Supplementary Materials

Nitrone or Oxaziridine? Further Insights into the Selectivity of Imine Oxidation Catalyzed by Methyltrioxorhenium

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General

Commercial reagents were used as received. All reactions were carried out under magnetic stirring and monitored by TLC on 0.25 mm silica gel plates (Merck F254). Column chromatography was carried out on silica gel (230–400 mesh, Merck). Yields refer to spectroscopically and analytically pure compounds unless otherwise stated. ^{1}H NMR spectra were recorded on a Varian Gemini-200 instrument at 25 °C. Chemical shifts are reported relative to $CDCl_3$ (^{1}H: 7.26 ppm). Integrals are in accordance with assignments, coupling constants are given in Hz. Splitting patterns are described by using the following abbreviations: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet.

Imine **1a** was purchased from Sigma-Aldrich (CAS n° 622-29-7) and used as received.

General Procedure for the Synthesis of Imines 1b-1e

Benzaldehyde (5.0 mmol) was added to a solution of a primary amine (5.0 mmol) in Methanol (10 mL) in the presence of anhydrous Na_2SO_4 (100mg) The reaction was performed at room temperature under magnetic stirring overnight and monitored by TLC. After this time, Na_2SO_4 was removed by filtration, and the solvent was removed in vacuo to afford the imines **1b**-**1e** directly as pure (*E*) products in quantitative yields.

General Procedure for the Synthesis of Imines 1f-1k

The aromatic aldehyde (5.0 mmol) was added to 2.0 mL of a 50% v/v solution of methylamine in water at 0 °C. The reaction was performed in a closed vial at room temperature under magnetic stirring overnight. After this time the solvent was removed in vacuo to afford the imines **1f**-**1k** directly as pure (*E*) stereoisomers in quantitative yields.

General Procedure for the Oxidation of Imines with UHP/MTO in MeOH (Method A):

To a stirred solution of the imine **1a-k** (1 mmol) in MeOH (2 mL), UHP (282 mg, 3 mmol) and MTO (5 mg, 0.02 mmol) were added sequentially. The resulting yellow solution was stirred at room temperature and monitored by TLC (for reaction time, see Table 1 and Table 2). After removal of the solvent under reduced pressure the reaction mixture was added with CH_2Cl_2 and the undissolved urea filtered off. Removal of the solvent afforded the crude product which was purified by flash column chromatography on silica gel, if necessary.

General Procedure for the Oxidation of Imines with UHP/MTO in [bmim]BF_4 (Method B):

To a stirred solution of the imine **1a-k** (3 mmol) in [bmim]BF_4 (0.5 mL), UHP (564 mg, 6 mmol) and MTO (7.5 mg, 0.03 mmol) were added sequentially. The resulting yellow solution was stirred at 50 °C (for reaction time, see Table 1 and Table 2) and monitored via ^{1}H NMR. The reaction mixture was extracted with AcOEt and the organic layer was washed with water (2 times). Finally, the organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to yield the crude product.

General Procedure for the Oxidation of Imines with UHP/MTO in [bmim]PF_6 (Method C):

To a stirred solution of the imine **1a**, **1b** or **1d** (1 mmol) in [bmim]PF_6 (2 mL), UHP (282 mg, 3 mmol) and MTO (5 mg, 0.02 mmol) were added sequentially. The resulting yellow solution was stirred at room temperature or 50 °C (for reaction time, see Table 1) and monitored via ^{1}H NMR. The reaction mixture was extracted with AcOEt and the organic layer was washed with water (2 times). Finally, the organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to yield the crude product.

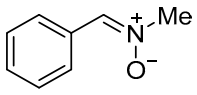
Procedure for the Oxidation of Imine 1a with MTO/H_2O_2 in [bmim]BF_4

To a stirred solution of the imine **1a** (1 mmol) in [bmim]BF_4 (1.8 mL), 35% H_2O_2 (0.2 mL) and MTO (7.5 mg, 0.03 mmol) were added sequentially. The resulting orange solution was stirred at room temperature for 20 h. After ^1H NMR control the reaction mixture was extracted with AcOEt and the organic layer was washed with water (2 times). Finally, the organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to yield the crude product.

Synthesis of nitrones 2a-d, f-k

Nitrones **2** were synthesized from the corresponding imines following the general procedure Method A or Method C. ^{1}H NMR spectra matched with the reported ones.

2-Methanamine, *N*-(phenylmethylene)-, *N*-oxide (2a) [70]

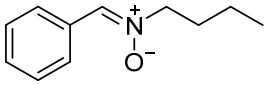


2a

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.24-8.17 (m, 2H), 7.40-7.28 (m, 4H), 3.78 (s, 3H).

Purification by flash column chromatography (eluent AcOEt/MeOH 10:1) of the crude mixture from the experiment in Entry 1, Table 1 afforded 92 mg of pure **2a** (68% yield).

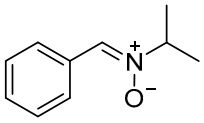
1-Buthanamine, *N*-(phenylmethylene)-, *N*-oxide (2b) [71]



2b

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.25-8.18 (m, 2H), 7.40-7.25 (m, 4H), 3.85 (t, J = 8.2 Hz, 2H), 1.92 (quint, J = 8.2 Hz, 2H), 1.48-1-21 (m, 2H), 1.00-0.84 (t, J = 7.2 Hz, 3H).

2-Propanamine, *N*-(phenylmethylene)-, *N*-oxide (2c) [71]

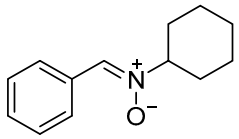


2c

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.28-8.20 (m, 2H), 7.45-7.35 (m, 4H), 4.30-4.14 (m, 1H), 1.28 (d, J = 7.8 Hz, 6H).

Purification by flash column chromatography (eluent AcOEt/MeOH 10:1) of the crude mixture from the experiment in Entry 15, Table 1 afforded 121 mg of pure **2c** (74% yield).

Cyclohexanamine, *N*-(phenylmethylene)-, *N*-oxide (2d) [72]

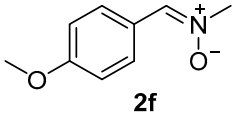


2d

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.25-8.15 (m, 2H), 7.43-7.25 (m, 4H), 3.81 (m, 1H), 2.10-1.80 (m, 6H), 1.76-1-65 (m, 1H), 1.40-1.08 (m,3H).

Purification by flash column chromatography (eluent AcOEt/MeOH 10:1) of the crude mixture from the experiment in Entry 19, Table 1 afforded 158 mg of pure **2d** (78% yield).

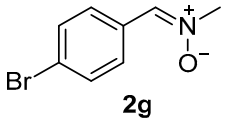
Methanamine, *N*-[(4-methoxyphenyl)methylene]-, *N*-oxide (2f) [71]



2f

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.69 (d, J = 8.2 Hz, 2H), 7.29 (s, 1H), 6.91 (d, J = 8.2 Hz, 2H), 3.82 (br s, 6H).

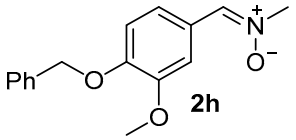
Methanamine, *N*-[(4-bromophenyl)methylene]-, *N*-oxide (2g) [73]



2g

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.07 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.33 (s, 1H), 3.84 (s, 3H).

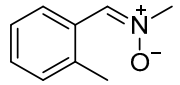
Methanamine, *N*-[[3-methoxy-4-(phenylmethoxy)phenyl]methylene]-, *N*-oxide (2h) [74]



2h

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.06 (s, 1H), 7.46-7.25 (m, 5H), 7.23 (d, J = 2.0 Hz, 1H), 6.96 (dd, J = 8.0, 2.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H) 5.39 (s, 2H), 3.91 (br s, 6H).

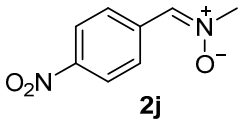
Methanamine, *N*-[(2-methylphenyl)methylene]-, *N*-oxide (2i) [75]



2i

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 9.08-9.03 (m, 1H), 7.52 (s, 1H), 7.29-7.15 (m, 3H), 3.88 (s, 3H), 2.34 (s, 3H).

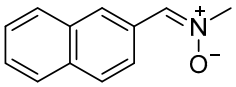
Methanamine, *N*-[(4-nitrophenyl)methylene]-, *N*-oxide (2j) [76]



2j

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.39 (d, J = 8.4 Hz, 2H), 8.25 (d, J = 8.4 Hz, 2H), 7.55 (s, 1H), 3.97 (s, 3H).

Methanamine, *N*-(2-naphthalenylmethylene)-, *N*-oxide (2k) [77]



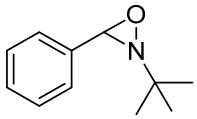
2k

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 9.15 (s, 1H), 7.94-7.79 (m, 4H), 7.54-7.45 (m, 3H), 3.91 (s, 3H).

Synthesis of Oxaziridine 3e

Oxaziridine **3e** was obtained from imine **1e** following the general procedure Method B. The ^{1}H NMR matched with the reported one.

2-(1,1-Dimethylethyl)-3-phenyloxaziridine (3e) [78]



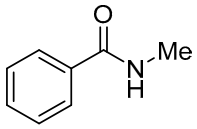
3e

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.45-7.32 (m, 5H), 4.67 (s, 1H), 1.15 (s, 9H).

Synthesis of Amides 4a-d, f-k

Amides **4** were synthesized from the corresponding imines following the general procedures Methods A-C. ^{1}H NMR spectra matched with the reported ones.

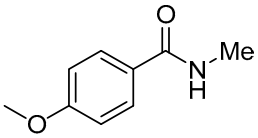
***N*-Methylbenzamide (4a)** [79]



4a

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.80-7.72 (m, 2H), 7.42-7.25 (m, 3H), 7.16 (br s, 1H), 2.88 (d, J = 5.5 Hz, 3H).

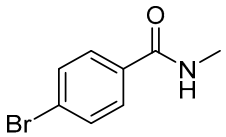
4-Methoxy-*N*-methylbenzamide (4f) [79]



4f

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.72 (d, J = 10.0 Hz, 2H), 6.86 (d, J = 10.0 Hz, 2H), 6.59 (br s, 1H), 3.75 (s, 1H), 2.89 (d, J = 4.0 Hz, 3H).

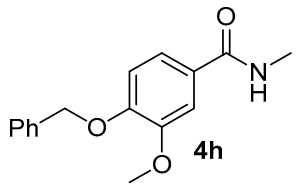
4-Bromo-*N*-methylbenzamide (4g) [80]



4g

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.14 (d, J = 2.0 Hz, 2H), 7.48 (d, J = 2.0 Hz, 2H), 7.76 (br s, 1H), 2.90 (d, J = 4.0 Hz, 3H).

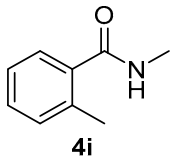
3-Methoxy-*N*-methyl-4-(phenylmethoxy)benzamide (4h) [81]



4h

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.44-7.23 (m, 5H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.03 (dd, *J* = 8.0, 2.0 Hz, 1H) 6.88 (d, *J* = 8.0 Hz, 1H), 6.68 (br s, 1H), 5.16 (s, 2H), 3.87 (s, 3H). 2.87 (d, *J* = 4.0 Hz, 3H).

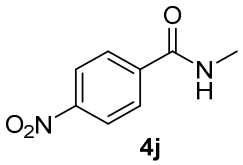
2-Methyl-*N*-methylbenzamide (4i) [82]



4i

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.34-7.18 (m, 4H), 6.04 (br s, 1H), 2.95 (d, *J* = 6.0 Hz, 3H), 3.88 (s, 3H), 2.42 (s, 3H).

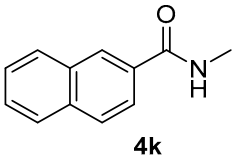
***N*-Methyl-4-nitrobenzamide (4j)** [79]



4j

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.37 (d, *J* = 8.0 Hz, 2H), 8.24 (d, *J* = 8.0 Hz, 2H), 5.16 (br s, 1H), 3.03 (d, *J* = 4.0 Hz, 3H).

***N*-Methyl-2-naphthalenecarboxamide (4k)** [79]

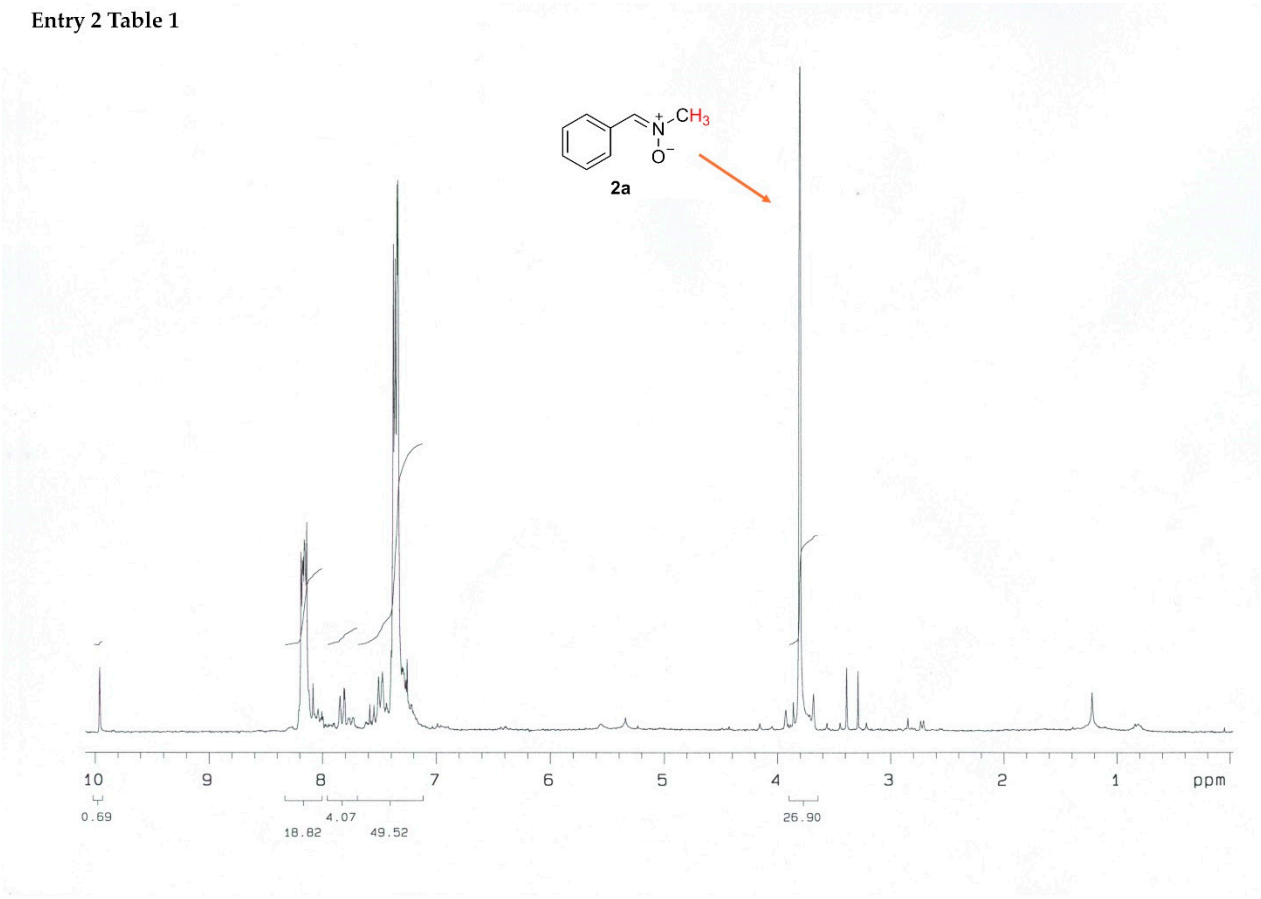


4k

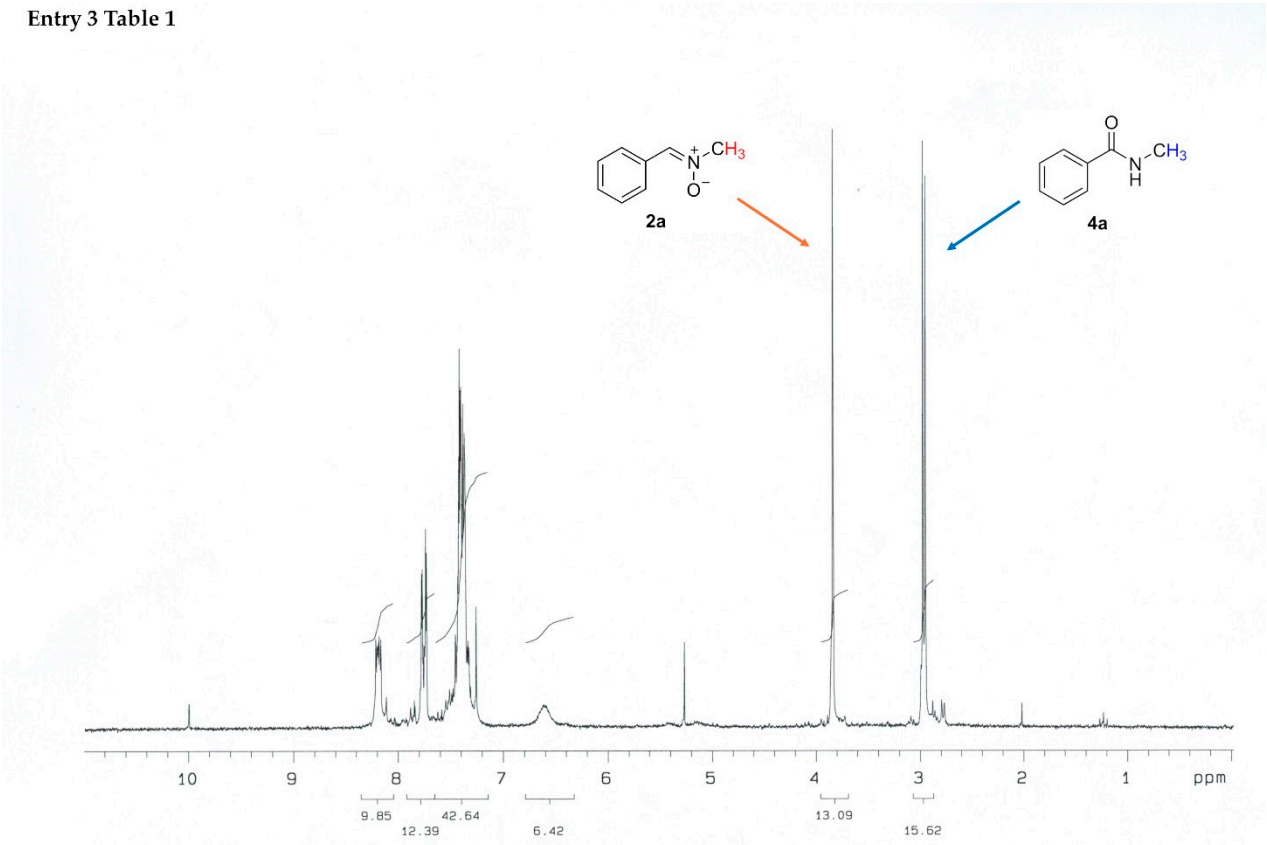
^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.36 (d, *J* = 2.0 Hz, 1H) 7.90-7.78 (m, 4H), 7.52-7.48 (m, 2H), 6.77 (br s, 1H), 3.02 (d, *J* = 4.0 Hz, 3H).

Representative examples of ^{1}H NMR spectra of the crude mixtures obtained from the oxidation of imine 1a

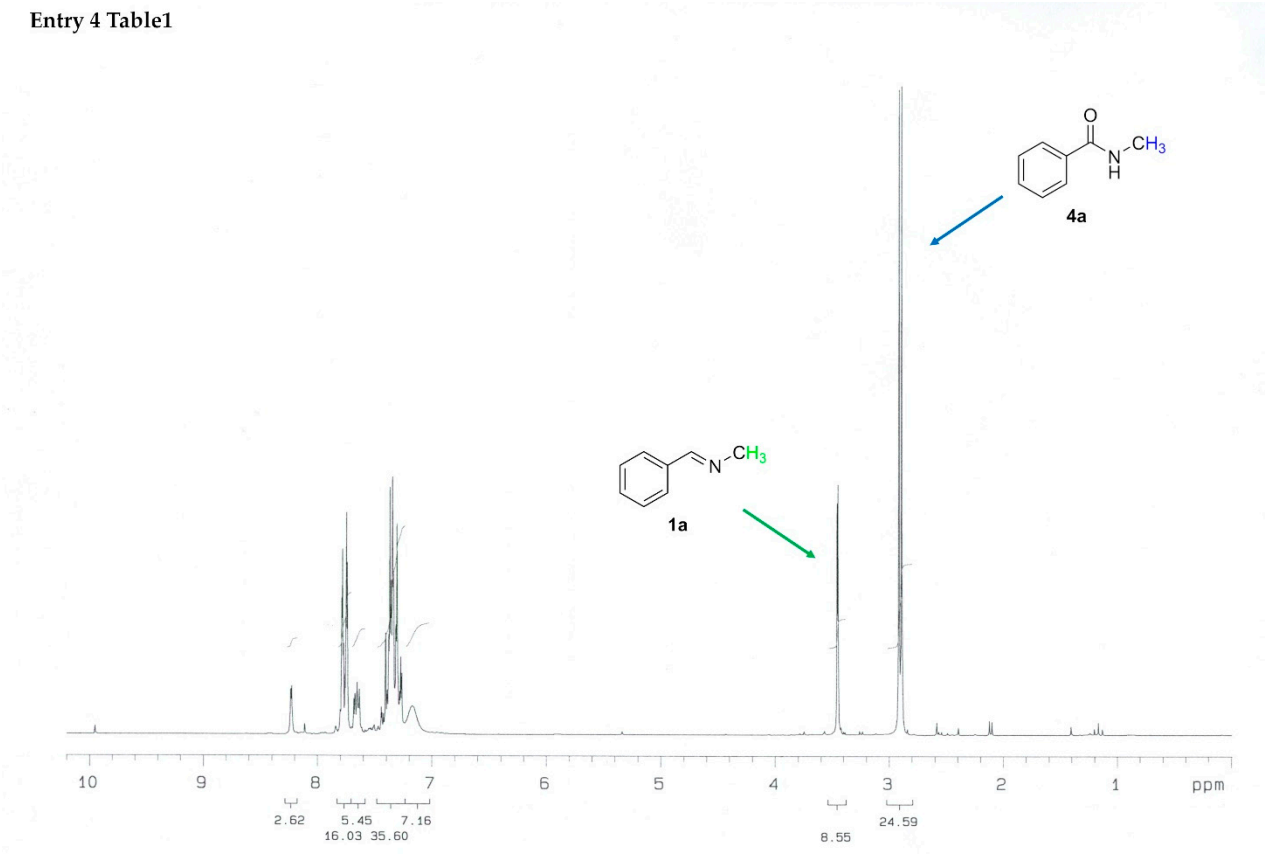
Entry 2 Table 1



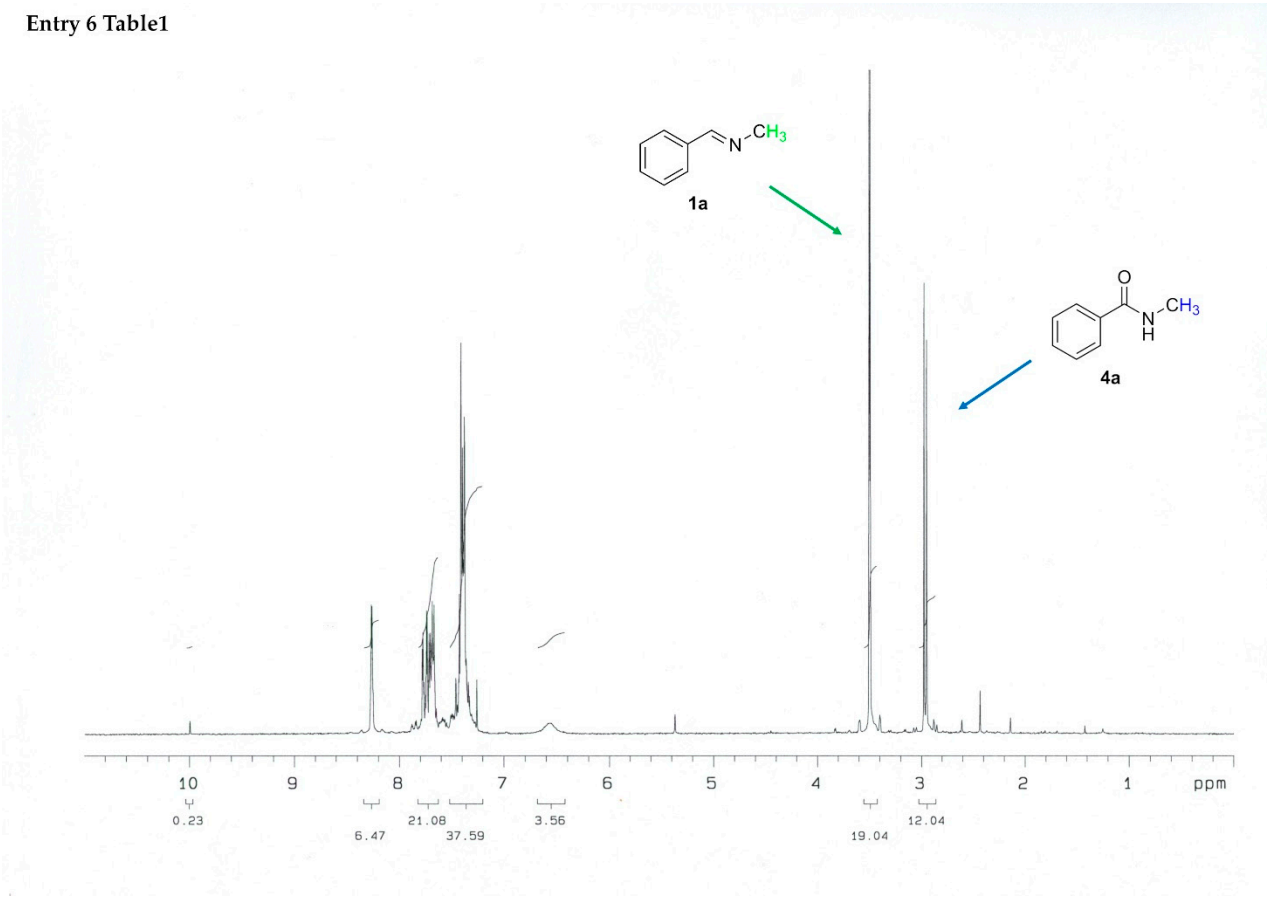
Entry 3 Table 1



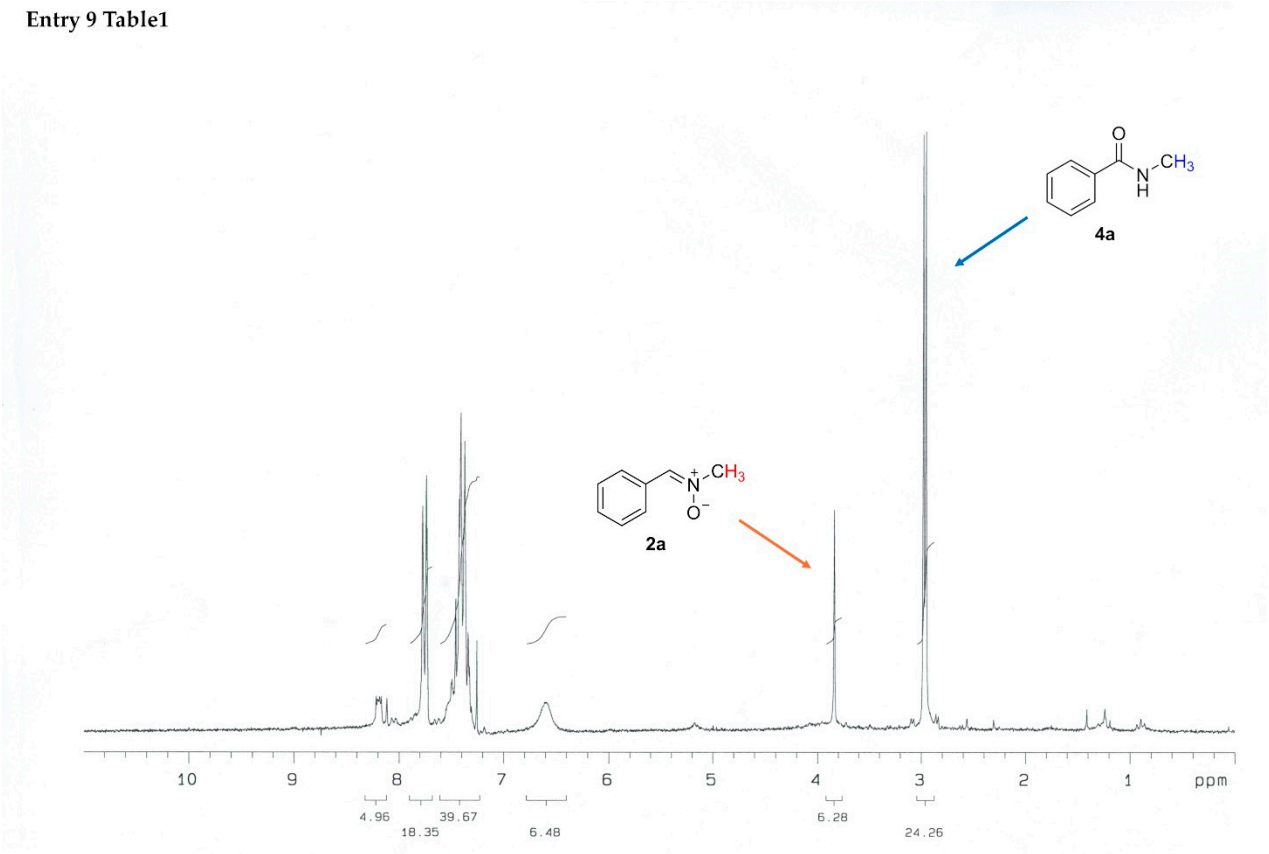
Entry 4 Table1



Entry 6 Table1



Entry 9 Table1



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