Supporting information

Zirconium Photocatalysis for Direct C(sp^3)−H Functionalization, Decarboxylative Amination, and Polystyrene Oxidative Degradation

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Content

1. General information

1.1. Materials and Methods

All reagents were purchased from Aldrich Chemical, Alfa Aesar, TCI, Adamas, Energy Chemical, or J&K at the highest commercial quality and used without further purification. Polystyrene standard (average Mw ~ 260,000) was purchased from J&K, and polystyrene standards (average Mw ~ 350,000 and average Mw ~ 192,000) were purchased from Macklin. Waste polystyrene materials were collected from daily life and used without further purification. Reactions were monitored by UPLC/MS and thin layer chromatography (TLC), using shortwave UV light as the visualizing agent, phosphomolybdic acid (PMA), $KMnO_4$ and heat, and I_2 as developing agents. NMR spectra were recorded on Varian 400 instruments and are calibrated using residual undeuterated solvent ($CHCl_3$ at 7.26 ppm ^1H NMR, 77.16 ppm ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ^1H NMR spectra were recorded at 500 MHz or 400 MHz, ^{13}C NMR spectra were recorded at 126 MHz or 101 MHz. GC analyses were performed on an Agilent 8890 gas chromatograph with an FID detector using a SH-I-5HT column (30m × 0.25 mm, 0.1 μm film). UPLC/MS analyses were performed on a Waters system with a Photodiode Array (PDA) detector and a Single Quadrupole (SQ) detector. High Resolution Mass spectra were obtained from on an Agilent 1290 LC-6540 QTOF Mass Spectrometer or an Agilent Technologies 7250 GCQTOF. HPLC analyses were carried out on Agilent 1200 Series system, using Daicel CHIRALCEL® columns or Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm). Weight-average molecular weights (M_w), number-average molecular weights (M_n) and dispersity index (PDI) of polymers were determined by gel permeation chromatography (GPC). GPC was performed using GPC−IR from Polymerchar. UV−Vis spectra was recorded on a Thermo Scientific NanoDrop spectrophotometer.

1.2. Reaction setup

The reactions were performed on PhotoSyn-10 parallel photoreactor. PhotoSyn-10 parallel photoreactor (5 W Blue LEDs, per lamp) was purchased from Shanghai Quanhuan Technology Co., Ltd., 4 mL sealing tubes were used for all 0.2 mmol scale reactions, and 25 mL sampling bottles with sealing caps were used for all 0.4 and 1.0 mmol scale reactions.

Figure S1 Left: Reaction sealing tubes，sampling bottles, and the manual bottle capping tools; Middle: The PhotoSyn-10 parallel photoreactor; Right: Parallel reaction setup under photoreactor.

2. Reaction development

2.1. Experimental phenomena

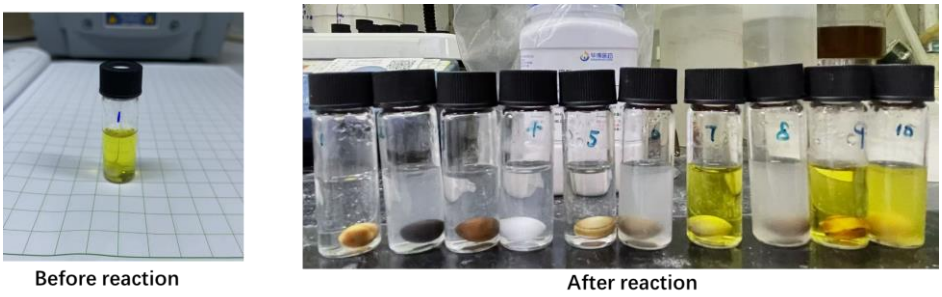


Figure S2 Color change of $ZrCl_4$-catalyzed alkane functionalization using DBAD as trapping reagents.

During the initial evaluation of the LMCT ability of $ZrCl_4$, the color change of each entry was recorded (**Figure S2**). *n*-hexane and DBAD were used as the substrates. Before the reaction, the addition of DBAD results in a yellow solution (**Figure S2**, left). After irradiated and reacted, entries 1−6 and entry 8 showed a complete disappearance of color, indicating the complete conversion of DBAD, while entry 7 and entries 9−10 still showed a yellow color, indicating the low transformation of these entries and the low yield of the final products (**Figure S2**, right).

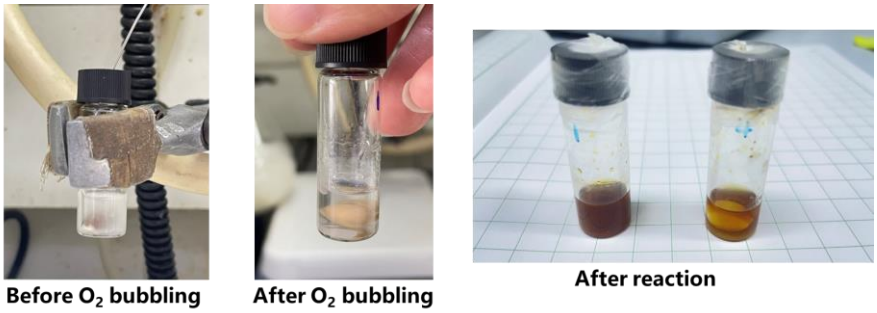
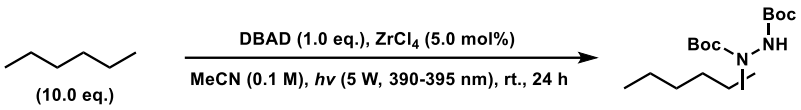


Figure S3 Color change of $ZrCl_4$-catalyzed PS degradation.

During the optimization of $ZrCl_4$-catalyzed PS degradation process, the color change was recorded (**Figure S3**). When the PS sample was completely dissolved in DCM, the solution was colorless and transparent. However, when the $ZrCl_4$/MeCN stock solution was added, the mixture became cloudy, mainly because of the low solubility of PS in MeCN (**Figure S3**, top left). Then, after O_2 bubbling under stirring, the mixture was separated, showing some undissolved PS solid in a transparent solution (**Figure S3**, top right). Just after 2−4 h stirring under light irradiation, the color of the mixture was darkened and turned into dark brown, and this color was kept until the reaction was stopped and taken out of the photoreactor (**Figure S3**, bottle).
Notice: O_2 ballon was attached to the sampling bottle throughout the photoreaction.

2.2. Control experiments based on *n*-hexane

Table S1 Control experiments on $ZrCl_4$ and light[a]



entry	deviations	total yield (%)
1	None	85%
2	no $ZrCl_4$	n.r.
3	in dark	n.r.

[a]Reaction conditions: *n*-hexane (2.0 mmol, 10.0 eq.), DBAD (0.2 mmol, 1.0 eq.), $ZrCl_4$ (0.01 mmol, 5.0 mol%), MeCN (2.0 mL, 0.1 M), Ar atmosphere, room temperature, 24 h, irradiation with 5 W LEDs.

2.3. Comparison with Ce system

As summarized in **Figure S4**, Equation (A) is the reproduction of Zuo's cerium condition[1] in our lab. Equation (B) is our optimized condition using $ZrCl_4$. Equation (C) and (D) are orthogonal experiments, where (C) only substituted the $CeCl_3$ in Zuo's condition into $ZrCl_4$, and (D) only substituted the $ZrCl_4$ in our condition into $CeCl_3$.

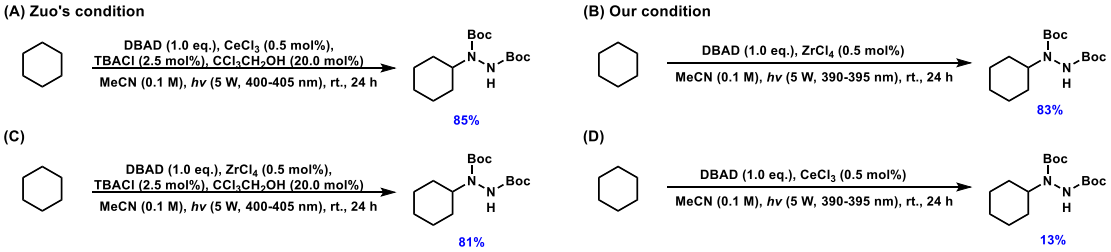


Figure S4 Comparison with Zuo's cerium system

Equation (A) and (B) showed that both catalytic systems have a close and high efficiency. In Equation (C), we observed a slight increase in yield from 60% to 81% when only an additional alcohol catalyst is added (Comparing to **Table 1**, entry 7). We would like to propose that an additional alcohol radical was also formed just as that in the Zuo's condition. In Equation (D), a sharp decrease was observed when no additional Cl source was added. This fits the previous reports that cerium can only present its photoactivity in the $[CeCl_6]^{2-}$ form[1,2]. However, $ZrCl_4$ can directly be activated without the need of another Cl source, showing its differences comparing to $CeCl_3$.

2.4. Unsuccessful examples of radical trapping reagents

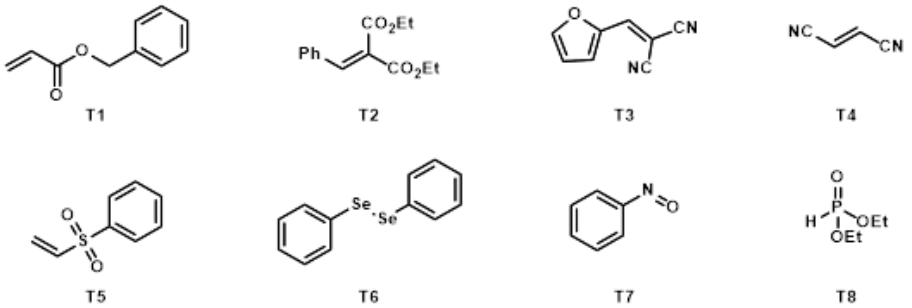
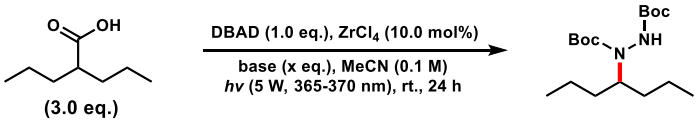


Figure S5 Unsuccessful examples of radical trapping reagents

Figure S5 listed the unsuccessful examples of radical trapping reagents in the direct C(sp^3)−H functionalization procedure using cyclohexane as the alkane species. **T1** gave a messy result; while **T2**, **T3**, **T6**−**T8** all showed almost no reaction. Although **T4** and **T5** reacted with cyclohexane to give the corresponding products, the low yield (< 10%) and the similar polarity between products and unreacted **T4** or **T5** on TLC make the purification very difficult. We proposed that these unsuccessful results attribute from the mismatch redox potential between the Zr(III)Cl_3 species and the radical adduct intermediates. Therefore, we believed that adding an additional photocatalyst (as the Zuo's Ce system[3]) or an appropriate oxidant or reductant can help promote the electron transfer from Zr(III) to the radical adducts, thus furnishing the catalytic circle to obtain the desired products.

2.5. Optimization for decarboxylative amination of acyclic acids

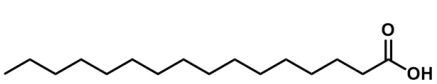
Table S2 Optimization of decarboxylative amination of acyclic acids[a]



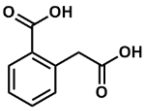
entry	base (x eq.)	yield (%)
1	K_2CO_3 (1.0)	n.r.
2	Cs_2CO_3 (1.0)	n.r.
3	NaOH (3.0)	n.r.
4	tBuOK (3.0)	decompose
5	DBU (3.0)	decompose
6	tBuOK (1.0)	39%
7	DBU (1.0)	69%

[a]Reaction conditions: valproic acid (0.6 mmol, 3.0 eq.), DBAD (0.2 mmol, 1.0 eq.), $ZrCl_4$ (0.01 mmol, 5.0 mol%), base, MeCN (2.0 mL, 0.1 M), Ar atmosphere, room temperature, 24 h, irradiation with 5 W LEDs. n.r. = no reaction.

2.6. Unsuccessful examples for decarboxylative amination

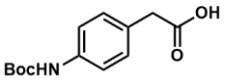


S1



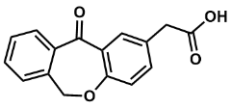
S2

Compound **S1** (palmitic acid) and compound **S2** (homophthalic acid) gave no desired decarboxylative amination product even when reaction time was lengthened to 48 h. We proposed that the limited solubility of these two substrates in the MeCN solvent result in their failure.



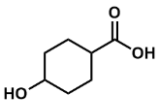
S3

After the reaction, compound **S3** was transformed to an inseparable mixture of the desired product and a byproduct that shows further hydrazination probably at the benzylic position with a total yield of 53%. This mixture was messy on ^{1}H NMR, and the byproduct was postulated according to LC−MS (with an excess ES^{+} = 230, which is the molecular weight of DBAD).

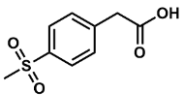


S4

Presumably due to the diphenyl ketone moiety in compound **S4** (Isoxepac), which is a light-sensitive functional group that can undergo Norrish-Yang type reaction, messy result was obtained. Efforts on isolating the product failed.

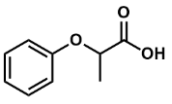


S5

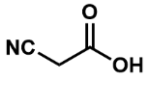


S6

Compounds with unprotected hydroxyl (**S5**) or sulphonyl (**S6**) group were not tolerated in this transformation. We proposed that alcohol -OH has a higher binding affinity to zirconium compared to carboxyl -COOH, which could be toxic to the LMCT process. On the other hand, phenyl sulphonyl group is considered to be sensitive to radicals (in many reports, phenyl sulphonyl group is a good leaving group under radical addition), thus resulting in messy result.



S7

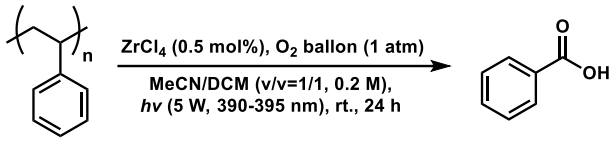


S8

Compound **S7** and **S8** showed no reaction under the present conditions. We believed that this may result from the mismatched pKa values of these two compounds and the bases (either K_2CO_3 or DBU) that we used.

2.7. Optimization of Zr-catalyzed PS degradation

Table S3 Reaction Optimization of PS degradation[a]



ca. 20.8 mg
(0.2 mmol per monounit)

entry	deviations	yield (%)
1	None	20%
2	no $ZrCl_4$	trace
3	in Ar	0%
4	$ZrCl_4$ (2.5 mol%)	22%
5[b]	48 h	30%
6[b]	MeCN/EA (v/v=1/2, 0.13 M)	0%

[a]Reaction conditions: PS samples (~20.8 mg, ~0.2 mmol per monounit), $ZrCl_4$ (0.001 mmol, 0.5 mol%), MeCN/DCM (v/v=1/1, 1.0 mL, 0.2 M), O_2 ballon (1 atm), room temperature, 48 h, irradiation with 5 W 390−395 nm LEDs, the BA yield was confirmed by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard; [b]2.5 mol% of $ZrCl_4$ was used.

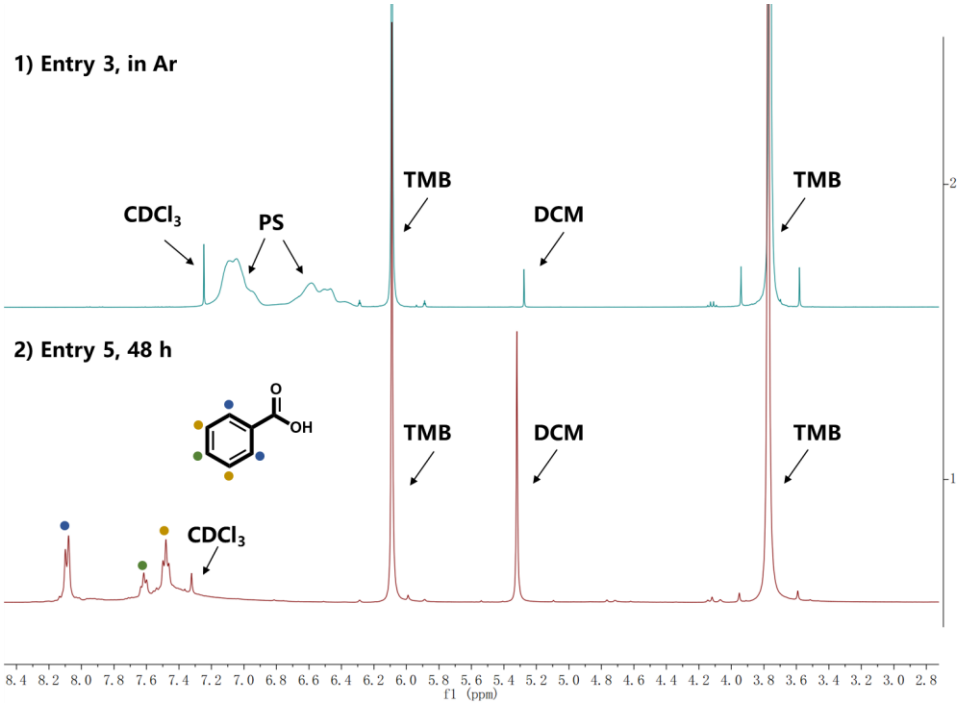


Figure S6 Crude ^{1}H NMR of entry 3 and entry 5. 1,3,5-trimethoxybenzene (TMB) was added as the internal standard.

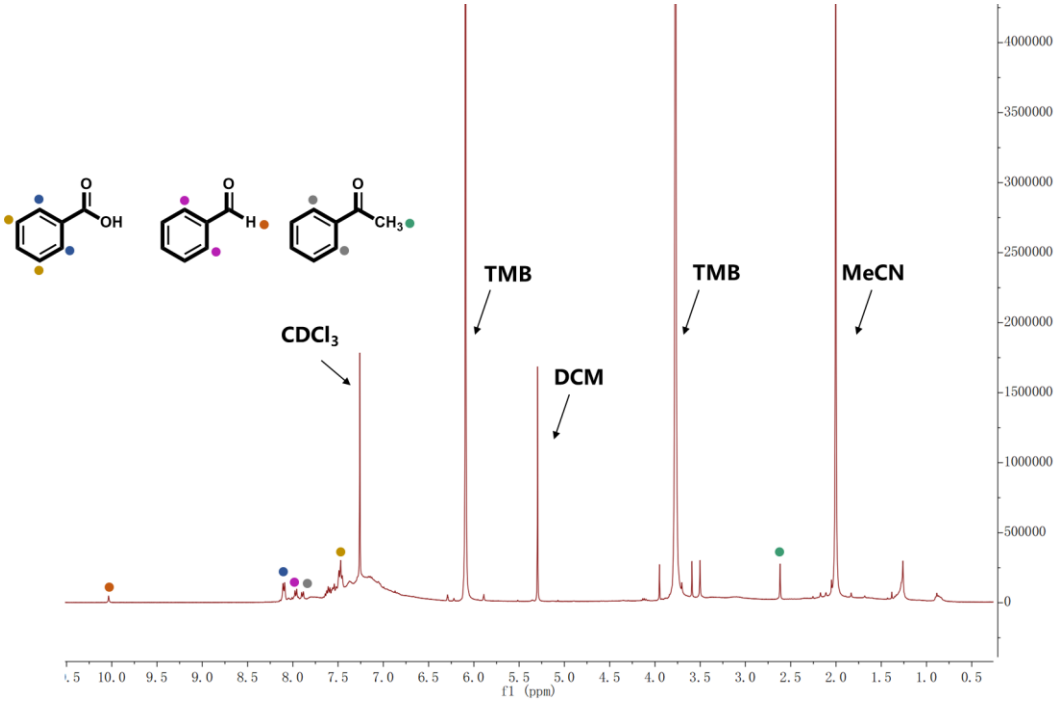


Figure S7 Small molecule products that can be visualized on crude ^{1}H NMR (Reaction optimization, entry 1). 1,3,5-trimethoxybenzene (TMB) was added as the internal standard. Signals for benzoic acid, benzaldehyde, and acetophenone were recorded.

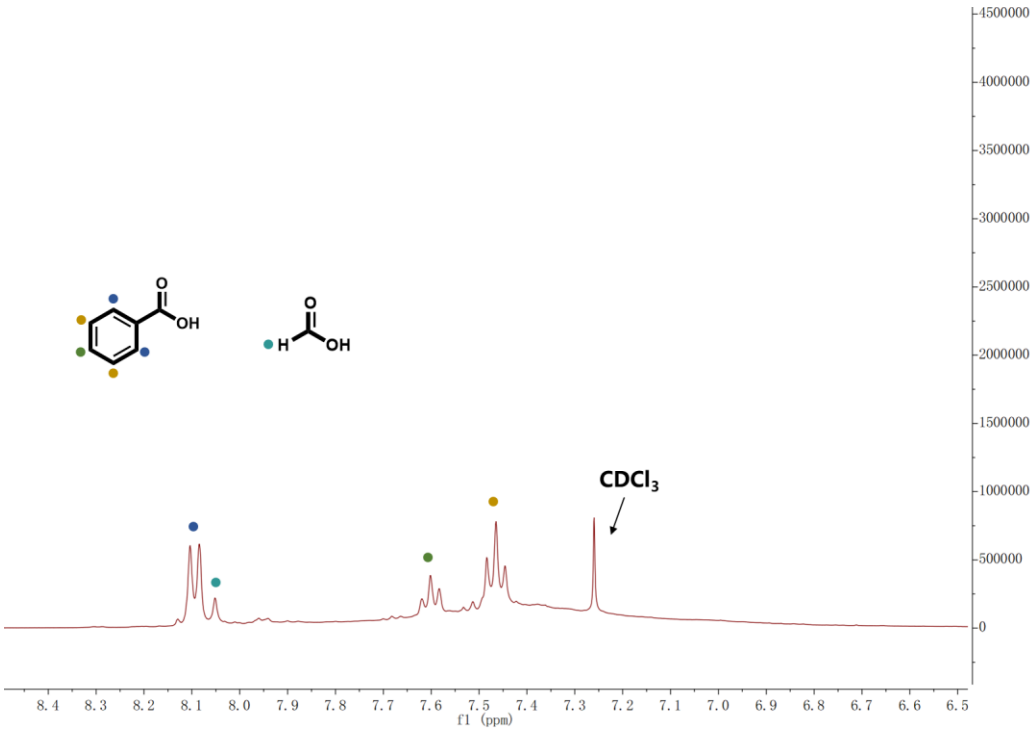


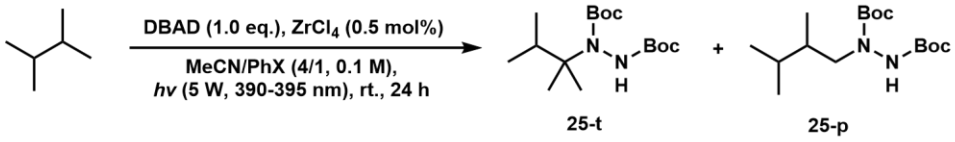
Figure S8 Small molecule products that can be visualized on crude ^{1}H NMR (degradation of EPS foam). 1,3,5-trimethoxybenzene (TMB) was added as the internal standard. Signals for benzoic acid and formic acid were recorded.

3. Studies of regioselectivity on feedstock alkanes

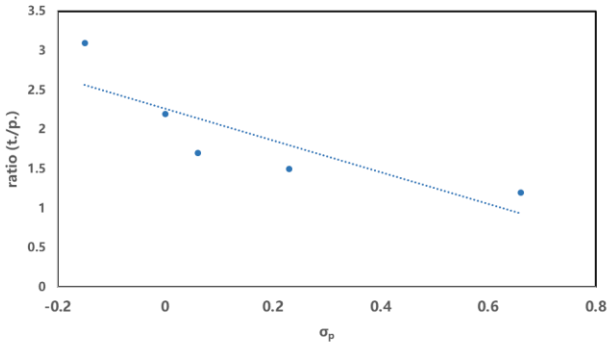
During our exploration on the $ZrCl_4$-catalyzed functionalization of feedstock alkanes, we unexpectedly found that introducing an appropriate amount of benzene (PhH) as a co-solvent markedly improved regioselectivity for adamantane functionalization, increasing the tertiary/secondary ratio from 1.1:1 to 2.6:1. To the best of our knowledge, the regioselectivity of feedstock alkane functionalization can often be modulated by ligands or substituents directly coordinated to the reactive center when oxygen-[1,4,5]or nitrogen-centered radicals[6–11], carbenes[12,13], or boron-based coupling partners[14–16] are employed. However, modulation of a single Cl·-based regioselectivity in non-boronation processes has remained a long-standing challenge[17,18]. This serendipitous observation prompted us to investigate the phenomenon in detail, with the aim of gaining mechanistic insight and developing a general strategy for controlling regioselectivity in Cl·-mediated reactions. Here, we used 2,4-dimethylbutane as a model substrate to evaluate the influence of different factors.

3.1. Arene electron density and regioselectivity

Scheme S1 Arene electron density and regioselectivity[a]



entry	X	σ_p	ratio (t./p.)[b]
1	-	-	1/1.3
2[c]	-^{i}Pr	-0.15	3.1/1
3	-H	0	2.2/1
4	-F	0.06	1.7/1
5	-Cl	0.23	1.5/1
6	-CN	0.66	1.2/1

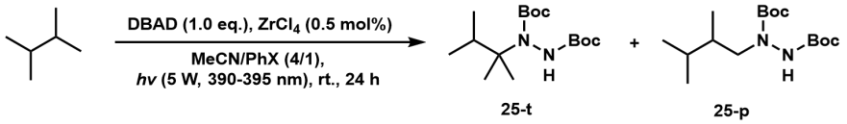


[a]Reaction conditions: 2,3-dimethylbutane (2.0 mmol, 10.0 eq.), DBAD (0.2 mmol, 1.0 eq.), $ZrCl_4$ (0.01 mmol, 5.0 mol%), cosolvents of MeCN and PhX (total: 2.0 mL, 0.1 M), Ar atmosphere, room temperature, 24 h, irradiation with 5 W LEDs; [b]The tertiary/primary product ratio was calculated from crude ^{1}H NMR; [c]The tertiary/primary product ratio was calculated from GC−MS.

The Hammett σ_p parameter[19] was used to quantify the influence of arene substituents (**Scheme S1**). Both electron-donating and electron-withdrawing groups inverted the regioselectivity, favoring substitution at the thermodynamically more stable tertiary site. A clear negative correlation emerged: as σ_p increased, the tertiary/primary product ratio decreased.

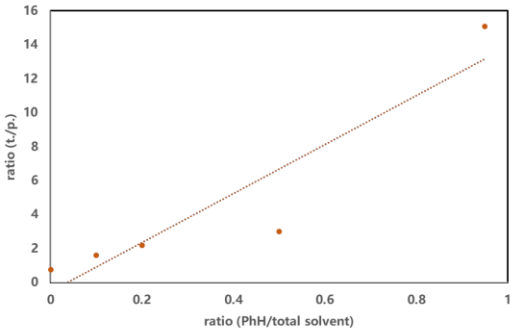
3.2. PhH proportion and regioselectivity

Scheme S2 PhH proportion and regioselectivity[a]



25-t 25-p

entry	conc.	MeCN/PhH	ratio (t./p.)[b]
1	0.1 M	1/0	1/1.3
2	0.1 M	9/1	1.6/1
3	0.1 M	4/1	2.2/1
4	0.1 M	1/1	3.0/1
5[c]	0.1 M	1/19	15.1/1
6	0.05 M	4/1	2.8/1
7	0.2 M	4/1	1.7/1
8	0.4 M	4/1	1.5/1



[a]Reaction conditions: 2,3-dimethylbutane (2.0 mmol, 10.0 eq.), DBAD (0.2 mmol, 1.0 eq.), $ZrCl_4$ (0.01 mmol, 5.0 mol%), cosolvents of MeCN and PhH, Ar atmosphere, room temperature, 24 h, irradiation with 5 W LEDs; [b]The tertiary/primary product ratio was calculated from crude ^{1}H NMR; [c]The tertiary/primary product ratio was calculated from GC−MS.

We next explored the effect of benzene loading (**Scheme S2**, entries 1−5). In all cases, tertiary substitution predominated, in contrast to the outcome without benzene. Under otherwise identical conditions, regioselectivity increased with benzene content, reaching a ratio of 15.1:1 when benzene served as the primary solvent (with only 0.1 mL of $ZrCl_4$/MeCN stock solution added). Varying the overall reaction concentration had little effect; instead, the selectivity trends correlated directly with the proportion of benzene (**Scheme S2**, entries 6−8).

Taken together, these findings suggest that a [Cl·---Ar] complex plays a pivotal role in modulating regioselectivity. In the absence of aromatic additives, hydrogen atom abstraction (HAT) by free Cl· is extremely rapid, and primary C−H bonds, which are both statistically and dynamically favored, are preferentially activated, leading to predominance of the primary-substituted product. Upon addition of aromatic co-solvents, Cl· engages in π-complexation with the arene, forming a [Cl·---Ar] intermediate. This interaction slows the HAT process, allowing activation to occur preferentially at the thermodynamically more favorable tertiary position. The experimental data supported this model: (1) electron-rich arenes, which stabilize Cl· more effectively, enhanced tertiary selectivity; (2) increasing the arene proportion increased the [Cl·---Ar] population and thus the tertiary/primary ratio; and (3) reactions proceeded more slowly in the presence of aromatic additives, consistent with reduced Cl· reactivity in the complexed form.

3.3. Density-Functional Theory (DFT) calculation results

To further elucidate the role of aromatic solvents in fine-tuning regioselectivity, we performed density functional theory (DFT) calculations (**Figure S9**).

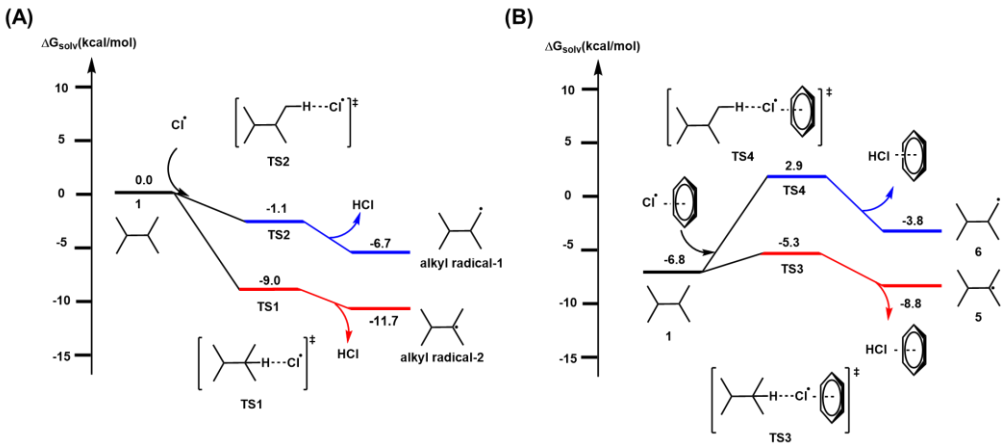


Figure S9 DFT calculation on regioselectivity. (A). single Cl radical-mediated HAT of 2,4-dimetyl butane; (B). [Cl·---Ar] complex-mediated HAT of 2,4-dimetyl butane.

Due to the high reactivity of Cl·, HAT from alkanes is exothermic and proceeds without a barrier, generating primary and tertiary radicals via **TS2** and **TS1**, respectively; and tertiary radicals are slightly more stable (**Figure S9A**). However, primary radicals are statistically more accessible and encounter less steric hindrance when reacting with DBAD, resulting in comparable, though slightly primary-favored, product ratios. In the presence of benzene, the [Cl·---Ar] pathway exhibits a markedly different energy profile (**Figure S9B**). π-Complexation stabilizes Cl· by 6.8 kcal mol^{-1}, rendering HAT at the primary position endothermic. The barrier for primary C–H activation via **TS4** increases to 9.7 kcal mol^{-1}, whereas tertiary activation via **TS3** requires only 1.5 kcal mol^{-1}. Furthermore, the primary radical lies 3.0 kcal mol^{-1} above the starting substrate, while the tertiary radical is 2.0 kcal mol^{-1} lower in energy. Collectively, these effects shift the thermodynamic preference strongly toward tertiary activation, accounting for the experimentally observed enhancement in regioselectivity upon addition of aromatic co-solvents.

3.4. Details for DFT calculations

In our calculations, Gaussian 16 program[20] was used to carry out total DFT calculations. Geometry optimizations were performed in gas phase by M062X[21,22] hybrid functional and using Def2-SVP[23] basis set for all elements. The vibrational frequencies calculations were conducted at the same level of theory to be sure whether every optimized stationary point is an energy minimum or a transition state and evaluate their thermal corrections at 298 K. The single point energies were calculated based on the gas-phase optimized structures by M062X hybrid functional and def2-QZVP[23] basis set

was used in calculations for all elements. The solvation free energies were evaluated by IEFPCM implicit solvent model[24] in single point calculations. In order to adjust the Gibbs free energies from 1 atm to 1 mol/L, a correction of $RTln(C_{sol}/C_{gas})$ (1.89kcal/mol) is added to energies of all species. C_{sol} represents the standard molar concentration in solution (1 mol/L), C_{gas} represents the standard molar concentrationin gas phase (0.0446 mol/L), and R represents the gas constant (8.314 J/(mol*K)).

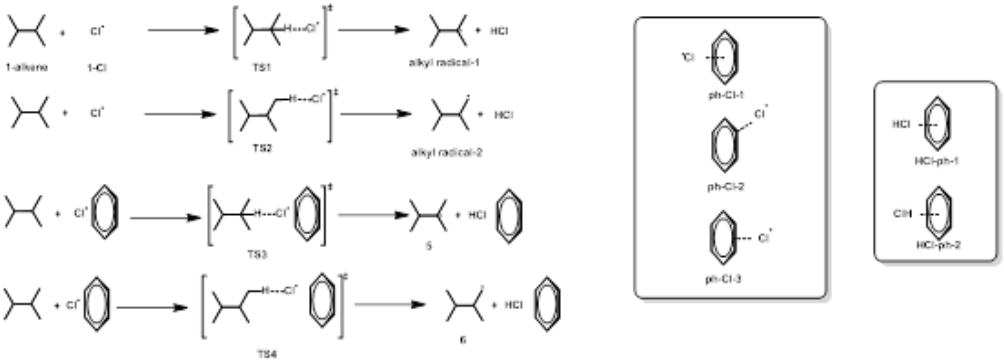


Figure S10 The presumable HAT pathways and different [Cl·---PhH] structures

Table S4 Zero-point correction (ZPE), thermal correction to enthalpy (TCH), thermal correction to Gibbs free energy (TCG), electronic energies (E), Gibbs free energies(G), enthalpies (H) (in Hartree), and imaginary frequencies (Im) of the structures calculated in corresponding level.

Filename	ZPE	TCH	TCG	EE	H	G	Im
1-alkane	-236.873	0.197373	0.15699	-237.061	-236.864	-236.904	-
1-Cl	-460.149	0.00236	-0.01568	-460.149	-460.146	-460.164	-
alkradical-1	-236.218	0.182937	0.141235	-236.392	-236.209	-236.25	-
alkradical-2	-236.225	0.183471	0.14042	-236.399	-236.215	-236.258	-
HCl	-460.811	0.010068	-0.01113	-460.818	-460.808	-460.829	-
hclph-1	-692.959	0.116279	0.07765	-693.067	-692.951	-692.99	-
hclph-2	-692.962	0.116313	0.077723	-693.071	-692.954	-692.993	-
ph-cl	-692.311	0.109209	0.069233	-692.413	-692.304	-692.344	-
ph-cl2	-692.311	0.109211	0.069238	-692.413	-692.304	-692.344	-
ph-cl3	-692.3	0.107529	0.072152	-692.402	-692.294	-692.329	-
phH	-232.147	0.106677	0.076264	-232.248	-232.141	-232.172	-
TS1	-697.044	0.192847	0.145337	-697.225	-697.032	-697.08	-200.039
TS2F-A	-697.031	0.192154	0.144915	-697.212	-697.02	-697.067	-373.691
TS2F-B	-697.031	0.191941	0.145399	-697.212	-697.02	-697.066	-424.008
TS2F-C	-697.031	0.19214	0.145673	-697.213	-697.02	-697.067	-357.15
TS3F-1	-929.192	0.30139	0.234602	-929.476	-929.174	-929.241	-198.456
TS3F-2	-929.191	0.301487	0.231532	-929.474	-929.173	-929.243	-212.241
TS4F-A1	-929.178	0.300634	0.232078	-929.461	-929.161	-929.229	-417.603
TS4F-A2	-929.178	0.300625	0.231749	-929.461	-929.161	-929.23	-421.673
TS4F-B1	-929.178	0.30051	0.234151	-929.462	-929.161	-929.227	-438.716
TS4F-B2	-929.178	0.300612	0.232688	-929.461	-929.16	-929.228	-423.703

4. Mechanism studies

4.1. TEMPO trapping and radical clock experiments

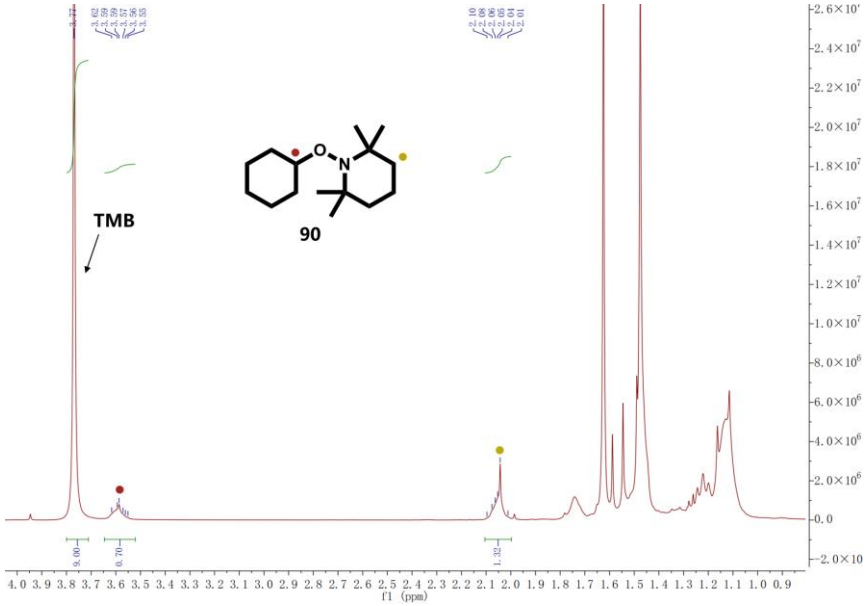


Figure S11 Crude ^{1}H NMR after adding 2.0 equiv. TEMPO in $ZrCl_4$-catalyzed hydrazination of cyclohexane. 1,3,5-trimethoxybenzene (TMB) was used as internal standard after the reaction. Characteristic signals match the literature[25].

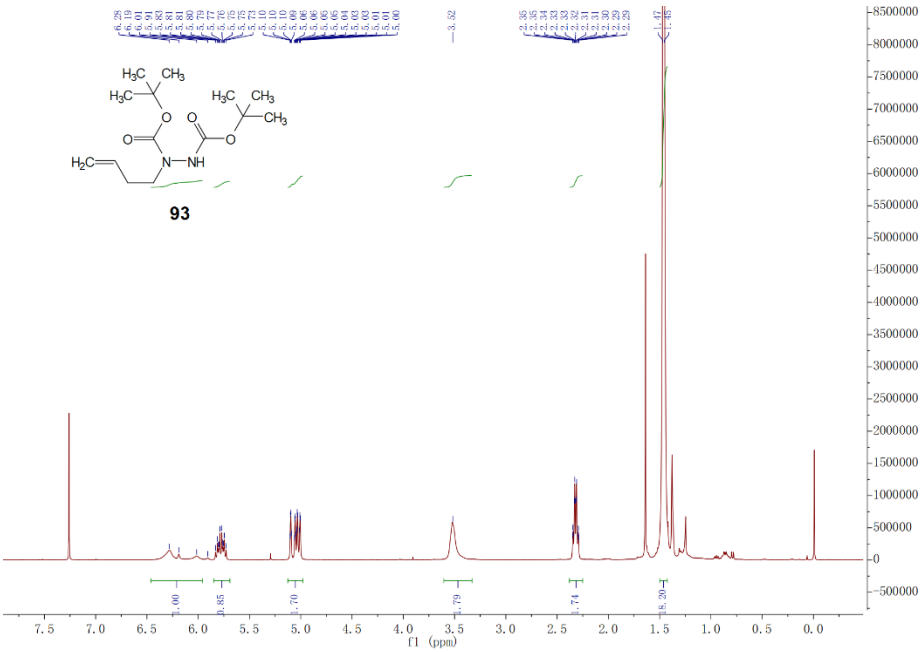


Figure S12 ^{1}H NMR of **93** using 2-cyclopropylacetic acid (**91**) as the decarboxylation substrate after purification.

4.2. Spin trapping experiments and EPR scanning

We carried out the electron paramagnetic resonance (EPR) spectroscopy using the solution of $ZrCl_4$ (0.05 M) and α-phenyl-N-tert-butylnitrone (PBN) (0.1 M) in different anhydrous solutions (all thoroughly deoxygenated before use). The mixture was stirred under light irradiation for 1 min, then a portion of the solution was taken out in a capillary tube for the detection.

The EPR spectrum strongly showed that the Cl radical was trapped as a Cl-PBN complex (g = 2.0067, A_N = 12.3 G, A_H = 0.8 G, $A_{Cl\text{-}35}$ = 6.2 G, $A_{Cl\text{-}37}$ = 5.3 G)[26,27], suggesting that chlorine radical is the key intermediate during the $ZrCl_4$-photocatalyzed reactions.

EPR experimental parameters:

CenterField	3496.70 G	Sweepwidth	120.0 G
FrequencyMon	9.816501 GHz	Power	20.00 mW
PowerAtten	10.0 dB	NbScansAcc	3
Gain	30 dB	Harmonic	1
ModAmp	2.000 G	ModFreq	100.00 kHz
Resolution	1500	Sweeptime	30.00 s

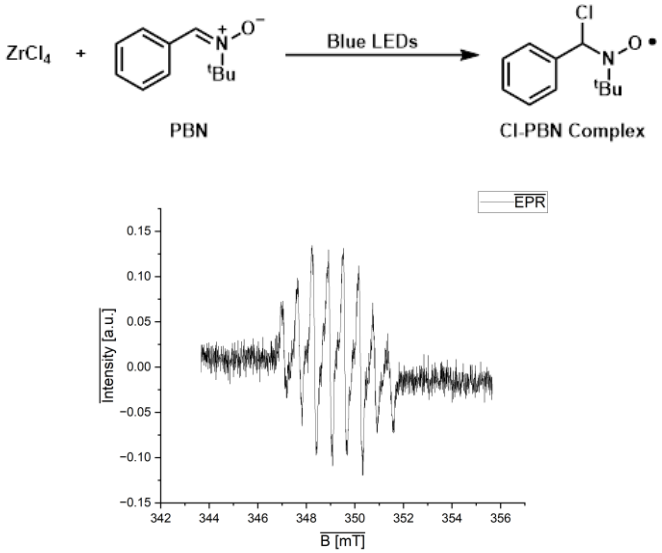


Figure S13 The EPR spectrum of $ZrCl_4$ and PBN in PhCN solution.

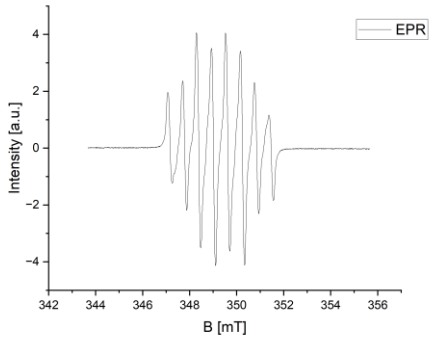


Figure S14 The EPR spectrum of $ZrCl_4$ and PBN in PhH solution

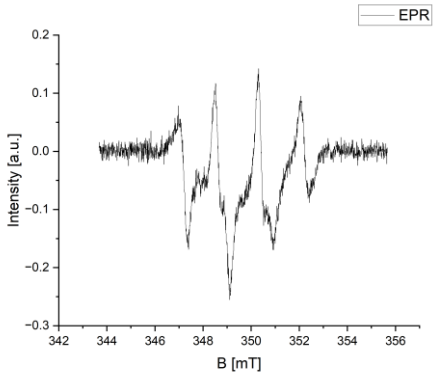


Figure S15 The EPR spectrum of $ZrCl_4$ and PBN in CD_3CN solution

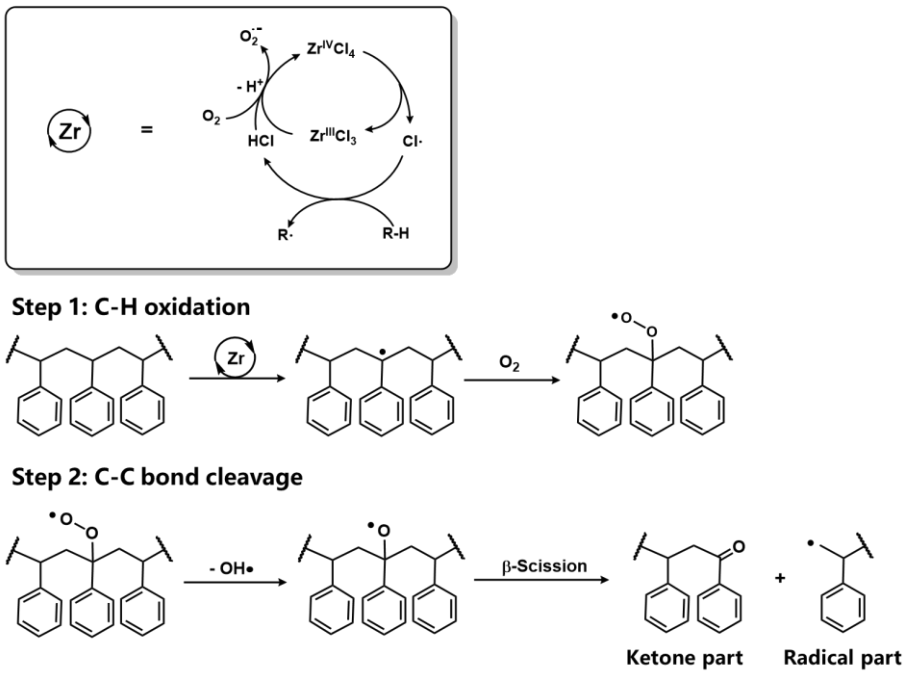
To analyze the EPR spectrum, we also conducted the quantum chemistry calculation on the assumed Cl-PBN complex. The complex was optimized under M062x/def2SVP level, and predicted EPR was calculated under M062x/def2TZVP level.

EPR calculation output:

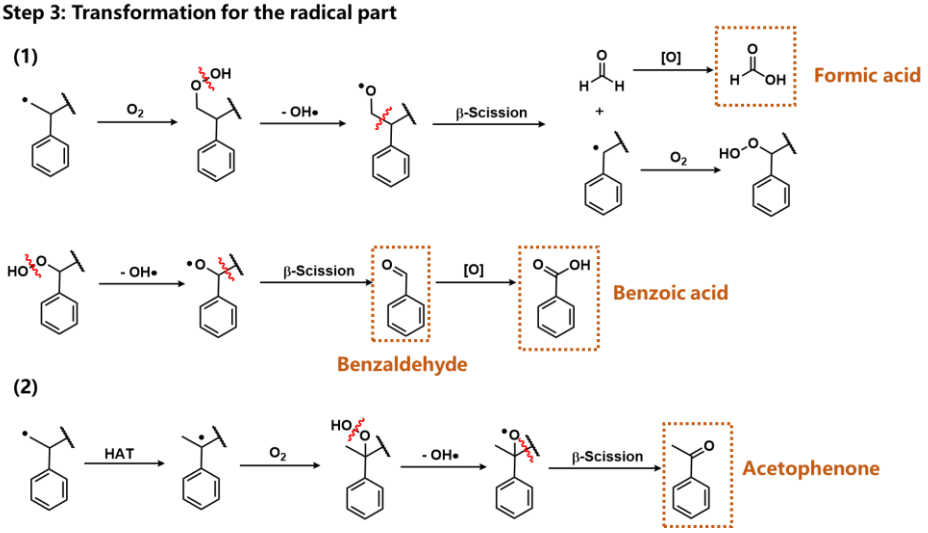
```
clear
Sys.g = 2.0066;
Sys.Nucs = '1H 35Cl,14N';
Sys.A = [0.8 6.3 12.6];
Exp.mwFreq = 9.385;
Sys.lwpp = 0.12;
Exp.Range = [332 336];
Exp.nPoints = 5001;
Exp.mwMode = 'perpendicular';
garlic(Sys,Exp);

clear
Sys.g = 2.0066;
Sys.Nucs = '1H,35Cl,14N';
Sys.A = [0.08 51 12.6];
```

```
Exp.mwFreq = 9.385;
Sys.lwpp = 0.05;
Exp.Range = [332 336];
Exp.nPoints = 5001;
Exp.mwMode = 'perpendicular';
garlic(Sys,Exp);
clear
Sys.g = [2.0036 2.0053 2.0109]
Sys.Nucs = '1H,35Cl,14N';
Sys.A = [0.8 6.3 12.6];
Exp.mwFreq = 9.816501;
Sys.lwpp = [0.035 0.01];
Exp.Range = [348 351];
Exp.nPoints = 1000;
Exp.modFreq = 100;
Exp.ModAmp = 0.2
Exp.nScans = 3
Exp.mwMode = 'perpendicular';
Exp.Temperature = 298
pepper(Sys,Exp);
```

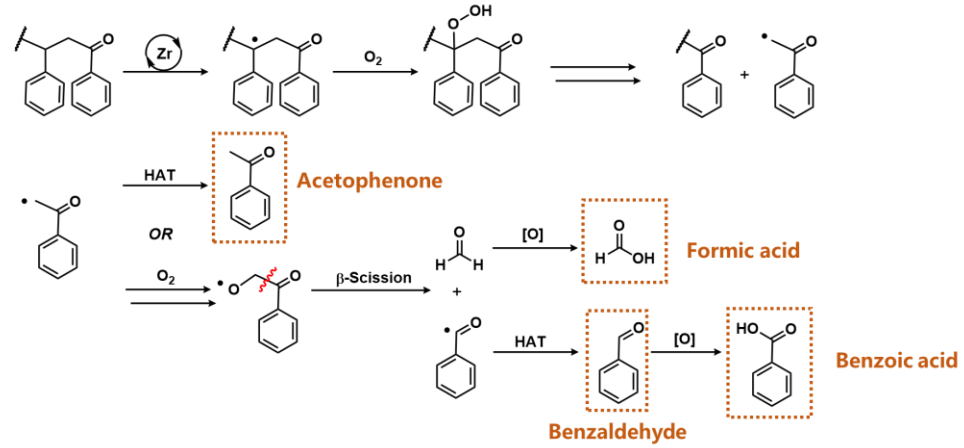
4.3. Proposed mechanism in PS degradation



Step 3: Transformation for the radical part



Step 4: Transformation for the ketone part



5. General procedure

5.1. Direct C(sp^3)−H activation on alkanes

General Procedure A: In an argon-filled glovebox, a flame-dried 25 mL sampling bottle equipped with a Teflon septum was charged with 46.0 mg $ZrCl_4$ (0.4 mmol). The bottle was sealed tightly and removed from the glovebox, and 20 mL anhydrous MeCN was added to prepare a stock solution. The solution was then stored under an argon atmosphere and in avoidance of light for each use.

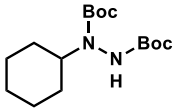
A flame-dried 4 mL vial equipped with a Teflon septum and magnetic stir bar was charged with DBAD (46.0 mg, 0.2 mmol, 1.0 eq.) or 2-benzylidenemalononitrile (30.8 mg, 0.2 mmol, 1.0 eq.) and alkanes (if solid, 2.0 mmol, 10.0 eq.). The vial was sealed, and then evacuated and back-filled with argon for 5 times. Next, alkanes (if liquid, 2mmol, 10.0 eq.) and 0.1 mL of the $ZrCl_4$ stock solution (0.001 mmol, 0.005 eq.) were added via syringe under argon. Finally, the remaining anhydrous MeCN (1.9 mL, total concentration: 0.1 M) was also added. The reaction mixture was then stirred and irradiated with 5 W 390−395 nm LEDs in the photoreactor at room temperature. After 24 h, the reaction mixture was concentrated in vacuum. Purification of the crude product by flash chromatography on silica gel afforded the desired product.

Notice:

1. All alkane substrates are commercially available;
2. To ensure the reproducibility, adding 100 mg $MgSO_4$ is sometimes recommended.

General Procedure B: In an argon-filled glovebox, a flame-dried 25 mL sampling bottle equipped with a Teflon septum was charged with 46.0 mg $ZrCl_4$ (0.4 mmol). The bottle was sealed tightly and removed from the glovebox, and 20 mL anhydrous MeCN was added to prepare a stock solution. The solution was then stored under an argon atmosphere and in avoidance of light for each use.

A flame-dried 4 mL vial equipped with a Teflon septum and magnetic stir bar was charged with different radical trapping reagents (0.2 mmol, 1.0 eq.). The vial was sealed, and then evacuated and back-filled with argon for 5 times. Next, cyclohexane (0.22 mL, 2.0 mmol, 10.0 eq.) and 0.1 mL of the $ZrCl_4$ stock solution (0.001 mmol, 0.005 eq.) were added via syringe under argon. Finally, the remaining anhydrous MeCN (1.9 mL, total concentration: 0.1 M) was also added. The reaction mixture was then stirred and irradiated with 5 W 390−395 nm LEDs in the photoreactor at room temperature. After 24 h, the reaction mixture was concentrated in vacuum. Purification of the crude product by flash chromatography on silica gel afforded the desired product.



Di-tert-butyl 1-cyclohexylhydrazine-1,2-dicarboxylate (**1**)

According to **General Procedure A**, cyclohexane (0.22 mL, 2.0 mmol, 10.0 eq.) and

DBAD were used as the substrates. Purification by silica gel chromatography (PE/EA = 30/1) afforded **1** as a white solid (55.3 mg, 88%).

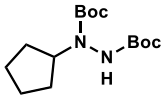
TLC: R_f = 0.4 (PE/EA = 10/1, $KMnO_4$ or PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (d, *J* = 95.7 Hz, 1H), 3.93 (d, *J* = 23.9 Hz, 1H), 1.90 – 1.69 (m, 4H), 1.66 – 1.53 (m, 2H), 1.45 (d, *J* = 5.4 Hz, 18H), 1.38 – 1.22 (m, 3H), 1.06 (ddt, *J* = 10.8, 7.1, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.47, 155.90, 154.86, 154.56, 81.35, 80.93, 80.81, 55.96, 30.24, 28.61, 28.38, 28.31, 25.68, 25.53.

NMR data matched with reference[28].

HRMS (ESI) m/z calcd. for $C_{16}H_{30}N_2O_4Na$ ($[M+Na]^+$) 337.2098, found 337.2098



Di-tert-butyl 1-cyclopentylhydrazine-1,2-dicarboxylate (**2**)

According to **General Procedure A**, cyclopentane (0.19 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (PE/EA = 30/1) afforded **2** as a white solid (46.4 mg, 77%).

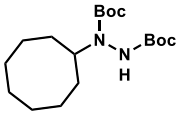
TLC: R_f = 0.4 (PE/EA = 10/1, $KMnO_4$ or PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, *J* = 93.7 Hz, 1H), 4.46 (s, 1H), 1.78 (s, 2H), 1.64 – 1.41 (m, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.43, 155.97, 155.19, 154.90, 81.40, 80.96, 80.65, 58.63, 29.01, 28.60, 28.37, 28.28, 23.78.

NMR data matched with reference[28].

HRMS (ESI) m/z calcd. for $C_{15}H_{28}N_2O_4Na$ ($[M+Na]^+$) 323.1941, found 323.1944



Di-tert-butyl 1-cyclooctylhydrazine-1,2-dicarboxylate (**3**)

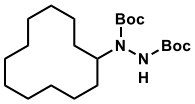
According to **General Procedure A**, cyclooctane (0.27 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (PE/EA = 30/1) afforded **3** as a white solid (60.6 mg, 89%).

TLC: R_f = 0.4 (PE/EA = 10/1, $KMnO_4$ or PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (d, *J* = 80.6 Hz, 1H), 4.33 – 4.00 (m, 1H), 1.72 – 1.59 (m, 5H), 1.56 – 1.38 (m, 27H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.39, 155.92, 154.69, 81.24, 81.01, 80.84, 56.93, 31.12, 28.39, 28.30, 26.73, 26.26, 24.69, 22.77.

HRMS (ESI) m/z calcd. for $C_{18}H_{34}N_2O_4Na$ ($[M+Na]^+$) 365.2411, found 365.2415



Di-tert-butyl 1-cyclododecylhydrazine-1,2-dicarboxylate (**4**)

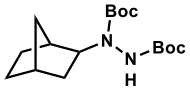
According to **General Procedure A**, cyclododecane (336.0 mg, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (From PE to PE/EA = 50/1) afforded **4** as a colorless oil (67.1 mg, 84%).

TLC: R_f = 0.4 (PE/EA = 10/1, $KMnO_4$ or PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (d, *J* = 64.3 Hz, 1H), 4.26 (d, *J* = 59.6 Hz, 1H), 1.61 – 1.13 (m, 40H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.53, 155.71, 155.15, 80.69, 69.21, 53.11, 51.98, 32.54, 28.37, 28.28, 27.93, 27.11, 24.30, 23.91, 23.45, 23.36, 23.03, 22.82, 22.64, 22.46, 22.15, 21.06.

HRMS (ESI) m/z calcd. for $C_{22}H_{42}N_2O_4Na$ ($[M+Na]^+$) 421.3037, found 421.3037



di-tert-butyl 1-bicyclo[2.2.1]heptan-2-yl)hydrazine-1,2-dicarboxylate (**5**)

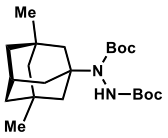
According to **General Procedure A**, norbornane (92.0 mg, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (From PE to PE/EA = 20/1) afforded **5** as a white solid (43.5 mg, 67%).

TLC: R_f = 0.4 (PE/EA = 10/1, $KMnO_4$ or PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, *J* = 98.1 Hz, 1H), 3.91 (dt, *J* = 10.9, 5.7 Hz, 1H), 2.56 – 2.11 (m, 2H), 1.79 – 1.53 (m, 2H), 1.44 (d, *J* = 5.8 Hz, 22H), 1.09 (t, *J* = 8.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.27, 155.91, 155.37, 155.12, 81.43, 81.09, 80.95, 80.71, 60.54, 59.42, 41.82, 40.93, 39.21, 36.24, 35.77, 28.63, 28.39, 28.32, 27.90, 27.34, 27.20.

HRMS (ESI) m/z calcd. for $C_{17}H_{30}N_2O_4Na$ ($[M+Na]^+$) 349.2098, found 349.2100



Di-tert-butyl 3,5-dimethyladamantan-1-yl)hydrazine-1,2-dicarboxylate (**6**)

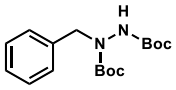
According to **General Procedure A**, 3,5-dimethyl adamantane (0.37 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (From PE to PE/EA = 20/1) afforded **6** as a colorless oil (48.5 mg, 62%).

TLC: R_f = 0.5 (PE/EA = 10/1, $KMnO_4$ or PMA)

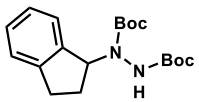
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 – 5.75 (m, 1H), 2.20 – 1.56 (m, 6H), 1.50 – 1.41 (m, 18H), 1.40 – 0.97 (m, 7H), 0.87 – 0.73 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.60, 156.38, 156.25, 154.54, 81.30, 80.98, 80.72, 61.77, 61.71, 51.81, 50.67, 46.61, 46.41, 46.25, 46.21, 44.61, 44.55, 44.34, 44.04, 43.57, 42.78, 40.02, 39.62, 39.43, 38.87, 38.50, 36.27, 35.74, 35.61, 35.55, 34.86, 34.69, 33.68, 32.93, 32.87, 32.01, 31.79, 31.62, 31.16, 31.04, 30.92, 30.72, 30.48, 30.42, 30.35, 30.13, 30.03, 29.46, 28.97, 28.74, 28.64, 28.45, 28.40, 28.36, 28.33, 28.28, 27.03, 26.56, 26.45.

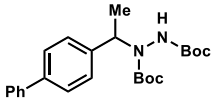
HRMS (ESI) m/z calcd. for $C_{22}H_{38}N_2O_4Na$ ([M+Na]$^+$) 417.2724, found 417.2724



Di-tert-butyl 1-benzylhydrazine-1,2-dicarboxylate (**7**)
According to **General Procedure A**, toluene (0.21 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (PE/EA = 20/1) afforded **7** as a white solid (16.6 mg, 26%).
TLC: R_f = 0.2 (PE/EA = 10/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (pd, *J* = 7.8, 7.0, 3.0 Hz, 5H), 6.06 (d, *J* = 110.5 Hz, 1H), 4.64 (s, 2H), 1.46 (d, *J* = 15.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.39, 154.87, 137.34, 128.65, 127.67, 81.46, 52.78, 28.38, 28.31.
NMR data matched with reference[29].
HRMS (ESI) m/z calcd. for $C_{17}H_{26}N_2O_4Na$ ([M+Na]$^+$) 345.1785, found 345.1782

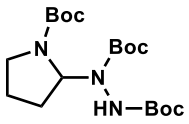


Di-tert-butyl 1-(2,3-dihydro-1H-inden-1-yl)hydrazine-1,2-dicarboxylate (**8**)
According to **General Procedure A**, indan (0.24 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (From PE to PE/EA = 20/1) afforded **8** as a colorless oil (37.3 mg, 54%).
TLC: R_f = 0.2 (PE/EA = 10/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.11 (m, 4H), 6.12 – 5.52 (m, 2H), 3.03 – 2.88 (m, 1H), 2.81 (dt, *J* = 15.8, 7.9 Hz, 1H), 2.45 – 2.04 (m, 2H), 1.50 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.95, 155.27, 144.21, 141.36, 127.97, 126.56, 125.07, 123.95, 81.42, 80.96, 64.45, 62.23, 30.53, 29.32, 28.38, 28.24, 27.02.
HRMS (ESI) m/z calcd. for $C_{19}H_{28}N_2O_4Na$ ([M+Na]$^+$) 371.1941, found 371.1939



Di-tert-butyl 1-(1-([1,1'-biphenyl]-4-yl)ethyl)hydrazine-1,2-dicarboxylate (**9**)
According to **General Procedure A**, 4-ethyl-1,1'-biphenyl (364.0 mg, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (PE/EA = 10/1) afforded **9** as a colorless oil (40.7 mg, 58%).
TLC: R_f = 0.2 (PE/EA = 10/1, UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (q, *J* = 9.3, 8.6 Hz, 5H), 7.46 – 7.31 (m, 4H), 6.11 – 4.96 (m, 2H), 1.58 – 1.46 (m, 21H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.75, 153.33, 140.94, 140.48, 128.91, 127.73, 127.42, 127.20, 127.18, 126.74, 83.52, 82.95, 81.55, 81.03, 67.18, 28.67, 28.56, 28.41, 28.31, 28.24, 28.18, 28.15, 27.54.

HRMS (ESI) m/z calcd. for $C_{24}H_{31}N_2O_4$ ([M-H]$^-$) 411.2289, found 411.2291



Di-tert-butyl 1-(1-(tert-butoxycarbonyl)pyrrolidin-2-yl)hydrazine-1,2-dicarboxylate (**10**)

According to **General Procedure A**, tert-butyl pyrrolidine-1-carboxylate (0.35 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (From PE/EA = 20/1 to PE/EA = 10/1) afforded **10** as a white solid (67.7 mg, 84%).

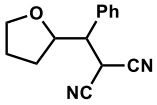
TLC: R_f = 0.3 (PE/EA = 10/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 – 5.58 (m, 2H), 3.55 – 3.22 (m, 2H), 2.24 – 1.97 (m, 2H), 1.97 – 1.64 (m, 2H), 1.43 (d, *J* = 8.3 Hz, 27H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.85, 154.30, 153.65, 81.85, 81.28, 80.17, 69.66, 46.68, 46.07, 46.02, 31.38, 28.65, 28.56, 28.35, 28.27, 28.09, 28.03, 22.77.

NMR data matched with reference[29].

HRMS (ESI) m/z calcd. for $C_{19}H_{35}N_3O_6Na$ ([M+Na]$^+$) 424.2418, found 424.2412



2-(phenyl(tetrahydrofuran-2-yl)methyl)malononitrile (**11**)

According to **General Procedure A**, tetrahydrofuran (0.16 mL, 2.0 mmol, 10.0 eq.) and 2-benzylidenemalononitrile were used as the substrates. Purification by silica gel chromatography (PE/EA = 10/1) afforded **11** as a colorless oil (29 mg, 64%). The combined NMR information of the two diastereomers were reported here.

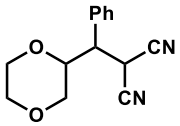
TLC: R_f = 0.5 (PE/EA = 5/1, I_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 8H), 7.34 – 7.29 (m, 2H), 4.55 (d, *J* = 4.2 Hz, 1H), 4.46 (td, *J* = 7.1, 3.2 Hz, 1H), 4.40 (dd, *J* = 10.5, 4.5 Hz, 2H), 4.00 – 3.92 (m, 1H), 3.91 – 3.82 (m, 1H), 3.75 (td, *J* = 6.6, 1.7 Hz, 2H), 3.28 (dd, *J* = 10.7, 3.2 Hz, 1H), 3.04 (dd, *J* = 10.3, 4.2 Hz, 1H), 2.05 – 1.85 (m, 4H), 1.83 – 1.72 (m, 1H), 1.50 – 1.37 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.61, 134.12, 129.39, 129.34, 129.25, 129.10, 129.07, 128.90, 128.63, 128.31, 128.04, 112.48, 112.45, 112.43, 112.31, 111.87, 78.19, 77.63, 68.97, 68.85, 52.11, 50.76, 30.47, 29.03, 27.47, 27.13, 25.91.

NMR data matched with reference[30].

HRMS (ESI) m/z calcd. for $C_{14}H_{13}N_2O$ ([M-H]$^-$) 225.1033, found 225.1036



2-((1,4-dioxan-2-yl)(phenyl)methyl)malononitrile (**12**)

According to **General Procedure A**, 1,4-Dioxane (0.17 mL, 2.0 mmol, 10.0 eq.) and 2-benzylidenemalononitrile were used as the substrates. Purification by silica gel chromatography (PE/EA = 20/1) afforded **12** as a colorless oil (41.9 mg, 87%). The combined NMR information of the two diastereomers were reported here.

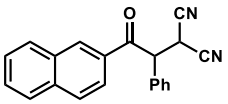
TLC: R_f = 0.5 (PE/EA = 5/1, I_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 10H), 4.56 (d, *J* = 4.2 Hz, 1H), 4.38 (d, *J* = 10.9 Hz, 1H), 4.19 – 4.11 (m, 1H), 4.11 – 4.04 (m, 1H), 3.94 – 3.78 (m, 4H), 3.79 – 3.70 (m, 1H), 3.67 (dd, *J* = 11.8, 2.7 Hz, 1H), 3.63 – 3.56 (m, 2H), 3.56 – 3.38 (m, 2H), 3.28 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.20 (dd, *J* = 11.7, 9.7 Hz, 1H), 3.11 (dd, *J* = 10.8, 4.2 Hz, 1H), 2.95 (dd, *J* = 11.6, 10.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.49, 132.68, 129.81, 129.65, 129.36, 129.32, 129.27, 129.13, 128.46, 112.31, 112.15, 112.12, 111.99, 111.64, 73.89, 73.85, 69.37, 69.00, 67.80, 67.24, 66.31, 66.29, 48.46, 48.39, 26.26, 26.18.

NMR data matched with reference[30].

HRMS (ESI) m/z calcd. for $C_{14}H_{13}N_2O_2$ ([M-H]$^-$) 241.0983, found 241.0986



2-(2-(naphthalen-2-yl)-2-oxo-1-phenylethyl)malononitrile (**13**)

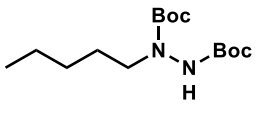
According to **General Procedure A**, 2-naphthaldehyde (312.0 mg, 2.0 mmol, 10.0 eq.) and 2-benzylidenemalononitrile were used as the substrates. Purification by silica gel chromatography (From PE/EA = 50/1 to PE/EA = 20/1) afforded **13** as a yellow oil (30.4 mg, 49%).

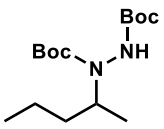
TLC: R_f = 0.2 (PE/EA = 10/1, UV & I_2)

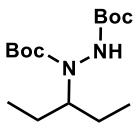
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 1.8 Hz, 1H), 7.94 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.83 (dd, *J* = 8.5, 4.4 Hz, 2H), 7.61 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.45 – 7.35 (m, 5H), 5.27 (d, *J* = 8.4 Hz, 1H), 4.60 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.09, 136.08, 132.36, 132.33, 131.84, 131.30, 130.23, 130.03, 129.94, 129.58, 129.07, 128.73, 127.95, 127.36, 124.17, 112.29, 111.71, 55.02, 27.03.

HRMS (ESI) m/z calcd. for $C_{21}H_{13}N_2O$ ([M-H]$^-$) 309.1033, found 309.1038







Di-tert-butyl 1-pentylhydrazine-1,2-dicarboxylate (**14-1**), di-tert-butyl 1-(pentan-2-yl)hydrazine-1,2-dicarboxylate (**14-2**), and di-tert-butyl 1-(pentan-3-yl)hydrazine-1,2-dicarboxylate (**14-3**)

According to **General Procedure A**, n-pentane (0.23 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (From

PE/EA = 30/1 to PE/EA = 20/1) afforded **14** as a colorless oil (43.0 mg, 71%). The three regio isomers can only be isolated on GC-MS, thus a combined NMR information is recorded here.

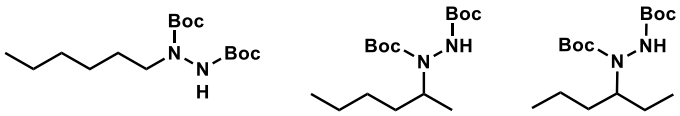
TLC: R_f = 0.4 (PE/EA = 10/1, $KMnO_4$ or PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 – 5.68 (m), 4.33 – 3.58 (m), 3.41 (t, *J* = 7.7 Hz), 1.58 – 1.20 (m), 1.08 (d), 0.88 (td).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 156.20, 155.76, 155.36, 154.92, 81.28, 81.09, 80.96, 80.83, 80.76, 80.68, 62.72, 60.47, 59.42, 54.01, 52.21, 49.52, 36.34, 28.98, 28.62, 28.43, 28.38, 28.35, 28.32, 28.29, 27.31, 27.29, 25.64, 25.63, 25.39, 25.23, 22.51, 19.76, 19.76, 18.50, 18.27, 18.02, 17.98, 14.14, 14.07, 11.32.

NMR data matched with reference[29].

HRMS (ESI) m/z calcd. for $C_{15}H_{30}N_2O_4Na$ ($[M+Na]^+$) 325.2098, found 325.2094



Di-tert-butyl 1-(hexan-2-yl)hydrazine-1,2-dicarboxylate (**15-1**), di-tert-butyl 1-(hexan-3-yl)hydrazine-1,2-dicarboxylate (**15-2**), and di-tert-butyl 1-hexylhydrazine-1,2-dicarboxylate (**15-3**)

According to **General Procedure A**, n-hexane (0.26 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (PE/EA = 20/1) afforded **15** as a colorless oil (45.7 mg, 72%). The three regio isomers can only be isolated on GC-MS, thus a combined NMR information is recorded here.

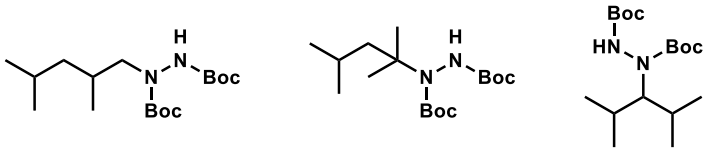
TLC: R_f = 0.4 (PE/EA = 10/1, $KMnO_4$ or PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 – 5.73 (m), 4.00 (t, *J* = 79.0 Hz), 3.40 (t, *J* = 7.2 Hz), 1.50 – 1.23 (m), 1.07 (d, *J* = 6.7 Hz), 0.87 (q, *J* = 7.4 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.54, 156.19, 155.62, 154.92, 81.41, 81.06, 80.74, 60.22, 59.41, 58.48, 54.31, 52.60, 52.15, 49.51, 34.66, 34.31, 33.84, 31.64, 28.76, 28.61, 28.42, 28.37, 28.34, 28.31, 28.28, 27.55, 26.48, 25.88, 25.56, 25.05, 22.71, 22.65, 19.78, 18.42, 18.05, 14.15, 14.13, 11.35.

NMR data matched with reference[29].

HRMS (ESI) m/z calcd. for $C_{16}H_{32}N_2O_4Na$ ($[M+Na]^+$) 339.2254, found 339.2246



Di-tert-butyl 1-(2,4-dimethylpentan-2-yl)hydrazine-1,2-dicarboxylate (**16-1**), di-tert-butyl 1-(2,4-dimethylpentan-3-yl)hydrazine-1,2-dicarboxylate (**16-2**), and di-tert-butyl 1-(2,4-dimethylpentyl)hydrazine-1,2-dicarboxylate (**16-3**)

According to **General Procedure A**, 2,4-dimethylpentane (0.30 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (From PE/EA = 40/1 to PE/EA = 30/1) afforded a mixture of **16-2** and **16-3** as a white solid (20.4 mg, 31%) and **16-1** as a colorless oil (26.4 mg, 40%). The two regio isomers

of **16-2** and **16-3** can only be isolated on GC-MS, thus a combined NMR information is recorded here.

16-1:

TLC: R_f = 0.4 (PE/EA = 10/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 – 5.86 (m, 1H), 3.28 (s, 2H), 1.82 (h, *J* = 7.0 Hz, 1H), 1.64 (dq, *J* = 8.6, 6.4 Hz, 1H), 1.45 (s, 18H), 1.37 (d, *J* = 4.6 Hz, 2H), 1.12 – 0.95 (m, 2H), 0.91 – 0.74 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.28, 155.18, 154.72, 81.38, 81.23, 80.81, 80.73, 68.73, 66.54, 62.38, 48.22, 28.64, 28.45, 28.42, 28.37, 28.31, 28.11, 26.93, 25.22, 24.66, 24.29, 20.01, 19.89.

HRMS (ESI) m/z calcd. for $C_{17}H_{34}N_2O_4Na$ ($[M+Na]^+$) 353.2411, found 353.2408

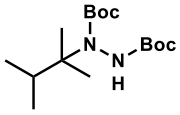
16-2 & **16-3**:

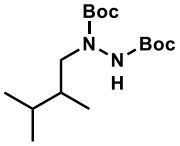
TLC: R_f = 0.5 (PE/EA = 10/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 – 5.18 (m), 3.59 (dq, *J* = 80.8, 7.0 Hz), 1.98 (dt, *J* = 12.7, 6.3 Hz), 1.70 – 1.56 (m), 1.49 – 1.41 (m), 1.24 (s), 0.92 (d, *J* = 6.7 Hz), 0.87 (d, *J* = 6.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.23, 155.88, 154.82, 81.26, 80.97, 80.72, 59.45, 57.25, 56.07, 43.93, 29.47, 28.64, 28.45, 28.37, 28.35, 25.31, 23.68, 22.14, 17.83.

HRMS (ESI) m/z calcd. for $C_{17}H_{34}N_2O_4Na$ ($[M+Na]^+$) 353.2411, found 353.2408





Di-tert-butyl 1-(2,3-dimethylbutan-2-yl)hydrazine-1,2-dicarboxylate (**17-1**), and di-tert-butyl 1-(2,3-dimethylbutyl)hydrazine-1,2-dicarboxylate (**17-2**)

According to **General Procedure A**, 2,3-dimethylbutane (0.26 mL, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (PE/EA = 60/1) afforded **17-1** and **17-2** separately as a white solid (**17-1**: 20.0 mg, 32%; **17-2**: 26.1 mg, 41%).

17-1:

TLC: R_f = 0.4 (PE/EA = 10/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, *J* = 116.7 Hz, 1H), 2.58 (hept, *J* = 6.9 Hz, 1H), 1.46 (d, *J* = 8.1 Hz, 21H), 1.09 (s, 3H), 0.86 (d, *J* = 7.3 Hz, 4H), 0.79 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.68, 156.29, 154.87, 154.49, 81.31, 80.72, 65.90, 33.94, 28.47, 28.39, 25.18, 20.72, 18.18, 17.90.

NMR data matched with reference[29].

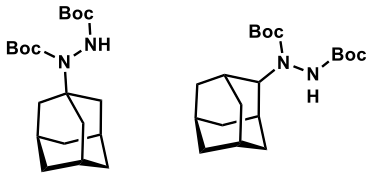
HRMS (ESI) m/z calcd. for $C_{16}H_{32}N_2O_4Na$ ($[M+Na]^+$) 339.2254, found 339.2252

17-2:

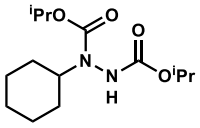
TLC: R_f = 0.3 (PE/EA = 10/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (dd, *J* = 107.8, 34.9 Hz, 1H), 3.51 – 3.07 (m, 2H),

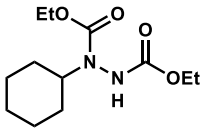
1.71 – 1.57 (m, 2H), 1.47 (s, 18H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.81 (dd, *J* = 9.0, 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.84, 155.67, 81.19, 80.71, 54.64, 53.75, 37.04, 28.67, 28.47, 28.38, 28.37, 20.63, 17.55, 13.06.
NMR data matched with reference[29].
HRMS (ESI) m/z calcd. for $C_{16}H_{32}N_2O_4Na$ ($[M+Na]^+$) 339.2254, found 339.2246



Di-tert-butyl 1-(adamantan-2-yl)hydrazine-1,2-dicarboxylate (**18-1**), and di-tert-butyl 1-(adamantan-1-yl)hydrazine-1,2-dicarboxylate (**18-2**)
According to **General Procedure A**, adamantane (272.0 mg, 2.0 mmol, 10.0 eq.) and DBAD were used as the substrates. Purification by silica gel chromatography (From PE to PE/EA = 20/1) afforded **18** as a white solid (25.5 mg, 35%). The two regio isomers of **18-1** and **18-2** are inseparable, thus a combined NMR information is recorded here.
TLC: R_f = 0.4 (PE/EA = 10/1, $KMnO_4$ or PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 – 5.76 (m), 4.00 (d, *J* = 43.5 Hz), 2.30 – 1.96 (m), 1.92 – 1.52 (m), 1.50 – 1.33 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.40, 156.30, 156.26, 154.64, 81.41, 81.24, 80.97, 80.75, 80.66, 62.83, 62.73, 60.11, 59.44, 40.43, 40.35, 38.52, 38.47, 37.85, 37.78, 37.59, 36.51, 33.30, 33.13, 32.18, 32.15, 31.94, 30.69, 30.48, 30.20, 28.64, 28.46, 28.44, 28.40, 28.38, 28.34, 27.64, 27.61, 27.27, 27.18.
NMR data matched with reference[29].
HRMS (ESI) m/z calcd. for $C_{20}H_{34}N_2O_4Na$ ($[M+Na]^+$) 389.2411, found 389.2401



Diisopropyl 1-cyclohexylhydrazine-1,2-dicarboxylate (**19**)
According to **General Procedure B**, diisopropyl azodicarboxylate (DIAD, 39.6 μL, 0.2 mmol, 1.0 eq.) and cyclohexane were used as the substrates. Purification by silica gel chromatography (PE/EA = 20/1) afforded **19** as a white solid (55.6 mg, 97%).
TLC: R_f = 0.4 (PE/EA = 5/1, $KMnO_4$ or PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (d, *J* = 40.7 Hz, 1H), 4.92 (ddt, *J* = 12.4, 9.4, 6.2 Hz, 2H), 3.96 (s, 1H), 1.97 – 1.65 (m, 4H), 1.59 (d, *J* = 13.4 Hz, 1H), 1.40 – 1.13 (m, 16H), 1.05 (dtt, *J* = 13.0, 9.2, 4.5 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.03, 156.71, 155.31, 69.83, 69.56, 56.83, 30.16, 25.58, 25.46, 22.18, 22.06.
NMR data matched with reference[29].
HRMS (ESI) m/z calcd. for $C_{14}H_{27}N_2O_4$ ($[M+H]^+$) 287.1965, found 287.1959



Diethyl 1-cyclohexylhydrazine-1,2-dicarboxylate (**20**)

According to **General Procedure B**, diethyl azodicarboxylate (DEAD, 28.8 μL, 0.2 mmol, 1.0 eq.) and cyclohexane were used as the substrates. Purification by silica gel chromatography (PE/EA = 20/1) afforded **20** as a colorless oil (40.7 mg, 79%).

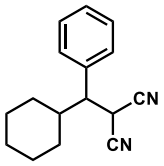
TLC: R_f = 0.2 (PE/EA = 5/1, $KMnO_4$ or PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (d, *J* = 52.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 4H), 4.05 – 3.82 (m, 1H), 1.88 – 1.69 (m, 4H), 1.65 – 1.49 (m, 1H), 1.40 – 1.18 (m, 10H), 1.05 (qt, *J* = 12.7, 3.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.44, 157.07, 155.88, 62.34, 62.01, 57.34, 30.16, 25.57, 25.51, 25.44, 14.64, 14.55.

NMR data matched with reference[29].

HRMS (ESI) m/z calcd. for $C_{12}H_{23}N_2O_4$ ($[M+H]^+$) 259.1652, found 259.1649



2-(cyclohexyl(phenyl)methyl)malononitrile (**21**)

According to **General Procedure B**, 2-benzylidenemalononitrile (30.8 mg, 0.2 mmol, 1.0 eq.) and cyclohexane were used as the substrates. Purification by silica gel chromatography (PE/EA = 30/1) afforded **21** as a yellowish oil (41.5 mg, 87%).

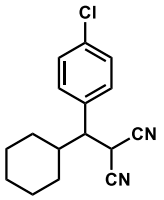
TLC: R_f = 0.5 (PE/EA = 5/1, I_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H), 7.35 – 7.28 (m, 2H), 4.20 (d, *J* = 5.5 Hz, 1H), 2.89 (dd, *J* = 9.8, 5.5 Hz, 1H), 2.08 – 1.96 (m, 1H), 1.92 (dt, *J* = 12.3, 3.2 Hz, 1H), 1.88 – 1.80 (m, 1H), 1.72 – 1.61 (m, 2H), 1.51 – 1.41 (m, 1H), 1.36 (ddd, *J* = 16.4, 8.1, 3.6 Hz, 1H), 1.28 – 1.01 (m, 3H), 0.90 – 0.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.80, 129.18, 128.79, 128.39, 112.36, 112.08, 52.34, 39.29, 31.23, 30.64, 27.20, 25.91, 25.89, 25.80.

NMR data matched with reference[29].

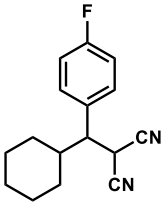
HRMS (ESI) m/z calcd. for $C_{16}H_{17}N_2$ ($[M-H]^-$) 237.1397, found 237.1399



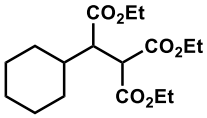
2-((4-chlorophenyl)(cyclohexyl)methyl)malononitrile (**22**)

According to **General Procedure B**, 2-(4-chlorobenzylidene)malononitrile (37.6 mg, 0.2 mmol, 1.0 eq.) and cyclohexane were used as the substrates. Purification by silica

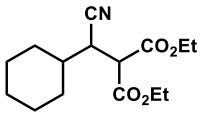
gel chromatography (PE/EA = 20/1) afforded **22** as a yellowish oil (50.8 mg, 93%).
TLC: R_f = 0.7 (PE/EA = 5/1, I_2)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.23 – 7.13 (m, 2H), 4.12 (d, *J* = 5.4 Hz, 1H), 2.79 (dd, *J* = 9.9, 5.4 Hz, 1H), 1.96 – 1.71 (m, 3H), 1.65 – 1.53 (m, 2H), 1.41 – 1.33 (m, 1H), 1.33 – 1.22 (m, 1H), 1.20 – 0.90 (m, 3H), 0.80 – 0.65 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 135.20, 134.82, 129.79, 129.46, 112.18, 111.77, 51.77, 39.21, 31.13, 30.68, 27.08, 25.85, 25.82, 25.74.
HRMS (ESI) m/z calcd. for $C_{16}H_{16}ClN_2$ ($[M-H]^-$) 271.1007, found 271.1015



2-(cyclohexyl(4-fluorophenyl)methyl)malononitrile (**23**)
According to **General Procedure B**, 2-(4-fluorobenzylidene)malononitrile (34.4 mg, 0.2 mmol, 1.0 eq.) and cyclohexane were used as the substrates. Purification by silica gel chromatography (PE/EA = 20/1) afforded **23** as a yellowish oil (47.1 mg, 92%).
TLC: R_f = 0.4 (PE/EA = 20/1, I_2)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 4.19 (d, *J* = 5.4 Hz, 1H), 2.87 (dd, *J* = 9.9, 5.3 Hz, 1H), 2.03 – 1.78 (m, 3H), 1.73 – 1.60 (m, 2H), 1.48 – 1.29 (m, 2H), 1.27 – 0.91 (m, 3H), 0.89 – 0.70 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.87, 161.90, 132.54, 132.51, 130.14, 130.08, 116.31, 116.14, 112.27, 111.85, 51.65, 39.31, 31.16, 30.69, 27.27, 25.87, 25.83, 25.75.
HRMS (ESI) m/z calcd. for $C_{16}H_{16}FN_2$ ($[M-H]^-$) 255.1303, found 255.1307



Triethyl 2-cyclohexylethane-1,1,2-tricarboxylate (**24**)
According to **General Procedure B**, triethyl ethene-1,1,2-tricarboxylate (48.8 mg, 0.2 mmol, 1.0 eq.) and cyclohexane were used as the substrates. Purification by silica gel chromatography (PE/EA = 10/1) afforded **24** as a colorless oil (64.4 mg, 98%).
TLC: R_f = 0.6 (PE/EA = 5/1, $KMnO_4$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 – 4.08 (m, 6H), 3.86 (d, *J* = 11.3 Hz, 1H), 3.05 (dd, *J* = 11.3, 3.8 Hz, 1H), 1.78 – 1.66 (m, 4H), 1.64 – 1.57 (m, 1H), 1.49 – 1.38 (m, 1H), 1.30 – 1.19 (m, 11H), 1.17 – 1.01 (m, 2H), 0.89 (qd, *J* = 13.1, 12.7, 3.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.45, 168.49, 168.36, 61.72, 61.65, 60.60, 52.48, 50.08, 38.55, 32.02, 28.54, 26.85, 26.54, 26.26, 14.33, 14.17, 14.05.
NMR data matched with reference[3].
HRMS (ESI) m/z calcd. for $C_{17}H_{29}O_6$ ($[M+H]^+$) 329.1959, found 329.1950



Diethyl 2-(cyano(cyclohexyl)methyl)malonate (**25**)

According to **General Procedure B**, diethyl 2-(cyanomethylene)malonate (39.4 mg, 0.2 mmol, 1.0 eq.) and cyclohexane were used as the substrates. Purification by silica gel chromatography (PE/EA = 10/1) afforded **25** as a colorless oil (40.9 mg, 73%).

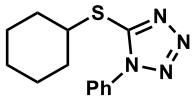
TLC: R_f = 0.6 (PE/EA = 5/1, $KMnO_4$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (dq, *J* = 9.0, 7.4 Hz, 4H), 3.67 (d, *J* = 9.7 Hz, 1H), 3.20 (dd, *J* = 9.7, 4.9 Hz, 1H), 1.89 – 1.74 (m, 3H), 1.72 – 1.65 (m, 2H), 1.56 – 1.42 (m, 1H), 1.31 – 1.17 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.48, 118.49, 62.50, 62.48, 51.46, 37.79, 37.34, 31.59, 28.68, 25.99, 25.77, 25.72, 14.17, 14.10, 14.07.

NMR data matched with reference[3].

HRMS (ESI) m/z calcd. for $C_{15}H_{27}NO_4$ ($[M+NH_4]^+$) 299.1965, found 299.1961



5-(cyclohexylthio)-1-phenyl-1H-tetrazole (**26**)

According to **General Procedure B**, 1,2-bis(1-phenyl-1H-tetrazol-5-yl)disulfane (70.8 mg, 0.2 mmol, 1.0 eq.) and cyclohexane were used as the substrates. Purification by silica gel chromatography (PE/EA = 20/1) afforded **26** as an off-white solid (49.4 mg, 95%).

TLC: R_f = 0.9 (PE/EA = 5/1, UV & PMA)

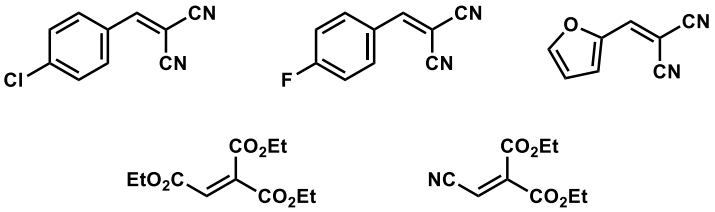
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.45 (m, 5H), 3.98 (tt, *J* = 10.4, 3.8 Hz, 1H), 2.25 – 2.12 (m, 2H), 1.81 – 1.68 (m, 2H), 1.62 (dddd, *J* = 12.3, 11.1, 6.0, 3.3 Hz, 1H), 1.57 – 1.38 (m, 4H), 1.35 – 1.22 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.11, 133.87, 130.09, 129.77, 124.09, 47.49, 33.27, 25.81, 25.50.

NMR data matched with reference[31].

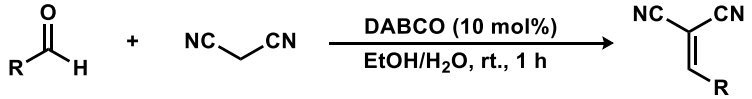
HRMS (ESI) m/z calcd. for $C_{13}H_{17}N_4S$ ($[M+H]^+$) 261.1168, found 261.1167

5.2. Synthesis of radical trapping reagents

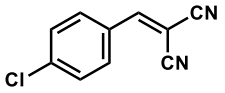


The above trapping reagents are not commercially available and were prepared according to the following protocols.

General procedure C



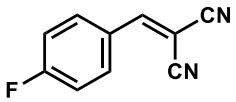
Following the literature[32,33] with a small modification, a 50 mL round-bottom flask equipped with a magnetic stir bar was charged with aldehydes (10.0 mmol, 1.0 eq.), which was then dissolved in a 16 mL EtOH/H_2O (v/v = 96/4) solution. While stirring, malononitrile (0.79 g, 12.0 mmol, 1.2 eq.) and DABCO (112.0 mg, 1.0 mmol, 0.1 eq.) were subsequently added. Large amount of precipitates can be seen in a few minutes. The mixture was then kept on stirring at room temperature for 1 h to ensure complete conversion. The precipitates were then filtered through a sand-core funnel and washed by cold water. Finally, the product was dried in vacuo as a powder and was used directly without further purification.



According to **General Procedure C**, 4-chlorobenzaldehyde (1.40 g, 10.0 mmol, 1.0 eq.) was used as the substrate to afford 2-(4-chlorobenzylidene)malononitrile as a white powder (1.76 g, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.73 (s, 1H), 7.56 – 7.48 (m, 2H).

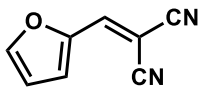
NMR data matched with reference[32].



According to **General Procedure C**, 4-fluorobenzaldehyde (1.07 mL, 10.0 mmol, 1.0 eq.) was used as the substrate to afford 2-(4-fluorobenzylidene)malononitrile as a white powder (1.40 g, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.74 (s, 1H), 7.26 – 7.20 (m, 2H).

NMR data matched with reference[33].

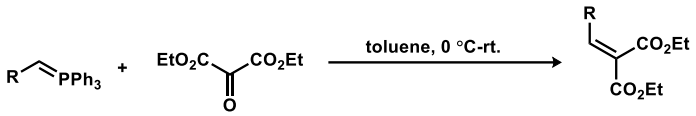


According to **General Procedure C**, furfural (0.83 mL, 10.0 mmol, 1.0 eq.) was used as the substrate to afford 2-(furan-2-ylmethylene)malononitrile as a dark red powder (1.29 g, 90%).

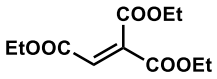
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 1.7 Hz, 1H), 7.51 (s, 1H), 7.37 (d, J = 3.7 Hz, 1H), 6.72 (dd, J = 3.8, 1.8 Hz, 1H).

NMR data matched with reference[32].

General Procedure D



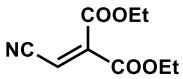
Following the literatures[3,34,35], a 25 mL round-bottom flask equipped with a magnetic stir bar was charged with ylides (5.0 mmol, 1.0 eq.). The flask was evacuated and backfilled by Ar for 3 times, then added with 10 mL anhydrous toluene. While stirring at 0 °C in ice bath, diethyl 2-oxomalonate (0.76 mL, 5.0 mmol, 1.0 eq.) was added dropwise through a syringe. After the addition, the flask was removed from ice and kept on stirring at room temperature for 3 h and was checked by TLC till completion. Solvent was concentrated in vacuo, and the crude products were purified through silica gel chromatography.



According to **General Procedure D**, ethyl (triphenylphosphoranylidene)acetate (1.74 g, 5.0 mmol, 1.0 eq.) was used as the substrate. Purification by silica gel chromatography (PE/EA = 20/1) afforded triethyl ethene-1,1,2-tricarboxylate as a colorless oil (868.0 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.26 (dq, *J* = 21.2, 7.1 Hz, 4H), 1.38 – 1.26 (m, 9H).

NMR data matched with reference[3].



According to **General Procedure D**, (cyanomethylene)triphenylphosphorane (1.50 g, 5.0 mmol, 1.0 eq.) was used as the substrate. Purification by silica gel chromatography (PE/EA = 20/1) afforded triethyl ethene-1,1,2-tricarboxylate as a colorless oil (290.1 mg, 29%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

NMR data matched with reference[3].

5.3. Decarboxylative functionalization of free aliphatic acids

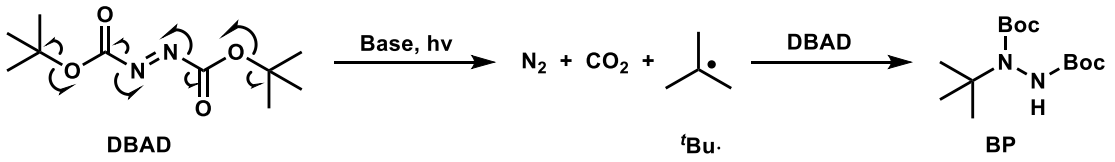
General Procedure E: In an argon-filled glovebox, a flame-dried 25 mL sampling bottle equipped with a Teflon septum was charged with 46.0 mg $ZrCl_4$ (0.4 mmol). The bottle was sealed tightly and removed from the glovebox, and 20 mL anhydrous MeCN was added to prepare a stock solution. The solution was then stored under an argon atmosphere and in avoidance of light for each use.

A flame-dried 4 mL vial equipped with a Teflon septum and magnetic stir bar was charged with DBAD, carboxylic acids, and bases (0.2 mmol, 1.0 eq.). The vial was sealed, and then evacuated and back-filled with argon for 5 times. Next, 2.0 mL of the $ZrCl_4$ stock solution (0.02 mmol, 0.1 eq.) were added via syringe under argon. The reaction mixture was then stirred and irradiated with 5 W LEDs (365−370 nm or

380−385 nm) in the photoreactor at room temperature. After 24-48 h, the reaction was completed with the monitoring of TLC. If the remaining acid had a great R_f difference in comparison with the product, the solvent was removed in vacuo and directly used for silica gel chromatography. If $MgSO_4$ was added, the mixture was first filtered through a sand-core funnel and washed by DCM for 3 times. The combined solvent was then removed in vacuo for purification. However, if the remaining acid had a very close R_f compared with the product, the mixture was first basified by saturated K_2CO_3 aqueous, then extracted by DCM for 3 times. The organic layers were combined, washed with brine for once, dried by Na_2SO_4, then concentrated in vacuum. Purification of the crude product by flash chromatography on silica gel afforded the desired product.

Notice:

1. To ensure the reproducibility, adding 100 mg $MgSO_4$ is sometimes recommended.
2. Among the decarboxylative amination processes, an off-white crystalline solid (TLC: R_f = 0.4, PE/EA = 10/1) can be isolated as a byproduct. The ^{1}H NMR spectrum showed that this byproduct is di-tert-butyl 1-(tert-butyl)hydrazine-1,2-dicarboxylate (^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (d, *J* = 92.1 Hz, 1H), 1.47 (s, 9H), 1.46 (s, 9H), 1.38 (s, 9H). **Figure S16**), which was in agreement with the reported data[36]. We proposed that under the basic conditions, DBAD might undergo a homolysis process (similar to that of AIBN), releasing CO_2 and N_2 to form a tert-butyl radical ^{t}Bu·, which was then trapped by another DBAD to form this byproduct.



DBAD ^{t}Bu· BP

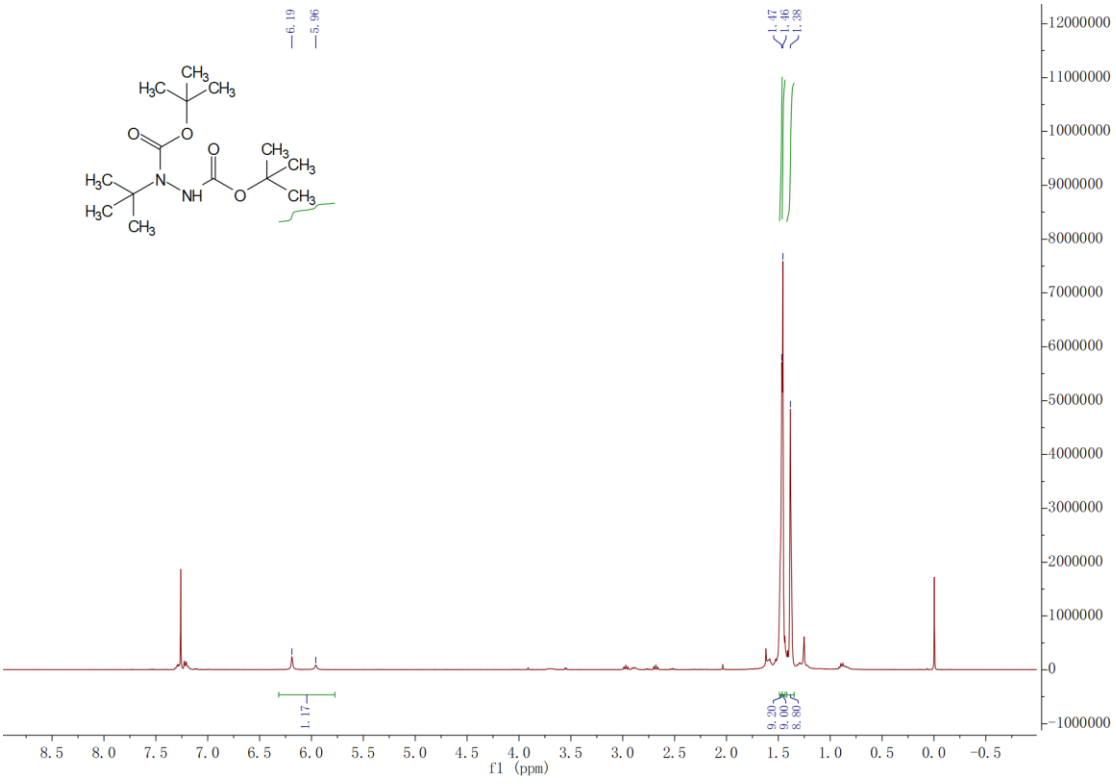
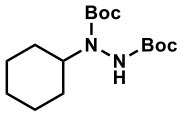
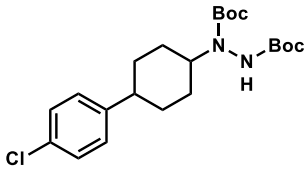


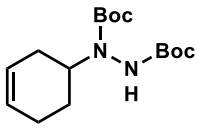
Figure S16 ^{1}H NMR spectrum of the byproduct di-tert-butyl 1-(tert-butyl)hydrazine-1,2-dicarboxylate



Di-tert-butyl 1-cyclohexylhydrazine-1,2-dicarboxylate (**1**)
According to **General Procedure E**, cyclohexanecarboxylic acid (25.6 mg, 0.2 mmol, 1.0 eq.), DBAD (69.0 mg, 0.3 mmol, 1.5 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **1** as a white solid (54.3 mg, 86%).

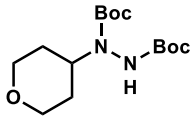


Di-tert-butyl 1-(4-(4-chlorophenyl)cyclohexyl)hydrazine-1,2-dicarboxylate (**28**)
According to **General Procedure E**, 4-(4-chlorophenyl)cyclohexanecarboxylic acid (142.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **28** as a white solid (47.3 mg, 56%). Two sets of signals were shown due to a mixture of *cis*/*trans*.
TLC: R_f = 0.6 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 3H), 7.18 – 7.09 (m, 1H), 6.63 – 6.03 (m, 1H), 4.38 – 3.87 (m, 1H), 2.58 – 2.30 (m, 1H), 2.28 – 1.85 (m, 4H), 1.83 – 1.55 (m, 4H), 1.53 – 1.43 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.43, 180.09, 156.22, 156.03, 155.20, 154.89, 145.31, 144.21, 131.78, 131.70, 131.35, 128.83, 128.78, 128.59, 128.54, 128.41, 128.21, 81.72, 81.21, 81.07, 80.74, 55.55, 54.63, 43.08, 42.88, 42.69, 41.33, 38.52, 33.29, 33.21, 30.01, 29.33, 29.18, 28.98, 28.62, 28.43, 28.39, 28.36, 28.33, 28.28, 28.21, 28.05, 27.28.
HRMS (ESI) m/z calcd. for $C_{22}H_{32}ClN_2O_4$ ($[M-H]^-$) 423.2056, found 423.2057

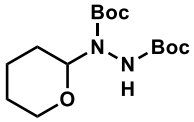


Di-tert-butyl 1-(cyclohex-3-en-1-yl)hydrazine-1,2-dicarboxylate (**29**)
According to **General Procedure E**, 3-cyclohexenecarboxylic acid (67.2 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **29** as a white solid (12.4 mg, 20%).
TLC: R_f = 0.5 (PE/EA = 5/1, PMA or I_2)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (d, J = 107.9 Hz, 1H), 5.61 (d, J = 2.5 Hz, 2H),

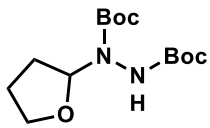
4.27 (s, 1H), 2.30 – 1.96 (m, 4H), 1.62 (d, *J* = 2.6 Hz, 2H), 1.48 – 1.45 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.21, 154.88, 126.34, 125.47, 81.15, 80.98, 59.44, 52.78, 28.64, 28.51, 28.42, 28.35, 28.19, 26.57, 25.61.
HRMS (ESI) m/z calcd. for $C_{16}H_{29}N_2O_4$ ($[M+H]^+$) 312.2122, found 312.2120



Di-tert-butyl 1-(tetrahydro-2H-pyran-4-yl)hydrazine-1,2-dicarboxylate (**30**)
According to **General Procedure E**, tetrahydro-2H-pyran-4-carboxylic acid (78.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **30** as a white solid (48.1 mg, 76%).
TLC: R_f = 0.5 (PE/EA = 2/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (d, *J* = 87.5 Hz, 1H), 4.21 (s, 1H), 3.96 (dt, *J* = 11.8, 3.1 Hz, 2H), 3.49 – 3.31 (m, 2H), 1.44 (d, *J* = 4.6 Hz, 22H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.96, 154.76, 81.58, 81.34, 81.06, 67.33, 53.40, 30.30, 28.32, 28.26.
HRMS (ESI) m/z calcd. for $C_{15}H_{28}N_2O_5Na$ ($[M+Na]^+$) 339.1890, found 339.1885

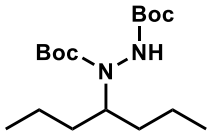


Di-tert-butyl 1-(tetrahydro-2H-pyran-2-yl)hydrazine-1,2-dicarboxylate (**31**)
According to **General Procedure E**, tetrahydro-2H-pyran-2-carboxylic acid (78.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **31** as a white solid (40.1 mg, 63%).
TLC: R_f = 0.4 (PE/EA = 5/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, *J* = 124.0 Hz, 1H), 5.16 (d, *J* = 83.0 Hz, 1H), 3.98 (d, *J* = 11.5 Hz, 1H), 3.55 (s, 1H), 1.98 – 1.49 (m, 6H), 1.46 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.46, 154.31, 84.26, 81.84, 80.86, 68.19, 28.31, 28.26, 27.91, 25.21, 23.16.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{15}H_{27}N_2O_5$ ($[M-H]^-$) 315.1925, found 315.1924

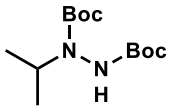


Di-tert-butyl 1-(tetrahydrofuran-2-yl)hydrazine-1,2-dicarboxylate (**32**)
According to **General Procedure E**, 2-tetrahydrofuroic acid (69.6 mg, 0.6 mmol, 3.0

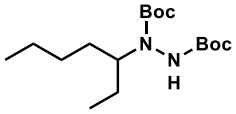
eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **32** as a white solid (38.0 mg, 63%).
TLC: R_f = 0.5 (PE/EA = 4/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (d, *J* = 54.0 Hz, 1H), 5.98 (d, *J* = 30.5 Hz, 1H), 3.95 (q, *J* = 6.8, 6.2 Hz, 1H), 3.72 (q, *J* = 7.1 Hz, 1H), 2.14 – 1.88 (m, 3H), 1.88 – 1.76 (m, 1H), 1.44 (d, *J* = 2.9 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.87, 154.36, 81.85, 81.39, 81.11, 68.54, 28.23, 25.36. NMR matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{14}H_{25}N_2O_5$ ($[M-H]^-$) 301.1769, found 301.1767



Di-tert-butyl 1-(heptan-4-yl)hydrazine-1,2-dicarboxylate (**33**)
According to **General Procedure E**, valproic acid (96 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 30/1) afforded **33** as a white solid (45.6 mg, 69%).
TLC: R_f = 0.4 (PE/EA = 10/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (s, 1H), 4.03 (d, *J* = 61.8 Hz, 1H), 1.47 (s, 22H), 1.35 – 1.21 (m, 4H), 0.90 (td, *J* = 7.2, 3.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.30, 155.52, 81.07, 80.72, 57.87, 56.52, 45.05, 34.96, 34.59, 28.37, 28.30, 20.70, 19.75, 14.12, 14.04.
HRMS (ESI) m/z calcd. for $C_{17}H_{38}N_3O_4$ ($[M+NH_4]^+$) 348.2857, found 348.2854



Di-tert-butyl 1-isopropylhydrazine-1,2-dicarboxylate (**34**)
According to **General Procedure E**, isobutyric acid (55.6 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **34** as a white solid (37.9 mg, 69%).
TLC: R_f = 0.3 (PE/EA = 10/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (d, *J* = 53.7 Hz, 1H), 4.36 (s, 1H), 1.46 (d, *J* = 4.8 Hz, 18H), 1.09 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.98, 154.80, 81.36, 80.89, 48.37, 28.38, 28.27, 19.85. NMR data matched with reference[36].
HRMS (ESI) m/z calcd. for $C_{13}H_{25}N_2O_4$ ($[M-H]^-$) 273.1820, found 273.1822



Di-tert-butyl 1-(heptan-3-yl)hydrazine-1,2-dicarboxylate (**35**)

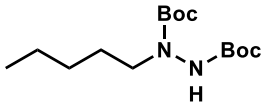
According to **General Procedure E**, 2-ethylhexanoic acid (95.4 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 30/1) afforded **35** as a colorless oil (37.1 mg, 56%).

TLC: R_f = 0.5 (PE/EA = 10/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (d, *J* = 28.2 Hz, 1H), 4.08 – 3.69 (m, 1H), 1.45 (d, *J* = 5.4 Hz, 20H), 1.30 (ddt, *J* = 31.2, 23.2, 6.3 Hz, 6H), 0.88 (q, *J* = 9.1, 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.97, 155.64, 80.99, 80.73, 60.57, 58.74, 32.20, 31.81, 28.78, 28.37, 28.31, 25.93, 25.64, 22.78, 22.66, 14.14, 11.34.

HRMS (ESI) m/z calcd. for $C_{17}H_{38}N_3O_4$ ($[M+NH_4]^+$) 348.2857, found 348.2856



Di-tert-butyl 1-pentylhydrazine-1,2-dicarboxylate (**14-1**)

According to **General Procedure E**, hexanoic acid (75.1 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 48 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **14-1** as a pale white solid (34.6 mg, 57%).

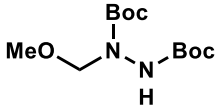
TLC: R_f = 0.3 (PE/EA = 10/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 – 5.90 (m, 1H), 3.49 – 3.28 (m, 2H), 1.53 (p, *J* = 7.4 Hz, 2H), 1.45 (d, *J* = 5.7 Hz, 18H), 1.35 – 1.20 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.52, 81.07, 59.41, 50.63, 49.50, 28.98, 28.61, 28.42, 28.34, 28.31, 27.28, 22.50, 14.13.

NMR data matched with reference[38].

HRMS (ESI) m/z calcd. for $C_{15}H_{31}N_2O_4$ ($[M+H]^+$) 303.2278, found 303.2278



Di-tert-butyl 1-(methoxymethyl)hydrazine-1,2-dicarboxylate (**36**)

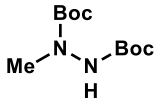
According to **General Procedure E**, methoxyacetic acid (50.0 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **36** as a colorless oil (50.8 mg, 92%).

TLC: R_f = 0.3 (PE/EA = 5/1, PMA)

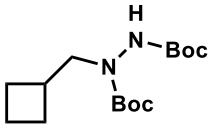
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (s, 1H), 4.79 (s, 2H), 3.35 (s, 3H), 1.46 (d, *J* = 4.6 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.97, 154.60, 82.37, 81.91, 81.42, 81.04, 56.28, 28.27, 28.19, 28.02.

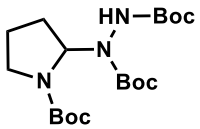
HRMS (ESI) m/z calcd. for $C_{12}H_{23}N_2O_5$ ([M-H]$^-$) 275.1612, found 275.1611



Di-tert-butyl 1-methylhydrazine-1,2-dicarboxylate (**37**)
According to **General Procedure E**, acetic acid (34.3 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 48 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **37** as a white solid (23.6 mg, 50%).
TLC: R_f = 0.5 (PE/EA = 5/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 – 6.08 (m, 1H), 3.09 (s, 3H), 1.45 (d, *J* = 6.1 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.89, 155.18, 81.26, 38.59, 37.58, 28.34.
NMR data matched with reference[28].
HRMS (ESI) m/z calcd. for $C_{11}H_{21}N_2O_4$ ([M-H]$^-$) 245.1507, found 245.1508

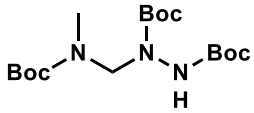


Di-tert-butyl 1-(cyclobutylmethyl)hydrazine-1,2-dicarboxylate (**38**)
According to **General Procedure E**, cyclobutylacetic acid (67.5 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 48 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **38** as a white crystalline solid (27.6 mg, 46%).
TLC: R_f = 0.4 (PE/EA = 10/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 – 5.86 (m, 1H), 3.46 (d, *J* = 7.4 Hz, 2H), 2.56 (hept, *J* = 7.6 Hz, 1H), 2.08 – 1.94 (m, 2H), 1.92 – 1.77 (m, 2H), 1.76 – 1.62 (m, 2H), 1.45 (d, *J* = 4.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.65, 81.05, 59.42, 55.69, 54.39, 34.02, 28.62, 28.43, 28.33, 26.20, 18.62.
HRMS (ESI) m/z calcd. for $C_{15}H_{27}N_2O_4$ ([M-H]$^-$) 299.1976, found 299.1978



Di-tert-butyl 1-(1-(tert-butoxycarbonyl)pyrrolidin-2-yl)hydrazine-1,2-dicarboxylate (**10**)
According to **General Procedure E**, L-proline (129.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (From PE/EA = 20/1 to 10/1) afforded **10** as a white solid (49.8 mg, 62%).

TLC: R_f = 0.3 (PE/EA = 5/1, PMA)



Di-tert-butyl 1-(((tert-butoxycarbonyl)(methyl)amino)methyl)hydrazine-1,2-dicarboxylate (**39**)

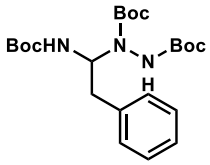
According to **General Procedure E**, Boc-sarcosine (113.4 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **39** as a white solid (48.0 mg, 61%).

TLC: R_f = 0.6 (PE/EA = 2/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 – 5.96 (m, 1H), 4.92 (s, 2H), 2.89 (d, *J* = 15.7 Hz, 3H), 1.44 (d, *J* = 8.5 Hz, 27H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.71, 155.03, 154.67, 81.68, 81.19, 80.08, 61.86, 34.23, 33.27, 28.42, 28.34, 28.26, 28.05.

HRMS (ESI) m/z calcd. for $C_{17}H_{34}N_3O_6$ ($[M+H]^+$) 376.2442, found 376.2439



Di-tert-butyl 1-(1-((tert-butoxycarbonyl)amino)-2-phenylethyl)hydrazine-1,2-dicarboxylate (**40**)

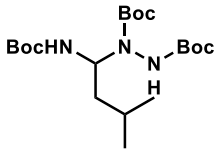
According to **General Procedure E**, 2-((tert-butoxycarbonyl)amino)-3-phenylpropanoic acid (159.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **40** as a pale white cloudy oil (80.5 mg, 89%).

TLC: R_f = 0.3 (PE/EA = 5/1, UV and PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.24 – 7.16 (m, 3H), 6.31 (s, 1H), 6.05 – 5.33 (m, 2H), 3.03 (s, 2H), 1.47 (d, *J* = 8.2 Hz, 9H), 1.39 (d, *J* = 12.5 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.23, 155.93, 154.63, 154.05, 136.95, 129.44, 129.20, 129.09, 128.66, 128.59, 128.50, 126.70, 126.07, 125.25, 81.81, 81.45, 79.64, 67.17, 39.45, 28.39, 28.27, 28.25, 28.21.

HRMS (ESI) m/z calcd. for $C_{23}H_{41}N_4O_6$ ($[M+NH_4]^+$) 469.3020, found 469.3020



Di-tert-butyl 1-(1-((tert-butoxycarbonyl)amino)-3-methylbutyl)hydrazine-1,2-dicarboxylate (**41**)

According to **General Procedure E**, N-tert-butoxycarbonyl-L-leucine (138.6 mg, 0.6

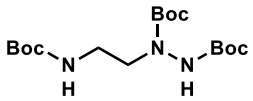
mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **41** as a foam-like white solid (42.5 mg, 51%).

TLC: R_f = 0.4 (PE/EA = 5/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 1H), 5.80 – 4.90 (m, 2H), 1.74 – 1.52 (m, 3H), 1.45 (d, *J* = 2.1 Hz, 18H), 1.41 (s, 9H), 0.92 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.94, 154.74, 154.26, 81.52, 79.70, 64.43, 52.69, 42.14, 28.46, 28.35, 28.29, 28.24, 24.49, 22.68, 22.61, 22.51.

HRMS (ESI) m/z calcd. for $C_{20}H_{43}N_4O_6$ ($[M+NH_4]^+$) 435.3177, found 435.3176



Di-tert-butyl 1-(2-((tert-butoxycarbonyl)amino)ethyl)hydrazine-1,2-dicarboxylate (**42**)

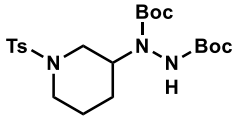
According to **General Procedure E**, 3-(tert-butyloxycarbonylamino)propionic acid (113.4 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (From PE/EA = 10/1 to 5/1) afforded **42** as a colorless oil (22.3 mg, 30%).

TLC: R_f = 0.2 (PE/EA = 5/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 55.4 Hz, 1H), 5.57 – 4.78 (m, 1H), 3.50 (t, *J* = 5.1 Hz, 2H), 3.28 (d, *J* = 8.3 Hz, 2H), 1.50 – 1.40 (m, 27H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.45, 155.44, 81.34, 79.24, 49.31, 38.28, 28.57, 28.33, 28.20, 28.05.

HRMS (ESI) m/z calcd. for $C_{17}H_{32}N_3O_6$ ($[M-H]^-$) 374.2296, found 374.2296



Di-tert-butyl 1-(1-tosylpiperidin-3-yl)hydrazine-1,2-dicarboxylate (**43**)

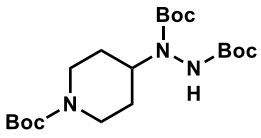
According to **General Procedure E**, 1-tosylpiperidine-3-carboxylic acid (56.6 mg, 0.2 mmol, 1.0 eq.), DBAD (69.0 mg, 0.3 mmol, 1.5 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 5/1) afforded **43** as a white solid (30.2 mg, 32%).

TLC: R_f = 0.4 (PE/EA = 2/1, UV & PMA)

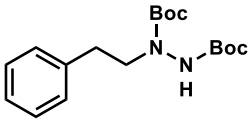
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 5.94 (d, *J* = 90.0 Hz, 1H), 3.78 (d, *J* = 89.7 Hz, 3H), 2.42 (s, 3H), 2.10 (s, 2H), 1.70 (dt, *J* = 24.8, 12.7 Hz, 3H), 1.44 (d, *J* = 10.5 Hz, 19H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.16, 154.39, 143.61, 133.53, 129.75, 127.83, 81.94, 81.42, 48.79, 46.00, 28.32, 28.23, 28.11, 27.98, 27.26, 24.03, 21.62.

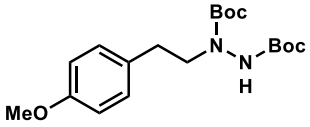
HRMS (ESI) m/z calcd. for $C_{22}H_{34}N_3O_6S$ ($[M-H]^-$) 468.21740, found 468.2178



Di-tert-butyl 1-(1-(tert-butoxycarbonyl)piperidin-4-yl)hydrazine-1,2-dicarboxylate (**44**)
According to **General Procedure E**, N-[(tert-butoxy)carbonyl]piperidine-4-carboxylic acid (137.4 mg, 0.2 mmol, 1.0 eq.), DBAD (69.0 mg, 0.3 mmol, 1.5 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (From PE/EA = 10/1 to 5/1) afforded **44** as a colorless oil (36.6 mg, 44%).
TLC: R_f = 0.6 (PE/EA = 2/1, PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (d, *J* = 100.0 Hz, 1H), 4.28 – 3.95 (m, 3H), 2.72 (t, *J* = 13.2 Hz, 2H), 1.86 – 1.63 (m, 2H), 1.63 – 1.53 (m, 2H), 1.51 – 1.38 (m, 27H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.96, 154.84, 81.47, 81.21, 79.65, 54.43, 43.21, 29.35, 28.57, 28.36, 28.32.
HRMS (ESI) m/z calcd. for $C_{20}H_{36}N_3O_6$ ($[M-H]^-$) 414.2609, found 414.2608

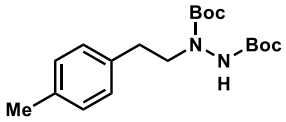


Di-tert-butyl 1-phenethylhydrazine-1,2-dicarboxylate (**45**)
According to **General Procedure E**, 3-phenylpropionic acid (90.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **45** as a white solid (44.6 mg, 66%).
TLC: R_f = 0.4 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.16 – 7.06 (m, 3H), 6.11 (d, *J* = 72.5 Hz, 1H), 3.62 (d, *J* = 7.9 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.38 (d, *J* = 19.7 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.71, 155.21, 139.17, 128.87, 128.58, 126.36, 81.28, 52.24, 51.07, 34.35, 34.01, 28.29, 28.26.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{18}H_{28}N_2O_4Na$ ($[M+Na]^+$) 359.1941, found 359.1932

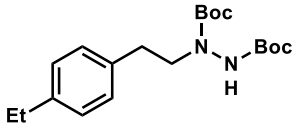


Di-tert-butyl 1-(4-methoxyphenethyl)hydrazine-1,2-dicarboxylate (**46**)
According to **General Procedure E**, 3-(4-methoxyphenyl)propionic acid (108.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **46** as a colorless oil (16.6 mg, 23%).

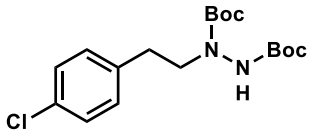
TLC: R_f = 0.3 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.8 Hz, 2H), 6.87 – 6.74 (m, 2H), 6.12 (d, *J* = 78.7 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 2H), 2.89 – 2.76 (m, 2H), 1.45 (d, *J* = 16.1 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.26, 155.28, 131.23, 129.84, 114.07, 81.33, 67.19, 55.41, 33.48, 33.11, 28.67, 28.33, 28.15, 28.08.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{19}H_{30}N_2O_5Na$ ($[M+Na]^+$) 389.2047, found 389.2043



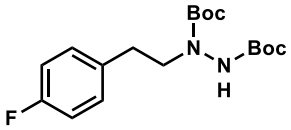
Di-tert-butyl 1-(4-methylphenethyl)hydrazine-1,2-dicarboxylate (**47**)
According to **General Procedure E**, 3-(4-methylphenyl)propionic acid (98.4 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 48 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **47** as a white solid (33.9 mg, 47%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 4H), 6.12 (d, *J* = 96.7 Hz, 1H), 3.67 (s, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.47 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.24, 136.06, 135.87, 129.30, 128.76, 81.26, 51.23, 33.90, 33.60, 28.33, 28.31, 21.12.
HRMS (ESI) m/z calcd. for $C_{19}H_{34}N_3O_4$ ($[M+NH_4]^+$) 368.2544, found 368.2539



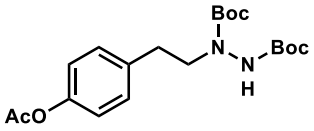
Di-tert-butyl 1-(4-ethylphenethyl)hydrazine-1,2-dicarboxylate (**48**)
According to **General Procedure E**, 3-(4-ethylphenyl)propionic acid (106.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 48 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **48** as a white solid (50.5 mg, 62%).
TLC: R_f = 0.6 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 4H), 6.44 – 5.78 (m, 1H), 3.68 (s, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.49 – 1.41 (m, 18H), 1.22 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.22, 142.29, 136.31, 128.81, 128.08, 81.21, 80.64, 59.40, 52.34, 51.16, 33.90, 33.60, 28.61, 28.56, 28.42, 28.30, 28.28, 28.20.
HRMS (ESI) m/z calcd. for $C_{20}H_{31}N_2O_4$ ($[M-H]^-$) 363.2289, found 363.2288



Di-tert-butyl 1-(4-chlorophenethyl)hydrazine-1,2-dicarboxylate (**49**)
According to **General Procedure E**, 3-(4-chlorophenyl)propionic acid (111.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **49** as a white solid (49.2 mg, 66%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.29 (t, *J* = 47.4 Hz, 1H), 3.68 (d, *J* = 7.9 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 1.48 (d, *J* = 18.0 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.17, 137.68, 132.15, 130.24, 128.67, 81.39, 52.17, 50.87, 33.73, 33.35, 28.29, 28.25, 28.03.
HRMS (ESI) m/z calcd. for $C_{18}H_{26}ClN_2O_4$ ($[M-H]^-$) 369.1587, found 369.1586

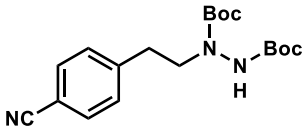


Di-tert-butyl 1-(4-fluorophenethyl)hydrazine-1,2-dicarboxylate (**50**)
According to **General Procedure E**, 3-(4-fluorophenyl)propionic acid (100.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 36 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **50** as a pale white solid (35.2 mg, 50%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.27 (m, 2H), 6.34 (d, *J* = 44.7 Hz, 1H), 3.68 (d, *J* = 7.7 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.48 – 1.35 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.87, 160.44, 155.18, 134.85, 130.30, 130.23, 115.44, 115.23, 81.36, 52.39, 51.09, 33.52, 33.22, 28.30, 28.27.
HRMS (ESI) m/z calcd. for $C_{18}H_{26}FN_2O_4$ ($[M-H]^-$) 353.1882, found 353.1881

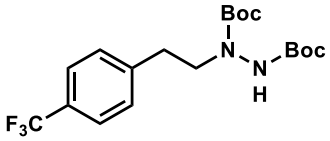


Di-tert-butyl 1-(4-acetoxyphenethyl)hydrazine-1,2-dicarboxylate (**51**)
According to **General Procedure E**, 3-(4-acetoxyphenyl)propionic acid (124.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **51** as a white solid (29.6 mg, 40%).
TLC: R_f = 0.2 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.92 (m, 2H), 6.10 (d, *J* = 90.6 Hz, 1H), 3.74 – 3.57 (m, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.48 – 1.41 (m, 18H).

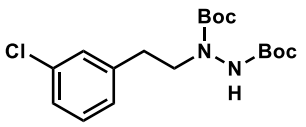
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.66, 155.25, 149.34, 136.80, 129.85, 121.68, 81.49, 50.97, 33.70, 28.36, 28.34, 21.26.
HRMS (ESI) m/z calcd. for $C_{20}H_{29}N_2O_6$ ([M-H]$^-$) 393.2031, found 393.2035



Di-tert-butyl 1-(4-cyanophenethyl)hydrazine-1,2-dicarboxylate (**52**)
According to **General Procedure E**, 3-(4-cyanophenyl)propionic acid (105.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **52** as a white solid (49.1 mg, 68%).
TLC: R_f = 0.2 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.50 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.19 (d, *J* = 57.1 Hz, 1H), 3.69 (d, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.48 – 1.40 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.86, 155.07, 145.05, 132.38, 132.34, 132.24, 129.80, 129.74, 119.03, 110.32, 82.11, 81.56, 51.78, 50.47, 34.51, 34.20, 28.29, 28.26, 28.23.
HRMS (ESI) m/z calcd. for $C_{19}H_{26}N_3O_4$ ([M-H]$^-$) 360.1929, found 360.1929

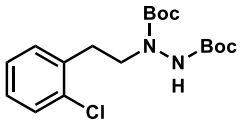


Di-tert-butyl 1-(4-(trifluoromethyl)phenethyl)hydrazine-1,2-dicarboxylate (**53**)
According to **General Procedure E**, 4-(trifluoromethyl)hydrocinnamic acid (130.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **53** as a white solid (37.9 mg, 47%).
TLC: R_f = 0.3 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.31 (q, *J* = 56.4, 53.3 Hz, 1H), 3.71 (t, *J* = 7.4 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 2H), 1.47 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.16, 143.45, 129.25, 128.64, 128.46, 125.75, 125.51, 125.48, 123.05, 120.35, 52.01, 50.68, 33.90, 28.30, 28.23.
HRMS (ESI) m/z calcd. for $C_{19}H_{26}F_3N_2O_4$ ([M-H]$^-$) 403.1850, found 403.1852

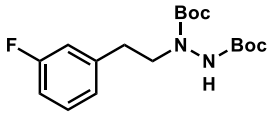


Di-tert-butyl 1-(3-chlorophenethyl)hydrazine-1,2-dicarboxylate (**54**)
According to **General Procedure E**, 3-(3-chlorophenyl)propionic acid (111.0 mg, 0.6

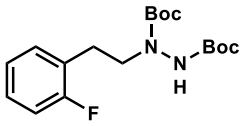
mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **54** as a white solid (45.5 mg, 61%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.0 Hz, 3H), 7.08 (s, 1H), 6.13 (d, *J* = 92.4 Hz, 1H), 3.68 (d, *J* = 7.7 Hz, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.45 (d, *J* = 20.0 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.17, 141.31, 134.36, 129.86, 129.05, 127.12, 126.63, 81.52, 50.86, 34.10, 33.80, 28.34, 28.29.
HRMS (ESI) m/z calcd. for $C_{18}H_{28}ClN_2O_4$ ($[M+H]^+$) 371.1732, found 371.1731



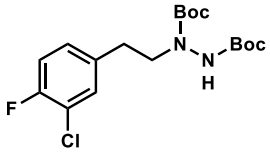
Di-tert-butyl 1-(2-chlorophenethyl)hydrazine-1,2-dicarboxylate (**55**)
According to **General Procedure E**, 3-(2-chlorophenyl)propionic acid (111.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **55** as a colorless oil (54.1 mg, 73%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.25 – 7.10 (m, 3H), 6.53 – 6.01 (m, 1H), 3.72 (t, *J* = 7.3 Hz, 2H), 3.00 (t, *J* = 8.4 Hz, 2H), 1.47 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.63, 155.12, 136.96, 134.33, 131.11, 129.61, 127.95, 127.01, 81.29, 50.40, 49.52, 32.26, 31.77, 28.30, 28.21.
HRMS (ESI) m/z calcd. for $C_{18}H_{31}ClN_3O_4$ ($[M+NH_4]^+$) 388.1997, found 388.1999



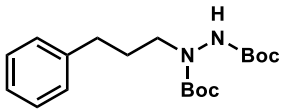
Di-tert-butyl 1-(3-fluorophenethyl)hydrazine-1,2-dicarboxylate (**56**)
According to **General Procedure E**, 3-(3-fluorophenyl)propionic acid (100.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 48 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **56** as a white solid (42.3 mg, 60%).
TLC: R_f = 0.4 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 7.9, 6.1 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 8.9 Hz, 2H), 6.15 (d, *J* = 79.0 Hz, 1H), 3.69 (t, *J* = 7.4 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H), 1.47 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.26, 161.82, 155.16, 141.81, 130.05, 129.97, 124.56, 115.86, 115.65, 113.39, 113.18, 81.44, 51.94, 50.83, 33.83, 28.31, 28.27.
HRMS (ESI) m/z calcd. for $C_{18}H_{28}FN_2O_4$ ($[M+H]^+$) 355.2027, found 355.2026



Di-tert-butyl 1-(2-fluorophenethyl)hydrazine-1,2-dicarboxylate (**57**)
According to **General Procedure E**, 3-(2-fluorophenyl)propionic acid (100.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **57** as a white solid (49.6 mg, 70%).
TLC: R_f = 0.4 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 2H), 7.10 – 6.92 (m, 2H), 6.52 – 5.87 (m, 1H), 3.71 (t, *J* = 7.2 Hz, 2H), 2.90 (d, *J* = 8.0 Hz, 2H), 1.47 (s, 18H).
^{13}C NMR (101 MHz, CDCl3) δ 162.76, 160.32, 155.69, 155.13, 131.27, 128.18, 126.19, 126.03, 124.25, 124.21, 115.45, 115.23, 81.28, 80.66, 49.69, 28.30, 28.18, 27.38.
HRMS (ESI) m/z calcd. for $C_{18}H_{26}FN_2O_4$ ($[M-H]^-$) 353.1882, found 353.1883

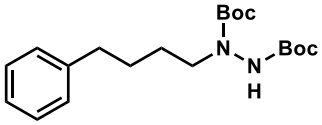


Di-tert-butyl 1-(3-chloro-4-fluorophenethyl)hydrazine-1,2-dicarboxylate (**58**)
According to **General Procedure E**, 3-(3-chloro-4-fluorophenyl)propanoic acid (121.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (From PE/EA = 20/1 to 10/1) afforded **58** as a foam-like white solid (32.4 mg, 42%).
TLC: R_f = 0.4 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.17 (d, *J* = 60.3 Hz, 1H), 3.65 (d, *J* = 7.6 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 1.45 (d, *J* = 21.9 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.17, 155.71, 155.16, 136.29, 130.88, 128.53, 120.91, 120.73, 116.68, 116.47, 81.55, 51.97, 33.12, 28.32, 28.27.
HRMS (ESI) m/z calcd. for $C_{18}H_{25}FClN_2O_4$ ($[M-H]^-$) 387.1492, found 387.1492

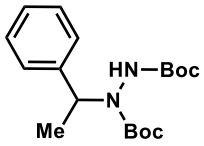


Di-tert-butyl 1-(3-phenylpropyl)hydrazine-1,2-dicarboxylate (**59**)
According to **General Procedure E**, 4-phenylbutyric acid (98.4 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **59** as an off-white solid (32.3 mg, 46%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 3H), 6.06

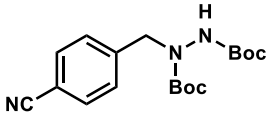
(d, J = 106.9 Hz, 1H), 3.41 (s, 2H), 2.63 – 2.48 (m, 2H), 1.82 (p, J = 7.3 Hz, 2H), 1.39 (d, J = 6.7 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.49, 155.32, 141.90, 128.47, 125.94, 81.22, 49.19, 33.18, 29.33, 28.33, 28.32.
HRMS (ESI) m/z calcd. for $C_{19}H_{30}N_2O_4Na$ ($[M+Na]^+$) 373.2098, found 373.2090



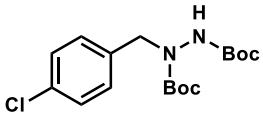
Di-tert-butyl 1-(4-phenylbutyl)hydrazine-1,2-dicarboxylate (**60**)
According to **General Procedure E**, 5-Phenylpentanoic acid (106.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **60** as an off-white solid (32.7 mg, 40%).
TLC: R_f = 0.6 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 8.8, 6.3 Hz, 2H), 7.18 (dd, J = 7.6, 4.9 Hz, 3H), 6.41 – 5.89 (m, 1H), 3.48 (d, J = 7.0 Hz, 2H), 2.64 (t, J = 7.1 Hz, 2H), 1.71 – 1.56 (m, 4H), 1.47 (d, J = 5.5 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.51, 142.43, 128.53, 128.41, 125.85, 81.17, 59.43, 50.93, 49.24, 35.67, 28.62, 28.35, 28.33, 27.23.
NMR data matched with reference[39].
HRMS (ESI) m/z calcd. for $C_{20}H_{31}N_2O_4$ ($[M-H]^-$) 363.2289, found 363.2286



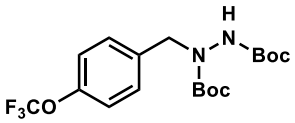
Di-tert-butyl 1-(1-phenylethyl)hydrazine-1,2-dicarboxylate (**61**)
According to **General Procedure E**, 2-phenylpropionic acid (82.0 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **61** as a white solid (43.8 mg, 65%).
TLC: R_f = 0.4 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 20.1, 4.8 Hz, 5H), 6.14 – 5.08 (m, 2H), 1.41 (d, J = 25.6 Hz, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.11, 155.74, 154.97, 154.71, 141.49, 128.48, 127.47, 127.25, 81.36, 80.92, 54.80, 28.35, 28.26, 27.48, 16.77.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{18}H_{28}N_2O_4Na$ ($[M+Na]^+$) 359.1941, found 359.1932



Di-tert-butyl 1-(4-cyanobenzyl)hydrazine-1,2-dicarboxylate (**62**)
According to **General Procedure E**, 4-cyanophenylacetic acid (96.6 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **62** as a colorless oil (62.8 mg, 91%).
TLC: R_f = 0.7 (PE/EA = 2/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 6.28 (d, *J* = 22.3 Hz, 1H), 4.65 (d, *J* = 18.1 Hz, 2H), 1.46 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.87, 155.22, 142.94, 132.39, 132.35, 129.36, 129.01, 118.83, 111.43, 82.05, 81.66, 81.48, 54.60, 53.30, 28.25, 28.21.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{18}H_{25}N_3O_4Na$ ($[M+Na]^+$) 370.1737, found 370.1738

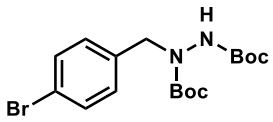


Di-tert-butyl 1-(4-chlorobenzyl)hydrazine-1,2-dicarboxylate (**63**)
According to **General Procedure E**, 4-chlorophenylacetic acid (102.6 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **63** as a colorless oil (37.5 mg, 53%).
TLC: R_f = 0.4 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.17 (d, *J* = 74.5 Hz, 1H), 4.56 (d, *J* = 16.5 Hz, 2H), 1.45 (d, *J* = 13.2 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.22, 135.85, 133.46, 130.37, 129.96, 128.72, 81.58, 53.96, 52.63, 28.32, 28.26.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{17}H_{24}ClN_2O_4$ ($[M-H]^-$) 355.1430, found 355.1427

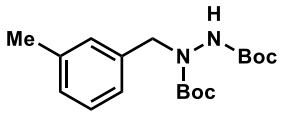


Di-tert-butyl 1-(4-(trifluoromethoxy)benzyl)hydrazine-1,2-dicarboxylate (**64**)
According to **General Procedure E**, 4-(trifluoromethoxy)phenylacetic acid (132.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **64** as a colorless oil (54.3 mg, 67%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) 7.37 – 7.28 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.20 (d, *J* = 70.9 Hz, 1H), 4.62 (s, 2H), 1.45 (d, *J* = 14.5 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.25, 148.77, 136.15, 130.97, 130.70, 129.98, 127.43, 124.45, 121.89, 121.10, 119.34, 116.78, 81.76, 81.53, 52.62, 28.33, 28.24.

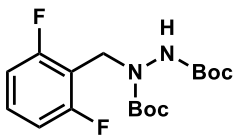
HRMS (ESI) m/z calcd. for $C_{18}H_{24}F_3N_2O_5$ ([M-H]$^-$) 405.1643, found 405.1643



Di-tert-butyl 1-(4-bromobenzyl)hydrazine-1,2-dicarboxylate (**65**)
According to **General Procedure E**, 4-bromo phenylacetic acid (129.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 380−385 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **65** as a white solid (50.2 mg, 63%).
TLC: R_f = 0.5 (PE/EA = 4/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.10 (d, *J* = 90.2 Hz, 1H), 4.58 (s, 2H), 1.46 (d, *J* = 12.9 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.39, 155.13, 136.38, 131.72, 131.58, 131.42, 131.11, 130.16, 128.62, 126.02, 121.59, 81.64, 52.68, 28.34, 28.28.
HRMS (ESI) m/z calcd. for $C_{17}H_{24}BrN_2O_4$ ([M-H]$^-$) 399.0925, found 399.0923

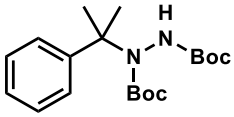


Di-tert-butyl 1-(3-methylbenzyl)hydrazine-1,2-dicarboxylate (**66**)
According to **General Procedure E**, 3-methyl phenylacetic acid (90.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **66** as a white solid (51.7 mg, 77%).
TLC: R_f = 0.6 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 3H), 6.10 (d, *J* = 107.5 Hz, 1H), 4.57 (d, *J* = 27.6 Hz, 2H), 2.34 (s, 3H), 1.47 (d, *J* = 15.9 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.54, 155.21, 138.20, 137.22, 129.18, 128.50, 128.33, 125.51, 81.28, 54.34, 52.98, 28.34, 28.26, 21.47.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{18}H_{27}N_2O_4$ ([M-H]$^-$) 335.1976, found 335.1976

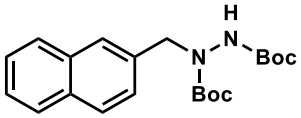


Di-tert-butyl 1-(2,6-difluorobenzyl)hydrazine-1,2-dicarboxylate (**67**)
According to **General Procedure E**, 2,6-difluorophenylacetic acid (103.2 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **67** as a white solid (51.2 mg, 72%).

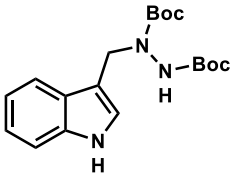
TLC: R_f = 0.4 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (p, *J* = 7.6 Hz, 1H), 6.92 – 6.76 (m, 2H), 6.48 – 5.86 (m, 1H), 4.72 (d, *J* = 34.3 Hz, 2H), 1.42 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.44, 160.96, 155.06, 154.74, 129.73, 112.59, 111.44, 111.38, 111.25, 111.19, 81.99, 81.51, 81.32, 81.17, 42.19, 40.77, 40.24, 28.60, 28.10.
HRMS (ESI) m/z calcd. for $C_{17}H_{24}F_2N_2O_4Na$ ($[M+Na]^+$) 381.1596, found 381.1592



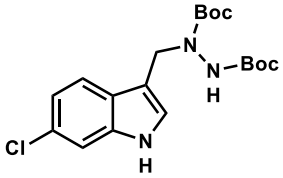
Di-tert-butyl 1-(2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (**68**)
According to **General Procedure E**, 2-phenylisobutyric acid (98.4 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 20/1) afforded **68** as a colorless oil (66.3 mg, 95%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.37 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.15 (m, 1H), 6.52 (d, *J* = 17.3 Hz, 1H), 1.72 (s, 3H), 1.55 (d, *J* = 18.8 Hz, 12H), 1.16 (d, *J* = 12.8 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.68, 154.77, 149.14, 128.09, 126.05, 124.72, 81.69, 81.24, 80.97, 63.83, 28.37, 27.99.
NMR data matched with reference[40].
HRMS (ESI) m/z calcd. for $C_{19}H_{29}N_2O_4$ ($[M-H]^-$) 349.2133, found 349.2130



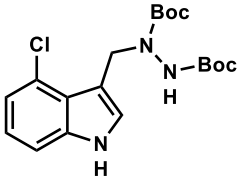
Di-tert-butyl 1-(naphthalen-2-ylmethyl)hydrazine-1,2-dicarboxylate (**69**)
According to **General Procedure E**, 2-naphthylacetic acid (111.6 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (From PE/EA = 20/1 to PE/EA = 10/1) afforded **69** as a colorless oil (39.4 mg, 53%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 3H), 7.71 (s, 1H), 7.46 (dp, *J* = 15.1, 6.8, 4.4 Hz, 3H), 6.13 (d, *J* = 82.9 Hz, 1H), 4.81 (s, 2H), 1.48 (d, *J* = 25.4 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.34, 134.73, 133.66, 133.43, 132.96, 128.43, 128.36, 128.31, 128.25, 128.12, 127.89, 127.80, 127.71, 126.30, 126.20, 126.03, 125.68, 124.74, 124.25, 81.49, 81.04, 53.06, 46.36, 28.38, 28.29.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{21}H_{27}N_2O_4$ ($[M-H]^-$) 371.1976, found 371.1978



Di-tert-butyl 1-((1H-indol-3-yl)methyl)hydrazine-1,2-dicarboxylate (**70**)
According to **General Procedure E**, indole-3-acetic acid (105.1 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 7/1) afforded **70** as a dark-purple solid (35.8 mg, 50%).
TLC: R_f = 0.2 (PE/EA = 4/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.10 (m, 3H), 6.06 (d, *J* = 91.5 Hz, 1H), 4.84 (s, 2H), 1.57 – 1.41 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.91, 155.49, 155.07, 136.47, 127.18, 124.57, 122.43, 122.34, 119.90, 119.43, 111.62, 111.48, 111.34, 81.66, 81.14, 44.07, 28.42, 28.34, 28.28, 28.16.
HRMS (ESI) m/z calcd. for $C_{19}H_{26}N_3O_4$ ($[M-H]^-$) 360.1929, found 360.1928

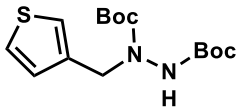


Di-tert-butyl 1-((6-chloro-1H-indol-3-yl)methyl)hydrazine-1,2-dicarboxylate (**71**)
According to **General Procedure E**, 6-chloroindole-3-acetic acid (125.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 8/1) afforded **71** as a purple solid (46.6 mg, 59%).
TLC: R_f = 0.2 (PE/EA = 4/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.34 (s, 1H), 7.16 – 7.02 (m, 2H), 6.08 (d, *J* = 96.2 Hz, 1H), 4.78 (s, 2H), 1.61 – 1.33 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.48, 155.13, 136.83, 128.23, 125.81, 125.17, 120.58, 120.23, 111.75, 111.30, 81.35, 45.23, 44.08, 28.53, 28.39, 28.31, 28.27.
HRMS (ESI) m/z calcd. for $C_{19}H_{25}ClN_3O_4$ ($[M-H]^-$) 394.1539, found 394.1541

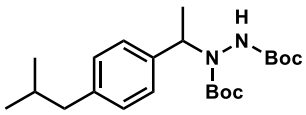


Di-tert-butyl 1-((4-chloro-1H-indol-3-yl)methyl)hydrazine-1,2-dicarboxylate (**72**)
According to **General Procedure E**, 4-chloroindole-3-acetic acid (125.8 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.)

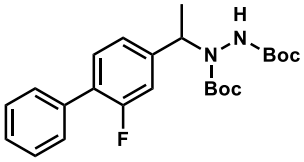
were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **72** as a black solid (30.9 mg, 39%).
TLC: R_f = 0.3 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.28 – 7.24 (m, 1H), 7.21 (s, 1H), 7.07 (q, *J* = 3.7, 2.9 Hz, 2H), 6.09 (d, *J* = 139.4 Hz, 1H), 5.06 (s, 2H), 1.49 (s, 9H), 1.39 (d, *J* = 5.9 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.58, 155.11, 137.90, 126.30, 124.24, 122.78, 120.87, 111.60, 110.20, 81.05, 45.14, 28.44, 28.31.
HRMS (ESI) m/z calcd. for $C_{19}H_{25}ClN_3O_4$ ($[M-H]^-$) 394.1539, found 394.1541



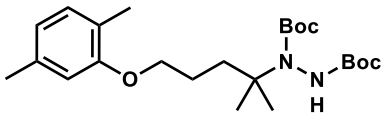
Di-tert-butyl 1-(thiophen-3-ylmethyl)hydrazine-1,2-dicarboxylate (**73**)
According to **General Procedure E**, 2-thiopheneacetic acid (85.2 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 reaction at 365−370 nm, purification by silica gel chromatography (From PE/EA = 20/1 to PE/EA = 10/1) afforded **73** as a white solid (48.0 mg, 73%).
TLC: R_f = 0.4 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 1H), 7.09 (s, 1H), 6.97 (d, *J* = 5.0 Hz, 1H), 6.09 (d, *J* = 97.0 Hz, 1H), 4.55 (s, 2H), 1.39 (d, *J* = 13.5 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.29, 154.97, 137.98, 128.40, 127.92, 126.03, 123.96, 123.39, 81.38, 49.55, 48.00, 28.33, 28.27.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{15}H_{24}N_2O_4SNa$ ($[M+Na]^+$) 351.1349, found 351.1340



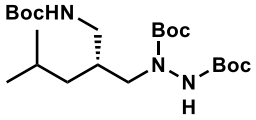
Di-tert-butyl 1-(1-(4-isobutylphenyl)ethyl)hydrazine-1,2-dicarboxylate (**74**)
According to **General Procedure E**, ibuprofen (123.6 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 15/1) afforded **74** as a colorless oil (47.4 mg, 60%).
TLC: R_f = 0.6 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.08 – 5.17 (m, 2H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.84 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.47 (dd, *J* = 32.6, 6.6 Hz, 21H), 0.89 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.69, 154.99, 140.92, 138.70, 129.19, 127.03, 81.27, 80.83, 54.43, 45.18, 30.29, 28.39, 28.28, 22.50, 16.95.
HRMS (ESI) m/z calcd. for $C_{22}H_{35}N_2O_4$ ($[M-H]^-$) 391.2602, found 391.2605



Di-tert-butyl 1-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)hydrazine-1,2-dicarboxylate (**75**)
According to **General Procedure E**, flurbiprofen (146.4 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (From PE/EA = 20/1 to 10/1) afforded **75** as a colorless oil (53.0 mg, 62%).
TLC: R_f = 0.6 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.40 – 7.33 (m, 2H), 7.18 (dt, *J* = 23.6, 13.9 Hz, 2H), 6.17 – 5.22 (m, 2H), 1.48 (d, *J* = 45.3 Hz, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.99, 158.52, 155.75, 154.86, 143.24, 135.68, 130.73, 129.06, 129.03, 128.99, 128.56, 128.36, 128.13, 127.98, 127.77, 123.27, 114.99, 114.75, 81.65, 81.16, 54.55, 28.37, 28.27, 16.94.
HRMS (ESI) m/z calcd. for $C_{24}H_{30}FN_2O_4$ ($[M-H]^-$) 429.2195, found 429.2193



Di-tert-butyl 1-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)hydrazine-1,2-dicarboxylate (**76**)
According to **General Procedure E**, gemfibrozil (150.0 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and DBU (29.8 μL, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (From PE/EA = 40/1 to 20/1) afforded **76** as a colorless oil (33.9 mg, 36%).
TLC: R_f = 0.7 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.5 Hz, 1H), 6.70 – 6.54 (m, 2H), 6.03 (d, *J* = 117.4 Hz, 1H), 3.93 (t, *J* = 6.3 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 2.06 (dq, *J* = 18.0, 10.8, 7.6 Hz, 1H), 1.93 – 1.67 (m, 3H), 1.52 – 1.19 (m, 24H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.16, 156.23, 154.84, 136.59, 130.41, 123.70, 120.76, 112.13, 81.50, 80.92, 80.80, 68.28, 61.98, 36.94, 28.44, 28.38, 28.07, 27.10, 26.55, 24.95, 21.54, 15.96.
NMR reference: [36]
HRMS (ESI) m/z calcd. for $C_{24}H_{39}N_2O_5$ ($[M-H]^-$) 435.2864, found 435.2861



Di-tert-butyl (R)-1-(2-(((tert-butoxycarbonyl)amino)methyl)-4-methylpentyl)hydrazine-1,2-dicarboxylate (**77**)

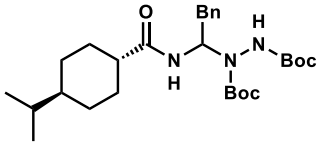
The substrate, Boc-protected pregabalin, was prepared according to the previous literature with a little modification. According to **General Procedure E**, Boc-pregabalin (155.4 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (From PE/EA = 15/1 to 10/1) afforded **77** as a colorless oil (24.8 mg, 28%).

TLC: R_f = 0.4 (PE/EA = 5/1, PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (d, *J* = 142.4 Hz, 1H), 4.99 (d, *J* = 131.9 Hz, 1H), 3.69 – 2.70 (m, 4H), 1.89 – 1.67 (m, 2H), 1.50 – 1.40 (m, 27H), 1.33 – 1.08 (m, 2H), 0.91 – 0.84 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.50, 155.99, 155.31, 83.61, 81.42, 79.05, 52.35, 41.33, 39.18, 35.24, 28.57, 28.49, 28.33, 28.17, 28.12, 25.26, 23.09, 22.76.

HRMS (ESI) m/z calcd. for $C_{22}H_{42}N_3O_6$ ($[M-H]^-$) 444.3079, found 444.3080



Di-tert-butyl 1-(1-((1r,4r)-4-isopropylcyclohexane-1-carboxamido)-2-phenylethyl)hydrazine-1,2-dicarboxylate (**78**)

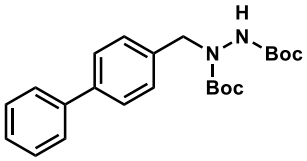
According to **General Procedure E**, nateglinide (190.4 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (PE/EA = 10/1) afforded **78** as a foam-like white solid (59.0 mg, 59%).

TLC: R_f = 0.7 (PE/EA = 2/1, UV & PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.14 (m, 5H), 7.03 – 5.56 (m, 3H), 3.43 – 2.79 (m, 2H), 2.06 – 1.67 (m, 5H), 1.53 – 1.34 (m, 24H), 0.86 – 0.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.32, 173.84, 155.86, 154.14, 137.00, 129.05, 128.63, 126.72, 82.13, 81.47, 66.32, 45.57, 43.37, 38.47, 32.88, 29.70, 29.67, 29.11, 28.25, 28.16, 27.00, 19.83.

HRMS (ESI) m/z calcd. for $C_{28}H_{45}N_3O_5Na$ ($[M+Na]^+$) 526.3251, found 526.3247



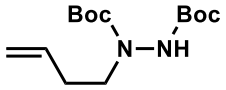
Di-tert-butyl 1-([1,1'-biphenyl]-4-ylmethyl)hydrazine-1,2-dicarboxylate (**79**)

According to **General Procedure E**, felbinac (127.2 mg, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. After 24 h reaction at 365−370 nm, purification by silica gel chromatography (From PE/EA = 15/1 to 10/1) afforded **79** as a pale white solid (33.5 mg, 42%).

TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 8.0 Hz, 4H), 7.44 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.39 – 7.29 (m, 3H), 6.13 (d, *J* = 108.6 Hz, 1H), 4.69 (s, 2H), 1.48 (d, *J* = 17.8 Hz, 18H).

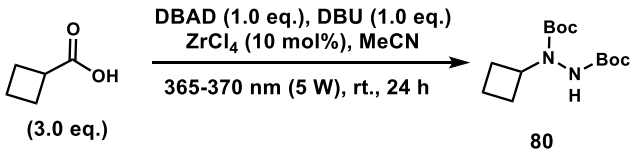
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.49, 155.22, 140.98, 140.66, 136.38, 128.92, 127.45, 127.40, 127.22, 127.01, 126.85, 81.47, 52.86, 28.40, 28.31.
NMR data matched with reference[37].
HRMS (ESI) m/z calcd. for $C_{23}H_{29}N_2O_4$ ([M-H]$^-$) 397.2133, found 397.2130



Di-tert-butyl 1-(but-3-en-1-yl)hydrazine-1,2-dicarboxylate (**93**)
According to **General Procedure E**, 2-cyclopropylacetic acid (55.8 μL, 0.6 mmol, 3.0 eq.), DBAD (46.0 mg, 0.2 mmol, 1.0 eq.), and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.) were used as the substrates. Purification by silica gel chromatography (PE/EA = 20/1) afforded **93** as a colorless oil (13.6 mg, 24%).
TLC: R_f = 0.5 (PE/EA = 5/1, UV & PMA)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 – 5.96 (m, 1H), 5.78 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.13 – 4.98 (m, 2H), 3.52 (s, 2H), 2.38 – 2.25 (m, 2H), 1.46 (d, *J* = 5.9 Hz, 18H).
NMR data matched with reference[36].
(**Figure S12**)

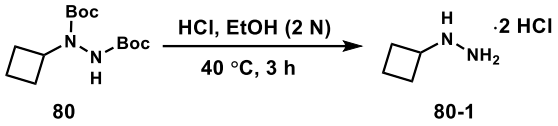
5.4. Syntheses of key pharmaceutical intermediates

Case 1: Cyclobutylation (telescoped synthesis)



In an argon-filled glovebox, a flame-dried 25 mL sampling bottle equipped with a Teflon septum was charged with 46.0 mg $ZrCl_4$ (0.4 mmol). The bottle was sealed tightly and removed from the glovebox, and 20 mL anhydrous MeCN was added to prepare a stock solution. The solution was then stored under an argon atmosphere and in avoidance of light for each use.
A flame-dried 25 mL sampling bottle equipped with a Teflon septa cap and magnetic stir bar was charged with DBAD (92.0 mg, 0.4 mmol, 1.0 eq.), cyclobutanecarboxylic acid (0.12 mL, 1.2 mmol, 3.0 eq.), and DBU (60.0 μL, 0.4 mmol, 1.0 eq.). The bottle was capped, and then evacuated and back-filled with argon for 5 times. Next, 4.0 mL of the $ZrCl_4$ stock solution (0.04 mmol, 0.1 eq.) were added via syringe under argon. The reaction mixture was then stirred and irradiated with 5 W LEDs (365−370 nm) in the photoreactor at room temperature. After 24 h, the reaction was completed with the monitoring of TLC (PE/EA = 10/1, PMA, R_f = 0.3).
The solution was concentrated in vacuo, then diluted with DCM, and washed by K_2CO_3 aqueous to remove excess acid. The aqueous was then extracted by DCM for 2 times. The organic layers were combined, washed with brine for once, dried by Na_2SO_4, then concentrated in vacuum to obtain the crude product **80**, which was used directly in the

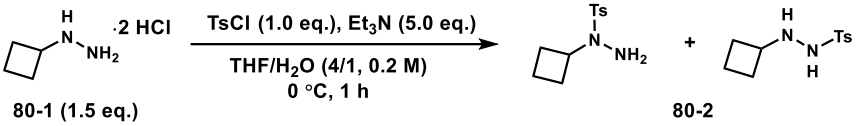
next step.



80 80-1

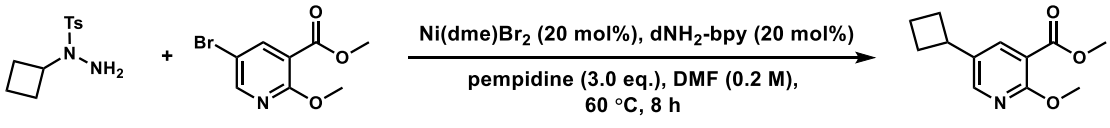
A 25 mL flask equipped with a stir bar magnetic stir bar was charged with **80**. The flask was then capped, evacuated and back-filled by Ar for 5 times. Under Ar atmosphere, 8.0 mL of 2N HCl-EtOH solution was added to the flask. The solution was then allowed to stir at 40 °C in oil bath for 3 h. The reaction was completed with the monitoring of TLC (No substrate remained). All solvent in the reaction was then removed in vacuo to obtain the crude product **80-1**, which was used directly in the next step.

The following reactions were carried out following the literature's procedure with a small modification[41].



80-1 (1.5 eq.) 80-2

A 25 mL flask equipped with a magnetic stir bar was charged with **80-1** (1.5 eq.), followed with 0.4 mL H_2O. The aqueous solution was cooled to 0 °C in ice bath, and under stirring, a 0.4 mL THF solution containing Et_3N (0.20 mL, 1.35 mmol, 5.0 eq.) was added. In another flask, TsCl (51.6 mg, 0.27 mmol, 1.0 eq.) was dissolved in 1.2 mL THF, and this clear solution was also added to the stirring flask dropwise under 0 °C in ice bath. The flask was then leaved to stir at 0 °C for 1.5 h. The reaction was completed with the monitoring of UPLC (no remaining signal for TsCl and two clear signals referring to two regioisomers of the products).
The solution was diluted by H_2O and DCM, and extracted with DCM for 3 times. Organic layers were combined, washed with brine for once, dried by Na_2SO_4, then concentrated in vacuum to obtain the crude mixture product **80-2**, which was used directly in the next step.

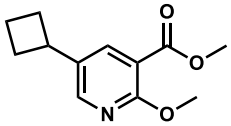


80-2 81 82

A flame-dried 5 mL sealed tube equipped with a stir bar was charged with 5-bromo-2-methoxynicotinate (**81**, 33.2 mg, 0.14 mmol, 1.0 eq.), $Ni(dme)Br_2$ (8.3 mg, 0.027 mmol, 20 mol%), dNH_2-bpy (5.0 mg, 0.027 mmol, 20 mol%). The tube was then capped, evacuated and back-filled with Ar for 5 times. Under Ar atmosphere, **80-2** (2.0 eq.) was dissolved in 0.7 mL anhydrous DMF in another flask. This DMF solution was then transferred to the sealed tube, and stirred at room temperature for a few minutes until all solid was dissolved. Next, while stirring under Ar atmosphere, pempidine (73.2 μL,

0.41 mmol, 3.0 eq.) was added quickly to the tube. The tube was finally evacuated and back-filled with Ar for 5 times, then quickly sealed with a solid cap. The tube was then allowed to stir at a pre-heated 60 °C oil bath for 8 h. The reaction was completed with the monitoring of TLC.

The solution was diluted and extracted by H_2O and EA for 3 times. Organic layers were combined, washed with brine for once, dried by Na_2SO_4, then concentrated in vacuum for silica gel chromatography (PE/EA = 20/1) to obtain the final product **82** as a yellowish oil.



Methyl 5-cyclobutyl-2-methoxynicotinate (**82**)

4 steps total yield: 21.3 mg, 71%

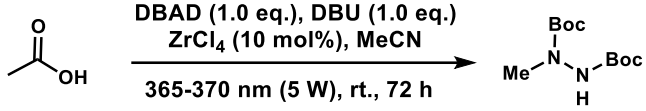
TLC: R_f = 0.4 (PE/EA = 10/1, UV)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, *J* = 2.7 Hz, 1H), 8.02 (t, *J* = 2.5 Hz, 1H), 4.01 (d, *J* = 2.7 Hz, 3H), 3.89 (d, *J* = 2.7 Hz, 3H), 3.49 (qd, *J* = 9.3, 8.8, 4.0 Hz, 1H), 2.42 – 2.23 (m, 2H), 2.06 (dddd, *J* = 32.2, 18.9, 9.4, 2.5 Hz, 3H), 1.94 – 1.74 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.97, 161.01, 148.79, 139.51, 133.93, 113.42, 54.18, 52.36, 37.03, 29.85, 18.53.

HRMS (ESI) m/z calcd. for $C_{12}H_{15}NO_3Na$ ($[M+Na]^+$) 244.0944, found 244.0940

Case 2: Methylation

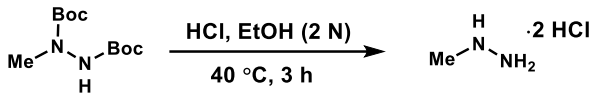


(3.0 eq.) 37

In an argon-filled glovebox, a flame-dried 25 mL sampling bottle equipped with a Teflon septum was charged with 46.0 mg $ZrCl_4$ (0.4 mmol). The bottle was sealed tightly and removed from the glovebox, and 20 mL anhydrous MeCN was added to prepare a stock solution. The solution was then stored under an argon atmosphere and in avoidance of light for each use.

A flame-dried 25 mL sampling bottle equipped with a Teflon septa cap and magnetic stir bar was charged with DBAD (92.0 mg, 0.4 mmol, 1.0 eq.), acetic acid (68.6 μL, 1.2 mmol, 3.0 eq.), and DBU (60.0 μL, 0.4 mmol, 1.0 eq.). The bottle was capped, and then evacuated and back-filled with argon for 5 times. Next, 4.0 mL of the $ZrCl_4$ stock solution (0.04 mmol, 0.1 eq.) were added via syringe under argon. The reaction mixture was then stirred and irradiated with 5 W LEDs (365−370 nm) in the photoreactor at room temperature. After 72 h, the reaction was completed with the monitoring of TLC (PE/EA = 5/1, PMA, R_f = 0.5).

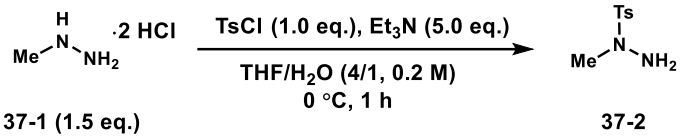
The solution was concentrated in vacuo, then purified by silica gel chromatography (PE/EA = 15/1) to obtain product **37** (60.2 mg, 61%).



37 37-1

A 25 mL flask equipped with a stir bar magnetic stir bar was charged with **37**. The flask was then capped, evacuated and back-filled by Ar for 5 times. Under Ar atmosphere, 4.8 mL of 2N HCl-EtOH solution was added to the flask. The solution was then allowed to stir at 40 °C in oil bath for 3 h. The reaction was completed with the monitoring of TLC (No substrate remained). All solvent in the reaction was then removed in vacuo to obtain the crude product **37-1**, which was used directly in the next step.

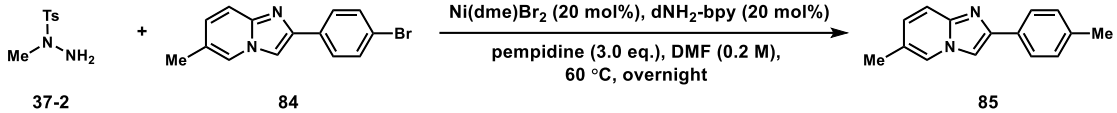
The following reactions were carried out following the literature's procedure with a small modification[41].



37-1 (1.5 eq.) 37-2

A 25 mL flask equipped with a magnetic stir bar was charged with **37-1** (1.5 eq.), followed with 0.24 mL H_2O. The aqueous solution was cooled to 0 °C in ice bath, and under stirring, a 0.24 mL THF solution containing Et_3N (0.11 mL, 0.80 mmol, 5.0 eq.) was added. In another flask, TsCl (30.6 mg, 0.16 mmol, 1.0 eq.) was dissolved in 0.72 mL THF, and this clear solution was also added to the stirring flask dropwise under 0 °C in ice bath. The flask was then leaved to stir at 0 °C for 1.5 h. The reaction was completed with the monitoring of UPLC (no remaining signal for TsCl and clear signal referring to products).

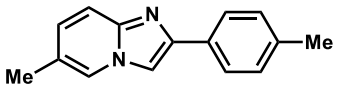
The solution was diluted by H_2O and DCM, and extracted with DCM for 3 times. Organic layers were combined, washed with brine for once, dried by Na_2SO_4, then concentrated in vacuum to obtain the crude mixture product **37-2**, which was used directly in the next step.



37-2 84 85

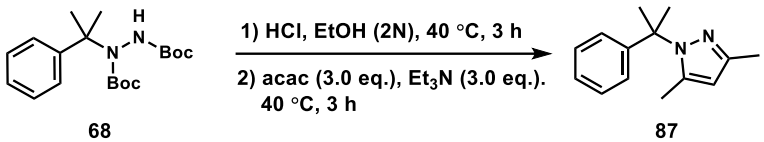
A flame-dried 5 mL sealed tube equipped with a stir bar was charged with 2-(4-bromophenyl)-6-methylimidazo[1,2-a]pyridine (**84**, 23.0 mg, 0.08 mmol, 1.0 eq.), $Ni(dme)Br_2$ (4.9 mg, 0.016 mmol, 20 mol%), dNH_2-bpy (3.0 mg, 0.016 mmol, 20 mol%). The tube was then capped, evacuated and back-filled with Ar for 5 times. Under Ar atmosphere, **37-2** (2.0 eq.) was dissolved in 0.4 mL anhydrous DMF in another flask. This DMF solution was then transferred to the sealed tube, and stirred at room temperature for a few minutes until all solid was dissolved. Next, while stirring under Ar atmosphere, pempidine (43.4 μL, 0.24 mmol, 3.0 eq.) was added quickly to the tube. The tube was finally evacuated and back-filled with Ar for 5 times, then quickly sealed with a solid cap. The tube was then allowed to stir at a pre-heated 60 °C oil bath

overnight.
The solution was diluted and extracted by H_2O and EA for 3 times. Organic layers were combined, washed with brine for once, dried by Na_2SO_4, then concentrated in vacuum for preparative TLC (DCM/MeOH = 100/1, 1 d $NH_3 \cdot H_2O$, for 3 times) to obtain the final product **85** as a white solid.
Notice: After the reaction, UPLC monitoring showed no signal of **37-2**, while **84** was not fully converted. Although the intact **84** and product **85** are almost the only two points that can be visualized from TLC, they have a very close retention time on UPLC and R_f value on TLC, and much effort is needed to obtain the pure **85**, resulting in relatively low yield.



6-methyl-2-(p-tolyl)imidazo[1,2-a]pyridine (**85**)
Yield: 7.1 mg, 40%
TLC: R_f = 0.2 (DCM/MeOH = 50/1, 1 d $NH_3 \cdot H_2O$, UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.73 (s, 1H), 7.54 (d, *J* = 9.2 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.01 (dd, *J* = 9.2, 1.7 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.53, 144.66, 137.85, 130.97, 129.56, 128.02, 125.99, 123.43, 122.21, 116.80, 107.62, 21.44, 18.25.
NMR data matched with reference[42].
HRMS (ESI) m/z calcd. for $C_{15}H_{14}N_2Na$ ($[M+Na]^+$) 245.1049, found 245.1051

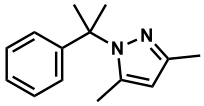
5.5. Syntheses of N-aromatic heterocycles



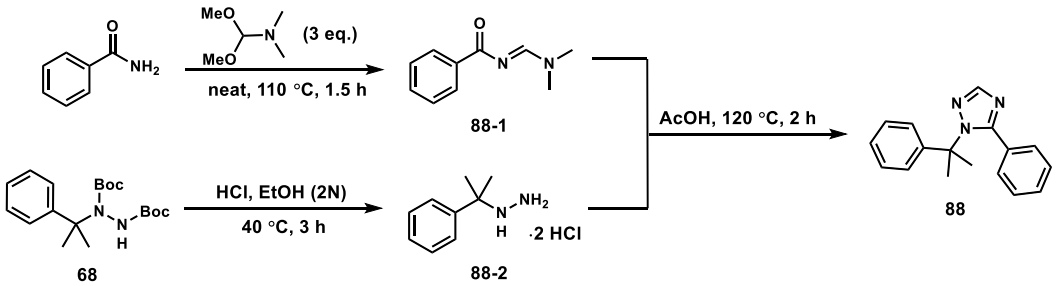
68 **87**

The reaction was carried out following a reported literature with a small modification[43]. A 25 mL flask equipped with a magnetic stir bar was charged with **68** (70.0 mg, 0.2 mmol, 1.0 eq.). The flask was then evacuated and back-filled with Ar for 5 times. Under Ar atmosphere, 4.0 mL of 2N HCl/EtOH solution was added. The resulted solution was then allowed to stir at 40 °C in oil bath for 3 h. The reaction was completed with the monitoring of TLC (No substrate remained). All solvent in the reaction was then removed in vacuo to obtain the crude product, which was used directly in the next step. A 10 mL flask equipped with a stir bar was added the following crude product, followed with acetylacetone (61.6 μL, 0.6 mmol, 3.0 eq.) and anhydrous Et_3N (111.0 μL, 0.8 mmol, 4.0 eq.). The mixture quickly turned burgundy red, and the flask was quickly plugged, evacuated and back-filled with Ar for 5 times, then added with anhydrous MeOH (0.6 mL, 0.3 M). This burgundy red solution was then allowed to stir at 50 °C in oil bath for 23 h. The solution was then extracted by H_2O and EA for 3 times. Organic

layers were combined, washed with brine for once, dried by Na_2SO_4, then concentrated in vacuum for silica gel chromatography (PE/EA = 25/1) to obtain the final product **87** as a white crystalline solid.



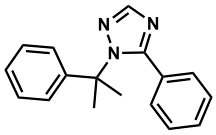
3,5-dimethyl-1-(2-phenylpropan-2-yl)-1H-pyrazole (**87**)
Yield: 26.4 mg, 62%
TLC: R_f = 0.7 (PE/EA = 5/1, UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.13 – 7.06 (m, 2H), 5.82 (s, 1H), 2.28 (s, 3H), 1.93 (s, 6H), 1.70 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.54, 145.45, 139.57, 128.61, 126.98, 125.21, 107.83, 63.42, 30.54, 13.82, 13.46.
NMR data matched with reference[44].
HRMS (ESI) m/z calcd. for $C_{14}H_{18}N_2Na$ ($[M+Na]^+$) 237.1362, found 237.1362



The reaction was carried out following reported literatures[45]. A 5 mL sealed tube equipped with a stir bar was charged with benzamide (60.5 mg, 0.5 mmol, 1.0 eq.) and N,N-Dimethylformamide dimethyl acetal (DMF-DMA, 0.2 mL, 1.5 mmol, 3.0 eq.). The tube was evacuated and back-filled with Ar for 5 times, then the tube was sealed and stirred at 110 °C in oil bath under neat condition for 1.5 h. The reaction was completed with the monitoring of UPLC, showing that **88-1** is the sole product. All solvents were transferred to a 10 mL flask, rinsed with DCM for 3 times, then removed in vacuo to obtain **88-1** as a white solid (84.3 mg, 96%). This solid was used directly for the next step.
A 25 mL flask equipped with a magnetic stir bar was charged with **68** (35.0 mg, 0.1 mmol, 1.0 eq.). The flask was then evacuated and back-filled with Ar for 5 times. Under Ar atmosphere, 2.0 mL of 2N HCl/EtOH solution was added. The resulted solution was then allowed to stir at 40 °C in oil bath for 3 h. The reaction was completed with the monitoring of TLC (No substrate remained). All solvent in the reaction was then removed in vacuo to obtain **88-2** as a crude product, which was used directly in the next step.
88-2 was dissolved in 0.36 mL AcOH (0.3 M), then this suspension was transferred to a 5 mL sealed tube equipped with a stir bar. While stirring at room temperature, **88-1** (35.0 mg, 0.2 mmol, 0.1 eq.) was added. The tube was then evacuated and back-filled with Ar for 5 times, and kept on stirring at room temperature for a few minutes till it

becomes a clear brown solution. Finally, the tube was sealed, and allowed to stir at 120 °C in oil bath for 2 h. The reaction was completed with the monitoring of UPLC and TLC, turning into an olive suspension.

The tube was cooled to room temperature, then while stirring, saturated K_2CO_3 aqueous was added till pH = 8. During this procedure, the suspension first turned back to brown solution, and finally became tan suspension. Next, the suspension was diluted with EA, and extracted by H_2O and EA for 3 times. Organic layers were combined, washed by brine once, dried by Na_2SO_4, then concentrated and purified by silica gel chromatography (PE/EA = 10/1) to obtain **88** as a colorless oil.



5-phenyl-1-(2-phenylpropan-2-yl)-1H-1,2,4-triazole (**88**)

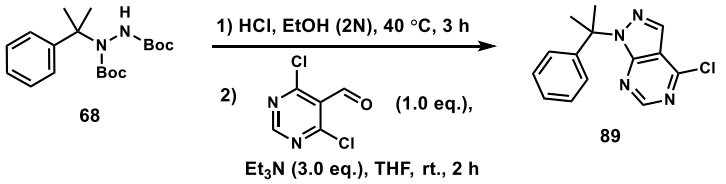
Yield: 8.5 mg, 32%

TLC: R_f = 0.4 (PE/EA = 2/1, UV & Anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 8.08 (s, 1H), 7.41 (ddd, *J* = 12.9, 7.9, 6.1 Hz, 3H), 7.36 – 7.27 (m, 3H), 7.18 (dd, *J* = 7.3, 1.9 Hz, 2H), 2.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.14, 144.90, 142.61, 131.52, 129.17, 128.86, 128.65, 127.91, 126.58, 125.35, 63.59, 29.76.

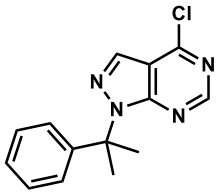
HRMS (ESI) m/z calcd. for $C_{17}H_{17}N_3Na$ ($[M+Na]^+$) 286.1315, found 286.1315



The reaction was carried out following a reported literature[46]. A 25 mL flask equipped with a magnetic stir bar was charged with **68** (35.0 mg, 0.1 mmol, 1.0 eq.). The flask was then evacuated and back-filled with Ar for 5 times. Under Ar atmosphere, 2.0 mL of 2N HCl/EtOH solution was added. The resulted solution was then allowed to stir at 40 °C in oil bath for 3 h. The reaction was completed with the monitoring of TLC (No substrate remained). All solvent in the reaction was then removed in vacuo to obtain the crude product, which was used directly in the next step.

A 10 mL flask equipped with a stir bar was added 2,6-dichloro-pyrimidine carbaldehyde (16.9 mg, 0.095 mmol, 1.0 eq.) and Et_3N (39.6 μL, 0.28 mmol, 3.0 eq.). The flask was evacuated and back-filled with Ar for 5 times, then 0.25 mL of anhydrous THF was added, and the resulting orange suspension was allowed to stir at 0 °C in ice bath for 10 min. In another flask containing the hydrochloride salt, 0.3 mL of anhydrous THF was added under Ar atmosphere. This suspension was then added dropwise to the stirring flask at °C, also under an Ar atmosphere. After the addition, the light-yellow suspension was warmed and allowed to stir at room temperature for 2 h. The reaction was completed with the monitoring of TLC (No substrate remained). All solvent in the

reaction was then removed in vacuo, and the crude product was extracted by DCM and H_2O for 3 times. Organic layers were combined, washed by brine once, then dried by Na_2SO_4. All solvents were removed in vacuo to obtain **89** as a yellow solid.

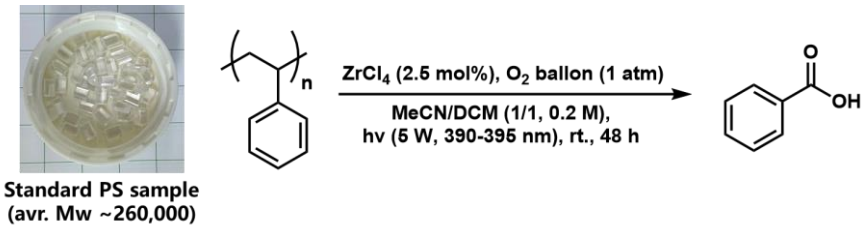


4-chloro-1-(2-phenylpropan-2-yl)-1H-pyrazolo[3,4-d]pyrimidine (**89**)
Yield: quantitative
TLC: R_f = 0.6 (PE/EA = 5/1, UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.71 (s, 1H), 7.52 – 7.16 (m, 5H), 1.69 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.28, 154.35, 146.94, 128.87, 128.74, 128.55, 127.18, 127.13, 126.11, 125.78, 60.01, 28.83.
HRMS (ESI) m/z calcd. for $C_{14}H_{14}ClN_4$ ($[M+H]^+$) 273.0901, found 273.0895

5.6. Oxidative degradation of polystyrene

General Procedure F: In an argon-filled glovebox, a flame-dried 25 mL sampling bottle equipped with a Teflon septum was charged with 46.0 mg $ZrCl_4$ (0.4 mmol). The bottle was sealed tightly and removed from the glovebox, and 20 mL anhydrous MeCN was added to prepare a stock solution. The solution was then stored under an argon atmosphere and in avoidance of light for each use.

A flame-dried 4 mL vial equipped with a Teflon septum and magnetic stir bar was charged with polystyrene samples (~20.8 mg, ~0.2 mmol per monounit), followed with 0.5 mL DCM. The mixture was sonicated for around 10 min until all solids were dissolved. The vial was sealed, and then evacuated and back-filled with O_2 for 5 times. Next, 0.5 mL of the $ZrCl_4$ stock solution (0.005 mmol, 0.025 eq.) were added via syringe under argon. The mixture was then bubbled with O_2 for 5 min, then stirred and irradiated with 5 W LEDs in the photoreactor at room temperature with a O_2 ballon attaching to the vial (1 atm). After 48 h, 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) was added to the mixture, then the mixture was concentrated in vacuum. 0.1 mL $CDCl_3$ was added to the crude product, then this mixture was dissolved in 0.4 mL $CDCl_3$, and crude ^{1}H NMR was then performed to calculate the NMR yield of benzoic acid after filtering through a syringe filter.



According to **General Procedure F**, 20.8 mg (0.2 mmol per monounit) standard PS sample (average M_w ~260,000) was dissolved in 0.5 mL DCM and 0.5 mL $ZrCl_4$ stock solution (1.15 mg, 0.005 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 30% NMR yield.

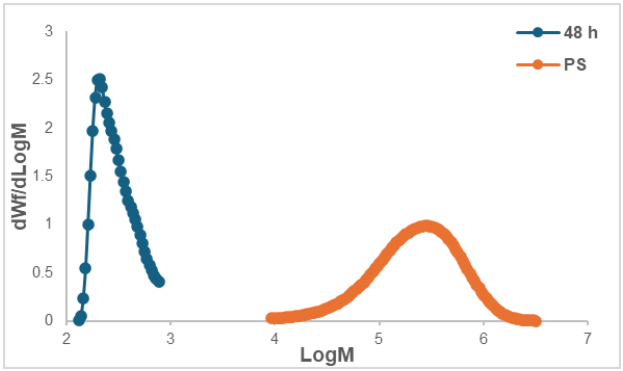
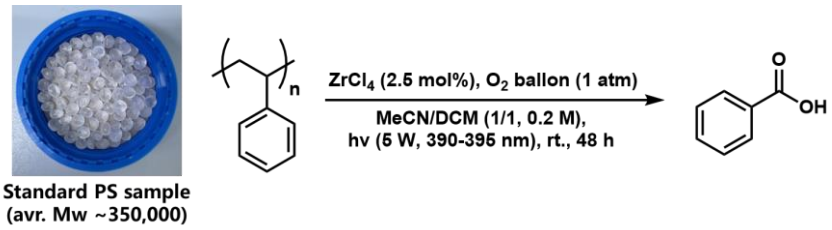


Figure S17 GPC results of PS standard 1 and degradation after 48 h



According to **General Procedure F**, 25.0 mg (0.24 mmol per monounit) standard PS sample (average M_w ~350,000) was dissolved in 0.6 mL DCM and 0.6 mL $ZrCl_4$ stock solution (1.4 mg, 0.006 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 30% NMR yield.

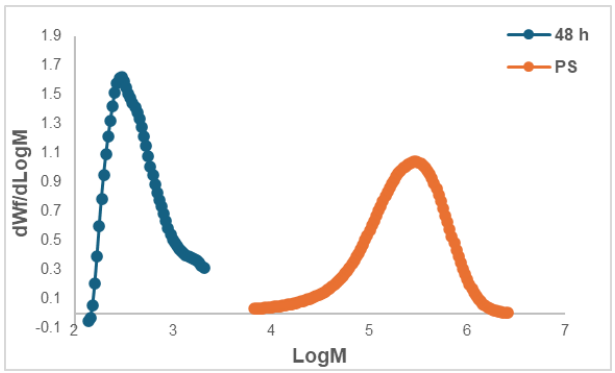
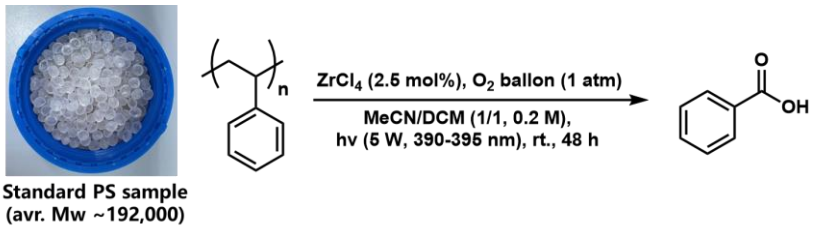


Figure S18 GPC results of PS standard 2 and degradation after 48 h



According to **General Procedure F**, 27.0 mg (0.26 mmol per monounit) standard PS sample (average M_w ~192,000) was dissolved in 0.65 mL DCM and 0.65 mL $ZrCl_4$ stock solution (1.5 mg, 0.0065 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 32% NMR yield.

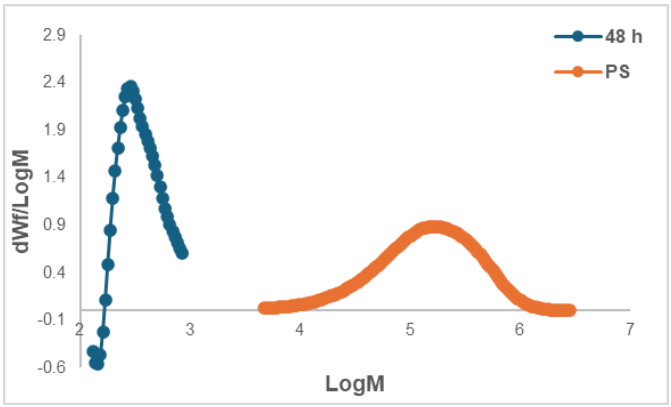
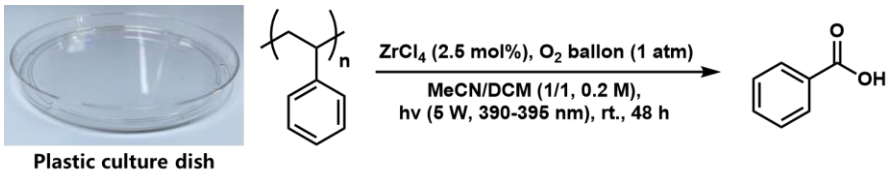


Figure S19 GPC results of PS standard 3 and degradation after 48 h



According to **General Procedure F**, 28.3 mg (0.27 mmol per monounit) plastic culture dish was dissolved in 0.68 mL DCM and 0.68 mL $ZrCl_4$ stock solution (1.6 mg, 0.007 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 67% NMR yield.

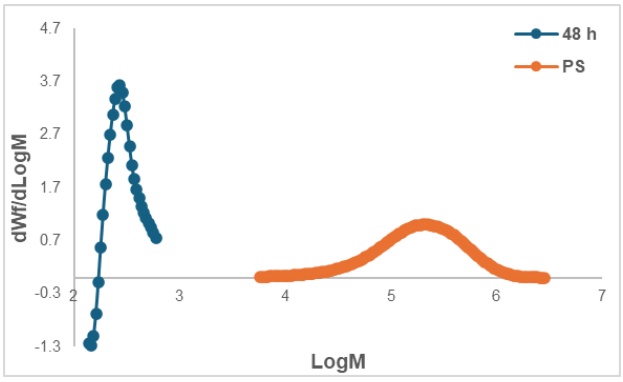
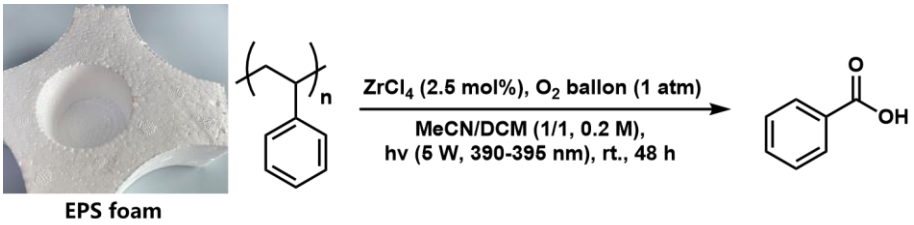


Figure S20 GPC results of plastic culture dish and degradation after 48 h



According to **General Procedure F**, 20.8 mg (0.2 mmol per monounit) EPS foam was dissolved in 0.5 mL DCM and 0.5 mL $ZrCl_4$ stock solution (1.15 mg, 0.005 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 24% NMR yield.

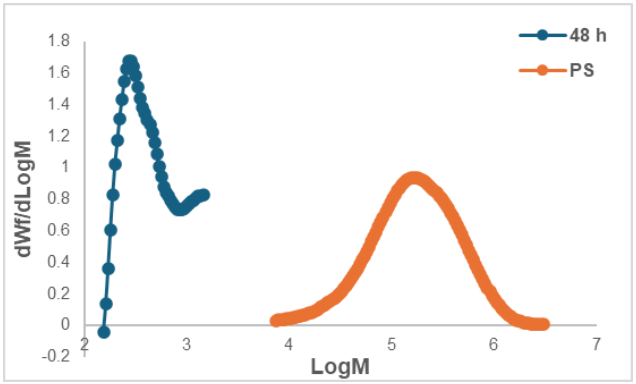
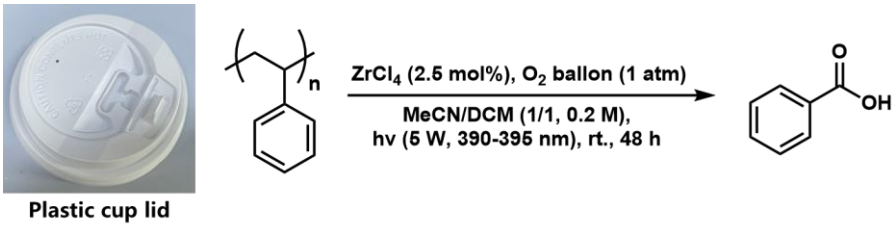


Figure S21 GPC results of EPS foam and degradation after 48 h



According to **General Procedure F**, 20.3 mg (0.2 mmol per monounit) plastic cup lid was dissolved in 0.5 mL DCM and 0.5 mL $ZrCl_4$ stock solution (1.15 mg, 0.005 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 25% NMR yield.

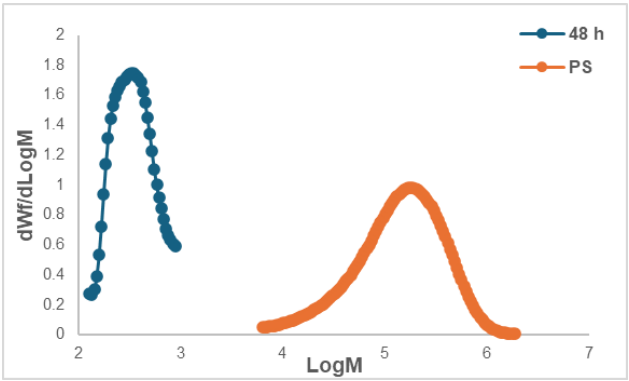
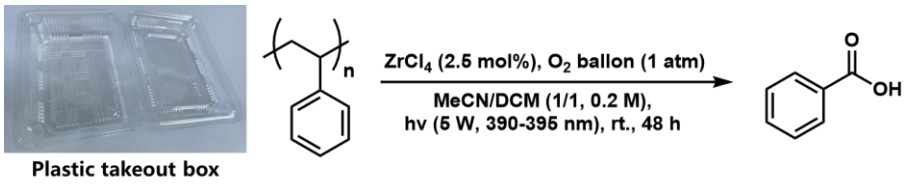


Figure S22 GPC results of plastic cup lid and degradation after 48 h



According to **General Procedure F**, 21.8 mg (0.21 mmol per monounit) plastic takeout box was dissolved in 0.54 mL DCM and 0.54 mL $ZrCl_4$ stock solution (1.2 mg, 0.005 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 23% NMR yield.

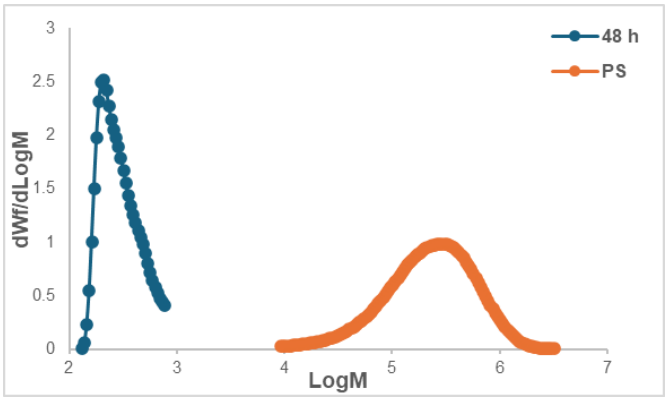
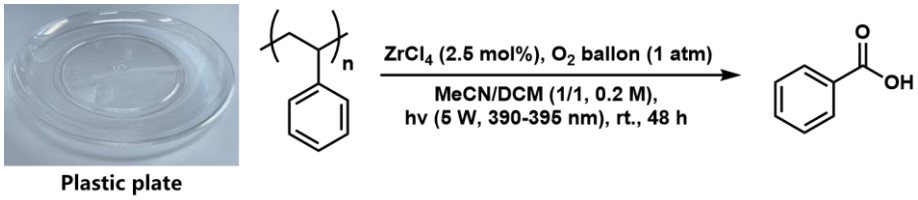


Figure S23 GPC results of plastic takeout box and degradation after 48 h



According to **General Procedure F**, 22.3 mg (0.21 mmol per monounit) plastic plate was dissolved in 0.54 mL DCM and 0.54 mL $ZrCl_4$ stock solution (1.2 mg, 0.005 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 25% NMR yield.

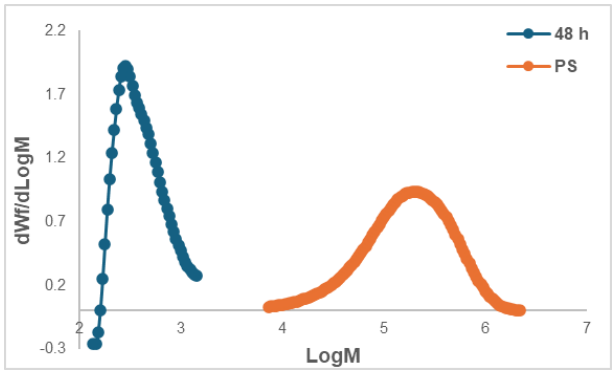
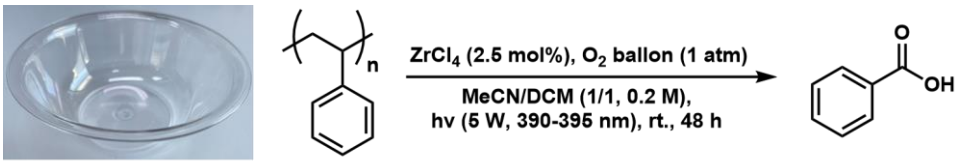


Figure S24 GPC results of plastic plate and degradation after 48 h



According to **General Procedure F**, 23.4 mg (0.22 mmol per monounit) plastic bowl was dissolved in 0.56 mL DCM and 0.56 mL $ZrCl_4$ stock solution (1.3 mg, 0.005 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 26% NMR yield.

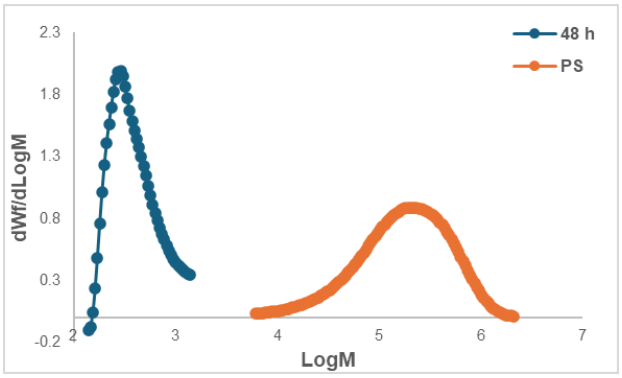
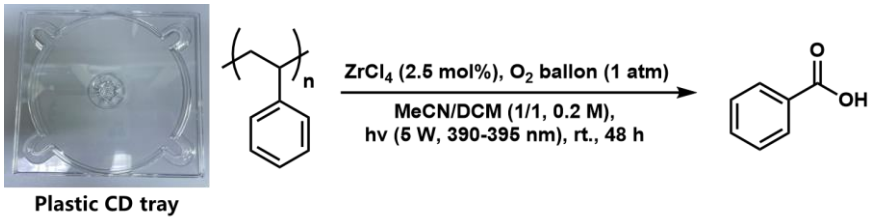


Figure S25 GPC results of plastic bowl and degradation after 48 h



According to **General Procedure F**, 28.7 mg (0.28 mmol per monounit) plastic CD tray was dissolved in 0.7 mL DCM and 0.7 mL $ZrCl_4$ stock solution (1.6 mg, 0.005 mmol, 0.025 eq.). After 48 h, benzoic acid was obtained in 39% NMR yield.

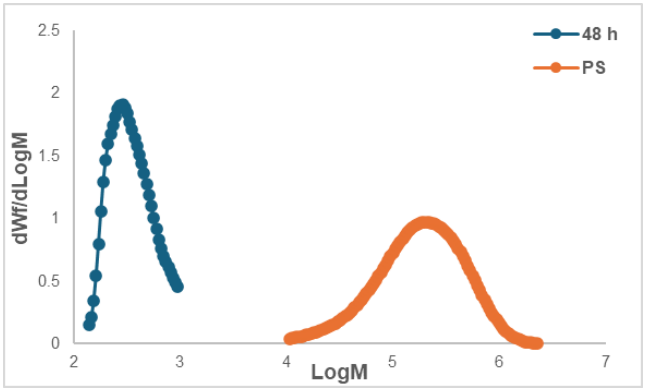


Figure S26 GPC results of plastic CD tray and degradation after 48 h

6. References

1. An, Q. *et al.* Identification of Alkoxy Radicals as Hydrogen Atom Transfer Agents in Ce-Catalyzed C–H Functionalization. *J. Am. Chem. Soc.* **145**, 359–376 (2023).
2. Yang, Q. *et al.* Photocatalytic C–H activation and the subtle role of chlorine radical complexation in reactivity. *Science* **372**, 847–852 (2021).
3. An, Q. *et al.* Cerium-Catalyzed C–H Functionalizations of Alkanes Utilizing Alcohols as Hydrogen Atom Transfer Agents. *J. Am. Chem. Soc.* **142**, 6216–6226 (2020).
4. Chen, M. S. & White, M. C. Combined Effects on Selectivity in Fe-Catalyzed Methylene Oxidation. *Science* **327**, 566–571 (2010).
5. Wang, Q. *et al.* Metal-Free Electrochemical C─H Chlorination of Terminal Alkanes. *Angew. Chem. Int. Ed.* **64**, e202504478 (2025).
6. Schmidt, V. A., Quinn, R. K., Brusoe, A. T. & Alexanian, E. J. Site-Selective Aliphatic C–H Bromination Using N-Bromoamides and Visible Light. *J. Am. Chem. Soc.* **136**, 14389–14392 (2014).
7. Quinn, R. K. *et al.* Site-Selective Aliphatic C–H Chlorination Using N-Chloroamides Enables a Synthesis of Chlorolissoclimide. *J. Am. Chem. Soc.* **138**, 696–702 (2016).
8. Lee, W., Jung, S., Kim, M. & Hong, S. Site-Selective Direct C–H Pyridylation of Unactivated Alkanes by Triplet Excited Anthraquinone. *J. Am. Chem. Soc.* **143**, 3003–3012 (2021).
9. McMillan, A. J. *et al.* Practical and Selective sp3 C−H Bond Chlorination via Aminium Radicals. *Angew. Chem. Int. Ed.* **60**, 7132–7139 (2021).
10. Yang, H.-B., Feceu, A. & Martin, D. B. C. Catalyst-Controlled C–H Functionalization of Adamantanes Using Selective H-Atom Transfer. *ACS Catal.* **9**, 5708–5715 (2019).
11. Matsumoto, A., Yamamoto, M. & Maruoka, K. Cationic DABCO-Based Catalyst for Site-Selective C–H Alkylation via Photoinduced Hydrogen-Atom Transfer. *ACS Catal.* **12**, 2045–2051 (2022).
12. Liu, Z. *et al.* Site-Selective C–H Benzylation of Alkanes with N-Triftosylhydrazones Leading to Alkyl Aromatics. *Chem* **6**, 2110–2124 (2020).
13. Álvarez, M., Molina, F. & Pérez, P. J. Carbene-Controlled Regioselective Functionalization of Linear Alkanes under Silver Catalysis. *J. Am. Chem. Soc.* **144**, 23275–23279 (2022).
14. Tu, J.-L., Hu, A.-M., Guo, L. & Xia, W. Iron-Catalyzed C(Sp3)–H Borylation, Thiolation, and Sulfinylation Enabled by Photoinduced Ligand-to-Metal Charge Transfer. *J. Am. Chem. Soc.* **145**, 7600–7611 (2023).
15. Wang, M., Huang, Y. & Hu, P. Terminal C (sp3)–H borylation through intermolecular radical sampling. *Science* **383**, 537–544 (2024).
16. Shu, C., Noble, A. & Aggarwal, V. K. Metal-free photoinduced C(sp3)–H borylation of alkanes. *Nature* **586**, 714–719 (2020).
17. Gonzalez, M. I. *et al.* Taming the Chlorine Radical: Enforcing Steric Control over Chlorine-Radical-Mediated C–H Activation. *J. Am. Chem. Soc.* **144**, 1464–1472

(2022).
18. Russell, G. A. Solvent Effects in the Reactions of Free Radicals and Atoms. II. Effects of Solvents on the Position of Attack of Chlorine Atoms upon 2,3-Dimethylbutane, Isobutane and 2-Deuterio-2-methylpropane[1]. *J. Am. Chem. Soc.* **80**, 4987–4996 (1958).
19. Hansch, C., Leo, A. & Taft, R. W. A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev.* **91**, 165–195 (1991).
20. Frisch, M. J. *et al.* Gaussian 16 Rev. B.01. (2016).
21. Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215–241 (2008).
22. Zhao, Y. & Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **41**, 157–167 (2008).
23. Weigend, F. & Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys Chem Chem Phys* **7**, 3297–3305 (2005).
24. Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **113**, 6378–6396 (2009).
25. Xia, R., Xie, M.-S., Niu, H.-Y., Qu, G.-R. & Guo, H.-M. Radical Route for the Alkylation of Purine Nucleosides at C6 via Minisci Reaction. *Org. Lett.* **16**, 444–447 (2014).
26. Walter, T. H. *et al.* Spin trapping in heterogeneous electron transfer processes. *Can. J. Chem.* **60**, 1621–1636 (1982).
27. Wang, H. S. *et al.* Visible light–triggered depolymerization of commercial polymethacrylates. *Science* **387**, 874–880 (2025).
28. Hu, A., Guo, J.-J., Pan, H. & Zuo, Z. Selective functionalization of methane, ethane, and higher alkanes by cerium photocatalysis. *Science* **361**, 668–672 (2018).
29. Jin, Y. *et al.* Convenient C(sp^3)–H bond functionalisation of light alkanes and other compounds by iron photocatalysis. *Green Chem.* **23**, 6984–6989 (2021).
30. Yamane, M., Kanzaki, Y., Mitsunuma, H. & Kanai, M. Titanium(IV) Chloride-Catalyzed Photoalkylation via C(sp3)–H Bond Activation of Alkanes. *Org. Lett.* **24**, 1486–1490 (2022).
31. Lu, Z., Putziger, J. & Lin, S. Light-activated hypervalent iodine agents enable diverse aliphatic C–H functionalization. *Nat. Chem.* **17**, 365–372 (2025).
32. Yu, Y. & Wang, Z. A Simple, Efficient and Green Procedure for Knoevenagel Condensation in Water or under Solvent-free Conditions. *J. Chin. Chem. Soc.* **60**, 288–292 (2013).
33. Laudadio, G. *et al.* C(sp^3)–H functionalizations of light hydrocarbons using decatungstate photocatalysis in flow. *Science* **369**, 92–96 (2020).
34. Huang, Y., Wang, M., Liu, W., Wu, Q. & Hu, P. Unraveling the Prominent Existence of Trace Metals in Photocatalysis: Exploring Iron Impurity Effects. *J. Org. Chem.*

89, 4156–4164 (2024).
35. Okuro, K. & Alper, H. Palladium-Catalyzed Intermolecular Cyclocarbonylation of 2-Iodoanilines with the Michael Acceptor, Diethyl Ethoxycarbonylbutendienoate. *J. Org. Chem.* **77**, 4420–4424 (2012).
36. Yatham, V. R., Bellotti, P. & König, B. Decarboxylative hydrazination of unactivated carboxylic acids by cerium photocatalysis. *Chem Commun* **55**, 3489–3492 (2019).
37. Feng, G., Wang, X. & Jin, J. Decarboxylative C–C and C–N Bond Formation by Ligand-Accelerated Iron Photocatalysis. *Eur. J. Org. Chem.* **2019**, 6728–6732 (2019).
38. Ratnam, S., Unone, S. & Janssen-Müller, D. 2,2'-Biquinoline-Based Recyclable Electroauxiliaries for the Generation of Alkyl Radicals via C−C Bond Cleavage. *Chem. – Eur. J.* **29**, e202301685 (2023).
39. Waser, J. & Carreira, E. M. Catalytic Hydrohydrazination of a Wide Range of Alkenes with a Simple Mn Complex. *Angew. Chem. Int. Ed.* **43**, 4099–4102 (2004).
40. Tamaki, S. *et al.* Mixed-Metal Ce-Zr-Mn Clusters as Photo-Catalysts for Decarboxylative Functionalization of Carboxylic Acids. *Angew. Chem. Int. Ed.* **64**, e202505639 (2025).
41. Tsien, J. *et al.* Accelerating Medicinal Chemistry: A C(sp3)-Rich Fragment Toolbox for Redox-Neutral Cross-Coupling. *Angew. Chem. Int. Ed.* **64**, e202517207 (2025).
42. Zhang, Y., Chen, Z., Wu, W., Zhang, Y. & Su, W. CuI-Catalyzed Aerobic Oxidative α-Aminaton Cyclization of Ketones to Access Aryl or Alkenyl-Substituted Imidazoheterocycles. *J. Org. Chem.* **78**, 12494–12504 (2013).
43. Liang, H. *et al.* Bench-Stable Cerium(IV) Benzoate: A Versatile LMCT Catalyst for Selective Dehydroxymethylative Functionalization. *ACS Catal.* **15**, 8069–8077 (2025).
44. Sheng, T. *et al.* Electrochemical decarboxylative N-alkylation of heterocycles. *Org. Lett.* **22**, 7594–7598 (2020).
45. Huang, H.-Y., Lin, X.-Y., Yen, S.-Y. & Liang, C.-F. Facile access to N-formyl imide as an N-formylating agent for the direct synthesis of N-formamides, benzimidazoles and quinazolinones. *Org Biomol Chem* **18**, 5726–5733 (2020).
46. Morrill, C., Babu, S., Almstead, N. G. & Moon, Y.-C. Synthesis of 1, 4-Disubstituted Pyrazolo [3, 4-d] pyrimidines from 4, 6-Dichloropyrimidine-5-carboxaldehyde: Insights into Selectivity and Reactivity. *Synthesis* **45**, 1791–1806 (2013).

7. NMR spectra data

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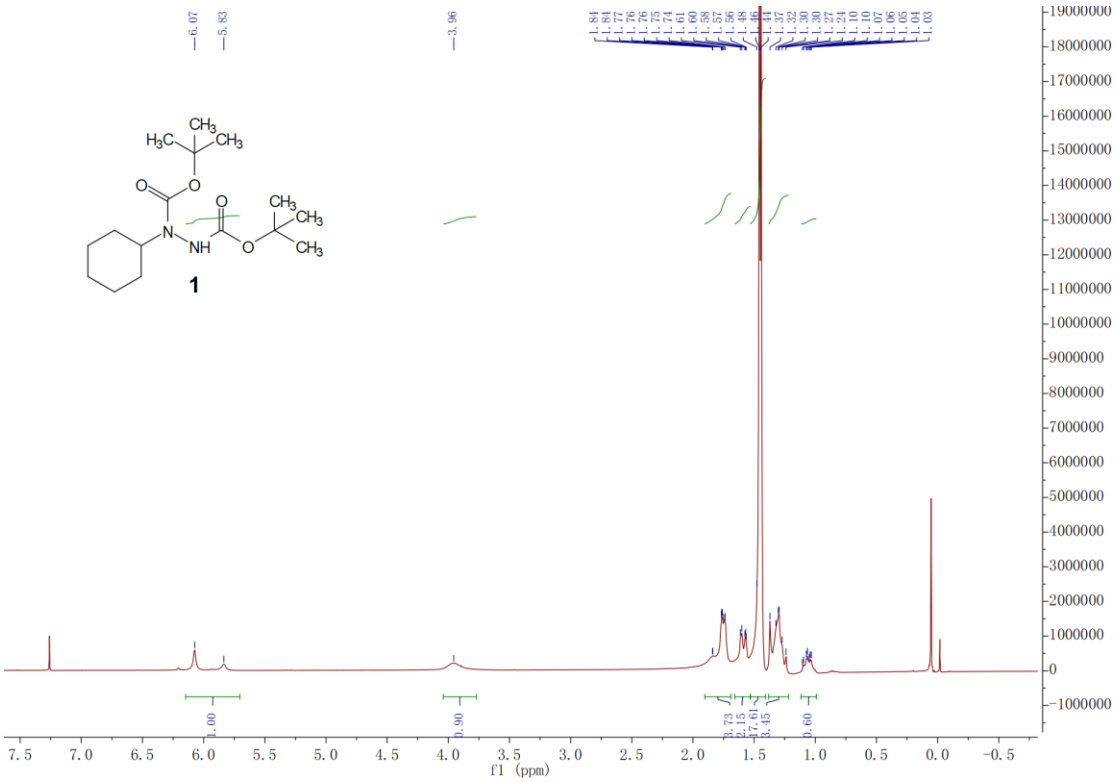

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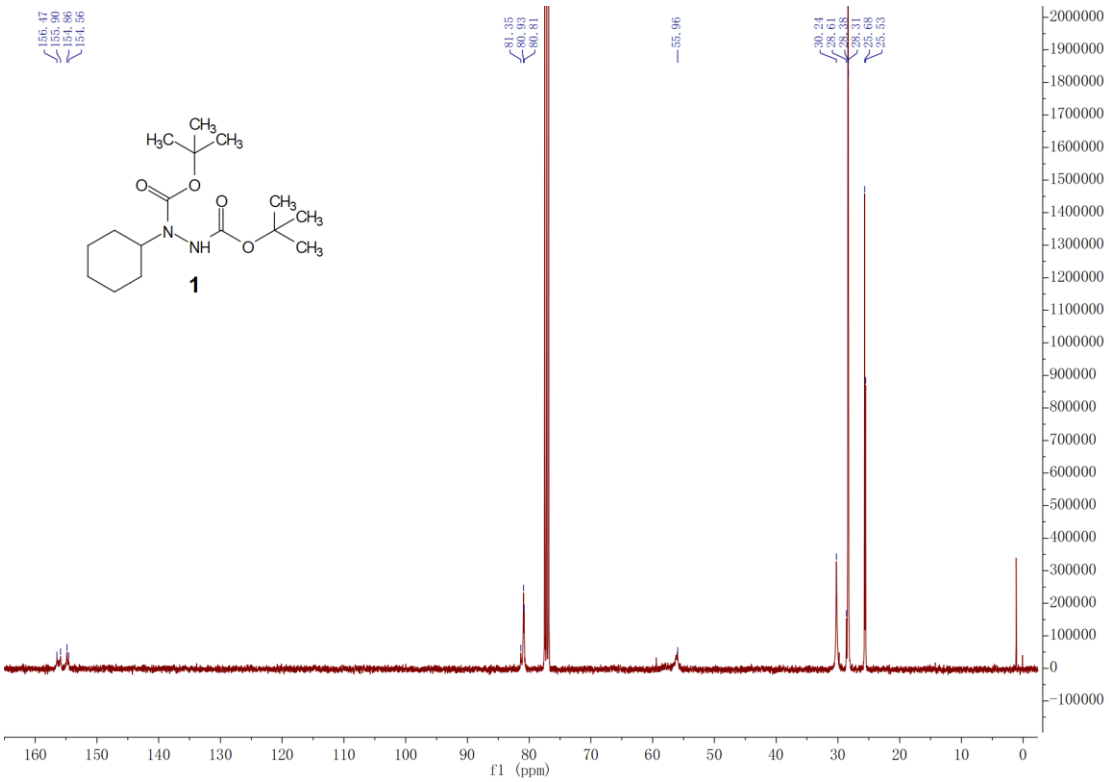

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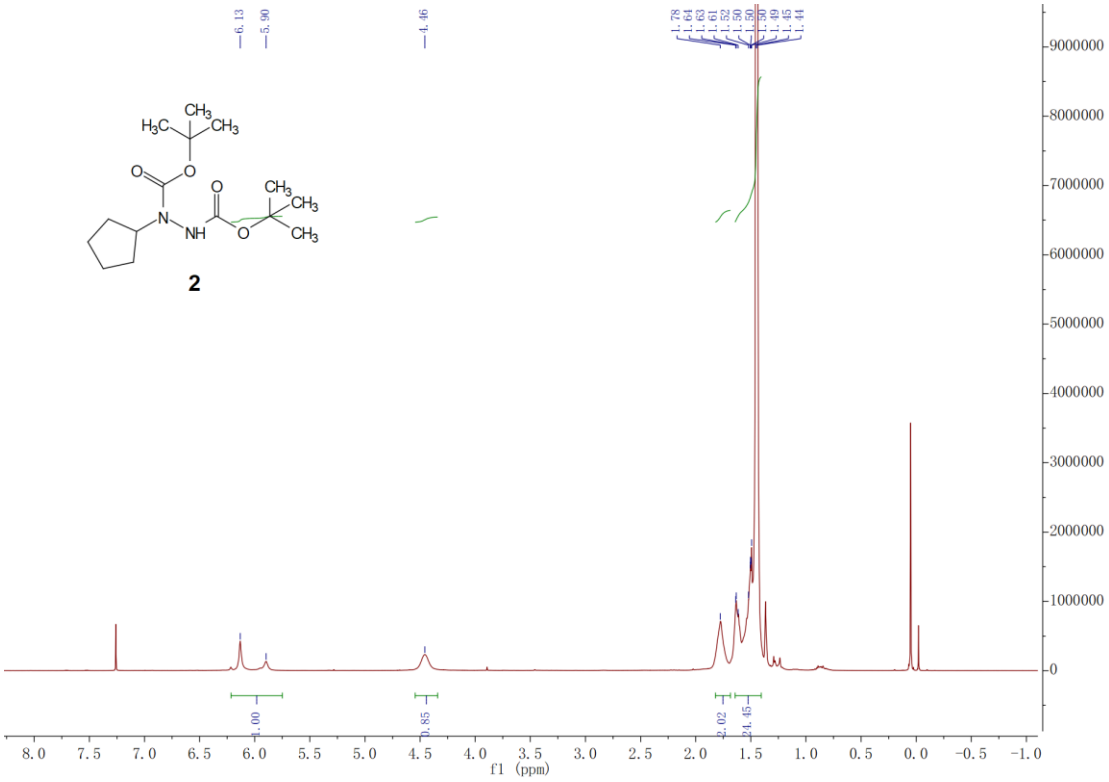

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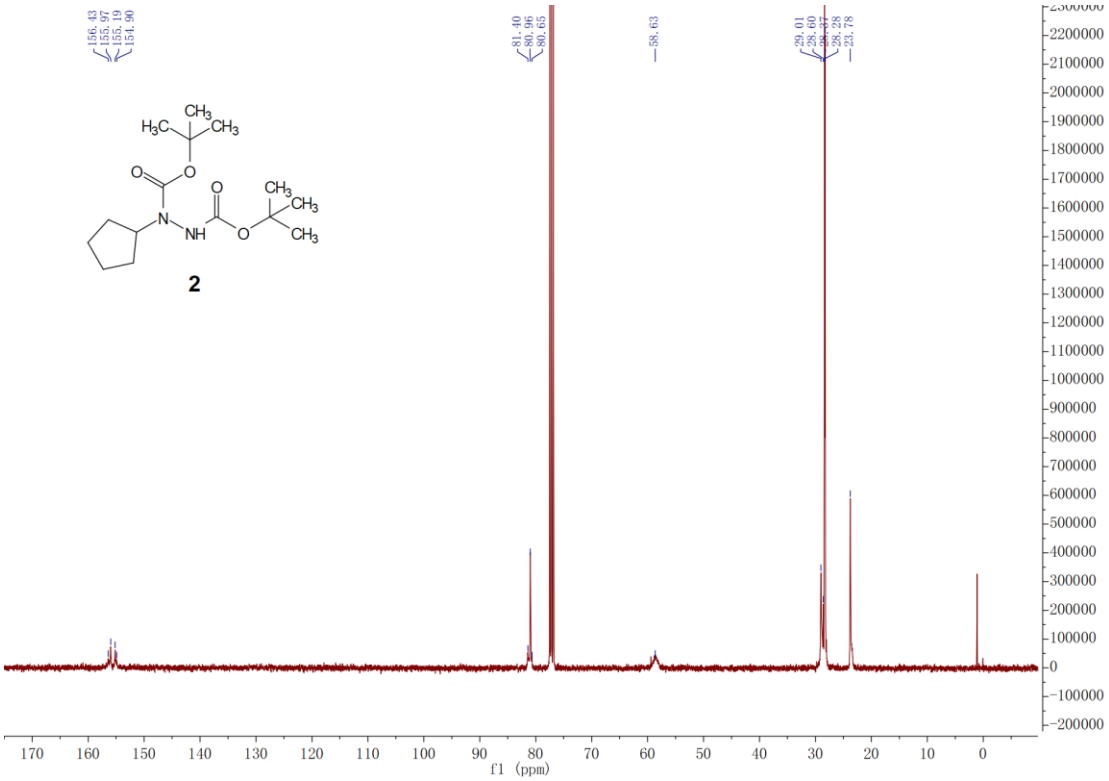

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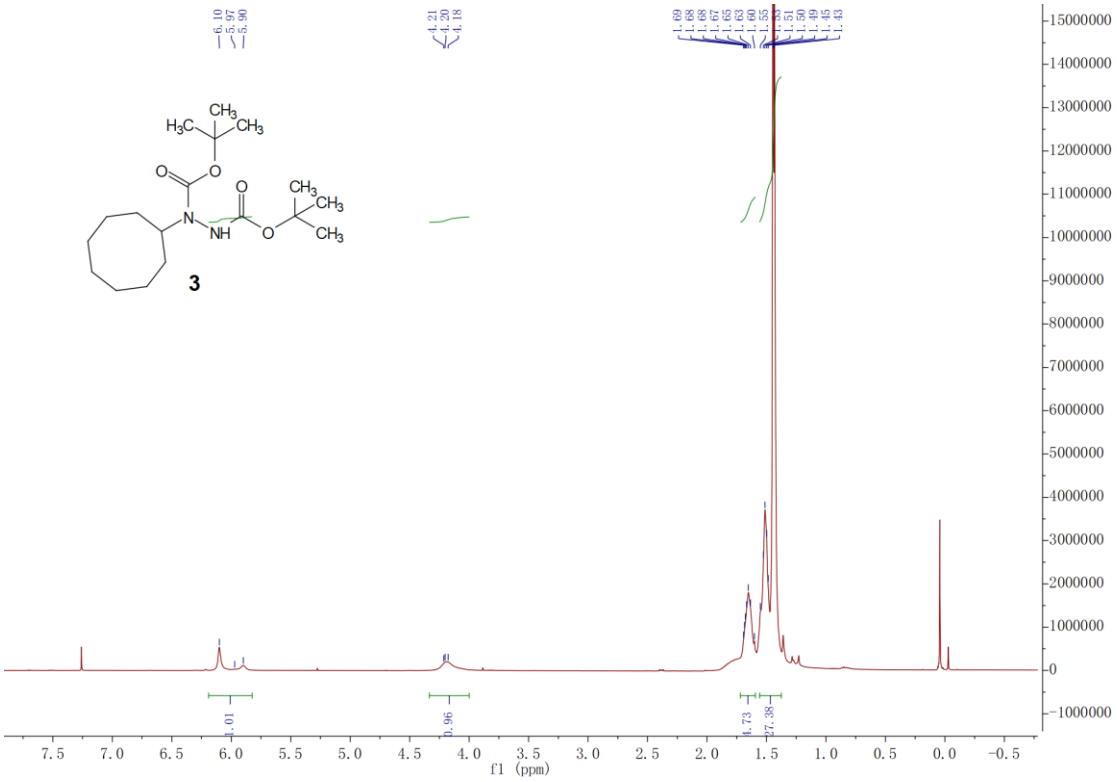

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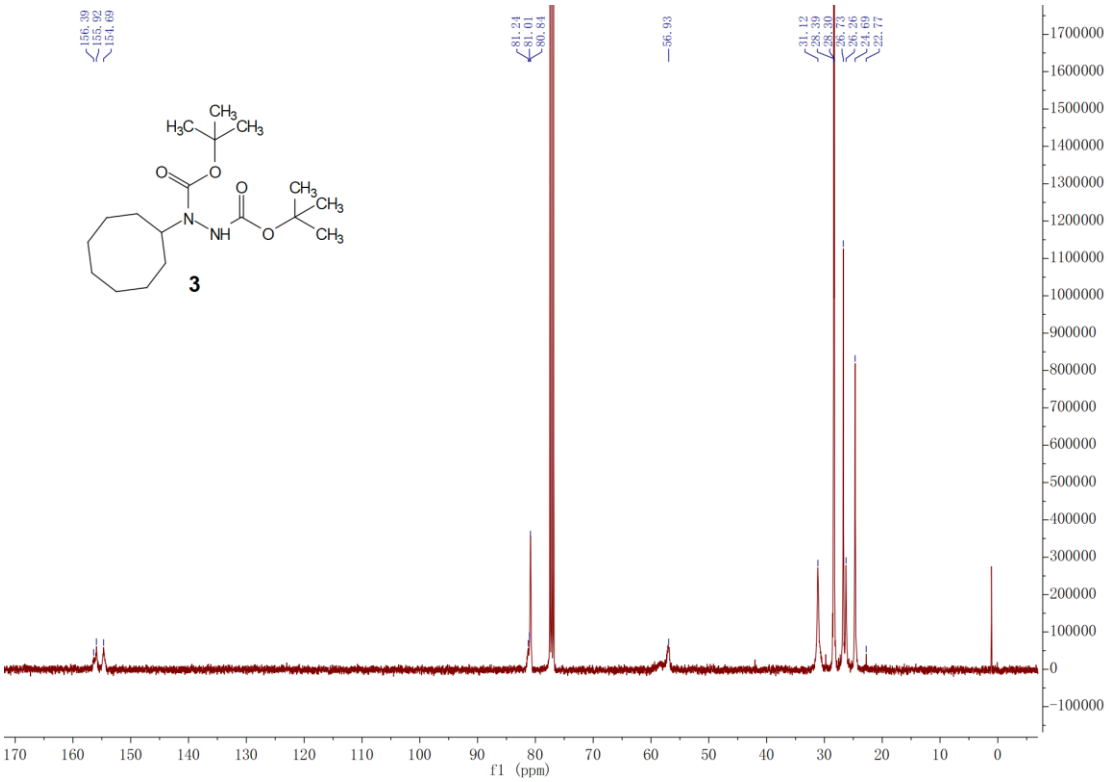

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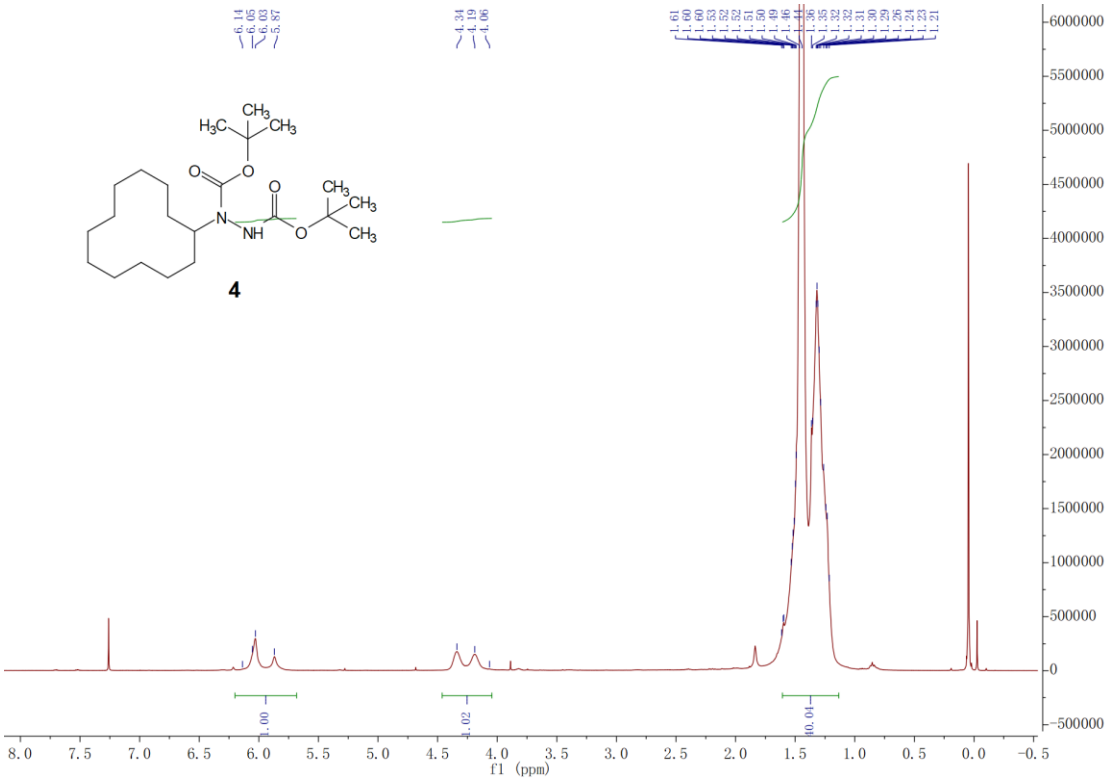

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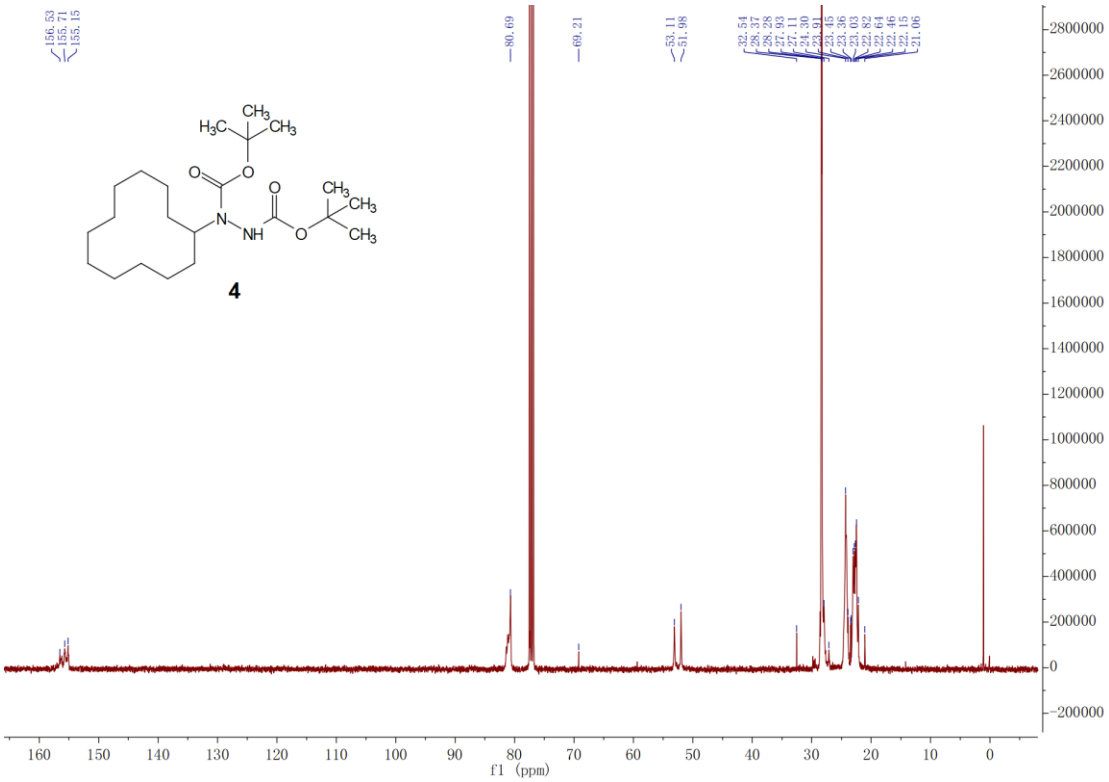

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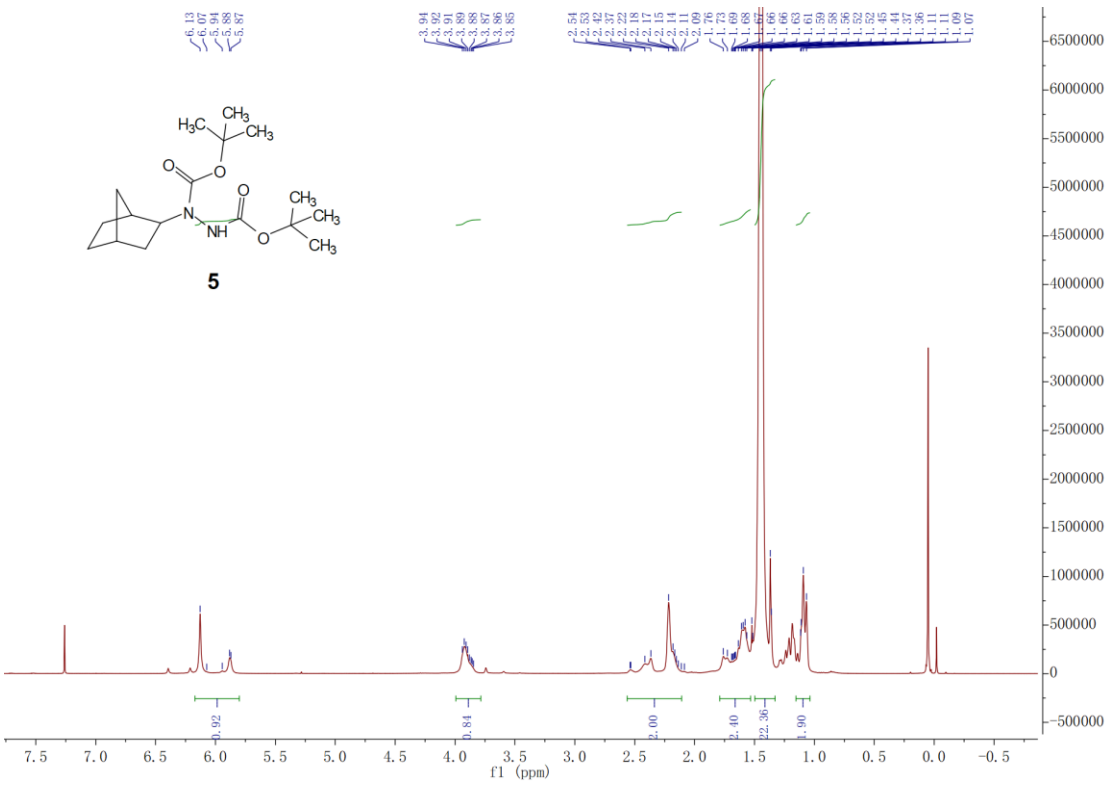

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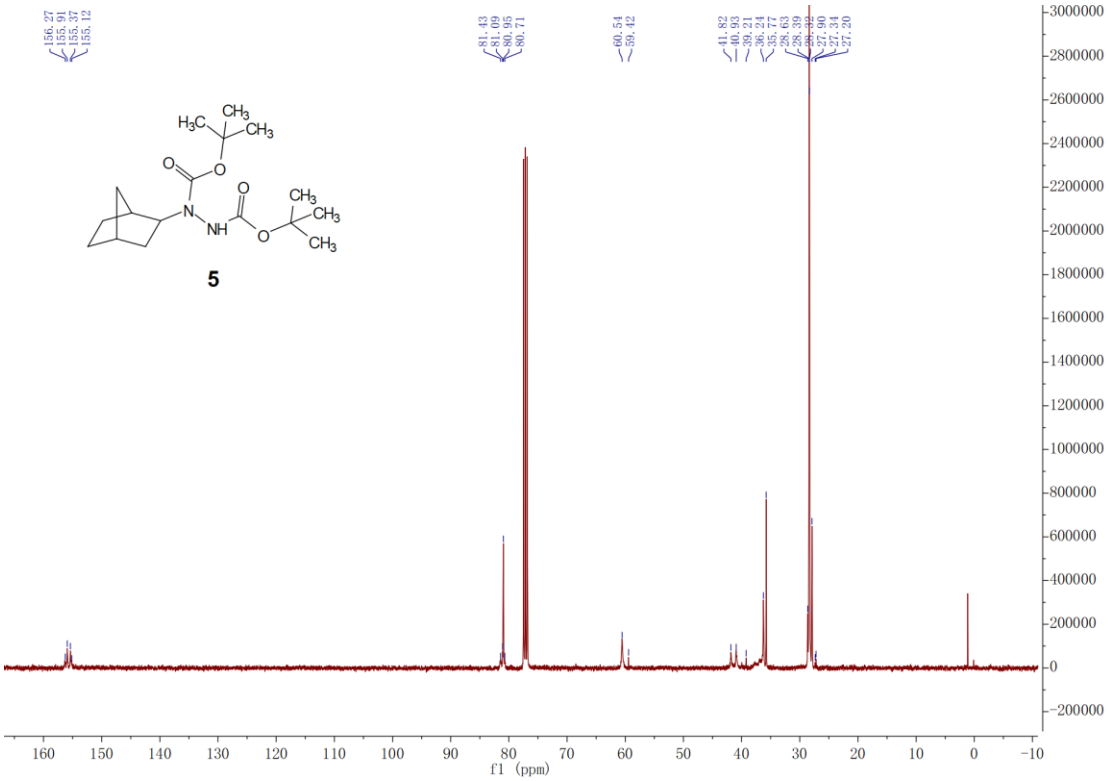

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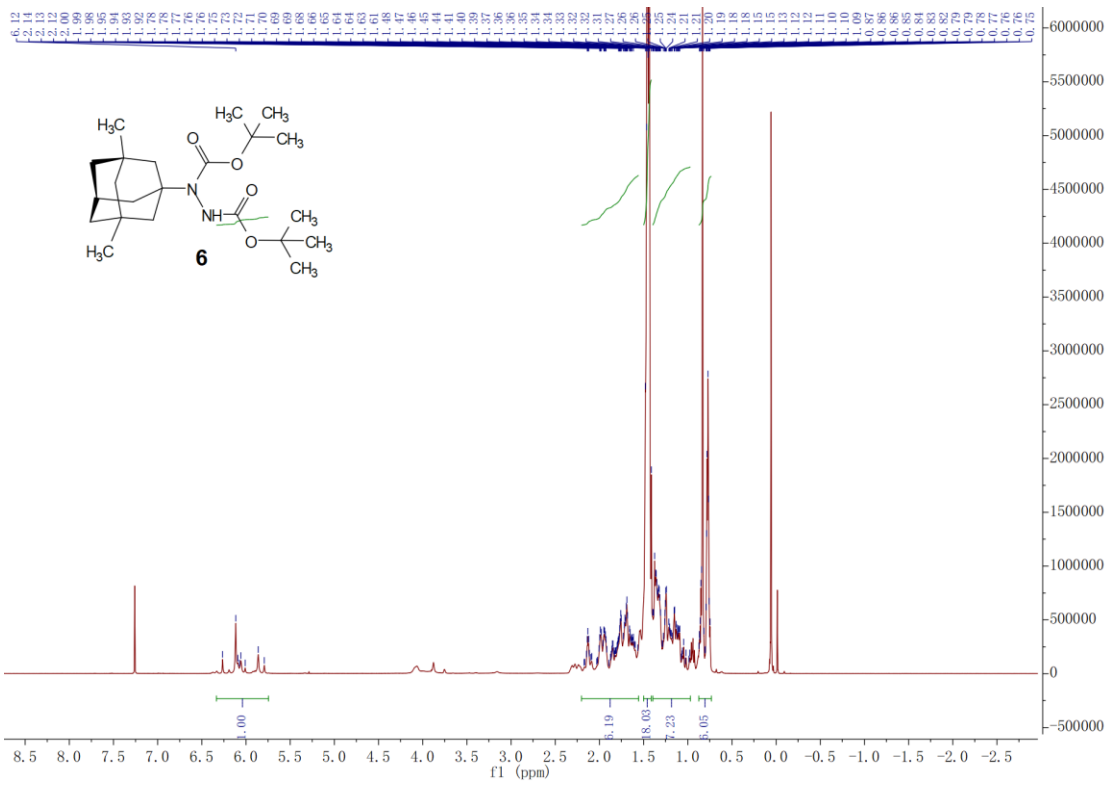

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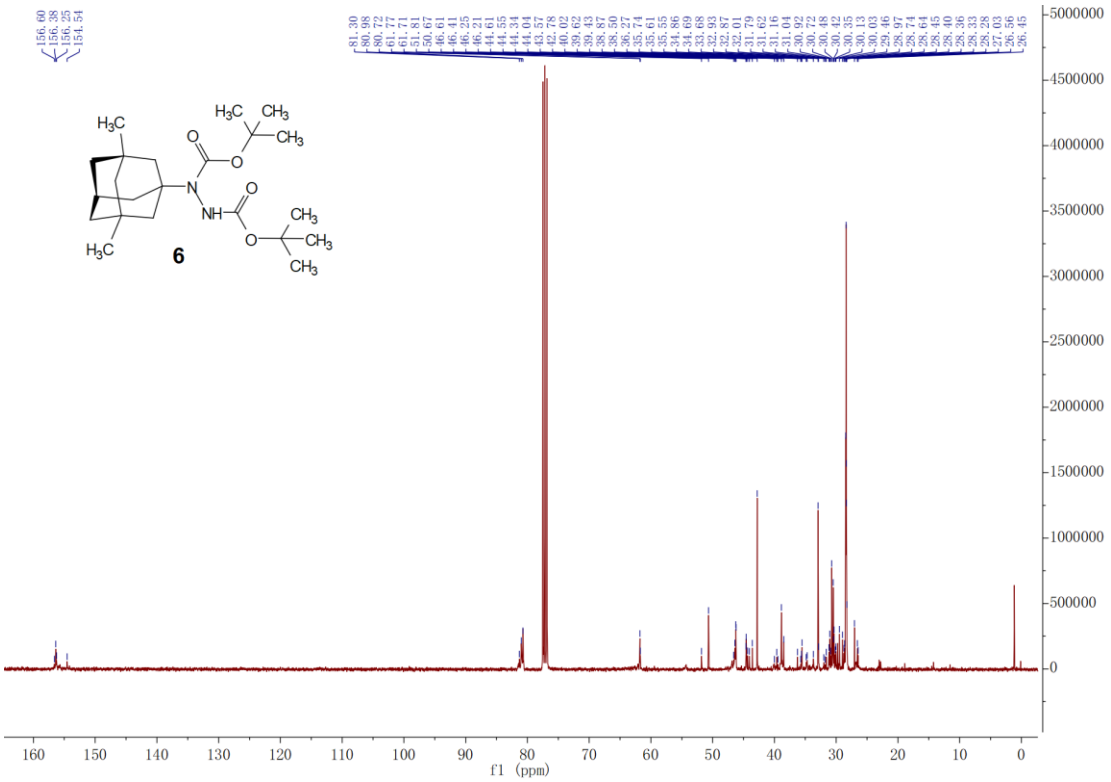

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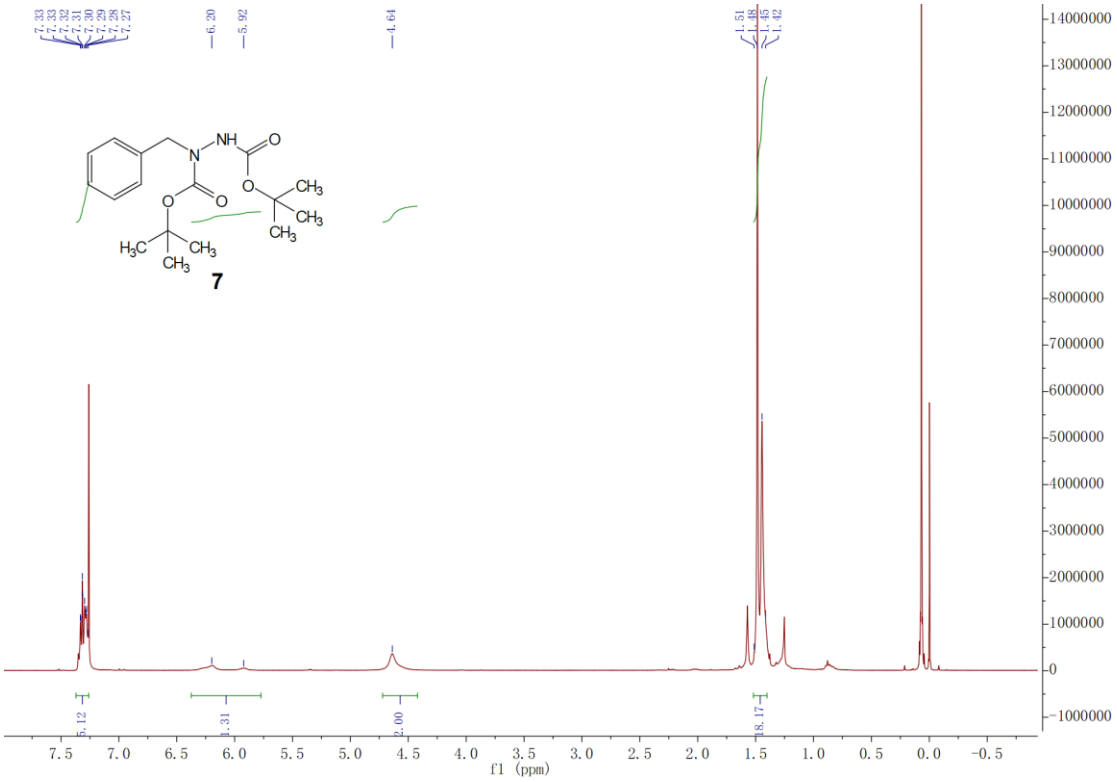

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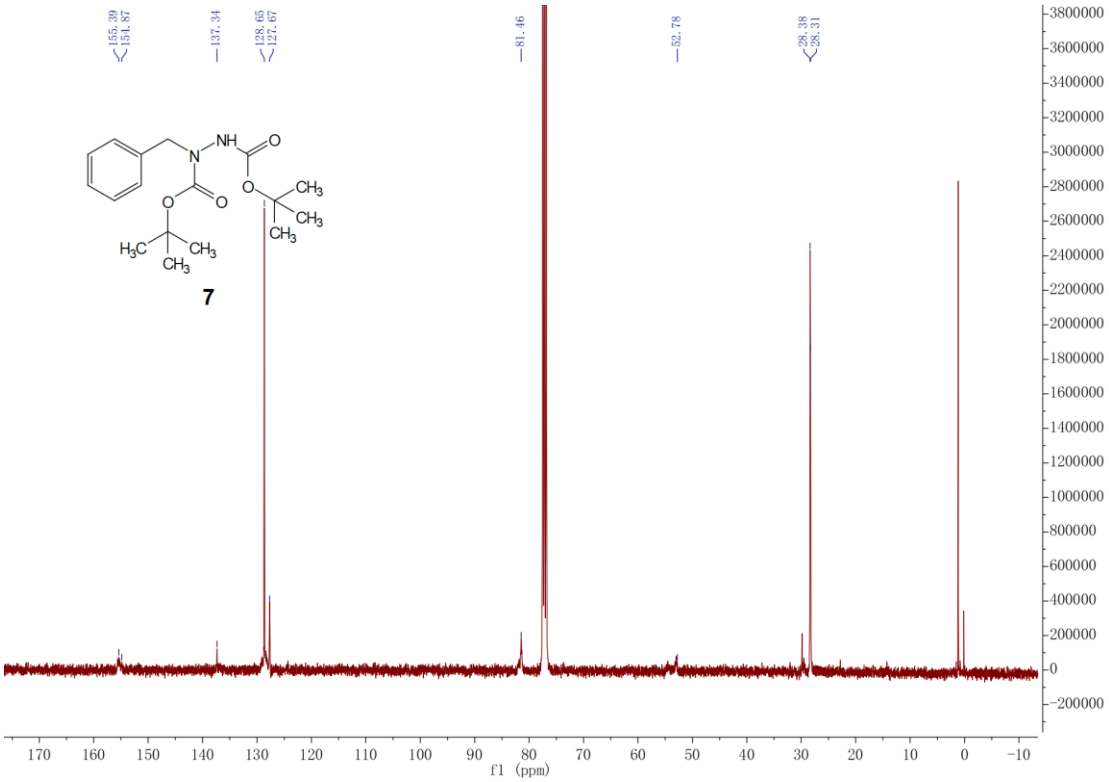

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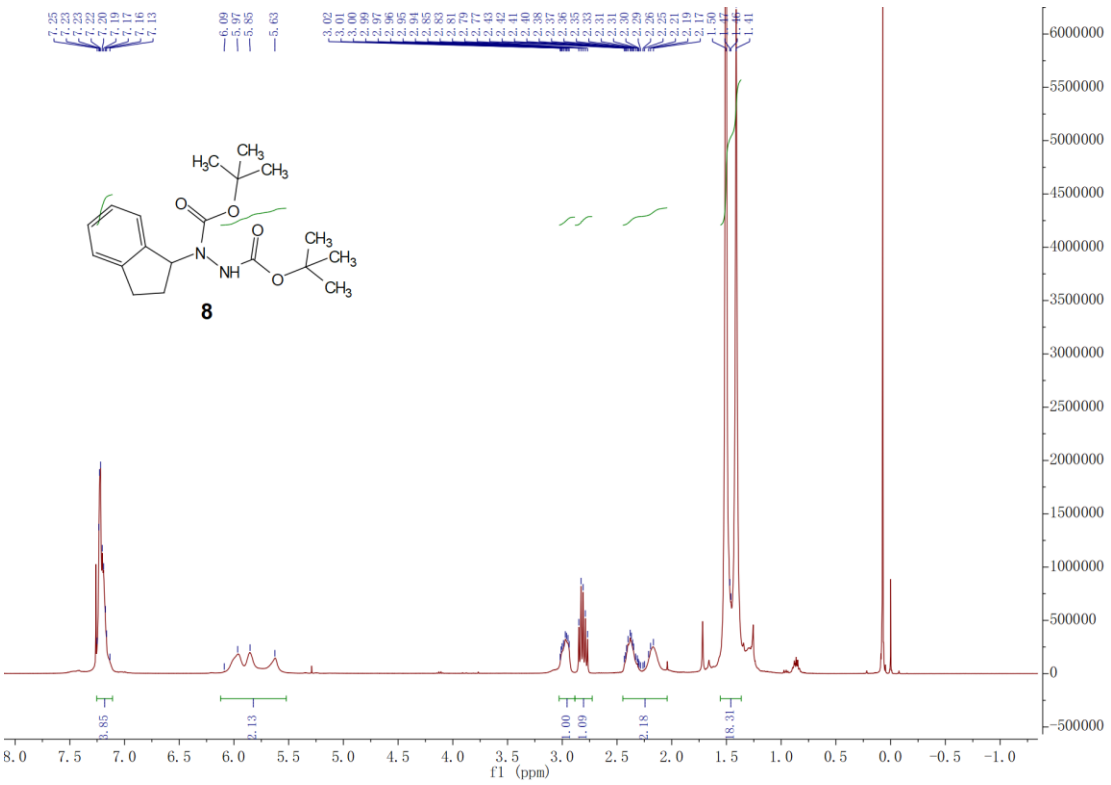

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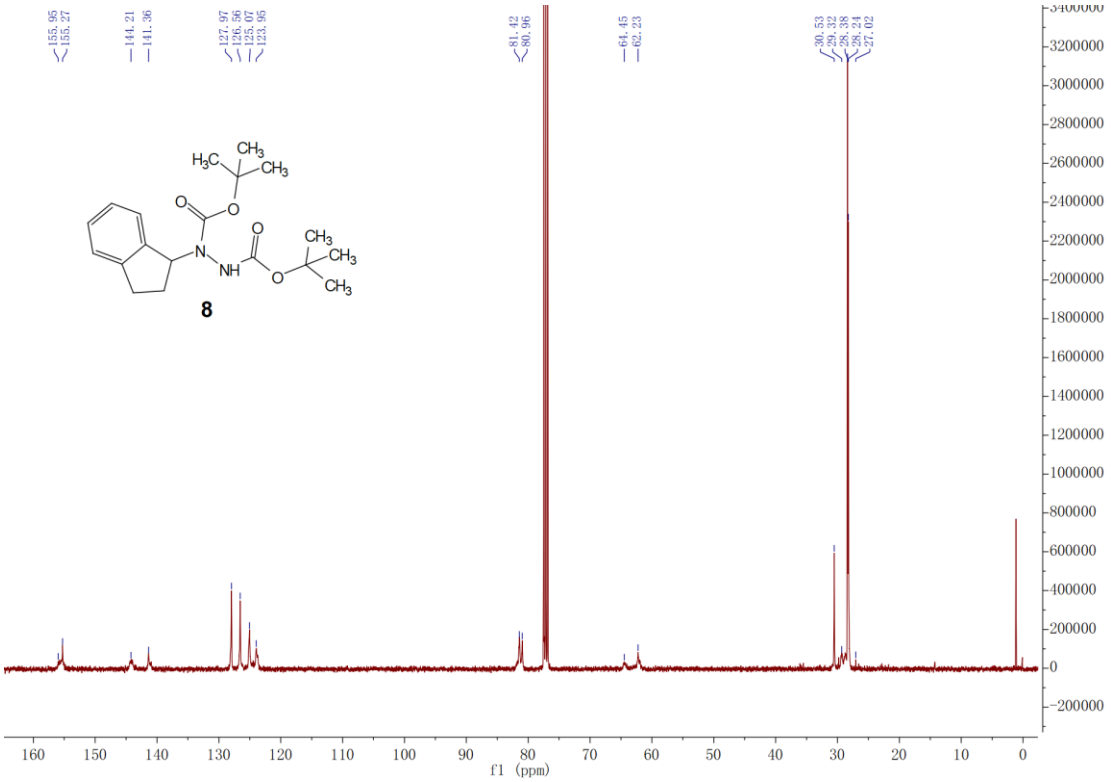

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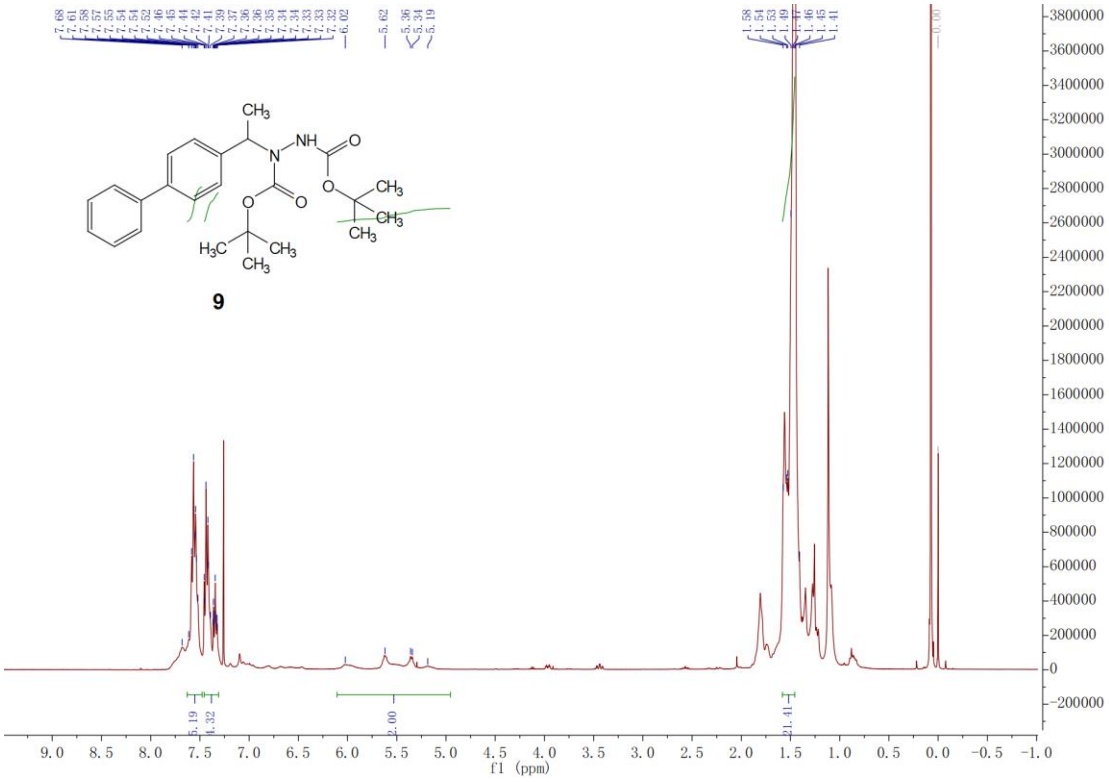

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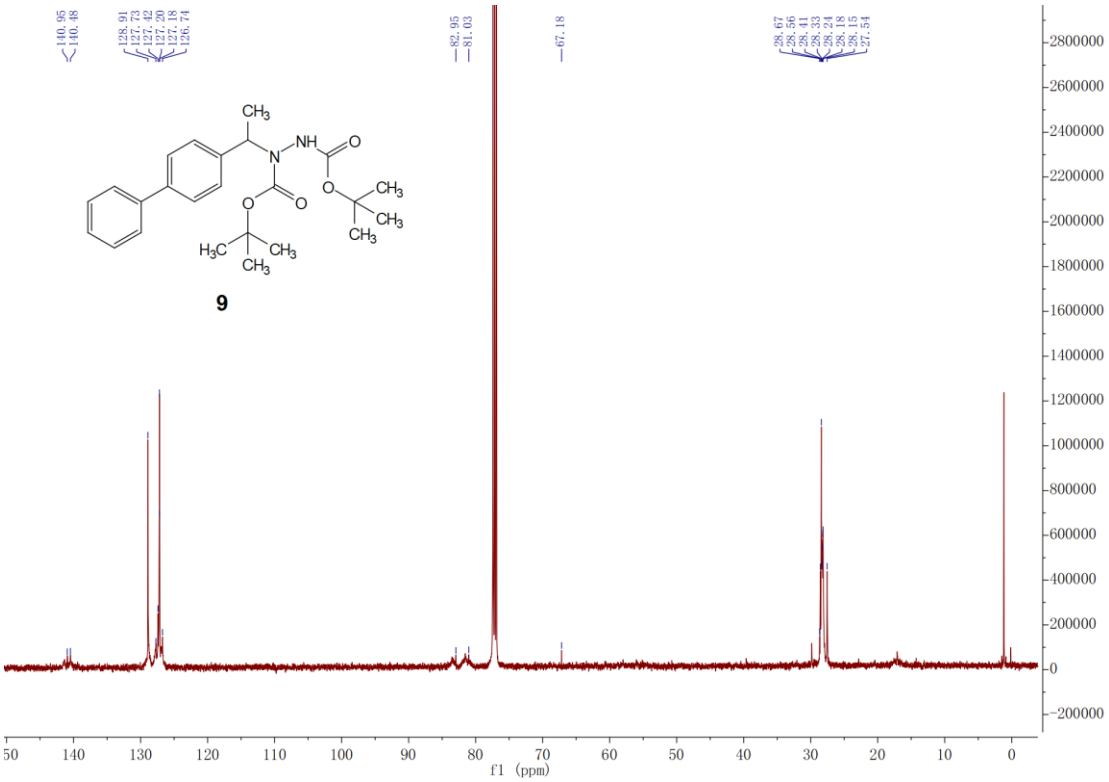

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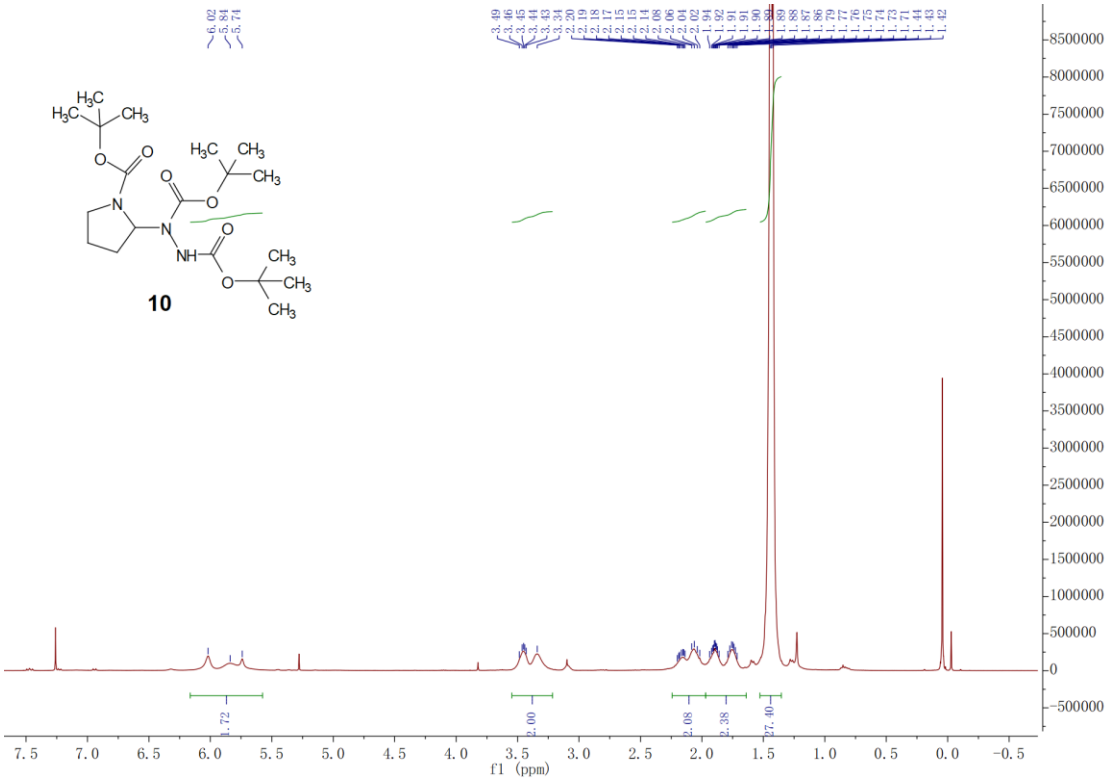

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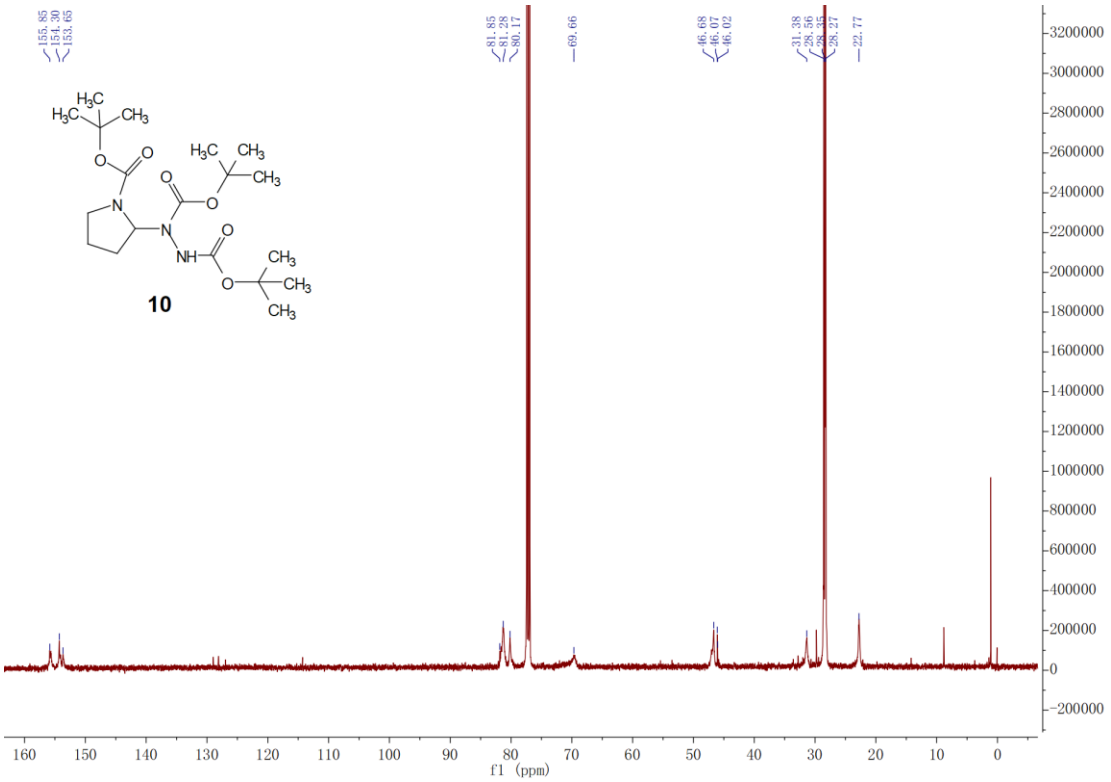

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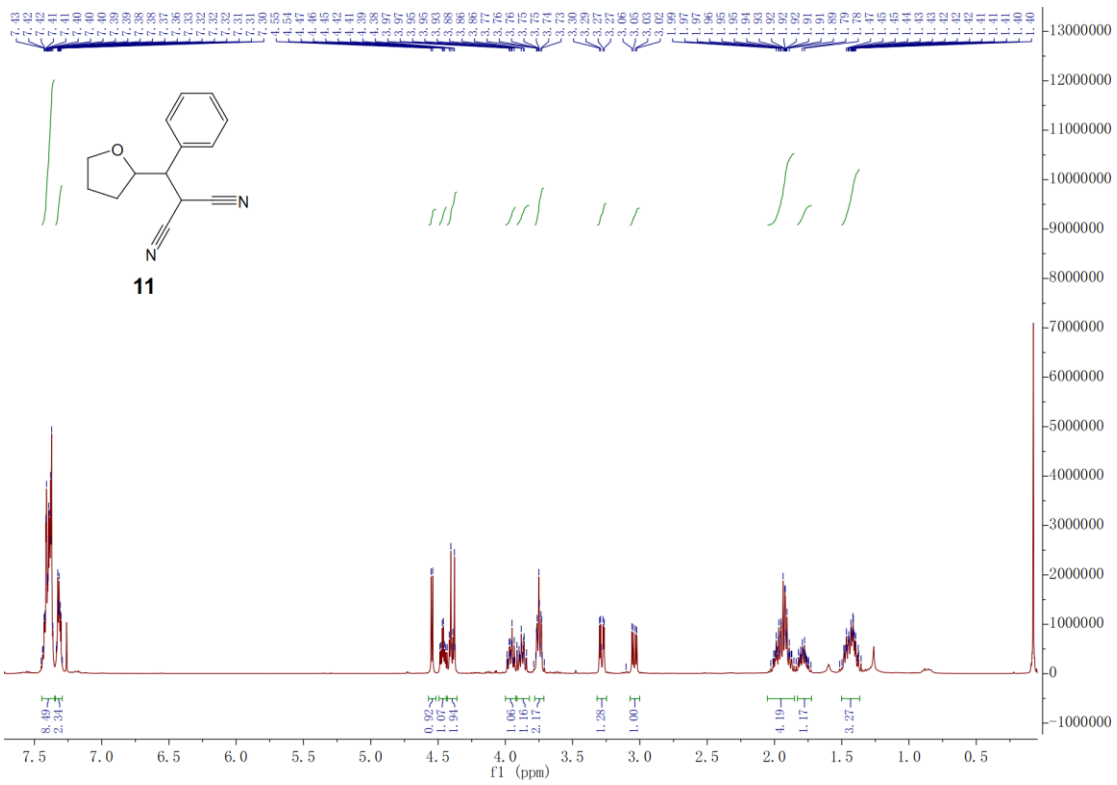

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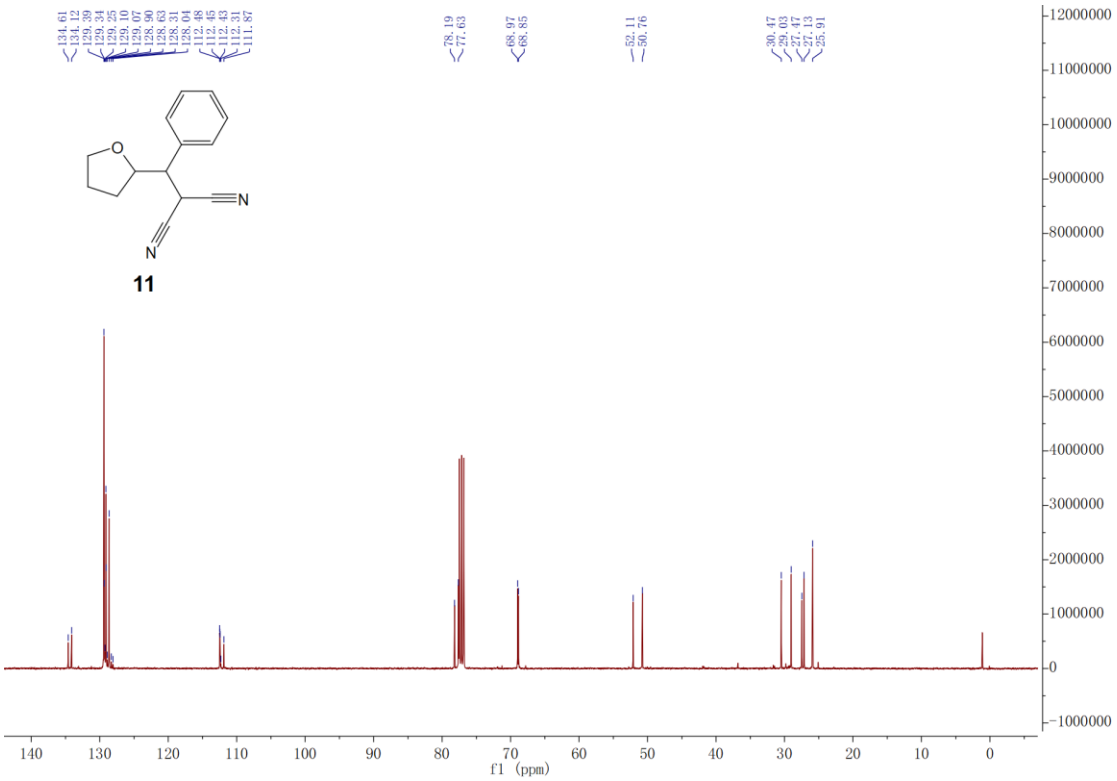

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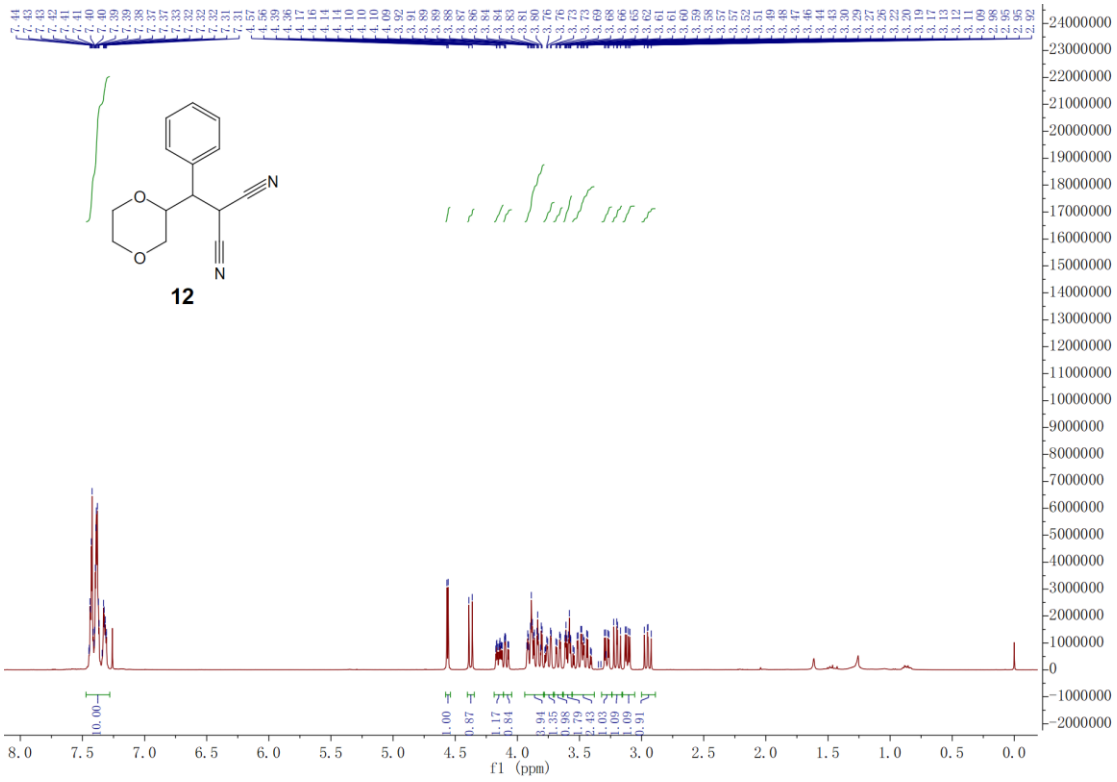

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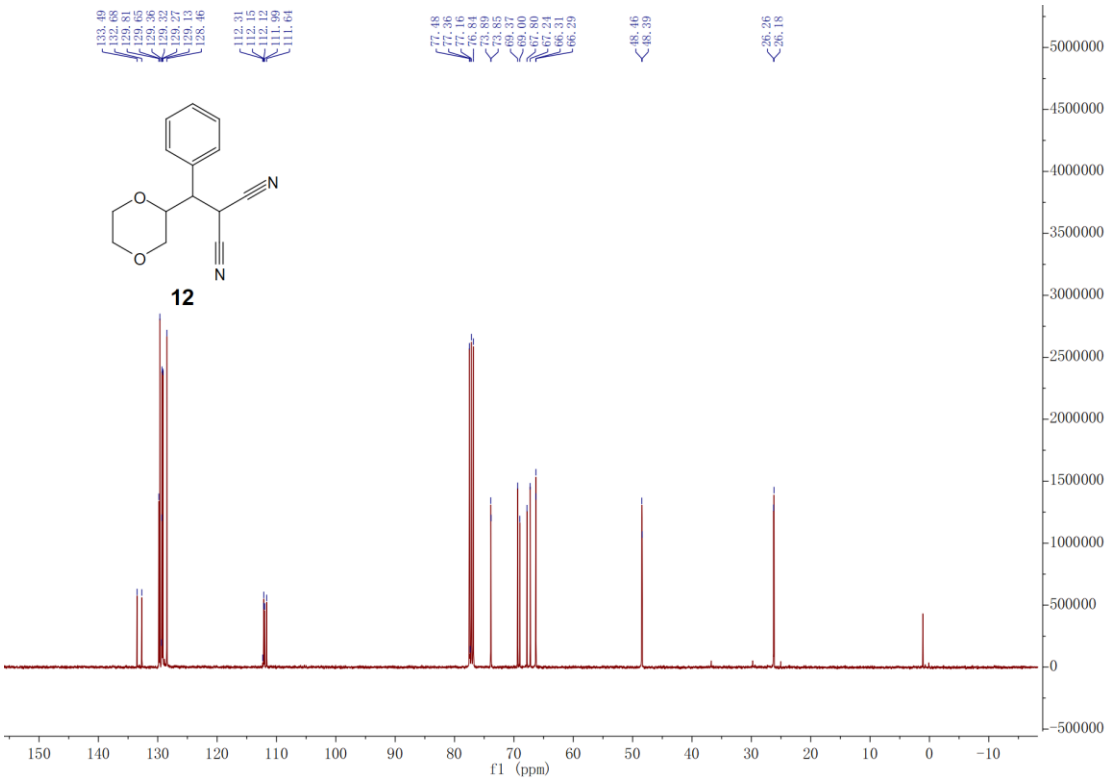

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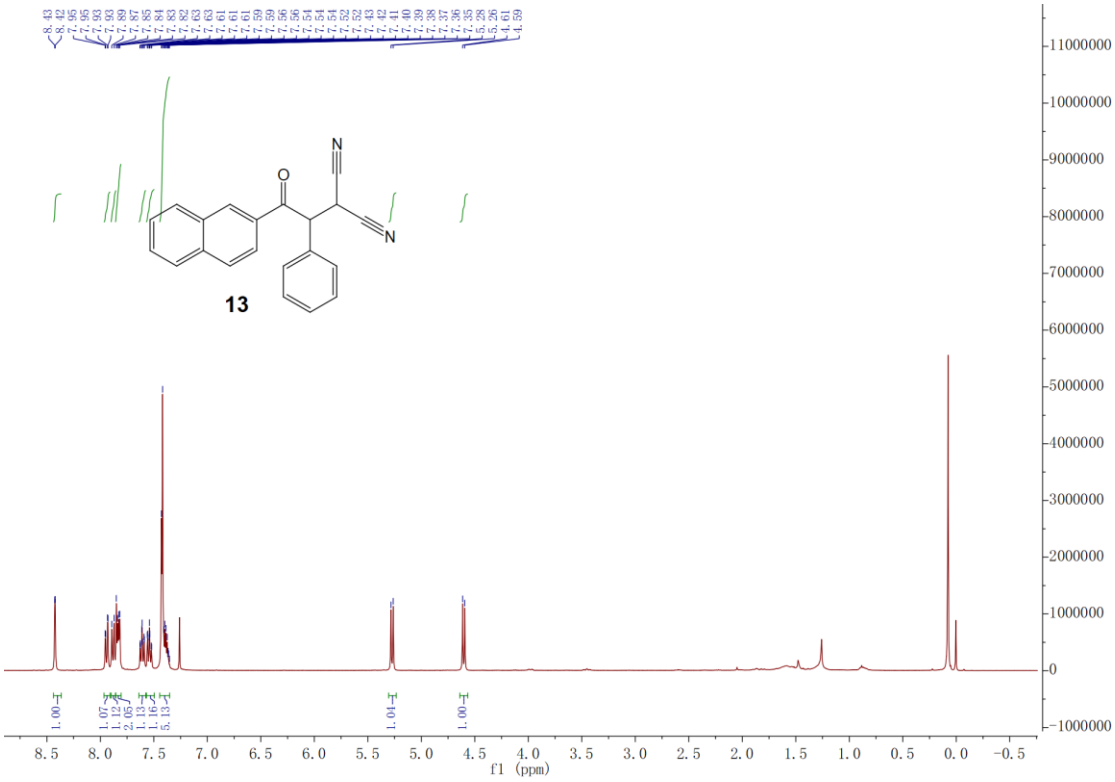

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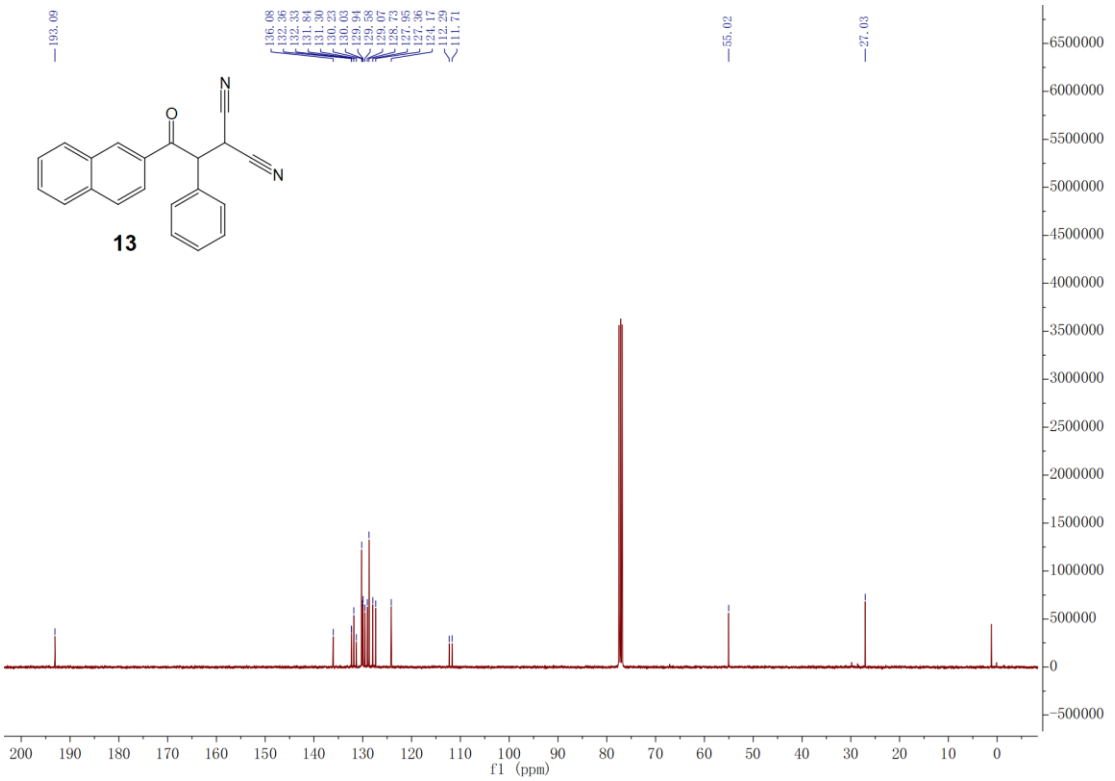

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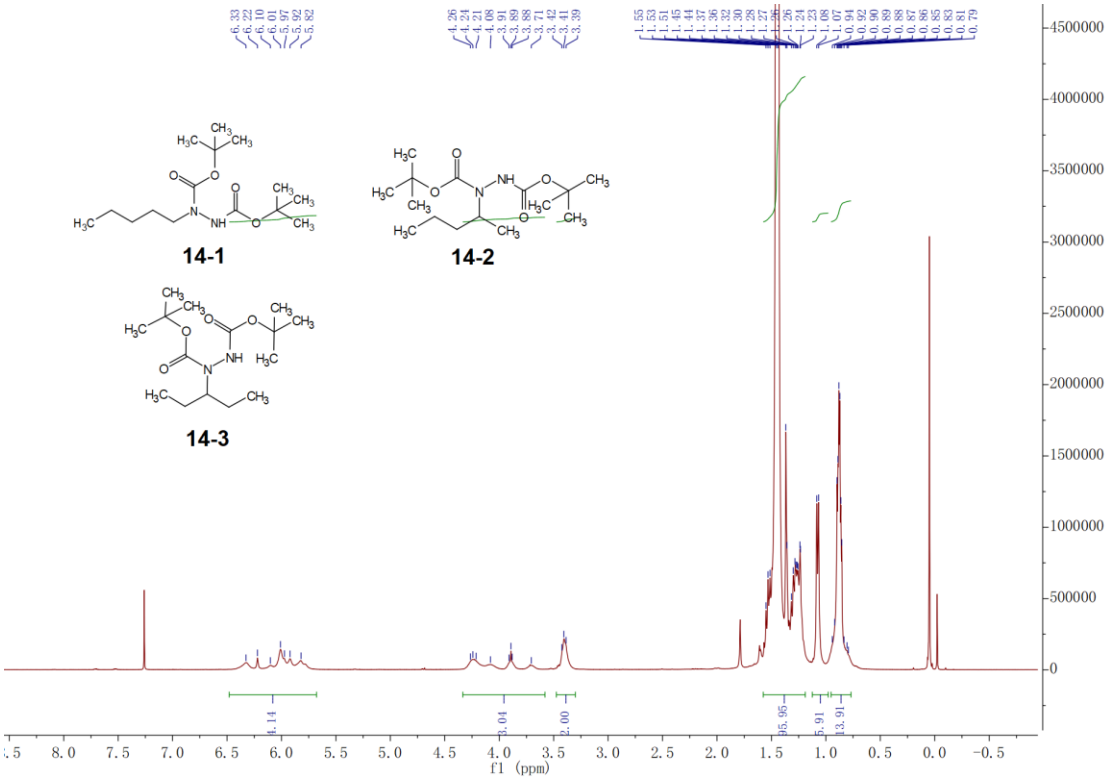

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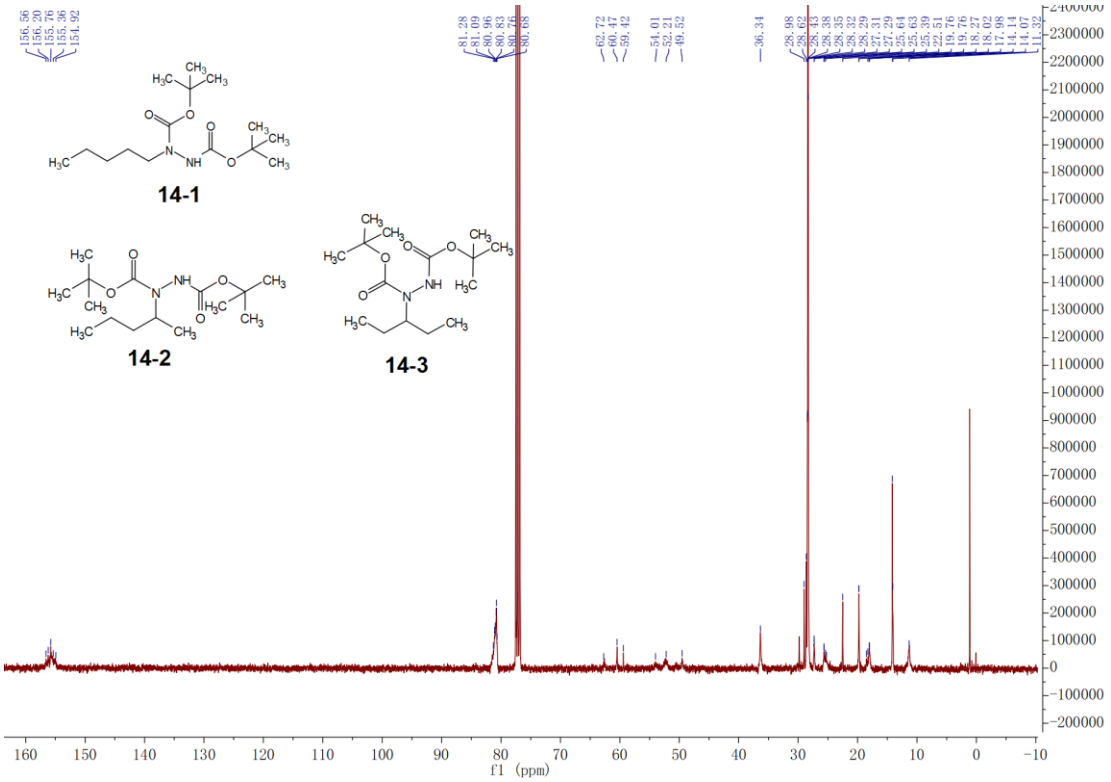
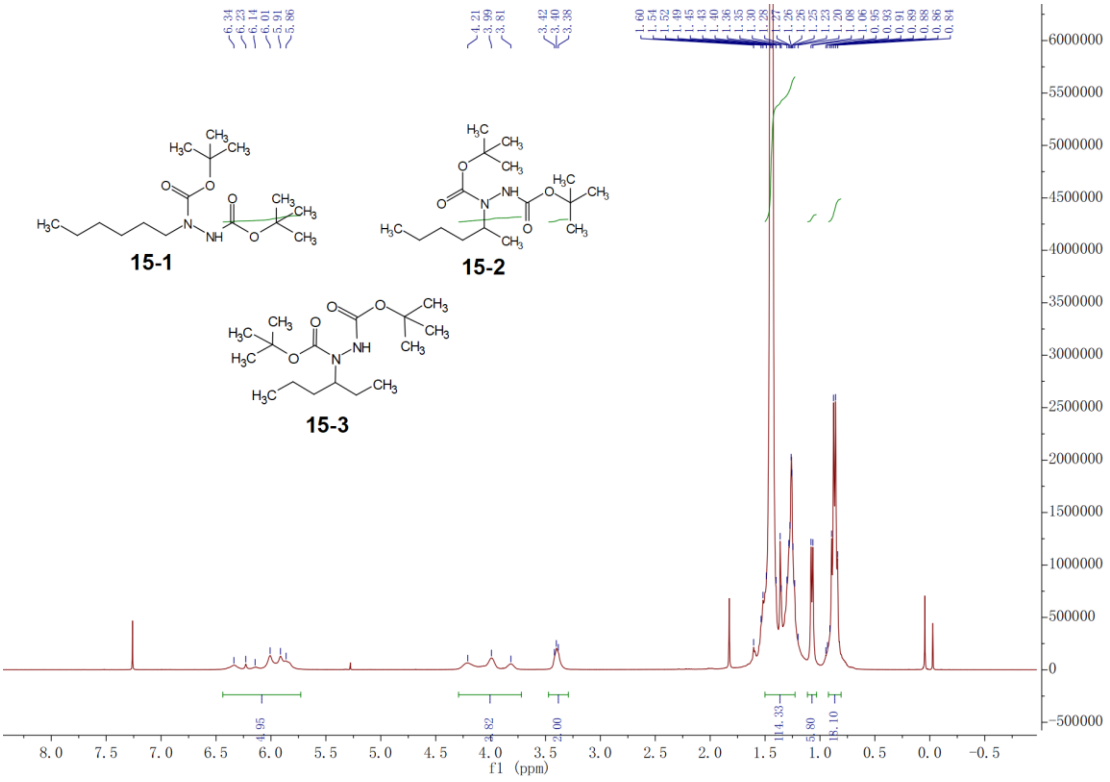
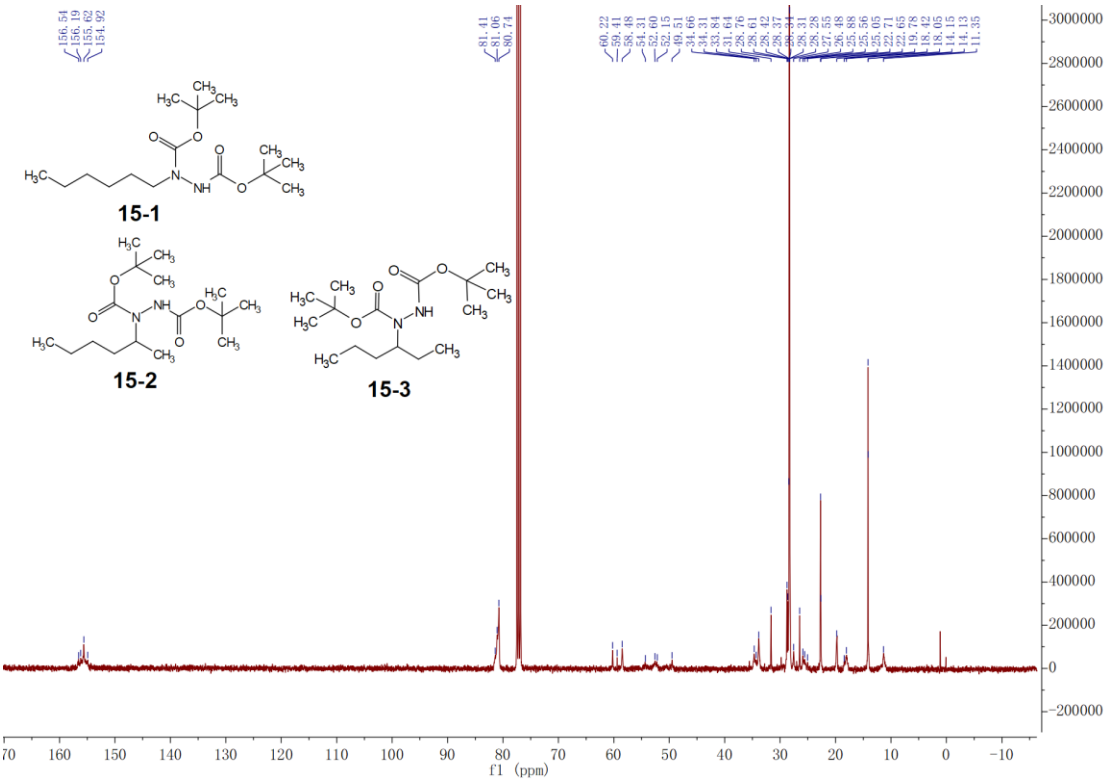


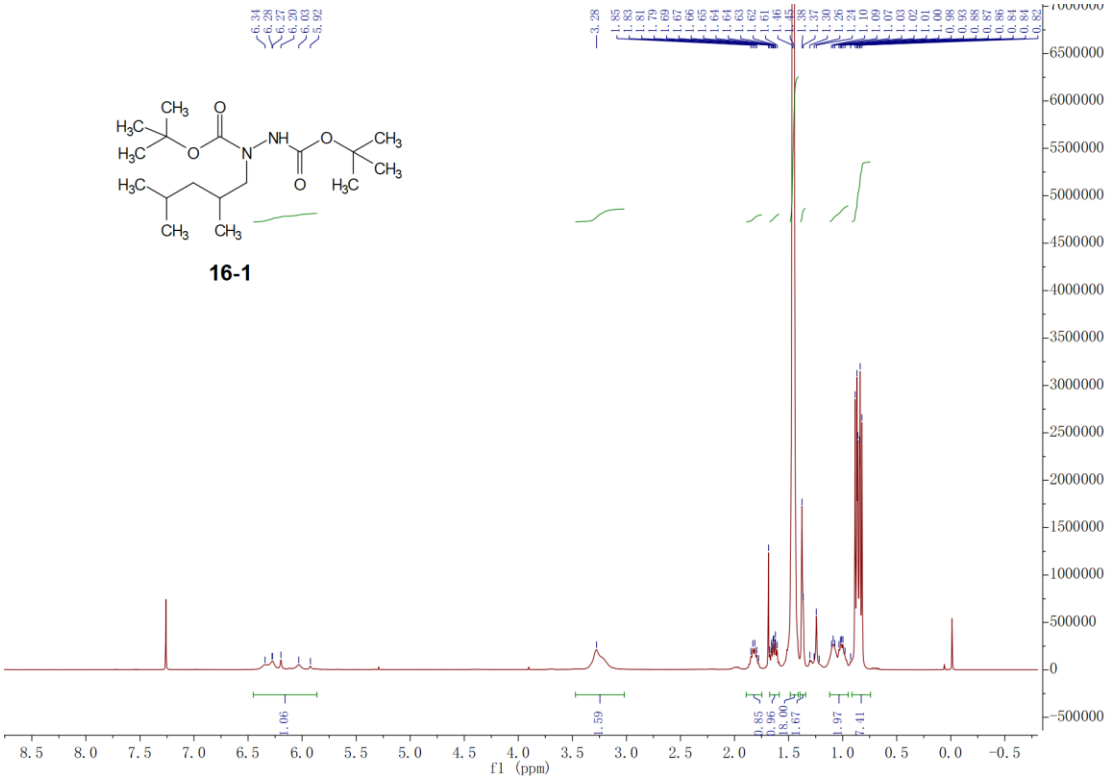
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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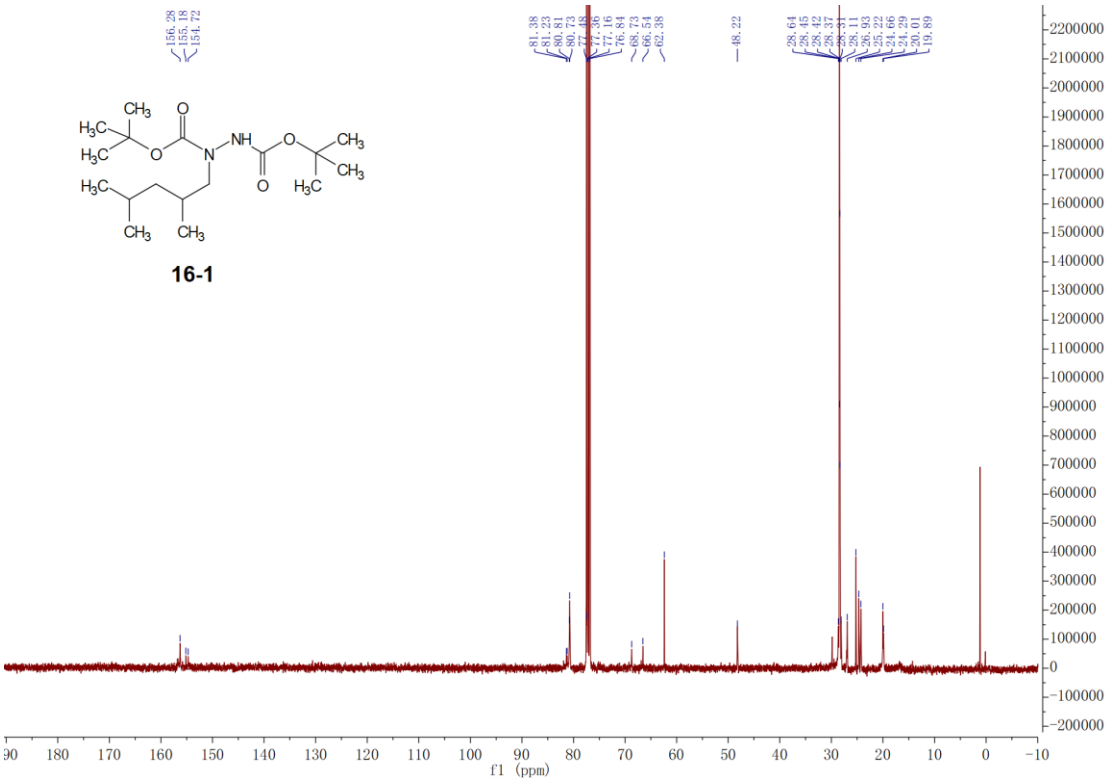

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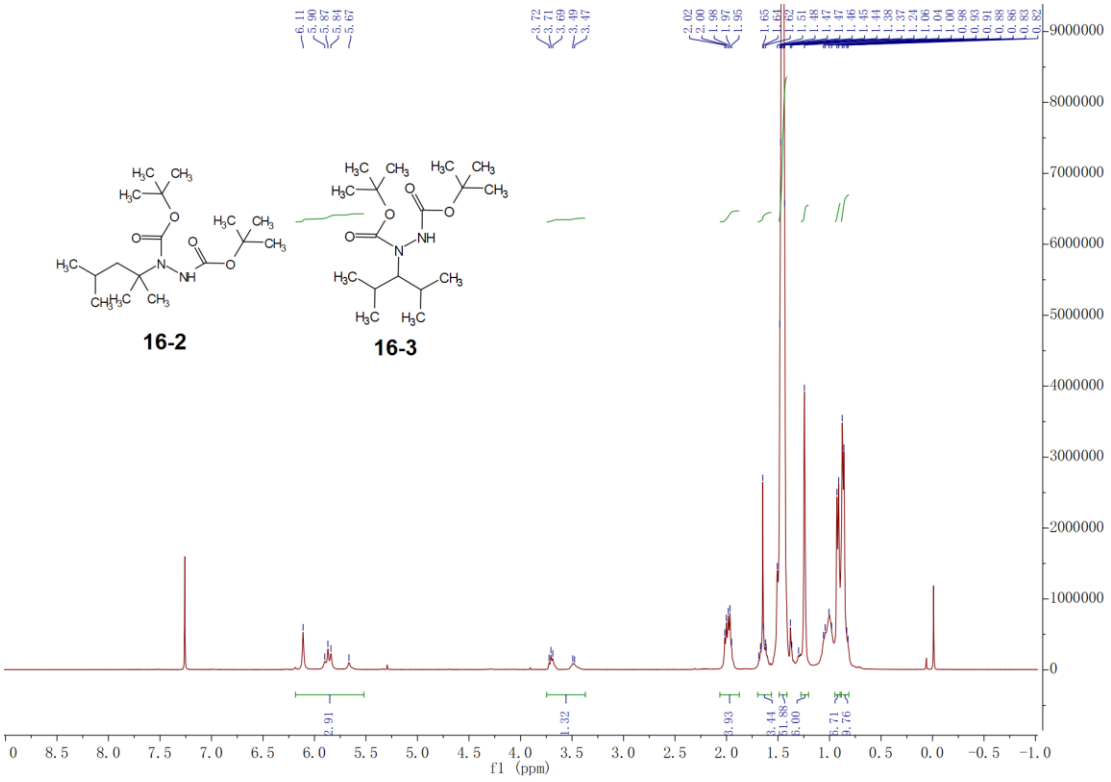

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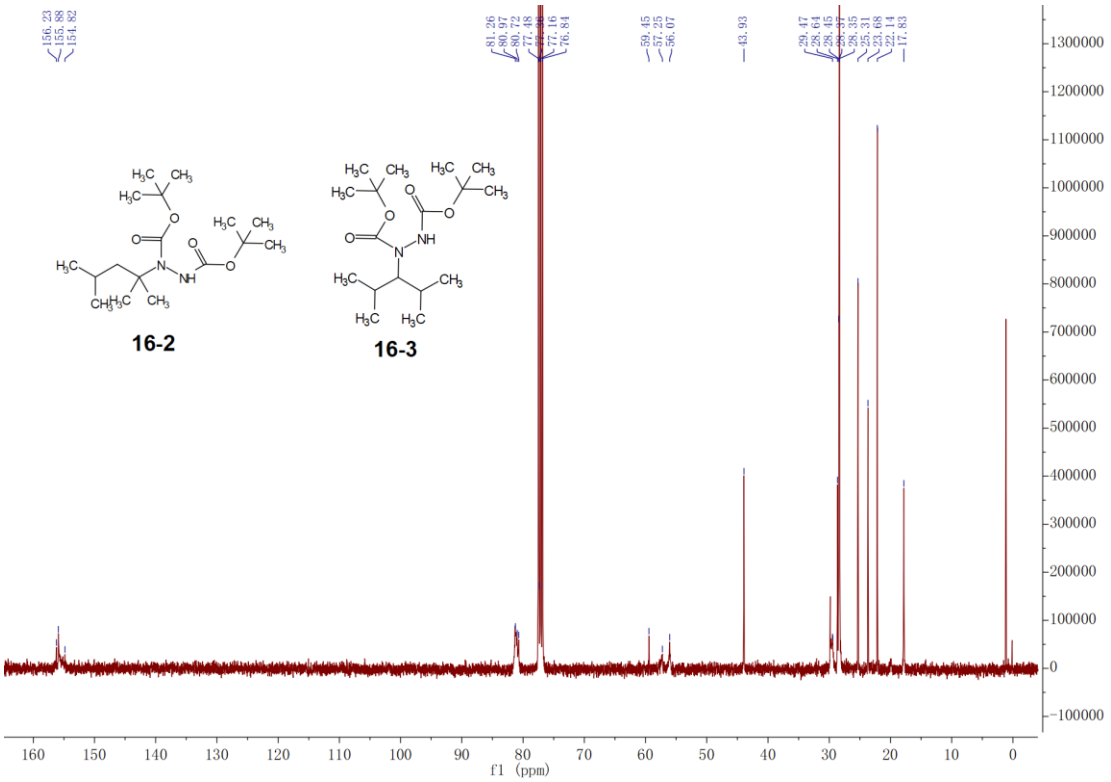
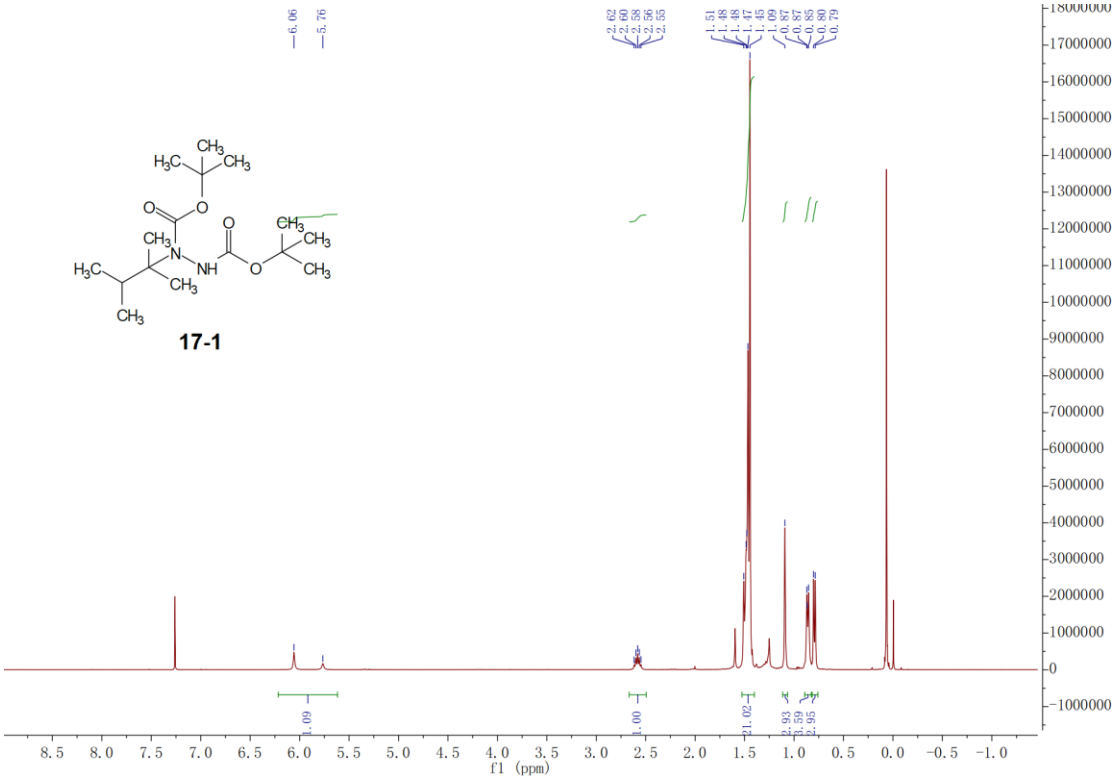


^{1}H NMR (400 MHz, $CDCl_3$)



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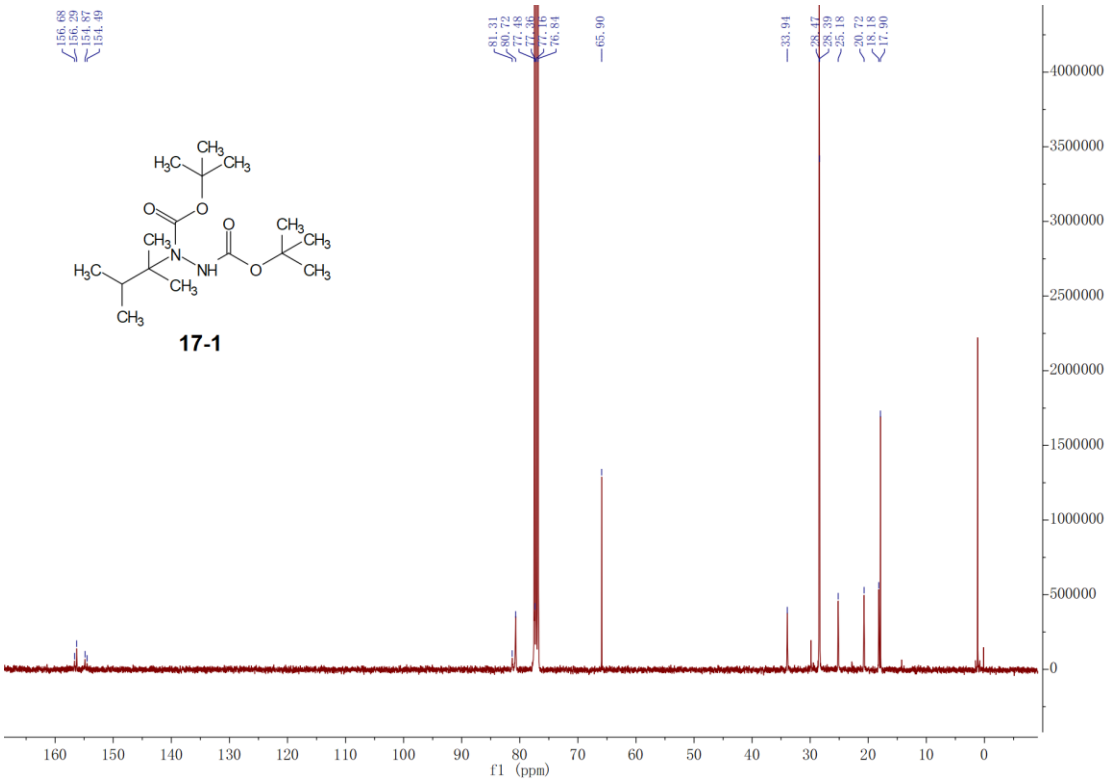

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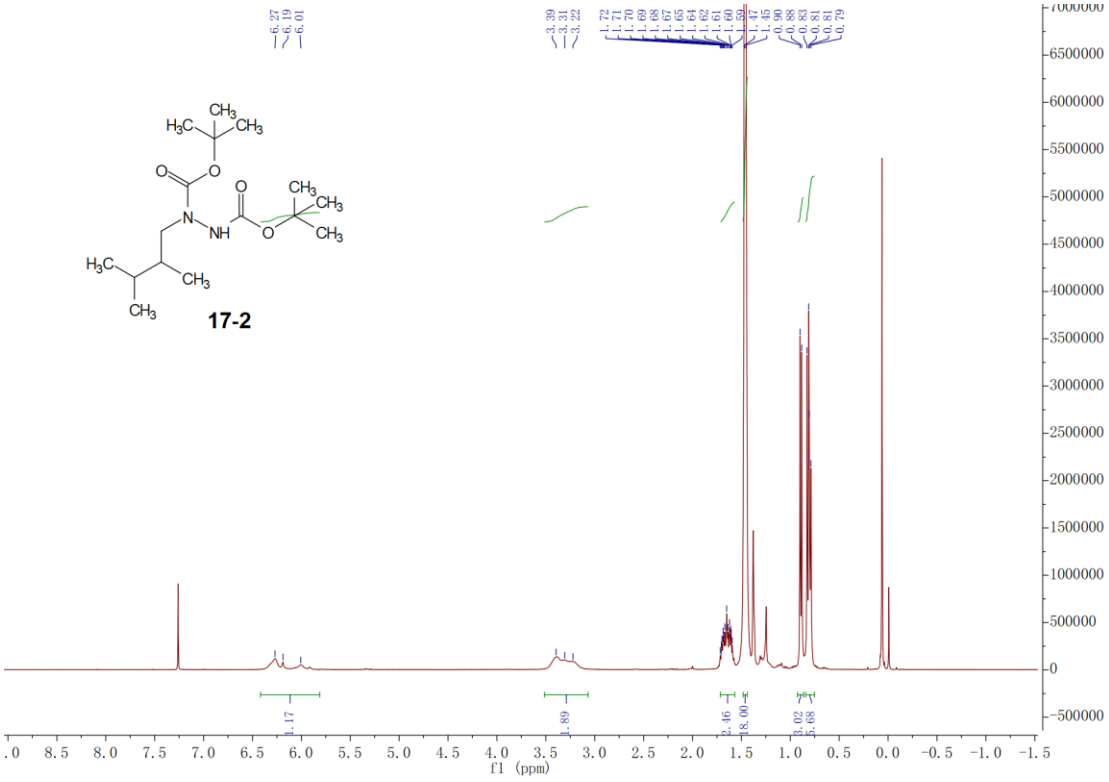

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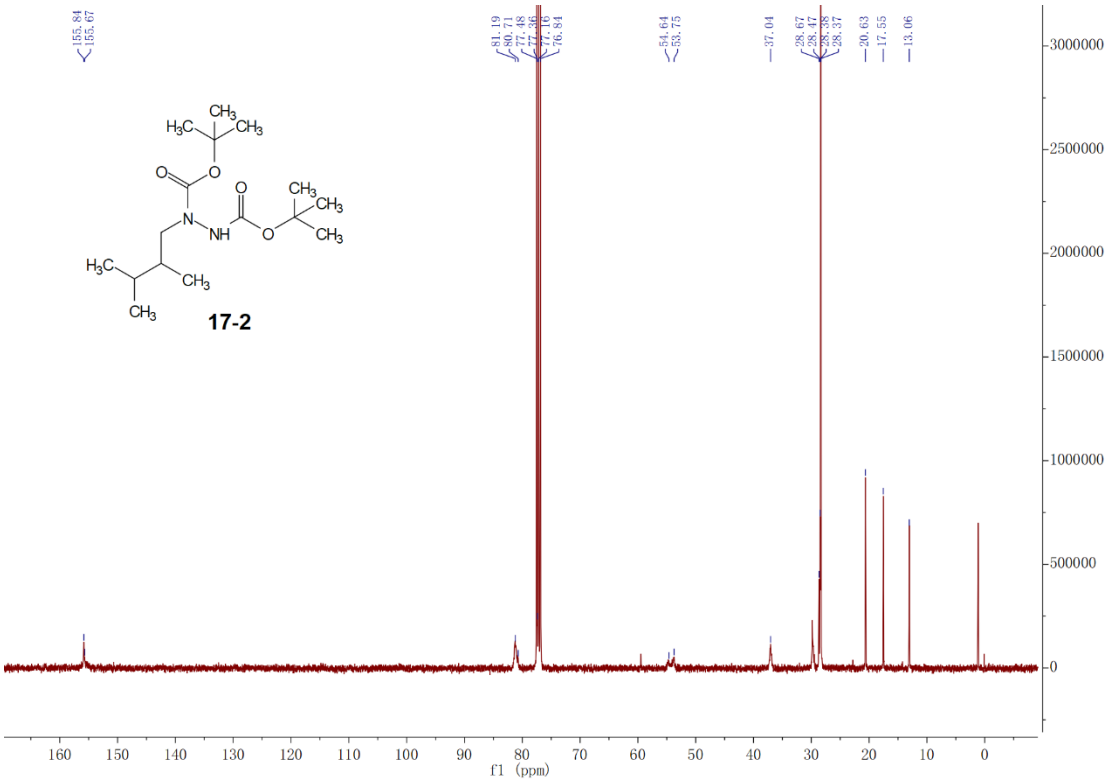

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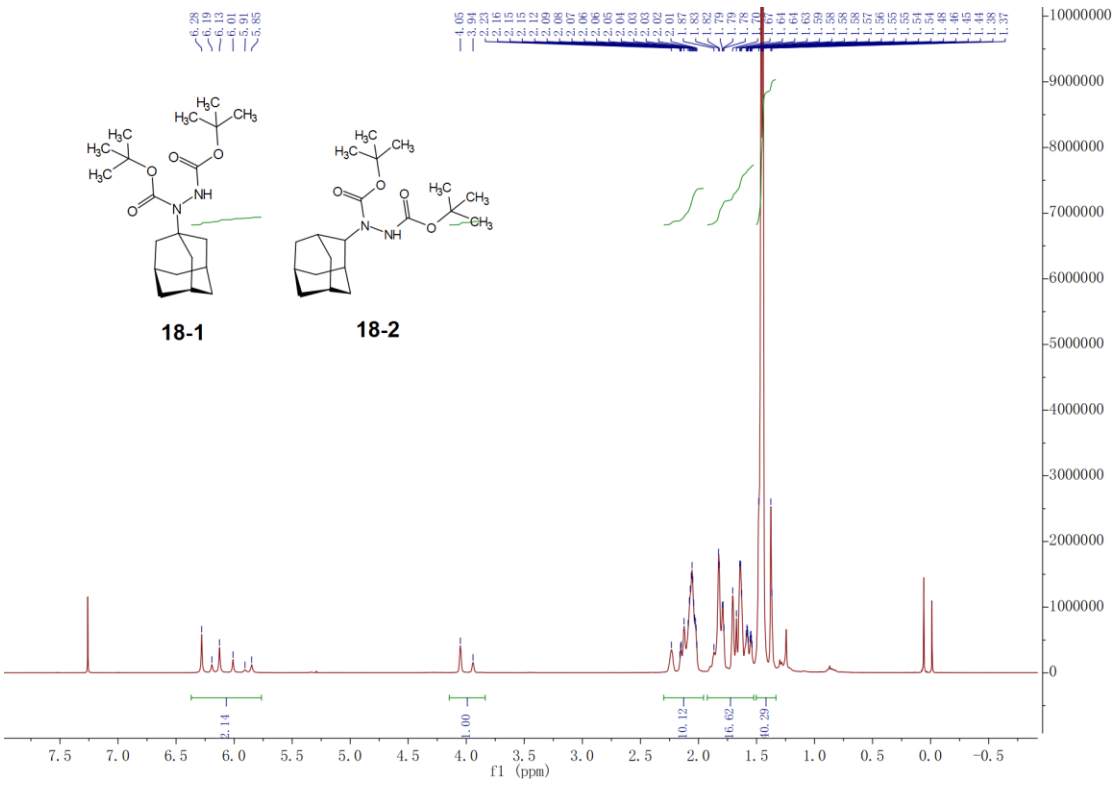

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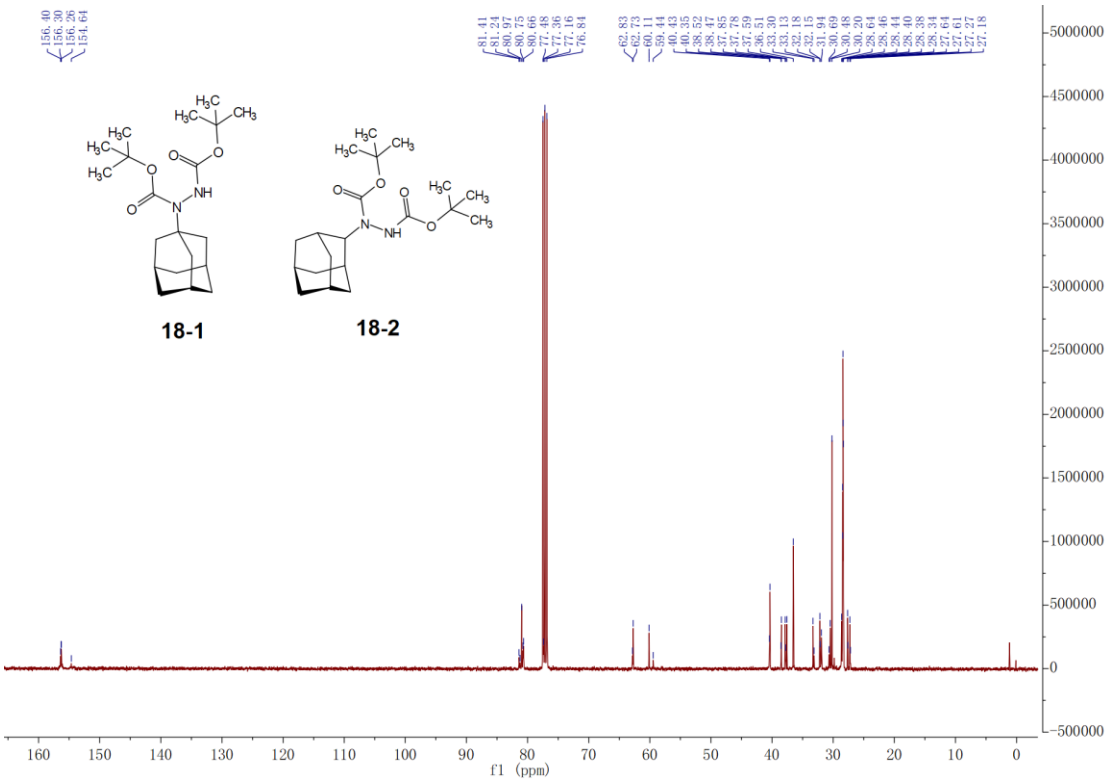

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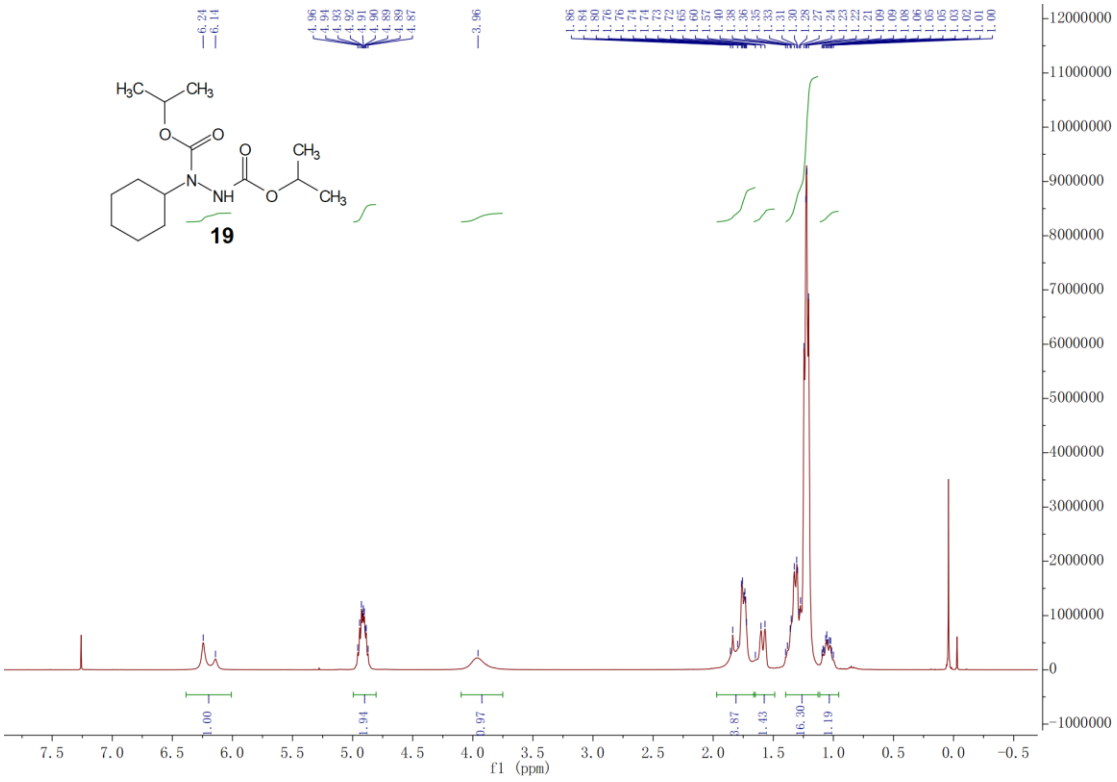

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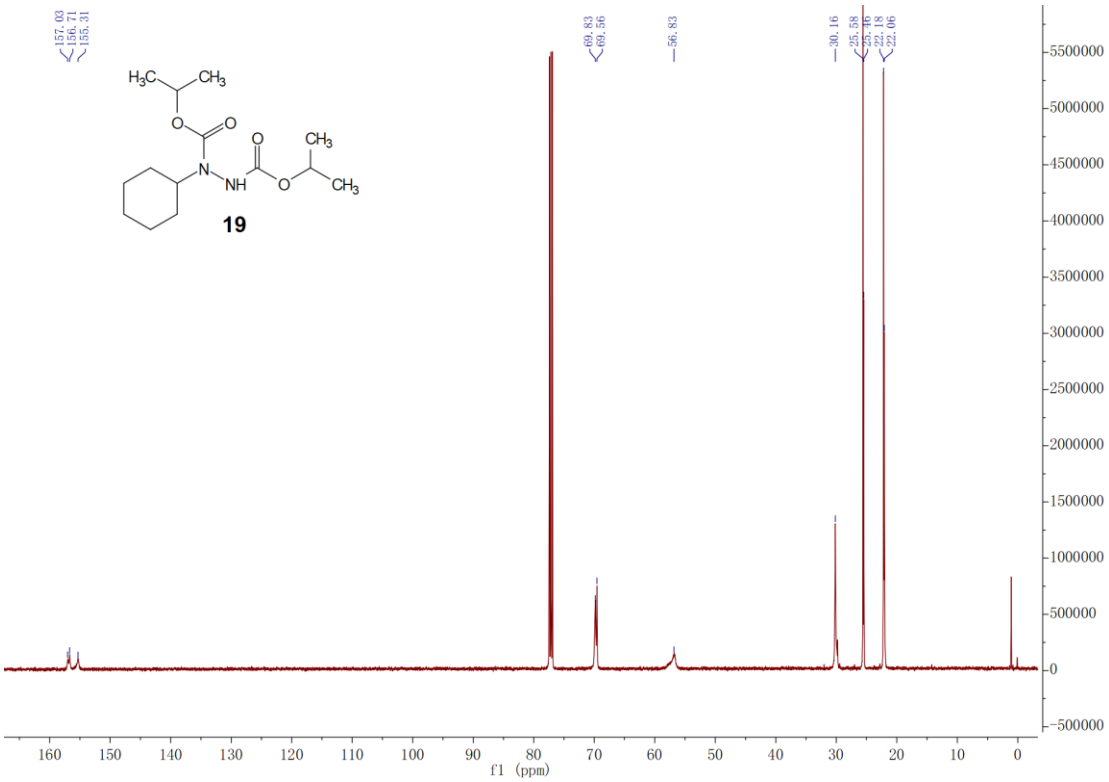

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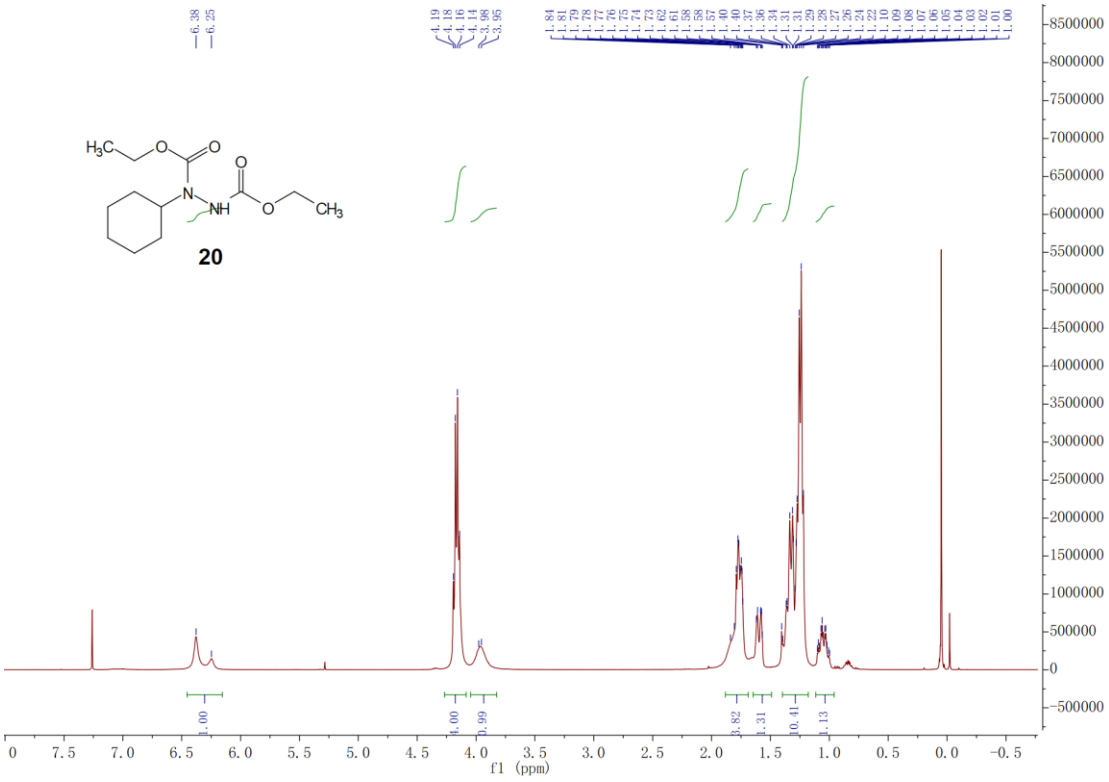

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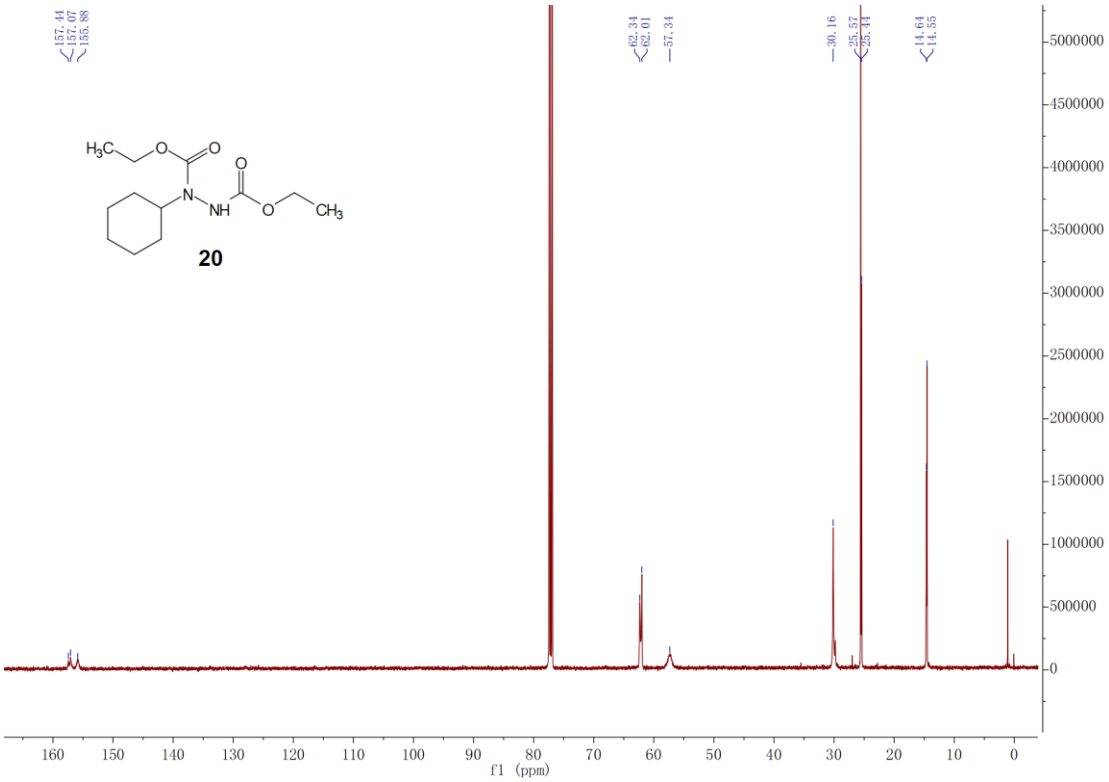

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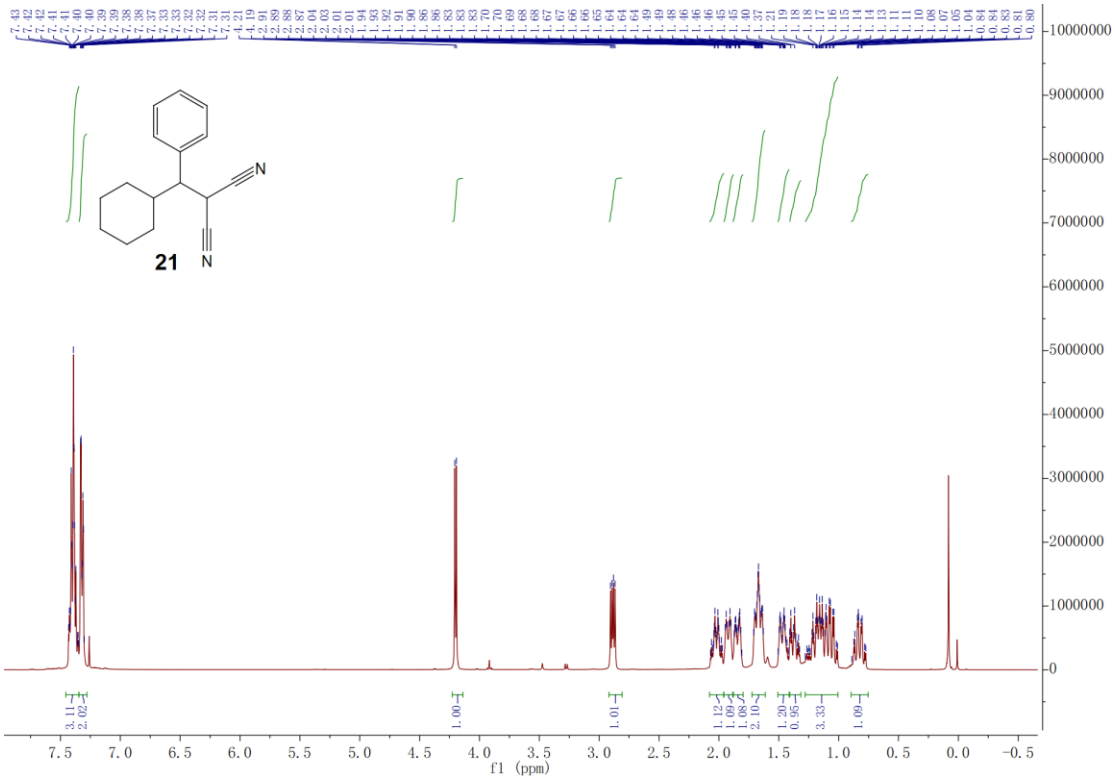

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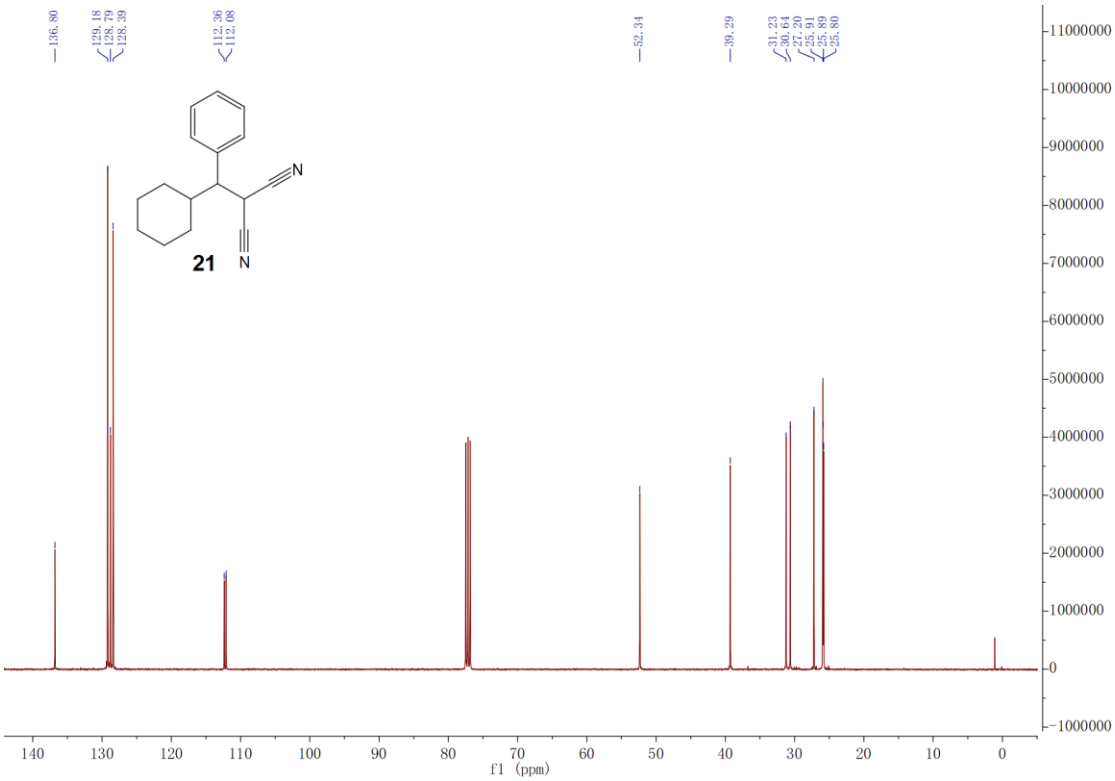

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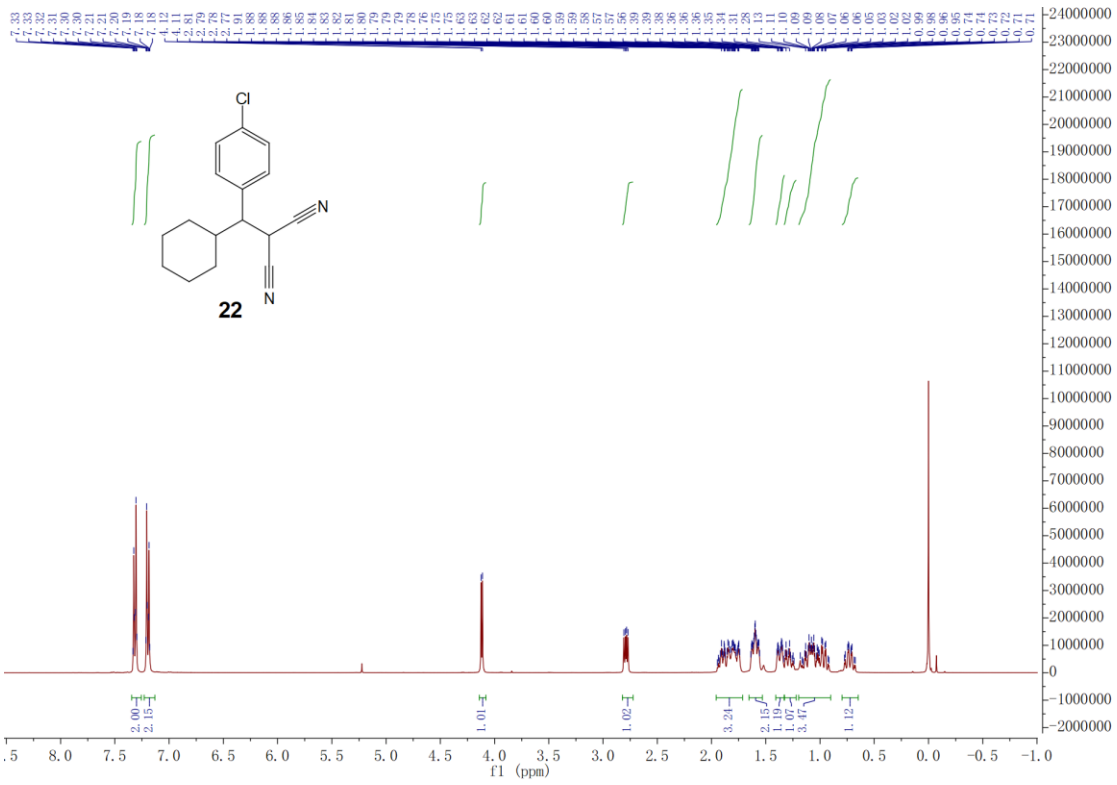

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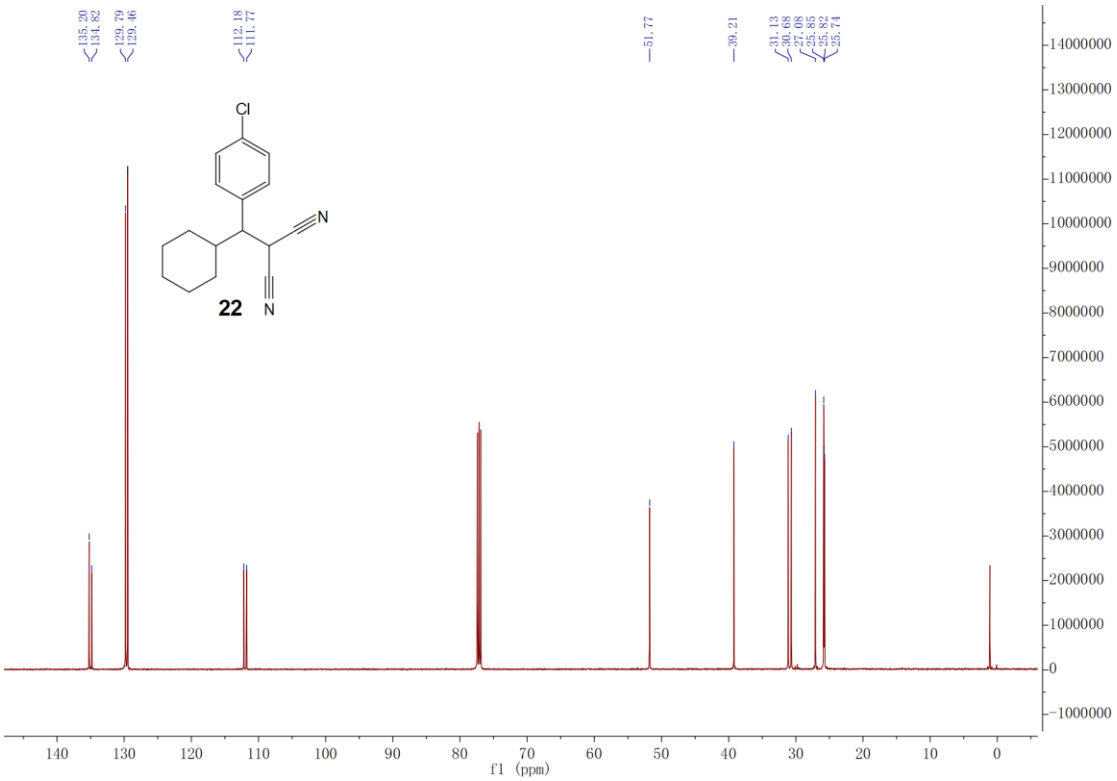

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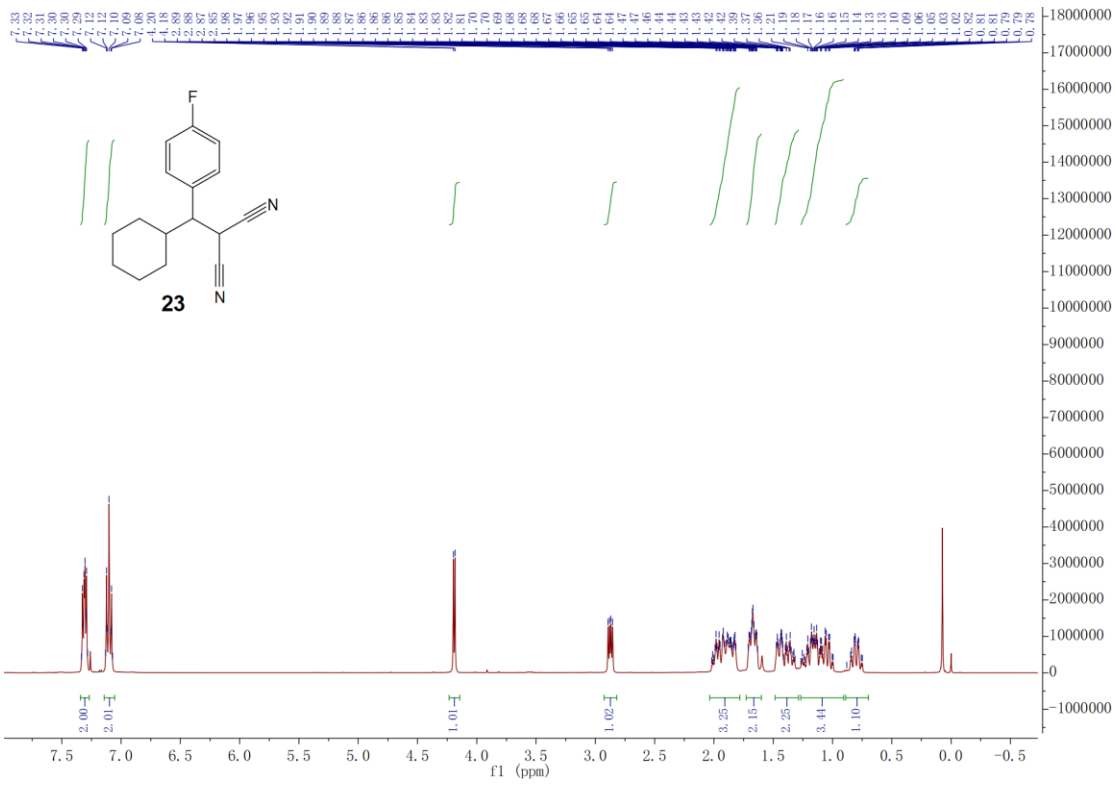

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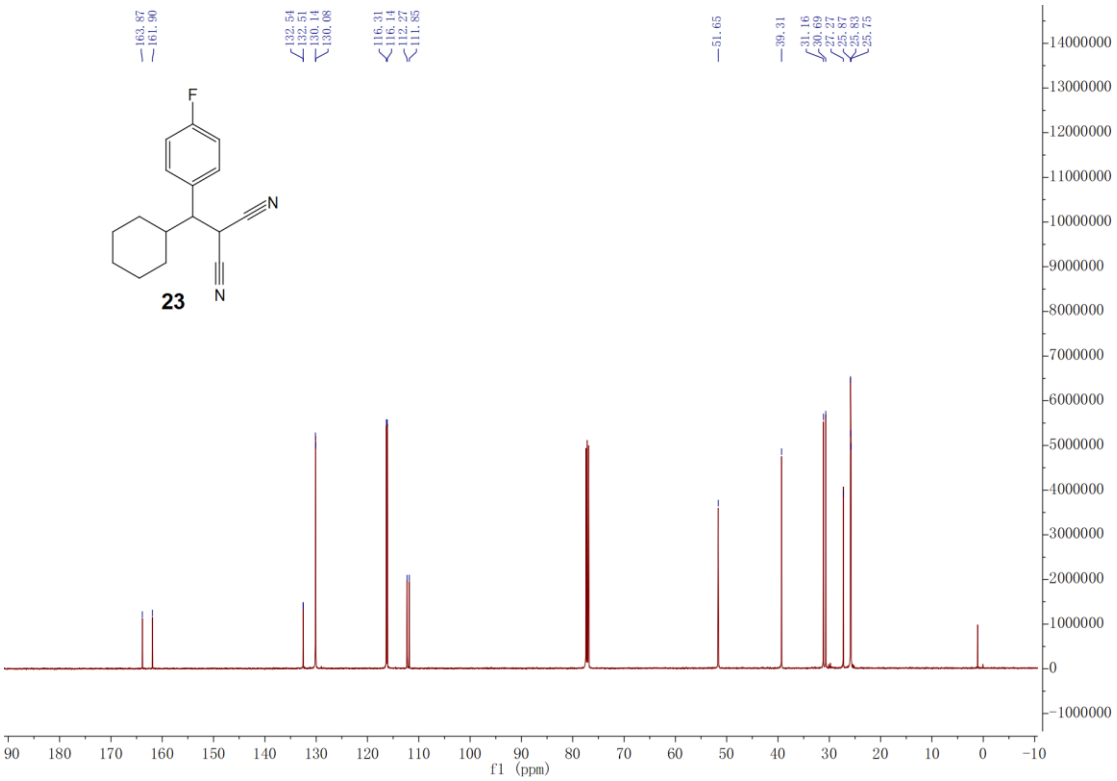

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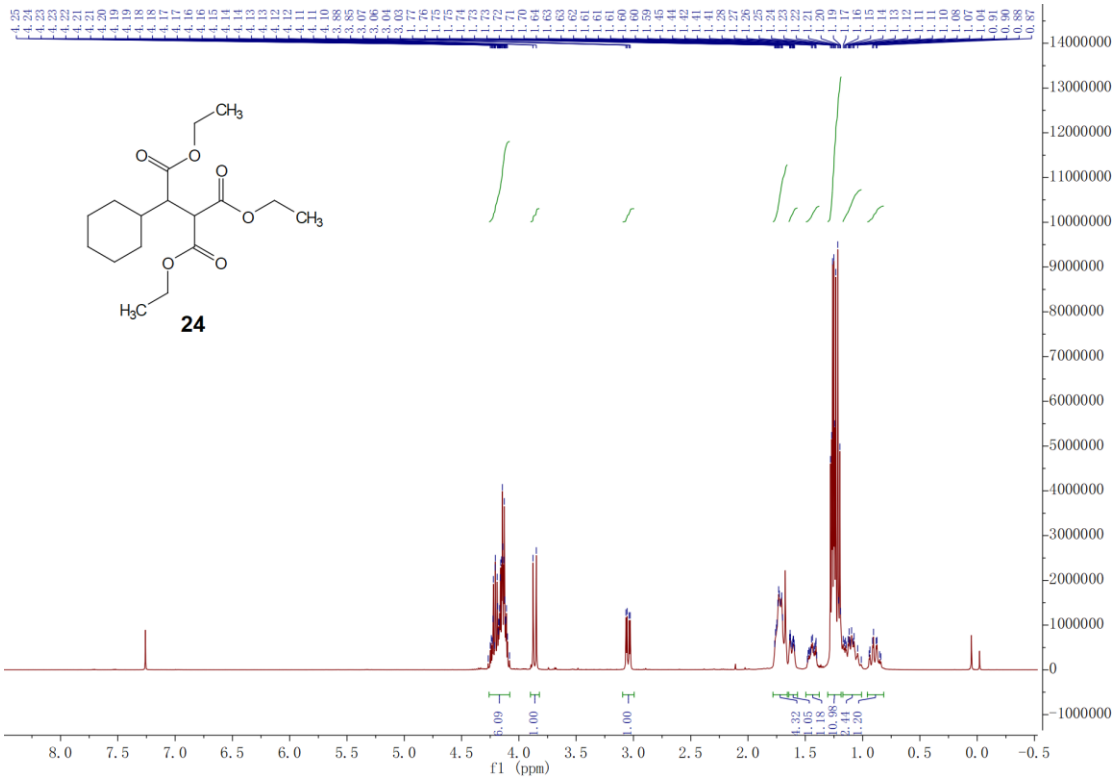

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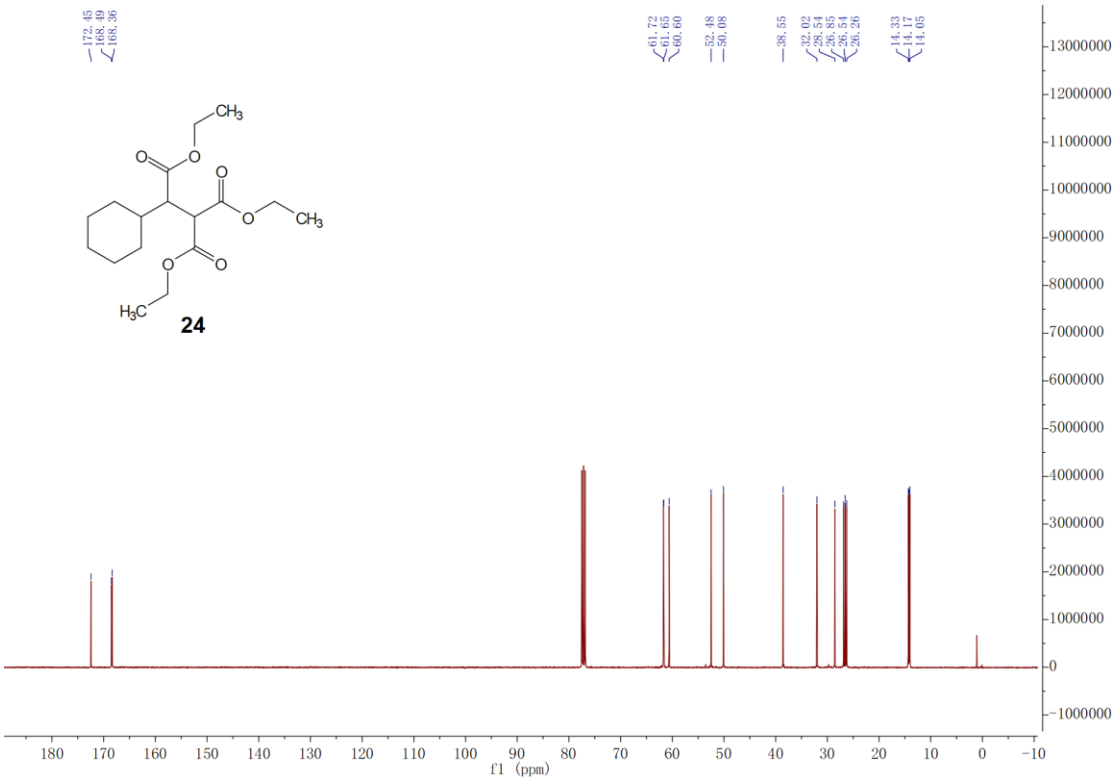

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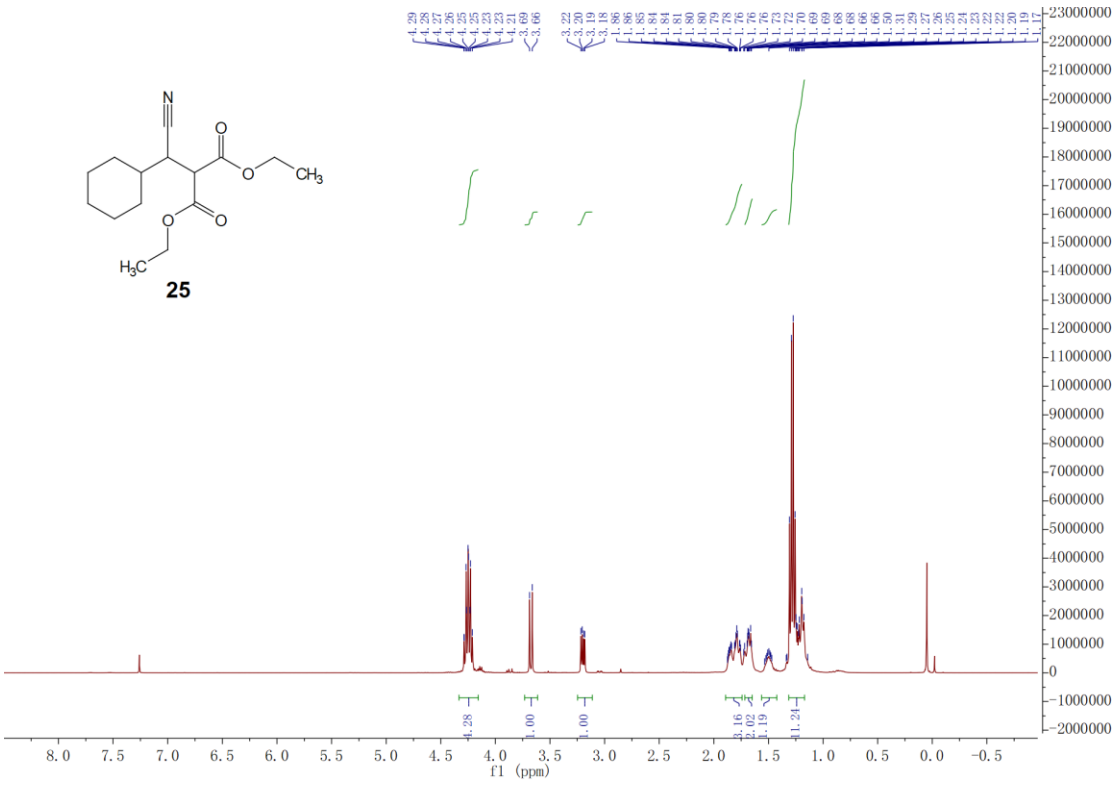

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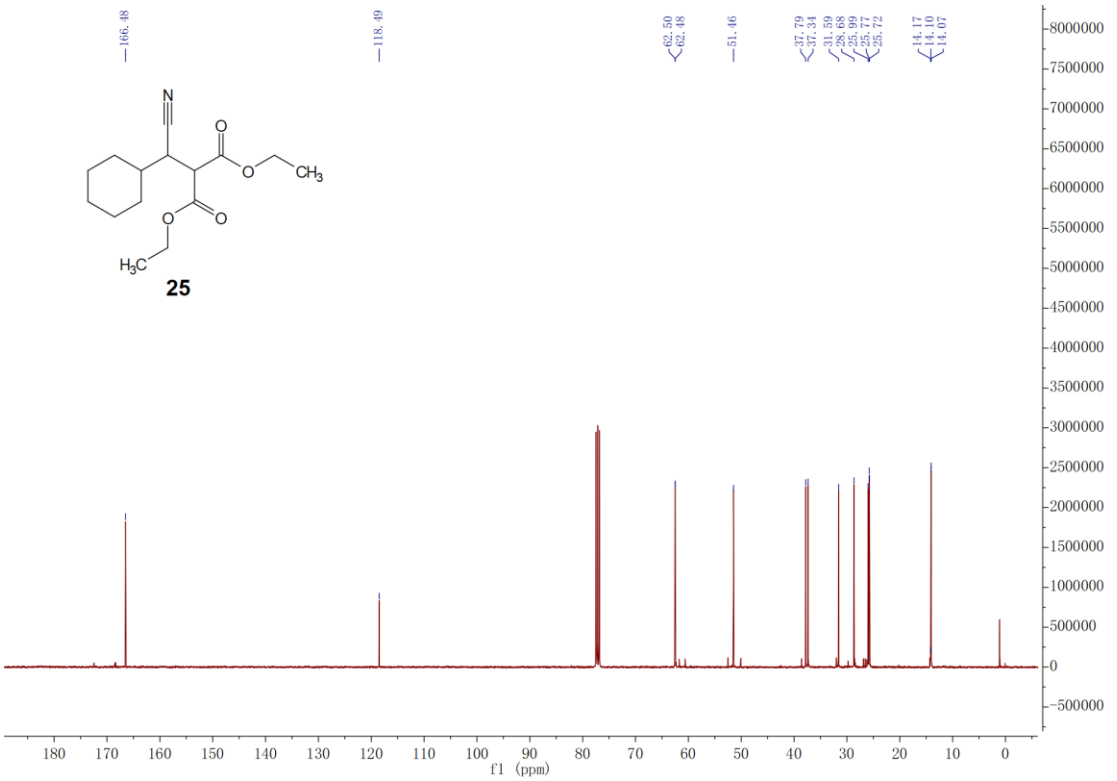

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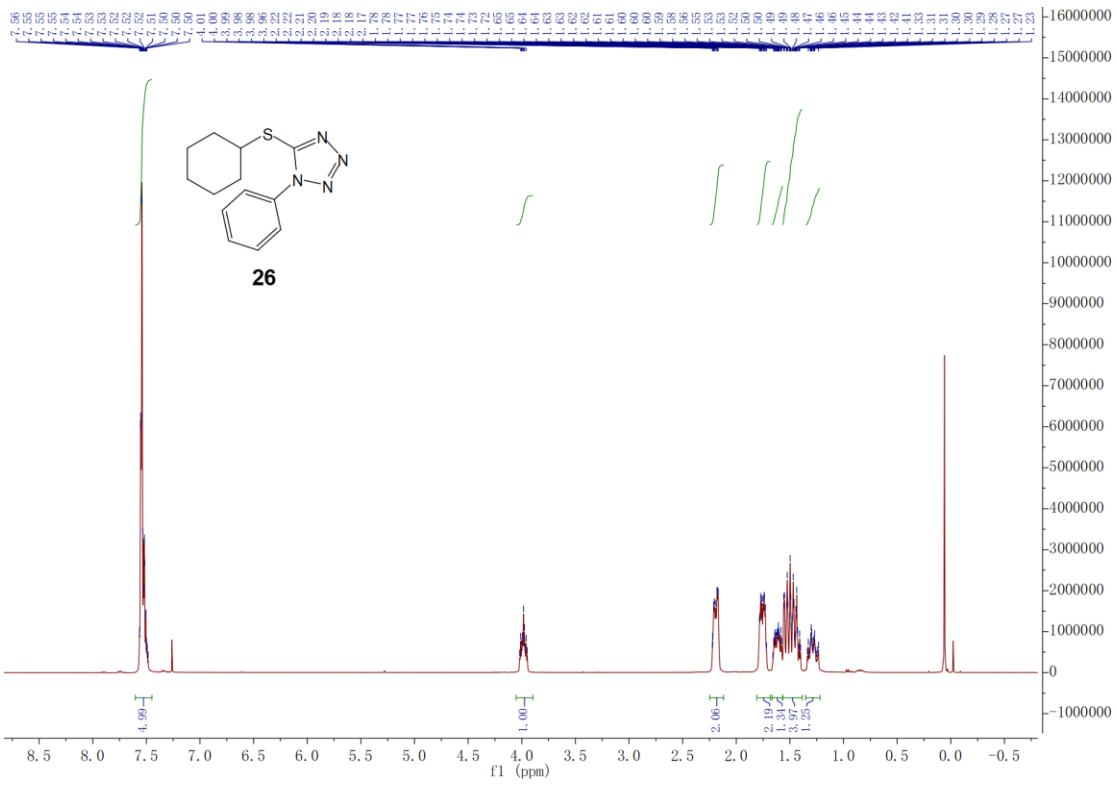

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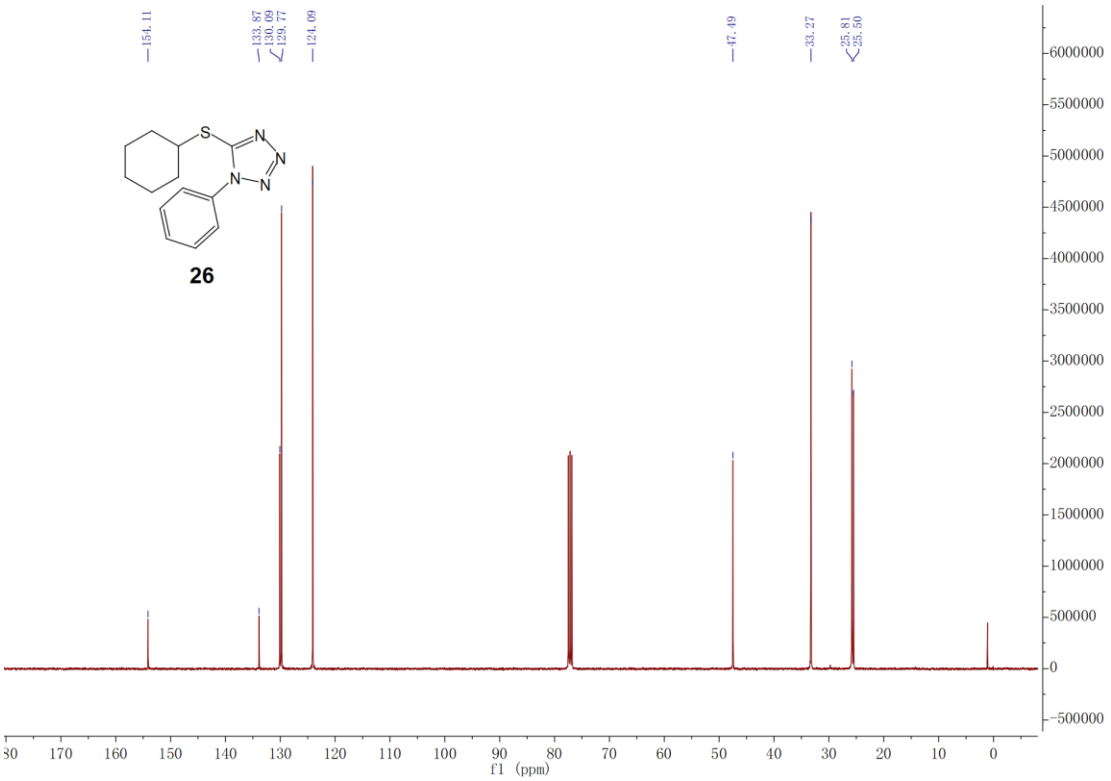

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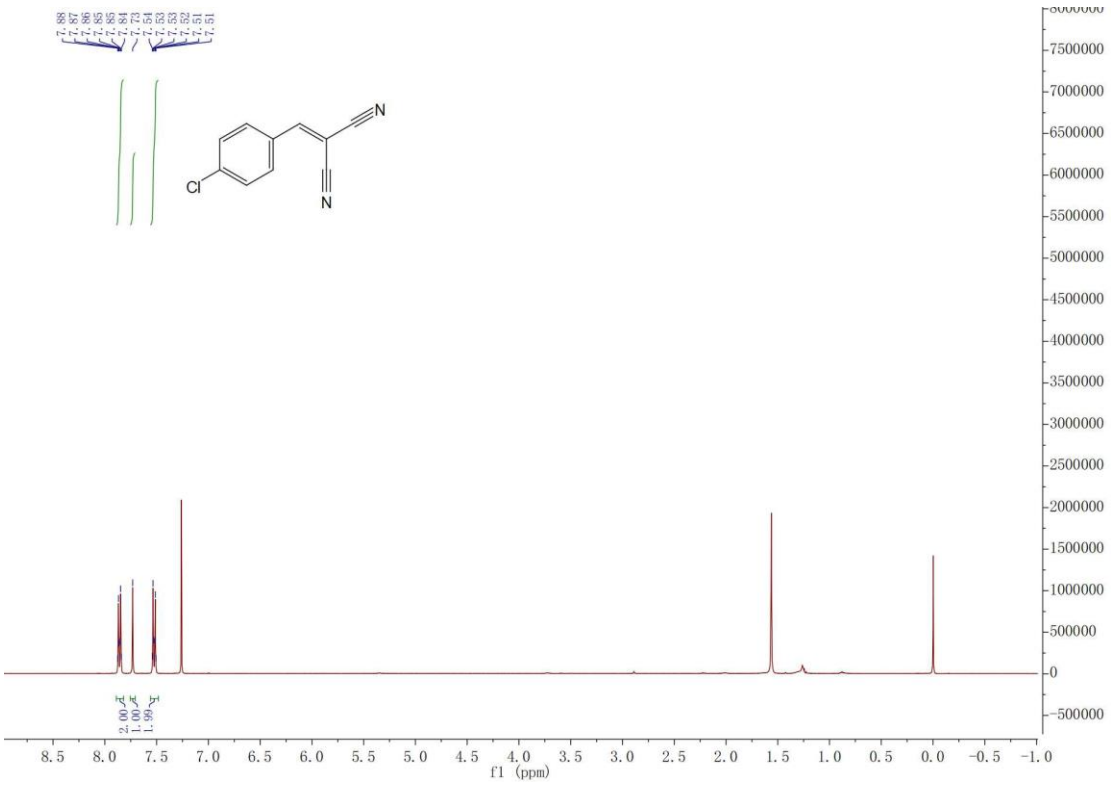

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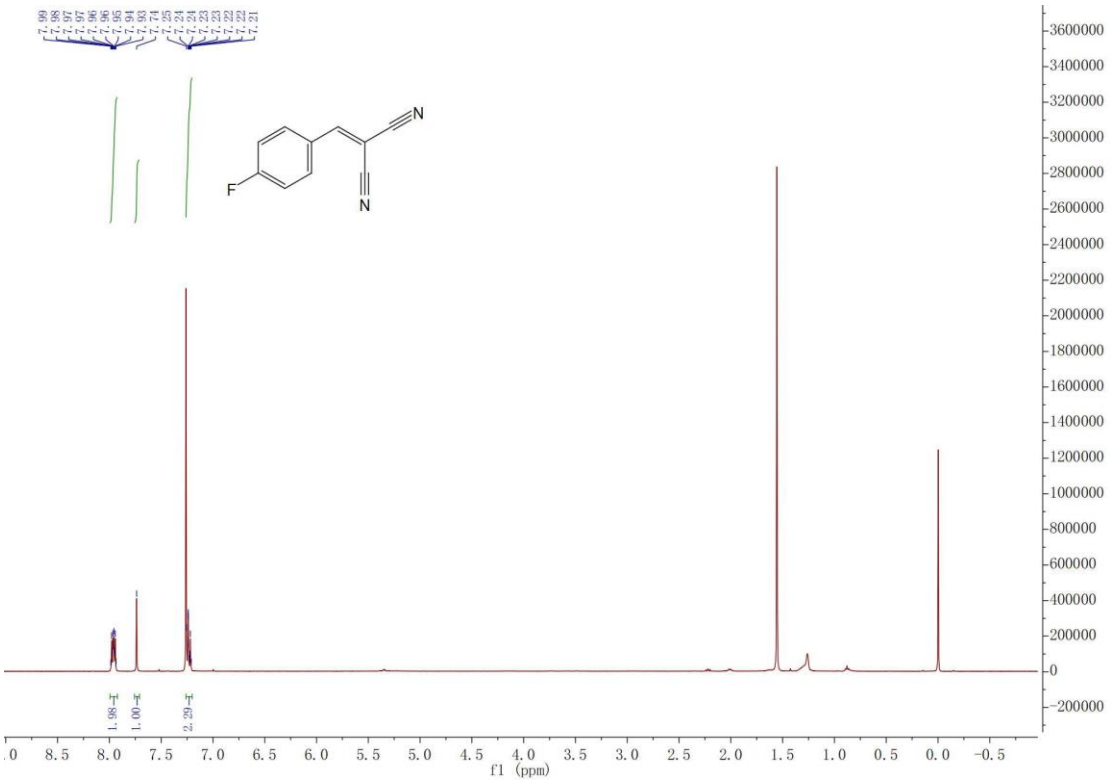

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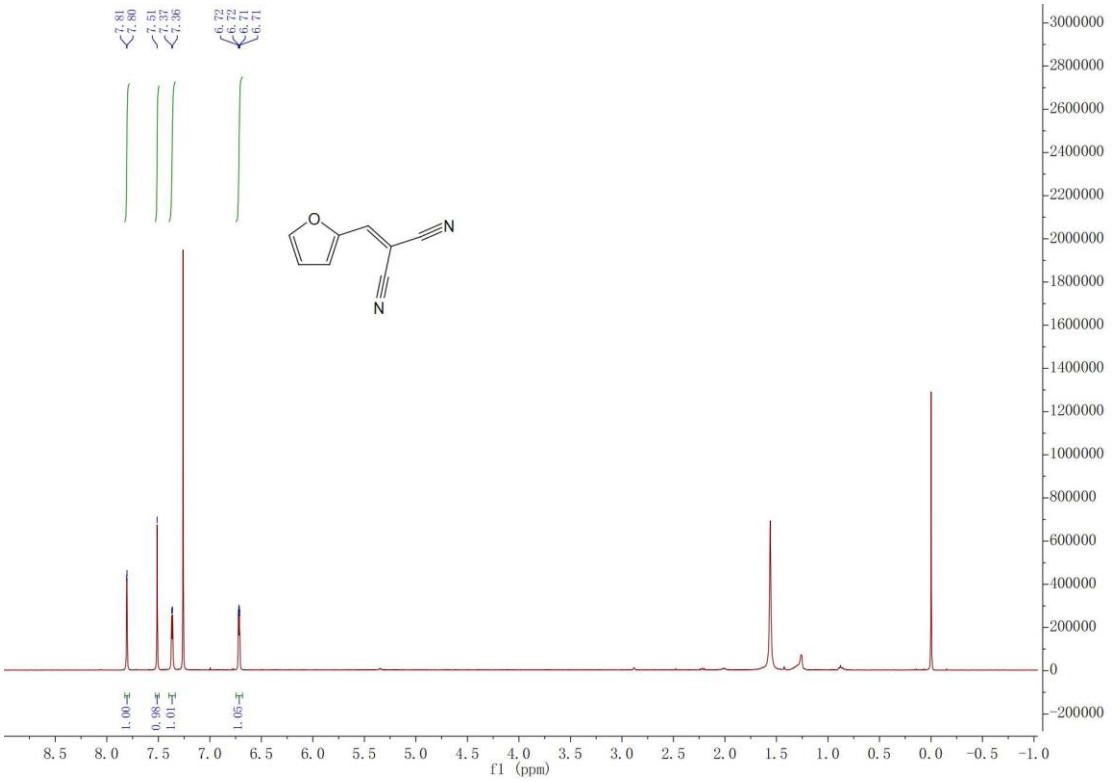

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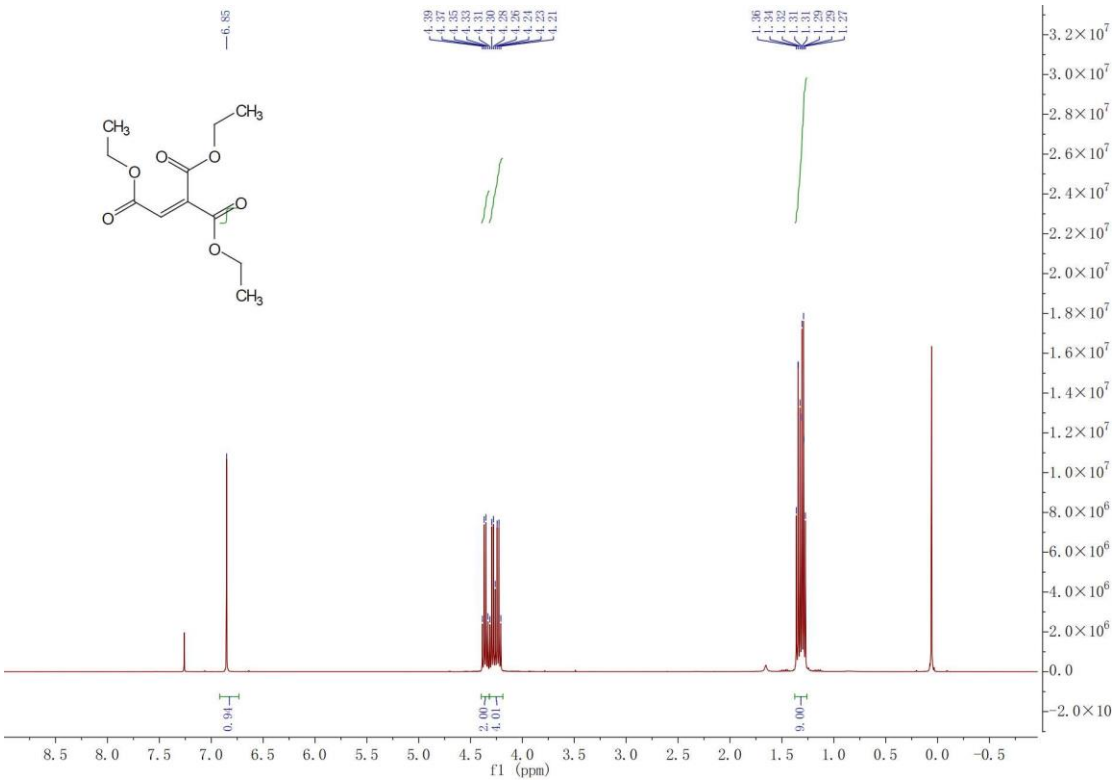

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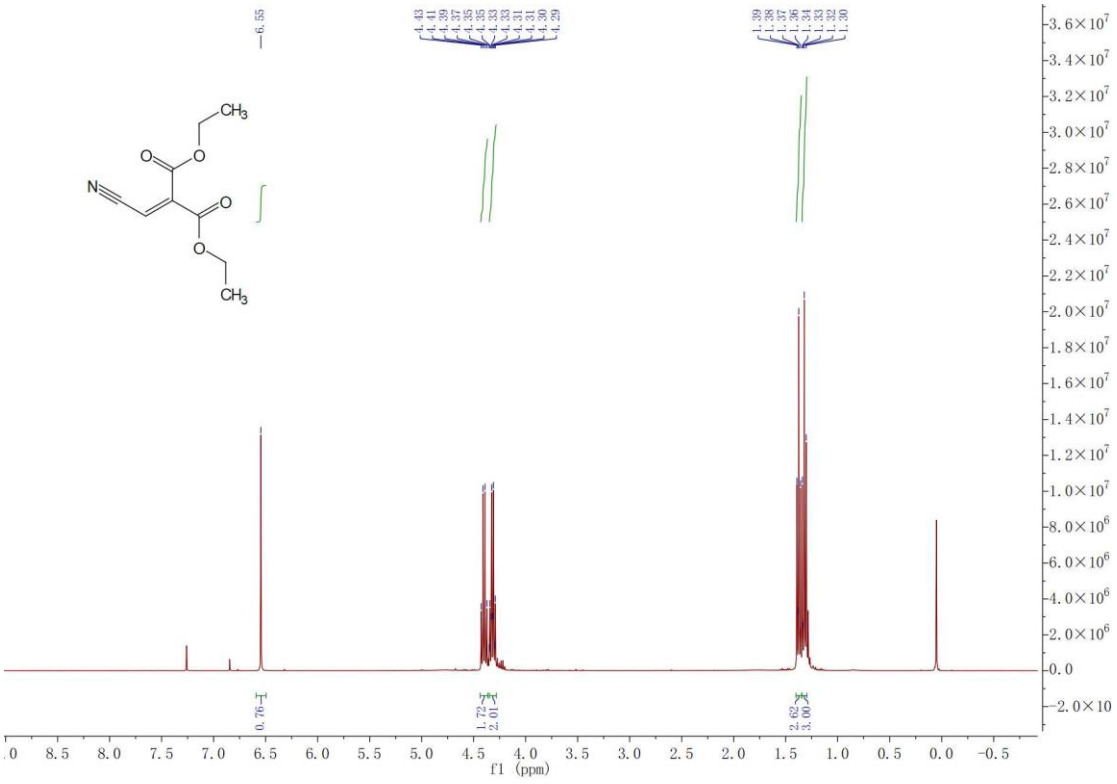

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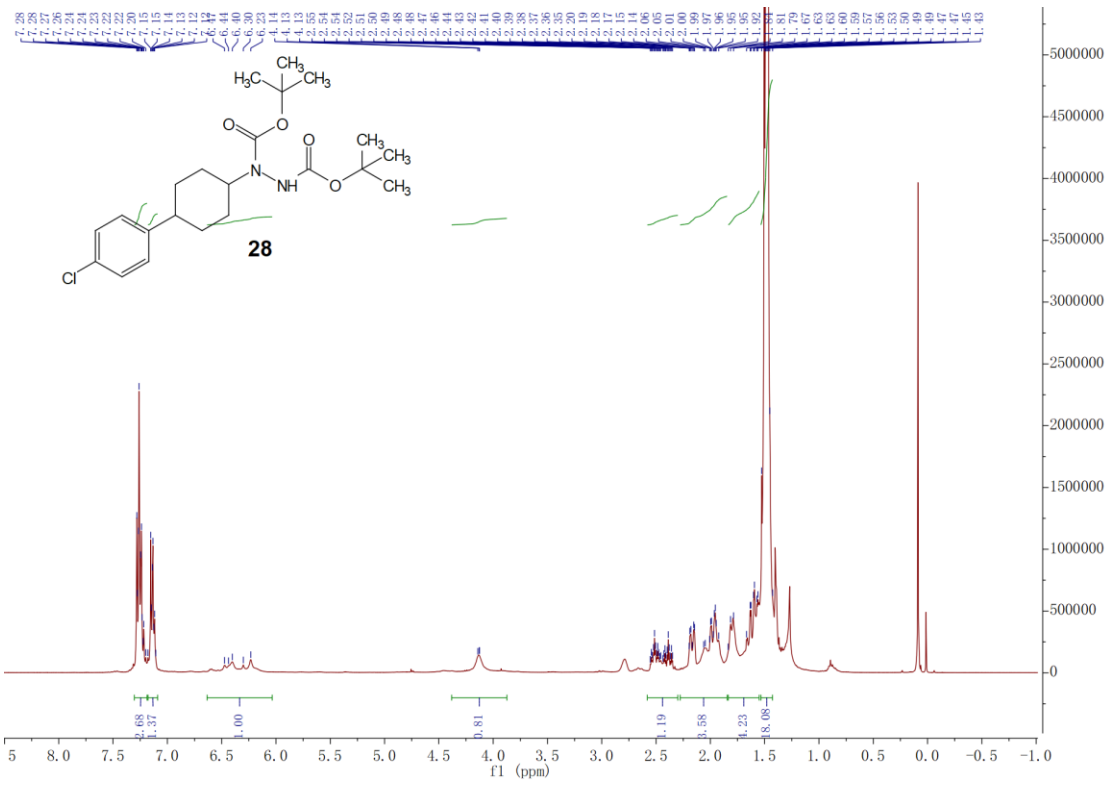

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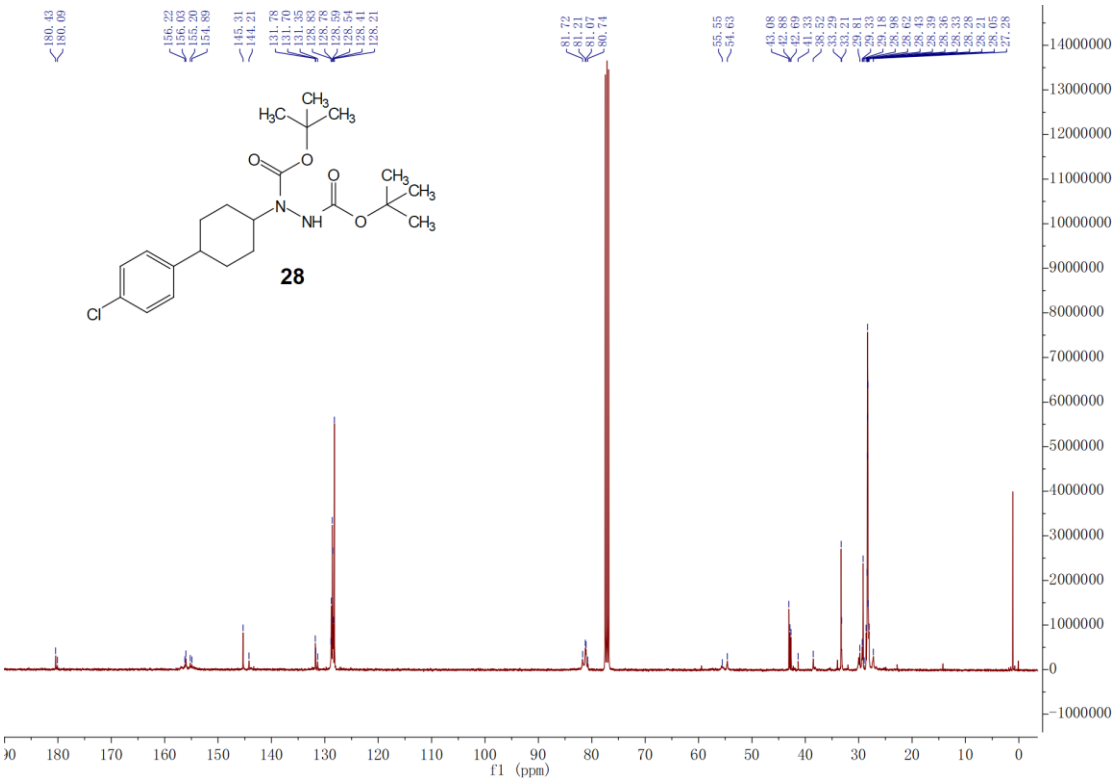

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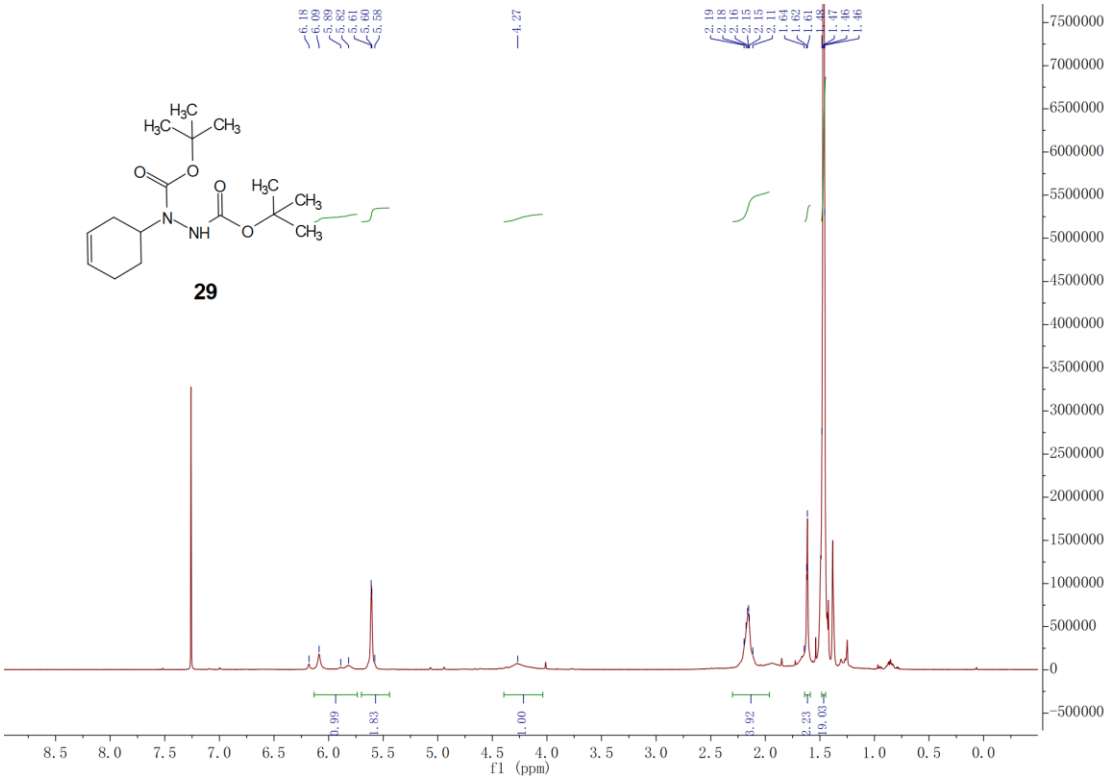

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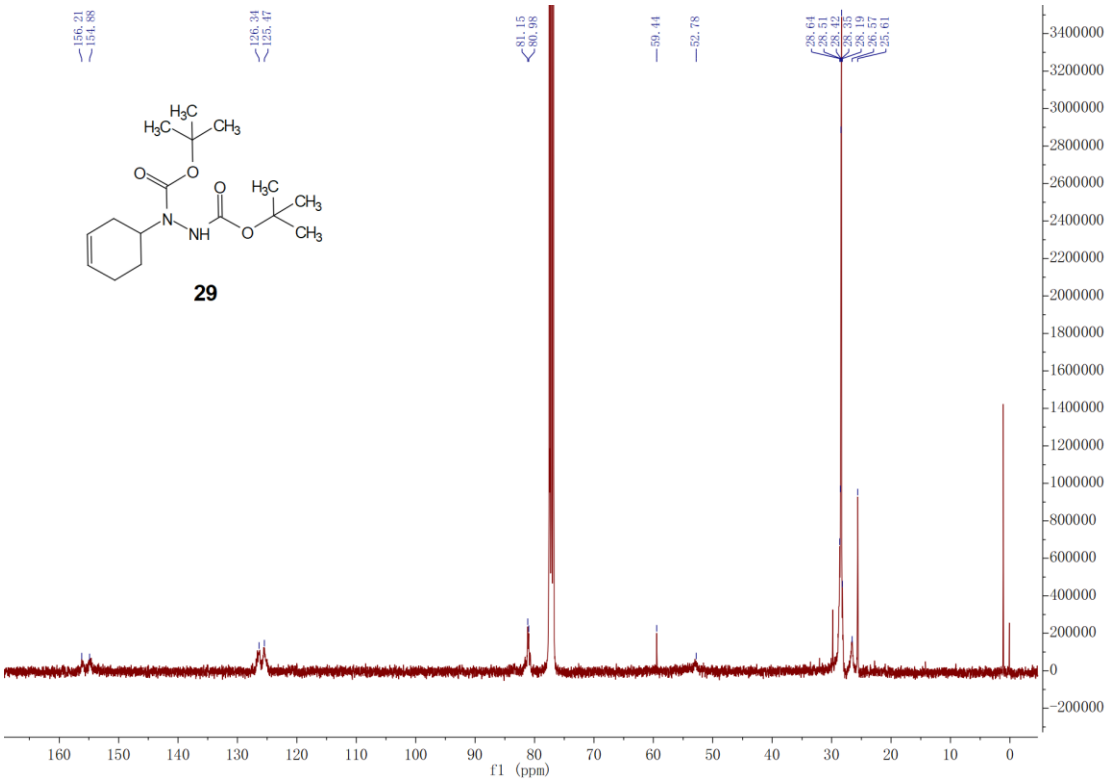

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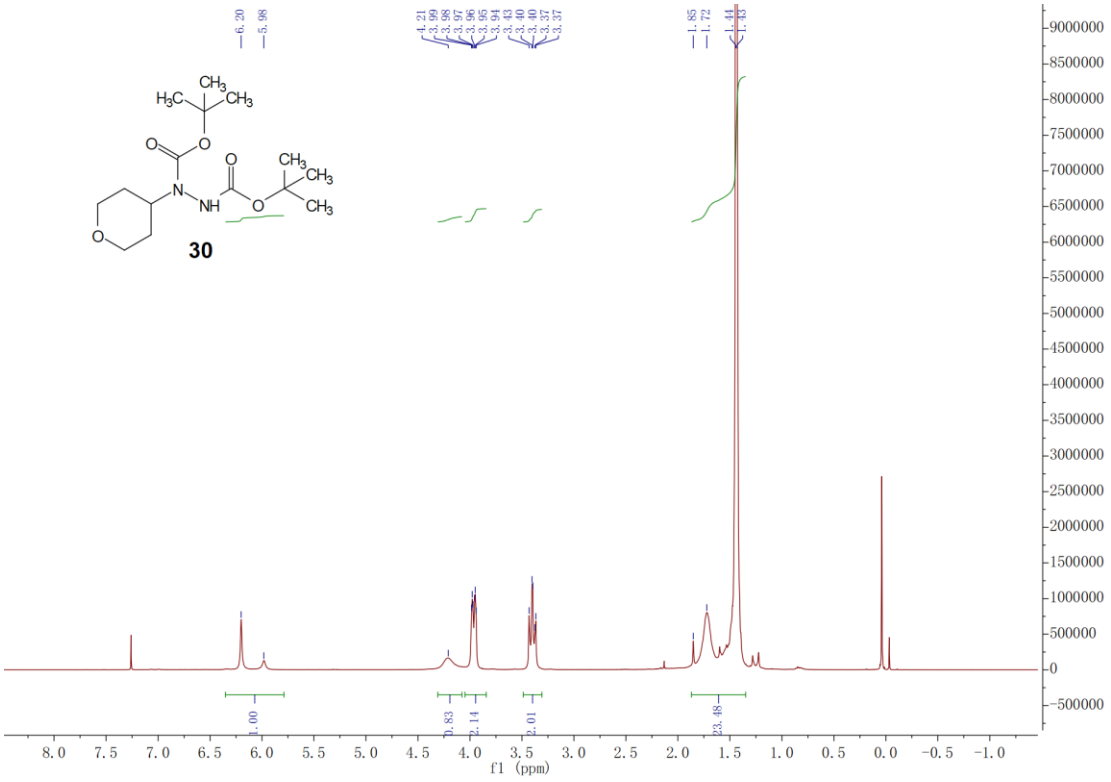

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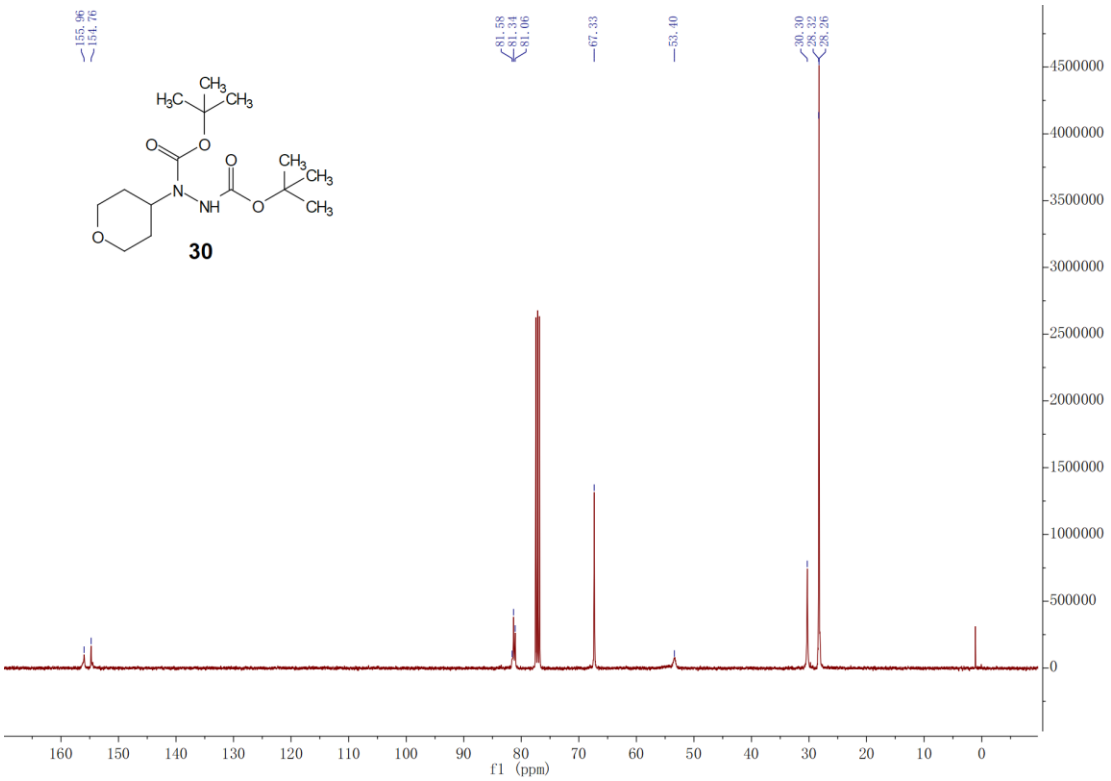

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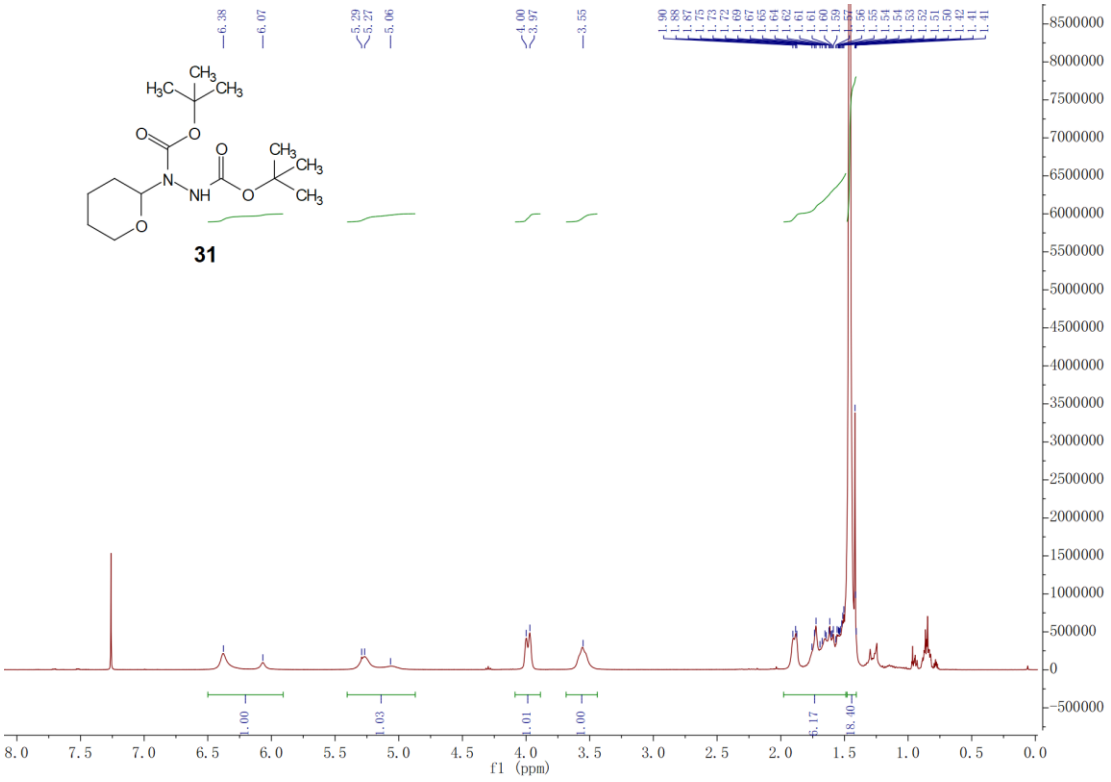

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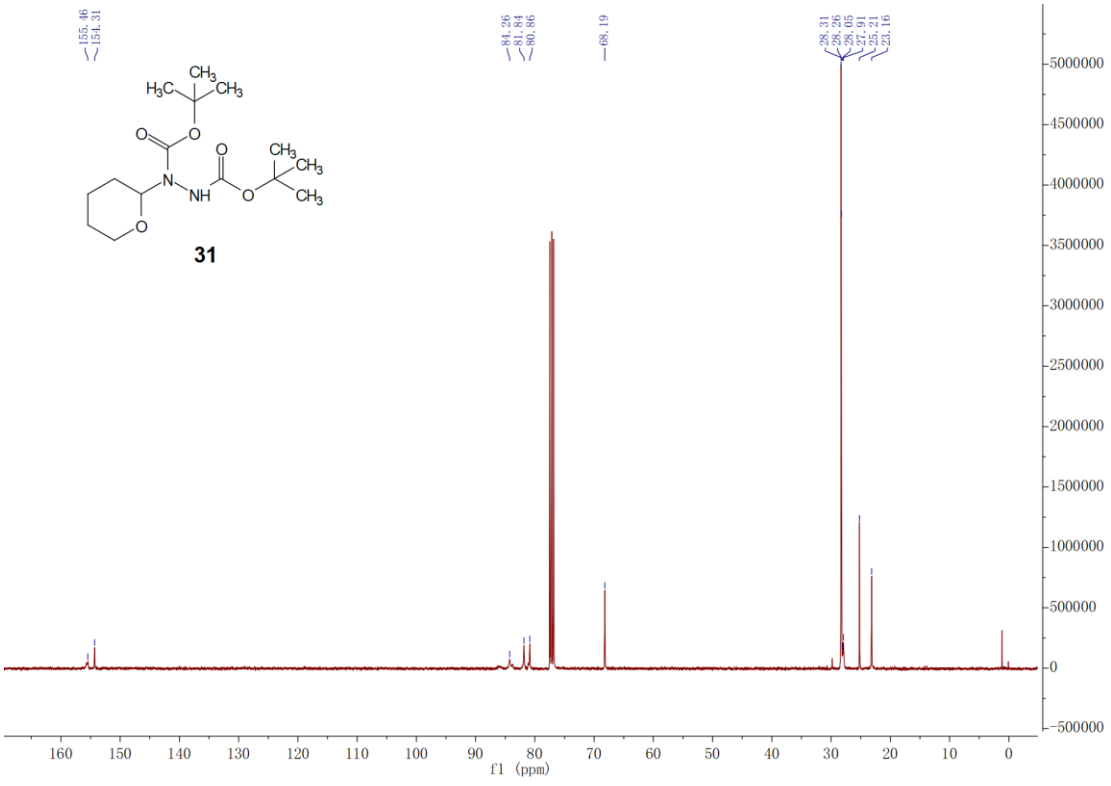

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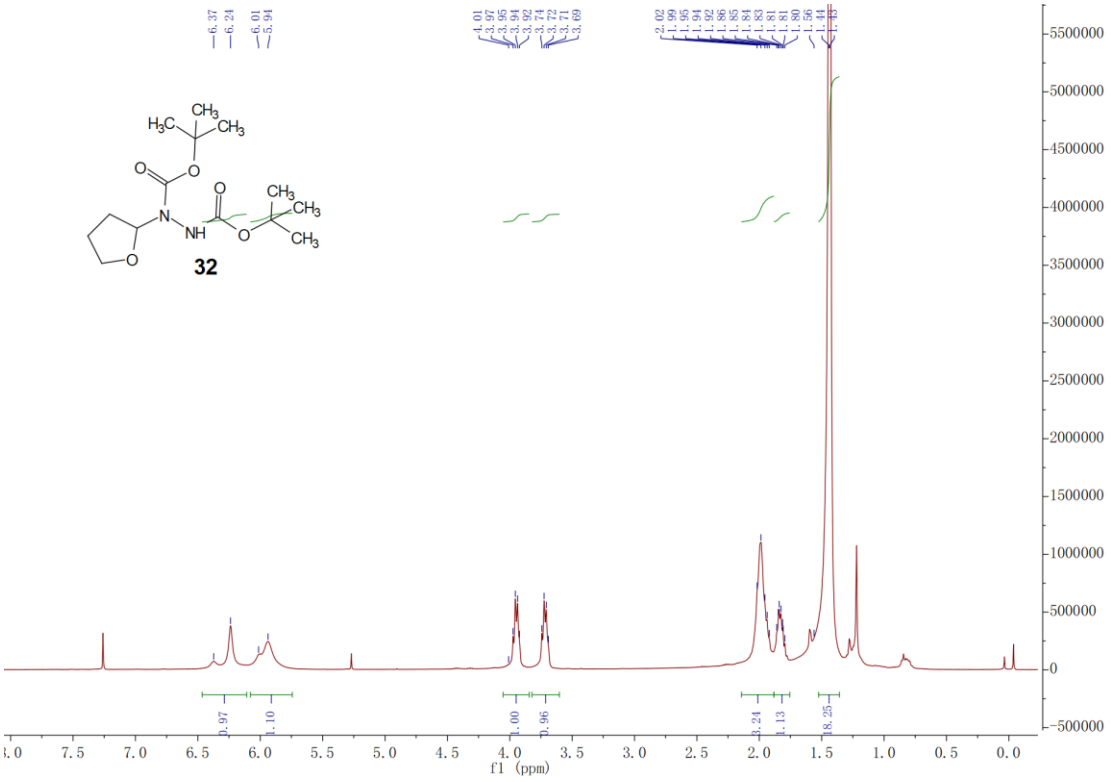

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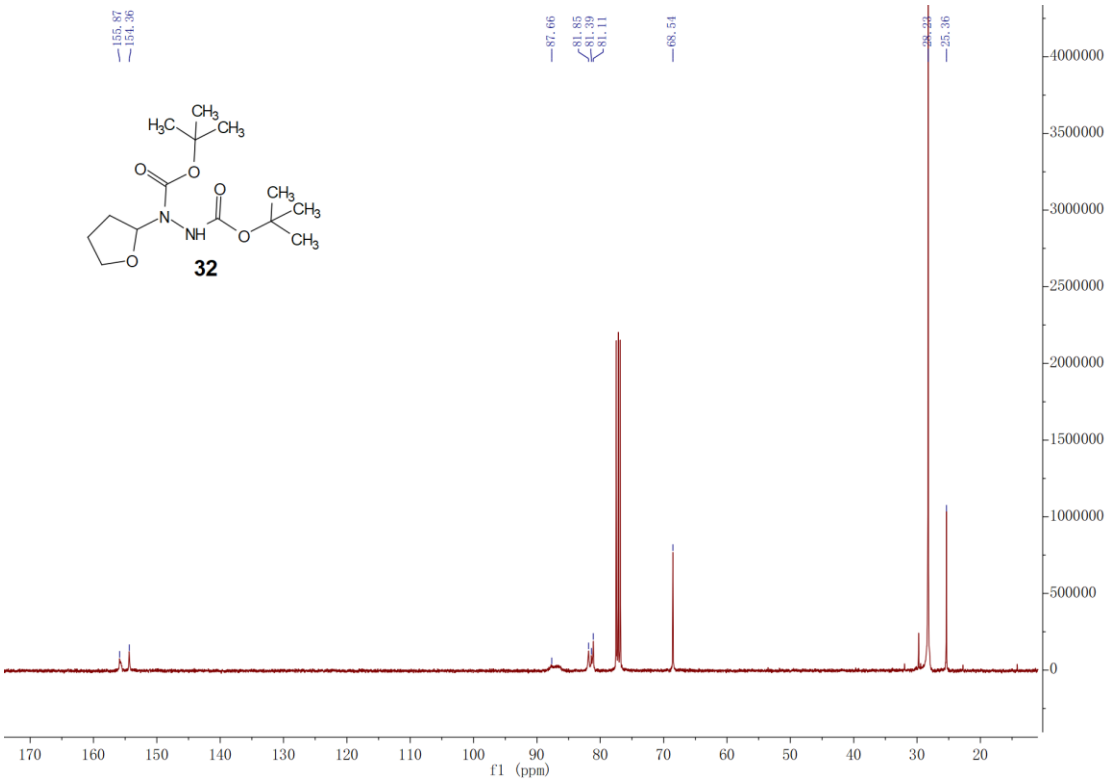

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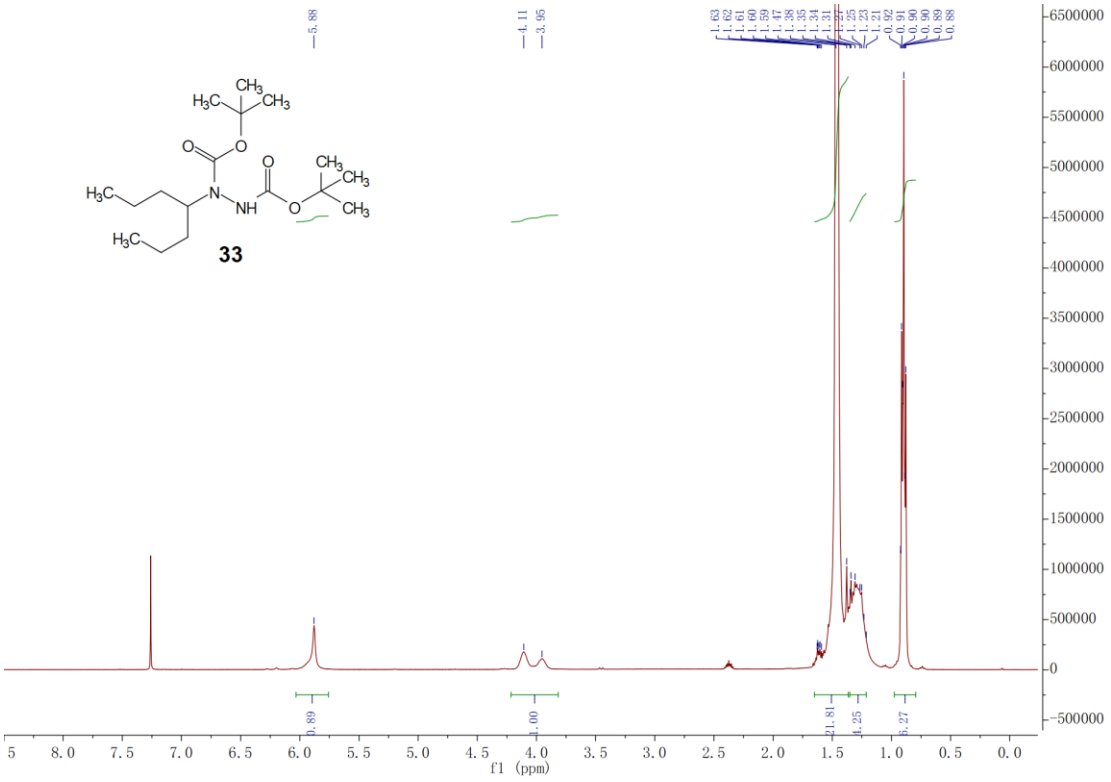

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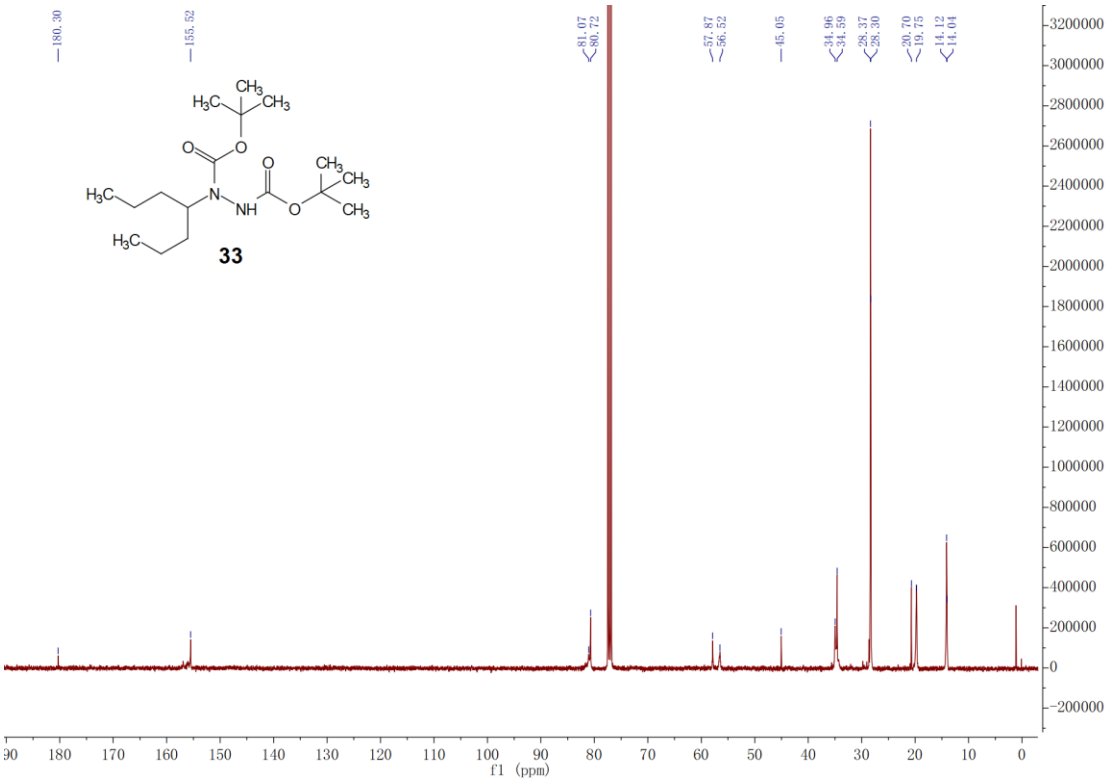

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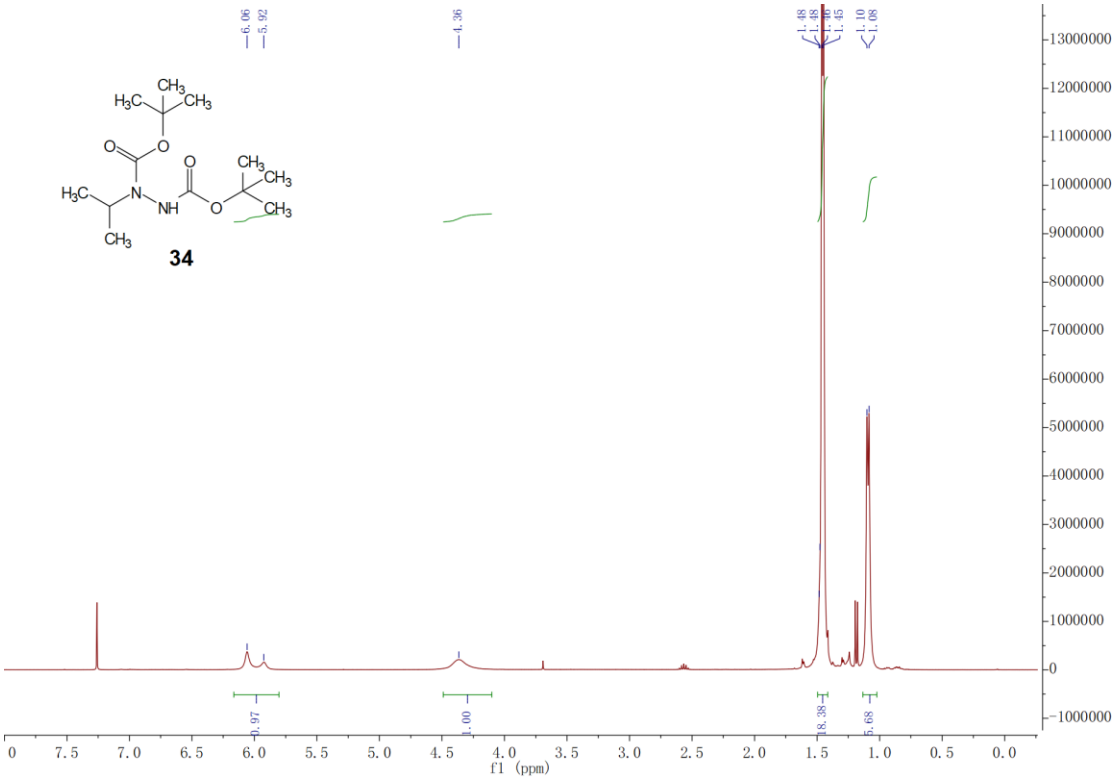

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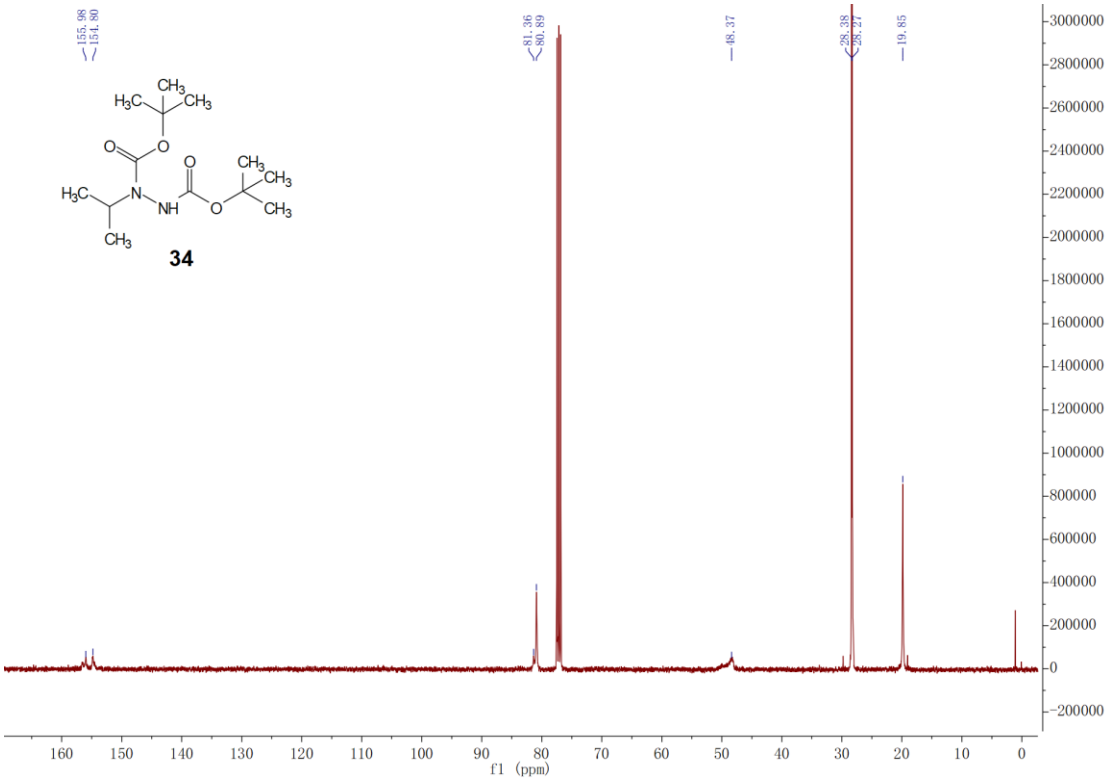

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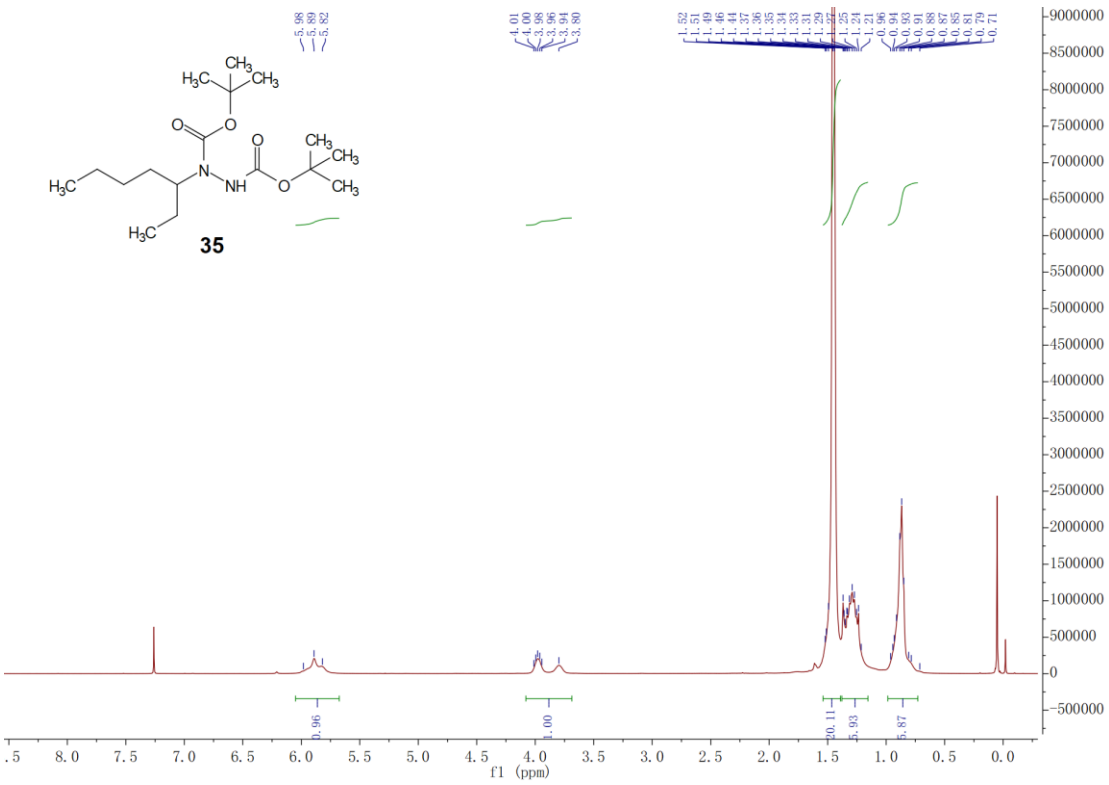
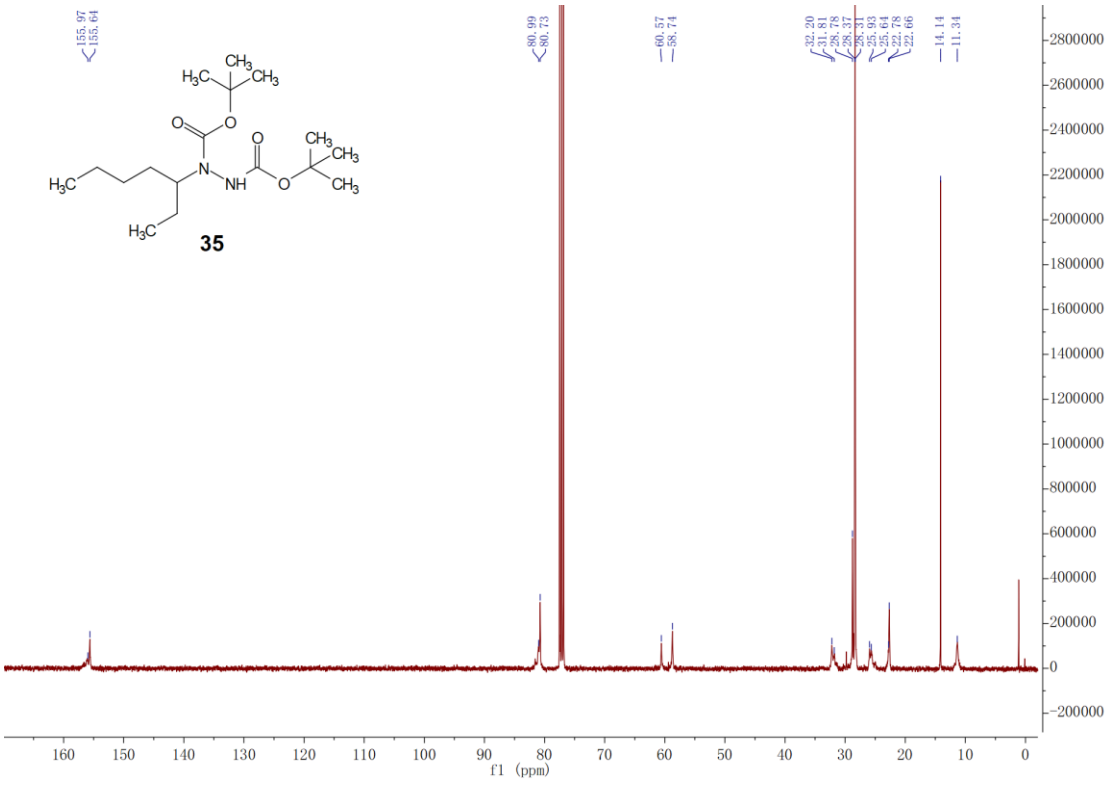


^{13}C NMR (101 MHz, $CDCl_3$)



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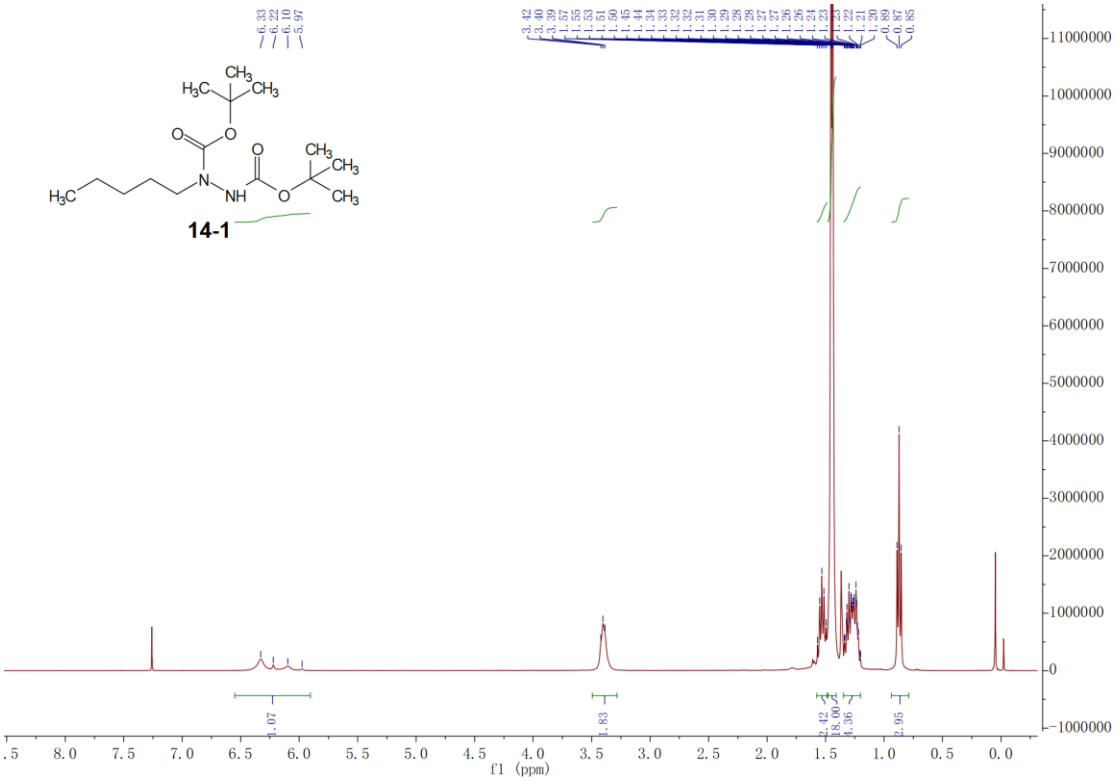

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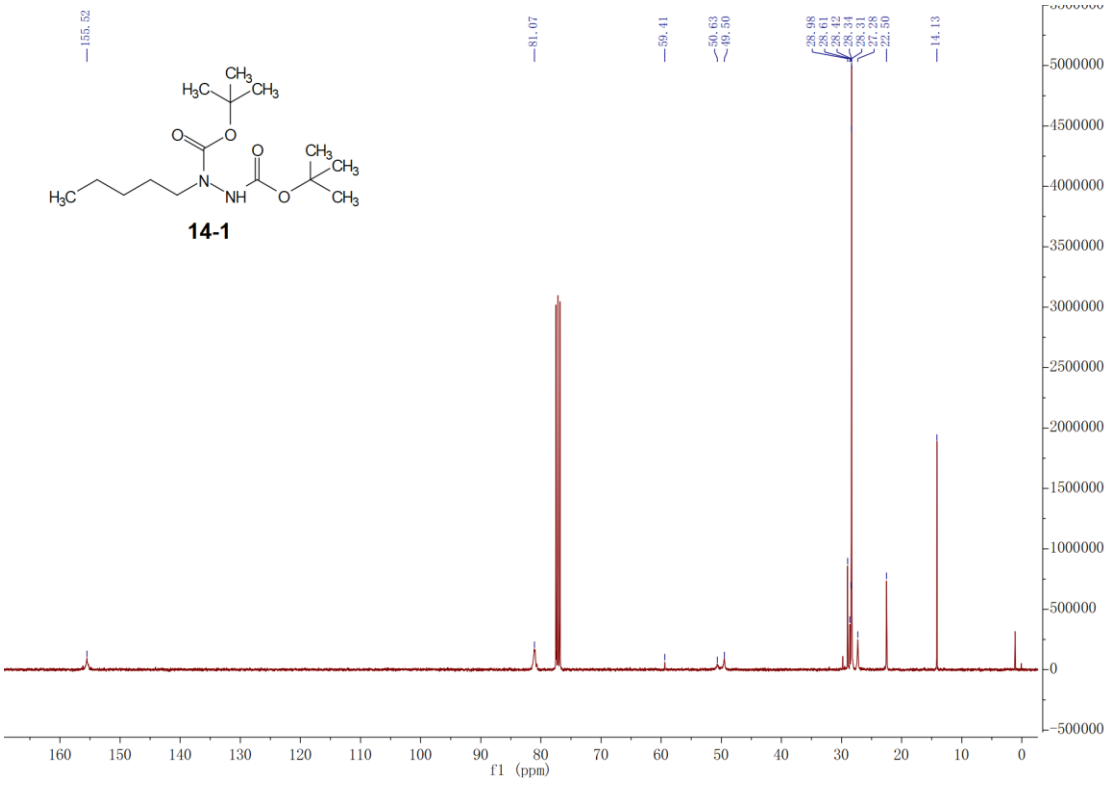

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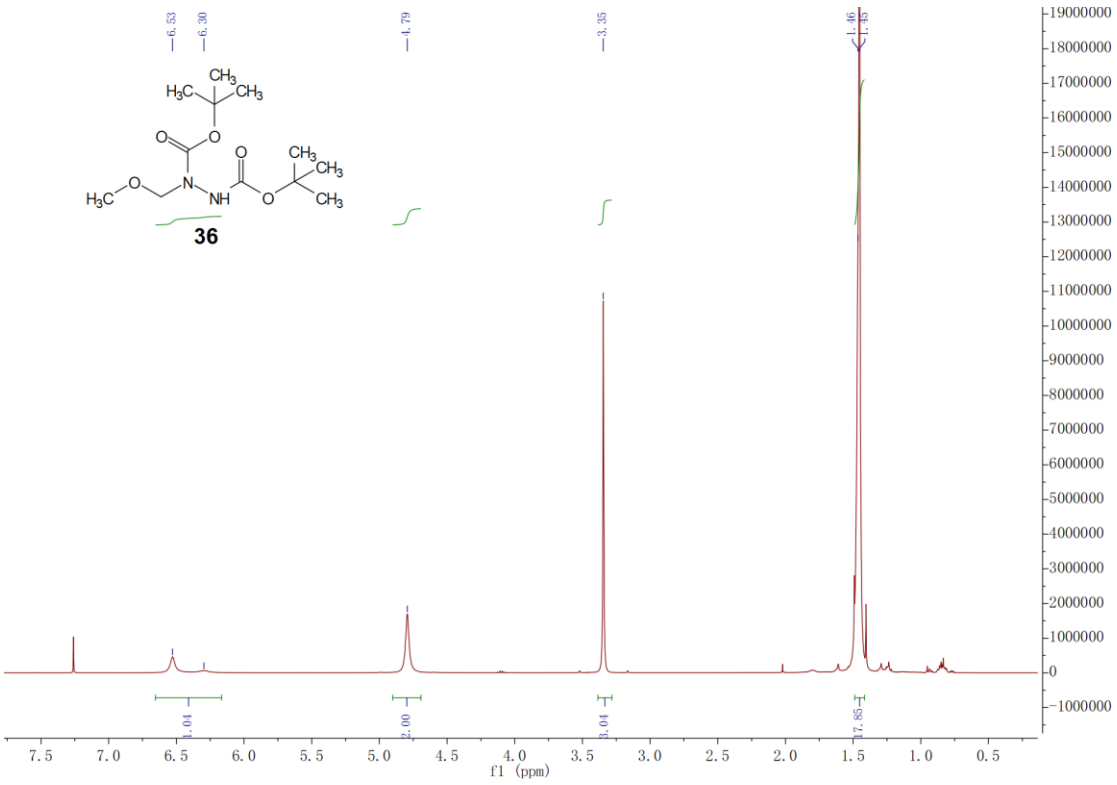

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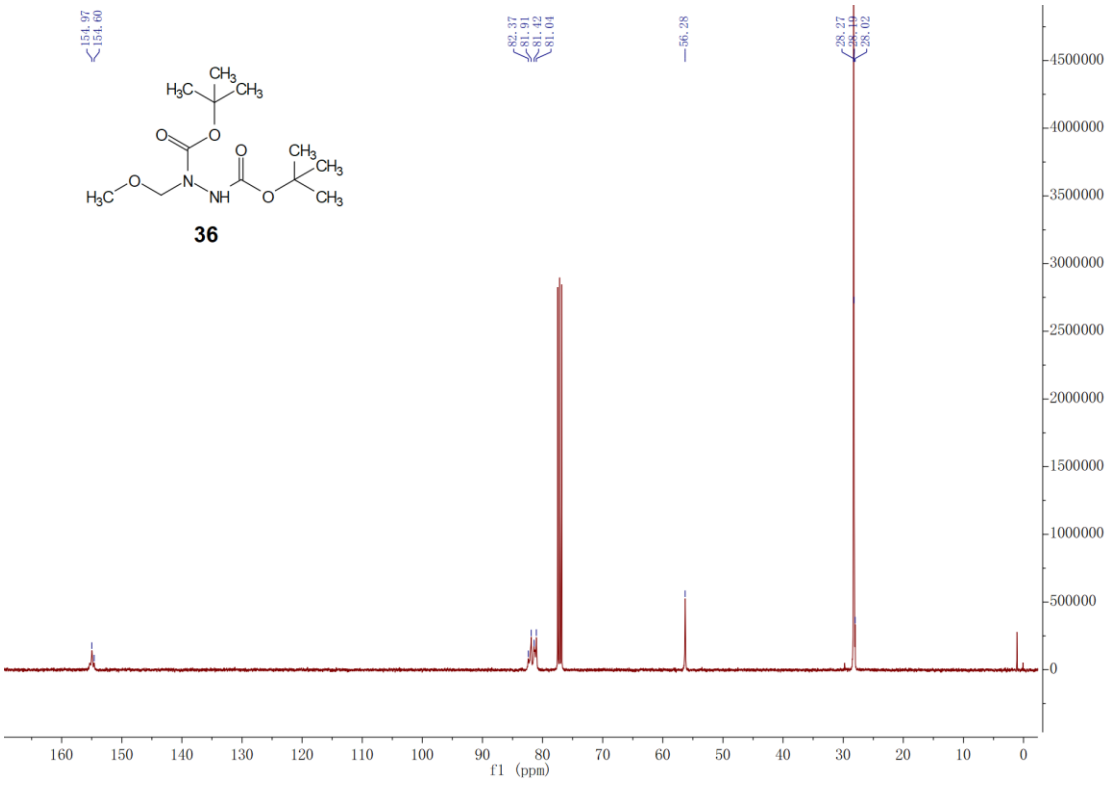
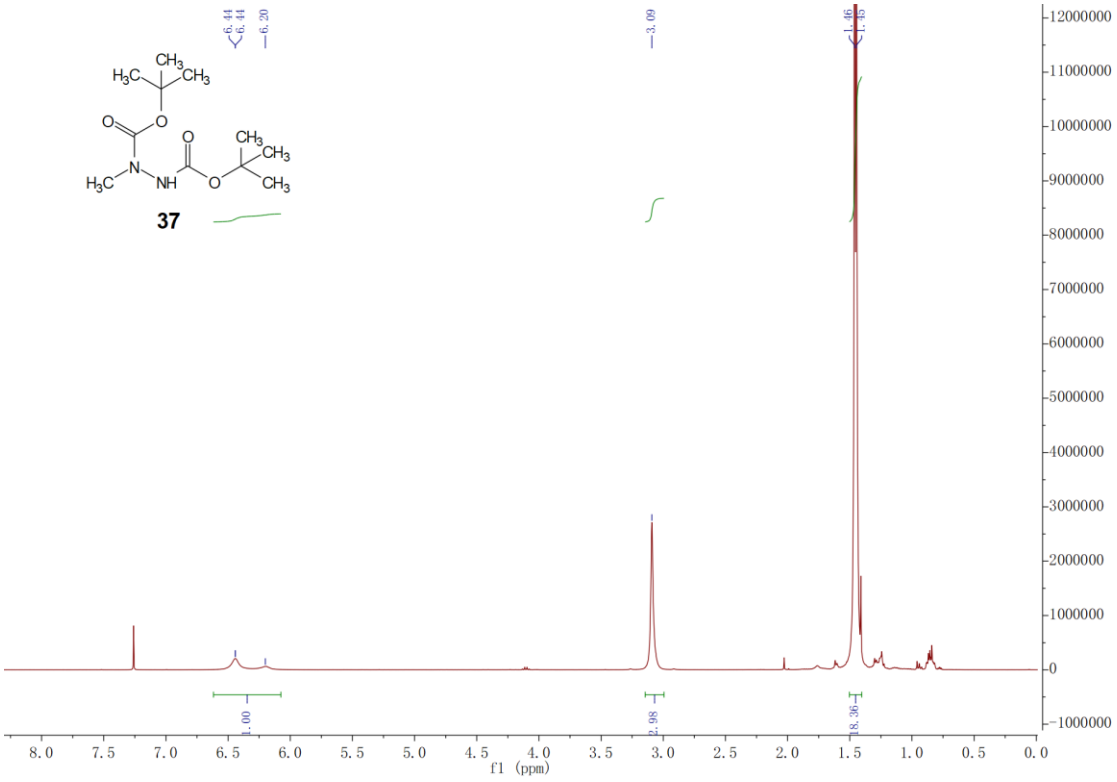
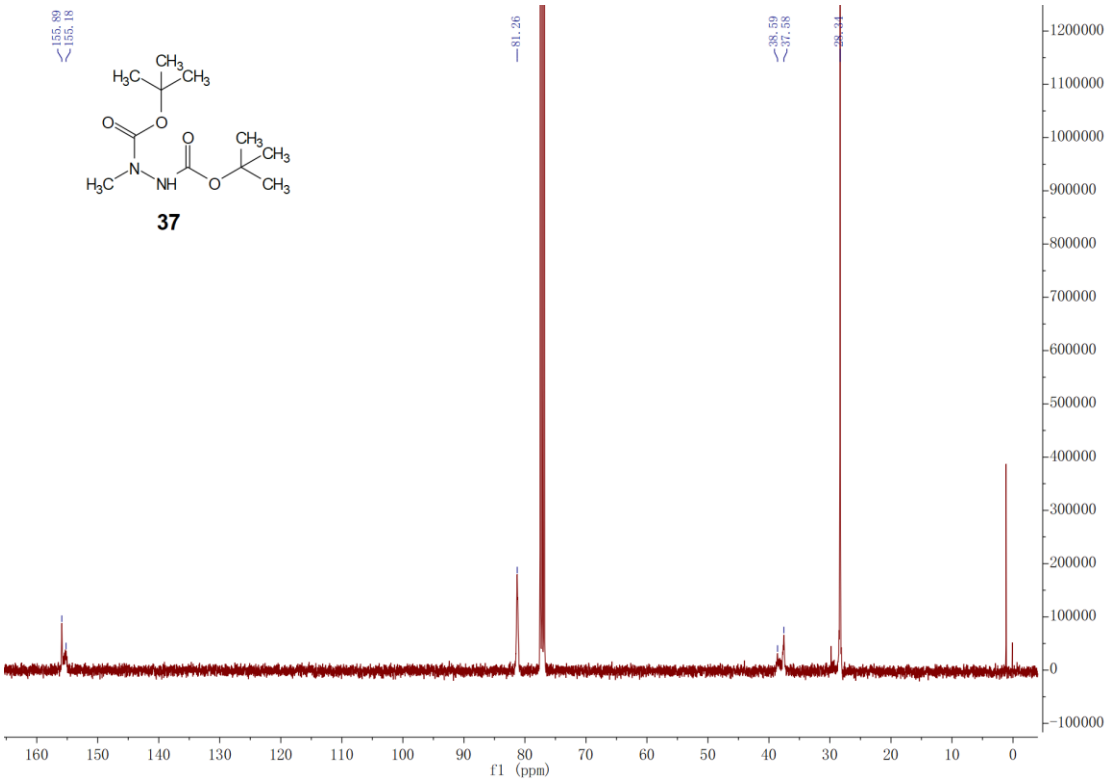


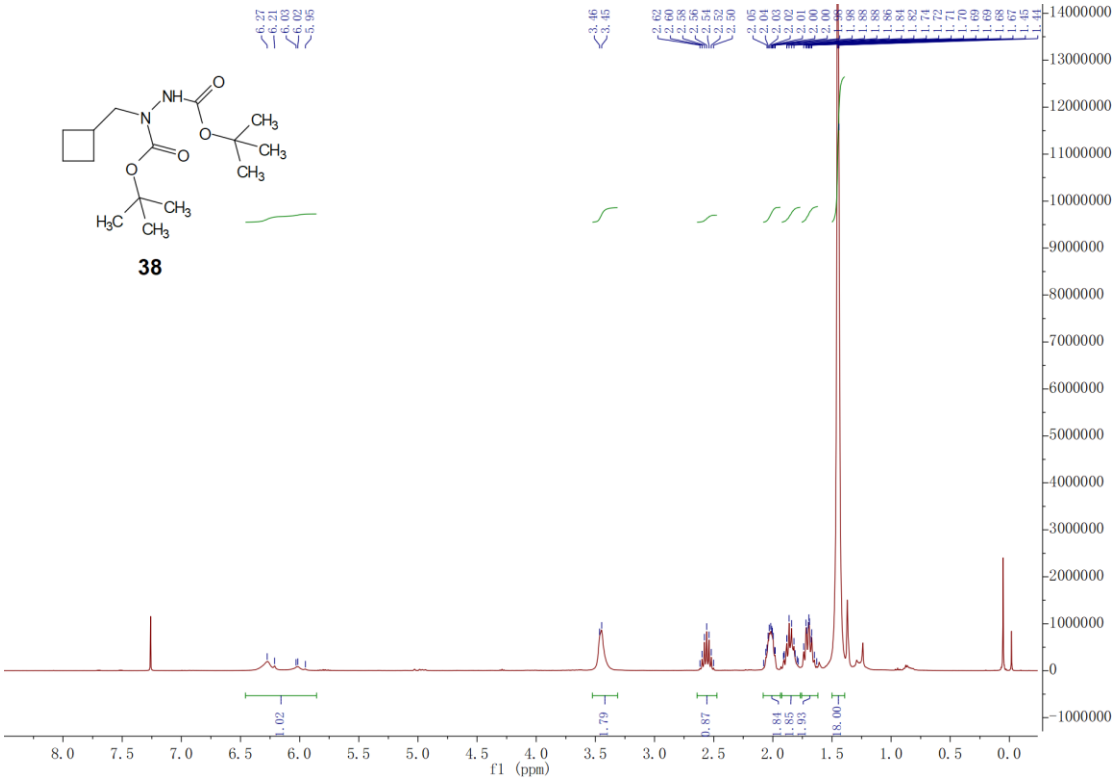
^{1}H NMR (400 MHz, $CDCl_3$)



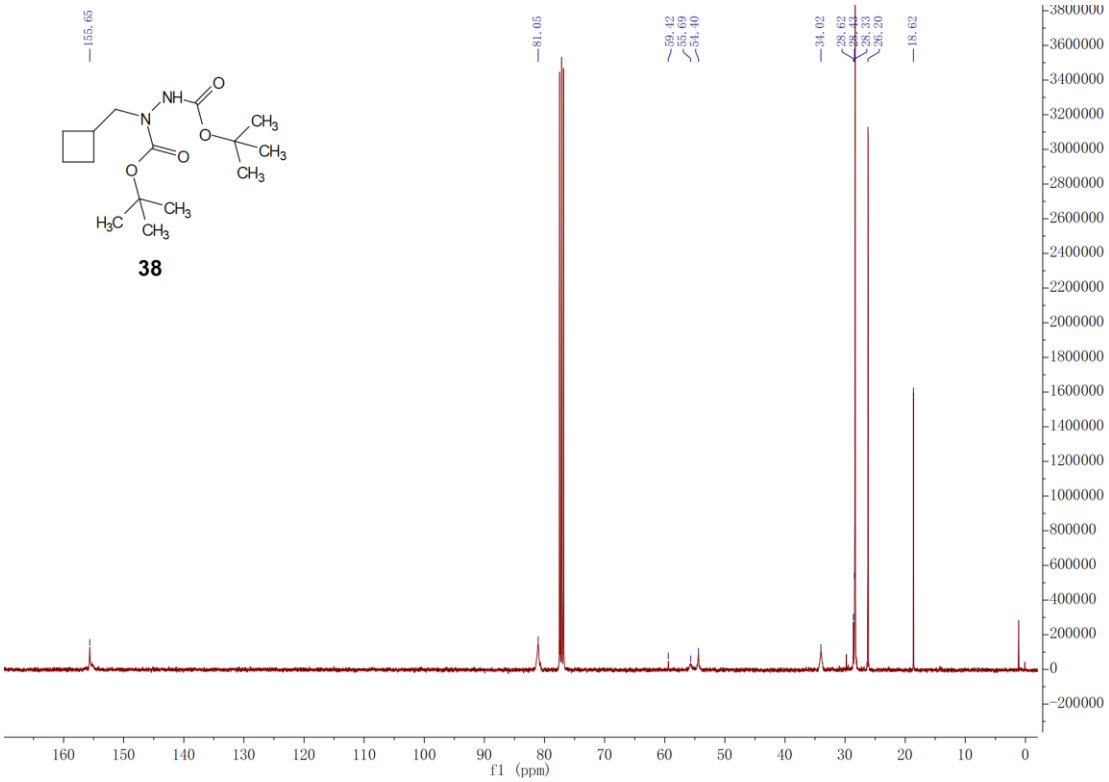
^{13}C NMR (101 MHz, $CDCl_3$)



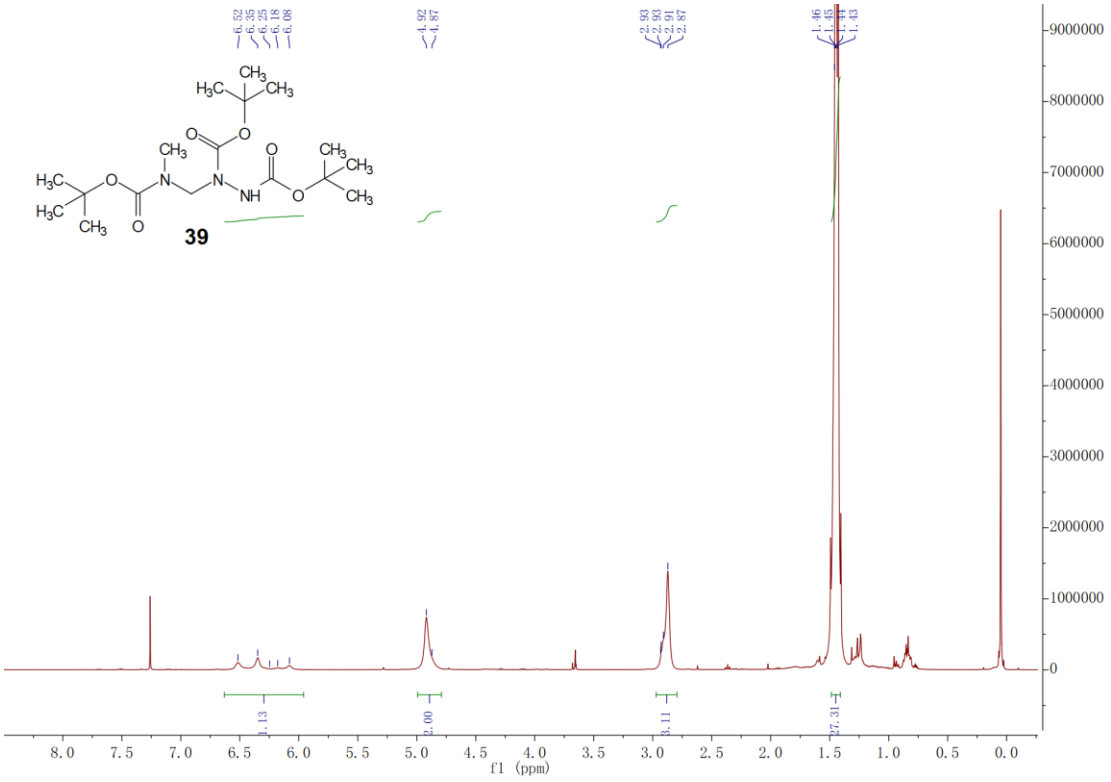
^{1}H NMR (400 MHz, $CDCl_3$)



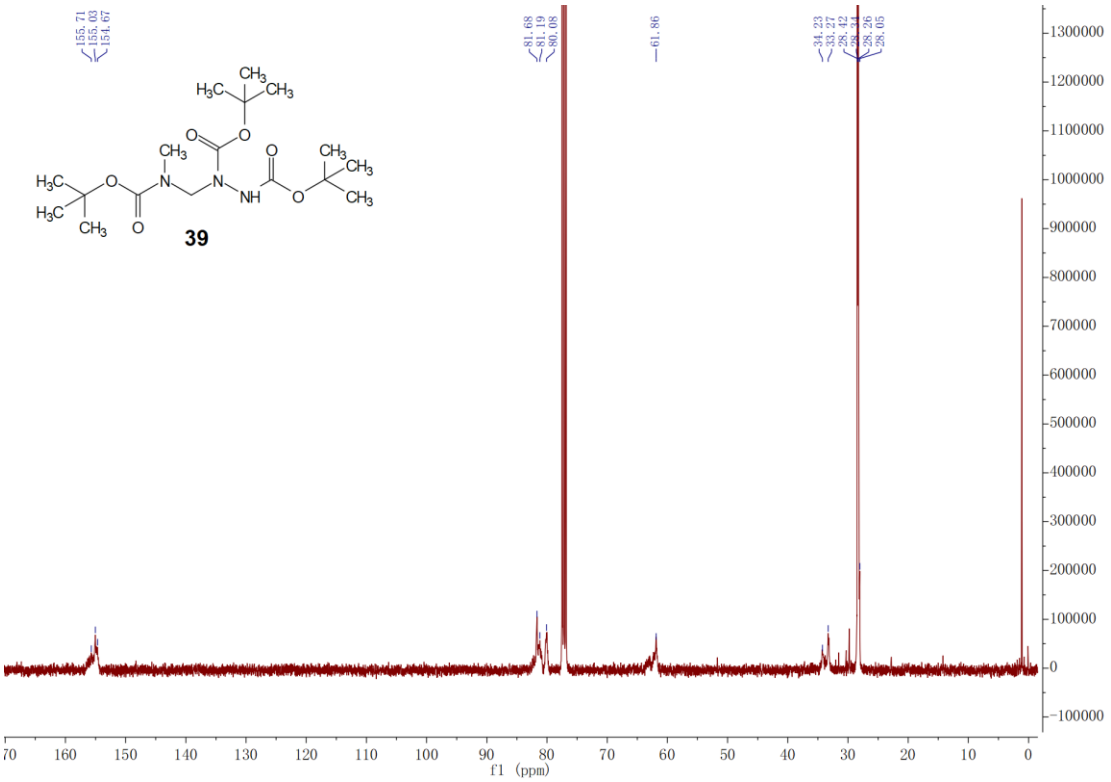
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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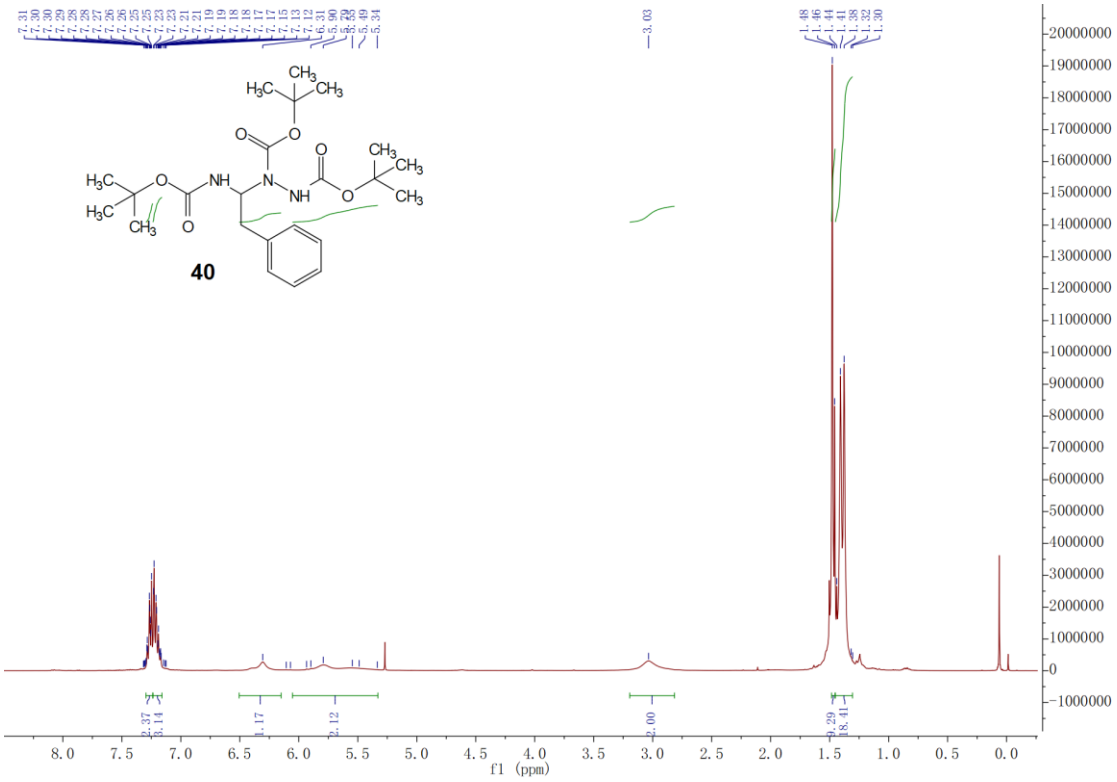
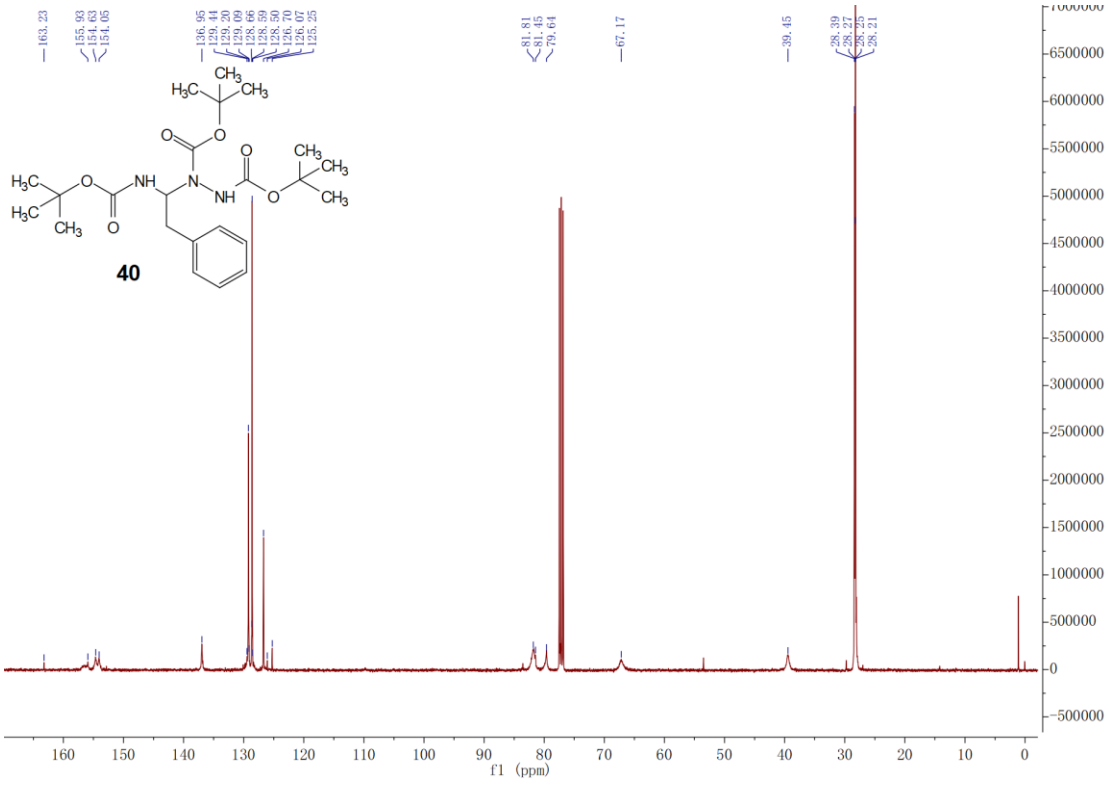
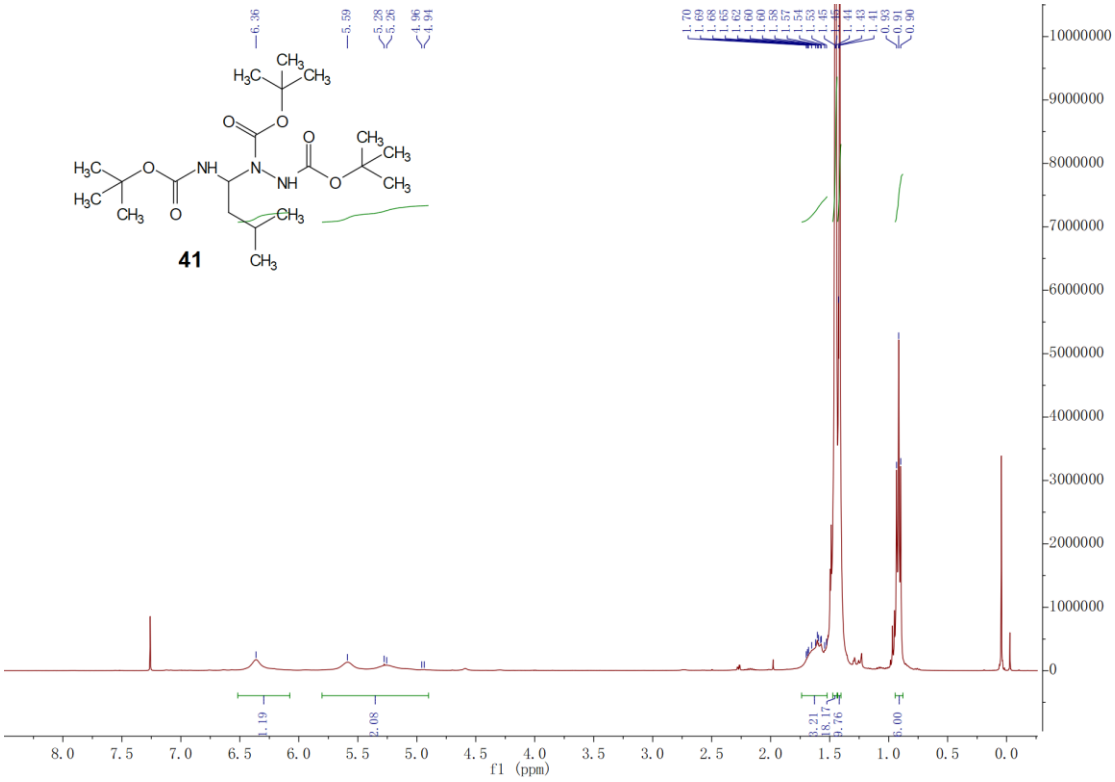


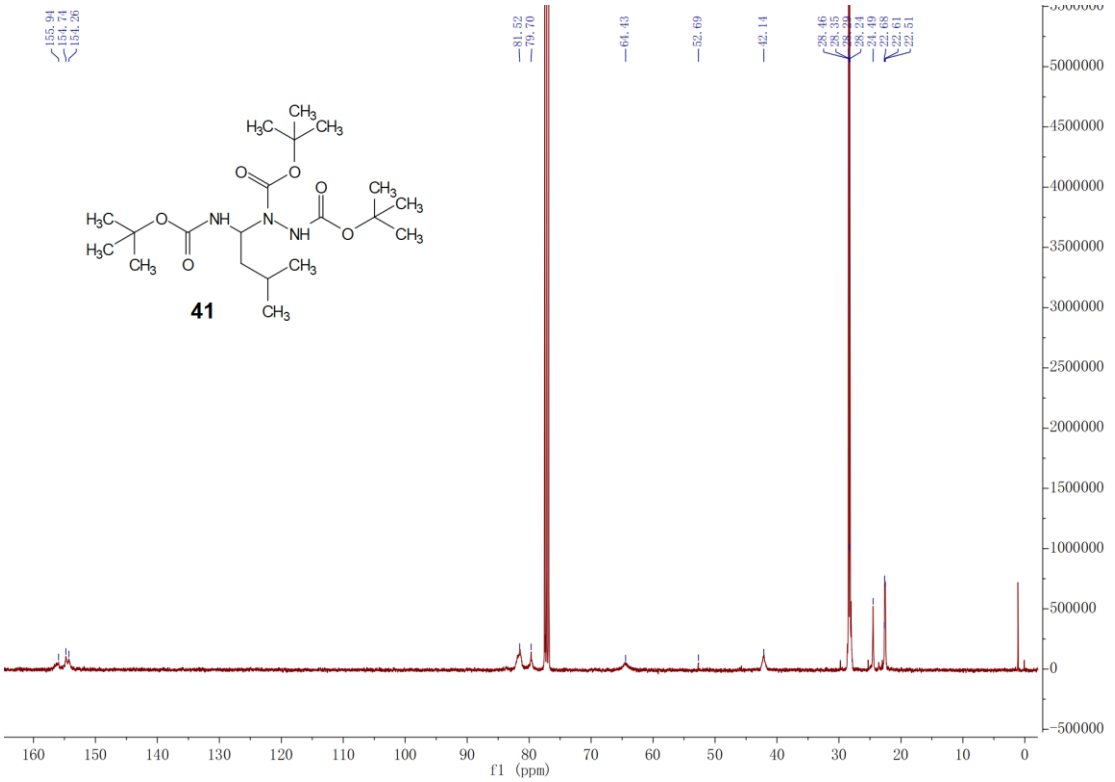
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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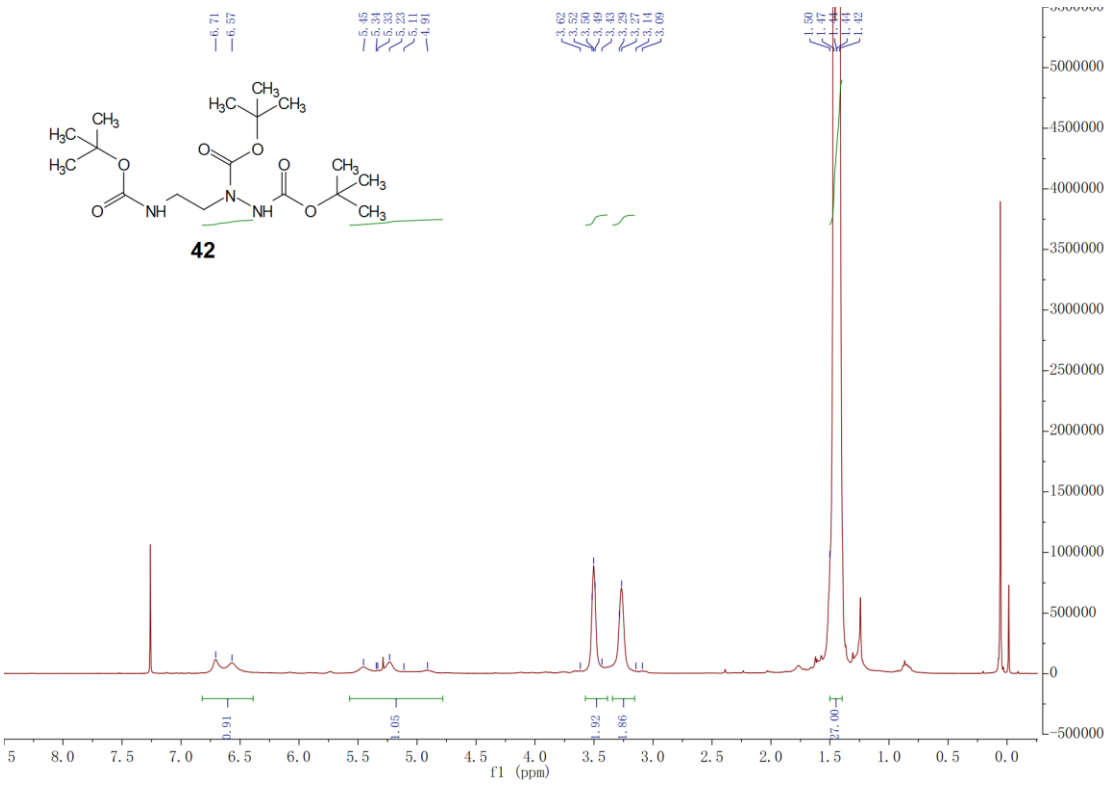
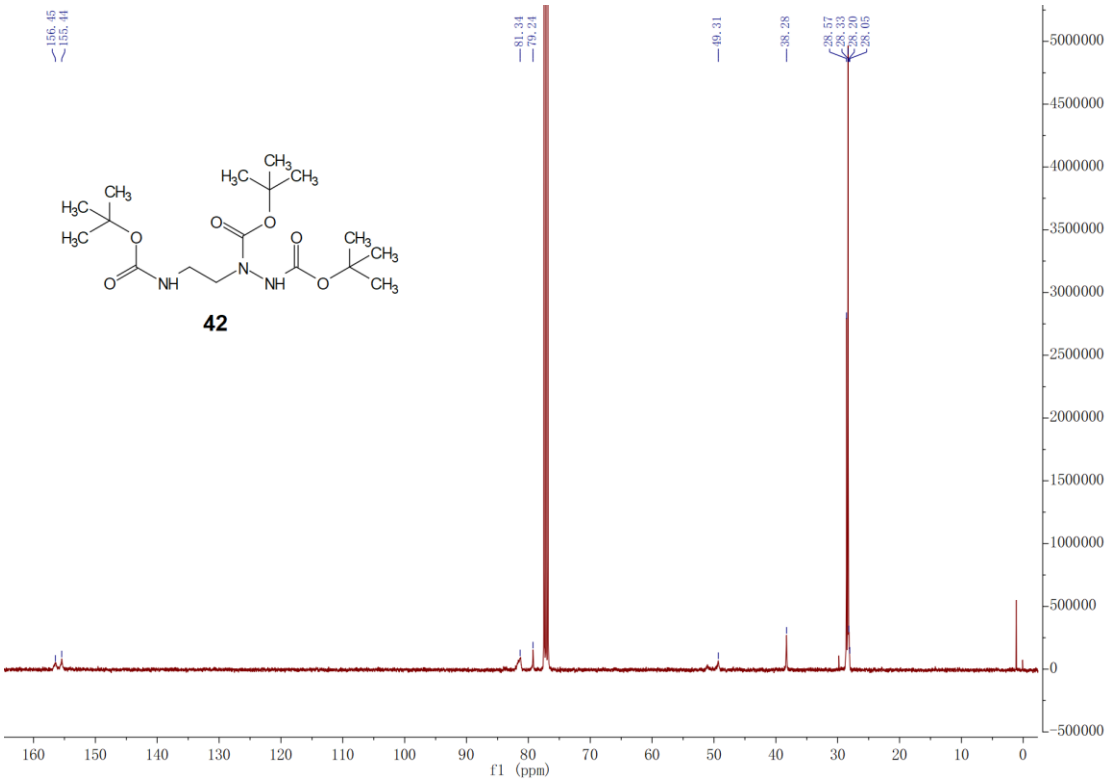


42

^{13}C NMR (101 MHz, $CDCl_3$)



42

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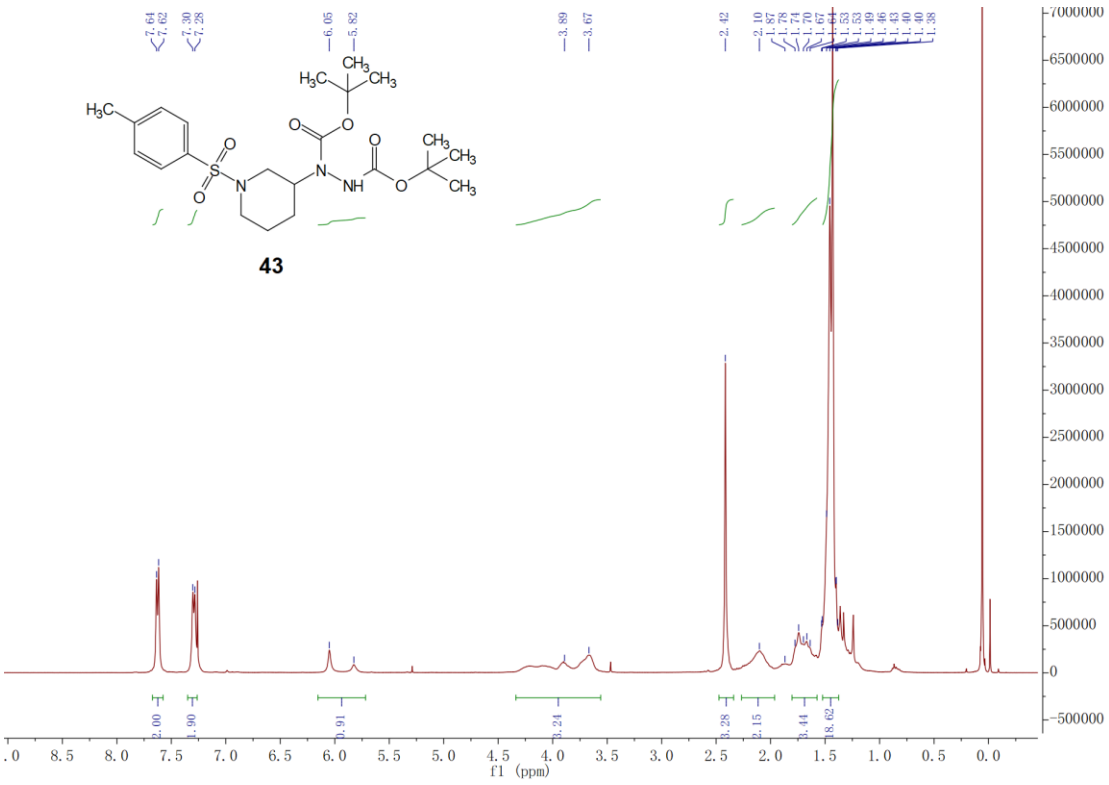

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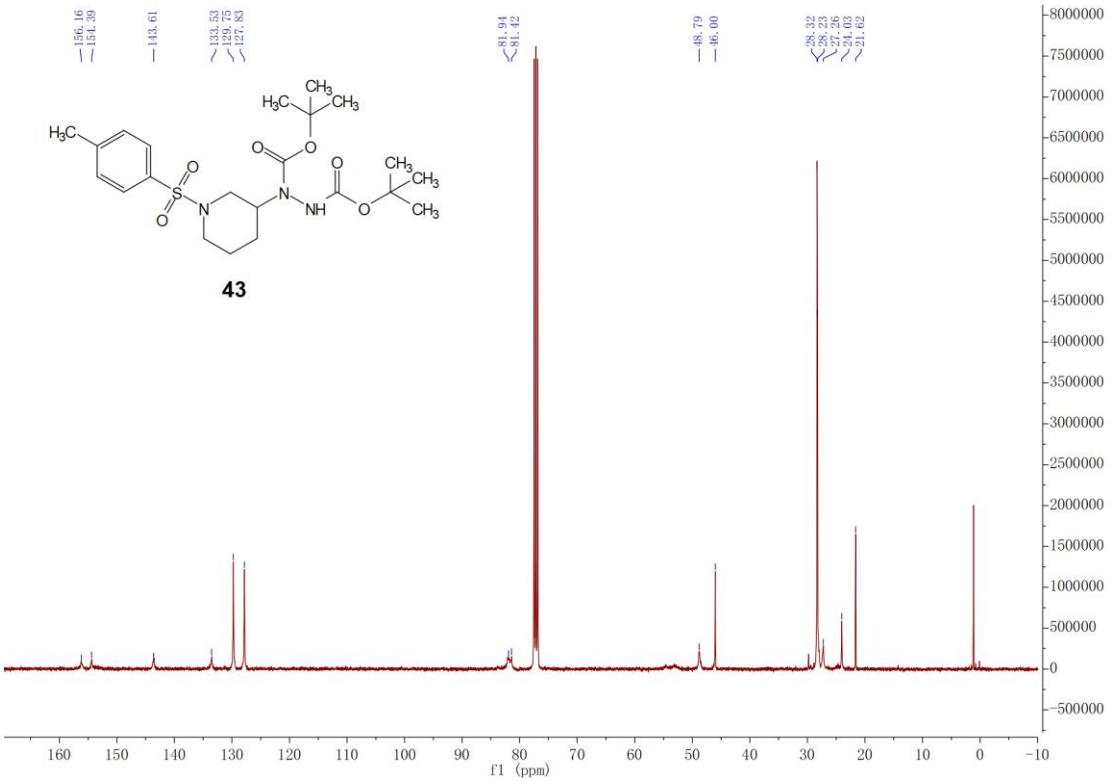
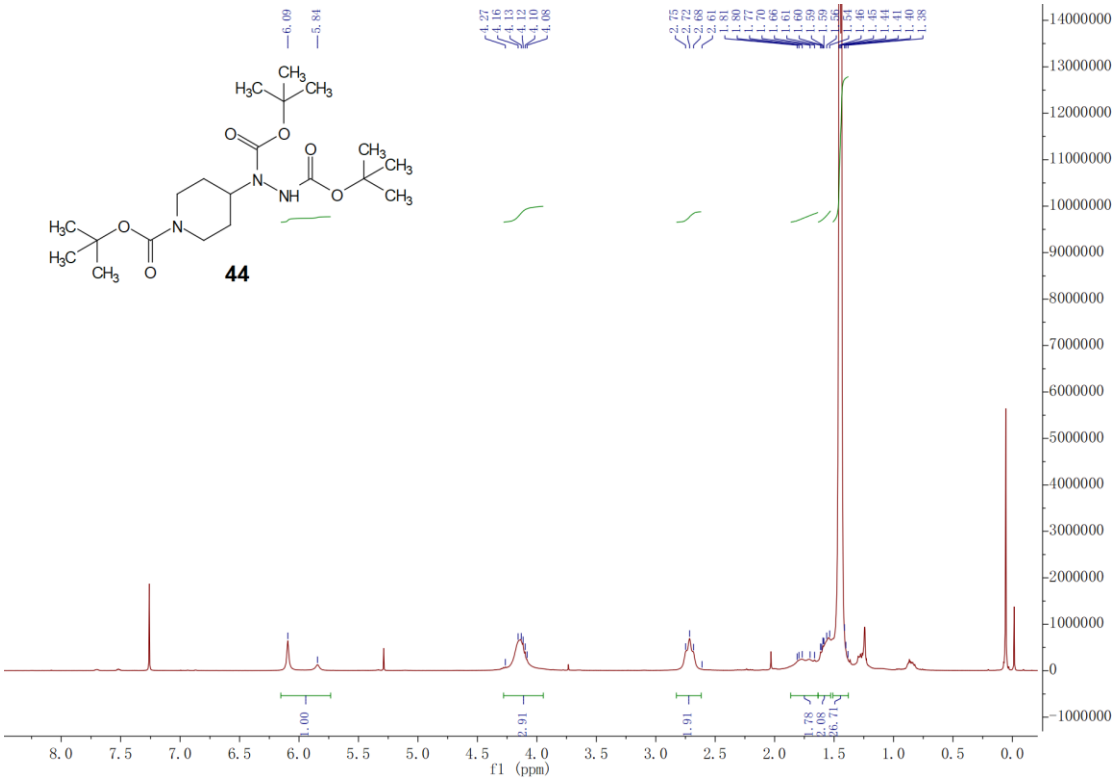
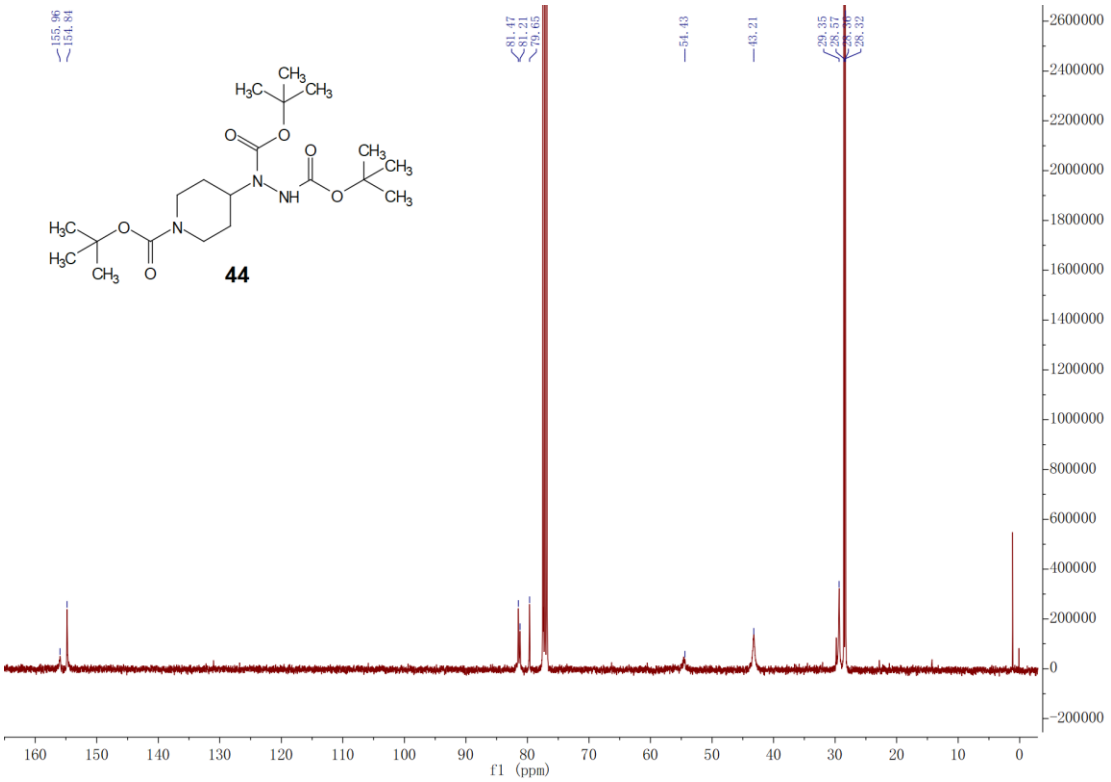


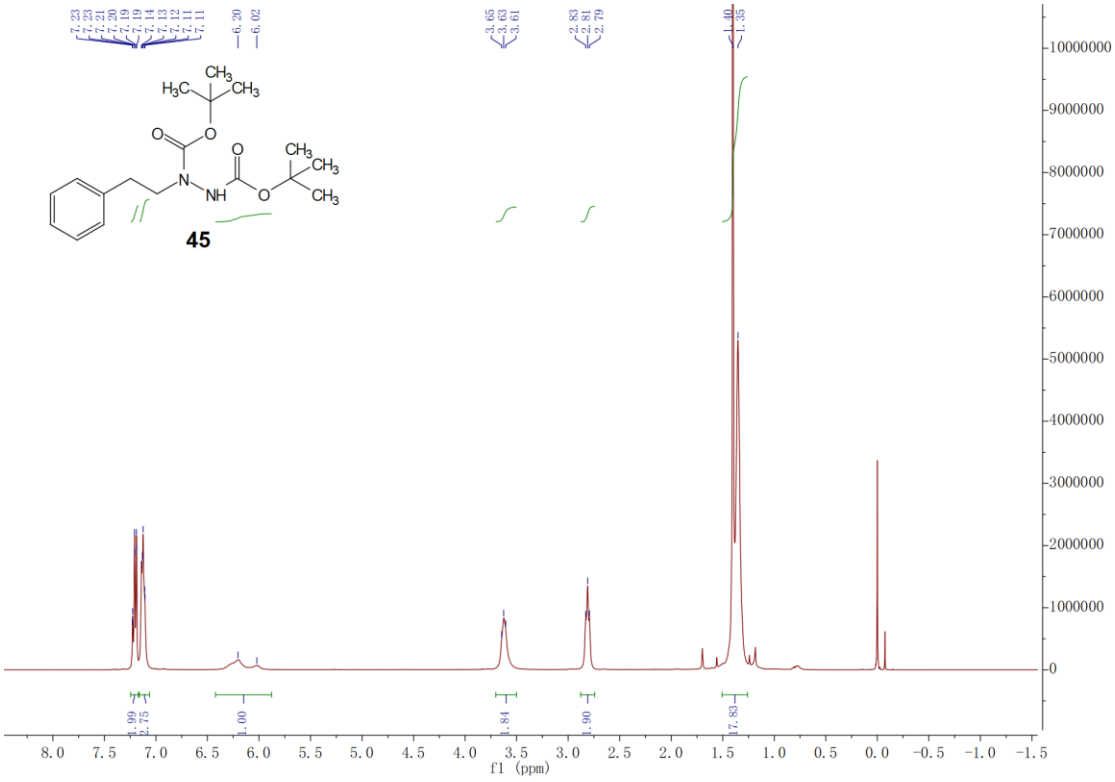
^{1}H NMR (400 MHz, $CDCl_3$)



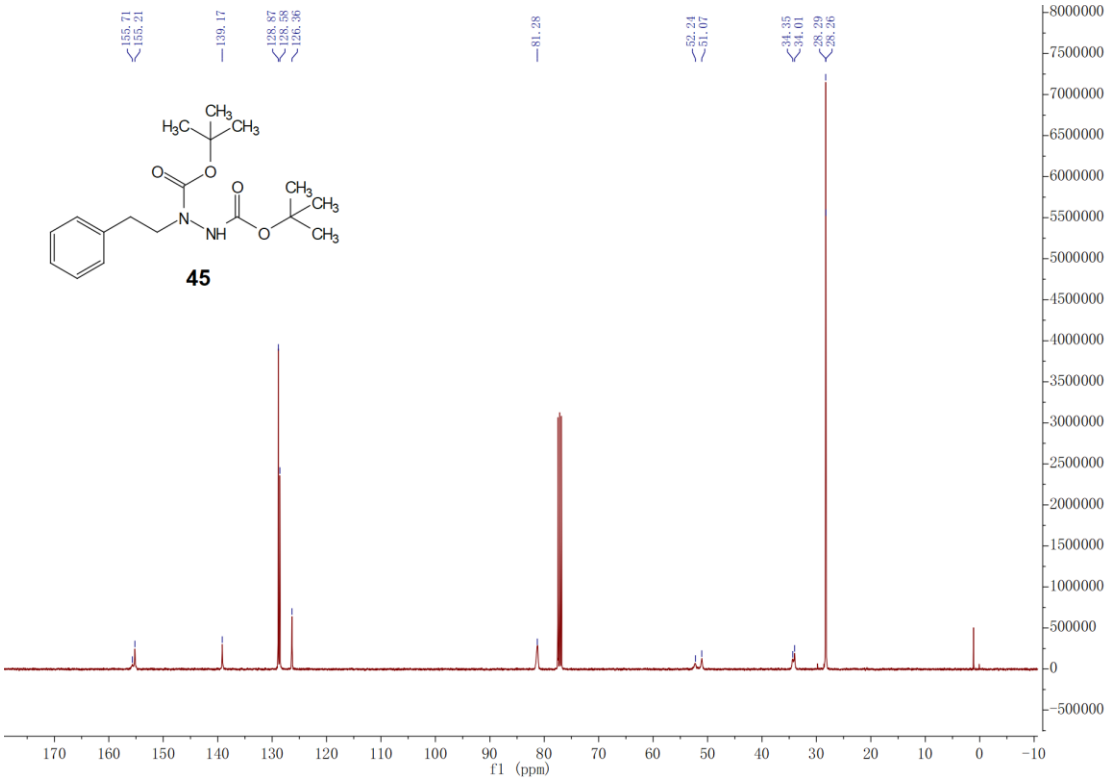
^{13}C NMR (101 MHz, $CDCl_3$)



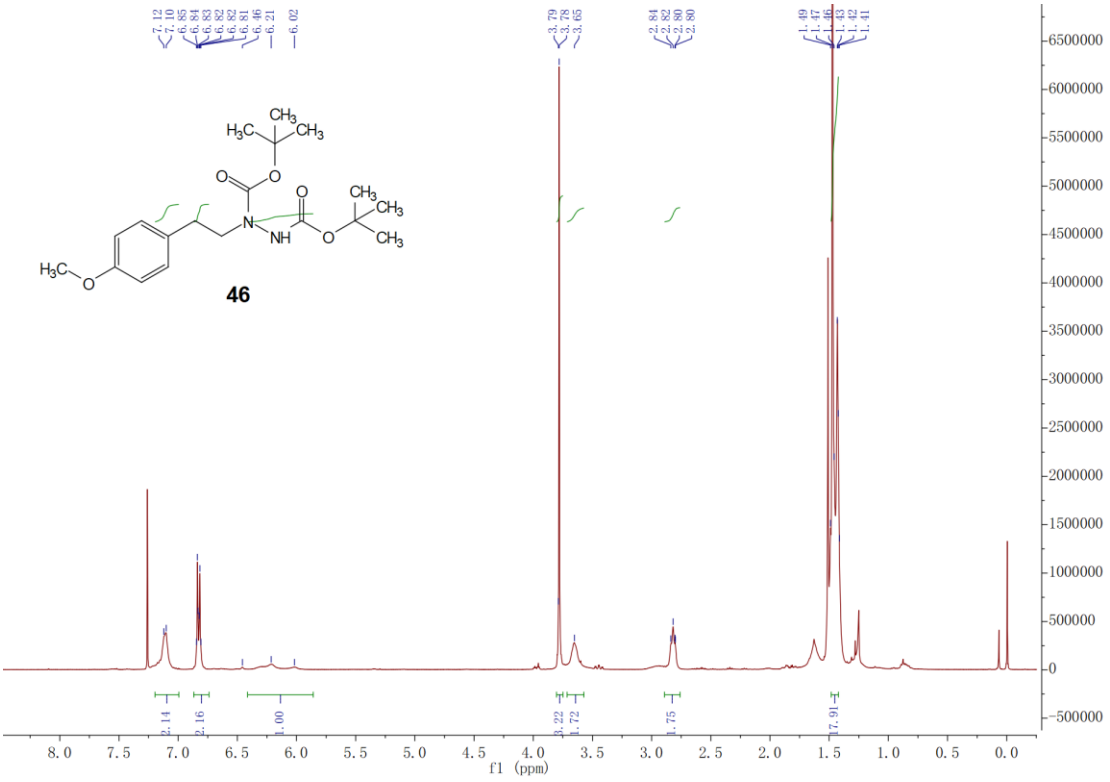
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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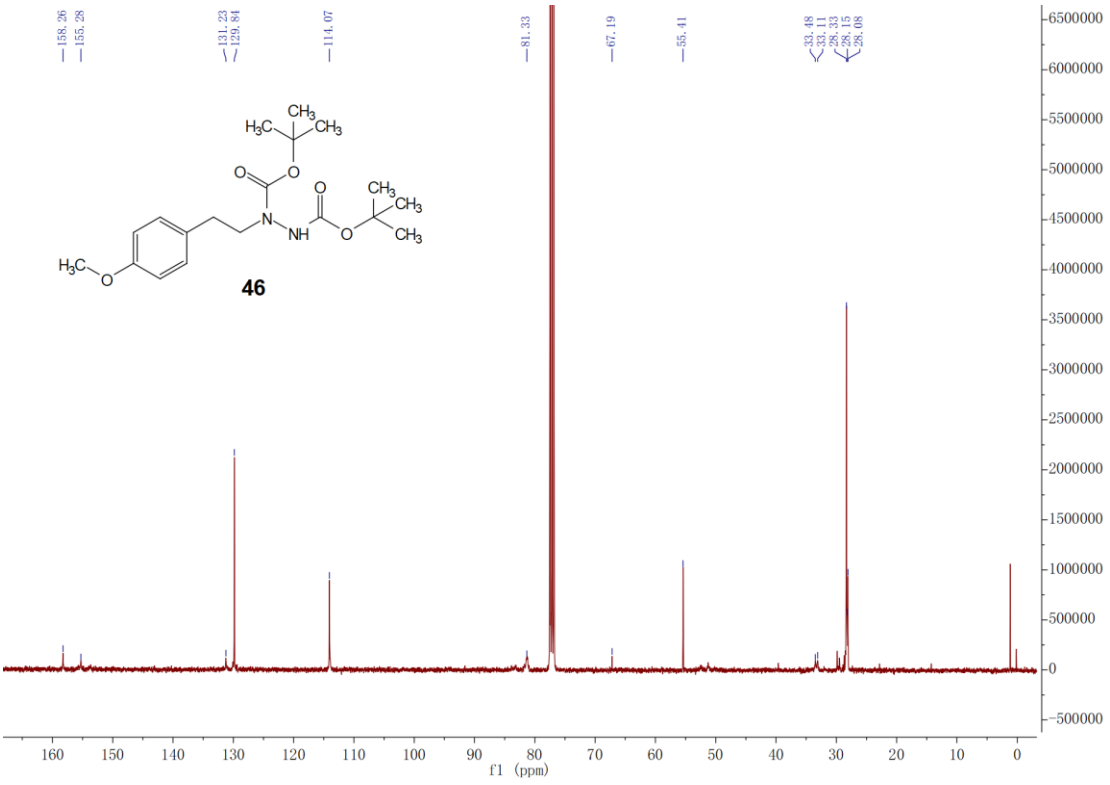

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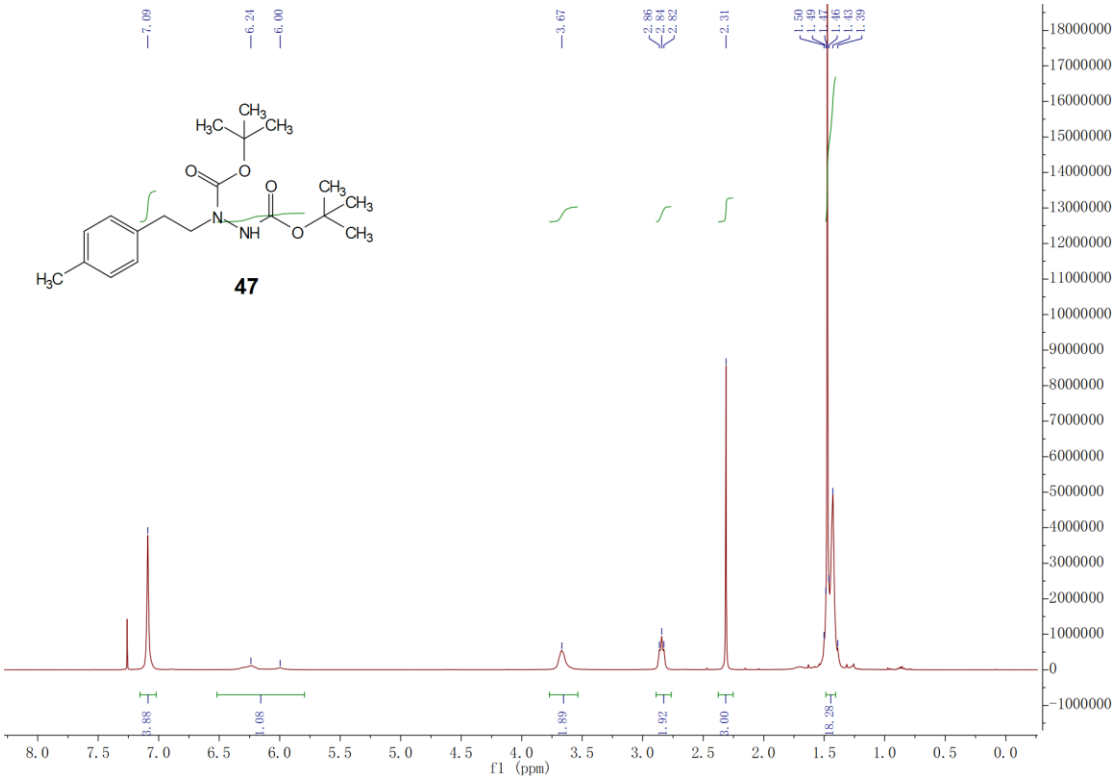

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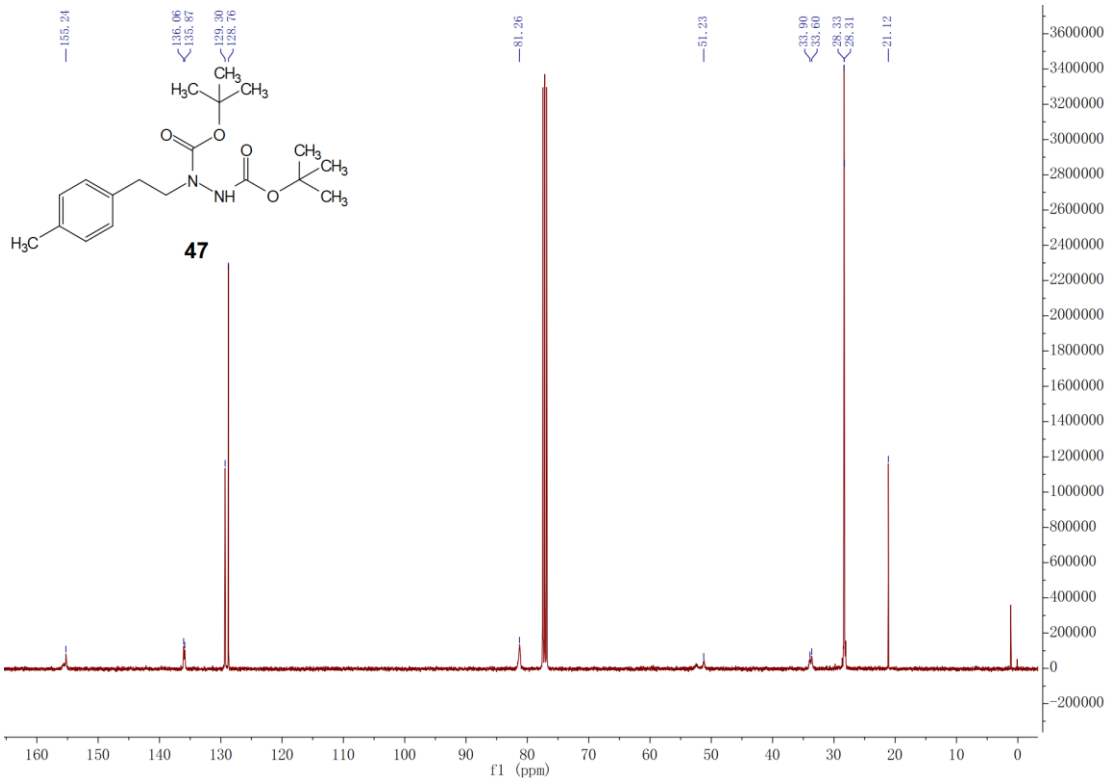
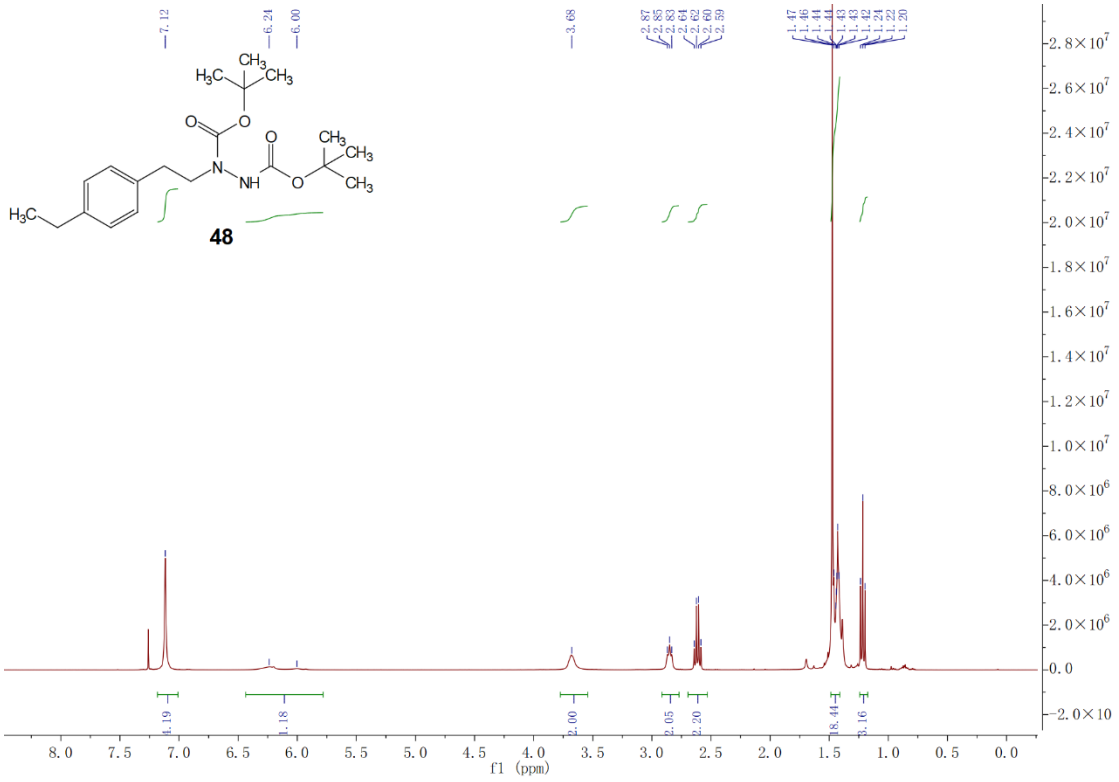


^{1}H NMR (400 MHz, $CDCl_3$)



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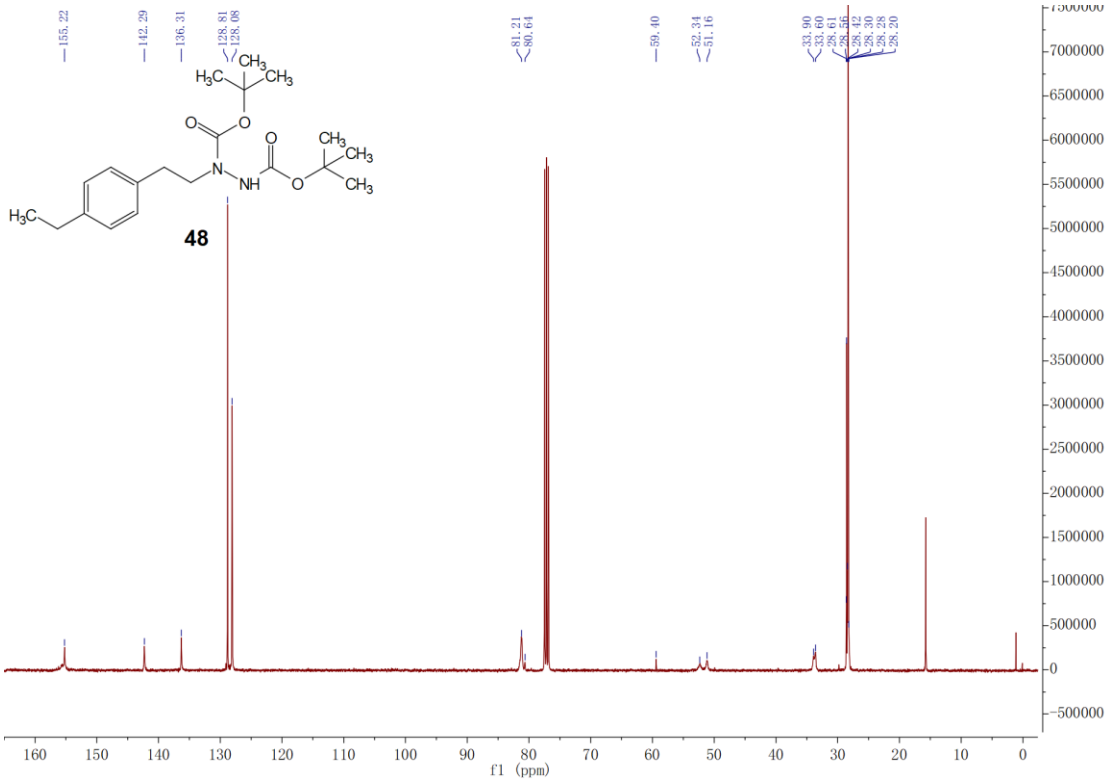

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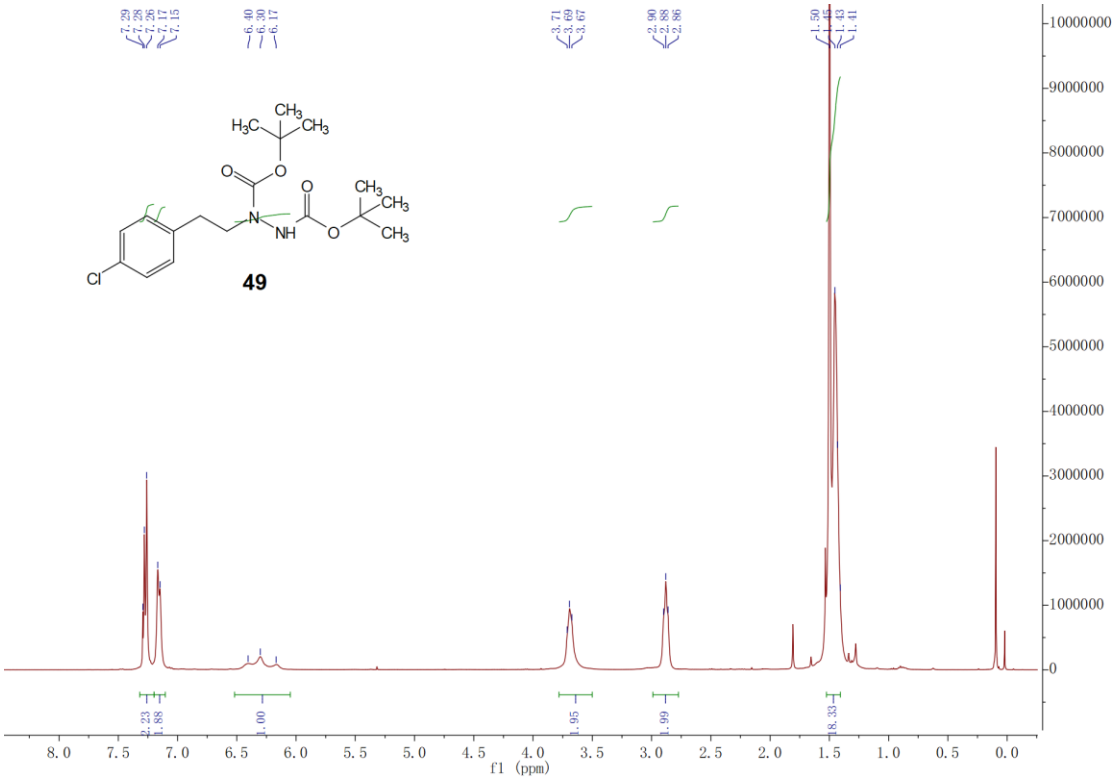
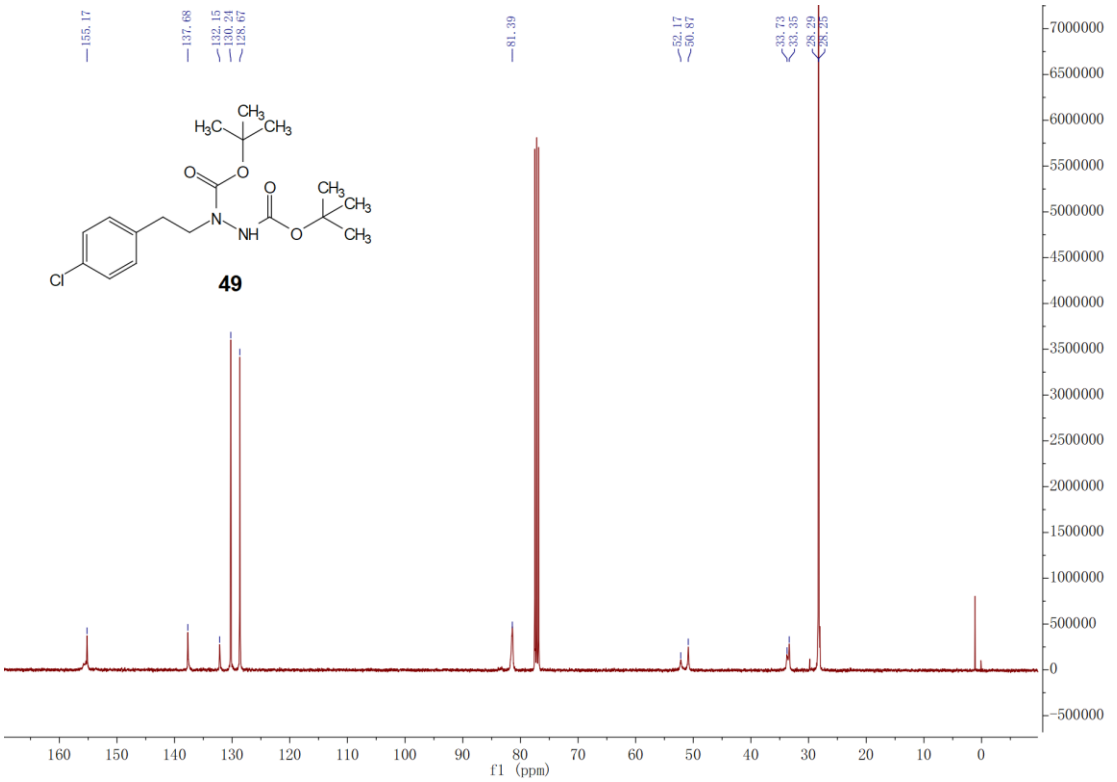


^{13}C NMR (101 MHz, $CDCl_3$)



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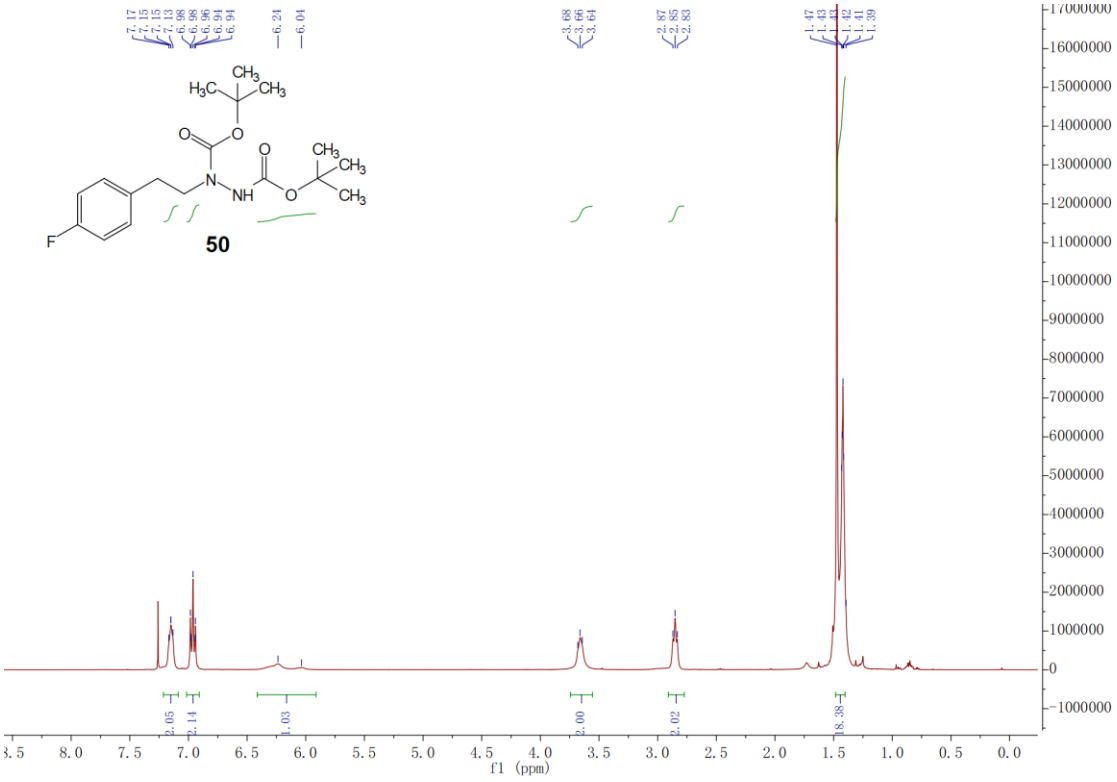

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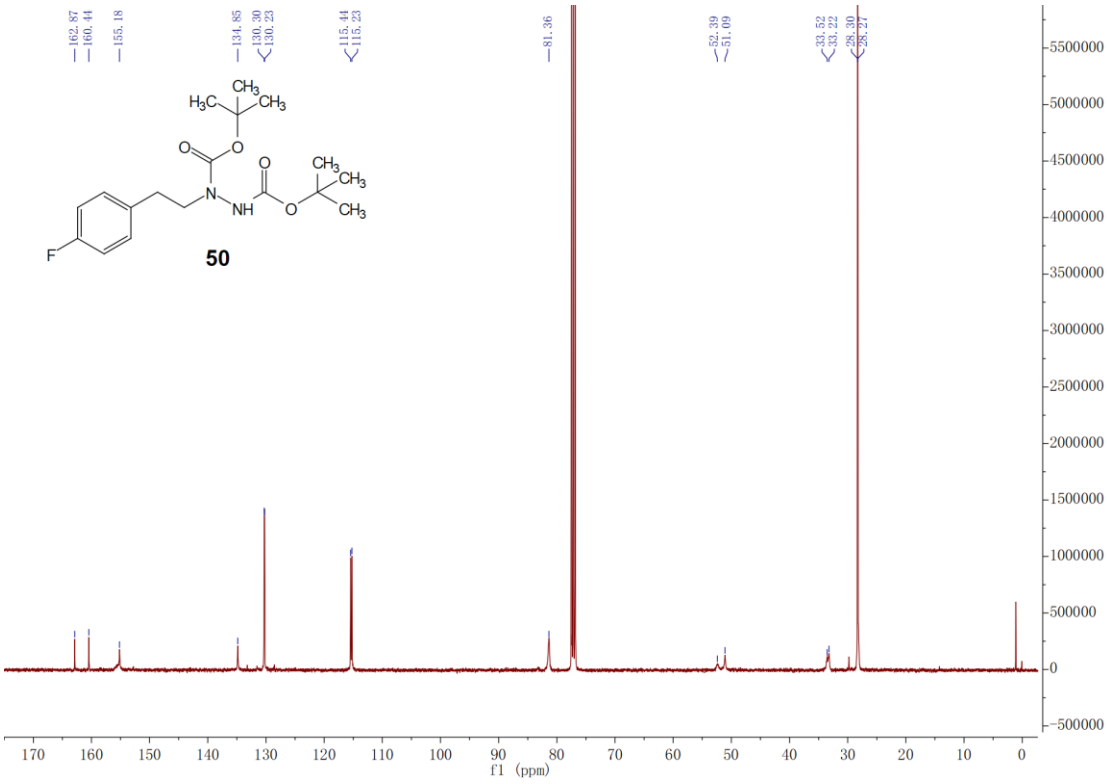

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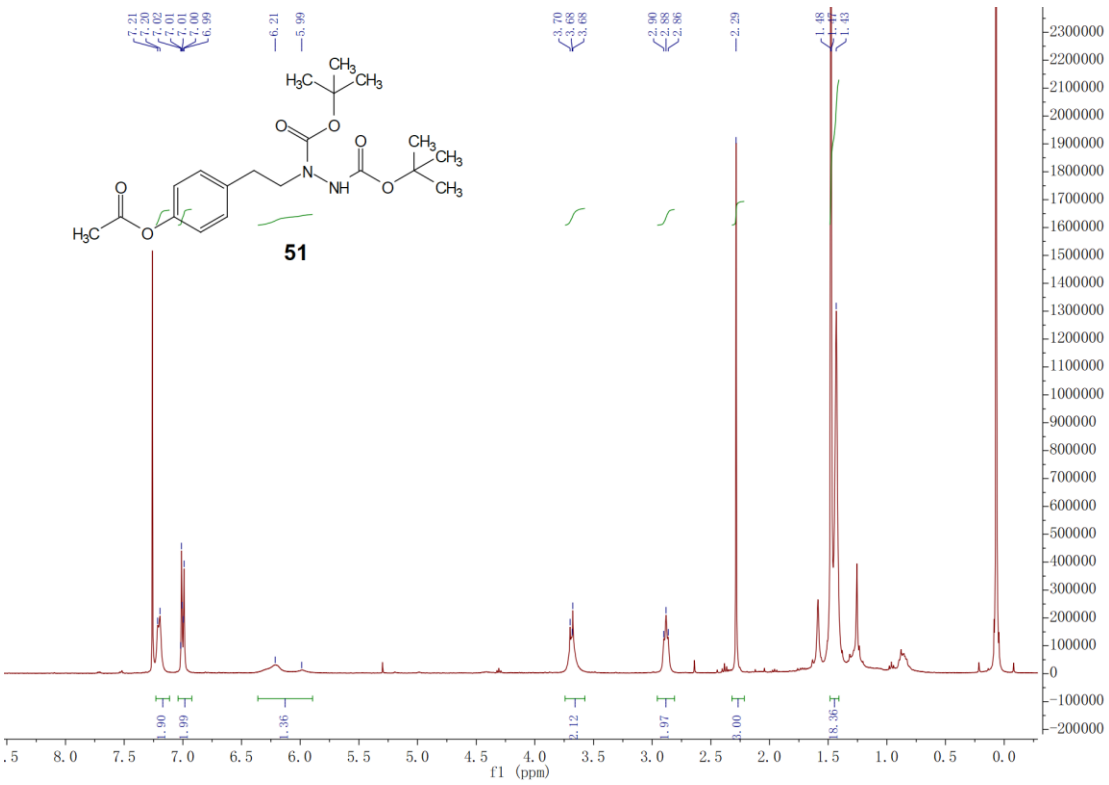

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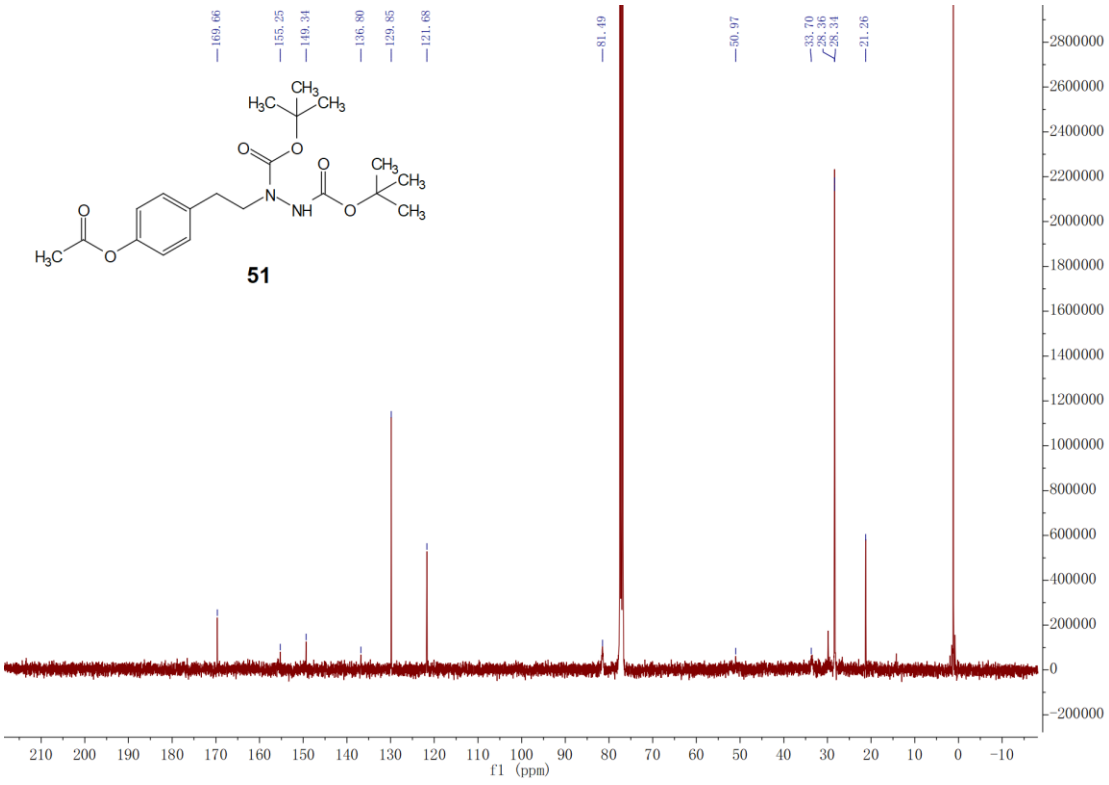

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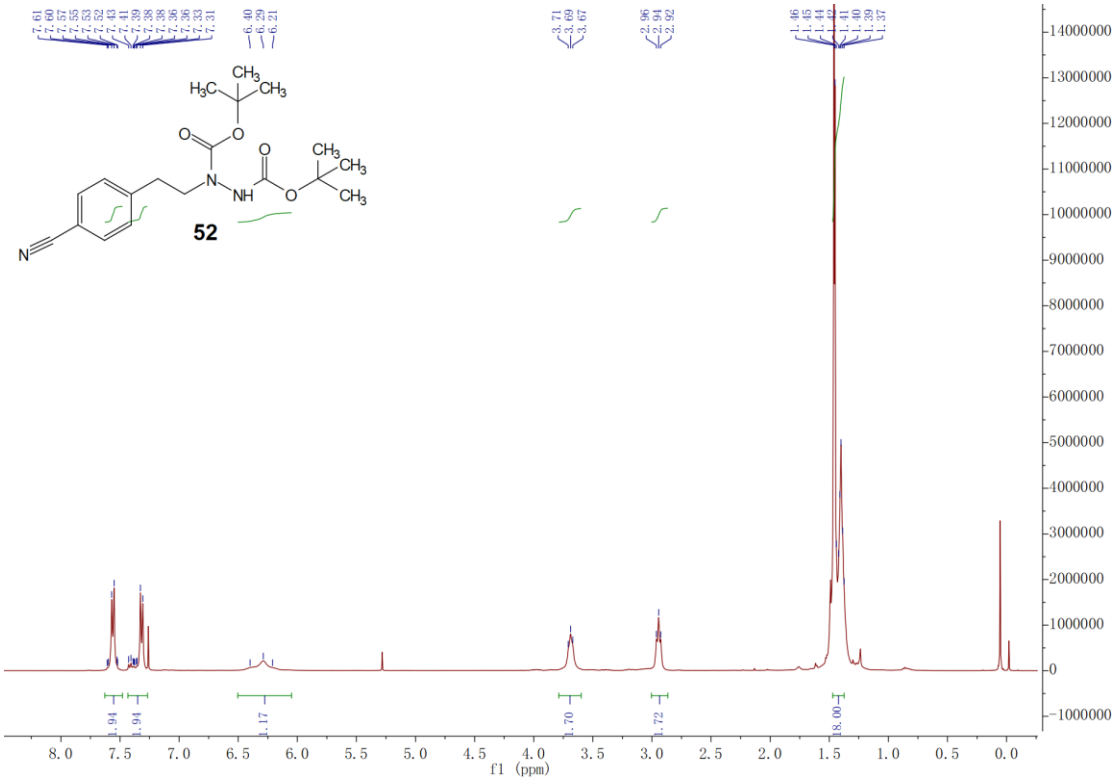

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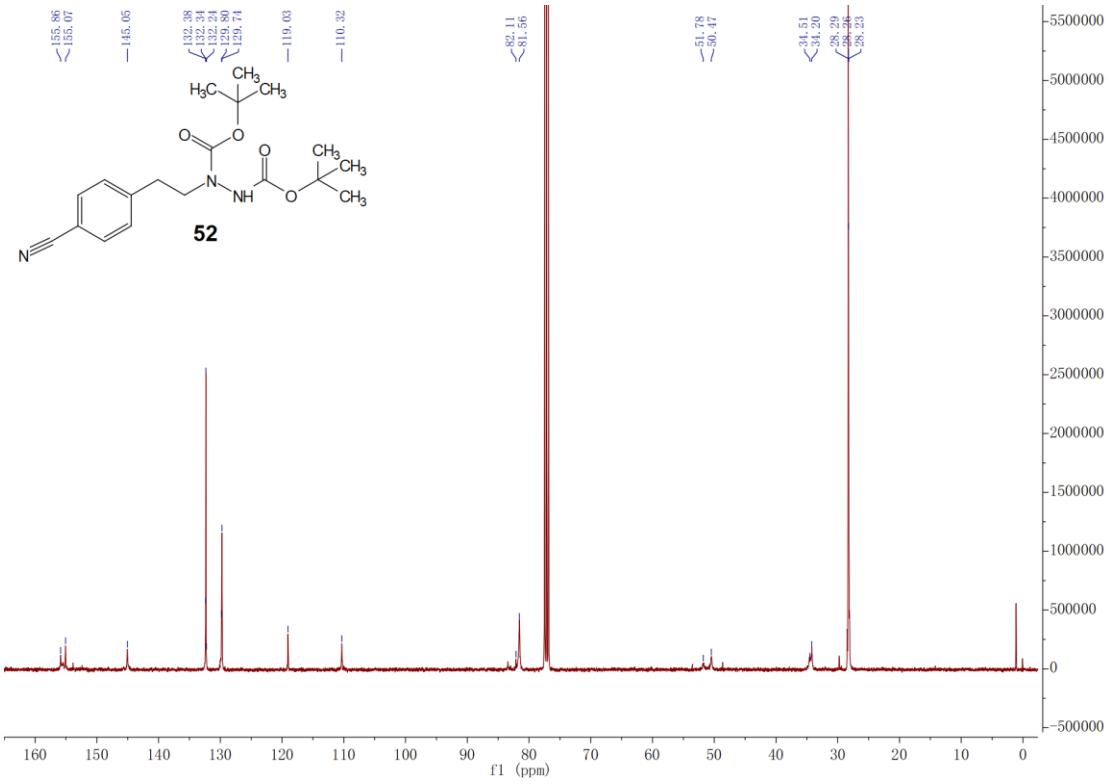

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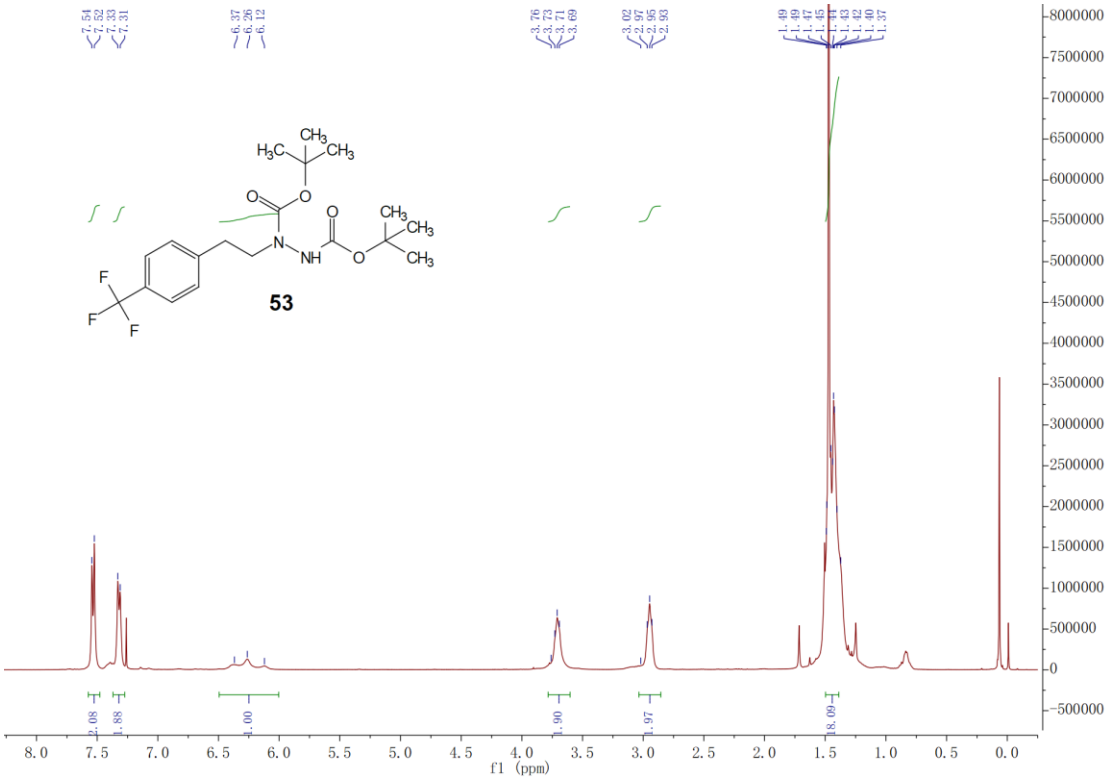
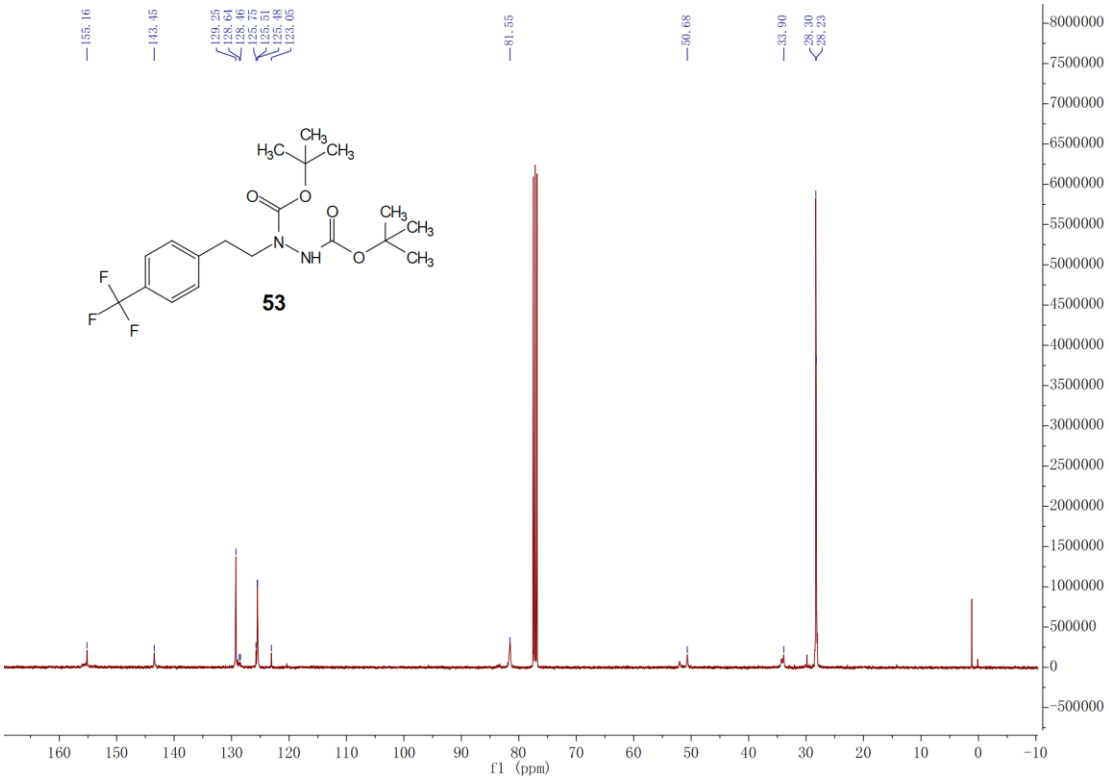
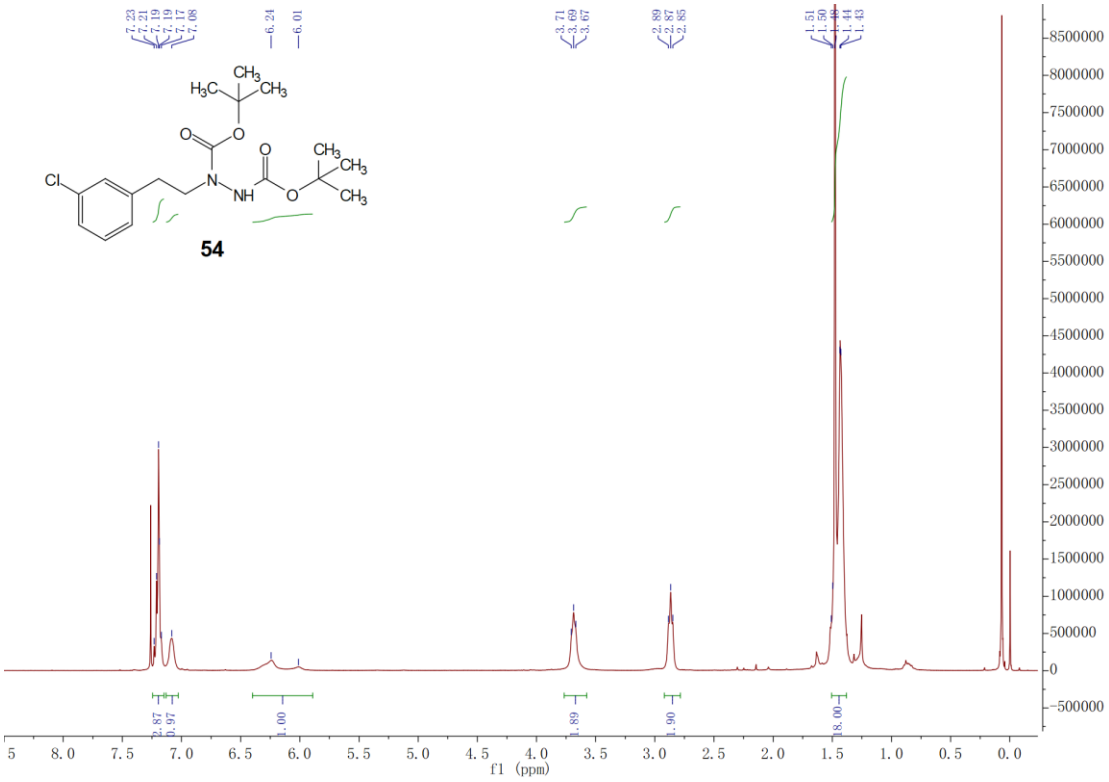


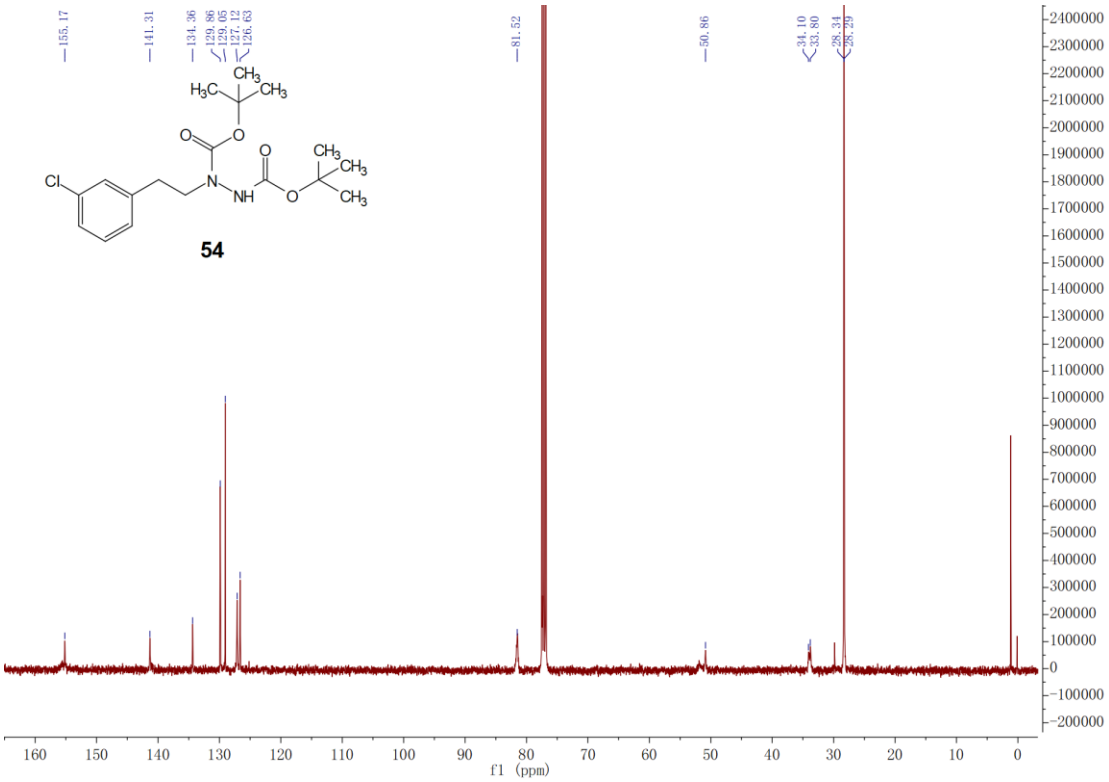
^{13}C NMR (101 MHz, $CDCl_3$)



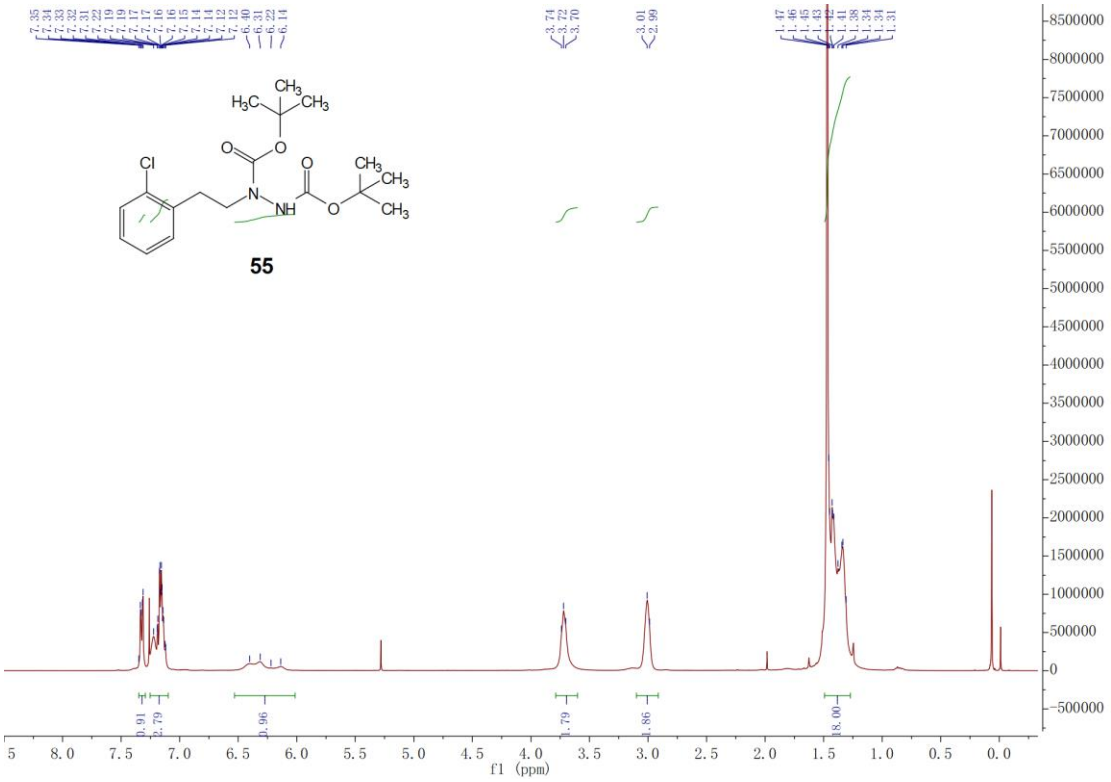
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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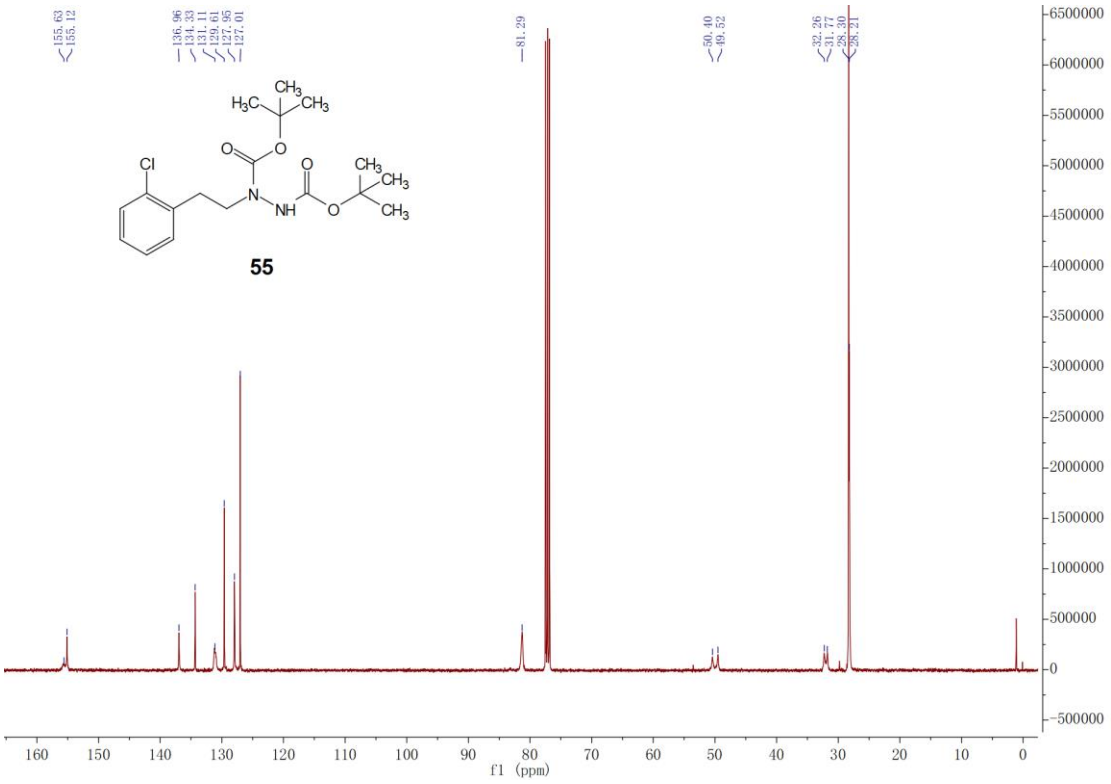

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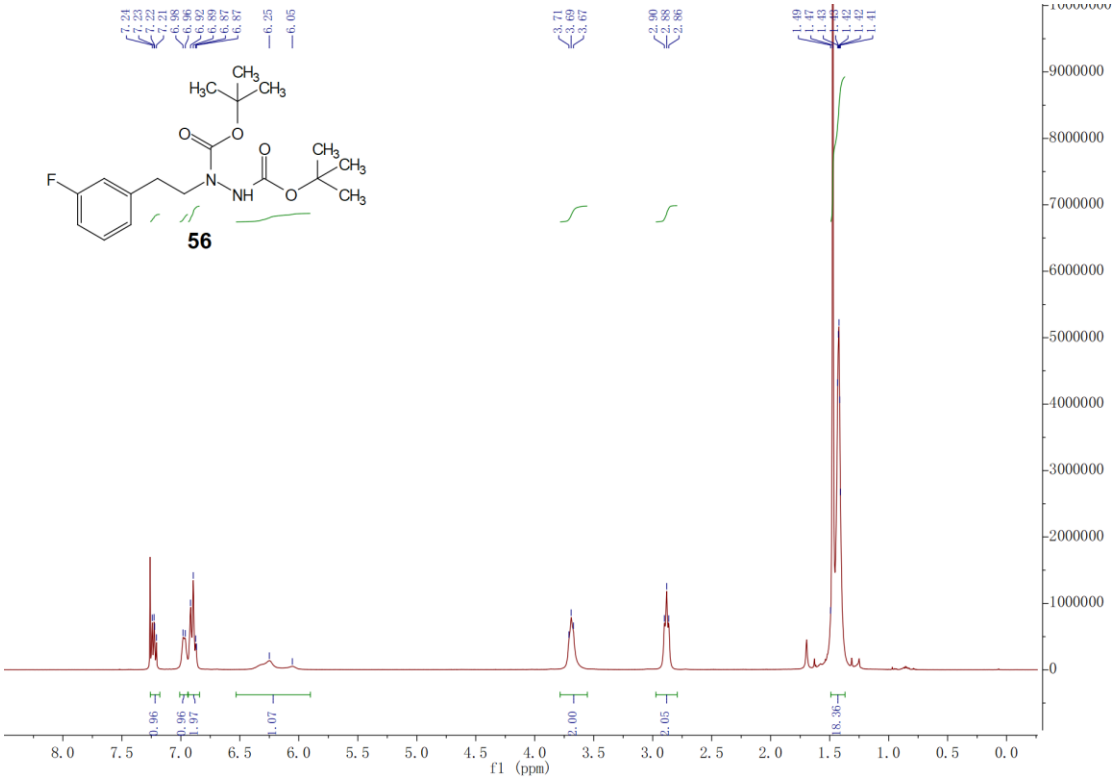

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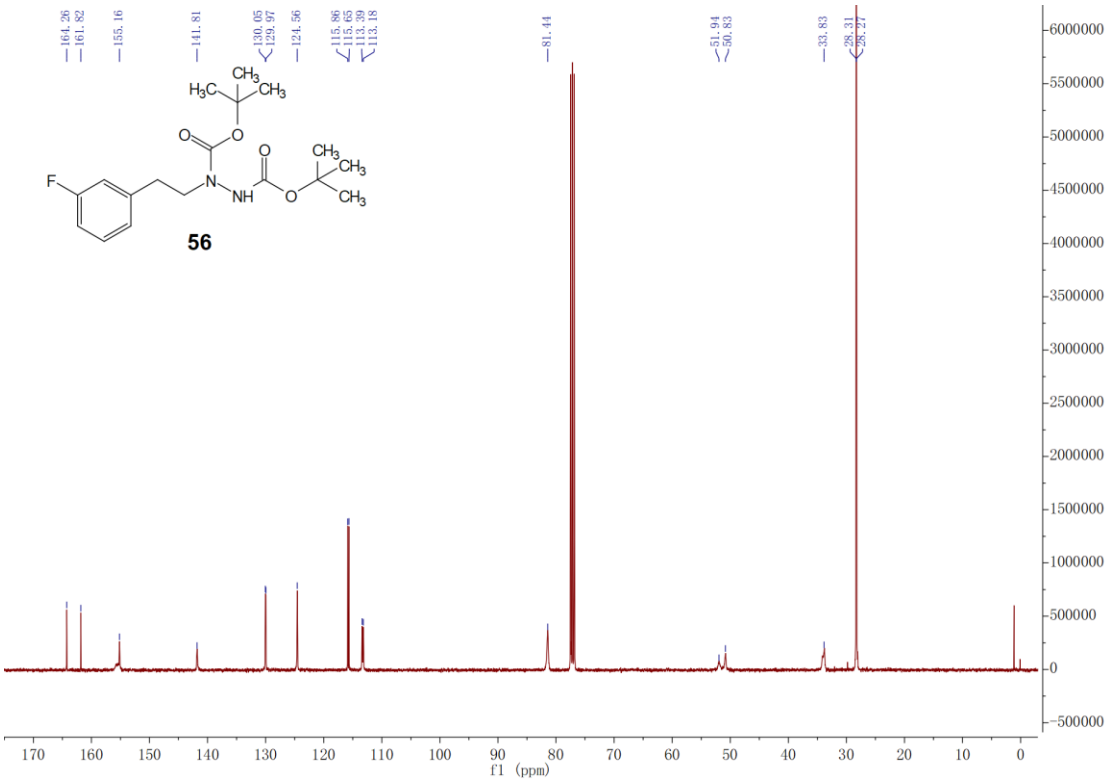

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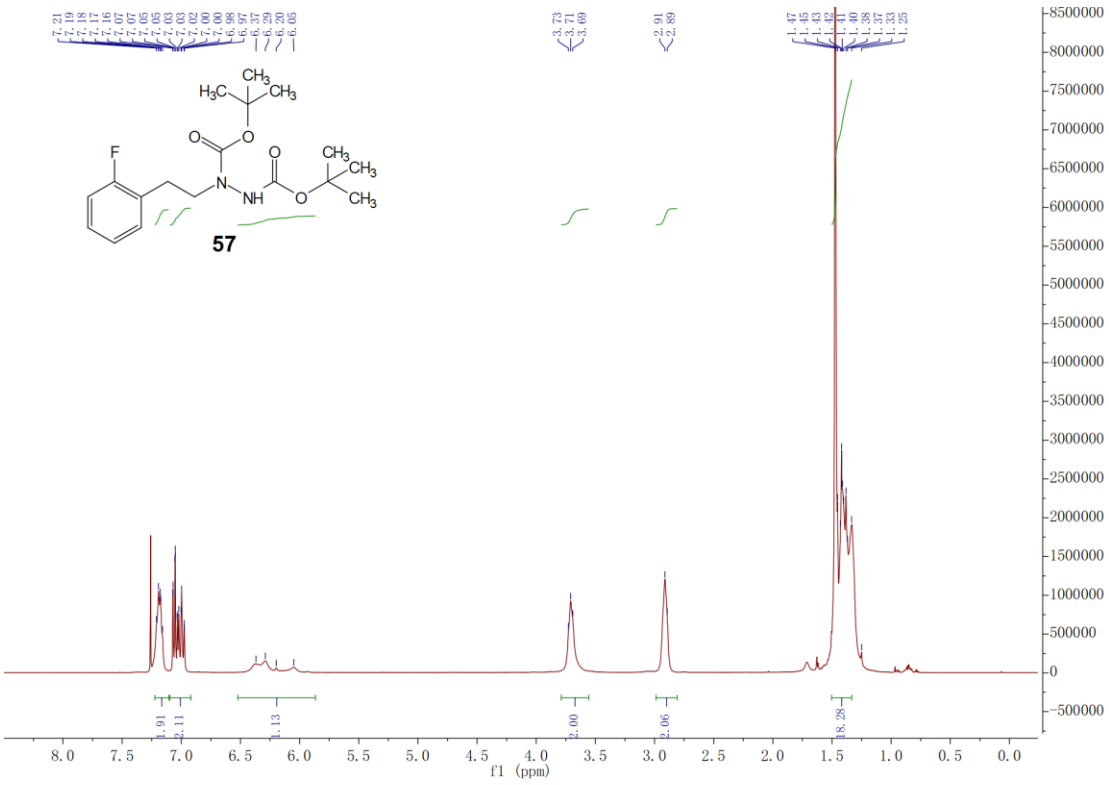
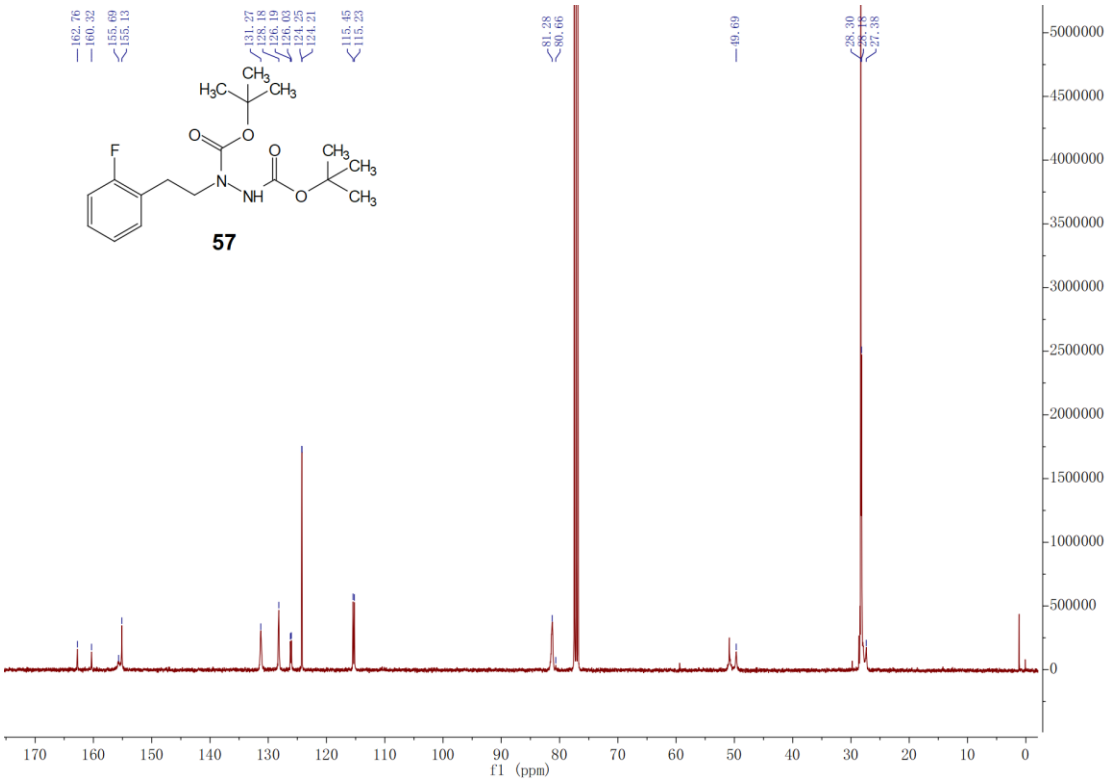


^{13}C NMR (101 MHz, $CDCl_3$)



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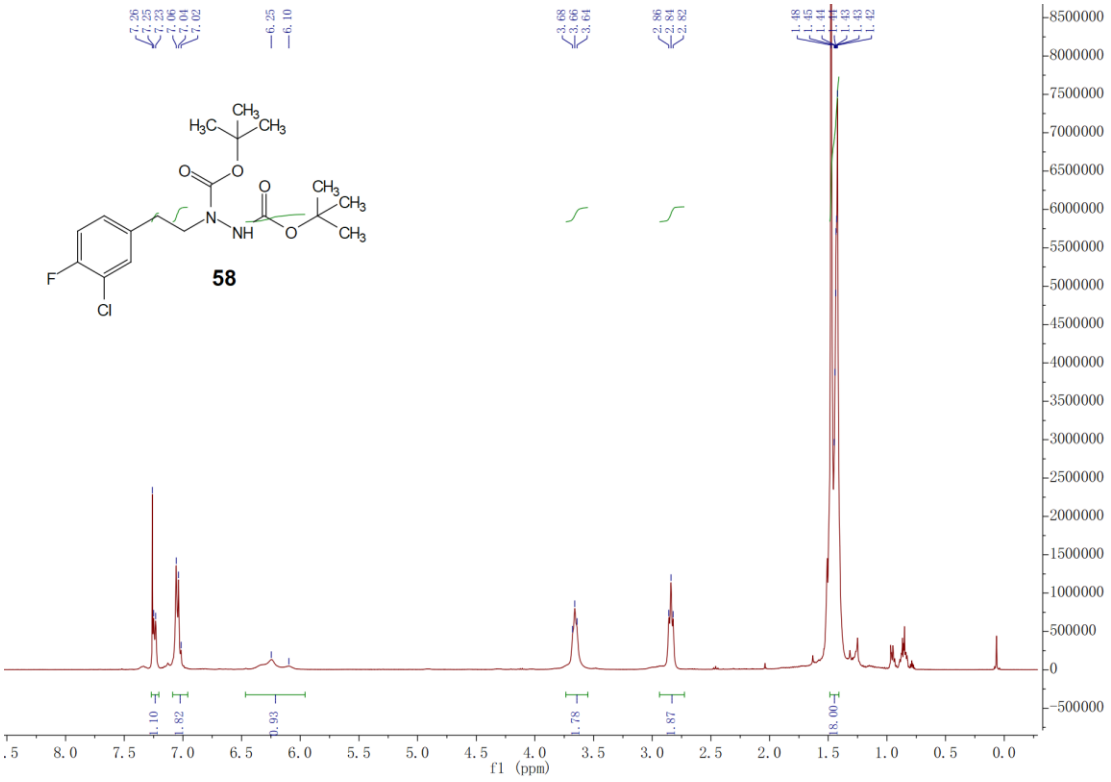
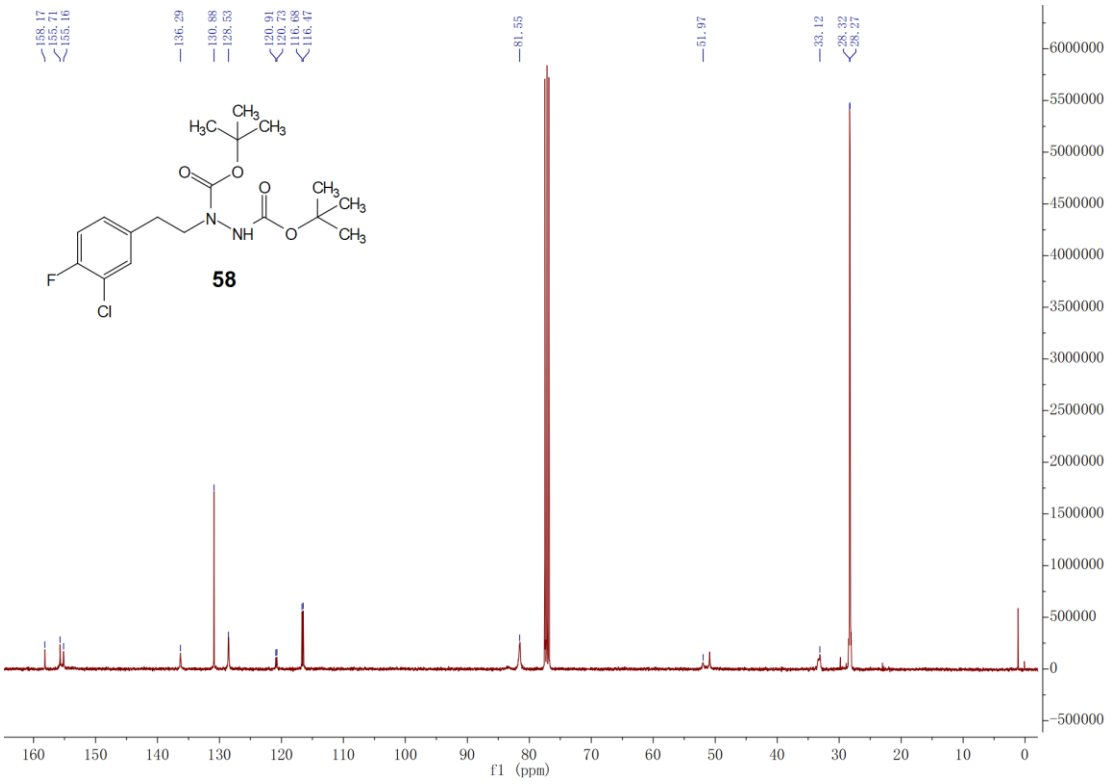
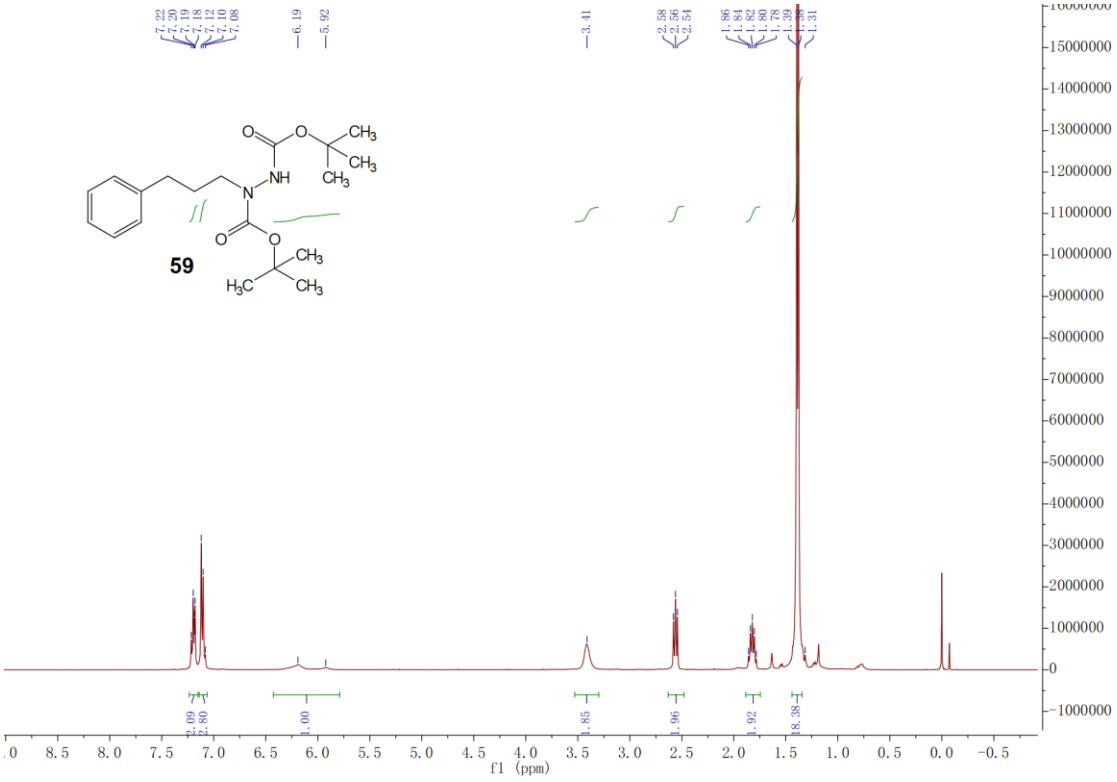


^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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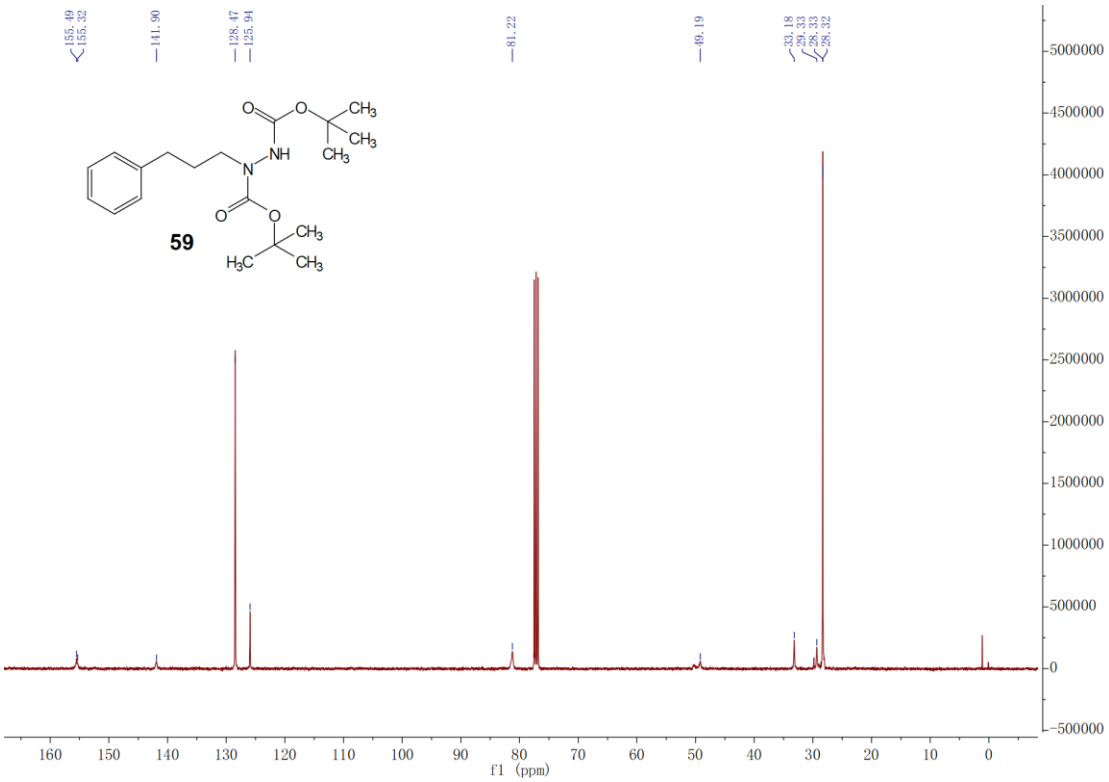

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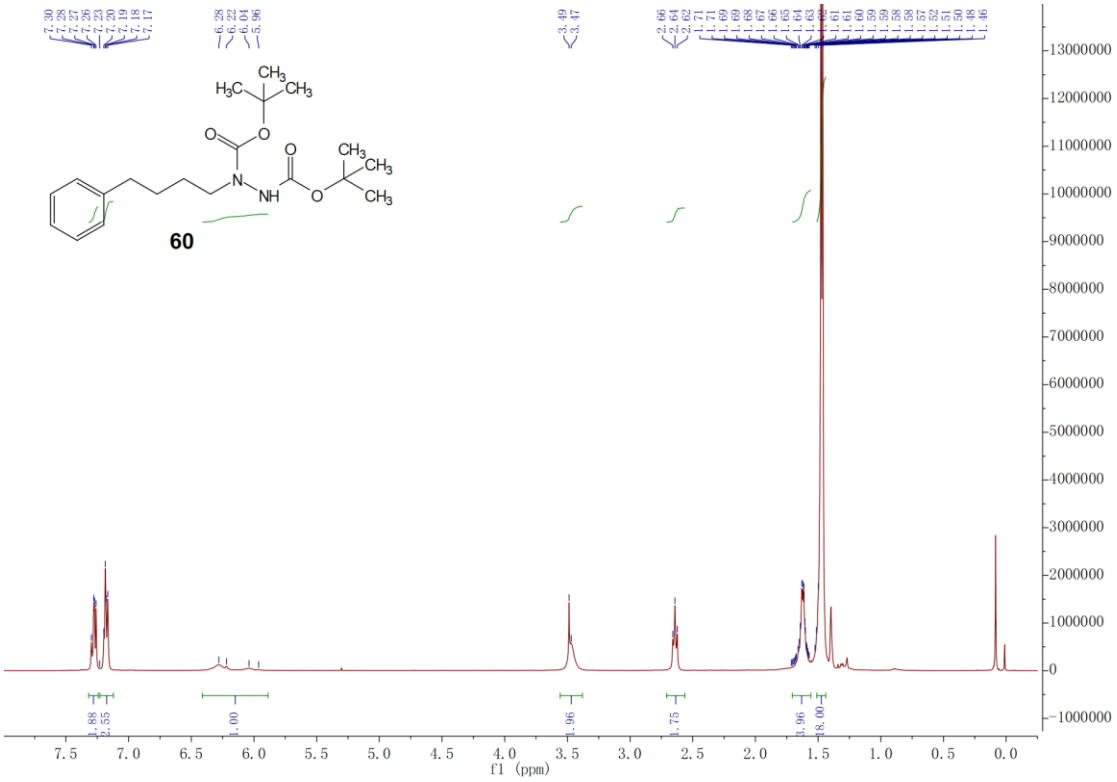

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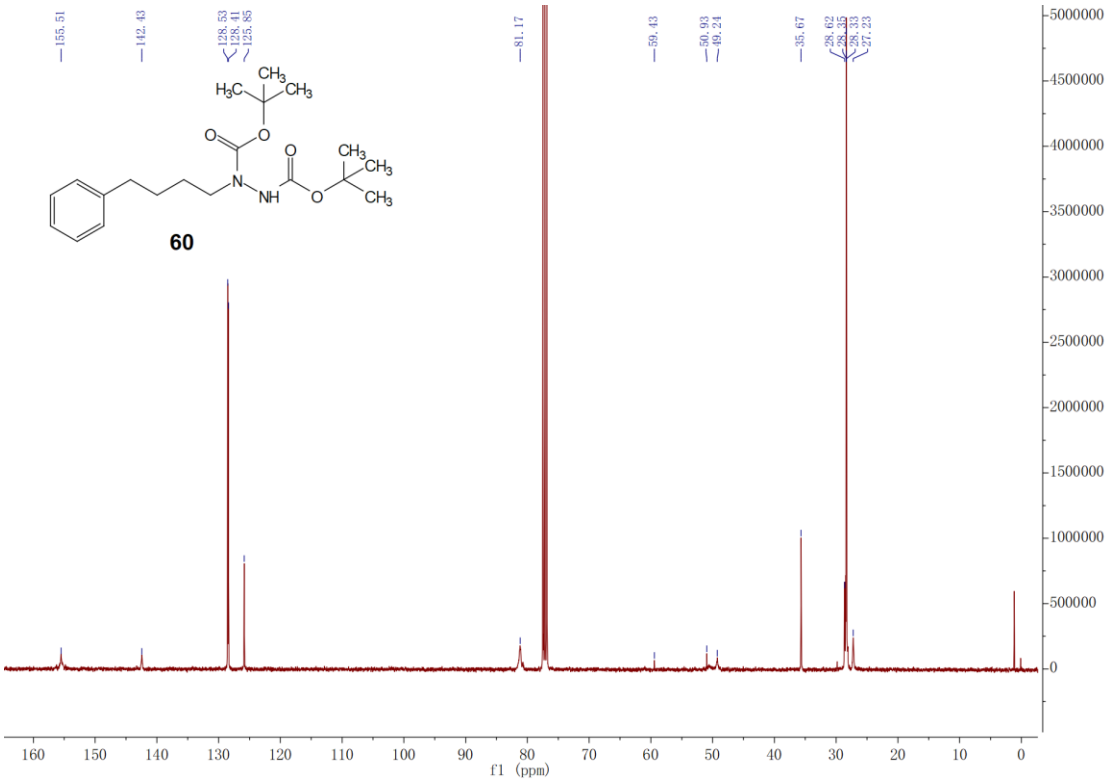

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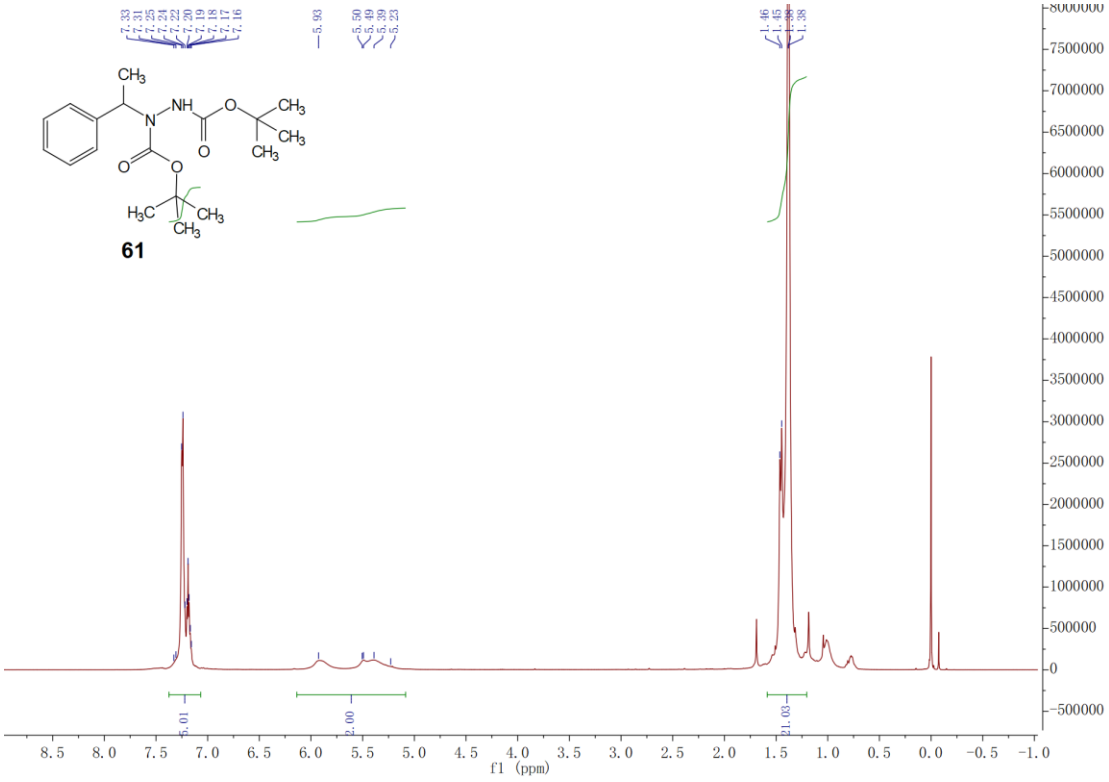
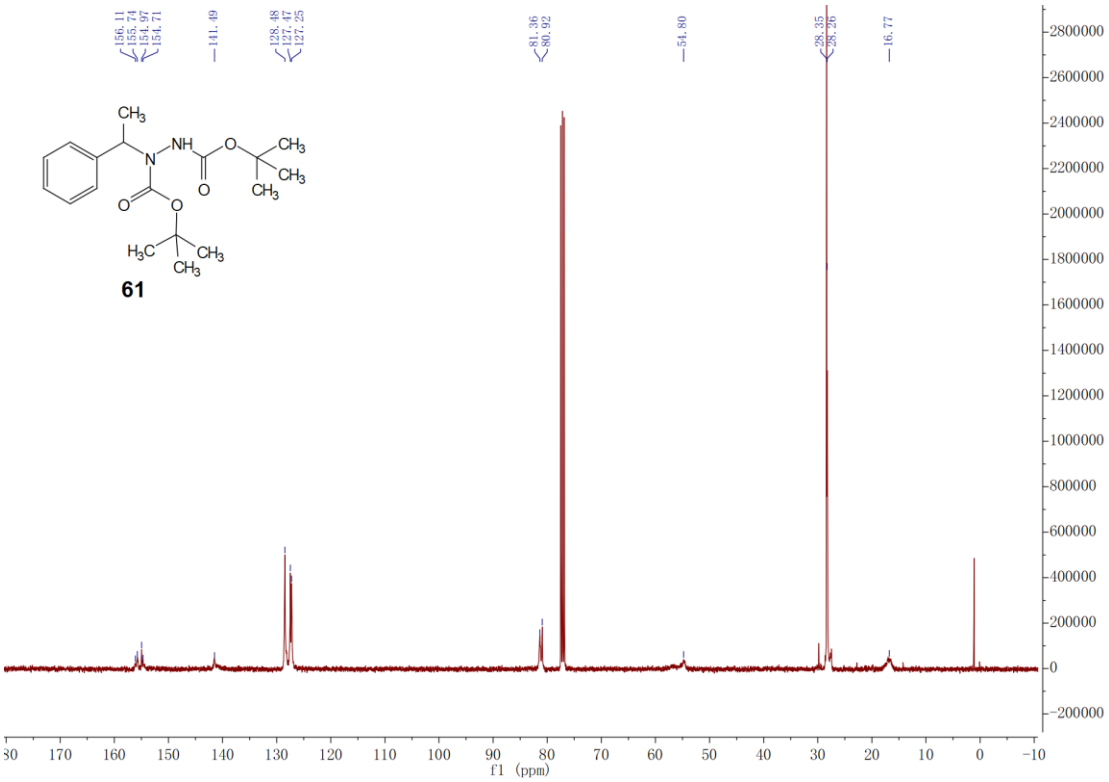


^{13}C NMR (101 MHz, $CDCl_3$)



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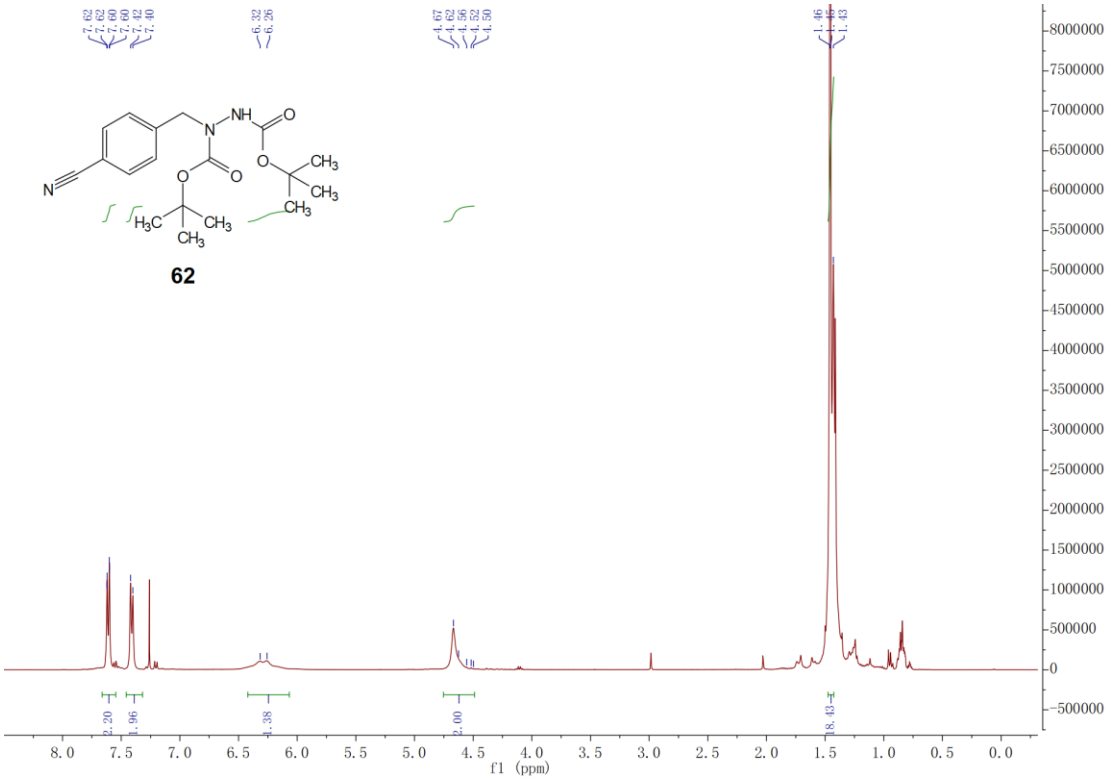

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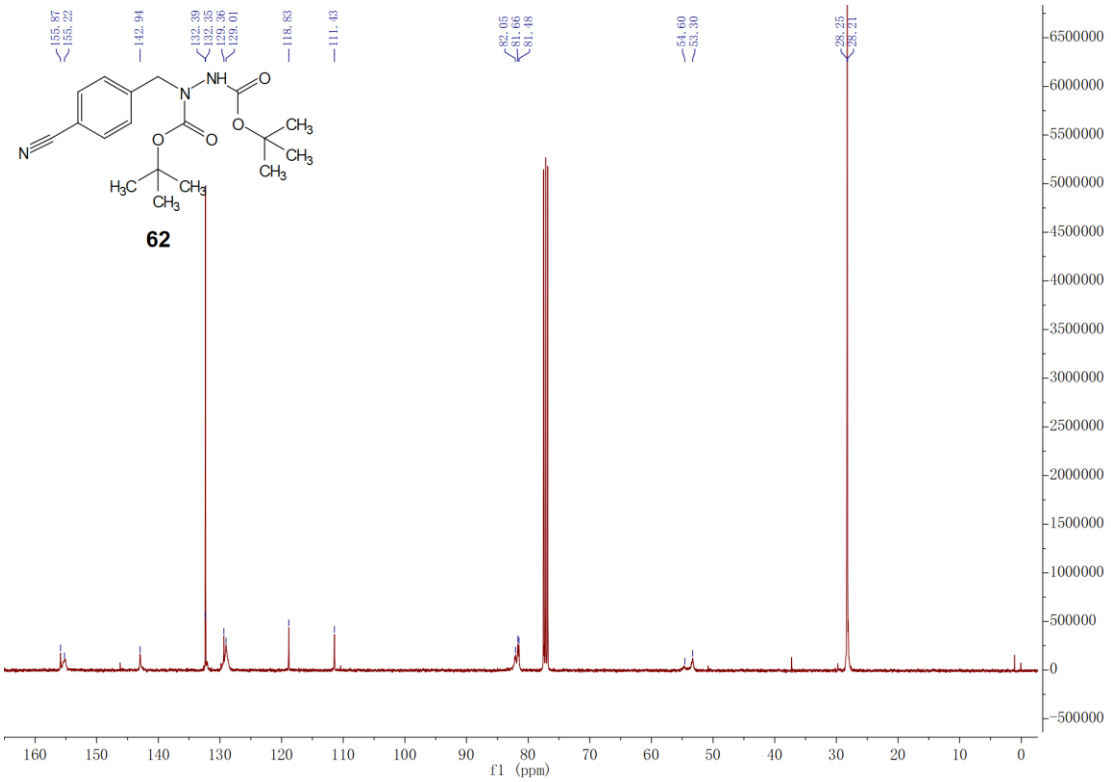

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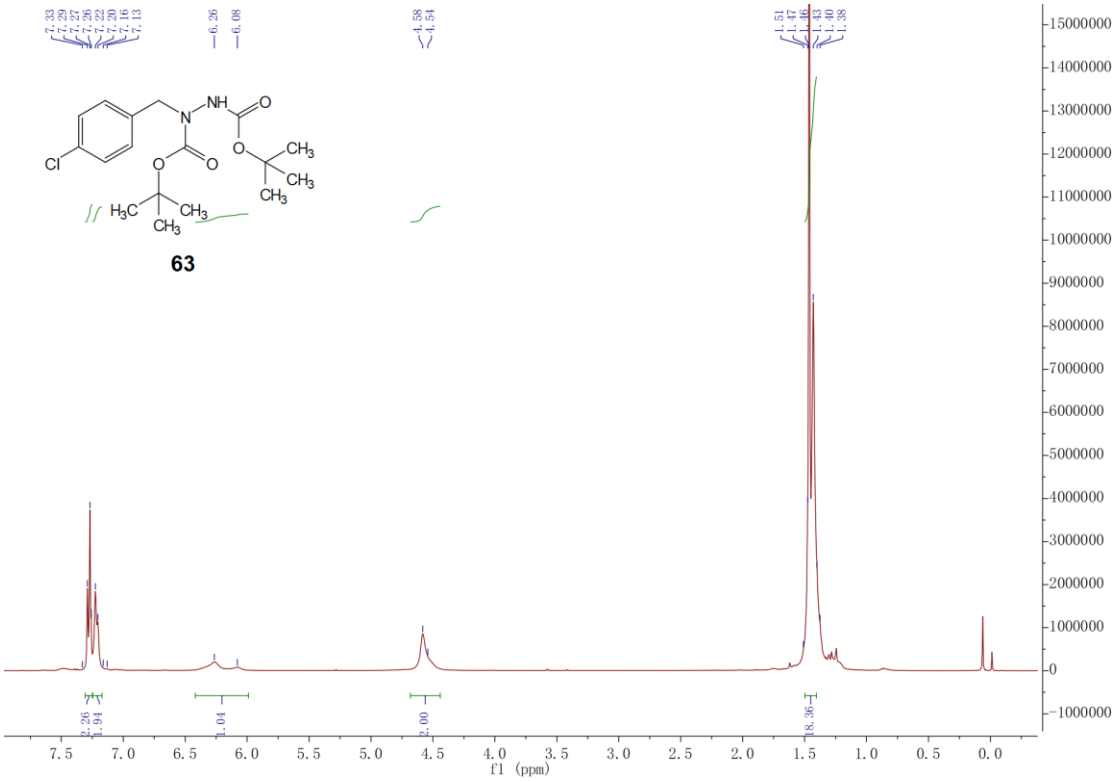

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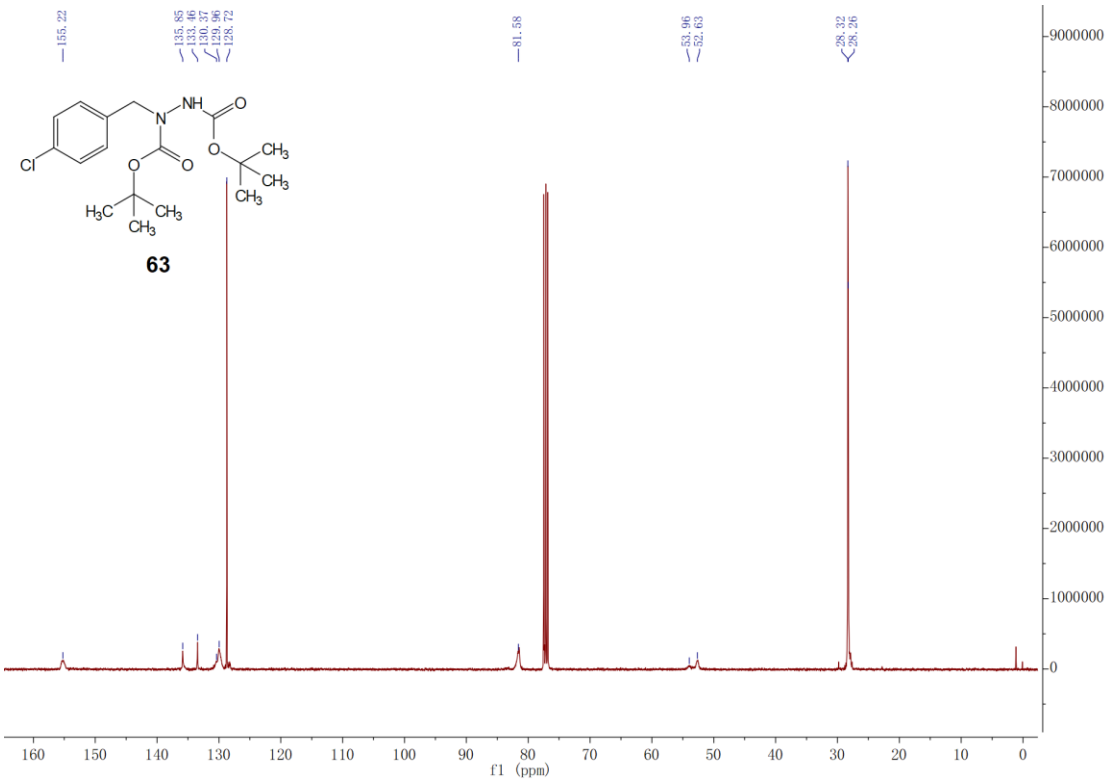

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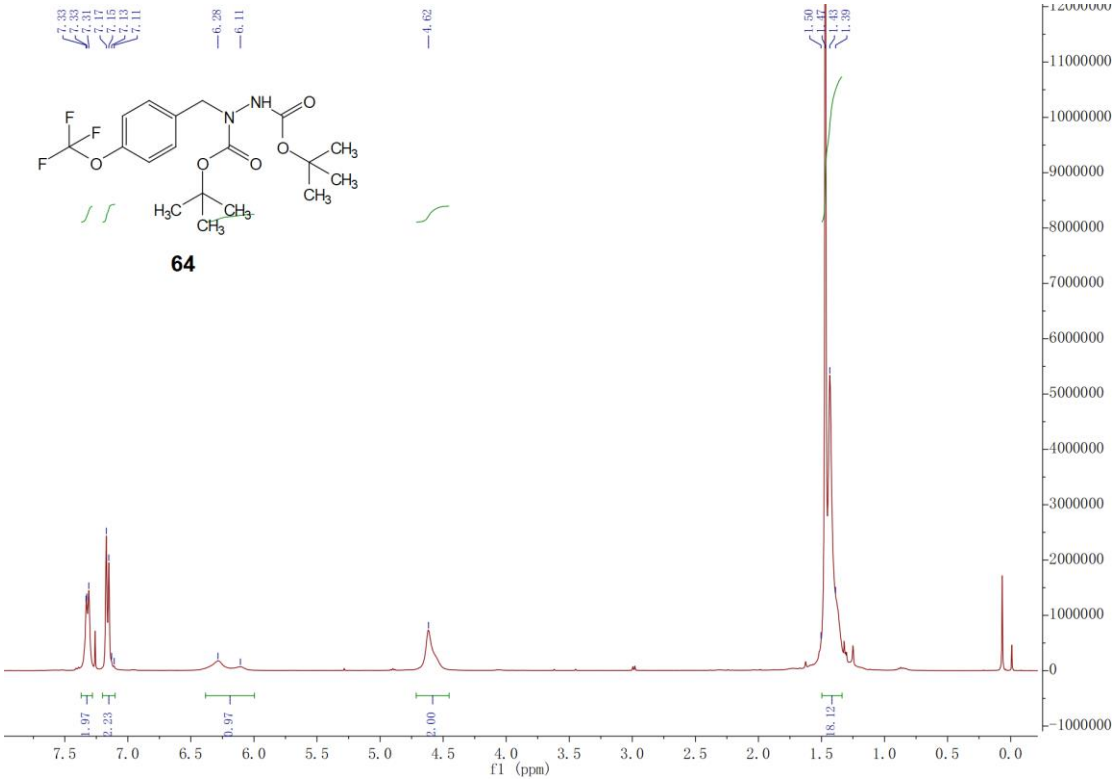
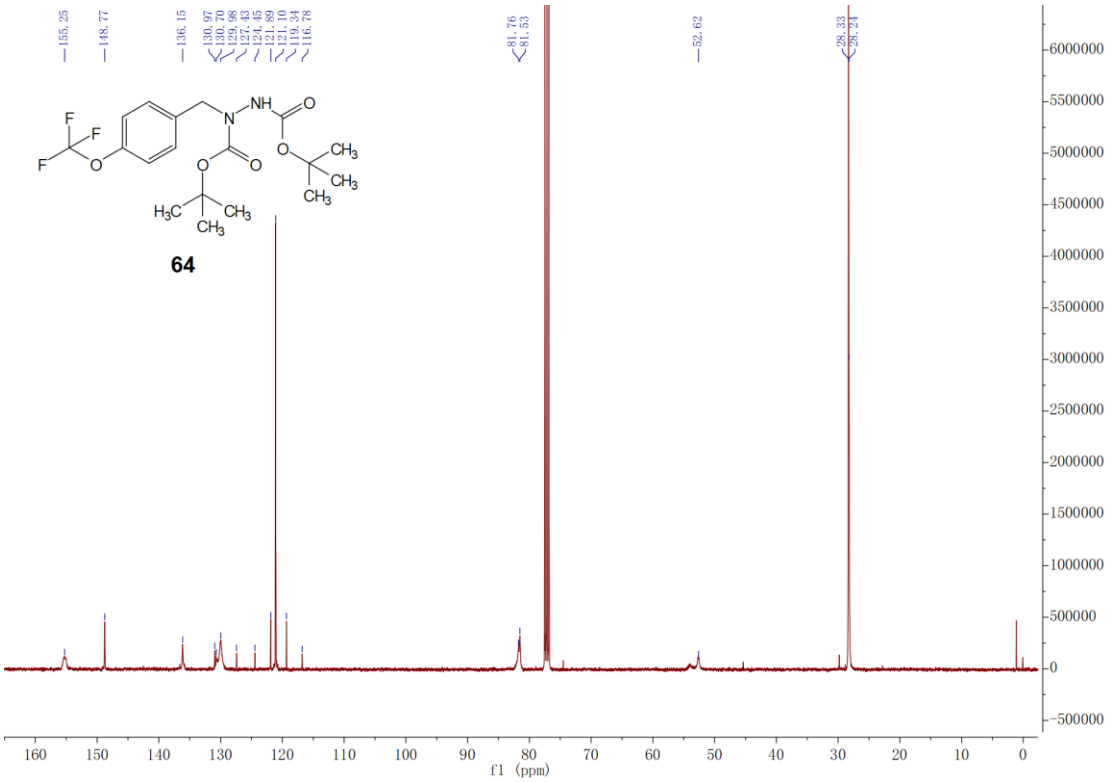
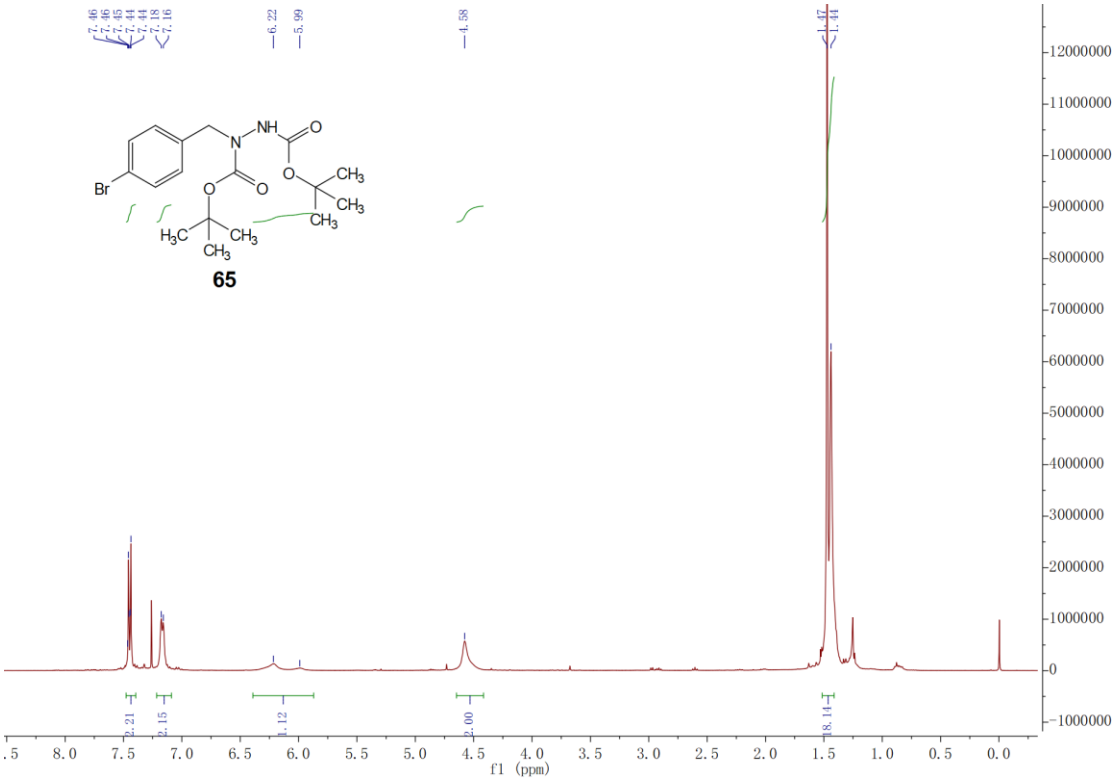
^{1}H NMR (400 MHz, $CDCl_3$)



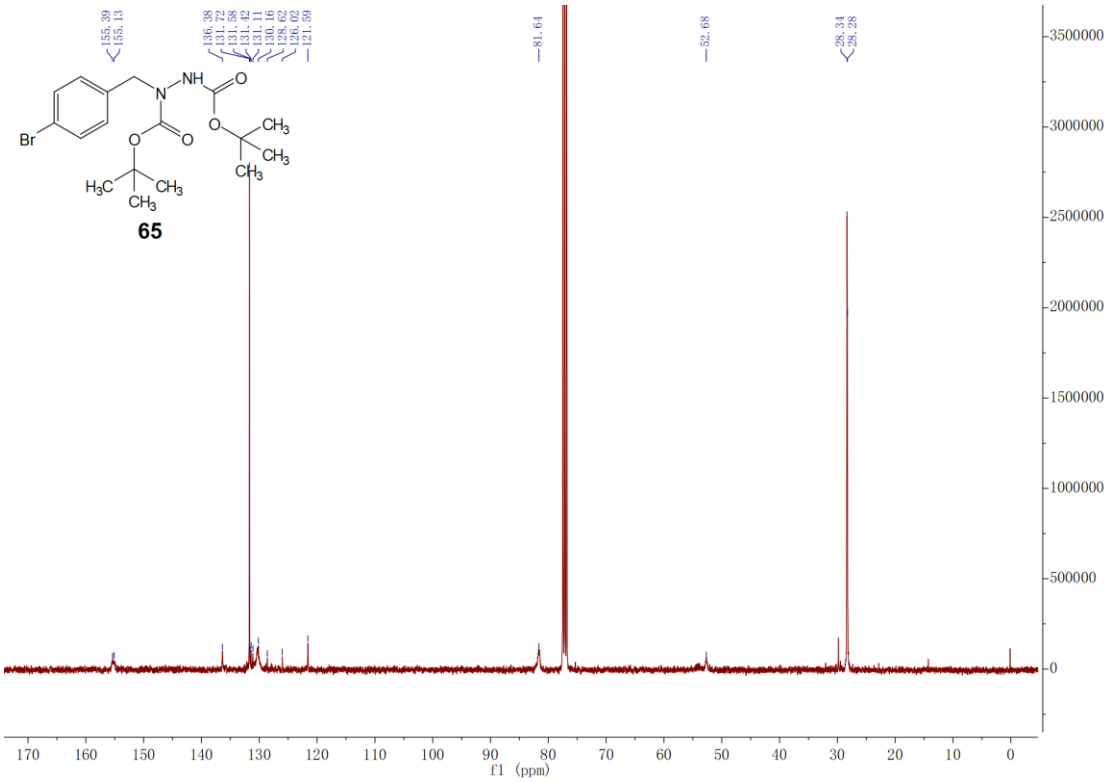
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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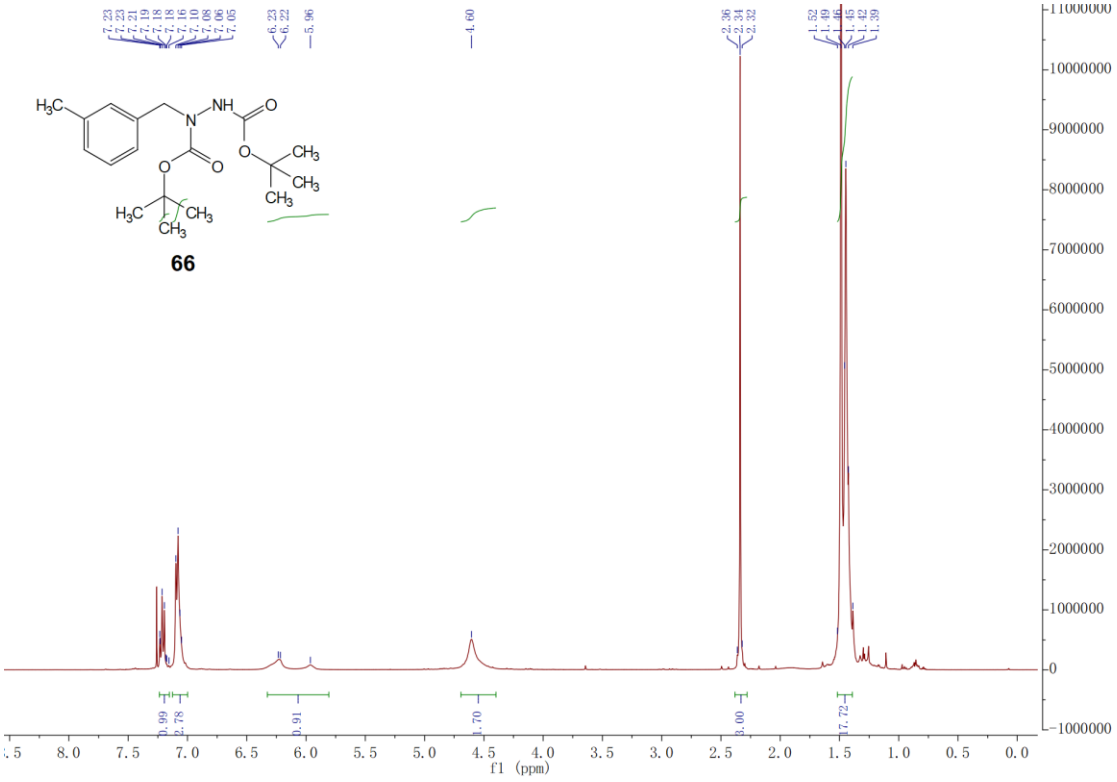

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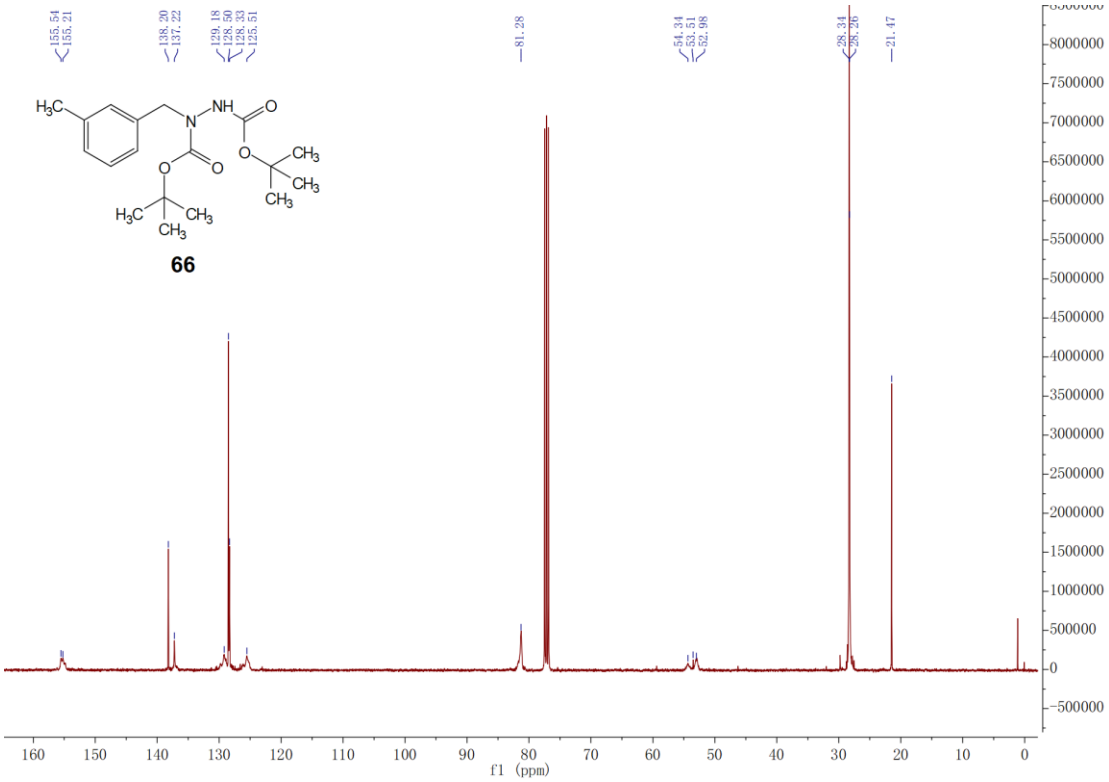

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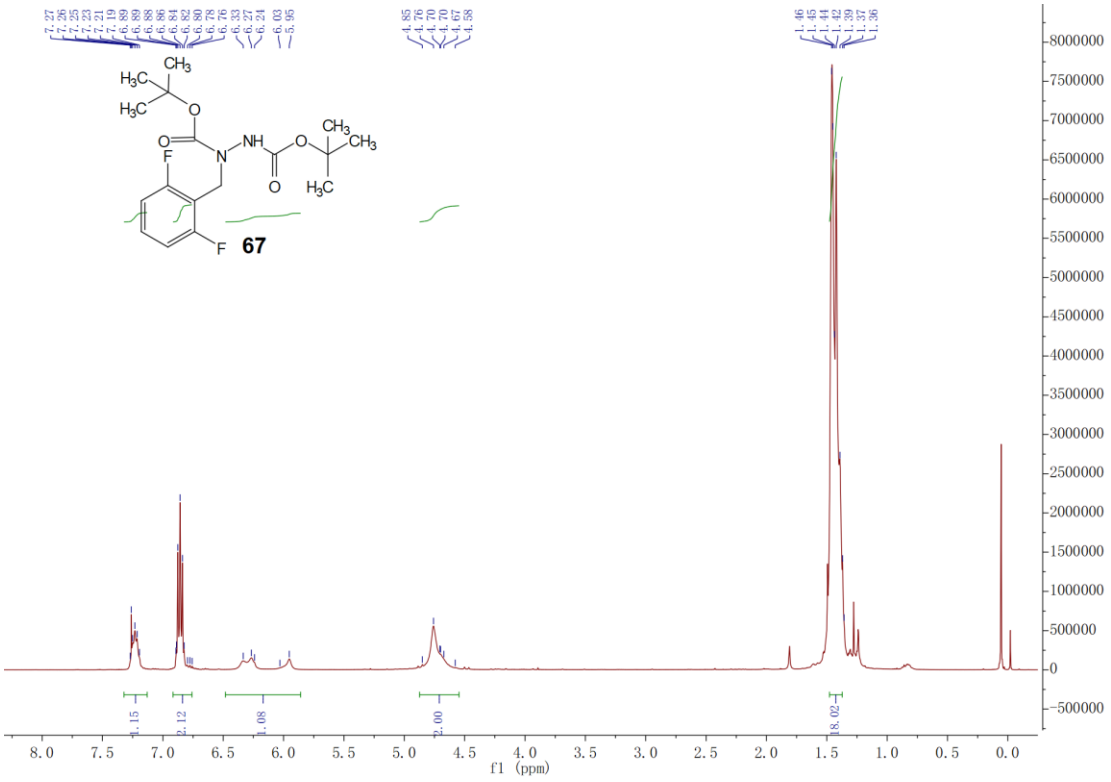
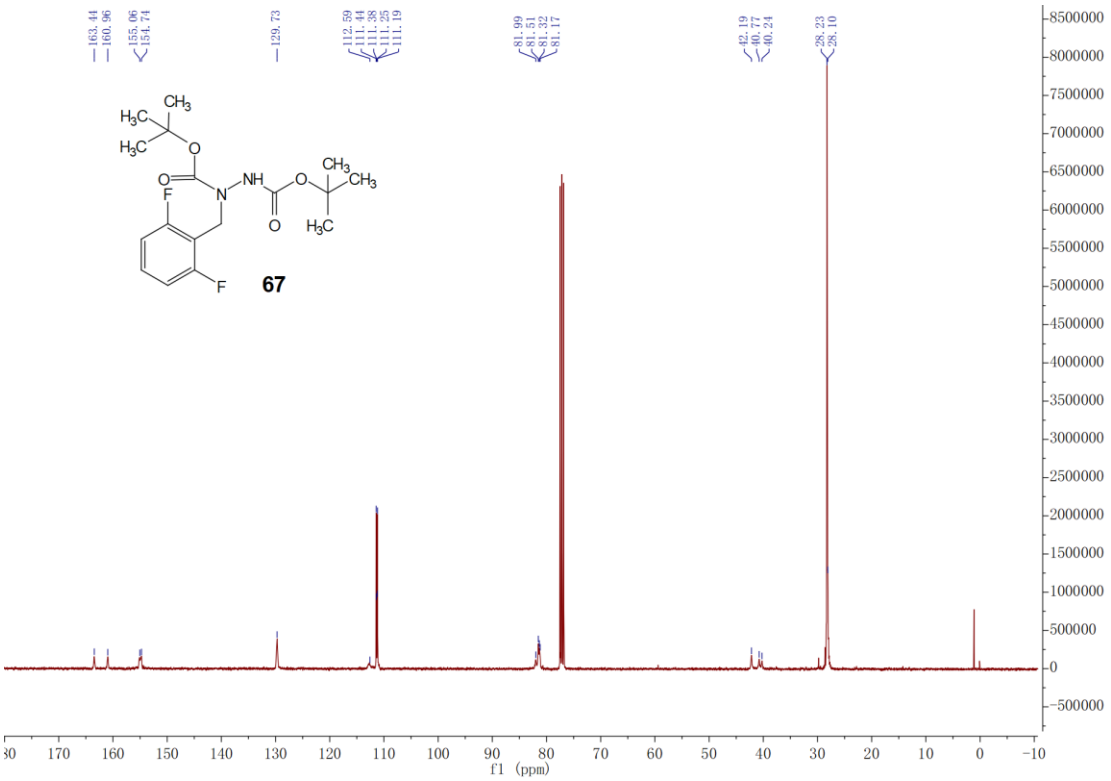


^{13}C NMR (101 MHz, $CDCl_3$)



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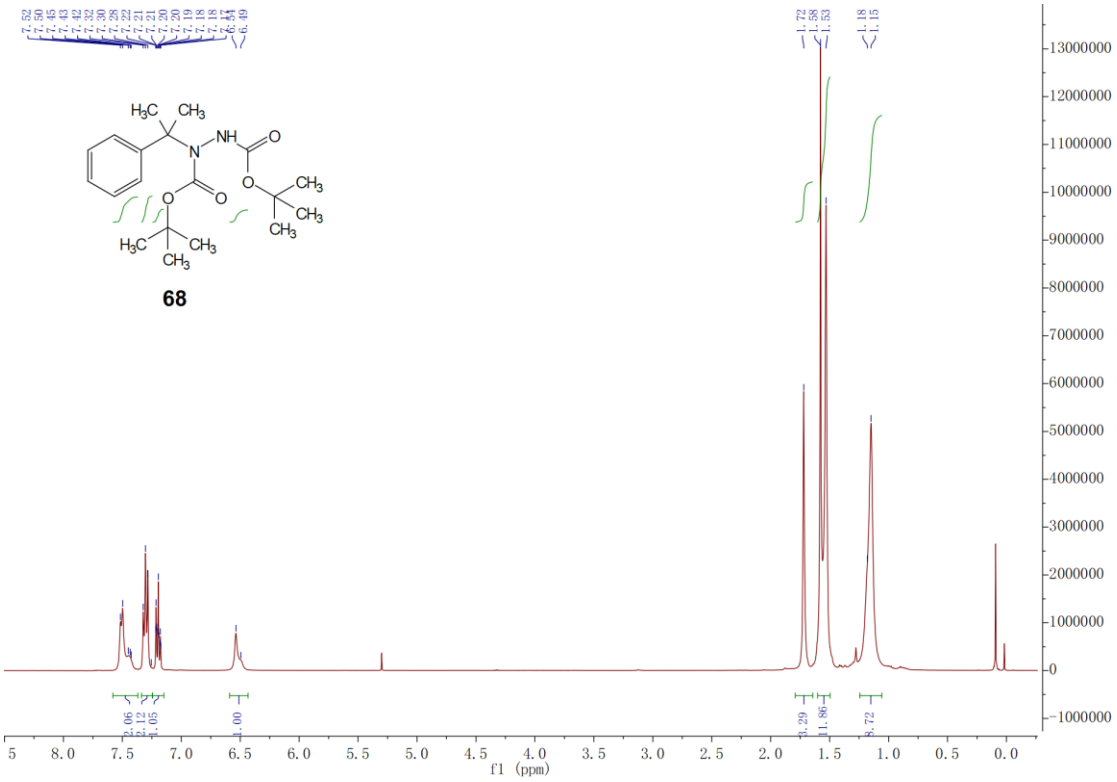
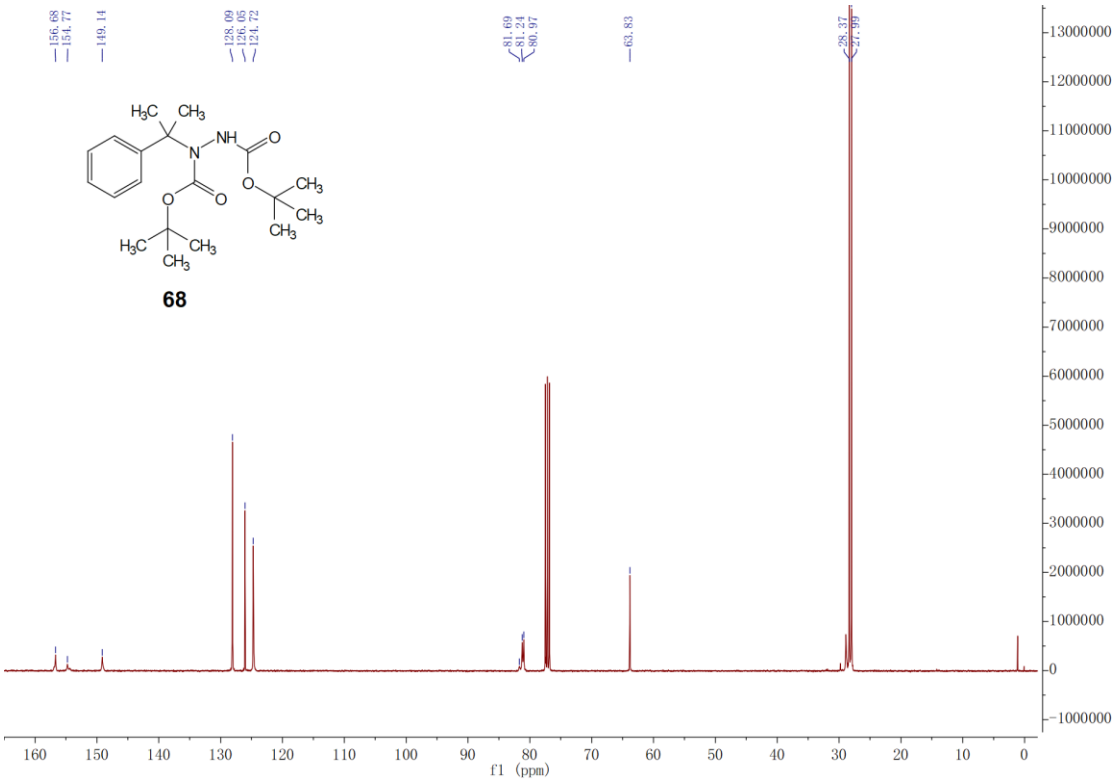


^{13}C NMR (101 MHz, $CDCl_3$)



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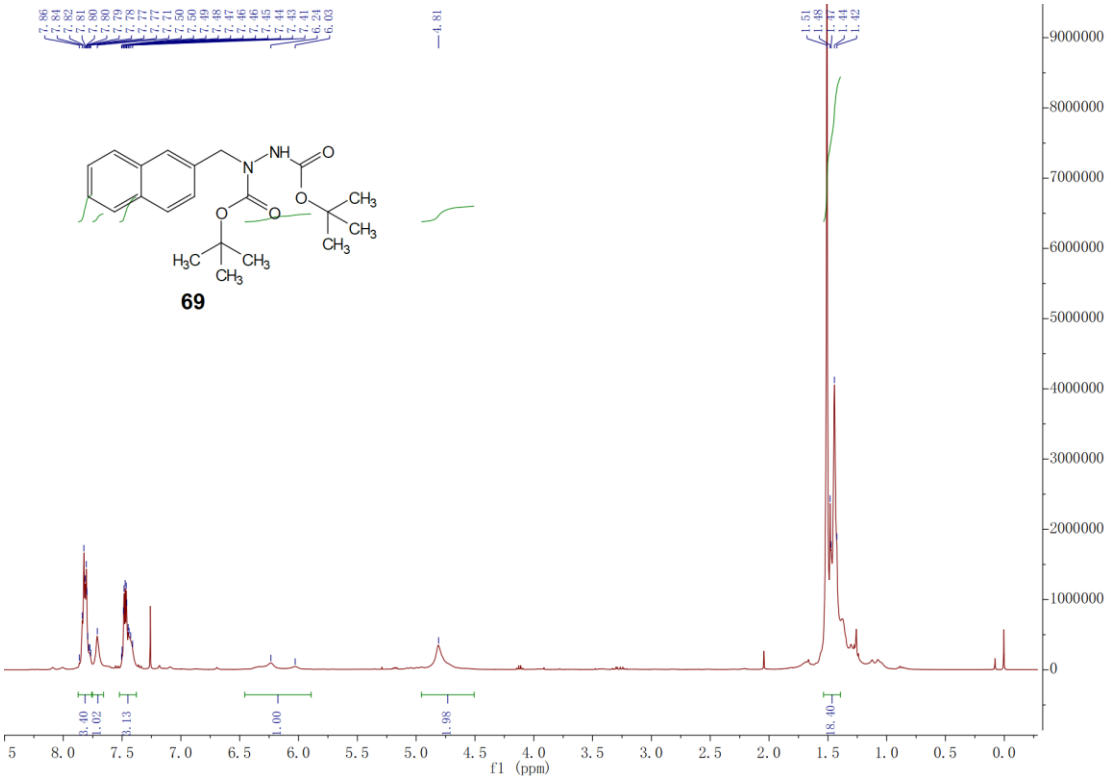

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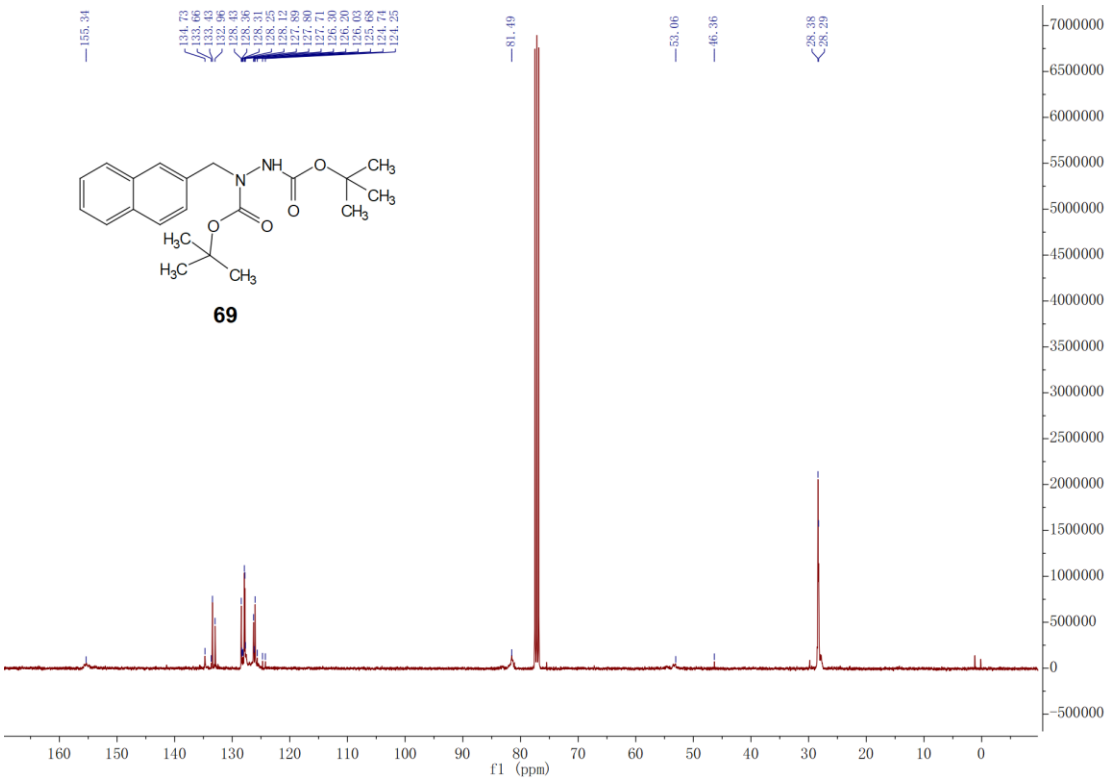

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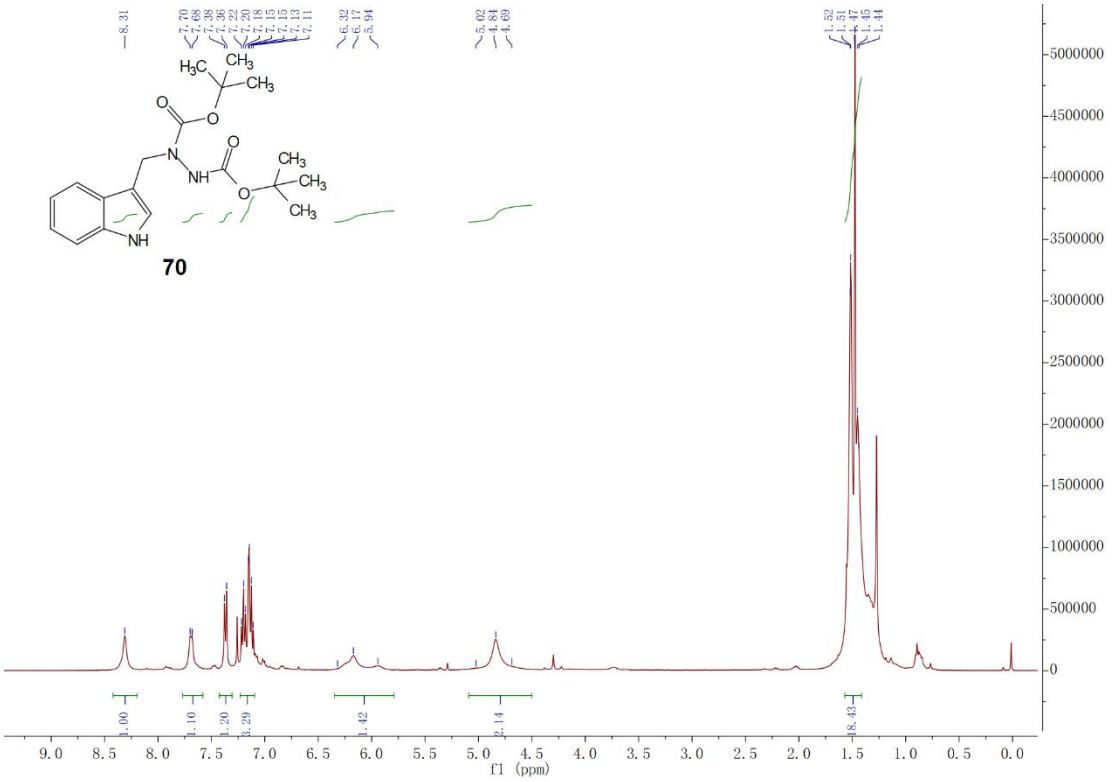

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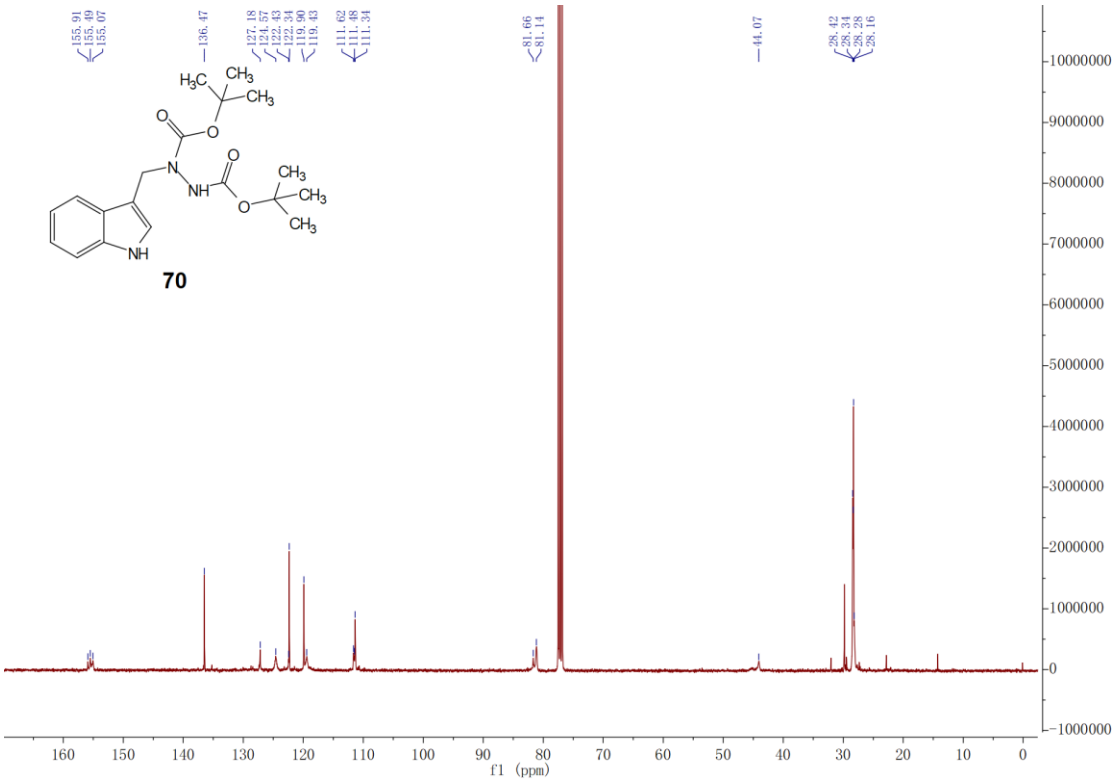

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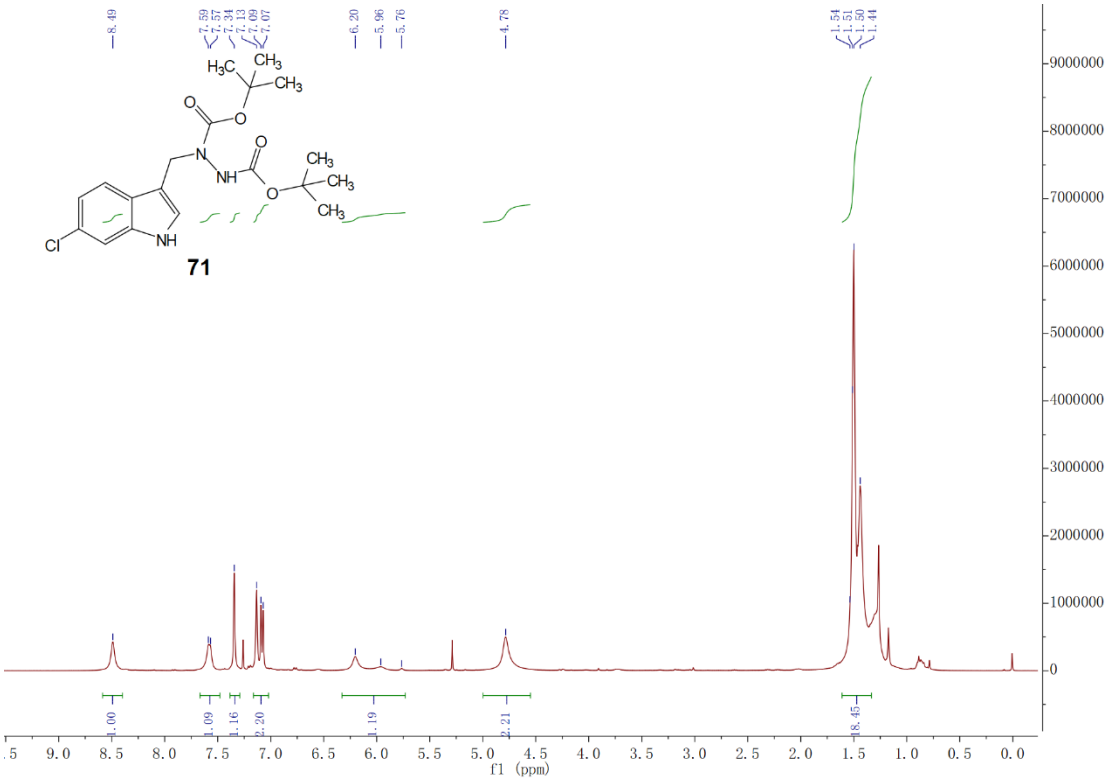

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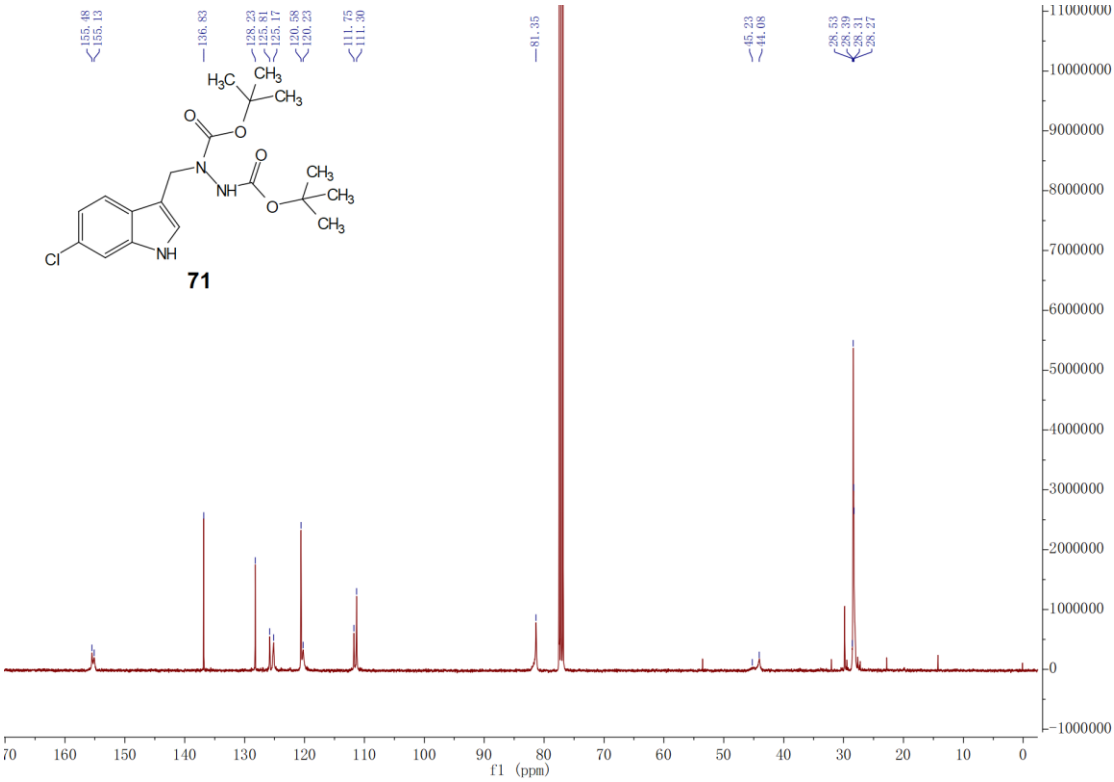

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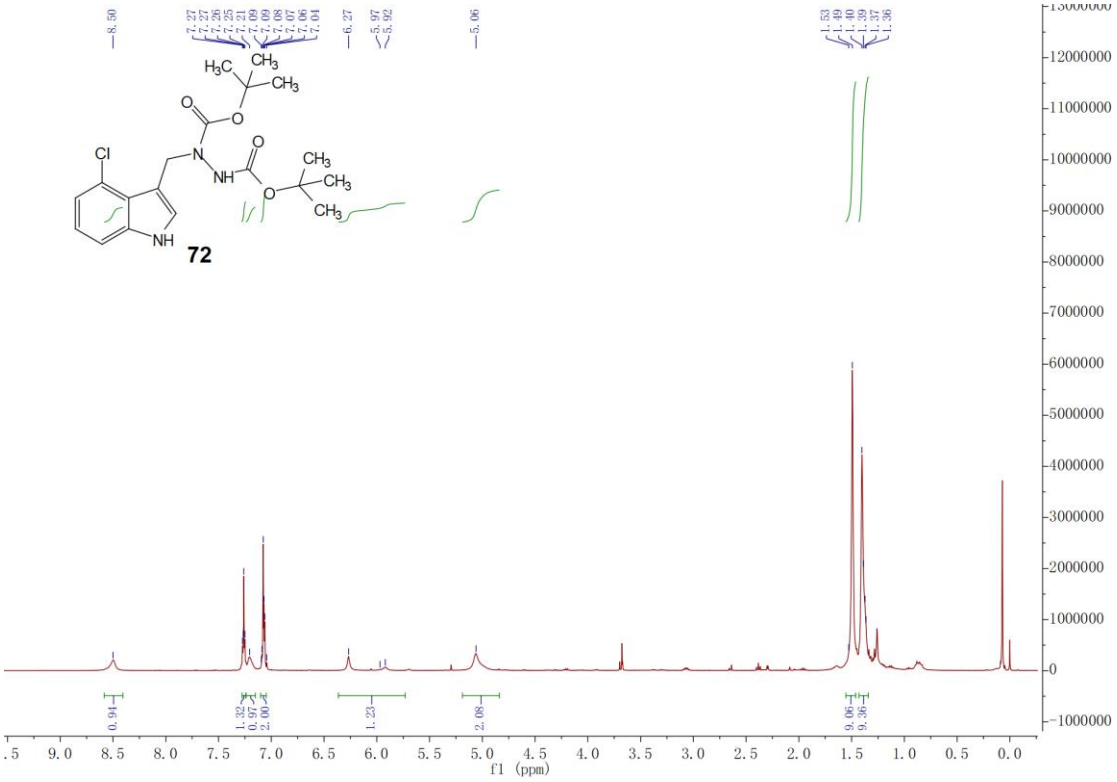

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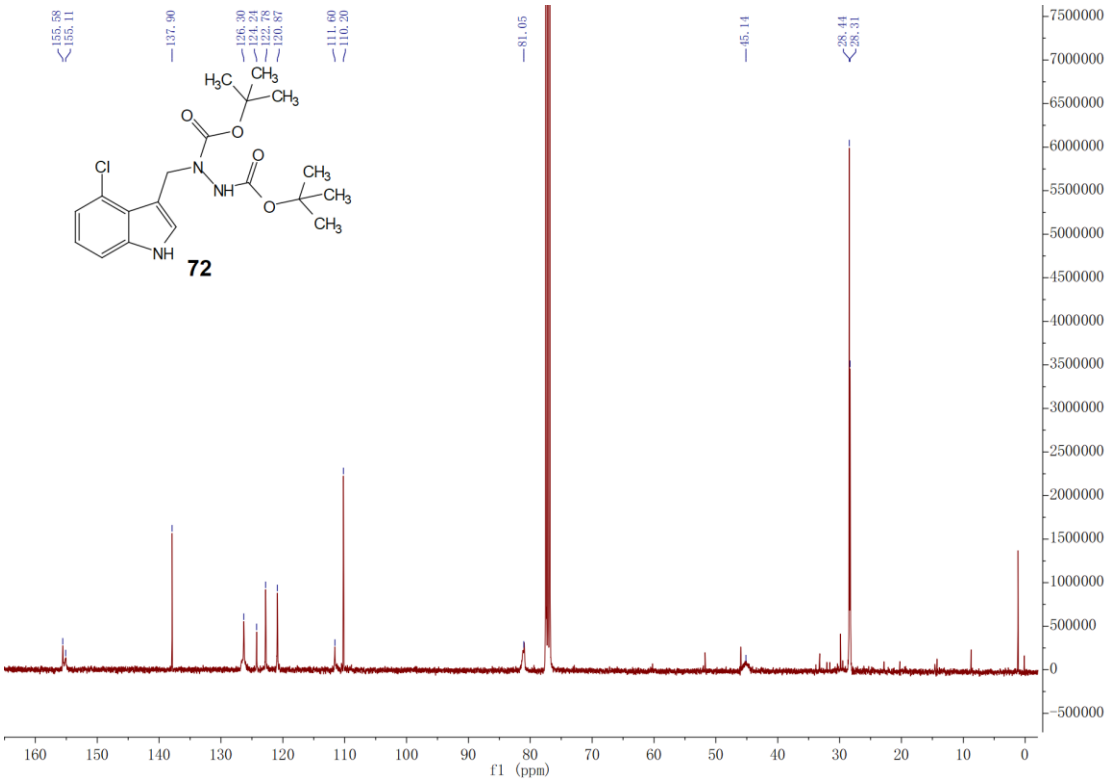

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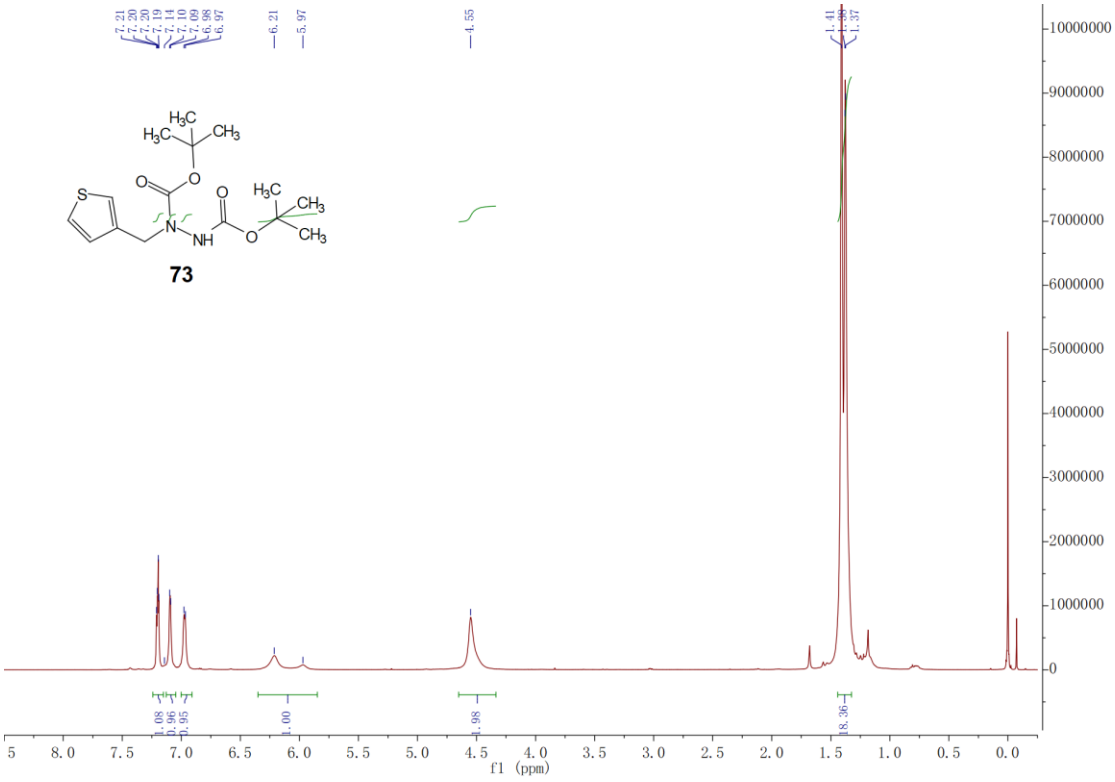

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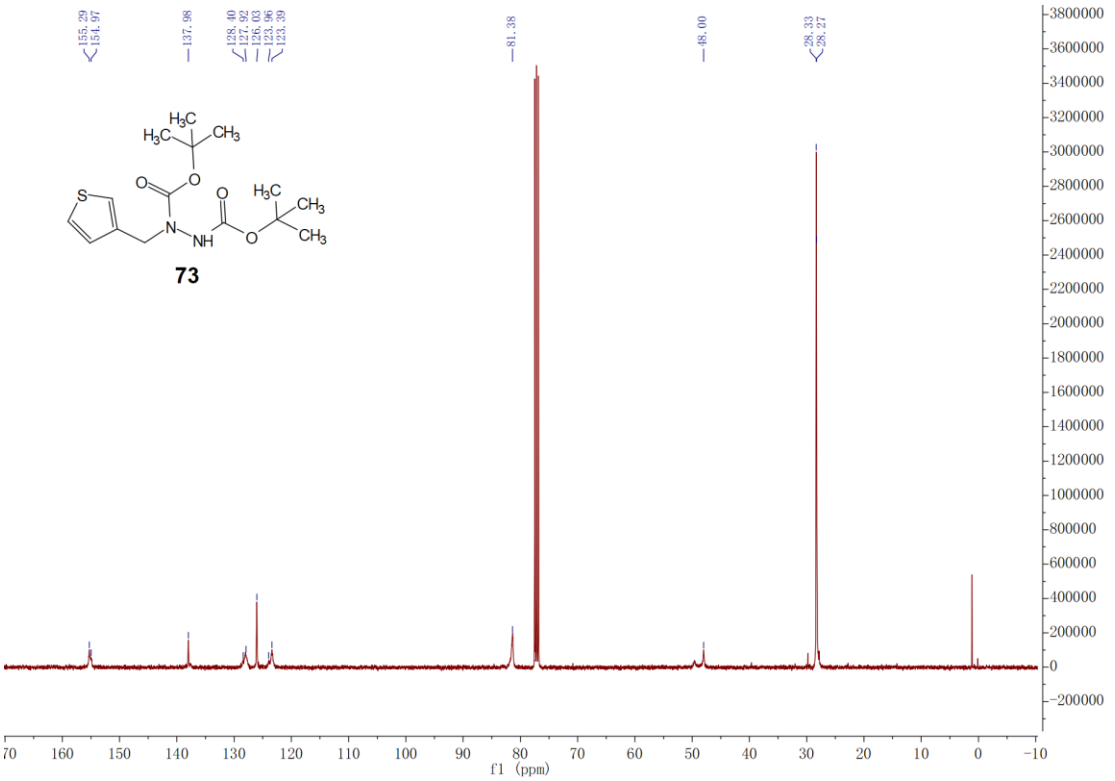

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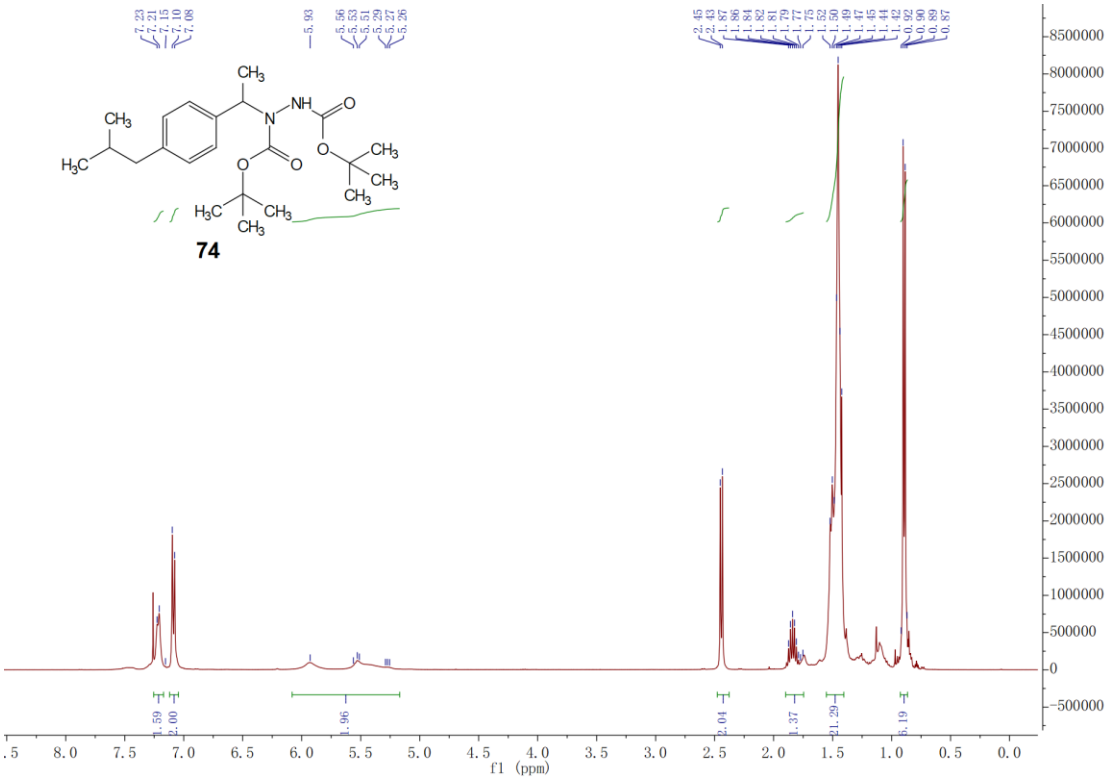

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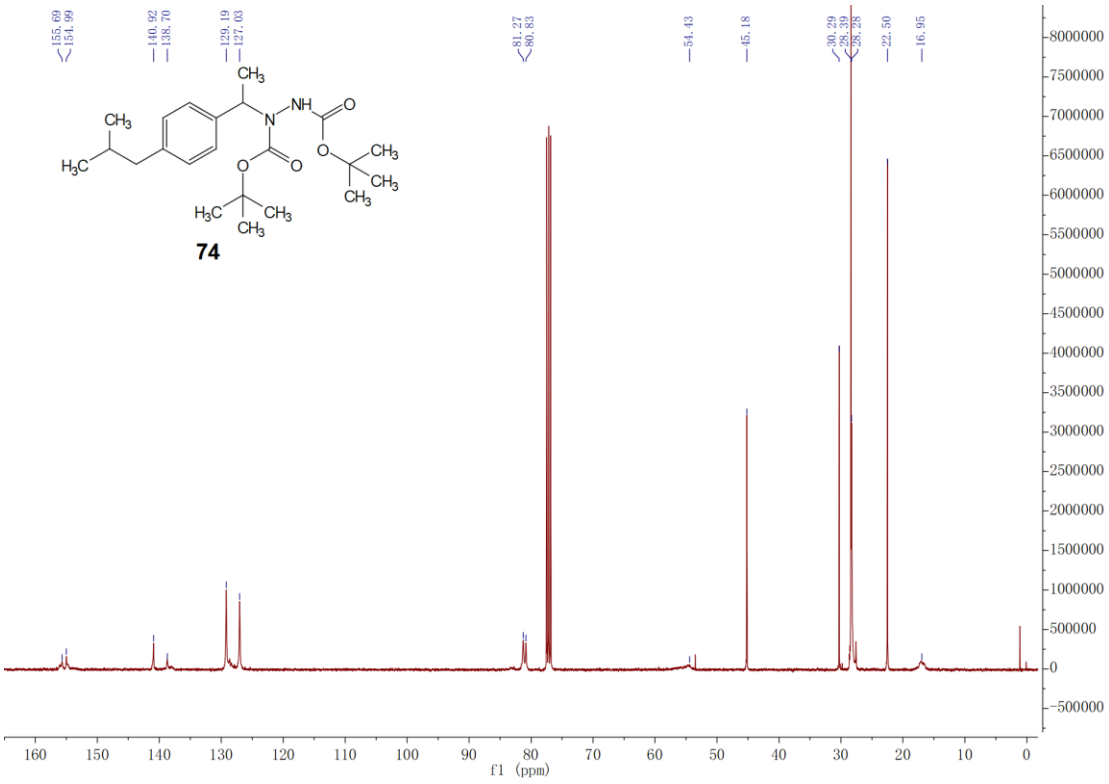

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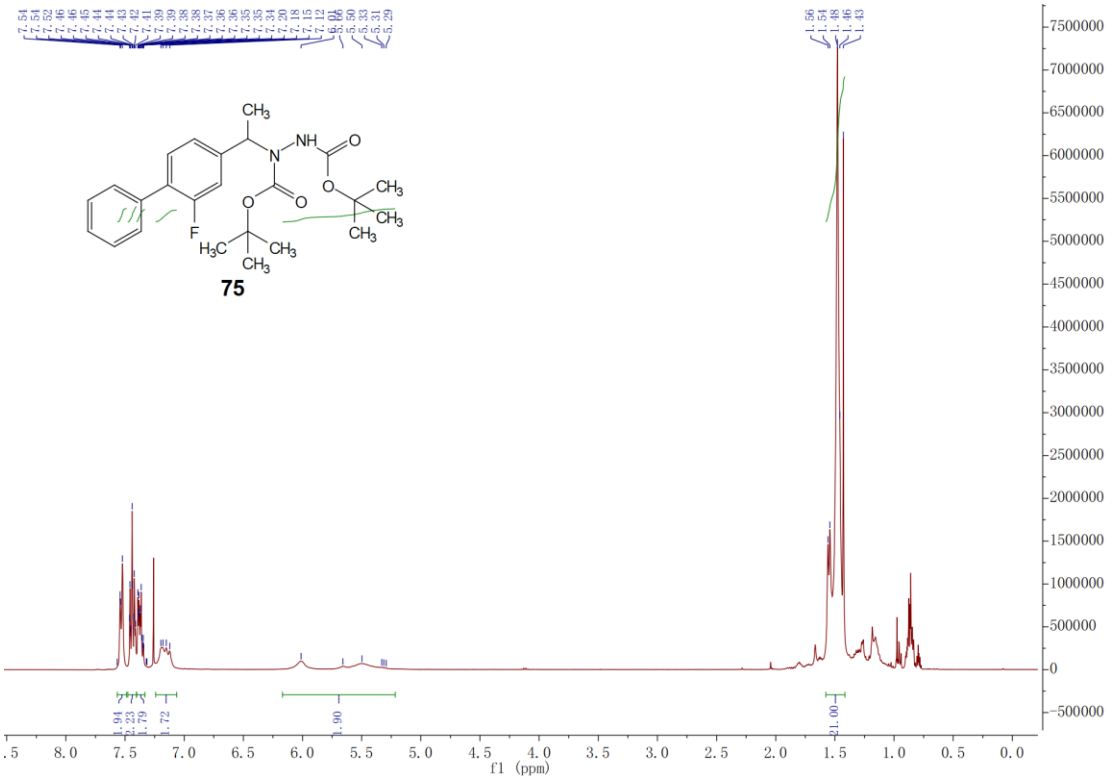

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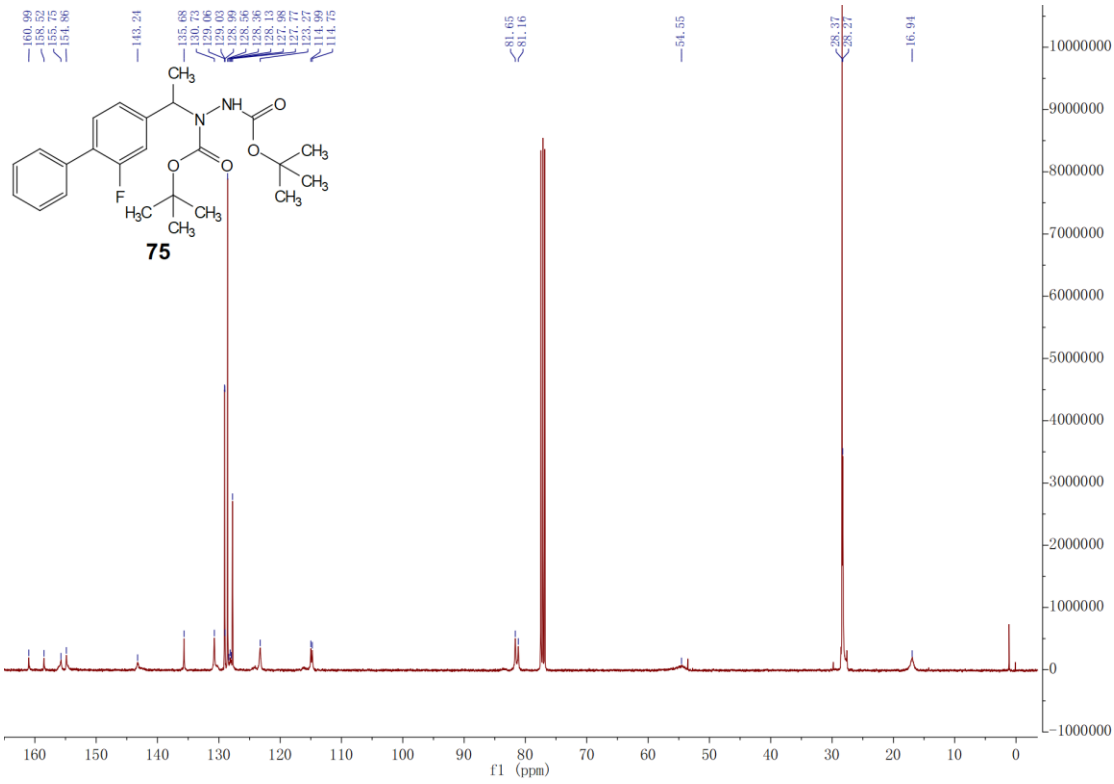

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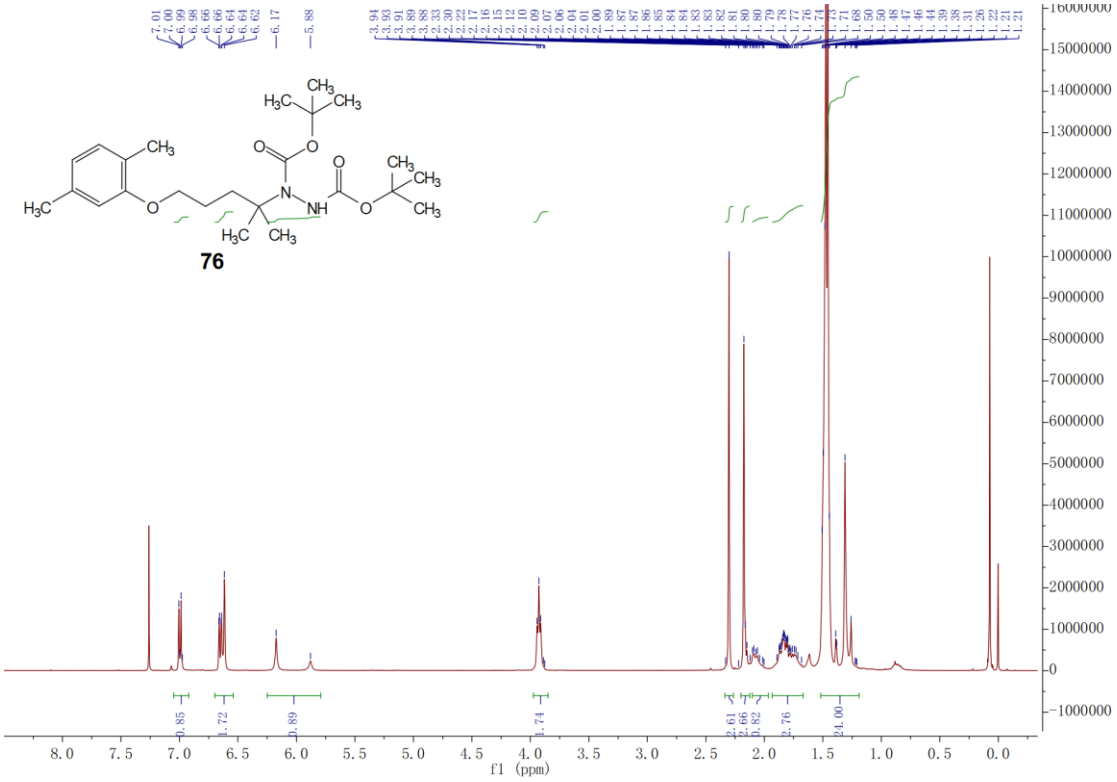

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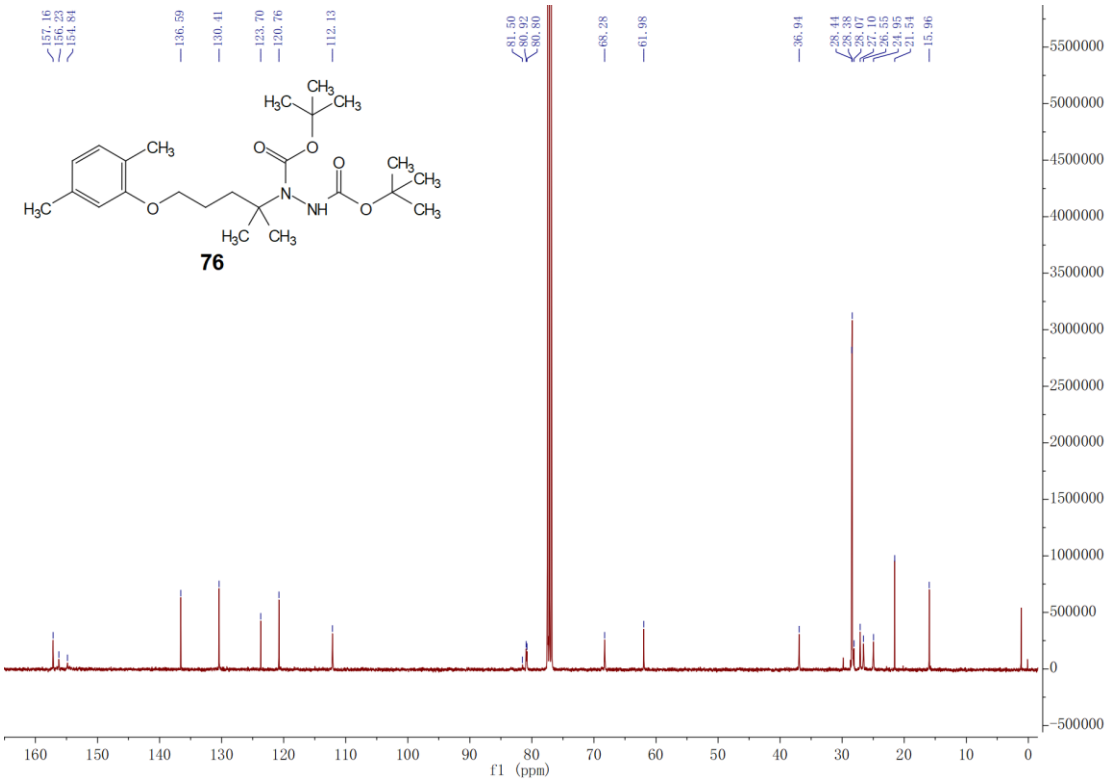

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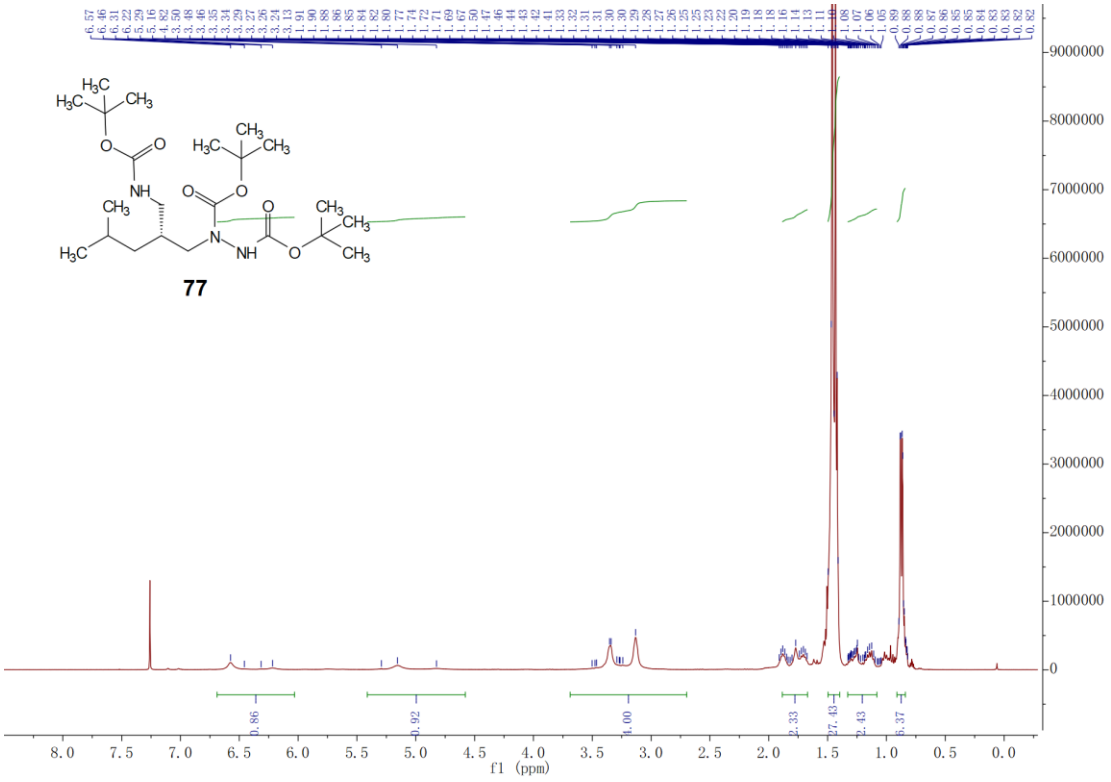

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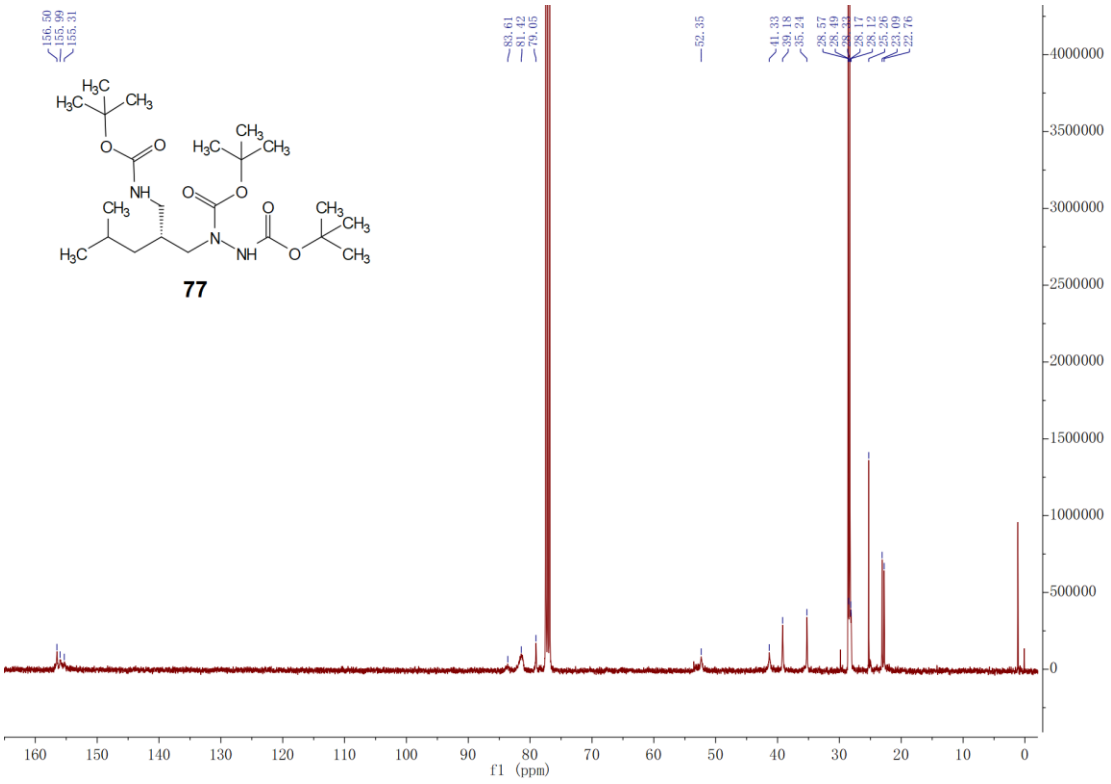

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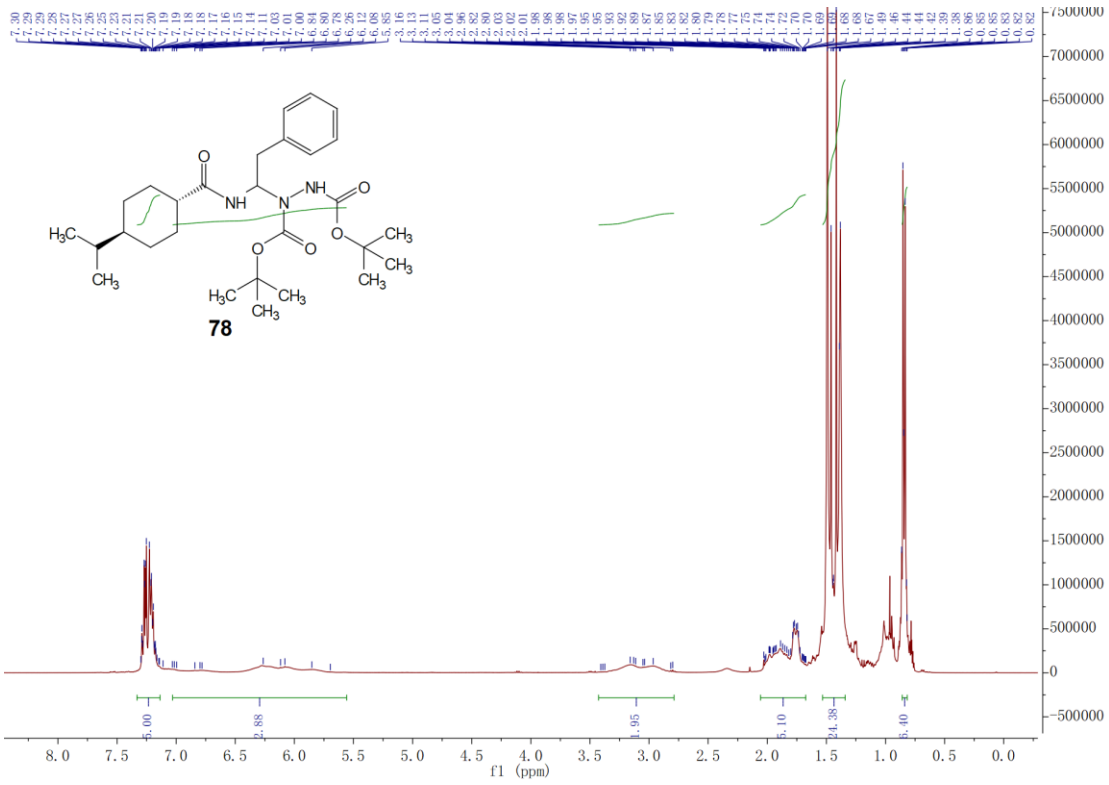

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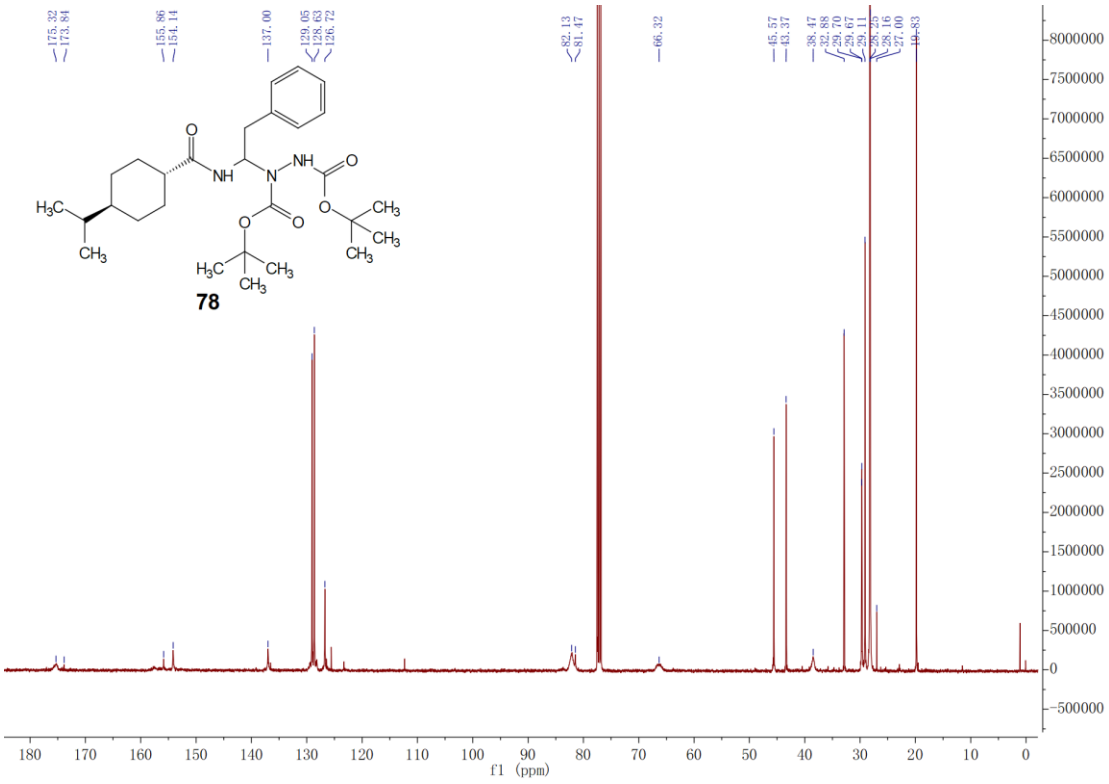
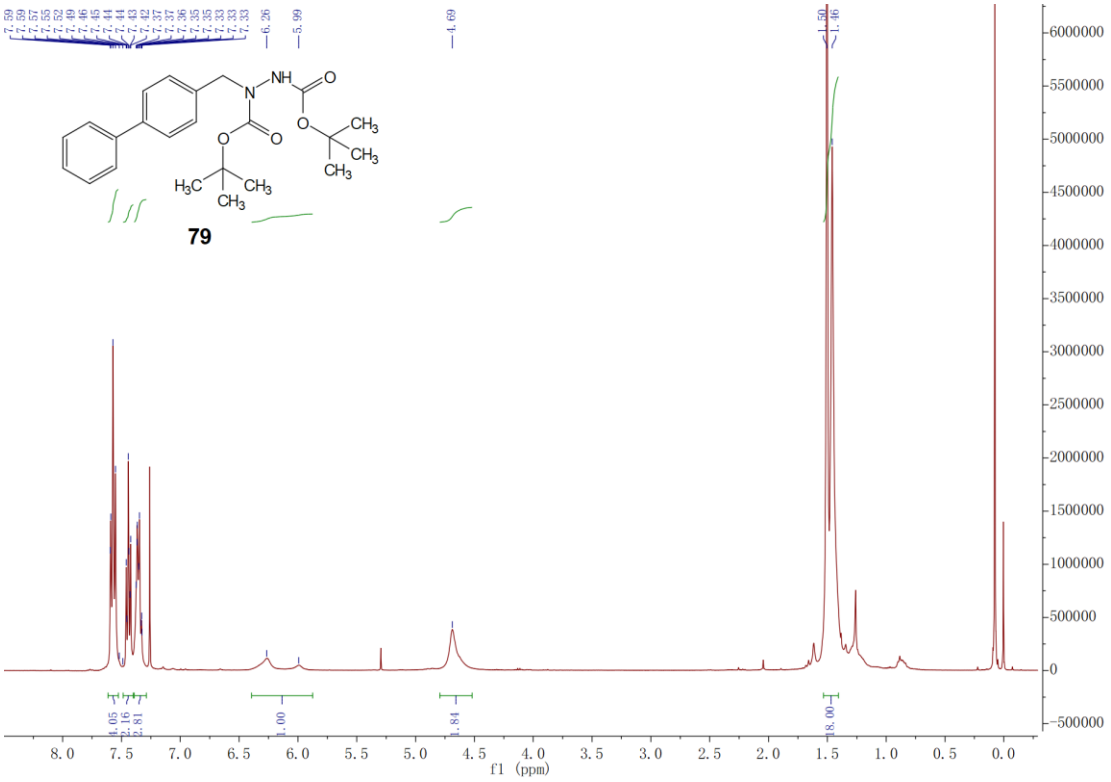


^{1}H NMR (400 MHz, $CDCl_3$)



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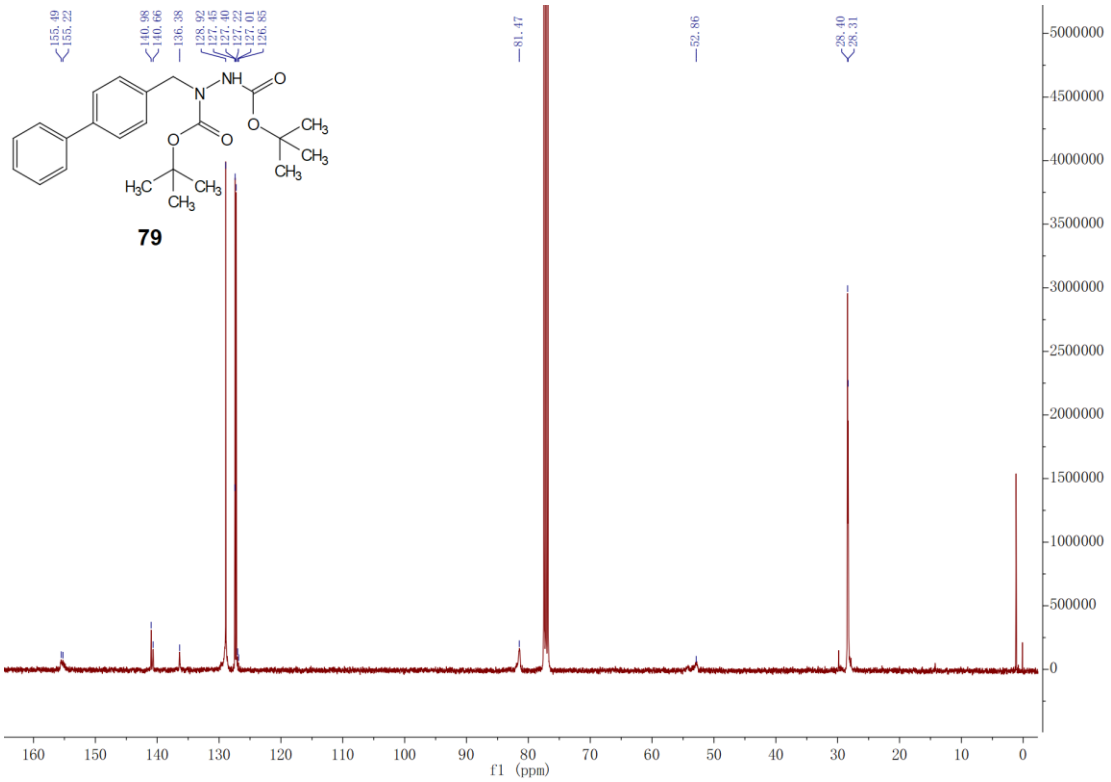

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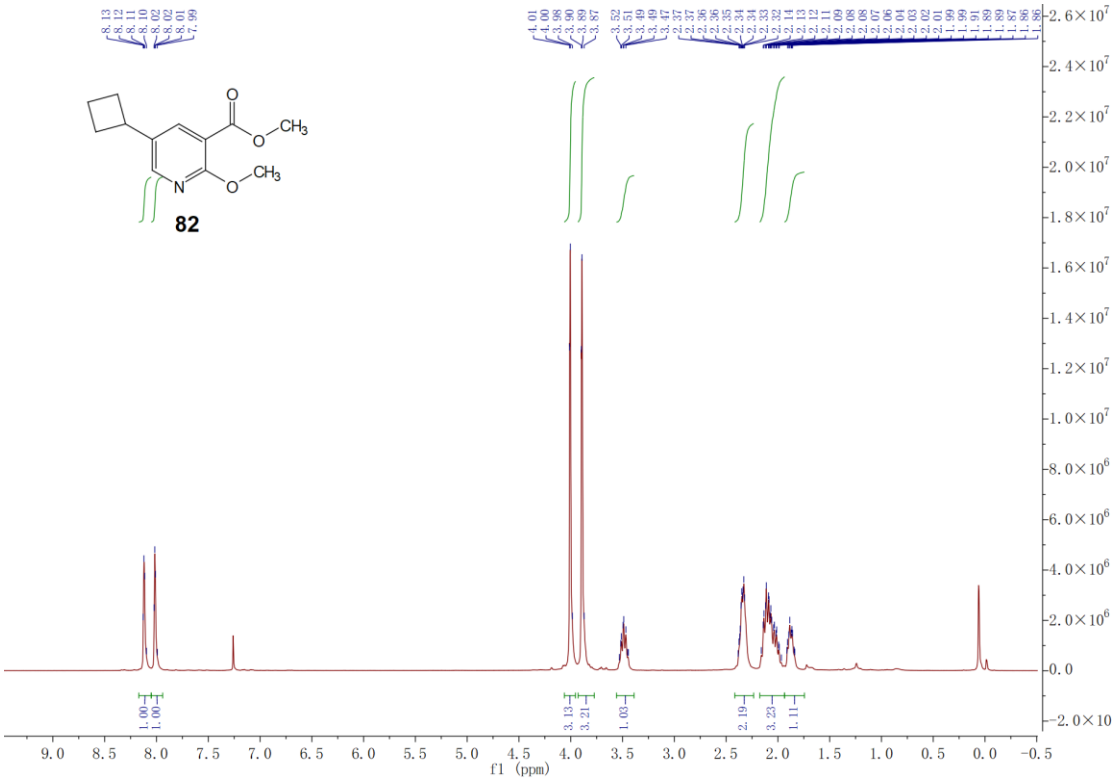

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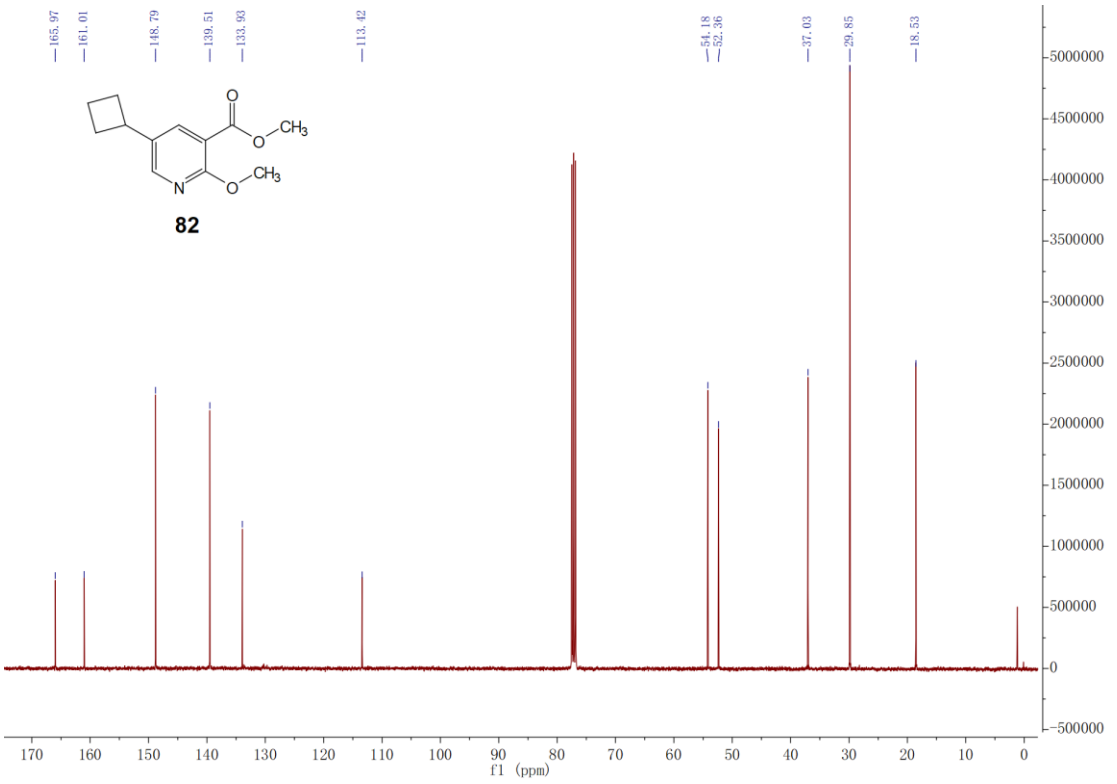

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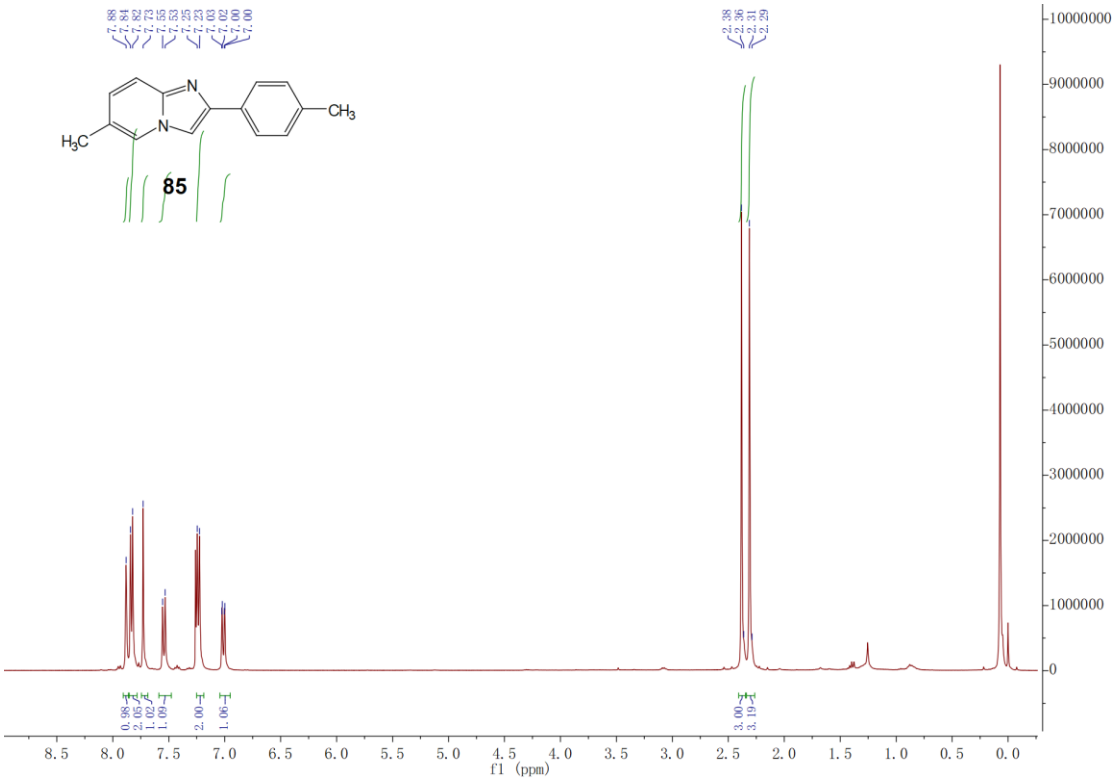

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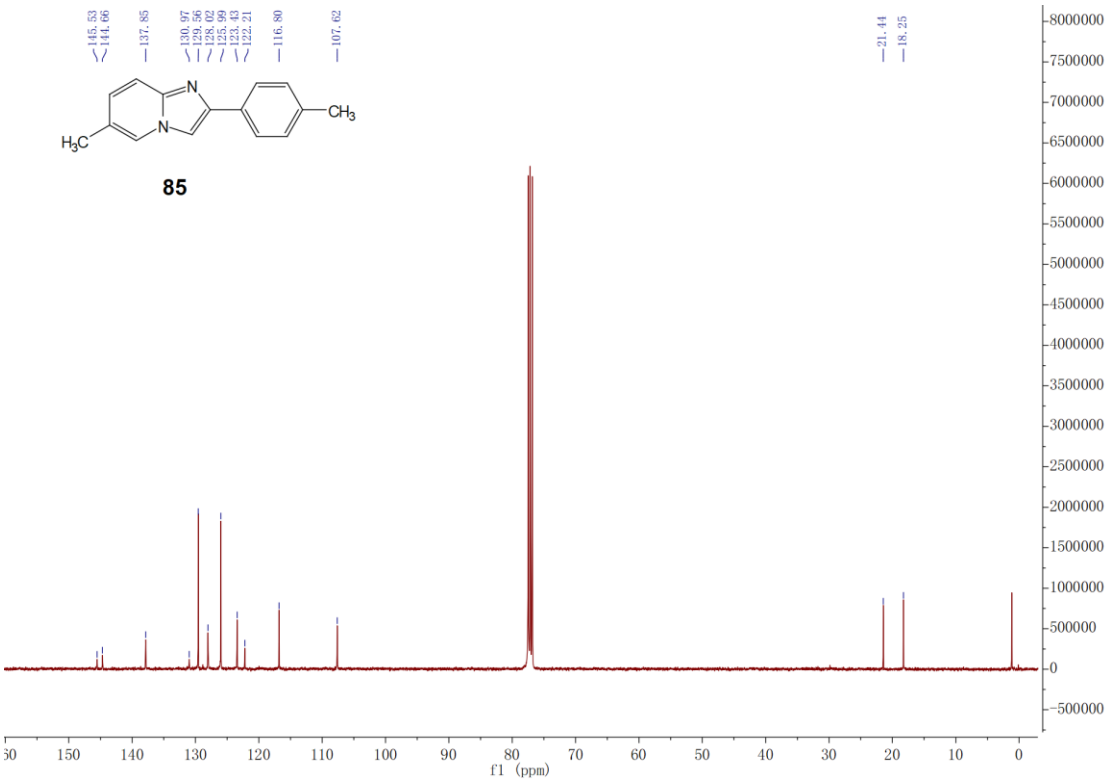

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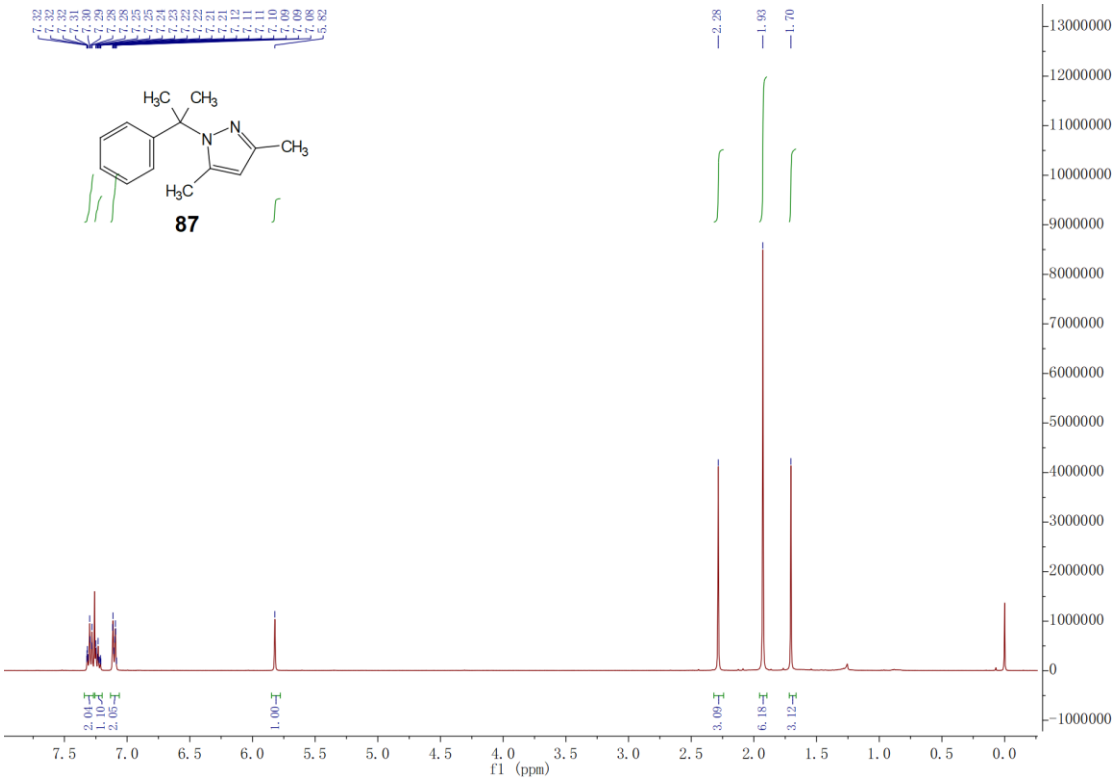

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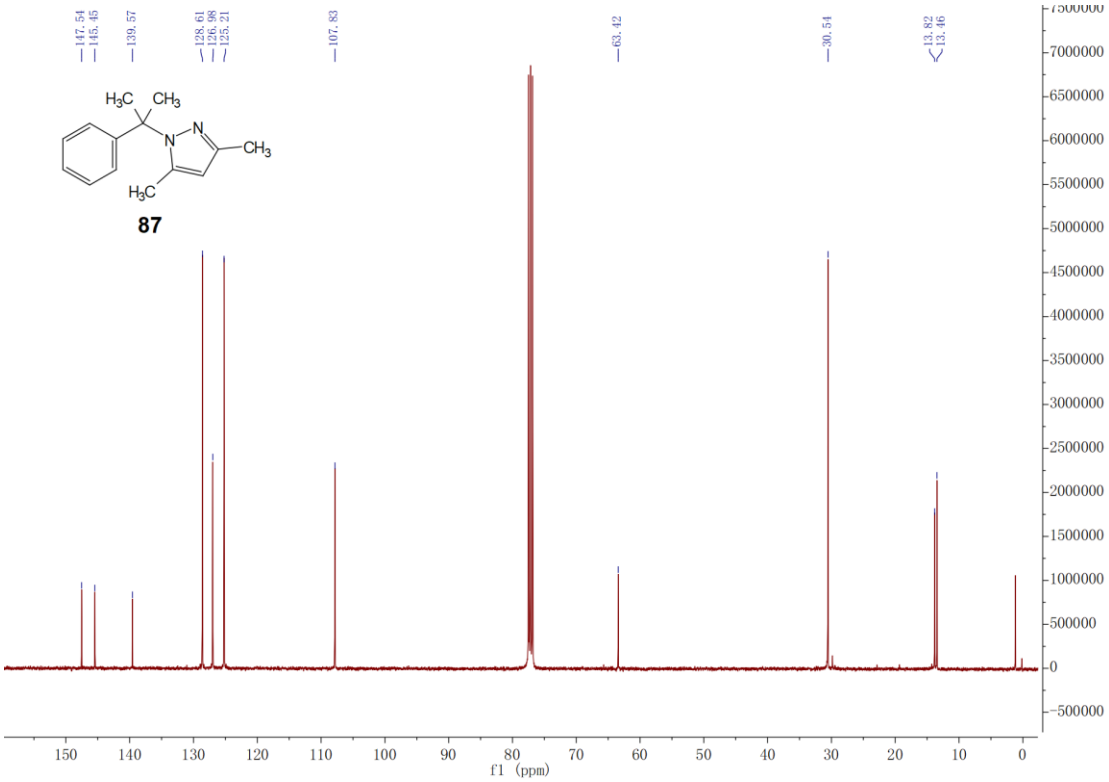

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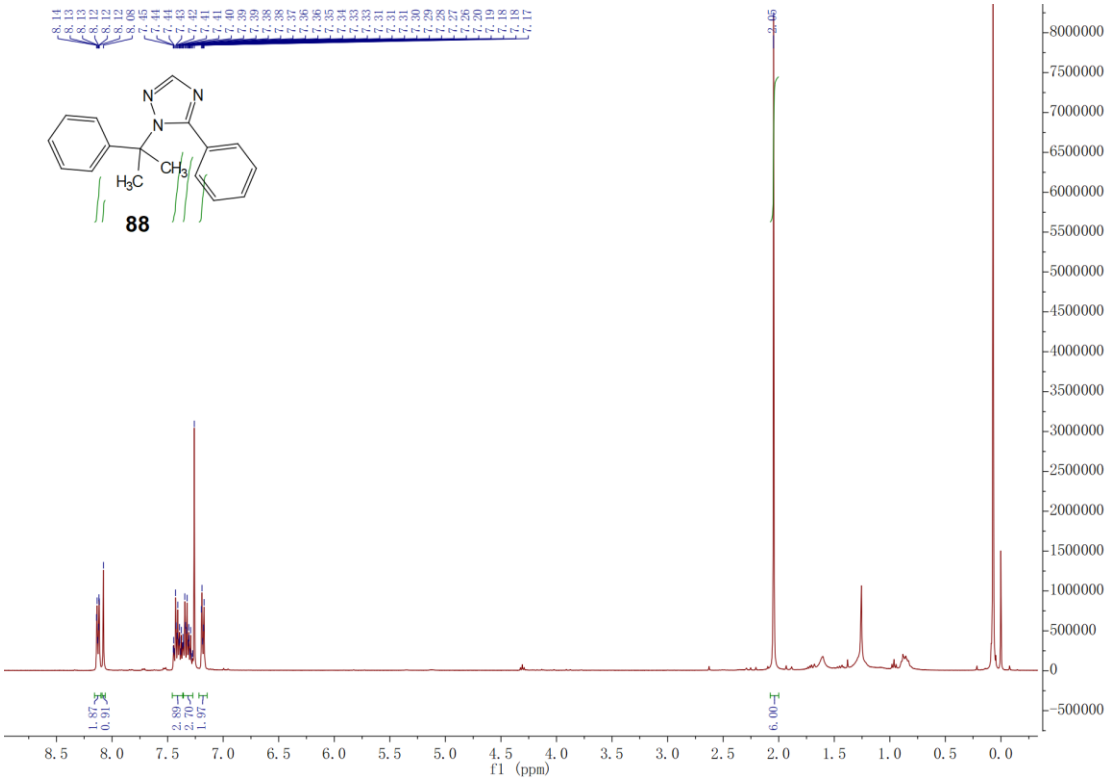

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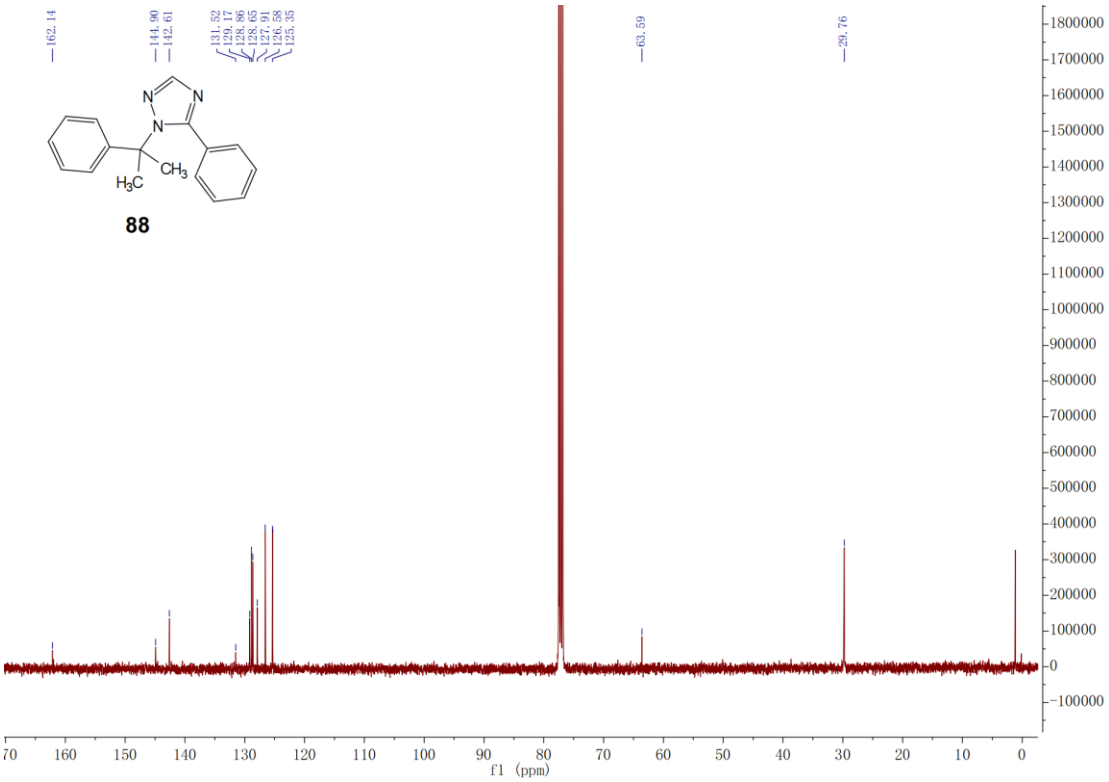

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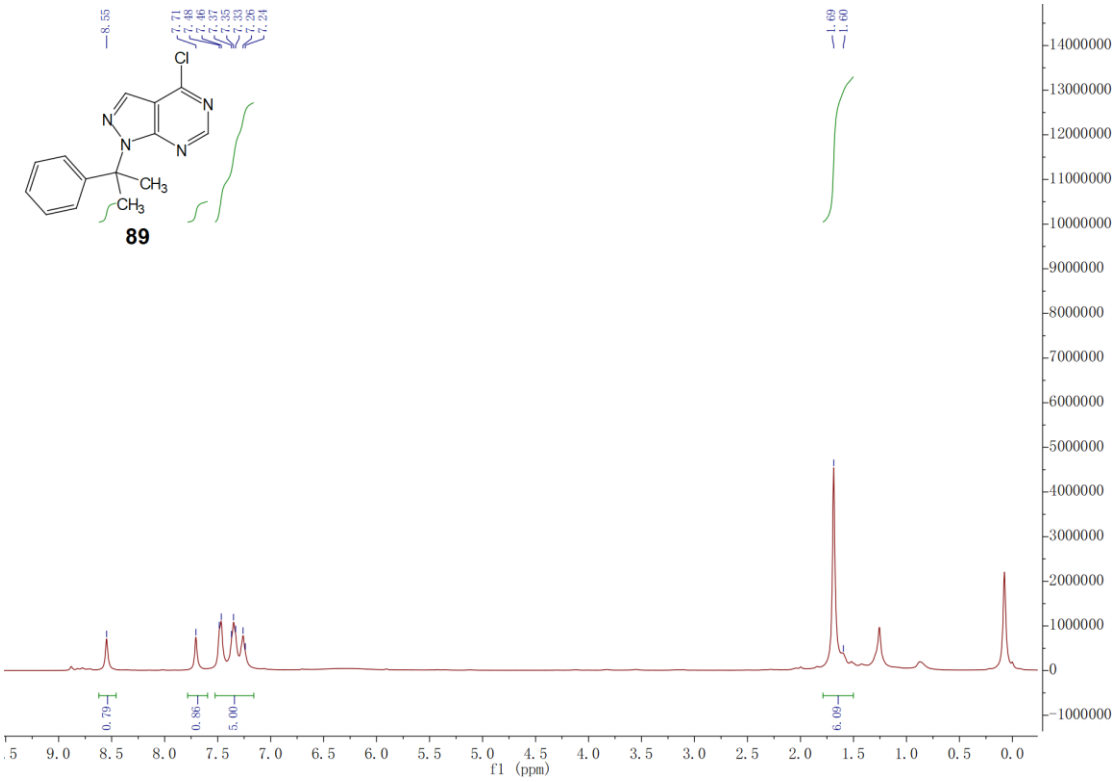

^{13}C NMR (101 MHz, $CDCl_3$)