Oxidation-Reduction Condensation of Diazaphosphites for Carbon-Heteroatom Bond Formation Based on Mitsunobu Mechanism

Hai Huang,[†,‡] Jun Yong Kang*[,†]

junyong.kang@unlv.edu

[†]Department of Chemistry and Biochemistry, University of Nevada Las Vegas,

4505 S. Maryland Parkway, Las Vegas, NV 89154-4003

[‡] Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Nanjing Tech University, No. 30 Puzhu Road (S), Nanjing 211816, People' s Republic of China

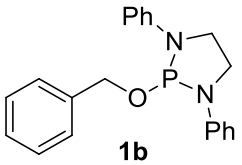
Supporting Information

1. General information.

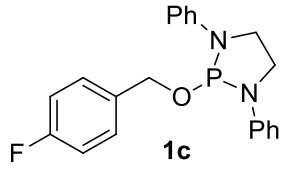
All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring bar. Dry solvents (THF, toluene, CH_3CN, Ether and DCM) were obtained by solvent purification system under argon. Morpholine was purchased from Alfa Aesar with a purity of more than 98%. All other commercially available reagents were purchased from Oakwood Chemicals with a purity of more than 98% and used as received without further purification. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on 0.25 mm aluminum-backed silica gel 60-F plates. Visualization was accompanied with UV light and $KMnO_4$ solution. Concentration under reduced pressure refers to the removal of volatiles using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr). Infrared (IR) spectra were recorded on a Shimadzu IRAffinity-1 spectrometer with KBr wafers or a film on KBr plate. High-resolution mass spectra (HRMS) were recorded on a Shimadzu LCMS-IT-TOF mass spectrometer using ESI (electrospray ionization). ^1H NMR spectra were recorded in $CDCl_3$ on 400 MHz NMR spectrometer (Varian Gemini 400 Hz). The ^1H chemical shifts are referenced to residual solvent signals at δ 7.26 ($CHCl_3$) or δ 0.00 (TMS). ^1H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), tt (triplet of triplets). ^{13}C NMR spectra were proton decoupled and recorded in $CDCl_3$ on 100.5 MHz NMR spectrometer. The ^{13}C chemical shifts are referenced to solvent signals at δ 77.16 ($CDCl_3$). ^{31}P NMR spectra were proton decoupled and recorded in $CDCl_3$ on 162 MHz NMR spectrometer. ^{31}P chemical shifts are reported relative to 85% H_3PO_4 (0.00 ppm) as an external standard.

2. Synthesis of diazaphosphites

To a solution of 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine (1.0 equiv) in DCM (0.1 M) were added achohol (1.0 equiv) and Et_3N (1.5 equiv) at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. After stirring for 2 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was subjected to flash column chromatography on silica gel (gradient eluent of hexanes/ether = 5/1) to give corresponding diazaphosphites **1.**

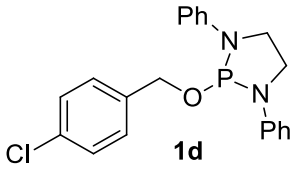


2-(Benzyloxy)-1,3-diphenyl-1,3,2-diazaphospholidine (1b). White solid; 434.0 mg, 42%; mp 83-84 °C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; IR ν (KBr, cm^{-1}) 3028, 2938, 2865, 1600, 1499, 1271, 1213, 1187, 1072, 987; 1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 4H), 7.20-7.14 (m, 7H), 7.11-7.08 (m, 2H), 6.93 (tt, *J* = 7.2, 1.2 Hz, 2H), 4.61 (d, *J* = 6.8 Hz, 2H), 3.92-3.86 (m, 2H), 3.86-3.79 (m, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 145.0 (d, *J* = 17.9 Hz), 138.0 (d, *J* = 2.9 Hz), 129.3, 128.2, 127.4, 127.3, 120.1 (d, *J* = 1.5 Hz), 115.4 (d, *J* = 13.5 Hz), 65.3, 47.4 (d, *J* = 9.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 103.6 ppm. HRMS (ESI): found $[M + H]^+$ values corresponding to 2-(benzyloxy)-1,3-diphenyl-1,3,2-diazaphospholidine 2-oxide; calcd for $C_{21}H_{21}N_2O_2P$ ($[M + H]^+$): 365.1413; found: 365.1415.



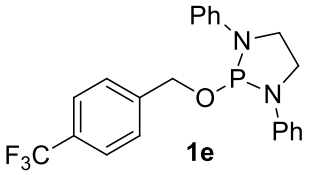
1c

2-((4-Fluorobenzyl)oxy)-1,3-diphenyl-1,3,2-diazaphospholidine (1c). white solid; 235.9 mg, 37%; mp 106-107 ^{o}C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; **IR** ν (KBr, cm^{-1}) 3024, 2931, 2866, 1597, 1508, 1488, 1284, 1272, 986; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.8 Hz, 4H), 7.17-7.12 (m, 4H), 7.06-7.00 (m, 2H), 6.94 (t, *J* = 7.2 Hz, 2H), 6.85 (tt, *J* = 8.8, 2.0 Hz, 2H), 4.57 (d, *J* = 7.2 Hz, 2H), 3.91-3.77 (m, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 162.2 (d, *J* = 244.1 Hz), 144.9 (d, *J* = 17.1 Hz), 133.9 (d, *J* = Hz), 129.3, 129.1 (d, *J* = 8.2 Hz), 120.2 (d, *J* = 1.4 Hz), 115.4 (d, *J* = 13.4 Hz), 115.1 (d, *J* = 21.5 Hz), 64.6, 47.4 (dd, *J* = 9.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 104.1 ppm; **HRMS** (ESI): m/z calcd for $C_{21}H_{20}FN_2OP$ ([M+H]$^{+}$): 367.1370; Found: 367.1360.



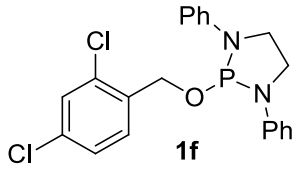
1d

2-((4-Chlorobenzyl)oxy)-1,3-diphenyl-1,3,2-diazaphospholidine (1d). White solid; 281.2 mg, 49%; mp 110-111 ^{o}C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; **IR** ν (KBr, cm^{-1}) 3026, 2925, 2863, 1595, 1488, 1470, 1284, 1272, 988; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 4H), 7.16-7.10 (m, 6H), 7.02-6.98 (m, 2H), 6.93 (tt, *J* = 7.2, 1.2 Hz, 2H), 4.57 (d, *J* = 7.2 Hz, 2H), 3.92-3.75 (m, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 144.9 (d, *J* = 17.1 Hz), 136.6 (d, *J* = 2.3 Hz), 133.2, 129.3, 128.6, 128.3, 120.0, 115.4 (d, *J* = 13.4 Hz), 64.6, 47.4 (d, *J* = 9.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 104.4 ppm; **HRMS** (ESI): m/z calcd for $C_{21}H_{20}ClN_2OP$ ([M+H]$^{+}$): 383.1075; Found: 383.1080.



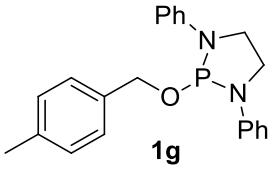
1e

1,3-Diphenyl-2-((4-(trifluoromethyl)benzyl)oxy)-1,3,2-diazaphospholidine (1e). White solid; 395.2 mg, 49%; mp 80-81 °C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; **IR** ν (KBr, cm^{-1}) 3062, 3029, 2929, 2855, 1597, 1499, 1329, 1273, 1166, 1116, 1067, 987; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.31-7.24 (m, 4H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.15-7.10 (m, 4H), 6.93 (tt, *J* = 7.6, 0.8 Hz, 2H), 4.67 (d, *J* = 7.2 Hz, 2H), 3.92-3.74 (m, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 144.8 (d, *J* = 17.1 Hz), 142.1, 129.7, 129.3, 127.2, 125.1 (q, *J* = 3.8 Hz), 124.1 (d, *J* = 268.0 Hz), 120.3, 115.4 (d, *J* = 14.2 Hz), 64.5, 47.4 (d, *J* = 9.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 104.9 ppm; **HRMS** (ESI): m/z calcd for $C_{22}H_{20}N_2OF_3P$ ($[M+H]^+$): 417.1338; Found: 417.1340.



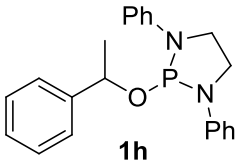
1f

2-((2,4-Dichlorobenzyl)oxy)-1,3-diphenyl-1,3,2-diazaphospholidine (1f). White solid; 342.7 mg, 55%; mp 76-77 °C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; **IR** ν (KBr, cm^{-1}) 3026, 2926, 2862, 1599, 1499, 1472, 1278, 1272, 1117, 1020, 991; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 5H), 7.17-7.11 (m, 5H), 7.00 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.93 (tt, *J* = 7.2, 1.2 Hz, 2H), 4.57 (d, *J* = 7.2 Hz, 2H), 3.96-3.75 (m, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 144.8 (d, *J* = 17.8 Hz), 134.5 (d, *J* = 2.3 Hz), 133.5, 132.6, 129.5, 129.3, 128.7, 127.0, 120.3 (d, *J* = 1.5 Hz), 115.4 (d, *J* = 14.1 Hz), 61.8, 47.5 (d, *J* = 9.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 104.9 ppm; HRMS (ESI): found $[M + H]^+$ values corresponding to *N*^{1},*N*^{2}-diphenylethane-1,2-diamine**;** calcd for $C_{14}H_{16}N_2$ ($[M + H]^+$):213.1386; found: 213.1395.



1g

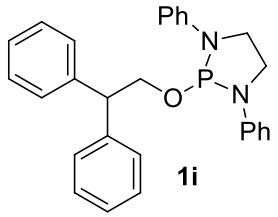
2-((4-Methylbenzyl)oxy)-1,3-diphenyl-1,3,2-diazaphospholidine (1g). White solid; 181.7 mg, 33%; mp 84-85 °C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; **IR** ν (KBr, cm^{-1}) 3034, 2921, 2859, 1599, 1497, 1473, 1276, 1125, 991; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 4H), 7.18-7.13 (m, 4H), 7.01-6.95 (m, 4H), 6.92 (tt, *J* = 7.6, 0.8 Hz, 2H), 4.56 (d, *J* = 6.4 Hz, 2H), 3.92-3.77 (m, 4H), 2.26 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 145.0 (d, *J* = 17.8 Hz), 137.2, 135.0 (d, *J* = 3.0 Hz), 129.3, 128.9, 127.5, 120.1, 115.4 (d, *J* = 14.2 Hz), 65.3, 47.4 (d, *J* = 10.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 103.4 ppm; HRMS (ESI): found [M + H]$^+$ values corresponding to N^1,N^2-diphenylethane-1,2-diamine; calcd for $C_{14}H_{16}N_2$ ([M + H]$^+$):213.1386; found: 213.1393.



1h

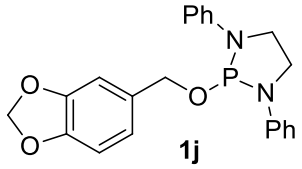
1,3-Diphenyl-2-(1-phenylethoxy)-1,3,2-diazaphospholidine (1h). White solid; 508.6 mg, 47%; mp 95-96 °C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; **IR** ν (KBr, cm^{-1}) 3062, 3028, 2975, 2868, 1597, 1496, 1473, 1281, 1058, 922; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2H), 7.20-7.15 (m, 2H), 7.10-7.04 (m, 7H), 6.96-6.87 (m, 3H), 6.84 (tt, *J* = 7.2, 1.2 Hz, 1H), 5.01-4.93 (m, 1H), 3.85 (ddd, *J* = 10.0, 6.4, 4.8 Hz, 1H), 3.76-3.68 (m, 1H), 3.62-3.48 (m, 2H), 1.31 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 145.0 (dd, *J* = 30.6, 18.6 Hz), 143.6, 129.2 (d, *J* = 1.5 Hz), 129.0, 128.0, 127.0, 125.4, 119.8 (dd, *J* = 6.7, 1.5 Hz), 115.4 (dd, *J* = 33.5, 14.2 Hz), 72.3, 47.0 (dd, *J* = 55.8, 9.6 Hz), 25.5 (d, *J* = 3.0 Hz); **^{31}P NMR**

(162 MHz, $CDCl_3$): δ 103.1 ppm; **HRMS** (ESI): m/z calcd for $C_{22}H_{23}N_2OP$ ($[M+H]^+$): 363.1621; Found: 363.1627.



1i

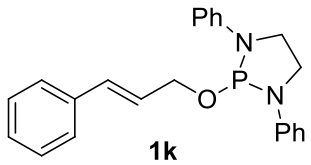
2-((4-Chlorobenzyl)oxy)-1,3-diphenyl-1,3,2-diazaphospholidine (1i). White solid; 260.9 mg, 40%; mp 147-148 °C; R_f = 0.50 (v_{hexane}/v_{ether}= 4:1), $v_{hexane}/v_{ether}/v_{DCM}$ (20/4/1) for column; **IR** ν (KBr, cm^{-1}) 3062, 3024, 2930, 2851, 1594, 1496, 1275, 1114, 980; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.2 Hz, 4H), 7.18-7.12 (m, 6H), 7.11-7.05 (m, 4H), 7.02-6.97 (m, 4H), 6.93 (td, *J* = 7.2, 0.8 Hz, 2H), 4.08-4.01 (m, 3H), 3.88-3.73 (m, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 145.0 (d, *J* = 17.9 Hz), 141.5, 129.3, 128.3, 128.2, 126.4, 120.1 (d, *J* = 1.5 Hz), 115.4 (d, *J* = 14.1 Hz), 65.9 (d, *J* = 3.9 Hz), 51.8 (d, *J* = 2.3 Hz), 47.5 (d, *J* = 9.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 103.4 ppm; **HRMS** (ESI): m/z calcd for $C_{28}H_{27}N_2OP$ ($[M+H]^+$): 439.1934; Found: 439.1925.



1j

2-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)-1,3-diphenyl-1,3,2-diazaphospholidine (1j). White solid; 164.2 mg, 28%; mp 126-127 °C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; **IR** ν (KBr, cm^{-1}) 3034, 2906, 2866, 1592, 1499, 1488, 1281, 1250, 1034, 985; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 4H), 7.17-7.12 (m, 4H), 6.93 (t, *J* = 7.2 Hz, 2H), 6.61 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.55-6.52 (m, 2H), 5.85 (s, 2 H), 3.91-3.76 (m, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 147.2 (d, *J* = 54.3 Hz), 144.9 (d, *J* = 17.2 Hz), 131.9 (d, *J* = 3.0 Hz), 129.6,

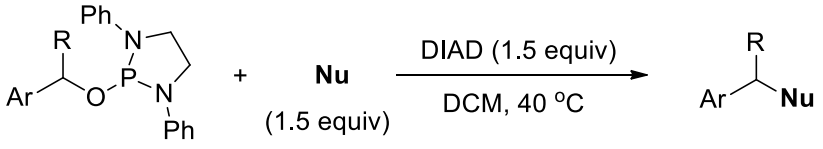
129.3, 122.3, 120.9, 120.1 (d, J = 1.5 Hz), 116.3 (d, J = 6.0 Hz), 115.3 (d, J = 14.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 103.7 ppm. HRMS (ESI): found $[M + H]^+$ values corresponding to N^1,N^2-diphenylethane-1,2-diamine**;** calcd for $C_{14}H_{16}N_2$ ($[M + H]^+$): 213.1386; found: 213.1381.



1k

2-(Cinnamyloxy)-1,3-diphenyl-1,3,2-diazaphospholidine (1k). White solid; 159.2 mg, 28%; mp 101-103 °C; R_f = 0.50 (v_{hexane}/v_{ether}= 5:1), v_{hexane}/v_{ether} (5/1) for column; **IR** ν (KBr, cm^{-1}) 3057, 3026, 2923, 2869, 1598, 1496, 1280, 1049, 923; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 4H), 7.25-7.12 (m, 9H), 6.93 (tt, J = 7.2, 1.2 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 6.01 (dt, J = 16.0, 5.6 Hz, 1H), 4.31-4.25 (m, 2H), 3.95-3.89 (m, 2H), 3.89-3.77 (m, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 145.0 (d, J = 17.9 Hz), 136.5, 131.7, 129.3, 128.4, 127.6, 126.4, 126.1 (d, J = 3.0 Hz), 120.1 (d, J = 1.5 Hz), 115.4 (d, J = 13.4 Hz), 64.1, 47.3 (d, J = 10.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 104.4 ppm; **HRMS** (ESI): m/z calcd for $C_{23}H_{23}N_2OP$ ($[M+H]^+$): 375.1621; Found: 375.1614.

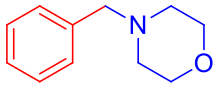
3. The general procedure for the substitution reaction.



1 **2** **3**

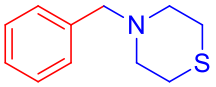
A mixture of diazaphosphites **1** (0.1 mmol), nucleophiles **2** (0.15 mmol), DIAD (26 μL, 0.15 mmol) and DCM (0.5 mL) in a 2 dram vial with a PTFE cap was stirred for 36 h at 40 °C. After stirring for 36 h at 40 °C, the reaction mixture was concentrated under reduced

pressure. The residue was subjected to flash column chromatography on silica gel to give corresponding products **3**.



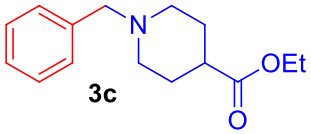
3a

4-Benzylmorpholine (3a)[1]: Pale yellow oil; 16.0 mg, 90%; R_f = 0.10 (v_{hexane}/v_{EtOAc}= 4:1), v_{hexane}/v_{EtOAc} (5/1, with 1% Et_3N) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 7.29-7.23 (m, 1H), 3.71 (t, *J* = 4.8 Hz, 4H), 3.50 (s, 2H), 2.44 (t, *J* = 4.4 Hz, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 137.7, 129.2, 128.2, 127.1, 67.0, 63.5, 53.6.



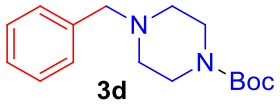
3b

4-Benzylthiomorpholine (3b)[2]: Pale yellow oil; 17.9 mg, 93%; R_f = 0.40 (v_{hexane}/v_{EtOAc}= 3:1), v_{hexane}/v_{EtOAc} (10/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 4H), 7.26-7.24 (m, 1H), 3.51 (s, 2H), 2.72-2.65 (m, 8H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 138.1, 129.0, 128.2, 127.1, 63.7, 54.9, 28.0.



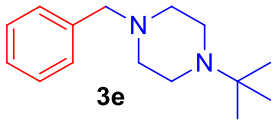
3c

Ethyl 1-benzylpiperidine-4-carboxylate (3c)[3]: Pale yellow oil; 19.2 mg, 78%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 3:1), v_{hexane}/v_{EtOAc} (6/1, with 1% Et_3N) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 4.4 Hz, 4H), 7.28-7.23 (m, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.48 (s, 2H), 2.85 (td, *J* = 12.0, 3.2 Hz, 2H), 2.31-2.23 (m, 1H), 2.02 (dt, *J* = 11.2, 4.0 Hz, 2H), 1.91-1.83 (m, 2H), 1.82-1.70 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 175.2, 138.4, 129.0, 128.2, 126.9, 63.2, 60.2, 52.9, 41.2, 28.3, 14.2.



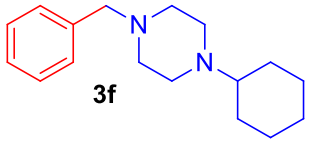
3d

***tert*-Butyl 4-benzylpiperazine-1-carboxylate (3d)**[4]: Pale yellow oil; 23.3 mg, 83%; R_f = 0.20 (v_{hexane}/v_{EtOAc}= 3:1), v_{hexane}/v_{EtOAc} (6/1, with 1% Et_3N) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 4.4 Hz, 4H), 7.29-7.23 (m, 1H), 3.51 (s, 2H), 3.42 (t, *J* = 4.8 Hz, 4H), 2.38 (t, *J* = 4.8 Hz, 4H), 1.46 (s, 9H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 154.8, 137.9, 129.1, 128.2, 127.1, 79.5, 63.0, 52.8, 28.4, 28.3.



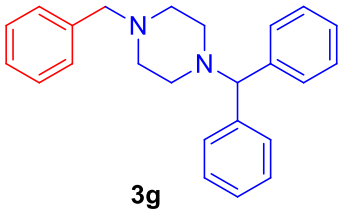
3e

1-Benzyl-4-(*tert*-butyl)piperazine (3e)[5]: Pale yellow oil; 16.5 mg, 72%; R_f = 0.10 (v_{EtOAc}/v_{MeOH}= 95:5), v_{EtOAc}/v_{MeOH} (95/5) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 4H), 7.27-7.21 (m, 1H), 3.51 (s, 2H), 2.60 (bs, 4H), 2.50 (bs, 4H), 1.46 (s, 9H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 138.1, 129.3, 128.1, 126.9, 63.1, 53.8, 45.6, 25.9, 21.9.



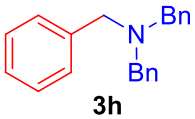
3f

1-Benzyl-4-cyclohexylpiperazine (3f)[6]: Pale yellow oil; 17.7 mg, 73%; R_f = 0.10 (v_{EtOAc}/v_{MeOH}= 98:2), v_{EtOAc}/v_{MeOH} (98/2) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 4.4 Hz, 4H), 7.28-7.22 (m, 1H), 3.51 (s, 2H), 2.63 (bs, 4H), 2.53 (bs, 4H), 2.27 (bs, 1H), 1.94-1.76 (m, 4H), 1.65-1.58 (m, 1H), 1.30-1.05 (m, 5H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 138.0, 129.3, 128.2, 127.0, 63.6, 63.1, 53.3, 48.8, 28.8, 26.2, 25.8.



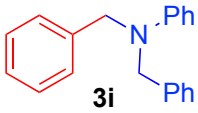
3g

1-Benzhydryl-4-benzylpiperazine (3g)[7]: White solid; 27.7 mg, 81%; R_f = 0.40 (v_{hexane}/v_{EtOAc}= 3:1), v_{hexane}/v_{EtOAc} (9/1-4/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 4H), 7.30-7.20 (m, 9H), 7.15 (tt, *J* = 7.2, 2.0 Hz, 2H), 4.22 (s, 1H), 3.51 (s, 2H), 2.47 (bs, 4H), 2.42 (bs, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 142.8, 138.1, 129.2, 128.4, 128.1, 128.0, 126.9, 126.8, 76.2, 63.1, 53.3, 51.9.



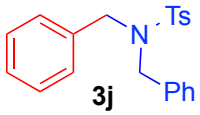
3h

Tribenzylamine (3h)[1]: Pale yellow oil; 23.2 mg, 81%; R_f = 0.50 (v_{hexane}/v_{EtOAc}= 8:1), v_{hexane}/v_{EtOAc} (10/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.36 (m, 6H), 7.36-7.28 (m, 6H), 7.22 (tt, *J* = 7.2, 1.2 Hz, 3H), 3.55 (s, 6H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 139.6, 128.7, 128.2, 126.8, 57.9.



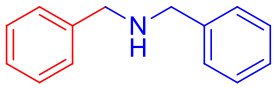
3i

***N,N*-Dibenzylaniline (3i)**[6]: Pale yellow oil; 18.5 mg, 68%; R_f = 0.05 (v_{hexane}/v_{EtOAc}= 100:1), v_{hexane}/v_{DCM} (20/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 4H), 7.27-7.22 (m, 6H), 7.19-7.17 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 4.65 (s, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 149.2, 138.6, 129.2, 128.6, 126.8, 126.6, 116.7, 112.4, 54.2.



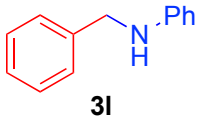
3j

***N,N*-dibenzyl-4-methylbenzenesulfonamide (3j)**[8]: White solid; 32.6 mg, 93%; R_f = 0.20 (v_{hexane}/v_{EtOAc}= 10:1), v_{hexane}/v_{EtOAc} (15/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (dt, *J* = 8.0, 1.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.23-7.18 (m, 6H), 7.08-7.03 (m, 4H), 4.31 (s, 4H), 2.44 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 143.2, 137.7, 135.7, 129.7, 128.6, 128.4, 127.6, 127.2, 50.5, 21.5.



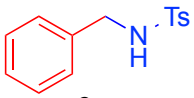
3k

Dibenzylamine (3k)[6]: Pale yellow oil; 8.8 mg, 45%; R_f = 0.20 (v_{hexane}/v_{EtOAc}= 4:1), v_{hexane}/v_{EtOAc} (5/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 8H), 7.27-7.23 (m, 2H), 3.81 (s, 4H), 1.61 (s, 1H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 140.4, 128.4, 128.1, 126.9, 53.2.



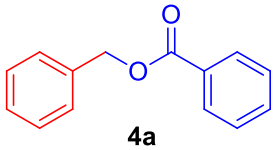
3l

***N*-Benzylaniline (3l)**[6]: Pale yellow oil; 7.0 mg, 38%; R_f = 0.40 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 4H), 7.30-7.29 (m, 1H), 7.20-7.19 (m, 2H), 6.71 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.66-6.61 (m, 2H), 4.33 (s, 2H), 4.01 (s, 1H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 148.1, 139.4, 129.3, 128.6, 127.5, 127.2, 117.5, 112.8, 48.3.



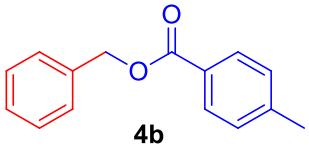
3m

***N*-benzyl-4-methylbenzenesulfonamide (3m)**[9]: White solid; 23.4 mg, 90%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 3:1), v_{hexane}/v_{EtOAc} (10/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.31-7.22 (m, 5H), 7.20-7.17 (m, 2H), 4.88 (t, *J* = 6.4 Hz, 1H), 4.10 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 143.5, 136.8, 136.3, 129.7, 128.6, 127.9, 127.8, 127.2, 47.2, 21.5.



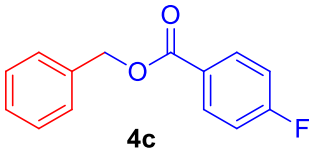
4a

Benzyl benzoate (4a)[10]: Pale yellow oil; 19.0 mg, 90%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 2H), 7.58-7.53 (m, 1H), 7.47-7.31 (m, 7H), 5.37 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 166.4, 136.0, 133.0, 129.7, 128.6, 128.4, 128.2, 128.1, 66.7.



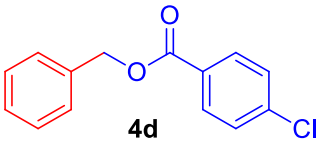
4b

Benzyl 4-methylbenzoate (4b)[10]: Pale yellow oil; 21.0 mg, 93%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.41-7.30 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.35 (s, 2H), 2.40 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 166.5, 143.7, 136.2, 129.7, 129.1, 128.6, 128.2, 128.1, 127.4, 66.5, 21.6.



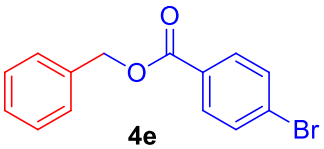
4c

Benzyl 4-fluorobenzoate (4c)[11]: Pale yellow oil; 20.8 mg, 90%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12-8.06 (m, 2H), 7.46-7.32 (m, 5H), 7.14-7.07 (m, 2H), 5.35 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 165.8 (d, *J* = 253.0 Hz), 165.4, 135.9, 132.2 (d, *J* = 9.7 Hz), 128.6, 128.3, 128.2, 126.4 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 22.3 Hz), 66.8.



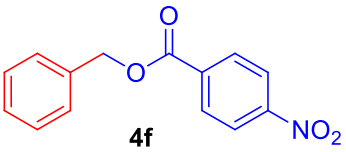
4d

Benzyl 4-chlorobenzoate (4d)[10]: Pale yellow oil; 22.2 mg, 91%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.46-7.32 (m, 7H), 5.35 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 165.6, 139.5, 135.8, 131.1, 128.7, 128.6, 128.5, 128.4, 128.2, 66.9.



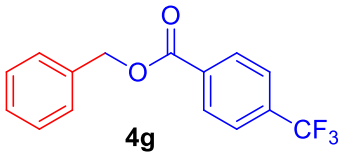
4e

Benzyl 4-bromobenzoate (4e)[10]: Pale yellow oil; 27.8 mg, 96%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.57 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.45-7.32 (m, 5H), 5.35 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 165.7, 135.8, 131.7, 131.2, 129.0, 128.6, 128.4, 128.2, 128.1, 66.9.



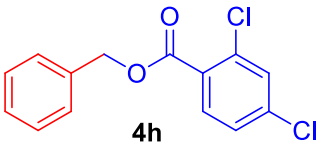
4f

Benzyl 4-nitrobenzoate (4f)[10]: White solid; 24.7 mg, 96%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30-8.22 (m, 4H), 7.48-7.34 (m, 5H), 5.41 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 164.5, 135.5, 135.2, 130.8, 128.7, 128.6, 128.4, 123.53, 123.52, 67.6.



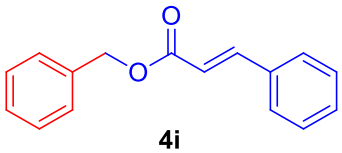
4g

Benzyl 4-(trifluoromethyl)benzoate (4g)[10]: Pale yellow oil; 25.4 mg, 91%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20-8.16 (m, 2H), 7.72-7.68 (m, 2H), 7.47-7.33 (m, 5H), 5.39 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 165.2, 135.5, 134.5 (d, J = 32.7 Hz), 133.3 (d, J = 1.5 Hz), 130.1, 128.7, 128.5, 128.3 (d, J = 1.5 Hz), 125.4 (q, J = 3.7 Hz), 123.6 (d, J = 271.6 Hz), 67.2.



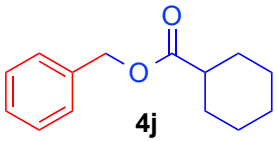
4h

Benzyl 2,4-dichlorobenzoate (4h)[11]: Pale yellow oil; 26.5 mg, 94%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.46-7.42 (m, 2H), 7.41-7.32 (m, 3H), 7.28 (dd, J = 8.8, 2.0 Hz, 1H), 5.36 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 164.5, 138.4, 135.3, 135.1, 132.6, 131.0, 128.6, 128.5, 128.4, 128.1, 127.0, 67.4.



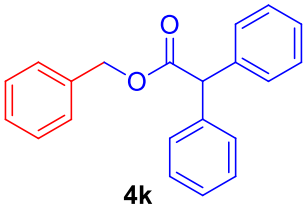
4i

Benzyl cinnamate (4i)[11]: Pale yellow oil; 19.3 mg, 81%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.53-7.49 (m, 2H), 7.44-7.31 (m, 8H), 6.49 (d, *J* = 16.0 Hz, 1H), 5.25 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 166.8, 145.2, 136.1, 134.4, 130.3, 128.9, 128.6, 128.3, 128.2, 128.1, 117.9, 66.4.



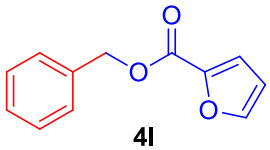
4j

Benzyl cyclohexanecarboxylate (4j)[11]: Pale yellow oil; 19.9 mg, 92%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 5.11 (s, 2H), 2.40-2.30 (m, 1H), 1.97-1.89 (m, 2H), 1.79-1.71 (m, 2H), 1.67-1.60 (m, 1H), 1.52-1.41 (m, 2H), 1.34-1.16 (m, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 175.9, 136.3, 128.5, 128.0, 127.9, 65.9, 43.2, 29.0, 25.7, 25.4.



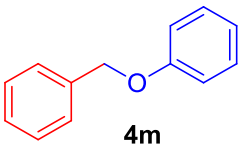
4k

Benzyl 2,2-diphenylacetate (4k)[12]: White solid; 27.8 mg, 92%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.23 (m, 15H), 5.18 (s, 2H), 5.07 (s, 1H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 172.3, 138.6, 135.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.3, 66.9, 57.0.



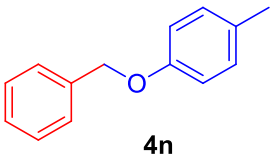
4l

Benzyl furan-2-carboxylate (4l)[13]: Pale yellow oil; 15.7 mg, 78%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.45-7.43 (m, 2H), 7.41-7.31 (m, 3H), 7.21 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.51-6.49 (m, 1H), 5.34 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 158.5, 146.4, 144.6, 135.6, 128.6, 128.4, 128.3, 118.2, 111.8, 66.5.



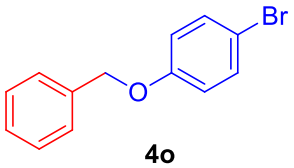
4m

(Benzyloxy)benzene (4m)[2]: Pale yellow oil; 12.2 mg, 66%; R_f = 0.10 (v_{hexane}), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.41-7.36 (m, 2H), 7.34-7.26 (m, 3H), 7.00-6.94 (m, 3H), 5.07 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 158.8, 137.1, 129.5, 128.6, 127.9, 127.5, 120.9, 114.8, 69.9.



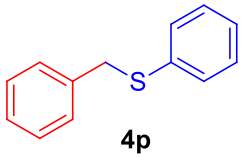
4n

1-(Benzyloxy)-4-methylbenzene (4n)[14]: Colourless oil; 13.3 mg, 67%; R_f = 0.10 (v_{hexane}), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2 H), 5.03 (s, 2H), 2.28 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 156.7, 137.3, 130.2, 129.9, 128.5, 127.9, 127.4, 114.7, 70.1, 20.5.



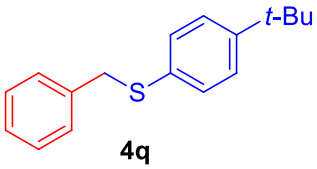
4o

1-(Benzyloxy)-4-bromobenzene (4o)[14]: White solid; 19.7 mg, 75%; R_f = 0.10 (v_{hexane}), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.29 (m, 7H), 6.86-6.81 (m, 2H), 5.02 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 157.9, 136.5, 132.3, 128.6, 128.1, 127.4, 116.7, 113.1, 70.2.



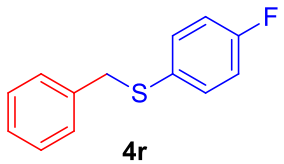
4p

Benzyl(phenyl)sulfane (4p)[15]: Pale yellow oil; 6.0 mg, 30%; R_f = 0.10 (v_{hexane}), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.20 (m, 9H), 7.17 (tt, J = 7.6, 1.2 Hz, 1H), 4.12 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 137.4, 136.3, 129.8, 128.8, 128.7, 128.5, 127.1, 126.3, 39.0.



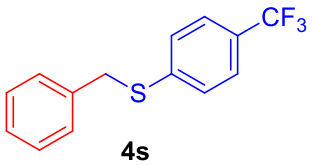
4q

Benzyl(4-(tert-butyl)phenyl)sulfane (4q)[16]: Colourless oil; 7.4 mg, 29%; R_f = 0.10 (v_{hexane}), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 9H), 4.10 (s, 2H), 1.30 (s, 9H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 149.7, 137.7, 132.9, 129.9, 128.8, 128.5, 127.1, 125.9, 39.4, 34.5, 31.3.



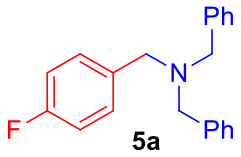
4r

Benzyl(4-fluorophenyl)sulfane (4r)[16]: Colourless oil; 7.2 mg, 33%; R_f = 0.10 (v_{hexane}), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.18 (m, 7H), 6.93 (tt, *J* = 8.8, 2.0 Hz, 2H), 4.02 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 161.1 (d, *J* = 245.6 Hz), 137.5, 133.4 (d, *J* = 8.2Hz), 130.8, 128.8, 128.5, 127.2, 115.9 (d, *J* = 21.5 Hz), 40.4.



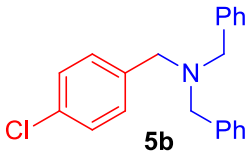
4s

Benzyl(4-(trifluoromethyl)phenyl)sulfane (4s)[17]: Colourless oil; 11.0 mg, 41%; R_f = 0.10 (v_{hexane}), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.37-7.25 (m, 7H), 4.19 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 142.0, 136.4, 128.7 (d, J = 3.8 Hz), 128.0, 127.6, 127.5, 125.6 (q, *J* = 3.7 Hz), 124.1 (d, *J* = 270.2 Hz), 37.7.



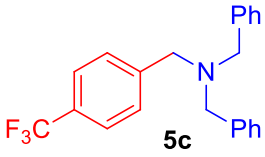
5a

***N,N*-Dibenzyl-1-(4-fluorophenyl)methanamine (5a)**[6]: Pale yellow oil; 25.2 mg, 85%; R_f = 0.60 (v_{hexane}/v_{EtOAc}= 4:1), v_{hexane}/v_{EtOAc} (50/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 10H), 7.22 (tt, *J* = 7.2, 2.4 Hz, 2H), 6.99 (t, *J* = 8.8 Hz, 2H), 3.53 (s, 4H), 3.50 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 161.9 (d, *J* = 243.3 Hz), 139.5, 135.3 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 7.4 Hz), 128.7, 128.2, 126.9, 115.0 (d, *J* = 20.9 Hz), 57.9, 57.1.



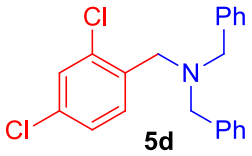
5b

***N,N*-Dibenzyl-1-(4-chlorophenyl)methanamine (5b)**[18]: Pale yellow oil; 26.3 mg, 82%; R_f = 0.60 (v_{hexane}/v_{EtOAc}= 4:1), v_{hexane}/v_{EtOAc} (50/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 4H), 7.38-7.30 (m, 5H), 7.29-7.20 (m, 5H), 3.53 (s, 4H), 3.50 (s, 2H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 139.4, 138.2, 132.5, 130.0, 128.7, 128.4, 128.3, 127.0, 57.9, 57.2.



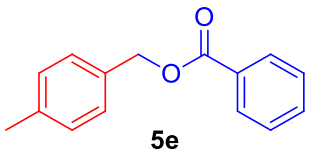
5c

***N,N*-Dibenzyl-1-(4-(trifluoromethyl)phenyl)methanamine (5c)**[19]: Pale yellow oil; 28.7 mg, 81%; R_f = 0.60 (v_{hexane}/v_{EtOAc}= 4:1), v_{hexane}/v_{EtOAc} (50/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 19.2, 8.4 Hz, 4H), 7.39 (d, *J* = 6.8 Hz, 4H), 7.32 (t, *J* = 7.2 Hz, 4H), 7.26-7.21 (m, 2H), 3.59 (s, 2H), 3.55 (s, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 144.0, 139.1, 129.2 (d, *J* = 32.0 Hz), 128.8, 128.7, 128.3, 127.0, 125.1 (q, *J* = 3.7 Hz), 124.3 (d, *J* = 270.2 Hz), 58.1, 57.4.



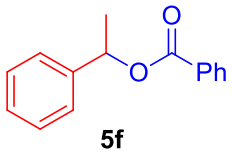
5d

***N,N*-Dibenzyl-1-(2,4-dichlorophenyl)methanamine (5d)**[20]: Pale yellow oil; 28.1 mg, 79%; R_f = 0.60 (v_{hexane}/v_{EtOAc}= 4:1), v_{hexane}/v_{EtOAc} (50/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 6.8 Hz, 4H), 7.33-7.28 (m, 5H), 7.25-7.20 (m, 3H), 3.63 (s, 2H), 3.58 (s, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 139.1, 135.9, 134.5, 132.8, 131.1, 129.0, 128.7, 128.3, 127.1, 127.0, 58.2, 54.1.



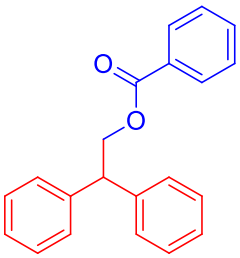
5e

4-Methylbenzyl benzoate (5e)[21]: Pale yellow oil; 15.6 mg, 82%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09-8.05 (m, 2H), 7.55 (tt, *J* = 6.4, 1.2 H, 1H), 7.45-7.40 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.33 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 166.5, 138.1, 133.0, 132.9, 130.2, 129.7, 129.2, 128.33, 128.30, 66.6, 21.2.



5f

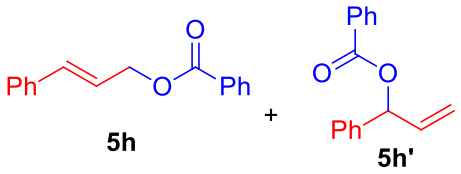
1-Phenylethyl benzoate (5f)[22]: Pale yellow oil; 13.6 mg, 71%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 2H), 7.58-7.52 (m, 1H), 7.47-7.40 (m, 4H), 7.39-7.33 (m, 2H), 7.32-7.24 (m, 1H), 6.14 (q, *J* = 6.4 Hz, 1H), 1.67 (dd, *J* = 6.8, 1.6 Hz, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 165.8, 141.8, 132.9, 130.5, 129.6, 128.5, 128.3, 127.9, 126.0, 72.9, 22.4.



5g

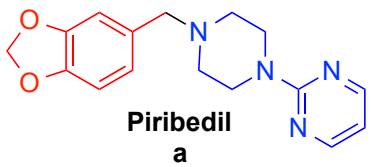
2,2-Diphenylethyl benzoate (5g)[23]: Pale yellow oil; 16.8 mg, 58%; R_f = 0.30 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.52 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.35-7.28 (m, 8H), 7.26-7.21 (m,

2H), 4.86 (d, *J* = 7.6 Hz, 2H), 4.52 (t, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 166.4, 141.2, 132.9, 130.1, 129.5, 128.6, 128.3, 128.2, 126.8, 67.2, 49.9.



5h **5h'**

Cinnamyl benzoate (**5h**) and 1-phenylallyl benzoate (**5h′**) was isolated as a mixture: Pale yellow oil; 11.3 mg, 47% yield; R_f = 0.35 (v_{hexane}/v_{EtOAc}= 16:1), v_{hexane}/v_{EtOAc} (100/1) for column; **Cinnamyl benzoate (5h)**[24]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13-8.06 (m, 2H), 7.59-7.54 (m, 2H), 7.48-7.40 (m, 2H), 7.38-7.32 (m, 2H), 7.28-7.24 (m, 2H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.40 (dt, *J* = 16.4, 6.0 Hz, 1H), 4.99 (dd, *J* = 6.4, 1.2 Hz, 2H); **1-Phenylallyl benzoate (5h′)**[25]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13-8.06 (m, 2H), 7.59-7.54 (m, 1H), 7.48-7.40 (m, 6H), 7.38- 7.30 (m, 1H), 6.52 (d, *J* = 6.0 Hz, 1H), 6.13 (ddd, *J* = 14.0, 13.2, 5.6 Hz, 1H), 5.40 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.30 (dt, *J* = 10.8, 1.2 Hz, 1H).



Piribedil a

2-(4-(Benzo[*d*][1,3]dioxol-5-ylmethyl)piperazin-1-yl)pyrimidine (Piribedil a)[1]: White solid; 16.8 mg, 56%; R_f = 0.15 (v_{hexane}/v_{EtOAc}= 2:1), v_{hexane}/v_{EtOAc} (2.5/1, with 2% Et_3N) for column; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 4.4 Hz, 2H), 6.89 (s, 1H), 6.76 (d, *J* = 0.4 Hz, 2H), 6.46 (t, *J* = 4.8 Hz, 1H), 5.95 (s, 2H), 3.82 (t, *J* = 4.8 Hz, 4H), 3.45 (s, 2H), 2.48 (t, *J* = 5.2 Hz, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 161.6, 157.7, 157.6, 147.6, 146.6, 131.9, 122.2, 109.7, 109.5, 107.9, 100.9, 62.8, 52.8, 43.7.

Reference

1. Hamid, M. H. S. A.; Allen, C. L.; Lamb, G. W.; Maxwell, A. C.; Maytum, H. C.; Watson, A. J. A.; Williams, J. M. J., *J. Am. Chem. Soc.* **2009,** *131*, 1766-1774.
2. Long, T. R.; Maity, P. K.; Samarakoon, T. B.; Hanson, P. R., *Org. Lett.* **2010,** *12*, 2904-2907.
3. O'Brien, C. J.; Nixon, Z. S.; Holohan, A. J.; Kunkel, S. R.; Tellez, J. L.; Doonan, B. J.; Coyle, E. E.; Lavigne, F.; Kang, L. J.; Przeworski, K. C., *Chem. Eur. J.* **2013,** *19*, 15281-15289.
4. Kovalenko, O. O.; Volkov, A.; Adolfsson, H., *Org. Lett.* **2015,** *17*, 446-449.
5. McDermott, B. P.; Campbell, A. D.; *Synlett* **2008,** *2008*, 875-879.
6. Du, Y.; Oishi, S.; Saito, S., *Chem. Eur. J.* **2011,** *17*, 12262-12267.
7. Borukhova, S.; Noël, T.; Hessel, V., *ChemSusChem* **2016,** *9*, 67-74.
8. Lai, J.; Chang, L.; Yuan, G., *Org. Lett.* **2016,** *18*, 3194-3197.
9. Zhu, M.; Fujita, K.-i.; Yamaguchi, R., *Org. Lett.* **2010,** *12*, 1336-1339.
10. Li, Y.; Du, W.; Deng, W.-P., *Tetrahedron* **2012,** *68*, 3611-3615.
11. Finney, E. E.; Ogawa, K. A.; Boydston, A. J., *J. Am. Chem. Soc.* **2012,** *134*, 12374-12377.
12. Carle, M. S.; Shimokura, G. K.; Murphy, G. K., *Eur. J. Org. Chem.* **2016,** *2016*, 3930-3933.
13. Green, R. A.; Pletcher, D.; Leach, S. G.; Brown, R. C. D., *Org. Lett.* **2015,** *17*, 3290-3293.
14. Wang, H.; Ma, Y.; Tian, H.; Yu, A.; Chang, J.; Wu, Y., *Tetrahedron* **2014,** *70*, 2669-2673.
15. Rostami, A.; Rostami, A.; Ghaderi, A., *J. Org. Chem.* **2015,** *80*, 8694-8704.
16. Li, Y.; Pu, J.; Jiang, X., *Org. Lett.* **2014,** *16*, 2692-2695.
17. Ham, J.; Yang, I.; Kang, H., *J. Org. Chem.* **2004,** *69*, 3236-3239.
18. Blondiaux, E.; Cantat, T., *Chem. Commun.* **2014,** *50*, 9349-9352.
19. Dombray, T.; Helleu, C.; Darcel, C.; Sortais, J.-B., *Adv. Synth. Catal.* **2013,** *355*, 3358-3362.
20. Unsalan, S.; Ulgen, M., *FABAD Farmasotik Bilimler Dergisi* **1997,** *22*, 103-109.
21. Zhang, C.; Feng, P.; Jiao, N., *J. Am. Chem. Soc.* **2013,** *135*, 15257-15262.
22. Squitieri, R. A.; Shearn-Nance, G. P.; Hein, J. E.; Shaw, J. T., *J. Org. Chem.* **2016,** *81*, 5278-5284.
23. Lim, S.; Ji, M.; Wang, X.; Lee, C.; Jang, H.-Y., *Eur. J. Org. Chem.* **2015,** *2015*, 591-595.
24. Correia, R.; DeShong, P., *J. Org. Chem.* **2001,** *66*, 7159-7165.
25. Stanley, L. M.; Bai, C.; Ueda, M.; Hartwig, J. F., *J. Am. Chem. Soc.* **2010,** *132*, 8918-8920.