Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Entries to 3,3′-Disubstituted Peroxyoxindole Derivatives and α-Peroxyamides via Azaoxyallyl Cation-Guided Addition of Hydroperoxides

Tishyasoumya Bera,[a,b] Bandana Singh,[a] Manoranjan Jana,[b] and Jaideep Saha *[a]

[a]*Department of Biological and Synthetic Chemistry, Centre of Biomedical Research (CBMR), SGPGIMS Campus. Raebareli Road, Lucknow 226014, Uttar Pradesh. India.*

E-mail: jaideep.saha@cbmr.res.in, jdsaha2000@gmail.com.

[b]*Department of Chemistry, University of Kalyani, Kalyani-741235, West Bengal, India*

Table of Contents

1. General Experimental

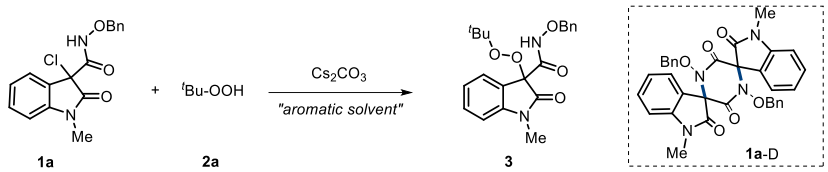
Unless otherwise noted, all reactions were conducted with oven or flame-dried glassware and maintaining an inert (under nitrogen or argon) atmosphere. Solvents were dried according to standard procedures and all reagents/catalysts were purchased commercially and used without any further purification. Reactions were monitored by TLC, using Merck silica gel 60 F 254 plates. The plates were visualized under UV light (254 nm) or by using 10% ethanolic phosphomolybdic acid (PMA) or 1% aqueous $KMnO_4$ or iodine. Flash column chromatography was performed using silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Avance III, Bruker 400 MHz and 100 MHz spectrometers respectively using $CDCl_3$ or CD_2Cl_2. ^{1}H NMR chemicals shift are expressed in ppm (δ) relative to δ = 7.26 for $CDCl_3$ and δ = 5.32 for CD_2Cl_2. ^{13}C NMR chemical shift are expressed in ppm (δ) relative to δ = 77.16 for $CDCl_3$ and δ = 54.00 for CD_2Cl_2 resonance. FT-IR experiments were performed on PerkinElmer Spectrum Version 10.03.08. HRMS and Electron Spray Ionization (ESI) (m/z) spectra were recorded on Agilent Technologies 6530 Accurate- Mass Q-TOF LC/MS.

Caution: Although we have not experienced any hazards in our study with this class of peroxides, but due to explosive nature of the peroxides in general, any preparative work should be carried out in the fume hood and a blast shield should be used.

Note: We used some commercially available hydroperoxides such as TBHP solution (5-6 M in decane) and Cumene hydroperoxide, which were obtained from Sigma-Aldrich. Other hydroperoxides were prepared following the literature method and discussed in the appropriate section of the Supporting Information.

2. Optimization Studies.

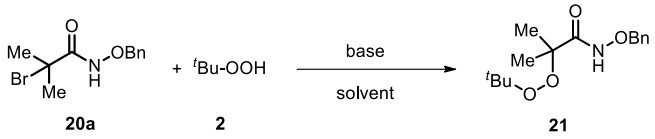
2.1. *Screening of aromatic solvents*



entry	*aromatic solvent*	*Conc.[M]*	*yield[b]*
1	$PhCF_3$	0.2	62
2	chlorobenzene	0.2	12
3	toluene	0.2	trace
4	benzene	0.2	0[c]
5	*O*-xylene	0.2	0[c]

Table S1. [a]Reaction conditions: **1a** (2.0 equiv) TBHP (10 equiv. 5-6 M TBHP in decane), [2.0 M]. [b]Yields of Isolated Products; [c]No product was detected by LC-MS analysis. For entries 2-5, dimer of **1a** (i.e., **1a**-D) was formed in significant amout .

2.2. *Optimization of reaction conditions with simple α-halohydroxamate [a]*



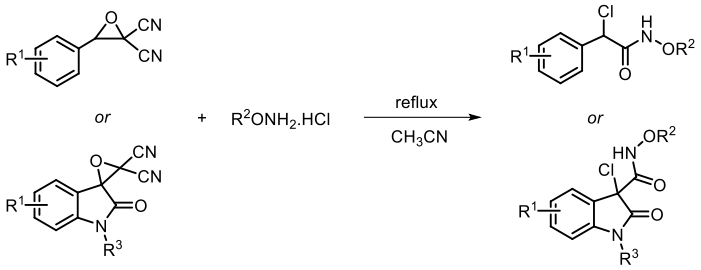
entry	*base*	*equiv*	*solvent [b]*	*yield (%)[c]*
1	Et_3N	2.0	HFIP	57
2	DBU	2.0	HFIP	c.m[d]
3	Na_2CO_3	2.0	HFIP	96
4	Na_2CO_3	4.0	HFIP	86
5	K_2CO_3	2.0	HFIP	70
6	Cs_2CO_3	2.0	HFIP	trace
7	Na_2CO_3	2.0	CH_3CN	41
8	Na_2CO_3	2.0	CH_2Cl_2	25
9[e]	Na_2CO_3	2.0	HFIP	74
10	Cs_2CO_3	2.0	$PhCF_3$	60

Table S2. Reaction conditions: [a] Reaction conditions: **20a** (2.0 equiv), **2** (1.0 equiv), base (2-4 equiv), TBHP (5.0 equiv; 5-6 M in decane), 1 h at room temperature. [b]Reaction concentration was 0.2 M. [c]Yields of the isolated products. [d]c.m= complex mixture. [e]10.0 equiv. of TBHP was used.

3. Preparation of Starting Materials.

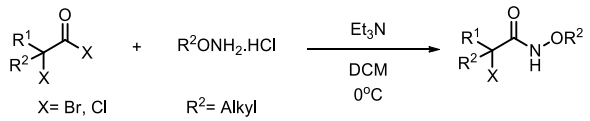
3.1 *General methods for the synthesis of α-halohydroxamates.*

Procedure I: [From epoxynitriles[1-2]]



A suspension of epoxynitrile or spiro-epoxynitrile (1.0 equiv) and corresponding hydroxylamine hydrochloride salt (1.2 equiv) in acetonitrile (0.1 M) was heated to reflux overnight. The suspension was cooled and the mixture was concentrated. The crude residue was purified by silica-gel column chromatography (using EtOAc-Hexane mixture as eluent) to afford the corresponding α-halohydroxamate products.

Procedure II: [From the α-haloacid halide[1]]



Triethyl amine (1.2 equiv) was added dropwise to a suspension of the *O*-benzyloxyamine hydrochloride (1.2 equiv) in DCM (0.25 M) at 0 °C. After 10 minutes, α-haloacid halide (1.0 equiv) was added dropwise at same temperature and stirred at this temperature until the starting material was consumed (TLC monitored). Reaction mixture was quenched with water (*ca*. 5.0 mL) and extracted with ethylacetate (10 mL x 2). Collected organic layer was dried over anhydrous Na_2SO_4 was concentrated in *vacuo*. Crude residue was purified by silica gel column chromatography (EtOAc:hexane) to afford the corresponding α-halohydroxamate products.

3.2 *List of α-halohydroxamate prepared in the study.*

A.

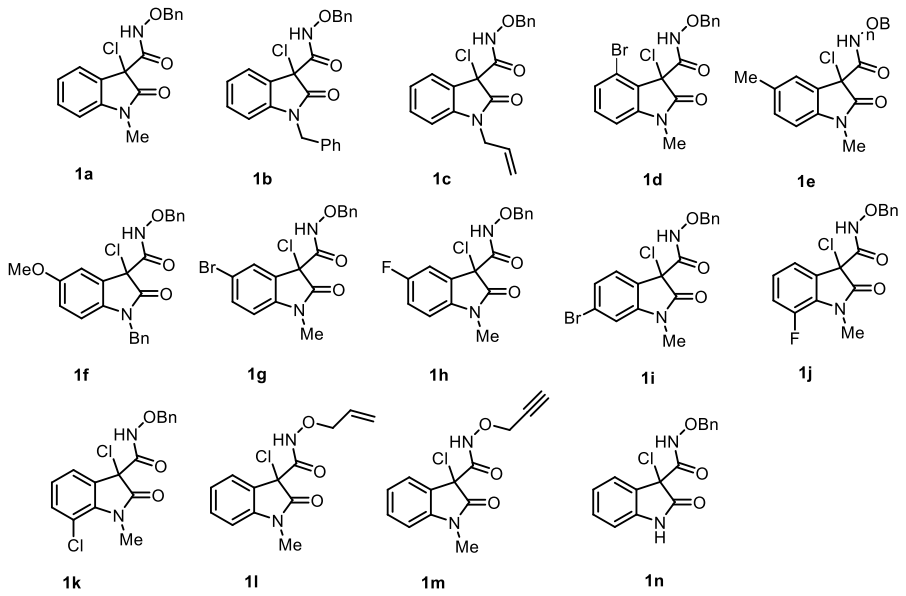


Figure S1: List of oxindole-based α-halohydroxamates.

B.

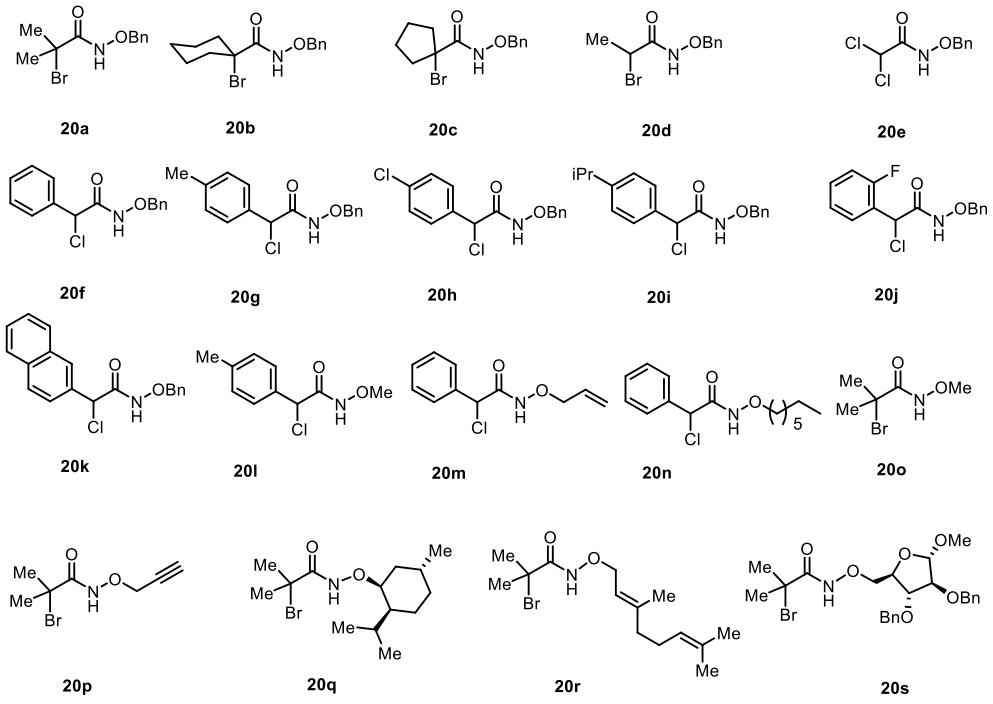
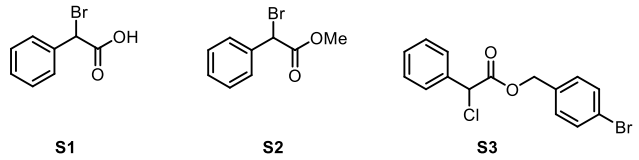


Figure S2: List of non-oxindole α-halohydroxamates used in the study.

***3.3** Preparation of Carboxylic acid derivatives (**S1-S3**)*

Carboxylic acid derivatives (**S1-S3**) were prepared according to the literature procedure.[3-4]

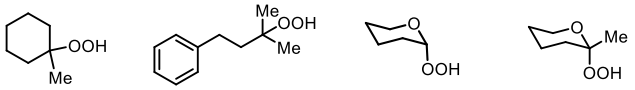


S1 **S2** **S3**

Figure S3: Structure of carboxylic acid derivatives prepared in the study

***3.4** Preparation of various alkyl hydroperoxides (HP **1**-**4**)*

Hydroperoxides **HP1-HP4** were prepared according to the literature procedure.[5-8]

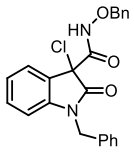


HP1 **HP2** **HP3** **HP4**

Figure S4: Structure of alkyl hydroperoxides prepared in the study

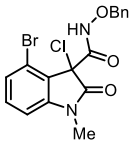
3.4 *Characterization of compounds (starting materials)*

1-Benzyl-N-(benzyloxy)-3-chloro-2-oxoindoline-3-carboxamide ***(1b)***



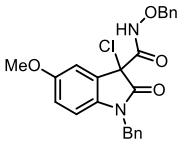
Compound **1b** was prepared using general procedure-I and isolated as reddish oil in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.47 - 7.45 (m , 2H), 7.40 - 7.39 (m, 3H), 7.35 - 7.33 (m, 2H), 7.31 - 7.26 (m, 4H), 7.14 (app t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.03 - 4.96 (m, 2H), 4.92 (s, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.3, 161.2, 142.2, 134.5, 134.4, 131.2, 129.6, 129.1, 128.7(2), 128.1, 127.1, 127.0, 125.8, 124.2, 110.2, 78.5, 60.5, 44.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{23}H_{19}ClN_2NaO_3$ calcd. 429.0982, found 429.1010.

N-(benzyloxy)-4-bromo-3-chloro-1-methyl-2-oxoindoline-3-carboxamide ***(1d)***



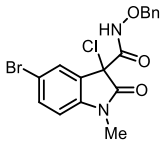
Compound **1d** was prepared using general procedure-I and isolated as reddish oil in 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.40 - 7.35 (m, 2H), 7.30 - 7.26 (m, 3H), 7.15 - 7.12 (m, 2H), 6.70 (d, *J* = 4.1 Hz, 1H), 4.87 (s, 2H), 3.08 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.3, 160.2, 145.8, 134.5, 132.5, 129.6, 129.0, 128.6, 127.5, 125.9, 120.5, 108.3, 78.7, 64.3, 27.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{14}BrClN_2NaO_3$ calcd. 432.9754, found, 432.9774.

1-Benzyl-N-(benzyloxy)-3-chloro-5-methoxy-2-oxoindoline-3-carboxamide ***(1f)***



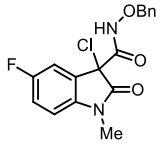
Compound **1f** was prepared using general procedure-I and isolated as yellow solid in 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.36 - 7.34 (m, 2H), 7.32 - 7.29 (m, 3H), 7.22 (dd, *J* = 12.5, 7.1 Hz, 4H), 7.17 - 7.15 (m, 2H), 6.71 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 1H), 4.91 (d, *J* = 11.1 Hz, 1H), 4.87 (d, *J* = 11.1 Hz, 1H),4.80 (s, 2H), 3.70 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.3, 161.2, 157.0, 135.3, 134.5, 129.6, 129.2, 129.1, 128.8, 128.2, 127.2, 126.7, 116.9, 113.4, 110.9, 78.6, 60.4, 56.0, 44.6; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{24}H_{21}ClN_2NaO_4$ calcd. 459.1082, found, 459.1088.

N-(benzyloxy)-5-bromo-3-chloro-1-methyl-2-oxoindoline-3-carboxamide ***(1g)***



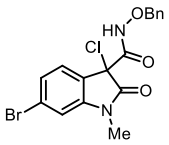
Compound **1g** was prepared using general procedure-I and isolated as red foam in 59% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.64 (s, 1H), 7.38 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.29 - 7.25 (m, 5H), 6.62 (d, *J* = 8.3 Hz, 1H), 4.85 - 4.79 (m, 2H), 3.06 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.3, 160.6, 142.0, 134.2, 134.1, 129.8, 129.5, 129.0, 128.6, 127.4, 116.6, 110.7, 78.4, 59.8, 27.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{14}BrClN_2NaO_3$ calcd. 432.9754, found, 432.9778.

N-(benzyloxy)-3-chloro-5-fluoro-1-methyl-2-oxoindoline-3-carboxamide ***(1h)***



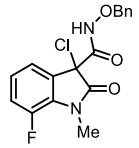
Compound **1h** was prepared using general procedure-I and isolated as reddish oil in 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.40 - 7.37 (m, 6H), 7.10 (s, 1H), 6.80 (s, 1H), 4.94 (s, 2H), 3.21 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.9, 160.6, 159.7 (d, *J* = 241.0 Hz), 138.9 (d, *J* = 1.0 Hz), 134.4, 129.6, 129.2, 128.7, 127.0 (d, *J* = 10.0 Hz), 117.9 (d, *J* = 23.0 Hz), 115.5 (d, *J* = 26.0 Hz), 109.9 (d, *J* = 7.0 Hz), 78.6, 59.6 (d, *J* = 3.0 Hz), 27.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{14}ClFN_2NaO_3$ calcd. 371.0569, found, 371.0546.

N-(benzyloxy)-6-bromo-3-chloro-1-methyl-2-oxoindoline-3-carboxamide ***(1i)***



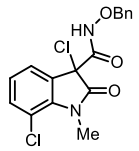
Compound **1i** was prepared using general procedure-I and isolated as reddish oil in 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.46 (d, *J* = 4.0 Hz, 1H), 7.39 - 7.35 (m, 5H), 7.27 - 7.26 (m, 1H), 7.00 (s, 1H), 4.92 (s, 2H), 3.15 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.7, 160.6, 144.1, 134.2, 129.4, 129.0, 128.6, 128.1, 127.0, 125.2, 112.7, 78.4, 59.8, 27.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{14}BrClN_2NaO_3$ calcd. 432.9754, found, 432.9759.

N-(benzyloxy)-3-chloro-7-fluoro-1-methyl-2-oxoindoline-3-carboxamide ***(1j)***



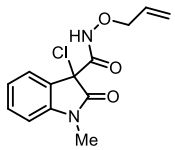
Compound **1j** was prepared using general procedure-I and isolated as reddish oil in 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.40 - 7.35 (m, 6H), 7.11 - 7.06 (m, 2H), 4.96 - 4.88 (m, 2H), 3.40 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.5, 160.8, 147.5 (d, *J* = 244.0 Hz), 134.3, 129.8 (d, *J* = 8.0 Hz), 129.5, 129.0, 128.6, 128.1 (d, *J* = 3.0 Hz), 124.7 (d, *J* = 6.0 Hz), 122.8 (d, *J* = 6.0 Hz), 119.1 (d, *J* = 19.0 Hz), 78.5, 60.2 (d, *J* = 5.0 Hz), 29.6 (d, *J* = 6.0 Hz); **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{14}ClFN_2NaO_3$ calcd. 371.0569, found, 371.0550.

N-(benzyloxy)-3,7-dichloro-1-methyl-2-oxoindoline-3-carboxamide ***(1k)***



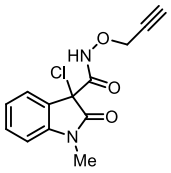
Compound **1k** was prepared using general procedure-I and isolated as red foam in 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.37 - 7.35 (m, 2H), 7.32 - 7.31 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.00 (app t, *J* = 7.9 Hz, 1H), 4.91 - 4.84 (m, 2H), 3.51 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.2, 160.7, 138.9, 134.3, 133.4, 129.5, 129.0, 128.6, 128.2, 125.7, 124.8, 116.2, 78.5, 59.7, 30.5; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{14}Cl_2N_2NaO_3$ calcd. 387.0279, found, 387.0280.

N-(allyloxy)-3-chloro-1-methyl-2-oxoindoline-3-carboxamide ***(1l)***



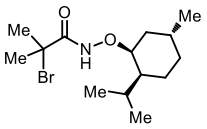
Compound **1l** was prepared using general procedure-I and isolated as white solid in 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.34 (app t, *J* = 7.8 Hz, 1H), 7.11 (app t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 5.96 - 5.88 (m, 1H), 5.35 - 5.24 (m, 2H), 4.42 - 4.34 (m, 2H), 3.18 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.8, 160.9, 142.8, 131.2(2), 126.7, 125.5, 123.9, 121.3, 109.0, 76.7, 60.1, 26.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{13}H_{13}ClN_2NaO_3$ calcd. 303.0507, found, 303.0504.

3-Chloro-1-methyl-2-oxo-N-(prop-2-yn-1-yloxy)indoline-3-carboxamide ***(1m)***



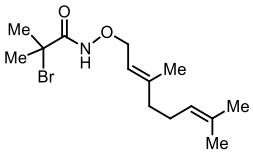
Compound **1m** was prepared using general procedure-I and isolated as white foam in 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.97(s, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.41 (app t, *J* = 7.8 Hz, 1H), 7.18 (app t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 4.60 (d, *J* = 15.5 Hz, 1H), 4.53 (d, *J* = 15.4 Hz, 1H), 3.26 (s, 3H), 2.60 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.1, 161.3, 143.0, 131.5, 127.4, 125.5, 124.4, 109.2, 76.8, 63.8, 59.9, 27.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{13}H_{11}ClN_2NaO_3$ calcd. 301.0350, found, 301.0339.

2-Bromo-N-(((1S,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-2-methylpropanamide ***(20q)***



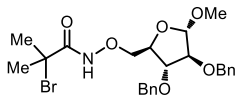
Compound **20q** was prepared using general procedure-II and isolated as white solid in 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 4.27 (s, 1H), 2.05 (d, *J* = 12.4 Hz, 1H), 1.92 - 1.86 (s, 5H), 1.76 - 1.72 (m, 4H), 1.67 - 1.63 (m, 1H), 1.39 - 1.29 (m, 1H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.89 - 0.85 (m, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.5, 81.5, 59.9, 47.7, 37.5, 35.1, 32.6, 32.5, 29.0, 26.4, 24.6, 22.4, 21.3, 21.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{14}H_{26}BrNNaO_2$ calcd. 342.1045, found, 342.1059.

(E)-2-Bromo-N-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-2-methylpropanamide ***(20r)***



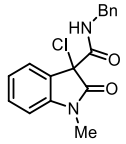
Compound **20r** was prepared using general procedure-II and isolated as white solid in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 5.34 (d, *J* = 5.0 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 4.41 - 4.38 (m, 2H), 2.02 - 1.96 (m, 4H), 1.88 (d, *J* = 4.2 Hz, 6H), 1.67 (d, *J* = 4.1 Hz, 3H), 1.60 (d, *J* = 3.6 Hz, 3H), 1.52 (d, *J* = 4.0 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.3, 145.3, 131.8, 123.6, 117.3, 72.1, 59.3, 46.0, 39.6, 32.2, 26.3, 25.6, 17.7, 16.6; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{14}H_{24}BrNNaO_2$ calcd. 340.0888, found, 340.0891.

N-(((2R,3R,4S,5S)-3,4-bis(benzyloxy)-5-methoxytetrahydrofuran-2-yl)methoxy)-2-bromo-2-methylpropanamide ***(20s)***



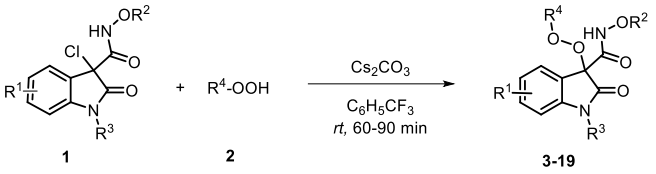
Compound **20s** was prepared using general procedure-II and isolated as white solid in 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.33 - 7.29 (m, 10H), 4.98 (s, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.56 - 4.48 (m, 3H), 4.32 - 4.23 (m, 1H), 4.15 - 4.10 (m, 1H), 4.06 (d, *J* = 5.5 Hz, 1H), 4.02 (s, 1H), 3.98 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.39 (s, 3H), 1.88 (s, 3H), 1.82 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.6, 137.4, 137.0, 128.6, 128.2(2), 128.1, 128.0, 107.5, 87.0, 82.3, 81.9, 74.7, 72.6, 72.0, 59.0, 55.1, 32.1(2); **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{24}H_{30}BrNNaO_6$ calcd. 532.1134, found, 532.1167.

N-Benzyl-3-chloro-1-methyl-2-oxoindoline-3-carboxamide ***(46)***



Compound **46** was prepared using general procedure-I and isolated as white solid in 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.31 - 7.18 (m, 6H), 7.07 (app t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 4.47 (dd, *J* = 15.0, 6.1 Hz, 1H), 4.34 (dd, *J* = 14.9, 5.7 Hz, 1H), 3.11 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.3, 163.7, 143.0, 137.2, 130.9, 128.6, 127.5(2), 126.5, 126.4, 123.8, 109.0, 61.3, 43.9, 26.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{15}ClN_2NaO_2$ calcd. 337.0720, found, 337.0716.

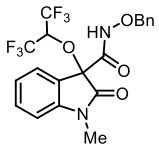
4. General Procedure for the preparation of 3-Peroxy-3-substituted Oxindole



To a solution of α-halohydroxamates (**1**) in $C_6H_5CF_3$ (2.0 M) was added hydroperoxide (2.0 to 10.0 equiv) and Cs_2CO_3 (2,0 equiv) under argon. The reaction was monitored by thin layer chromatography (TLC) until the disappearance of the starting material was observed (*ca*. 60-90 minutes). The solvent was removed under vacuo (Note: bath temperature was maintained < 30 ^oC) and the crude product was purified by flash column chromatography to obtain the desired peroxy-derivatives **3-19**.

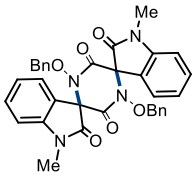
5. Characterization of the side products

N-(benzyloxy)-3-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-1-methyl-2-oxoindoline-3-carboxamide ***(1a-HFIP)***



Formation of compound **1a-HFIP** was noted during the optimization process (Table 1 from the main text; entries 1-2). This compound was obtained in ca. 50-75% yield and was purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) and isolated as yellow foam. R_f 0.4 (1:4 EtOAc /Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.51 - 7.39 (m, 6H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.16 (app t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 4.99 - 4.93 (m, 2H), 4.42 - 4.34 (m, 1H), 3.21 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.5, 162.2, 145.8, 134.4, 133.0, 129.7, 129.2, 128.8, 126.7, 124.0, 123.4 (q, *J* = 80.3 Hz), 120.6, 109.8, 84.0, 78.8, 71.5 (q, *J* = 34.0 Hz), 26.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{20}H_{16}F_6N_2NaO_4$ calcd. 485.0912, found, 485.0910.

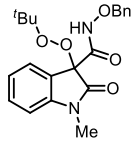
(3R,5'R)-1',4'-bis(benzyloxy)-1,1''-dimethyldispiro[indoline-3,2'-piperazine-5',3''-indoline]-2,2'',3',6'-tetraone ***(1a-D)***



Formation of compound **1a-D** was noted during the optimization process (Table 1 from the main text; entries 3-4 in 20-25% yield). This compound can be formed in higher yield in absence of TBHP. α-Chlorohydroxamate **1a** (0.05g, 0.31 mmol) was transformed into dimer product **1a-D** in DCM (1.0 M) with Cs_2CO_3 (0.20 g, 0.62 mmol) and purified by silica gel column chromatography (using 2:3 EtOAc: Hexanes as eluent) to give the title compound as yellow foam in 73% (0.065g) yield. R_f 0.2 (1:4 EtOAc /Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 - 7.41 (m, 3H), 7.28 - 7.22 (m, 8H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.15 - 7.09 (m, 3H), 6.99 (d, *J* = 7.0 Hz, 2H), 6.89 (dd, *J* = 7.8, 4.6 Hz, 2H), 4.93 - 4.78 (m, 4H), 3.25 (d, *J* = 3.0 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.7, 168.6, 163.6(2), 145.5, 144.6, 144.5, 137.0, 134.1, 132.1, 131.0, 129.7, 128.9, 128.4, 128.2, 128.0, 125.2, 124.9, 124.3, 124.1, 123.4, 123.1, 109.5, 109.2, 82.8, 78.8, 77.4, 70.6, 27.1, 27.0; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{34}H_{28}N_4NaO_6$ calcd. 611.1907, found, 611.1905.

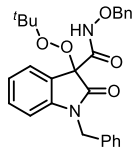
6. Characterization of various 3-Peroxy-3-substituted oxindoles

N-(benzyloxy)-3-(tert-butylperoxy)-1-methyl-2-oxoindoline-3-carboxamide ***(3)***



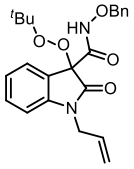
Following the general procedure, α-chlorohydroxamate **1a** (0.100g, 0.31 mmol) was transformed into peroxy-compound **3** with TBHP (0.6 mL, 3.1 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to afford the title compound as yellow foam in 62% (0.072g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2979, 2929, 1732, 1693, 1613, 1471, 1368, 1191, 751; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.46 (d, *J* = 6.5 Hz, 3H), 7.39 - 7.36 (m, 4H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H),3.20 (s, 3H), 1.08 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.7, 162.5, 144.8, 134.9, 131.0, 129.7, 129.0, 128.7, 127.3, 124.5, 123.2, 108.7, 86.2, 82.1, 78.7, 26.7, 26.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{21}H_{24}N_2NaO_5$ calcd. 407.1583, found, 407.1554.

1-Benzyl-N-(benzyloxy)-3-(tert-butylperoxy)-2-oxoindoline-3-carboxamide ***(4)***



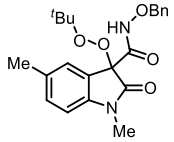
Following the general procedure, α-chlorohydroxamate **1b** (0.100g, 0.25 mmol) was transformed into peroxy-compound **4** with TBHP (0.5 mL, 2.5 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to afford the title compound as white foam in 67% (0.076g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2981, 2927, 1723, 1681, 1613, 1467, 1364, 1179, 748; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.47 - 7.43 (m, 3H), 7.41 - 7.37 (m, 3H), 7.27 - 7.20 (m, 6H), 7.05 (app t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 5.00 (d, *J* = 11.0 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.71 (d, *J* = 16.0 Hz, 1H), 1.09 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.3, 162.0, 144.0, 135.0, 134.8, 130.9, 129.7, 129.0, 128.9, 128.7, 127.7, 127.0, 126.9, 124.5, 123.2, 109.8, 86.4, 82.1, 78.7, 44.0, 26.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{28}N_2NaO_5$ calcd. 483.1896, found, 483.1925.

1-Allyl-N-(benzyloxy)-3-(tert-butylperoxy)-2-oxoindoline-3-carboxamide ***(5)***



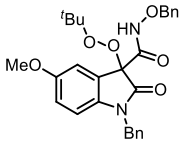
Following the general procedure, α-chlorohydroxamate **1c** (0.100g, 0.28 mmol) was transformed into peroxy compound **5** with TBHP (0.5 mL, 2.8 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as yellow oil in 65% (0.075g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2980, 2928, 1729, 1692, 1610, 1475, 1463, 1114, 750; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.47 - 7.45 (m, 3H), 7.41 - 7.36 (m, 3H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 5.85 - 5.76 (m, 1H), 5.23 - 5.17 (m, 2H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.43 (dd, *J* = 16.8, 4.3 Hz, 1H), 4.20 (dd, *J* = 16.8, 4.4 Hz, 1H), 1.08 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.8, 162.2, 144.0, 134.9, 130.9, 130.3, 129.7, 129.0, 128.7, 127.1, 124.5, 123.1, 117.5, 109.6, 86.3, 82.1, 78.6, 42.5, 26.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{23}H_{26}N_2NaO_5$ calcd. 433.1739, found, 433.1738.

N-(benzyloxy)-3-(tert-butylperoxy)-1,5-dimethyl-2-oxoindoline-3-carboxamide ***(7)***



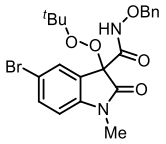
Following the general procedure, α-chlorohydroxamate **1e** (0.05g, 0.15 mmol) was transformed into peroxy compound **7** with TBHP (0.3 mL, 1.5 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as colourless oil in 60% (0.035g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2984, 2927, 1731, 1694, 1624, 1502, 1362, 1193, 1117, 740; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.46 (d, *J* = 5.8 Hz, 2H), 7.40 - 7.36 (m, 3H), 7.28 (s, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 3.17 (s, 3H), 2.34 (s, 3H), 1.08 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.7, 162.7, 142.4, 135.0, 132.7, 131.3, 129.7, 129.0, 128.7, 128.0, 124.4, 108.4, 86.3, 82.0, 78.6, 26.7, 26.3, 21.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{22}H_{26}N_2NaO_5$ calcd. 421.1739, found, 421.1755.

1-Benzyl-N-(benzyloxy)-3-(tert-butylperoxy)-5-methoxy-2-oxoindoline-3-carboxamide ***(8)***



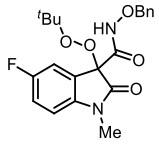
Following the general procedure, α-chlorohydroxamate **1f** (0.100g, 0.23 mmol) was transformed into peroxy compound **8** with TBHP (0.4 mL, 2.3 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:3 Acetone: Hexanes as eluent) to give the title compound as yellow oil in 64% (0.072g) yield. R_f 0.3 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2983, 2932, 1727, 1686, 1613, 1462, 1371, 1188, 749; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 7.37 - 7.36 (m, 2H), 7.31 - 7.27 (m, 3H), 7.21 - 7.12 (m, 5H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.65 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.42 (d, *J* = 8.6 Hz, 1H), 4.97 (d, *J* = 16.0 Hz, 1H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.59 (d, *J* = 16.0 Hz, 1H), 3.65 (s, 3H), 1.01 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.1, 161.9, 156.2, 137.2, 135.0, 134.8, 129.7, 129.0, 128.8, 128.7, 127.7, 127.0, 125.6, 115.8, 113.8, 110.3, 86.7, 82.2, 78.7, 55.9, 44.1, 26.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{28}H_{30}N_2NaO_6$ calcd. 513.2002, found, 513.2029.

N-(benzyloxy)-5-bromo-3-(tert-butylperoxy)-1-methyl-2-oxoindoline-3-carboxamide ***(9)***



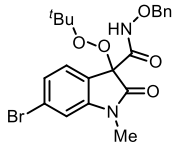
Following the general procedure, α-chlorohydroxamate **1g** (0.05g, 0.12 mmol) was transformed into peroxy compound **9** with TBHP (0.2 mL, 1.2 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as white foam in 55% (0.031g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2980, 2931, 1727, 1695, 1617, 1488, 1365,1192,750; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.56 (s, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.47 - 7.45 (m, 2H), 7.42 - 7.36 (m, 3H), 6.72 (d, *J* = 8.3 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 3.18 (s, 3H), 1.09 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.2, 161.8, 143.9, 134.8, 133.8, 130.3, 129.7, 129.1, 128.8, 126.4, 115.9, 110.2, 86.0, 82.4, 78.7, 26.9, 26.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{21}H_{23}BrN_2NaO_5$ calcd 487.0668, found 487.0657.

N-(benzyloxy)-3-(tert-butylperoxy)-5-fluoro-1-methyl-2-oxoindoline-3-carboxamide ***(10)***



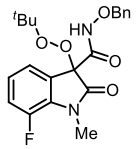
Following the general procedure, α-chlorohydroxamate **1h** (0.05g, 0.14 mmol) was transformed into peroxy compound **10** with TBHP (0.25 mL, 1.4 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as white foam in 59% (0.034g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2980, 2933, 1732, 1692, 1624, 1494, 1363, 1188, 730; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.47 - 7.45 (m, 2H), 7.41 - 7.37 (m, 3H), 7.22 (dd, *J* = 7.6, 2.6 Hz, 1H), 7.12 - 7.06 (m, 1H), 6.76 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 3.19 (s, 3H), 1.09 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.5, 161.8, 159.3 (d, *J* = 241.0 Hz), 140.7 (d, *J* = 2.0 Hz), 134.8, 129.7, 129.1, 128.8, 126.0 (d, *J* = 8.0 Hz), 117.3 (d, *J* = 24.0 Hz), 115.5 (d, *J* = 25.0 Hz), 109.3 (d, *J* = 8.0 Hz), 86.2 (d, *J* = 2.0 Hz), 82.3, 78.7, 26.9, 26.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{21}H_{23}FN_2NaO_5$ calcd. 425.1489, found, 425.1463.

N-(benzyloxy)-6-bromo-3-(tert-butylperoxy)-1-methyl-2-oxoindoline-3-carboxamide ***(11)***



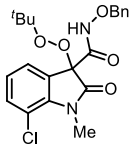
Following the general procedure, α-chlorohydroxamate **1i** (0.05g, 0.12 mmol) was transformed into peroxy compound **11** with TBHP (0.22 mL, 1.2 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as yellow foam in 63% (0.036g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2981, 2933, 1732, 1692, 1624, 1494, 1363,1188,747; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.47 - 7.44 (m, 2H), 7.41 - 7.35 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.26 - 7.24 (m, 1H), 7.00 (d, *J* = 1.2 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 3.18 (s, 3H), 1.08 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.6, 161.8, 146.1, 134.8, 129.7, 129.1, 128.8, 128.5, 126.1, 124.9, 123.4, 112.4, 85.8, 82.3, 78.7, 26.9, 26.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{21}H_{23}BrN_2NaO_5$ calcd. 487.0668, found, 487.0695.

N-(benzyloxy)-3-(tert-butylperoxy)-7-fluoro-1-methyl-2-oxoindoline-3-carboxamide ***(12)***



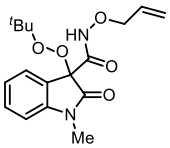
Following the general procedure, α-chlorohydroxamate **1j** (0.05g, 0.14 mmol) was transformed into peroxy compound **12** with TBHP (0.25 mL, 1.4 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as yellow oil in 45% (0.026g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2978, 2924, 1743, 1694, 1632, 1480, 1367,1242,1123,741; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.47 - 7.45 (m, 2H), 7.40 - 7.38 (m, 3H), 7.25 (d, *J* = 8.0 Hz,1H), 7.14 - 7.09 (m, 1H), 7.06 - 7.01 (m, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 3.41 (d, *J* = 2.6 Hz, 3H), 1.08 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.5, 161.8, 147.8 (d, *J* = 242.0 Hz), 134.8, 131.5 (d, *J* = 8.0 Hz), 129.7, 129.1, 128.8, 127.1 (d, *J* = 3.0 Hz), 123.8 (d, *J* = 6.0 Hz), 123.1 (d, *J* = 3.0 Hz), 119.1 (d, *J* = 19.0 Hz), 86.1 (d, *J* = 3.0 Hz), 82.3, 78.7, 29.4 (d, *J* = 6.0 Hz), 26.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{21}H_{23}FN_2NaO_5$ calcd. 425.1489, found, 425.1491.

N-(benzyloxy)-3-(tert-butylperoxy)-7-chloro-1-methyl-2-oxoindoline-3-carboxamide ***(13)***



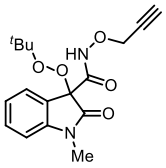
Following the general procedure, α-chlorohydroxamate **1k** (0.05g, 0.14 mmol) was transformed into peroxy compound **13** with TBHP (0.25 mL, 1.4 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as yellow oil in 48% (0.028g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2981, 2927, 1740, 1695, 1610, 1464, 1364, 1191, 1114, 748; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.46 - 7.45 (m, 2H), 7.42 - 7.37 (m, 3H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.02 (app t, *J* = 7.4 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 3.57 (s, 3H), 1.08 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.1, 161.8, 140.7, 134.8, 133.4, 129.7, 129.1, 128.8, 127.1, 125.8, 124.0, 116.0, 85.6, 82.3, 78.7, 30.3, 26.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{21}H_{23}ClN_2NaO_5$ calcd 441.1193, found 441.1195.

N-(allyloxy)-3-(tert-butylperoxy)-1-methyl-2-oxoindoline-3-carboxamide ***(14)***



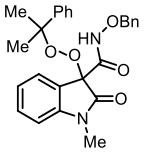
Following the general procedure, α-chlorohydroxamate **1l** (0.05g, 0.15 mmol) was transformed into peroxy compound **14** with TBHP (0.3 mL, 1.5 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as colourless oil in 60% (0.035g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2984, 2933, 1734, 1692, 1613, 1471, 1369, 1190, 1117, 750; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.05 - 5.95 (m, 1H), 5.38 (dd, *J* = 21.0, 13.8 Hz, 2H), 4.49 - 4.40 (m, 2H), 3.19 (s, 3H), 1.13 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.8, 162.4, 144.8, 131.7, 131.0, 127.3, 124.5, 123.2, 121.5, 108.7, 86.1, 82.1, 77.6, 26.7, 26.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{22}N_2NaO_5$ calcd. 357.1426, found, 357.1448.

3-(Tert-butylperoxy)-1-methyl-2-oxo-N-(prop-2-yn-1-yloxy)indoline-3-carboxamide ***(15)***



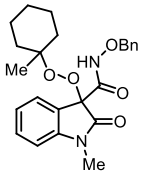
Following the general procedure, α-chlorohydroxamate **1m** (0.05g, 0.15 mmol) was transformed into peroxy compound **15** with TBHP (0.3 mL, 1.5 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as white foam in 57% (0.033g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2981, 2933, 2127, 1731, 1693, 1613, 1471, 1369, 1193, 750; **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 9.63 (s, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.62 - 4.53 (m, 2H), 3.19 (s, 3H), 2.67 (s, 1H), 1.16 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2) δ 169.8, 163.2, 145.5, 131.6, 127.5, 124.9, 123.4, 109.3, 86.6, 82.7, 77.9, 77.1, 64.3, 27.0, 26.5; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{20}N_2NaO_5$ calcd. 355.1270, found, 355.1267.

N-(benzyloxy)-1-methyl-2-oxo-3-((2-phenylpropan-2-yl)peroxy)indoline-3-carboxamide ***(16)***



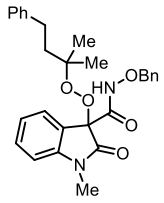
Following the general procedure, α-chlorohydroxamate **1n** (0.05g, 0.15 mmol) was transformed into peroxy compound **16** with Cumene hydroperoxide (67 µl, 0.45 mmol, 3.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as yellow foam in 58% (0.039g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2983, 2933, 1729, 1695, 1613, 1471, 1370, 1155, 732; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.34 - 7.33 (m, 4H), 7.31 - 7.30 (m, 3H), 7.18 - 7.16 (m, 5H), 7.05 (app t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.82 (d, *J* = 11.0 Hz, 1H), 3.14 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.9, 161.9, 144.9, 144.3, 134.8, 131.1, 129.7, 129.0, 128.7, 128.2, 127.4, 126.9, 125.5, 124.3, 123.3, 108.7, 86.5, 84.6, 78.6, 26.8(2), 26.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{26}N_2NaO_5$ calcd 469.1739, found, 469.1707.

N-(benzyloxy)-1-methyl-3-((1-methylcyclohexyl)peroxy)-2-oxoindoline-3-carboxamide ***(17)***



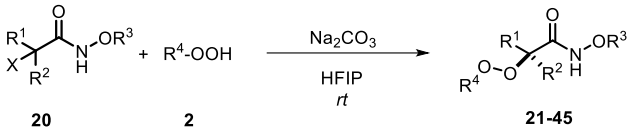
Following the general procedure, α-chlorohydroxamate **1a** (0.05g, 0.15 mmol) was transformed into peroxy compound **17** with HP1 (0.039 g, 0.3 mmol, 2.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as colourless oil in 48% (0.031g) yield. R_f 0.4 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2934, 1737, 1698, 1610, 1471, 1369, 1114, 1091, 754; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.47 (d, *J* = 6.9 Hz, 3H), 7.39 - 7.36 (m, 4H), 7.10 (app t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 3.20 (s, 3H), 1.64 - 1.56 (m, 4H), 1.32 - 1.25 (m, 6H), 1.04 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.8, 162.6, 144.9, 138.5, 135.0, 131.0, 129.6, 128.8, 127.2, 124.7, 123.2, 108.7, 86.1, 83.0, 78.7, 35.0, 34.8, 26.7, 25.5, 24.4, 22.3, 22.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{24}H_{28}N_2NaO_5$ calcd. 447.1896, found, 447.1884.

*N-(benzyloxy)-1-methyl-3-((2-methyl-4-phenylbutan-2-yl)peroxy)-2-oxoindoline-3-carboxamide **(18)***



Following the general procedure, α-chlorohydroxamate **1a** (0.05g, 0.15 mmol) was transformed into peroxy compound **18** with HP2 (0.054g, 0.3 mmol, 2.0 equiv) and purified by silica gel column chromatography (using 1:4 Acetone: Hexanes as eluent) to give the title compound as colourless oil in 50% (0.036g) yield. R_f 0.35 (1:4 Acetone/Hexanes); **FT-IR** (v cm^{-1}): 2929, 1731, 1692, 1622, 1463, 1369, 1117, 1088, 750; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.49 - 7.45 (m, 3H), 7.41 - 7.35 (m, 4H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.15 - 7.09 (m, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 3.21 (s, 3H), 2.45 - 2.41 (m, 2H), 1.73 - 1.69 (m, 2H), 1.12 (s, 3H), 1.11 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.9, 169.2, 144.9, 142.4, 134.9, 131.1, 129.6, 129.0, 128.8, 128.5, 128.4, 127.2, 125.9, 124.4, 123.3, 108.7, 86.2, 83.8, 78.7, 40.9, 30.2, 26.8, 24.5(2); **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{28}H_{30}N_2NaO_5$ calcd. 497.2052, found, 497.2077.

7. General procedure for the preparation of α-peroxyamides

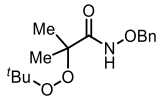


20 **2** **21-45**

To a solution of α-halohydroxamates **20** in HFIP (0.2 M) was added hydroperoxide (2.0 to 5.0 equiv) and base (2.0 equiv) under argon atmosphere. The reaction was monitored by thin layer chromatography (TLC) until the disappearance of the starting material was observed (*ca*. 60-90 minutes). The solvent was removed under vacuo (bath temperature was maintained at 30 ^{o}C) and the crude product was purified by flash column chromatography to obtain the peroxy products **21-45**.

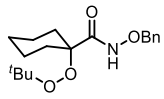
8.Charcterization of α-peroxyamides

*N-(benzyloxy)-2-(tert-butylperoxy)-2-methylpropanamide **(21)***



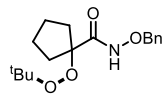
Following the general procedure, α-bromohydroxamate **20a** (0.100g, 0.37 mmol) was transformed into peroxy compound **21** with TBHP (0.4 mL, 1.85 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as white solid in 96% (0.100g) yield. R_f 0.4 (1:4 EtOAc/Hexanes); **FT-IR** (v cm^{-1}): 2978, 2930, 1672, 1496, 1362, 1196, 1046, 746; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.37 - 7.36 (m, 2H), 7.32 - 7.27 (m, 3H), 4.86 (s, 2H), 1.34 (s, 6H), 1.06 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 172.4, 135.5, 129.3, 128.7(2), 83.4, 80.5, 78.1, 26.4, 23.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{15}H_{23}NNaO_4$ calcd. 304.1525, found, 304.1544.

*N-(benzyloxy)-1-(tert-butylperoxy)cyclohexanecarboxamide **(22)***



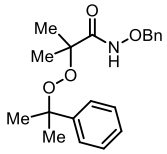
Following the general procedure, α-bromohydroxamate **20b** (0.100g, 0.32mmol) was transformed into peroxy compound **22** with TBHP (0.32 mL, 1.6 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 93% (0.096 g) yield. R_f 0.4 (1:4 EtOAc/Hexanes); **FT-IR** (v cm^{-1}): 2978, 2936, 1689, 1454, 1364, 1194, 1026, 750; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.40 - 7.39 (m, 2H), 7.37 - 7.31 (m, 3H), 4.89 (s, 2H), 1.87 - 1.84 (m, 4H), 1.62 - 1.40 (m, 5H), 1.31 - 1.21 (m, 1H), 1.10 (s, 9H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ172.8, 135.7, 129.1, 128.7, 84.4, 80.1, 77.9, 30.6, 26.5, 25.0, 21.0; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{18}H_{27}NNaO_4$ calcd. 344.1838, found, 344.1835.

N-(benzyloxy)-1-(tert-butylperoxy)cyclopentane-1-carboxamide ***(23)***



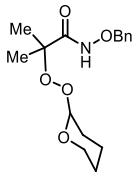
Following the general procedure, α-bromohydroxamate **20c** (0.100g, 0.34 mmol) was transformed into peroxy compound **23** with TBHP (0.31 mL, 1.7 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 87% (0.090g) yield. R_f 0.4 (1:4 EtOAc/Hexanes); **FT-IR** (v cm^{-1}): 2975, 2930, 1666, 1499, 1363, 1194, 989, 727; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.44 - 7.42 (m, 2H), 7.39 - 7.32 (m, 3H), 4.93 (s, 2H), 2.14 - 2.07 (m, 2H), 1.95 - 1.90 (m, 2H), 1.77 - 1.69 (m, 4H), 1.10 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 172.5, 135.6, 129.2, 128.8, 128.7, 93.5, 80.4, 78.1, 35.2, 26.5, 25.0; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{25}NNaO_4$ calcd. 330.1681, found, 330.1698.

N-(benzyloxy)-2-methyl-2-((2-phenylpropan-2-yl)peroxy)propanamide ***(26)***



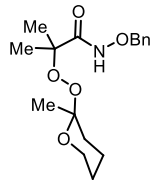
Following the general procedure, α-bromohydroxamate **20a**(0.100g, 0.4mmol) was transformed into peroxy compound **26** with cumene peroxide (0.12 g, 0.8 mmol, 2.0 equiv) and purified by silica gel column chromatography (using 1:3EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 87% (0.110g) yield. R_f 0.3 (1:4 EtOAc/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ8.91 (s, 1H), 7.45 - 7.43 (m, 2H), 7.38 (d, J = 5.0 Hz, 3H), 7.30 - 7.26 (m, 5H), 4.94 (s, 2H), 1.52 (s, 6H), 1.40 (s, 6H);**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 172.0, 144.5, 135.5, 129.2, 128.8, 128.7, 128.2, 127.4, 125.4, 83.7, 82.9, 78.0, 26.3, 23.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{20}H_{25}NNaO_4$ calcd. 366.1681, found, 366.1681.

N-(benzyloxy)-2-methyl-2-((tetrahydro-2H-pyran-2-yl)peroxy)propanamide ***(27)***



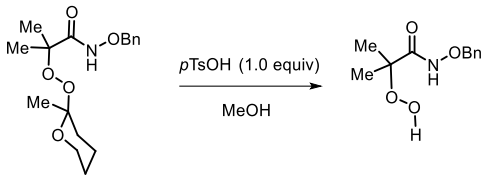
Following the general procedure, α-bromohydroxamate **20a** (0.100g, 0.4 mmol) was transformed into peroxy compound **27** with THP-hydroperoxide (**HP3**) (0.095 g,0.8 mmol, 2.0 equiv) and purified by silica gel column chromatography (using 1:3 E_2O: Hexanes as eluent) to give the title compound as colorless oil in 75% (0.085 g) yield. R_f 0.4 (1:3 E_2O/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.43 - 7.41 (m, 2H), 7.38 - 7.33 (m, 3H), 4.96 - 4.87 (m, 3H), 3.84 - 3.79 (m, 1H), 3.53 - 3.47 (m, 1H), 1.82 (s, 1H), 1.69 - 1.66 (m, 3H), 1.53 (s, 3H), 1.51 -1.47 (m, 2H), 1.38 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.9, 135.9, 129.3, 128.7, 128.6, 102.0, 84.9, 78.0, 64.6, 27.6, 24.9, 24.1, 22.0, 20.9; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{16}H_{23}NNaO_5$ calcd. 332.1474, found, 332.1470.

N-(benzyloxy)-2-methyl-2-((2-methyltetrahydro-2H-pyran-2-yl)peroxy)propanamide ***(28)***



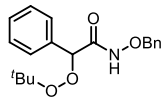
Following the general procedure, α-bromohydroxamate **20a** (0.100g, 0.4 mmol) was transformed into peroxy compound **28** with THP-hydroperoxide (HP4) (0.106 g,0.8 mmol, 2.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 64% (0.076g) yield. R_f 0.4 (1:4 EtOAc /Hexanes); **FT-IR** (v cm^{-1}): 2990, 2942, 1681, 1457, 1377, 1168, 1047, 743; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.42 - 7.40 (m, 2H), 7.38 - 7.32 (m, 3H), 4.95 (d, *J* = 11.6 Hz, 1H), 4.91 (d, *J* = 11.6 Hz, 2H), 3.59 - 3.56 (m, 2H), 1.81 (s, 1H), 1.66 - 1.63 (m, 2H), 1.48 (s, 6H), 1.44 - 1.41 (m, 3H), 1.32 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 172.3, 135.7, 129.1, 128.8, 128.7, 102.8, 84.1, 78.1, 62.4, 32.8, 24.6, 24.2, 24.0, 22.9, 19.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{25}NNaO_5$ calcd. 346.1630, found, 346.1628.

N-(benzyloxy)-2-hydroperoxy-2-methylpropanamide ***(29)***



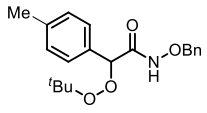
To a solution of α-peroxy amide **27** (0.050 g, 0.16 mmol) in dry methanol (1 mL, 0.16 M) under argon was added *p*-toluenesulfonic acid (0.028 g, 0.16 mmol) and the reaction mixture was stirred at room temperature for 12 h. Upon completion of the reaction as determined by the disappearance of starting material, the reaction solvent was removed under reduced pressure and the crude product was purified by flash silica gel column chromatography (using 3:7EtOAc/Hexanes as eluent) to obtain **29** as white solid in 66% yield (0.024g). R_f 0.4 (3:7 EtOAc/Hexanes);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 9.22 (s, 1H), 7.41 - 7.39 (m, 2H), 7.37 - 7.34 (m, 3H), 4.90 (s, 2H), 1.43 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 172.2, 135.1, 129.6, 129.0, 128.7, 85.0, 78.4, 22.9; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{11}H_{15}NNaO_4$ calcd. 248.0899, found, 248.0888.

N-(benzyloxy)-2-(tert-butylperoxy)-2-phenylacetamide ***(30)***



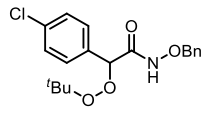
Following the general procedure, α-chlorohydroxamate **20f** (0.100g, 0.36mmol) was transformed into peroxy-compound **30** with TBHP (0.4 mL, 1.8 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:3 E_2O: Hexanes as eluent) to give the title compound as colorless oil in 70% (0.084g) yield. R_f 0.4 (1:3Et_2O/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.32 - 7.28 (m, 4H), 7.25 -7.19 (m, 6H), 5.22 (s, 1H), 4.86 (s, 2H), 1.08 (s, 9H);**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.0, 135.3, 133.7, 129.6, 129.4,128.9, 128.8, 128.7, 128.1, 86.6, 82.3, 78.4, 26.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{23}NNaO_4$ calcd. 352.1525, found, 352.1507.

N-(benzyloxy)-2-(tert-butylperoxy)-2-(p-tolyl)acetamide ***(31)***



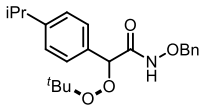
Following the general procedure, α-chlorohydroxamate **20g** (0.100g, 0.35mmol) was transformed into peroxy compound **31** with TBHP (0.4 mL, 1.75 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 75% (0.089g) yield. R_f 0.4 (1:3 Et_2O /Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ9.11 (s, 1H), 7.45 -7.41 (m, 2H), 7.40 - 7.38 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.31 (s, 1H), 4.99 (s, 2H), 2.35 (s, 3H), 1.20 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.1, 139.4, 135.3, 130.7, 129.5(2), 128.9, 128.7, 128.2, 86.5, 82.1, 78.4, 26.3, 21.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{20}H_{25}NNaO_4$ calcd. 366.1681, found, 366.1691.

N-(benzyloxy)-2-(tert-butylperoxy)-2-(4-chlorophenyl)acetamide ***(32)***



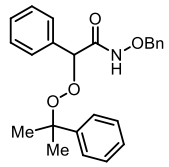
Following the general procedure, α-chlorohydroxamate **20h** (0.100g, 0.32mmol) was transformed into peroxy compound **32** with TBHP (0.32 mL, 1.6 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 72% (0.085 g) yield. R_f 0.4 (1:3Et_2O/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ9.06 (s, 1H), 7.42 -7.41 (m, 2H), 7.38 - 7.37 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.29 (s, 1H), 4.97 (s, 2H), 1.19 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ167.5, 135.4, 135.2, 132.3, 129.5, 129.4, 129.0(2), 128.7, 85.6, 82.4, 78.4, 26.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{22}ClNNaO_4$ calcd 386.1135, found, 386.1135.

N-(benzyloxy)-2-(tert-butylperoxy)-2-(4-isopropylphenyl)acetamide ***(33)***



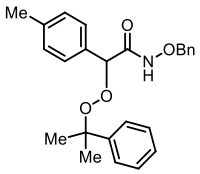
Following the general procedure, α-chlorohydroxamate **20i** (0.100g, 0.31mmol) was transformed into peroxy compound **33** with TBHP (0.28 mL, 1.6 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 71% (0.083g) yield. R_f 0.4 (1:3Et_2O/Hexanes); **FT-IR** (v cm^{-1}): 2964, 2927, 1675, 1457, 1363, 1196, 1020, 740; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.45 - 7.44 (m, 2H), 7.39 - 7.38 (m, 3H), 7.26 - 7.20 (m, 4H), 5.33 (s, 1H), 5.00 (s, 2H), 2.95 - 2.88 (m, 1H), 1.26 (s, 3H), 1.24 (s, 3H), 1.22 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 150.2, 135.3, 130.9, 129.5, 128.8, 128.7, 128.2, 126.9, 86.5, 82.1, 78.4, 34.0, 26.3, 23.9; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{22}H_{29}NNaO_4$ calcd. 394.1994, found, 394.1961.

N-(benzyloxy)-2-phenyl-2-((2-phenylpropan-2-yl)peroxy)acetamide ***(34)***



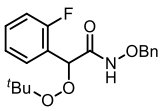
Following the general procedure, α-chlorohydroxamate **20f** (0.100g, 0.36mmol) was transformed into peroxy compound **34** with cumene hydroperoxide (0.11 g, 0.72 mmol, 2.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 61% (0.087g) yield. R_f 0.4 (1:3 Et_2O /Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.50 - 7.41 (m, 7H), 7.38 - 7.28 (m, 6H), 7.08 (d, *J* = 7.3 Hz, 2H), 5.32 (s, 1H), 5.01 (s, 2H), 1.62 (s, 3H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.5, 144.1, 135.2, 133.3, 129.5, 129.3, 128.9, 128.7, 128.6, 128.3, 128.2, 127.7, 125.7, 86.2, 84.5, 78.4, 26.2, 26.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{24}H_{25}NNaO_4$ calcd. 414.1681, found, 414.1676.

N-(benzyloxy)-2-((2-phenylpropan-2-yl)peroxy)-2-(p-tolyl)acetamide ***(35)***



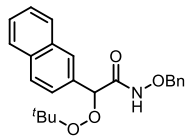
Following the general procedure, α-chlorohydroxamate **20g** (0.100g, 0.35 mmol) was transformed into peroxy compound **35** with cumene hydroperoxide (0.107 g, 0.7 mmol, 2.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 67% (0.094g) yield. R_f 0.4 (1:3 Et_2O /Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ8.96 (s, 1H), 7.45 - 7.43 (m, 2H), 7.39 - 7.37 (m, 6H), 7.33 - 7.29 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 5.24 (s, 1H), 4.98 (s, 2H), 2.30 (s, 3H), 1.58 (s, 3H), 1.55 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ167.8, 144.1, 139.4, 135.3, 130.3, 129.5, 129.4, 128.9, 128.7, 128.3(2), 127.7, 125.8, 86.2, 84.4, 78.4, 26.3, 26.2, 21.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{27}NNaO_4$ calcd. 428.1838, found, 428.1810.

N-(benzyloxy)-2-(tert-butylperoxy)-2-(2-fluorophenyl)acetamide ***(36)***



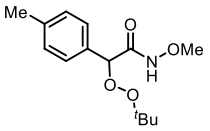
Following the general procedure, α-chlorohydroxamate **20j** (0.100g, 0.34 mmol) was transformed into peroxy compound **36** with TBHP (0.3 ml, 1.7 mmol, 10.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 64% (0.076g) yield. R_f 0.4 (1:3 Et_2O /Hexanes); **FT-IR** (v cm^{-1}): 2981, 2933, 1681, 1492, 1454, 1365, 1234, 1193, 1026, 754; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.48 - 7.47 (m, 2H), 7.40 - 7.33 (m, 4H), 7.20 - 7.17 (m, 1H), 7.11 - 7.06 (m, 2H), 5.65 (s, 1H), 5.02 (s, 2H), 1.17 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 161.4(d, *J* = 248.0 Hz), 135.3, 131.5(d, *J* = 8.0 Hz), 130.1(d, *J* = 3.0 Hz), 129.5, 129.0, 128.8, 124.4(d, *J* = 3.0 Hz), 121.2(d, *J* = 14.0 Hz), 115.9(d, *J* = 22.0 Hz), 82.4, 80.3(d, *J* = 3.0 Hz), 78.5, 26.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{22}FNNaO_4$ calcd. 370.1431, found, 370.1437.

N-(benzyloxy)-2-(tert-butylperoxy)-2-(naphthalen-2-yl)acetamide ***(37)***



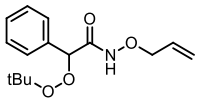
Following the general procedure, α-chlorohydroxamate **20k** (0.100g, 0.36mmol) was transformed into peroxy compound **37** with TBHP (0.4 mL, 1.8 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as white foam in 69% (0.080g) yield. R_f 0.4 (1:3 Et_2O /Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.70 - 7.67 (m, 4H), 7.37 - 7.35 (m, 2H), 7.33 - 7.29 (m, 3H), 7.24 - 7.23 (m, 3H), 5.37 (s, 1H), 4.86 (s, 2H), 1.09 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.9, 135.3, 133.7, 133.2, 131.1, 129.6, 129.0, 128.7, 128.6, 128.4, 127.8, 126.9, 126.5, 125.3, 86.7, 82.4, 78.4, 26.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{23}H_{25}NNaO_4$ calcd. 402.1681, found, 402.1687.

2-(tert-butylperoxy)-N-methoxy-2-(p-tolyl)acetamide ***(38)***



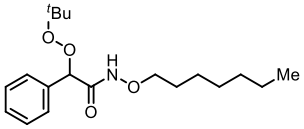
Following the general procedure, α-chlorohydroxamate **20l** (0.100g, 0.47mmol) was transformed into peroxy compound **38** with TBHP (0.5 mL, 2.35 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:3 E_2O: Hexanes as eluent) to give the title compound as colorless oil in 77% (0.097g) yield. R_f 0.4 (1:3E_2O/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 5.36 (s, 1H), 3.86 (s, 3H), 2.38 (s, 3H), 1.30 (s, 9H);**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.4, 139.4, 130.7, 129.5, 128.1, 86.3, 82.2, 64.5, 26.3, 21.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{14}H_{21}NNaO_4$ calcd. 290.1368, found, 290.1368.

*N-(allyloxy)-2-(tert-butylperoxy)-2-phenylacetamide **(39)***



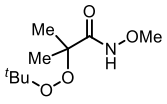
Following the general procedure, α-chlorohydroxamate **20m** (0.05g, 0.22mmol) was transformed into peroxy compound **39** with TBHP (0.2 mL, 1.11 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 60% (0.037g) yield. R_f 0.4 (1:3 Et_2O /Hexanes); **FT-IR** (v cm^{-1}): 2981, 2933, 1675, 1454, 1363, 1194, 696; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.39 - 7.32 (m, 5H), 6.08 - 5.97 (m, 1H), 5.39 - 5.33 (m, 3H), 4.48 (dd, *J* = 15.1, 6.4 Hz, 2H), 1.26 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.1, 133.7, 132.1, 129.5, 128.8, 128.2, 121.3, 86.7, 82.4, 77.6, 26.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{15}H_{21}NNaO_4$ calcd. 302.1368, found, 302.1342.

*2-(Tert-butylperoxy)-N-(heptyloxy)-2-phenylacetamide **(40)***



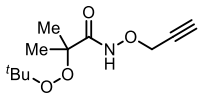
Following the general procedure, α-chlorohydroxamate **20n** (0.100g, 0.35mmol) was transformed into peroxy compound **40** with TBHP (0.32 mL, 1.11 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:3 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 67% (0.080g) yield. R_f 0.4 (1:3 Et_2O /Hexanes); **FT-IR** (v cm^{-1}): 2958, 2930, 1669, 1454, 1363, 1196, 1018, 732; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.43 - 7.36 (m, 5H), 5.35 (s, 1H), 4.03 - 3.93 (m, 2H), 1.73 - 1.66 (m, 3H), 1.42 - 1.35 (m, 6H), 1.27 (s, 9H), 0.89 - 0.86 (m, 4H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.0 133.8, 129.4, 128.8, 128.1, 86.6, 82.3, 77.1, 31.8, 29.2, 28.0, 26.4, 25.8, 22.7, 14.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$: $C_{19}H_{31}NNaO_4$ calcd. 360.2151, found, 360.2132.

*2-(Tert-butylperoxy)-N-methoxy-2-methylpropanamide **(41)***



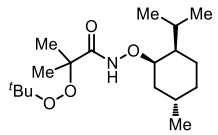
Following the general procedure, α-bromohydroxamate **20o** (0.100g, 0.51mmol) was transformed into peroxy compound **41** with TBHP (0.5 mL, 2.55 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 94% (0.099g) yield. R_f 0.35 (1:4 EtOAc/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ9.10 (s, 1H), 3.71 (s, 3H), 1.37 (s, 6H), 1.20 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 172.8, 83.3, 80.6, 64.2, 26.5, 23.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_9H_{19}NNaO_4$ calcd. 228.1212, found, 228.1208.

*2-(Tert-butylperoxy)-2-methyl-N-(prop-2-yn-1-yloxy)propenamide **(42)***



Following the general procedure, α-bromohydroxamate **20p** (0.05g, 0.23 mmol) was transformed into peroxy-compound **42** with TBHP (0.2 mL, 1.15 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as white solid in 67% (0.035g) yield. R_f 0.4 (1:4 EtOAc/Hexanes); **FT-IR** (v cm^{-1}): 2984, 2936, 2123, 1693, 1474, 1365, 1193, 1171, 1052; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 4.52 (d, *J* = 1.3 Hz, 2H), 2.51 (s, 1H), 1.41 (s, 6H), 1.23 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 172.8, 83.4, 80.7, 78.0, 76.1, 63.4, 26.5, 23.4; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{11}H_{19}NNaO_4$ calcd. 252.1212, found, 252.1208.

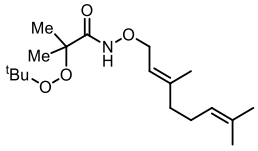
*2-(tert-butylperoxy)-N-(((1R,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)-2-methylpropanamide **(43)***



Following the general procedure, α-bromohydroxamate **20q** (0.100g, 0.31 mmol) was transformed into peroxy compound **43** with TBHP (0.3 mL, 1.85 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as white solid in 85% (0.088g) yield. R_f 0.4 (1:4 EtOAc/Hexanes); **FT-IR** (v cm^{-1}): 2927, 2868, 1697, 1460, 1364, 1193, 1168, 1052; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 4.30 (s, 1H), 2.15 (d, *J* = 12.4 Hz, 1H), 1.78 - 1.63 (m, 4H), 1.41 (s, 3H), 1.38

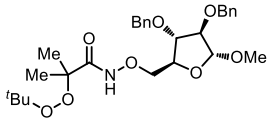
(s, 3H), 1.23 (s, 9H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.97 - 0.93 (m, 1H), 0.89 (s, 3H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.85 (s, 3H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 171.8, 83.6, 80.8, 80.5, 47.7, 37.2, 35.2, 29.1, 26.5, 26.3, 24.7, 23.7, 23.1, 22.4, 21.5, 21.0; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{18}H_{35}NNaO_4$ calcd. 352.2464, found, 352.2471.

*(E)-2-(tert-butylperoxy)-N-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-2-methylpropanamide **(44)***



Following the general procedure, α-bromohydroxamate **20r** (0.100g, 0.32 mmol) was transformed into peroxy compound **44** with TBHP (0.3 mL, 1.85 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as white solid in 96% (0.062g) yield. R_f 0.4 (1:4 EtOAc/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 5.42 (t, *J* = 7.3 Hz, 1H), 5.07 - 5.06 (m, 1H), 4.43 (d, *J* = 7.4 Hz, 2H), 2.10 - 2.03 (m, 4H), 1.73 (s, 3H), 1.66 (s, 3H), 1.58 (s, 3H), 1.41 (s, 6H), 1.23 (s, 9H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 172.5, 144.8, 132.0, 123.8, 117.8, 83.5, 80.5, 72.3, 39.8, 26.6, 26.5, 25.8, 23.4, 17.8, 16.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{18}H_{33}NNaO_4$ calcd. 350.2307, found, 350.2307.

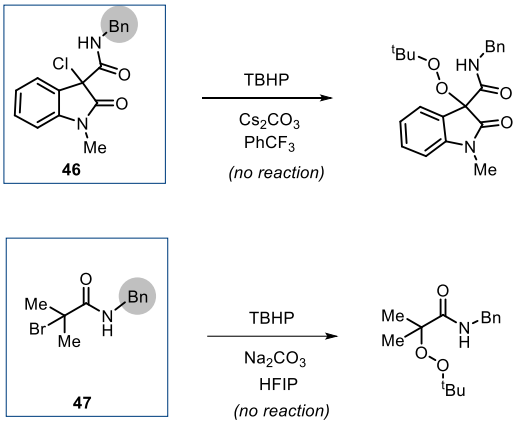
*N-(((2S,3S,4R,5R)-3,4-bis(benzyloxy)-5-methoxytetrahydrofuran-2-yl)methoxy)-2-(tert-butylperoxy)-2-methylpropanamide **(45)***



Following the general procedure, α-bromohydroxamate **20s** (0.100g, 0.20 mmol) was transformed into peroxy compound **45** with TBHP (0.2 mL, 1.85 mmol, 5.0 equiv) and purified by silica gel column chromatography (using 1:4 EtOAc: Hexanes as eluent) to give the title compound as white solid in 78% (0.080g) yield. R_f 0.4 (1:4 EtOAc/Hexanes); **FT-IR** (v cm^{-1}): 2987, 2927, 1694, 1454, 1363, 1193,1109,739; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.35 - 7.25 (m, 10H), 4.94 (s, 1H), 4.59 - 4.52 (m, 2H), 4.51 - 4.45 (m, 2H), 4.30 - 4.27 (m, 1H), 4.10 (dd, *J* = 11.4, 3.3 Hz, 1H), 4.04 (dd, *J* = 11.6, 5.6 Hz, 1H), 3.98 - 3.96 (m, 2H), 3.37 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.20 (s, 9H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 172.1, 137.6, 137.4, 128.5, 128.0(2), 127.9, 107.6, 87.7, 83.3, 80.4, 80.3, 75.6, 72.5, 72.0, 55.0, 26.5, 23.4, 23.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{28}H_{39}NNaO_8$ calcd. 540.2573, found, 540.2590.

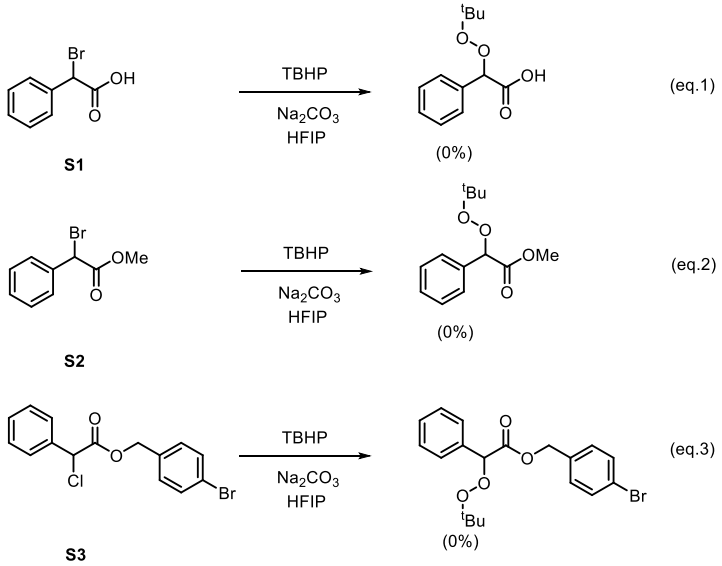
9. Control Experiment

(a)Reaction with α-haloamide: Amide **46** and **47** were employed under standard reaction conditions in presence of *tert*-butylhydroperoxide (TBHP). These reactions did not afford any peroxy-containing product and unreacted starting material was left in the reaction mixture.



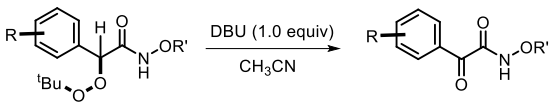
Scheme S1. Control experiments with amides **46**/**47** having N-benzyl residue.

(b) *Reaction with different carboxylic acid derivative:* Carboxylic acid derivatives (**S1-S3**) were employed under standard reaction conditions with *tert*-butylhydroperoxide (TBHP). These reactions did not afford any peroxy-containing product and only unreacted starting material was left in the reaction mixture. These reactions strongly suggests that, despite the higher nucleophilicity of hydroperoxide due to α-effect, S_N1/S_N2 -type substitution is not operative on α-halocarboxylic acid derivatives.



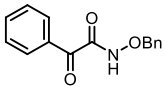
Scheme S2. Control experiments with carboxylic acid derivative.

10. Kornblum-DelaMare rearrangement α-peroxyamides



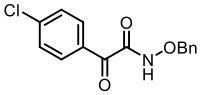
To a solution of α-peroxyhydroxamate in dry CH_3CN (0.2 M) was added DBU (1.0 eq), and the reaction mixture was stirred at room temperature for 12 h. The solvent was removed under vacuo and the crude product was purified by flash column chromatography to obtain the α-ketohydroxamates (**48-51**).

*N-(benzyloxy)-2-oxo-2-phenylacetamide (**48**)*



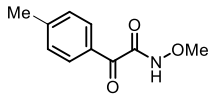
Following the general procedure, compound **30** (0.050 g, 0.15 mmol) was transformed into α-ketohydroxamates **48** and purified by silica gel column chromatography (using 1:3 Acetone: Hexanes as eluent) to give the title compound as colorless oil in 63% (0.024 g) yield. R_f 0.4 (1:3 Acetone/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.25 (d, *J* = 6.5 Hz, 2H), 7.66 - 7.63 (m, 1H), 7.50 -7.44 (m, 4H), 7.40 (d, *J* = 4.8 Hz, 3H), 5.03 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.2, 159.4, 135.0, 134.7, 133.1(2), 129.5, 129.2, 128.9, 128.8, 78.8; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{15}H_{13}NNaO_3$ calcd. 278.0793, found, 278.0788.

*N-(benzyloxy)-2-(4-chlorophenyl)-2-oxoacetamide (**49**)*



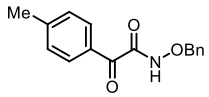
Following the general procedure, compound **32** (0.050 g, 0.14 mmol) was transformed into α-ketohydroxamates **49** and purified by silica gel column chromatography (using 1:3 Acetone: Hexanes as eluent) to give the title compound as colorless oil in 55% (0.022 g) yield. R_f 0.4 (1:3 Acetone/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.22 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 4H), 7.41 - 7.40 (m, 3H), 5.04 (s, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.7, 158.8, 141.8, 134.7, 132.5, 131.4, 129.4, 129.2, 129.1, 128.9, 78.8; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{15}H_{12}NNaO_3$ calcd. 312.0403, found, 312.0396.

*N-methoxy-2-oxo-2-(p-tolyl)acetamide (**50**)*



Following the general procedure, compound **38** (0.050g, 0.19mmol) was transformed into α-ketohydroxamates **50** and purified by silica gel column chromatography (using 1:3 Acetone:Hexanes as eluent) to give the title compound as colorless oil in 55% (0.019 g) yield. R_f 0.4 (1:3 Acetone/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ9.45 (s, 1H), 8.21 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 2.43 (s, 3H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 159.6, 146.4, 131.3, 129.6, 125.2, 64.8, 22.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{10}H_{11}NNaO_3$ calcd. 216.0637, found, 216.0628.

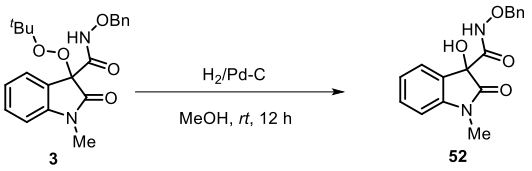
*N-(benzyloxy)-2-oxo-2-(p-tolyl)acetamide (**51**)*



Following the general procedure, compound **31** (0.050 g, 0.15 mmol) was transformed into α-ketohydroxamates **51** and purified by silica gel column chromatography (using 1:3 Acetone: Hexanes as eluent) to give the title compound as colorless oil in 65% (0.025 g) yield. R_f 0.4 (1:3 Acetone/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.17 (d, J = 7.9 Hz, 2H), 7.44 -7.42 (m, 2H), 7.40 - 7.39 (m, 3H), 7.28 (d, J = 7.9 Hz, 2H), 5.02 (s, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 159.7, 146.4, 134.7, 131.2, 130.6, 129.6, 129.5, 129.2, 128.9, 78.8, 22.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{16}H_{15}NNaO_3$ calcd. 292.0950, found, 292.0944.

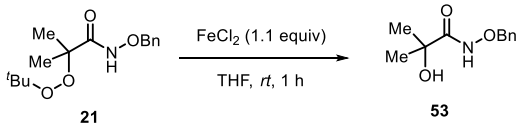
11. Applications:

N-(benzyloxy)-3-hydroxy-1-methyl-2-oxoindoline-3-carboxamide ***(52)***



Palladium on carbon (10% w/w, 15 mg) was added to a solution of 3-Peroxy-3-substituted Oxindole **3** (0.050 g, 0.13 mmol) in MeOH (1.3 mL, 0.1 M) and the reaction mixture was stirred at room temperature under a hydrogen balloon for 12 h. Upon completion of the reaction as determined by the disappearance of starting material, the reaction mixture was filtered through celite and thoroughly washed with eyhylacetate. Then filtrate was concentrated under reduced pressure and the crude product was purified by flash silica gel column chromatography (using 1:1 EtOAc/Hexanes as eluent) to obtain **52** as white foam in 64 % yield (0.026g). R_f 0.2 (2:3 EtOAc/Hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.36 - 7.32 (m, 6H), 7.21 (d, *J* = 6.6 Hz, 1H), 7.09 - 7.04 (m, 1H), 6.81 (d, *J* = 7.1 Hz, 1H), 4.87 (s, 2H), 3.13 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 174.2, 165.9, 144.5, 134.9, 130.9, 129.6, 129.0, 128.6, 127.5, 124.3, 123.7, 109.2, 78.4, 78.1, 26.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{17}H_{16}N_2NaO_4$ calcd. 335.1008, found, 335.1020.

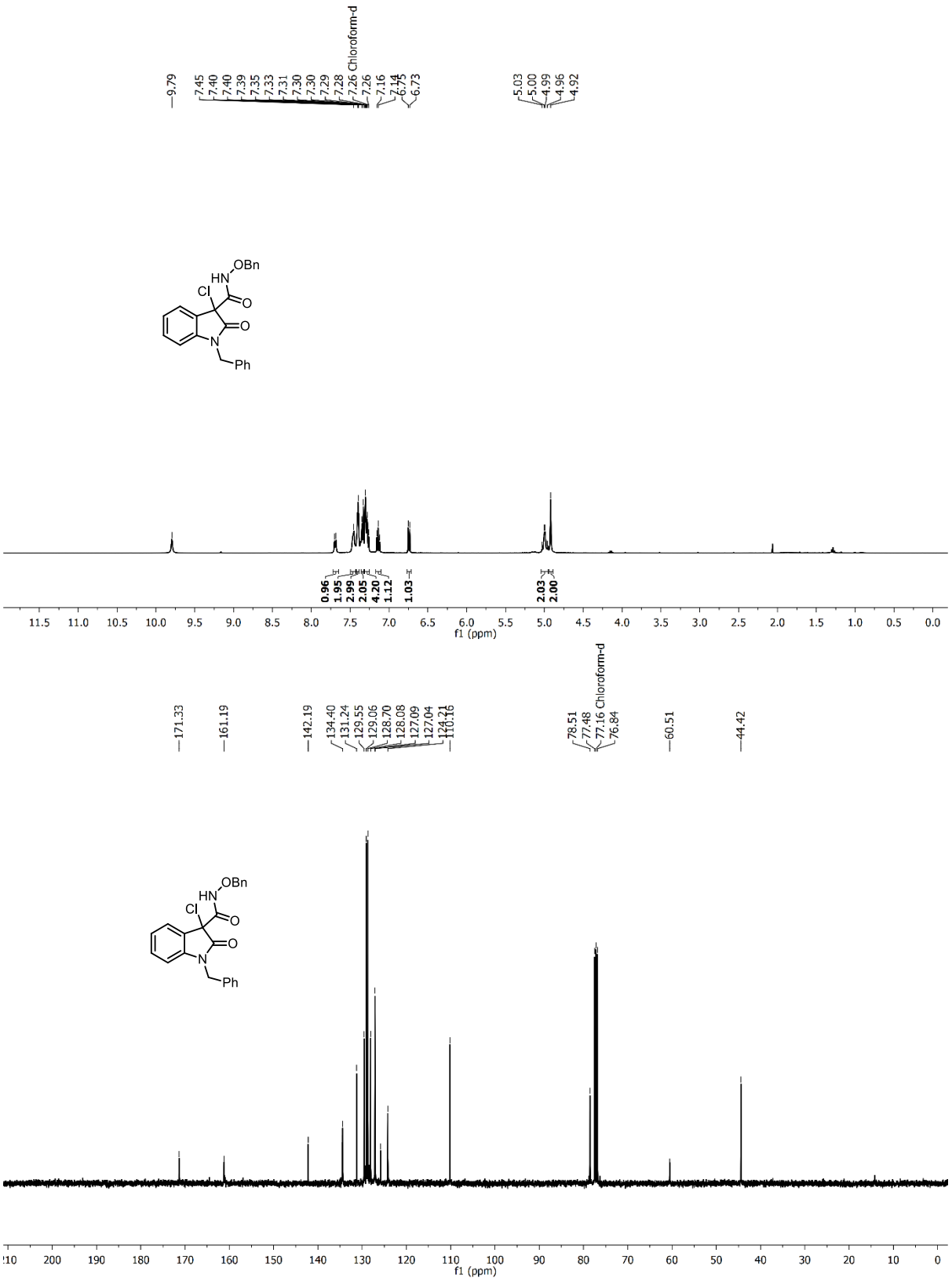
N-(benzyloxy)-2-hydroxy-2-methylpropanamide ***(53)***



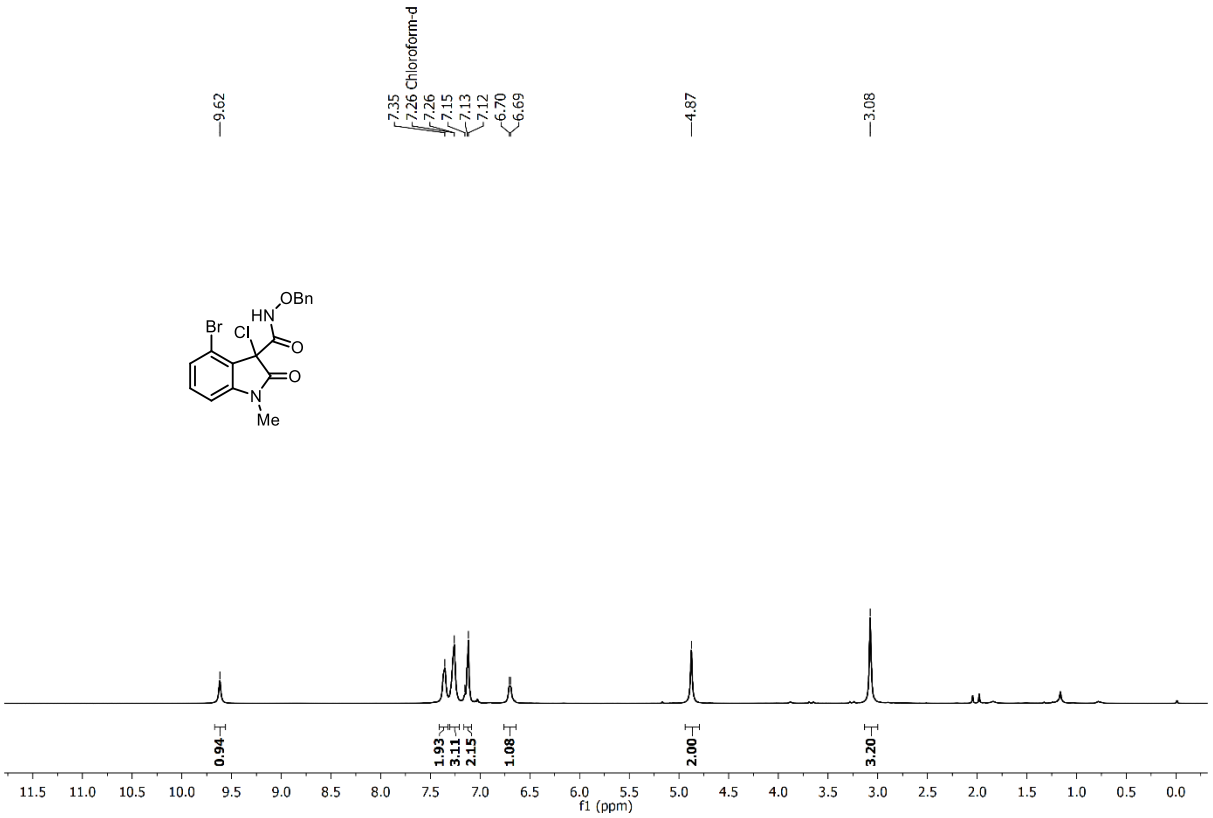
To a solution of α-peroxy amide **21** (0.050 g, 0.18 mmol) in THF (1.8 mL, 0.1 M) under argon was added $FeCl_2$ (0.025 g, 0.20 mmol) and the reaction mixture was stirred at room temperature for 1 h. Upon completion of the reaction as determined by the disappearance of starting material, the reaction solvent was removed under reduced pressure and the crude product was purified by flash silica gel column chromatography (using 3:7 EtOAc/Hexanes as eluent) to obtain **53** as white solid in 72% yield (0.024g). R_f 0.4 (3:7 EtOAc/Hexanes). Compound **53** is reported in the literature and spectral data was matched to that of the reported.[9]

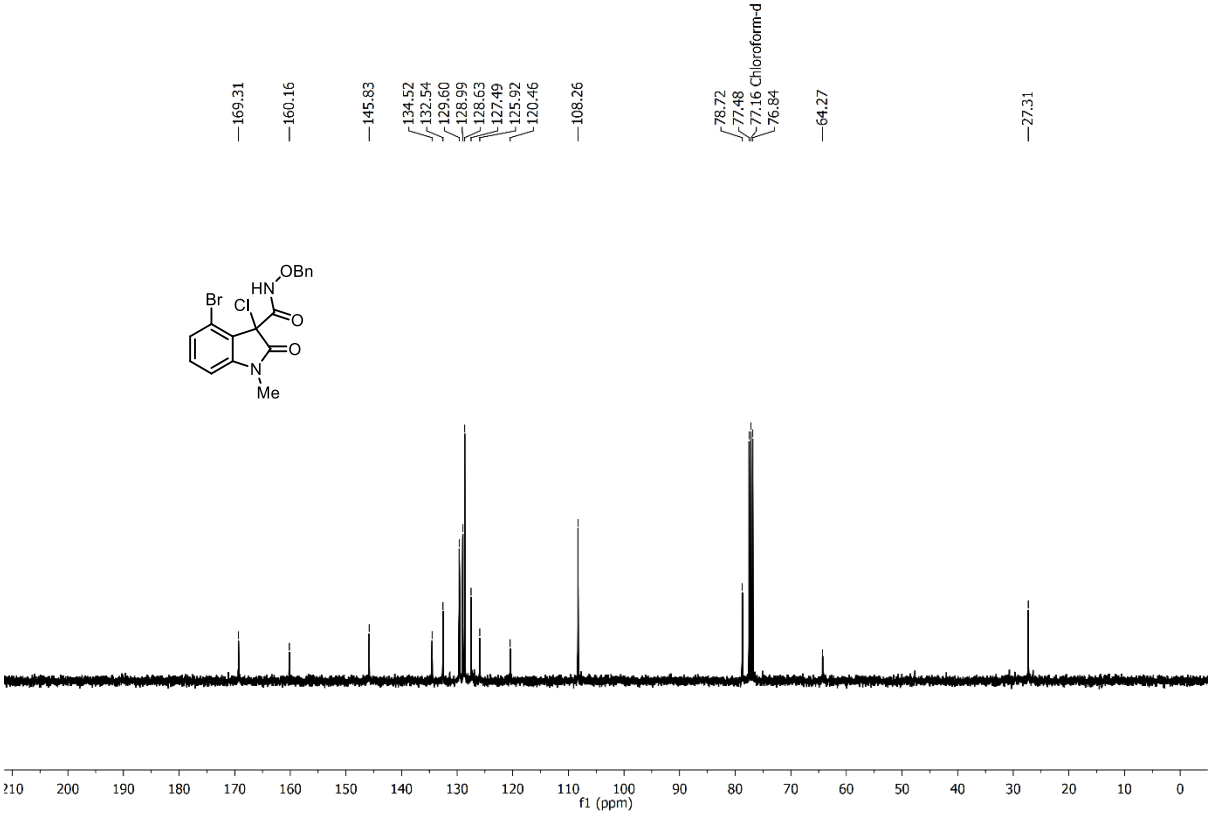
12. NMR Spectra of new compounds

^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1b)***

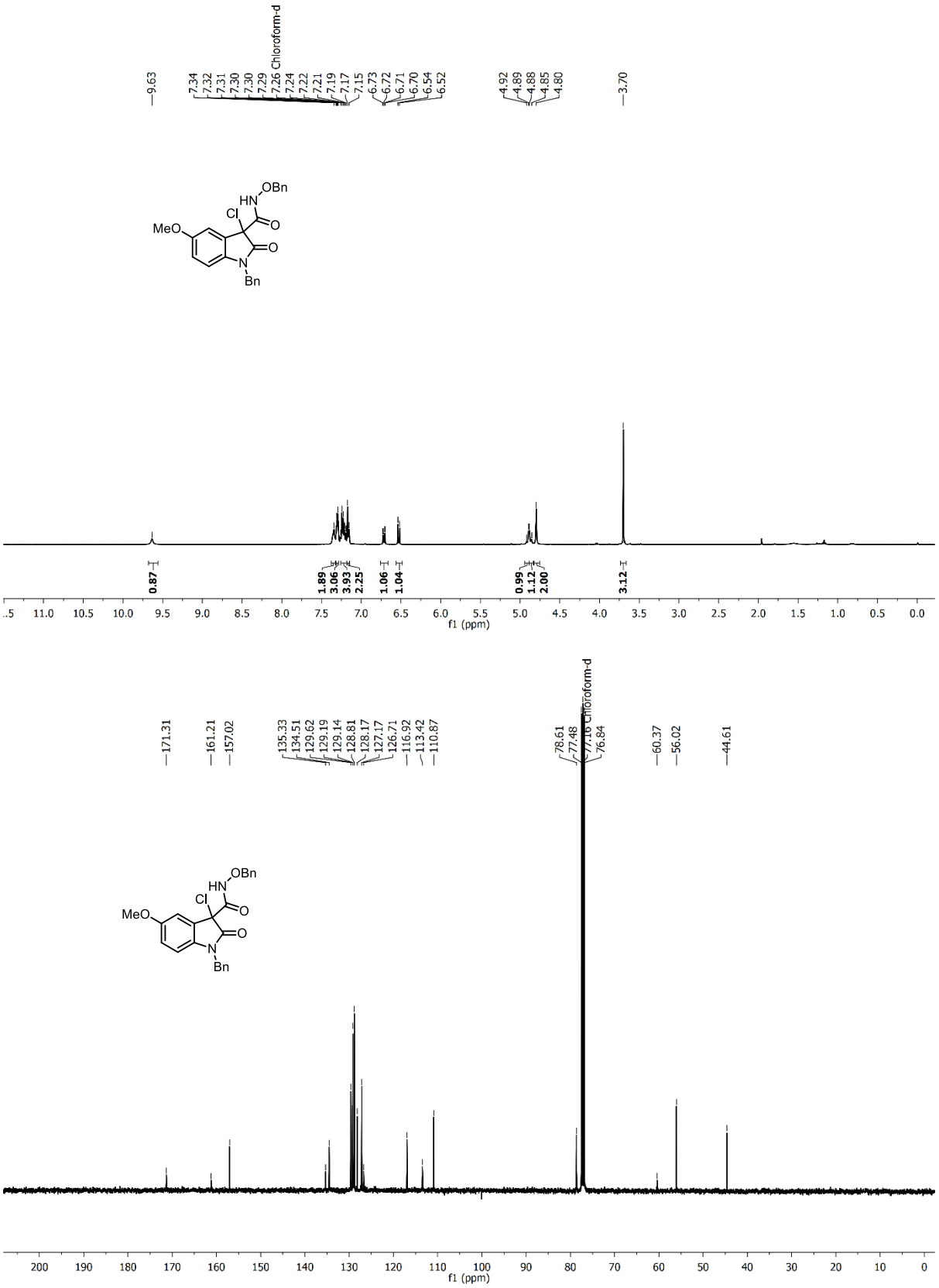


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1d)***

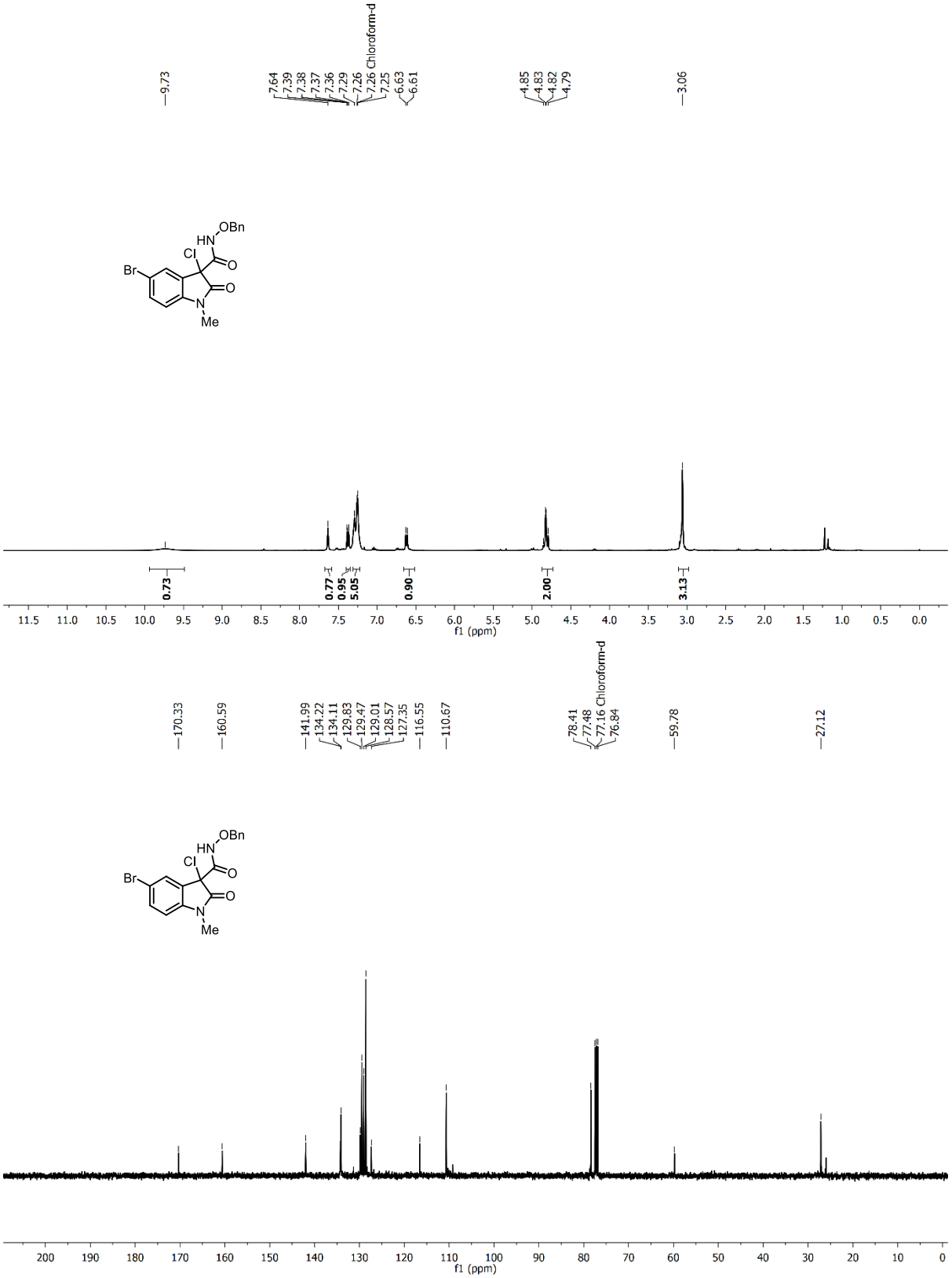




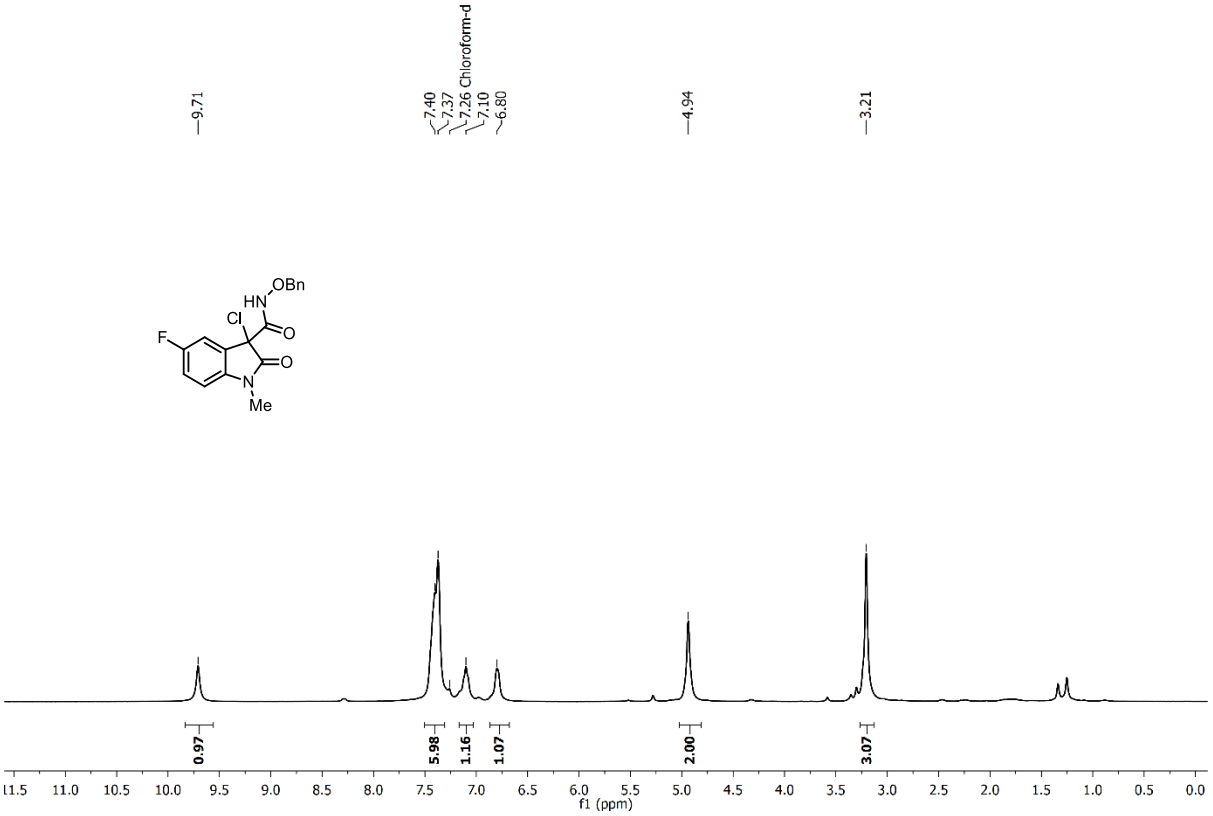
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1f)***

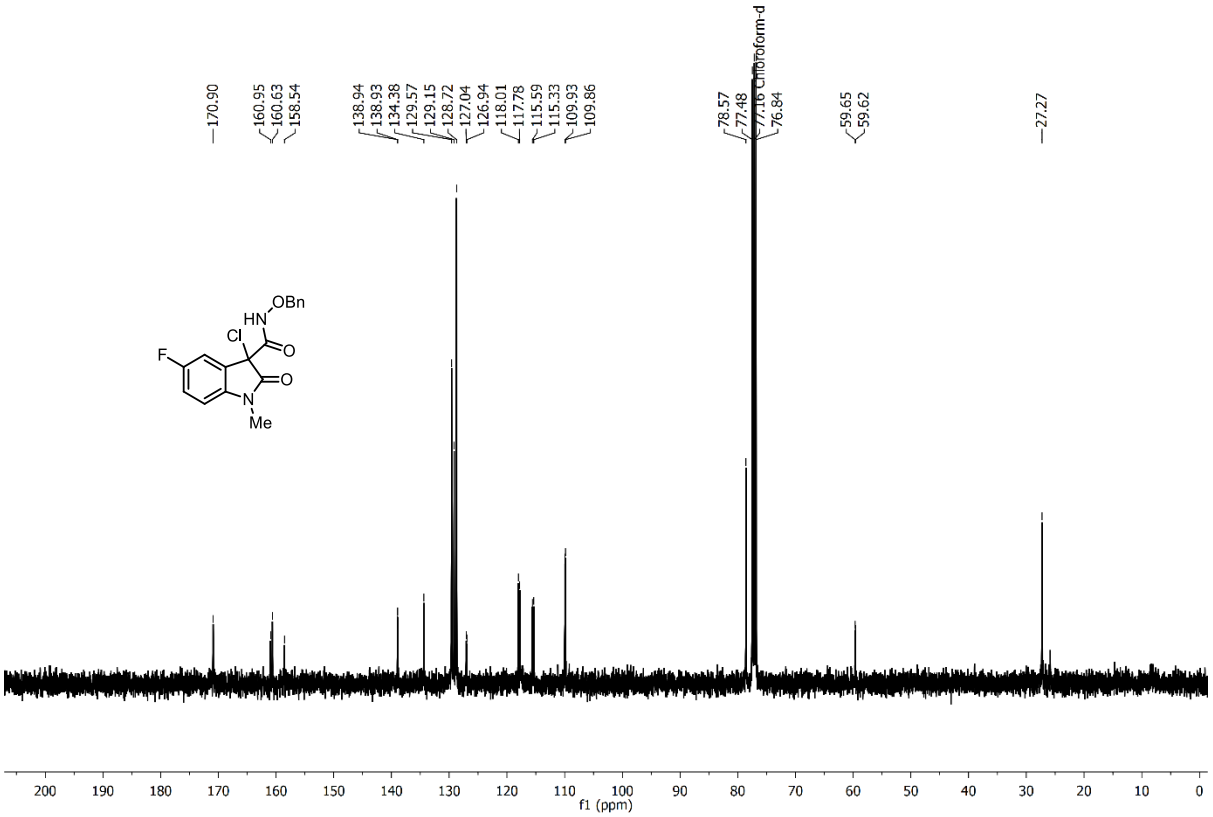


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1g)***

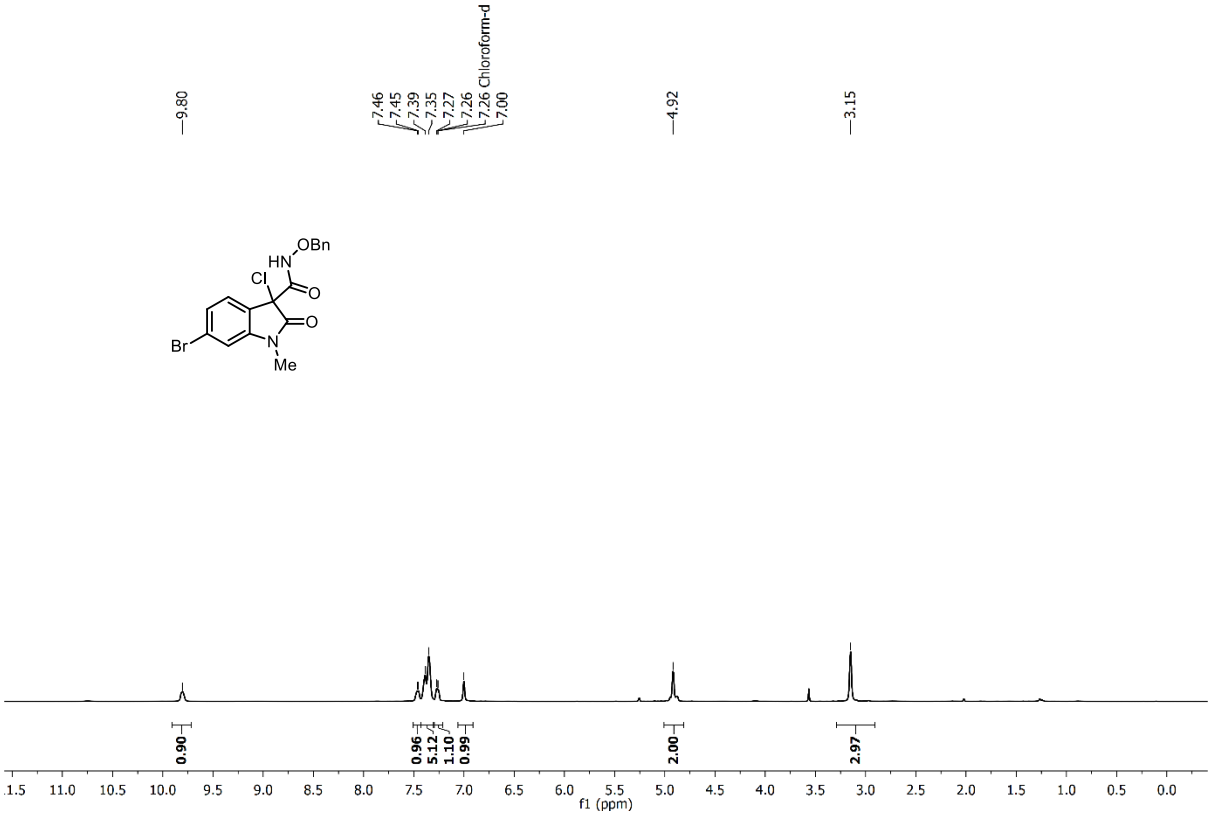


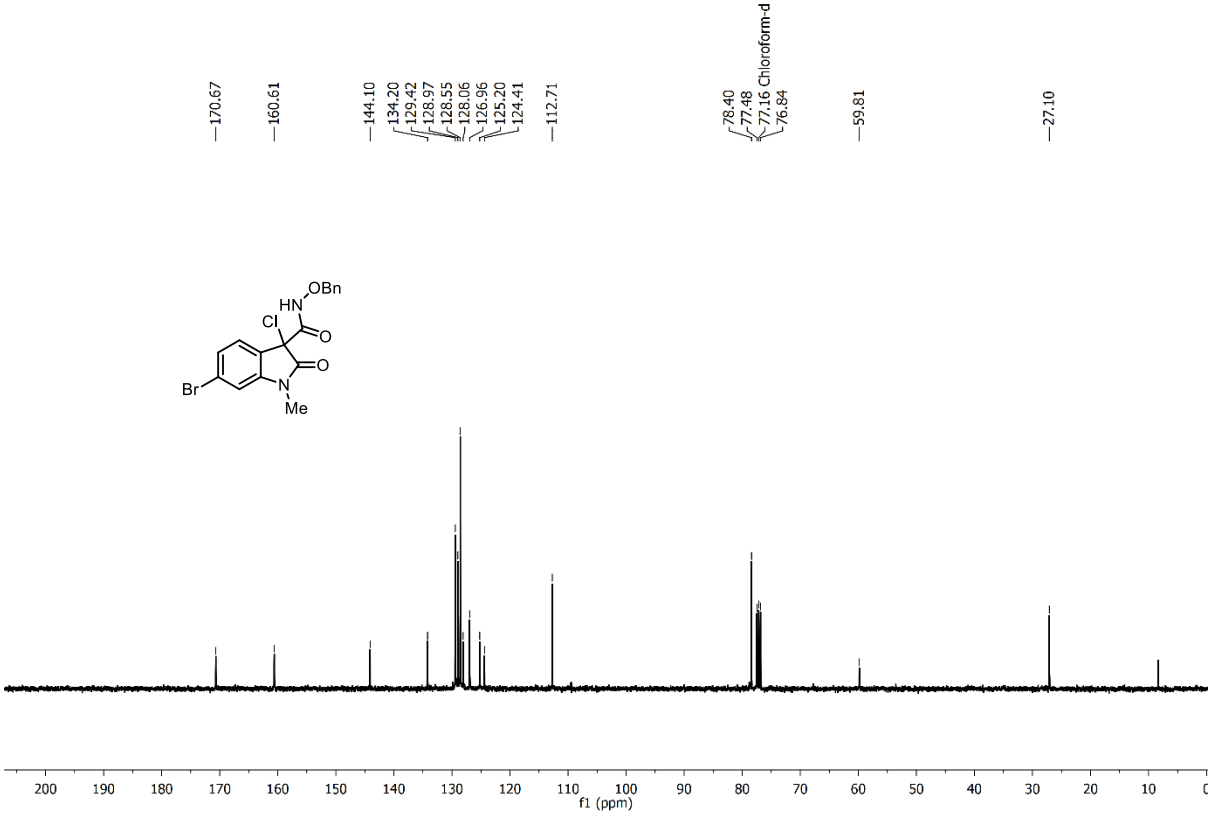
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1h)***



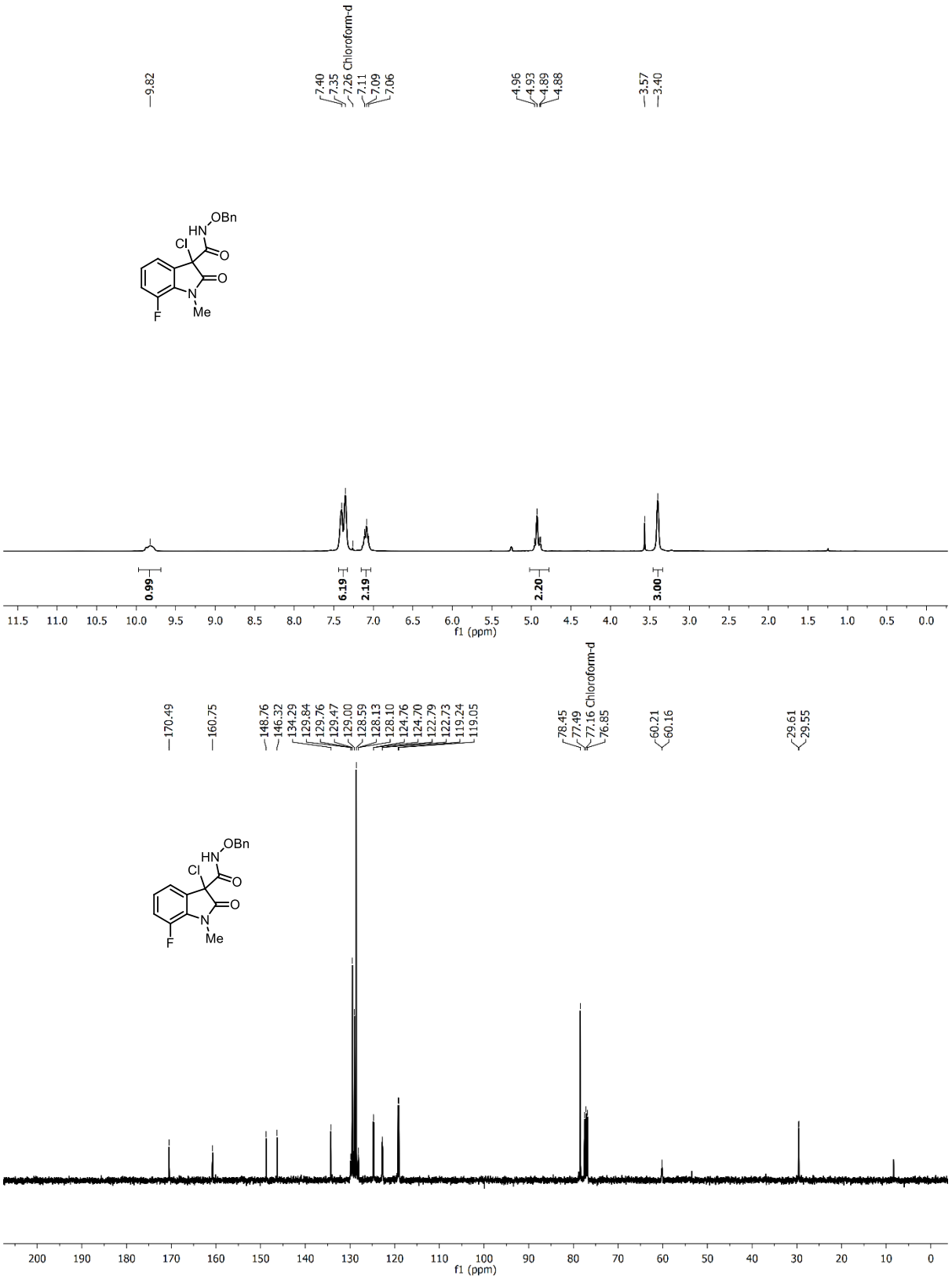


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1i)***

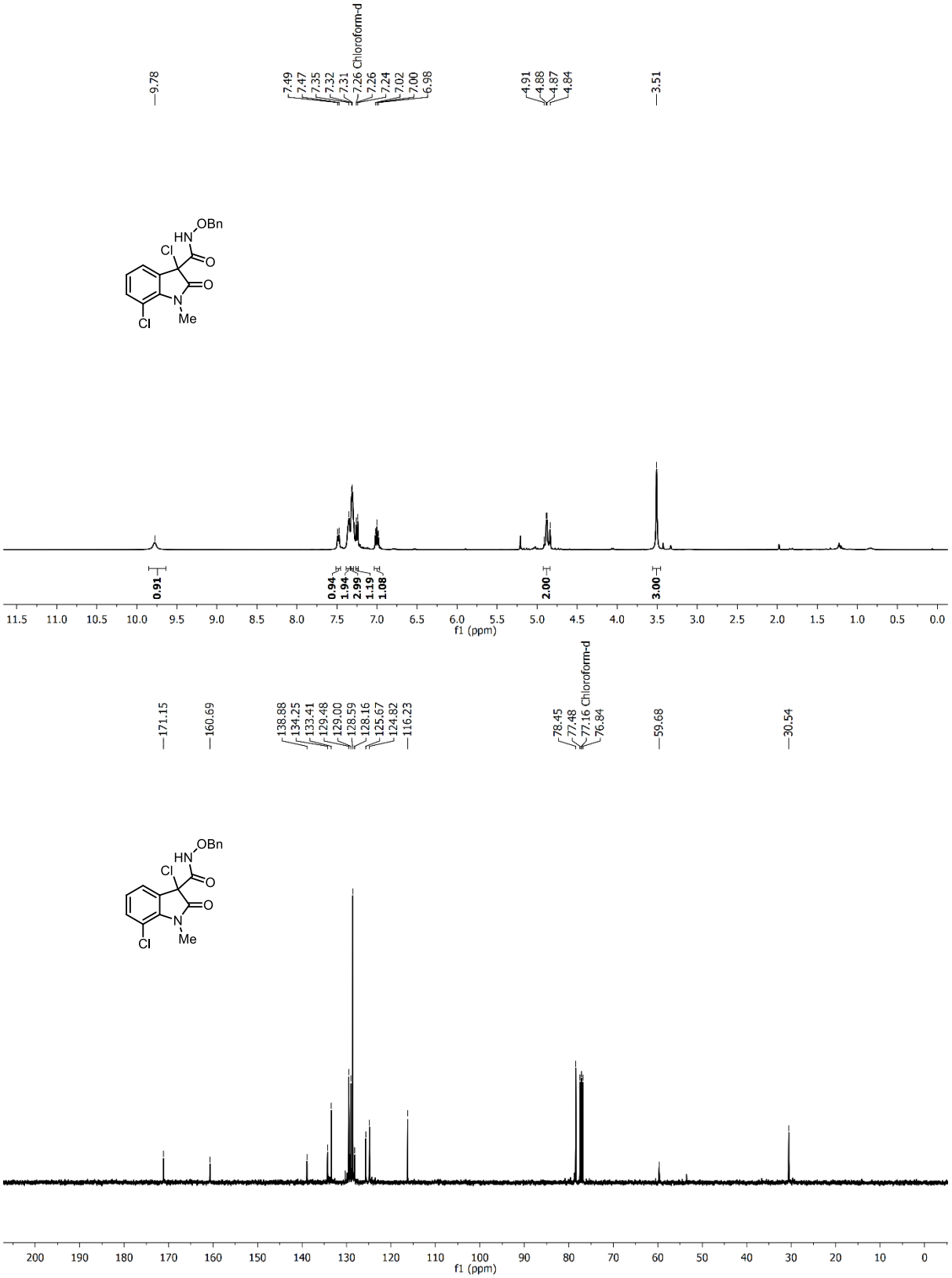




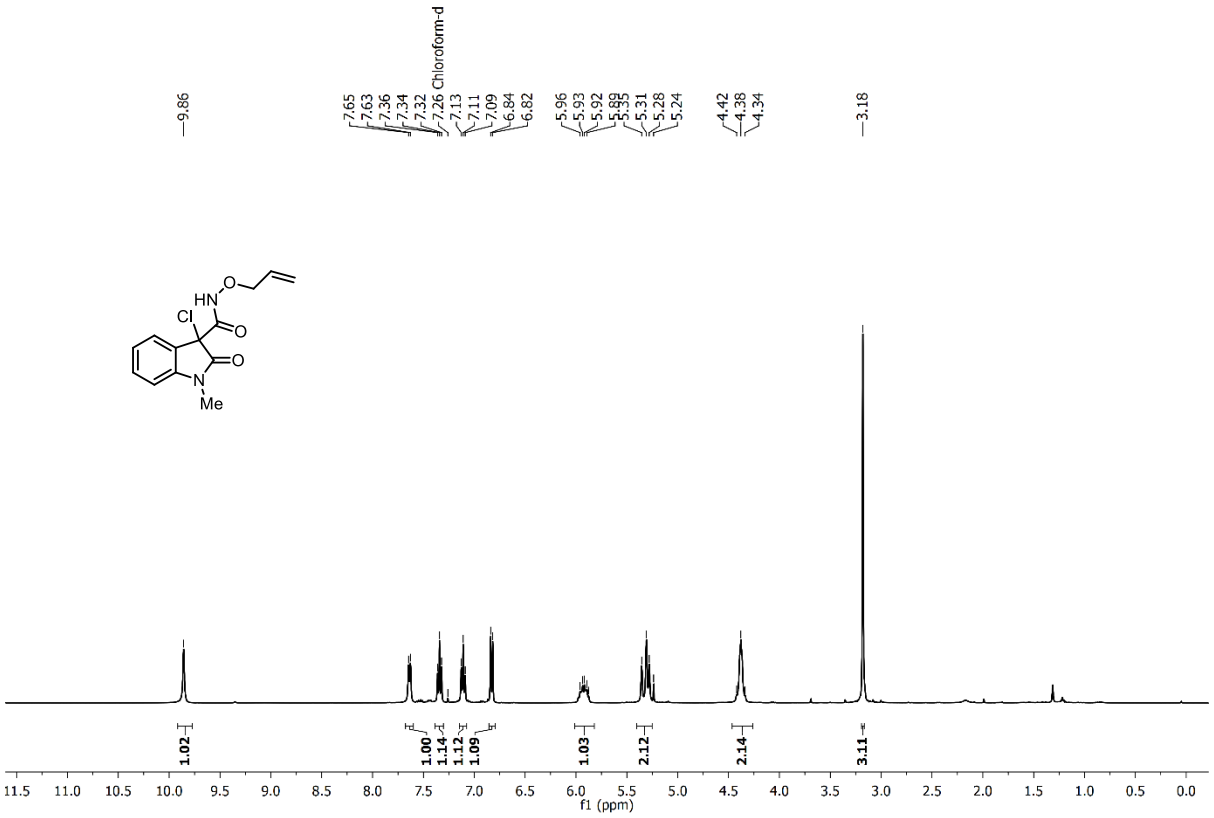
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1j)***

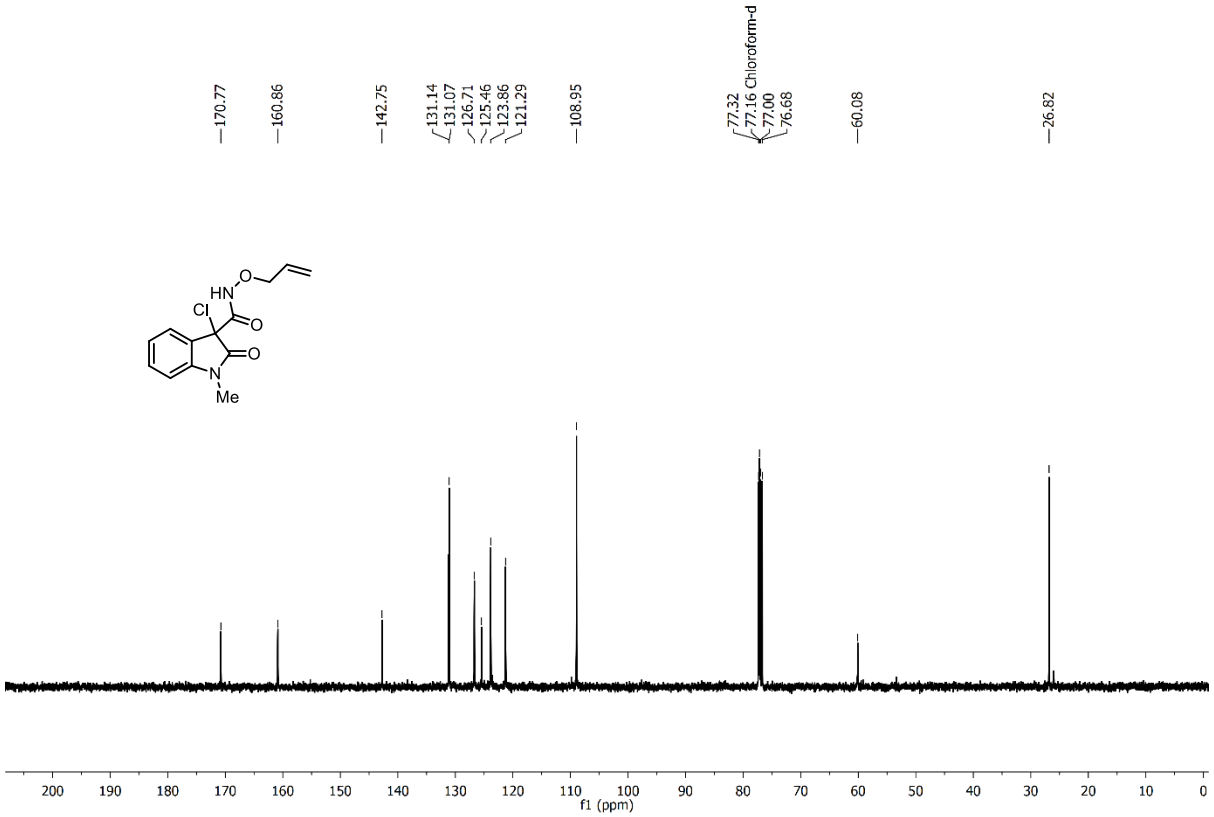


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1k)***

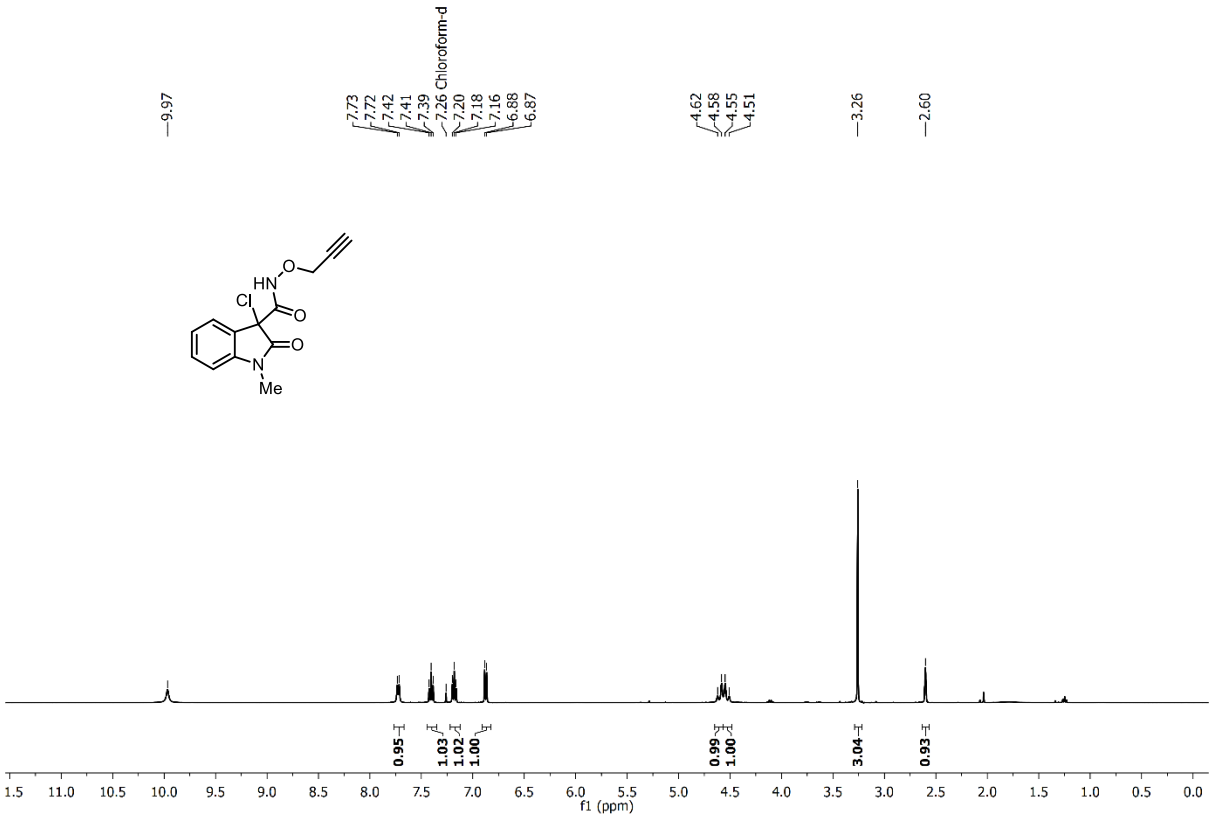


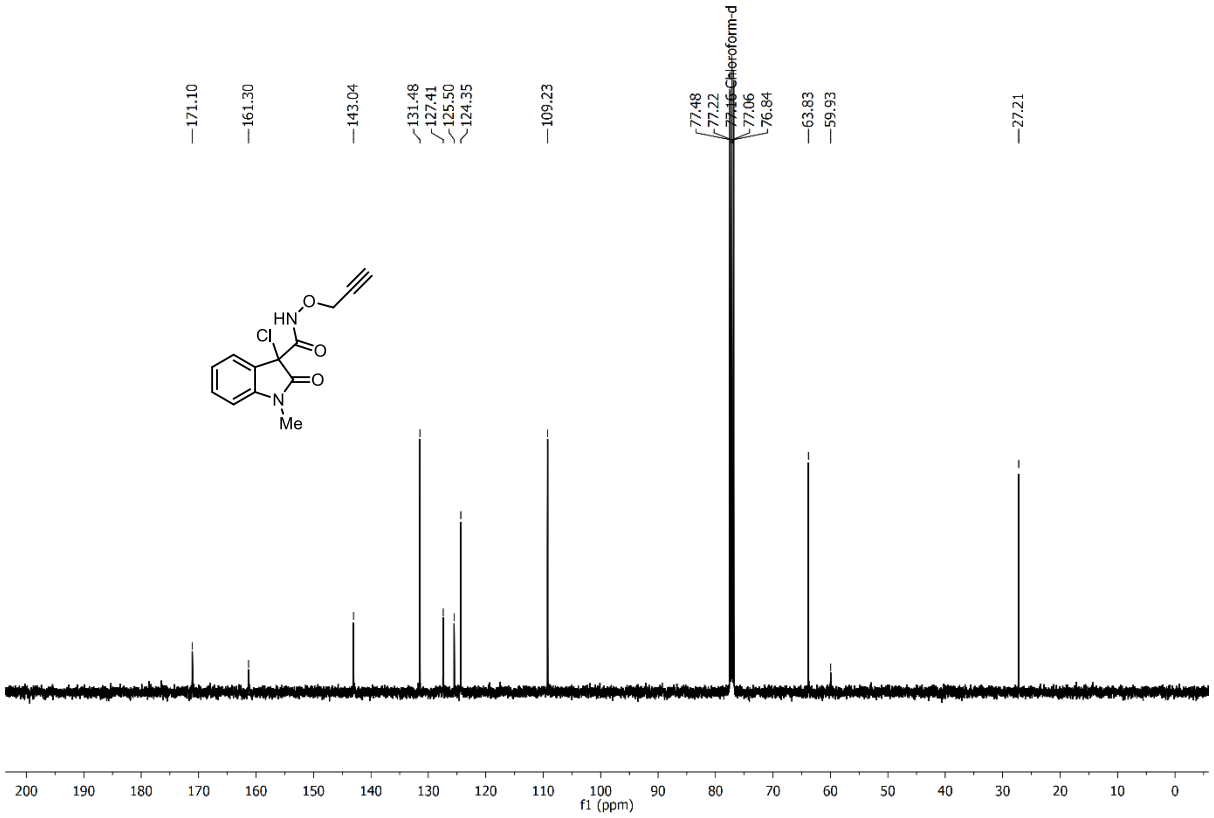
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1l)***



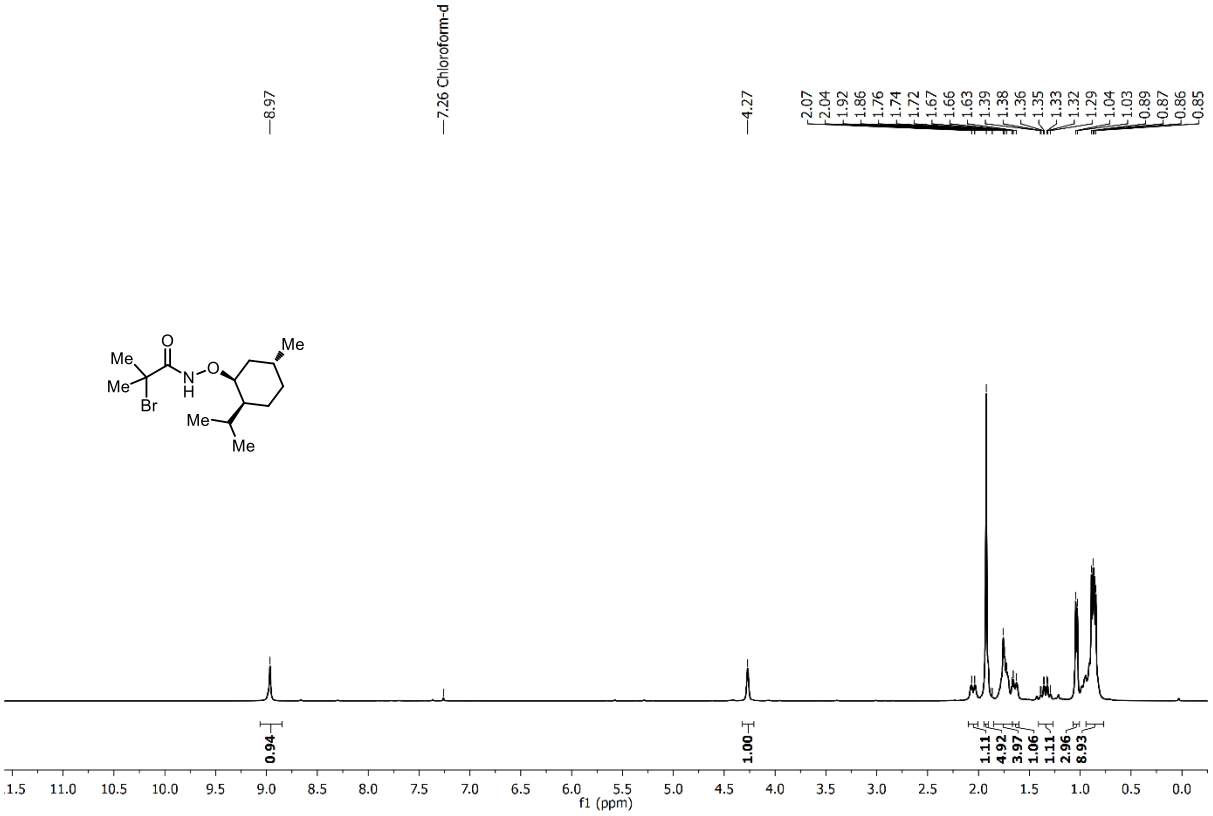


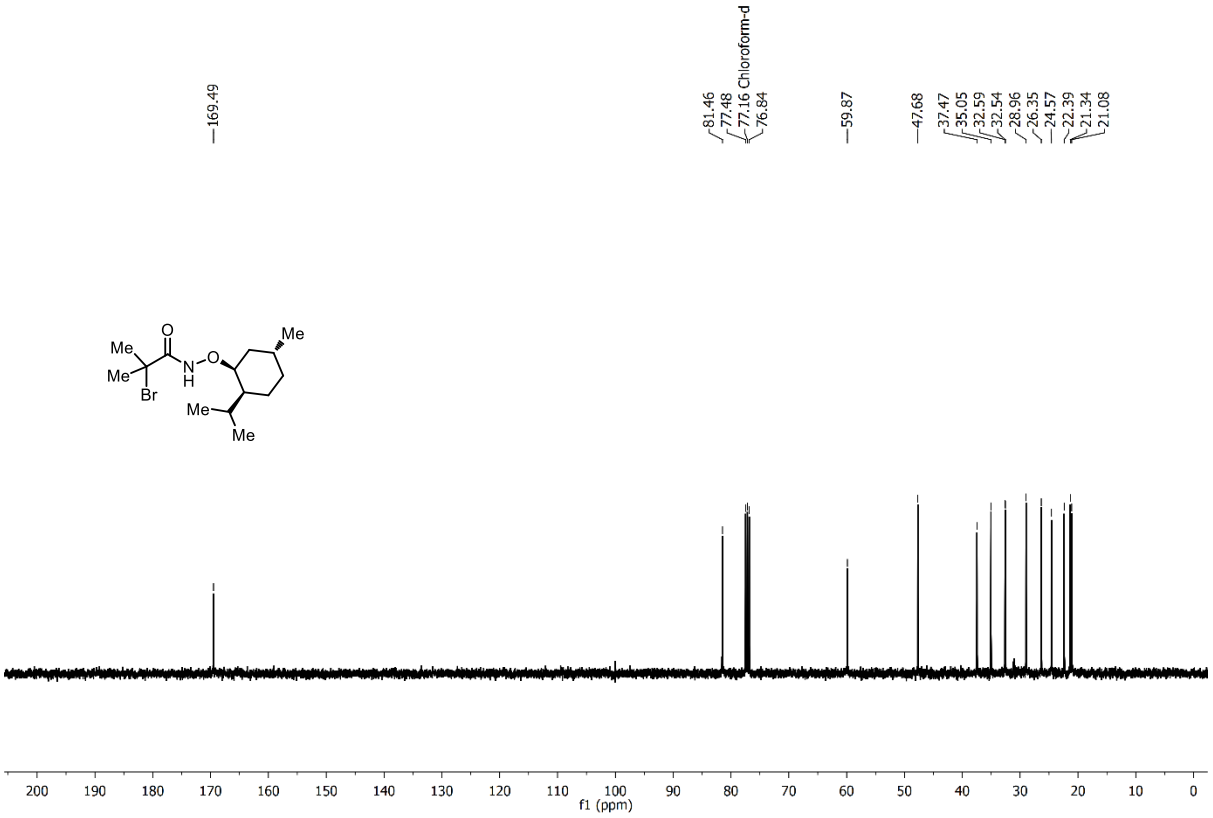
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1m)***



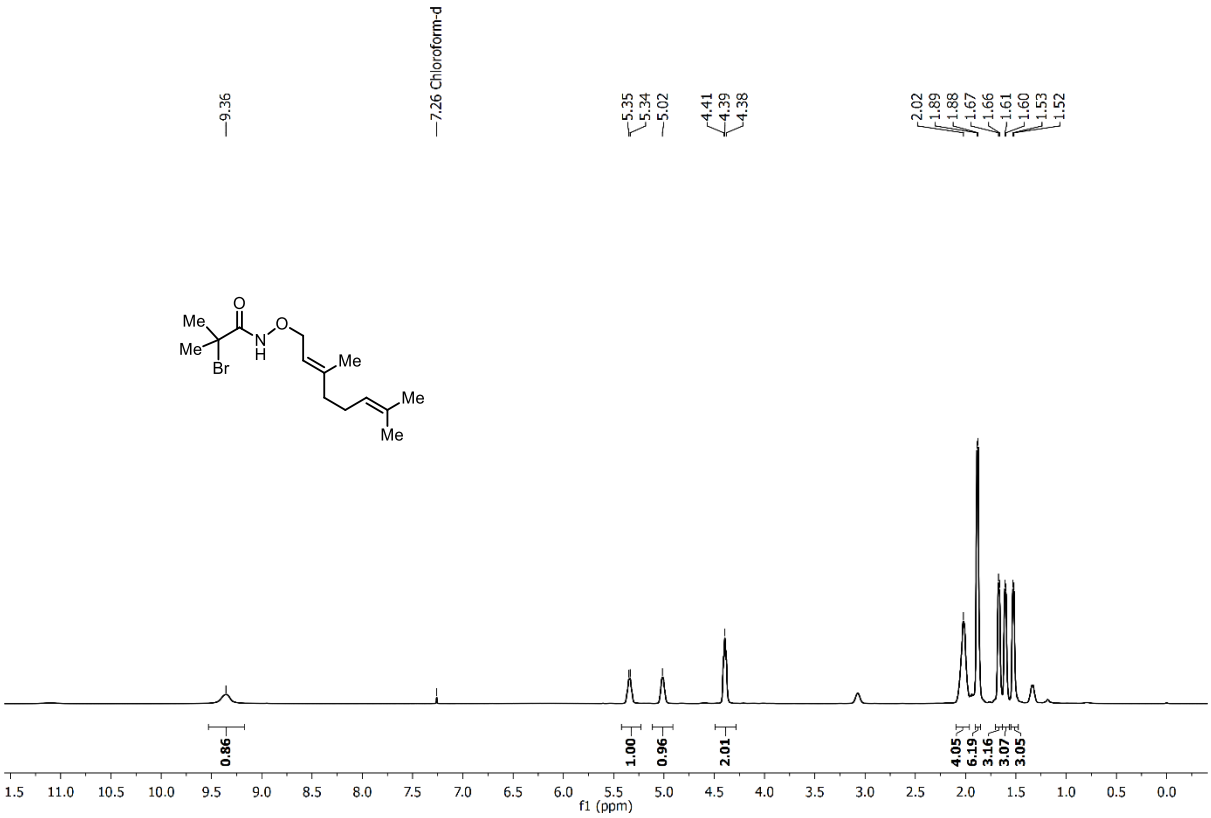


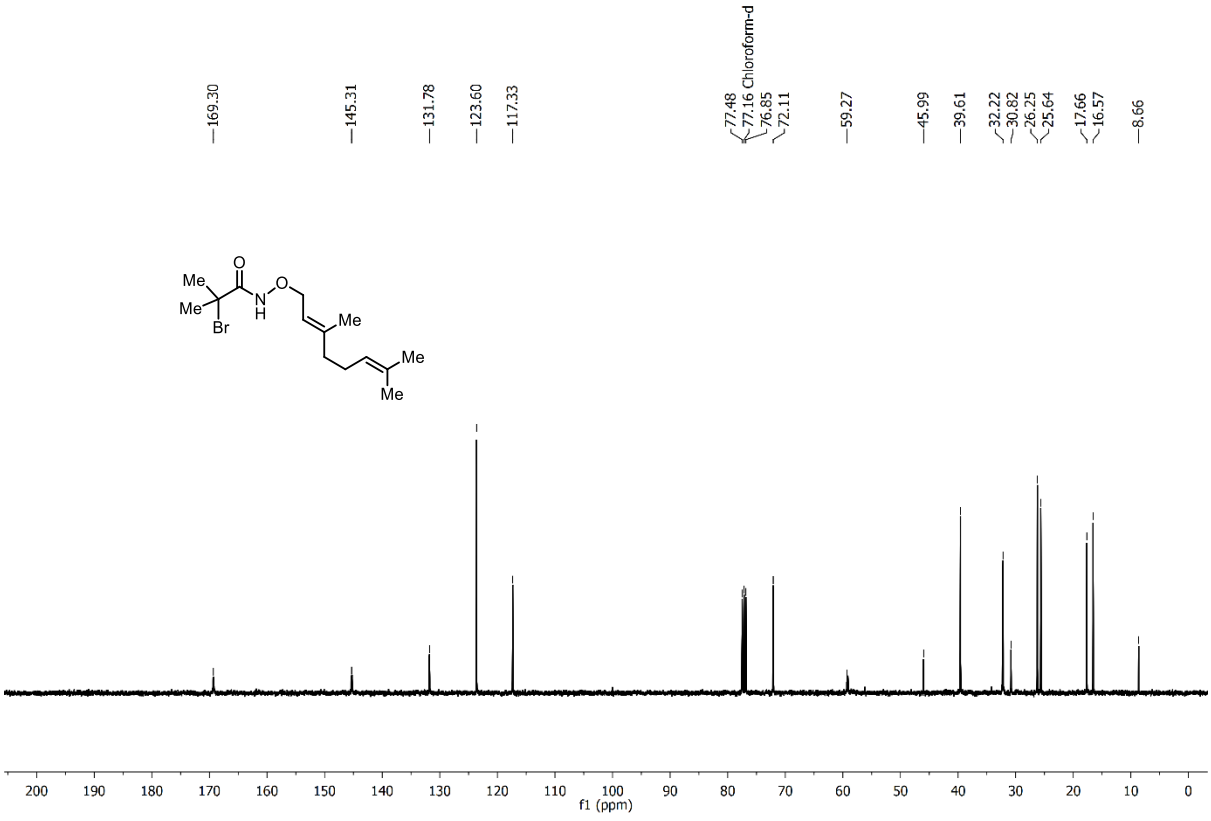
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(20q)***



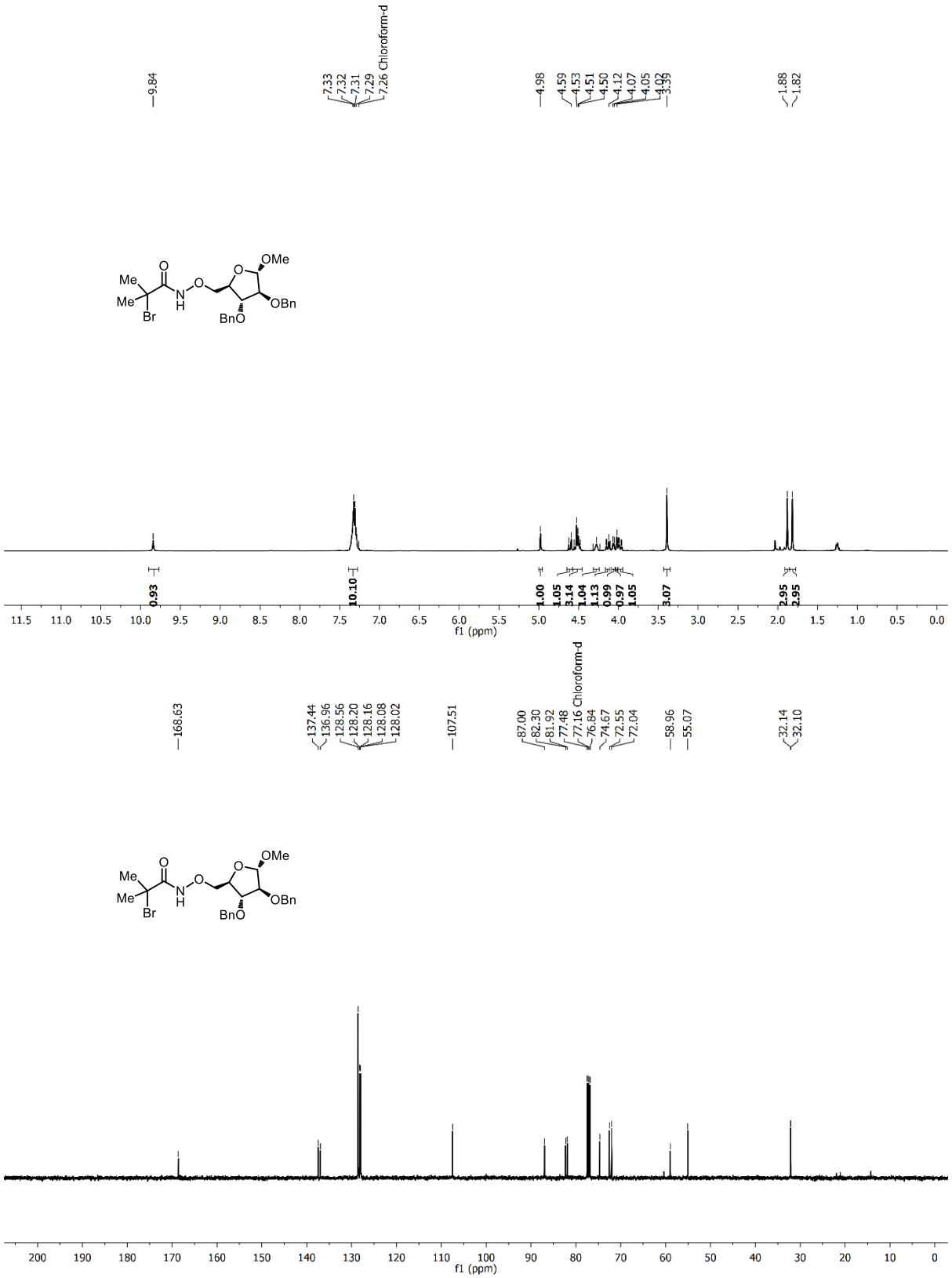


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(20r)***

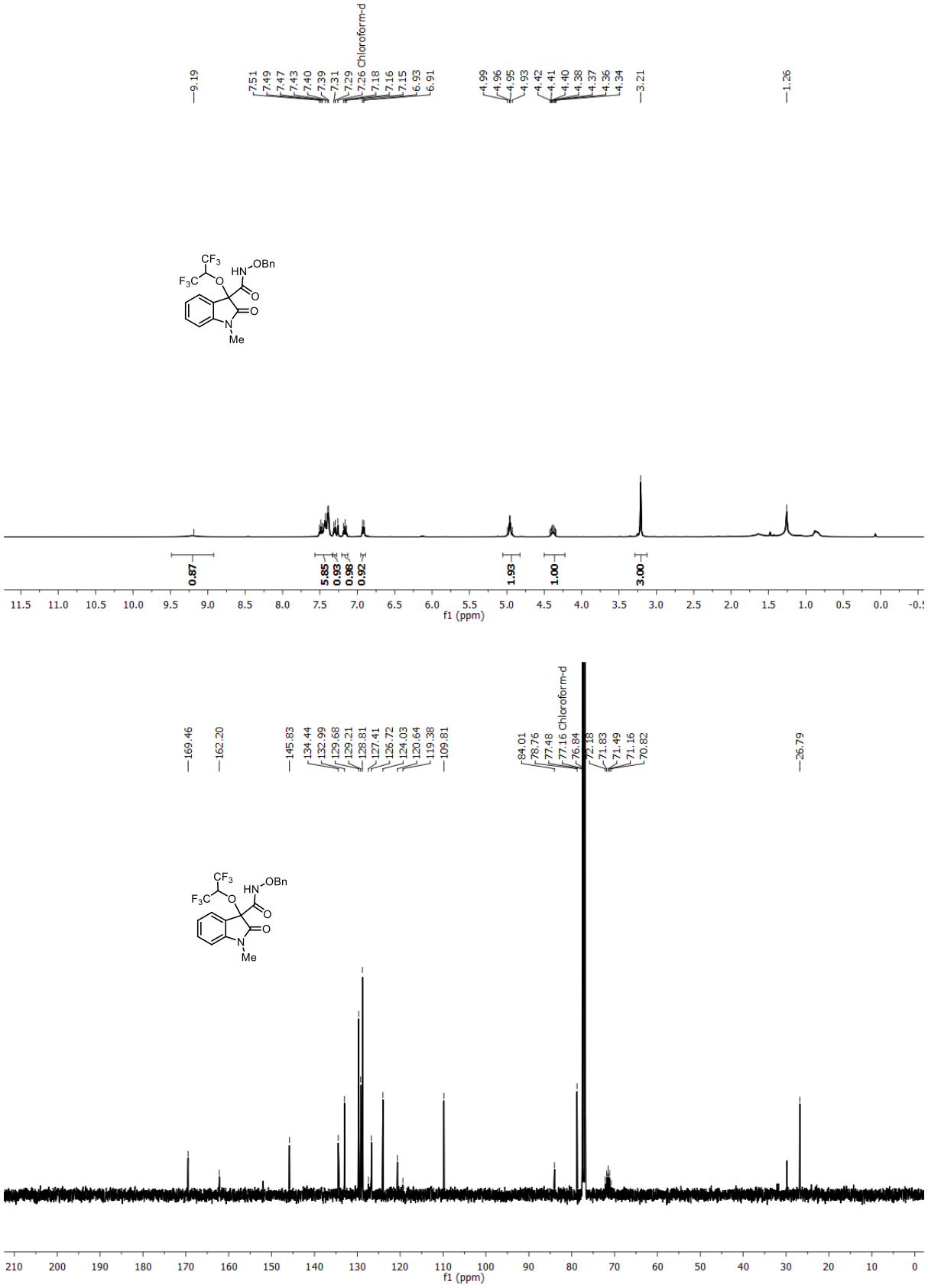




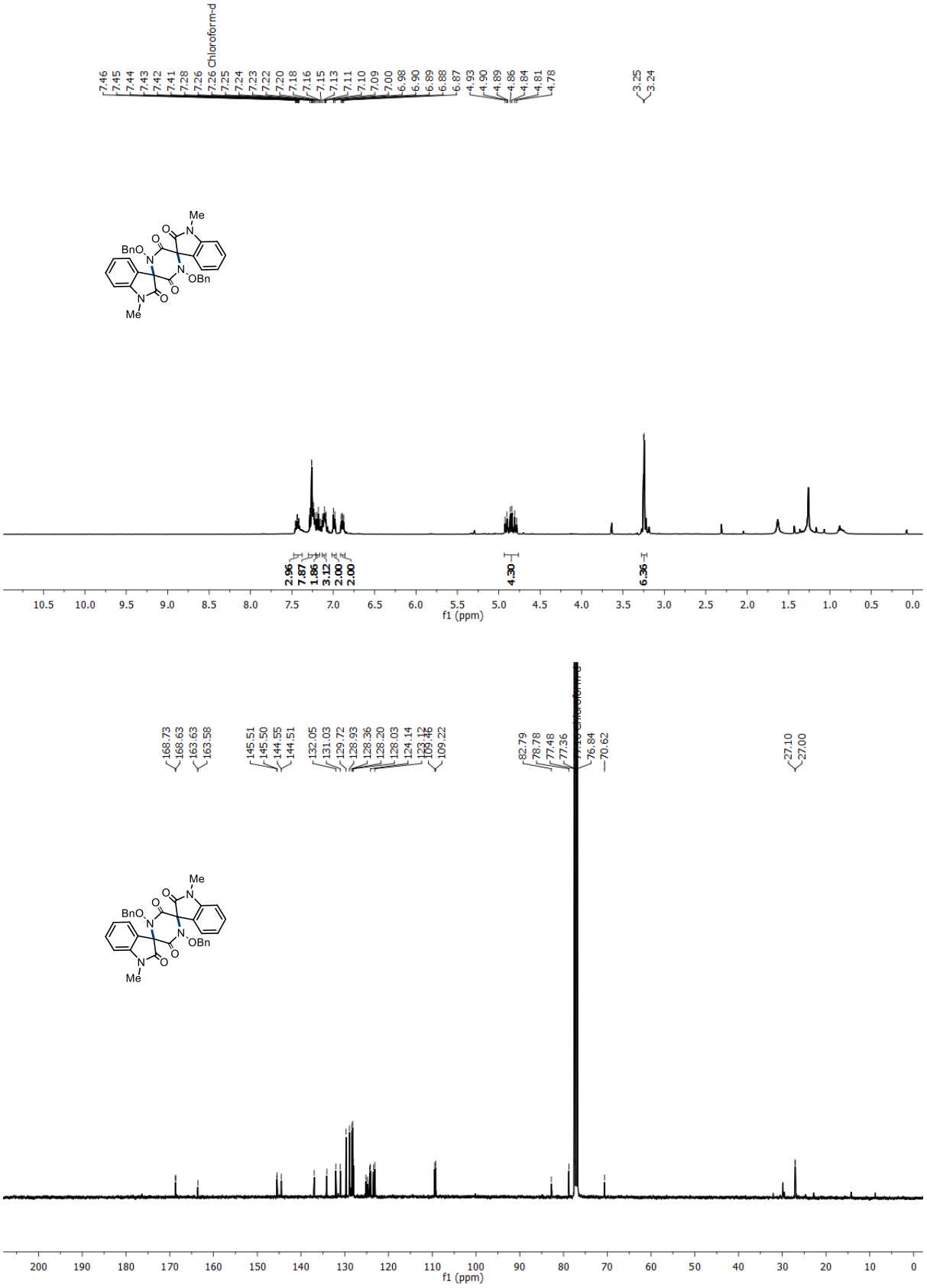
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(20s)***



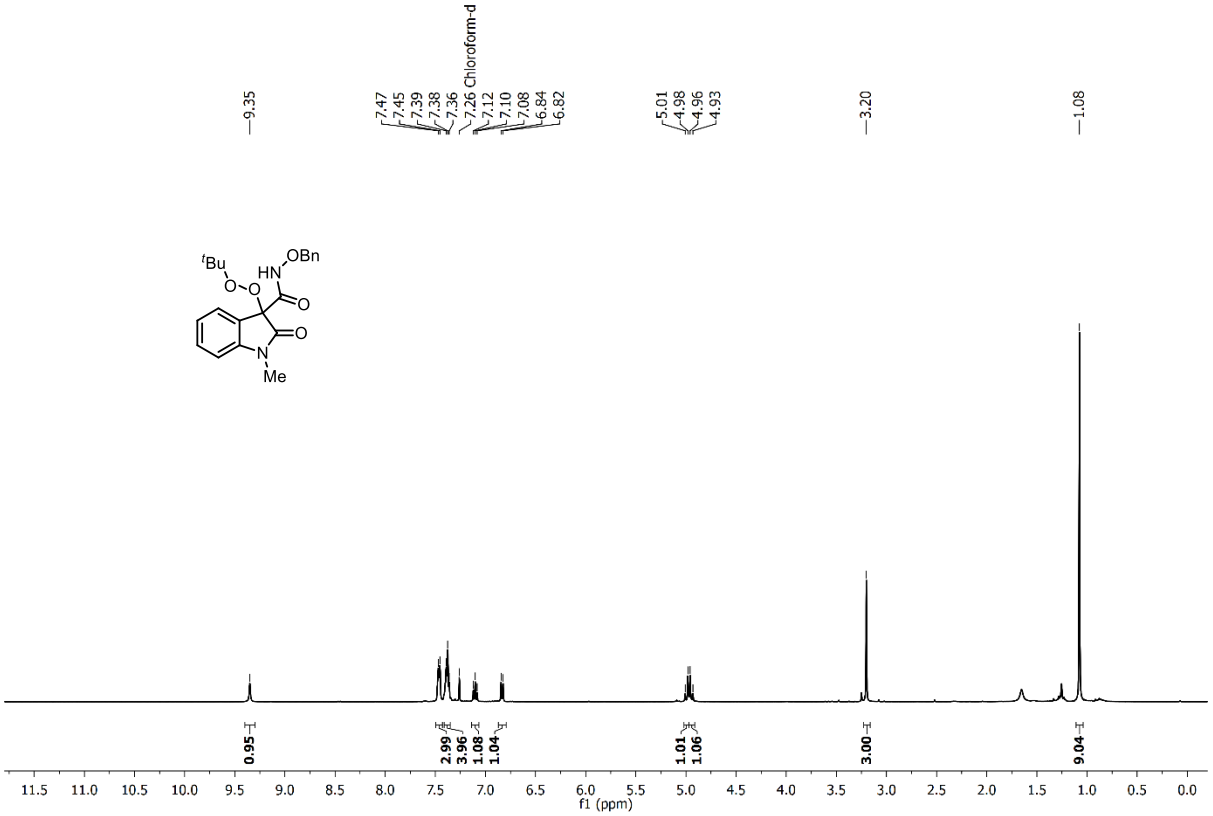
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1a-HFIP)***

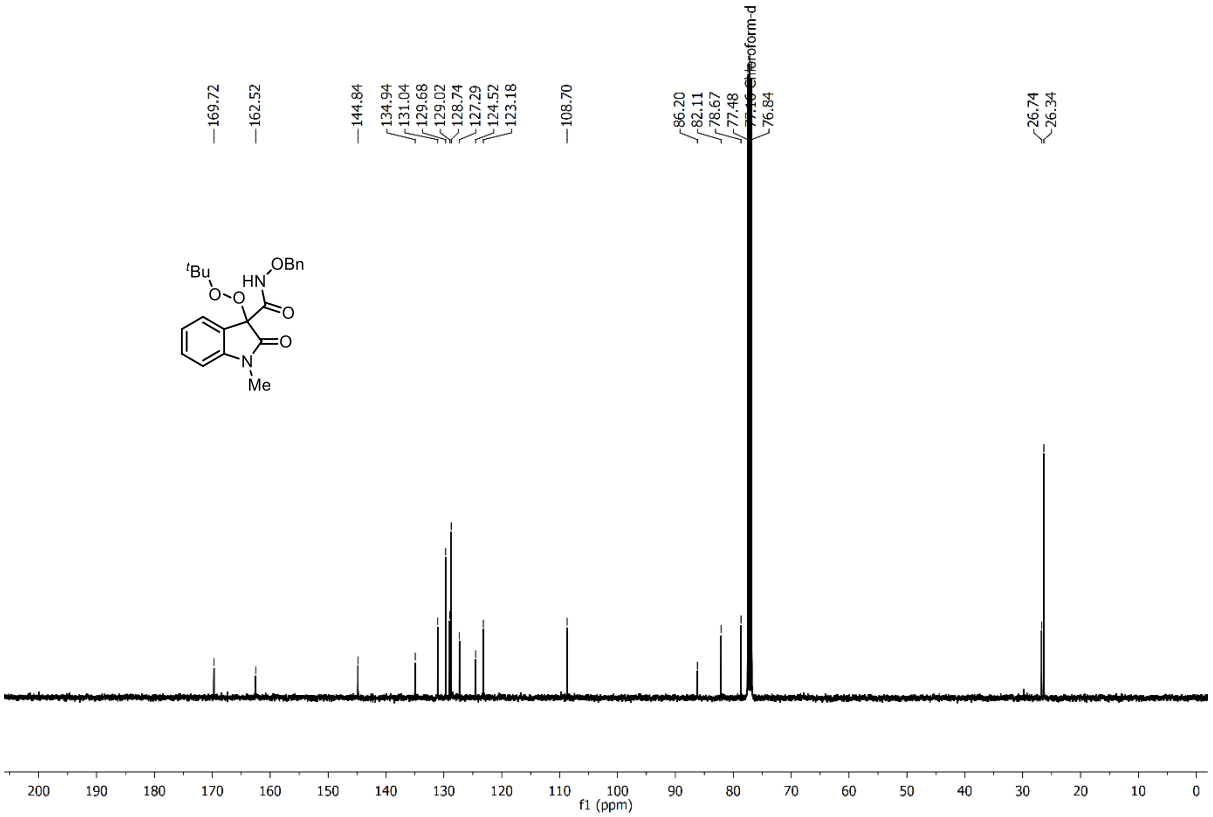


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1a-D)***

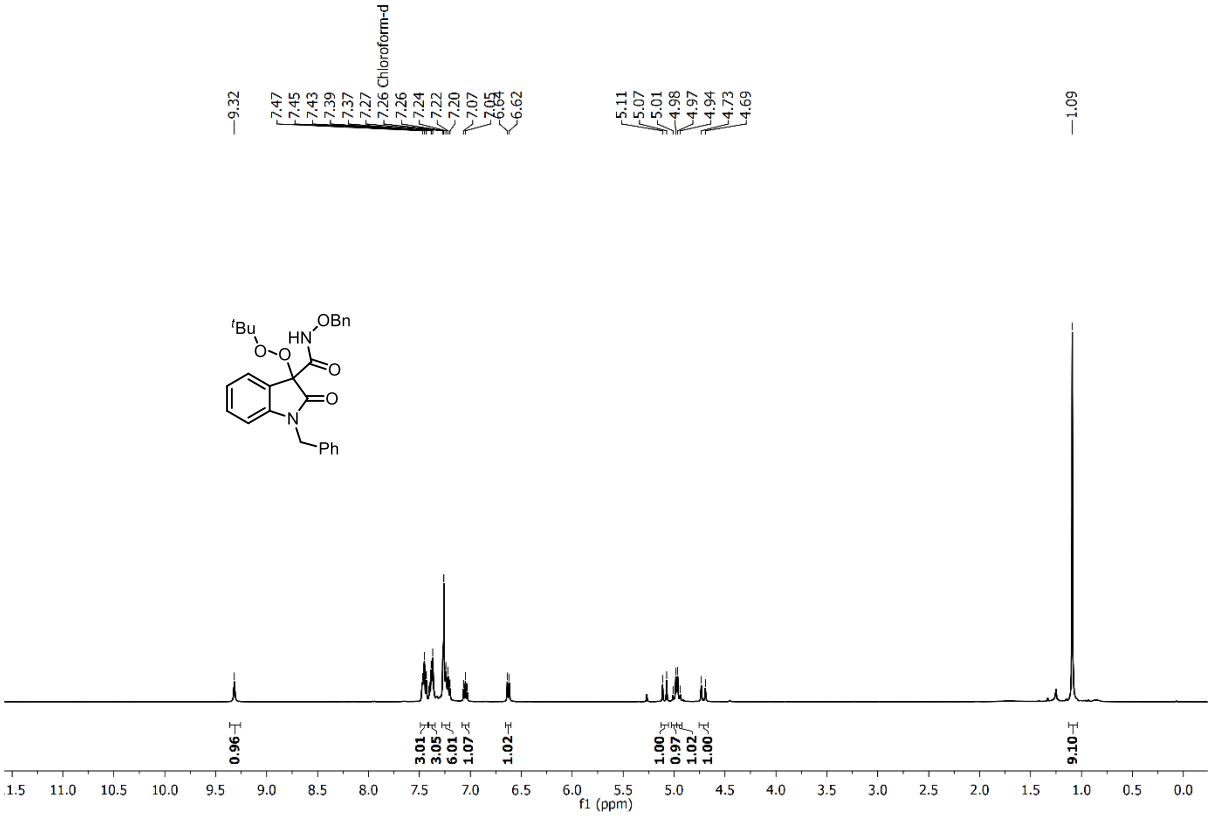


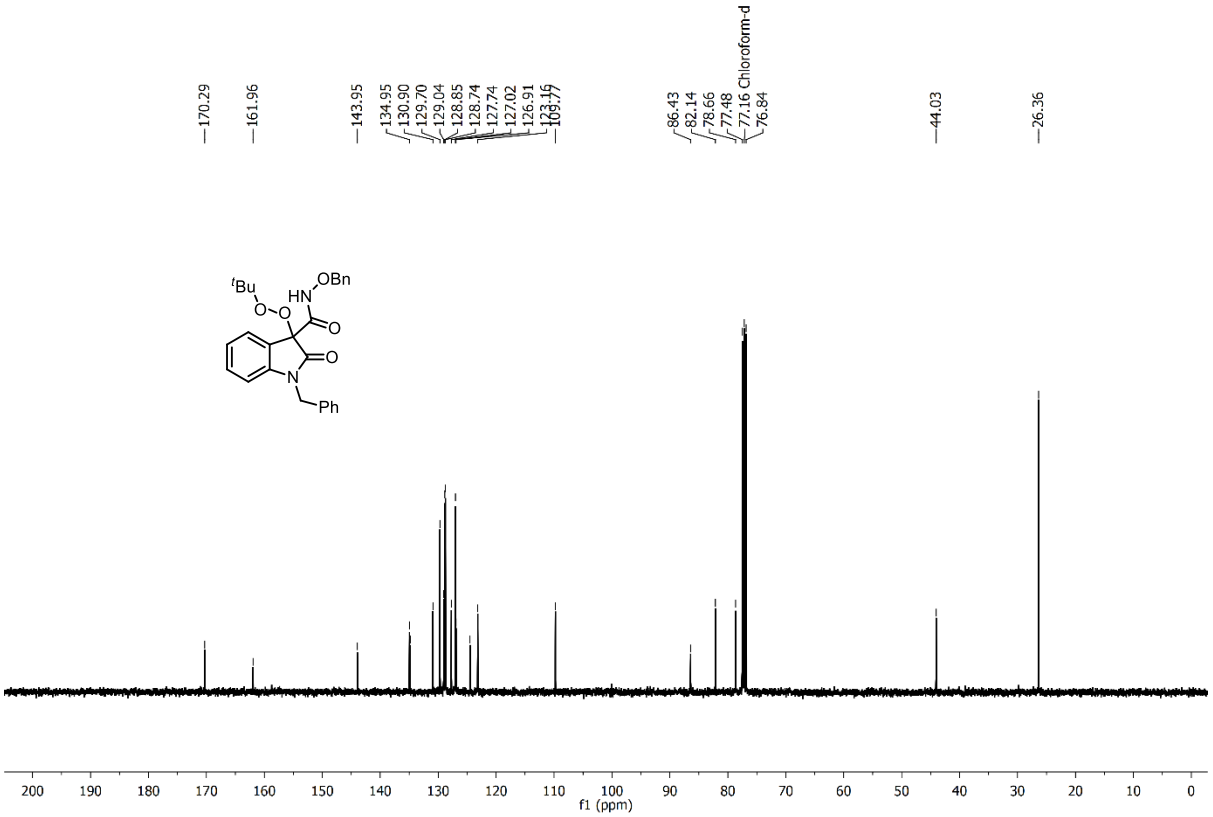
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(3)***



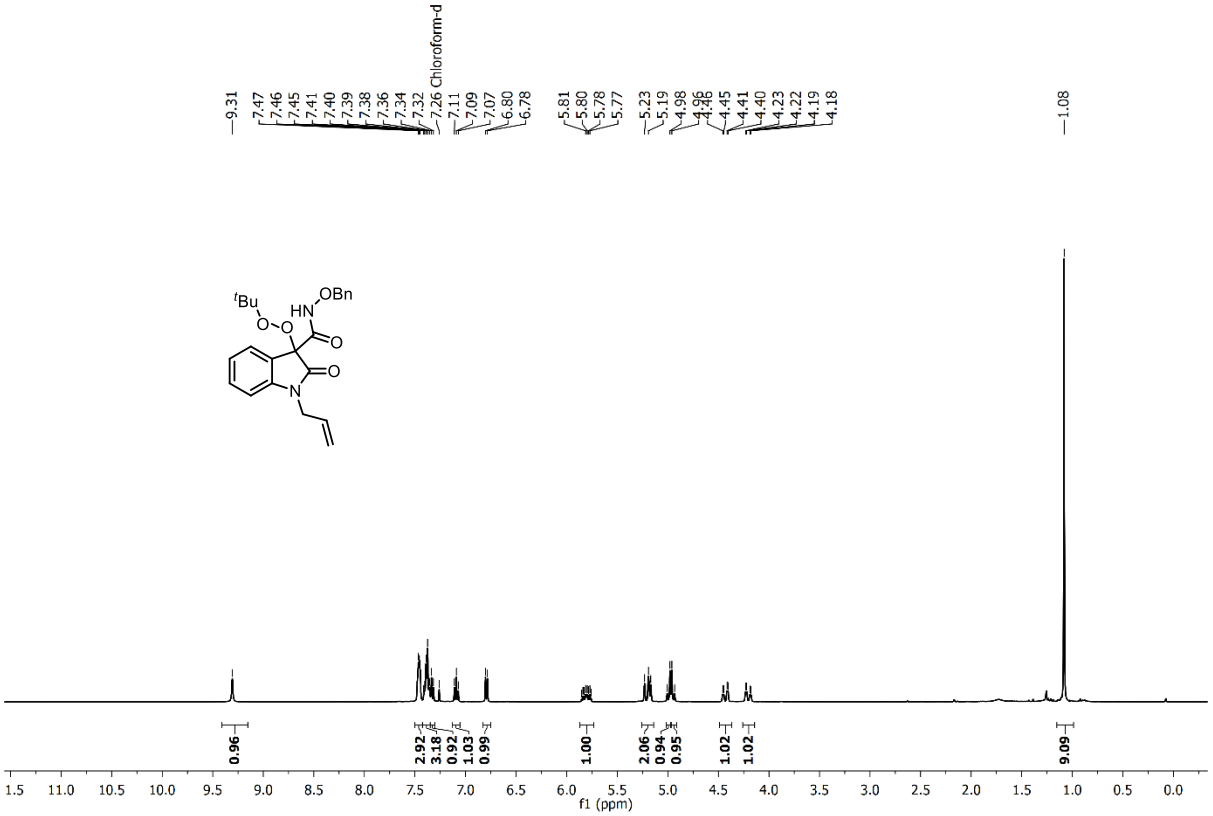


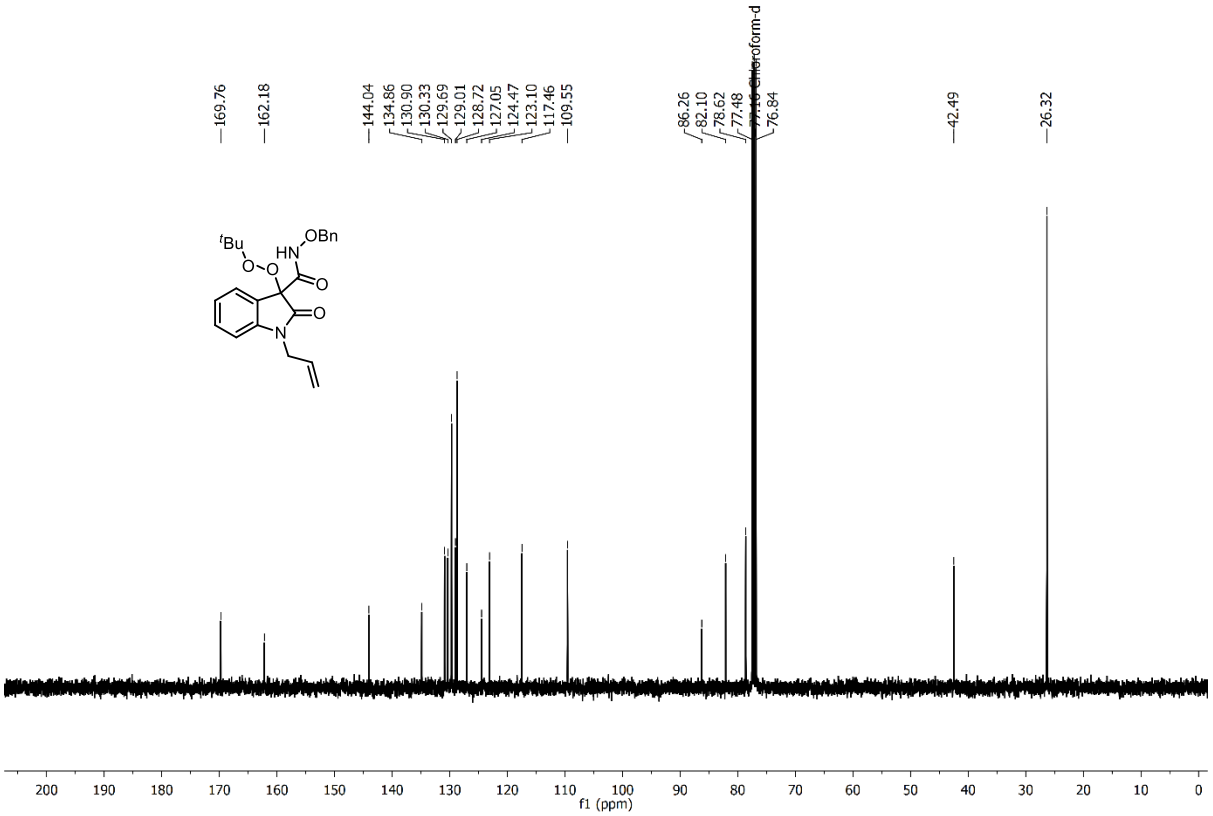
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(4)***



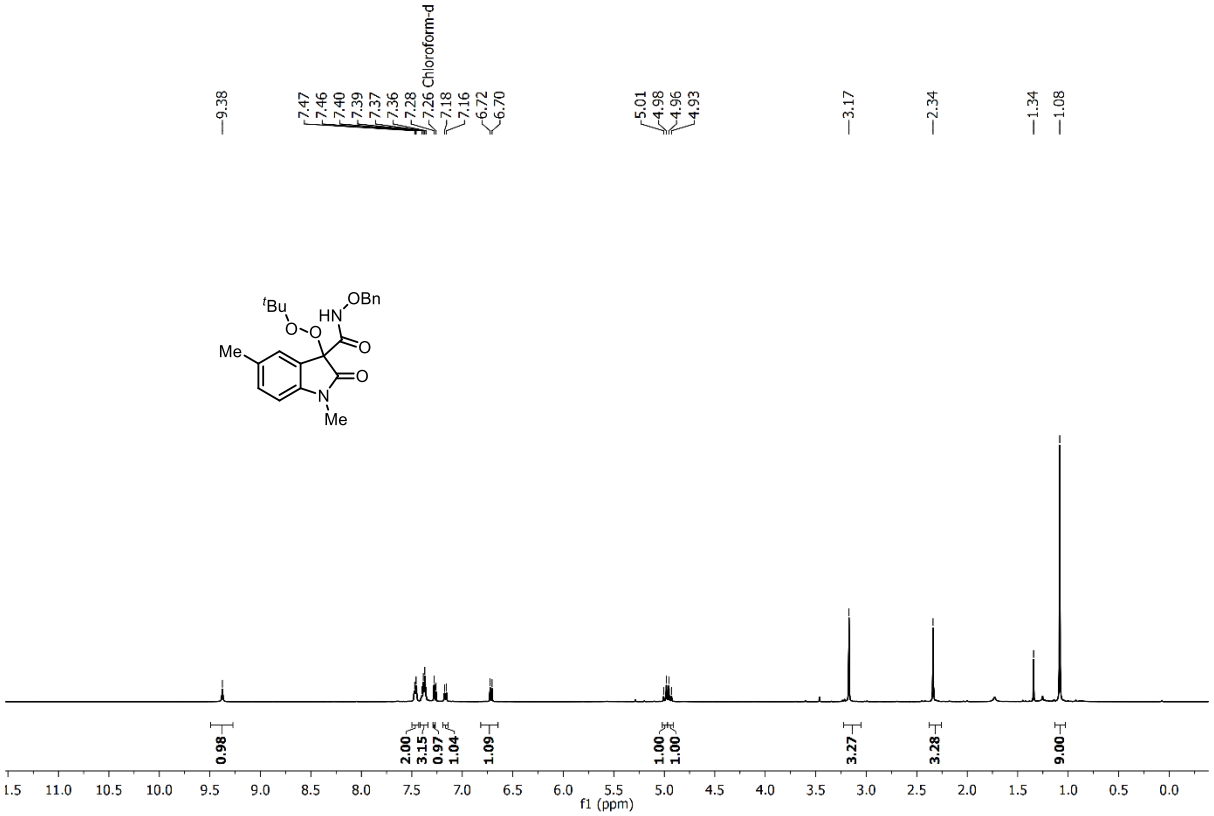


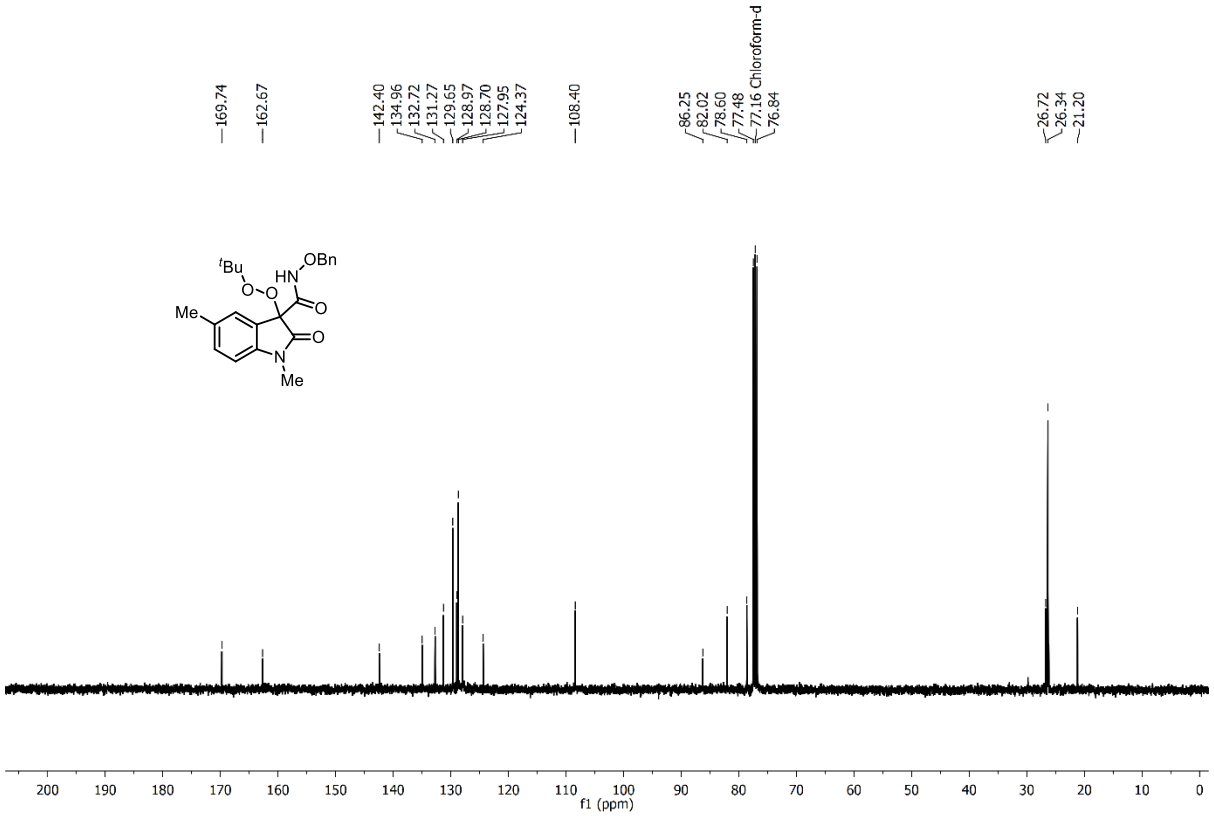
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(5)***



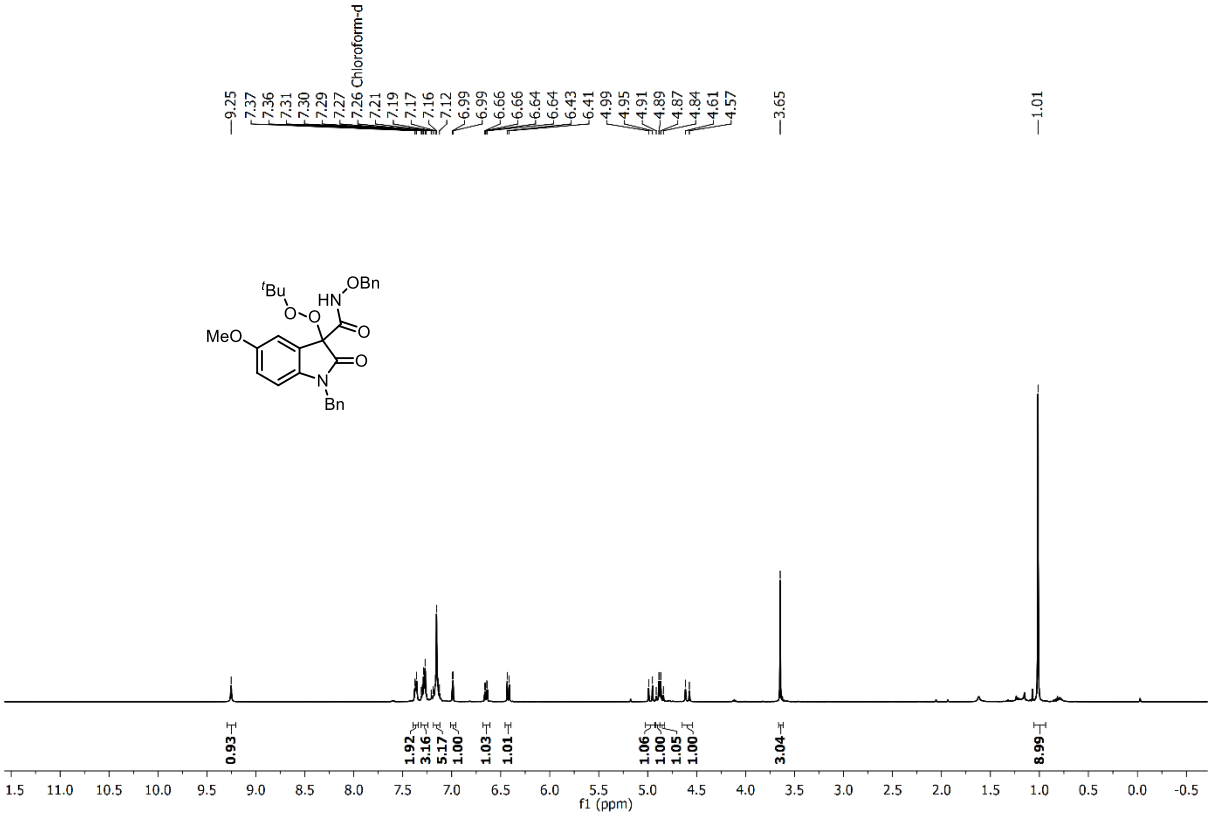


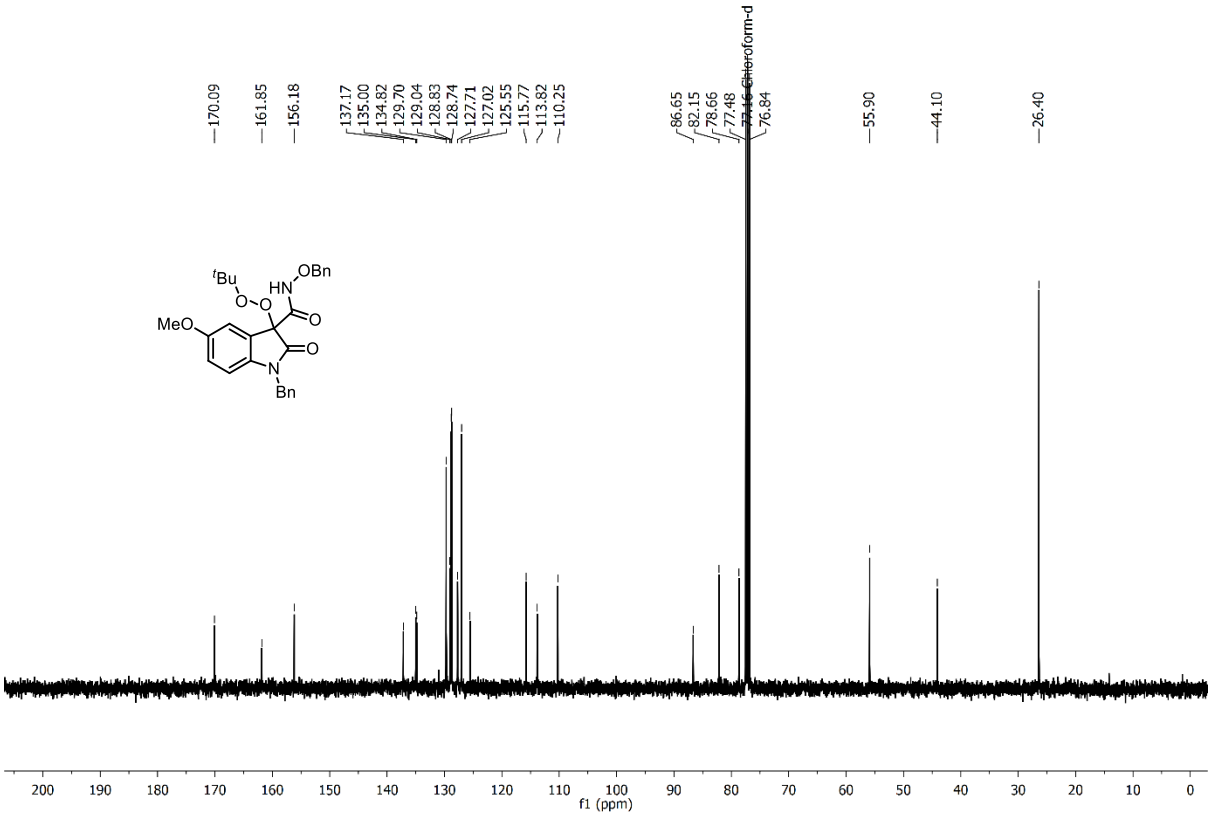
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(7)***



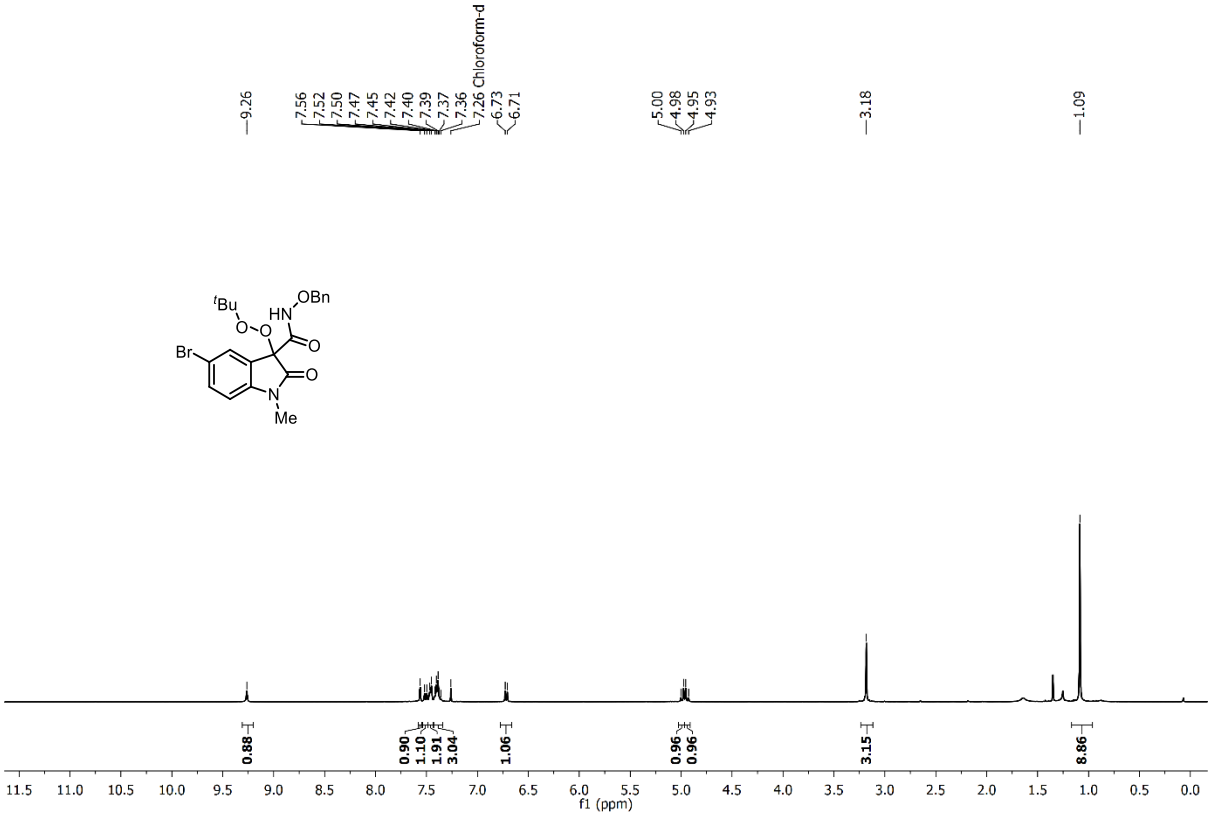


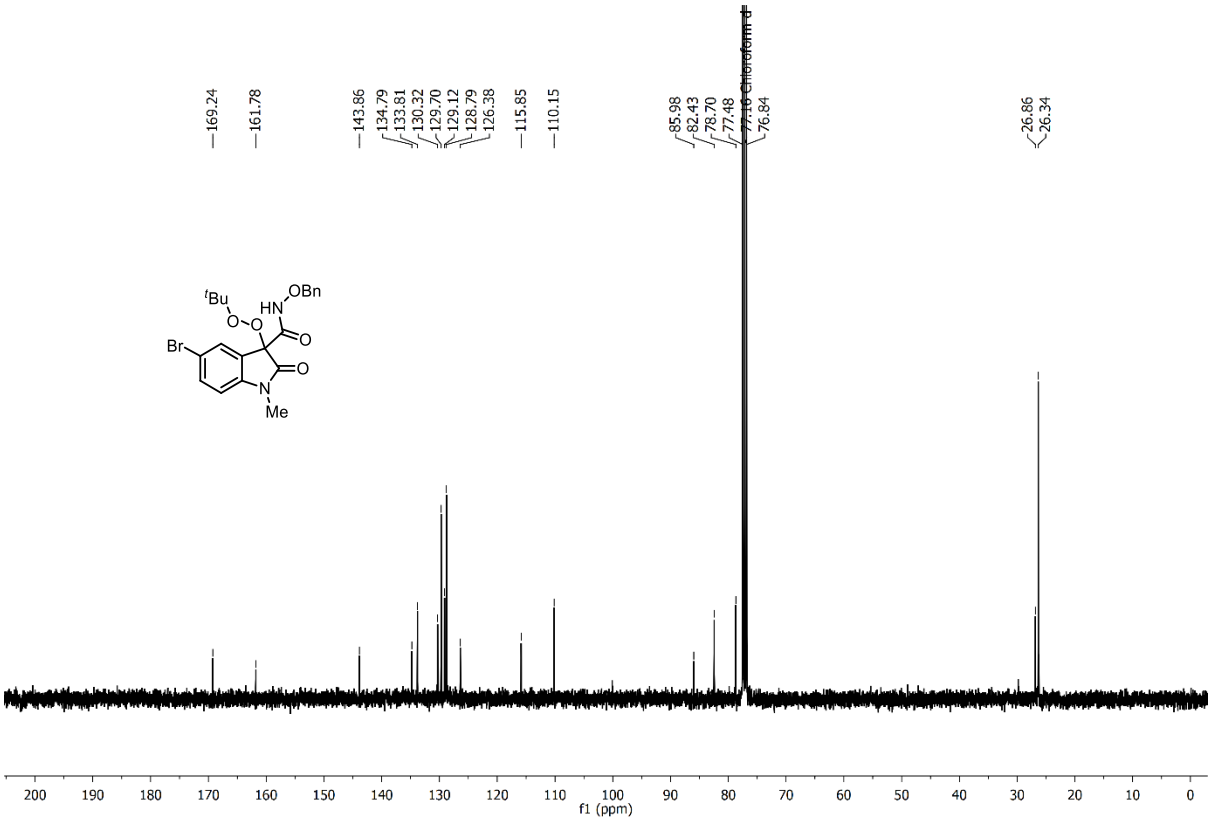
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(8)***



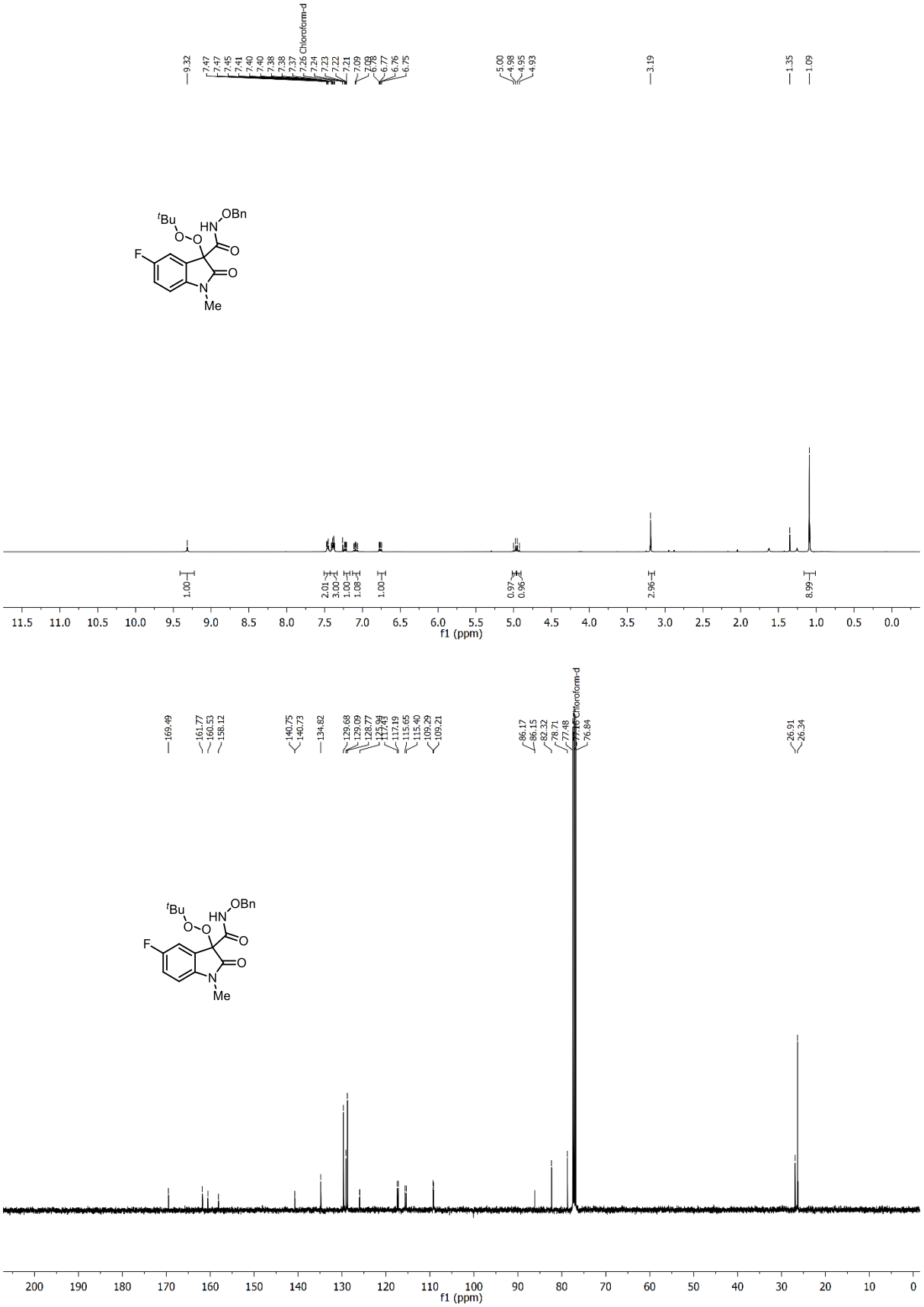


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(9)***

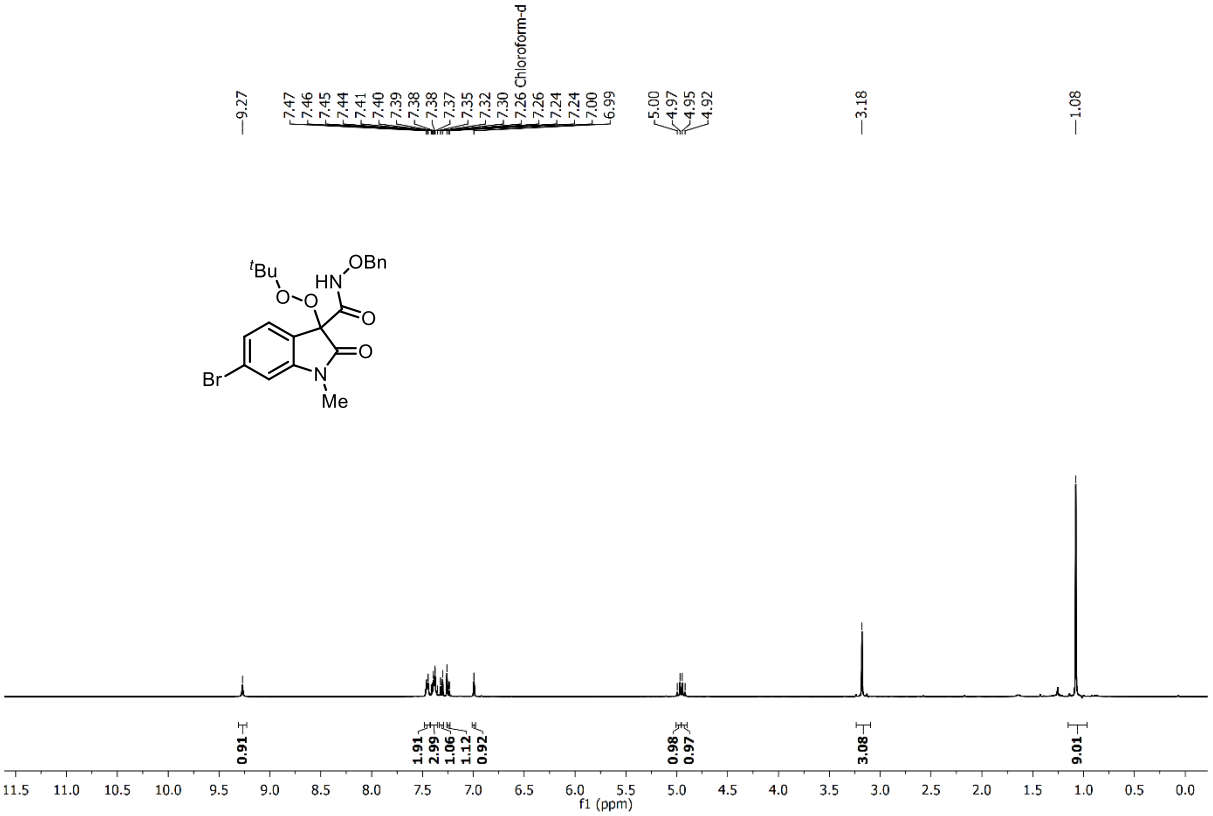


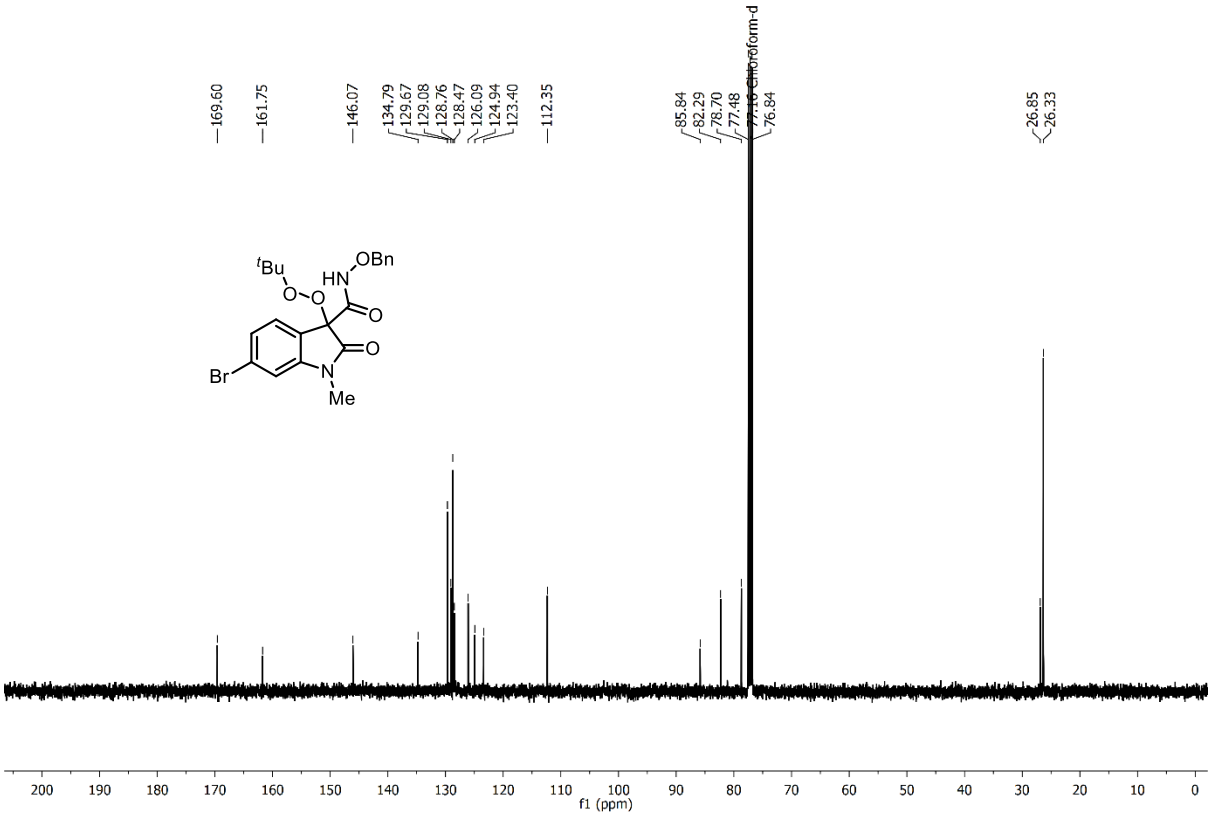


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(10)***

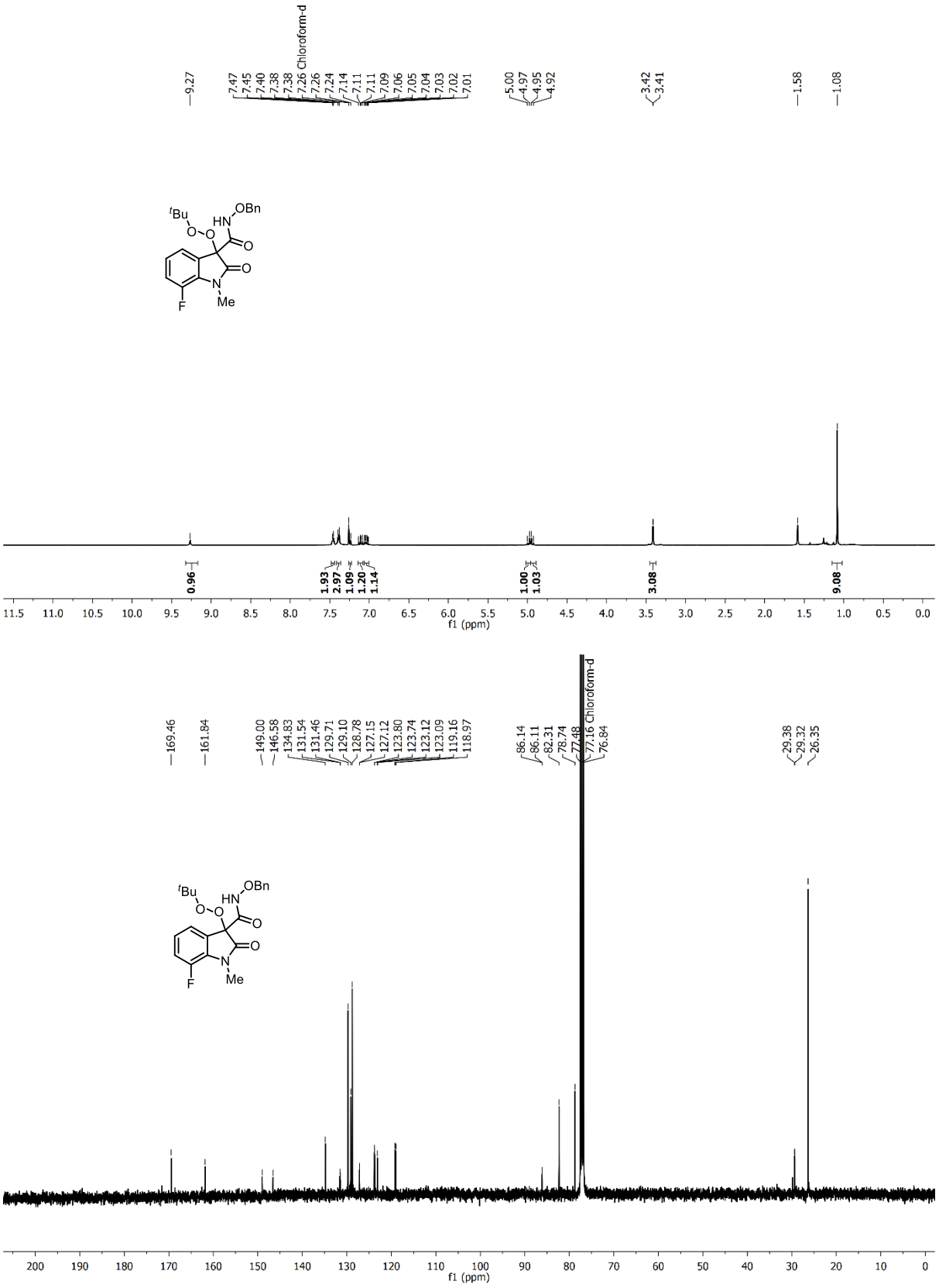


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(11)***

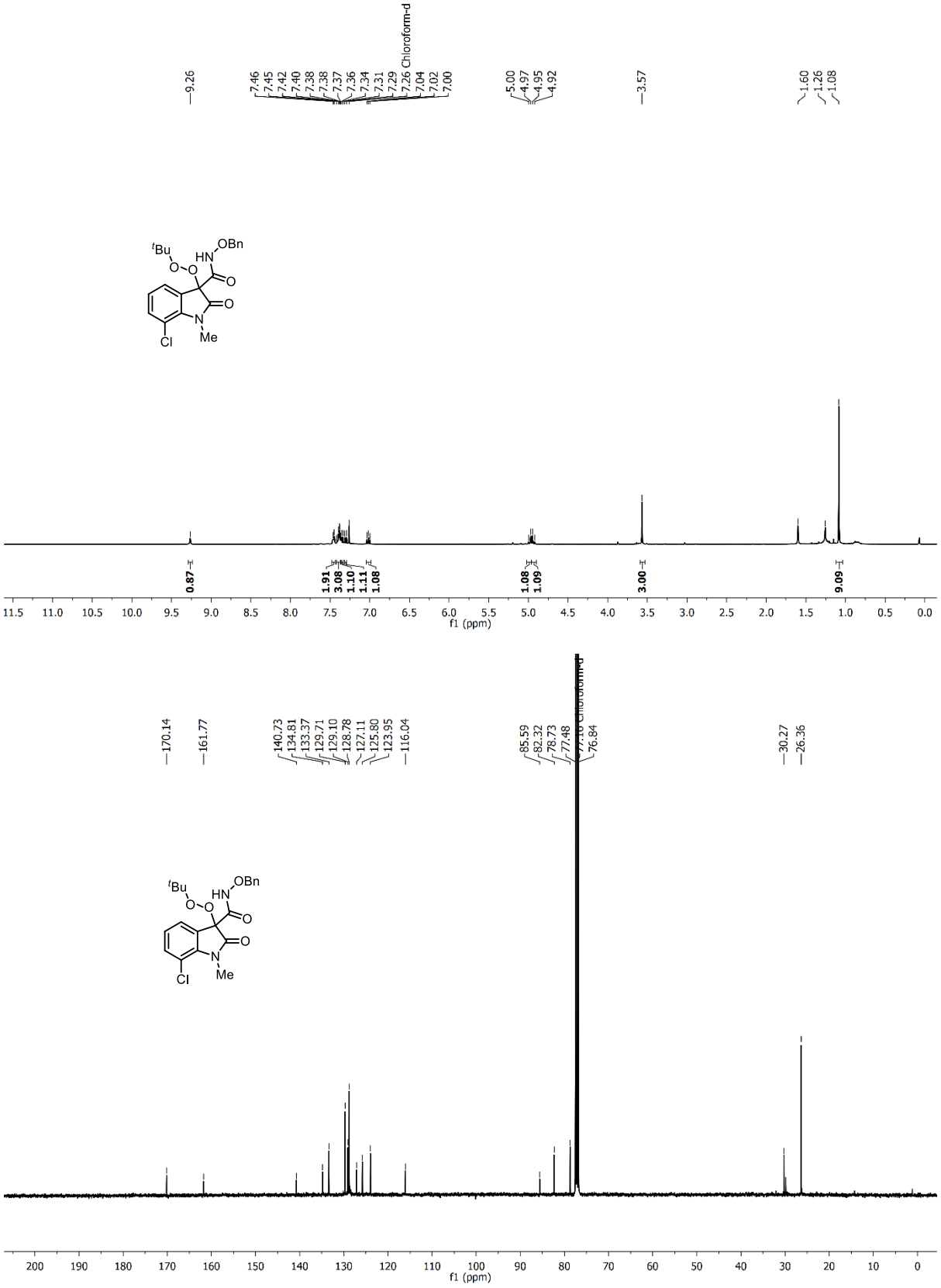




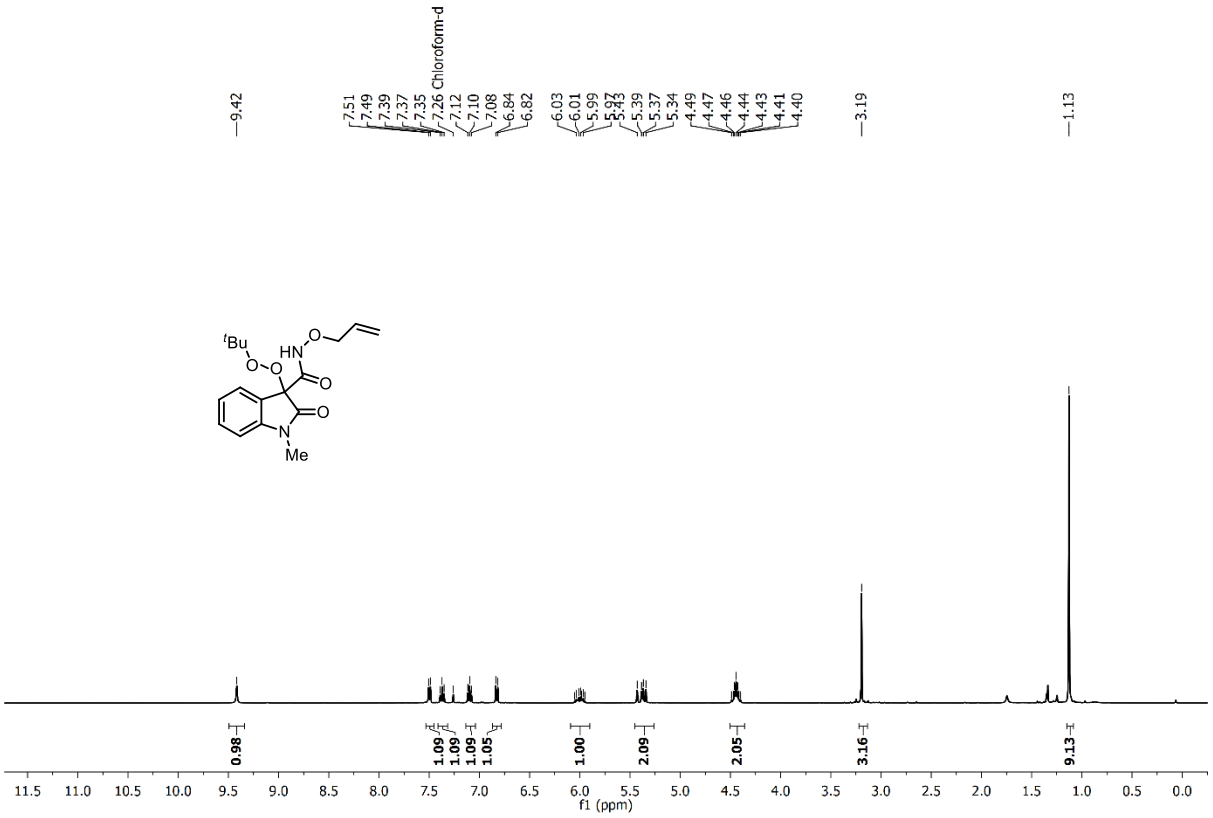
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(12)***

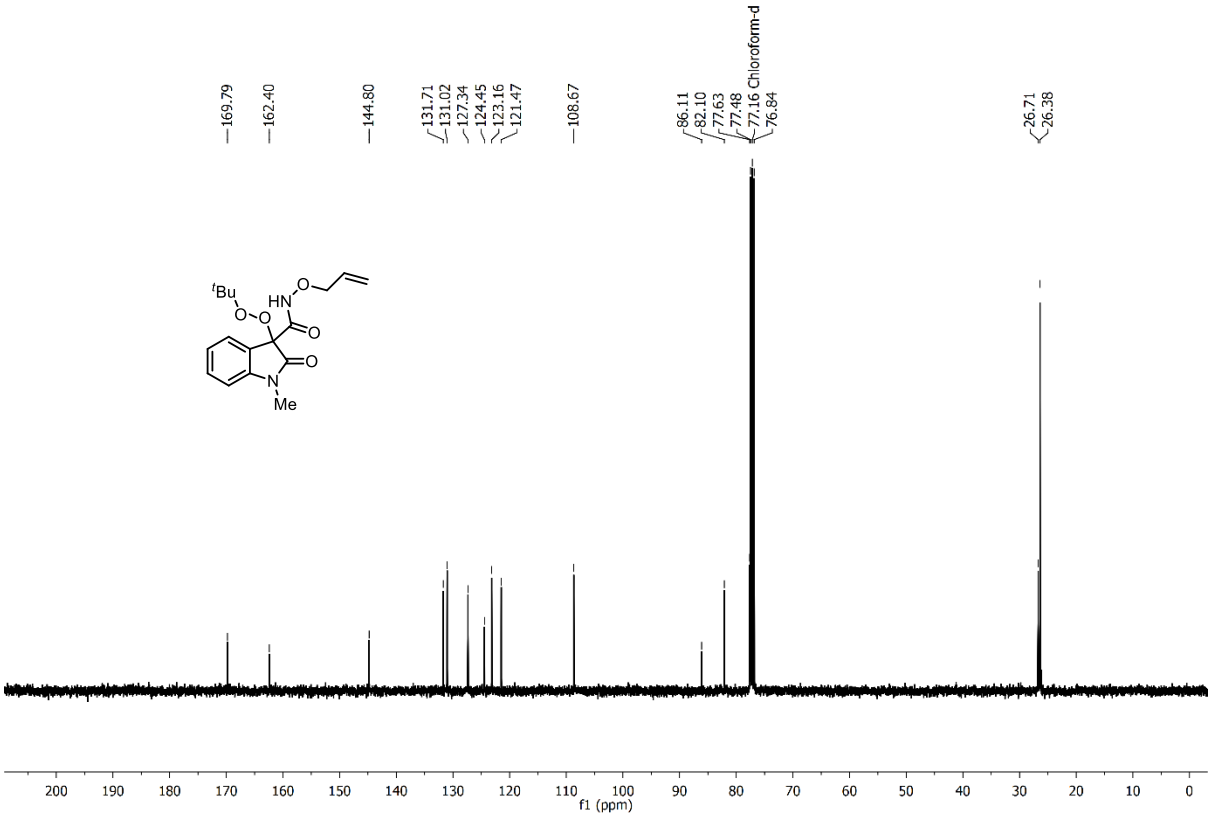


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(13)***

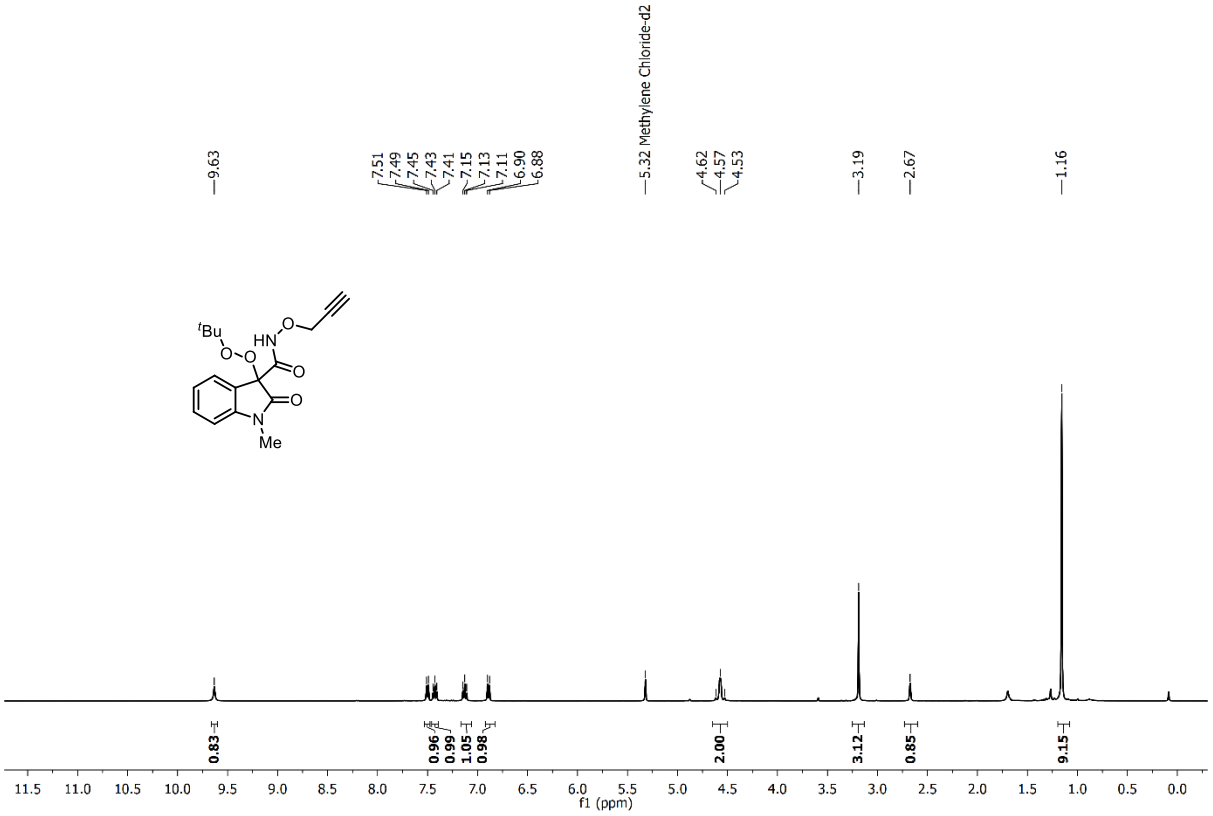


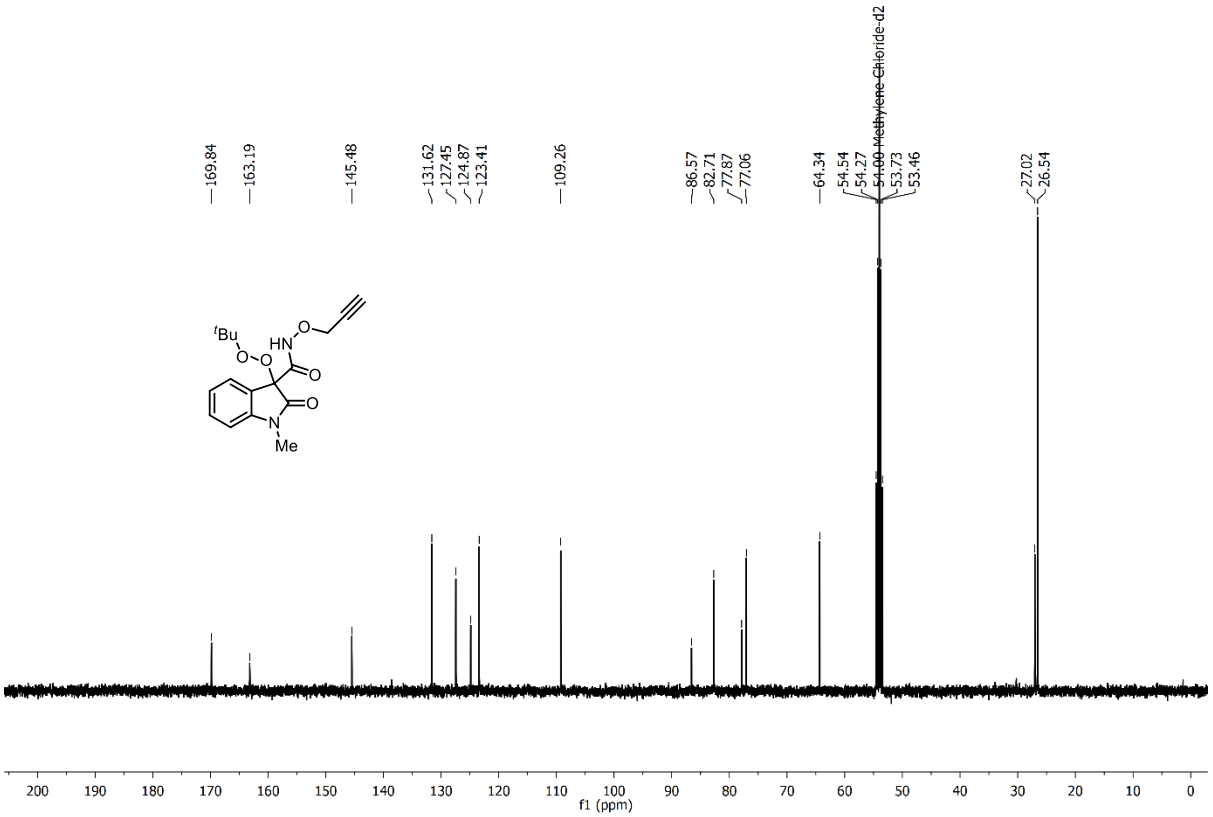
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(14)***



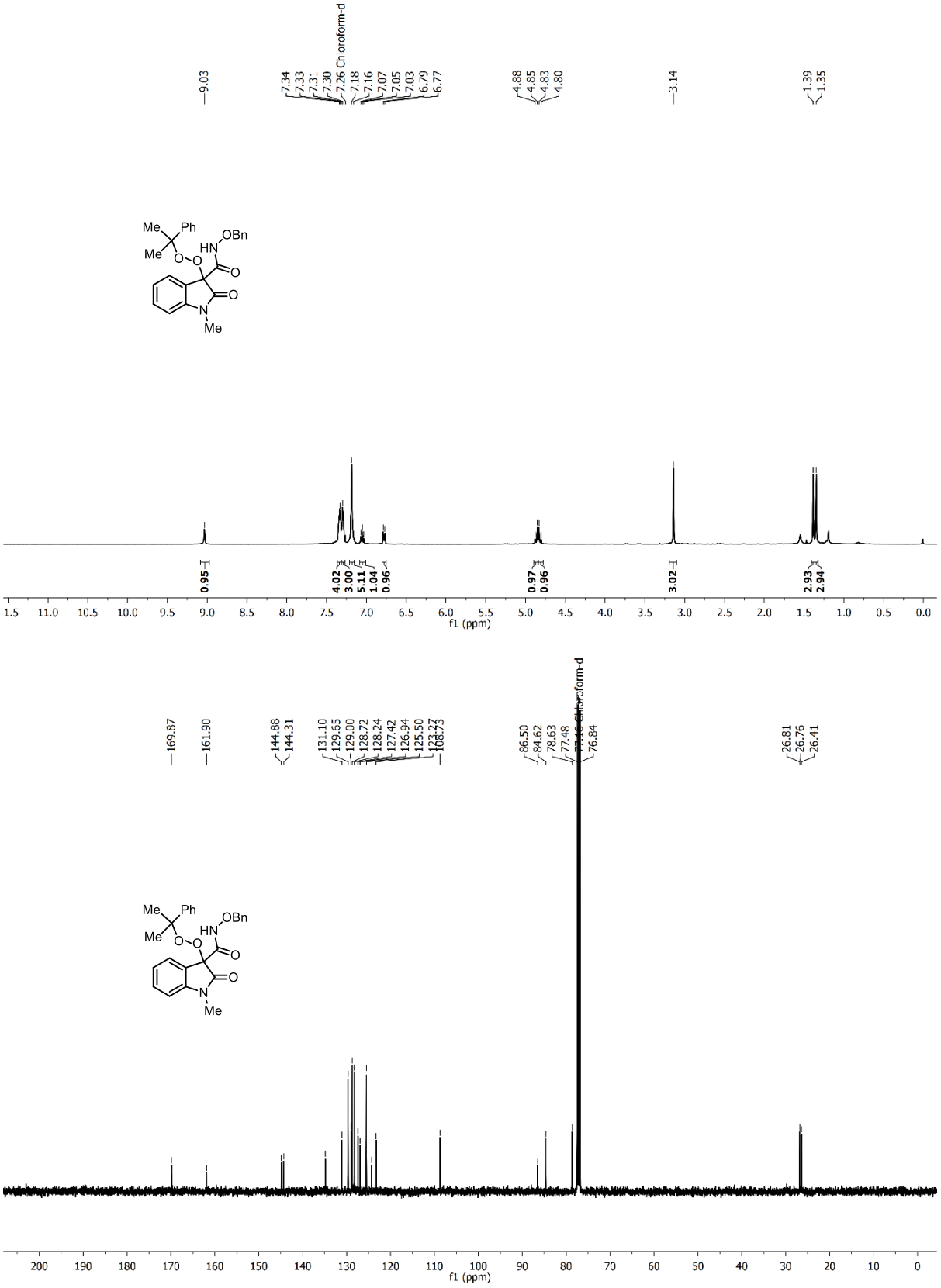


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in CD_2Cl_2 ***(15)***

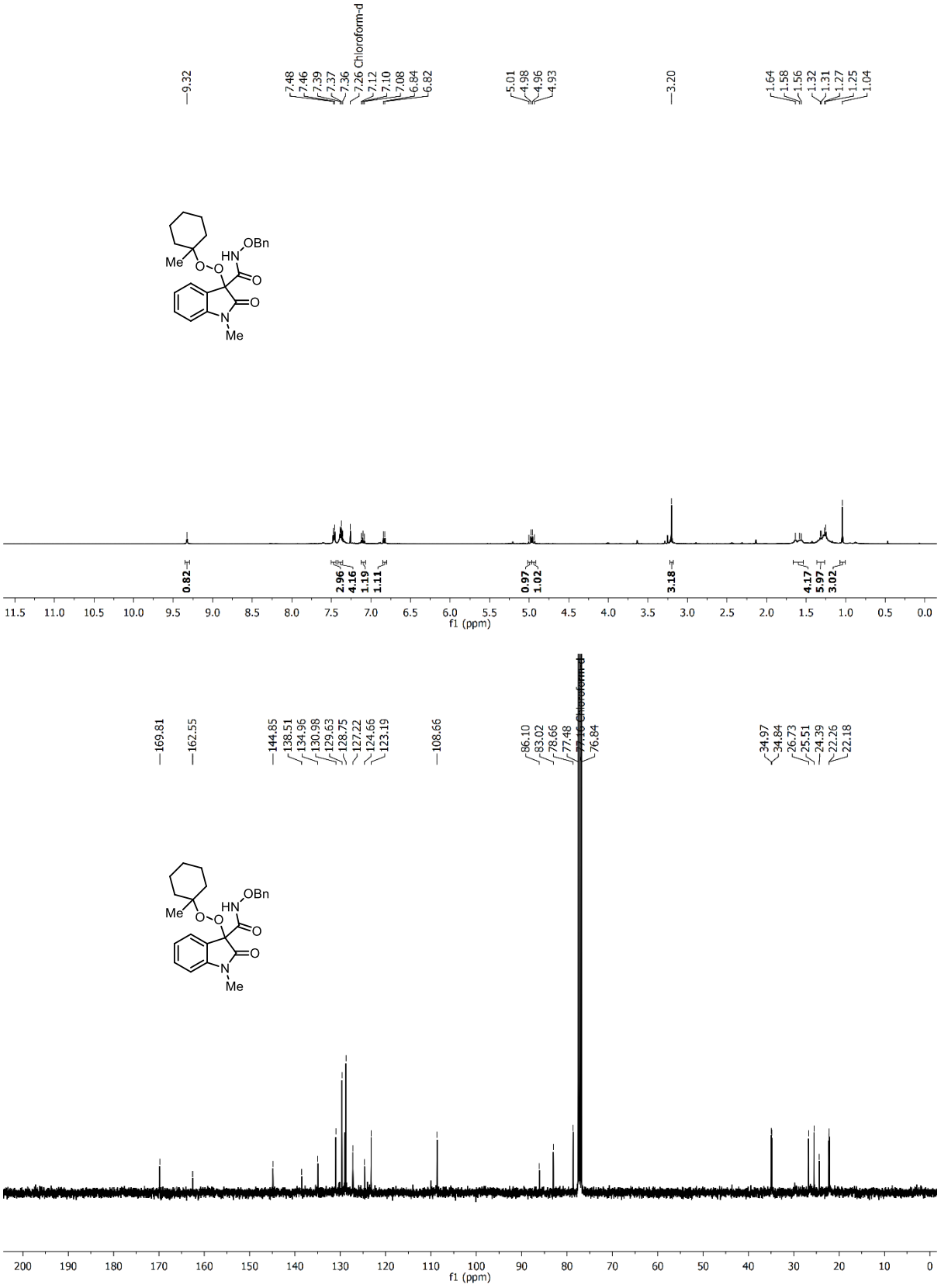




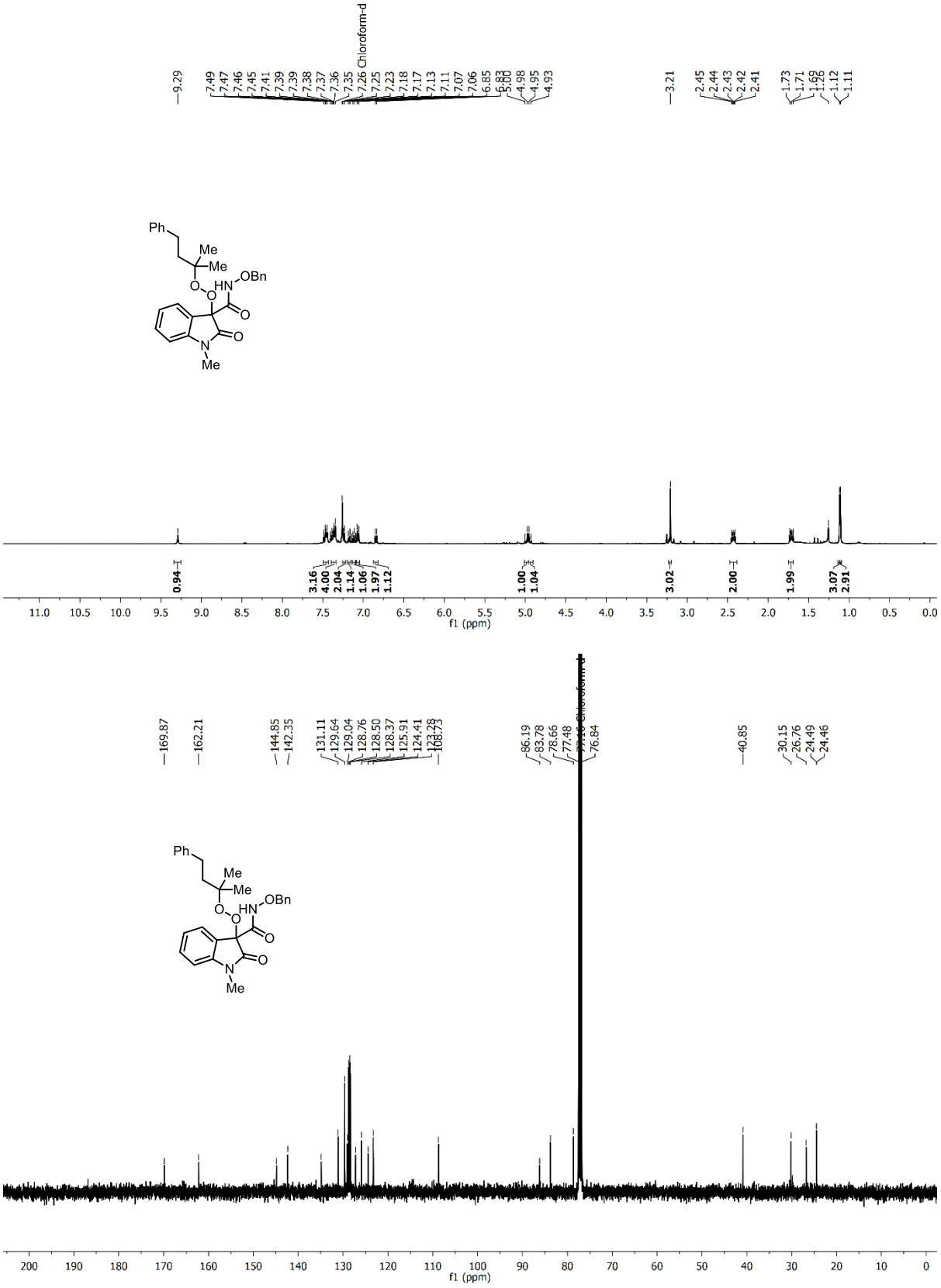
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(16)***



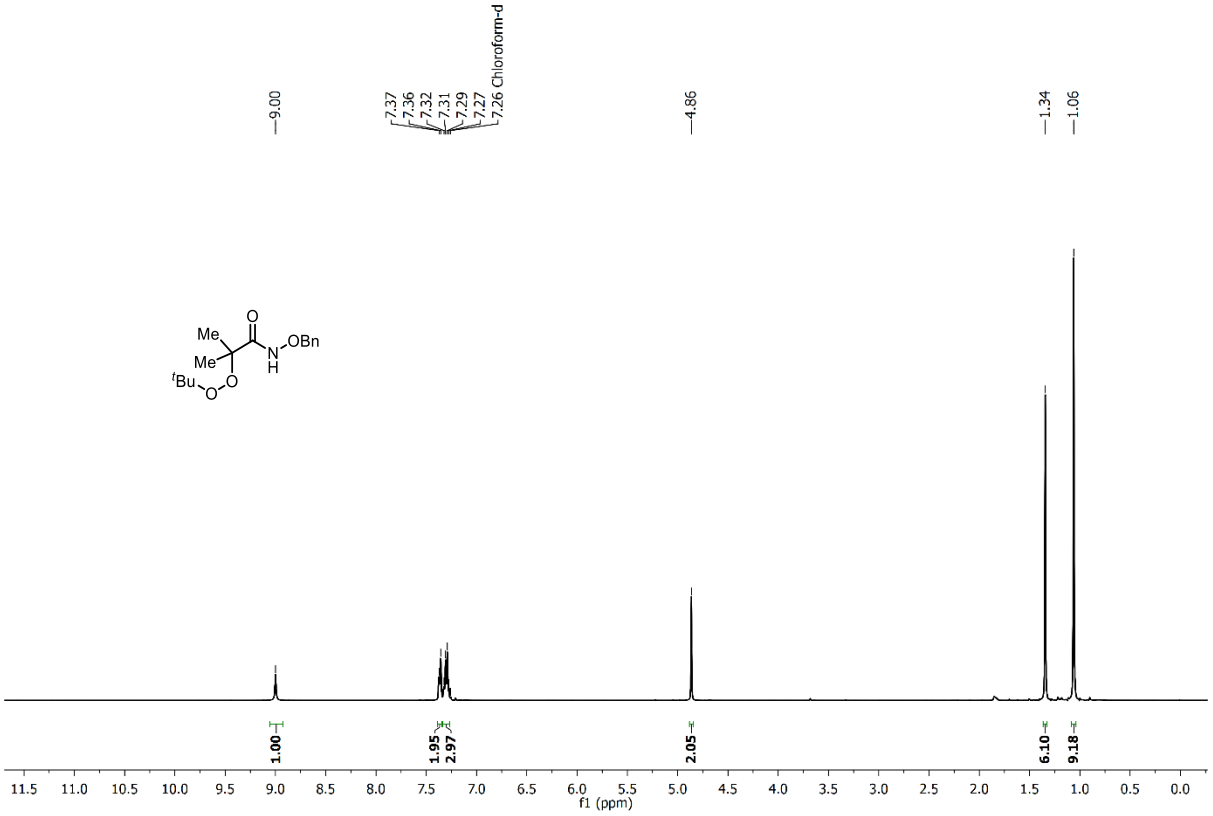
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(17)***

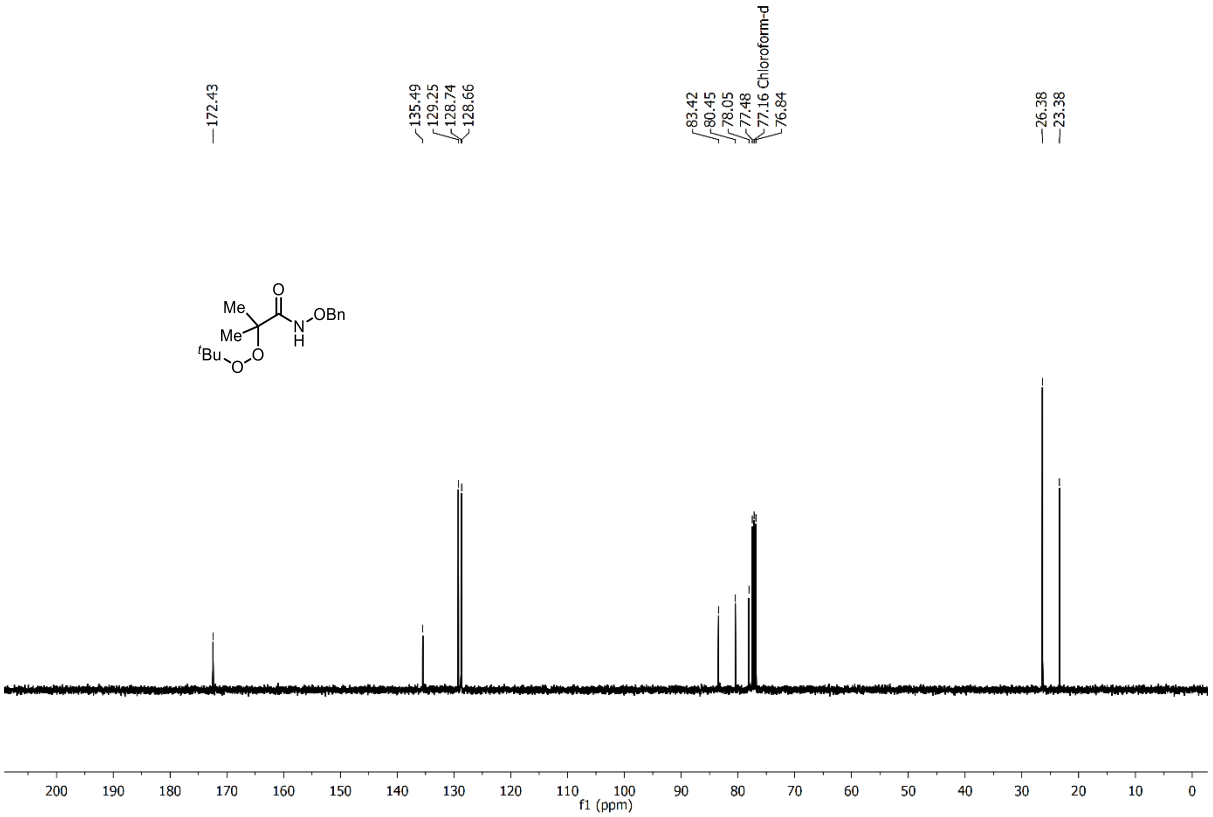


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(18)***

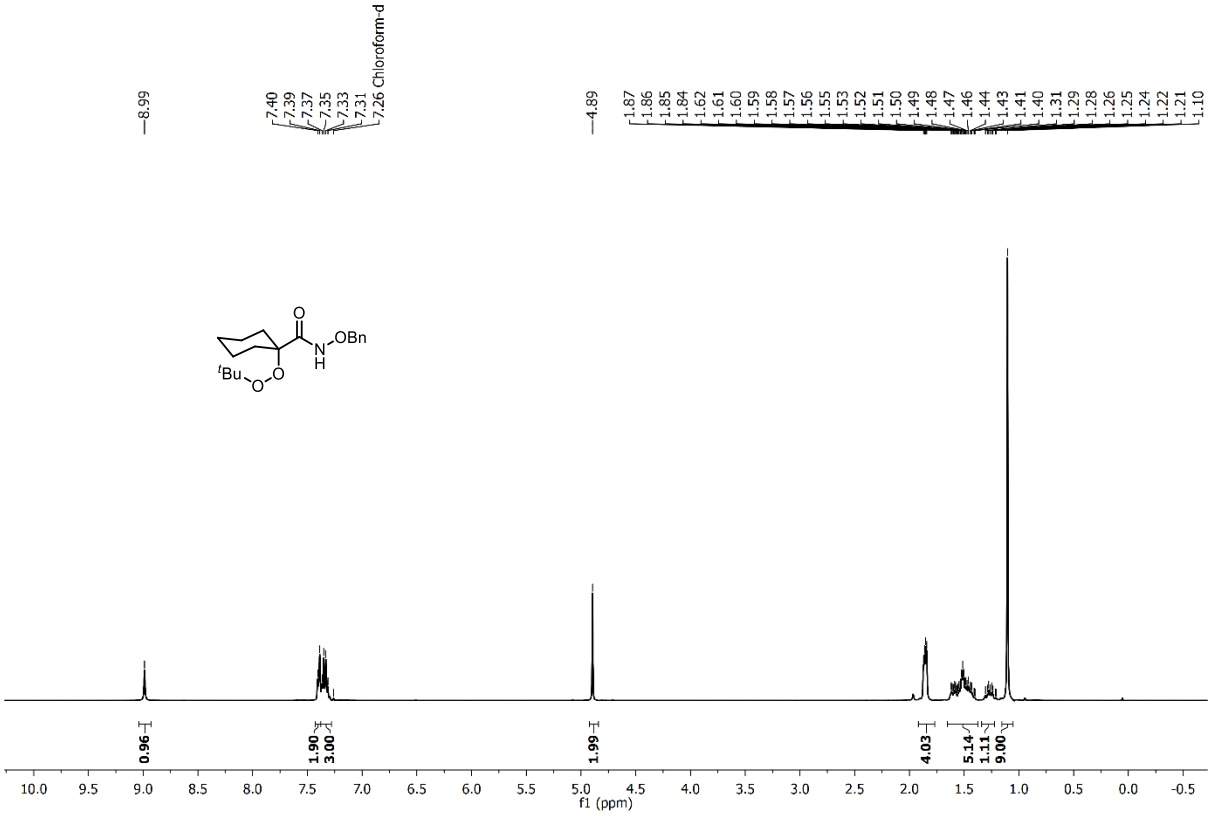


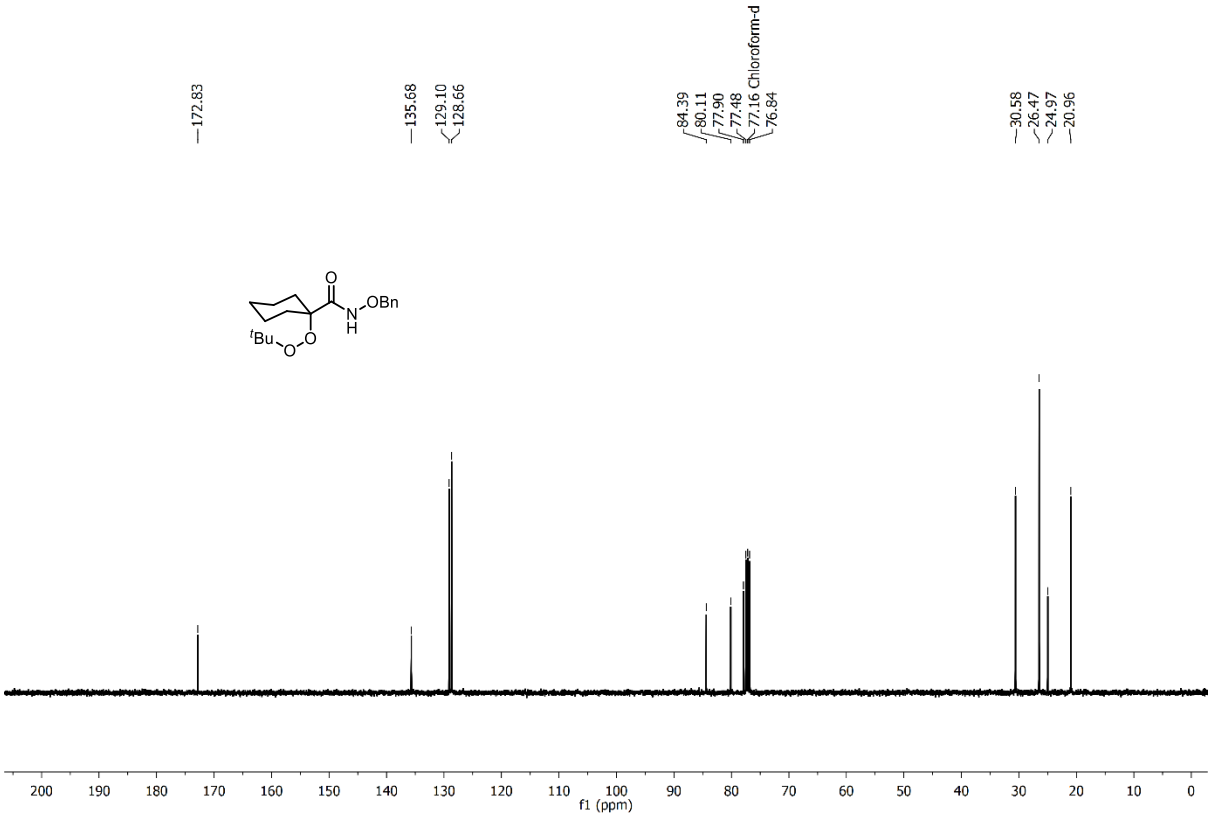
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(21)***



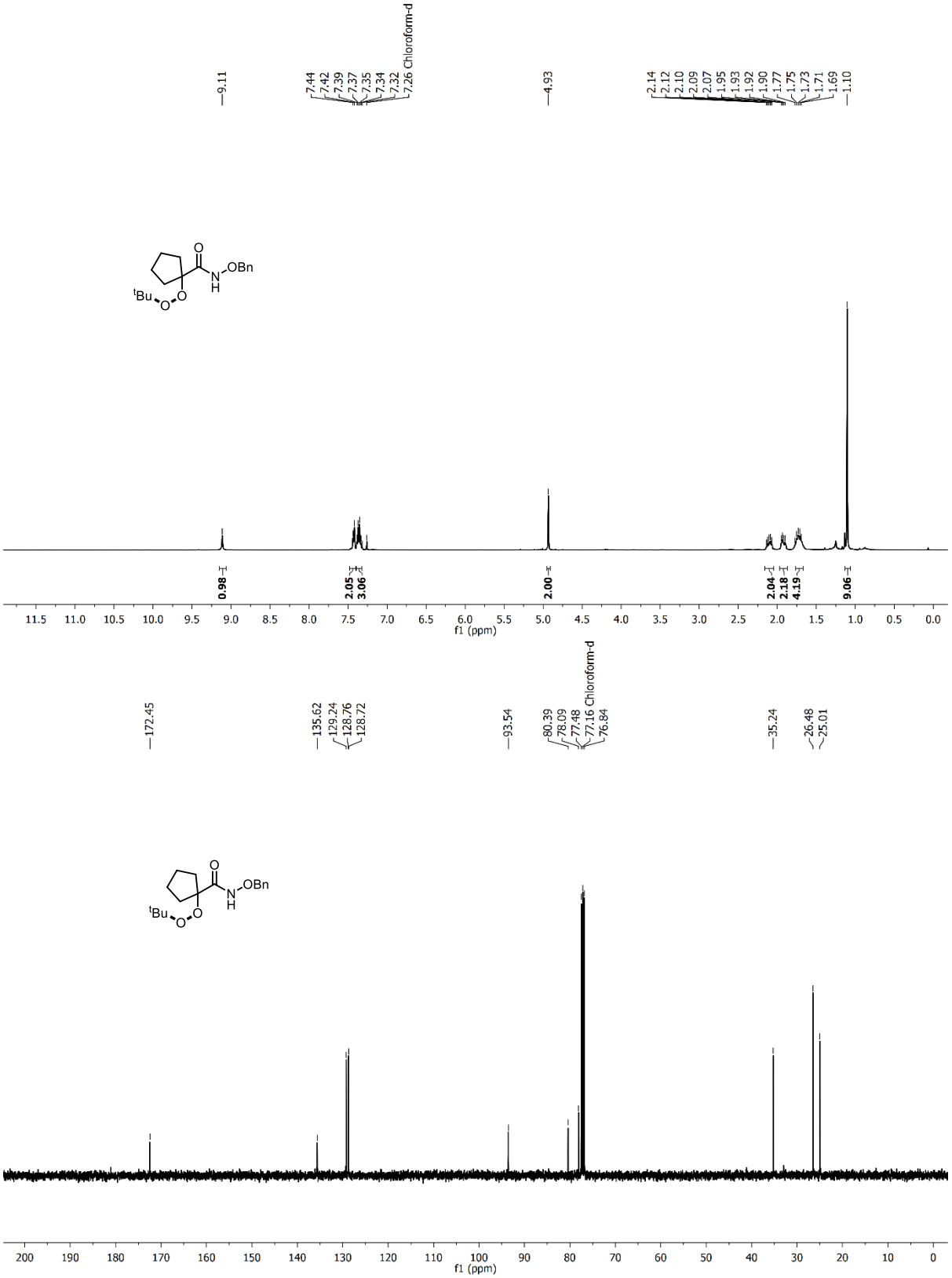


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(22)***

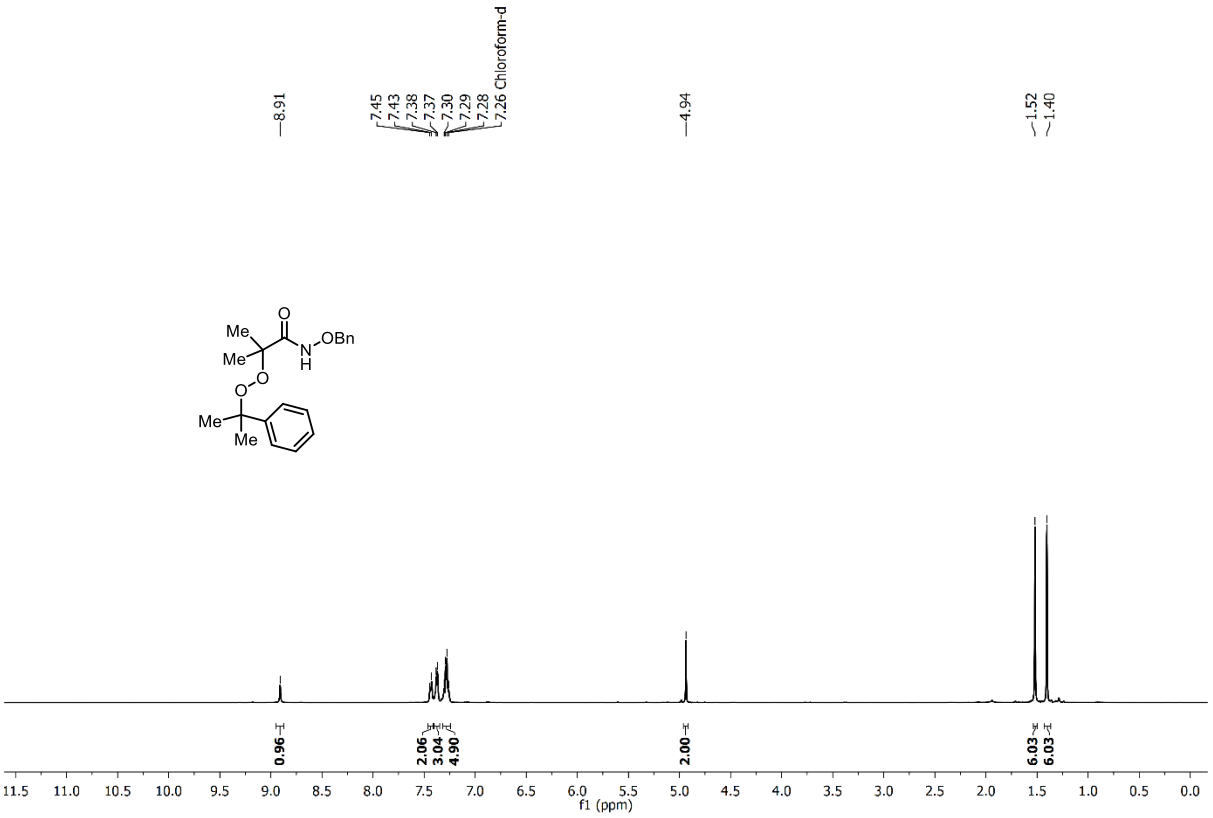


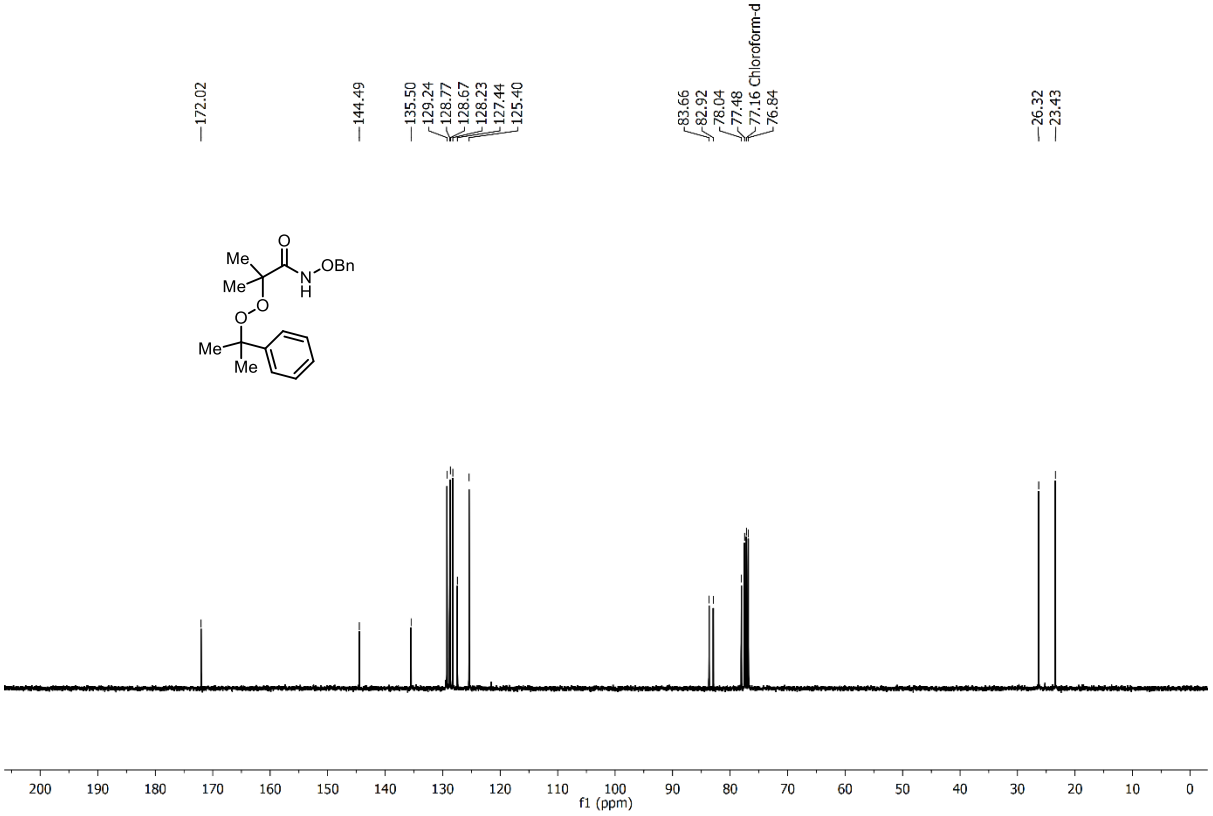


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(23)***

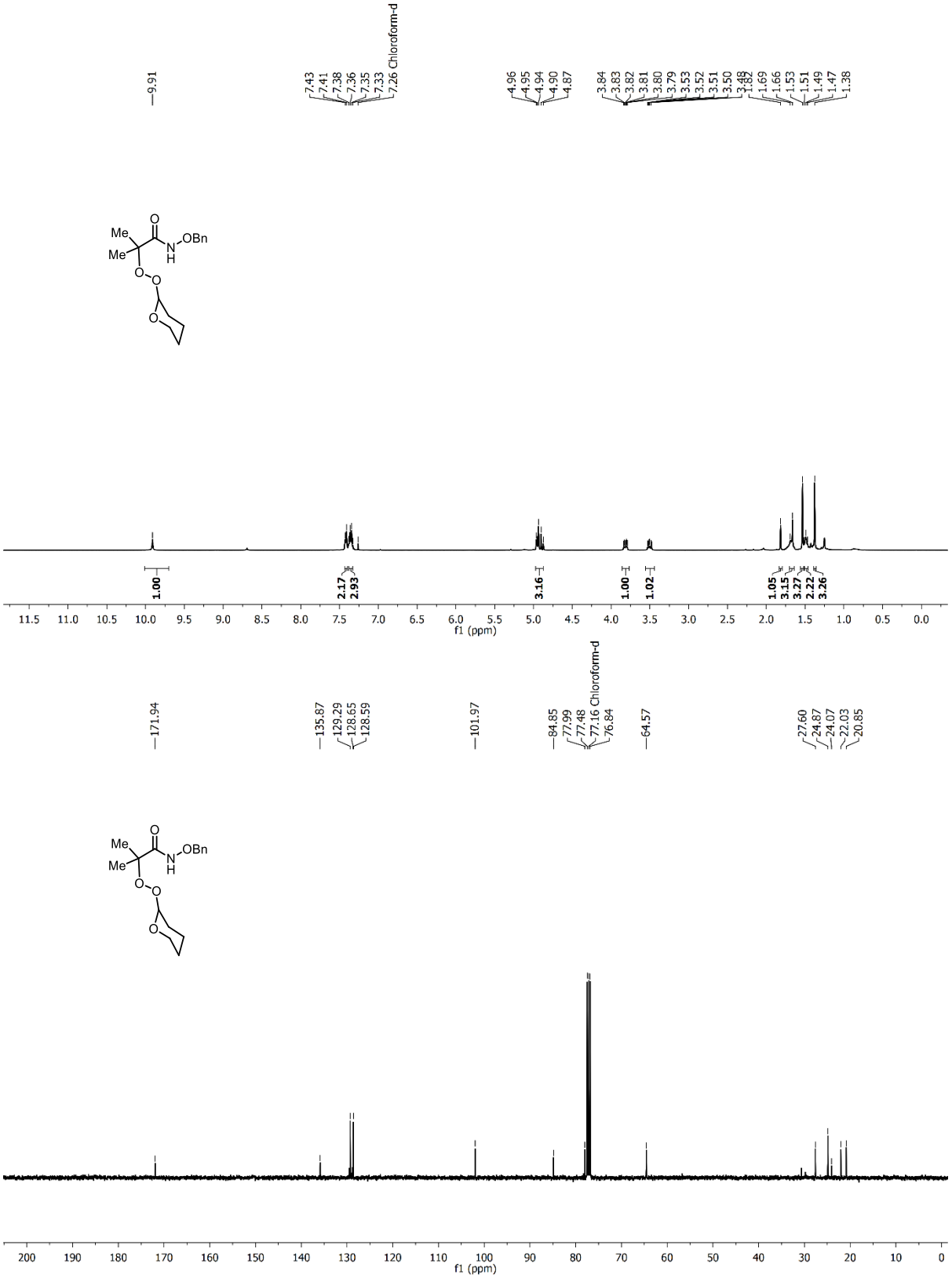


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(26)***

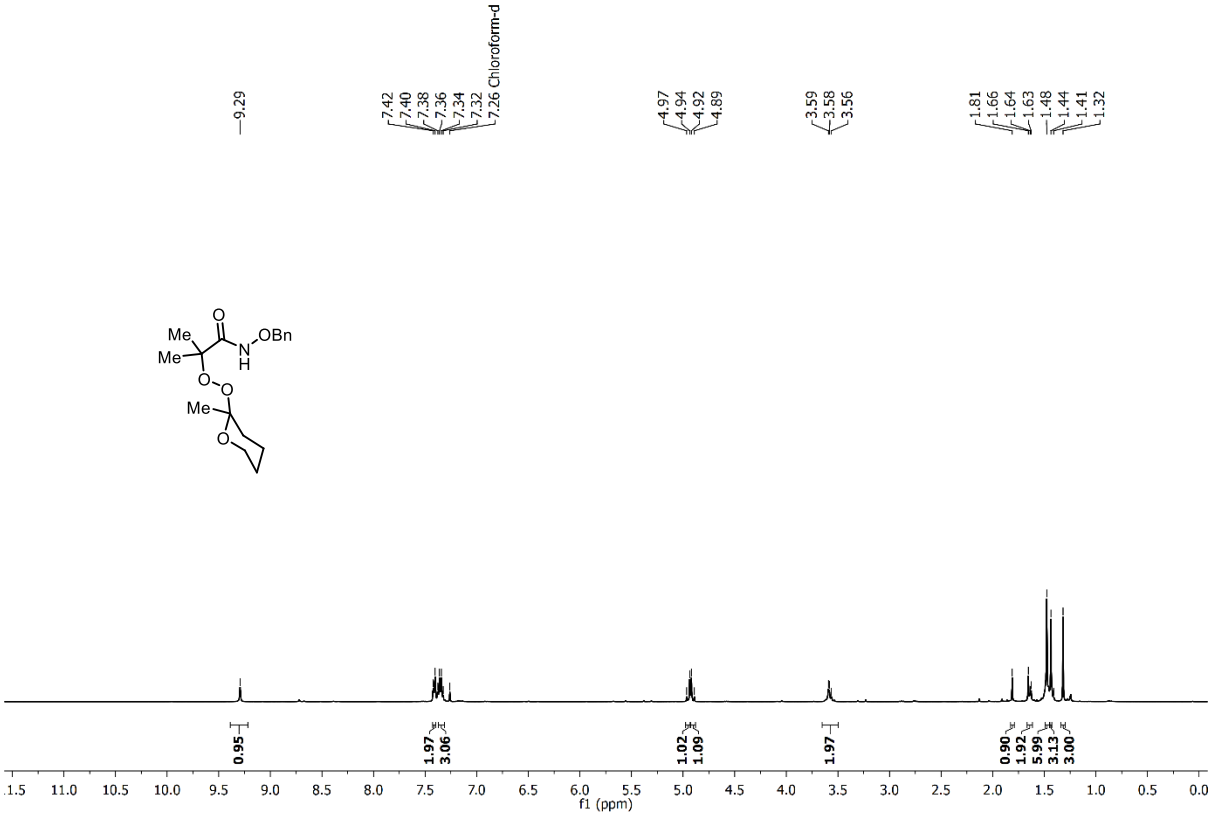


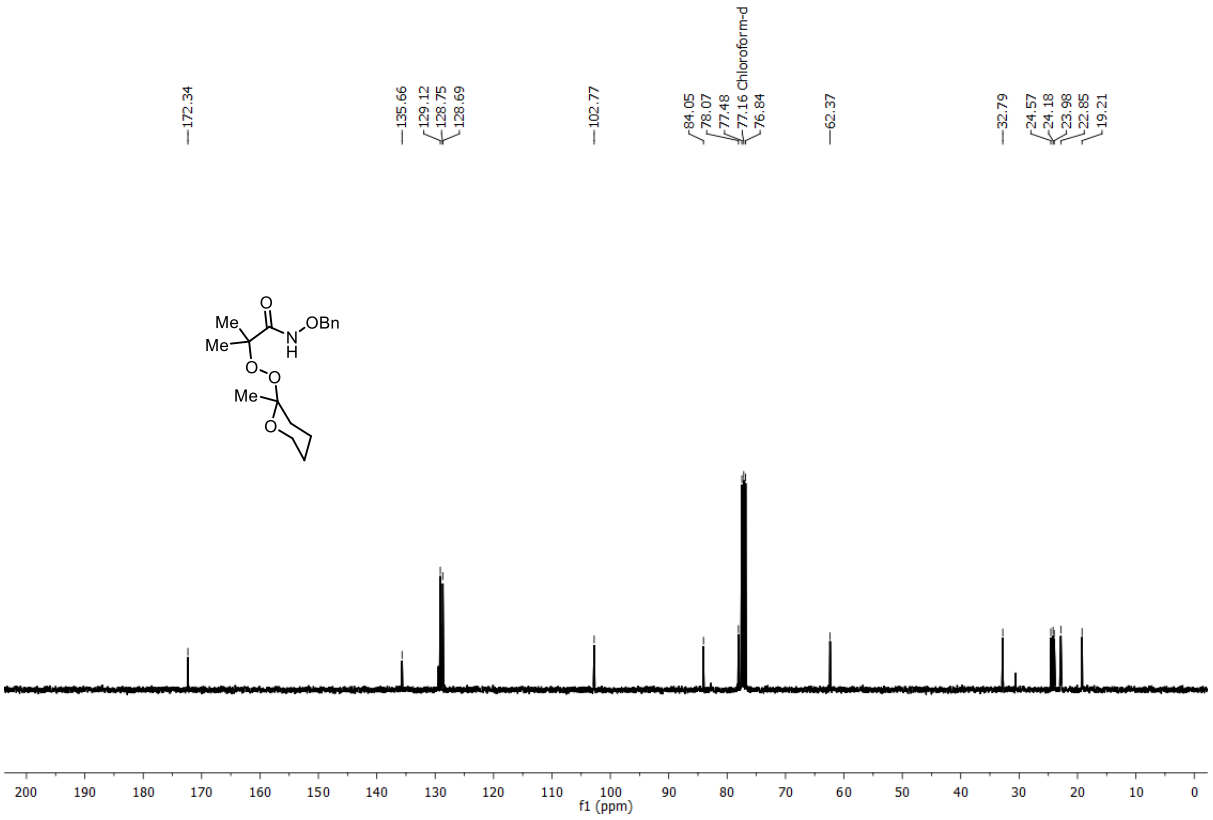


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(27)***

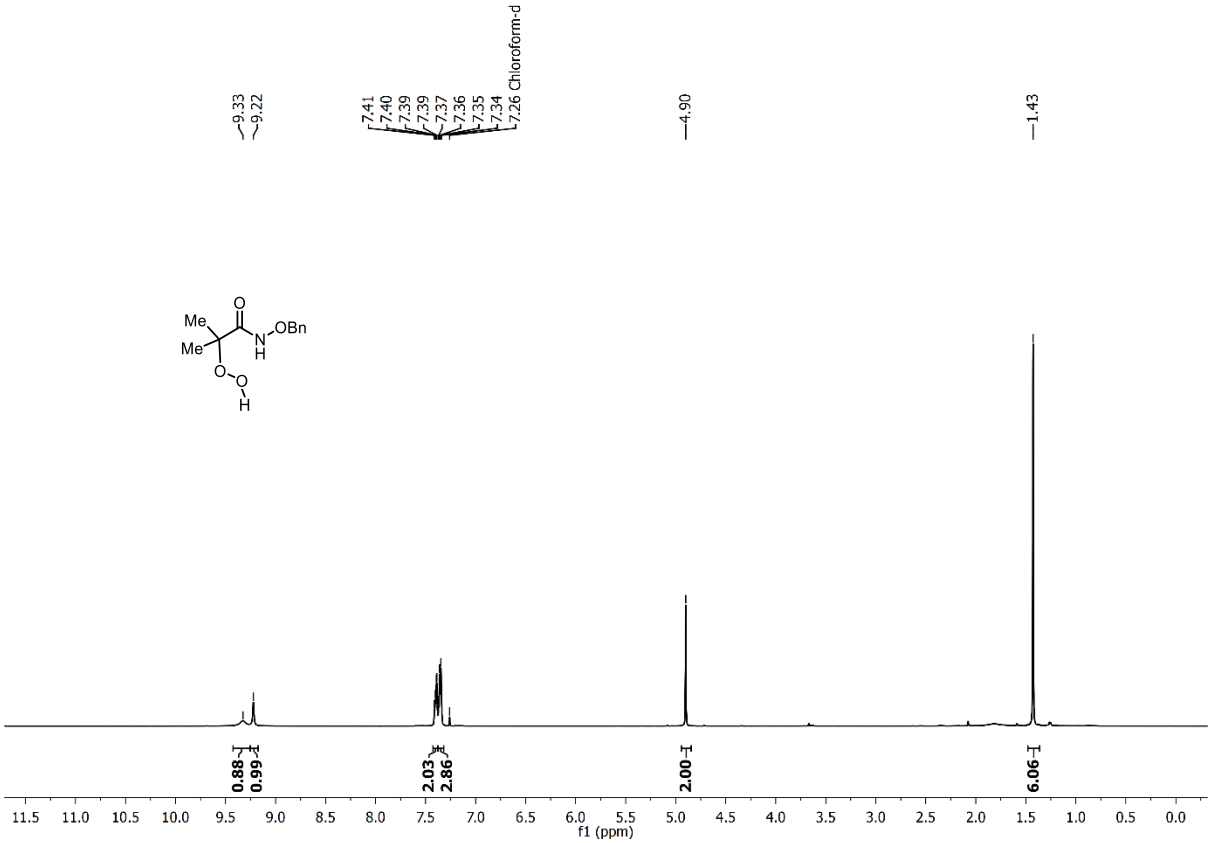


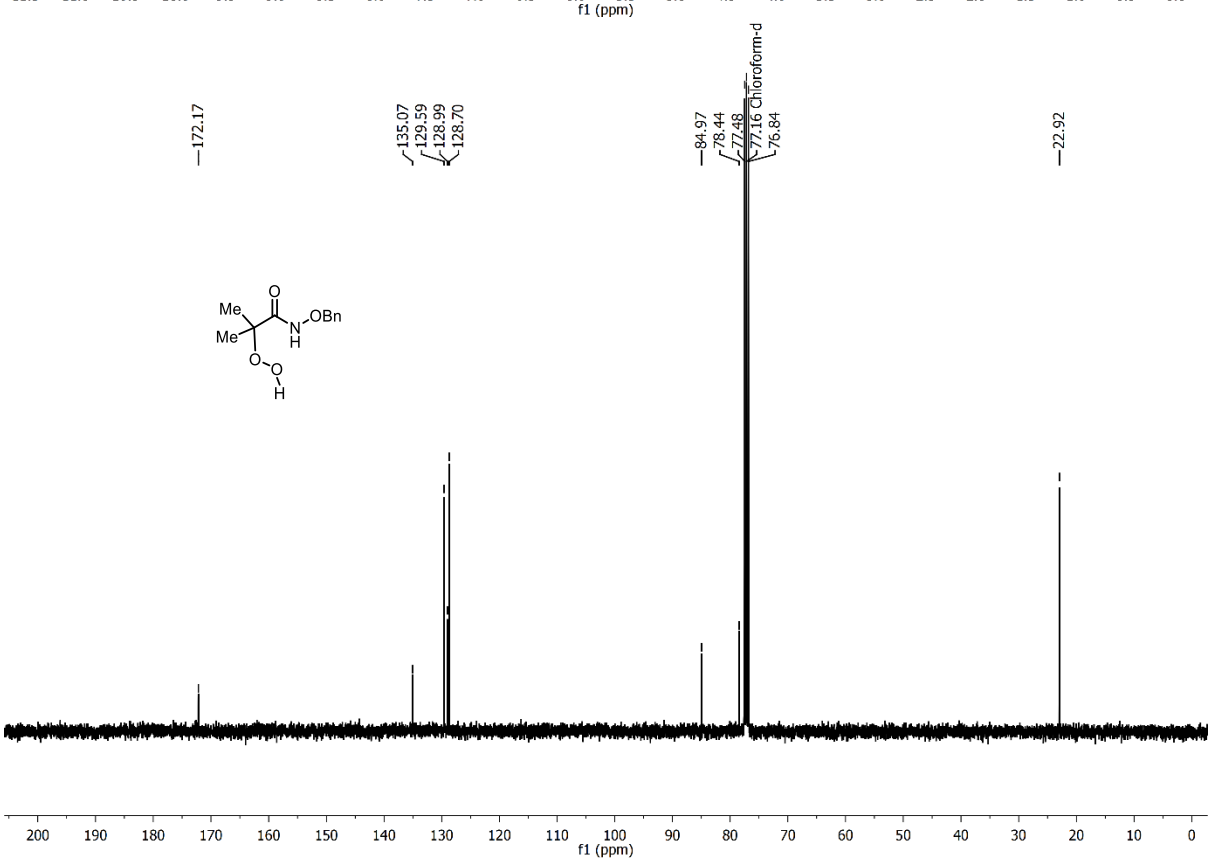
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(28)***



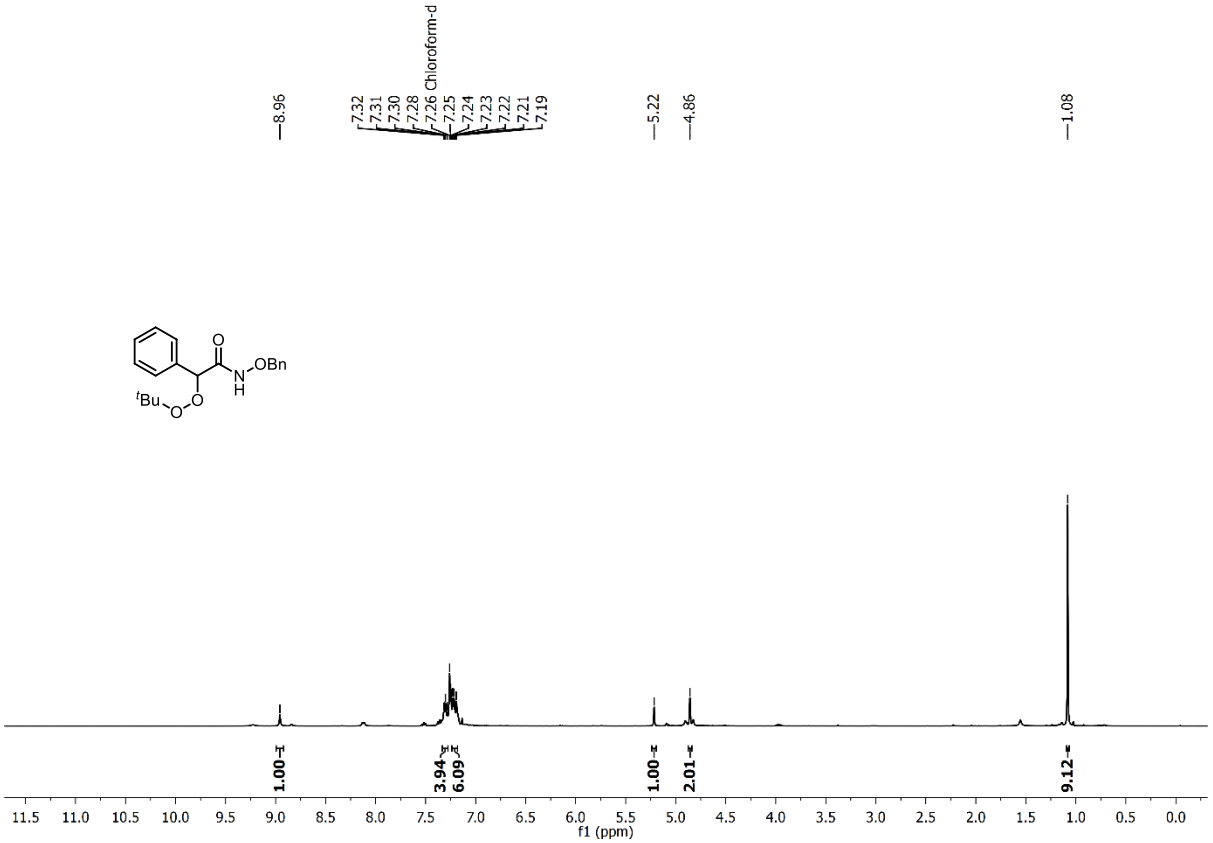


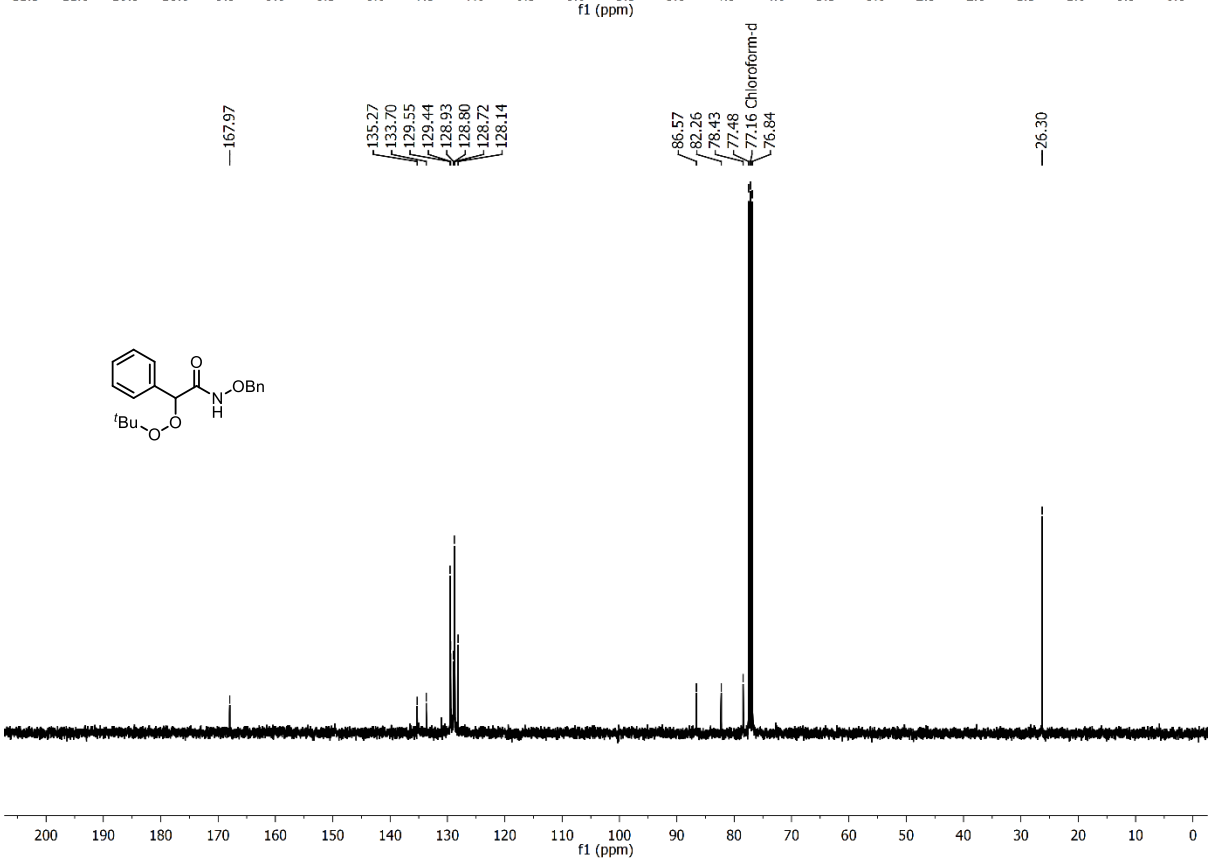
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(29)***



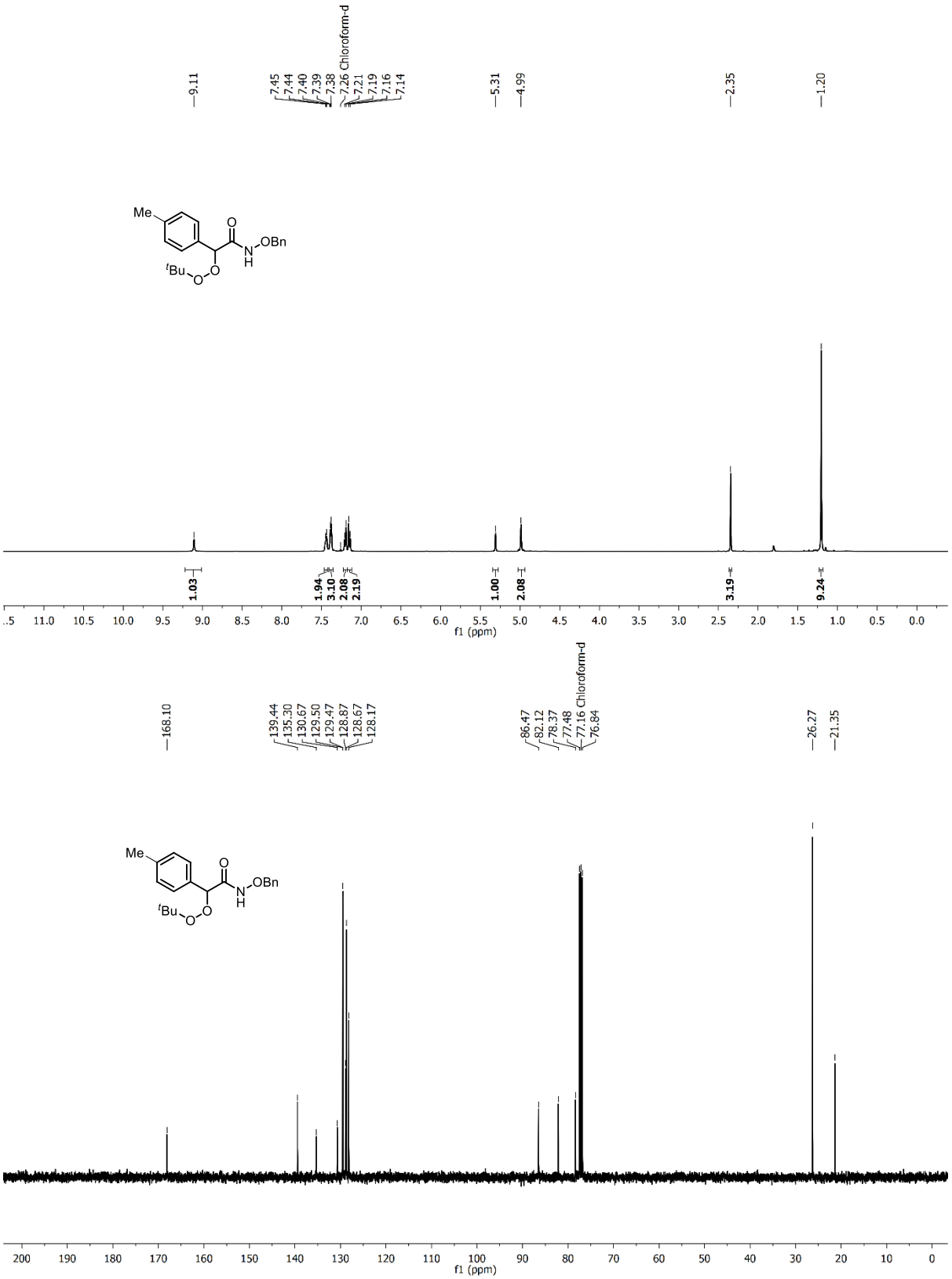


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(30)***

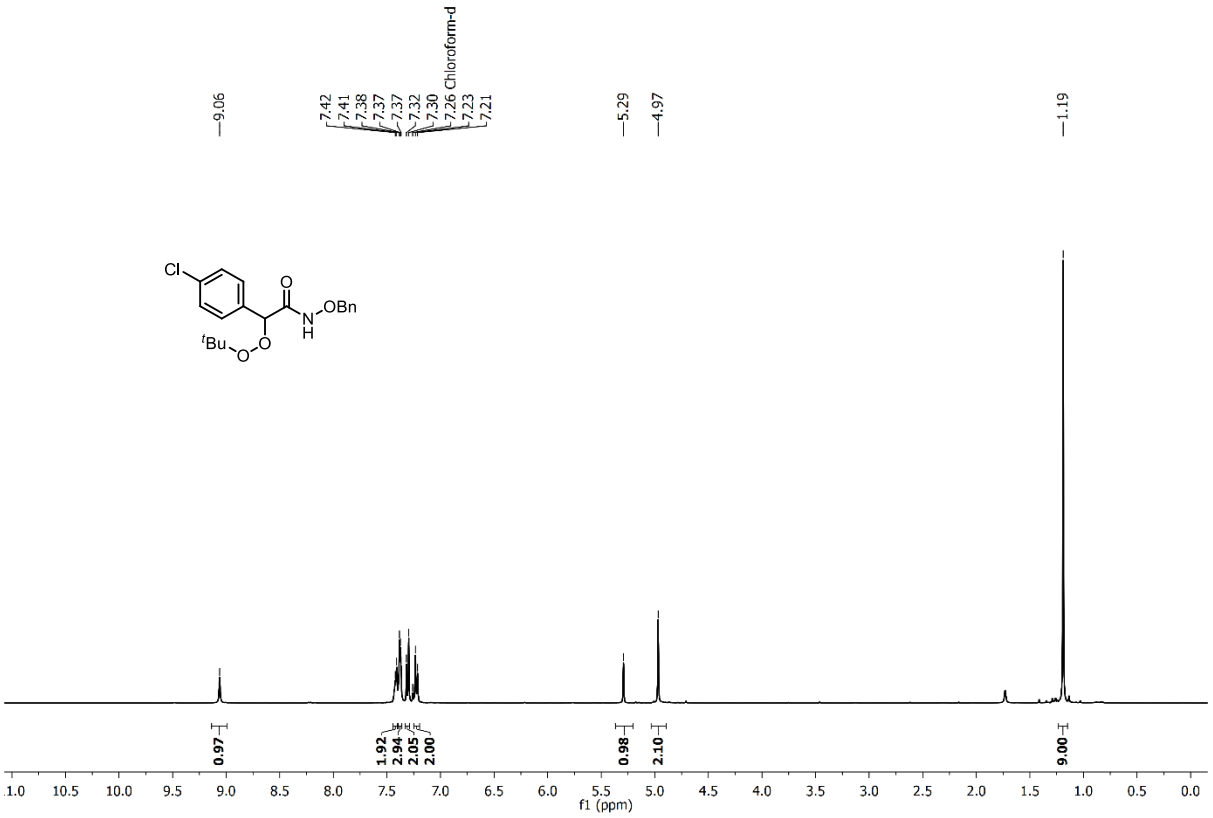


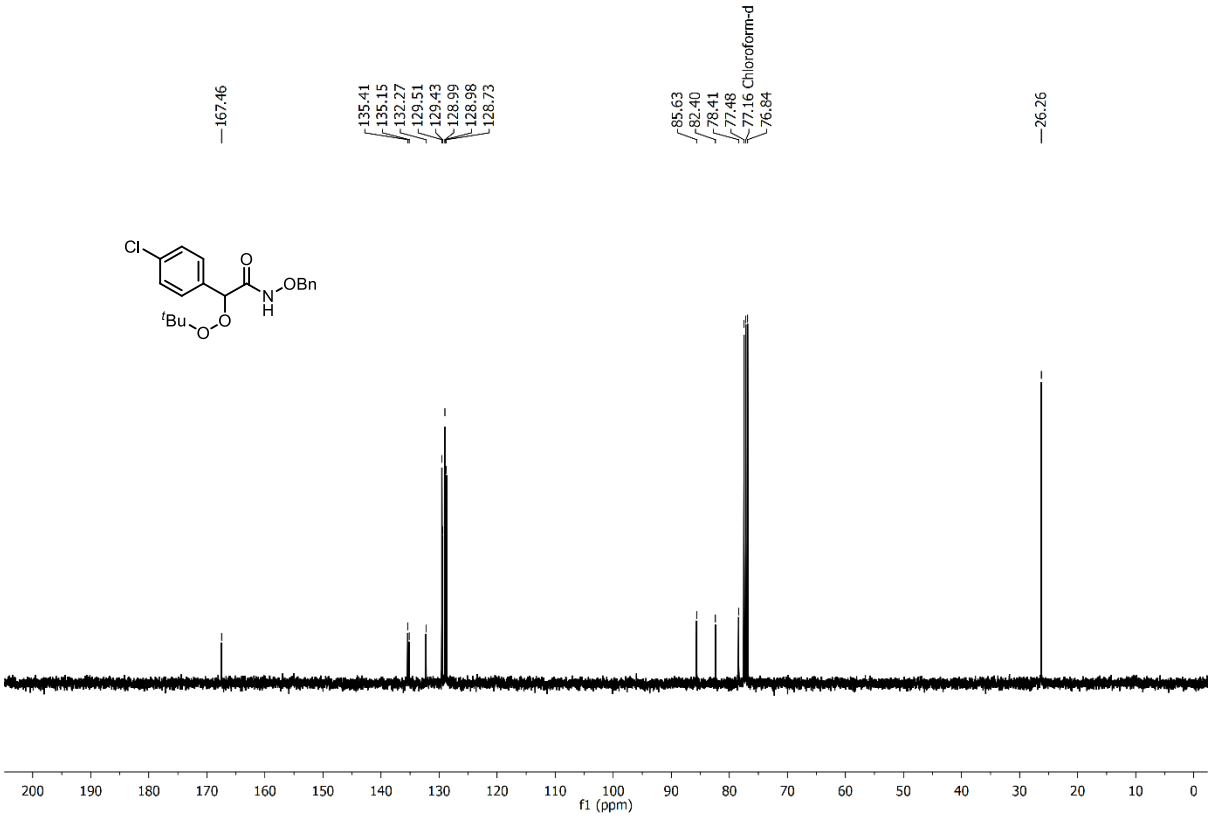


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(31)***

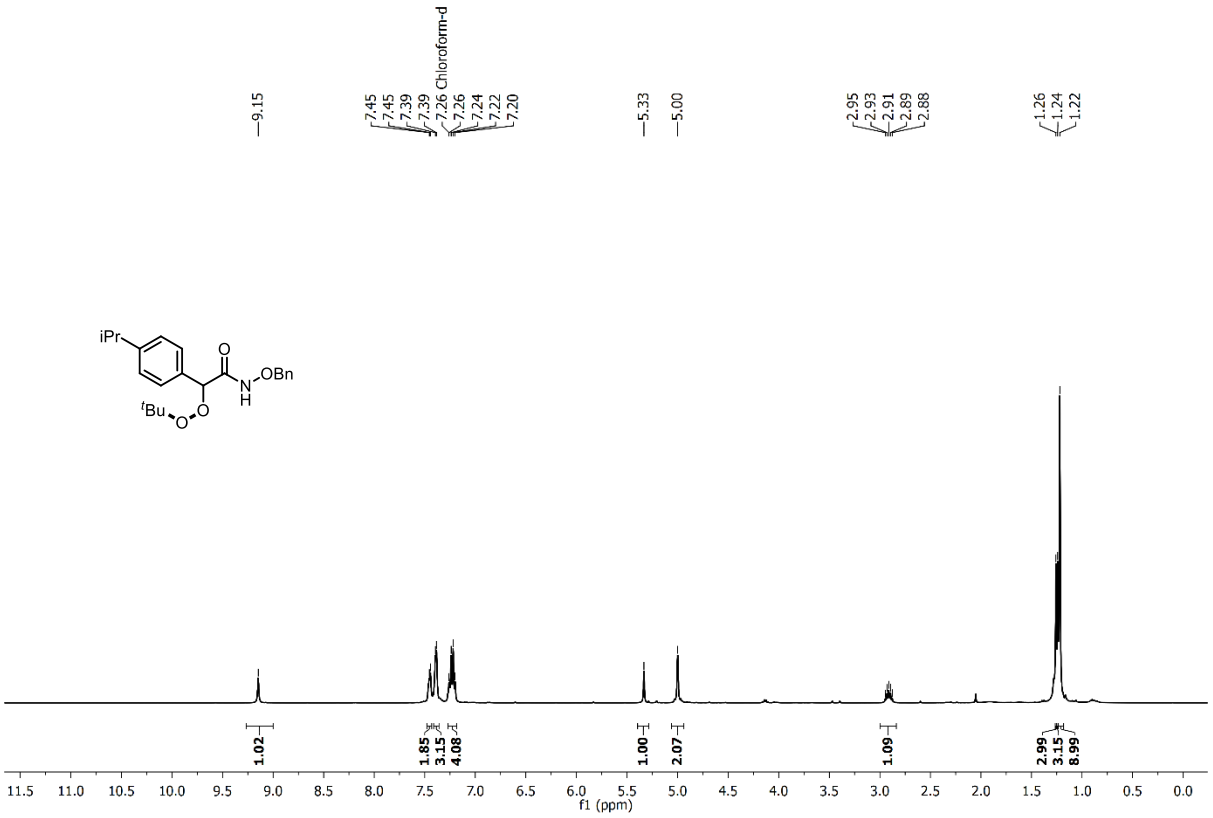


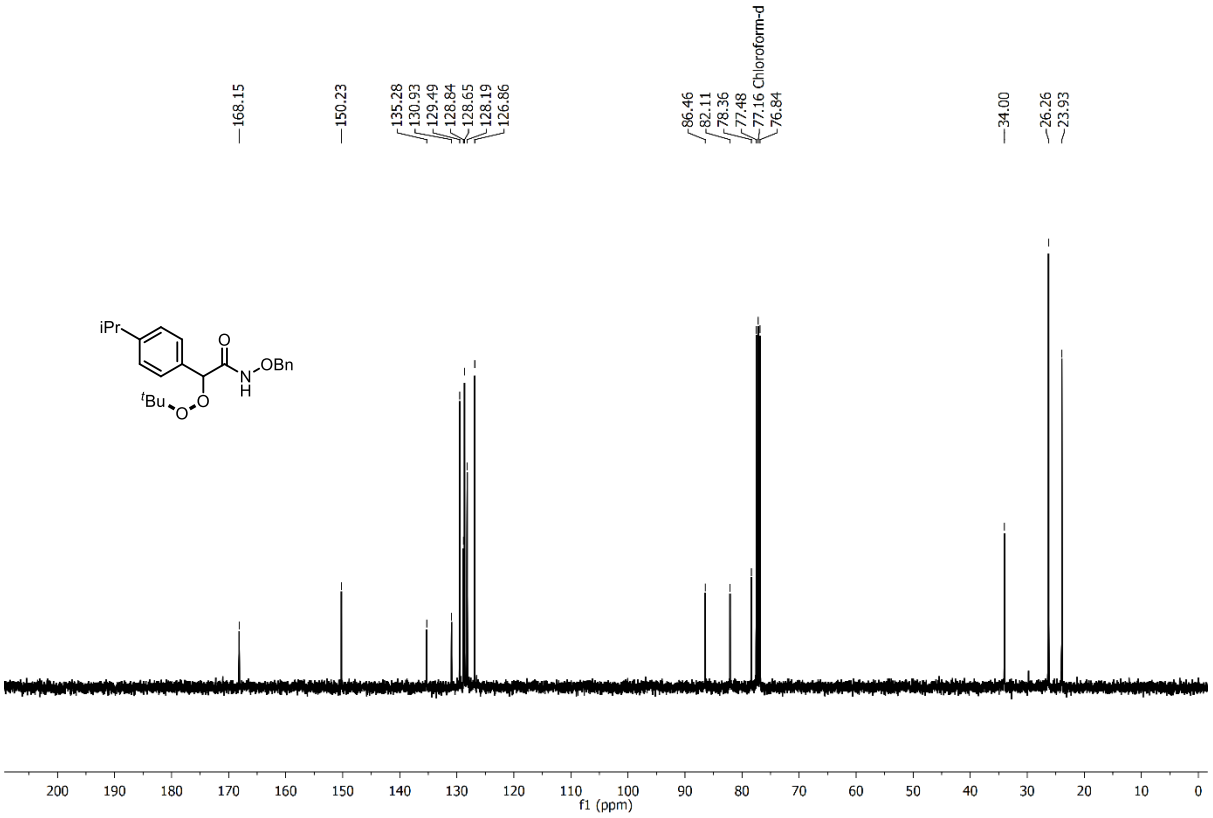
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(32)***



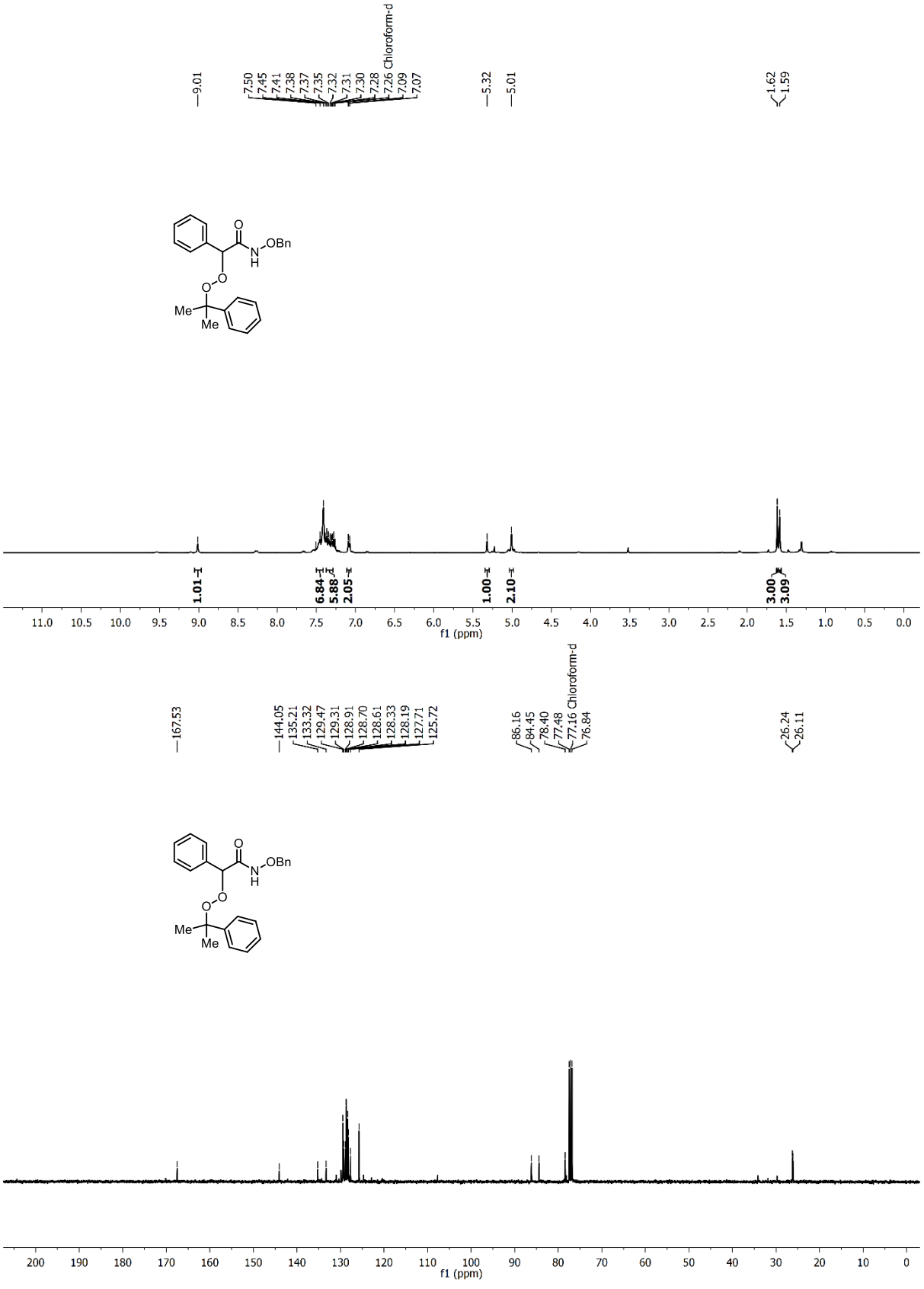


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(33)***

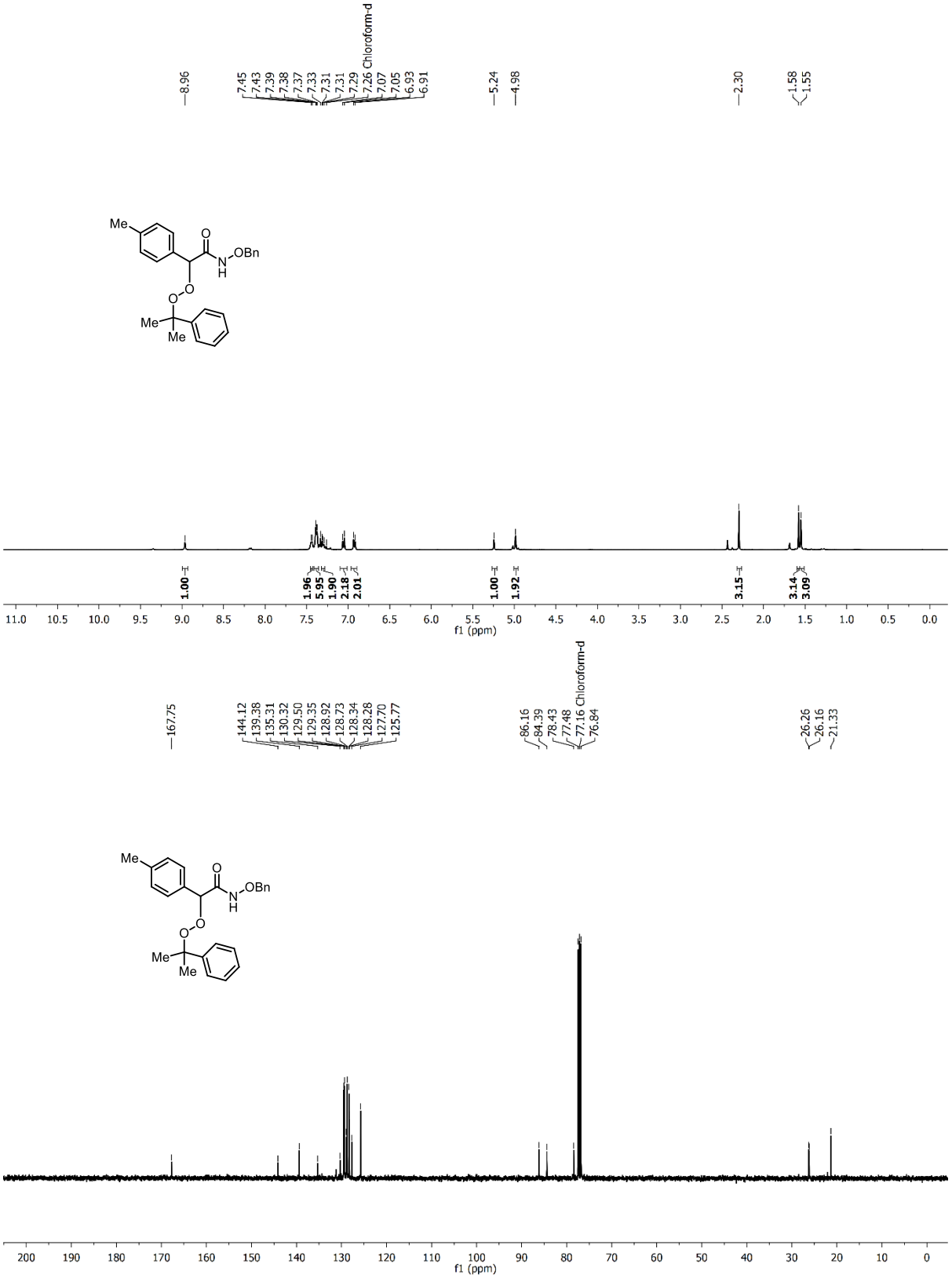




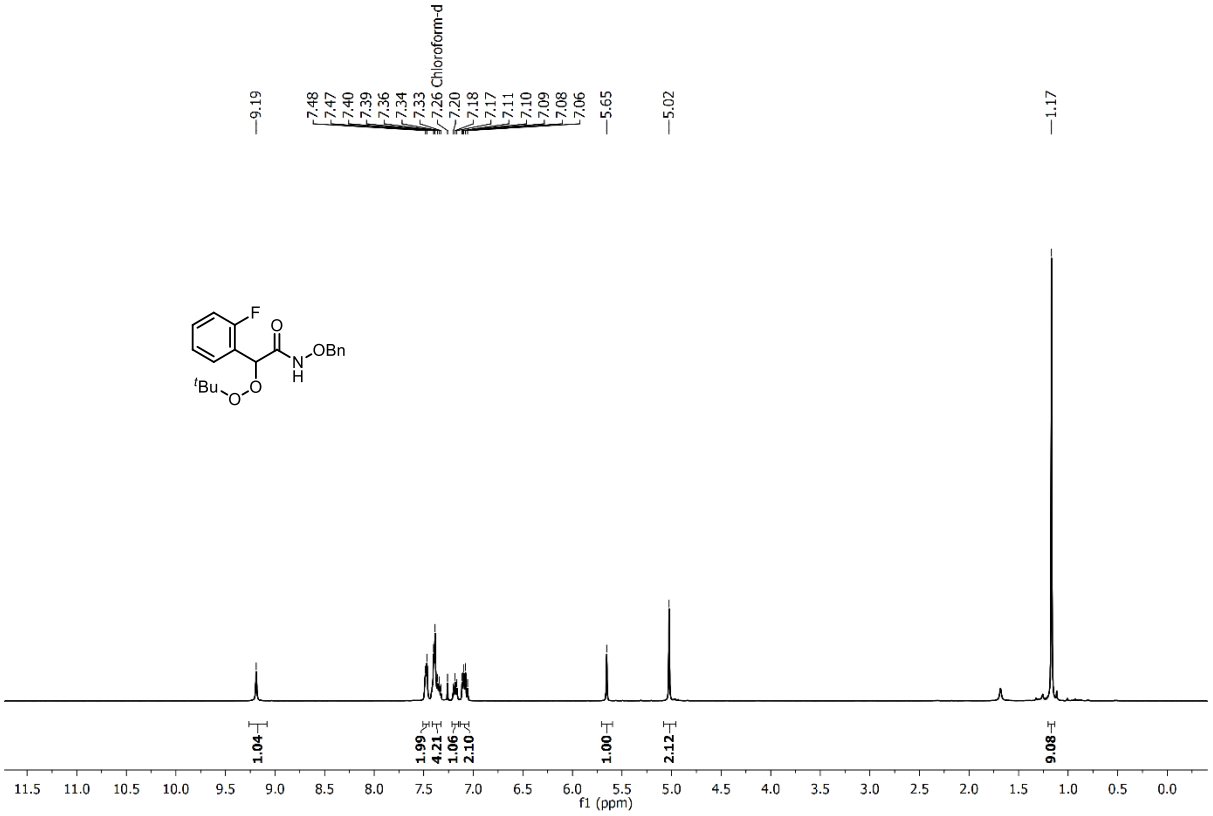
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(34)***

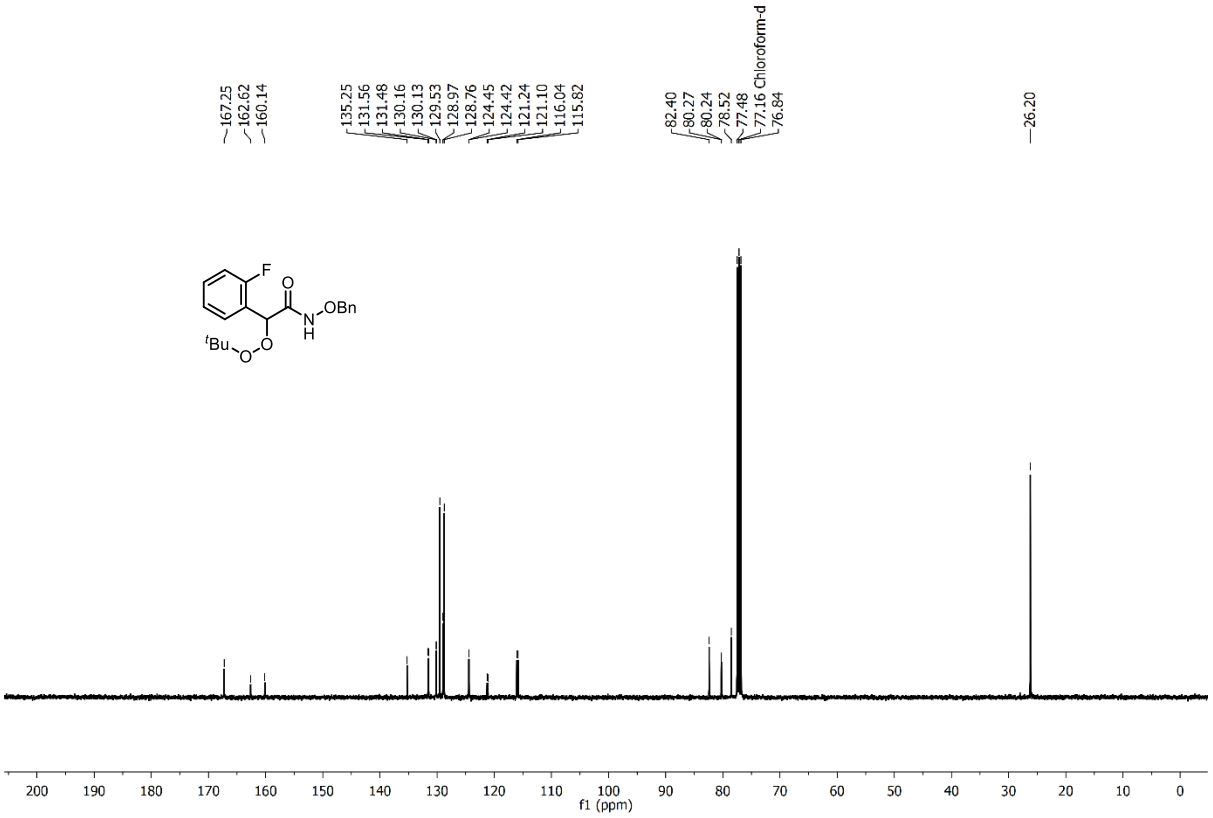


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(35)***

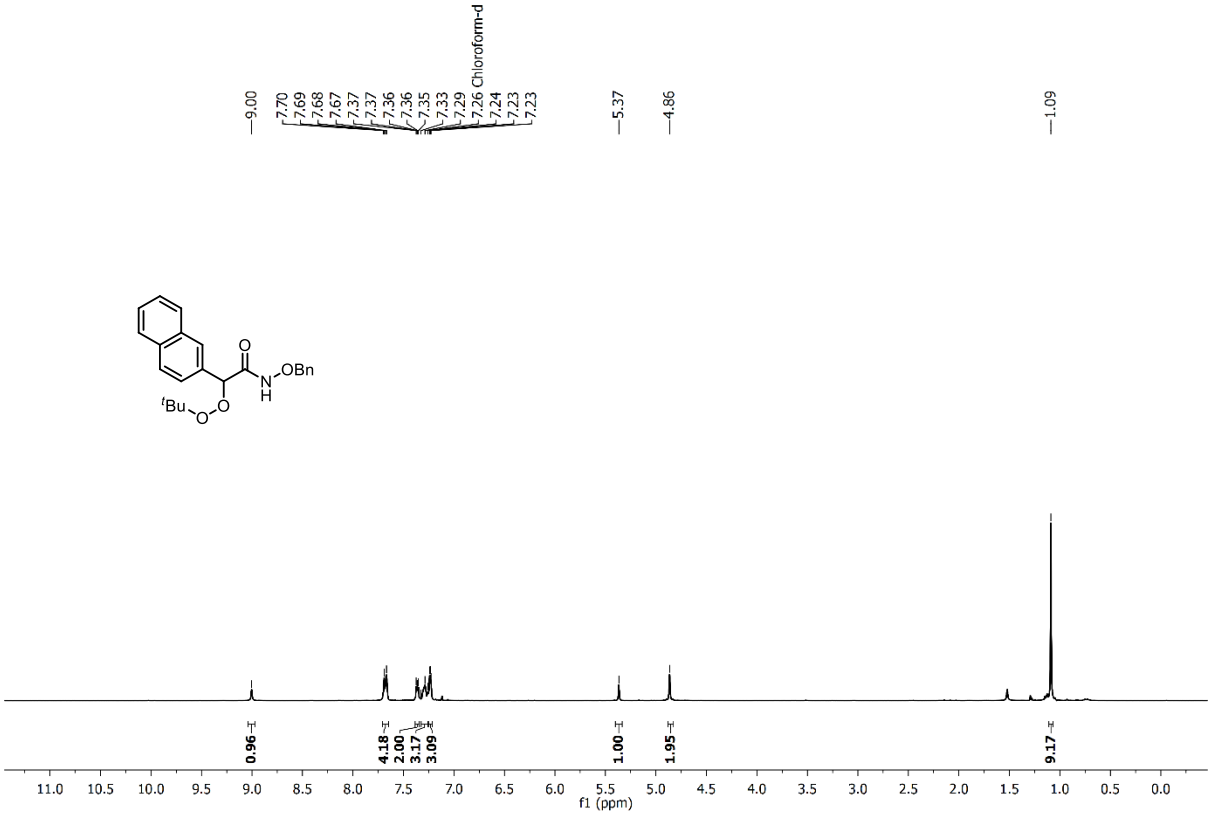


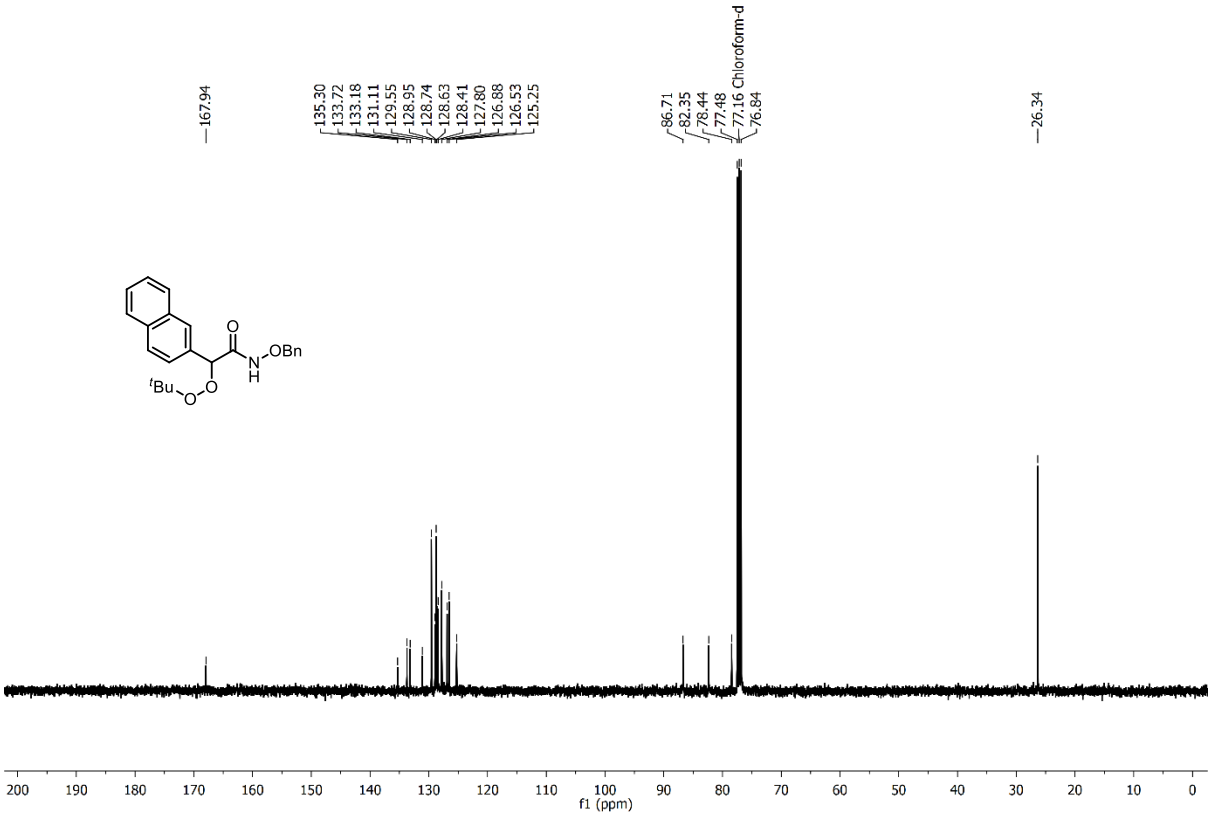
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(36)***



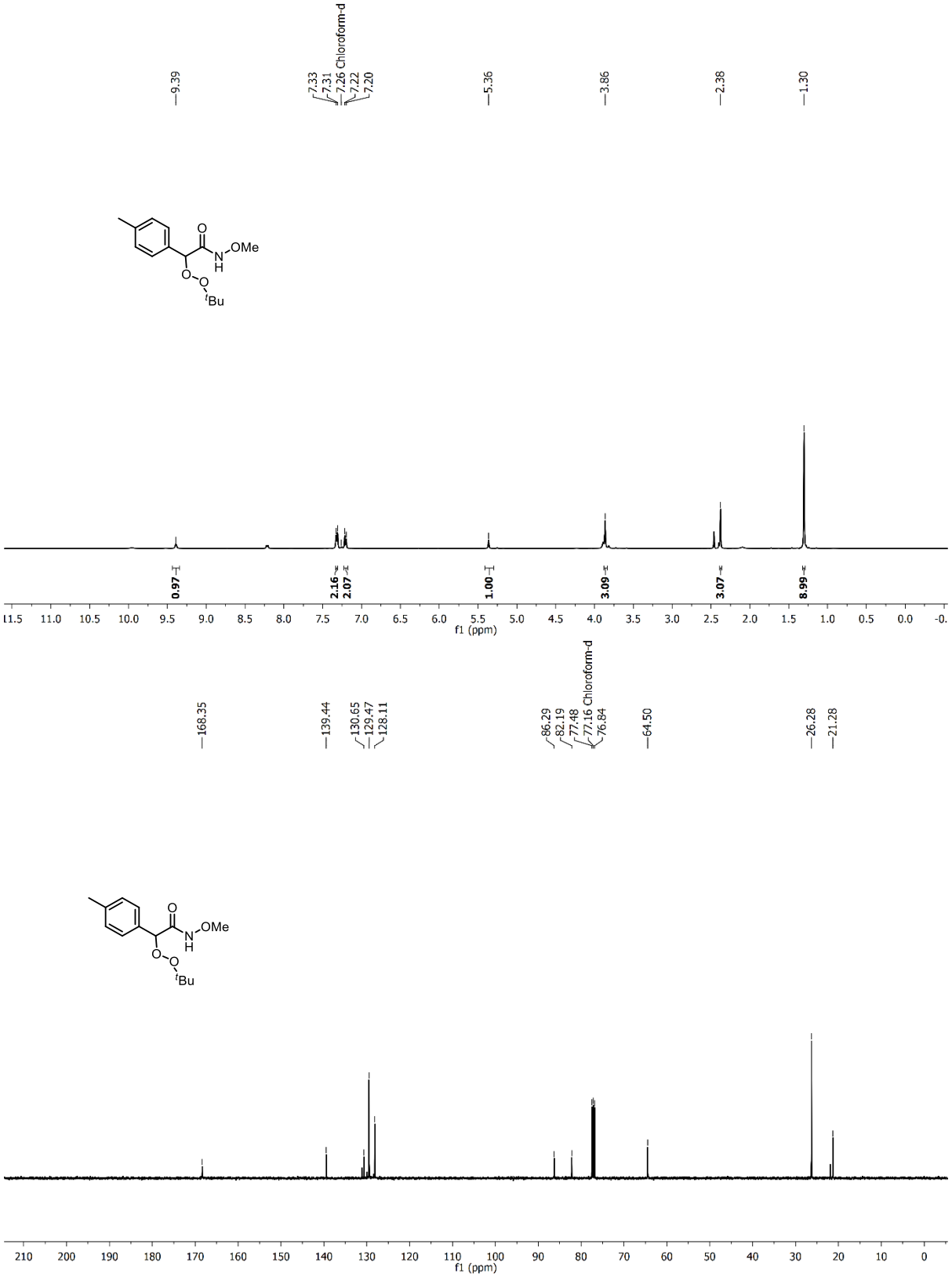


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(37)***

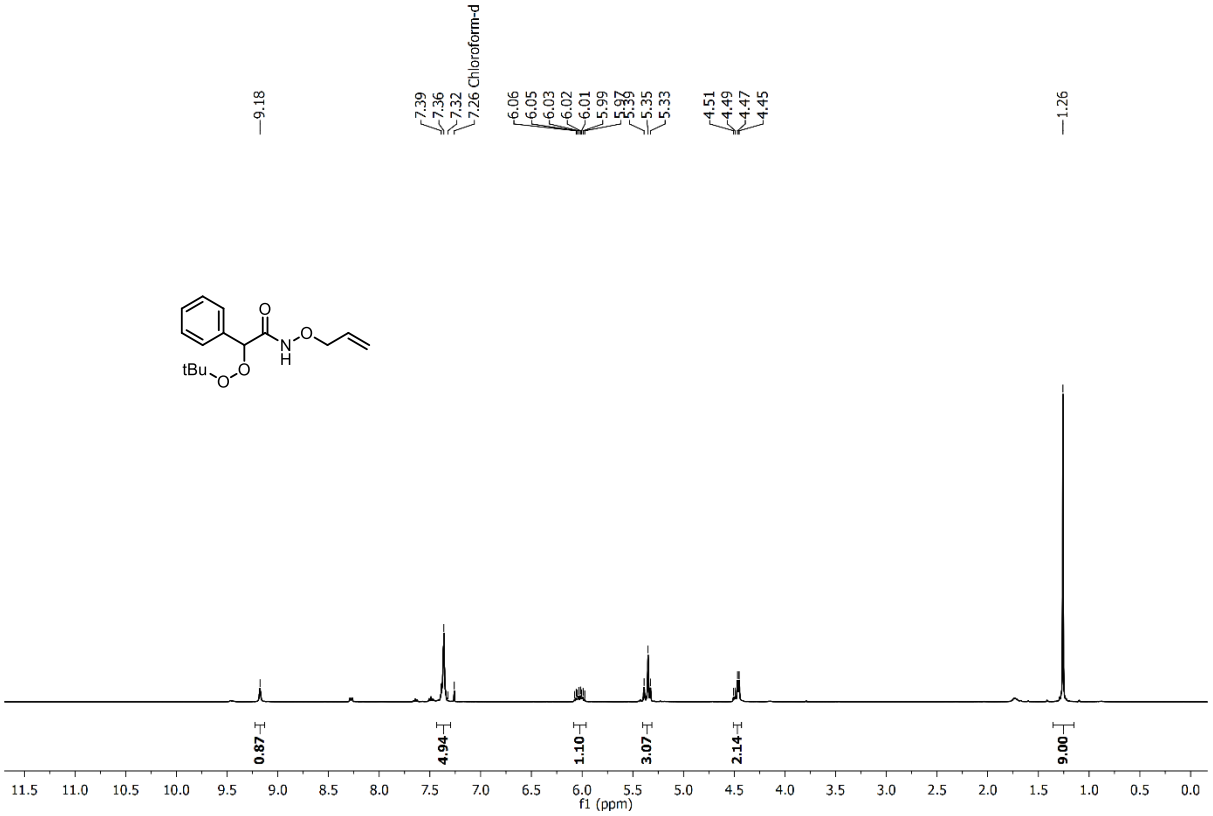


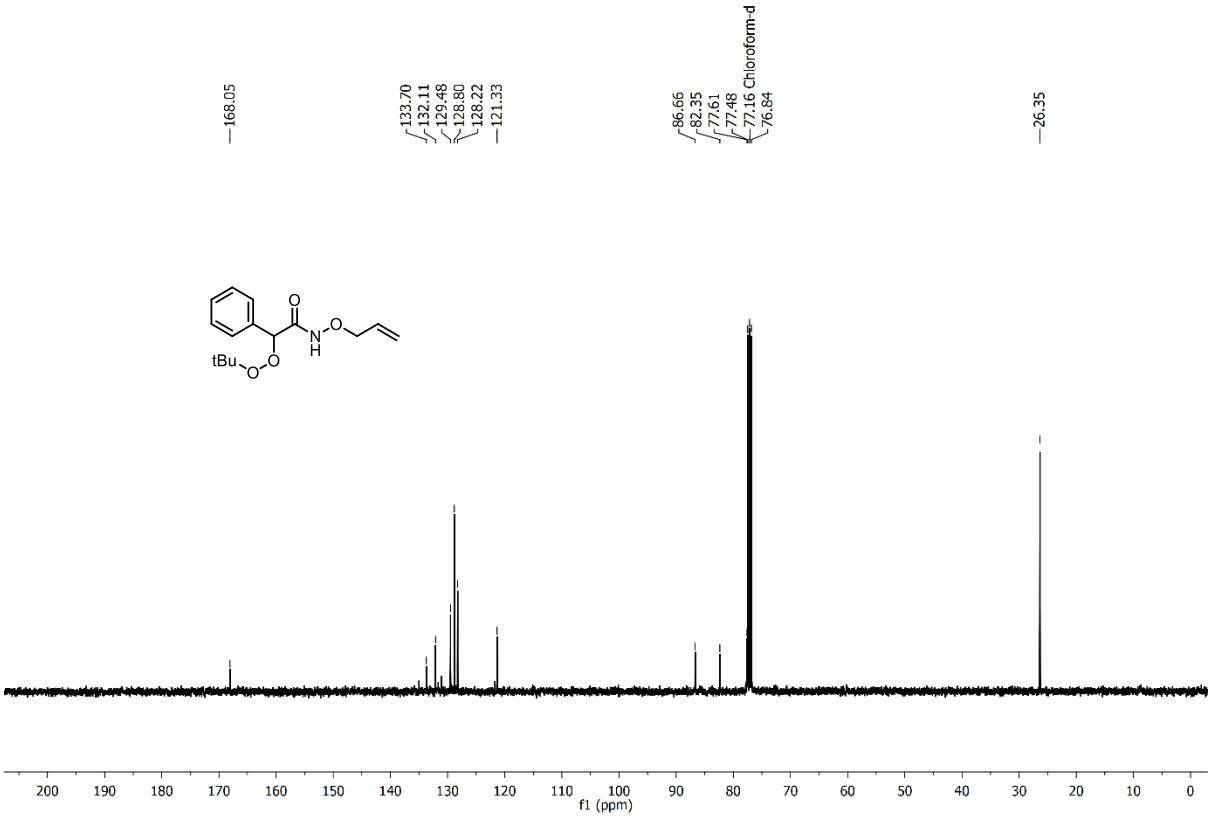


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(38)***

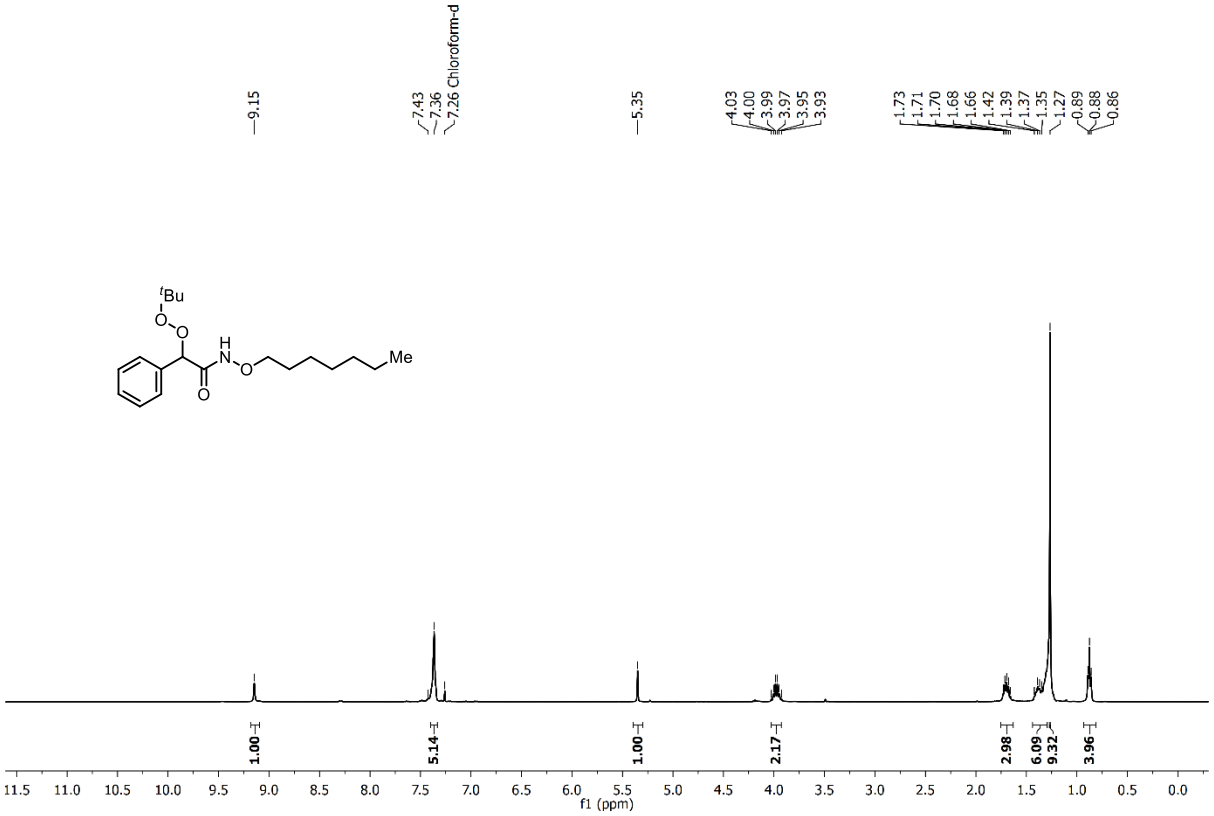


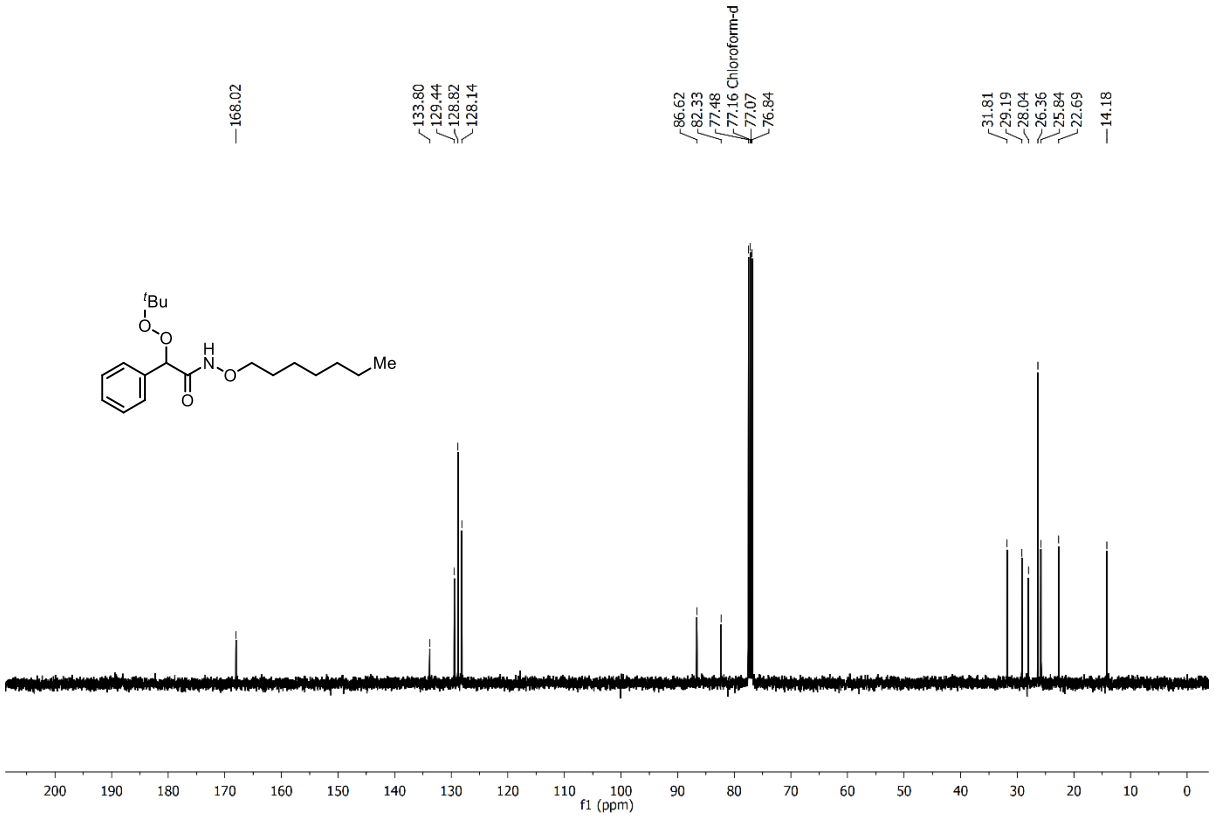
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(39)***



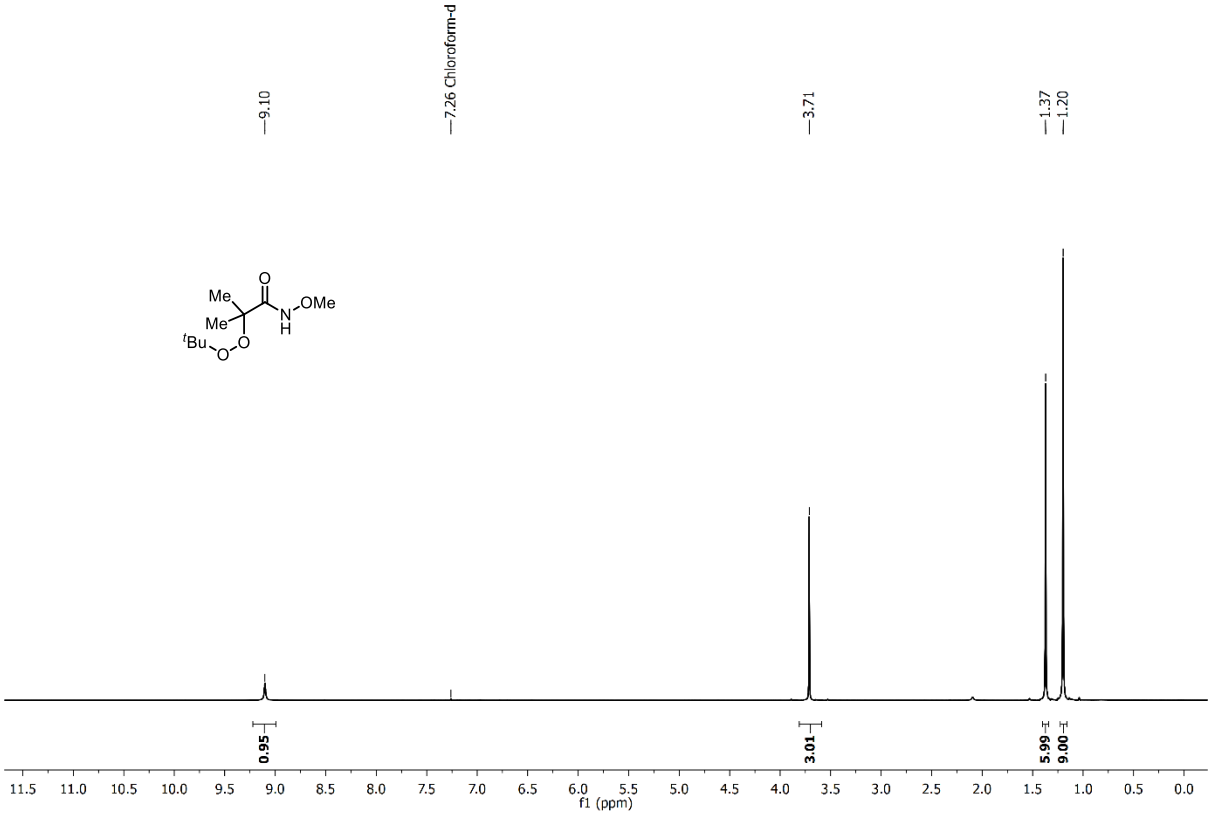


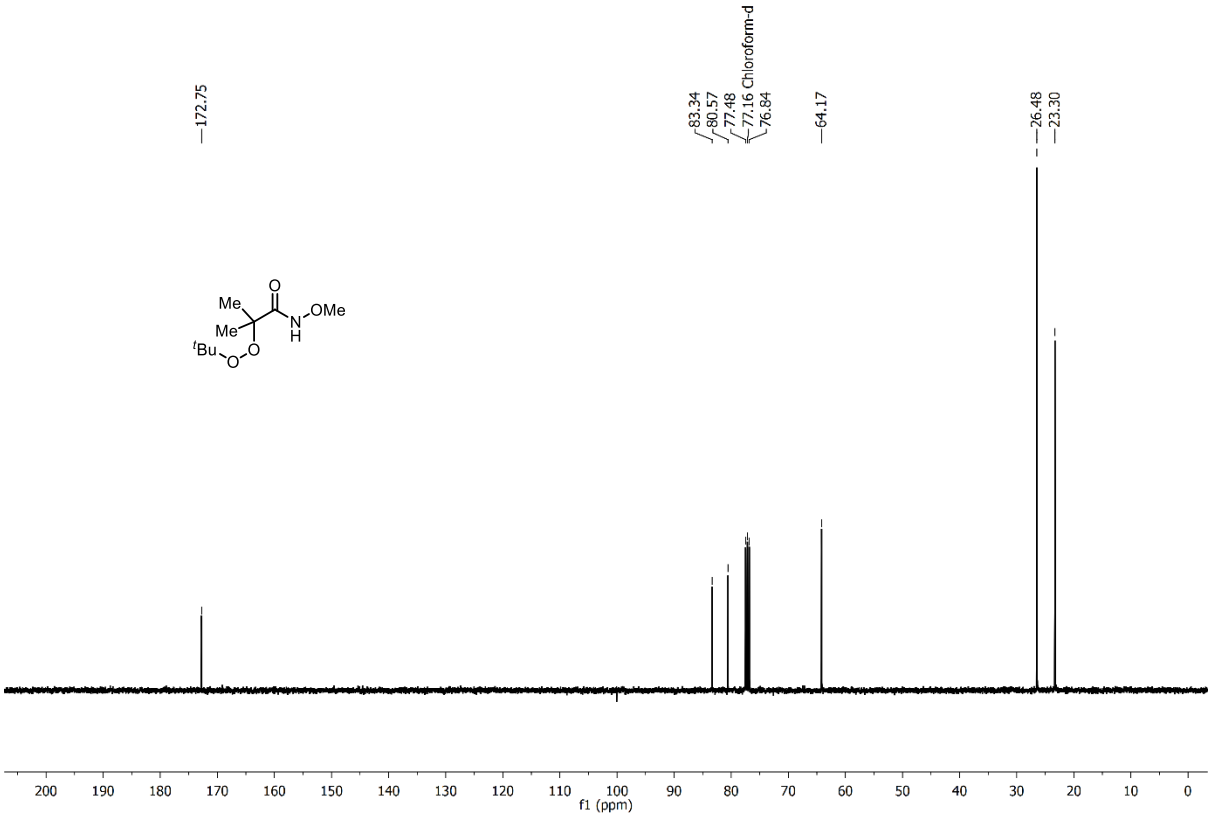
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(40)***



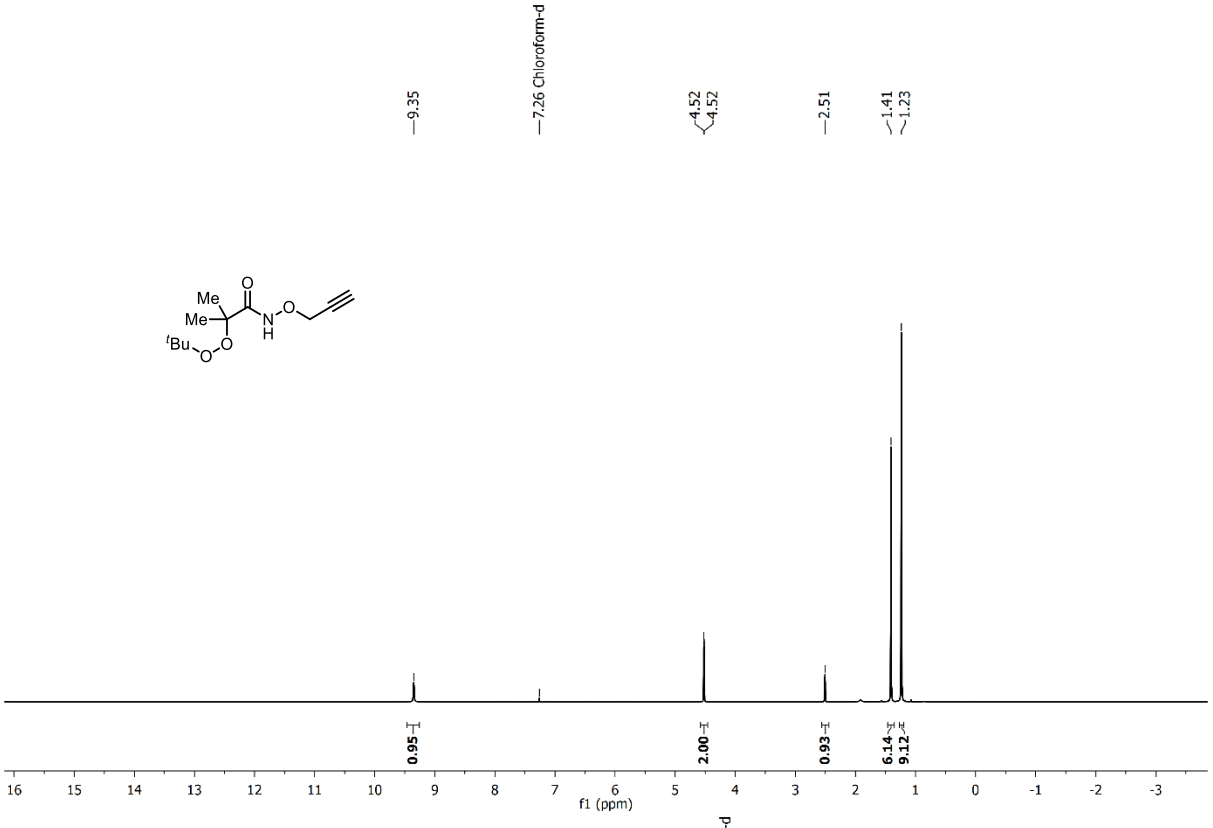


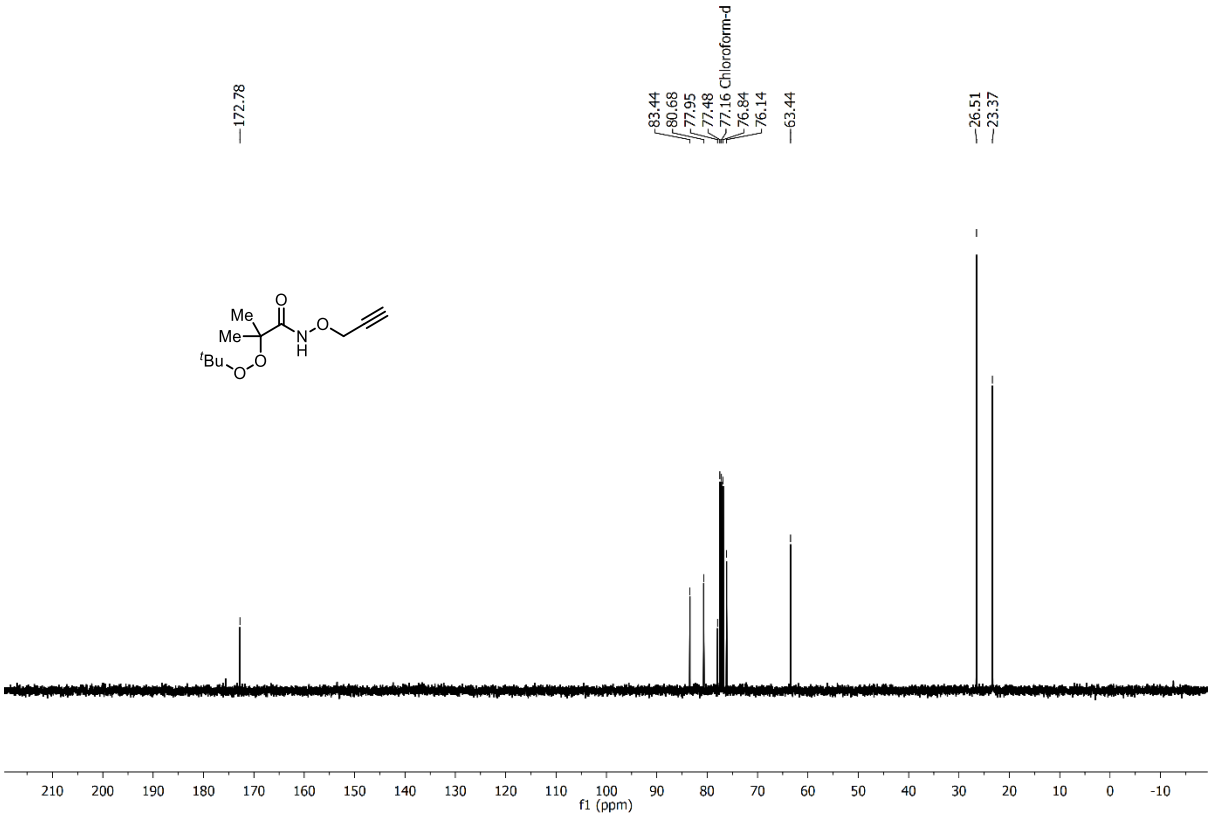
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(41)***



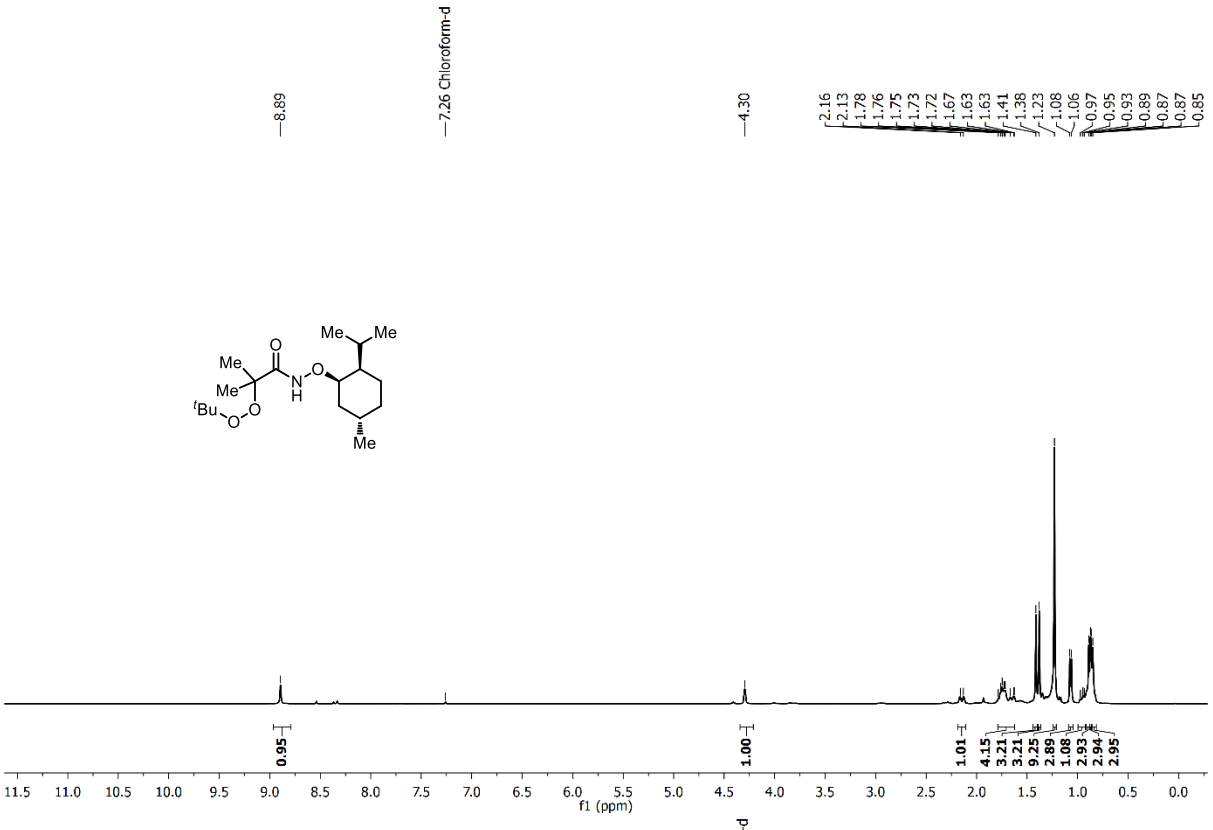


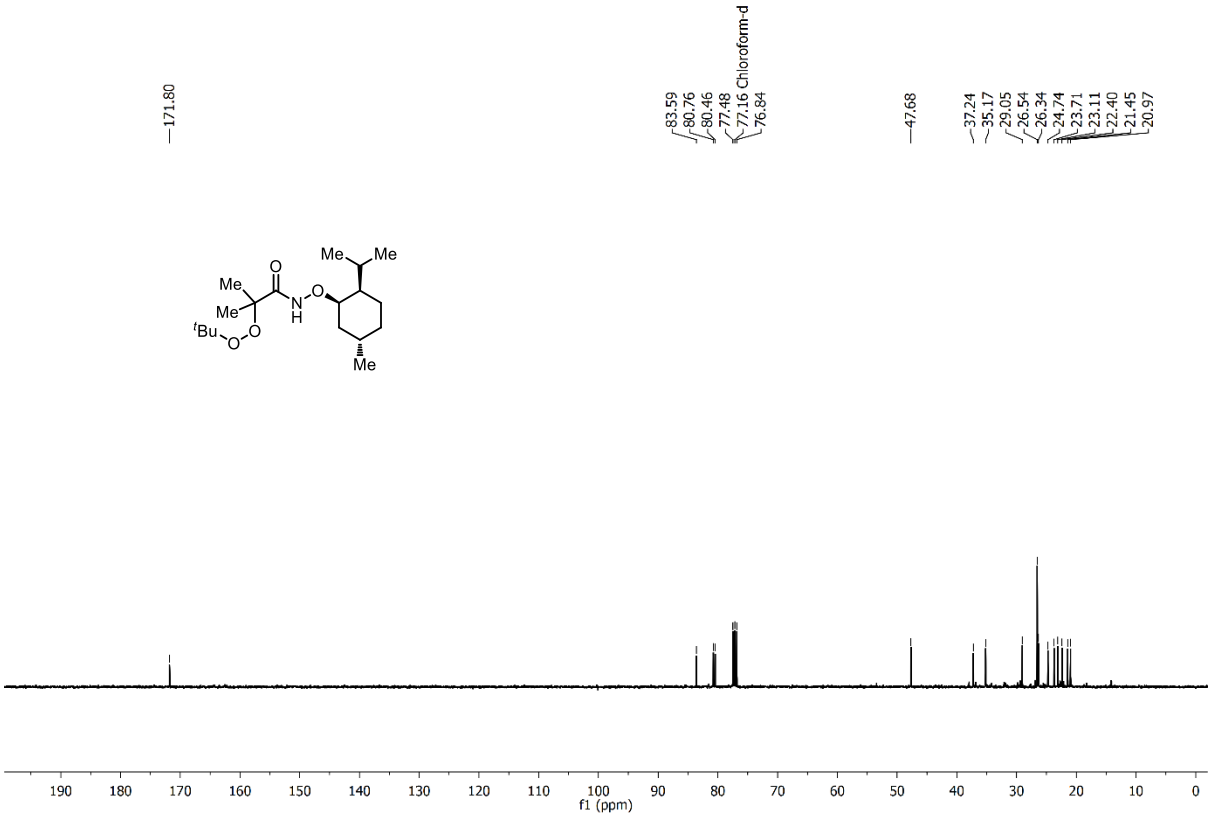
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(42)***



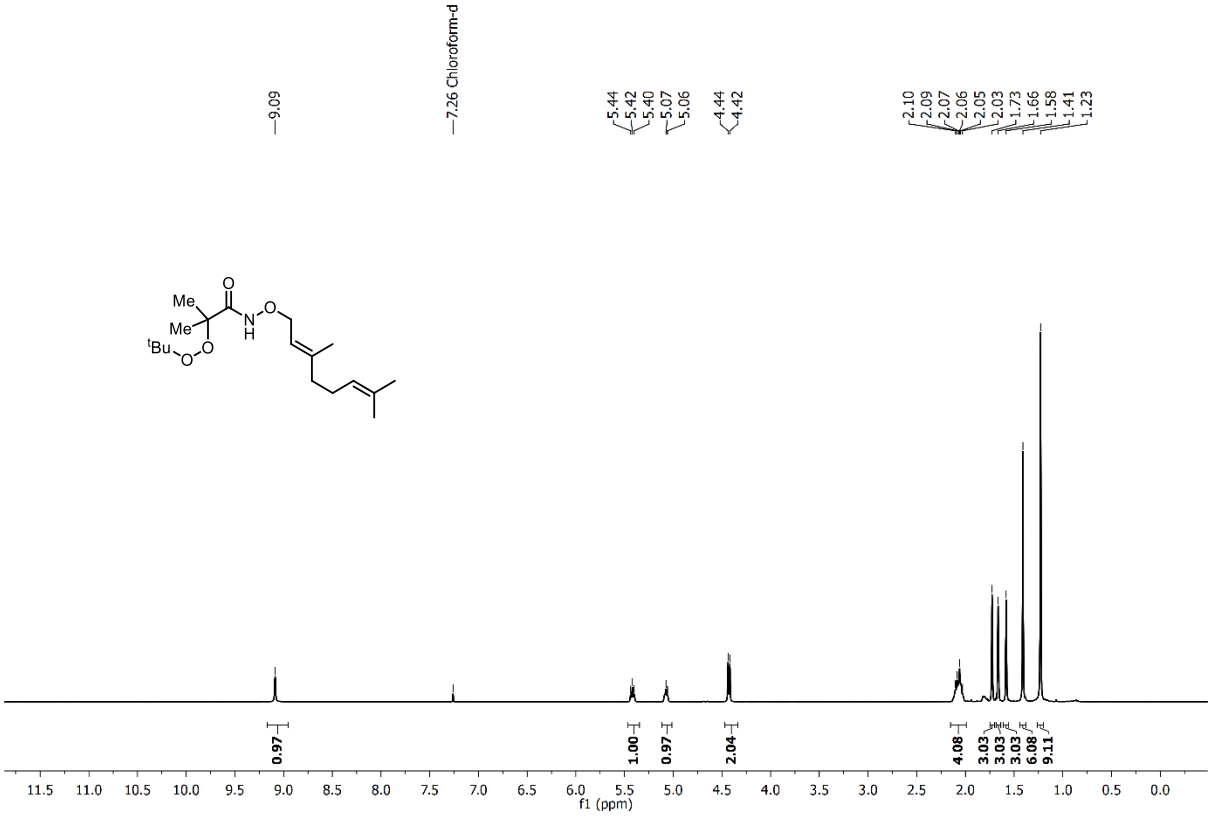


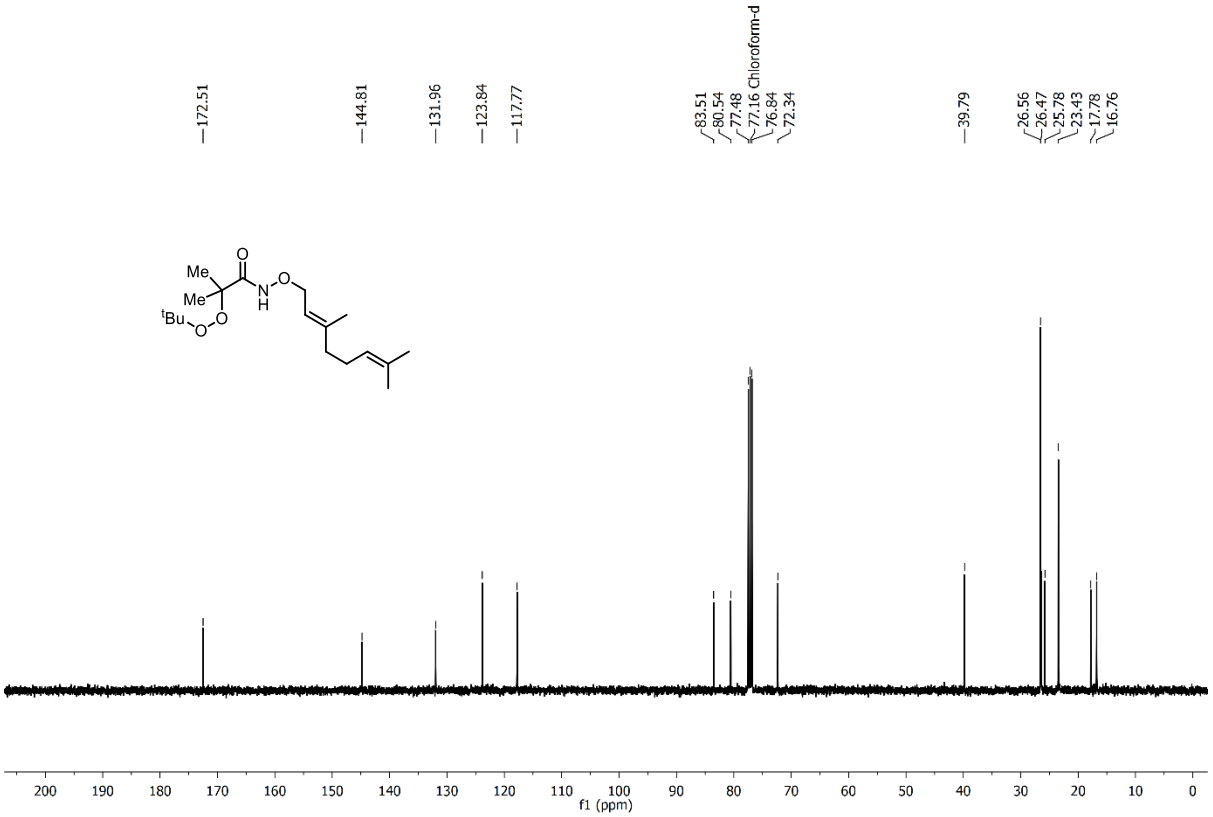
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(43)***



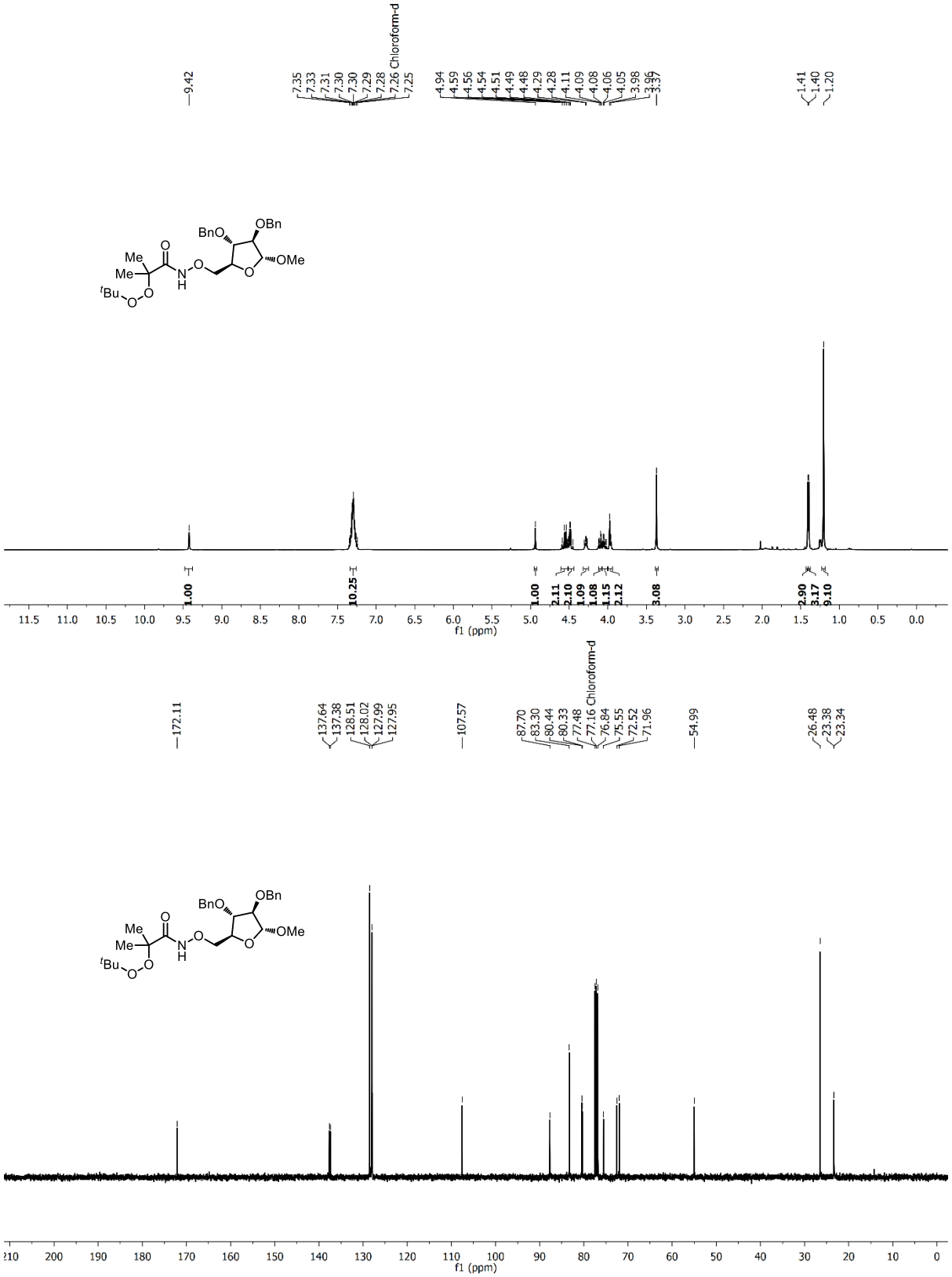


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(44)***

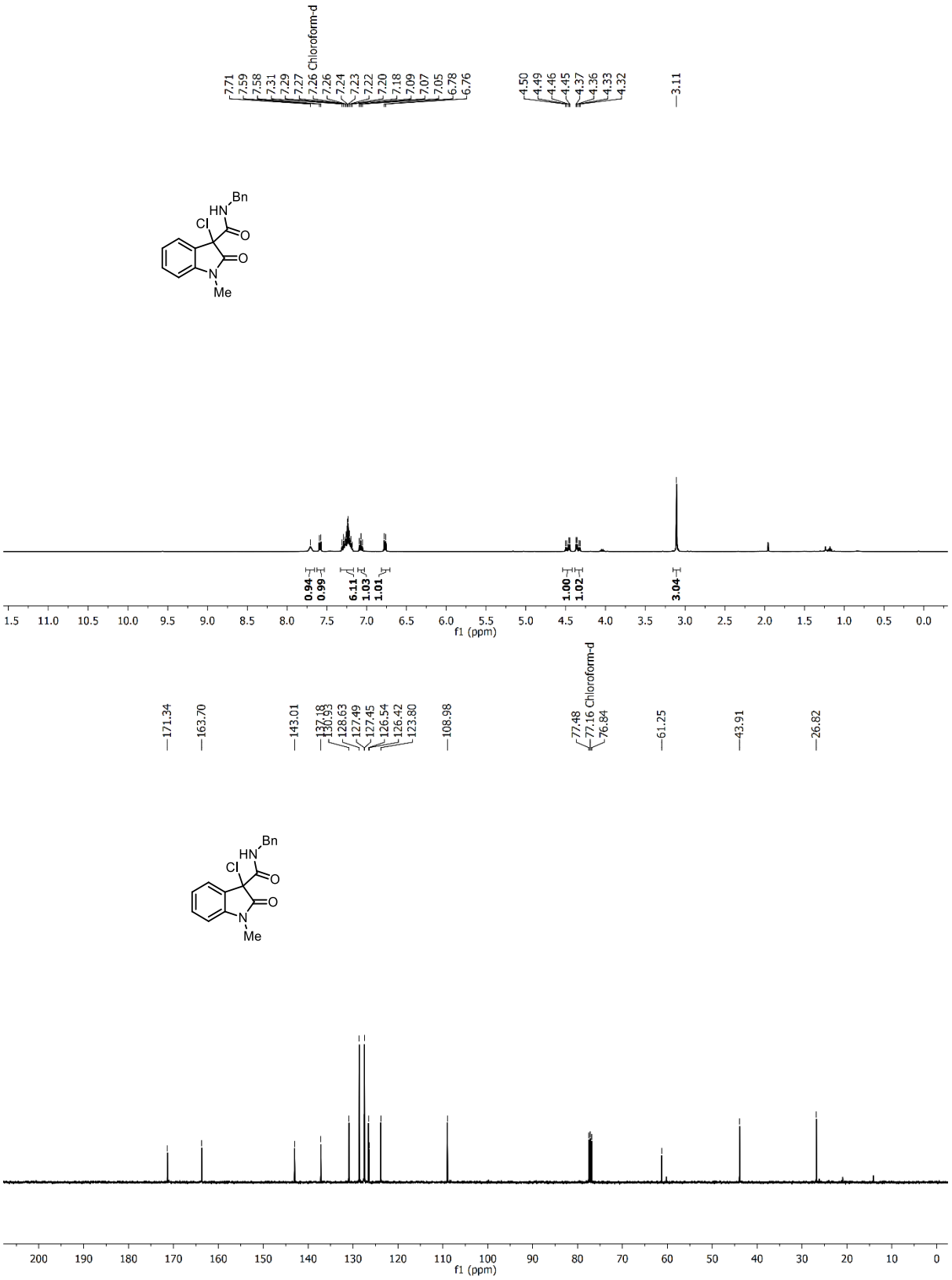




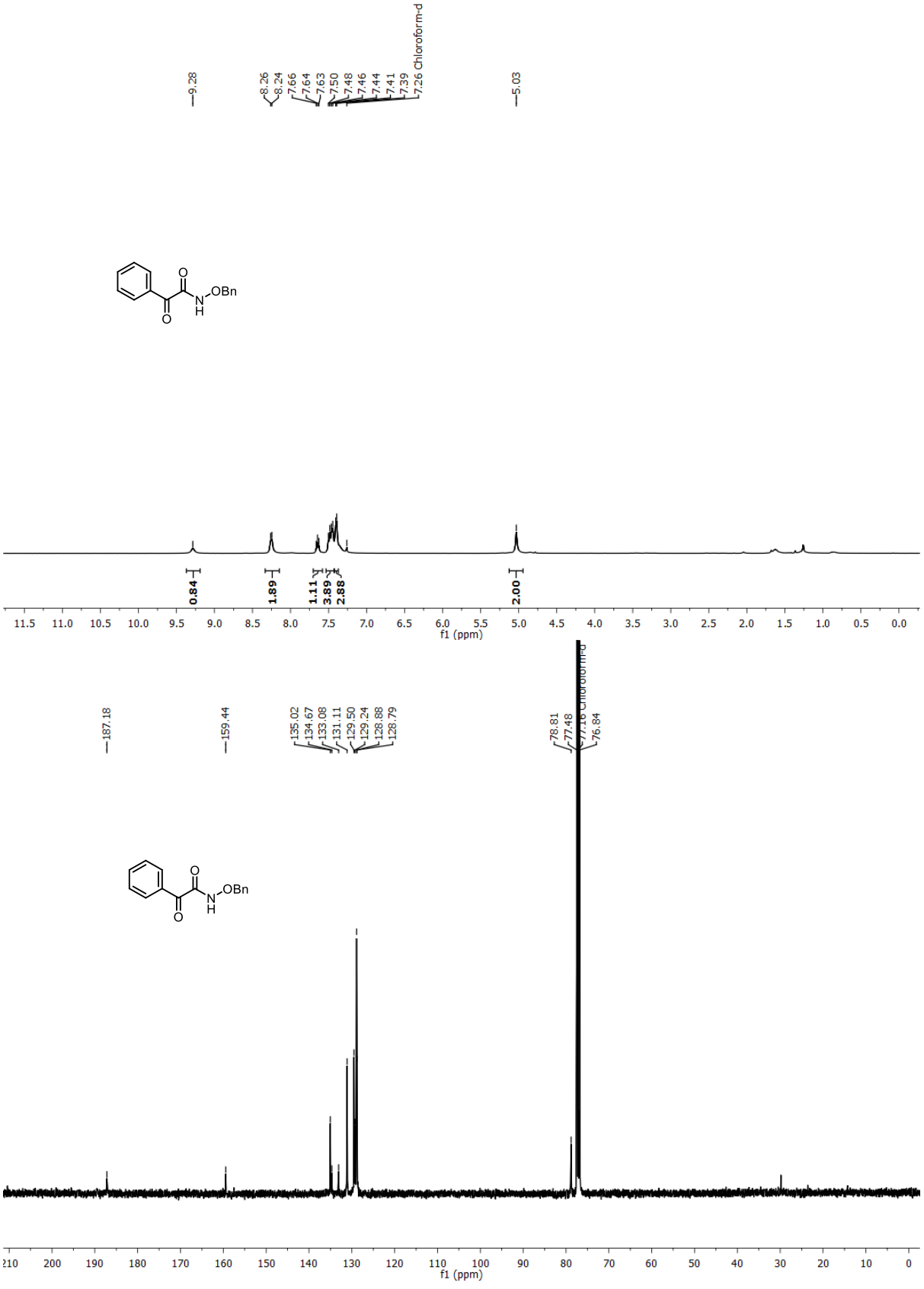
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(45)***



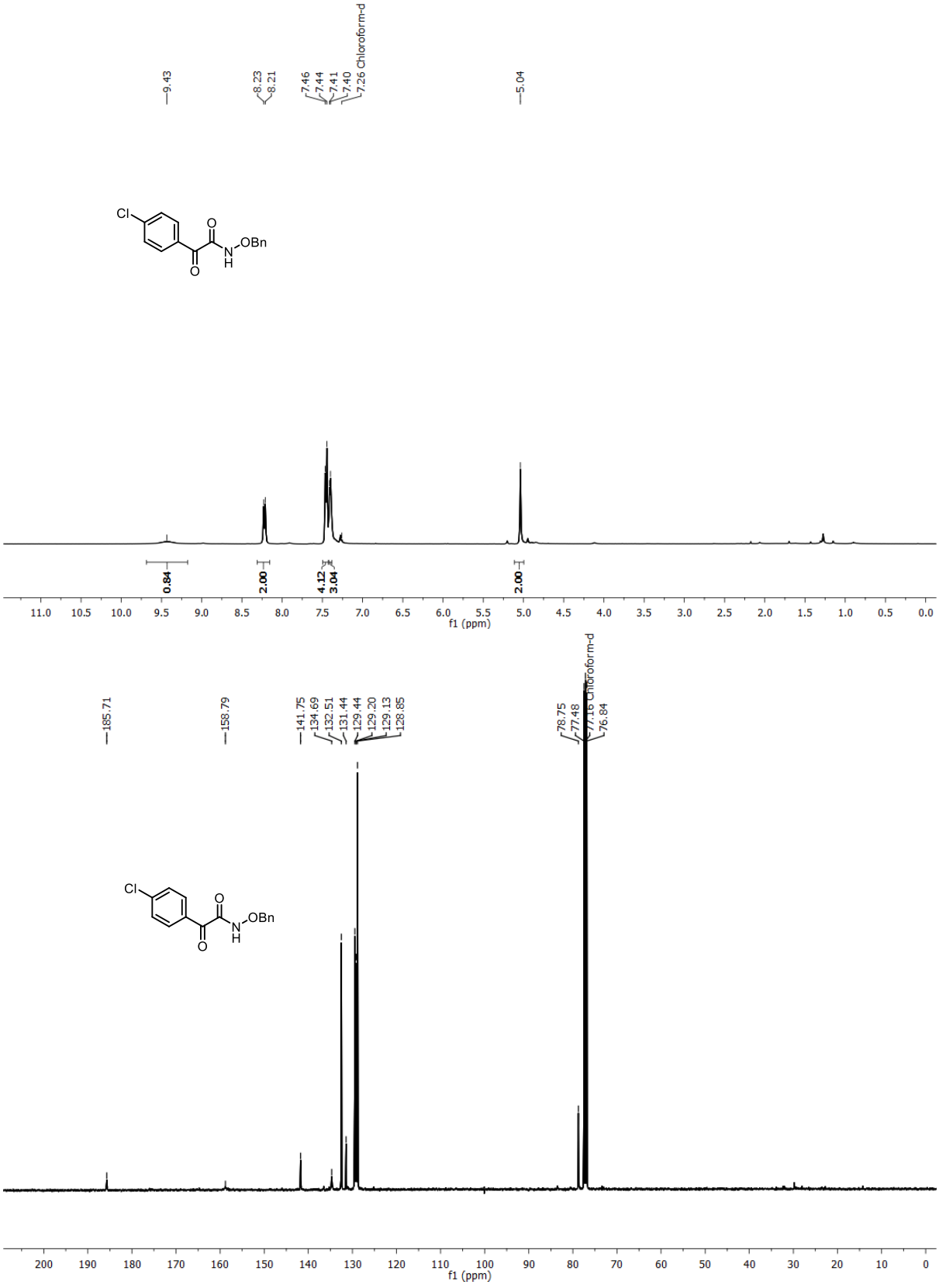
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(46)***



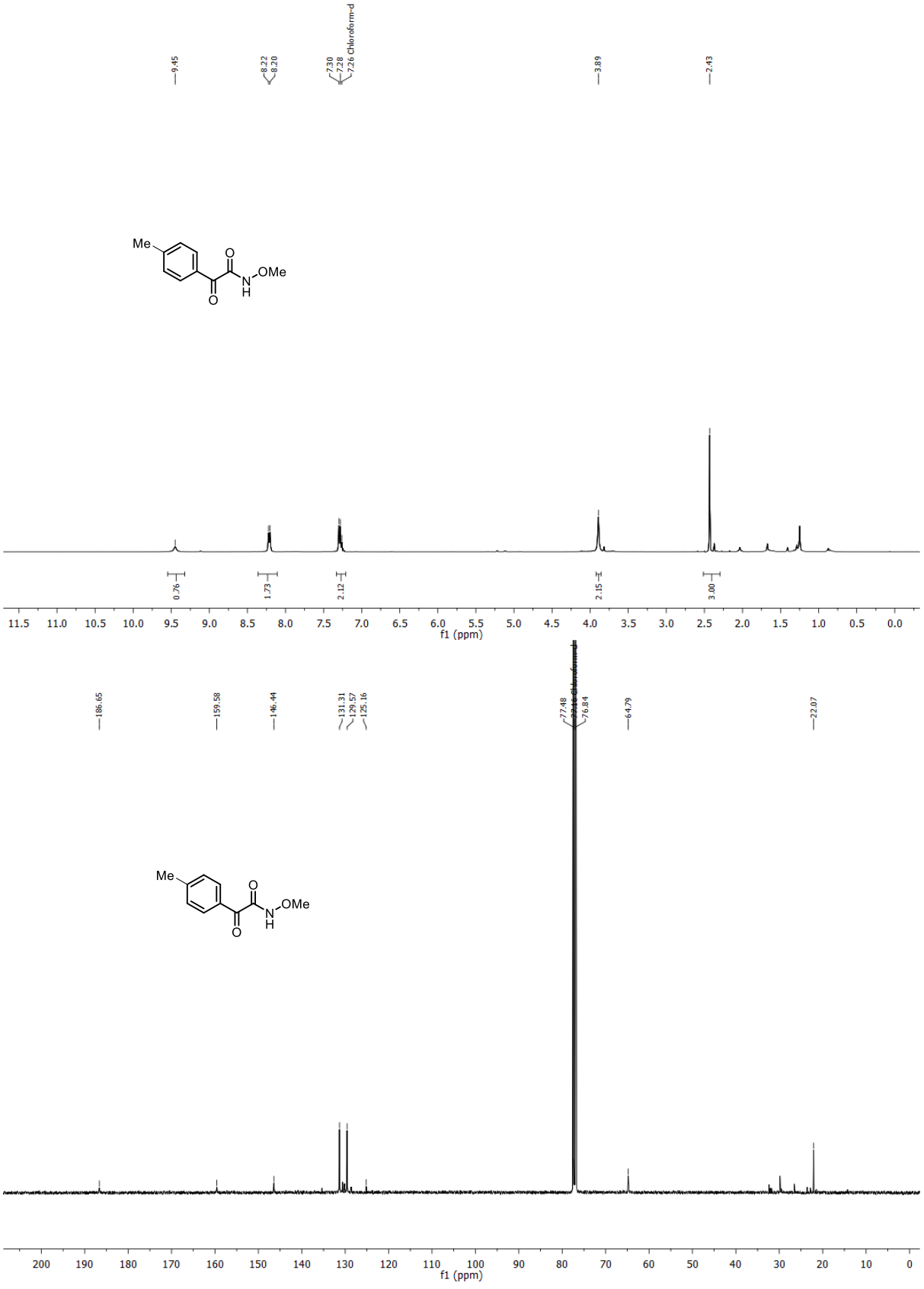
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(48)***



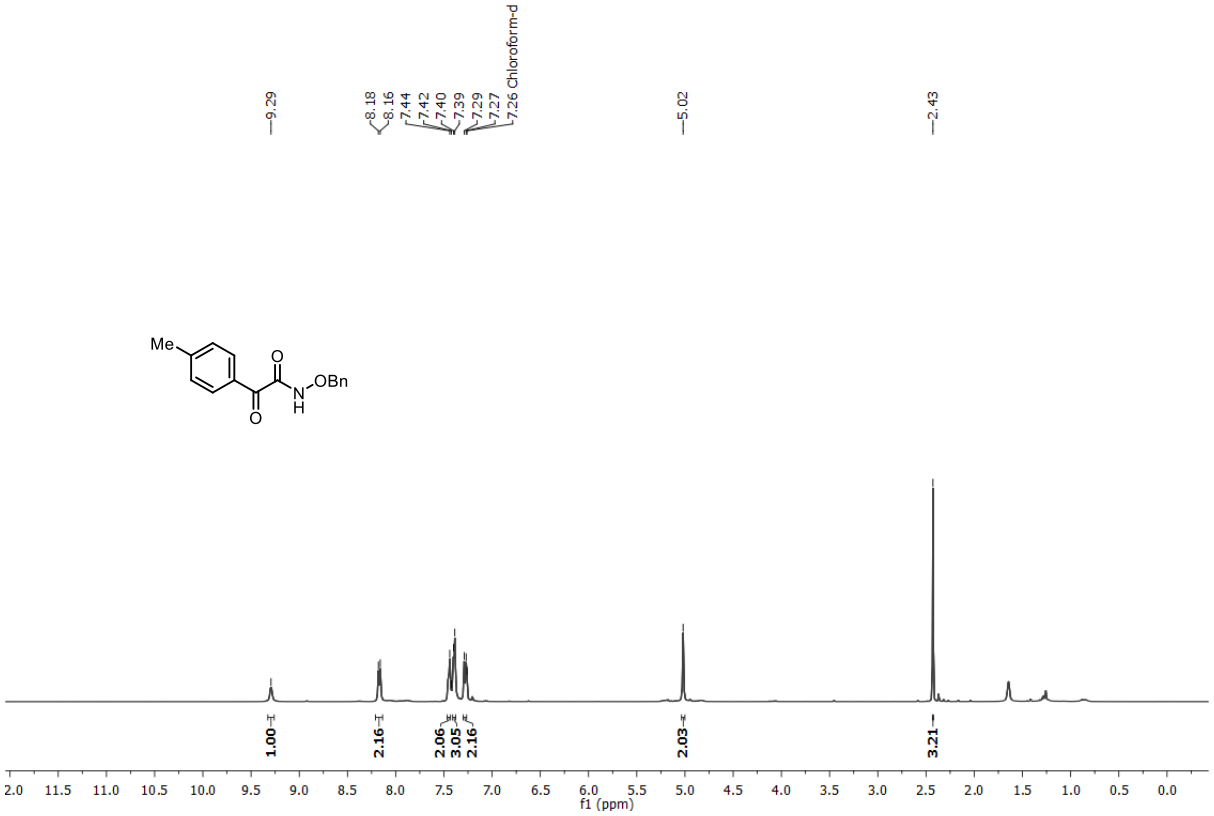
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(49)***

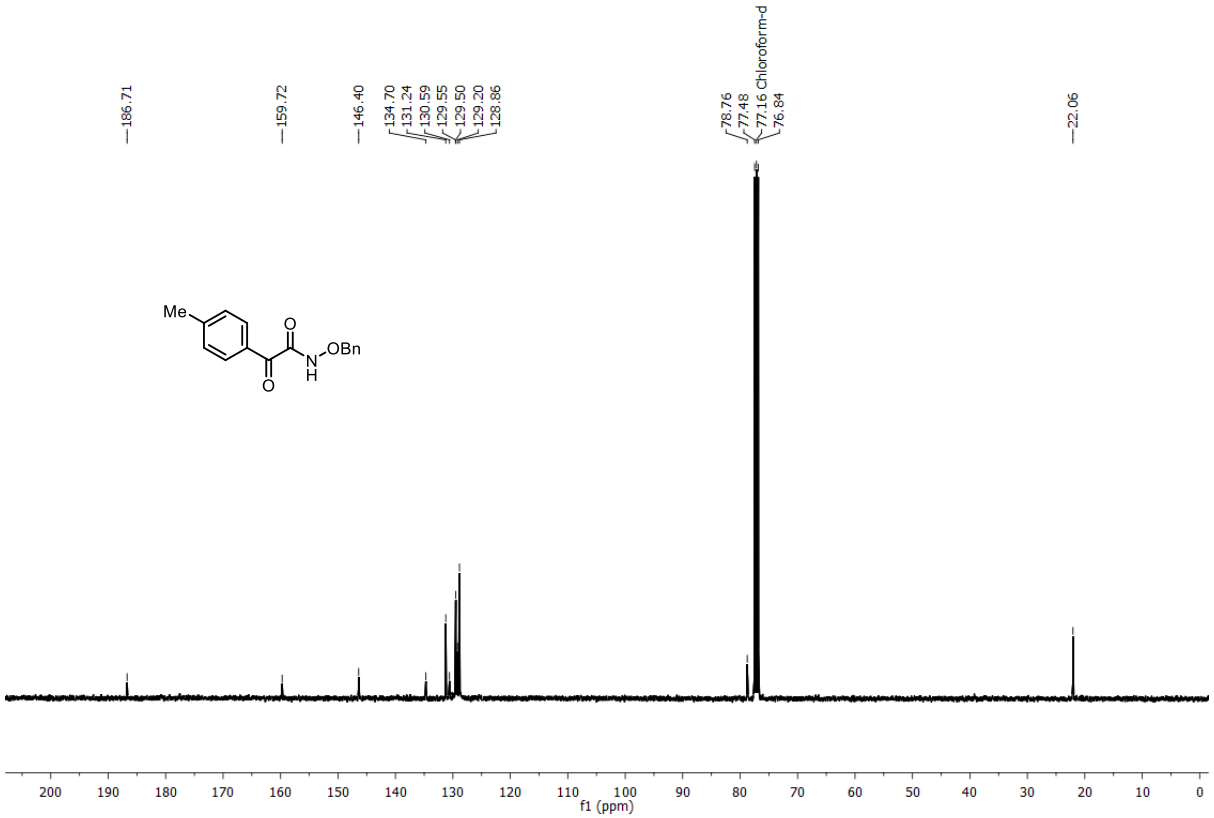


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(50)***

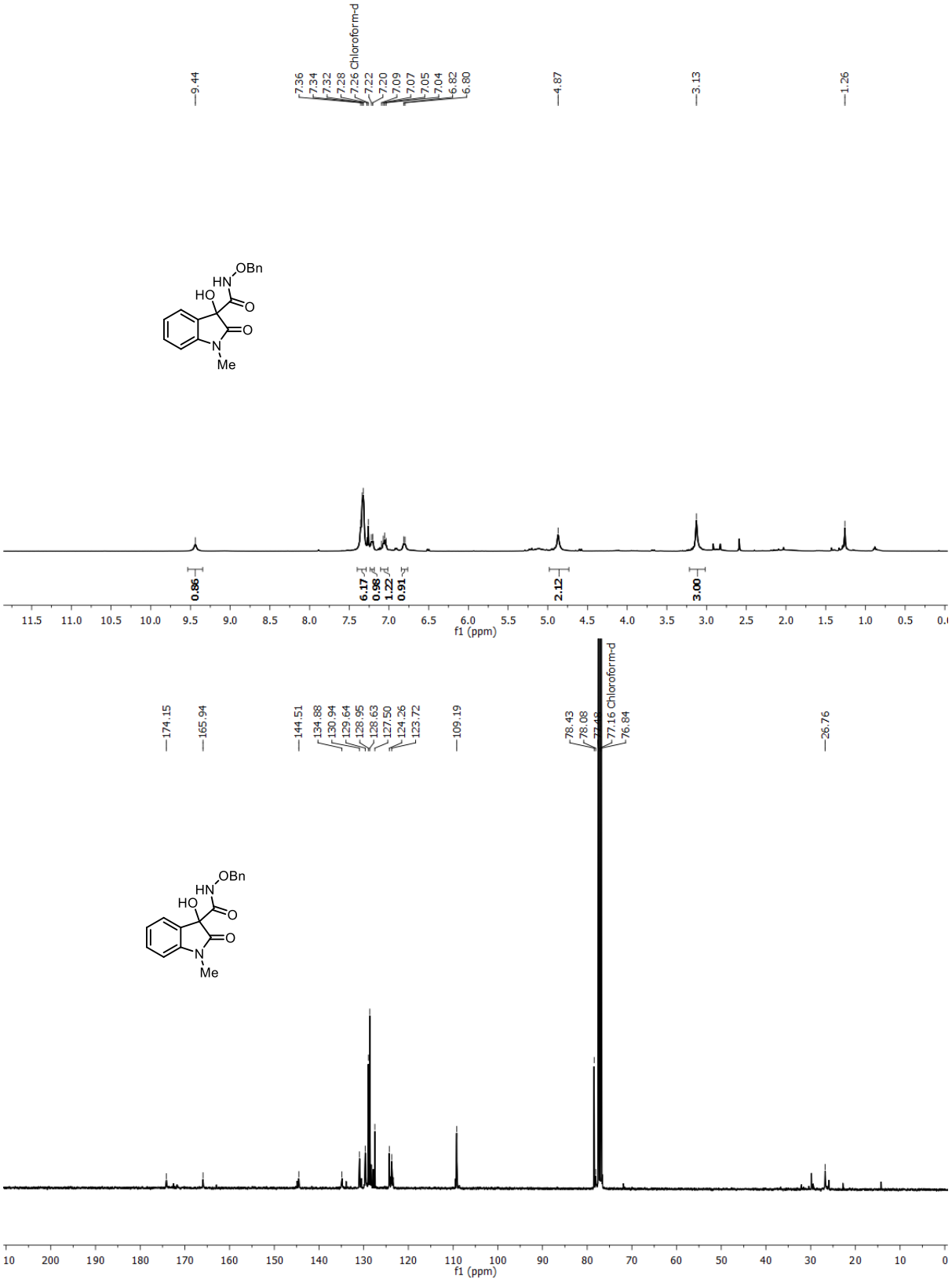


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(51)***





^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(52)***



13. Reference

1. C. S. Jeffrey, K. L. Barnes, J. A. Eickhoff and C. R. Carson, *J. Am. Chem. Soc.* 2011, **133**, 7688−7691.
2. H-J. Leng, Q-Z. Li, P. Xiang, Q-S. Dai, Z-Q. Jai, C. Gou, X. Zhang and J-L. Li, *Org. Lett.* **23,** 1451-1456.
3. J. Lihui,B. Liwei, Y. Xinyi, Z. Xiaowei and J. Zhiyong, *J. Org. Chem*. 2016, **81**, 9620-9629.
4. C. Simon, E. Benjamin, T-G. Ludouie, W. Sara A.M. *J. Am. Chem. Soc.* 2020, 142,5549-5555.
5. P. H. Dussault, T. K. Trullinger and F. Noor-e-Ain, *Org. Lett.* 2002, **4**, 4591-4593.
6. S. Kyasa, R. N. Meier, R. A. Pardini, T. K. Truttmann, K. T. Kuwata and P. H. Dussault, *J. Org. Chem.* 2015, **80**, 12100.
7. T.G. Driver, J. R. Harris and K.A. Woerpel, *J. Am. Chem. Soc.* 2007, **129**, 3836-3837.
8. J. Hill, A. A. Hettikankanamalage and D. Crich, *J. Am. Chem. Soc.* 2020, **142,** 14820-14825.
9. C. Y. Lee and S.-G. Kim, *Eur. J. Org. Chem*. 2021, 1607-1614.