Anionic phenoxy-amido rare-earth complexes as efficient catalysts for amidation of aldehydes with amines

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Table S1 Crystallographic data for complexes **1-4**

Compound	**1**	**2**	**3**	**4**
formula	$C_{56}H_{86}F_2Li_2N_3O_4Si_2Y$	$C_{56}H_{86}F_2Li_2N_3O_4Si_2Yb$	$C_{56}H_{86}F_2Li_2N_3O_4Si_2Sm$	$C_{56}H_{86}F_2Li_2N_3NdO_4Si_2$
*f*w	1062.25	1146.38	1123.69	1117.58
T(K)	223(2)	223(2)	223(2)	223(2)
crystal system	tetragonal	tetragonal	tetragonal	tetragonal
space group	$I4_1cd$	$I4_1cd$	$I4_1cd$	$I4_1cd$
crystal size (mm^3)	0.90× 0.60 × 0.40	0.30×0.25× 0.20	0.60 × 0.38 × 0.25	0.40×0.18× 0.10
a (Å)	21.175(2)	21.174(1)	21.239(1)	21.269(1)
b (Å)	21.175(2)	21.174(1)	21.239(1)	21.269(1)
c (Å)	26.984(3)	26.954(2)	27.125(2)	27.168(2)
V ($Å^3$)	12100(2)	12085(2)	12236(1)	12290(1)
Z	8	8	8	8
D_{calcd} (g cm^{-3})	1.166	1.260	1.220	1.208
μ (mm^{-1})	1.052	1.636	1.047	0.932
F(000)	4528	4776	4712	4696
θ_{max} (deg)	25.50	27.48	27.48	25.49
collected reflns	13836	36312	24559	30256
unique reflns	4733	6901	5573	5690
obsd reflns [$I > 2.0\sigma(I)$]	3529	5613	4818	4250
no. of variables	298	307	307	227
GOF	1.035	1.242	1.167	1.252
R	0.0599	0.0654	0.0500	0.0977
w*R*	0.1539	0.1286	0.1186	0.1385
largest diff peak, hole ($e.Å^{-3}$)	0.591, -0.427	0.515, -0.706	0.445,-0.612	0.391, -0.410

Table S2 Crystallographic data for complexes **5-8**

Compound	**5**	**6**	**7**	**8**
formula	$C_{56}H_{86}Cl_2Li_2N_3O_4Si_2Sm$	$C_{56}H_{86}Cl_2Li_2N_3O_4Si_2Nd$	$C_{56}H_{86}Br_2Li_2N_3O_4Si_2Sm$	$C_{56}H_{86}Br_2Li_2N_3O_4Si_2Nd$
*f*w	1156.59	1150.48	1245.51	1239.40
T(K)	223(2)	223(2)	223(2)	223(2)
crystal system	tetragonal	tetragonal	tetragonal	tetragonal
space group	$I4_1cd$	$I4_1cd$	$I4_1cd$	$I4_1cd$
crystal size (mm^3)	0.40 × 0.30 × 0.20	0.80 × 0.60 × 0.40	0.40 × 0.38 × 0.30	0.80 × 060 × 0.50
a (Å)	21.558(2)	21.6935(8)	21.658(2)	21.687(2)
b (Å)	21.558(2)	21.6935(8)	21.658(2)	21.687(2)
c (Å)	26.692(2)	26.918(1)	26.562(3)	26.622(3)
V ($Å^3$)	12405(2)	12668(1)	12460(2)	12522(2)
Z	8	8	8	8
D_{calcd} (g cm^{-3})	1.239	1.206	1.328	1.315
μ (mm^{-1})	1.114	0.983	2.306	2.186
F(000)	4840	4824	5128	5112
θ_{max} (deg)	27.49	26.37	27.50	27.45
collected reflns	20011	21602	28574	25396
unique reflns	5725	5093	6440	5836
obsd reflns [$I > 2.0\sigma(I)$]	4246	2943	5218	4427
no. of variables	315	297	318	317
GOF	1.186	1.014	1.240	1.099
R	0.0737	0.0441	0.0680	0.0479
w*R*	0.1341	0.0849	0.0986	0.1099
largest diff peak, hole ($e.Å^{-3}$)	0.439, -0.785	0.608, -0.380	0.879, -0.771	0.835, -0.858

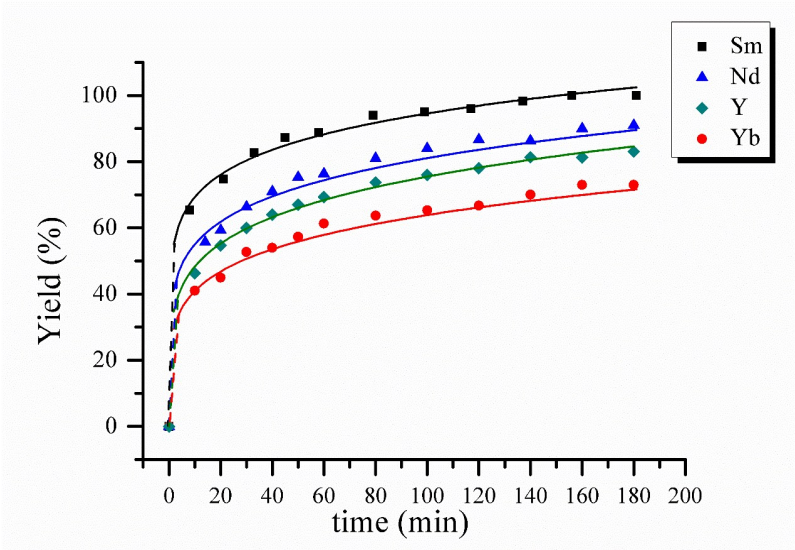


Fig. S1. The yield *vs.* reaction time plots for the amidation of benzaldehyde with *N*-methyl-benzylamine catalyzed by complexes **1** (Y), **2** (Yb), **3** (Sm) and **4** (Nd). Procedure: The catalyst (9.16 mg, 0.01 mmol) and d_8-THF (0.5 mL) was added to the NMR tube, and then *N*-methyl-benzylamine was added (0.065 mL, 0.5 mmol). The solution was kept for half an hour at room temperature, and then benzaldehyde was

added (0.15 mL, 1.5 mmol). Ferrocene (0.05 mmol, 9.3 mg) was used as the internal standard. The reaction was monitored by ^{1}H NMR spectroscopy for 3 h.

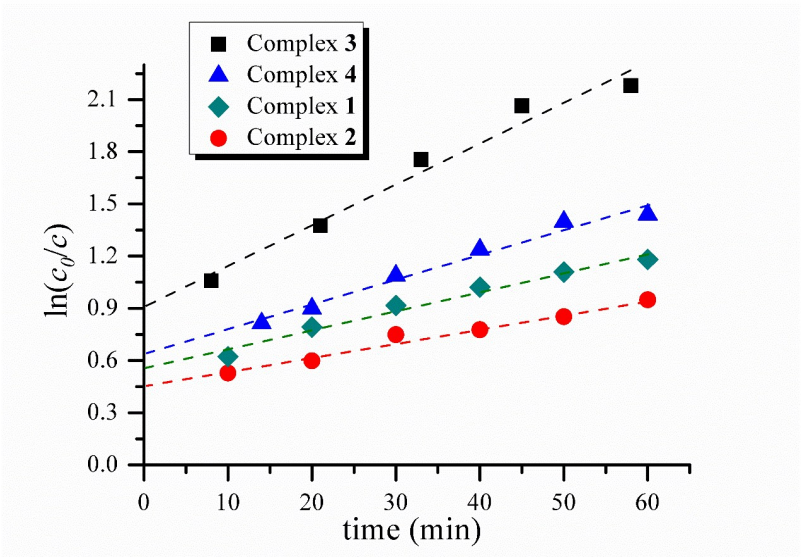
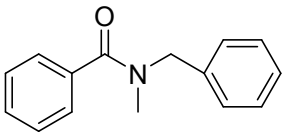


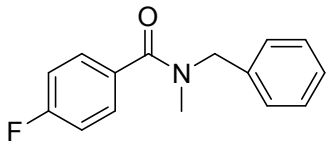
Fig. S2 Kinetics of the amidation of benzaldehyde with *N*-methyl-benzylamine catalyzed by complexes **1-4** in d_8-THF. (a) Complex **1**, k_{app} = 0.011 min^{-1} (linear fit, R^2 = 0.9715); (b) complex **2**, k_{app} = 0.0082 min^{-1} (linear fit, R^2 = 0.9711); (c) complex **3**, k_{app} = 0.0236 min^{-1} (linear fit, R^2 = 0.9623); (d) complex **4**, k_{app} = 0.0144 min^{-1} (linear fit, R^2 = 0.9609).

Spectroscopic data for the products

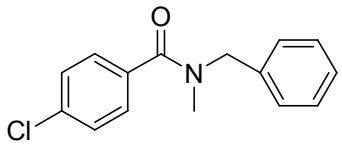


N-Benzyl-*N*-methylbenzamide (**13aa**). Purified by column chromatography (ethyl acetate: petroleum eater = 1:7). Colorless oil : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.85 (s, 1.5H), 3.02 (s, 1.5H), 4.51 (s, 1H), 4.76 (s, 1H), 7.16-7.47 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 33.1, 36.9, 50.7, 55.1, 126.7, 126.9, 127.4, 128.1, 128.3, 128.6, 128.7, 129.5, 136.1, 136.5, 136.9, 171.5, 172.2.

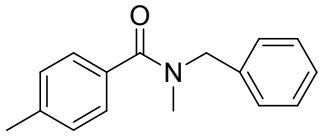
N-Benzyl-*N*-methyl-4-fluorobenzamide (**13ba**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:7). Colorless oil : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.88 (s, 1.5H), 3.04 (s, 1.5H), 4.52 (s, 1H), 4.75 (s, 1H), 7.08-7.49 (m, 9H); ^{13}C NMR



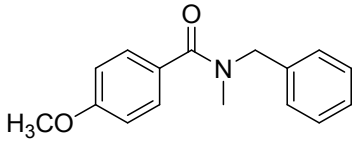
(100 MHz, $CDCl_3$) δ = 33.4, 36.9, 50.8, 55.1, 115.3, 115.6, 126.5, 127.6, 128.2, 128.8, 129.2, 132.1, 136.4, 136.8, 161.7, 165.0, 170.6, 171.4.



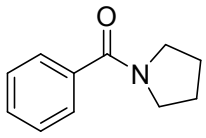
N-Benzyl-N-methyl-4-chlorobenzamide (**13ca**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:7). Colorless oil : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.85 (s, 1.5H), 3.02 (s, 1.5H), 4.49 (s, 1H), 4.73 (s, 1H), 7.15-7.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 33.3, 36.9, 50.8, 55.1, 126.5, 127.6, 128.1, 128.3, 128.4, 128.6, 132.9, 134.3, 135.7, 136.2, 136.6, 139.6, 170.5, 171.2.



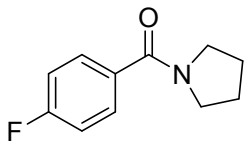
N-Benzyl-N-methyl-4-methylbenzamide (**13da**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:7). White solid : mp 67–68 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.36 (s, 3H), 2.90 (s, 1.5H), 2.97 (s, 1.5H), 4.52 (s, 1H), 4.73 (s, 1H), 7.19-7.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 33.4, 37.3, 51.0, 55.4, 126.9, 127.1, 127.3, 127.7, 128.3, 128.9, 129.2, 133.5, 137.0, 137.3, 139.9, 172.9



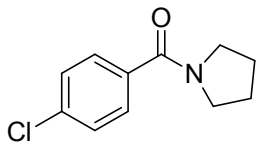
N-Benzyl-N-methyl-4-methoxybenzamide(**13ea**).Purified by column chromatography (ethyl acetate : petroleum ester = 1:7). Colorless oil : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.93 (s, 1.5H), 2.99 (s, 1.5H), 3.81 (s, 3H), 4.59 (s, 1H), 4.73 (s, 1H), 6.88-7.46 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 33.2, 37.0, 51.0, 55.1, 64.7, 113.5, 126.5, 127.4, 128.1, 128.4, 128.7, 128.9, 136.9, 160.6.



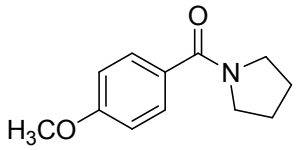
N-Benzoylpyrrolidine (**13ab**). Purified by column chromatography (ethyl acetate: petroleum ester = 1: 3). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.84-2.00 (m, 4H), 3.42 (t, J = 6.8 Hz, 2H), 3.65 (t, J = 6.8 Hz, 2H), 7.39-7.40 (m, 3H), 7.51-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.4, 26.4, 46.1, 49.6, 127.0, 128.2, 129.7, 137.2, 169.7.



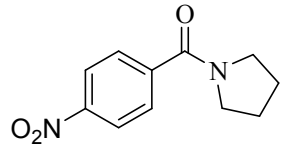
N-(*p*-Fluorobenzoyl)pyrrolidine (**13bb**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:3). White solid: mp 89-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.93 (brs, 4H), 3.55 (brs, 4H), 7.07-7.12 (m, 2H), 7.53-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.4, 26.3, 46.3, 49.7, 115.1, 115.4, 129.3, 129.4, 133.1, 133.2, 161.7, 165.0, 166.6.



N-(*p*-Chlorobenzoyl)pyrrolidine (**13cb**). Purified by column chromatography (ethyl acetate: petroleum ester = 1 : 3). White solid: mp 74-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.85-2.00 (m, 4H), 3.41 (t, J = 6.4 Hz, 2H), 3.63 (t, J = 6.8 Hz, 2H), 7.28-7.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.3, 26.3, 46.2, 49.5, 128.4, 128.5, 135.4, 135.7, 166.4.

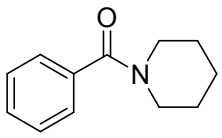


N-(*p*-Methoxybenzoyl)pyrrolidine (**13eb**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:3). White solid: mp 78-79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.89 (t, J = 6.8 Hz, 4H), 3.53 (t, J = 6.8 Hz, 4H), 3.80 (s, 3H), 6.87 (m, 2H), 7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.5, 26.4, 46.3, 49.7, 55.3, 113.3, 129.1, 129.3, 160.7, 169.4.

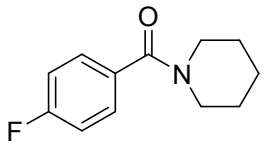


N-(*p*-Nitrobenzoyl)pyrrolidine (**13fb**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:6). White solid : mp 75-76 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.87-

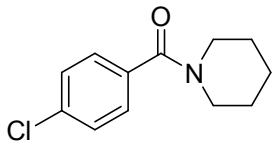
1.98 (m, 4H), 3.34-3.37 (m, 2H), 3.62-3.65 (m, 2H), 7.64-7.66 (m, 2H), 8.23-8.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.1, 27.1, 47.1, 50.2, 124.4, 128.9, 143.9, 149.1, 168.1.



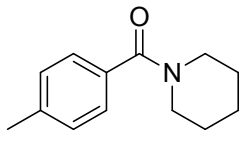
N-Benzoylpiperidine (**13ac**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:7). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.52 (brs, 2H), 1.68 (brs, 4H), 3.34 (brs, 2H), 3.72 (brs, 2H), 7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.5, 25.5, 26.4, 43.0, 48.7, 126.7, 128.3, 129.3, 136.4, 170.2.



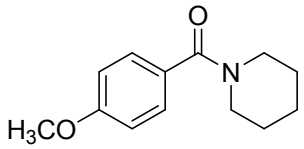
N-(*p*-Fluorobenzoyl)piperidine (**13bc**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:7) . White solid : mp56-57 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.54 (brs, 2H), 1.68 (brs, 4H), 3.35 (brs, 2H), 3.69 (brs, 2H), 7.07-7.11 (m, 2H), 7.39-7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.5, 25.5, 26.4, 43.2, 48.7, 115.2, 115.5, 128.9, 129.0, 132.3, 132.4, 161.5, 164.8, 169.3.



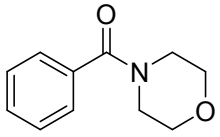
N-(*p*-Chlorobenzoyl)piperidine (**13cc**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:7) . White solid : mp79-80 ^{o}C: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.52 (brs, 2H), 1.68 (brs, 4H), 3.33 (brs, 2H), 3.69 (brs, 2H), 7.28-7.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.5, 25.5, 26.5, 43.2, 48.7, 128.2, 128.3, 128.5, 128.6, 133.1, 134.7, 135.4, 139.4, 169.2.



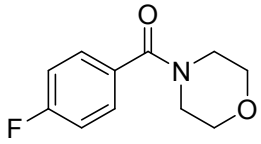
N-(p-Methylbenzoyl)piperidine (**13dc**). Purified by column chromatography (ethyl acetate: ester = 1:7). Colorless oil : ^{1}H NMR (400MHz, $CDCl_3$) δ = 1.52-1.67 (brs, 6H), 2.37 (s, 3H), 3.36 (s, 2H), 3.69 (s, 2H), 7.18-7.19 (m, 2H), 7.28-7.30 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 16.8, 20.1, 21.1, 21.9, 38.6, 44.2, 122.3, 124.4, 128.9, 134.9, 165.8.



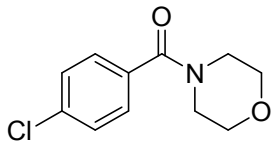
N-(*p*-Methoxybenzoyl)piperidine (**13ec**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:7). Colorless oil : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.60 (brs, 2H), 1.67 (brs, 4H), 3.45 (brs, 2H), 3.64 (brs, 2H), 3.82 (s, 3H), 6.89-6.91 (m, 2H), 7.36-7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.5, 26.0, 43.2, 48.7, 55.2, 113.5, 128.5, 128.7, 160.4, 170.2.



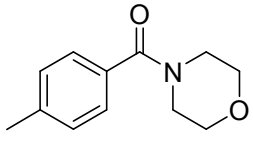
N-Benzoylmorpholine (**13ad**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:5). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.44-3.78 (m, 8H), 7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 43.1, 48.8, 67.6, 127.8, 129.3, 130.6, 136.1, 171.2.



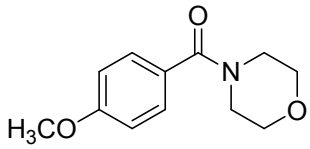
N-(p-Fluorobenzoyl)morpholine (**13bd**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:5). Colorless oil : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.49-3.70 (m, 8H), 7.08-7.12 (m, 2H), 7.39-7.43(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 43.1, 48.4, 67.0, 115.7, 116.0, 129.6, 129.7, 131.5, 162.0, 165.3, 169.7.



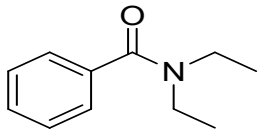
N-(p-Chlorobenzoyl)morpholine (**13cd**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:5). White solid: mp 76 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.45-3.73 (m, 8H), 7.34-7.40 (m, 4H); ^{13}C NMR (100 MHz, CDCl3) δ = 42.8, 48.5, 67.0, 128.9, 129.0, 133.8, 136.2, 169.5.



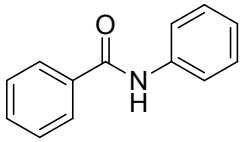
N-(p-Methylbenzoyl)morpholine (**13dd**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:5). White solid : mp 76-77 ^{o}C : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.36 (s, 3H), 3.67 (m, 8H), 7.19-7.21 (m, 2H); 7.28-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 42.8, 48.4, 67.1, 127.4, 129.3, 132.5, 140.3, 170.8.



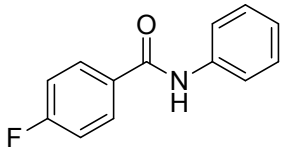
N-(*p*-Methoxybenzoyl)morpholine (**13ed**). Purified by column chromatography (ethyl acetate: petroleum ester = 1: 5). Colorless oil : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.63-3.67 (m, 8H), 3.81 (s, 3H); 6.90 (m, 2H); 7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 43.3, 48.4, 55.8, 67.3, 114.1, 127.6, 129.5, 161.1, 170.6.



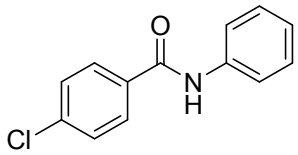
N-diethylbenzamide (**13ae**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:15). Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.17 (d, *J* = 57.5 Hz, 6H), 3.40 (d, *J* = 117.7 Hz, 4H), 7.31-7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.0, 14.3, 39.3, 43.4, 126.3, 126.9, 128.5, 129.2, 137.4, 171.4.



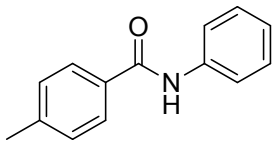
Phenylbenzamide (**13ah**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:15). White solid: mp 162-163 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14-7.89 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 120.2, 124.6, 127.0, 128.8, 129.1, 131.8, 134.9, 137.9, 165.7.



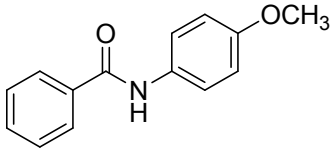
N-Phenyl-4-fluorobenzamide (**13bh**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:15). White solid : mp 188-189 ^{o}C; ^{1}H NMR (400 MHz, DMSO) δ = 7.07-7.12 (m, 1H), 7.32-7.39 (m, 4H), 7.74-7.77 (m, 2H), 8.01-8.05 (m, 2H), 10.25 (m, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 115.9, 116.2, 121.1, 124.4, 129.3, 131.1, 132.1, 139.7, 163.1, 165.1, 166.4.



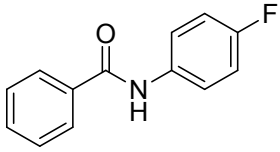
N-Phenyl-4-chlorobenzamide (**13ch**). Purified by column chromatography (ethyl acetate : petroleum ester = 1:15). White solid : mp 202-203 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (m, 1H), 7.36-7.40 (m, 2H), 7.47 (d, 2H), 7.61-7.64 (m, 2H), 7.82 (d, 2H); ^{13}C NMR (100 MHz, DMSO) δ = 164.2, 138.9, 131.1, 130.1, 128.4, 123.5, 120.2, 115.2, 115.0



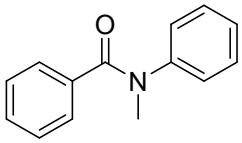
N-Phenyl-4-methylbenzamide (**13dh**). Purified by column chromatography (ethyl acetate : petroleum ester = 1:15). White solid : mp149-150 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.43 (s, 3H), 7.14 (m, 1H), 7.29 (m, 2H), 7.35-7.40 (m, 2H), 7.63-7.65 (d, 2H), 7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 120.7, 124.5, 127.6, 129.2, 129.6, 132.3, 138.4, 142.4, 166.1



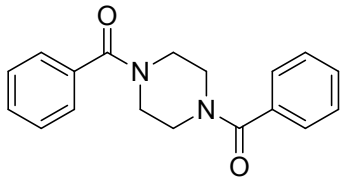
N-(*p*-Methoxy)phenylbenzamide (**13ai**). Purified by column chromatography (ethyl acetate: petroleum ester = 1:15). White solid : mp 160-161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.82 (s, 3H), 6.92 (m, 2H), 7.47-7.56 (m, 5H), 7.75 (brs, 1H), 7.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.5, 114.2, 122.0, 126.9, 128.7, 130.9, 131.7, 135.0, 156.6, 165.6.



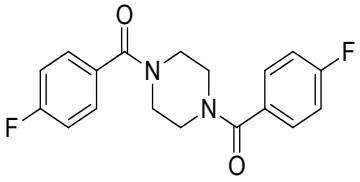
N-(*p*-Fluoro)phenylbenzamide (**13aj**). Purified by column chromatography (ethyl acetate : petroleum ester = 1 : 15). White solid : mp 185-186 ^{o}C, ^{1}H NMR (400 MHz, DMSO) δ = 7.06-7.09 (m, 2H) , 7.48-7.62 (m, 5H), 7.79 (s, 1H), 7.87 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ = 115.7, 116.0, 122.8, 123.0, 128.3, 129.1, 132.3, 135.5, 136.2, 166.1.



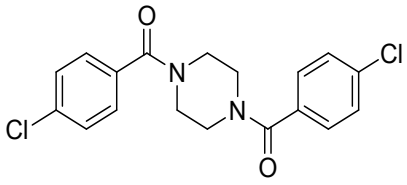
N-Phenyl-N-methylbenzamide (**13ak**). Purified by column chromatography (ethyl acetate: petroleum ester = 1: 7). White solid: mp 104-106 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.43 (s, *3*H), 6.97 (d, *J* = 7.7 Hz, 2H), 7.01-7.19 (m, 6H), 7.24(d, *J* = 1.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =38.2, 126.3, 126.7, 127.5, 128.5, 129.0, 129.4, 135.7, 144.7, 170.4.



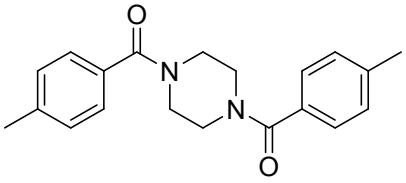
N,N'-Dibenzoylpiperazidine (**13am**). Purified by column chromatography (ethyl acetate : petroleum ester = 1 : 1). White solid: mp 196-197 ^{o}C , ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.64 (d, *J* = 87.3 Hz, 8H), δ = 7.41 (s, 10H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 48.1, 127.6, 129.2,130.7, 135.7, 171.2.



N,N'-di(p-Fluorobenzoyl)piperazidine (**13bm**). Purified by column chromatography (ethyl acetate: petroleum ester = 1 : 1). White solid: mp 258 - 259 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.63 (brs, 8H), 7.11 (m, 4H), 7.43 (m, 4H); ^{13}C NMR (100 MHz, DMSO) δ = 26.5, 132.8, 134.6, 138.1, 145.2, 175.2.

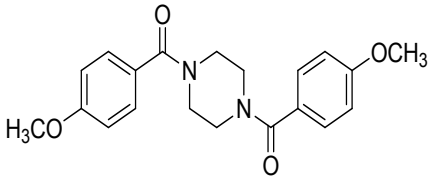


N,N'-di(*p*-Chlorobenzoyl)piperazidine (**13cm**). Purified by column chromatography (ethyl acetate: petroleum ester = 1 : 1). White solid: mp 223-224 ^{o}C, ^{1}H NMR (300 MHz, DMSO) δ = 3.63 (m, 8H), 7.49 (d, *J* = 12.2 Hz, 8H); ^{13}C NMR (75 MHz, DMSO) δ = 41.7, 128.6, 129.0, 134.4, 168.2.

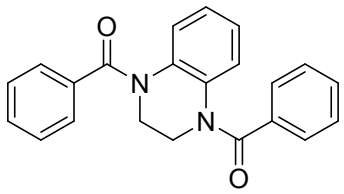


N,N'-di(p-Methylbenzoyl)piperazidine (**13dm**). Purified by column chromatography (ethyl acetate:

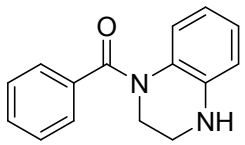
petroleum ester = 1 : 1). White solid: mp 213 -214 ^{o}C, ^{1}H NMR (300 MHz, DMSO) δ = 2.39 (s, 6H), 3.55 (brs, 8H), δ 7.34 (d, *J* = 13.6 Hz, 8H); ^{13}C NMR (75 MHz, DMSO) δ = 20.9, 42.0, 127.2, 128.9, 132.7, 139.4, 169.3.



N,N'-di(*p*-Methoxybenzoyl)piperazidine (**13em**). Purified by column chromatography (ethyl acetate: petroleum ester = 1 : 1). White solid: mp 204-205 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.65(s, 8H), 3.83 (d, *J* = 6.5 Hz, 6H), 6.92 (d, *J* = 8.6 Hz, 4H), 7.40 (d, *J* = 8.6 Hz, 4H)); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.4, 113.9, 127.2, 129.3, 161.0, 170.7.



N,N'-diBenzoyl-1,2,3,4-tetrahydro-quinoxaline (**13an**). Purified by column chromatography (ethyl acetate: petroleum ester = 1: 5). White solid : mp 205 -207 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.15 (s, 4H), 6.76 (s, 4H), 7.36 (t, *J* = 7.4 Hz, 4H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 46.3, 124.8, 125.4, 128.5, 128.7 131.0, 133.7, 135.2, 169.6.



1-Benzoyl-1,2,3,4-tetrahydro-quinoxaline (**13an-2**). Purified by column chromatography (ethyl acetate: petroleum ester = 1: 5). White solid : mp 161 -163 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.52 (s, 2H), 3.96 (s, 2H), 4.16 (s, 1H), 6.36 (s, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.84 (m, 1H) , 7.33 (m, 3H), 7.45 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 42.8, 114.6, 116.3, 124.7, 125.2, 125.8, 128.2, 128.7, 130.2, 135.9, 137,1.