Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Metal-free, oxidative C(sp^3)-H arylation of amides with zeolite catalysts

Jannick Vercammen,[1*] Besir Krasniqi,[1] Dirk E. De Vos[1]*

[1]*Centre for Membrane Separations, Adsorption, Catalysis, and Spectroscopy for Sustainable Solutions (cMACS), KU Leuven, Leuven, Belgium*

*Correspondence to: Jannick.vercammen@kuleuven.be (J.V.); dirk.devos@kuleuven.be (D.D.V.).

Oxidant Screening

Table S1. Oxidative coupling of NMP and *N*-methylpyrrole with different oxidants.[a]

Entry	Oxidant	Conv. [%] [d]	Yield [%] [d]	3a : 3b : 3c
1	Oxygen (atm)	54	54	37 : 57 : 6
2	Benzoquinone	<1	<1	-
3	H_2O_2	<1	<1	-
	Dibenzyl peroxide	<1	<1	-
4	TBHP	<1	<1	-
5	DTBP	<1	<1	-
6	Dicumyl peroxide	11	11	29 : 68 : 3
8	TBPB	68	68	36 : 60 : 4
9	TBEC	84	84	37 : 57 : 4

[a] Reaction conditions: 100 mg CBV-780, 2 mL NMP, 1.5 mmol *N*-methylpyrrole, 1.65 mmol oxidans, 100°C, 16 hours.

Solvent Screening

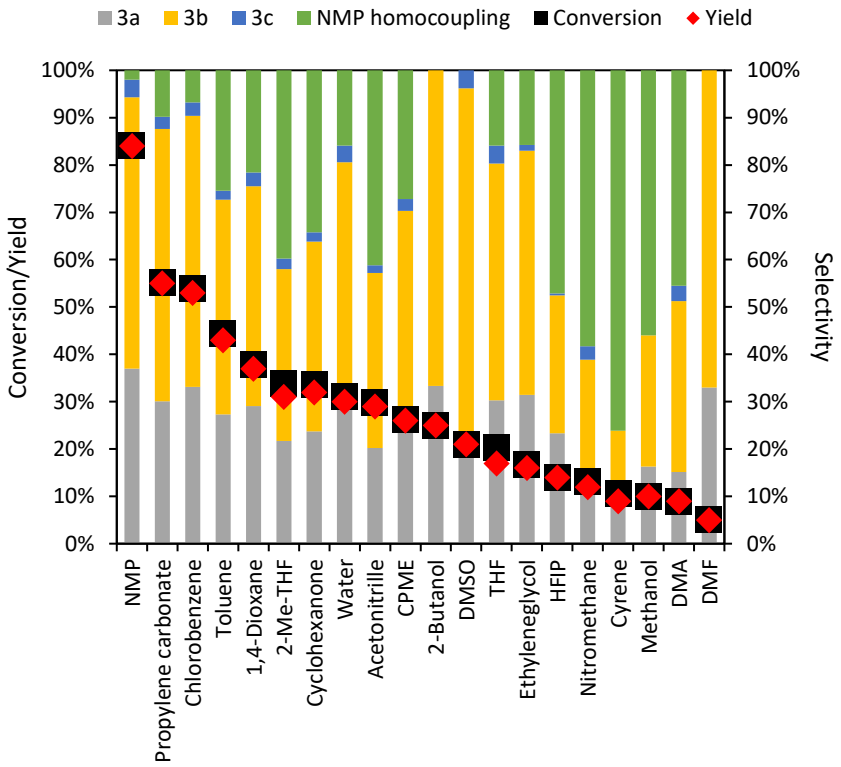


Figure S2. Oxidative coupling of NMP and *N*-methylpyrrole in different solvents. Reaction conditions: 100 mg CBV-780, 2 mL solvent, 1.5 mmol *N*-Methylpyrrole, 3 mmol NMP, 1.65 mmol TBEC.

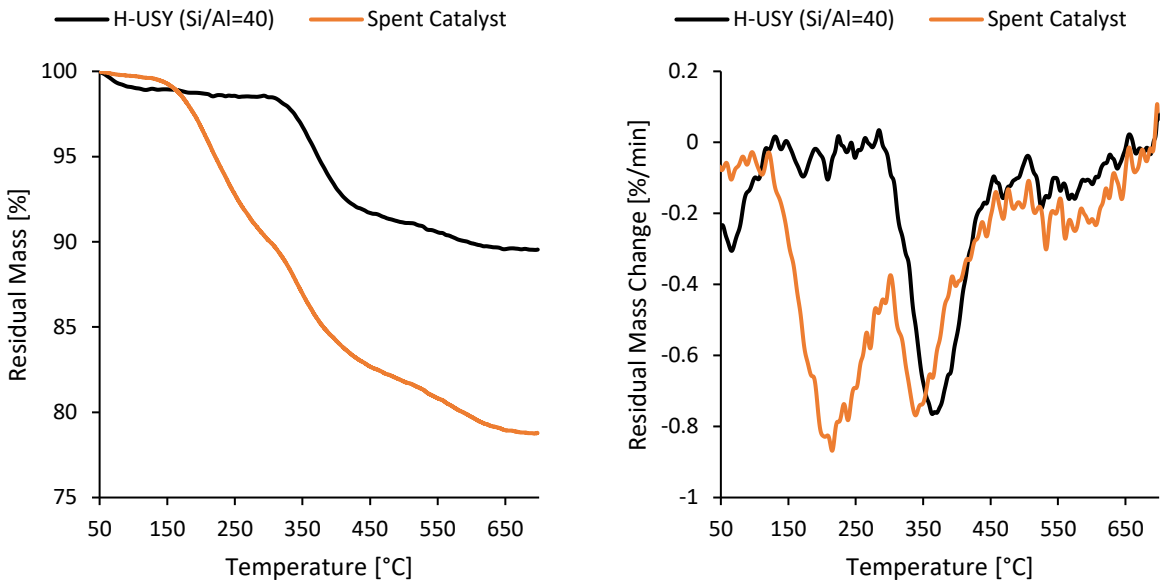


Figure S3. Thermogravimetric analysis on CBV-780 before reaction and after 5 runs (Table 1). Thermographic analysis was carried out on a NETZCH STA 449 F3 Jupiter under a flow of synthetic air (20:60 flow of O_2:N_2) with a heating rate of 10 K/min.

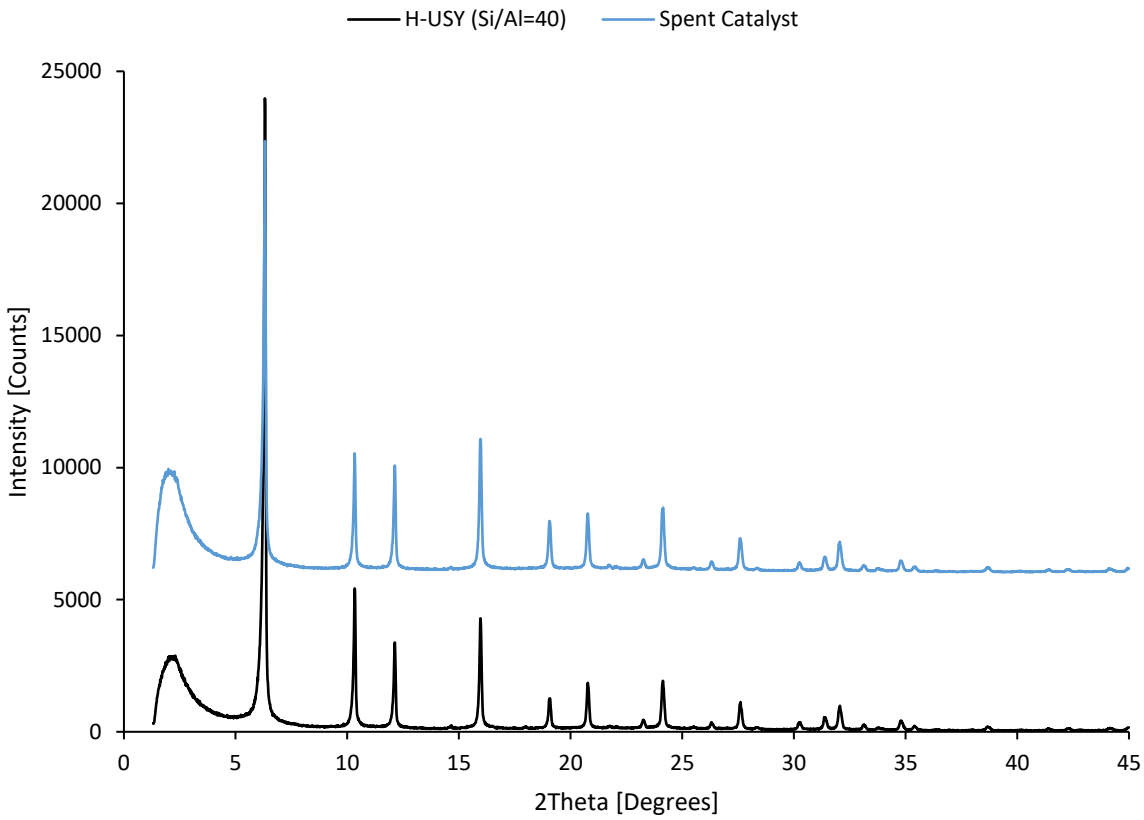


Figure S4. Powder X-ray diffractogram of CBV-780 before reaction and after 5 runs (Table 4). Powder X-ray diffraction (PXRD) were recorded on a Malvern PANalytical Empyrean diffractometer equipped with a PIXcel 3D 1x1 detector. The powder samples were put onto a 96-well plate and patterns were recorded at room temperature in transmission geometry within a 1.3°- 50° 2θ-range with a step size of 0.013° and analyzed via PANalytical Data Viewer software.

Product Characterization

GC-MS

1-methyl-5-(1-methyl-1H-pyrrol-2-yl)pyrrolidin-2-one (Table 1): GC-MS (EI, 70 eV): m/z (rel int., %): 179 (9), 178 (87), 177 (100), 122 (23), 121 (78), 120 (38), 108 (11), 107 (21), 106 (16), 94 (33), 82 (11).

1-methyl-5-(1-methyl-1H-pyrrol-3-yl)pyrrolidin-2-one (Table 1): GC-MS (EI, 70 eV): m/z (rel int., %): 179 (11), 178 (100), 177 (26), 122 (13), 121 (77), 120 (43), 107 (23), 106 (16), 94 (34).

5-((1H-pyrrol-1-yl)methyl)-1-methylpyrrolidin-2-one (Table 1): GC-MS (EI, 70 eV): m/z (rel int., %): 179 (6), 178 (60), 177 (9), 163 (9), 149 (11), 135 (6), 122 (7), 121 (9), 108 (9), 107 (18), 95 (18), 94 (100), 93 (20), 92 (6), 82 (5), 80 (7), 78 (5), 69 (5), 67 (7), 66 (5), 65 (7), 53 (10).

1-methyl-5-(1-methyl-1H-indol-3-yl)pyrrolidin-2-one (Table 2, Entry 1): GC-MS (EI, 70 eV): m/z (rel int., %): 229 (16), 228 (100), 227 (76), 172 (18), 171 (65), 170 (36), 157 (13), 156 (18), 144 (35), 131 (12).

1-methyl-5-(1H-pyrrol-3-yl)pyrrolidin-2-one (Table 2, Entry 2): GC-MS (EI, 70 eV): m/z (rel int., %): 164 (100), 163 (70), 108 (31), 107 (88), 106 (63), 98 (11), 93 (17), 92 (13), 80 (54), 79 (18), 68 (22).

5-(1H-indol-3-yl)-1-methylpyrrolidin-2-one (Table 2, Entry 3): GC-MS (EI, 70 eV): m/z (rel int., %): 215 (14), 214 (100), 213 (72), 158 (20), 157 (63), 156 (35), 143 (15), 142 (15), 130 (35), 129 (11), 115 (11).

5-(1H-imidazol-1-yl)-1-methylpyrrolidin-2-one (Table 2, Entry 4): GC-MS (EI, 70 eV): m/z (rel int., %): 165 (14), 98 (100), 70 (47), 69 (15), 68 (16).

1-methyl-5-(1H-pyrazol-1-yl)pyrrolidin-2-one (Table 2, Entry 5): GC-MS (EI, 70 eV): m/z (rel int., %): 165 (1), 99 (6), 98 (100), 97 (60), 70 (8), 69 (12), 68 (52).

1-methyl-5-(1H-1,2,4-triazol-1-yl)pyrrolidin-2-one (Table 2, Entry 6): GC-MS (EI, 70 eV): m/z (rel int., %): 165 (0.02), 99 (6), 98 (100), 97 (31), 70 (13), 69 (12), 68 (15), 55 (6), 54 (5).

1-methyl-5-(2H-1,2,3-triazol-2-yl)pyrrolidin-2-one (Table 2, Entry 7): GC-MS (EI, 70 eV): m/z (rel int., %): 165 (0.07), 99 (7), 98 (100), 97 (31), 96 (3), 70 (15), 69 (8), 68 (12), 55 (6).

5-(1H-benzo[d][1,2,3]triazol-1-yl)-1-methylpyrrolidin-2-one (Table 2, Entry 8): GC-MS (EI, 70 eV): m/z (rel int., %): 216 (4), 98 (100), 97 (4).

1-methyl-5-(5-methylfuran-2-yl)pyrrolidin-2-one (Table 2, Entry 9): GC-MS (EI, 70 eV): m/z (rel int., %): 180 (12), 179 (100), 178 (61), 164 (62), 162 (12), 136 (55), 124 (15), 123 (18), 122 (62), 121 (17), 108 (28), 107 (26), 98 (19), 95 (41), 94 (17), 79 (23), 77 (16), 68 (12), 55 (14), 53 (15), 51 (17).

1-methyl-5-(5-methylthiophen-2-yl)pyrrolidin-2-one (Table 2, Entry 10): GC-MS (EI, 70 eV): m/z (rel int., %): 196 (15), 195 (100), 194 (86), 180 (41), 138 (41), 137 (14), 124 (13), 123 (21), 111 (21), 98 (23), 97 (15), 69 (22).

1-methyl-5-(pyridin-2-yl)pyrrolidin-2-one (Table 2, Entry 11): GC-MS (EI, 70 eV): m/z (rel int., %): 176 (9), 148 (12), 147 (100), 119 (32), 118 (34), 117 (11), 106 (53), 98 (67), 93 (31), 78 (18), 51 (14).

N-(1-methyl-5-oxopyrrolidin-2-yl)acetamide (Table 2, Entry 12): GC-MS (EI, 70 eV): m/z (rel int., %): 156 (13), 141 (12), 128 (23), 113 (86), 99 (31), 98 (100), 97 (85), 85 (13), 84 (12), 70 (19), 69 (74), 68 (48), 58 (13), 57 (29), 56 (31), 55 (19), 54 (11).

N-(1-methyl-5-oxopyrrolidin-2-yl)benzamide (Table 2, Entry 13): GC-MS (EI, 70 eV): m/z (rel int., %): 218 (28), 161 (12), 113 (18), 105 (100), 98 (65), 97 (42), 77 (75), 69 (27), 68 (19), 51 (24).

methyl (1-methyl-5-oxopyrrolidin-2-yl)carbamate (Table 2, Entry 14): GC-MS (EI, 70 eV): m/z (rel int., %): 172 (9), 157 (96), 144 (30), 113 (35), 98 (100), 97 (21), 85 (14), 70 (18), 69 (14), 68 (21), 59 (16), 56 (14), 55 (12).

N-(1-methyl-5-oxopyrrolidin-2-yl)furan-2-carboxamide (Table 2, Entry 15) : GC-MS (EI, 70 eV): m/z (rel int., %): 208 (51), 113 (12), 112 (13), 98 (84), 97 (39), 96 (10), 95 (100), 70 (11), 69 (26), 68 (27), 55 (10).

1,3,7-trimethyl-8-(1-methyl-5-oxopyrrolidin-2-yl)-1H-purine-2,6(3H,7H)-dione (Table 2, Entry 16): GC-MS (EI, 70 eV): m/z (rel int., %): 293 (2), 292 (16), 291 (100), 235 (48), 234 (23), 221 (14), 220 (72), 208 (47), 207 (12), 194 (12), 193 (11), 81 (12), 67 (19).

5-(benzo[d]thiazol-2-yl)-1-methylpyrrolidin-2-one (Table 2, Entry 17): GC-MS (EI, 70 eV): m/z (rel int., %): 232 (23), 204 (17), 203 (100), 176 (8), 175 (37), 174 (15), 163 (6), 162 (33), 161 (45), 149 (10), 136 (11), 135 (6), 134 (6), 109 (7), 108 (12), 98 (66), 70 (16), 69 (20), 68 (12), 63 (5), 55 (5).

1-methyl-5-(1H-pyrrolo[2,3-b]pyridin-3-yl)pyrrolidin-2-one (Table 2, Entry 18): GC-MS (EI, 70 eV): m/z (rel int., %): 216 (13), 215 (100), 214 (62), 159 (15), 158 (53), 157 (28), 144 (14), 143 (11), 132 (11), 131 (30), 119 (11).

5-(1-methyl-1H-pyrrol-2-yl)pyrrolidin-2-one (Table 3, Entry 1): GC-MS (EI, 70 eV): m/z (rel int., %): 165 (9), 164 (84), 163 (32), 135 (30), 134 (31), 121 (10), 120 (19), 108 (28), 107 (100), 106 (13), 94 (16), 82 (21), 80 (25), 53 (10).

1-cyclohexyl-5-(1-methyl-1H-pyrrol-2-yl)pyrrolidin-2-one (Table 3, Entry 2): GC-MS (EI, 70 eV): m/z (rel int., %): 247 (18), 246 (100), 165 (22), 164 (39), 163 (40), 161 (25), 135 (18), 121 (34), 120 (74), 108 (18), 107 (75), 106 (20), 98 (12), 94 (31), 93 (11), 84 (12), 81 (13), 80 (13), 79 (12), 55 (14).

1-cyclohexyl-5-(1-methyl-1H-pyrrol-3-yl)pyrrolidin-2-one (Table 3, Entry 2): GC-MS (EI, 70 eV): m/z (rel int., %): 247 (17), 246 (100), 164 (51), 163 (66), 161 (16), 148 (13), 139 (16), 135 (20), 134 (12), 122 (12), 121 (42), 120 (81), 118 (12), 108 (24), 107 (92), 106 (16), 98 (12), 97 (11), 94 (33), 82 (11), 81 (14), 79 (11), 77 (11), 55 (16).

5-((1H-pyrrol-1-yl)methyl)-1-cyclohexylpyrrolidin-2-one (Table 3, Entry 2): GC-MS (EI, 70 eV): m/z (rel int., %): 247 (18), 246 (100), 165 (32), 164 (38), 163 (32), 122 (12), 121 (59), 120 (47), 108 (38), 107 (52), 106 (31), 94 (27).

5-(1-methyl-1H-pyrrol-2-yl)-1-octylpyrrolidin-2-one (Table 3, Entry 3): GC-MS (EI, 70 eV): m/z (rel int., %): 277 (2), 276 (10), 178 (12), 177 (100), 120 (8),) 108 (18, 94 (13).

5-(1-methyl-1H-pyrrol-3-yl)-1-octylpyrrolidin-2-one (Table 3, Entry 3): GC-MS (EI, 70 eV): m/z (rel int., %): 277 (11), 276 (59), 178 (42), 164 (14), 163 (20), 149 (13), 148 (14), 135 (12), 121 (47), 120 (100), 108 (16), 107 (78), 106 (15), 98 (10), 97 (12), 94 (67), 84 (11), 82 (10), 81 (10), 55 (11).

5-((1H-pyrrol-1-yl)methyl)-1-octylpyrrolidin-2-one (Table 3, Entry 3): GC-MS (EI, 70 eV): m/z (rel int., %): 277 (11), 276 (55), 275 (16), 219 (10), 191 (11), 178 (28), 177 (16), 164 (10), 163 (20), 149 (12), 148 (21), 121 (41), 120 (100), 108 (15), 107 (65), 95 (10), 94 (85).

5-(1-methyl-1H-pyrrol-2-yl)-1-butylpyrrolidin-2-one (Table 3, Entry 4): GC-MS (EI, 70 eV): m/z (rel int., %): 220 (55), 219 (16), 177 (16), 163 (32), 148 (19), 135 (25), 122 (23), 121 (38), 120 (100), 109 (10), 108 (19), 107 (69), 106 (13), 94 (91).

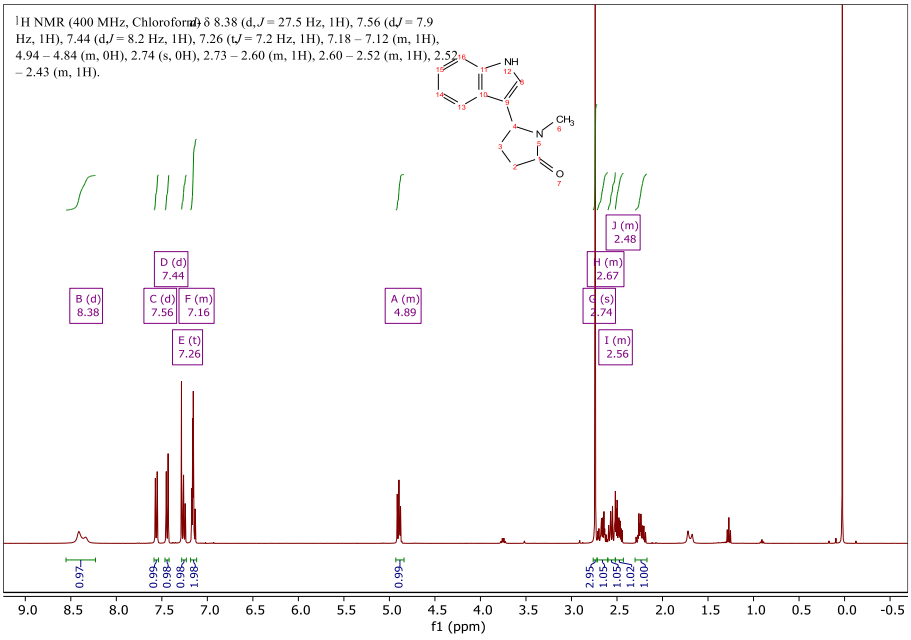
5-(1-methyl-1H-pyrrol-3-yl)-1-butylpyrrolidin-2-one (Table 3, Entry 4): GC-MS (EI, 70 eV): m/z (rel int., %): 221 (10), 220 (69), 164 (10), 163 (31), 148 (10), 139 (11), 135 (32), 122 (40), 121 (48), 120 (100), 109 (13), 108 (18), 107 (79), 106 (21), 97 (13), 94 (77), 93 (10), 84 (19), 82 (11), 80 (14), 79 (11), 77 (10).

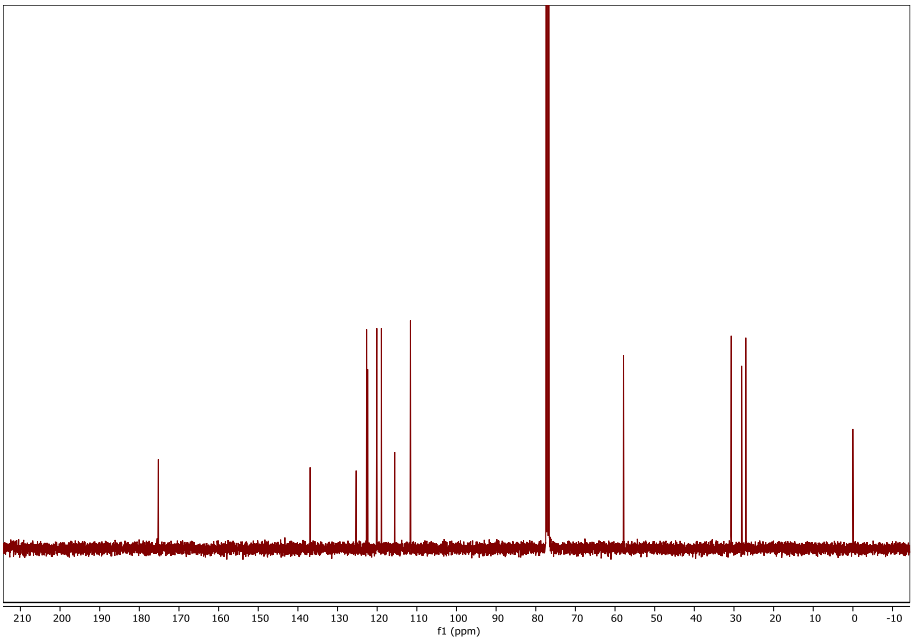
5-((1H-pyrrol-1-yl)methyl)-1-butylpyrrolidin-2-one (Table 3, Entry 4): GC-MS (EI, 70 eV): m/z (rel int., %): 220 (16), 178 (12), 177 (100), 120 (10), 108 (35), 94 (19).

Product isolation

Once the reaction was complete, the crude mixture was poured into a saturated solution of $NaHCO_3$ to precipitate the indole/pyrazole derivatives. The resulting product was then transferred to a round-bottom flask and dissolved in $CHCl_3$. Next, the solution was subjected to rotary evaporation to remove the $CHCl_3$, and this process was repeated several times until any residual NMP was completely removed. Finally, the pure product was obtained through crystallization using THF/MeOH as a solvent at a temperature of -20°C.

5-(1H-indol-3-yl)-1-methylpyrrolidin-2-one (Table 2, Entry 3, 156 mg, 73% yield)





1-methyl-5-(1H-pyrazol-1-yl)pyrrolidin-2-one (Table 2, Entry 5, 123 mg, 75% yield)