Supporting information
For

Sodium Carbonate Promoted [3+2] Annulation of α-Halohydroxamates and Isocyanates

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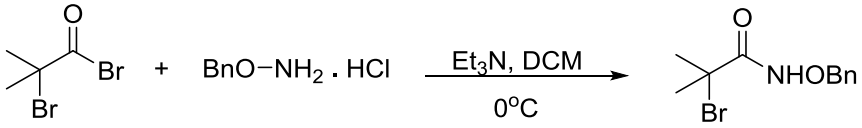
Content

1 General Information and Starting Materials

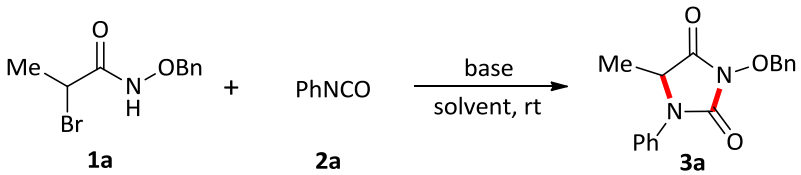
All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise specified. Dichloromethane was purified by passage through a bed of activated alumina. All other reagents and solvents were purchased from Energy Chemical or J&K Chemical Company and used without any further purification. TLC information was recorded on GF 254 (Qingdao Haiyang Chemical Co., Ltd. P. R. China) plates and developed by staining with $KMnO_4$ or ceric ammonium molybdate (CAM). Purification of reaction products was carried out by flash chromatography using Silica gel (200 - 300 mesh, Qingdao Haiyang Chemical Co. Ltd. P. R. China). Melting point was measured on X-4 digital display micro-melting point detector. ^{1}H NMR spectra were measured on Varian 400 (400 MHz), spectrometers and are reported in ppm (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad; integration; coupling constant(s) in Hz), using TMS as an internal standard (TMS at 0.00 ppm) in $CDCl_3$. ^{13}C NMR spectra were recorded on V400 spectrometer and reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm). High-resolution mass spectra were obtained using an Agilent 6230 TOF LC/MS with an (atmospheric pressure photo-ionization (APPI) or electrospray (ESI) source with purine and HP-0921 as an internal calibrants. HR-EI-MS were performed on an API-Qstar-Pulsar-1 spectrometer.

1.1 General procedure A for synthesis of α-haloamide



To a solution of *O*-benzylhydroxylamine HCl (1 g, 6.3 mmol, 1 equiv) in dicholoromethane (30 mL) was added trimethylamine (0.88 mL, 6.3 mmol, 1 equiv). The reaction mixture was then cooled to 0 ℃. Next, 2-bromo-2-methylpropanoyl bromide (0.75 mL, 6.3 mmol, 1 eq) was added dropwise to the reaction mixture. The reaction was stirred for 4 h at 0 ℃. After 4 h, the reaction mixture was then allowed to warm to room temperature and quenched by water. The resulting mixture was then washed with brine (x3). The combined organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The crude reaction mixture was purified by silica gel chromatography (ethyl acetate/hexanes) to give haloamide as a white solid (1.3 g, 80%).

1.2 General Procedure B for the [3+2]-cycloaddition of isocyanates with α-halo amides:

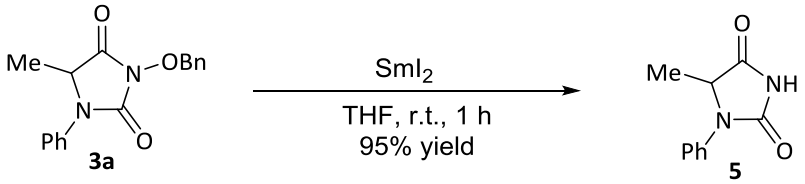


To a solution of isocyanates **2a** (1.0 equiv.) in CH_3CN (1.5 M) was added

α-haloamide **1a** (1.0 equiv) and sodium carbonate (2 equiv) and stirred at room temperature and the reaction progress monitored by TLC (hexanes:ethyl acetate = 3:1) until complete consumption of the α-haloamide (For reaction time, see substrate tables). The mixture was filtered through the short pad of celite and the filtrate was concentrated under reduced pressure. The residue was purified via flash column chromatography (hexanes: ethyl acetate, 50:1 to 15:1) to provide the desired cycloadducts.

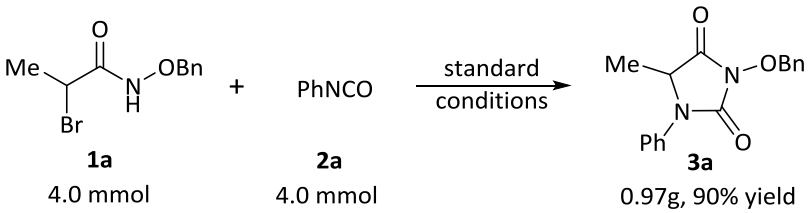
2 Experimental Results

2.1 Synthesis of 5-methyl-1-phenylimidazolidine-2,4-dione from thiazolidinone 3a



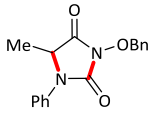
To a solution of **3a** (100 mg, 0.34 mmol) in anhydrous THF (0.1 mL), 0.1 mol/L SmI_2 solution in THF (10.2 mL) was added. The reaction was stirred at room temperature for 15 min under nitrogen. The reaction was quenched with saturated solution of ammonium chloride (10 mL) and extracted with ethyl acetate (20 mL x 3). The volatiles were removed under reduced pressure and the residue was purified via flash column chromatography (3:1 hexanes: ethyl acetate) to provide title compound as a white solid 61mg **5**.

2.2 Scalable Synthesis



To a solution of isocyanates **2a** (4.0 mmol) in CH_3CN (1.5 M) was added α-haloamide **1a** (4.0 mmol) and sodium carbonate (8.0 mmol) and stirred at room temperature and the reaction progress monitored by TLC (hexanes:ethyl acetate = 3:1) until complete consumption of the α-haloamide. The mixture was filtered through the short pad of celite and the filtrate was concentrated under reduced pressure. The residue was purified via flash column chromatography (hexanes: ethyl acetate, 50:1 to 15:1) to provide the desired **3a** in 90% (0.97 g).

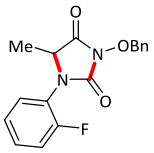
3 Characterization



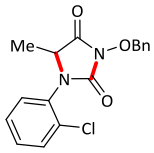
3-(Benzyloxy)-5-methyl-1-phenylimidazolidine-2,4-dione (**3a**)

Colorless oil, 109 mg, 95%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 2H), 7.43-7.22 (m, 8H), 5.24 (s, 2H), 4.48 (q, 1H, *J* = 7.2 Hz), 1.38 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 150.6, 135.1, 133.3, 130.2, 129.5, 129.4, 128.6, 125.8,

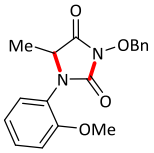
121.7, 79.4, 54.2, 15.4. HRMS (EI) (positive) *m/z* 319.1059 $[M+Na]^+$ (calcd for $C_{17}H_{16}N_2O_3Na$ 319.1059).



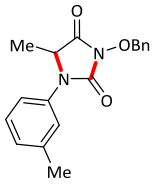
3-(Benzyloxy)-1-(2-fluorophenyl)-5-methylimidazolidine-2,4-dione (**3b**)
Colorless oil, 99 mg, 80%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 2H), 7.42-7.32 (m, 5H), 7.24-7.17 (m, 2H), 5.25 (s, 2H), 4.43 (q, 1H, *J* = 7.2 Hz), 1.28 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.42, 159.0, 156.5, 151.1, 133.3, 130.3, 129.6, 129.5, 129.0, 128.5, 125.0, 124.9, 122.1, 122.0, 117.0, 116.8, 79.3, 56.1, 15.3. HRMS (EI) (positive) *m/z* 337.0964 $[M+Na]^+$ (calcd for $C_{17}H_{15}FN_2O_3Na$ 337.0964).



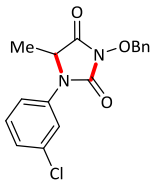
3-(Benzyloxy)-1-(2-chlorophenyl)-5-methylimidazolidine-2,4-dione (**3c**)
Colorless oil, 102 mg, 81%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.27 (m, 9H), 5.25 (s, 2H), 4.41 (q, 1H, *J* = 7.2 Hz), 1.28 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 151.3, 133.3, 133.2, 131.8, 130.8, 130.7, 130.4, 130.3, 129.5, 129.4, 128.5, 128.0, 79.3, 56.2, 15.3. HRMS (EI) (positive) *m/z* 353.0669 $[M+Na]^+$ (calcd for $C_{17}H_{15}ClN_2O_3Na$ 353.0669).



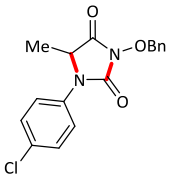
3-(Benzyloxy)-1-(2-methoxyphenyl)-5-methylimidazolidine-2,4-dione (**3d**)
Colorless oil, 99 mg, 78%, 5h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31-8.29 (m, 1H), 7.58-7.56 (m, 2H), 7.47-7.44 (m, 3H), 7.14-6.93 (m, 3H), 5.26-5.24 (m, 3H), 3.94 (s, 3H), 1.77 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 148.4, 133.4, 130.1, 129.5, 128.9, 126.7, 124.3, 121.1, 119.8, 110.2, 79.1, 55.9, 20.9. HRMS (EI) (positive) *m/z* 349.1167 $[M+Na]^+$ (calcd for $C_{18}H_{18}N_2O_4Na$ 349.1164).



3-(Benzyloxy)-5-methyl-1-(m-tolyl)imidazolidine-2,4-dione (**3e**)
Colorless oil, 109 mg, 91%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (m, 2H), 7.42-7.40 (m, 3H), 7.32-7.25 (m, 2H), 7.15-7.05 (m, 2H), 5.24 (s, 2H), 4.45 (q, 1H, *J* = 7.2 Hz), 2.39 (s, 3H), 1.37 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 150.7, 139.5, 135.0, 133.4, 130.2, 129.5, 128.6, 126.7, 122.7, 118.8, 79.4, 54.3, 21.5, 15.4. HRMS (EI) (positive) *m/z* 333.1215 $[M+Na]^+$ (calcd for $C_{18}H_{18}N_2O_3Na$ 333.1215).

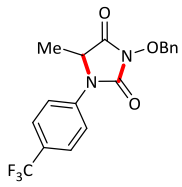


3-(Benzyloxy)-1-(3-chlorophenyl)-5-methylimidazolidine-2,4-dione (**3f**)
White solid, m.p.:51-53^{o}C, 109 mg, 85%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.20 (m, 9H), 5.23 (s, 2H), 4.45 (q, 1H, *J* = 7.2 Hz), 1.40 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 150.5, 136.4, 135.2, 133.2, 130.4, 130.2, 129.6, 128.6, 125.7, 121.5, 119.1, 79.4, 54.1, 15.4. HRMS (EI) (positive) *m/z* 353.0667 $[M+Na]^+$ (calcd for $C_{17}H_{15}ClN_2O_3Na$ 353.0669).



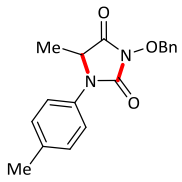
3-(Benzyloxy)-1-(4-chlorophenyl)-5-methylimidazolidine-2,4-dione (**3g**)
Colorless oil, 113 mg, 88%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H), 7.42-7.33 (m, 7H), 5.23 (m, 2H), 4.45 (q, 1H, *J* = 7.2 Hz), 1.28 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 150.5, 133.7, 133.2, 131.1, 130.2, 129.6, 129.5, 128.6, 122.7, 79.4, 54.2, 15.3. HRMS (EI) (positive) *m/z*

353.0672 $[M+Na]^+$ (calcd for $C_{17}H_{15}ClN_2O_3Na$ 353.0669).



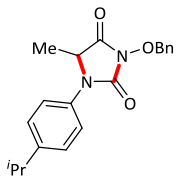
3-(Benzyloxy)-5-methyl-1-(4-(trifluoromethyl)phenyl)imidazolidine-2,4-dione (**3h**)

White solid, m.p.:77-78°C, 120 mg, 85%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.67 (m, 2H), 7.57-7.53 (m, 4H), 7.42-7.40 (m, 3H), 5.24 (s, 2H), 4.53 (q, 1H, *J* = 7.2 Hz), 1.42 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 150.5, 138.4, 133.1, 130.2, 129.6, 128.6, 126.6, 126.5, 120.5, 79.5, 63.8, 15.4. HRMS (EI) (positive) *m/z* 387.0932 $[M+Na]^+$ (calcd for $C_{18}H_{15}F_3N_2O_3Na$ 387.0932).



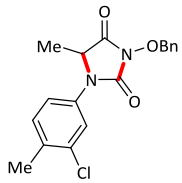
3-(Benzyloxy)-5-methyl-1-(p-tolyl)imidazolidine-2,4-dione (**3i**)

Colorless oil, 111 mg, 92%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 2H), 7.41-7.39 (m, 3H), 7.27-7.21 (m, 4H), 5.23 (s, 2H), 4.42 (q, 1H, *J* = 7.2 Hz), 2.36 (s, 3H), 1.35 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 150.7, 135.8, 133.4, 132.5, 130.2, 130.0, 129.5, 128.5, 122.0, 79.3, 54.4, 21.0, 15.4. HRMS (EI) (positive) *m/z* 333.1213 $[M+Na]^+$ (calcd for $C_{18}H_{18}N_2O_3Na$ 333.1215).



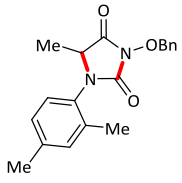
3-(Benzyloxy)-1-(4-isopropylphenyl)-5-methylimidazolidine-2,4-dione (**3j**)

White solid, m.p.:64-66°C, 115 mg, 88%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 2H), 7.41-7.38 (m, 3H), 7.31-7.09 (m, 4H), 5.24 (s, 2H), 4.44 (q, 1H, *J* = 7.2 Hz), 2.96-2.90 (m, 1H), 1.37 (d, 3H, *J* = 7.2 Hz), 1.27 (d, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 150.8, 146.8, 133.3, 132.6, 130.2, 129.5, 128.6, 127.4, 126.8, 122.1, 120.2, 79.4, 54.5, 33.7, 24.0, 15.4. HRMS (EI) (positive) *m/z* 361.1528 $[M+Na]^+$ (calcd for $C_{20}H_{22}N_2O_3Na$ 361.1528).



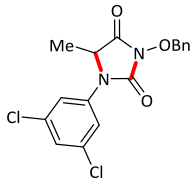
3-(Benzyloxy)-1-(3-chloro-4-methylphenyl)-5-methylimidazolidine-2,4-dione (**3k**)

Colorless oil, 111 mg, 83%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.53 (m, 2H), 7.43-7.40 (m, 4H), 7.28-7.25 (m, 1H), 7.19-7.16 (m, 1H), 5.23 (s, 2H), 4.42 (q, 1H, *J* = 7.2 Hz), 2.38 (s, 3H), 1.38 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 150.5, 135.0, 133.8, 133.7, 133.2, 131.4, 130.2, 129.5, 128.6, 122.3, 119.8, 79.4, 54.3, 19.5, 15.4. HRMS (EI) (positive) *m/z* 367.0825 $[M+Na]^+$ (calcd for $C_{18}H_{17}ClN_2O_3Na$ 367.0825).



3-(Benzyloxy)-1-(2,4-dimethylphenyl)-5-methylimidazolidine-2,4-dione (**3l**)

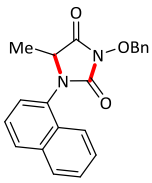
Colorless oil, 96 mg, 76%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (m, 2H), 7.42-7.40 (m, 3H), 7.00 (s, 2H), 6.89 (s, 1H), 5.24 (s, 1H), 4.44 (q, 1H, *J* = 7.2 Hz), 2.35 (s, 6H), 1.37 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 150.7, 139.2, 134.8, 133.4, 130.2, 129.5, 128.5, 127.8, 119.8, 79.3, 54.4, 21.4, 15.5. HRMS (EI) (positive) *m/z* 347.1370 $[M+Na]^+$ (calcd for $C_{19}H_{20}N_2O_3Na$ 347.1372).



3-(Benzyloxy)-1-(3,5-dichlorophenyl)-5-methylimidazolidine-2,4-dione (**3m**)

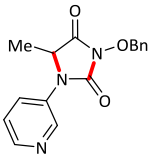
Colorless oil, 127 mg, 90%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.52 (m, 2H), 7.42-7.36 (m, 5H), 7.22-7.21 (m, 1H), 5.22 (s, 2H), 4.42 (q, 1H, *J* = 7.2

Hz), 1.41 (d, 3H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 150.3, 137.2, 135.8, 133.0, 130.2, 129.7, 128.6, 125.5, 119.1, 79.5, 53.9, 15.4. HRMS (EI) (positive) *m/z* 387.0279 $[M+Na]^+$ (calcd for $C_{17}H_{14}Cl_2N_2O_3Na$ 387.0279).



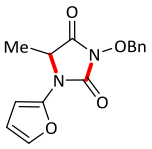
3-(Benzyloxy)-5-methyl-1-(naphthalen-1-yl)imidazolidine-2,4-dione (**3n**)

White solid, m.p.:76-78^{o}C, 112 mg, 83%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H), 7.63-7.35 (m, 10H), 5.35 (s, 2H), 4.42 (m, 1H), 1.27 (d, 3H, *J* = 7.2 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 134.7, 133.3, 130.5, 129.6, 128.6, 127.4, 126.8, 125.5, 79.1, 15.6. HRMS (EI) (positive) *m/z* 369.1215 $[M+Na]^+$ (calcd for $C_{21}H_{18}N_2O_3Na$ 369.1215).



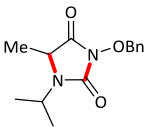
3-(Benzyloxy)-5-methyl-1-(pyridin-3-yl)imidazolidine-2,4-dione (**3o**)

Colorless oil, 92 mg, 80%, 5h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, 1H, *J* = 2.6 Hz), 8.47 (d, 1H, *J* = 4.7 Hz), 7.88-7.86 (m, 1H), 7.54-7.51 (m, 2H), 7.40-7.34 (m, 4H), 5.22 (s, 2H), 4.52 (q, 1H, *J* = 7.2 Hz), 1.40 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 150.6, 146.5, 142.2, 133.1, 132.2, 130.2, 129.6, 128.9, 128.6, 123.9, 79.5, 53.9, 15.3. HRMS (EI) (positive) *m/z* 320.1011 $[M+Na]^+$ (calcd for $C_{16}H_{15}N_3O_3Na$ 320.1011).



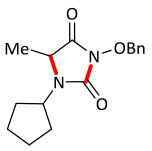
3-(Benzyloxy)-1-(furan-2-yl)-5-methylimidazolidine-2,4-dione (**3p**)

Colorless oil, 92 mg, 83%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H), 7.42-4.41 (m, 3H), 7.25-7.24 (m, 1H), 6.46-6.45 (m, 1H), 6.30-6.29 (m, 1H), 5.22 (s, 2H), 4.37 (q, 1H, *J* = 7.2 Hz), 1.47 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 149.8, 141.9, 138.7, 133.1, 130.2, 129.6, 128.6, 111.6, 100.4, 79.5, 55.5, 16.1. HRMS (EI) (positive) *m/z* 309.0851 $[M+Na]^+$ (calcd for $C_{15}H_{14}N_2O_4Na$ 309.0851).



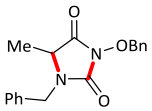
3-(Benzyloxy)-1-isopropyl-5-methylimidazolidine-2,4-dione (**3q**)

Colorless oil, 82 mg, 81%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-741 (m, 5H), 5.17 (m, 2H), 4.02 (q, 1H, *J* = 7.2 Hz), 1.71 (d, 3H, *J* = 7.2 Hz), 1.23 (d, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 133.6, 130.0, 129.5, 128.9, 79.0, 43.1, 22.7, 22.6, 20.9. HRMS (EI) (positive) *m/z* 285.1213 $[M+Na]^+$ (calcd for $C_{14}H_{18}N_2O_3Na$ 285.1215).



3-(Benzyloxy)-1-cyclopentyl-5-methylimidazolidine-2,4-dione (**3r**)

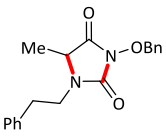
White solid, m.p.:50-51^{o}C, 117 mg, 85%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.42 (m, 5H), 5.22-5.14 (m, 3H), 4.19-4.14 (m, 1H), 2.06-2.00 (m, 2H), 1.72-1.62 (m, 7H), 1.52-1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 133.6, 130.0, 129.5, 128.9, 79.0, 52.5, 33.1, 33.0, 23.6, 20.9. HRMS (EI) (positive) *m/z* 311.1371 $[M+Na]^+$ (calcd for $C_{16}H_{20}N_2O_3Na$ 311.1372).



1-Benzyl-3-(benzyloxy)-5-methylimidazolidine-2,4-dione (**3s**)

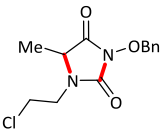
Colorless oil, 111 mg, 92%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.33 (m, 10H), 5.24-5.17 (m, 3H), 4.50-4.48 (m, 2H), 1.71 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 137.5, 133.5, 130.1, 129.5, 128.9, 128.8, 127.7, 79.1, 44.6, 20.8.

HRMS (EI) (positive) *m/z* 333.1214 $[M+Na]^+$ (calcd for $C_{18}H_{18}N_2O_3Na$ 333.1215).



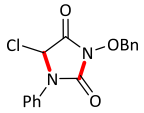
3-(Benzyloxy)-5-methyl-1-phenethylimidazolidine-2,4-dione (**3t**)

Colorless oil, 117 mg, 93%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.41 (m, 5H), 7.37-7.33 (m, 2H), 7.29-7.24 (m, 3H), 5.12 (m, 2H), 3.60 (q, 2H, *J* = 7.2 Hz), 2.91 (t, 2H, *J* = 7.2 Hz), 1.70 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 138.5, 133.4, 130.0, 129.5, 128.9, 128.8, 128.7, 126.7, 78.9, 41.8, 35.7, 20.8. HRMS (EI) (positive) *m/z* 347.1373 $[M+Na]^+$ (calcd for $C_{19}H_{20}N_2O_3Na$ 347.1372).



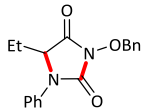
3-(Benzyloxy)-1-(2-chloroethyl)-5-methylimidazolidine-2,4-dione (**3u**)

White solid, m.p.:66-68^{o}C, 93 mg, 90%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.49 (m, 2H), 7.44-7.42 (m, 3H), 5.19-5.09 (m, 3H), 3.69-3.65 (m, 4H), 1.70 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 133.3, 130.1, 129.6, 128.9, 79.0, 43.1, 42.3, 20.8. HR-EI-MS (positive) *m/z* 305.0673 $[M+Na]^+$ (calcd for $C_{13}H_{15}ClN_2O_3Na$ 305.0669).



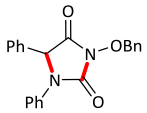
3-(Benzyloxy)-5-chloro-1-phenylimidazolidine-2,4-dione (**4a**)

White solid, m.p.:44-46^{o}C, 108 mg, 80%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.36 (m, 5H), 5.93 (s, 1H), 4.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 153.5, 138.0, 134.2, 129.6, 129.3, 129.2, 128.2, 124.2, 121.1, 78.6, 64.4. HRMS (EI) (positive) *m/z* 339.0516 $[M+Na]^+$ (calcd for $C_{16}H_{13}ClN_2O_3Na$ 339.0512).



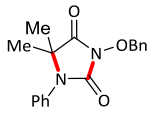
3-(Benzyloxy)-5-ethyl-1-phenylimidazolidine-2,4-dione (**4b**)

Colorless oil, 100 mg, 87%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.46-7.40 (m, 7H), 7.27-7.23 (m, 1H), 5.24 (s, 2H), 4.55 (q, 1H, *J* = 7.2 Hz), 2.01-1.81 (m, 2H), 0.71 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 151.2, 135.0, 133.5, 130.0, 129.5, 129.4, 128.6, 125.9, 121.9, 79.4, 58.8, 21.4, 6.81. HRMS (EI) (positive) *m/z* 333.1215 $[M+Na]^+$ (calcd for $C_{18}H_{18}N_2O_3Na$ 333.1215).



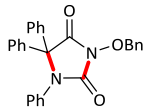
3-(Benzyloxy)-1,5-diphenylimidazolidine-2,4-dione (**4c**)

White solid, m.p.:100-101^{o}C, 92 mg, 82%, 6h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H), 7.44-7.27 (m, 10H), 7.20-7.10 (m, 3H), 5.36 (s, 1H), 5.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 151.1, 136.0, 133.2, 132.1, 130.2, 129.5, 129.3, 129.2, 128.6, 126.9, 125.1, 120.3, 79.4, 62.4. HRMS (EI) (positive) *m/z* 381.1215 $[M+Na]^+$ (calcd for $C_{22}H_{18}N_2O_3Na$ 381.1215).



3-(Benzyloxy)-5,5-dimethyl-1-phenylimidazolidine-2,4-dione (**4d**)

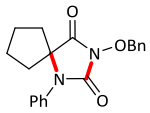
Colorless oil, 92 mg, 80%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.40 (m, 10H), 5.14 (s, 2H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 156.5, 135.4, 131.2, 129.8, 129.1, 129.0, 128.6, 128.3, 125.9, 79.9, 64.4, 22.0. HRMS (EI) (positive) *m/z* 333.1215 $[M+Na]^+$ (calcd for $C_{18}H_{18}N_2O_3Na$ 333.1215)



3-(Benzyloxy)-1,5,5-triphenylimidazolidine-2,4-dione (**4e**)

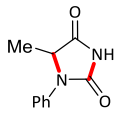
White solid, m.p.:79-80^{o}C, 82 mg, 75%, 6h. ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.82-7.80 (m, 1H), 7.63-7.61 (m, 2H), 7.48-7.46 (m, 2H), 7.37-7.32 (m, 11H), 7.22-7.13 (m, 3H), 7.10-6.99 (m, 1H), 5.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 163.5, 139.4, 137.4, 133.5, 130.2, 129.6, 129.2, 129.0, 128.9, 128.7, 128.4, 127.9, 126.4, 125.3, 124.7, 124.2, 120.0, 108.0, 78.3, 61.8. HRMS (EI) (positive) *m/z* 457.1529 $[M+Na]^+$ (calcd for $C_{28}H_{22}N_2O_3Na$ 457.1528)



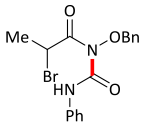
3-(Benzyloxy)-1-phenyl-1,3-diazaspiro[4.4]nonane-2,4-dione (**4f**)

Colorless oil, 88 mg, 78%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.57 (m, 4H), 7.46-7.37 (m, 5H), 7.20-7.16 (m, 1H), 5.42 (s, 2H), 2.56-2.51 (m, 2H), 2.37-2.31 (m, 2H), 2.05-2.00 (m, 2H), 1.83-1.79 (m, 2H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 149.1, 137.0, 133.9, 130.0, 129.2, 129.1, 128.6, 124.7, 120.4, 77.8, 68.2, 40.8, 22.6. HRMS (EI) (positive) *m/z* 359.1376 $[M+Na]^+$ (calcd for $C_{20}H_{20}N_2O_3Na$ 359.1372)



5-Methyl-1-phenylimidazolidine-2,4-dione (**5**)

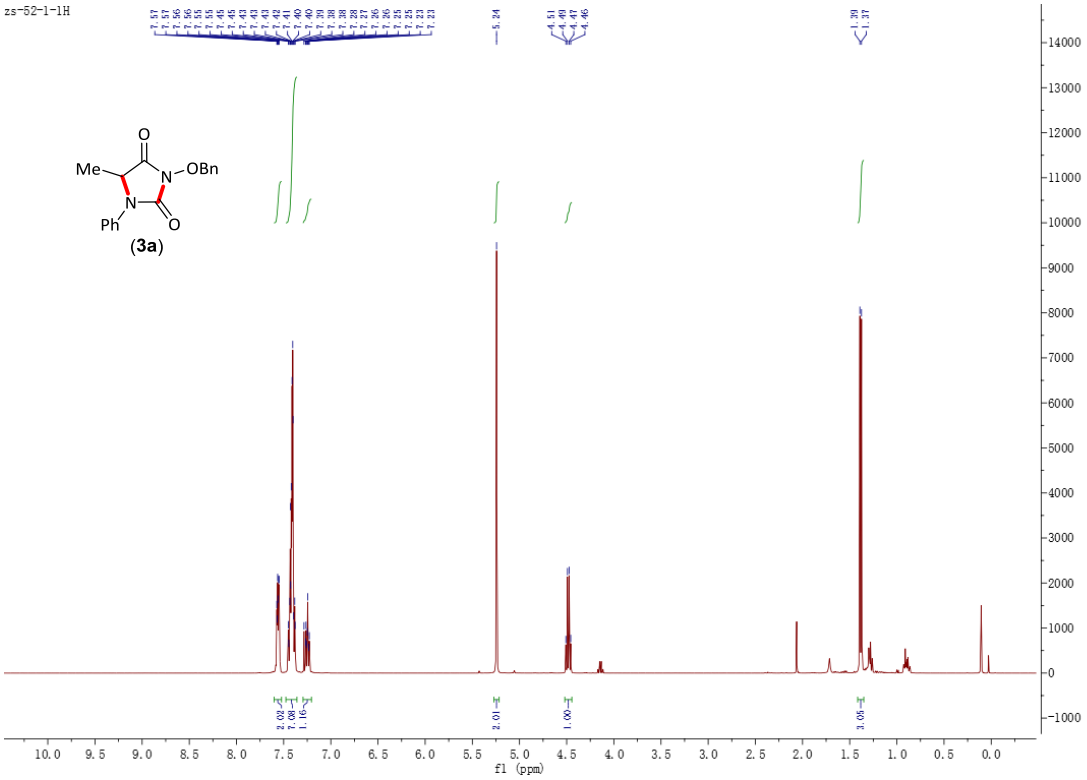
White solid, 61 mg, 95%, 1h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (s, 1H), 7.44-7.43 (m, 4H), 7.28-7.24 (m, 1H), 4.65 (q, 1H, *J* = 7.2 Hz), 1.50 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 154.2, 135.3, 129.4, 125.8, 122.2, 57.6, 16.5. HRMS (EI) (positive) *m/z* 213.0639 $[M+Na]^+$ (calcd for $C_{10}H_{10}N_2O_2Na$ 213.0640)

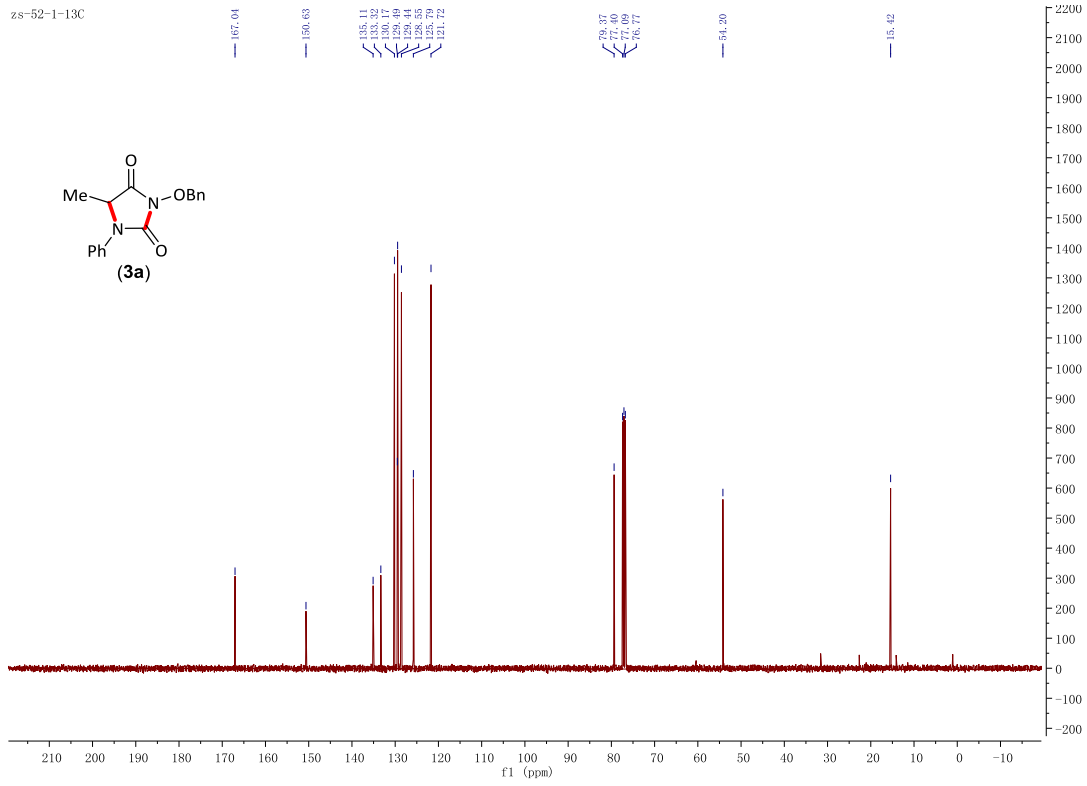


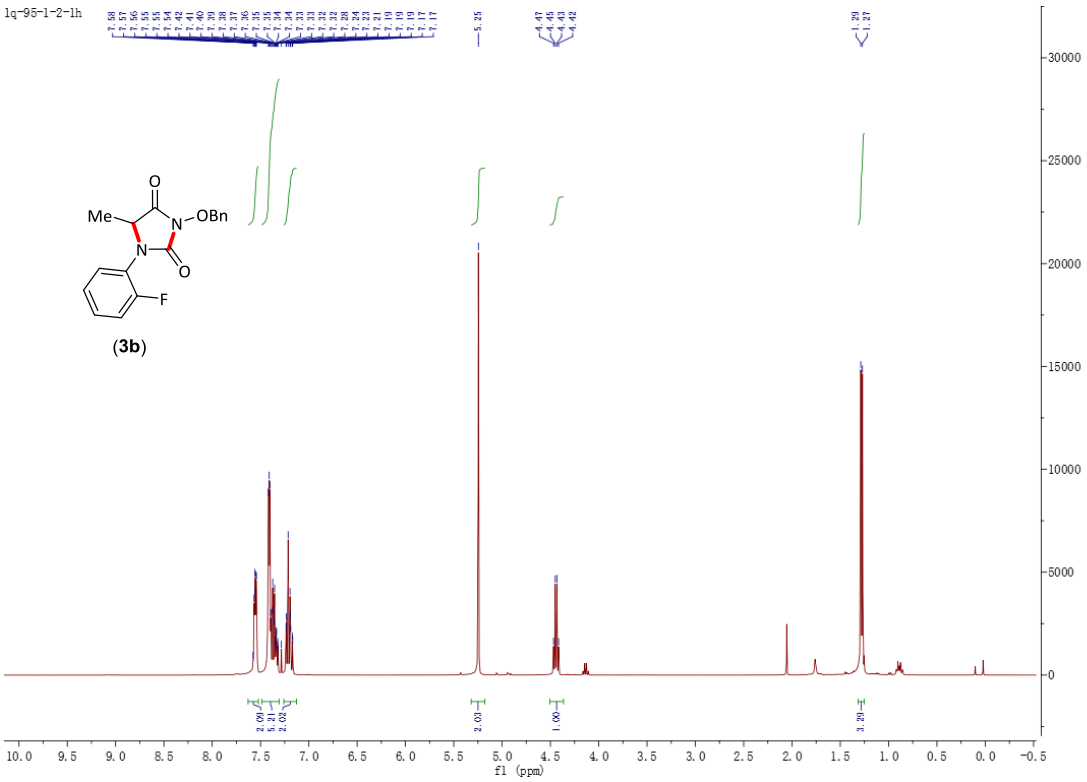
N-(Benzyloxy)-2-bromo-N-(phenylcarbamoyl)propanamide (**6**)

White solid, m.p.: 67-68^{o}C, 139 mg, 95%, 4h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.2 (s, 1H), 7.57-7.54 (m, 4H), 7.49-7.44 (m, 3H), 7.41-7.37 (m, 2H), 7.20-7.16 (m, 1H), 5.31 (m, 2H), 5.10 (s, 1H), 1.74 (d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 148.6, 136.8, 133.3, 130.1, 129.6, 129.2, 129.0, 124.8, 120.4, 79.3, 38.3, 20.8. HRMS (EI) (positive) *m/z* 399.0320 $[M+Na]^+$ (calcd for $C_{17}H_{17}BrN_2O_3Na$ 399.0320)

4 NMR Spectra



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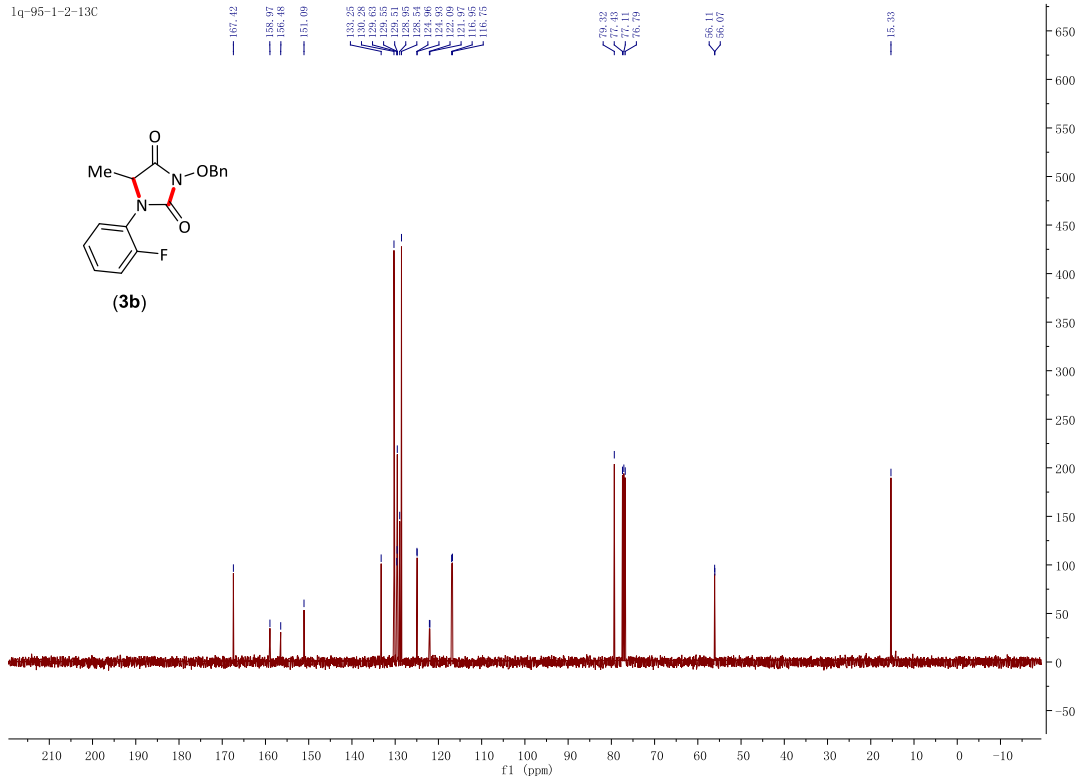
O
F
(3b)
f1 (ppm)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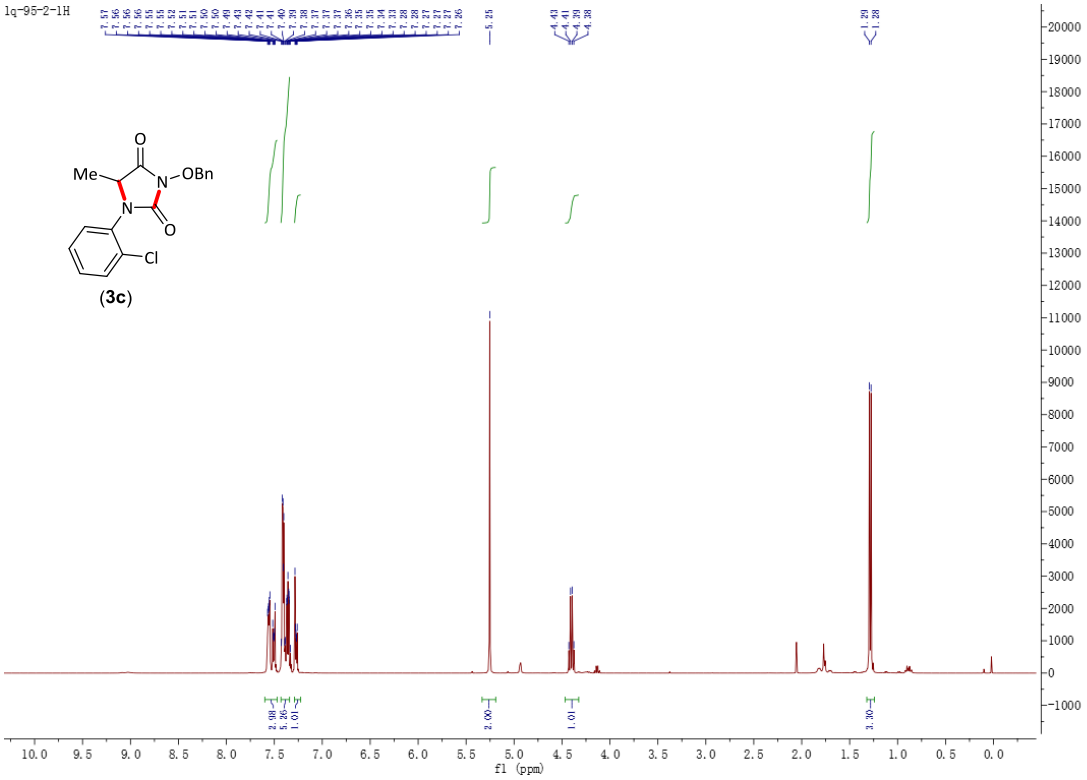
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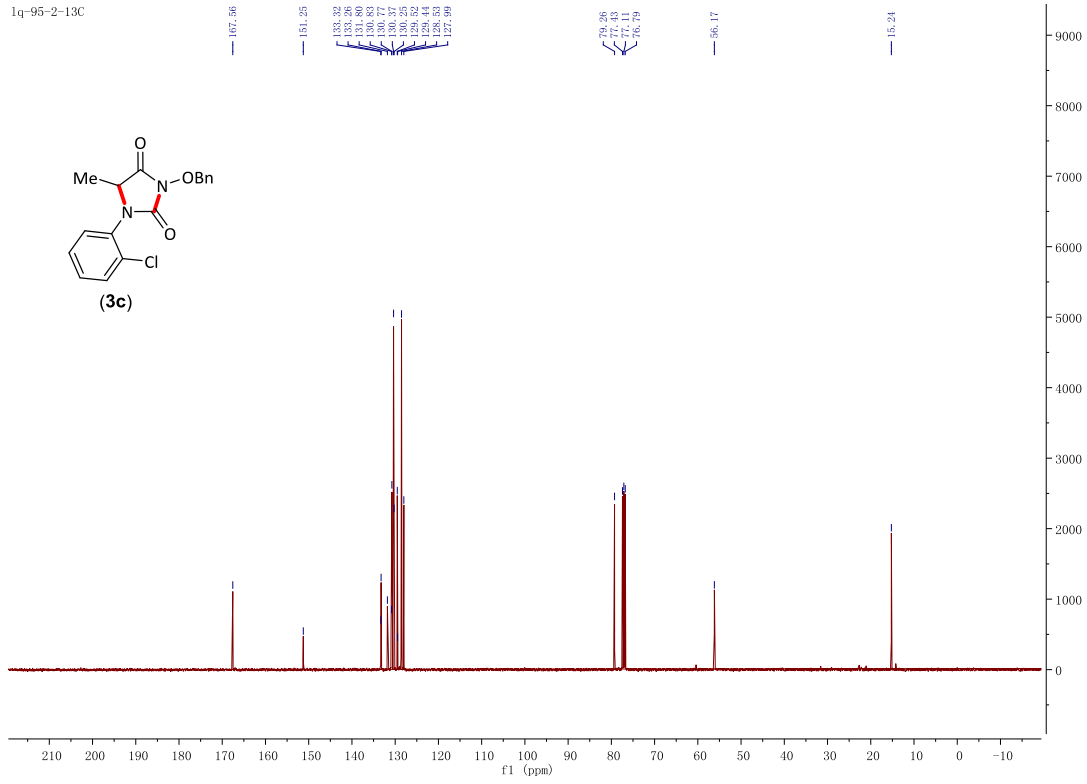
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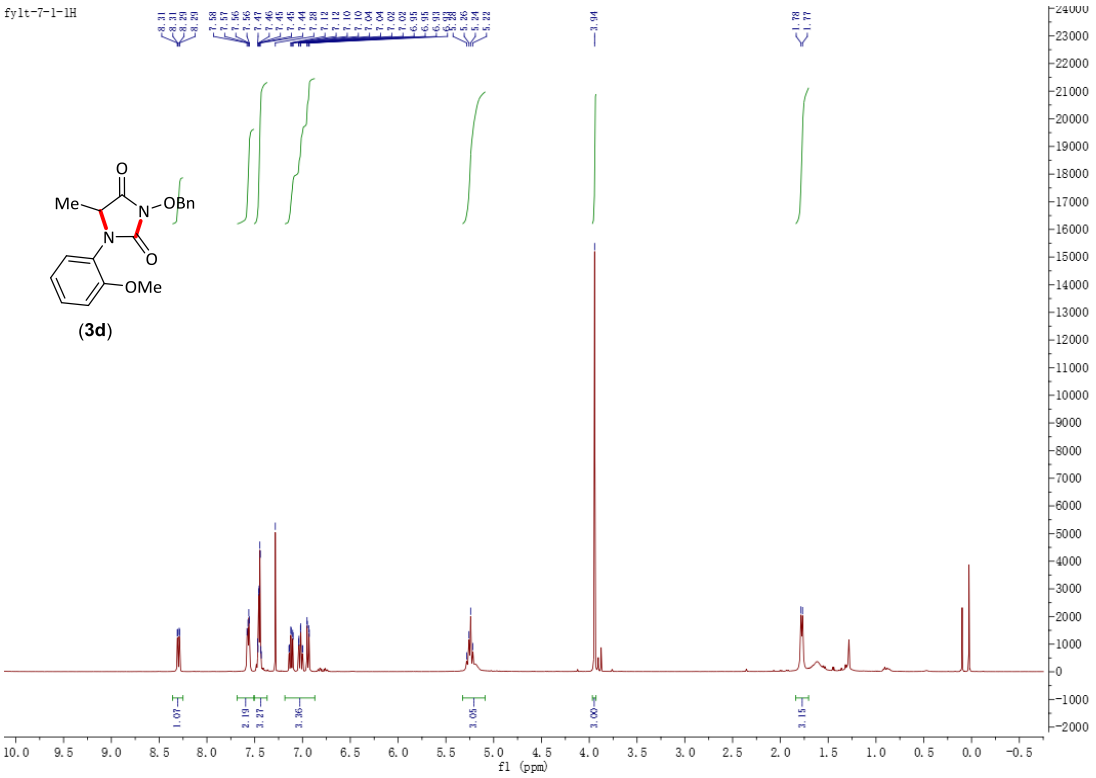
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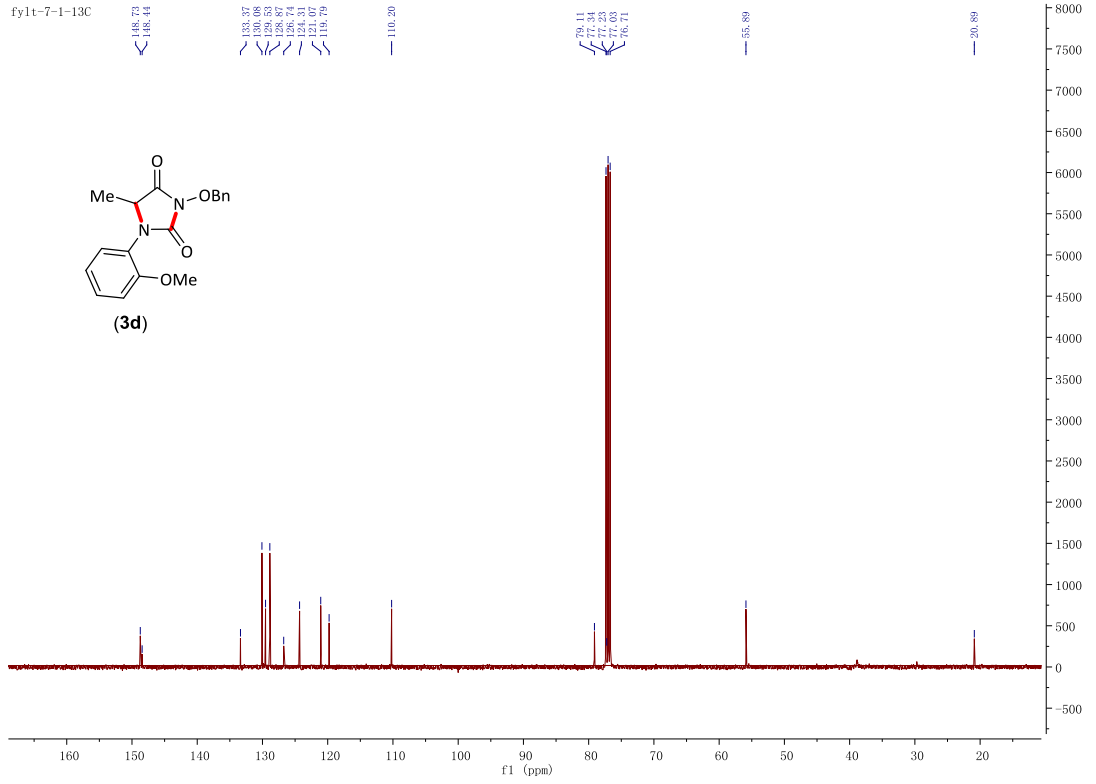
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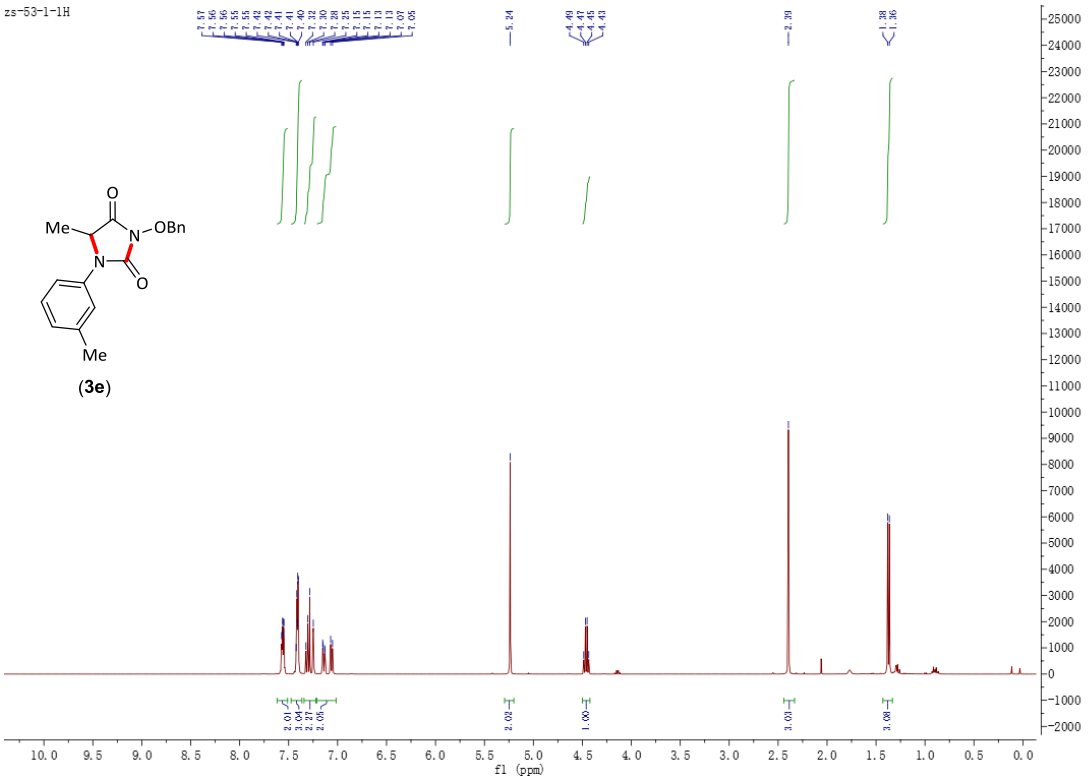
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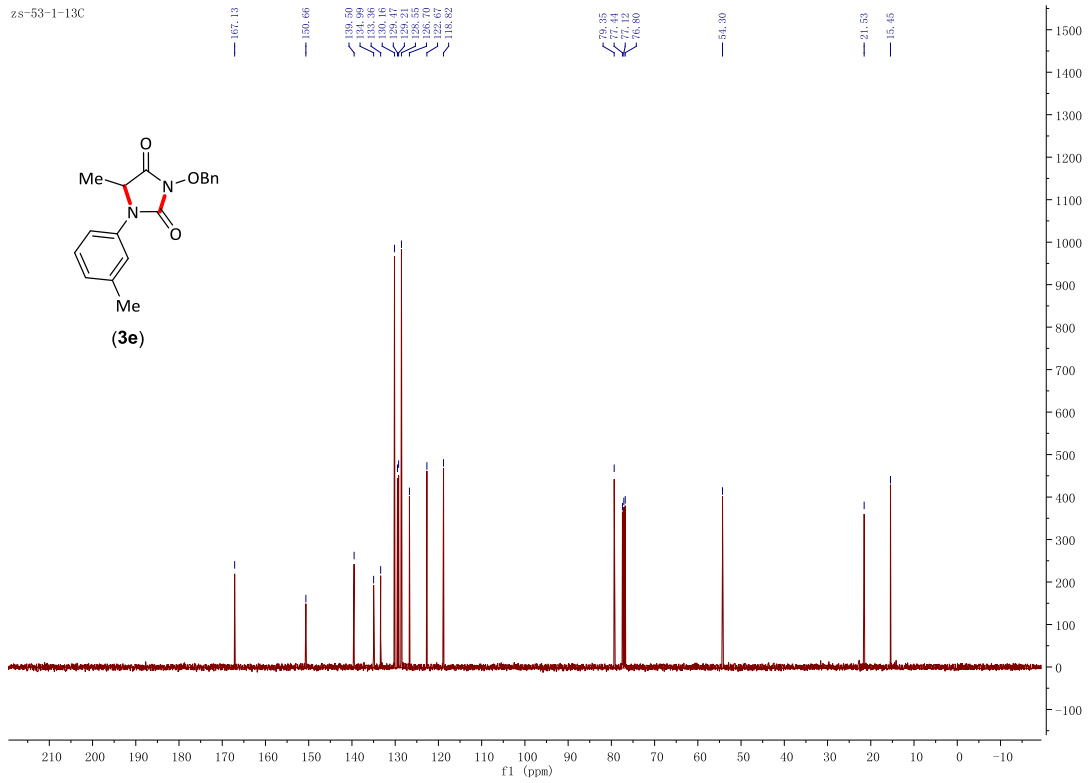
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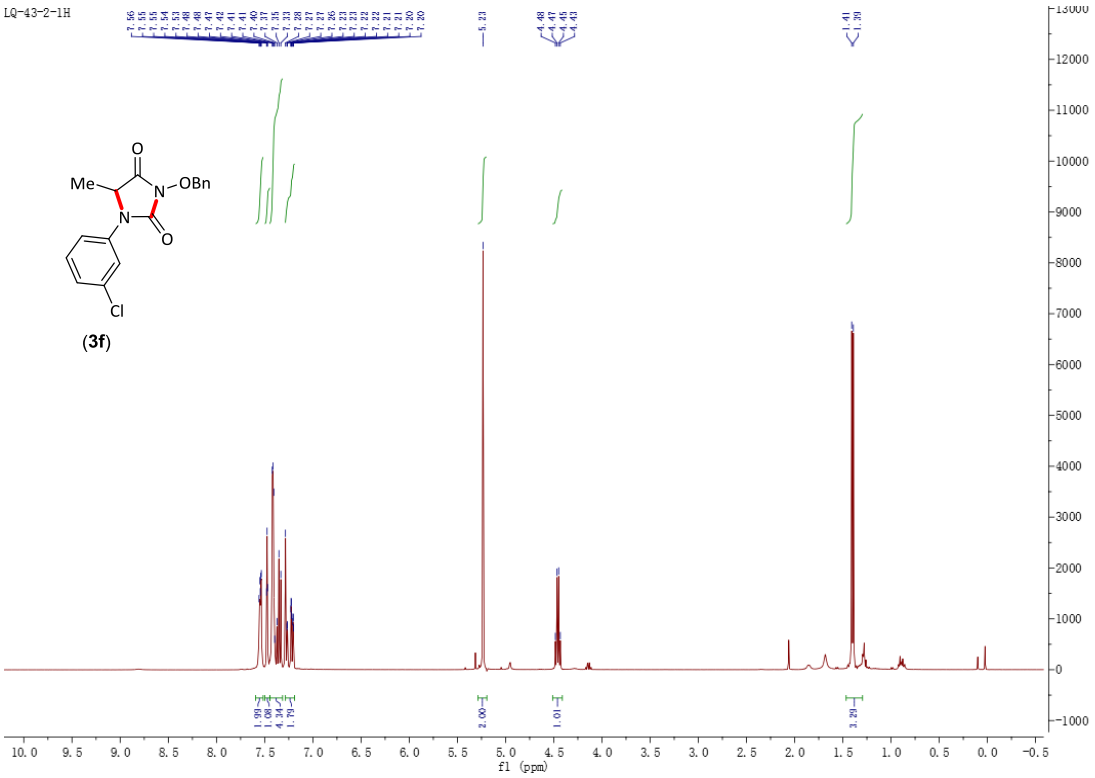
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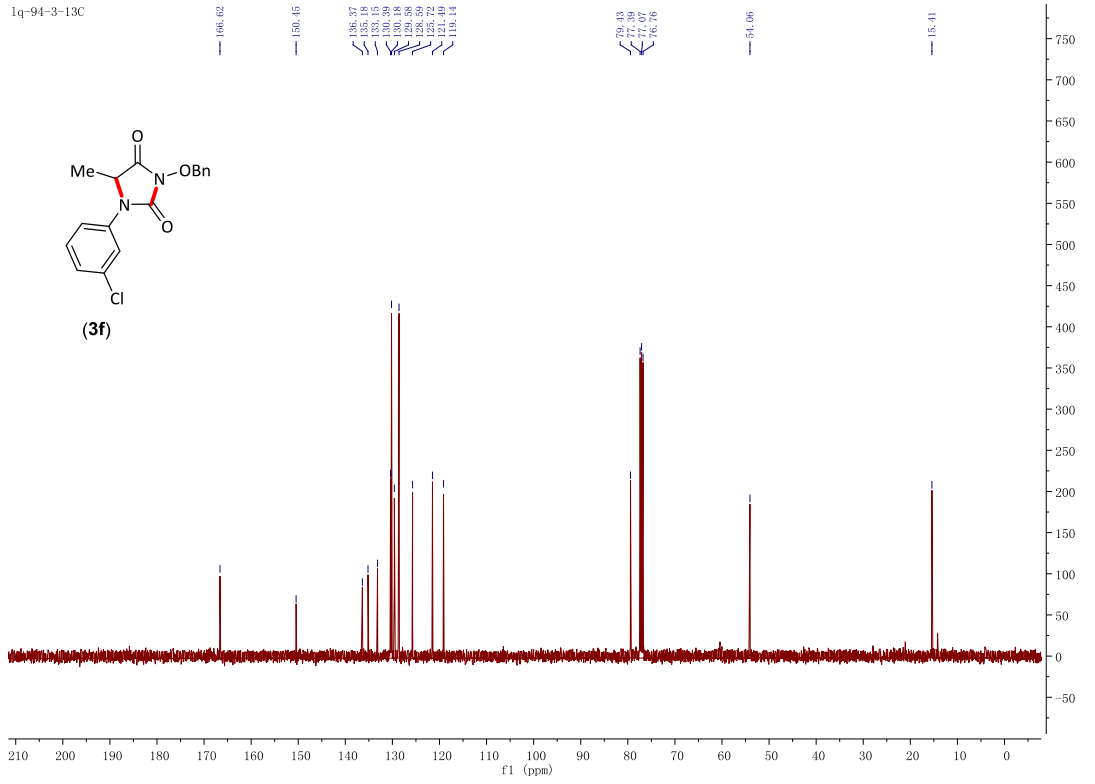
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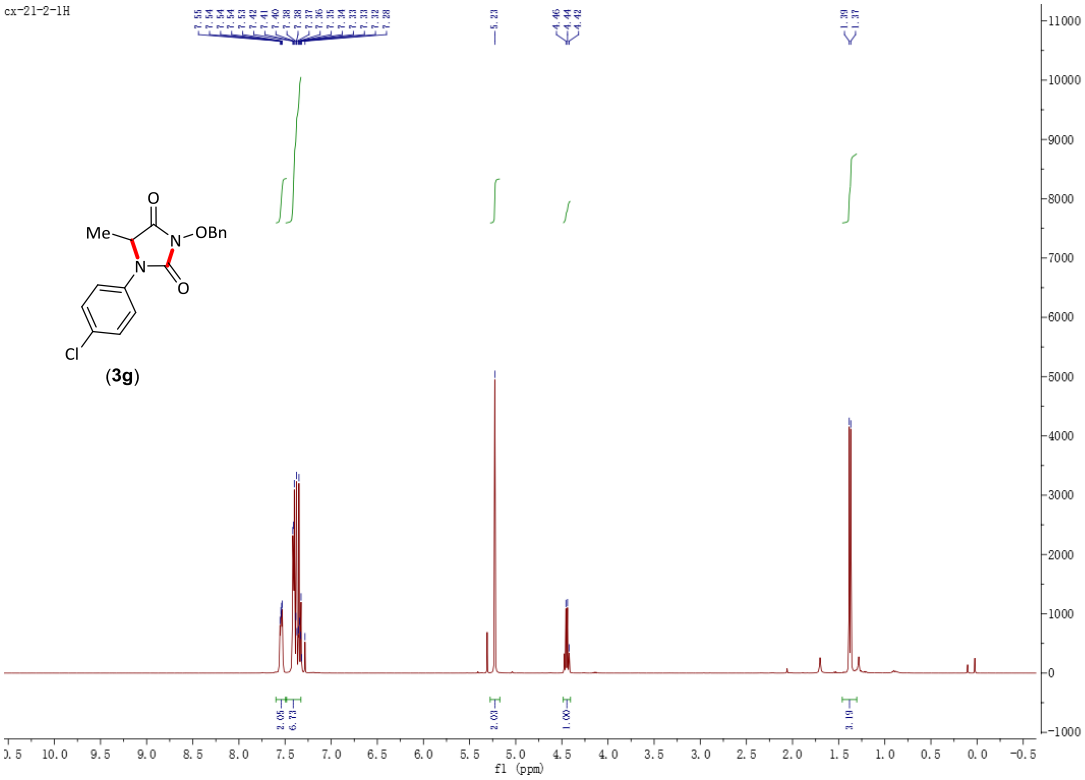
f1 (ppm)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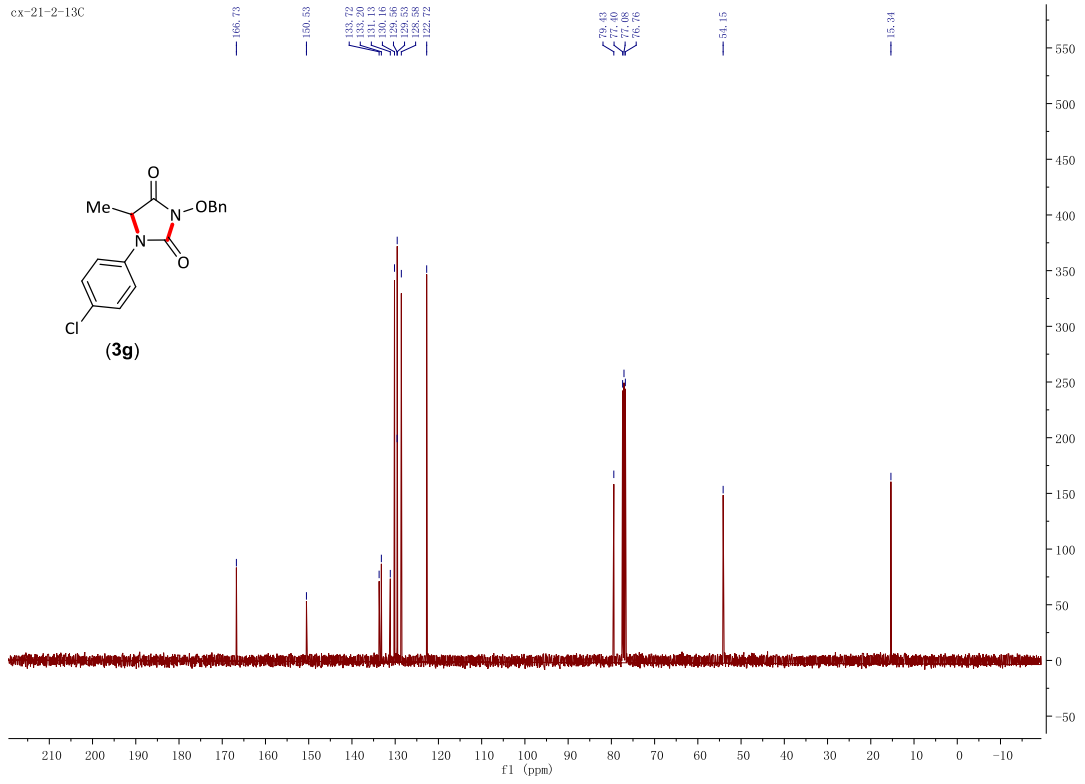
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Cl
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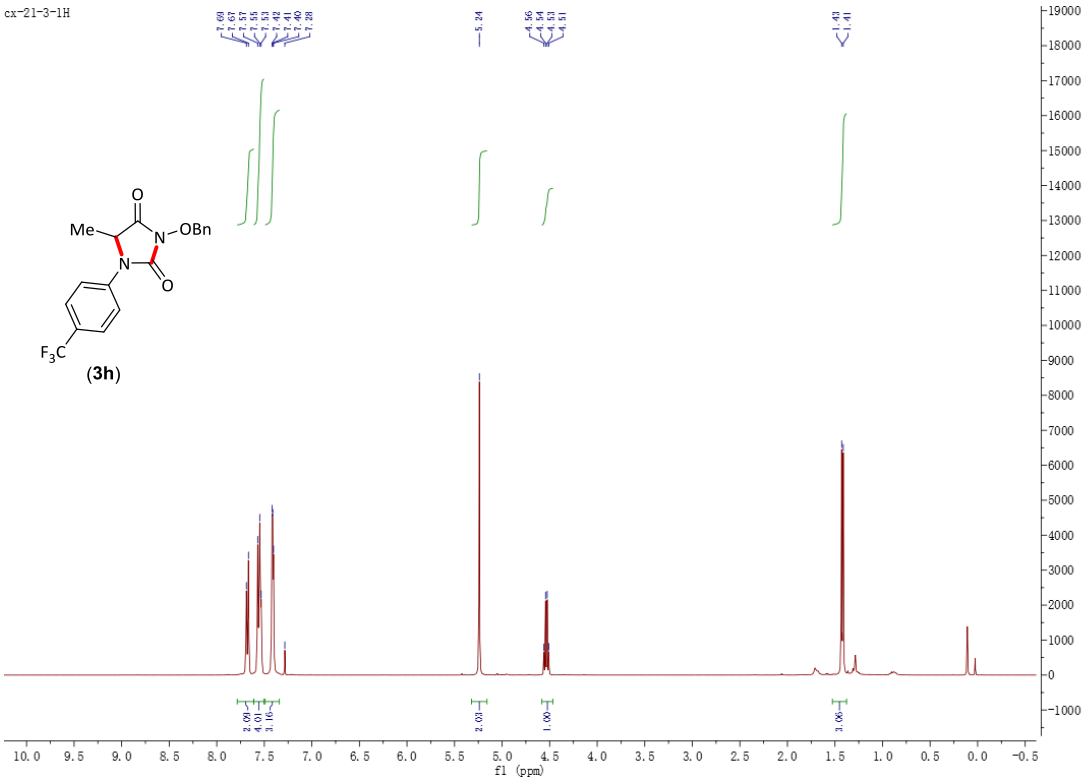
f1 (ppm)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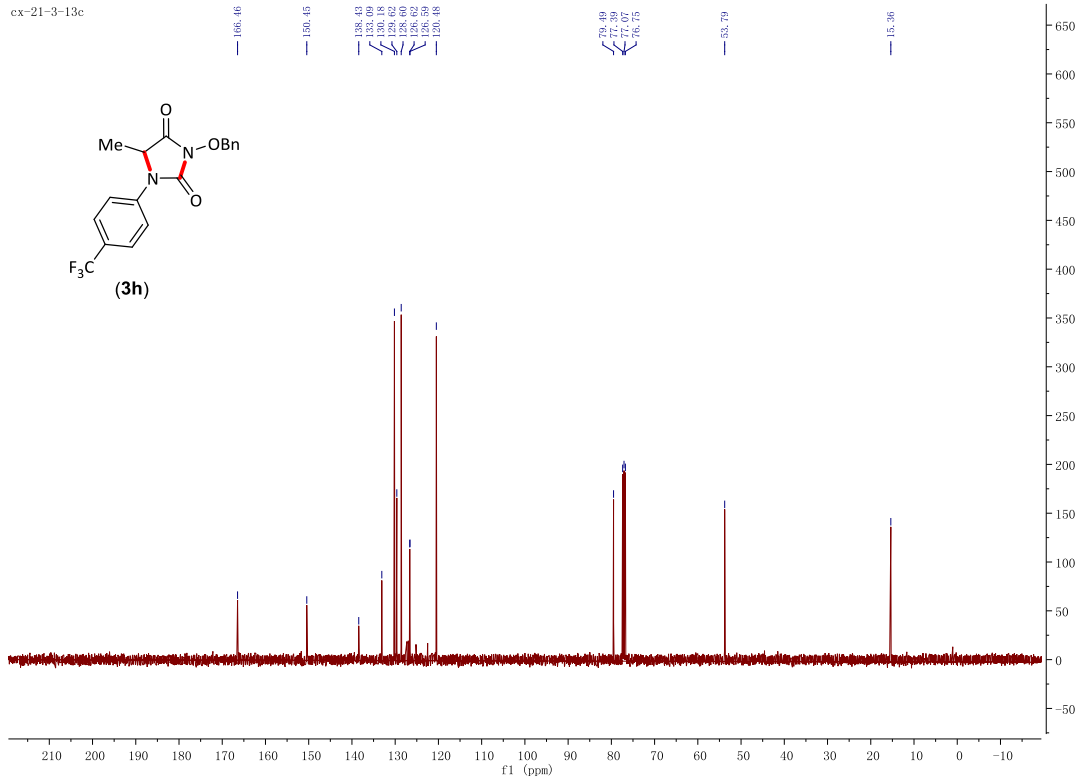
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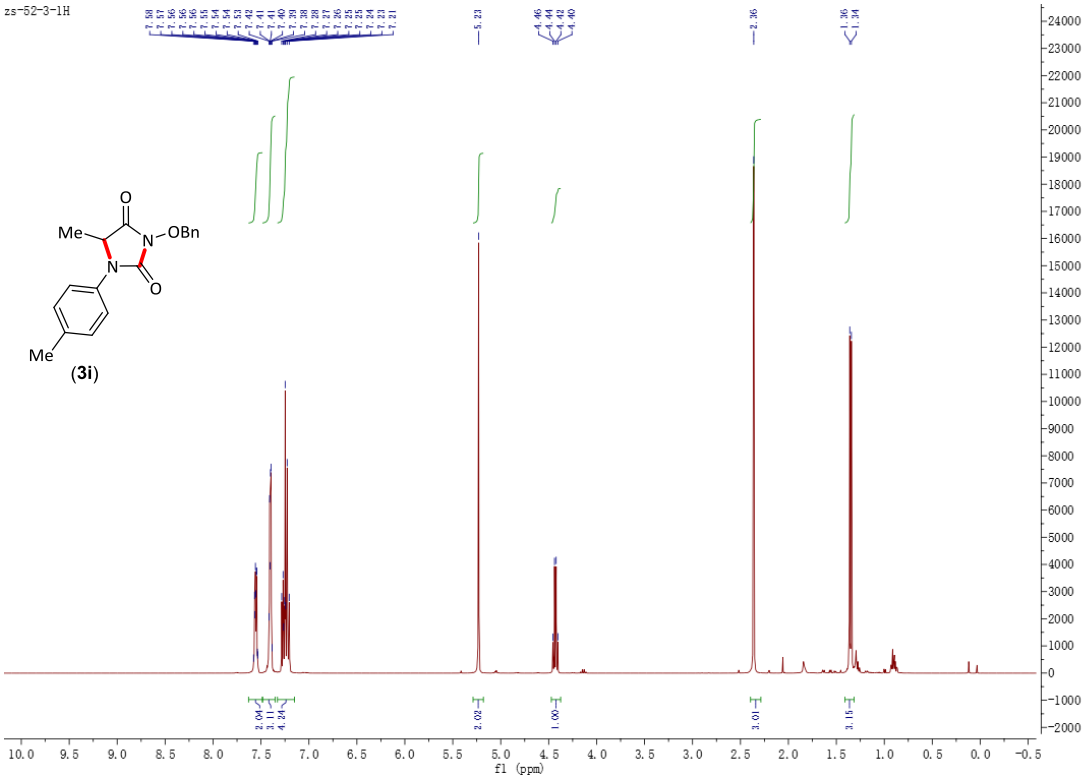
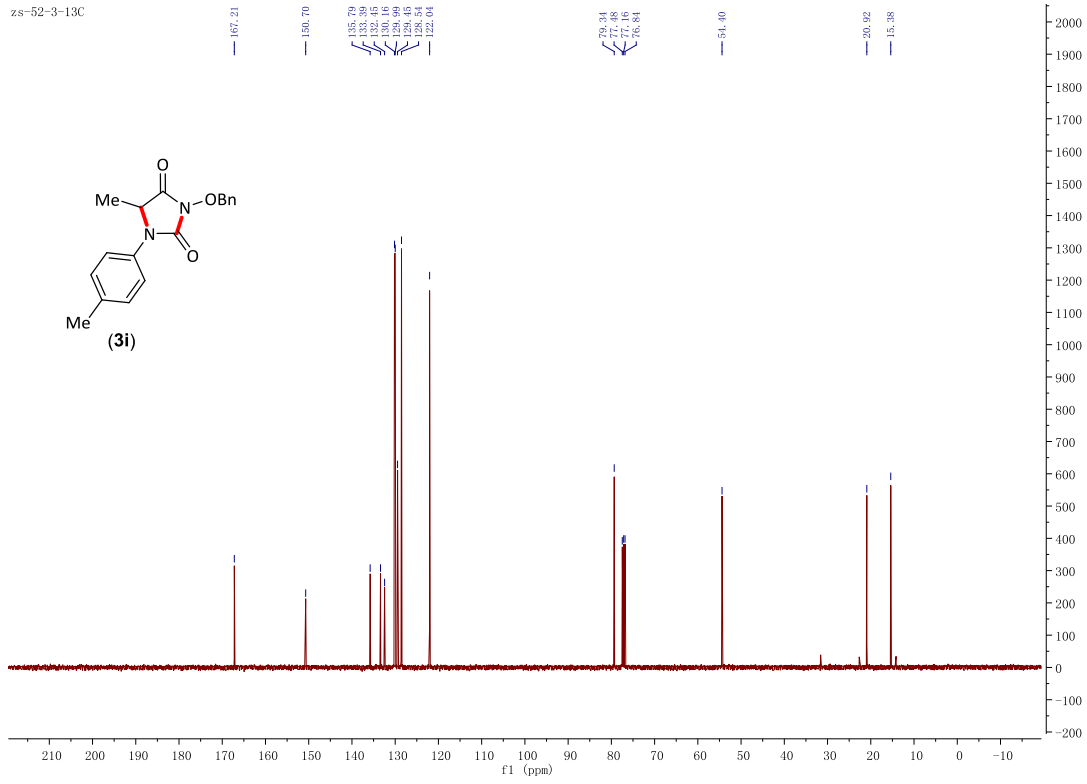
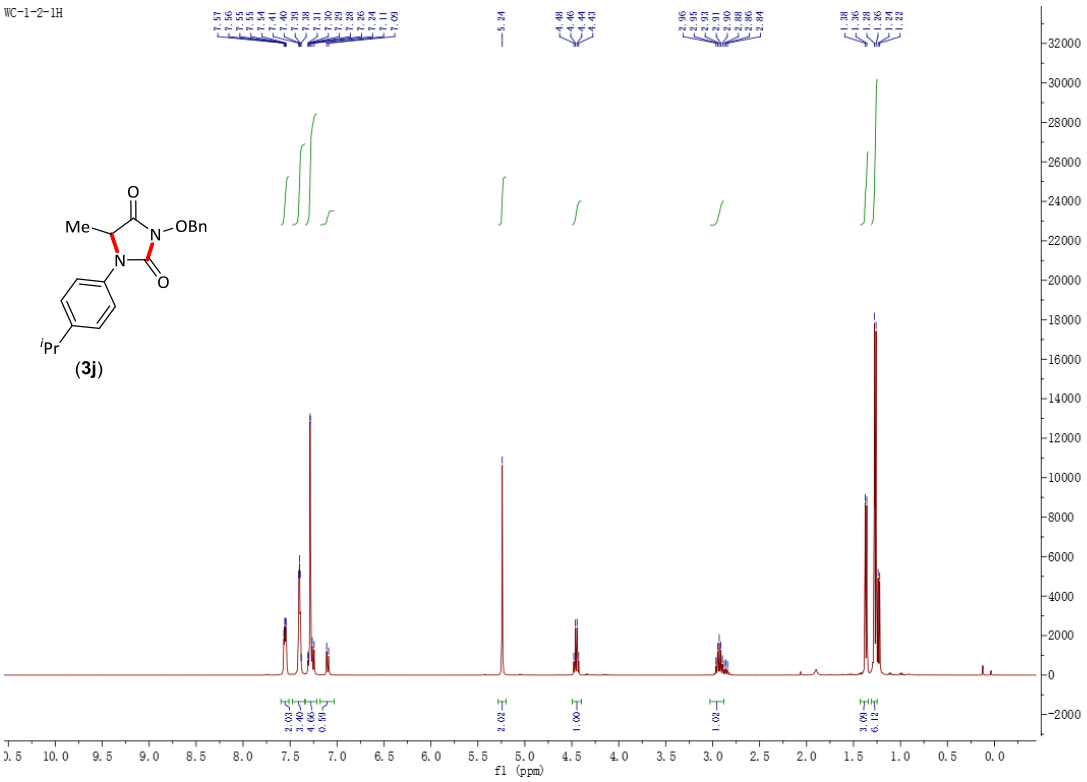
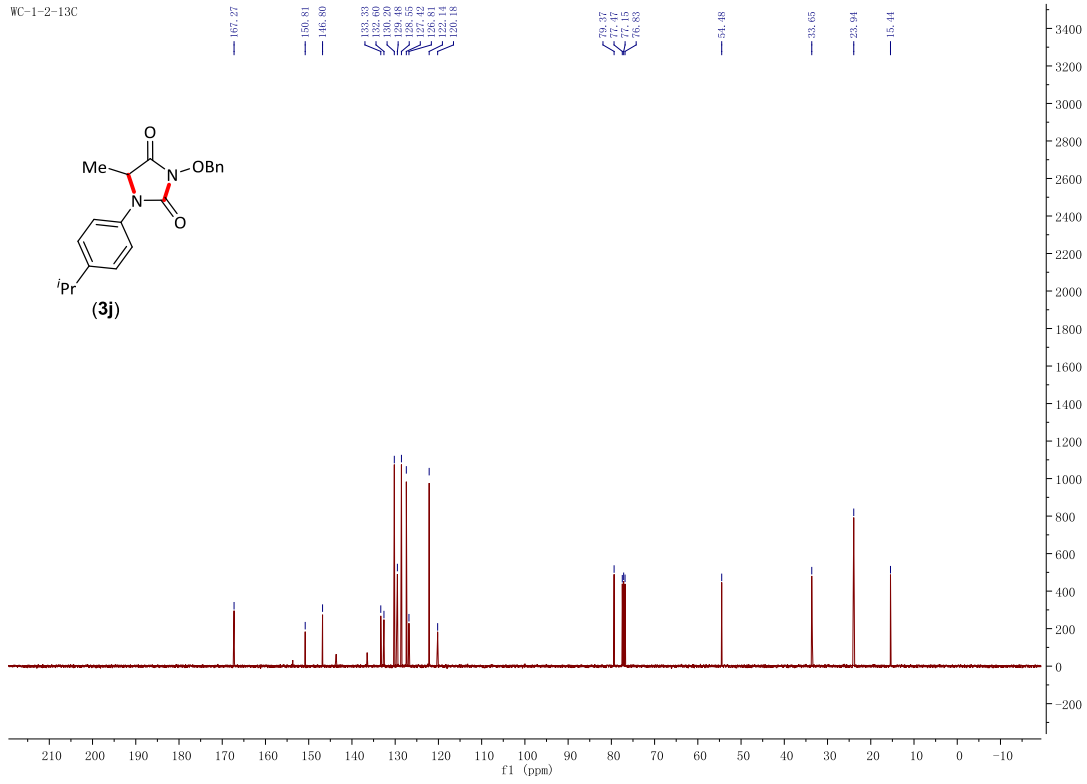
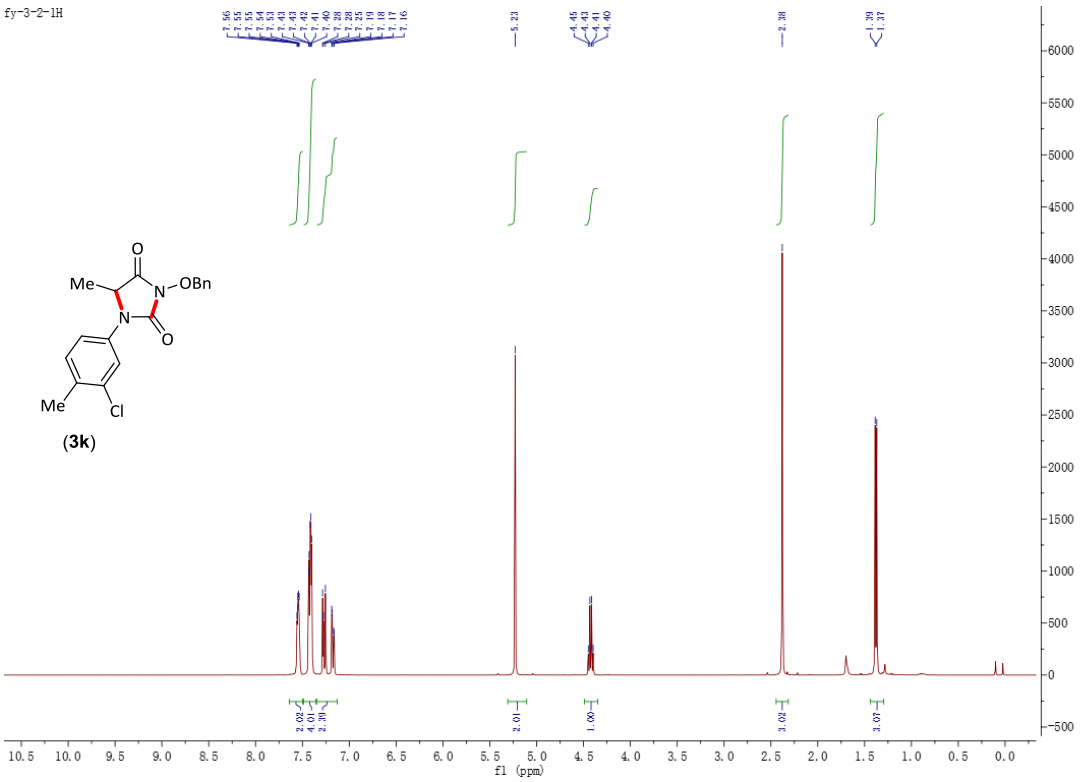
Me
OBn
(3h)
f1 (ppm)

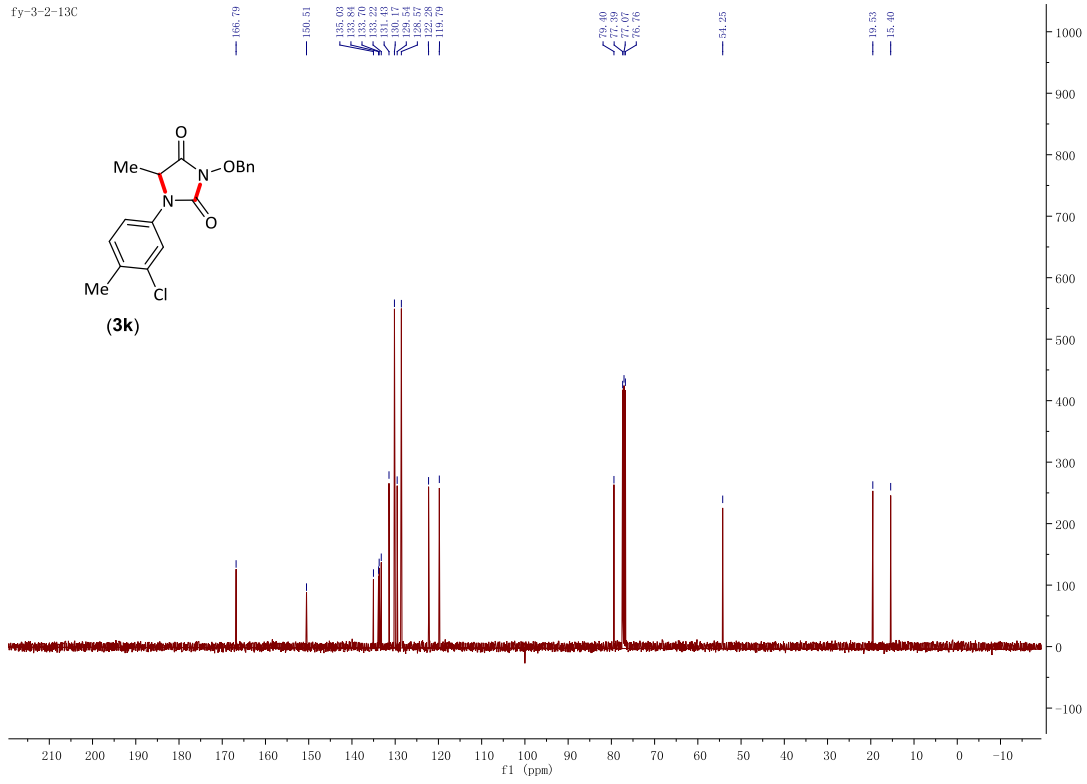

zs-52-3-1H
Me
OBn
Me
(3i)
f1 (ppm)

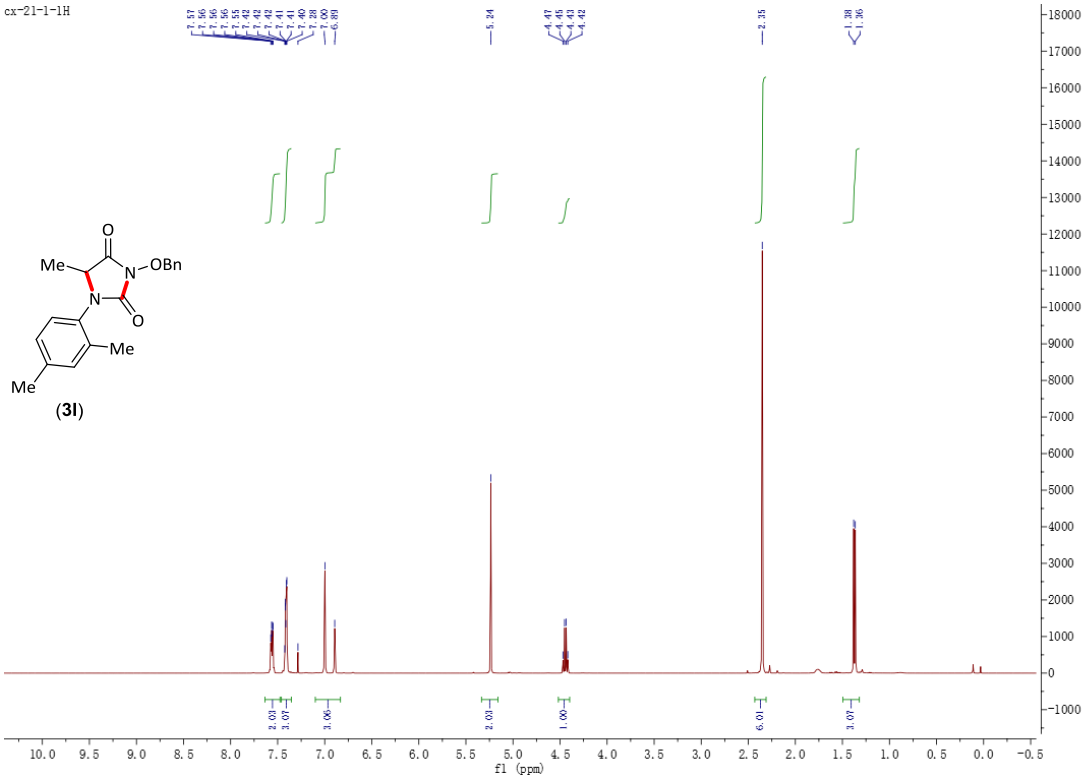

zs-52-3-13C
Me
OBn
Me
(3i)
f1 (ppm)

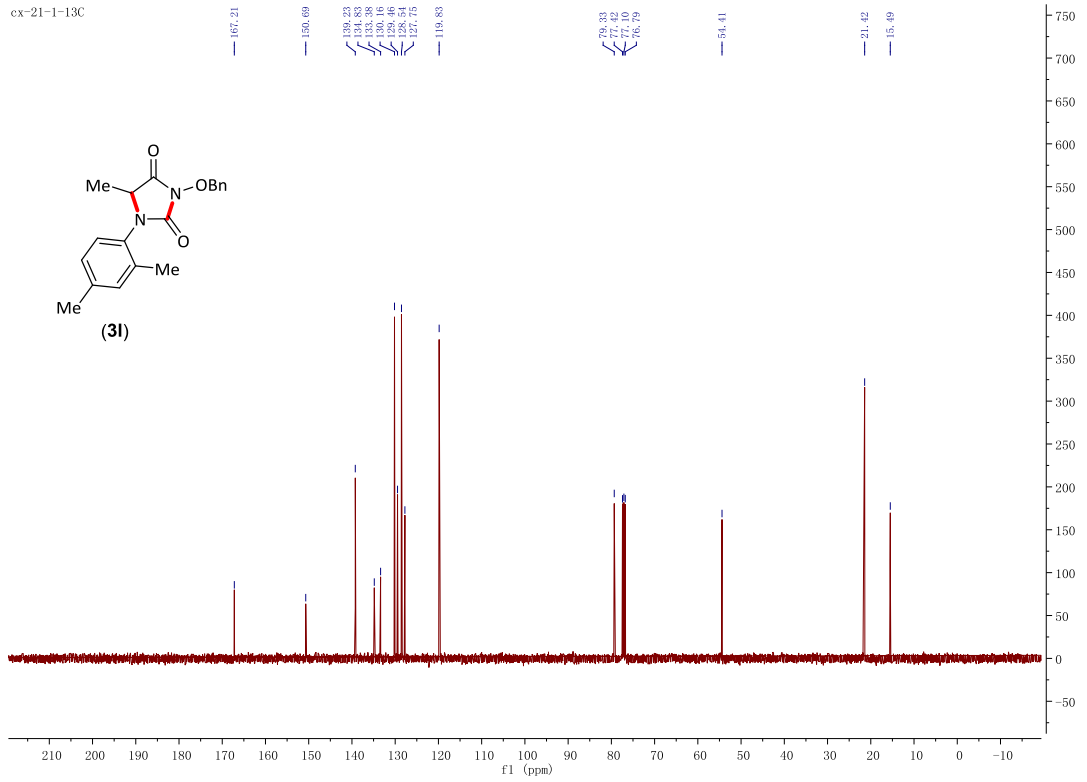

WC-1-2-1H
Me
OBn
iPr
(3j)
f1 (ppm)

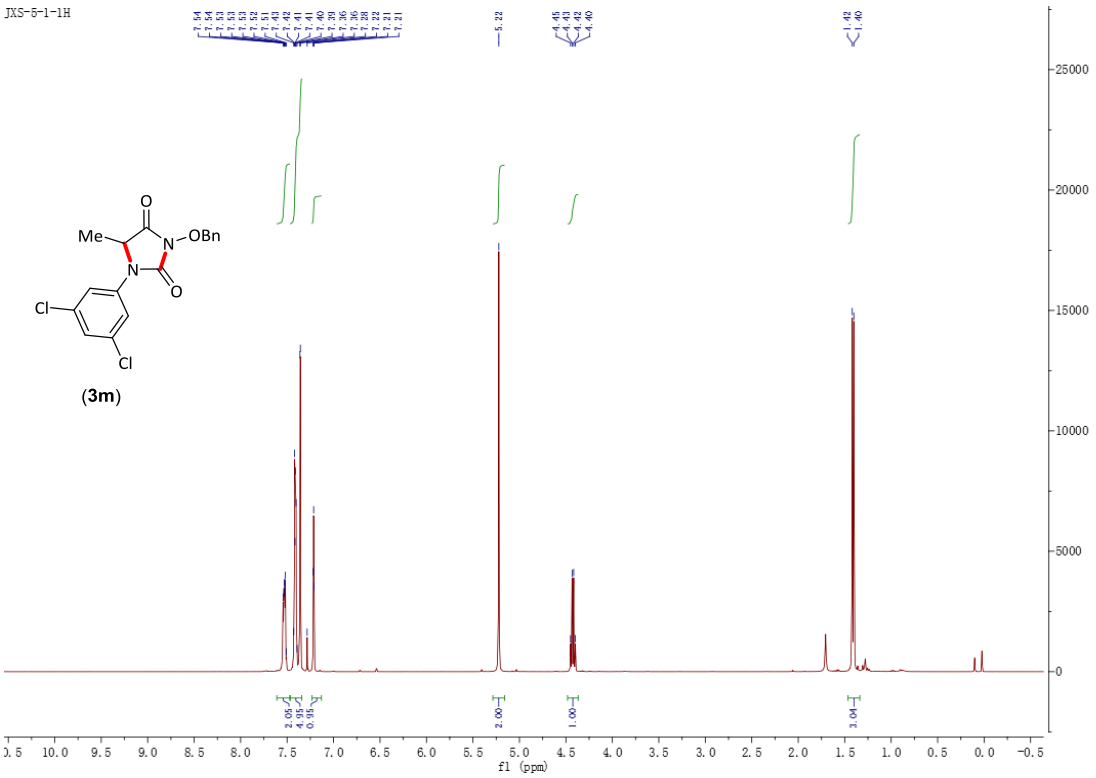

WC-1-2-13C
Me
OBn
iPr
(3j)
f1 (ppm)

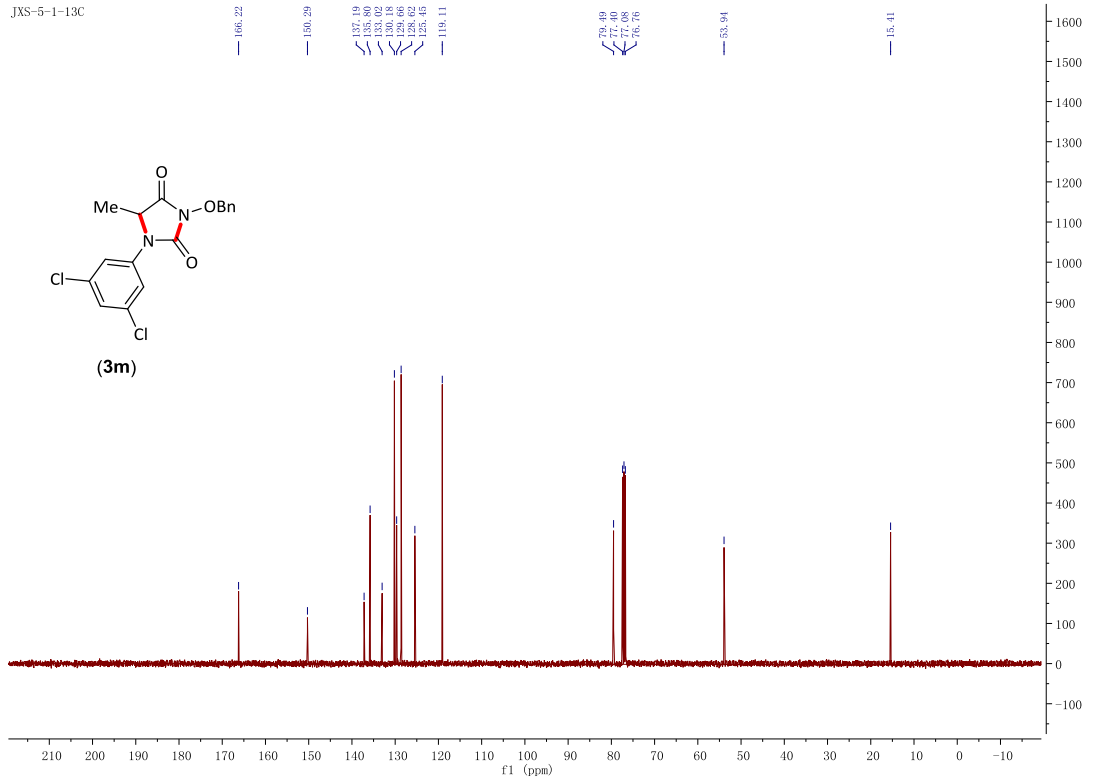

fy-3-2-1H
Me
N
OBn
O
Me
Cl
(3k)
f1 (ppm)

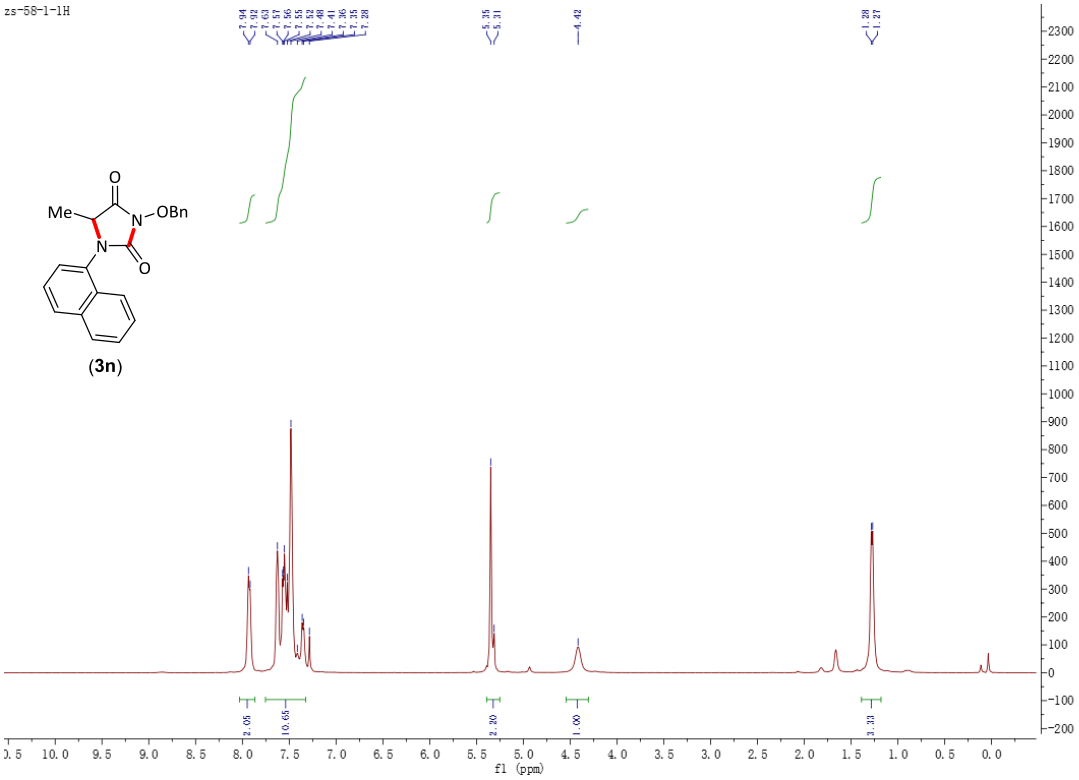

fy-3-2-13C
Me
N
OBn
O
Me
Cl
(3k)
f1 (ppm)

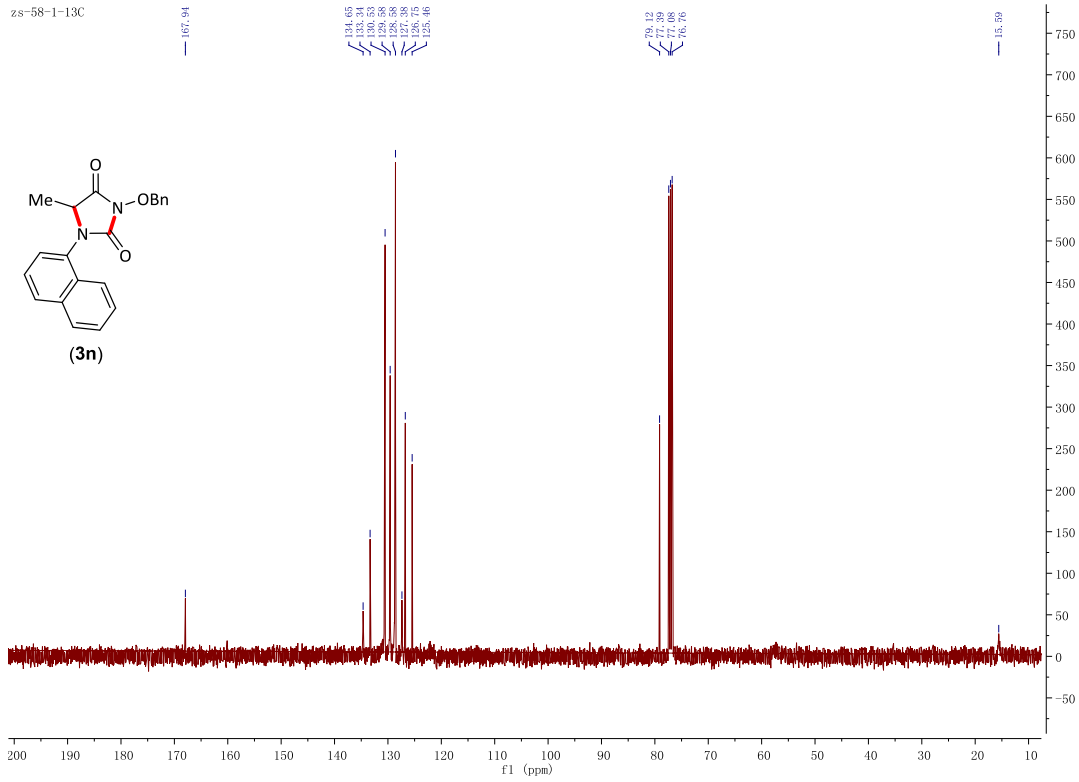

cx-21-1-1H
Me
N
OBn
O
O
Me
Me
(3l)
f1 (ppm)

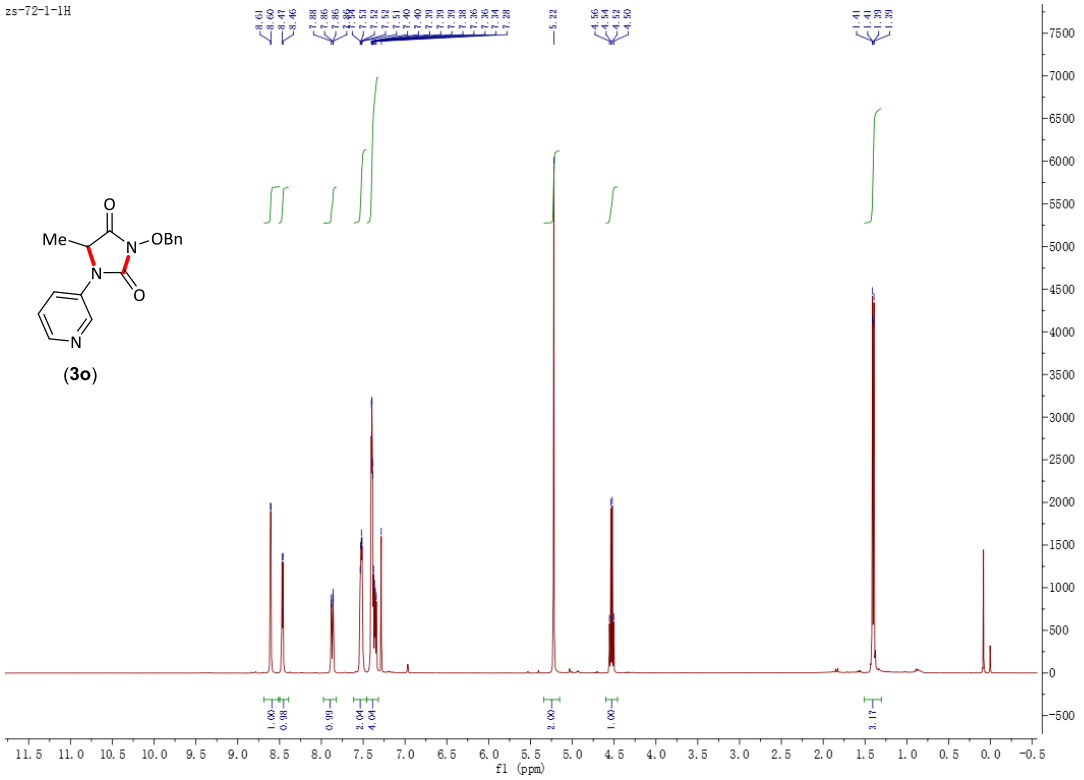

cx-21-1-13C
Me
N
OBn
O
O
Me
Me
(3l)
f1 (ppm)

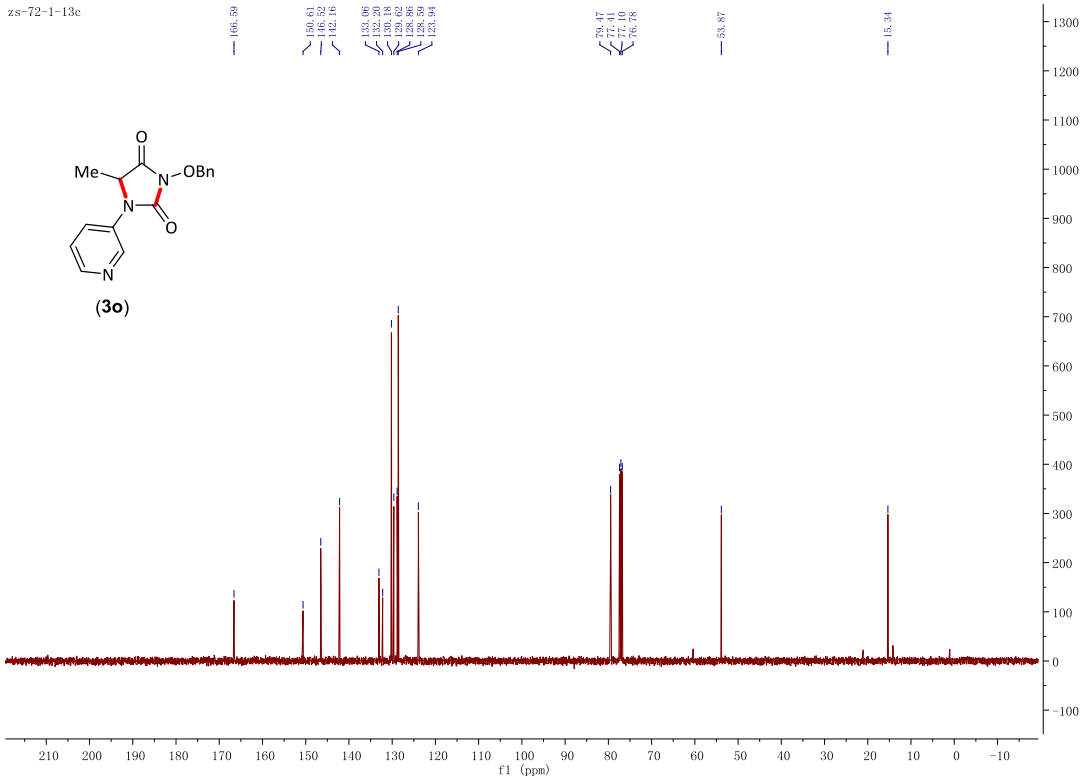

JXS-5-1-1H
Me
N
OBn
O
O
Cl
Cl
(3m)
f1 (ppm)

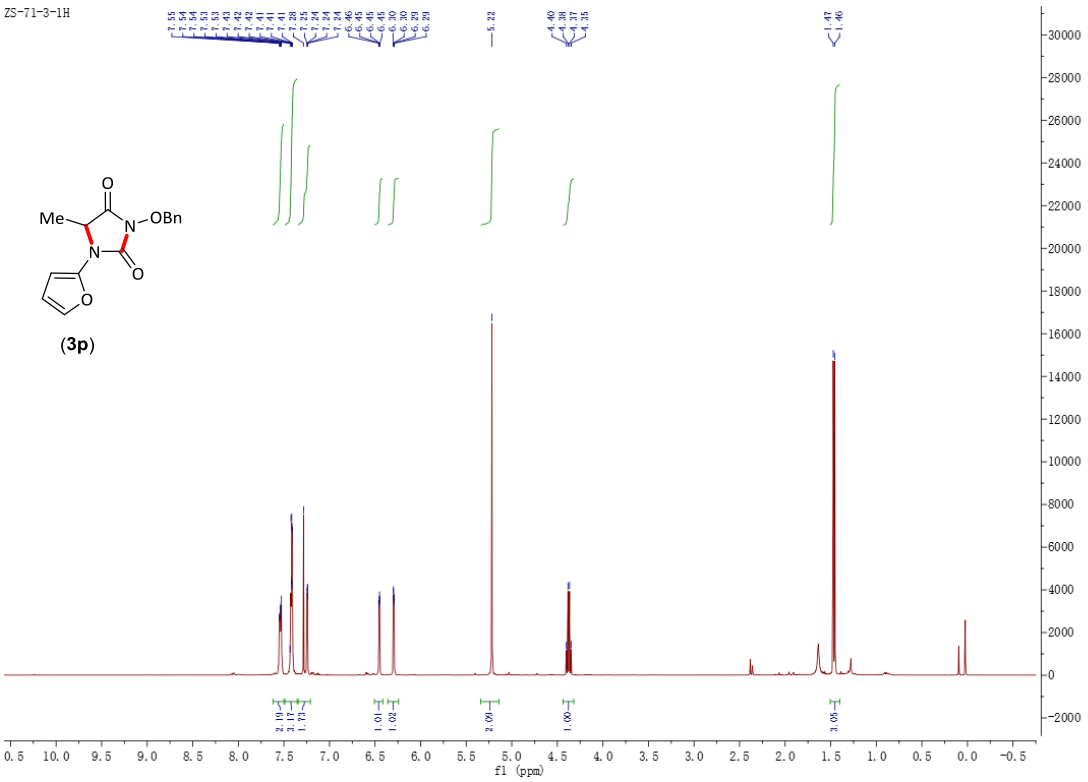

JXS-5-1-13C
Me
N
OBn
O
O
Cl
Cl
(3m)
f1 (ppm)

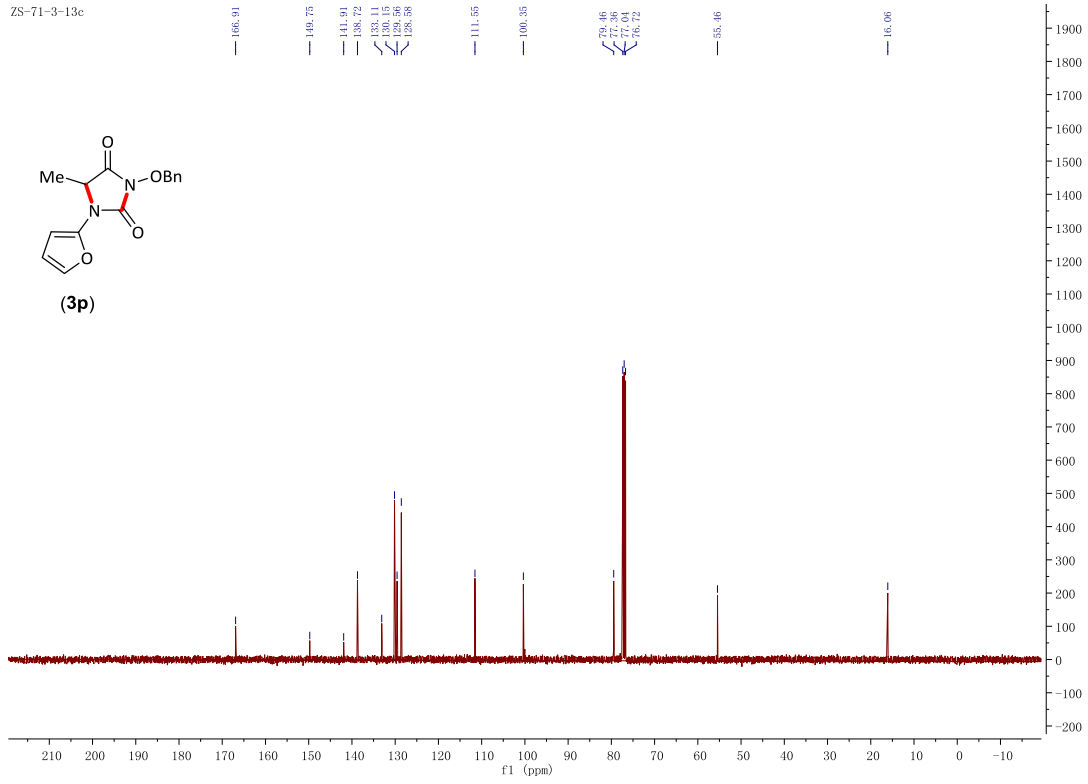

zs-58-1-1H
Me
OBn
O
N
(3n)
f1 (ppm)

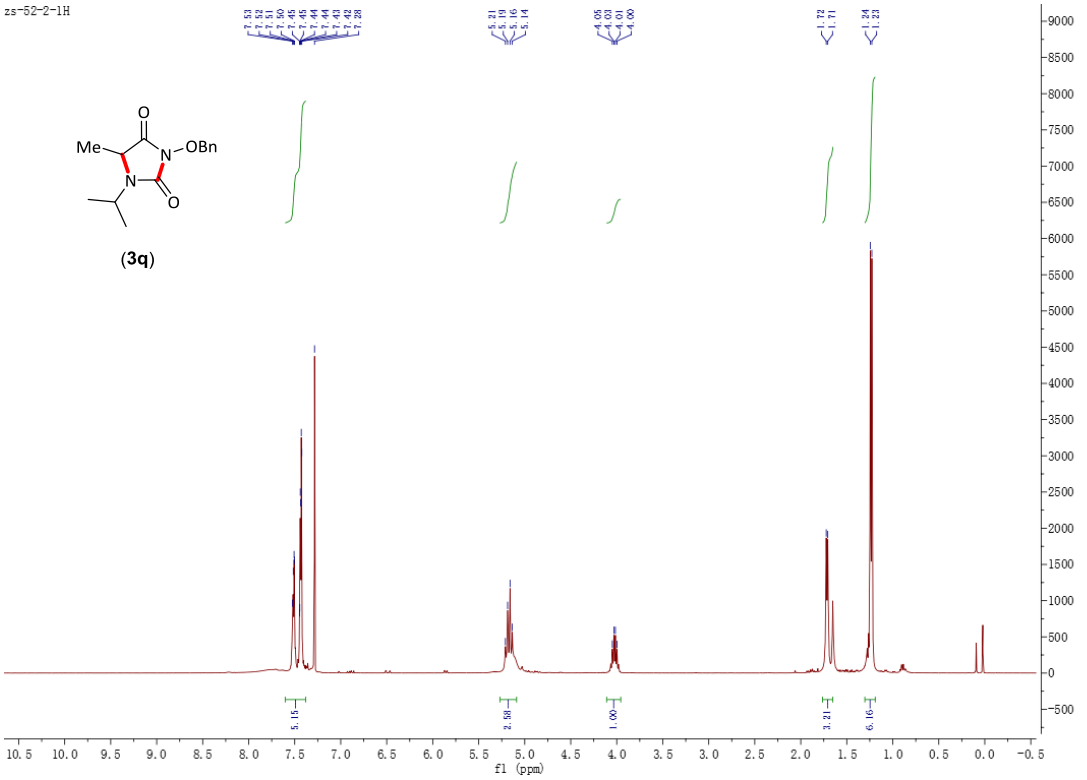

zs-58-1-13C
Me
OBn
O
N
(3n)
f1 (ppm)

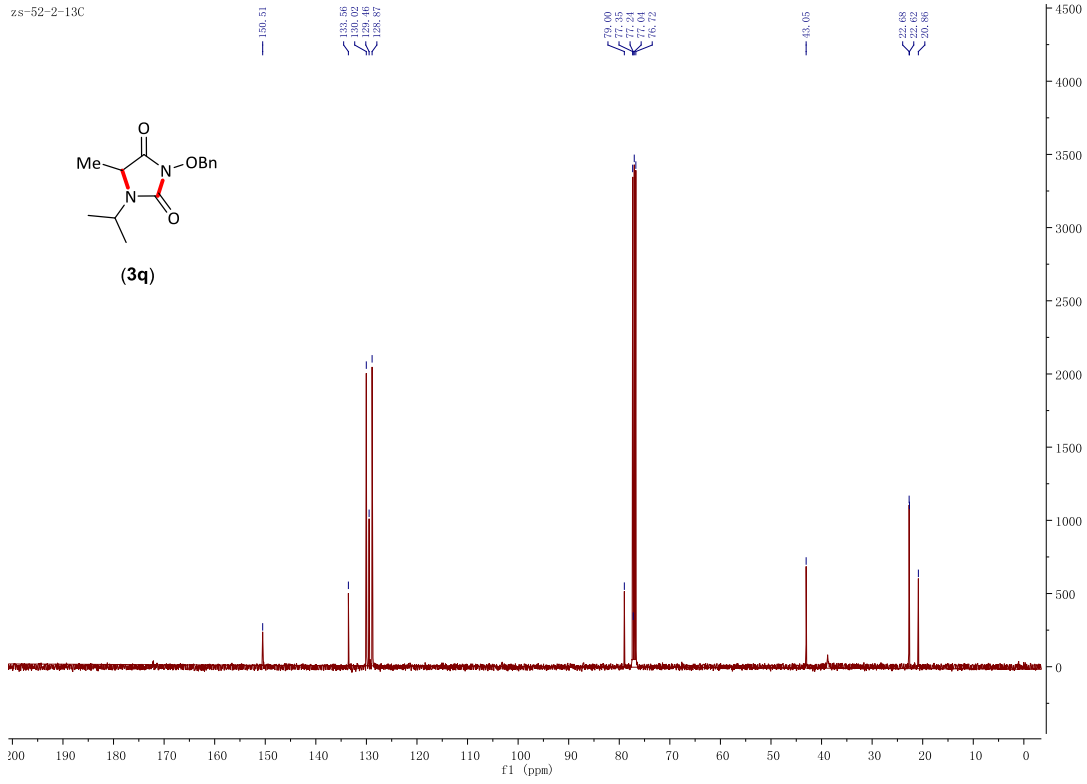

zs-72-1-1H
Me
OBn
(3o)
f1 (ppm)

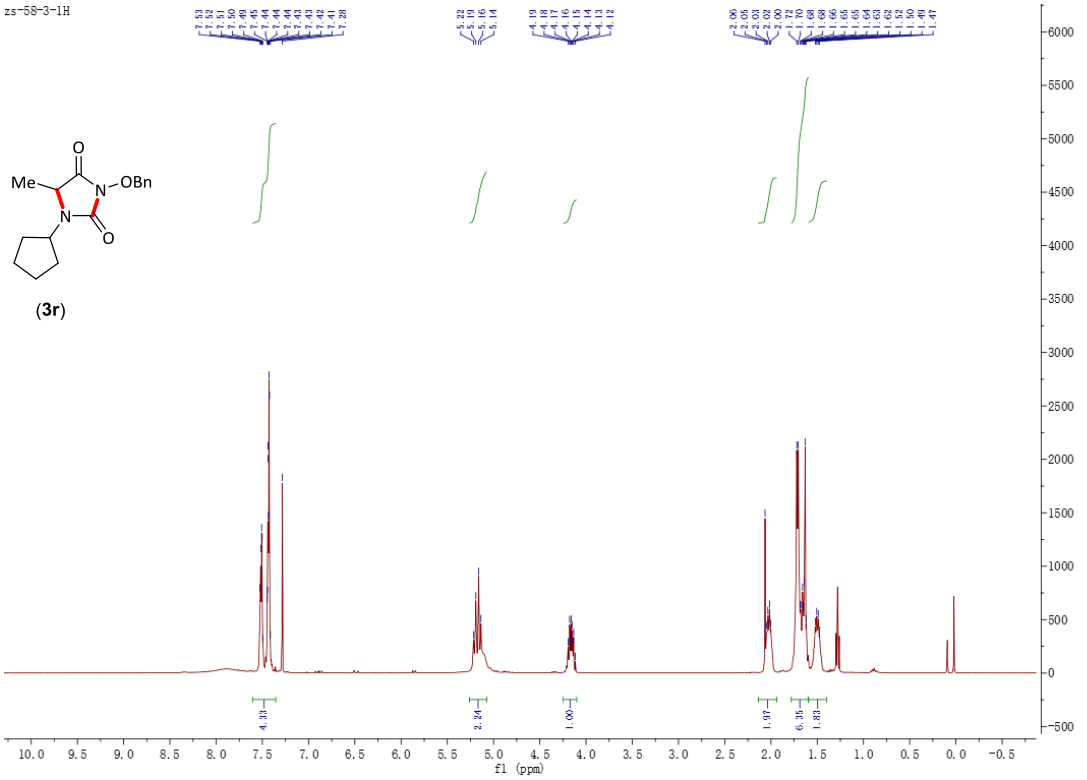

zs-72-1-13c
Me
OBn
(3o)
f1 (ppm)

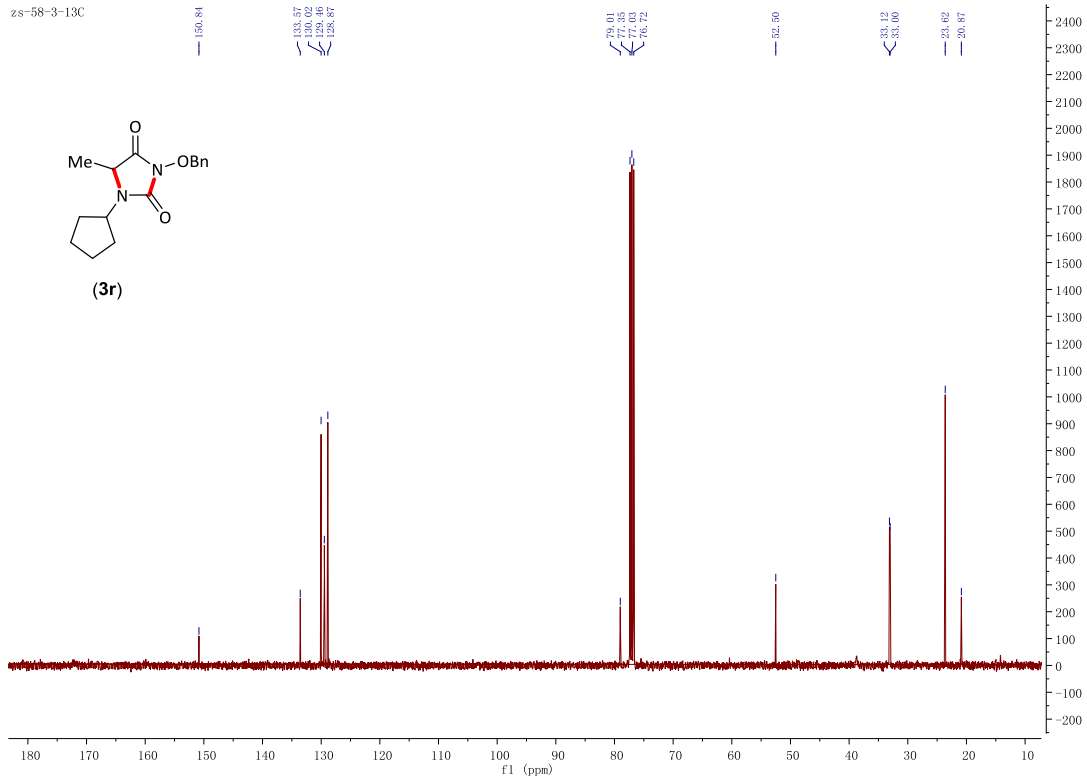

ZS-71-3-1H
Me
OBn
(3p)
f1 (ppm)

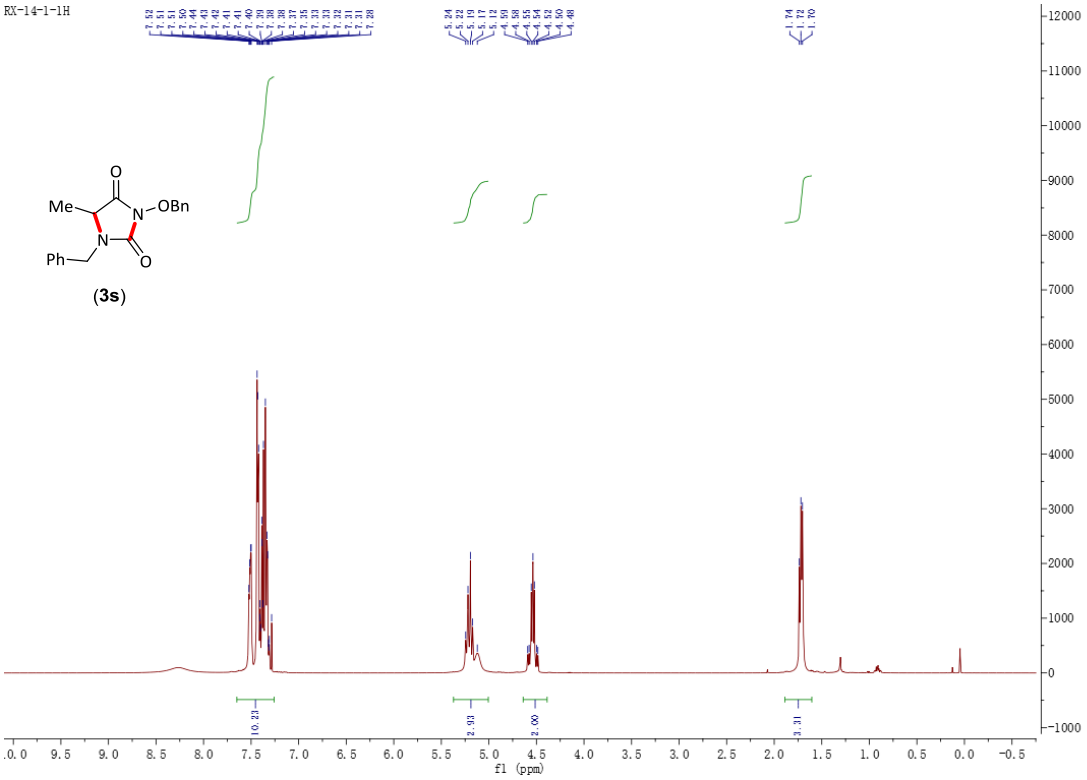

ZS-71-3-13c
Me
OBn
(3p)
f1 (ppm)

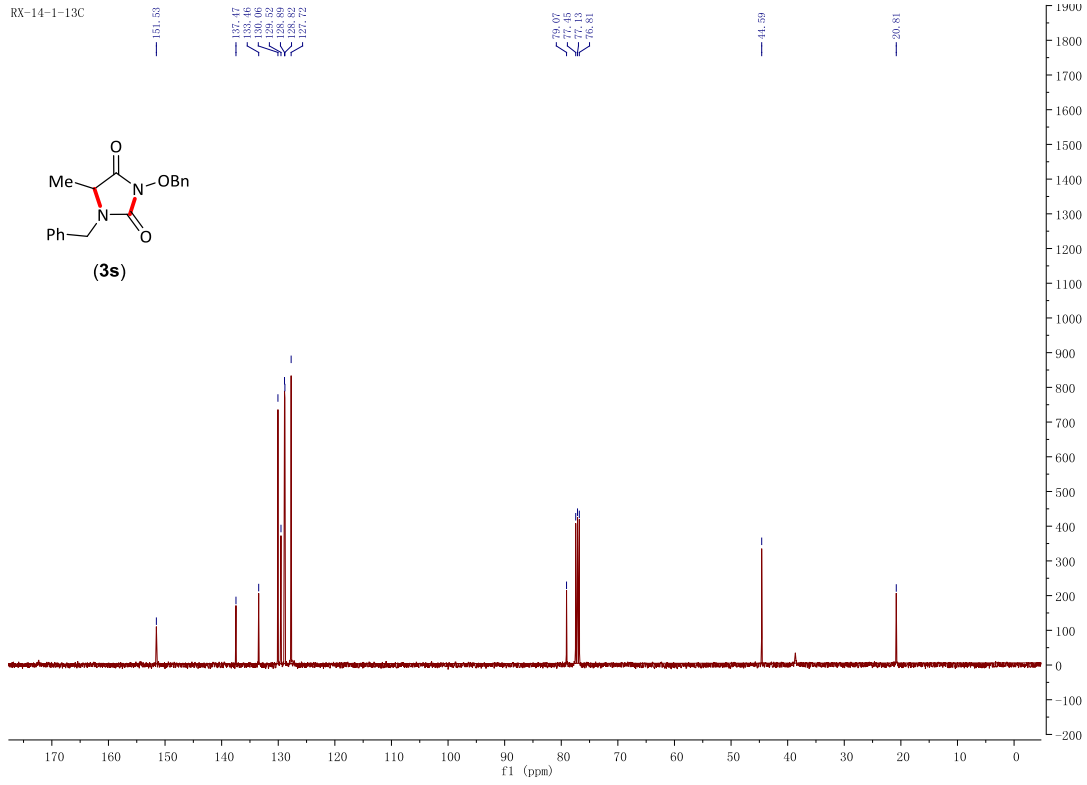

zs-52-2-1H
Me
N
OBn
O
O
(3q)
f1 (ppm)

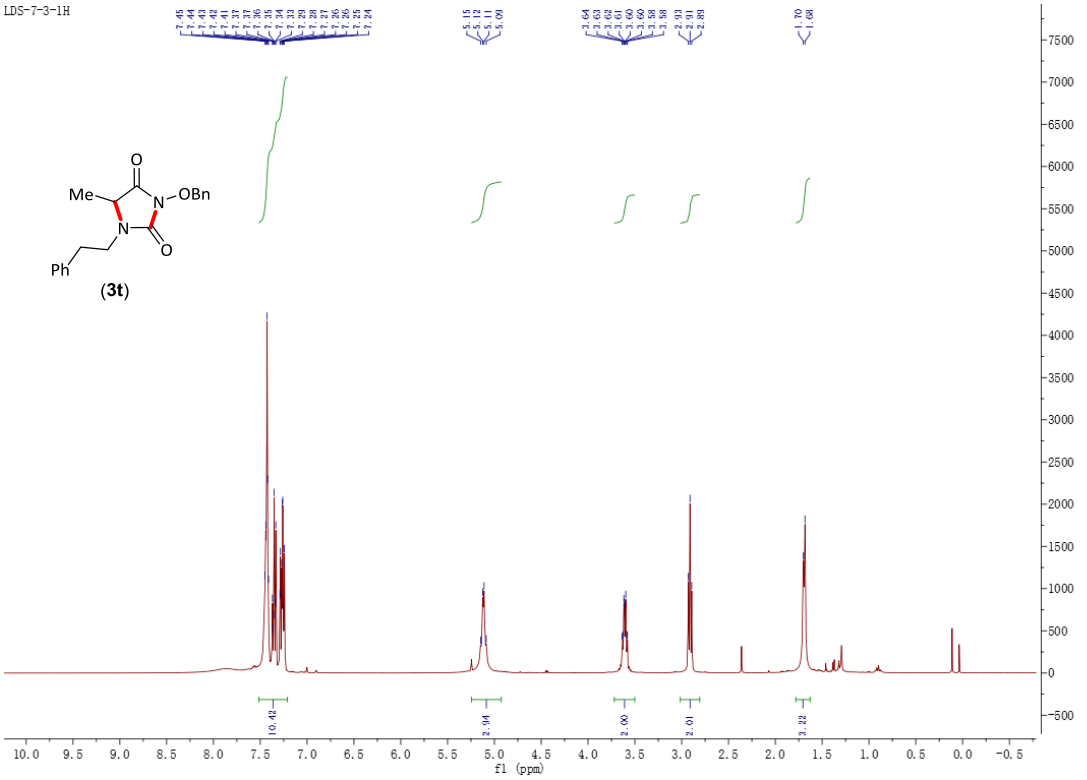

zs-52-2-13C
Me
N
OBn
O
O
(3q)
f1 (ppm)

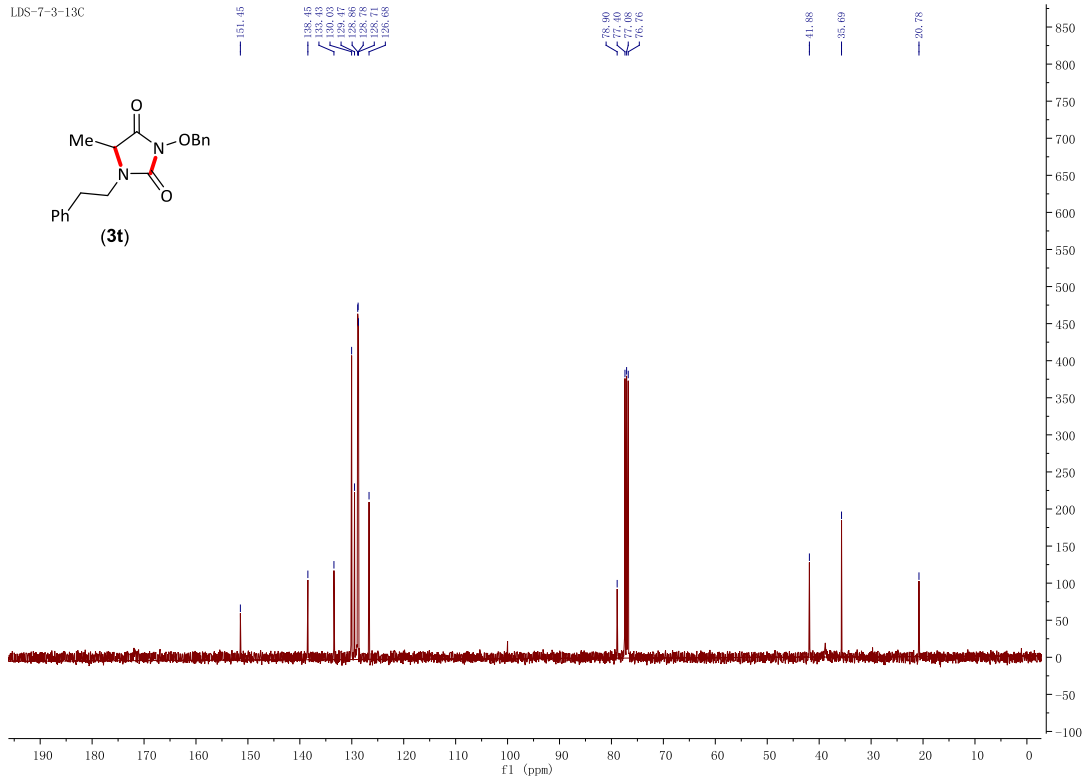

zs-58-3-1H
Me
OBn
O
N
O
(3r)
f1 (ppm)

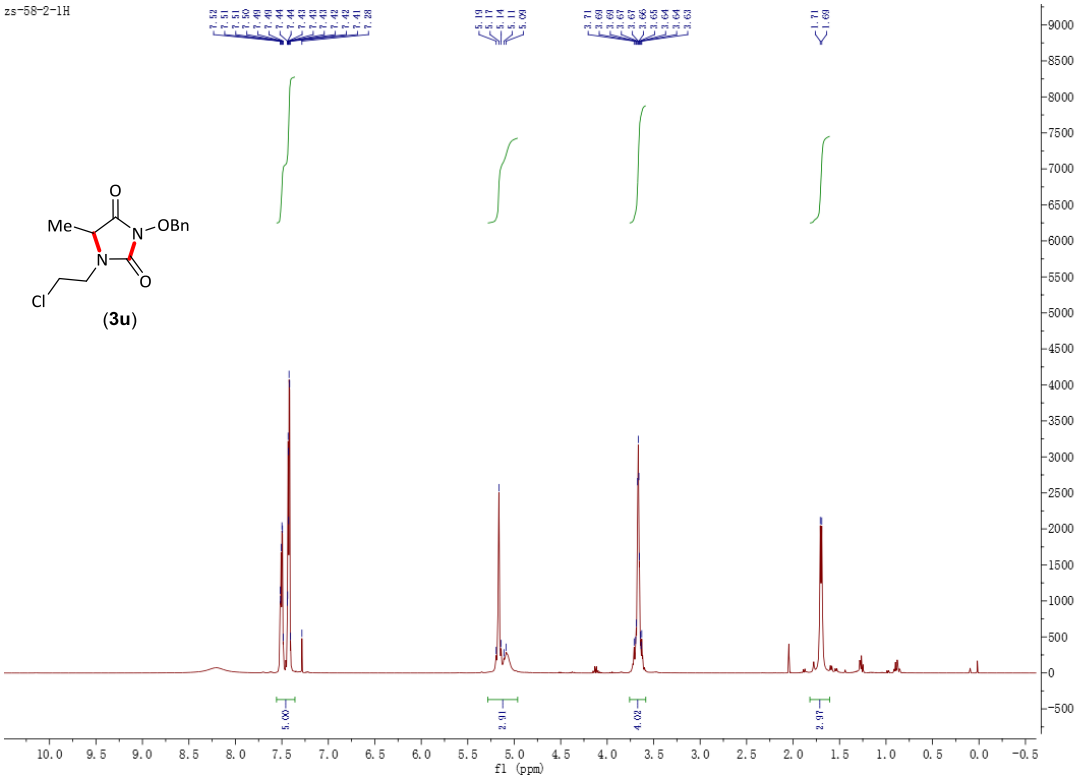

zs-58-3-13C
Me
OBn
O
N
O
(3r)
f1 (ppm)

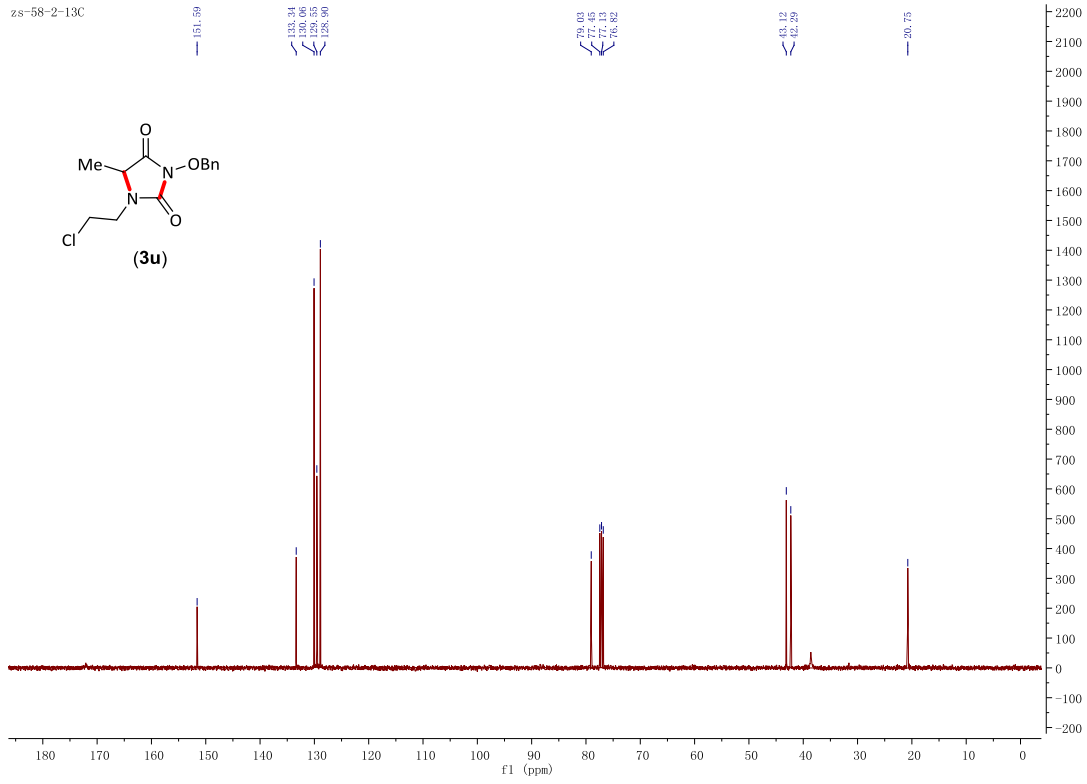

RX-14-1-1H
Me
OBn
N
Ph
O
(3s)
f1 (ppm)

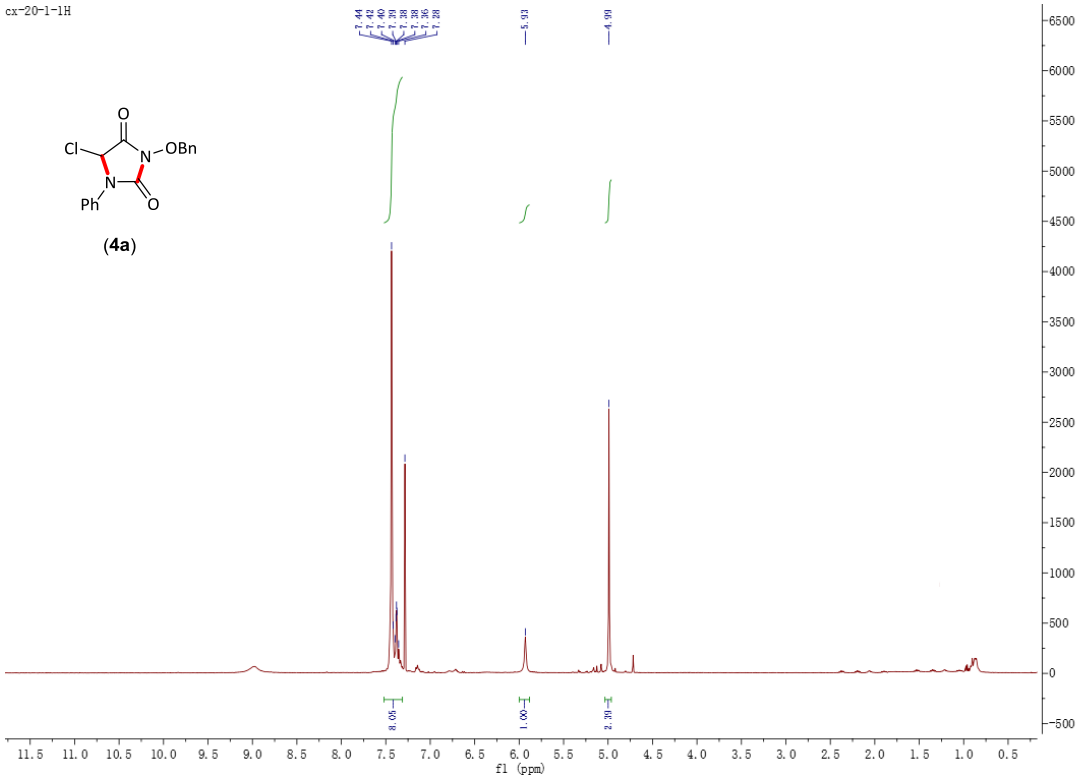

RX-14-1-13C
Me
OBn
N
Ph
O
(3s)
f1 (ppm)

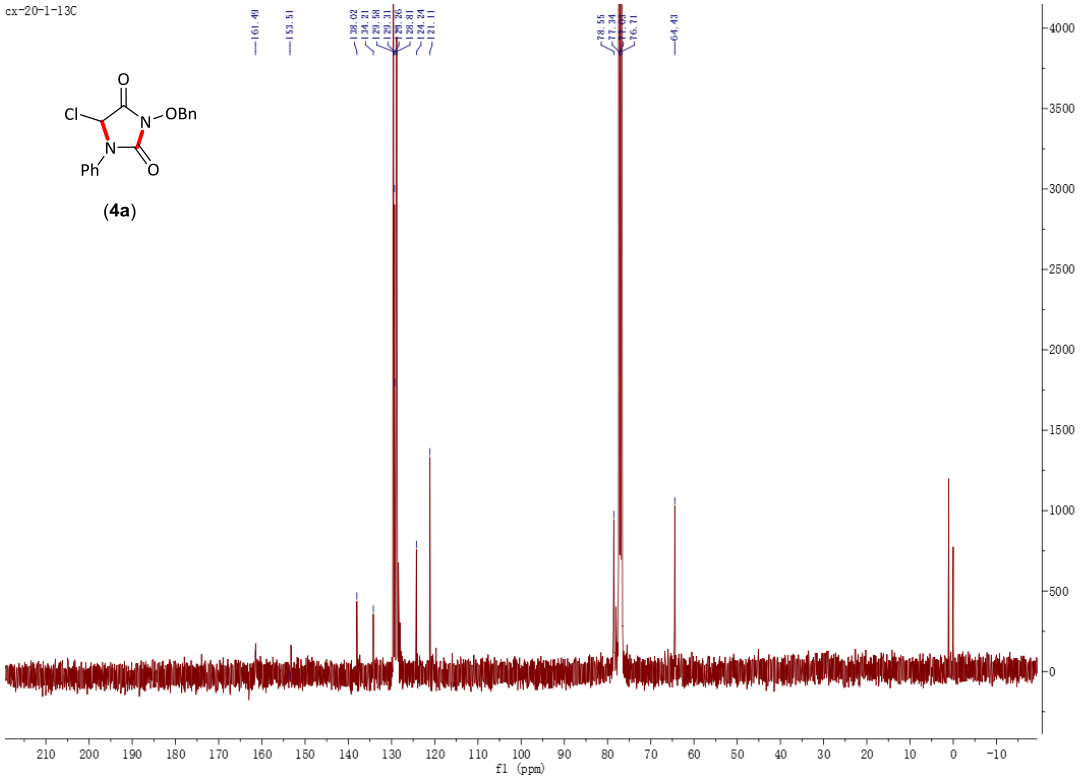

LDS-7-3-1H
Me
OBn
Ph
(3t)
f1 (ppm)

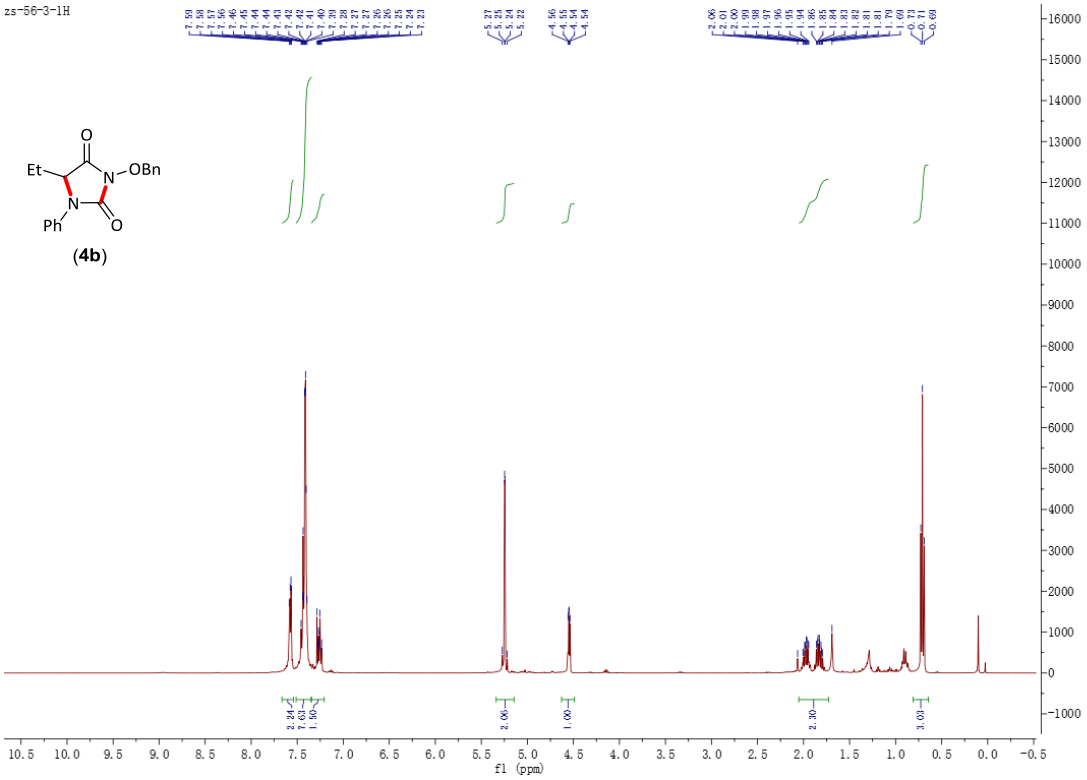

LDS-7-3-13C
Me
OBn
Ph
(3t)
f1 (ppm)

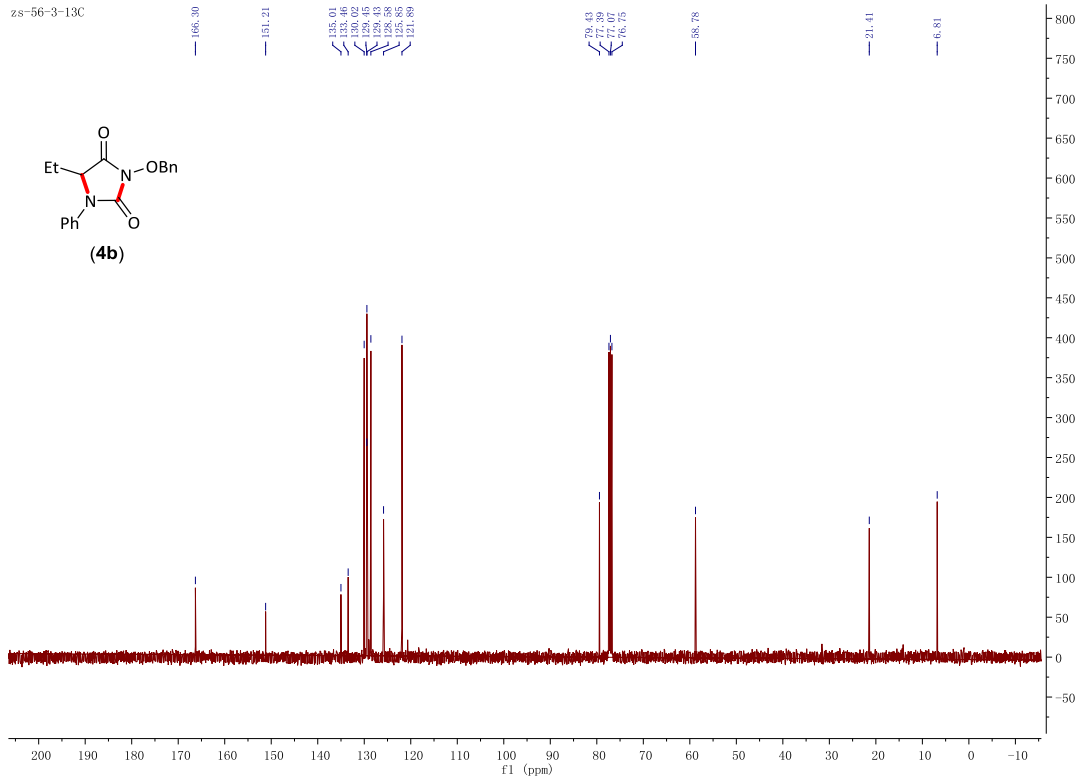

zs-58-2-1H
Me
N
OBn
N
O
O
Cl
(3u)
f1 (ppm)

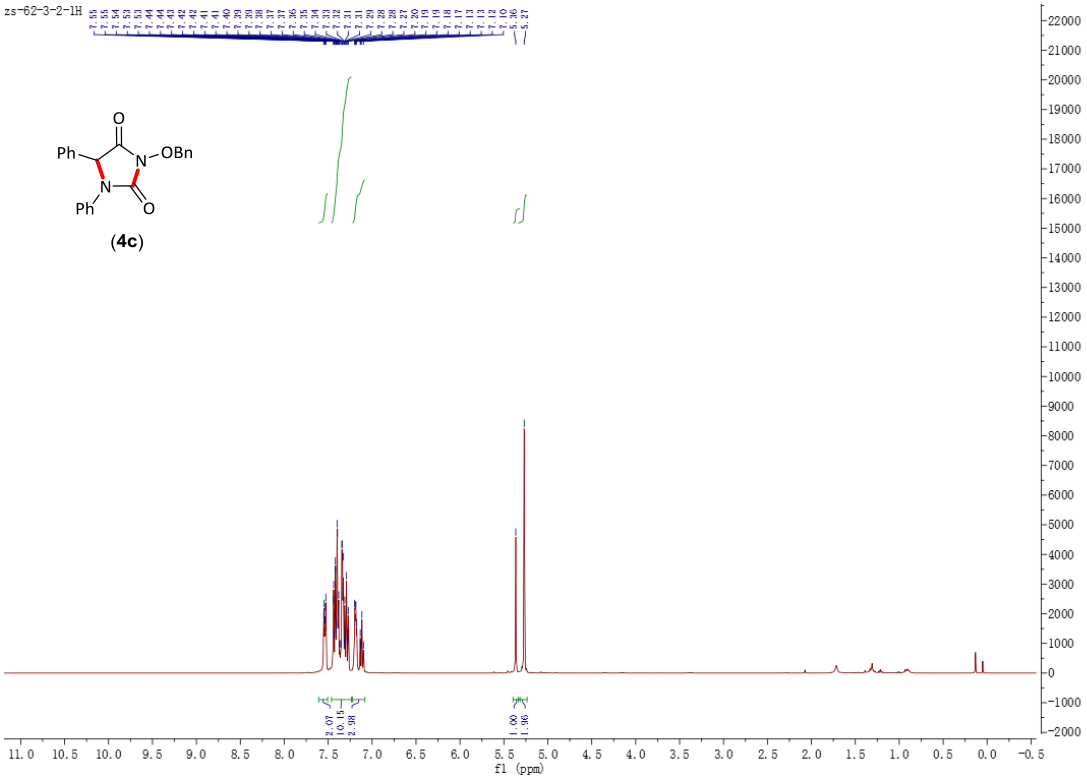

zs-58-2-13C
Me
N
OBn
N
O
O
Cl
(3u)
f1 (ppm)

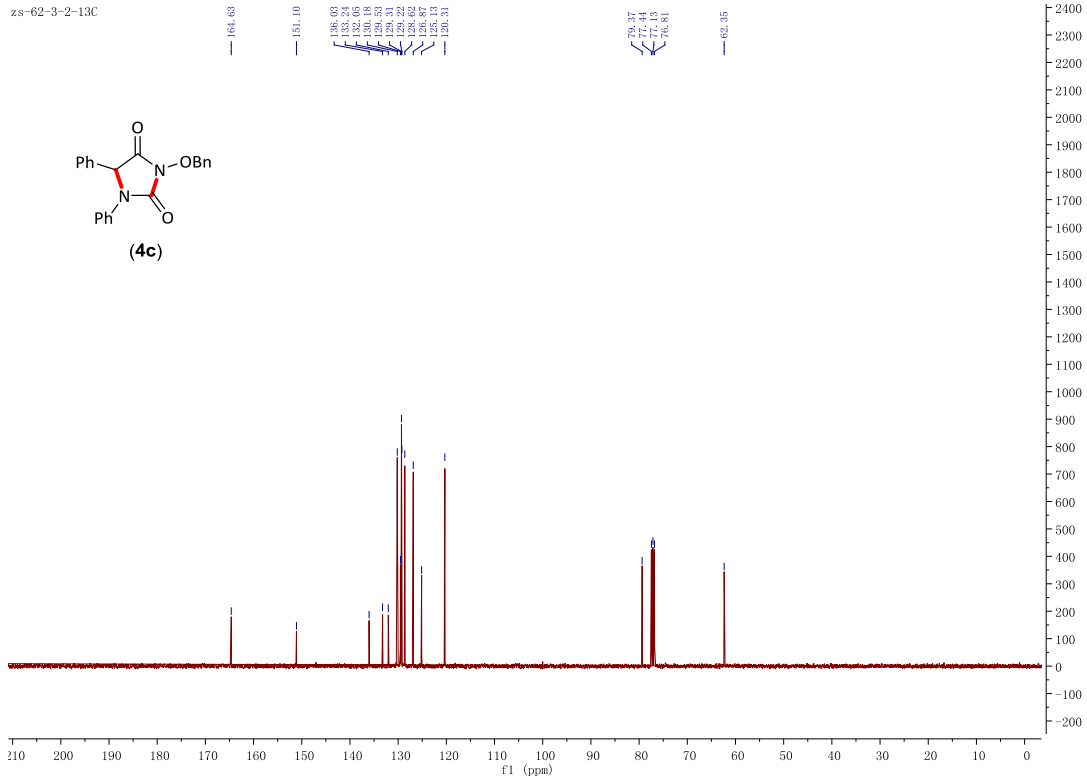

cx-20-1-1H
Cl
O
N
OBn
N
Ph
O
(4a)
7.44
7.42
7.40
7.39
7.38
7.38
7.36
7.28
5.93
4.99
8.05
1.00
2.39
f1 (ppm)

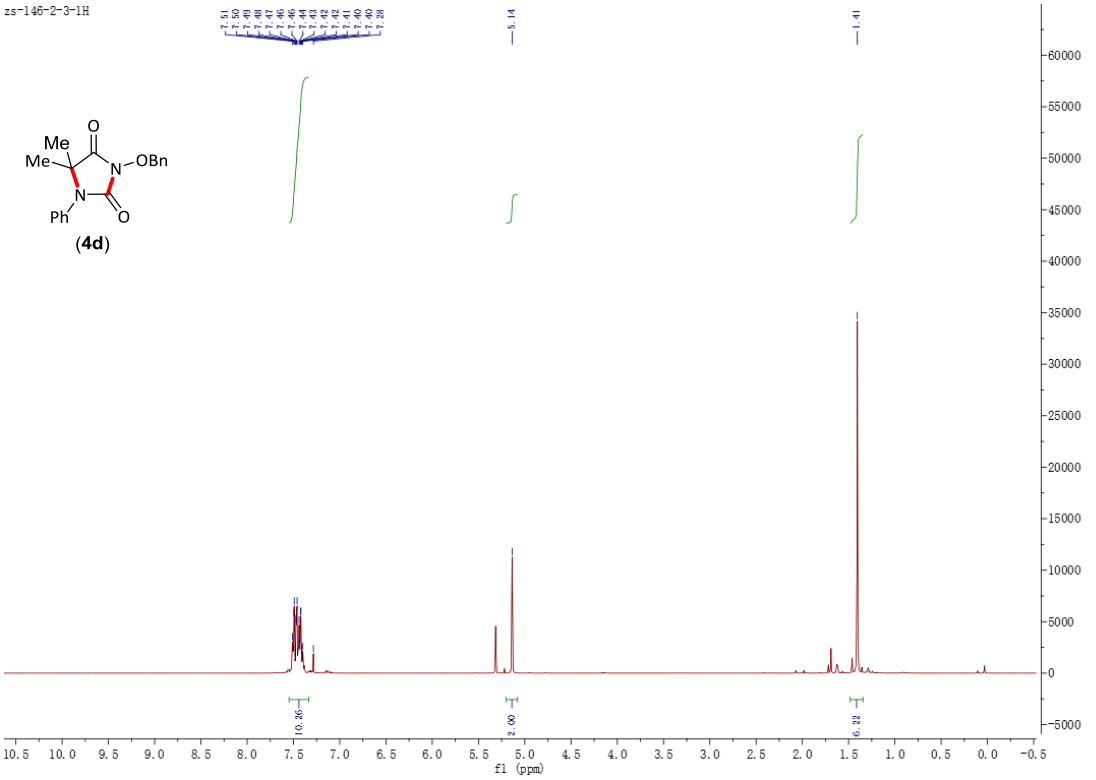

cx-20-1-13C
Cl
O
N
OBn
N
Ph
O
(4a)
161.49
153.51
138.02
134.21
129.36
129.31
129.26
128.81
124.24
121.11
78.55
77.34
77.00
76.71
64.43
f1 (ppm)

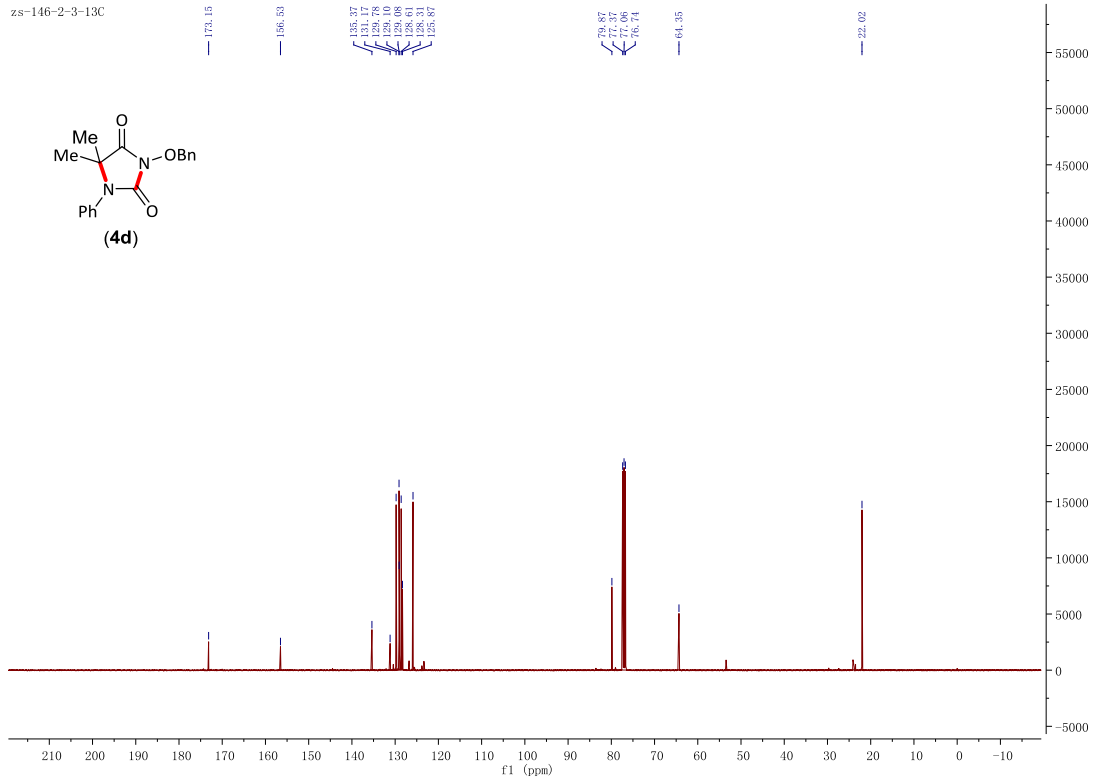

zs-56-3-1H
Et
OBn
N
N
Ph
O
O
(4b)
f1 (ppm)

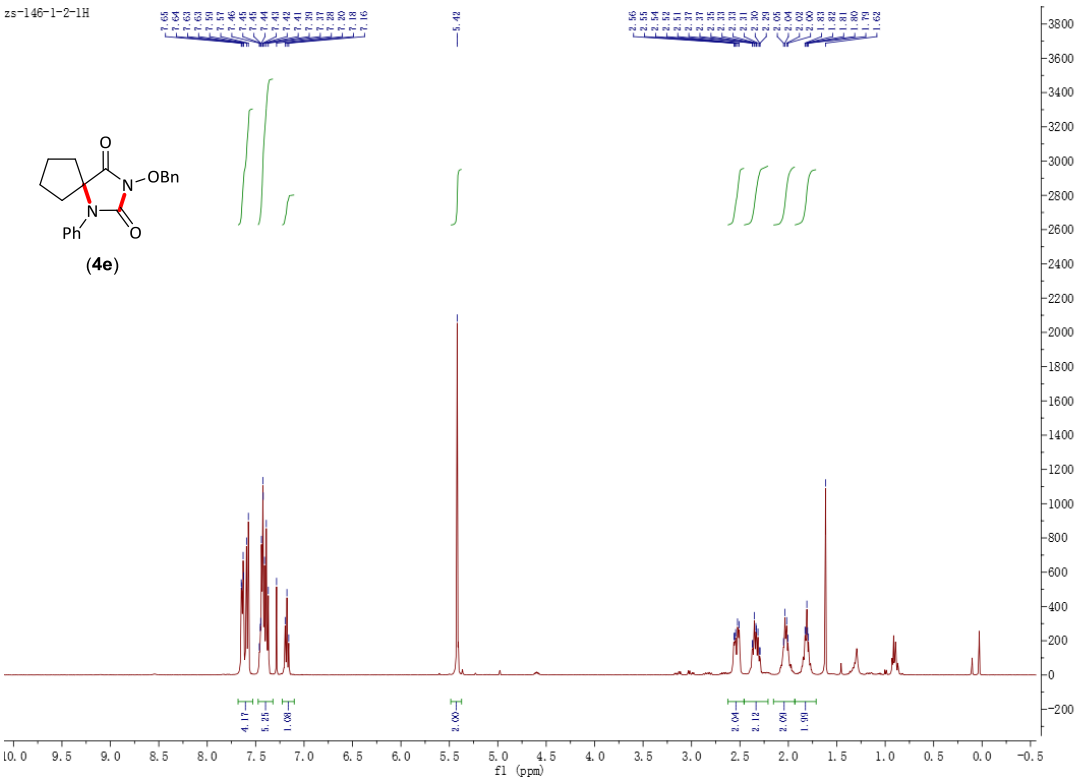

zs-56-3-13C
Et
OBn
N
N
Ph
O
O
(4b)
f1 (ppm)

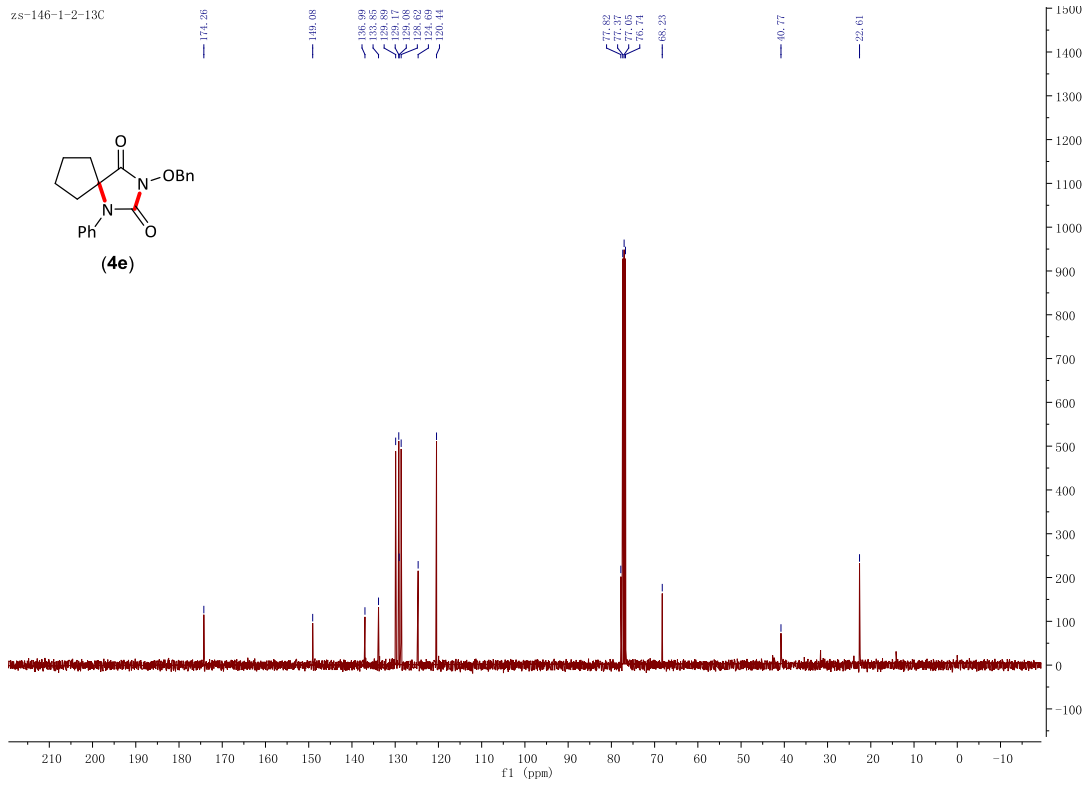

zs-62-3-2-1H
Ph
N
OBn
N
Ph
O
O
(4c)
f1 (ppm)

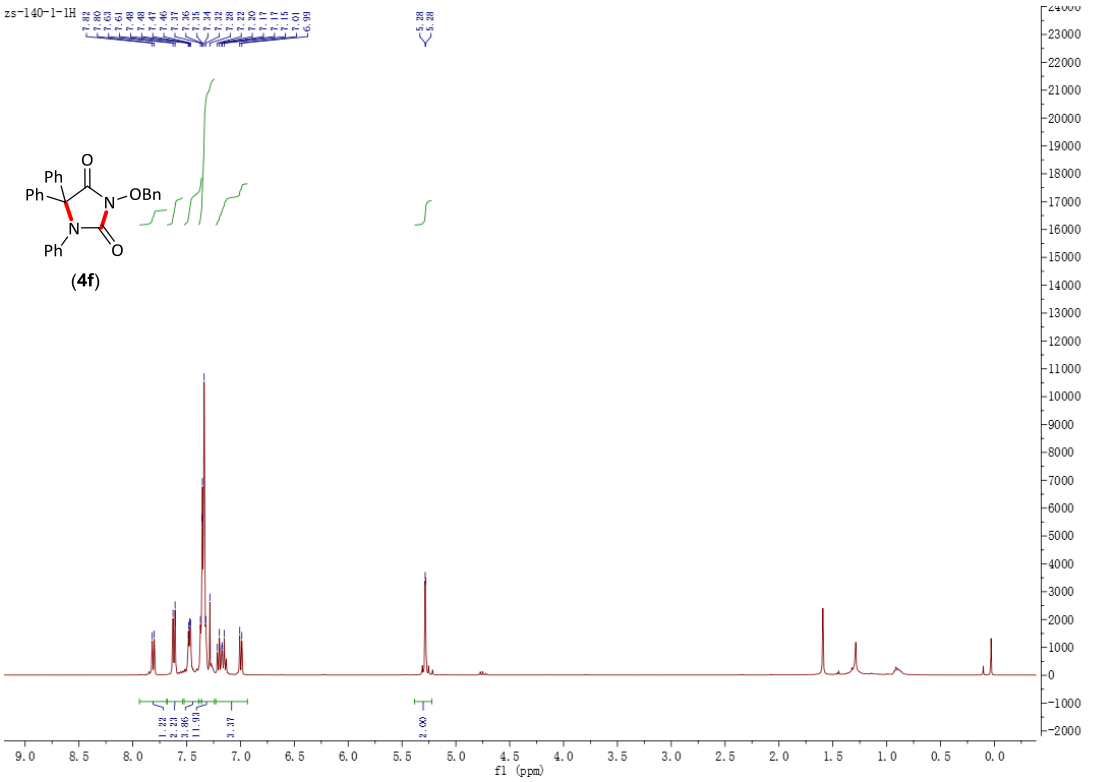

zs-62-3-2-13C
Ph
N
OBn
N
Ph
O
O
(4c)
f1 (ppm)

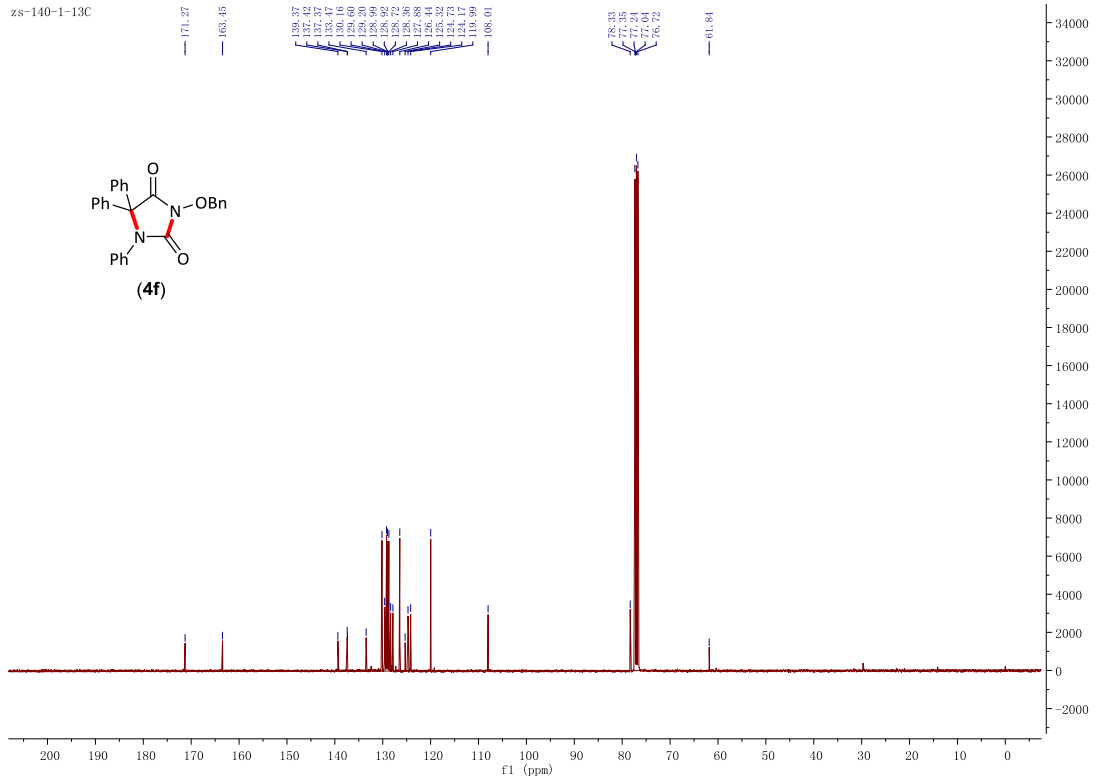

zs-146-2-3-1H
Me
Me
O
N
OBn
N
Ph
O
(4d)
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.40
7.28
5.14
1.41
10.26
2.00
6.22
f1 (ppm)

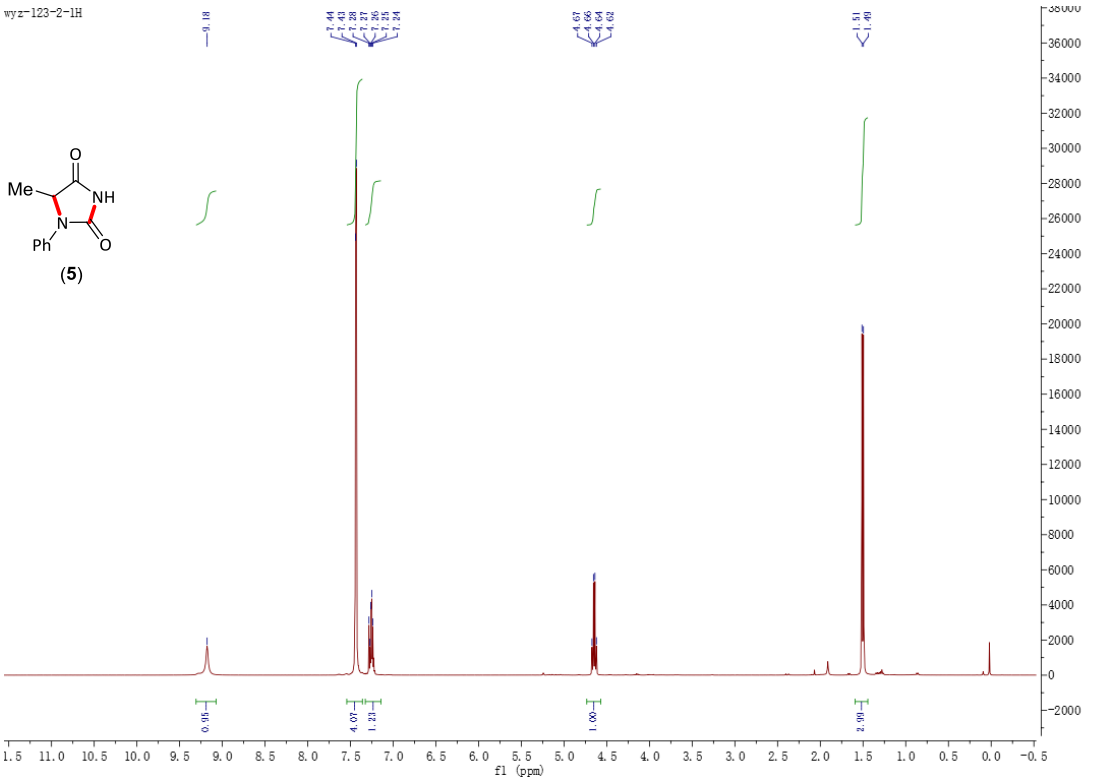

zs-146-2-3-13C
Me
Me
O
N
OBn
N
Ph
O
(4d)
173.15
166.53
135.37
133.17
129.78
129.10
129.08
128.61
128.31
125.87
79.87
77.37
77.06
76.74
64.35
22.02
f1 (ppm)

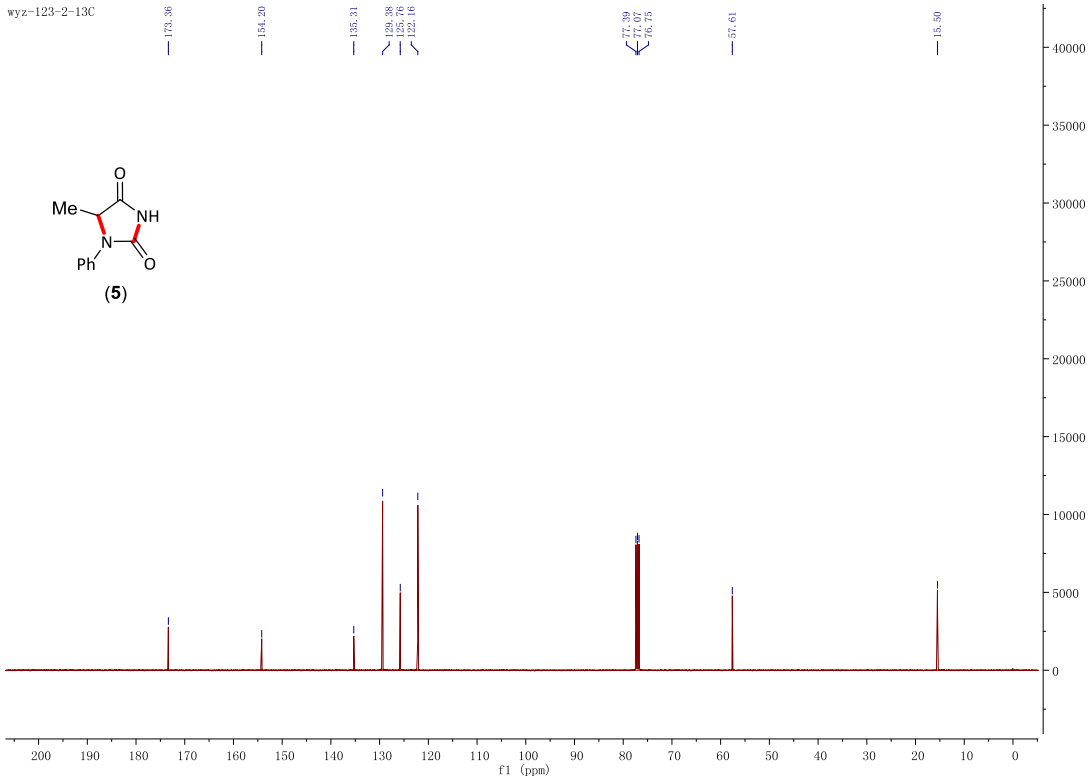

zs-146-1-2-1H
OBn
Ph
O
N
(4e)
f1 (ppm)

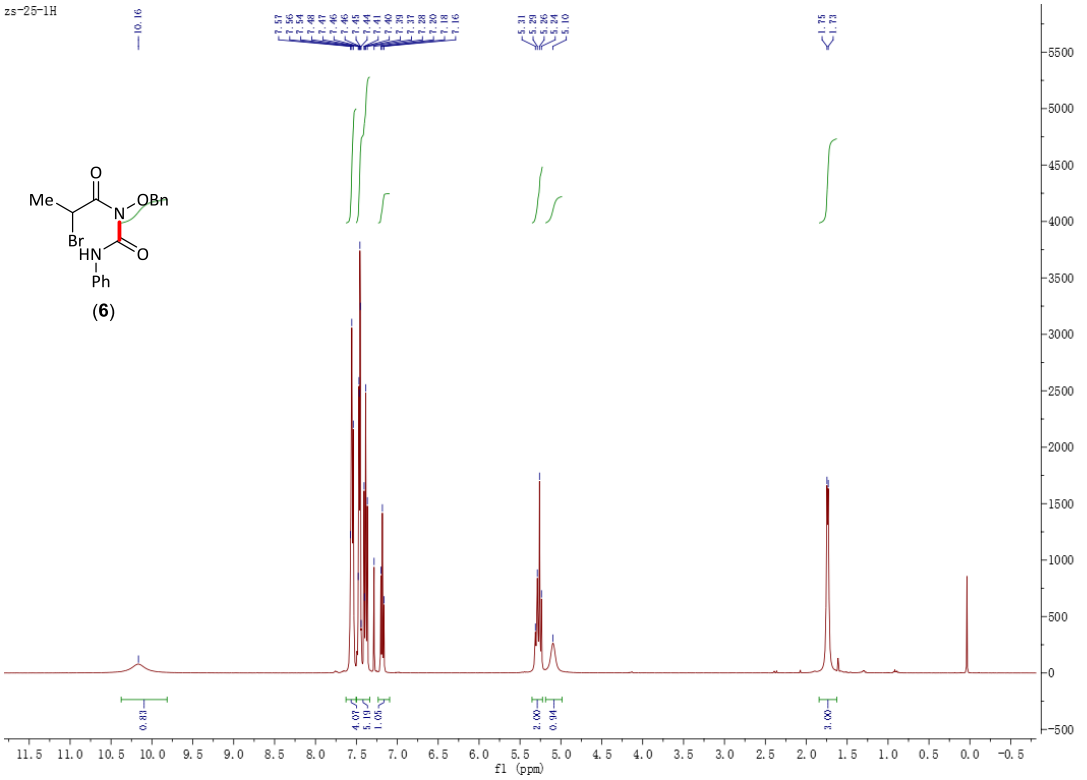

zs-146-1-2-13C
OBn
Ph
O
N
(4e)
f1 (ppm)

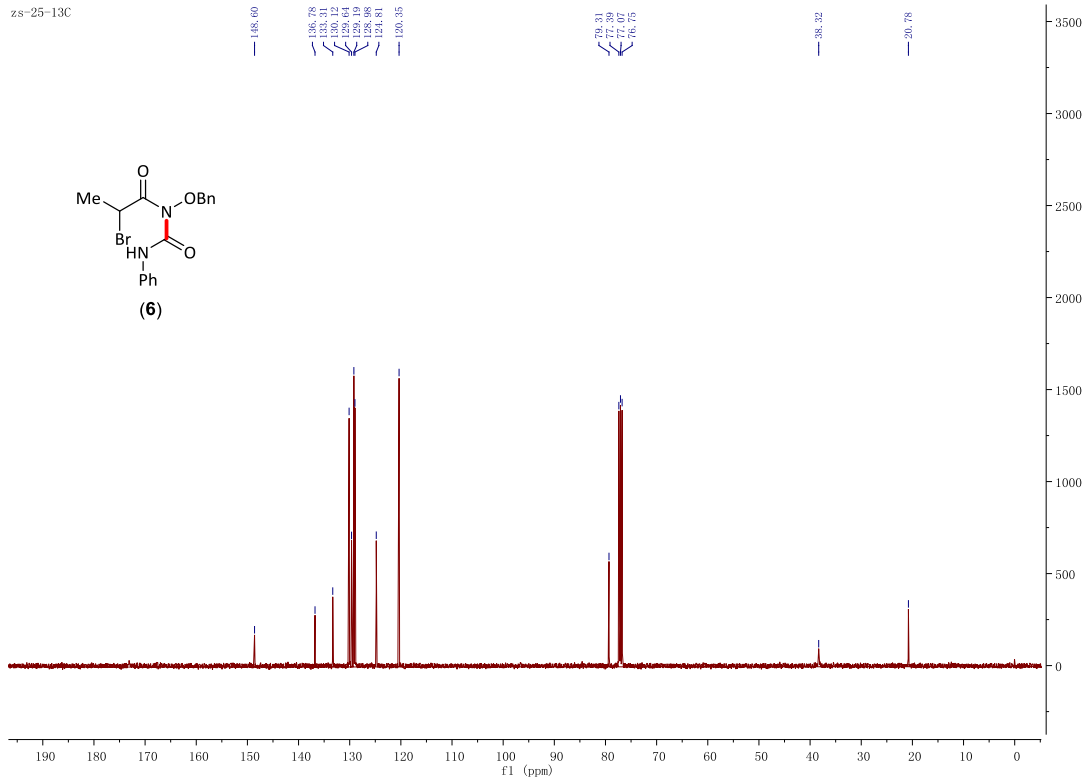

zs-140-1-1H
Ph
Ph
O
N
OBn
N
Ph
O
(4f)
f1 (ppm)


zs-140-1-13C
Ph
Ph
O
N
OBn
N
Ph
O
(4f)
f1 (ppm)


wyz-123-2-1H
Me
NH
N
Ph
O
O
(5)
f1 (ppm)


wyz-123-2-13C
Me
NH
N
Ph
O
O
(5)
f1 (ppm)





5 Checkcif for **3h**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) T

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: T

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=17.298(2) b=5.9353(8) c=33.483(4)
alpha=90 beta=90 gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	3437.7(7)	3437.7(8)
Space group	P b c a	P b c a
Hall group	: -P 2ac 2a	-P 2ac 2a
Moiety formula	C18 H15 F3 N2 O3	?
Sum formula	C18 H15 F3 N2 O3	C18 H15 F3 N2 O3
Mr	364.32	364.32
Dx,g cm-3	1.408	1.408
Z	8	8
Mu (mm-1)	0.118	0.118
F000	1504.0	1504.0
F000’	1505.00	
h,k,lmax	21,7,41	21,7,41
Nref	3383	3381
Tmin,Tmax	0.986,0.988	
Tmin’	0.986	

Correction method= Not given

Data completeness= 0.999 Theta(max)= 25.995

R(reflections)= 0.0529(2596) wR2(reflections)= 0.1451(3381)

S = 1.038 Npar= 264

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range        3.5 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference F1       --C1       .       0.16 Ang.
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       F1'      0.088 Check
PLAT480_ALERT_4_C Long H...A H-Bond Reported H11B     ..O2       .       2.65 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H11A     ..O1       .       2.61 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.785 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          2 Report
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.         0 Info
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Alert level G

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PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         8 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         7 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         3 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records         2 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records         1 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    F1'      --C1       .       5.4 s.u.
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of        C1 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        12% Note
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O3             110.2 Degree
PLAT432_ALERT_2_G Short Inter X...Y Contact  O1       ..C10             2.85 Ang.
                                            1/2-x,-1/2+y,z  =      6_655 Check
PLAT793_ALERT_4_G Model has Chirality at C8          (Centro SPGR)         R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        55 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         2 Note
PLAT955_ALERT_1_G Reported (CIF) and Actual (FCF) Lmax Differ by .         1 Units
```

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   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  15 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  10 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 26/09/2018; check.def file version of 13/09/2018

Datablock T - ellipsoid plot