Supporting Information

[3+2]-Annulation of Azaoxyallyl Cations and Thiocarbonyls for the Assembly of Thiazolidin-4-ones

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1. General Experimental.

Unless otherwise noted, all the reactions were conducted under an inert atmosphere (nitrogen or argon) using oven or flame-dried glassware. Solvents were dried following the standard procedures and for THF, it was freshly distilled before use. Unless otherwise mentioned, all reagents or catalysts were purchased from commercial sources and used without any further purification. Reactions were monitored by TLC, using Merck silica gel 60 F 254 plates. Visualization of the TLC plates were performed either 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, ^{13}C and ^{19}F NMR spectra were recorded on Avance III, Bruker at 400 MHz, 100 MHz and 376 MHz spectrometers respectively using $CDCl_3$. ^{1}H NMR chemicals shift are expressed in ppm (δ) relative to δ = 7.26 for $CDCl_3$. ^{13}C NMR chemical shift are expressed in ppm (δ) relative to δ = 77.16 for $CDCl_3$ 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.

2. Preparation of starting materials.

2.1 Thioketones

*(a) Following Thioketone (**Figure S1**) were used in the study and were prepared according to the literature procedure.*[1]

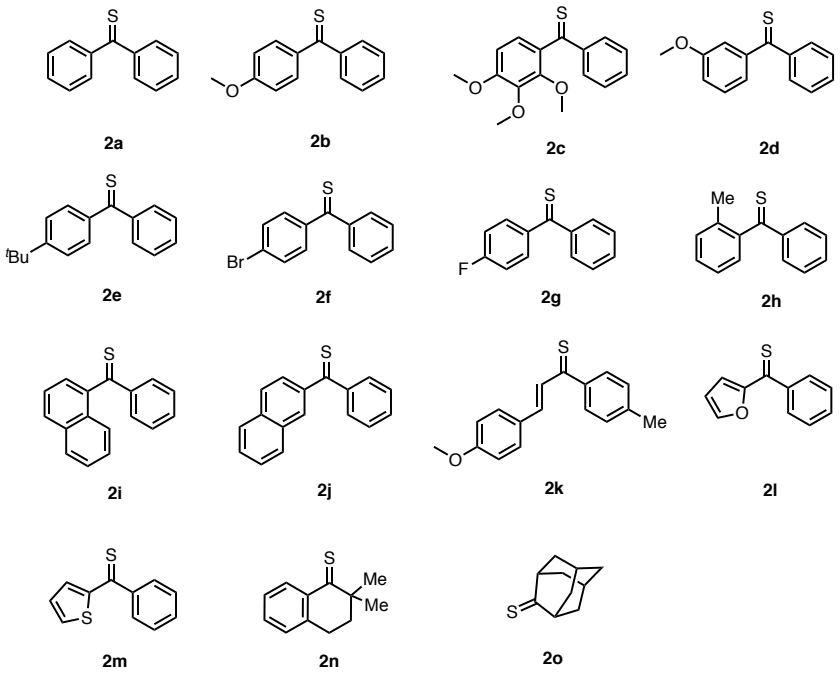
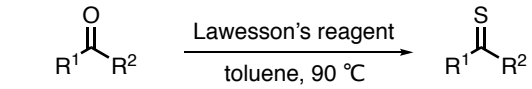


Figure S1: List of thioketones used in the study.

(b) General Procedure for the Preparation of Thioketones.



for cyclic and acyclic ketones

R^1, R^2 = alkyl, aryl

Respective ketone (0.60 mmol, 1.0 equiv) and Lawesson's reagent (0.36 mmol, 0.6 equiv) were suspended in dry toluene (10 ml). The reaction mixture was then heated to reflux for 8-12 h. The solvent was removed in *vacuo* and the colored residue was then passed through a short silica gel column and eluted with DCM-hexane mixture. The colored fractions (blue) were quickly collected, and the solvent was removed under reduced pressure to give the crude thioketone as a strong-smelling oil, which was immediately used in the reaction without further characterizations.

2.2 Thioamides

(a) Following thioamides (**Figure S2**) were used in the study and were prepared according to the literature procedure.[2]

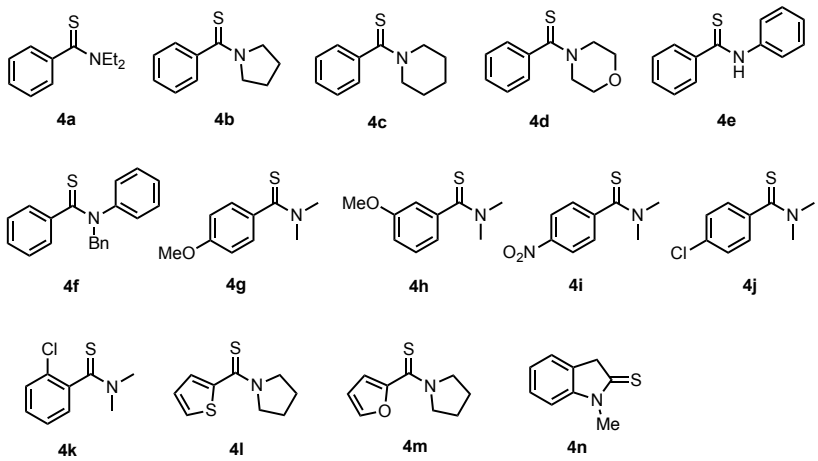
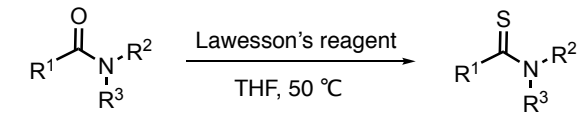


Figure S2: List of thioamide derivatives used in the study.

(b). General Procedure for the Preparation of Thioamides.

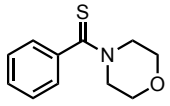


R^1= alkyl, aryl
R^2, R^3 = akyl, aryl

Respective amide (0.60 mmol, 1.00 equiv) and Lawesson's reagent (0.30 mmol, 0.5 equiv) were suspended in dry THF (2 ml). The reaction mixture was then heated to 50 °C for 6-8 h. After complete consumption of the amide (TLC controlled), the solvent was removed in vacuo and the crude product was purified by column chromatography (ethyl acetate/hexane) to afford the corresponding thioamide products. Compounds 4a-4c, 4e-4f, 4i, 4n are known compounds and prepared following the reported method. Other compounds were prepared following the similar method describes above.

(c) Characterization of newly synthesized thioamides:

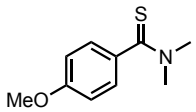
morpholino(phenyl)methanethione (4d):



4d

Following the general procedure, reaction between morpholino(phenyl)methanone (0.120 g, 0.62 mmol, 1.0 equiv) and lawsson's reagent (0.127 g, 0.31 mmol, 0.5 equiv) afforded the corresponding thioamide **4d**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as yellow oil in 78% (0.102 g) yield. R_f 0.2 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 3H), 7.28-7.26 (m, 2H), 4.44 - 4.42 (m, 2H), 3.89-3.86 (m, 2H), 3.63-3.62 (m, 2H), 3.60-3.58 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0, 142.5, 128.9, 128.6, 125.9, 66.8, 66.6, 52.5, 49.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{11}H_{14}NOS$ 208.0796 mass found 208.0785.

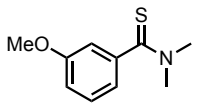
4-methoxy-N,N-dimethylbenzothioamide (4g):



4g

Following the general procedure, reaction between 4-methoxy-N,N-dimethylbenzamide (0.090 g, 0.5 mmol, 1.0 equiv) and Lawesson's reagent (0.101 g, 0.25 mmol, 0.5 equiv) afforded the corresponding thioamide **4g**, which was purified by silica gel column chromatography (3:97 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 71% (0.070 g) yield. R_f 0.3 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 3.59 (s, 3H), 3.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.4, 160.1, 135.9, 128.0, 113.6, 55.5, 44.4, 43.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{10}H_{14}NOS$ 196.0796, mass found 196.0783.

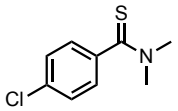
3-methoxy-N,N-dimethylbenzothioamide (4h):



4h

Following the general procedure, reaction between 3-methoxy-N,N-dimethylbenzamide (0.120 g, 0.67 mmol, 1.0 equiv) and Lawesson's reagent (0.134 g, 0.33 mmol, 0.5 equiv) afforded the corresponding thioamide **4h**, which was purified by silica gel column chromatography (3:97 EtOAc:Hexane as eluent) to give the title compound as yellow oil in 83% (0.108 g) yield. R_f 0.3 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 1H), 6.87-6.84 (m, 3H), 3.81 (s, 3H), 3.60 (s, 3H), 3.17 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0, 159.5, 144.7, 129.6, 117.9, 114.5, 111.4, 55.5, 44.2, 43.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{10}H_{14}NOS$ 196.0796, mass found 196.0783.

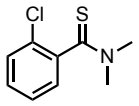
4-chloro-N,N-dimethylbenzothioamide (4j):



4j

Following the general procedure, reaction between 4-chloro-N,N-dimethylbenzothioamide (0.135 g, 0.0.73 mmol, 1.0 equiv) and Lawesson's reagent (0.147 g, 0.36 mmol, 0.5 equiv) afforded the corresponding thioamide **4j**, which was purified by silica gel column chromatography (3:97 EtOAc:Hexane as eluent) to give the title compound as yellow oil in 73% (0.106 g) yield. R_f 0.35 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 3.53 (s, 3H), 3.11 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 141.8, 134.7, 128.7, 128.4, 127.4, 125.8, 44.3, 43.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_9H_{11}ClNS$ 200.0301, mass found 200.0281.

2-chloro-N,N-dimethylbenzothioamide (4k):

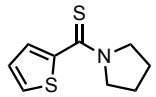


4k

Following the general procedure, reaction between 2-chloro-N,N-dimethylbenzothioamide (0.060 g, 0.32 mmol, 1.0 equiv) and Lawesson's reagent (0.066 g, 0.16 mmol, 0.5 equiv) afforded the corresponding thioamide **4k**, which was purified by silica gel column

chromatography (3:97 EtOAc:Hexane as eluent) to give the title compound as yellow oil in 73% (0.048 g) yield. R_f 0.35 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.6 Hz, 1H), 7.29 - 7.18 (m, 3H), 3.57 (s, 3H), 3.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 142.1, 129.7, 129.5, 128.3, 127.8, 127.4, 43.0, 42.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_9H_{11}ClNS$ 200.0301, mass found 200.0286.

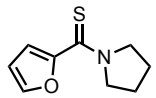
pyrrolidin-1-yl(thiophen-2-yl)methanethione(4l):



4l

Following the general procedure, reaction between pyrrolidin-1-yl(thiophen-2-yl)methanone (0.90 g, 0.50 mmol, 1.0 equiv) and Lawesson's reagent (0.100 g, 0.25 mmol, 0.5 equiv) afforded the corresponding thioamide **4l**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as yellow oil in 75% (0.074 g) yield. R_f 0.2 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 5.2 Hz, 1H), 7.27 (d, *J* = 4.0 Hz, 1H), 6.99 (t, *J* = 4.8 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 3.86 (t, *J* = 6.4 Hz, 2H), 2.08-2.01 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 146.5, 130.5, 127.0, 55.3, 54.4, 26.9, 24.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_9H_{12}NS_2$ 198.0411, mass found 198.0398.

furan-2-yl(pyrrolidin-1-yl)methanethione(4m):



4m

Following the general procedure, reaction between furan-2-yl(pyrrolidin-1-yl)methanone (0.122g, 0.73 mmol, 1.0 equiv) and Lawesson's reagent (0.149 g, 0.37mmol, 0.5 equiv) afforded the corresponding thioamide **4m**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as yellow oil in 72% (0.096 g) yield. R_f 0.2 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.29 (d, *J* = 3.2 Hz, 1H), 6.47-6.46 (m, 1H), 4.00 (q, *J* = 7.2 Hz, 4H), 2.11 - 1.97 (m, 4H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.5, 153.0, 143.8, 118.9, 112.2, 55.0, 53.6, 27.0, 23.9 ; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_9H_{12}NOS$ 182.0640, mass found 182.0626.

2.3 α-Halohydroxamate derivatives.

*Following haloamides (**Figure S3**) were used in the study and were prepared according to the literature procedure.*[3]

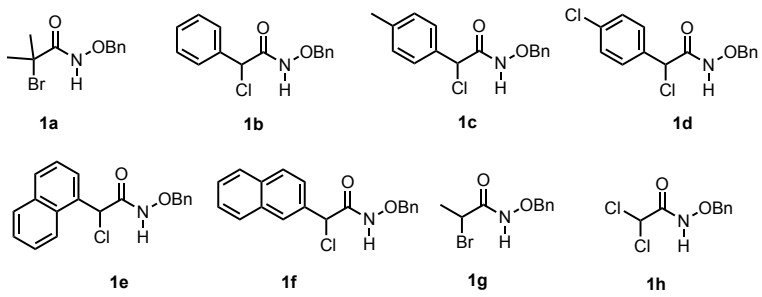
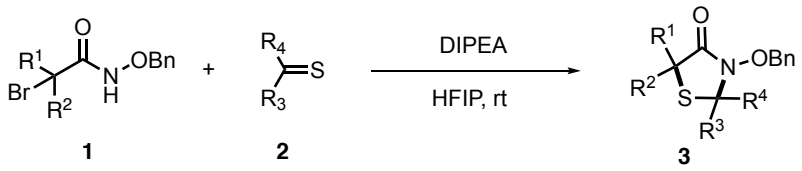


Figure S3: List of α-halo hydroxamate derivatives used in the study.

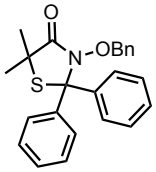
3. General procedure for [3+2]-annulation of α-halo hydroxamates (precursor to azaoxyallyl cation) and thioketones.



To a solution of α-bromo hydroxamate (**1**, 1.0 equiv) and thioketone (**2**, 1.0 equiv) in $(CF_3)_2CHOH$ (0.4 M), was added DIPEA (2.0 equiv) dropwise. The reaction mixture was stirred at room temperature and the reaction progress was monitored by thin layer chromatography (TLC). Upon completion of the reaction (*ca*. 0.5-1 h), HFIP was removed under reduced pressure and the crude was purified by silica gel column chromatography (using ethyl acetate-hexane mixture as eluent) to afford the corresponding thiazolidin-4-one products (**3**).

4. Characterization of thiazolidin-4-one products (3)

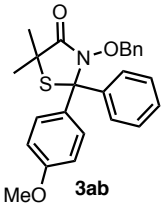
3-(benzyloxy)-5, 5-dimethyl-2, 2-diphenylthiazolidin-4-one (3aa):



3aa

Following the general procedure, reaction between diphenylmethanethione **2a** (0.042 g, 0.2 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.2 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3aa**, which was purified by silica gel column chromatography (using 3:97 EtOAc:Hexane as eluent) to give the title compound as white solid in 80% (0.068 g) yield. R_f 0.2 (1:9 EtOAc:Hexane); **mp** 127.0 - 128.5 ºC ; **FT-IR** (v cm^{-1}): 2971, 2926, 1703, 1493, 1446, 1382, 1215, 1134, 1002; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 4H), 7.29-7.25 (m, 6H), 7.18-7.14 (m, 3H), 6.99-6.98 (m, 2H), 4.26 (s, 2H), 1.45 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 141.8, 134.1, 129.8, 129.1, 128.7, 128.4, 128.3, 128.2, 78.0, 74.3, 46.7, 29.0; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{24}H_{23}NNaO_2S$, 412.1347, mass found 412.1340.

3-(benzyloxy)-2-(4-methoxyphenyl)-5, 5-dimethyl-2-phenylthiazolidin-4-one (3ab):

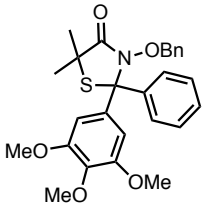


3ab

Following the general procedure, reaction between (4-methoxyphenyl)(phenyl)methanethione **2b** (0.046 g, 0.2 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.2 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ab**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as white solid in 87% (0.074 g) yield. R_f 0.3 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 4H), 7.29-7.24 (m, 3H), 7.21-7.17 (m, 3H), 7.04 (dd, *J*= 7.6 Hz, 2.4 Hz, 2H), 6.84-6.80 (m, 2H), 4.42 (d, *J* = 8.8 Hz, 1H), 4.21 (d, *J* = 8.8 Hz, 1H), 3.76 (s, 3H), 1.51 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$)

δ 172.1, 159.7, 142.7, 134.2, 133.1, 130.8, 129.8, 128.7, 128.6, 128.3, 128.1, 113.4, 78.0, 74.1, 55.41, 46.6, 29.0, 28.8; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{25}H_{26}NO_3S$ 420.1633, mass found 420.1625.

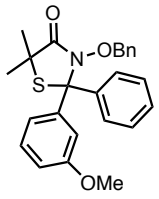
3-(benzyloxy)-5, 5-dimethyl-2-phenyl-2-(3,4,5-trimethoxyphenyl)thiazolidin-4-one (3ac):



3ac

Following the general procedure, reaction between phenyl (3,4,5-trimethoxyphenyl) methanethione **2c** (0.058 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ac**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 64 % (0.068 g) yield. R_f 0.2 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.40 (m, 2H), 7.35-7.29 (m, 6H), 6.78 (s, 2H), 5.08 (s, 2H), 3.84 (s, 3H), 3.76 (s, 6H), 1.50 (s, 3H), 1.47 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 152.9, 142.6, 138.4, 138.3, 138.0, 128.6, 128.3, 128.3, 127.8, 127.1, 104.6, 97.6, 76.5, 61.0, 56.2, 54.5, 29.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{27}H_{29}NNaO_5S$ 502.1664, mass found 502.1657.

3-(benzyloxy)-2-(3-methoxyphenyl)-5, 5-dimethyl-2-phenylthiazolidin-4-one (3ad):

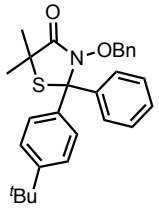


3ad

Following the general procedure, reaction between (3-methoxyphenyl)(phenyl)methanethione **2d** (0.046 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ad**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 70% (0.054 g) yield. R_f ,0.3 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.34-7.30 (m, 3H), 7.24-7.20 (m, 4H), 7.12-7.07 (m, 2H), 7.05 (dd, *J* = 7.2, 2.4 Hz, 2H) 6.87-6.85 (m, 1H), 4.35 (d, *J* = 8.8 Hz, 1H), 4.31 (d, *J* = 8.8 Hz, 1H), 3.72 (s, 3H), 1.52 (s, 3H), 1.50 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 159.4, 143.5, 141.9, 134.3, 129.8, 129.2, 129.1, 128.8, 128.4, 128.3,

128.2, 121.6, 115.2, 113.8, 78.0, 74.3, 55.4, 46.7, 29.1, 29.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{25}H_{26}NO_3S$, 420.1633, mass found 420.1617.

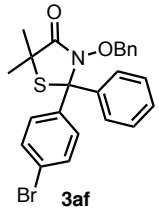
3-(benzyloxy)-2-(4-(tert-butyl) phenyl)-5,5-dimethyl-2-phenylthiazolidin-4-one (3ae):



3ae

Following the general procedure, reaction between (4-(tert-butyl) phenyl)(phenyl) methanethione **2e** (0.050 g, 0.20 mmol,1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ae**, which was purified by silica gel column chromatography (5:95: EtOAc:Hexane as eluent) to give the title compound as colorless oil in 67% (0.060 g) yield. R_f 0.3 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.44-7.37 (m, 5H), 7.32-7.25 (m, 3H), 7.06 (d, *J* = 6.8 Hz, 2H), 4.53 (d, *J* = 8.8 Hz, 1H), 4.29 (d, *J* = 8.8 Hz, 1H), 1.63 (s, 3H), 1.55 (s, 3H), 1.39 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 151.7, 142.5, 138.2, 134.2, 129.9, 129.2, 128.9, 128.8, 128.3, 128.2, 128.2, 125.6, 78.1, 74.2, 46.7, 34.7, 31.4, 29.1, 29.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{28}H_{32}NO_2S$ 446.2154, mass found 446.2142.

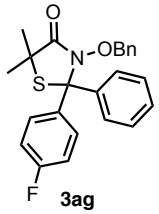
3-(benzyloxy)-2-(4-bromophenyl)-5,5-dimethyl-2-phenylthiazolidin-4-one (3af):



3af

Following the general procedure, reaction between (4-bromophenyl)(phenyl)methanethione **2f** (0.055 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3af**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 54% (0.054 g) yield. R_f 0.4 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 6.0, 2.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.38-7.33 (m, 5H), 7.25-7.21 (m, 3H), 7.05 (s, 1H), 7.033 (d, *J* = 1.6 Hz, 1H), 4.46 (d, *J* = 8.8 Hz, 1H), 4.24 (d, *J* = 8.8 Hz, 1H), 1.54 (s, 3H), 1.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 141.6, 141.0, 134.0, 131.4, 130.6, 129.8, 129.3, 128.9, 128.8, 128.4, 128.4, 122.5, 78.2, 73.9, 46.8, 29.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{24}H_{23}BrNO_2S$, 470.0612, mass found 470.0603.

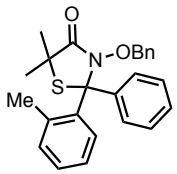
3-(benzyloxy)-2-(4-fluorophenyl)-5, 5-dimethyl-2-phenylthiazolidin-4-one (3ag):



3ag

Following the general procedure, reaction between (4-fluorophenyl)(phenyl)methanethione **2g** (0.044 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ag**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 72% (0.059 g) yield. R_f 0.4 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.44(m, 4H), 7.29-7.24 (m, 3H), 7.19-7.15 (m, 3H), 7.00 (dd, *J* = 6.8,1.2 Hz,2H), 6.98-6.92 (m, 2H), 4.30 (s, 2H), 1.45 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 162.5 (d, *J* = 247.2 Hz), 141.7, 137.6 (d, *J* = 3.2 Hz) 134.0, 131.1 (d, *J* = 8.2 Hz), 129.7, 128.9, 128.8, 128.5, 128.3, 128.2, 115.0 (d, *J* = 21.4 Hz),, 78.1, 73.8, 46.7, 29.0, 28.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$calculated for $C_{24}H_{22}FNNaO_2S$ 430.1253, mass found 430.1244.

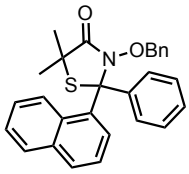
3-(benzyloxy)-5, 5-dimethyl-2-phenyl-2-(o-tolyl) thiazolidin-4-one (3ah):



3ah

Following the general procedure, reaction between phenyl(o-tolyl)methanethione **2h** (0.042g, 0.20 mmol,1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ah**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 74% (0.060 g) yield. R_f 0.2 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 4H), 7.30-7.18 (m, 6H), 7.15 (t, J=7.6 Hz 2H), 7.10-7.06 (m, 2H), 4.85 (d, *J* = 8.8 Hz, 1H), 3.49 (d, *J* = 8.8 Hz, 1H), 1.88 (s, 3H), 1.74 (s, 3H), 1.35 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 142.0, 138.7, 135.8, 134.1, 132.3, 129.9, 129.1, 128.8, 128.5, 128.3, 127.9, 125.8, 77.8, 74.2, 46.4, 29.5, 28.9, 21.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{25}H_{25}NNaO_2S$ 426.1504, mass found 426.1501.

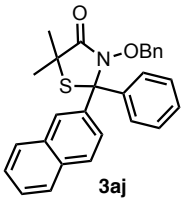
3-(benzyloxy)-5,5-dimethyl-2-(naphthalen-1-yl)-2-phenylthiazolidin-4-one (3ai):



3ai

Following the general procedure, reaction between naphthalen-1-yl(phenyl)methanethione **2i** (0.050, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ai**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as white solid in 68% (0.063 g) yield. R_f 0.5 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 13.2, 8.0 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.46-7.34 (m, 5H), 7.28-7.16 (m, 7H), 7.07-7.03 (m, 2H), 4.90 (d, *J* = 8.8 Hz, 1H), 3.49 (d, *J* = 8.8 Hz, 1H), 1.75 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 139.5, 139.0, 134.8, 134.1, 130.0, 129.8, 129.3, 129.2, 128.9, 128.3, 128.2, 126.8, 125.5, 125.4, 124.9, 124.0, 78.2, 74.2, 47.0, 29.7, 29.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$calculated for $C_{28}H_{26}NO_2S$ 440.1684, mass found 440.1675.

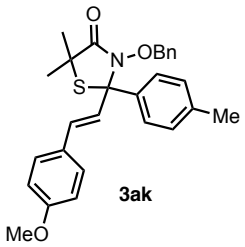
3-(benzyloxy)-5,5-dimethyl-2-(naphthalen-2-yl)-2-phenylthiazolidin-4-one (3aj):



3aj

Following the general procedure, reaction between naphthalen-2-yl(phenyl)methanethione **2j** (0.050 g, 0.20 mmol,1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3aj**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as white solid in 72% (0.063 g) yield. R_f 0.5 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.92-7.86 (m, 3H), 7.71-7.69 (m, 2H), 7.61-7.55 (m, 3H), 7.47-7.44 (m, 3H), 7.33-7.24 (m, 3H), 7.09 (d, *J* = 6.8 Hz, 2H), 4.59 (d, *J* = 8.8 Hz, 1H), 4.29 (d, *J* = 8.8 Hz, 1H), 1.68 (s, 3H), 1.57 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 141.1, 139.6, 134.1, 132.9, 132.7, 129.8, 129.7, 128.8, 128.7, 128.7, 128.3, 128.3, 128.0, 127.6, 127.0, 127.0, 126.9, 126.6, 78.2, 74.5, 46.8, 29.2, 29.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{28}H_{26}NO_2S$ 440.1684, mass found 440.1677.

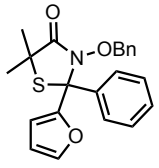
3-(benzyloxy)-2-(4-methoxyphenyl)-5, 5-dimethyl-2-(4-methylstyryl) thiazolidin-4-one (3ak):



3ak

Following the general procedure, reaction between 3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-ene-1-thione **2k** (0.054 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ak**, which was purified by silica gel column chromatography (5:95: EtOAc:Hexane as eluent) to give the title compound as reddish oil in 65% (0.061g) yield. R_f 0.35 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.29-7.24 (m, 3H), 7.22-7.17 (m, 4H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.48 (d, *J* =16.0 Hz 1H), 4.96 (d, *J* = 9.2 Hz, 1H), 4.56 (d, *J* = 9.2 Hz, 1H), 3.82 (s, 3H), 2.40 (s, 3H), 1.63 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 159.8, 138.7, 137.1, 134.5, 131.8, 129.8, 129.1, 128.8, 128.7, 128.7, 128.4, 128.3, 127.7, 114.2, 78.6, 72.2, 55.4, 46.7, 29.3, 28.9, 21.2; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{28}H_{29}NNaO_3S$, 482.1766 mass found 482.1752.

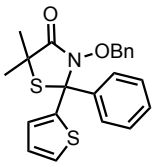
3-(benzyloxy)-2-(furan-2-yl)-5, 5-dimethyl-2-phenylthiazolidin-4-one (3al):



3al

Following the general procedure, reaction between furan-2-yl(phenyl)methanethione **2l** (0.038 g, 0.20 mmol , 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3al**, which was purified by silica gel column chromatography (5:95: EtOAc:Hexane as eluent) to give the title compound as white solid in 78% (0.058 g) yield. R_f 0.3 (1:9 EtOAc:Hexane); **mp** 108 -109 ºC ; **FT-IR** (v cm^{-1}): 2926, 1705, 1449, 1383, 1016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 3H), 7.37-7.33 (m, 3H), 7.27-7.23 (m, 3H), 7.17-7.14 (m, 2H), 6.46 (dd, *J* = 4.0, 1.0 Hz, 1H), 6.39 (dd, *J* = 4.0, 2.0 Hz, 1H), 4.57 (d, *J* = 9.0 Hz, 1H), 4.40 (d, *J* = 9.0 Hz, 1H), 1.57 (s, 3H), 1.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 152.3, 143.4, 139.8, 134.3, 129.7, 128.8, 128.8, 128.4, 128.3, 128.1, 112.3, 111.0, 78.2, 68.8, 46.7, 29.2, 29.0; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{22}H_{21}NaNO_3S$, 402.1140 mass found 402.1128.

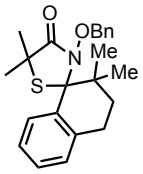
3-(benzyloxy)-5, 5-dimethyl-2-phenyl-2-(thiophen-2-yl) thiazolidin-4-one (3am):



3am

Following the general procedure, reaction between phenyl(thiophen-2-yl)methanethione **2m** (0.041 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol,1.0 equiv) afforded the corresponding thiazolidin-4-one **3am**, which was purified by silica gel column chromatography (5:95: EtOAc:Hexane as eluent) to give the title compound as white solid in 97% (0.078g) yield. R_f 0.3(1:9 EtOAc:Hexane); **mp** 115 -117.5 ºC ; **FT-IR** (v cm^{-1}): 3400, 2926, 1704, 1448, 1383, 1235, 1014; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.45 (dd, 3.6, 1.2 Hz, 1H) 7.33-7.28, (m, 6H), 7.20 (dd, *J* = 7.2, 3.6 Hz, 2H), 7.07 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 4.8, 3.6 Hz, 1H) 4.89 (d, *J* = 8.8 Hz, 1H), 4.11 (d, *J* = 8.8 Hz, 1H), 1.67 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 145.8, 143.21, 134.3, 131.2, 129.7, 128.8, 128.3, 128.3, 128.2, 128.2, 127.3, 127.3, 78.3, 70.5, 47.2, 28.9, 28.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{22}H_{22}NO_2S_2$, 396.1092, mass found, 396.1084.

3'-(benzyloxy)-2,2,5',5'-tetramethyl-3,4-dihydro-2H-spiro[naphthalene-1,2'-thiazolidin]-4'-one (3an):

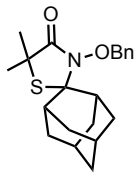


3an

Following the general procedure, reaction between 2,2-dimethyl-3,4-dihydronaphthalene-1(2H)-thione **2n** (0.038 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3an,** which was purified by silica gel column chromatography (5:95: EtOAc:Hexane as eluent) to give the title compound as white solid in 81% (0.065 g, 0.16 mmol) yield. R_f 0.4 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.48 (m, 1H), 7.37 (d, *J* = 6.8 Hz, 2H), 7.34-7.29 (m, 2H), 7.28-7.22 (m, 1H), 7.17-7.13 (m, 2H), 7.04-6.99 (m, 1H), 5.03 (d, *J* = 14.0 Hz, 1H), 5.03 (d, *J* = 14.0 Hz, 1H) 2.86-2.73 (m, 2H), 1.79-1.74 (m, 2H), 1.73 (s, 3H), 1.64 (s, 3H), 1.06 (s, 3H), 1.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.1, 140.0, 138.5, 134.8, 128.8, 128.3, 128.2,

127.8, 127.7, 126.5, 126.1, 100.5, 76.2, 53.6, 39.9, 33.8, 33.6, 29.9, 25.4, 24.7, 22.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{23}H_{28}NO_2S$, 382.1841 mass found, 382.1836.

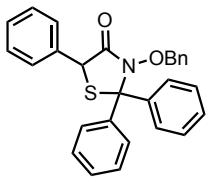
3'-(benzyloxy)-5',5'-dimethylspiro[adamantane-2,2'-thiazolidin]-4'-one (3ao):



3ao

Following the general procedure, reaction between adamantane-2-thione **2o (**0.033 g, 0.2 mmol, 1.0 equiv) and α-bromo hydroxamate **1a (**0.055 g, 0.2 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one (**3ao**), which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 58% (0.042g) yield. R_f 0.2 (5:95: EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.30-7.25 (m, 1H), 5.03 (s, 2H), 2.35 (d, *J* = 12.4 Hz, 2H), 2.10 (s, 2H), 1.84 (s, 6H), 1.74-1.64 (m, 4H), 1.61 (s, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.9, 138.6, 128.2, 128.0, 127.5, 100.7, 76.02, 52.4, 41.6, 37.3, 36.1, 34.1, 32.0, 26.5, 26.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{21}H_{28}NO_2S$ 358.1841, mass found 358.1831.

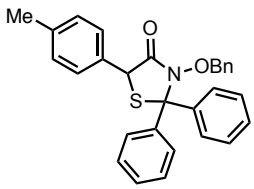
3-(benzyloxy)-2, 2, 5-triphenylthiazolidin-4-one (3ba):



3ba

Following the general procedure, reaction between diphenylmethanethione **2a** (0.040 g, 0.20 mmol 1.0 equiv) and α-bromo hydroxamate **1b** (0.055 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ba**, which was purified by silica gel column chromatography (5:95: EtOAc:Hexane as eluent) to give the title compound as white solid in 82% (0.073 g) yield. R_f 0.3 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.74 (m, 2H), 7.54 -7.49 (m, 2H), 7.48-7.44 (m, 3H), 7.44-7.34 (m, 8H), 7.30-7.23 (m, 3H), 7.10 (d, *J* = 6.4 Hz, 2H), 4.85 (s, 1H), 4.69 (d, *J* = 8.8 Hz, 1H), 4.20 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 142.3, 139.6, 136.1, 134.1, 130.2, 129.9, 129.2, 129.2, 129.0, 128.8, 128.6, 128.4, 128.4, 128.3, 128.2, 128.0, 78.4, 75.4, 46.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{28}H_{24}NO_2S$ 438.1528, mass found 438.1517.

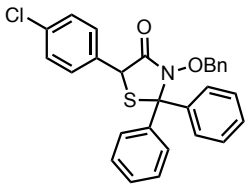
3-(benzyloxy)-2,2-diphenyl-5-(p-tolyl)thiazolidin-4-one (3ca):



3ca

Following the general procedure, reaction between diphenylmethanethione **2a** (0.040 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1c** (0.058 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ca**, which was purified by silica gel column chromatography (5:95: EtOAc:Hexane as eluent) to give the title compound as white solid in 83% (0.075 g) yield. R_f 0.3 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.50-7.45 (m, 3H), 7.44-7.38 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32-7.26 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14-7.10 (m, 2H), 4.84 (s, 1H), 4.74 (d, *J* = 8.8 Hz, 1H), 4.22 (d, *J* = 8.8 Hz, 1H), 2.40 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 142.3, 139.6, 138.4, 134.1, 133.0, 130.2, 130.9, 129.6, 129.1, 129.0, 128.8, 128.4, 128.3 (2), 127.9, 78.3, 75.3, 46.4, 21.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{28}H_{24}NO_2S$ 452.1684, mass found 452.1675.

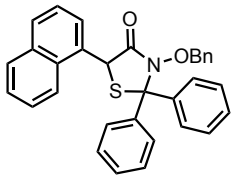
3-(benzyloxy)-5-(4-chlorophenyl)-2, 2-diphenylthiazolidin-4-one (3da):



3da

Following the general procedure, reaction between diphenylmethanethione **2a** (0.040 g, 0.20 mmol, 1.0 equiv) and α-chloro hydroxamate **1d** (0.063 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3da**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as yellow solid in 76% (0.073g) yield. R_f 0.2(1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.62 (m, 2H), 7.46-7.43 (m, 2H), 7.40-7.36 (m, 3H), 7.35-7.31 (m, 3H), 7.29-7.24 (m, 4H), 7.22-7.16 (m, 3H), 7.02 (dd, *J* = 8.0, 1.6Hz, 2H), 4.75 (s, 1H), 4.54 (d, *J* = 8.8 Hz, 1H), 4.16 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 134.5, 134.0, 130.5, 130.0, 129.9, 129.2, 129.1, 128.9, 128.5, 128.4, 128.3, 128.1, 78.5, 75.5, 46.1. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for, $C_{28}H_{22}ClNNaO_2S$ 494.0957 mass found 494.0939.

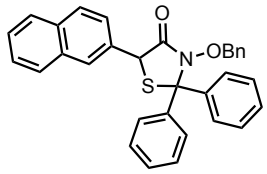
3-(benzyloxy)-5-(naphthalen-1-yl)-2,2-diphenylthiazolidin-4-one (3ea):



3ea

Following the general procedure, reaction between diphenylmethanethione **2a** (0.040 g, 0.2 mmol, 1.0 equiv) and α-chloro hydroxamate **1e** (0.065 g, 0. 2mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ea**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as brown solid in 69% (0.064g) yield. R_f 0.3 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.93-7.88 (m, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.80-7.75 (m, 2H), 7.58-7.39 (m, 12H), 7.32-7.25 (m, 3H), 7.13 (d, *J* = 6.4 Hz, 2H), 5.59 (s, 1H), 4.82 (d, *J* = 8.8 Hz, 1H), 4.21 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 142.6, 139.4, 134.2, 134.1, 132.1, 131.9, 130.4, 130.0, 129.3 (2), 129.2, 128.9, 128.5 (2), 128.4, 128.2, 127.9, 127.3, 126.7, 126.1, 125.7, 123.4, 78.4, 75.9, 43.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{32}H_{26}NO_2S$, 488.1684 mass found, 488.1672.

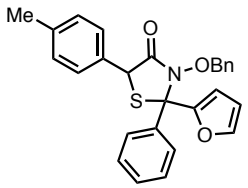
3-(benzyloxy)-5-(naphthalen-2-yl)-2,2-diphenylthiazolidin-4-one (3fa):



3fa

Following the general procedure, reaction between diphenylmethanethione **2a** (0.040 g, 0.20 mmol, 1.0 equiv) and α-chloro hydroxamate **1f** (0.065 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3fa**, which was purified by silica gel column chromatography (5:95: EtOAc:Hexane as eluent) to give the title compound as yellow solid in 74% (0.072 g) yield. R_f 0.2 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91-7.83 (m, 2H), 7.82-7.77 (m, 4H), 7.59-7.46 (m, 8H), 7.45-7.39 (m, 3H), 7.31-7.25 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 2H), 5.05 (s, 1H), 4.70 (d, *J* = 8.8 Hz, 1H), 4.28 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 142.2, 139.8, 134.1, 133.3, 133.2, 130.2, 130.0, 129.2, 129.0, 128.8, 128.5, 128.4, 128.3, 128.1, 127.8, 126.6, 126.5, 126.2, 78.5, 75.6, 47.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{32}H_{26}NO_2S$ 488.1684, mass found 488.1670.

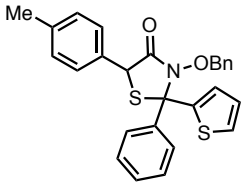
3-(benzyloxy)-2-(furan-2-yl)-2-phenyl-5-(p-tolyl) thiazolidin-4-one (3cl):



3cl

Following the general procedure, reaction between furan-2-yl(phenyl)methanethione **2l** (0.038 g, 0.2 mmol, 1.0 equiv) and α-chloro hydroxamate **1c** (0.058 g, 0.2 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3cl**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as mixture of diastereomers (d.r = 2:1) in 74% (0.065 g) combined yield. R_f 0.4 (3:7 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 1H), 7.58 (s, 1H), 7.50-7.46 (m, 2.5H), 7.43-7.41 (m, 1.0H), 7.39-7.33 (m, 3H), 7.29-7.22 (m, 8H), 7.21-7.17 (m, 2H), 7.16-7.12 (m, 3H), 7.09 (d, *J* = 6.4 Hz, 1H), 6.53 (d, *J* = 3.2 Hz, 0.5H), 6.49 (d, *J* = 3.2 Hz, 1H), 6.45 (brs, 1H), 6.39 (d, *J* = 0.8 Hz, 0.5H), 4.87 (s, 0.5 H), 4.79 - 4.77 (m, 2H), 4.56 (d, *J* = 9.2 Hz, 0.5H), 4.42 (d, *J* = 8.8Hz, 1H), 4.37 (d, *J* = 9.2 Hz, 1H), 2.32 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 168.0, 152.4, 151.4, 144.0, 143.4, 140.4, 138.5, 137.7, 134.3, 133.1, 129.9, 129.8, 129.7, 128.7, 129.5, 129.0 (2), 128.9, 128.8, 128.7, 128.6 (2),128.4 (2), 127.3, 113.9, 111.3, 110.8 (2), 78.4, 70.0, 69.4, 47.1, 46.3, 21.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{27}H_{24}NO_3S$ 442.1477, mass found 442.1467.

3-(benzyloxy)-2-phenyl-2-(thiophen-2-yl)-5-(p-tolyl) thiazolidin-4-one (3cm):

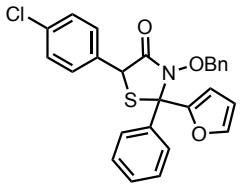


3cm

Following the general procedure, reaction between phenyl(thiophen-2-yl)methanethione **2m** (0.040 g, 0.20 mmol, 1.0 equiv) and α-chloro hydroxamate **1c** (0.058 g, 0.20 mmol,1.0 equiv) afforded the corresponding thiazolidin-4-one **3cm**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as mixture of diastereomers (d.r = 2:1) in 79% (0.072 g) combined yield. R_f 0.3 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.2, 3.6 Hz, 1H), 7.44 (d, J=4.8 Hz 1H), 7.42-7.38 (m, 2H), 7.34 (d, *J* = 5.2 Hz, 0.5H), 7.31-7.26 (m, 6H), 7.22-7.16 (m, 5H), 7.15-7.08 (m,

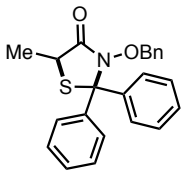
6.5H), 7.05-6.99 (m, 3H), 6.97-6.94 (m, 0.5H), 4.92 (s, 0.5H), 4.88 (d, *J* =9.2 Hz, 1H), 4.71-4.68 (m, 1.5H), 4.38 (d, *J* = 9.2 Hz, 0.5H), 4.04 (d, *J* = 9.2 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 1.3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8 (2),145.5, 144.8, 142.6, 141.5, 138.6, 138.3, 134.4, 134.3, 132.9, 132.8, 131.8, 130.1, 129.9, 129.8, 129.7, 129.5, 129.1, 128.9 (2), 128.8 (2), 128.4 (2), 128.3 (2), 127.7, 127.5, 127.2, 126.9, 78.7, 78.4, 72.0, 71.4, 47.7, 46.6, 21.3, 21.2; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for, $C_{27}H_{23}NNaO_2S_2$, 480.1068 mass found, 480.1059.

3-(benzyloxy)-5-(4-chlorophenyl)-2-(furan-2-yl)-2-phenylthiazolidin-4-one (3dl):



3dl

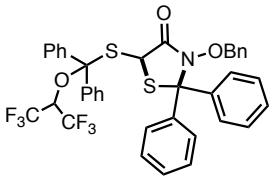
Following the general procedure, reaction between furan-2-yl(phenyl)methanethione **2l** (0.038 g, 0.20 mmol, 1.0 equiv) and α-chloro hydroxamate **1d** (0.062 g, 0.20 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3dl**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as mixture of diastereomers (d.r =1.3:1) in 77 % (0.071 g) combined yield. R_f 0.4 (3:7 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.55(m, 1.7H), 7.53 (s, 1H), 7.46-7.42 (m, 3H), 7.38-7.34 (m, 2.7H), 7.34-7.30 (m, 3H), 7.24-7.16 (m, 9.5H), 7.15-7.11 (m, 2H), 7.06 (d, *J* = 6.4 Hz, 1.7H), 6.45 (*app* t, *J* = 3.2 Hz, 2H), 6.41-6.38 (m, 1H), 6.37-6.35 (m, 1H), 4.84 (s, 0.7H), 4.75 (s, 1H), 4.66 (d, *J* = 9.2 Hz, 1H), 4.44 (s, 1.5H), 4.35 (d, *J* = 9.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 167.4, 152.0, 151.2, 144.0, 143.5, 139.8, 137.7, 134.6 (2), 134.5 (2), 134.1, 130.4 (2), 129.9, 129.8, 129.5, 129.1 (2), 128.9 (2), 128.7, 128.6 (2), 128.4 (2), 127.4, 113.9, 111.3 (2), 110.9, 78.5, 78.4, 70.1, 69.6, 46.7, 45.9; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{26}H_{21}ClNO_3S$, 462.0931 mass found, 462.0917.



3ga

Following the general procedure, reaction between diphenylmethanethione **2a** (0.039 g, 0.2 mmol, 1.0 equiv) and α-bromo hydroxamate **1g** (0.051 g, 0.2 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ga**, which was purified by silica gel column

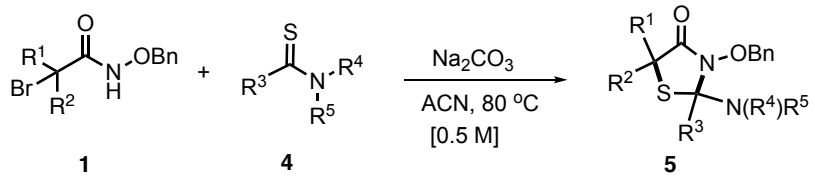
chromatography (using 3:97 EtOAc:Hexane as eluent) to give the title compound as white solid in 30% (0.023 g) yield. R_f 0.2 (5:95 EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 2H), 7.46-7.40 (m, 2H), 7.39 -7.35 (m, 3H), 7.34-7.29 (m, 3H), 7.25-7.19 (m, 3H), 7.03 (d, *J* = 6.0 Hz, 2H), 4.54 (d, *J* = 8.8 Hz, 1H), 4.13 (d, *J* = 8.8 Hz, 1H), 3.72 (q, *J* = 7.0 Hz, 1H), 1.56 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.02, 141.7, 140.40, 134.2, 129.8, 128.9, 128.8, 128.3, 128.3(2), 128.2, 78.3, 75.4, 37.1, 18.15. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{23}H_{22}NO_2S$ mass, 376.1371 found 376.1368.



3ha

Following the general procedure, reaction between diphenylmethanethione **2a** (0.039 g, 0.2 mmol, 1.0 equiv) and α-bromo hydroxamate **1h** (0.046 g, 0.2 mmol, 1.0 equiv) afforded the corresponding thiazolidin-4-one **3ha**, which was purified by silica gel column chromatography (using 2:98 EtOAc:Hexane as eluent) to give the title compound as white solid in 28% (0.041 g) yield. R_f 0.3 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H), 7.40-7.34 (m, 4H), 7.33-7.30 (m, 3H), 7.29-7.25 (m, 7H), 7.24-7.20 (m, 4H), 7.19-7.13 (m, 3H), 6.95 (d, *J* = 6.8 Hz, 2H), 5.32 (sept, *J* =6.0 Hz, 1H), 4.55 (s, 1H), 4.37 (d, *J* = 8.8 Hz, 1H), 4.25 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 141.9, 140.8, 140.4, 140.0, 133.9, 129.8, 129.3, 129.3, 128.9, 128.9(2), 128.7, 128.6, 128.4, 128.4(2), 128.3, 128.3(2) 127.9, 127.7, 125.5-116.1 (m, CF_3), 98.9, 78.3, 76.0, 71.0 (hept J_{FC} = 32.8 Hz), 45.8. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{38}H_{29}F_6NNaO_3S_2$, 748.1391, mass found 748.1373.

5. General procedure for [3+2]-annulation of α-haloamides (precursor to azaoxyallyl cation) and thioamides to 2-aminothiazolidin-4-one derivatives (5).

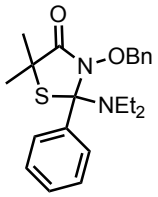


1 **4** **5**

To a solution of thioamide (**4**, 1.0 equiv) and haloamide (**1**, 2.0 equiv) in acetonitrile (0.5 M) was added Na_2CO_3 (4.0 equiv) and the reaction mixture was heated at 80 ^oC for 1 h. Upon completion of the reaction (TLC controlled), reaction mixture was passed through celite and thoroughly washed with ethyl acetate. The filtrate was concentrated under vacuo and the crude product was purified by silica gel column chromatography to afford the 2-aminothiazolidin-4-one derivatives (**5**).

6. Characterization of thiazolidin-4-one products (5)

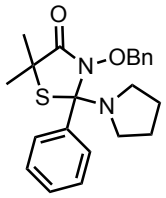
3-(diethylamino)-5, 5-dimethyl-2-phenylthiazolidin-4benzyloxy)-2-one (5aa):



5aa

Following the general procedure, reaction between *N,N*-diethylbenzothioamide **4a** (0.102 g, 0.5 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.286 g, 1.05 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5aa**, which was purified by silica gel column chromatography (5:95, EtOAc:Hexane as eluent) to give the title compound as colorless oil in 70% (0.142 g) yield. R_f 0.4 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04(d, *J* = 6.8 Hz, 2H), 7.42-7.37 (m, 3H), 7.32 (*br* s, 5H), 4.91 (d, *J* = 8.8 Hz, 1H), 4.00 (d, *J* = 8.8 Hz, 1H), 2.67-2.60 (m, 4H), 1.69 (s, 3H), 1.62 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 141.4, 134.7, 129.4, 129.1, 128.9, 128.6, 128.4, 128.3, 94.0, 76.2, 45.4, 45.0, 30.9, 28.4, 15.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{22}H_{29}N_2O_2S$, 385.1950 mass found 385.1943.

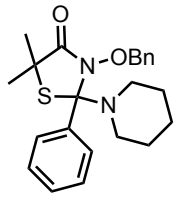
3-(benzyloxy)-5,5-dimethyl-2-phenyl-2-(pyrrolidin-1-yl)thiazolidin-4-one (5ab):



5ab

Following the general procedure, reaction between phenyl(pyrrolidin-1-yl)methanethione **4b** (0.070 g, 0.36 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.198 g, 0.73 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5ab,** which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as white solid in 85% (0.119 g) yield. R_f 0.3 (5:95 EtOAc:Hexane); **mp** 97-98 ºC; **FT-IR** (v cm^{-1}): 2970, 1698, 1447, 1382, 1330, 1140, 1015; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.2 Hz, 2H), 7.46 -7.41(m, 3H), 7.32-7.26 (m, 5H) 4.8 (d, *J* = 8.4 Hz, 1H), 3.81 (d, *J* = 8.4 Hz, 1H), 2.72-2.68 (m, 2H), 2.59-2.52 (m, 2H), 1.85-1.79 (m, 4H), 1.76 (s, 3H), 1.72 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 139.9, 134.4, 129.9, 129.8, 129.3, 128.7, 128.3 (2), 92.3, 76.8, 48.0, 44.9, 31.7, 27.6, 24.0; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{22}H_{26}N_2NaO_3S$ 405.1613, mass found 405.1601.

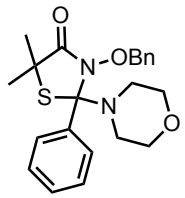
3-(benzyloxy)-5, 5-dimethyl-2-phenyl-2-(piperidin-1-yl) thiazolidin-4-one (5ac):



5ac

Following the general procedure, reaction between phenyl(piperidin-1-yl)methanethione **4c** (0.164 g, 0.8 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.433 g, 1.59 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5ac**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as white solid in 87% (0.256 g) yield. R_f 0.3 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 6.8 Hz, 2H), 7.47-7.41 (m, 3H), 7.32-7.28(m, 5H), 4.85 (d, *J* = 8.8 Hz, 1H), 3.70 (d, *J* = 8.8 Hz, 1H), 2.47-2.38 (m, 4H), 1.77 (s, 3H), 1.72 (s, 3H), 1.68-1.58 (m, 4H), 1.53-1.48 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 139.7, 134.3, 129.7, 129.5, 129.1, 128.6, 128.3, 128.2, 93.1, 76.6, 47.5, 44.6, 31.4, 27.9, 25.3, 24.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{23}H_{29}N_2O_2S$ 397.1950, mass found 397.1944.

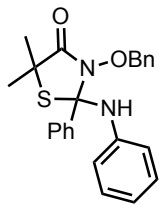
3-(benzyloxy)-5,5-dimethyl-2-morpholino-2-phenylthiazolidin-4-one (5ad):



5ad

Following the general procedure, reaction between morpholino (phenyl)methanethione **4d** (0.095 g, 0.46 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.248 g, 0.91 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5ad**, which was purified by silica gel column chromatography (5:95, EtOAc:Hexane as eluent) to give the title compound as white solid in 85% (0.183g) yield. R_f 0.3 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.8 Hz, 2H), 7.45-7.39 (m, 3H), 7.28-7.25 (m, 3H), 7.23-7.18 (m, 2H), 4.79 (d, *J* = 8.8 Hz, 1H), 3.75-3.67 (m, 4H), 3.64 (d, *J* = 8.8 Hz, 1H), 2.48-2.40 (m, 4H), 1.71 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 138.5, 134.2, 130.0, 129.7, 129.6, 128.8, 128.6, 128.3, 92.3, 76.8, 66.3, 46.8, 44.9, 31.5, 27.7; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{22}H_{26}N_2NaO_3S$ 421.1562, mass found 421.1551.

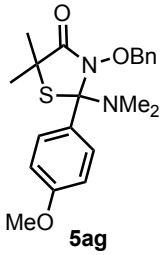
3-(benzyloxy)-5, 5-dimethyl-2-phenyl-2-(phenylamino) thiazolidin-4-one (5ae):



5ae

Following the general procedure, reaction between *N*-phenylbenzothioamide **4e** (0.113 g, 0.53 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.287 g, 1.06 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5ae**, which was purified by silica gel column chromatography (3:97 EtOAc:Hexane as eluent) to give the title compound as white solid in 60% (0.287 g) yield. R_f 0.25 (5:95 EtOAc:Hexane); **mp** 123 -124 ºC ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.45-7.40 (m, 3H), 7.31-7.27 (m, 3H), 7.20-7.15 (m, 4H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.82 (d, *J* = 8.8 Hz, 1H), 4.75 (s, 1H), 4.37 (d, *J* = 8.8 Hz, 1H), 1.62 (s, 3H), 1.47 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 142.9, 140.5, 134.3, 129.9, 129.3, 129.0, 128.9, 128.8, 128.5, 128.0, 120.9, 118.9, 84.4, 78.4, 46.7, 29.6, 29.0; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{24}H_{24}N_2NaO_2S$ 427.1456, mass found 427.1451.

3-(benzyloxy)-2-(dimethylamino)-2-(4-methoxyphenyl)-5, 5-dimethylthiazolidin-4-one (5ag):

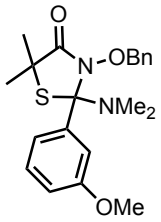


5ag

Following the general procedure, reaction between 4-methoxy-*N,N*-dimethylbenzothioamide **4g** (0.050 g, 0.25 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.138 g, 0.51 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5ag**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 62% (0.061 g) yield. R_f 0.2 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.29-7.21 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.83 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 3H), 3.69 (d, *J* = 8.8 Hz, 1H), 2.16 (s, 6H), 1.72 (s, 3H), 1.67(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 160.4, 134.3, 131.4, 131.3, 129.9, 128.8, 128.4, 113.6, 93.6,

77.0, 55.5, 44.8, 39.2, 31.8, 27.6; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{21}H_{26}N_2NaO_3S$, 409.1562, mass found 409.1552.

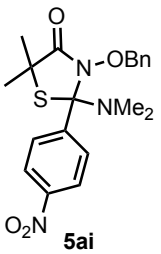
3-(benzyloxy)-2-(dimethylamino)-2-(3-methoxyphenyl)-5, 5-dimethylthiazolidin-4-one (5ah):



5ah

Following the general procedure, reaction between 3-methoxy-*N,N*-dimethylbenzothioamide **4h** (0.108 g, 0.55 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.298 g, 1.10 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5ah**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 72% (0.153 g) yield. R_f 0.2 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.32-7.25 (m, 5H), 6.99 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.71 (d, *J* = 8.4 Hz, 1H), 2.21 (s, 6H), 1.78 (s, 3H), 1.71 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 159.7, 141.0, 134.2, 129.8, 129.3, 128.7, 128.3, 122.2, 115.4, 115.0, 93.7, 76.8, 55.3, 44.7, 39.0, 31.6, 27.5; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{21}H_{26}N_2NaO_3S$ 409.1562, mass found 409.1554.

3-(benzyloxy)-2-(dimethylamino)-5,5-dimethyl-2-(4-nitrophenyl)thiazolidin-4-one (5ai):

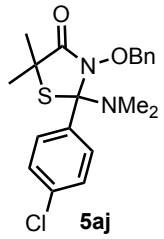


5ai

Following the general procedure, reaction between *N,N*-dimethyl-4-nitrobenzothioamide **4i** (0.107 g, 0.51 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.276 g, 1.02 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5ai**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as yellow oil in 65% (0.132 g) yield. R_f 0.25 (1:9 EtOAc:Hexane); **FT-IR** (v cm^{-1}): 2960, 1702, 1605, 1523, 1457, 1383, 1239, 1014; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.8 Hz, 2H), 8.29 (d, *J* = 8.8 Hz, 2H), 7.38-7.33 (m, 3H), 7.29-7.26 (m, 2H), 5.01 (d, *J* = 8.8 Hz, 1H), 4.07

(d, *J* = 8.8 Hz, 1H), 2.27 (s, 6H), 1.82 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 148.3, 146.6, 133.8, 130.8, 129.6, 129.0, 128.5, 123.4, 92.6, 77.0, 45.1, 39.0, 31.6, 27.6; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{20}H_{23}N_3NaO_4S$ 424.1307, mass found 424.1301.

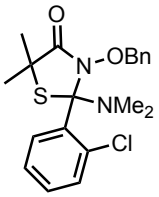
3-(benzyloxy)-2-(4-chlorophenyl)-2-(dimethylamino)-5,5-dimethylthiazolidin-4-one (5aj):



5aj

Following the general procedure, reaction between 4-chloro-*N,N*-dimethylbenzothioamide **4j** (0.106 g, 0.53 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.285 g, 1.06 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5aj**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as mixture of diastereomers (5:1) in 80% (0.170 g) yield. R_f 0.25 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.8 Hz, 0.4 H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J*=7.6 Hz, 0.4H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.29-7.24 (m, 3.6H), 7.23-7.20 (m, 2.4 H), 4.88 (d, *J* = 8.8 Hz, 1H), 4.83 (d, *J* = 8.8 Hz, 0.2 H), 3.81 (d, *J* = 8.8 Hz, 1H), 3.61 (d, *J* = 8.8 Hz, 0.2H), 2.17 (s, 1.2 H), 2.14 (s, 6H), 1.74 (s, 0.6H), 1.71 (s, 3H), 1.67 (s, 3.6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 170.9, 139.4, 138.1, 135.2, 134.1, 134.0, 131.3, 129.9, 129.8, 128.7, 129.3, 128.8, 128.7, 128.5, 128.4, 128.3, 93.8, 93.1, 76.9, 44.8, 44.7, 39.0, 39.0, 31.7, 31.6, 27.5, 27.5; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{20}H_{23}ClN_2NaO_2S$ 413.1066, mass found 413.1052.

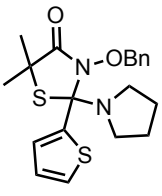
3-(benzyloxy)-2-(2-chlorophenyl)-2-(dimethylamino)-5,5-dimethylthiazolidin-4-one (5ak):



5ak

Following the general procedure, reaction between 2-chloro-*N,N*-dimethylbenzothioamide **4k** (0.040 g, 0.20 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.108 g, 0.40 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5ak**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as mixture of diastereomers (5:1) in 58% (0.045 g) yield. R_f 0.25 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.8Hz, 0.4H), 7.46-7.40 (m, 3H), 7.34 (d, *J* = 7.1 Hz, 0.4H), 7.31 (dd, *J* = 7.2 Hz, 2.0 Hz, 1H), 7.28-7.24 (m, 3.0H), 7.19 – 7.13(m, 1H), 7.11 – 7.04 (m, 2H), 5.25 (d, *J* = 8.8 Hz, 1H), 4.98 (d, *J* = 8.8 Hz, 1H), 4.75 (d, *J* = 8.8 Hz, 0.2H), 3.51 (d, *J* = 8.8 Hz, 0.2H), 2.60 (s, 6H), 2.10 (s, 1.2H), 1.66 (s, 0.6H), 1.60 (s, 0.6H), 1.54 (s, 3H), 1.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 171.0, 140.5, 139.5, 134.8, 134.2, 132.9, 131.9, 130.0, 129.9, 129.6, 129.4, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 127.5, 126.9, 93.9, 91.5, 76.9, 76.8, 46.2, 44.8, 39.1, 38.8, 31.7, 29.5, 29.2, 27.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for, $C_{20}H_{24}ClN_2O_2S$, 391.1247 mass found 391.1256.

3-(benzyloxy)-5,5-dimethyl-2-(pyrrolidin-1-yl)-2-(thiophen-2-yl)thiazolidin-4-one (5al):

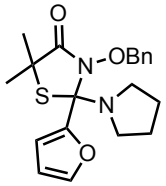


5al

Following the general procedure, reaction between pyrrolidin-1-yl(thiophen-2-yl)methanethione **4l** (0.050 g, 0.25 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.137 g, 0.0.51 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5al**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 90% (0.089 g) yield. R_f 0.25 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 3.2 Hz, 1H), 7.40-7.34 (m,3H), 7.33-7.30 (m, 3H), 7.06 (*app* t, *J* = 4.0 Hz, 1H), 4.96 (d, *J* = 8.8 Hz, 1H), 4.04 (d, *J* = 8.8 Hz, 1H), 2.73-2.66 (m, 2H), 2.62-

2.56, (m, 2H), 1.85-1.78 (m, 4H), 1.74 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 146.1, 134.5, 129.9, 129.0, 128.8, 128.4, 127.9, 127.1, 88.0, 77.2, 48.6, 45.3, 31.6, 27.6, 24.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{20}H_{25}N_2O_2S_2$ 389.1357, mass found 389.1354.

3-(benzyloxy)-2-(furan-2-yl)-5, 5-dimethyl-2-(pyrrolidin-1-yl) thiazolidin-4-one (5am):



5am

Following the general procedure, reaction between furan-2-yl(pyrrolidin-1-yl)methanethione **4m** (0.074 g, 0.41 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.221 g, 0.82 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5am**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as pale green solid in 73% (0.111 g) yield. R_f 0.3 (1:9 EtOAc:Hexane); **mp** 96 -97 ºC ;**FT-IR** (v cm^{-1}): 2970, 1697, 1457, 1383, 1160, 1141, 1014; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.38-7.34 (m, 2H), 7.30-7.26 (m, 3H), 6.76 (d, *J* = 4.0 Hz, 1H), 6.42 (brs, 1H), 4.87 (d, *J* = 9.2 Hz, 1H), 4.26 (d, *J* = 9.2 Hz, 1H), 2.74-2.69 (m, 2H), 2.63-2.56 (m, 2H), 1.86-1.79 (m, 4H), 1.67 (s, 3H), 1.64 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 152.5, 143.2, 134.6, 129.8, 128.7, 128.2, 112.2, 111.0, 85.7, 77.3, 47.9, 45.1, 31.5, 27.7, 24.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for, $C_{20}H_{25}N_2O_3S$, 373.1586 mass found 373.1568.

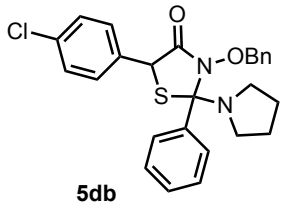
3'-(benzyloxy)-1,5' ,5'-trimethylspiro[indoline-2,2'-thiazolidin]-4'-one (5an):

5an

Following the general procedure, reaction between 1-methylindoline-2-thione **4n** (0.096 g, 0.58 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.319 g, 1.16 mmol, 2.0 equiv) afforded the corresponding spiro thiazolidin-4-one **5an**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as yellow solid in 55% (0.0.114 g) yield. R_f 0.35 (1:4 EtOAc:Hexane); **FT-IR** (v cm^{-1}): 3292, 2924, 1703, 1610, 1487, 1364, 1309, 1207, 1079; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 3H), 7.29-7.23 (m, 3H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.90-6.84 (t, *J* = 7.6Hz, 1H), 6.57 (d, *J* = 8.0 Hz,

1H), 5.17 (d, *J* = 8.8 Hz, 1H), 4.99 (d, *J* = 8.8 Hz, 1H), 3.88 (d, *J* = 16.8 Hz, 1H), 3.50 (d, *J* = 16.8 Hz, 1H), 2.89 (s, 3H), 1.80 (s, 3H), 1.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 148.9, 134.5, 129.7, 129.0, 128.5, 128.0, 125.3, 123.8, 118.9, 106.4, 92.3, 77.9, 46.2, 43.7, 31.0, 29.5, 28.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for, $C_{20}H_{23}N_2O_2S$, 355.1480 mass found 355.1452.

3-(benzyloxy)-5-(4-chlorophenyl)-2-phenyl-2-(pyrrolidin-1-yl)thiazolidin-4-one (5db):



5db

Following the general procedure, reaction between phenyl(pyrrolidin-1-yl)methanethione **4b** (0.040 g, 0.21 mmol, 1.0 equiv) and α-chloro hydroxamate **1d** (0.130 g, 0.42 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **5db**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as mixture of diastereomers (4:1) in 70% (0.068 g) combined yield. R_f 0.3 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 0.5H), 7.41-7.32 (m, 4.5H), 7.27-7.25 (m, 4H), 7.21 (s, 1H), 7.19-7.14 (m, 3.5H), 7.11-7.07 (m, 2H), 4.97 (s, 0.25H), 4.91 (d, *J* = 8.8 Hz, 0.25H), 4.79 (s, 1H), 4.69 (d, *J* = 8.4 Hz, 1H), 3.96 (d, *J* = 8.8 Hz, 0.25 H), 3.74 (d, *J* = 8.4 Hz, 1H), 2.77-2.70 (m, 0.5H), 2.60-2.52 (m, 4.5H), 1.78-1.69(m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 165.4, 140.0, 138.5, 137.4, 135.2, 134.4, 134.2 (2), 134.0, 130.1, 130.0, 129.8, 129.7 (2), 129.5, 129.3, 129.2, 129.0, 128.9, 128.6, 128.5, 128.4 (2), 125.7, 93.8, 93.7, 77.7, 48.5, 48.3, 46.9, 45.1, 24.4, 24.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{26}H_{26}ClN_2O_2S$ 465.1404, mass found 465.1393.

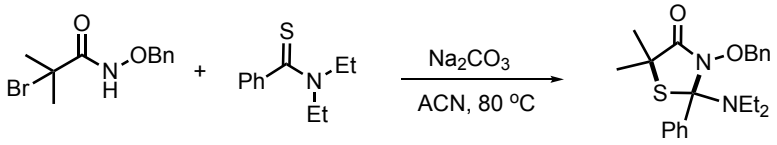
7. Gram scale preparation.

compound **3aa**

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

To a solution of α-haloamide (**1a**, 1.04 g, 3.83 mmol, 1.0 equiv) and thioketone (**2a**, 0.76 g, 3.83 mmol, 1.0 equiv) in $(CF_3)_2CHOH$ (9.5 mL, 0.4 M), was added DIPEA (1.3 mL, 7.66 mmol, 2.0 equiv) dropwise. The reaction mixture was stirred at room temperature and the reaction progress was monitored by thin layer chromatography (TLC). Upon completion of the reaction HFIP was removed under reduced pressure and the crude was purified by silica gel column chromatography (using 3:97 ethyl acetate-hexane mixture as eluent) to afford the corresponding thiazolidin-4-one products **3aa** in 72% (1.07 g) yield.

compound **5aa**

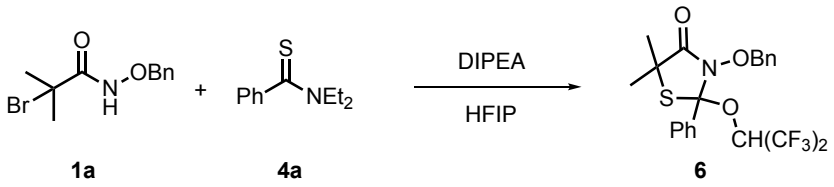


1a **4a** **5aa**

To a solution of thioamide (**4a**, 1.08 g, 5.58 mmol, 1.0 equiv) and haloamide (**1a**, 3.03 g, 11.2 mmol, 2 equiv) in acetonitrile (11.1 mL, 0.5 M) was added Na_2CO_3 (2.37 g, 22.3 mmol, 4.0 equiv) and the reaction mixture was heated at 80°C for 1h. Upon completion of the reaction (TLC controlled), reaction mixture was passed through celite and thoroughly washed with ethyl acetate. The filtrate was concentrated under vacuo and the crude product was purified by silica gel column chromatography (using 3:97 ethyl acetate-hexane mixture as eluent) to afford the 2-aminothiazolidin-4-one derivatives **5aa** in 64% (1.37 g) yield.

8. Synthesis of compound 6.

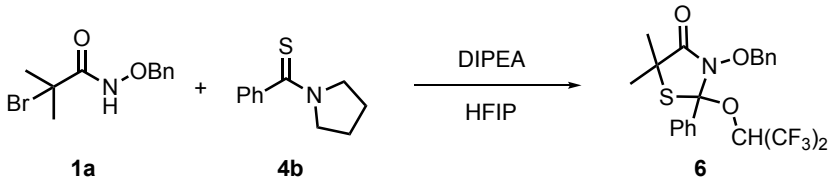
procedure 1.



1a **4a** **6**

N,N-diethylbenzothioamide **4a** (0.116 g, 0.60 mmol, 1.0 equiv) and α-bromo hydroxamate **1a** (0.162 g, 0.60 mmol, 1.0 equiv) were taken in HFIP (0.4 M) and was added DIPEA (0.20 mL, 1.2 mmol, 2.0 equiv). The reaction mixture was stirred at room temperature for 45 minutes until the disappearence of the starting materials were observed (TLC controlled). The solvent was removed in vacuo and the crude product was purified by silica gel column chromatography (3:97 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 76% (0.154 g) yield. R_f 0.5 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.32-7.29 (m, 3H), 7.28-7.21 (m, 5H), 5.56 (sept, J = 6.0 Hz,1H), 4.92 (s, 2H), 1.60 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 152.5, 138.2, 131.6, 130.1, 128.6, 128.3 (2), 127.9, 124.9-116.5 (m, CF_3), 76.3, 67.6 (hept, J_{FC} = 34.5 Hz), 50.4, 25.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.90. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{21}H_{20}F_6NO_3S$ 480.1068 mass found, 480.1065.

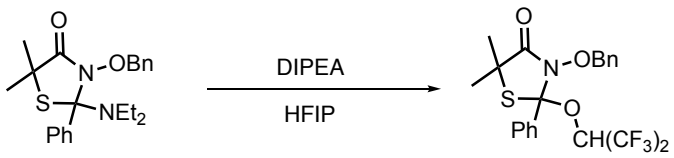
procedure 2.



1a **4b** **6**

To a solution of α-haloamide **1a** (0.085 g, 0.31 mmol, 1.0 equiv) and thioamide **4b** (0.060 g, 0.31 mmol, 1.0 equiv) in $(CF_3)_2CHOH$ (0.4 M), was added DIPEA (0.1 mL, 0.62 mmol, 2.0 equiv) dropwise. The reaction mixture was stirred at room temperature and the reaction progress was monitored by thin layer chromatography (TLC). Upon completion of the reaction, HFIP was removed under reduced pressure and the crude was purified by silica gel column chromatography (using 2:98 ethyl acetate-hexane mixture as eluent) to afford the corresponding thiazolidin-4-one products **6** in 65% (0.098 g) yield. Spectral data (^{1}H/^{13}C NMR) was matched to that of the previously prepared **6**.

*procedure 3 (from **5aa**).*



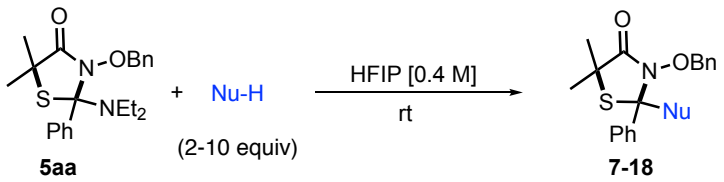
5aa **6**

Compound **5aa** (0.03 g, 0.08 mmol, 1.0 equiv) was taken in HFIP (0.2 mL) and stirred for 5 minute. Complete disappearence of **5aa** and formation of product **6** was observed by TLC analysis**.** HFIP was removed under reduced pressure and the crude was purified by silica gel chromatography (using 2:98 ethyl acetae-hexane mixture as eluent) to afford the corresponding thiazolidin-4-one product **6** in 90% (0.034 g) yield.

NMR experiment.

Compound **5aa** (0.010 g, 0.02 mmol) was taken in 0.3 mL of $CDCl_3$ and to this mixture was added HFIP (0.2 mL). ^1H NMR was recorded immediately.

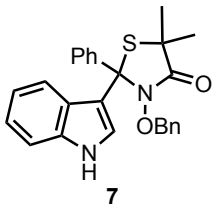
9. General Procedure for the C-2 Modification of Thiazolidin-4-ones with Various Nucleophiles (7-18):



To a solution of compound **5aa** (1.0 equiv) in HFIP (0.4 M) was added the corresponding nucleophile (2-10 equiv) at room temperature. Progress of the reaction was monitored by TLC and upon completion of the reaction, the solvent was removed in vacuo and the crude was purified by silica gel column chromatography (using ethyl acetate/hexane mixture as eluent) to afford the corresponding 2-substituted thiazolidin-4-one derivatives (**7**-**18**).

10. Characterization of Various C-2 substituted Thiazolidin-4-ones (7-18):

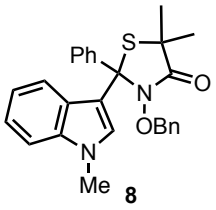
3-(benzyloxy)-2-(1H-indol-3-yl)-5,5-dimethyl-2-phenylthiazolidin-4-one (7):



7

Following the general procedure, reaction between **5aa** (0.040 g, 0.10 mmol, 1.0 equiv) and 1*H*-indole (0.024 g, 0.20 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **7**, which was purified by silica gel column chromatography (1:4 EtOAc:Hexane as eluent) to give the title compound as white solid in 92% (0.041 g) yield. R_f 0.3 (1:4 EtOAc:Hexane); **mp** 139 -140 ºC ; **FT-IR** (v cm^{-1}): 3322, 2925, 1681, 1491, 1457, 1363, 1129, 1013; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63-8.52 (m, 1H), 7.71-7.66 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43-7.39 (m, 4H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.32-7.21 (m, 4H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.63 (d, *J* = 8.8 Hz, 1H), 4.42 (d, *J* = 8.8 Hz, 1H), 1.67 (s, 3H), 1.63 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9, 142.3, 137.0, 134.3, 129.9, 128.7, 128.3, 128.2 (2), 126.2, 126.0, 122.6, 121.7, 120.1, 116.6 (2), 78.4, 70.3, 46.9, 29.2, 29.0; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}N_2NaO_2S$, 451.1456, mass found 451.1449.

3-(benzyloxy)-5, 5-dimethyl-2-(1-methyl-1H-indol-3-yl)-2-phenylthiazolidin-4-one (8):

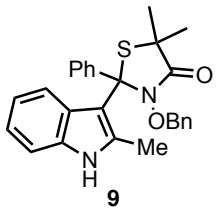


8

Following the general procedure, reaction between **5aa** (0.03 g, 0.08 mmol, 1.0 equiv) and 1-methyl-1*H*-indole (0.020 g, 0.16 mmol, 2.0 equiv) afforded thiazolidin-4-one derivative **8**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as pale yellow solid in 91% (0.031 g) yield. R_f 0.35 (1:4 EtOAc:Hexane); **mp** 154 -155 ºC ;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.39-7.35 (m, 4H), 7.34-7.25 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 4.62 (d, *J* = 9.2 Hz, 1H), 4.34 (d, *J* = 9.2 Hz, 1H), 3.82 (s, 3H), 1.64 (s, 3H), 1.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 142.8, 137.9, 134.5, 130.6, 129.9, 128.6, 128.2

(2), 126.8, 122.2, 121.9, 119.7, 114.8, 109.6, 78.4, 70.21, 46.87, 33.08, 29.19, 29.11; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{27}H_{26}N_2NaO_2S$ 465.1613, mass found 465.1604.

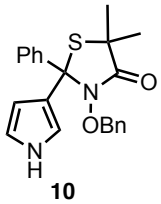
3-(benzyloxy)-5, 5-dimethyl-2-(2-methyl-1H-indol-3-yl)-2-phenylthiazolidin-4-one (9):



9

Following the general procedure, reaction between **5aa** (0.030 g, 0.08 mmol, 1.0 equiv) and 2-methyl-1H-indole (0.020 g, 0.16 mmol, 2.0 equiv) afforded thiazolidin-4-one derivative **9**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as brown solid in 90% (0.032 g) yield. R_f 0.3 (1:4 EtOAc:Hexane); **mp** 170 -171 ºC ;**FT-IR** (v cm^{-1}): 3316, 2925, 1677, 1489, 1458, 1384, 1140, 1019; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14-8.05 (m, 1H), 7.74 (s, 2H), 7.39-7.34 (m, 4H), 7.28-7.25 (m, 1H), 7.22-7.15 (m, 3H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.00-6.94 (m, 3H), 4.50 (d, *J* = 8.8Hz, 1H), 4.21 (d, *J* = 8.8 Hz, 1H), 2.08 (s, 3H), 1.62 (s, 3H), 1.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 142.7, 135.1, 134.5, 134.3, 129.6, 128.6, 128.4, 128.3, 128.2, 127.7, 121.6, 121.4, 119.7, 111.5, 110.4, 78.0, 71.1, 46.7, 29.3, 29.0, 14.2; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{27}H_{26}N_2NaO_2S$ 465.1613, mass found 465.1599.

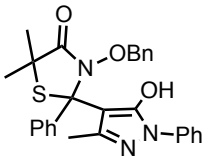
3-(benzyloxy)-5, 5-dimethyl-2-phenyl-2-(1H-pyrrol-3-yl) thiazolidin-4-one (10):



10

Following the general procedure, reaction between **5aa** (0.040 g, 0.10 mmol, 1.0 equiv) and 1*H*-pyrrole (0.014 g, 0.20 mmol, 2.0 equiv) afforded thiazolidin-4-one derivative **10**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as brown solid in 91% (0.036 g) yield. R_f 0.2 (1:4 EtOAc:Hexane); **mp** 141 - 142.5 ºC ; **FT-IR** (v cm^{-1}): 3340, 2972, 2927, 1691, 1456, 1384, 1033, 1016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.53-7.48 (m, 2H), 7.41-7.34 (m, 6H), 7.28-7.24 (m, 2H), 6.95-6.91 (m, 1H), 6.46-6.42 (m, 1H), 6.34-6.30 (m, 1H), 4.86 (d, *J* = 8.8 Hz, 1H), 4.16 (d, *J* = 8.8 Hz, 1H), 1.68 (s, 3H), 1.52 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 142.3, 134.3, 129.9, 129.4, 128.9, 128.4 (2), 128.3, 127.6, 119.4, 113.0, 109.2, 78.4, 69.2, 46.9, 28.9, 28.8; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{22}H_{22}N_2NaO_2S$ 401.1300, mass found 401.1297.

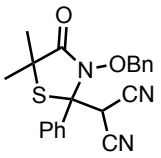
3-(benzyloxy)-5,5-dimethyl-2-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-2-phenylthiazolidin-4-one (11):



11

Following the general procedure, reaction between **5aa** (0.030 g, 0.08 mmol, 1.0 equiv) and 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (0.135 g, 0.80 mmol, 10.0 equiv) afforded the corresponding thiazolidin-4-one derivative **11**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as light brown solid in 95% (0.036 g) yield; R_f 0.3 (1:4 EtOAc:Hexane); **mp** 173 -174 ºC ;**FT-IR** (v cm^{-1}): 2924, 1697, 1617, 1498, 1458, 1401, 1380, 1016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.36-7.25 (m, 5H), 7.20-7.15 (m, 4H), 7.10-7.05 (m, 2H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.53 (d, *J* = 8.4 Hz, 1H), 1.57 (s, 3H), 1.54 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 149.4, 149.0, 141.6, 138.3, 133.3, 130.2, 129.3, 129.0, 128.8, 128.8, 128.6, 127.7, 126.5, 122.2, 97.6, 79.4, 69.0, 47.3, 29.4, 28.8, 15.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{28}H_{28}N_3O_3S$ 486.1851, mass found 486.1841.

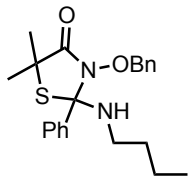
(3-(benzyloxy)-5, 5-dimethyl-4-oxo-2-phenylthiazolidin-2-yl)malononitrile (12):



12

Following the general procedure, reaction between **5aa** (0.020 g, 0.052 mmol, 1.0 equiv) and (0.034 g, 0.52 mmol, 10.0 equiv) afforded the corresponding thiazolidin-4-one derivative **12 ,** which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 86% (0.017g) yield. R_f 0.25 (5:95 EtOAc:Hexane); **FT-IR** (v cm^{-1}): 2923, 1712, 1448, 1386, 1134, 1016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 2H), 7.44-7.39 (m, 3H), 7.28-7.21 (m, 3H), 7.19- 7.17 (m, 2H), 5.05 (d, *J* = 8.8 Hz, 1H), 4.95 (s, 1H), 4.35 (d, *J* = 8.8 Hz, 1H), 1.76 (s, 3H), 1.67 (s, 3H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 135.9, 133.4, 130.5, 130.0, 129.5, 129.5, 128.7, 127.3, 110.8, 110.5, 78.8, 71.1, 47.6, 35.4, 31.3, 28.2; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{21}H_{19}N_3NaO_2S$ 400.1096, mass found 400.1087.

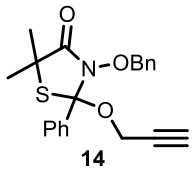
3-(benzyloxy)-2-(butylamino)-5,5-dimethyl-2-phenylthiazolidin-4-one (13):



13

Following the general procedure, reaction between **5aa** (0.030 g, 0.08 mmol, 1.0 equiv) and butan-1-amine (0.057 g, 0.80 mmol, 10.0 equiv) afforded the corresponding thiazolidin-4-one derivative **13**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as mixture of isomers. Each isomer was isolated separately by silica gel column chromatography. Yield of one isomer (**13a**), 26% (0.08 g); R_f 0.35 (5:95 EtOAc:Hexane). Yield of other isomer (**13b**) is 36% (0.011g) R_f 0.3 (5:95 EtOAc:Hexane). NMR data of **13a**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.37-7.29 (m, 3H), 7.27-7.25 (m, 4H), 7.23 (brs, 1H), 5.05 (d, *J* = 9.2 Hz, 1H), 4.72 (d, *J* = 9.2 Hz, 1H), 2.99-2.89 (m, 1H), 2.57-2.49 (m, 1H), 2.23 (brs, 1H), 1.66 (s, 3H), 1.63 (s, 3H), 1.53-1.50 (m, 2H), 1.40-1.35 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.2, 142.7, 135.0, 129.4, 128.8, 126.6, 128.5, 126.8, 86.6, 77.9, 46.3, 42.5, 32.1, 30.7, 29.2, 20.6, 14.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for, $C_{22}H_{29}NO_2S$, 385.1950 mass found 385.1928. NMR data of **13b**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.41-7.36 (m, 3H), 7.34-7.28 (m, 5H), 6.96 (s, 1H), 5.08 (s, 2H), 3.10 (q, *J* = 6.8 Hz, 2H), 1.59 (s, 6H), 1.43-1.39 (m, 2H), 1.34-1.29 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 153.2, 138.0, 132.4, 130.0, 128.7, 128.5, 128.3, 128.3, 127.9, 76.7, 53.5, 39.8, 31.7, 26.6, 20.2, 14.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{22}H_{29}NO_2S$ 385.1950, mass found 385.1936

3-(benzyloxy)-5,5-dimethyl-2-phenyl-2-(prop-2-yn-1-yloxy)thiazolidin-4-one (14):

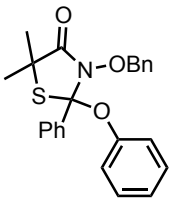


14

Following the general procedure, reaction between **5aa** (0.050 g, 0.13 mmol, 1.0 equiv) and prop-2-yn-1-ol (0.073 g, 1.30 mmol, 10.0 equiv) afforded the corresponding thiazolidin-4-one derivative **14**, which was purified by silica gel column chromatography (1:9 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 62% (0.030 g) yield. R_f 0.3 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 6.4 Hz, 2H), 7.29-7.25 (m, 3H), 7.15-7.09 (m, 3H), 7.06-7.03 (m, 2H), 4.80 (d, *J* = 8.8 Hz, 1H), 4.27 (dd, *J* = 14.0, 2.4 Hz,

1H), 4.17 (d, *J* = 8.8 Hz, 1H), 4.02 (dd, *J* = 14.0, 2.4 Hz, 1H), 2.33 (t, *J* = 2.0 Hz, 1H), 1.60 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 138.6, 134.2, 129.7, 129.5, 128.9, 128.5, 128.4, 127.8, 99.0, 78.6, 78.2, 75.1, 52.8, 46.6, 30.2, 28.7; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{21}H_{21}NNaO_3S$ 390.1140, mass found 390.1132.

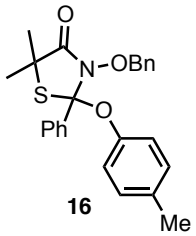
3-(benzyloxy)-5,5-dimethyl-2-phenoxy-2-phenylthiazolidin-4-one (15):



15

Following the general procedure, reaction between **5aa** (0.021 g, 0.05 mmol, 1.0 equiv) and phenol (0.051 g, 0.50 mmol, 10.0 equiv) afforded thiazolidin-4-one derivative **15**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 75% (0.017 g) yield. R_f 0.3 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 6.8, 3.2 Hz, 2H), 7.40-7.32 (m, 5H), 7.31-7.26 (m, 5H), 7.22 (*app* t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 5.02 (s, 2H), 1.70 (s, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 153.5, 151.4, 138.1, 132.1, 130.0, 129.5, 128.9, 128.4 (2), 128.3, 127.8, 125.8, 121.6, 76.6, 51.4, 26.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{24}H_{24}NO_3S$ 406.1477, mass found 406.1470.

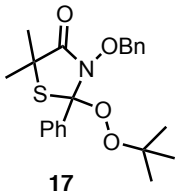
3-(benzyloxy)-5,5-dimethyl-2-phenyl-2-(p-tolyloxy)thiazolidin-4-one (16):



16

Following the general procedure, reaction between **5aa** (0.050 g, 0.013 mmol, 1.0 equiv) and *p*-cresol (0.140 g, 0.13 mmol, 10.0 equiv) afforded the corresponding thiazolidin-4-one derivative **16**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 83% (0.045 g) yield. R_f 0.3 (5:95 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 6.8, 3.2 Hz, 2H), 7.35-7.32 (m, 3H), 7.33-7.28 (m, 5H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.02 (s, 2H), 2.30 (s, 3H), 1.69 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 153.5, 149.2, 138.1, 135.4, 132.2, 130.0 (2), 128.8, 128.4 (2), 128.3, 127.8, 121.3, 76.5, 51.5, 26.2, 21.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{25}H_{26}NO_3S$ 420.1633, mass found 420.1618.

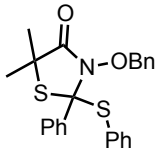
3-(benzyloxy)-2-(tert-butylperoxy)-5,5-dimethyl-2-phenylthiazolidin-4-one (17):



17

Following the general procedure, reaction between **5aa** (0.040 g, 0.13 mmol, 1.0 equiv) and tert-butyl peroxide solution (0.05 ml, 0.26 mmol, 2.0 equiv, 5-6 M in decane) afforded the corresponding thiazolidin-4-one **17**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 78% (0.040 g) yield. R_f 0.4 (3:97 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* =7.6, 3.6 Hz, 2H), 7.39-7.35 (m, 3H), 7.27-7.24 (m, 5H), 5.06 (d, *J* = 9.2 Hz, 1H), 4.81 (d, *J* = 9.2 Hz, 1H), 1.76 (s, 3H), 1.67 (s, 3H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 136.9, 135.05, 129.5, 129.4, 128.6, 128.5, 128.3, 126.9, 100.9, 82.4, 77.9, 46.9, 30.5, 27.7, 27.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{22}H_{27}NNaO_4S$ 424.1558, mass found 424.1546.

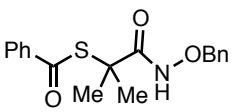
3-(benzyloxy)-5, 5-dimethyl-2-phenyl-2-(phenylthio) thiazolidin-4-one (18):



18

Following the general procedure, reaction between **5aa** (0.041 g, 0.11 mmol, 1.0 equiv) and thiophenol (0.023 g, 0.22 mmol, 2.0 equiv) afforded the corresponding thiazolidin-4-one **18**, which was purified by silica gel column chromatography (5:95 EtOAc:Hexane as eluent) to give the title compound as colorless oil in 80% (0.036 g) yield. R_f 0.35 (1:9 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.49-7.45 (m, 2H), 7.36-7.30 (m, 3H), 7.28-7.23 (m, 8H), 5.13 (d, *J* = 8.8 Hz, 1H), 4.30 (d, *J* = 8.8 Hz, 1H), 1.46 (s, 3H), 0.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 139.9, 138.1, 134.4, 130.9, 129.9, 129.7, 129.4, 129.0, 128.9, 128.7, 128.5, 128.2, 83.0, 77.7, 47.1, 31.4, 26.8; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{24}H_{23}NNaO_2S_2$ 444.1068, mass found 444.1060.

(1-((benzyloxy)amino)-2-methyl-1-oxopropan-2-yl) benzothioate (19):

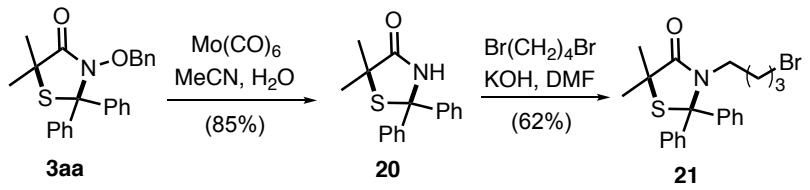


19

Compound **5aa** (0.040 g, 0.10 mmol, 1.0 equiv) was taken in HFIP (0.3 mL) and was added

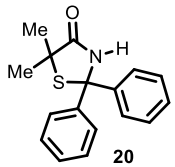
TBAF (0.2 mL, 0.20 mmol, 2.0 equiv, 1.0 M in THF). The reaction mixture was then heated at 50^{o}C for 8h. Upon disappearence of the starting material (TLC controlled), the solvent was removed in vacuo and the reaction mixture was purified by silica gel column chromatography (1:4 EtOAc:Hexane as eluent) to give compound **19** as colorless oil in 30% (0.010 g) yield. R_f 0.25 (1:4 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.60 (*app*t, *J* = 7.2Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39-7.35 (m, 2H), 7.25-7.20 (m, 3H), 4.92 (s, 2H), 1.68 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.8, 171.5, 136.7, 135.5, 134.1, 129.5, 128.8, 128.7, 128.6, 127.6, 78.1, 50.6, 26.2; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for, $C_{18}H_{19}NNaO_3S$, 352.0983 mass found 352.0969.

11. Further Studies: Preparation and characterization of compounds 20-21



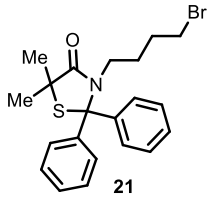
(Scheme 6 *from main text***)**

5,5-dimethyl-2,2-diphenylthiazolidin-4-one (20):



To a solution of thiazolidine-4-one **3aa** (0.078 g, 0.20 mmol, 1.0 equiv) in acetonitrile/water (9:1, 2 mL), $Mo(CO)_6$ (0.063 g, 0.24 mmol, 1.2 equiv) was added and the reaction was stirred at 120 ºC under argon for 12 h. After cooling to room temperature, the mixture was the filtered through celite and thoroughly washed with ethyl acetate. Then, filtrate was concentrated under vacuo, and the resulting residue was purified by silica gel column chromatography (3:7 EtOAc/hexane) to afford **20** as white solid in 85% (0.049 g) yield. R_f 0.25 (30:70 EtOAc:Hexane) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.37 (d, J = 7.2 Hz, 4H), 7.29-7.19 (m, 6H), 1.45 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.5, 144.8, 128.4, 127.9, 127.1, 69.9, 52.6, 28.4; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calculated for $C_{17}H_{17}NNaOS$ 306.0929, mass found 306.0921.

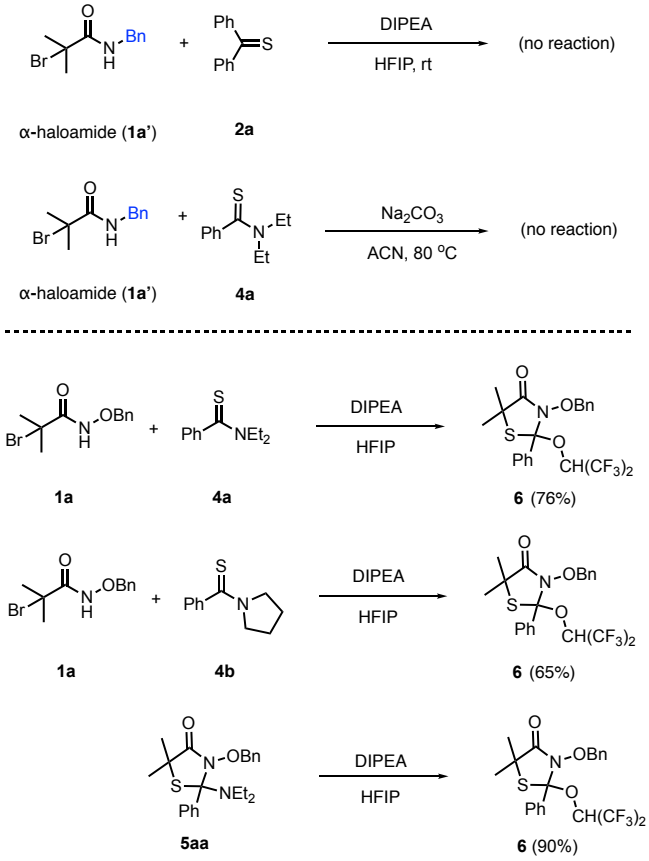
3-(4-bromobutyl)-5,5-dimethyl-2,2-diphenylthiazolidin-4-one (21):



To a solution of thiazolidine-4-one **20** (0.029 g, 0.10 mmol, 1.0 equiv) in anhydrous DMF (1mL), under N_2 atmosphere was added KOH (0.017 g, 0.30 mmol, 3.0 equiv) was added and the reaction was stirred for 30 minutes, which provided yellow solution. After getting yellow solution,1,4 dibromobutane (0.023 mL, 0.20 mmol, 2.0 equiv) was added and stirred the reaction at room temperature until the consumption of the starting material. The reaction mixture was quenched with water and extracted with ethyl acetate. The organic layer was

concentrated under vacuo, and the resulting residue was purified by silica gel column chromatography (3:7 EtOAc/hexane) to afford **21** as colorless oil in 62% (0.026 g) yield. R_f 0.3 (3:7 EtOAc:Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 4H), 7.38-7.32 (m, 6H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H), 1.53-1.47 (m, 8H), 0.90-0.82 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 142.9, 128.8, 128.4 (2), 75.2, 51.3, 44.7, 32.8, 30.3, 29.3, 26.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calculated for $C_{21}H_{25}BrNOS$ 418.0840, mass found 418.0822.

12. Control Experiments.



NMR Experiment.

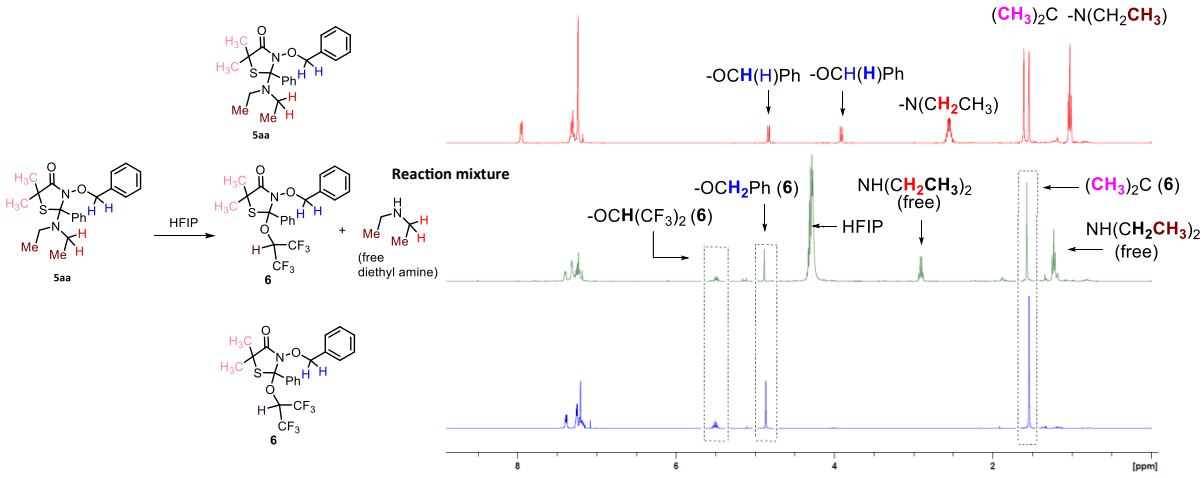
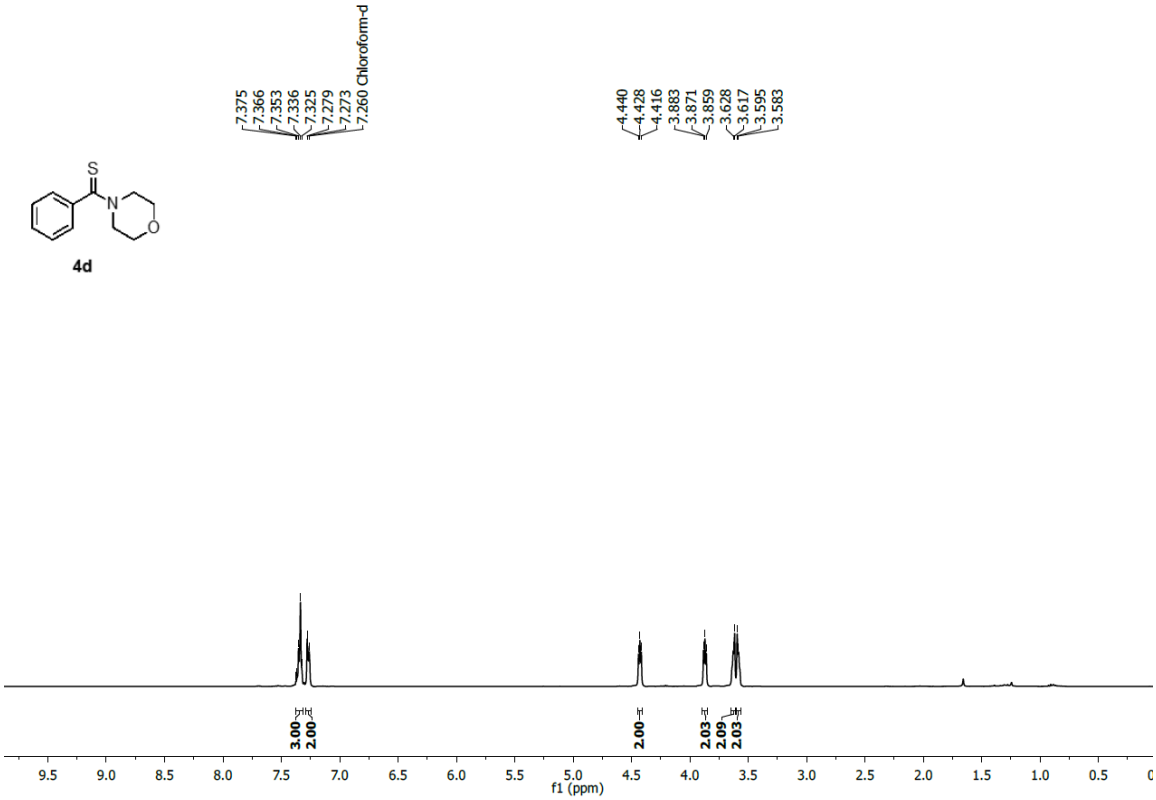
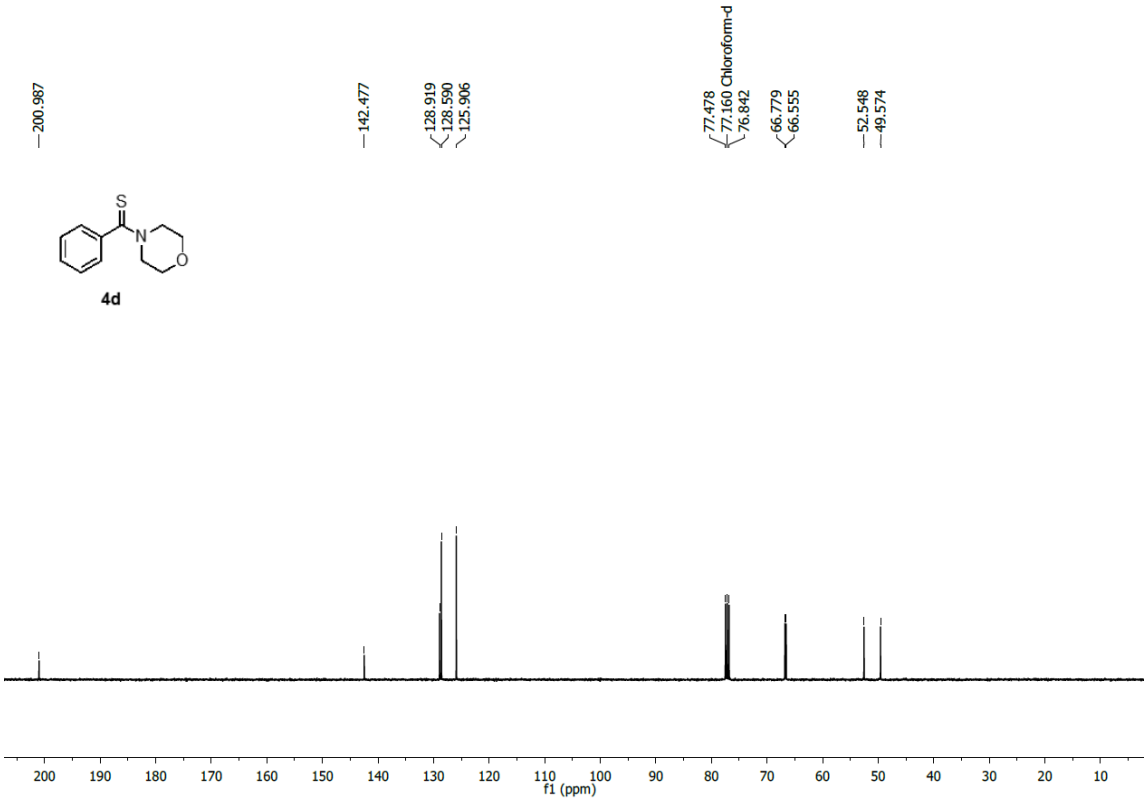


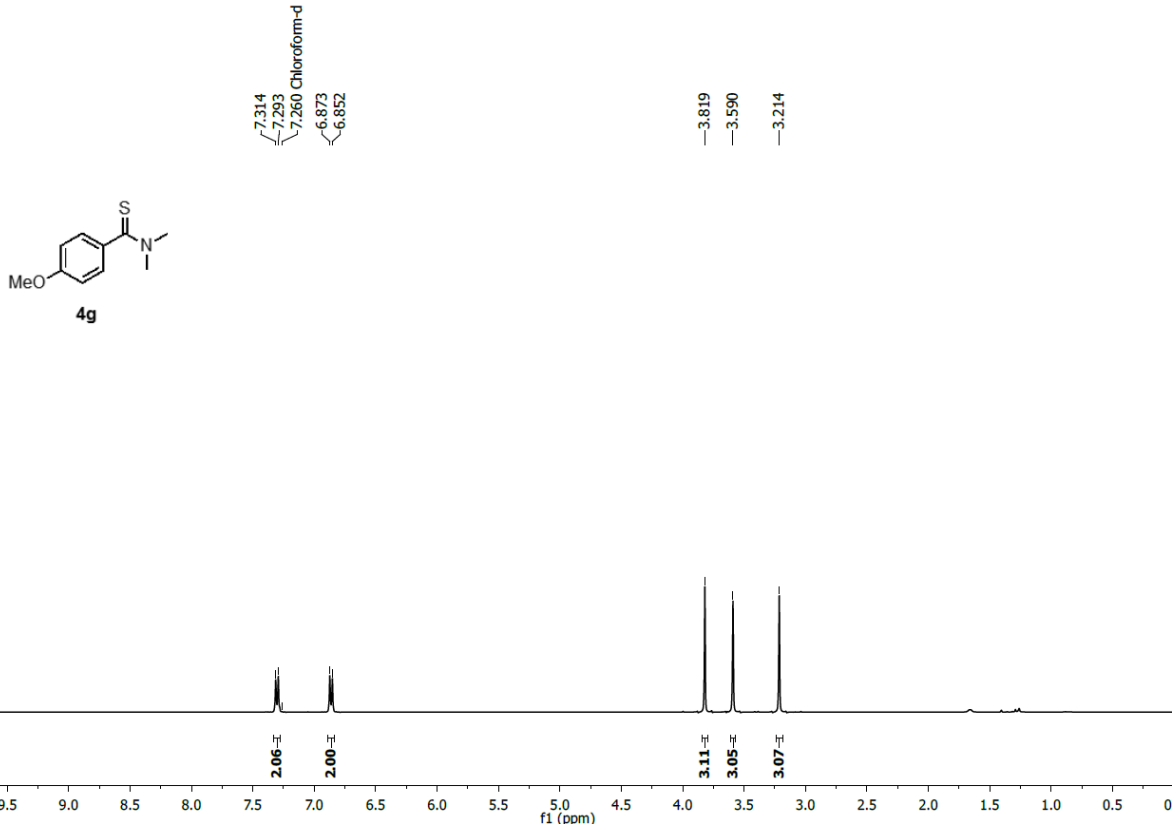
Figure S4: Stacked NMR spectras of pure **5aa**, reaction of **5aa** in HFIP and pure compound **6**.

Note: Compound **5aa** (0.010 g, 0.02 mmol) was taken in 0.3 mL of $CDCl_3$ and to this mixture was added HFIP (0.2 mL). ^1H NMR was recorded immediately. It was clear from the crude NMR that, compound 5aa was fully converted to compound **6** and free Et_2NH was released in the reaction mixture. No traces of **5aa** was remained in the reaction mixture.

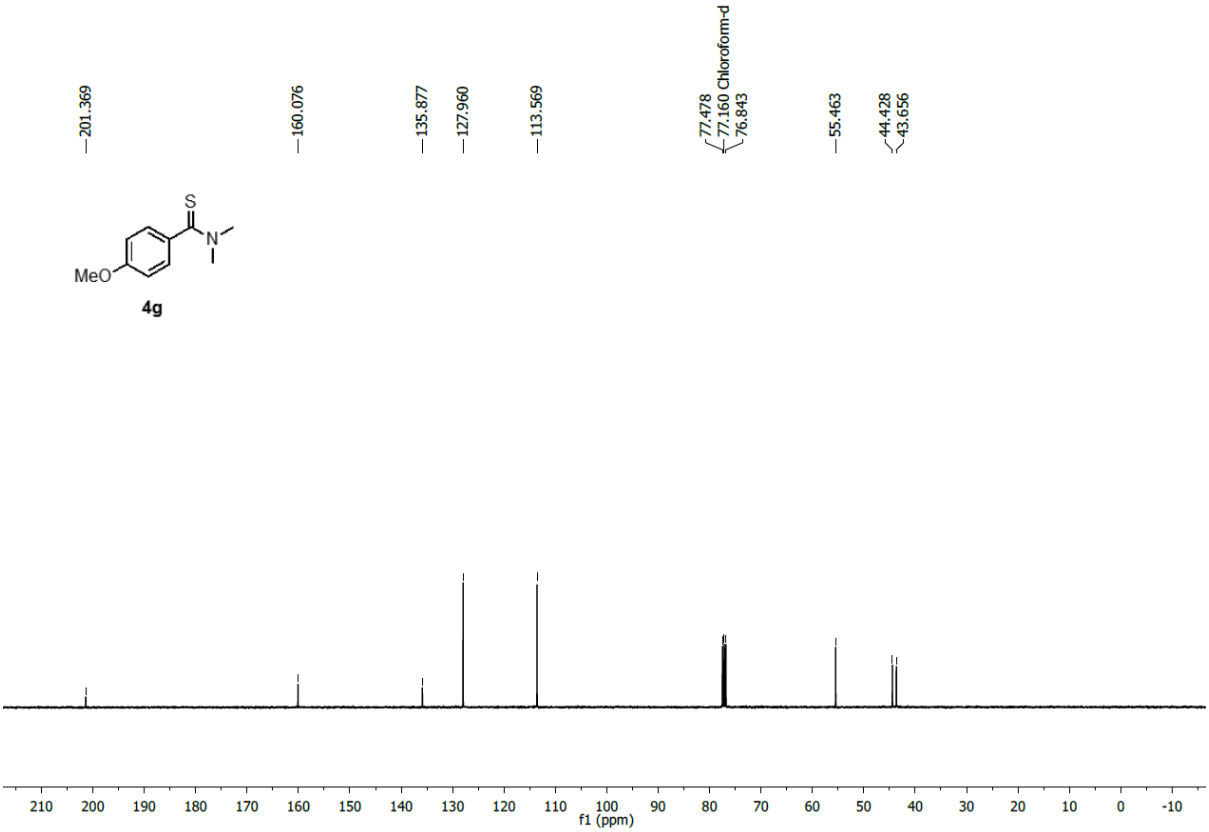
13. NMR Spectra of New Compounds



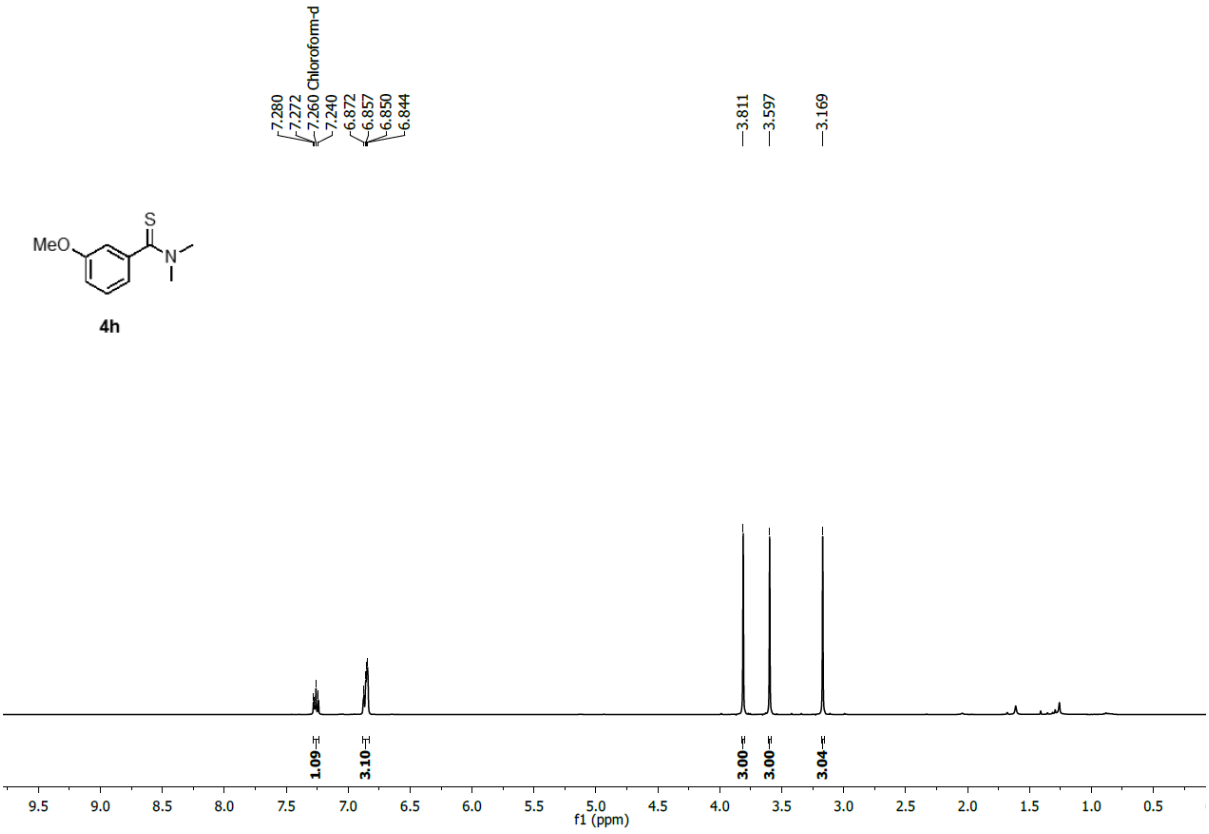


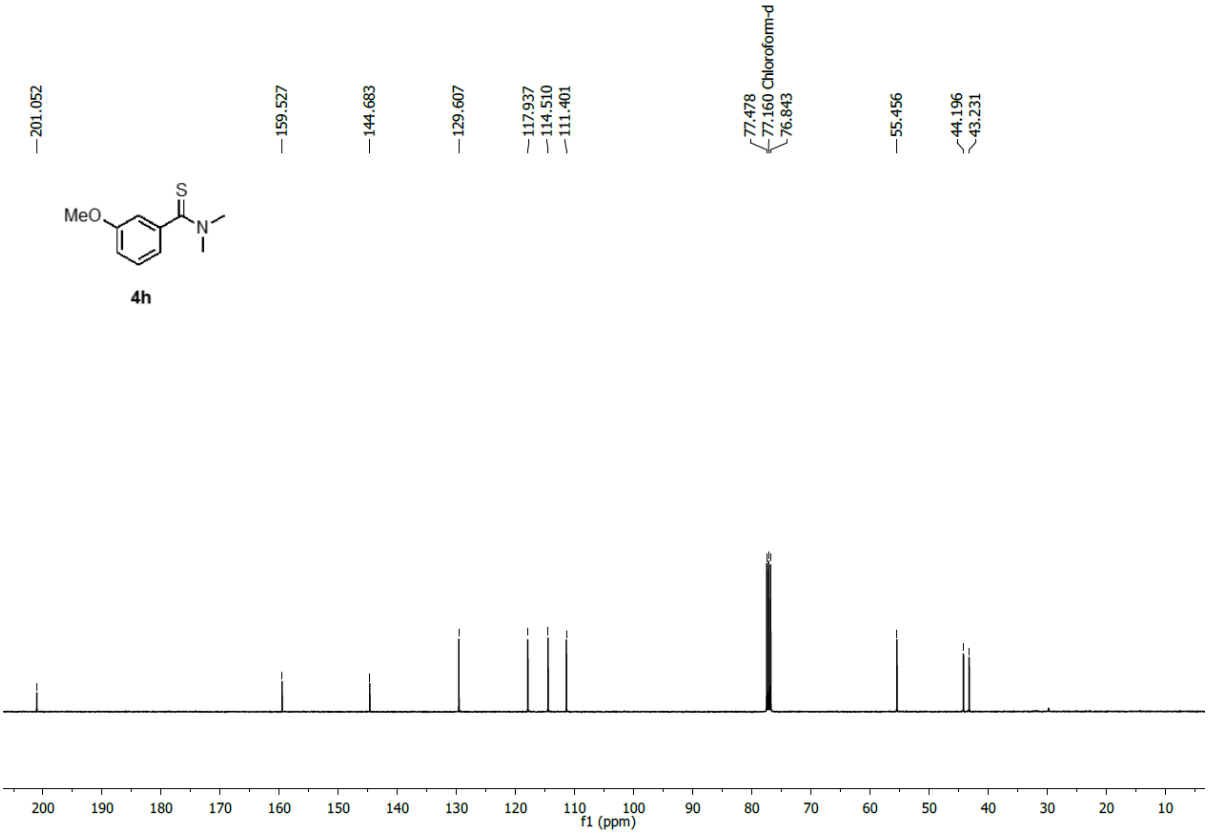

7.314
7.293
7.260 Chloroform-d
6.873
6.852
3.819
3.590
3.214
S
N
MeO
2.06
2.00
3.11
3.05
3.07
f1 (ppm)

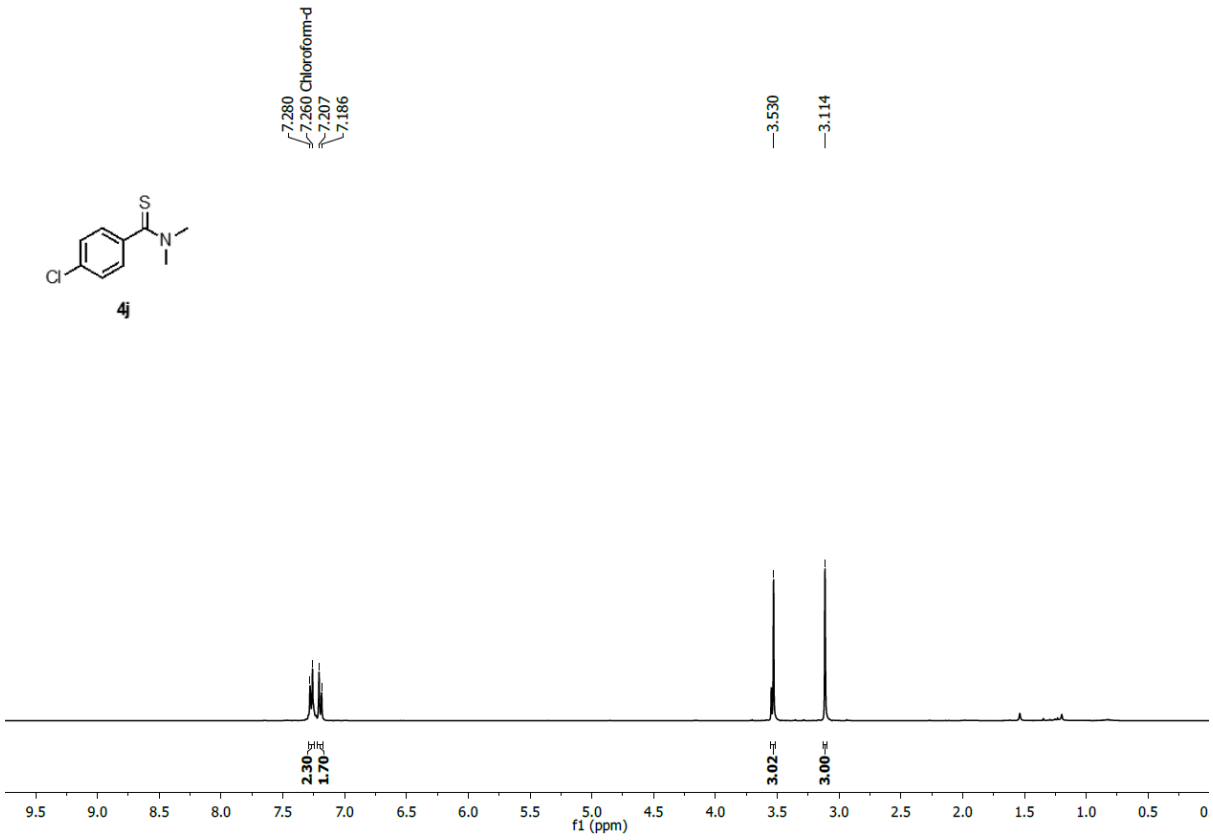
4g

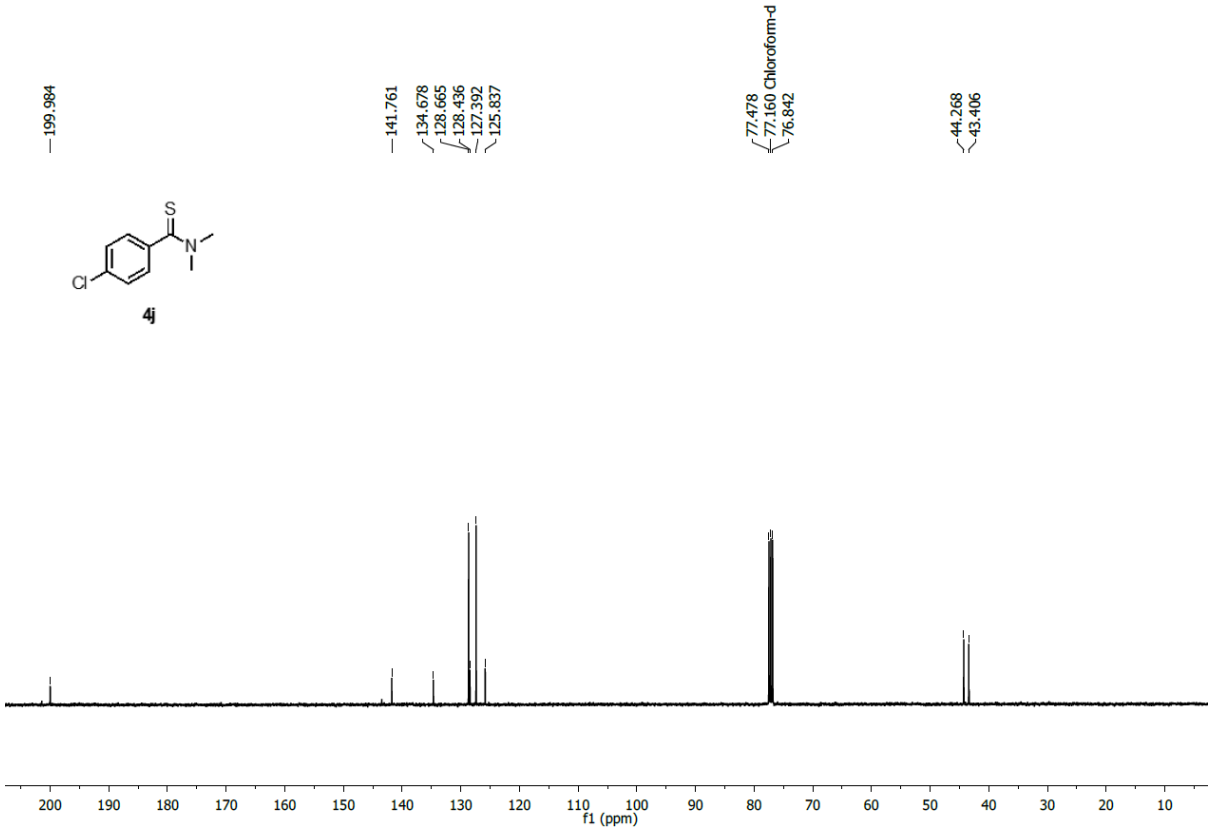

201.369
160.076
135.877
127.960
113.569
77.478
77.160 Chloroform-d
76.843
55.463
44.428
43.656
S
N
MeO
f1 (ppm)

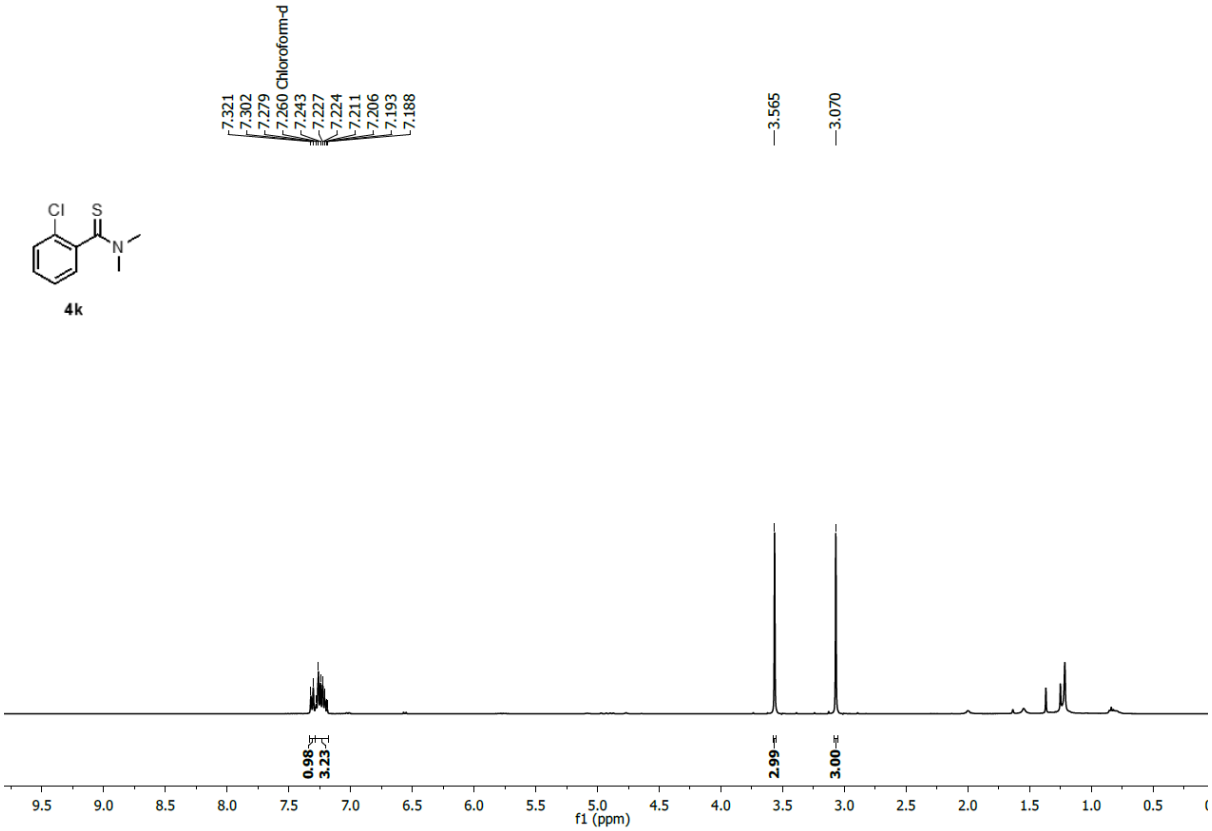
4g

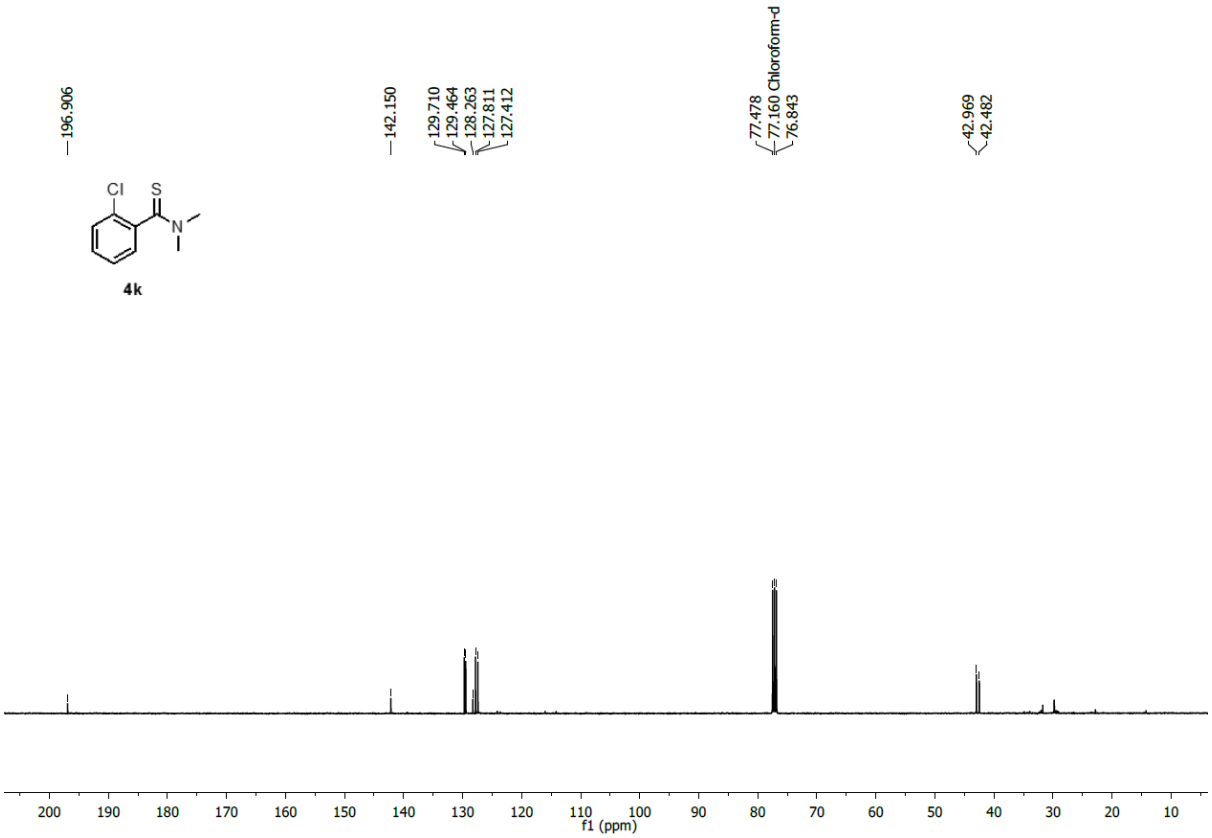

7.280
7.272
7.260 Chloroform-d
7.240
6.872
6.857
6.850
6.844
3.811
3.597
3.169
MeO
S
N
4h
1.09
3.10
3.00
3.00
3.04
f1 (ppm)

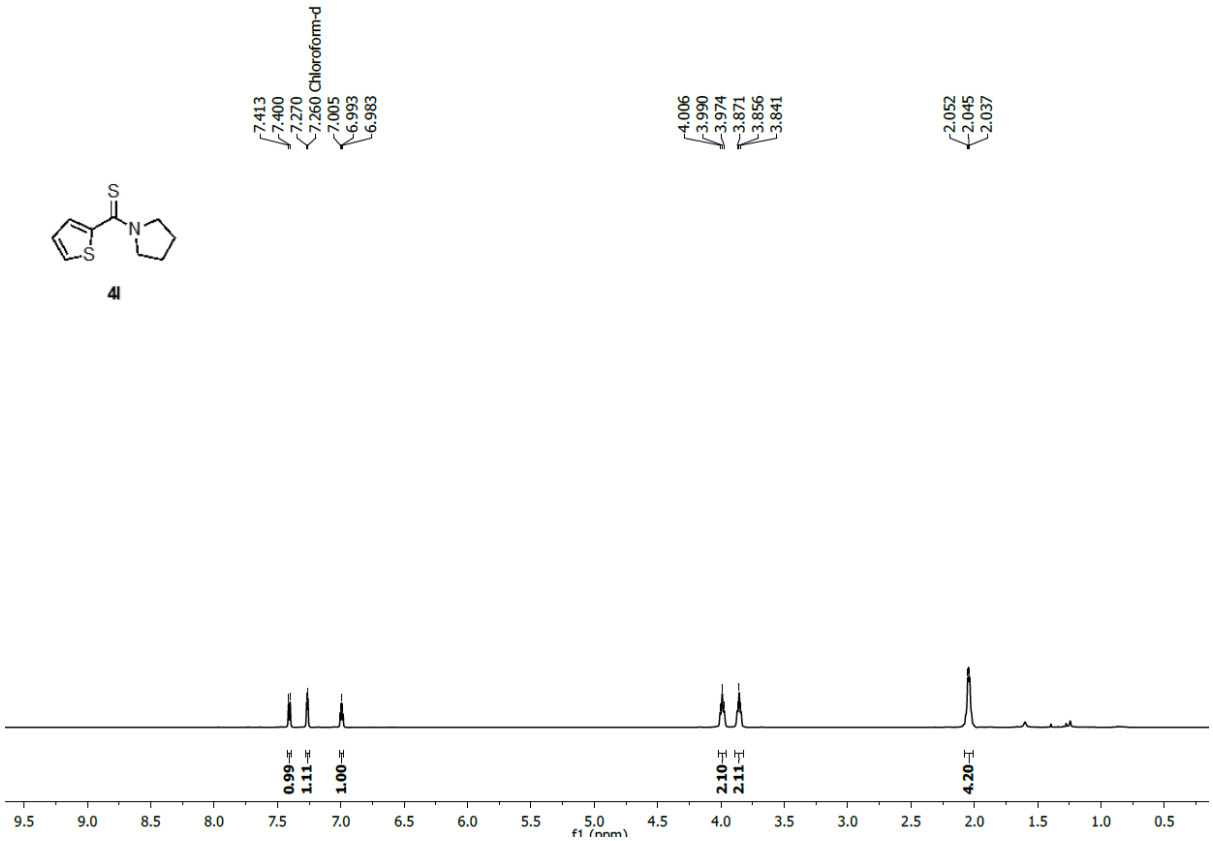

201.052
159.527
144.683
129.607
117.937
114.510
111.401
77.478
77.160 Chloroform-d
76.843
55.456
44.196
43.231
MeO
S
N
4h
f1 (ppm)

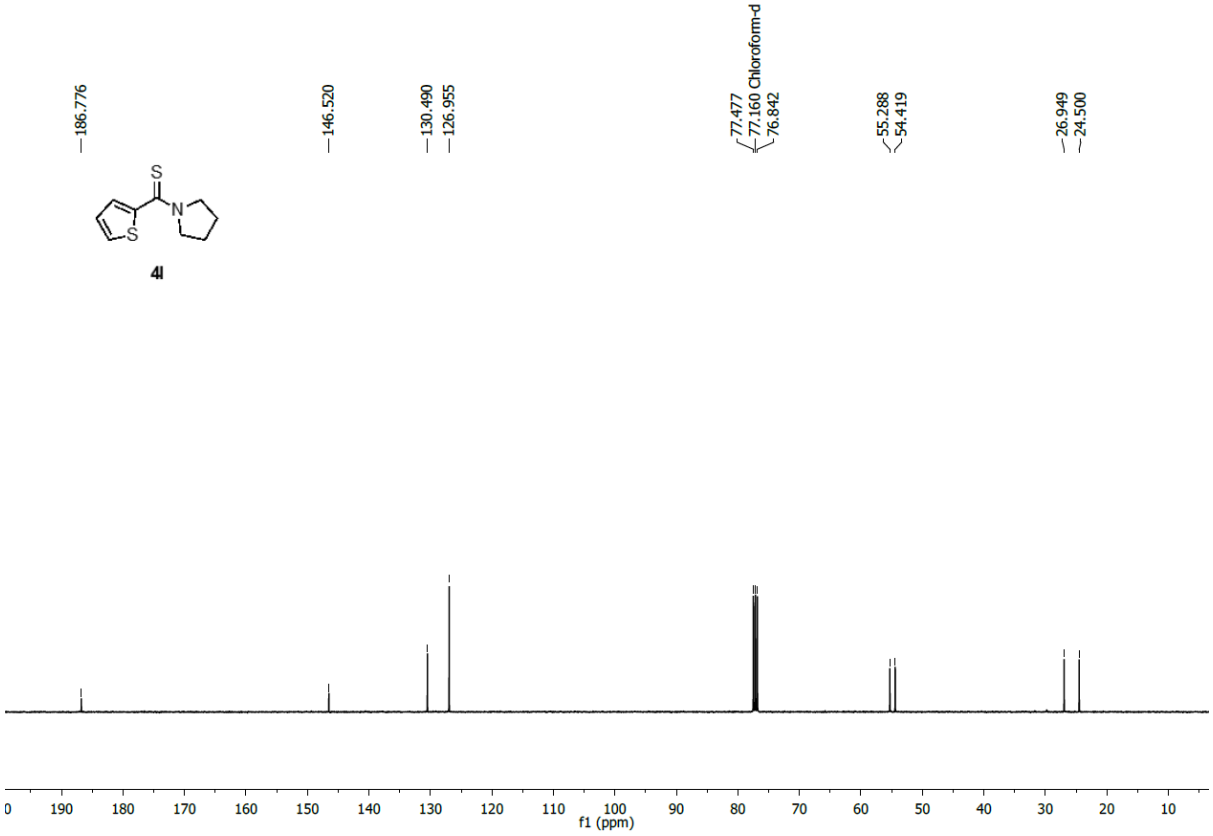

7.280
7.260 Chloroform-d
7.207
7.186
3.530
3.114
S
N
Cl
4j
2.30
1.70
3.02
3.00
f1 (ppm)

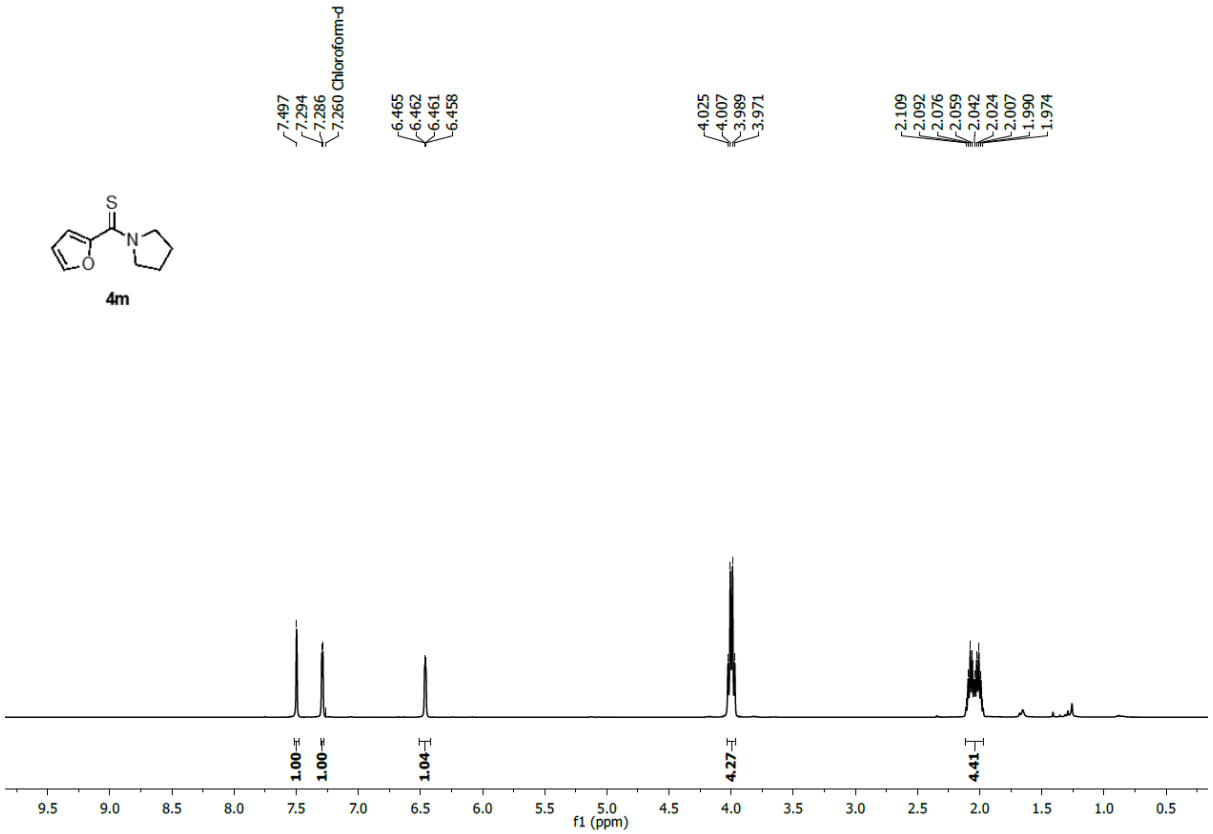

199.984
141.761
134.678
128.665
128.436
127.392
125.837
77.478
77.160 Chloroform-d
76.842
44.268
43.406
S
N
Cl
4j
f1 (ppm)


7.321
7.302
7.279
7.260 Chloroform-d
7.243
7.227
7.224
7.211
7.206
7.193
7.188
3.565
3.070
Cl
S
N
4k
0.98
3.23
2.99
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


196.906
142.150
129.710
129.464
128.263
127.811
127.412
77.478
77.160 Chloroform-d
76.843
42.969
42.482
Cl
S
N
4k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.413
7.400
7.270
7.260 Chloroform-d
7.005
6.993
6.983
4.006
3.990
3.974
3.871
3.856
3.841
2.052
2.045
2.037
S
N
S
4l
0.99
1.11
1.00
2.10
2.11
4.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


186.776
146.520
130.490
126.955
77.477
77.160 Chloroform-d
76.842
55.288
54.419
26.949
24.500
S
N
S
4l
0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.497
7.294
7.286
7.260 Chloroform-d
6.465
6.462
6.461
6.458
4.025
4.007
3.989
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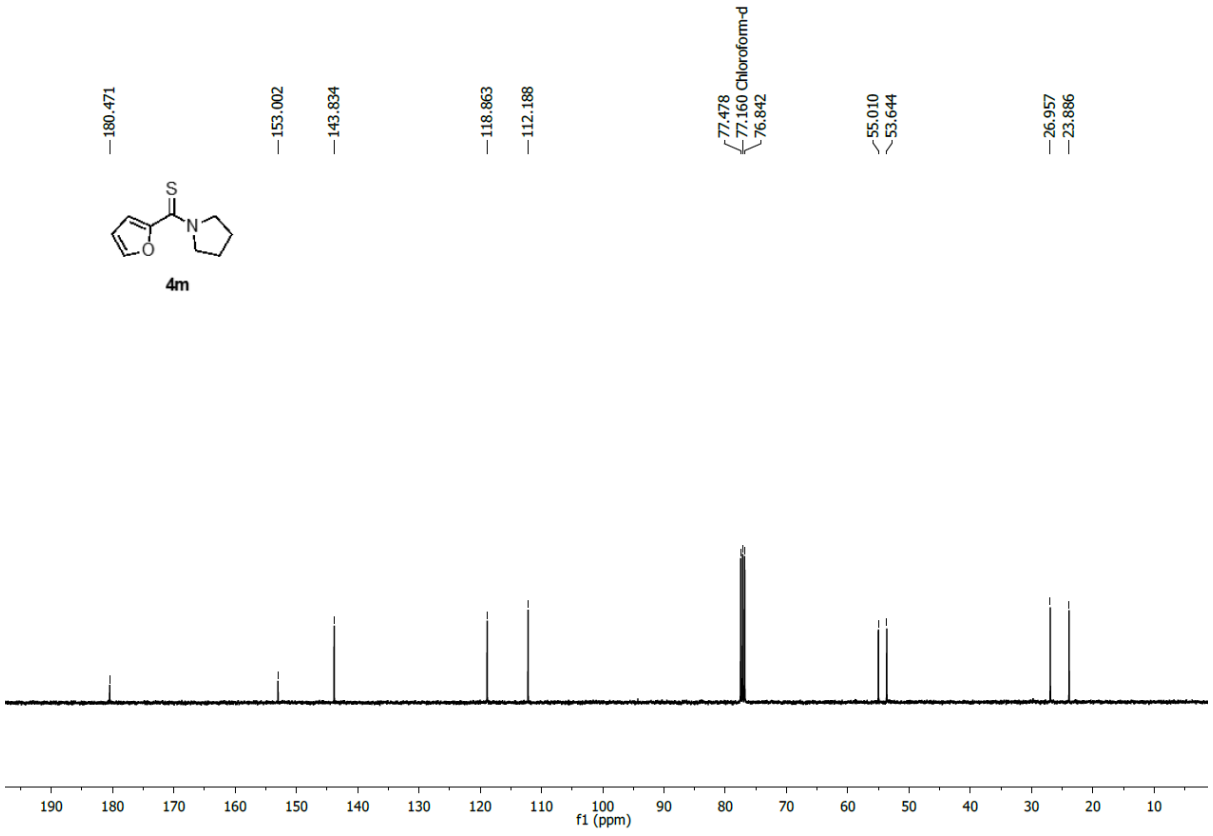
2.092
2.076
2.059
2.042
2.024
2.007
1.990
1.974
S
N
O
4m
1.00
1.00
1.04
4.27
4.41
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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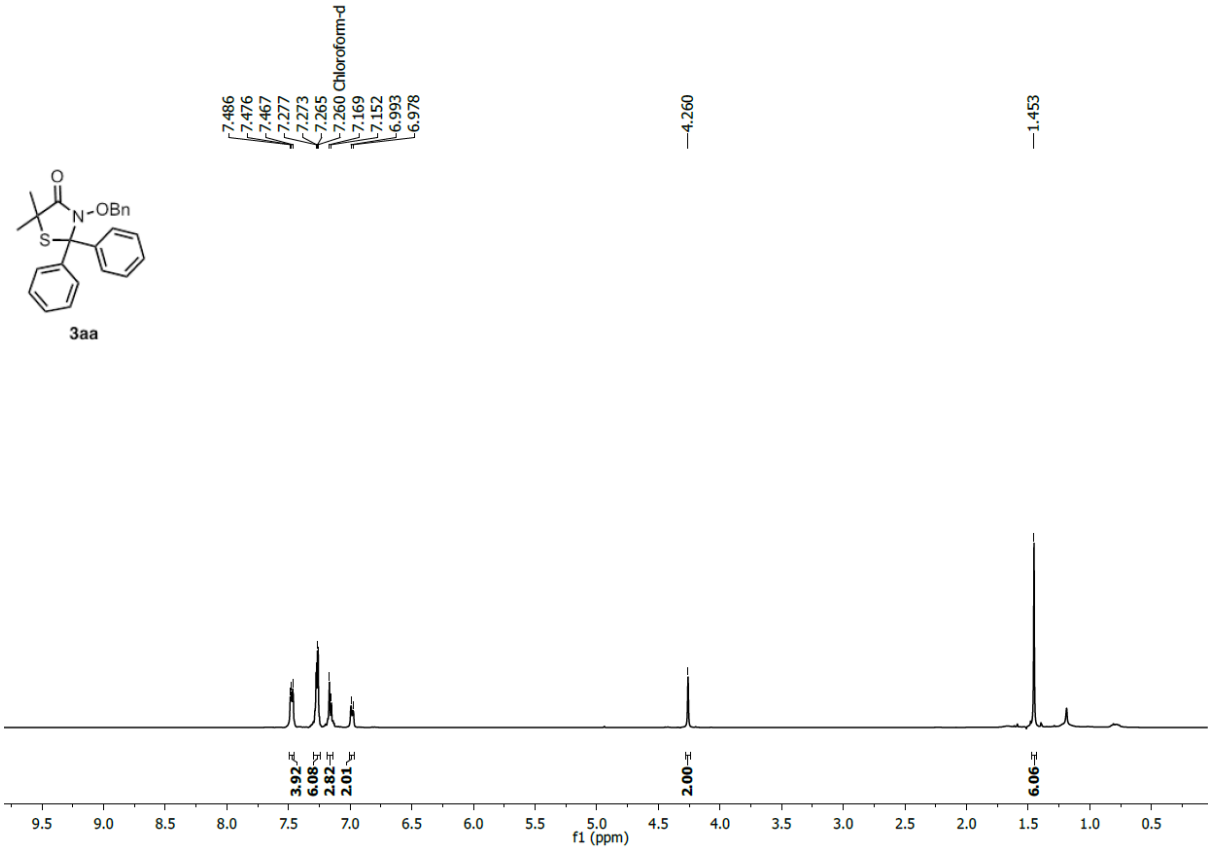
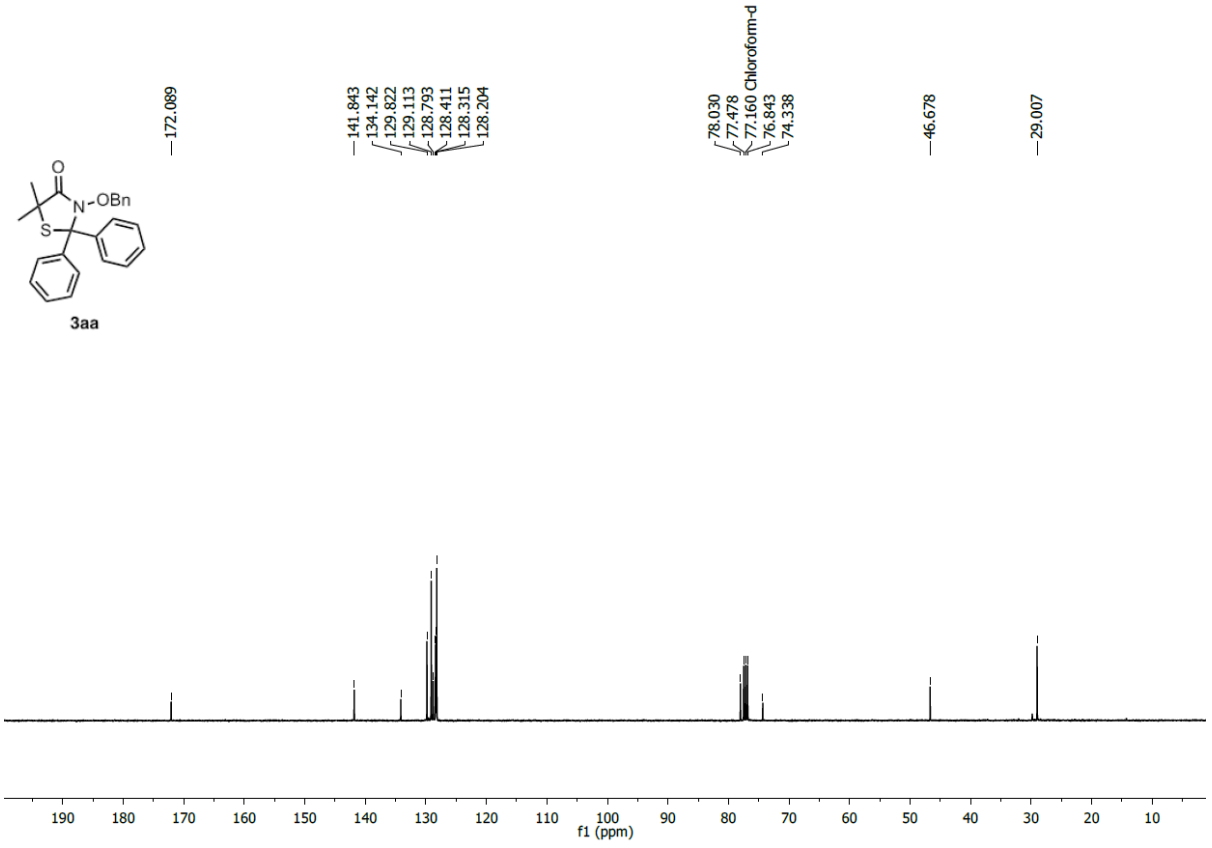
153.002
143.834
118.863
112.188
77.478
77.160 Chloroform-d
76.842
55.010
53.644
26.957
23.886
S
N
O
4m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.486
7.476
7.467
7.277
7.273
7.265 Chloroform-d
7.260
7.169
7.152
6.993
6.978
4.260
1.453
O
N-OBn
S
3aa
3.92
6.08
2.82
2.01
2.00
6.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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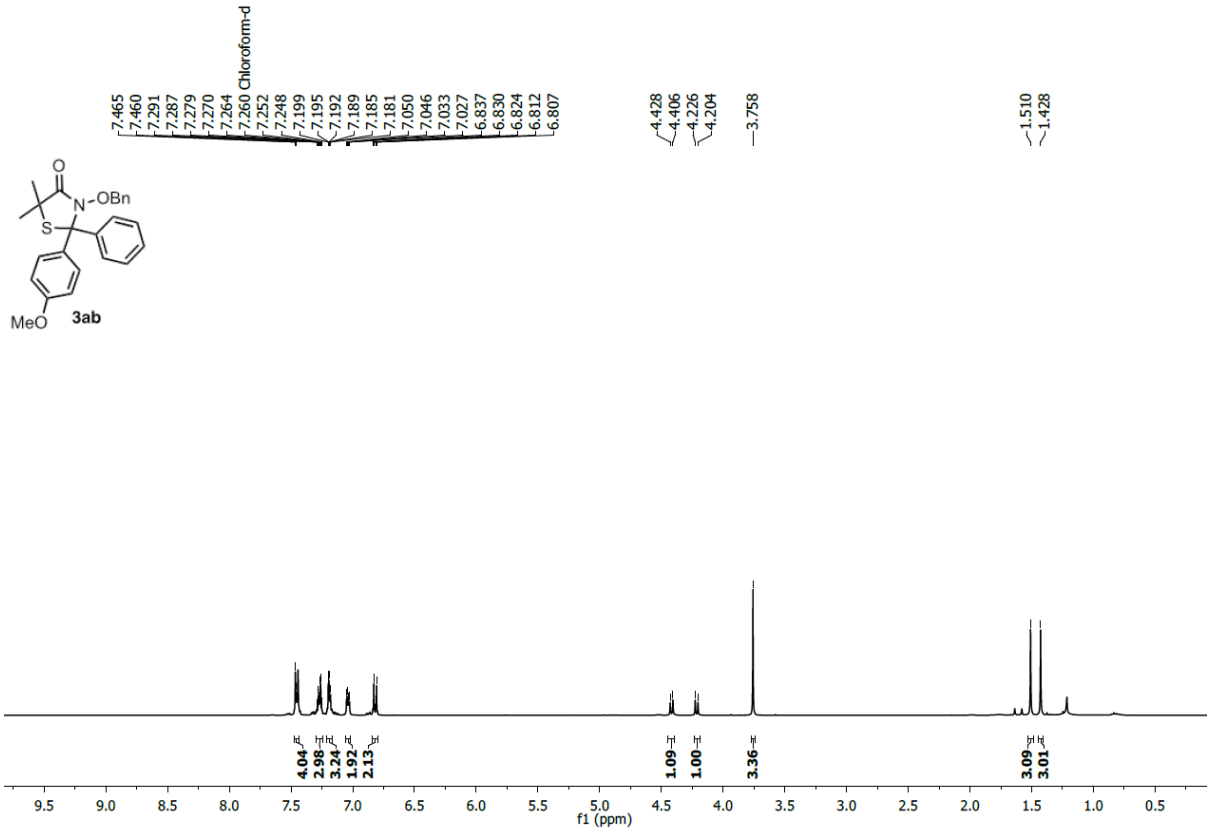
134.142
129.822
129.113
128.793
128.411
128.315
128.204
78.030
77.478
77.160 Chloroform-d
76.843
74.338
46.678
29.007
O
N-OBn
S
3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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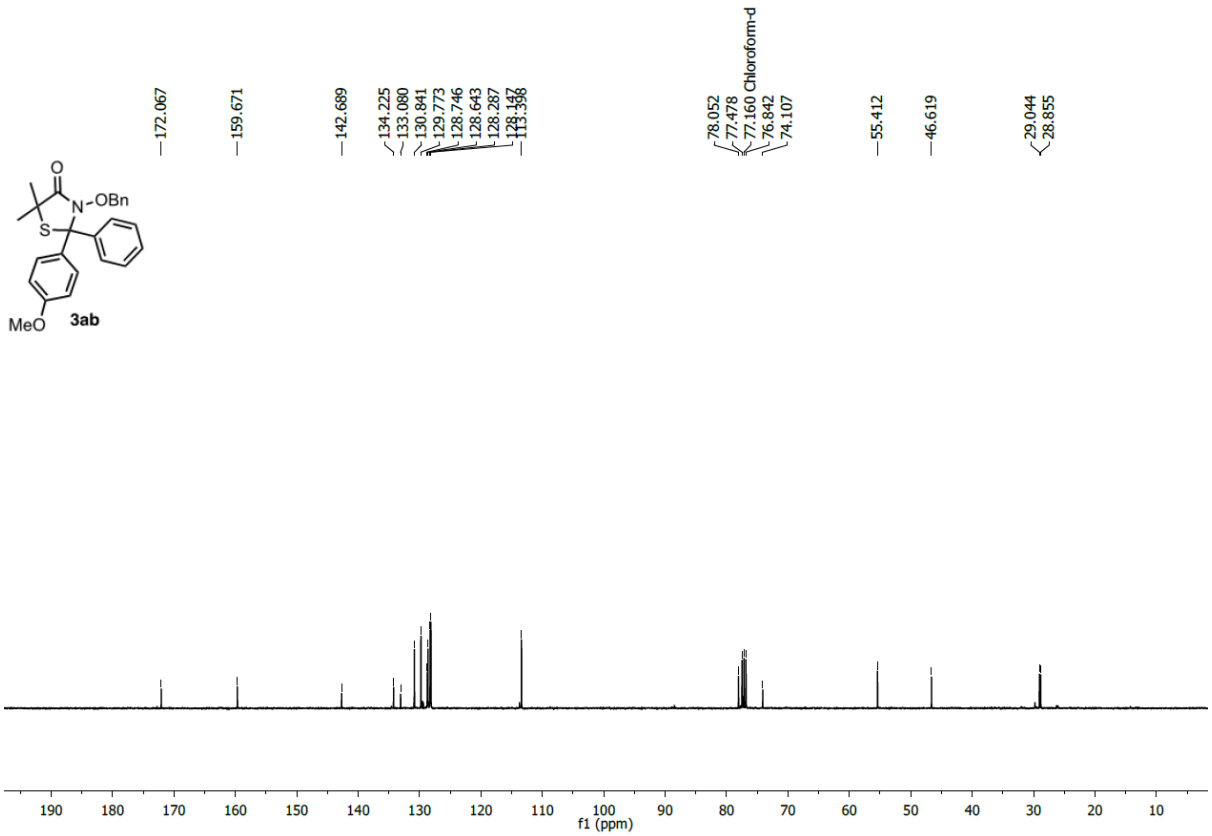
7.460
7.291
7.287
7.279
7.270
7.264
7.260 Chloroform-d
7.252
7.248
7.199
7.195
7.192
7.189
7.185
7.181
7.050
7.046
7.033
7.027
6.837
6.830
6.824
6.812
6.807
4.428
4.406
4.226
4.204
3.758
1.510
1.428
N-OBn
S
MeO
3ab
4.04
2.98
3.24
1.92
2.13
1.09
1.00
3.36
3.09
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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128.147
113.396
78.052
77.478
77.160 Chloroform-d
76.842
74.107
55.412
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28.855
N-OBn
S
MeO
3ab
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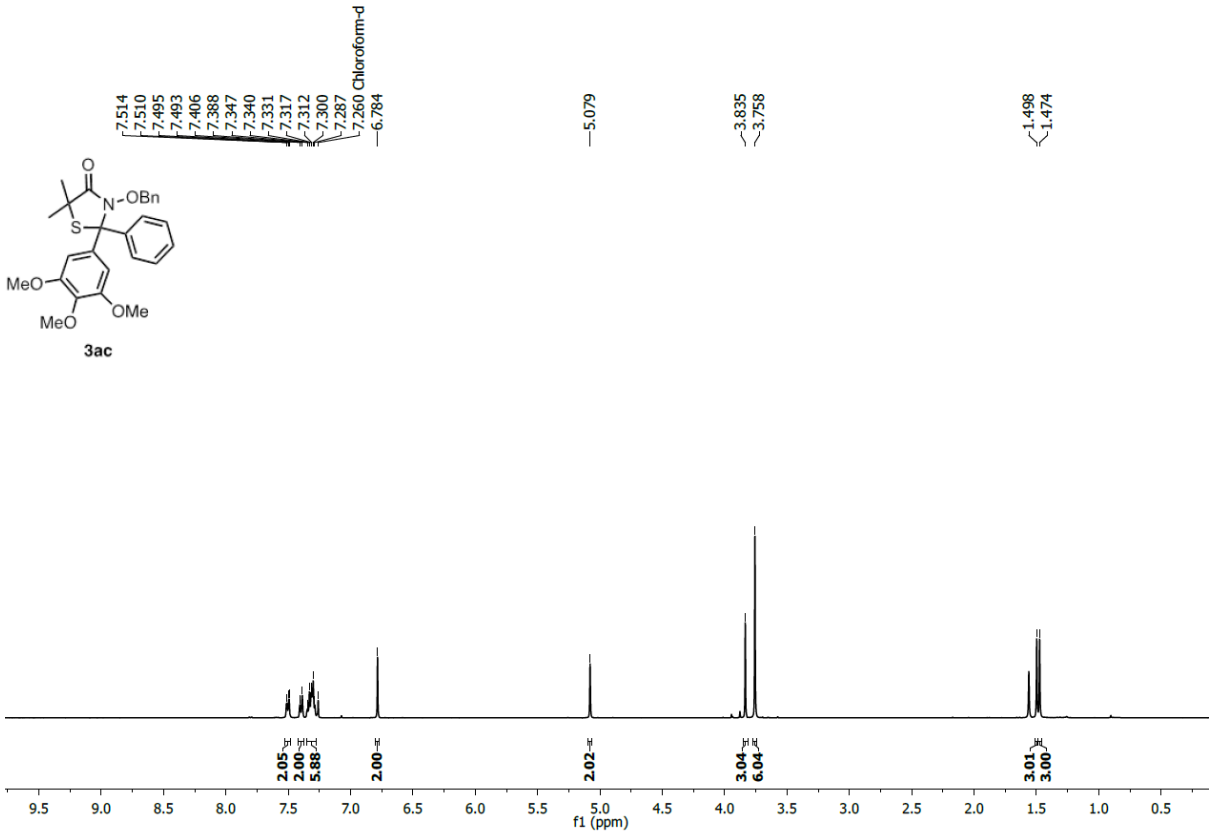
f1 (ppm)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7.510
7.495
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7.406
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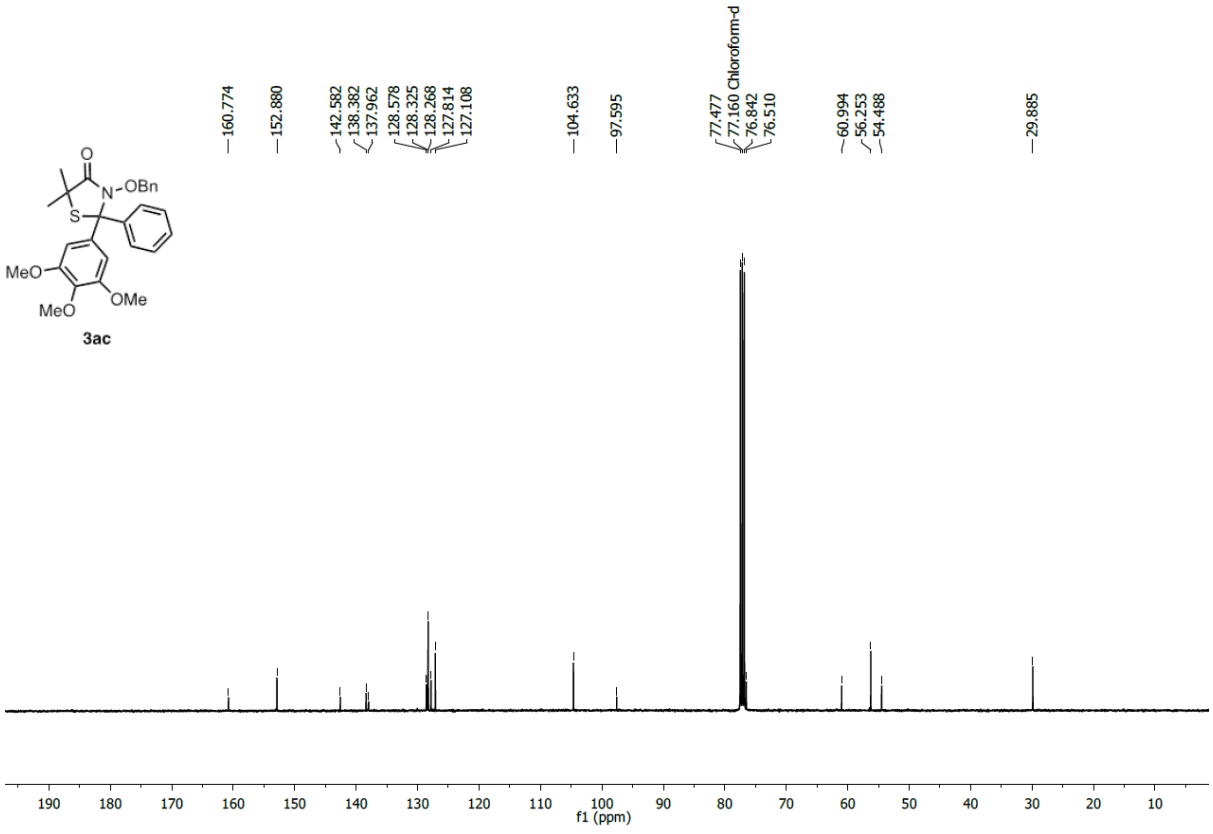
7.347
7.340
7.331
7.317
7.312
7.300
7.287
7.260 Chloroform-d
6.784
5.079
3.835
3.758
1.498
1.474
O
N
OBn
S
MeO
MeO
OMe
3ac
2.05
2.00
5.88
2.00
2.02
3.04
6.04
3.01
3.00
f1 (ppm)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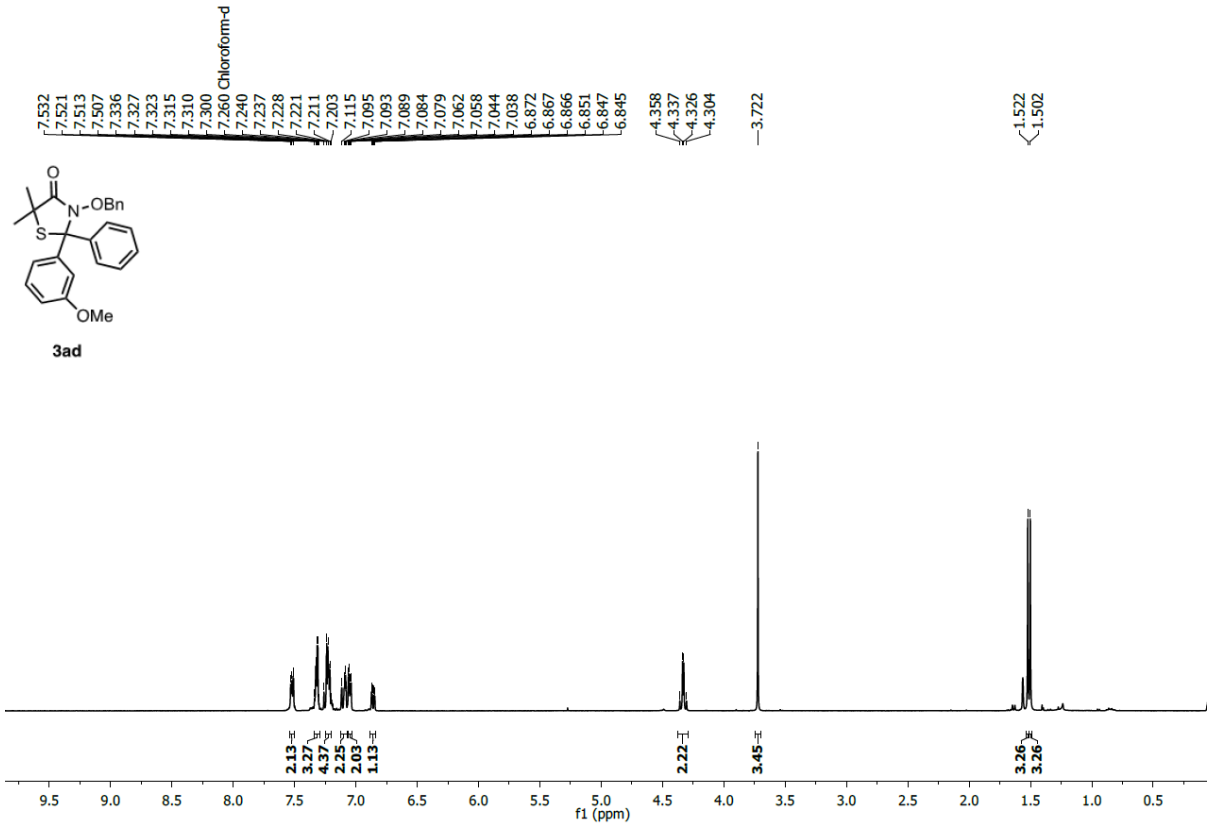
97.595
77.477
77.160 Chloroform-d
76.842
76.510
60.994
56.253
54.488
29.885
O
N
OBn
S
MeO
MeO
OMe
3ac
f1 (ppm)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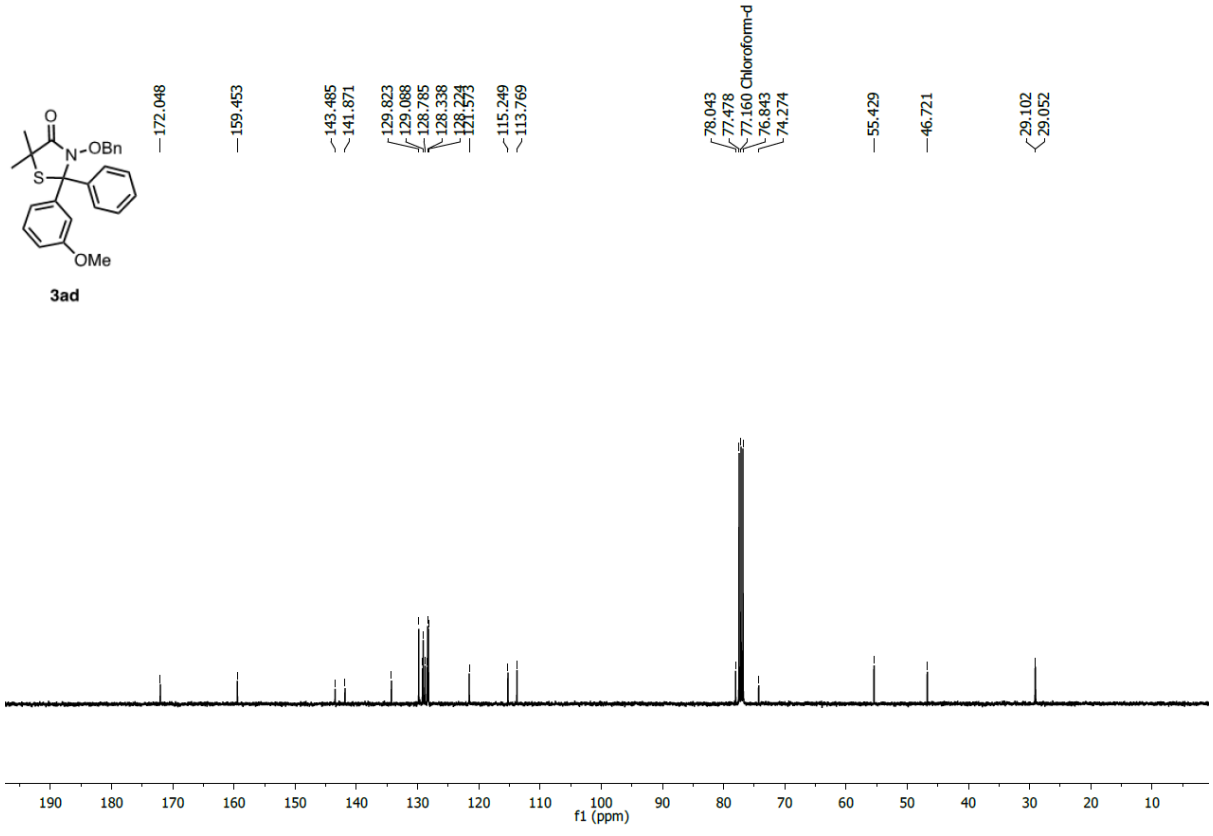
7.521
7.513
7.507
7.336
7.327
7.323
7.315
7.310
7.300
Chloroform-d
7.260
7.240
7.237
7.228
7.221
7.211
7.203
7.115
7.095
7.093
7.089
7.084
7.079
7.062
7.058
7.044
7.038
6.872
6.867
6.866
6.851
6.847
6.845
4.358
4.337
4.326
4.304
3.722
1.522
1.502
O
N-OBn
S
OMe
3ad
2.13
3.27
4.37
2.25
2.03
1.13
2.22
3.45
3.26
3.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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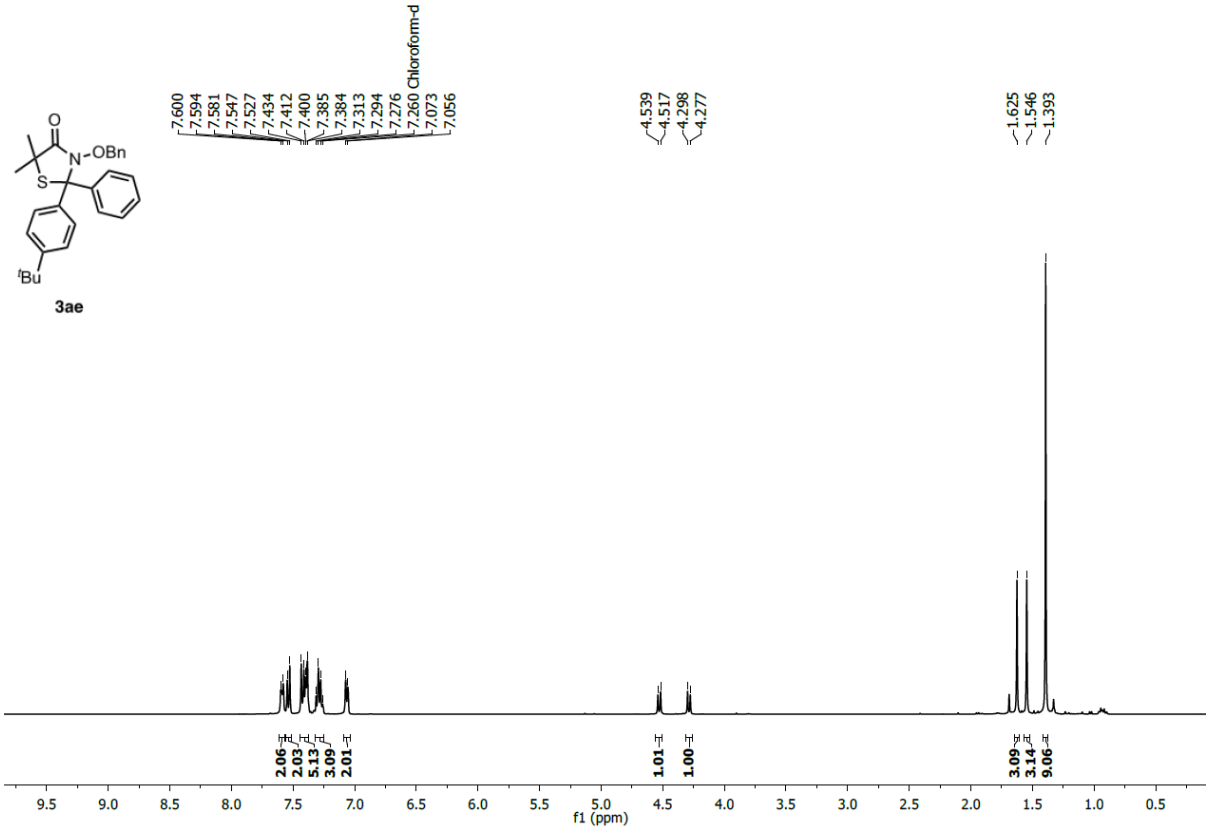
143.485
141.871
129.823
129.088
128.785
128.338
121.573
115.249
113.769
78.043
77.478
77.160
Chloroform-d
76.843
74.274
55.429
46.721
29.102
29.052
O
N-OBn
S
OMe
3ad
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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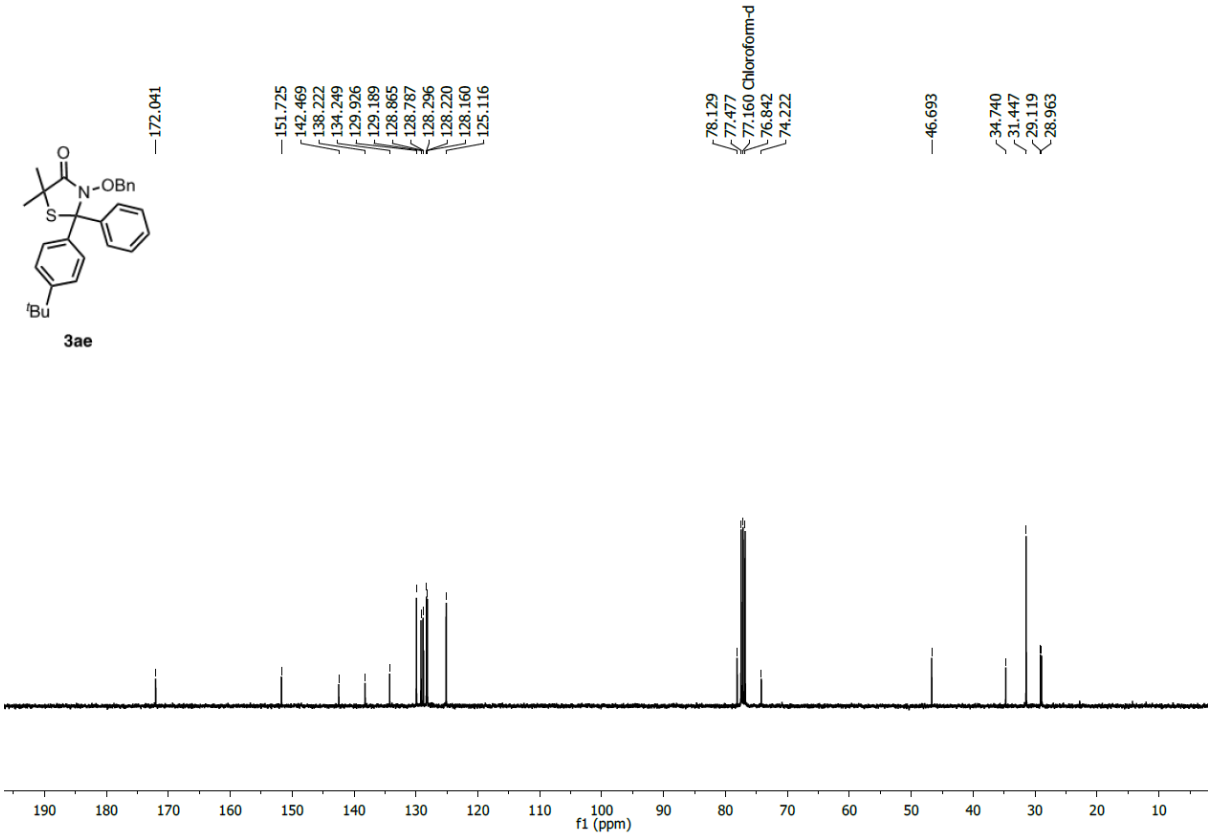
7.594
7.581
7.547
7.527
7.434
7.412
7.400
7.385
7.384
7.313
7.294
7.276
7.260 Chloroform-d
7.073
7.056
4.539
4.517
4.298
4.277
1.625
1.546
1.393
O
N-OBn
S
tBu
3ae
2.06
2.03
5.13
3.09
2.01
1.01
1.00
3.09
3.14
9.06
f1 (ppm)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138.222
134.249
129.926
129.189
128.865
128.787
128.296
128.220
128.160
125.116
78.129
77.477
77.160 Chloroform-d
76.842
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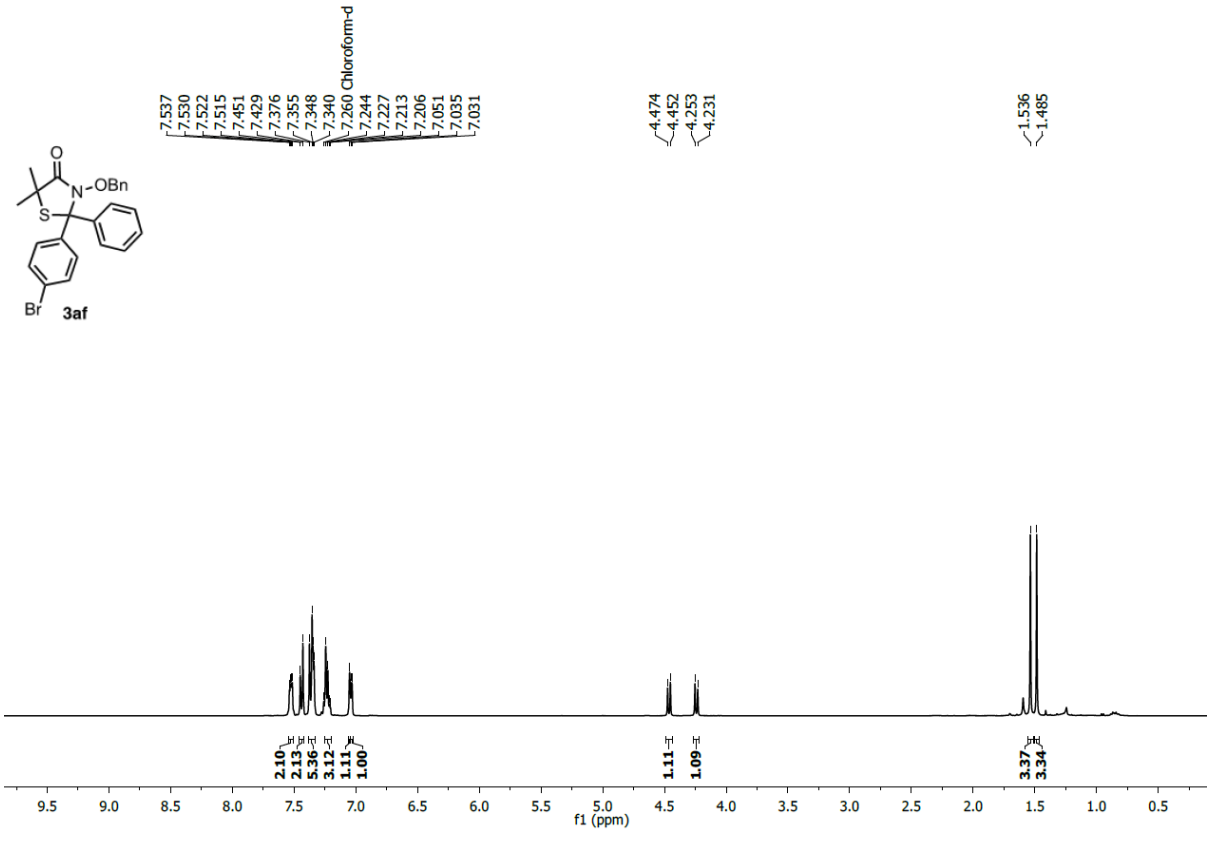
34.740
31.447
29.119
28.963
O
N-OBn
S
tBu
3ae
f1 (ppm)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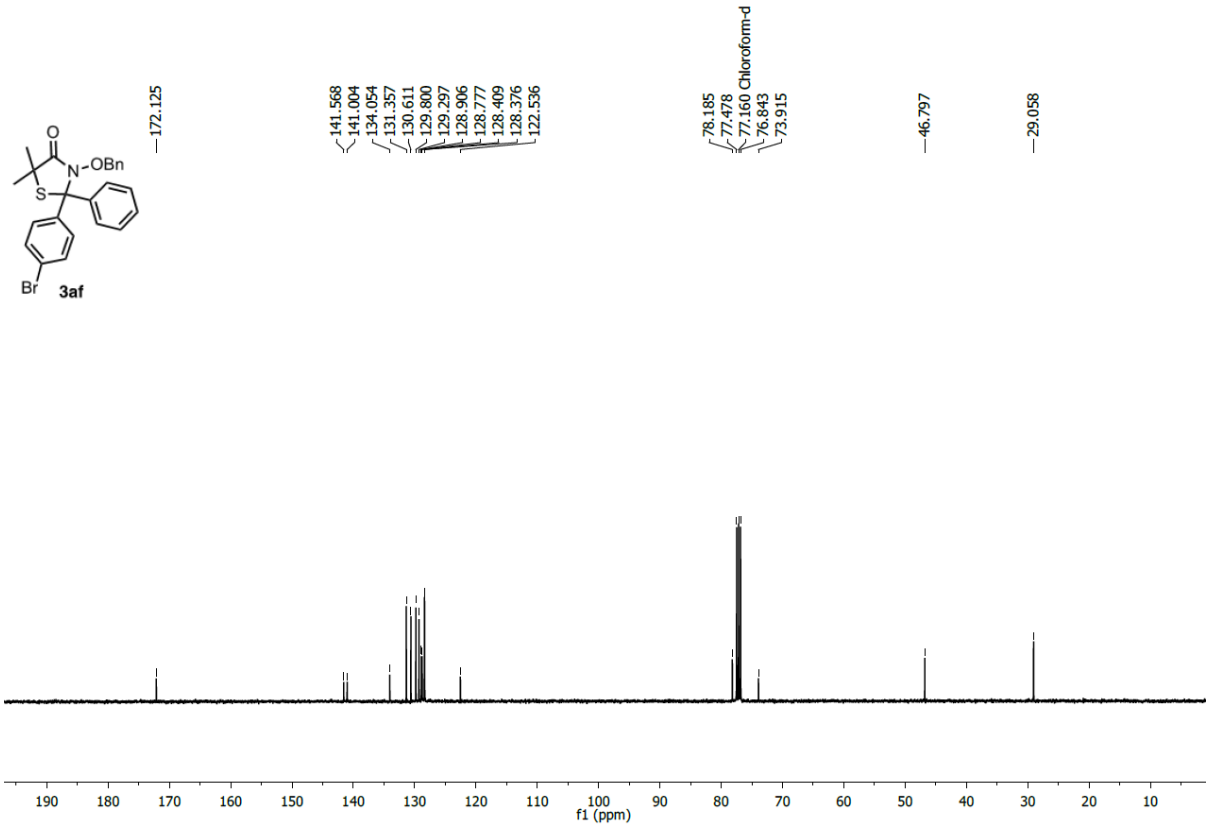
7.530
7.522
7.515
7.451
7.429
7.376
7.355
7.348
7.340
7.260 Chloroform-d
7.244
7.227
7.213
7.206
7.051
7.035
7.031
4.474
4.452
4.253
4.231
1.536
1.485
O
N-OBn
S
Br
3af
2.10
2.13
5.36
3.12
1.11
1.00
1.11
1.09
3.37
3.34
f1 (ppm)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134.054
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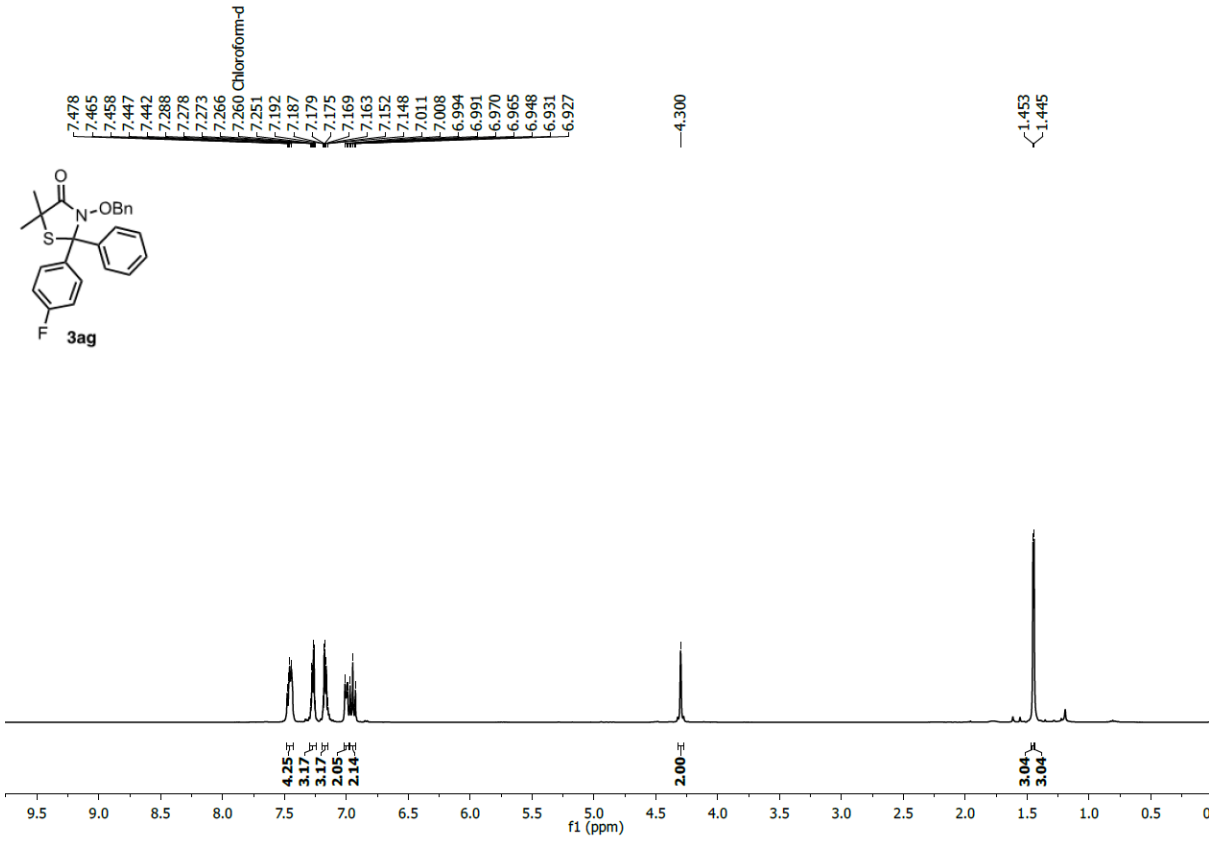
130.611
129.800
129.297
128.906
128.777
128.409
128.376
122.536
78.185
77.478
77.160 Chloroform-d
76.843
73.915
46.797
29.058
O
N-OBn
S
Br
3af
f1 (ppm)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7.458
7.447
7.442
7.288
7.278
7.273
7.266
7.260 Chloroform-d
7.251
7.192
7.187
7.179
7.175
7.169
7.163
7.152
7.148
7.011
7.008
6.994
6.991
6.970
6.965
6.948
6.931
6.927
4.300
1.453
1.445
O
N-OBn
S
F
3ag
4.25
3.17
3.17
2.05
2.14
2.00
3.04
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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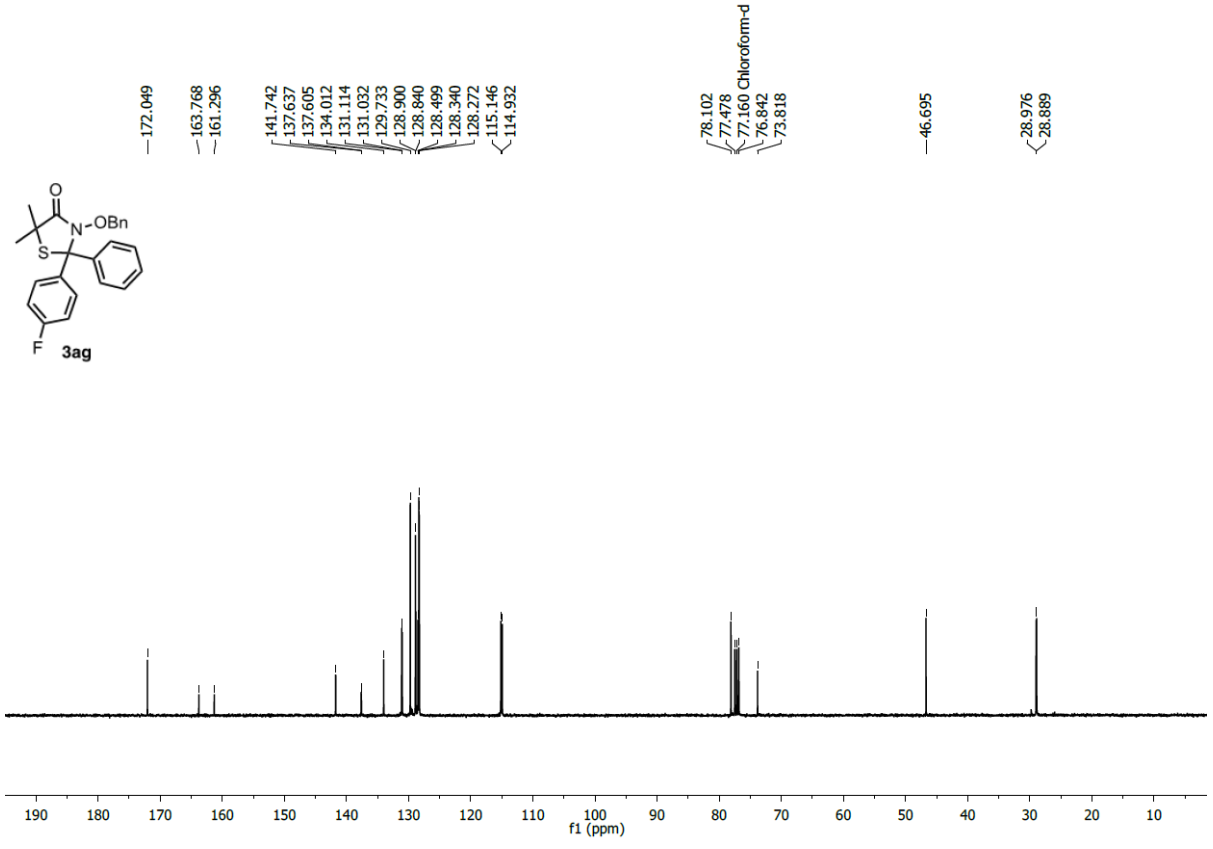
1.0
0.5
f1 (ppm)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137.605
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131.114
131.032
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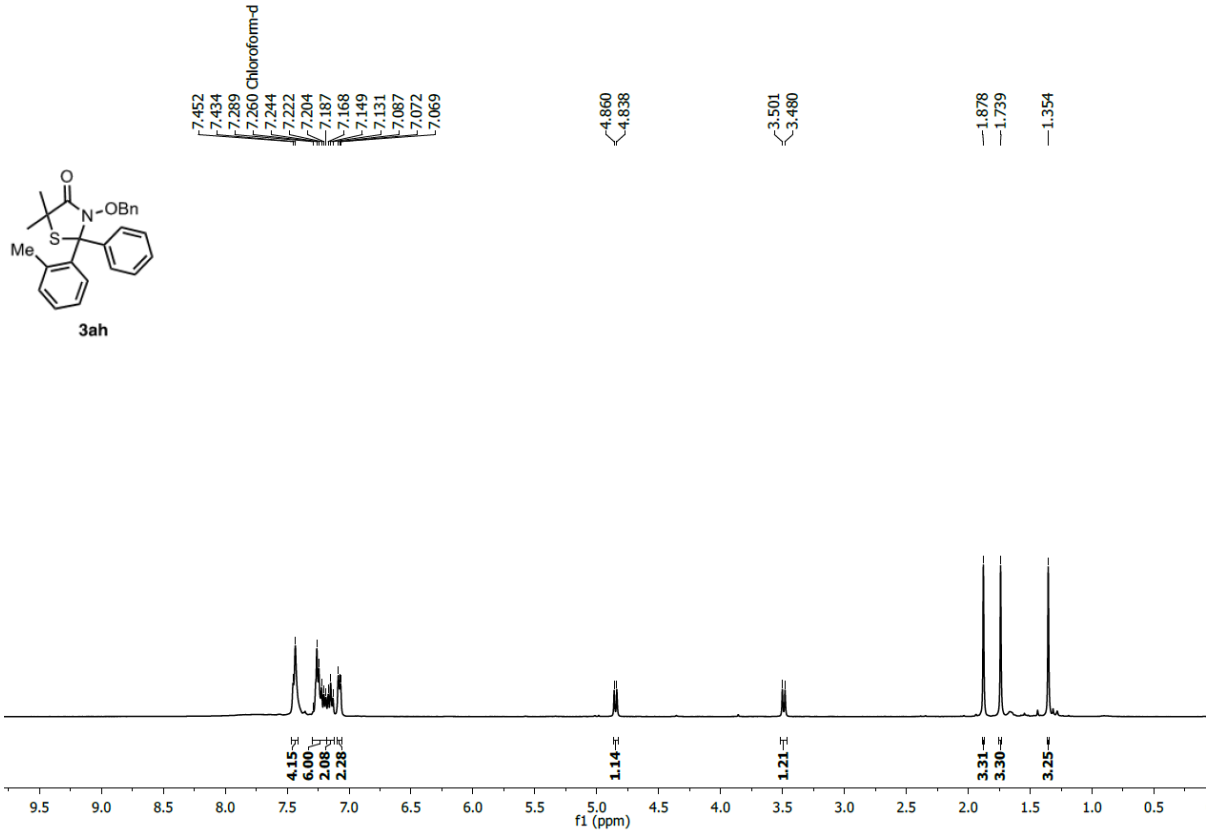
128.900
128.840
128.499
128.340
128.272
115.146
114.932
78.102
77.478
77.160 Chloroform-d
76.842
73.818
46.695
28.976
28.889
O
N-OBn
S
F
3ag
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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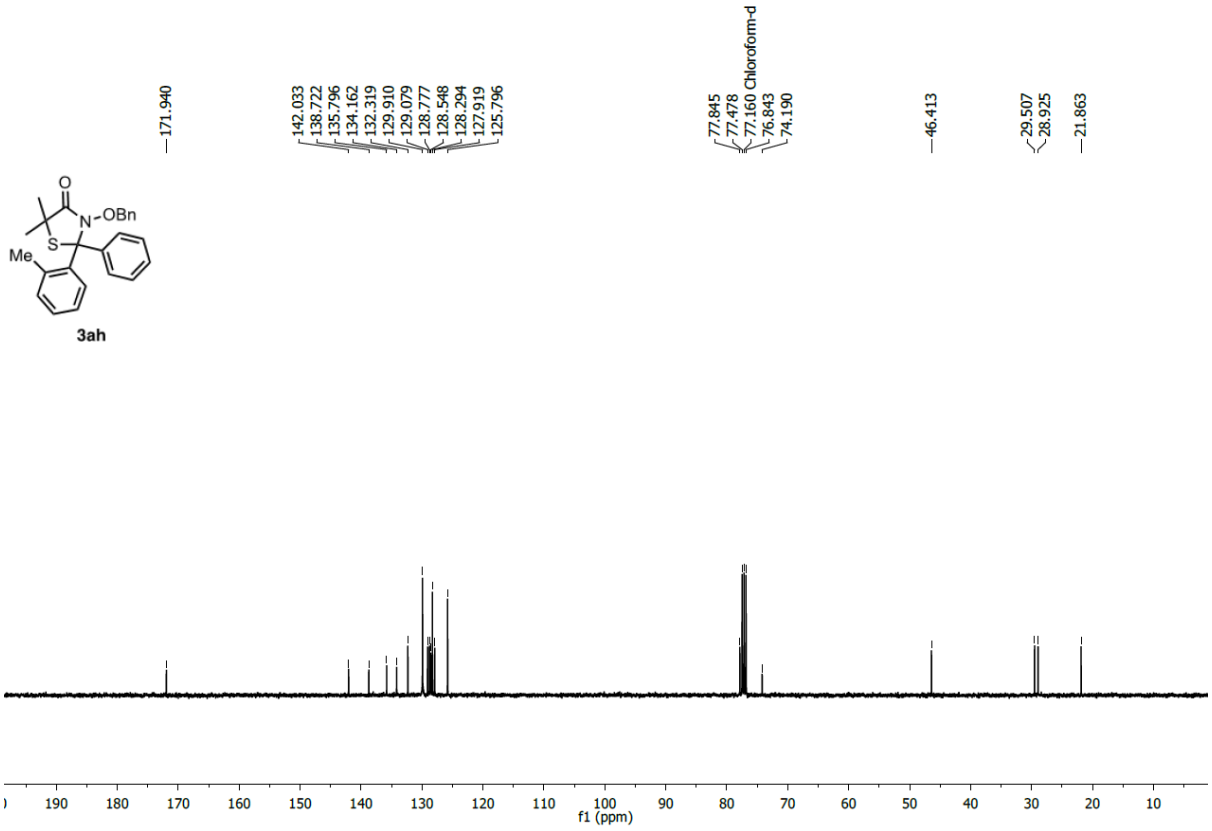
7.222
7.204
7.187
7.168
7.149
7.131
7.087
7.072
7.069
4.860
4.838
3.501
3.480
1.878
1.739
1.354
O
N-OBn
S
Me
3ah
4.15
6.00
2.08
2.28
1.14
1.21
3.31
3.30
3.25
f1 (ppm)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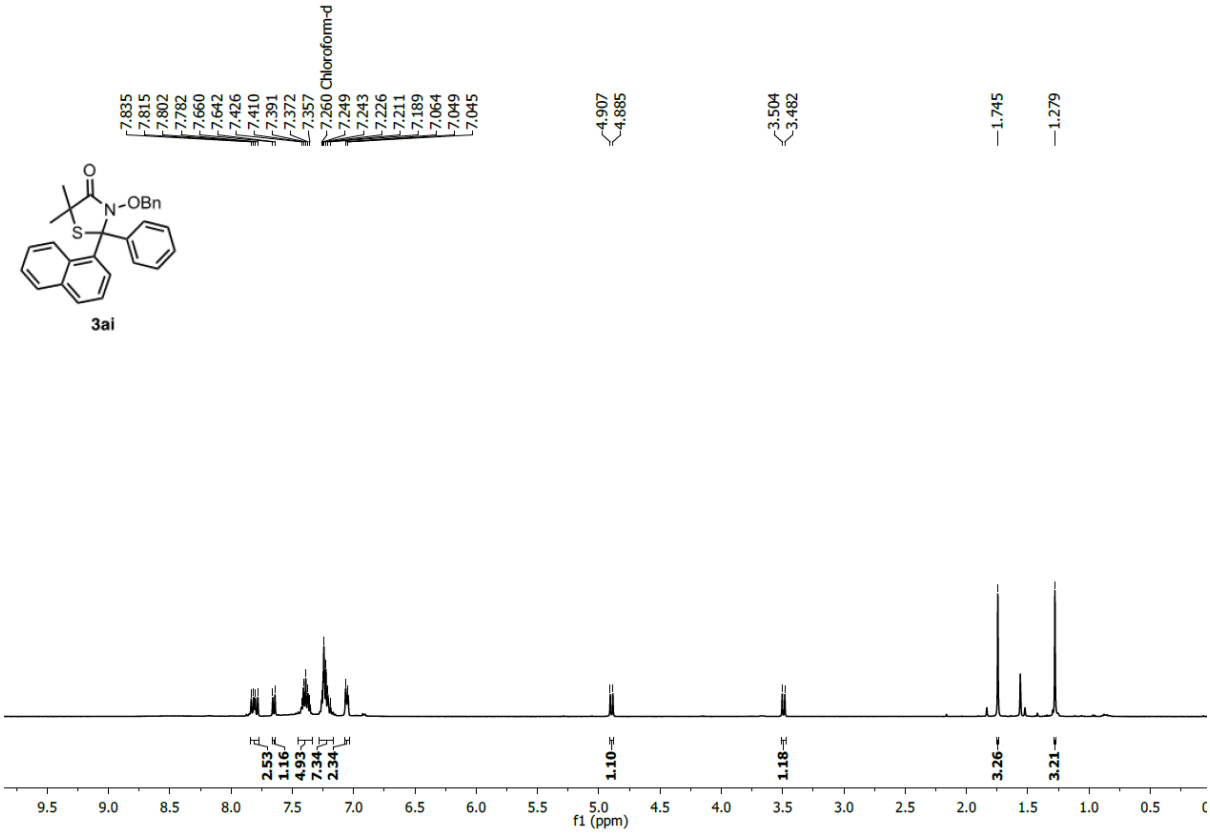
129.079
128.777
128.548
128.294
127.919
125.796
77.845
77.478
77.160 Chloroform-d
76.843
74.190
46.413
29.507
28.925
21.863
O
N-OBn
S
Me
3ah
f1 (ppm)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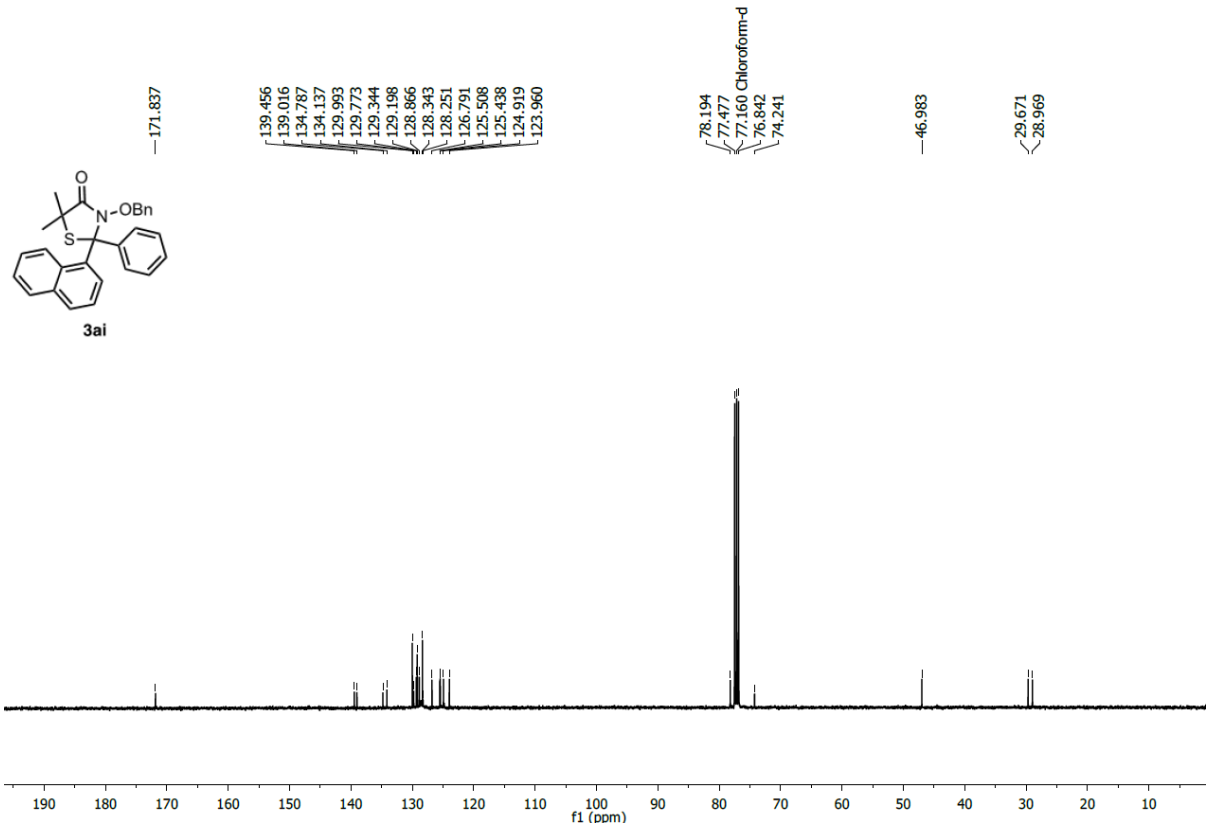
7.357
7.260 Chloroform-d
7.249
7.243
7.226
7.211
7.189
7.064
7.049
7.045
4.907
4.885
3.504
3.482
1.745
1.279
O
N-OBn
S
3ai
2.53
1.16
4.93
7.34
2.34
1.10
1.18
3.26
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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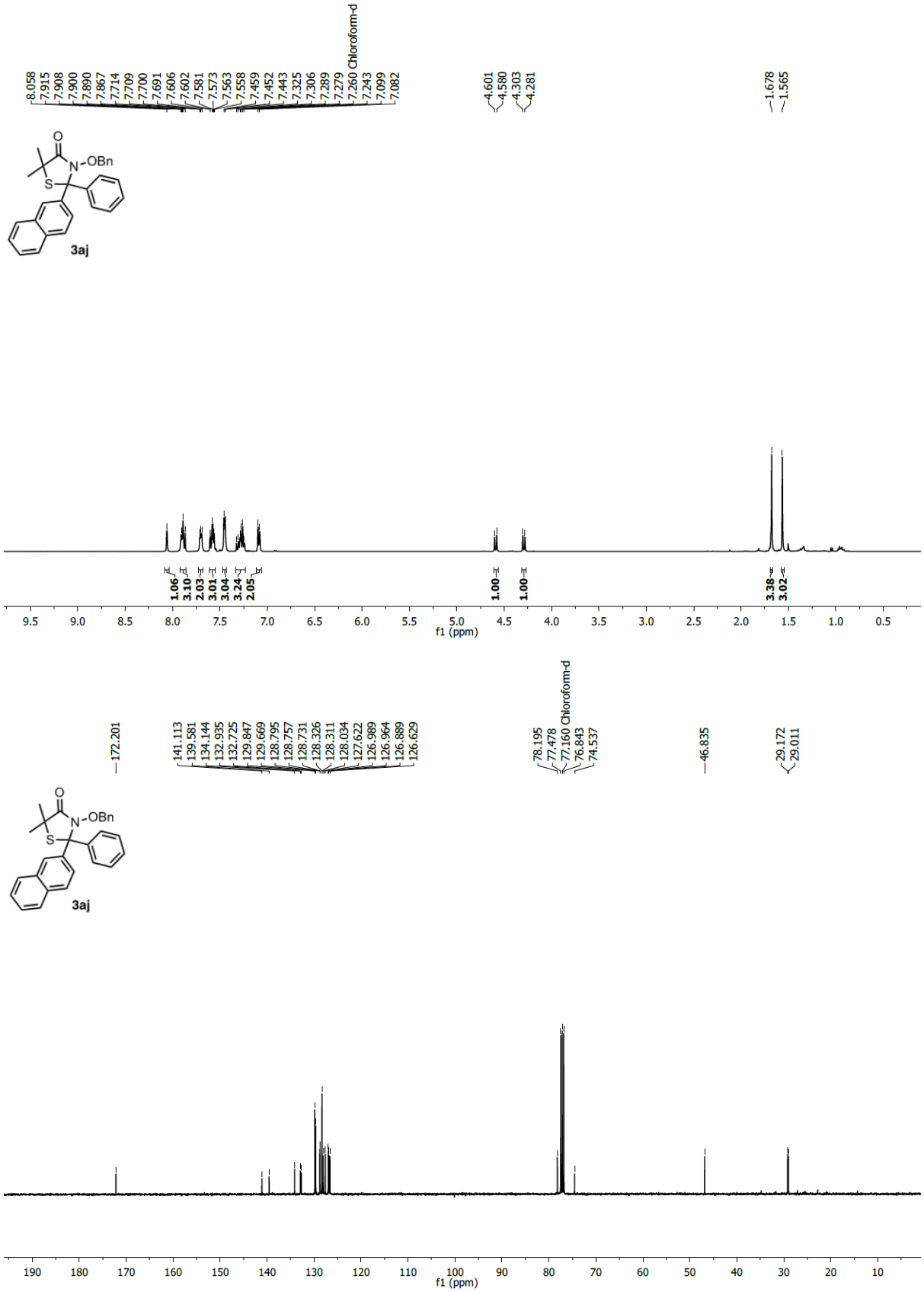
129.344
129.198
128.866
128.343
128.251
126.791
125.508
125.438
124.919
123.960
78.194
77.477
77.160 Chloroform-d
76.842
74.241
46.983
29.671
28.969
O
N-OBn
S
3ai
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.709
7.700
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7.606
7.602
7.581
7.573
7.563
7.558
7.459
7.452
7.443
7.325
7.306
7.289
7.279
7.260 Chloroform-d
7.243
7.099
7.082
4.601
4.580
4.303
4.281
1.678
1.565
O
N-OBn
S
3aj
1.06
3.10
2.03
3.01
3.04
3.24
2.05
1.00
1.00
3.38
3.02
f1 (ppm)
172.201
141.113
139.581
134.144
132.935
132.725
129.847
129.669
128.795
128.757
128.731
128.326
128.311
128.034
127.622
126.989
126.964
126.889
126.629
78.195
77.478
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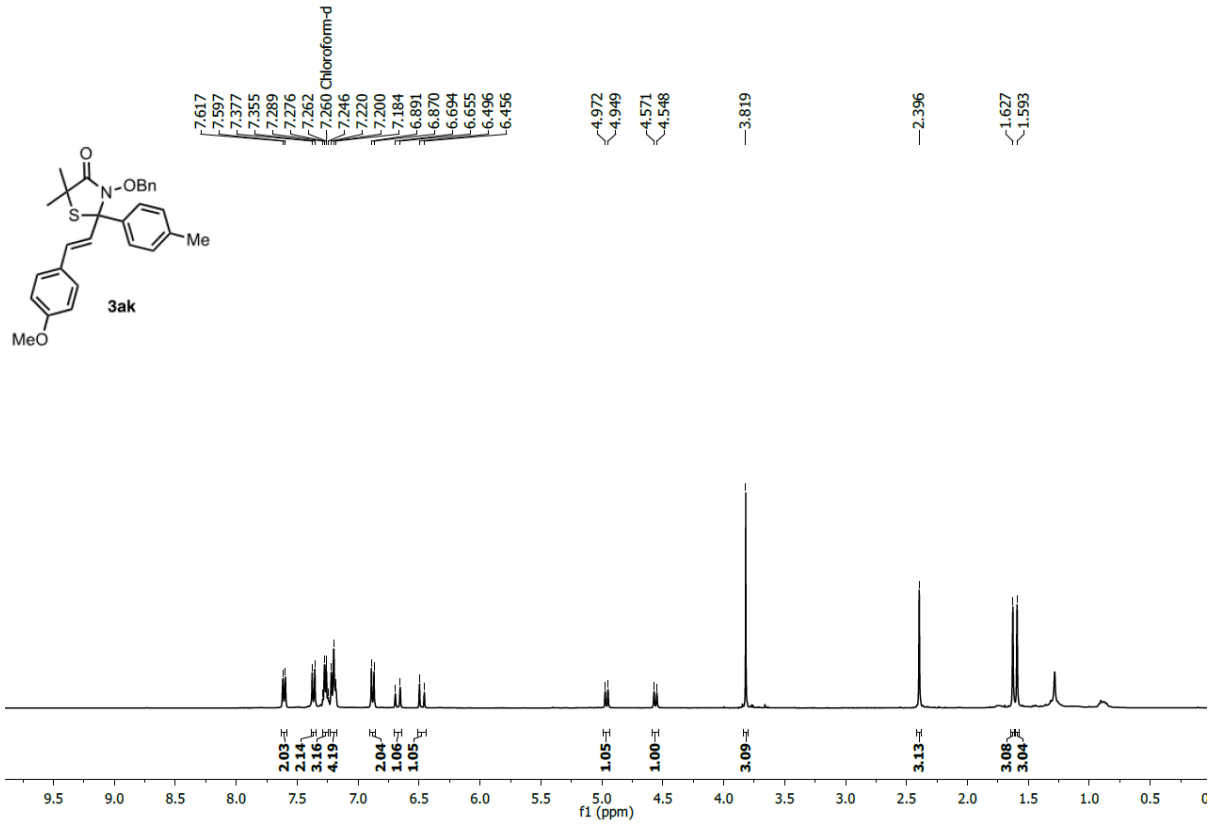
O
N-OBn
S
3aj
f1 (ppm)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7.262
Chloroform-d
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6.870
6.694
6.655
6.496
6.456
4.972
4.949
4.571
4.548
3.819
2.396
1.627
1.593
O
N-OBn
S
Me
3ak
MeO
2.03
2.14
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1.05
1.05
1.00
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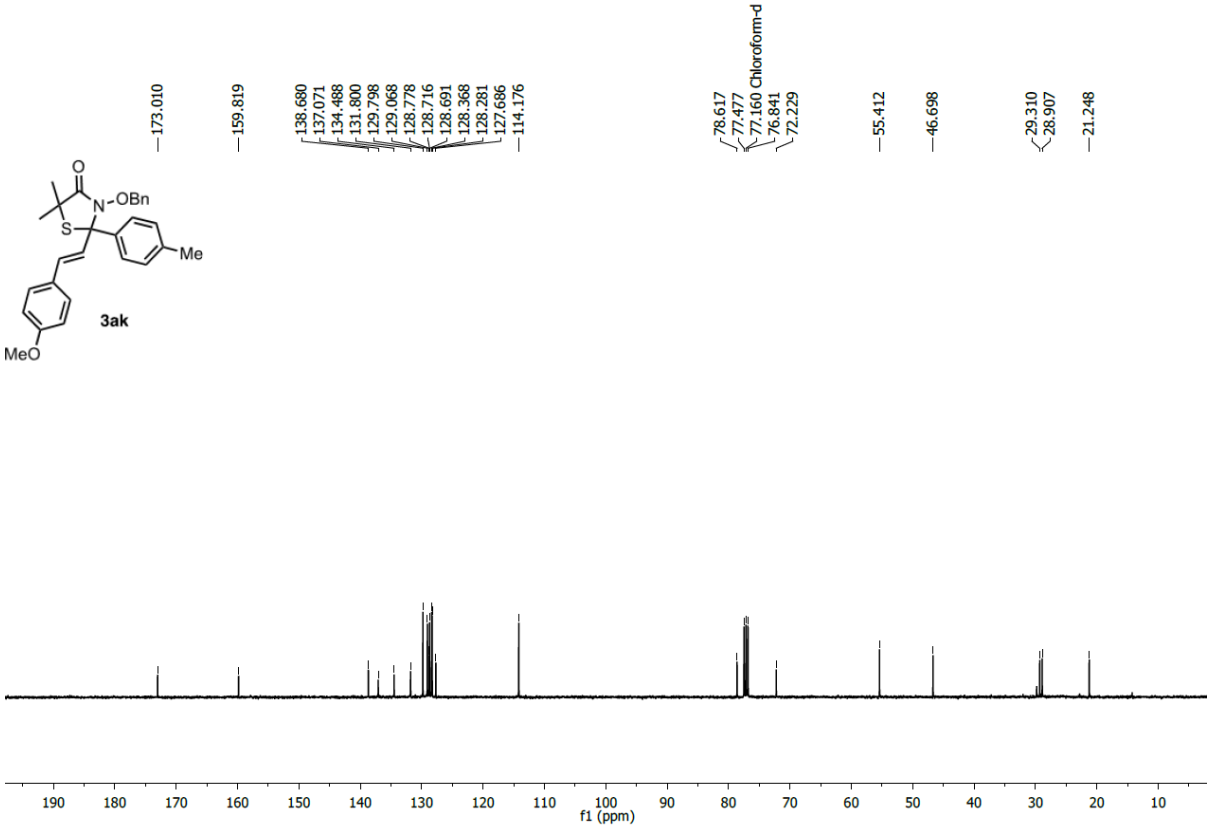
3.13
3.08
3.04
f1 (ppm)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128.281
127.686
114.176
78.617
77.477
77.160
Chloroform-d
76.841
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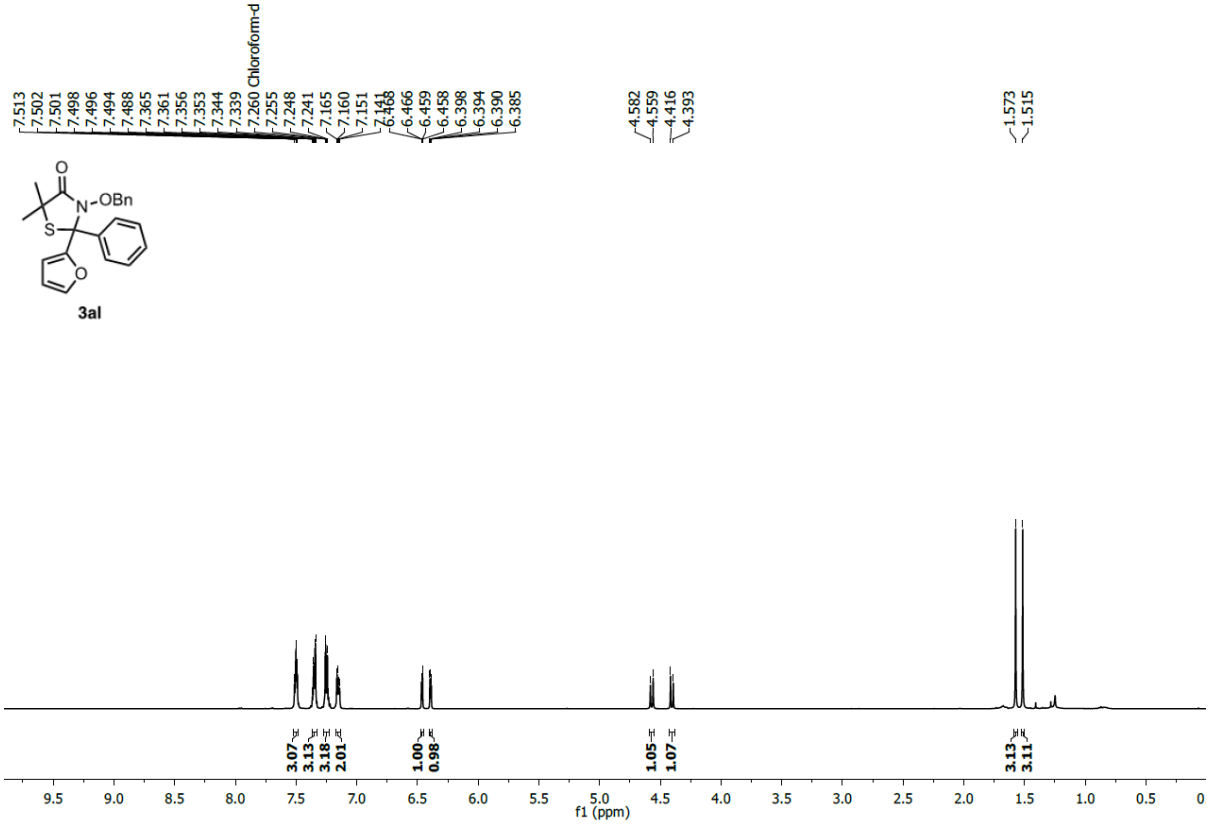
46.698
29.310
28.907
21.248
O
N-OBn
S
Me
3ak
MeO
f1 (ppm)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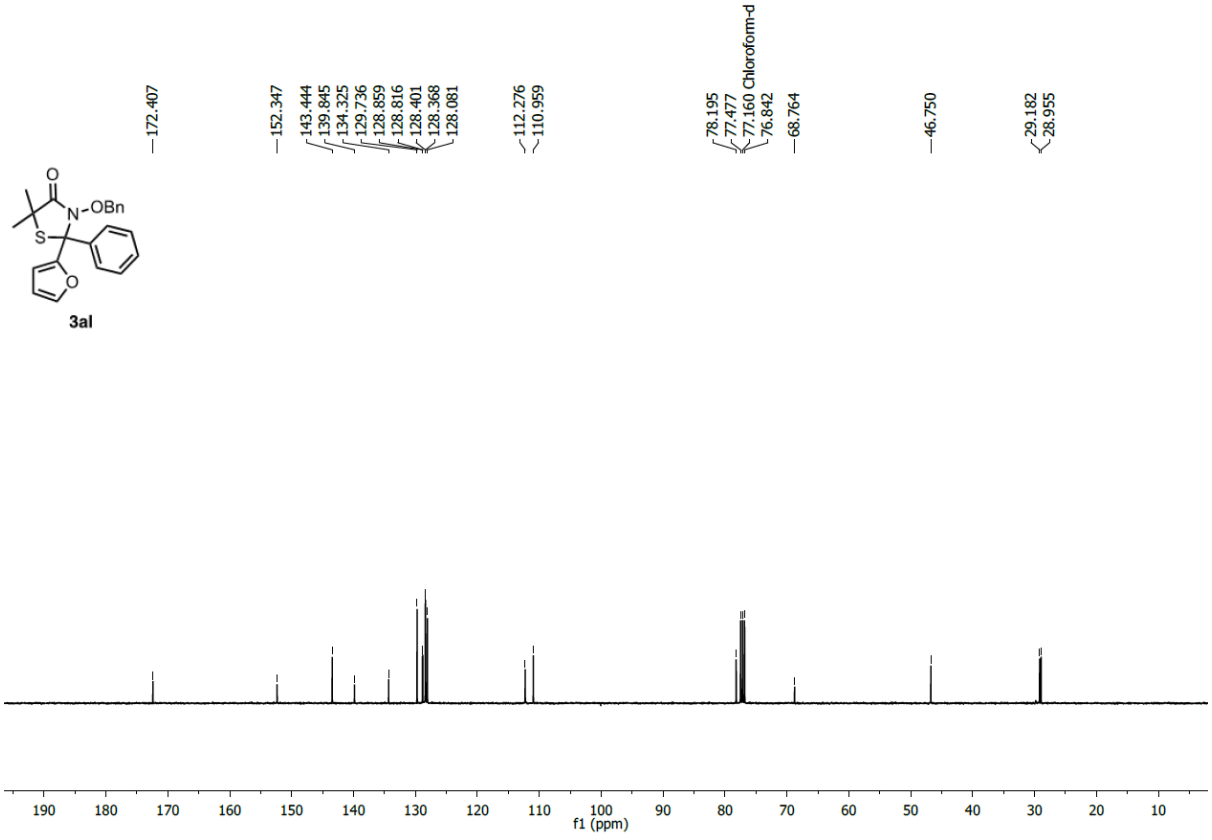
7.356
7.353
7.344
7.339
7.260 Chloroform-d
7.255
7.248
7.241
7.165
7.160
7.151
7.141
6.468
6.466
6.459
6.458
6.398
6.394
6.390
6.385
4.582
4.559
4.416
4.393
1.573
1.515
O
N-OBn
S
O
3al
3.07
3.13
3.18
2.01
1.00
0.98
1.05
1.07
3.13
3.11
f1 (ppm)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129.736
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128.816
128.401
128.368
128.081
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110.959
78.195
77.477
77.160 Chloroform-d
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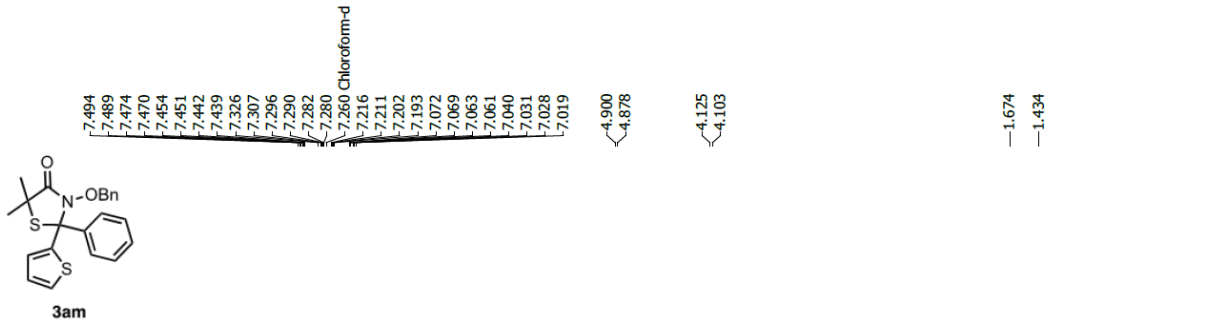
68.764
46.750
29.182
28.955
O
N-OBn
S
O
3al
f1 (ppm)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7.282
7.280
Chloroform-d
7.260
7.216
7.211
7.202
7.193
7.072
7.069
7.063
7.061
7.040
7.031
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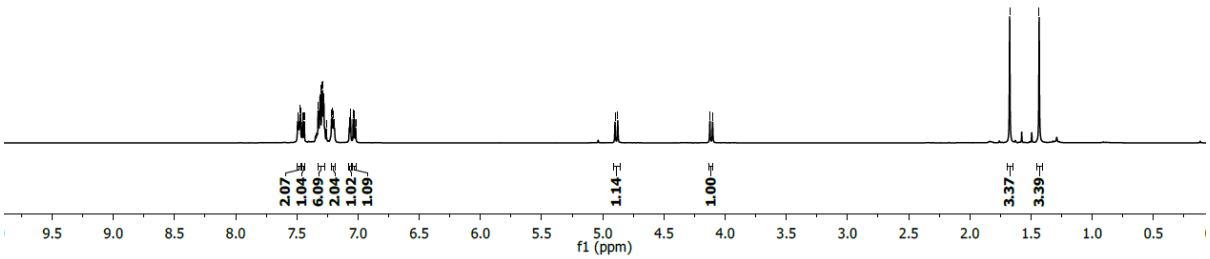
1.434
O
N
OBn
S
S

3am


2.07
1.04
6.09
2.04
1.02
1.09
1.14
1.00
3.37
3.39
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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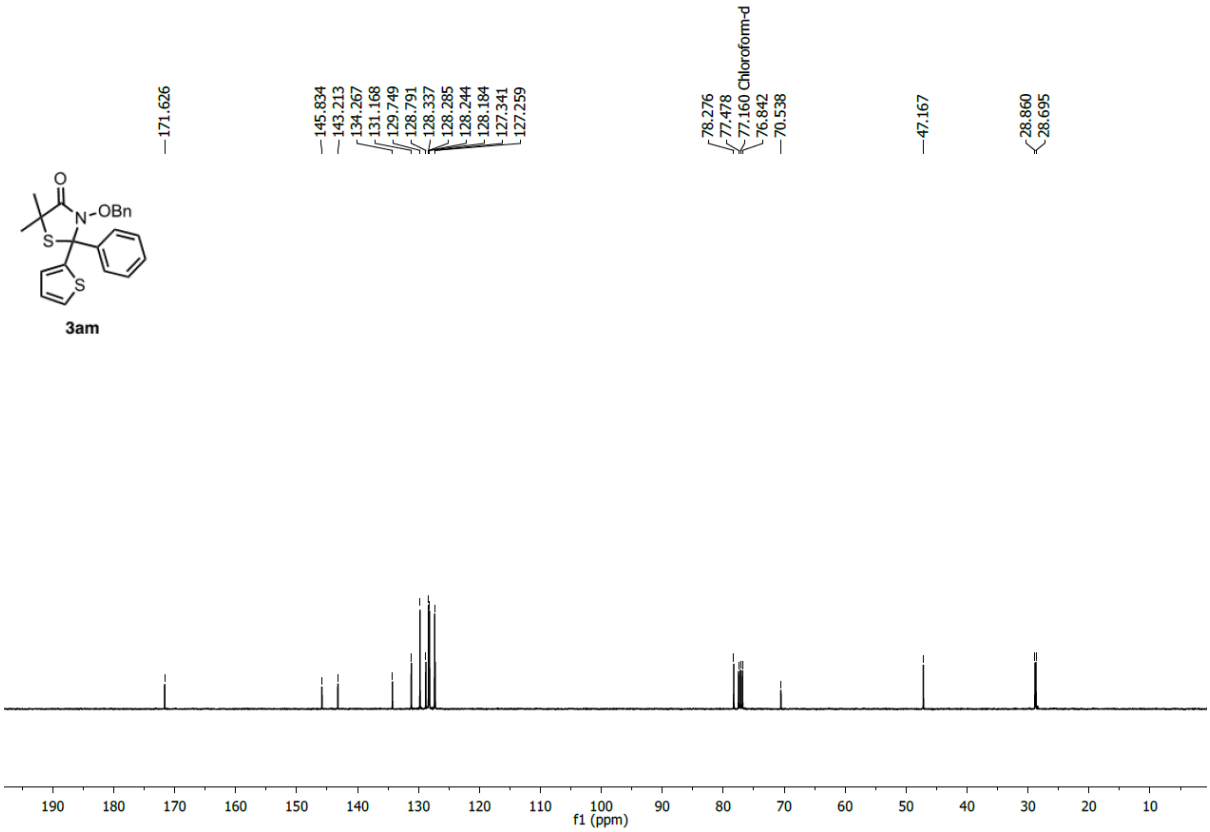
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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143.213
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131.168
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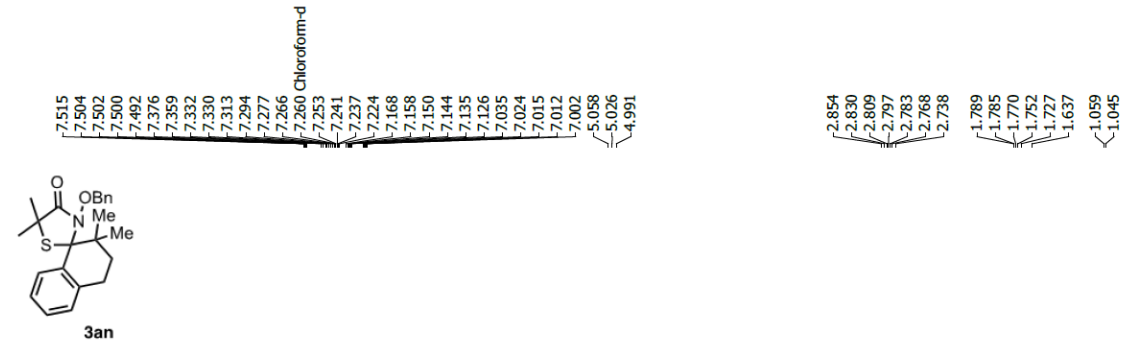
128.791
128.337
128.285
128.244
128.184
127.341
127.259
78.276
77.478
77.160
Chloroform-d
76.842
70.538
47.167
28.860
28.695
O
N
OBn
S
S

3am

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.504
7.502
7.500
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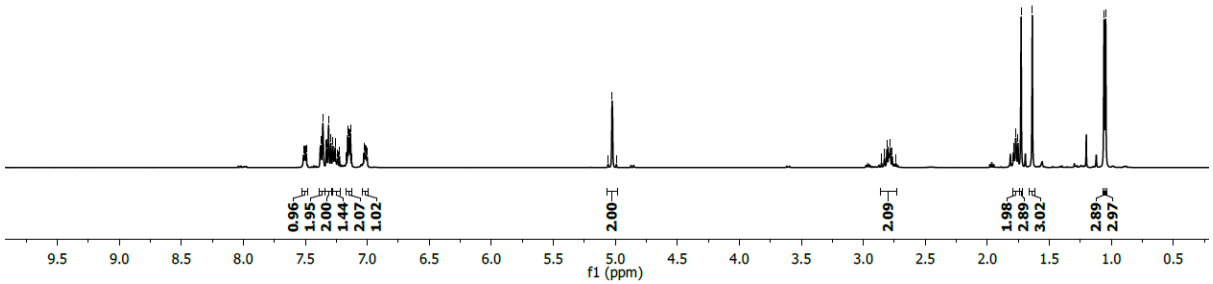
7.359
7.332
7.330
7.313
7.294
7.277
7.266
7.260 Chloroform-d
7.253
7.241
7.237
7.224
7.168
7.158
7.150
7.144
7.135
7.126
7.035
7.024
7.015
7.012
7.002
5.058
5.026
4.991
2.854
2.830
2.809
2.797
2.783
2.768
2.738
1.789
1.785
1.770
1.752
1.727
1.637
1.059
1.045
O
OBn
N
Me
S
Me

3an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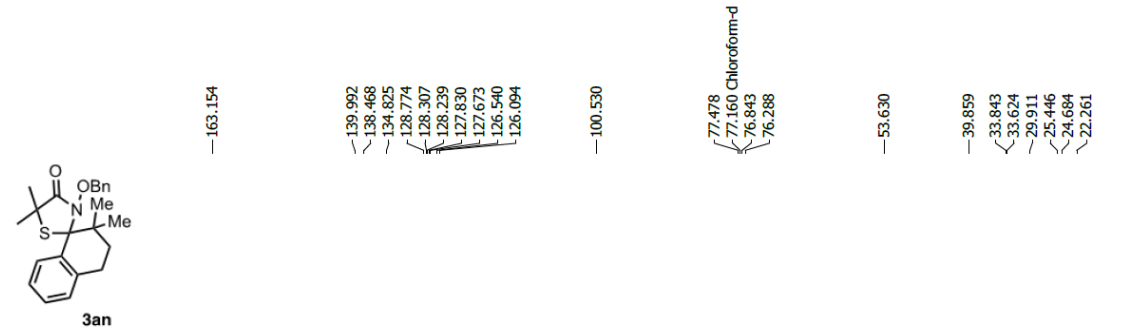
1.95
2.00
1.44
2.07
1.02
2.00
2.09
1.98
2.89
3.02
2.89
2.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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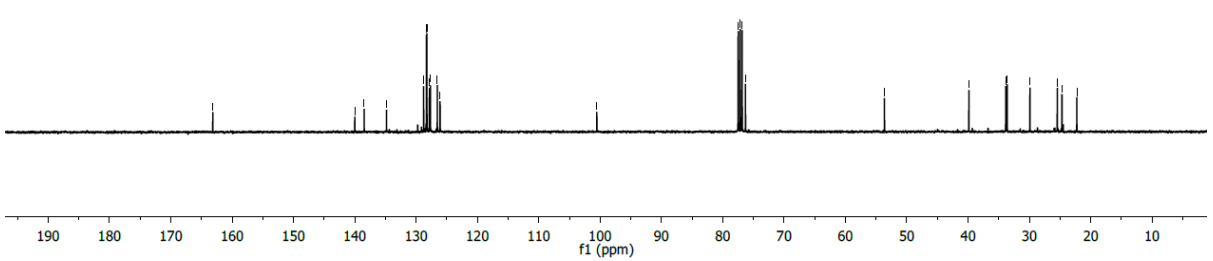
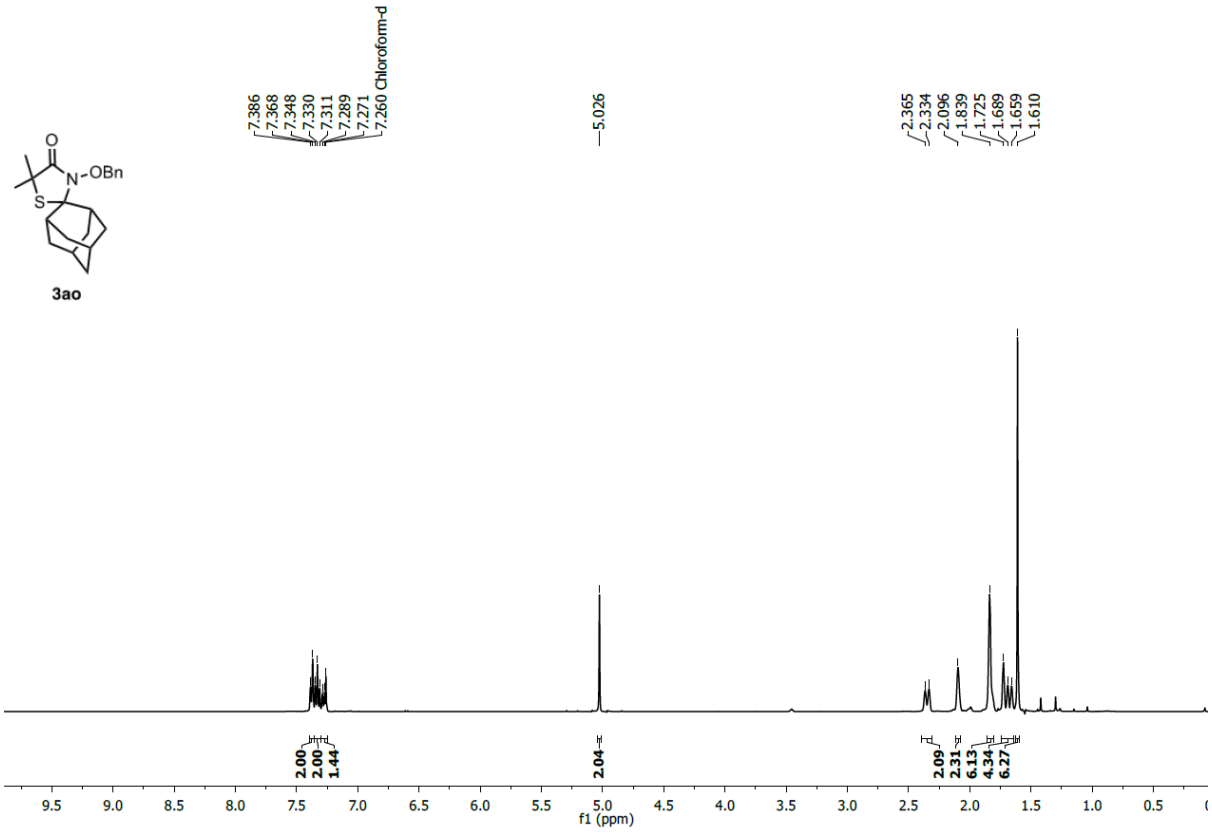
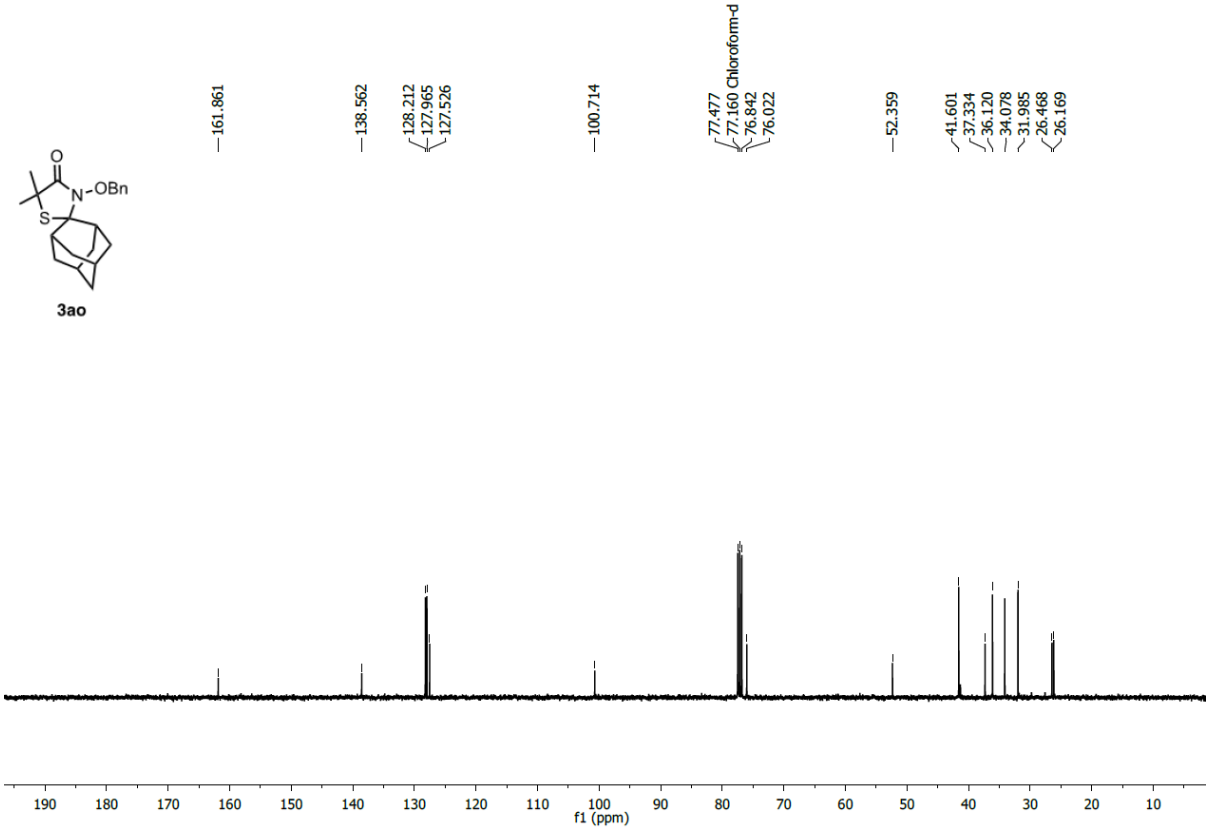
139.992
138.468
134.825
128.774
128.307
128.239
127.830
127.673
126.540
126.094
100.530
77.478
77.160 Chloroform-d
76.843
76.288
53.630
39.859
33.843
33.624
29.911
25.446
24.684
22.261
O
OBn
N
Me
S
Me

3an


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.386
7.368
7.348
7.330
7.311
7.289
7.271
7.260 Chloroform-d
5.026
2.365
2.334
2.096
1.839
1.725
1.689
1.659
1.610
N-OBn
O
S
3ao
2.00
2.00
1.44
2.04
2.09
2.31
6.13
4.34
6.27
f1 (ppm)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127.965
127.526
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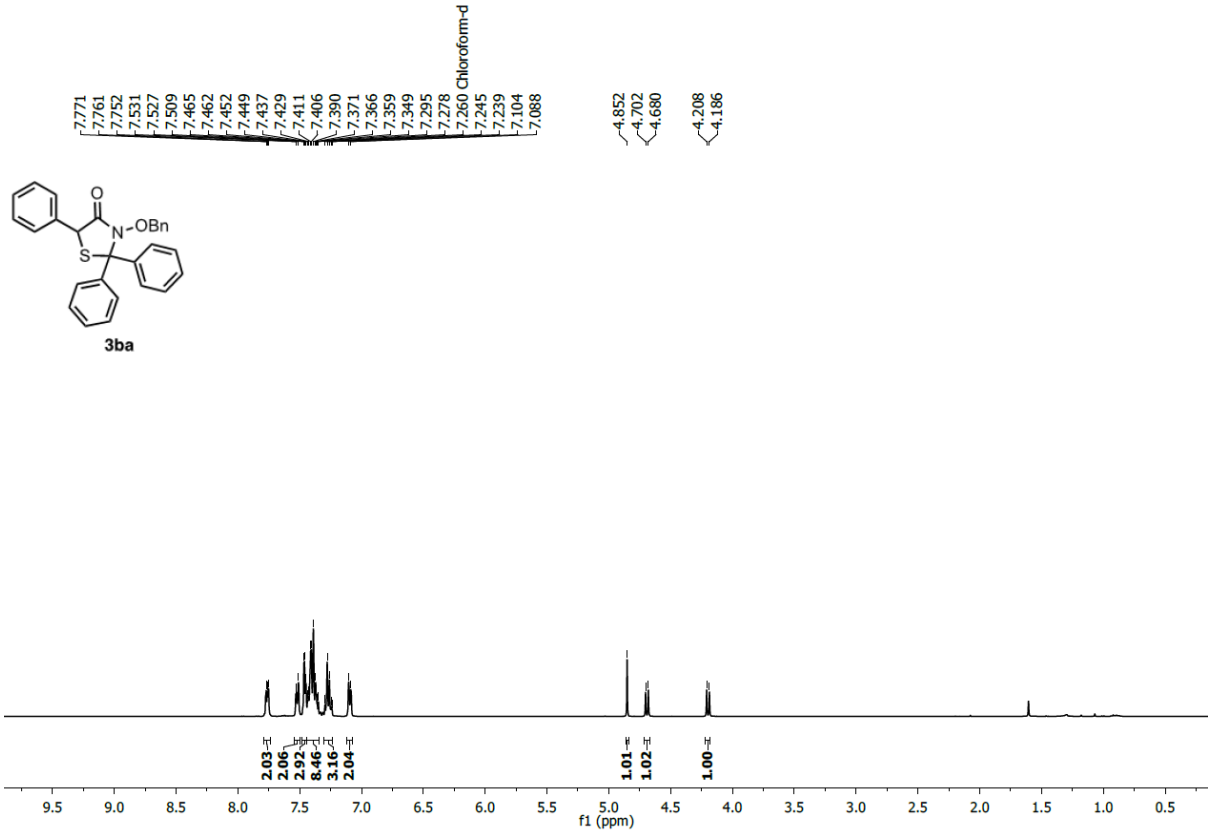
77.477
77.160 Chloroform-d
76.842
76.022
52.359
41.601
37.334
36.120
34.078
31.985
26.468
26.169
N-OBn
O
S
3ao
f1 (ppm)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7.761
7.752
7.531
7.527
7.509
7.465
7.462
7.452
7.449
7.437
7.429
7.411
7.406
7.390
7.371
7.366
7.359
7.349
7.295
7.278
7.260 Chloroform-d
7.245
7.239
7.104
7.088
4.852
4.702
4.680
4.208
4.186
O
N-OBn
S
3ba
2.03
2.06
2.92
8.46
3.16
2.04
1.01
1.02
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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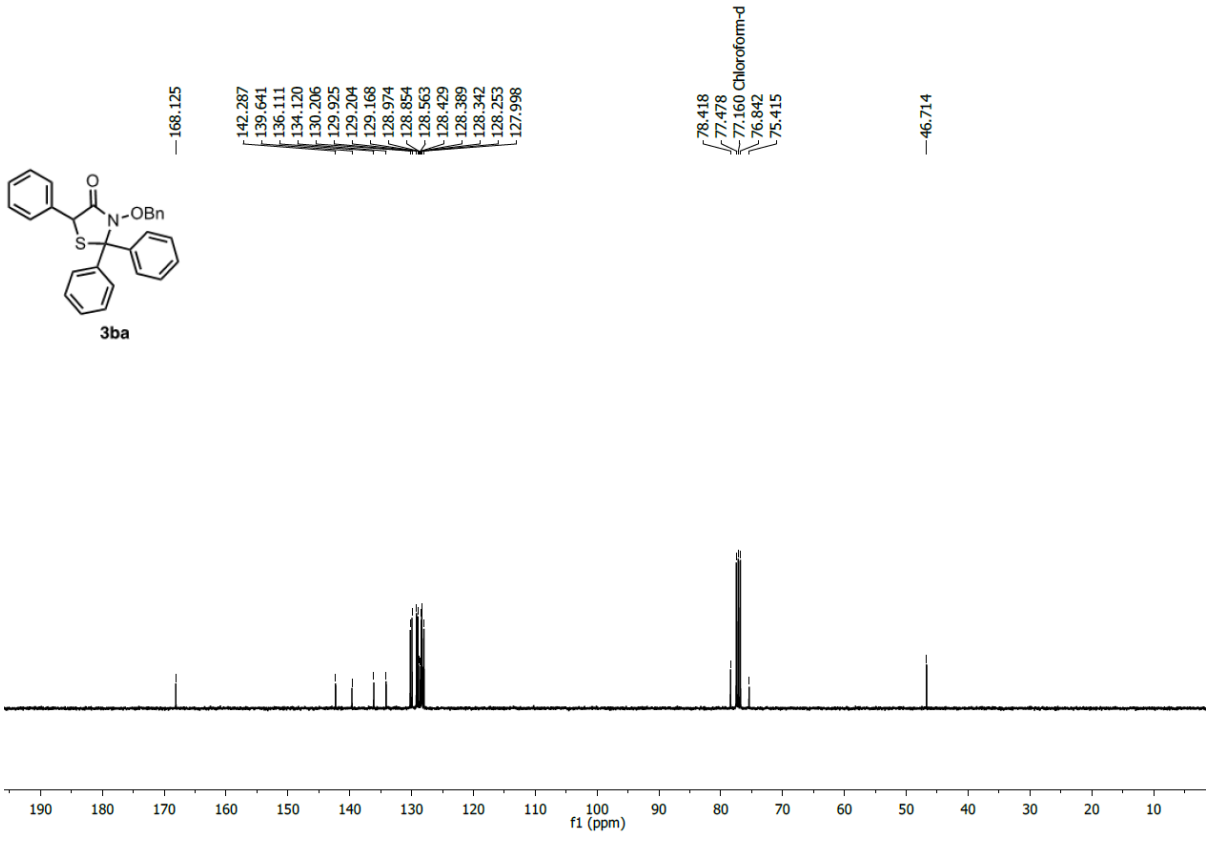
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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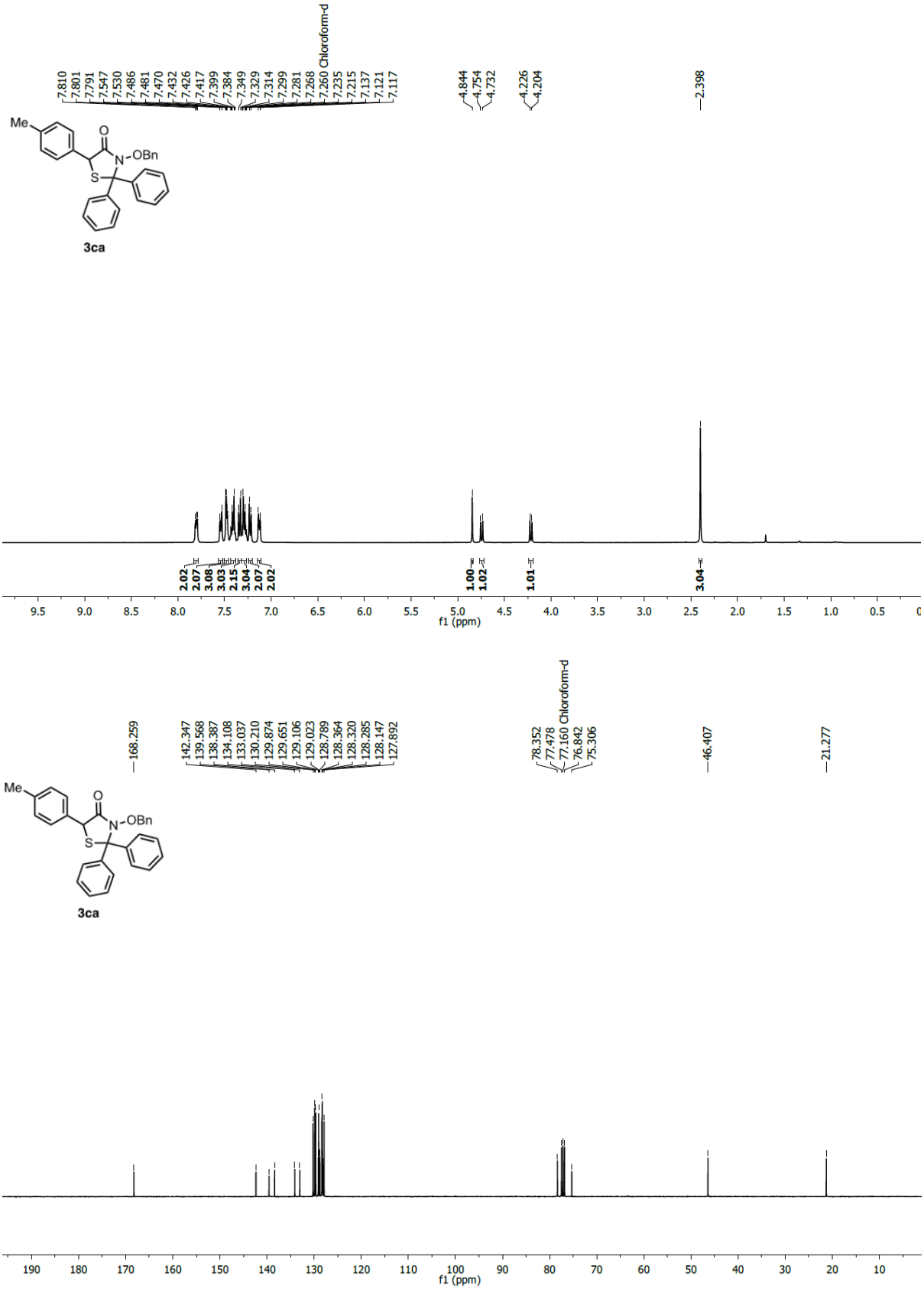
142.287
139.641
136.111
134.120
130.206
129.925
129.204
129.168
128.974
128.854
128.563
128.429
128.389
128.342
128.253
127.998
78.418
77.478
77.160 Chloroform-d
76.842
75.415
46.714
O
N-OBn
S
3ba
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.791
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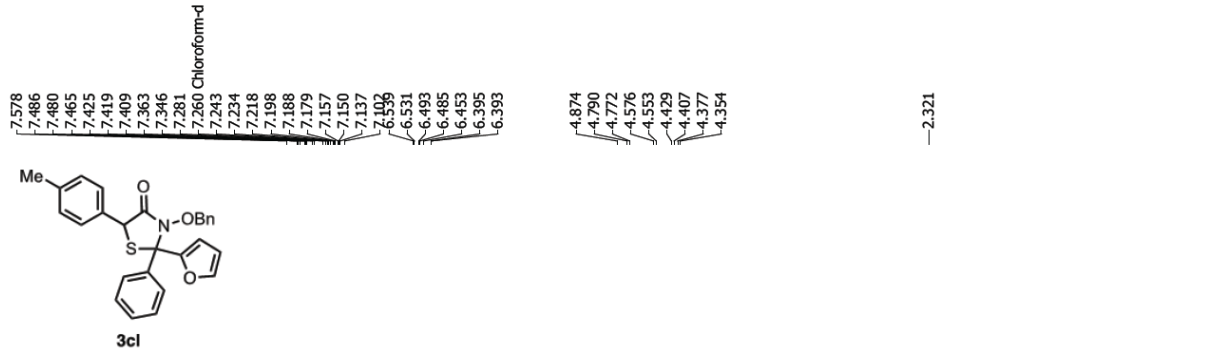
7.530
7.486
7.481
7.470
7.432
7.426
7.417
7.399
7.384
7.349
7.329
7.314
7.299
7.281
7.268
Chloroform-d
7.260
7.235
7.215
7.137
7.121
7.117
4.844
4.754
4.732
4.226
4.204
2.398
Me
O
N-OBn
S
3ca
2.02
2.07
3.08
3.03
2.15
3.04
2.07
2.02
1.00
1.02
1.01
3.04
f1 (ppm)
168.259
142.347
139.568
138.387
134.108
133.037
130.210
129.874
129.651
129.106
129.023
128.789
128.364
128.320
128.285
128.147
127.892
78.352
77.478
77.160
Chloroform-d
76.842
75.306
46.407
21.277
f1 (ppm)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7.486
7.480
7.465
7.425
7.419
7.409
7.363
7.346
7.281
7.260 Chloroform-d
7.243
7.234
7.218
7.198
7.188
7.179
7.157
7.150
7.137
7.102
6.539
6.531
6.493
6.485
6.453
6.395
6.393
4.874
4.790
4.772
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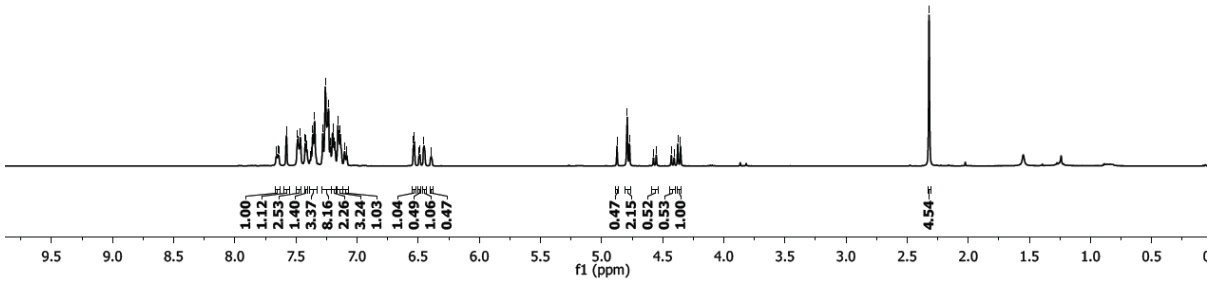
4.553
4.429
4.407
4.377
4.354
2.321
Me
O
N-OBn
S
O

3cl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2.53
1.40
3.37
8.16
2.26
3.24
1.03
1.04
0.49
1.06
0.47
0.47
2.15
0.52
0.53
1.00
4.54
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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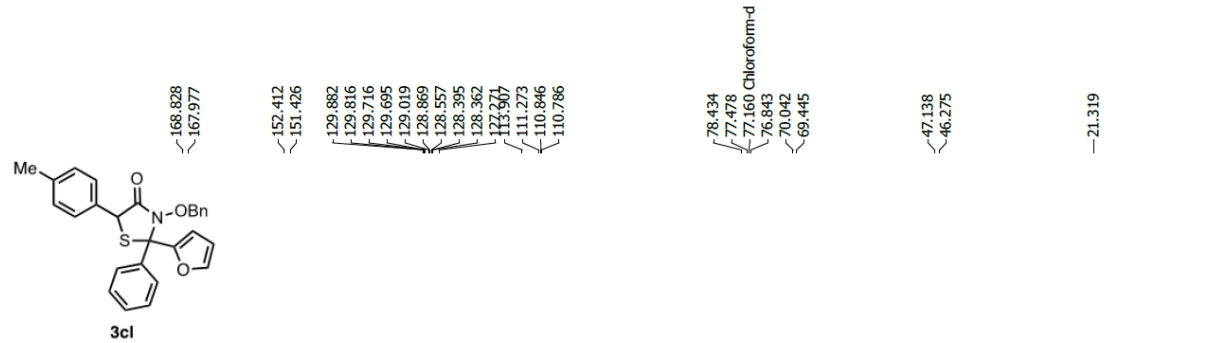
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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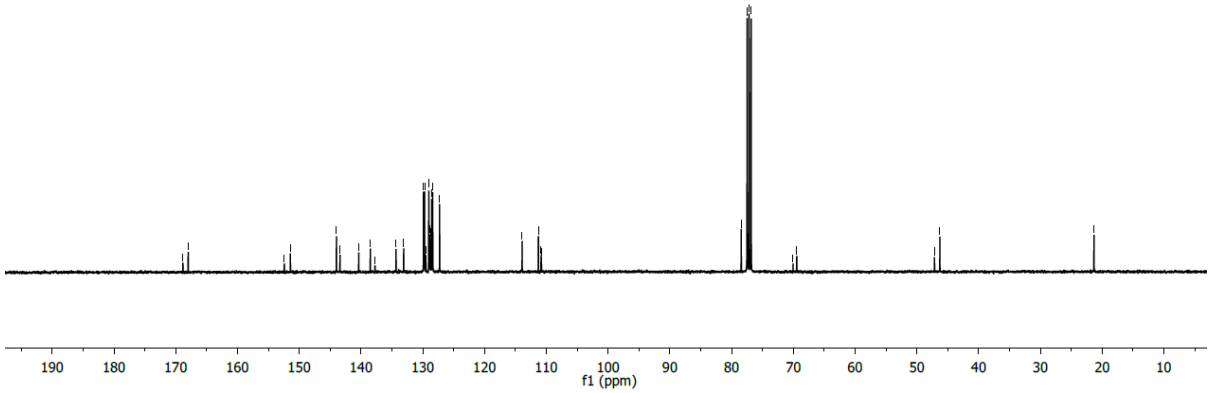
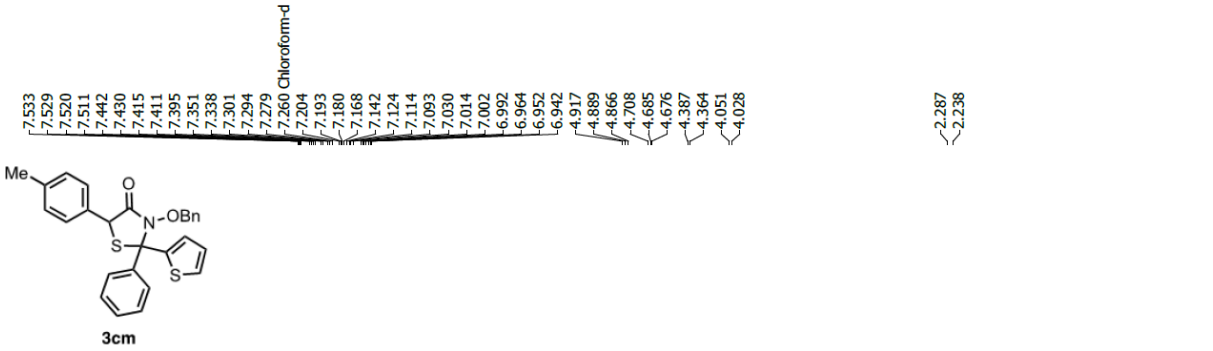
167.977
152.412
151.426
129.882
129.816
129.716
129.695
129.019
128.869
128.557
128.395
128.362
127.271
113.907
111.273
110.846
110.786
78.434
77.478
77.160 Chloroform-d
76.843
70.042
69.445
47.138
46.275
21.319
Me
O
N-OBn
S
O

3cl


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.529
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7.442
7.430
7.415
7.411
7.395
7.351
7.338
7.301
7.294
7.279
7.260 Chloroform-d
7.204
7.193
7.180
7.168
7.142
7.124
7.114
7.093
7.030
7.014
7.002
6.992
6.964
6.952
6.942
4.917
4.889
4.866
4.708
4.685
4.676
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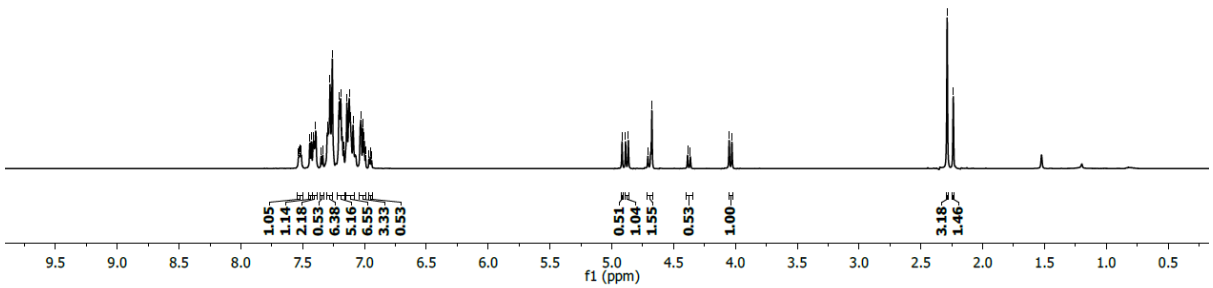
4.364
4.051
4.028
2.287
2.238
Me
O
N-OBn
S
S

3cm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2.18
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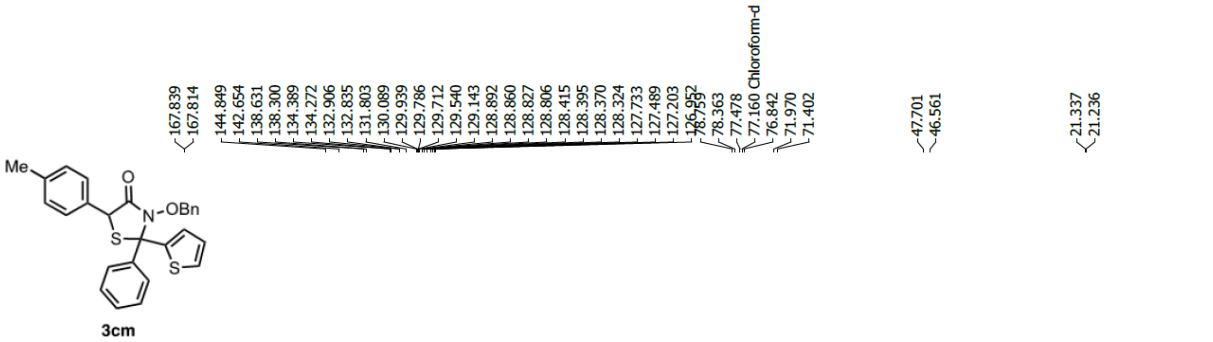
6.38
5.16
6.55
3.33
0.53
0.51
1.04
1.55
0.53
1.00
3.18
1.46
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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134.272
132.906
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130.089
129.939
129.786
129.712
129.540
129.143
128.892
128.860
128.827
128.806
128.415
128.395
128.370
128.324
127.733
127.489
127.203
126.952
78.759
78.363
77.478
77.160 Chloroform-d
76.842
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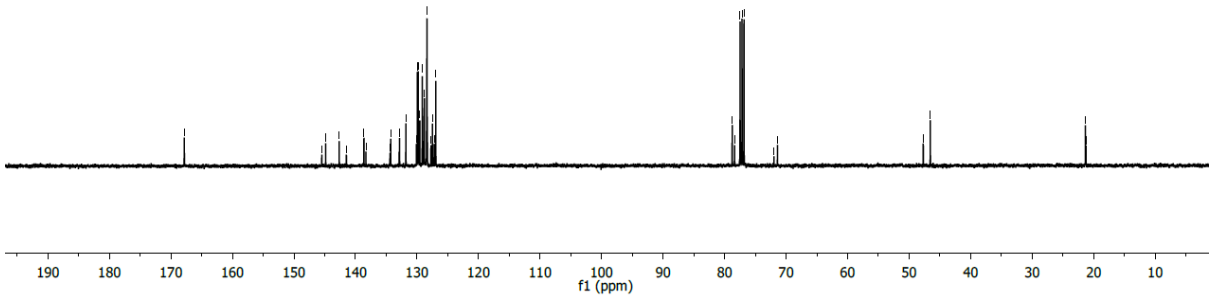
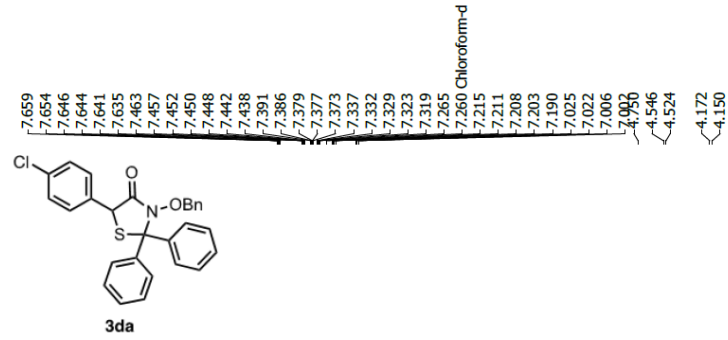
71.402
47.701
46.561
21.337
21.236
Me
O
N-OBn
S
S

3cm


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.448
7.442
7.438
7.391
7.386
7.379
7.377
7.373
7.337
7.332
7.329
7.323
7.319
7.265
Chloroform-d
7.215
7.211
7.208
7.203
7.190
7.025
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7.006
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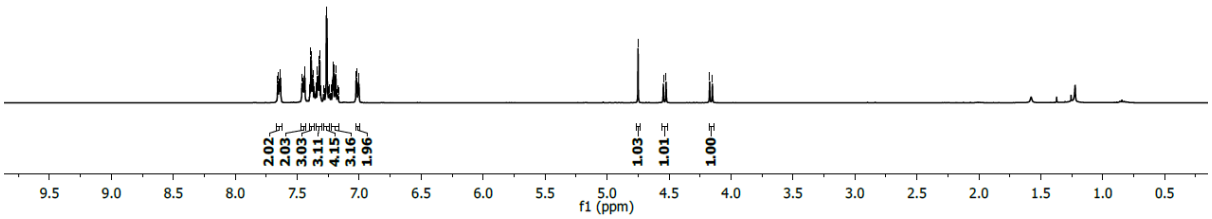
4.550
4.546
4.524
4.172
4.150
Cl
O
N
OBn
S

3da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3.16
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1.03
1.01
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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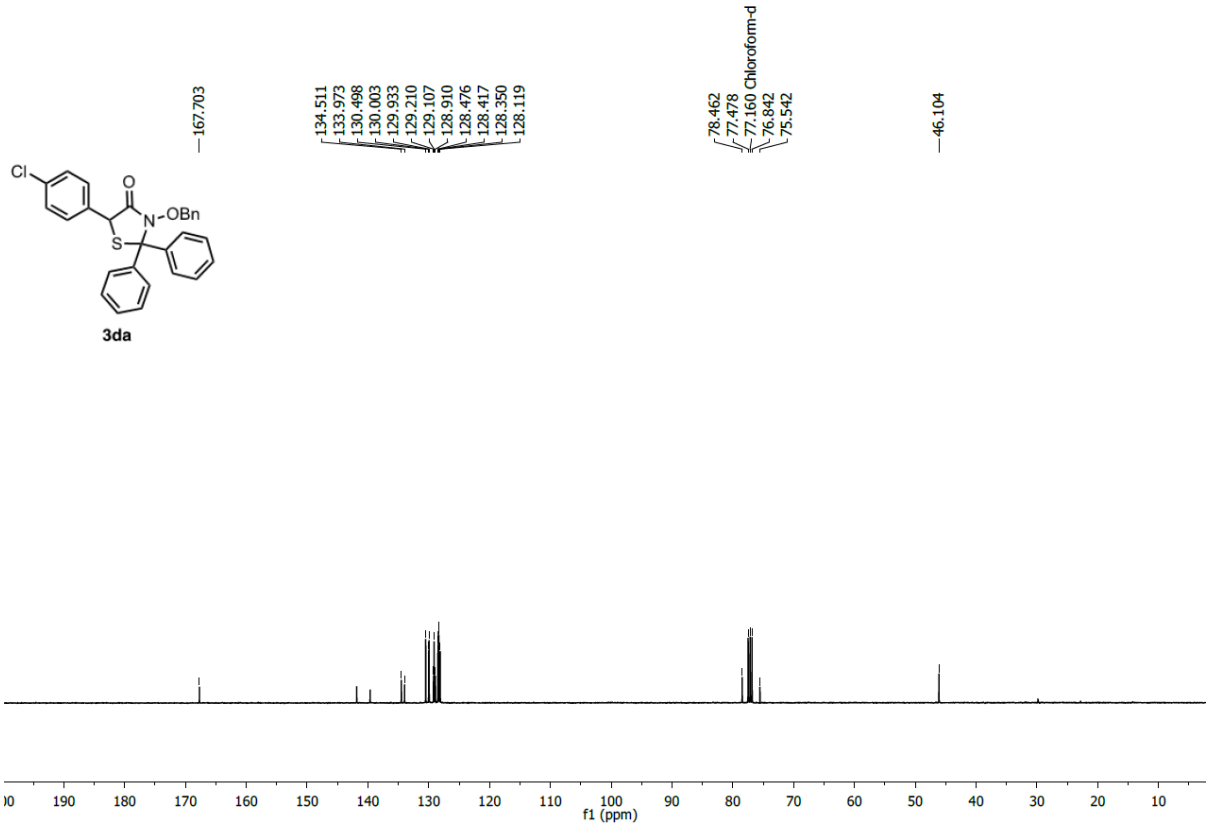
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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130.003
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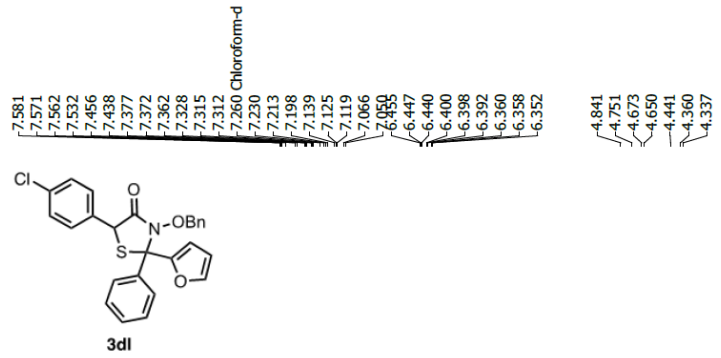
129.210
129.107
128.910
128.476
128.417
128.350
128.119
78.462
77.478
77.160
Chloroform-d
76.842
75.542
46.104
Cl
O
N
OBn
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3da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7.438
7.377
7.372
7.362
7.328
7.315
7.312
7.260 Chloroform-d
7.230
7.213
7.198
7.139
7.125
7.119
7.066
7.050
6.455
6.447
6.440
6.400
6.398
6.392
6.360
6.358
6.352
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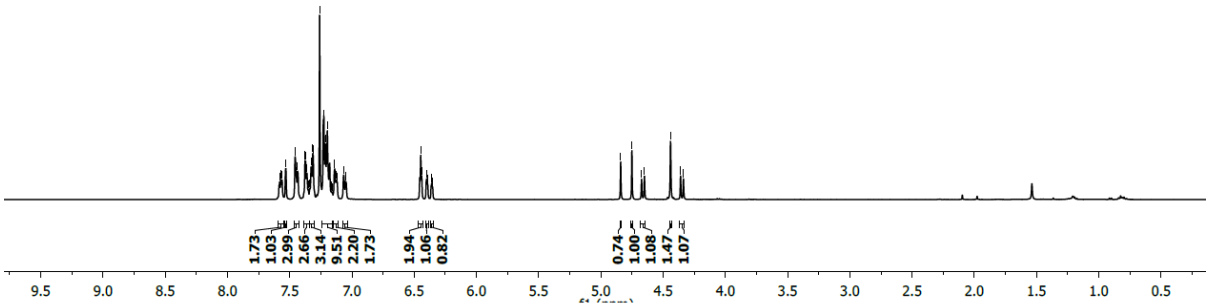
4.673
4.650
4.441
4.360
4.337
Cl
O
N-OBn
S
O

3dl


1.73
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3.14
9.51
2.20
1.73
1.94
1.06
0.82
0.74
1.00
1.08
1.47
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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3.5
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2.5
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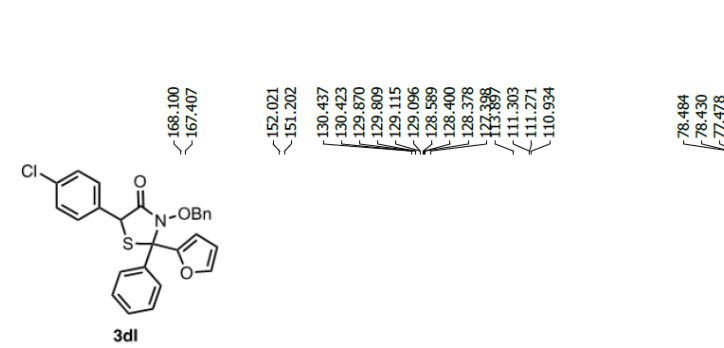
1.5
1.0
0.5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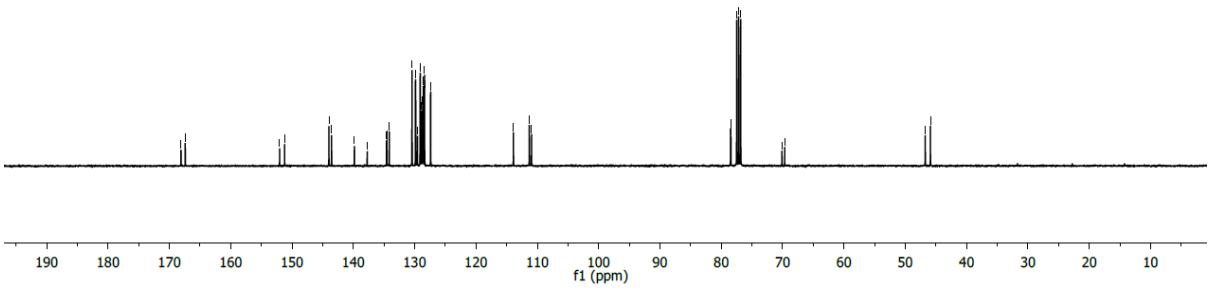
130.423
129.870
129.809
129.115
129.096
128.589
128.400
128.378
111.303
111.271
110.934
78.484
78.430
77.478
77.160 Chloroform-d
76.842
70.097
69.650
46.738
45.891
Cl
O
N-OBn
S
O

3dl


190
180
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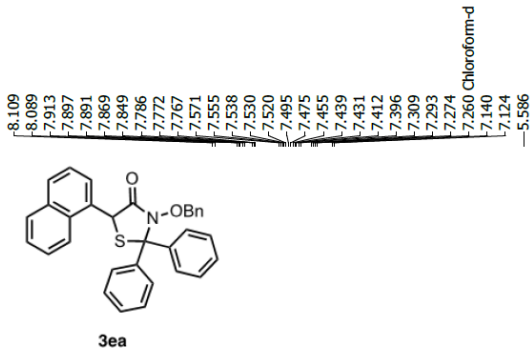
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.109
8.089
7.913
7.897
7.891
7.869
7.849
7.786
7.772
7.767
7.571
7.555
7.538
7.530
7.520
7.495
7.475
7.455
7.439
7.431
7.412
7.396
7.309
7.293
7.274
7.260 Chloroform-d
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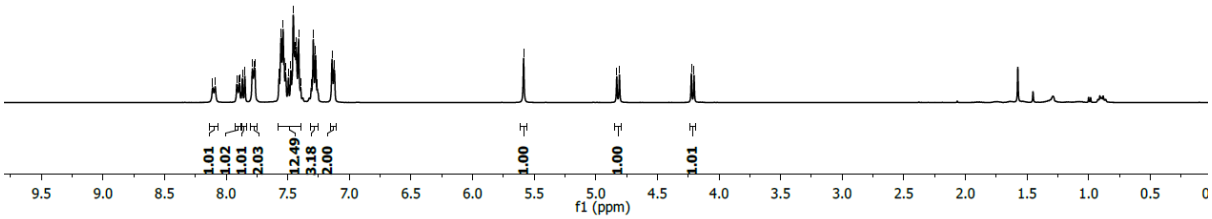
7.124
5.586
4.830
4.808
4.225
4.203
O
N-OBn
S

3ea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1.02
1.01
2.03
12.49
3.18
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1.00
1.00
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
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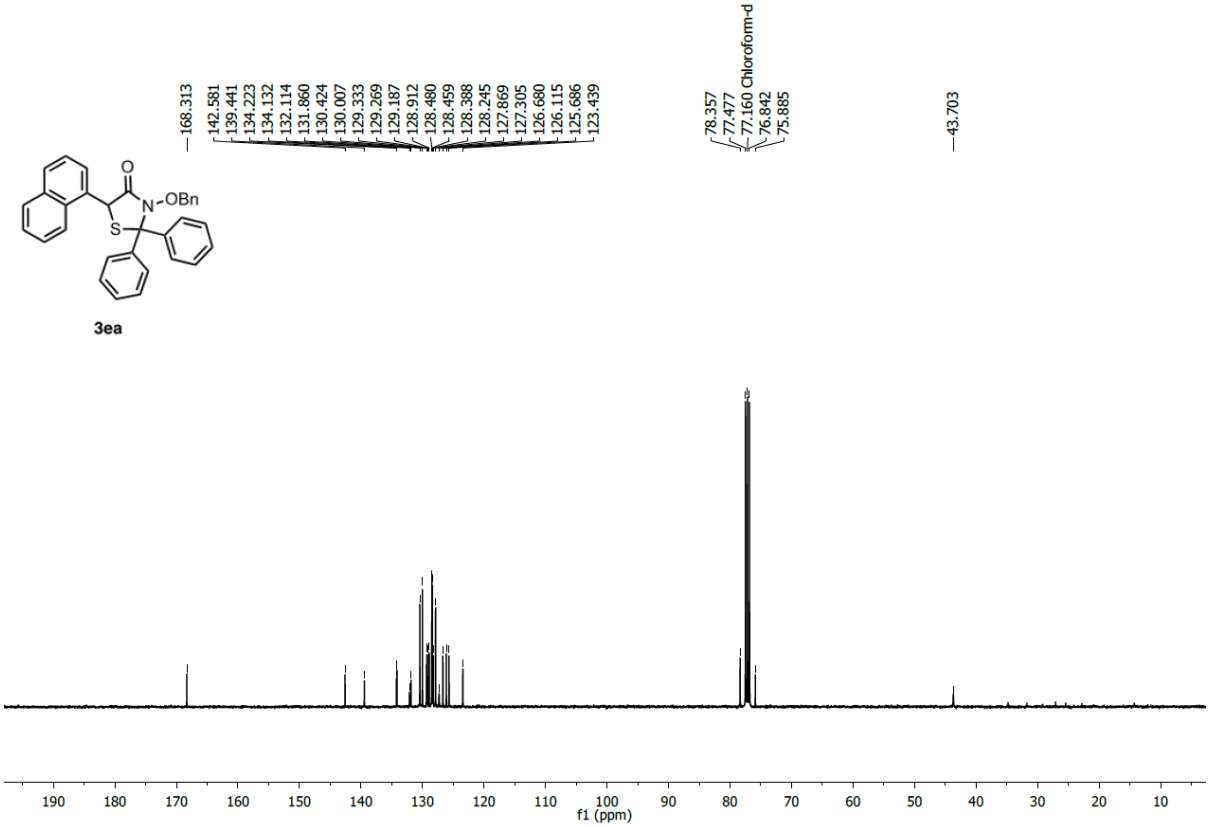
f1 (ppm)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134.223
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130.424
130.007
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129.269
129.187
128.912
128.480
128.459
128.388
128.245
127.869
127.305
126.680
126.115
125.686
123.439
78.357
77.477
77.160 Chloroform-d
76.842
75.885
43.703
O
N-OBn
S
190
180
170
160
150
140
130
120
110
100
90
80
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60
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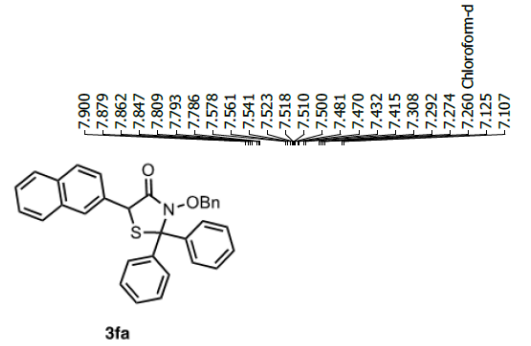
40
30
20
10
f1 (ppm)

3ea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7.578
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7.541
7.523
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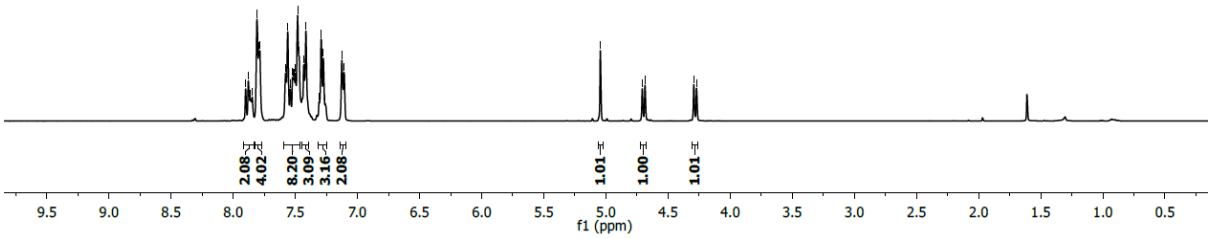
7.510
7.500
7.481
7.470
7.432
7.415
7.308
7.292
7.274
7.260 Chloroform-d
7.125
7.107
5.045
4.708
4.686
4.293
4.271
O
N-OBn
S

3fa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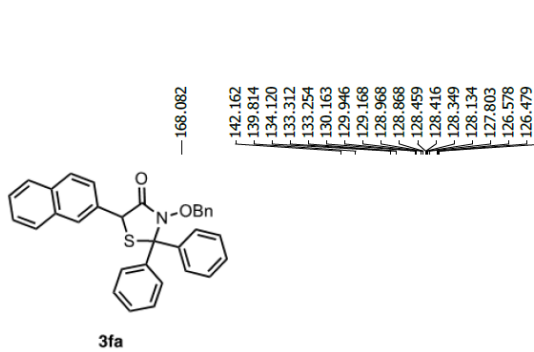
4.02
8.20
3.09
3.16
2.08
1.01
1.00
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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139.814
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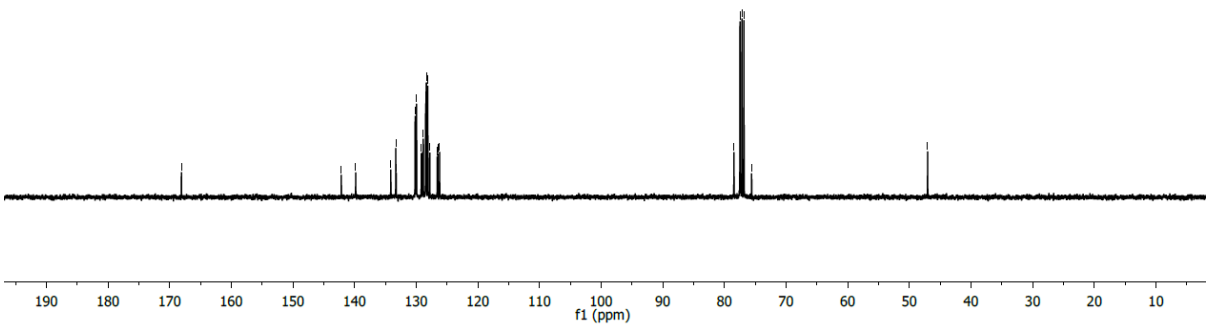
128.416
128.349
128.134
127.803
126.578
126.479
126.204
78.461
77.477
77.160 Chloroform-d
76.842
75.592
47.041
O
N-OBn
S

3fa


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.606
7.598
7.450
7.440
7.430
7.379
7.373
7.364
7.335
7.324
7.311
7.260 Chloroform-d
7.244
7.231
7.214
7.201
7.193
7.042
7.027
4.555
4.533
4.139
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3.729
3.711
3.693
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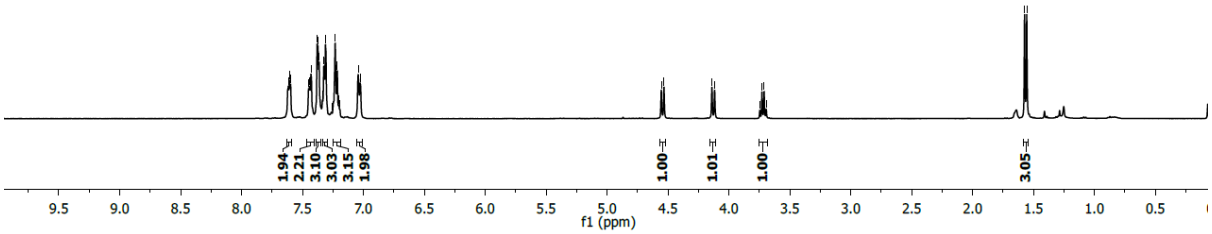
1.556
Me
O
N
OBn
S

3ga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1.01
1.00
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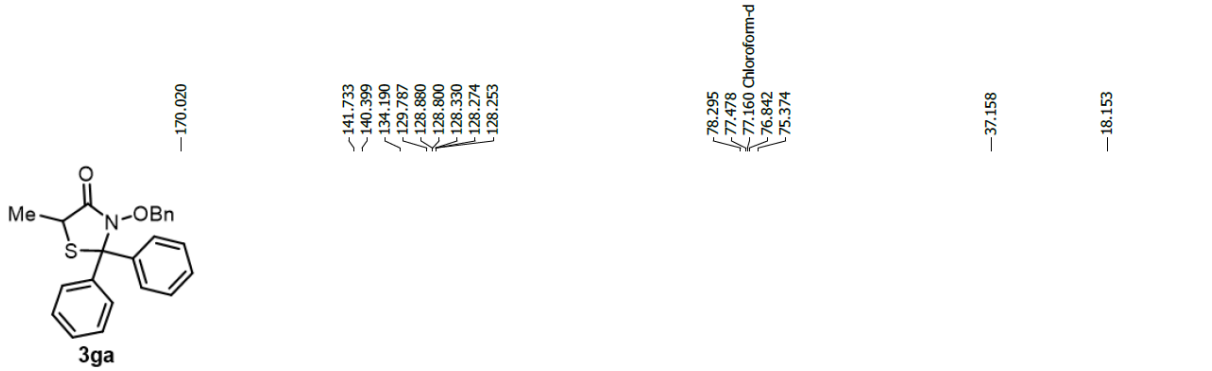
f1 (ppm)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140.399
134.190
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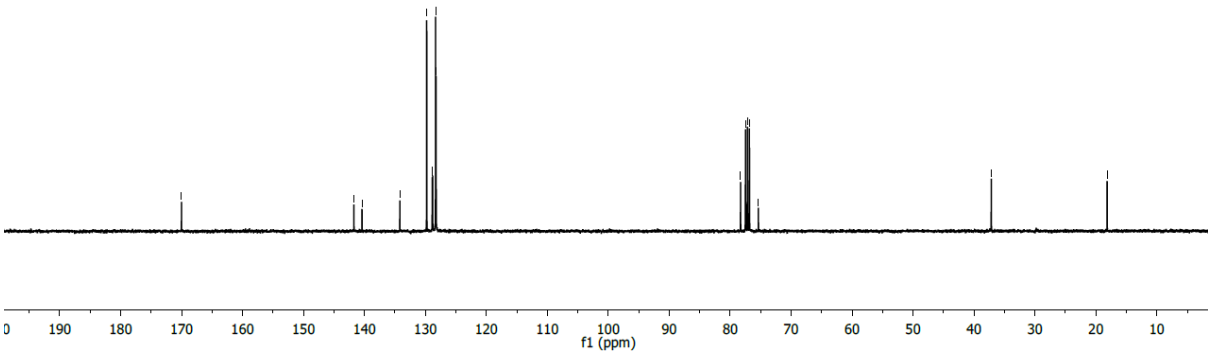
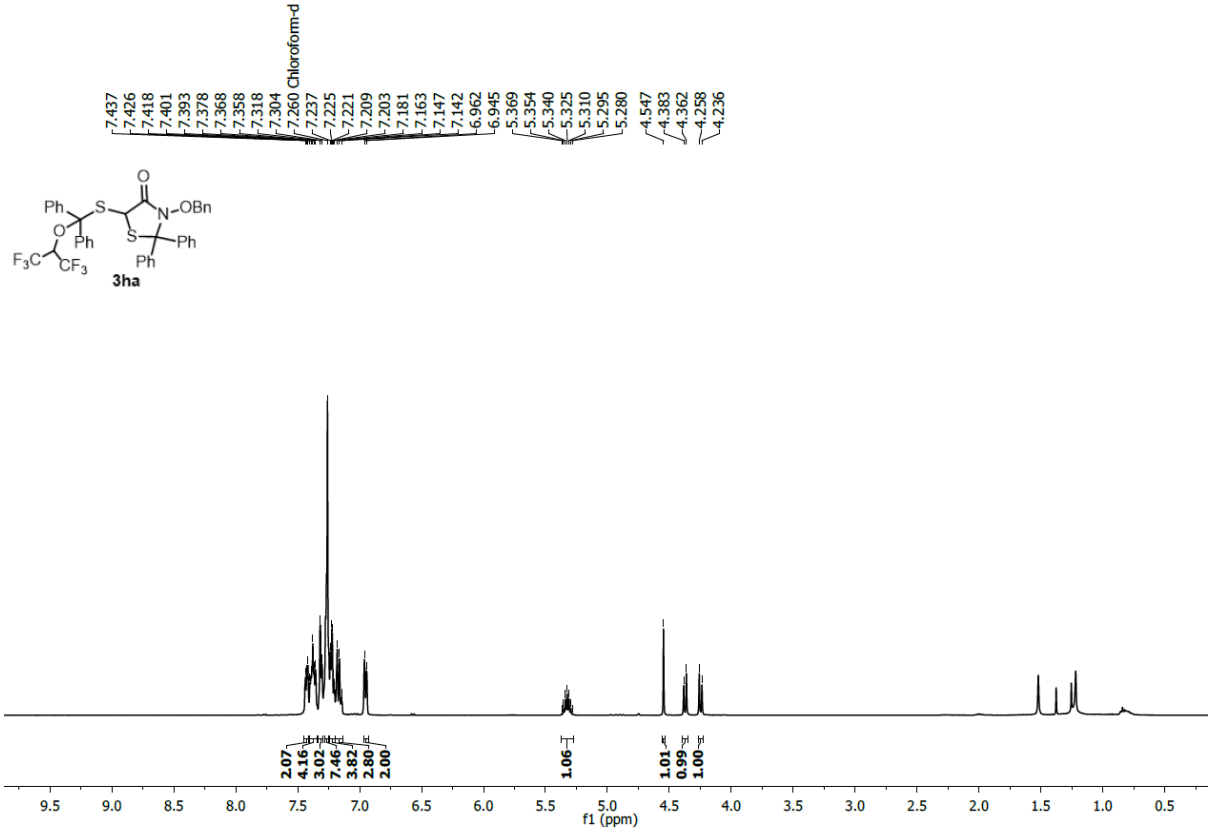
128.880
128.800
128.330
128.274
128.253
78.295
77.478
77.160 Chloroform-d
76.842
75.374
37.158
18.153
Me
O
N
OBn
S

3ga


f1 (ppm)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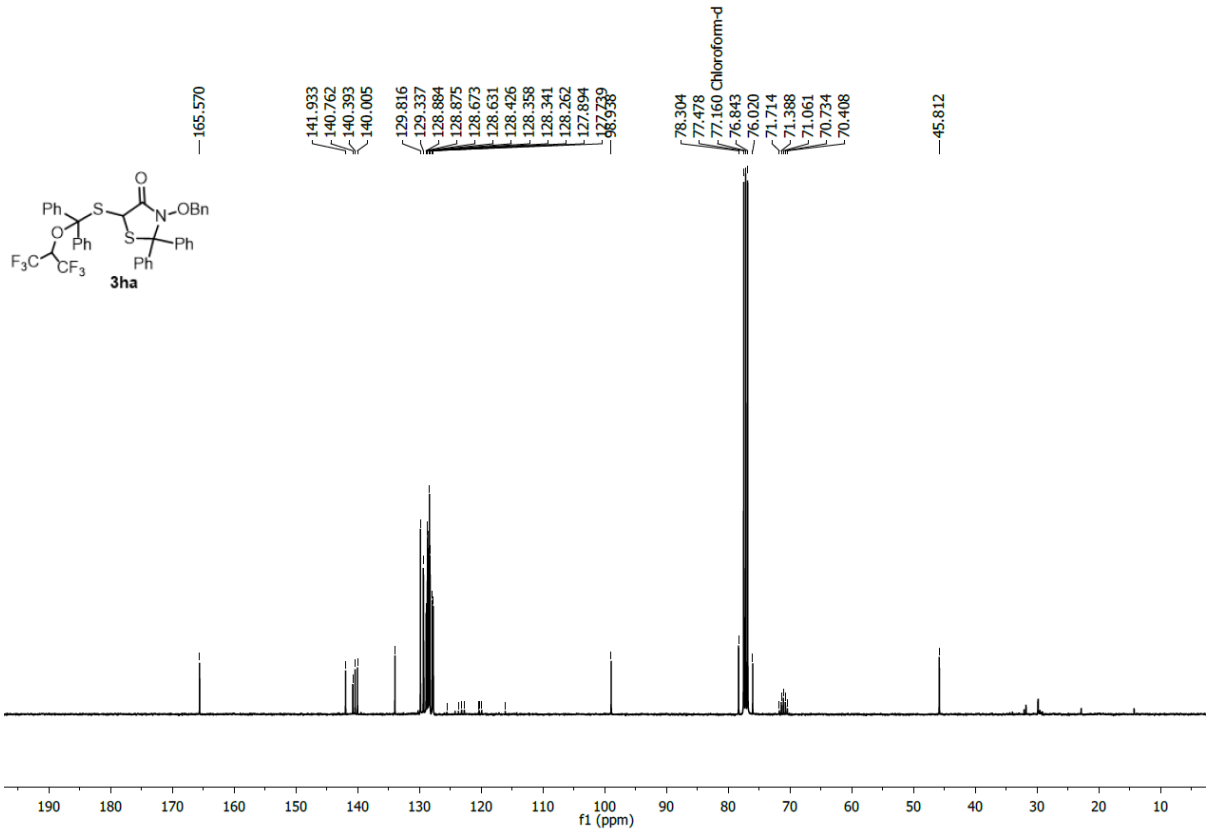
7.426
7.418
7.401
7.393
7.378
7.368
7.358
7.318
7.304
7.260 Chloroform-d
7.237
7.225
7.221
7.209
7.203
7.181
7.163
7.147
7.142
6.962
6.945
5.369
5.354
5.340
5.325
5.310
5.295
5.280
4.547
4.383
4.362
4.258
4.236
Ph
S
O
N
OBn
Ph
O
Ph
S
Ph
F3C
CF3
Ph
3ha
2.07
4.16
3.02
7.46
3.82
2.80
2.00
1.06
1.01
0.99
1.00
f1 (ppm)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129.337
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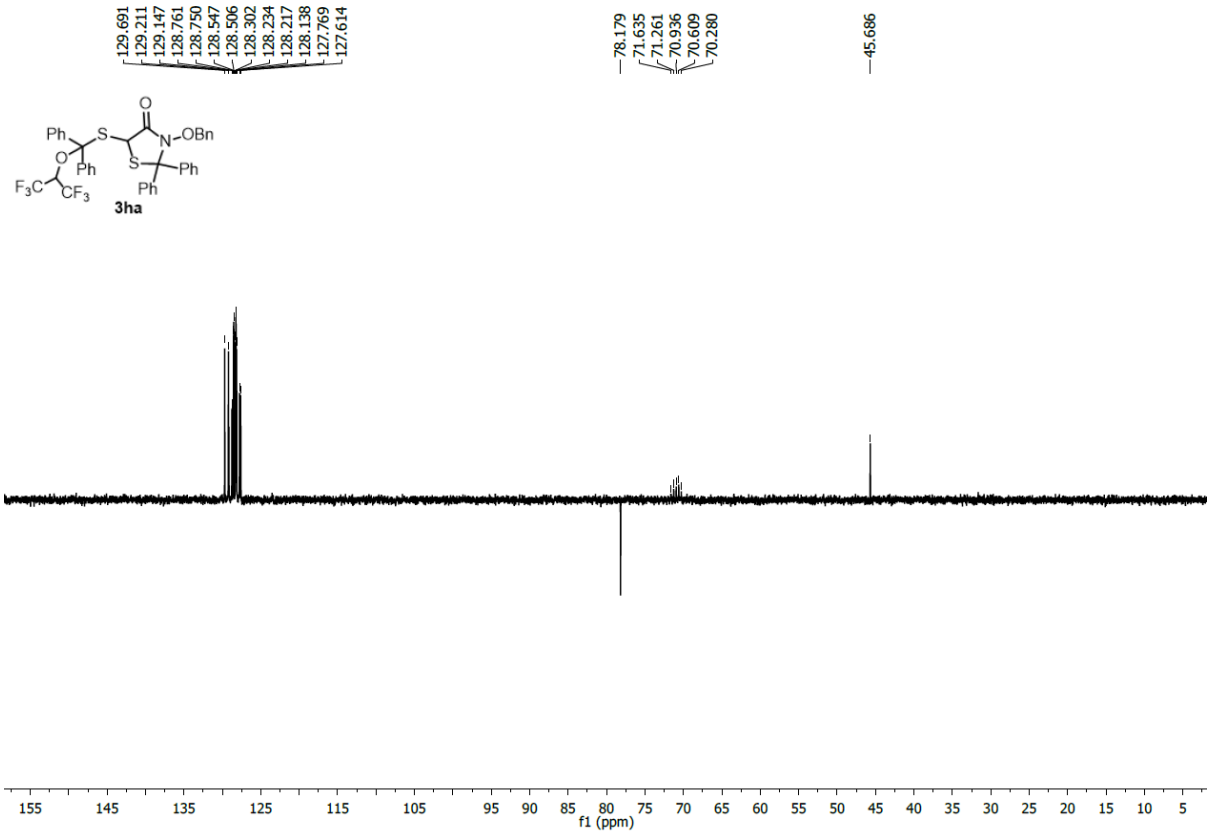
128.631
128.426
128.358
128.341
128.262
127.894
127.739
98.938
78.304
77.478
77.160 Chloroform-d
76.843
76.020
71.714
71.388
71.061
70.734
70.408
45.812
Ph
S
O
N
OBn
Ph
O
Ph
S
Ph
F3C
CF3
Ph
3ha
f1 (ppm)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129.147
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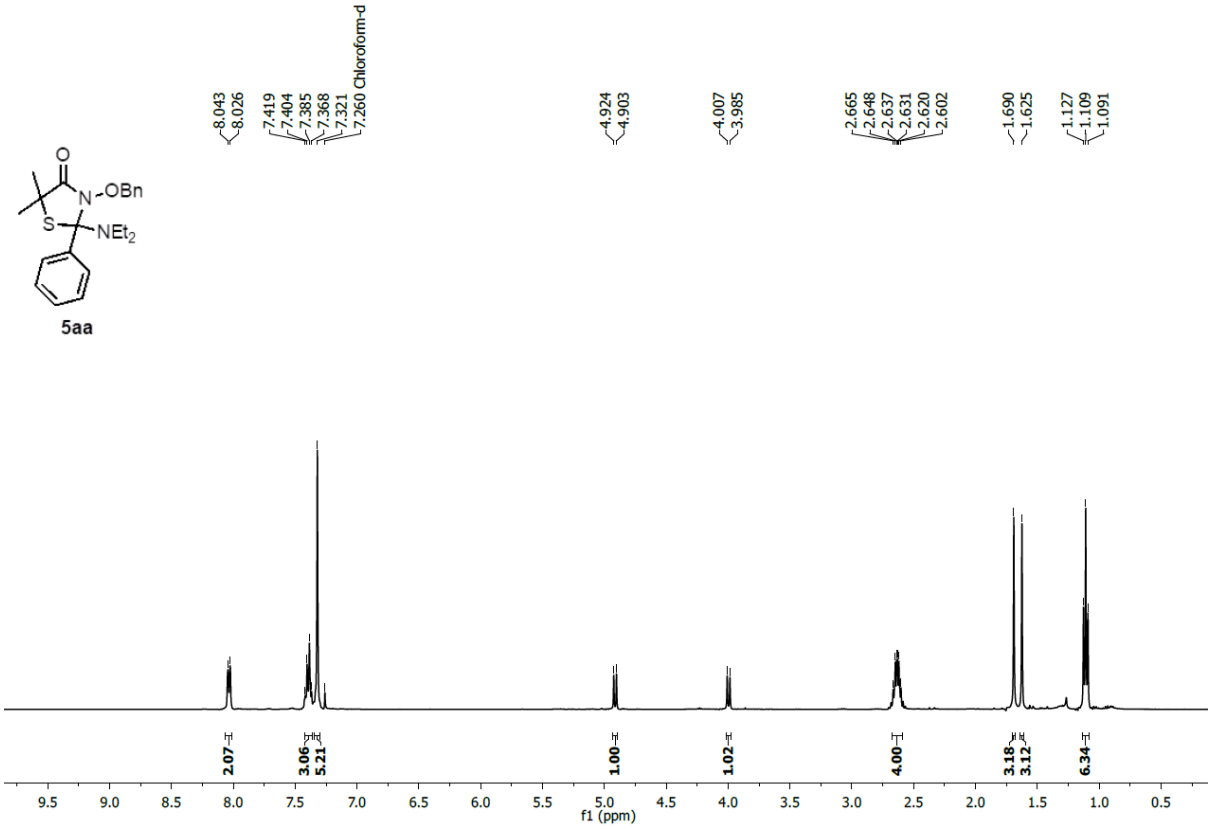
128.750
128.547
128.506
128.302
128.234
128.217
128.138
127.769
127.614
78.179
71.635
71.261
70.936
70.609
70.280
45.686
O
Ph
S
N
OBn
O
Ph
S
Ph
F3C
CF3
Ph
3ha
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)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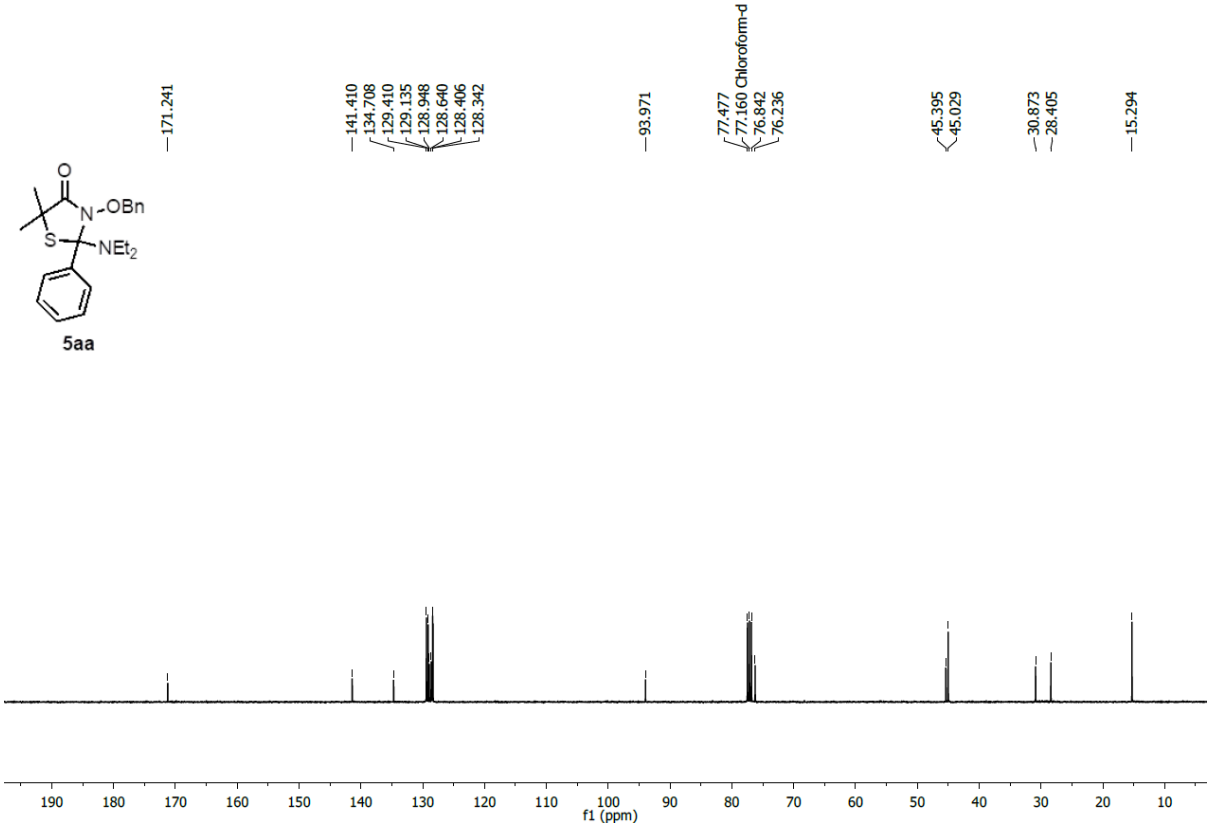
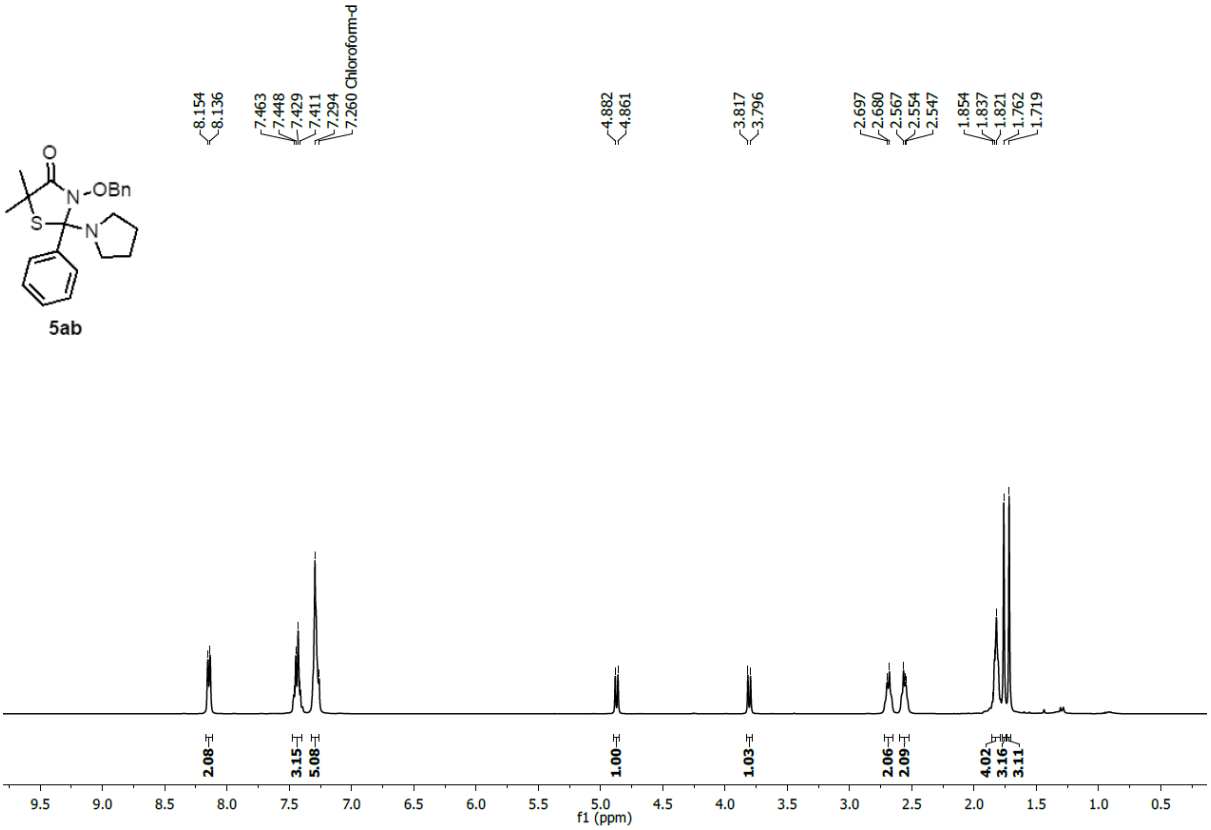
8.026
7.419
7.404
7.385
7.368
7.321
7.260 Chloroform-d
4.924
4.903
4.007
3.985
2.665
2.648
2.637
2.631
2.620
2.602
1.690
1.625
1.127
1.109
1.091
O
N-OBn
S
NEt2
5aa
2.07
3.06
5.21
1.00
1.02
4.00
3.18
3.12
6.34
f1 (ppm)


171.241
141.410
134.708
129.410
129.135
128.948
128.640
128.406
128.342
93.971
77.477
77.160 Chloroform-d
76.842
76.236
45.395
45.029
30.873
28.405
15.294
O
N-OBn
S
NEt2
5aa
f1 (ppm)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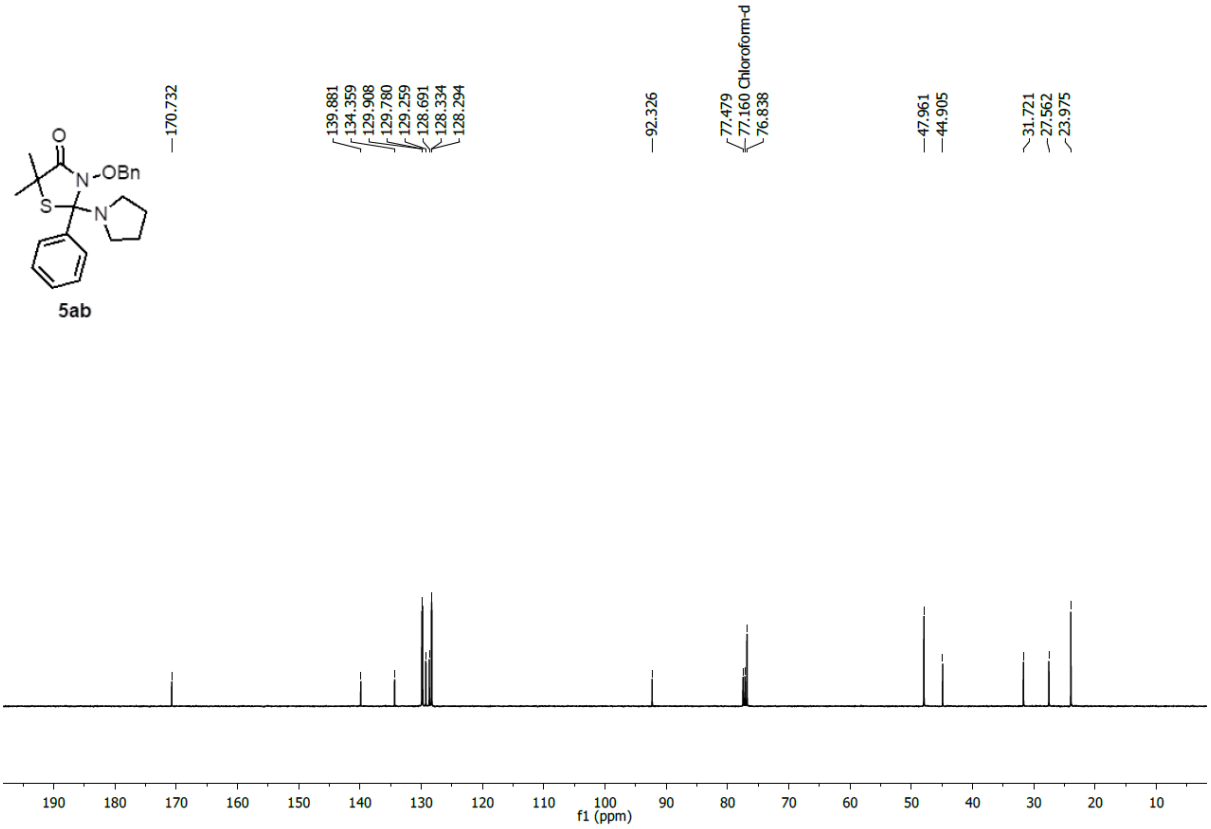
8.136
7.463
7.448
7.429
7.411
7.294
7.260 Chloroform-d
4.882
4.861
3.817
3.796
2.697
2.680
2.567
2.554
2.547
1.854
1.837
1.821
1.762
1.719
O
N-OBn
S
N
5ab
2.08
3.15
5.08
1.00
1.03
2.06
2.09
4.02
3.16
3.11
f1 (ppm)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134.359
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129.259
128.691
128.334
128.294
92.326
77.479
77.160 Chloroform-d
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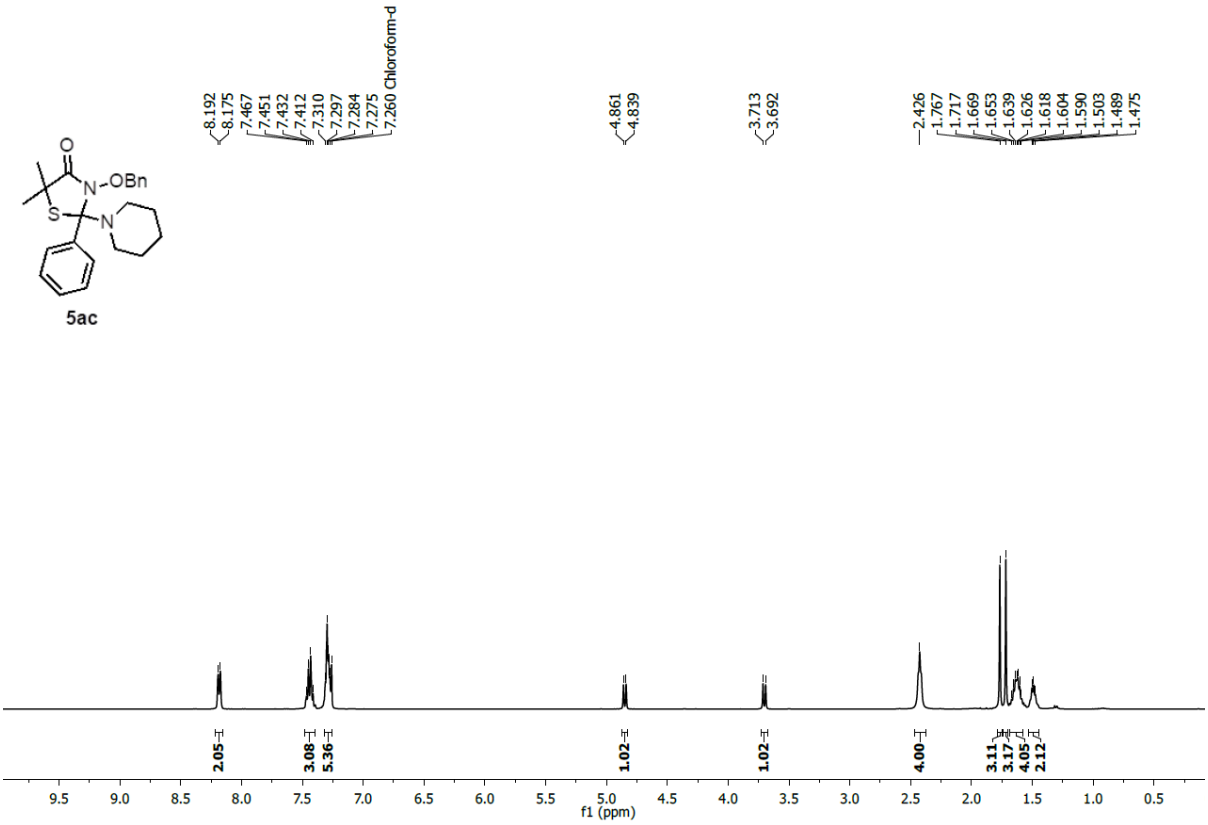
44.905
31.721
27.562
23.975
O
N-OBn
S
N
5ab
f1 (ppm)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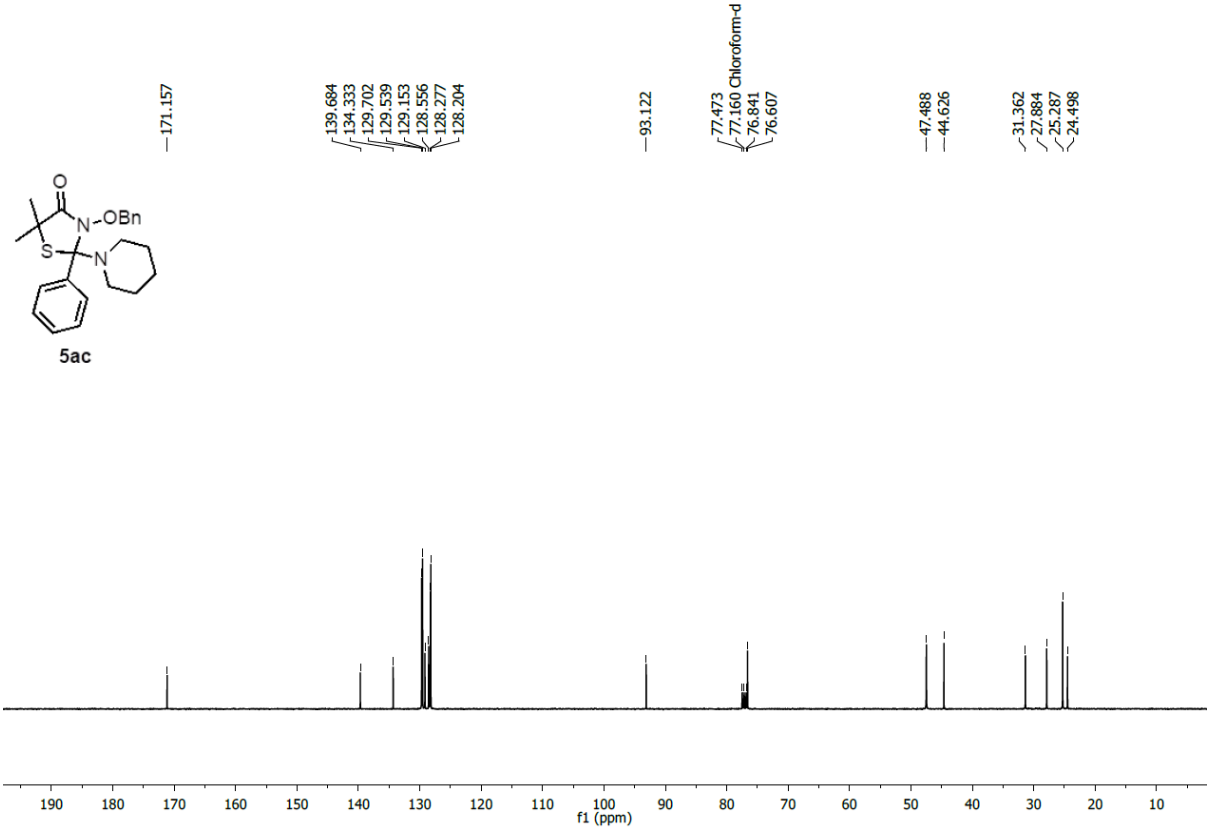
8.175
7.467
7.451
7.432
7.412
7.310
7.297
7.284
7.275
7.260 Chloroform-d
4.861
4.839
3.713
3.692
2.426
1.767
1.717
1.669
1.653
1.639
1.626
1.618
1.604
1.590
1.503
1.489
1.475
O
N-OBn
S
N
5ac
2.05
3.08
5.36
1.02
1.02
4.00
3.11
3.17
4.05
2.12
f1 (ppm)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77.473
77.160 Chloroform-d
76.841
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25.287
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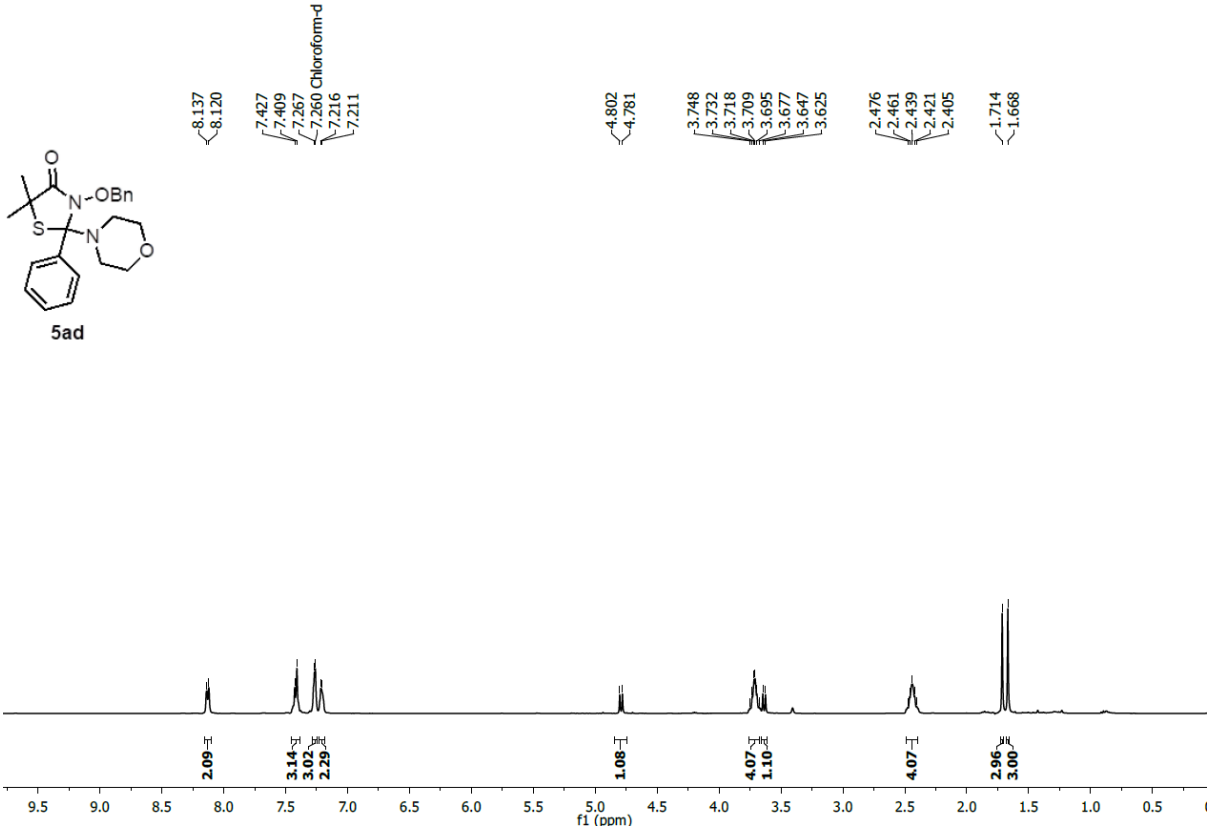
O
N-OBn
S
N
5ac
f1 (ppm)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7.267
7.260 Chloroform-d
7.216
7.211
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4.781
3.748
3.732
3.718
3.709
3.695
3.677
3.647
3.625
2.476
2.461
2.439
2.421
2.405
1.714
1.668
O
N-OBn
S
N
O
5ad
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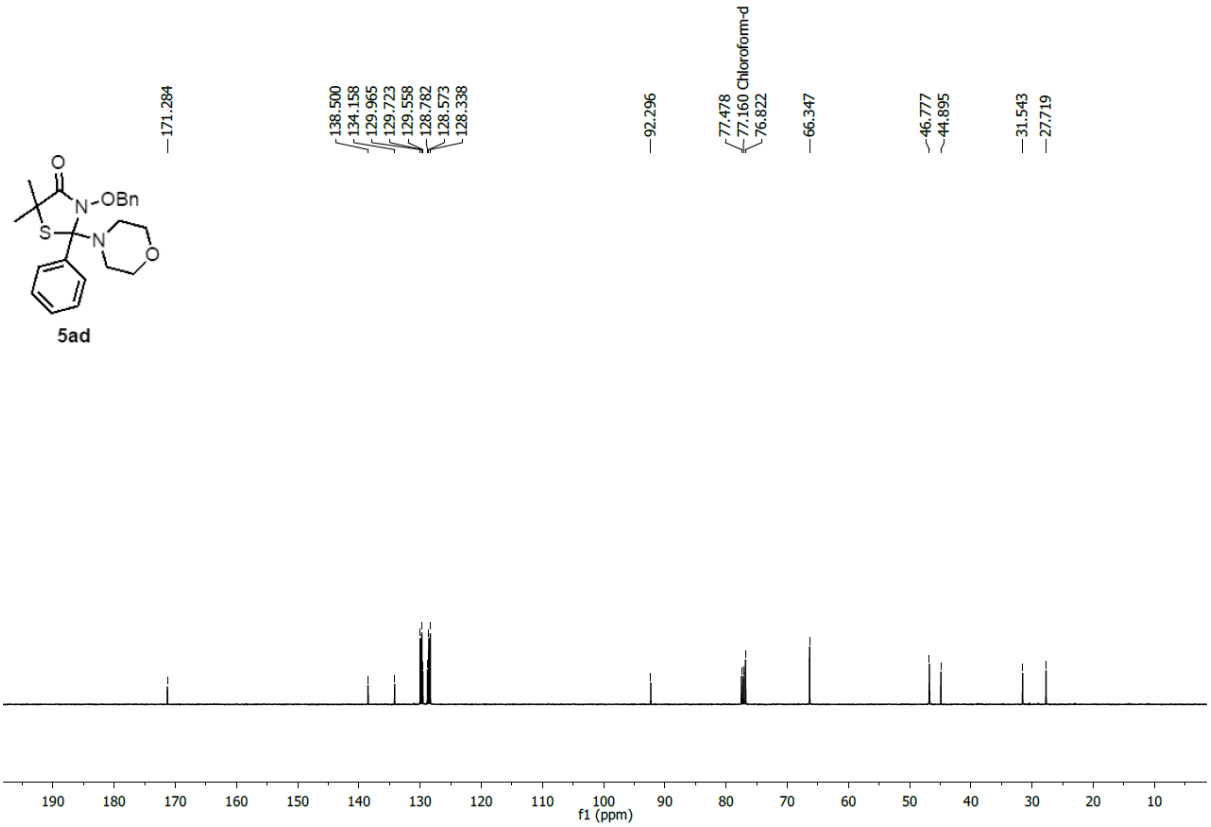
3.14
3.02
2.29
1.08
4.07
1.10
4.07
2.96
3.00
f1 (ppm)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128.573
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92.296
77.478
77.160 Chloroform-d
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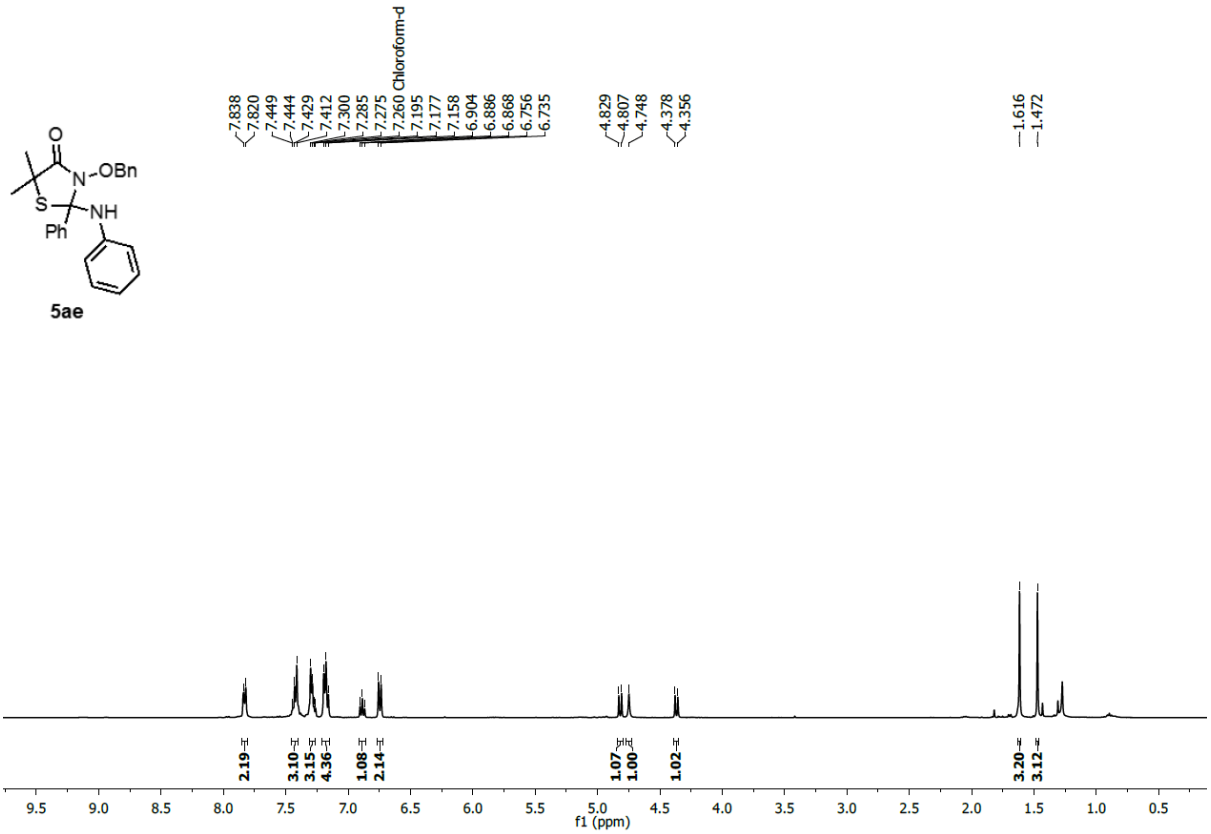
O
N-OBn
S
N
O
5ad
f1 (ppm)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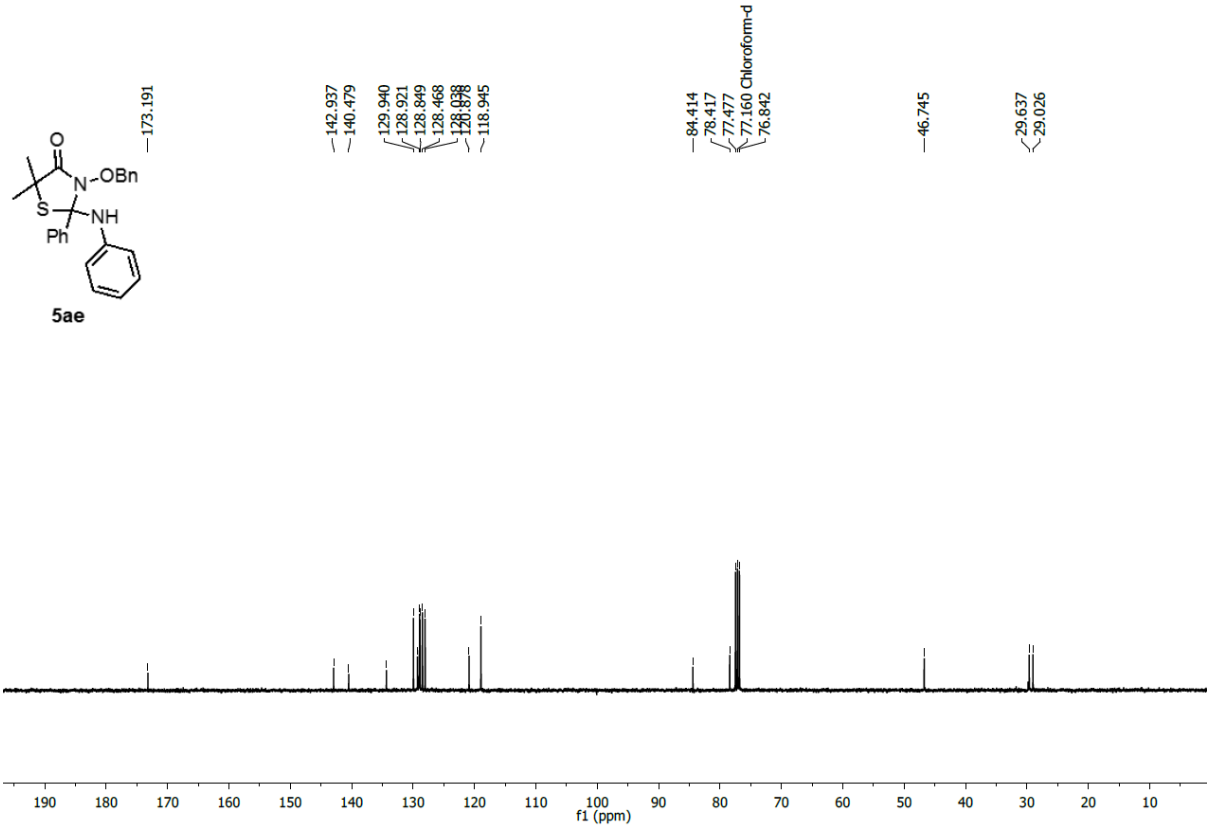
7.444
7.429
7.412
7.300
7.285
7.275
7.260 Chloroform-d
7.195
7.177
7.158
6.904
6.886
6.868
6.756
6.735
4.829
4.807
4.748
4.378
4.356
1.616
1.472
O
N-OBn
S
NH
Ph
5ae
2.19
3.10
3.15
4.36
1.08
2.14
1.07
1.00
1.02
3.20
3.12
f1 (ppm)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128.921
128.849
128.468
118.945
84.414
78.417
77.477
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76.842
46.745
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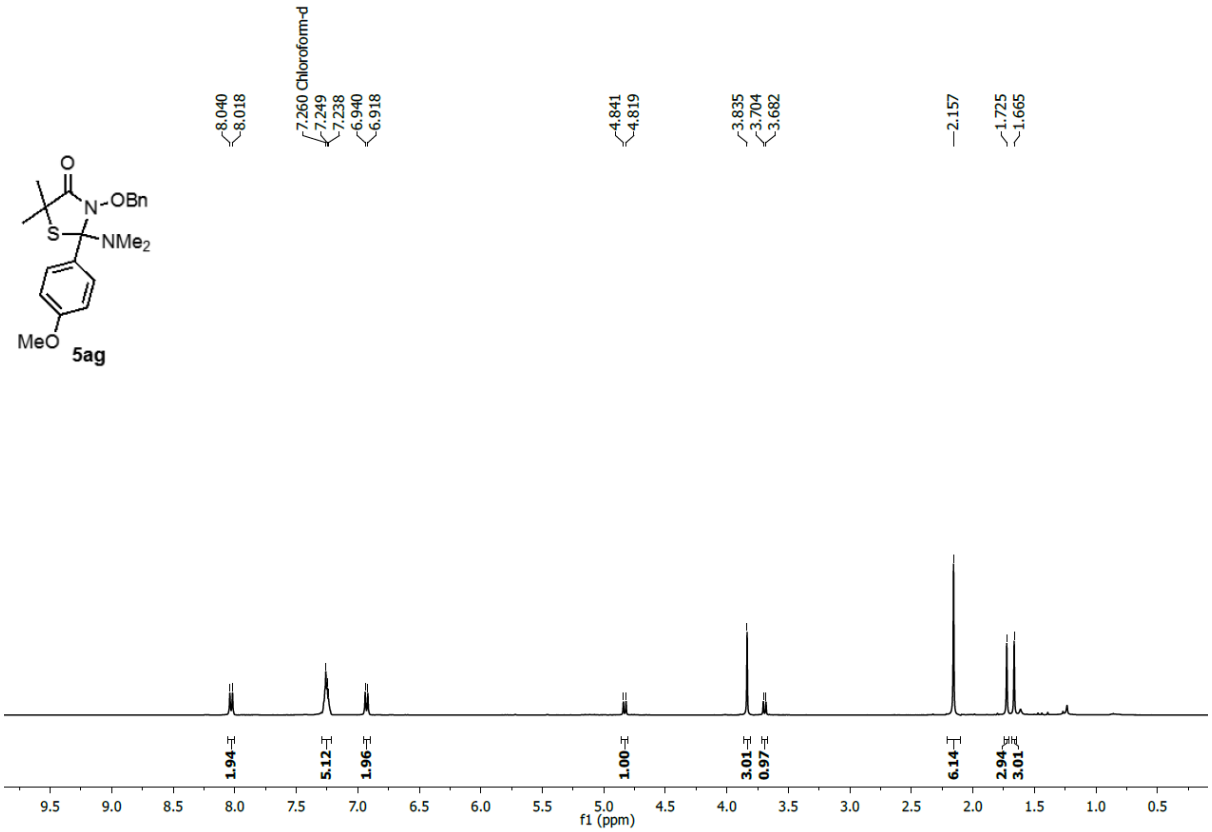
O
N-OBn
S
NH
Ph
5ae
f1 (ppm)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6.918
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4.819
3.835
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2.157
1.725
1.665
O
N-OBn
S
NMe2
MeO
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1.96
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6.14
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3.01
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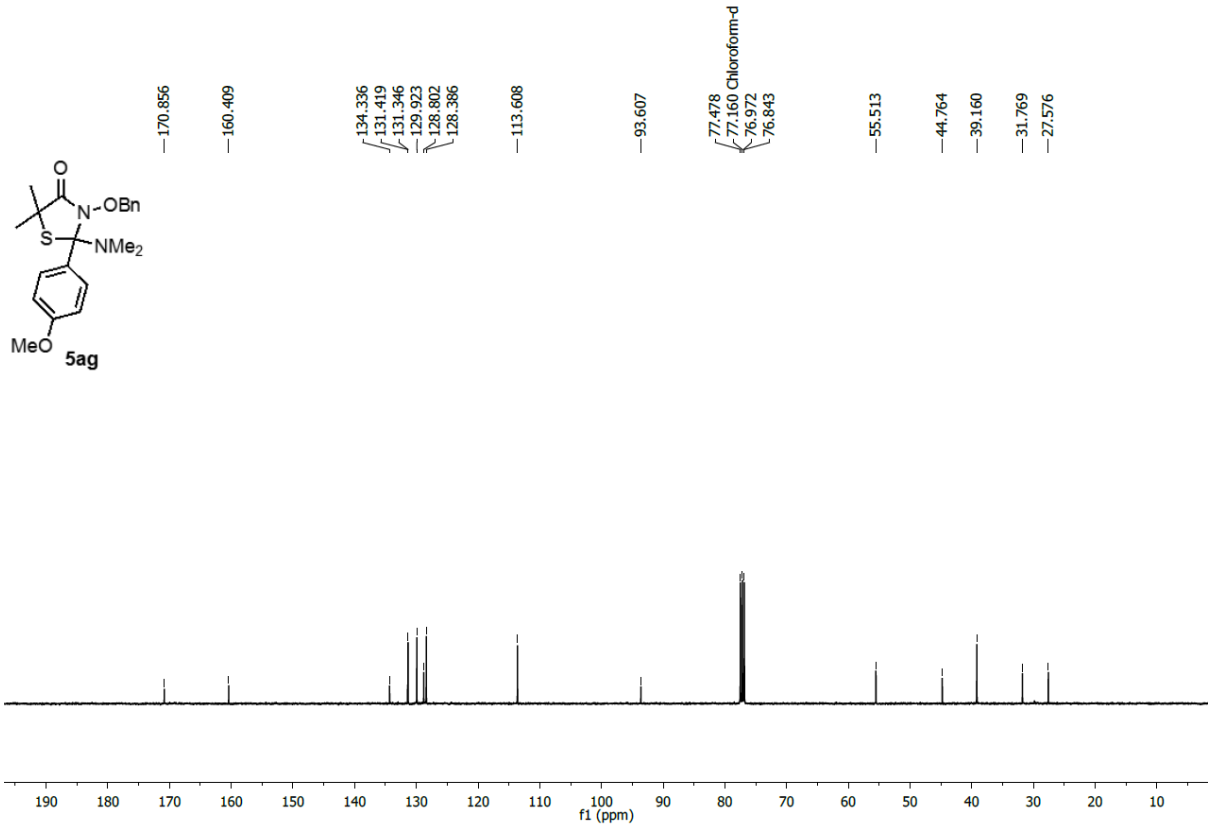
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131.419
131.346
129.923
128.802
128.386
113.608
93.607
77.478
77.160 Chloroform-d
76.972
76.843
55.513
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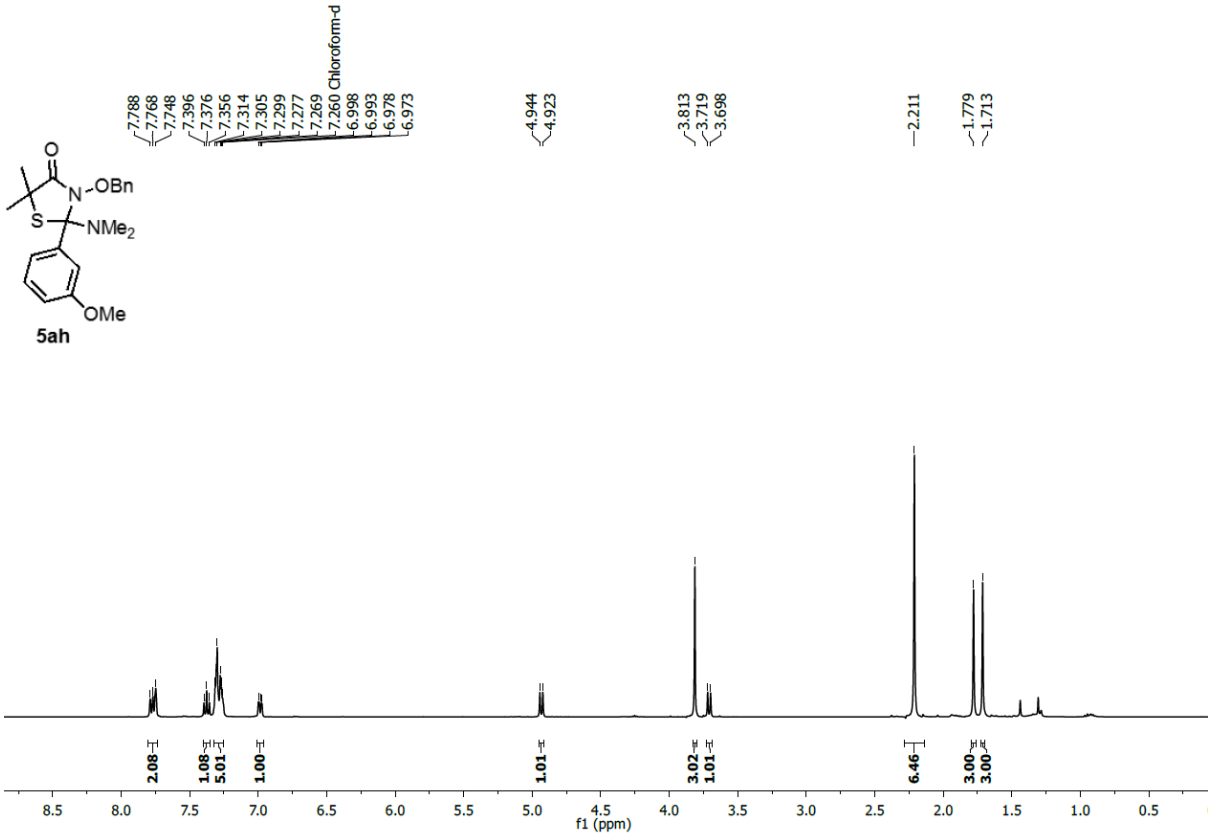
39.160
31.769
27.576
O
N-OBn
S
NMe2
MeO
5ag
f1 (ppm)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7.356
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7.305
7.299
7.277
7.269
7.260 Chloroform-d
6.998
6.993
6.978
6.973
4.944
4.923
3.813
3.719
3.698
2.211
1.779
1.713
O
N
OBn
S
NMe2
OMe
5ah
2.08
1.08
5.01
1.00
1.01
3.02
1.01
6.46
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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1.5
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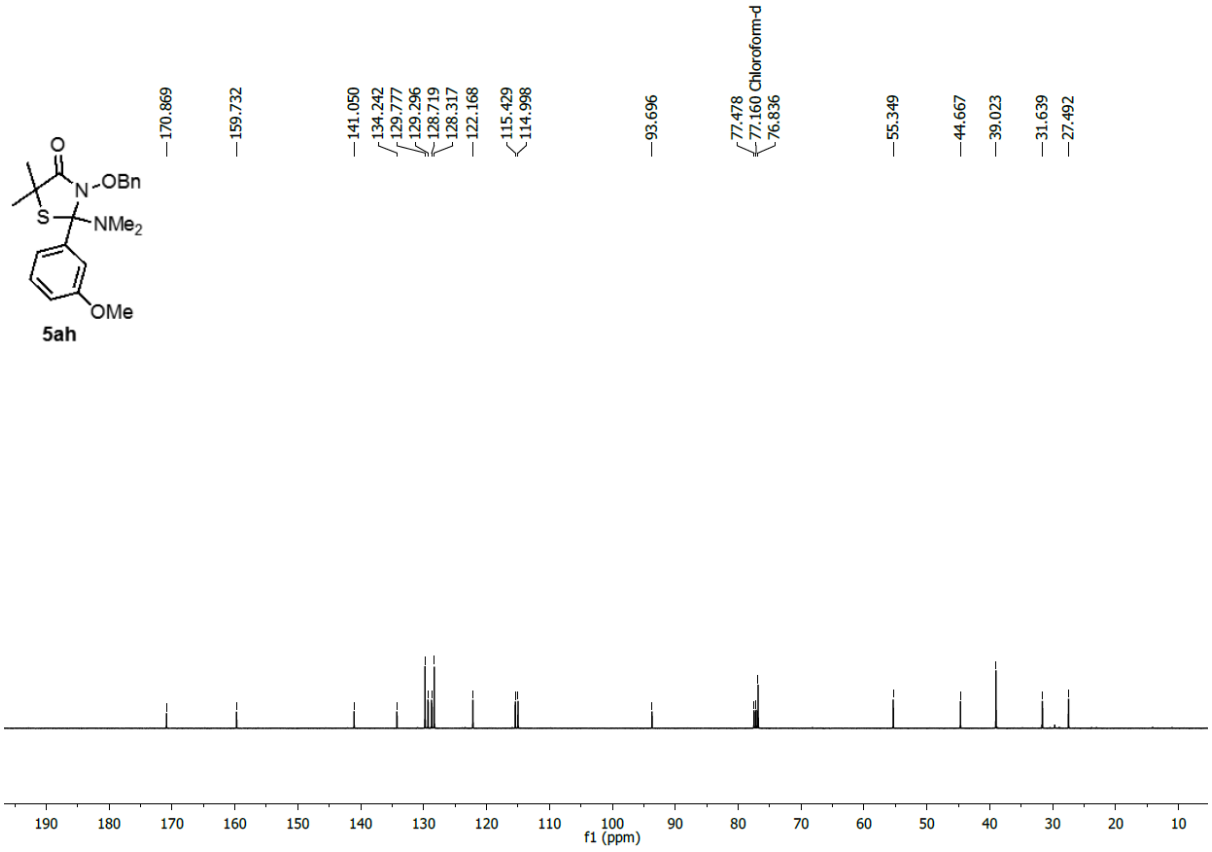
f1 (ppm)


170.869
159.732
141.050
134.242
129.777
129.296
128.719
128.317
122.168
115.429
114.998
93.696
77.478
77.160 Chloroform-d
76.836
55.349
44.667
39.023
31.639
27.492
O
N
OBn
S
NMe2
OMe
5ah
190
180
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120
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100
90
80
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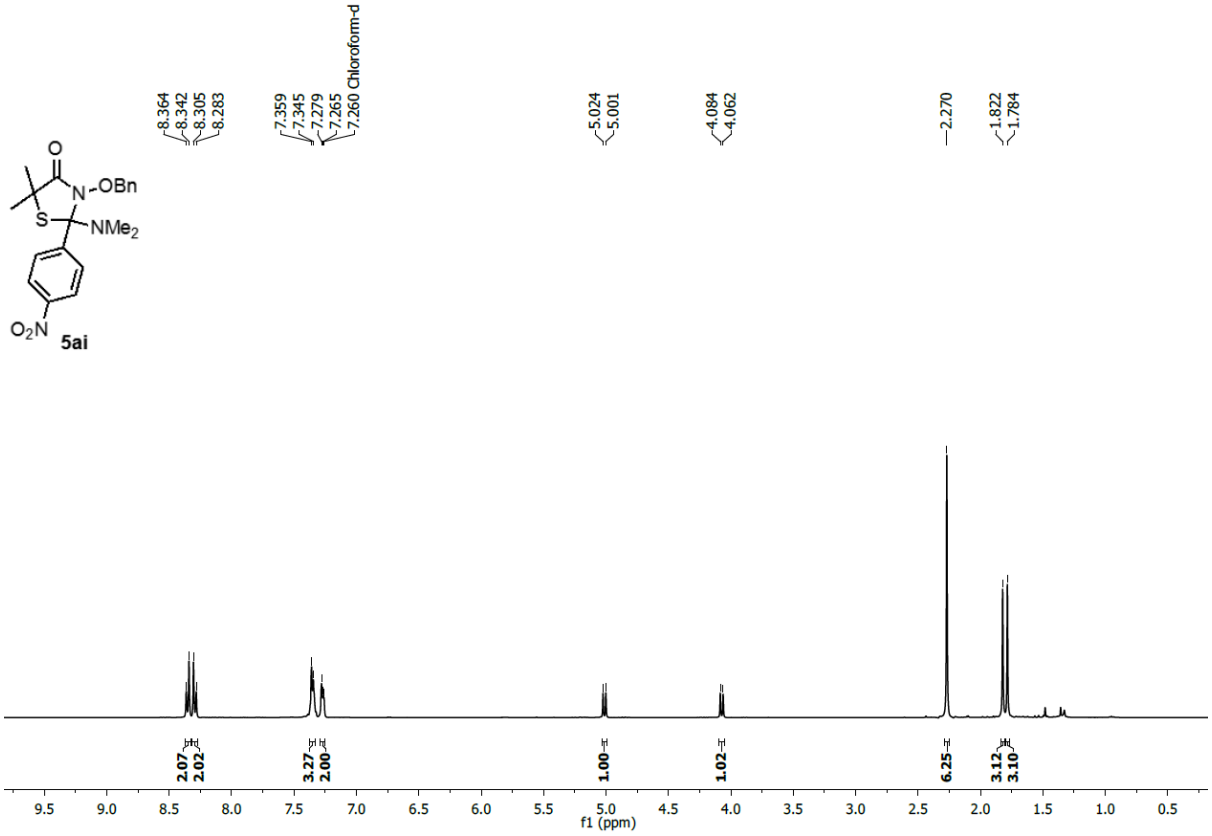
60
50
40
30
20
10
f1 (ppm)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8.283
7.359
7.345
7.279
7.265
7.260 Chloroform-d
5.024
5.001
4.084
4.062
2.270
1.822
1.784
O
N
OBn
S
NMe2
O2N
5ai
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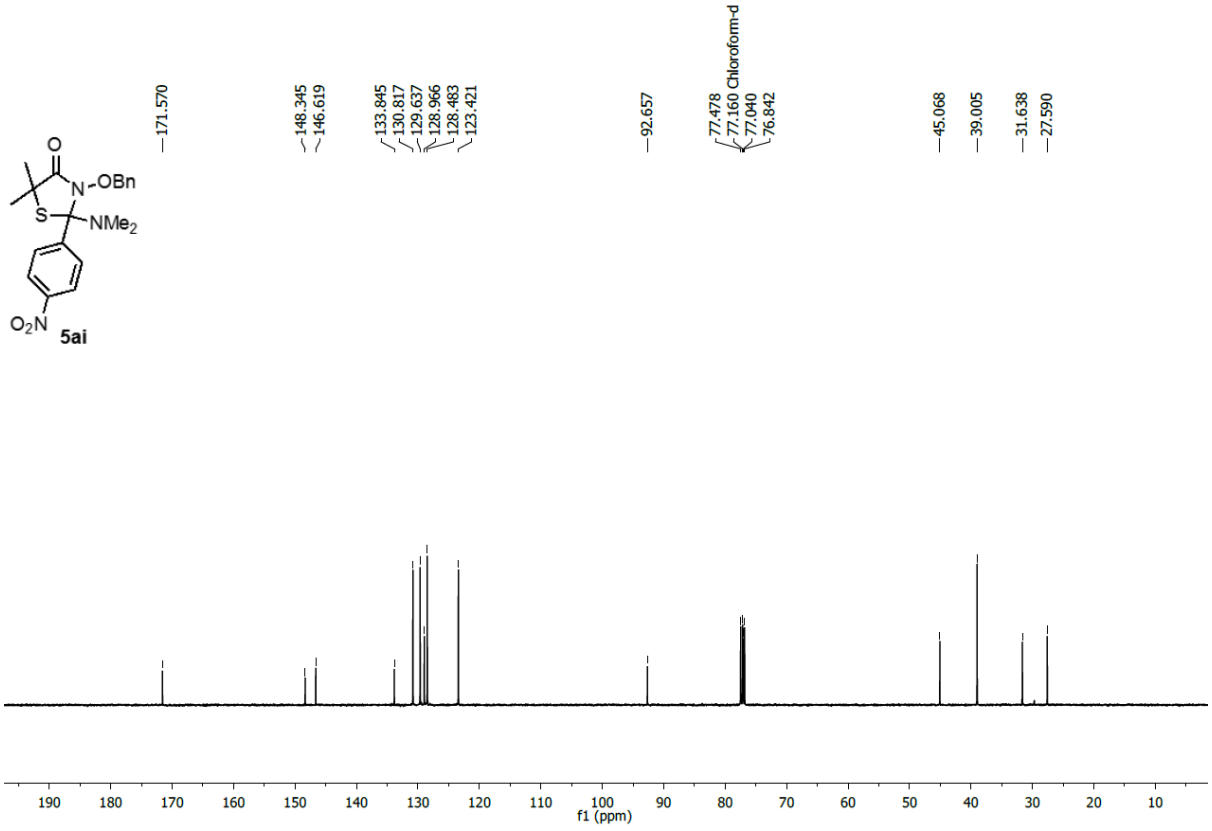
2.02
3.27
2.00
1.00
1.02
6.25
3.12
3.10
f1 (ppm)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77.160 Chloroform-d
77.040
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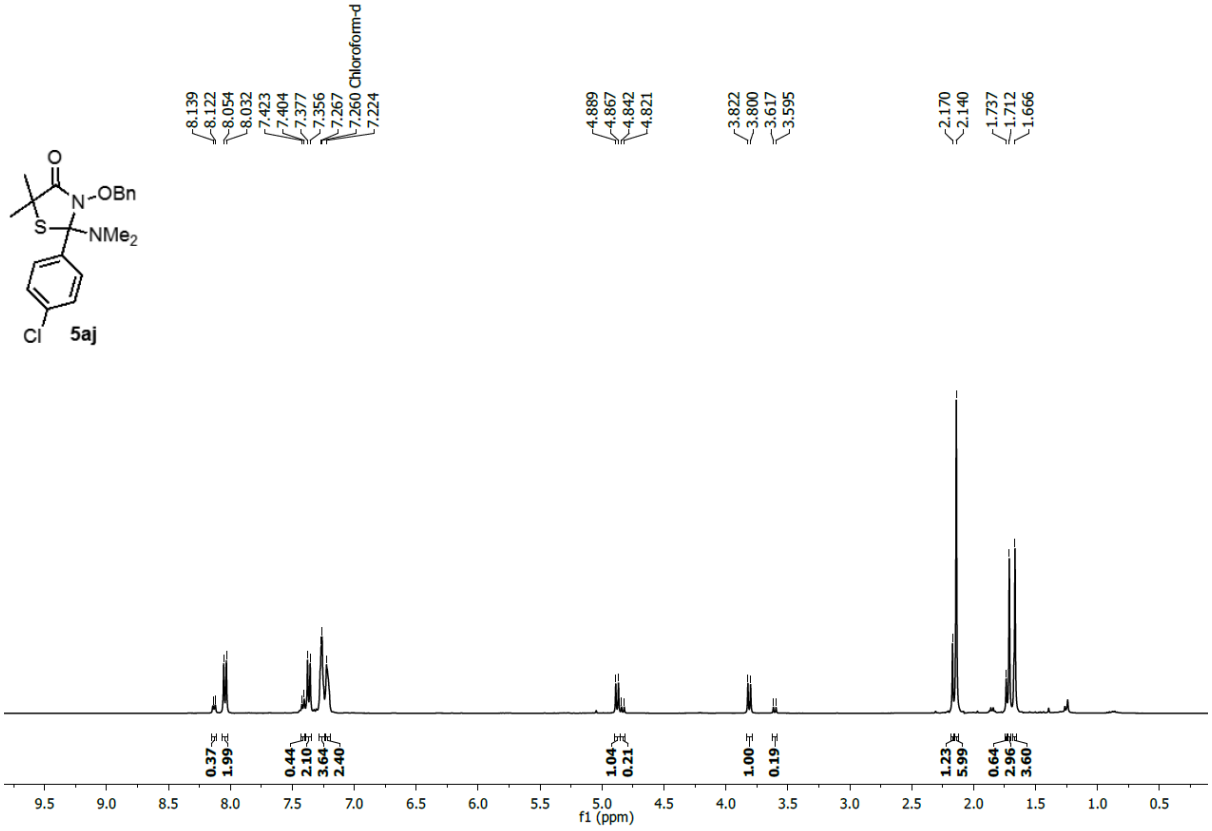
39.005
31.638
27.590
O
N
OBn
S
NMe2
O2N
5ai
f1 (ppm)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8.032
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7.404
7.377
7.356
7.267
7.260 Chloroform-d
7.224
4.889
4.867
4.842
4.821
3.822
3.800
3.617
3.595
2.170
2.140
1.737
1.712
1.666
O
N
OBn
S
NMe2
Cl
5aj
0.37
1.99
0.44
2.10
3.64
2.40
1.04
0.21
1.00
0.19
1.23
5.99
0.64
2.96
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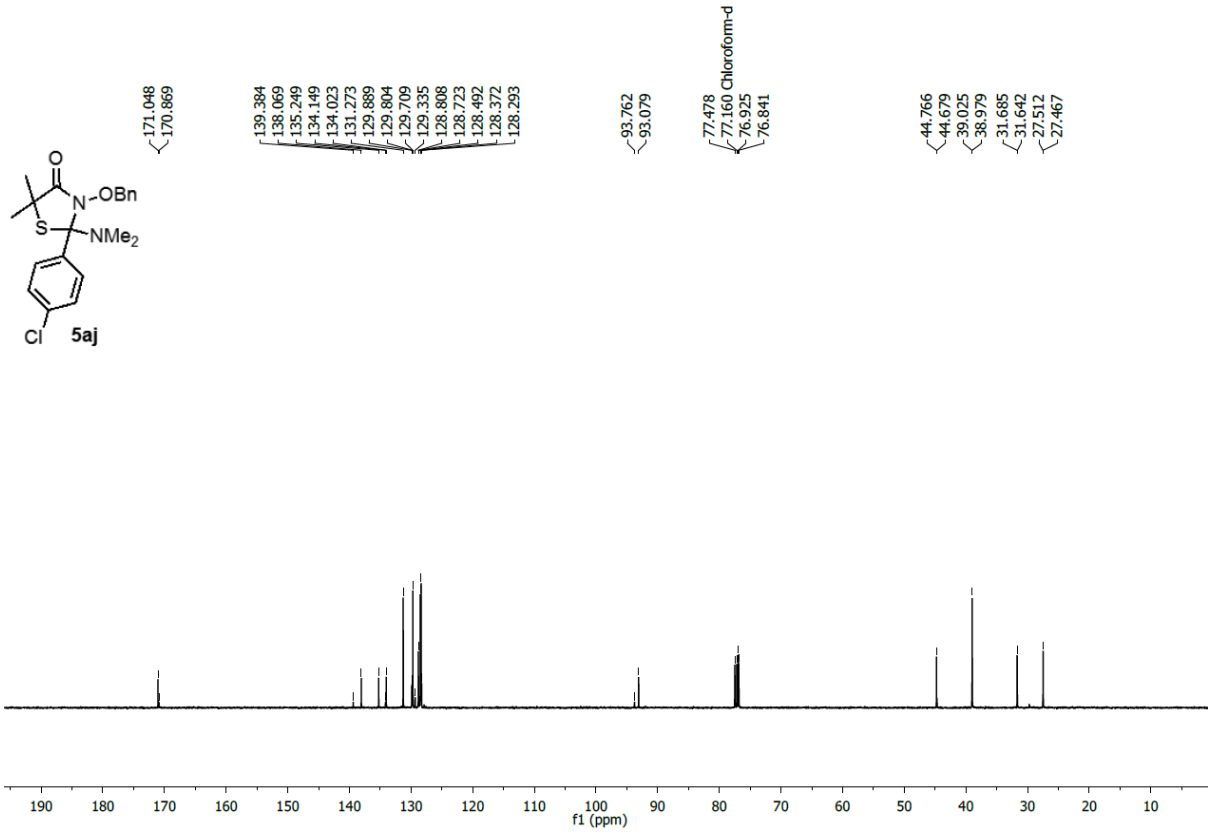
f1 (ppm)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128.808
128.723
128.492
128.372
128.293
93.762
93.079
77.478
77.160 Chloroform-d
76.925
76.841
44.766
44.679
39.025
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31.642
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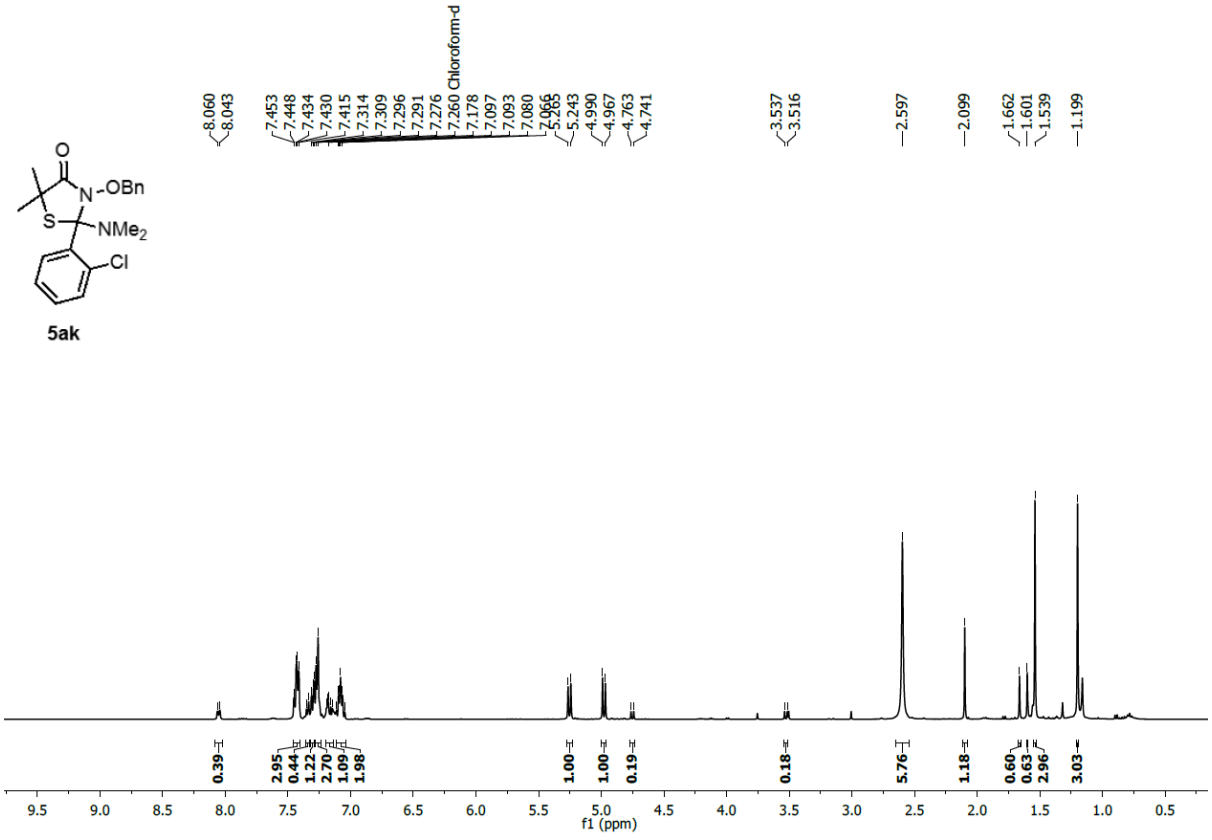
27.467
O
N
OBn
S
NMe2
Cl
5aj
f1 (ppm)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7.415
7.314
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7.276
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7.178
7.097
7.093
7.080
7.066
5.265
5.243
4.990
4.967
4.763
4.741
3.537
3.516
2.597
2.099
1.662
1.601
1.539
1.199
O
N-OBn
S
NMe2
Cl
0.39
2.95
0.44
1.22
2.70
1.09
1.98
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1.00
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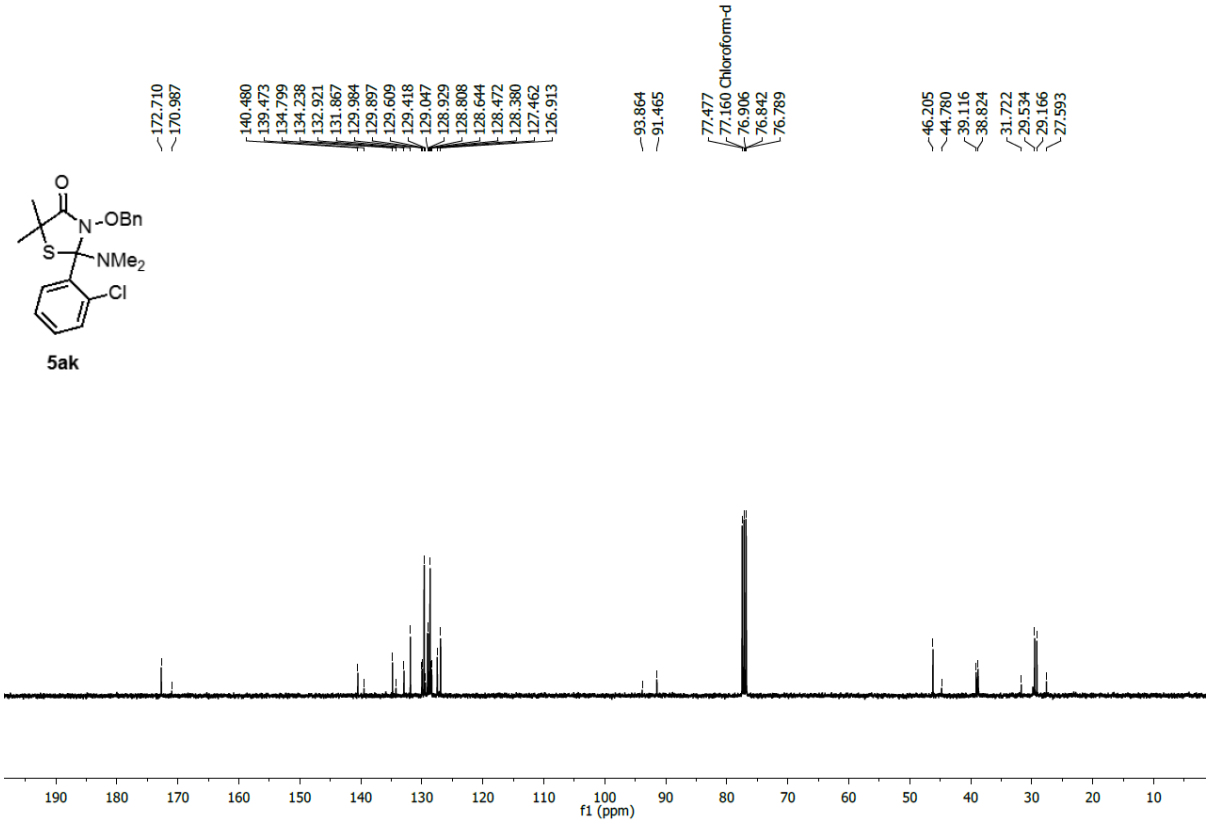
0.18
5.76
1.18
0.60
0.63
2.96
3.03
f1 (ppm)

5ak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128.929
128.808
128.644
128.472
128.380
127.462
126.913
93.864
91.465
77.477
77.160 Chloroform-d
76.906
76.842
76.789
46.205
44.780
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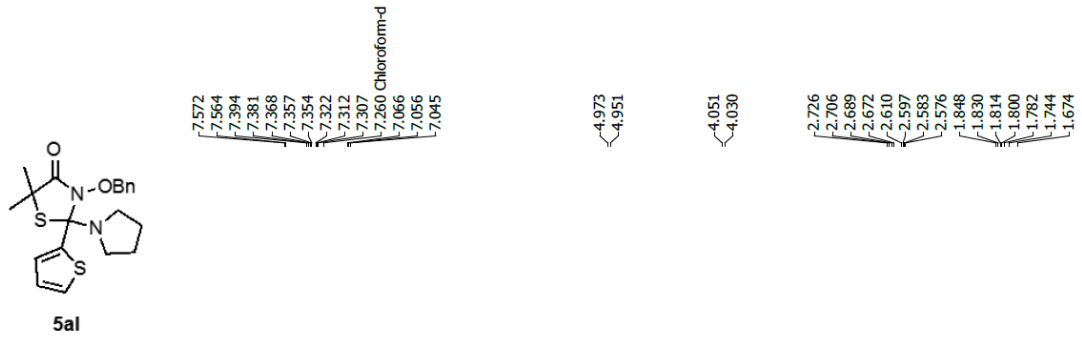
27.593
O
N-OBn
S
NMe2
Cl
f1 (ppm)

5ak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7.394
7.381
7.368
7.357
7.354
7.322
7.312
7.307
7.260 Chloroform-d
7.066
7.056
7.045
4.973
4.951
4.051
4.030
2.726
2.706
2.689
2.672
2.610
2.597
2.583
2.576
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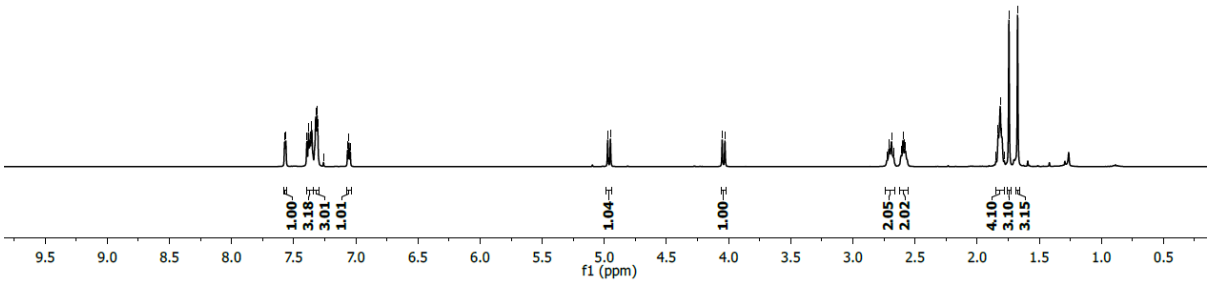
1.814
1.800
1.782
1.744
1.674
O
N
OBn
S
N
S

5al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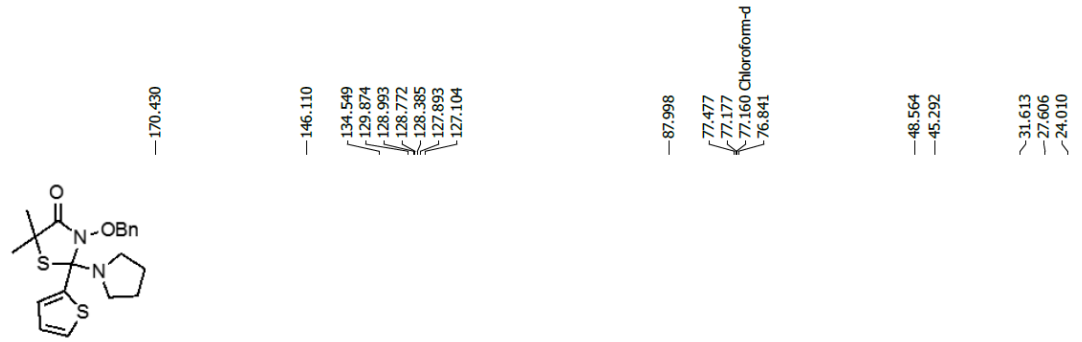
3.18
3.01
1.01
1.04
1.00
2.05
2.02
4.10
3.10
3.15
f1 (ppm)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129.874
128.993
128.772
128.385
127.893
127.104
87.998
77.477
77.177
77.160 Chloroform-d
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48.564
45.292
31.613
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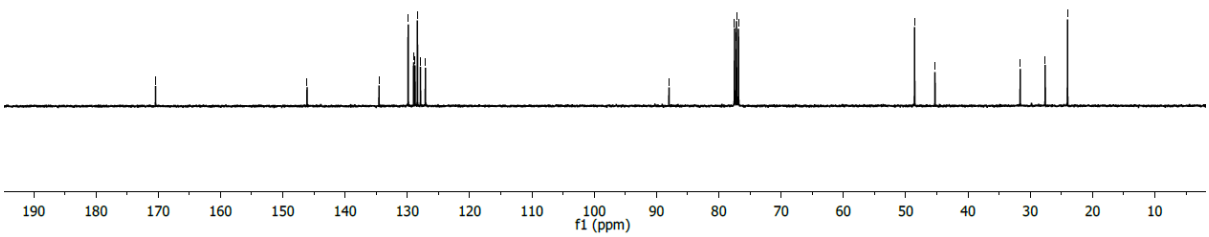
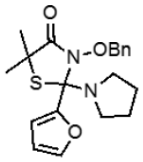
24.010
O
N
OBn
S
N
S

5al


f1 (ppm)


O
N-OBn
S
N
O

5am

7.513
7.365
7.352
7.290
7.281
7.276
7.260 Chloroform-d
6.755
6.747
6.417
4.884
4.861
4.272
4.248
2.740
2.721
2.703
2.685
2.617
2.605
2.592
2.583
1.862
1.845
1.827
1.796
1.667
1.638
1.00
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1.00
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1.06
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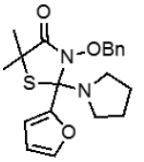
2.10
4.29
3.11
3.15
f1 (ppm)


O
N-OBn
S
N
O

5am

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143.217
134.576
129.846
128.699
128.268
112.185
110.989
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77.478
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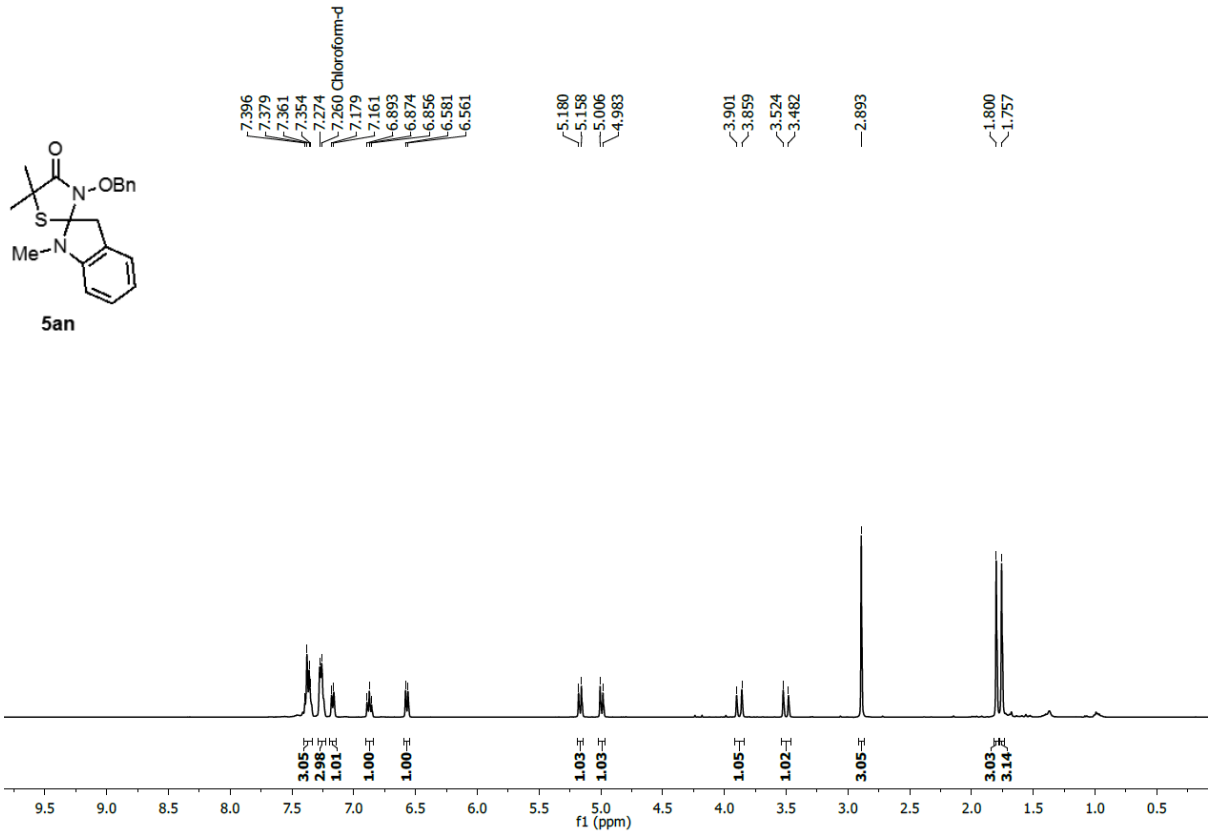
77.160 Chloroform-d
76.842
47.954
45.070
31.535
27.678
24.051
f1 (ppm)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7.274
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7.179
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6.874
6.856
6.581
6.561
5.180
5.158
5.006
4.983
3.901
3.859
3.524
3.482
2.893
1.800
1.757
O
N-OBn
S
Me-N
5an
3.05
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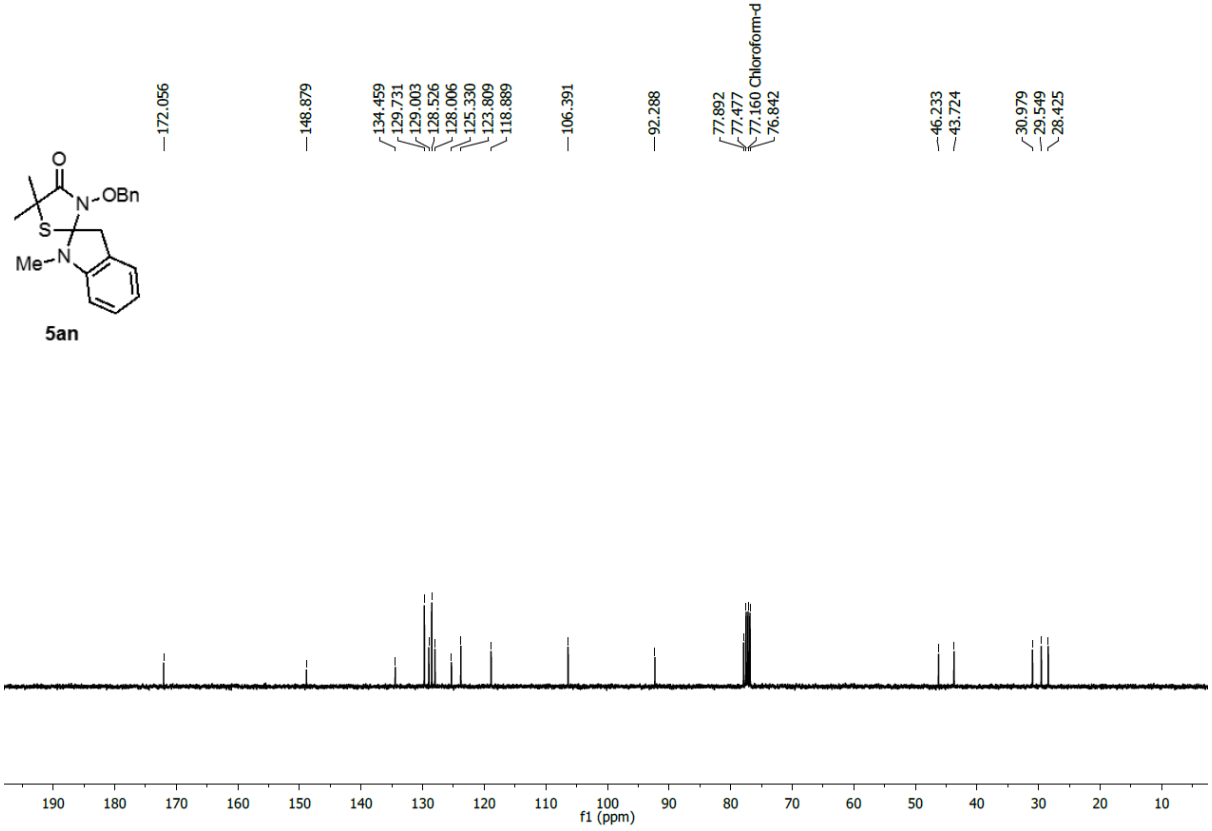
1.01
1.00
1.00
1.03
1.03
1.05
1.02
3.05
3.03
3.14
f1 (ppm)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125.330
123.809
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77.892
77.477
77.160 Chloroform-d
76.842
46.233
43.724
30.979
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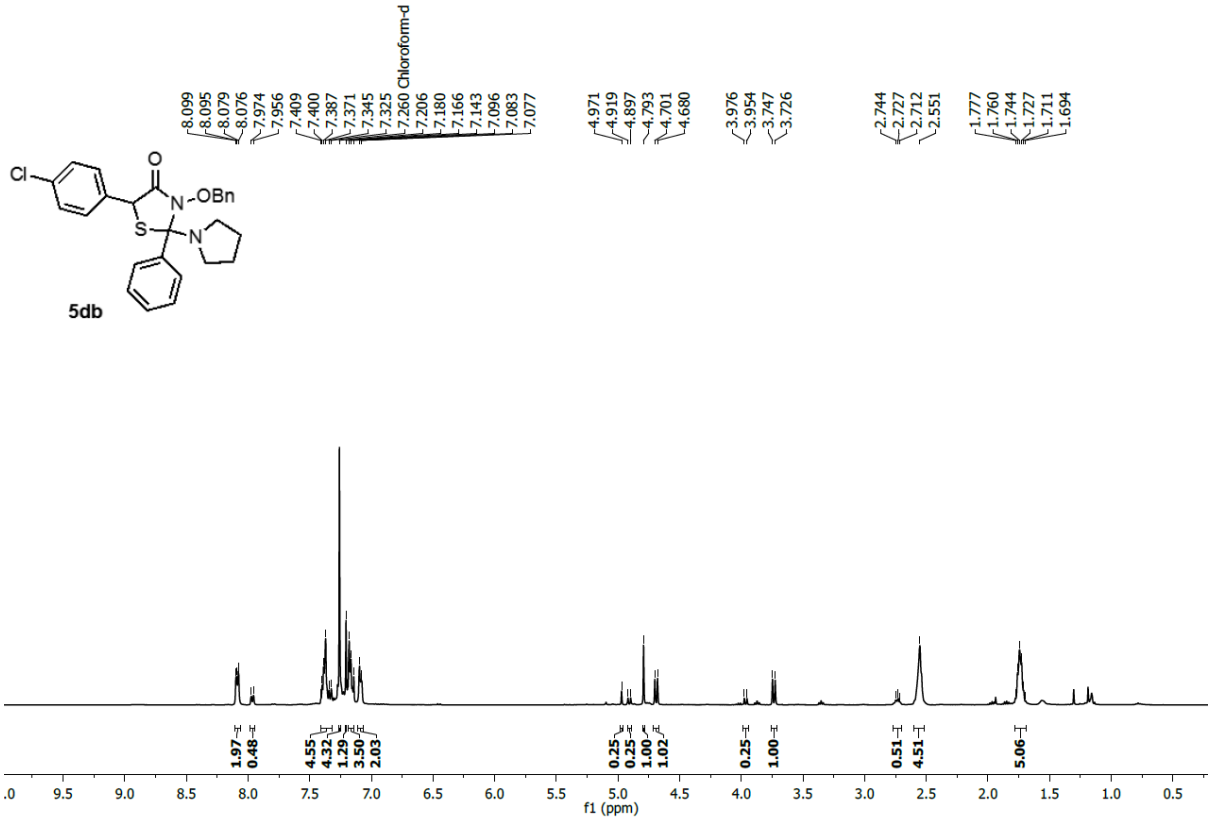
28.425
O
N-OBn
S
Me-N
5an
f1 (ppm)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7.400
7.387
7.371
7.345
7.325
7.260 Chloroform-d
7.206
7.180
7.166
7.143
7.096
7.083
7.077
4.971
4.919
4.897
4.793
4.701
4.680
3.976
3.954
3.747
3.726
2.744
2.727
2.712
2.551
1.777
1.760
1.744
1.727
1.711
1.694
Cl
O
N
OBn
S
N
5db
1.97
0.48
4.55
4.32
1.29
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0.25
1.00
1.02
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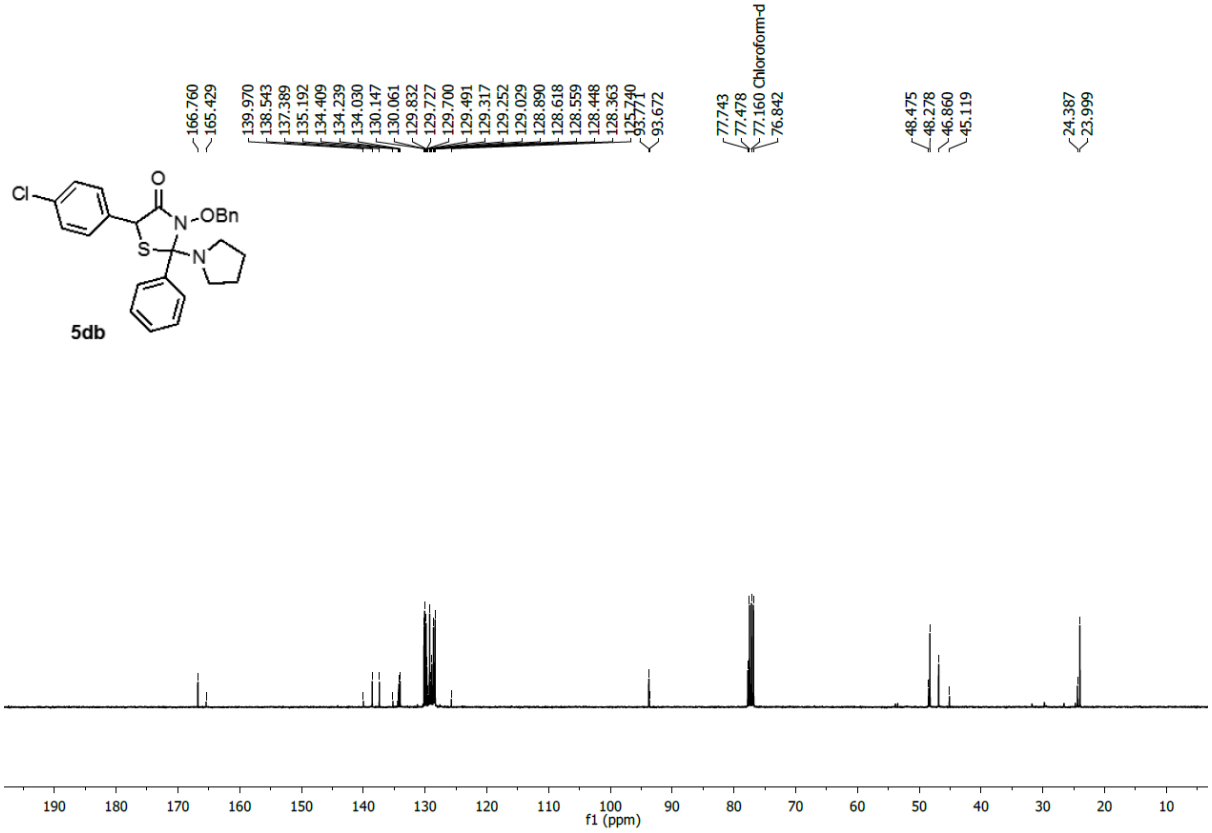
1.00
0.51
4.51
5.06
f1 (ppm)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134.239
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130.147
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129.700
129.491
129.317
129.252
129.029
128.890
128.618
128.559
128.448
128.363
125.740
93.771
93.672
77.743
77.478
77.160 Chloroform-d
76.842
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N
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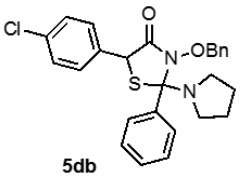
5db
f1 (ppm)


Cl
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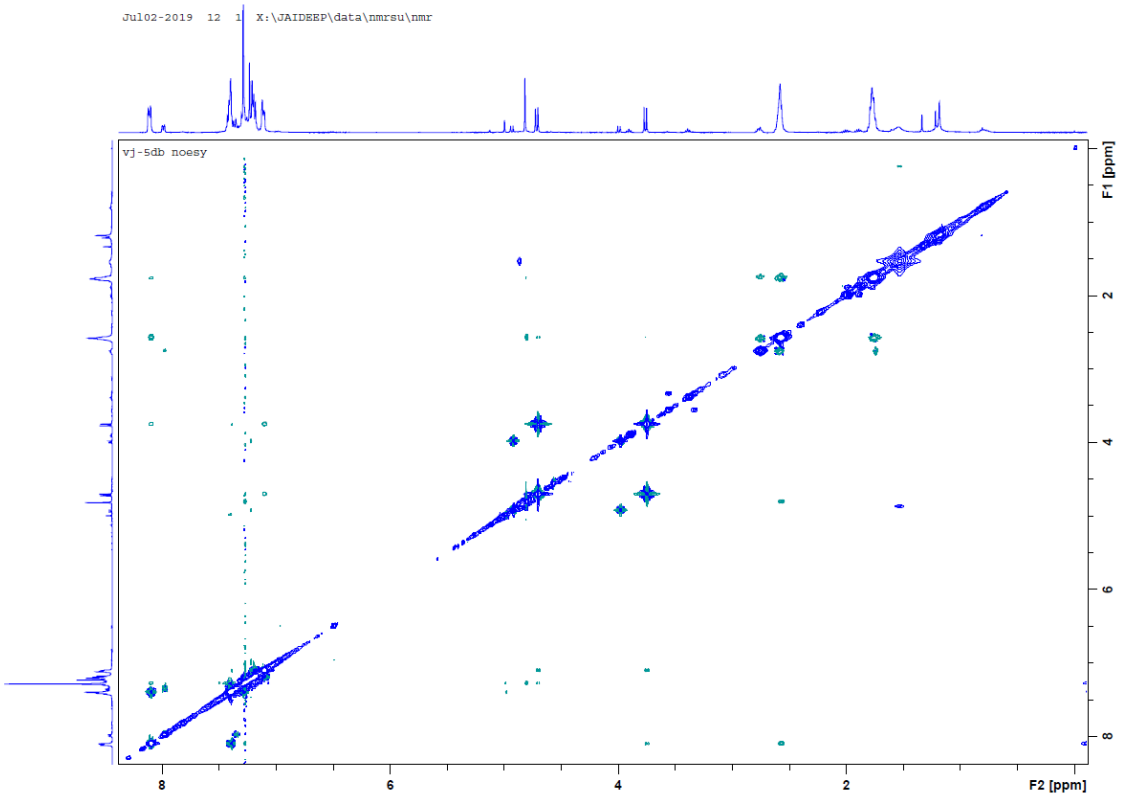
N
OBn
S
N

5db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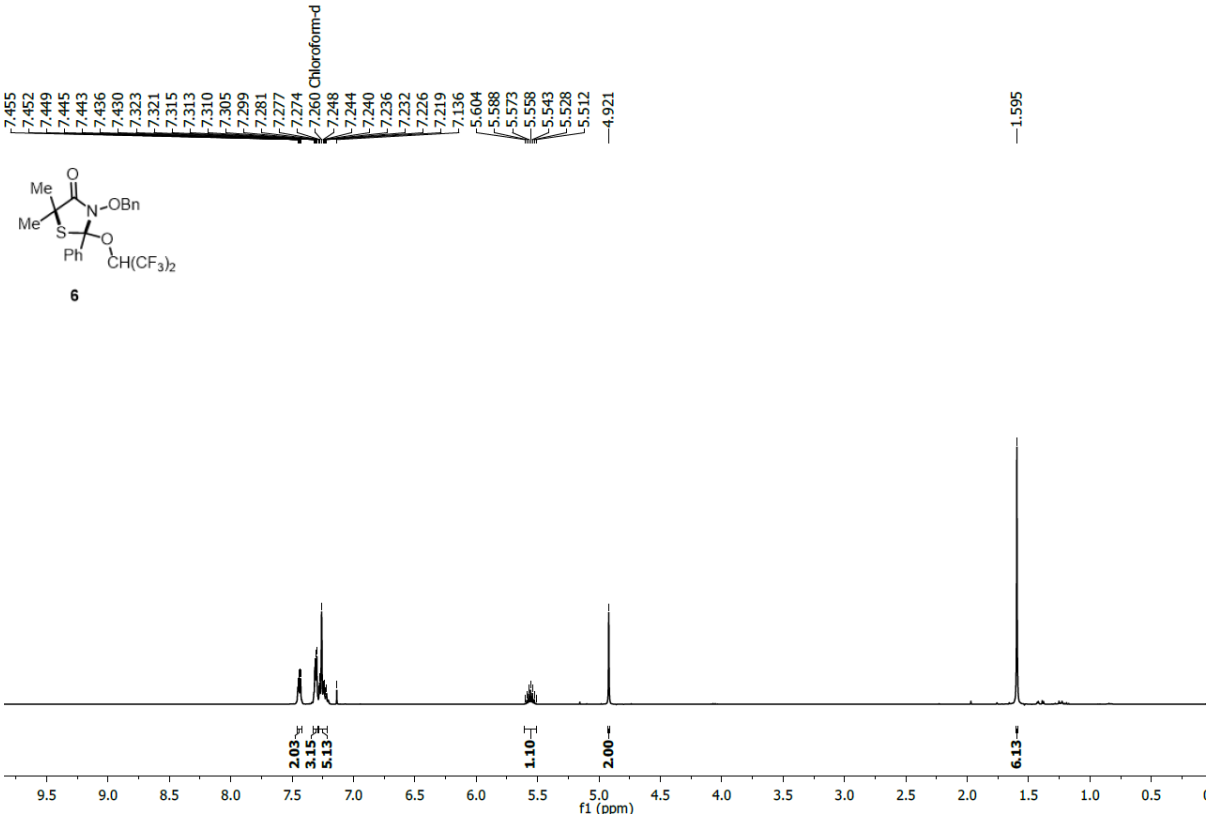
vj-5db noesy
F1 [ppm]
F2 [ppm]
8
6
4
2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7.299
7.281
7.277
7.274
7.260 Chloroform-d
7.248
7.244
7.240
7.236
7.232
7.226
7.219
7.136
5.604
5.588
5.573
5.558
5.543
5.528
5.512
4.921
1.595
Me
O
N
OBn
Me
S
Ph
O
CH(CF3)2
6
2.03
3.15
5.13
1.10
2.00
6.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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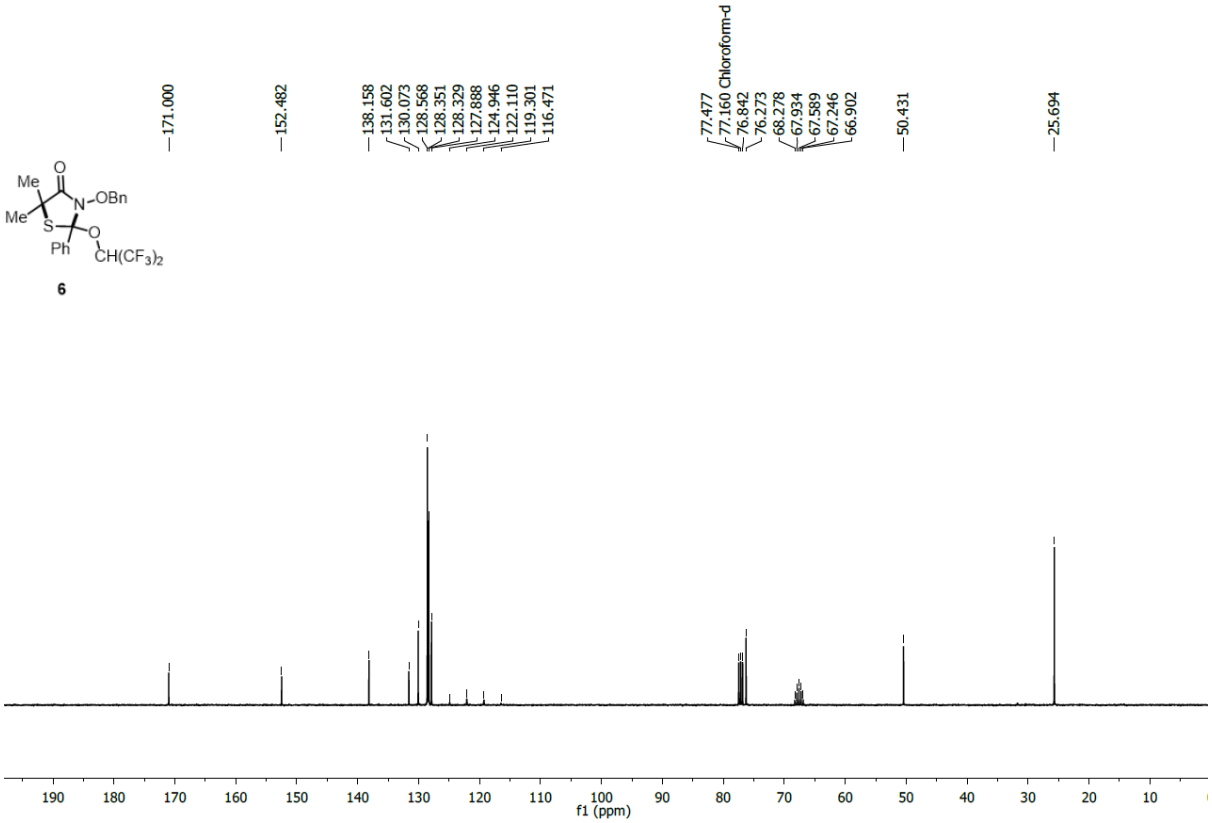
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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152.482
138.158
131.602
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128.568
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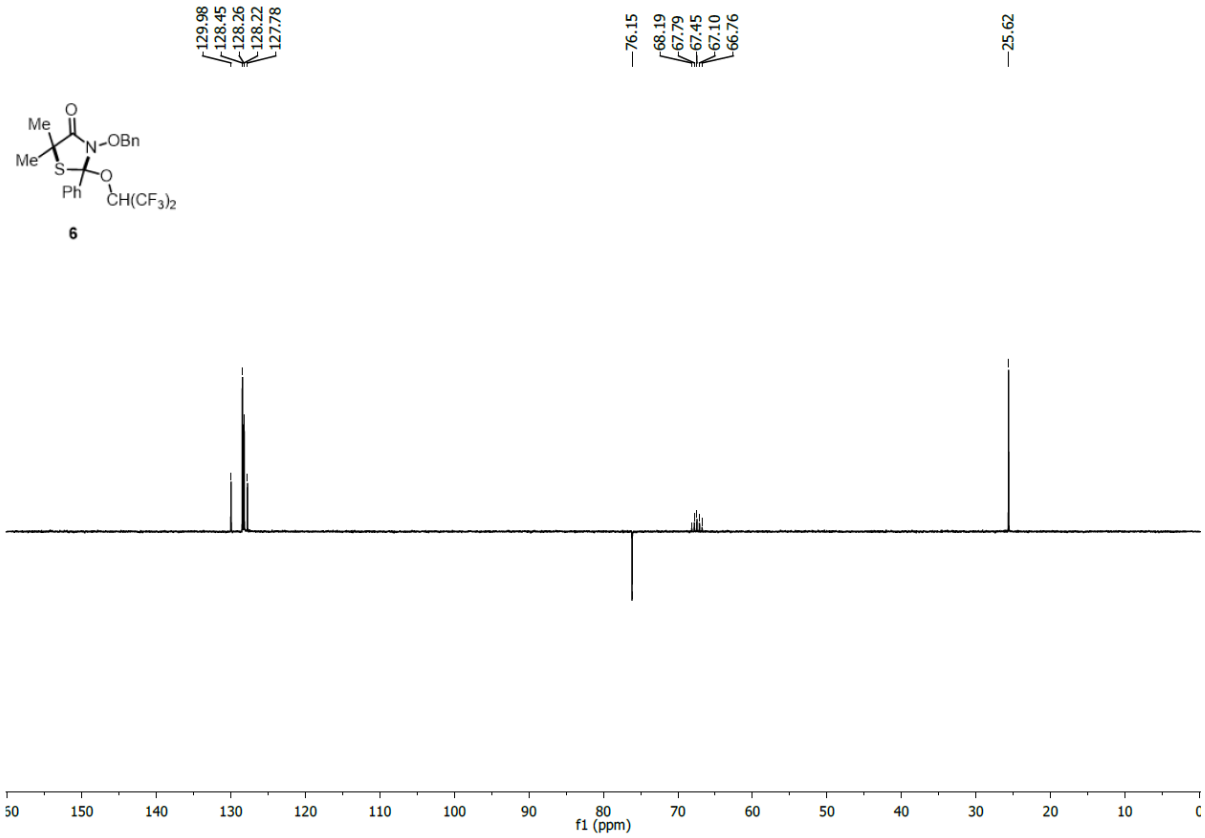
124.946
122.110
119.301
116.471
77.477
77.160 Chloroform-d
76.842
76.273
68.278
67.934
67.589
67.246
66.902
50.431
25.694
Me
O
N
OBn
Me
S
Ph
O
CH(CF3)2
6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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128.22
127.78
76.15
68.19
67.79
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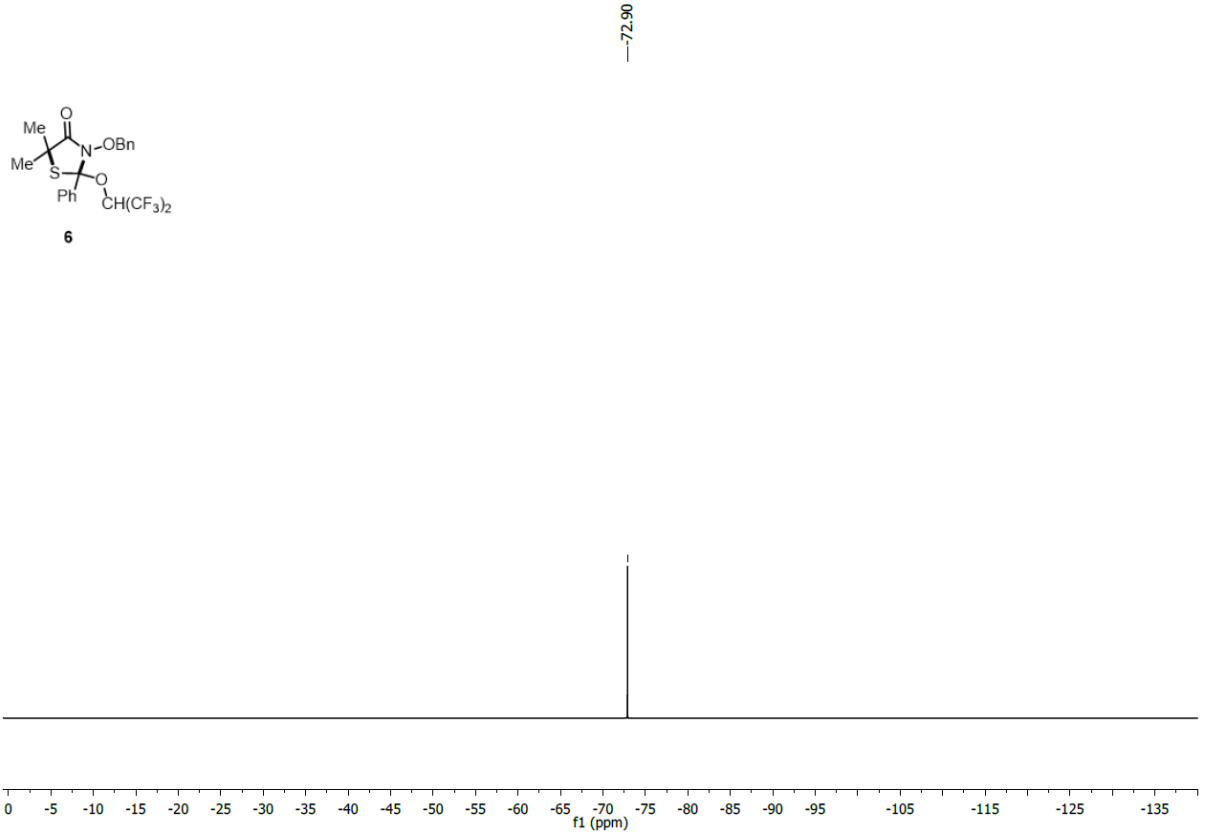
66.76
25.62
Me
Me
O
N
OBn
S
O
Ph
CH(CF3)2
6
f1 (ppm)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Me
Me
O
N
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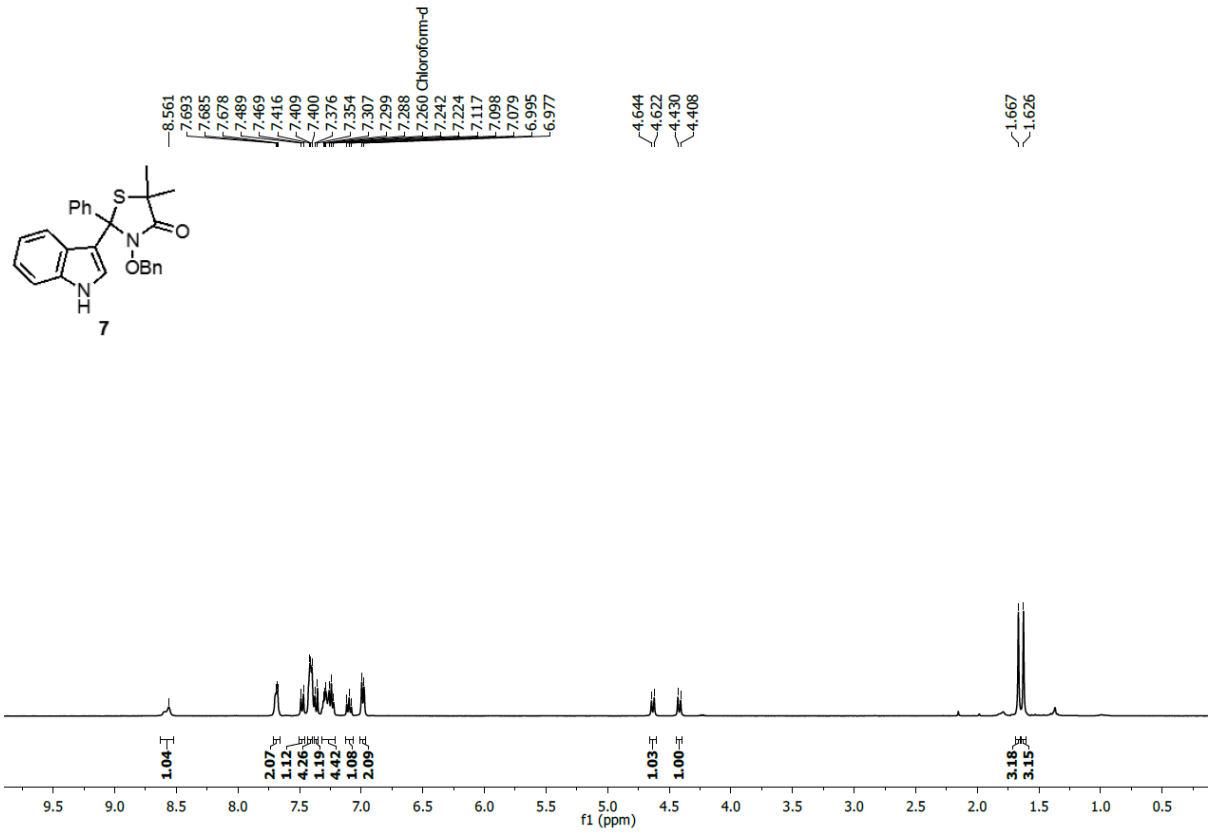
S
O
Ph
CH(CF3)2
6
f1 (ppm)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7.299
7.288
7.260 Chloroform-d
7.242
7.224
7.117
7.098
7.079
6.995
6.977
4.644
4.622
4.430
4.408
1.667
1.626
Ph
S
N
O
OBn
H
7
1.04
2.07
1.12
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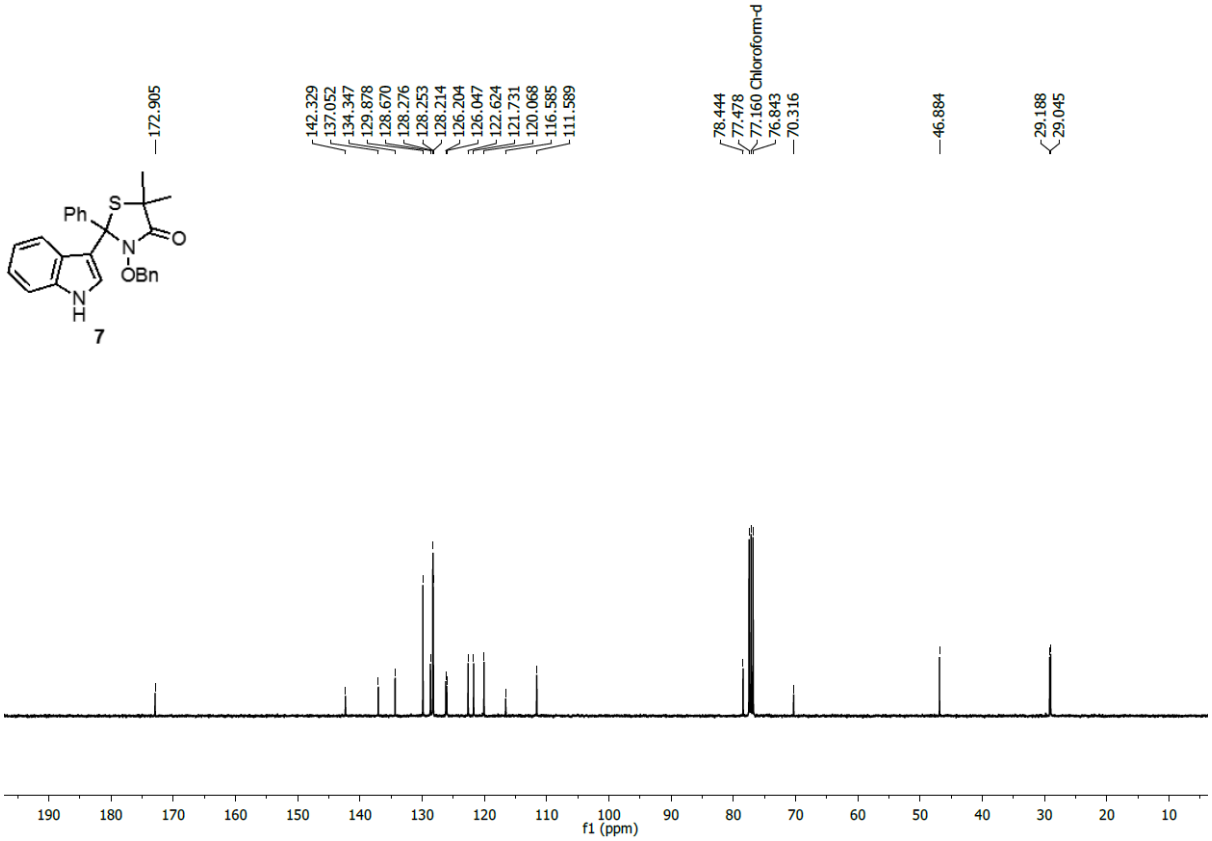
3.15
f1 (ppm)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128.214
126.204
126.047
122.624
121.731
120.068
116.585
111.589
78.444
77.478
77.160 Chloroform-d
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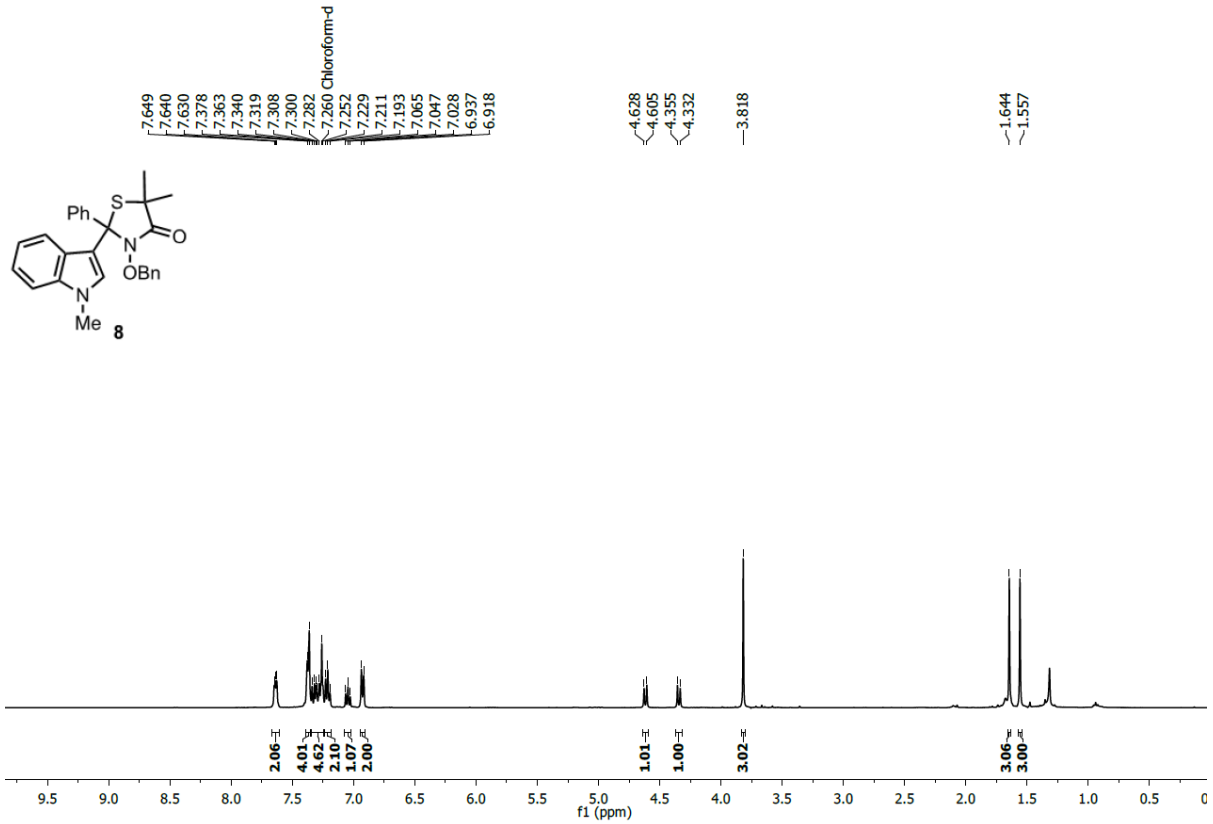
70.316
46.884
29.188
29.045
Ph
S
N
O
OBn
H
7
f1 (ppm)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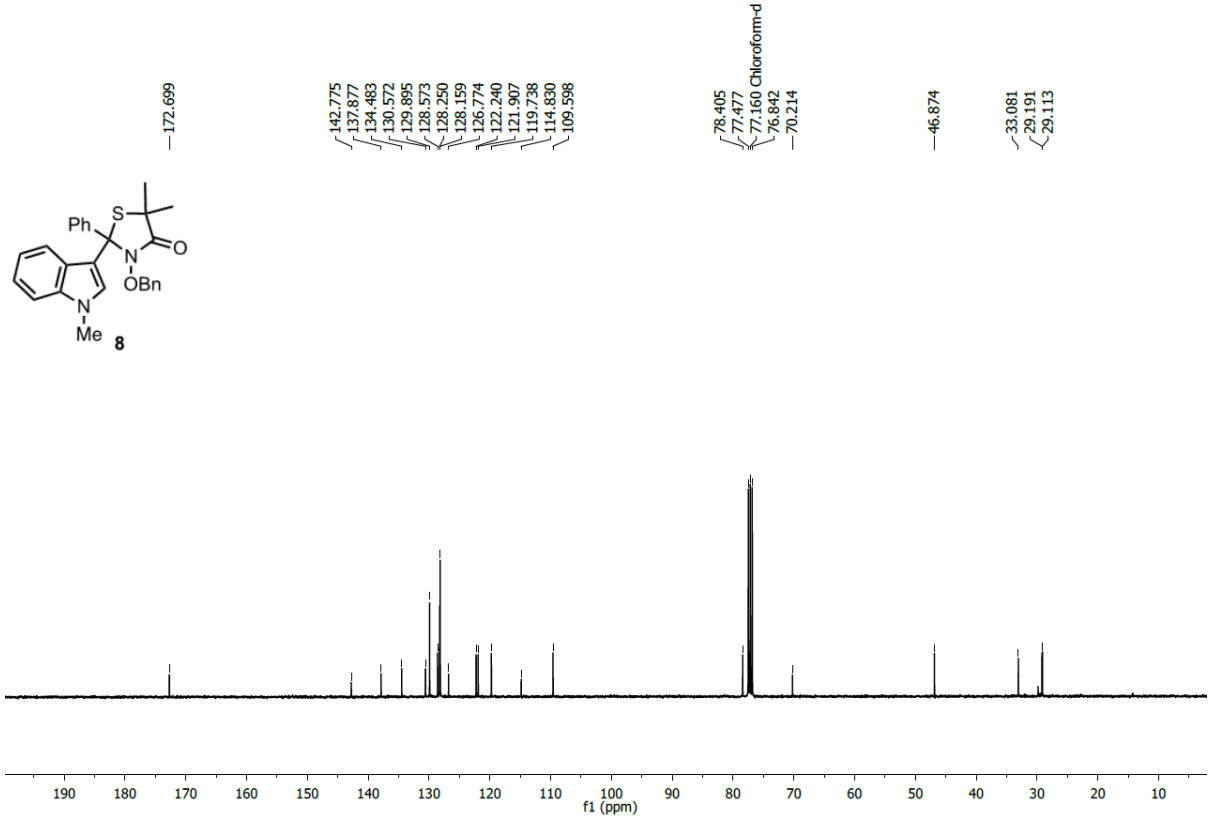
7.282
Chloroform-d
7.260
7.252
7.229
7.211
7.193
7.065
7.047
7.028
6.937
6.918
4.628
4.605
4.355
4.332
3.818
1.644
1.557
Ph
S
O
N
OBn
N
Me
8
2.06
4.01
4.62
2.10
1.07
2.00
1.01
1.00
3.02
3.06
3.00
f1 (ppm)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114.830
109.598
78.405
77.477
77.160
Chloroform-d
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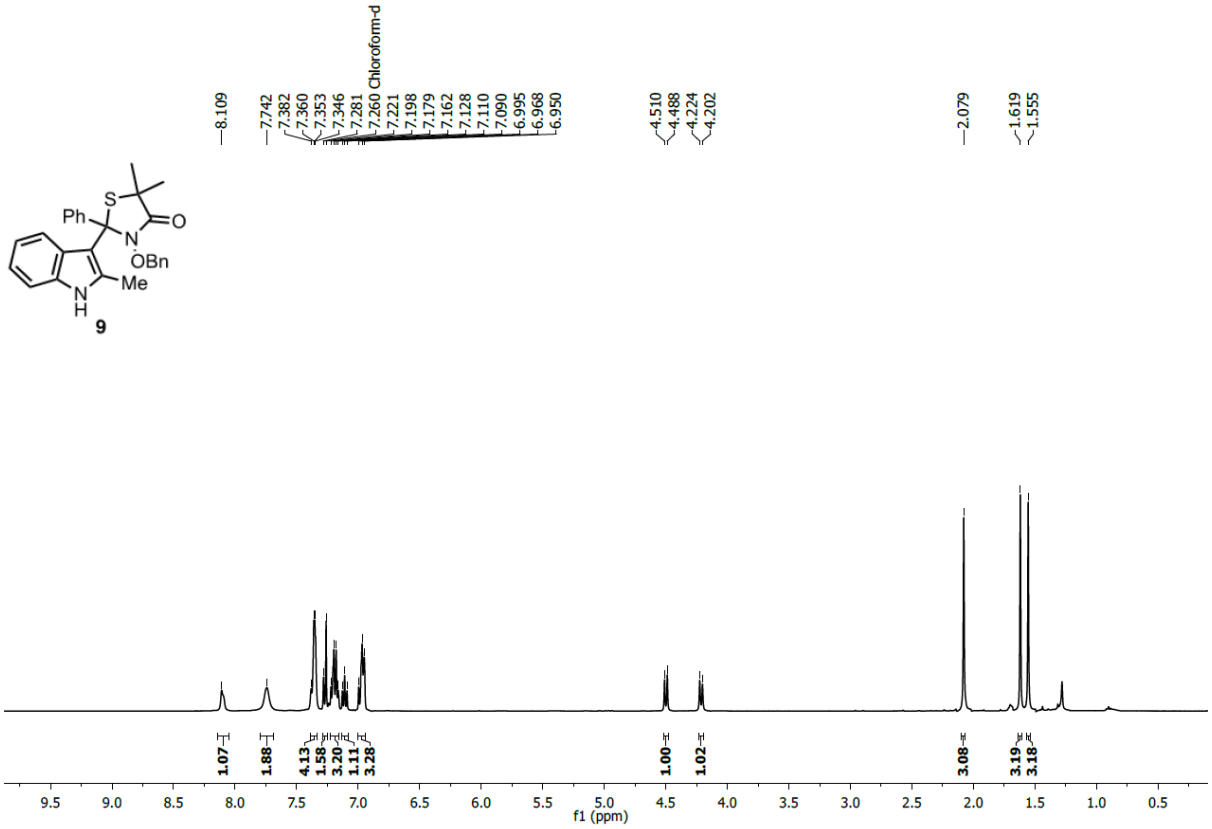
29.191
29.113
Ph
S
O
N
OBn
N
Me
8
f1 (ppm)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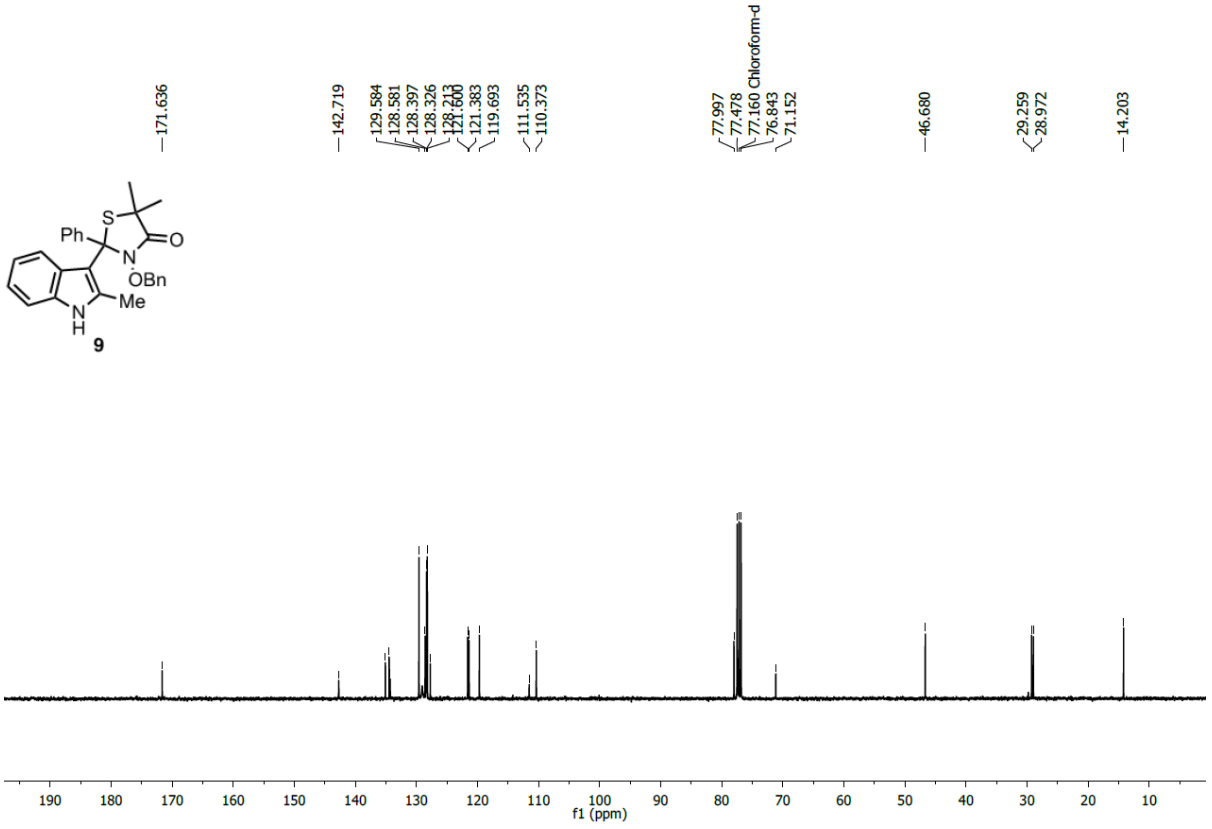
6.995
6.968
6.950
4.510
4.488
4.224
4.202
2.079
1.619
1.555
Ph
S
O
N
OBn
Me
N
H
9
1.07
1.88
4.13
1.58
3.20
1.11
3.28
1.00
1.02
3.08
3.19
3.18
f1 (ppm)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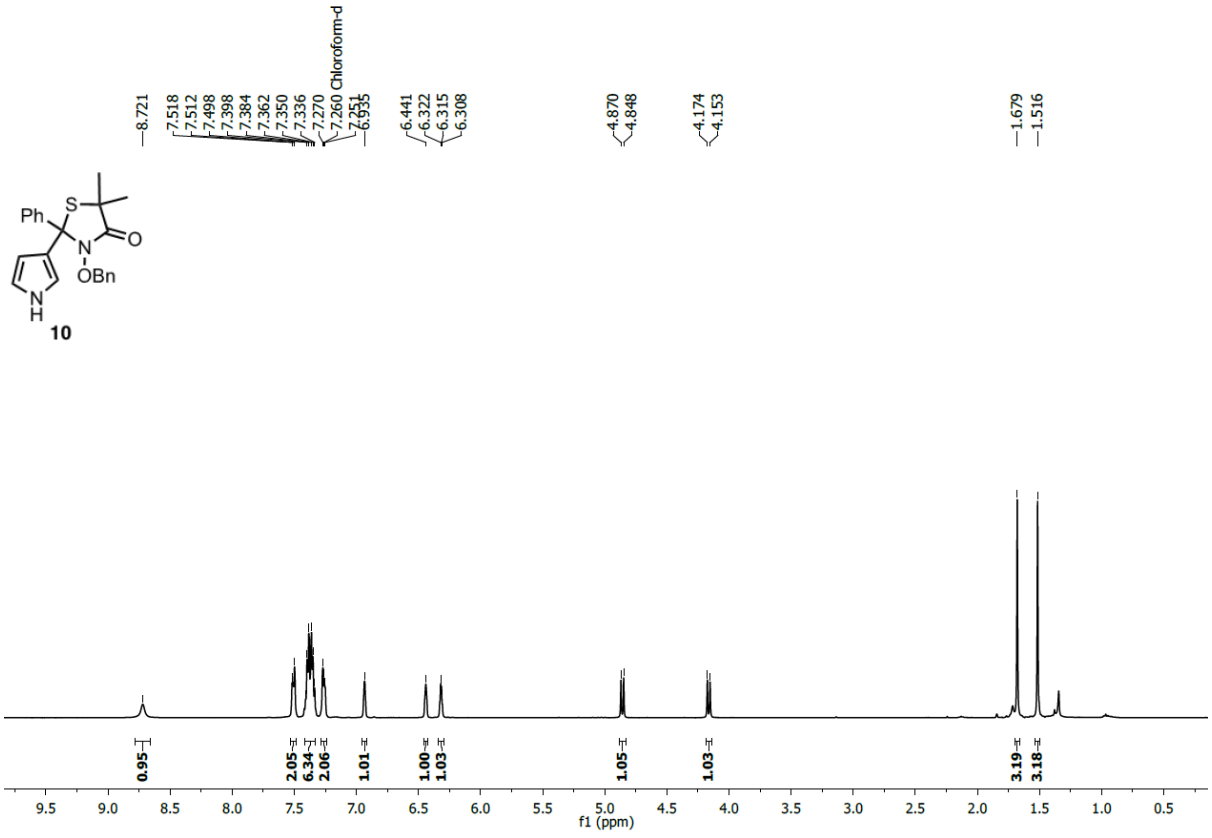
129.584
128.581
128.397
128.326
121.600
121.383
119.693
111.535
110.373
77.997
77.478
77.160 Chloroform-d
76.843
71.152
46.680
29.259
28.972
14.203
Ph
S
O
N
OBn
Me
N
H
9
f1 (ppm)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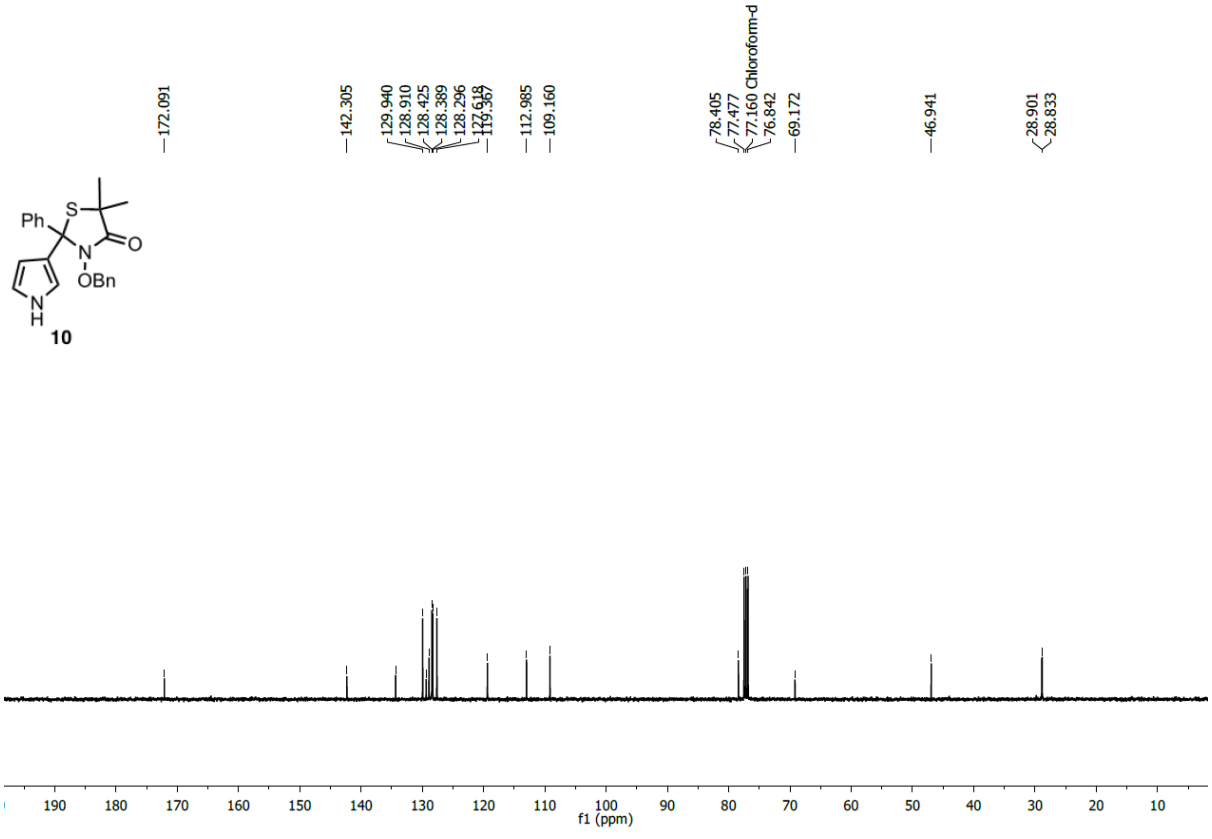
7.398
7.384
7.362
7.350
7.336
7.270
Chloroform-d
7.251
6.935
6.441
6.322
6.315
6.308
4.870
4.848
4.174
4.153
1.679
1.516
Ph
S
O
N
OBn
H
10
0.95
2.05
6.34
2.06
1.01
1.00
1.03
1.05
1.03
3.19
3.18
f1 (ppm)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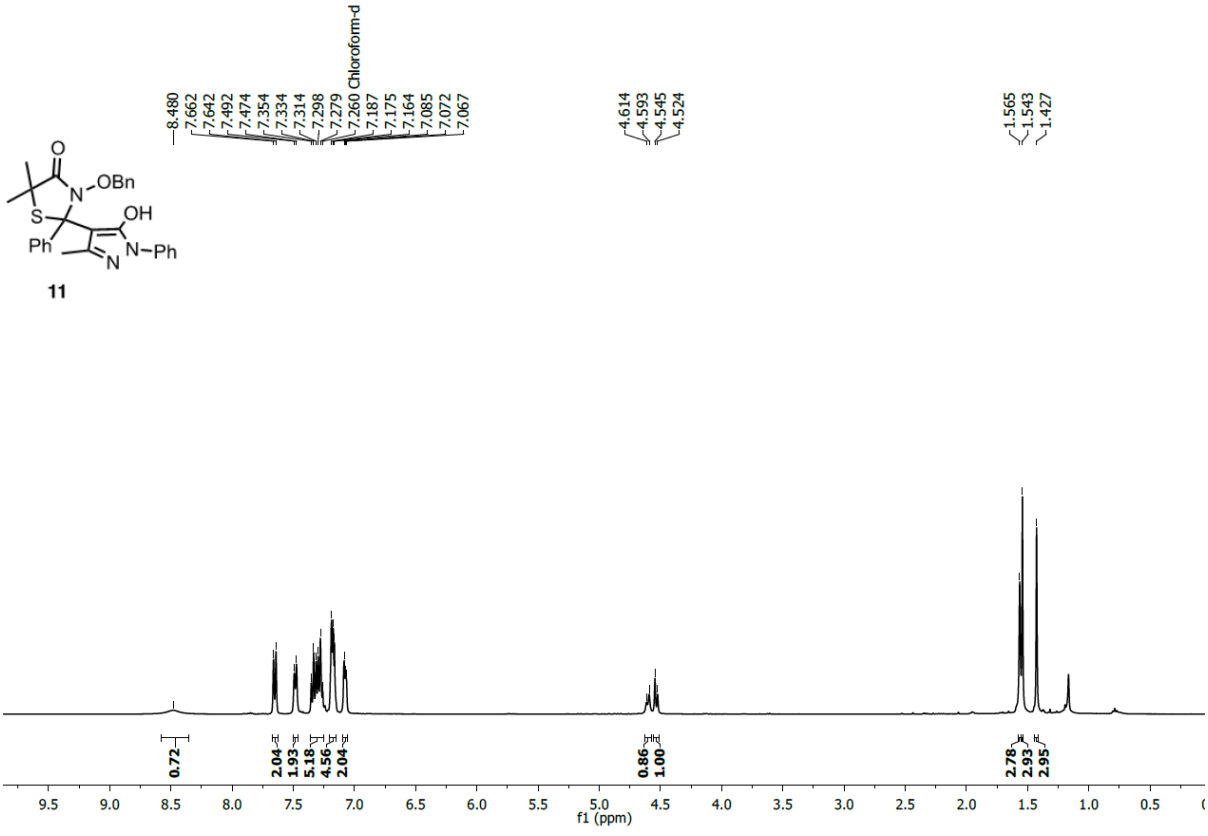
128.425
128.389
128.296
127.618
119.367
112.985
109.160
78.405
77.477
77.160
Chloroform-d
76.842
69.172
46.941
28.901
28.833
Ph
S
O
N
OBn
H
10
f1 (ppm)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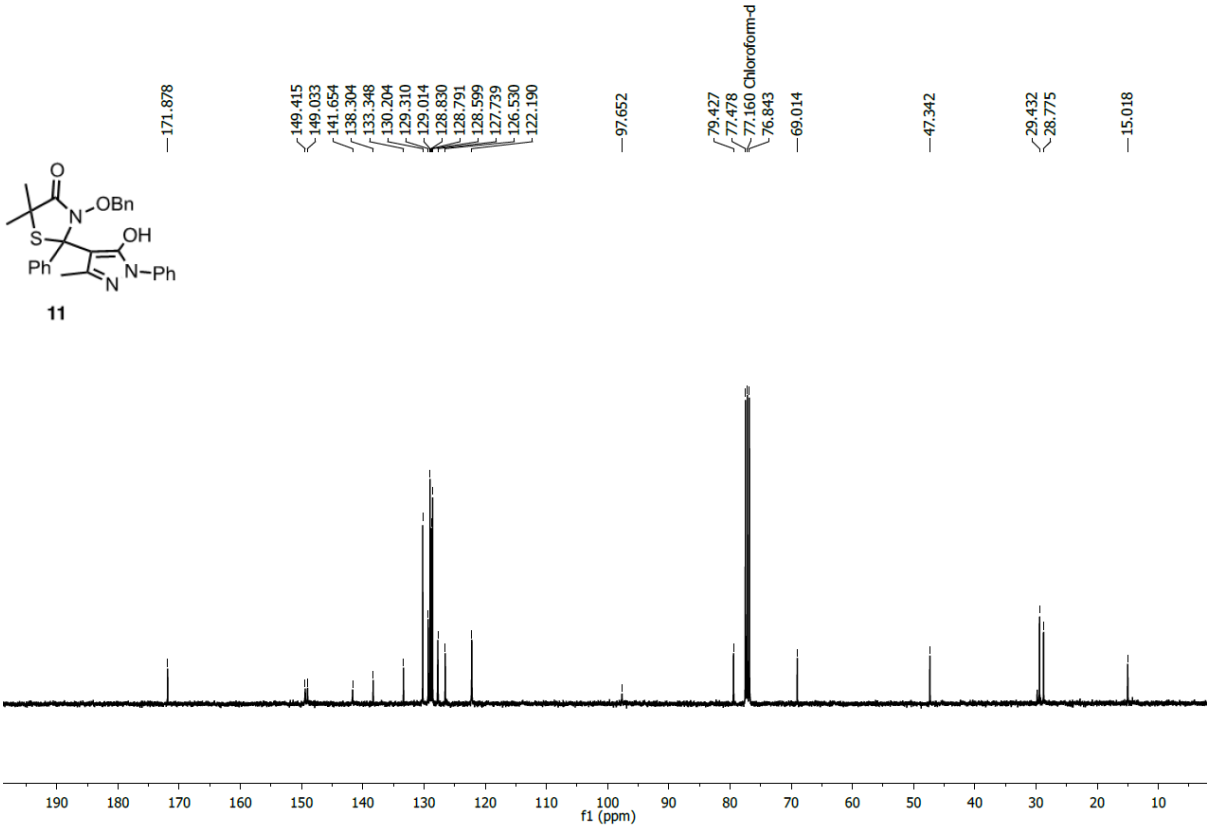
7.662
7.642
7.492
7.474
7.354
7.334
7.314
7.298
7.279
7.260 Chloroform-d
7.187
7.175
7.164
7.085
7.072
7.067
4.614
4.593
4.545
4.524
1.565
1.543
1.427
O
N
OBn
S
OH
Ph
N
N–Ph
0.72
2.04
1.93
5.18
4.56
2.04
0.86
1.00
2.78
2.93
2.95
f1 (ppm)

11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149.033
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138.304
133.348
130.204
129.310
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128.791
128.599
127.739
126.530
122.190
97.652
79.427
77.478
77.160 Chloroform-d
76.843
69.014
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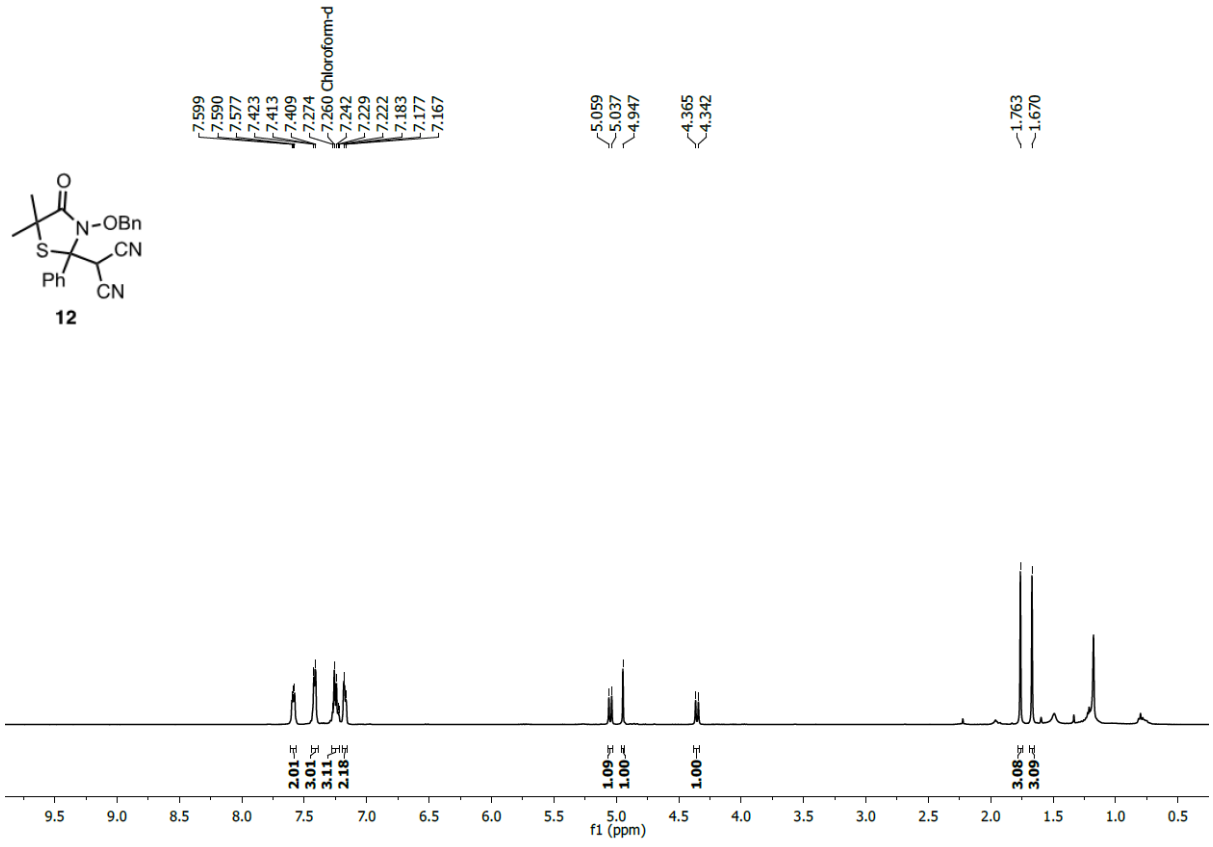
28.775
15.018
O
N
OBn
S
OH
Ph
N
N–Ph
f1 (ppm)

11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7.590
7.577
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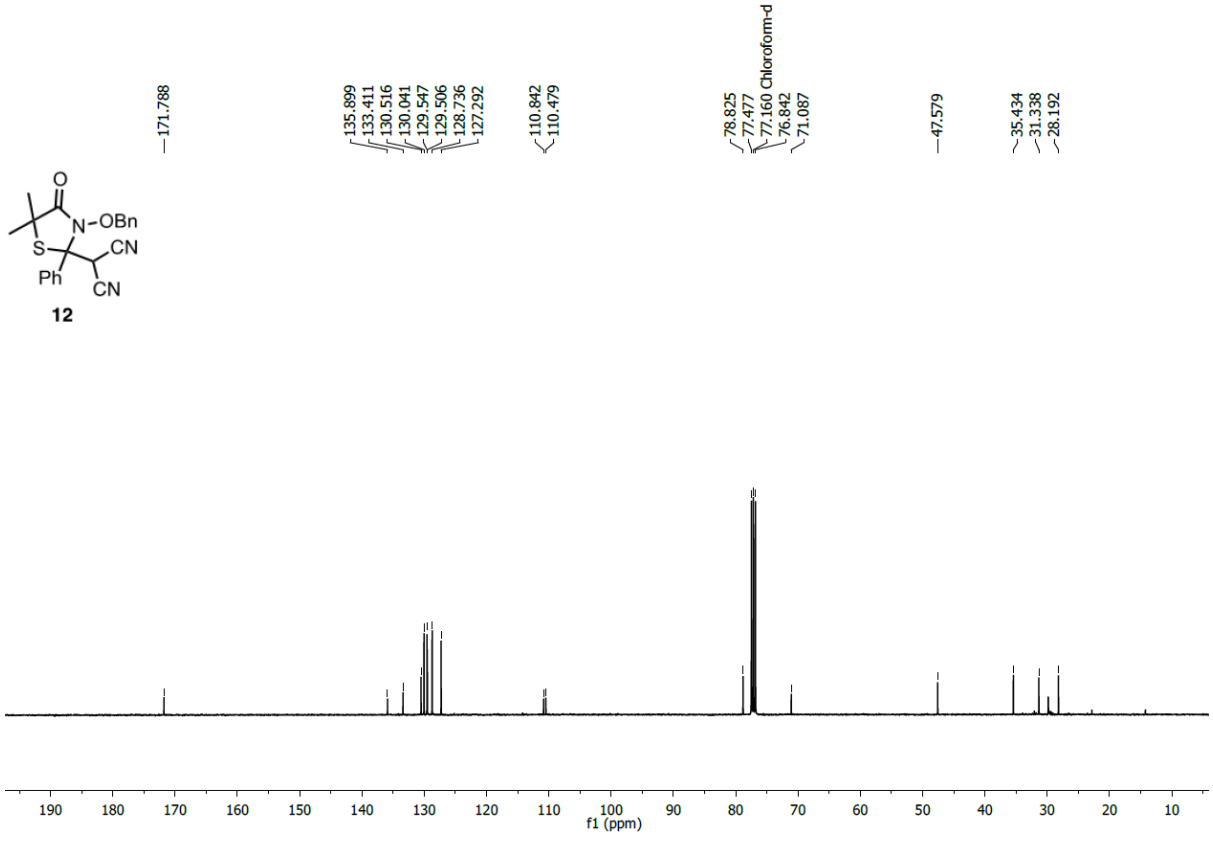
7.413
7.409
7.274
7.260 Chloroform-d
7.242
7.229
7.222
7.183
7.177
7.167
5.059
5.037
4.947
4.365
4.342
1.763
1.670
O
N-OBn
S
CN
Ph
CN
12
2.01
3.01
3.11
2.18
1.09
1.00
1.00
3.08
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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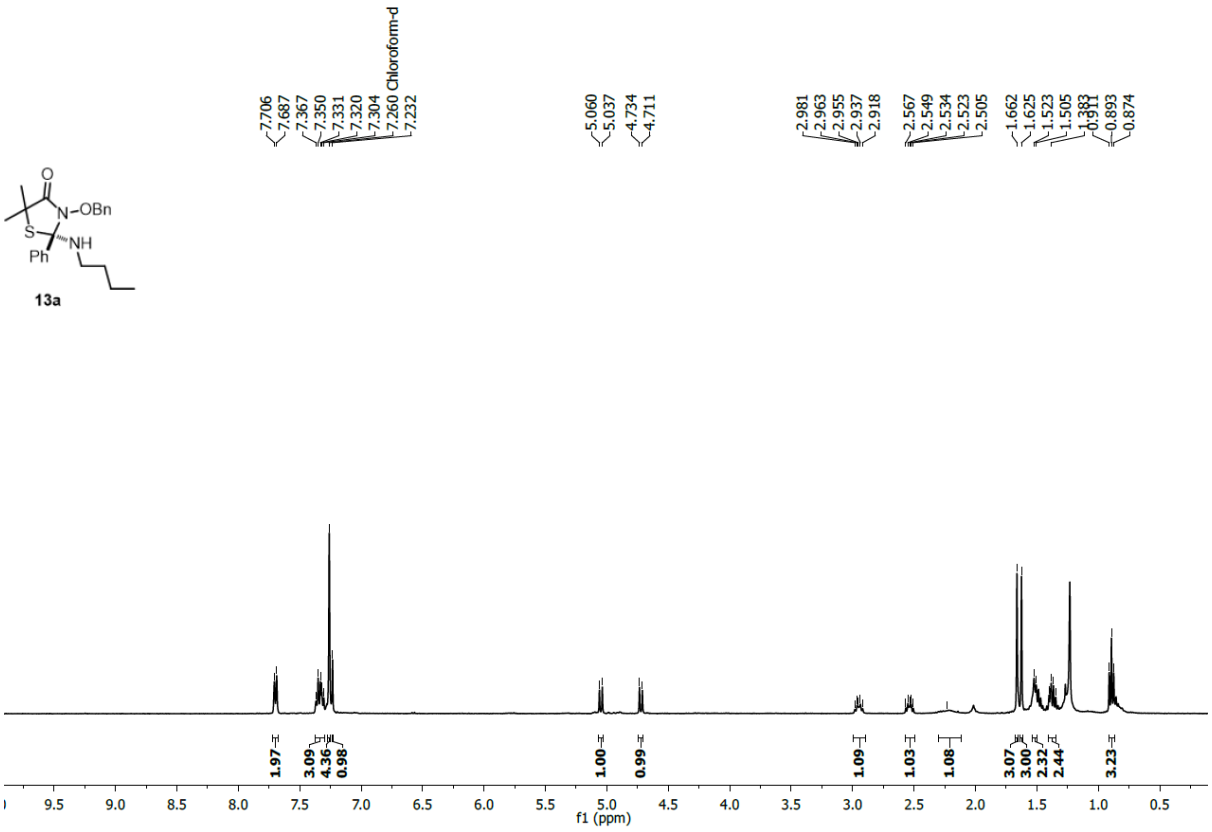
130.516
130.041
129.547
129.506
128.736
127.292
110.842
110.479
78.825
77.477
77.160 Chloroform-d
76.842
71.087
47.579
35.434
31.338
28.192
O
N-OBn
S
CN
Ph
CN
12
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.687
7.367
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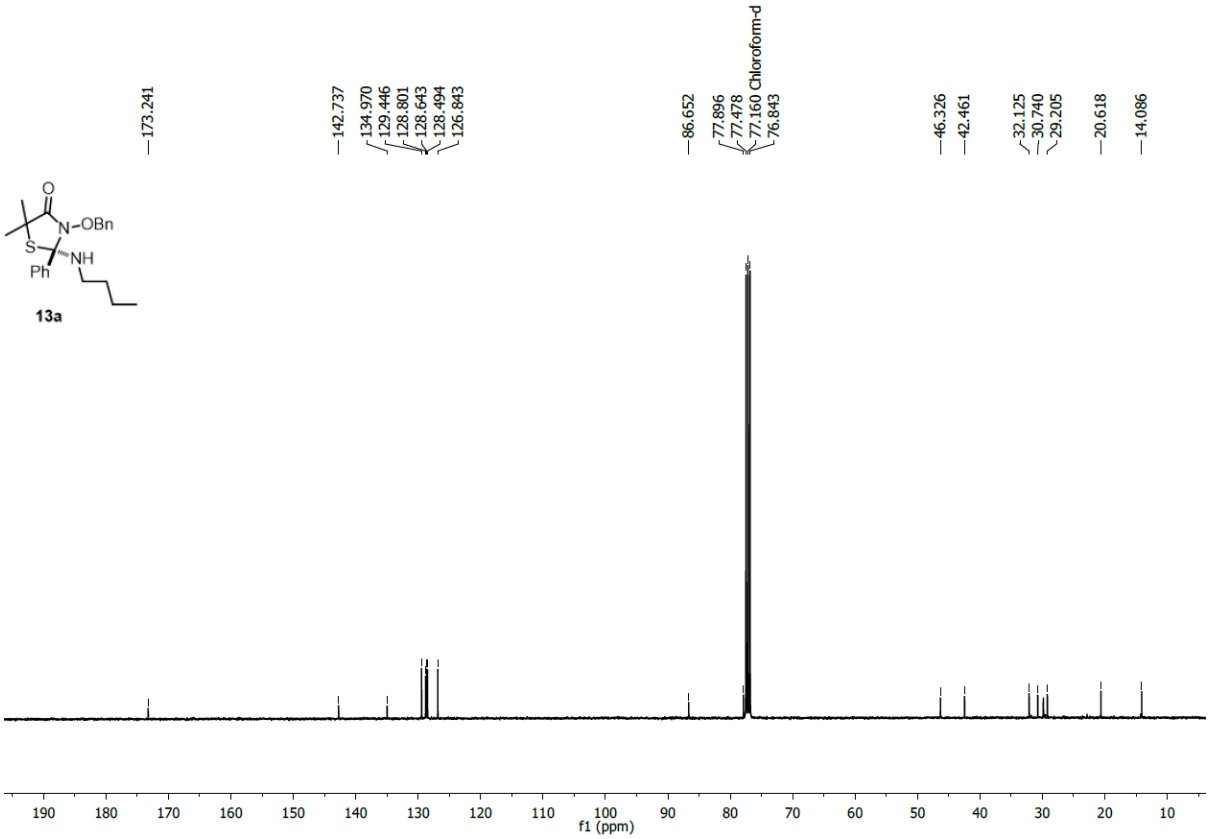
7.331
7.320
7.304
7.260 Chloroform-d
7.232
5.060
5.037
4.734
4.711
2.981
2.963
2.955
2.937
2.918
2.567
2.549
2.534
2.523
2.505
1.662
1.625
1.523
1.505
1.383
0.911
0.893
0.874
O
N-OBn
S
NH
Ph
13a
1.97
3.09
4.36
0.98
1.00
0.99
1.09
1.03
1.08
3.07
3.00
2.32
2.44
3.23
f1 (ppm)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142.737
134.970
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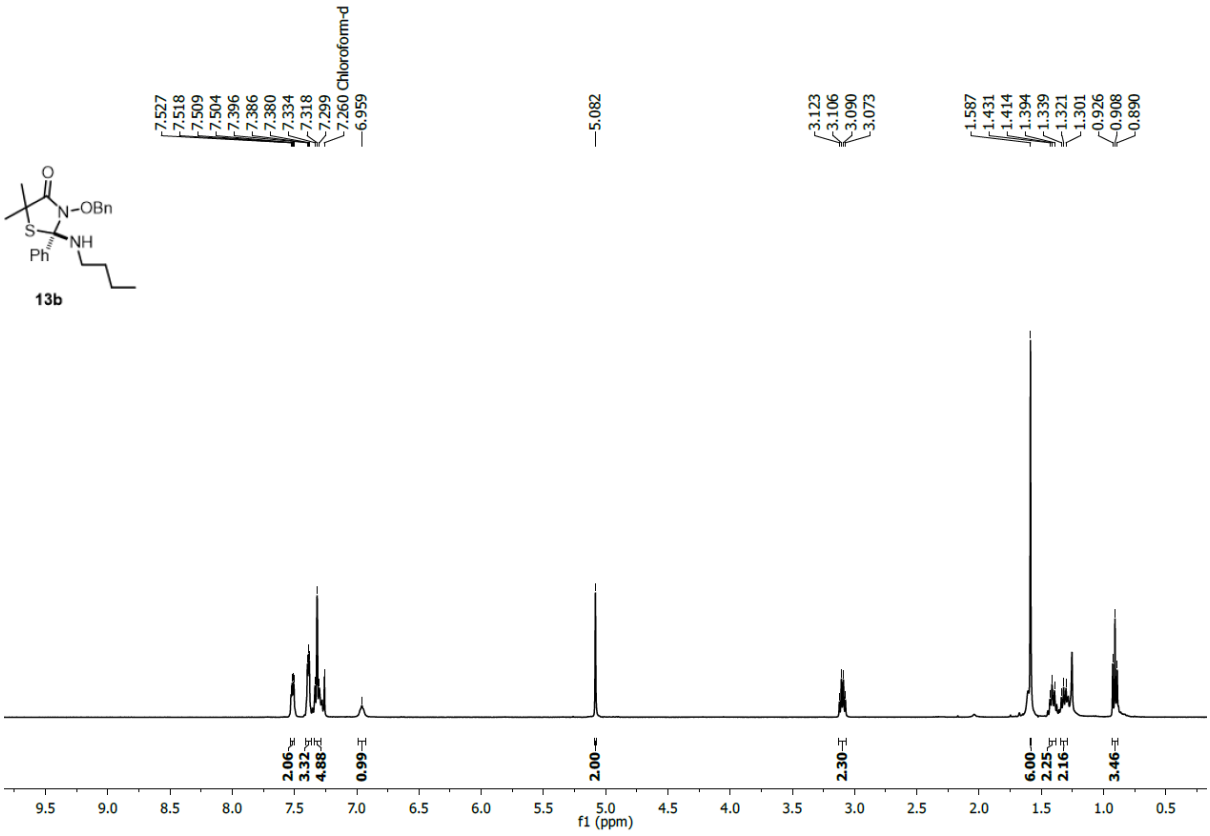
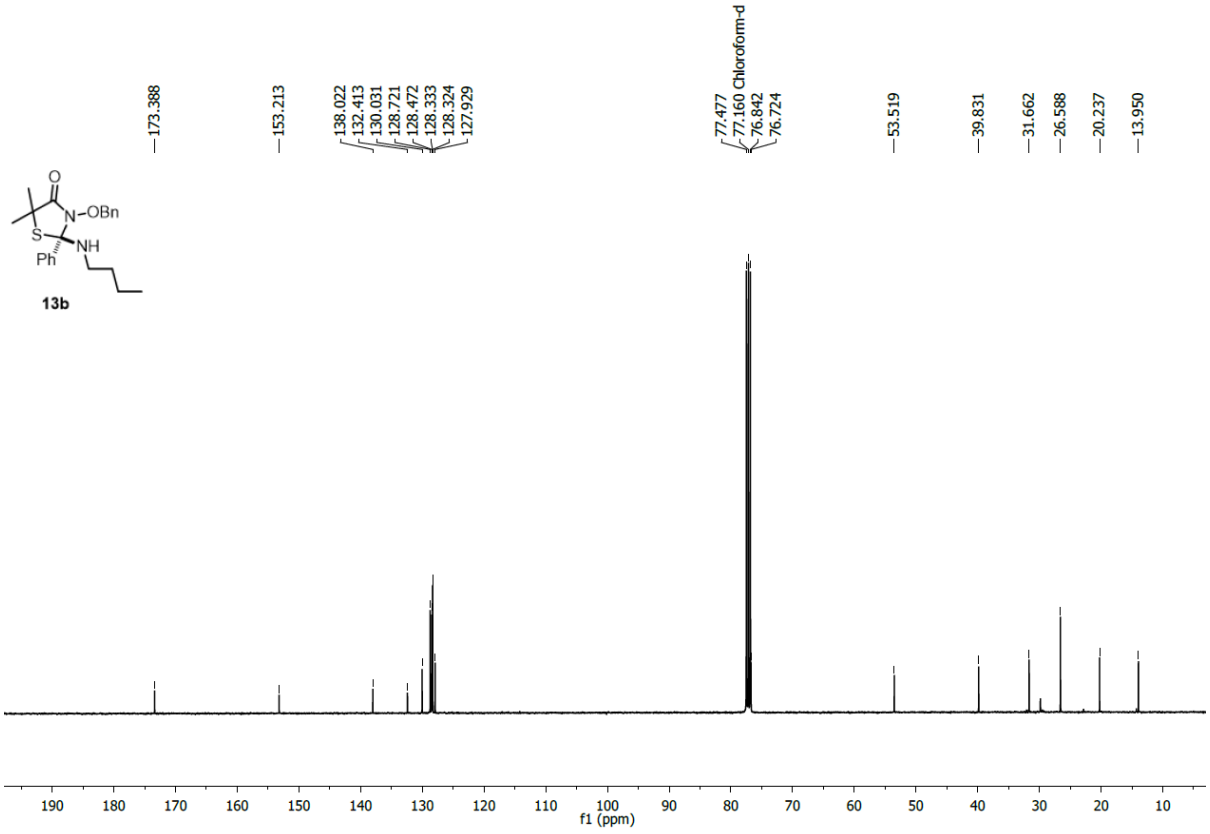
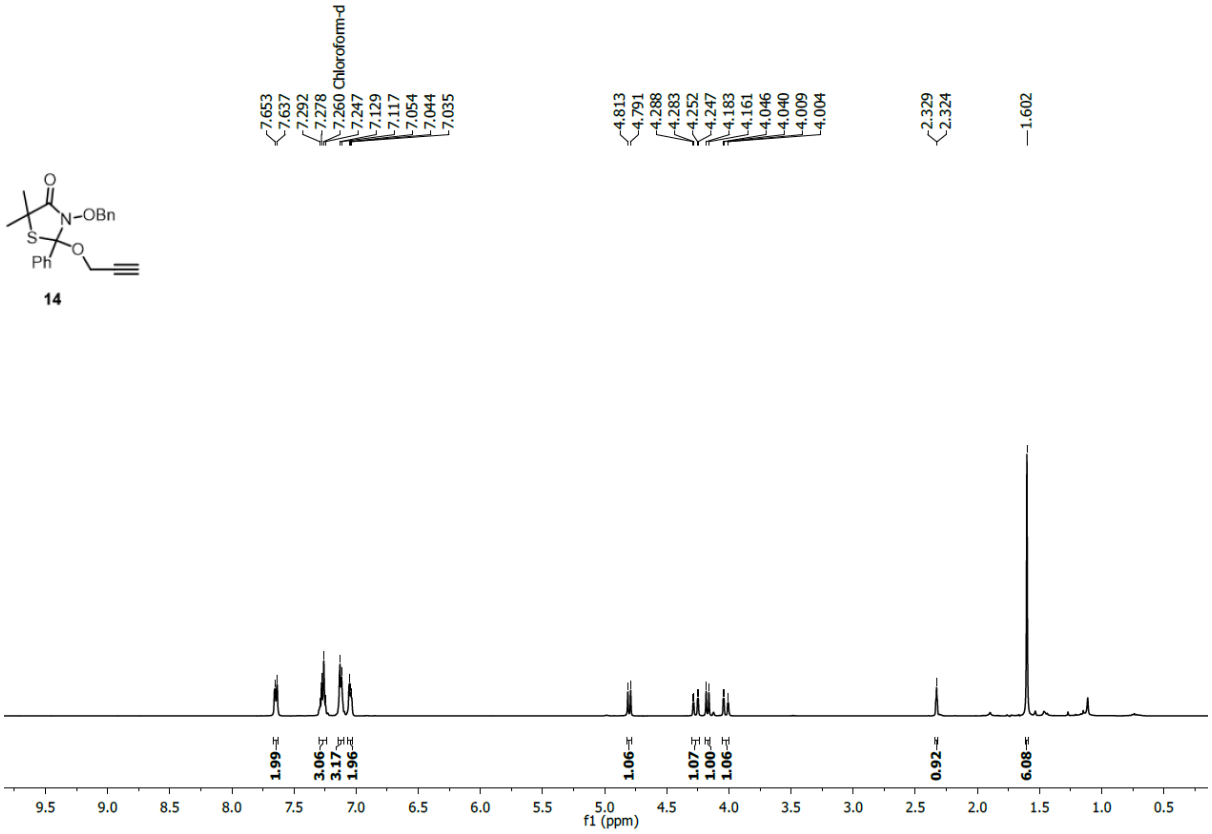
128.801
128.643
128.494
126.843
86.652
77.896
77.478
77.160 Chloroform-d
76.843
46.326
42.461
32.125
30.740
29.205
20.618
14.086
O
N-OBn
S
NH
Ph
13a
f1 (ppm)


7.527
7.518
7.509
7.504
7.396
7.386
7.380
7.334
7.318
7.299
7.260 Chloroform-d
6.959
5.082
3.123
3.106
3.090
3.073
1.587
1.431
1.414
1.394
1.339
1.321
1.301
0.926
0.908
0.890
O
N-OBn
S
NH
Ph
13b
2.06
3.32
4.88
0.99
2.00
2.30
6.00
2.25
2.16
3.46
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


173.388
153.213
138.022
132.413
130.031
128.721
128.472
128.333
128.324
127.929
77.477
77.160 Chloroform-d
76.842
76.724
53.519
39.831
31.662
26.588
20.237
13.950
O
N-OBn
S
NH
Ph
13b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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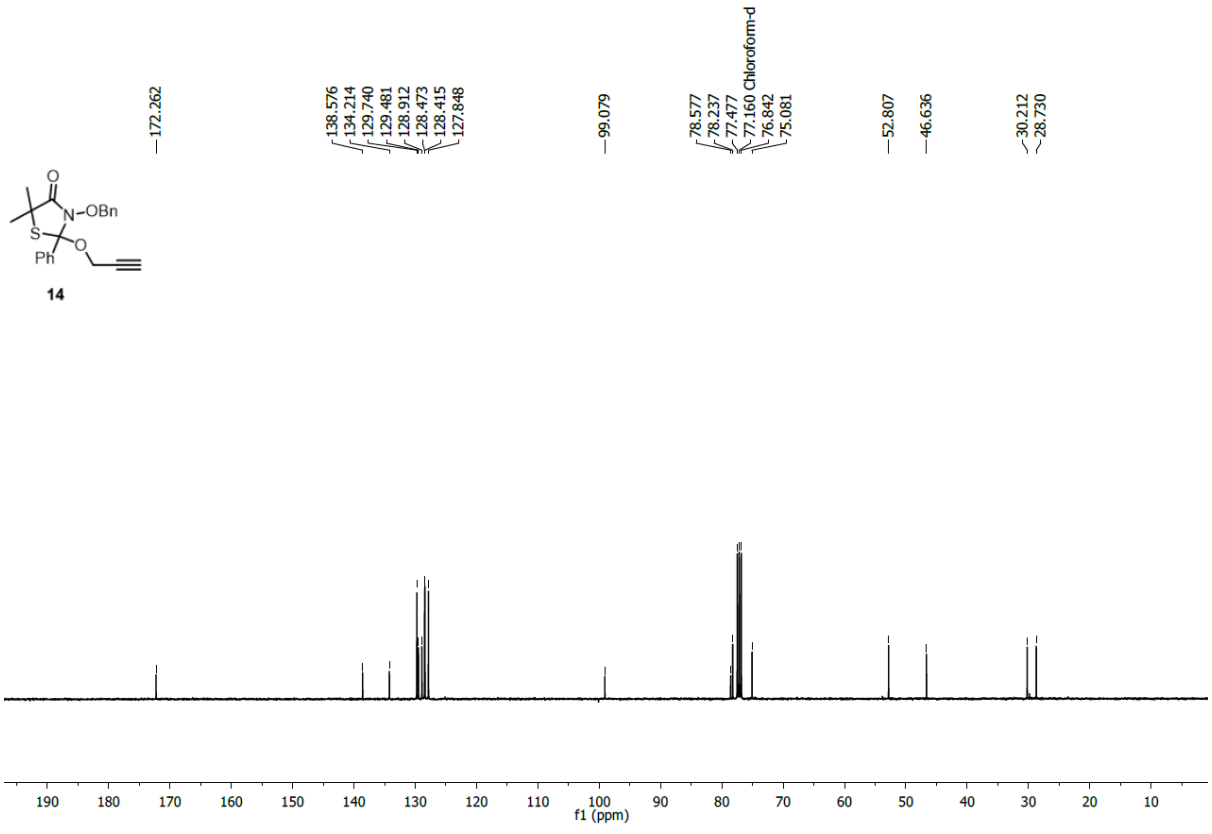
7.637
7.292
7.278
7.260 Chloroform-d
7.247
7.129
7.117
7.054
7.044
7.035
4.813
4.791
4.288
4.283
4.252
4.247
4.183
4.161
4.046
4.040
4.009
4.004
2.329
2.324
1.602
O
N-OBn
S
O
Ph
14
1.99
3.06
3.17
1.96
1.06
1.07
1.00
1.06
0.92
6.08
f1 (ppm)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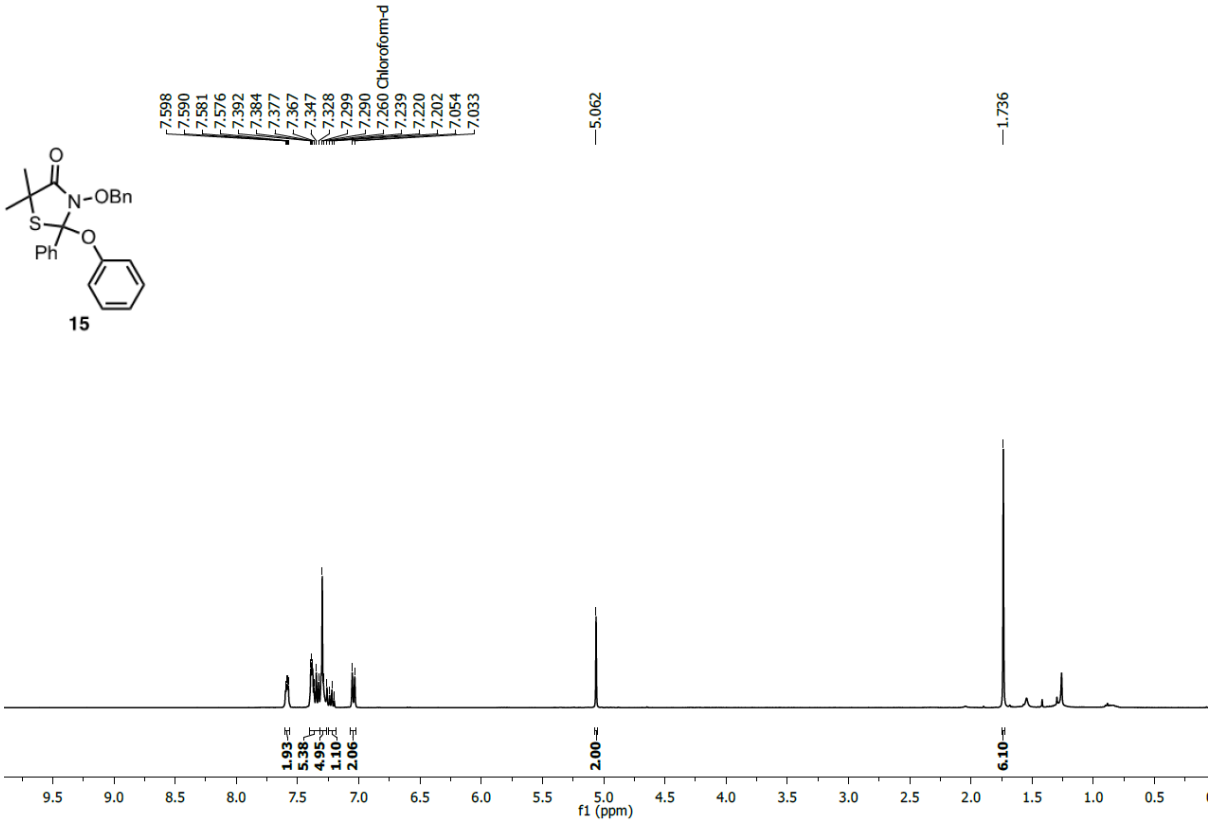
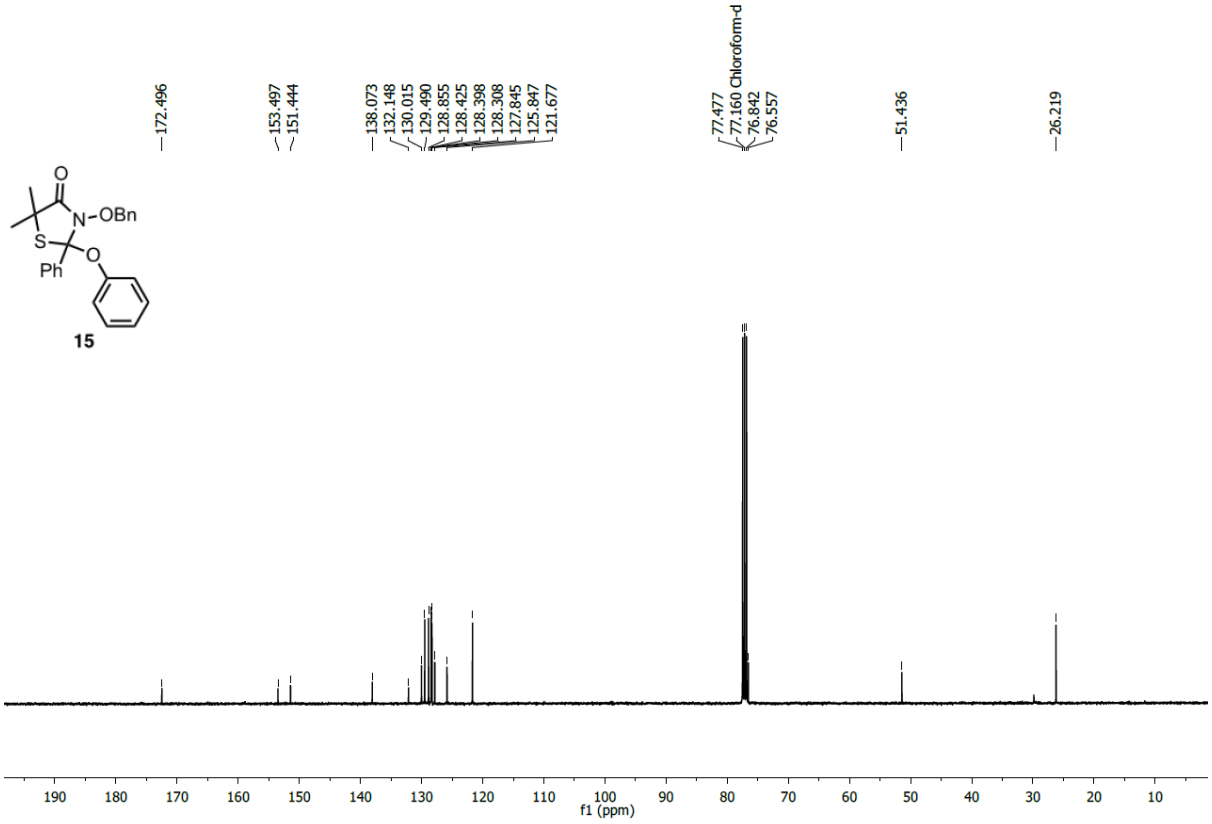
138.576
134.214
129.740
129.481
128.912
128.473
128.415
127.848
99.079
78.577
78.237
77.477
77.160 Chloroform-d
76.842
75.081
52.807
46.636
30.212
28.730
O
N-OBn
S
O
Ph
14
f1 (ppm)


7.598
7.590
7.581
7.576
7.392
7.384
7.377
7.367
7.347
7.328
7.299
7.290
Chloroform-d
7.260
7.239
7.220
7.202
7.054
7.033
5.062
1.736
O
N-OBn
S
Ph
O
15
1.93
5.38
4.95
1.10
2.06
2.00
6.10
f1 (ppm)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132.148
130.015
129.490
128.855
128.425
128.398
128.308
127.845
125.847
121.677
77.477
77.160
Chloroform-d
76.842
76.557
51.436
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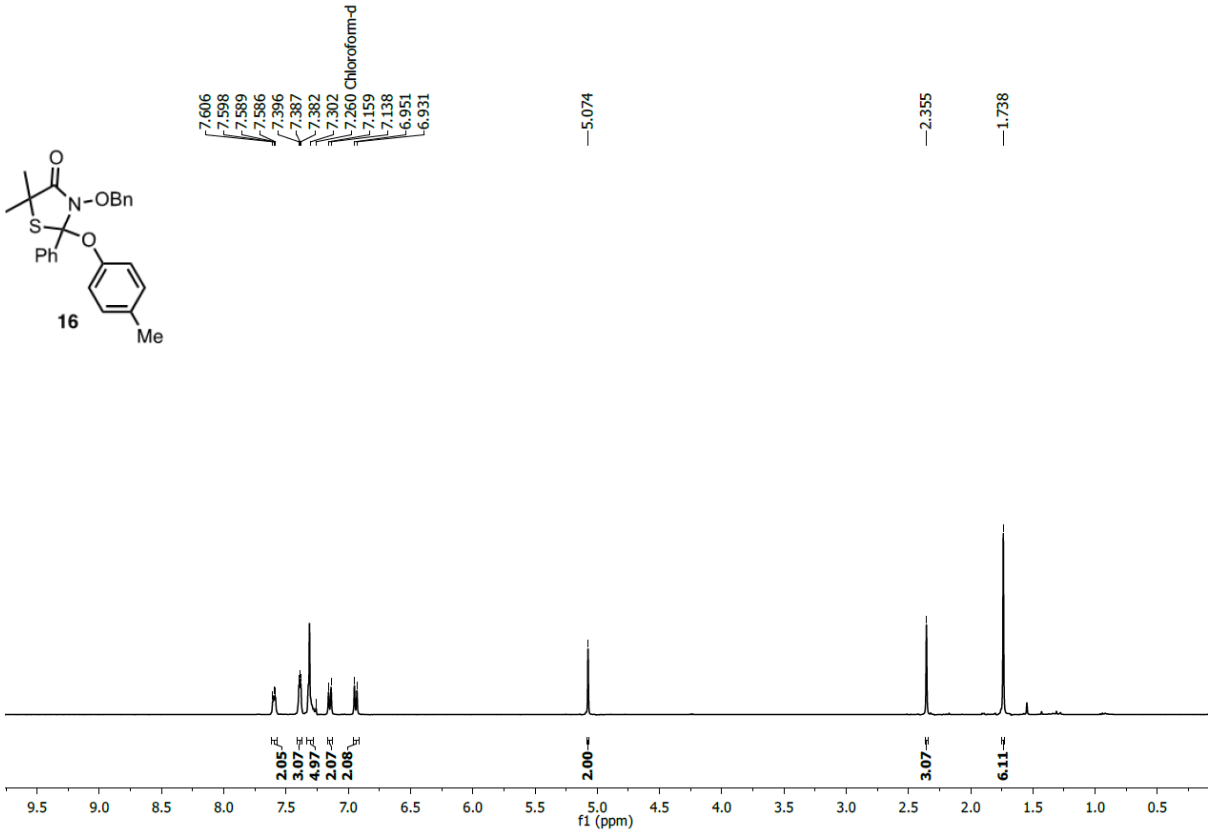
O
N-OBn
S
Ph
O
15
f1 (ppm)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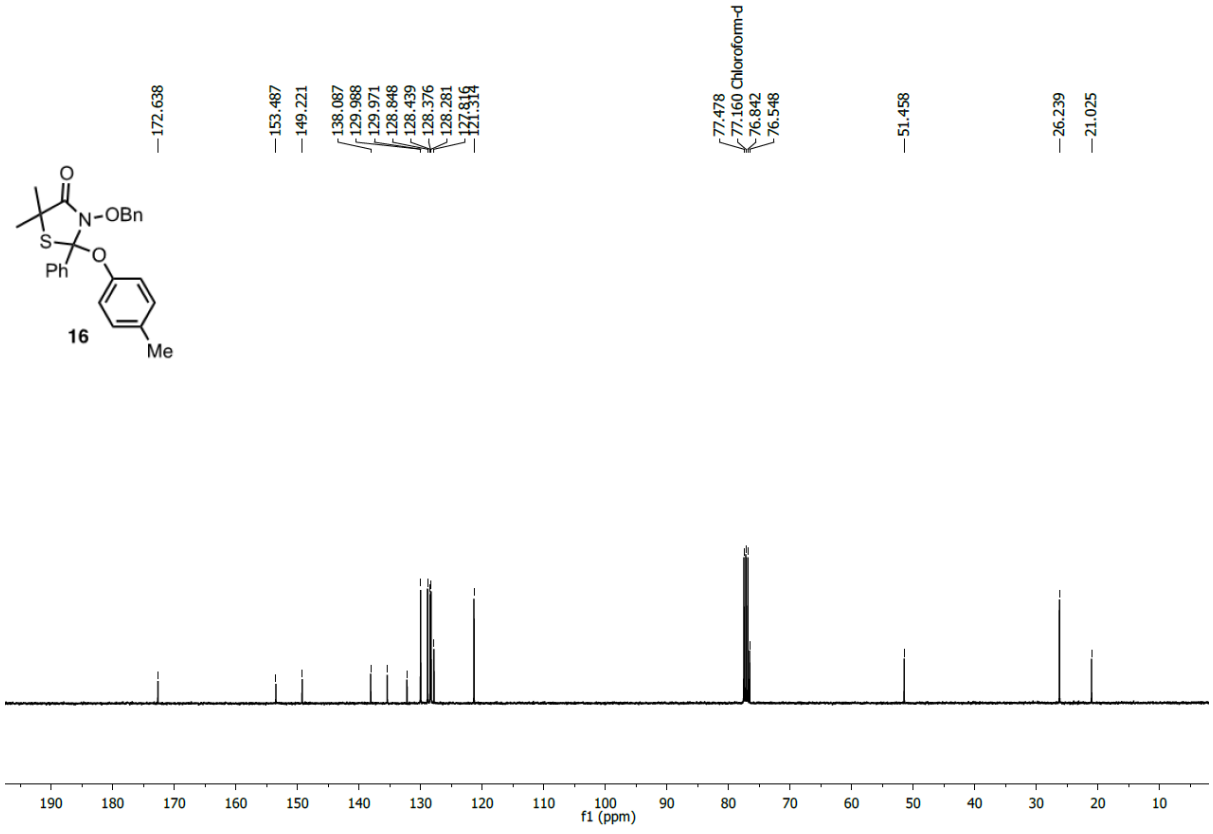
7.302
7.260 Chloroform-d
7.159
7.138
6.951
6.931
5.074
2.355
1.738
O
N-OBn
S
Ph
O
16
Me
2.05
3.07
4.97
2.07
2.08
2.00
3.07
6.11
f1 (ppm)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153.487
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138.087
129.988
129.971
128.848
128.439
128.376
128.281
127.816
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77.478
77.160 Chloroform-d
76.842
76.548
51.458
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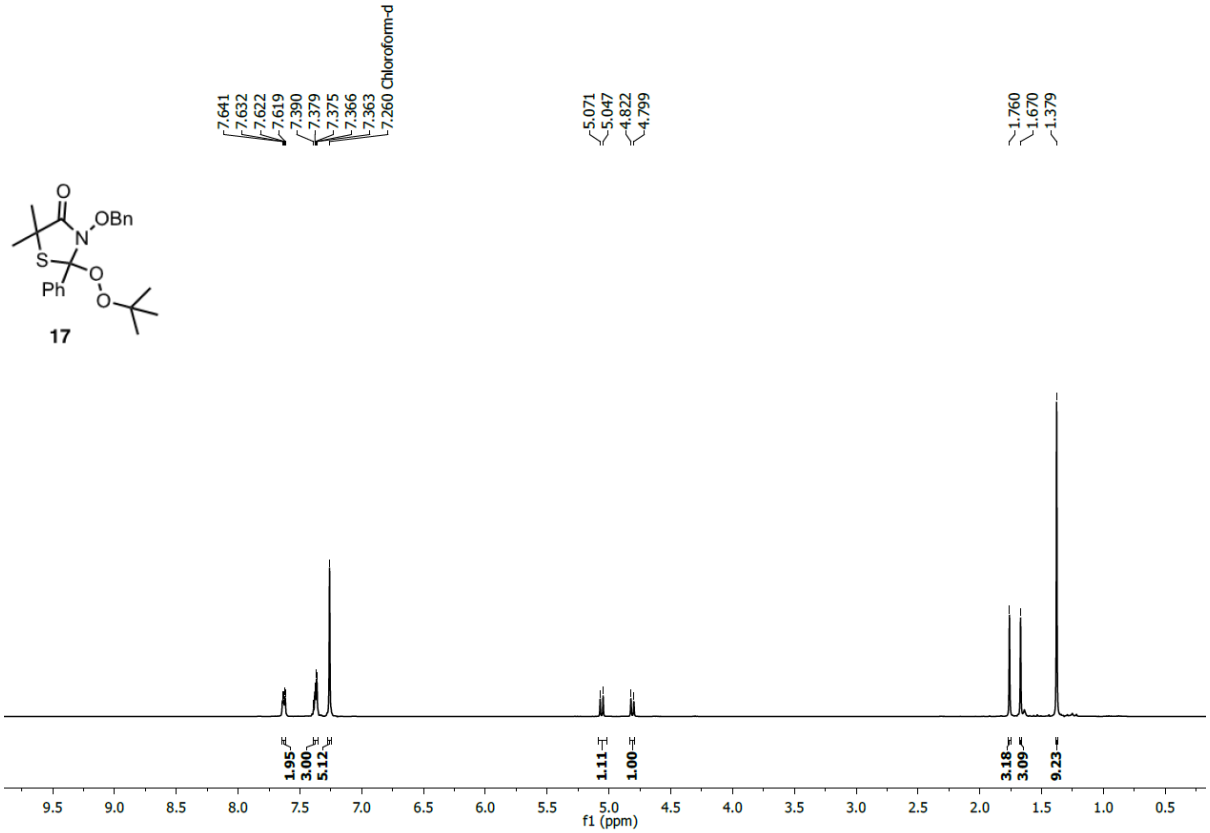
21.025
O
N-OBn
S
Ph
O
16
Me
f1 (ppm)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7.375
7.366
7.363
7.260 Chloroform-d
5.071
5.047
4.822
4.799
1.760
1.670
1.379
O
OBn
N
S
Ph
O
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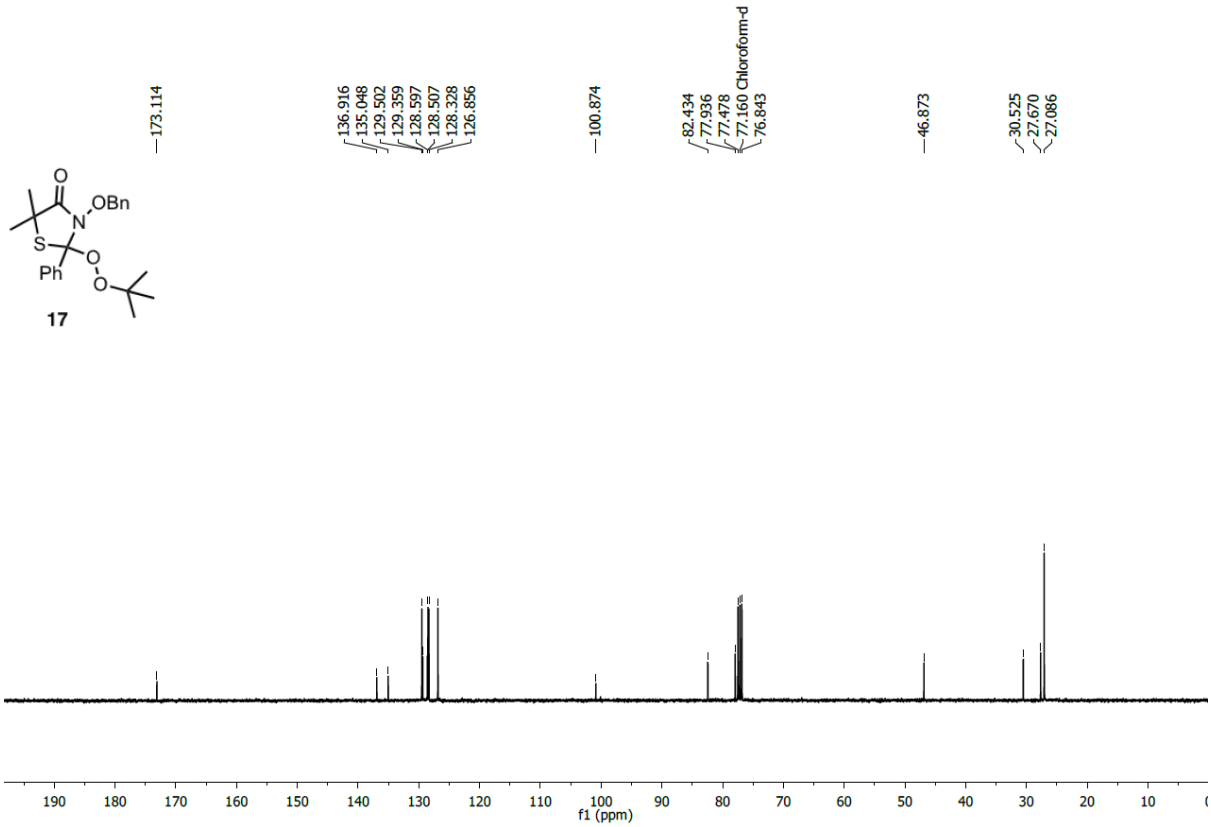
1.95
3.00
5.12
1.11
1.00
3.18
3.09
9.23
f1 (ppm)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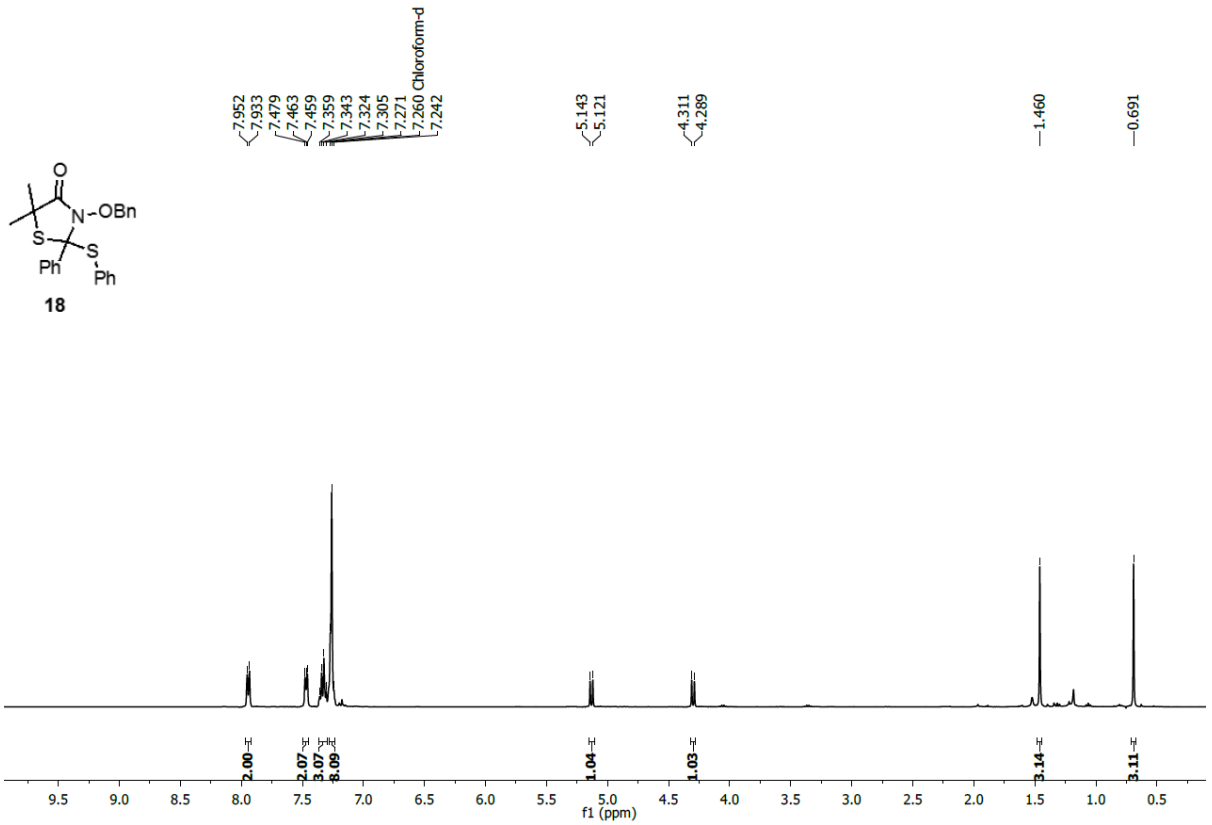
129.359
128.597
128.507
128.328
126.856
100.874
82.434
77.936
77.478
77.160 Chloroform-d
76.843
46.873
30.525
27.670
27.086
O
OBn
N
S
Ph
O
O
17
f1 (ppm)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7.359
7.343
7.324
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7.271
7.260 Chloroform-d
7.242
5.143
5.121
4.311
4.289
1.460
0.691
O
N-OBn
S
S
Ph
Ph
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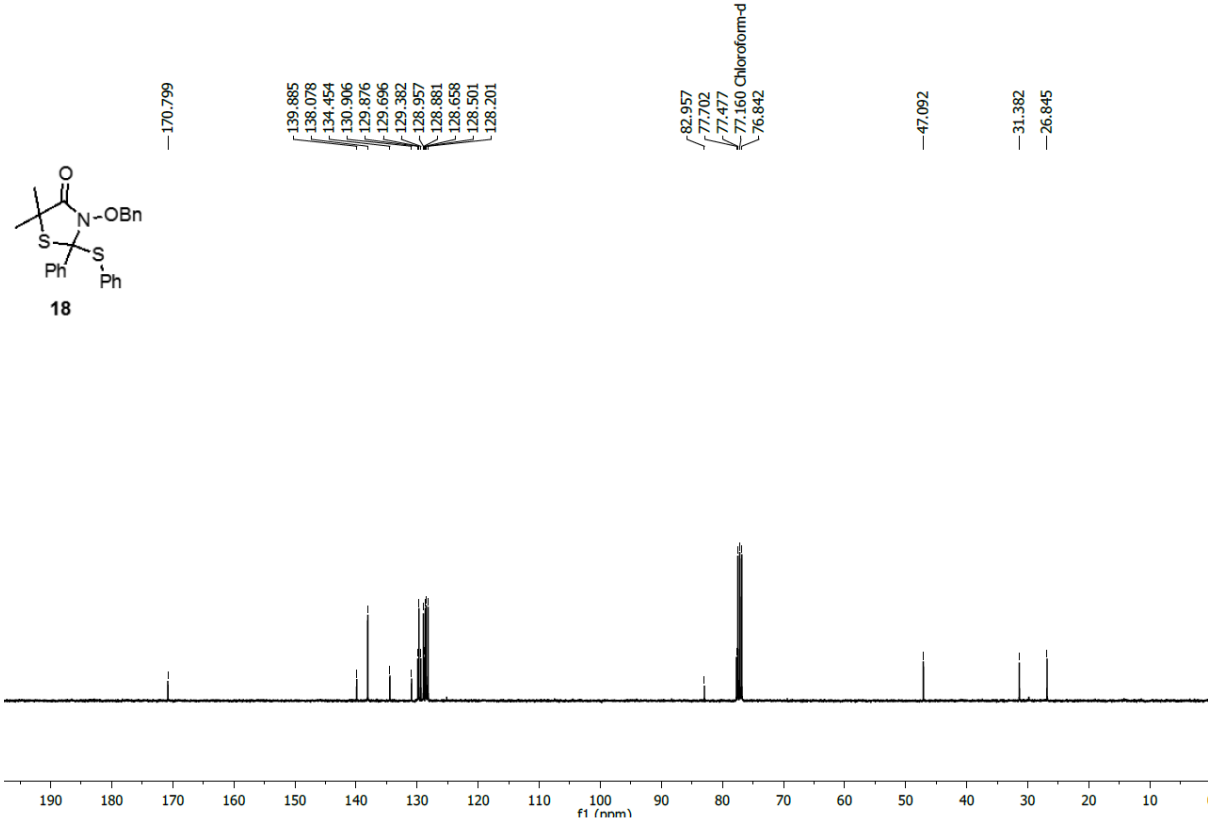
2.00
2.07
3.07
8.09
1.04
1.03
3.14
3.11
f1 (ppm)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128.658
128.501
128.201
82.957
77.702
77.477
77.160 Chloroform-d
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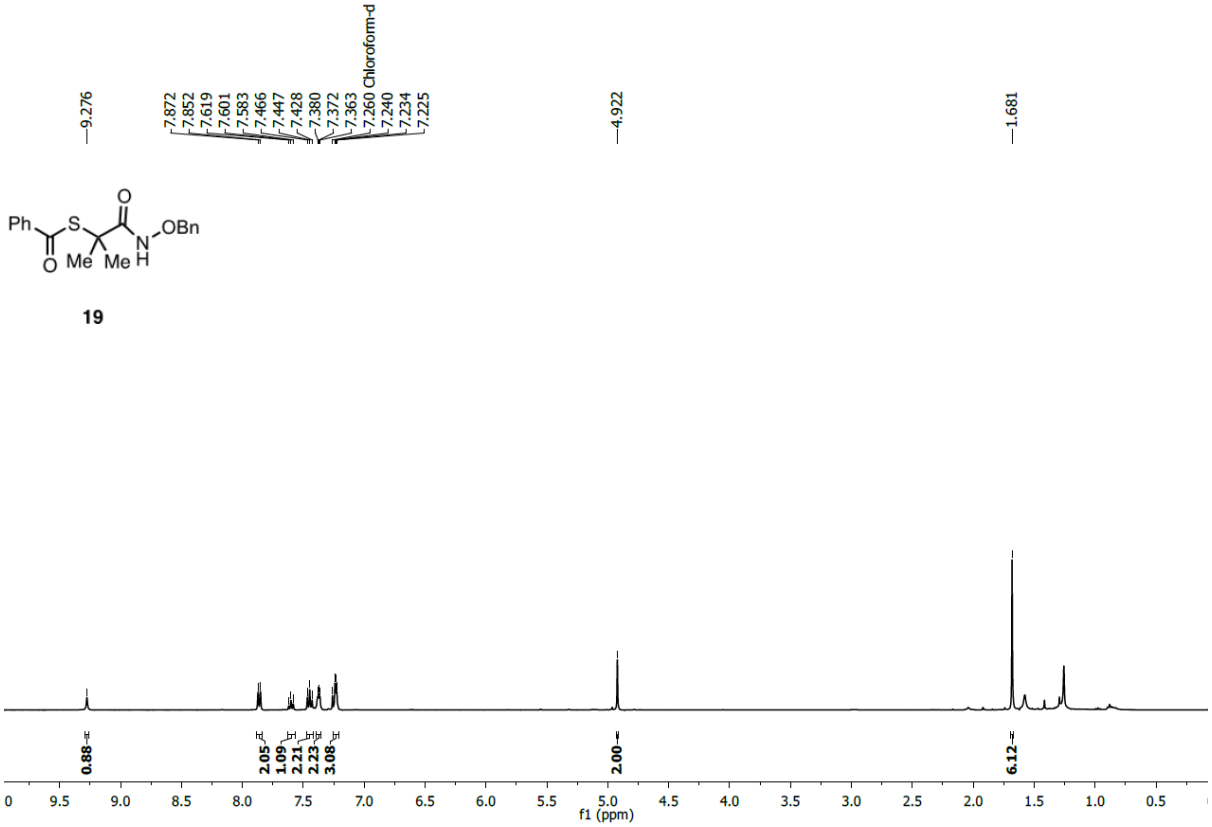
47.092
31.382
26.845
O
N-OBn
S
S
Ph
Ph
18
f1 (ppm)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7.372
7.363
Chloroform-d
7.260
7.240
7.234
7.225
4.922
1.681
Ph
S
O
N
H
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Me
Me
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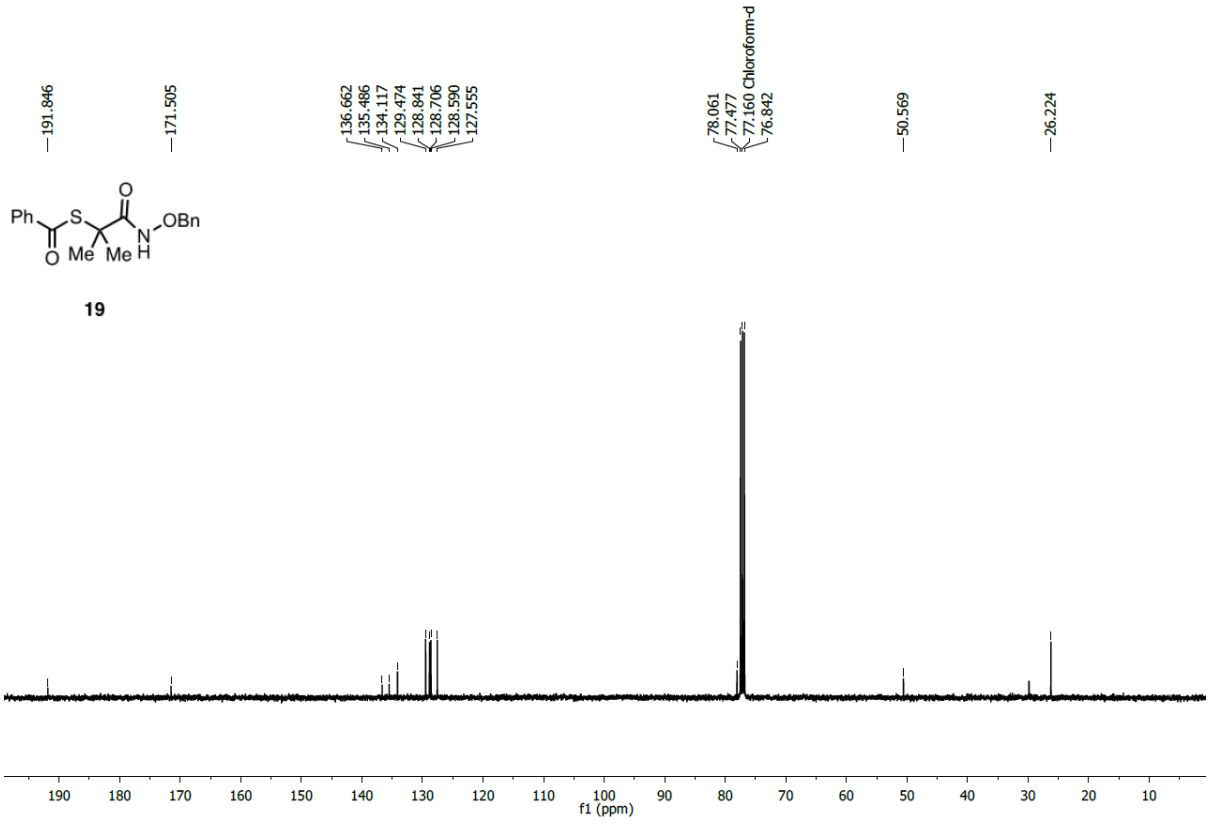
2.23
3.08
2.00
6.12
f1 (ppm)

19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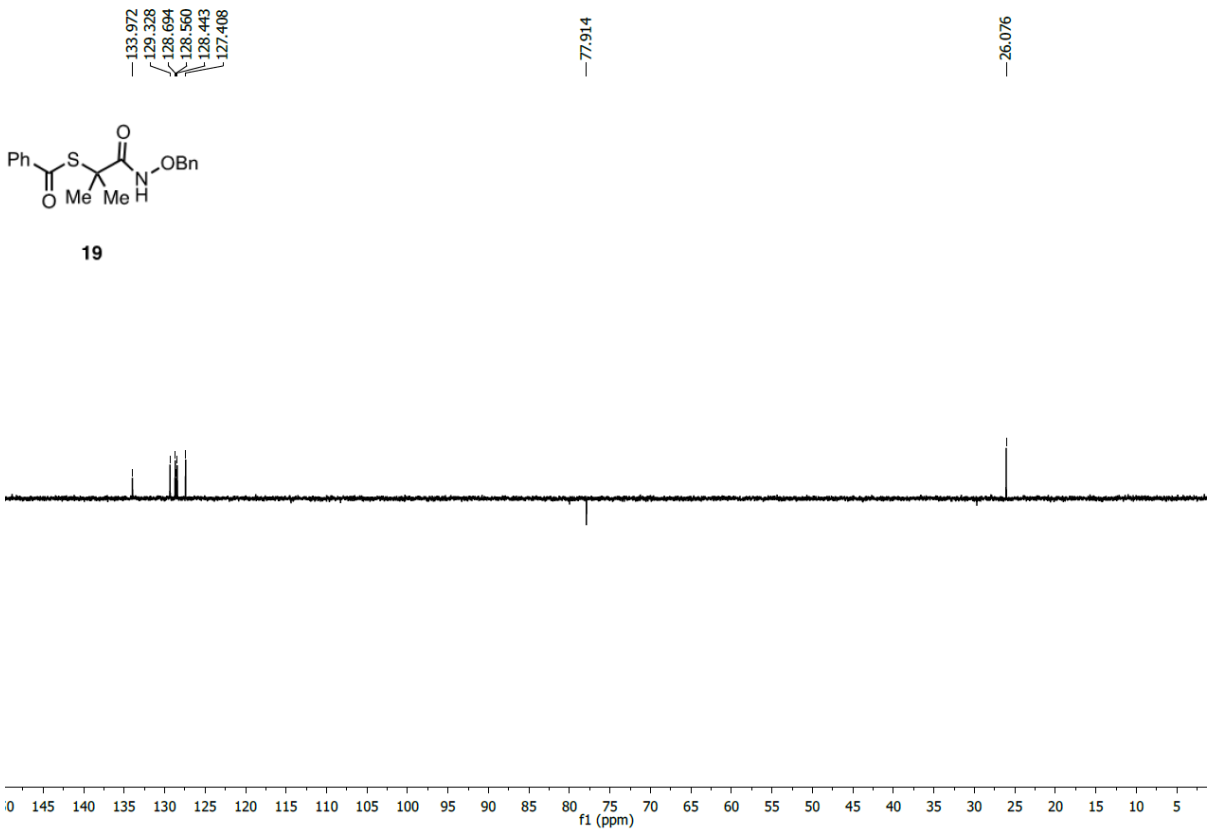
135.486
134.117
129.474
128.841
128.706
128.590
127.555
78.061
77.477
77.160
Chloroform-d
76.842
50.569
26.224
Ph
S
O
N
H
OBn
Me
Me
f1 (ppm)

19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129.328
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128.560
128.443
127.408
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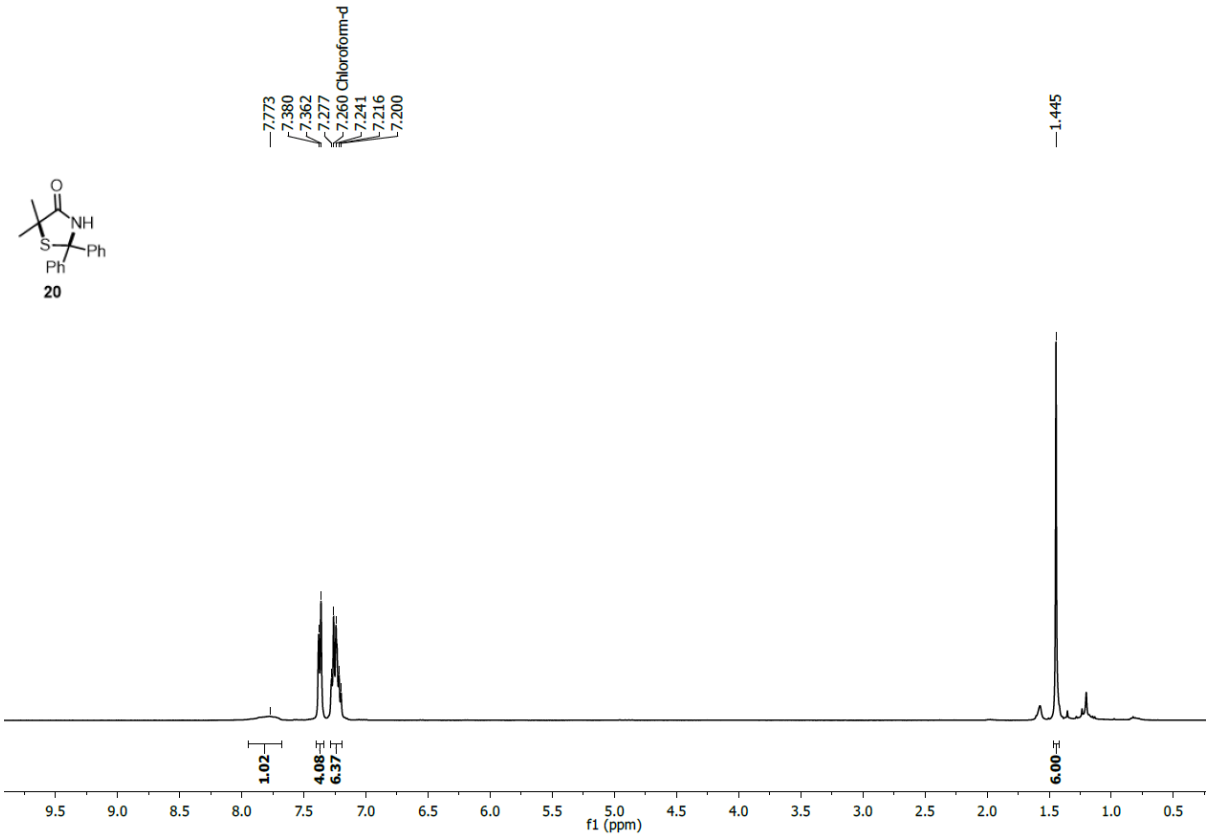
26.076
Ph
S
O
N
H
OBn
Me
Me
O
19
f1 (ppm)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7.380
7.362
7.277
7.260 Chloroform-d
7.241
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O
NH
S
Ph
Ph
20
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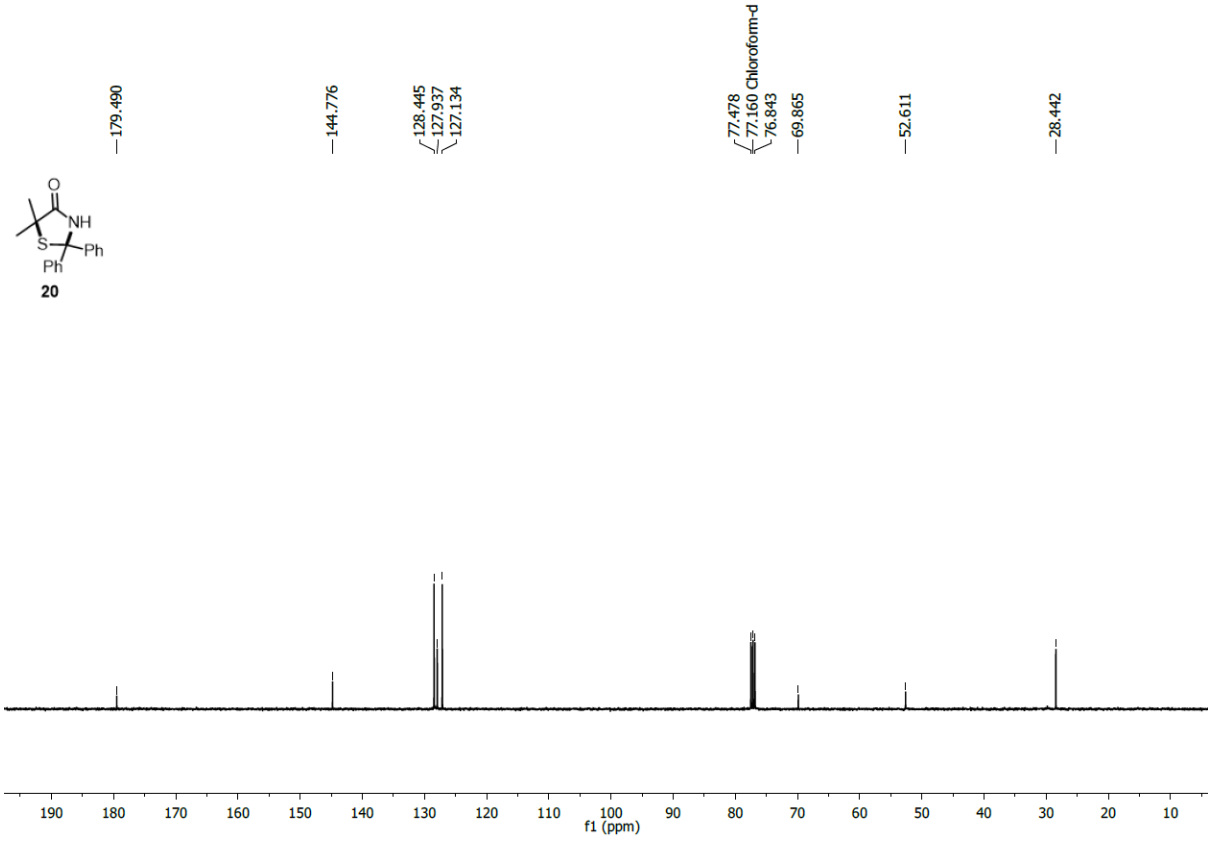
4.08
6.37
6.00
f1 (ppm)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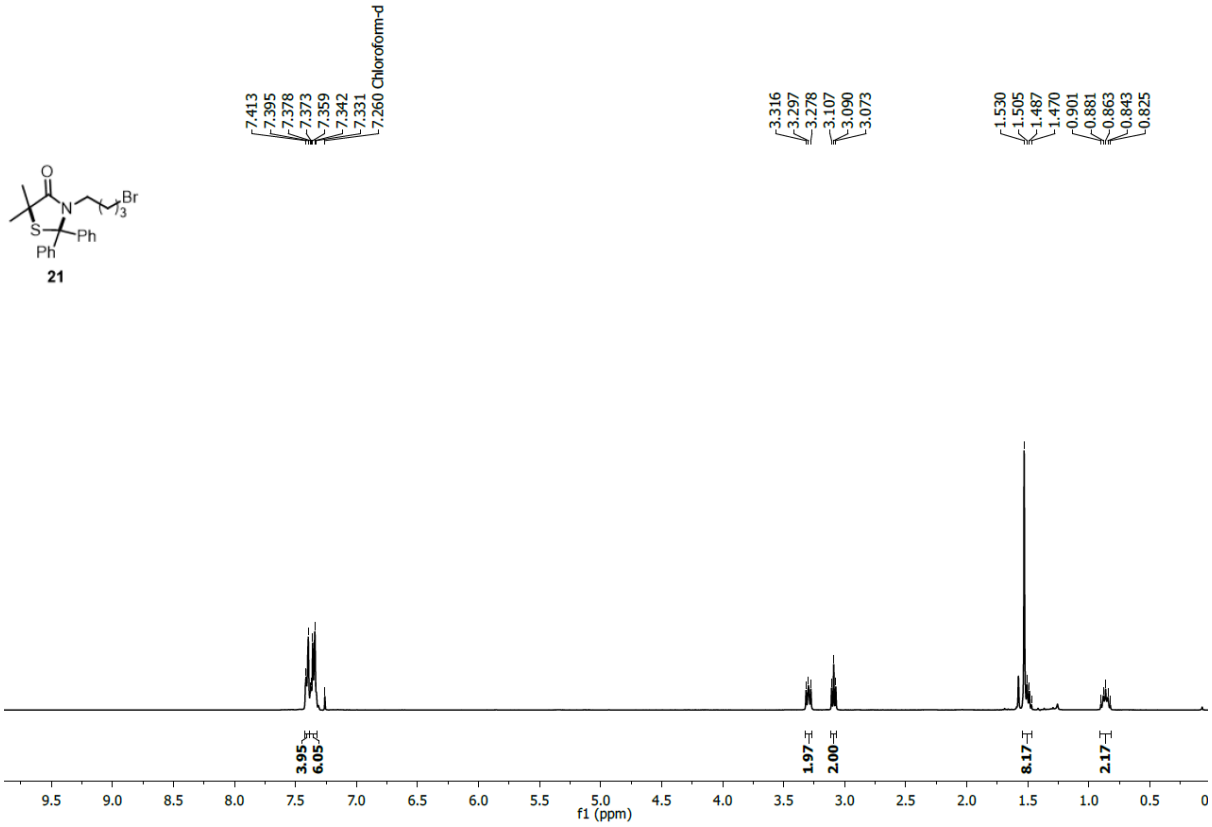
144.776
128.445
127.937
127.134
77.478
77.160 Chloroform-d
76.843
69.865
52.611
28.442
O
NH
S
Ph
Ph
20
f1 (ppm)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7.373
7.359
7.342
7.331
7.260 Chloroform-d
3.316
3.297
3.278
3.107
3.090
3.073
1.530
1.505
1.487
1.470
0.901
0.881
0.863
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Br
Ph
Ph
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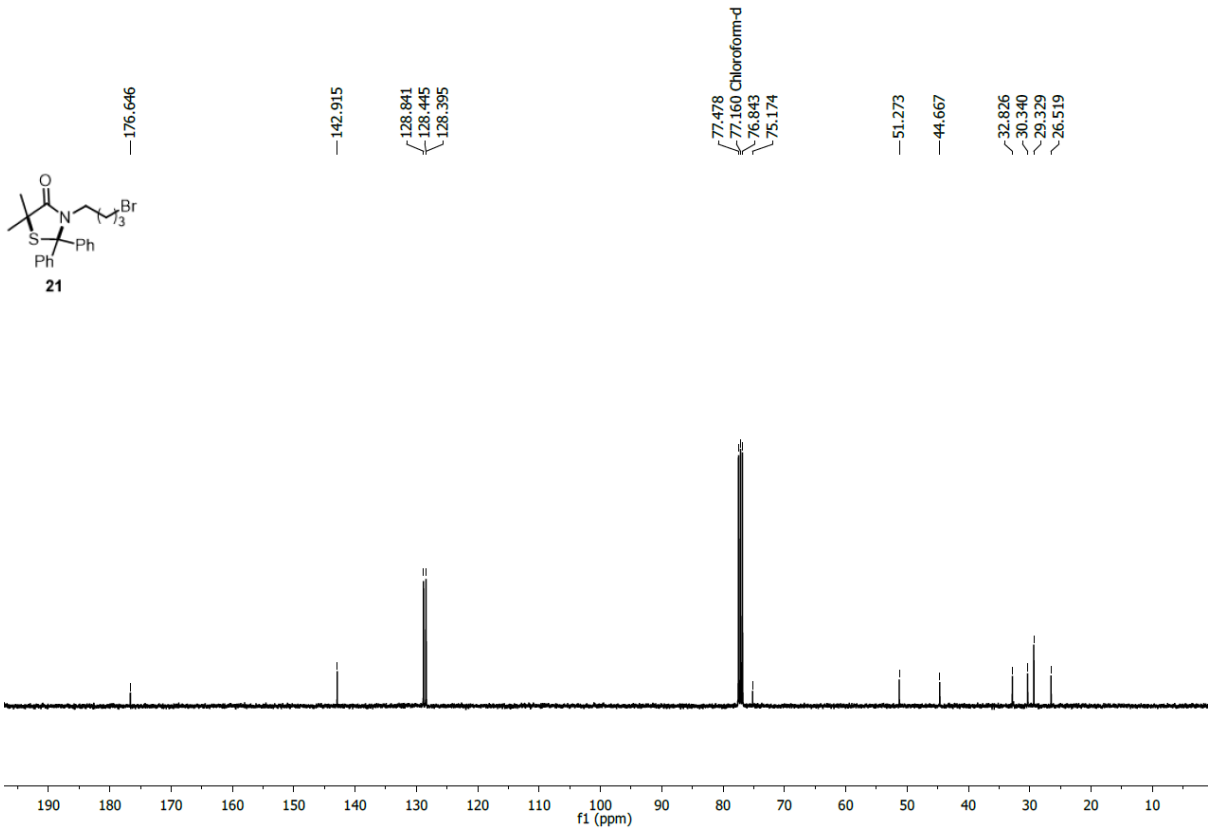
2.00
8.17
2.17
f1 (ppm)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142.915
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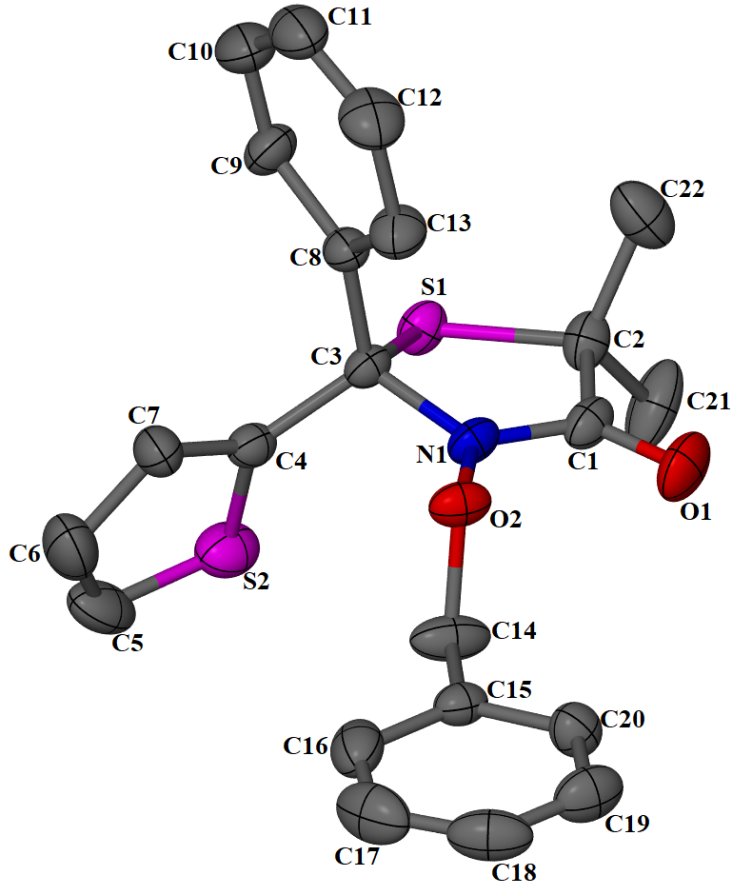
77.160 Chloroform-d
76.843
75.174
51.273
44.667
32.826
30.340
29.329
26.519
Br
Ph
Ph
21
f1 (ppm)

14. Crystallographic Data

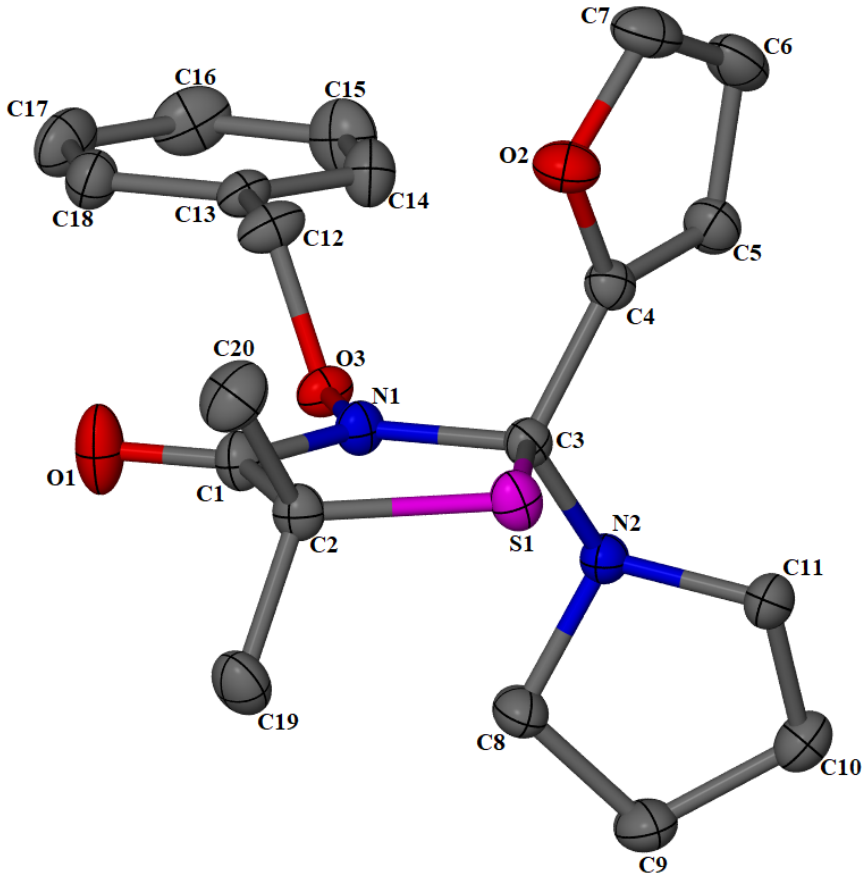
Crystal structures of all the compounds were determined by Single Crystal X-ray Diffraction (SCD) experiment. The structures of **3am** and **5am** were determined on Bruker D8 Quest equipped with a micro-focus anode (Mo) and a PHOTON II CMOS detector. Integration and scaling of data were performed by SAINT[1] and SADABS program[2]. The structures were solved by direct methods using SHELXT-2018[3] and refined by full-matrix least-squares on F^2 using SHELXL-2018/3 version[3]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed at calculated positions using riding models.

ORTEP diagram: Atoms are shown with 30% probability of thermal ellipsoids

Compound: *3am* [CCDC No. 1918619]



Compound: 5am [CCDC No. 1918620]



References:

1. SAINT, Version 6.45; Bruker AXS Inc.: Madison, WI, 2003.

2. SADABS, Version 2.05; Bruker AXS Inc.: Madison, WI, 2002.

3. Sheldrick, G. M. *Acta Cryst. Sect. A.* **2015**, *71*, 3-8

Table S1. Crystal data and refinement parameters

Code	**3am**	**5am**
Empirical formula	C_{22} H_{21} N_1 O_2 S_2	C_{20} H_{24} N_2 O_3 S_1
Formula weight	395.52	372.47
Wavelength/ Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*P*2$_1$/*c*	*P*2$_1$/*n*
Crystal size (mm$^{3)}$	0.47 x 0.43 x 0.27	0.44 x 0.35 x 0.26
a/Å	8.9931(3)	10.7320(8)
b/Å	9.8904(4)	10.5315(7)
c/Å	23.2963(8)	17.0367(12)
α/(°)	90	90
β/(°)	93.1270(10)	100.807(3)
γ/(°)	90	90
V/Å^3	2069.01(13)	1891.4(2)
Z	4	4
D_{cal} /g cm^{-3}	1.270	1.308
T/K	298	298
μ/mm^{-1}	0.274	0.193
F_{000}	832	792
Theta ranges for data collection	3.2° to 28.3°	2.4° to 30.4°
Index ranges	-10 ≤ h ≤ 11, -13 ≤ k ≤ 13, -31 ≤ l ≤ 30	-15 ≤ h ≤ 15, -14 ≤ k ≤ 14, -24 ≤ l ≤ 24
Reflections measured	29550	31791
Unique reflections	5087	5653
Observed reflections	3845	4555
Parameters	246	237
Data completeness	0.989	0.989
R_{int}	0.028	0.027
final *R* (I >2σ(I))	0.0699	0.0397

final *R* (all data)	0.0889	0.0538
final wR_2 (I >2σ(I))	0.2183	0.1018
final wR_2 (all data)	0.2459	0.1143
GOF on F^2	1.064	1.046
Highest peak and deepest hole	0.39 & -0.63	0.23 & -0.24
CCDC No.	1918619	1918620

15. Reference.

1. (a) Pedersen,B.S.;Scheibye,S.; Nilsson,N.H.; Lawesson, S.O. *Bull. Soc. Chim. Belg*. **1978**, 87, 223.(b) Mloston, G.; Urbaniak, K.; Gebicki, K.; Grzelak, P.; Heimgartner, H. Hetaryl Thioketones: Synthesis and Selected Reactions. *Heteroatom Chemistry*. **2014,** *25*, 548. (c) Grzelak, P.; Utecht, G.; Jasinski, M.; Mloston, G. First (3+2)-Cycloadditions of Thiochalcones as C=S Dipolarophiles: Efficient Synthesis of 1,3,4-Thiadiazoles via Reactions with Fluorinated Nitrile Imines. *Synthesis*. **2017**, *49*, 2129. (d) Greidanus J. *Can. J. Chem.* **1970**, *48*, 3530.

2. (a) Scheibye, S.; Pedersen, B.S.; Lawesson, S.O. *Bull. Sot. Chim. Belg.* **1978,** *87,*229. (b) Raucher S.; Kein, P. *Tetrahedron Lett*. **1980,** *21*, 406. (c) Sundberg, R. J.; Walters, C.P.; Bloom J.D. Borohydride and Cyanoborohydride Reduction of Thioimonium Salts: A Convenient Route for transformation of amides to Amines. *J. Org. Chem.* **1981**, *46*, 3730. (d) Palani V.; Chen J.; Hoye T.R. Reactions of HDDA-derived Benzynes with Thioamides: Synthesis of Dihydrobenzothiazino-Heterocyclics. *Org. Lett.* **2016**, *18*, 24, 6312. (e) Ransborg L.K.; Albrecht L.; Weise C.F.; Bak J.R.; and Jørgensen K.A. Optically Active Thiophenes via an Organocatalytic One-Pot Methodology. *Org. Lett.* **2012**, *14,* 3, 724. (f) Hori, T.; Otani, Y.; Kawahata, M.;Yamaguchi, K.; Ohwada, T. Nonplanar Structures of Thioamides Derived from 7-Azabicyclo[2.2.1]heptane. Electronically Tunable Planarity of thioamides. *J. Org. Chem.* **2008,** *73*, 22.

3. See reference **1b** and **1j** from the maintext.