Supporting Information

Dearomative hydroamination of heteroarenes catalyzed by the phenolate photocatalyst

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1 General Information

All reactions were set up using standard Schlenk techniques and carried out under nitrogen atmosphere with anhydrous solvents unless otherwise noted. Anhydrous solvents, such as DMAc, DMF, DMSO and THF, were purchased from J&K and used as received. Commercially available chemicals were purchased from J&K, Adamas, Acros Organics, Aldrich Chemical, TCI, Bide Pharmatech, Chengdu RZBT Chemical Reagent Co. Ltd or Energy Chemical and used as received unless otherwise stated.

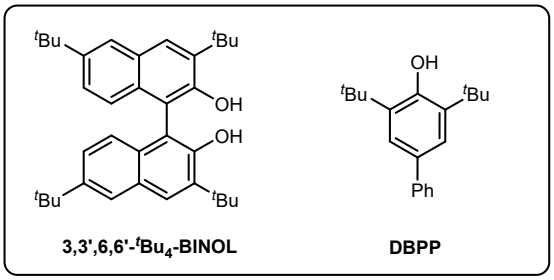
^{1}H and ^{19}F NMR spectra were recorded on a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{19}F: 376 MHz). ^{13}C NMR spectra were recorded on a Brüker Advance 400 spectrometer (^{13}C: 101 MHz) or 600 spectrometer (^{13}C: 151 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm, DMSO-d_6: δH = 2.50 ppm, δC = 39.52 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad.

UPLC yields were recorded on Waters ACQUITY UPLC M-Class. High resolution mass spectra (HRMS) were recorded on a SHIMADZU LCMS-IT-TOF. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected with UV light (254 nm).

2 Preparation of Catalysts and Substrates

2.1 Preparation of catalysts

Potocatalysts 3,3',6,6'-^{t}Bu$_4$-BINOL,[1] and DBPP[2] were known compounds and prepared according to the literature procedures.



2.2 Preparation of substrates

The substrates **1c**,[3] **1e**,[3] **1h**[4] and **1o**[4] in Table 2 were prepared according to the procedures described in the literature reported before.

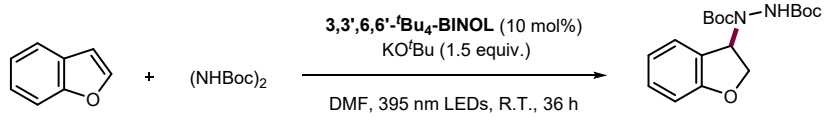
3 Optimization of the Reaction Conditions

3.1 Example of procedure for optimization

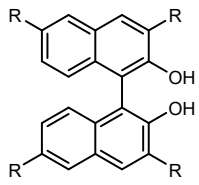
The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with **2a** (1.0 mmol, 5.0 equiv.), 3,3',6,6'-^{t}Bu$_4$-BINOL (10.2 mg, 0.02 mmol, 0.1 equiv.). The tube was then transferred to glovebox to add KO^{t}Bu (0.3 mmol, 33.7 mg, 1.5 equiv.). Subsequently, DMF (3.5 mL) and **1a** (0.2 mmol, 1.0 equiv.) were added under nitrogen atmosphere. Once added, the tube was sealed, then stirred in water bath and irradiated with a 30 W 395 nm LED lamp (1 cm away, with a cooling fan to keep the reaction temperature at room temperature) for 36 h. Then, the reaction mixture was diluted with 2 mL EA and quenched by 1 mL 2N HCl (aq.) and stirred for 1 min. Benzonitrile was added as internal standard and the reaction mixture was analyzed by UPLC.

Figure S1: 395 nm LED Photoreactor

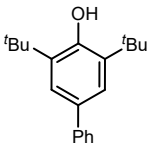
Table S1 Optimization of the Reaction Conditions[a]



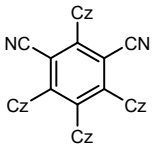
1a **2a** **3aa**



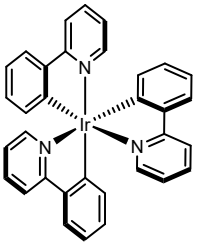
3,3',6,6'-^{t}Bu$_4$-BINOL, R = ^{t}Bu
BINOL, R = H



DBPP



4CzIPN



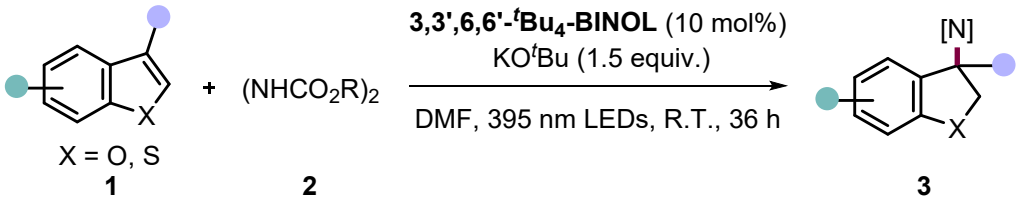
***fac*-Ir(ppy)$_3$**

Entry	Variation from standard conditions	Yield[b]
1	**none**	**87% (80%)**
2	BINOL instead of 3,3',6,6'-^{t}Bu$_4$-BINOL	52%
3	DBPP instead of 3,3',6,6'-^{t}Bu$_4$-BINOL	55%
4[c]	4CzIPN instead of 3,3',6,6'-^{t}Bu$_4$-BINOL	17%
5[c]	*fac*-Ir(ppy)$_3$ instead of 3,3',6,6'-^{t}Bu$_4$-BINOL	6%
6	NaO^{t}Bu instead of KO^{t}Bu	75%
7	KOMe instead of KO^{t}Bu	75%
8	K_2CO_3 instead of KO^{t}Bu	37%
9	DMSO instead of DMF	50%
10	DMAc instead of DMF	52%
11	THF instead of DMF	12%
12	450 nm LEDs	52%
13	2 mol% 3,3',6,6'-^{t}Bu$_4$-BINOL	73%
14	2.0 equiv. (NHBoc)$_2$	68%
15	w/o 3,3',6,6'-^{t}Bu$_4$-BINOL	11%
16	w/o KO^{t}Bu	N.D.
17	w/o light	N.D.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), 3,3',6,6'-^{t}Bu$_4$-BINOL (10 mol%), KO^{t}Bu (0.3 mmol), DMF (3.5 mL), 30 W 395 nm LEDs, R.T., 36 h. [b]Determined by ultraperformance liquid chromatography (UPLC) with benzonitrile as internal standard. Isolated yield in parentheses. [c]4CzIPN (2 mol%) or *fac*-Ir(ppy)$_3$ (2 mol%) was used. LED = lightemitting diode; R.T. = room temperature; Cz = carbazolyl; ppy = 2-phenylpyridine; DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide; DMAc = *N*,*N*-dimethylacetamide; THF = tetrahydrofuran; N.D. = not detected.

4 Experimental Procedures and Characterization Data

4.1 General experimental procedure



The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with **1** (0.2 mmol, 1.0 equiv., if solid), **2** (1.0 mmol, 5.0 equiv.) and 3,3',6,6'-^{t}Bu$_4$-BINOL (10.2 mg, 0.02 mmol, 0.1 equiv.). The tube was then transferred to glovebox to add KO^{t}Bu (0.3 mmol, 33.7 mg, 1.5 equiv.). Subsequently, DMF (3.5 mL) and **1** (if liquid) were added under nitrogen atmosphere. Once added, the tube was sealed, then stirred in water bath and irradiated with a 30 W 395 nm LED lamp (1 cm away, with a cooling fan to keep the reaction temperature at room temperature) for 36 h. Then, the reaction mixture was diluted with 2 mL EA, 2 mL H_2O and quenched by 1 mL 2N HCl (aq.) and stirred for 1 min. After that, it was extracted by EA for 5 times and the combined organic phases were concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE:EA = 50:1-10:1) to give the pure desired product.

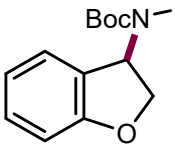
4.2 Scale-up experimental procedure

The oven-dried Schlenk bottle (500 mL) containing a stirring bar was charged with **2a** (50 mmol, 5.0 equiv.) and 3,3',6,6'-^{t}Bu$_4$-BINOL (1 mmol, 510 mg, 0.1 equiv.). The tube was then transferred to glovebox to add KO^{t}Bu (15 mmol, 1.68 g, 1.5 equiv.). Subsequently, DMF (175 mL) and **1a** (10 mmol, 1.0 equiv.) were added under nitrogen atmosphere. Once added, the bottle was sealed, then stirred in water bath and irradiated with four 30 W 395 nm LED lamps for 36 h. Then, the reaction mixture was diluted with 100 mL EA, 100 mL H_2O and quenched by 50 mL 2N HCl (aq.) and stirred for 1 min. After that, it was extracted by EA for 5 times and the combined organic phases were concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE:EA = 50:1-10:1) to give the pure desired product.

4.3 Characterization data

Due to the presence of rotamers of the amide moieties in the products, the NMR spectra of the products appear complex.[5]

Di-*tert*-butyl 1-(2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3aa**)

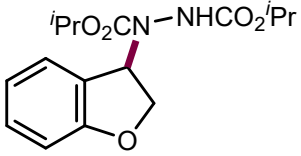


56.0 mg, 80% yield, light yellow solid; Mp: 96 - 97 °C;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.20 (m, 2H), 6.95 - 6.80 (m, 2H), 6.20 - 5.58 (m, 2H), 4.75 - 4.50 (m, 2H), 1.51 (s, 9H), 1.43 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.0, 155.6, 154.6, 130.1, 125.3, 124.4, 120.6, 110.2, 81.9, 81.3, 73.7, 58.9, 28.2, 28.1; **HRMS (ESI+):** calculated m/z for : $C_{18}H_{26}N_2O_5Na^+$ [M+Na]$^+$:373.1734, found: 373.1730.

Diisopropyl 1-(2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ab**)

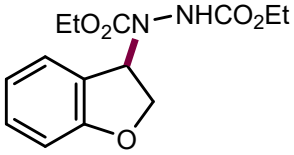


46.4 mg, 72% yield; yellow liquid;

R_f (PE/EA = 5:1) = 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 2H), 6.94 - 6.80 (m, 2H), 6.22 - 5.70 (m, 2H), 5.08 - 4.82 (m, 2H), 4.74 - 4.47 (m, 2H), 1.27 (d, *J* = 6.4 Hz, 6H), 1.20 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.0, 156.2, 155.2, 130.4, 125.3, 123.9, 120.7, 110.3, 73.5, 70.7, 70.0, 59.4, 22.0, 21.9, 21.8; **HRMS (ESI+):** calculated m/z for: $C_{16}H_{22}N_2O_5Na^+$ $[M+Na]^+$:345.1421, found: 345.1423.

Diethyl 1-(2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ac**)

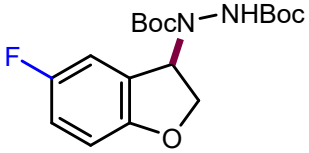


47.6 mg, 81% yield; yellow liquid;

R_f (PE/EA = 3:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.21 (m, 2H), 6.97 - 6.80 (m, 2H), 6.27 (br s, 1H), 5.97 (br s, 1H), 4.77 – 4.53 (m, 2H), 4.35 - 4.04 (m, 4H), 1.34 - 1.27 (m, 3H), 1.27 - 1.15 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.0, 156.4, 155.6, 130.5, 125.3, 123.6, 120.8, 110.3, 73.7, 62.9, 62.2, 59.6, 14.5, 14.3; **HRMS (ESI+):** calculated m/z for: $C_{14}H_{18}N_2O_5Na^+$ $[M+Na]^+$:317.1108, found: 317.1111.

Di-*tert*-butyl 1-(5-fluoro-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ba**)

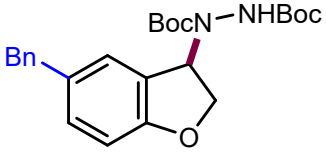


55.4 mg, 75% yield, light yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 - 6.85 (m, 2H), 6.75 (dd, *J* = 8.8, 4.0 Hz, 1H), 6.21 - 5.64 (m, 2H), 4.77 - 4.43 (m, 2H), 1.50 (s, 9H), 1.43 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.9, 157.0, 154.6, 125.4, 116.7, 116.6, 112.0, 110.5, 82.1, 81.5, 74.2, 59.0, 28.2, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.4 - 124.5 (m); **HRMS (ESI+):** calculated m/z for: $C_{18}H_{25}FN_2O_5Na^+$ $[M+Na]^+$:391.1645, found: 391.1647.

Di-*tert*-butyl 1-(5-benzyl-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ca**)

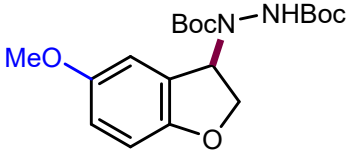


79.9 mg, 91% yield, light yellow liquid;

R_f (PE/EA = 5:1) = 0.3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.27 (m, 2H), 7.25 - 7.16 (m, 3H), 7.15 - 6.96 (m, 2H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.23 - 5.60 (m, 2H), 4.80 - 4.47 (m, 2H), 3.94 (s, 2H), 1.49 (s, 9H), 1.44 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.5, 155.7, 154.8, 141.5, 133.6, 130.8, 128.8, 128.5, 126.1, 125.5, 124.6, 110.0, 81.9, 81.3, 74.0, 58.9, 41.3, 28.2, 28.1; **HRMS (ESI+):** calculated m/z for: $C_{25}H_{32}N_2O_5Na^+$ $[M+Na]^+$:463.2209, found: 463.2207.

Di-*tert*-butyl 1-(5-methoxy-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3da**)

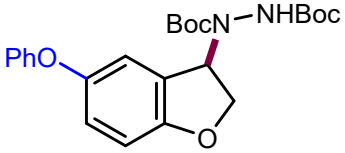


59 mg, 78% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 - 6.67 (m, 3H), 6.35 - 5.63 (m, 2H), 4.75 - 4.37 (m, 2H), 3.75 (s, 3H), 1.54 - 1.38 (m, 18H) ; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.6, 155.1, 154.7, 154.1, 125.2, 116.1, 110.3, 81.9, 81.3, 73.8, 59.4, 56.0, 28.2, 28.1; **HRMS (ESI+):** calculated m/z for: $C_{19}H_{28}N_2O_6Na^+$ $[M+Na]^+$:403.1840, found: 403.1844.

Di-*tert*-butyl 1-(5-phenoxy-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ea**)

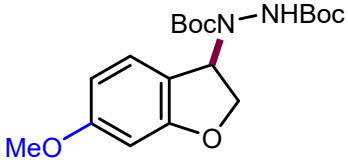


67.2 mg, 76% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

1H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.27 (m, 2H), 7.11 - 6.89 (m, 5H), 6.80 (d, *J* = 8.6 Hz, 1H), 6.35 - 5.65 (m, 2H), 4.86 - 4.42 (m, 2H),1.59 - 1.33 (m, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 157.6, 155.2, 154.5, 150.4, 129.7, 125.6, 122.5, 122.0, 117.5, 116.9, 110.7, 82.0, 81.4, 74.2, 59.2, 28.2, 28.1; **HRMS (ESI+):** calculated m/z for: $C_{24}H_{30}N_2O_6Na^+$ $[M+Na]^+$:465.1997, found: 465.1996.

Di-*tert*-butyl 1-(6-methoxy-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3fa**)

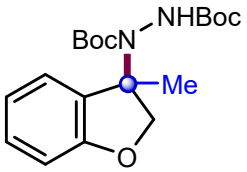


49.8 mg, 65% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (br s, 1H), 6.46 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.40 (d, *J* = 2.3 Hz, 1H), 6.20 - 5.61 (m, 2H), 4.79 - 4.45 (m, 2H), 3.79 (s, 3H), 1.53 - 1.38 (m, 18 H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.6, 161.9, 155.7, 154.7, 125.5, 107.0, 96.0, 81.8, 81.3, 75.0, 58.5, 55.5, 28.2, 28.1; **HRMS (ESI+):** calculated m/z for: $C_{19}H_{28}N_2O_6Na^+$ $[M+Na]^+$:403.1840, found: 403.1839.

Di-*tert*-butyl 1-(3-methyl-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ga**)

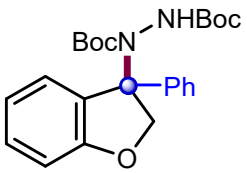


67.9 mg, 93% yield; light yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.12 (m, 2H), 6.93 -6.74 (m, 2H), 6.35 - 5.93 (m, 1H), 5.07 - 4.87 (m, 1H), 4.46 - 4.27 (m, 1H), 1.80 - 1.70 (m, 3H), 1.57 - 1.23 (m, 18H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 155.8, 154.3, 129.5, 126.5, 125.3, 120.2, 110.1, 82.6, 81.9, 81.2, 69.1, 28.2, 28.1, 27.6; **HRMS (ESI+):** calculated m/z for: $C_{19}H_{28}N_2O_5Na^+$ $[M+Na]^+$: 387.1896, found: 387.1900.

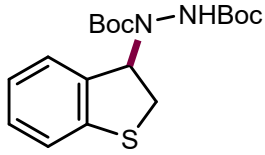
Di-*tert*-butyl 1-(3-phenyl-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ha**)



72.9 mg, 86% yield, light yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 - 7.49 (m, 1H), 7.39 - 7.30 (m, 3H), 7.29 - 7.06 (m, 3H), 6.95 - 6.76 (m, 2H), 6.51 - 6.18(m, 1H), 5.26 - 5.12 (m, 1H), 5.03 - 4.47 (m, 1H), 1.48 - 1.19 (m, 18H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.7, 156.1, 154.0, 143.5, 130.0, 128.5, 127.1, 126.9, 125.2, 124.4, 120.8, 110.6, 82.7, 82.3, 81.3, 75.5, 28.1, 27.9; **HRMS (ESI+):** calculated m/z for: $C_{24}H_{30}N_2O_5Na^+$ $[M+Na]^+$: 449.2047, found: 449.2049.



Di-*tert*-butyl 1-(2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3ia**)

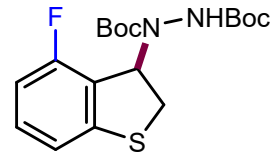
51.3 mg, 70% yield, light yellow liquid;

R_f (PE/EA = 10:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 - 6.94 (m, 4H), 6.33 - 5.68 (m, 2H), 3.68 - 3.30 (m, 2H), 1.49 (s, 9H), 1.41 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.3, 154.7, 142.1, 136.8, 129.0, 124.5, 124.3, 122.7, 81.9, 81.3, 64.0, 34.9, 28.2, 28.1; **HRMS (ESI+):** calculated m/z for: $C_{18}H_{26}N_2O_4SNa^+$ $[M+Na]^+$:

389.1511, found: 389.1514.

Di-*tert*-butyl 1-(4-fluoro-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3ja**)

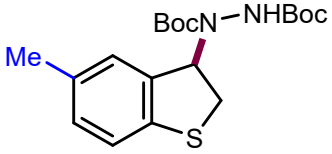


53.0 mg, 69% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 - 7.18 (m, 1H), 7.13 - 7.01 (m, 1H), 7.00 - 6.66 (m, 1H), 6.34 - 5.73 (m, 2H), 3.77 - 3.43 (m, 2H), 1.51 (s, 9H), 1.43 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.5, 154.7, 131.1, 129.0, 124.3, 122.7, 118.4, 111.3 (d, *J* = 21.0 Hz), 81.9, 81.3, 64.1, 36.0, 28.2, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.6, -120.3 (m); **HRMS (ESI+):** calculated m/z for: $C_{18}H_{25}FN_2O_4SNa^+$ $[M+Na]^+$: 407.1417, found: 407.1418.

Di-*tert*-butyl 1-(5-methyl-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3ka**)

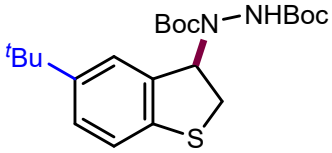


63.2 mg, 83% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 - 6.75 (m, 3H), 6.28 - 5.77 (m, 2H), 3.66 - 3.37 (m, 2H), 2.30 (s, 3H), 1.52 (s, 9H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 154.7, 138.5, 136.8, 134.1, 129.9, 125.2, 122.4, 81.8, 81.2, 64.0, 35.1, 28.2, 28.1, 21.0; **HRMS (ESI+):** calculated m/z for: $C_{19}H_{28}N_2O_4SNa^+$ $[M+Na]^+$: 403.1662, found: 403.1666.

Di-*tert*-butyl 1-(5-(tert-butyl)-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3la**)

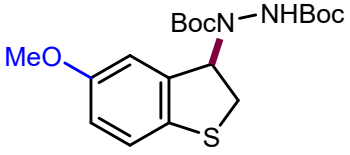


64.2 mg, 76% yield, white solid; Mp: 147 - 148 °C;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 6.96 (m, 3H), 6.37 - 5.61 (m, 2H), 3.77 - 3.30 (m, 2H), 1.53 (s, 9H), 1.44 (s, 9H), 1.31 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.5, 154.8, 147.9, 138.9, 136.6, 126.4, 122.1, 121.4, 81.9, 81.3, 64.1, 35.2, 34.5, 31.5, 28.2; **HRMS (ESI+):** calculated m/z for: $C_{22}H_{34}N_2O_4SNa^+$ $[M+Na]^+$: 445.2132, found: 445,2134.

Di-*tert*-butyl 1-(5-methoxy-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ma**)

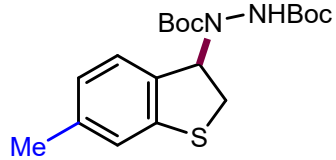


62.8 mg, 79% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.5 Hz, 1H), 6.90 - 6.48 (dd, *J* = 8.5, 2.5 Hz, 2H), 6.30 – 5.72 (m, 2H), 3.76 (s, 3H), 3.63-3.42 (m, 2H), 1.50 (s, 9H), 1.41 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.6, 155.4, 154.7, 138.5, 132.6, 123.1, 114.8, 110.9, 81.9, 81.2, 64.0, 55.6, 35.6, 28.2, 28.1; **HRMS (ESI+):** calculated m/z for: $C_{19}H_{28}N_2O_5SNa^+$ $[M+Na]^+$: 419.1617, found: 419.1621.

Di-*tert*-butyl 1-(6-methyl-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3na**)



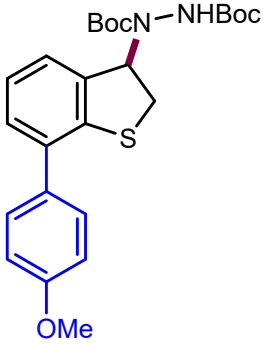
62.6 mg, 87% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 - 6.75 (m, 3H), 6.20 - 5.67 (m, 2H), 3.65 - 3.35 (m, 2H), 2.29 (s, 3H), 1.49 (s, 9H), 1.41 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.4, 154.7, 142.2, 139.1, 133.9, 125.3, 124.3, 123.2, 81.8, 81.2,

63.8, 35.2, 28.2, 28.1, 21.2; **HRMS (ESI+):** calculated m/z for: $C_{19}H_{28}N_2O_4SNa^+$ $[M+Na]^+$: 403.1662, found: 403.1658.

Di-*tert*-butyl 1-(7-(4-methoxyphenyl)-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3oa**)

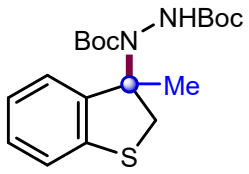


60.0 mg, 64% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.4;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.36 - 7.21 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H),7.01 - 6.97 (m, 2H), 6.35 - 5.90 (m, 2H), 3.84 (s, 3H), 3.56 -3.37 (m, 2H), 1.53 (s, 9H), 1.45 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.2, 155.4, 154.7, 140.5, 137.6, 136.5, 132.8, 129.2, 129.2, 125.0, 122.7, 113.9, 81.9, 81.3, 64.6, 55.3, 34.1, 28.3, 28.2; **HRMS (ESI+):** calculated m/z for: $C_{25}H_{32}N_2O_5SNa^+$ $[M+Na]^+$: 495.1930, found: 495.1935.

Di-*tert*-butyl 1-(3-methyl-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3pa**)

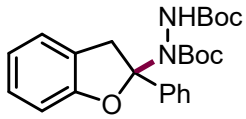


58.5 mg, 77% yield, yellow liquid;

R_f (PE/EA = 5:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 - 6.95 (m, 4H), 6.59 - 6.27 (m, 1H), 4.19 - 3.79 (m,1H), 3.24 - 2.99 (m, 1H), 1.67 -1.58 (m, 3H), 1.53 - 1.43 (m, 9H), 1.27 - 1.14 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 154.2, 128.1, 127.8, 124.3, 124.1, 122.8, 122.4, 81.9, 81.2, 74.4, 43.3, 28.3, 28.2, 27.9, 27.8, 26.0; **HRMS (ESI+):** calculated m/z for: $C_{19}H_{28}N_2O_4SNa^+$ $[M+Na]^+$: 403.1667, found: 403.1672.

Di-*tert*-butyl 1-(2-phenyl-2,3-dihydrobenzofuran-2-yl)hydrazine-1,2-dicarboxylate (**3qa**)



50.5 mg, 59% yield, yellow liquid;

R_f (PE:EA = 10:1) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 - 7.46 (m, 2H), 7.38 -7.21 (m, 3H), 7.20 - 7.03 (m, 2H), 7.00 - 6.77 (m, 2H), 6.38 -5.86 (m, 1H), 4.40 - 3.88 (m, 1H), 3.67 - 3.20 (m, 1H), 1.60 - 1.12 (m, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 156.3, 153.9, 144.7, 128.3, 128.1, 127.1, 125.6, 124.3, 124.3, 121.2, 109.5, 103.2, 82.5, 81.5, 44.2, 28.2, 27.8; **HRMS (ESI+):** calculated m/z for: $C_{24}H_{30}N_2O_5Na^+$ $[M+Na]^+$: 449.2052, found: 449.2054.

5 Mechanistic Studies

5.1 UV-Vis experiments

The UV-Vis absorption spectra of DMF solutions (1/10 of the concentration as in the reaction conditions) of benzothiophene **1i**, 3,3',6,6'-^{t}Bu$_4$-BINOL, mixtures of 3,3',6,6'-^{t}Bu$_4$-BINOL and KO^{t}Bu, mixtures of **1i**, 3,3',6,6'-^{t}Bu$_4$-BINOL and KO^{t}Bu were recorded in 10 mm path quartz cuvettes equipped with a Teflon® septum under N_2 atmosphere. The solutions were analyzed using a PUXI TU-1901 UV-Vis spectrophotometer.

Upon mixing with KO^{t}Bu, the deprotonated anion of 3,3',6,6'-^{t}Bu$_4$-BINOL (ArO$^-$) exhibited redshifted absorption into the visible light range. In the presence of **1i**, the absorption spectrum of ArO$^-$ did not show a bathochromic shift, thus we did not prefer the possible existence of electron-donor-acceptor (EDA) complex. This process can also be followed by naked eye, as the colorless solution of 3,3',6,6'-^{t}Bu$_4$-BINOL was immediately turned to a primrose yellow upon addition of KO^{t}Bu and no new color change after **1i** was added to the solution of the ArO$^-$.

Note: All solutions are tested after filtration.

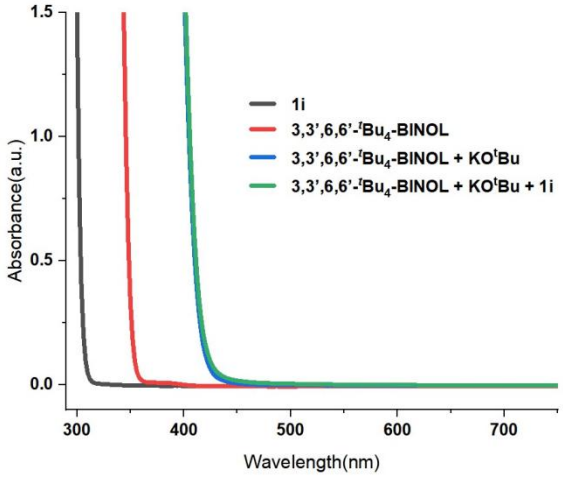


Figure S2: UV-Vis absorption spectra of different reaction components

5.2 Stern-Volmer quenching experiments

Fluorescence emission quenching experiments were measured on a RF-5301PC Spectrofluorophotometer with a 4 mL quartz cuvette with a cap. Anhydrous DMF was degassed by N_2 bubbling for 30 minutes before use. ArO$^-$ was irradiated at 372 nm and the emission spectrum was recorded from 400 nm to 750 nm. In a typical experiment, the emission spectrum of a 5.0×10^{-5} M solution of ArO$^-$ (freshly prepared in situ by the deprotonation of 3,3',6,6'-^{t}Bu$_4$-BINOL with 4.0 equiv. of KO^{t}Bu) in DMF was collected. A stock solution of **1i** in 1 mL DMF was prepared. Then, different amounts of this stock solution were added to a solution of ArO$^-$ (10^{-5} M) in DMF (2.4 mL).

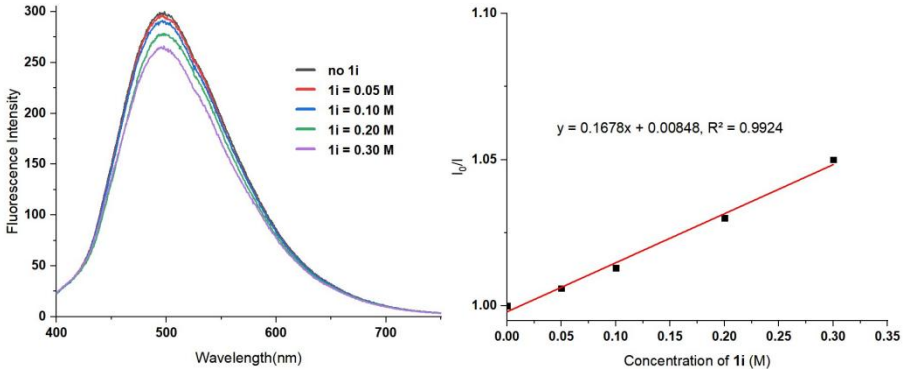


Figure S3: Stern-Volmer quenching experiments with benzothiophene **1i**

5.3 EPR studies

To an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added **1i** (0.01 mmol, 1.0 equiv.) and 3,3',6,6'-^{t}Bu$_4$-BINOL (0.01 mmol, 1.0 equiv.). The tube was moved into the glovebox where was added the KO^{t}Bu (0.02 mmol, 2.0 equiv.). The tube was sealed and removed from the glovebox. Subsequently, degassed dry DMF (1.0 mL) was added under nitrogen atmosphere. Once added, the tube was sealed, then stirred and irradiated with a 30 W 395 nm LED lamp for 2 min. Finally, the reaction system was quickly taken out into a capillary and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.854317 GHz.

The solution gave rise to obvious EPR signal, which could be attributed to the in situ formed phenoxyl radical species (ArO•) (g = 2.0057). No signal was observed in the absence of light irradiation, **1i** or 3,3',6,6'-^{t}Bu$_4$-BINOL. This result suggested that photo-induced electron transfer occurred from the ArO^{-*} to **1i**.

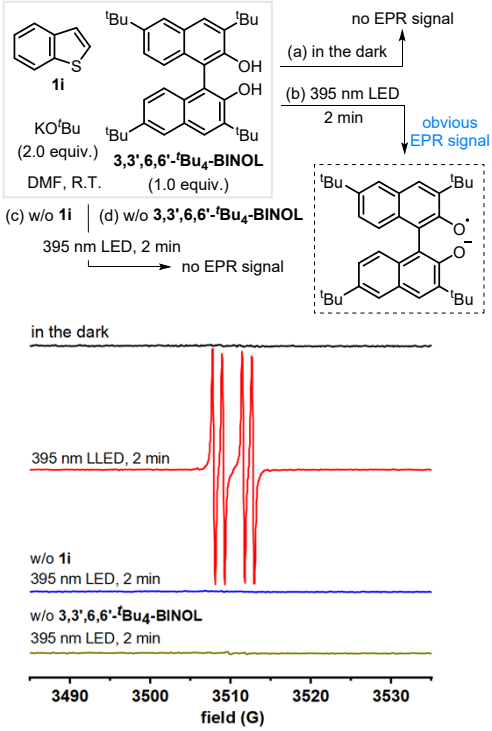
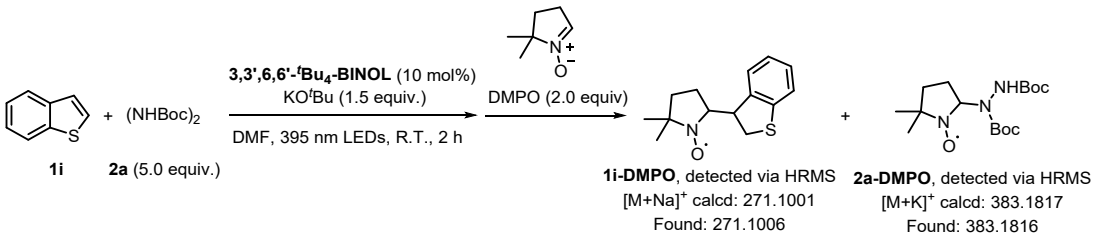


Figure S4: EPR measurements under different conditions

The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with **1i** (0.2 mmol, 1.0 equiv.), **2a** (1.0 mmol, 5.0 equiv.) and 3,3',6,6'-^{t}Bu$_4$-BINOL (10.2 mg, 0.02 mmol, 0.1 equiv.). The tube was then transferred to glovebox to add KO^{t}Bu (0.3 mmol, 33.7 mg, 1.5 equiv.). Subsequently, DMF (3.5 mL) was added under nitrogen atmosphere. Once added, the tube was sealed, then stirred in water bath and irradiated with a 30 W 395 nm LED lamp (1 cm away, with a cooling fan to keep the reaction temperature at room temperature) for 2 h. Then, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 2.0 equiv.) was added under nitrogen atmosphere and the reaction mixture was stirred at room temperature for about 5 min. Finally, the reaction system was quickly taken out into a capillary and submitted to EPR analysis. The major radical species observed in EPR spectrum was as an adduct between a *N*-centered radical and DMPO. The small triplet with equal intensity (aγ-N = 3.3 G) was indicative of an *N*-centered radical being trapped. To further confirm the structure of this trapping product, the reaction solution was sujected for HRMS analysis, and the proposed structure **2a-DMPO** was observed.



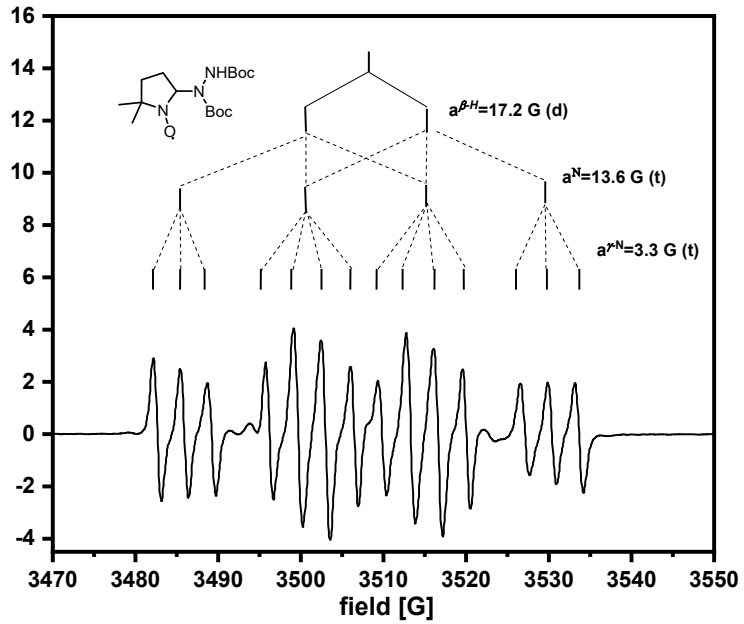
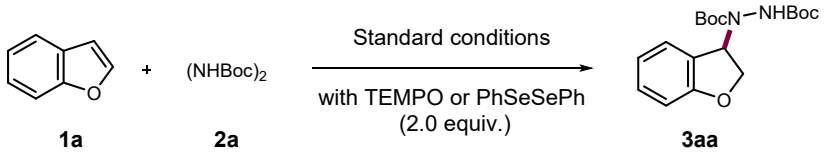


Figure S5: EPR measurements with DMPO as an additive

5.4 Control experiments with TEMPO or PhSeSePh

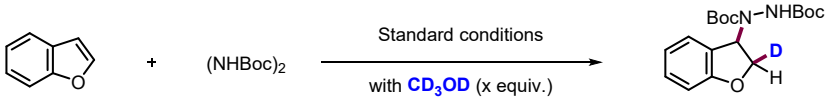


1a **2a** **3aa**

TEMPO: **3aa**, N.D.
PhSeSePh: **3aa**, N.D.

The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with **2a** (1.0 mmol, 5.0 equiv.) and 3,3',6,6'-^{t}Bu$_4$-BINOL (10.2 mg, 0.02 mmol, 0.1 equiv.). The tube was then transferred to glovebox to add KO^{t}Bu (0.3 mmol, 33.7 mg, 1.5 equiv.). Subsequently, DMF (3.5 mL), **1a** (0.2 mmol, 1.0 equiv.) and TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv.) were added under nitrogen atmosphere. Once added, the tube was sealed, then stirred in water bath and irradiated with a 30 W 395 nm LED lamp (1 cm away, with a cooling fan to keep the reaction temperature at room temperature) for 36 h. Then, the reaction mixture was analyzed by HRMS and TLC. The reaction was totally inhibited and product **3aa** was not observed.

5.5 Deuterium-labeling experiments



1a **2a** **3aa**

x = 30, 67% yield, 62% **D**
x = 50, 62% yield, 81% **D**

The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with **2a** (1.0 mmol, 5.0 equiv.) and 3,3',6,6'-^{t}Bu$_4$-BINOL (10.2 mg, 0.02 mmol, 0.1 equiv.). The tube was then transferred to glovebox to add KO^{t}Bu (0.3 mmol, 33.7 mg, 1.5 equiv.). Subsequently, DMF (3.5 mL), CD_3OD (216 mg, 6 mmol, 30 equiv.) or CD_3OD (360 mg, 10 mmol, 50 equiv.) and **1a** (0.2 mmol, 1.0 equiv.) were added under nitrogen atmosphere. Once added, the tube was sealed, then stirred in water bath and irradiated with a 30 W 395 nm LED lamp (1 cm away, with a cooling fan to keep the reaction temperature at room temperature) for 36 h. Then, the reaction mixture was diluted with 2 mL EA, 2 mL H_2O and quenched by 1 mL 2N HCl (aq.) and stirred for 1 min. After that, it was extracted by EA for 5 times and the combined organic phases were concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE:EA = 50:1-10:1) to give the pure desired product.

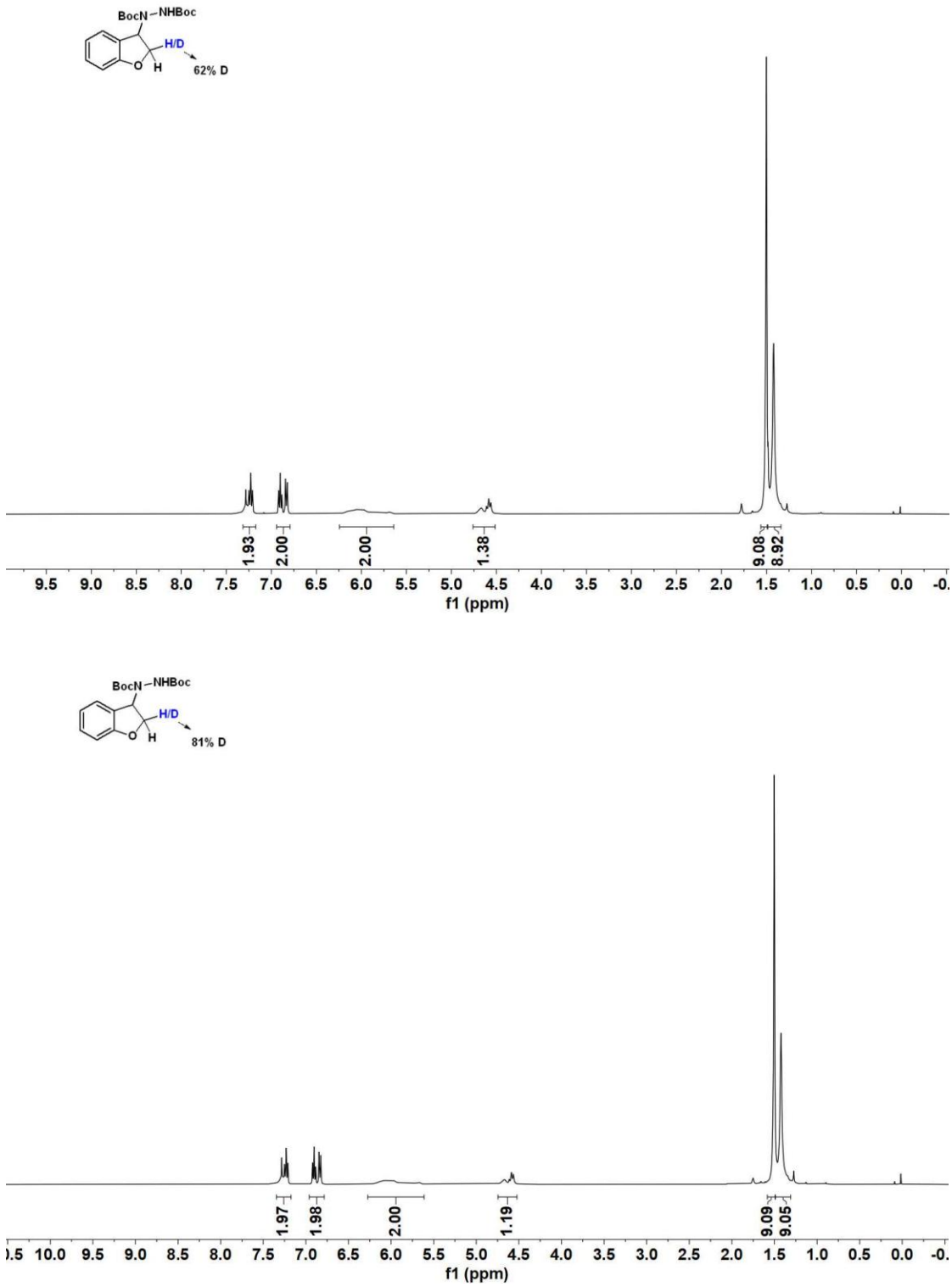
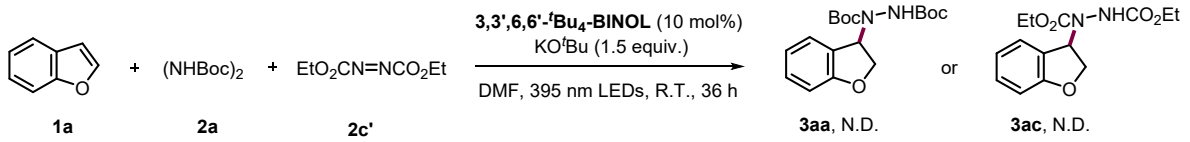


Figure S6: ^{1}H NMR Spectra of compound **3aa**

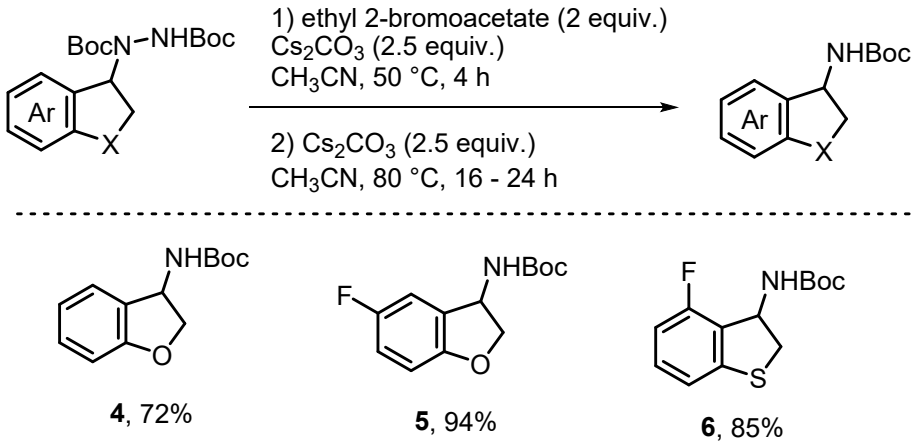
5.6 Control experiments with diethyl azodicarboxylate as an additive



1a + $(NHBoc)_2$ (**2a**) + $EtO_2CN{=}NCO_2Et$ (**2c'**) → **3aa**, N.D. or **3ac**, N.D.

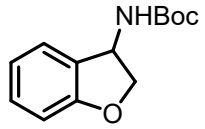
The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with **2a** (0.4 mmol, 2.0 equiv.), **2c** (0.4 mmol, 2.0 equiv.) and 3,3',6,6'-^{t}Bu$_4$-BINOL (10.2 mg, 0.02 mmol, 0.1 equiv.). The tube was then transferred to glovebox to add KO^{t}Bu (0.3 mmol, 33.7 mg, 1.5 equiv.). Subsequently, DMF (3.5 mL) and **1a** (0.2 mmol, 1.0 equiv.) were added under nitrogen atmosphere. Once added, the tube was sealed, then stirred in water bath and irradiated with a 30 W 395 nm LED lamp (1 cm away, with a cooling fan to keep the reaction temperature at room temperature) for 36 h. Then, the reaction mixture was analyzed by HRMS and TLC. The reaction was totally inhibited and product **3aa** and **3ac** were not observed.

6 Product Derivatization



The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with **3** (0.1 mmol). The tube was then transferred to glovebox to add Cs_2CO_3 (2.5 equiv.). Subsequently, CH_3CN (2.5 mL) and 2-bromoacetate (2 equiv.) were added under nitrogen atmosphere. Once added, the tube was sealed, then stirred in an oil bath at 50 °C for 4 h. After completion (TLC), the resulting mixture was diluted with saturated NH_4Cl solution and then extracted by EA with three times. The combined organic phase was concentrated in vacuo to give the intermediate without further purification. Next, the oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with Cs_2CO_3 (3.0 equiv.) in glovebox. Subsequently, the obtained intermediate was dissolved in CH_3CN (3.5 mL) and then added to the reaction tube. Once added, the tube was sealed, then stirred in an oil bath at 80 °C for 16 - 24 h. After completion (TLC), the resulting mixture was diluted with saturated NH_4Cl solution and then extracted by EA with three times. The residue was purified by silica gel flash column chromatography (PE:EA = 30:1-20:1) to give the pure desired product.

tert-Butyl (2,3-dihydrobenzofuran-3-yl)carbamate (**4**)



16.9 mg, 72% yield, white solid;

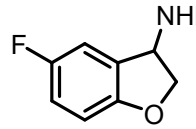
R_f (PE/EA = 10:1) = 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.31 (m, 1H), 7.29 - 7.19 (m, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.38 - 5.33 (m, 1H), 4.89 - 4.83 (m, 1H), 4.66 (dd, *J* = 10.0, 7.8 Hz, 1H), 4.34 (dd, *J* = 10.0, 4.0 Hz, 1H), 1.46 (s, 9H);

GC-MS: calculated m/z : 235.1, found: 235.1.

The spectroscopic data matches the previously reported data.[6]

tert-Butyl (5-fluoro-2,3-dihydrobenzofuran-3-yl)carbamate (**5**)



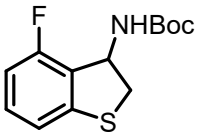
23.9 mg, 94% yield, white solid, Mp: 75 - 76 °C;

R_f (PE/EA = 10:1) = 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 - 7.01 (m, 1H), 6.95 - 6.86 (m, 1H), 6.74 (dd, *J* = 8.9, 4.0 Hz, 1H), 5.46 - 5.26 (m, 1H), 4.98 - 4.80 (m, 1H), 4.68 (dd, *J* = 9.1 Hz, 1H), 4.33 (dd, *J* = 10.1, 4.3 Hz, 1H), 1.46 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.7 (d, *J* = 238.5 Hz), 156.2, 155.2, 127.7 (d, *J* = 8.1 Hz), 116.8 (d, *J* = 24.2 Hz), 112.2 (d, *J* = 24.7 Hz), 110.8 (d, *J* = 8.3 Hz), 80.4, 78.6, 53.1, 28.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.2 (s);

HRMS (ESI+): calculated m/z for: $C_{13}H_{16}FNO_3Na^+$ $[M+Na]^+$: 276.1006, found: 276.1003.

tert-Butyl (4-fluoro-2,3-dihydrobenzo[*b*]thiophen-3-yl)carbamate (**6**)



22.9 mg, 85% yield, white solid, Mp: 73 - 74 °C;

R_f (PE/EA = 10:1) = 0.5;

^{1}H NMR (400 MHz, DMSO) δ 7.56 - 7.46 (m, 1H), 7.27 - 7.16 (m, 1H), 7.07 - 6.97 (m, 1H), 6.87 - 6.75 (m, 1H), 5.50 - 5.41 (m, 1H), 3.59 (dd, *J* = 11.6, 7.6 Hz, 1H), 3.16 (dd, *J* = 11.6, 5.3 Hz, 1H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, DMSO) δ 159.3 (d, *J* = 249.2 Hz), 154.8, 144.2 (d, *J* = 5.0 Hz), 131.1 (d, *J* = 8.0 Hz), 125.4 (d, *J* = 17.0 Hz), 118.4 (d, *J* = 3.3 Hz), 111.5 (d, *J* = 20.7 Hz), 78.2, 54.9, 28.2; **^{19}F NMR** (376 MHz, DMSO) δ -117.8;

HRMS (ESI+): calculated m/z for: $C_{13}H_{17}FNO_2S^+$ $[M+H]^+$: 270.0959, found: 270.0958.

Note: One aromatic signal missing in ^{13}C spectrum due to overlap.

7 Other Unsuccessful Attempts

7.1 Attempts on the dearomative amination of indoles

we attempted dearomative amination reactions of indoles under standard reaction conditions. With 1-Boc-indole as the substrate, the corresponding dearomative amination product **3ra** could be isolated in 26% yield. We also observed the formation of indole as the main side product. With 1-methylindole as the substrate, only a trace amount of product was detected by ESI-MS. With indole as the substrate, we could not detect the formation of the target product. Instead, the reaction mainly produced the byproduct tert-butyl 2-(1H-indole-3-carbonyl)hydrazine-1-carboxylate in 65% yield.

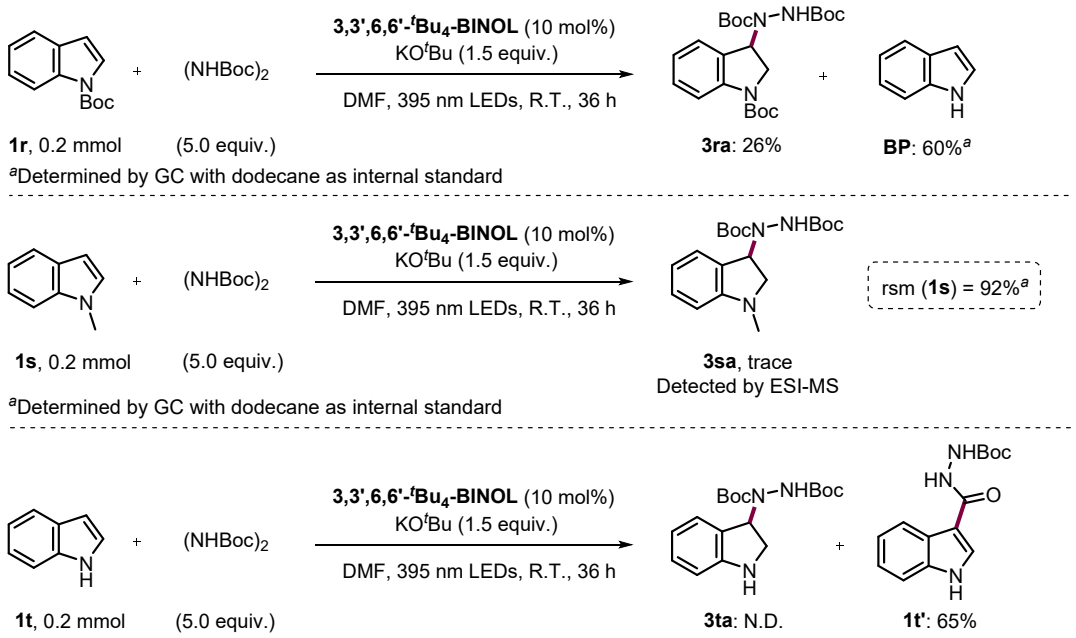
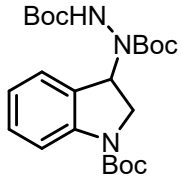


Figure S7: Reaction results of diffenrent indoles

Di-*tert*-butyl-1-(1-(*tert*-butoxycarbonyl)indolin-3-yl)hydrazine-1,2-dicarboxylate (**3ra**)



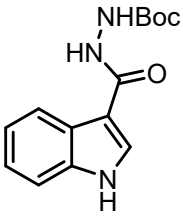
23.0 mg, 26%, yellow liquid;

R_f (PE:EA = 5:1) = 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.28 - 7.25 (m, 3H), 6.97 (t, J = 7.5 Hz, 1H), 5.89 (s, 2H), 4.06 (s, 2H), 1.54 (s, 9H), 1.48 (s, 9H), 1.41 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.6, 154.7, 152.3, 143.9, 129.7, 124.8, 122.4, 115.1, 81.9, 81.3, 80.8, 56.1, 51.1, 28.5, 28.3, 28.1;

HRMS (ESI+): calculated m/z for: $C_{23}H_{35}N_3O_6Na^+$ [M+Na]$^+$: 472.2418, found: 472.2418.

tert-Butyl 2-(1*H*-indole-3-carbonyl)hydrazine-1-carboxylate (**1t'**)



36.0 mg, 65%, white solid, Mp: 156 - 157 °C;

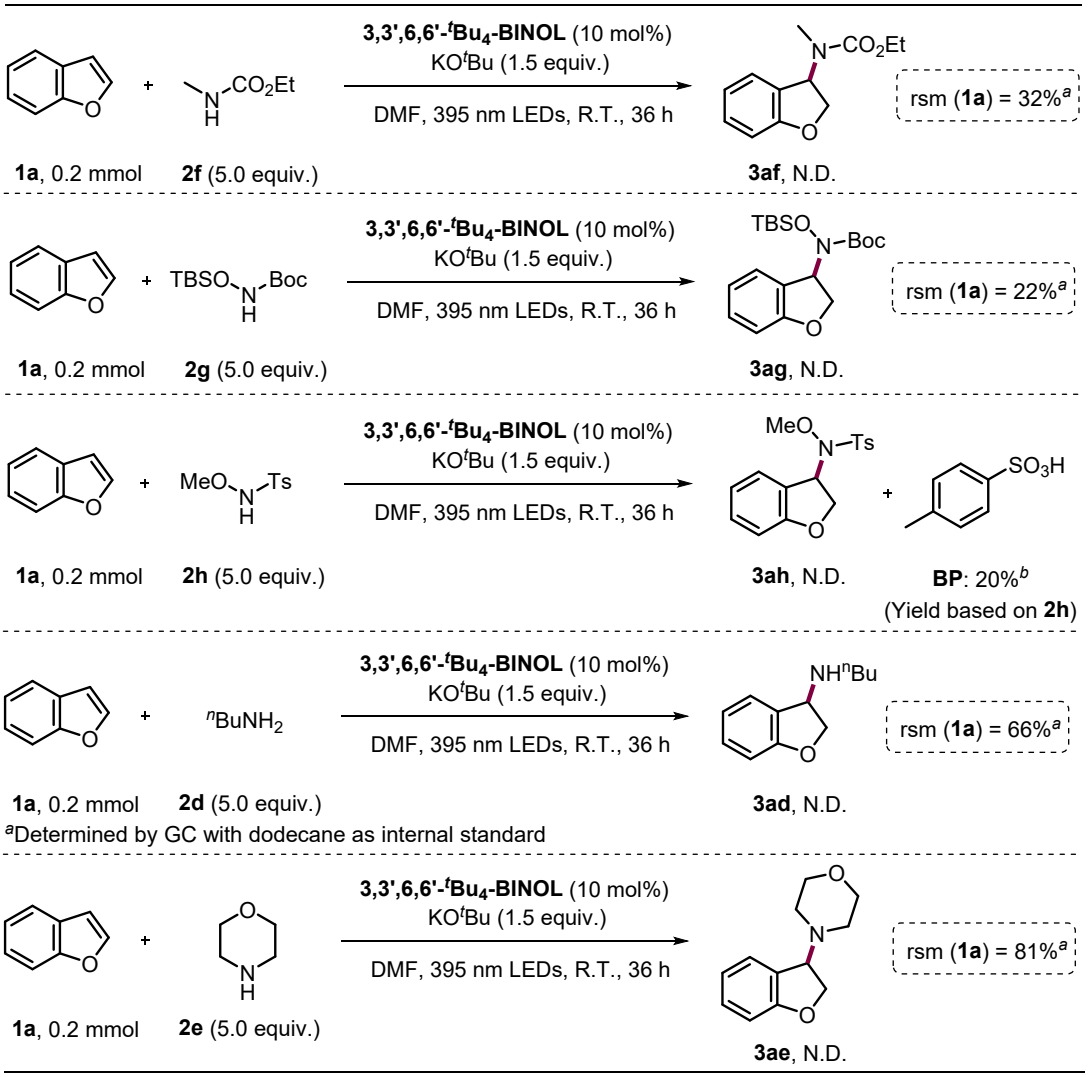
R_f (PE:EA = 5:1) = 0.2;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.12 (d, J = 8.3 Hz, 1H), 7.39 (d, J = 3.7 Hz, 1H), 7.28 (s, 1H), 7.24 - 7.16 (m, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.81 (s, 1H), 6.26 (s, 1H), 1.40 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.6, 152.5, 135.4, 129.9, 124.5, 123.0, 122.7, 121.0, 114.9, 108.5, 82.5, 28.1;

HRMS (ESI+): calculated m/z for: $C_{14}H_{17}N_3O_3Na^+$ [M+Na]$^+$: 298.1162, found: 298.1158.

7.2 Attempts on the dearomative amination using other amination reagents

The reactivity of other amination reagents, including *N*-methylcarbamate, *N*-methoxysulfonamide, *N*-silyloxy tert-butyl carbonate, primary and secondary aliphatic amine, were tested under standard reaction conditions. The TLC of these reactions was messy and the amination products could not be detected. A certain amount of the byproduct *p*-toluenesulfonic acid was observed when using *N*-methoxysulfonamide as the amination reagent.



[a]Determined by GC with dodecane as internal standard

[b]Determined by UPLC with PhCN as internal standard

Figure S8: Reaction results of other amination reagents

8 References

(1) J.-P. Yue, J.-C. Xu, H.-T. Luo, X.-W. Chen, H.-X. Song, Y. Deng, L. Yuan, J.-H. Ye and D.-G. Yu, *Nat. Catal.*, 2023, **6**, 959.

(2) K. Liang, Q. Liu, L. Shen, X. Li, D. Wei, L. Zheng and C. Xia, *Chem. Sci.*, 2020, **11**, 6996.

(3) W. Yu, X.-H. Xu and F.-L. Qing, *New J. Chem.*, 2016, **40**, 6564.

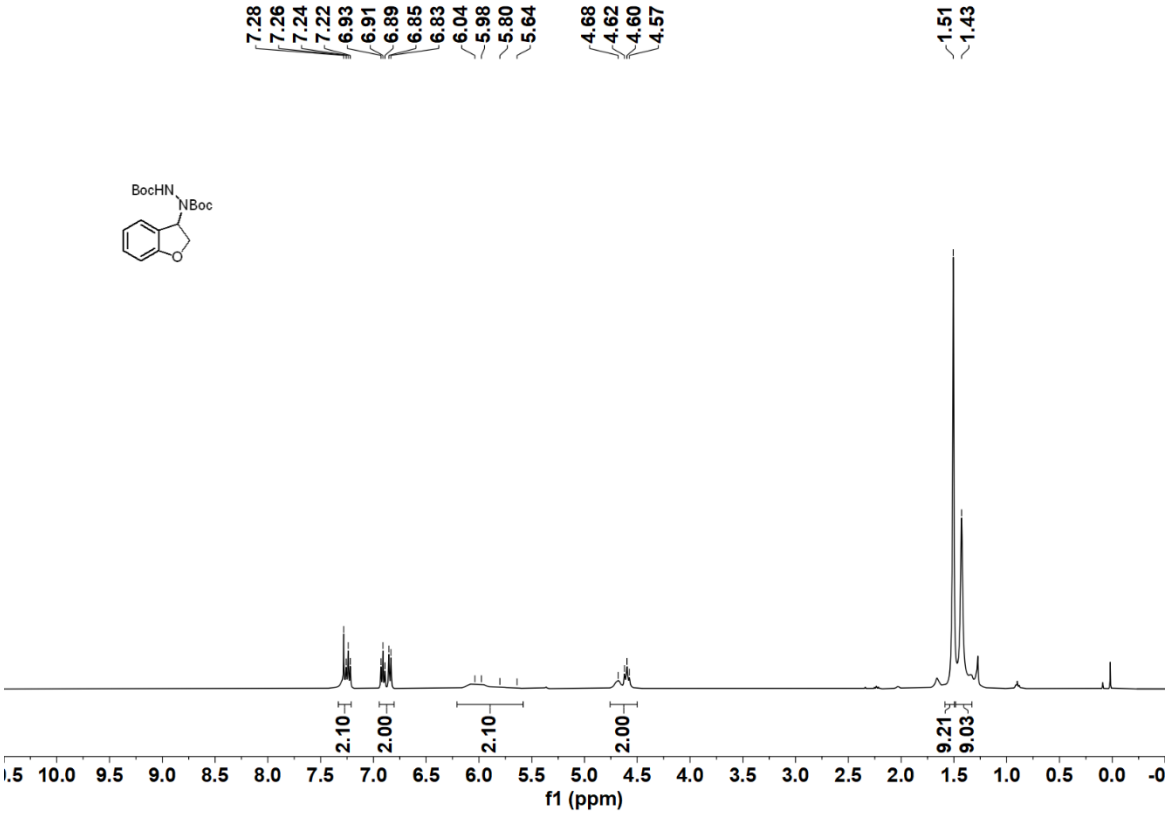
(4) J. Liu, M. Tian, A. Li, L. Ji, D. Qiu and X. Zhao, *Tetrahedron Lett.*, 2021, **66**, 152809.

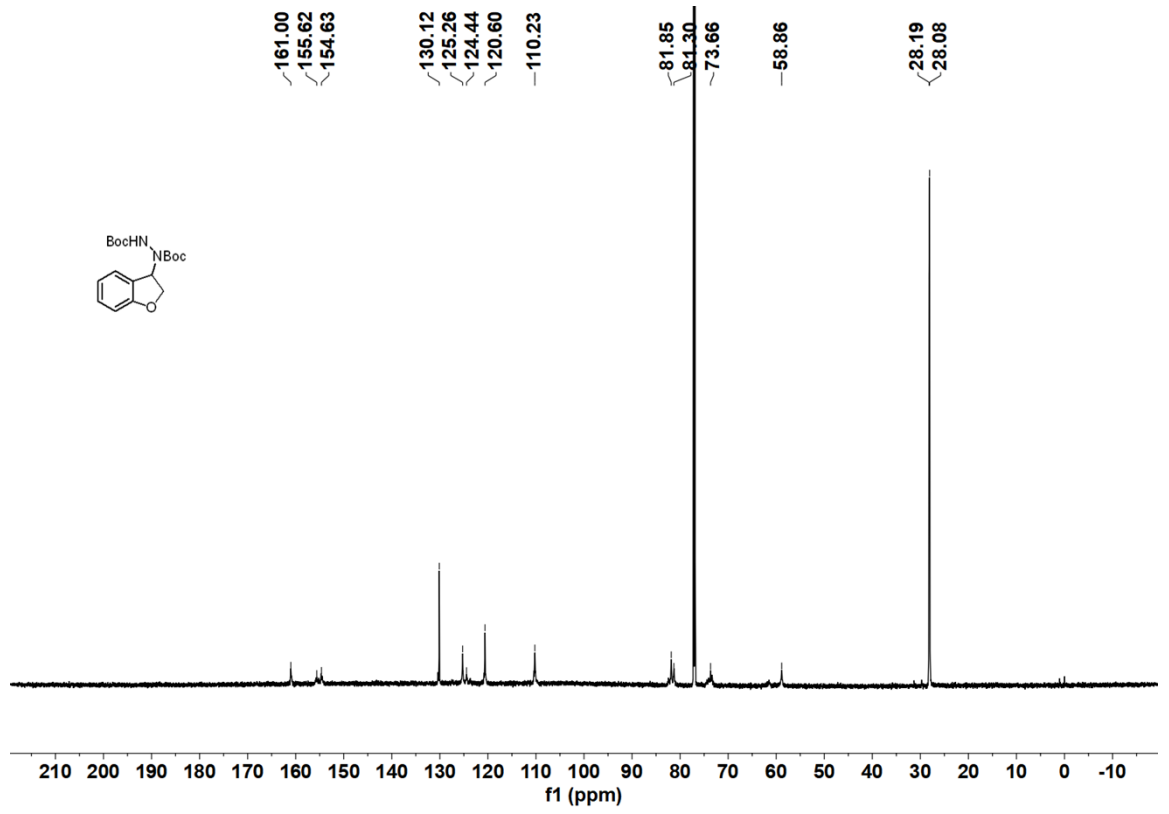
(5) Z. Ye, W. Xie, D. Wang, H. Liu and X. Yang, *ACS Catal.*, 2024, **14**, 4958.

(6) H. Chiba, Y. Sakai, S. Oishi, N. Fujii and H. Ohno, *Tetrahedron Lett.* 2012, **53**, 6273.

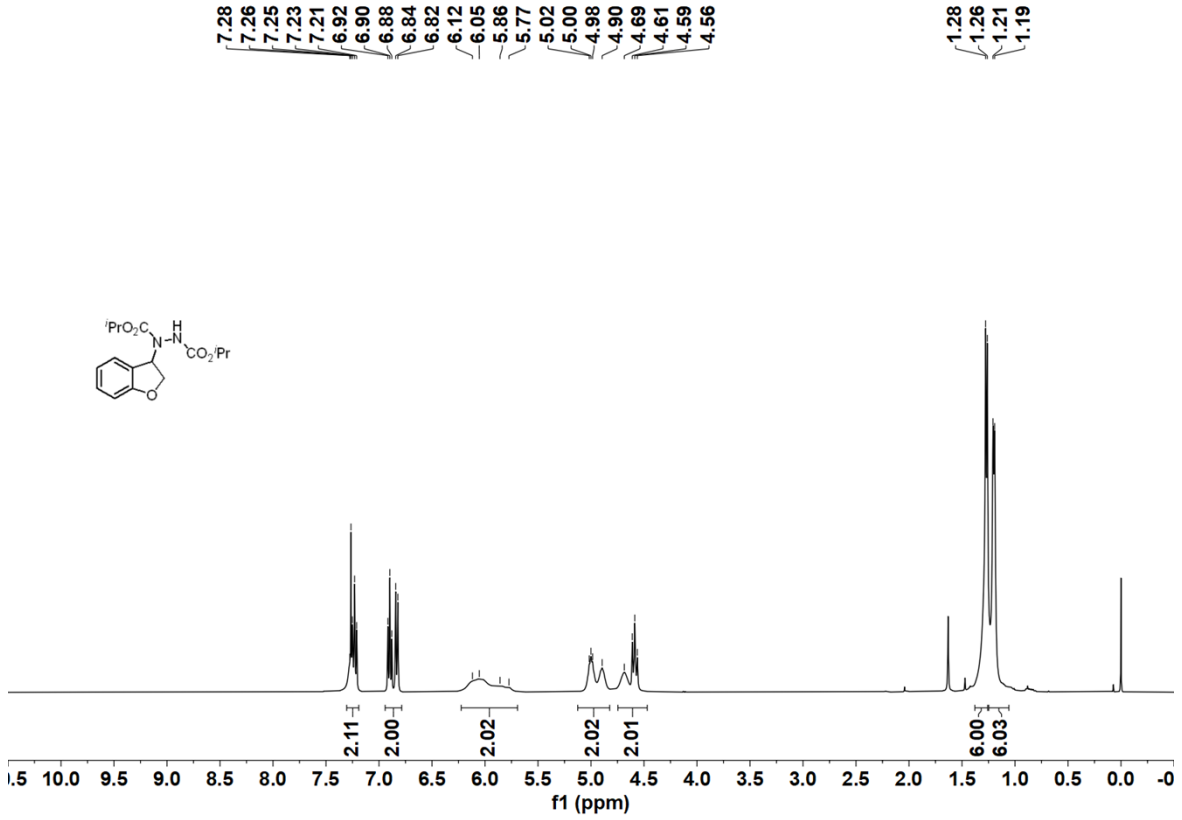
9 NMR Spectra

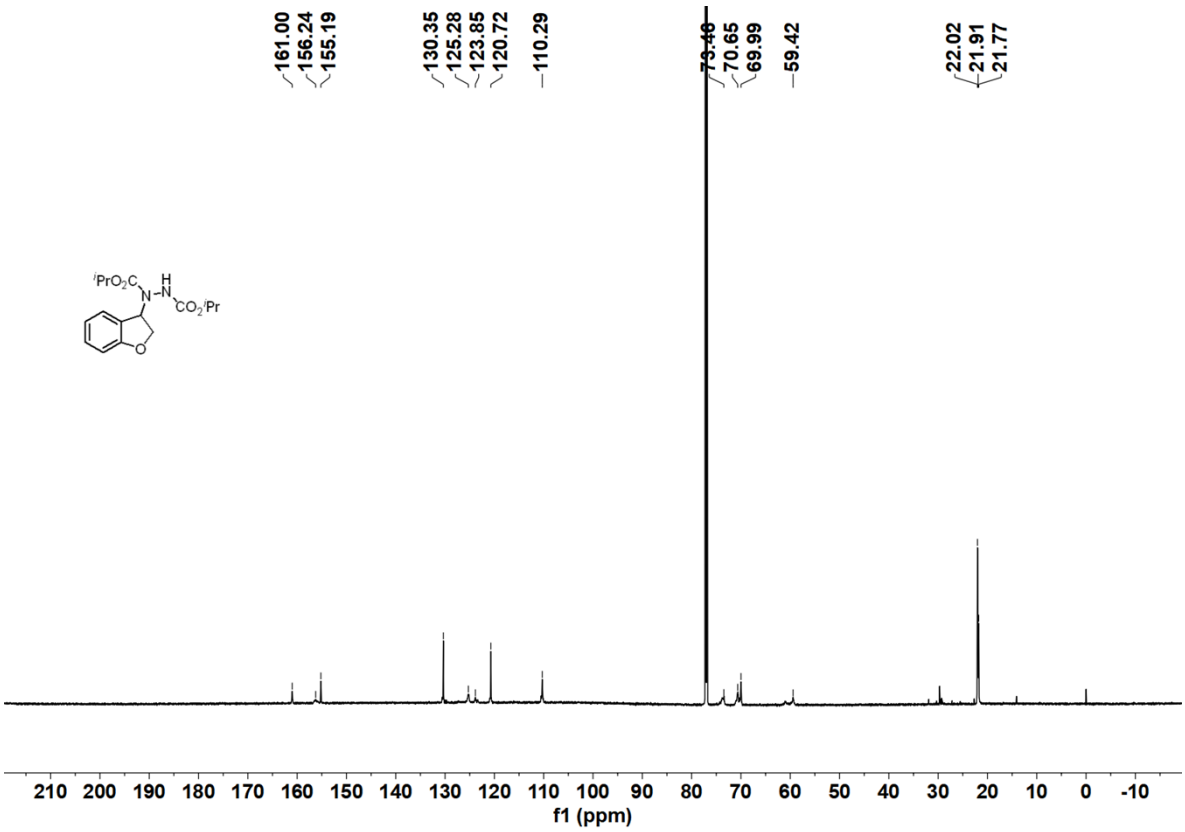
Di-*tert*-butyl 1-(2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3aa**)



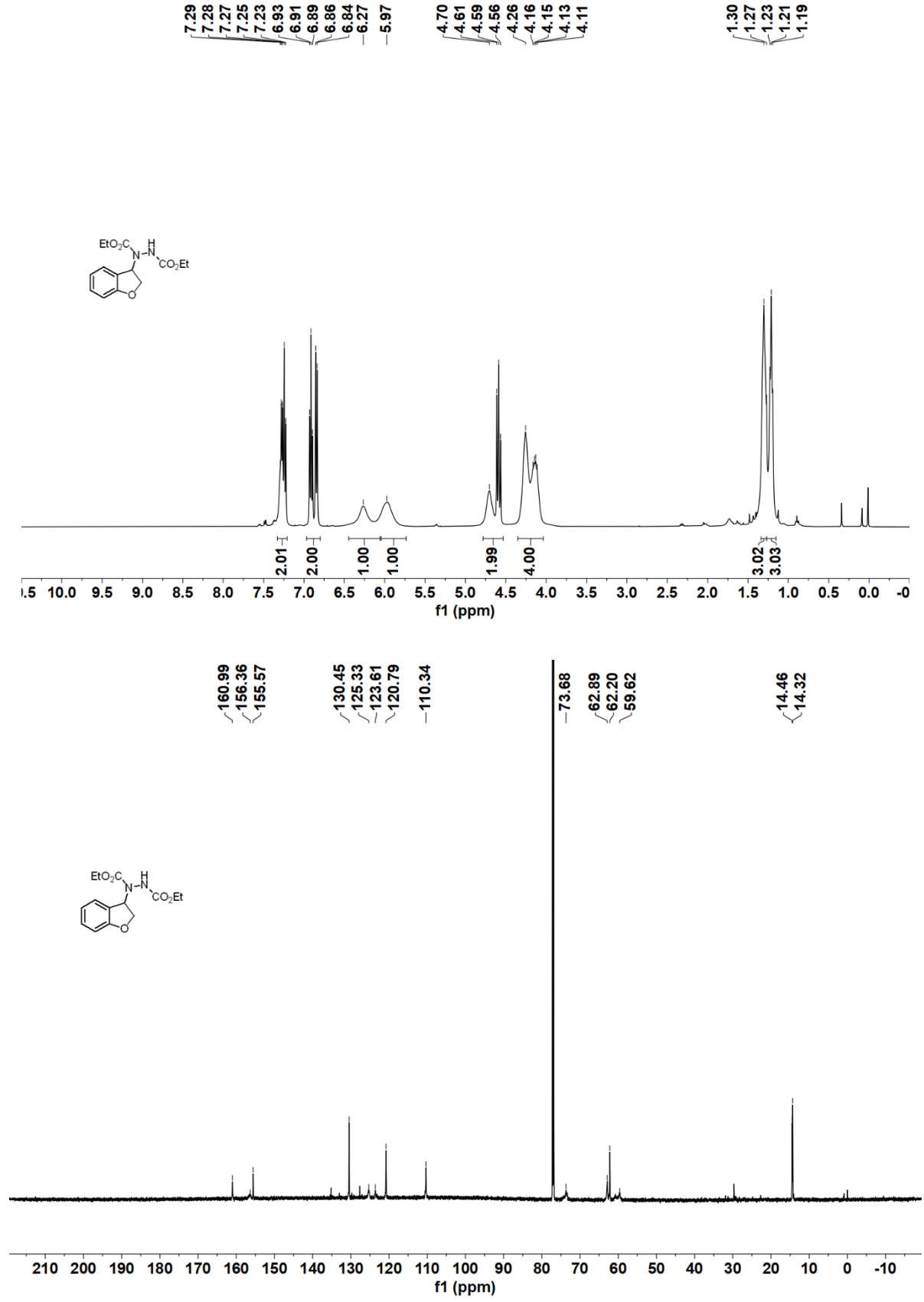


Diisopropyl 1-(2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ab**)

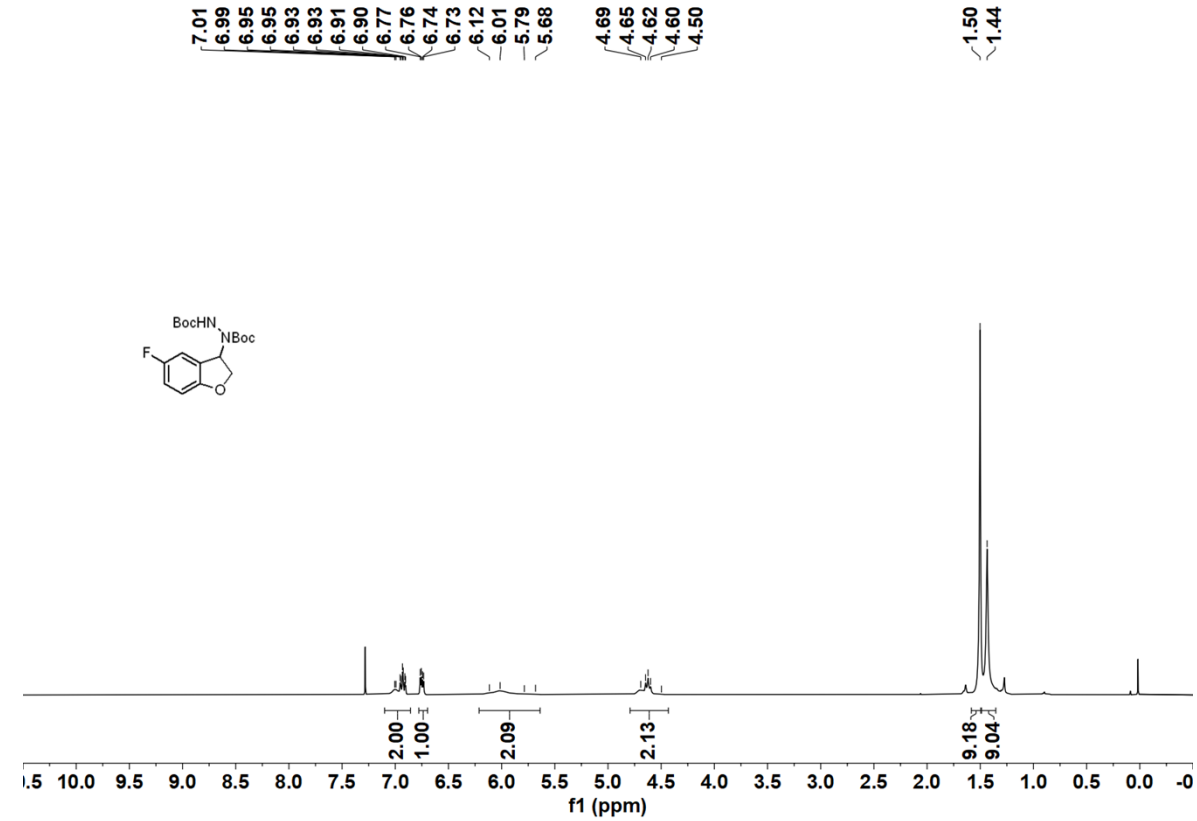


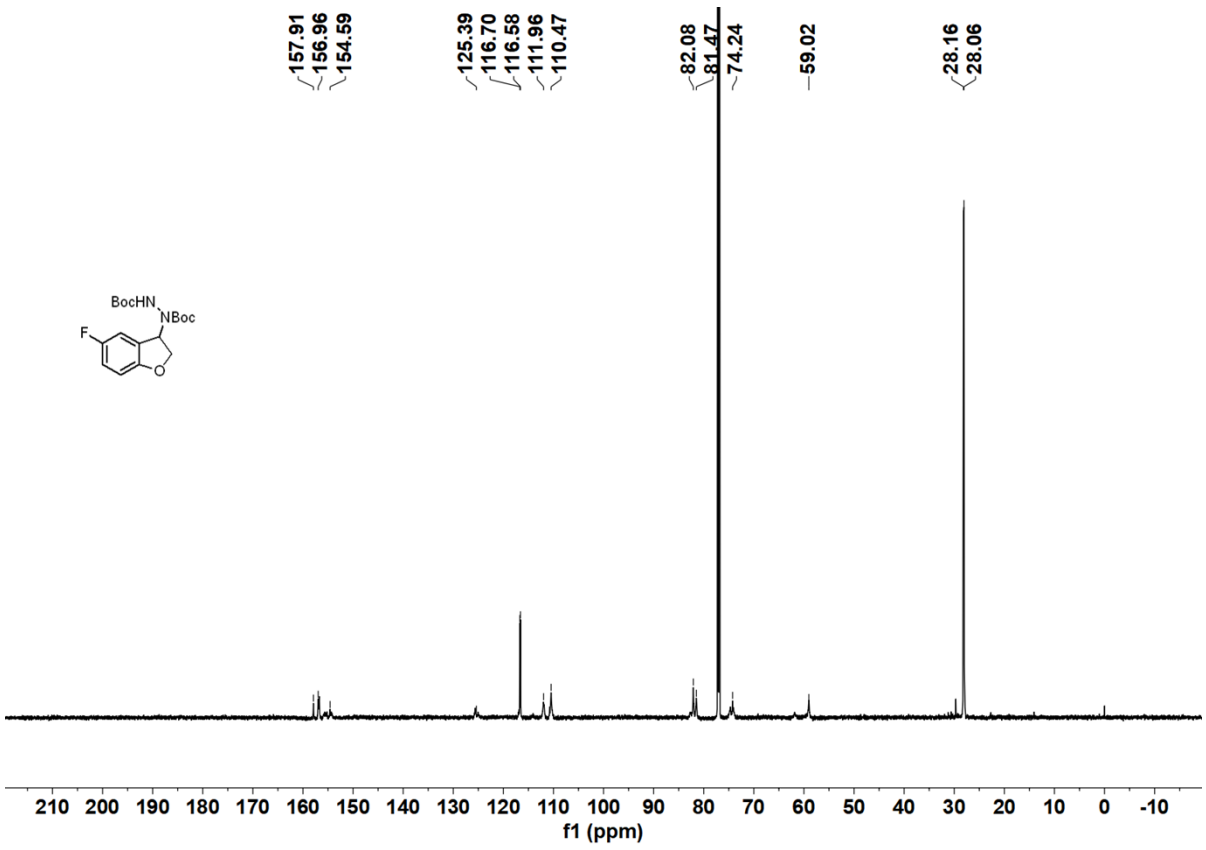


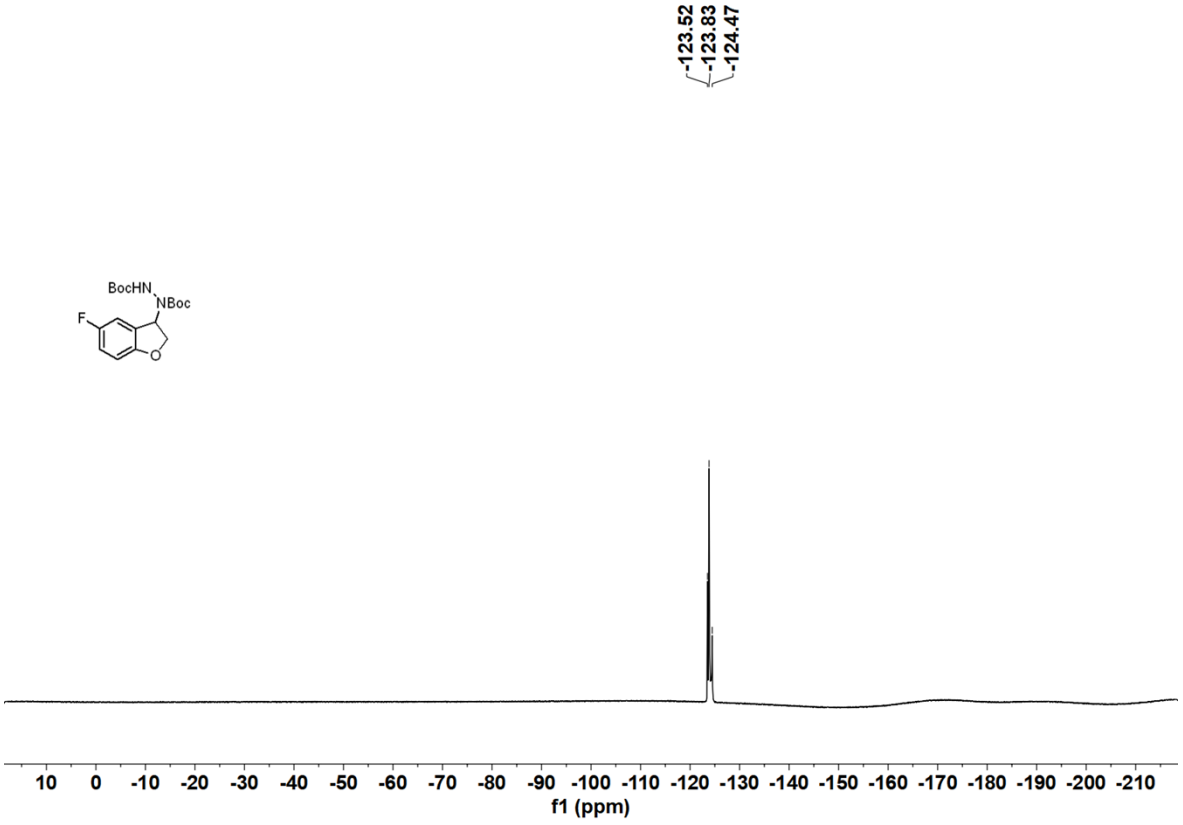
Diethyl 1-(2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ac**)



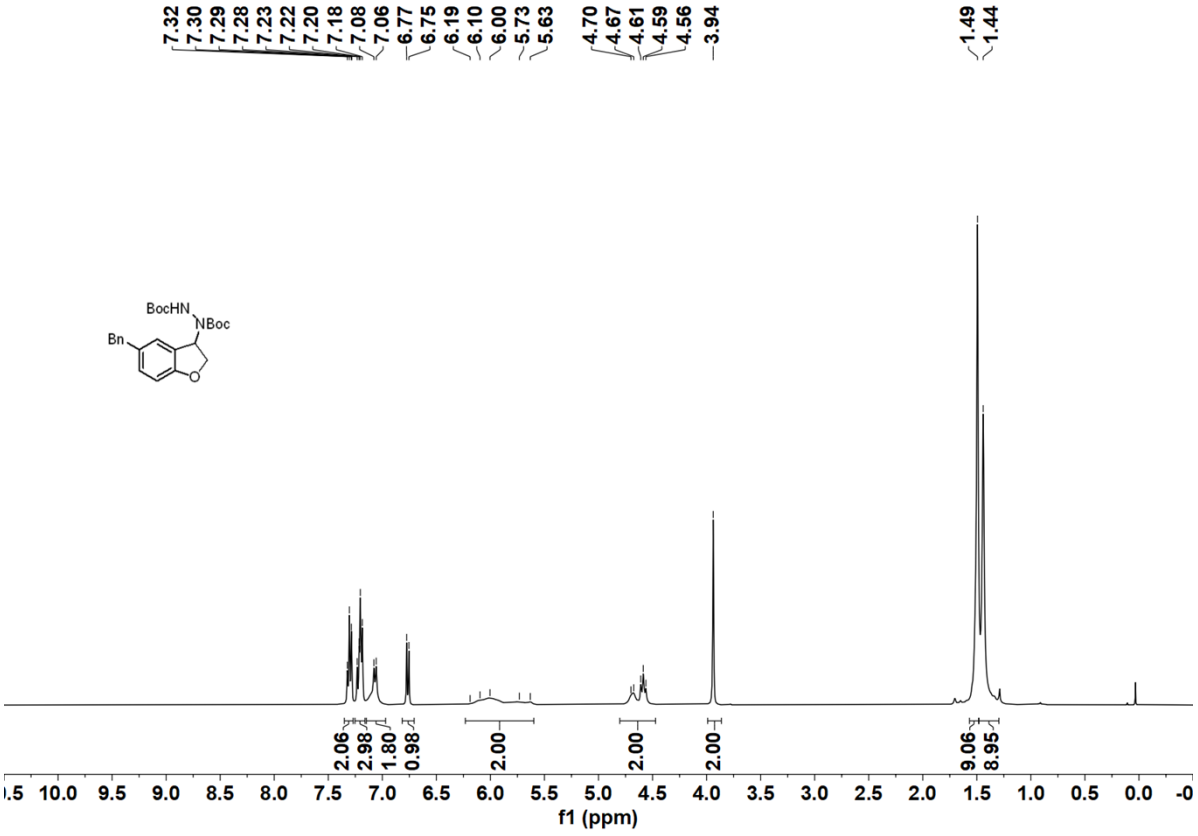
Di-*tert*-butyl 1-(5-fluoro-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate(**3ba**)

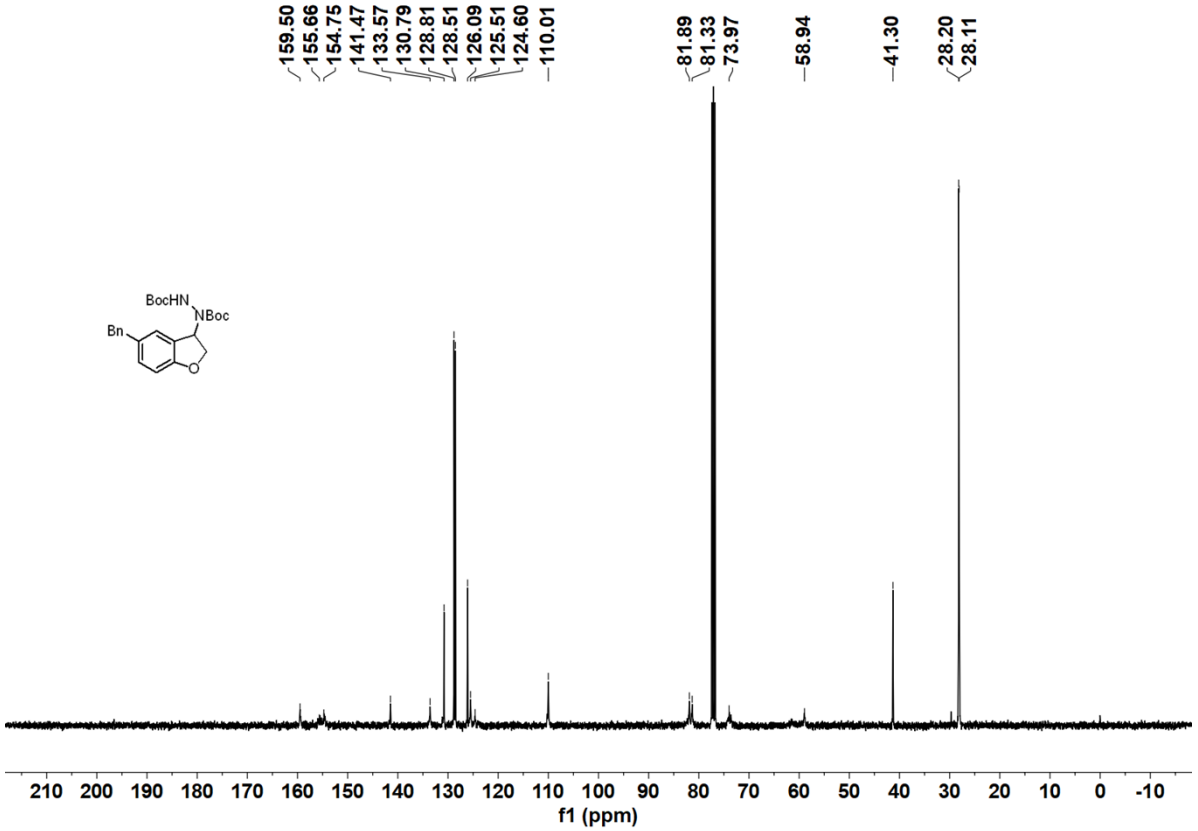

7.01
6.99
6.95
6.95
6.93
6.93
6.91
6.90
6.77
6.76
6.74
6.73
6.12
6.01
5.79
5.68
4.69
4.65
4.62
4.60
4.50
1.50
1.44
BocHN
NBoc
F
O
2.00
1.00
2.09
2.13
9.18
9.04
f1 (ppm)


157.91
156.96
154.59
125.39
116.70
116.58
111.96
110.47
82.08
81.47
74.24
59.02
28.16
28.06
BocHN
NBoc
F
O
f1 (ppm)

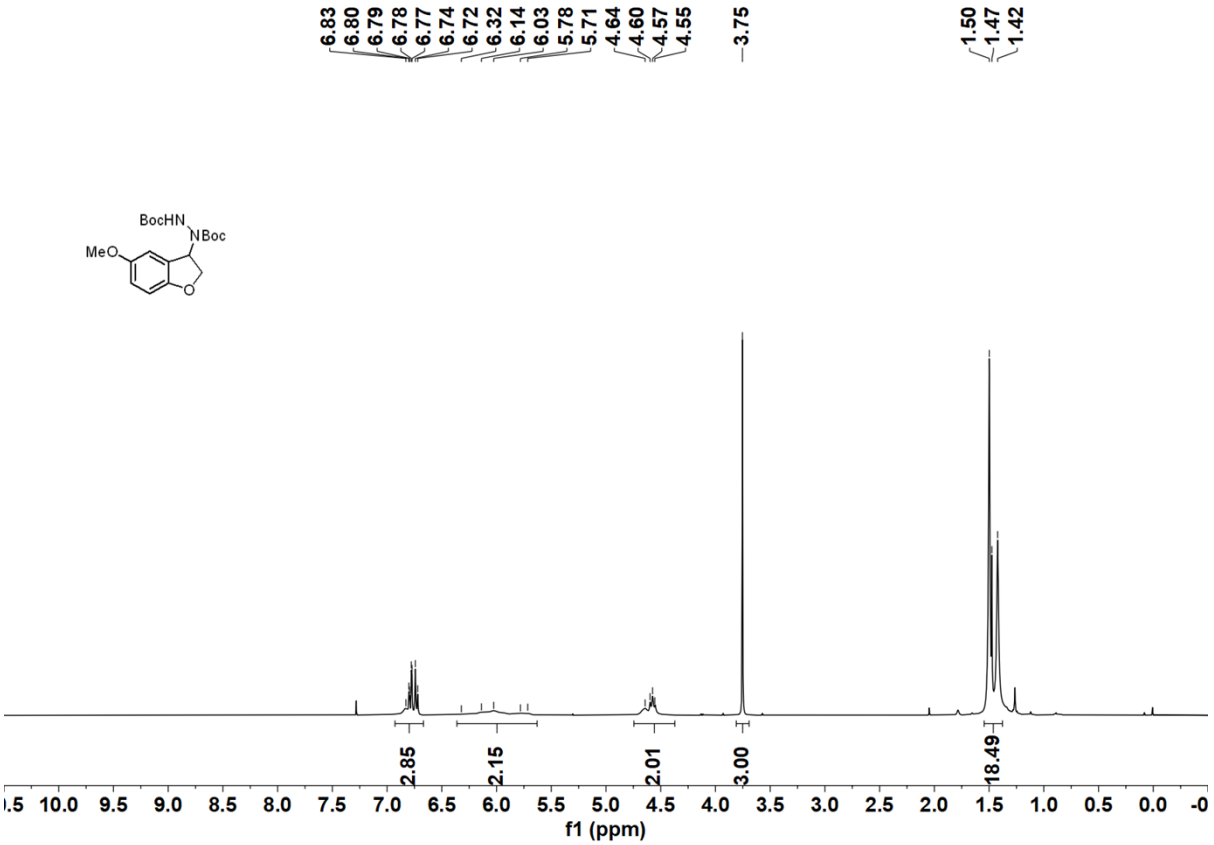


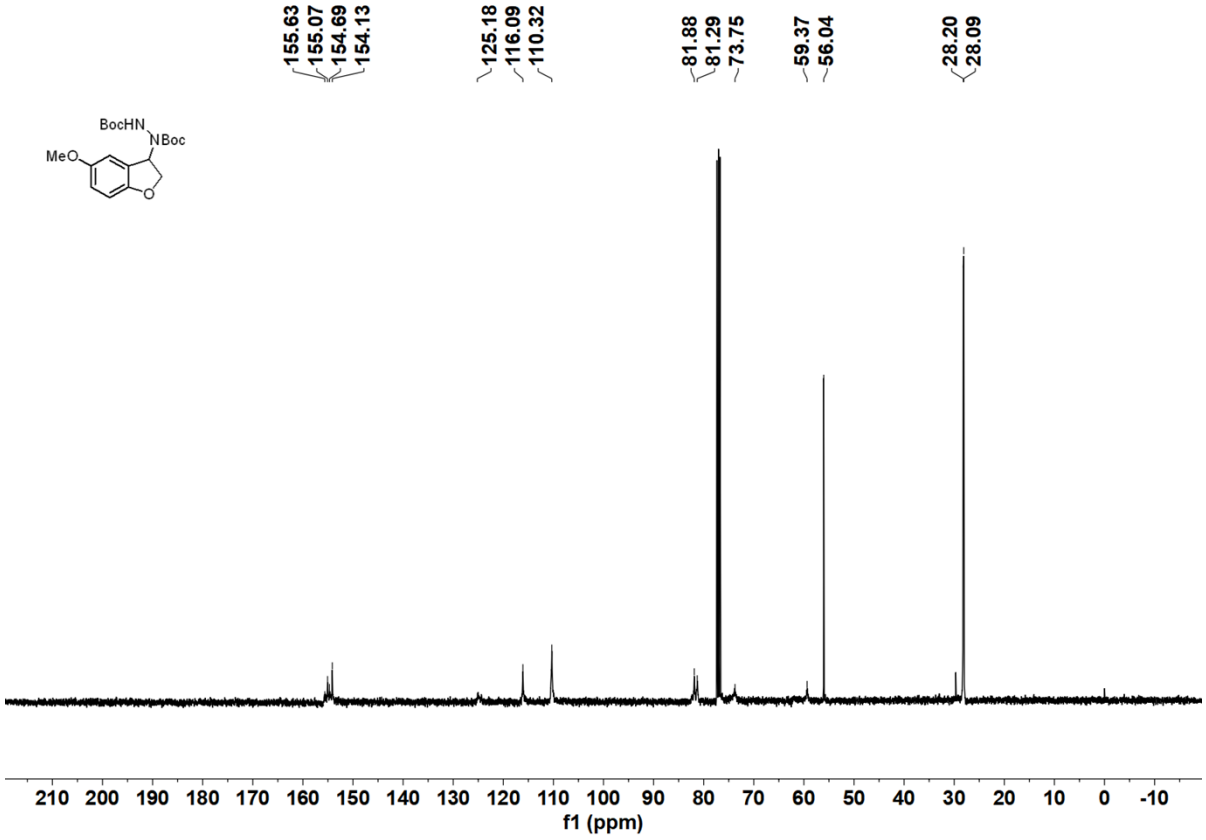
Di-*tert*-butyl 1-(5-benzyl-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ca**)



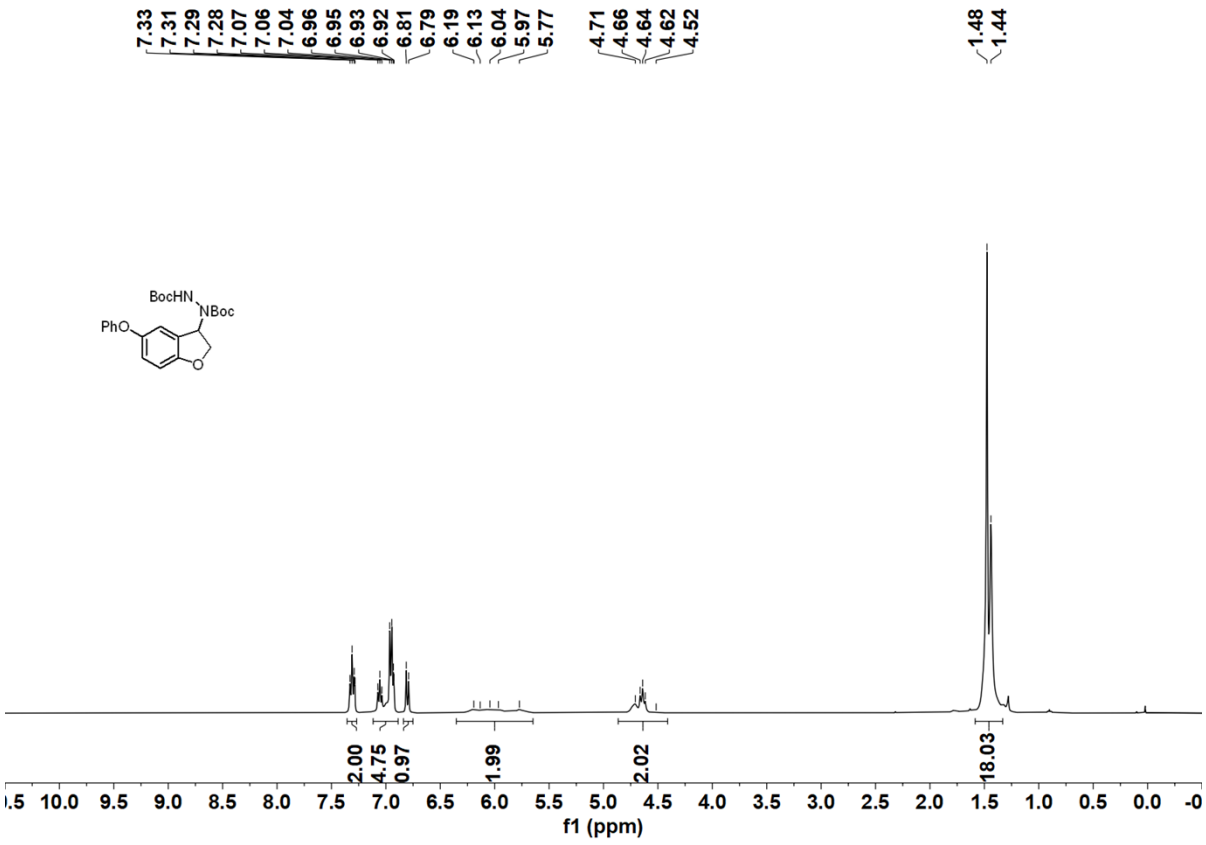


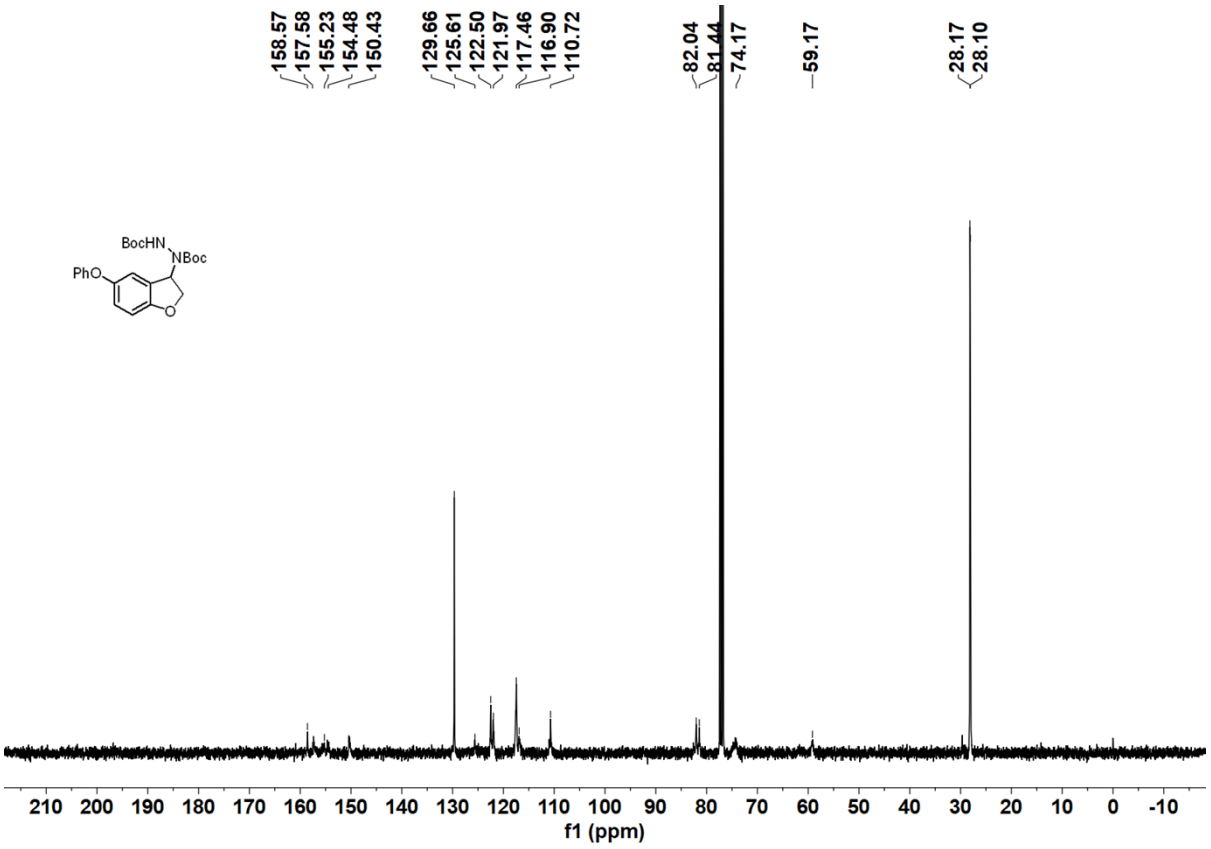
Di-*tert*-butyl 1-(5-methoxy-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate **(3da)**



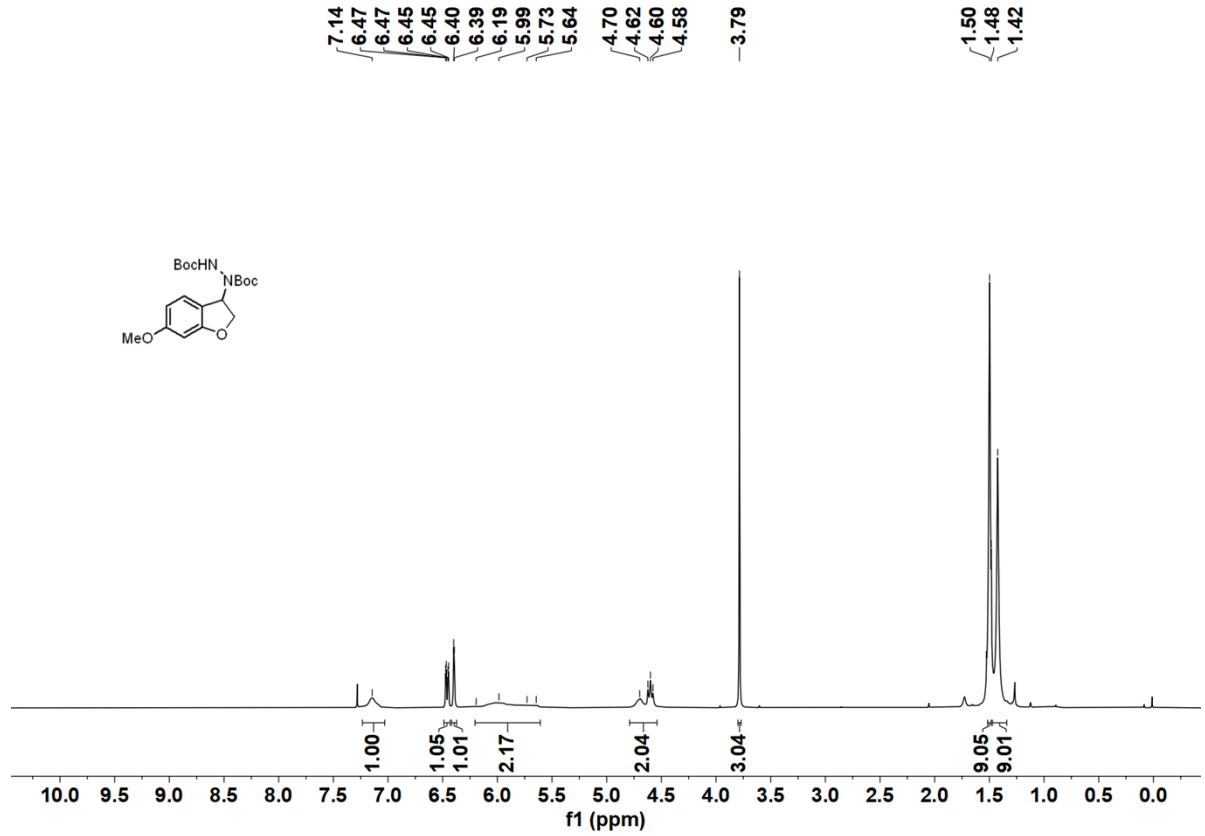


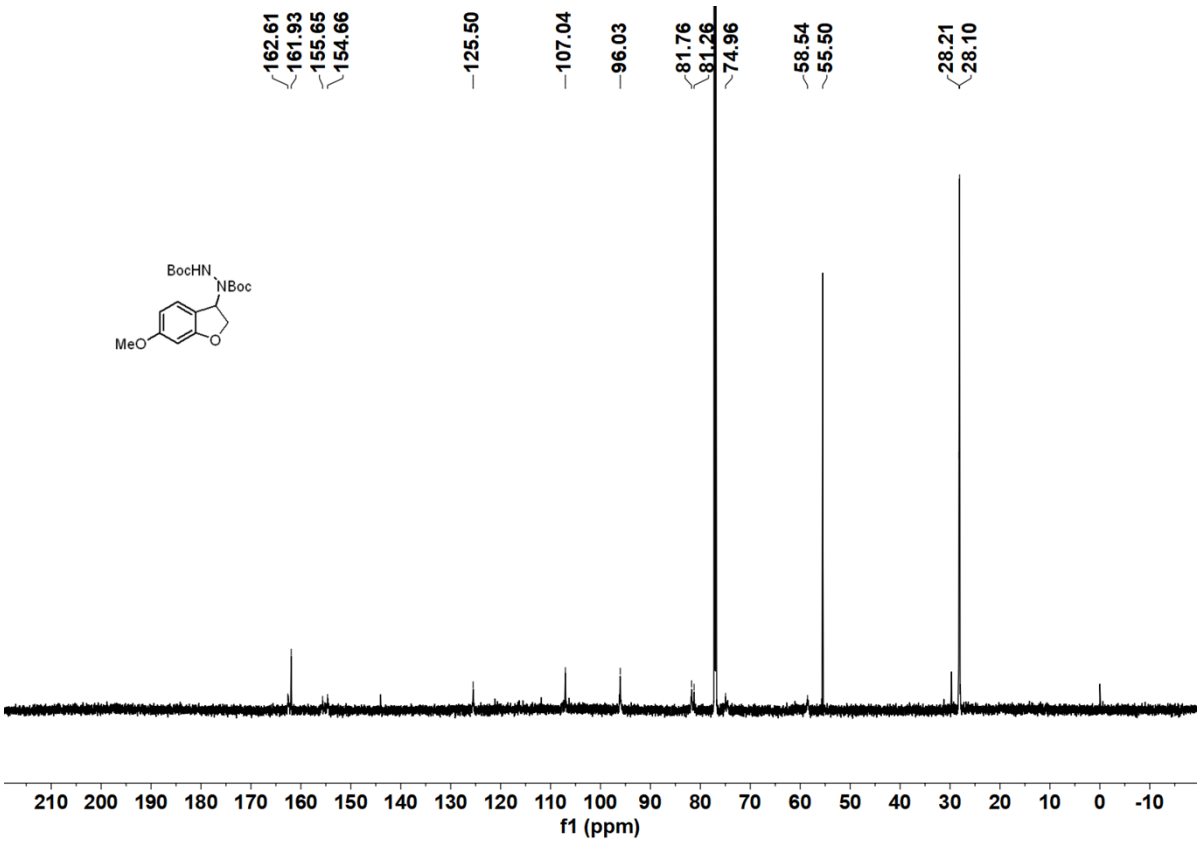
Di-*tert*-butyl 1-(5-phenoxy-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ea**)



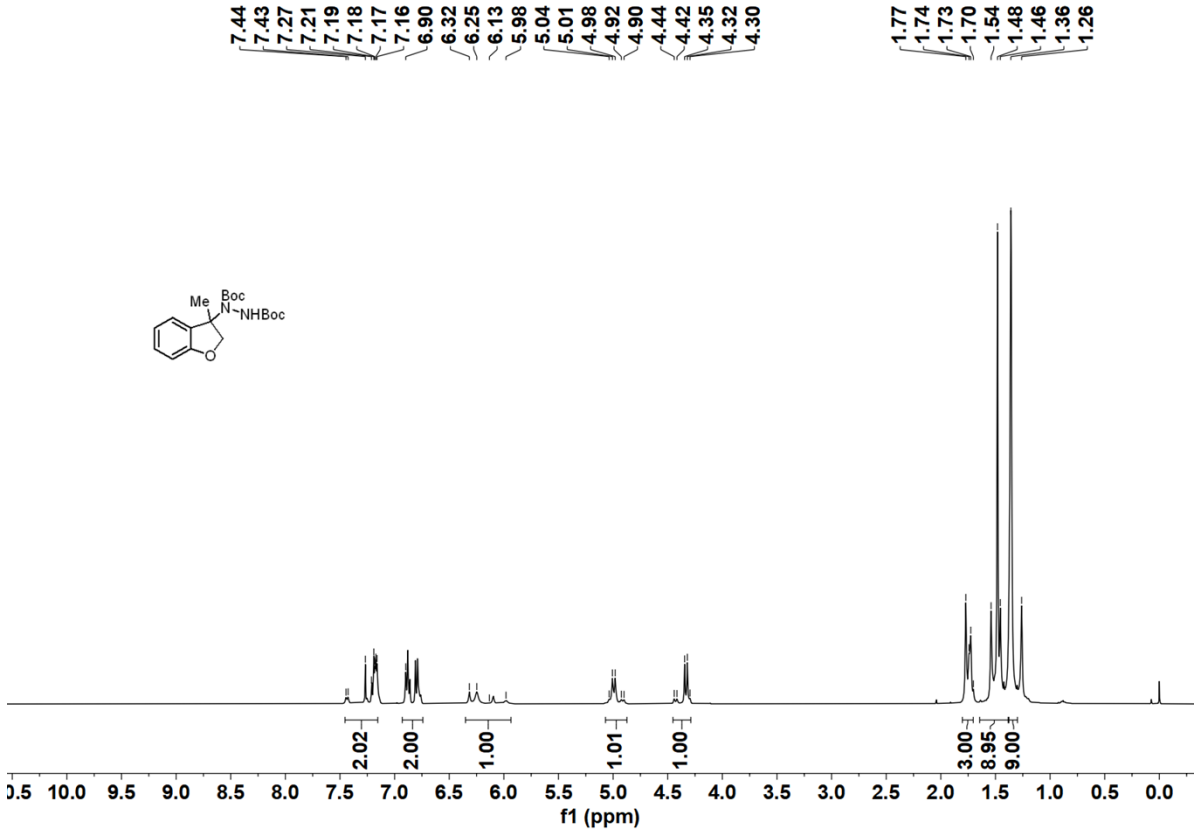


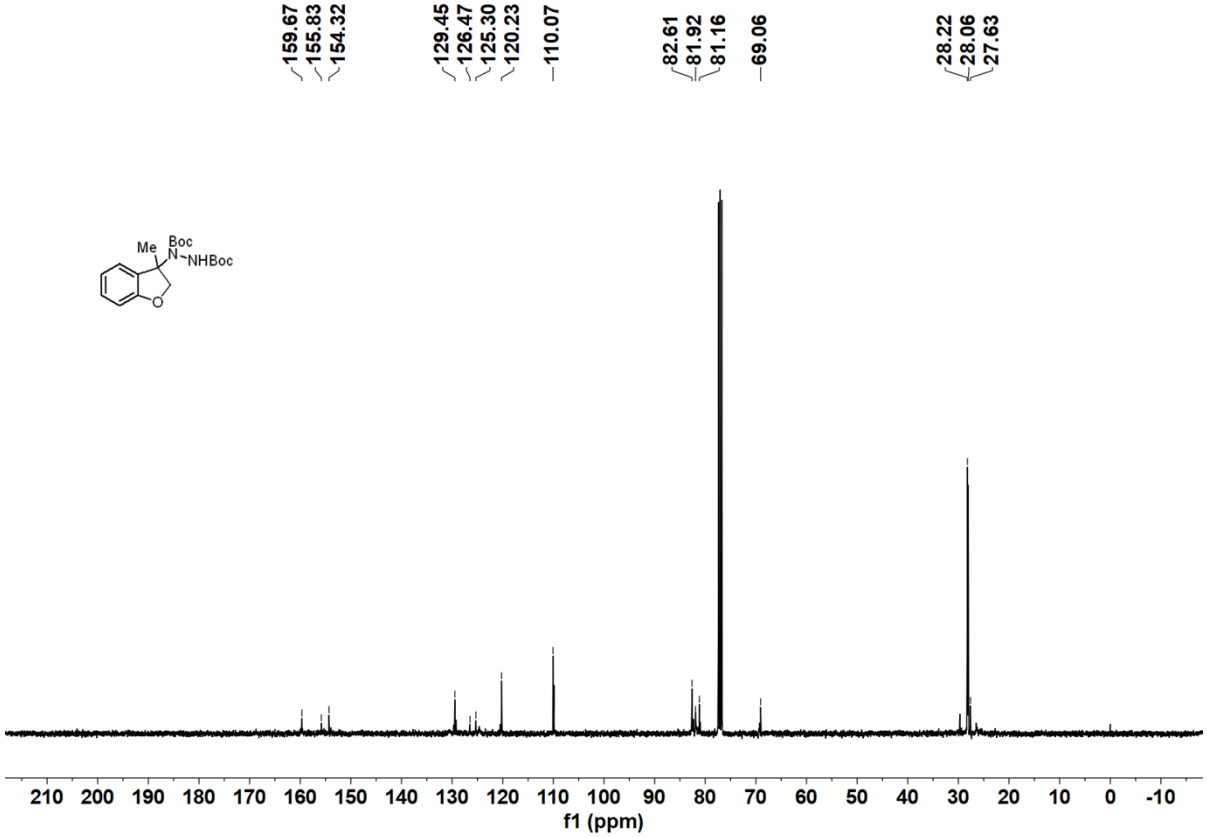
Di-*tert*-butyl 1-(6-methoxy-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3fa**)



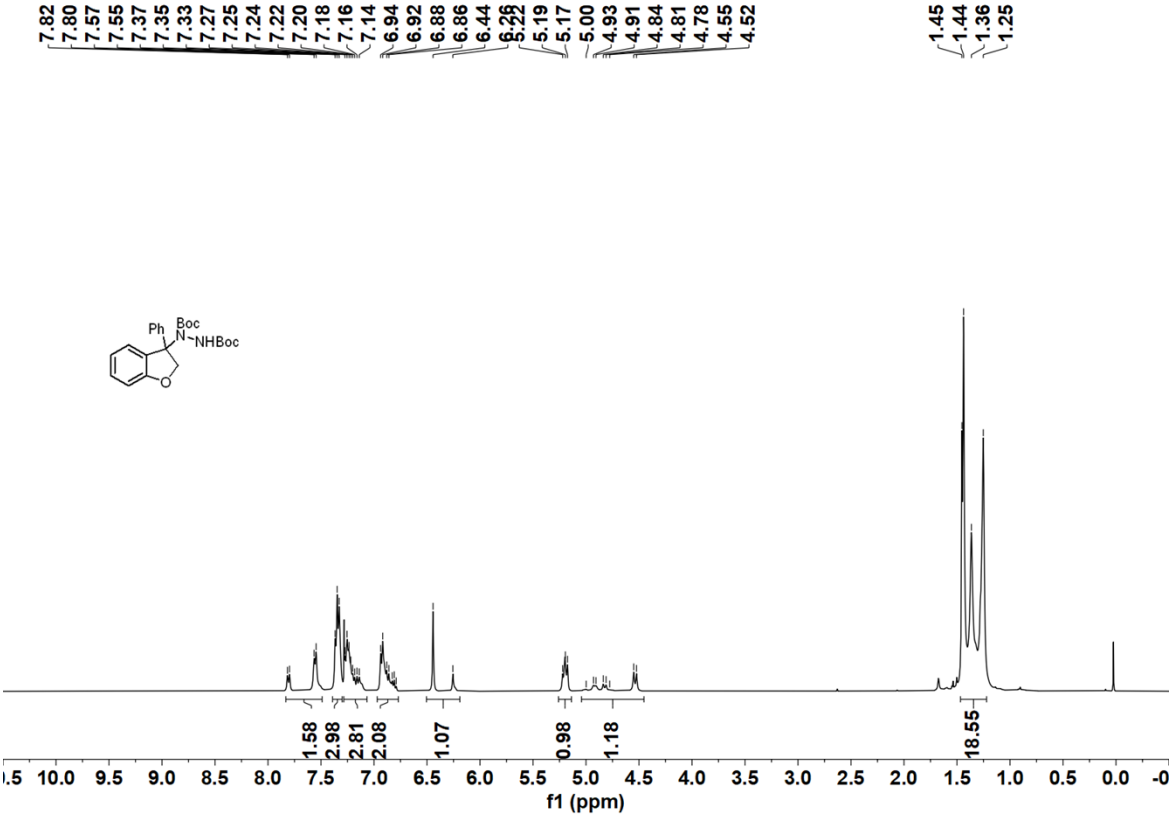


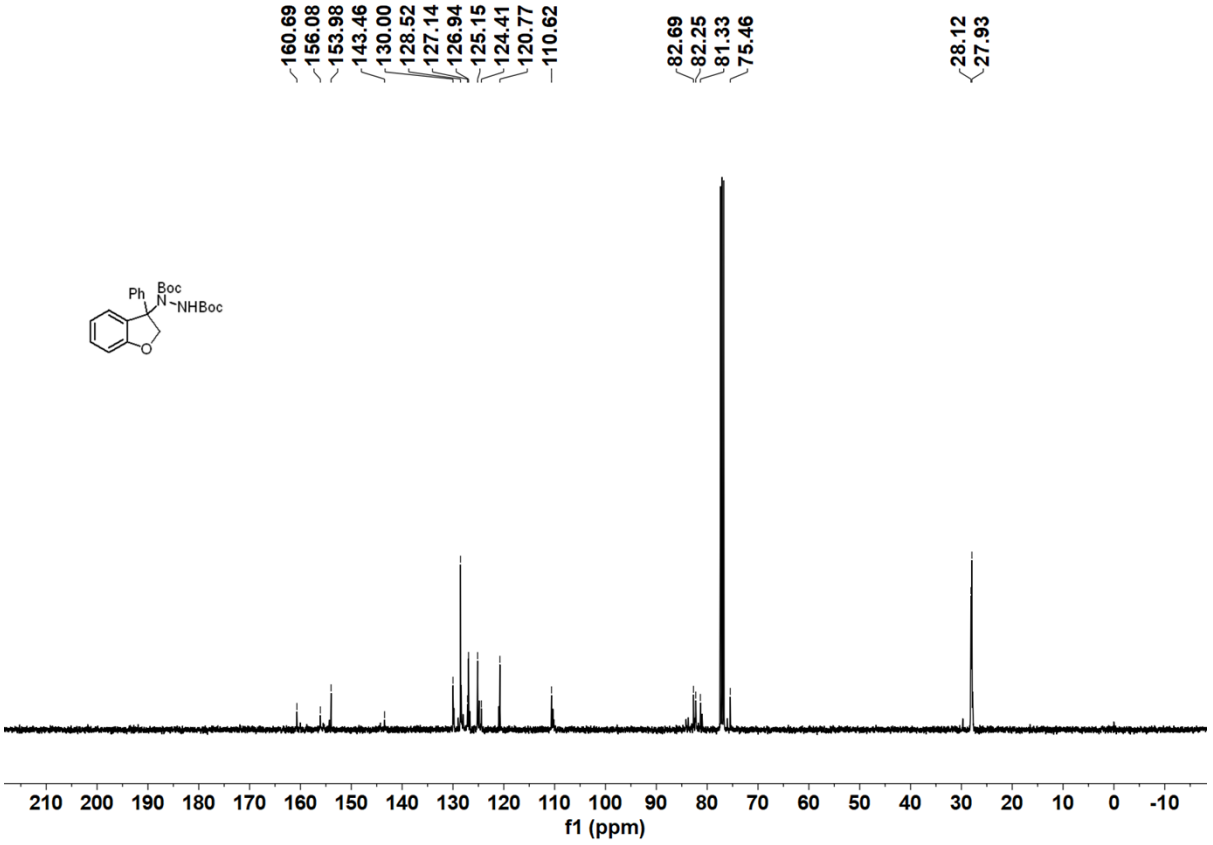
Di-*tert*-butyl 1-(3-methyl-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ga**)



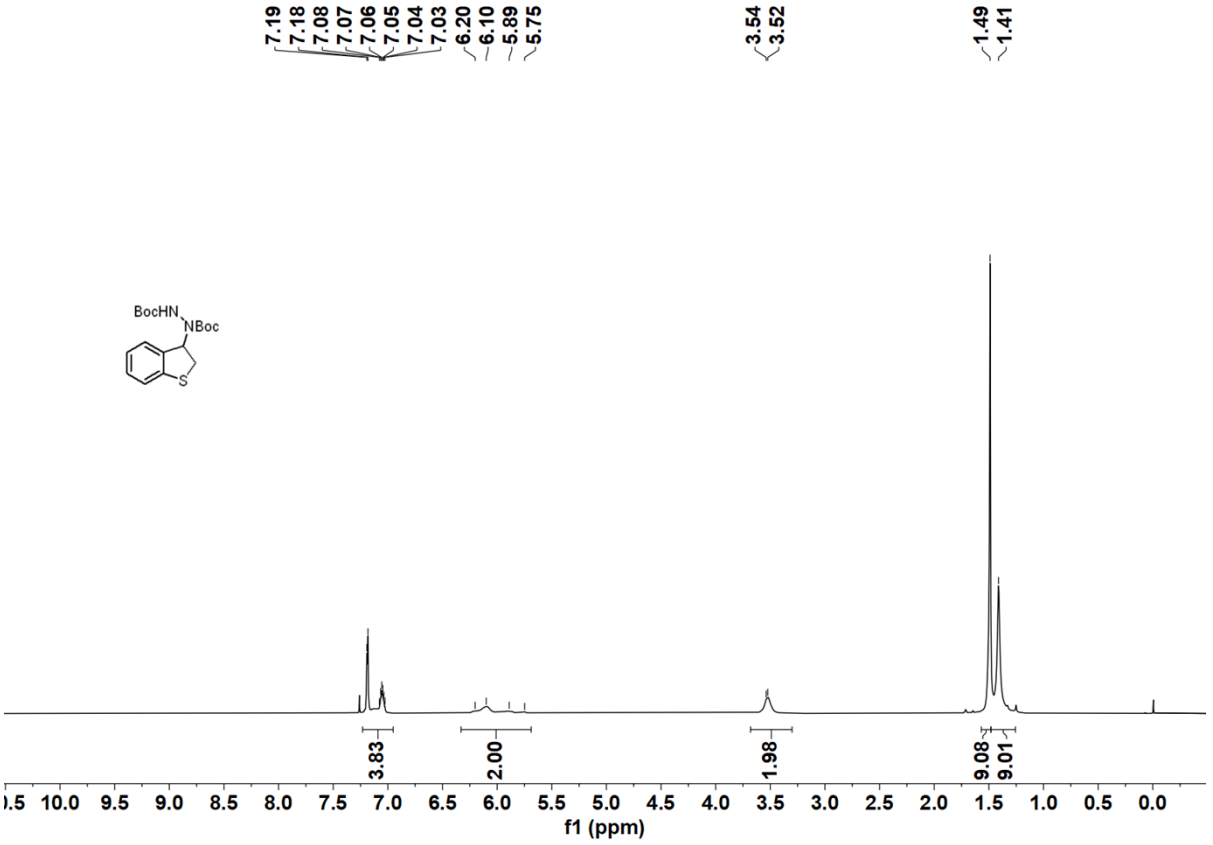


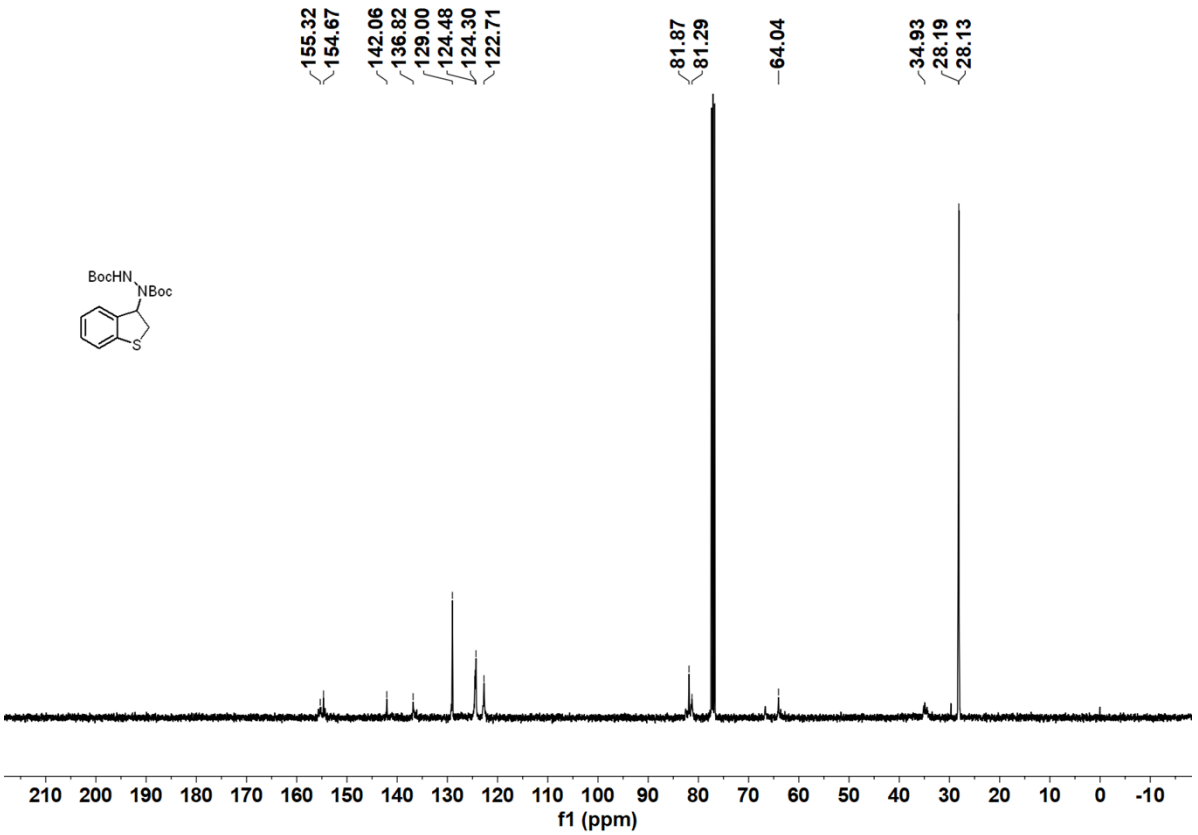
Di-*tert*-butyl 1-(3-phenyl-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ha**)



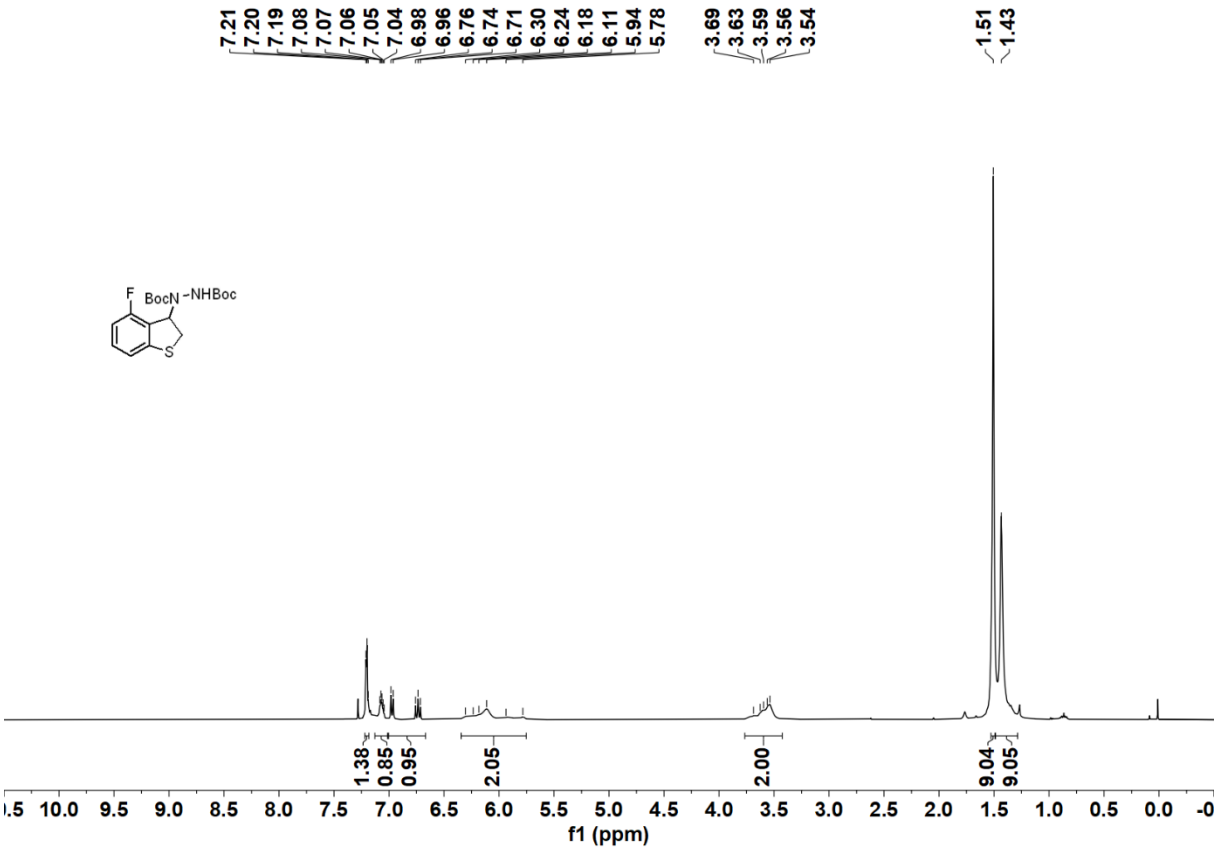


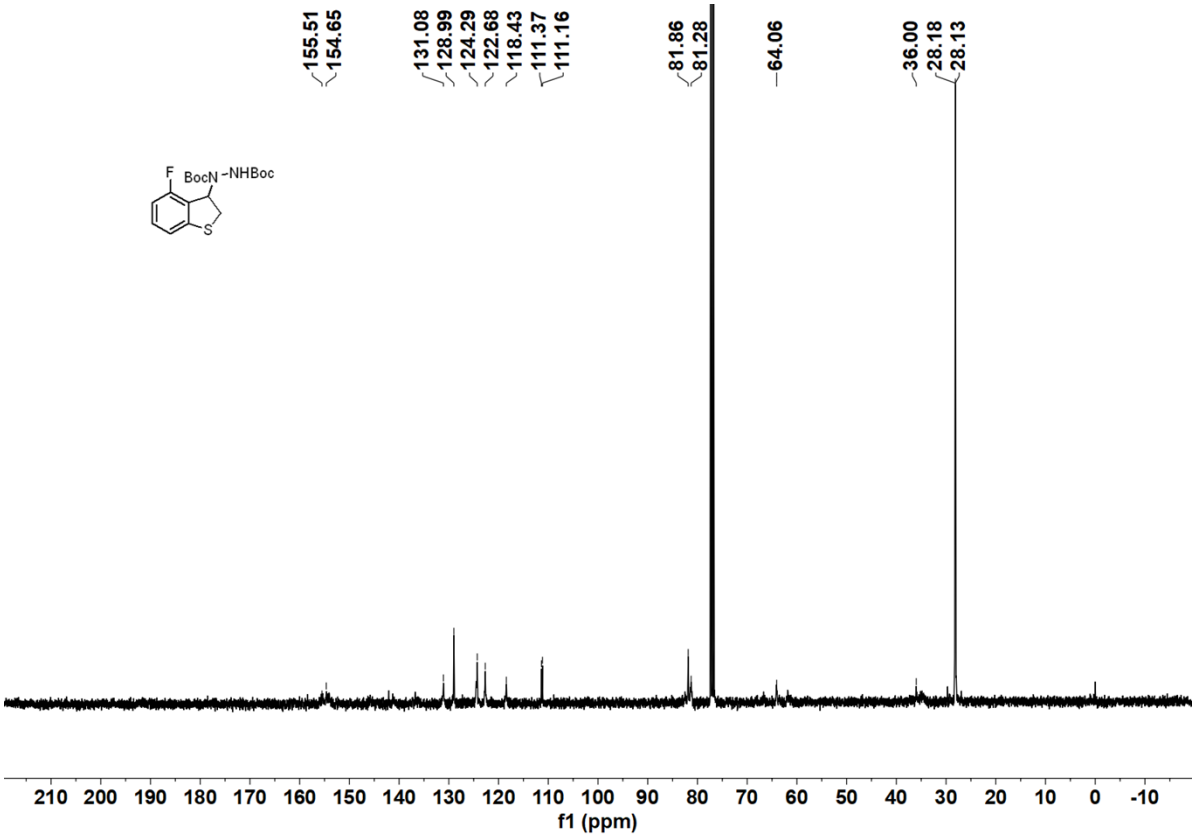
Di-*tert*-butyl 1-(2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3ia**)





Di-*tert*-butyl 1-(4-fluoro-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3ja**)




155.51
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111.37
111.16
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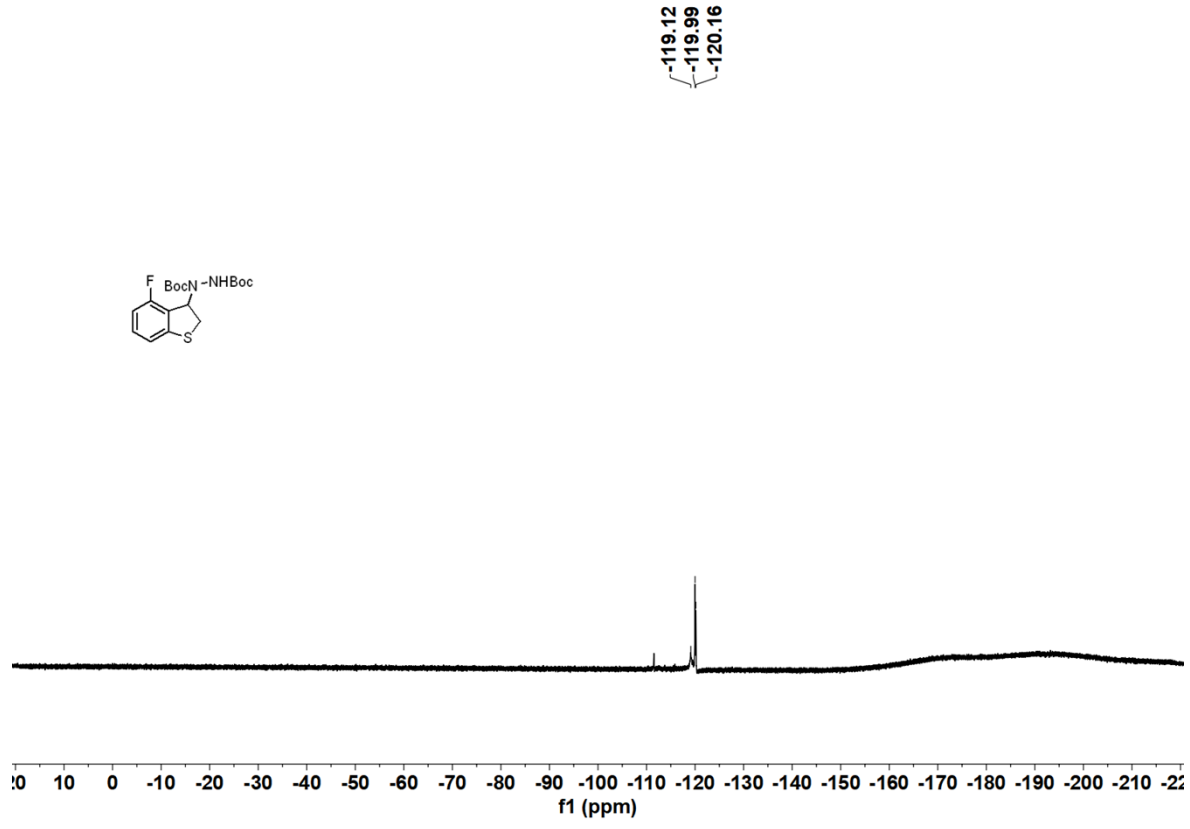
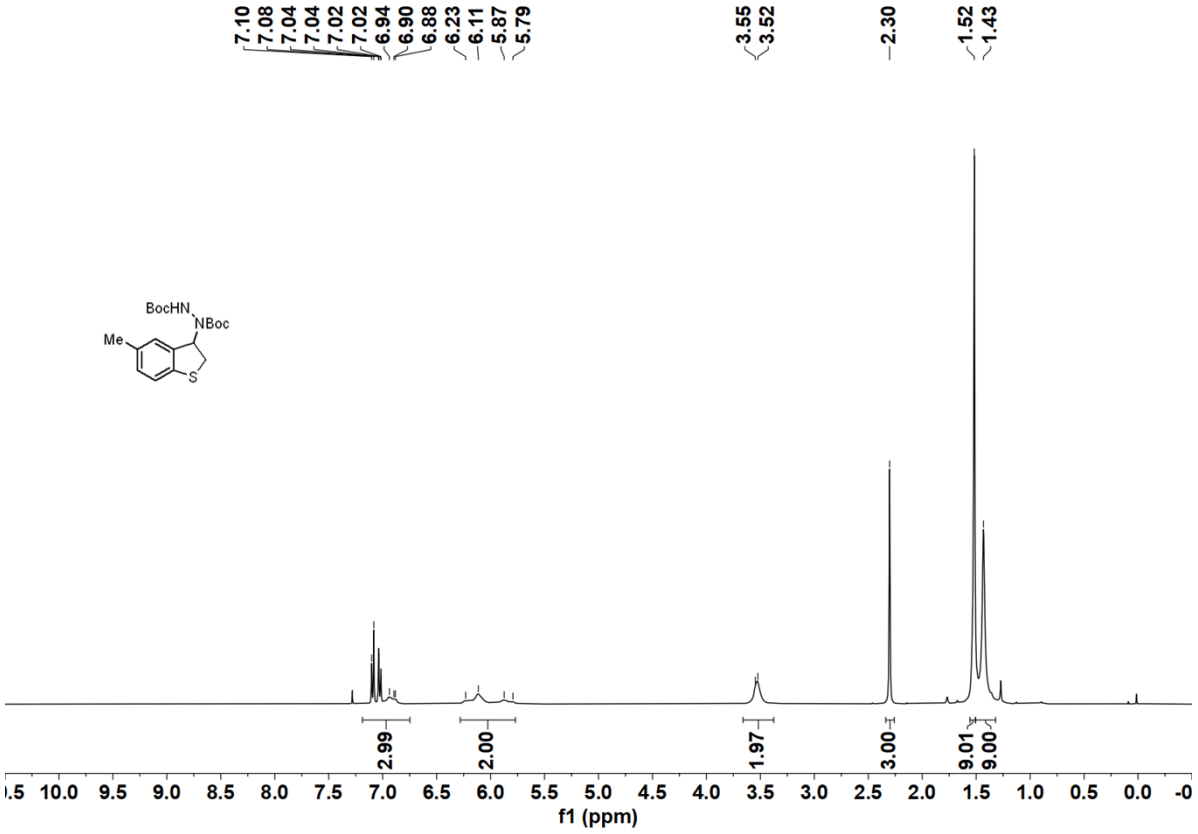
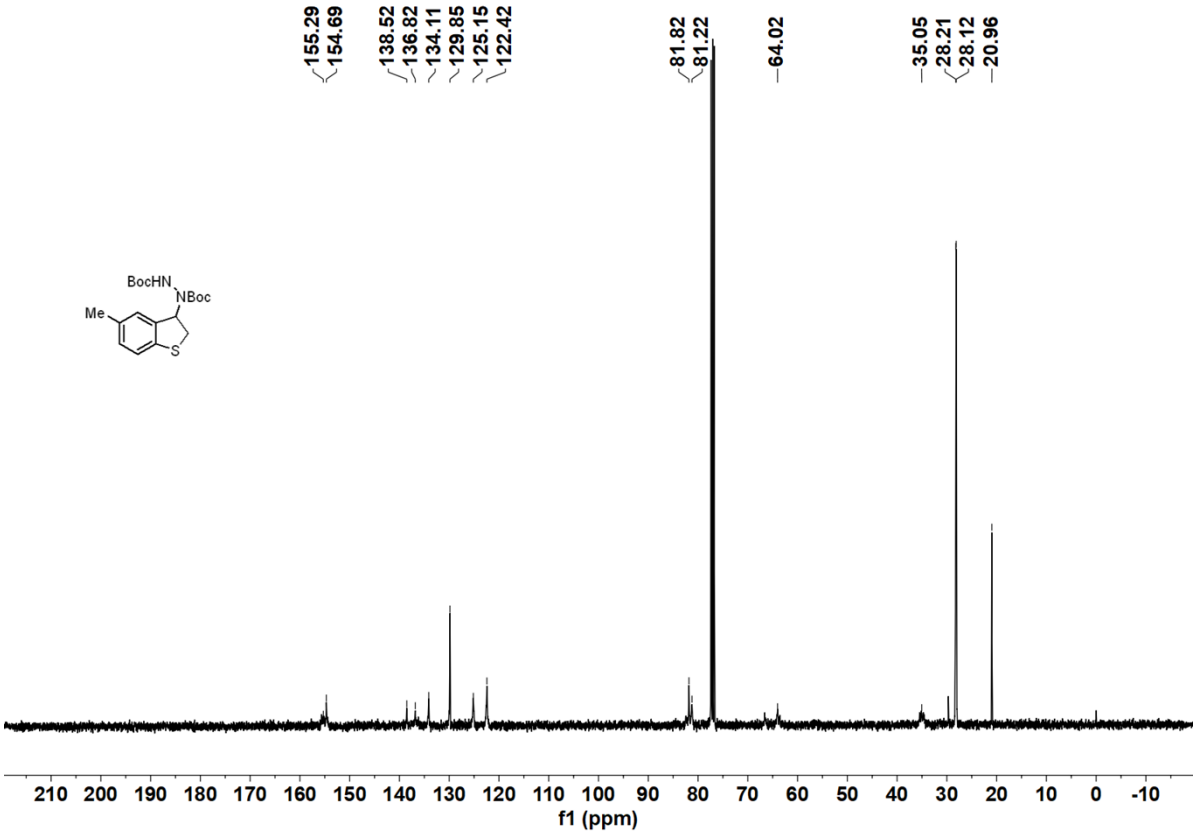
81.28
64.06
36.00
28.18
28.13
F
BocN
NHBoc
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

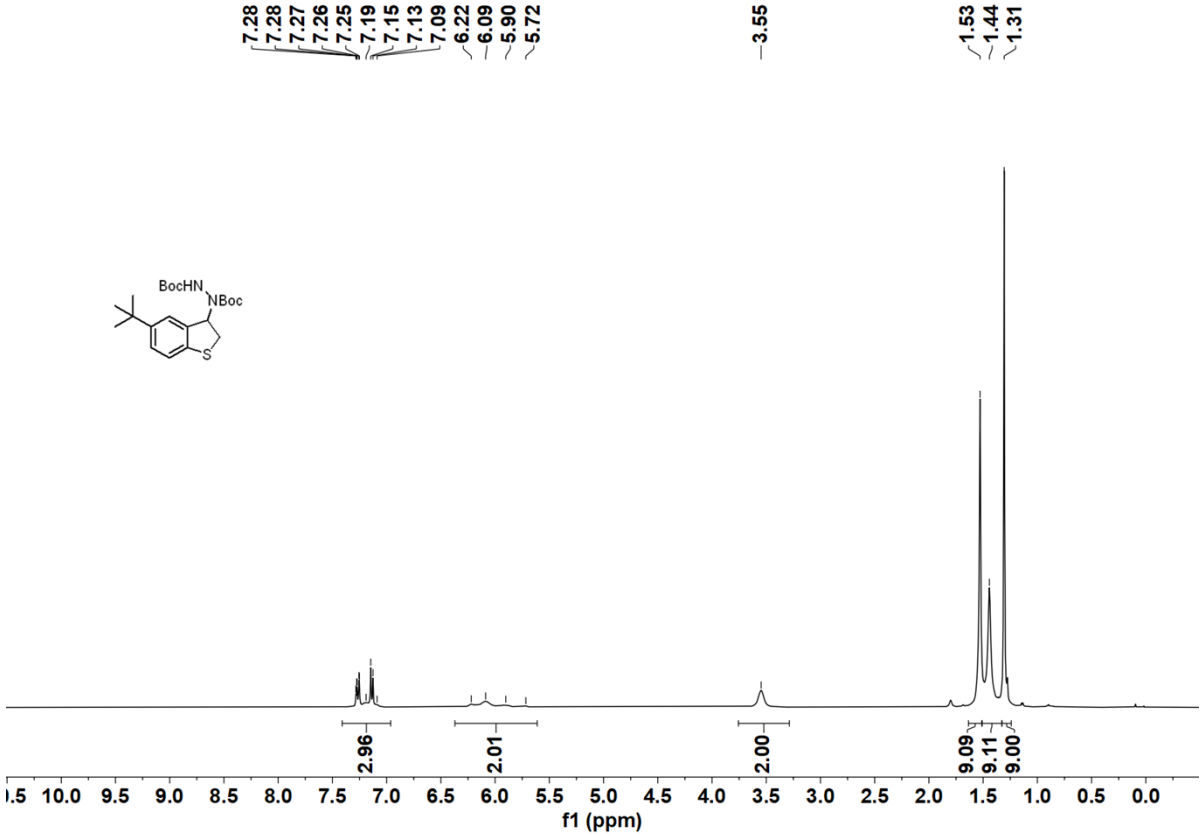

-119.12
-119.99
-120.16
F
BocN
NHBoc
S
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

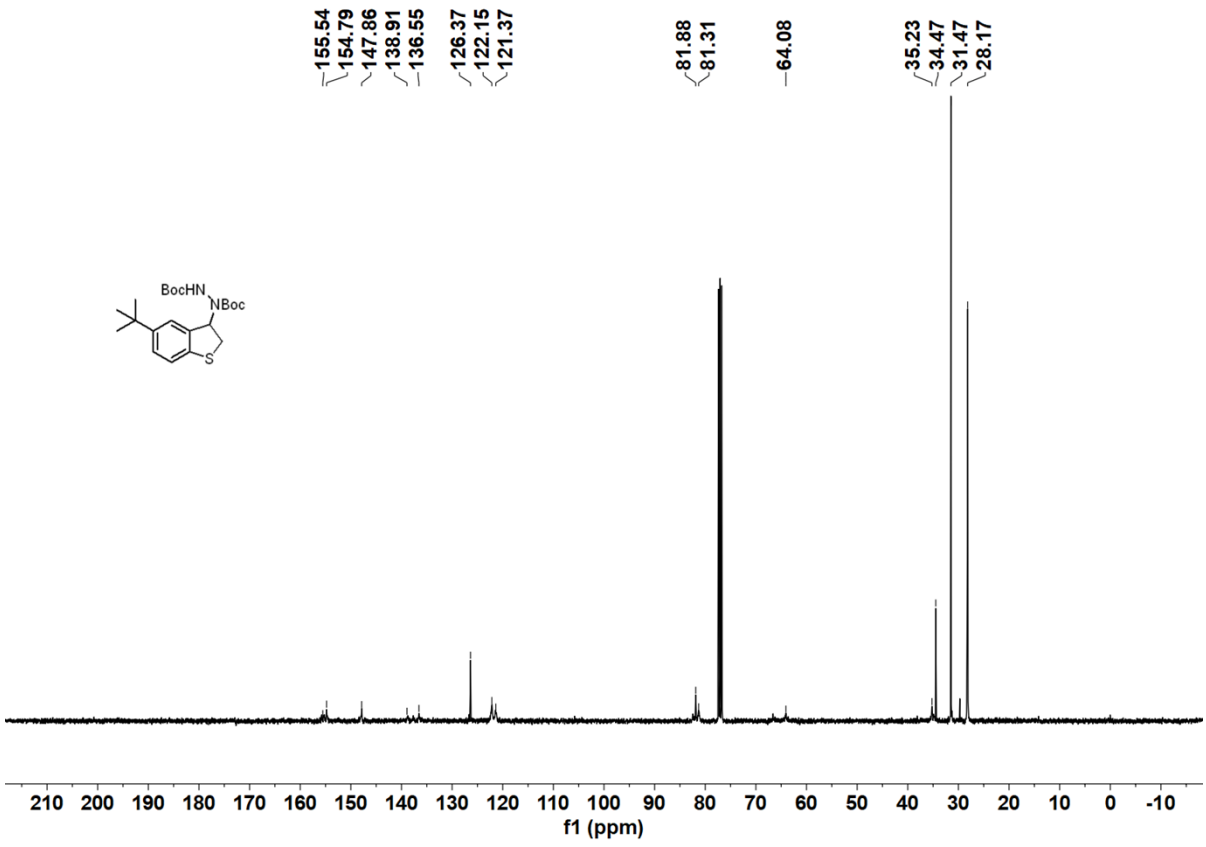
Di-*tert*-butyl 1-(5-methyl-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3ka**)



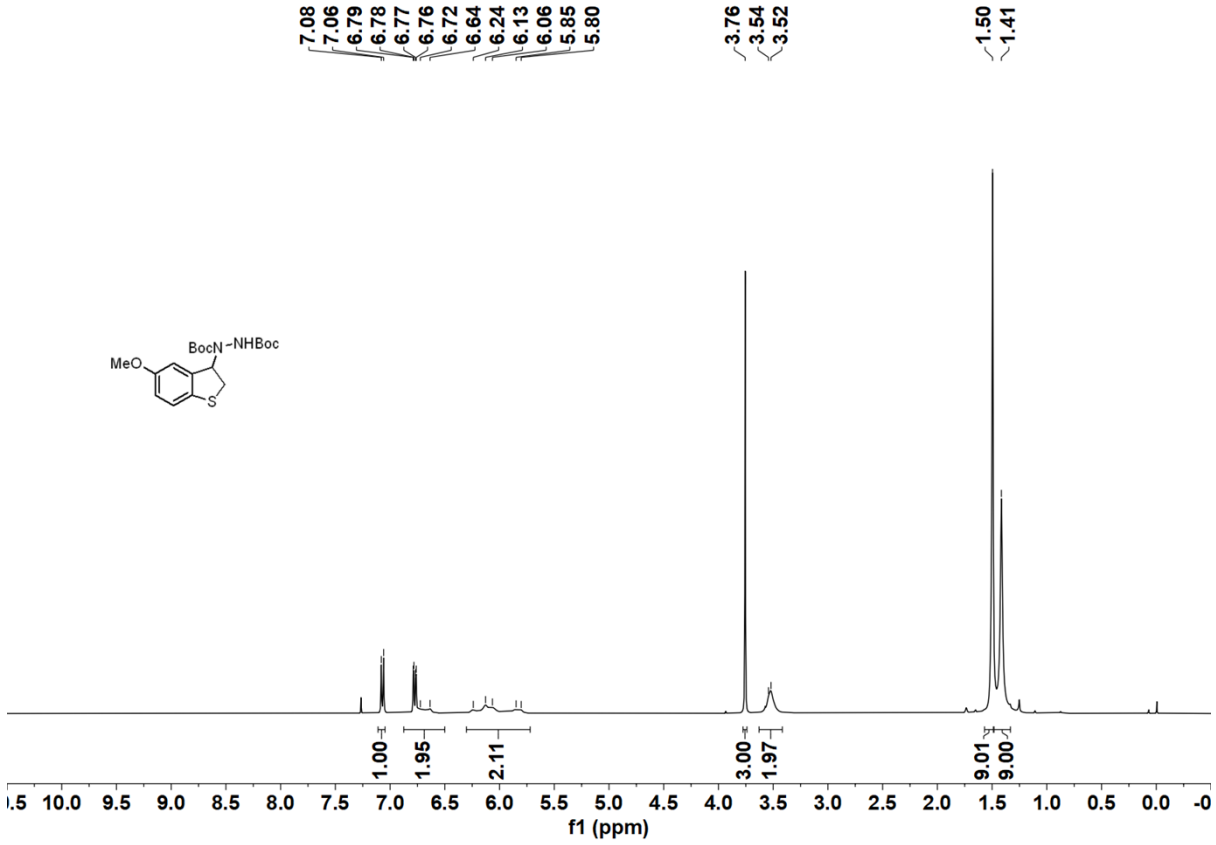


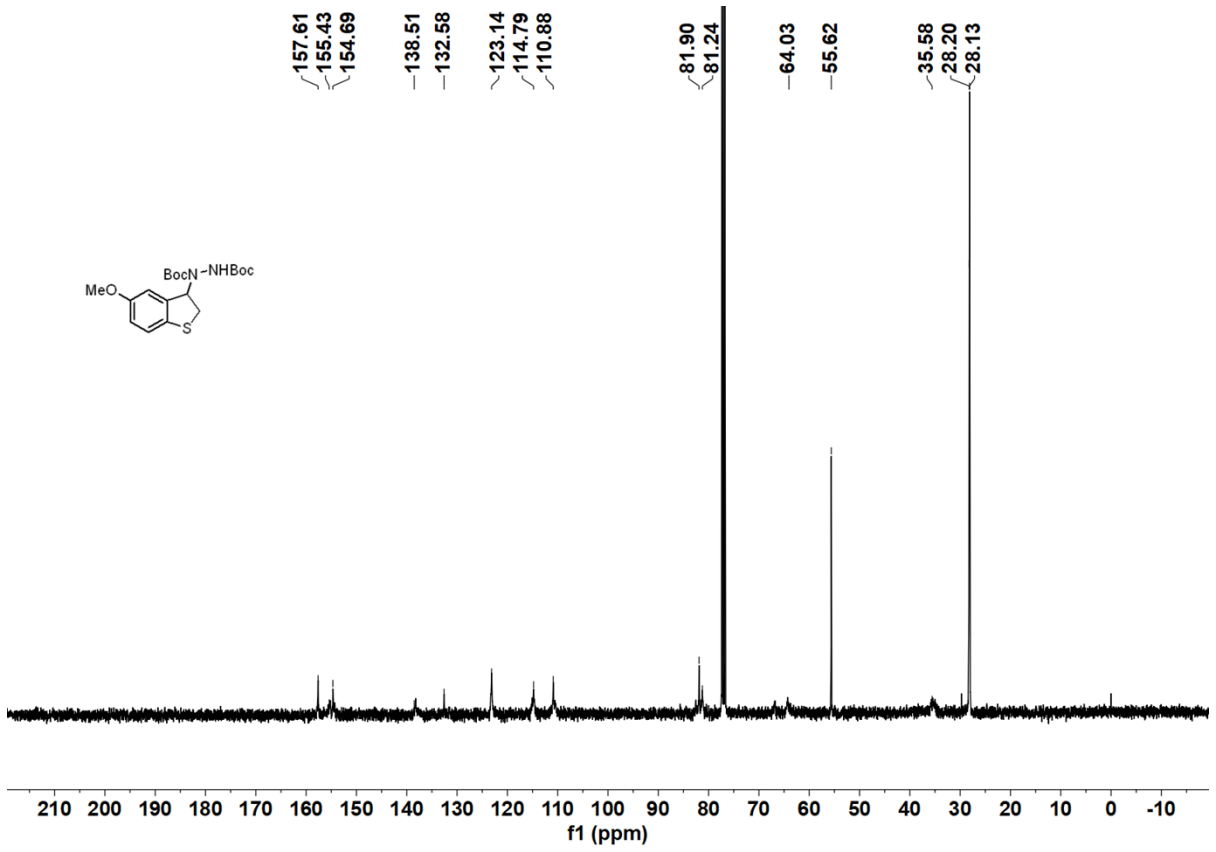
Di-*tert*-butyl 1-(5-(tert-butyl)-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3la**)



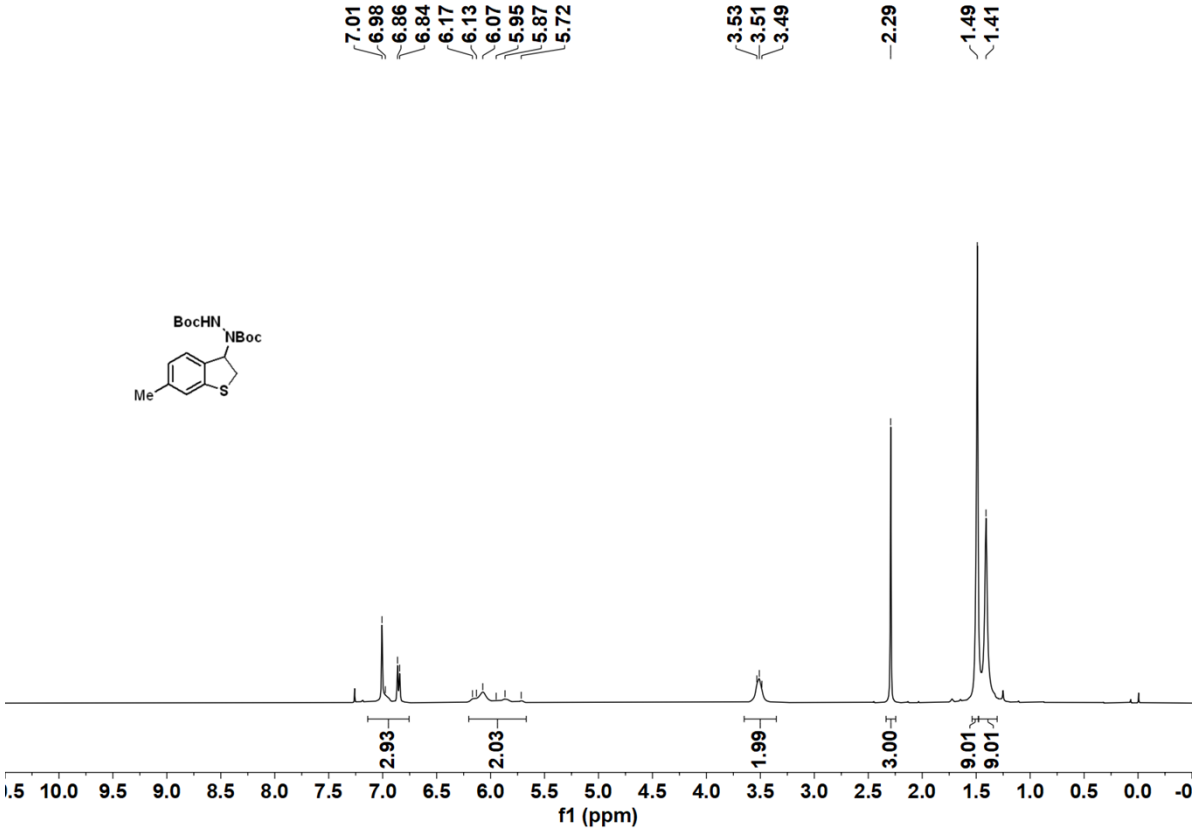


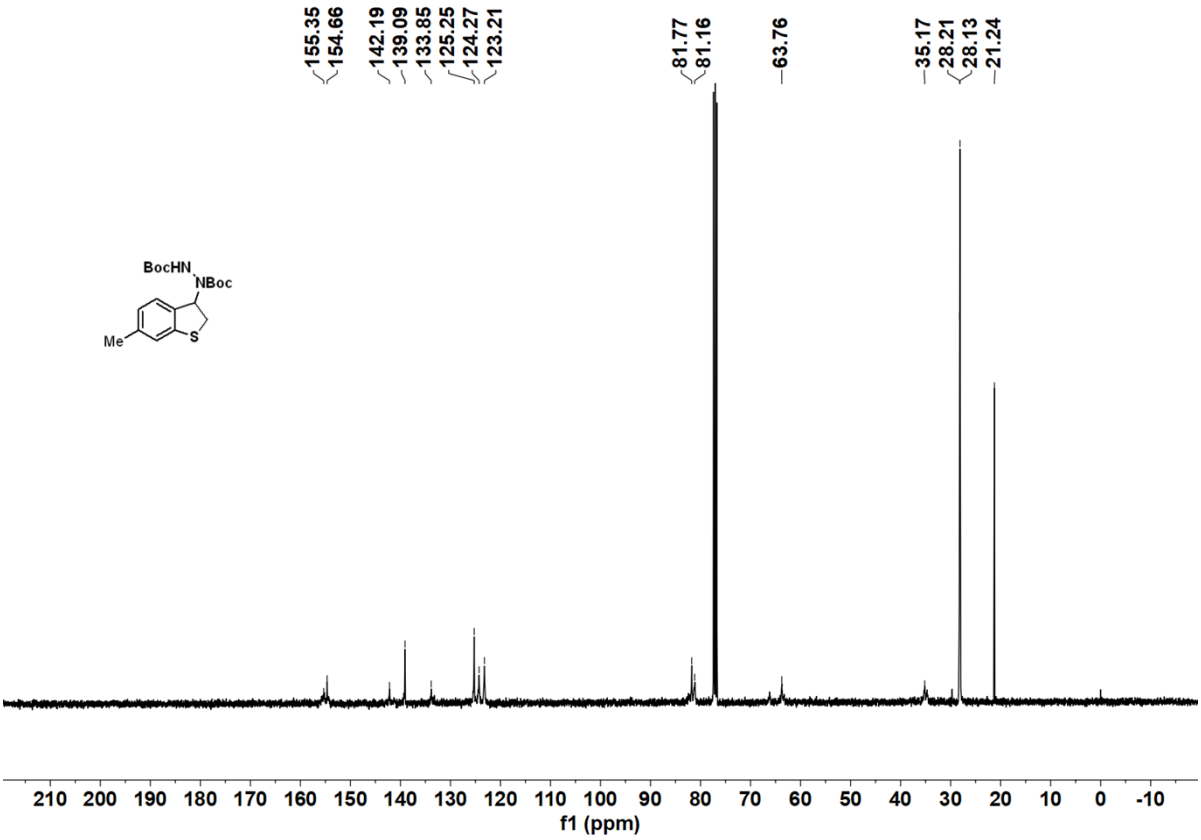
Di-*tert*-butyl 1-(5-methoxy-2,3-dihydrobenzofuran-3-yl)hydrazine-1,2-dicarboxylate (**3ma**)



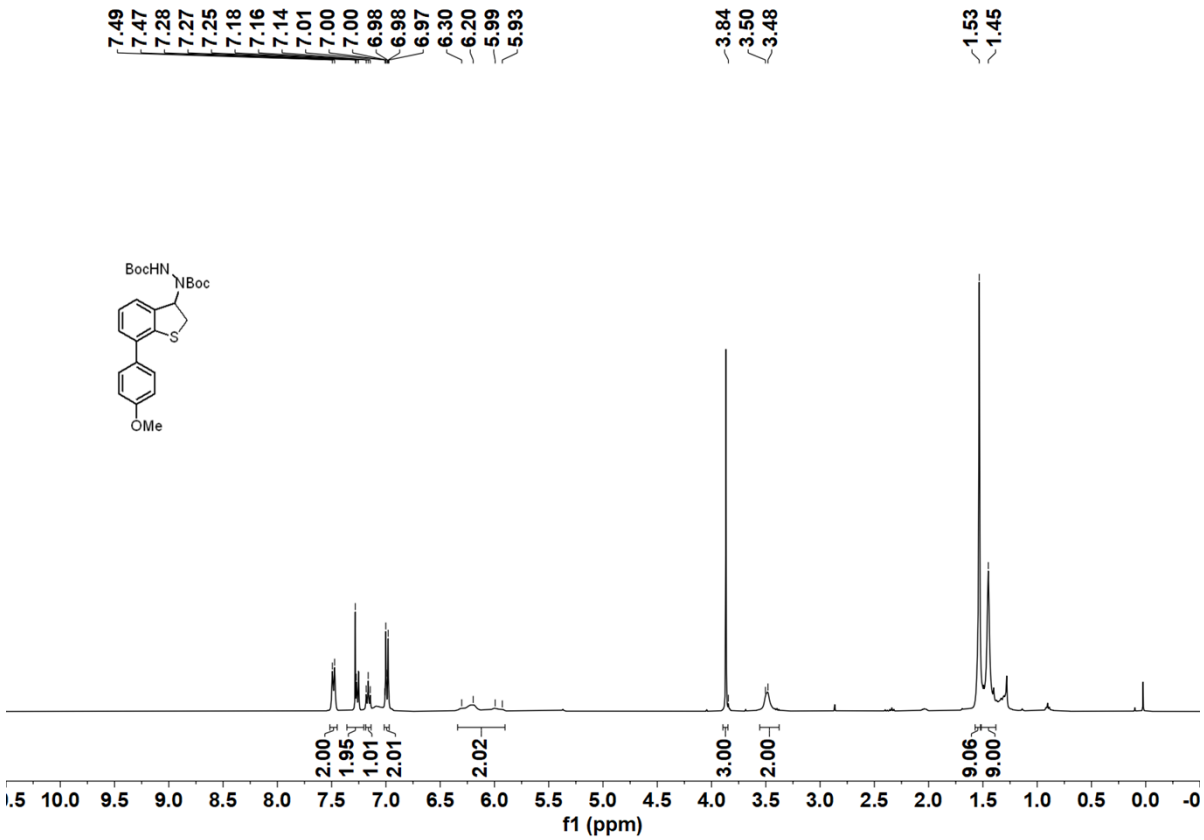


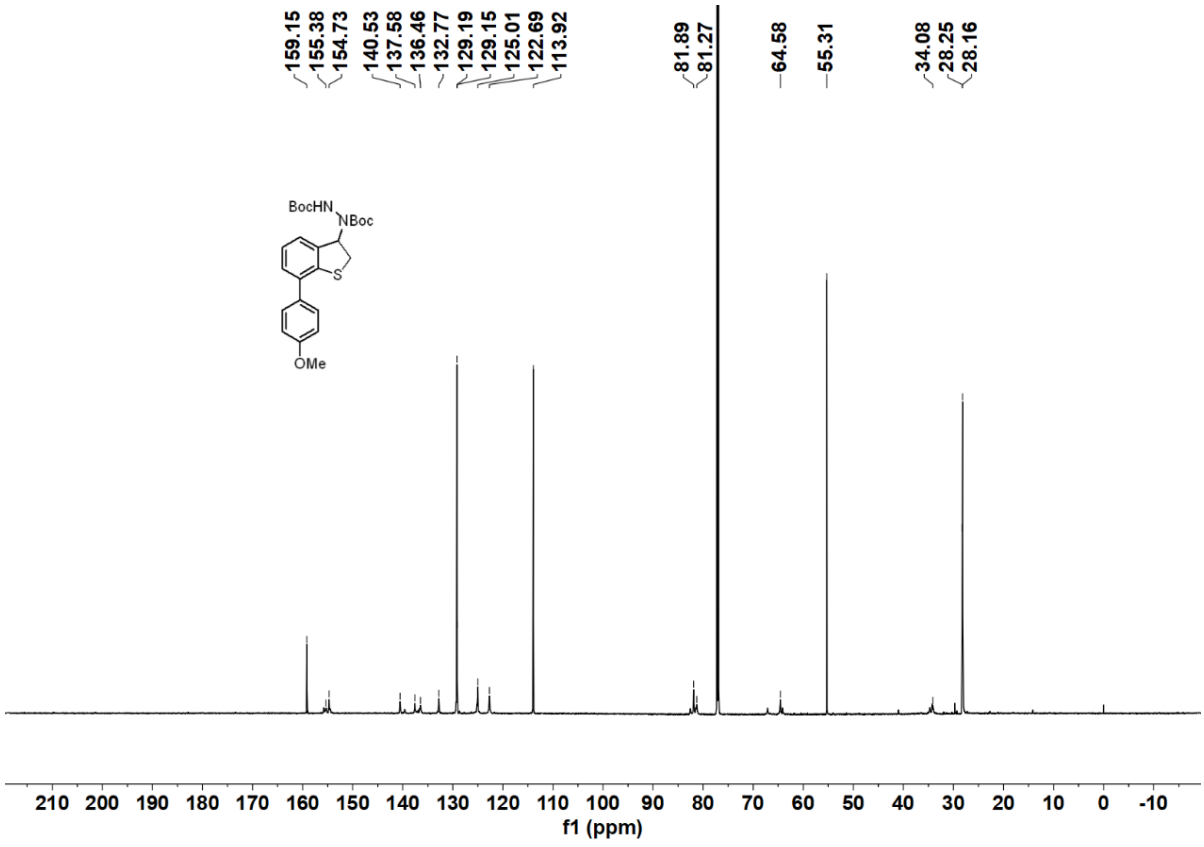
Di-*tert*-butyl 1-(6-methyl-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3na**)



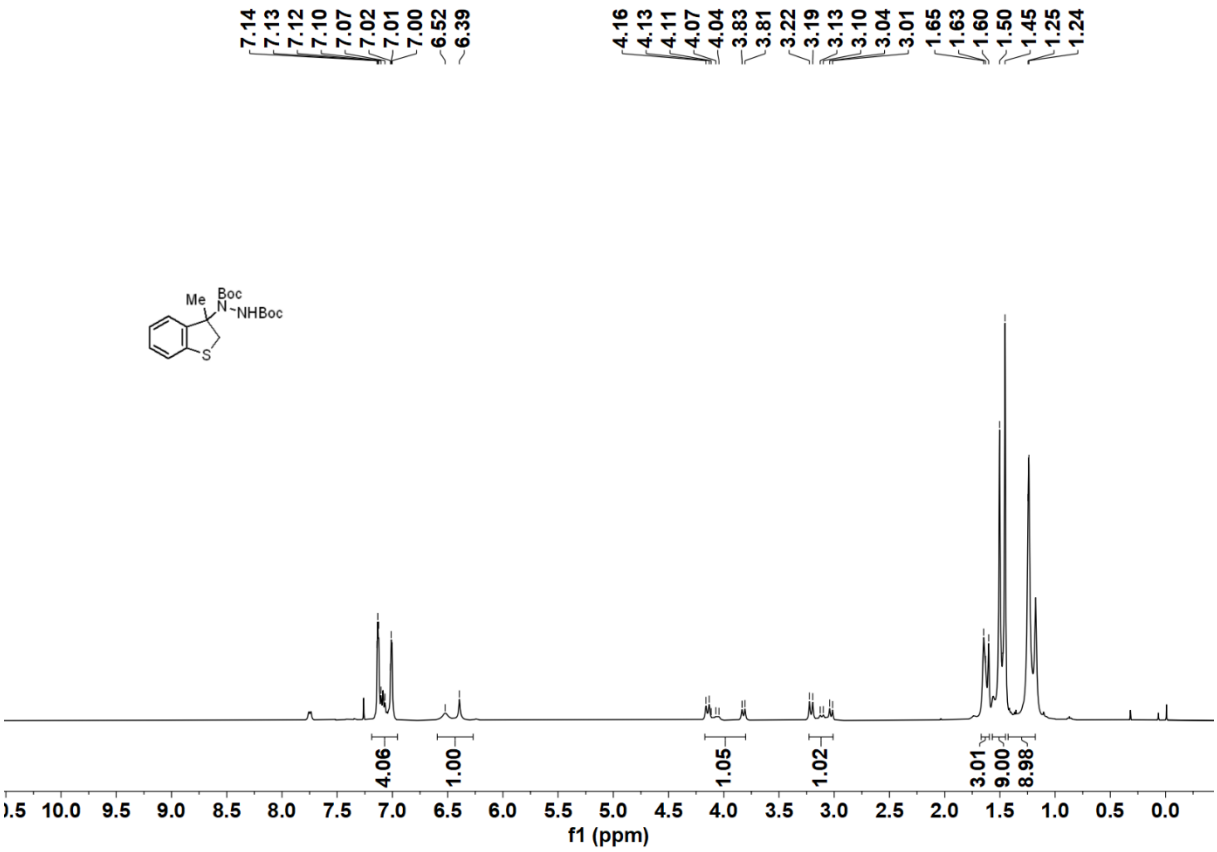


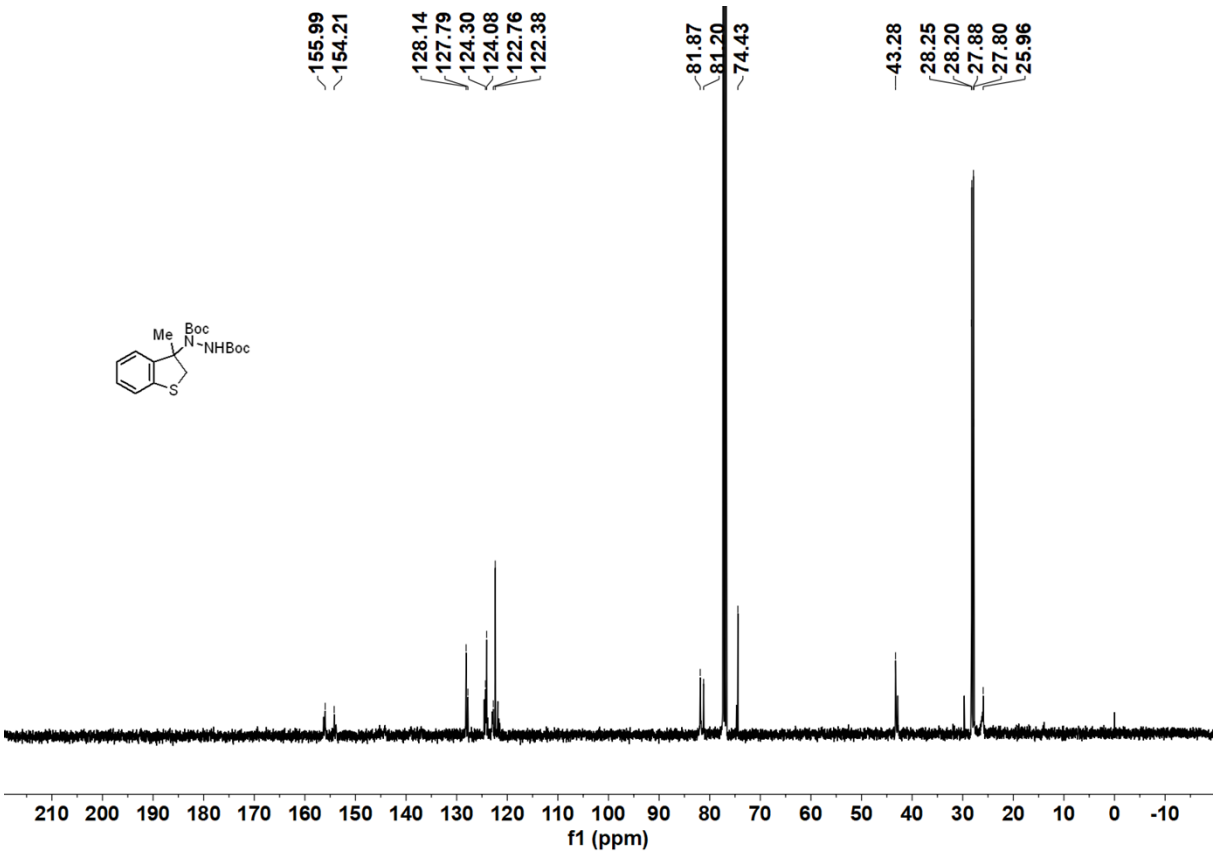
Di-*tert*-butyl 1-(7-(4-methoxyphenyl)-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2-dicarboxylate (**3oa**)



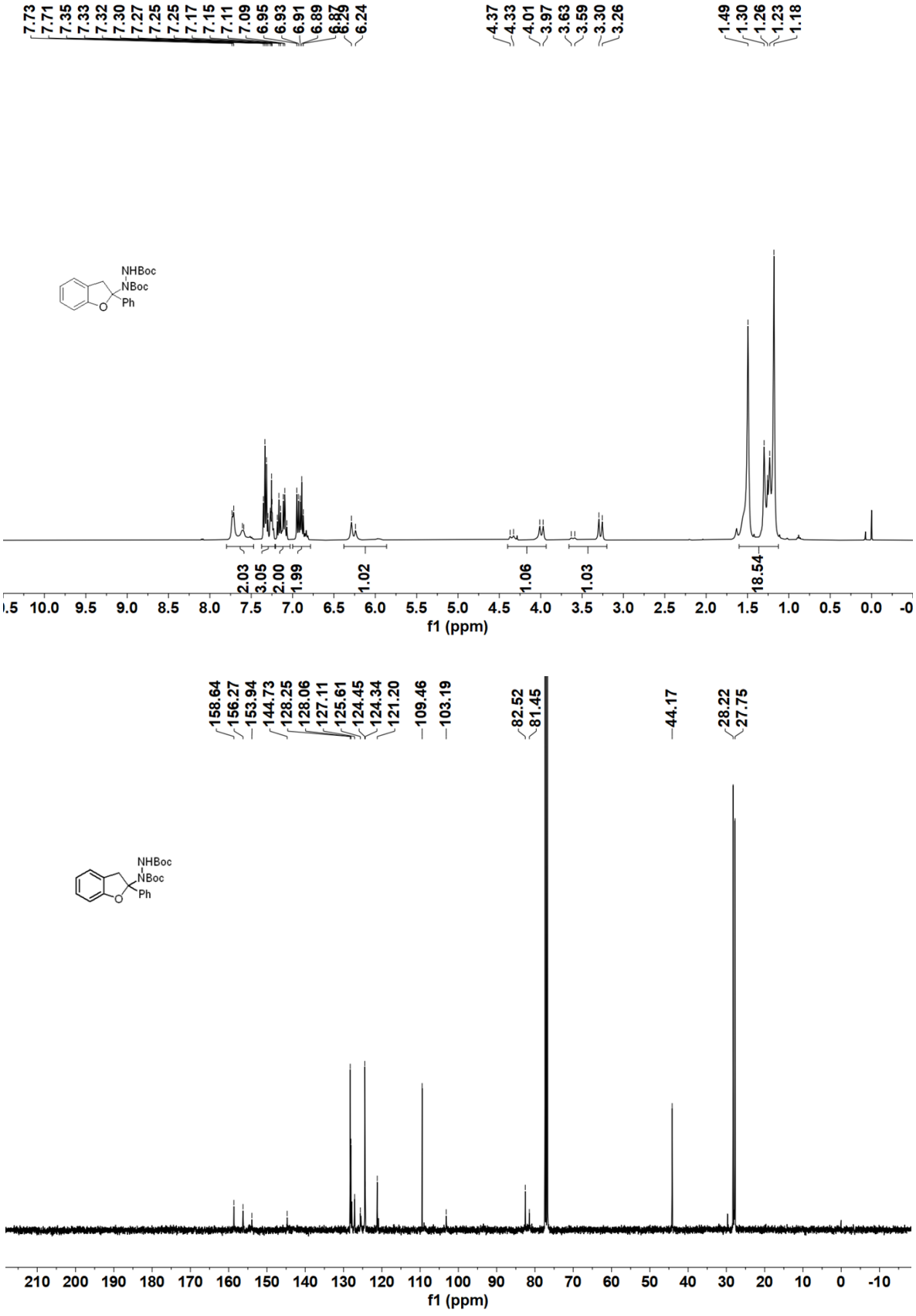


Di-*tert*-butyl 1-(3-methyl-2,3-dihydrobenzo[b]thiophen-3-yl)hydrazine-1,2dicarboxylate (**3pa**)

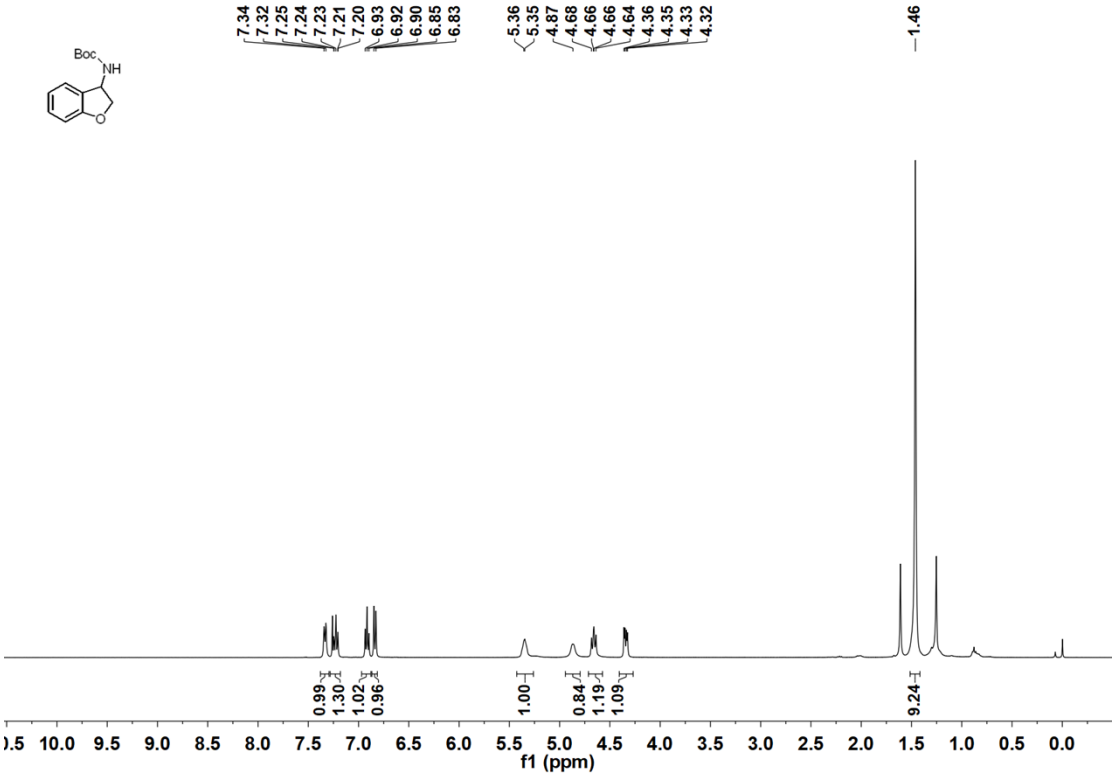




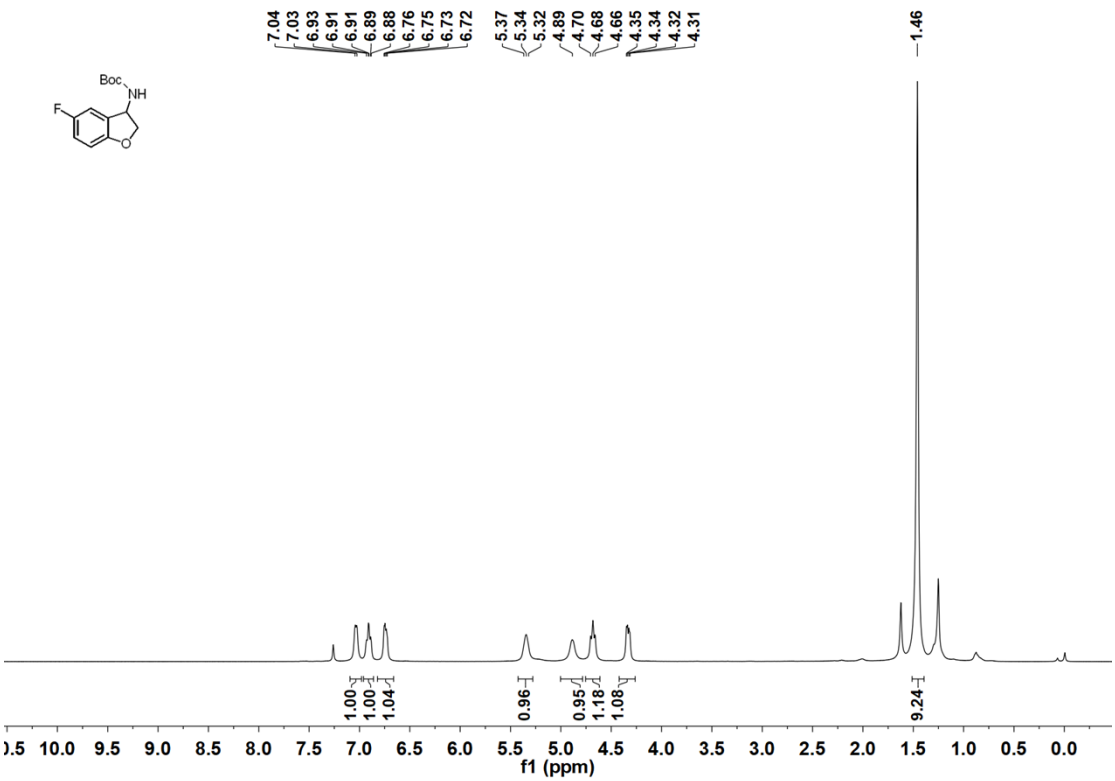
Di-*tert*-butyl 1-(2-phenyl-2,3-dihydrobenzofuran-2-yl)hydrazine-1,2-dicarboxylate (**3qa**)

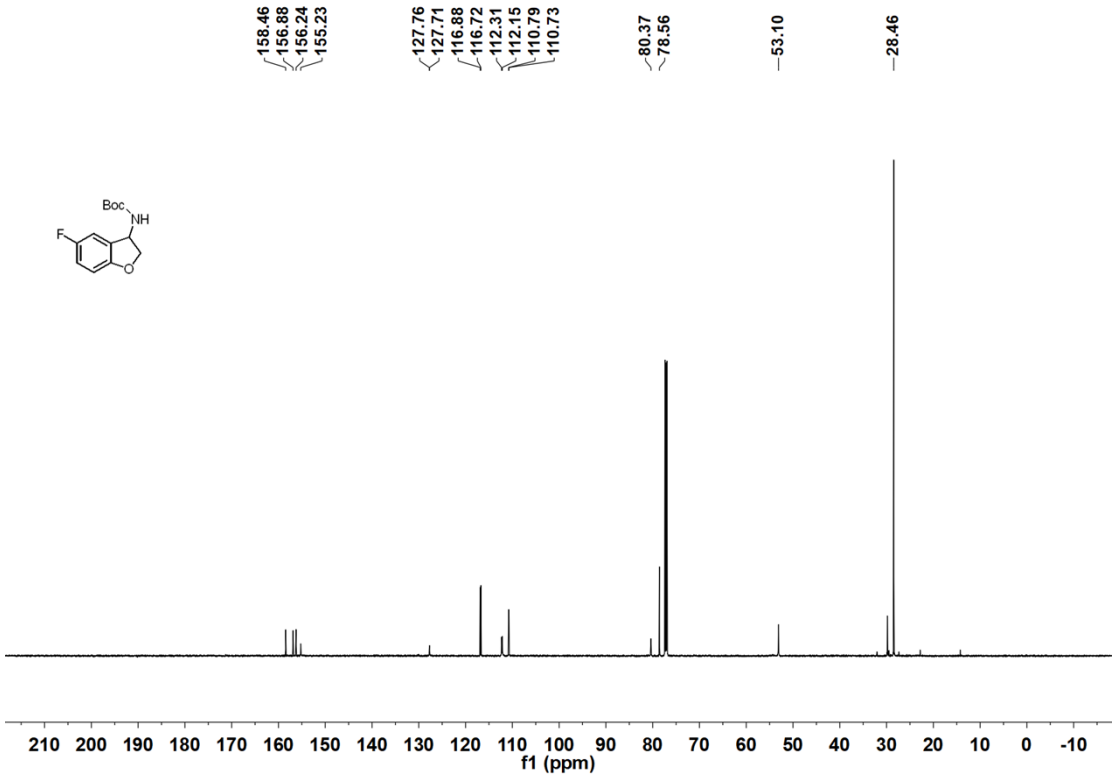


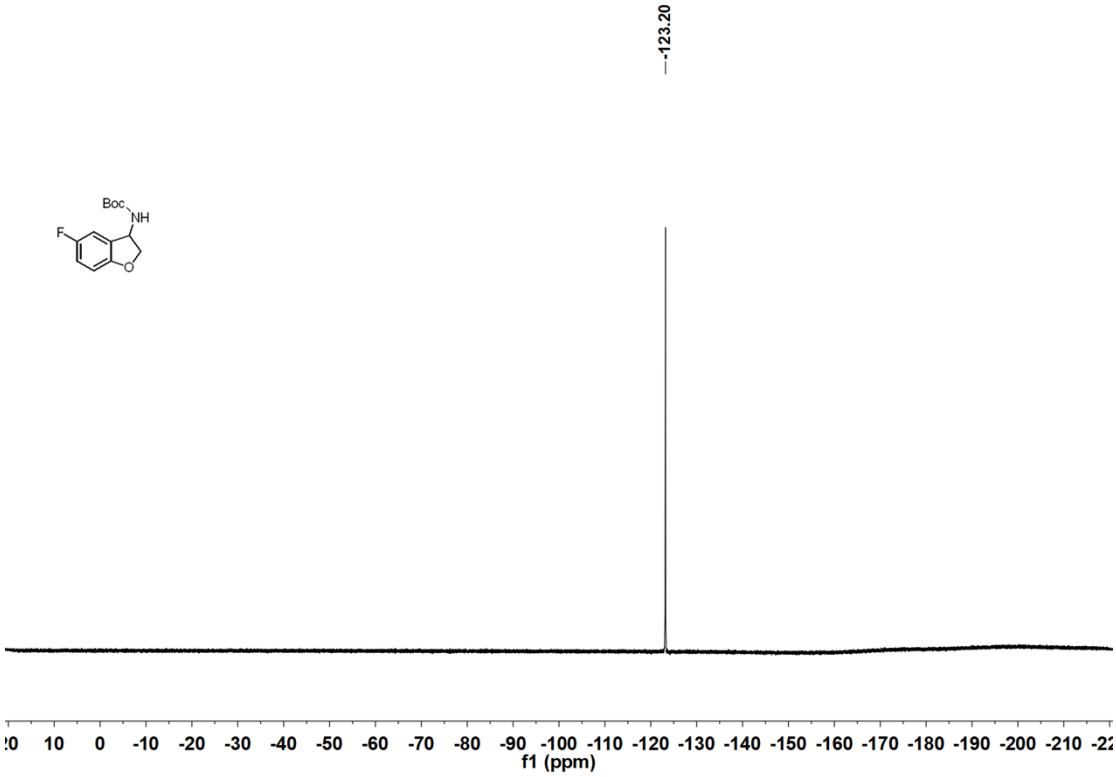
tert-Butyl (2,3-dihydrobenzofuran-3-yl)carbamate (**4**)



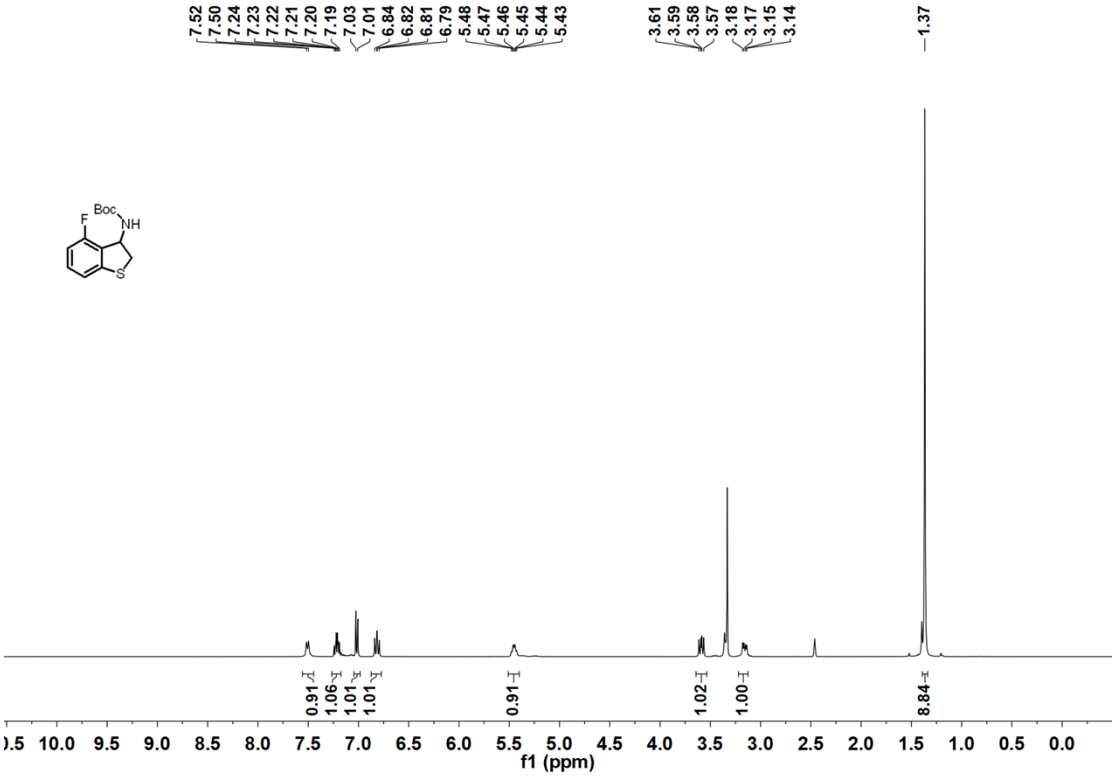
tert-Butyl (5-fluoro-2,3-dihydrobenzofuran-3-yl)carbamate (**5**)

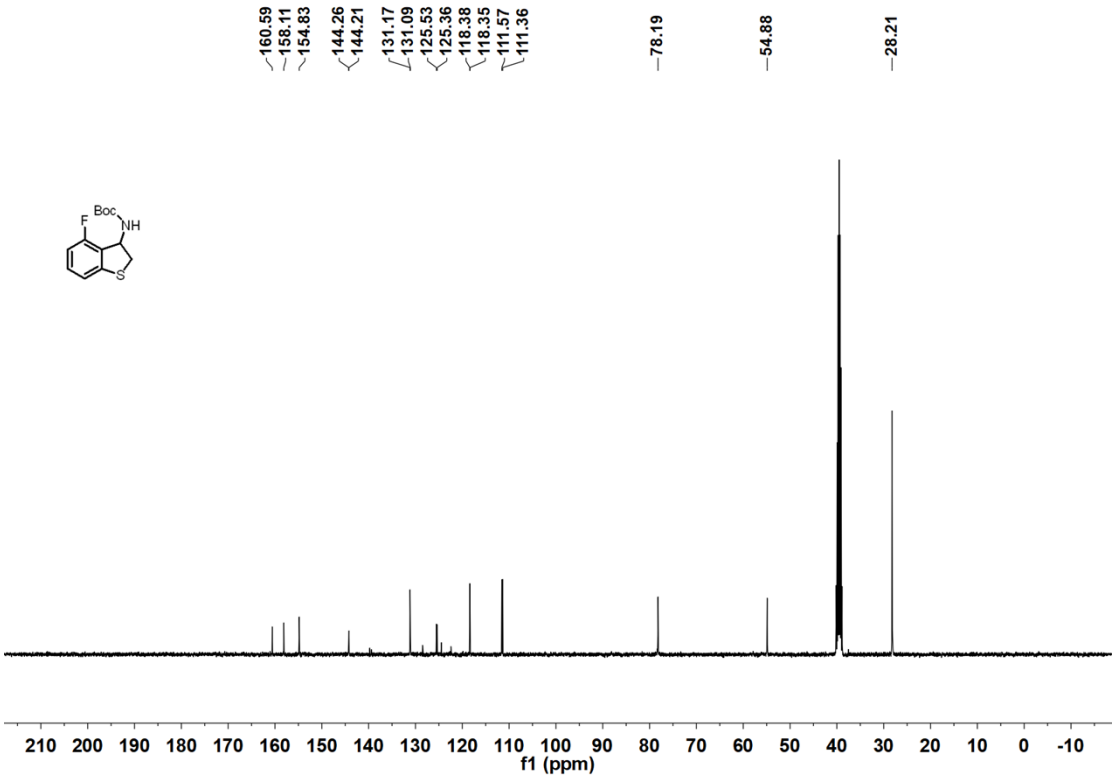


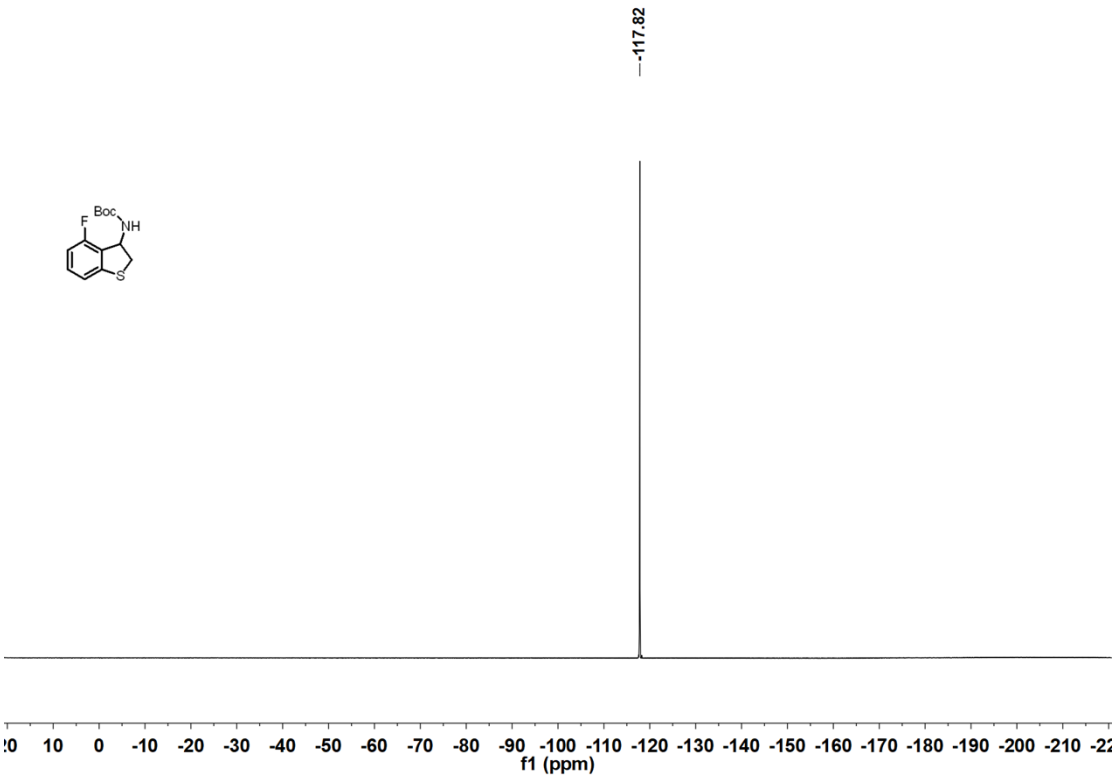

158.46
156.88
156.24
155.23
127.76
127.71
116.88
116.72
112.31
112.15
110.79
110.73
80.37
78.56
53.10
28.46
Boc
NH
F
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-123.20
Boc
NH
F
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

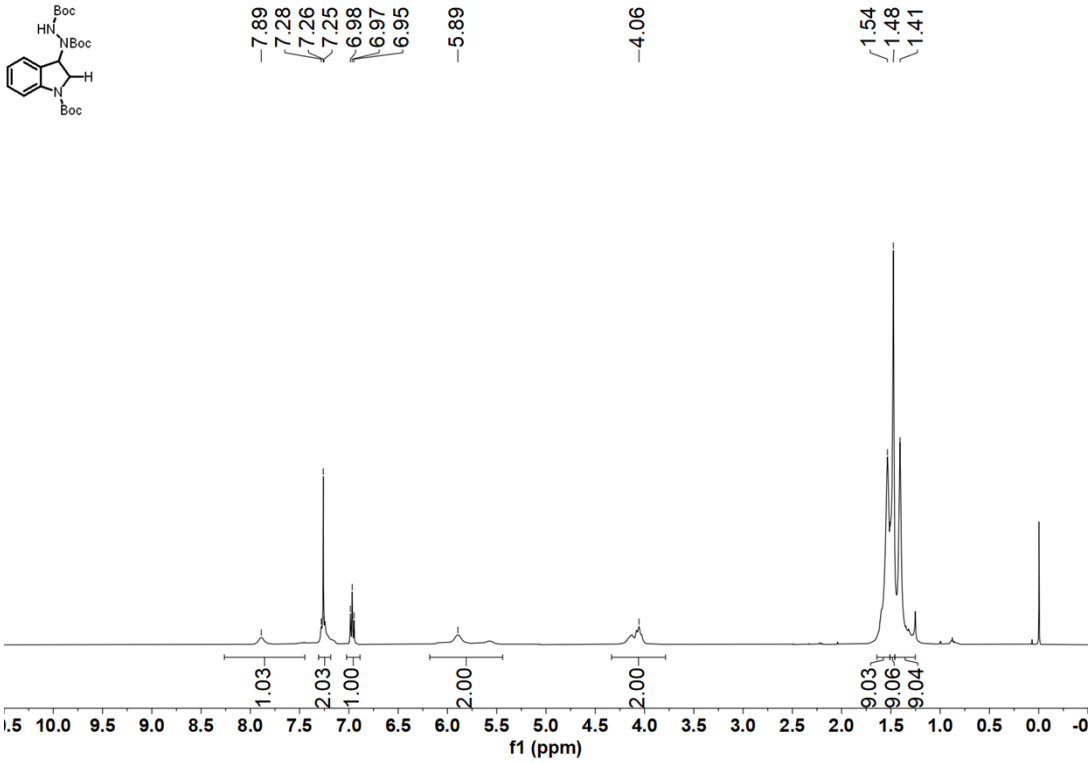
tert-Butyl (4-fluoro-2,3-dihydrobenzo[*b*]thiophen-3-yl)carbamate (**6**)

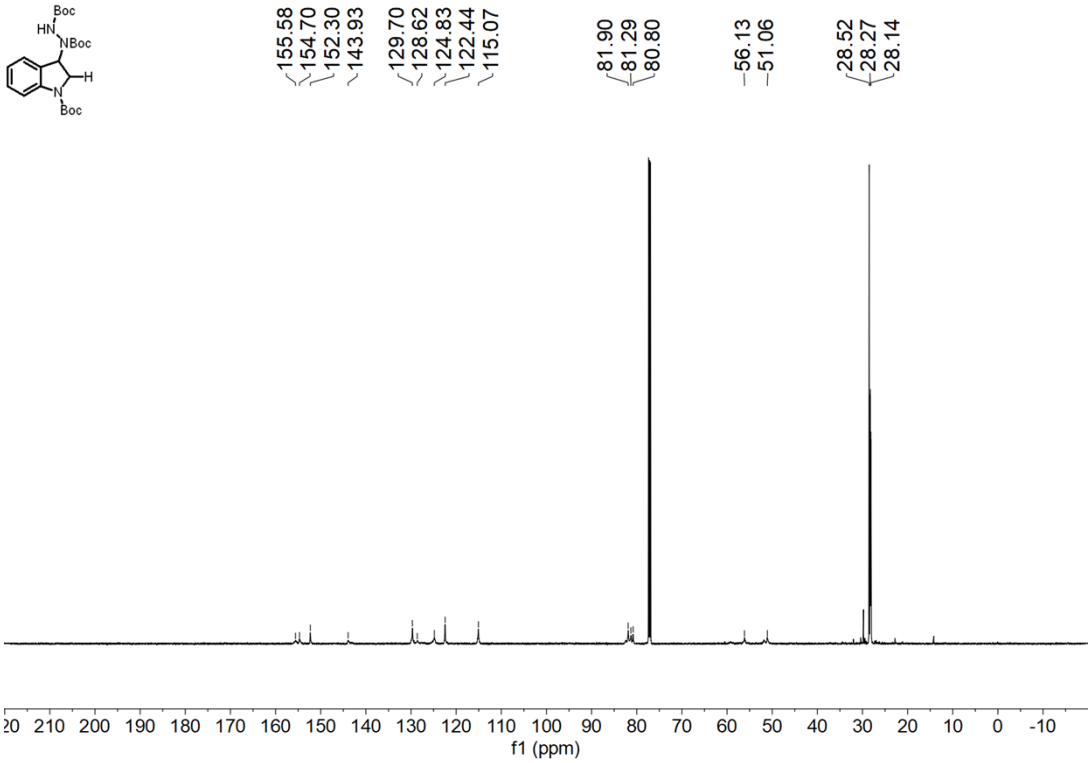




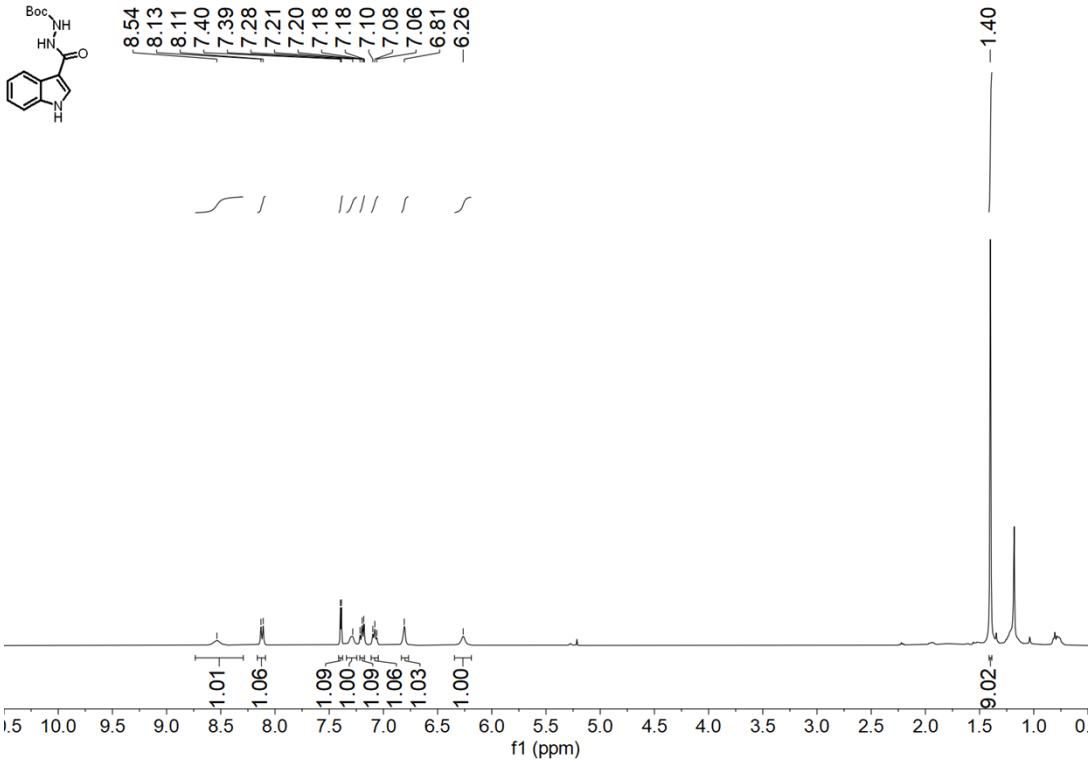


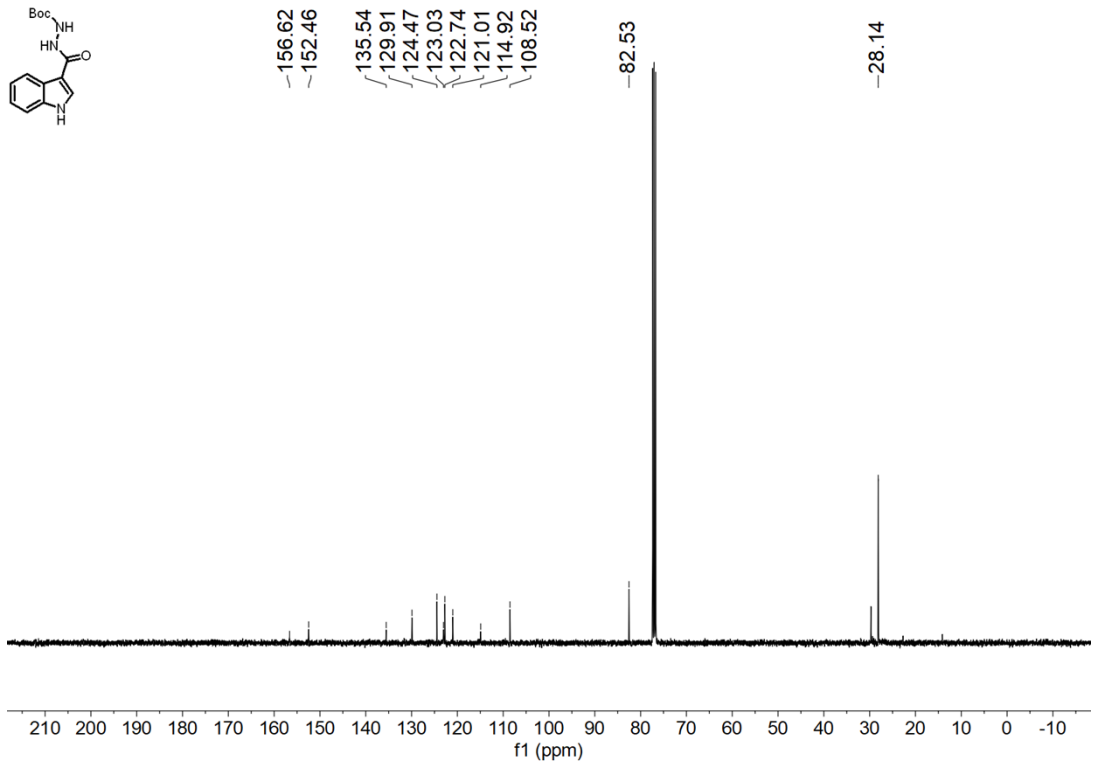
Di-*tert*-butyl-1-(1-(*tert*-butoxycarbonyl)indolin-3-yl)hydrazine-1,2-dicarboxylate (**3ra**)





tert-Butyl 2-(1*H*-indole-3-carbonyl)hydrazine-1-carboxylate (**1t'**)




Boc
NH
HN
O
N
H
156.62
152.46
135.54
129.91
124.47
123.03
122.74
121.01
114.92
108.52
82.53
28.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)