

6. ANEXOS

6.1. Mecanismo de reacción.

En el grupo de investigación donde se realizó este Trabajo Fin de Grado se han llevado a cabo cálculos computacionales¹ confirmándose la preferencia por la cara menos impedida, así como la esperada coordinación del átomo de litio con el oxígeno de la nitrona. En la Figura 1, a modo de ejemplo, se ilustran dos estados de transición correspondientes a la adición de litiometilfosfonato de dimetilo a una nitrona modelo. La estructura de transición correspondiente a la cara menos impedida es kcal/mol más estable que aquella correspondiente a la cara más impedida.

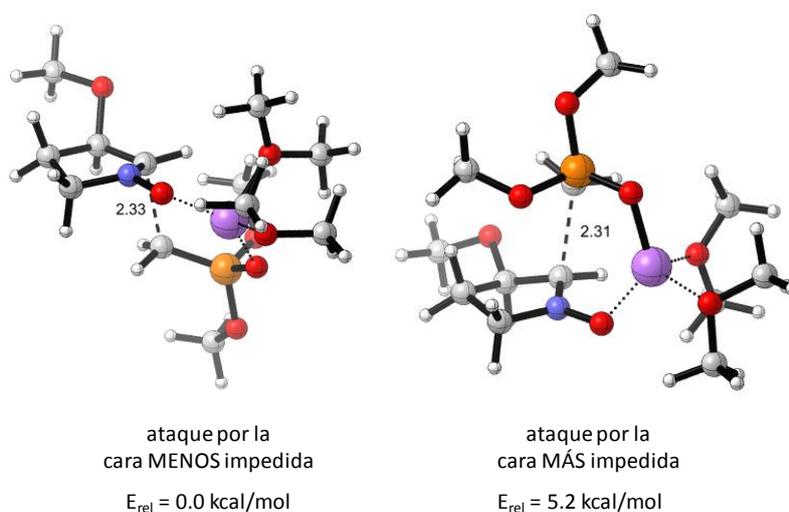


Figura 1. Estructuras optimizadas (B3LYP-D3BJ/def2TZVP/PCM=THF) de transición (se incluyen dos moléculas discretas de disolvente para completar la esfera de coordinación del litio)

Los modelos de la reacción confirman que la especie atacante es, en realidad, aquella en la que el litio está coordinado al átomo de oxígeno, pudiéndose plantear un mecanismo para la reacción como el ilustrado en la Figura 2.

¹ Los cálculos computacionales han sido llevados a cabo por parte de los directores de este Trabajo Fin de Grado limitándose la participación de la autora a la interpretación de los modelos.

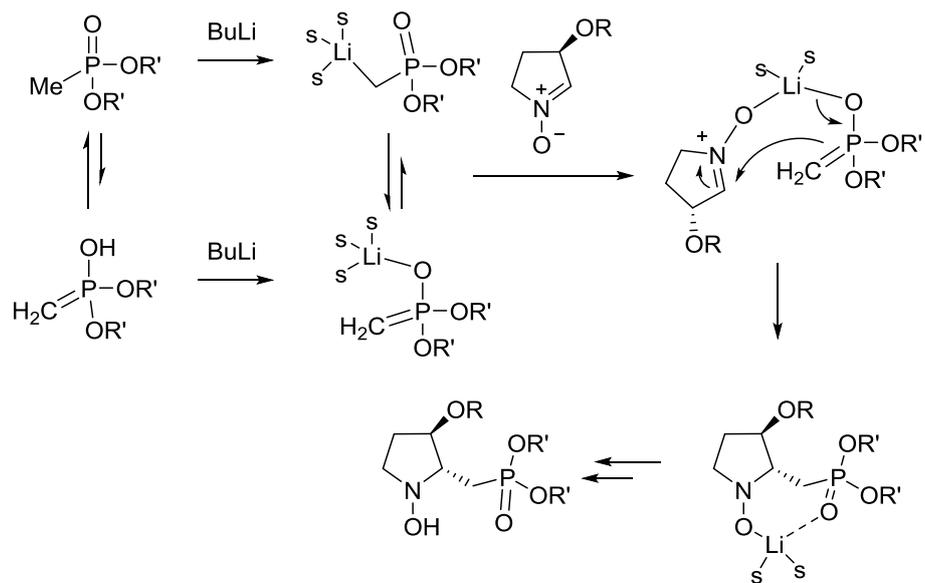


Figura 2. Mecanismo detallado de la adición de litiometilfosfonatos a nitronas cíclicas

6.2. Espectros

6.2.1. Espectros de los sustratos de partida

6.2.1.1. Nitronas cíclicas

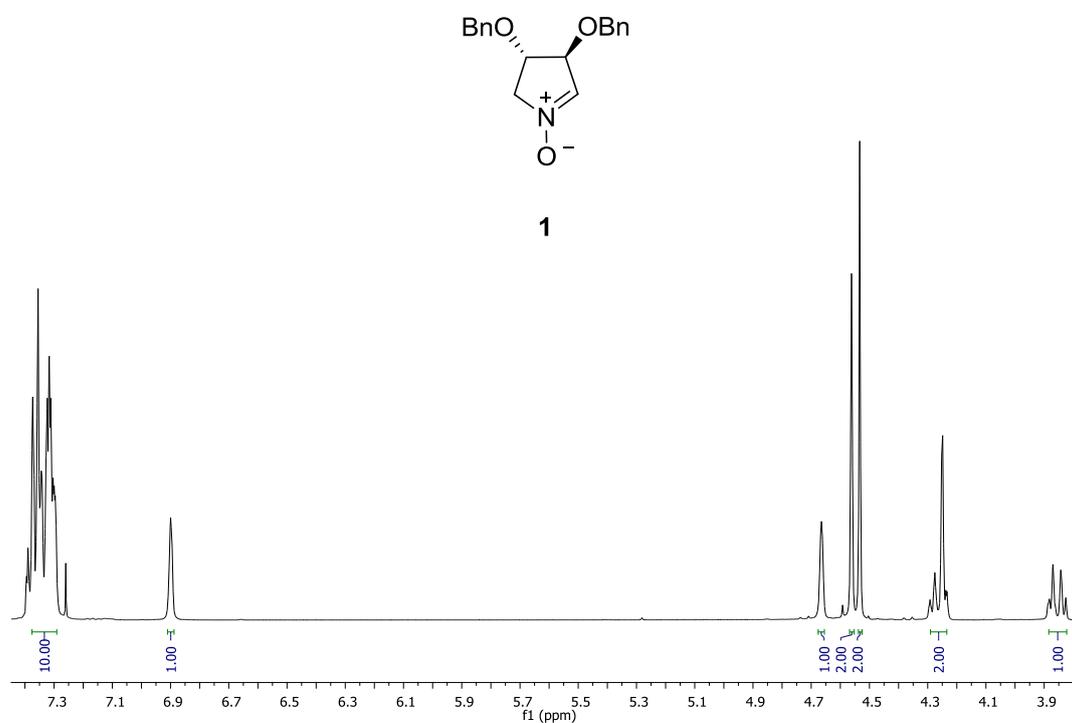


Figura 3a: ^1H RMN (400 MHz, CDCl_3)

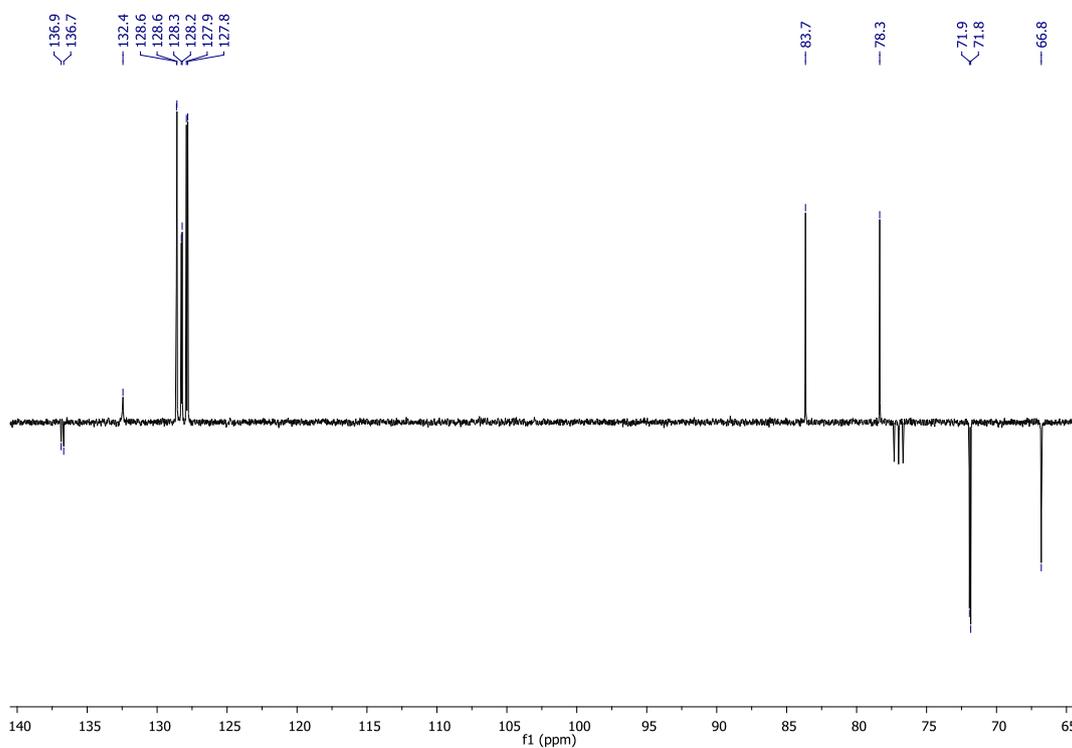


Figura 3b: ^{13}C RMN (100 MHz, CDCl_3)

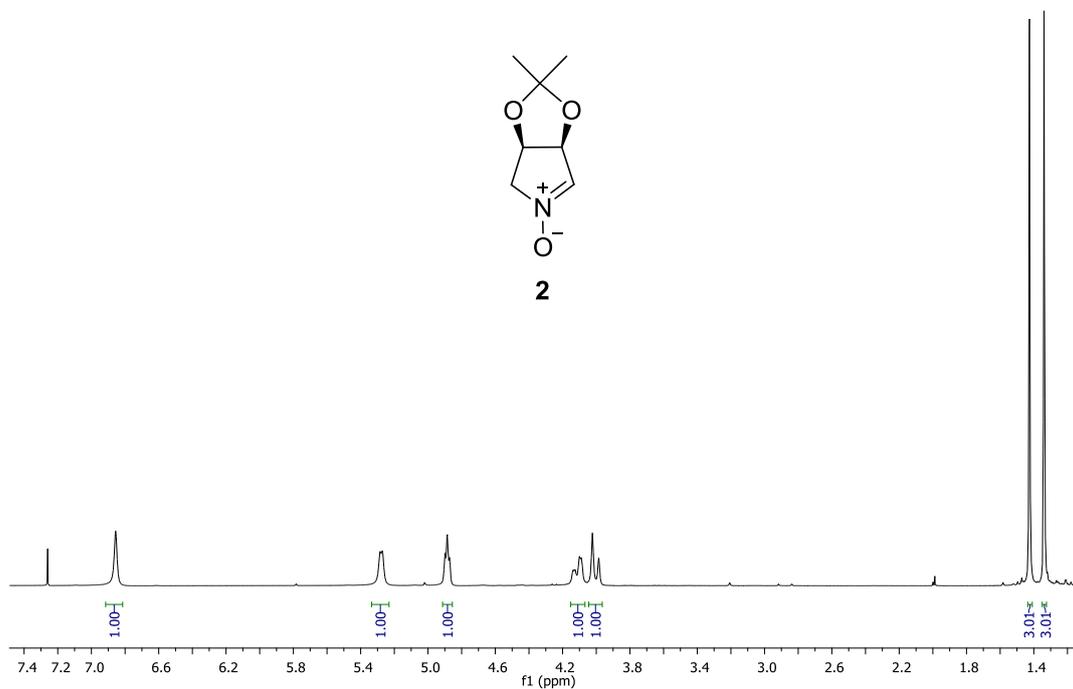


Figura 4a: ^1H RMN (400 MHz, CDCl_3)

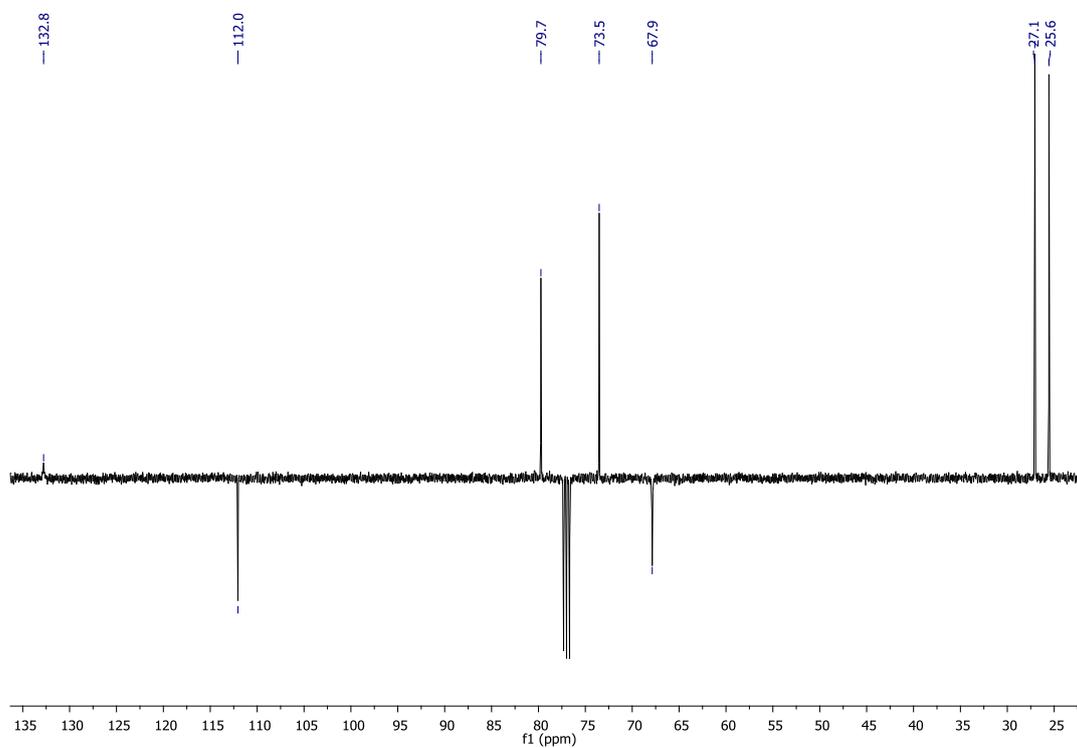


Figura 4b: ^{13}C RMN (100 MHz, CDCl_3)

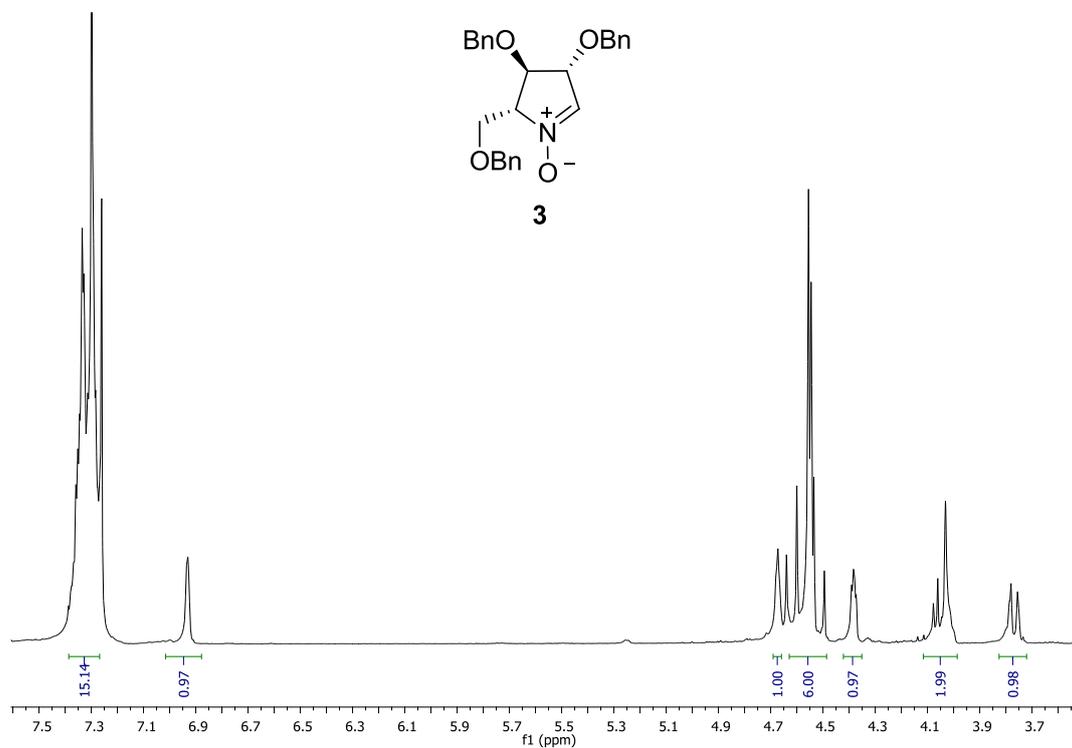


Figura 5a: ^1H RMN (400 MHz, CDCl_3)

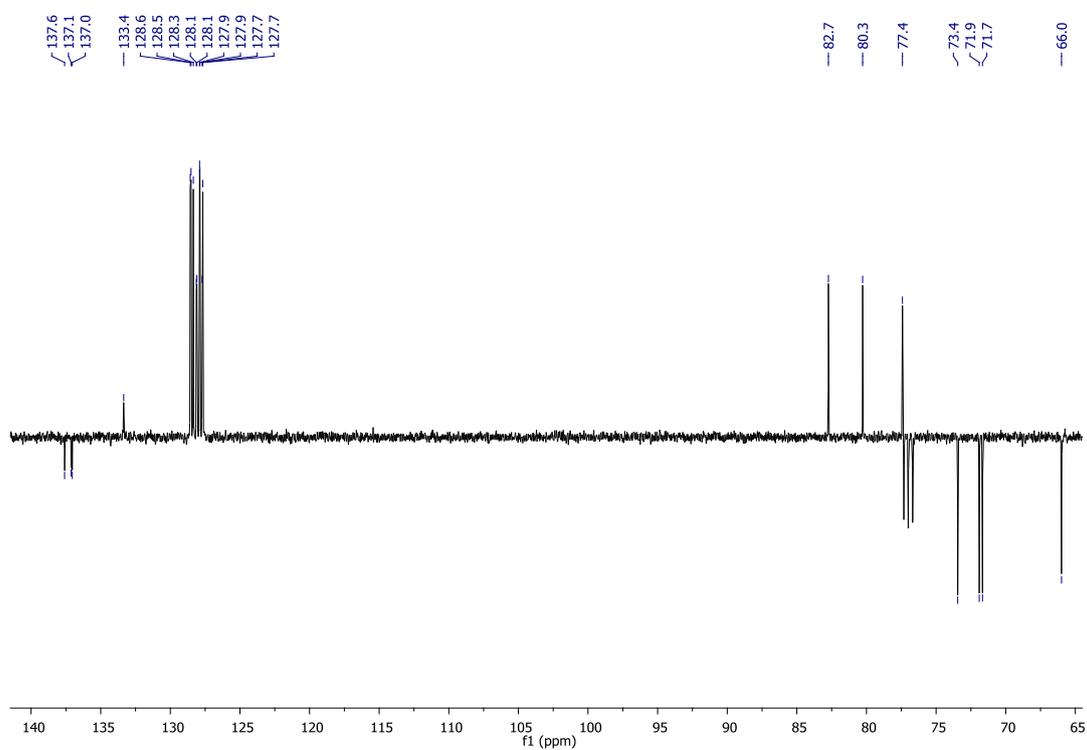


Figura 5b: ^{13}C RMN (100 MHz, CDCl_3)

6.2.1.2. Metilfosfonatos no comerciales

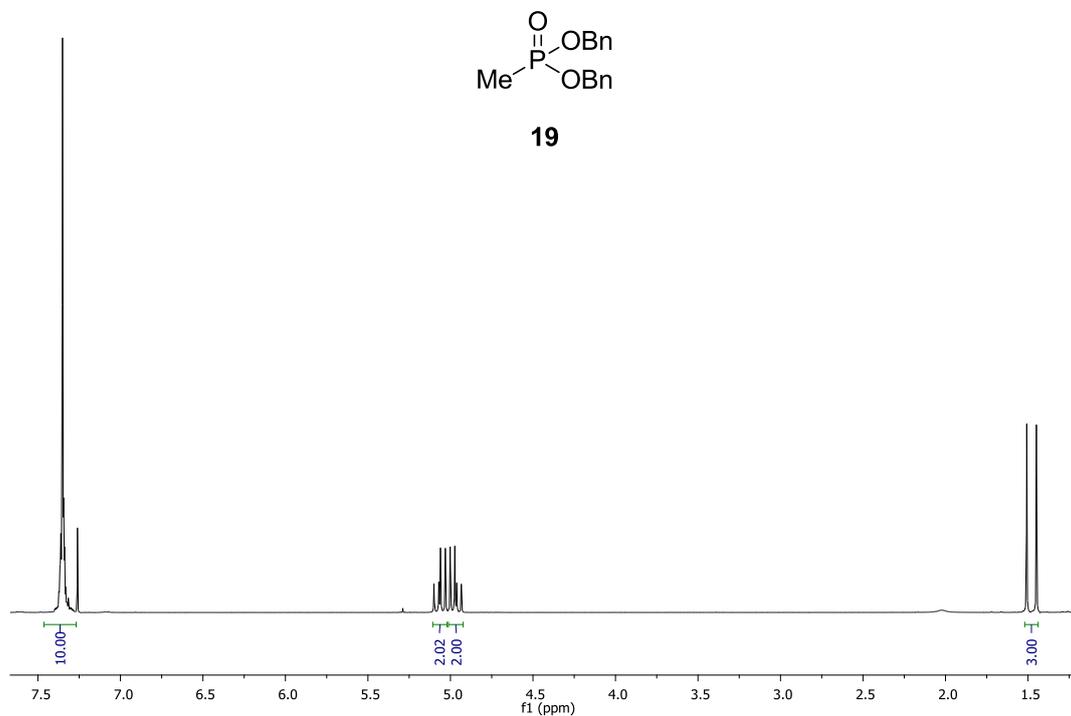


Figura 6a: ^1H RMN (300 MHz, CDCl_3)

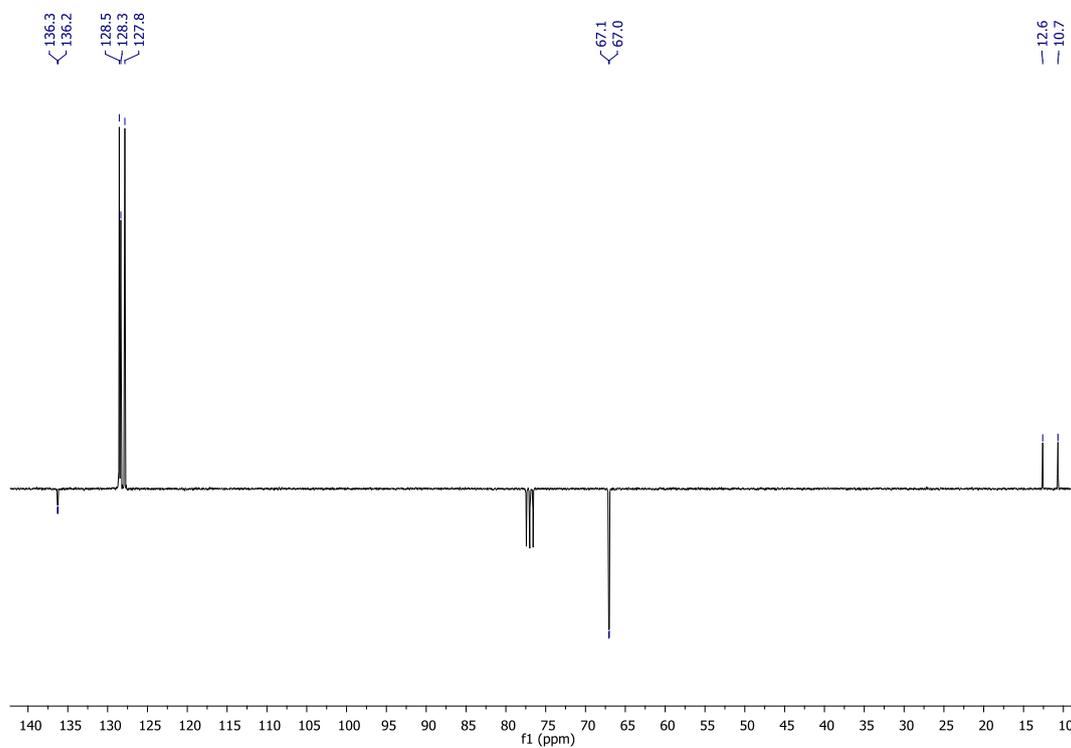


Figura 6b: ^{13}C RMN (75.5 MHz, CDCl_3)

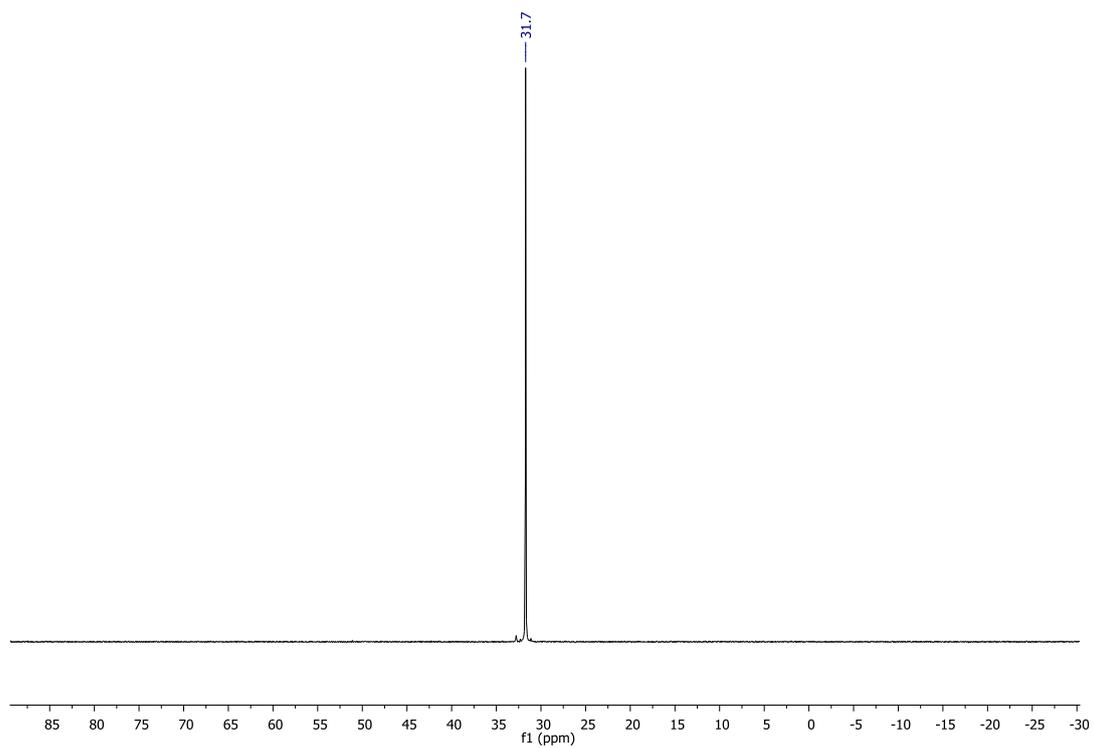
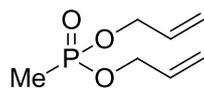


Figura 6c: ^{31}P RMN (121.5 MHz, CDCl_3)



20

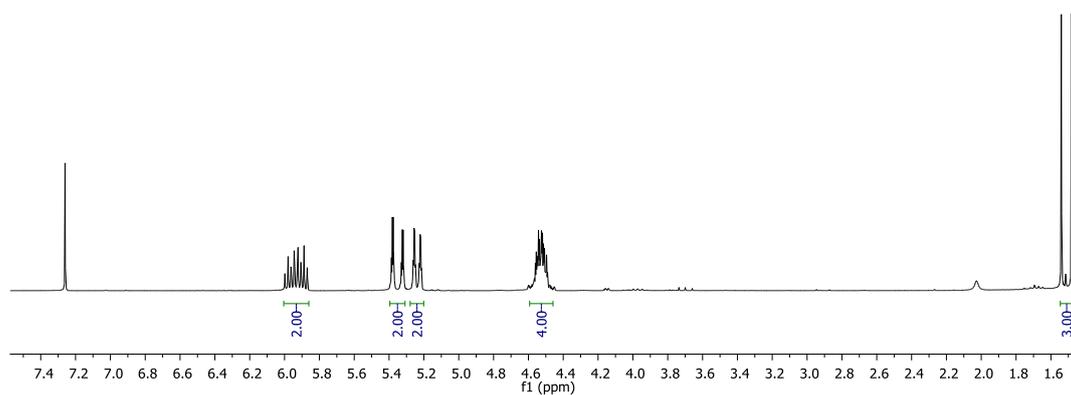


Figura 7a: ^1H RMN (300 MHz, CDCl_3)

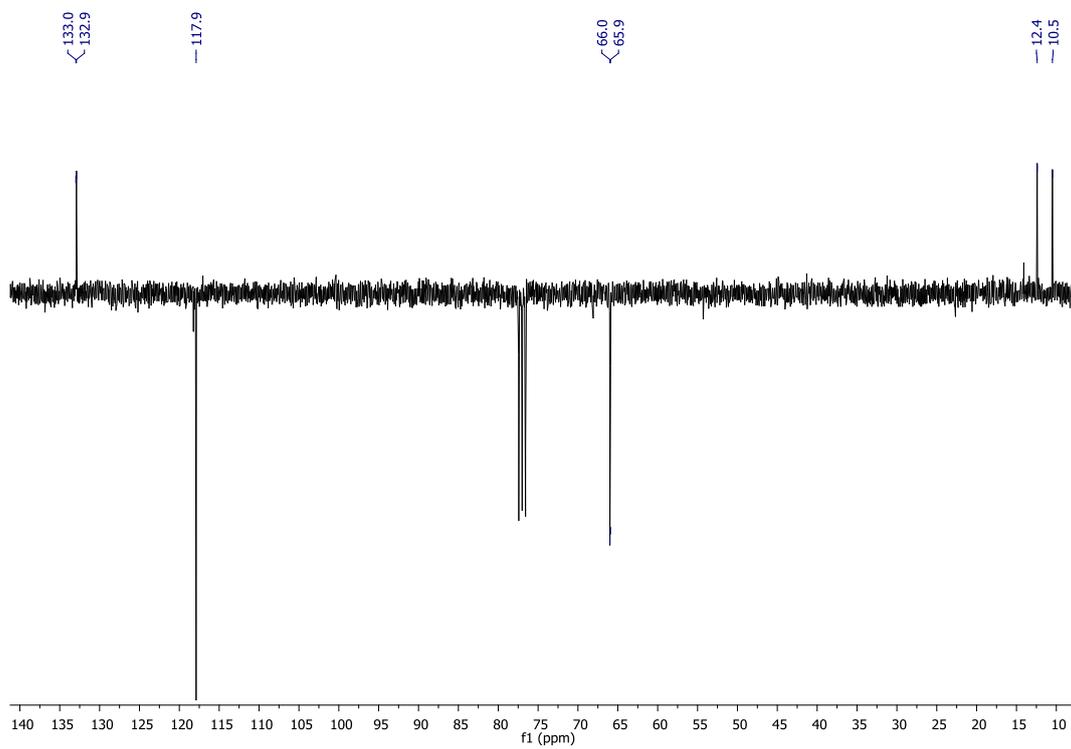


Figura 7b: ^{13}C RMN (75.5 MHz, CDCl_3)

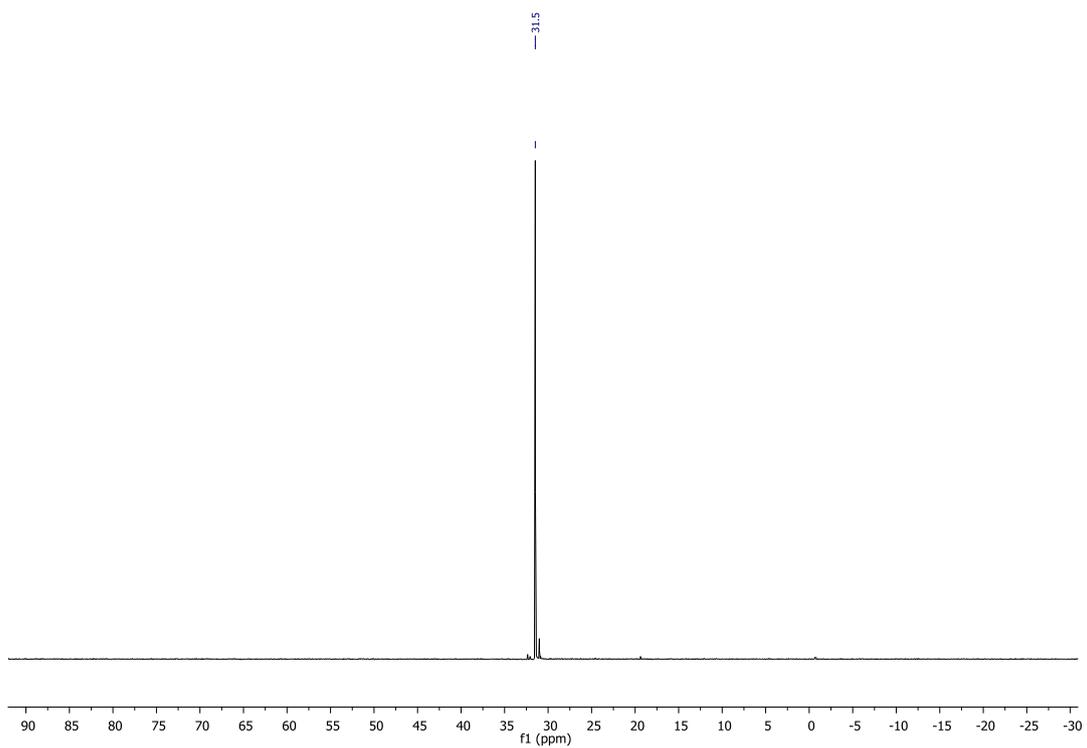


Figura 7c: ^{31}P RMN (121.5 MHz, CDCl_3)

6.2.2. Espectros de los productos de adición

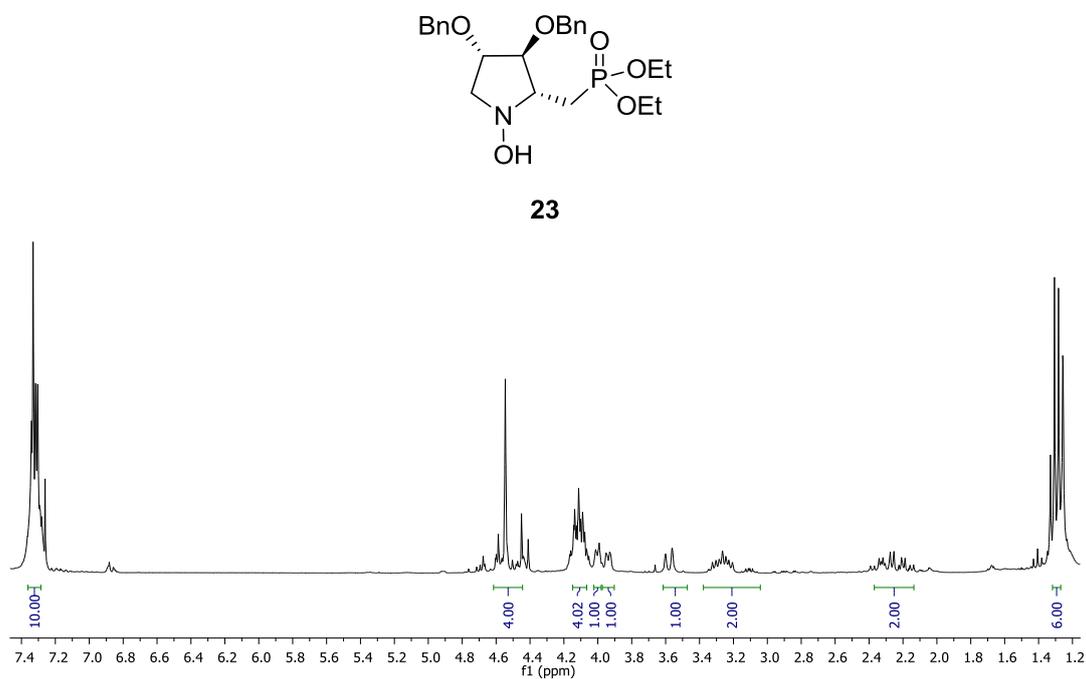


Figura 8a: ^1H RMN (300 MHz, CDCl_3)

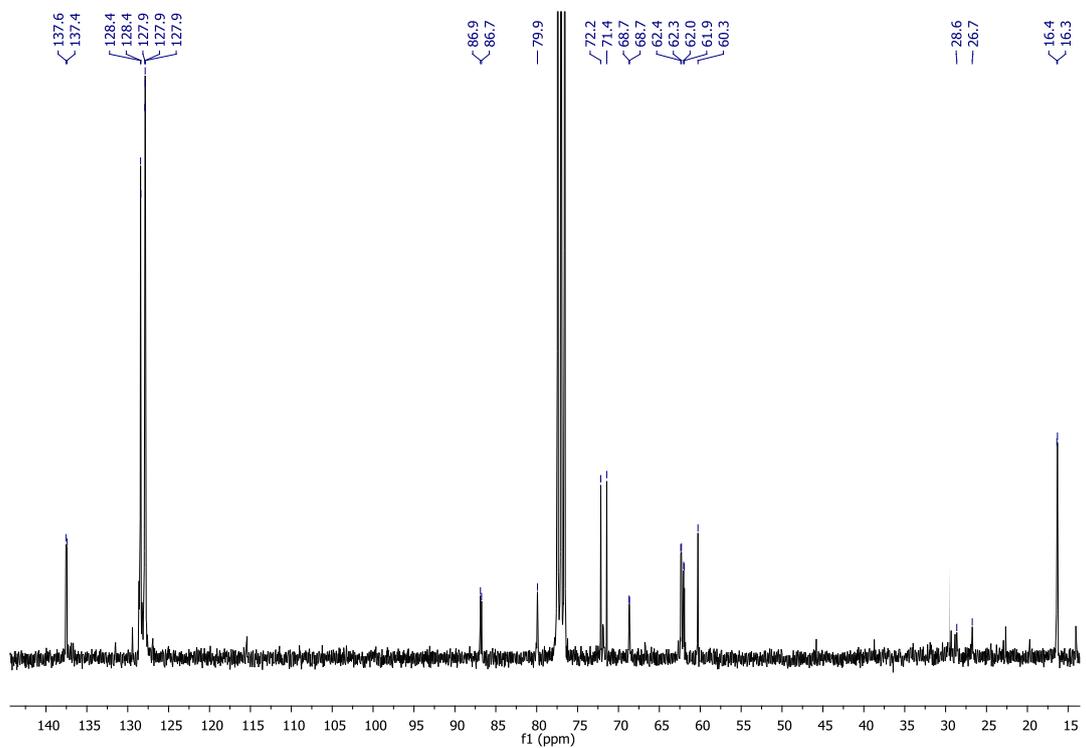


Figura 8b: ^{13}C RMN (75.5 MHz, CDCl_3)

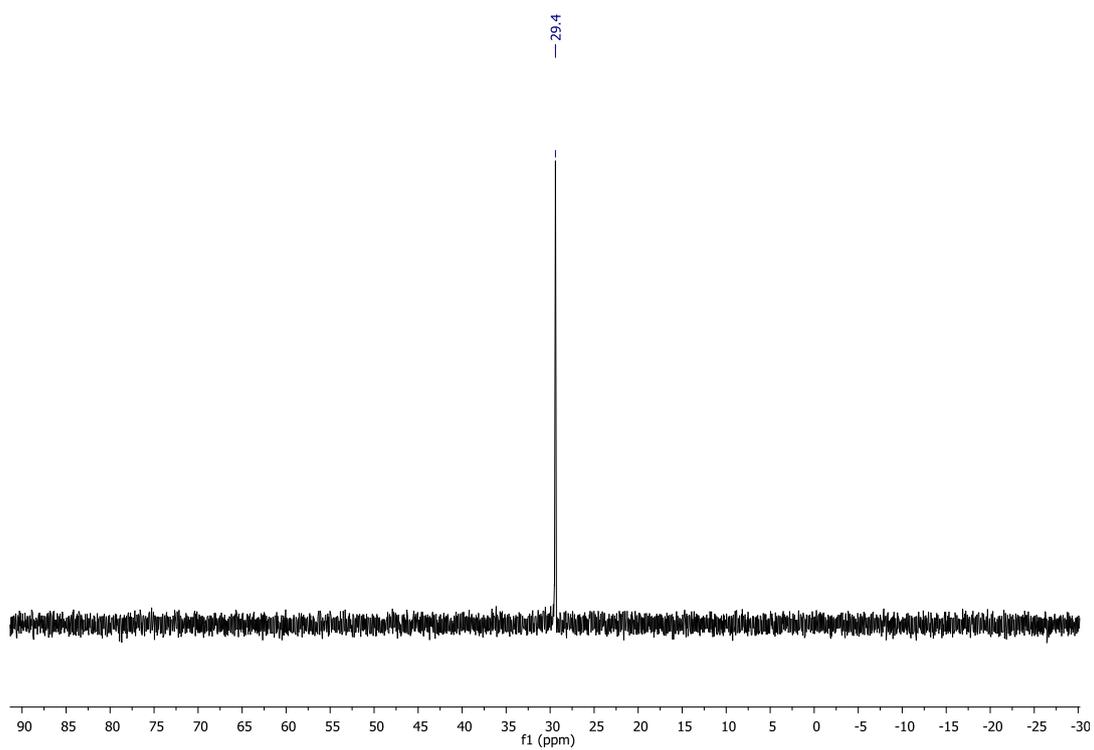


Figura 8c: ^{31}P RMN (121.5 MHz, CDCl_3)

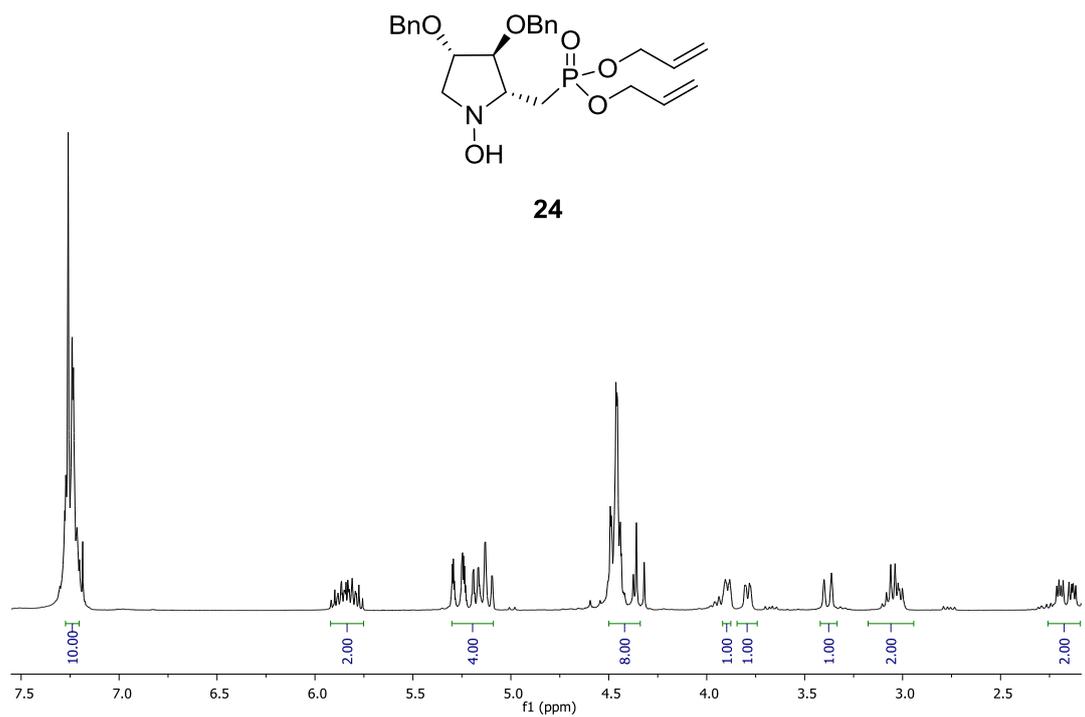


Figura 9a: ^1H RMN (300 MHz, CDCl_3)

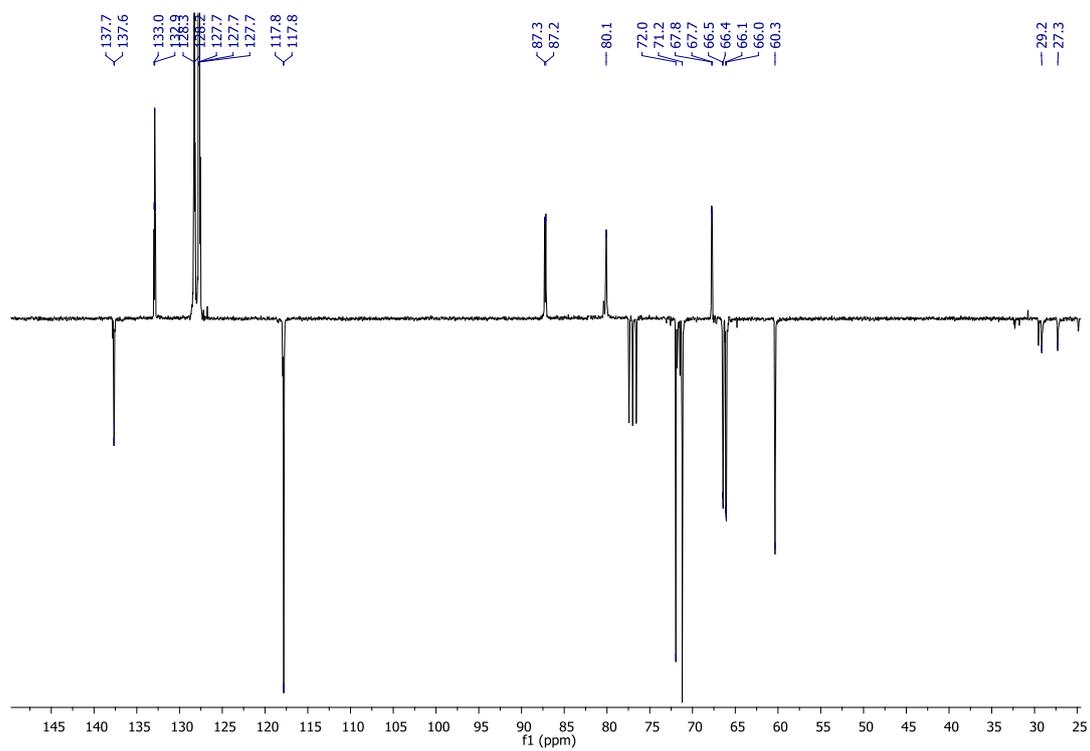


Figura 9b: ^{13}C RMN (75.5 MHz, CDCl_3)

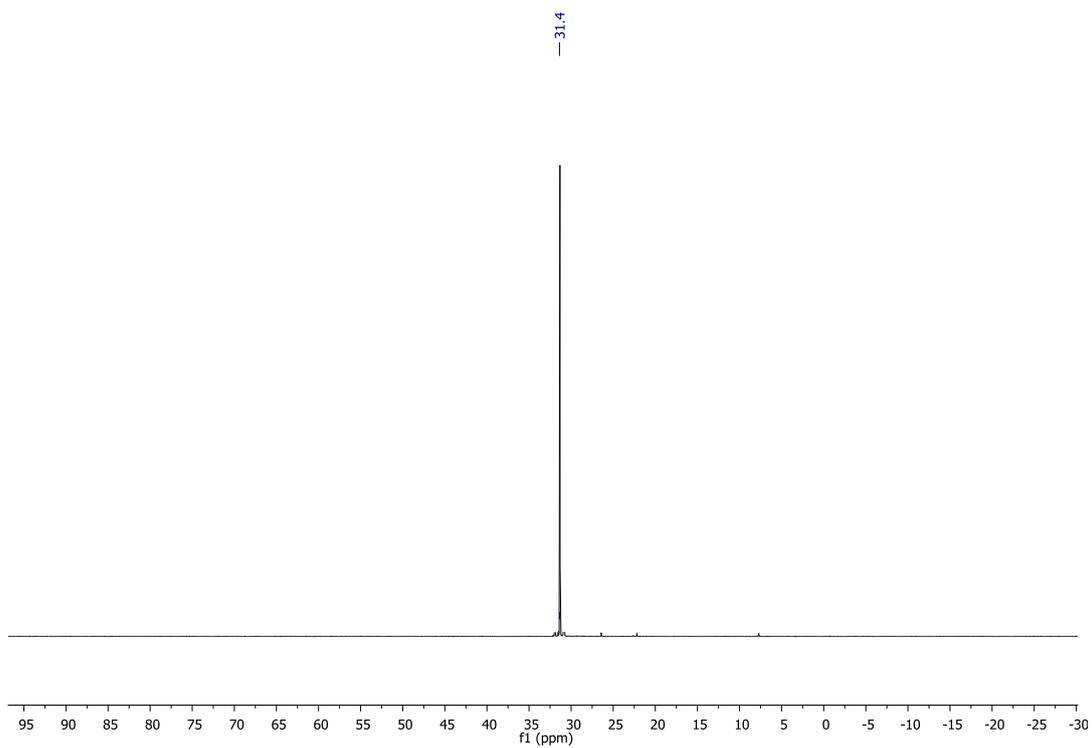


Figura 9c: ^{31}P RMN (121.5 MHz, CDCl_3)

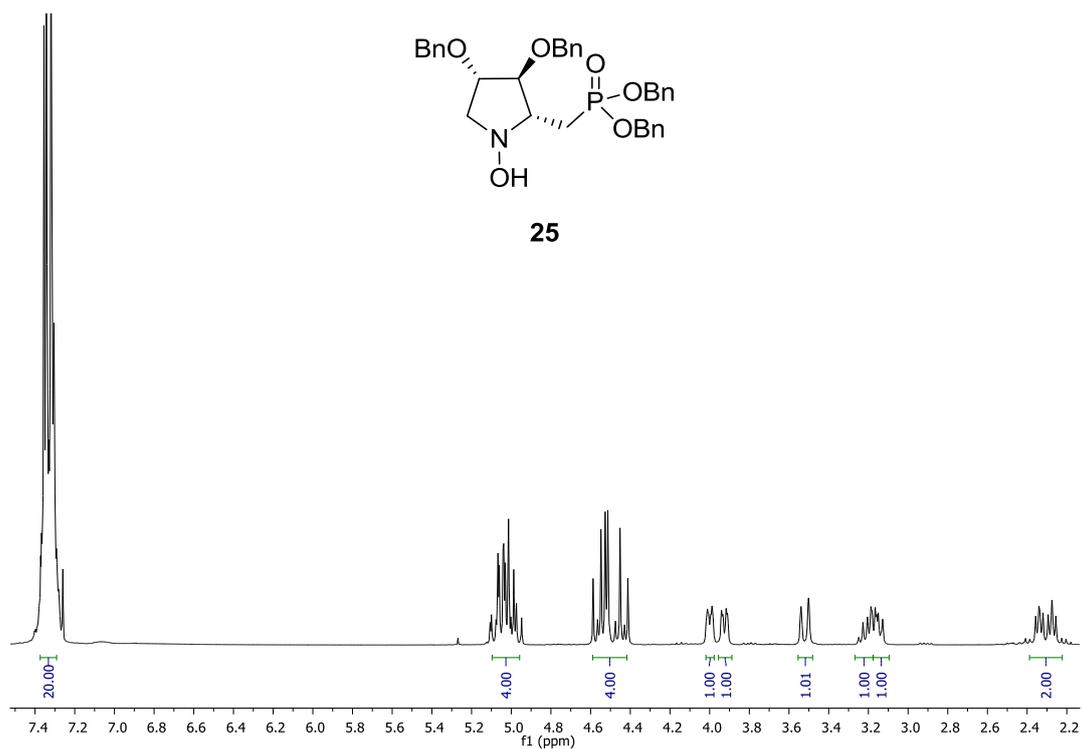


Figura 10a: ^1H RMN (300 MHz, CDCl_3)

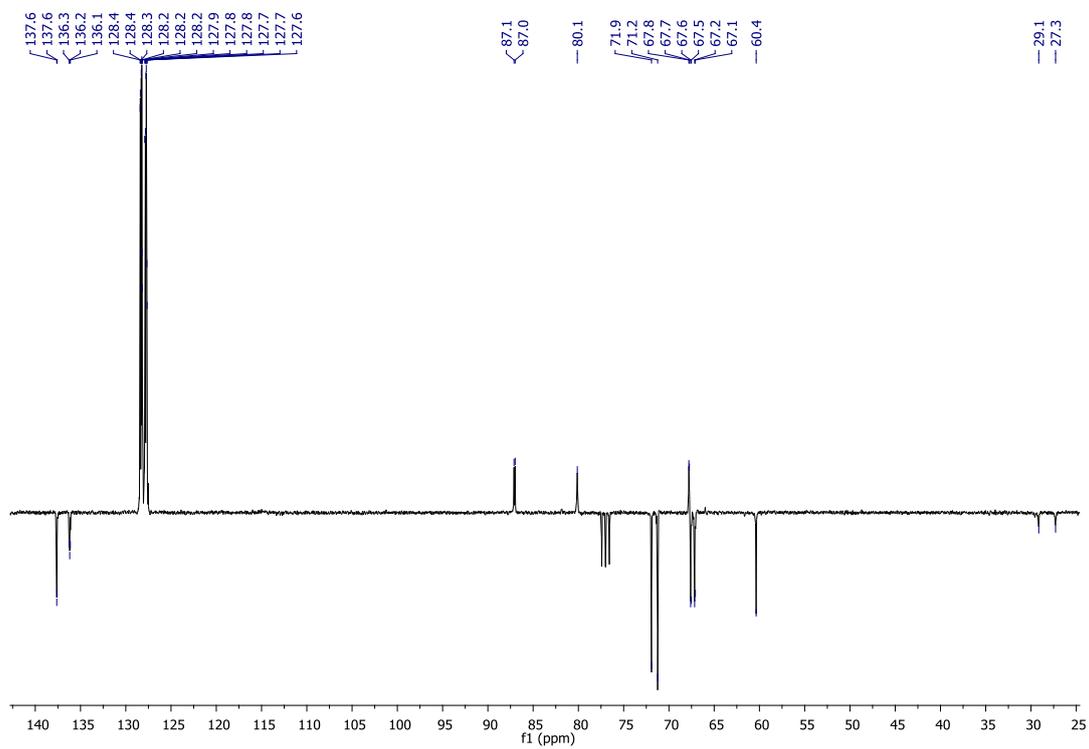


Figura 10b: ^{13}C RMN (75.5 MHz, CDCl_3)

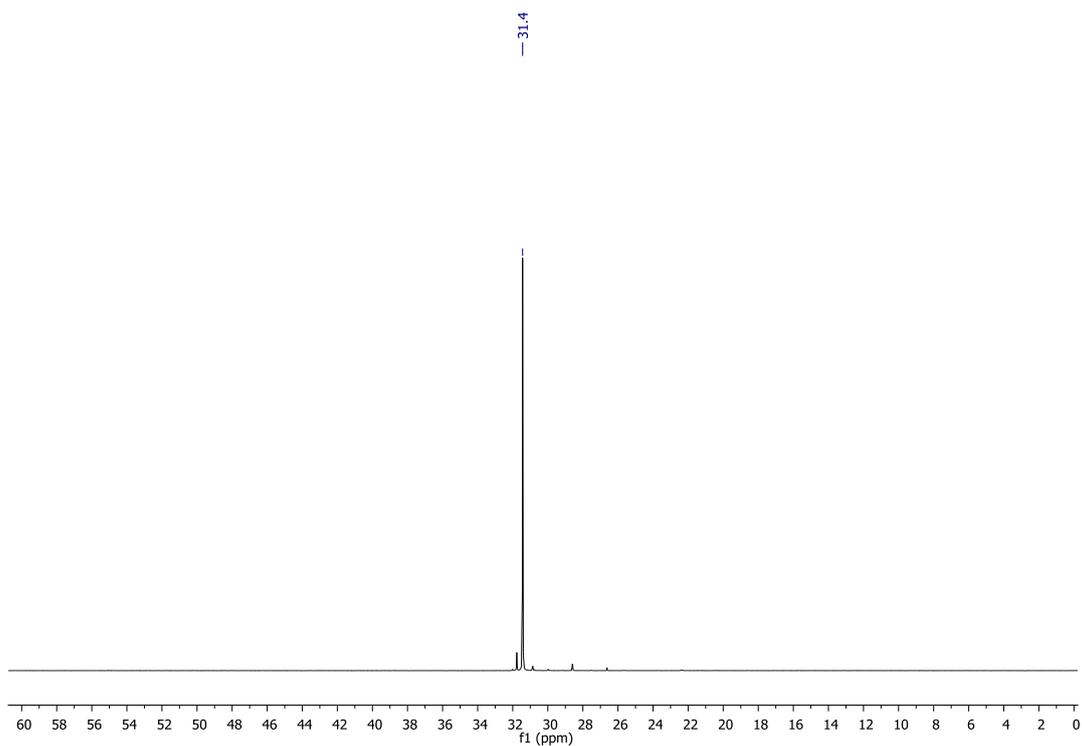


Figura 10c: ^{31}P RMN (121.5 MHz, CDCl_3)

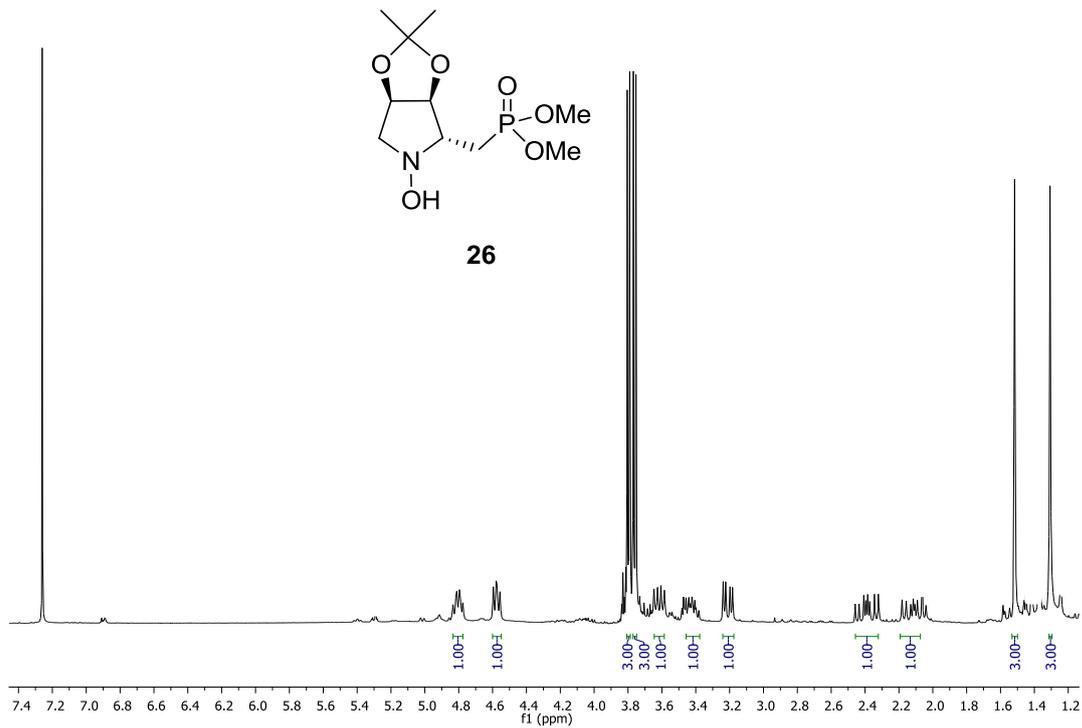


Figura 11a: ^1H RMN (300 MHz, CDCl_3)

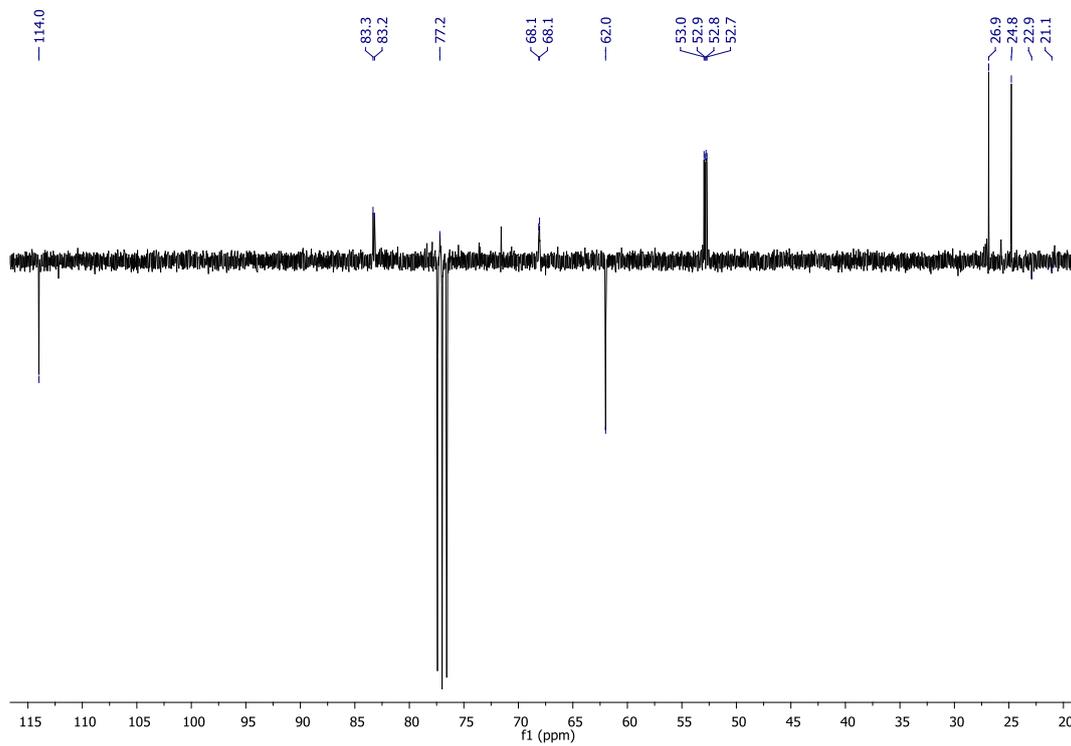


Figura 11b: ^{13}C RMN (75.5 MHz, CDCl_3)

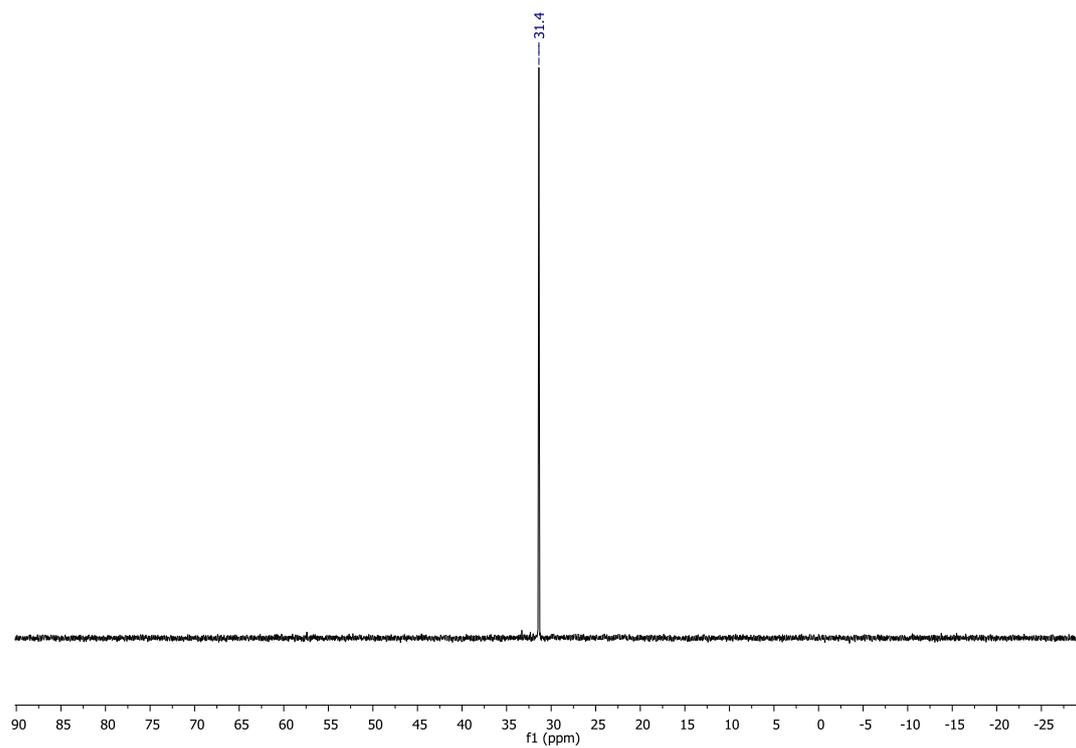


Figura 11c: ^{31}P RMN (121.5 MHz, CDCl_3)

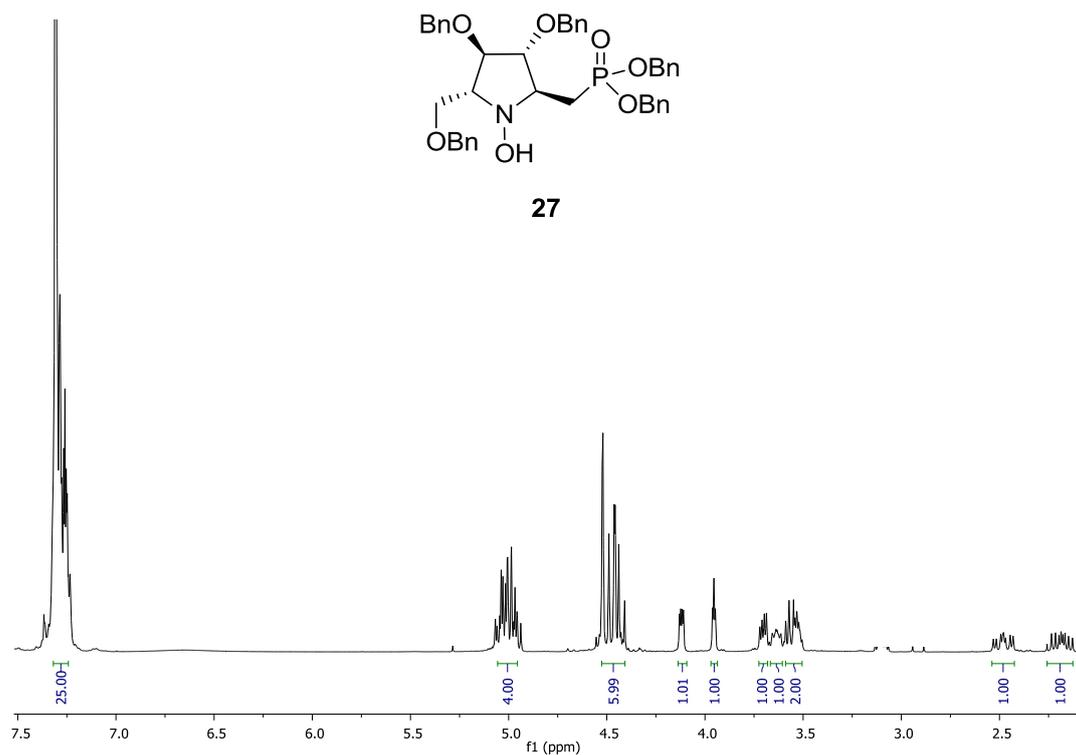


Figura 12a: ^1H RMN (400 MHz, CDCl_3)

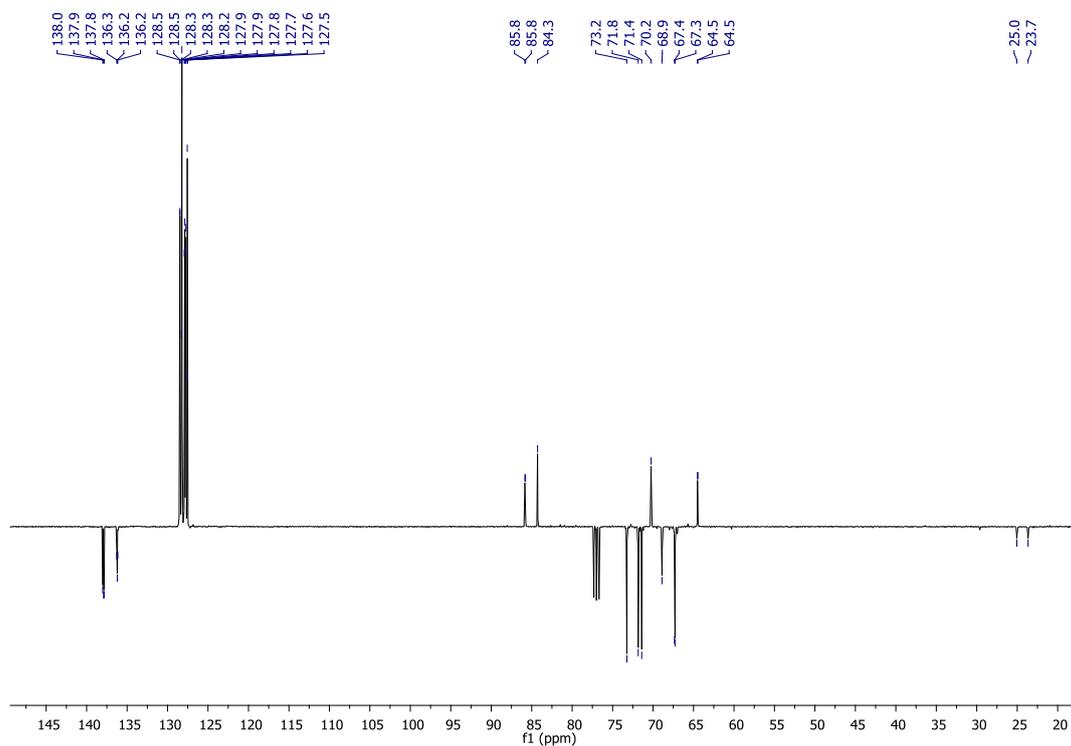


Figura 12b: ^{13}C RMN (100 MHz, CDCl_3)

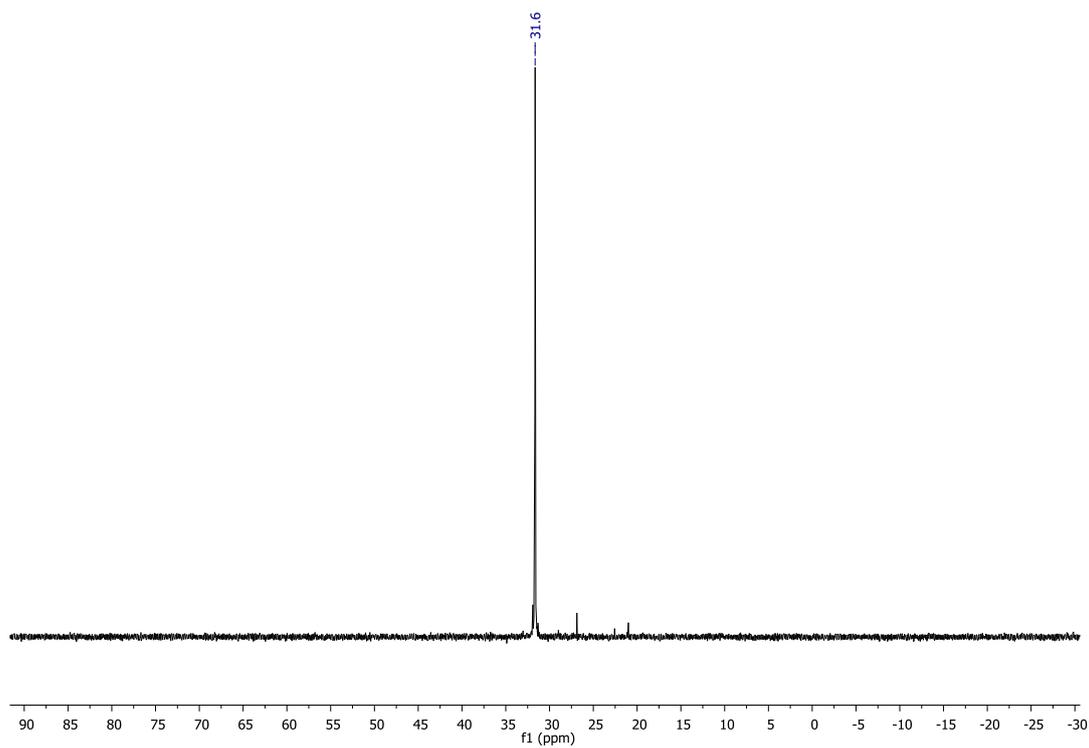


Figura 12c: ^{31}P RMN (162 MHz, CDCl_3)

6.2.3. Espectros del producto final

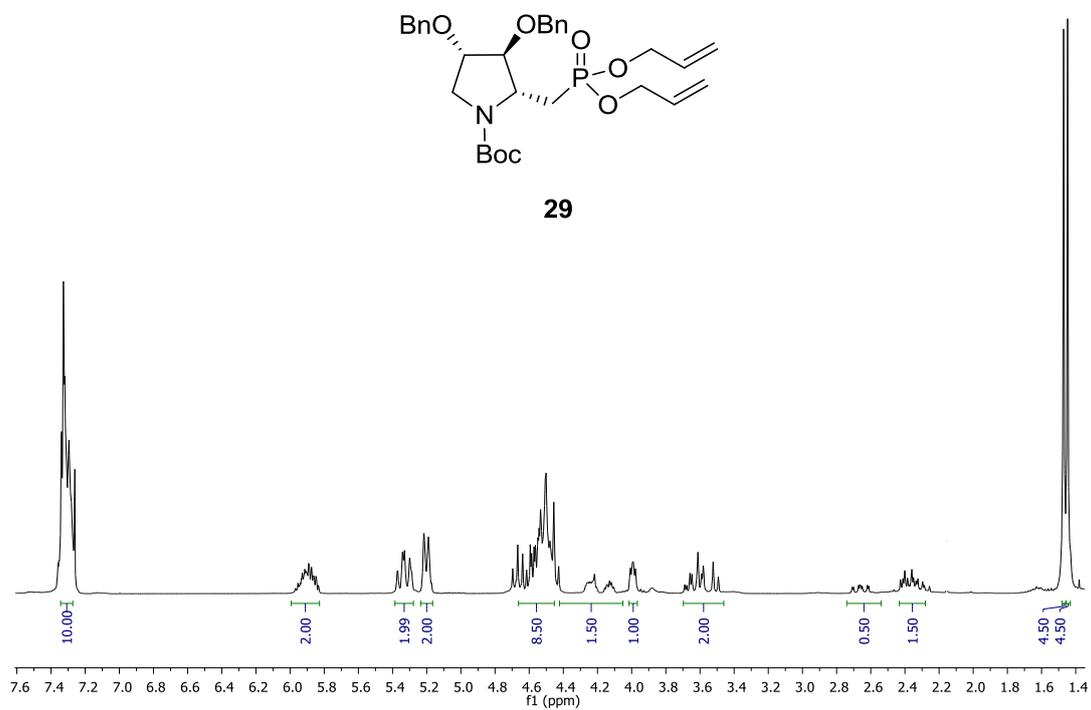


Figura 13a: ^1H RMN (400 MHz, CDCl_3)

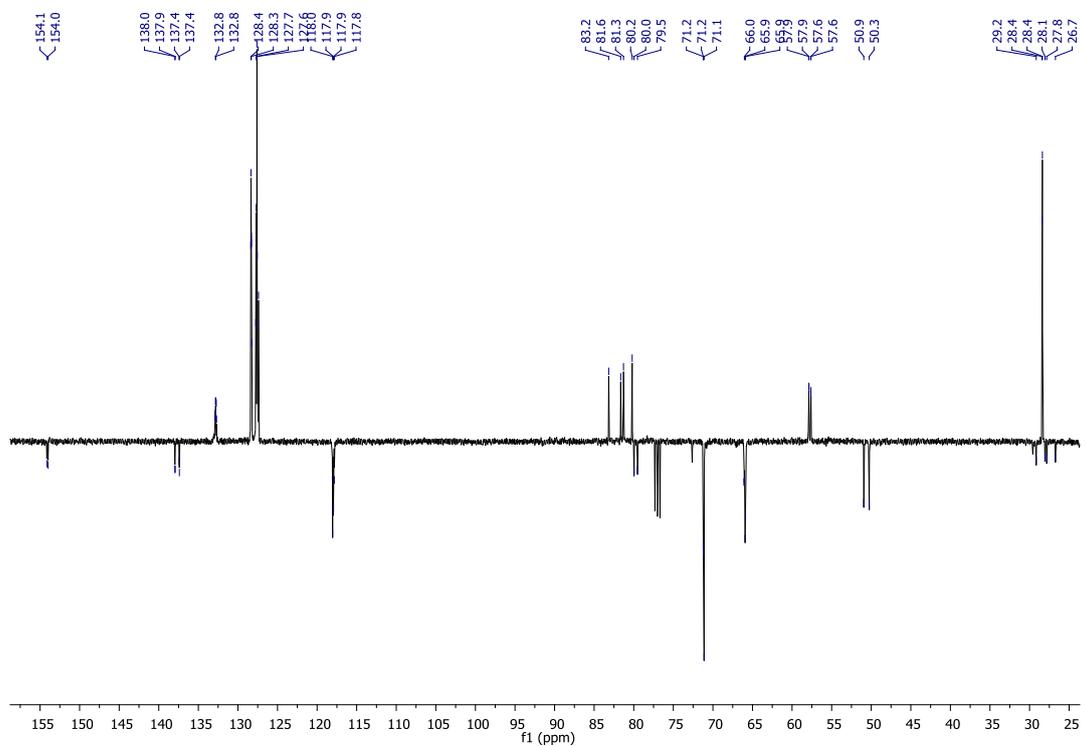


Figura 13b: ^{13}C RMN (100 MHz, CDCl_3)

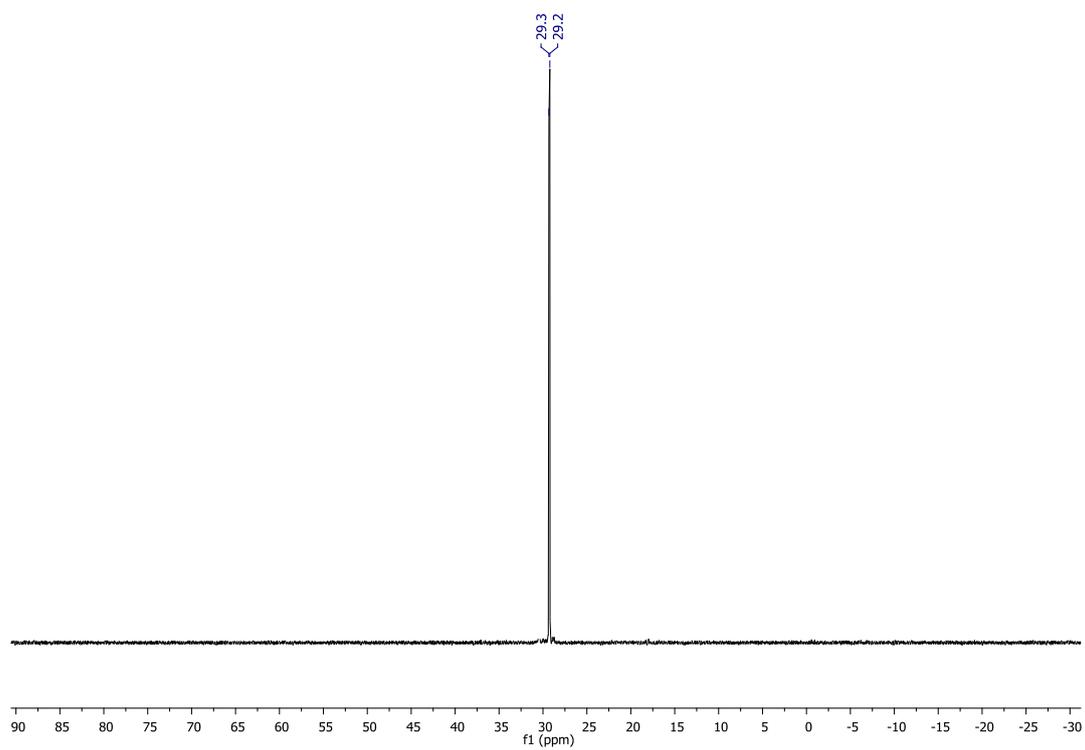


Figura 13c: ^{31}P RMN (162 MHz, CDCl_3)