Asymmetric Hydrogenation using Covalently Immobilized Ru-BINOL-AP@MSNs Catalyst

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Supporting Information

Table of Contents

1. General Information

S-BINOL, $RuCl_3 \cdot 3H_2O$, IPA, NaOH, CTAB, sodium hydride, dimethylformamide, methoxy methyl chloride, diethyl ether, toluene, Acetophenone and its derivatives, KOH and $NaHCO_3$ was procured from Loba Chemie, India. (3-aminopropyl)trimethoxysilane was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). TEOS was purchased from Sisco Research Laboratories Pvt. Ltd.(SRL) – India. all of these reagents are of analytical grade and used as received without further purification.

2. Characterization's Techniques Information

For the characterization of as-prepared materials such as MSNs, AP@MSNs, BINOL-AP@MSNs and Ru-BINOL-AP@MSNs different physicochemical techniques have been employed. ^{13}C CP MAS NMR using the model: JEOL, JAPAN ECZR Series 600 MHz NMR SPECTROMETER at SAIF, IIT Bombay, Mumbai, India. XPS spectra were performed on Specs, Phoibios 225 spectrometer with Al Kα radiation (1486.6 eV), Synchrotrons Utilisation Section, Raja Ramanna Centre for Advanced Technology, Indore, India. The quantitative analysis of Fe metal ion of the nanocatalysts was carried out by ICP-AES using the model: ARCOS, Simultaneous ICP Spectrometer at SAIF, IIT, Mumbai. The structure determinations of as-prepared materials were performed on Bruker AXS D8 Advance X-ray powder diffractometer with a CuKα (λ=1.54058) target and movable detector, which scans the intensity of diffracted radiation within the range of 5°–80° as a function of the angle 2θ between the incident and diffracted beams. Transmission electron microscopy (HR-TEM) of as-prepared materials was performed on Model HRTEM: JEOL/JEM 2100 at Sophisticated Test & instrumentation centre Cochin University of Science and Technology Cochin. Field Emission Scanning Electron Microscopy (FESEM) of as-prepared materials was performed the images were taken at 5 keV and Model: Auriga at Synchrotrons Utilisation Section, Raja Ramanna Centre for Advanced Technology, Indore, India. BET surface area and pore size distribution measure on micromeritics. FTIR spectra of as prepared materials were performed in the range: 4000-400 cm^{-1} on a model: FTIR - 8400S Shimadzu using KBr pellets. Thermogravimetric analysis of the as-prepared materials was performed on Shimadzu TGA-50 instrument (50 to 700 °C at 10 °C min^{-1} in air atmosphere) at the Applied Chemistry Department, Faculty of Technology & Engineering, The Maharaja Sayajirao University of Baroda, Vadodara, India.

3. Spectral Data for Modified *S*-BINOL

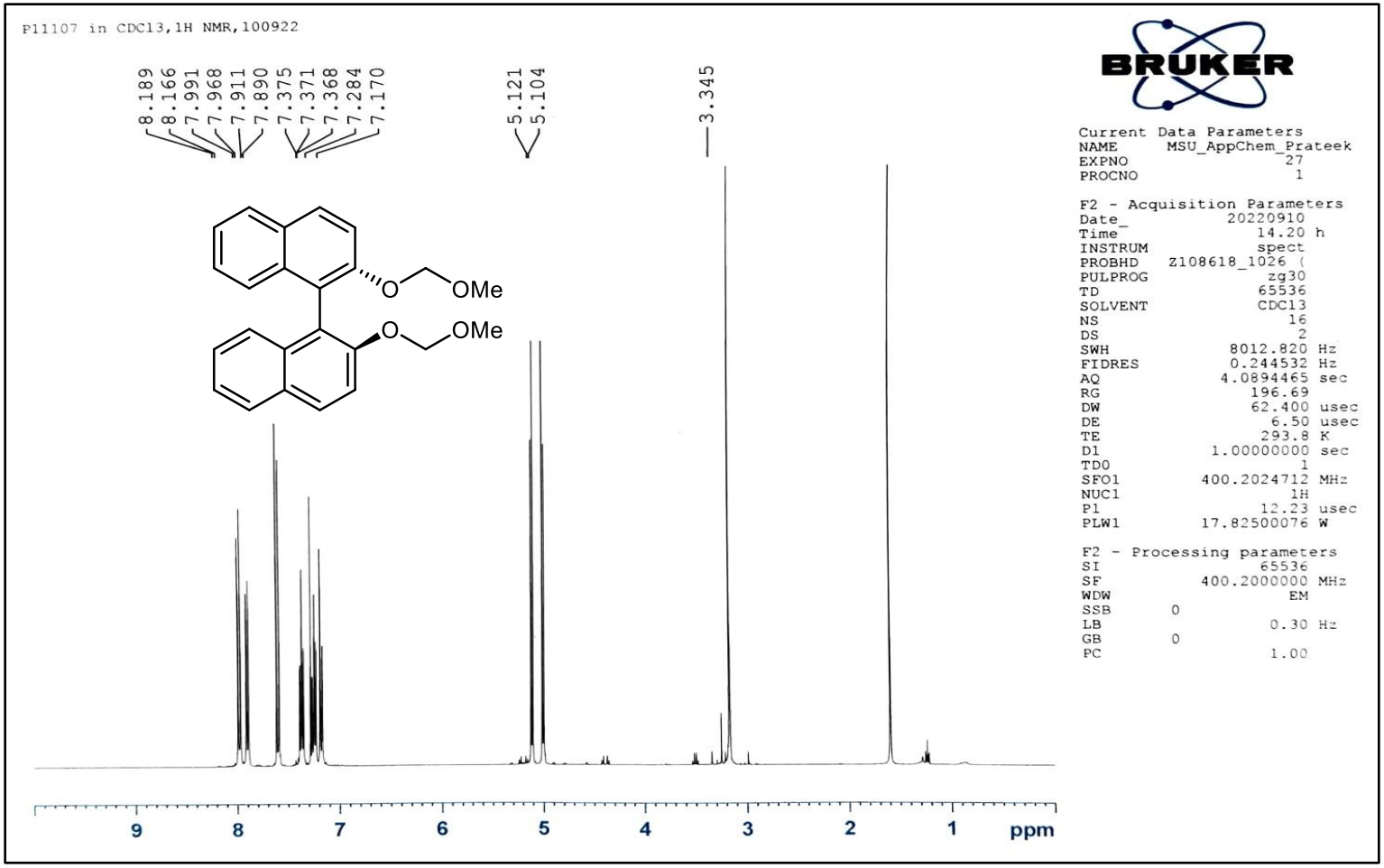


Fig. S1. ^{1}H NMR spectra of the 2-(methoxymethoxy)-1-(2-(methoxymethoxy)-naphthalen-1-yl)naphthalene.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, 2H), 7.99 (d, 2H), 7.89 (d, 2H), 7.36 (m, 2H), 7.28 (m, 4H), 5.12 (d, 2H), 5.10 (d, 2H), 3.34 (s, 6H).

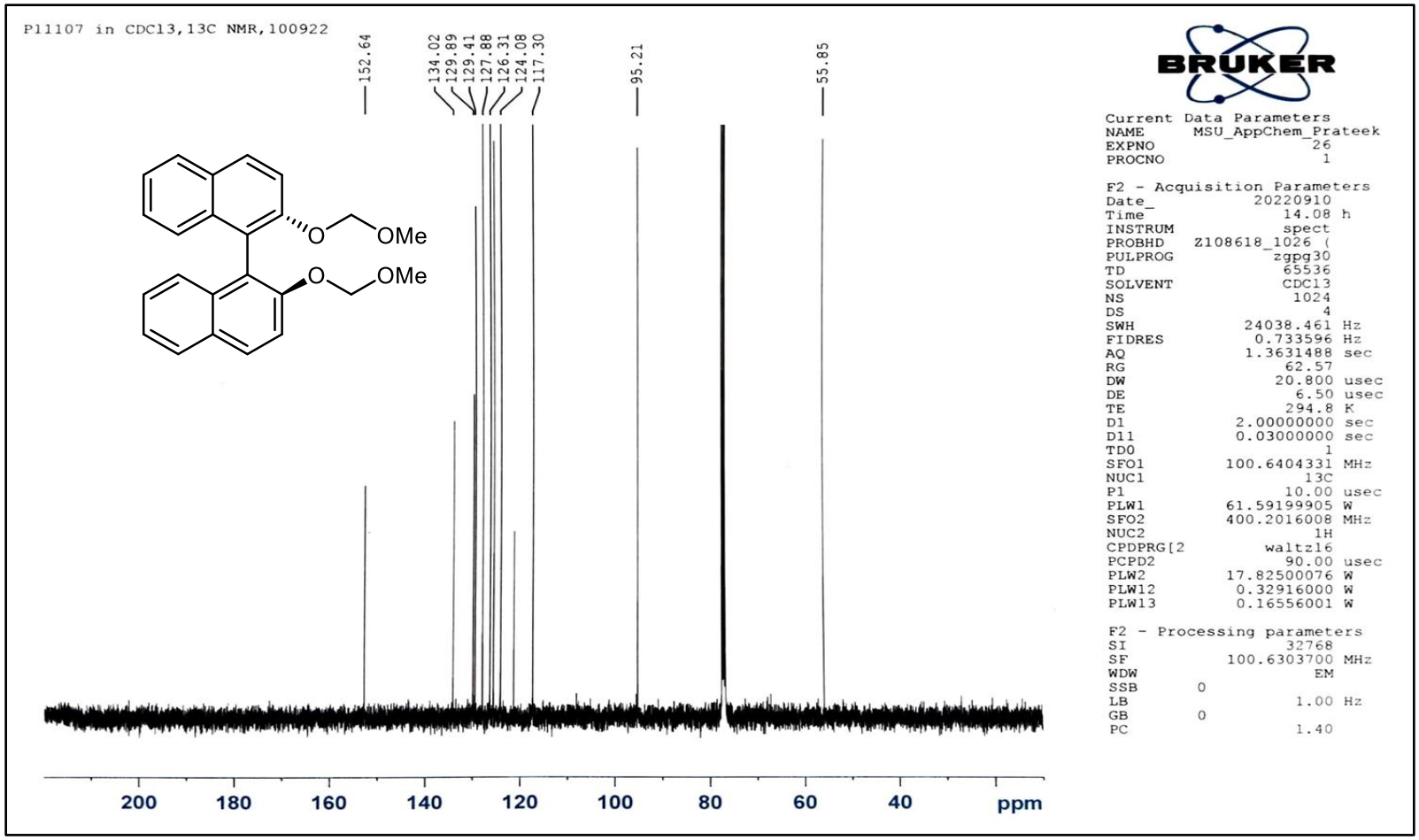


Fig. S2. ^{13}C NMR spectra of the 2-(methoxymethoxy)-1-(2-(methoxymethoxy)-naphthalen-1-yl)naphthalene.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.64, 134.02, 129.89, 129.41, 127.88, 126.31, 124.08, 117.30, 95.21 and 55.85.

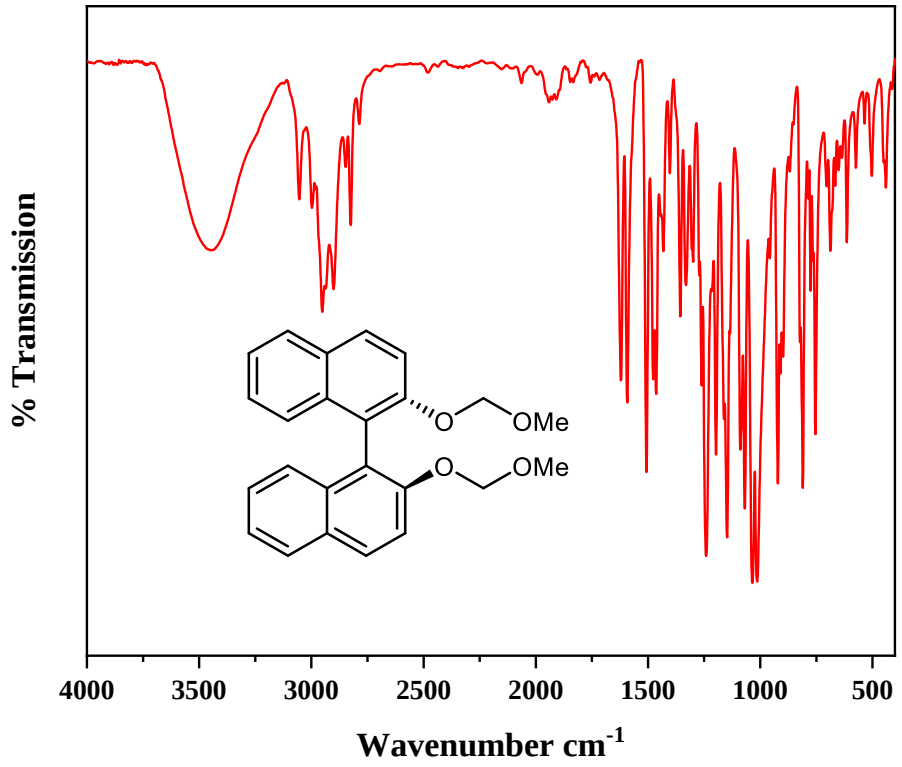


Fig. S3. FTIR spectra of the 2-(methoxymethoxy)-1-(2-(methoxymethoxy)-naphthalen-1-yl)naphthalene.

4. Characterization Data for Catalyst

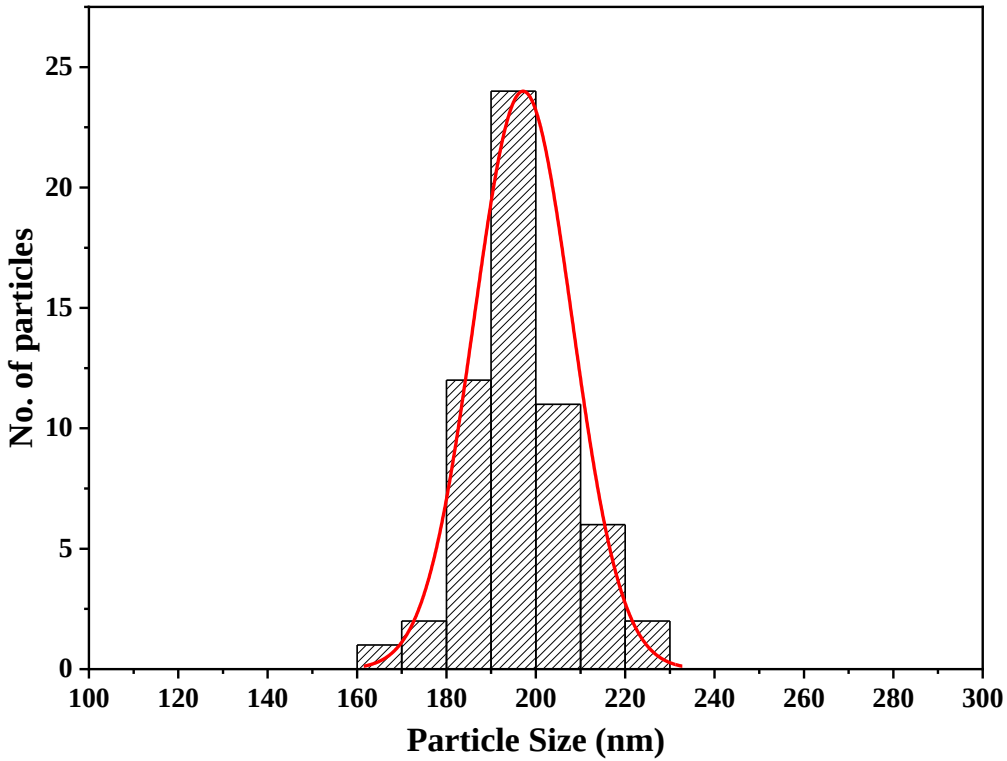


Fig. S4. Histogram graph of MSNs.

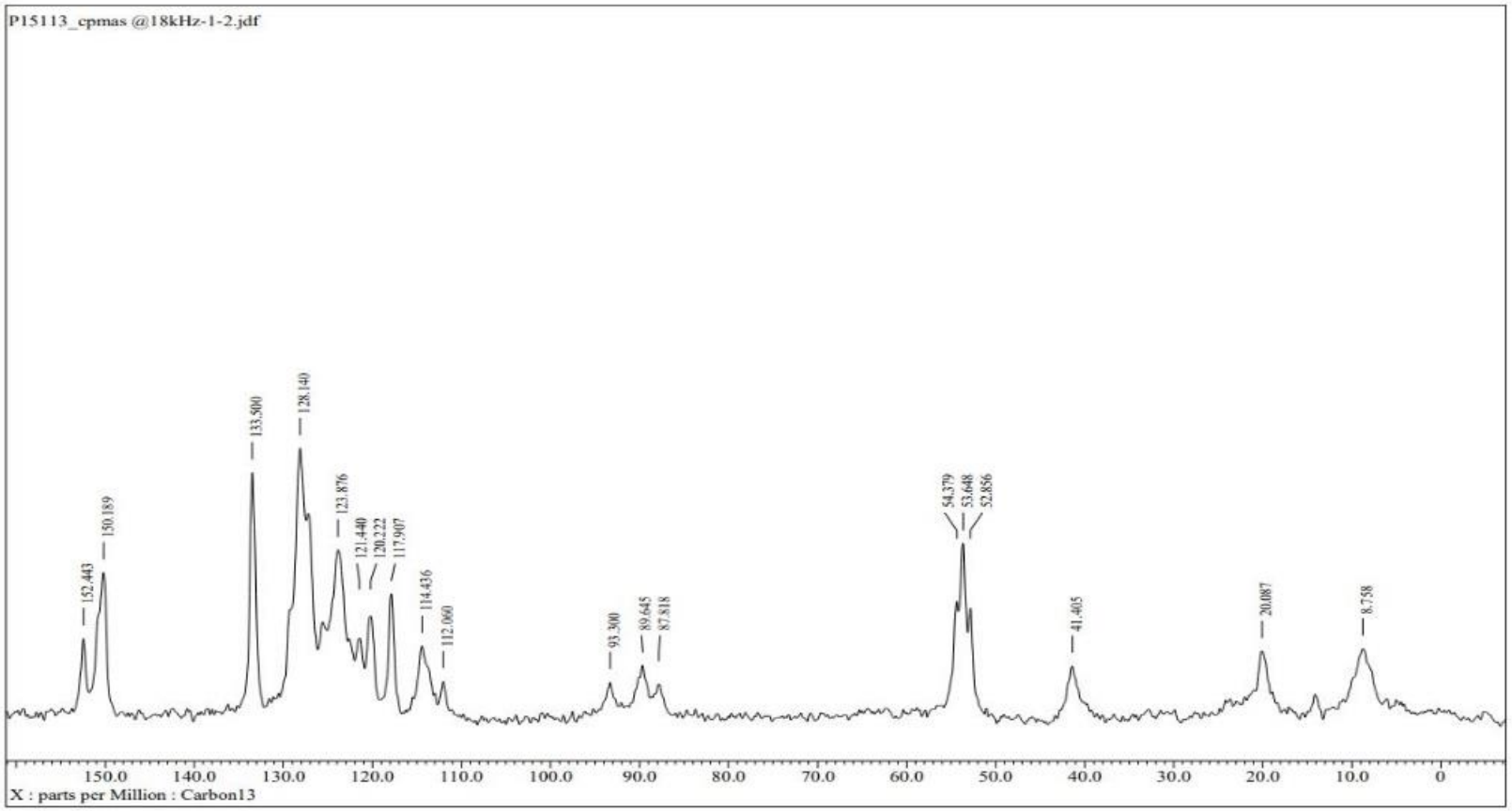


Fig. S5. ^{13}C CP MAS NMR spectra of Ru-BINOL-AP@MSNs.

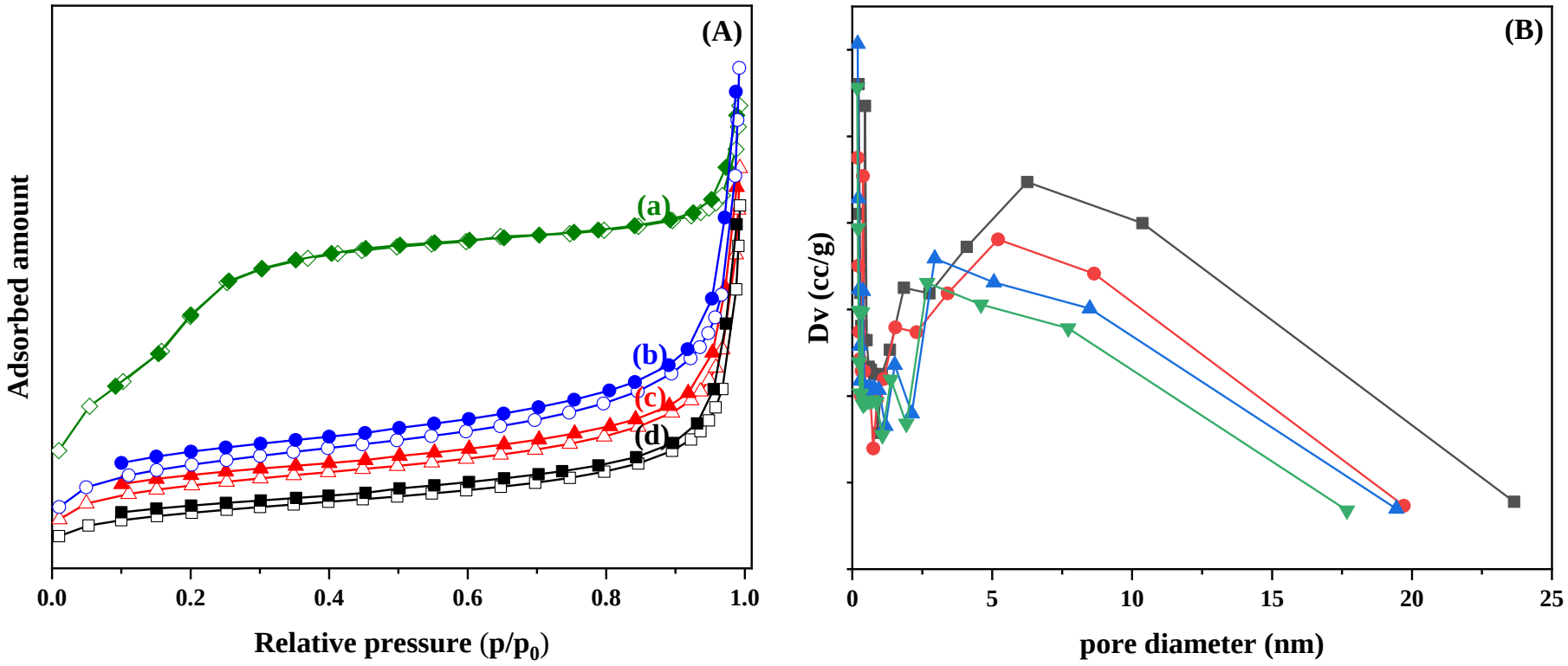


Fig. S6. (A) N_2 adsorption− desorption isotherms of (a) MSNs, (b) AP@MSNs, (c) BINOL-AP@MSNs and (d) Ru-BINOL-AP@MSNs. (B) BJH pore size distributions of (a) MSNs, (b) AP@MSNs, (c) BINOL-AP@MSNs and (d) Ru-BINOL-AP@MSNs.

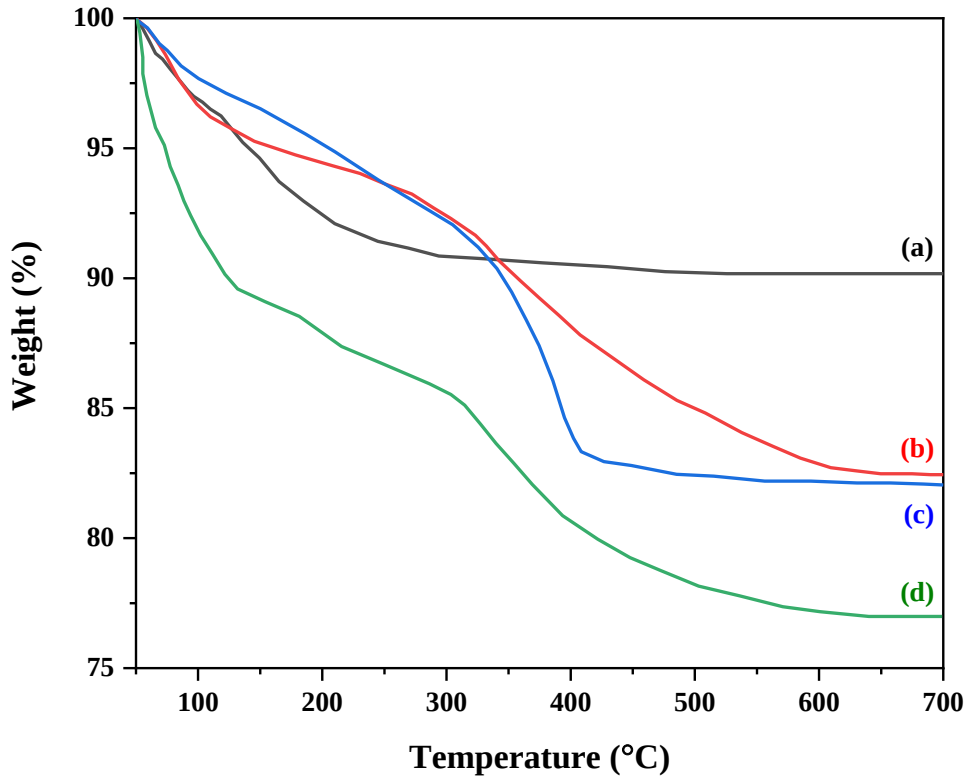


Fig. S7. TGA curves of (a) MSNs, (b) AP@MSNs, (c) BINOL-AP@MSNs and, (d) Ru-BINOL-AP@MSNs.

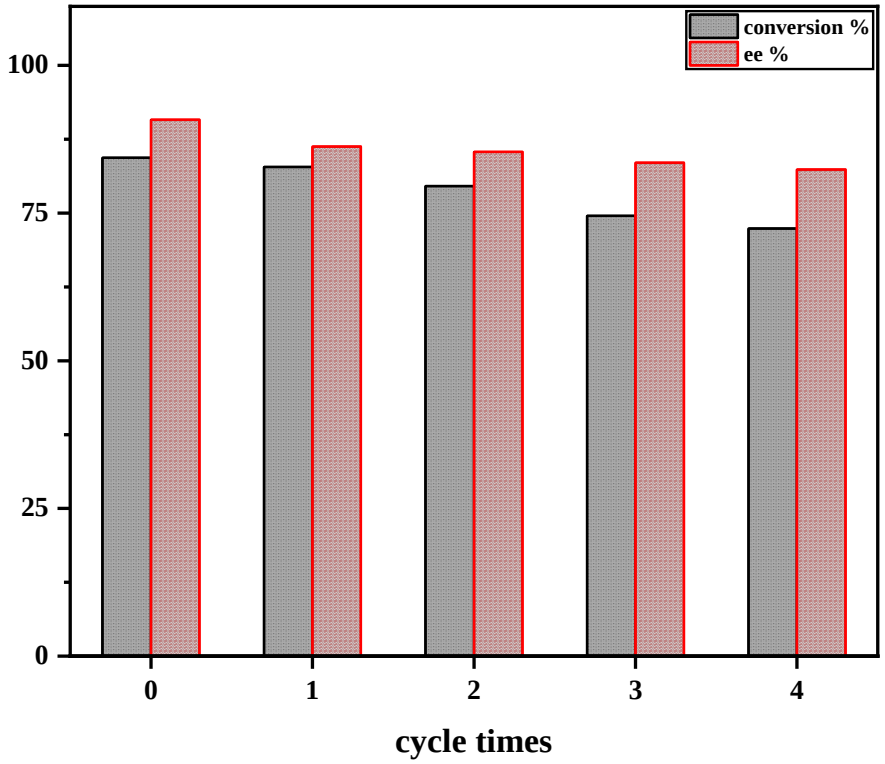


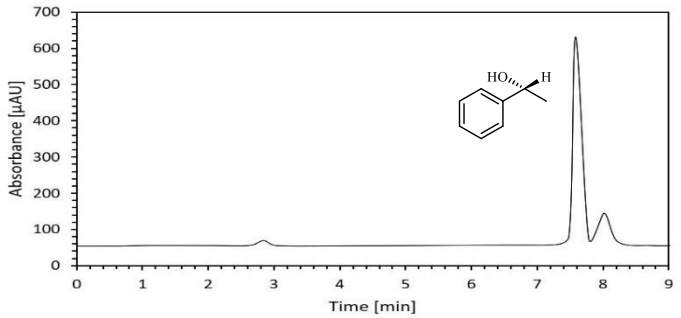
Fig. S8. Recyclability test of Ru-BINOL-AP@MSNs catalyst over asymmetric hydrogenation reaction.

5. Chromatographic data for Products

Column: Chiralpak OJ-H (250 x 4.6) mm, 20µ (make: Diacel), Mobile phase: (n-Hexane and isopropanol (80:20)), Flow rate: 1.0 mL/min, Detection: 280 nm.

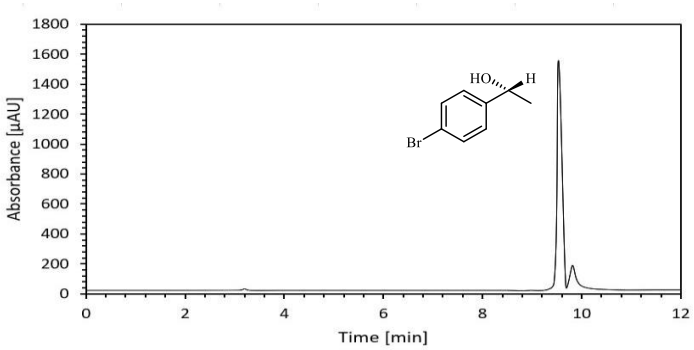
Enantiomeric excess (ee%) was calculated from the chromatographic data by the following equation:

$$(ee\%) = \left[\frac{peak\ area\ 1 - peak\ area\ 2}{peak\ area\ 1 + peak\ area\ 2}\right] \times 100$$



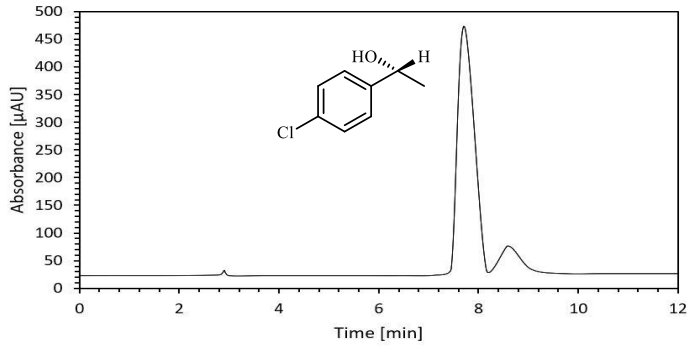
1st cycle of Ru-BINOL-AP@MSNs as a catalyst			
Peak	Ret. Time	Area	Area %
1	7.57	9549693	95.42
2	8.15	458726	4.58
Total		10008419	100

Fig. S9. Chiral HPLC spectra of the Acetophenone as a reactant.



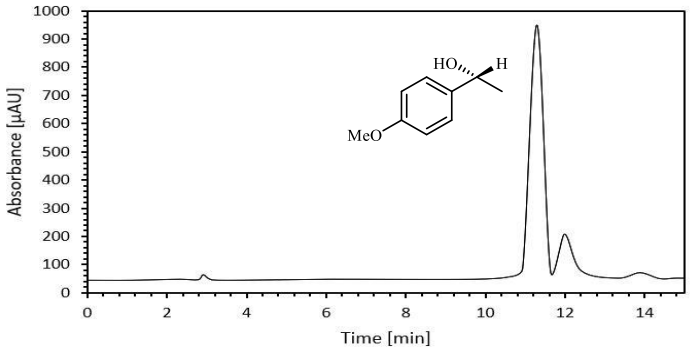
4-Br Acetophenone as a reactant			
Peak	Ret. Time	Area	Area %
1	9.53	10125974	95.96
2	9.81	426105	4.04
Total		10552079	100

Fig. S10. Chiral HPLC spectra of the 4-Br Acetophenone as a reactant.



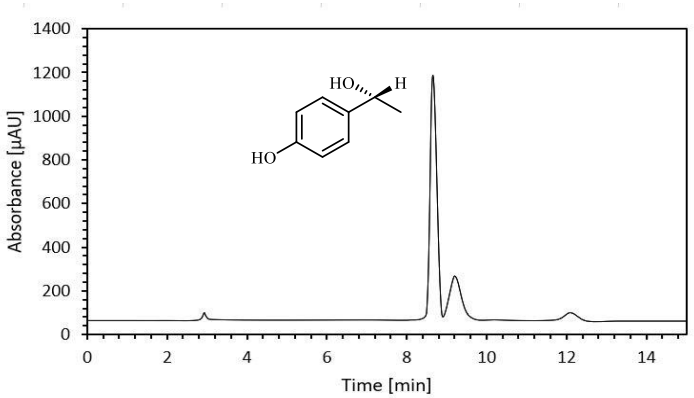
4-Cl Acetophenone as a reactant			
Peak	Ret. Time	Area	Area %
1	7.71	11896478	93.26
2	8.58	860247	6.74
Total		12756725	100

Fig. S11. Chiral HPLC spectra of the 4-Cl Acetophenone as a reactant.



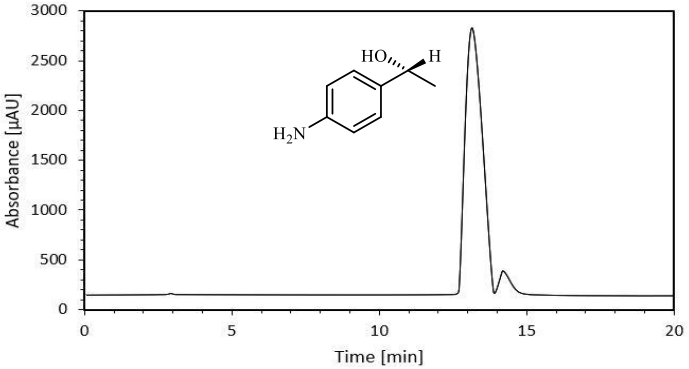
4-OMe Acetophenone as a reactant			
Peak	Ret. Time	Area	Area %
1	11.30	12015478	92.99
2	11.99	905147	7.01
Total		12920625	100

Fig. S12. Chiral HPLC spectra of the 4-OMe Acetophenone as a reactant.



4-OH Acetophenone as a reactant			
Peak	Ret. Time	Area	Area %
1	8.80	10255974	91.47
2	9.19	956188	8.53
Total		11212162	100

Fig. S13. Chiral HPLC spectra of the 4-OH Acetophenone as a reactant.



4-NH_2 Acetophenone as a reactant			
Peak	Ret. Time	Area	Area %
1	13.12	11257848	90.26
2	14.16	1214874	9.74
Total		12472722	100

Fig. S14. Chiral HPLC spectra of the 4-NH_2 Acetophenone as a reactant.

6. NMR and FTIR Spectra for Products

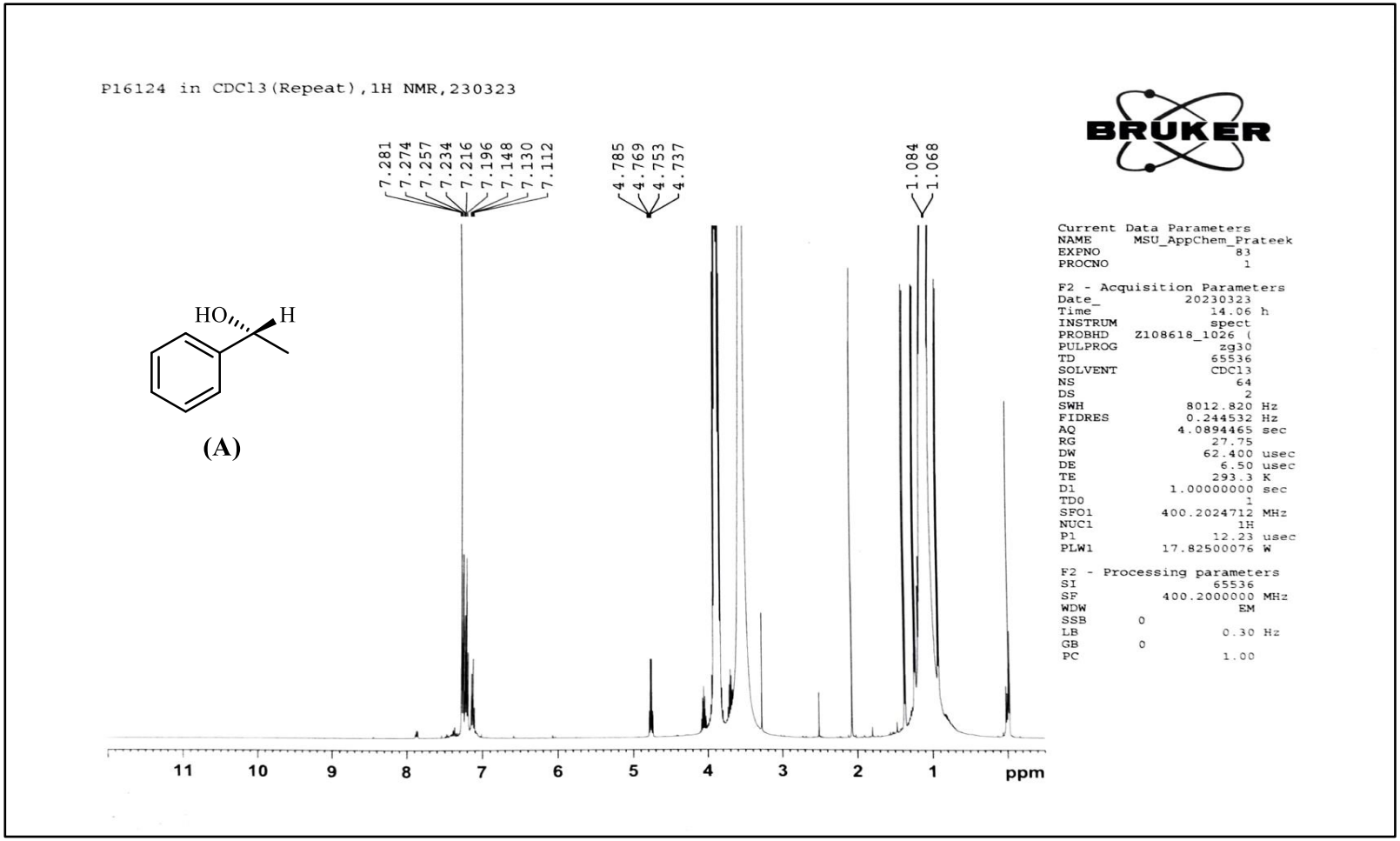


Fig. S15. ^{1}H NMR spectra of the product (A).

^{1}H NMR spectra of the product (A). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, ArH), 7.21 (m, ArH), 4.78 (m, -OH), 4.73(d, 1H), 1.08 (d, 3H).

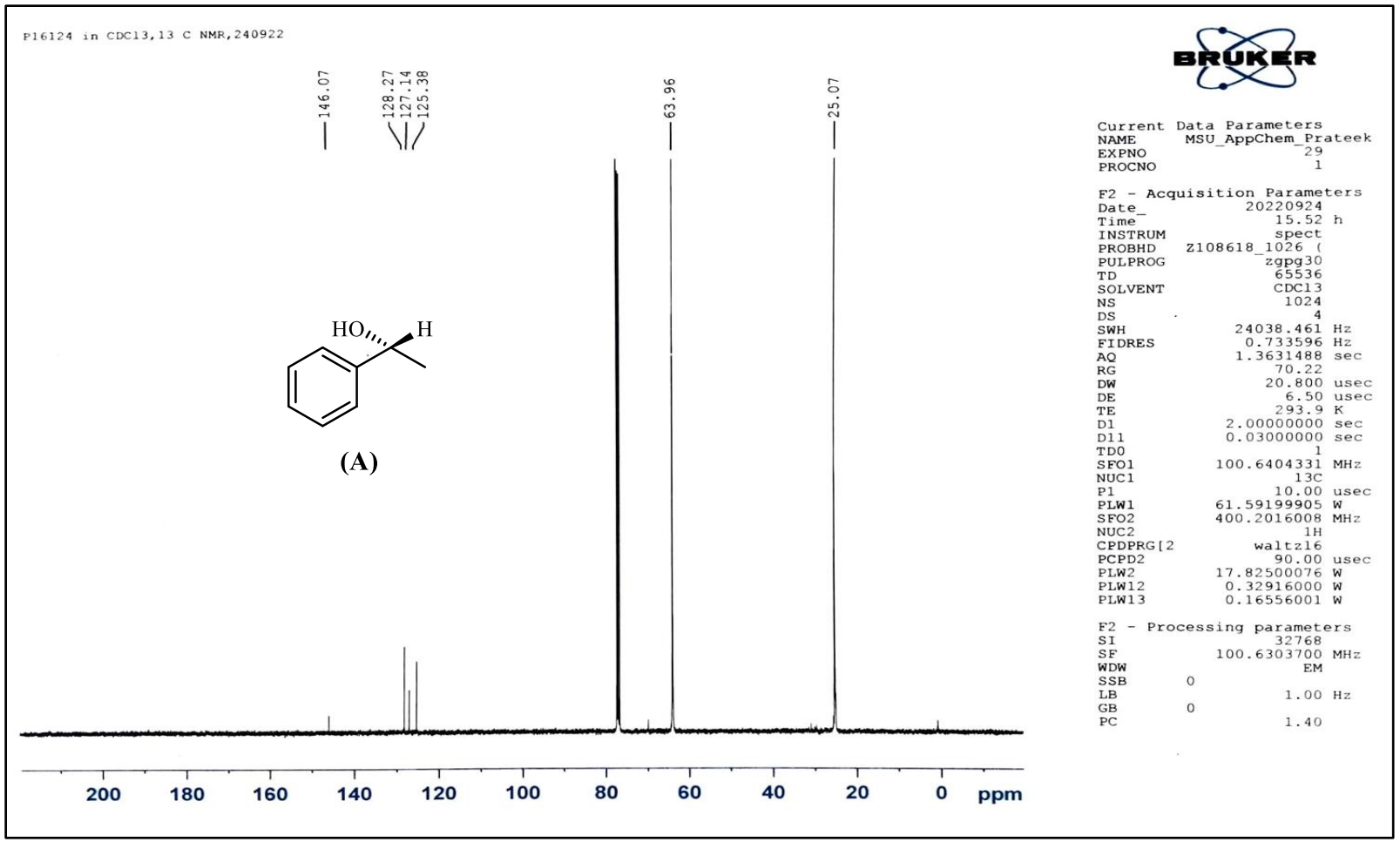


Fig. S16. ^{13}C NMR spectra of the product (A).

^{13}C NMR spectra of the product (A). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.04, 128.33, 127.22 125.39, 70.02 and 25.16.

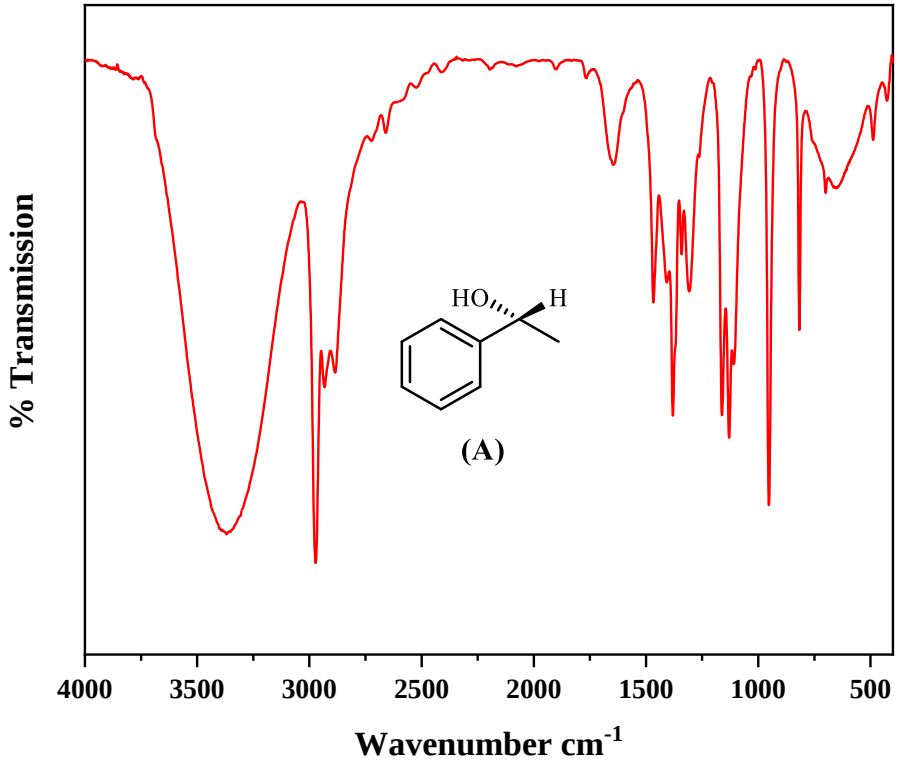


Fig. S17. FTIR spectra of the product (A)

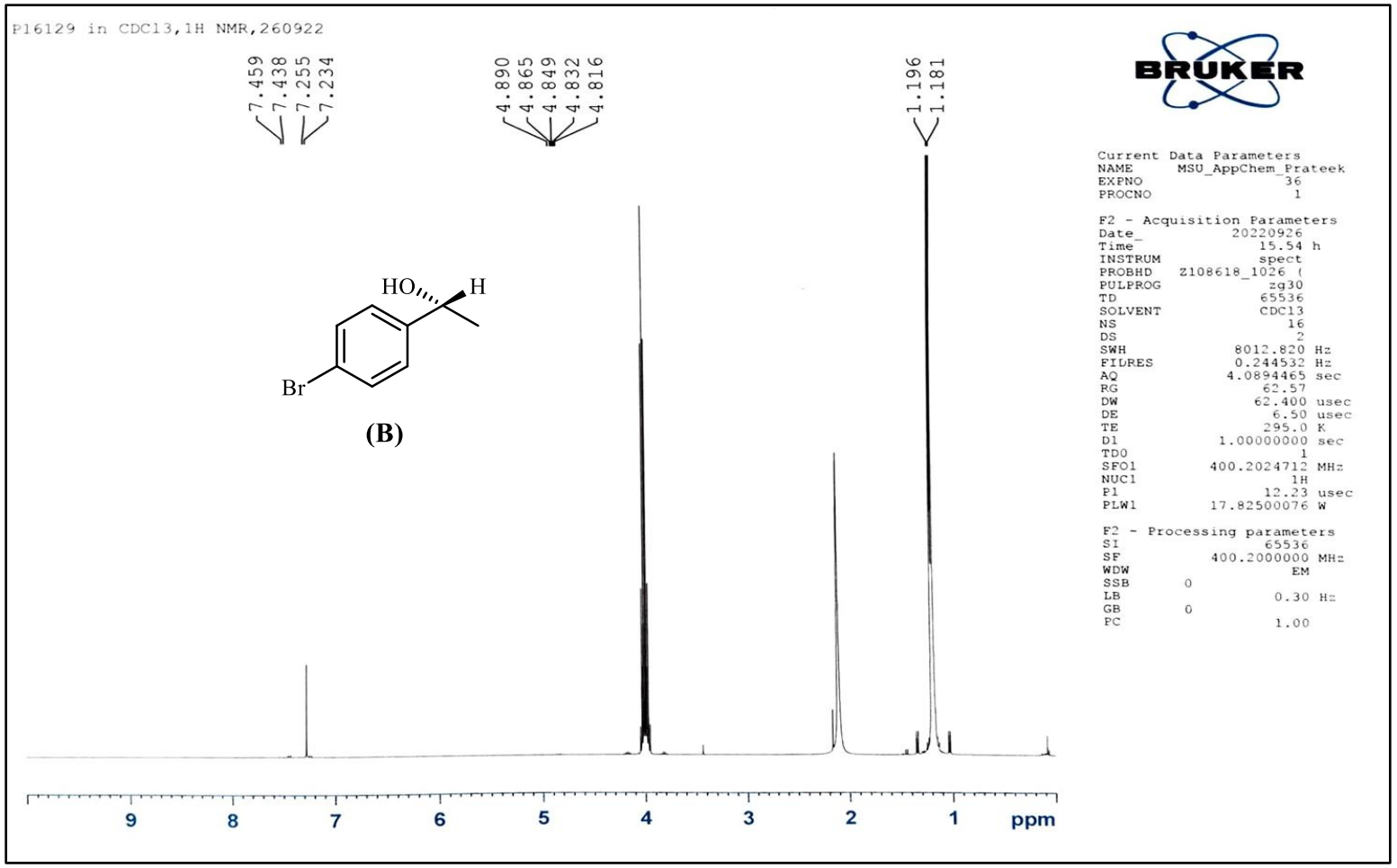


Fig. S18. ^{1}H NMR spectra of the product (B).

^{1}H NMR spectra of the product (B). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, ArH), 7.25 (m, ArH), 4.89 (m, -OH), 4.83(d, 1H), 1.19 (d, 3H).

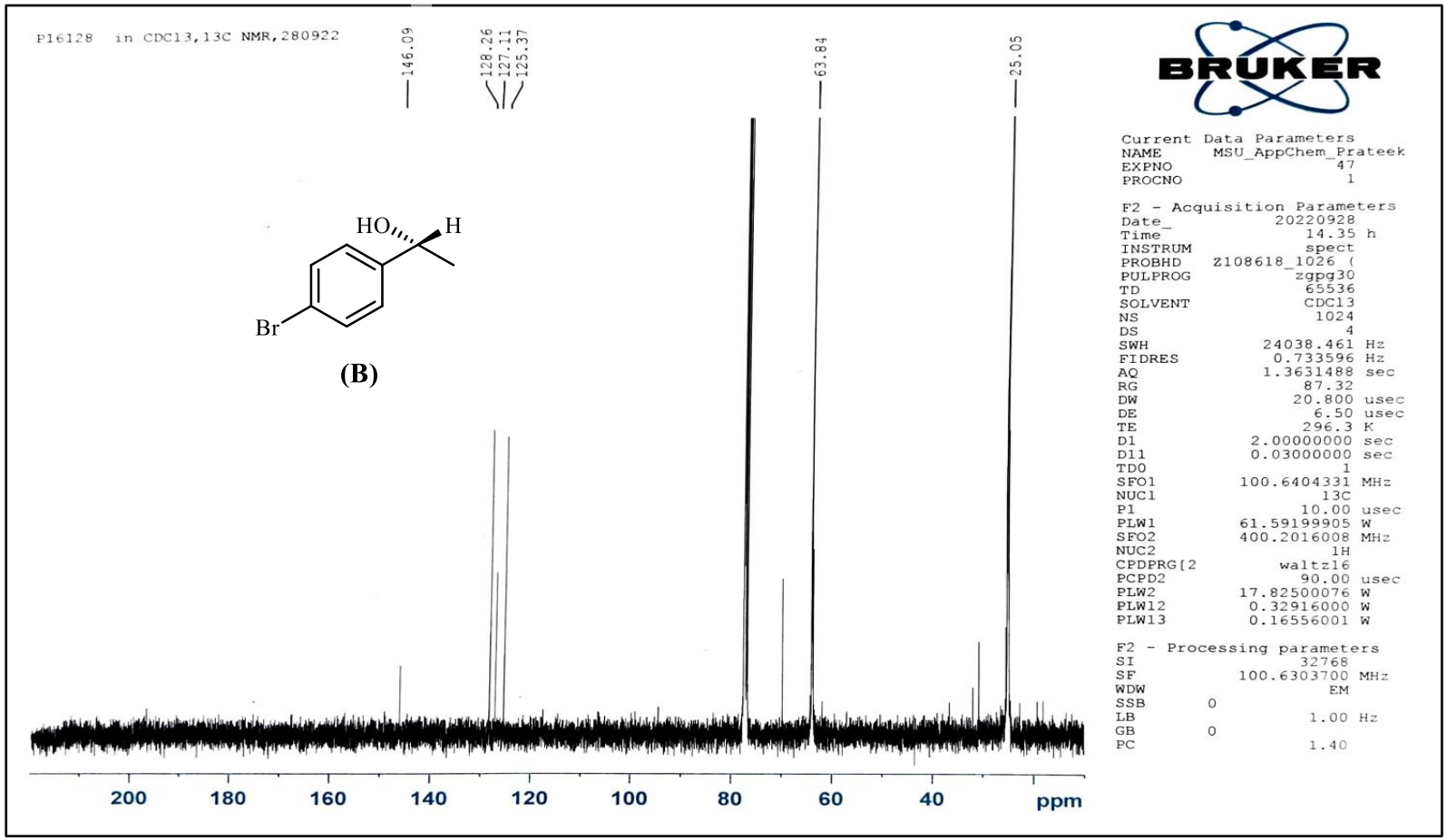


Fig. S19. ^{13}C NMR spectra of the product (B).

^{13}C NMR spectra of the product (B). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 146.09, 128.26, 127.11, 125.37, 63.84 and 25.05.

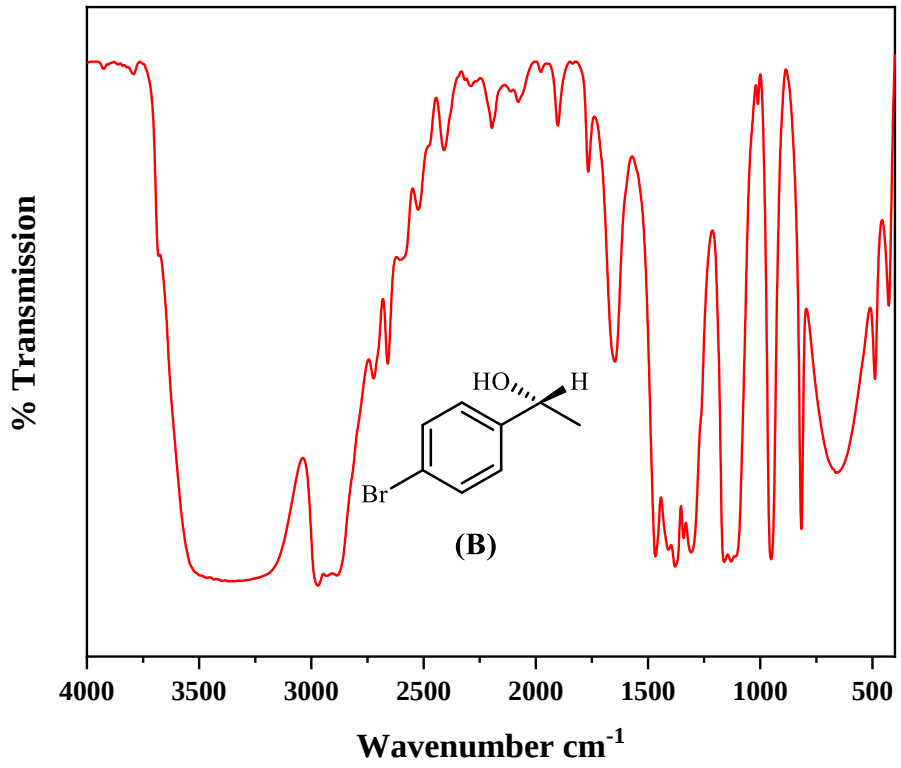


Fig. S20. FTIR spectra of the product (B).

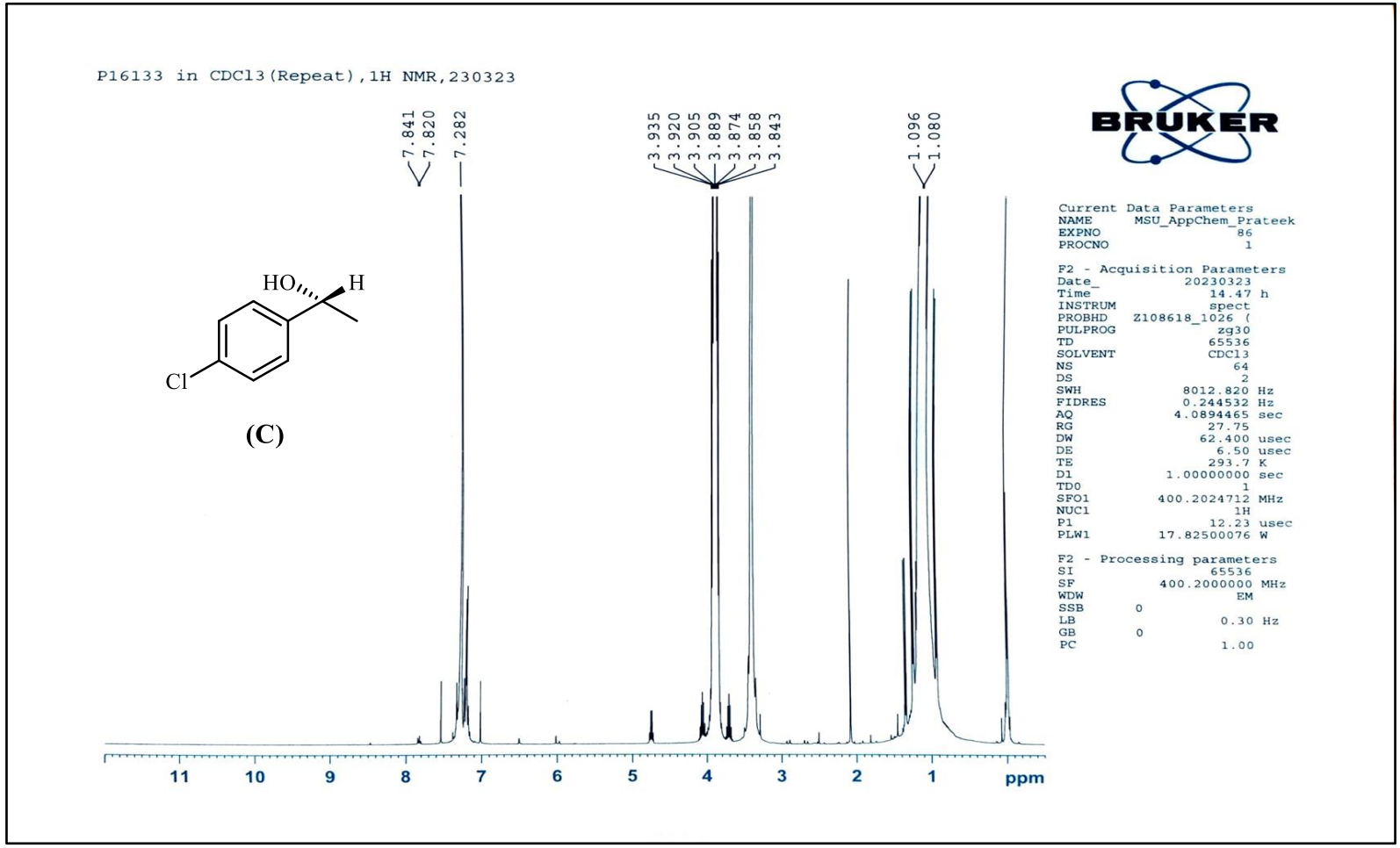


Fig. S21. ^{1}H NMR spectra of the product (C).

^{1}H NMR spectra of the product (C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 (m, ArH), 7.28 (m, ArH), 3.93 (m, -OH), 3.90 (d, 1H), 1.09 (d, 3H).

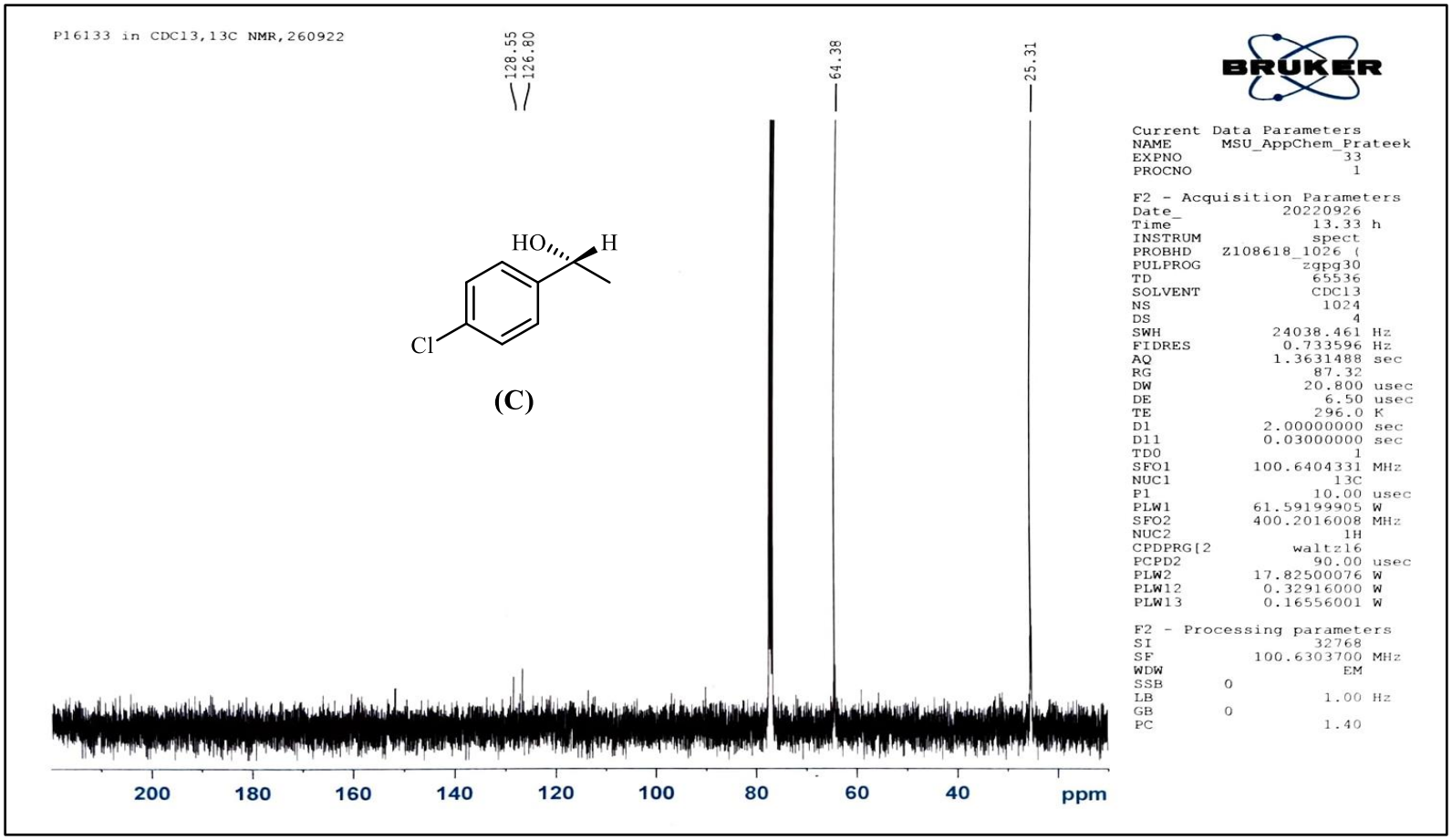


Fig. S22. ^{13}C NMR spectra of the product (C).

^{13}C NMR spectra of the product (C). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 144.2, 133.2, 128.55, 126.80, 64.38, 25.31

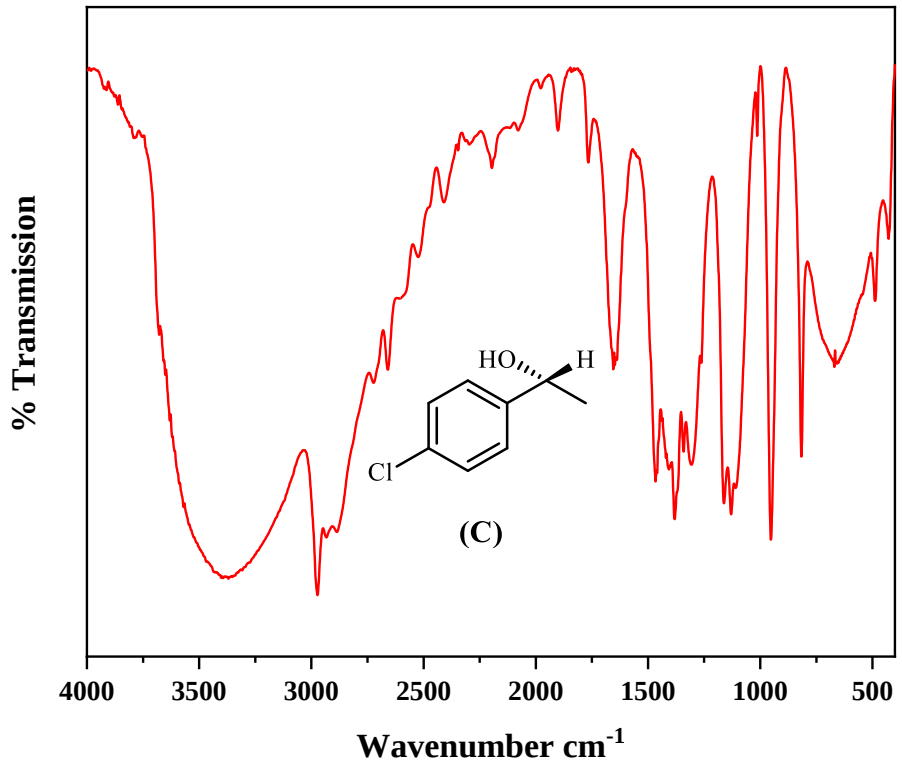


Fig. S23. FTIR spectra of the product (C).

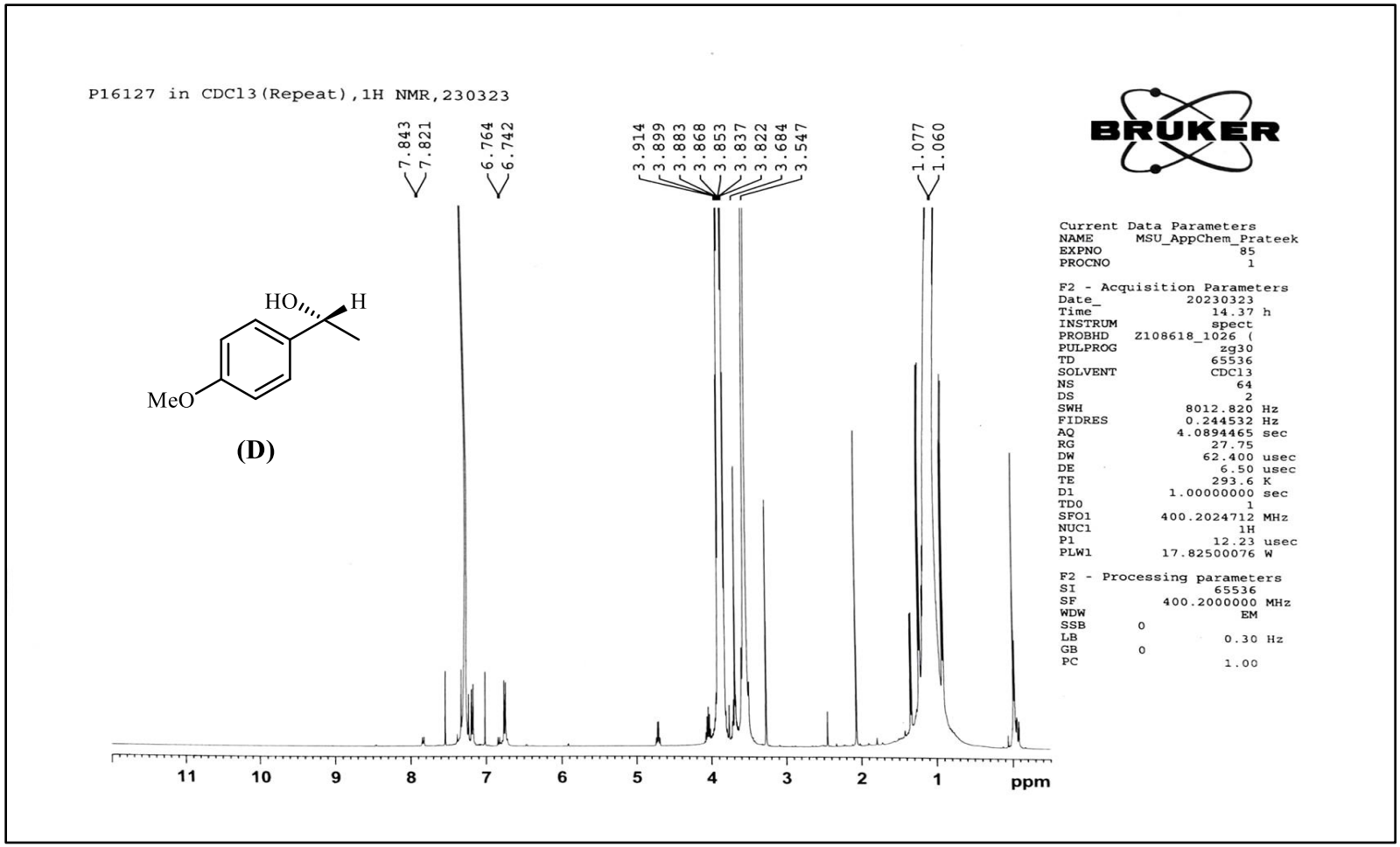


Fig. S24. ^{1}H NMR spectra of the product (D).

^{1}H NMR spectra of the product (D). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 (m, ArH), 6.76 (m, ArH), 3.91 (m, -OH), 3.88 (d, 1H), 3.54 (s, -OCH_3), 1.07 (d, 3H).

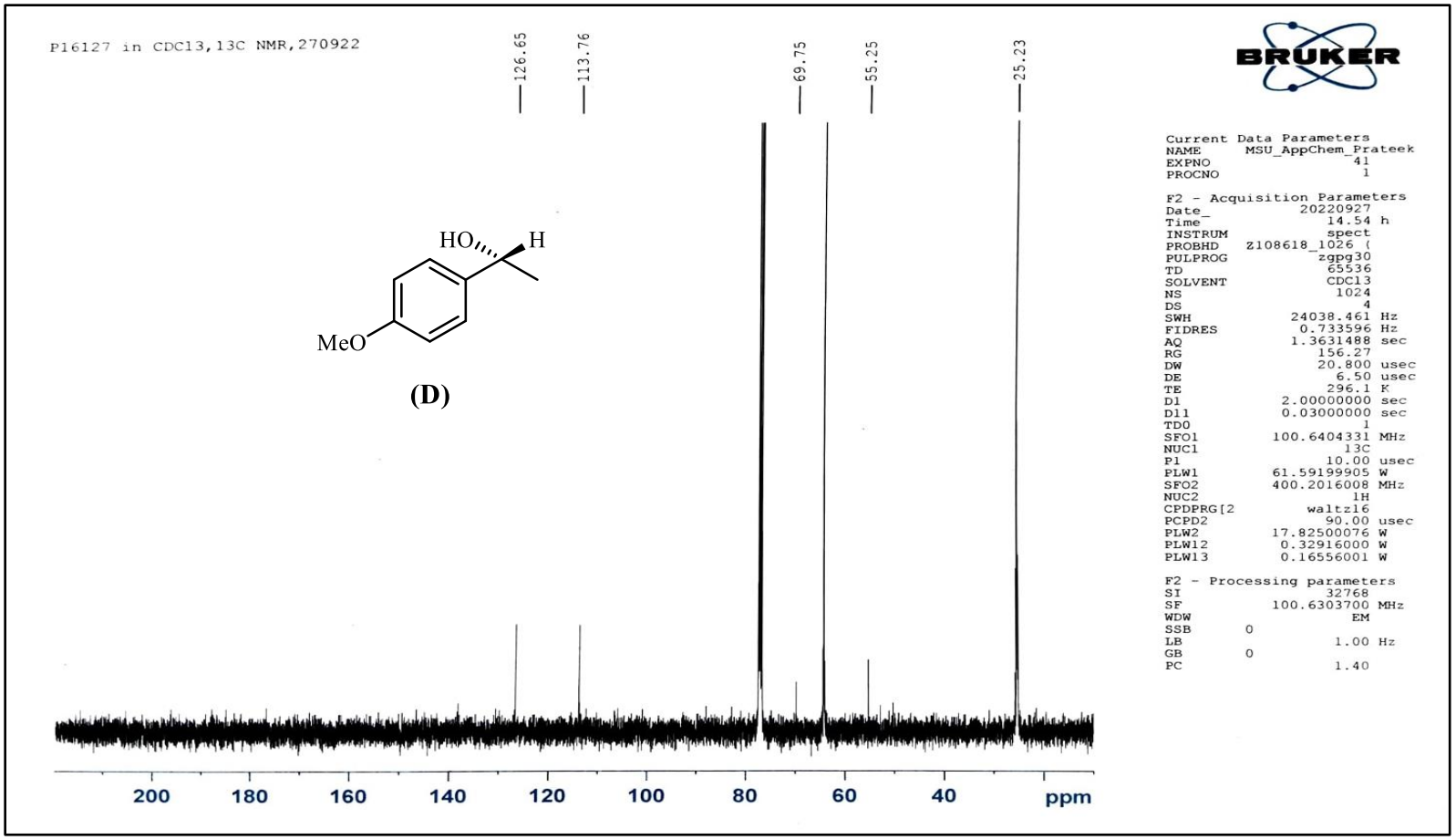


Fig. S25. ^{13}C NMR spectra of the product (D).

^{13}C NMR spectra of the product (D). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 126.65, 113.76, 69.75, 55.25, 25.23.

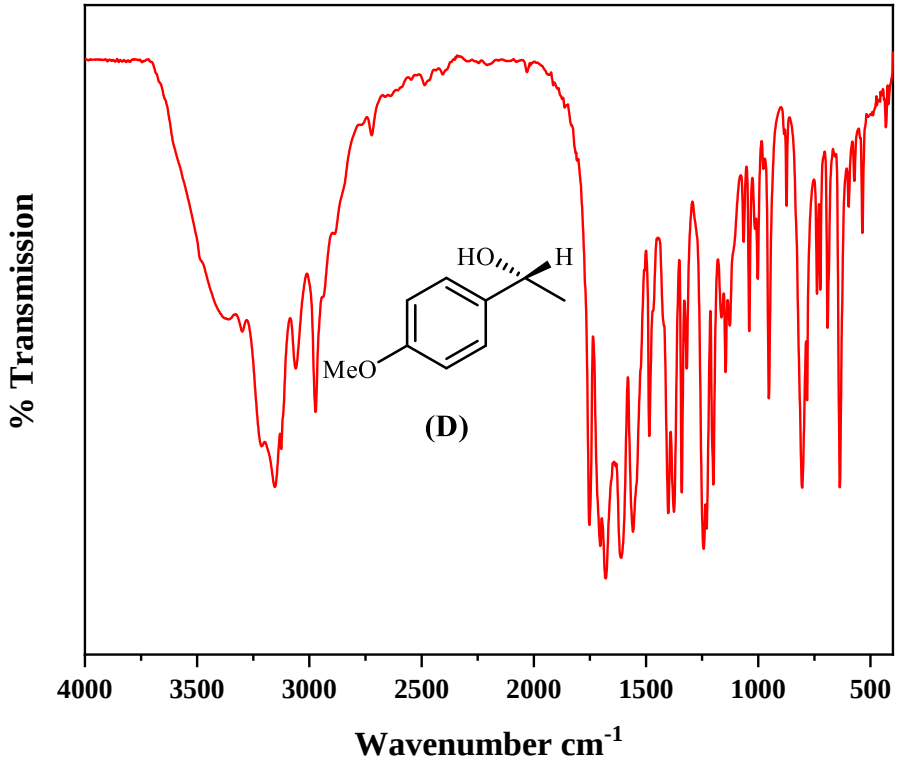


Fig. S26. FTIR spectra of the product (D).

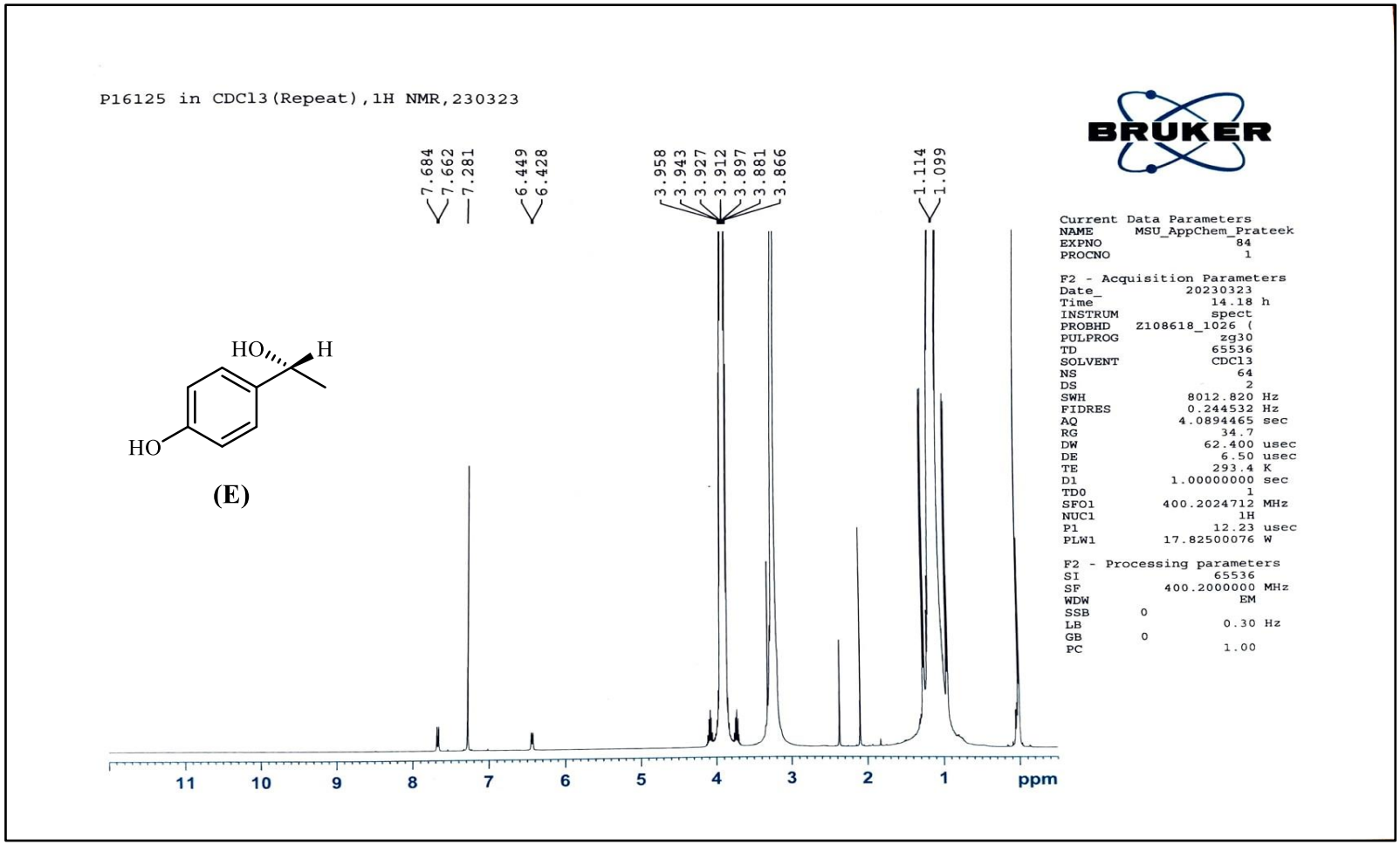


Fig. S27. ^{1}H NMR spectra of the product (E).

^{1}H NMR spectra of the product (E). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.68 (s, (P)-OH), 7.28 (m, ArH), 6.44 (m, ArH), 3.95 (m, -OH), 3.91 (d, 1H), 1.11 (d, 3H).

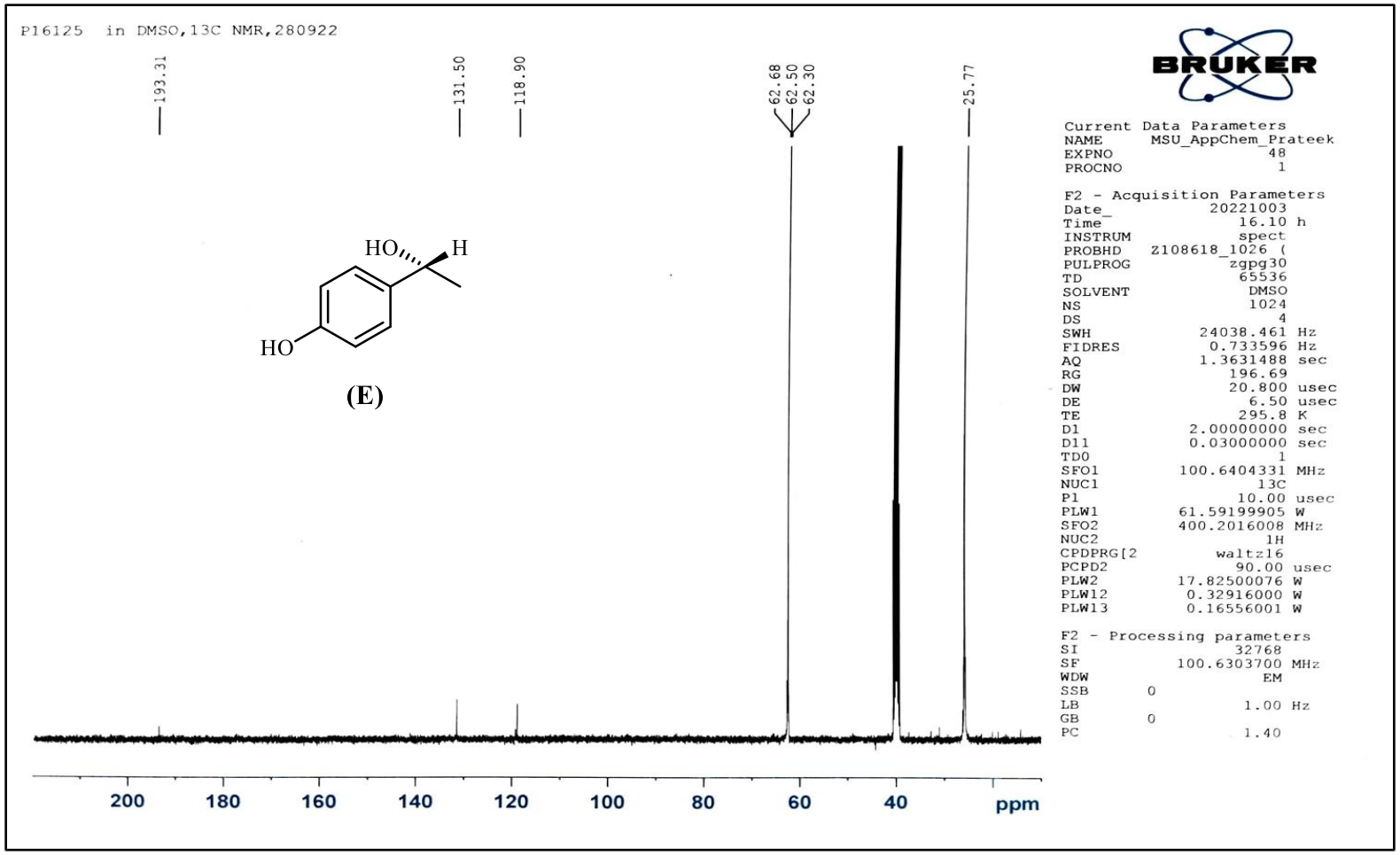


Fig. S28. ^{13}C NMR spectra of the product (E).

^{13}C NMR spectra of the product (E). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 193.31, 131.50, 118.90, 62.50, 25.8.

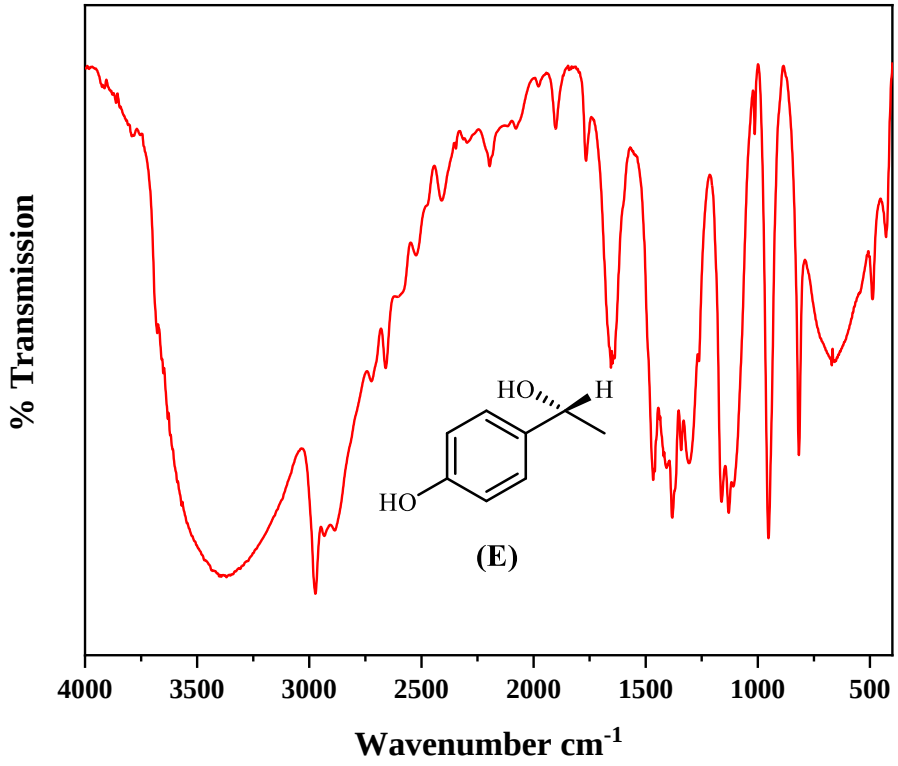


Fig. S29. FTIR spectra of the product (E).

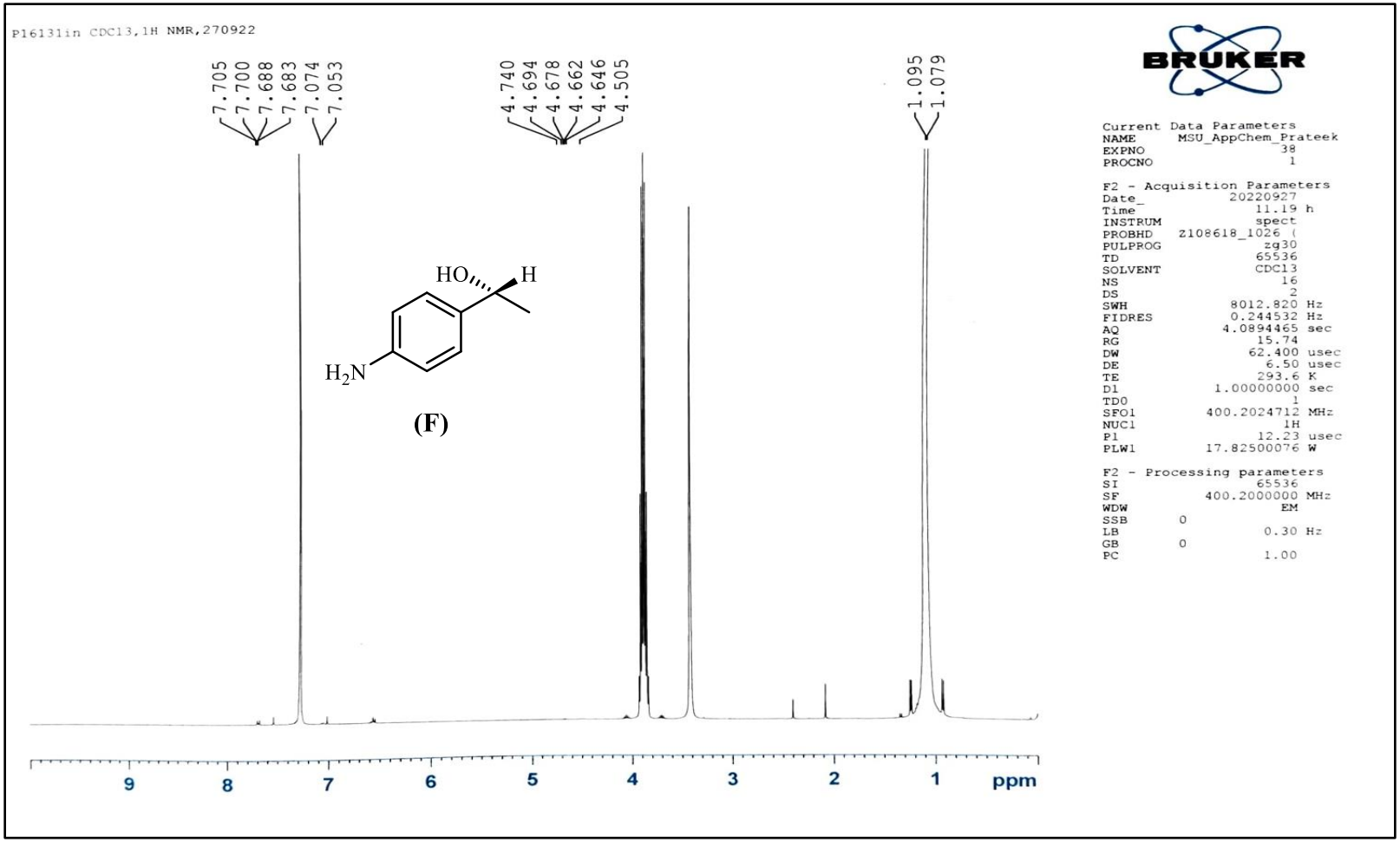


Fig. S30. ^{1}H NMR spectra of the product (F).

^{1}H NMR spectra of the product (F). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.70 (m, ArH), 7.07 (m, ArH), 4.74 (m, -OH), 4.66 (s, -NH_2), 4.50 (d, 1H), 1.09 (d, 3H).

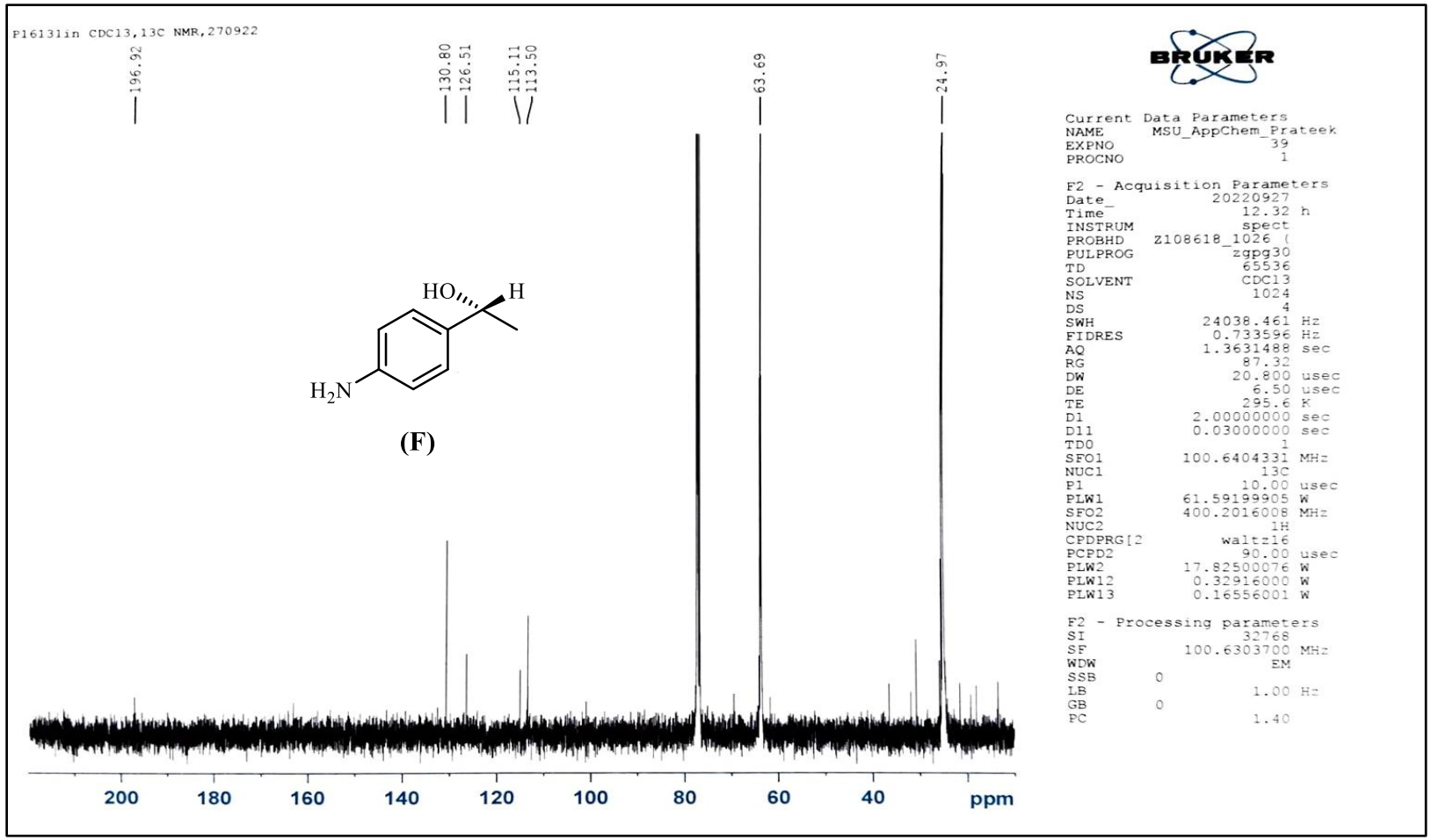


Fig. S31. ^{13}C NMR spectra of the product (F).

^{13}C NMR spectra of the product (F). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 196.92, 130.80, 126.51, 115.11, 63.69, 24.97.

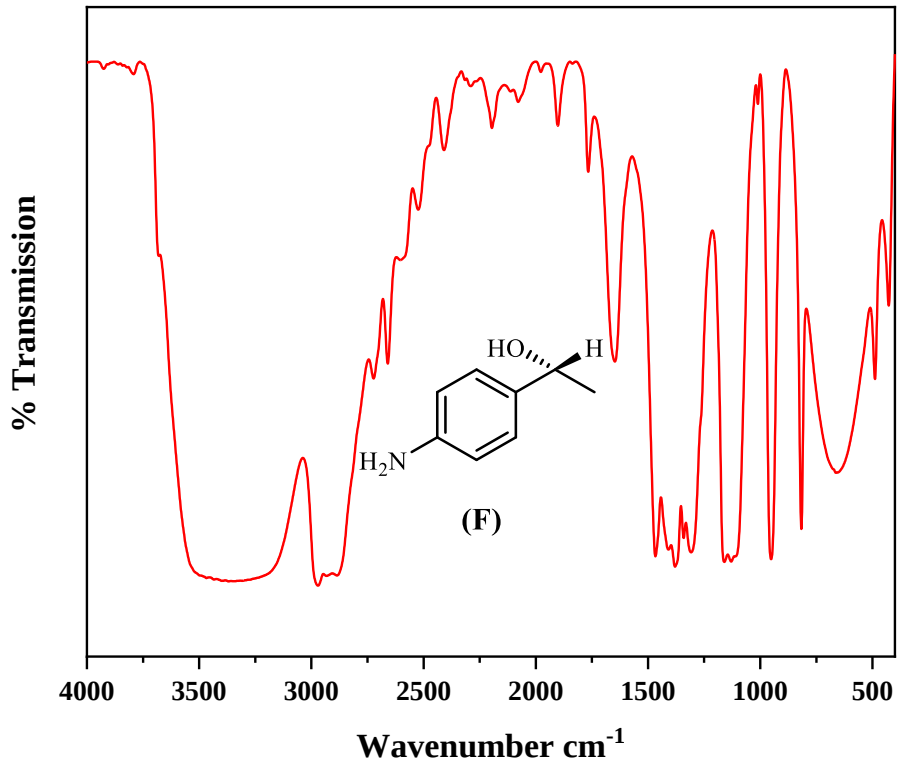


Fig. S32. FTIR spectra of the product (F).