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After finishing in the top four, Villarreal won the right to start dreaming about their first adventure in the Champions League in 2005/06, the most important club competition on the planet. And the Submarine went on a journey that caused a stir in Europe and throughout the world: easily beating English side Everton in their qualifying play-off match, then leading their group in the Group stages and passing the hurdles one by one until, with what was very bad luck, they were stopped in the Semi-finals by an Arsenal side who were made to suffer to the end to get to the Final of the competition. The Yellows made their debut in the world's biggest competition in style, against a less than Manchester United on 14th September 2005. It was a very even game that finished in a 0-0 draw and the Submarine made their intentions clear.

Villarreal's first victory in the Champions League came on Match Day 4 in the Group stages, with the Submarine playing in Group D. The Yellows visited the Da Luz stadium and beat Benfica 0-1, with a wonder goal by Marcos Senna from about 25 yards out. A key result to finish the initial phase in first place with 10 points, two games won and four drawn. Villarreal were already among the 16 best teams in Europe in their first time participating in the Champions League. A success that wouldn't finish there and far from it.

The Yellows went up against Glasgow Rangers in the Round of 16. The Scottish side, one of Europe's classics, hosted the Submarine on 22nd February 2006. Riquelme, from the penalty spot, and Diego Forl were the goal scorers for the Yellows, who went away with a valuable 2-2 draw. The second leg at El Madrigal finished in a 1-1 draw, enough to take the Submarine through to the Quarter-finals. Arruabarrena, with his goal, was already beginning to establish himself as the team's hero in the Champion