Supporting Information

Photocatalyst- and additive-free site-specific C(sp^3)-H hydrazination of glycine derivatives and peptides

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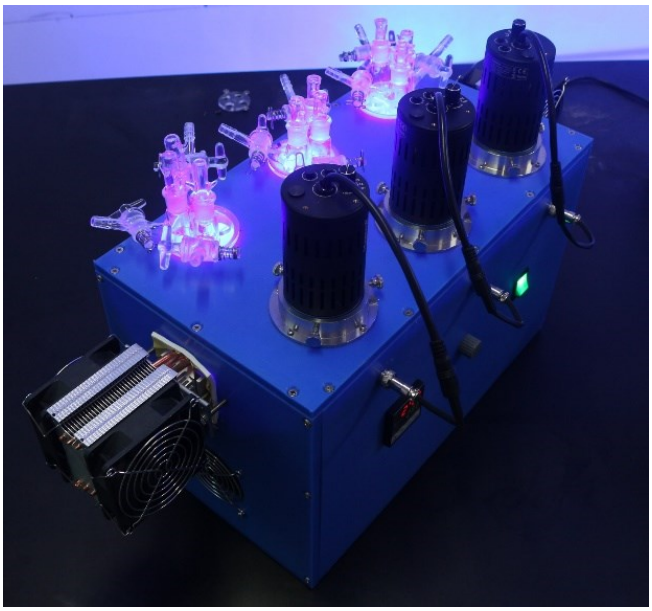
1. General Information

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity≥99.9%) unless otherwise mentioned. Commercial reagents were purchased from Adamas, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Büchi rotary evaporator. The blue LED lamps were purchased from Kessil company (PR160–390 nm, 427 nm, 440 nm, 456 nm, 467 nm). The Photo Reaction Setup was purchased from Anhui kemi machinery technology Co., Ltd.



Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H-NMR data are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. UV-Vis spectrum was measured by UV-

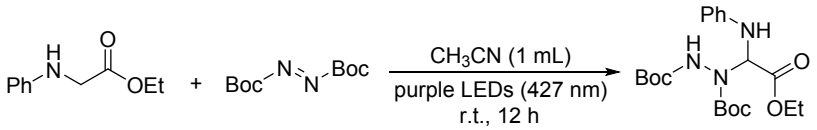
3600. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. Preparation of Substrates

Esters, amides of N-aryl-substituted glycine[1] and N-aryl-substituted peptides[2] were all prepared according to the previous reports.

3. Investigation of the Key Reaction Parameters

Table S1 Study of parameters controlling the reaction (For ester substrates)



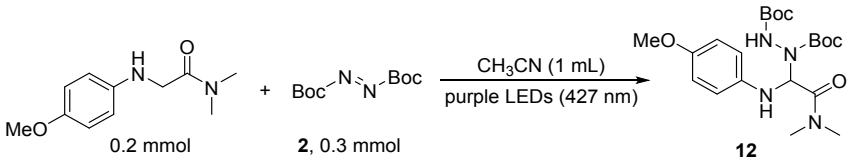
1, 0.2 mmol **2**, 0.3 mmol **3**

10 mmol scale, 95%, 3.885g

entry	variations from standard conditions	**3**, yield (%)[a]
1	**none**	**96**
2	DMF instead of CH_3CN	86
3	DMSO instead of CH_3CN	90
4	Acetone instead of CH_3CN	92
5	$PhCF_3$ instead of CH_3CN	96
6	THF instead of CH_3CN	76
7	MeOH instead of CH_3CN	82
8	DCM instead of CH_3CN	87
9	365 nm instead of 456 nm	82
10	390 nm instead of 456 nm	92
11	440 nm instead of 456 nm	95
12	456 nm instead of 456 nm	92
13	467 nm instead of 456 nm	90
14	520 nm instead of 456 nm	56
15	**2**, (0.24 mmol)	88
16	H_2O (2 equiv)	96
17	In the air	51
18	In dark	12

[a]Reaction condition: **1** (0.2 mmol), **2** (0.3 mmol) in CH_3CN (1 mL), irradiation by 40 W purple LEDs (427 nm) at room temperature for 12 h under argon atmosphere. Isolated yield.

Table S2 Study of parameters controlling the reaction (For amide substrates)



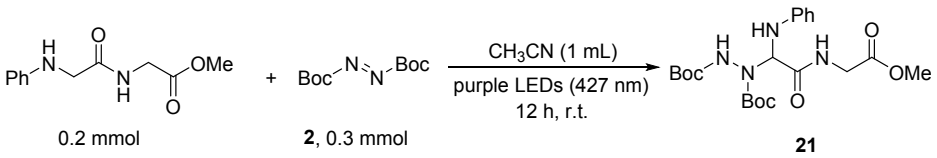
0.2 mmol **2**, 0.3 mmol **12**

entry	variations from standard conditions	**12**, yield (%)[a]
1	none	44
2	DMF instead of CH_3CN	51
3	DMSO instead of CH_3CN	36
4	Acetone instead of CH_3CN	55
5	$PhCF_3$ instead of CH_3CN	82
6	Toluene instead of CH_3CN	**80**
7	THF instead of CH_3CN	33
8	**$PhCF_3$ instead of CH_3CN**	**86**[b]

[a]Reaction condition: N,N-dimethyl-2-(p-tolylamino)acetamide (0.2 mmol), **2** (0.3 mmol) in CH_3CN (1 mL),

irradiation by 40 W purple LEDs (427 nm) at room temperature for 12 h under argon atmosphere. Isolated yield. [b]**2** (0.4 mmol).

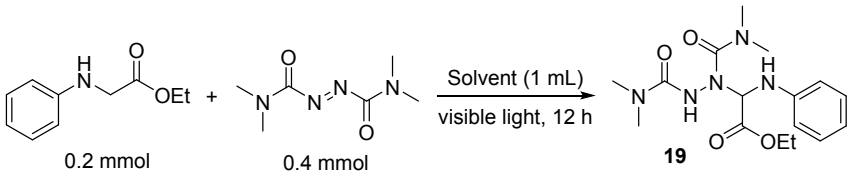
Table S3 Study of parameters controlling the reaction (For peptide substrates)



entry	variations from standard conditions	**21**, yield (%)[a]
1	none	15
2	DMF instead of CH_3CN	n.r.
3	DMSO instead of CH_3CN	n.r.
4	Acetone instead of CH_3CN	trace
5	$PhCF_3$ instead of CH_3CN	trace
6	THF instead of CH_3CN	trace
7	MeOH instead of CH_3CN	n.r.
8	DCM instead of CH_3CN	28
9	$CHCl_3$ instead of CH_3CN	52
10	DCE instead of CH_3CN	71
11	**DCE instead of CH_3CN**	**82[b]**

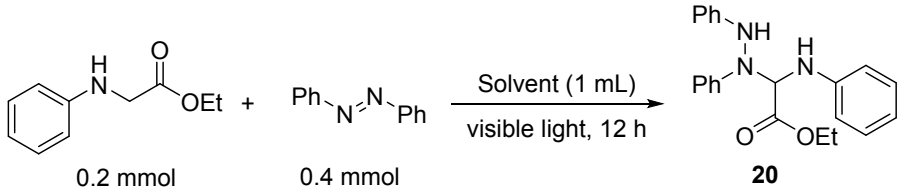
[a]Reaction condition: Dipeptide (0.2 mmol), **2** (0.3 mmol) in CH_3CN (1 mL), irradiation by 40 W purple LEDs (427 nm) at room temperature for 12 h under argon atmosphere. Isolated yield. [b]**2** (0.4 mmol).

Table S4 Optimization condition of the substrate 19



	wavelength	**solvent**	**19**, yield
1	427 nm	CH_3CN	0
2	427 nm	$PhCF_3$	0
3	427 nm	DCM	0
4	427 nm	DMF	0
5	427 nm	DMSO	0
6	427 nm	MeOH	0
7	427 nm	Acetone	0
8	427 nm	CH_3NO_2	0
9	390 nm	CH_3CN	0
10	467 nm	CH_3CN	0

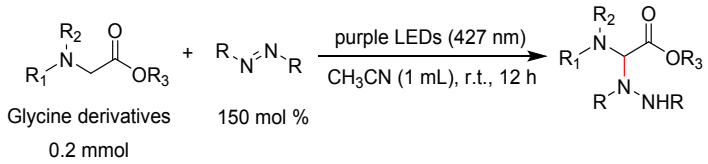
Table S5 Optimization condition of the substrate 20



	wavelength	solvent	**20**, yield
1	427 nm	CH_3CN	0
2	427 nm	$PhCF_3$	0
3	427 nm	DCM	0
4	427 nm	DMF	0
5	427 nm	DMSO	0
6	427 nm	MeOH	0
7	427 nm	Acetone	0
8	427 nm	CH_3NO_2	0
9	390 nm	CH_3CN	0
10	467 nm	CH_3CN	0

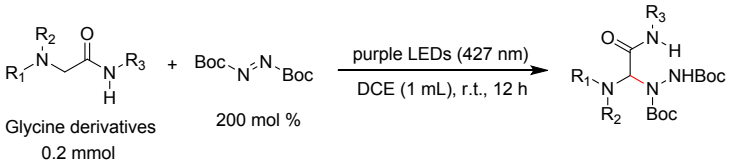
4. General Procedure and Spectral Data

4.1 General Procedure A



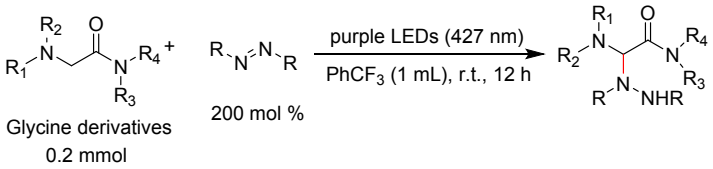
Glycine derivatives (0.2 mmol), azo compounds (150 mol %, 0.3 mmol) were placed in a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, anhydrous CH_3CN (1 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with purple LEDs (427 nm), maintained at approximately room temperature (28 ± 2 ^{o}C) by a desk fan in the air-conditioned room of 25 ^{o}C for 12 h. The mixture was then quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

4.2 General Procedure B



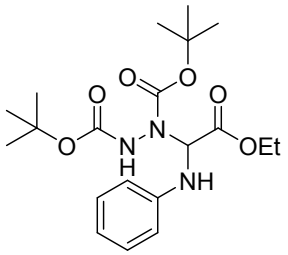
Glycine derivatives (0.2 mmol), azo compounds (200 mol %, 0.4 mmol) were placed in a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, anhydrous DCE (1 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with purple LEDs (427 nm), maintained at approximately room temperature (28 ± 2 ^{o}C) by a desk fan in the air-conditioned room of 25 ^{o}C for 12 h. The mixture was then quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

4.3 General Procedure C



Glycine derivatives (0.2 mmol), azo compounds (200 mol %, 0.4 mmol) were placed in a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, anhydrous $PhCF_3$ (1 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with purple LEDs (427 nm), maintained at approximately room temperature (28 ± 2 ^{o}C) by a desk fan in the air-conditioned room of 25 ^{o}C for 12 h. The mixture was then quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

4.4 Spectral Data

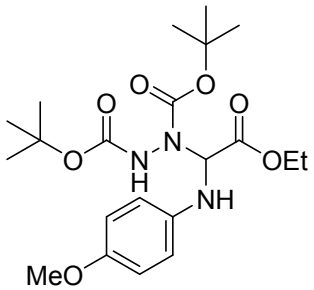


di-tert-butyl-1-(2-ethoxy-2-oxo-1-(phenylamino)ethyl)hydrazine-1,2-dicarboxylate (3): Following the general procedure A, obtained in 96% yield as a pale yellow viscous liquid (78.5 mg, eluent: petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 6.79 – 6.76 (m, 3H), 6.11 (m, 2H), 4.27 (s, 2H), 1.80 – 1.19 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 154.5, 143.9, 129.3, 119.0, 113.8, 82.1, 81.3, 67.4, 62.4, 28.1, 27.8, 14.0.

HRMS (ESI) calcd for $C_{20}H_{32}N_3O_6^+$[M+H]$^+$: 410.2286, found: 410.2289.

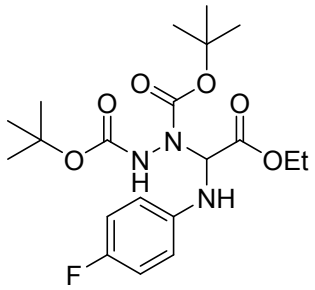


di-tert-butyl-1-(2-ethoxy-1-((4-methoxyphenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (4): Following the general procedure A, obtained in 89% yield as a pale yellow viscous liquid (78.1 mg, eluent: petroleum ether/ ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 – 6.66 (m, 4H), 6.30 – 5.79 (m, 2H), 4.18 (d, J = 7.0 Hz, 2H), 3.67 (s, 3H), 1.50 – 1.32 (m, 18H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 154.6, 153.2, 137.8, 115.2, 114.9, 82.1, 81.2, 65.9, 62.2, 55.7, 28.1, 27.9, 14.0.

HRMS (ESI) calcd for $C_{21}H_{34}N_3O_7^+$[M+H]$^+$: 440.2391, found: 440.2394.

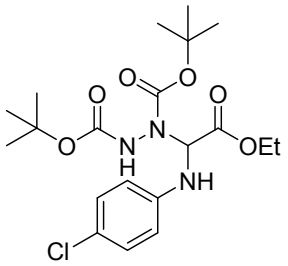


di-tert-butyl-1-(2-ethoxy-1-((4-fluorophenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (5): Following the general procedure A, obtained in 96% yield as a pale yellow viscous liquid (82.0 mg, eluent: petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, J = 8.6 Hz, 2H), 6.71 (s, 2H), 6.14 – 5.93 (m, 2H), 4.25 – 4.21 (m, 2H), 1.60 – 1.30 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 156.7 (d, *J* = 236.9 Hz), 140.3, 123.4 (d, J = 8.7 Hz), 115.8 (d, J = 22.4 Hz), 114.9, 82.3, 81.4, 66.0, 62.4, 28.1, 27.9, 14.0.

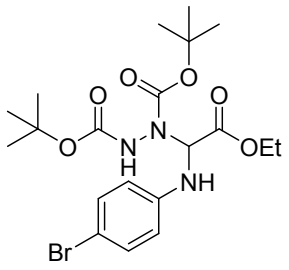
HRMS (ESI) calcd for $C_{20}H_{31}FN_3O_6^+[M+H]^+$: 428.2191, found: 428.2195.



di-tert-butyl-1-(1-((4-chlorophenyl)amino)-2-ethoxy-2-oxoethyl)hydrazine-1,2-dicarboxylate (6): Following the general procedure A, obtained in 92% yield as a pale viscous liquid (81.5 mg, eluent: petroleum ether/ethyl acetate = 5:1). (Ref. *Tetrahedron Letters,* **2016***, 57,* 2179)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 2H), 6.69 (d, J = 7.4 Hz, 2H), 6.15 – 5.93 (m, 2H), 4.29 – 4.21 (m, 2H), 1.61 – 1.19 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 154.5 142.7, 129.2, 123.8, 115.0, 82.4, 81.4, 65.2, 62.5, 28.1, 27.9, 14.1.

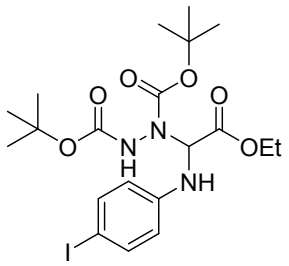


di-tert-butyl-1-(1-((4-bromophenyl)amino)-2-ethoxy-2-oxoethyl)hydrazine-1,2-dicarboxylate (7): Following the general procedure A, obtained in 88% yield as a pale viscous liquid (85.7 mg, eluent: petroleum ether/ ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 6.9 Hz, 2H), 6.29 – 5.79 (m, 2H), 4.37 – 4.13 (m, 2H), 1.51 – 1.32 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 154.5, 143.2, 132.0, 115.5, 111.0, 82.4, 81.4, 62.5, 60.3, 28.1, 27.9, 14.0.

HRMS (ESI) calcd for $C_{20}H_{31}BrN_3O_6^+[M+H]^+$: 488.1391, found: 488.1393.

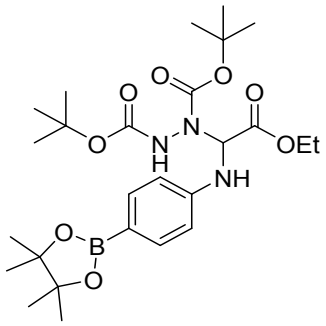


di-tert-butyl-1-(2-ethoxy-1-((4-iodophenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (8): Following the general procedure A, obtained in 90% yield as a pale viscous liquid (96.3 mg, eluent: petroleum ether/ ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 6.7 Hz, 2H), 6.04 (m, 2H), 4.29 – 4.20 (dd, J = 10.6, 7.0 Hz, 2H), 1.71 – 1.11 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 154.5, 143.5, 137.9, 123.2, 116.1, 82.4, 81.5, 67.4, 62.5, 28.1, 27.9, 14.0.

HRMS (ESI) calcd for $C_{20}H_{31}IN_3O_6^+[M+H]^+$: 536.1252, found: 536.3142.

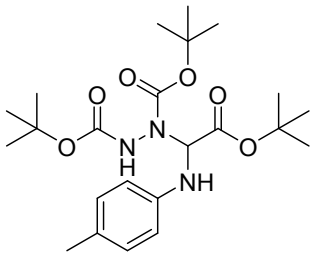


di-tert-butyl-1-(2-ethoxy-2-oxo-1-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)ethyl)hydrazine-1,2-dicarboxylate (9): Following the general procedure A, obtained in 71% yield as a pale viscous liquid (76.0 mg, eluent: petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.5 Hz, 2H), 6.73 (d, J = 8.1 Hz, 2H), 6.22 – 5.96 (d, J = 105.1 Hz, 2H), 4.30 – 4.21 (m, 2H), 1.58 – 1.27 (m, 33H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 182.5, 170.9, 136.4, 121.1, 113.0, 85.4, 83.3, 82.3, 62.4, 59.8, 28.1, 27.9, 24.8, 14.0.

HRMS (ESI) calcd for $C_{26}H_{43}BN_3O_8^+$[M+H]$^+$: 536.3138, found: 536.3142.

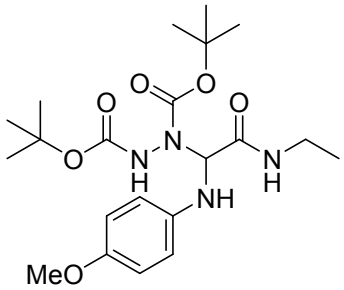


di-tert-butyl-1-(2-(tert-butoxy)-2-oxo-1-(p-tolylamino)ethyl)hydrazine-1,2-dicarboxylate (10): Following the general procedure A, obtained in 72% yield as a pale yellow oil (64.9 mg, eluent: petroleum ether/ ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 8.2 Hz, 2H), 6.66 (d, J = 7.9 Hz, 2H), 6.16 – 5.67 (m, 2H), 2.23 (s, 3H), 1.62 – 1.31 (m, 27H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 155.7, 129.8, 121.5, 119.6, 113.9, 83.1, 82.1, 81.5, 60.4, 28.2, 28.1, 27.8, 20.4.

HRMS (ESI) calcd for $C_{23}H_{38}N_3O_6^+$[M+H]$^+$: 452.2755, found: 452.2759.

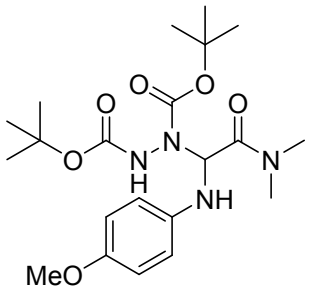


di-tert-butyl-1-(2-(ethylamino)-1-((4-methoxyphenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (11): Following the general procedure B, obtained in 65% yield as a pale viscous liquid (58.6 mg, eluent: petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.29 (s, 2H), 6.93 (d, J = 8.9 Hz, 1H), 6.95 – 6.67 (m, 1H), 6.34 – 5.64 (m, 2H), 3.90 – 3.70 (m, 3H), 3.51 – 3.22 (m, 2H), 1.47 (s, 18H), 1.25 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 160.0, 155.7, 150.9, 140.6, 123.3, 114.6, 82.6, 81.5, 55.7, 55.5, 34.1, 28.2, 28.1, 14.8.

HRMS (ESI) calcd for $C_{21}H_{35}N_4O_6^+$[M+H]$^+$: 439.2551, found: 439.2546.

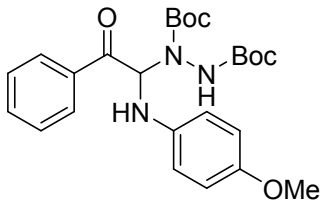


di-tert-butyl-1-(2-(dimethylamino)-1-((4-methoxyphenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (12): Following the general procedure C, obtained in 86% yield as a pale yellow solid (75.3 mg, eluent: petroleum ether/ ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (s, 4H), 6.77 – 6.27 (m, 2H), 3.74 (s, 3H), 3.21 (s, 3H), 2.95 (s, 3H), 1.52 – 1.33 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 154.7, 154.3, 152.7, 138.0, 115.3, 114.9, 81.9, 80.9, 63.4, 55.7, 36.8, 36.3, 28.1, 28.0.

HRMS (ESI) calcd for $C_{21}H_{35}N_4O_6^+$[M+H]$^+$: 439.2551, found: 439.2556.

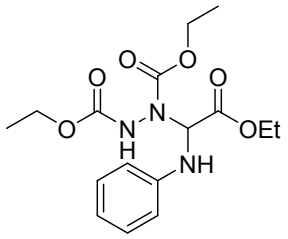


di-tert-butyl-1-(1-((4-methoxyphenyl)amino)-2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (13): Following the general procedure C, obtained in 62% yield as a pale yellow solid (78.3 mg, eluent: petroleum ether/ ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 7.94 (m, 2H), 7.67 – 7.45 (m, 3H), 6.98 – 6.82 (m, 4H), 6.05 – 5.02 (m, 2H), 3.75 (s, 3H), 1.54 – 0.89 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 154.8, 133.9, 131.4, 130.6, 129.1, 128.6, 123.5, 121.5, 115.1, 82.3, 81.2, 64.7, 55.7, 28.2, 28.1.

HRMS (ESI) calcd for $C_{25}H_{34}IN_3O_6^+[M+H]^+$: 472.2442, found: 472.2448.

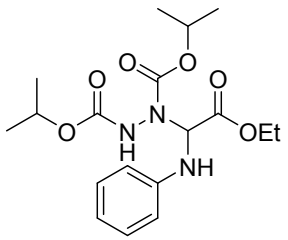


diethyl 1-(2-ethoxy-2-oxo-1-(phenylamino)ethyl)hydrazine-1,2-dicarboxylate (16): Following the general procedure A, obtained in 96% yield as a pale yellow viscous liquid (67.8 mg, eluent: petroleum ether/ ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 7.3 Hz, 2H), 6.88 – 6.67 (m, 3H), 6.17 (m, 2H), 4.44 – 4.01 (m, 6H), 1.32 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 155.4, 143.5, 129.4, 119.3, 113.8, 68.1, 63.0, 62.5, 62.1, 14.4, 14.2, 14.1.

HRMS (ESI) calcd for $C_{16}H_{24}N_3O_6^+[M+H]^+$: 354.1660, found: 354.1594.

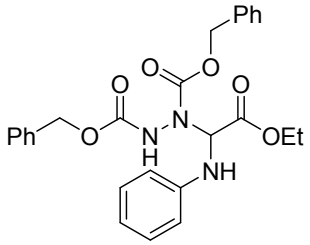


diisopropyl 1-(2-ethoxy-2-oxo-1-(phenylamino)ethyl)hydrazine-1,2-dicarboxylate (17): Following the general procedure A, obtained in 94% yield as a pale yellow viscous liquid (71.6 mg, eluent: petroleum ether/ ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 7.8 Hz, 2H), 6.86 – 6.67 (m, 3H), 6.19 (m, 2H), 4.95 (m, 2H), 4.40 – 4.18 (m, 2H), 1.50 – 0.9 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 155.1, 143.5, 129.3, 119.2, 113.8, 70.8, 69.9, 66.8, 62.4, 21.9, 21.6, 14.0.

HRMS (ESI) calcd for $C_{18}H_{28}N_3O_6^+$[M+H]$^+$: 382.1973, found: 382.1980.

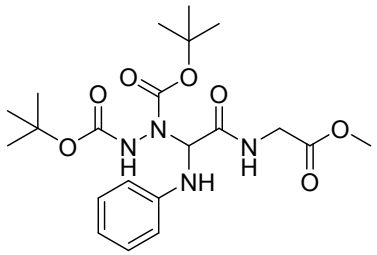


dibenzyl 1-(2-ethoxy-2-oxo-1-(phenylamino)ethyl)hydrazine-1,2-dicarboxylate (18): Following the general procedure A, obtained in 92% yield as a pale yellow viscous liquid (87.7 mg, eluent: petroleum ether/ ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.08 (m, 12H), 6.85 – 6.53 (m, 3H), 6.46 – 5.97 (m, 2H), 5.39 – 5.08 (m, 4H), 4.52 – 4.01 (m, 2H), 1.39 – 1.09 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 155.4, 143.3, 135.5, 135.4, 129.4, 128.5, 128.3, 128.1 119.5, 113.8, 68.4, 67.4, 65.7, 62.6, 14.0.

HRMS (ESI) calcd for $C_{26}H_{28}N_3O_6^+$[M+H]$^+$: 478.1973, found: 478.1976.



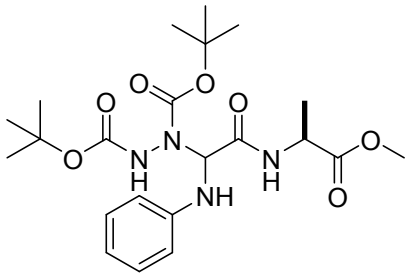
di-tert-butyl-1-(2-((2-methoxy-2-oxoethyl)amino)-2-oxo-1-(phenylamino)ethyl)hydrazine-1,2-dicarboxylate (21): Following the general procedure B, obtained in 82% yield as a pale yellow solid (74.1 mg, eluent: petroleum

ether/ ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 2H), 6.86 – 6.67 (m, 3H), 6.35 – 6.25 (m, 1H), 6.03 – 5.12 (m, 2H), 4.21 – 4.01 (m, 2H), 3.75 (s, 3H), 1.47 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 168.1, 155.7, 129.4, 125.4, 119.8, 113.9, 82.8, 81.5, 60.3, 52.2, 41.7, 28.2, 28.1.

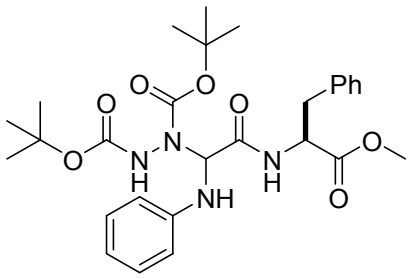
HRMS (ESI) calcd for $C_{21}H_{33}N_4O_7^+$[M+H]$^+$: 453.2344, found: 453.2351.



di-tert-butyl-1-(2-((1-methoxy-1-oxopropan-2-yl)amino)-2-oxo-1-(phenylamino)ethyl)hydrazine-1,2-dicarboxylate (22): Following the general procedure B, obtained in 78% yield as a pale yellow viscous liquid (72.7 mg, eluent: petroleum ether/ ethyl acetate = 2:1). (d.r. = 1.9:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 7.3 Hz, 2H), 6.81 – 6.60 (m, 3H), 6.60 – 6.25 (m, 1H), 5.92 – 5.35 (m, 2H), 4.66 – 4.43 (m, 1H), 3.75 (s, 3H), 1.47 (d, J = 2.1 Hz, 21H).

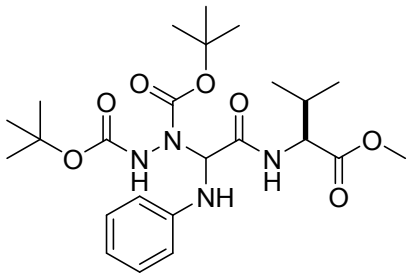
HRMS (ESI) calcd for $C_{22}H_{35}N_4O_7^+$[M+H]$^+$: 467.2500, found: 467.2507.



di-tert-butyl-1-(2-((1-methoxy-1-oxo-3-phenylpropan-2-yl)amino)-2-oxo-1-(phenylamino)ethyl)hydrazine-1,2-dicarboxylate (23): Following the general procedure B, obtained in 83% yield as a pale yellow viscous liquid (90.0 mg, eluent: petroleum ether/ ethyl acetate = 2:1). (d.r. = 1.7:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 7H), 6.82 – 6.68 (m, 3H), 6.45 – 6.06 (m, 1H), 5.78 – 5.35 (m, 2H), 4.97 – 4.59 (m, 1H), 3.75 – 3.63 (m, 3H), 3.27 – 3.00 (m, 2H), 1.57 – 1.38 (m, 18H).

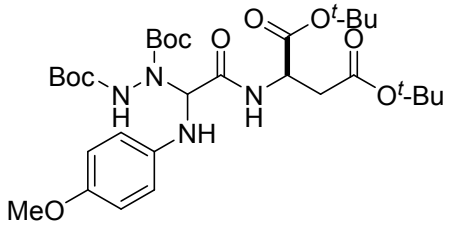
HRMS (ESI) calcd for $C_{28}H_{39}N_4O_7^+[M+H]^+$: 543.2813, found: 543.2820.



di-tert-butyl-1-(2-((1-methoxy-1-oxo-3-phenylpropan-2-yl)amino)-2-oxo-1-(pheylamino)ethyl)hydrazine-1,2-dicarboxylate (24): Following the general procedure B, obtained in 65% yield as a pale yellow viscous liquid (64.2 mg, eluent: petroleum ether/ ethyl acetate = 2:1). (d.r. = 1.1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.2 Hz, 2H), 6.81 – 6.71(m, 3H), 6.48– 5.35 (m, 3H), 4.58 – 4.28 (m, 1H), 3.73 (s, 3H), 2.31 – 2.19 (m, 1H), 1.51 – 1.43 (m, 18H), 1.08 – 0.91 (m, 6H).

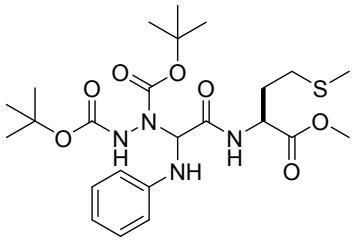
HRMS (ESI) calcd for $C_{24}H_{39}N_4O_7^+[M+H]^+$: 495.2813, found: 495.2819.



di-tert-butyl-1-(2-((1,4-di-tert-butoxy-1,4-dioxobutan-2-yl)amino)-1-((4-methoxyphenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (25): Following the general procedure B, obtained in 91% yield as a pale yellow viscous liquid (116.1 mg, eluent: petroleum ether/ ethyl acetate = 2:1). (d.r. = 1.1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 6.42 (m, 4H), 6.33 – 5.77 (m, 2H), 5.53 – 5.02 (m, 1H), 4.71 – 4.62 (m, 1H), 3.83 – 3.55 (m, 3H), 3.01 – 2.49 (m, 2H), 1.38 (d, J = 9.7 Hz, 36H).

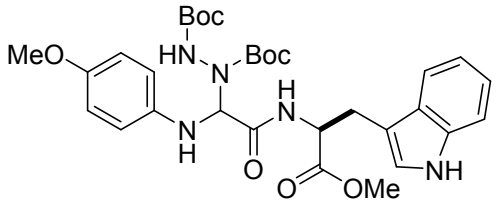
HRMS (ESI) calcd for $C_{31}H_{51}N_4O_{10}^+[M+H]^+$: 639.3600, found: 639.3612.



di-tert-butyl-1-(2-((3-(1H-indol-3-yl)-1-methoxy-1-oxopropan-2-yl)amino)-1-((4-methoxyphenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (26): Following the general procedure B, obtained in 71% yield as a pale yellow viscous liquid (74.7 mg, eluent: petroleum ether/ ethyl acetate = 2:1). (d.r. = 1.1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 7.5 Hz, 2H), 6.86 – 6.64 (m, 3H), 6.51 – 6.20 (m, 1H), 5.88 – 5.36 (m, 1H), 4.87 – 4.69 (m, 1H), 4.68 – 4.52 (m, 1H), 3.75 (s, 3H), 2.58 (d, J = 7.0 Hz, 2H), 2.24 – 1.98 (m, 5H), 1.46 (d, J = 4.4 Hz, 18H).

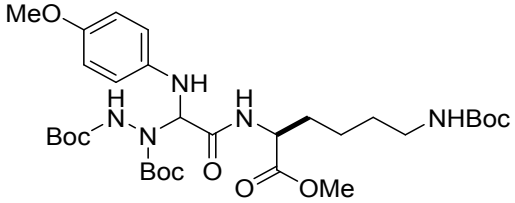
HRMS (ESI) calcd for $C_{24}H_{39}N_4O_7S^+[M+H]^+$: 527.2534, found: 527.2541.



di-tert-butyl-1-(2-((3-(1H-indol-3-yl)-1-methoxy-1-oxopropan-2-yl)amino)-1-((4-methoxyphenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (27): Following the general procedure B, obtained in 69% yield as a pale yellow viscous liquid (84.3 mg, eluent: petroleum ether/ ethyl acetate = 1:1). (d.r. = 1.1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 7.84 (m, 1H), 7.54 – 7.38 (m, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.11 – 6.84 (m, 3H), 6.83 – 6.46 (m, 4H), 6.28 – 5.31 (m, 2H), 5.06 – 4.29 (m, 2H), 3.70 – 3.48 (m, 6H), 3.29 – 3.19 (m, 2H), 1.67 – 0.45 (m, 18H).

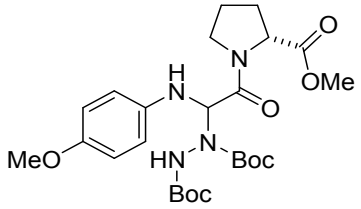
HRMS (ESI) calcd for $C_{31}H_{42}N_5O_8^+[M+H]^+$: 612.3028, found: 612.3043.



28: Following the general procedure B, obtained in 86% yield as a pale yellow viscous liquid (112.3 mg, eluent: petroleum ether/ ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 – 6.66 (m, 4H), 6.39 – 5.44 (m, 2H), 5.27 – 4.28 (m, 3H), 3.78 – 3.63 (m, 6H), 3.10 (d, J = 5.6 Hz, 2H), 1.88 – 1.73 (m, 2H), 1.55 – 1.24 (m, 31H). (d.r. = 1:1)

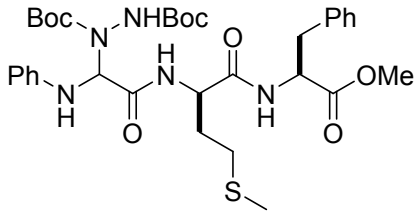
HRMS (ESI) calcd for $C_{31}H_{52}N_5O_{10}^+[M+H]^+$: 654.3079, found: 654.3722.



di-tert-butyl-1-(2-(2-(methoxycarbonyl)pyrrolidin-1-yl)-1-((4-methoxyphenyl)amino)-2-oxoethyl)hydrazine-1,2-dicarboxylate (29): Following the general procedure B, obtained in 62% yield as a pale yellow viscous liquid (64.7 mg, eluent: petroleum ether/ ethyl acetate = 1:1). (d.r. = 2.2:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 4H), 6.30 – 6.10 (m, 1H), 4.83 – 4.21 (m, 1H), 4.15 – 3.23 (m, 8H), 2.47 – 1.83 (m, 4H), 1.61 – 1.01 (m, 18H).

HRMS (ESI) calcd for $C_{25}H_{39}N_4O_8^+[M+H]^+$: 523.2762, found: 523.2766.

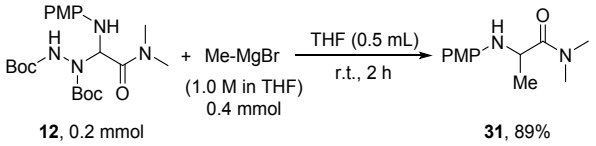


di-tert-butyl-1-(2-((1-((1-methoxy-1-oxo-3-phenylpropan-2-yl)amino)-4-(methylthio)-1-oxobutan-2-yl)amino)-2-oxo-1-(phenylamino)ethyl)hydrazine-1,2-dicarboxylate (30): Following the general procedure B, obtained in 88% yield as a pale yellow viscous liquid (118.4 mg, eluent: petroleum ether/ethyl acetate = 1:1). (d.r. = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.10 (m, 8H), 6.84 – 6.70 (m, 3H), 6.47 – 6.24 (m, 1H), 6.02 – 4.98 (m, 2H), 4.87 – 4.81 (m, 1H), 4.54 (d, *J* = 6.6 Hz, 1H), 3.85 – 3.55 (m, 3H), 3.28 – 2.96 (m, 2H), 2.67 – 2.34 (m, 2H), 2.22 – 1.87 (m, 5H), 1.55 – 1.21 (m, 18H).

HRMS (ESI) calcd for $C_{33}H_{48}N_5O_8S^+[M+H]^+$: 674.3218, found: 674.3231.

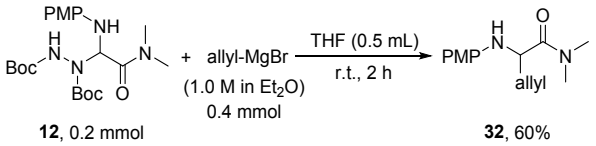
5. Further transformation of the products



12 (0.2 mmol) were placed in a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). Then anhydrous THF (0.5 mL) were added using a gastight syringe under argon atmosphere. To the mixture, MeMgBr (1.0 M in THF, 0.4 mmol) was added at 0 ^{o}C under argon atmosphere. The reaction system was warmed to room temperature and stirred for 2 h. Subsequently, water (5 mL) was added to the tube. The resulting mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (q, J = 9.0 Hz, 4H), 4.32 (q, J = 6.7 Hz, 1H), 3.68 (s, 3H), 3.00 (s, 3H), 2.89 (s, 3H), 1.34 (d, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 154.2, 137.9, 117.7, 114.9, 55.7, 52.0, 36.8, 35.9, 17.7.

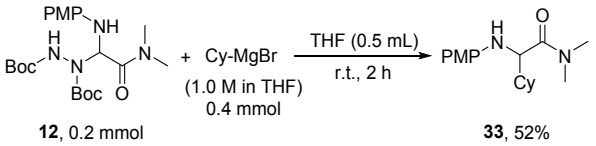


12 (0.2 mmol) were placed in a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). Then anhydrous THF (0.5 mL) were added using a gastight syringe under argon atmosphere. To the mixture, allylMgBr (1.0 M in Et_2O, 0.4 mmol) was added at 0 ^{o}C under argon atmosphere. The reaction system was warmed to room temperature and stirred for 2 h. Subsequently, water (5 mL) was added to the tube. The resulting mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.7 Hz, 2H), 5.73

(dq, J = 10.0, 7.2 Hz, 1H), 5.08 (dd, J = 17.9, 13.6 Hz, 2H), 4.33 (t, J = 6.2 Hz, 1H), 3.68 (s, 3H), 2.97 (s, 3H), 2.88 (s, 3H), 2.53 (t, J = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 153.3, 140.0, 133.4, 118.3, 116.5, 114.9, 55.7, 55.3, 37.0, 35.8, 29.7.



12 (0.2 mmol) were placed in a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). Then anhydrous THF (0.5 mL) were added using a gastight syringe under argon atmosphere. To the mixture, CyMgBr (1.0 M in THF, 0.4 mmol) was added at 0 ^{o}C under argon atmosphere. The reaction system was warmed to room temperature and stirred for 2 h. Subsequently, water (5 mL) was added to the tube. The resulting mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, J = 8.9 Hz, 2H), 6.65 (d, J = 8.9 Hz, 2H), 4.02 (d, J = 5.8 Hz, 1H), 3.73 (s, 3H), 3.05 (s, 3H), 2.93 (s, 3H), 1.92 – 1.67 (m, 6H), 1.26 – 1.10 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 153.0, 141.9, 116.4, 114.9, 60.8, 55.8, 41.8, 37.3, 35.7, 30.2, 28.8, 26.5, 26.4, 26.3.

6. Continuous-flow Chemistry

Continuous-flow setup

The continuous-flow photo-microreactor was made up of Plunger pump (0-10 mL, 0.01 ml/min), Kessil lamps (390 nm, 427 nm, 440 nm, 456 nm, 467 nm), PFA coil (Ø = 1000 µm, L = 10 m), reaction tube, ballon, check valve and reaction mixture collector.

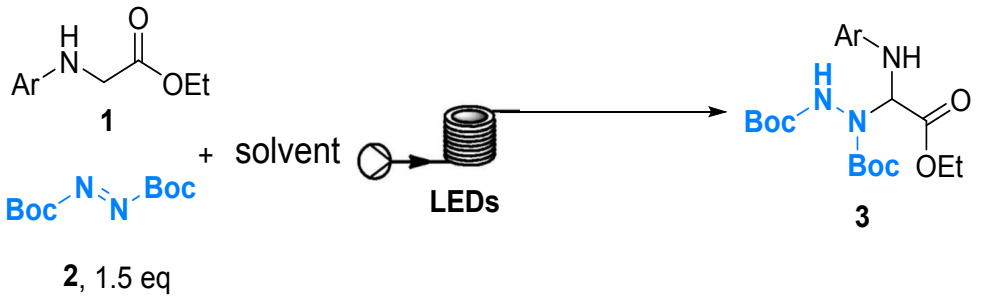
Continuous-flow reaction device: a) Kessil light; b) Plunger pump; c) PFA coil; d) light cover; e) Connection of main component; f) Irradiation mode; g) Irradiation with cover; h) Operating mode.

General procedure for the continuous-flow system

Glycine derivatives, azo compounds were placed in a 100 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, anhydrous CH_3CN were added using a gastight syringe under argon atmosphere. The mixture was stirred in the dark for 10 minutes until all solids were dissolved. After that, inserted a balloon on the rubber plug for argon atmosphere protection.

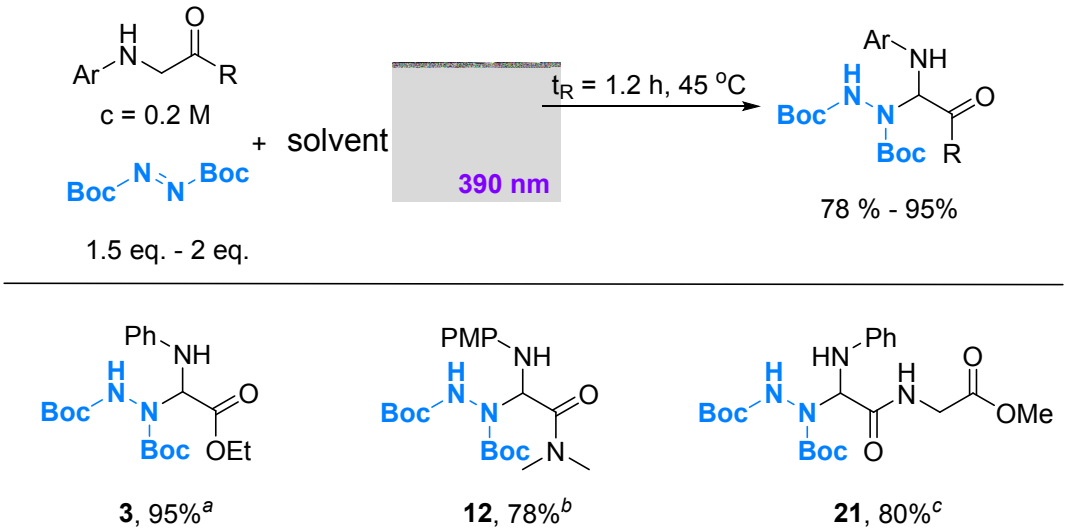
Purge the argon to replace all the air in the PFA coil and then pump the corresponding solvent to fill up the reaction coil. Next, the reaction mixture was pumped into the PFA coil under the irradiation of LEDs (390 nm - 467 nm) with a small fan (20°C- 45 °C) at the speed of 0.1 or 0.13 mL/min. After the reaction is stable, collect 20 minutes of samples for result analysis. The sample was then quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

Reaction condition optimization



	Wavelength	Solvent	Temperture	Concentration	Residence time	Yield
1	467 nm	CH_3CN	30°C	0.2 M	1 h	66
2	456 nm	CH_3CN	30°C	0.2 M	1 h	72
3	440 nm	CH_3CN	30°C	0.2 M	1 h	76
4	427 nm	CH_3CN	30°C	0.2 M	1 h	80
5	390 nm	CH_3CN	30°C	0.2 M	1 h	82
6	390 nm	CH_3CN	30°C	0.1 M	1 h	75
7	390 nm	CH_3CN	30°C	0.4 M	1 h	80
8	390 nm	CH_3CN	20°C	0.2 M	1 h	61
9	390 nm	CH_3CN	45°C	0.2 M	1 h	88
10	**390 nm**	**CH_3CN**	**45°C**	**0.2 M**	**1.2h**	**95**
11	390 nm	$PhCF_3$	45°C	0.2 M	1.2 h	92
12	390 nm	Acetone	45°C	0.2 M	1.2 h	90

Continuous-flow system for different substrates



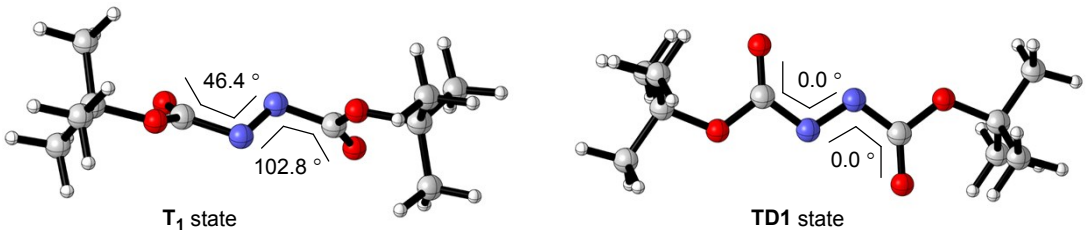
[a]Reaction condition: Glycine derivatives (10 mmol), azo compounds (15 mmol), CH_3CN (50 mL), 390 nm LED (40 W), 45 °C, 1.2 h. [b]azo compounds (20 mmol), $PhCF_3$ instead of CH_3CN; [c]azo compounds (20 mmol), DCE instead of CH_3CN.

7. DFT Calculation

Computational Methods:

All calculations were performed with Gaussian 16, Rev. C01.[3] The DFT functional of B3LYP,[4] associated with the Grimme empirical dispersion correction (GD3BJ),[5] was used for geometry optimization of all intermediates and transition states. The 6-31G(d)[6] basis set was employed on all elements. Frequency analysis was performed at the same level of theory with the geometry optimization to confirm that the optimized structures are local minima or transition states, and to gain the thermal correction to Gibbs free energy. Single-point energy calculations were conducted on the basis of optimized structures, and with the M06[7] functional, including Grimme empirical dispersion correction (GD3), and the 6-311+G(d,p)[8] basis set was employed. The solvent effects were taken into account in all calculations by employing the SMD[9] (Acetonitrile) solvation model. The intrinsic reaction coordinate (IRC)[10] calculations were performed to ensure that the transition state connects the correct reactants and products. The time-dependent density functional theory (TD-DFT) excited states calculations were performed at the same level of the geometry optimization and single-point energy calculations. All energies in this study are corrected Gibbs free energy, and are given in kcal/mol. The geometries of the optimized structures were drawn with CYLview.[11]

The **T1** state is the vertical excited state of **D0**, and the structure is distorted, while the **TD1** is obtained by the relaxation of **T1** state, and its structure is coplanar. The related dihedral angel (O-C-N-N) is also shown below:



Marcus theory calculations for the single electron transfer.

We used the Marcus theory to estimate the barriers for the single electron transfer (SET) processes. The DFT calculations were performed at the M06-D3/6-311+G(d,p) level of theory in acetonitrile at 298K

The SET pathway is shown as:

TD1 + **S0** → **D1** + **S1** (1)

The following equation was used to calculate the activation free energy of activation in the SET pathway:

$$\Delta G_{SET}{}^{\neq} = \Delta G_0{}^{\neq}[1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0{}^{\neq}}]^2 \qquad (2)$$

Here, $\Delta_r G^{\theta}$= 4.8 kcal/mol is the reaction energy of **eq. 1** obtained from DFT calculations. The intrinsic barrier is determined using $\Delta G_0^{\neq} = \lambda_0/4$, where λ_0 is the solvent reorganization energy that can be calculated as follows:

$$\lambda_0 = \sqrt{\lambda_1 \lambda_2} \qquad (3)$$

Where λ_1 and λ_2 are the reorganization energies of electron donor and acceptor, respectively. Here we follow the suggestion in the Amador-Bedolla's study.[12] and the idealized parabolic potential energy surface for reactants (G1(x)) and products (G2(x)) in the electron self-exchange process based on the Marcus−Hush theory are used to calculate the reorganization energy. Thus,

first we proceed to compute λ_1 through

$$G_2(x_1) - G_1(x_1) = \lambda_1 + \Delta G_1 \qquad (4)$$

λ_1 = 27.76 kcal/mol

and to compute λ_2 we use

$$G_1(x_2) - G_2(x_2) = \lambda_2 + \Delta G_2 \qquad (5)$$

λ_2 = 20.64 kcal/mol:

leading to

$$\Delta G_0{}^{\neq} = \frac{\lambda_0}{4} = 5.30\ kcal/mol \qquad (6)$$

Thus,

$$\Delta G_{SET}{}^{\neq} = 5.3 * \left[1 + \frac{4.8}{4 * 5.3}\right]^2 = 8.0\ kcal/mol \qquad (7)$$

The directly 1,2-hydrogen shift process from **S2** to **S3** was shown in Figure S1 below:

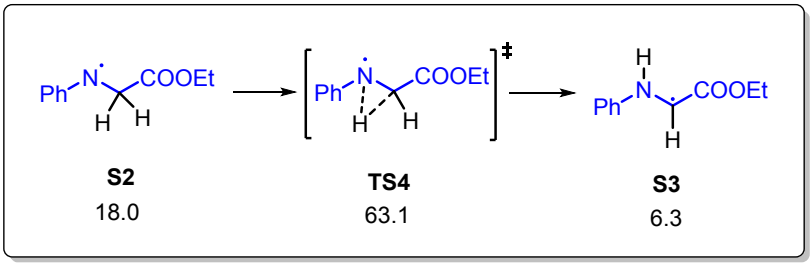


Figure S1. The Gibbs free energies of the directly 1, 2-hydrogen shift process.

Mulliken charges and spin densities (Figure S2, A) indicate that the N−H cleavage from **D1S1** to **D2S2** cannot be characterized by hydrogen atom transfer (HAT) process. The Δe = 0.905 and Δρ = -0.018 implied that a proton is obtained when **D1** fragment generating **D2** fragment via the proton transfer (PT) process. Simultaneously, the charge and spin density distribution of **D1S1** also indicate that the previous single electron transfer (SET) process is reasonable. However, the thermodynamic instability of **D1S1** ion pair complex) allows it to easily generate an electrically neutralized **D2S2** complex via **TS0**. Differently, when generating **S3S0** from **S0S2** (via **TS1**), during the process of generating **S0** from **S2** fragment, the Δe = 0.133 and Δρ = -1.017 strongly implies hydrogen atom transfer character (Figure S2, B).

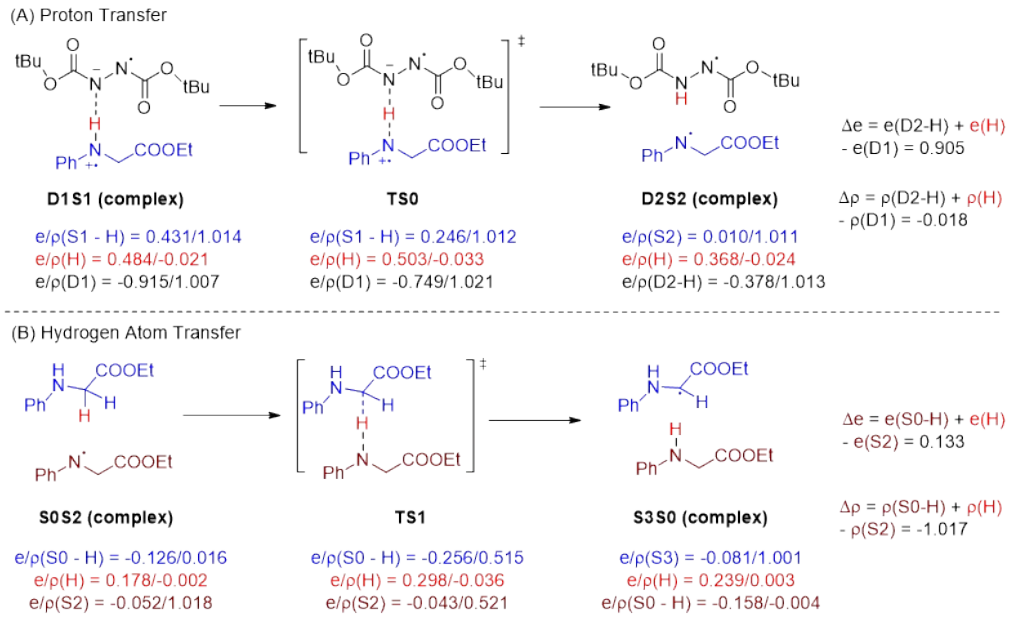


Figure S2. Populations of Mulliken charges (e) and Mulliken spin densities (ρ) for the key structures involved in the proton transfer (A) and hydrogen atom transfer (B) process.

In addition, we can also draw similar conclusions from the electrostatic potential surface of the transition states (Figure S3).[13] For **TS0**, the electrostatic distribution on

both sides of the proton is significantly different, negative charges are concentrated on the left and positive charges are distributed on the right. While in **TS1**, the electrostatic distribution on both sides of the hydrogen atom is relatively uniform.

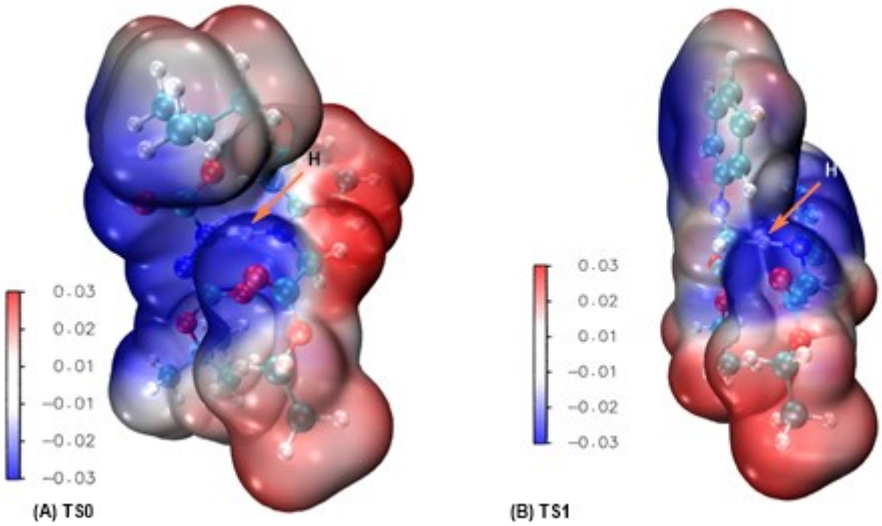


Figure S3. Electrostatic potential surface of transition states **TS0** and **TS1**.

Calculated energies of all stationary points

$\Delta G_{sol} = \Delta E_{sol} + \Delta G_{corr}$

ΔE_{sol} refers to the solvation single point energy by M06-D3/6–311+G(d,p).

ΔG_{corr} refers to the thermal correction to the Gibbs free energy calculated at B3LYP-D3(BJ)/6–31G(d) level of theory.

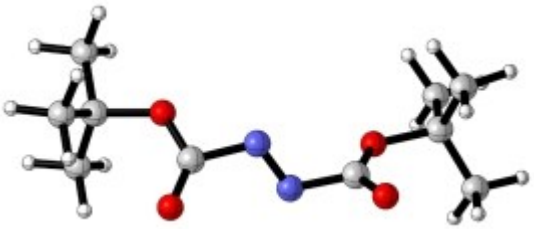
ΔG_{sol} refers to the sum of the solvation single point energy and the thermal correction to the Gibbs free energy.

Table S6. The ΔG_{corr}, ΔE_{sol} and ΔG_{sol} of Optimized Structures

Number	ΔE_{sol} (Hartree)	ΔG_{corr} (Hartree)	ΔG_{sol} (kcal/mol)
D0	-802.023532	0.233128	-503131.0157
TD1	-801.978929	0.232829	-503103.2145
S0	-593.875808	0.176789	-372551.7152
D1	-802.167226	0.234414	-503220.3777
D1'	-802.799179	0.246039	-503609.6394
S1	-593.681701	0.177055	-372429.7446
S1'	-593.0838709	0.167334	-372060.7003
D1S1	-1395.882433	0.430755	-875659.0452
TS0	-1395.880145	0.429246	-875658.5565
TS0'	-1395.862326	0.42727	-875648.6145
D2	-802.6453956	0.247100	-503512.4730
S2	-593.2242832	0.161846	-372152.2542
TS1	-1187.097615	0.359046	-744689.6077
TS1'	-1395.89595804	0.433236	-875665.9754
S3	-593.2436792	0.162673	-372163.9064
P0	-1395.319551	0.426589	-875308.4459
TS2	-2197.972793	0.699097	-1378809.8980
TS2'	-1989.204345	0.627318	-1247850.777
P1	-1395.975848	0.442014	-875710.5985
TS3	-1395.832810	0.433002	-875626.4961
TS4	-553.8525128	0.132403	-347464.5739

The Cartesian coordinates of all stationary points.

D0



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N	-0.33166600	-0.54587700	0.42507600
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C	3.74685100	0.62490200	-0.03234500
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H	-3.90882700	-0.69569300	-1.76965600
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H	4.81868300	2.46197000	-0.34703800
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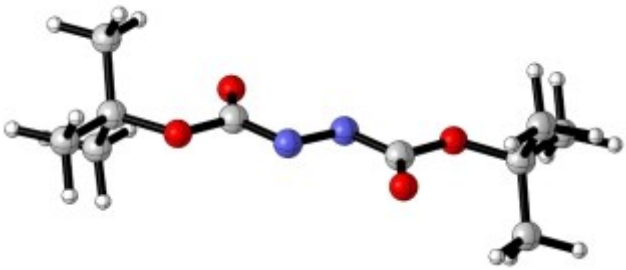
D1



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N	-0.53720600	-0.40163400	0.00001600
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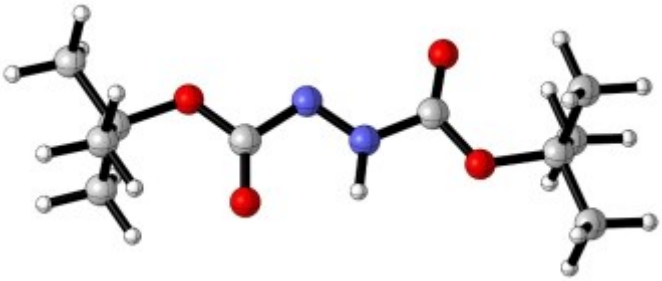
D2



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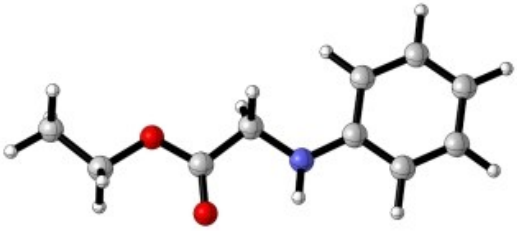
S0



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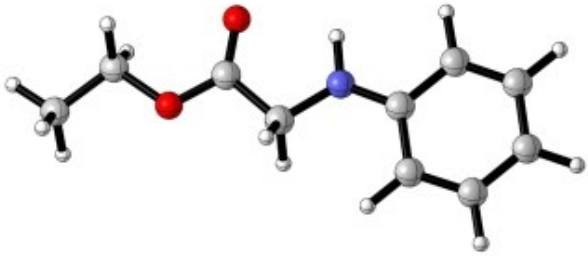
S1



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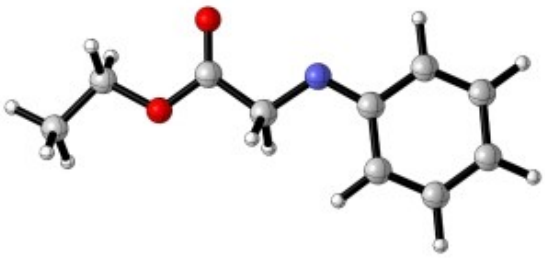
S2



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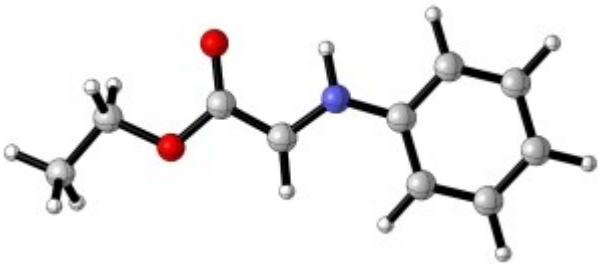
S3



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C	-4.15641700	-0.84284400	-0.00032900
C	-4.56150300	0.49638400	-0.00028700
H	-3.89194400	2.54666200	-0.00015200
H	-1.49814700	1.98727000	-0.00004200
H	-2.49001500	-2.21259000	-0.00029300

H	-4.89724300	-1.63756300	-0.00041100
H	-5.61693900	0.75116400	-0.00033800
N	-0.49244400	-0.53609000	-0.00009200
C	0.61731800	0.24697300	0.00008500
H	0.52714100	1.32221900	0.00021700
C	1.88088200	-0.42452400	0.00008300
O	2.01485900	-1.65342900	-0.00014600
O	2.92540500	0.44564900	0.00017700
C	4.23932700	-0.15026900	0.00014200
H	4.34415300	-0.78786700	0.88463200
H	4.34446800	-0.78704800	-0.88490800
H	-0.29730300	-1.53508700	-0.00017800
C	5.25124800	0.97646400	0.00083100
H	6.26489400	0.56026200	0.00078700
H	5.13753900	1.60667200	-0.88823400
H	5.13726200	1.60582000	0.89046400

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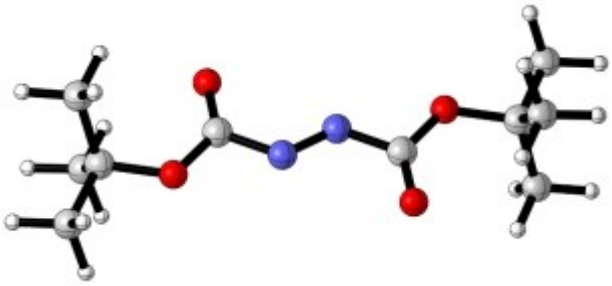

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C	1.79718800	0.40713700	-0.00103400
O	1.89883100	1.62115100	0.00025100
N	0.56672300	-0.25981000	-0.00284600
C	-1.79720800	-0.40706900	-0.00101900
O	-1.89886200	-1.62108300	0.00029600
N	-0.56674300	0.25987800	-0.00285600
O	-2.74992600	0.52092800	-0.00134700
O	2.74989900	-0.52087000	-0.00130400
C	-4.18680600	0.13540300	0.00054300
C	4.18680700	-0.13542400	0.00060700
C	4.88694200	-1.49040600	0.00000600
H	5.97095300	-1.34087300	0.00109700
H	4.61448700	-2.06808500	0.88920700
H	4.61606000	-2.06648600	-0.89071400
C	4.50140000	0.64600300	1.27389900
H	4.00048400	1.61603900	1.28455700
H	4.19545500	0.07612800	2.15768000

H	5.58217400	0.81254700	1.33079900
C	4.50404200	0.64851500	-1.27048900
H	5.58491200	0.81531200	-1.32475200
H	4.20006500	0.08031200	-2.15602300
H	4.00300600	1.61849900	-1.28033600
C	-4.88704100	1.49033800	-0.00008200
H	-5.97104100	1.34072800	0.00099700
H	-4.61464000	2.06804900	0.88911500
H	-4.61619000	2.06642800	-0.89080500
C	-4.50133100	-0.64604800	1.27383500
H	-4.00030300	-1.61602700	1.28451000
H	-4.19546500	-0.07613000	2.15761600
H	-5.58208700	-0.81271300	1.33071500
C	-4.50393900	-0.64858700	-1.27054400
H	-5.58479000	-0.81550500	-1.32481400
H	-4.20001500	-0.08036200	-2.15608200
H	-4.00279300	-1.61851600	-1.28037300

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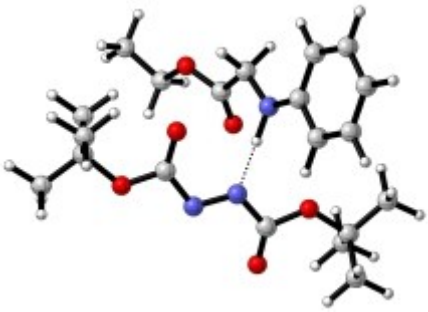

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C	-1.67470100	2.13698500	-0.28188400
C	-2.53731800	1.47171300	-1.21169600
C	-3.52607700	2.18272200	-1.85967800
C	-3.68699000	3.55734100	-1.61488300
H	-2.96903000	5.28531600	-0.53172500
H	-1.18882400	4.05527600	0.64378000
H	-2.40061300	0.41137600	-1.37915000
H	-4.18048700	1.67739600	-2.56258600
H	-4.46766500	4.11053500	-2.12716300
N	-0.73440000	1.40587200	0.33457700
C	0.26671700	1.96076900	1.22080900
H	0.96449600	2.58608500	0.65720900
H	-0.20806200	2.58641300	1.98606100
C	1.01019300	0.84556600	1.93138900

O	0.52361400	-0.22712900	2.22000200
O	2.24395600	1.24304300	2.25595900
C	3.04843500	0.28198500	2.99389600
H	2.51504700	0.01408300	3.91050000
H	3.15284800	-0.61688300	2.38044300
C	1.72288500	-0.73891300	-1.07794900
O	1.62053500	0.47251700	-0.86551800
N	0.75074100	-1.71197900	-0.92131800
C	-1.38551400	-2.10607200	-0.24782000
O	-1.32860500	-3.32527900	-0.34205800
N	-0.40166600	-1.17233100	-0.52978400
O	-2.47662500	-1.40412600	0.16830200
O	2.85602500	-1.34132500	-1.50723800
C	-3.71240200	-2.07149900	0.58218100
C	4.09371400	-0.57757700	-1.70148900
H	-0.60505900	0.37678800	0.02477500
C	-4.31232800	-2.84740900	-0.59117800
H	-3.67208800	-3.68276600	-0.87931700
H	-5.29641200	-3.23728400	-0.30833500
H	-4.44249400	-2.18600500	-1.45532000
C	-3.44448700	-2.96422600	1.79496900
H	-2.96473700	-2.38483900	2.59186600
H	-4.39297900	-3.35549200	2.17901600
H	-2.79826100	-3.80316000	1.53160500
C	-4.61414300	-0.89924400	0.96832400
H	-4.78609100	-0.24211100	0.10944600
H	-5.58187000	-1.27085400	1.32058500
H	-4.15553300	-0.30894900	1.76887900
C	3.90251700	0.48418300	-2.78628100
H	3.21556900	1.26572300	-2.45878600
H	4.87000600	0.93988500	-3.02448600
H	3.50767400	0.02525800	-3.69978500
C	5.07896700	-1.64718300	-2.17096400
H	6.06306900	-1.19972200	-2.34405300
H	5.18311900	-2.43395600	-1.41618000
H	4.73669300	-2.10525800	-3.10518900
C	4.55052900	0.02494600	-0.37127900
H	4.65891100	-0.76270000	0.38242500
H	5.52577100	0.50653800	-0.50365900
H	3.83740200	0.76532400	-0.00724200
C	4.38234400	0.93298600	3.28375700
H	4.25443000	1.83620000	3.88990500
H	5.01326000	0.23123500	3.84003200
H	4.90013800	1.20229500	2.35762600

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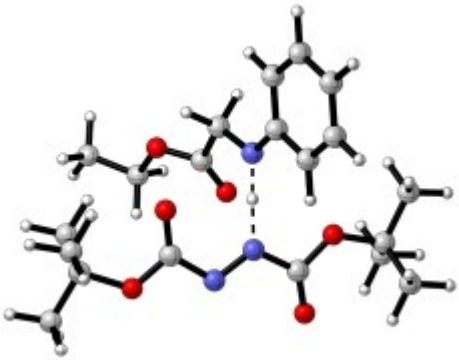

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C	-1.69699500	2.06876000	-0.12239100
C	-2.49547500	1.57166900	-1.20194000
C	-3.43626800	2.38538000	-1.80242000
C	-3.61600800	3.70647800	-1.36095900
H	-2.97879700	5.23489000	0.02732700
H	-1.28901400	3.81679300	1.12020000
H	-2.35219400	0.54974700	-1.52762000
H	-4.03794300	2.00061500	-2.61991700
H	-4.35811300	4.34069400	-1.83573300
N	-0.80276500	1.23326800	0.43103100
C	0.10418100	1.67768500	1.46520500
H	0.77833600	2.44977000	1.08225700
H	-0.45191900	2.11224100	2.30734700
C	0.90606700	0.51033600	2.01012100
O	0.48990400	-0.62504600	2.11403300
O	2.10892700	0.92285400	2.42599700
C	2.95871500	-0.09256400	3.02524300
H	2.43383200	-0.52368200	3.88279600
H	3.11928900	-0.88297700	2.28718200
C	1.75301200	-0.54982700	-1.15403300
O	1.62325800	0.62843400	-0.82036800
N	0.78393700	-1.54375800	-1.11669700
C	-1.35941900	-2.03311400	-0.46380900
O	-1.27404500	-3.23403800	-0.66179600
N	-0.37373000	-1.07222300	-0.66731100
O	-2.44827800	-1.37700100	-0.00053900
O	2.89379000	-1.09808500	-1.61793000
C	-3.66869700	-2.08720000	0.40250900
C	4.13202800	-0.30908900	-1.70703600
H	-0.58575300	0.13873900	-0.10068200

C	-4.28024600	-2.80418400	-0.80088900
H	-3.63627900	-3.61395800	-1.14789300
H	-5.25293800	-3.22257100	-0.51992400
H	-4.43682900	-2.09773100	-1.62379400
C	-3.35338000	-3.04033400	1.55543600
H	-2.85662300	-2.49859300	2.36803500
H	-4.28564200	-3.46412100	1.94414100
H	-2.70650800	-3.85668700	1.22913700
C	-4.57414900	-0.95015400	0.87282200
H	-4.76855400	-0.24662400	0.05662700
H	-5.53073500	-1.35399800	1.21948400
H	-4.10697700	-0.40262700	1.69821100
C	3.95175500	0.85229300	-2.68557700
H	3.24959200	1.59236700	-2.29909200
H	4.91925400	1.33777100	-2.85417800
H	3.58306100	0.48244300	-3.64889900
C	5.13546300	-1.32133300	-2.25642900
H	6.11861000	-0.85169300	-2.36250100
H	5.23042400	-2.17727500	-1.57989200
H	4.81782300	-1.68746400	-3.23859700
C	4.55035800	0.16047000	-0.31259300
H	4.65034800	-0.69751900	0.36100800
H	5.52281800	0.66120500	-0.37416700
H	3.82197500	0.85546200	0.10676900
C	4.25181000	0.57869300	3.43147600
H	4.06868500	1.37231800	4.16378100
H	4.91734600	-0.16301200	3.88632300
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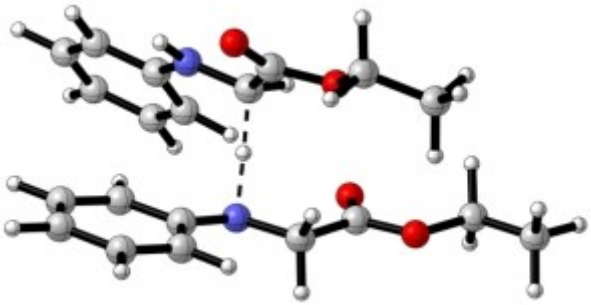

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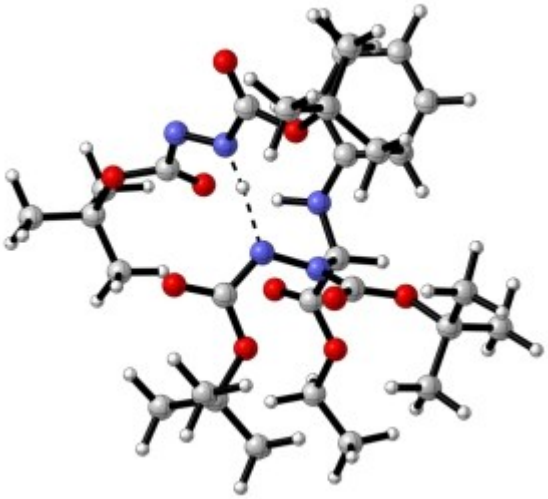
C	0.55342500	1.74846600	-1.11648800
C	1.96382900	1.69076700	-0.97940200
C	2.71345100	2.84628500	-0.80348300

C	2.08844000	4.09929500	-0.77636300
H	0.20655400	5.14263100	-0.91773700
H	-1.14054400	3.10987900	-1.19603200
H	2.44699900	0.72090400	-1.02717400
H	3.79235500	2.77265900	-0.69487900
H	2.67538900	5.00364400	-0.64506600
N	-0.11066100	0.54334500	-1.26771700
C	-1.55568700	0.59937200	-1.34228500
H	-2.02642300	1.20386200	-0.55324800
H	-1.86861100	1.05095900	-2.29565700
C	-2.15945200	-0.79198300	-1.27222400
O	-1.54683600	-1.84060800	-1.24925700
O	-3.49888100	-0.70556400	-1.24019600
C	-4.22172000	-1.95832800	-1.11637800
H	-3.95987400	-2.59827100	-1.96414100
H	-3.89543100	-2.45525600	-0.19798000
C	3.47658800	-2.89606700	-0.99357800
C	2.44161500	-2.19741800	-0.37429200
C	2.73223800	-1.31064900	0.68128300
C	4.07146100	-1.12760900	1.08036100
C	5.09080100	-1.82925000	0.44710700
C	4.80322900	-2.72365800	-0.59063600
H	3.24027300	-3.57490300	-1.80853500
H	1.42096500	-2.31490600	-0.72178800
H	4.29262500	-0.43395600	1.88745400
H	6.11828200	-1.67751800	0.76646900
H	5.60263400	-3.26945300	-1.08256800
N	1.73660000	-0.60738400	1.33243500
C	0.37083700	-0.69147400	1.03331400
H	0.16408900	-0.18729600	-0.15543400
H	-0.01004400	-1.70378300	0.89809500
C	-0.45004200	0.16640400	1.91954900
O	-0.00304200	1.05901500	2.62338900
O	-1.75820700	-0.11095900	1.78233600
C	-2.68462600	0.75828400	2.48598900
H	-2.51985200	0.64283800	3.56153000
H	-2.46523600	1.79463900	2.21388100
H	2.01171900	0.16834300	1.92689600
C	-4.08261000	0.34787800	2.07653700
H	-4.27757600	-0.69669200	2.34237400
H	-4.81332600	0.97778200	2.59549300
H	-4.22181700	0.46552500	0.99816800
C	-5.69889500	-1.63190000	-1.09006300
H	-6.27417700	-2.56090600	-1.01183800

H	-5.94827500	-0.99943000	-0.23162500
H	-6.00260500	-1.11500200	-2.00665800

TS2



ATOM	X	Y	Z
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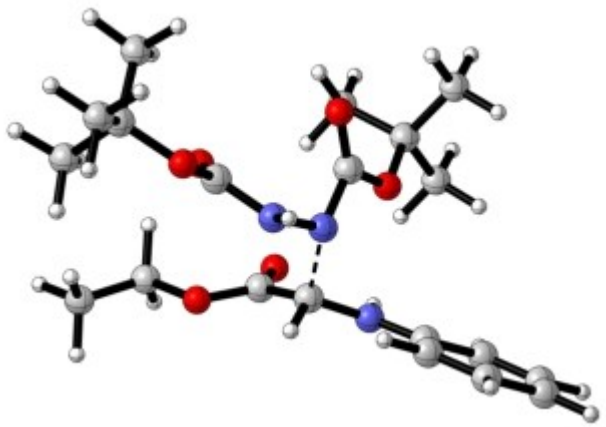
O	-2.32477300	-1.71447400	1.15370500
N	-1.74322900	-3.06356100	-0.65756200
C	0.53450600	-3.23611700	-1.21424400
O	0.47781600	-4.38348600	-1.61114700
N	-0.53657900	-2.51129700	-0.68795800
O	1.59898700	-2.42410200	-1.16397800
O	-3.85589700	-2.42356500	-0.37224900
C	2.86966400	-2.75748400	-1.83893000
C	-4.98309100	-1.65982900	0.22057600
H	-0.41476900	-1.44067800	-0.57434900
C	3.39702500	-2.34279600	2.38958700
C	2.51179800	-1.30799800	2.16030700
C	1.11560600	-1.58322500	2.10160300
C	0.65493400	-2.92666000	2.24686400
C	1.56052200	-3.94303300	2.47216500
C	2.93492600	-3.66141700	2.55143300
H	4.46101000	-2.13491700	2.43485000
H	2.88126900	-0.30142900	2.00881500
H	-0.40881500	-3.12355000	2.17680300
H	1.20791700	-4.96297700	2.58455600
H	3.64363000	-4.46395500	2.72750500
N	0.18648600	-0.61814500	1.92872500
C	0.46704600	0.77073700	1.59206600
H	1.36561100	1.11842000	2.09224100
C	-0.71662600	1.63095100	2.05284600

O	-1.78864000	1.18348200	2.40262300
O	-0.38135400	2.91469300	2.00457400
C	-1.42418700	3.87207300	2.34372400
H	-2.21236700	3.79041400	1.59042000
H	-1.84187200	3.59798900	3.31609300
H	-0.78856400	-0.91873300	1.77854900
C	-1.21815600	0.91148200	-1.28283100
O	-2.04888900	0.38533100	-2.03038900
N	-0.33666500	0.16649800	-0.57354500
C	1.68230500	1.48207800	-0.47624900
O	1.77734600	1.55085200	-1.69050700
N	0.62447000	0.86748200	0.16133200
O	2.55051500	1.97065900	0.43035200
O	-1.13223300	2.25529800	-1.05956700
C	3.65045000	2.87347000	0.03157600
C	-1.74642400	3.20928600	-1.98335000
C	-0.78591500	5.24246500	2.36505700
H	-1.54832300	5.99273800	2.60076100
H	-0.00133900	5.29571700	3.12722600
H	-0.34844400	5.48855200	1.39244800
C	4.27927600	3.23490100	1.37422100
H	4.65727200	2.33924800	1.87877000
H	5.11577800	3.92322000	1.21805900
H	3.54502800	3.72050100	2.02554500
C	4.64449300	2.12677100	-0.85499400
H	4.20150500	1.86992500	-1.81805100
H	5.51991500	2.76219400	-1.02801100
H	4.98071000	1.20891400	-0.36087400
C	3.06548100	4.11104600	-0.64677300
H	2.30796300	4.57181300	-0.00339900
H	3.86309300	4.84198000	-0.81677200
H	2.61172400	3.86045100	-1.60728400
C	3.49186500	-3.99956900	-1.20633000
H	4.48812300	-4.15879500	-1.63305800
H	3.59950000	-3.86447500	-0.12596100
H	2.88439800	-4.88695000	-1.39293800
C	3.71179800	-1.51351800	-1.56732400
H	3.21123900	-0.62340800	-1.95849500
H	3.86466900	-1.38148500	-0.49163500
H	4.68963600	-1.61323600	-2.04920600
C	2.61099700	-2.92826800	-3.33453700
H	3.56598800	-3.05980500	-3.85410000
H	1.98539200	-3.80120800	-3.53391200
H	2.11873800	-2.03751500	-3.73963900

C	-5.28496700	-2.19894000	1.61692600
H	-4.46050500	-2.00213700	2.30450500
H	-6.18625400	-1.71053500	2.00326700
H	-5.47014100	-3.27808500	1.58015700
C	-4.65680400	-0.16544300	0.21631100
H	-4.27707700	0.13451900	-0.76474400
H	-5.57287500	0.39691000	0.42792600
H	-3.90661100	0.08974100	0.96663200
C	-6.12491800	-1.96777200	-0.74403500
H	-6.30941100	-3.04597100	-0.79574600
H	-7.03998700	-1.47505500	-0.40094700
H	-5.89043400	-1.60401200	-1.74994400
C	-3.27182300	3.13064000	-1.89919000
H	-3.59638400	3.20713900	-0.85496900
H	-3.71710300	3.96261500	-2.45701100
H	-3.63719000	2.18940300	-2.31114300
C	-1.25130400	4.55834400	-1.46374100
H	-1.62898900	4.74745100	-0.45496600
H	-0.15680500	4.58080300	-1.43617100
H	-1.60067400	5.36392600	-2.11812400
C	-1.22714400	2.96479300	-3.40128000
H	-1.57194100	2.00243800	-3.78448800
H	-1.58366700	3.75728200	-4.06846400
H	-0.13202900	2.97212900	-3.40339500

TS3



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N	-0.25077000	-0.29211500	-0.68798300
C	2.14653600	-0.25092100	-0.71836000
O	2.26570600	0.49680600	0.23500200

N	0.94855700	-0.80494900	-1.13593400
H	0.93055400	-1.23141300	-2.05543600
O	3.12523100	-0.71803700	-1.51557400
O	-1.52136200	1.47707800	-0.22312600
C	4.52621800	-0.29653300	-1.32330400
C	-1.74914300	2.89708100	0.08285600
C	-3.85953800	-2.67787700	-1.89678400
C	-2.83762300	-2.21629300	-1.12252500
C	-3.12999100	-1.34238700	0.00092300
C	-4.51736700	-0.97734300	0.28050200
C	-5.51834200	-1.45953600	-0.51040400
C	-5.22419000	-2.32030700	-1.61257400
H	-3.64717400	-3.32294900	-2.74384500
H	-1.80876700	-2.47613100	-1.34133600
H	-4.71688800	-0.31811200	1.12026600
H	-6.54961500	-1.18634000	-0.30769800
H	-6.02573300	-2.70459600	-2.23336100
N	-2.17872800	-0.88769400	0.82951200
H	-2.43795700	-0.18023900	1.51676200
C	-0.78926200	-1.07535000	0.72887300
C	-0.14533300	-0.58249700	1.95845000
O	-0.56916300	0.36782700	2.63327200
O	0.99735800	-1.26231400	2.22446100
C	1.84162200	-0.69980000	3.24622200
H	2.16504000	0.29306200	2.91904300
H	1.26575000	-0.58680300	4.17063500
H	-0.49337200	-2.08316200	0.45043400
C	-2.95864500	2.83870700	1.01415500
H	-3.25433500	3.85066200	1.30936400
H	-3.80789800	2.36135100	0.51323200
H	-2.71496000	2.26726200	1.91555100
C	-2.07913600	3.65993900	-1.19859200
H	-1.22121900	3.67980200	-1.87278400
H	-2.92354200	3.18896400	-1.71432000
H	-2.36034600	4.68967400	-0.95106200
C	-0.53252500	3.46384500	0.81441300
H	-0.28126200	2.81908300	1.66281300
H	0.33345800	3.52914900	0.15240600
H	-0.76451200	4.46706500	1.18807900
C	5.25713300	-1.05610400	-2.42750900
H	6.32515000	-0.81825500	-2.39671600
H	5.13830300	-2.13709500	-2.29797500
H	4.86735500	-0.77736200	-3.41222000
C	5.02186800	-0.73335200	0.05454300

H	4.51608100	-0.18397200	0.84951700
H	4.84994300	-1.80585400	0.19749400
H	6.09900600	-0.54752400	0.12757000
C	4.64000200	1.21266300	-1.53442000
H	4.22938600	1.49175200	-2.51101900
H	4.10573500	1.76183100	-0.75720400
H	5.69543600	1.50468700	-1.50969800
C	3.01568900	-1.63797800	3.43387200
H	3.57571300	-1.75344300	2.50052000
H	3.69271200	-1.23531300	4.19551800
H	2.67781300	-2.62734300	3.76192700

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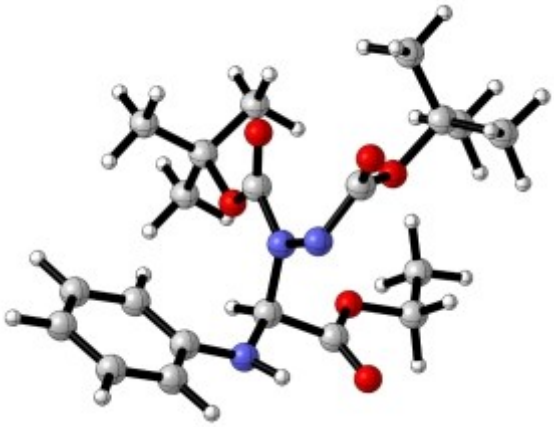

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C	-3.34494300	0.83710500	0.52532000
C	-4.28364400	1.87021800	0.35661600
C	-5.39139000	1.68931400	-0.46615900
C	-5.58851900	0.48005900	-1.14085500
H	-4.78693600	-1.48980000	-1.49751200
H	-2.83247300	-1.19184900	-0.05248400
H	-4.13087400	2.81250000	0.87719300
H	-6.10361900	2.50180800	-0.58320500
H	-6.45159000	0.34273400	-1.78536600
N	-2.26655000	1.04786500	1.39216800
C	-1.10332500	0.24217100	1.32915400
H	-1.31755100	-0.80905800	1.50306900
C	-0.07013700	0.74395800	2.34599800
O	-0.13290400	1.82173400	2.89872900
O	0.91538000	-0.13928000	2.46341400
C	2.07483800	0.26791200	3.24610000
H	2.48386900	1.17609600	2.79432100

H	1.74317400	0.50089900	4.26148000
H	-2.06493700	2.02122700	1.59638900
C	0.93760200	1.77977500	-1.23787800
O	0.91260000	2.53967500	-2.18639800
N	-0.20923000	1.55334400	-0.44909100
C	-0.00317200	-0.82953200	-0.73891500
O	0.34331200	-0.75002700	-1.89976700
N	-0.39805900	0.31659700	-0.00001800
O	-0.10794200	-1.90831300	0.02303000
O	2.00937400	1.20096100	-0.67916000
C	0.22747600	-3.26580200	-0.49648400
C	3.35764200	1.31391200	-1.27913600
C	3.05722200	-0.88081900	3.21370200
H	3.95345300	-0.60712500	3.78069400
H	2.62364200	-1.77950000	3.66503200
H	3.35493900	-1.11096300	2.18598900
C	3.81702000	2.76903800	-1.22197200
H	4.85990500	2.83292000	-1.55064900
H	3.20731600	3.40244800	-1.86914000
H	3.75724500	3.14730400	-0.19558000
C	4.19842800	0.43540100	-0.35706800
H	5.23960700	0.43360400	-0.69497100
H	4.16760300	0.81124000	0.67079100
H	3.82814000	-0.59506500	-0.36548100
C	3.34309000	0.75505600	-2.70009400
H	4.36914600	0.72413900	-3.08213600
H	2.93912100	-0.26159200	-2.70459600
H	2.74136500	1.37591000	-3.36622700
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H	1.90296100	-2.66287900	-1.75159700
H	2.32398200	-2.96341000	-0.04659000
H	1.98345000	-4.32439400	-1.13322800
C	-0.70444900	-3.61076800	-1.65335000
H	-0.53391500	-4.65195700	-1.94657700
H	-1.75090400	-3.50926500	-1.34637800
H	-0.52282600	-2.97193800	-2.51945100
C	-0.04227000	-4.14582000	0.71842200
H	0.18410000	-5.18778900	0.47262200
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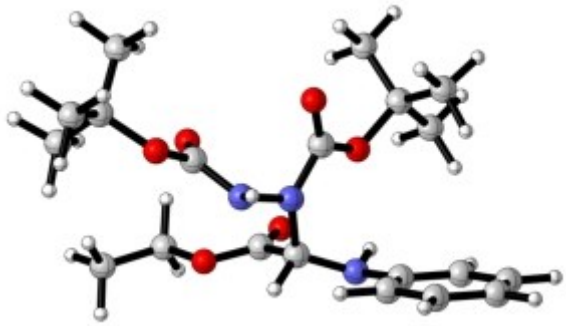

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C	2.14739100	0.45355500	-0.48238600
O	2.29583200	0.16406200	0.69040100
N	0.96881500	0.22731700	-1.19274100
H	0.82208000	0.81404800	-2.00889200
O	3.04695300	0.98255400	-1.31862800
O	-1.48752700	0.57551600	1.27087000
C	4.41185500	1.32400000	-0.85741000
C	-2.19614900	1.50105500	2.18191800
C	-3.49732900	0.07823700	-3.24944300
C	-2.55373000	-0.52855200	-2.41899800
C	-2.92486400	-0.97085400	-1.13759600
C	-4.25365200	-0.78430100	-0.71460700
C	-5.18451600	-0.17492200	-1.55188400
C	-4.81509800	0.26282200	-2.82757200
H	-3.19014600	0.41452100	-4.23633500
H	-1.53525200	-0.65192300	-2.77078200
H	-4.54525500	-1.12357900	0.27609200
H	-6.20456400	-0.03980000	-1.20191600
H	-5.54100700	0.74127700	-3.47828000
N	-2.03148600	-1.61551000	-0.27501000
H	-2.31604400	-1.58121200	0.69833200
C	-0.62330300	-1.43137700	-0.41451400
C	0.08900600	-2.16131500	0.72890900
O	-0.35964100	-2.27709000	1.85161000
O	1.27431000	-2.60921300	0.31917600
C	2.16350700	-3.12744900	1.34529300
H	2.32682100	-2.33357800	2.07840700
H	1.67093500	-3.96859300	1.84114700
H	-0.26503400	-1.83331500	-1.36262900
C	-3.14483700	0.56286400	2.92299700
H	-3.71793700	1.12700600	3.66553900

H	-3.84687600	0.09373200	2.22613900
H	-2.58338700	-0.22299500	3.43833100
C	-2.97393600	2.52953600	1.36425300
H	-3.60172900	3.12435400	2.03628800
H	-2.30210300	3.20194400	0.82767600
H	-3.62508500	2.02542500	0.64201300
C	-1.19477100	2.13714100	3.14309800
H	-1.73637600	2.71742600	3.89787700
H	-0.61711600	1.36065300	3.65635800
H	-0.50636900	2.80012400	2.61665900
C	4.32953400	2.39100300	0.23236400
H	3.75253600	3.25244000	-0.12107700
H	3.86202700	1.99933200	1.13746800
H	5.34023800	2.73298800	0.47946800
C	5.05705300	1.88362300	-2.12188000
H	6.08784800	2.18327500	-1.90836100
H	5.07174000	1.12954500	-2.91578800
H	4.50771500	2.76001600	-2.48138000
C	5.13160200	0.06038000	-0.39036100
H	4.68223700	-0.33926000	0.51996900
H	5.09919300	-0.70680700	-1.17159600
H	6.18165900	0.29776000	-0.18830100
C	3.44615400	-3.54086500	0.65909500
H	4.14949400	-3.92708100	1.40480800
H	3.26085400	-4.32770300	-0.07994600
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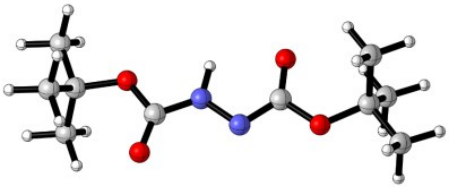

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O	1.68934600	1.33581500	-0.03311900
N	0.64699200	-0.74453200	-0.04329000
C	-1.75398500	-0.50968100	-0.01800600
O	-2.02538100	-1.71045900	-0.00881300
N	-0.52645100	0.03217200	-0.04106000
O	-2.67604100	0.51213600	-0.00894300
O	2.86517400	-0.66237600	-0.06326700
C	-4.10668700	0.22586500	0.01300300
C	4.15665200	-0.01219100	0.01620700
C	-4.73332400	1.62070300	0.01593700
H	-4.43814600	2.17852800	-0.87948200
H	-5.82557000	1.54353100	0.03209600
H	-4.41238900	2.18636600	0.89747100
C	-4.51938500	-0.53868800	-1.24741500
H	-4.20124300	0.00848400	-2.14234200
H	-4.06929100	-1.53240200	-1.26433500
H	-5.61012900	-0.64065300	-1.27943900
C	-4.48252200	-0.52746100	1.29159300
H	-4.13787300	0.02712700	2.17203400
H	-5.57190900	-0.62817800	1.35665900
H	-4.03276400	-1.52141200	1.30384000
C	4.29753800	0.76616600	1.32928400
H	5.31601300	1.15985200	1.42913400
H	3.58817700	1.59451500	1.36007300
H	4.10302900	0.10430700	2.18174300
C	4.39569400	0.88505400	-1.20364400
H	5.42044100	1.27528200	-1.19184800
H	4.26197300	0.30783700	-2.12644100
H	3.69234600	1.71862800	-1.20739900
C	5.13822000	-1.18715100	-0.00139600
H	5.02585200	-1.76920400	-0.92298600
H	6.17050600	-0.82476100	0.05535800
H	4.95738500	-1.85338300	0.84954100

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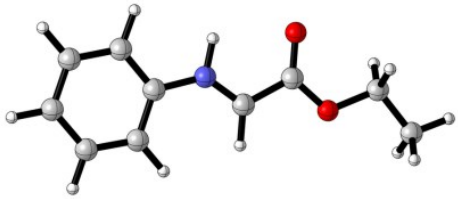

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N	0.46569800	-0.46241700	0.01514700
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C	-0.59239300	0.27127900	-0.00753700
C	2.25513300	1.22950700	0.03576100
C	2.74420400	-1.16868800	-0.02883500
H	0.27866800	-1.47469000	0.04292600
C	-1.90153100	-0.45255100	0.01488700
H	-0.53566800	1.35165400	-0.04565200
C	3.61885700	1.48995000	0.02343100
H	1.54374500	2.04695900	0.07305600
C	4.10632600	-0.88765500	-0.04147500
H	2.38510000	-2.19351300	-0.05115500
O	-2.90265300	0.40644000	-0.01114900
O	-1.96408800	-1.66698700	0.05077000
C	4.54368700	0.43820400	-0.01574600
H	3.96488000	2.51789100	0.04694900
H	4.82223600	-1.70225700	-0.07086100
C	-4.25459300	-0.16189500	0.00429700
H	5.60683400	0.65706600	-0.02416300
H	-4.35238300	-0.75827000	0.91514800
H	-4.34604800	-0.82196600	-0.86208400
C	-5.22614600	0.99343400	-0.04065600
H	-5.09439200	1.58274100	-0.95376700
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H	-5.09957100	1.64831000	0.82738300

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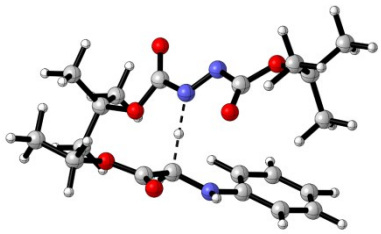

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C	-1.67891400	3.22742800	1.29635400
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C	-1.29390000	0.96037000	2.04542100
C	-2.56739300	0.95019300	2.65333600
C	-3.37898500	2.07343600	2.57690300
C	-2.94176000	3.21809100	1.89817200
H	-1.33825200	4.10961700	0.76258500
H	0.11866500	2.12504800	0.87822700
H	-2.90007000	0.05582400	3.17246100
H	-4.35907100	2.05766400	3.04402700
H	-3.58136100	4.09309600	1.83688200
N	-0.52043900	-0.17600400	2.12227500
C	0.71172700	-0.35611000	1.49929000
H	0.55253100	-0.24030000	0.24140700
H	1.43176500	0.44581400	1.66830400
C	1.24677500	-1.72938600	1.71932000
O	0.60721800	-2.64120000	2.21610100
O	2.49542000	-1.83588800	1.25130300
C	3.10537600	-3.15264100	1.32230600
H	3.18441600	-3.44283800	2.37426100
H	2.44899100	-3.86655700	0.81652700
C	-1.64558300	-0.67763900	-1.26495600
O	-1.50575300	-1.42388400	-0.30247100
N	-0.64115900	0.07953100	-1.87270200
C	1.54933100	0.82534900	-1.67730400
O	1.67414800	1.18789200	-2.83396600
N	0.44555900	0.16075300	-1.14015000
O	2.43736800	0.97789500	-0.67839100
O	-2.78537500	-0.46144900	-1.94166300
C	3.80431900	1.47283200	-0.91982200
C	-4.04862600	-1.09590800	-1.52344100
H	-0.98286300	-1.03573600	2.41305300
C	-4.40842700	-0.64905000	-0.10633700
H	-5.41678900	-0.99979900	0.13876500
H	-3.70948200	-1.05257100	0.62737800
H	-4.39952900	0.44392800	-0.03853600
C	-5.04989900	-0.54114300	-2.53413200
H	-4.76413900	-0.81833800	-3.55433900
H	-6.04621900	-0.94614600	-2.33054000
H	-5.09893000	0.55103300	-2.47036400
C	-3.93745200	-2.61505300	-1.64938500
H	-4.91769100	-3.06654200	-1.46155100
H	-3.62258400	-2.89065600	-2.66194800
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C	4.52268700	0.53207100	-1.88583400
H	4.07086200	0.56017600	-2.87943900
H	5.57213600	0.83311200	-1.97170100
H	4.48978900	-0.49586400	-1.50854300
C	3.75615600	2.91318500	-1.42591200
H	3.16924500	3.53617800	-0.74193300
H	4.77384200	3.31621400	-1.46781000
H	3.31482700	2.96963700	-2.42246200
C	4.42707700	1.40144000	0.47241100
H	4.37869300	0.37899500	0.85964700
H	5.47524700	1.71361700	0.42802900
H	3.89762700	2.06309600	1.16652700
C	4.46038000	-3.05752100	0.65624500
H	5.10197900	-2.33380000	1.16990000
H	4.95046900	-4.03668400	0.68973300
H	4.36043400	-2.75754600	-0.39226700

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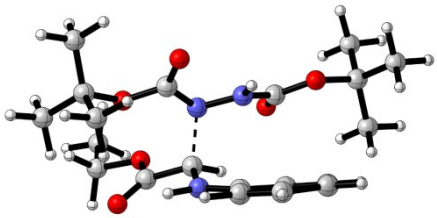

ATOM	X	Y	Z
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C	-1.90445800	1.31204900	-1.54935200
C	-0.57501600	1.94178900	-1.35127300
C	-0.48656000	3.33667300	-1.08052400
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O	2.09008100	-2.01498700	-1.36831100
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C	1.25178000	0.22976100	1.35146600
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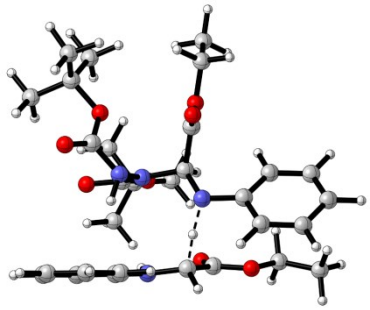
TS2’



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H	-2.22618500	-1.23885100	3.44715700
H	-2.36726500	-0.12666100	4.82327600
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H	1.27496900	0.00795300	3.88065800
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H	-3.86128600	-1.93138300	1.51315200
H	-5.29401400	-2.77337200	0.88128400
C	-5.28396200	-0.20026500	-0.08527100
H	-5.39918200	0.52390800	-0.89331600
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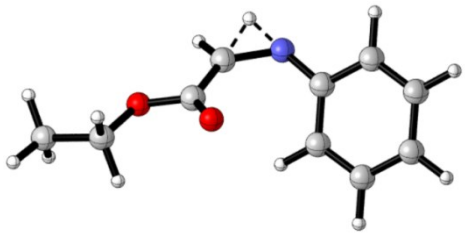
TS4



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C	1.23675500	-1.35797800	-0.37818300
H	0.59732700	-2.03498000	0.50846600
H	1.85951500	-2.06713200	-0.91468800
C	1.87658600	-0.13603700	0.13131600
O	1.37053000	0.71385500	0.84813900
O	3.17677600	-0.11772300	-0.24930800
C	3.95697900	0.97128800	0.27507000
H	3.54963800	1.93110000	-0.05440400
H	3.97612900	0.94142900	1.36819300
C	5.37592536	0.77180476	-0.28919736
H	6.01416723	1.55375172	0.06591708
H	5.75803864	-0.17435917	0.03277044
H	5.34146109	0.79741980	-1.35833537

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9. NMR Spectra

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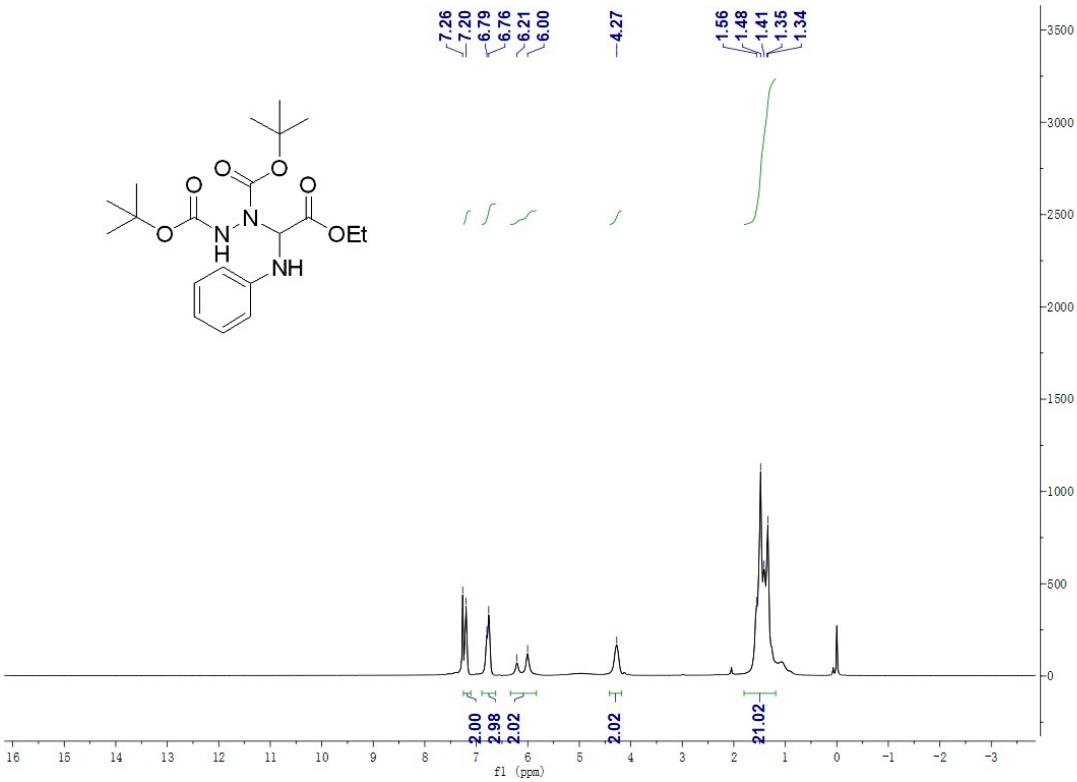

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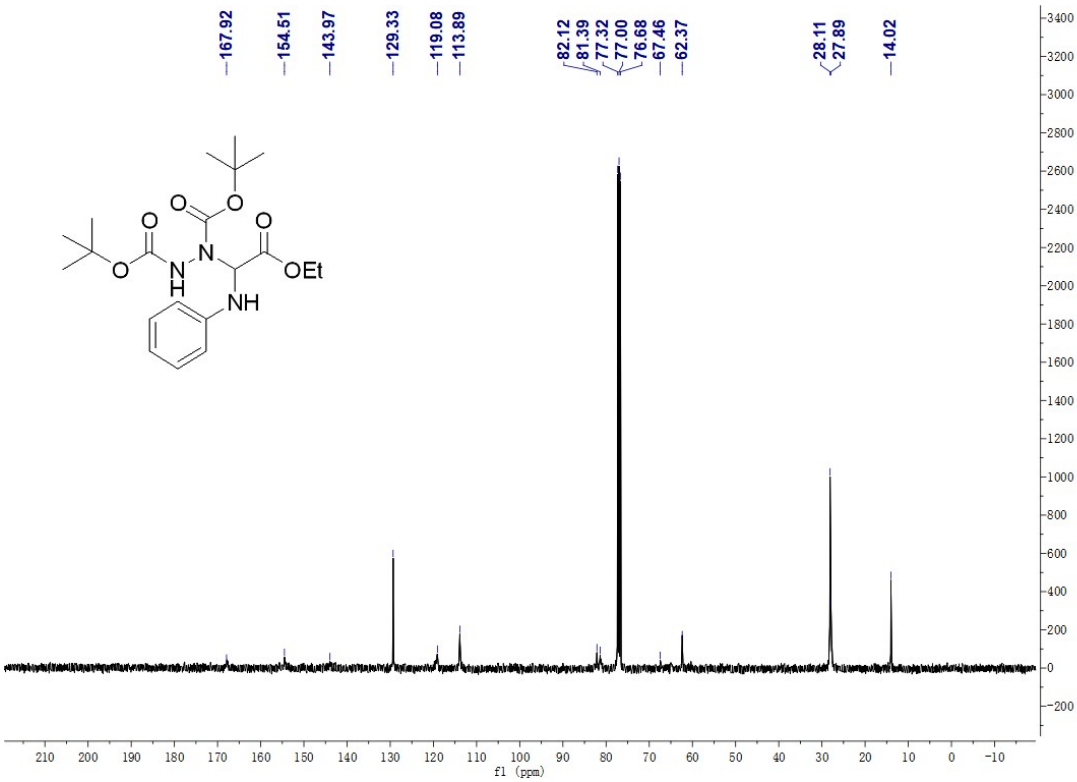

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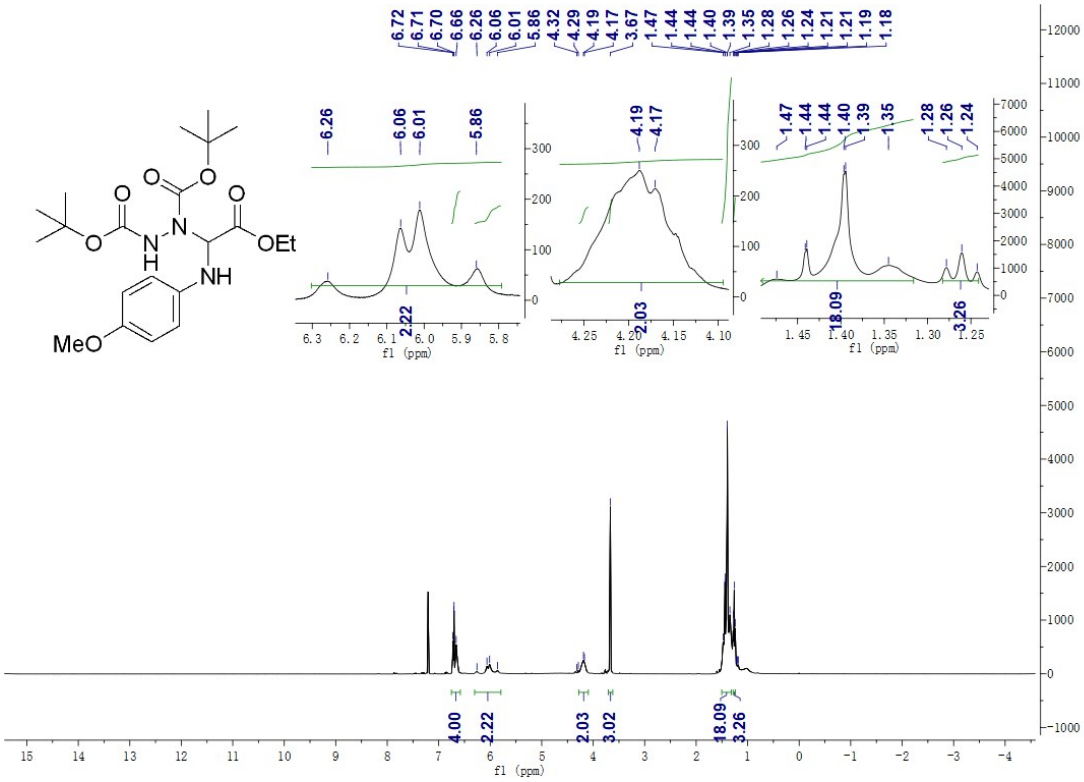

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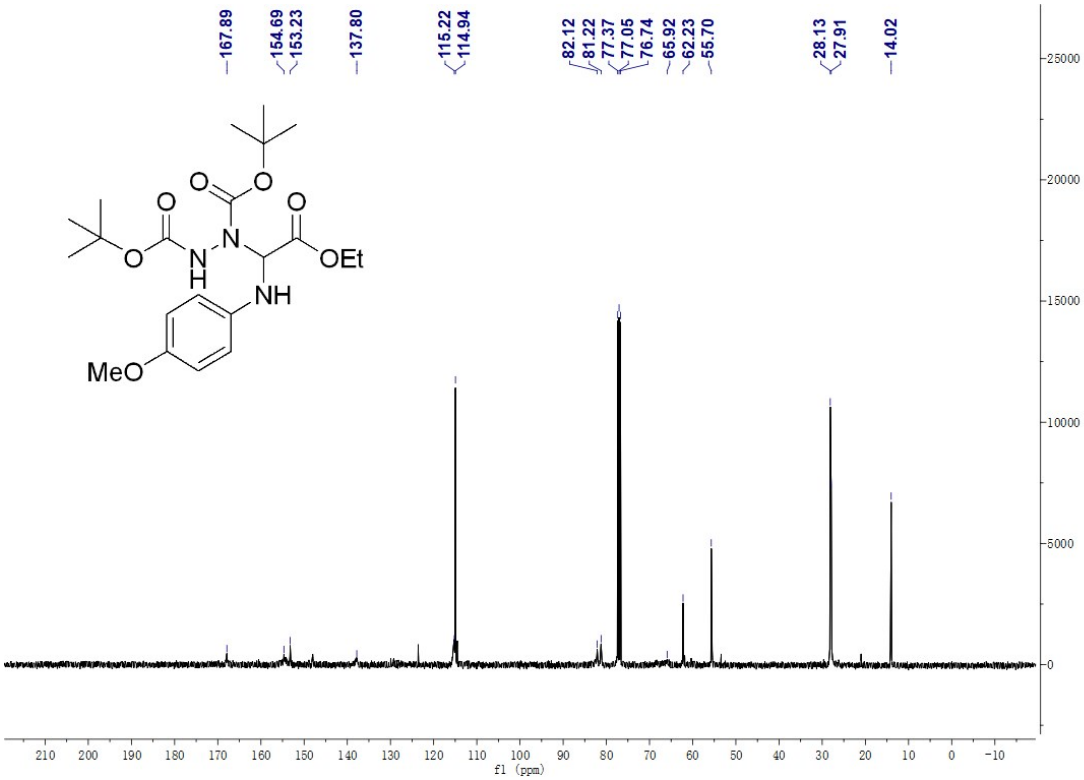

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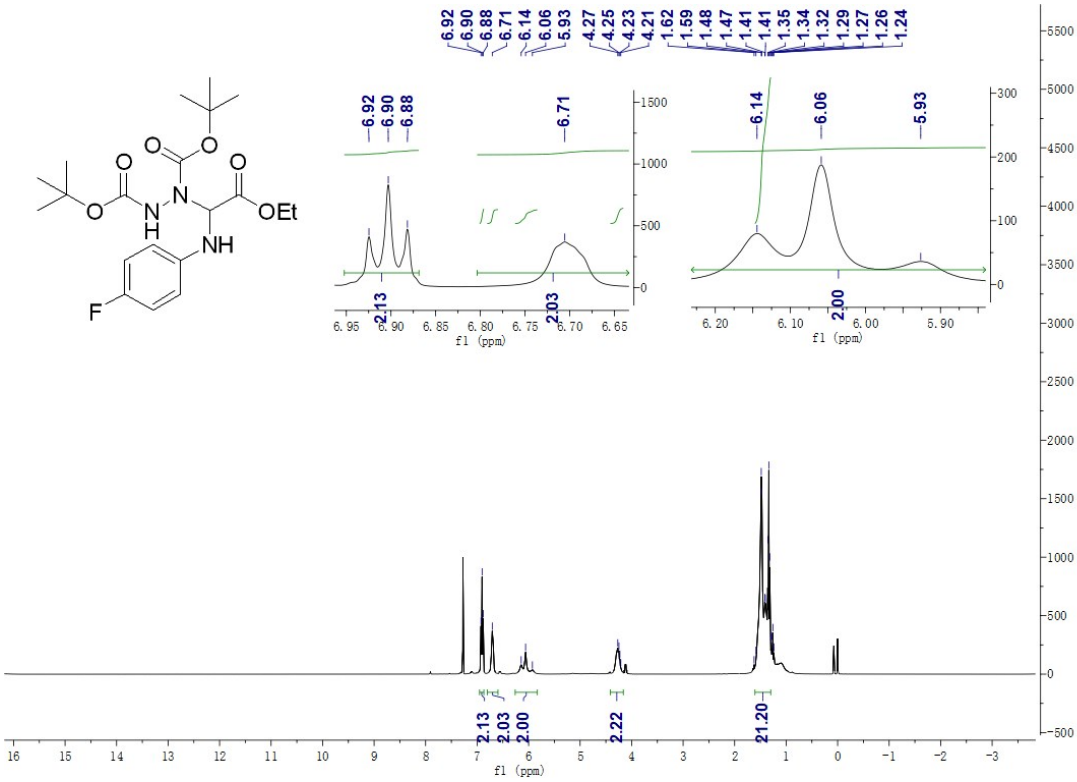

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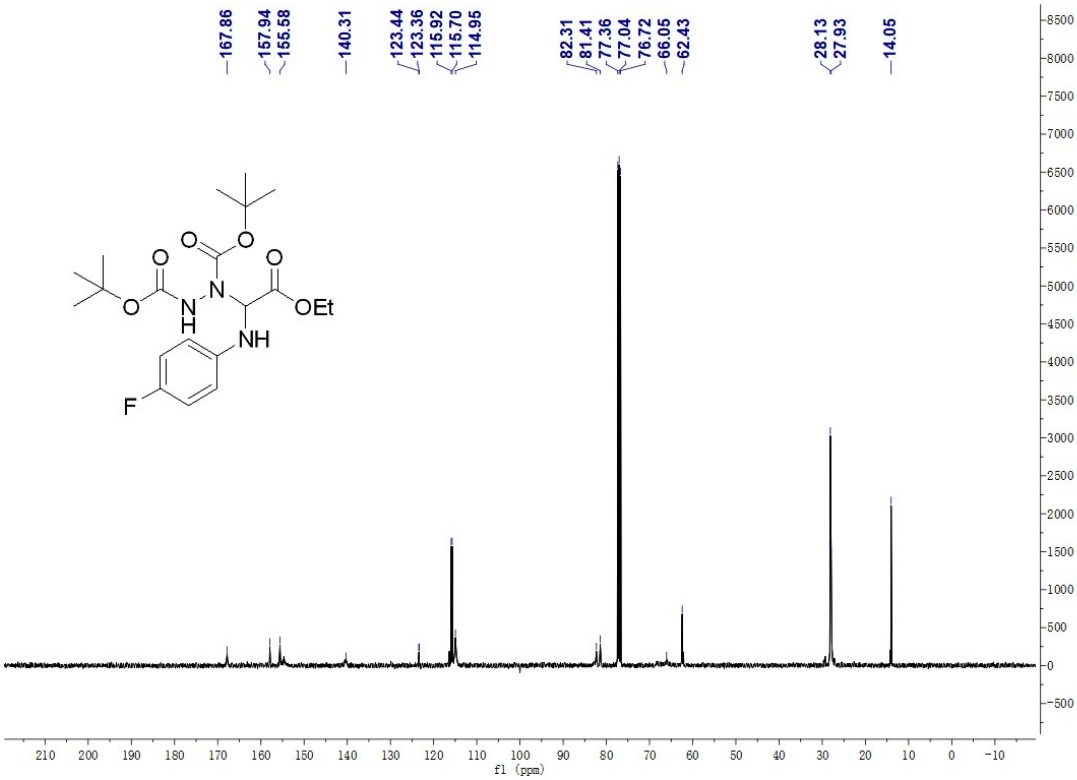

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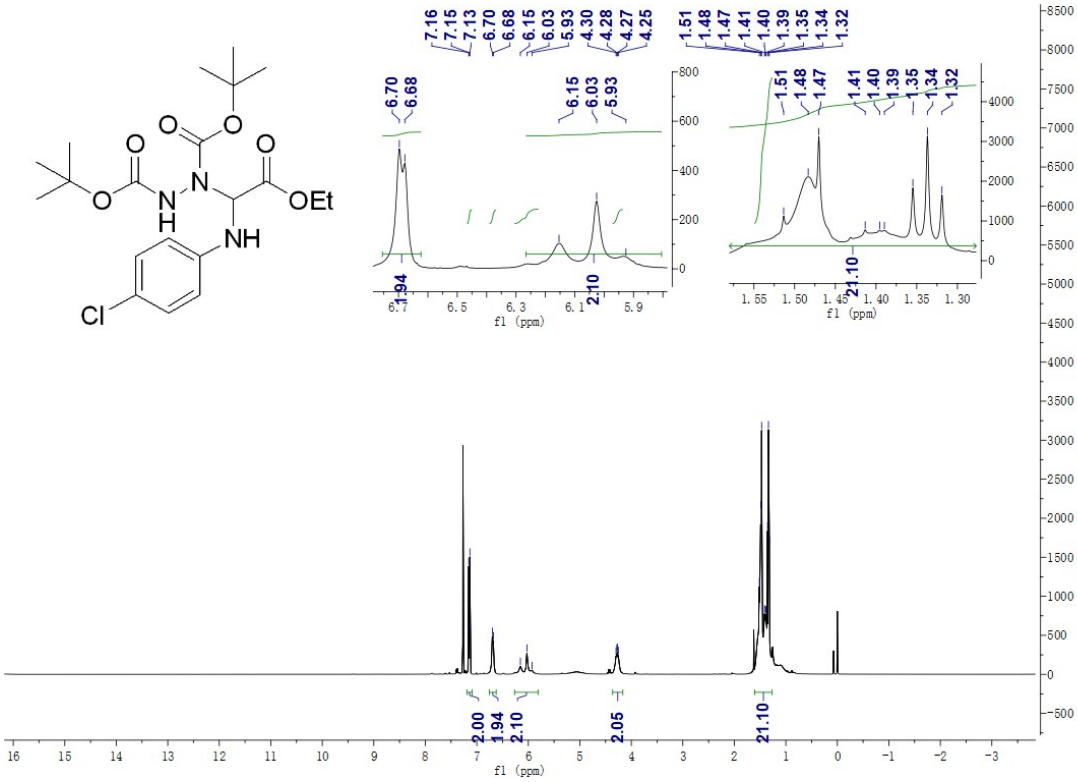

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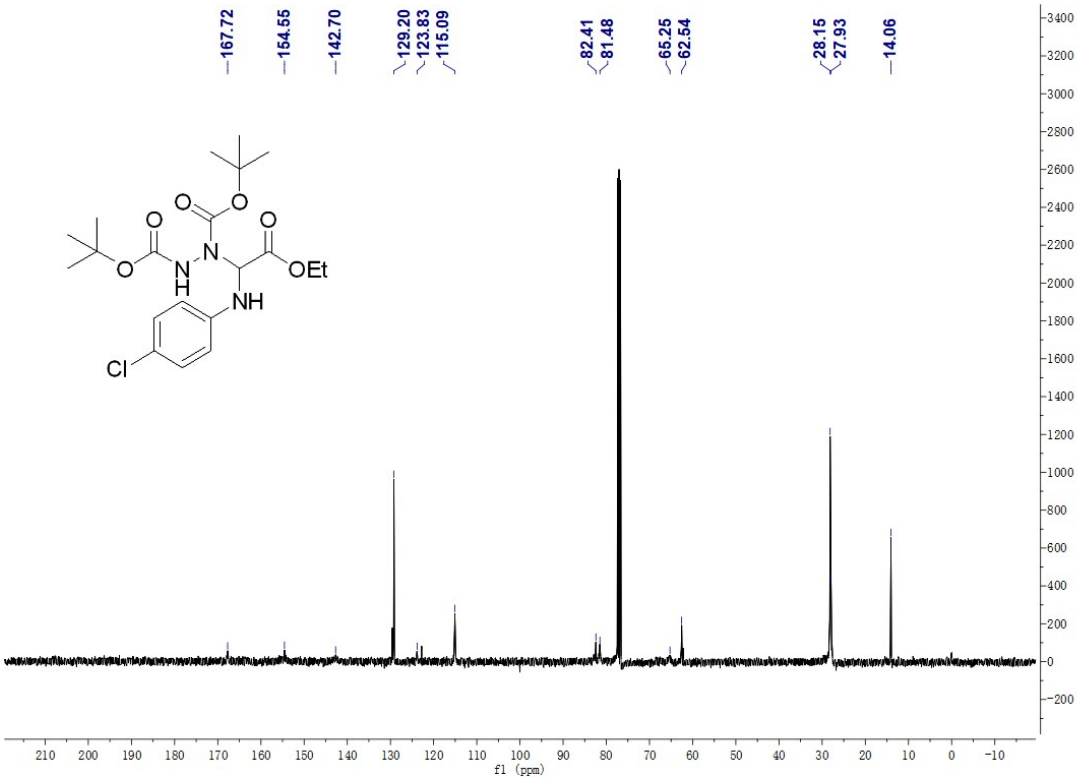

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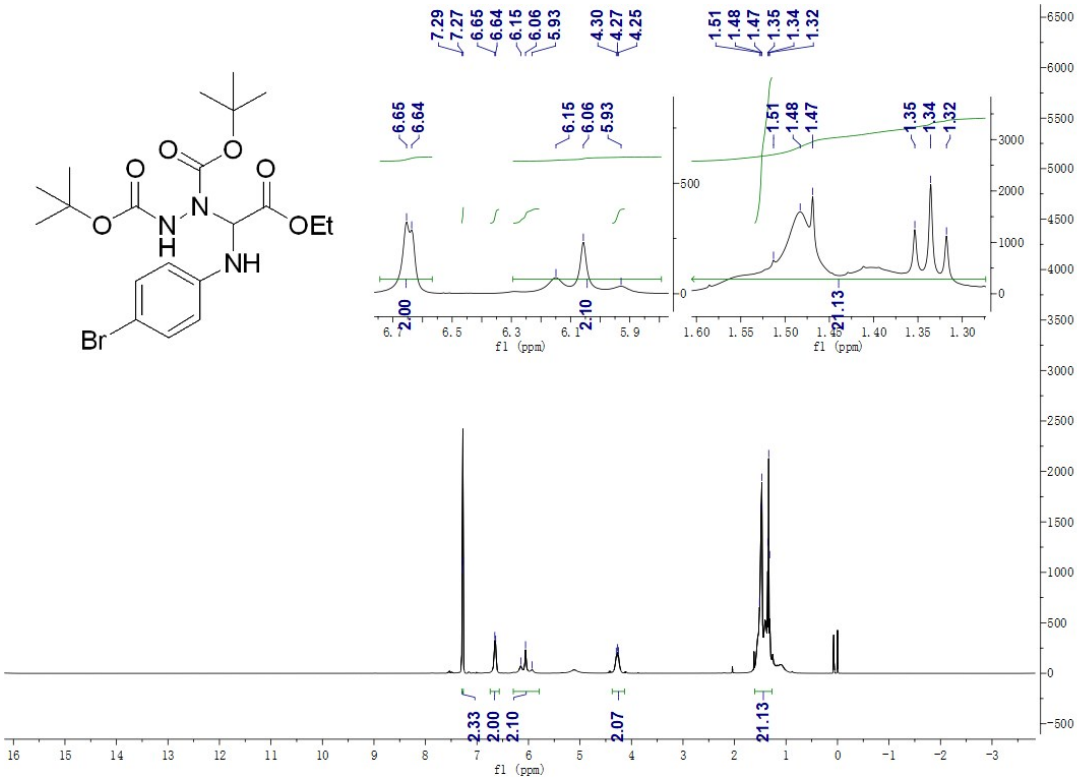

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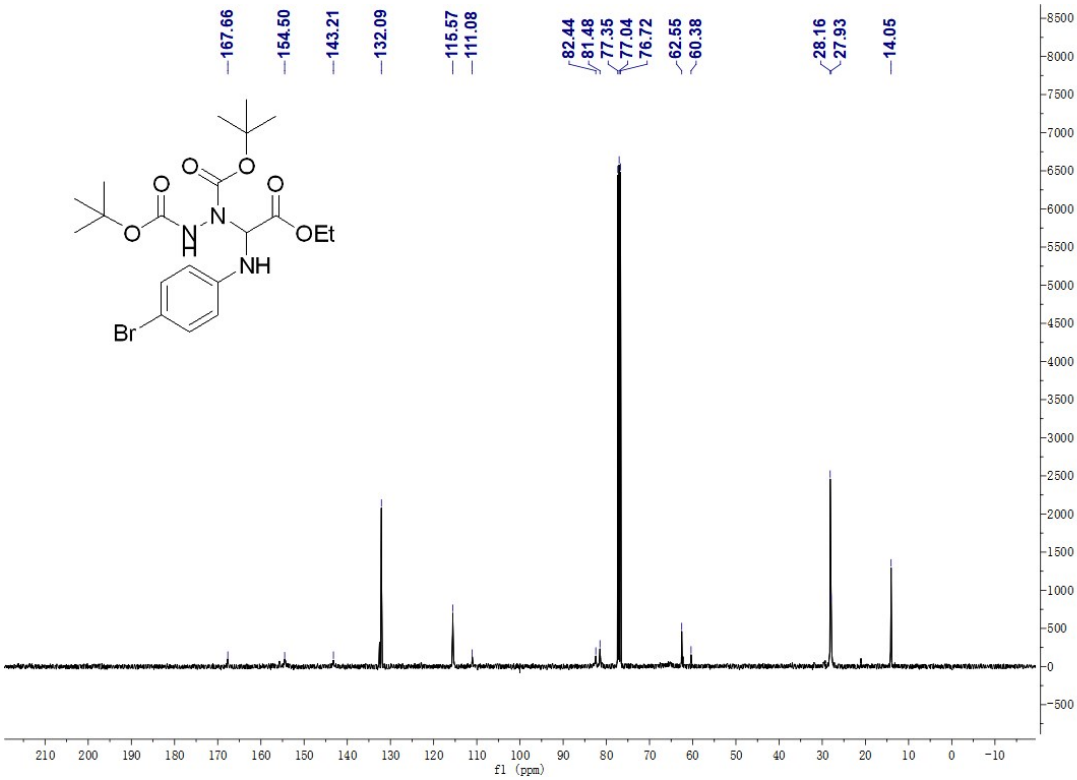

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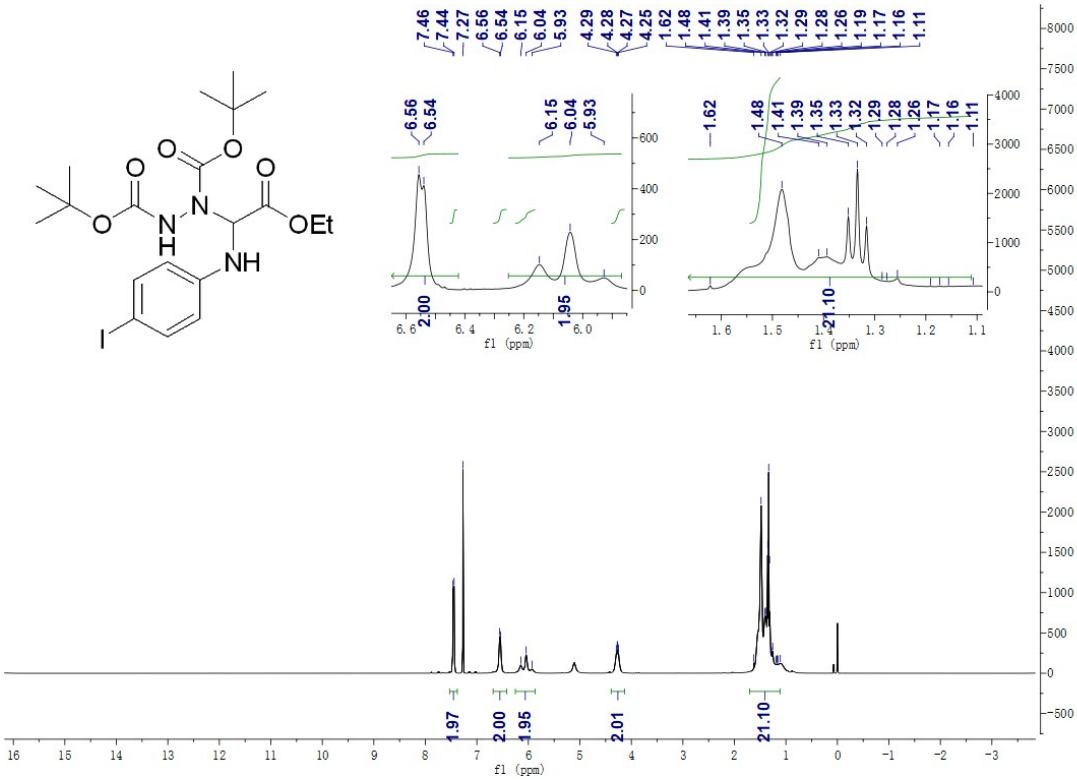

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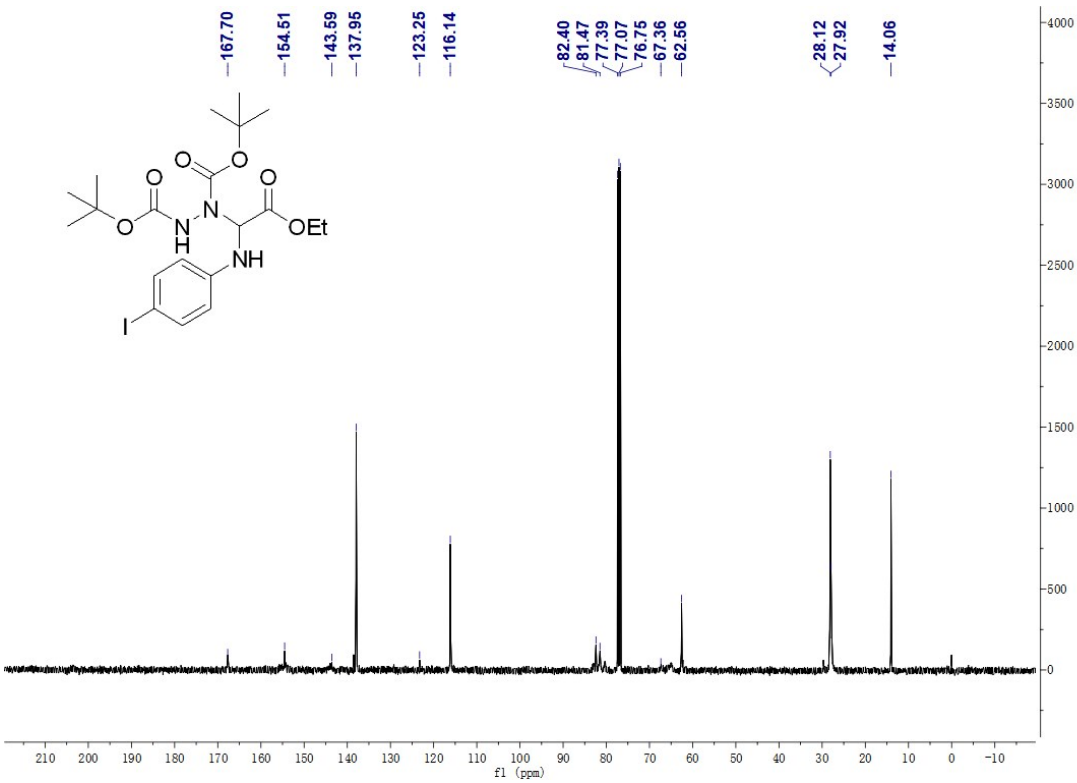

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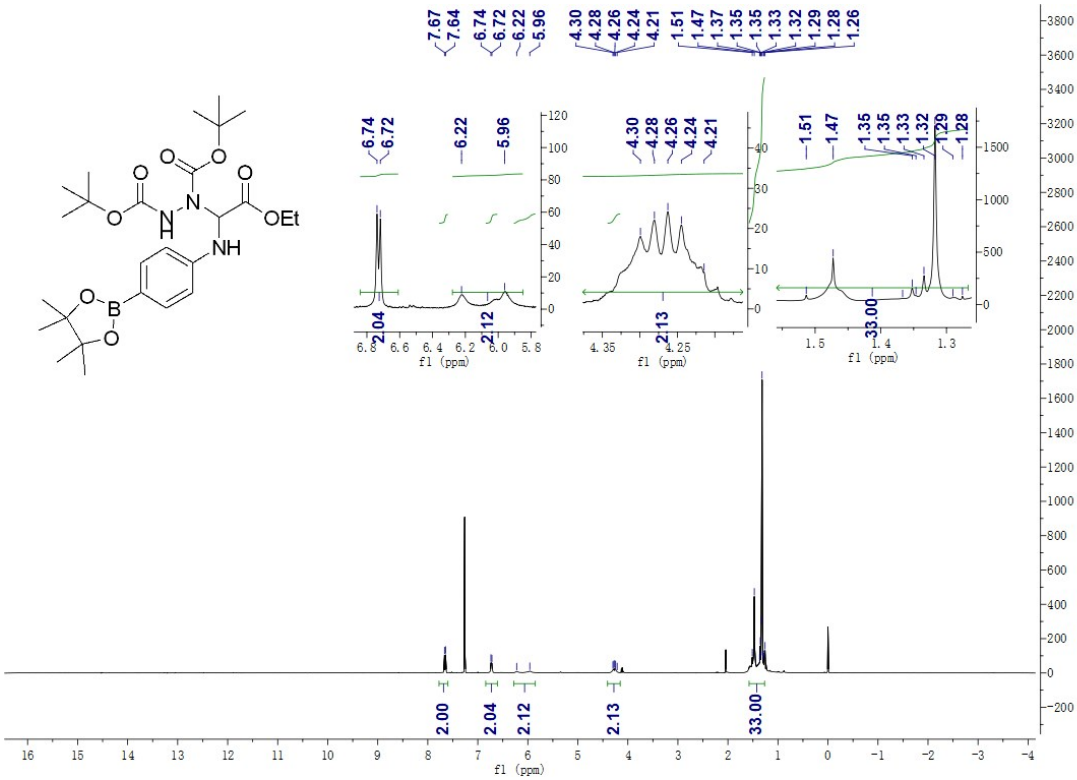

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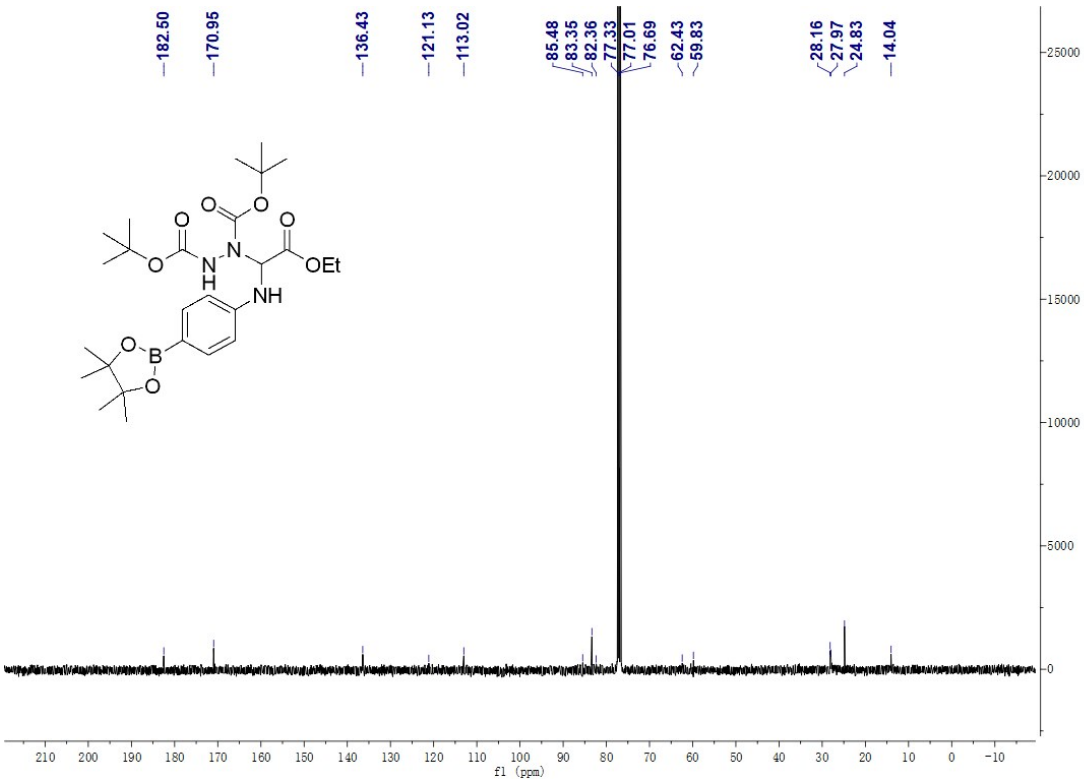

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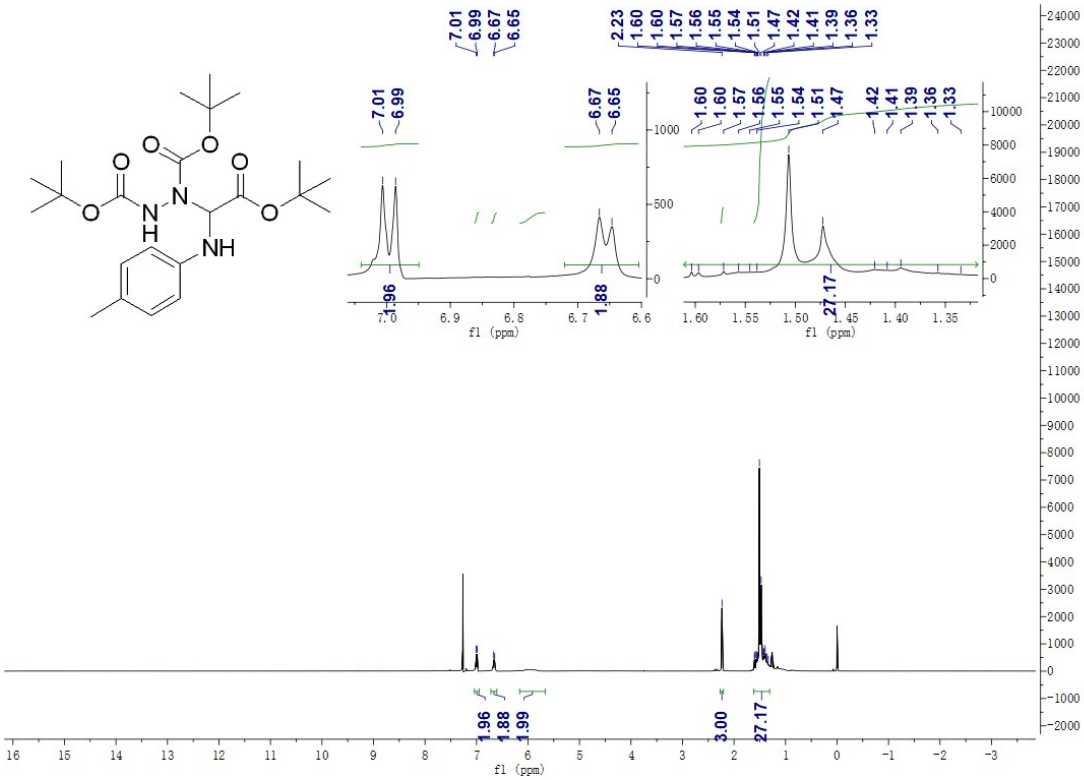

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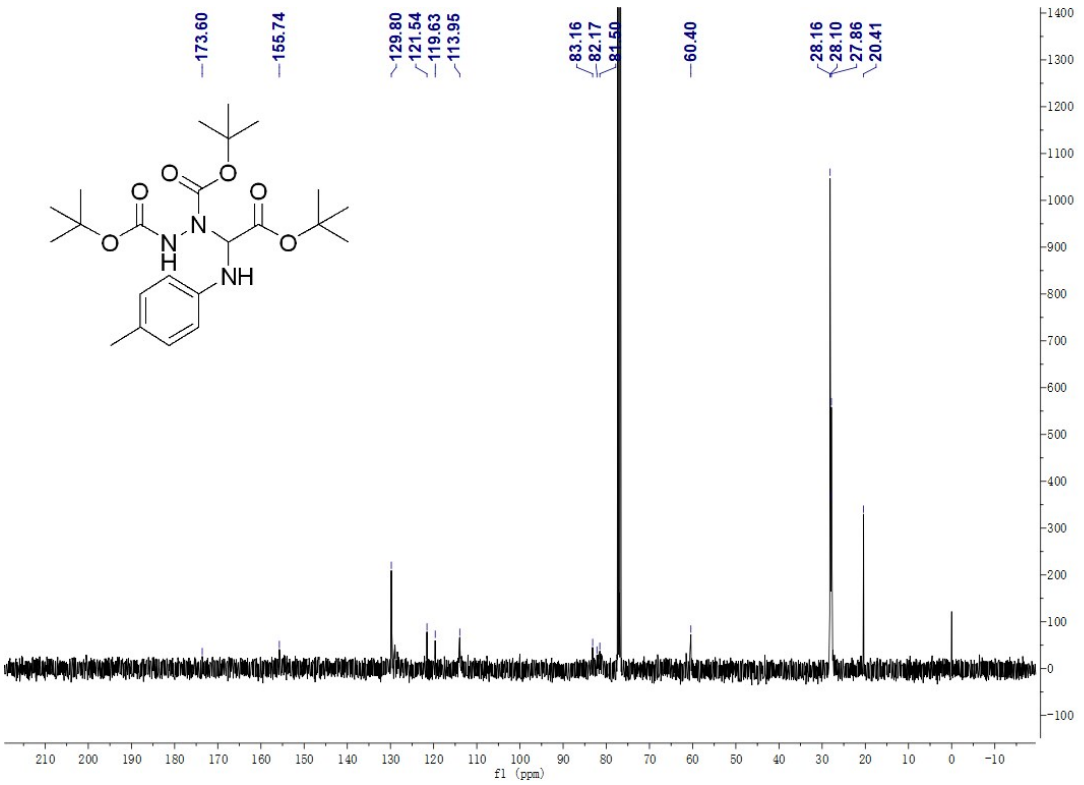
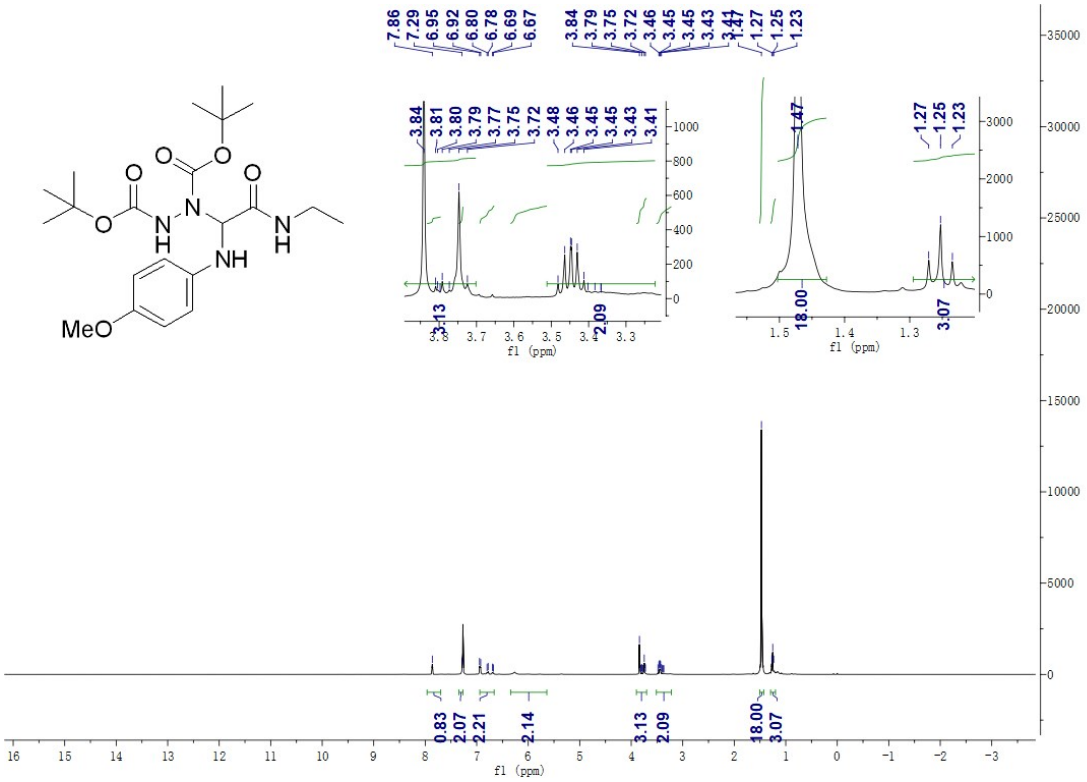
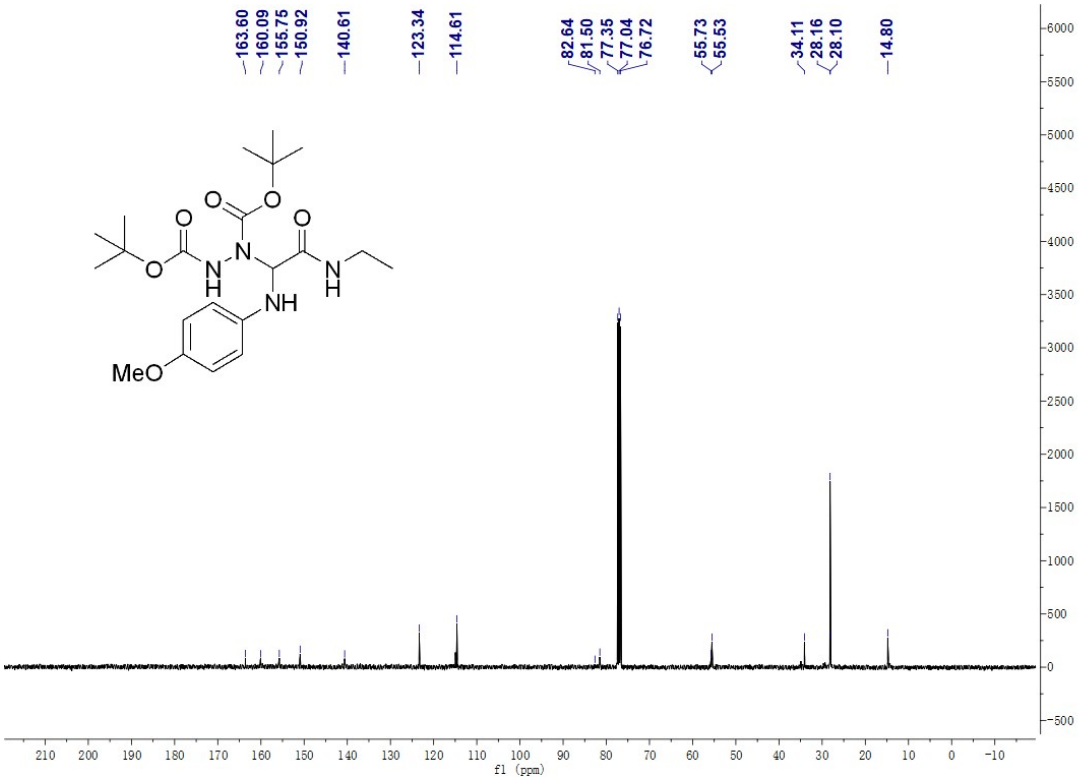


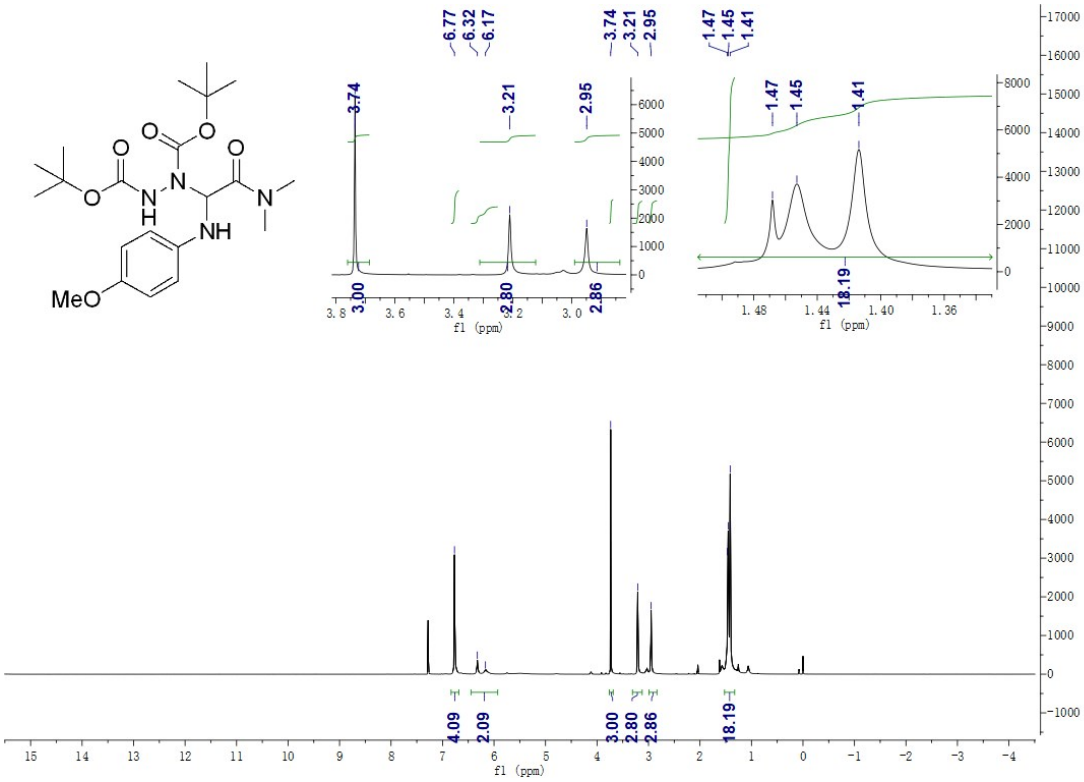
^{1}H NMR of **11**



^{13}C NMR of **11**



^{1}H NMR of **12**



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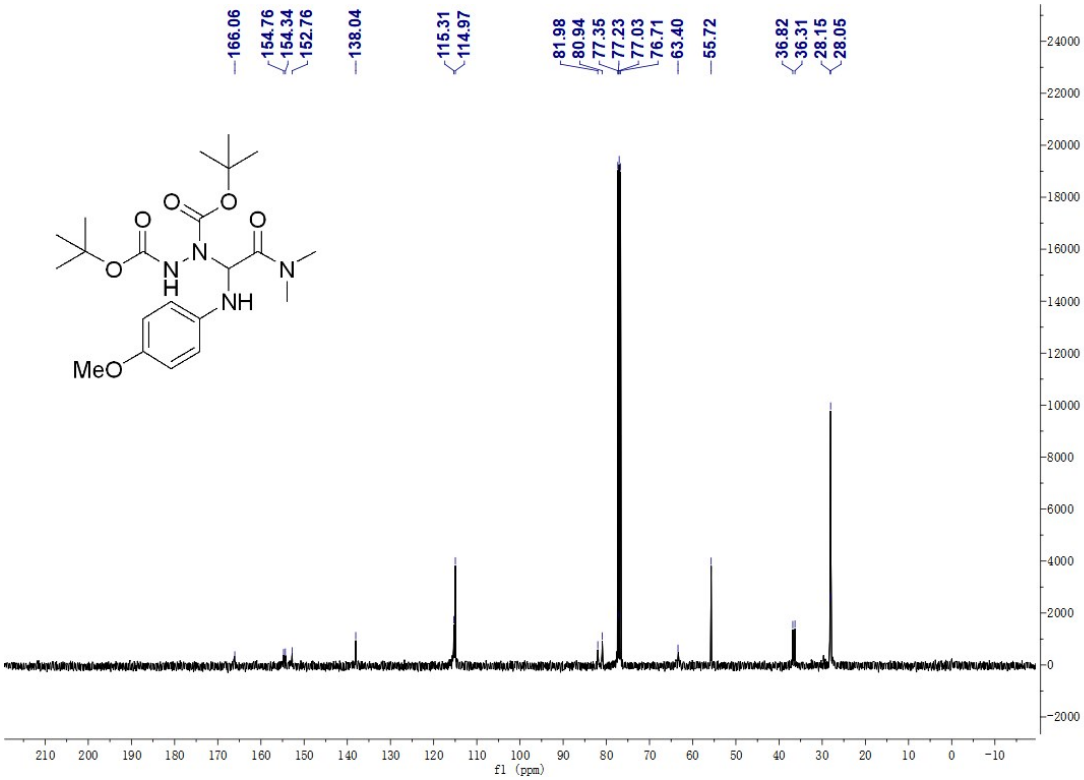
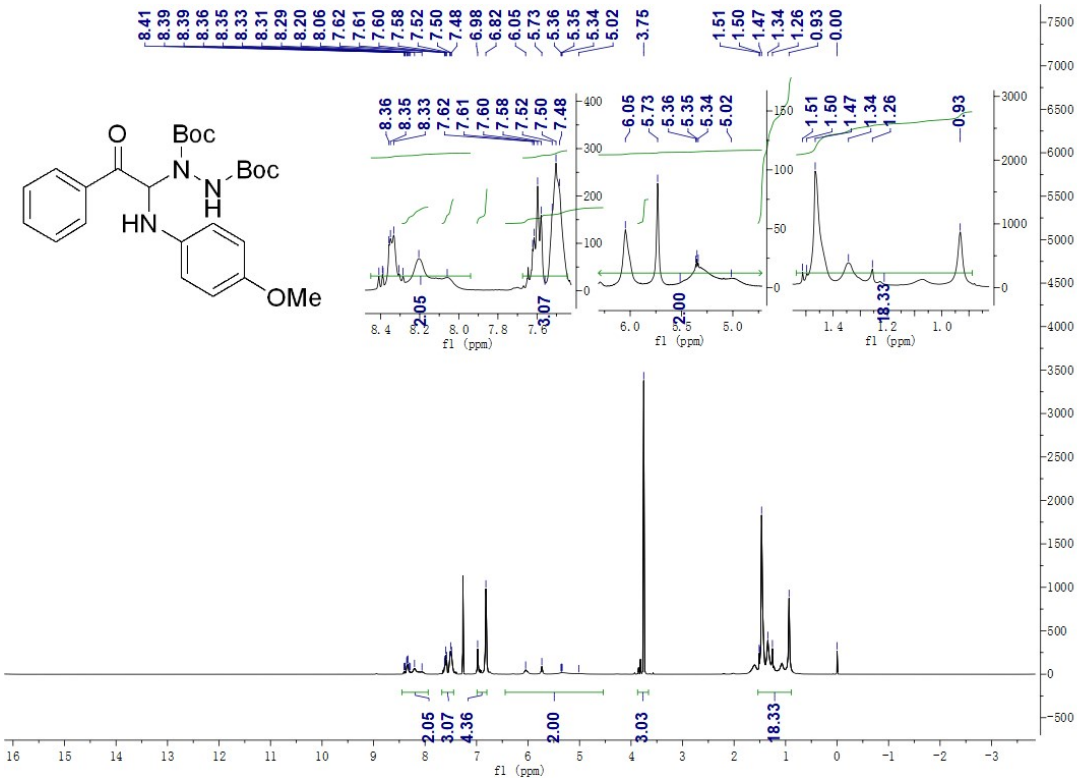
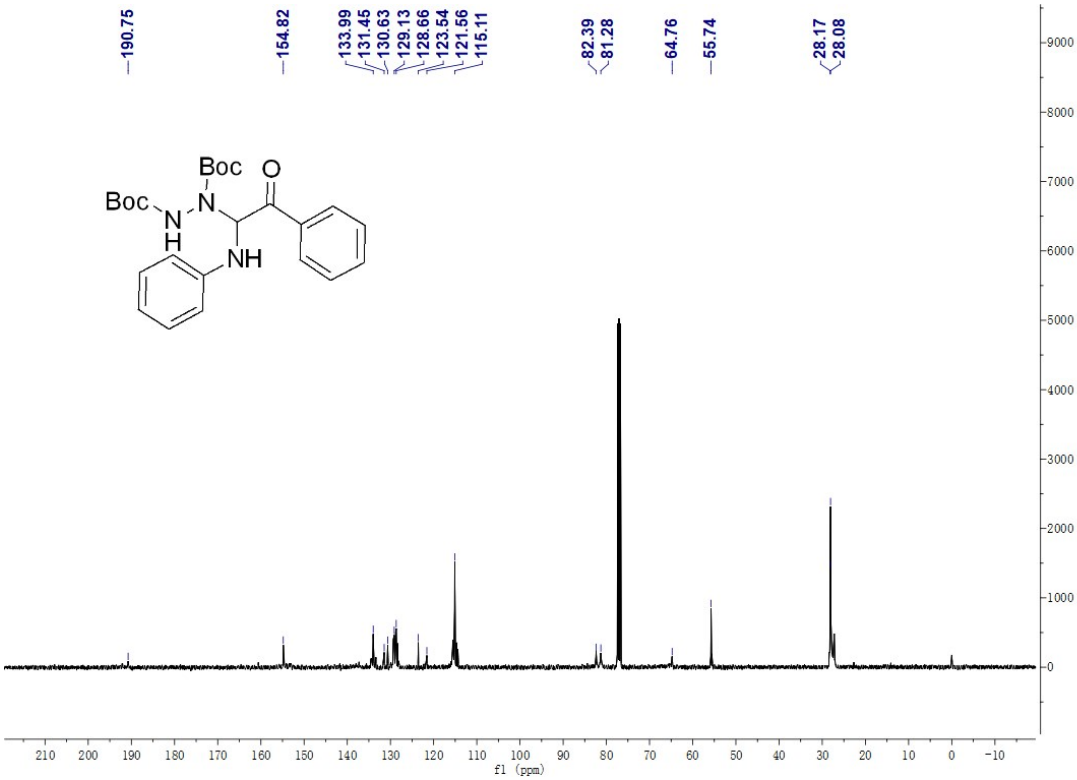


^{1}H NMR of **13**



^{13}C NMR of **13**



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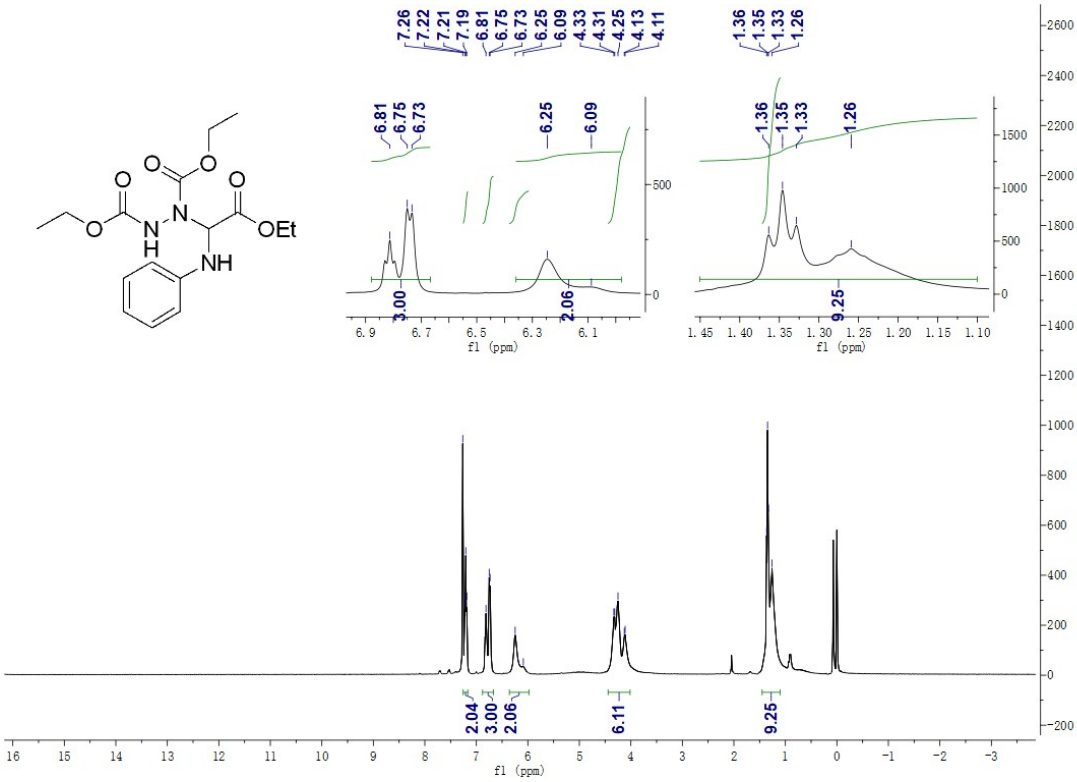
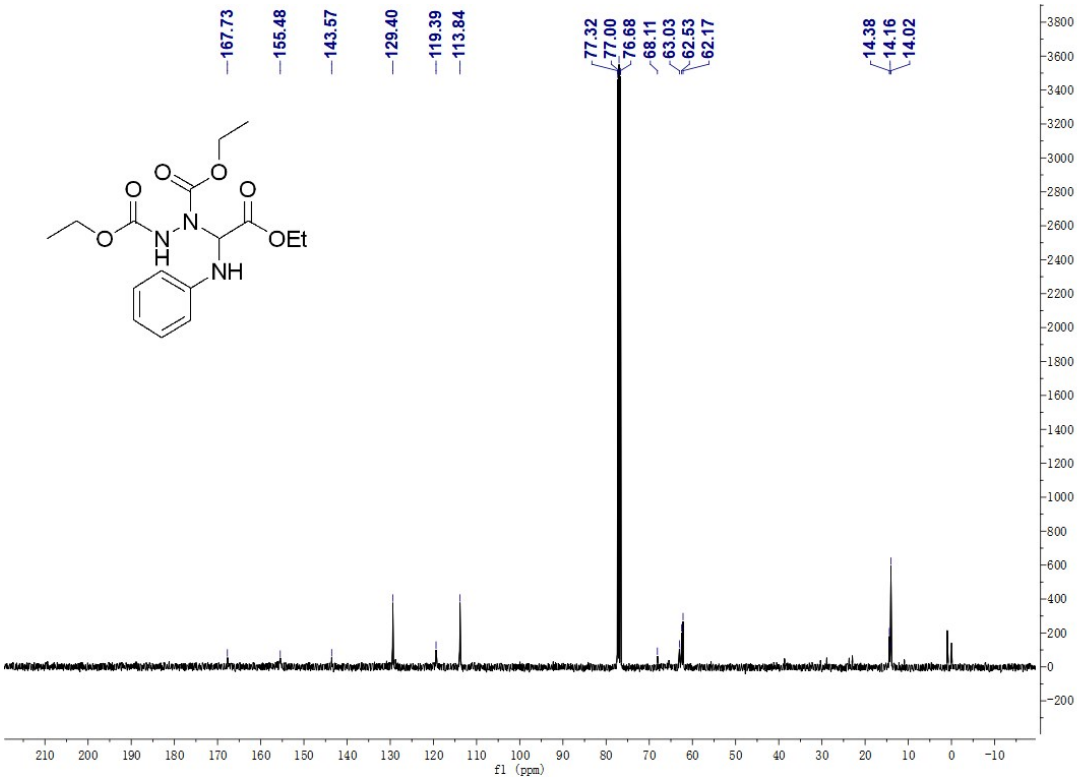
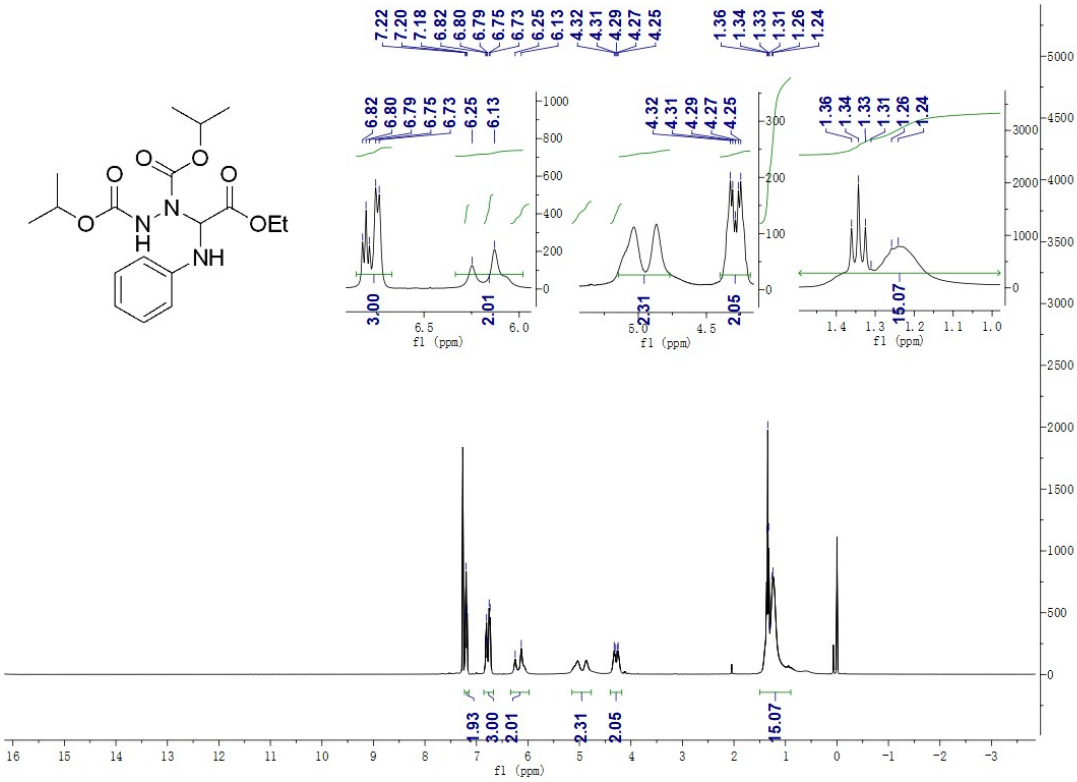


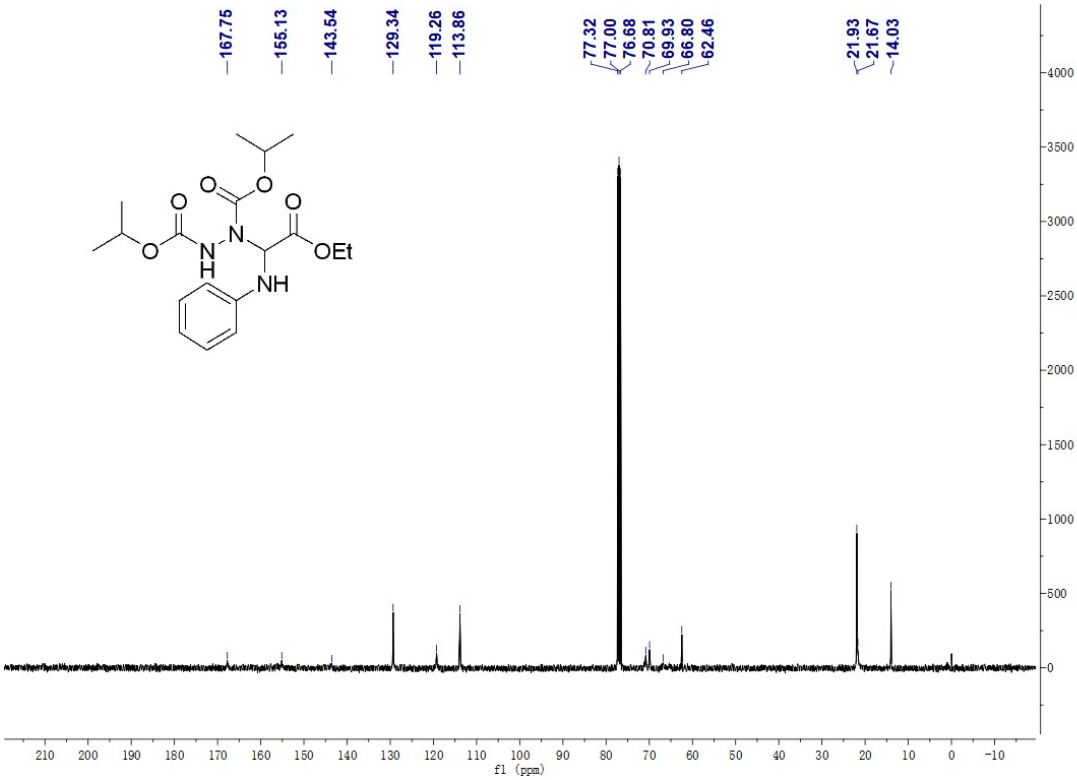
^{13}C NMR of **16**



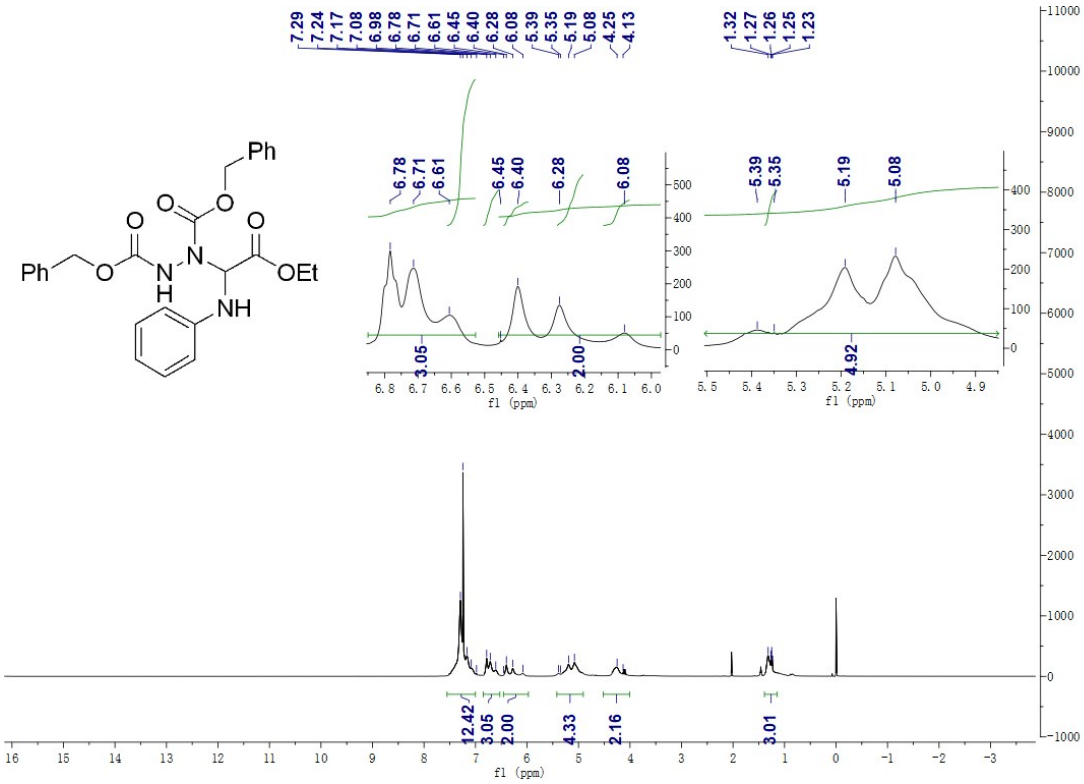
^{1}H NMR of **17**



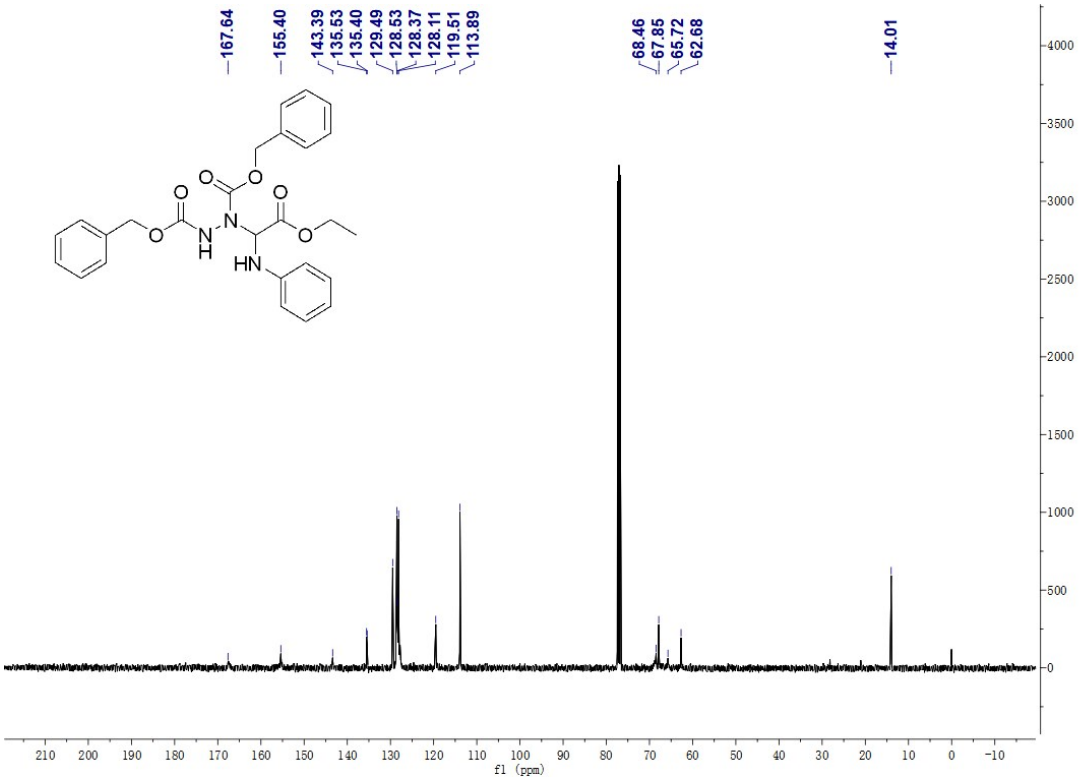
^{13}C NMR of **17**



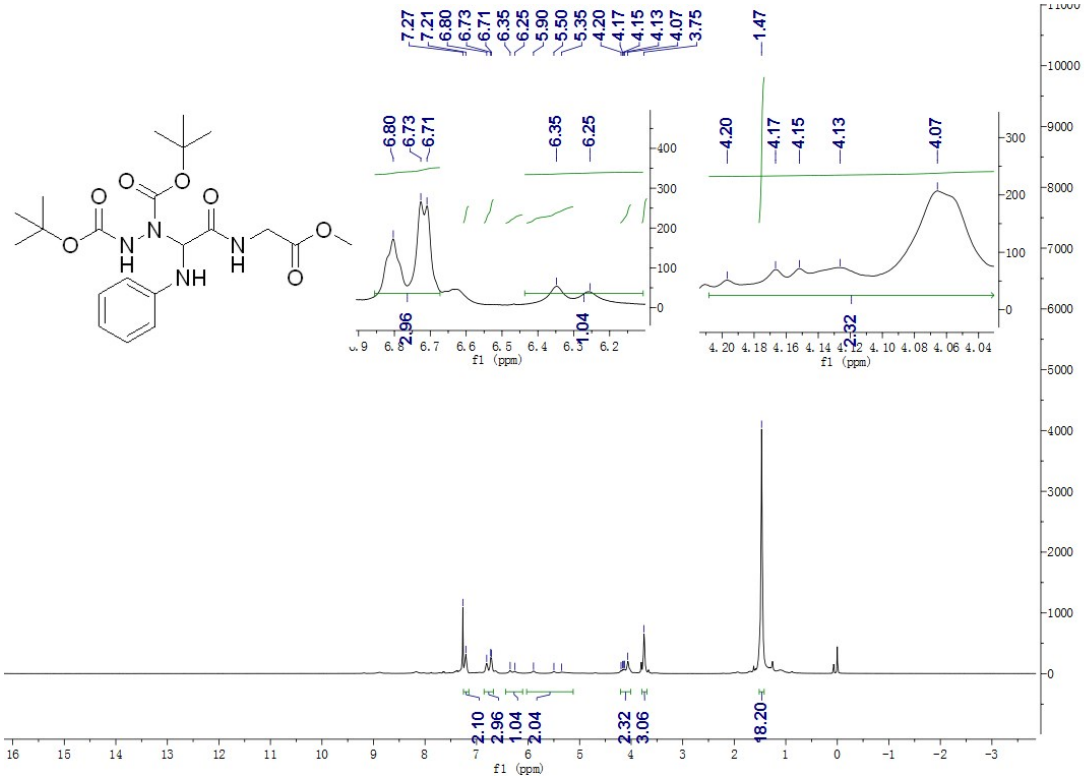
^{1}H NMR of **18**



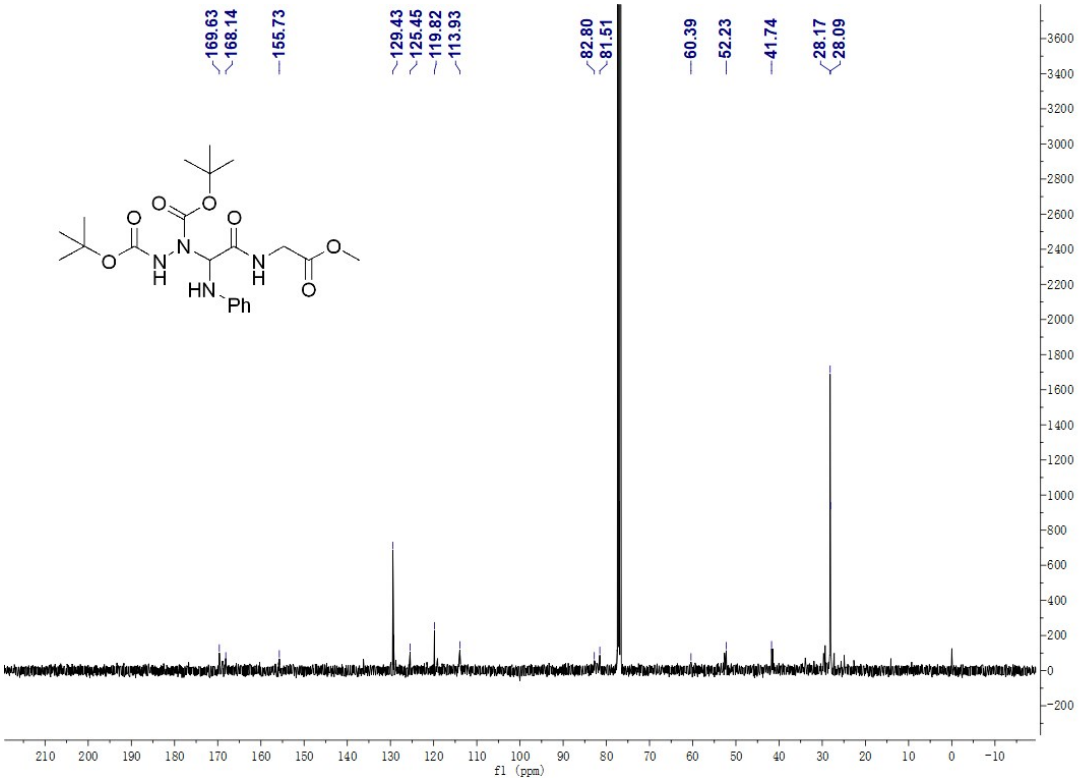
^{13}C NMR of **18**



^{1}H NMR of **21**



^{13}C NMR of **21**



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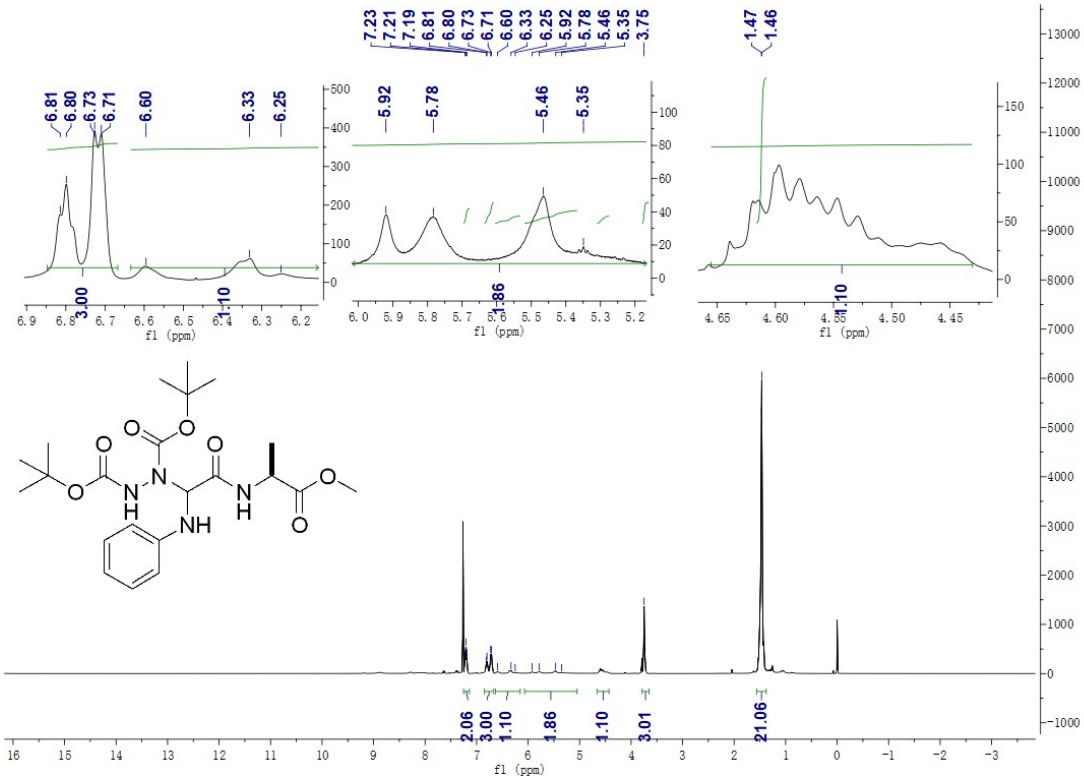
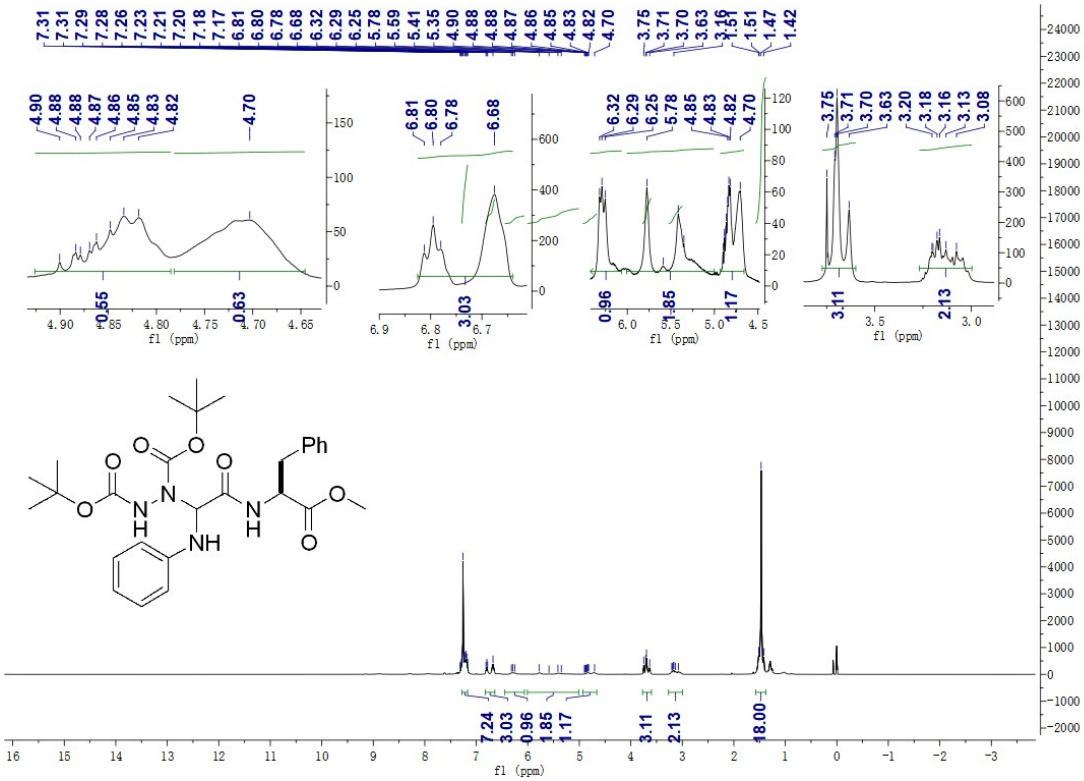
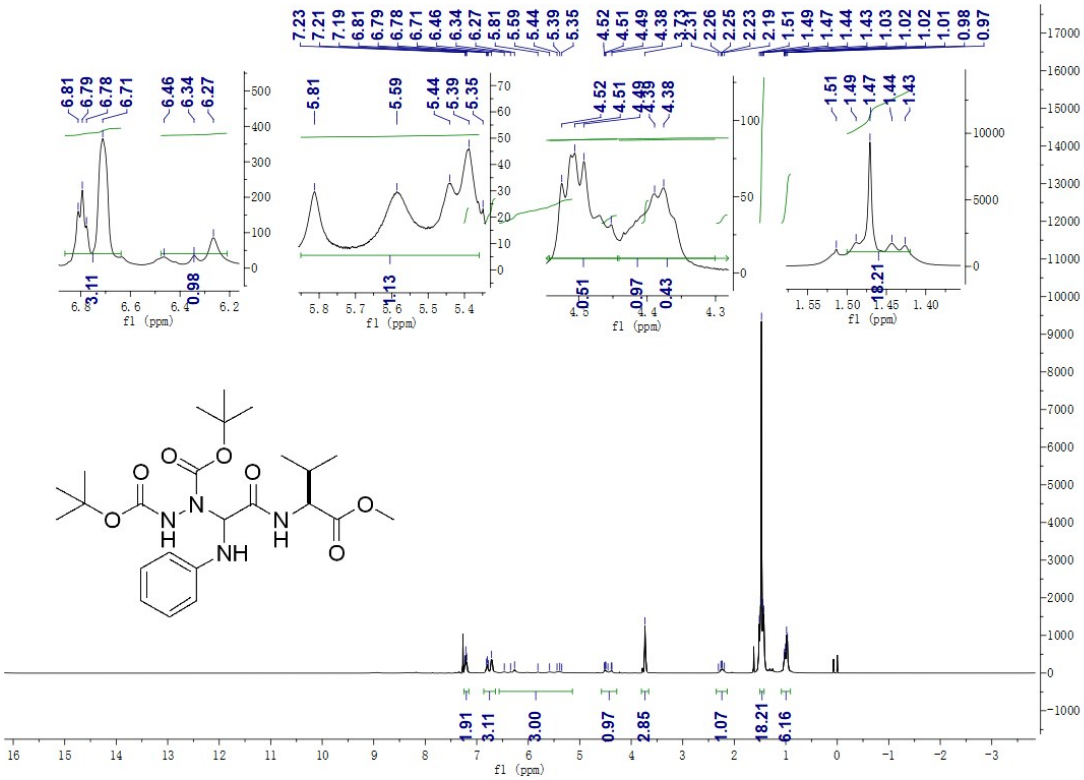


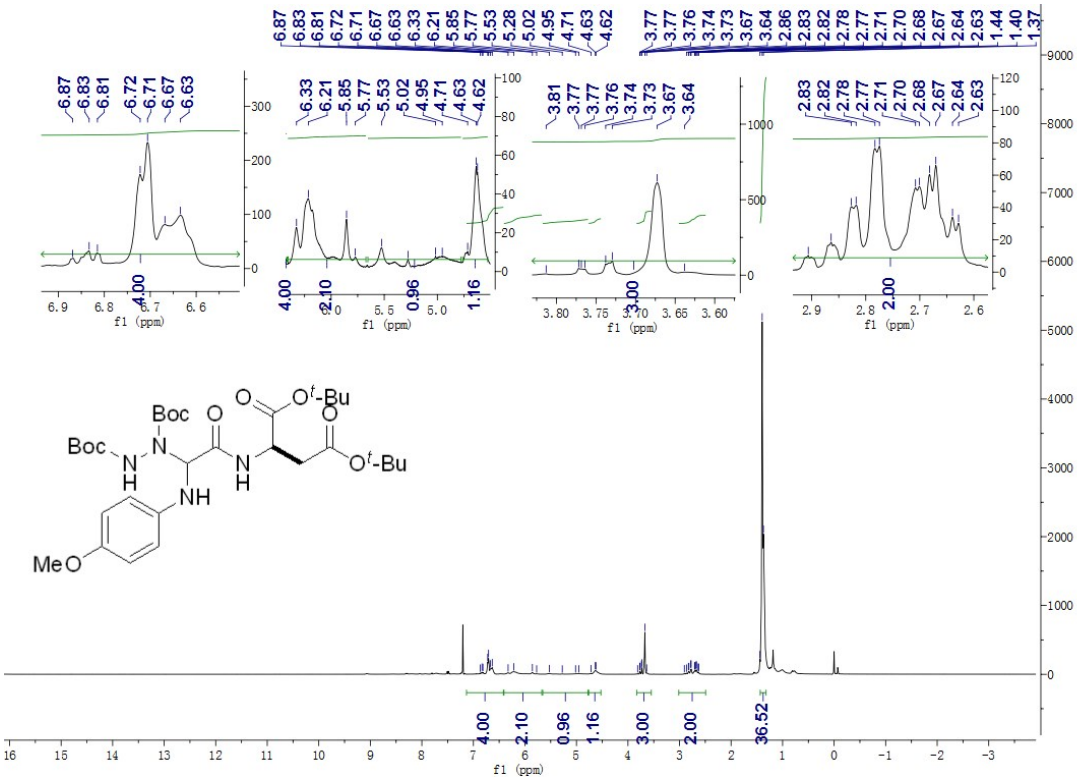
^{1}H NMR of **23**



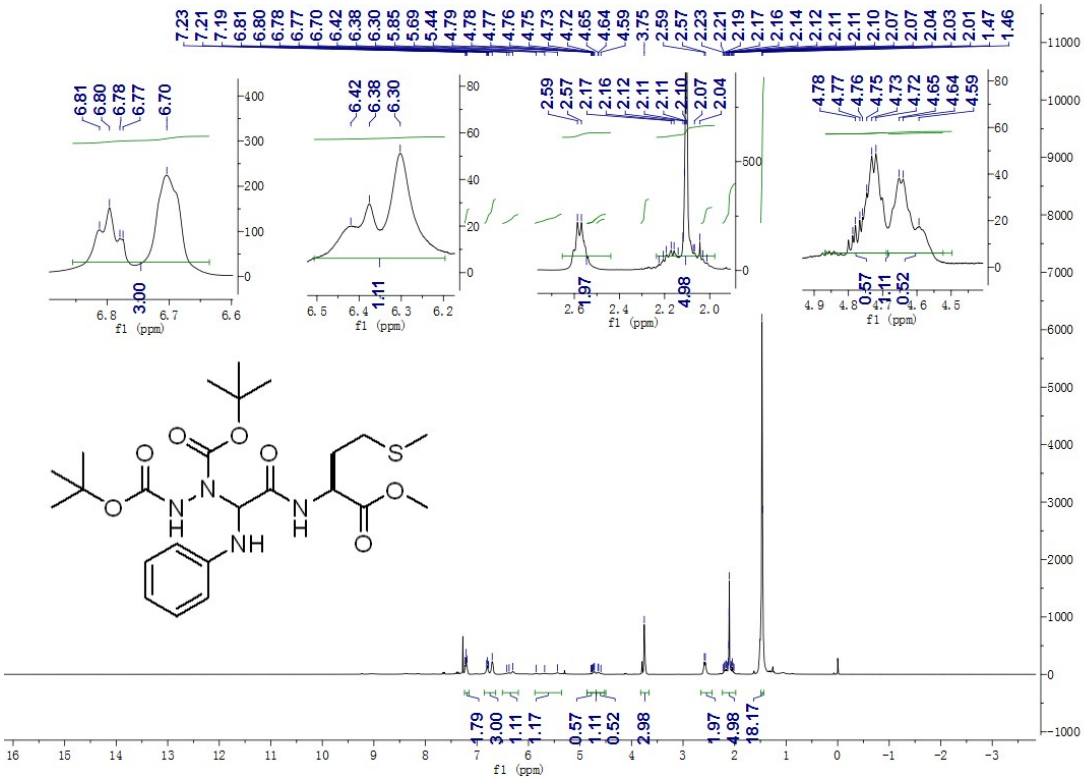
^{1}H NMR of **24**



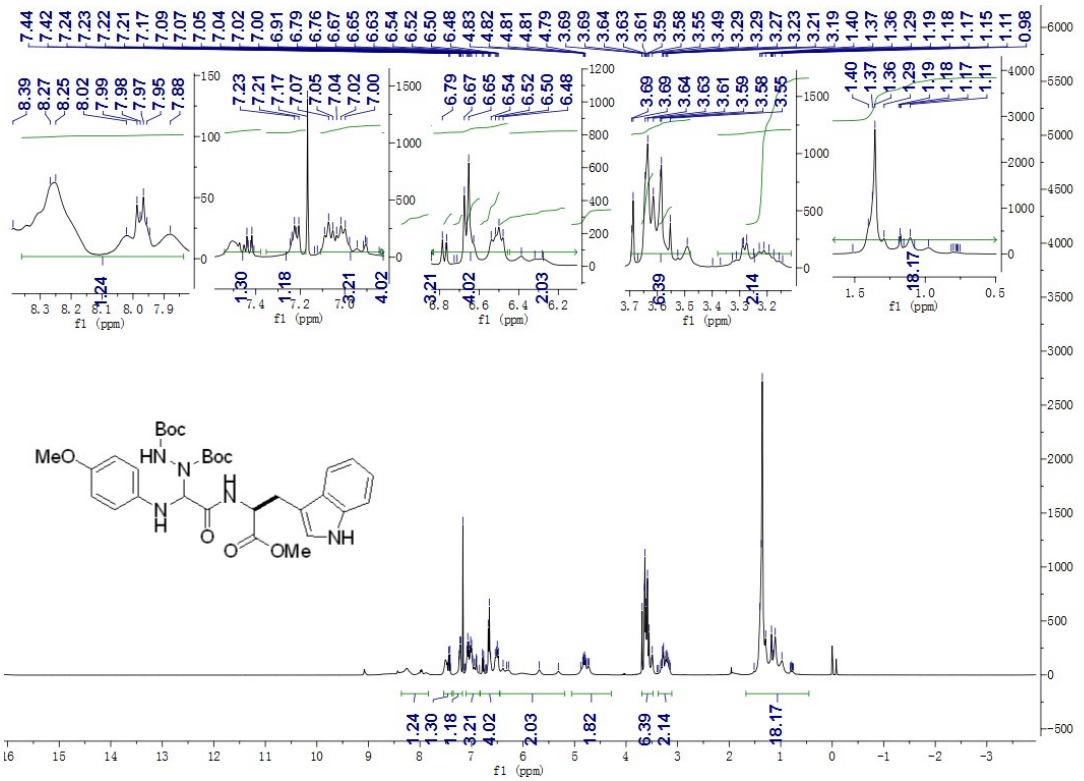
^{1}H NMR of **25**



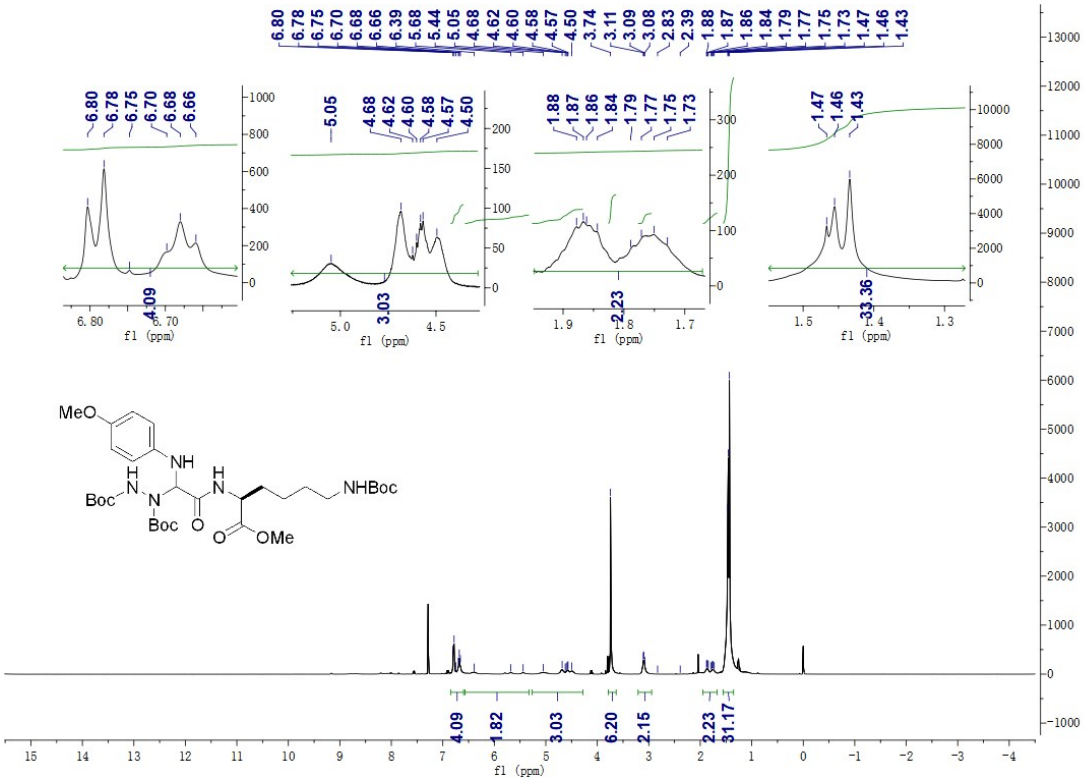
^{1}H NMR of **26**



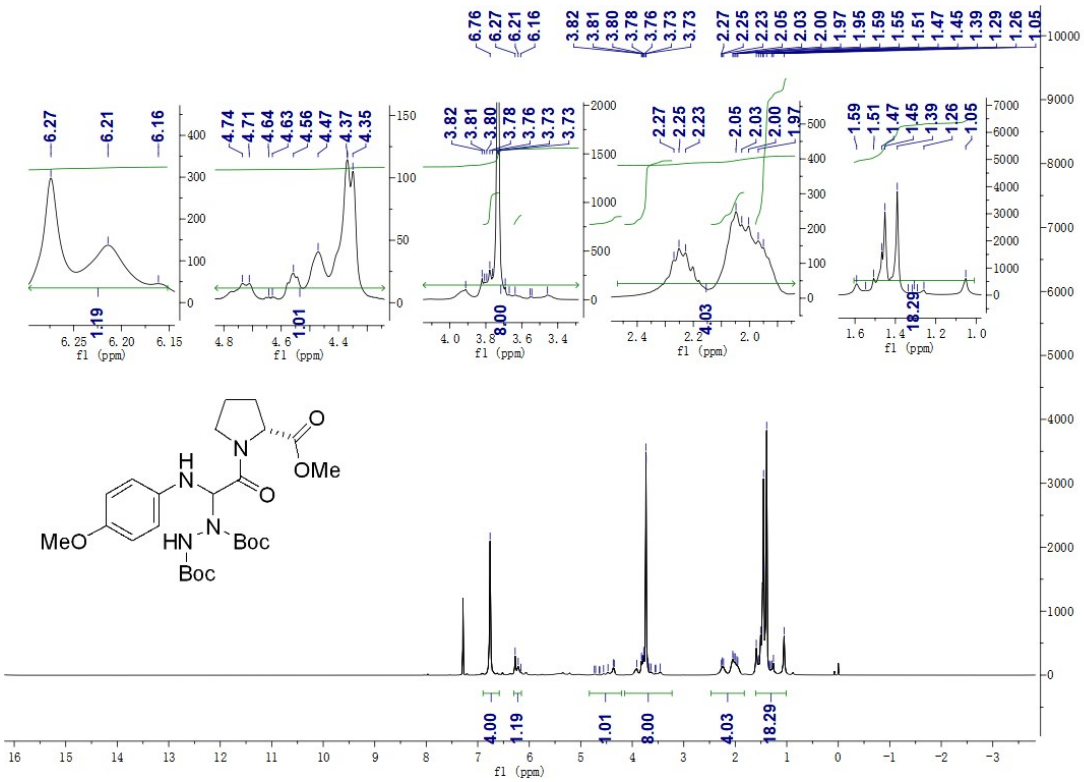
^{1}H NMR of **27**



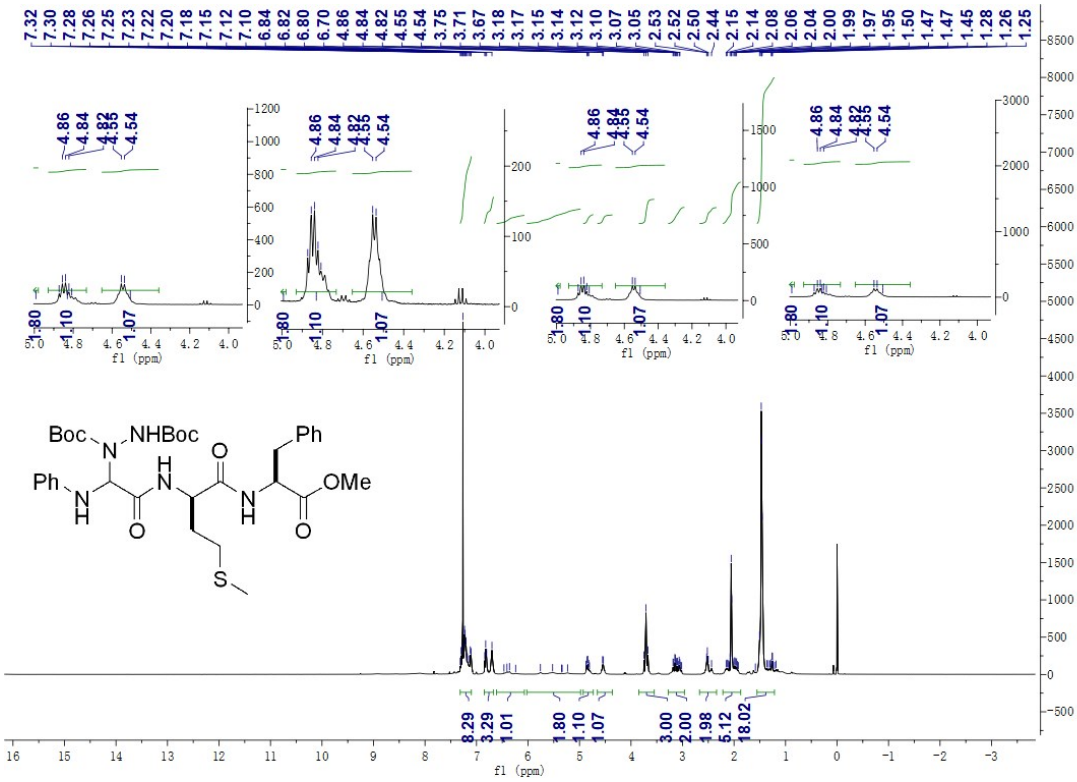
^{1}H NMR of **28**



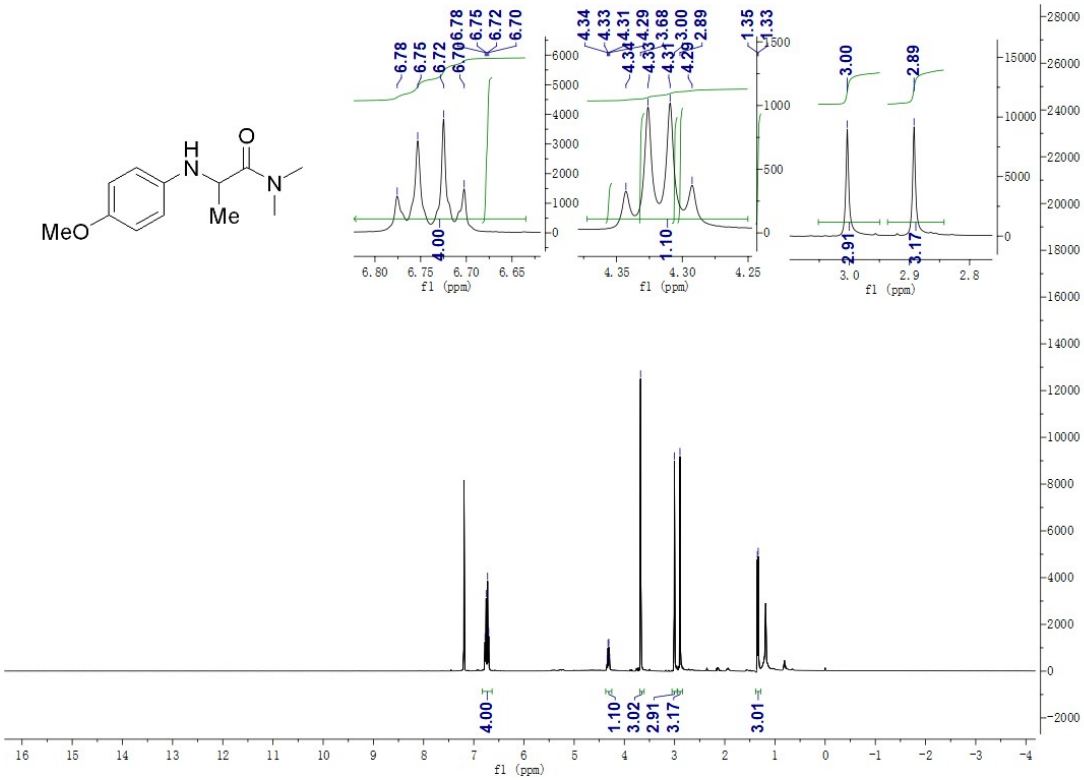
^{1}H NMR of **29**



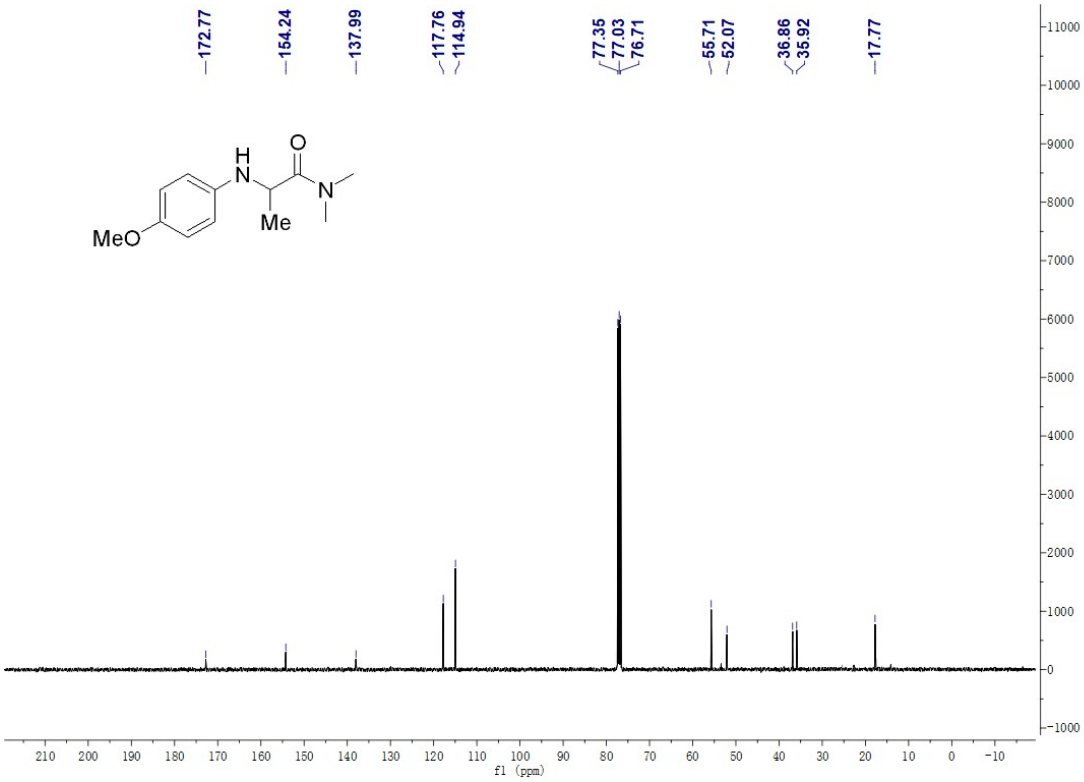
^{1}H NMR of **30**



^{1}H NMR of **31**



^{13}C NMR of **31**



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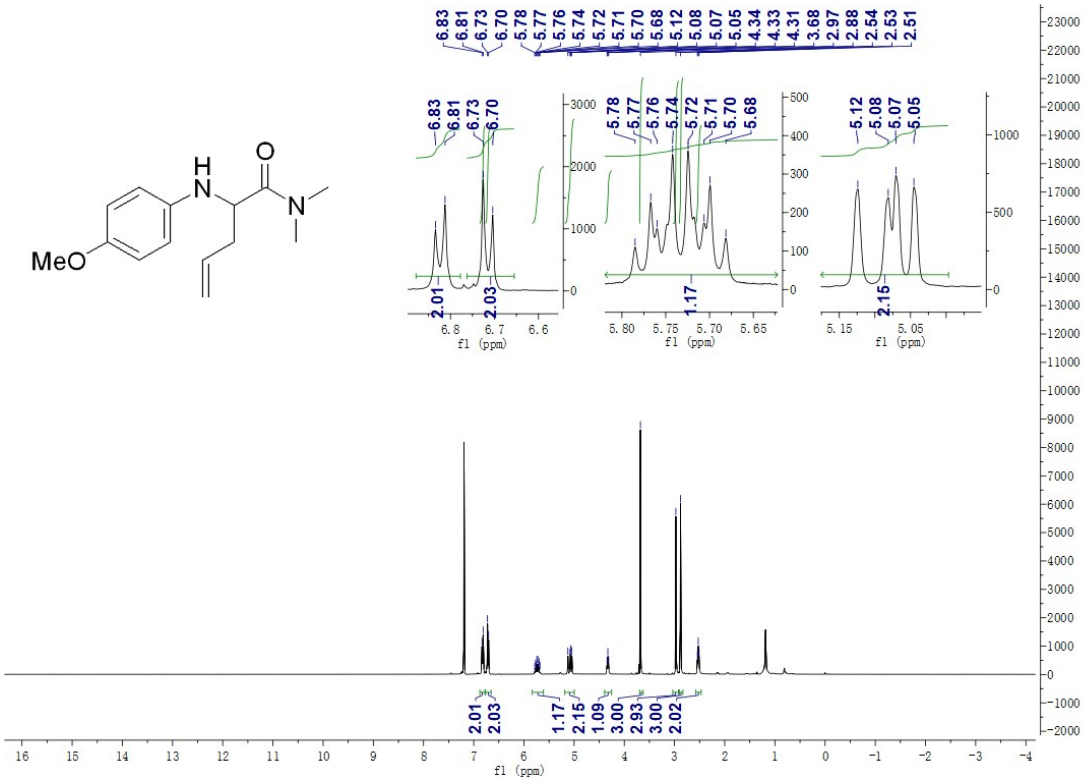

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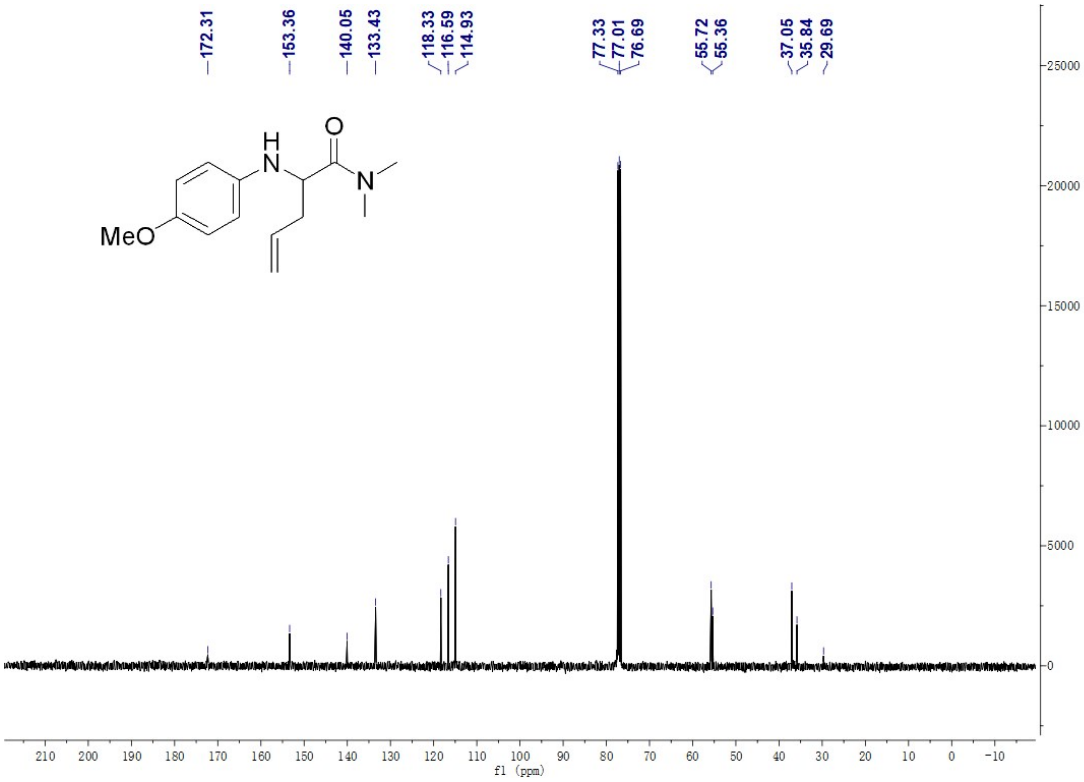

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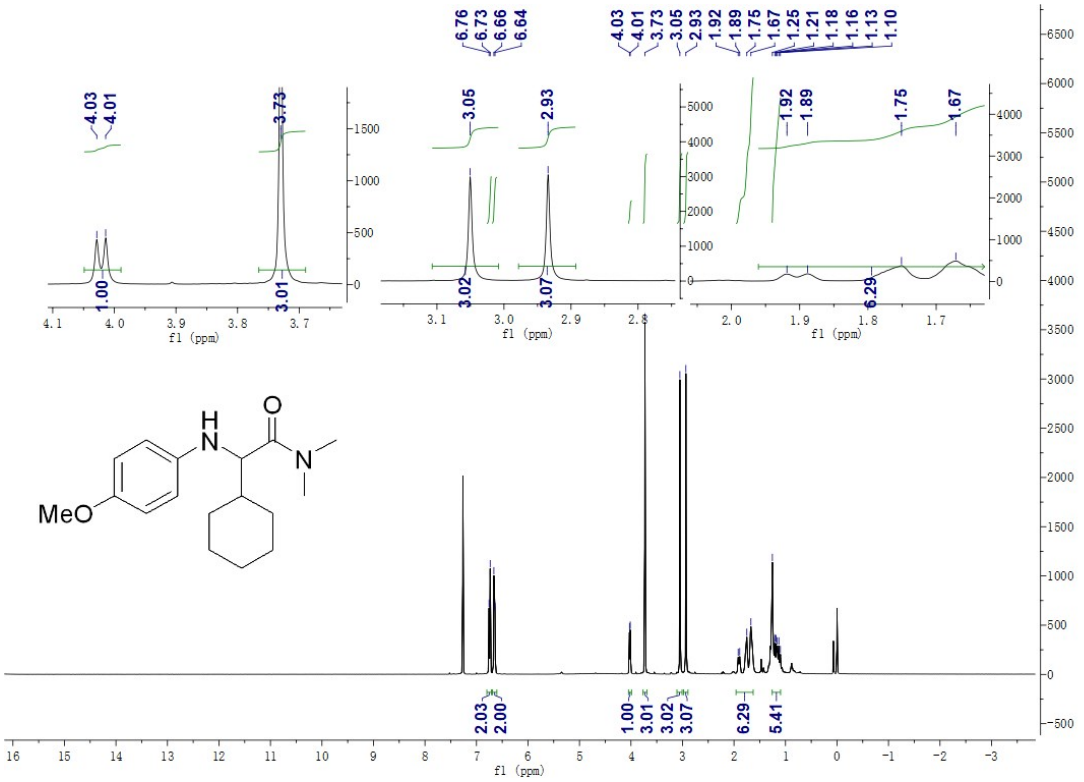

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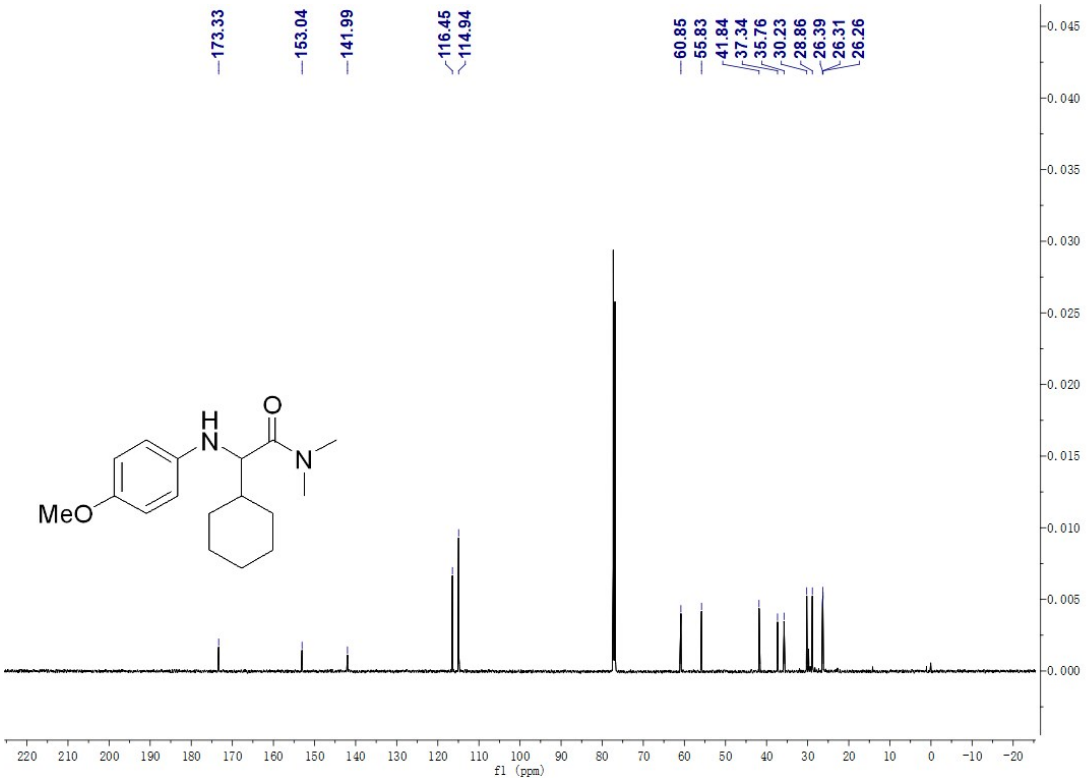
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41.84
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26.31
26.26
MeO
H
N
O
N
f1 (ppm)