Supporting Information

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Boron Compounds as Additives for the Cationic Polymerization Using Coumarin Derivatives in Epoxy Silicones

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Study of Coum-a complexation:

Addition of BF_3•OEt_2 and $B(C_6F_5)_3$ to **Coum-a** leads to a significant variation in ^{1}HNMR spectrum (Figures 1- 6).

Very broad signals were observed for protons (H^5, H^6, H^8) of the nitrogen substituted aromatic ring when BF_3•OEt_2 was added, whereas H^4 (β-position respect to C=O) moves at higher frequencies (Figure 2). Protons relative CH_2 (H^{11}) of Et_2N group became broad and move to higher frequencies (Figure 3). It is noteworthy that, when 1 equivalent of BF_3•OEt_2 was added, the two CH_2 of the Et_2N group give two distinct broad signals (Figure 3E).

Addition of $B(C_6F_5)_3$ results in a less markable changes in the signal relative to CH_2 (H^{11}) of Et_2N group, that slightly move to higher frequencies (Figure 6). In the aromatic region the addition of $B(C_6F_5)_3$ gives quite similar results observed for BF_3OEt_2 (Figure 5).

Due the broadness of the signal was not possible to collect ^{13}CNMR spectrum after the addition of BF_3•OEt_2.

From the results obtained, a coordination of boranes to the nitrogen atom seems very probable for **Coum-a**.

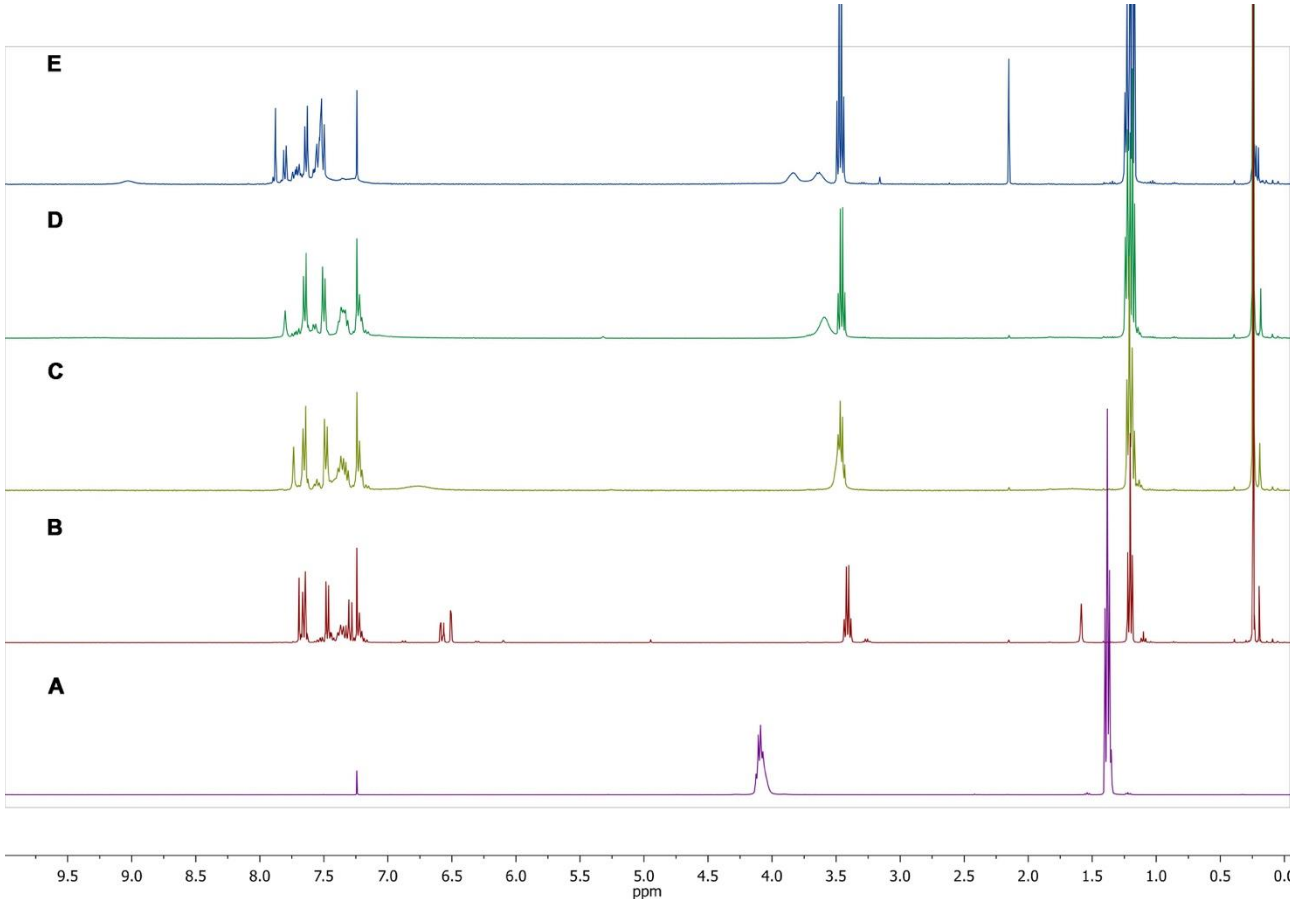


Figure 1. [1]HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) BF_3•OEt_2; (B) **Coum-a**; (C): **Coum-a** + 0.25 equiv of BF_3•OEt_2; (D): **Coum-a** + 0.5 equiv of BF_3•OEt_2; (E): **Coum-a** + 1 equiv of BF_3•OEt_2.

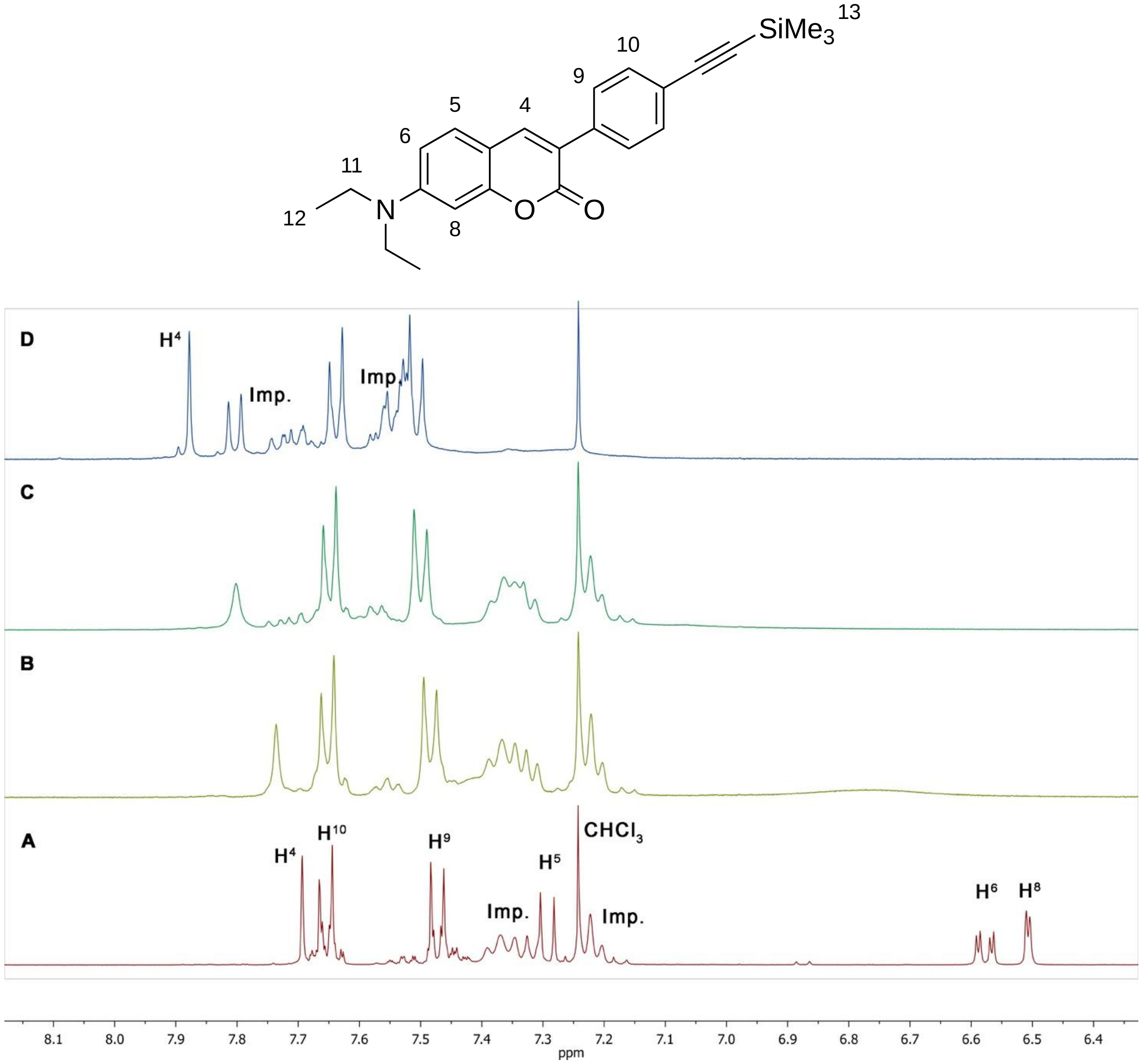


Figure 2. Aromatic region ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-a**; (B): **Coum-a** + 0.25 equiv of BF_3•OEt_2; (C): **Coum-a** + 0.5 equiv of BF_3•OEt_2; (D): **Coum-a** + 1 equiv of BF_3•OEt_2.

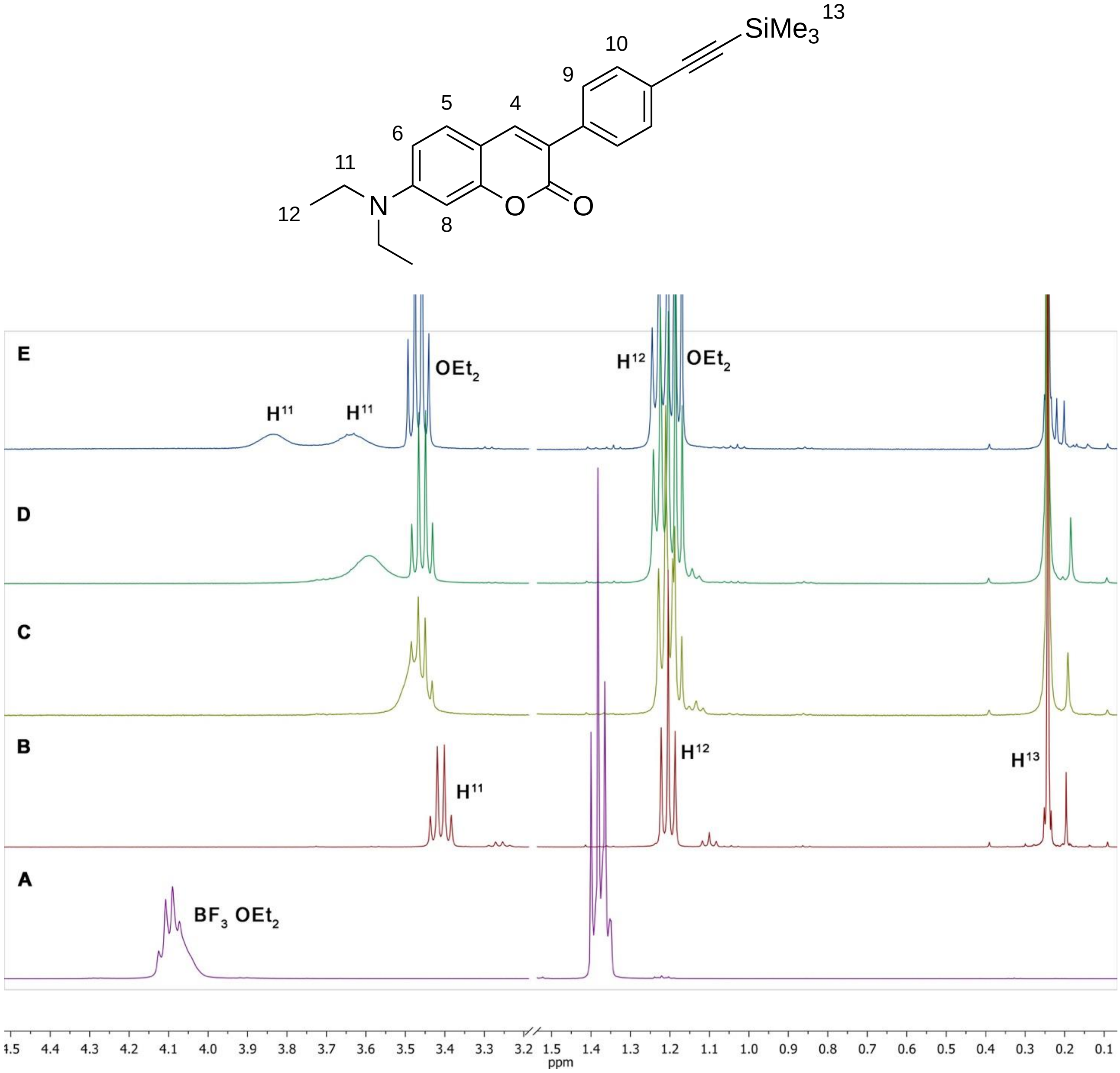


Figure 3. Aliphatic region ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) BF_3•OEt_2; (B) **Coum-a**; (C): **Coum-a** + 0.25 equiv of BF_3•OEt_2; (D): **Coum-a** + 0.5 equiv of BF_3•OEt_2; (E): **Coum-a** + 1 equiv of BF_3•OEt_2.

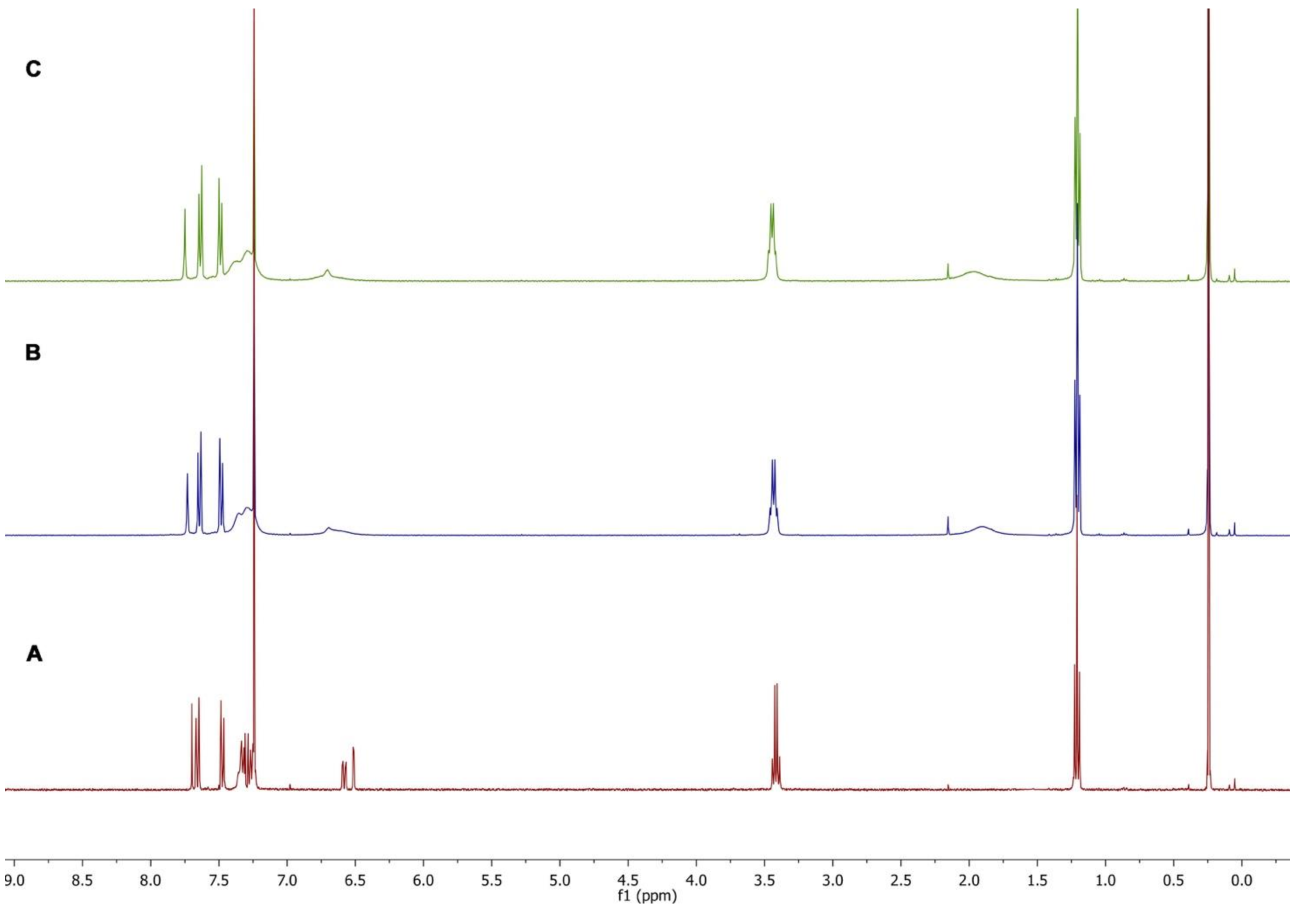


Figure 4. ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-a**; (B): **Coum-a** + 0.5 equiv of $B(C_6F_5)_3$; (C): **Coum-a** + 1.0 equiv of $B(C_6F_5)_3$.

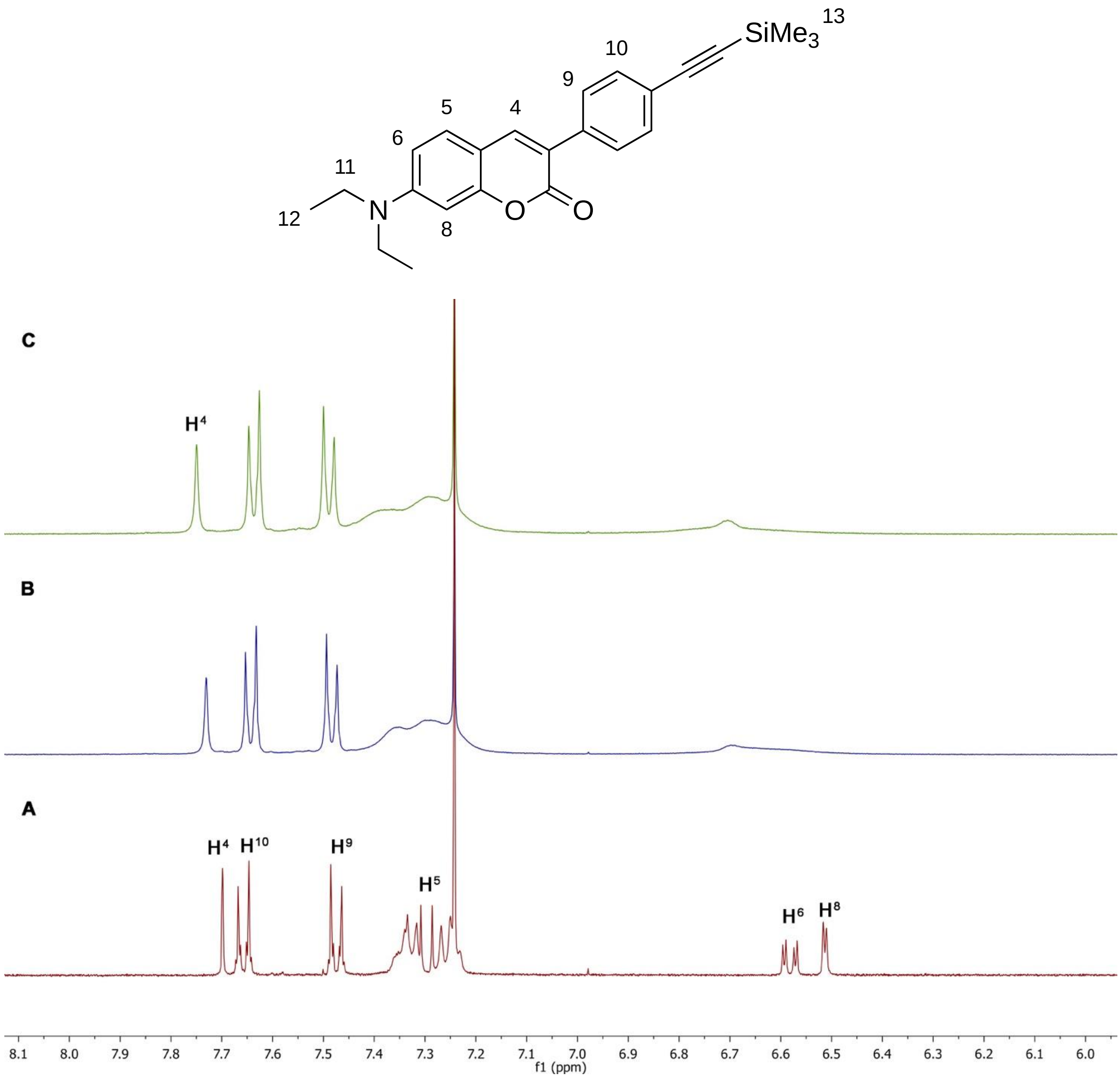


Figure 5. Aromatic region of ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-a**; (B): **Coum-a** + 0.5 equiv of $B(C_6F_5)_3$; (C): **Coum-a** + 1.0 equiv of $B(C_6F_5)_3$.

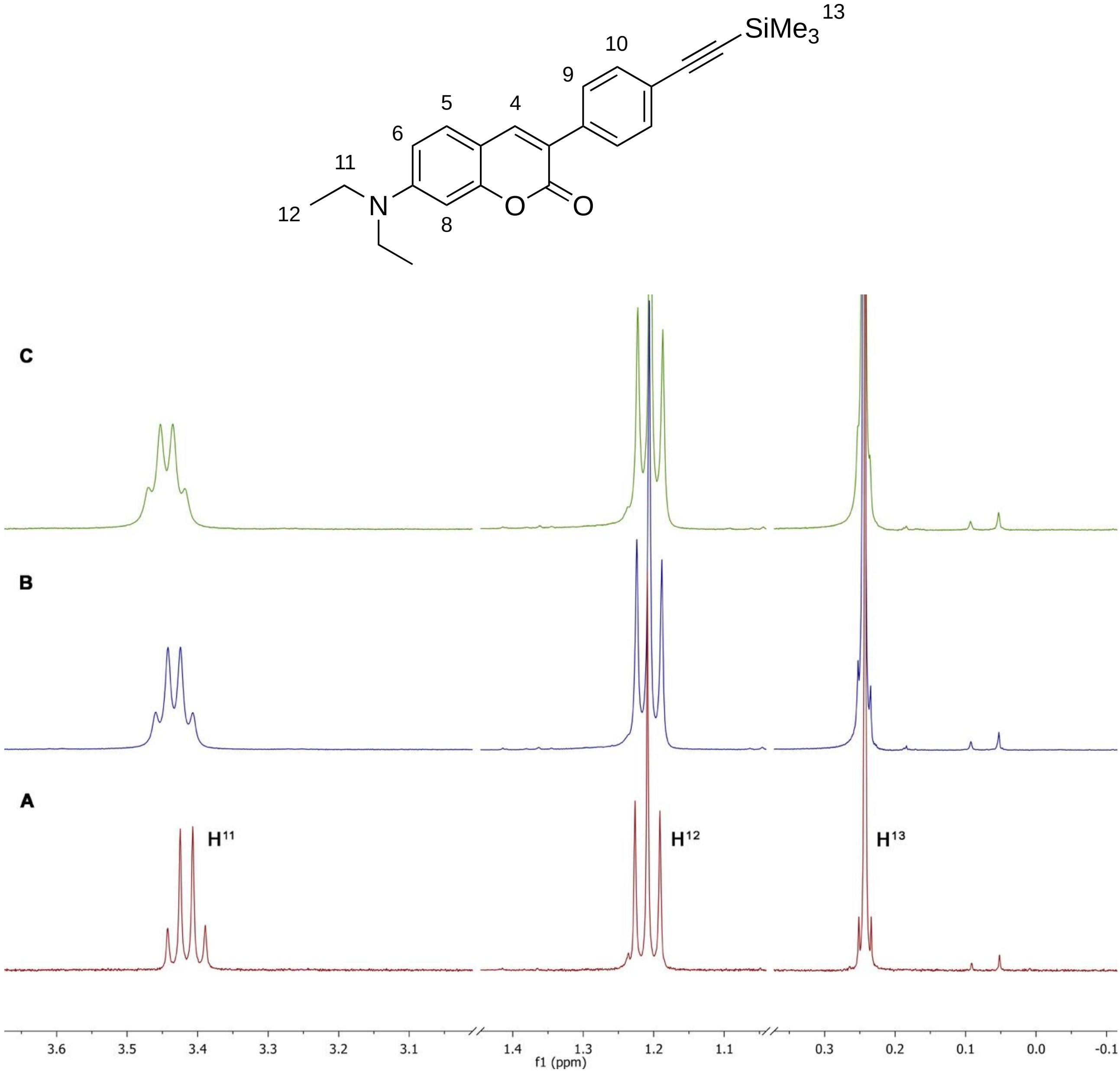


Figure 6. Aliphatic region of ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-a**; (B): **Coum-a** + 0.5 equiv of $B(C_6F_5)_3$; (C): **Coum-a** + 1.0 equiv of $B(C_6F_5)_3$.

Study of Coum-b complexation:

Coum-b presented a less pronounced change in the ^{1}HNMR signal compared to Coumarin-a. Both with BF_3•OEt_2 (Figures 7-9) and $B(C_6F_5)_3$ (Figures 10-12), there are slight changes in the aromatic signals related to the coumarin system, but only the signal relative to H^4 (β-position respect to C=O) shows a shift at higher frequencies (Figures 8) with BF_3•OEt_2. When $B(C_6F_5)_3$ was added, 5 equivalents are needed to observe appreciable shift in the H^4 signal (Figure 11). The signal relative to the aliphatic chain of phenol ether remains untouched (Figures 6 and 12).

Remarkable ^{13}CNMR shift of the signals relative to the α,β-unsaturated ester region was recorded by the addition of 5 equivalents of $B(C_6F_5)_3$ (Figures 13-17). C^4 (β-position respect to C=O) and C^{12} (*ipso* carbon of nitrophenyl substituent) move to higher frequencies and low field respectively. Less pronounced changes were observed for carbonyl group (C^2), C^3 (α-position respect to C=O) and for the phenolic ring (C^7 and C^6).

These results were in according with minor ability to coordinate boranes from the **Coum-b** respect to **Coum-a**. From the signals involved in the changes in NMR spectra, it is possible to suppose a coordination of the carbonyl group with boranes for **Coum-b**.

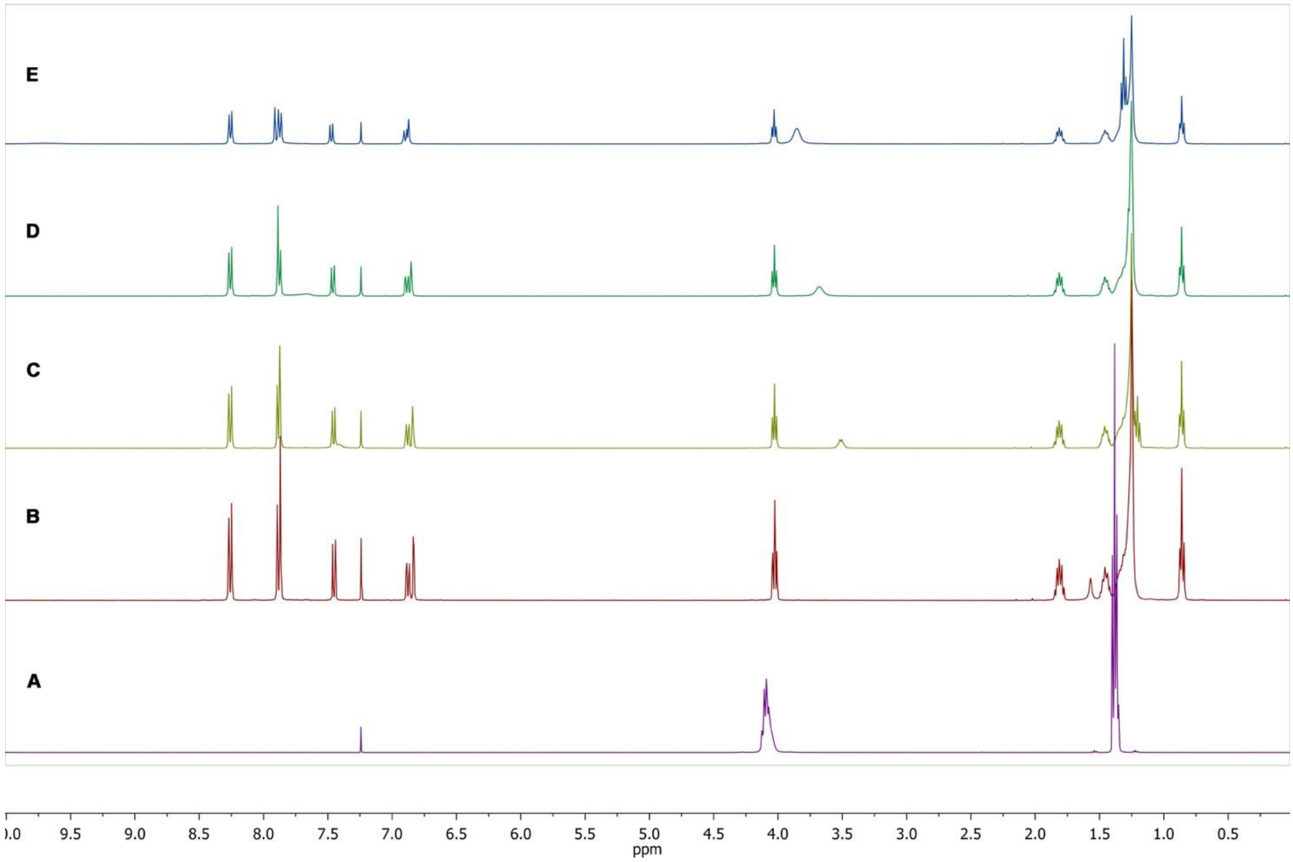


Figure 7. [1]HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) BF_3•OEt_2; (B) **Coum-b**; (C): **Coum-b** + 0.25 equiv of BF_3•OEt_2; (D): **Coum-b** + 0.5 equiv of BF_3•OEt_2; (E): **Coum-b** + 1 equiv of BF_3•OEt_2.

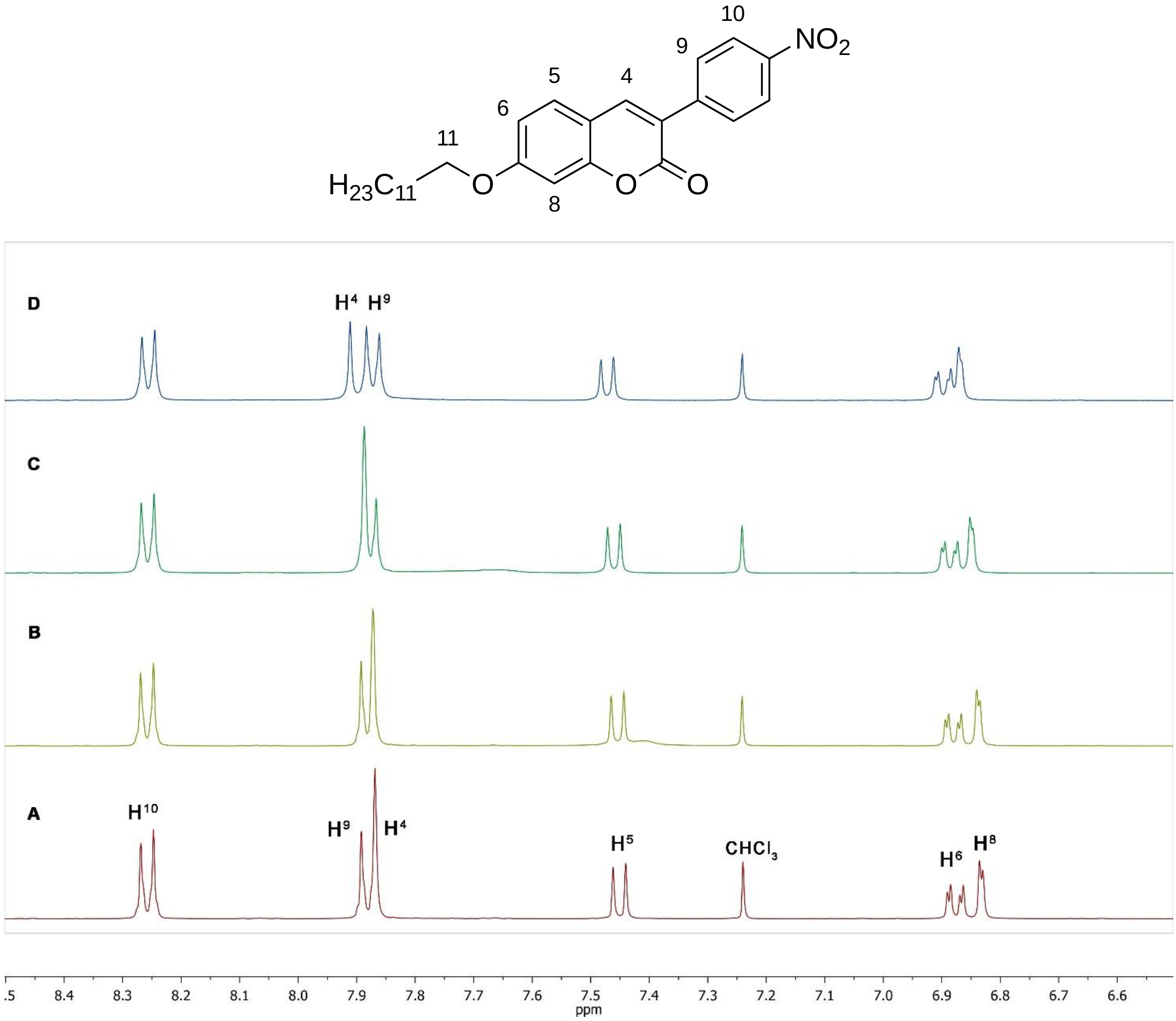


Figure 8. Aromatic region ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-b**; (B): **Coum-b** + 0.25 equiv of BF_3•OEt_2; (C): **Coum-b** + 0.5 equiv of BF_3•OEt_2; (D): **Coum-b** + 1 equiv of BF_3•OEt_2.

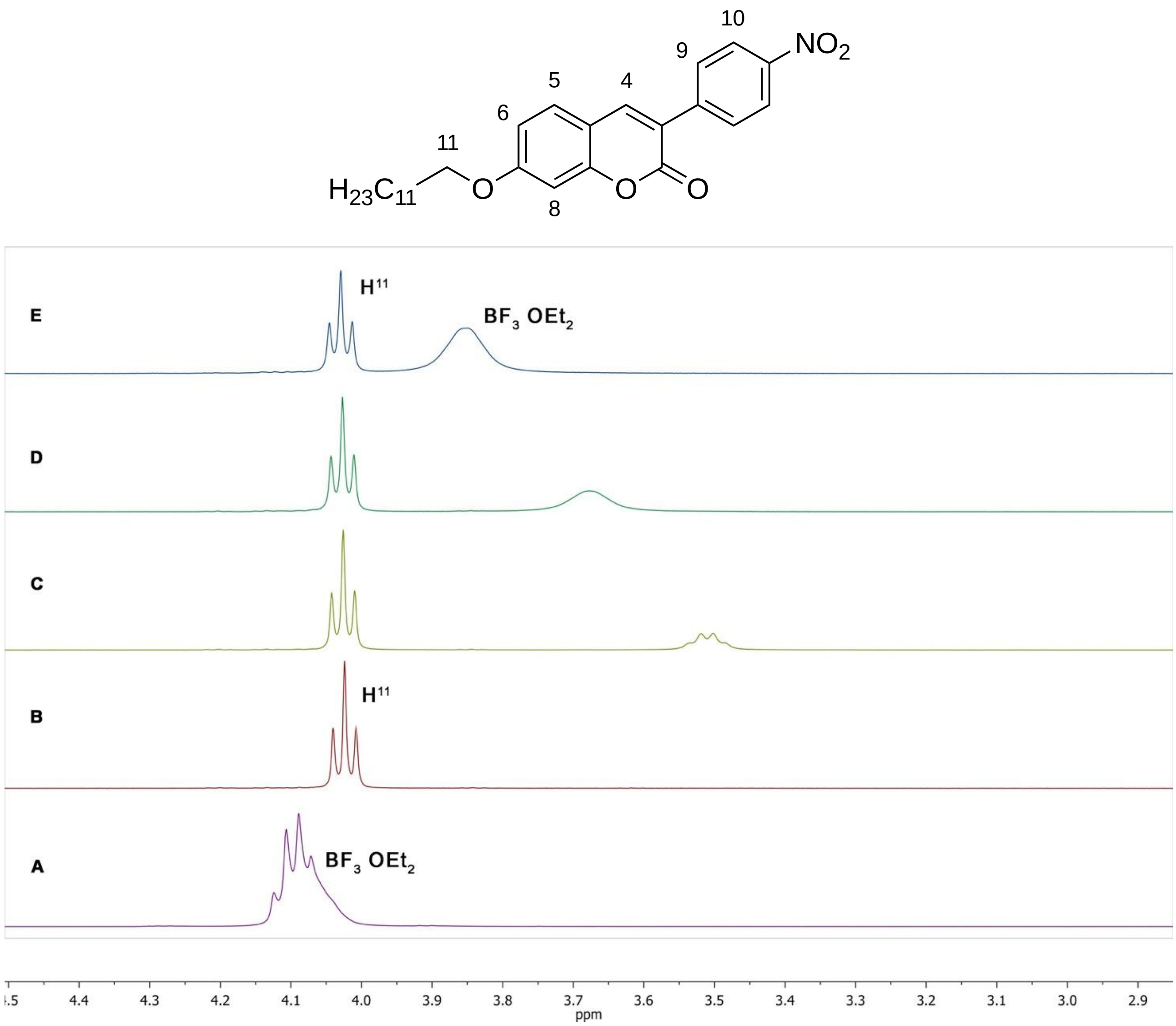


Figure 9. 2.5-4.5 ppm region [1]HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) BF_3•OEt_2; (B) **Coum-b**; (C): **Coum-b** + 0.25 equiv of BF_3•OEt_2; (D): **Coum-b** + 0.5 equiv of BF_3•OEt_2; (E): **Coum-b** + 1 equiv of BF_3•OEt_2.

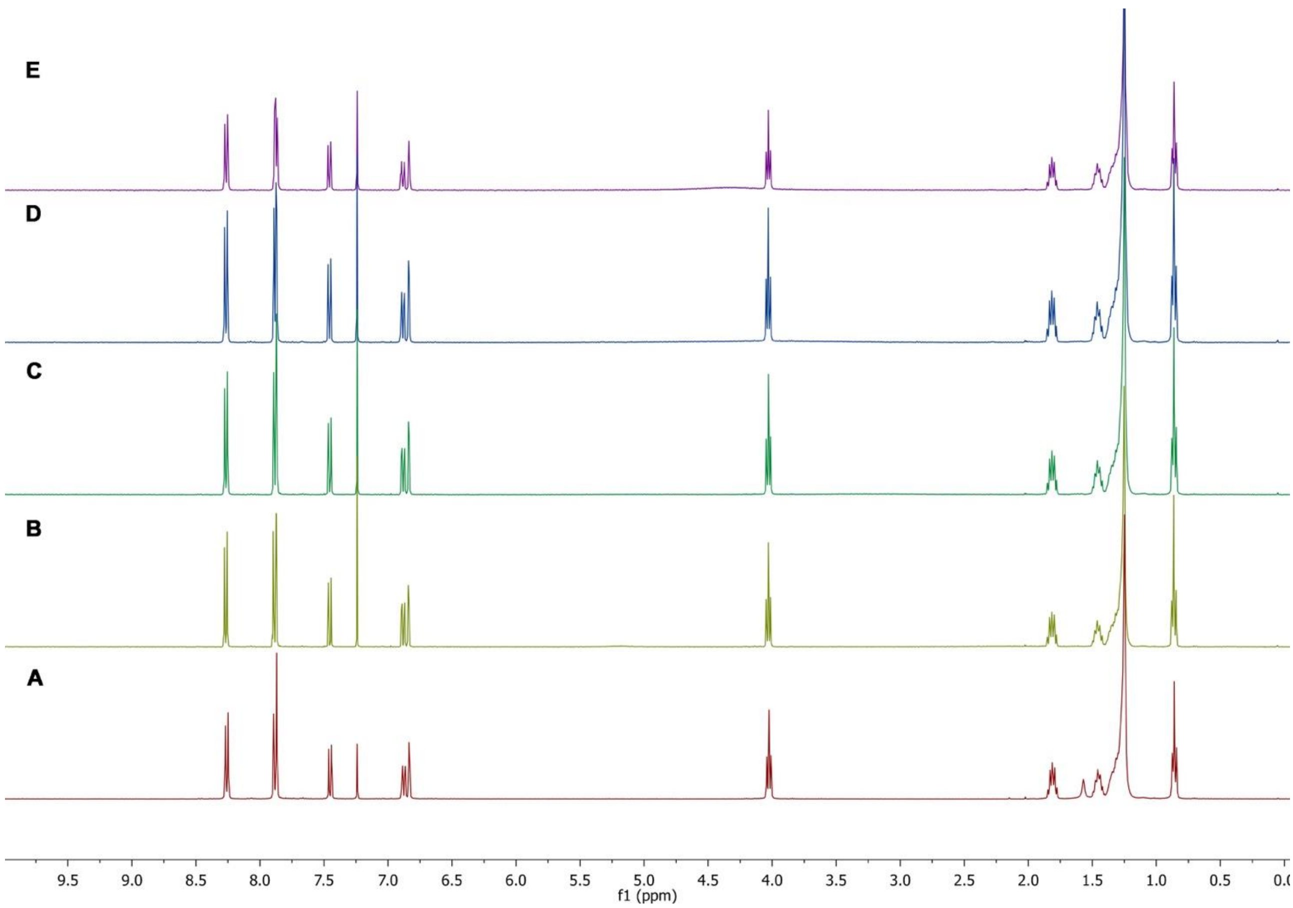


Figure 10. [1]HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-b**; (B): **Coum-b** + 0.5 equiv of $B(C_6F_5)_3$; (C): **Coum-b** + 1.0 equiv of $B(C_6F_5)_3$; (D): **Coum-b** + 2.0 equiv of $B(C_6F_5)_3$; (E): **Coum-b** + 5.0 equiv of $B(C_6F_5)_3$.

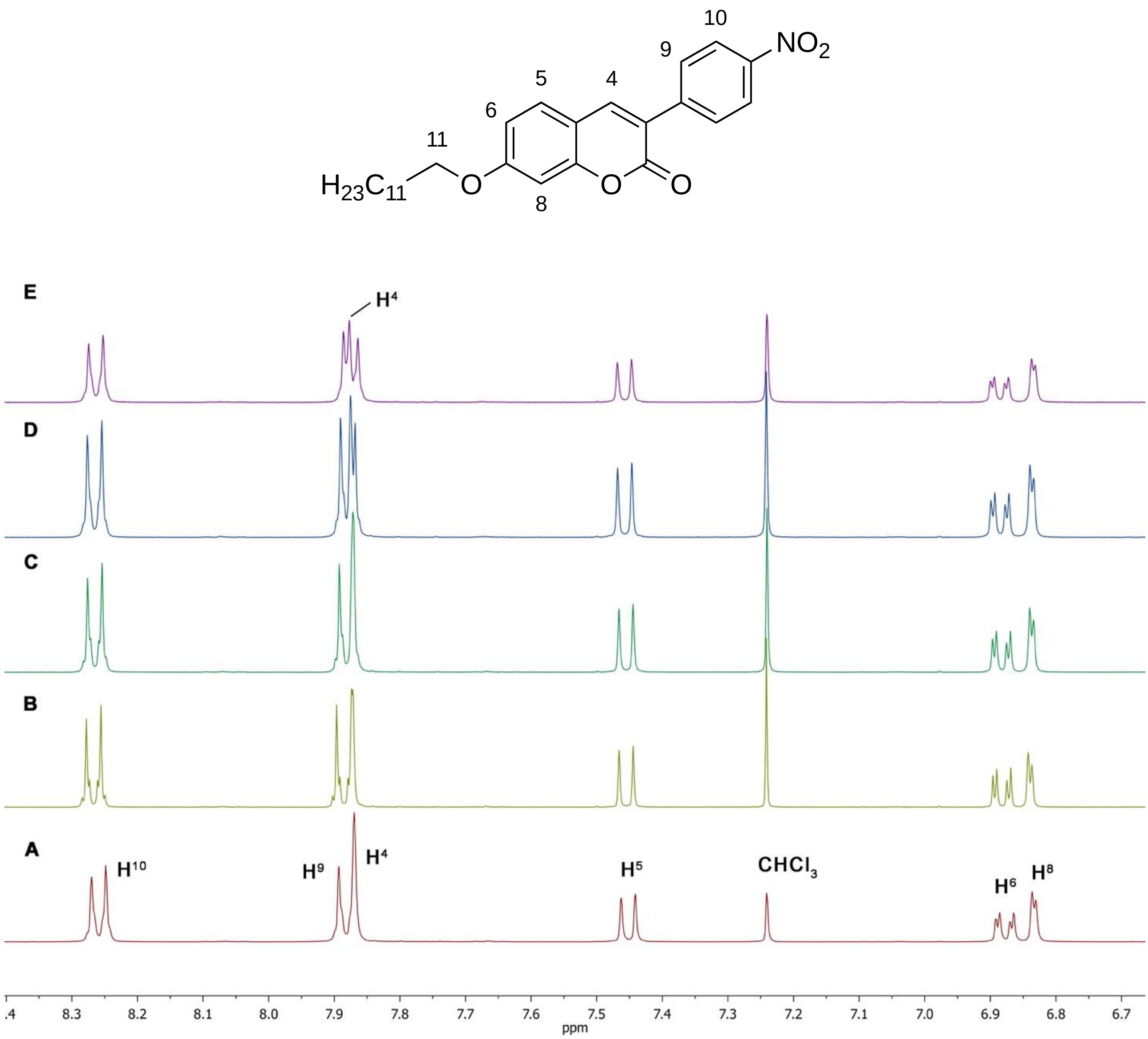


Figure 11. Aromatic region of ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-b**; (B): **Coum-b** + 0.5 equiv of $B(C_6F_5)_3$; (C): **Coum-b** + 1.0 equiv of $B(C_6F_5)_3$; (D): **Coum-b** + 2.0 equiv of $B(C_6F_5)_3$; (E): **Coum-b** + 5.0 equiv of $B(C_6F_5)_3$.

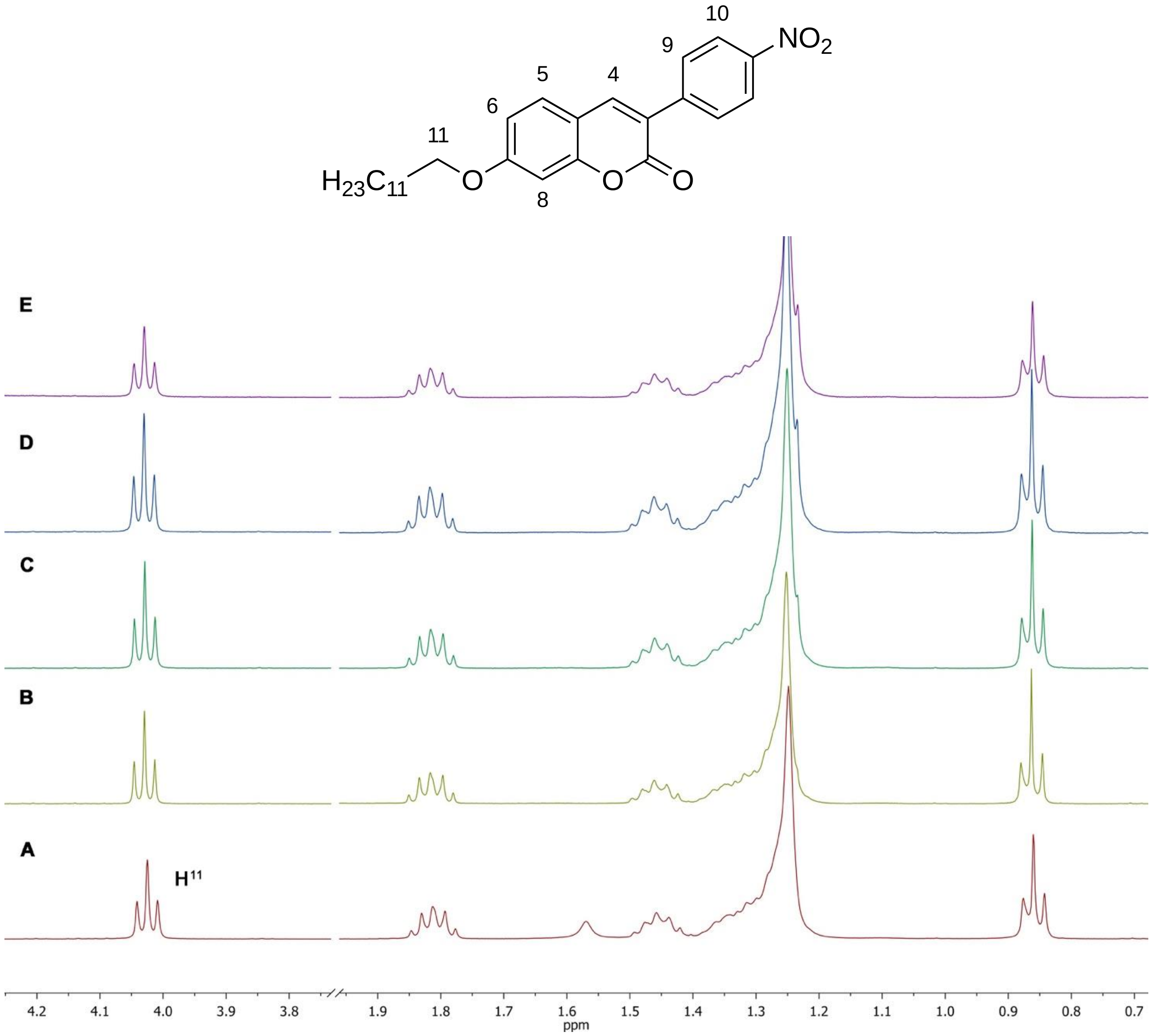


Figure 12. Alipahtic region of ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-b**; (B): **Coum-b** + 0.5 equiv of $B(C_6F_5)_3$; (C): **Coum-b** + 1.0 equiv of $B(C_6F_5)_3$; (D): **Coum-b** + 2.0 equiv of $B(C_6F_5)_3$; (E): **Coum-b** + 5.0 equiv of $B(C_6F_5)_3$.

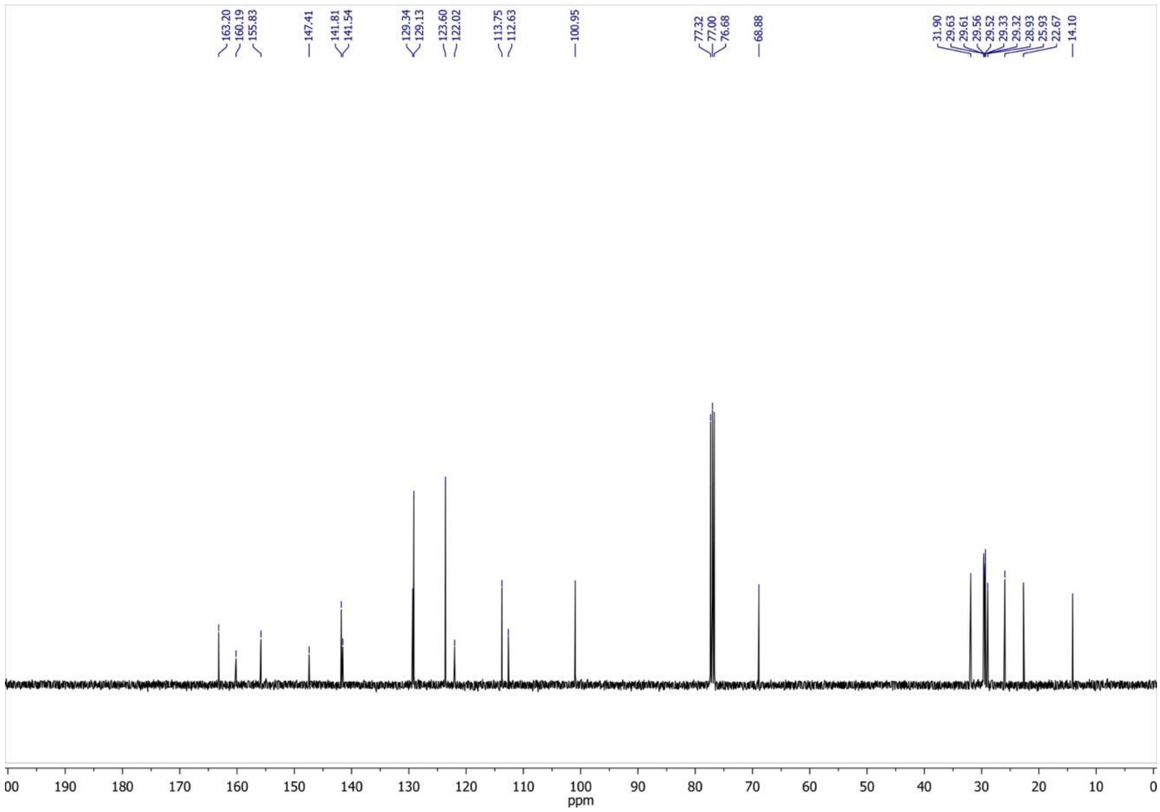


Figure 13. ^{13}CNMR (100 MHz, $CDCl_3$, 25 °C) spectrum of **Coum-b**.

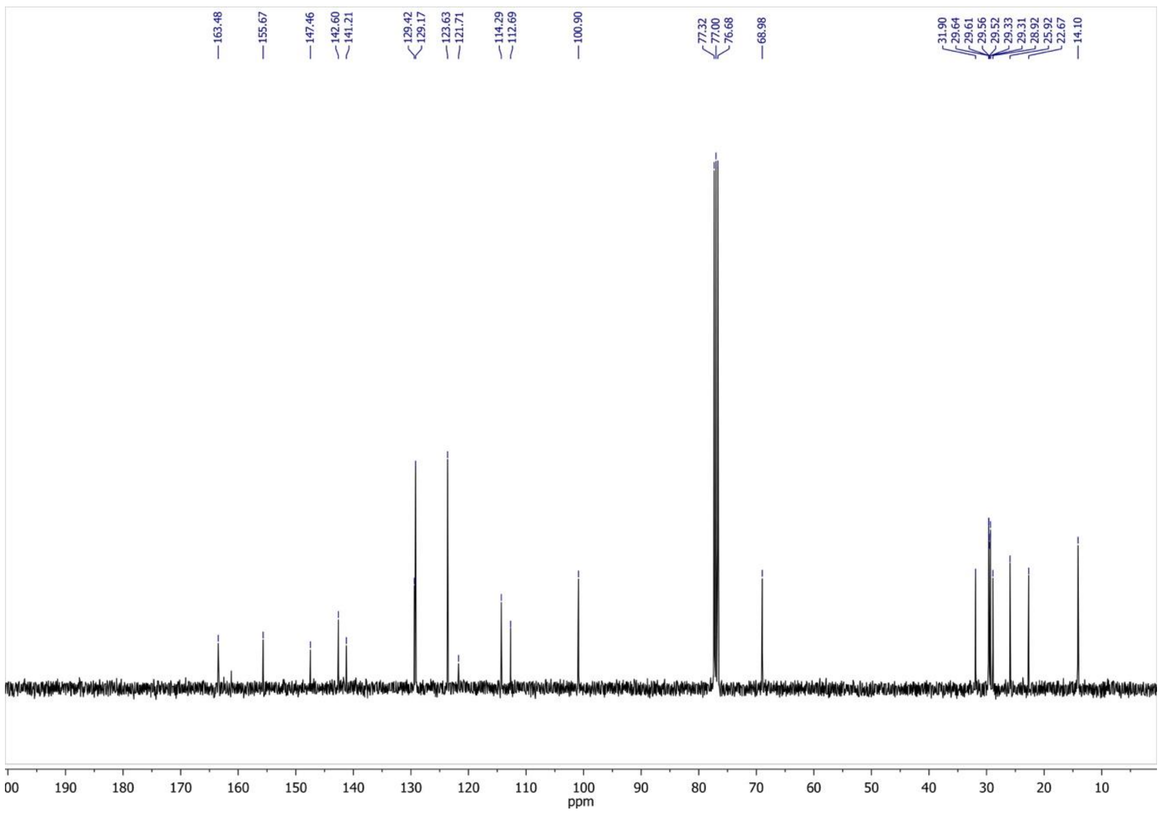


Figure 14. ^{13}CNMR (100 MHz, $CDCl_3$, 25 °C) spectrum of **Coum-b** + 5 equiv of $B(C_6F_5)_3$.

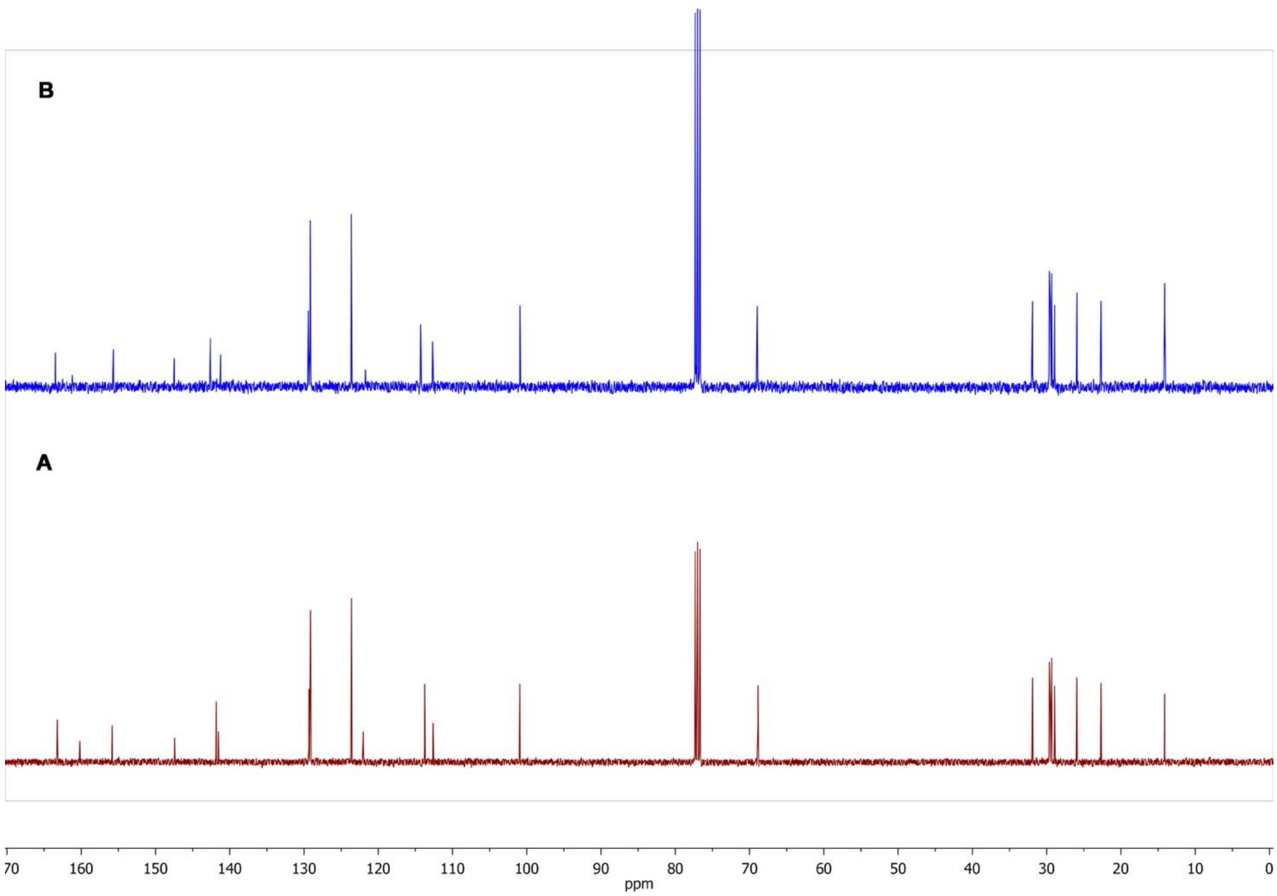
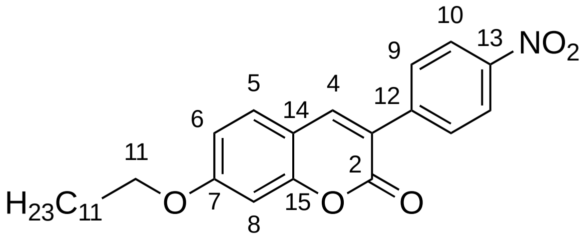


Figure 15. ^{13}CNMR (100 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-b**; (B) **Coum-b** + 5 equiv of $B(C_6F_5)_3$.



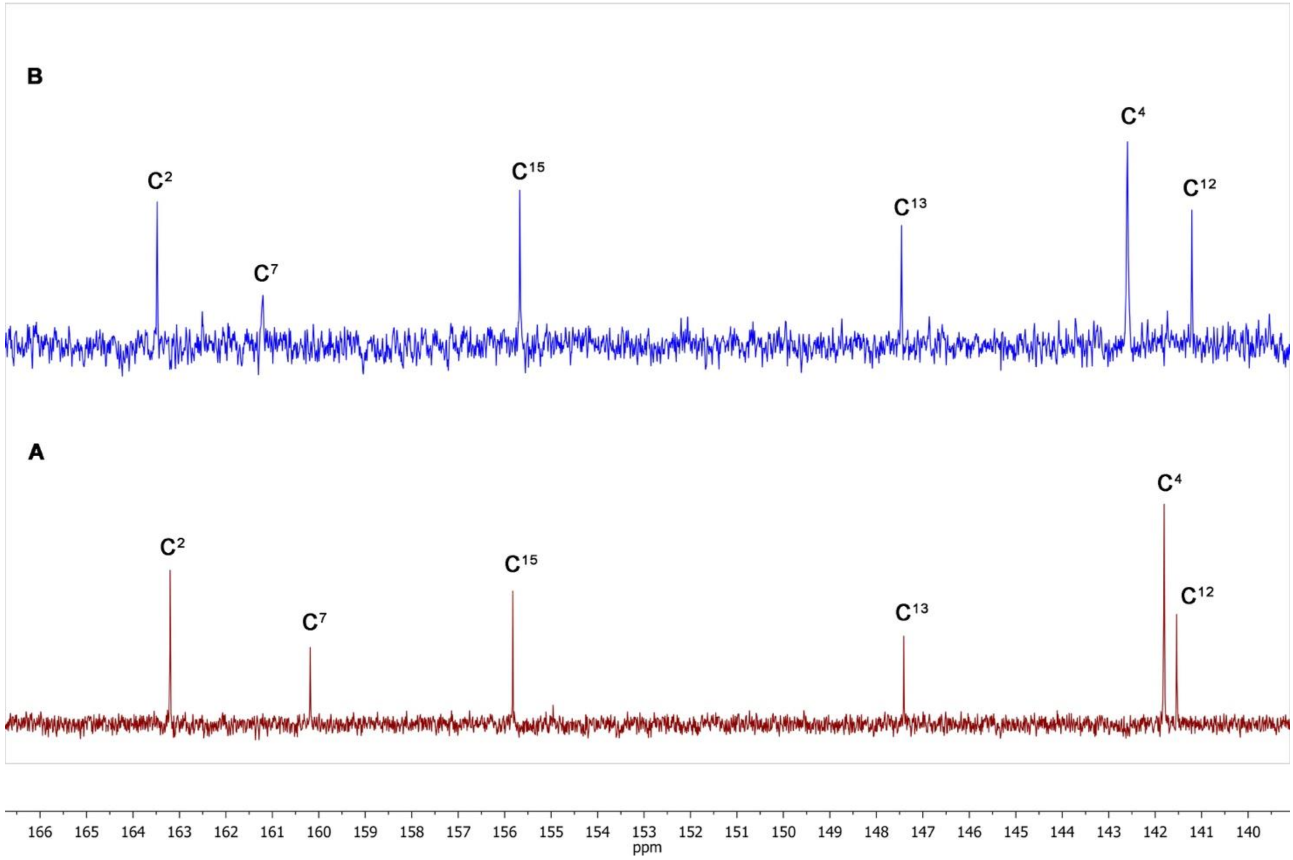
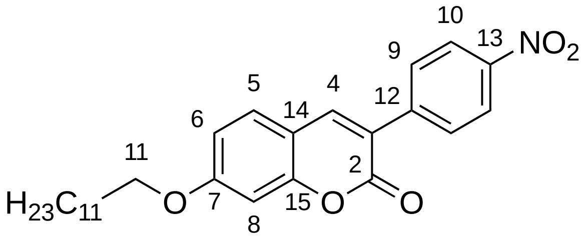


Figure 16. Aromatic region ^{13}CNMR (100 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-b**; (B) **Coum-b** + 5 equiv of $B(C_6F_5)_3$.



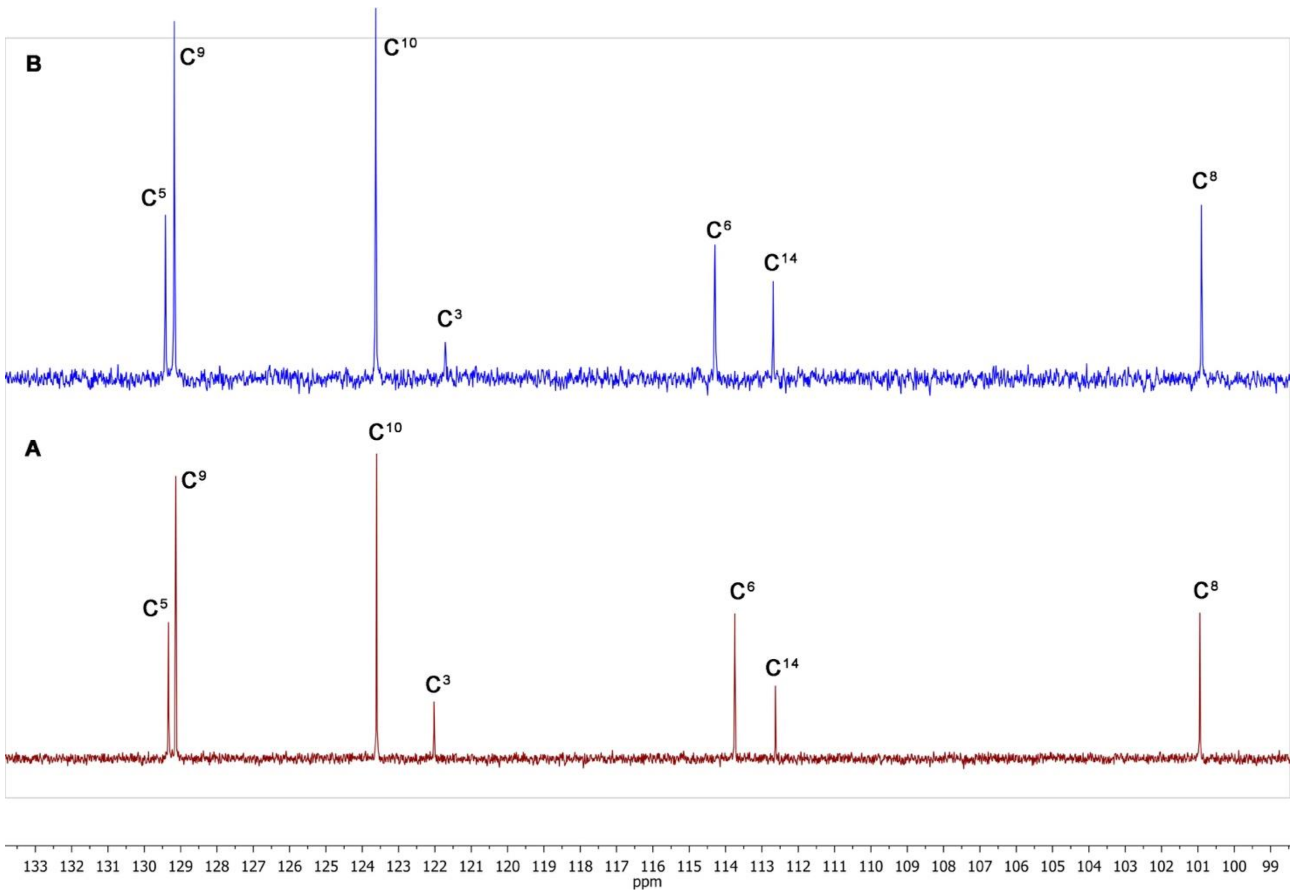


Figure 17. Aromatic region ^{13}CNMR (100 MHz, $CDCl_3$, 25 °C) spectra of: (A) **Coum-b**; (B) **Coum-b** + 5 equiv of $B(C_6F_5)_3$.