Supporting Information

Mercury-Catalyzed Rearrangement of Ketoximes into Amides and Lactams in

Acetonitrile

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Sl. No	Index	Page No
	Experimental Section	
1	General.....	-S3-
2	Synthesis of <i>N</i> -phenylbenzamide.....	-S3-
3	Syntheses of <i>N</i> -(4-fluorophenyl)benzamide and 4-fluoro- <i>N</i> -phenylbenzamide.....	-S3-
4	Syntheses of <i>N</i> -(4-methoxyphenyl)benzamide and 4-methoxy- <i>N</i> -phenylbenzamide.....	-S4-
5	Synthesis of 4-chloro- <i>N</i> -(4-chlorophenyl)benzamide.....	-S5-
6	Synthesis of 4-methyl- <i>N</i> - <i>p</i> -tolylbenzamide.....	-S5-
7	Synthesis of <i>N</i> -phenylpropionamide.....	-S6-
8	Synthesis of <i>N</i> -(4-fluorophenyl)propionamide.....	-S7-
9	Synthesis of <i>N</i> -(4-methoxyphenyl)propionamide.....	-S8-
10	Synthesis of <i>N</i> - <i>p</i> -tolylpropionamide.....	-S8-
11	Synthesis of <i>N</i> -phenylacetamide.....	-S9-
12	Synthesis of <i>N</i> -(2-chlorophenyl)acetamide.....	-S10-
13	Synthesis of <i>N</i> -(2-bromophenyl)acetamide.....	-S10-
14	Synthesis of <i>N</i> -(4-bromophenyl)acetamide.....	-S11-
15	Synthesis of <i>N</i> -(2-iodophenyl)acetamide.....	-S12-
16	Synthesis of <i>N</i> -(2-methoxyphenyl)acetamide.....	-S12-
17	Synthesis of <i>N</i> -(3-methoxyphenyl)acetamide.....	-S13-

Sl. No	Index	Page No
18	Synthesis of <i>N</i> -(4-methoxyphenyl)acetamide.....	-S14-
19	Synthesis of <i>N-p</i> -tolylacetamide.....	-S14-
20	Synthesis of <i>N-o</i> -tolylacetamide.....	-S15-
21	Synthesis of piperidin-2-one.....	-S16-
22	Synthesis of azepan-2-one.....	-S16-
23	Synthesis of 7- <i>tert</i> -butylazepan-2-one.....	-S17-
24	Synthesis of azocan-2-one.....	-S18-
25	References.....	-S19-
26	¹ H NMR Spectrum of <i>N</i> -phenylbenzamide.....	-S20-
27	¹ H NMR Spectrum of <i>N</i> -(4-fluorophenyl)benzamide and 4-fluoro- <i>N</i> -phenylbenzamide.....	-S21-
28	¹ H NMR Spectrum of <i>N</i> -(4-methoxyphenyl)benzamide and 4- methoxy- <i>N</i> -phenylbenzamide.....	-S22-
29	¹ H NMR Spectrum of 4-chloro- <i>N</i> -(4-chlorophenyl)benzamide.....	-S23-
30	¹ H NMR Spectrum of 4-methyl- <i>N-p</i> -tolylbenzamide.....	-S24-
31	¹ H NMR Spectrum of <i>N</i> -phenylpropionamide.....	-S25-
32	¹ H NMR Spectrum of <i>N</i> -(4-fluorophenyl)propionamide.....	-S26-
33	¹ H NMR Spectrum of <i>N</i> -(4-methoxyphenyl)propionamide.....	-S27-
34	¹ H NMR Spectrum of <i>N-p</i> -tolylpropionamide.....	-S28-
35	¹ H NMR Spectrum of <i>N</i> -phenylacetamide.....	-S29-
36	¹ H NMR Spectrum of <i>N</i> -(2-chlorophenyl)acetamide.....	-S30-
37	¹ H NMR Spectrum of <i>N</i> -(2-bromophenyl)acetamide.....	-S31-
38	¹ H NMR Spectrum of <i>N</i> -(4-bromophenyl)acetamide.....	-S32-
39	¹ H NMR Spectrum of <i>N</i> -(2-iodophenyl)acetamide.....	-S33-
40	¹ H NMR Spectrum of <i>N</i> -(2-methoxyphenyl)acetamide.....	-S34-
41	¹ H NMR Spectrum of <i>N</i> -(3-methoxyphenyl)acetamide.....	-S35-
42	¹ H NMR Spectrum of <i>N</i> -(4-methoxyphenyl)acetamide.....	-S36-
43	¹ H NMR Spectrum of <i>N-p</i> -tolylacetamide.....	-S37-
44	¹ H NMR Spectrum of <i>N-o</i> -tolylacetamide.....	-S38-
45	¹ H NMR Spectrum of piperidin-2-one.....	-S39-
46	¹ H NMR Spectrum of azepan-2-one.....	-S40-
47	¹ H NMR Spectrum of 7- <i>tert</i> -butylazepan-2-one.....	-S41-
48	¹ H NMR Spectrum of azocan-2-one.....	-S42-

Experimental section

General. All solvents used herein were distilled prior to use. Reagent grade reagents were purchased and were used without further purification. Thin layer chromatography was performed on Silica gel 60 F plates eluting with the solvents indicated. Flash column chromatography was performed on Silica gel 230-400 mesh slurry packed in glass columns with eluent as indicated. ^1H NMR spectra were acquired at 400 MHz by using CDCl_3 and DMSO-d_6 as solvents (See the individual compounds for the specific solvents used).

Mercury-catalyzed rearrangement of oximes: synthesis of *N*-phenylbenzamide (Table 3, entry 1).¹ The experimental procedure for the synthesis of *N*-phenylbenzamide is presented in the manuscript. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 7.91 (1H, br.s), 7.85-7.83 (2H, m), 7.62 (2H, d, $J = 8.04\text{Hz}$), 7.54-7.49 (1H, m), 7.46-7.43 (2H, m), 7.36-7.32 (2H, m), 7.14-7.11 (1H, m).

Syntheses of *N*-(4-fluorophenyl)benzamide and 4-fluoro-*N*-phenylbenzamide (Table 3, entry 2). To a solution of (4-fluorophenyl)phenylmethanone oxime (252 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried

over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford an isomeric mixture of *N*-(4-fluorophenyl)benzamide and 4-fluoro-*N*-phenylbenzamide as an off-white solid (207 mg, 82%). mp 167-178°C. ^1H NMR δ_{H} (400 MHz; DMSO- d_6 ; Me $_4$ Si; 25°C) 10.32 (1H, br.s), 10.27 (1H, br.s), 8.07-8.02 (2H, m), 7.96 (2H, d, J = 7.04Hz), 7.83-7.81 (1H, m), 7.79-7.76 (3H, m), 7.61-7.58 (1H, m), 7.56-7.51 (2H, m), 7.39-7.34 (4H, m), 7.20 (2H, t, J = 9.02Hz), 7.13-7.09 (1H, m).

Syntheses of *N*-(4-methoxyphenyl)benzamide and 4-methoxy-*N*-phenylbenzamide (Table 3, entry 3). To a solution of (4-methoxyphenyl)phenylmethanone oxime (227 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford an isomeric mixture of *N*-(4-methoxyphenyl)benzamide and 4-methoxy-*N*-phenylbenzamide as a white solid (193 mg, 85%). mp 148-161°C. ^1H NMR δ_{H} (400 MHz; DMSO- d_6 ; Me $_4$ Si; 25°C)

10.15 (1H, br.s), 10.10 (1H, br.s), 7.99-7.95 (3H, m), 7.78 (2H, d, $J = 8.04\text{Hz}$), 7.70 (2H, d, $J = 9.04\text{Hz}$), 7.59-7.50 (2H, m), 7.54-7.50 (3H, m), 7.34 (2H, t, $J = 8.02\text{Hz}$), 7.07 (2H, d, $J = 9.04\text{Hz}$), 6.94 (2H, d, $J = 9.04\text{Hz}$), 3.84 (3H, s), 3.75 (3H, s).

Synthesis of 4-chloro-N-(4-chlorophenyl)benzamide (Table 3, entry 4).² To a solution of *bis*-(4-chlorophenyl)methanone oxime (266 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford 4-chloro-N-(4-chlorophenyl)benzamide as a white solid (237 mg, 89%). mp 205-207°C. ¹H NMR δ_{H} (400 MHz; DMSO- d_6 ; Me₄Si; 25°C) 10.44 (1H, br.s), 7.98 (2H, d, $J = 8.52\text{Hz}$), 7.81 (2H, d, $J = 8.56\text{Hz}$), 7.61 (2H, d, $J = 8.52\text{Hz}$), 7.41 (2H, d, $J = 8.52\text{Hz}$).

Synthesis of 4-methyl-N-*p*-tolylbenzamide (Table 3, entry 5).³ To a solution of di-*p*-

tolylmethanone oxime (225 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford 4-methyl-*N-p*-tolylbenzamide as an off-white solid (218 mg, 97%). mp 159-160°C. ¹H NMR δ_H(400 MHz; CDCl₃; Me₄Si; 25°C) 8.06 (1H, br.s), 7.72 (2H, d, *J* = 8.04Hz), 7.50 (2H, d, *J* = 8.52Hz), 7.18 (2H, d, *J* = 8.04Hz), 7.10 (2H, d, *J* = 8.52Hz), 2.37 (3H, s), 2.30 (3H, s).

Synthesis of *N*-phenylpropionamide (Table 3, entry 6).⁴ To a solution of 1-phenylpropan-1-one oxime (149 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by

flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-phenylpropionamide as a pale-yellow solid (146 mg, 98%). mp 103-104°C. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 7.83 (1H, br.s), 7.53 (2H, d, $J = 8.04\text{Hz}$), 7.28 (2H, t, $J = 7.52\text{Hz}$; 8.56Hz), 7.08 (1H, t, $J = 7.52\text{Hz}$, 7.04Hz), 2.37 (2H, q, $J = 7.53\text{Hz}$), 1.22 (3H, t, $J = 7.52\text{Hz}$).

Synthesis of *N*-(4-fluorophenyl)propionamide (Table 3, entry 7).⁵ To a solution of 1-(4-fluorophenyl)propan-1-one oxime (167 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-(4-fluorophenyl)propionamide as an off-white solid (142 mg, 85%). mp 118-119°C. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 7.83 (1H, br.s), 7.48-7.45 (2H, m), 6.97 (2H, t, $J = 9.04\text{Hz}$; 8.52Hz), 2.37 (2H, q, $J = 7.69\text{Hz}$), 1.22 (3H, t, $J = 7.78\text{Hz}$).

Synthesis of *N*-(4-methoxyphenyl)propionamide (Table 3, entry 8). To a solution of 1-(4-methoxyphenyl)propan-1-one oxime (179 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane - methanol (100:4) eluent system to afford *N*-(4-Methoxyphenyl)propionamide as a light-brown solid (159 mg, 89%). mp 93-94°C. ¹H NMR δ_H(400 MHz; CDCl₃; Me₄Si; 25°C) 7.72 (1H, br.s), 7.40 (2H, d, *J* = 9.04Hz), 6.81 (2H, d, *J* = 9.00Hz), 3.76 (3H, s), 2.34 (2H, q, *J* = 7.52Hz), 1.21 (3H, t, *J* = 7.78Hz).

Synthesis of *N-p*-tolylpropionamide (Table 3, entry 9).⁶ To a solution of 1-*p*-tolylpropan-1-one oxime (163 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered.

The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-*p*-tolylpropionamide as an off-white solid (153 mg, 94%). mp 122-124°C. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 7.68 (1H, br.s), 7.39 (2H, d, $J = 8.04\text{Hz}$), 7.08 (2H, d, $J = 8.56\text{Hz}$), 2.35 (2H, q, $J = 7.52\text{Hz}$), 2.29 (3H, s), 1.21 (3H, t, $J = 7.52\text{Hz}$).

Synthesis of *N*-phenylacetamide (Table 3, entry 10).⁴ To a solution of 1-phenylethanone oxime (135 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-phenylacetamide as a white solid (132 mg, 98%). mp 114-116°C. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 8.44 (1H, br.s), 7.50 (2H, d, $J = 8.52\text{Hz}$), 7.25 (2H, t, $J = 7.78\text{Hz}$), 7.05 (1H, t, $J = 7.24\text{Hz}$), 2.09 (3H, s).

Synthesis of *N*-(2-chlorophenyl)acetamide (Table 3, entry 11).⁷ To a solution of 1-(2-chlorophenyl)ethanone oxime (170 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-(2-chlorophenyl)acetamide as an off-white solid (141 mg, 83%). mp 90-91°C. ¹H NMR δ_{H} (400 MHz; CDCl₃; Me₄Si; 25°C) 8.34 (1H, d, *J* = 8.04Hz), 7.65 (1H, br.s), 7.35 (1H, dd, *J* = 8.02Hz; 1.50Hz), 7.28-7.24 (1H, m), 7.03 (1H, t, *J* = 7.28Hz), 2.23 (3H, s).

Synthesis of *N*-(2-bromophenyl)acetamide (Table 3, entry 12).⁸ To a solution of 1-(2-bromophenyl)ethanone oxime (214 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered.

The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-(2-bromophenyl)acetamide as a pale-yellow solid (169 mg, 79%). mp 97-99°C. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 8.31 (1H, d, J = 8.52Hz), 7.68 (1H, br.s), 7.54 (1H, dd, J = 8.04Hz; 1,52Hz), 7.31 (1H, dt, J = 1.26Hz; 8.04Hz), 6.99 (1H, t, J = 7.28Hz), 2.25 (3H, s).

Synthesis of *N*-(4-bromophenyl)acetamide (Table 3, entry 13).⁹ To a solution of 1-(4-bromophenyl)ethanone oxime (214 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-(4-bromophenyl)acetamide as a white solid (180 mg, 84%). mp 166-167°C. ^1H NMR δ_{H} (400MHz; $\text{DMSO}-d_6$; Me_4Si ; 25°C) 10.04 (1H, br.s), 7.55 (2H, d, J = 8.52Hz), 7.46 (2H, d, J = 9.00Hz), 2.03 (3H, s).

Synthesis of *N*-(2-iodophenyl)acetamide (Table 3, entry 14).¹⁰ To a solution of 1-(2-iodophenyl)ethanone oxime (261 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-(2-iodophenyl)acetamide as a colorless solid (193 mg, 74%). mp 109-110°C. ¹H NMR δ_{H} (400 MHz; CDCl₃; Me₄Si; 25°C) 8.19 (1H, d, *J* = 8.04Hz), 7.78 (1H, d, *J* = 8.00Hz), 7.46 (1H, br.s), 7.34 (1H, dt, *J* = 1.00Hz; 7.78Hz), 6.85 (1H, t, *J* = 7.52Hz), 2.24 (3H, s).

Synthesis of *N*-(2-methoxyphenyl)acetamide (Table 3, entry 15).¹¹ To a solution of 1-(2-methoxyphenyl)ethanone oxime (165 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and

filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-(2-methoxyphenyl)acetamide as a white solid (117 mg, 71%). mp 85-86°C. ¹H NMR δ_H(400 MHz; CDCl₃; Me₄Si; 25°C) 8.36 (1H, dd, *J* = 1.81, 7.83Hz), 7.77 (1H, br.s), 7.08 – 6.93 (2H, m), 6.87 (1H, dd, *J* = 1.83Hz, 8.09Hz), 3.87 (3H, s), 2.21 (3H, s).

Synthesis of *N*-(3-methoxyphenyl)acetamide (Table 3, entry 16).¹² To a solution of 1-(3-methoxyphenyl)ethanone oxime (165 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-(3-methoxyphenyl)acetamide as an off-white solid (135 mg, 82%). mp 87-88°C. ¹H NMR δ_H(400 MHz; CDCl₃; Me₄Si; 25°C) 7.75 (1H, br.s), 7.29 – 7.17 (2H, m), 6.94 (1H, d, *J* = 8.05Hz), 6.63 (1H, dd, *J* = 2.09Hz; 8.04Hz), 3.80 (3H, s), 2.17 (3H, s).

Synthesis of *N*-(4-methoxyphenyl)acetamide (Table 3, entry 17).¹³ To a solution of 1-(3-methoxyphenyl)ethanone oxime (165 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N*-(4-methoxyphenyl)acetamide as a light-brown solid (149 mg, 90%). mp 129-130°C. ¹H NMR δ_{H} (400 MHz; CDCl₃; Me₄Si; 25°C) 7.38 (2H, d, *J* = 9.01Hz), 7.06 (1H, br.s), 6.84 (2H, d, *J* = 9.02Hz), 3.80 (3H, s), 2.15 (3H, s).

Synthesis of *N-p*-tolylacetamide (Table 3, entry 18).³ To a solution of 1-*p*-tolylethanone oxime (149 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then

acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N-p*-tolylacetamide as an off-white solid (139 mg, 93%). mp 149-151°C. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 7.66 (1H, br.s), 7.37 (2H, d, $J = 8.04\text{Hz}$), 7.09 (2H, d, $J = 8.04\text{Hz}$), 2.30 (3H, s), 2.13 (3H, s).

Synthesis of *N-o*-tolylacetamide (Table 3, entry 19).¹⁴ To a solution of 1-*o*-tolylethanone oxime (149 mg, 1 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (33 mg, 0.12 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford *N-o*-tolylacetamide as a pale-yellow solid (115 mg, 77%). mp 125-126°C. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 7.62 (1H, d, $J = 8.00\text{Hz}$), 7.37 (1H, br.s), 7.16 (2H, t, $J = 6.02\text{Hz}$), 7.08-7.04 (1H, m), 2.21 (3H, s), 2.13 (3H, s).

Synthesis of piperidin-2-one (Table 3, entry 20).¹⁵ To a solution of cyclopentanone oxime (198 mg, 2 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (165 mg, 0.6 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford piperidin-2-one as a colorless liquid (166 mg, 84%). ¹H NMR δ_{H} (400 MHz; CDCl₃; Me₄Si; 25°C) 7.44 (1H, br.s), 3.34 – 3.29 (2H, m), 2.36 – 2.32 (2H, m), 2.02 – 1.84 (4H, m).

Synthesis of azepan-2-one (Table 3, entry 21).¹⁵ To a solution of cyclohexanone oxime (226 mg, 2 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (165 mg, 0.6 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material

was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford azepan-2-one (208 mg, 92%). mp 70-71°C. ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 7.46 (1H, br.s), 3.21-3.16 (2H, m), 2.45-2.40 (2H, m), 1.75-1.71 (2H, m), 1.68-1.62 (4H, m).

Synthesis of 7-*tert*-butylazepan-2-one (Table 3, entry 22). To a solution of 2-*tert*-butylcyclohexanone oxime (339 mg, 2 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (165 mg, 0.6 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford 7-*tert*-butylazepan-2-one as a colorless oil (302 mg, 89%). ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 5.68 (1H, br.s), 3.03 (1H, dd, $J = 9.54\text{Hz}$; 6.02Hz), 2.52 (1H, dt, $J = 2.19\text{Hz}$; 12.80Hz), 2.45 – 2.40 (1H, m), 2.04 – 2.00 (1H, m), 1.97 – 1.92 (1H, m), 1.90 – 1.85 (1H, m), 1.60 – 1.45 (2H, m), 1.27 – 1.18 (1H, m), 0.96 (9H, s).

Synthesis of azocan-2-one (Table 3, entry 23). To a solution of cycloheptanone oxime (254 mg, 2 mmol in 5 mL acetonitrile) in a two-necked flask equipped with reflux condenser under nitrogen atmosphere, was added mercury(II) chloride (165 mg, 0.6 mmol). After being stirred at 80°C for 8 hr, the reaction mixture was allowed to cool and then acetonitrile (5 mL) was added to dissolve the solid formed. The solvent was stripped off and the organic material was taken up in dichloromethane (4x10 mL). The combined organic layers were washed with brine, dried over magnesium sulphate, and filtered. The filtrate was evaporated under reduced pressure and the residue obtained was purified by flash-column chromatography over silica gel (230-400 mesh) with a dichloromethane-methanol (100:4) eluent system to afford azocan-2-one as a colorless oil (122 mg, 48%). ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si ; 25°C) 7.28 (1H, br.s), 3.36 – 3.34 (2H, m), 2.44 (2H, t, $J = 6.52\text{Hz}$), 1.93 – 1.86 (2H, m), 1.82 – 1.79 (2H, m), 1.63 – 1.58 (2H, m), 1.55 – 1.49 (2H, m).

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- (15) ^1H NMR was compared with the authentic sample.

Entry 6 in Table 3

400MHz ^1H -NMR Spectrum of N-Phenylpropionamide in CDCl_3

Entry 23 in Table 3