Supplementary Information

Annulative coupling of sulfoxonium ylides with 2-amino(thio)phenols: Easy access to 2-acyl benzox(thio)azoles

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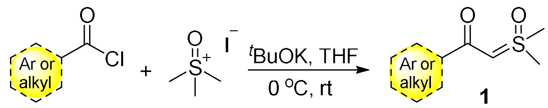
Table of contents

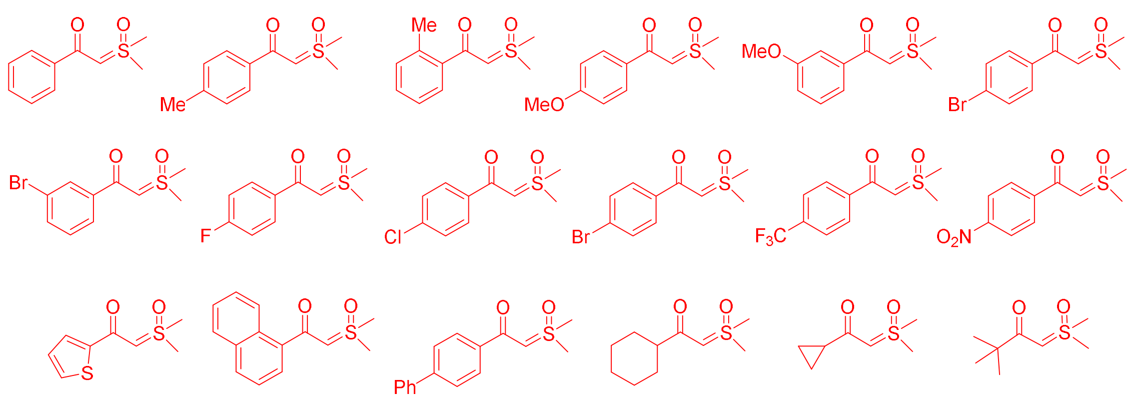
1. General information: Substrate **1** was synthesized according to the known literature procedure.[1] All the substrates **2** and **4** were purchased from Merck, TCI, Spectrochem chemicals. All the chemicals and solvents were used as received without further purification. Progress of the reactions was monitored by TLC using precoated aluminium plates of Merck Kieselgel 60 F254. Column chromatography was performed on silica gel (100-200 mesh) using a mixture of *n*-hexane/ethyl acetate. ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra were recorded in $CDCl_3$ on JEOL ECS and Brucker operating at 500/126/471 and 600/151/565 MHz, respectively. Chemical shifts are reported in δ (ppm), referenced to TMS and are referenced to the residual deuterium in the solvent (^{1}H NMR: $CDCl_3$ at 7.26 ppm) and carbon of the solvent peak (^{13}C{^{1}H} NMR: $CDCl_3$ at 77.160 ppm), respectively. NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, tt = triplet of triplet, m = multiplet) etc. The coupling constants *J*, are reported in Hertz (Hz). Mass spectra were recorded on SCIEX X500R QTOF (TOF-MS) mass spectrometer.

2. General experimental procedure for the synthesis of substituted sulfoxonium ylides

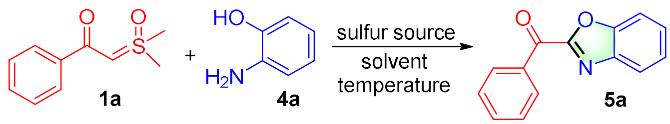


Sulfoxonium ylides were prepared according to the known literature procedure.[1] In brief, trimethylsulfoxonium iodide (18.0 mmol, 3.0 equiv.) was added to a stirred solution of potassium *tert*-butoxide (24.0 mmol, 4.0 equiv.) in anhydrous THF (25 mL) at ambient temperature. The mixture was then refluxed for 2 hours, cooled to 0 ºC, and subsequently, a solution of acyl chlorides (6.0 mmol, 1.0 equiv.) in THF (5 mL) was added. After that, the reaction was warmed to room temperature and stirred for an additional 3 h. After the completion of the reaction as monitored by TLC, the solvent was evaporated under reduced pressure, and water (20 mL) and DCM (30 mL) were added to the resultant slurry. The organic layer was separated, and the aqueous layer was washed with DCM (3 x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. After removing the solvent under vacuum, the crude product was purified by a mixture of EtOAc/diethyl ether with constant stirring, resulting in the precipitation of pure ylide. These ylides were filtered through a Buchner funnel under vacuum and washed with cold EtOAc/diethylether to afford the corresponding sulfoxonium ylides as solid compounds; R_f = 0.4 (95:5 EtOAc/MeOH).

3. Structures of sulfoxonium ylide used in this study



4. Table S1: Synthesis of 2-substituted Benzoxazole Derivatives: Optimization[a]



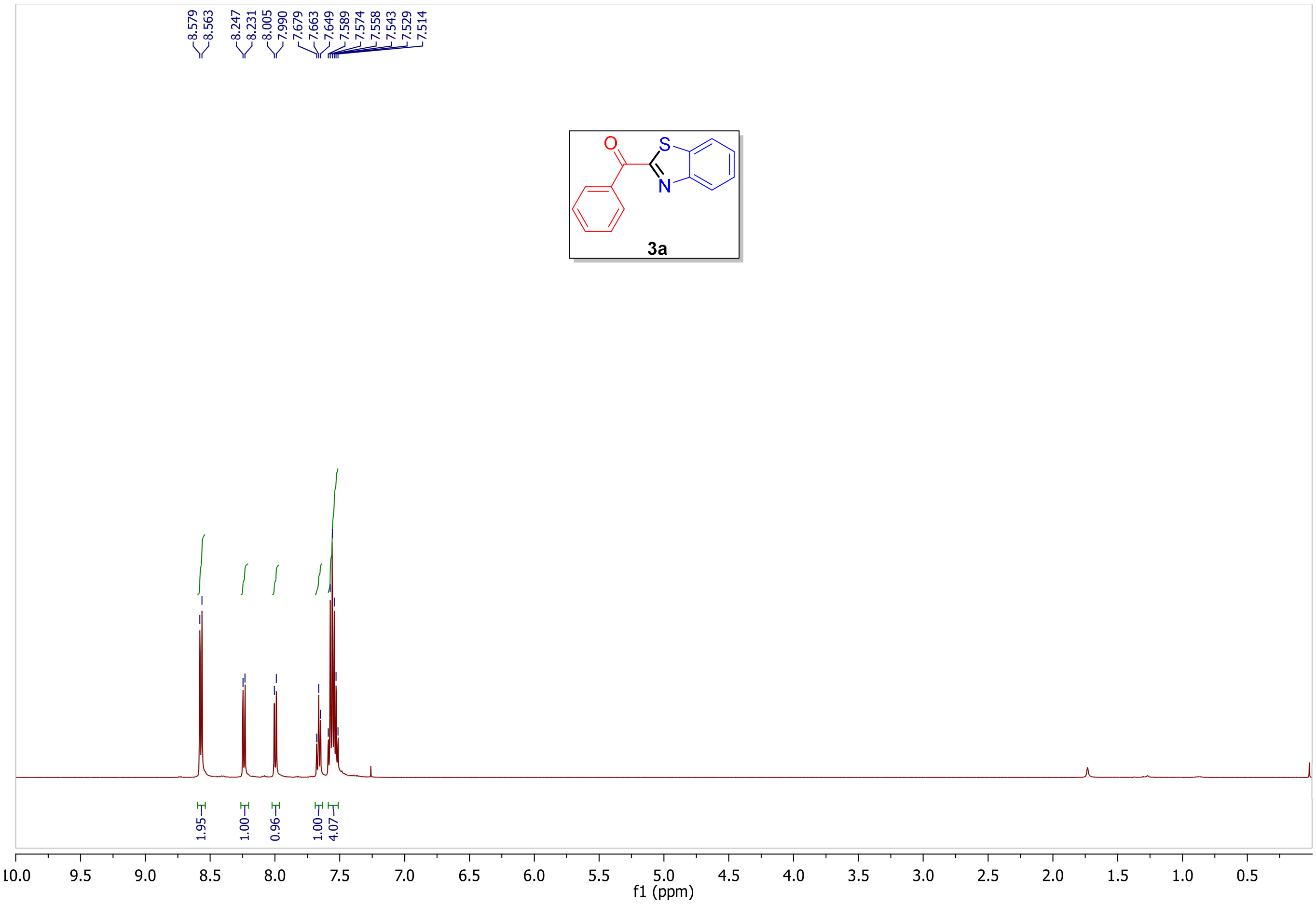
entry	solvent	sulfur source	temp (°C)	yield[b] of 3a (%)
1	DMF	S_8	100	58
2	DMSO	S_8	100	61
3	THF	S_8	60	52
4	Toluene	S_8	100	47
5	CH_3CN	S_8	60	36
6	EtOAc	S_8	60	n.d. [c]
7	CH_3OH	S_8	60	65
8	H_2O	S_8	100	trace
9	CH_3OH	S_8	rt	trace
10	CH_3OH	S_8	100	n.d.
11[d]	CH_3OH	S_8	60	48
12[d]	CH_3OH	S_8	60	63
13	DMSO	$K_2S_2O_8$	100	n.d.
14	DMSO	$Na_2S{\cdot}9H_2O$	100	trace

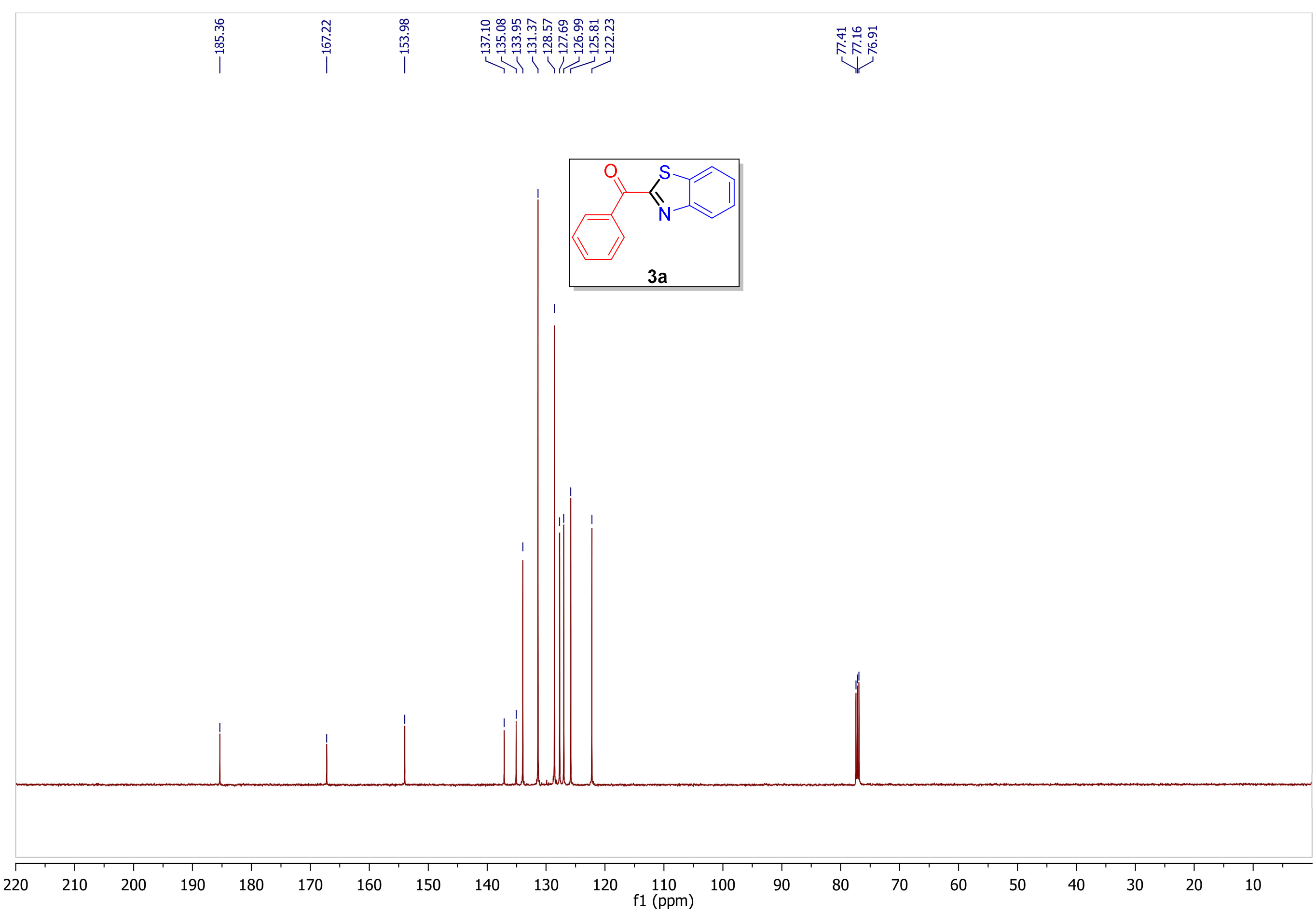
[a] General conditions: All reactions, unless otherwise noted, were conducted in an open round-bottom flask with **1a** (0.5 mmol), 2-aminophenol **4a** (0.75 mmol), and S_8 (0.75 mmol) in 3 mL of solvent at 60 °C. [b] Isolated yield. [c] n.d.: not detected. [d] 0.5 mmol (entry 11) and 1.0 mmol (entry 12) sulfur were used.

5. References

1. *(a)* S. Kumar, S. Nunewar and V. Kanchupalli, *Asian. J. Chem.*, 2022, 11, e202100689; *(b)* P. Zhou, W.-T. Yang, A. U. Rahman, G. Li and B. Jiang, *J. Org. Chem.*, 2020, 85, 360–366; *(c)* S. Zhu, K. Shi, H. Zhu, Z. K. Jia, X. F. Xia, D. Wang and L. H. Zou, *Org. Lett.*, 2020, 22, 1504–1509; *(d)* Y. Yuan and X. F. Wu, *Org. Lett.*, 2019, 21, 5310–5314.

^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3a**





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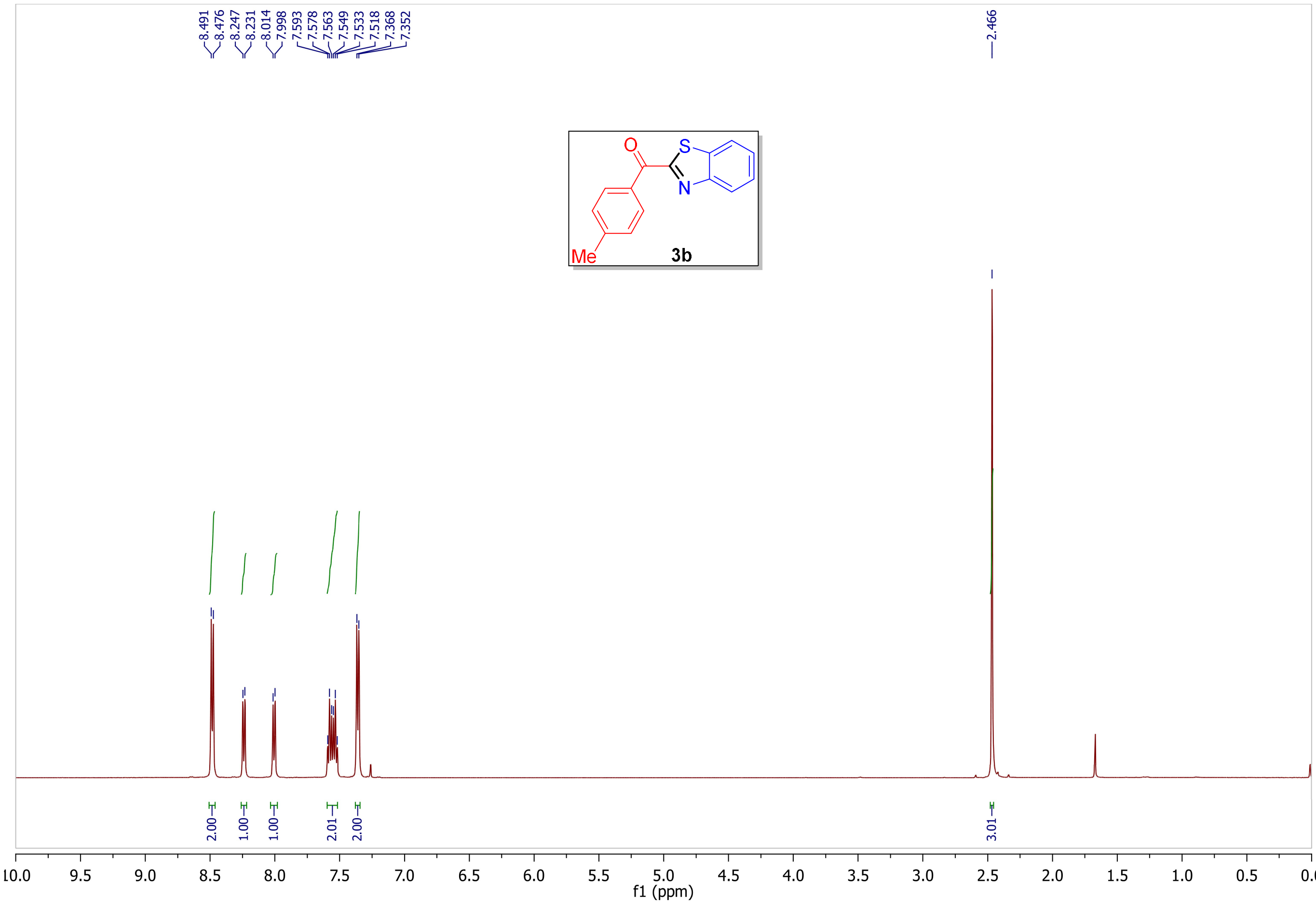

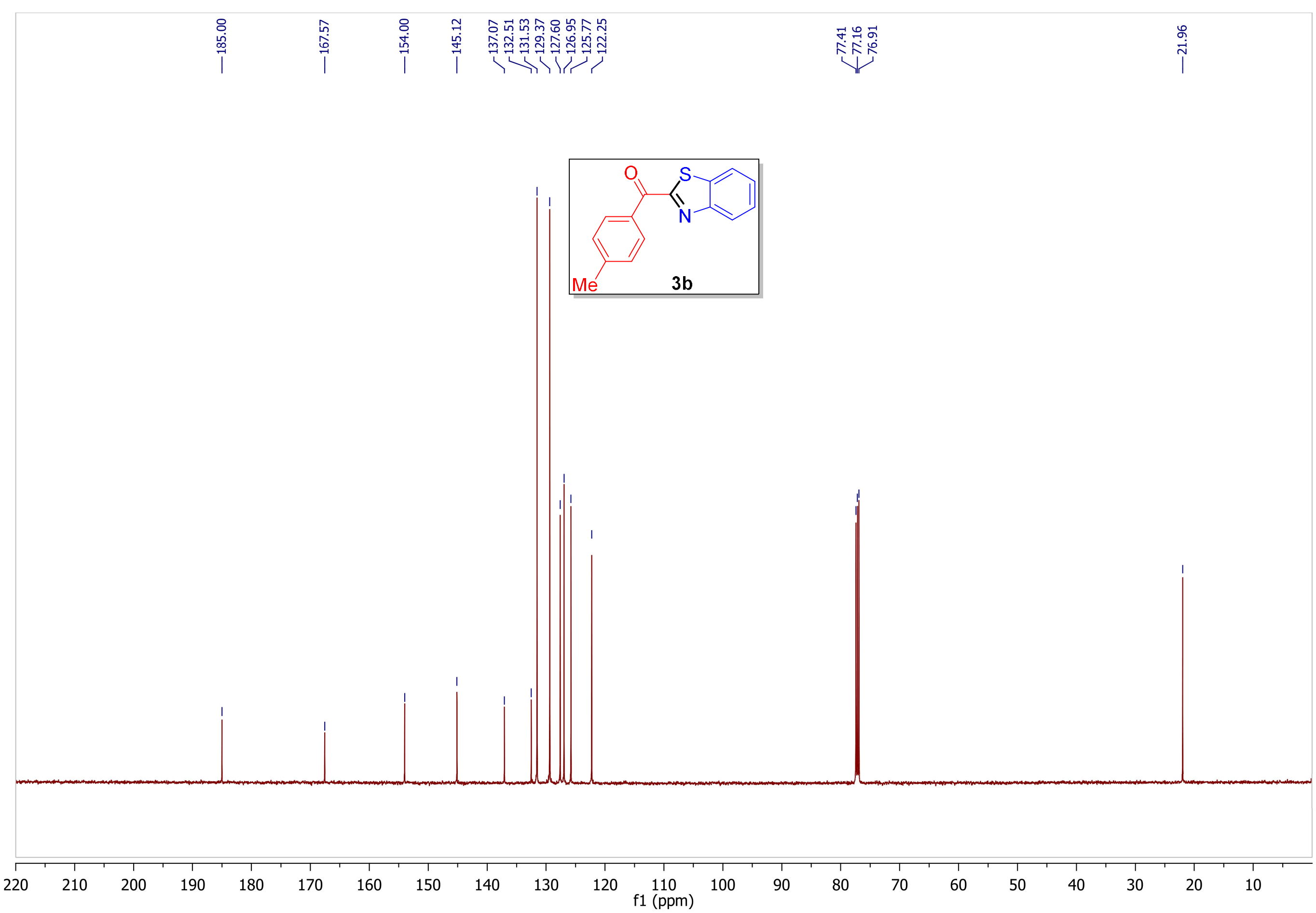

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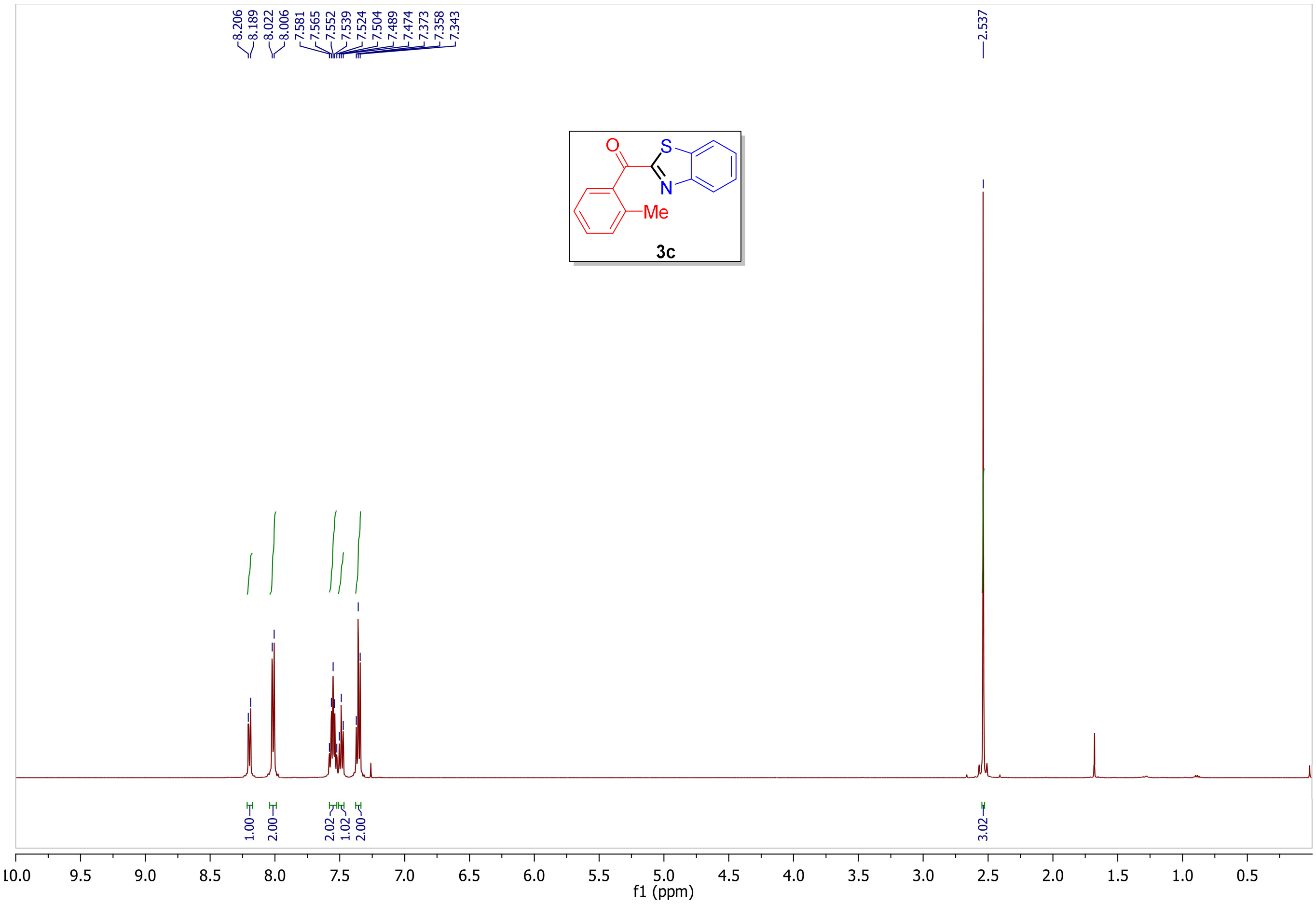

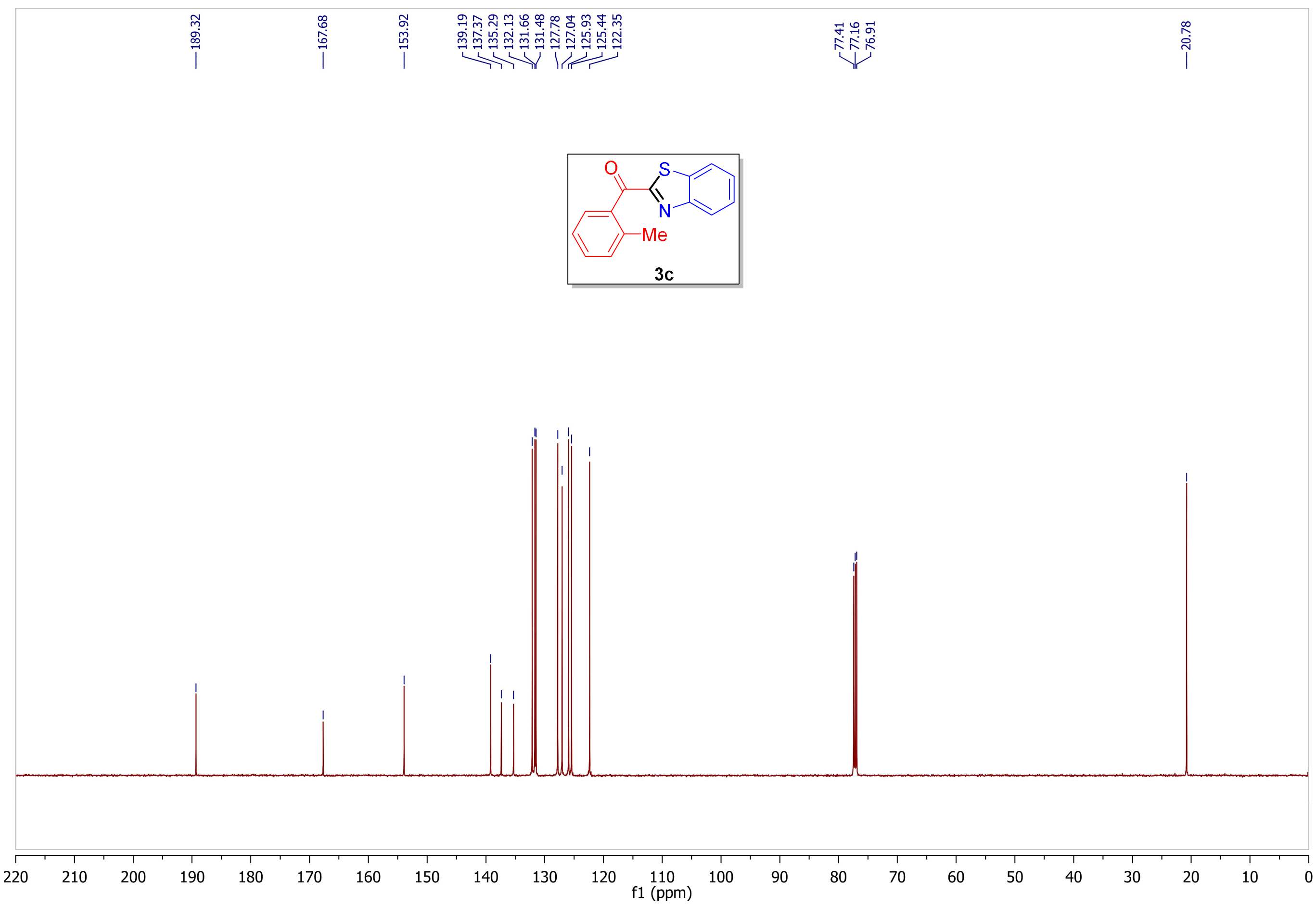

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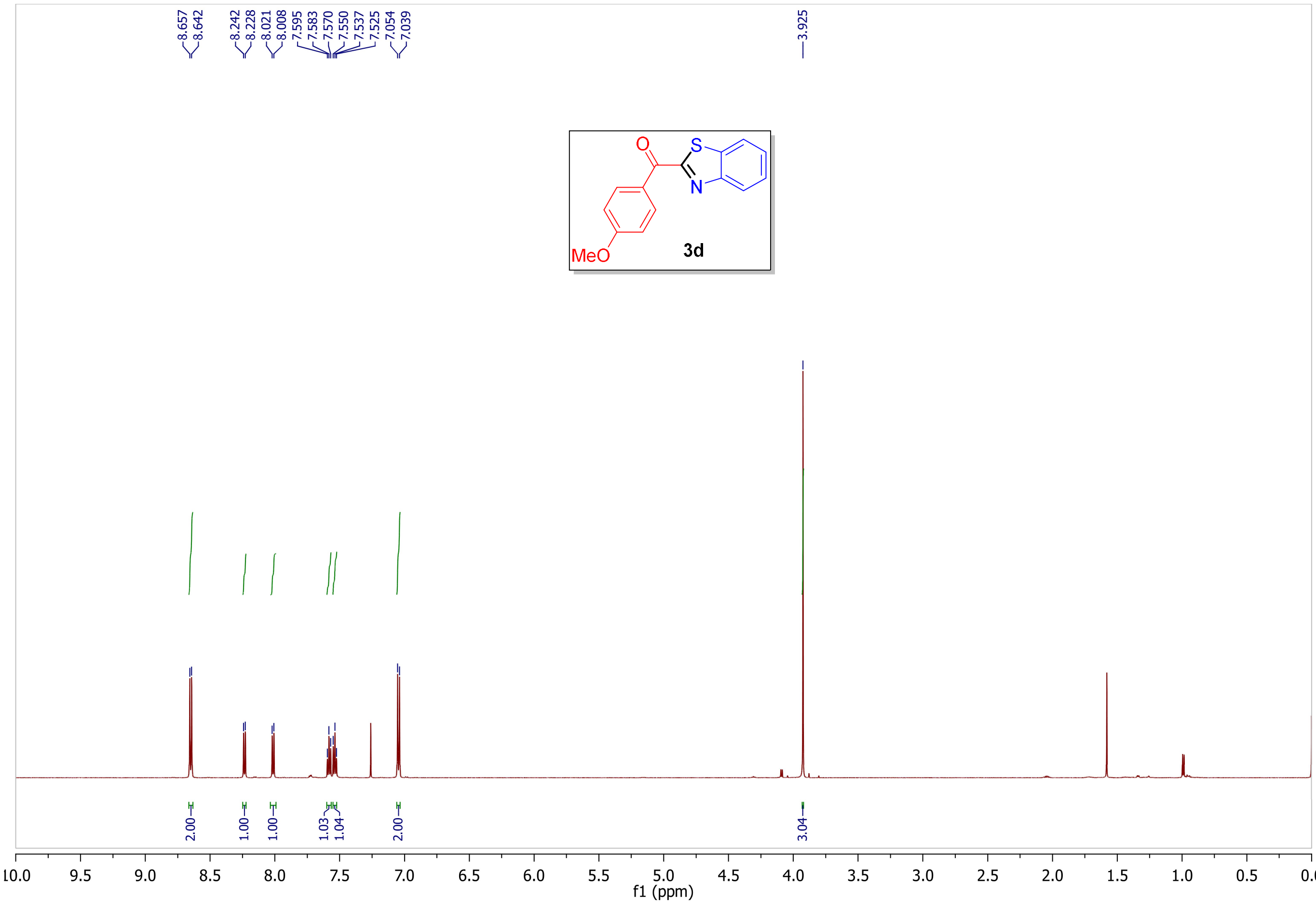

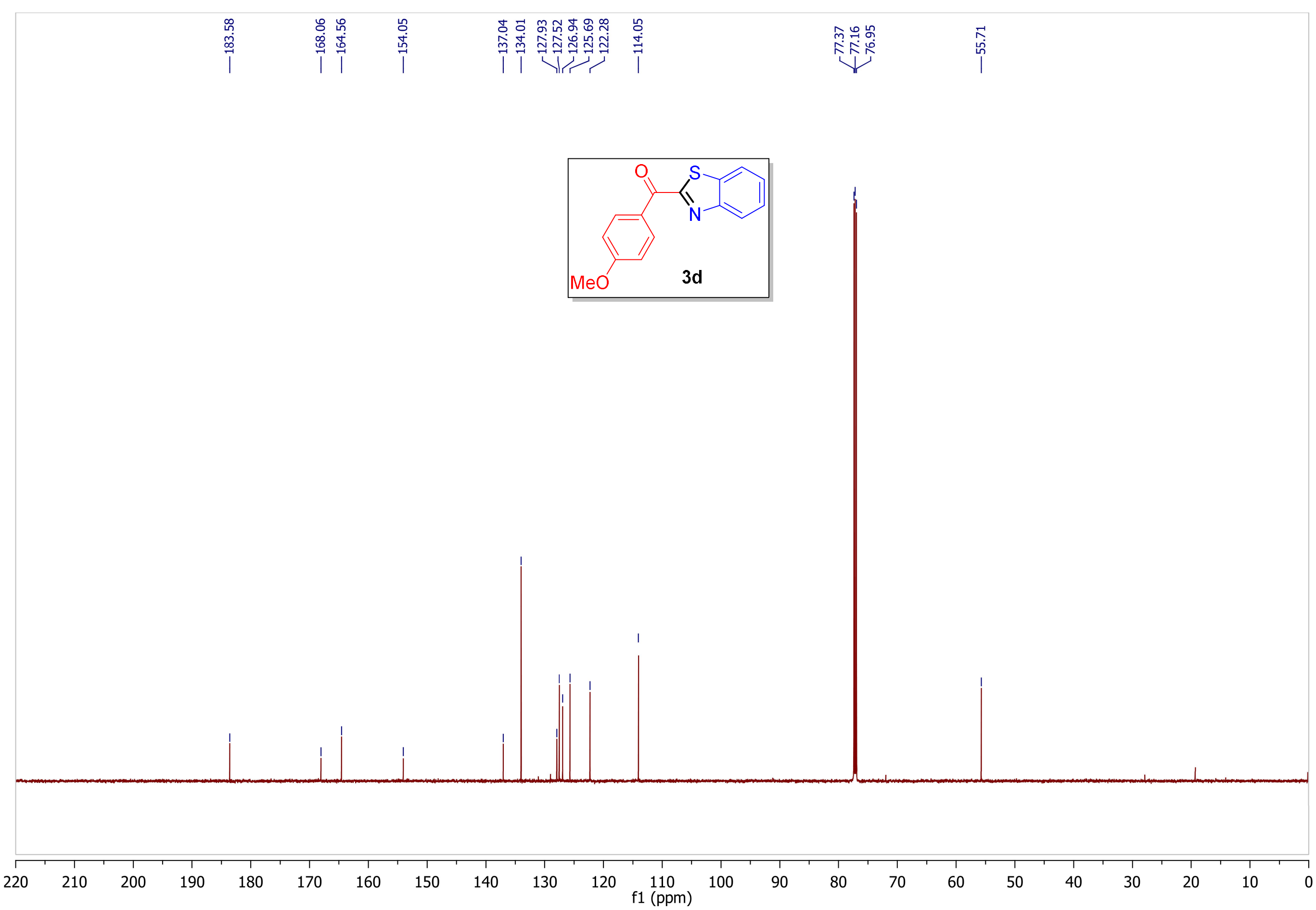

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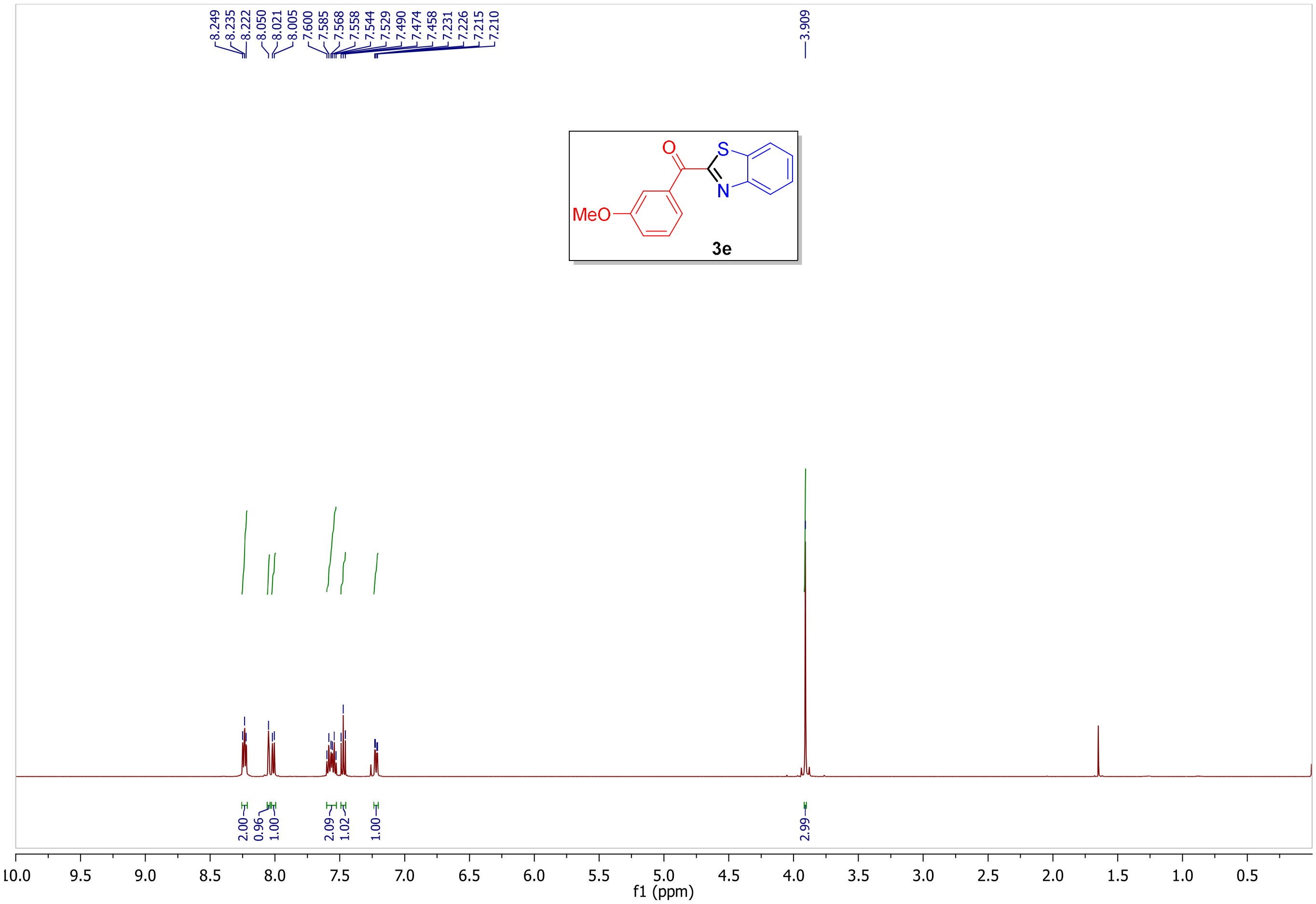

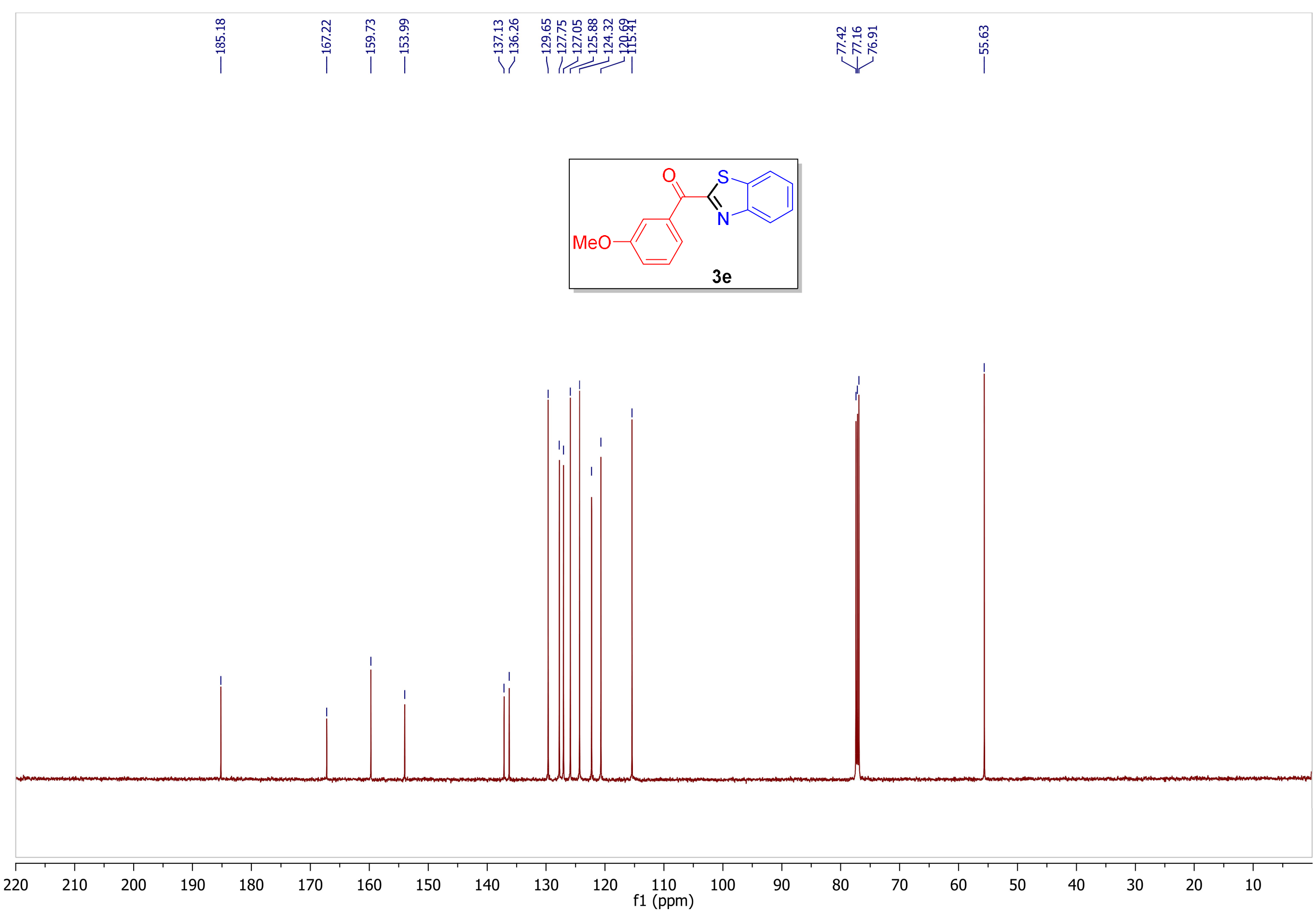

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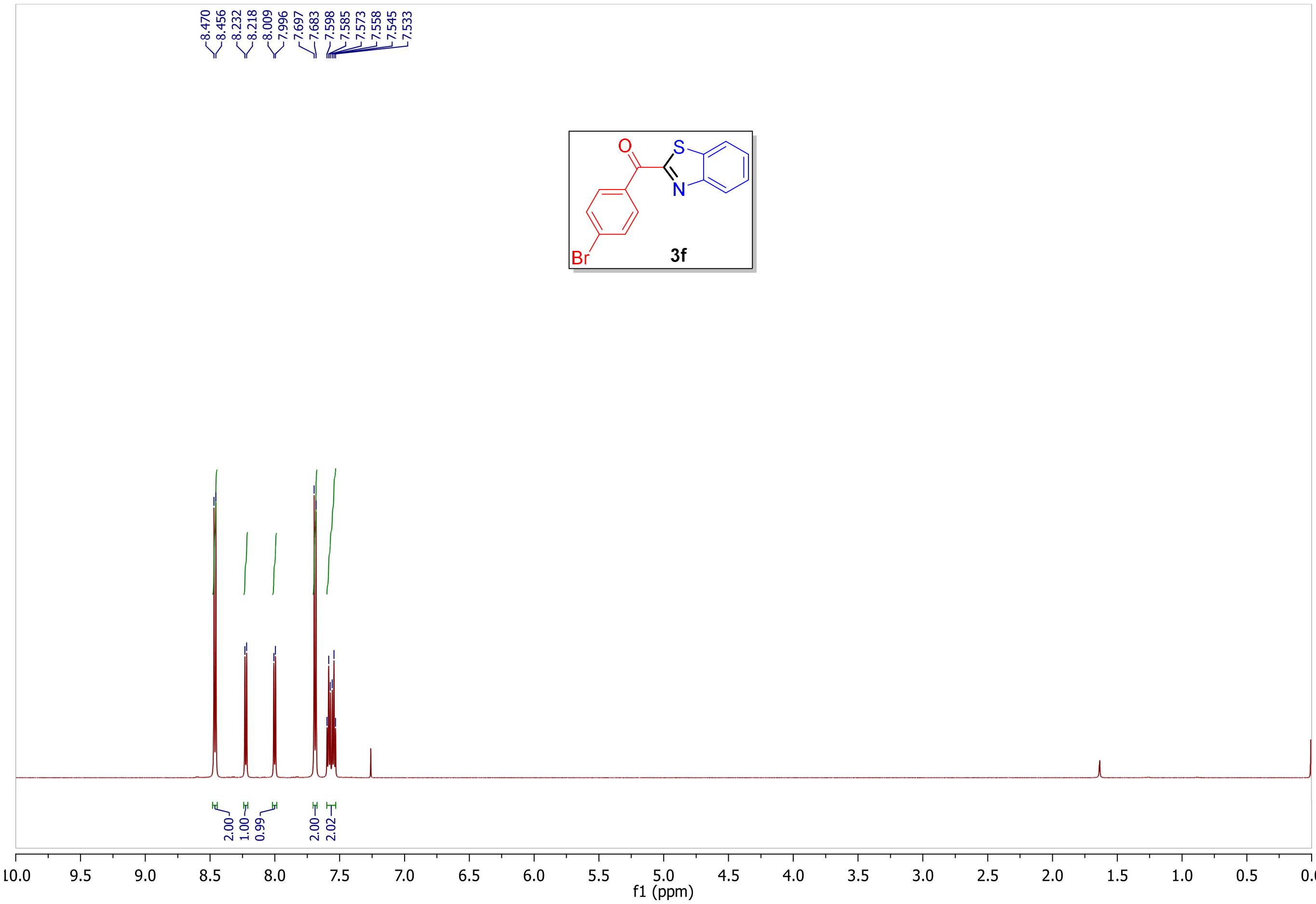

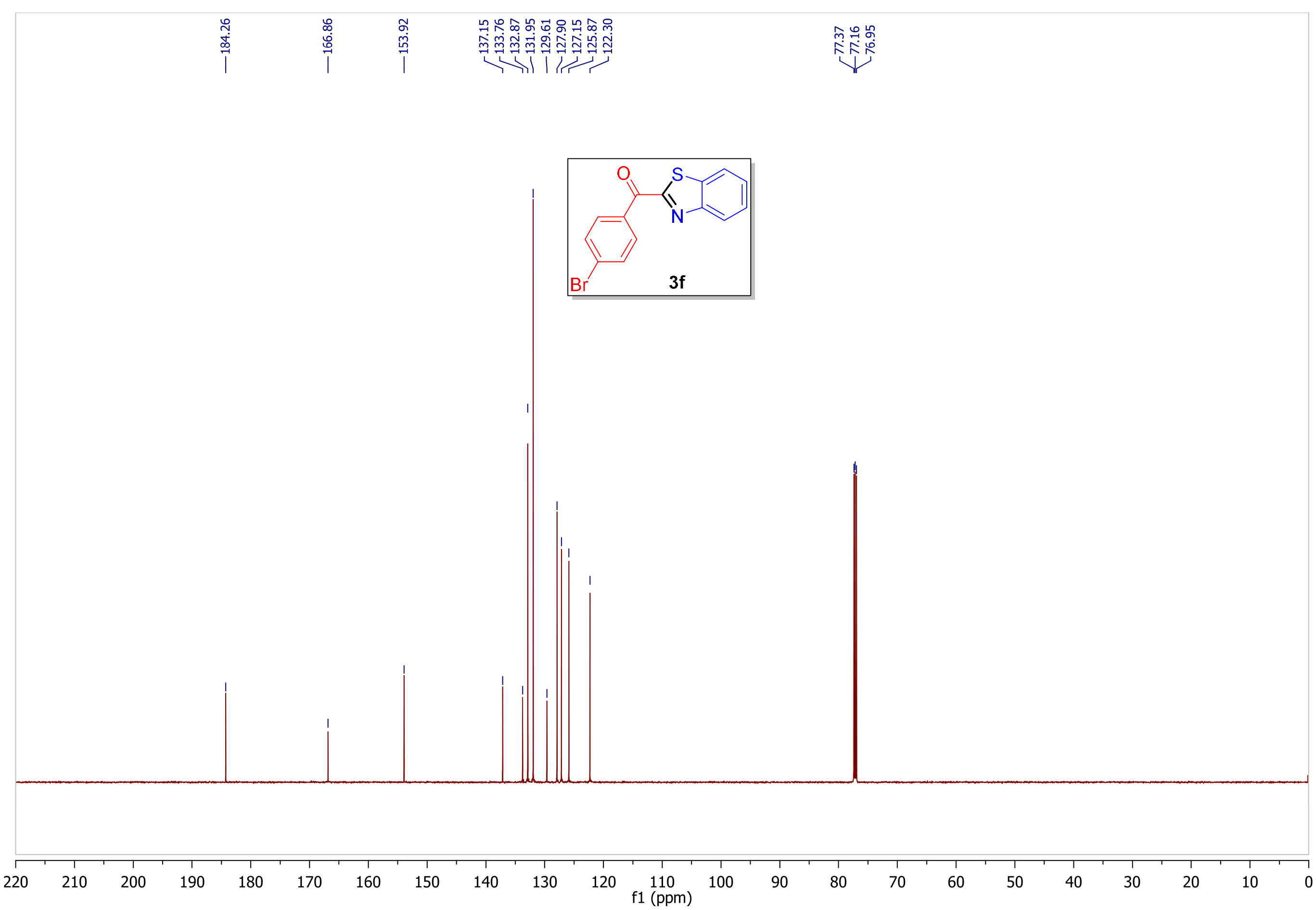

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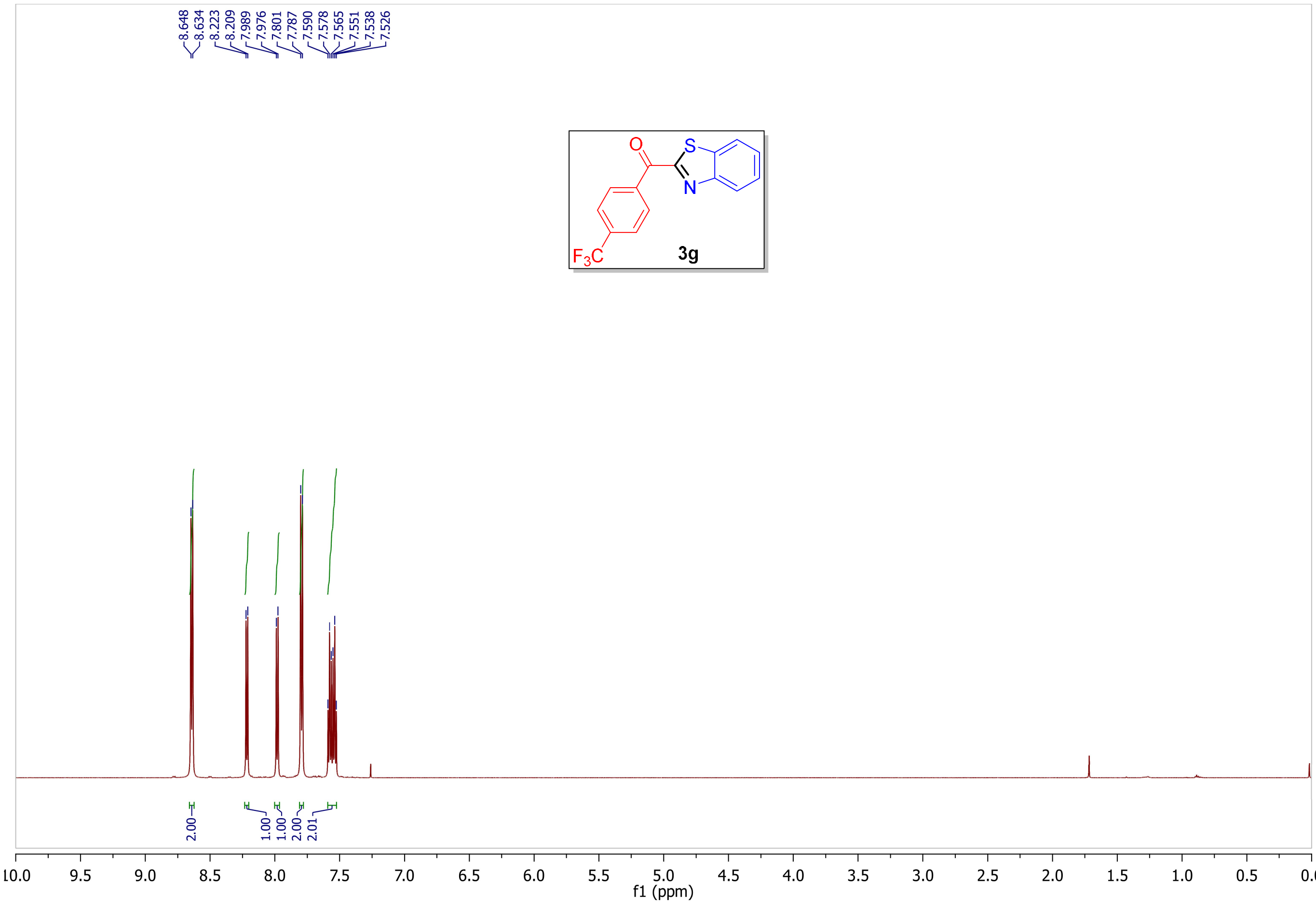

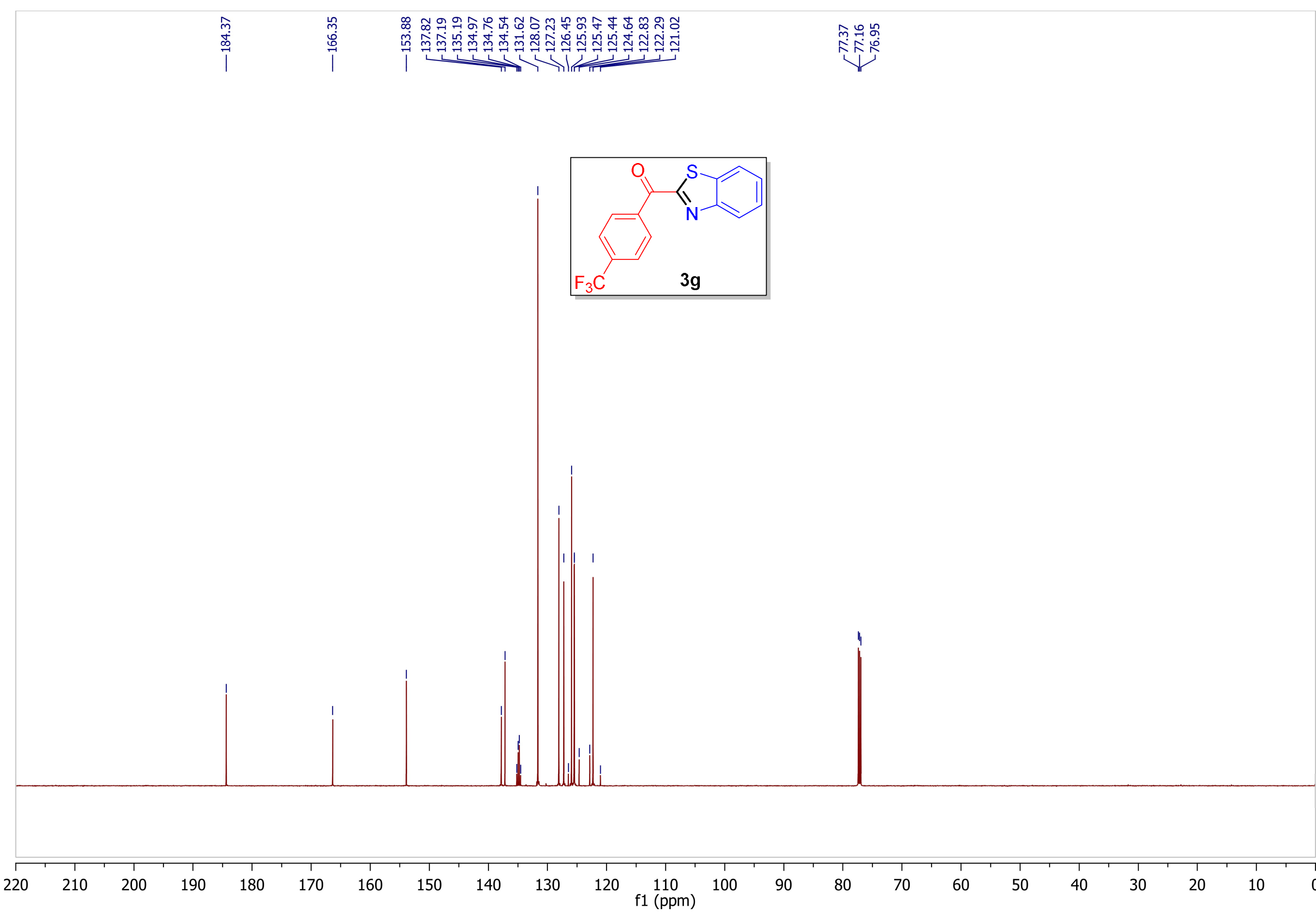

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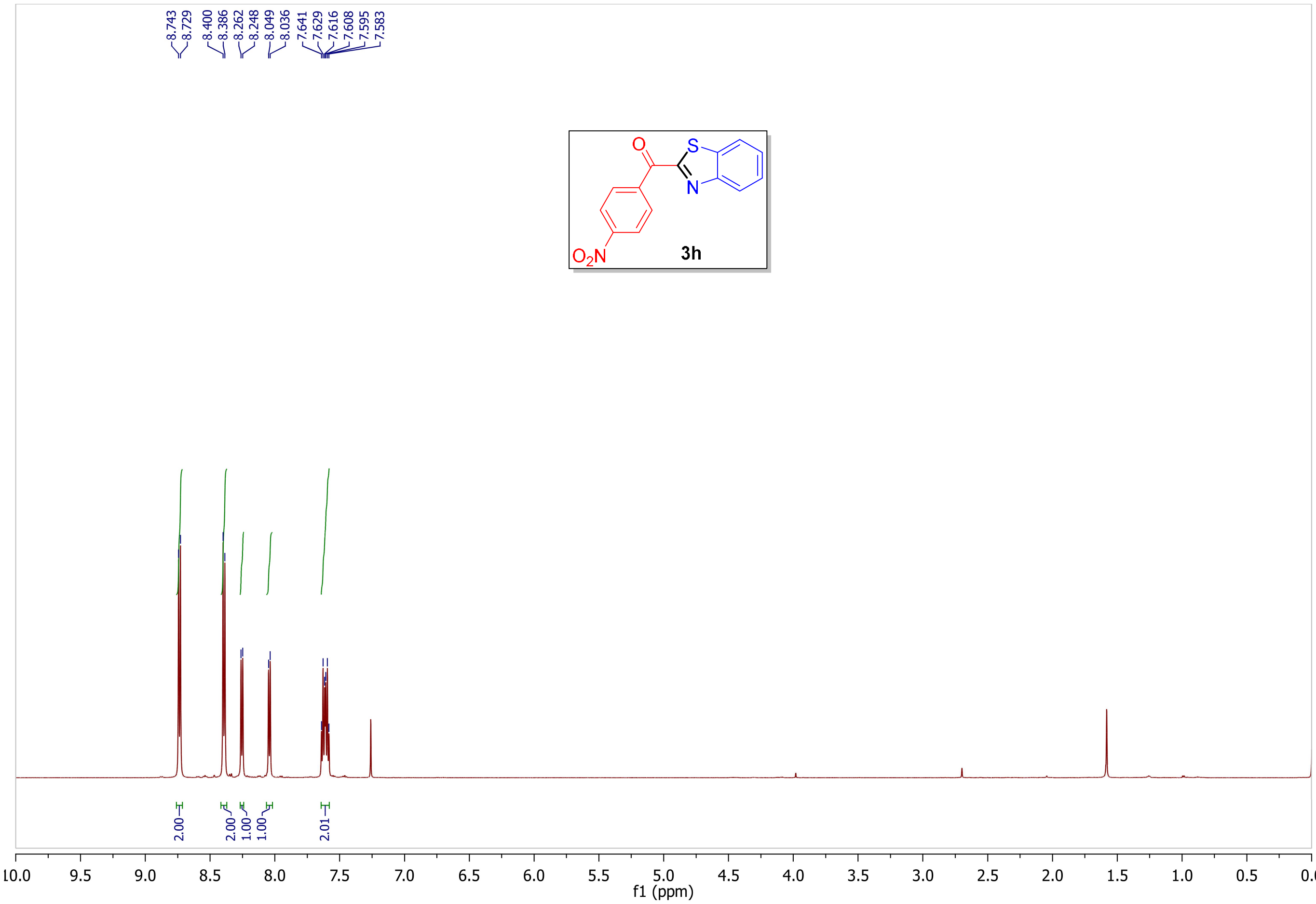

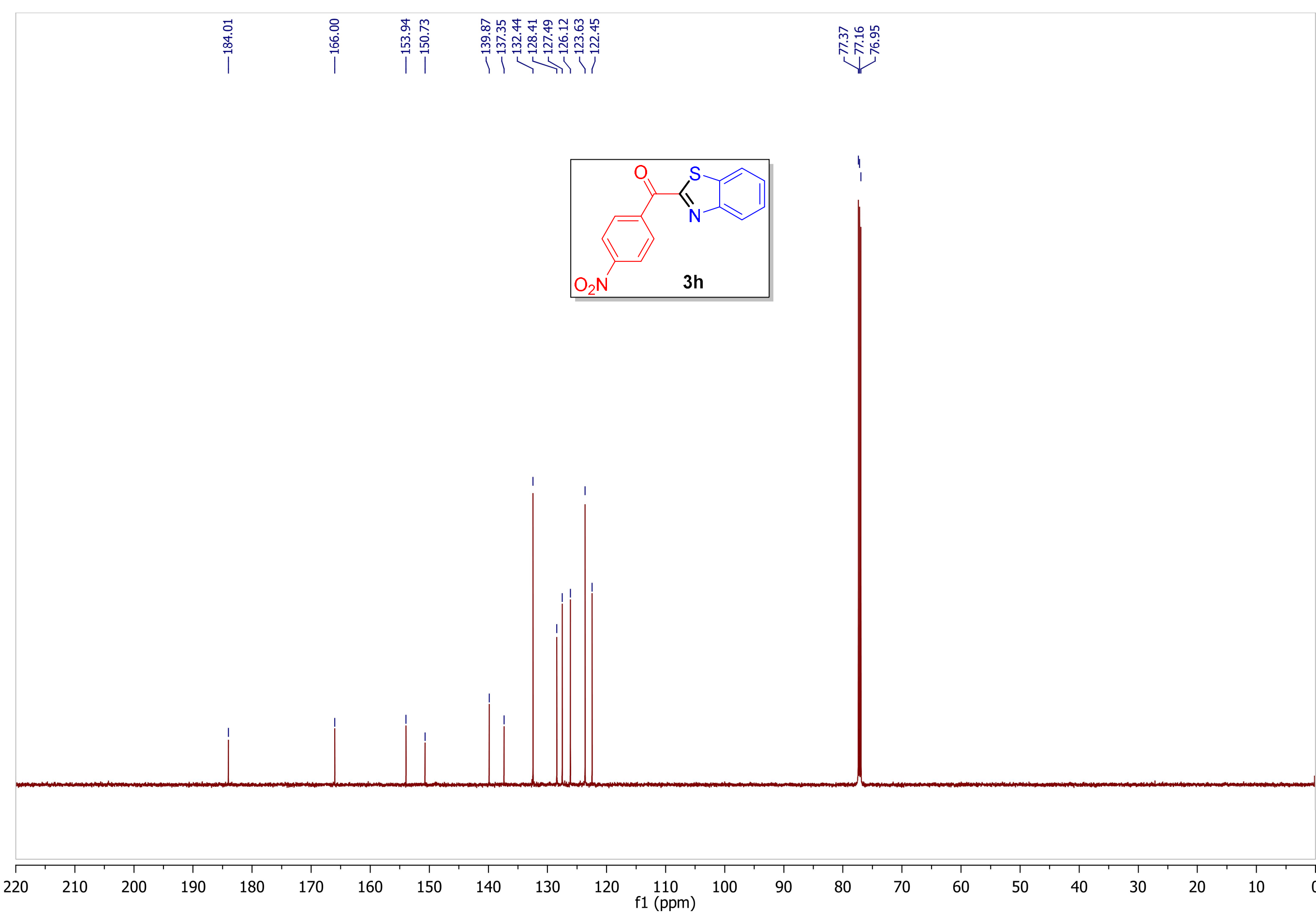

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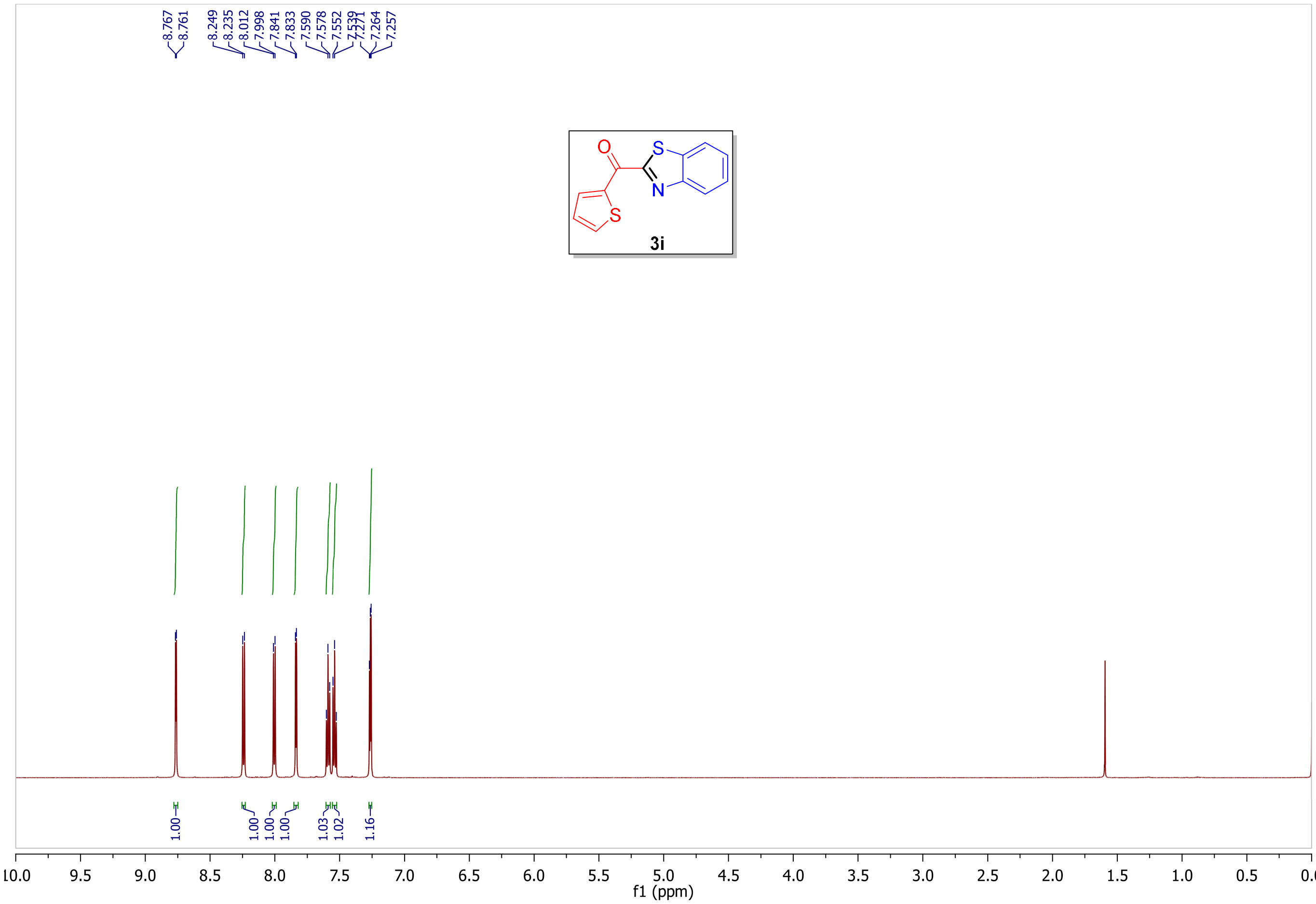

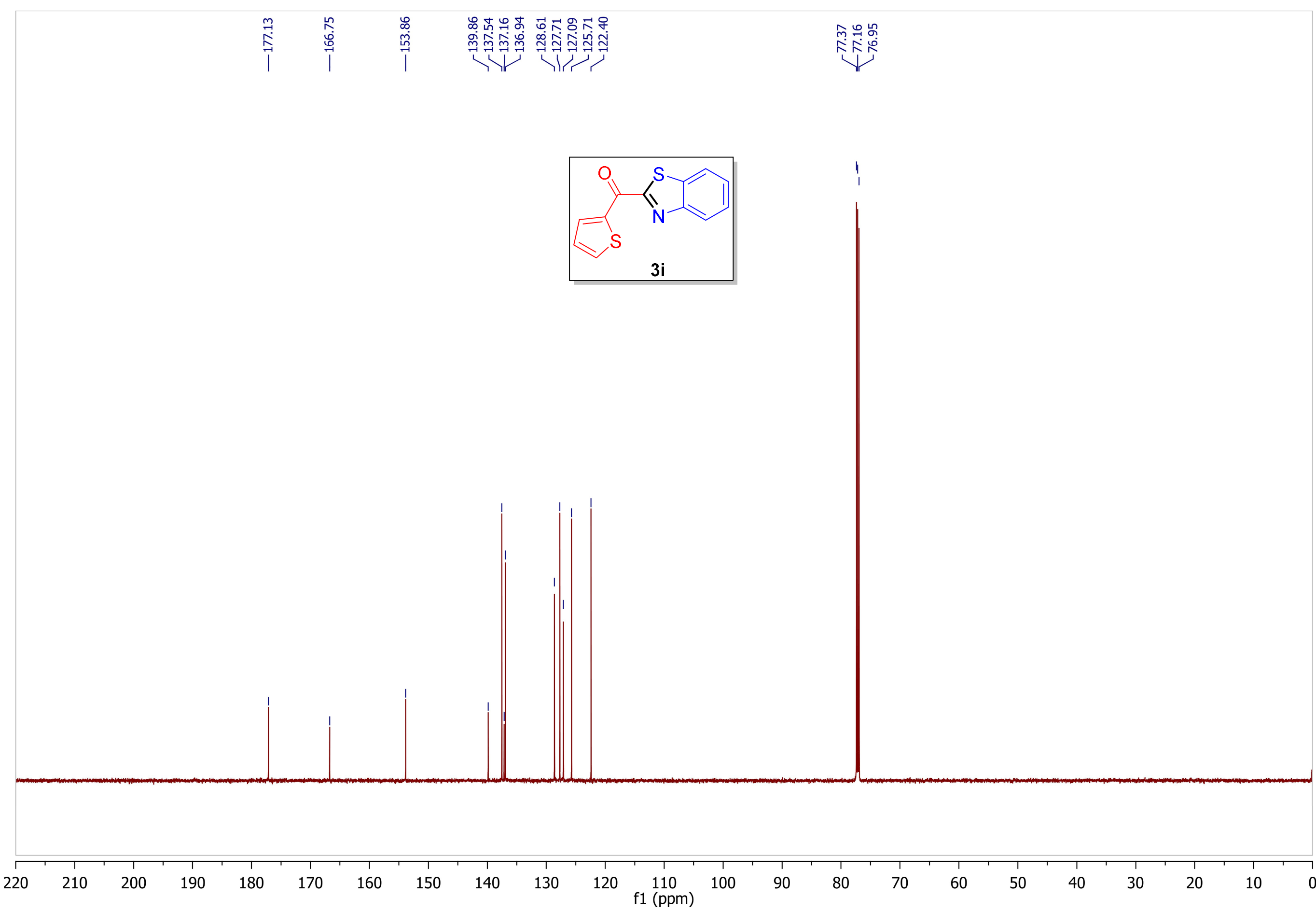

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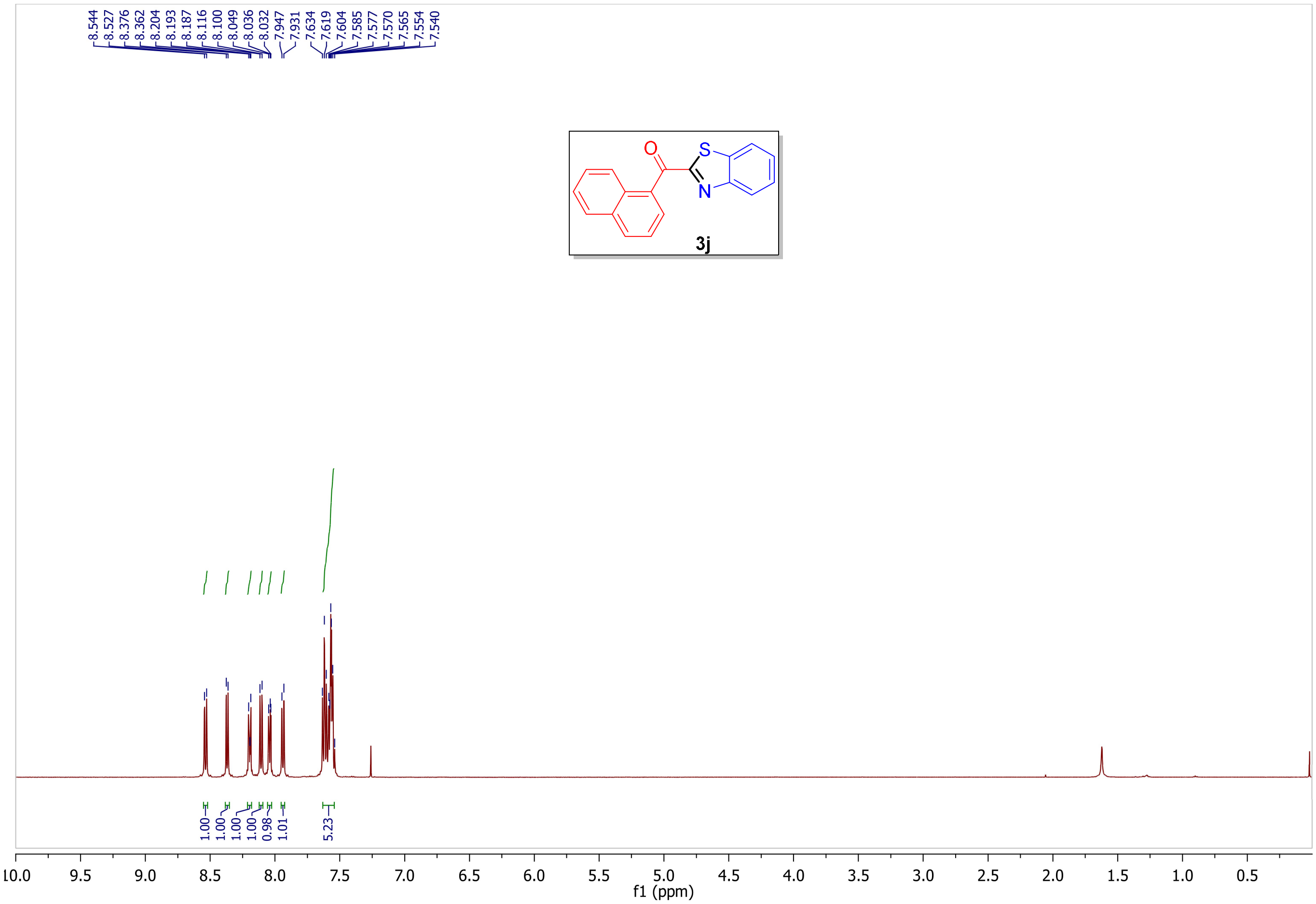

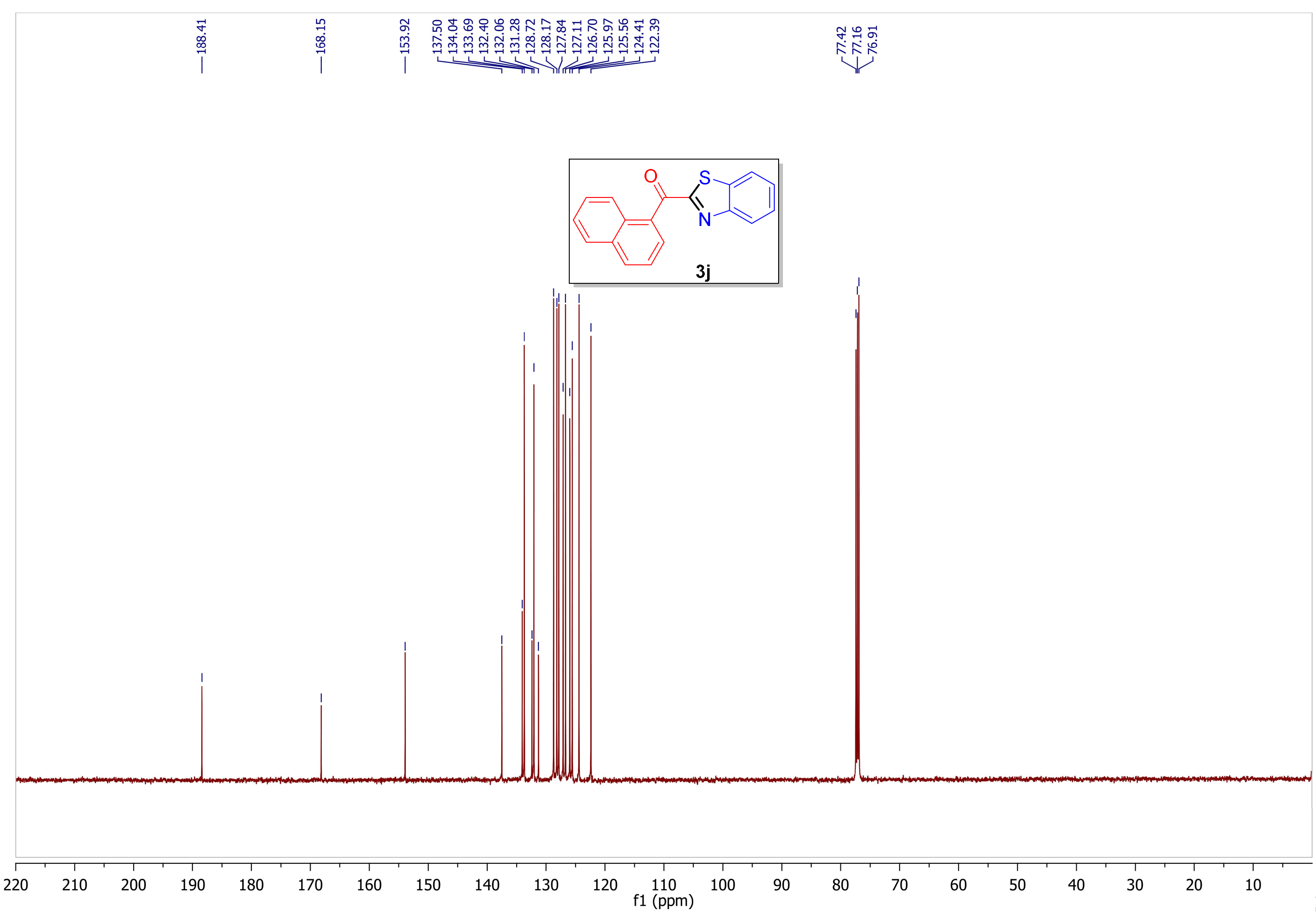

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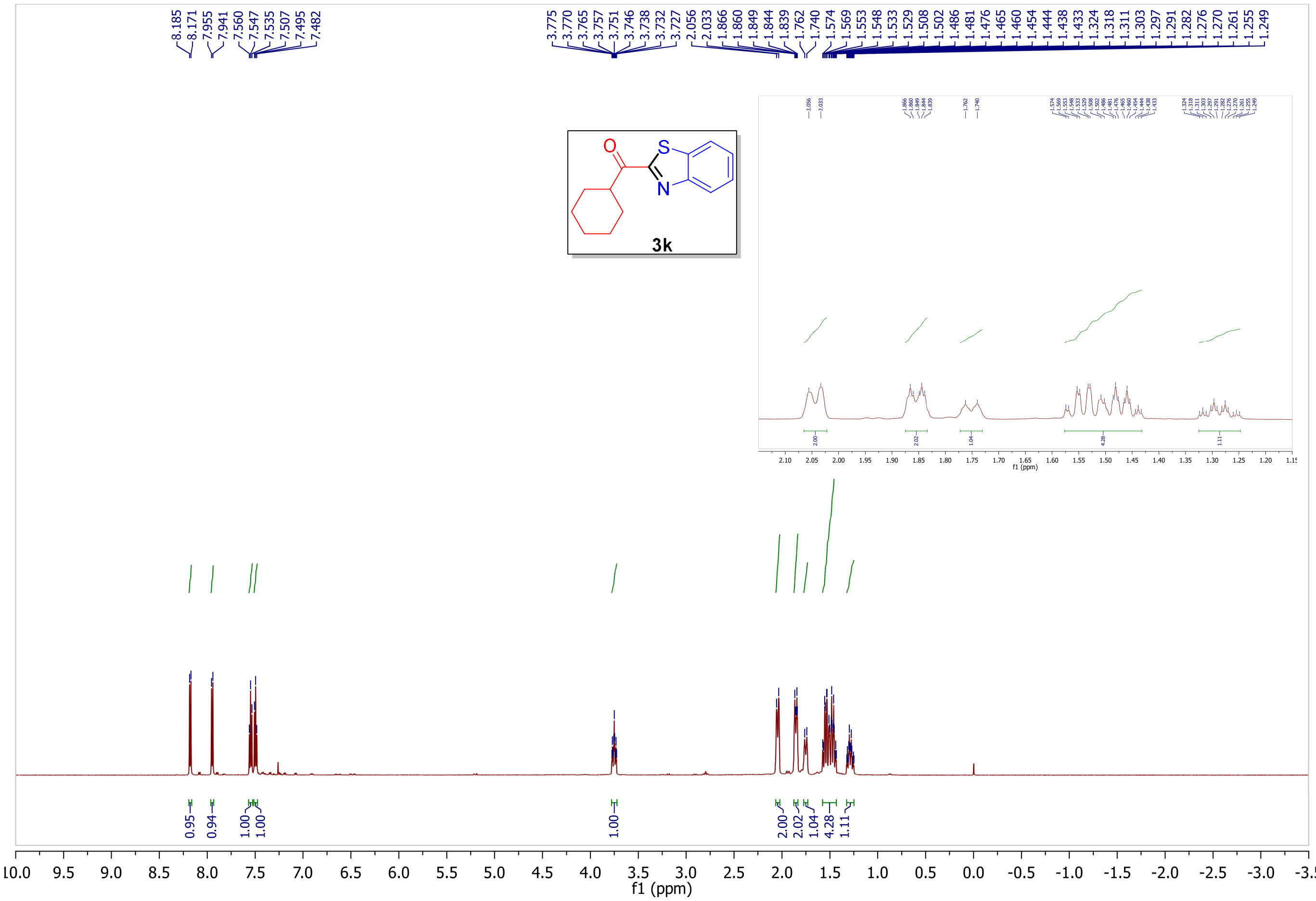

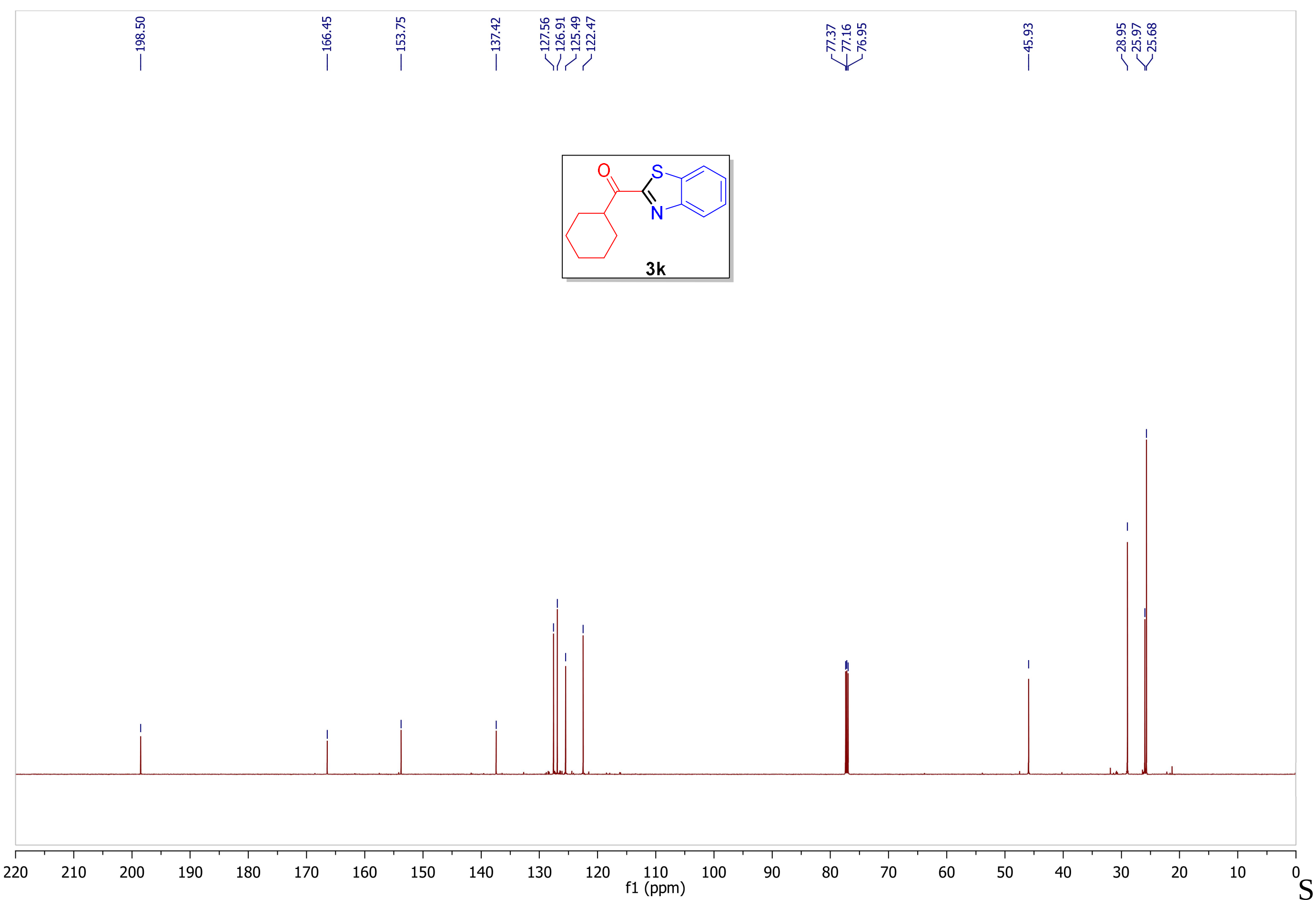

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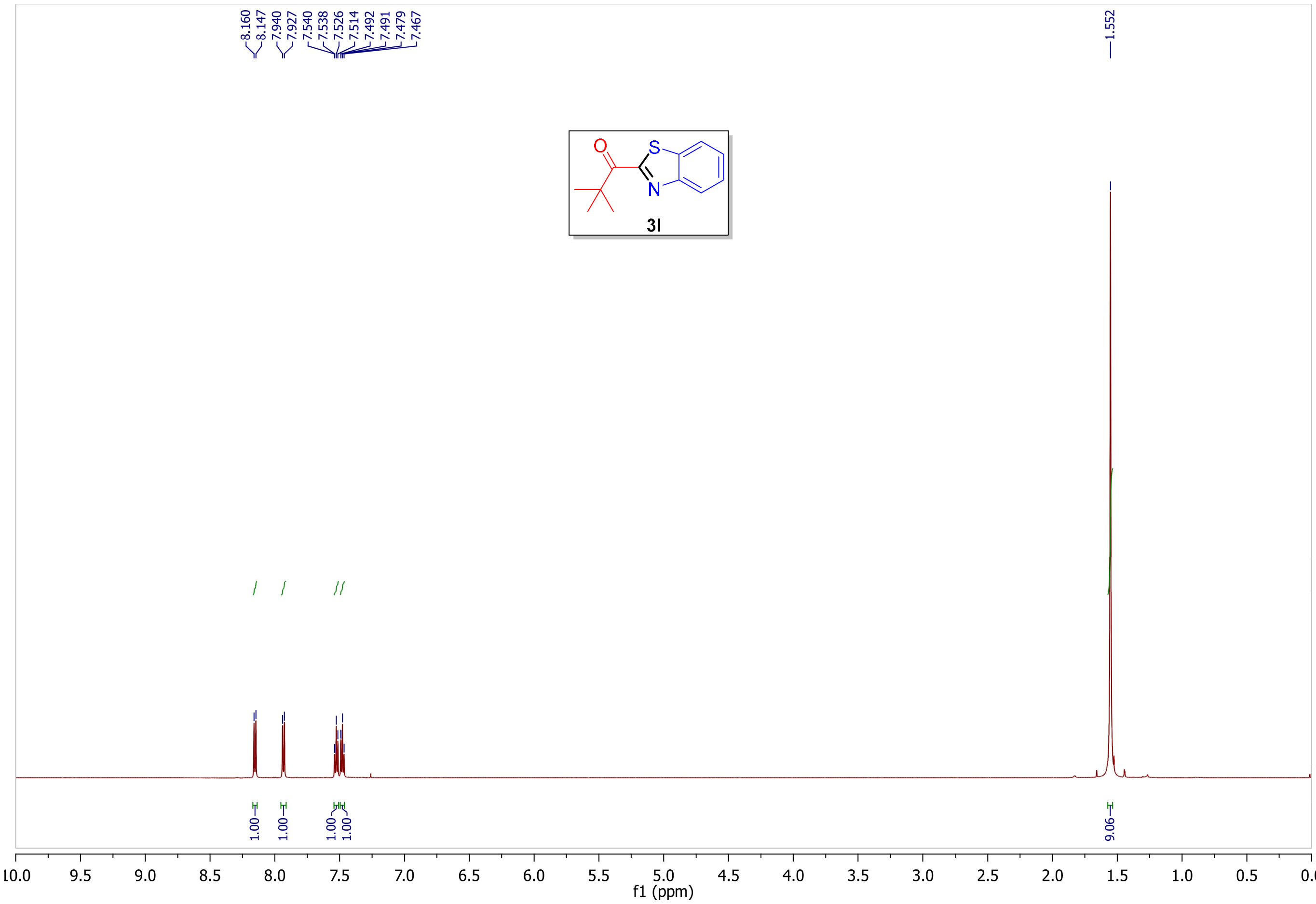

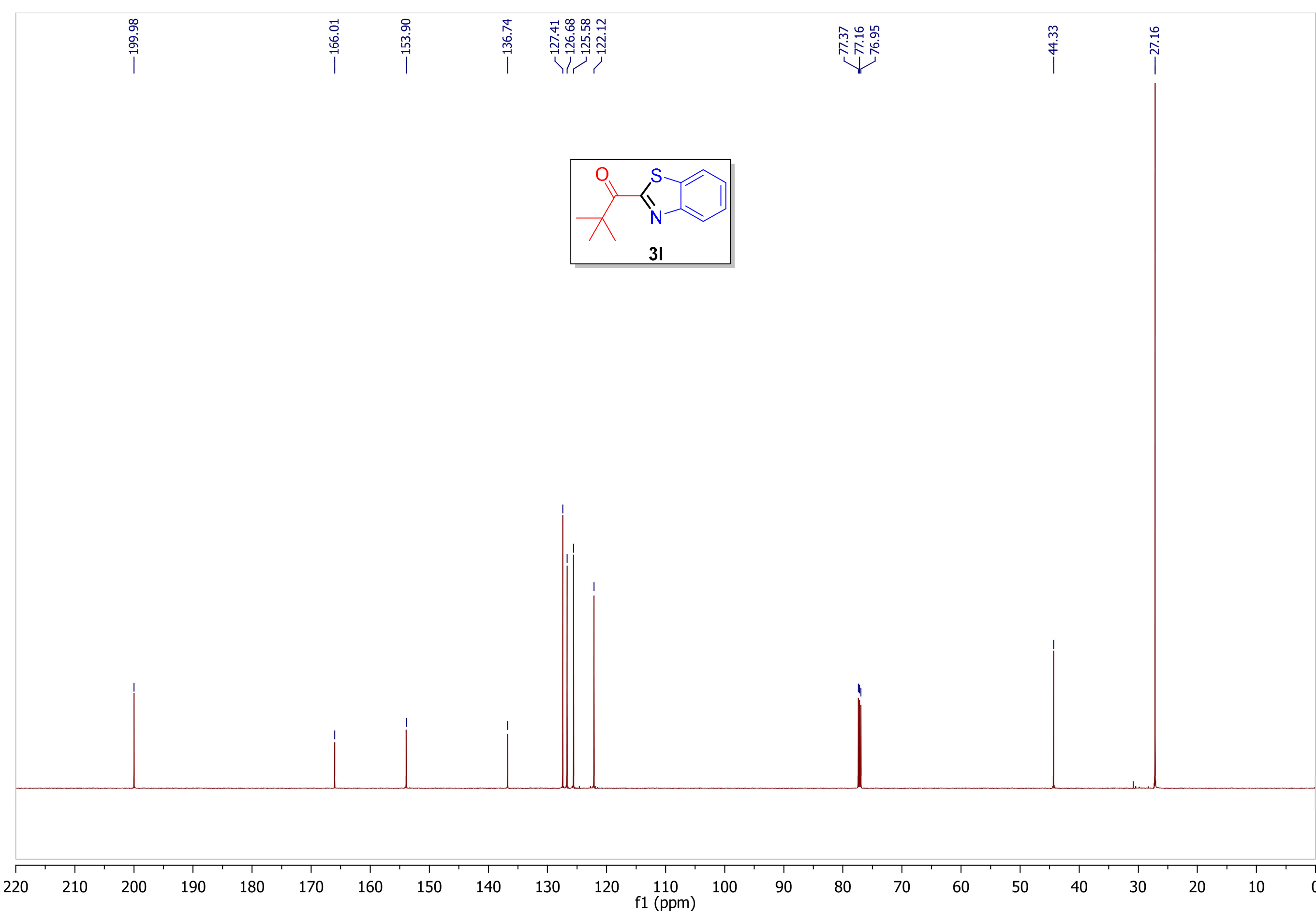

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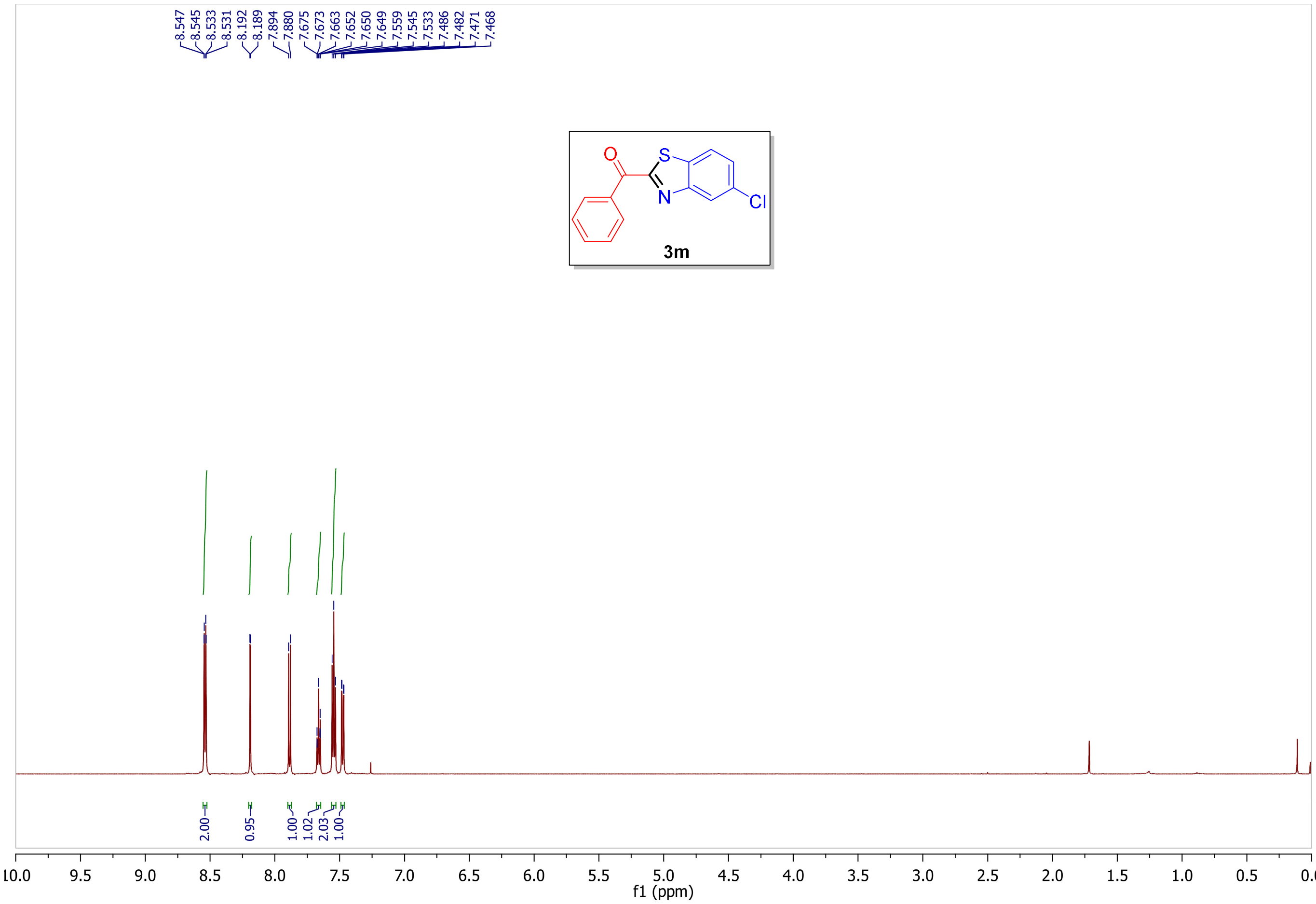

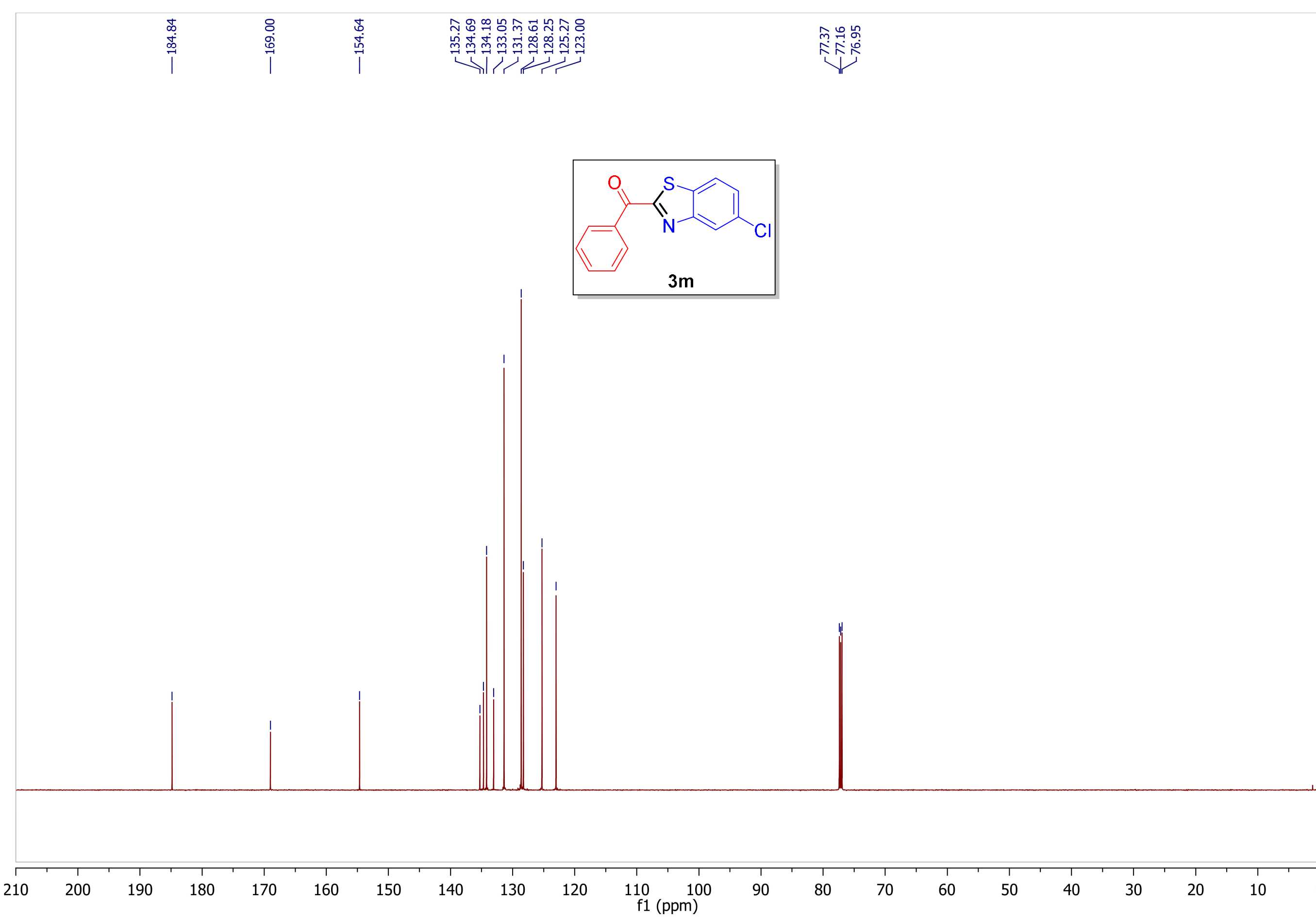

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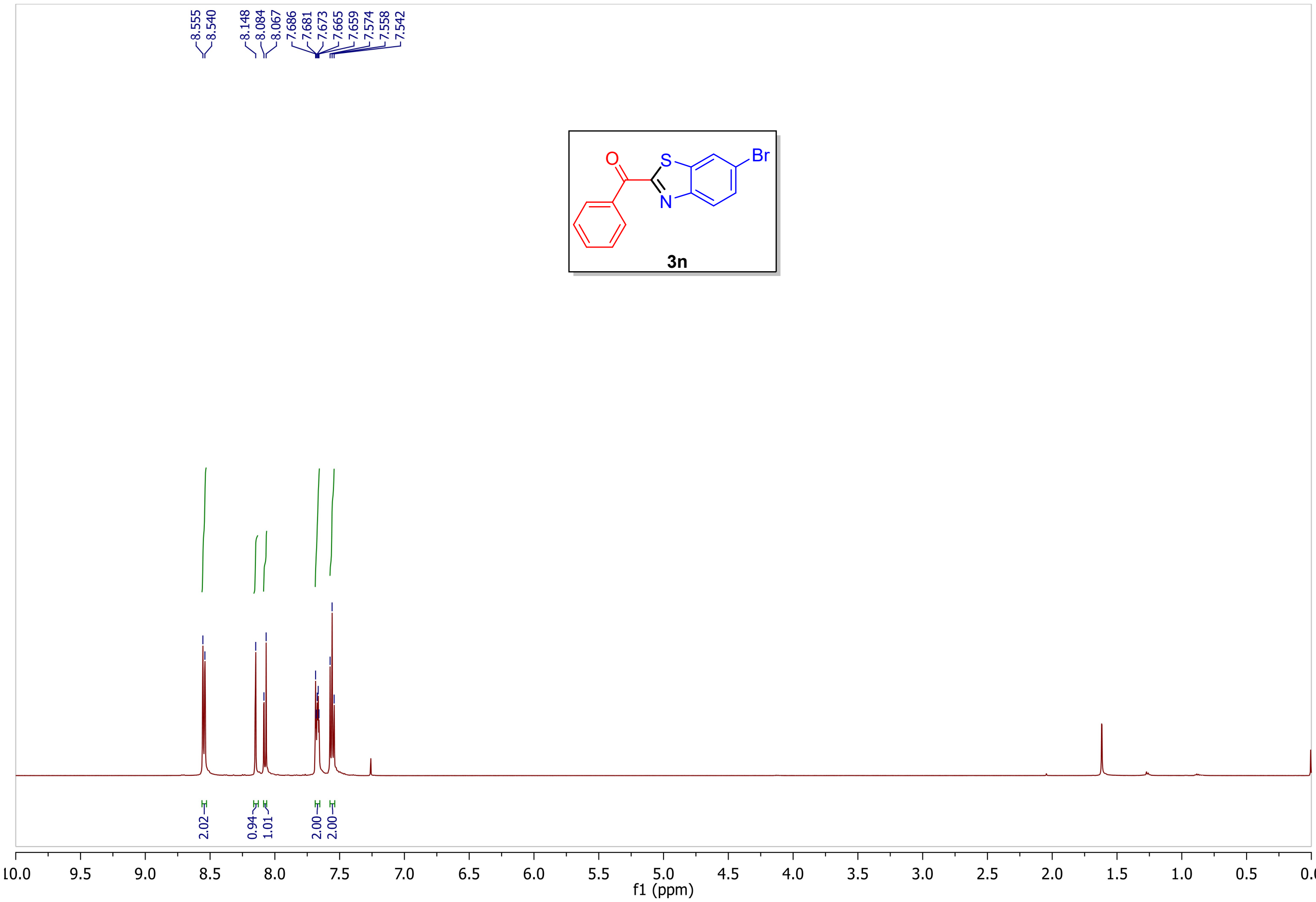

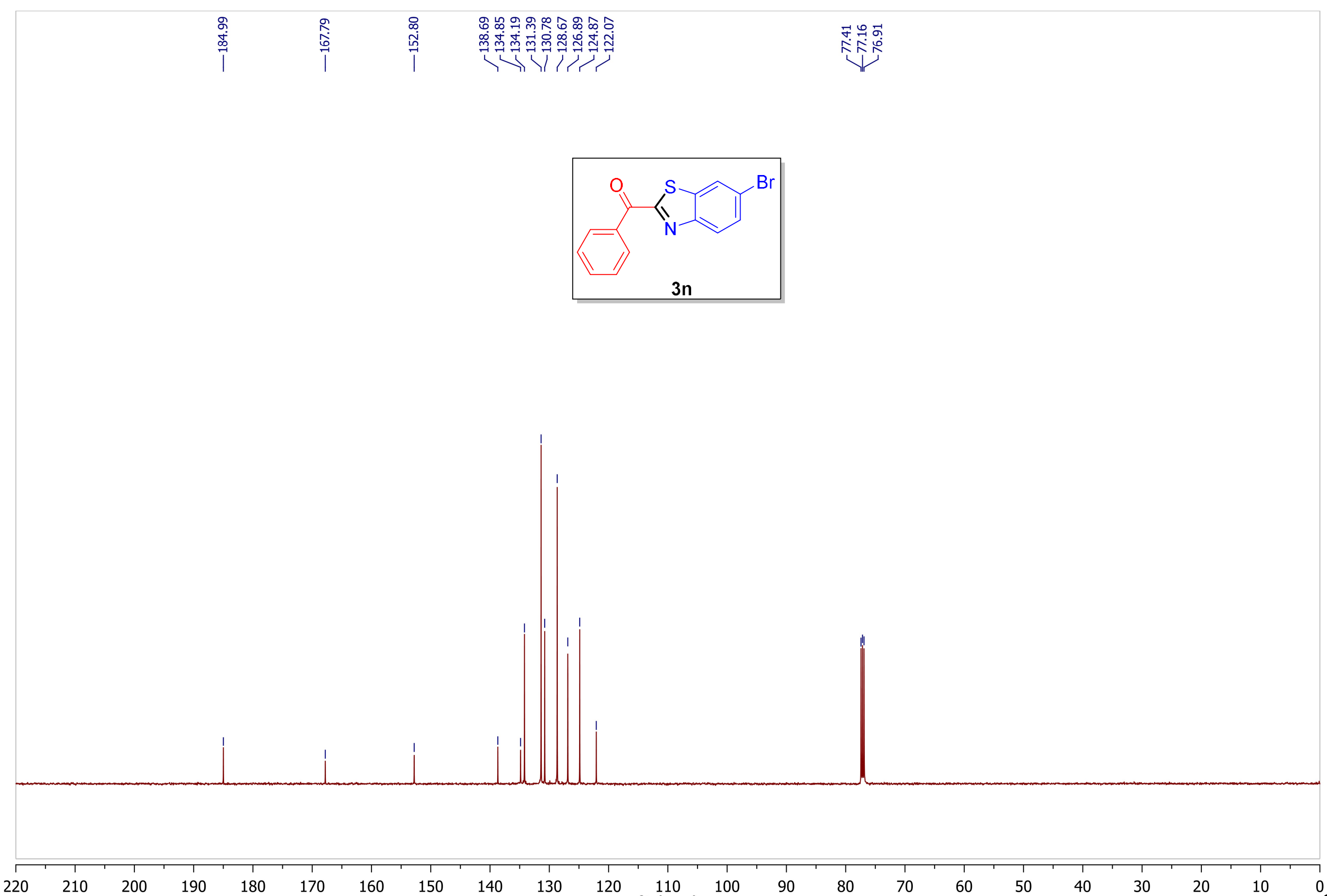

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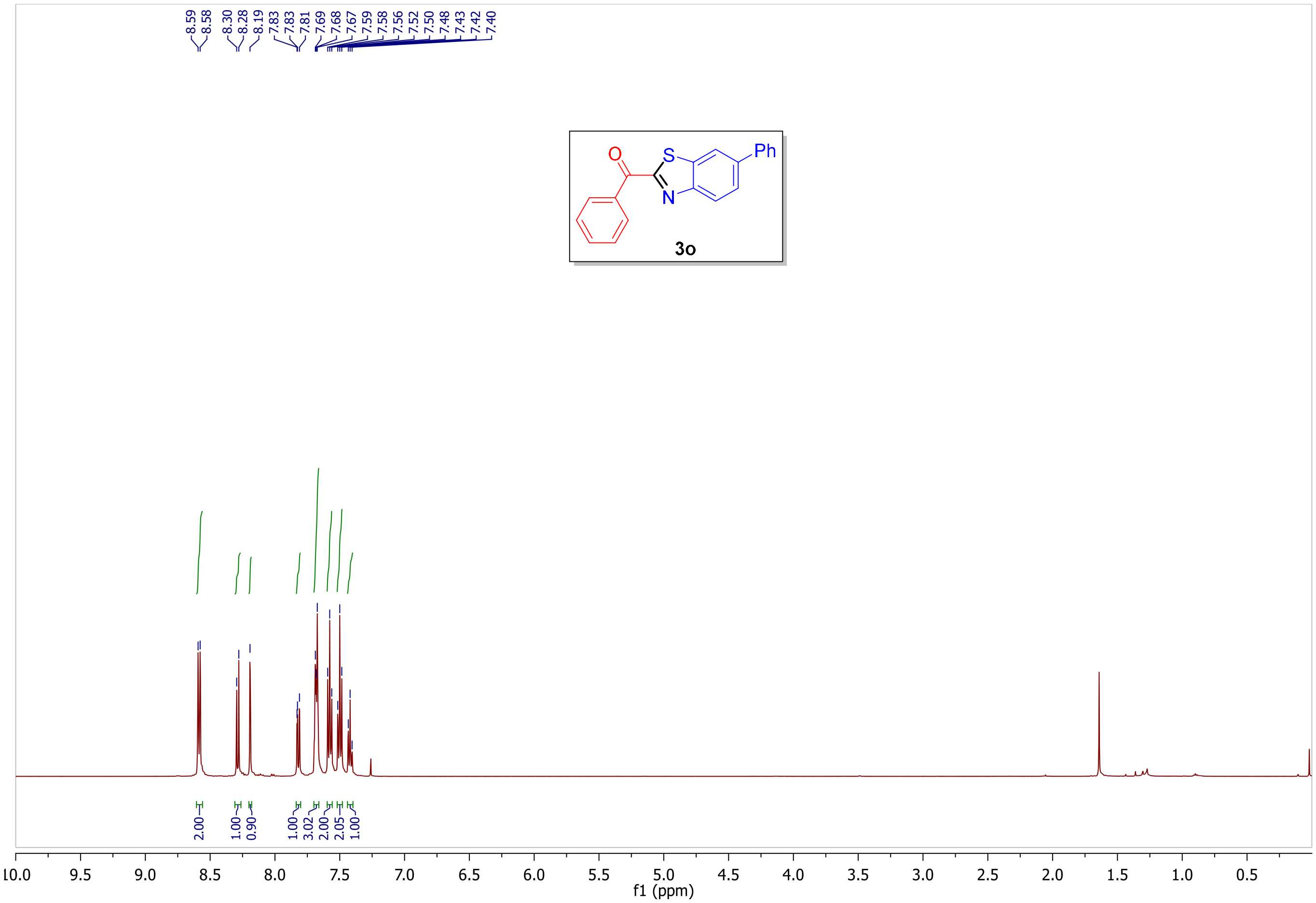

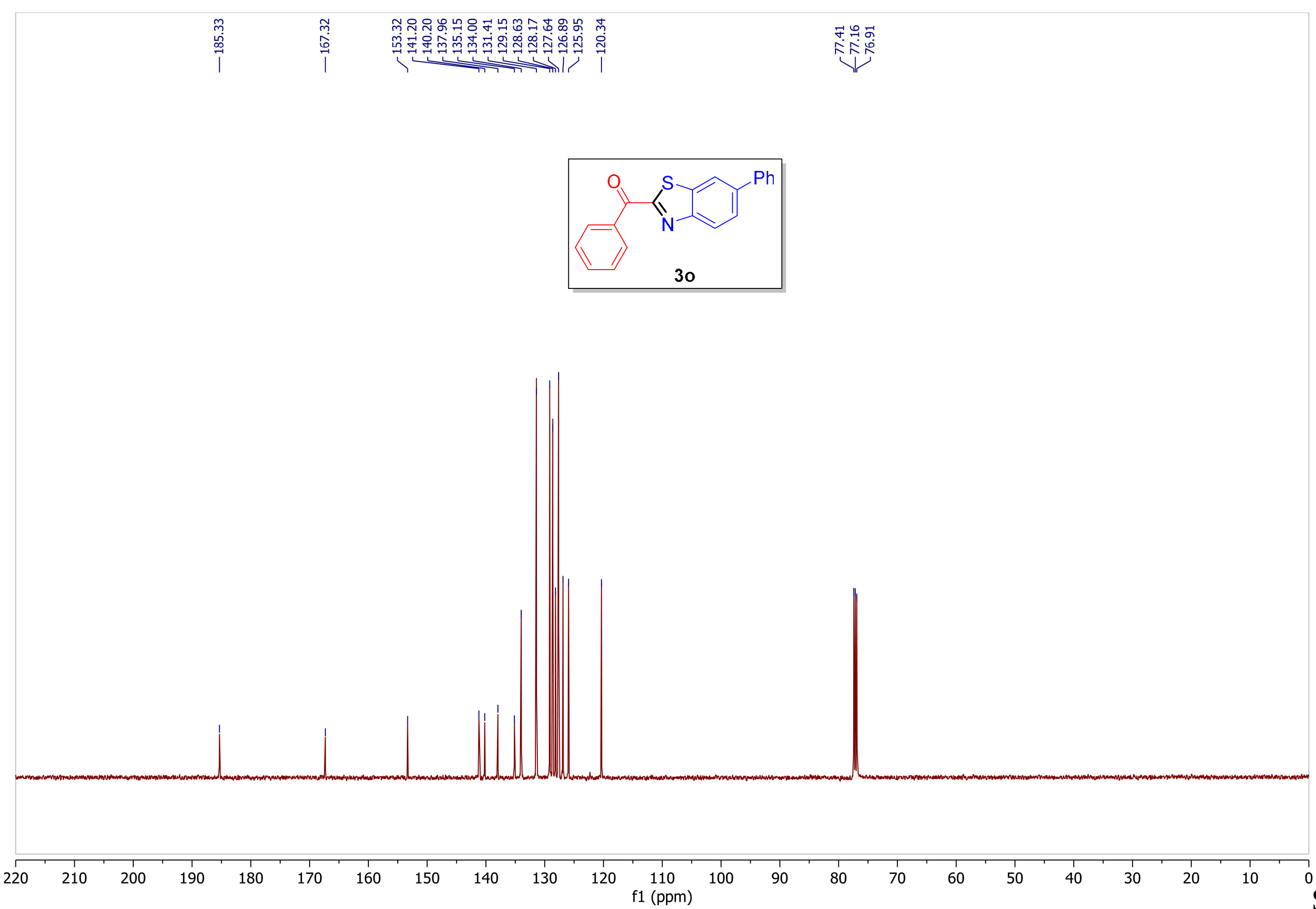

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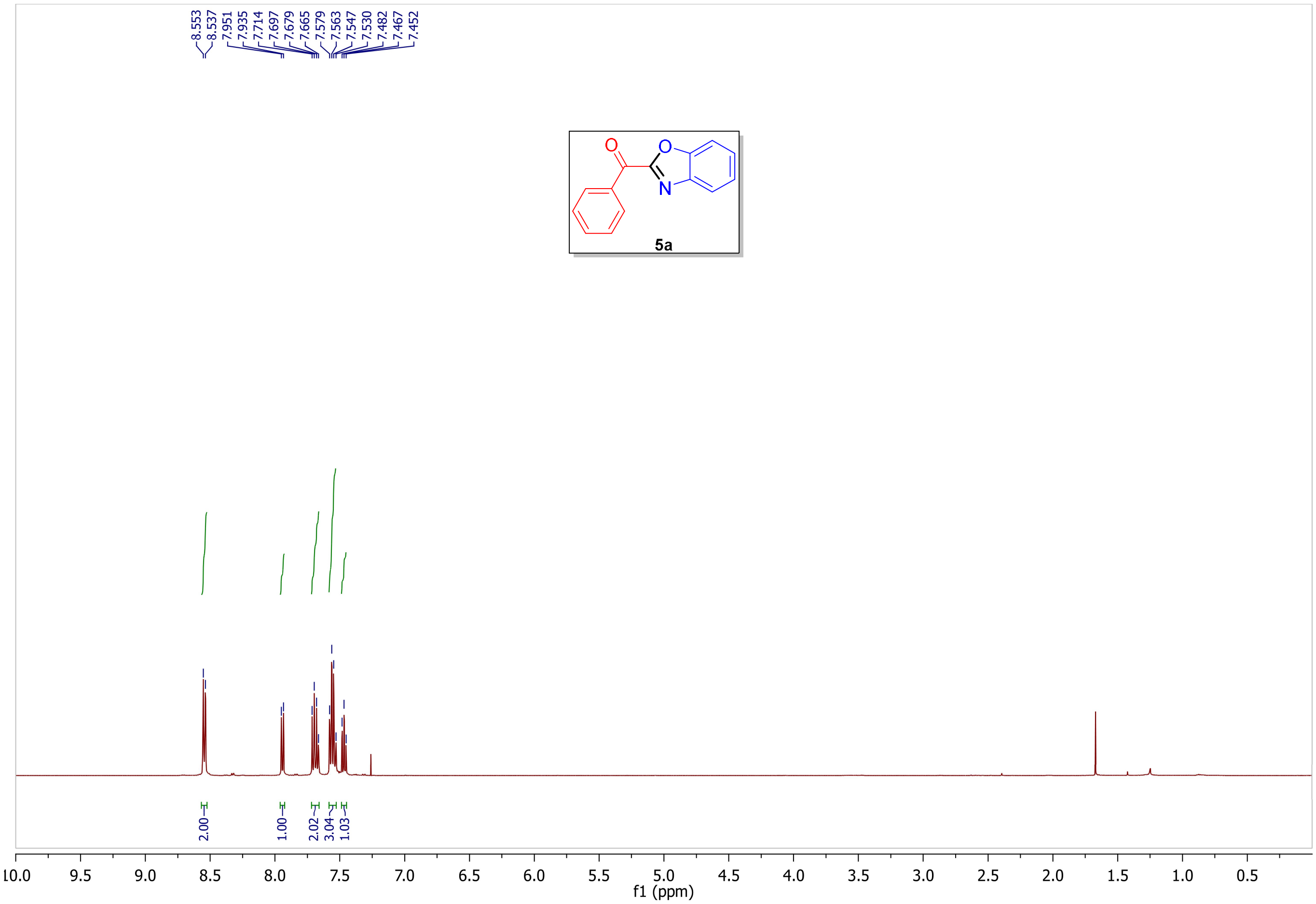

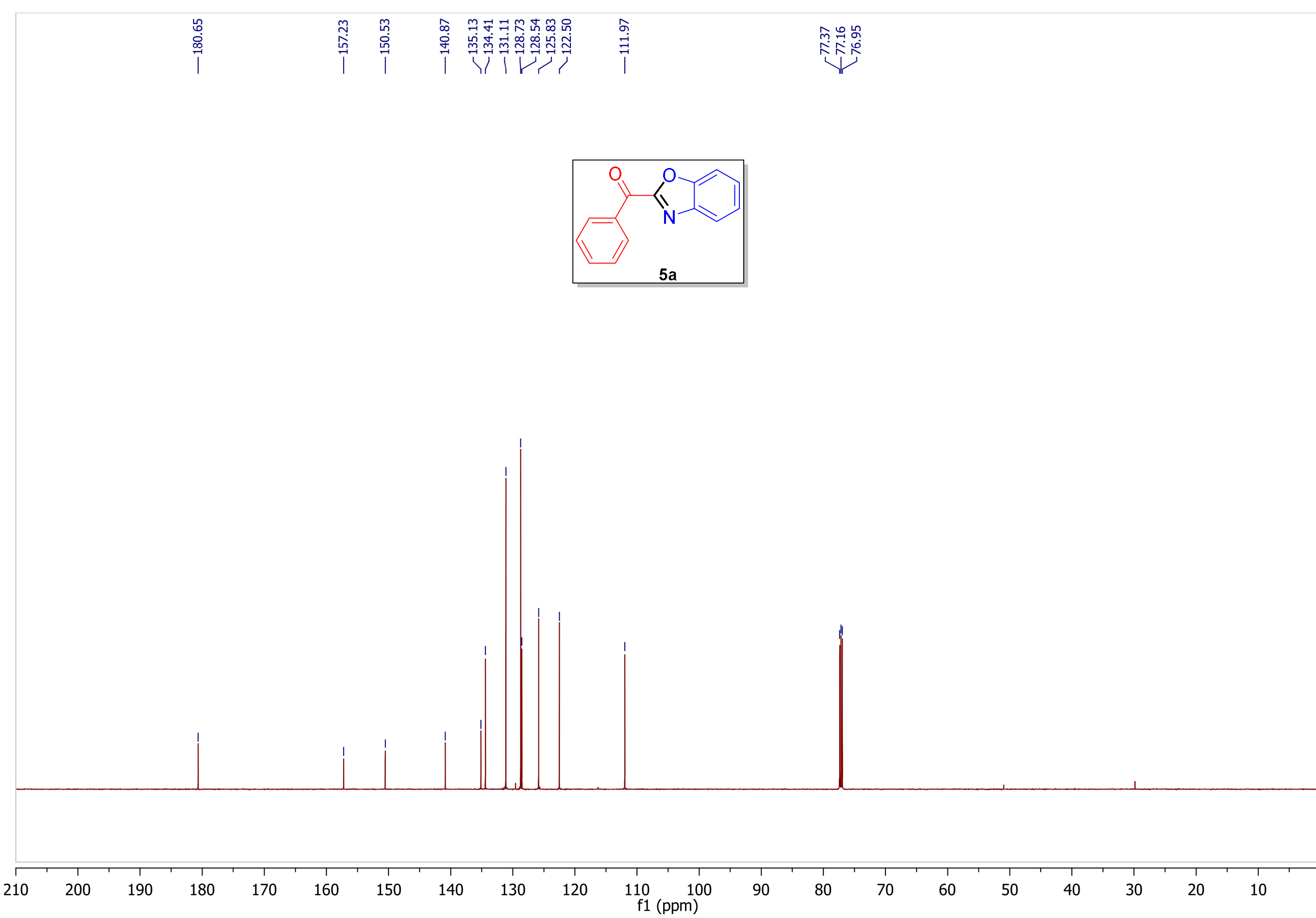

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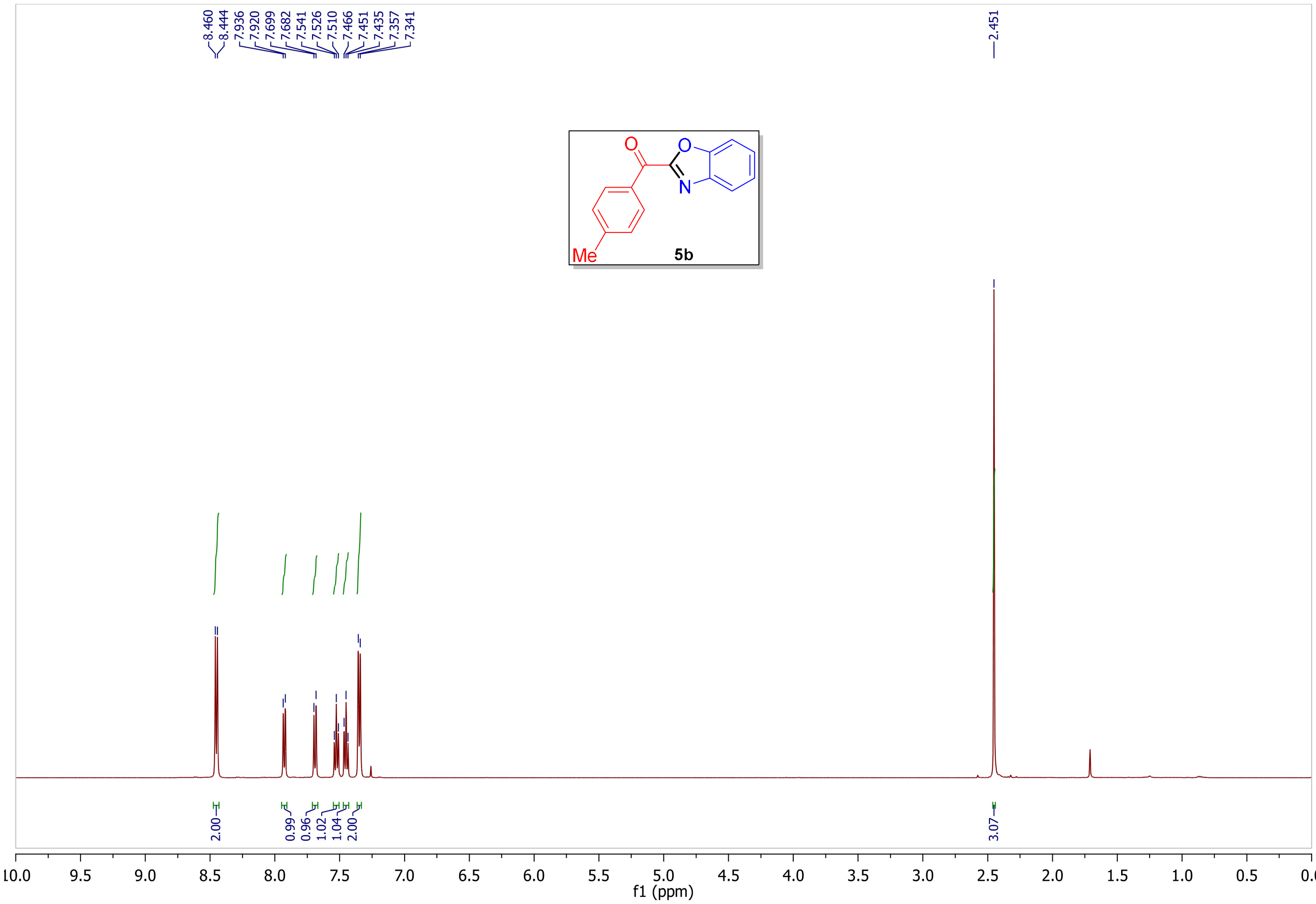

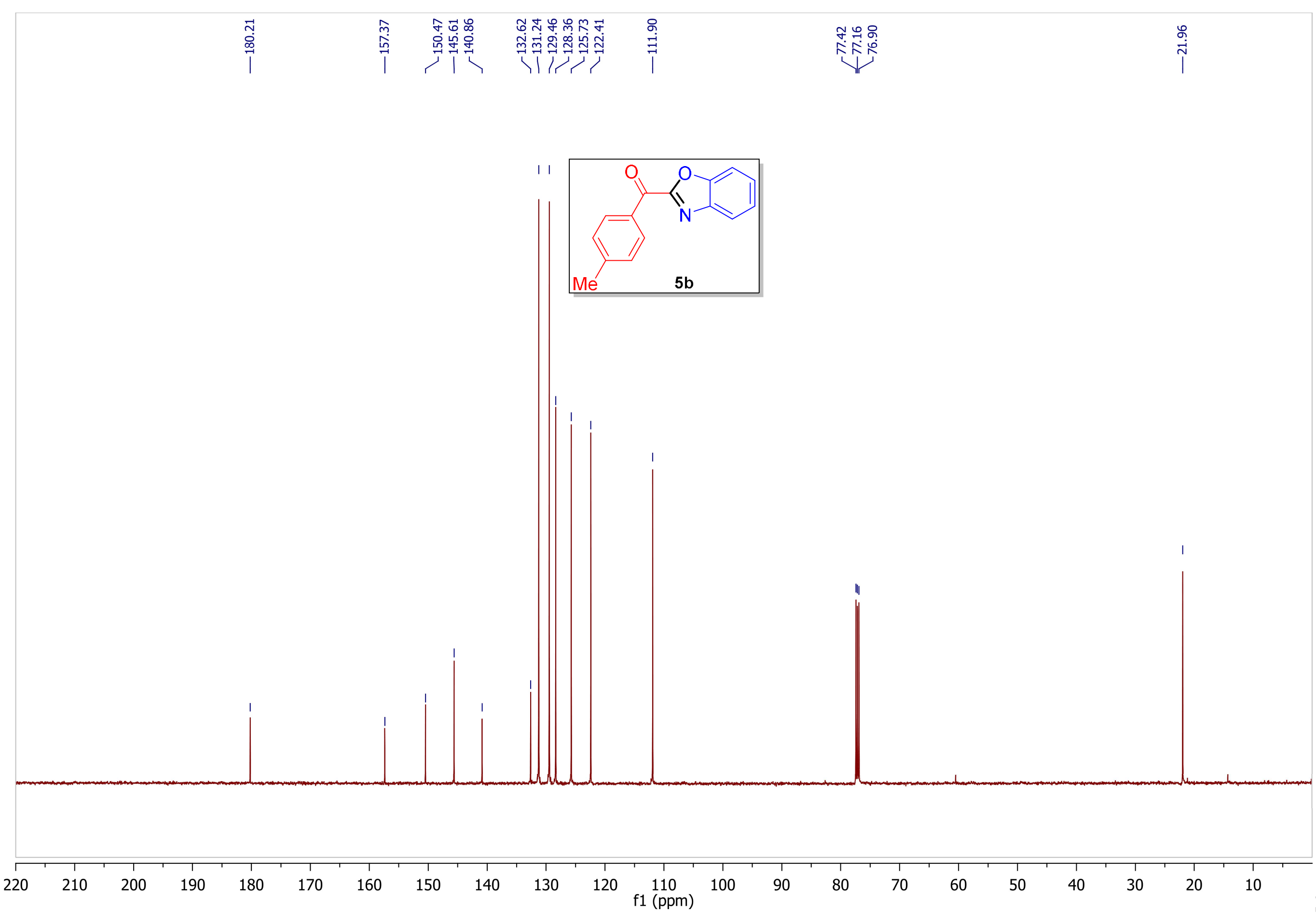

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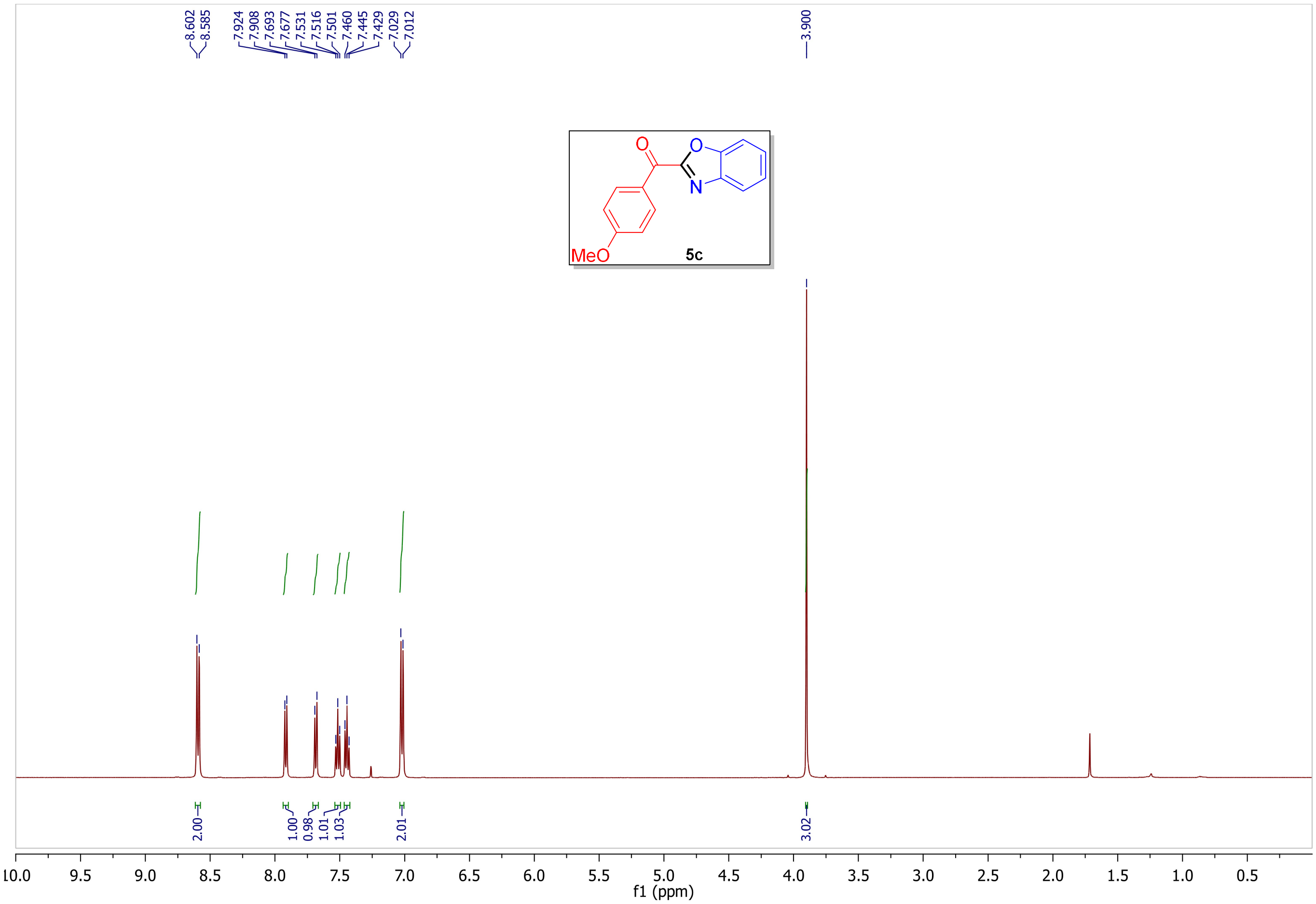

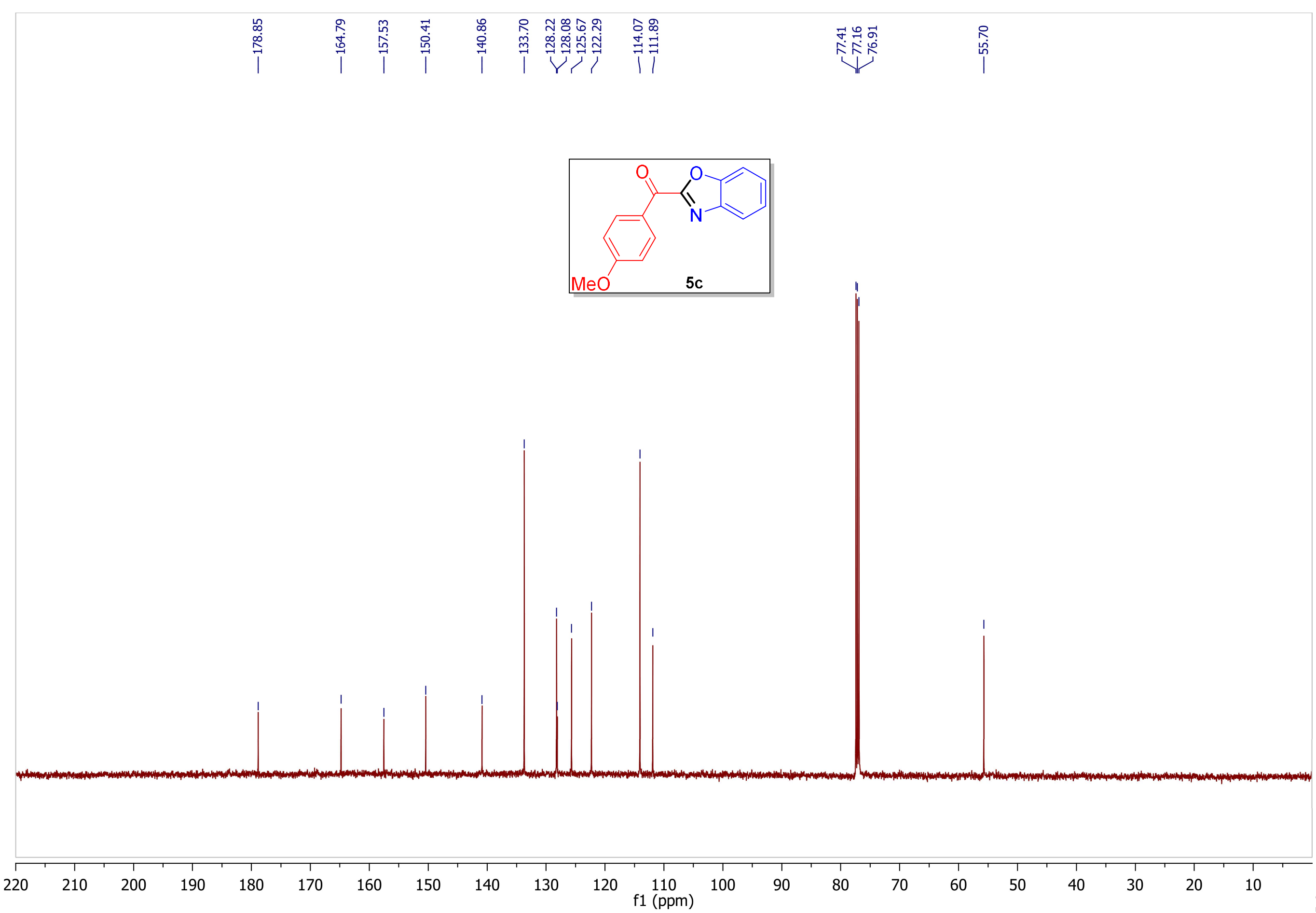

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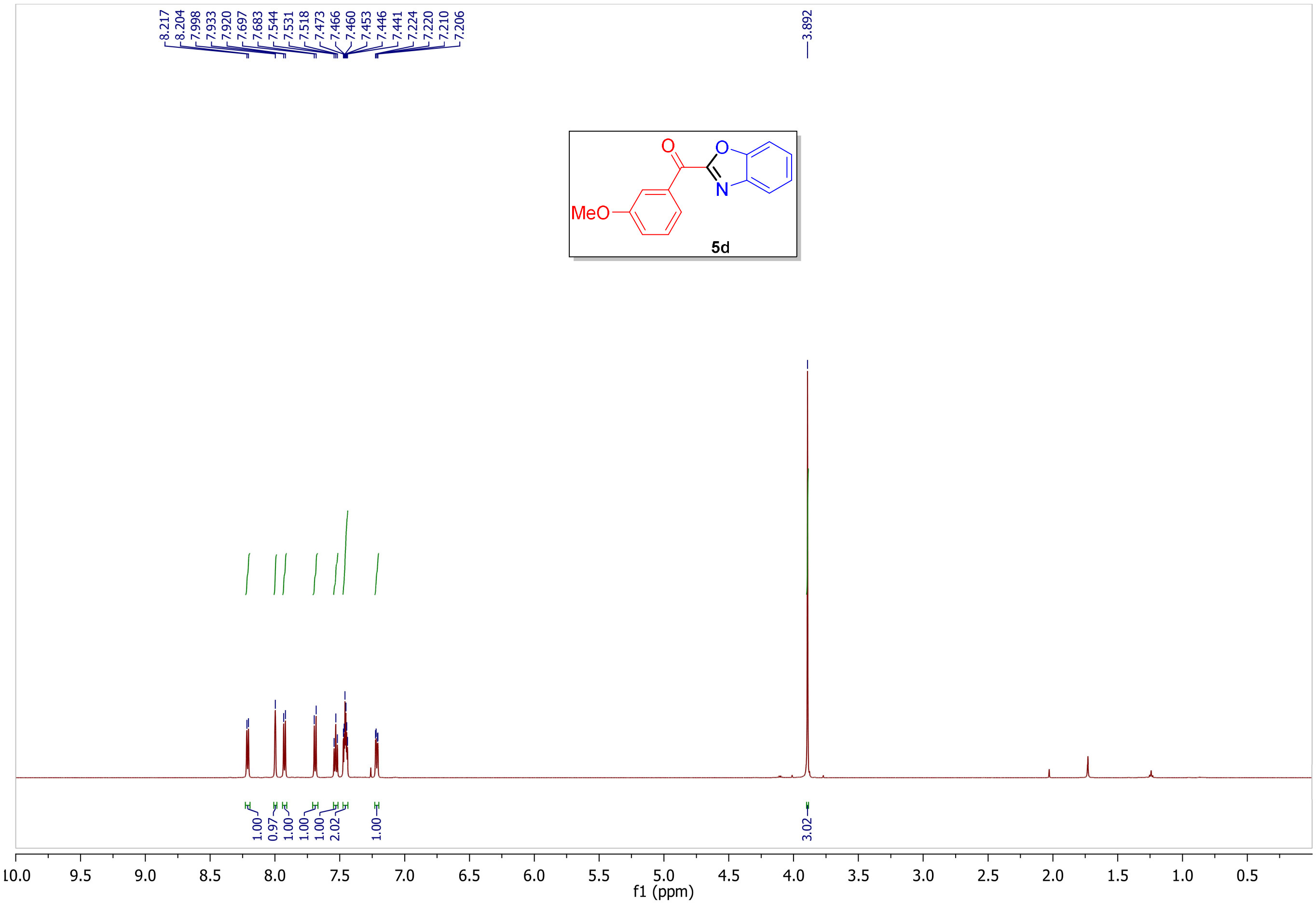

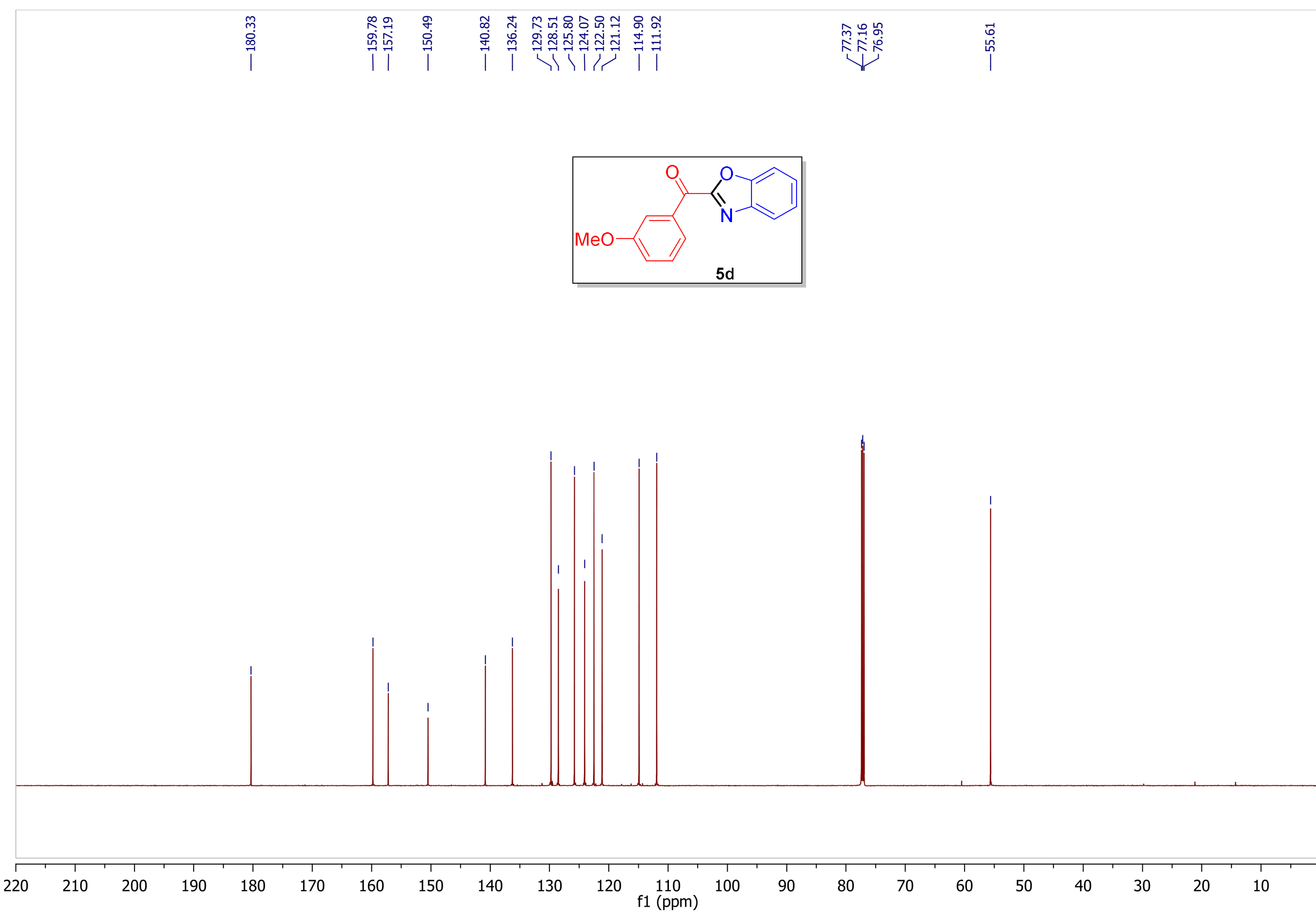

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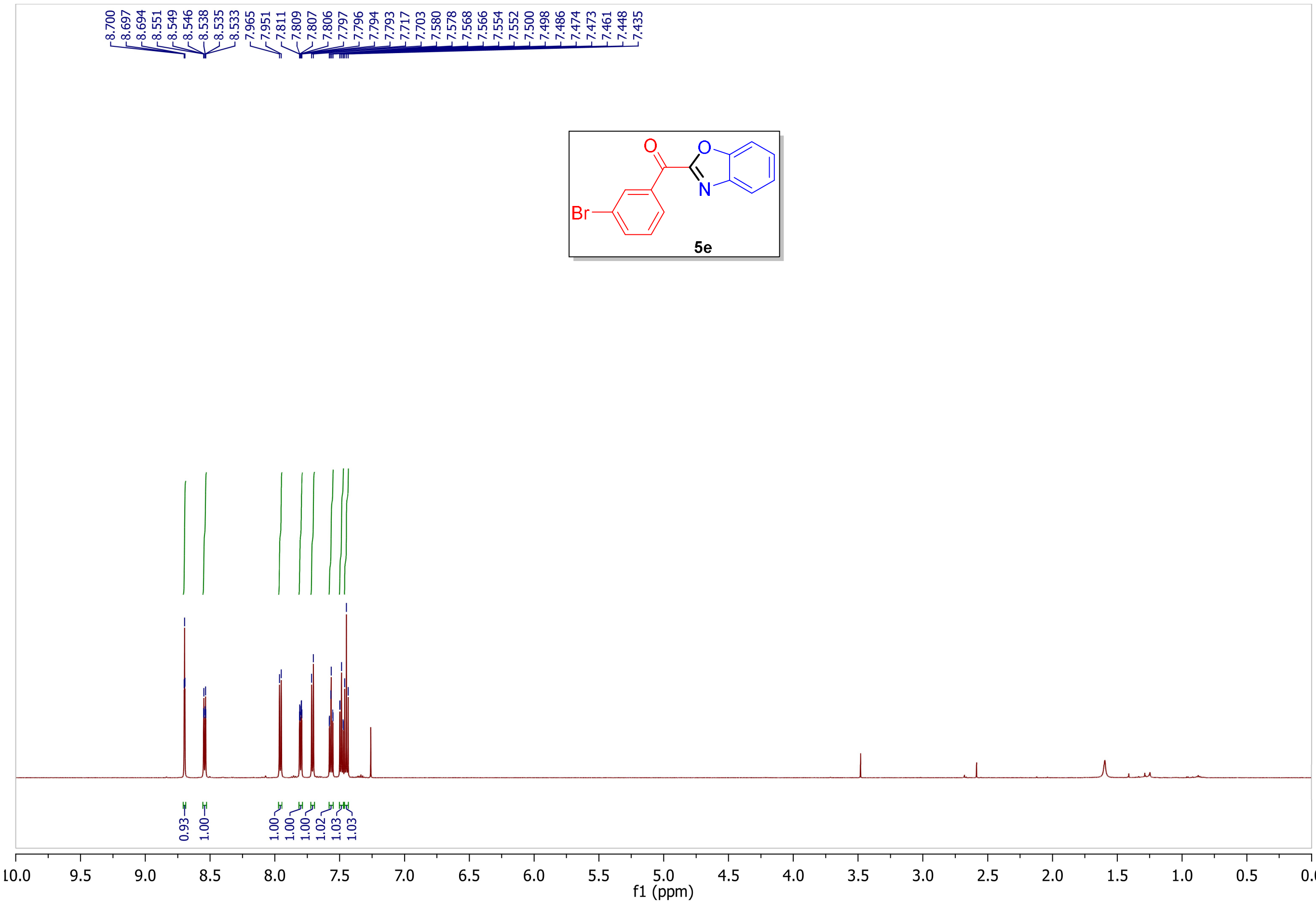

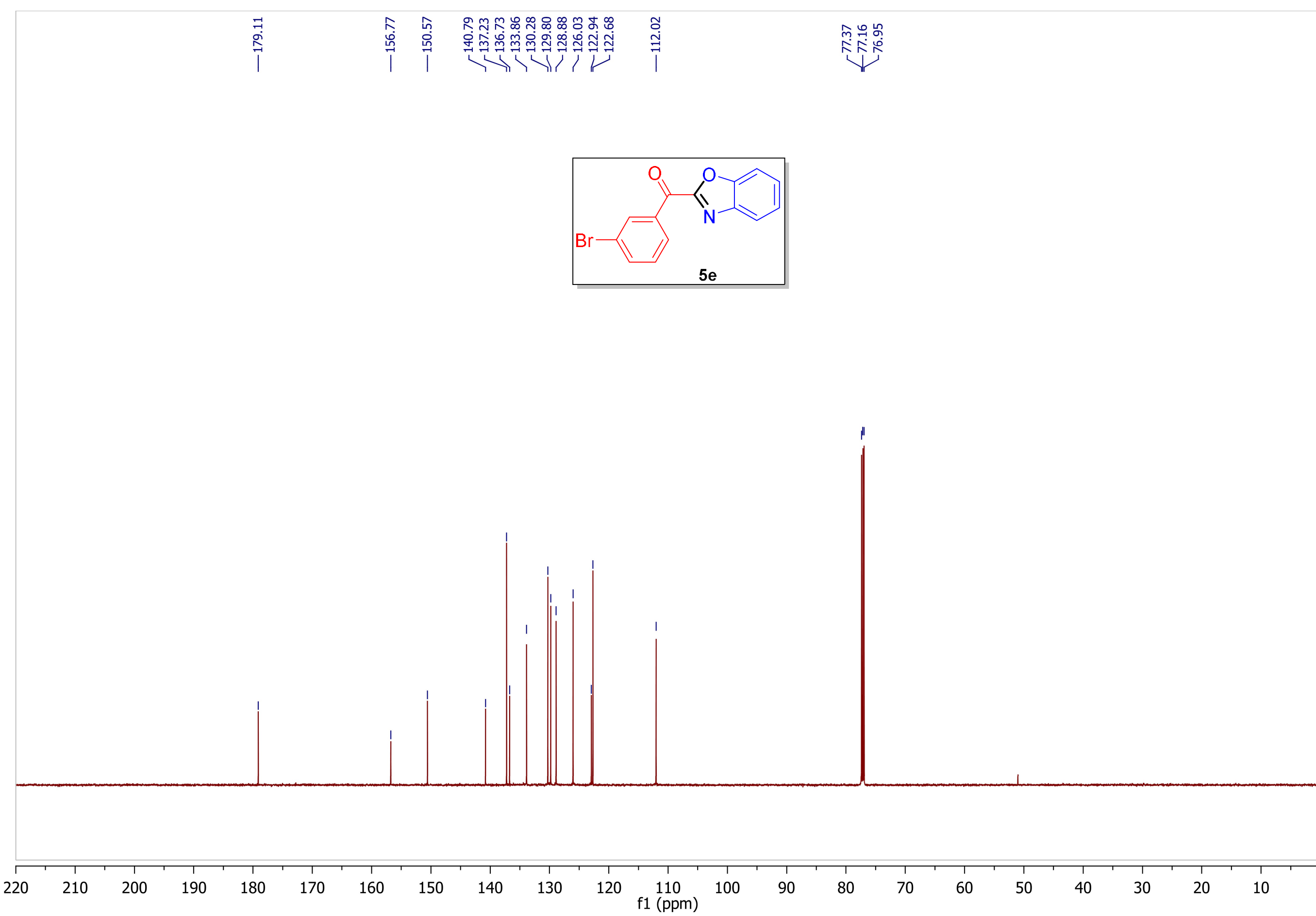

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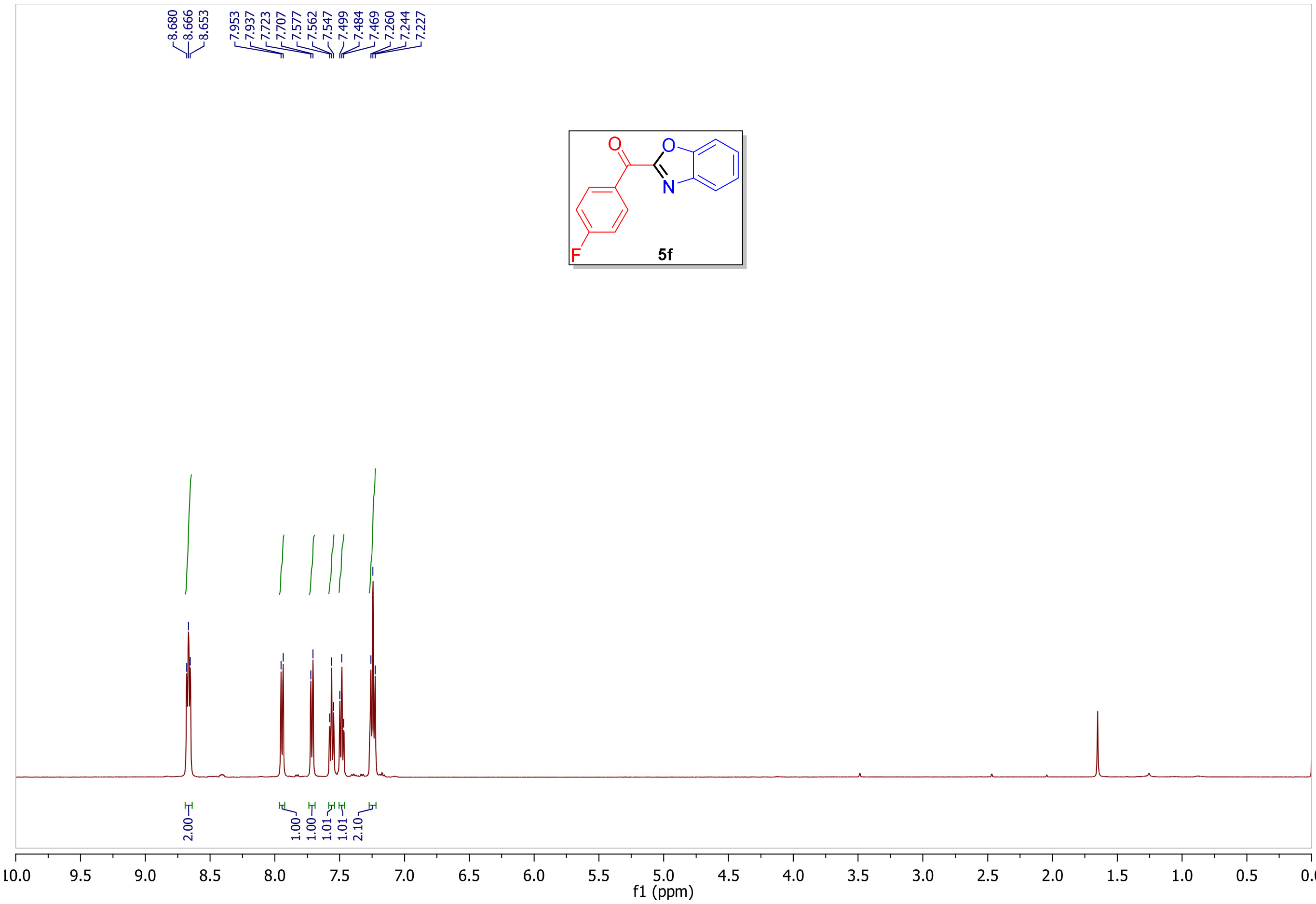

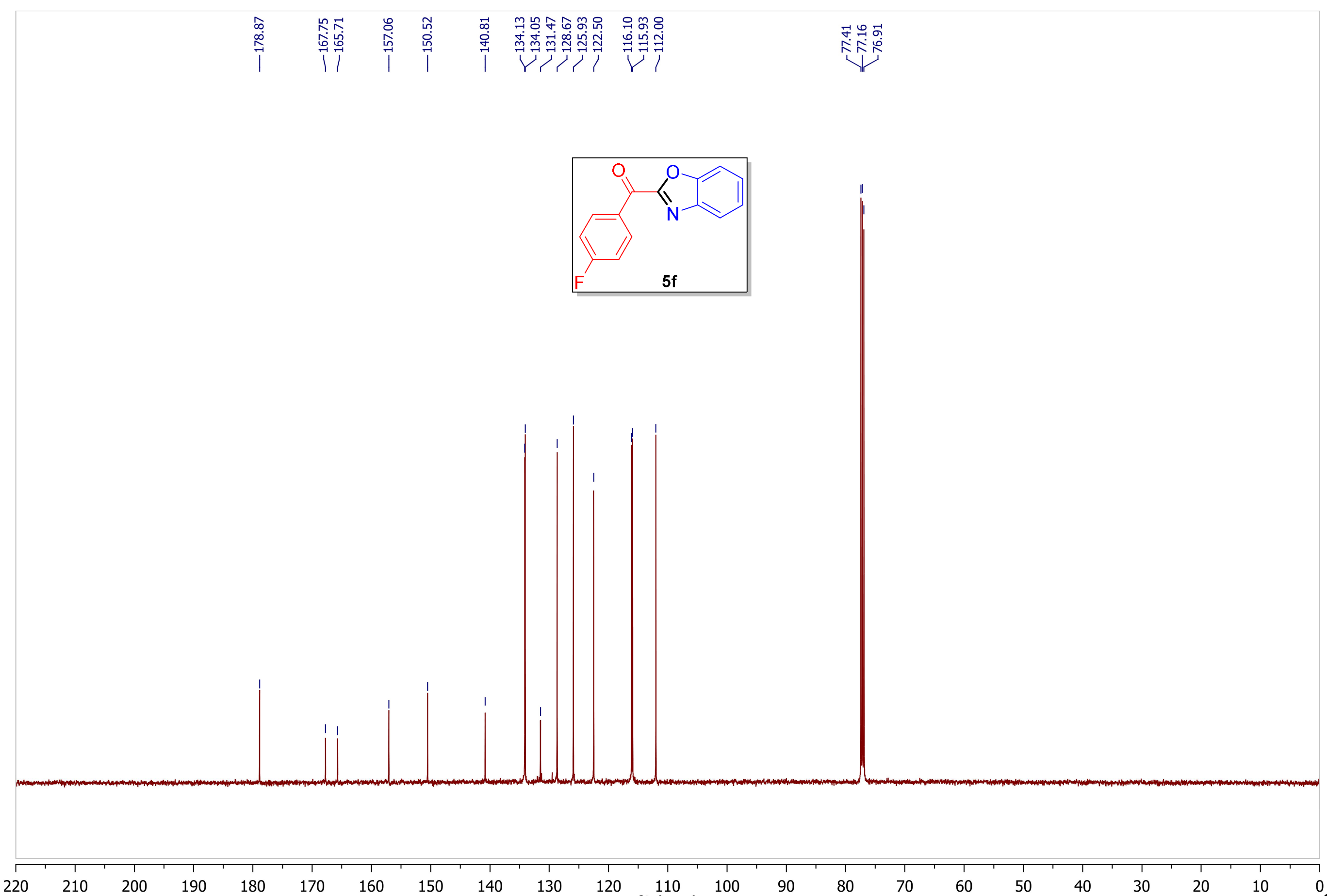

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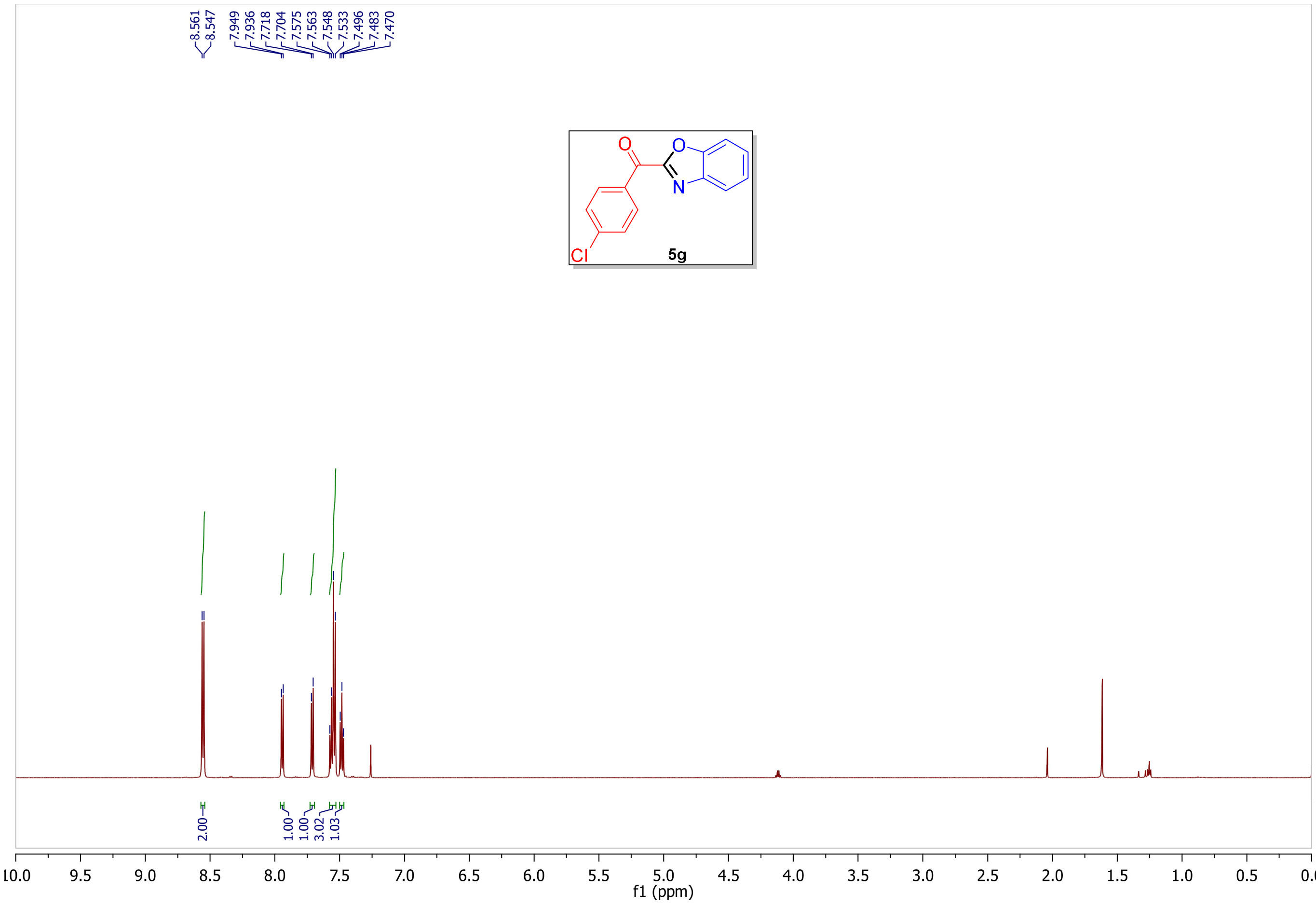

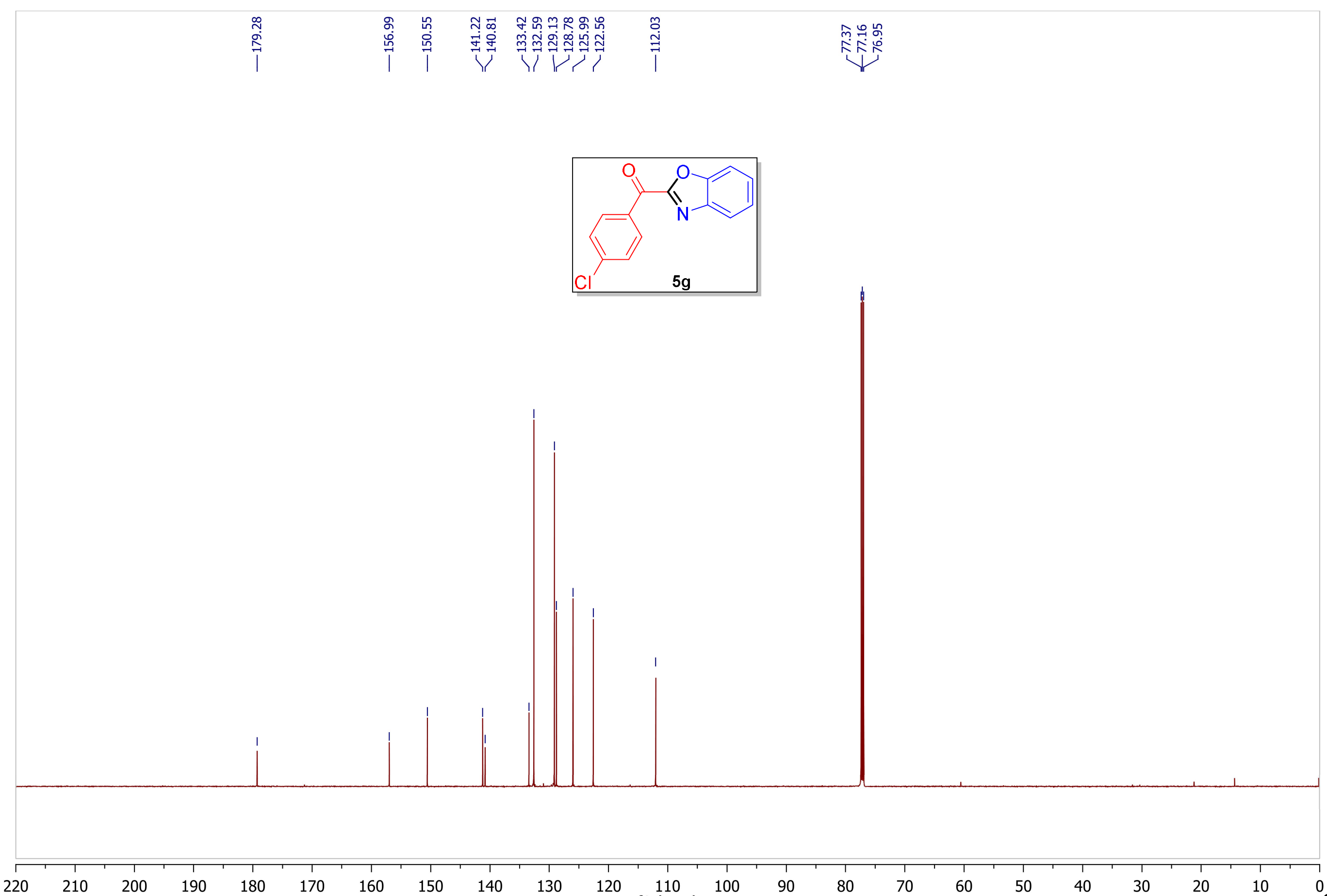

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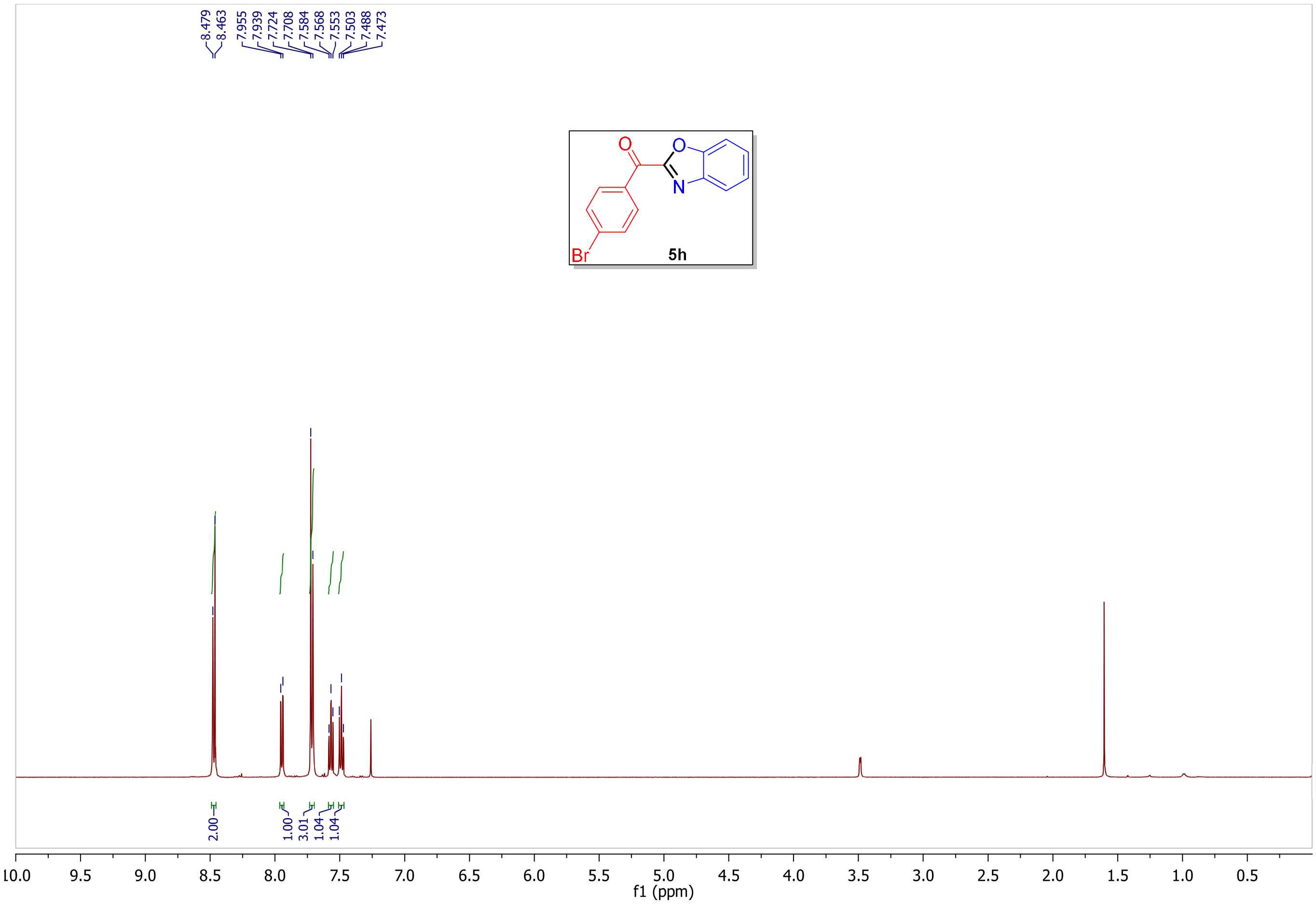

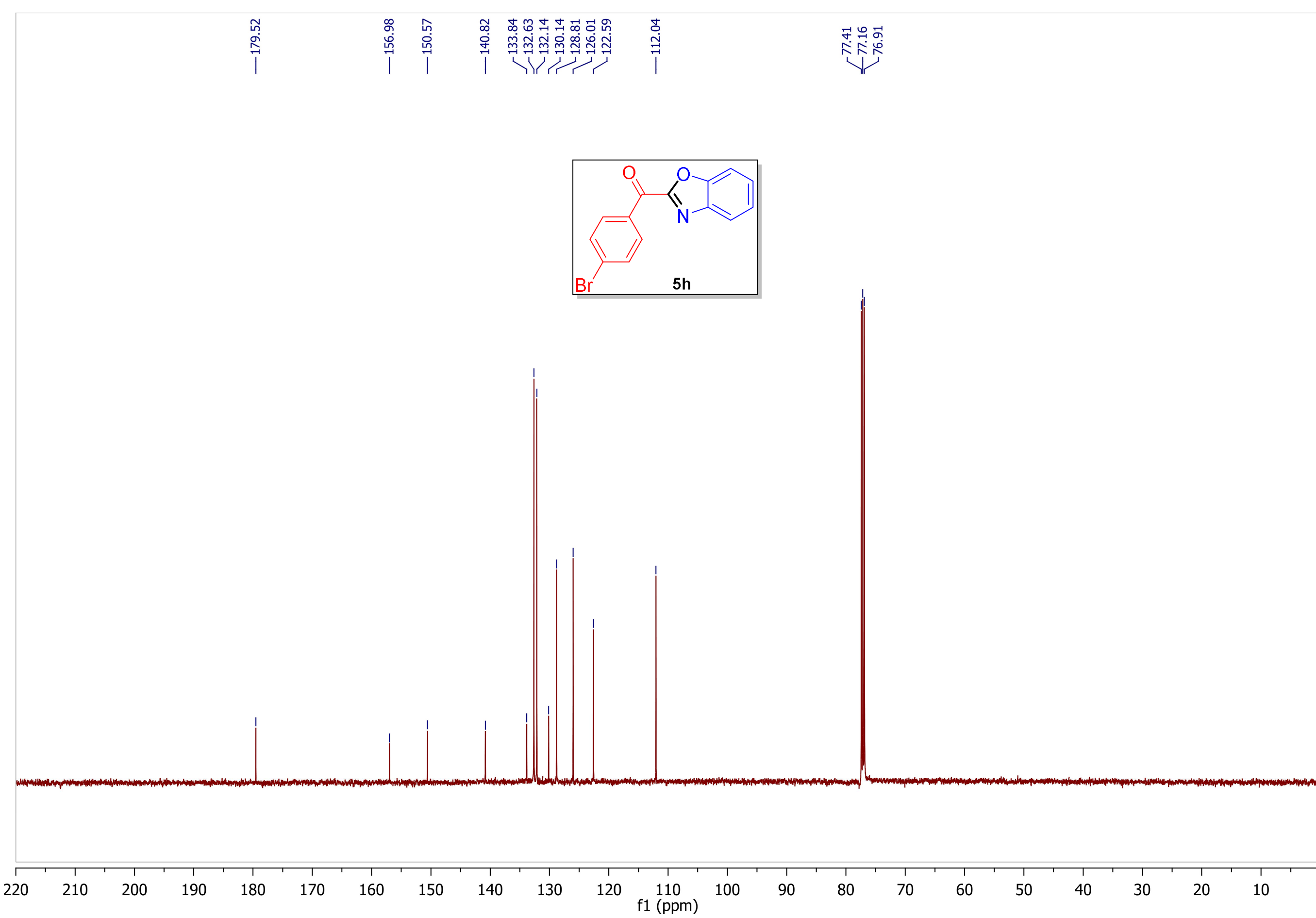

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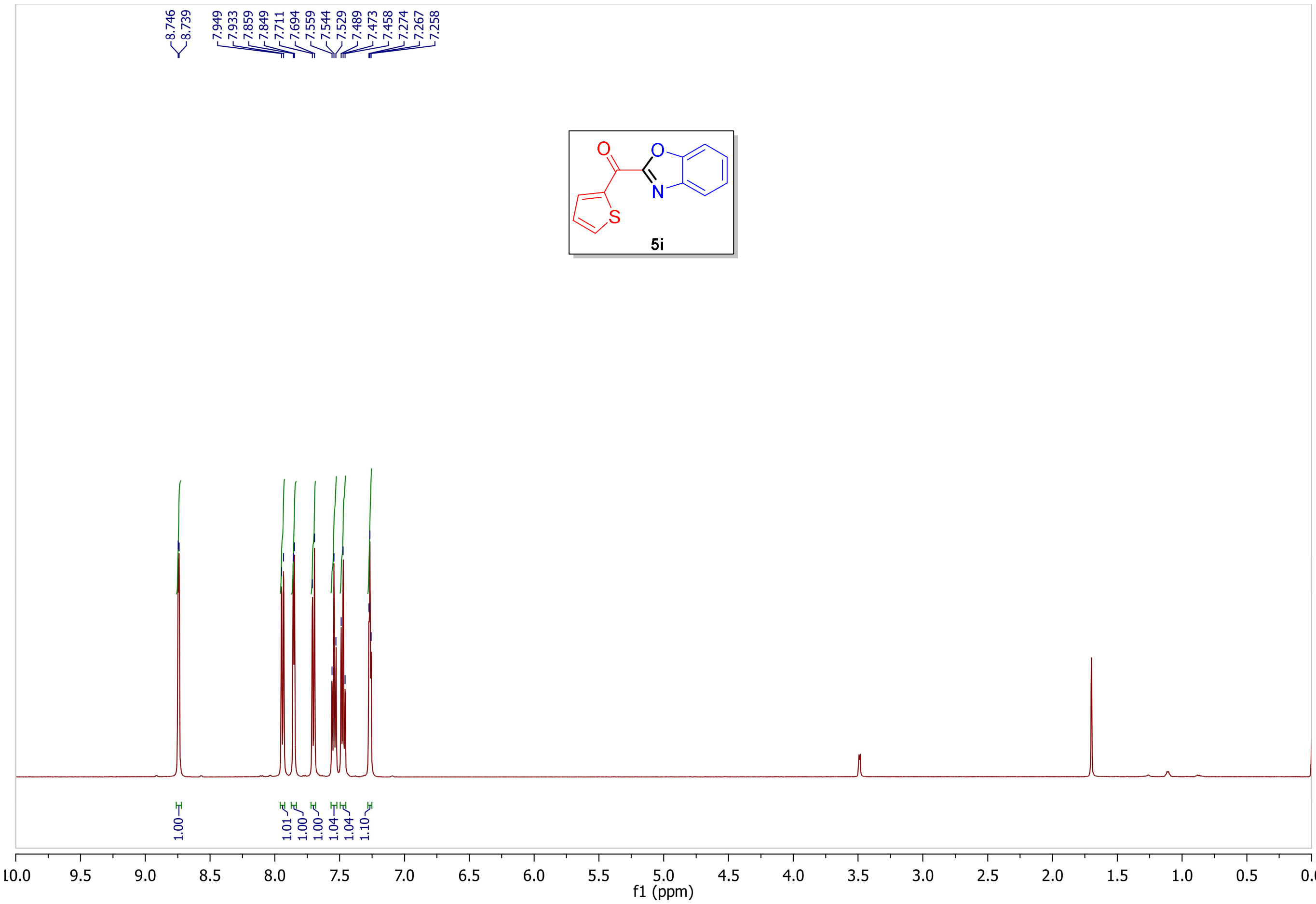

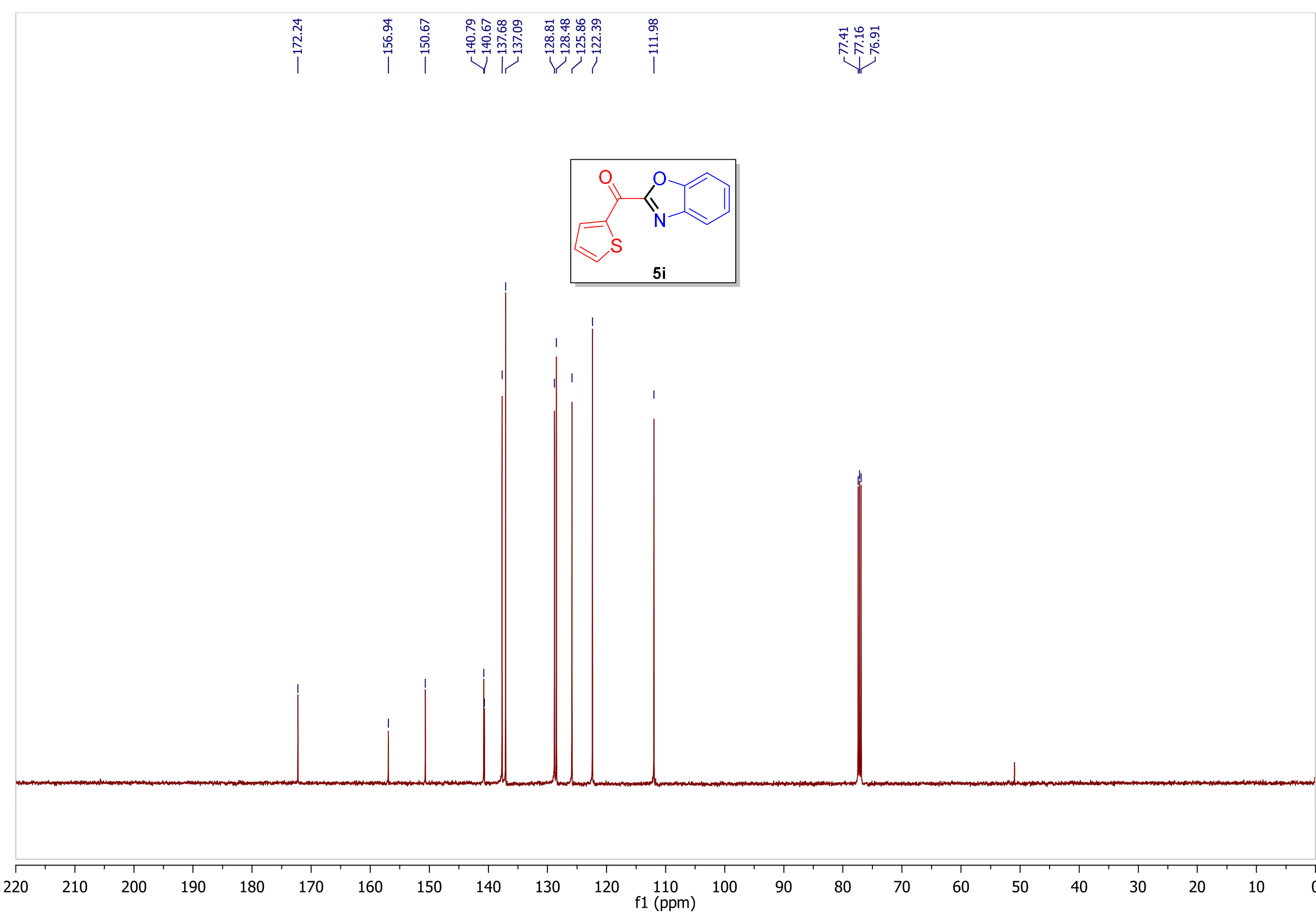

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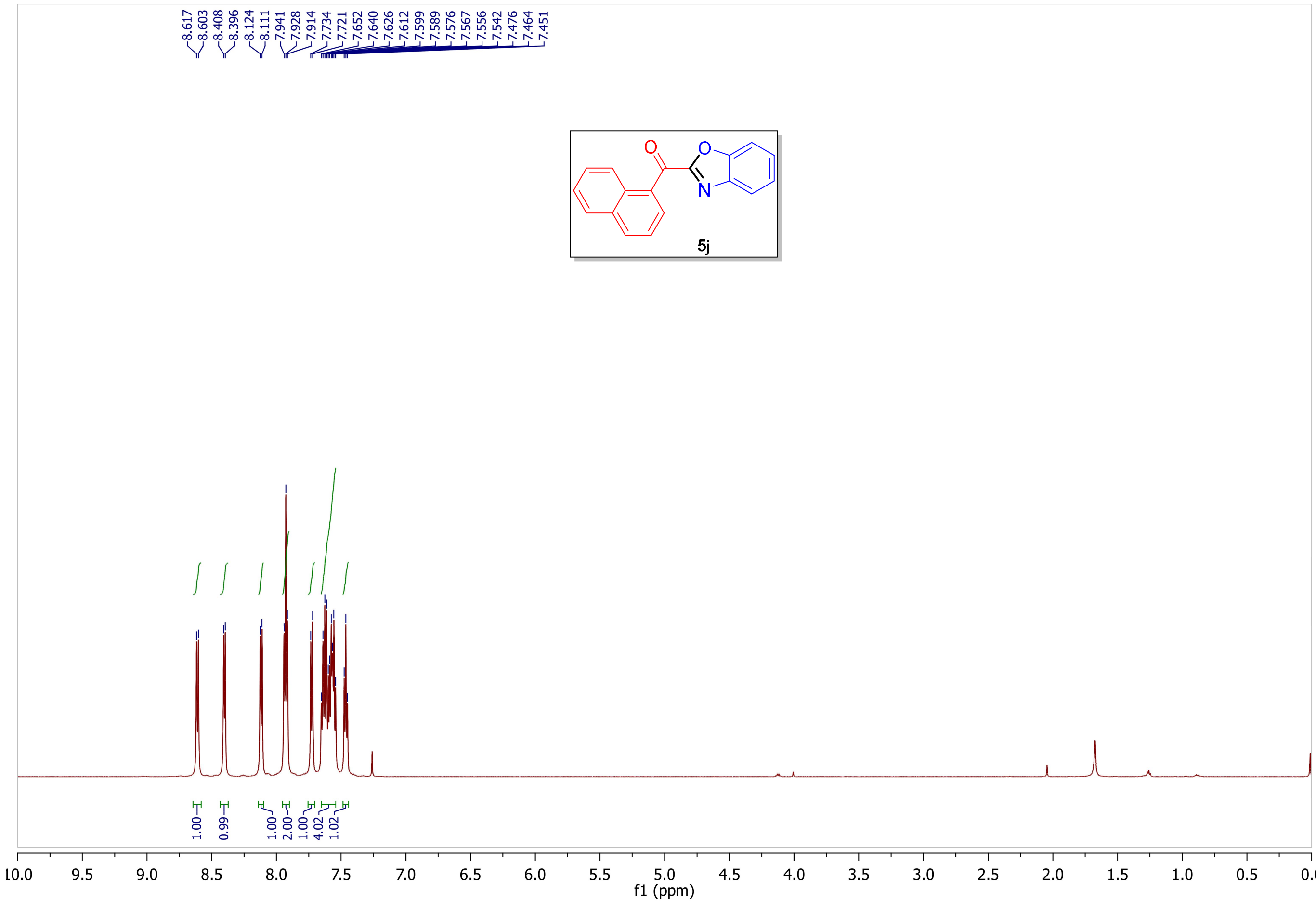
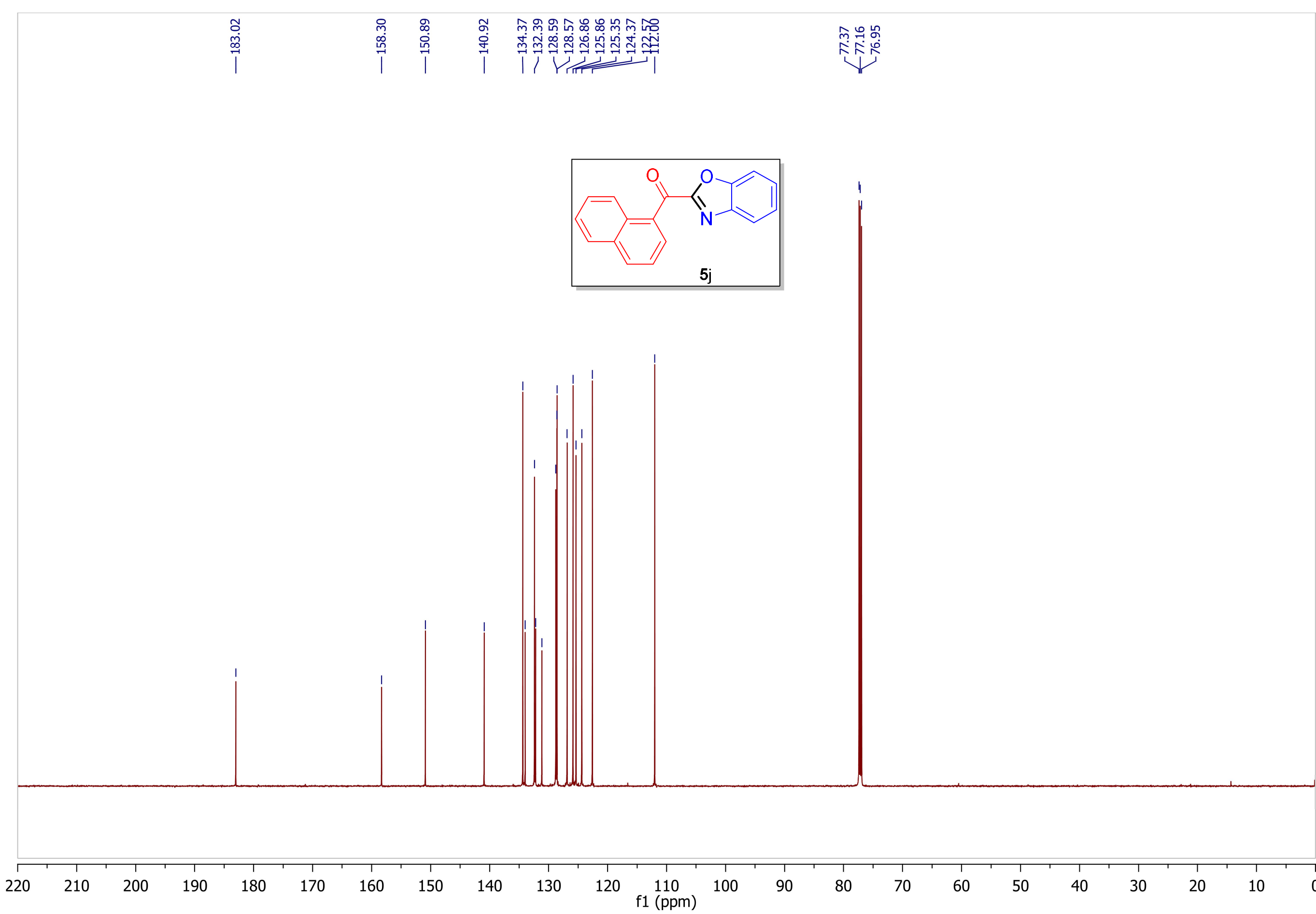
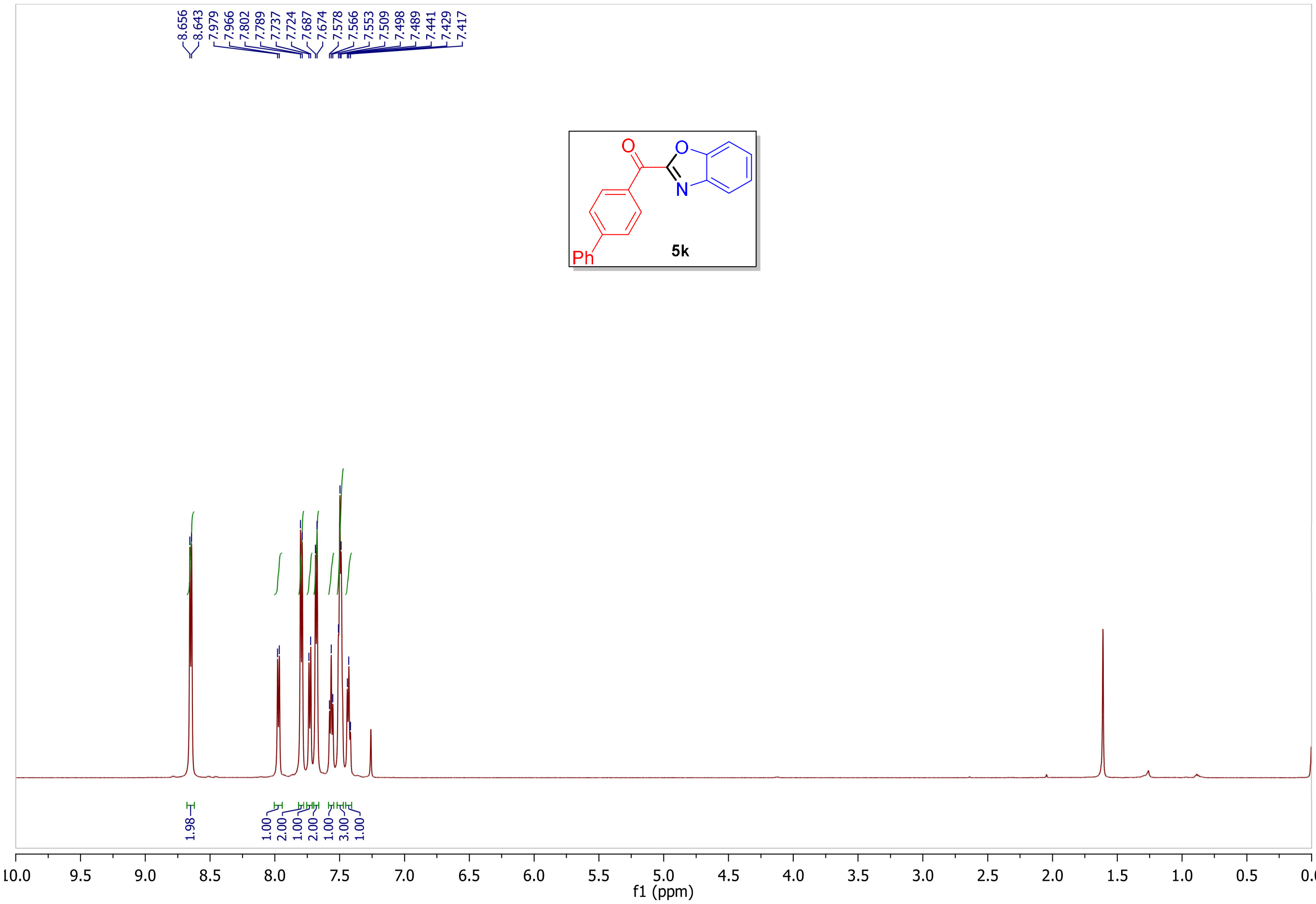
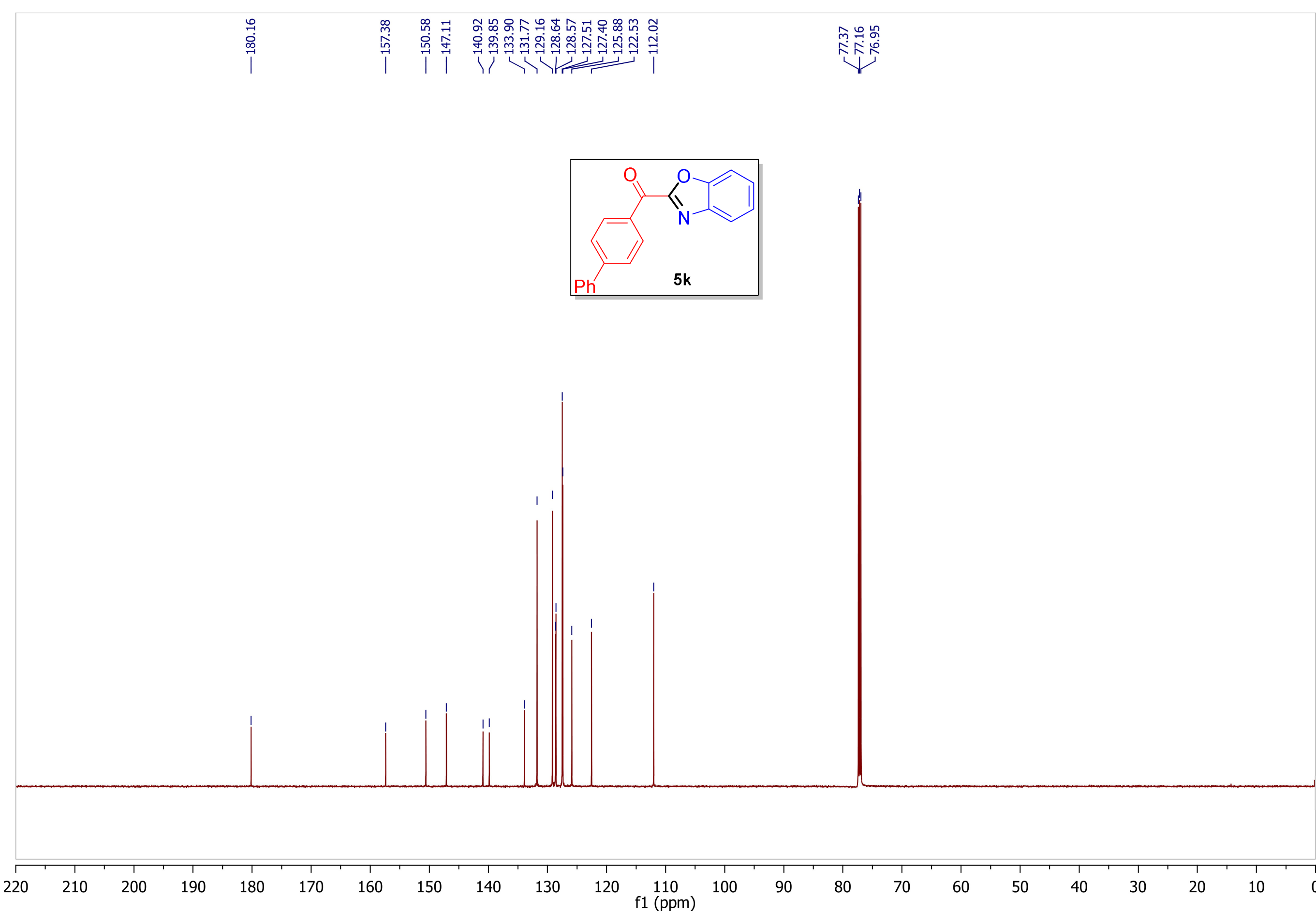


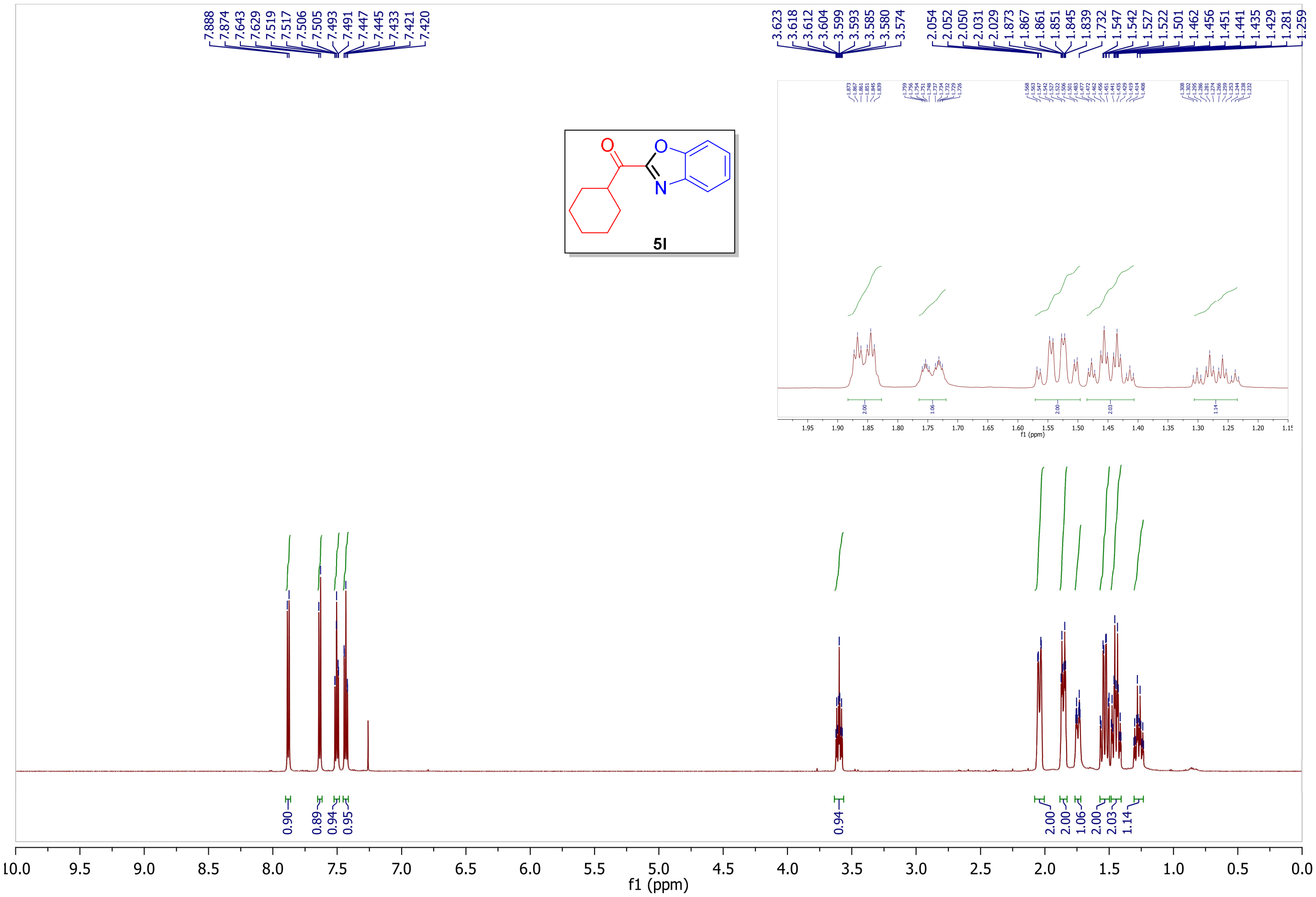


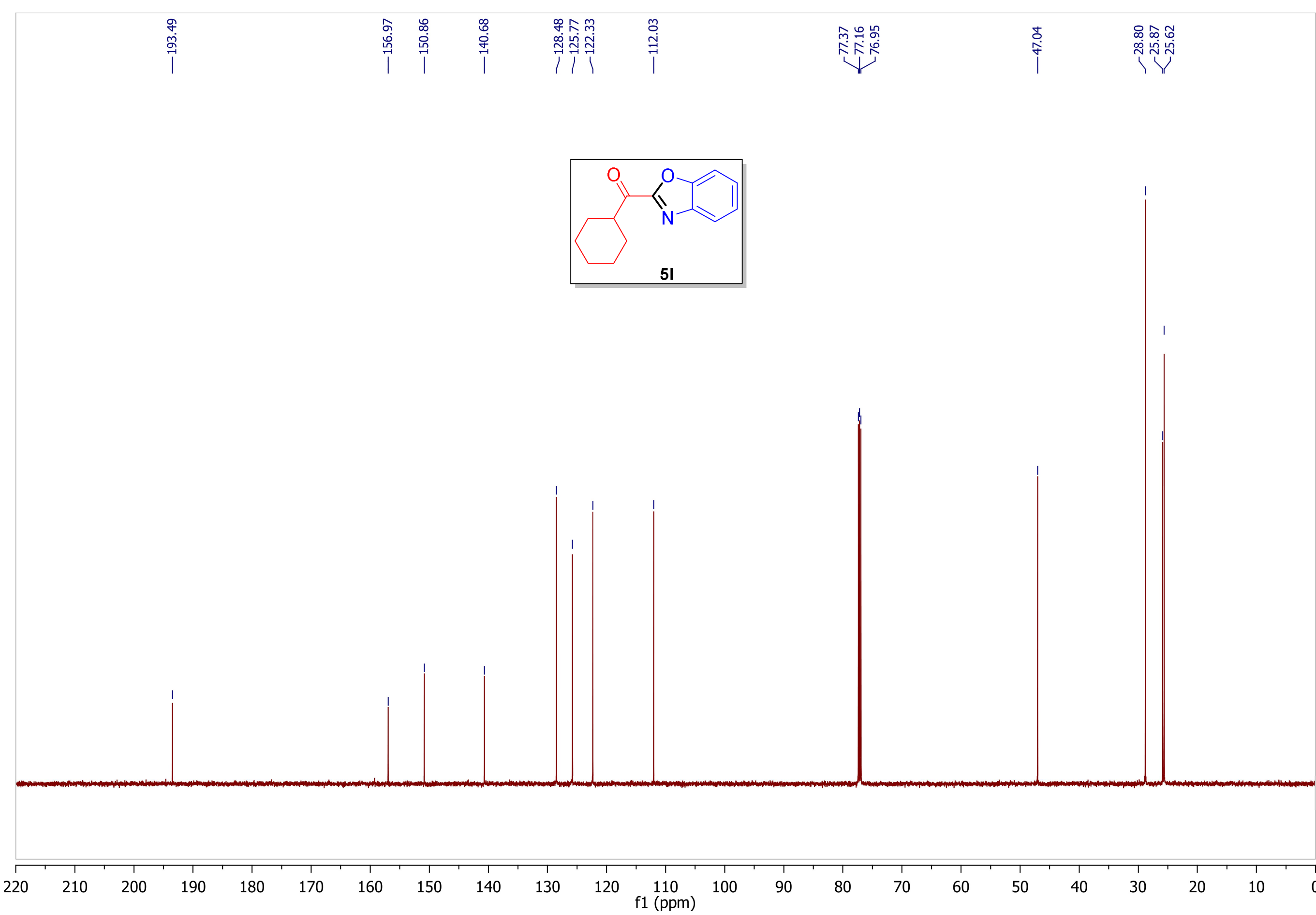
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$), **5k**



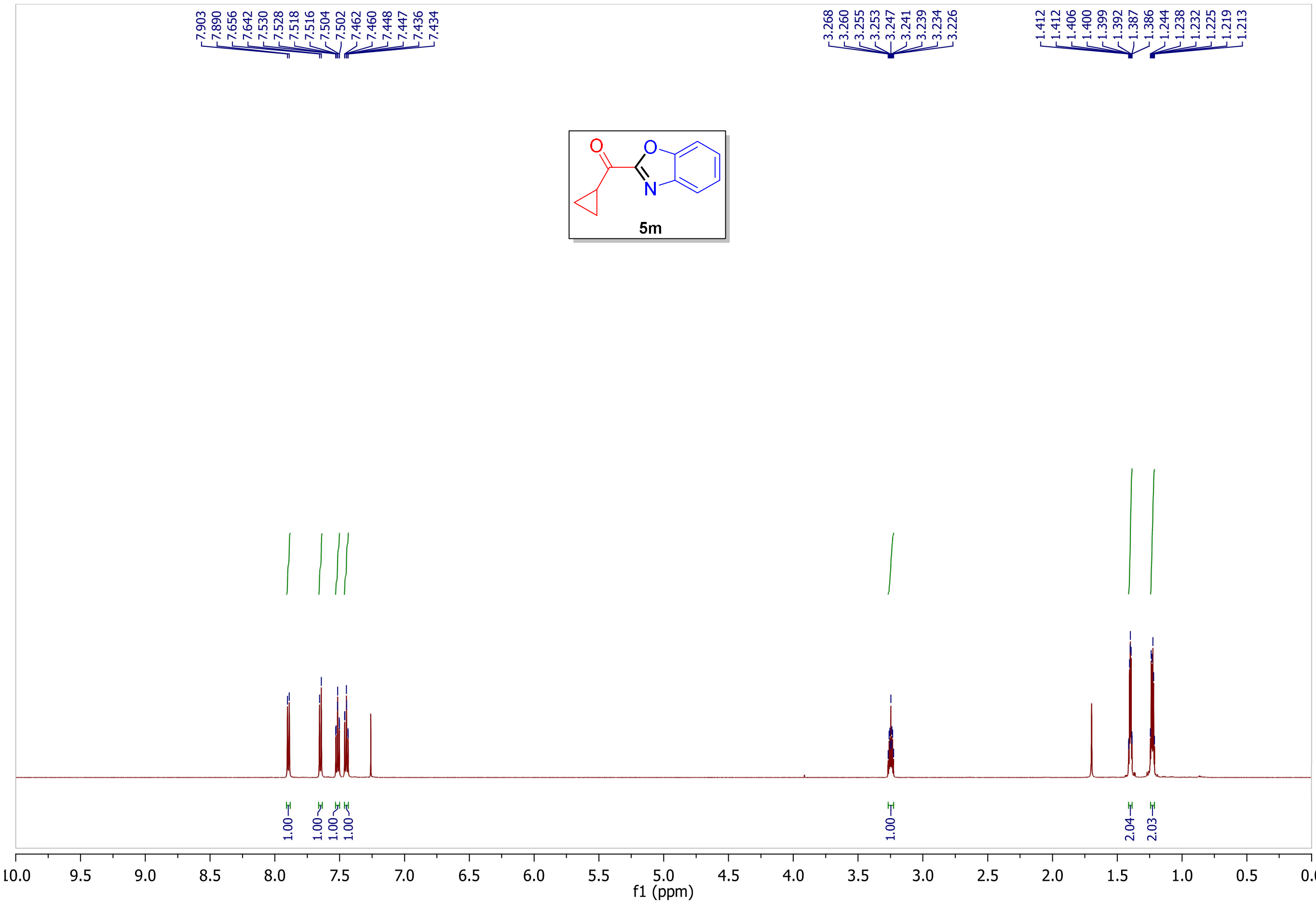


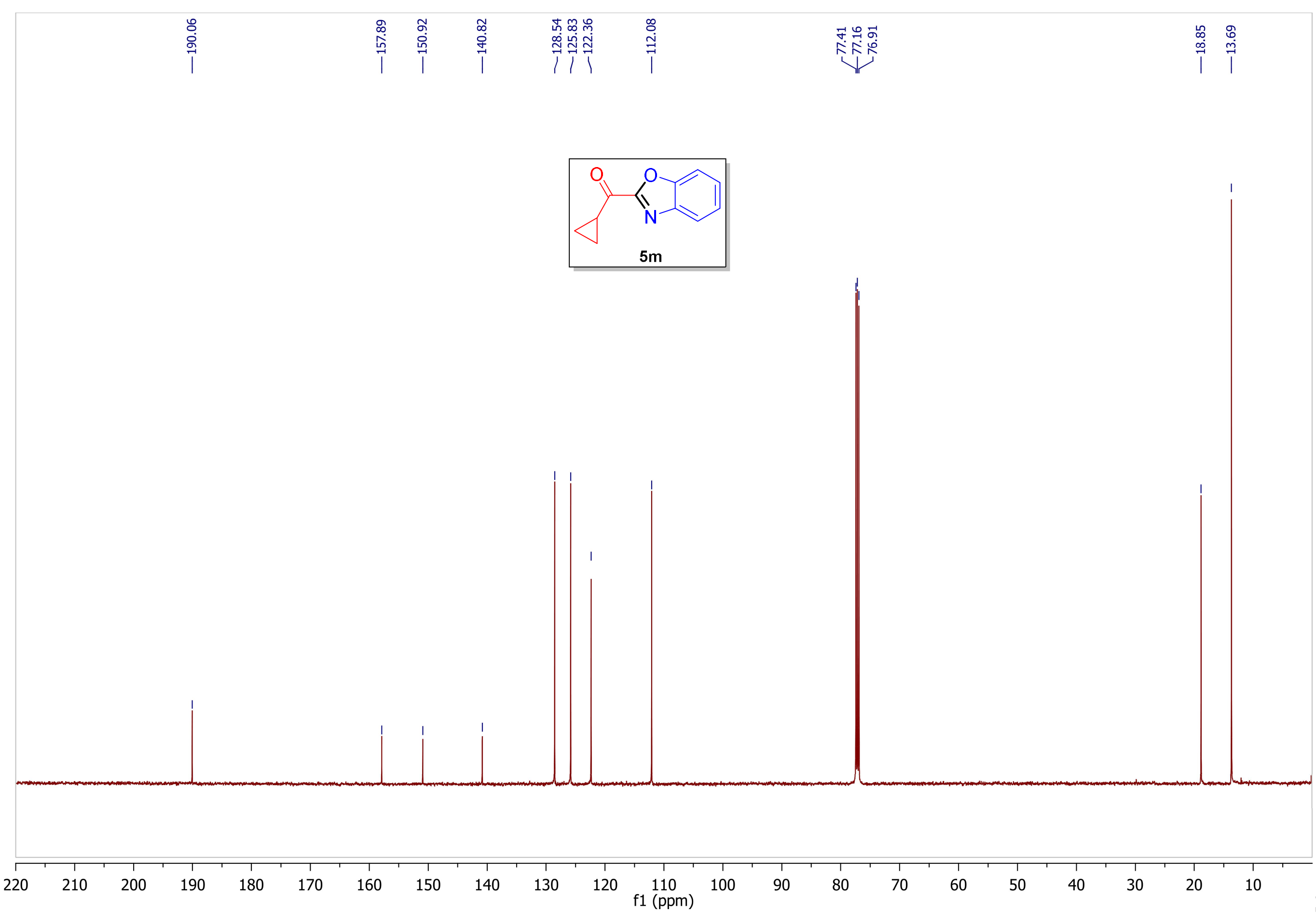
[1]H NMR (600 MHz, $CDCl_3$) and [13]C{[1]H} NMR (151 MHz, $CDCl_3$), **5l**



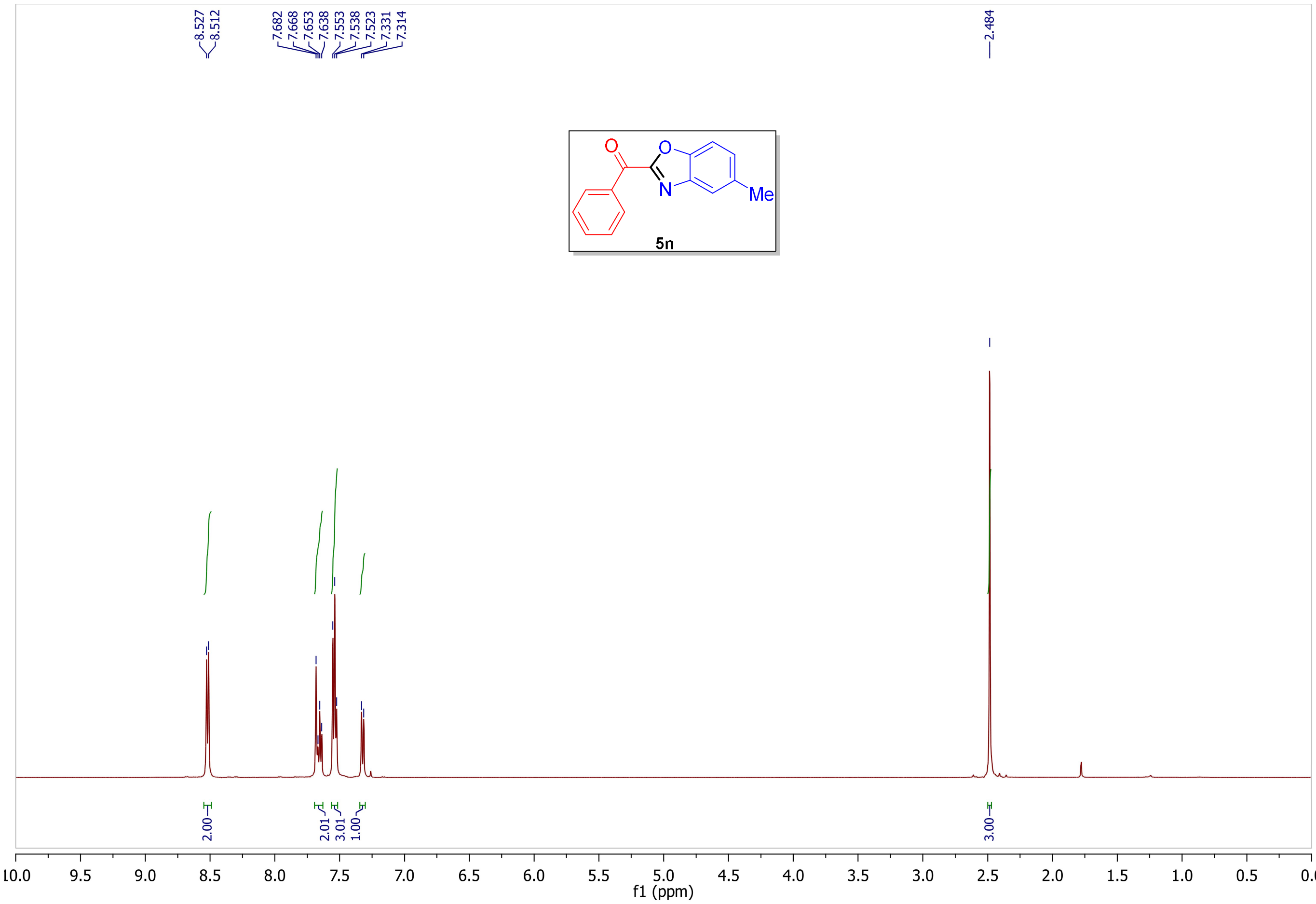


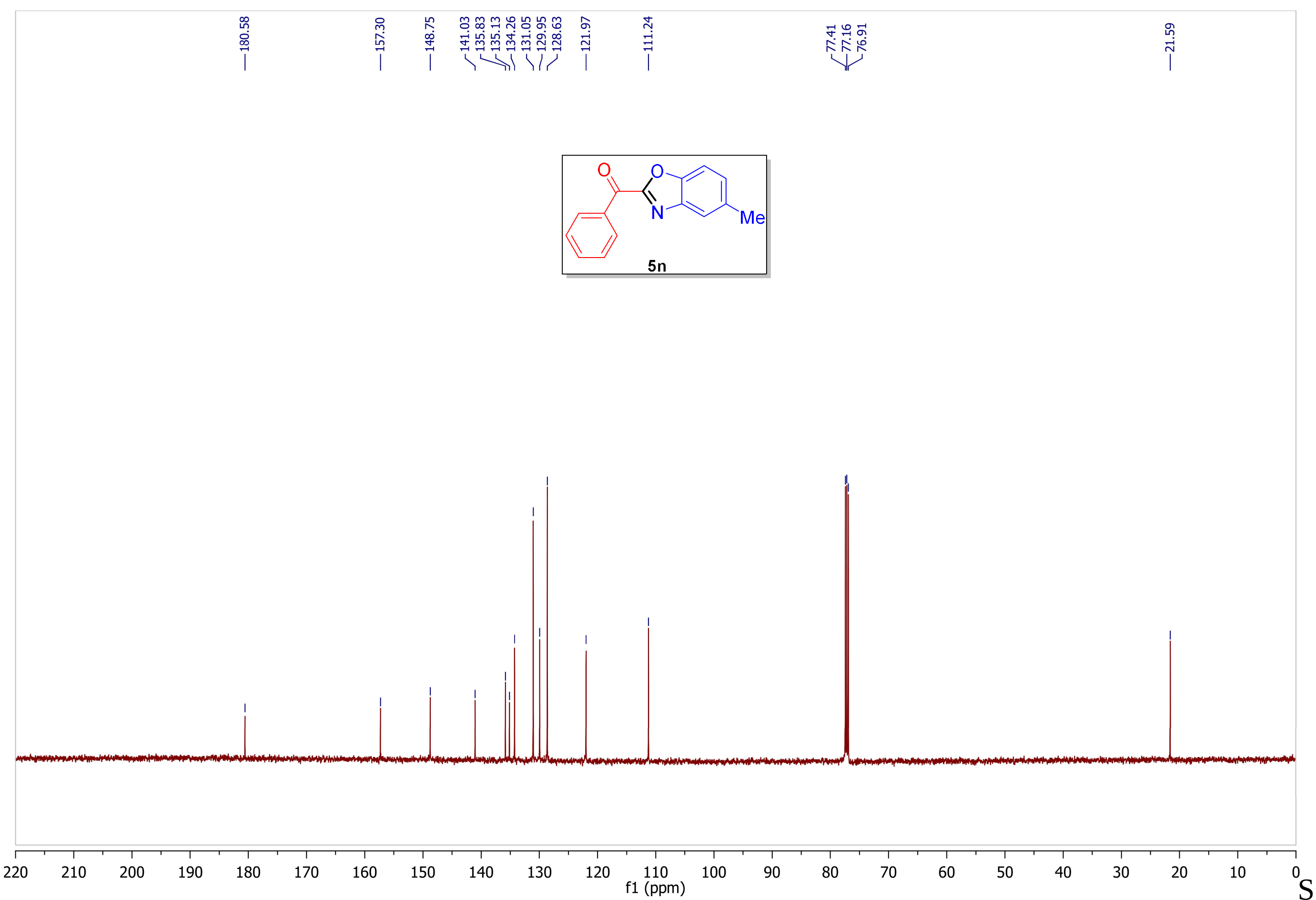
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **5m**



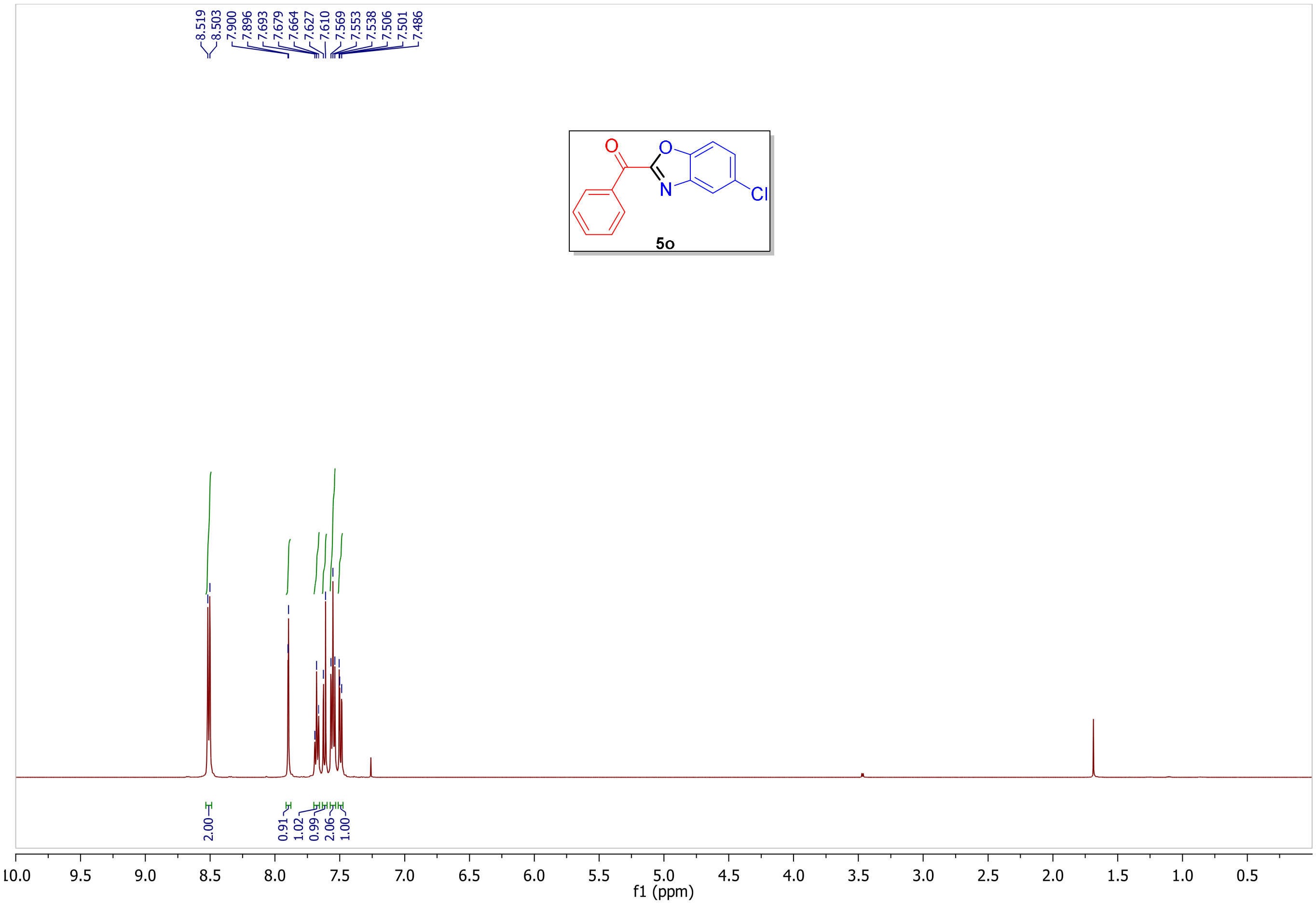


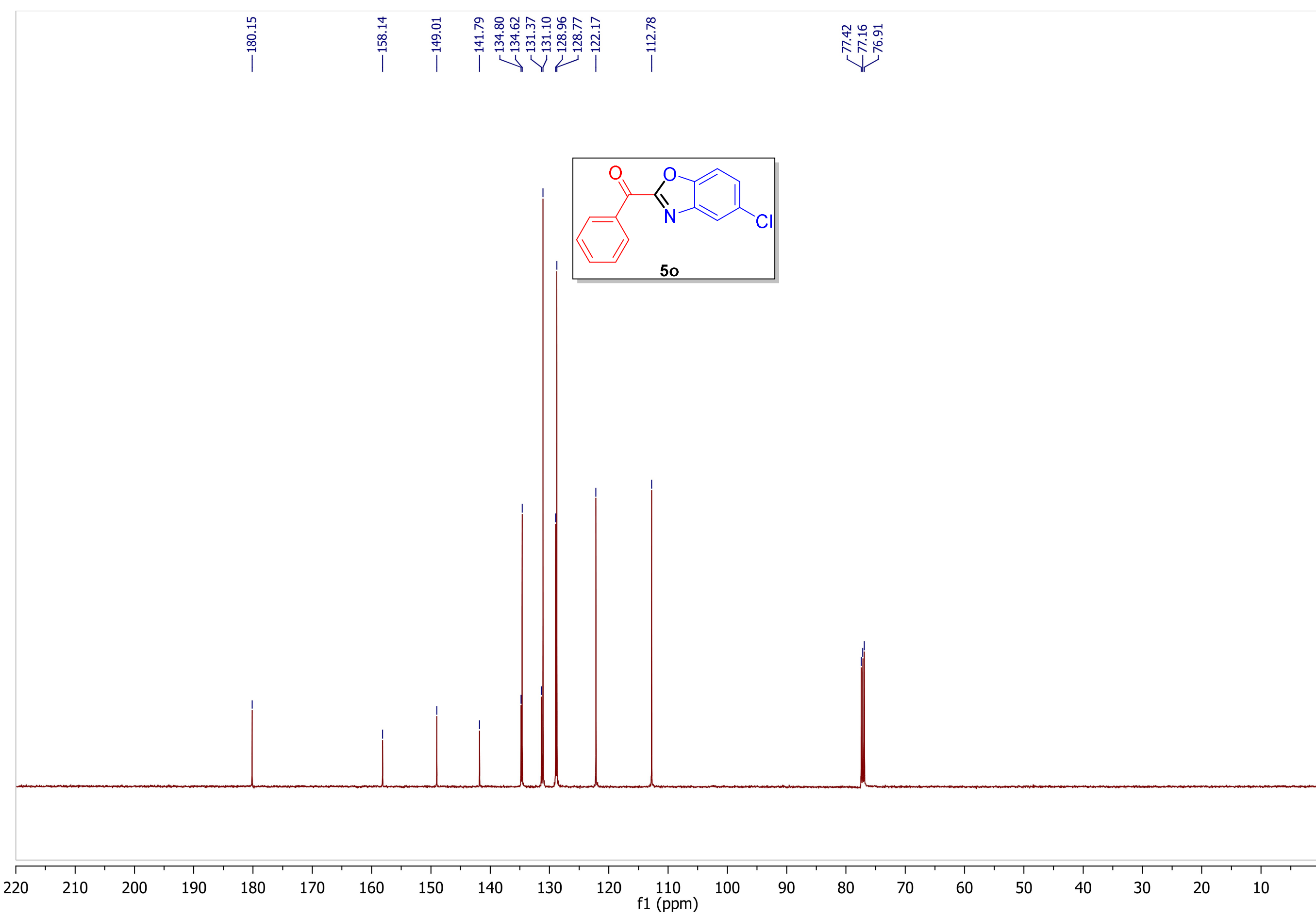
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **5n**



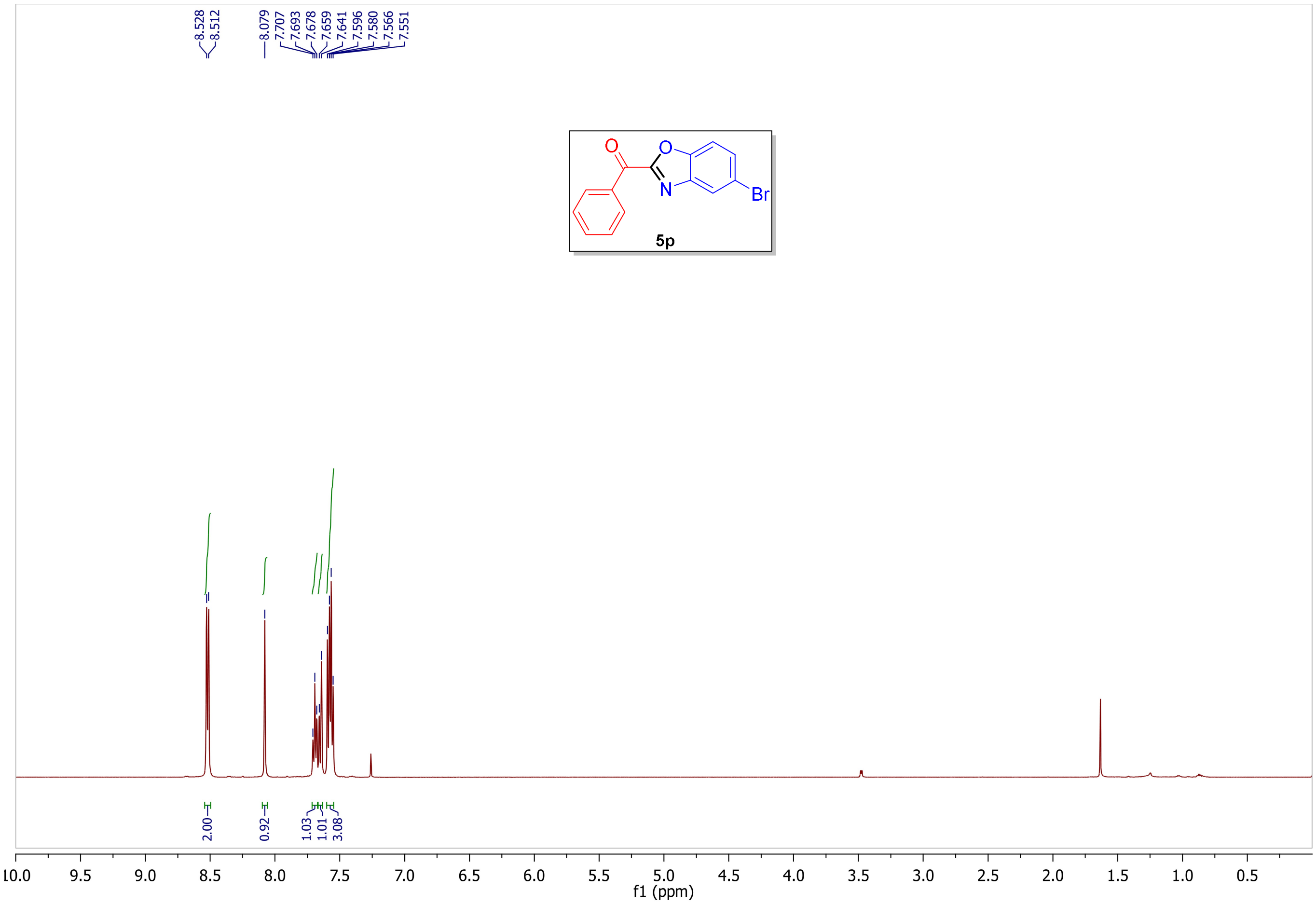


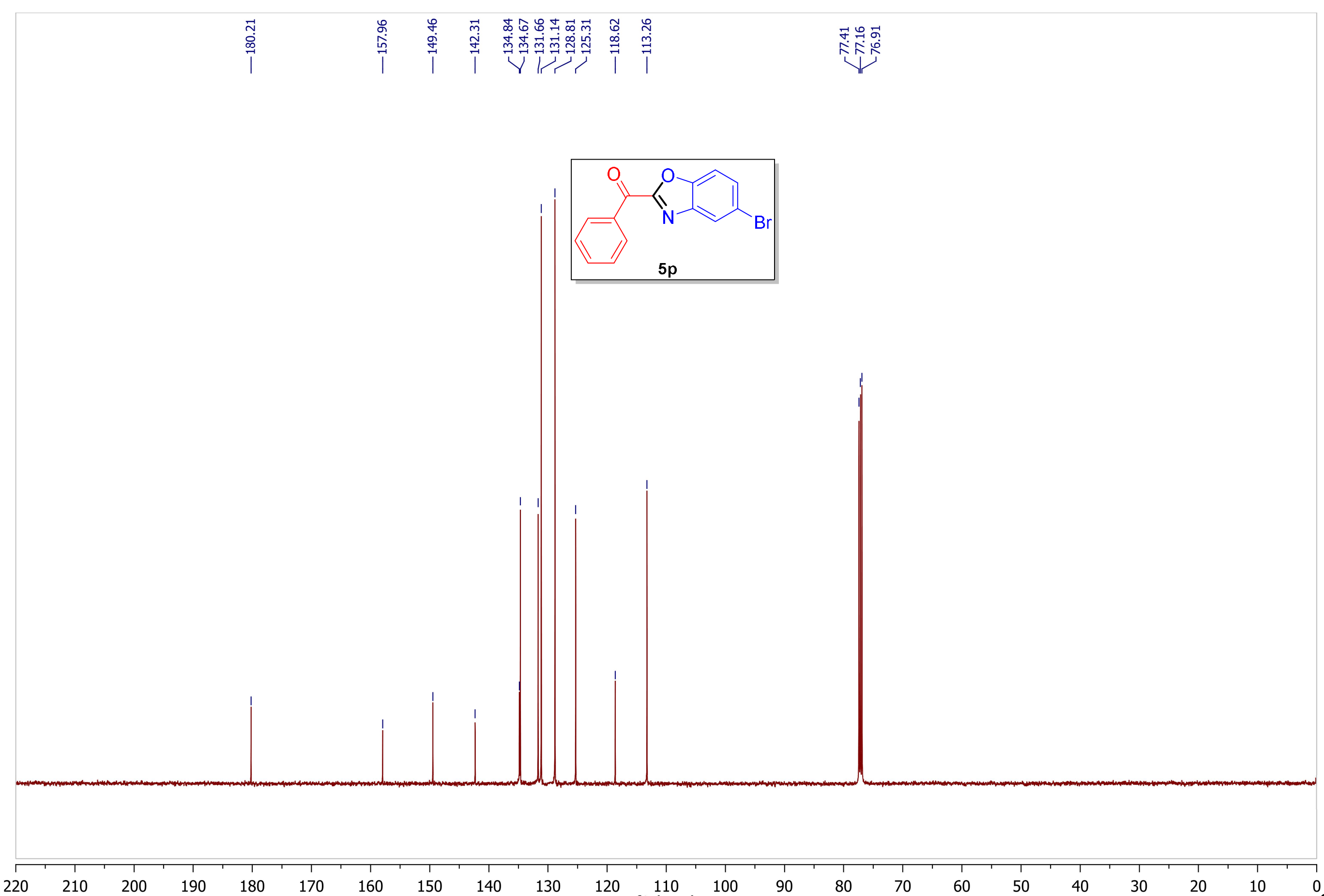
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **5o**



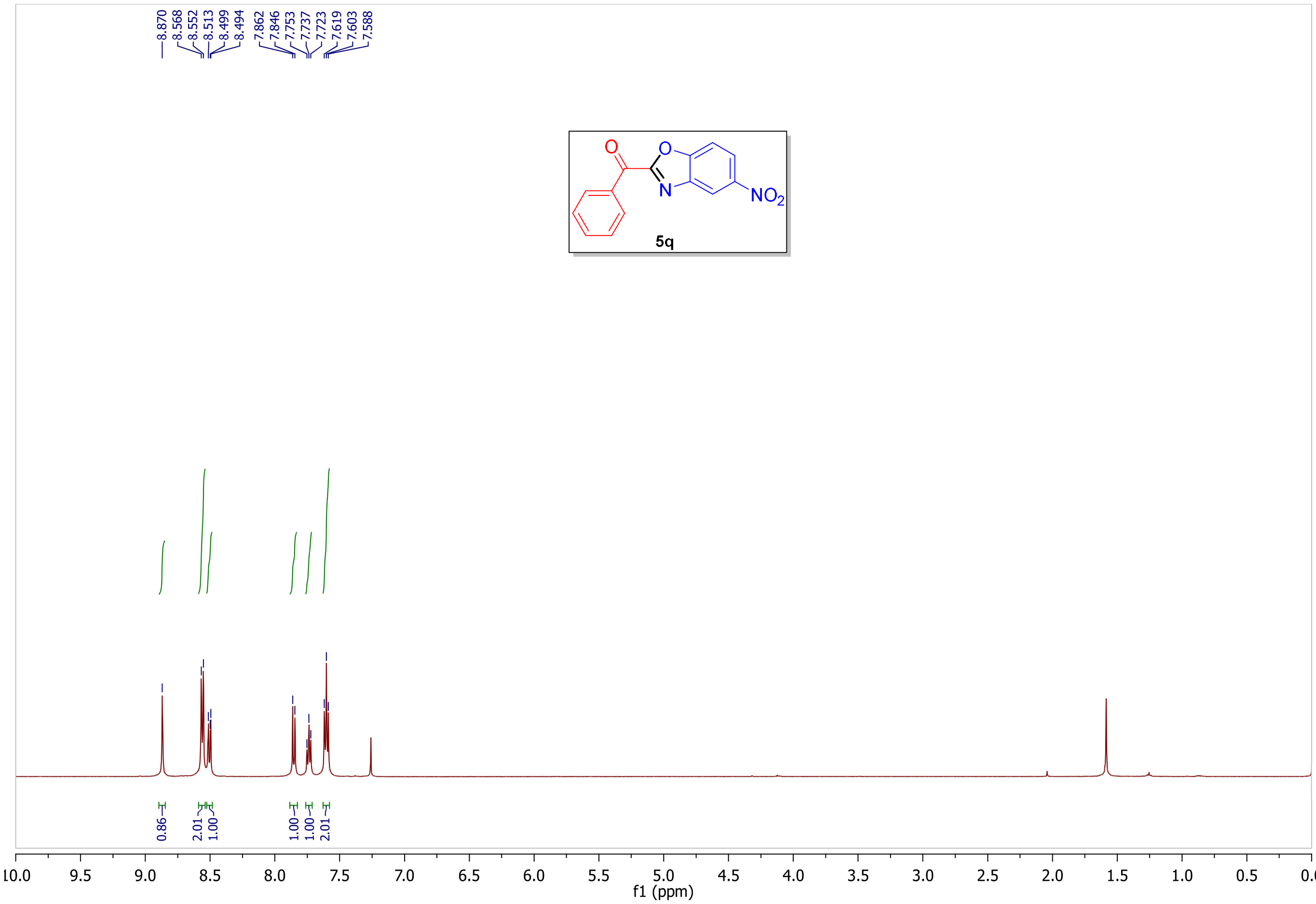


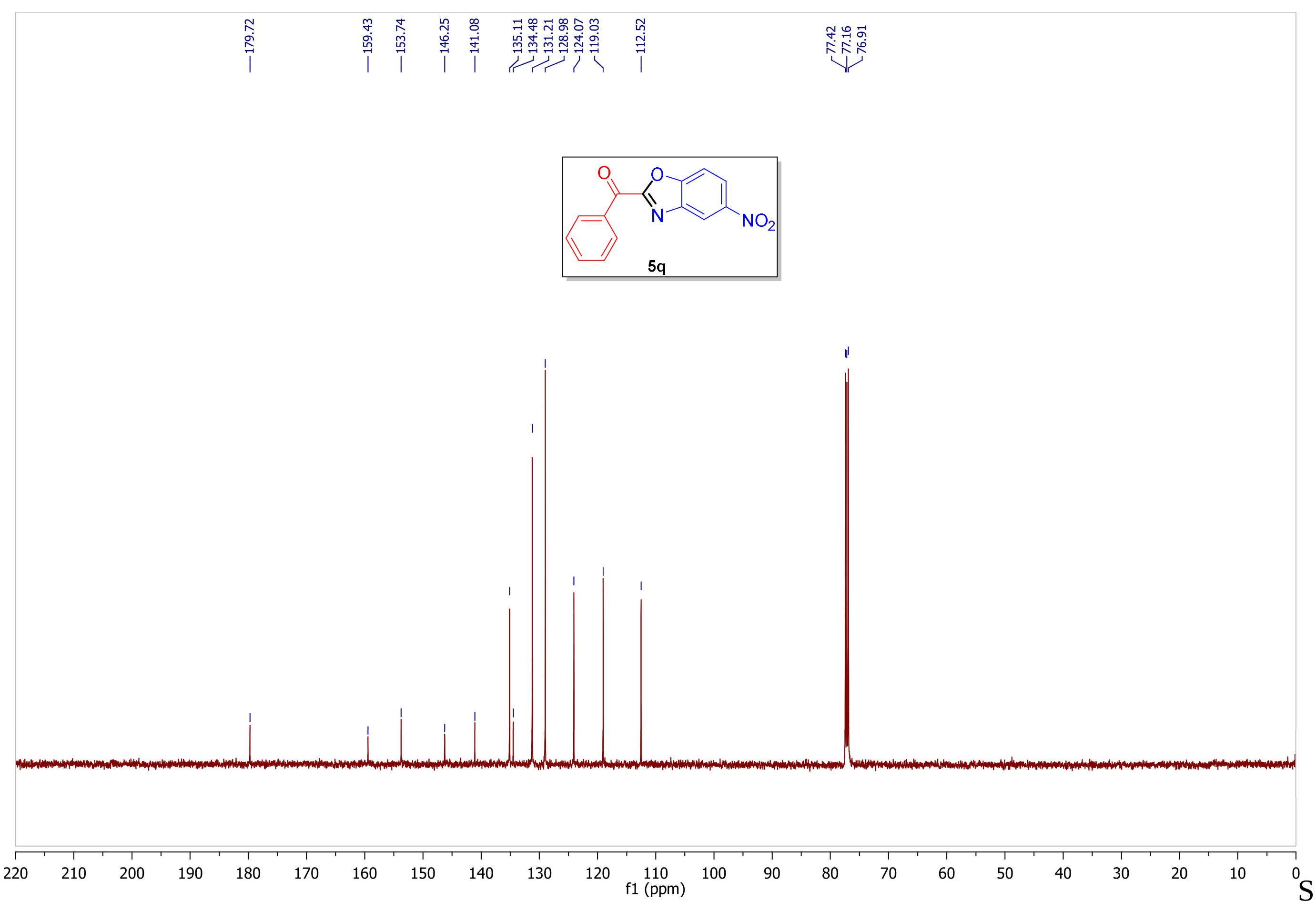
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **5p**



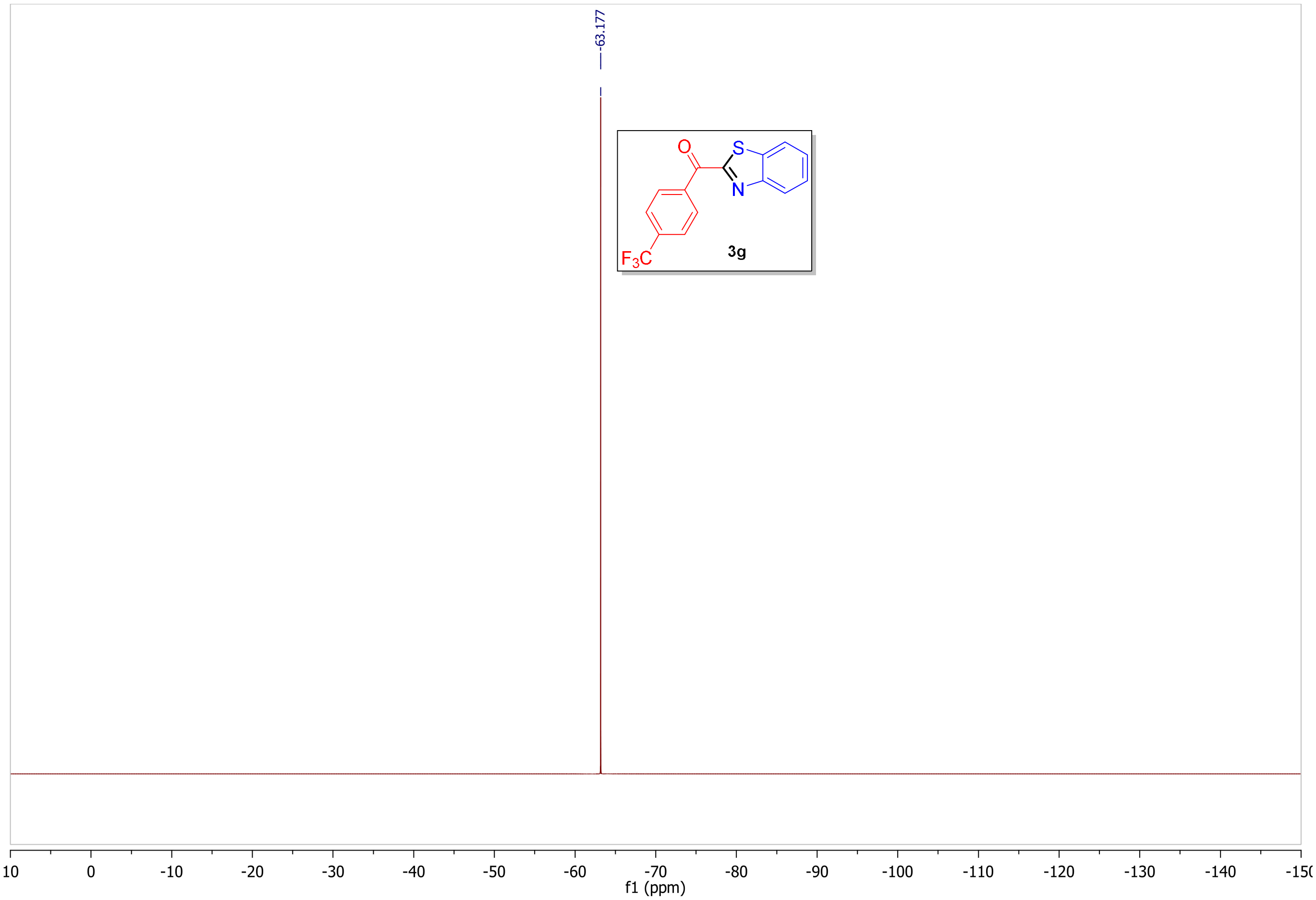


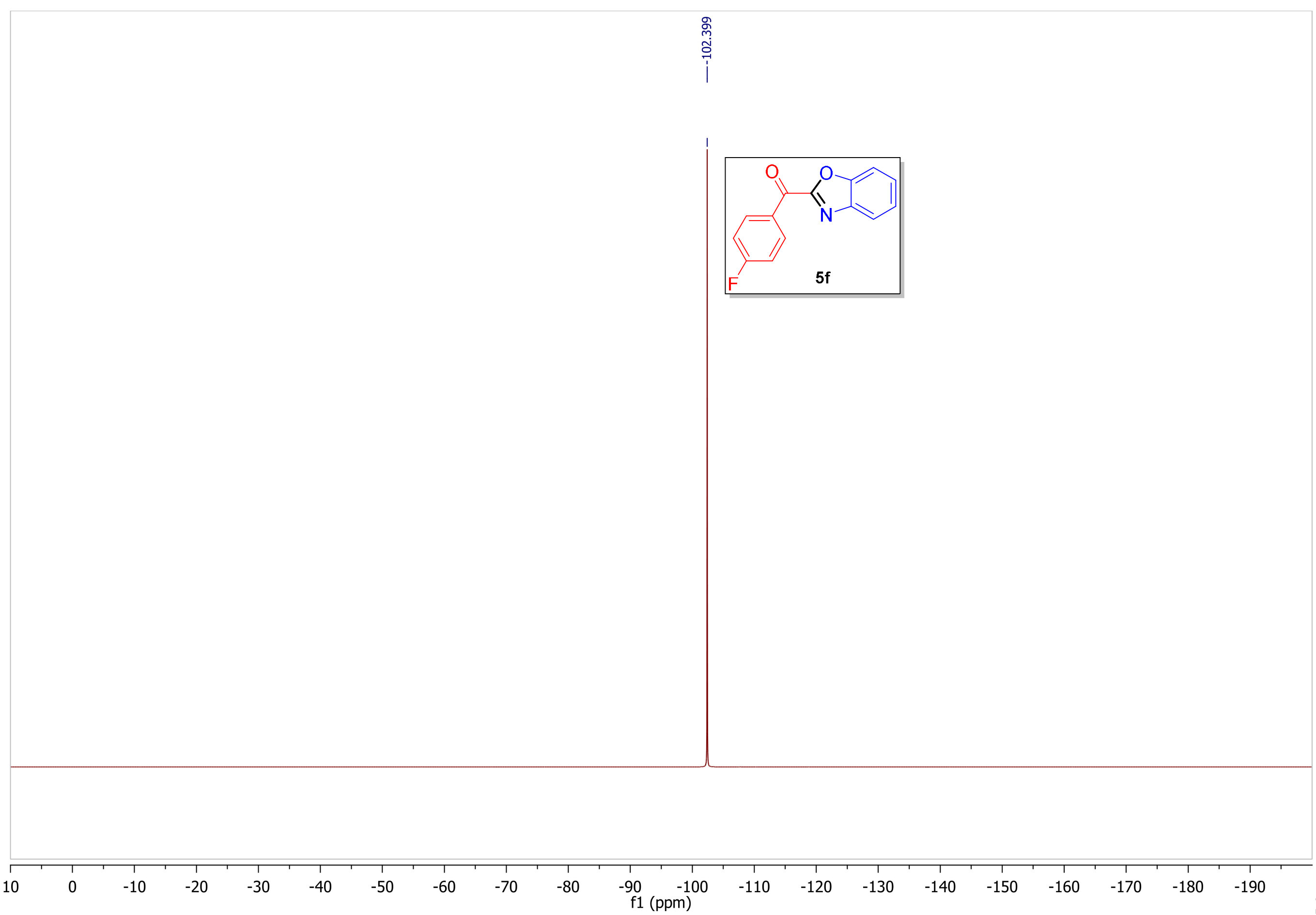
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **5q**





^{19}F NMR (565 MHz, $CDCl_3$), **3g** and ^{19}F NMR NMR (471 MHz, $CDCl_3$), **5f**





HRMS Spectra of Intermediate III or IV