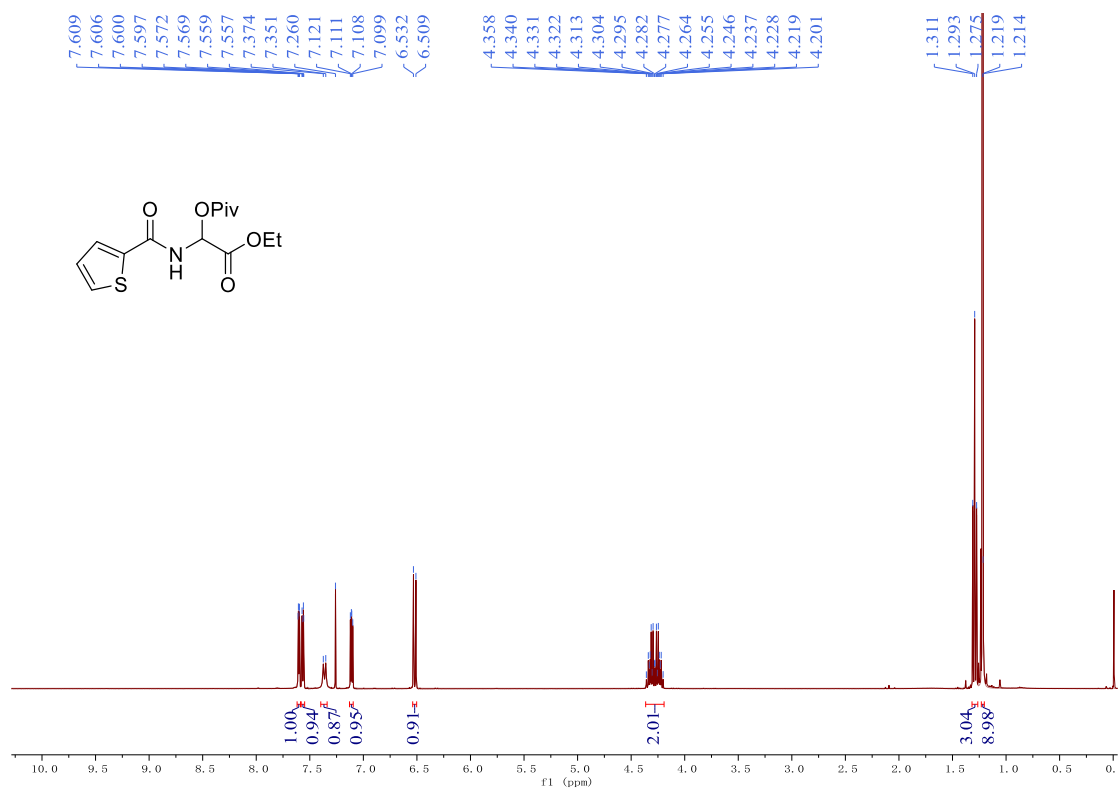
HRMS (ESI) *m/z* ([*M*+*H*]⁺) calcd for C₈H₁₄ClNO₂: 191.0785. Found 191.0787.

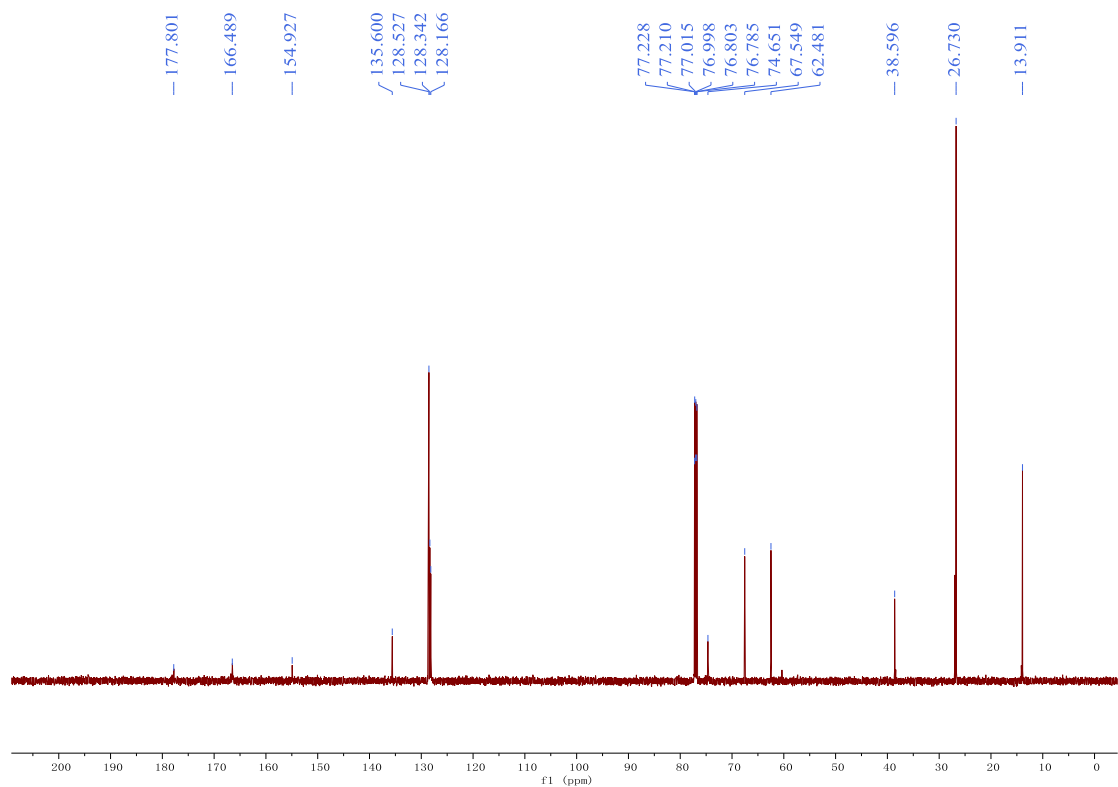
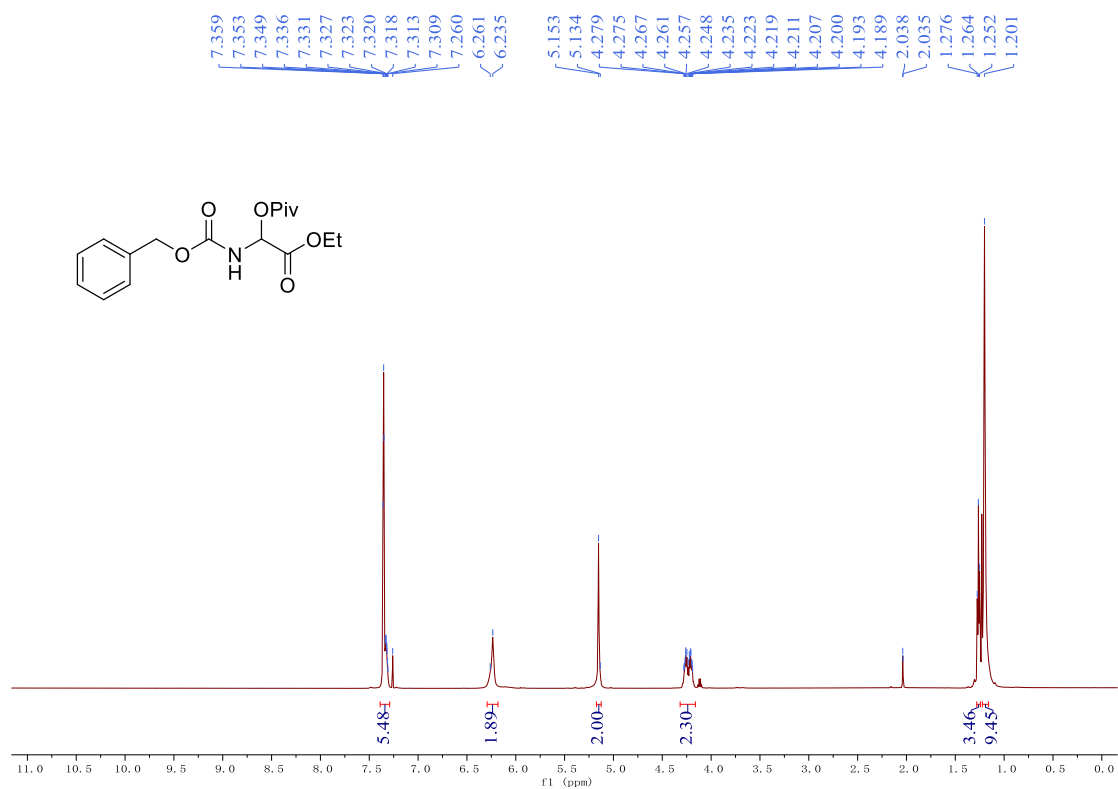
II. Copy of NMR Spectral Data

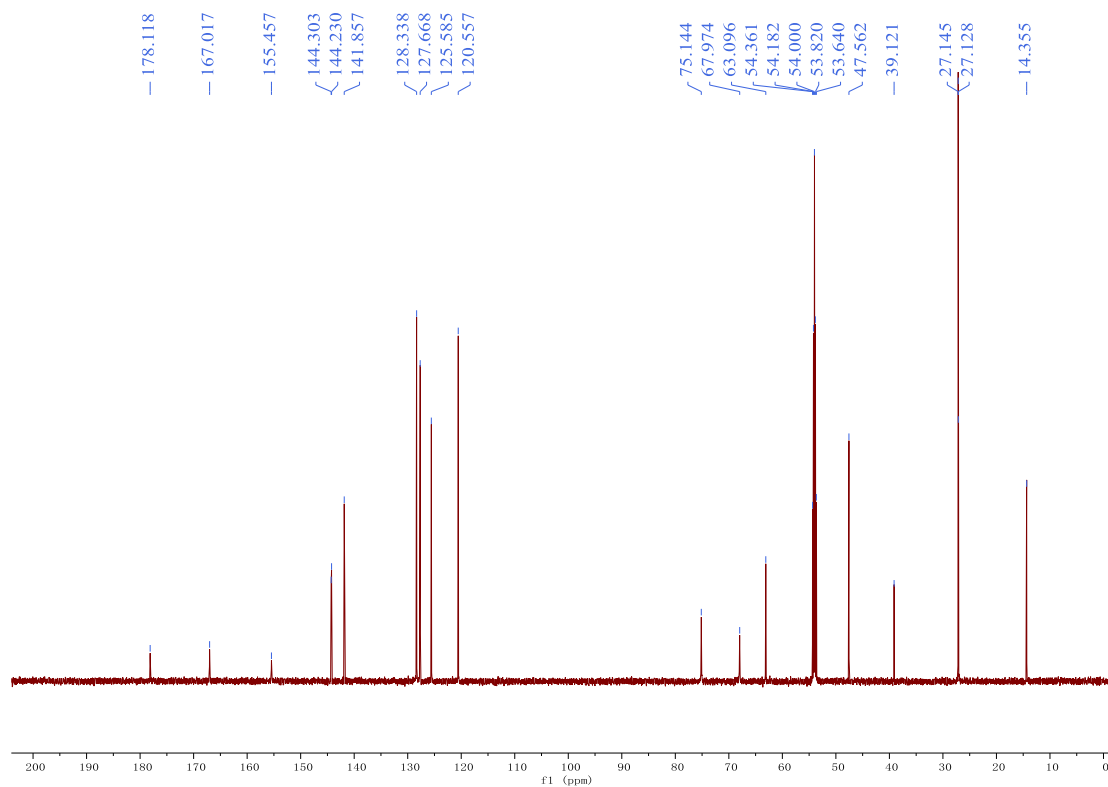
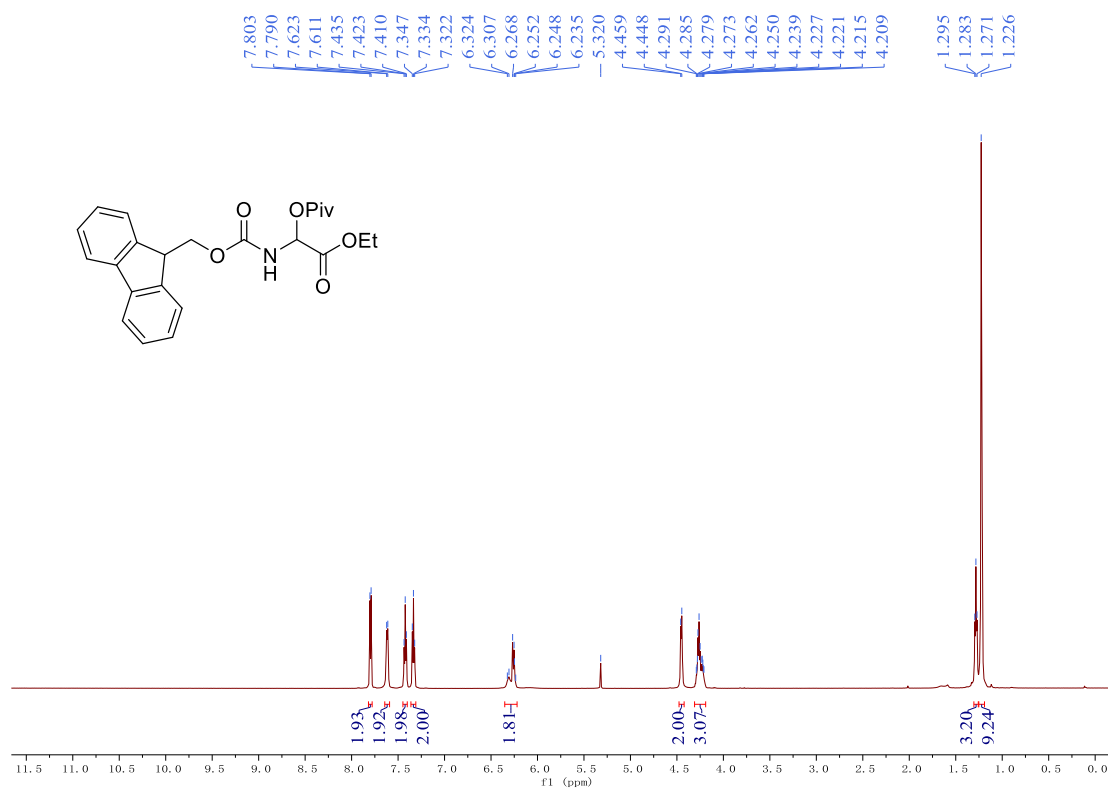


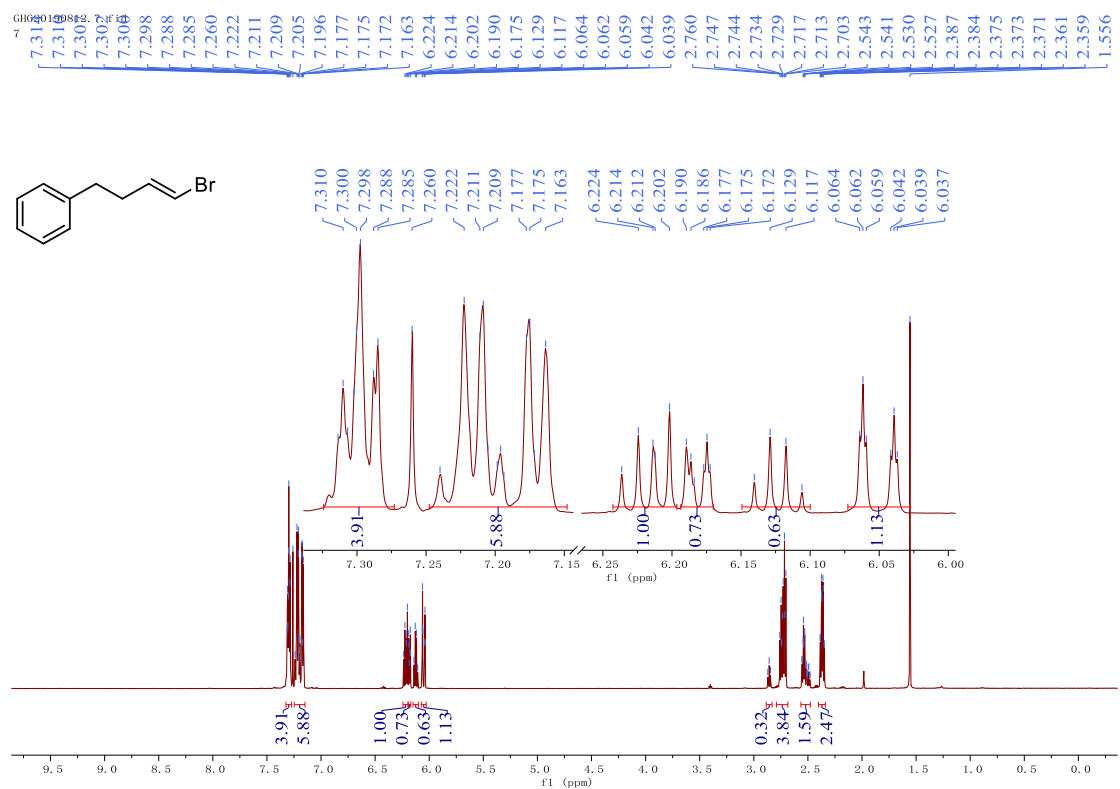
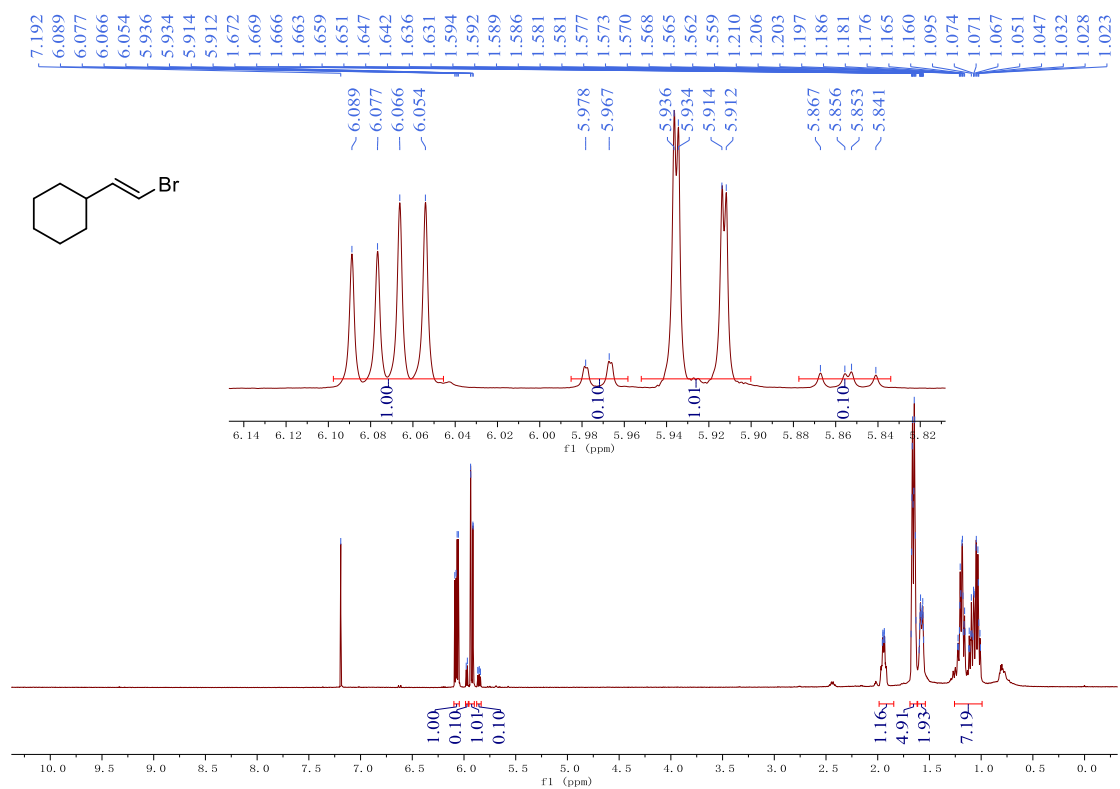


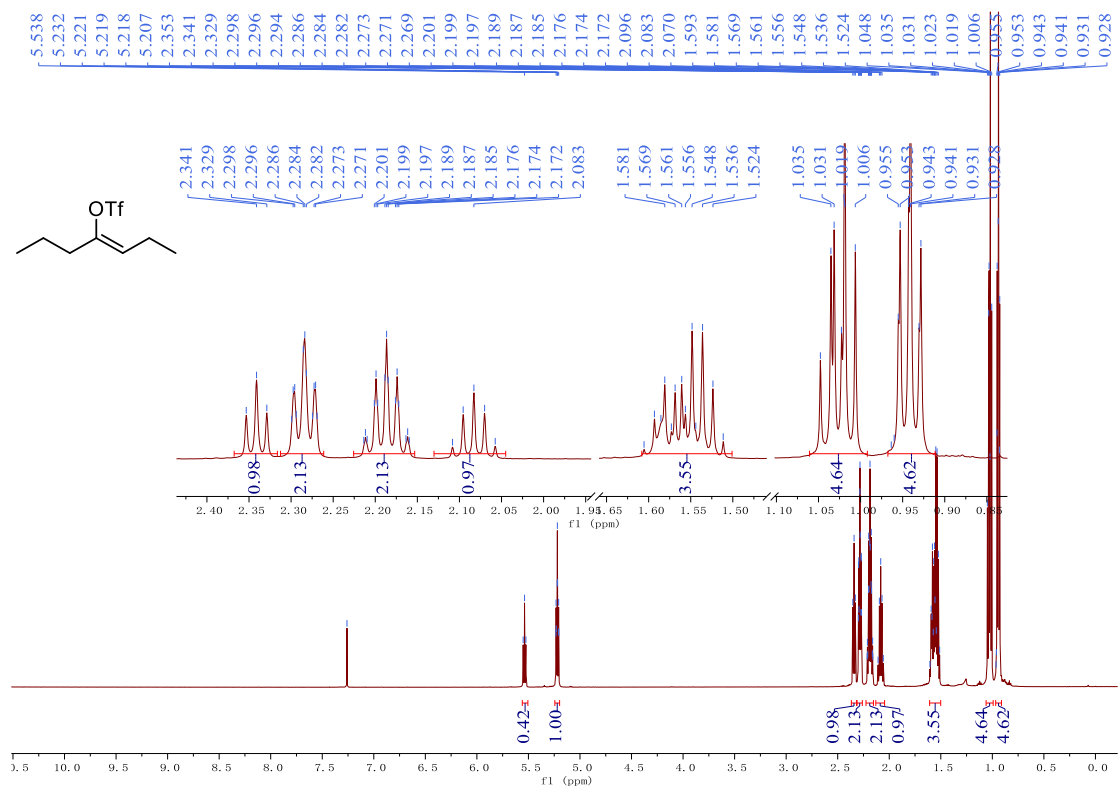
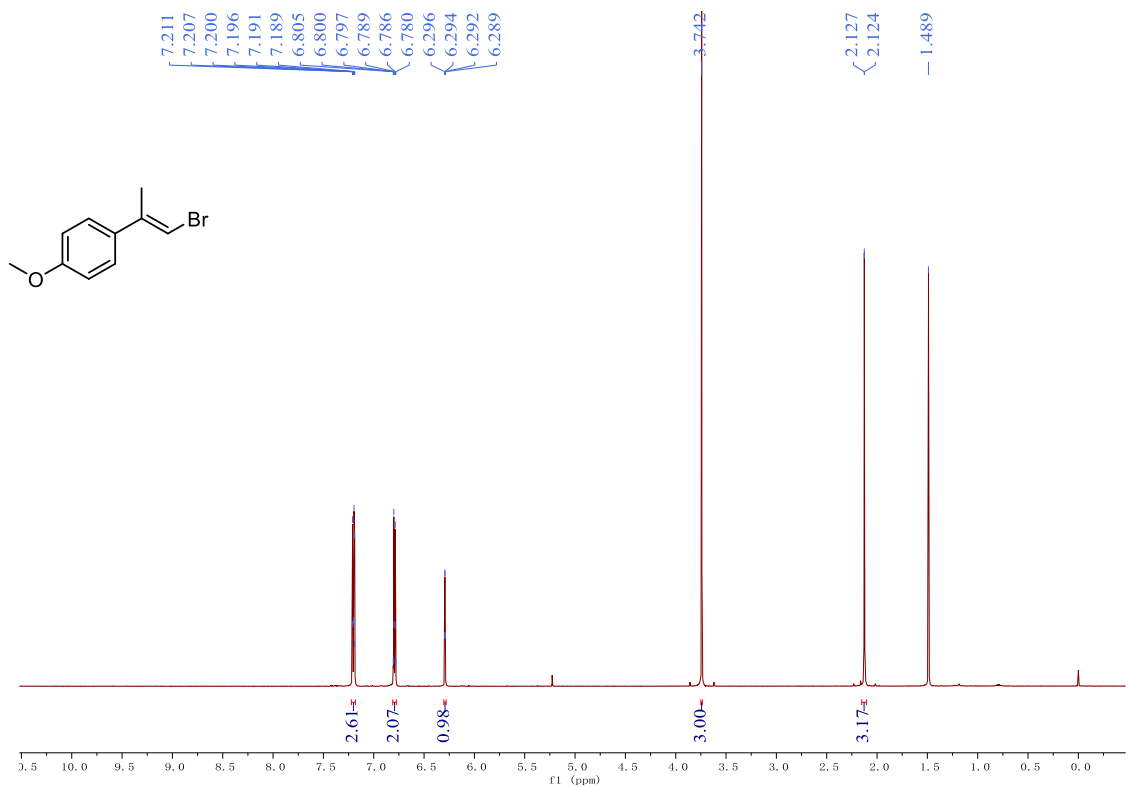


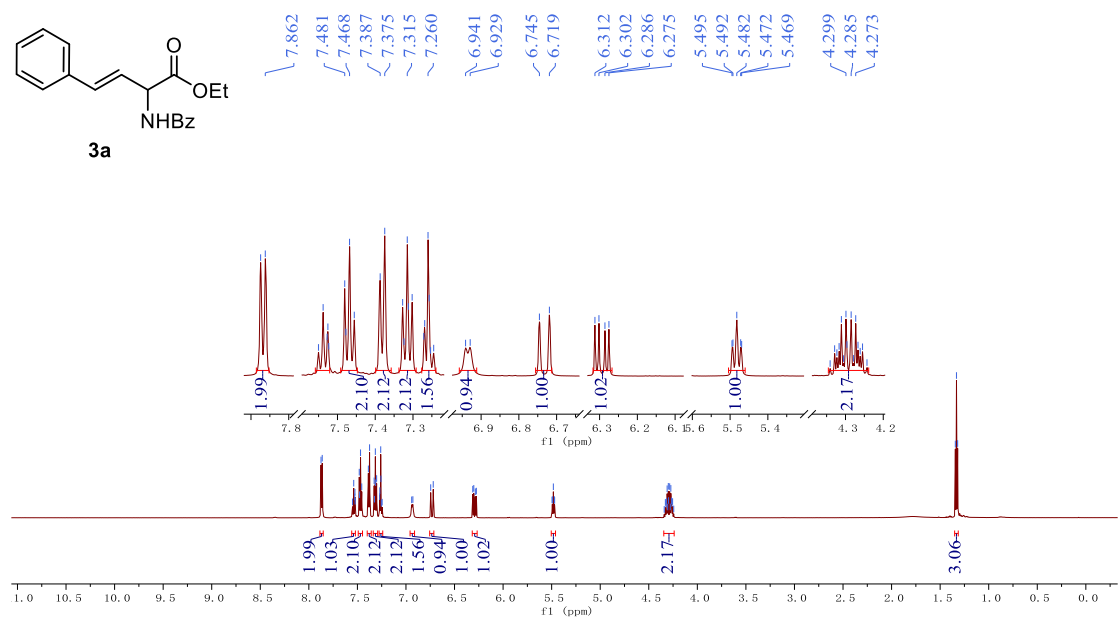
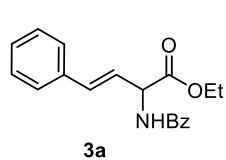
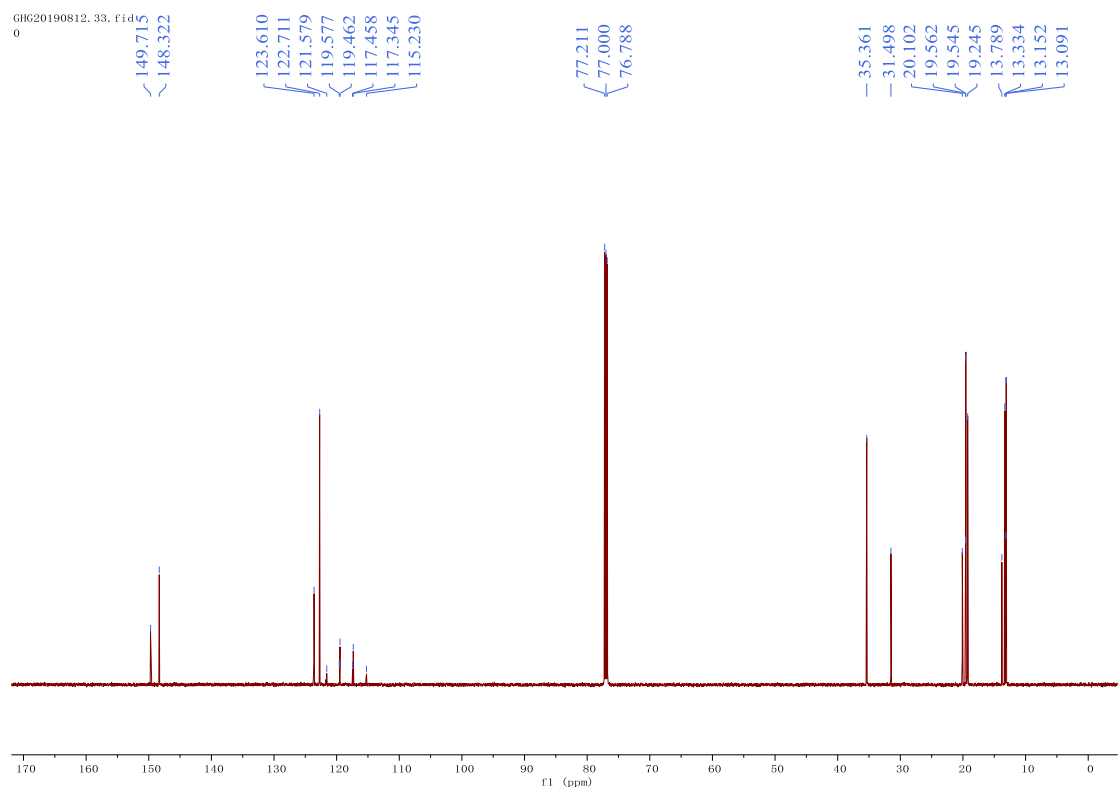


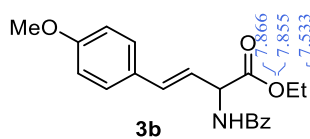
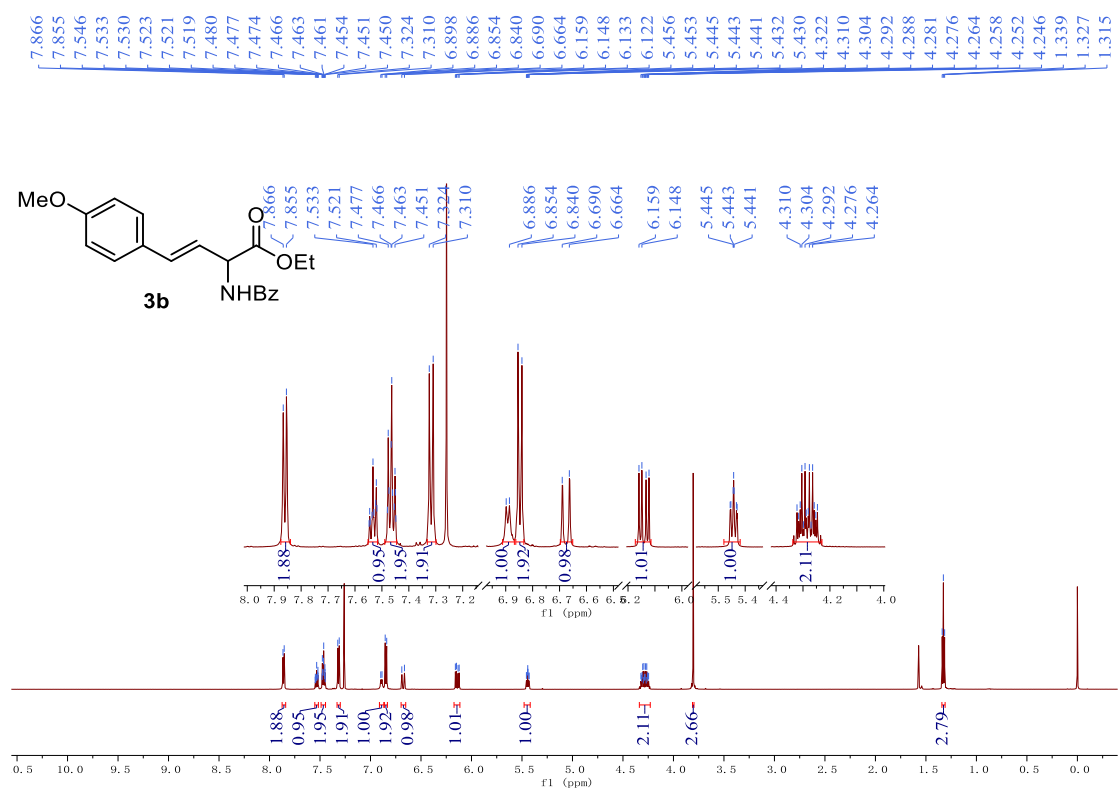
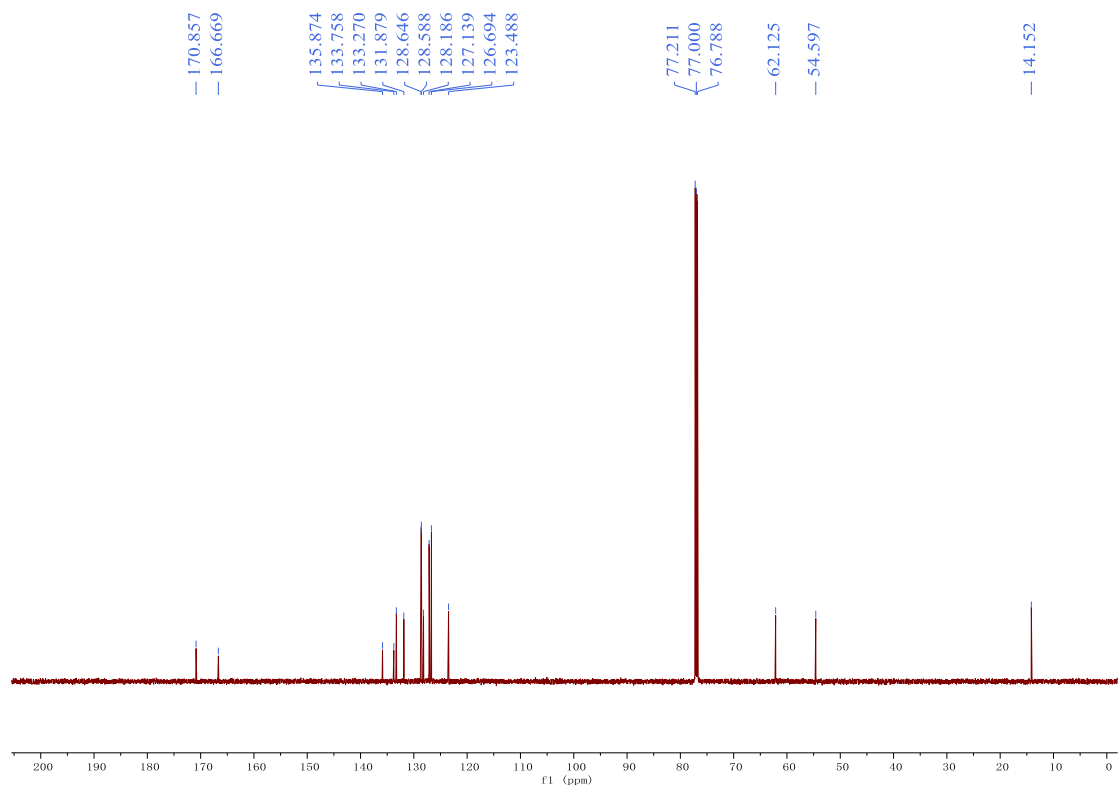


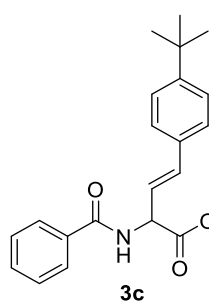
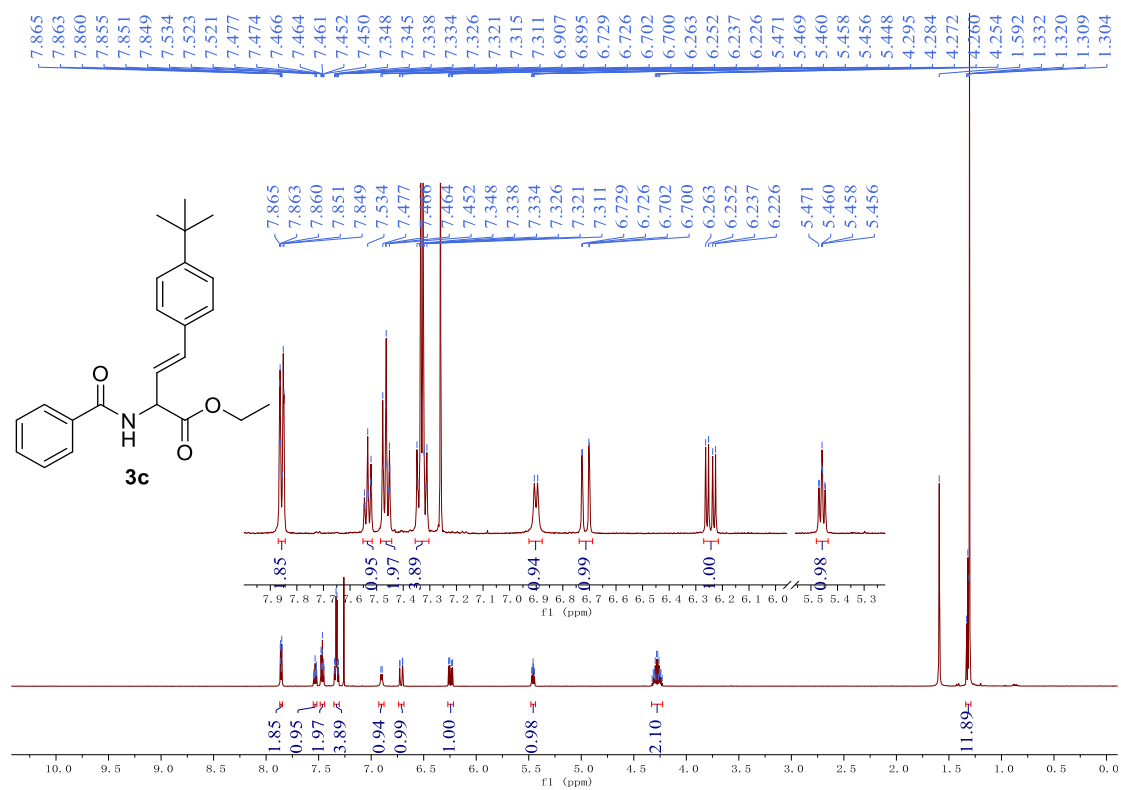
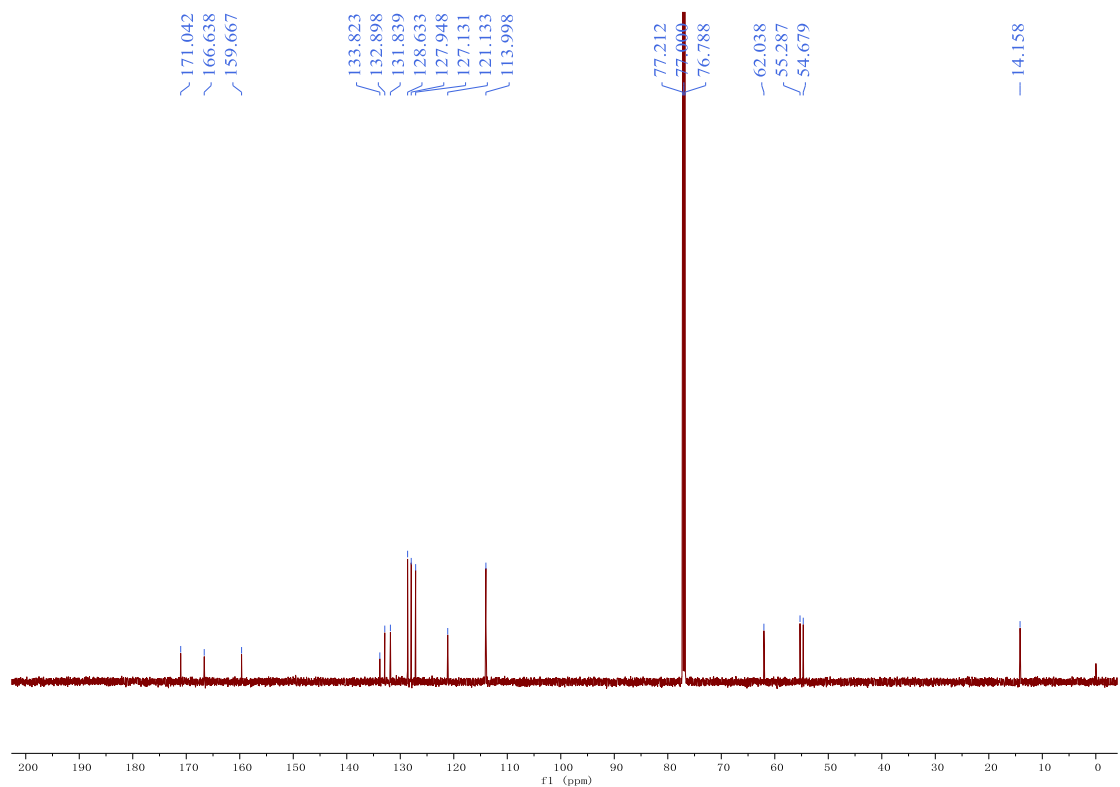


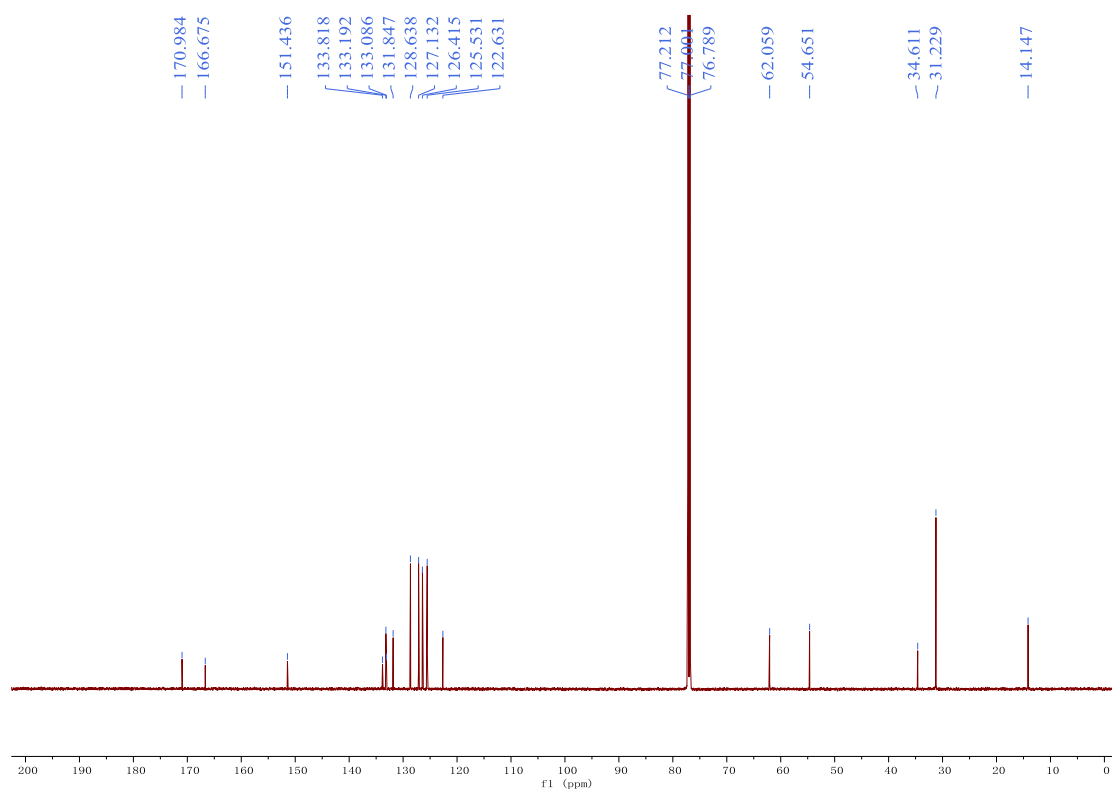


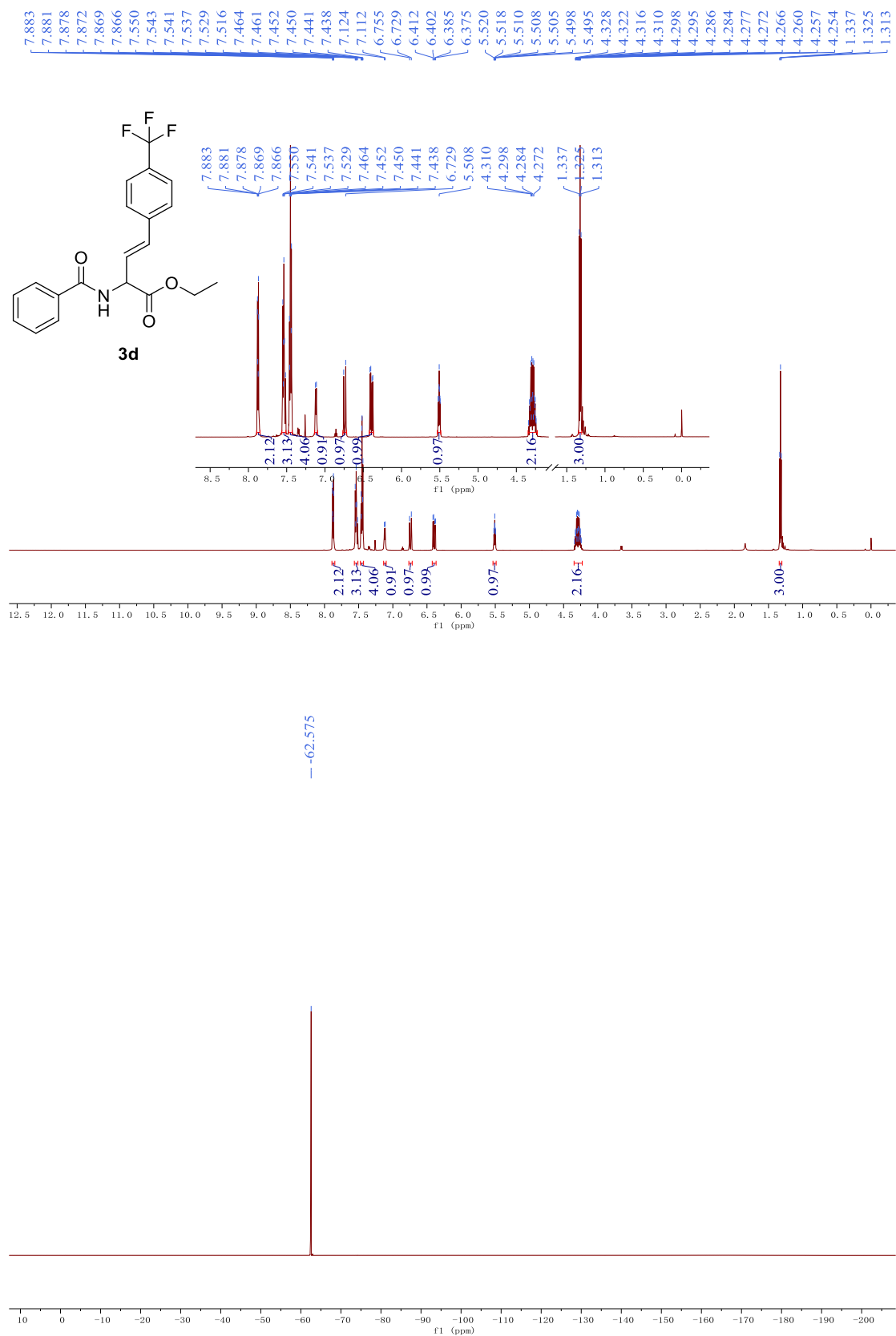


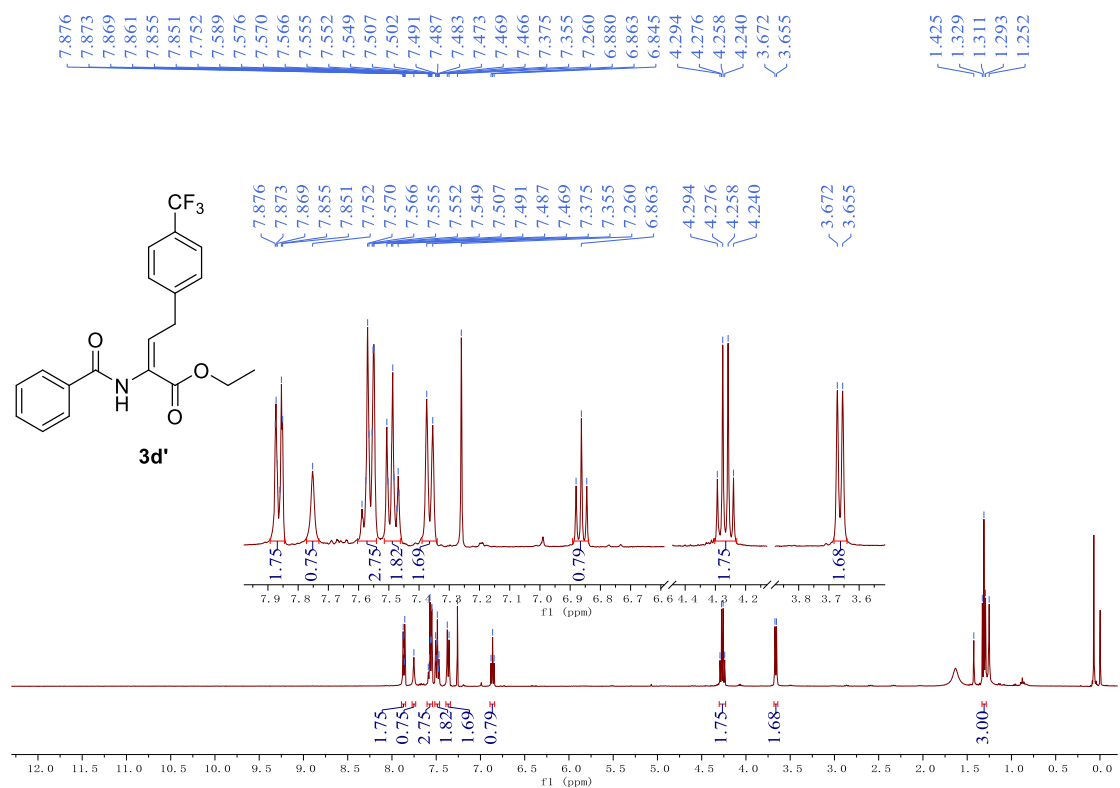
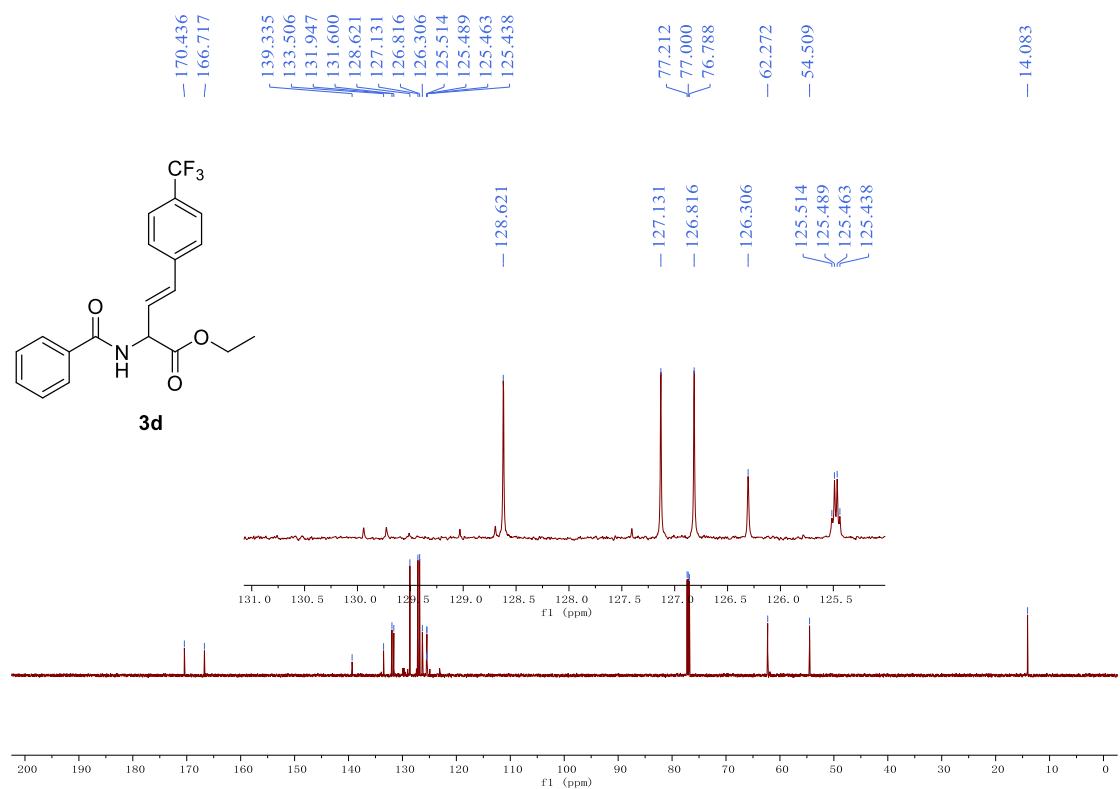


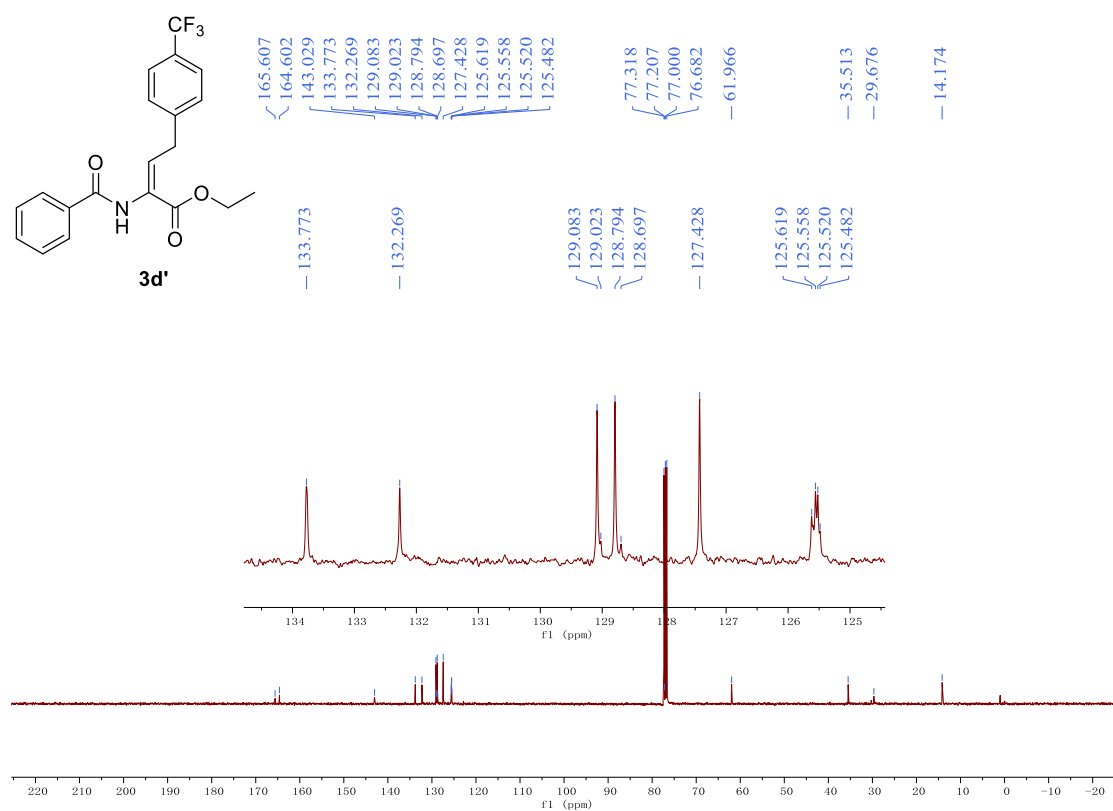
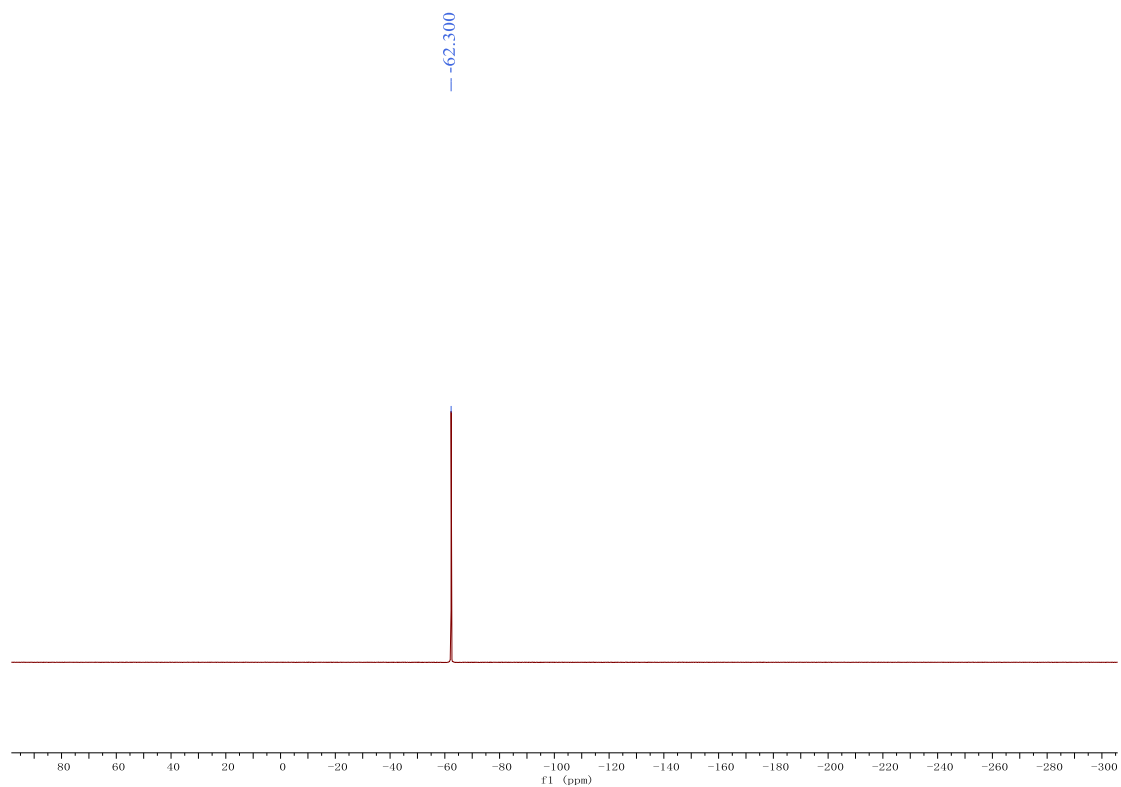


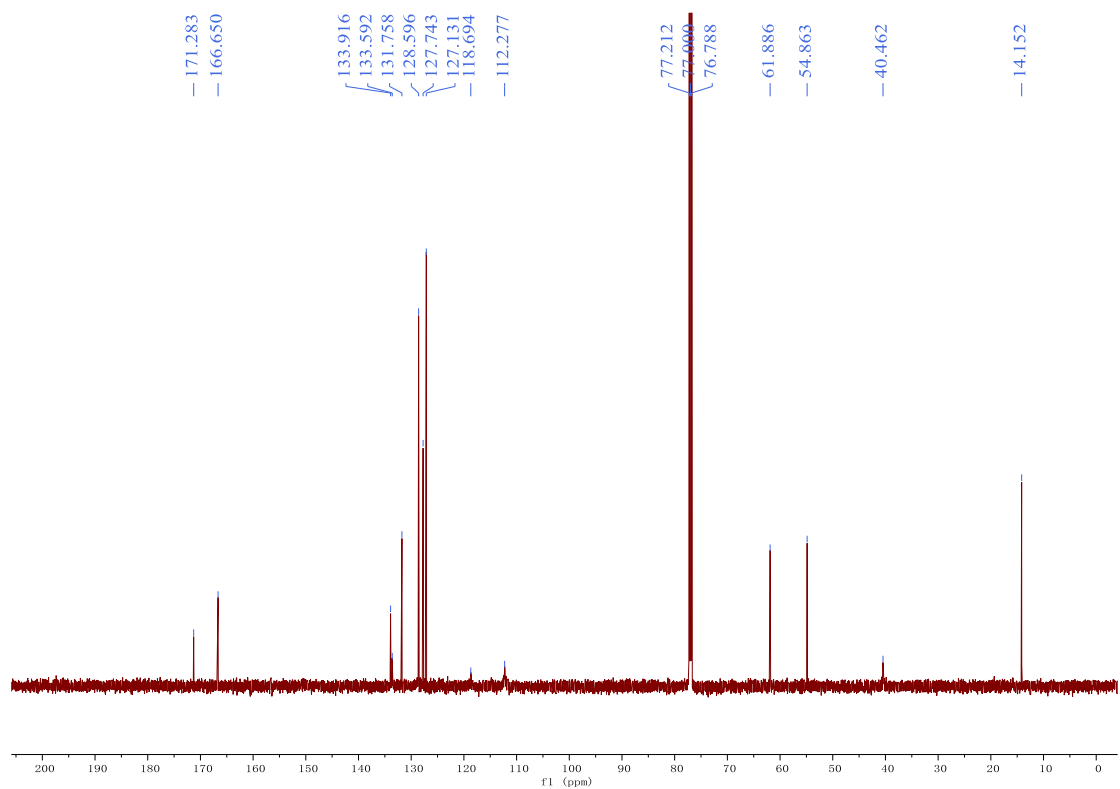
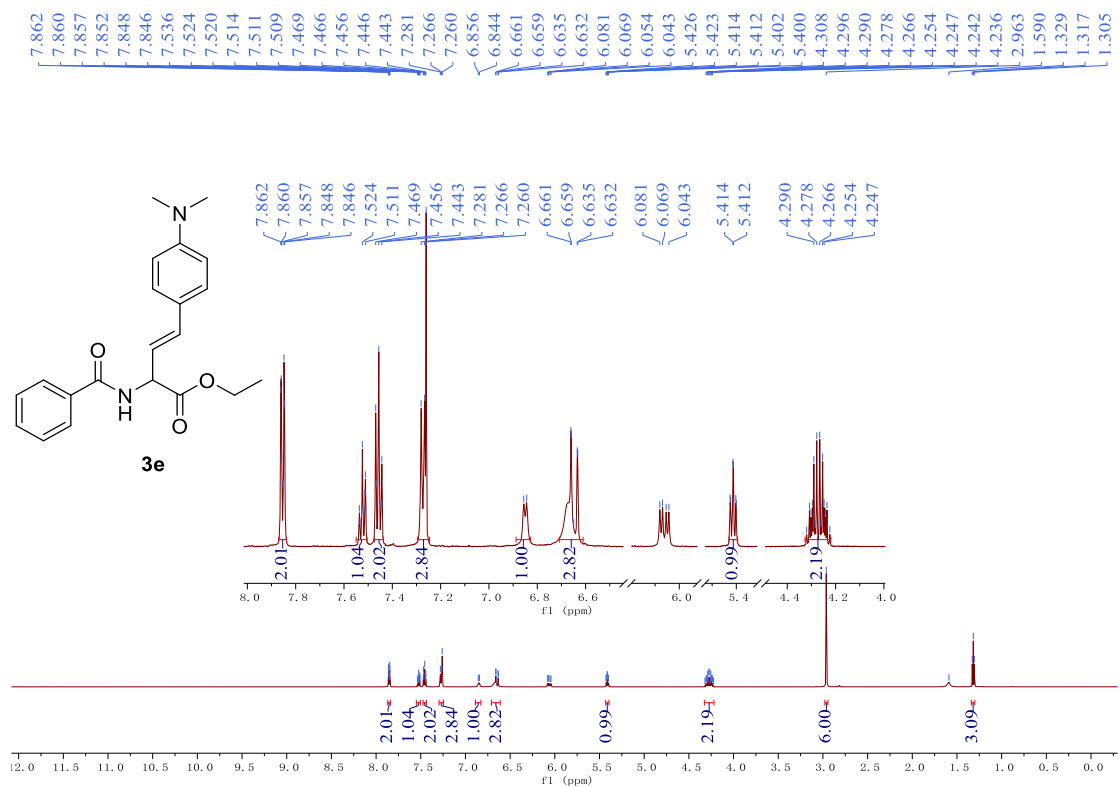


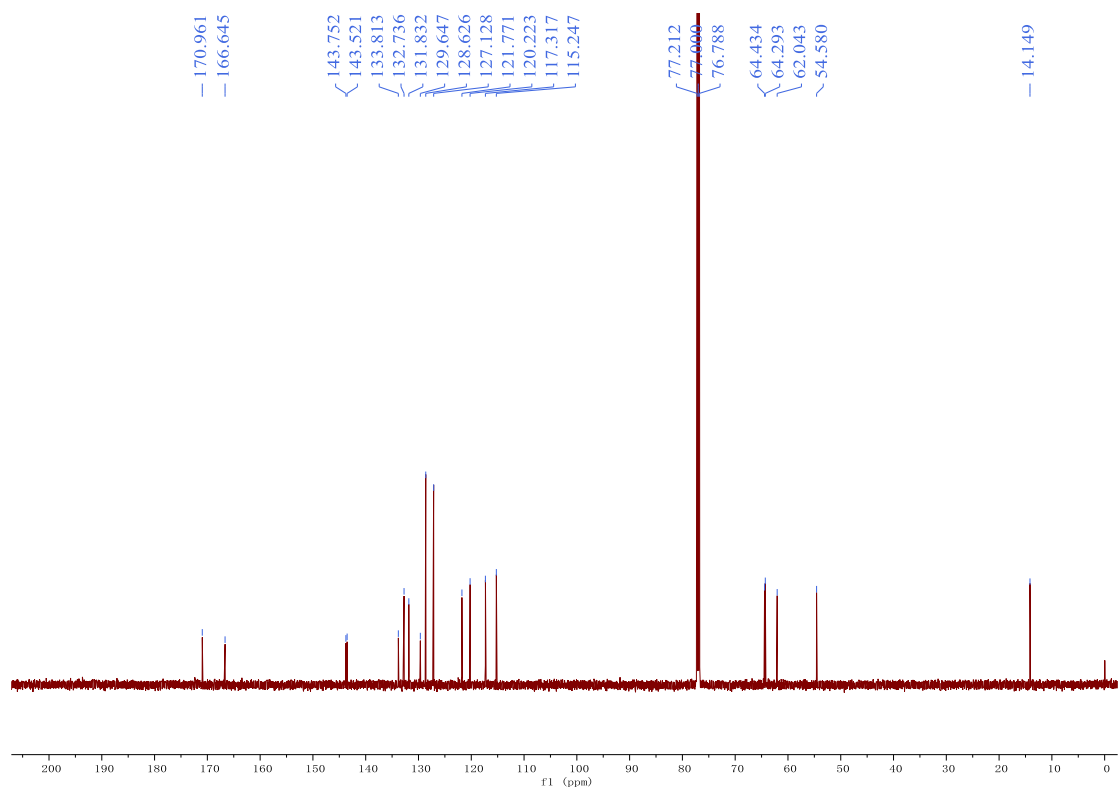
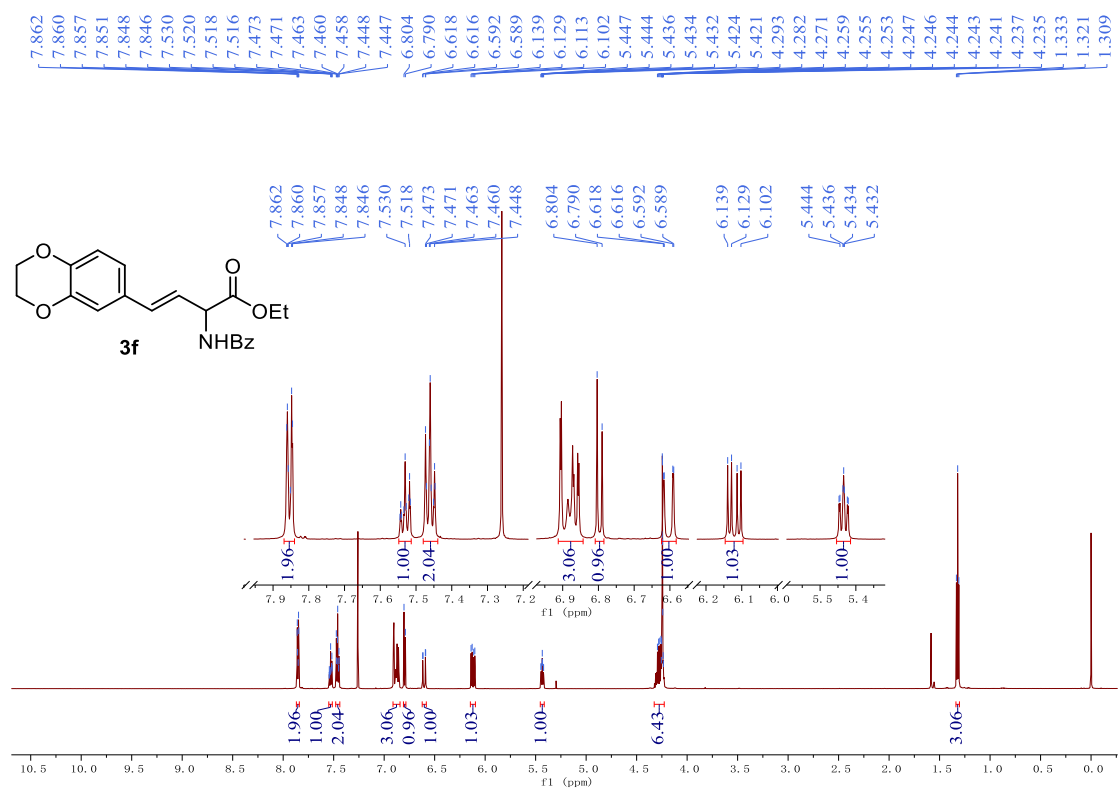


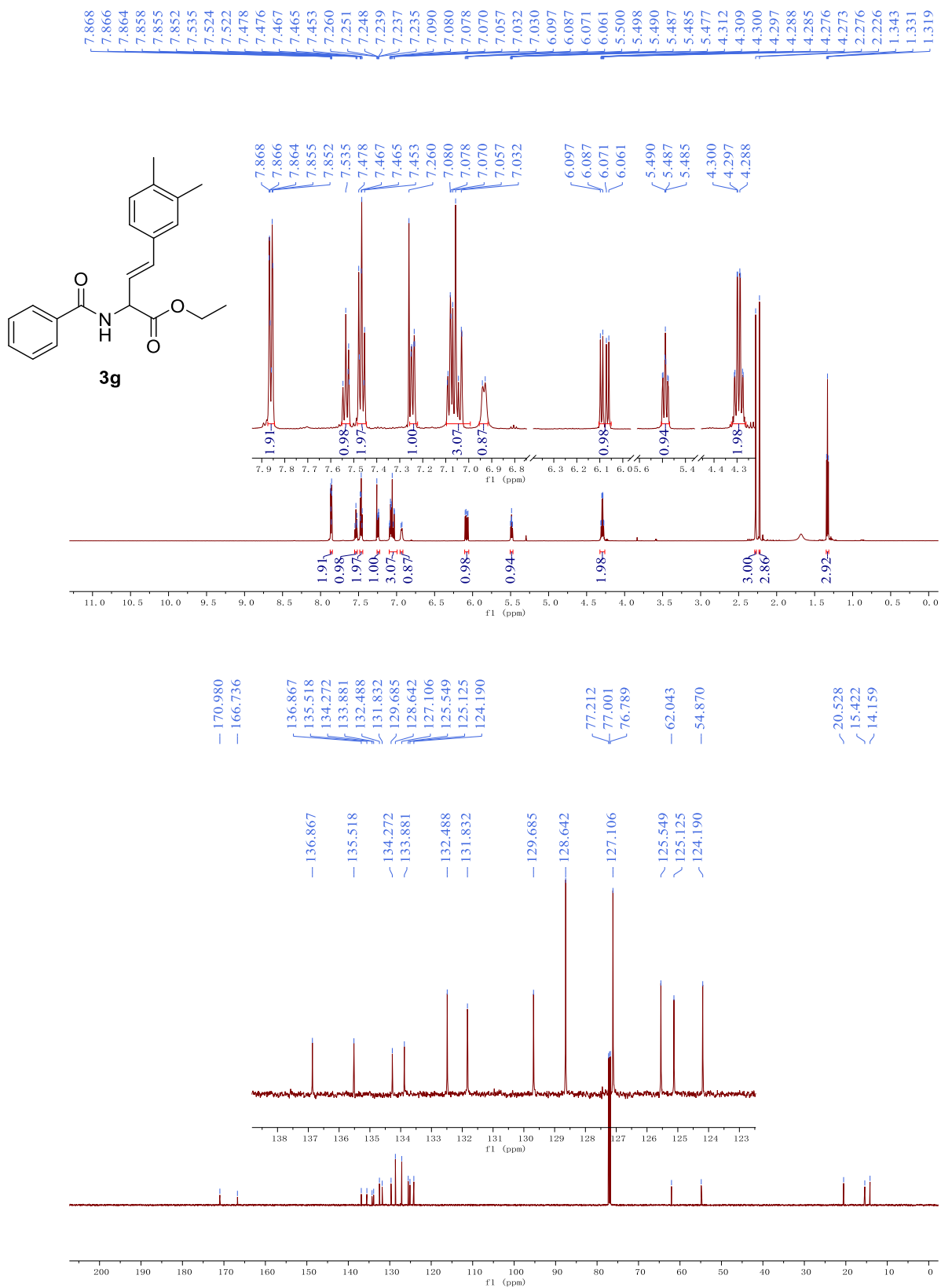


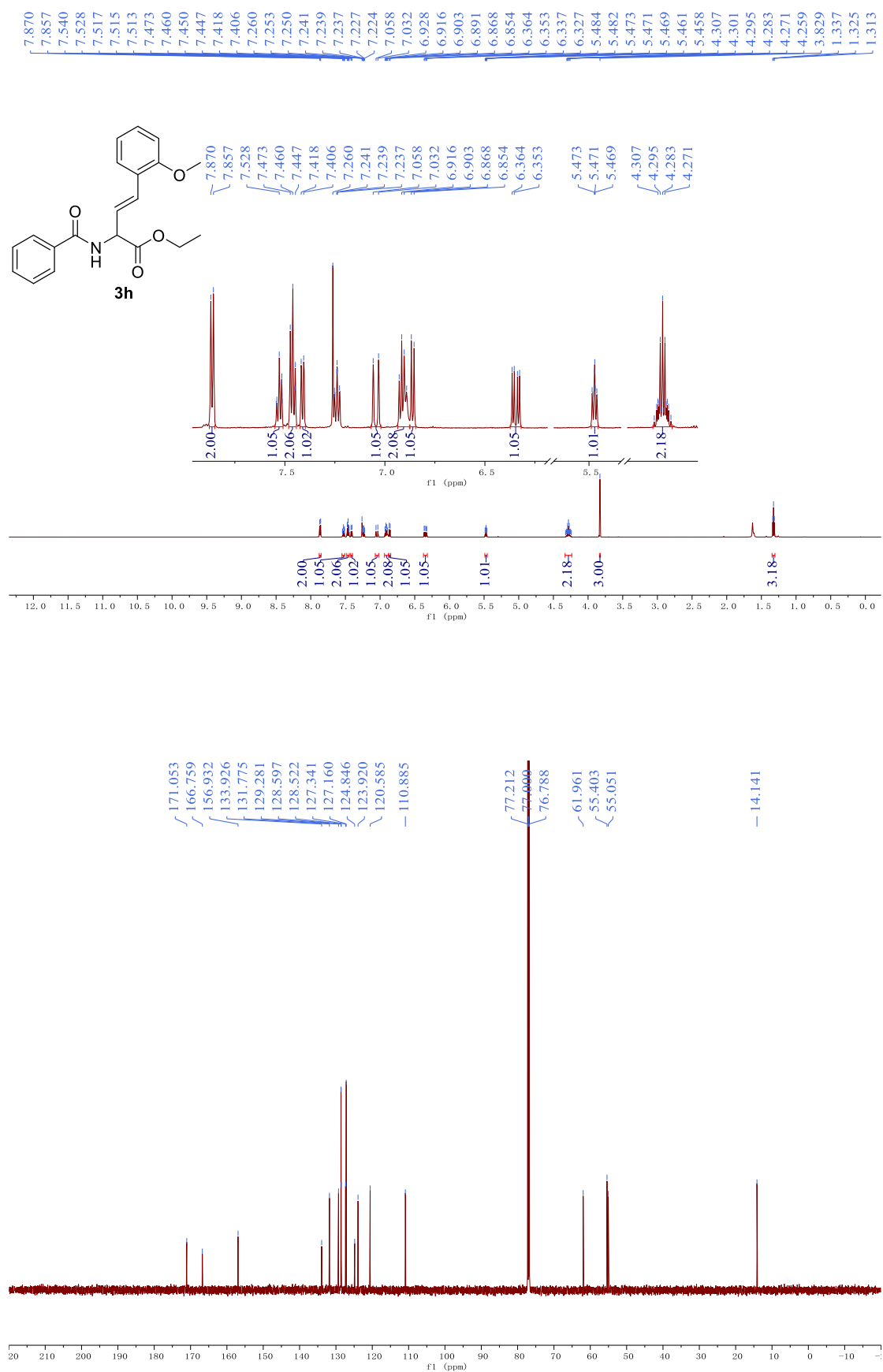


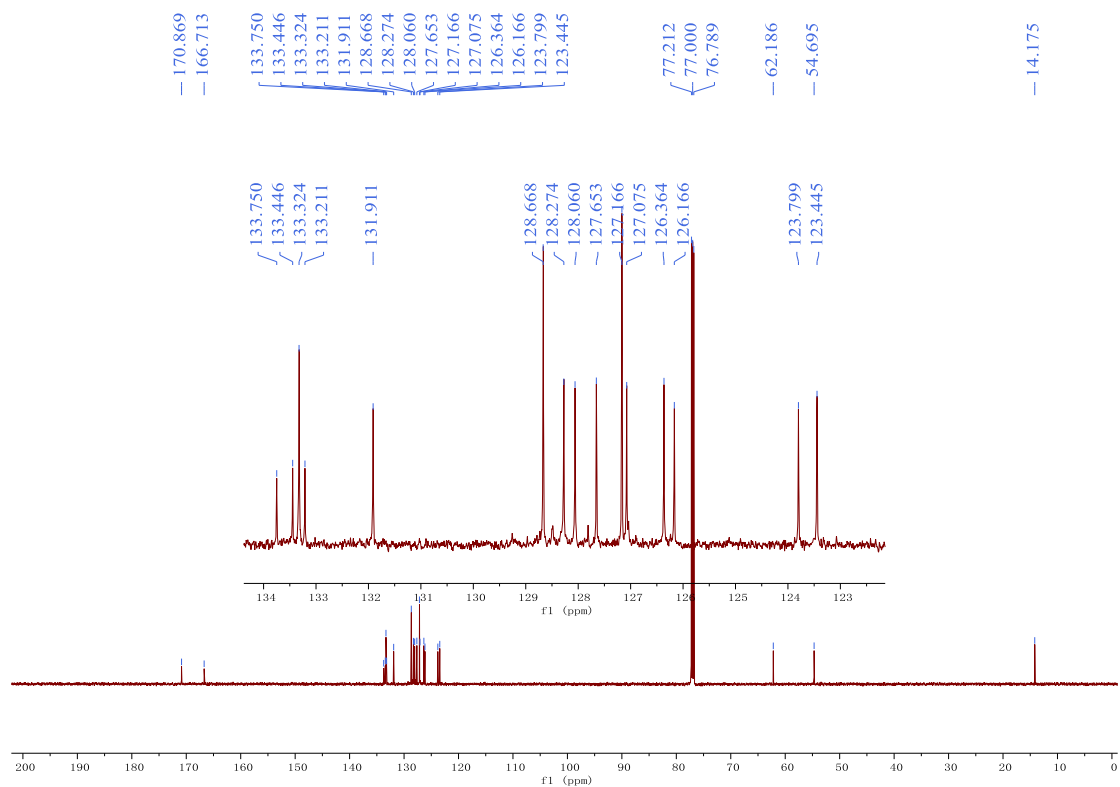
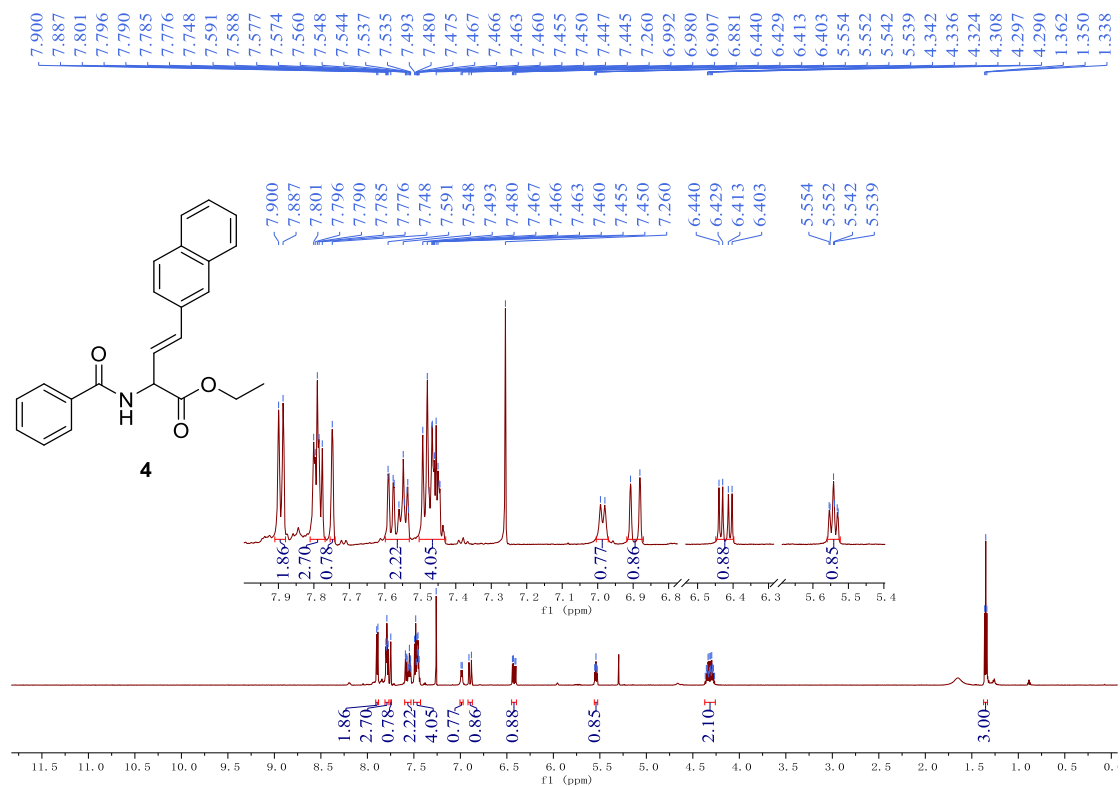


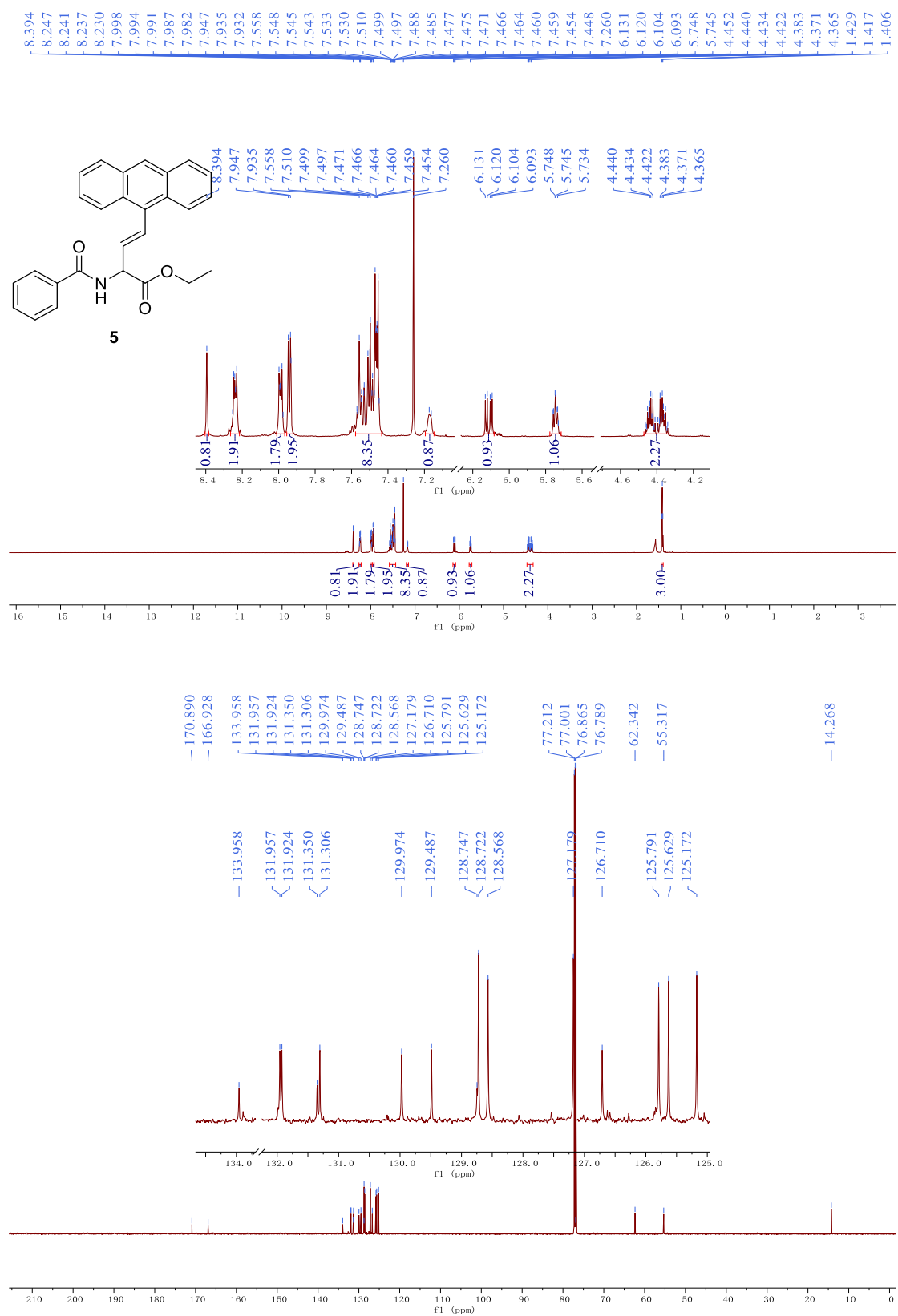


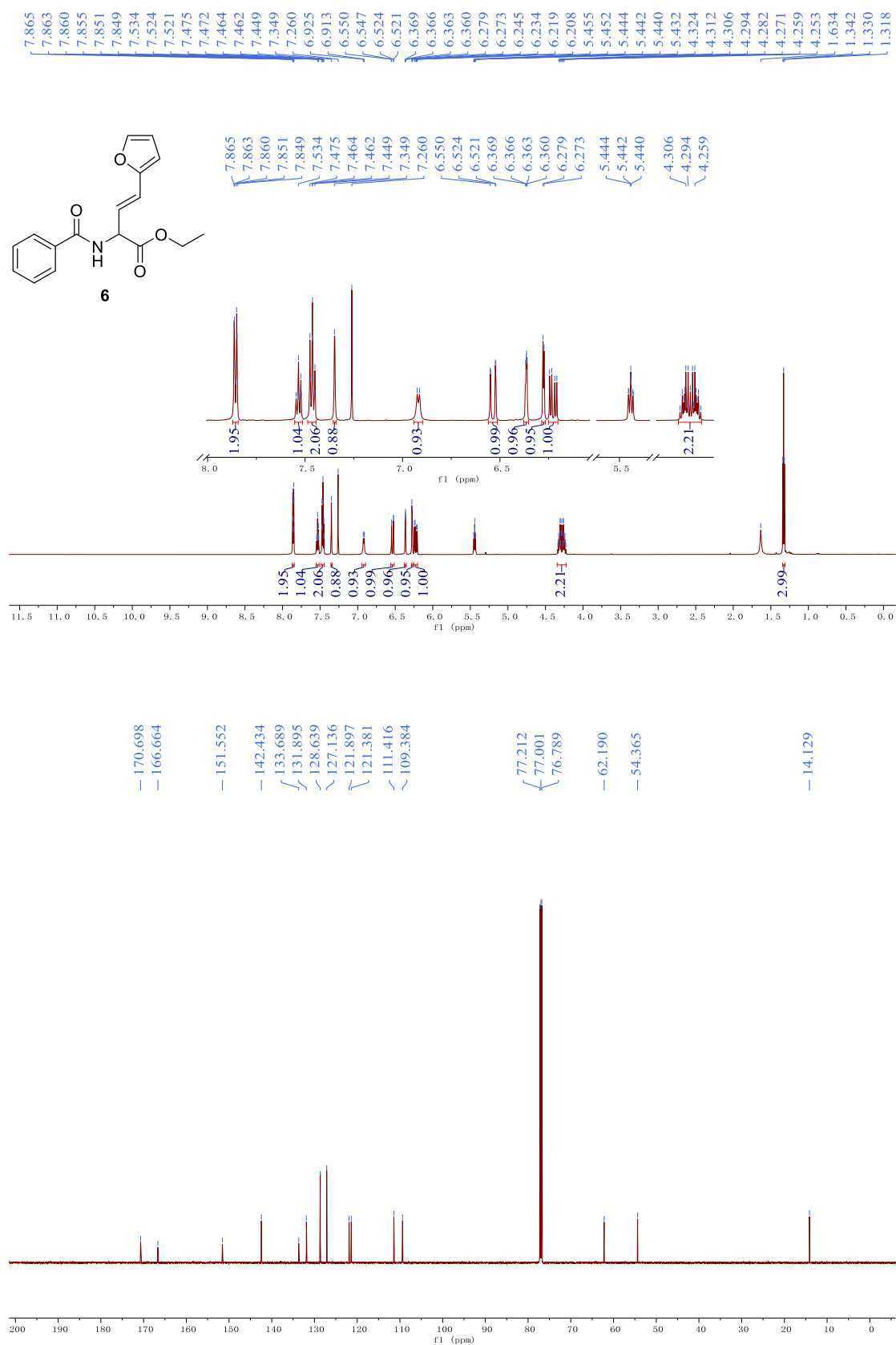


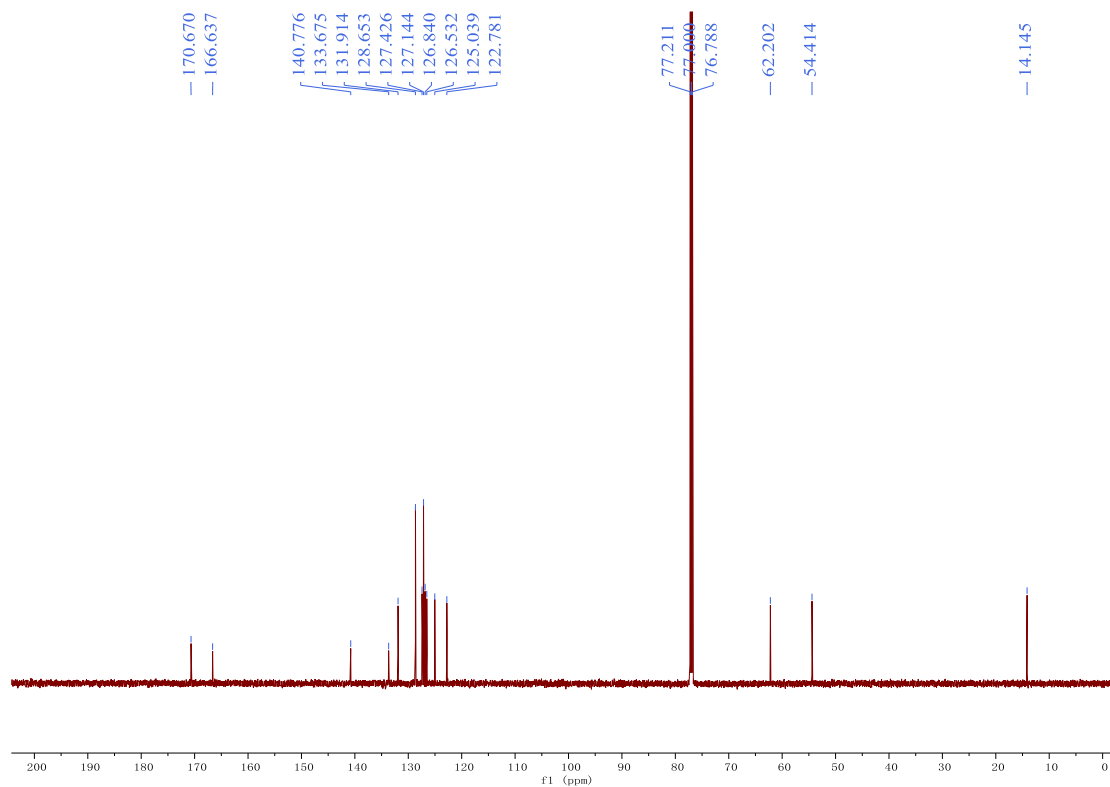
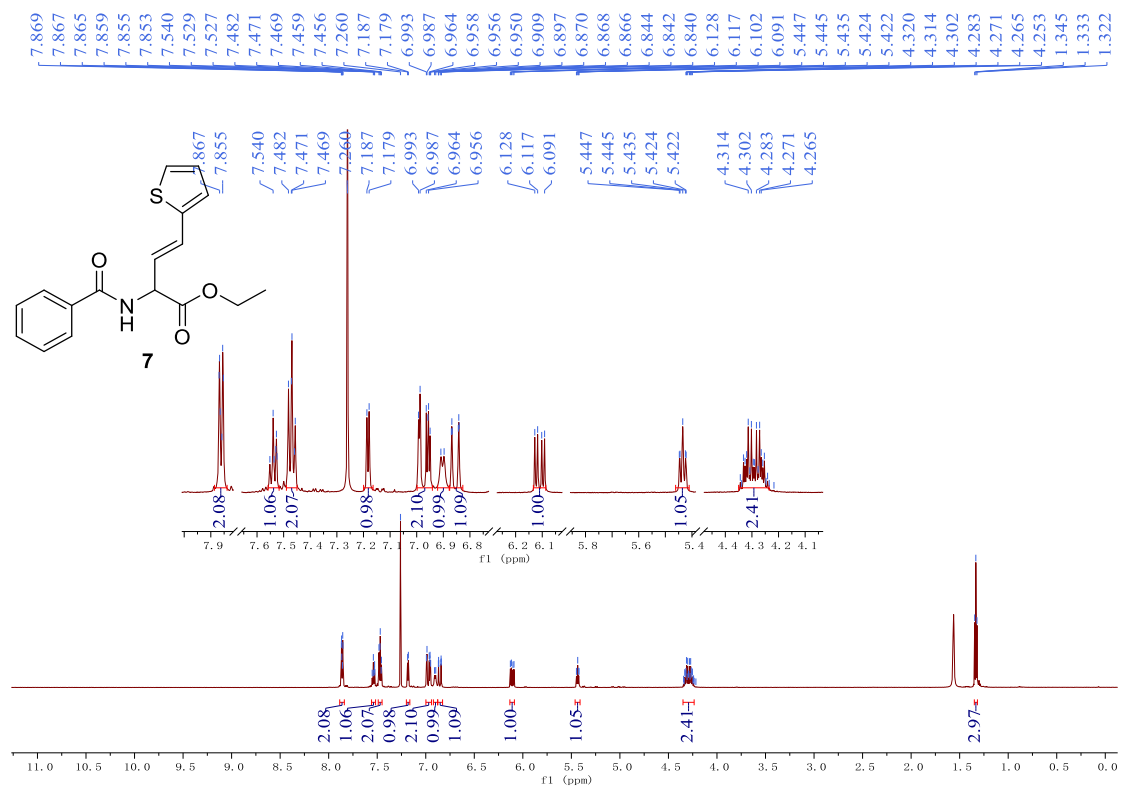


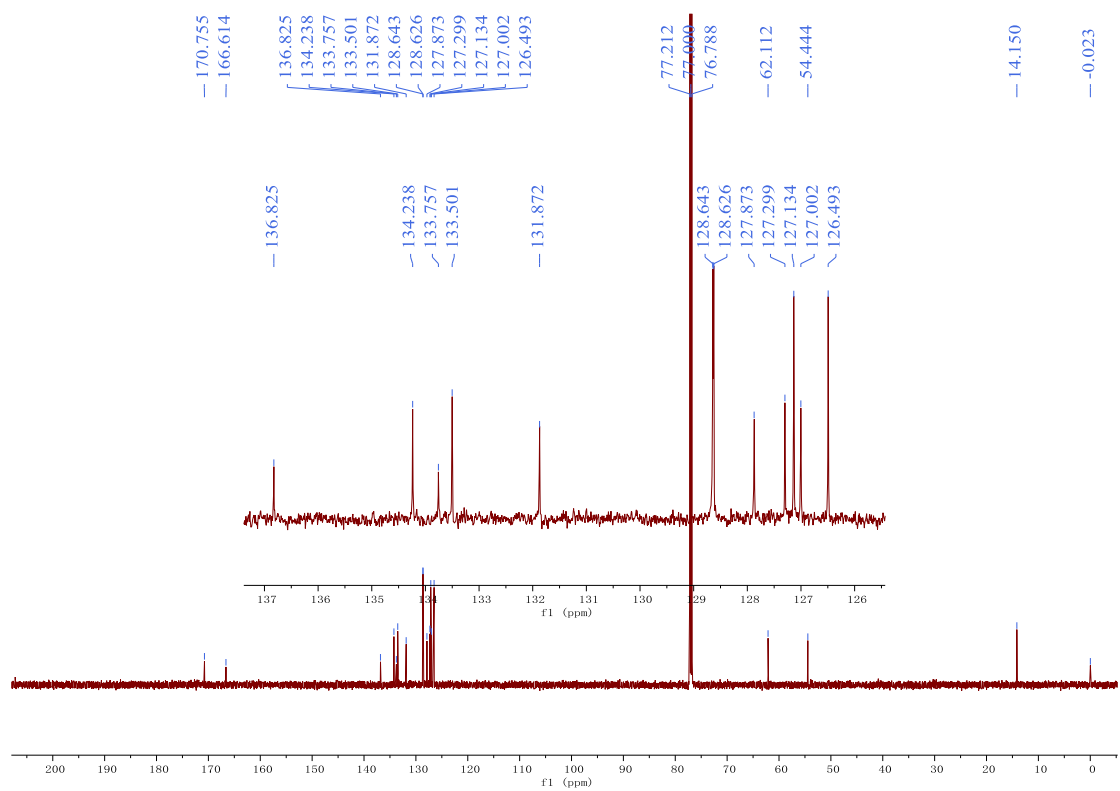
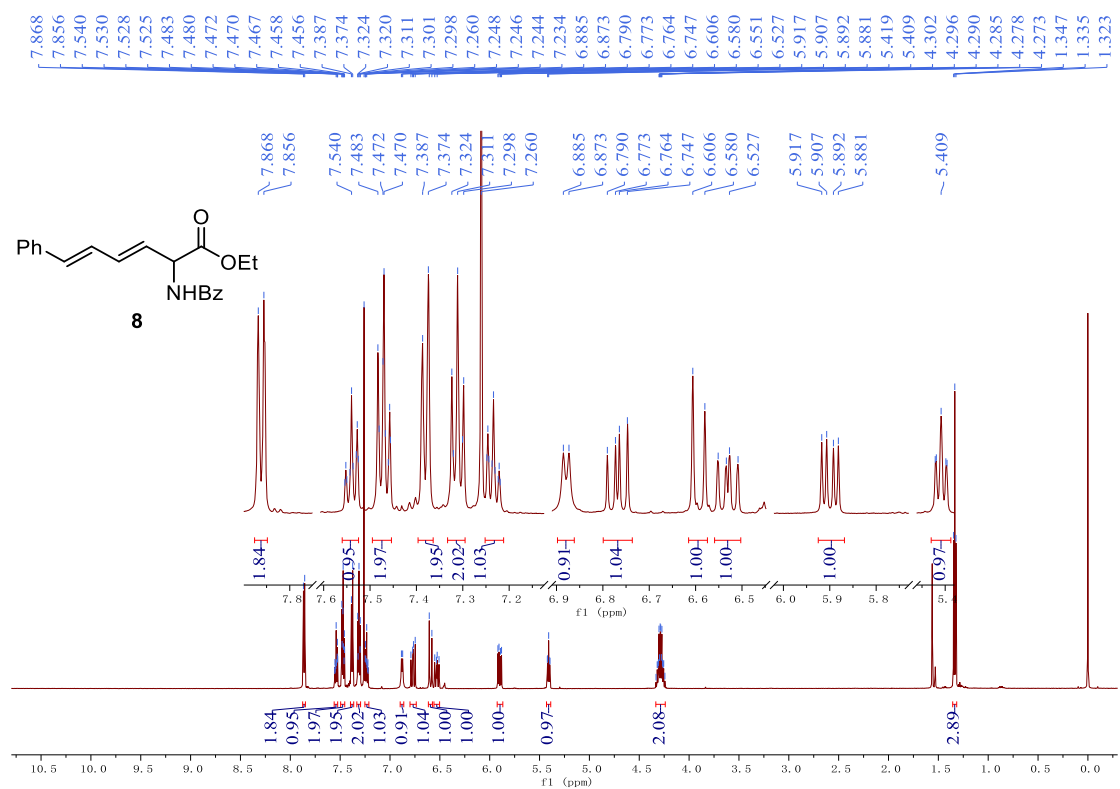


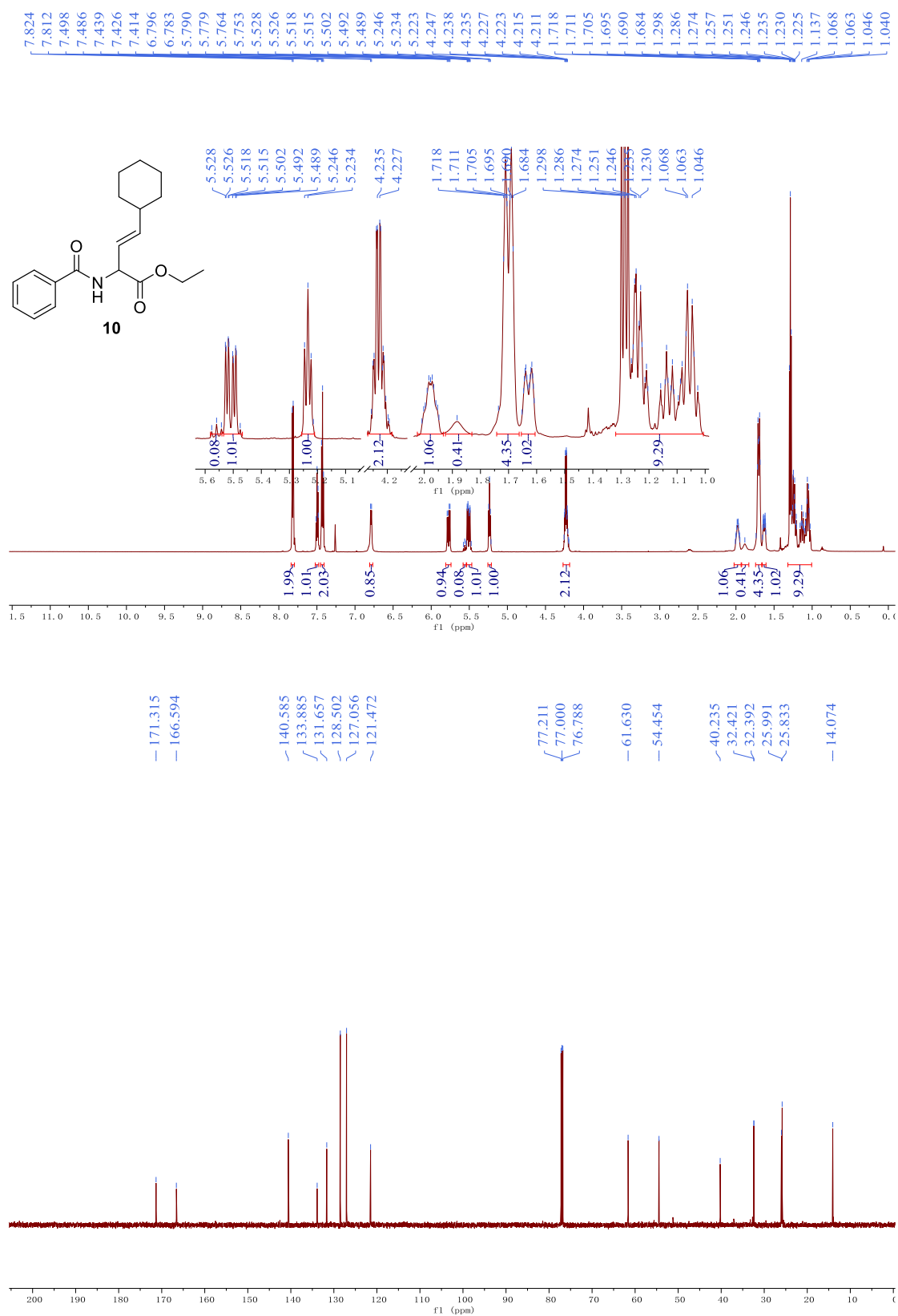


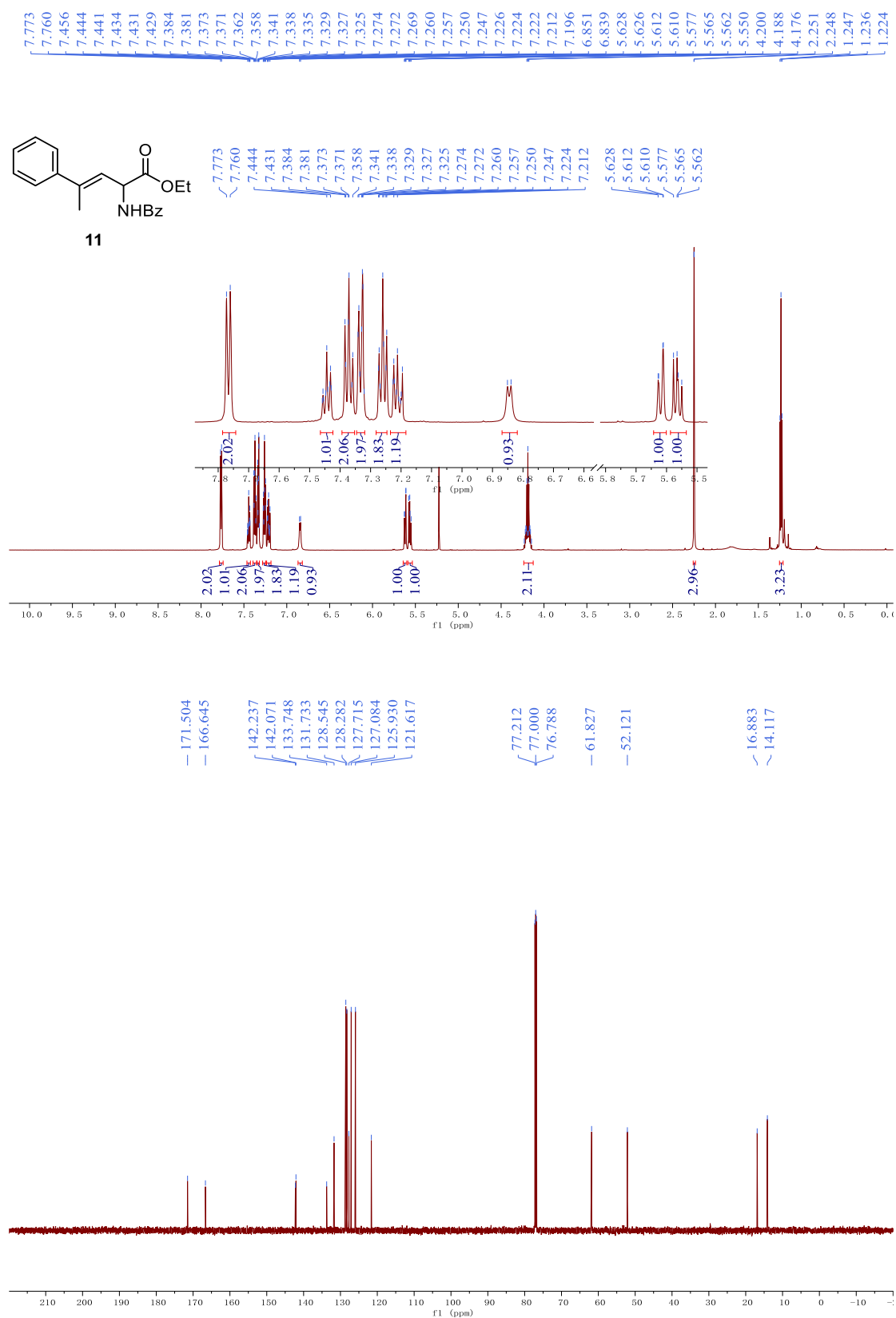


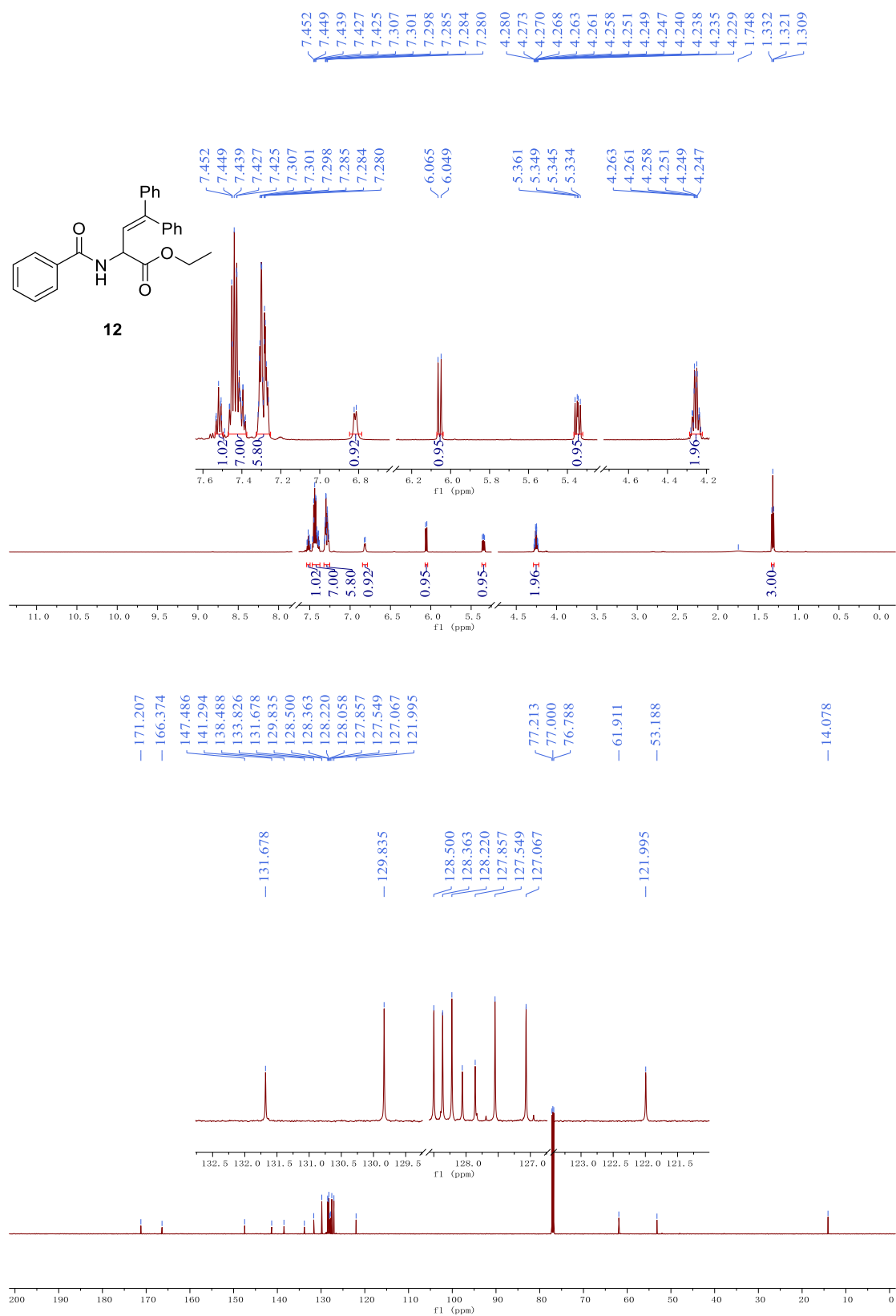


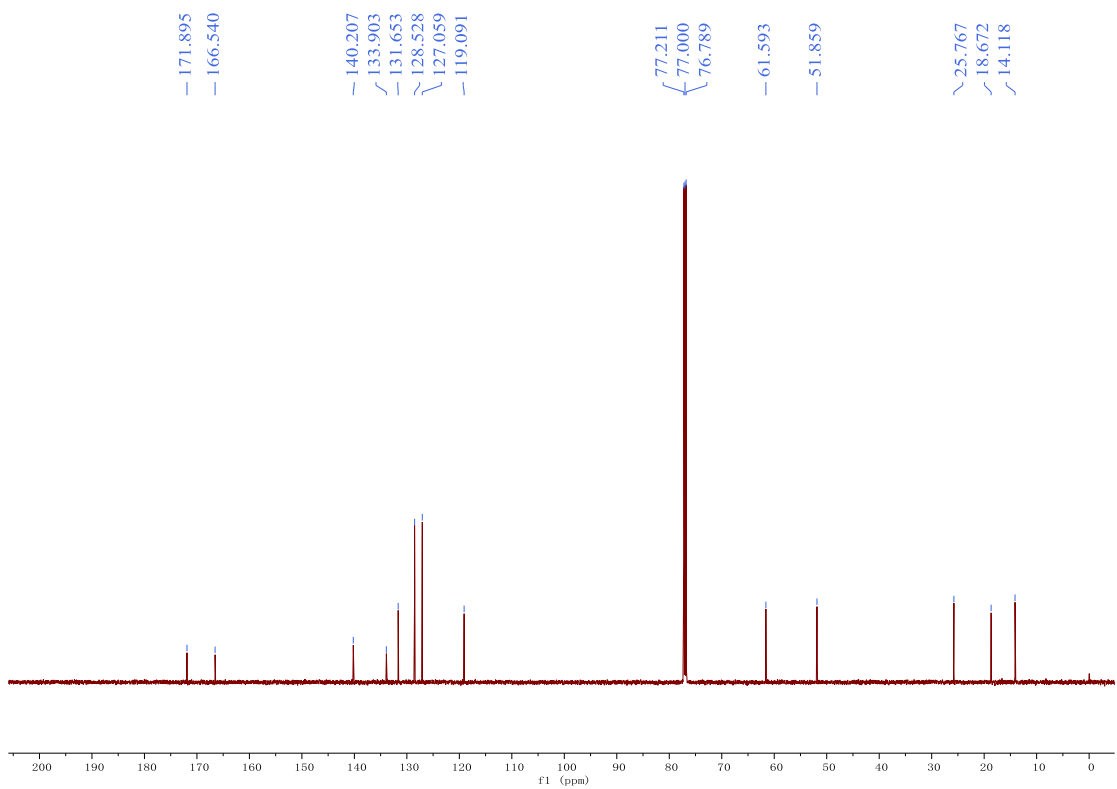
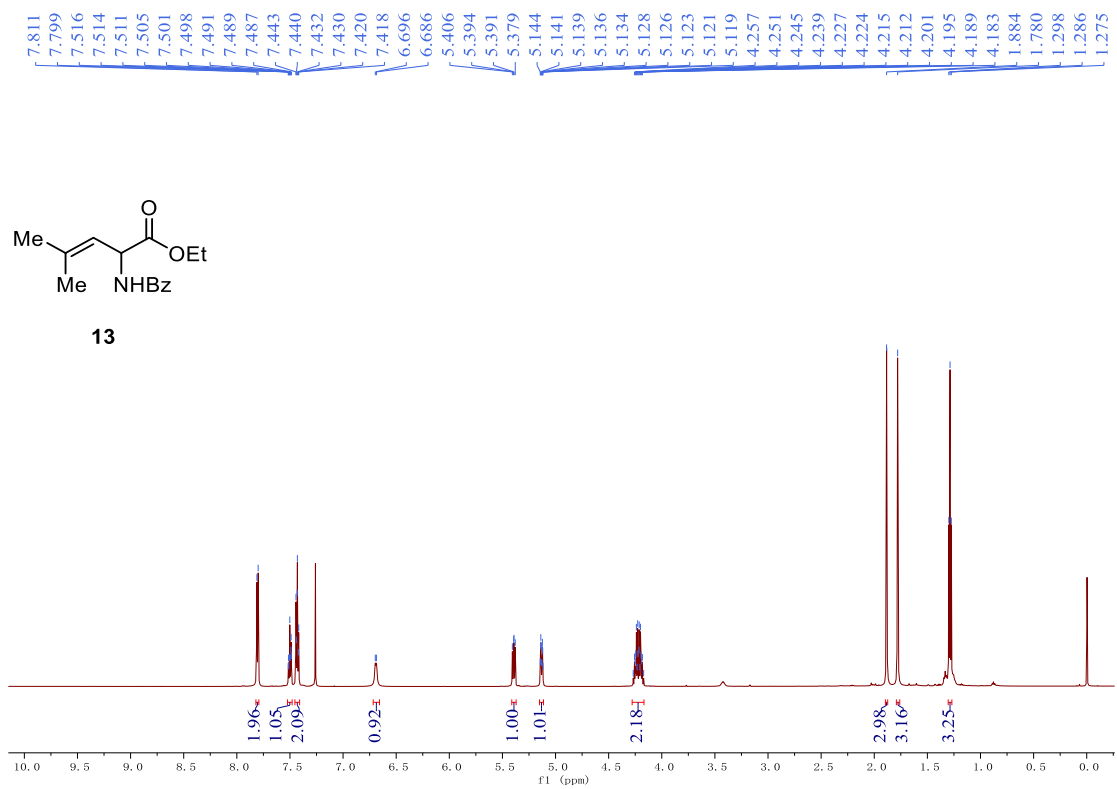


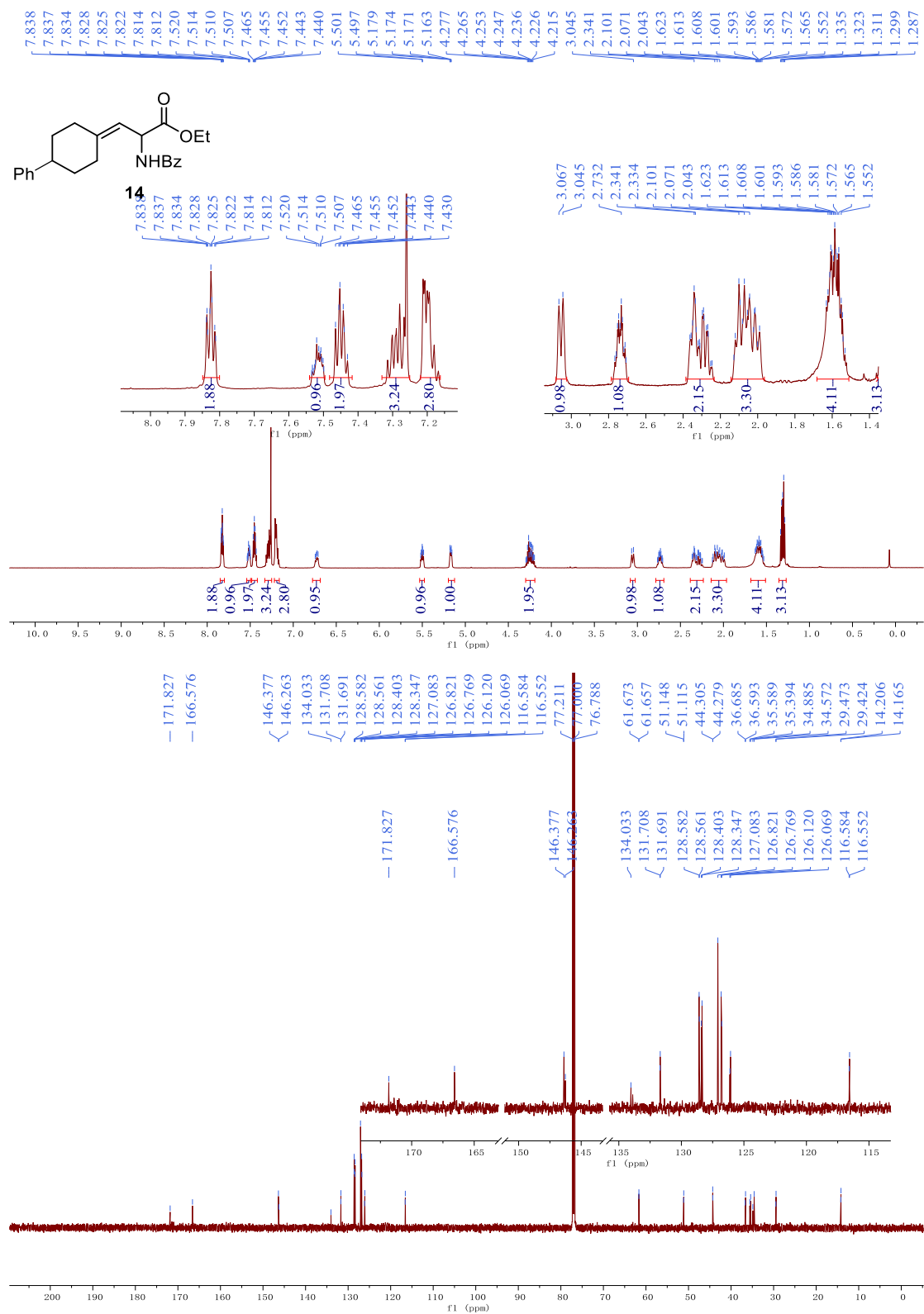


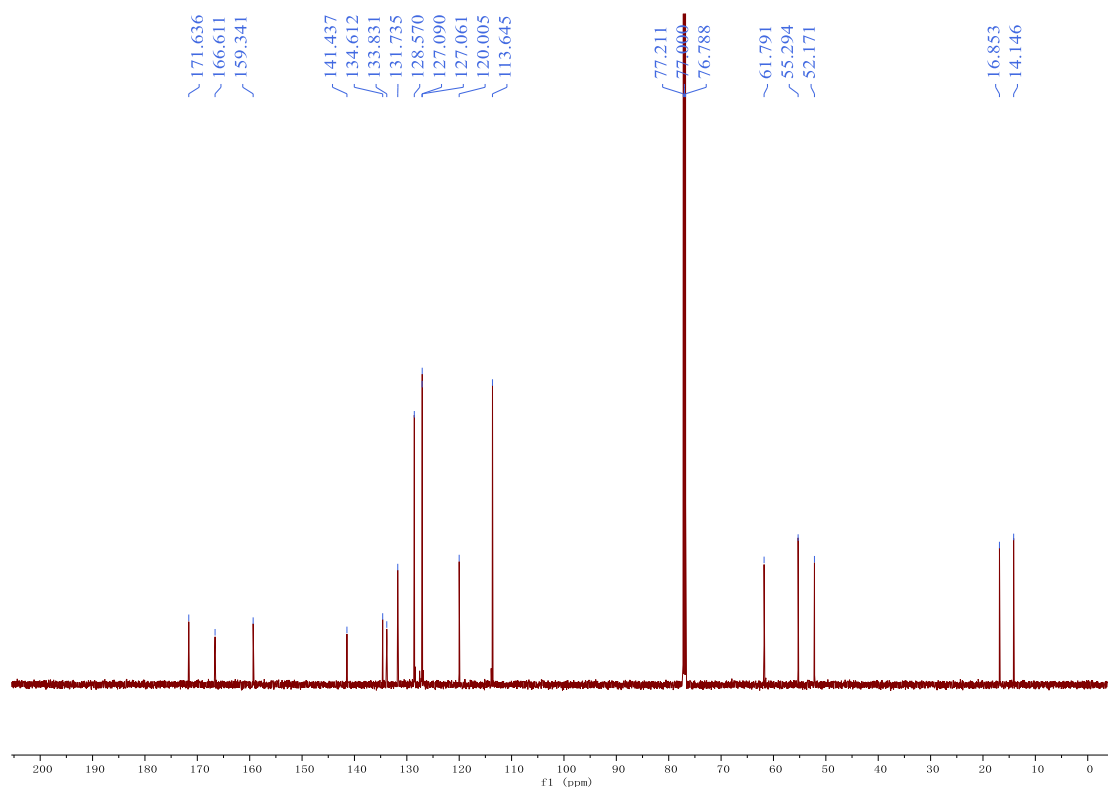
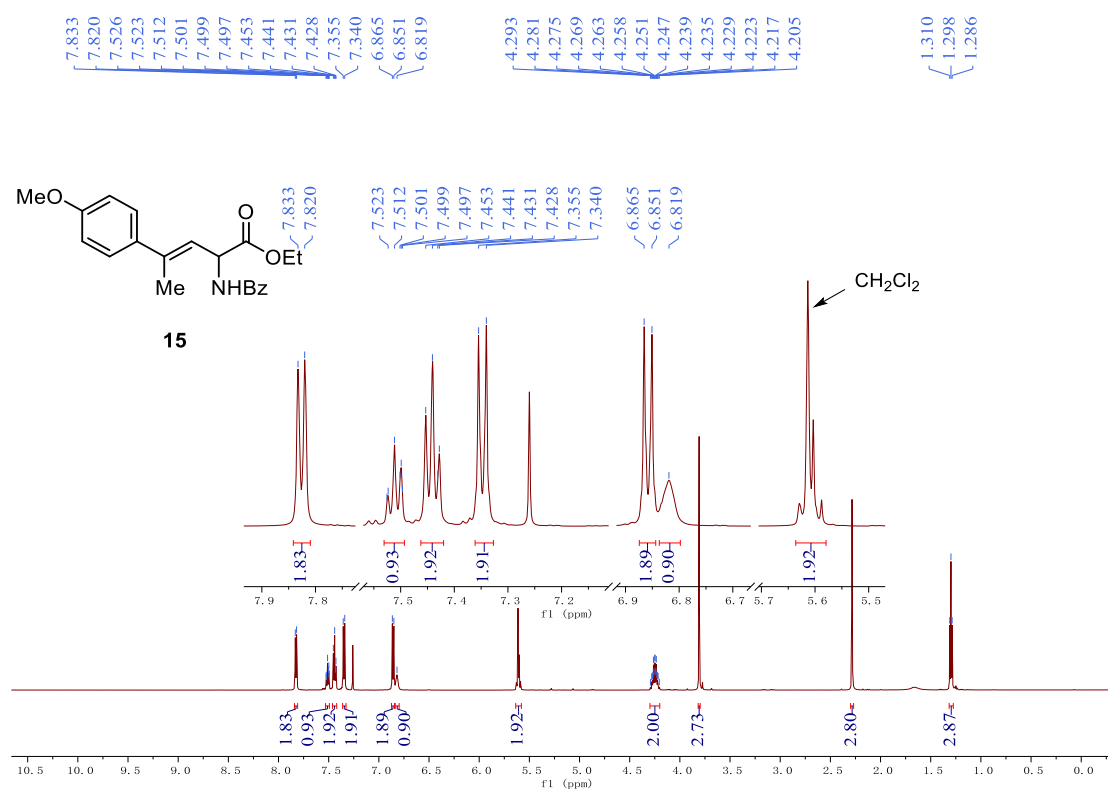


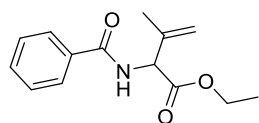




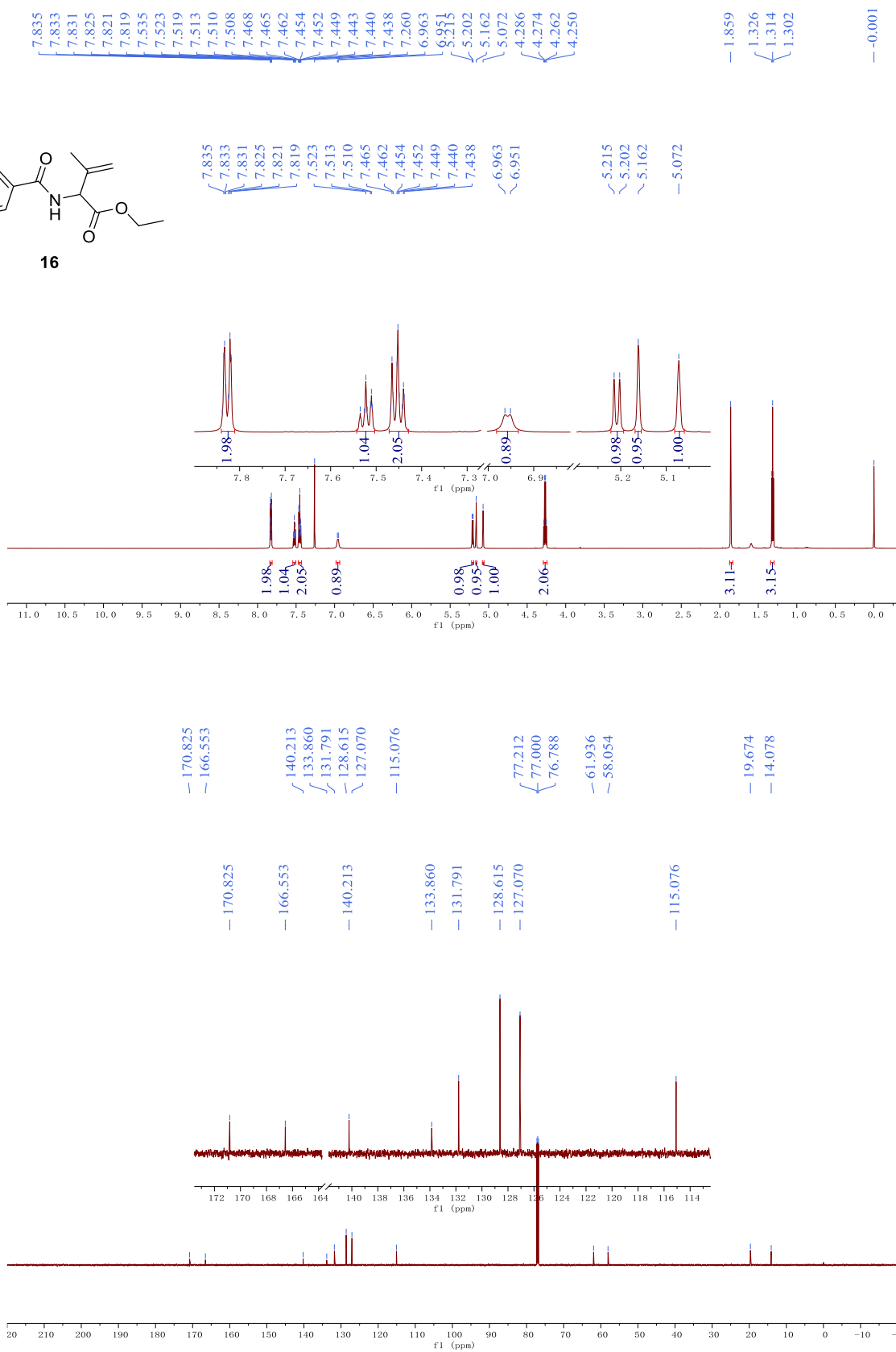


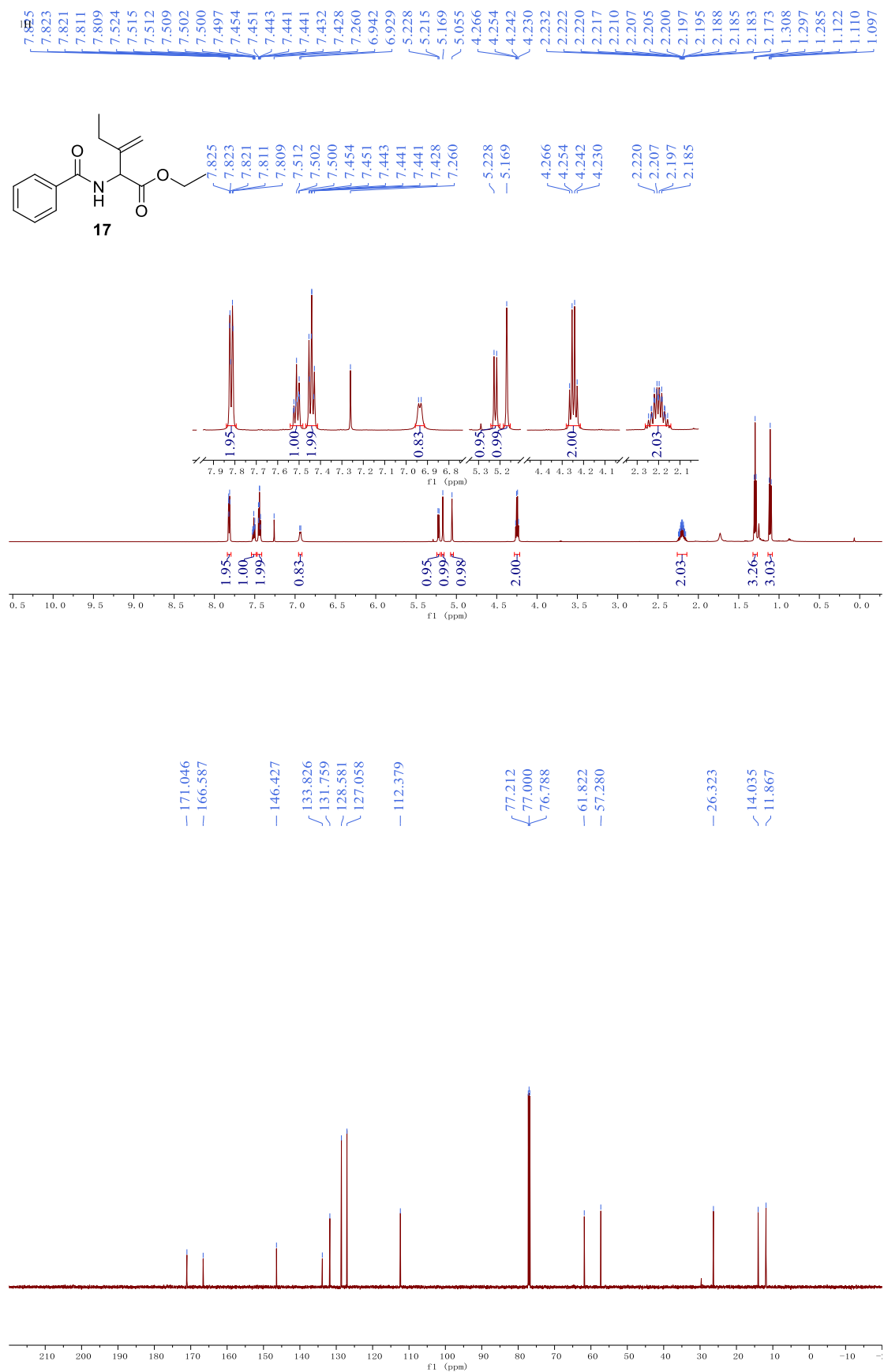


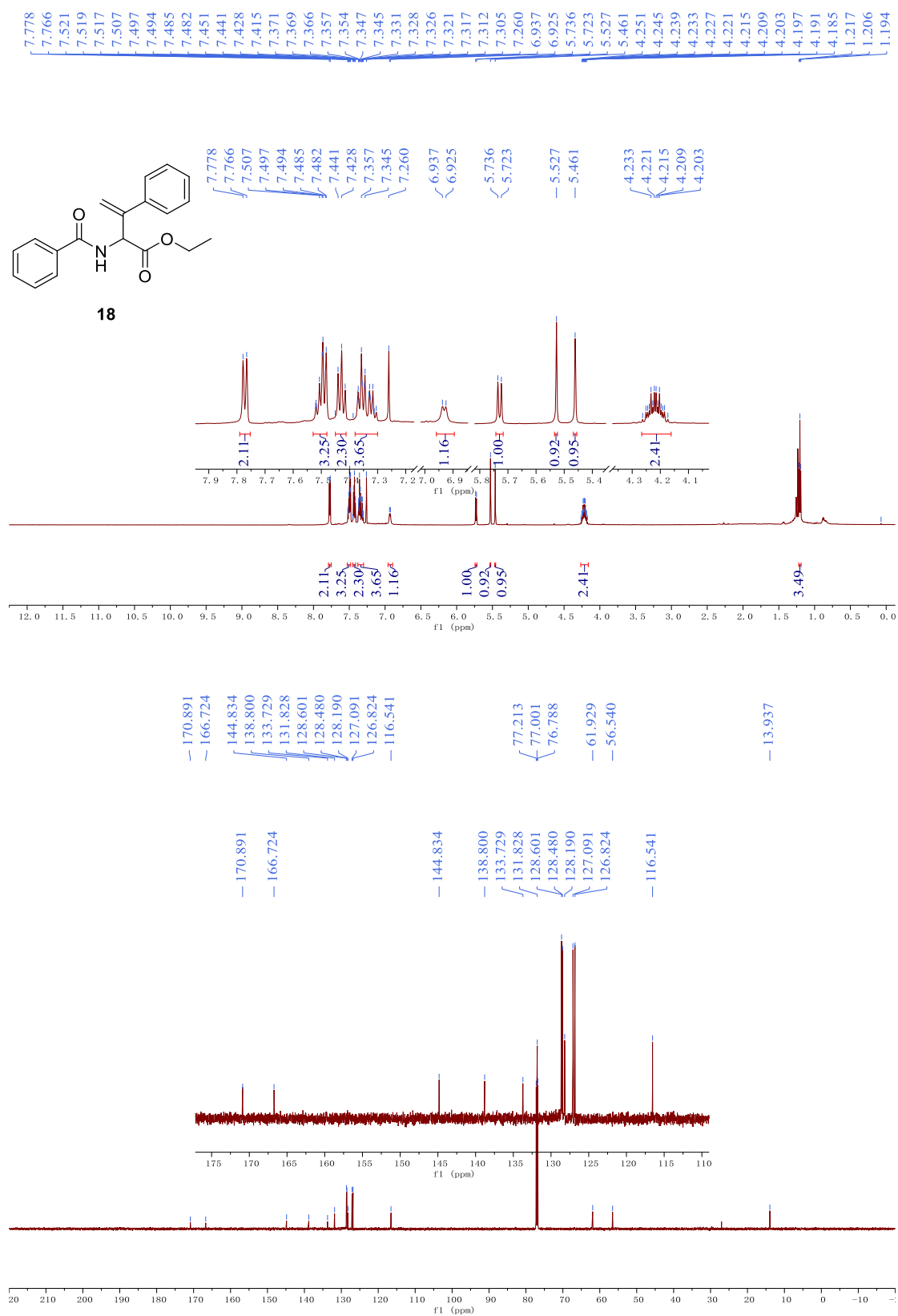


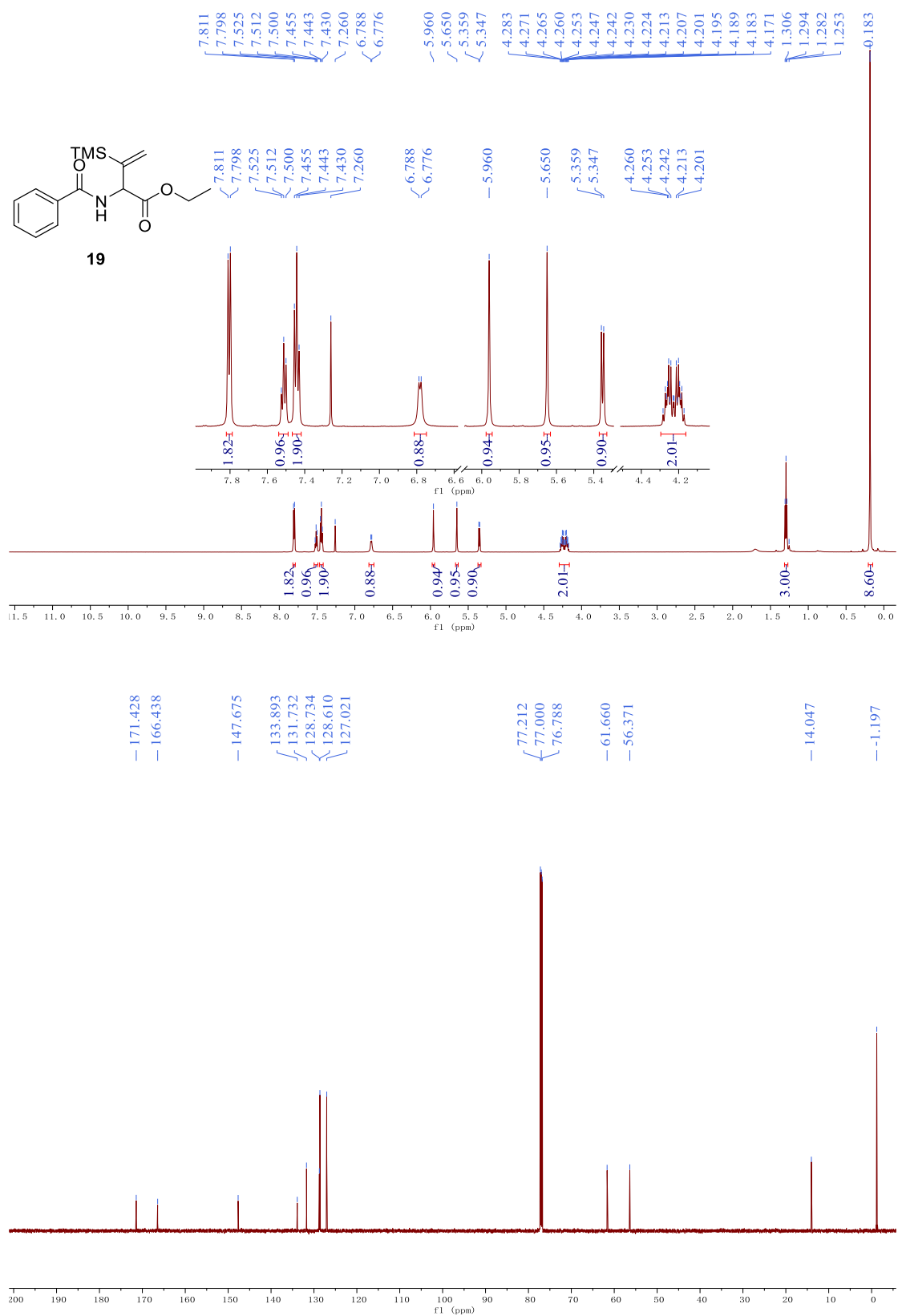


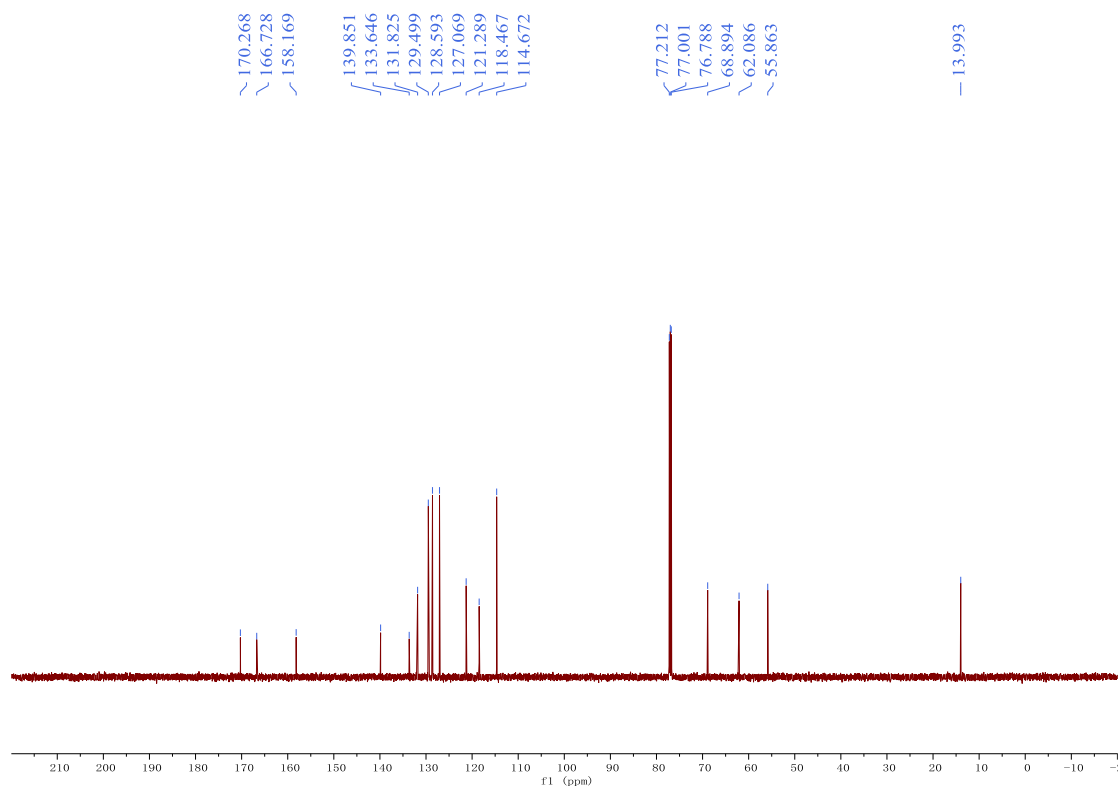
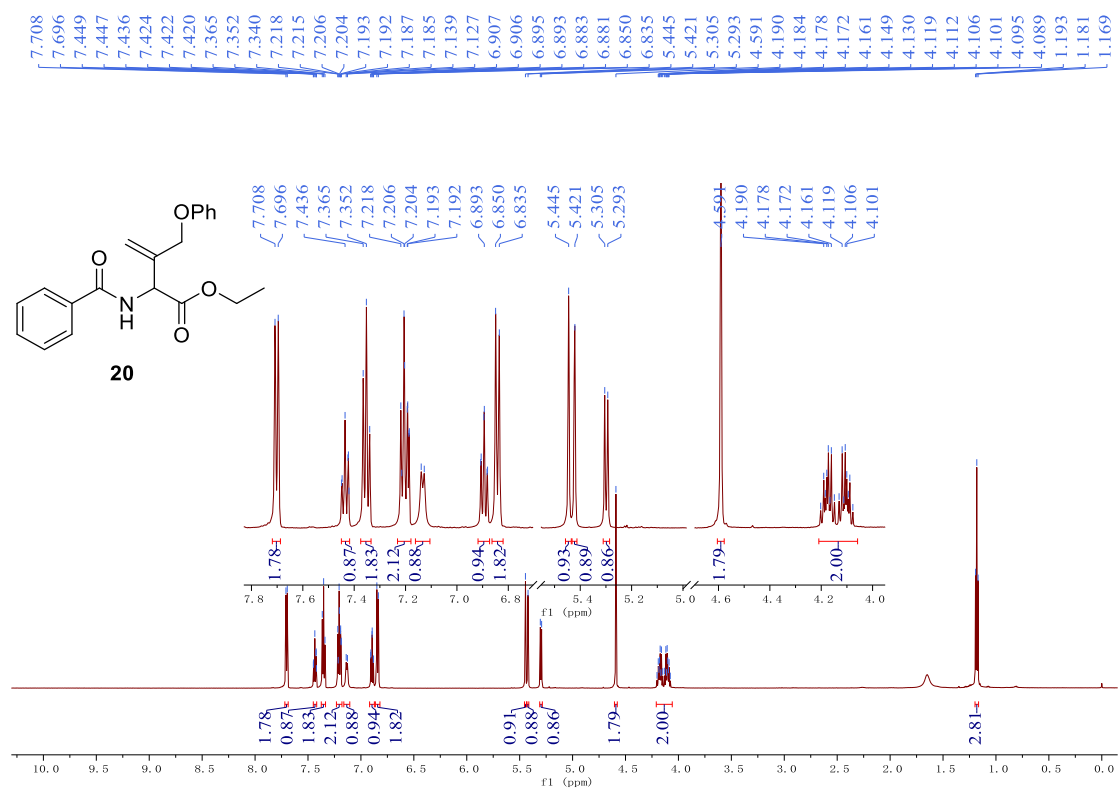
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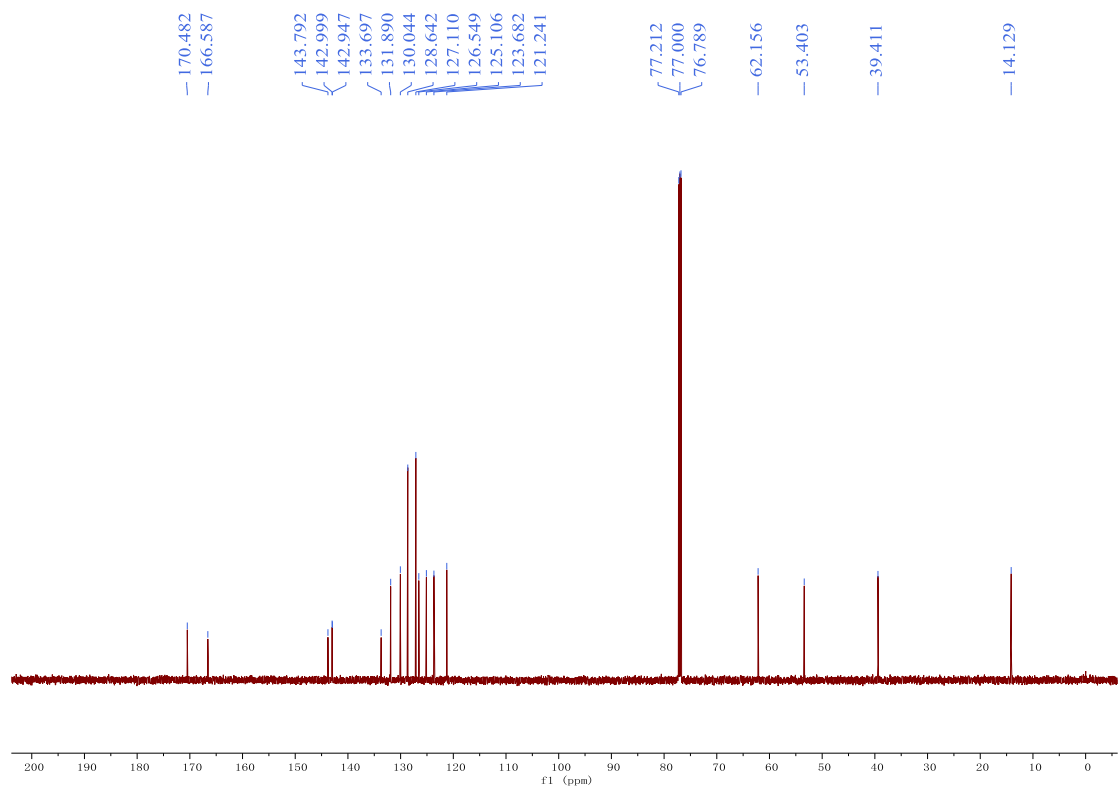
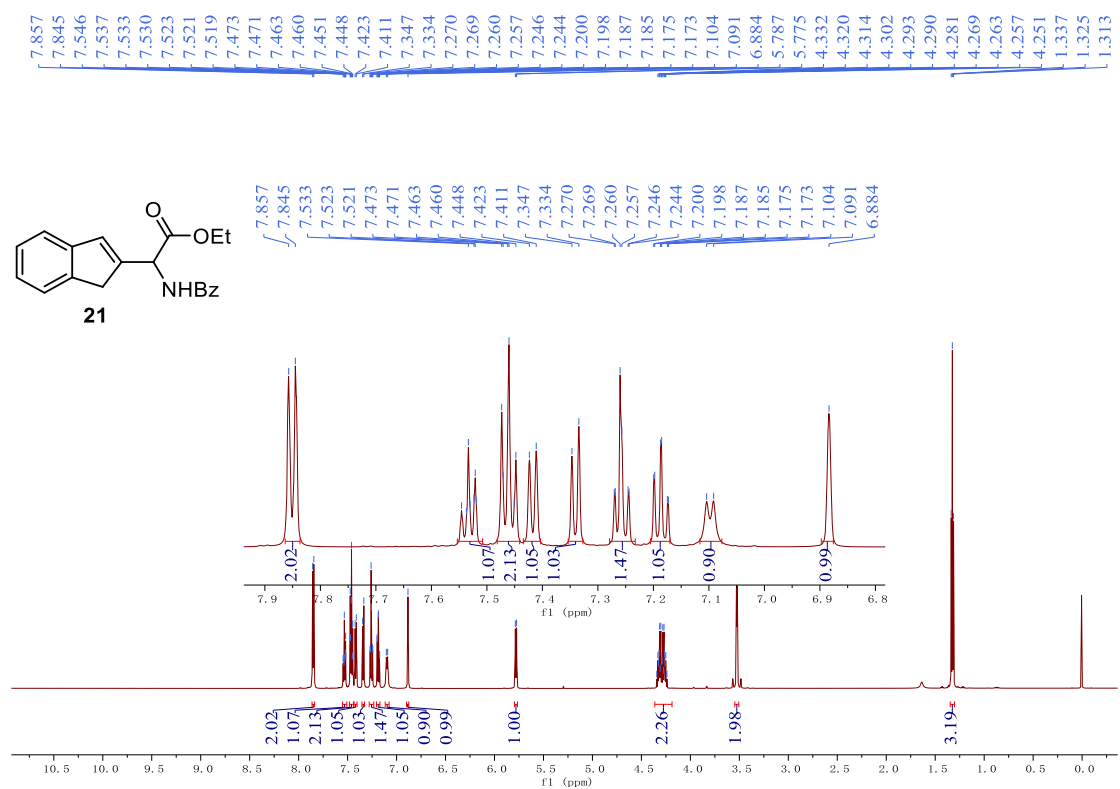


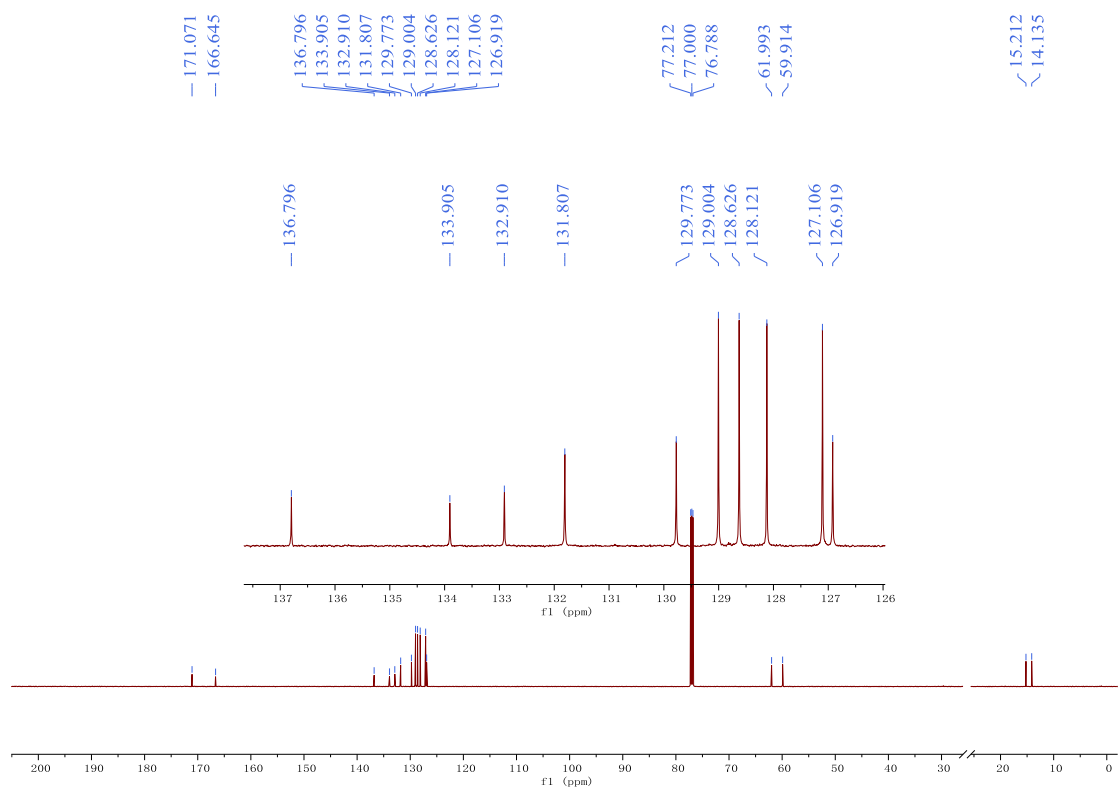
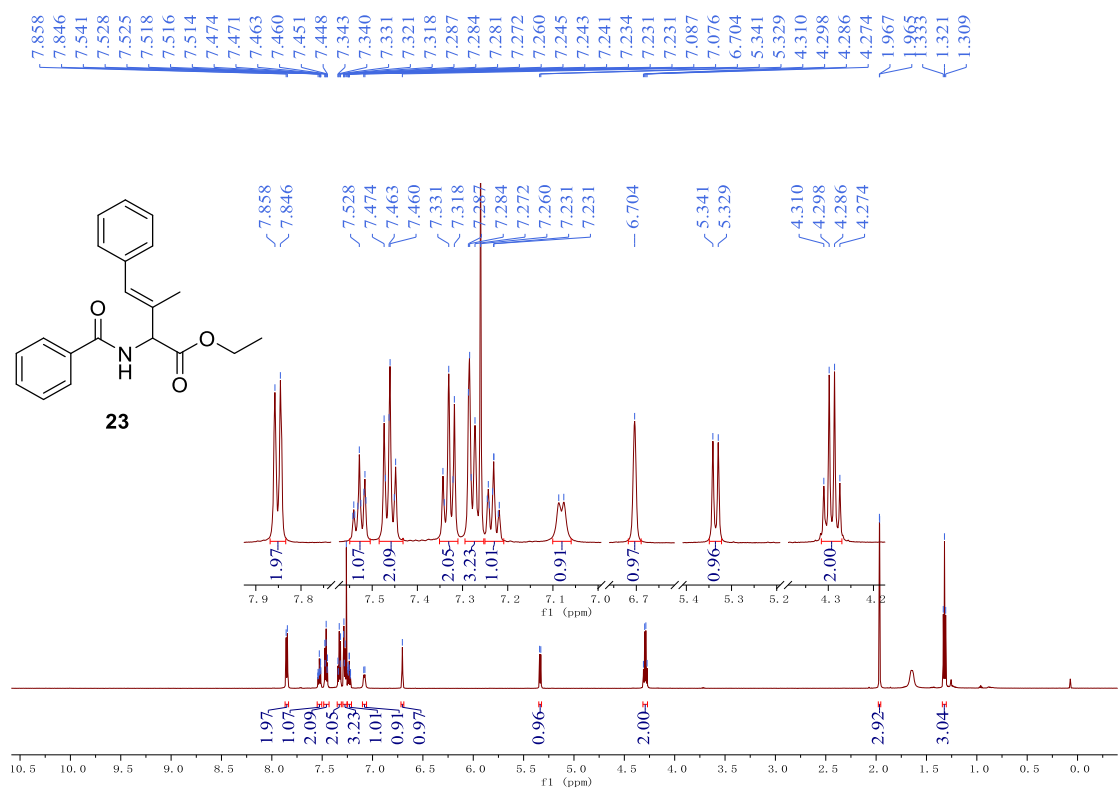


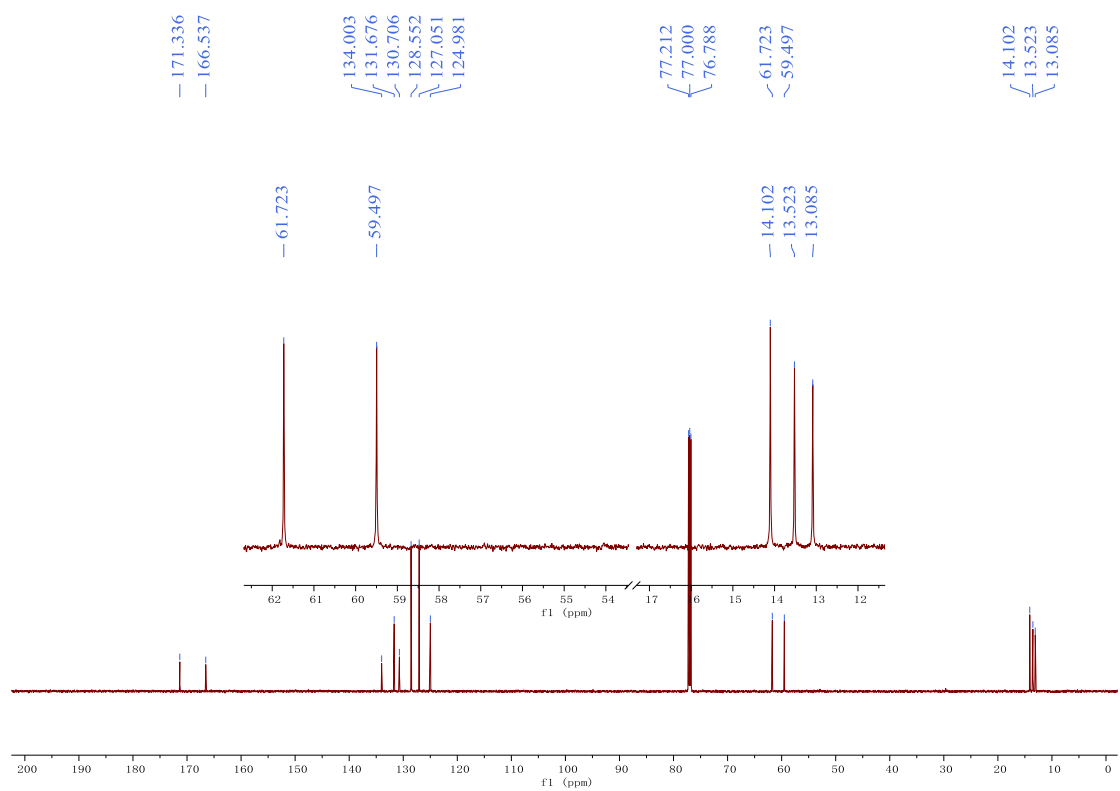
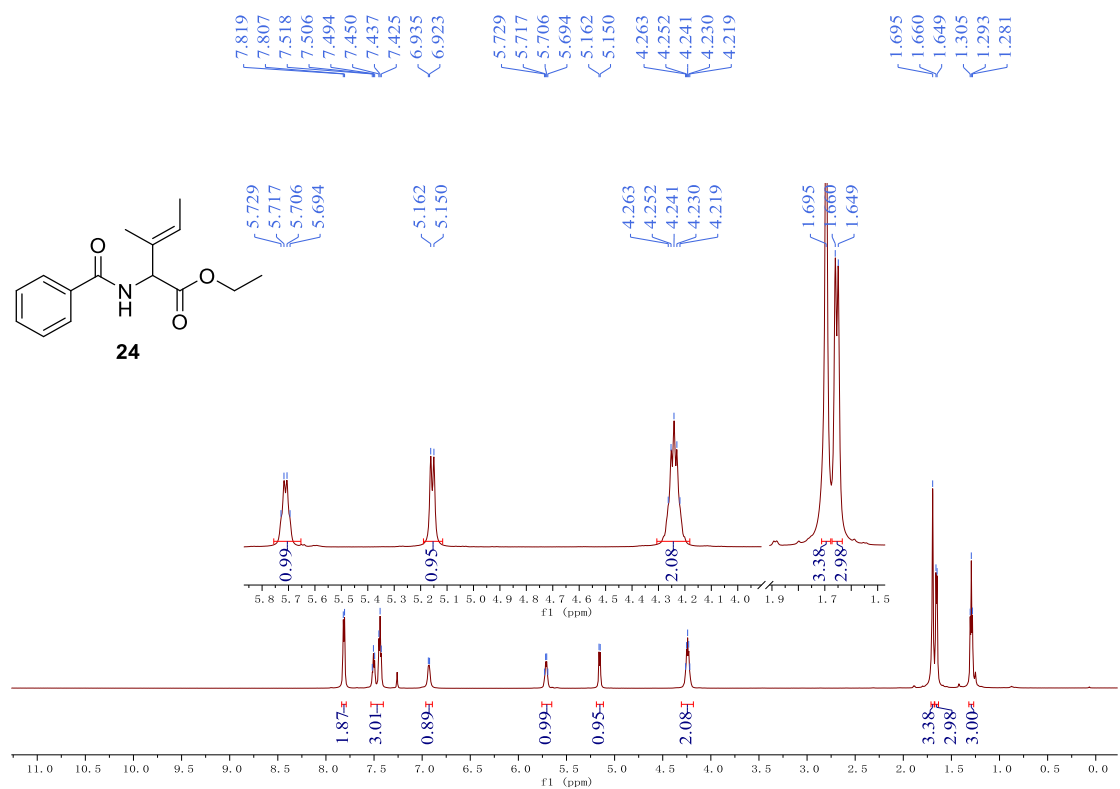


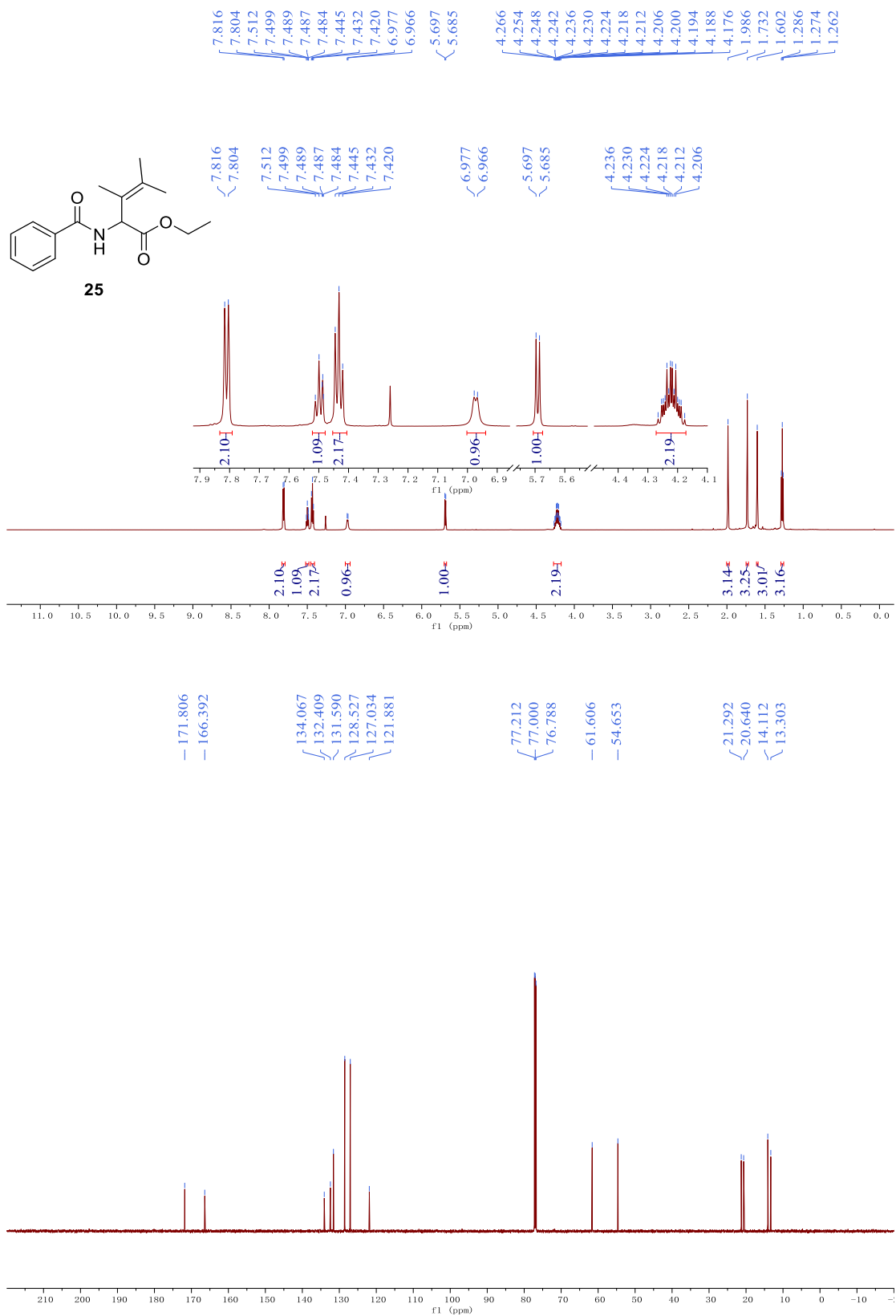


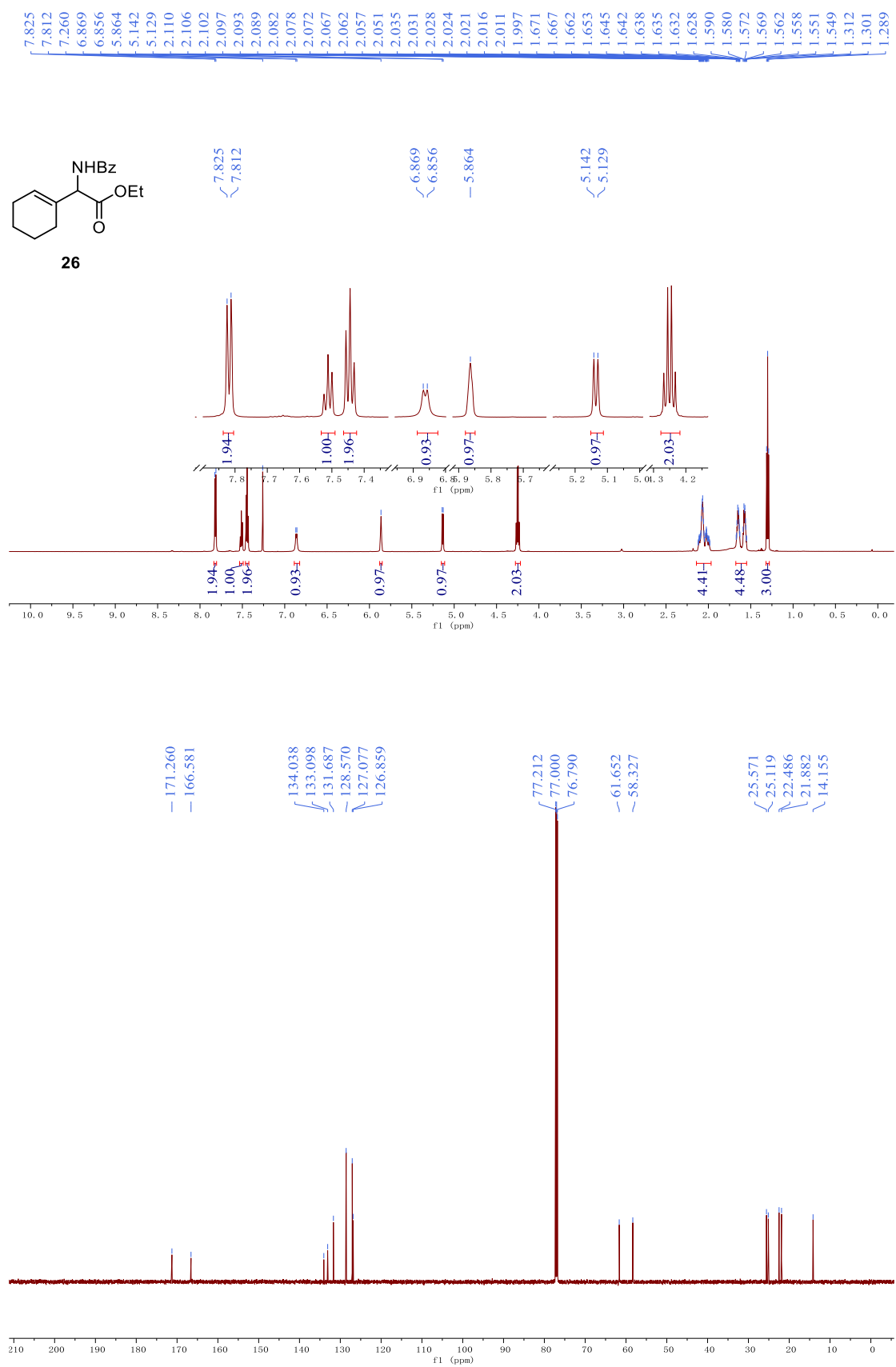


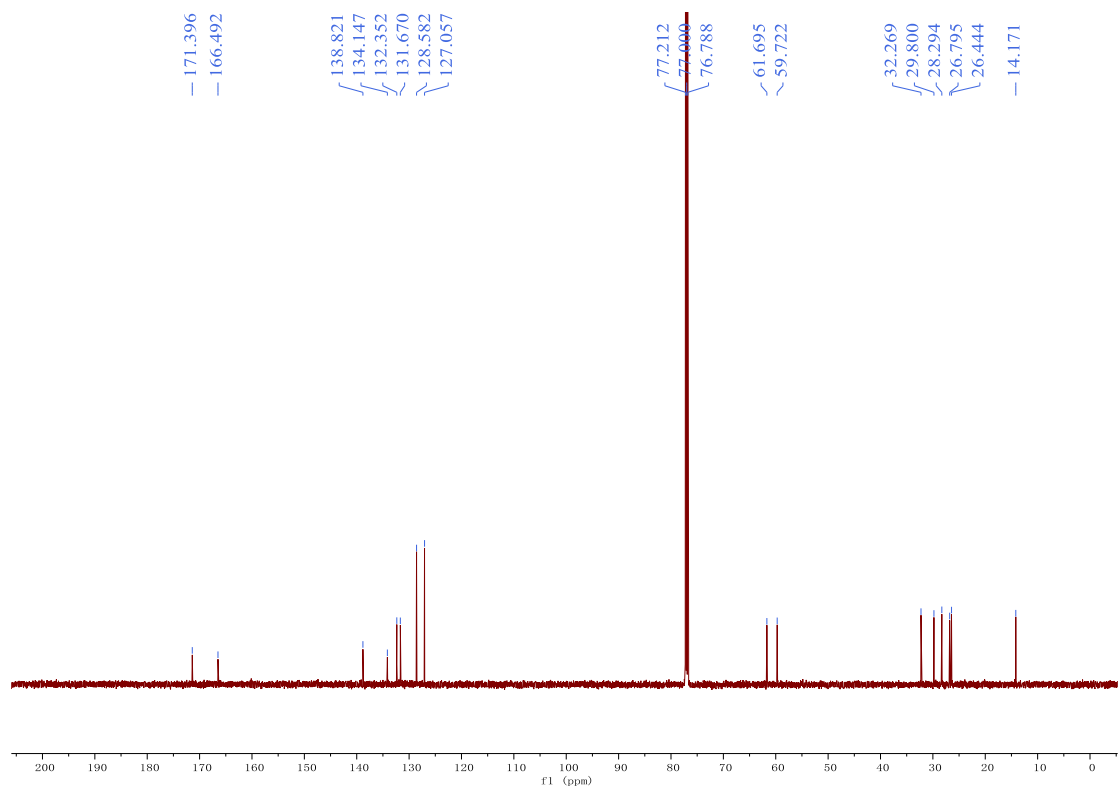
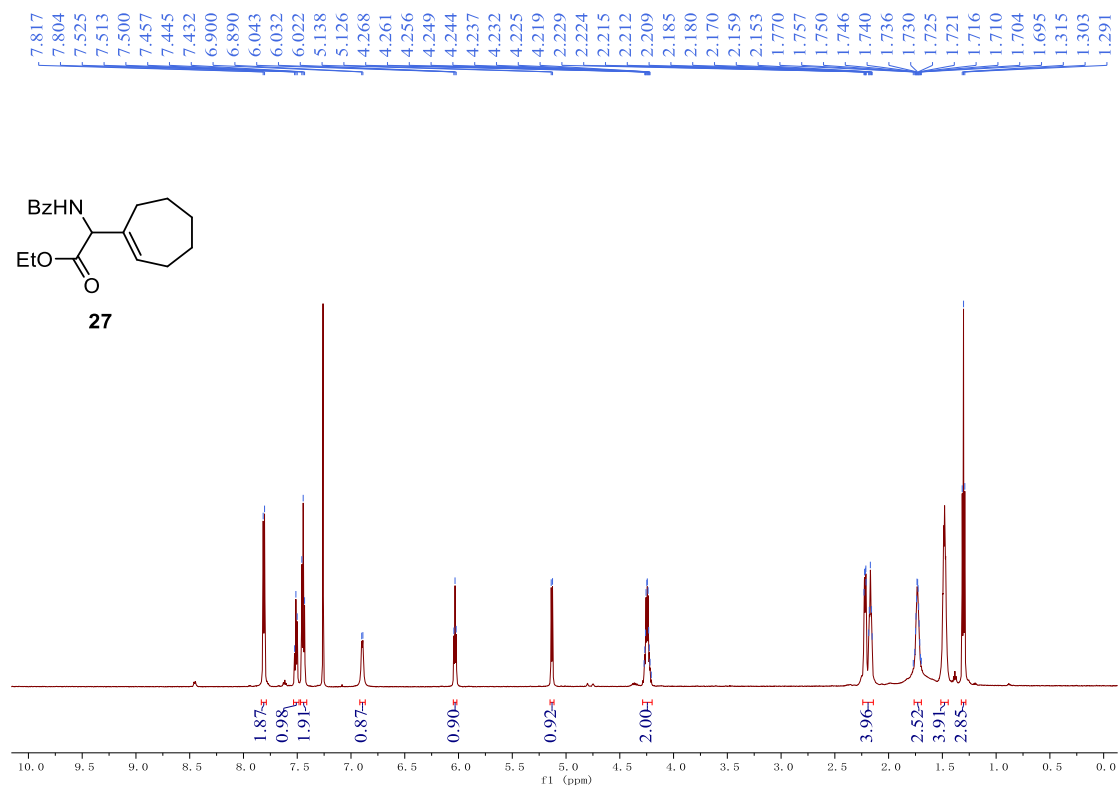


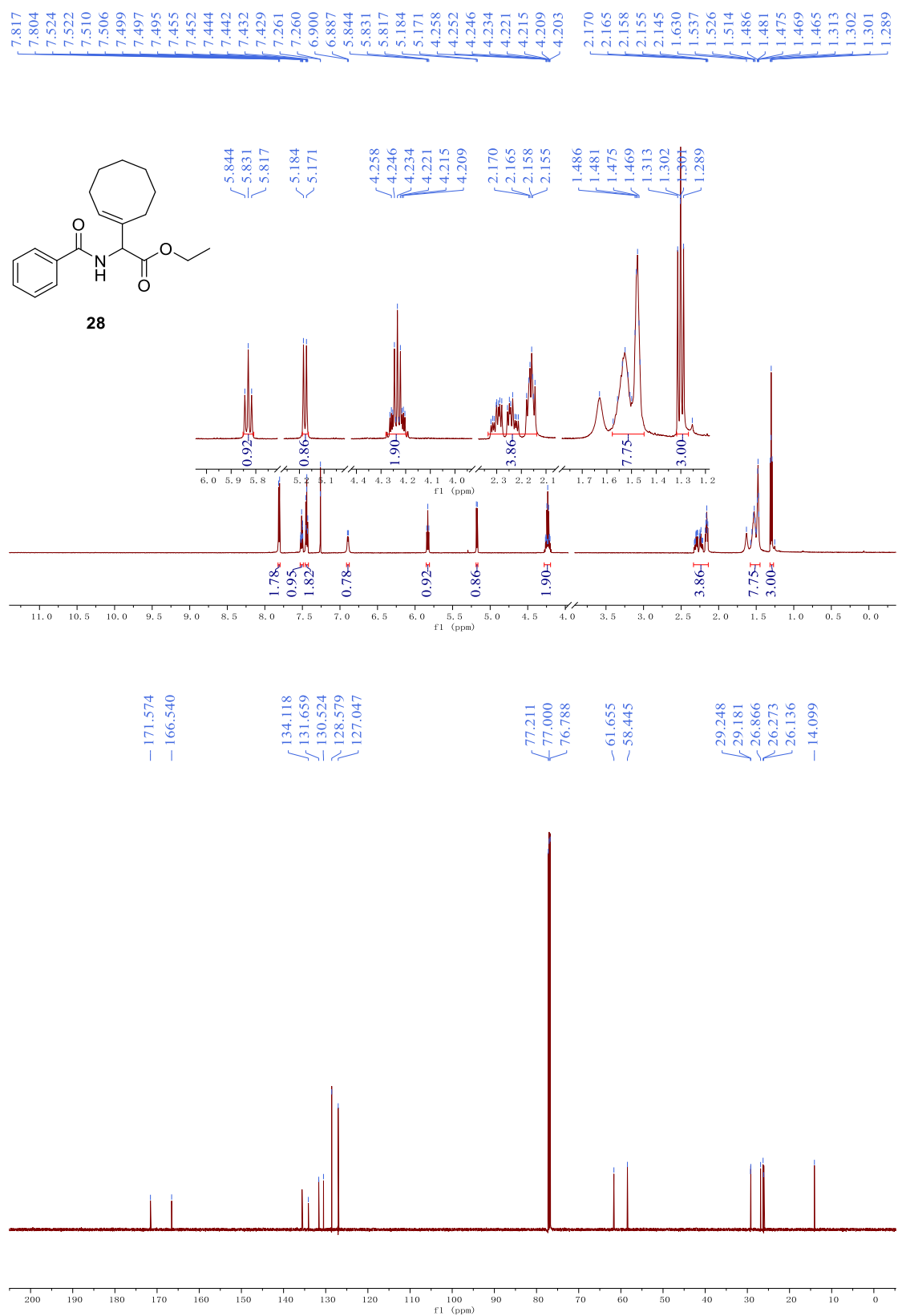


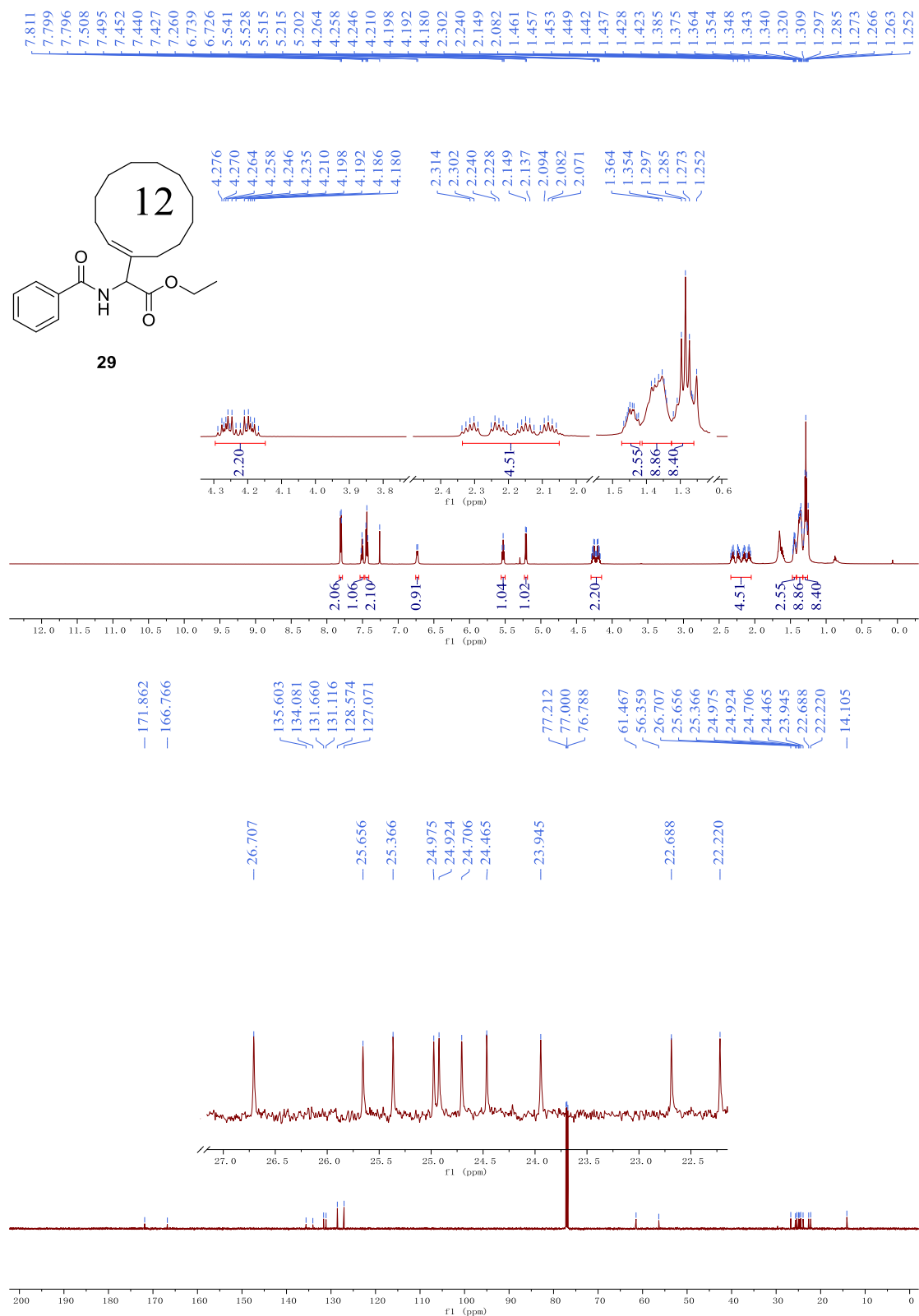


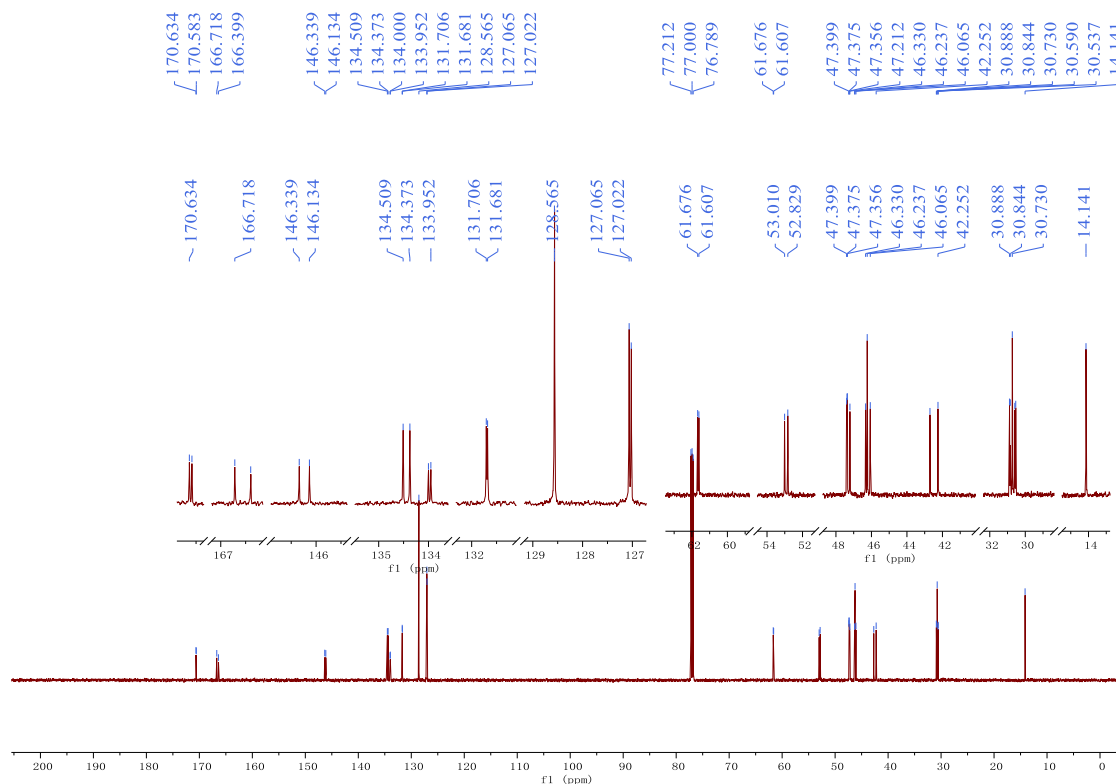
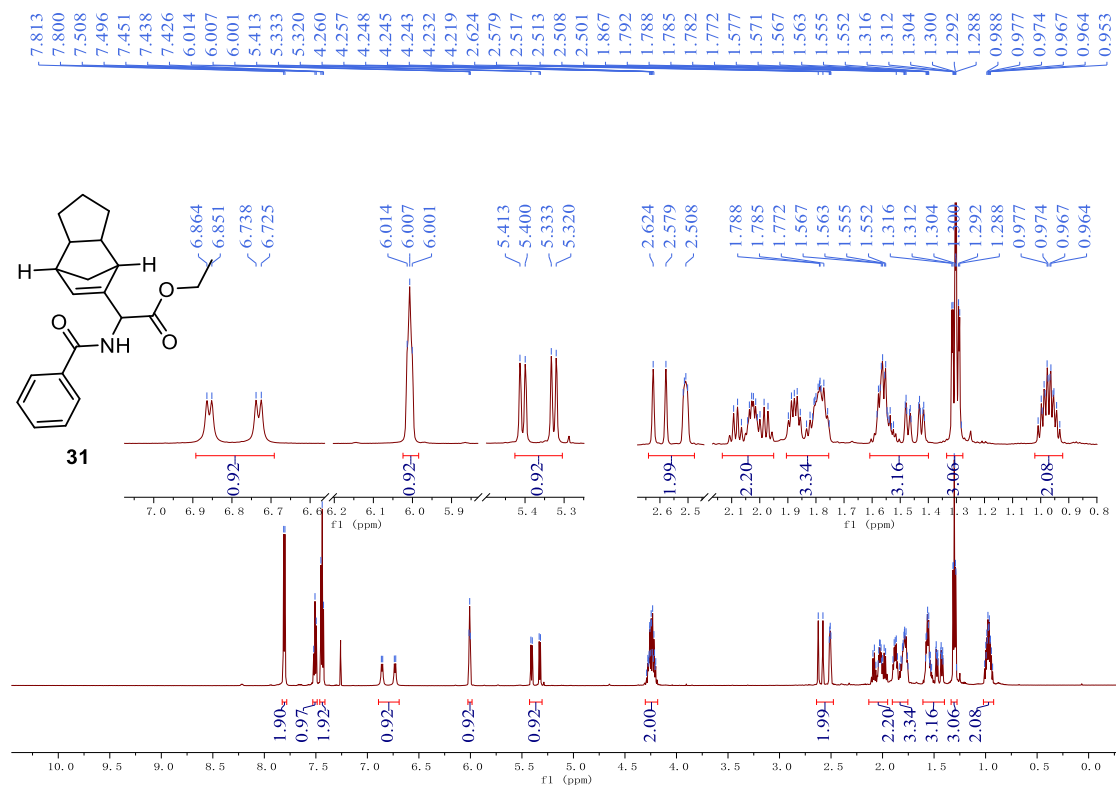


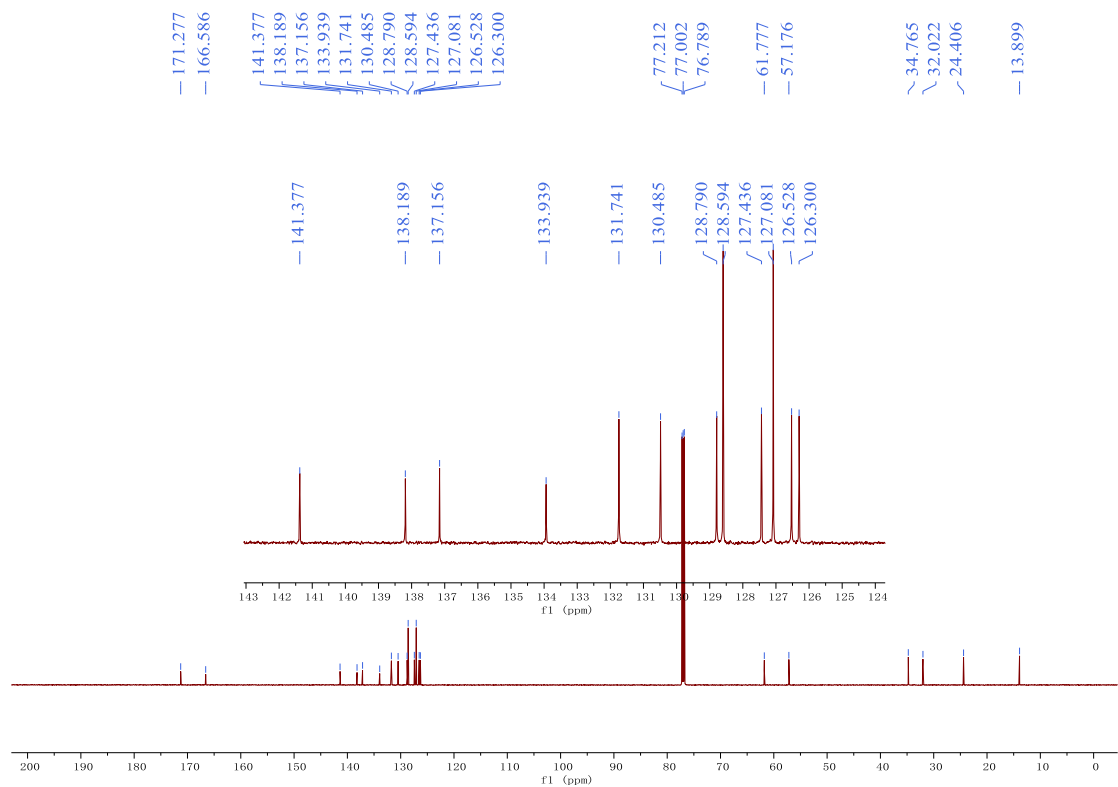
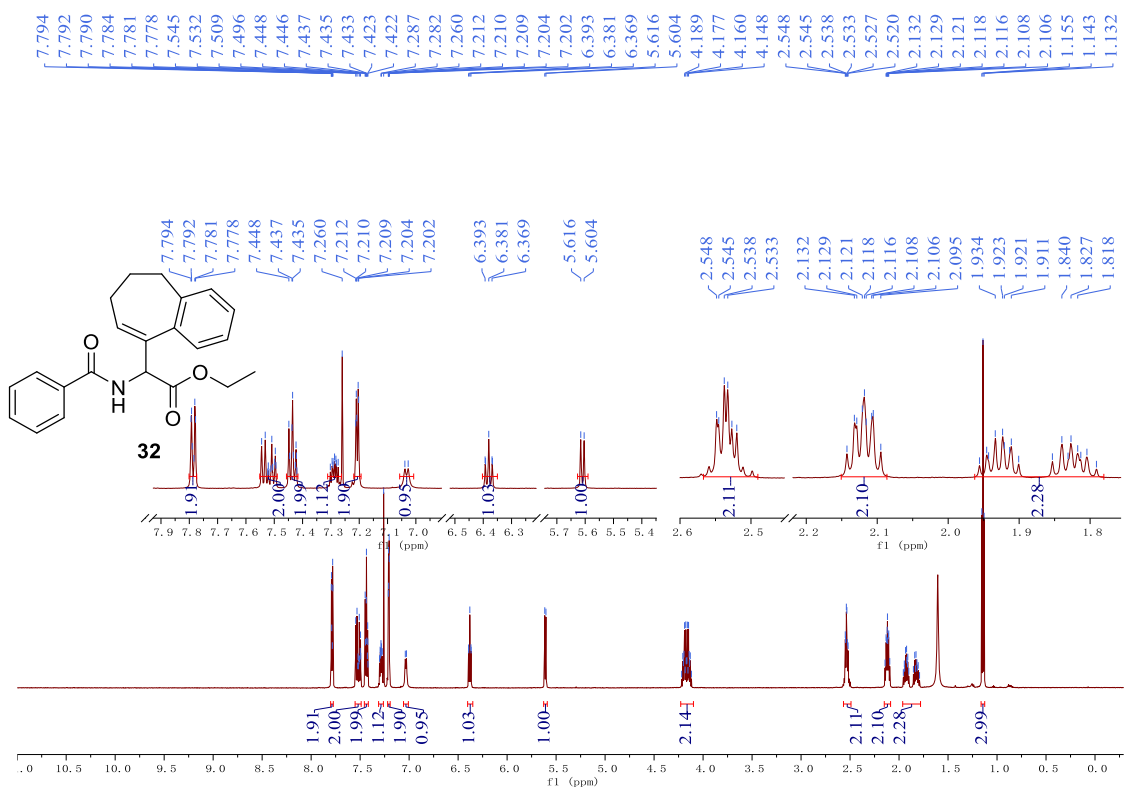


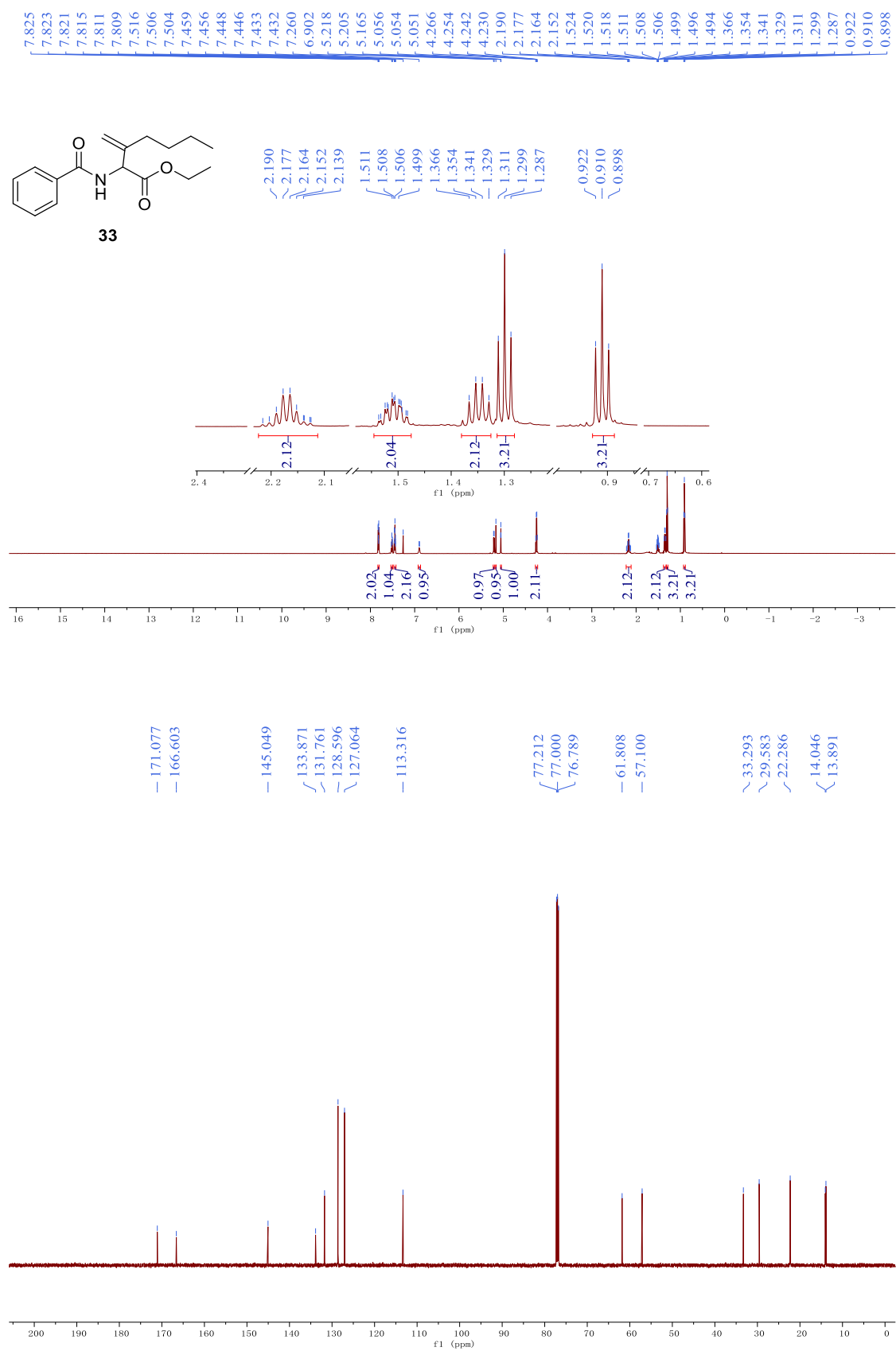


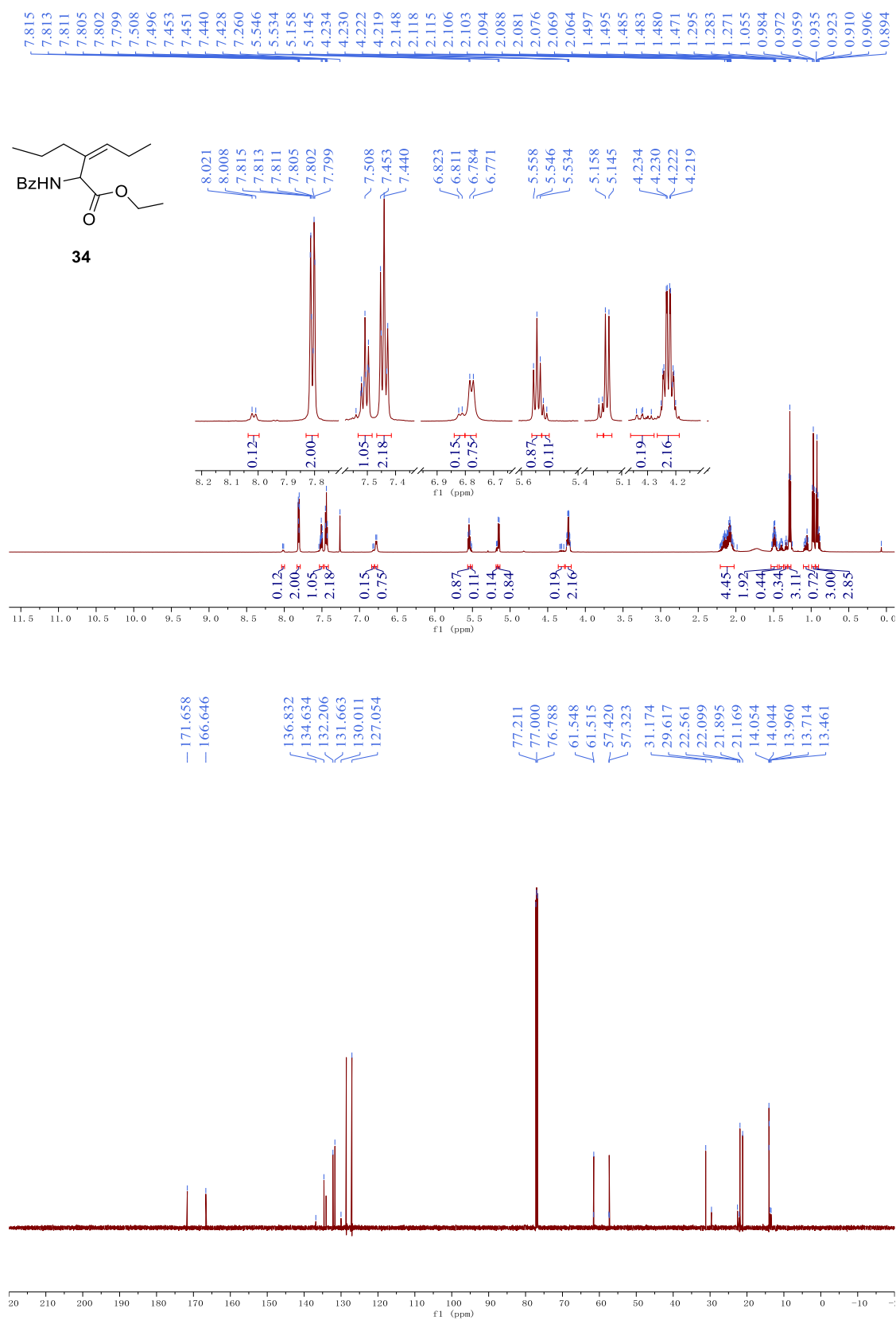


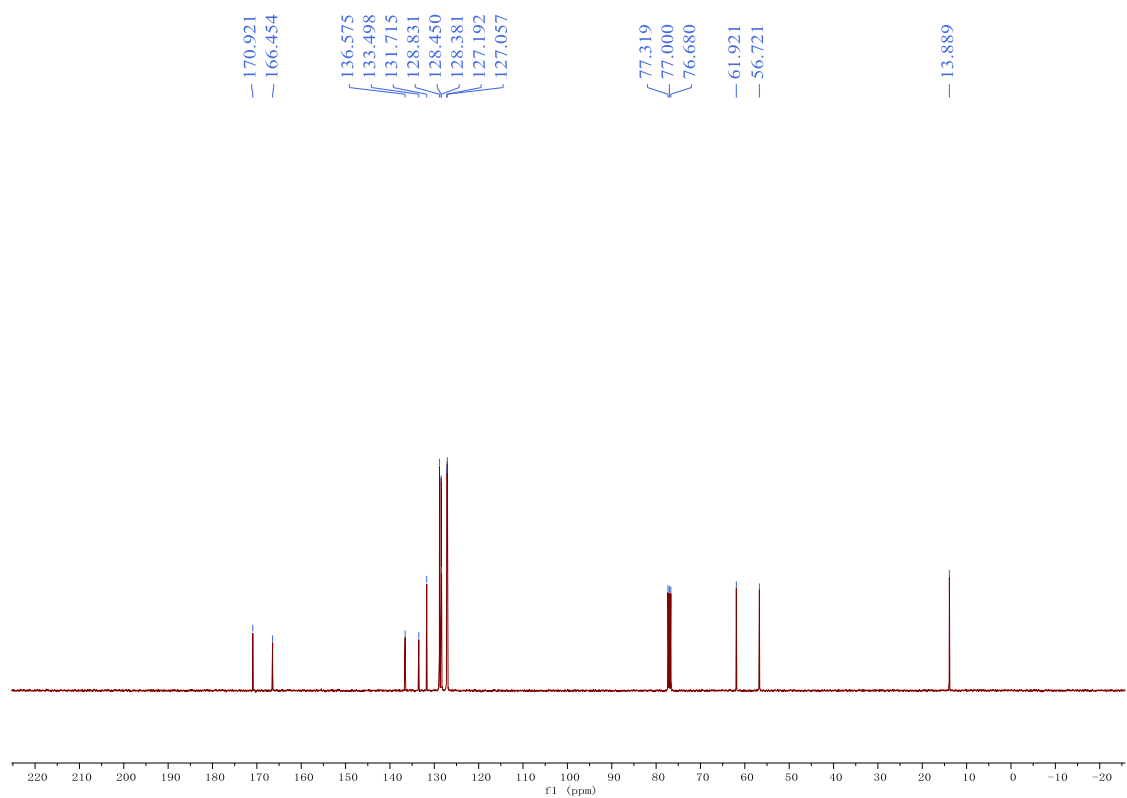
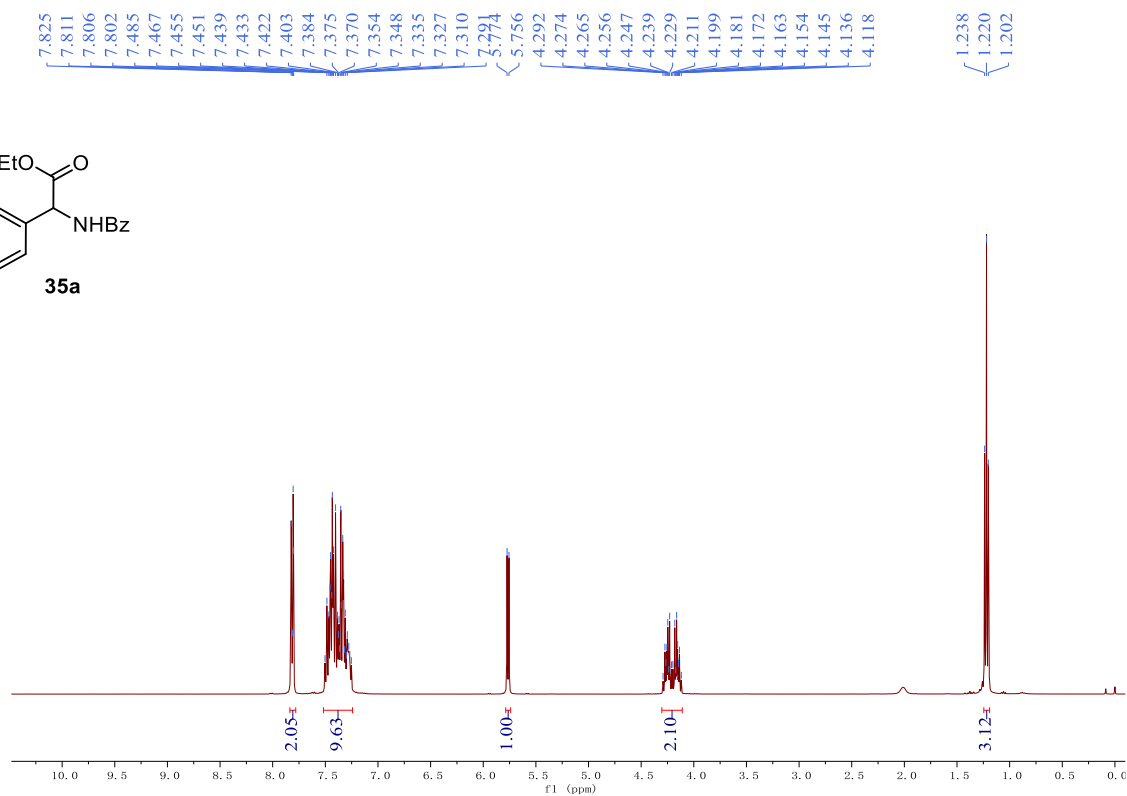
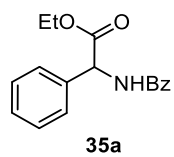


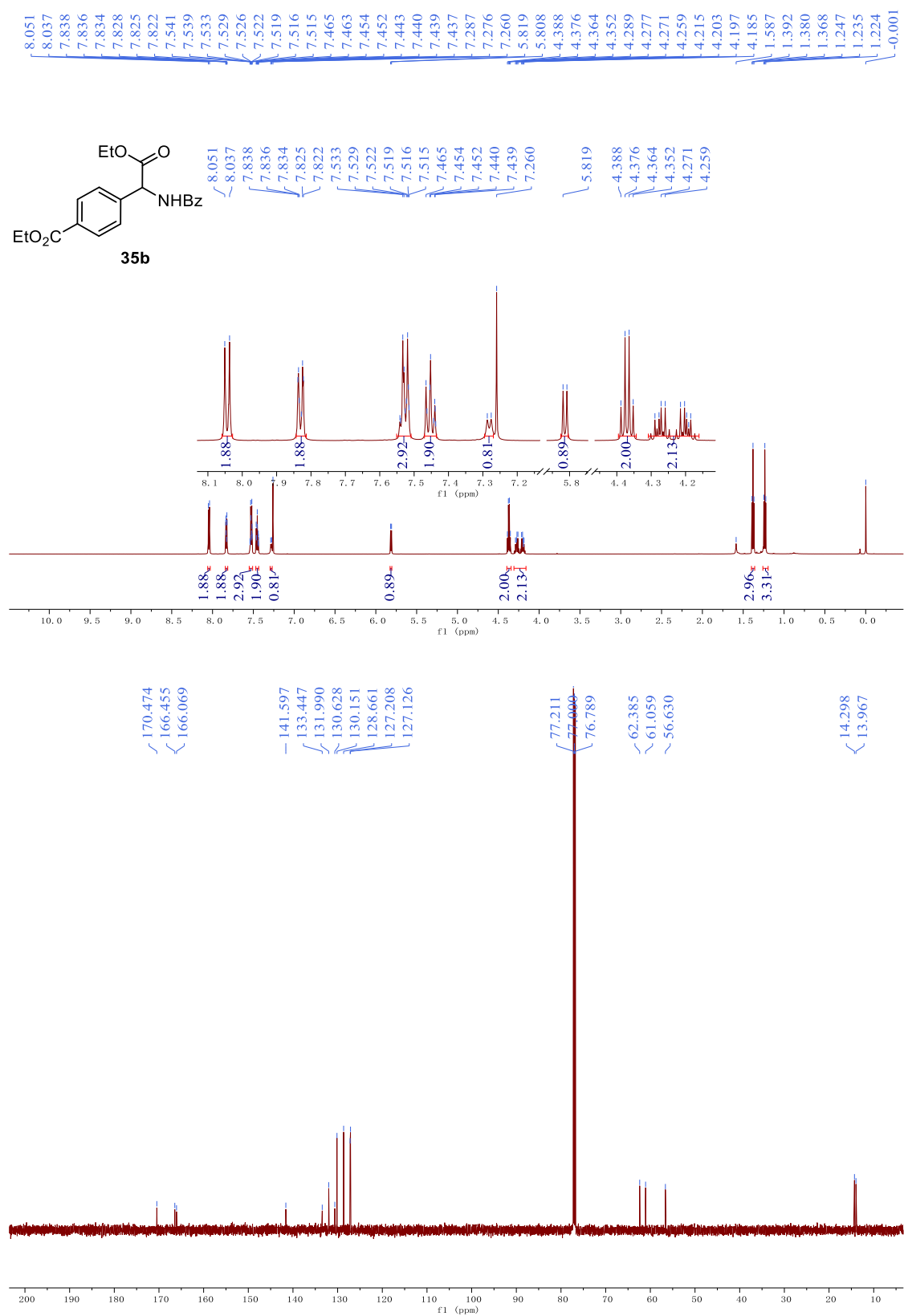


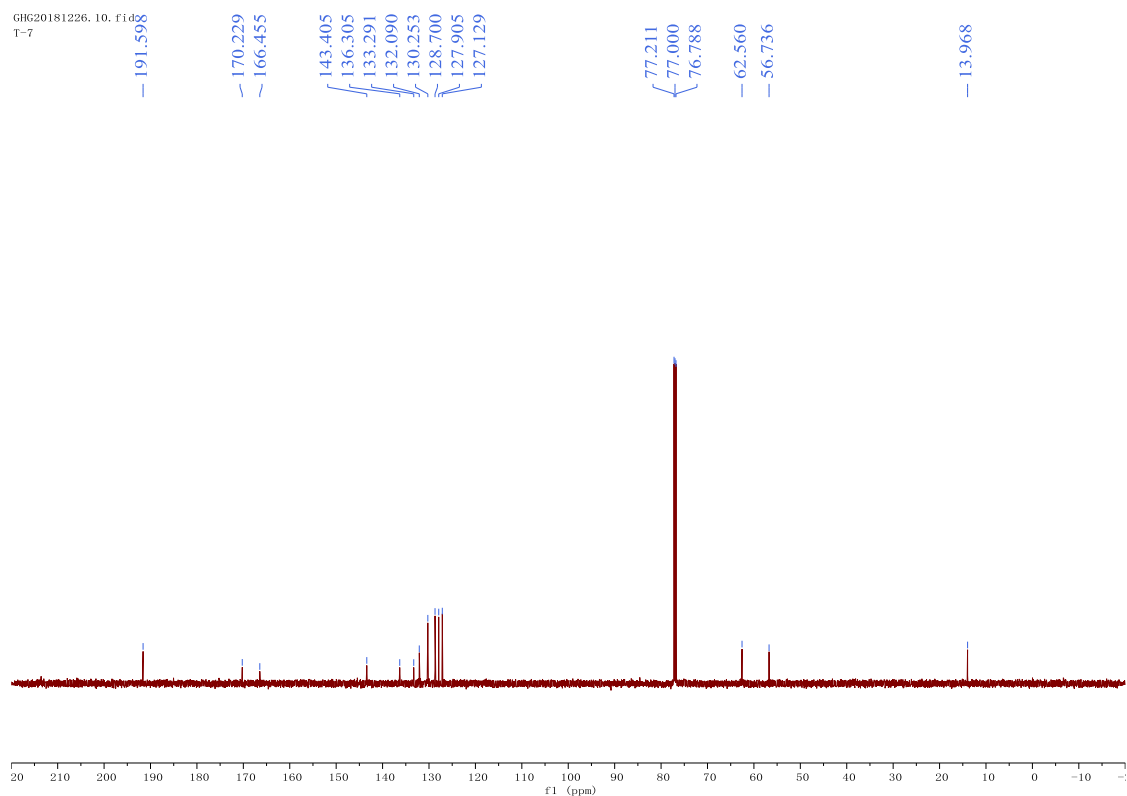
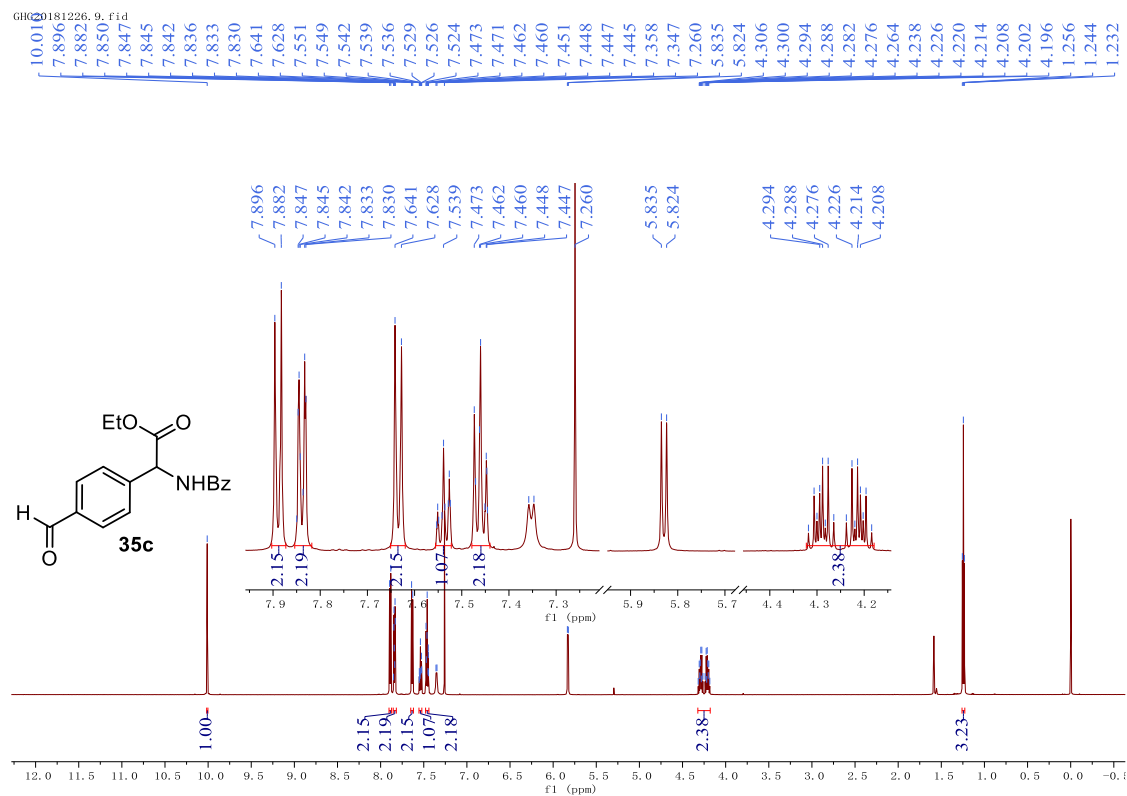


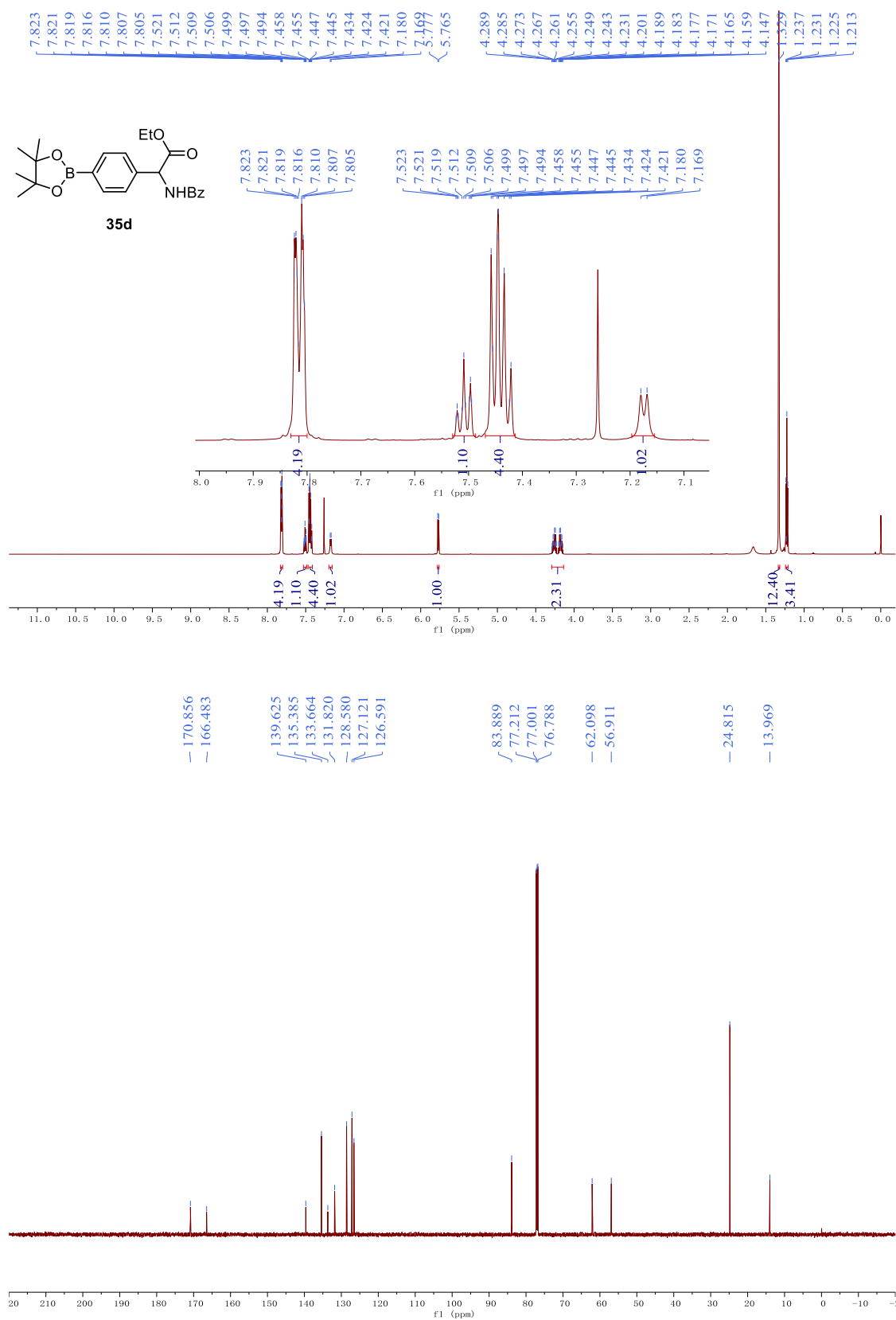


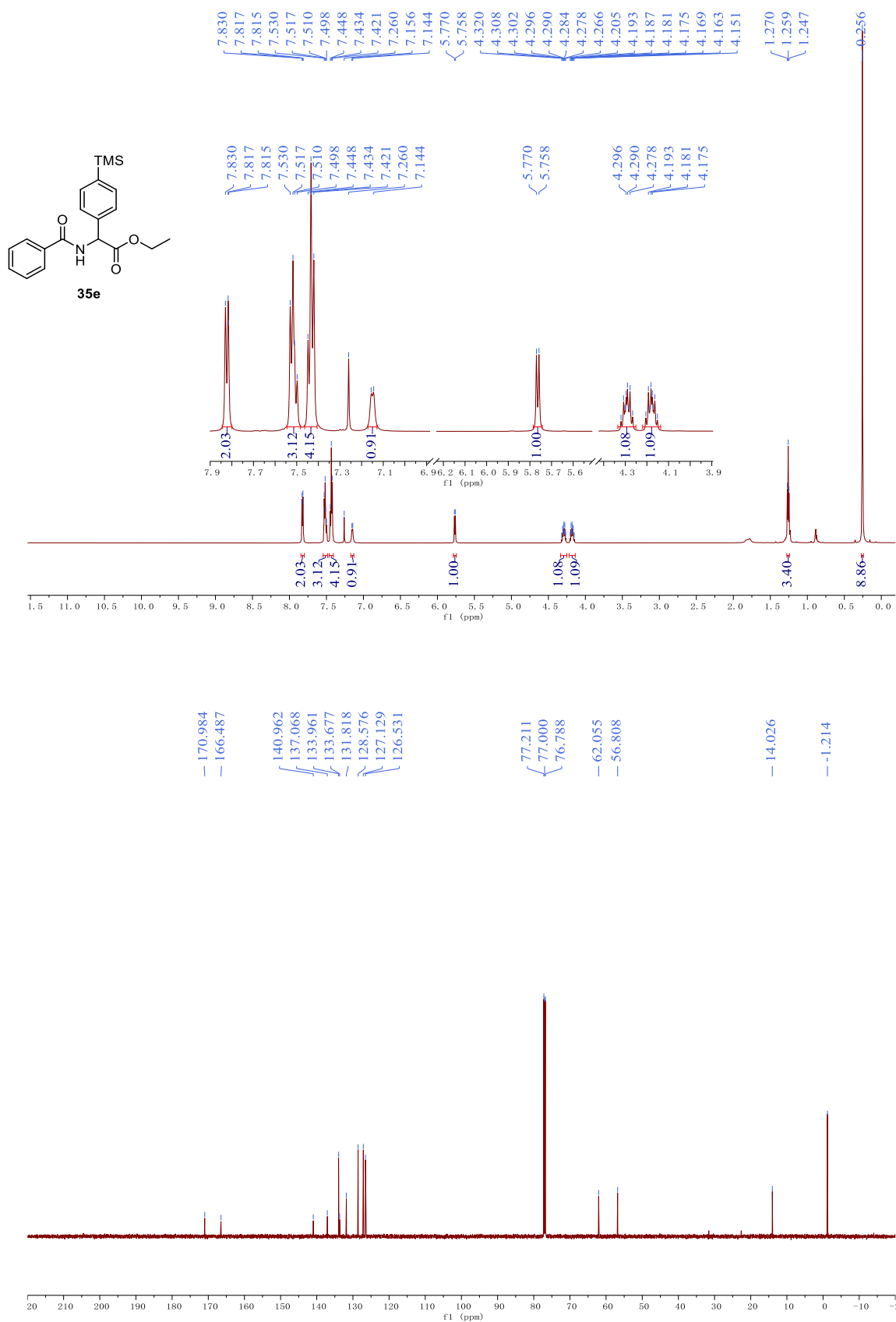


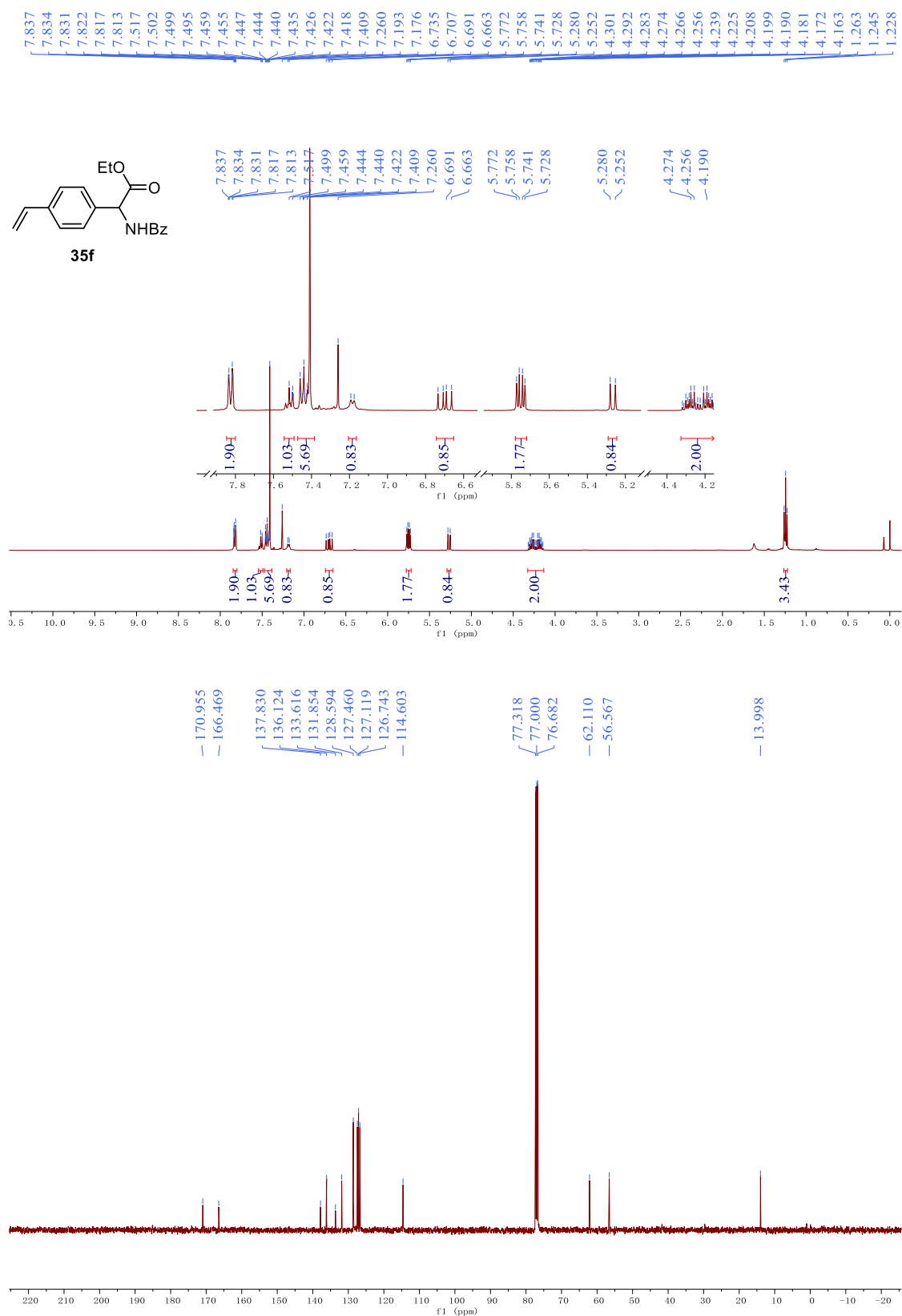


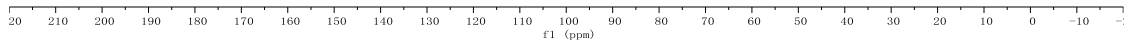
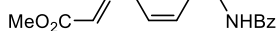


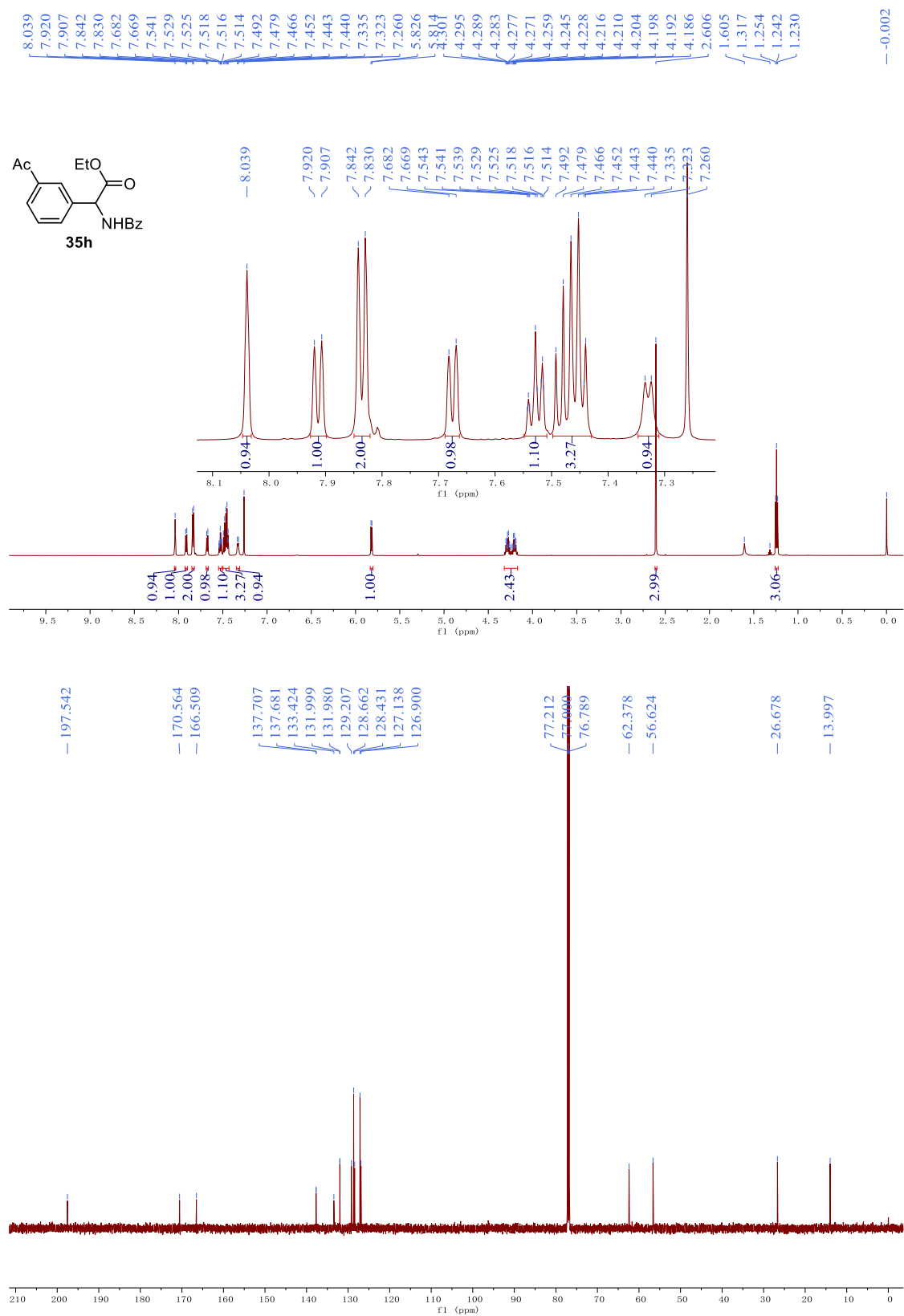


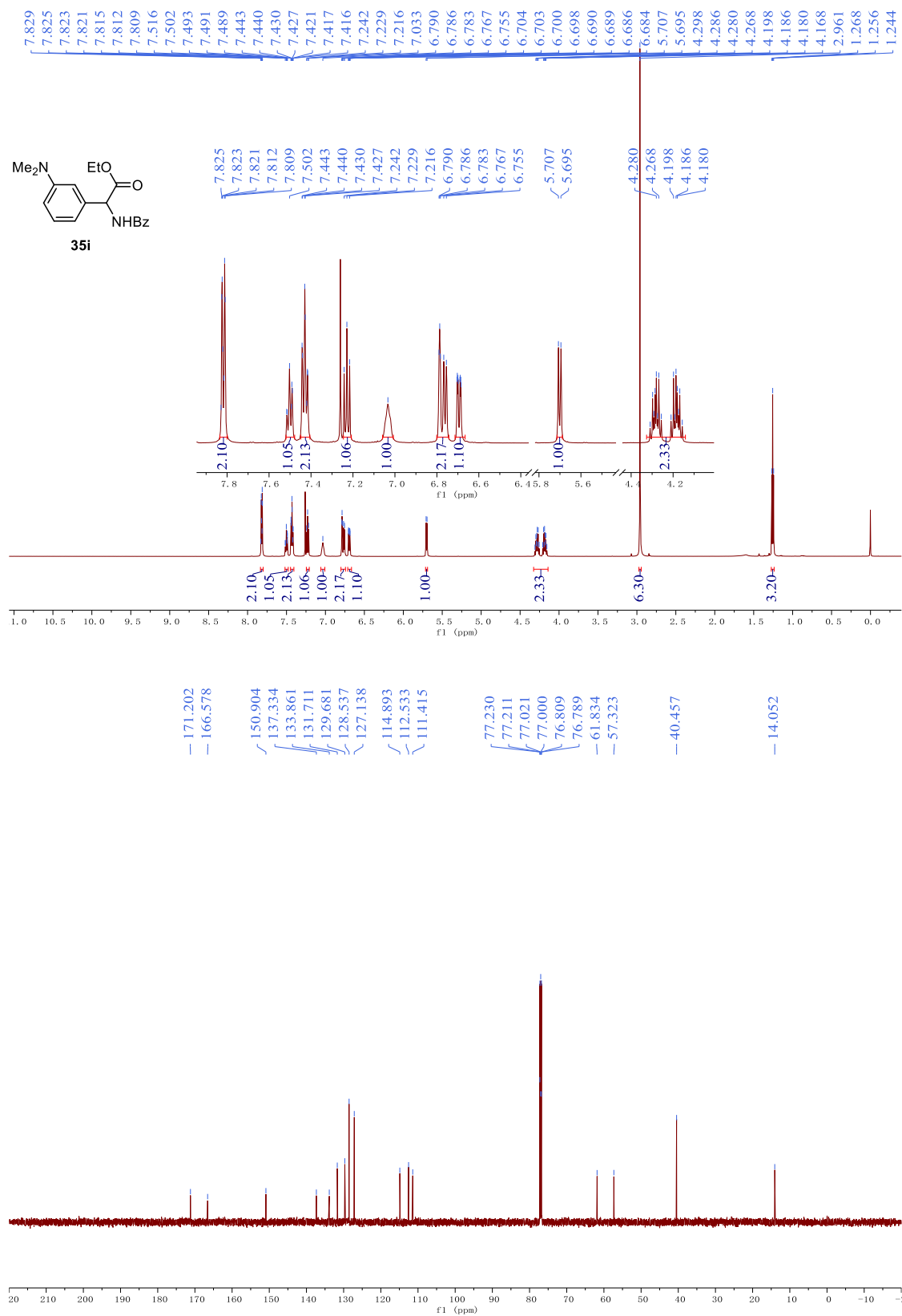


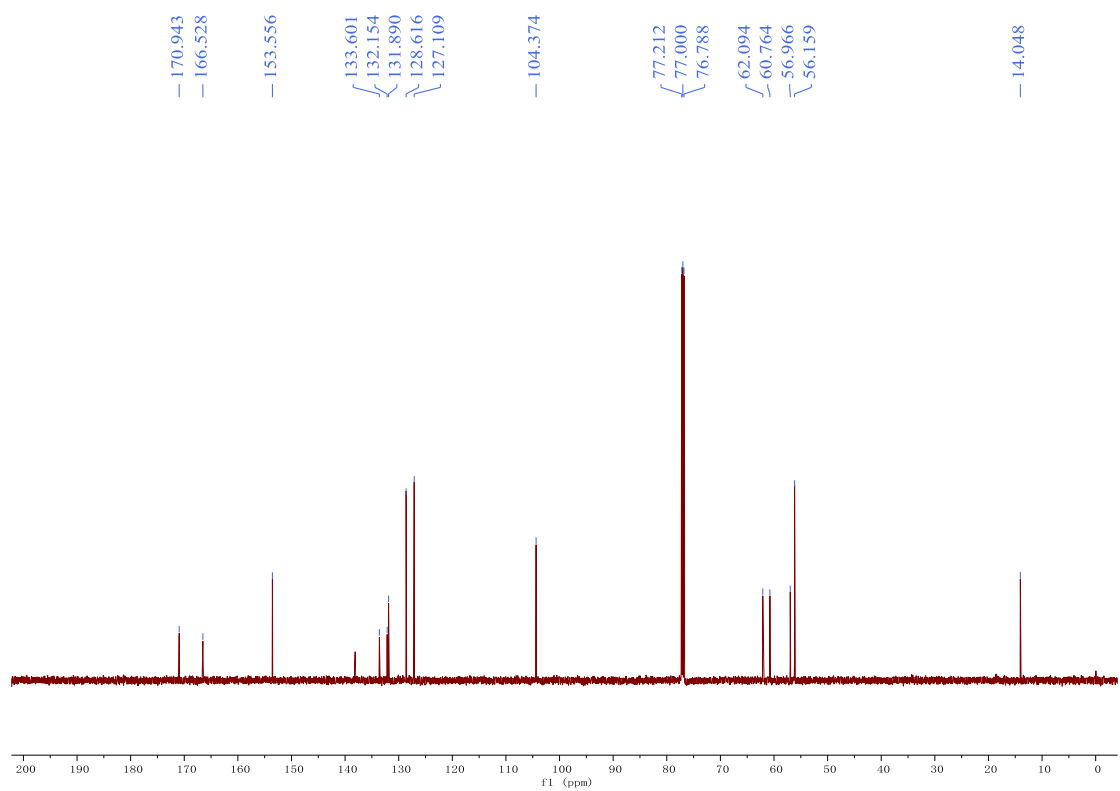
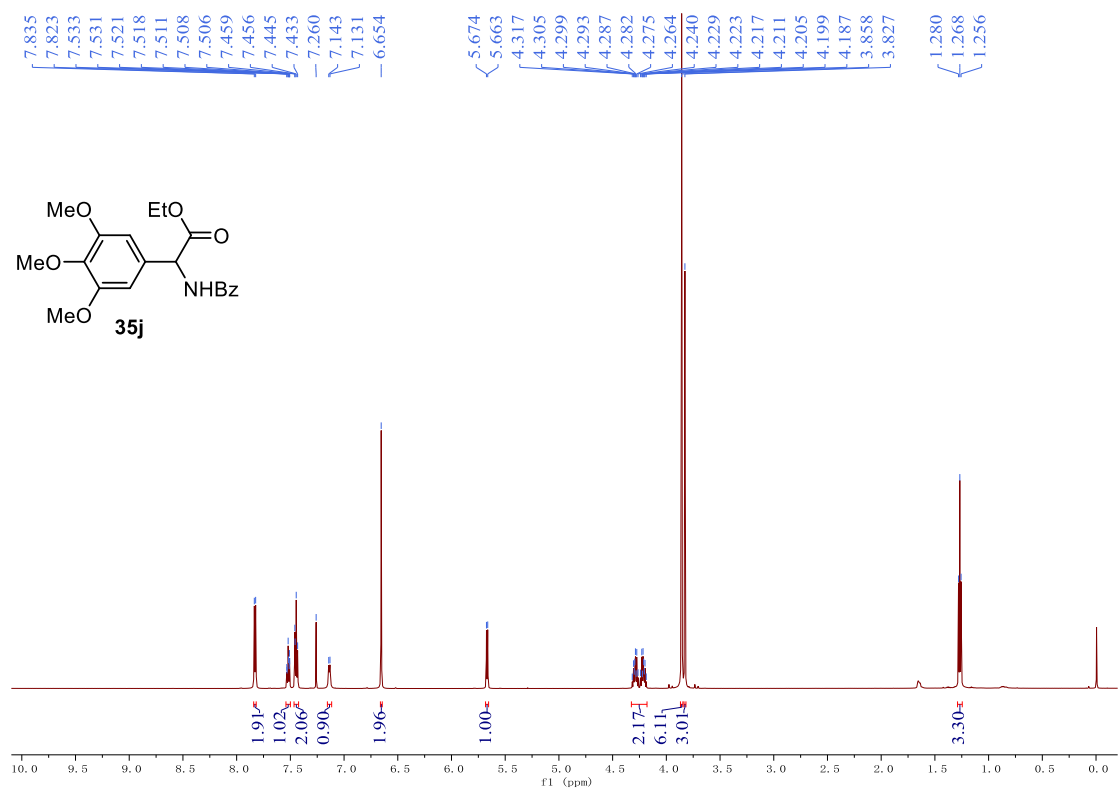


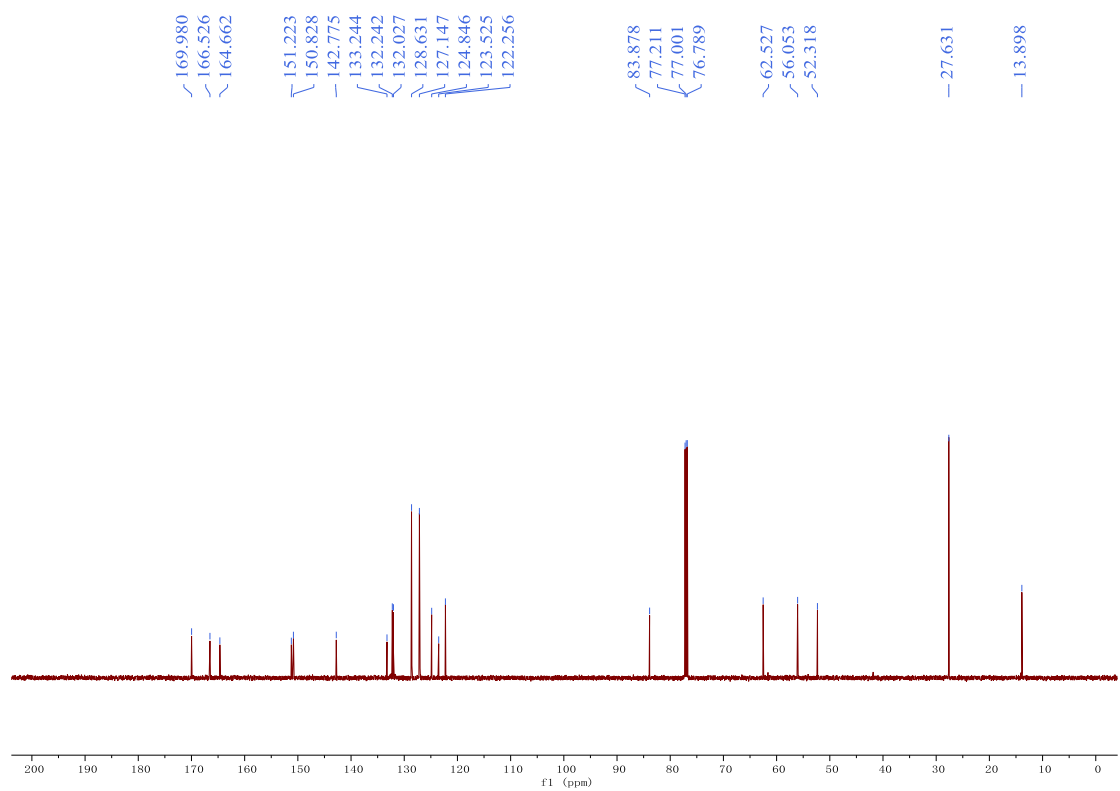
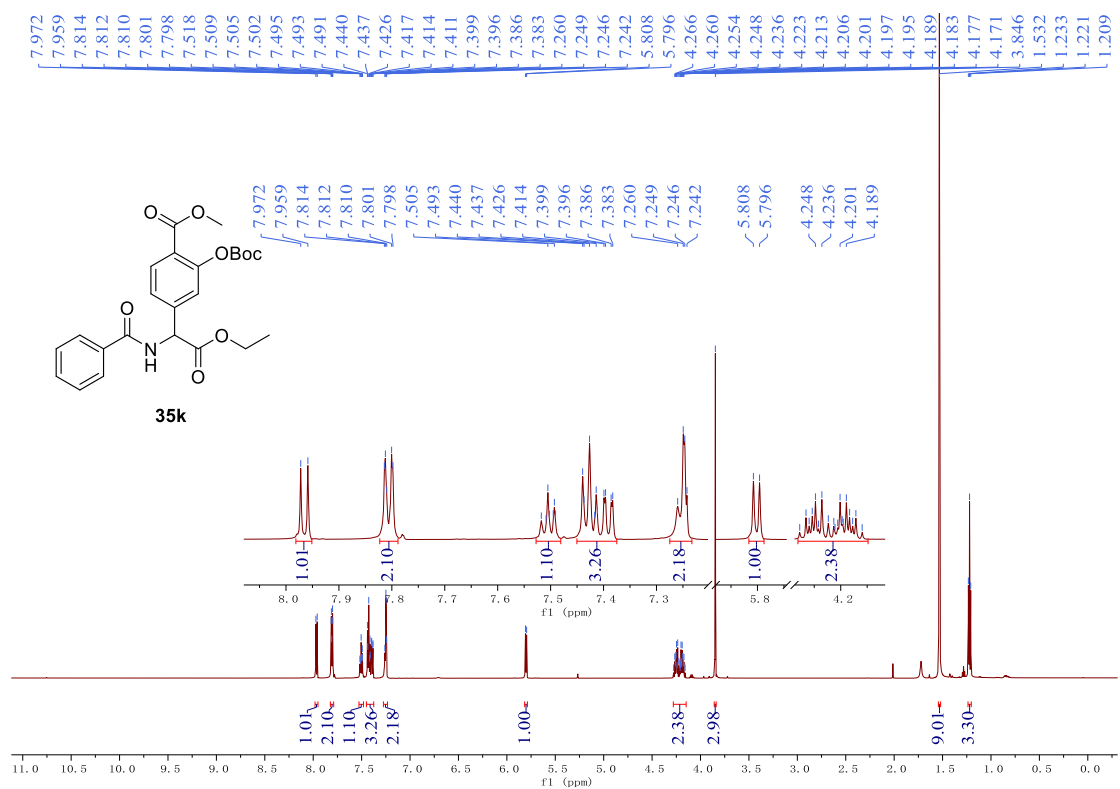


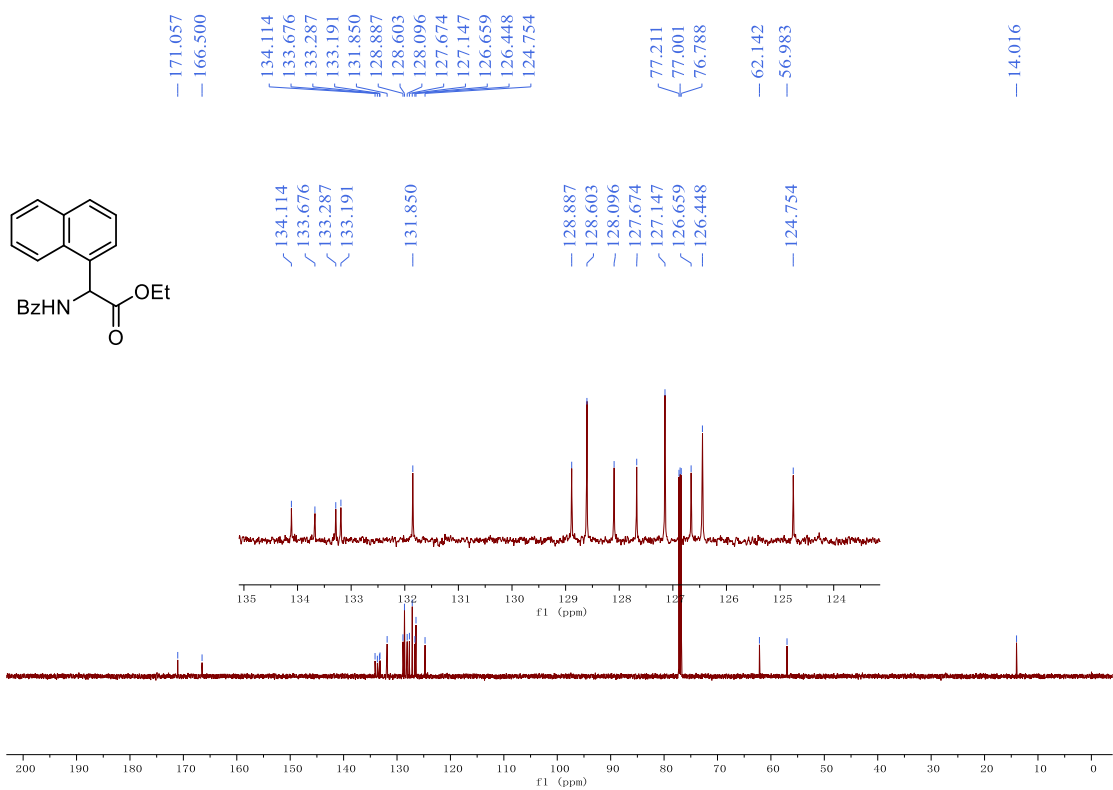
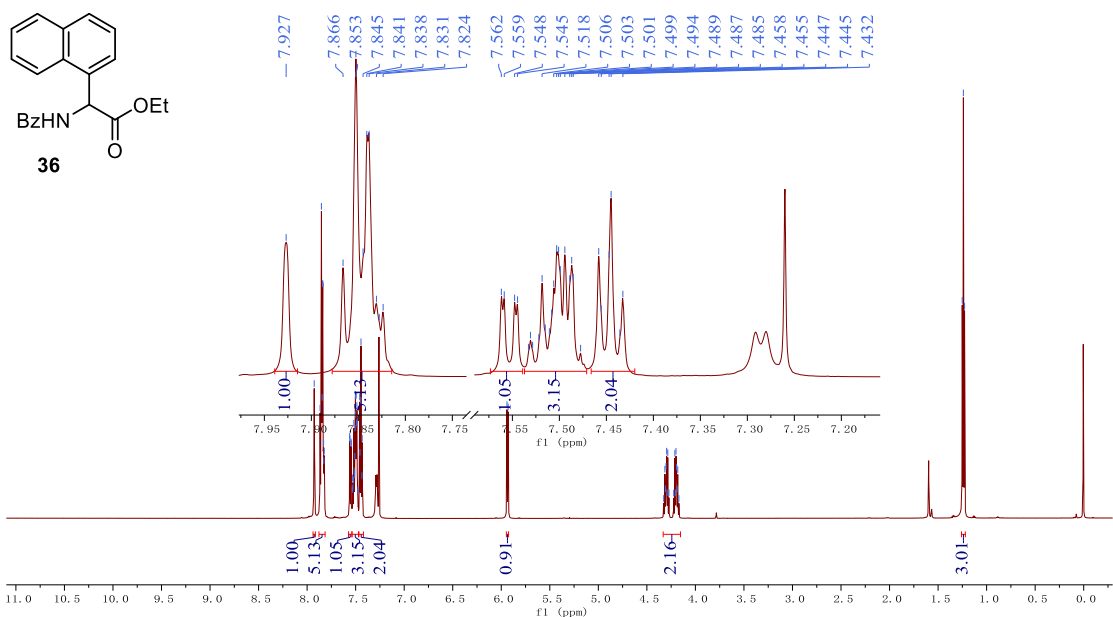


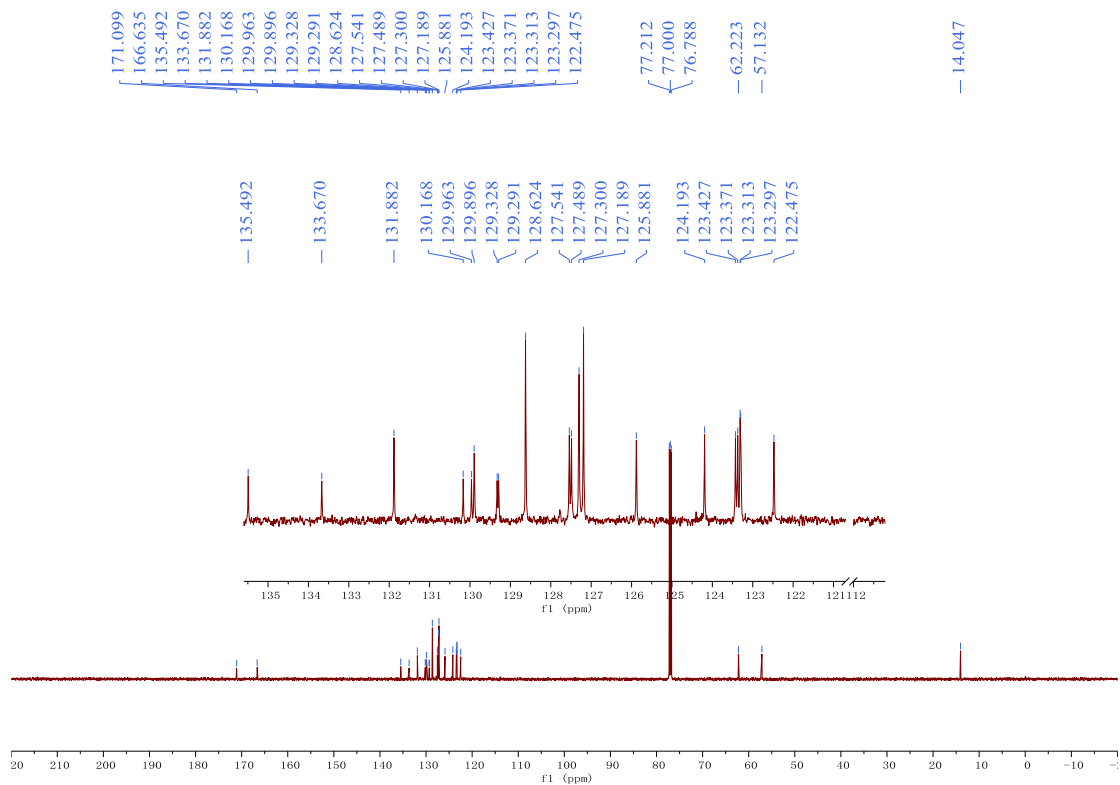
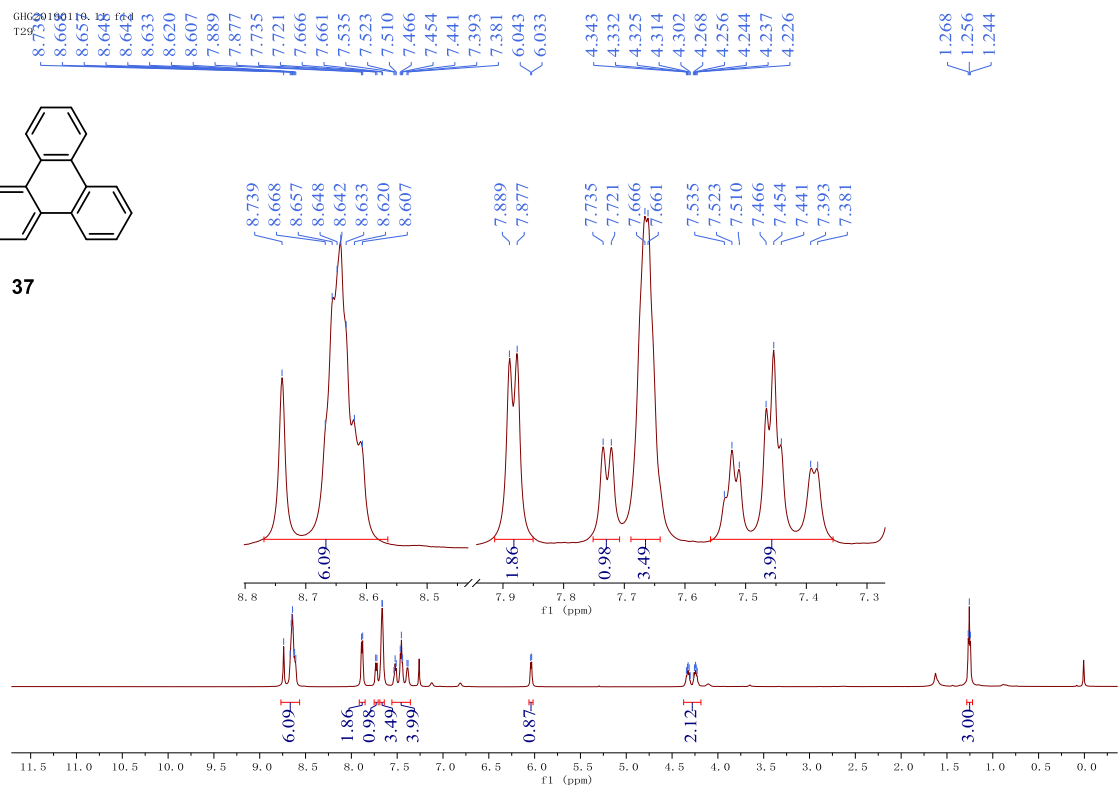
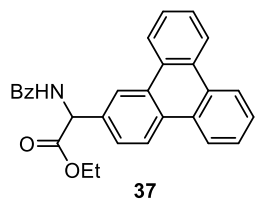


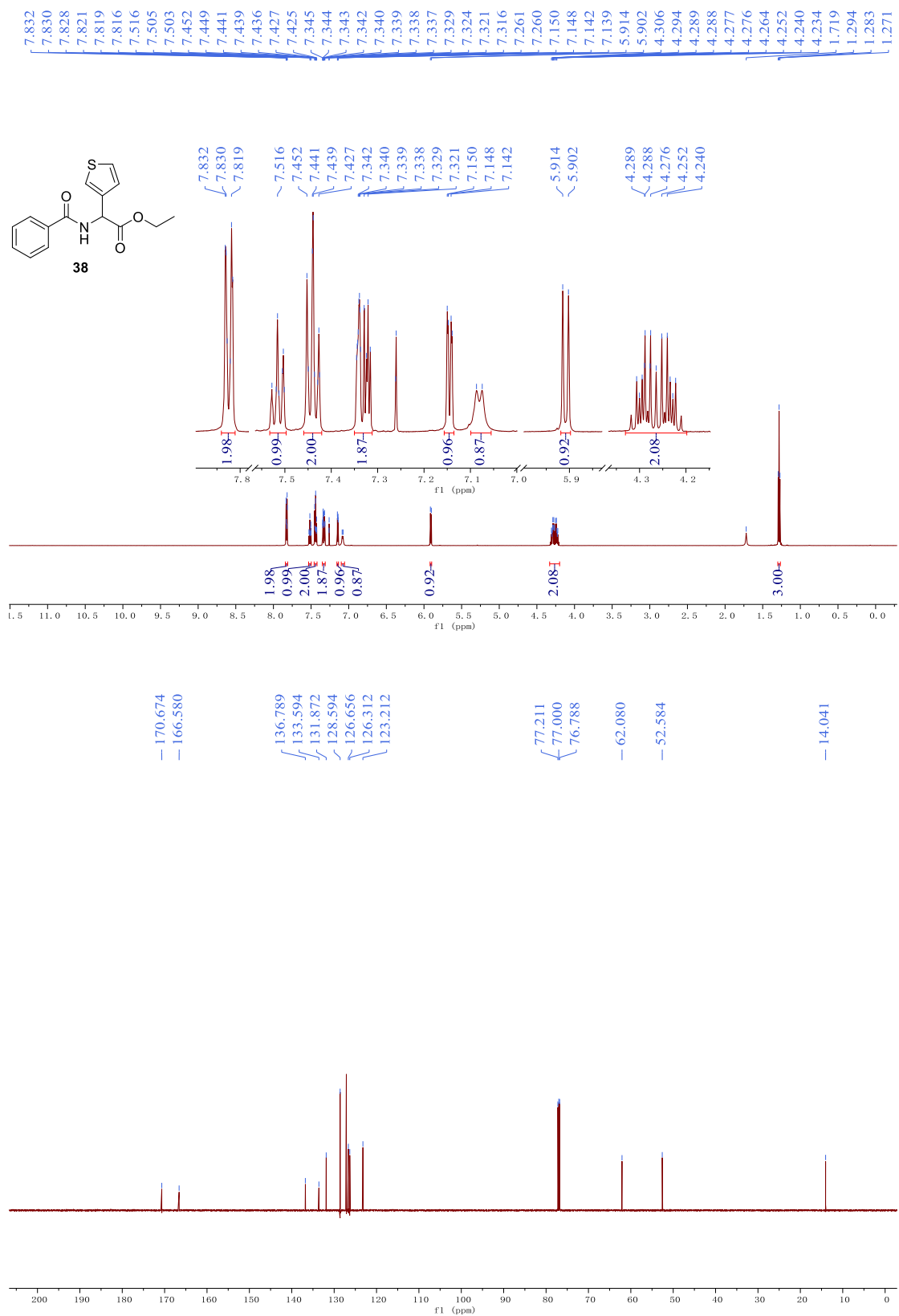


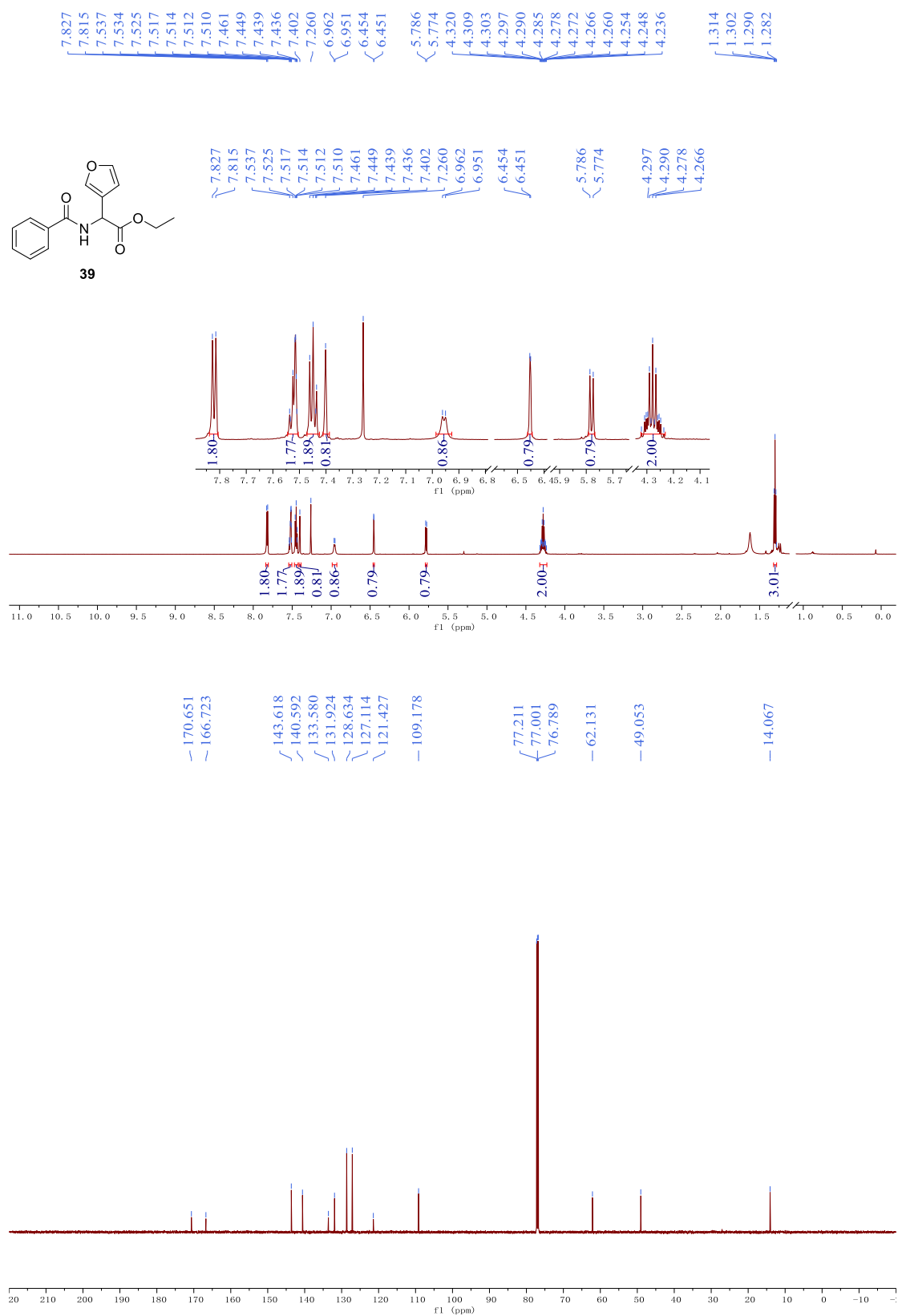


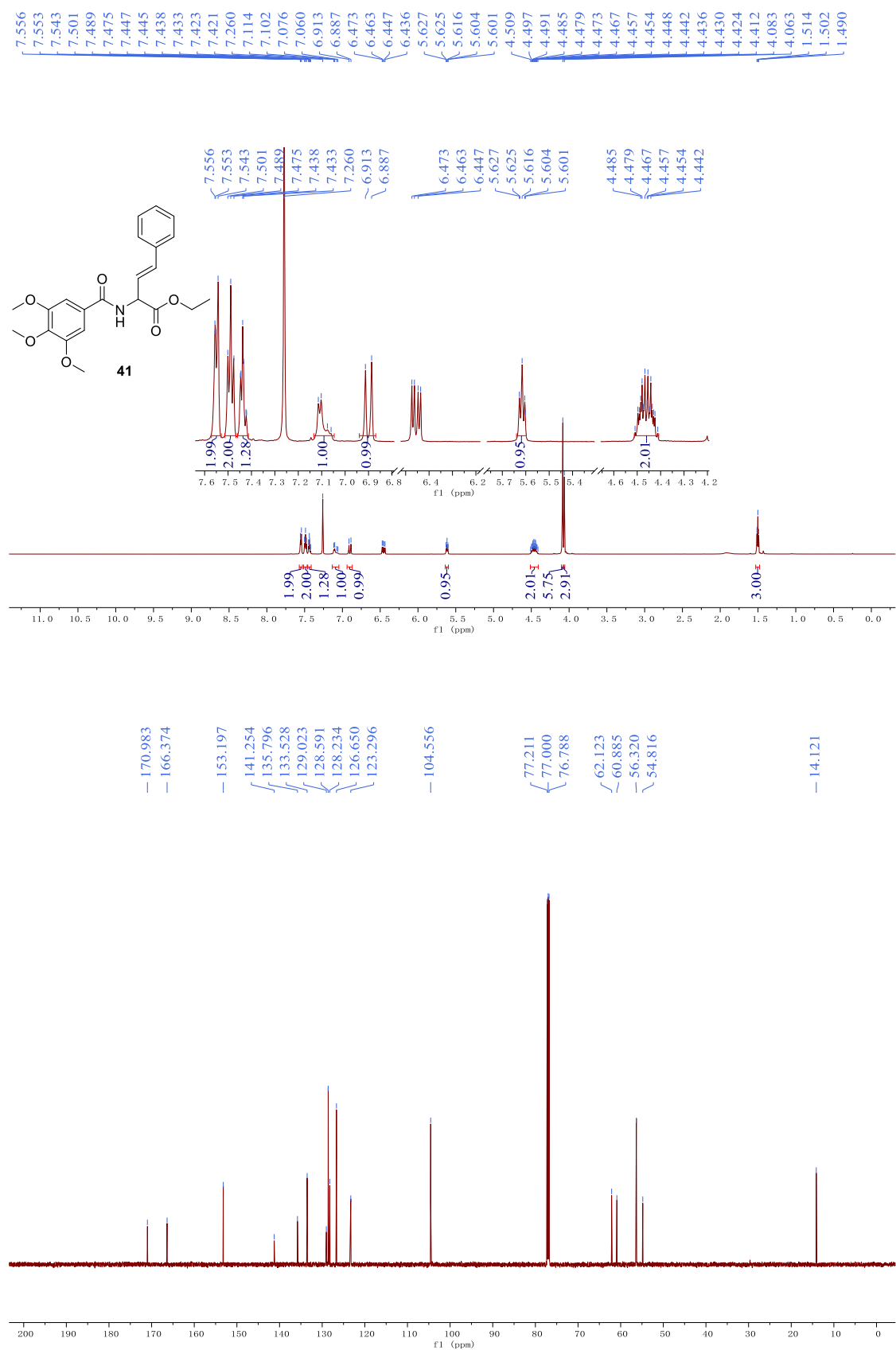


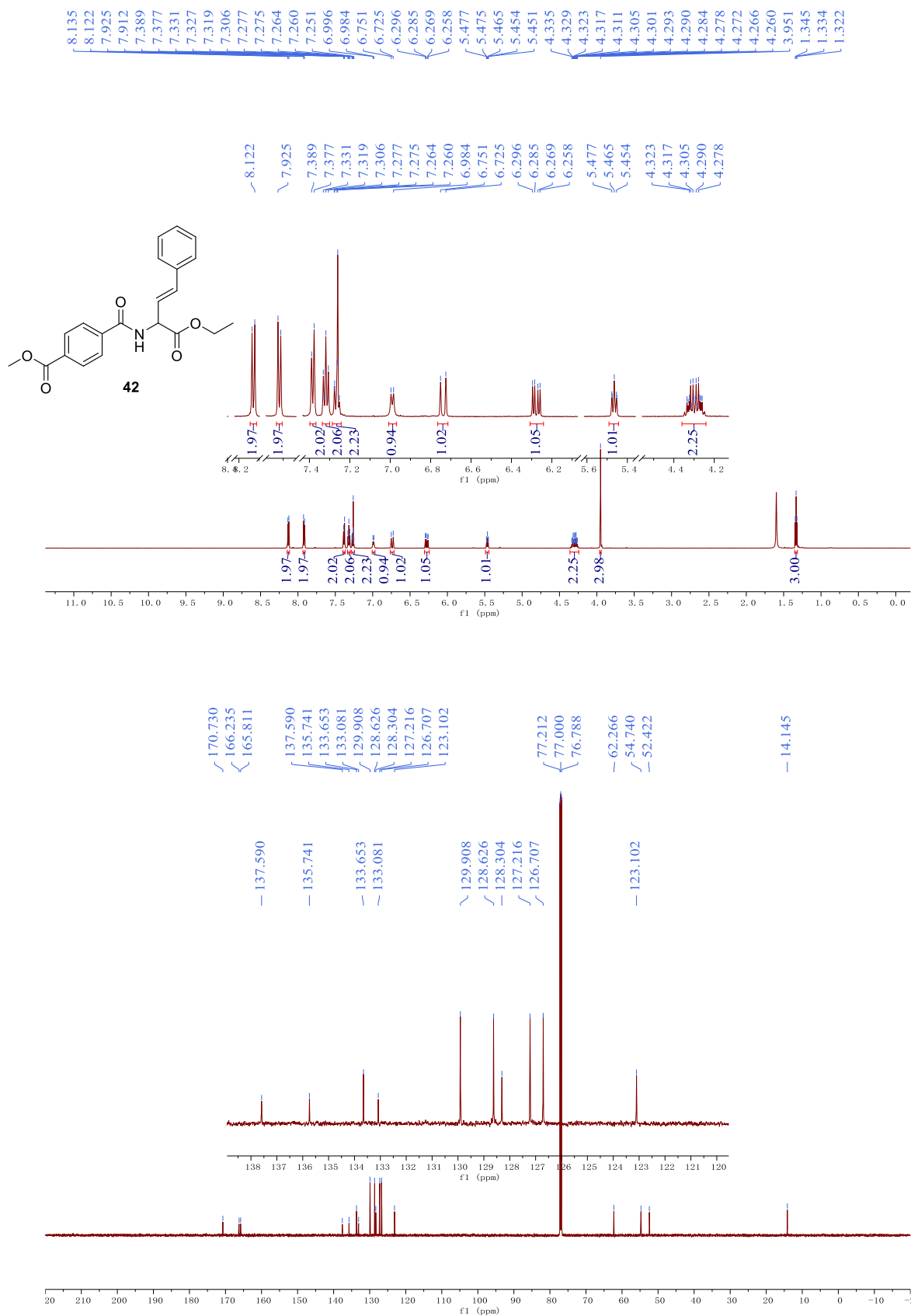


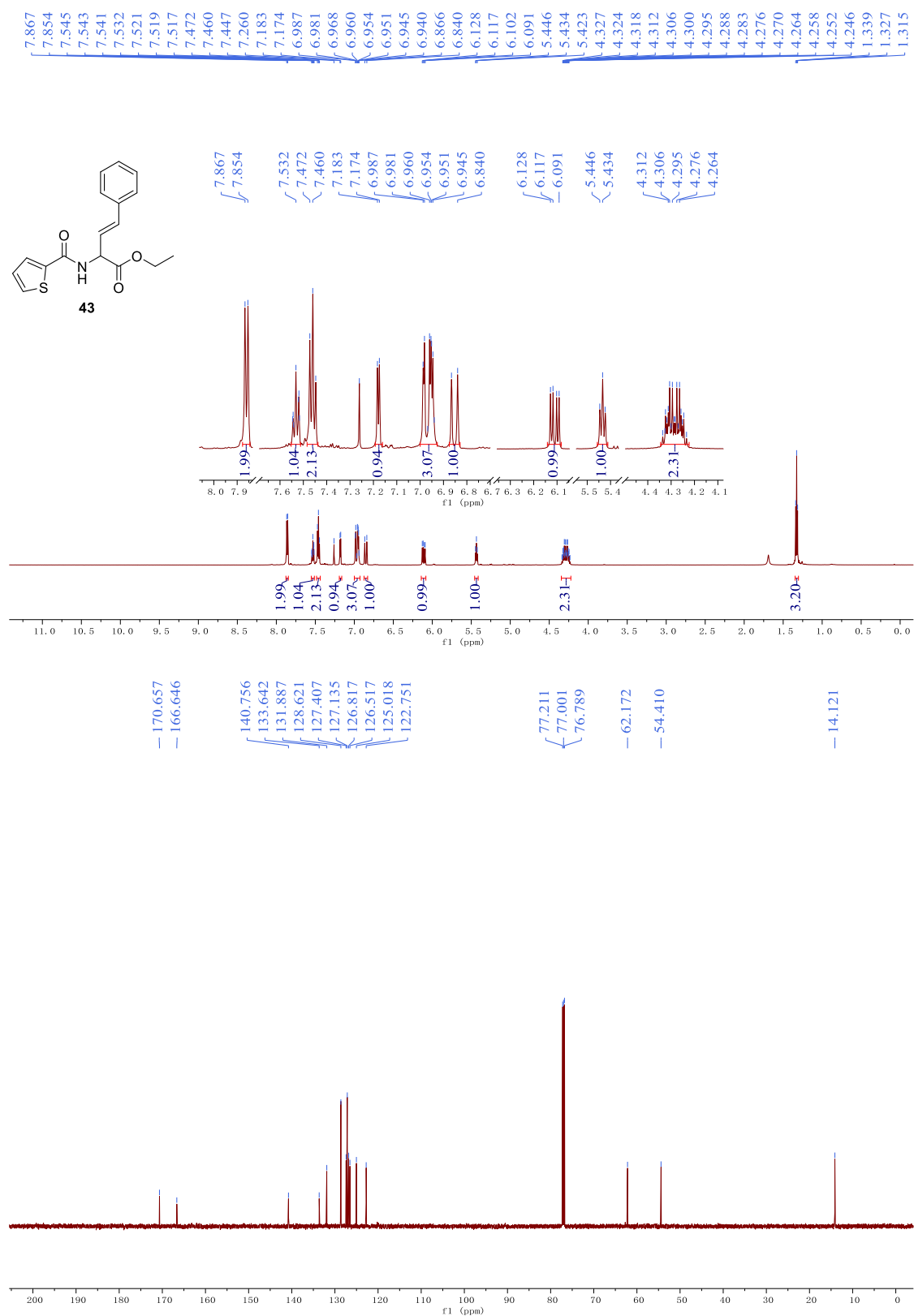


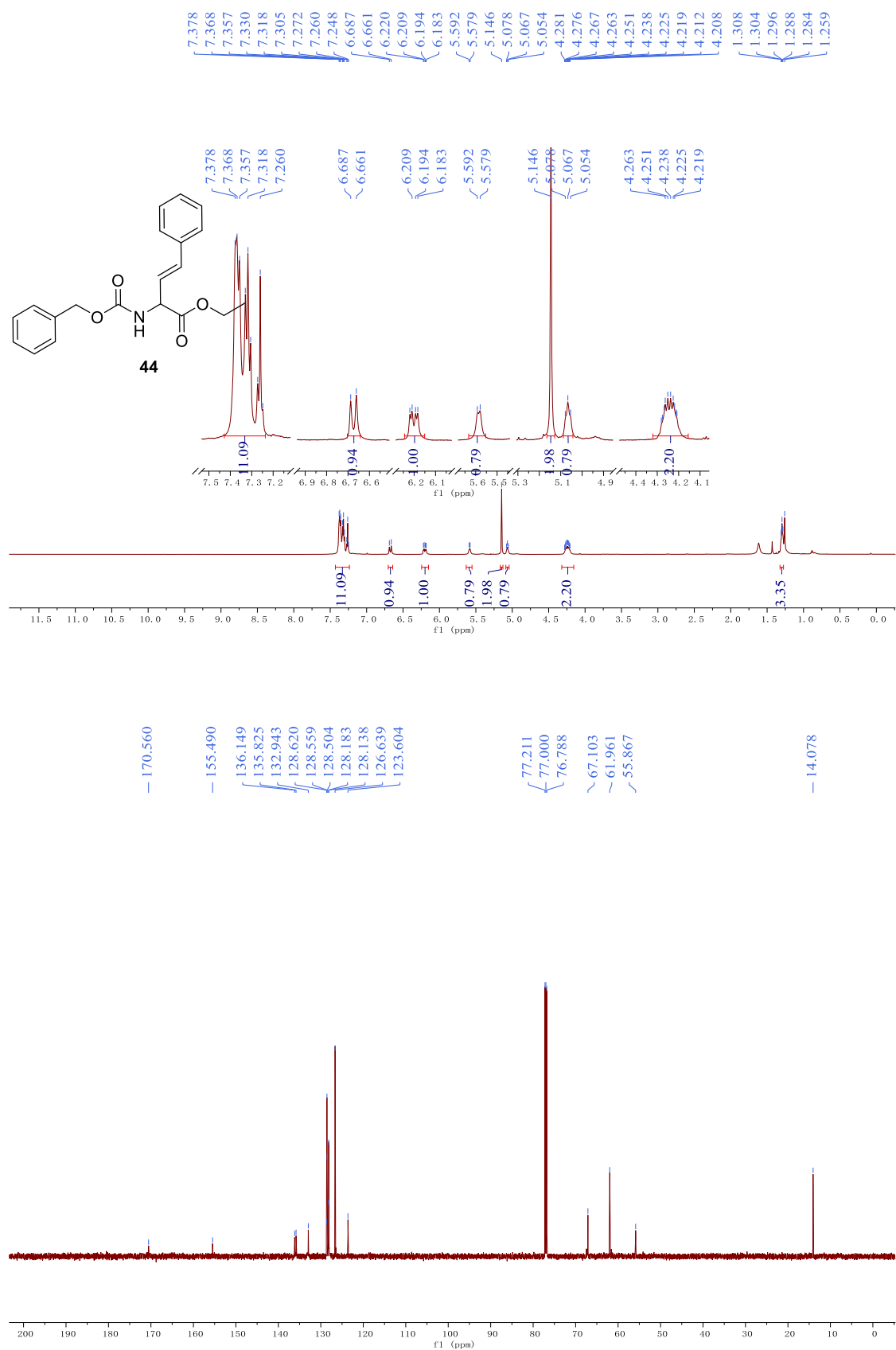


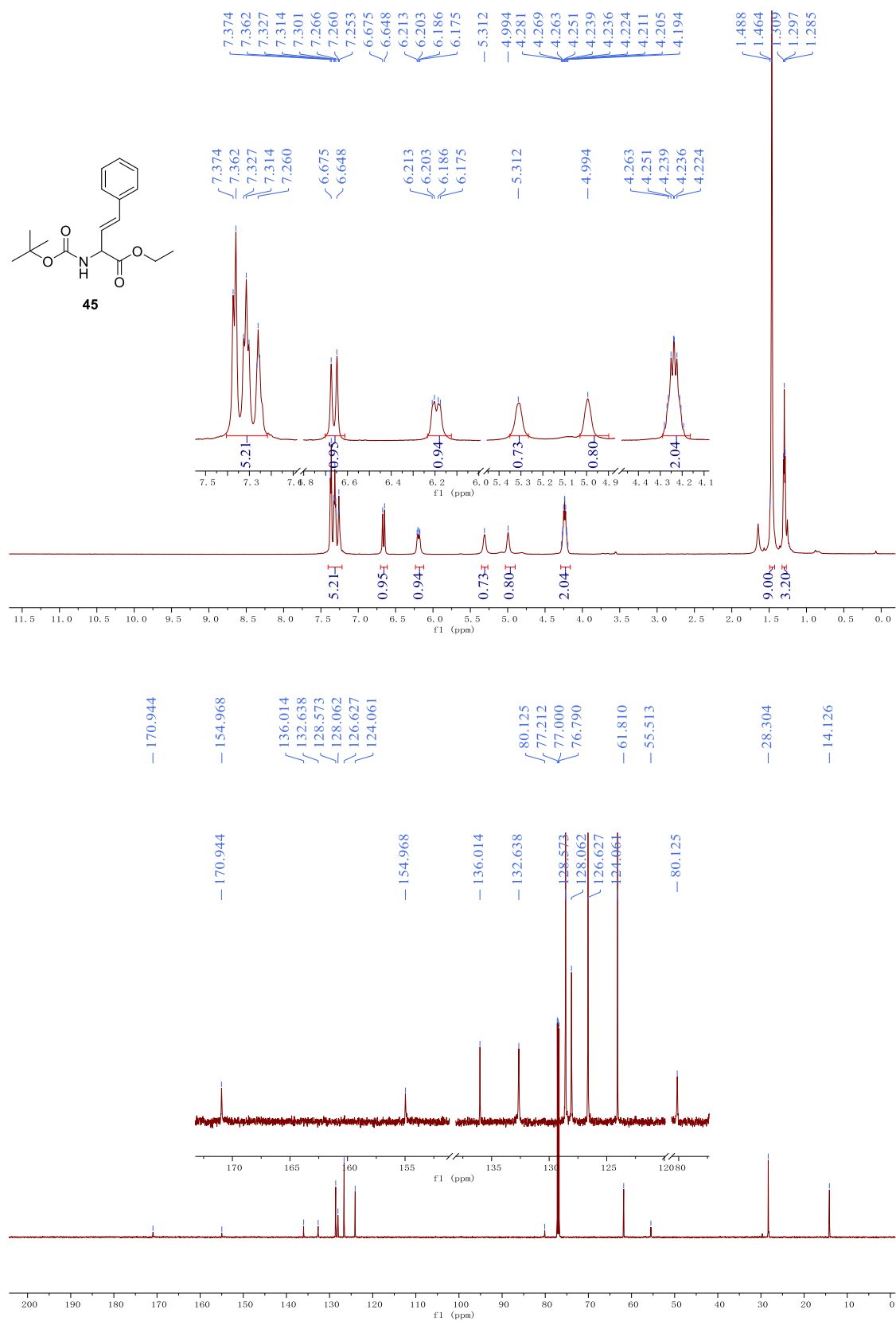


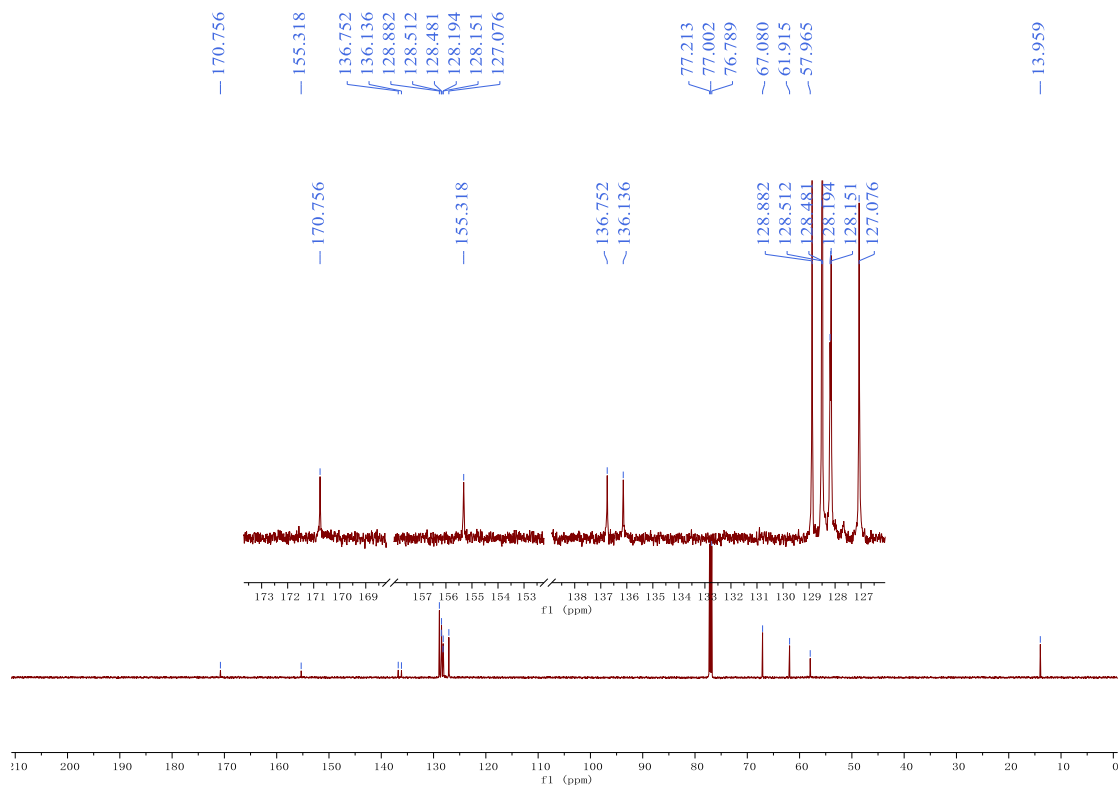
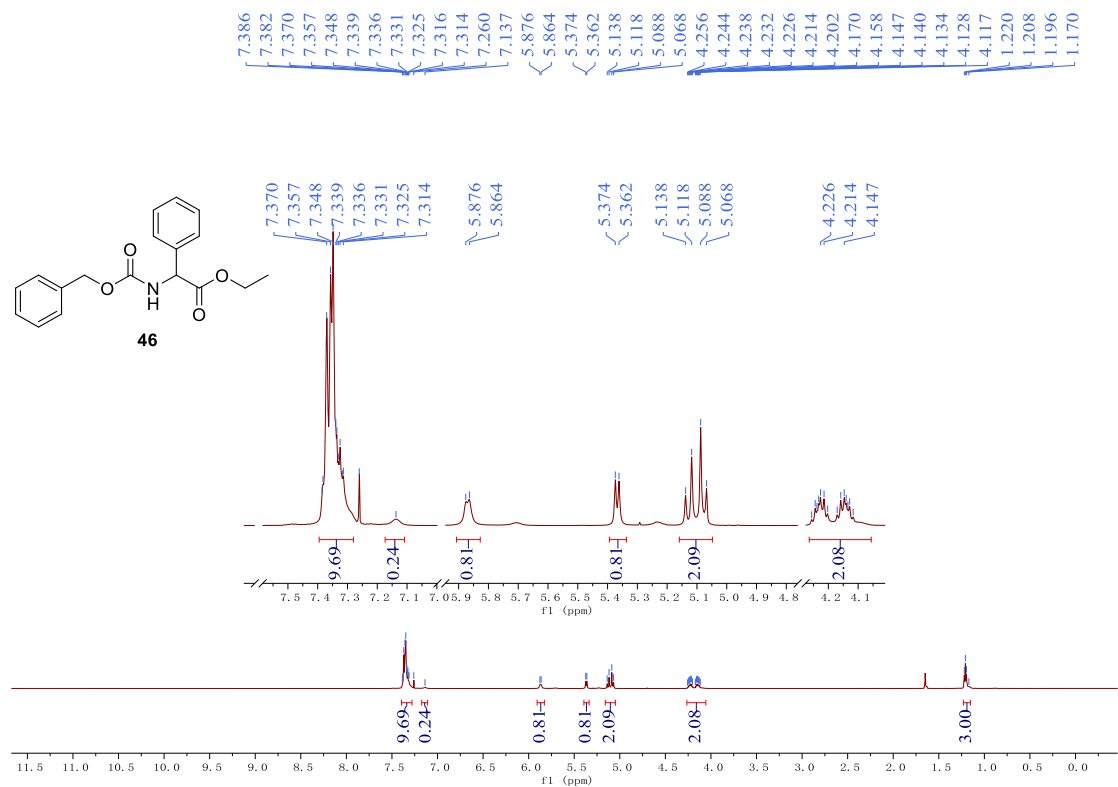
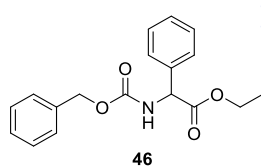


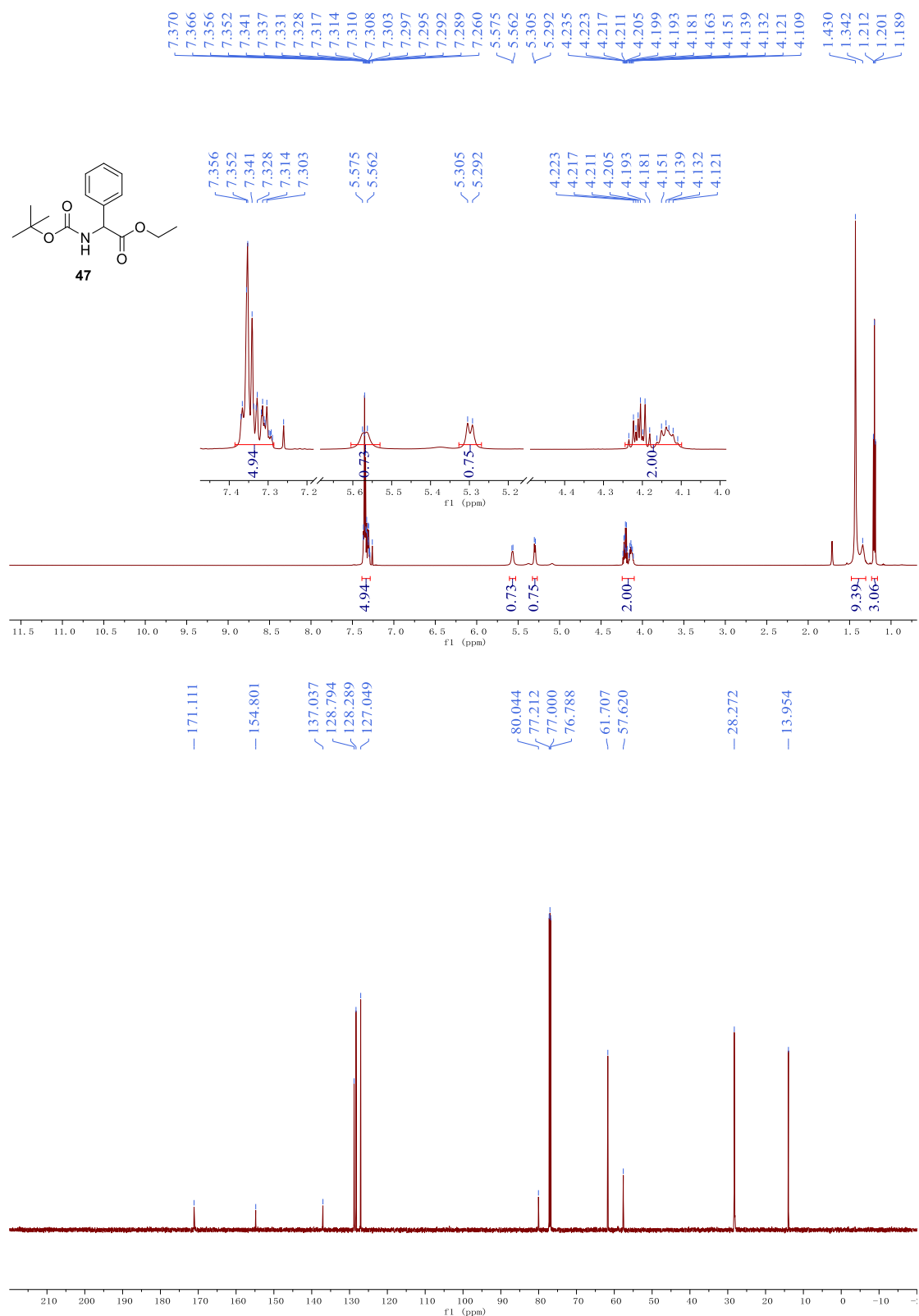


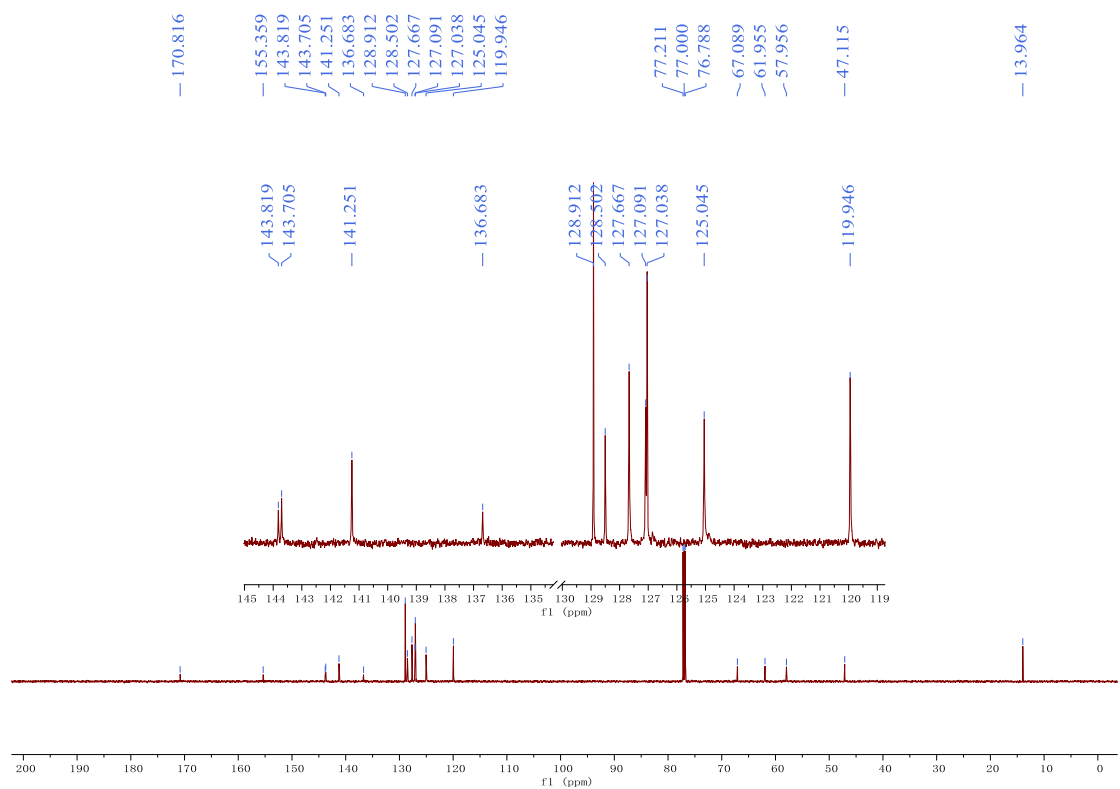
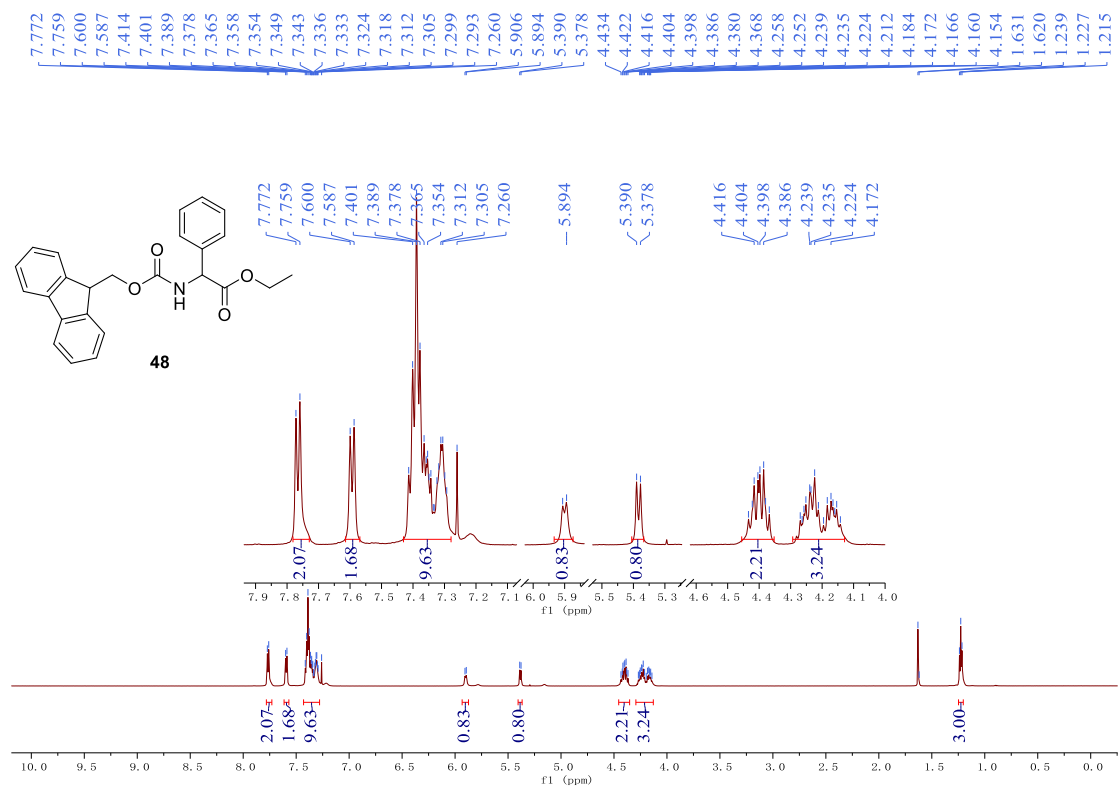


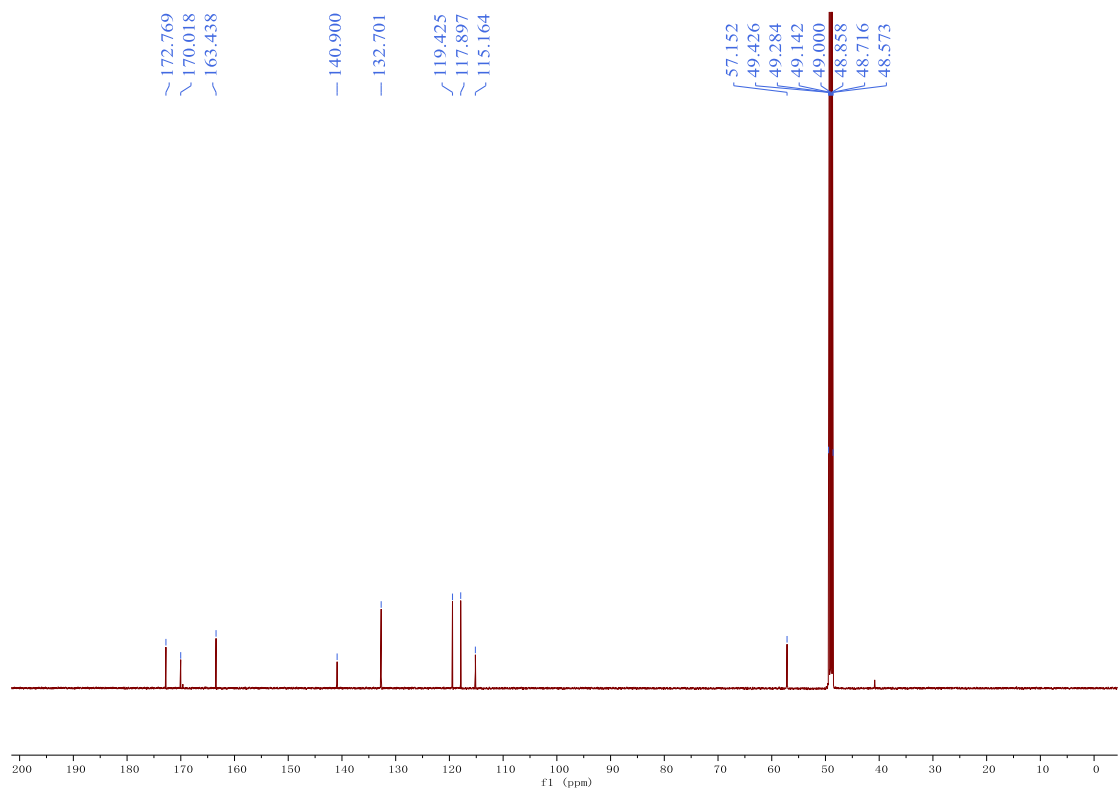
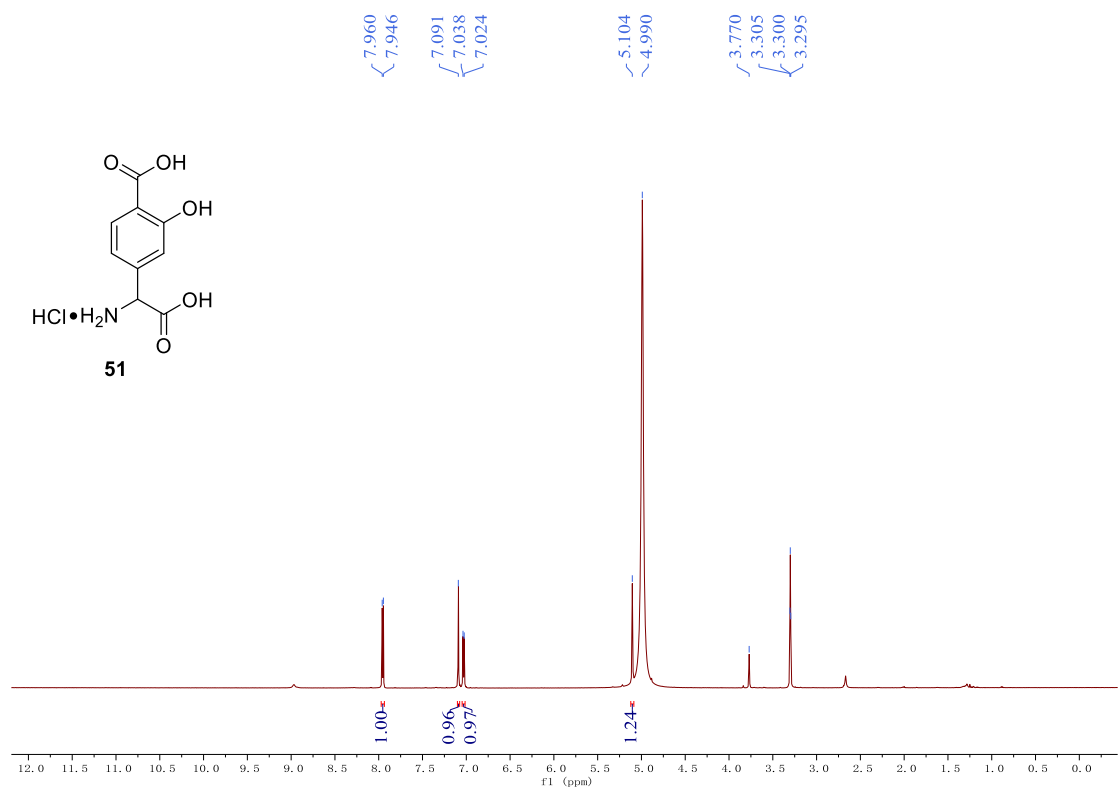


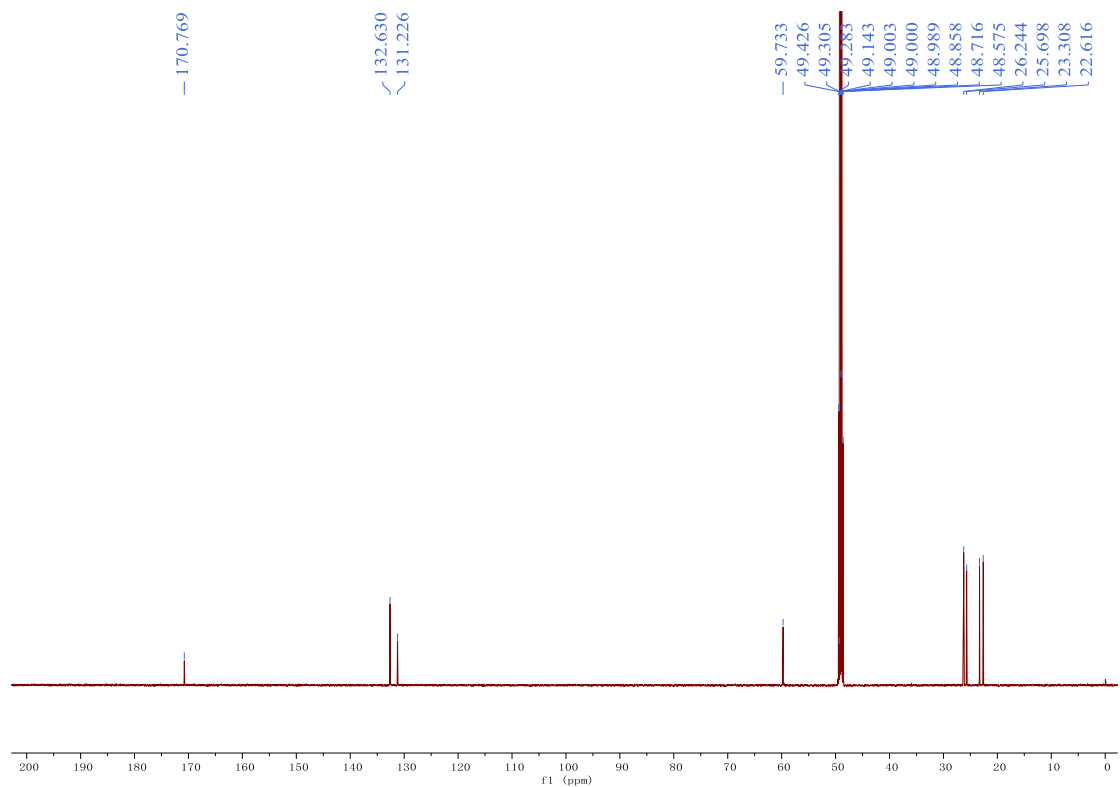
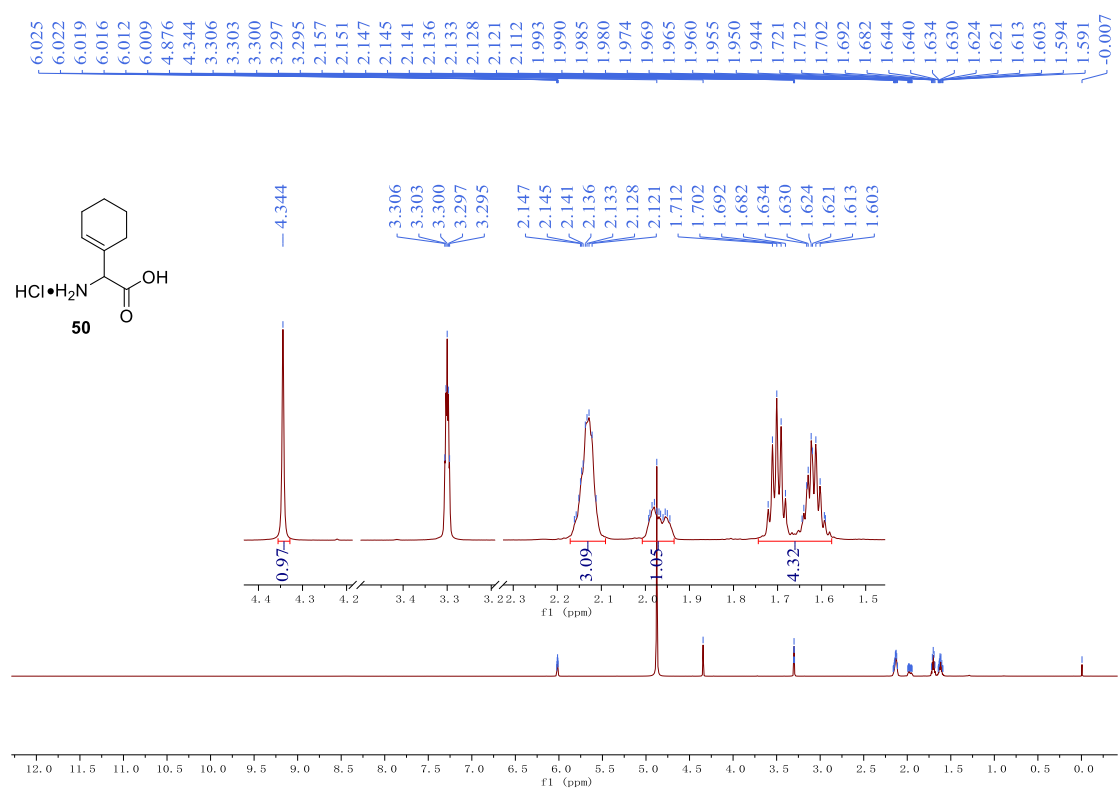












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