Supplementary Material (ESI) for Chemical Communications

Supporting Information

For

Remarkable Ligand Effect on the Palladium Catalyzed Double Carbonylation of Aryl Iodides

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General Comments.

1H-NMR spectra were recorded on a JEOL AL400 using tetramethylsilane as an internal standard. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in herts (Hz). The following abbreviations are used: s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet, br= broad singlet. Mass spectra were recorded on JEOL JMS- DX303 or JEOL JMS-AX500 spectrometer. IR spectra were measured with SensIR ATR FT-IR.

Procedures and Characterization

(Table 1, entry 1)

A test tube was charged with 4-iodonitrobenzene (124.6 mg, 0.5 mmol), $Pd_2(dba)_3$□ $CHCl_3$ (5.1 mg, 0.005 mmol) and triphenylphosphine (5.0 mg, 0.02mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 3 h. After the reaction, solvent was removed under reduced pressure.

(Table 1, entry 2)

A test tube was charged with 4-iodonitrobenzene (124.9 mg, 0.5 mmol), $Pd_2(dba)_3$□ $CHCl_3$ (4.3 mg, 0.005 mmol) and DPPF (5.8 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 14 h. After the reaction, solvent was removed under reduced pressure.

(Table 1, entry 3)

A test tube was charged with 4-iodonitrobenzene (124.5 mg, 0.5 mmol), $Pd_2(dba)_3$□ $CHCl_3$ (4.8 mg, 0.005 mmol) and DPPP (4.8 mg, 0.01mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and pyrrolidine (0.1 ml, 1 mmol) were added. The mixture was stirred at room temperature for 14 h. After the reaction, solvent was removed under reduced pressure.

(Table 1, entry 4)

A test tube was charged with 4-iodonitrobenzene (124.9 mg, 0.5 mmol), $Pd_2(dba)_3$□$CHCl_3$ (4.4 mg, 0.005 mmol) and *t*-Bu_3P□HBF_4 (6.9 mg, 0.02 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and pyrrolidine (0.1 ml, 1 mmol) were added. The mixture was stirred at room temperature for 3 h. After the reaction, solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (7/3) to give 1-(4-nitrophenyl)-2-pyrrolidin-1-yl-ethane-1, 2-dione (90.5 mg, 73 %).

(Table 1, entry 5)

A test tube was charged with 4-iodonitrobenzene (125.7 mg, 0.5 mmol), $Pd_2(dba)_3$□$CHCl_3$ (4.6 mg, 0.005 mmol) and PCy_3□HBF_4 (8.3 mg, 0.02 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 24 h. After the reaction, solvent was removed under reduced pressure.

(Table 1, entry 6)

A test tube was charged with 4-iodonitrobenzene (126 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (4.9 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 2 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (7/3) to give 1-(4-nitrophenyl)-2-pyrrolidin-1-yl-ethane-1, 2-dione (97 mg, 78 %).

(Table 1, entry 7)

A test tube was charged with 4-iodonitrobenzene (126.3 mg,, 0.5 mmol), and Pd(*t*-$Bu_3P)_2$ (5.7 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and triethylamine (0.1 ml, 0.7 mmol) were added. The mixture was stirred at room temperature for 24 h. After the reaction, solvent was removed under reduced pressure.

(Table 1, entry 8)

A test tube was charged with 4-iodonitrobenzene (126.3 mg, 0.5 mmol), $Pd_2(dba)_3$□ $CHCl_3$ (5.2 mg, 0.05 mmol) *t*-Bu_3P□HBF_4 (6.2 mg, 0.02 mmol) and DABCO (114.5 mg, 1 mmol). Under carbon monoxide atmosphere THF (5 ml) and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 14 h. After the reaction, solvent was removed under reduced pressure.

(Table 1, entry 9)

A test tube was charged with 4-iodonitrobenzene (124.4 mg, 0.5 mmol) Pd(*t*-$Bu_3P)_2$ (2.4 mg, 0.01mmol) and Cs_2CO_3 (324.7 mg, 1 mmol). Under carbon monoxide atmosphere THF (5 ml), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 1.5 h. After the reaction, solvent was removed under reduced pressure.

(Table 1, entry 10)

A test tube was charged with 4-iodonitrobenzene (125.2 mg, 0.5 mmol) Pd(*t*-$Bu_3P)_2$ (2.7 mg, 0.01 mmol), and K_3PO_4 (217.5 mg, 1 mmol). Under carbon monoxide atmosphere THF (5 ml) and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 1.5 h. After the reaction, solvent was removed under reduced pressure.

(Table 1, entry 11)

A test tube was charged with 4-iodonitrobenzene (124 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (2.7 mg, 0.005 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and butylamine (0.1 ml, 1 mmol) were added. The mixture was stirred at room temperature for 12 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (4/1) to give *N*-butyl-2-(4-nitrophenyl)-2-oxoacetamide (58 mg, 45 %).

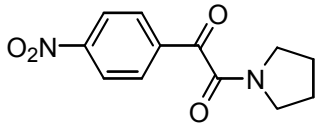
(Table 1, entry 12)

A test tube was charged with 4-iodonitrobenene (125 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (5.5 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and *tert*-butylamine (0.1 ml, 0.92 mmol) were added. The mixture was stirred at room temperature for 7 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (4/1) to give *N*-*tert*-butyl-2-(4-nitrophenyl)-2-oxoacetamide (68 mg, 55 %).

(Table 1, entry 13)

A test tube was charged with 4-iodonitrobenzene (124 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (5.5 mg, 0.01 mmol). Under carbonmonoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and diethylamine (0.1 ml, 0.97 mmol) were added. The mixture was stirred at room temperature for 9 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (7/3) to give N, *N*-diethyl-2-(4-nitrophenyl)-2-oxoacetamide (106 mg, 85 %)

1-(4-Nitro-phenyl)-2-pyrrolidin-1-yl-ethane-1,2-dione (5a)



mp 117 °C

IR (neat) (cm^{-1}): 2964, 2881, 1683, 1627, 1552, 733

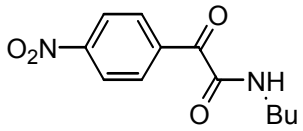
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 1.96-2.02 (4H, m), 3.50 (2H, t, *J* = 6.8 Hz), 3.67 (2H, t, *J* = 6.8Hz), 8.20 (2H, d, *J* = 9.0 Hz), 8.33 (2H, d, *J* = 9.0 Hz).

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 23.9, 25.9, 45.6, 46.9, 123.9, 131.0, 137.6, 150.9, 163.1

MS *m/z*: 248

HRMS *m/z* Calcd for $C_{13}H_{15}NO_3$: 248.0797. Found: 248.0776

_N_-n-Butyl-2-(4-nitrophenyl)-2-oxoacetamide (5b)



mp 69 °C

IR (neat) (cm^{-1}): 3384, 2958, 1656, 1598, 1522, 1472. 1349, 872, 816, 739

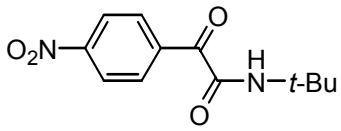
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 0.97 (3H, t, *J*=7.3 Hz), 1.37-1.47 (2H, m), 1.57-1.66 (2H, m), 3.39-3.45 (2H, m), 7.19 (1H, br), 8.02 (2H, d, *J*=9.3 Hz), 8.53 (2H, d, *J*=9.3 Hz)

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 13.7, 20.1, 31.2, 39.3, 123.3, 132.2, 137.8, 150.6, 160.3, 186.0

MS *m/z*: 250 (M^+)

HRMS *m/z* Calcd for $C_{12}H_{14}N_2O_4$: 250.0954. Found: 250.0961

***N-tert*-Butyl-2-(4-nitrophenyl)-2-oxoacetamide (5c)**



mp 88 °C

IR (neat) (cm^{-1}): 3388, 2970, 1671, 1602, 1517, 1351, 831, 740

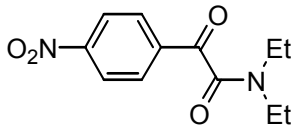
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 1.47 (9H, s), 7.00 (1H, br), 8.29 (2H, d, *J* = 9.2 Hz), 8.49 (2H, d, *J* = 9.2 Hz)

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 28.2, 51.9, 123.3, 132.3, 138.1, 150.7, 159.8, 186.9

MS *m/z*: 250 (M^+)

HRMS *m/z* Calcd for $C_{12}H_{14}N_2O_4$: 250.0954. Found: 250.0942

***N*, *N*-Diethyl-2-(4-nitrophenyl)-2-oxoacetamide (5d)**



mp 84 °C

IR (neat) (cm^{-1}): 2971, 1739, 1690, 1636, 1526, 1347, 1225, 1027, 789, 708

400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 1.19 (3H, t, *J* = 7.1 Hz), 1.31 (3H, t, *J* = 7.1 Hz), 3.27 (2H, q, *J* = 7.1 Hz), 3.59 (2H, q, *J* = 7.1 Hz), 8.13 (2H, d, *J* = 9.0 Hz), 8.35 (2H, d, *J* = 9.0 Hz)

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 12.9, 14.3, 39.2, 42.2, 124.0, 130. 6, 137.6, 150.8, 165.2, 188.9

MS *m/z*: 250 (M^+)

HRMS *m/z* Calcd for $C_{12}H_{14}N_2O_4$: 250.0954.Found: 250.9700

(Table 2, entry 1)

A test tube was charged with 4-iodobenzonitrile (117 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (4.9 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were was stirred at room temperature for 1.5 h. After the reaction, solvent was removed and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (7/3) to give 4-(2-oxo-2-pyrrolidin-1-ylacetyl)benzonitrile (107 mg, 92 %).

(Table 2, entry 2)

A test tube was charged with 4-iodobenzonitrile (117 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (5.7 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and butylamine (0.1 ml, 1 mmol) were added. The mixture was stirred at room temperature for 12 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (4/1) to give *N*-butyl-2-(4-cyanophenyl)-2-oxoacetamide (67 mg, 60 %).

(Table 2, entry 3)

A test tube was charged with 4-iodobenzoic acid ethyl ester (138 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (5.2 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 2 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (7/3) to give 4-(2-oxo-2-pyrrolidin-1-ylacetyl)benzoic acid ethyl ester (136 mg, 99 %).

(Table 2, entry 4)

A test tube was charged with 4-iodobenzoic acid ethyl ester (142 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (4.9 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and butylamine (0.1 ml, 1 mmol) were added. The mixture was stirred at room temperature for 12 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (4/1) to give 4-butylamino oxalyl-benzoic acid ethyl ester (108 mg, 76 %).

(Table 2, entry 5)

A test tube was charged with 4-iodobenzene (103 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (5.2 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 24 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (1/1) to give 1-phenyl-2-pyrrolidine-1-yl-ethane-1,2-dione (94 mg, 92 %).

(Table 2, entry 6)

A test tube was charged with 4-iodobenzene(115 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (5.0 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and butylamine (0.1 ml, 1 mmol) were added. The mixture was stirred at room temperature for 12 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (4/1) to give N-butyl-2-oxo-2-phenylacetamide (74 mg, 64 %).

(Table 2, entry 7)

A test tube was charged with 4-iodoanisole (115 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (5.5 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml, 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 24 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (1/1) to give 1-(4-methoxyphenyl)-2-pyrrolidin-1-ylethane-1, 2-dione (107 mg, 93 %).

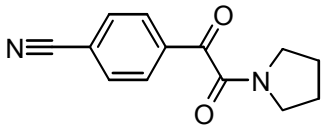
(Table 2, entry 8)

A test tube was charged with 4-iodoanisole (117 mg, 0.5 mmol) and Pd(*t*-$Bu_3P)_2$ (5.0 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (1 ml), DBU (0.15 ml, 1 mmol), and butylamine (0.1 ml, 1 mmol) were added. The mixture was stirred at room temperature for 12 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (4/1) to give N-butyl-2(4-methoxyphenyl)-2-oxoaceamide (109 mg, 73 %).

(Table 2, entry 9)

A test tube was charged with methyl-2-iodobenzoate (130.0 mg, 0.5 mmol), Pd(*t*-$Bu_3P)_2$ (5.8 mg, 0.01 mmol). Under carbon monoxide atmosphere THF (5 ml), DBU (0.15 ml 1 mmol), and pyrrolidine (0.1 ml, 1.2 mmol) were added. The mixture was stirred at room temperature for 3.5 h. After the reaction, solvent was removed under reduced pressure. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (1/1) to give 2-(2-oxo-2-pyrrolidin-1-yl-acetyl)-benzoic acid metyl ester (88.7 mg, 68%).

4-(2-Oxo-2-pyrrolidine-1-ylacetyl)benzonitrile (9a)



mp 86-90 ^{o}C

IR (neat) (cm^{-1}): 2973, 2883, 2231, 1686, 1632, 1451, 760

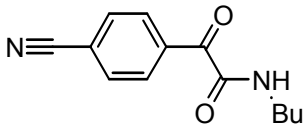
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 1.95-2.01 (4H, m), 3.48 (2H, t, *J* = 6.8 Hz), 3.64 (2H, t, *J* = 7.0 Hz), 7.80 (2H, d, *J* = 8.5 Hz), 8.13 (2H, d, *J* = 8.5Hz)

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 23.8, 25.8, 45.5, 46.7, 117.3, 117,6, 130.2, 132.5, 136.0, 163.2, 189.3

MS *m/z*: 228

HRMS *m/z* Calcd for $C_{13}H_{12}N_2O_2$: 228.0899. Found: 228.0876

***N*-butyl-2-(4-cyanophenyl)-2-oxoacetamide (9b)**



mp 44 ^{o}C

IR (neat) (cm^{-1}): 3298, 2931, 2236, 1652, 1526, 1229, 795

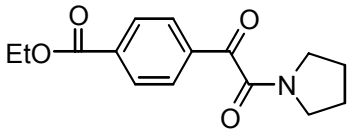
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 0.96 (3H, t, *J* = 7.3 Hz), 1.36-1.46 (2H, m), 1.56-1.65 (2H, m), 3.37-3.43 (2H, m), 7.17 (1H, br), 7.77 (2H, d, *J* = 8.8 Hz), 8.45 (2H, d, *J* = 8.8 Hz)

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 13.7, 20.0, 31.2, 39.3, 117.2, 117.7, 131.4, 132.0, 136.4, 160.4, 186.3

MS *m/z*: 230 (M^+)

HRMS *m/z* Calcd for $C_{13}H_{14}N_2O_2$: 230.1055. Found: 230.1070

4-(2-Oxo-2-pyrrolidin-1-ylacetyl)benzoic acid ethyl ester (9c)



oil

IR (neat) (cm^{-1}): 2979, 2881, 1717, 1683, 1636, 1449, 1013, 737, 687

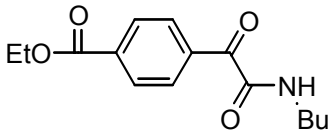
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 1.42 (3H, t, *J* = 7.1 Hz), 1.93-2.01 (4H, m), 3.45 (2H, t, *J* = 6.6 Hz), 3.67 (2H, t, *J* = 7.1 Hz), 4.41 (2H, q, *J* = 7.1 Hz), 8.06 (2H, d, *J* = 8.5 Hz), 8.15 (2H, d, *J* = 8.5 Hz)

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 14.1, 23.9, 25.8, 45.3, 46.6, 61.5, 129.7, 129.8, 135.3, 136.0, 164.1, 165.4, 190.6

MS *m/z*: 275

HRMS *m/z* Calcd for $C_{15}H_{17}NO_4$: 275.1158. Found: 275.1151

4-Butylamino oxalyl-benzoic acid ethyl ester (9d)



oil

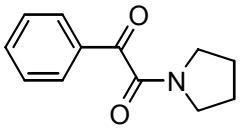
IR (neat) (cm^{-1}): 3355, 2960, 1719, 1663, 1522, 1270, 757.

400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 0.97 (3H, t, *J* = 7.3 Hz), 1.36-1.46 (5H,m), 1.56-1.65 (2H, m), 3.37-3.43 (2H, m), 4.41 (2H, q, J=7.2), 7.11 (1H, br), 8.12 (2H, d, *J* = 8.8 Hz), 8.39 (2H, d, *J* = 8.8 Hz).

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 13.7, 14.3, 20.1, 31.3, 39.3, 61.5, 129.3, 131.0, 135.0, 136.5, 161.0, 165.5, 187.2.

MS *m/z*: 277 (M^+)

1-Phenyl-2-pyrrolidine-1-yl-ethane-1,2-dione (9e)



oil

IR (neat) (cm^{-1}): 2956, 2881, 1675, 1630, 1596, 1443, 1241, 1013

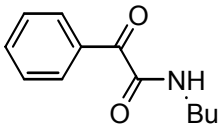
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 1.91-2.01 (4H, m), 3.43 (2H, t, *J* = 6.6 Hz), 3.66 (2H, t, *J* = 6.8 Hz), 7.48-7.54 (2H, m), 7.61-7.67 (1H, m), 7.98-8.03 (2H, m)

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 23.9, 25.7, 45.1, 46.5, 128.9, 129.7, 132.8, 134.5, 164.8, 191.5

MS *m/z*: 203

HRMS *m/z* Calcd for $C_{12}H_{13}NO_2$: 203.0946. Found: 203.0934

N-Butyl-2-oxo-2-phenylacetamide (9f)



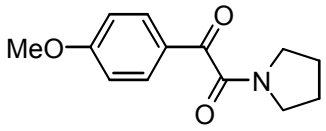
oil

IR (neat) (cm^{-1}): 3334, 2960, 1661, 1559, 1540, 1227, 688

400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 0.96 (3H, t, *J* = 7.3 Hz), 1.35-1.47 (2H, m), 1.55-1.64 (2H, m), 3.37-3.43 (2H, m), 7.12 (1H, br), 7.45-7.54 (2H, m), 7.60-7.64 (1H, m), 8.32-8.35 (2H, m)

MS *m/z*: 205 (M^+)

1-(4-methoxy-phenyl)-2-pyrrolidin-1-ylethane-1, 2-dione (9g)



oil

IR (neat) (cm^{-1}): 2956, 1665, 1629, 1594, 1246, 1015, 710.

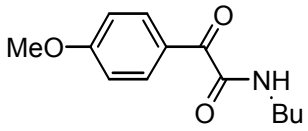
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 1.91-1.98 (4H, m), 3.42 (2H, t, *J* = 6.3 Hz), 3.64 (2H, t, *J* = 6.3 Hz), 3.89 (3H, s), 6.96 (2H, d, *J* = 9.0 Hz), 7.97 (2H, d, *J* = 9.0 Hz).

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 23.9, 25.8, 45.1, 46.6, 55.5, 114.2, 125.9, 132.2, 164.7, 165.2, 190.2

MS *m/z*: 233

HRMS *m/z* Calcd for $C_{13}H_{15}NO_3$: 233.1052. Found: 233.1037

N-Butyl-2(4-methoxyphenyl)-2-oxoaceamide (9h)



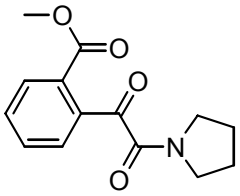
mp 65 ^{o}C

IR (neat) (cm^{-1}): 3244, 2960, 1669, 1630, 1559, 1509, 1266, 687.

400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 0.95 (3H, t, *J* = 7.5 Hz), 1.33 (2H, m), 1.52 (2H, m), 3.34-3.41 (2H, m), 3.88 (3H, s), 6.94 (2H, d, *J* = 8.9 Hz), 7.21 (1H, br), 8.41 (2H, d, *J* = 8.9 Hz)

MS *m/z*: 235 (M^{+})

2-(2-Oxo-2-pyrrolidin-1-yl-acetyl)benzoic acid methyl ester (9i)



oil

IR (neat) (cm^{-1}): 2973, 2952, 2877, 1733, 1708, 1634, 1594, 1287, 795.

400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 1.88-1.97 (2H, m), 1.98-2.07 (2H, m) 3.51 (2H, t, *J*=6.5 Hz), 3.86 (3H, s), 3.92 (2H, t, *J*=7.0Hz), 7.51-7.59 (1H, m), 7.63 (1H, s), 7.64 (1H, s), 7.91 (2H, d, *J*=7.5Hz).

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 23.8, 26.4, 46.3, 47.4, 52.5, 129.0, 129.6, 130.2, 131.0, 132.4, 139.2, 162.6, 167.1, 192.3.

MS *m/z*: 261

HRMS *m/z* Calcd for $C_{14}H_{15}NO_4$:261.1001. Found: 261.0989.

(Table 3, entry 1)

A test tube was charged with 4-iodoanisole (128 mg, 0.5 mmol), $[Pd(C_3H_5)Cl]_2$ (2.3mg, 0.005 mmol), triphenylphosphine (5.6 mg, 0.01 mmol), and $Mo(CO)_6$ (207.1 mg, 0.75 mmol). The test tube was backfilled with argon. And then DBU (0.15 ml 1 mmol), THF (5 ml), benzylamine (0.1 ml, 0.92 mmol) were added. The tube was sealed with screwcap and the mixture was stirred at room temperature for 24 h. After the reaction, solvent was removed.

(Table 3, entry 2)

A test tube was charged with 4-iodoanisole (117 mg, 0.5 mmol), $[Pd(C_3H_5)Cl]_2$ (2.5 mg, 0.005 mmol), triphenylphosphine (5.4 mg, 0.02 mmol) $Mo(CO)_6$ (197.8 mg, 0.75 mmol) and DABCO (111.5 mg, 1 mmol). The test tube was backfilled with argon. And then THF (5 ml) and benzylamine (0.1 ml, 0.92 mmol) were added. The tube was sealed with screwcap and the mixture was stirred at room temperature for 24 h. After the reaction, solvent was removed.

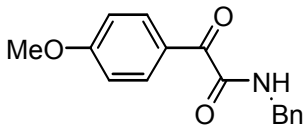
(Table 3, entry 3)

A test tube was charged with 4-iodoanisole (125 mg, 0.53 mmol), Pd(t-Bu_3P)$_2$ (5.3 mg, 0.01 mmol), and $Mo(CO)_6$ (199 mg, 0.75 mmol). The test tube was backfilled with argon. And then DBU (0.15 ml 1 mmol), THF (1 ml), benzylamine (0.1 ml, 0.92 mmol) were added. The tube was sealed with screwcap and the mixture was stirred at room temperature for 24h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (4/1) to give *N*-benzyl-2-(4-methoxyphenyl)-2-oxoacetamide (100 mg, 70 %) was obtained.

(Table 3, entry 4)

A test tube was charged with 4-iodoanisole (116 mg, 0.5 mmol), Pd(t-Bu_3P)$_2$ (5.3 mg, 0.01 mmol), $Mo(CO)_6$ (199 mg, 0.75 mmol), and DABCO (131 mg, 1.2 mmol). The test tube was backfilled with argon. THF (1 ml) and benzyl amine (0.1 ml, 0.92 mmol) were added. The tube was sealed with screwcap and the mixture was stirred at room temperature for 24 h. After the reaction, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using hexane/ethyl acetate (7/3) to give *N*-benzyl-4-methoxybenzamide (81 mg, 67%).

***N*-Benzyl-2-(4-methoxyphenyl)-2-oxoacetamide (10)**



mp 89 ^{o}C

IR (neat) (cm^{-1}): 3236, 1671, 1632, 1596, 1559, 1266, 1173, 1025, 858, 698

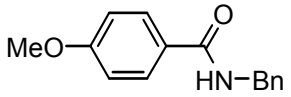
400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 3.89 (3H, s), 4.56 (2H, d, J = 5.6 Hz), 6.95 (2H, d, J = 9.0 Hz), 7.27-7.40 (5H, m), 7.45 (1H, br), 8.44 (2H, d, J = 9.0 Hz)

100MHz ^{13}C-NMR($CDCl_3$/TMS)δ(ppm): 43.4, 55.5, 113.8, 126.3, 127.7, 127.8, 128.7, 133.9, 137.1, 161.9, 164.6, 185.2

MS *m/z*: 269 (M^+)

HRMS *m/z* Calcd for $C_{16}H_{15}NO_3$: 269.1052. Found: 269.1052

_N_-Benzyl-4-methoxybenzamide (11)



mp 128 ^{o}C

IR (neat) (cm^{-1}): 3253, 2956, 1630, 1507, 1248, 841, 721

400MHz ^{1}H-NMR($CDCl_3$/TMS)δ(ppm): 3.84 (3H, s), 4.63 (2H, d, J = 5.4 Hz), 6.33 (1H, br), 6.91 (2H, d, J = 8.8 Hz), 7.26-7.38 (5H, m), 7.75 (2H, d, J = 8.8 Hz)

MS m/z: 241 (M^+)