

**RSC Advances**  
**Supporting Information**

**Synthesis a new type, cost-effective and insensitive energetic  
materials by nitration of solid bituminous hydrocarbons**

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**Table 1**

**Nitro natural asphalt synthesis with HNO<sub>3</sub>**

17.5 mL of HNO<sub>3</sub> was poured into a 100 mL round-bottom flask ice bath, and then 2 g of natural asphalt was slowly added. After 30 minutes, the reaction mixture was heated to 60 °C for 5 hours. Afterwards the completion of the reaction, 300 mL of distilled water was added to it. After filtering and washing, it was dried in the oven for 3 hours at a temperature of 80 °C.

**Nitro natural asphalt synthesis by HNO<sub>3</sub>/ H<sub>2</sub>SO<sub>4</sub>/AC<sub>2</sub>O (5 mL), HNO<sub>3</sub>/ H<sub>2</sub>SO<sub>4</sub>/AC<sub>2</sub>O (10 mL) and HNO<sub>3</sub>/ H<sub>2</sub>SO<sub>4</sub>/P<sub>2</sub>O<sub>5</sub> (10 g)**

First, 2 g of natural asphalt was slowly added to the HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture with a ratio of (17.5 mL/20 mL) to a 100 mL round-bottom flask in an ice bath. In the next step, 5 (entry 4), 10 mL AC<sub>2</sub>O (entry 5) and 10 g of P<sub>2</sub>O<sub>5</sub> (entry 6) are added to the reaction mixture for 20 minutes. After half an hour, a temperature of 60 °C is given to it for 5 hours. The reaction mixture is poured into 300 ml of distilled water. After filtering, the precipitate obtained is kept in an oven at 80 °C for 3 hours to dry. After the synthesis of the above products, the IR spectrum was applied to identify them. Their FTIR spectra indicate that groups NO<sub>2</sub> of three synthesized compounds have two peaks around 1350-1550 cm<sup>-1</sup>. The color of nitro products obtained from the above three methods was dark brown, brown and light brown respectively. In addition, they were completely dissolved in aprotic solvents such as DMSO and decomposed at a temperature higher than 300 °C.

**Nitro natural asphalt synthesis by HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/CaCl<sub>2</sub>**

This synthesis method is summarized as follows: 2 g of natural asphalt powder was slowly added to a mixture of HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> with a ratio of 17.5 mL:20 mL to a round-bottom flask in an ice water bath. Gradually, 10 g of CaCl<sub>2</sub> was poured into it. After one hour, the reaction temperature was increased to 60 °C for 5 hours. After the completion of the reaction, we added it to 300 mL of distilled water. Then it was dried at 80 °C for 3 hours after filtering and washing. Finally, a gray precipitate was obtained which was not capable of burning and its FTIR spectrum showed that it was not nitrated.

**Nitro natural asphalt synthesis by NaNO<sub>2</sub>/ KHSO<sub>4</sub>/ H<sub>2</sub>O<sub>2</sub><sup>1</sup>**

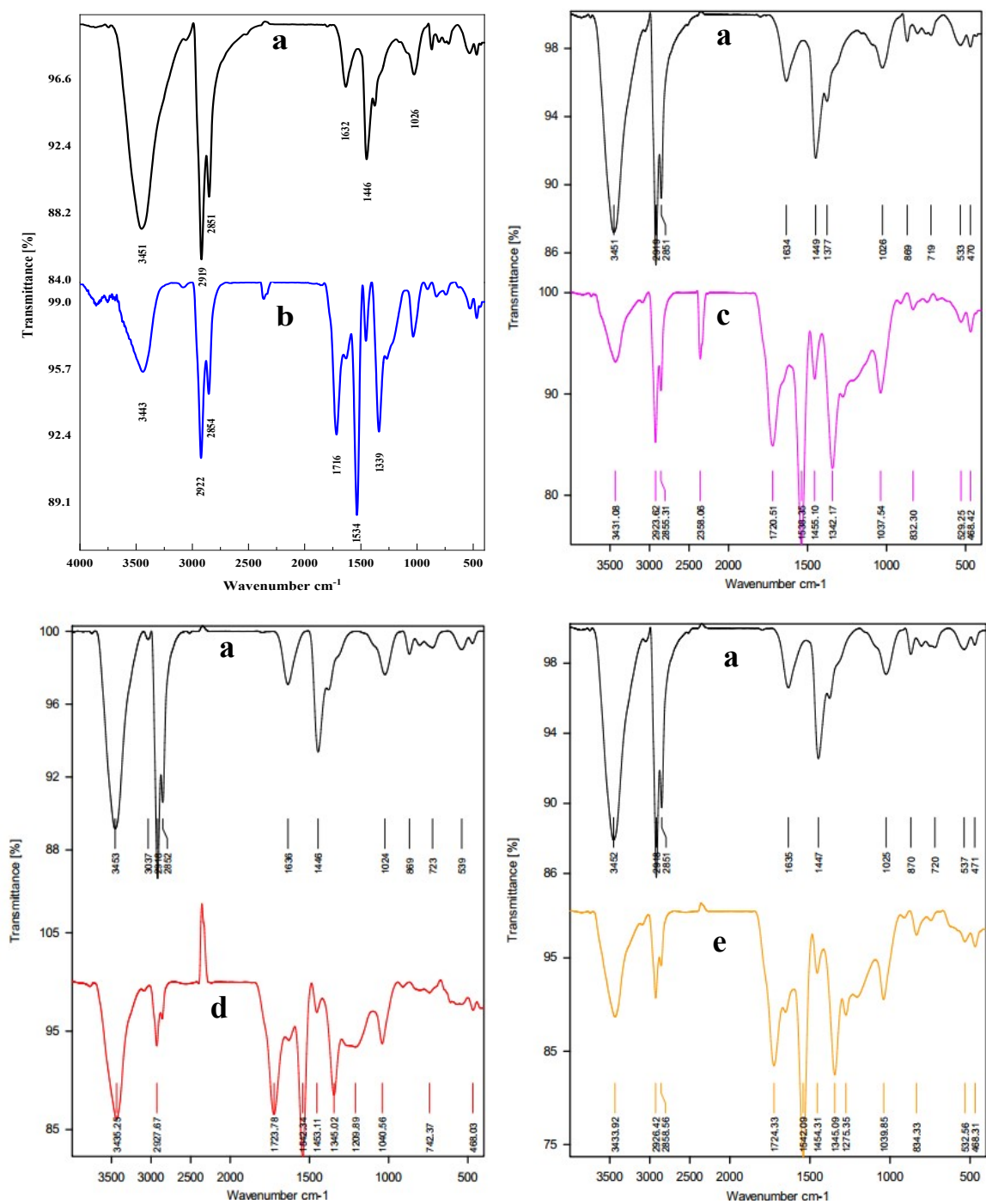
Natural asphalt (1 g), sodium nitrite (0.8 g) and hydrogen peroxide (0.03 g) were mixed in acetonitrile for 6 h at a temperature of 60 °C in a round-bottom flask. After the completion of the reaction, the resulting mixture was added to 300 ml of distilled water. The precipitate was filtered and placed at a temperature of 80 °C (3 hours) to dry. The FTIR spectrum of the synthesized compound demonstrated that it was not nitrated.

**Table S1.** OB values of NA-NO<sub>2</sub>, PP-NO<sub>2</sub> and PB-NO<sub>2</sub>

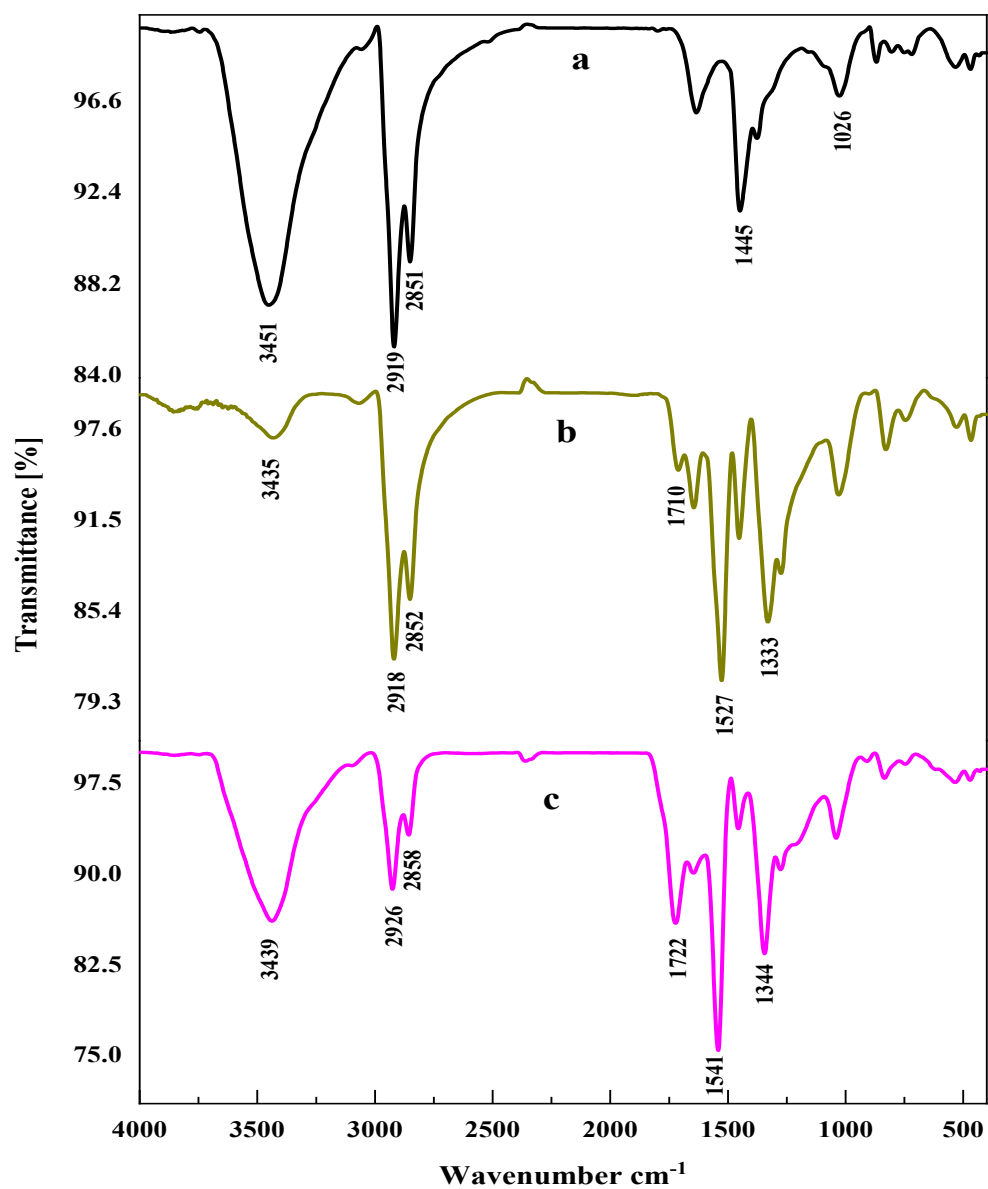
Sample	Formula	OB [Ω]
NA-NO <sub>2</sub>	C <sub>46.91</sub> H <sub>4.68</sub> N <sub>6.11</sub> S <sub>5.52</sub> O <sub>36</sub> 78	-66.51
PP-NO <sub>2</sub>	C <sub>48.99</sub> H <sub>2.53</sub> N <sub>8.18</sub> S <sub>6.33</sub> O <sub>33</sub> 97	-69.42
PB-NO <sub>2</sub>	C <sub>50.42</sub> H <sub>7.42</sub> N <sub>6.67</sub> S <sub>10.99</sub> O <sub>2</sub> 4.50	-87.67

The above results confirm that the OB obtained from the EMDB V 1.0 software related to NA-NO<sub>2</sub>, PP-NO<sub>2</sub> and PB-NO<sub>2</sub> is consistent with the calculations of the mentioned formula.<sup>2</sup>

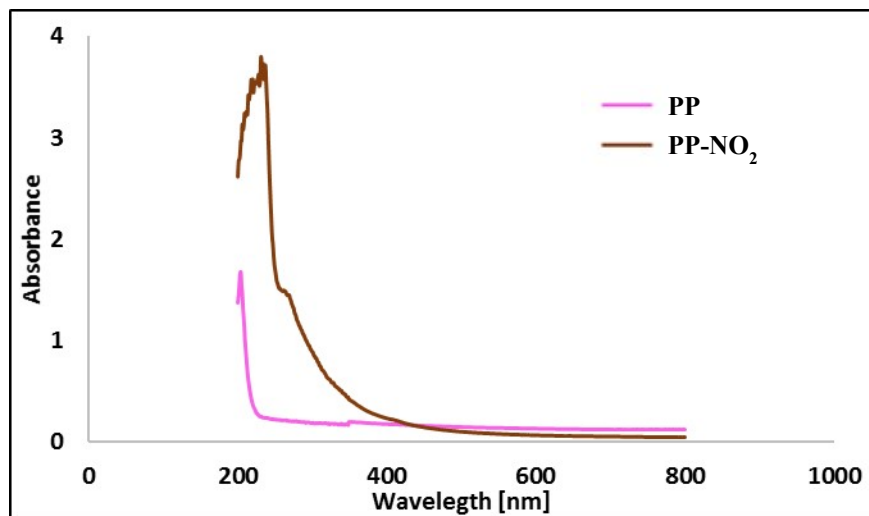
$$OB\% = \frac{d - 2a - \frac{b}{2}}{\text{Molecular mass of explosive (M)}} \times 1600$$



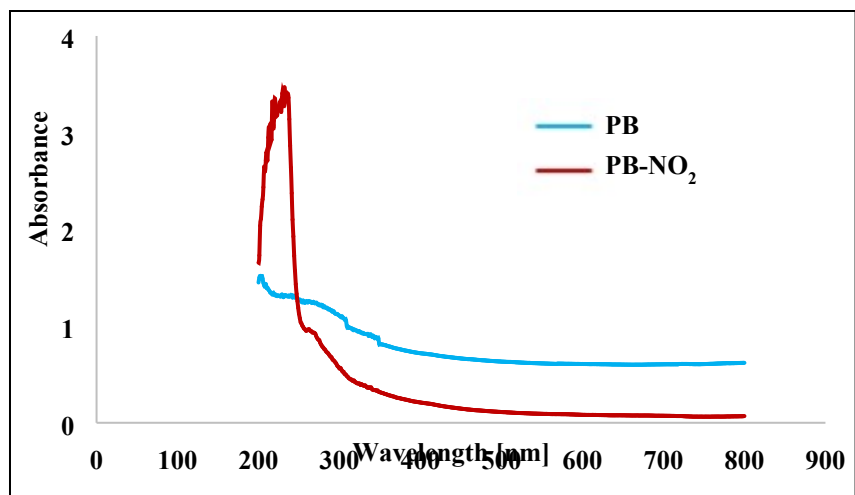
**Figure S1.** FT-IR spectra of NA (a), NA-NO<sub>2</sub> (with only HNO<sub>3</sub>) (b), NA-NO<sub>2</sub> (5 mL AC<sub>2</sub>O) (c), NA-NO<sub>2</sub> (10 mL AC<sub>2</sub>O) (d) and NA-NO<sub>2</sub> (10 g P<sub>2</sub>O<sub>5</sub>) (e).



**Figure S2.** FT-IR spectra of NA (a), NA-NO<sub>2</sub> (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> with acid ratio 2:3) (b), NA-NO<sub>2</sub> (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> with acid ratio 4:5) (c).



**Figure S3.** UV-Visible absorption spectra for PP and PP-NO<sub>2</sub>.



**Figure S4.** UV-Visible absorption spectra for PB and PB-NO<sub>2</sub>.



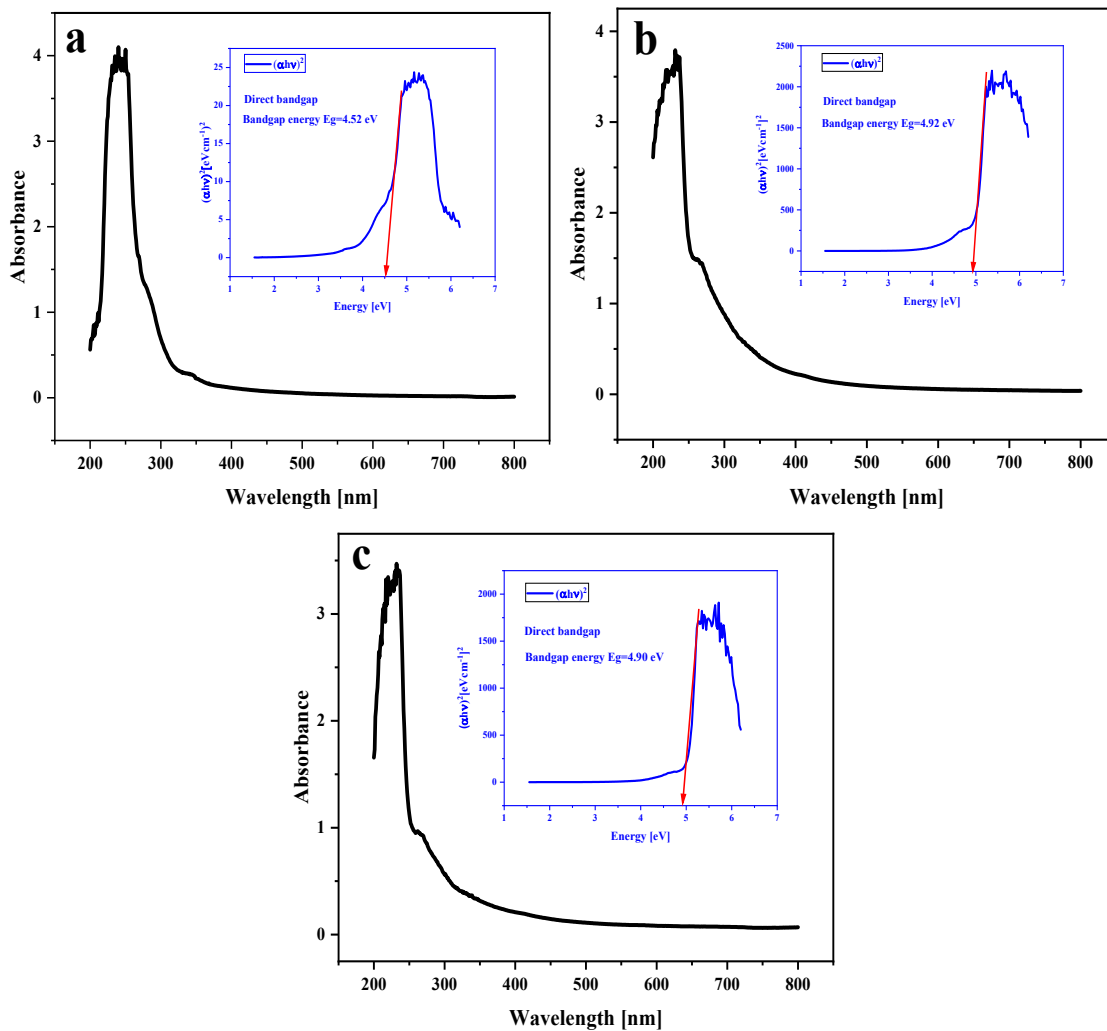


Figure S5. Direct band gap energies NA-NO<sub>2</sub> (a), PP-NO<sub>2</sub> (b) and PB-NO<sub>2</sub> (c).

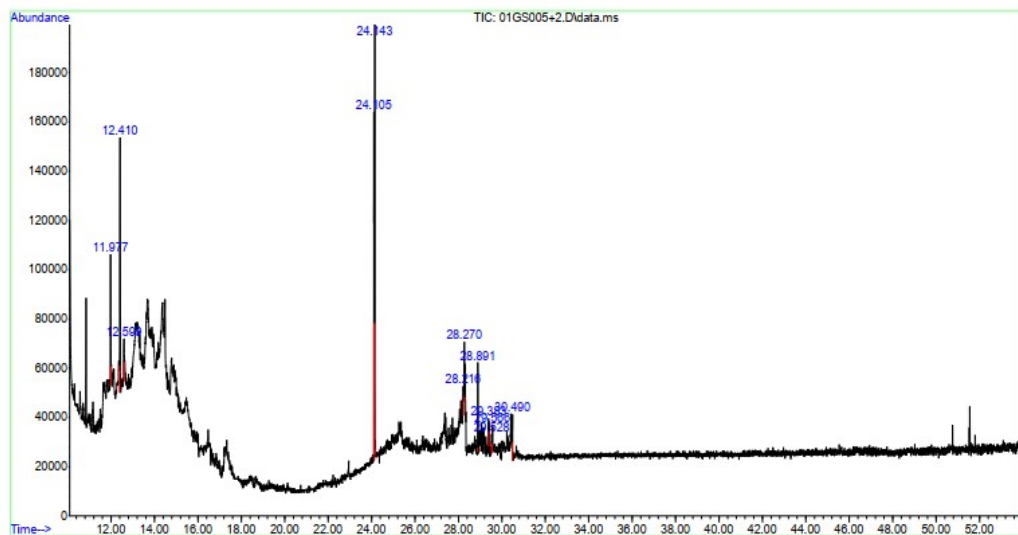


Figure S6. GC Chromatogram for NA-NO<sub>2</sub>.

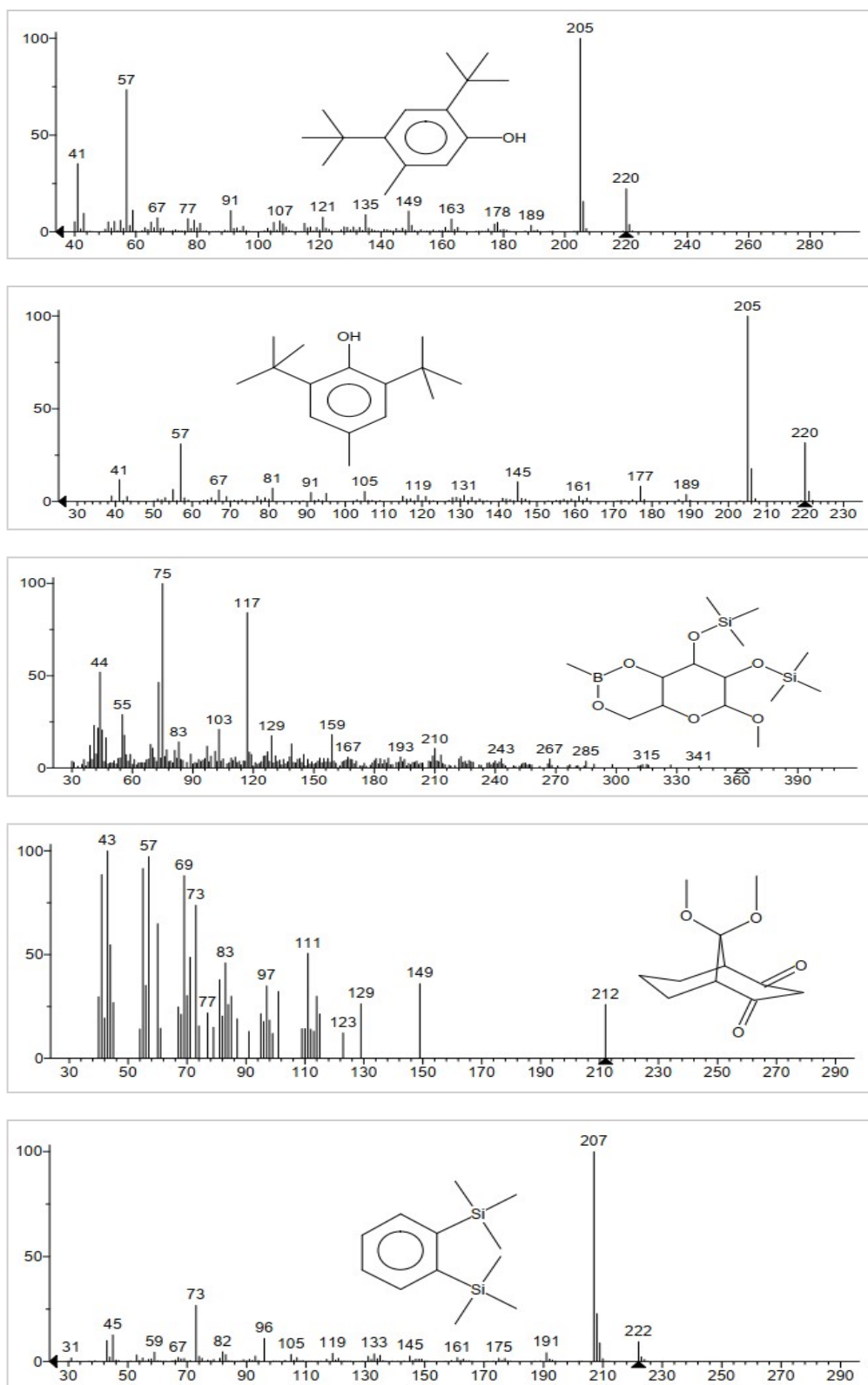


Figure S7. Mass spectra of fragmented molecules in NA-NO<sub>2</sub>.

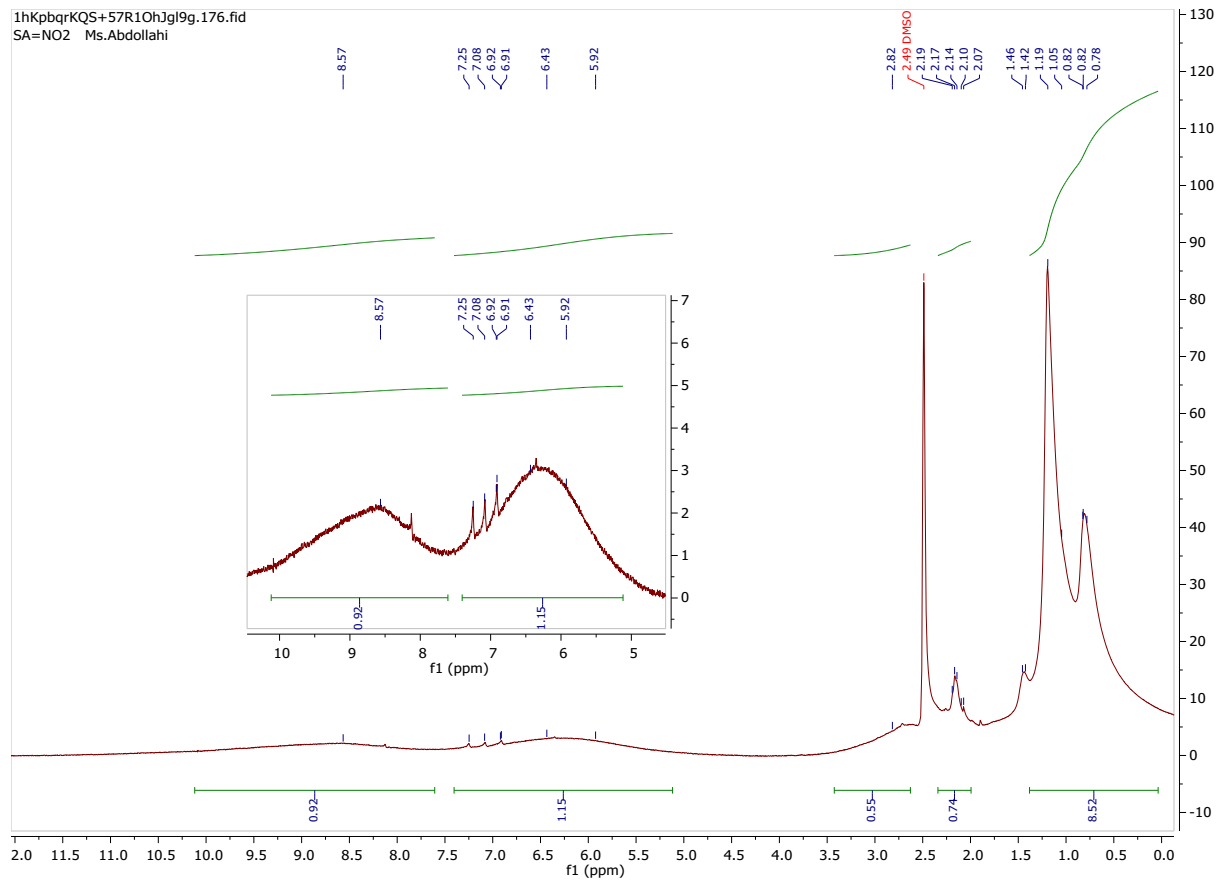


Figure S8.  $^1\text{H-NMR}$  spectrum of  $\text{NA-NO}_2$

## REFERENCES

- 1 S. Muppidi, C. R. Kamatala, S. C. Voruvala and S. K. Mukka, *Chem. Data Collect.*, 2019, **21**, 100222.
- 2 C. M. Tarver, *Propellants, Explos. Pyrotech.*, 2010, **35**, 494–494.