

Electronic Supplementary Information

A facile access to 2,5-diaryl fulleropyrrolidines: magnesium perchlorate-mediated reaction of [60]fullerene with arylmethamines and arylaldehydes

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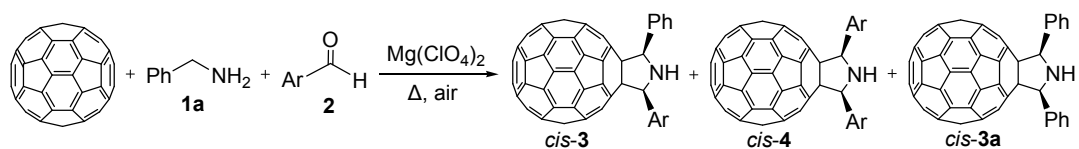
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Reaction of C₆₀ with 2-chlorobenzaldehyde (2g) and 3-nitrobenzaldehyde (2i) in the presence of benzylamine (1a) and Mg(ClO₄)₂ under different conditions

To improve the product selectivity of the reaction of C₆₀ with 2-chlorobenzaldehyde (2g) and 3-nitrobenzaldehyde (2i) in the presence of benzylamine (1a) and Mg(ClO₄)₂, various reaction conditions have been screened. The reaction conditions and yields for the Mg(ClO₄)₂-mediated reactions of C₆₀ with 1a, 2g and 2i are summarized in Table S1. As can be seen from Table S1, increasing the amount of benzylamine (1a) from 5 to 10 equiv could selectively obtain the unsymmetrical 2,5-diaryl fulleropyrrolidine *cis*-3i in 38% isolated yield, while raising the amount of 2-chlorobenzaldehyde (2g) from 5 to 10 equiv had no benefit to the product selectivity of *cis*-3i and *cis*-4a. As for 3-nitrobenzaldehyde (2i), decreasing the reaction temperature from 160 to 120 °C together with varying the amount of benzylamine (1a) and 3-nitrobenzaldehyde (2i) (from 5 to 10 equiv) did not improve the product selectivity of *cis*-3k and *cis*-4c. Furthermore, increasing the amount of benzylamine (1a) from 5 to 10 equiv usually led to the formation of another 2,5-diaryl fulleropyrrolidine *cis*-3a, which would further reduce the selectivity of the reaction of C₆₀ with benzylamine (1a) and 3-nitrobenzaldehyde (2i) in the presence of Mg(ClO₄)₂.

Table S1 Optimization of reaction conditions for the reaction of C₆₀ with benzylamine 1a and arylaldehydes 2g,i bearing electron-withdrawing groups under the assistance of Mg(ClO₄)₂^a



Amine 1	Aldehyde 2	Molar ratio (C ₆₀ /Mg(ClO ₄) ₂)/ 1a/2)	Time (h)	Product <i>cis</i> - 3	Yield of <i>cis</i> - 3 ^b (%)	Product <i>cis</i> - 4	Yield of <i>cis</i> - 4 ^b (%)	Yield of <i>cis</i> - 3a ^b (%)
		1:2:5:5	22	3i	29 (52)	4a	25 (45)	trace
		1:2:10:5	24	3i	38 (93)	4a	trace	trace
		1:2:5:10	23	3i	32 (57)	4a	22 (39)	trace
		1:2:10:5	26	3k	23 (52)	4c	9 (20)	10 (23)
		1:2:5:10	24	3k	18 (56)	4c	8 (25)	trace
		1:2:5:5	4^c	3k	38 (57)	4c	26 (39)	trace
		1:2:10:5	4^c	3k	36 (57)	4c	11 (17)	13 (21)
		1:2:5:10	3.5^c	3k	23 (44)	4c	24 (46)	trace

^a All reactions were performed in chlorobenzene (10 mL) under air conditions at 120 °C unless otherwise indicated. ^b Isolated yield, those in parentheses were based on consumed C₆₀. ^c The reaction was conducted at 160 °C in *o*-dichlorobenzene (6 mL).

