

Supplementary Information

Coal fly ash derived zeolite: A solid-state base for convenient synthesis of diphenyl ethers

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S1. Different fusion conditions and corresponding XRD analysis for the synthesis of Sodalite

Table S1 Variation in the time and temperature of the fusion for Sodalite synthesis

S.No.	Sample name	Fusion temperature (°C)	Fusion time (h)
1.	F550-0.5	550	0.5
2.	F750-0.5	750	0.5
3.	F750-2	750	2

Table S1 above shows the fusion of **FA**, NaOH and sodium aluminate at different times and temperatures. XRD analysis was used to analyze the effect of fusion time and temperature on the synthesis of Sodalite. Noticeable changes can be seen in the XRD spectra as sodium silicate and sodium aluminate phases appear (ICDD card no. 049-0003), and the peak due to quartz at 26.8 begins to diminish.¹ Finally, sample *F750-2* shows a diminished quartz peak with broadening, indicating its reduced crystallinity. Therefore, a temperature of 750 °C for 2h was used to synthesize pure-phase Sodalite.

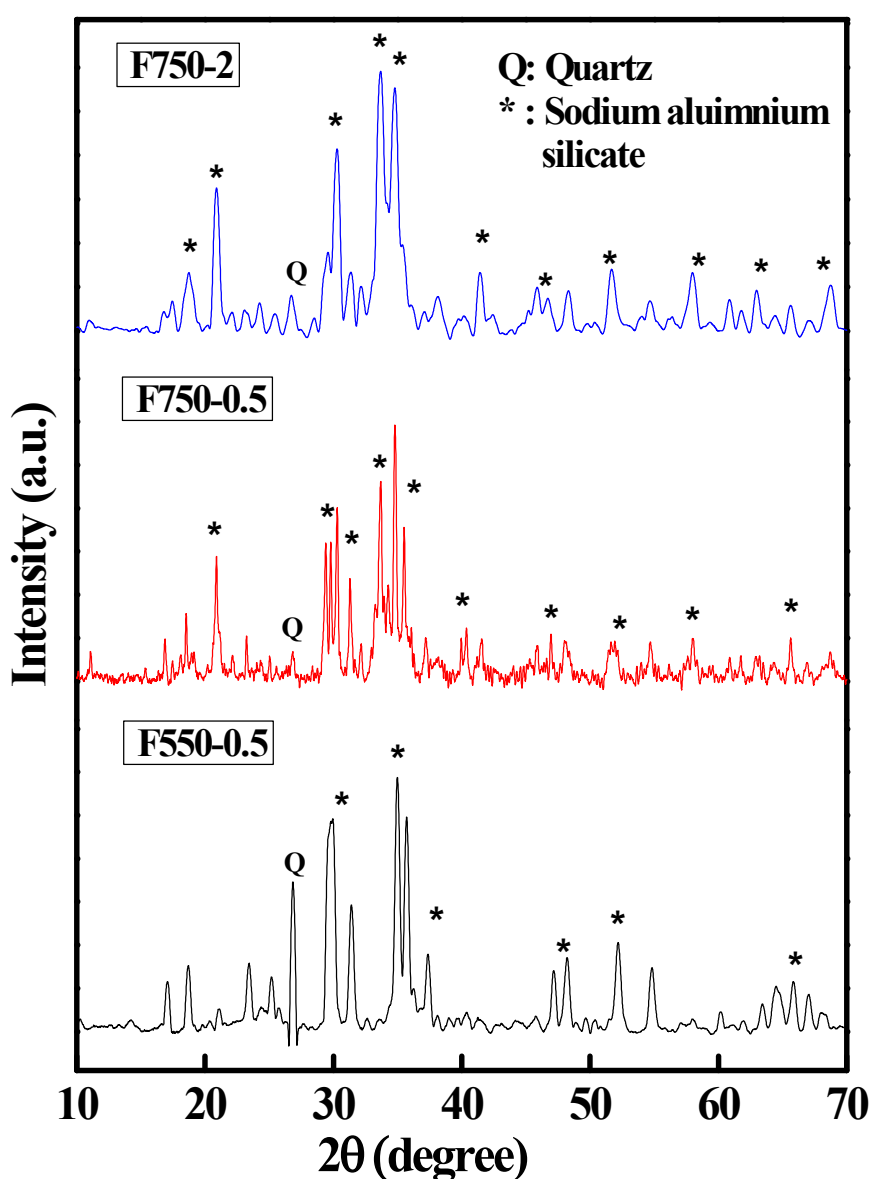


Fig. S1. Noticeable changes can be seen in the XRD spectra as sodium silicate and sodium aluminate phases appear (ICDD card no. 049-0003), and the peak due to quartz at 26.8 begins to diminish at 750 °C for 2h (F750-2).¹

S2. Calculation for the percent yield using NMR Spectrum

The percent yield formula was modified from the reported literature.² The percent yield was calculated using the following expression for a functional group with equal hydrogens appearing in both reactant and product.

$$\% \text{ Yield} = \frac{I_p}{I_p + I_r} \times 100 \quad (\text{Equation -1})$$

where

I_r : Integration of the same substituent in the reactant (From NMR)

I_p : Integration of the same substituent in the product (From NMR)

For example, for the reaction in **Scheme S1**, the percent yield was calculated by considering the OCH₃ hydrogens in both reactant and product.

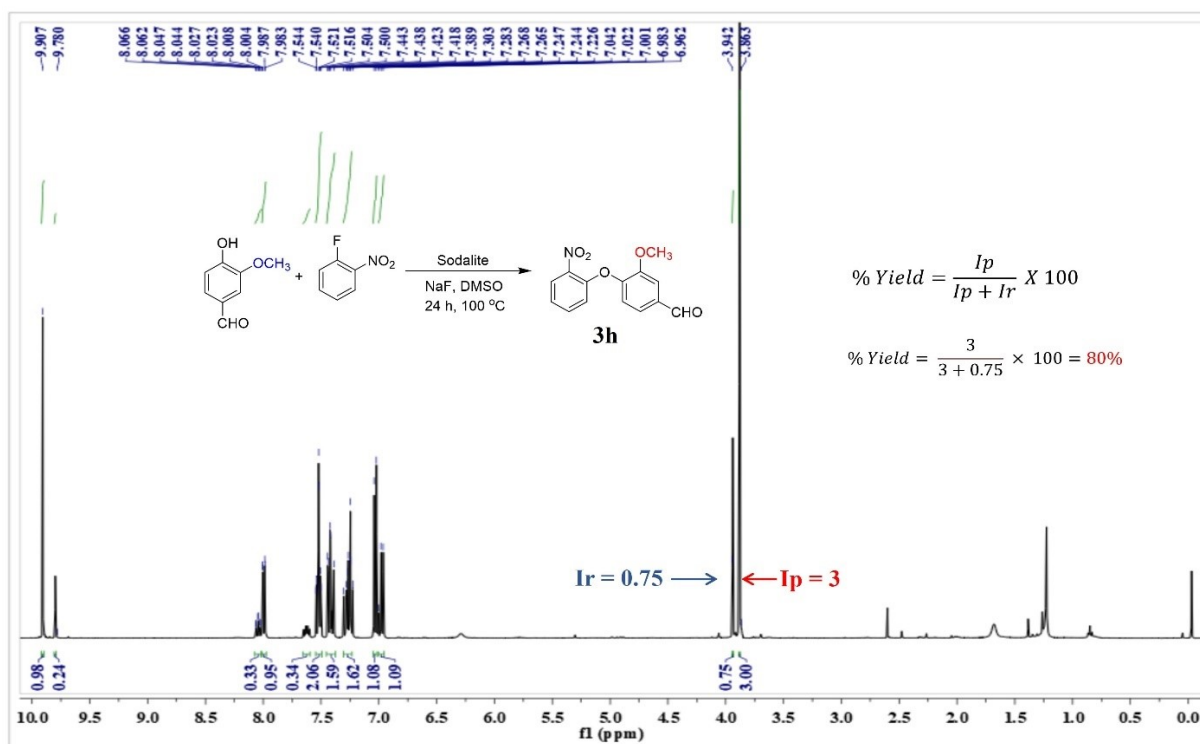


Fig. S2. NMR spectra of compound 3h showing 80 percent yield of the reaction by considering peaks of OCH₃ hydrogens at 3.942 and 3.863 δ values and evaluating integration values I_r (0.75) and I_p (3.0) for the reactant (A) and product (C) in Equation-1.

S3. Calculation of per cent yield for different reactions carried out as shown in Table-3 of the manuscript.

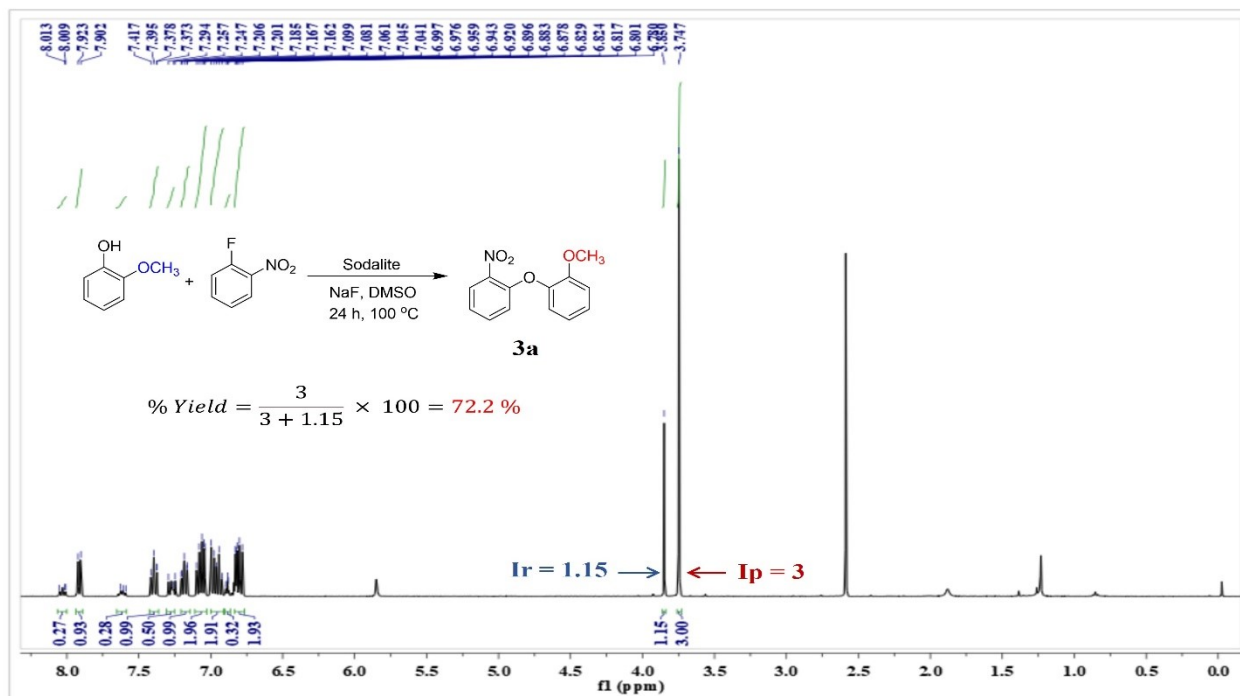


Fig. S3a. NMR spectra of compound 3a showing percent yield by considering the integration of OCH₃ hydrogens in reactant and product.

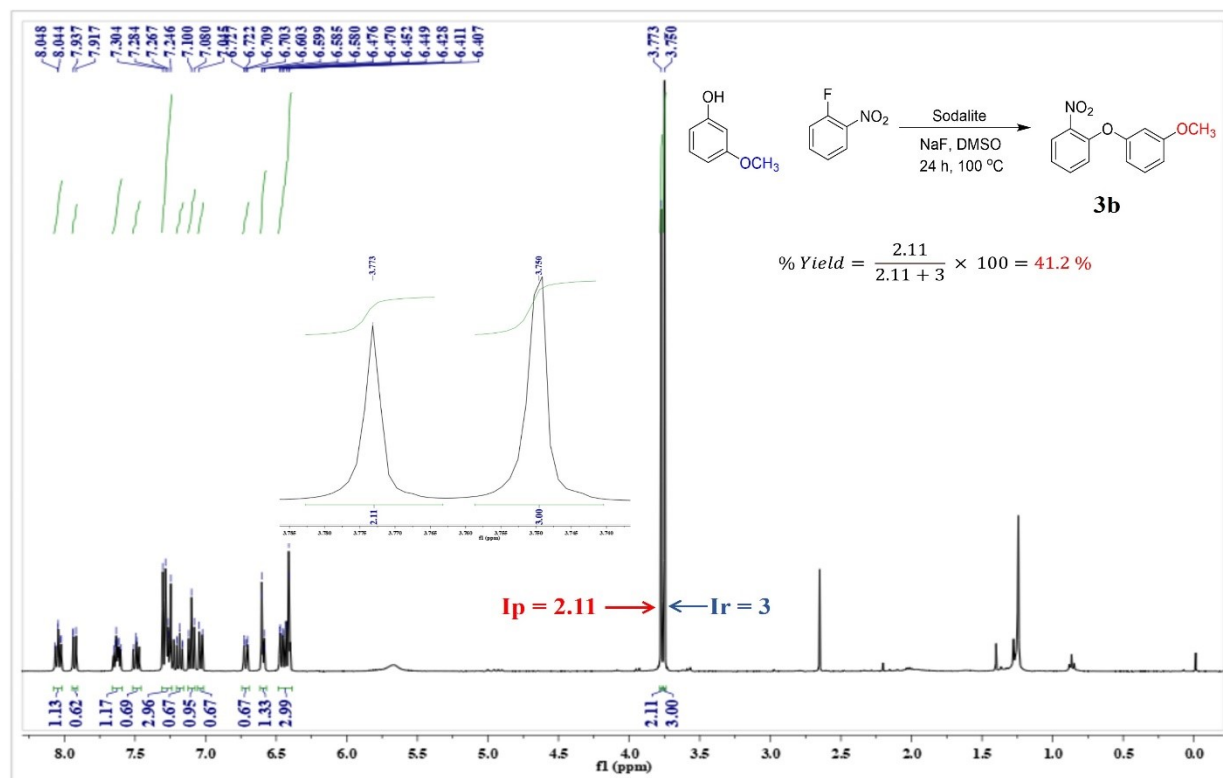


Fig. S3b. NMR spectra of compound 3b showing percent yield by considering the integration of OCH₃ hydrogens in reactant and product.

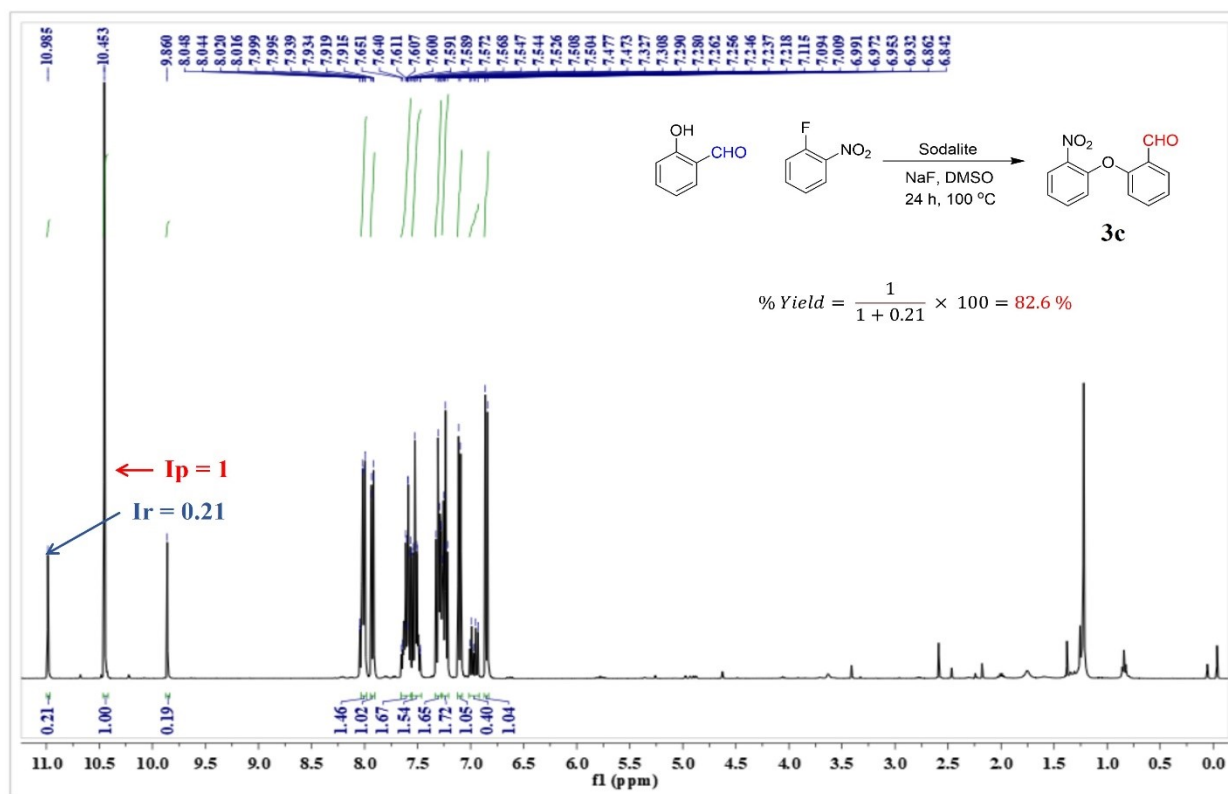


Fig. S3c. NMR spectra of compound 3c showing percent yield by considering the integration of CHO hydrogen in reactant and product.

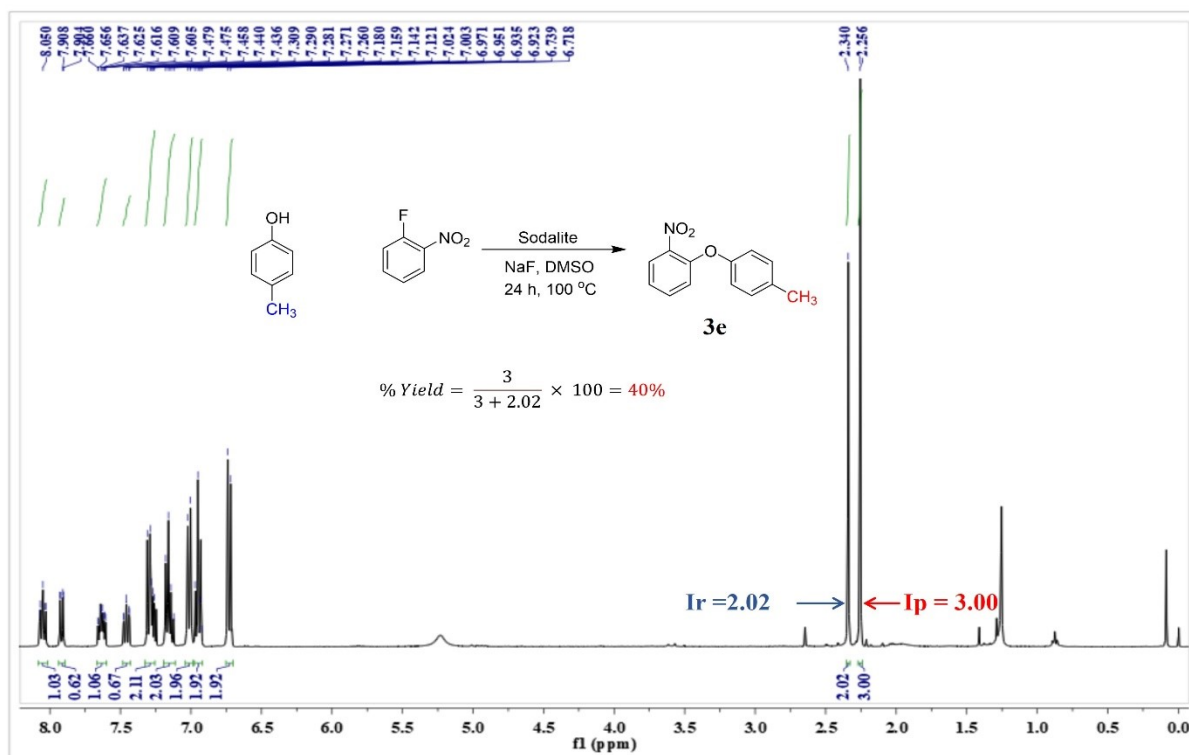


Fig. S3d. NMR spectra of compound **3e** showing percent yield by considering the integration of OCH₃ hydrogens in reactant and product.

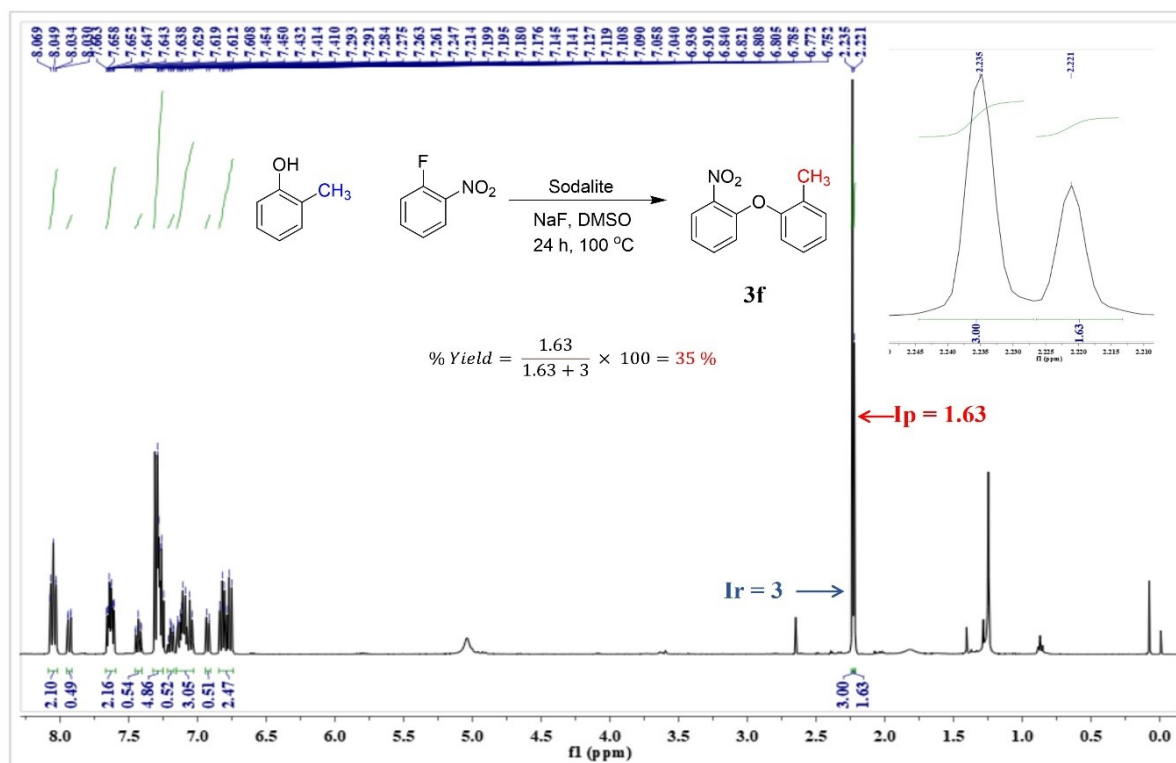


Fig. S3e. NMR spectra of compound **3f** showing percent yield by considering the integration of CH₃ hydrogens in reactant and product.

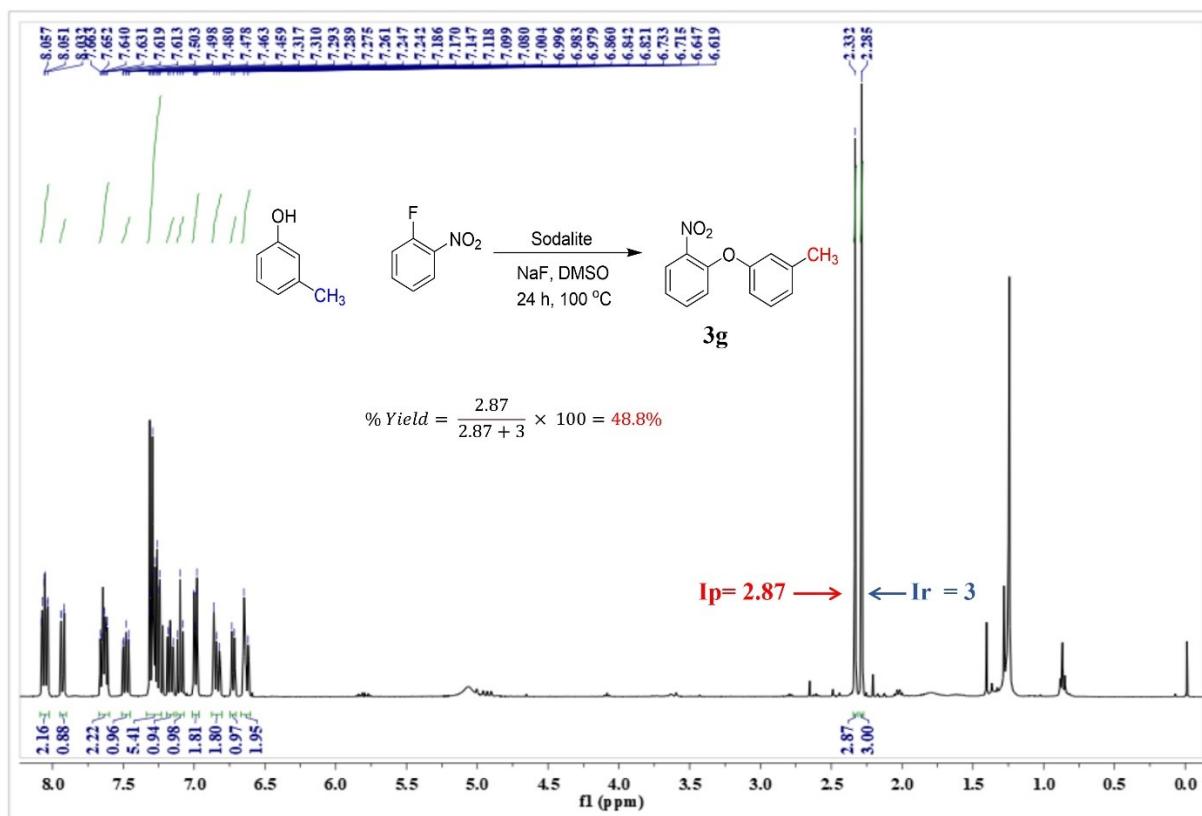


Fig. S3f. NMR spectra of compound 3g showing percent yield by considering the integration of CH₃ hydrogens in reactant and product.

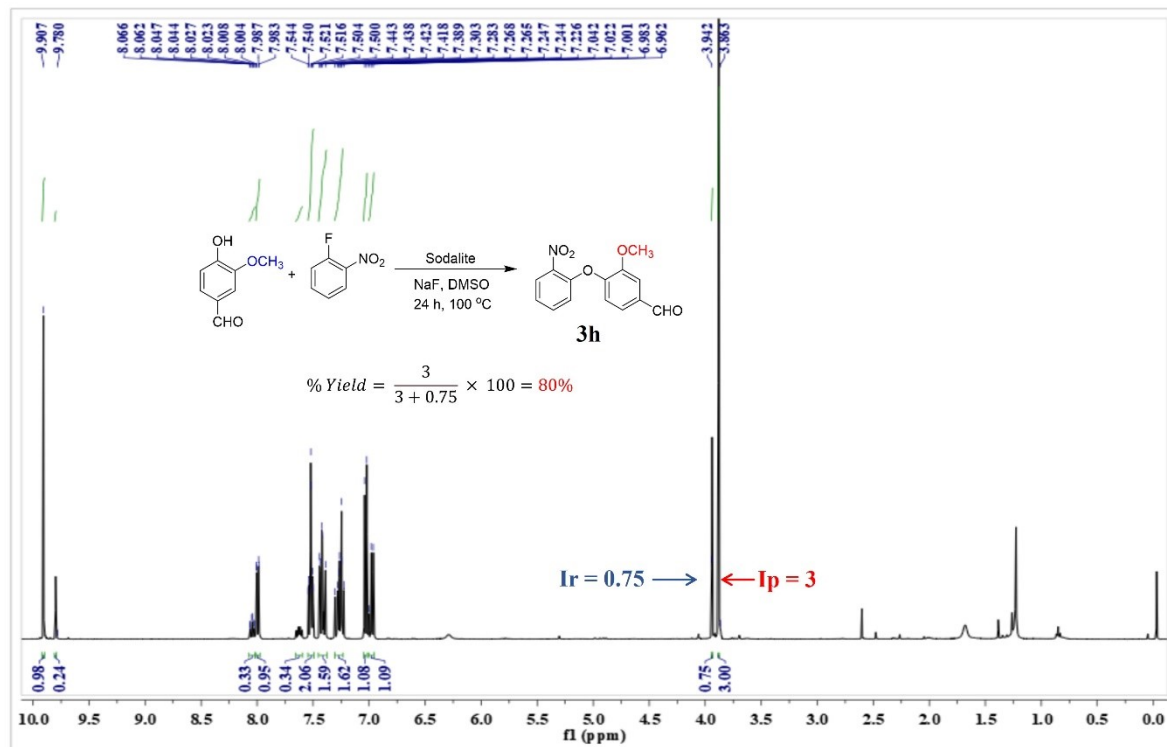


Fig. S3g. NMR spectra of compound 3h showing percent yield by considering the integration of OCH₃ hydrogens in reactant and product.

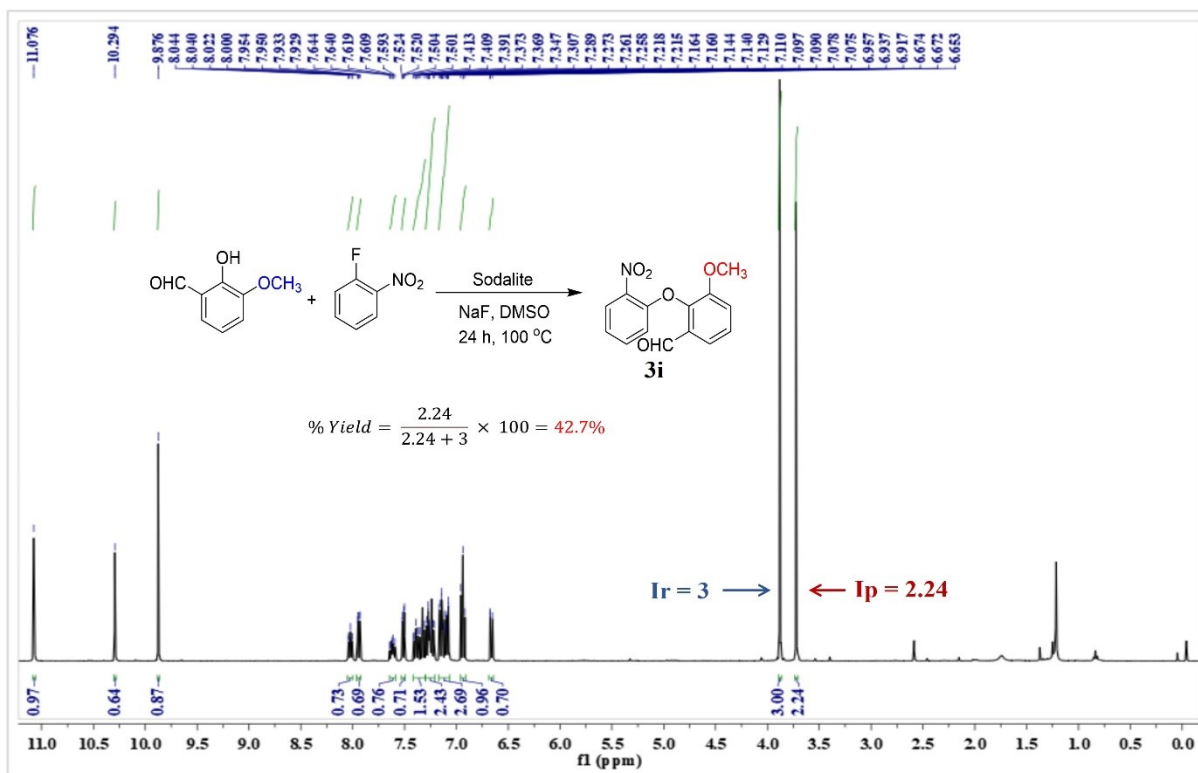


Fig. S3h. NMR spectra of compound **3i** showing percent yield by considering the integration of OCH_3 hydrogens in reactant and product.

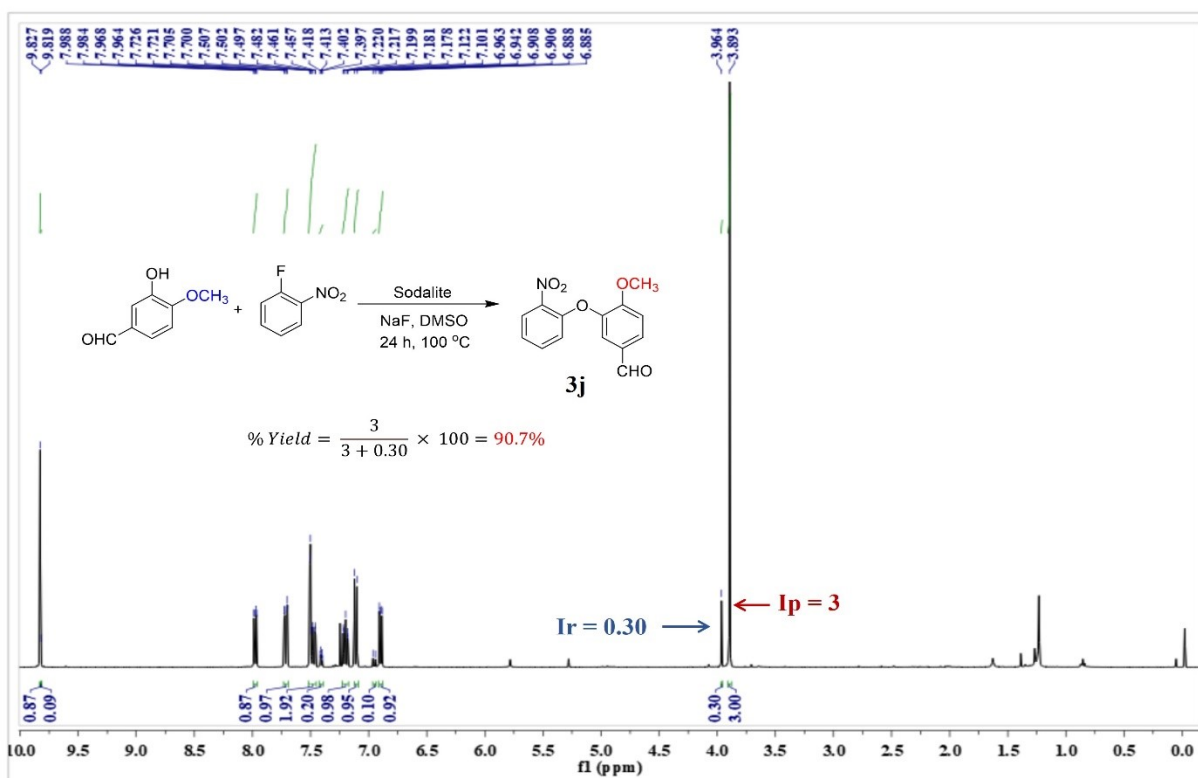


Fig. S3i. NMR spectra of compound 3j showing percent yield by considering the integration of OCH₃ hydrogens in reactant and product.

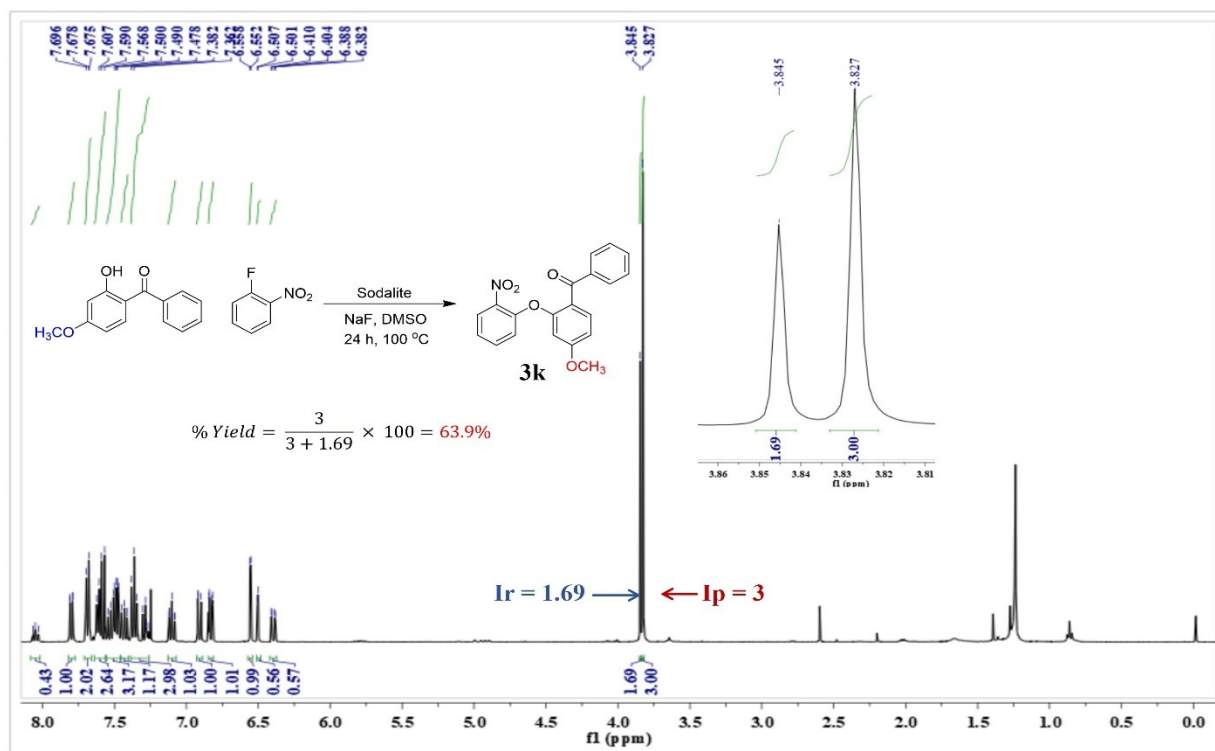


Fig. Sj. NMR spectra of compound 3k showing percent yield by considering the integration of OCH₃ hydrogens in reactant and product.

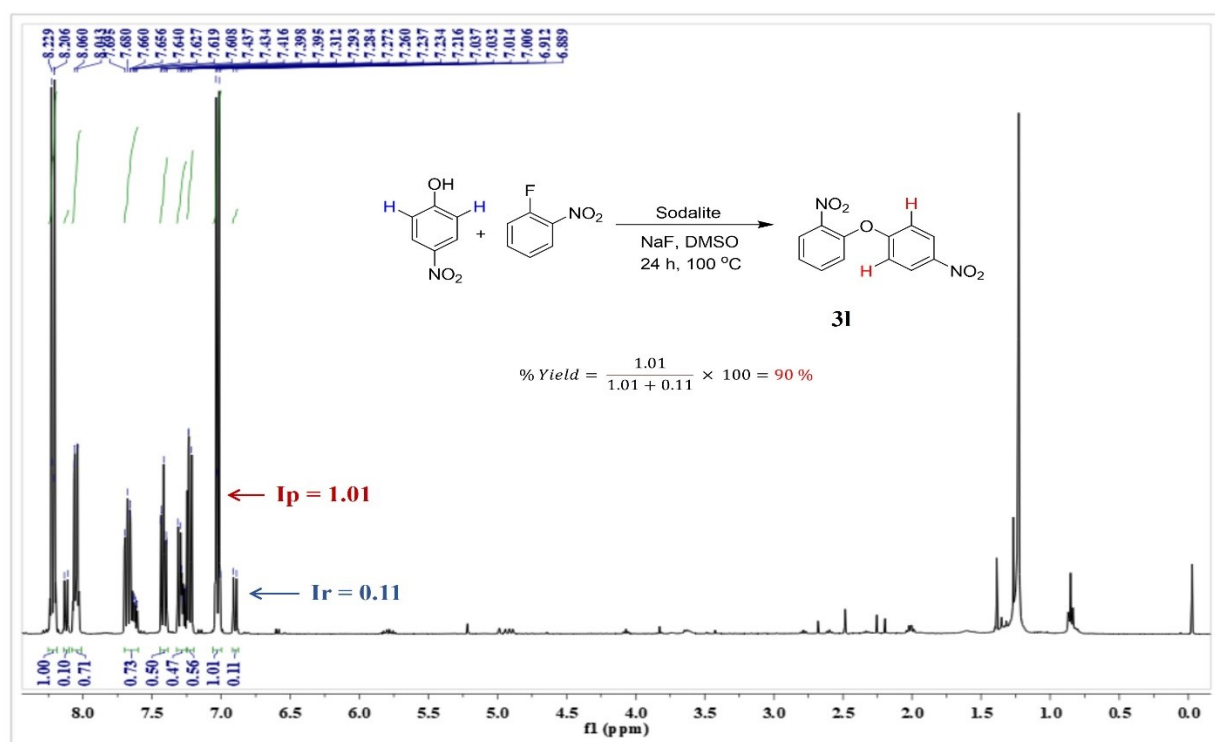


Fig. S3k. NMR spectra of compound 3l showing percent yield by considering the integration of aromatic hydrogens in reactant and product.

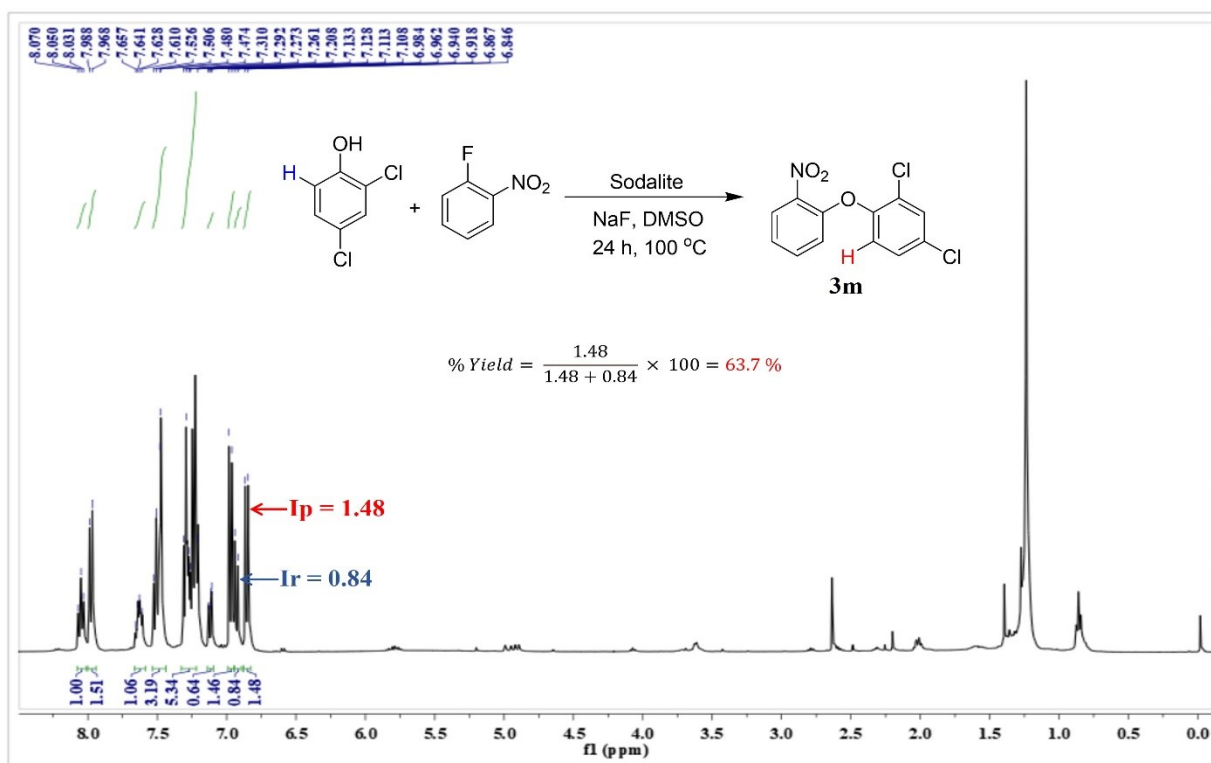


Fig. S31. NMR spectra of compound **3m** showing percent yield by considering the integration of aromatic hydrogens in reactant and product.

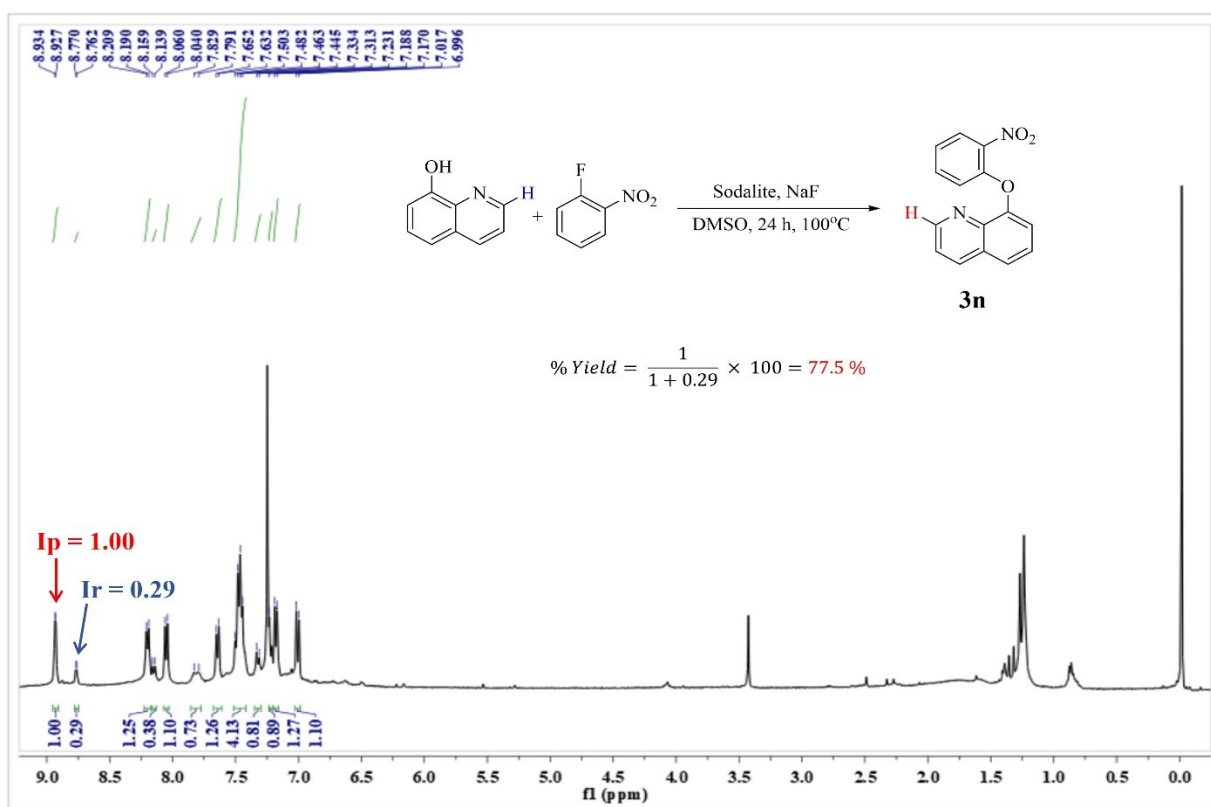


Fig. S3m. NMR spectra of compound 3n showing percent yield by considering the integration of aromatic hydrogens in reactants and product.

S4. Complete characterization of the representative compound 3n

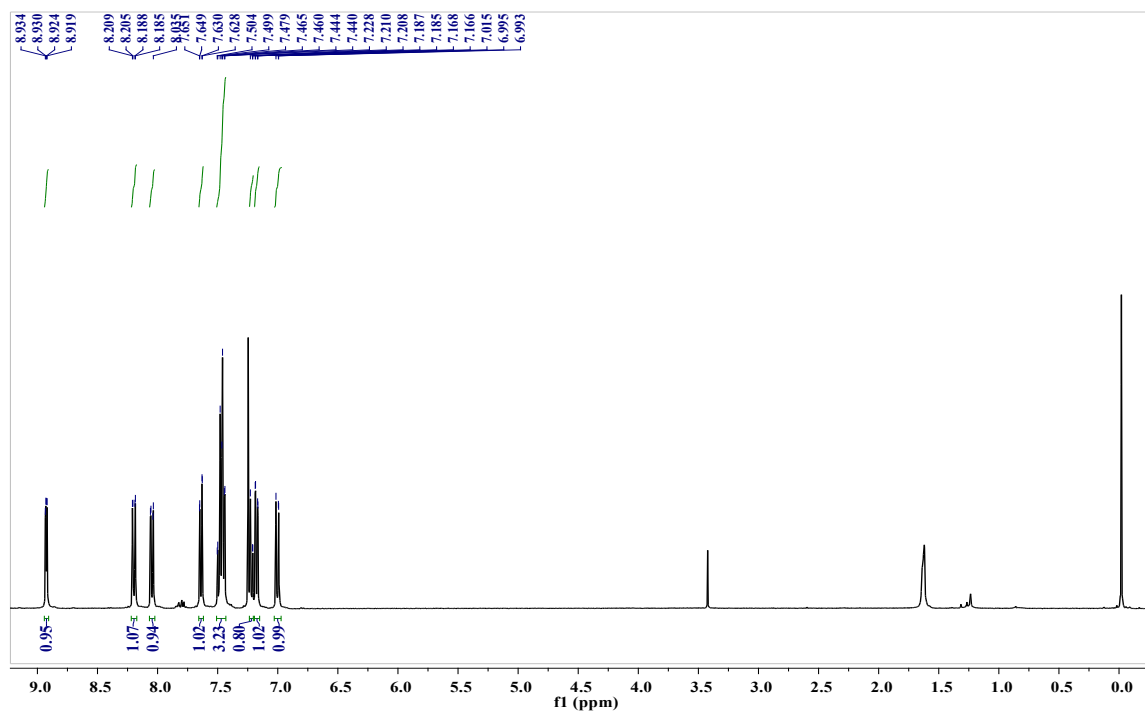


Fig. S4a. ¹³C NMR spectra of compound 3n.

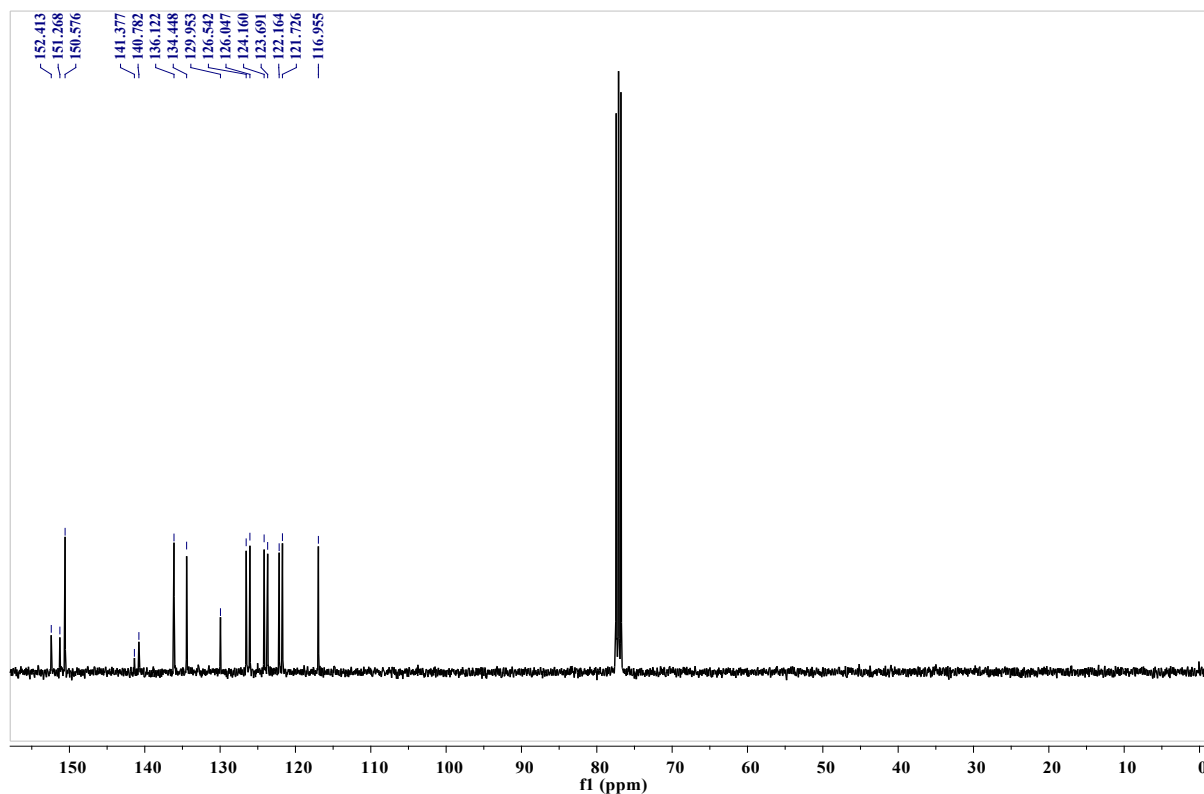


Fig. S4b. ^{13}C NMR spectra of compound 3n.

^1H NMR (CDCl_3 , 400MHz): $\delta(\text{ppm})$ 8.93 (dd, $^2J = 4.2$ Hz, $^3J = 5.8$ Hz, 1H, ArH), $\delta(\text{ppm})$ 8.20 (dd, $^2J = 8.36$ Hz, $^3J = 8.24$ Hz, 1H, ArH), $\delta(\text{ppm})$ 8.05 (dd, $^2J = 8.24$ Hz, $^3J = 8.08$ Hz, 1H, ArH), $\delta(\text{ppm})$, 7.64 (dd, $^2J = 8.4$ Hz, $^3J = 8.48$ Hz, 1H, ArH), $\delta(\text{ppm})$ 7.47 (m, 3H, ArH), $\delta(\text{ppm})$ 7.22 (m, 1H, ArH), $\delta(\text{ppm})$ 7.18 (dd, $^2J = 7.88$ Hz, $^3J = 7.8$ Hz, 1H, ArH), $\delta(\text{ppm})$ 7.00 (dd, $^2J = 8.08$ Hz, $^3J = 8.84$ Hz, 1H, ArH); ^{13}C (CDCl_3 , 100MHz): $\delta(\text{ppm})$ 152.4, 151.2, 150.5, 141.3, 140.7, 136.1, 134.4, 129.9, 126.5, 126.0, 124.1, 123.6, 122.1, 121.7, 116.9; HRMS (ESI) Calcd. for $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 267.0771 Found; 267.0785.

S5. Optimization of time and temperature for synthesis of diphenyl ethers

Initial optimization of the reaction conditions for time and temperature to synthesize diphenyl ether was done using 3 mol percent of Sodalite as a solid state base and DMSO as a solvent.

Table S2. Optimization of time and temperature for synthesis of diphenyl ether.

Entry	Time (h)	Temperature ($^{\circ}\text{C}$)	Percent yield
1.	56	Room temperature	3
2.	14	75	11
3.	24	75	15
4.	14	100	17
5.	24	100	20

Table S2 shows that the highest yield was observed in **Entry 5** and the condition optimized for diphenyl ether synthesis was 100 °C for 24 h.

S6. Hot filtration test

The hot filtration test was carried out by filtering out the model reaction (Scheme 2) through a heated Celite pad after a reaction for 8 h.³

The reaction was set up as described in section 2.6 for the synthesis of product 3a. After 8h the reaction mixture was filtrated hot using celite bed and the filtrate was divided into two parts. Part 1 was washed with DCM (3×10 mL) and water (5×10 mL), and the percent yield of the obtained DPE was calculated using ¹H NMR as described above. Part -2 of the reaction mixture was further heated under similar conditions described in section 2.6 for another 16h. After completion of the time, it was also washed with DCM (3×10 mL) and water (5×10 mL). The yield was again calculated using ¹H NMR. This was done to check if the removal of Sodalite affects the reaction yield and confirm whether it reacts in a homogeneous or heterogeneous fashion³. The NMR spectra (Fig S6) below display hot filtration after 8h (HF-8H) and 16h (HF-16H), which show the percent yield in each case.

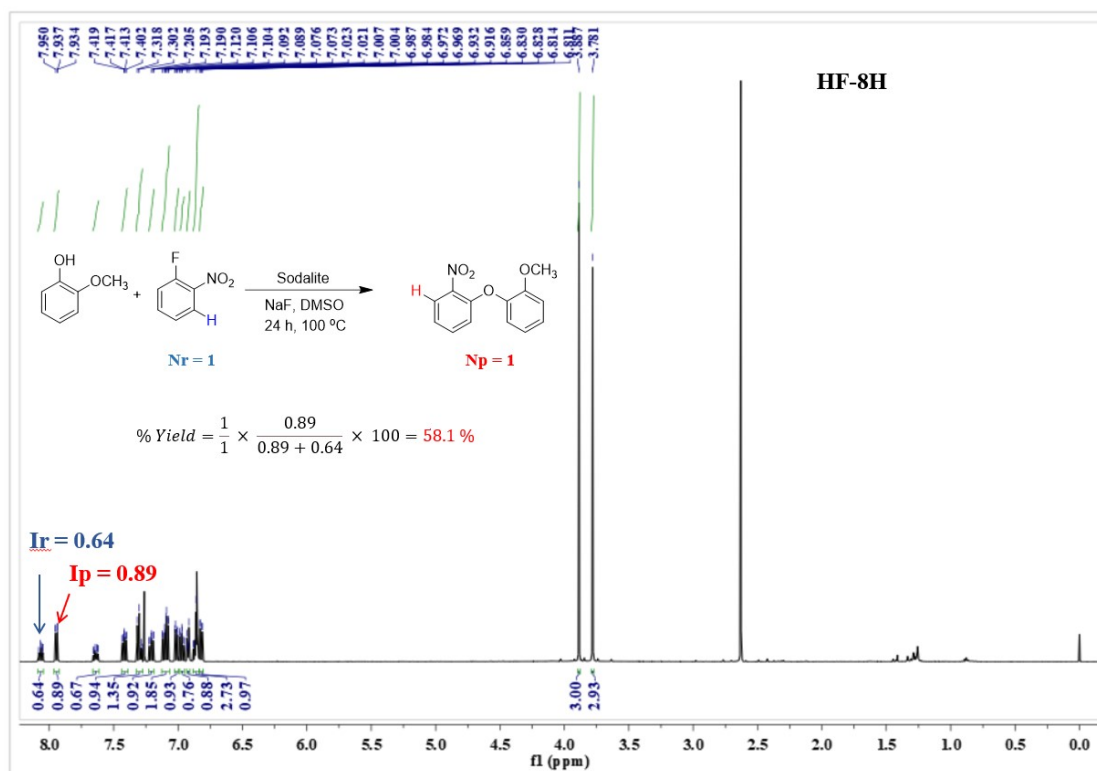


Fig. S6a. NMR spectra of compound 3a showing percent yield by considering the integration of aromatic hydrogens in reactant and product.

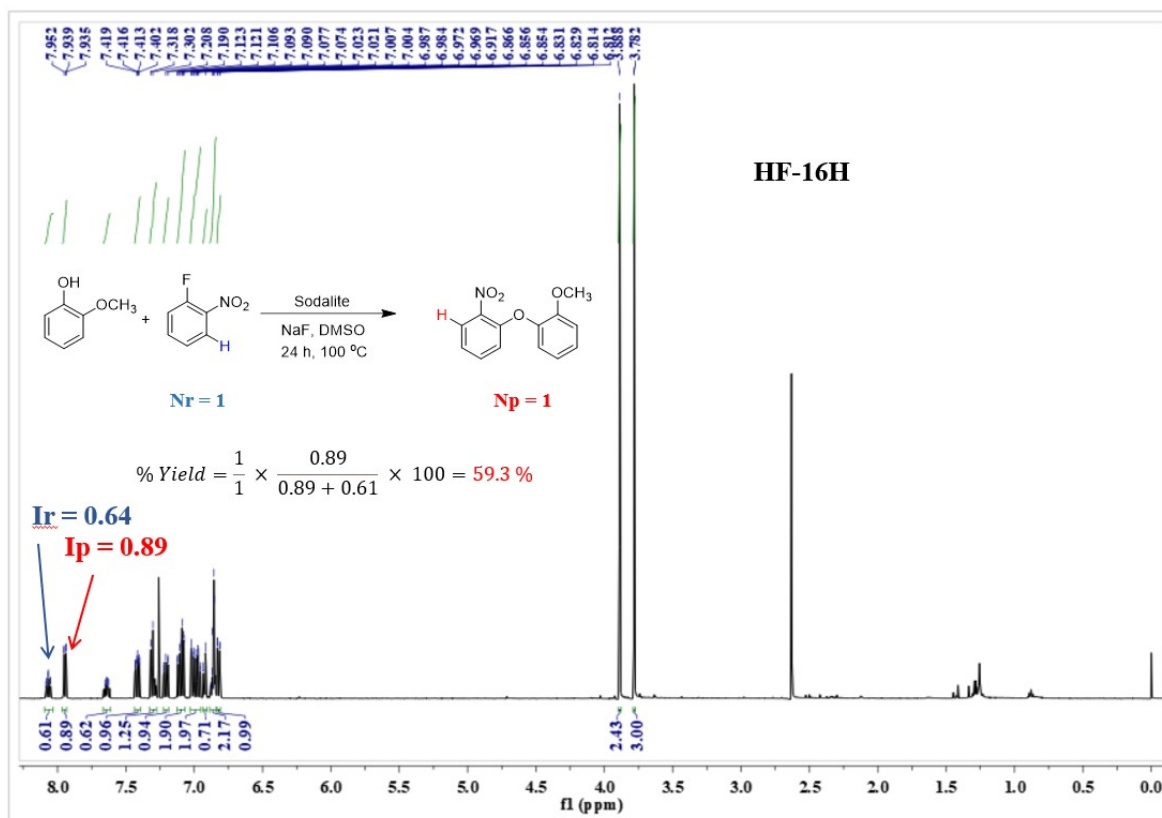


Fig. S6b. NMR spectra of compound 3a showing percent yield by considering the integration of aromatic hydrogens in reactant and product.

S7. References

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- 2 J. K. Satyarthi, D. Srinivas and P. Ratnasamy, *Energy and Fuels*, 2009, **23**, 2273–2277.
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