Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Copper-Catalyzed Oxidative Decarboxylative Coupling of α-Keto Acids and Sulfoximines

Chaleena Pimpasri, Ladawan Sumunnee and Sirilata Yotphan*

Center of Excellence for Innovation in Chemistry (PERCH-CIC),

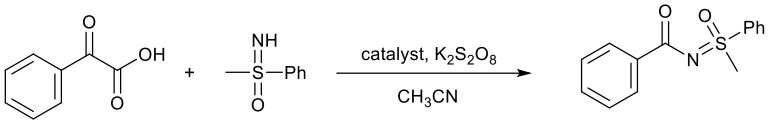
Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

E-mail: sirilata.yot@mahidol.ac.th

Table of Contents

I. Reaction Optimization

Table S1. Effect of Metal Catalyst[a]

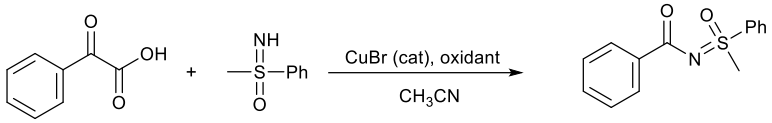


1a 2a 3a

entry	catalyst	mol%	%yield[b]
1	$AgNO_3$	10	trace
2	AgOAc	10	9
3	Ag_2CO_3	10	trace
4	$NiCl_2$	10	50
5	$Pd(OAc)_2$	10	23
6	$Fe(OAc)_2$	10	no reaction
7	**CuBr**	**10**	**75**
8	$CuBr_2$	10	68
9	CuBr	5	65
10	CuBr	20	74
11	CuBr[c]	10	13
12	-	-	trace

[a]Conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), $K_2S_2O_8$ (0.55 mmol), CH_3CN (3 mL), 1 h. [b]GC yield.
[c]10 mol% of $AgNO_3$ (co-catalyst) was added to the reaction.

Table S2. Effect of Oxidant and Temperature [a]



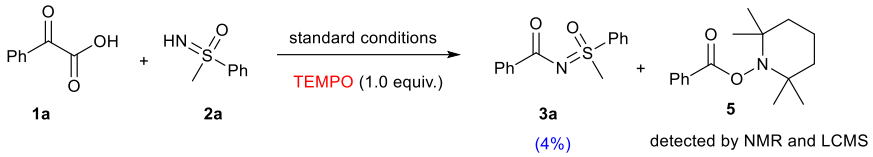
1a 2a 3a

entry	oxidant	equiv.	temperature (°C)	%yield[b]
1	$K_2S_2O_8$	1.1	rt	43
2	$K_2S_2O_8$	1.1	40	48
3	$K_2S_2O_8$	1.1	50	55
4	$K_2S_2O_8$	1.1	60	61
5	$K_2S_2O_8$	1.1	70	73
6	**$K_2S_2O_8$**	**1.1**	**75**	**75**
7	$K_2S_2O_8$	1.1	80	71
8	$K_2S_2O_8$	2.0	75	69
9	$K_2S_2O_8$	3.0	75	64
10	TBHP	1.1	75	2
11	DTBP	1.1	75	20
12	-	-	75	trace

[a]Conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), CuBr (0.05 mmol), CH_3CN (3 mL), 1 h. [b]GC yield.

II. Miscellaneous Experiments

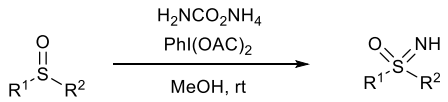
Control experiment



2,2,6,6-Tetramethylpiperidin-1-yl benzoate (radical coupling adduct **5**): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.49−7.45 (m, 2H), 1.83−1.68 (m, 3H), 1.62−1.58 (m, 2H), 1.49−1.45 (m, 2H), 1.28 (s, 6H), 1.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 132.6, 129.3, 128.2, 60.1, 38.8, 31.7, 20.6, 16.7.

(Reference: S. Yang, H. Tan, W. Ji, X. Zhang, P. Li, and L. Wang, *Adv. Synth. Catal.*, 2017, **359**, 443.)

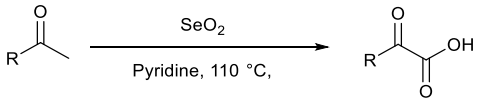
General Procedure for the Preparation of *NH*-Sulfoximine



The sulfoxide (4.0 mmol, 1.0 equiv.), $PhI(OAc)_2$ (3.87 g, 12.0 mmol, 3.0 equiv.), ammonium carbamate ($H_2NCO_2NH_4$,1.25 g, 16.0 mmol, 4.0 equiv.) and MeOH (8.0 mL) were added to a 50 mL round bottom flask equipped with a magnetic stir bar. The reaction was stirred for 30 min at room temperature in an open flask. Upon completion, a solvent was removed *in vacuo* and the crude residue was purified by flash silica gel (SiO_2) column chromatography

(Reference: M. Zenzola, R. Doran, L. Degennaro, R. Luisi and J. A. Bull, *Angew. Chem. Int. Ed.*, 2016, **55**, 7203.)

General Procedure for the Preparation of *α*-keto acid



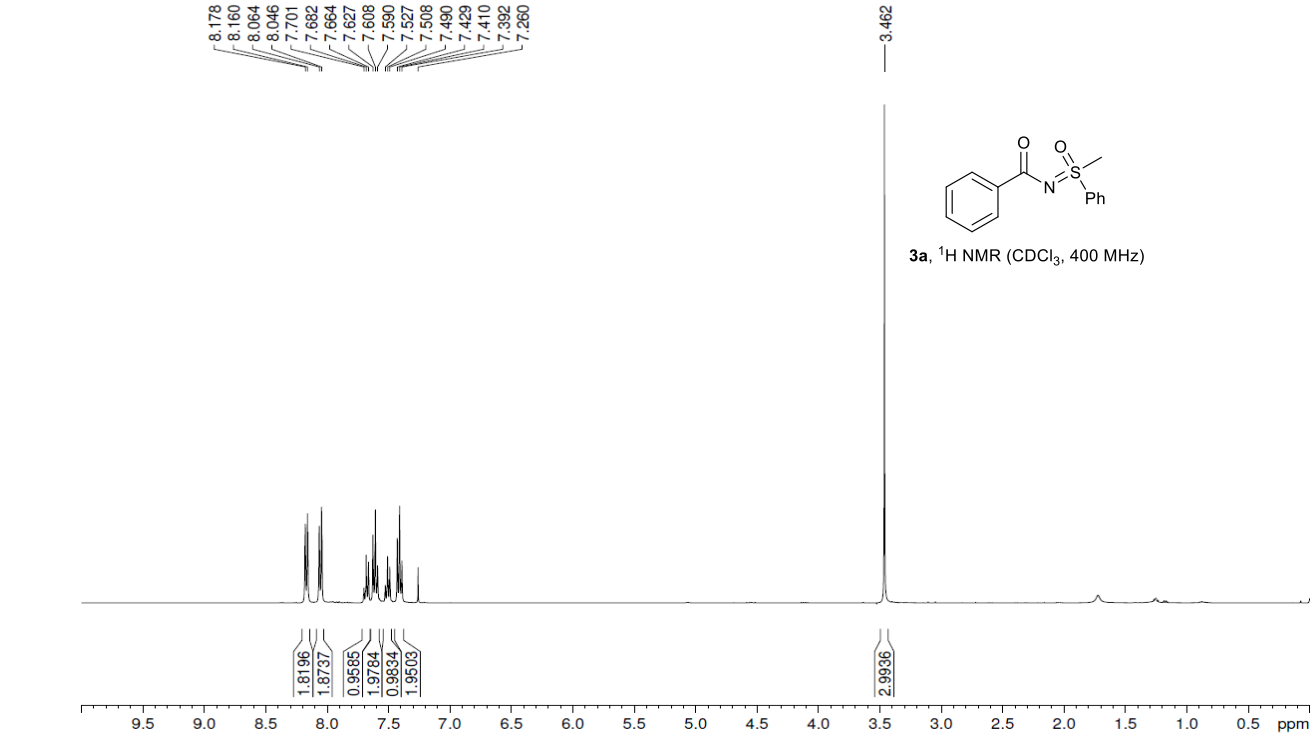
Substituted aryl-methylketone (10.0 mmol, 1.0 equiv.), selenium dioxide (SeO_2, 1.65 g, 15.0 mmol, 1.5 equiv.), and anhydrous pyridine (4 mL, 50 mmol) were added, respectively, to a 50 mL round bottom flask equipped with a magnetic bar. The reaction mixture was heated in an oil bath under Ar at 110 ºC for 4 h. Upon completion (monitoring by TLC), the reaction mixture was cooled to room temperature and filtered. The residue was washed with ethyl acetate (50 mL). The combined filtrate was treated with 1 M HCl (20 mL), the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). Then, the combined organic layers were treated with 1 M NaOH (50 mL), and the aqueous layer

was separated. The organic layer was extracted with water (25 mL) and the combined aqueous layers were added dropwise with 1 M HCl until pH = 1−2. The mixture was extracted with ethyl acetate (3 × 50 mL), and the combined organic layers were dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting α-keto acid was used in the copper-catalyzed decarboxylative aroylation without further purification.

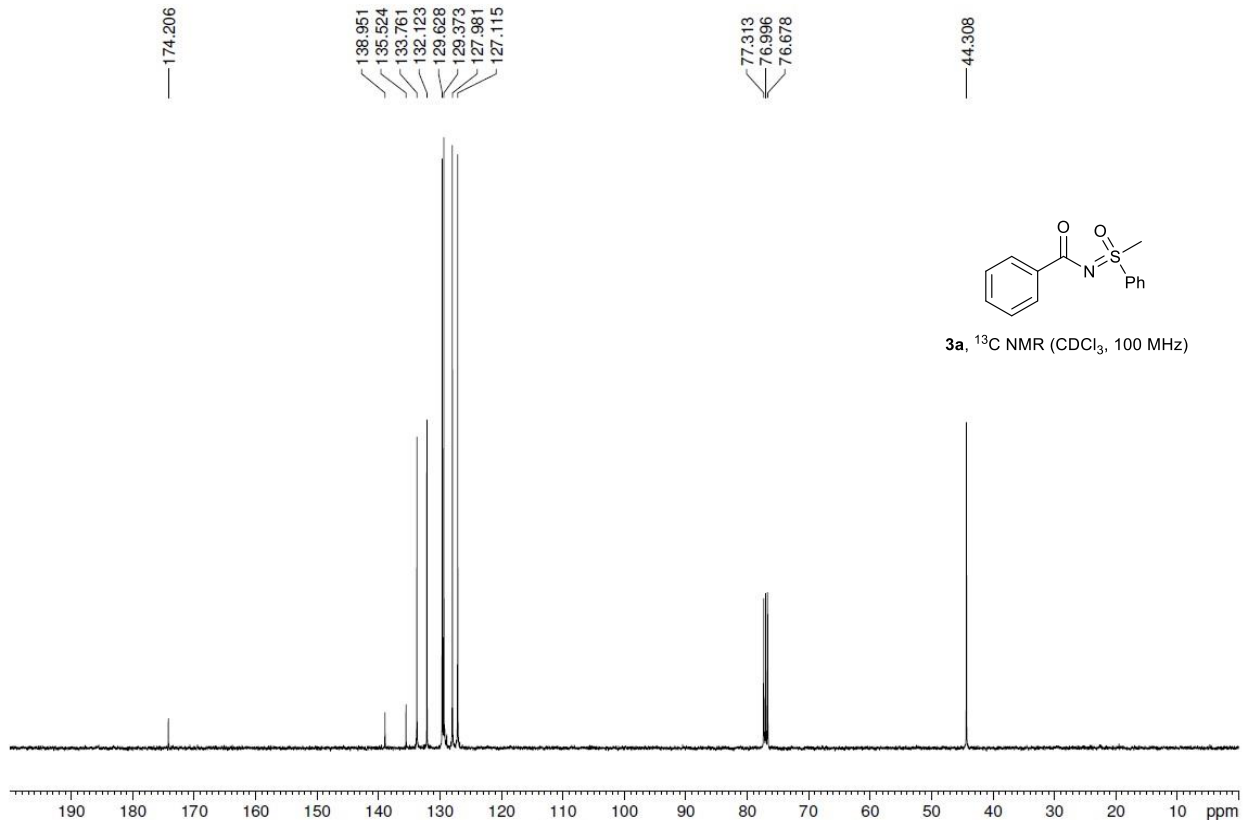
(Reference: K. Wadhwa, C.-X. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun.*, 2008, **38**, 4434.)

III. Spectral Data of Compounds 3a−3i and 4a−4n

N-Benzoyl-*S*-methyl-*S*-phenyl sulfoximine (3a)

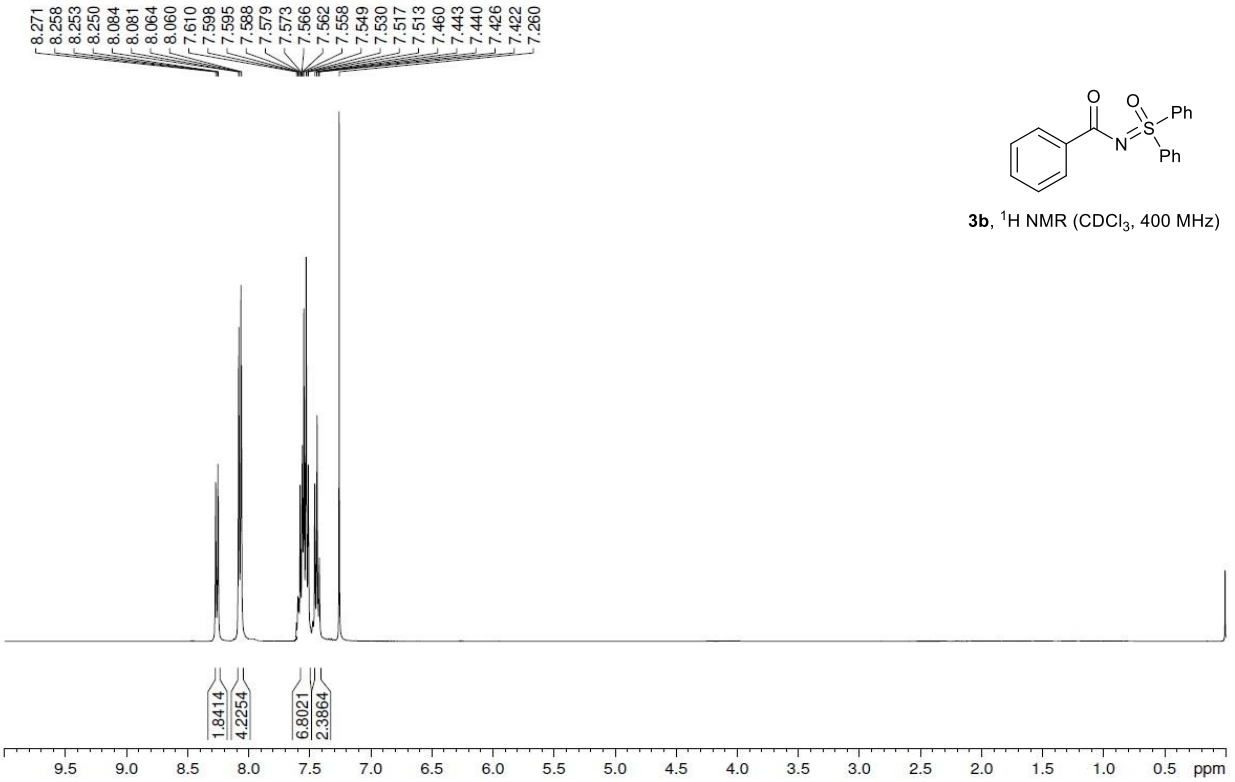


3a, ^{1}H NMR ($CDCl_3$, 400 MHz)

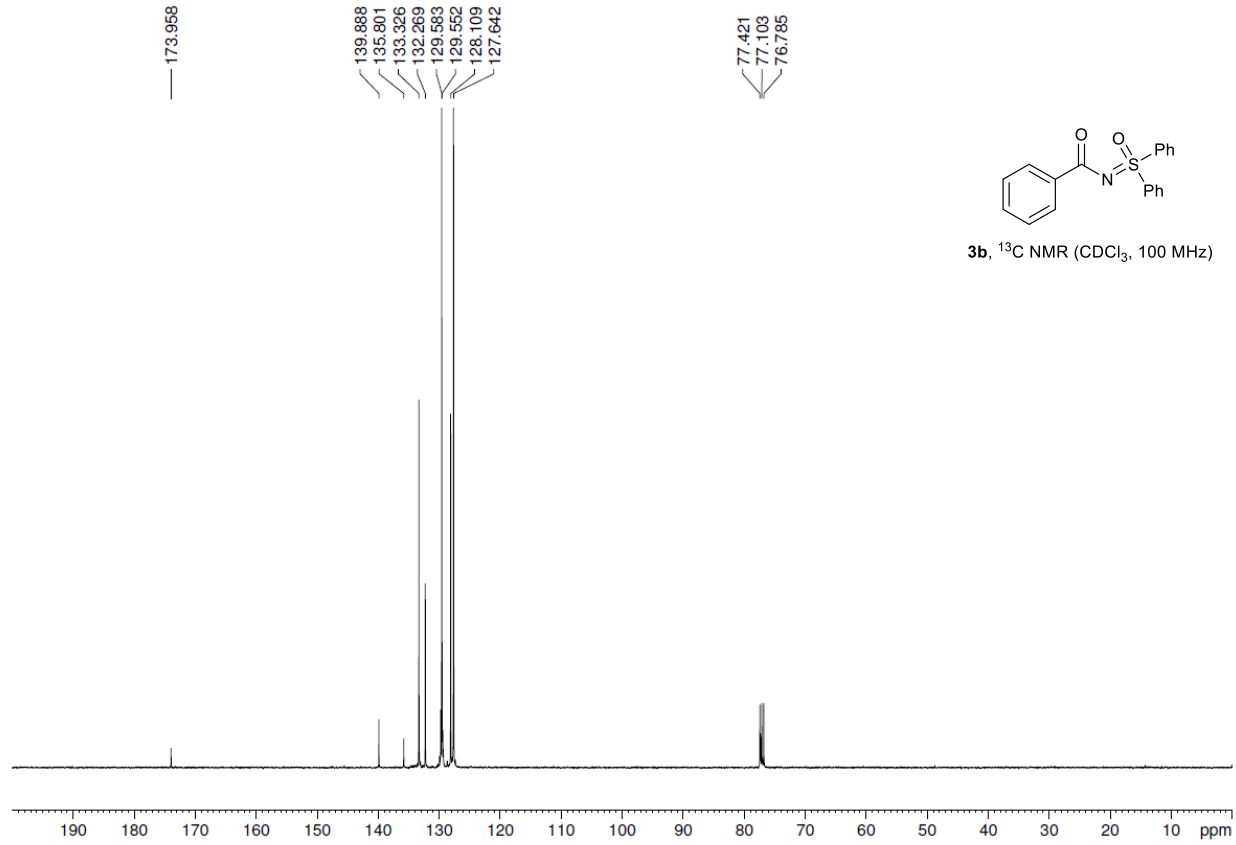


3a, ^{13}C NMR ($CDCl_3$, 100 MHz)

N-Benzoyl-*S,S*-diphenyl sulfoximine (3b)

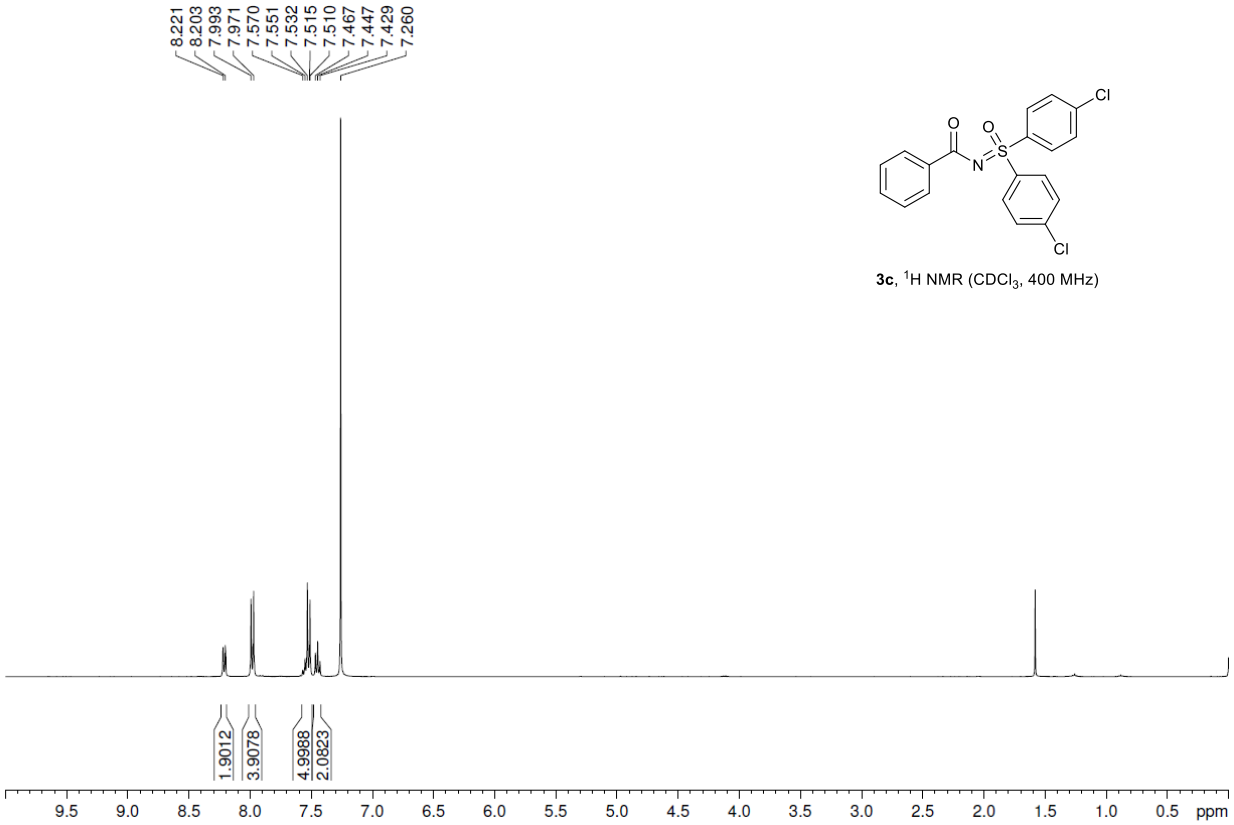


3b, ^{1}H NMR ($CDCl_3$, 400 MHz)

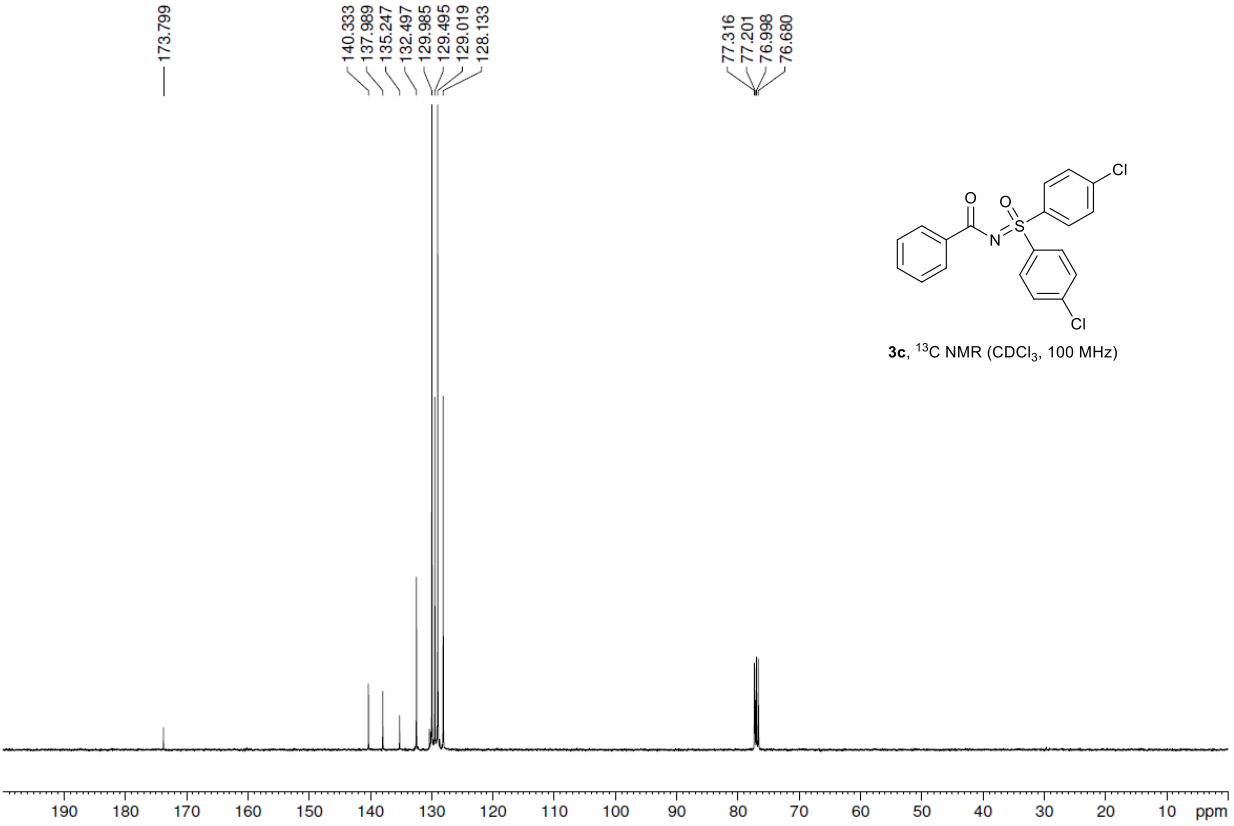


3b, ^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-Benzoyl-_S,S_-di-4-chlorophenyl sulfoximine (3c)

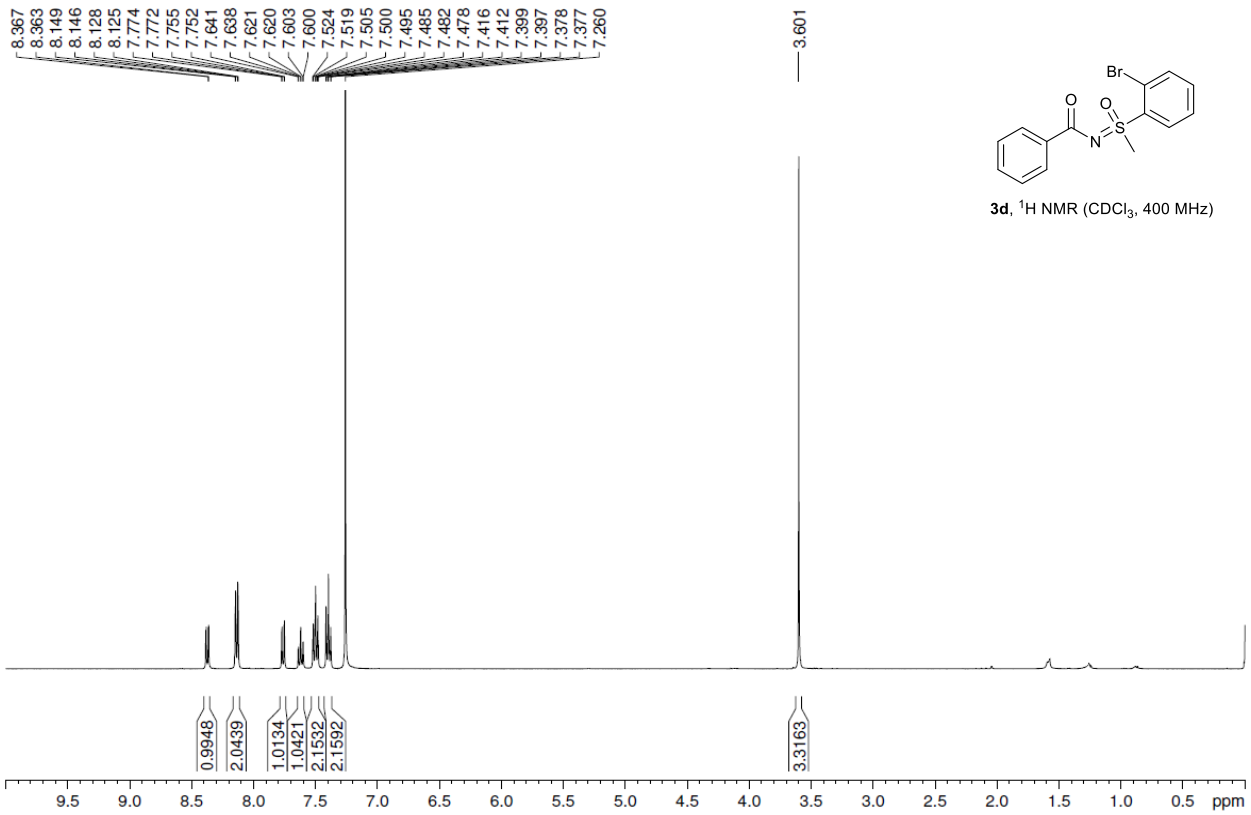


3c, ^{1}H NMR ($CDCl_3$, 400 MHz)

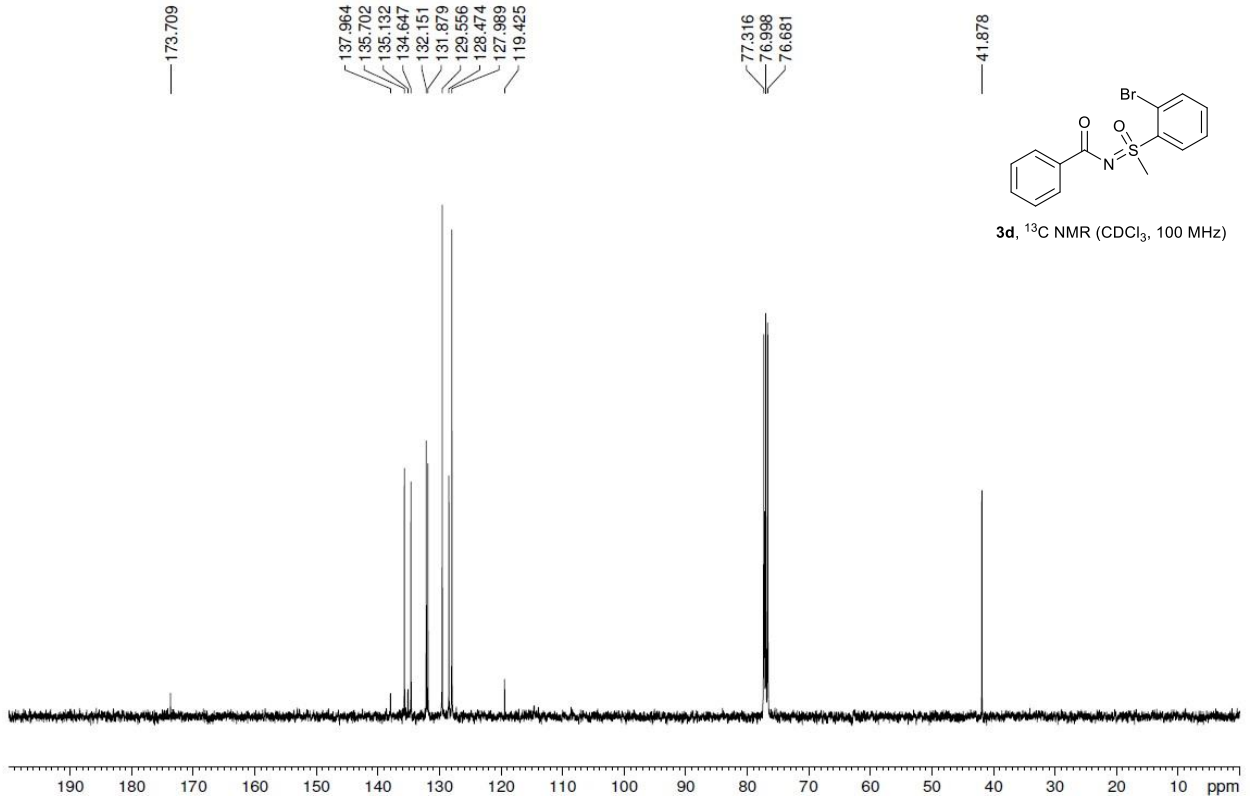


3c, ^{13}C NMR ($CDCl_3$, 100 MHz)

N-Benzoyl-*S*-(2-bromophenyl)-*S*-methyl sulfoximine (3d)

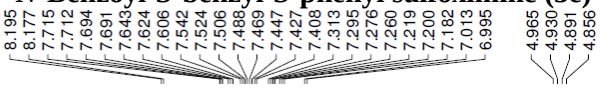


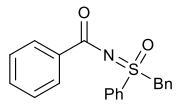
3d, ^{1}H NMR ($CDCl_3$, 400 MHz)



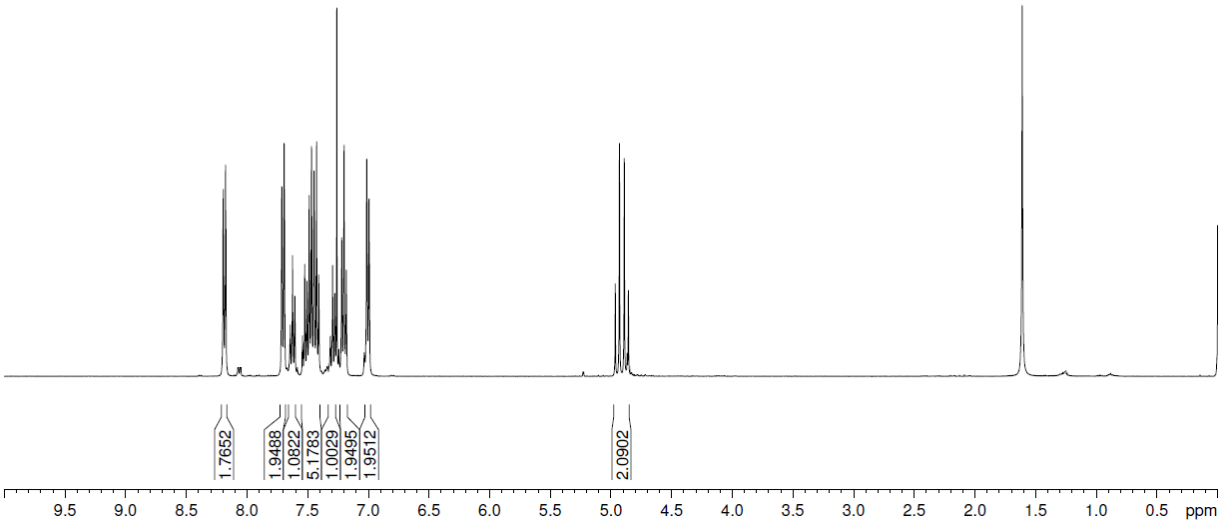
3d, ^{13}C NMR ($CDCl_3$, 100 MHz)

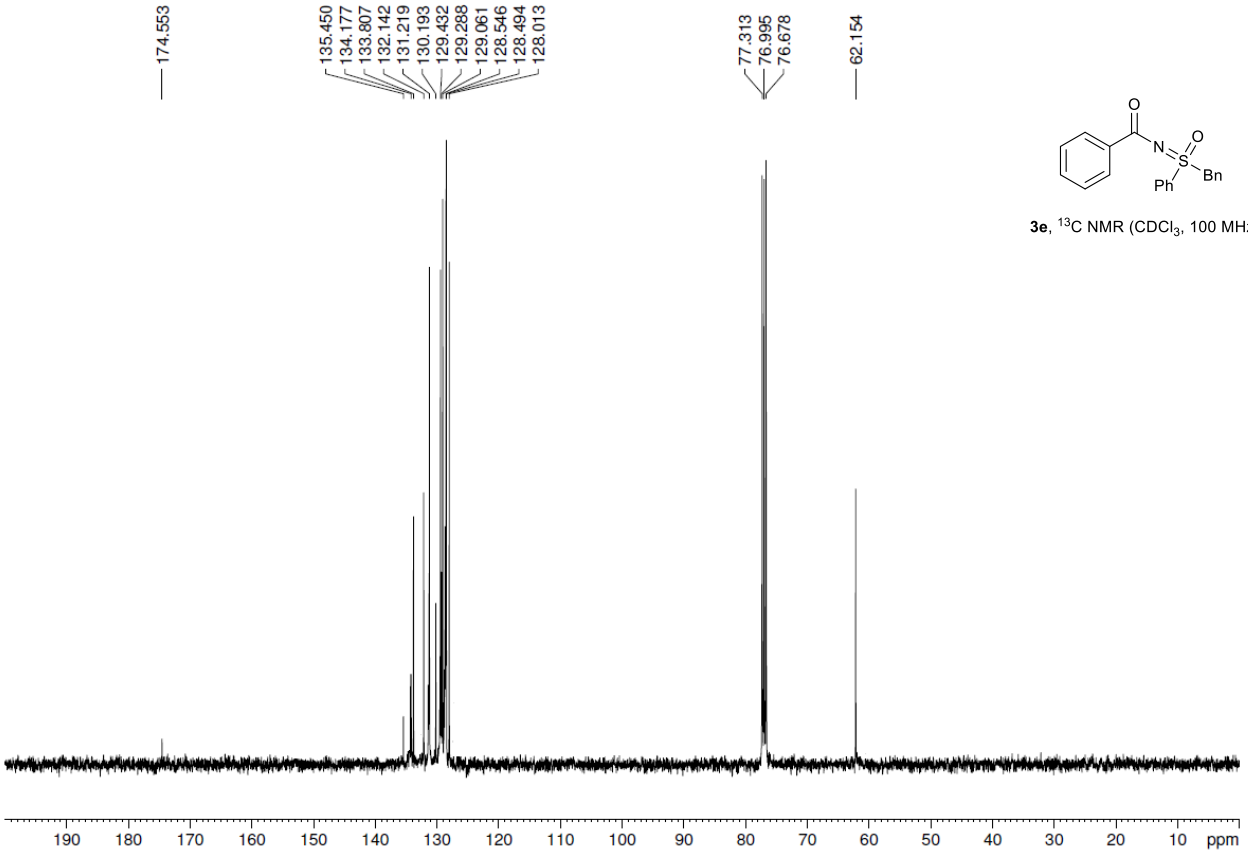
N-Benzoyl-*S*-benzyl-*S*-phenyl sulfoximine (3e)





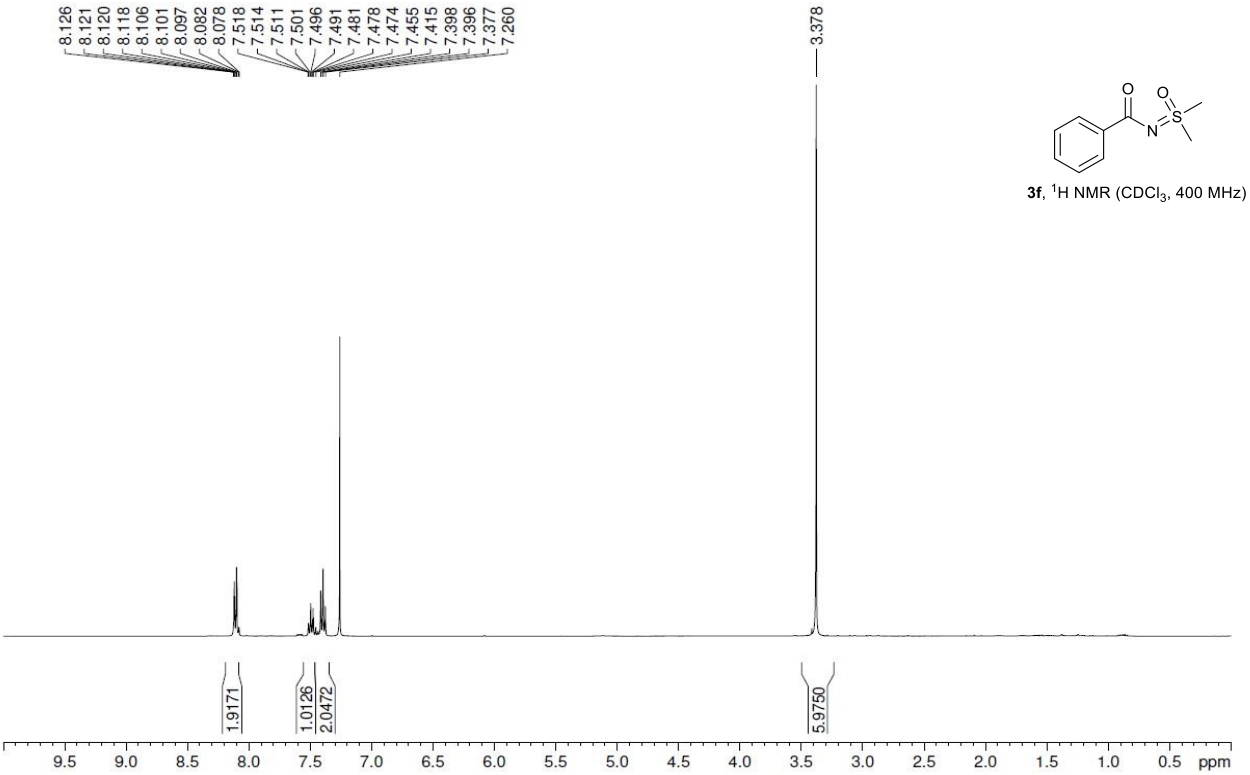
3e, ^{1}H NMR ($CDCl_3$, 400 MHz)



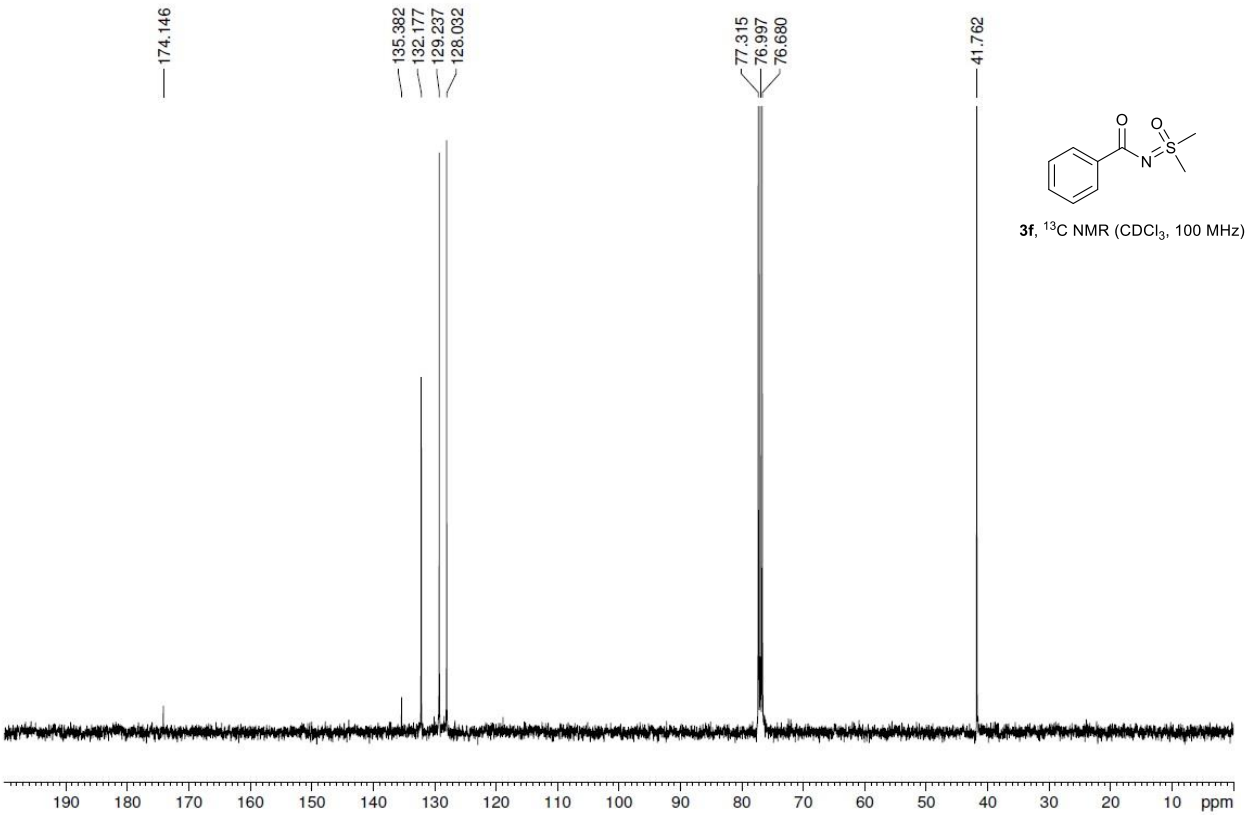


3e, ^{13}C NMR ($CDCl_3$, 100 MHz)

***N*-Benzoyl-*S,S*-dimethyl sulfoximine (3f)**

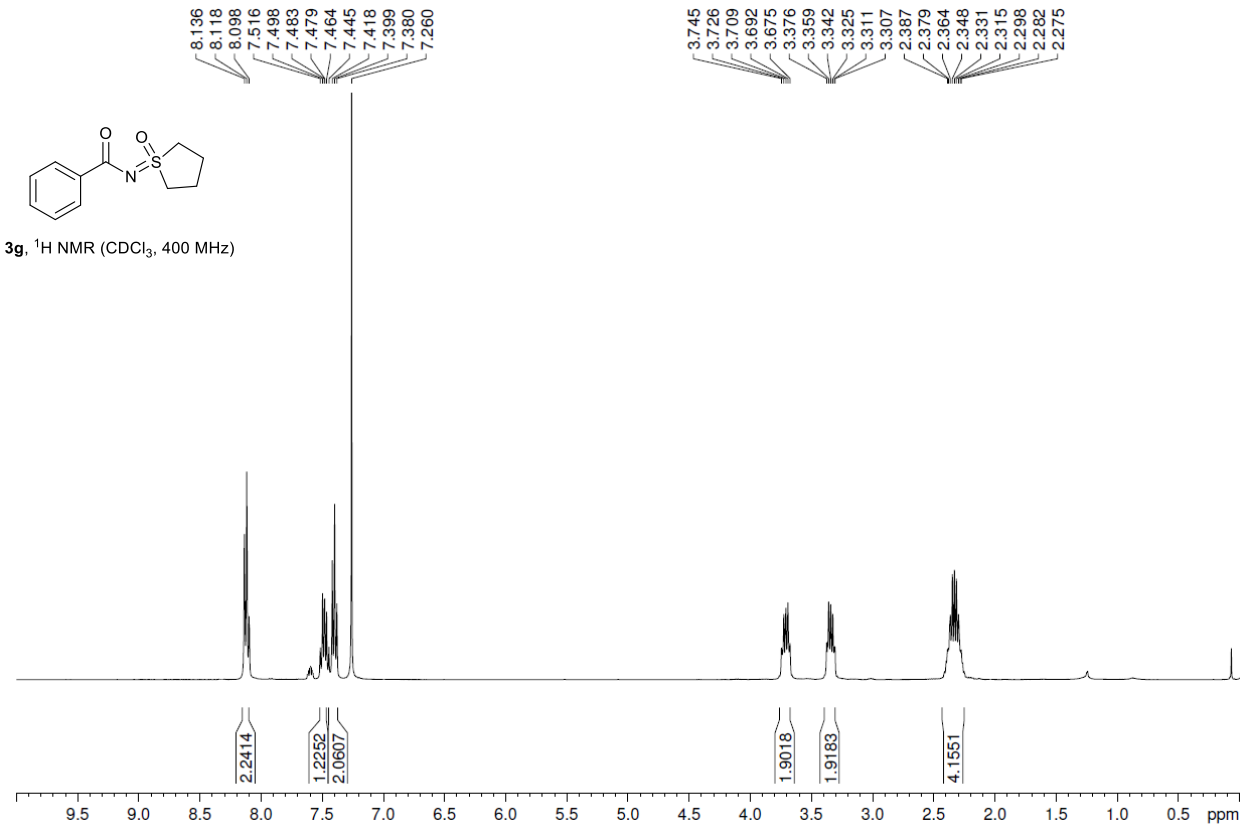


3f, ^{1}H NMR ($CDCl_3$, 400 MHz)

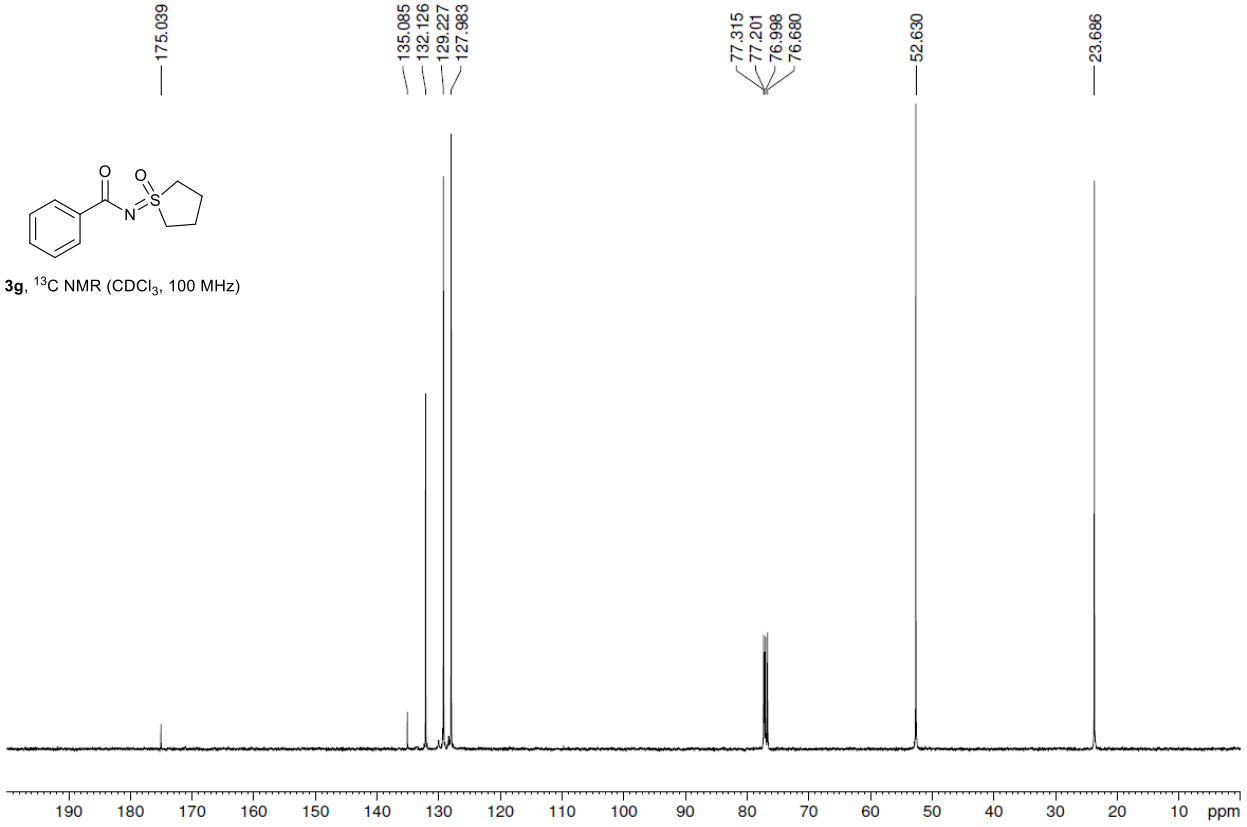


3f, ^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-Benzoyl-_S,S_-tetramethylene sulfoximine (3g)

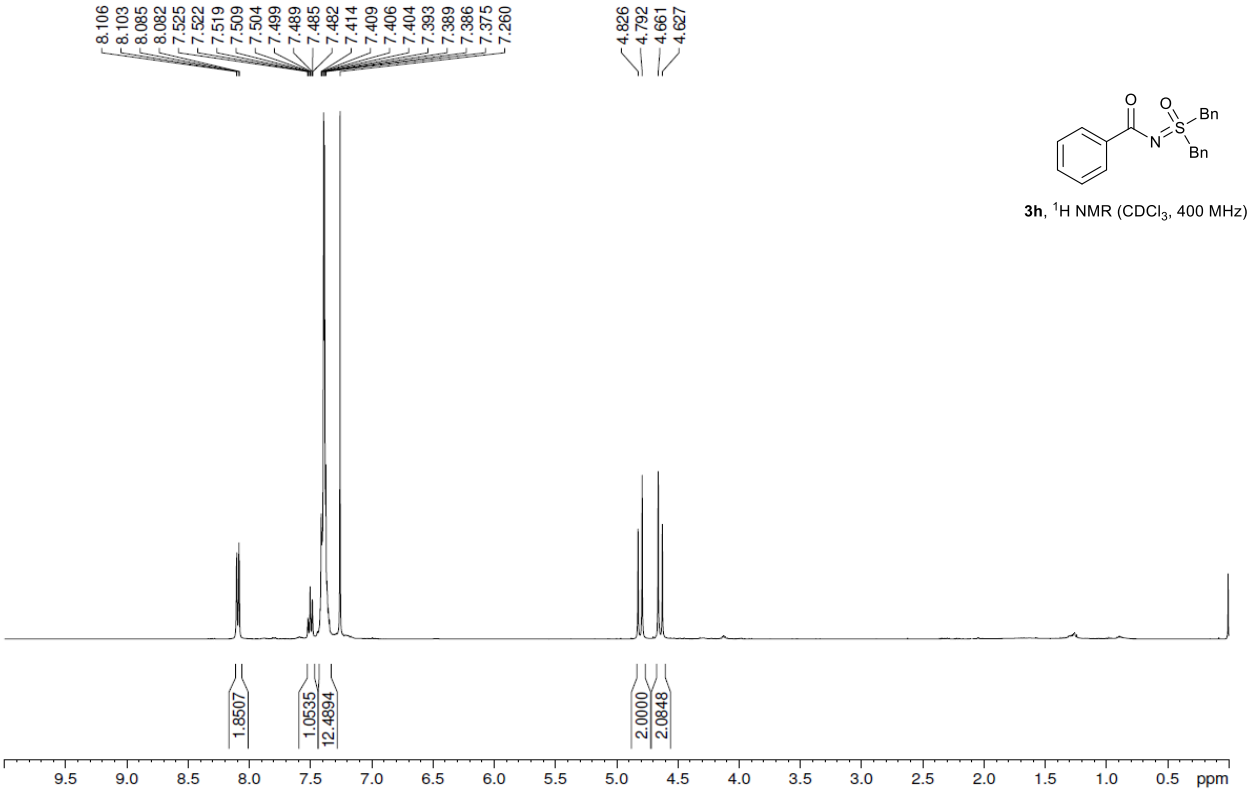


3g, ^{1}H NMR ($CDCl_3$, 400 MHz)

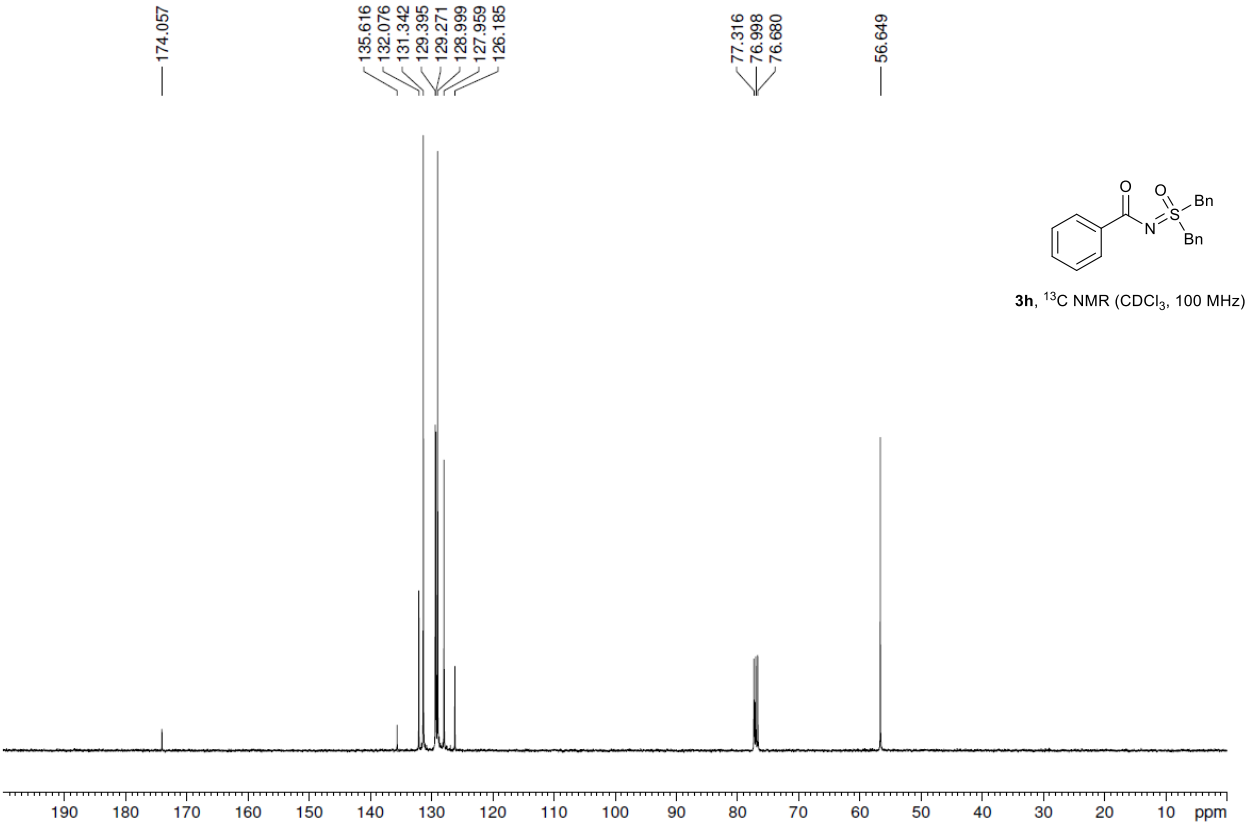


3g, ^{13}C NMR ($CDCl_3$, 100 MHz)

N-Benzoyl-*S,S*-dibenzyl sulfoximine (3h)

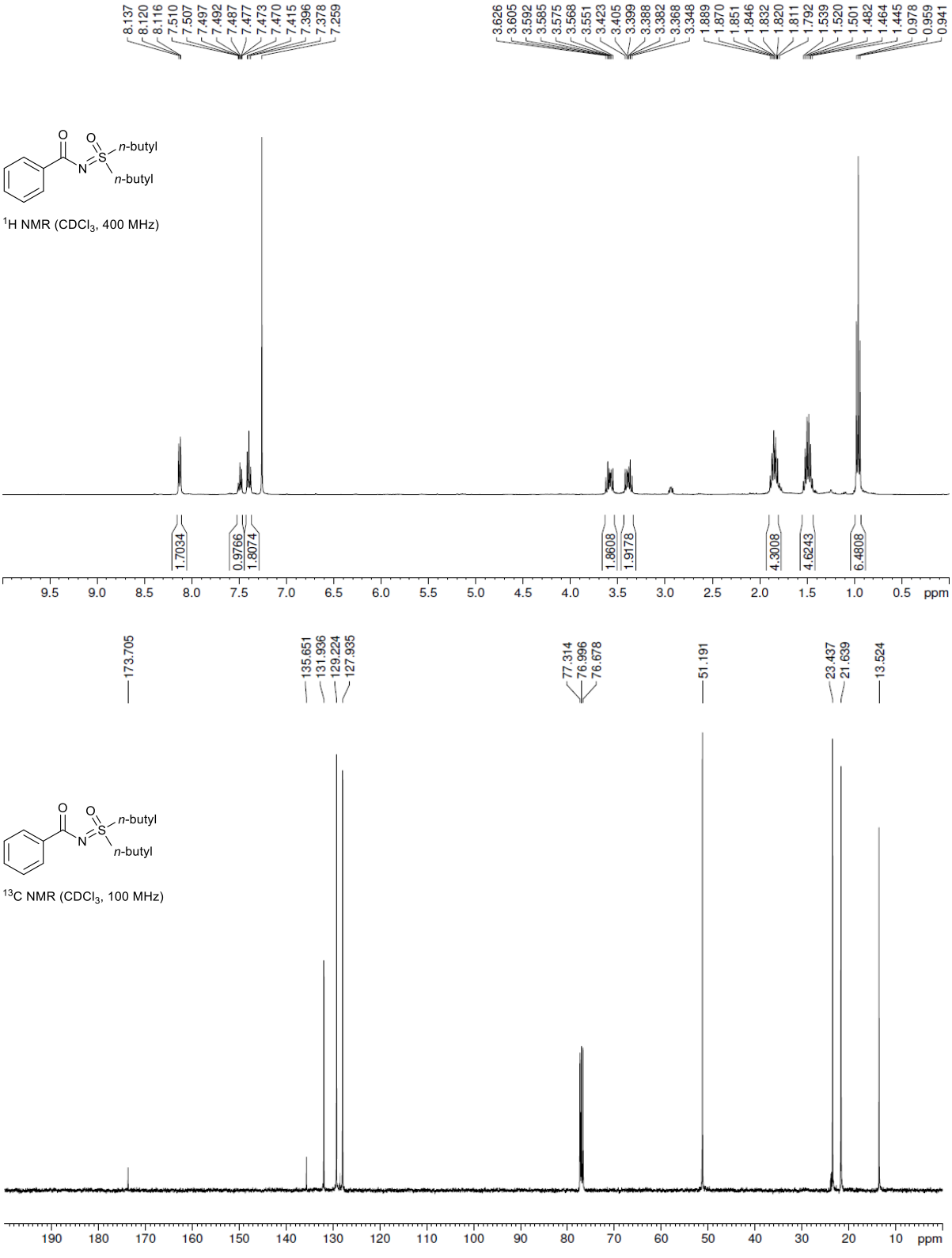


3h, ^{1}H NMR ($CDCl_3$, 400 MHz)

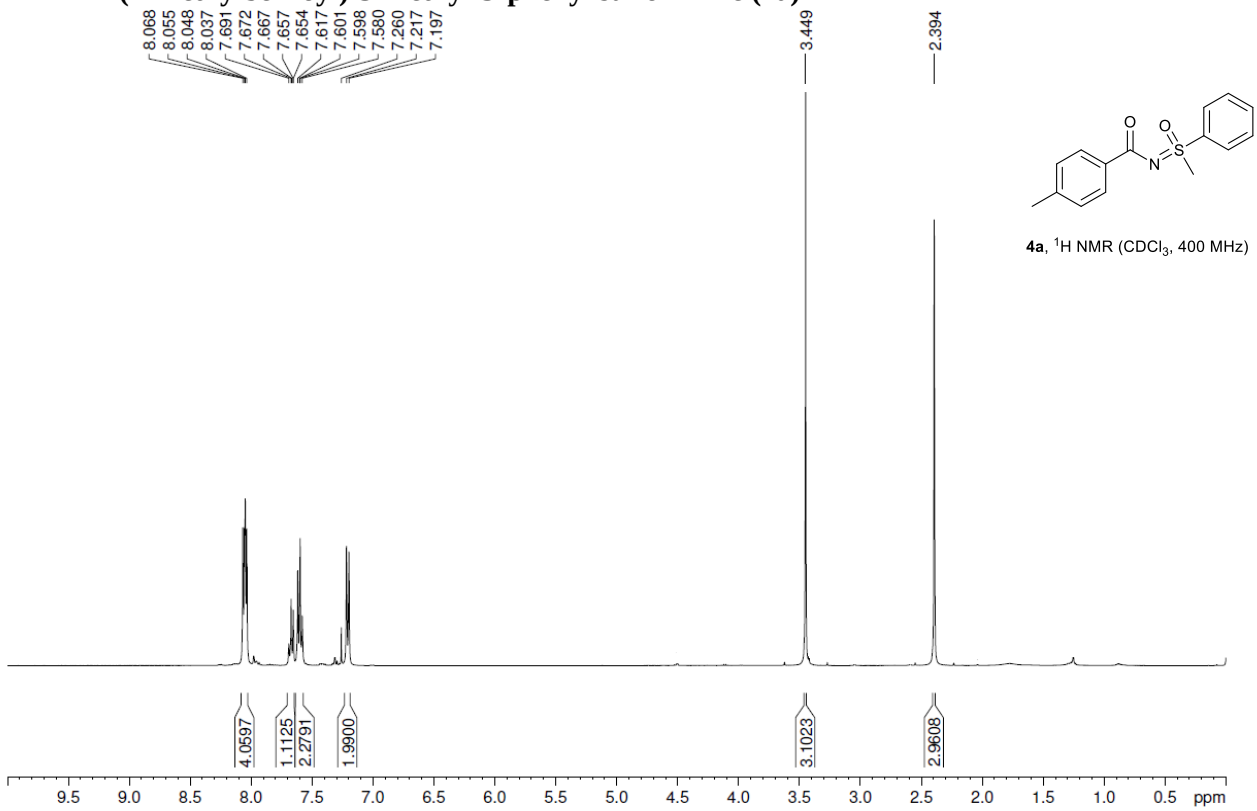


3h, ^{13}C NMR ($CDCl_3$, 100 MHz)

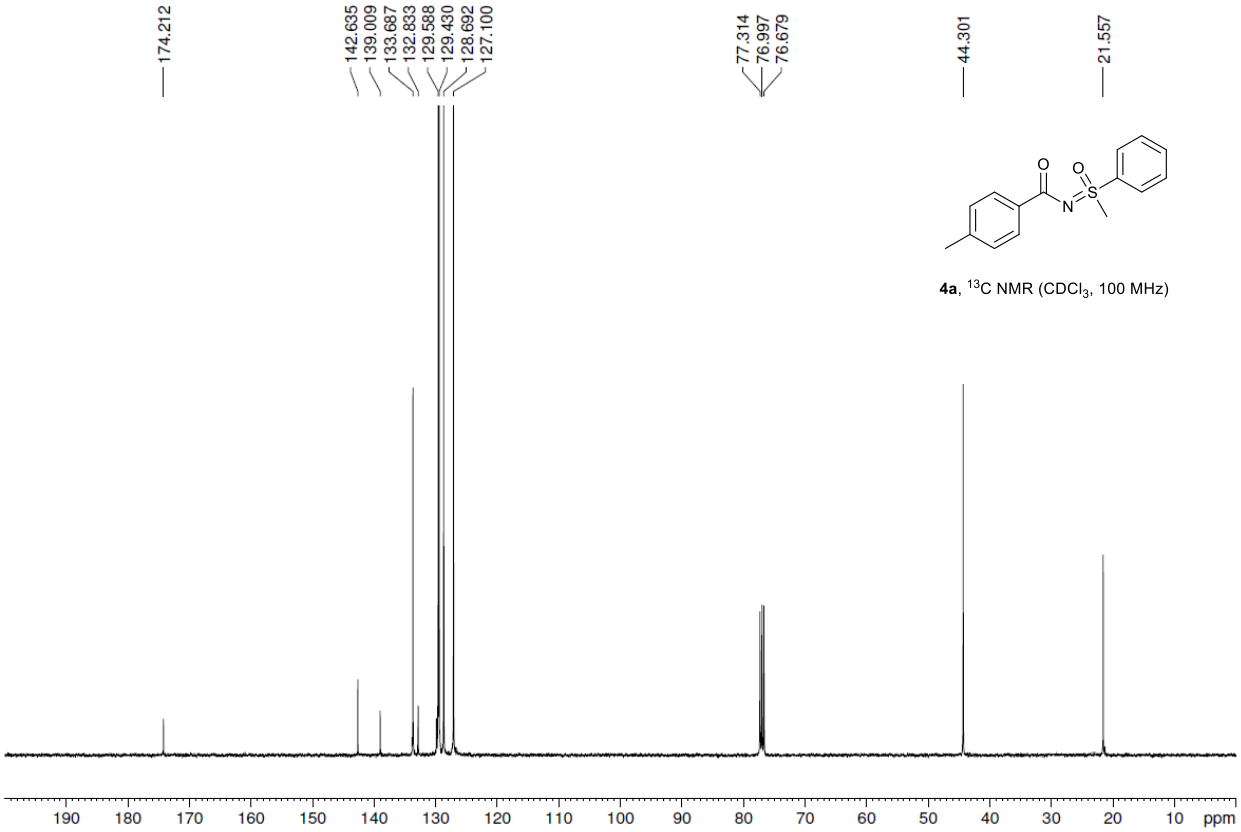
N-Benzoyl-*S*,*S*-di-*n*-butyl sulfoximine (3i)



_N_-(4-Methylbenzoyl)-_S_-methyl-_S_-phenyl sulfoximine (4a)

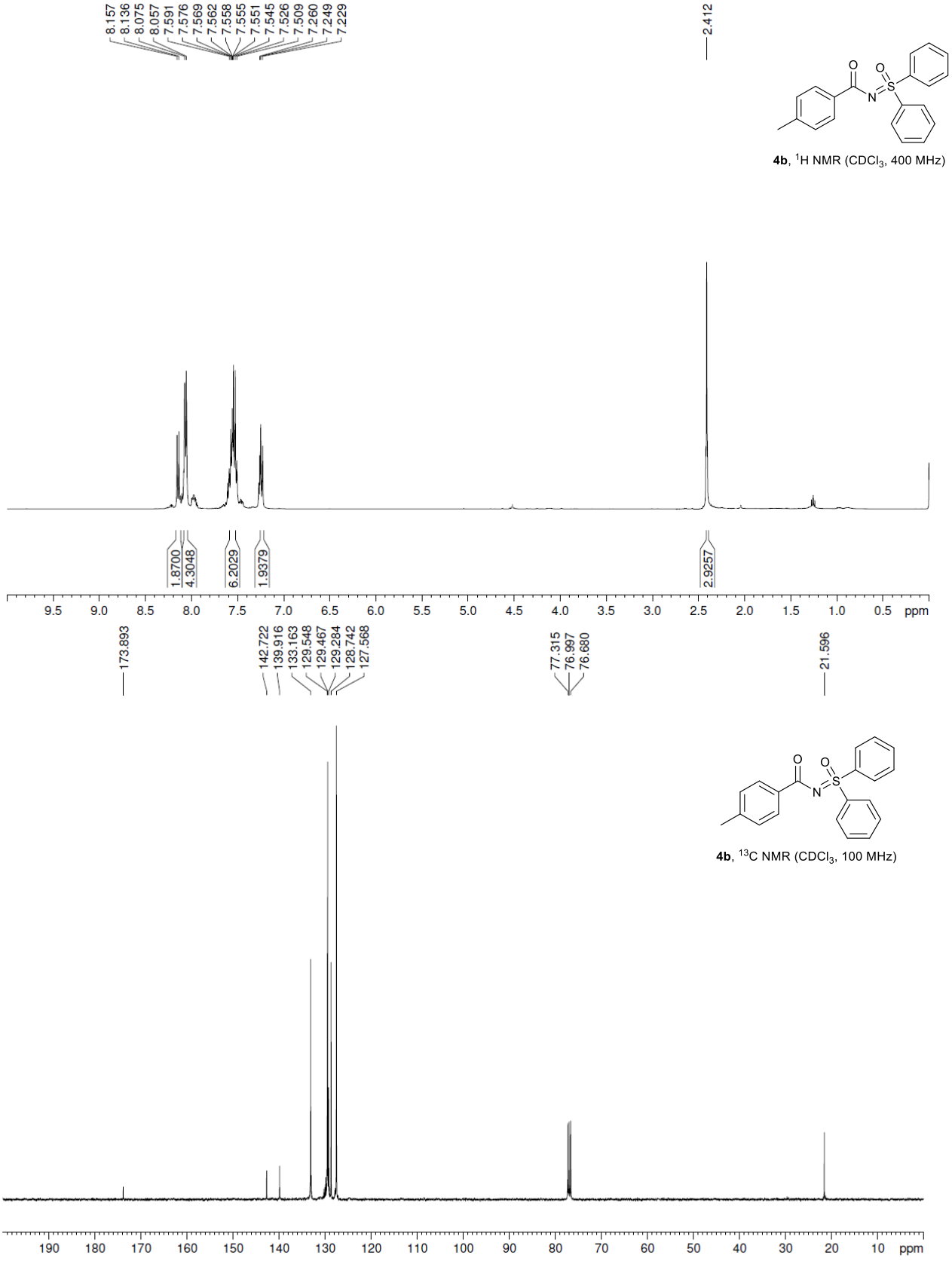


4a, ^{1}H NMR ($CDCl_3$, 400 MHz)



4a, ^{13}C NMR ($CDCl_3$, 100 MHz)

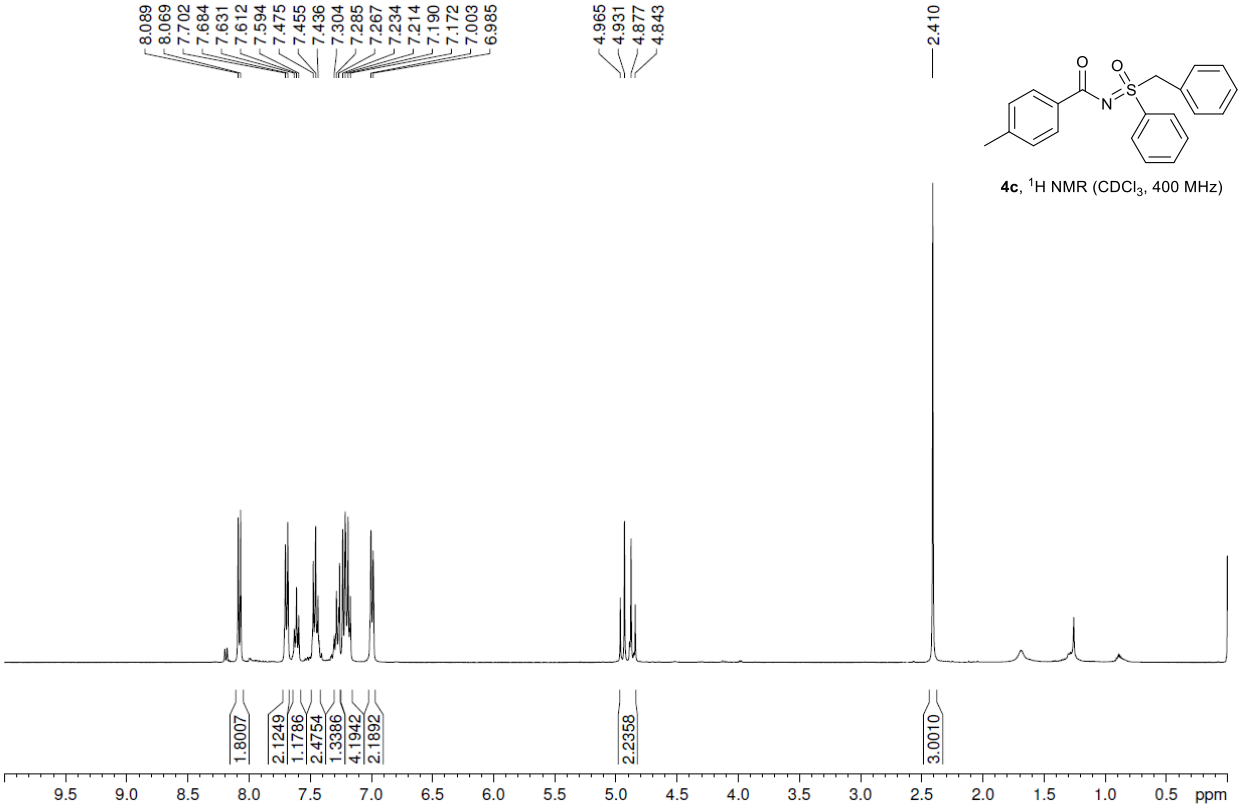
_N_-(4-Methylbenzoyl)-_S,S_-diphenyl sulfoximine (4b)



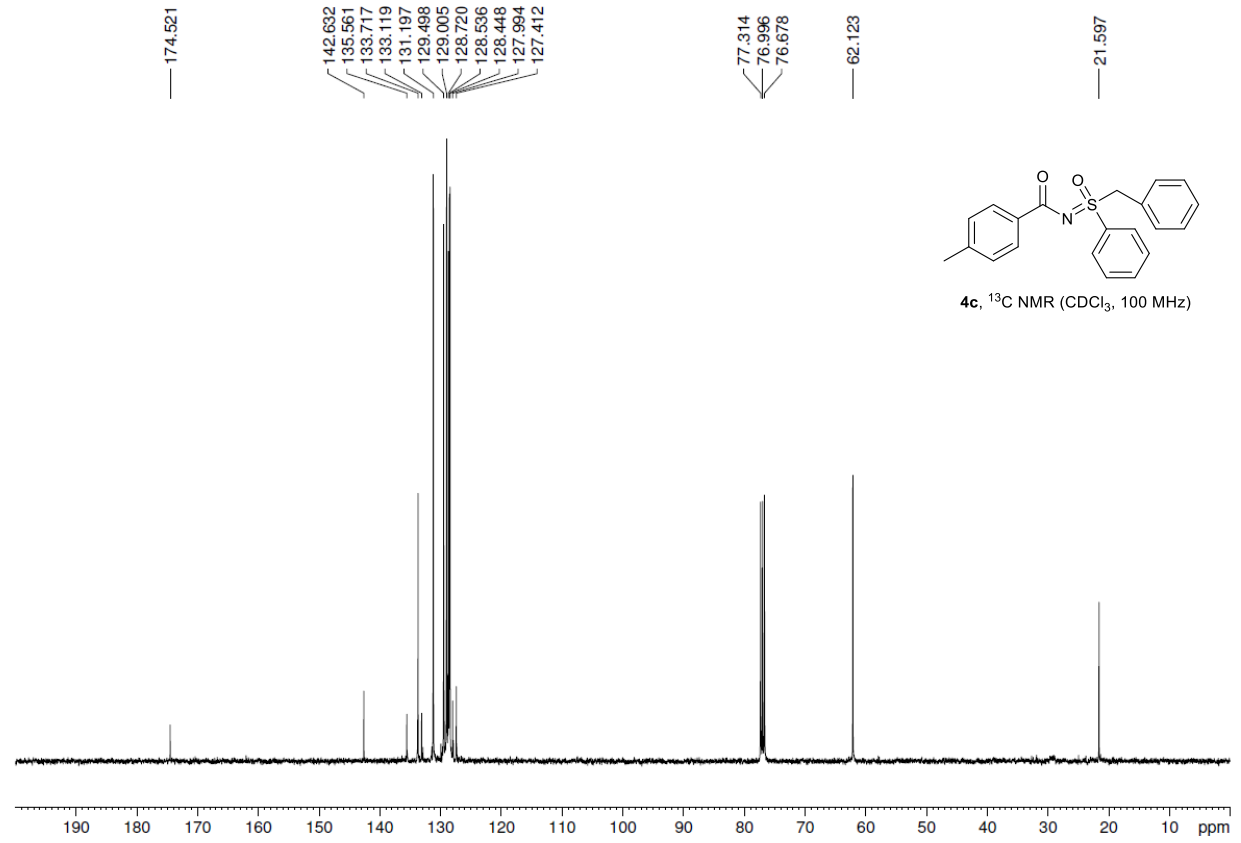
4b, ^{1}H NMR ($CDCl_3$, 400 MHz)

4b, ^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(4-Methylbenzoyl)-_S_-benzyl-_S_-phenyl sulfoximine (4c)

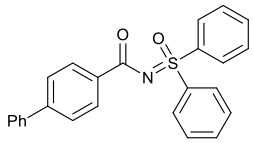


4c, ^{1}H NMR ($CDCl_3$, 400 MHz)

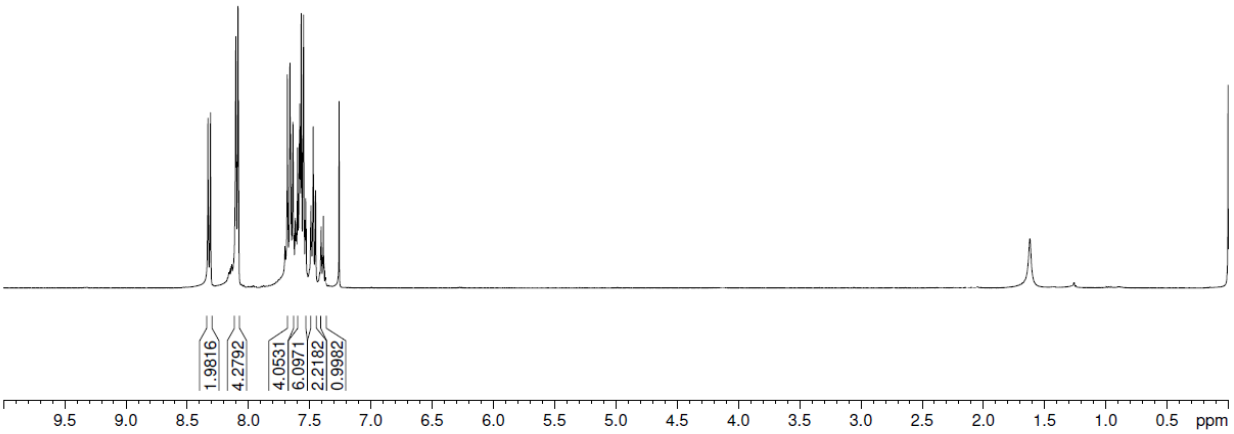


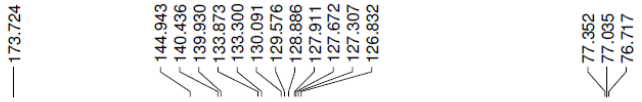
4c, ^{13}C NMR ($CDCl_3$, 100 MHz)

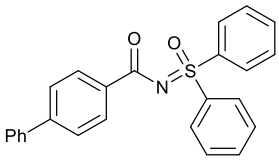
_N_-(4-Phenylbenzoyl)-_S,S_-diphenyl sulfoximine (4d)



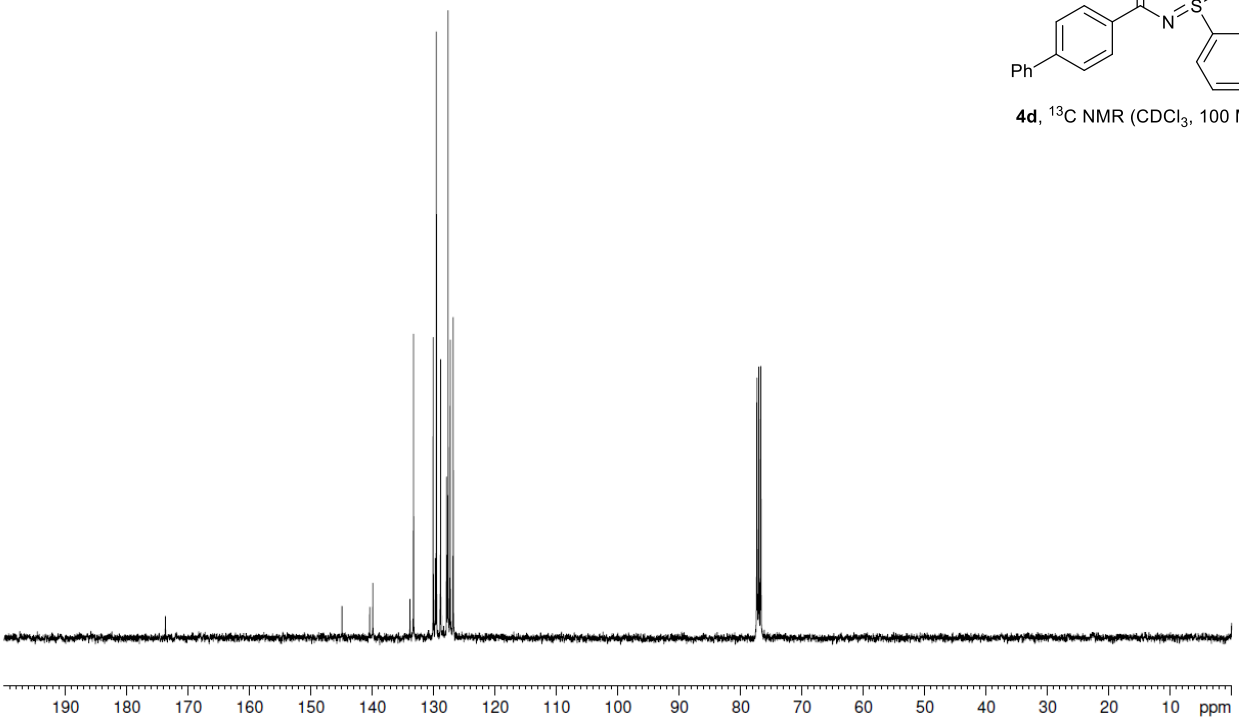
4d, ^{1}H NMR ($CDCl_3$, 400 MHz)



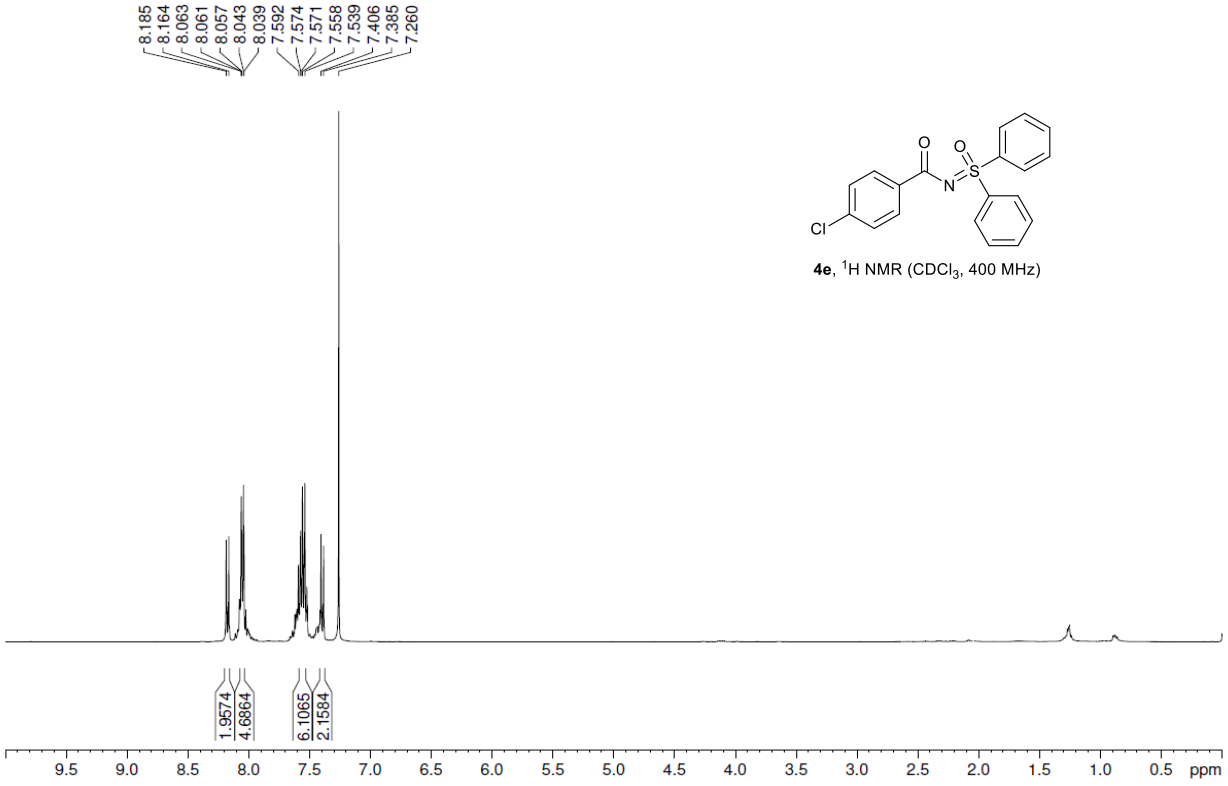




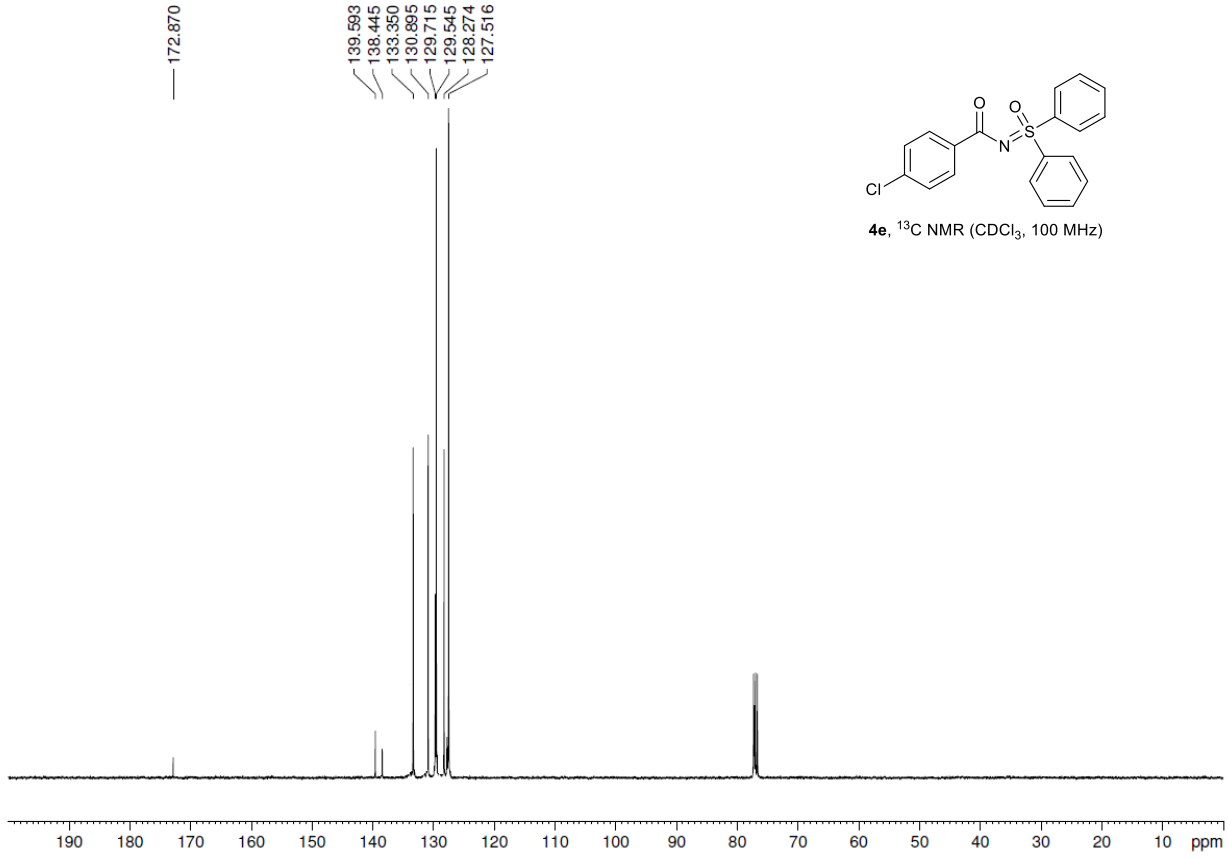
4d, ^{13}C NMR ($CDCl_3$, 100 MHz)



***N*-(4-Chlorobenzoyl)-*S*,*S*-diphenyl sulfoximine (4e)**.

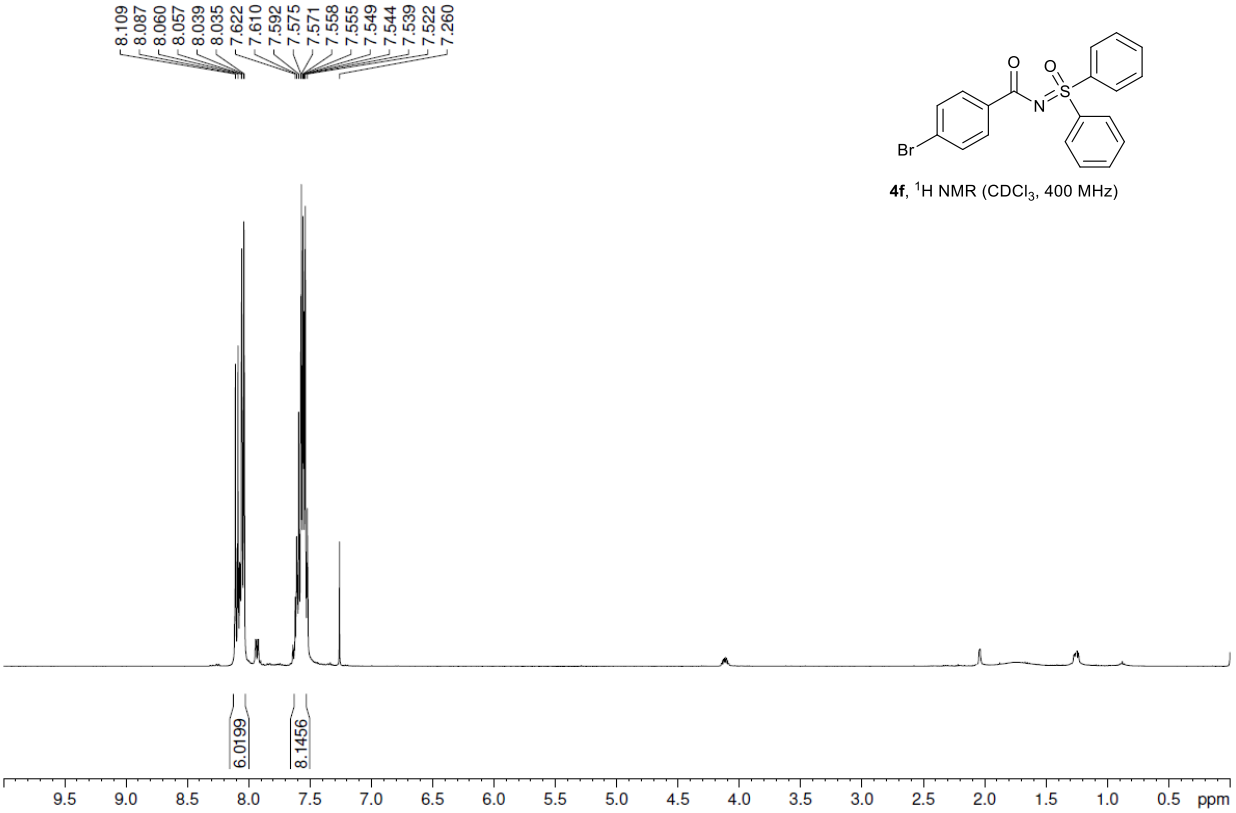


4e, ^{1}H NMR ($CDCl_3$, 400 MHz)

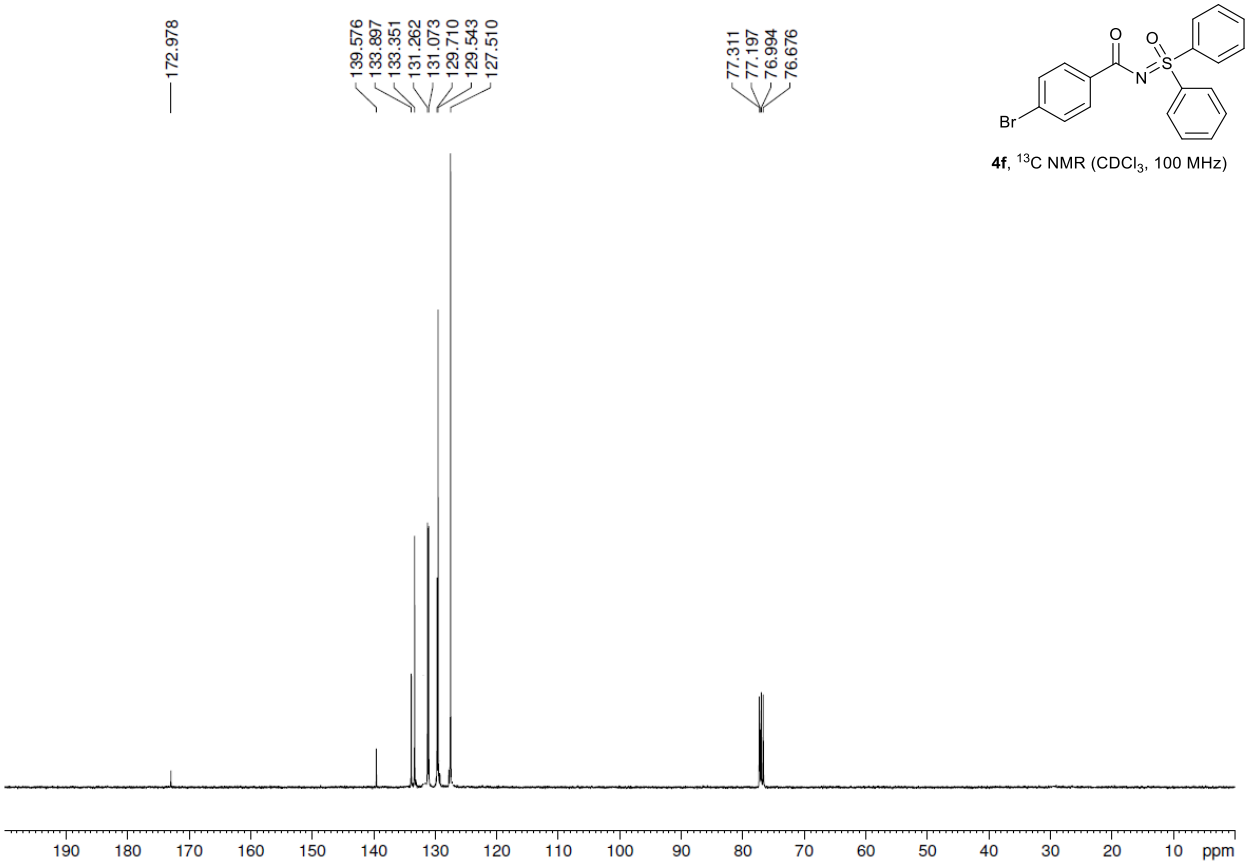


4e, ^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(4-Bromobenzoyl)-_S,S_-diphenyl sulfoximine (4f)

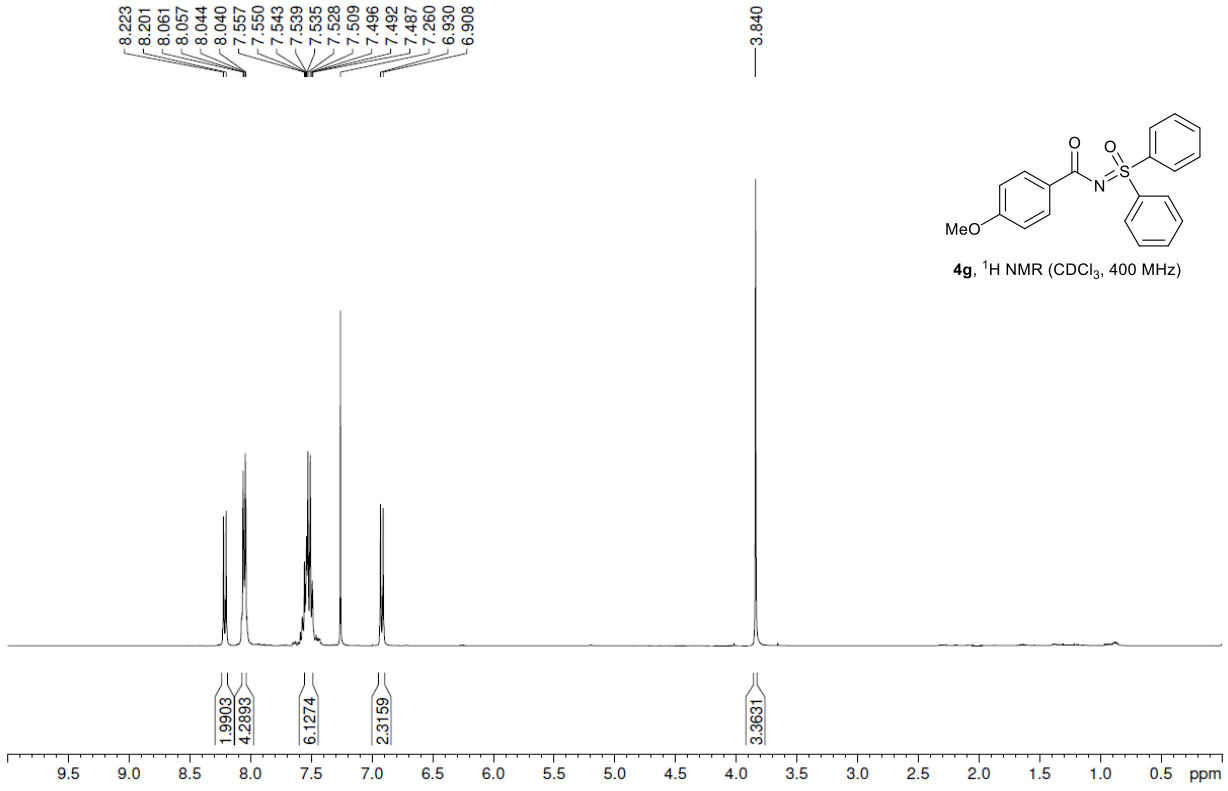


4f, ^{1}H NMR ($CDCl_3$, 400 MHz)

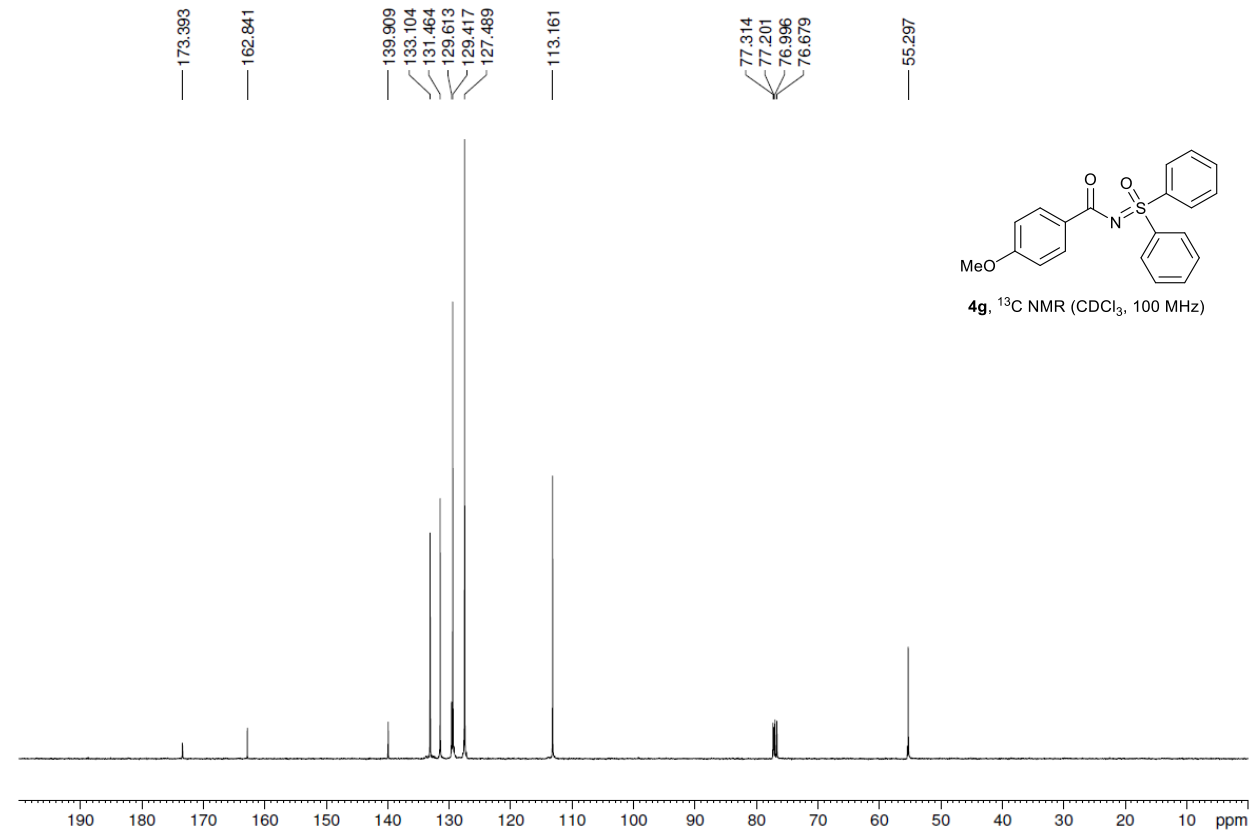


4f, ^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(4-Methoxybenzoyl)-_S,S_-diphenyl sulfoximine (4g)

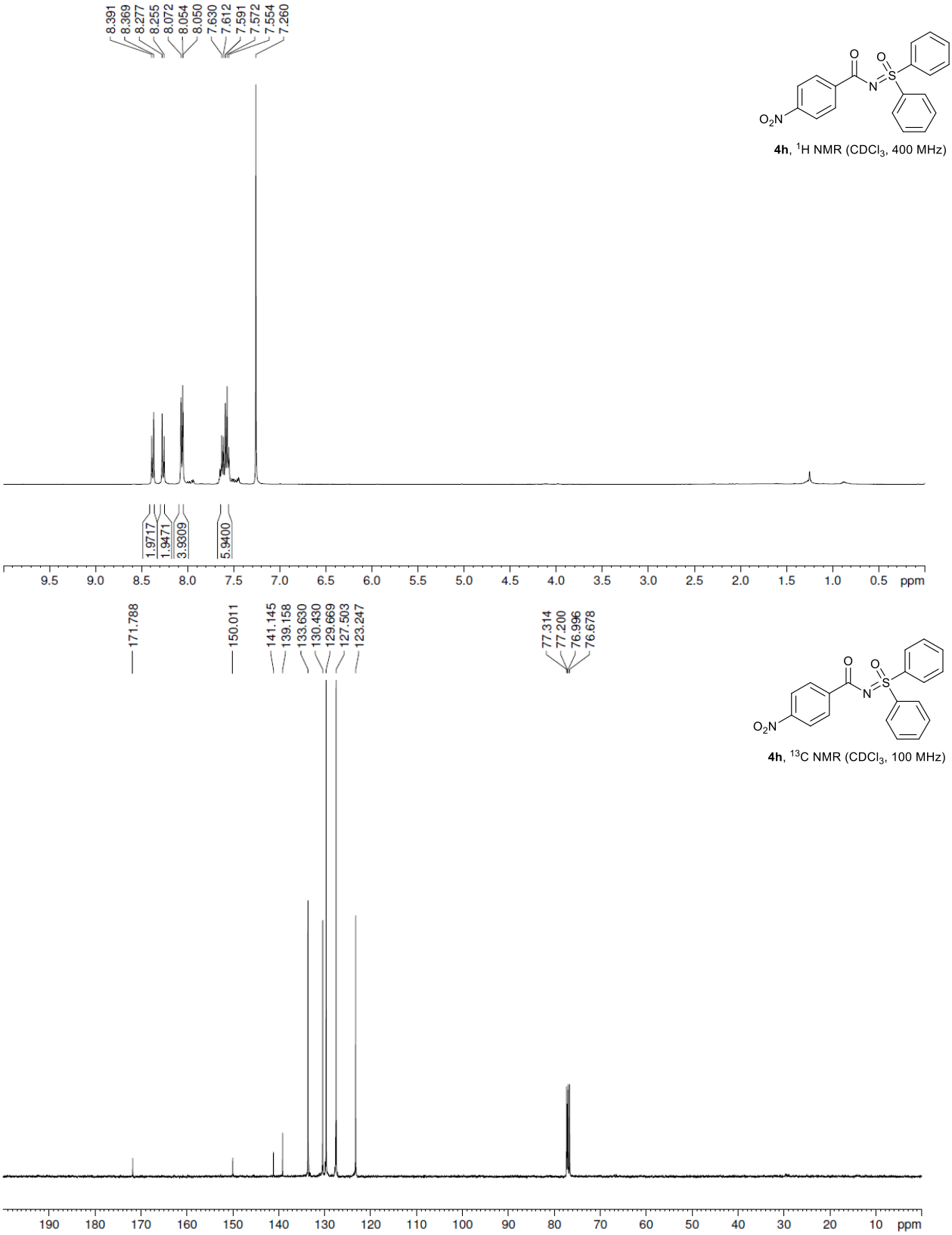


4g, ^{1}H NMR ($CDCl_3$, 400 MHz)



4g, ^{13}C NMR ($CDCl_3$, 100 MHz)

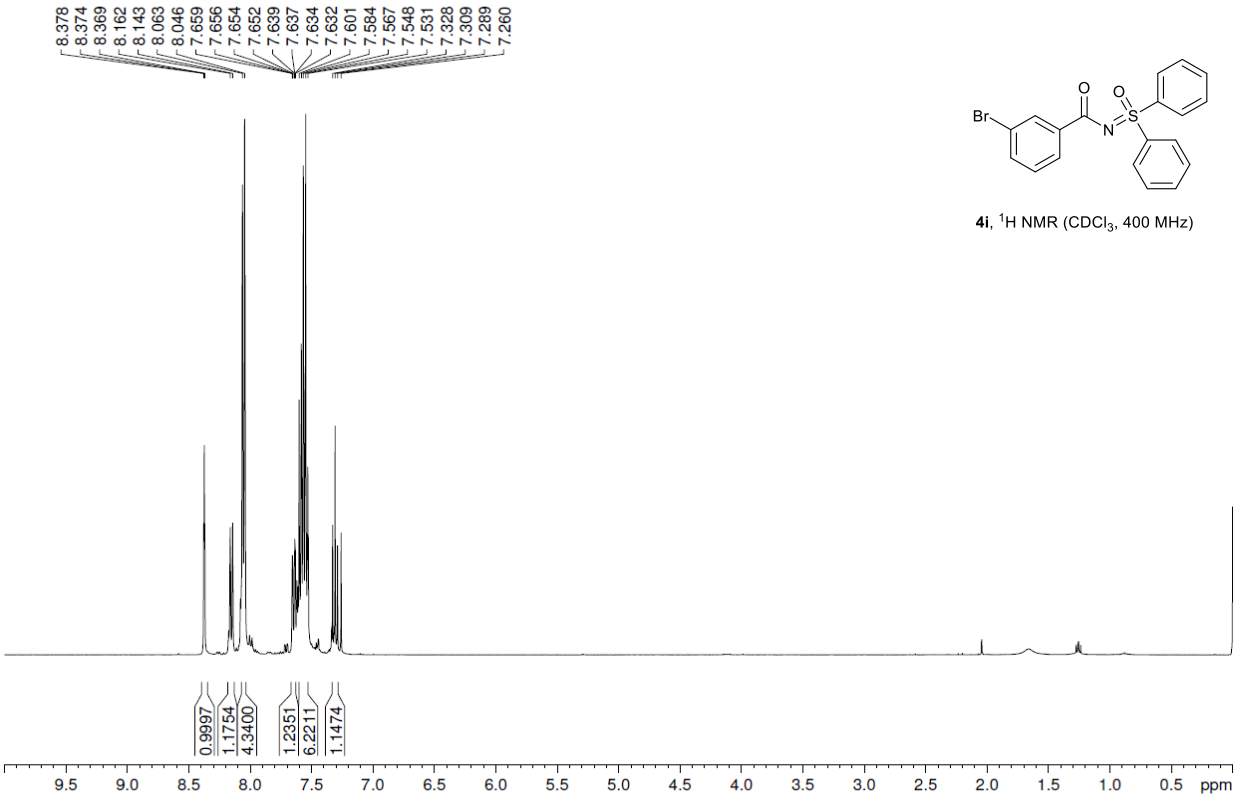
N-(4-Nitrobenzoyl)-*S*,*S*-diphenyl sulfoximine (4h)



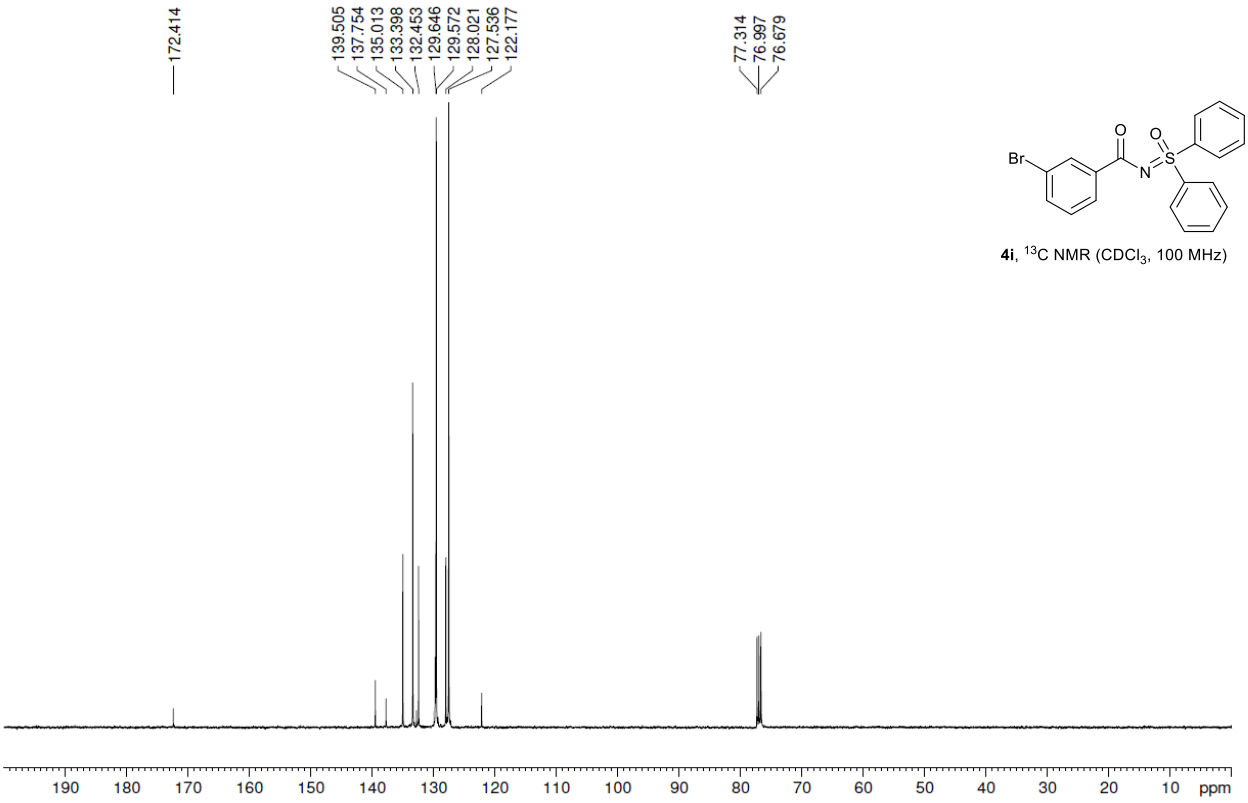
4h, ^{1}H NMR ($CDCl_3$, 400 MHz)

4h, ^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(3-Bromobenzoyl)-_S,S_-diphenyl sulfoximine (4i)

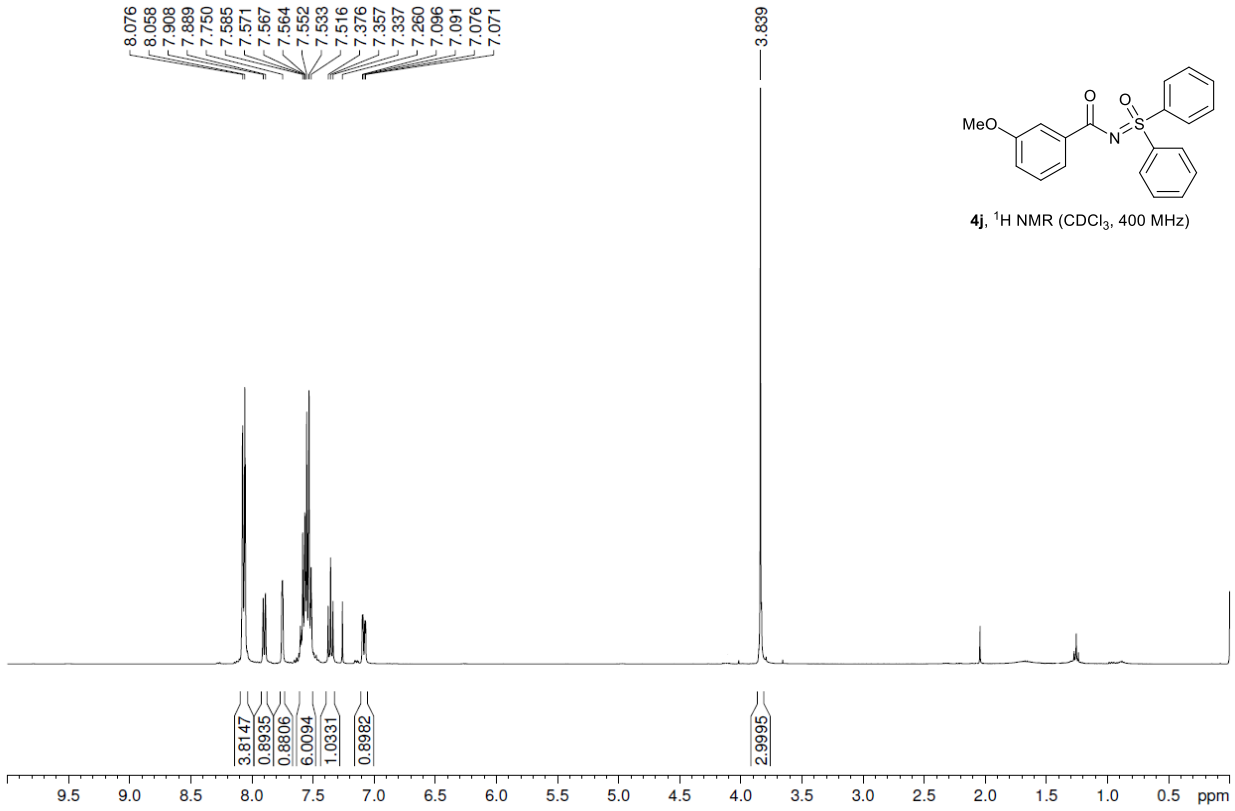


4i, ^{1}H NMR ($CDCl_3$, 400 MHz)

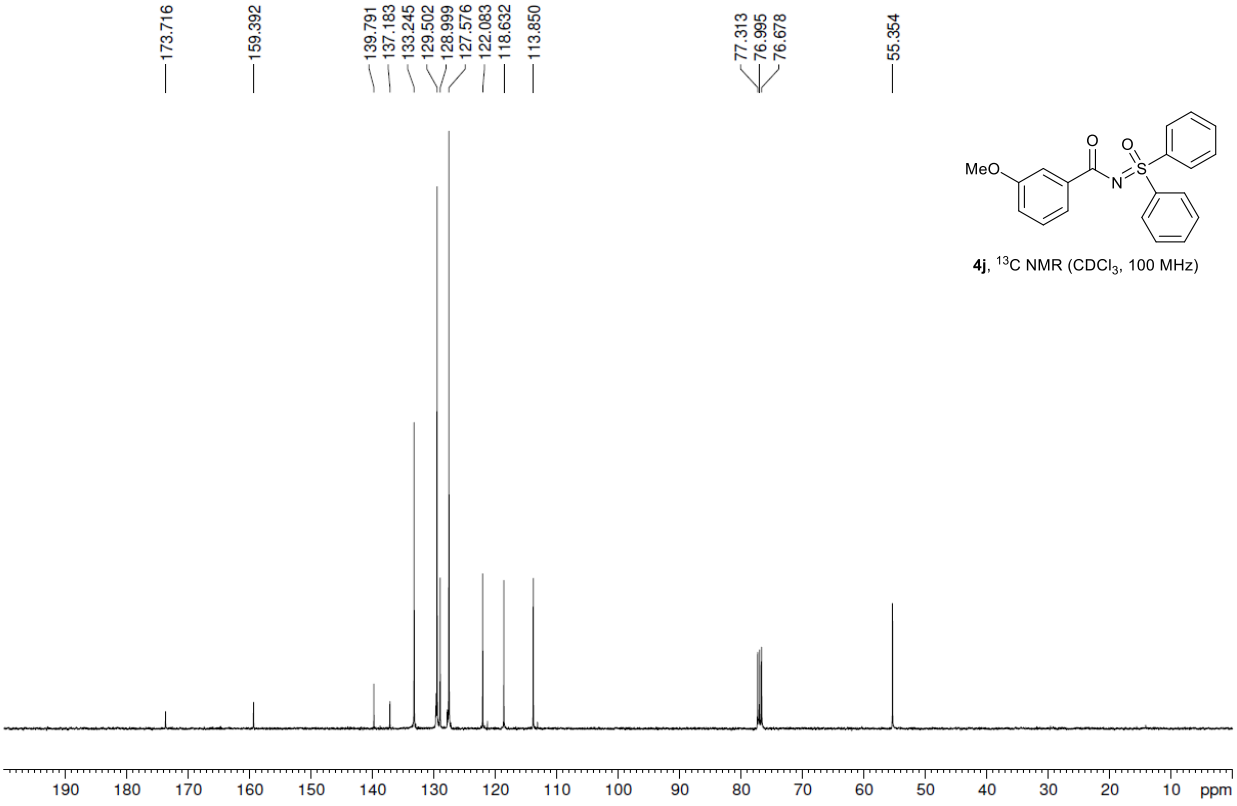


4i, ^{13}C NMR ($CDCl_3$, 100 MHz)

***N*-(3-Methoxybenzoyl)-*S*,*S*-diphenyl sulfoximine (4j)**

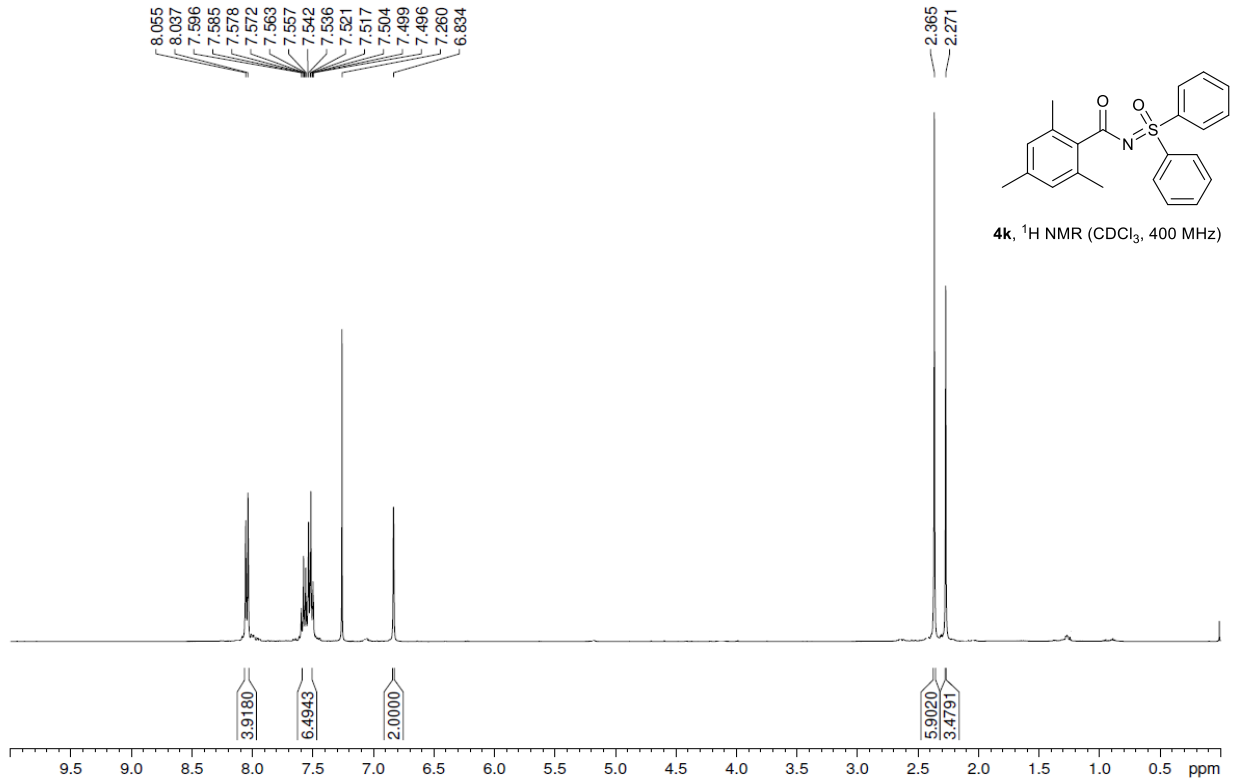


4j, ^{1}H NMR ($CDCl_3$, 400 MHz)

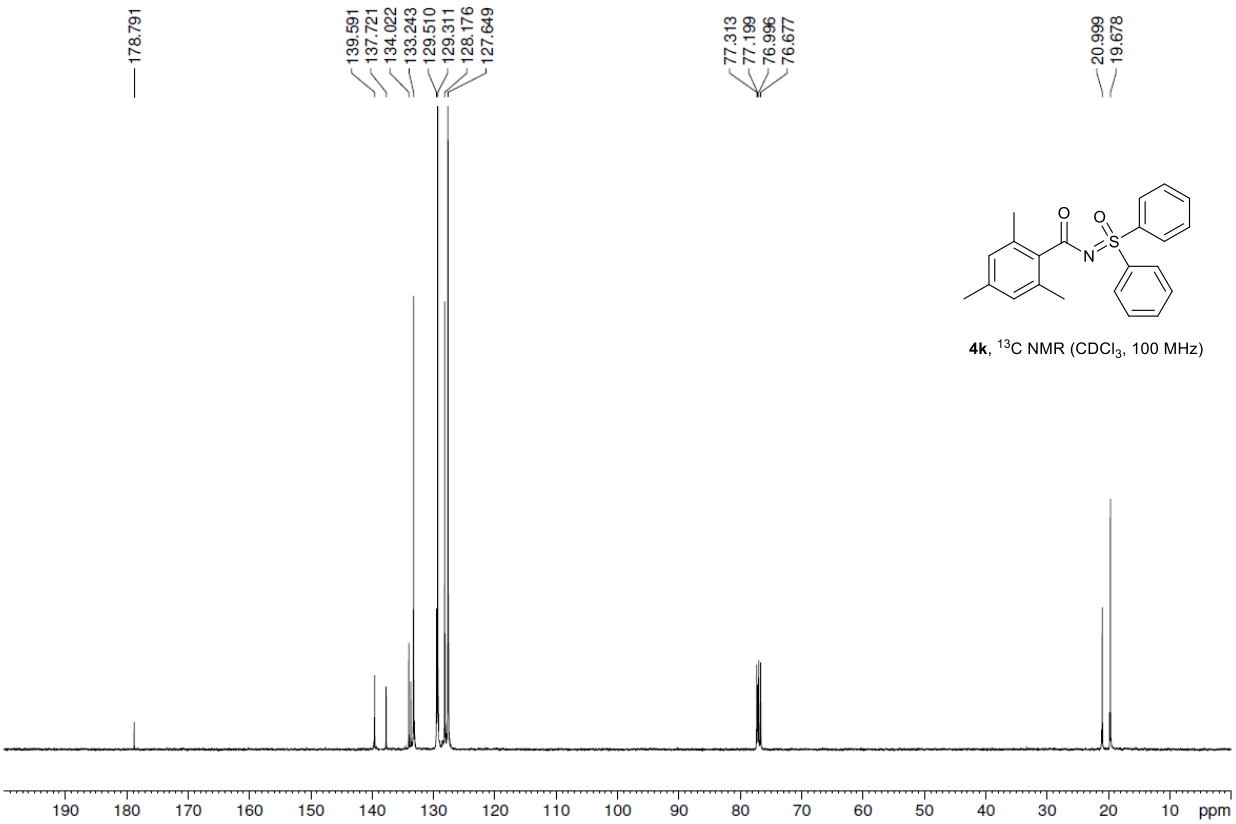


4j, ^{13}C NMR ($CDCl_3$, 100 MHz)

***N*-(2,4,6-Trimethylbenzoyl)-*S*,*S*-diphenyl sulfoximine (4k)**

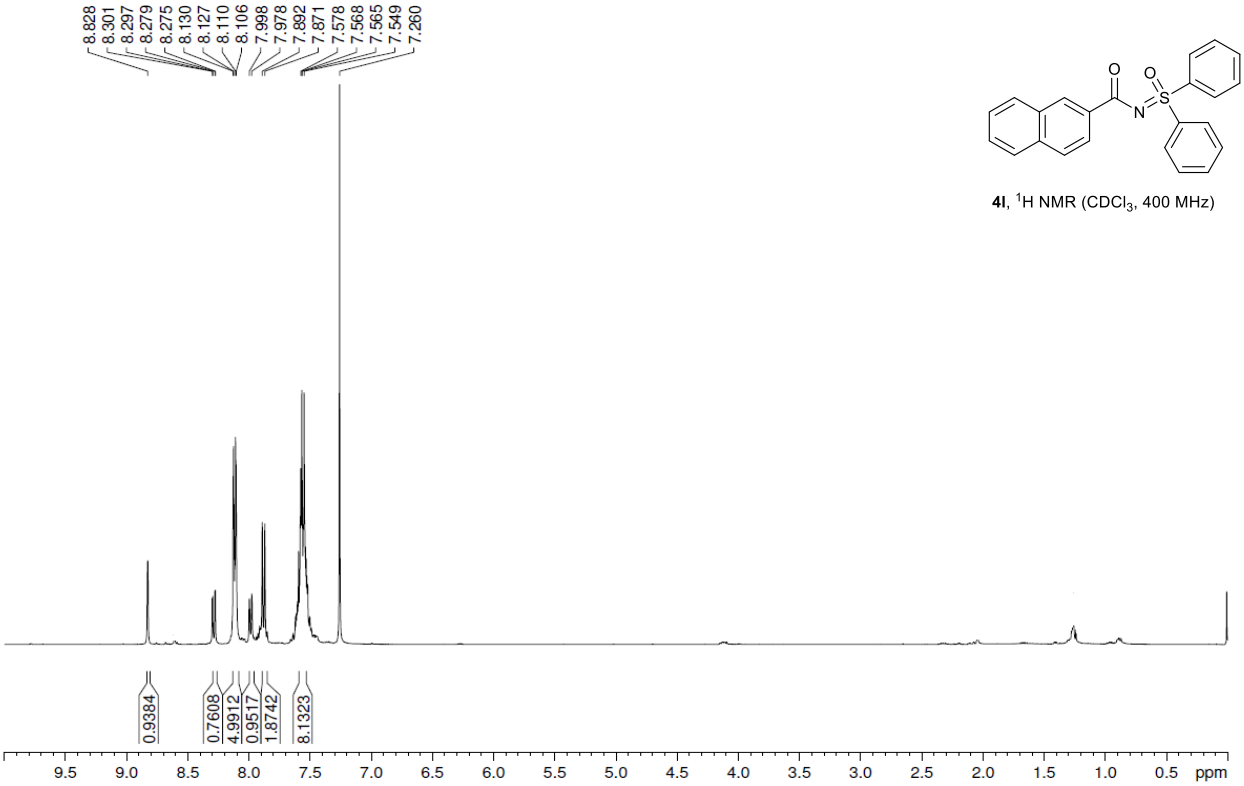


4k, ^{1}H NMR ($CDCl_3$, 400 MHz)

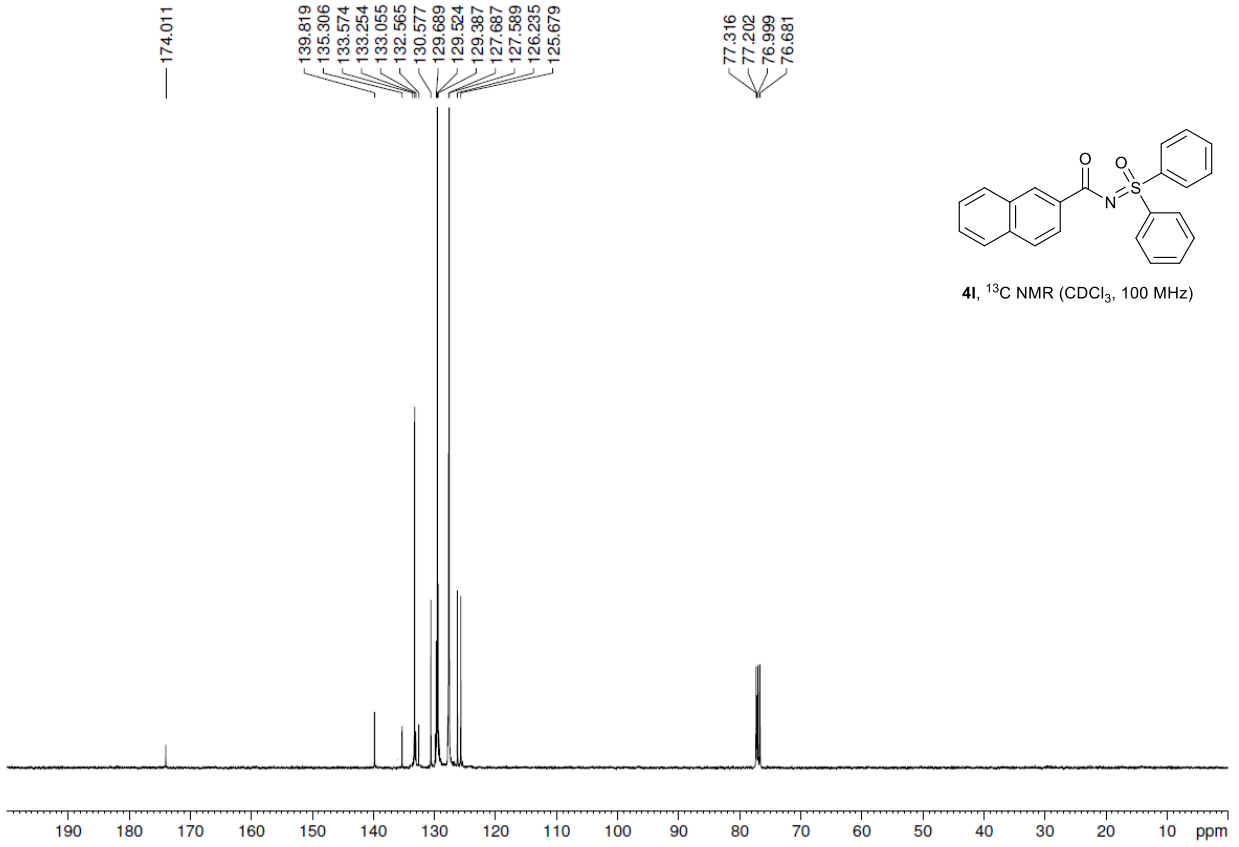


4k, ^{13}C NMR ($CDCl_3$, 100 MHz)

***N*-(2-Naphthoyl)-*S*,*S*-diphenyl sulfoximine (4l)**

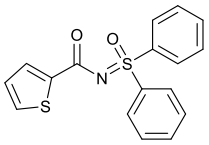


4l, ^{1}H NMR ($CDCl_3$, 400 MHz)

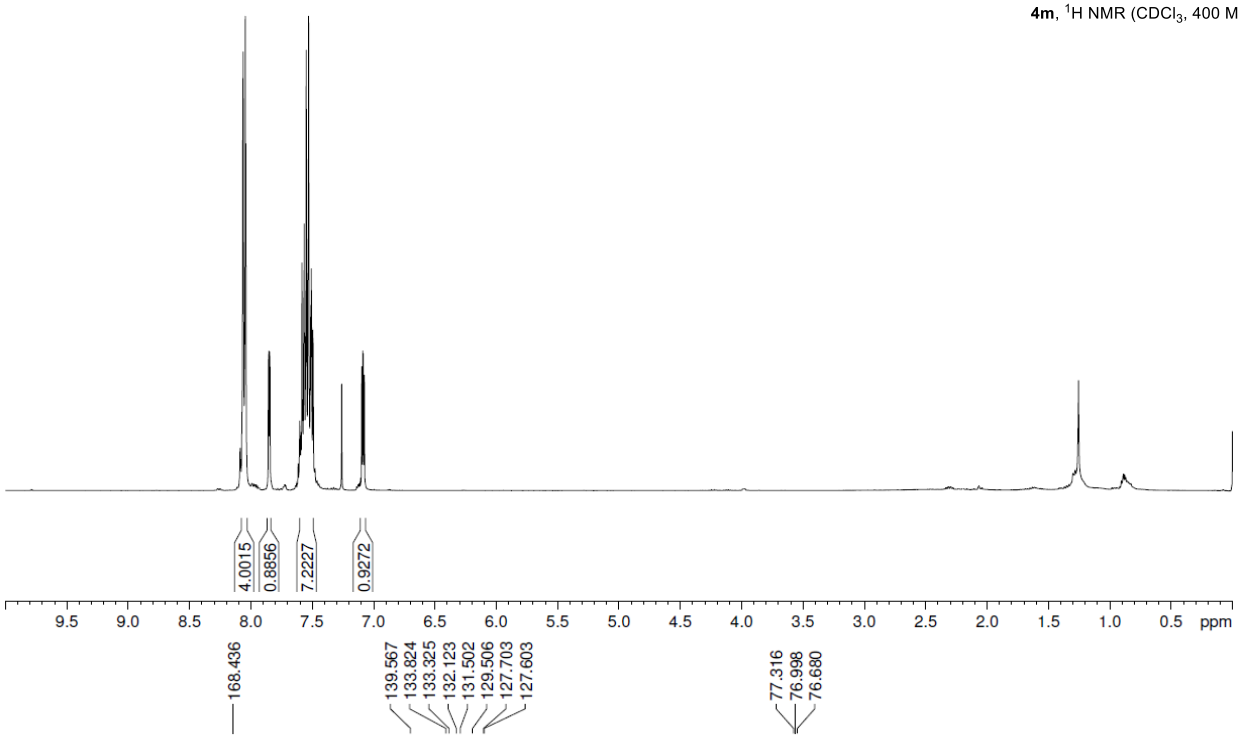


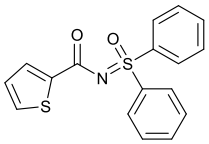
4l, ^{13}C NMR ($CDCl_3$, 100 MHz)

_N_-(Thiophene-2-carbonyl)-_S,S_-diphenyl sulfoximine (4m)



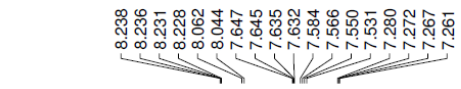
4m, ^{1}H NMR ($CDCl_3$, 400 MHz)

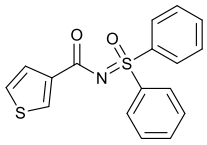




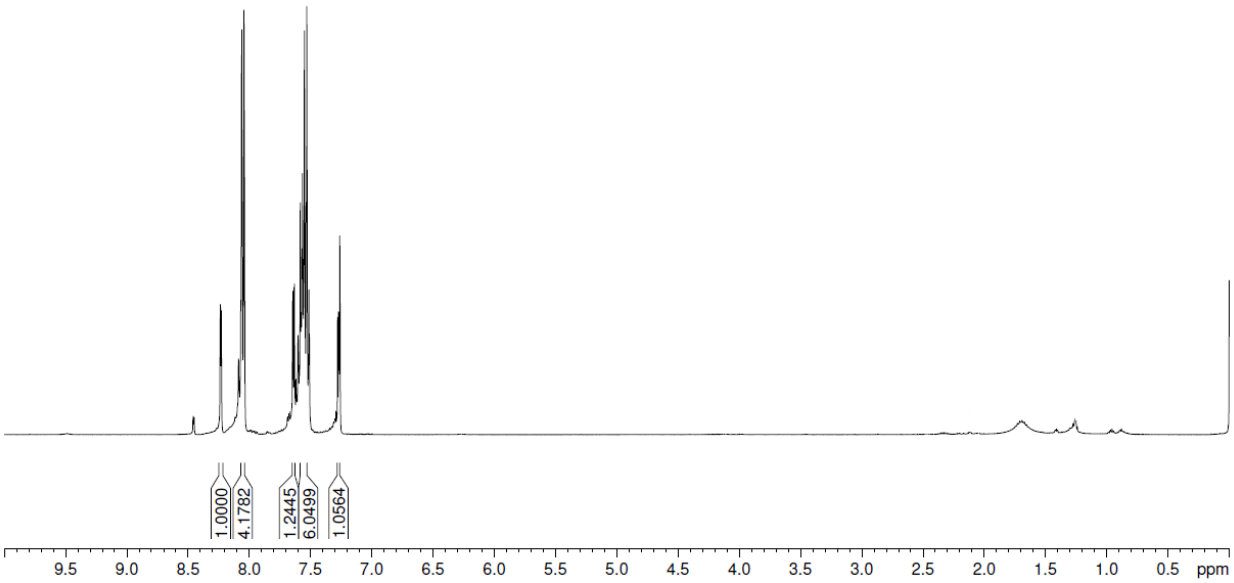
4m, ^{13}C NMR ($CDCl_3$, 100 MHz)

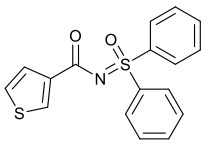
_N_-(Thiophene-3-carbonyl)-_S,S_-diphenyl sulfoximine (4n)





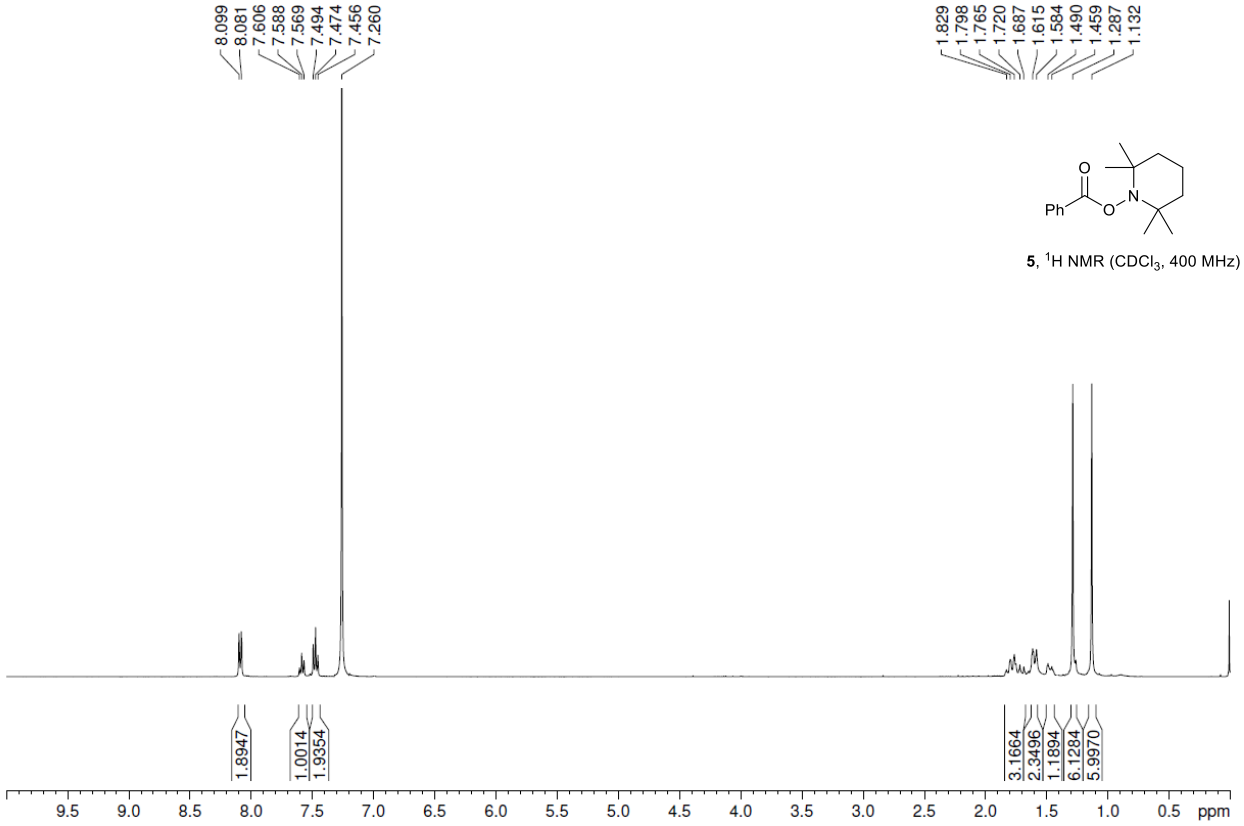
4n, ^{1}H NMR ($CDCl_3$, 400 MHz)



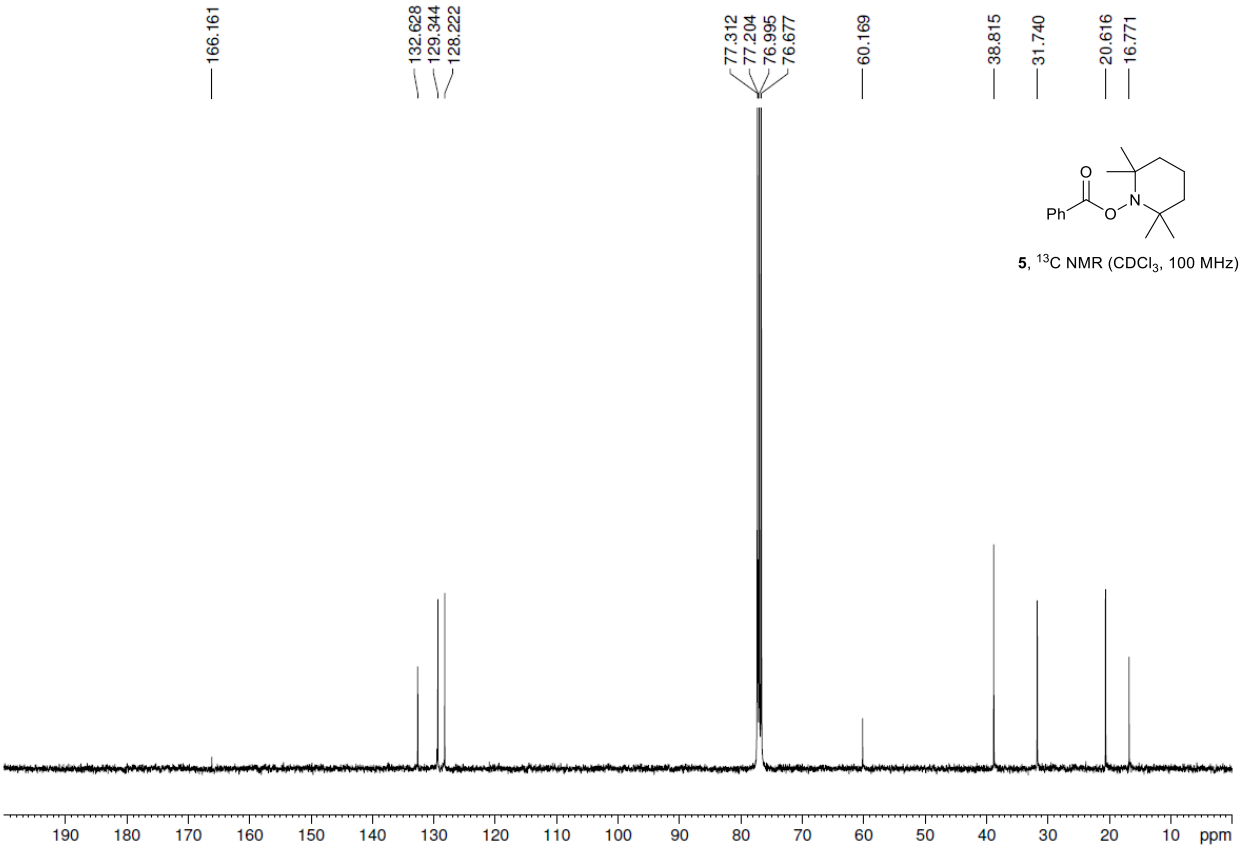


4n, ^{13}C NMR ($CDCl_3$, 100 MHz)

2,2,6,6-Tetramethylpiperidin-1-yl benzoate (5)



5, ^{1}H NMR ($CDCl_3$, 400 MHz)



5, ^{13}C NMR ($CDCl_3$, 100 MHz)