Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Nickel-catalyzed coupling of isocyanates with 1,3-iodoesters and halobenzenes: a novel method for the synthesis of imide and amide derivatives

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Experimental section

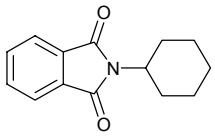
General procedure for the cycloaddition of isocyanates with iodobenzoates: To a screw-capped vial were added $NiBr_2$(dppe) (62 mg, 0.10 mmol), dppe (40 mg, 0.10 mmole), Zn (128 mg, 2.0 mmol). The vial was sealed with septum and flushed several times with nitrogen. Iodobenzoate (1.0 mmol), isocyanate (5.0 mmol), triethylamine (10 mg, 0.10 mmol) and acetonitrile (2.0 mL) were injected into the reaction mixture via a syringe (Solid isocyanates and dimethoxyiodobenzoate could be added to vial immediately after the catalyst.). The septum was removed, and the vial was sealed with a screw cap quickly under nitrogen. The reaction mixture was stirred at 80 ^oC for 36 h. The crude reaction mixture was diluted with CH_2Cl_2, filtered through a thin Celite pad, and concentrated *in vacuo*. The residue was chromatographed on a silica gel column using hexane and EA as the eluent to give the pure product. (Since isocyanates are toxic, the reaction and the following work-up should be carried out in a well-ventilated hood).

Products **3a-o** were obtained according to this procedure. Spectral data for these compounds are listed below.

General procedure for the synthesis of amide: $NiBr_2$(dppe) (62 mg, 0.10 mmol), dppe (40 mg, 0.10 mmole) and Zn (128 mg, 2.0 mmol) were placed in a screw-capped vial. The vial was sealed with a septum and flushed several times with nitrogen. Bromobenzene or iodobenzene (1.0 mmol), isocyanate (2.0 mmol) and acetonitrile (2.0 mL) were injected into the reaction mixture via a syringe (Solid isocyanates and solid halobenzene could be added to the vial immediately after the catalyst.). The septum was removed, and the vial was sealed with a screw cap quickly under nitrogen. The reaction mixture was stirred at 80 ^oC for 16 h. The crude reaction mixture was diluted with CH_2Cl_2, filtered through a thin Celite pad, and concentrated *in vacuo*. The residue was chromatographed on a silica gel column using hexane and EA as the eluent to give the pure product.

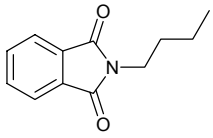
Products **9a-f** were obtained according to this procedure. Spectral data for these compounds are listed below.

2-Cyclohexylisoindoline-1,3-dione (3a):



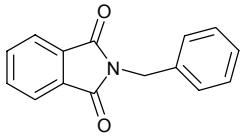
white solid, mp: 169-171 ^oC; IR (KBr): 1770 (m, $\nu_{C=O}$), 1707 (s, $\nu_{C=O}$) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ1.23-1.39 (m, 3 H), 1.68 (d, J = 8 Hz, 3 H), 1.83 (d, J = 8 Hz, 2 H) , 2.18 (d, q, J_1 = 12 Hz, J_2 = 3 Hz, 2 H), 4.08 (t, t, J_1 = 12 Hz, J_2 = 3.5 Hz, 1 H), 7.66 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H), 7.79 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ25.1, 26.0, 29.8, 50.9, 123.0, 132.0, 133.7, 168.5; HRMS: $C_{14}H_{15}NO_2$ calculated 229.1103, found 229.1100.

2-Butylisoindoline-1,3-dione (3b):



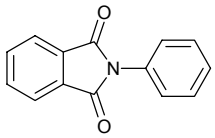
white solid, mp: 105-107 ^{o}C; IR (KBr): 1772 (m, $\nu_{C=O}$), 1714 (s, $\nu_{C=O}$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ0.92 (t, J = 8 Hz, 3 H), 1.33 (m, 2 H), 1.63 (m, 2 H), 3.66 (t, J = 7.5 Hz, 2 H), 7.67 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H) , 7.81 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ13.6, 20.1, 30.6, 37.8, 123.1, 132.2, 133.8, 168.5; HRMS: $C_{12}H_{13}NO_2$ calculated 203.0946, found 203.0946.

2-Benzylisoindoline-1,3-dione (3c):



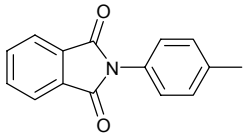
white solid, mp: 113-115 ^{o}C; IR (KBr): 1770 (m, $\nu_{C=O}$), 1702 (s, $\nu_{C=O}$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ4.83 (s, 2 H), 7.25 (t, J = 6 Hz, 1 H), 7.31 (t, J = 6 Hz, 2 H), 7.42 (d, J = 6 Hz, 2 H), 7.69 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H) , 7.83 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ41.6, 123.4, 127.8, 128.6, 128.7, 132.1, 134.0, 136.3, 168.1; HRMS: $C_{15}H_{11}NO_2$ calculated 237.0790, found 237.0791.

2-Phenylisoindoline-1,3-dione (3d):



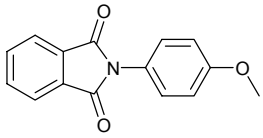
white solid, mp: 208-210 ^{o}C; IR (KBr): 1732 (m, $\nu_{C=O}$), 1698 (s, $\nu_{C=O}$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ7.39-7.43 (m, 3 H), 7.49 (t, J = 7.5 Hz, 2 H), 7.78 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H) , 7.95 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ123.8, 126.6, 128.1, 129.1, 131.8 (2C), 134.4, 167.3; HRMS: $C_{14}H_9NO_2$ calculated 223.0633, found 223.0630.

2-*p*-Tolylisoindoline-1,3-dione (3e):



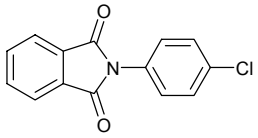
white solid, mp: 207-209 ^{o}C; IR (KBr): 1746 (m, $\nu_{C=O}$), 1716 (s, $\nu_{C=O}$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ2.39 (s, 3 H), 7.29 (s, 4 H), 7.76 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H), 7.93 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ21.2, 123.7, 126.5, 128.9, 129.8, 131.8, 134.3, 138.2, 167.4; HRMS: $C_{15}H_{11}NO_2$ calculated 237.0790, found 237.0791.

2-(4-Methoxyphenyl)isoindoline-1,3-dione (3f):



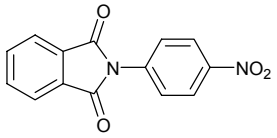
white solid, mp: 143-145 ^{o}C; IR (KBr): 1704 (s, $\nu_{C=O}$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ3.83 (s, 3 H), 7.00 (d, J = 9 Hz, 2 H), 7.31 (d, J = 9 Hz, 2 H), 7.76 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H), 7.93 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ55.5, 114.5, 123.7, 124.2, 127.9, 131.8, 134.3, 159.2, 167.6; HRMS: $C_{15}H_{11}NO_3$ calculated 253.0739, found 253.0741.

2-(4-Chlorophenyl)isoindoline-1,3-dione (3g):



white solid, mp: 194-196 ^{o}C; IR (KBr): 1716 (m, $\nu_{C=O}$), 1699 (s, $\nu_{C=O}$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ7.39 (d, J = 9 Hz, 2 H), 7.46 (d, J = 9 Hz, 2 H), 7.79 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H), 7.94 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ123.9, 127.7, 129.3, 130.2, 131.6, 134.6, 136.4, 167.0; HRMS: $C_{14}H_8ClNO_2$ calculated 257.0244, found 257.0242.

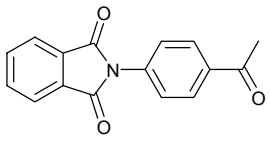
2-(4-Nitrophenyl)isoindoline-1,3-dione (3h):



white solid, mp: 250-252 ^{o}C; IR (KBr): 1731 (s, $\nu_{C=O}$), 1715 (s,

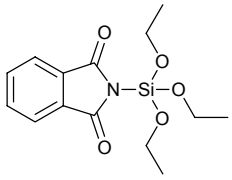
$\nu_{C=O}$), 1520 (s, $\nu_{N=O}$), 1350 (s, $\nu_{N=O}$) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ7.76 (d, J = 9 Hz, 2 H), 7.83 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H) , 7.99 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H), 8.36 (d, J = 9 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ124.2, 124.4, 126.3, 131.3, 135.0, 137.5, 146.4, 166.4; HRMS: $C_{14}H_8N_2O_4$ calculated 268.0484, found 268.0485.

2-(4-Acetlyphenyl)isoindoline-1,3-dione (3i):



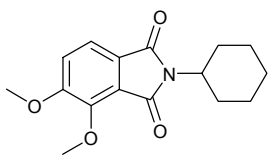
white solid, mp: 245-247 °C**;** IR (KBr): 1748 (m, $\nu_{C=O}$), 1732 (m, $\nu_{C=O}$), 1716 (s, $\nu_{C=O}$), 1683 (s, $\nu_{C=O}$) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ2.63 (s, 3 H), 7.61 (d, J = 9 Hz, 2 H), 7.81 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H), 7.97 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H), 8.09 (d, J = 9 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ30.0, 124.0, 126.1, 128.4, 129.2, 131.6, 134.7, 136.0, 166.9, 198.5; HRMS: $C_{16}H_{11}NO_3$ calculated 265.0739, found 265.0744.

2-(Triethoxysilyl)isoindoline-1,3-dione (3j):



yellow oil; IR (KBr):1768 (s, $\nu_{C=O}$), 1702 (s, $\nu_{C=O}$), 1103, 1079 (s, $\nu si\text{-}_O$) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ1.19 (t, J = 7.5 Hz, 9 H), 3.79 (q, J = 7 Hz, 6 H), 7.68 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H), 7.82 (d, d, J_1 = 6 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ18.2, 58.4, 123.1, 132.1, 133.8, 168.4; HRMS: $C_{14}H_{19}NO_5Si$ calculated 309.1032, found 309.1032.

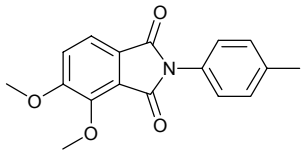
2-Cyclohexyl-4,5-dimethoxyisoindoline-1,3-dione (3k):



white solid, mp: 95-97 °C; IR (KBr): 1763 (m, $\nu_{C=O}$), 1704 (s,

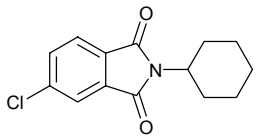
$\nu_{C=O}$), 1270 (s, ν_{C-O}) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ1.23-1.35 (m, 3 H), 1.68 (d, J = 8 Hz, 3 H), 1.81 (d, J = 8 Hz, 2 H), 2.17 (d, q, J_1 = 12 Hz, J_2 = 3.5 Hz, 2 H), 3.90 (s, 3 H), 4.02 (t, t, J_1 = 12 Hz, J_2 = 3.5 Hz, 1 H), 4.09 (s, 3 H), 7.05 (d, J = 8 Hz, 1 H), 7.46 (d, J = 8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ25.1, 26.0, 29.7, 50.8, 56.5, 62.4, 115.6, 119.1, 122.0, 124.7, 146.9, 157.6, 166.3, 167.7; HRMS: $C_{16}H_{19}NO_4$ calculated 289.1314, found 289.1308.

4,5-Dimethoxy-2-p-tolylisoindoline-1,3-dione (3l):



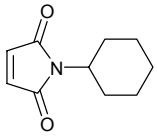
white solid, mp: 173-175 °C; IR (KBr): 1764 (m, $\nu_{C=O}$), 1717 (s, $\nu_{C=O}$), 1270 (s, ν_{C-O}) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ2.38 (s, 3 H), 3.95 (s, 3 H), 4.15 (s, 3 H), 7.14 (d, J = 8 Hz, 1 H), 7.28 (s, 4 H), 7.62 (d, J = 8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ21.2, 56.6, 62.6, 116.1, 119.9, 121.7, 124.2, 126.5, 129.1, 129.7, 138.0, 147.5, 157.9, 165.4, 166.8; HRMS: $C_{17}H_{15}NO_4$ calculated 297.1001, found 297.1002.

5-chloro-2-cyclohexylisoindoline-1,3-dione (3m):



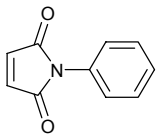
white solid, mp: 118-120 °C; IR (KBr): 1770 (m, $\nu_{C=O}$), 1702 (s, $\nu_{C=O}$) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ1.20-1.38 (m, 3 H), 1.68 (d, J = 8 Hz, 3 H), 1.84 (d, J = 8 Hz, 2 H), 2.18 (d, q, J_1 = 12 Hz, J_2 = 3.5 Hz, 2 H), 4.07 (t, t, J_1 = 12 Hz, J_2 = 3.5 Hz, 1 H), 7.63 (d, d, J_1 = 6 Hz, J_2 = 1.5 Hz, 1 H), 7.72 (d, J = 8 Hz, 1 H), 7.75 (d, J = 1.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ25.0, 25.9, 29.8, 51.2, 123.5, 124.3, 130.1, 133.7, 133.8, 140.4, 167.1, 167.5; HRMS: $C_{14}H_{14}ClNO_2$ calculated 263.0713, found 263.0716.

1-Cyclohexyl-1*H*-pyrrole-2,5-dione (3n):



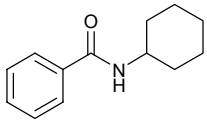
white solid, mp: 86-88 ^{o}C; IR (KBr): 1771 (m, $\nu_{C=O}$), 1697 (s, $\nu_{C=O}$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ1.19-1.34 (m, 3 H), 1.63-1.65 (m, 3 H), 1.80-1.82 (m, 2 H), 1.99-2.04 (m, 2 H), 3.82 (t, t, J_1 = 12 Hz, J_2 = 4 Hz, 1 H), 6.60 (s, 2H) ;^{13}C NMR (125 MHz, $CDCl_3$): δ25.0, 25.9, 29.9, 50.8, 133.9, 170.9; HRMS: $C_{10}H_{13}NO_2$ calculated 179.0946, found 179.0946.

1-Phenyl-1*H*-pyrrole-2,5-dione (3o):



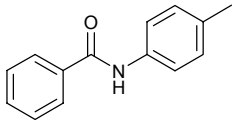
yellow solid, mp: 89-91 ^{o}C; IR (KBr): 1764 (m, $\nu_{C=O}$), 1716 (s, $\nu_{C=O}$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ6.84 (s, 2H), 7.32 (d, J = 7.5 Hz, 2 H), 7.33 (m, 1 H), 7.45 (t, J = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ126.1, 128.0, 129.1, 131.2, 134.2, 169.5; HRMS: $C_{10}H_7NO_2$ calculated 173.0477, found 173.0479.

***N*-Cyclohexylbenzamide (9a):**



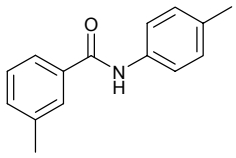
white solid, mp: 135-137 ^{o}C; IR (KBr): 1627 (s, $\nu_{C=O}$), 1538 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ1.17-1.24 (m, 3 H), 1.30-1.37 (m, 2 H), 1.57-1.62 (m, 1 H), 1.63-1.65 (m, 2 H), 1.87-2.02 (m, 2 H), 3.88-3.91 (m, 1 H), 6.28 (s, broad, N-H, 1 H), 7.33 (t, J = 7.5 Hz, 2 H), 7.41 (t, J = 7.5 Hz, 1 H), 7.72 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ24.8, 25.4, 33.0, 48.6, 126.8, 128.3, 131.0, 134.9, 166.6; HRMS: $C_{13}H_{17}NO$ calculated 203.1310, found 203.1310.

***N-p*-Tolylbenzamide (9b):**



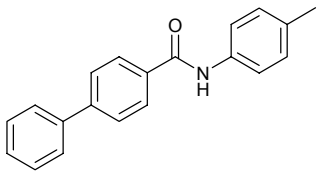
white solid, mp: 141.5-143.5 ^{o}C; IR (KBr): 1651 (s, $\nu_{C=O}$), 1542 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ2.32 (s, 3 H), 7.16 (d, *J* = 8 Hz, 2 H), 7.45-7.54 (m, 5H), 7.76 (s, broad, N-H, 1 H), 7.84 (d, *J* = 8 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ20.9, 120.2, 127.0, 128.8, 129.6, 131.7, 134.3, 135.0, 135.3, 165.6; HRMS: $C_{14}H_{13}NO$ calculated 211.0997, found 211.0998.

3-Methyl-*N*-*p*-tolylbenzamide (9c):



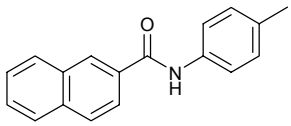
yellow oil; IR (KBr): 1635 (s, $\nu_{C=O}$), 1534 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ2.32 (s, 3 H), 2.40 (s, 3 H), 7.14 (d, *J* = 8 Hz, 2 H), 7.32-7.34 (m, 2 H), 7.50 (d, *J* = 8 Hz, 2 H), 7.61 (d, *J* = 8 Hz, 1 H), 7.66 (s, 1 H), 7.78 (s, broad, N-H, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ20.9, 21.4, 120.2, 123.9, 127.7, 128.9, 129.5, 132.4, 134.1, 135.0, 135.4, 138.6, 165.8; HRMS: $C_{15}H_{15}NO$ calculated 225.1154, found 225.1152.

4-Phenyl-*N*-*p*-tolylbenzamide (9d):



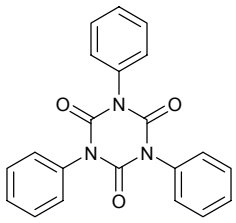
white solid, mp:217.5-218.5 ^{o}C; IR (KBr): 1652 (s, $\nu_{C=O}$), 1542 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ2.33 (s, 3 H), 7.17 (d, *J* = 7.5 Hz, 2 H), 7.38 (t, *J* = 7 Hz, 1 H), 7.46 (t, *J* = 7 Hz, 2 H), 7.52 (d, *J* = 7.5 Hz, 2 H), 7.62 (d, *J* = 7.5 Hz, 2 H), 7.69 (d, *J* = 7.5 Hz, 2 H), 7.80 (s, broad, N-H, 1 H), 7.93 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ20.9, 120.2, 127.2, 127.4, 127.5, 128.1, 128.9, 129.6, 133.7, 134.3, 135.3, 139.9, 144.6, 165.3; HRMS: $C_{20}H_{17}NO$ calculated 287.1310, found 287.1311.

***N-p*-Tolyl-2-naphthamide (9e):**



white solid, mp: 178-180 ^{o}C; IR (KBr): 1653 (s, $\nu_{C=O}$), 1542 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ2.34 (s, 3 H), 7.18 (d, *J* = 7.5 Hz, 2 H), 7.54-7.56 (m, 4 H), 7.87-7.94 (m, 5 H), 8.35 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ20.9, 120.3, 123.5, 126.9, 127.5, 127.8, 127.8, 128.7, 128.9, 129.6, 132.3, 132.7, 134.3, 134.8, 135.4, 165.7; HRMS: $C_{18}H_{15}NO$ calculated 261.1154, found 261.1155.

1,3,5-Triphenyl-1,3,5-triazinane-2,4,6-trione (5d):



white solid, mp: 282-284 ^{o}C; IR (KBr): 1702 (s, $\nu_{C=O}$) cm^{-1} ; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.5 Hz, 6 H), 7.44 (t, *J* = 7.5 Hz, 3 H), 7.49 (t, *J* = 7.5 Hz , 6 H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ128.4, 129.3, 133.6, 148.7 ; HRMS: $C_{21}H_{15}N_3O_3$ calculated 257.1113 found 257.1116.