

[Supporting Information]

Dual-functional click-triazole: a metal chelator and immobilization linker for the construction of heterogeneous palladium catalyst and its application for aerobic oxidation of alcohols

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General Experimental

All reagents were purchased from commercial suppliers and used without purification unless otherwise stated. Anhydrous *N,N*-Dimethylformamide (DMF), acetonitrile (CH₃CN) were distilled from calcium hydride (CaH₂). Anhydrous toluene was dried from sodium. Pluronic P123 (average $M_r \cong 5800$) were purchased from Sigma-Adrich Company. Palladium (II) acetate was purchased from Acros Organics. Column chromatography was performed with silica gel (300-400 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). GC-MS analysis of determination of selectivity was performed on the instrument of Agilent 7890 GC-QQQ. NMR spectra were recorded on Bruker AVANCE III 500MHz instrument with TMS as internal standard. Coupling constants were reported in Hertz (Hz). FT-IR spectra were recorded on Nicolet 6700 FT-IR spectrometer by mixing the solid with KBr. UV-Vis spectra was recorded on SHIMADZU, UV-2450 spectrophotometer using BaSO₄ as the reference. The content of palladium was measured by inductively coupled plasma mass spectrometry (ICP-MS) on PerkinElmer Elan DRC-e ICP-MS. Elemental analysis of the solids was determined by chemical combustion using Flash EA 1112. The microstructure observation was carried out with a Tecnai G2 F30 S-Twin analytical transmission electron microscope (TEM) operating at 300 kV. X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert PRO powder diffractometer equipped with a X'Celerator detector using Cu K α radiation ($\lambda = 0.1541$ nm). The working voltage of the instrument was 40 kV and the working current was 40 mA. The patterns were collected with a 2θ range from 0.5 to 6° and a scanning rate of 0.01° s⁻¹. Nitrogen sorption isotherms were determined at 77 K on a Quantachrome autosorb iQ system in static measurement mode. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. The samples were out-gassed at 473 K for 10 h prior to sorption measurements.

Caution: Sodium azide is potentially explosive. Great care is needed when treating this compound.

Experimental Sections

a) Synthesis and characterization of PdL_n@SBA-15

Synthesis of SBA-15:¹ The SBA-15 has been synthesized following the procedure reported by Zhao *et al.* Pluronic P123 (4.0 g, average $M_r = 5800$) was dissolved in water (30.0 mL) and 2 M HCl solution (120.0 mL) with stirring at 40 °C for 1 h. Then 8.50 g of tetraethoxysilane (TEOS) was added and the mixture was stirred at 40 °C for 20 h. The obtained gel was then loaded in a polypropylene bottle, sealed using teflon tape and kept at 373 K for 48 h under static conditions. Then the bottle was removed from the oven, and was allowed to cool to ambient temperature. The contents were then filtered and the residue was washed thoroughly with water until the pH of the water became neutral. After the white solid was dried, it was then underwent a calcination process at 773 K for 16 h in air with a slow heating rate of 1 °C/min. The SBA-15 was obtained as a white powder.

Synthesis of Azide@SBA-15:² To a 500 mL three-necked round-bottom flask, 3-chloropropyltriethoxysilane (16.000 g, 66.4 mmol) was added to a solution of NaN₃ (6.480 g, 1.5 equiv. 99.6 mmol) and tetrabutylammonium bromide (TBAB, 0.2 equiv., 4.280 g, 13.3 mmol) in dry acetonitrile (200.0 mL) under nitrogen atmosphere. Under nitrogen atmosphere the reaction mixture was stirred under reflux for 24 h. After the reaction, the solvent was removed under reduced pressure. The crude mixture was then diluted in Et₂O (60 ml) and the suspension was filtered and washed with Et₂O (2×20 mL). The combined solvent was removed and the product 3-azidopropyltriethoxysilane was obtained as a pure and colorless liquid. Yield: 13.321 g, 81%. ¹H NMR (500 MHz, CDCl₃): δ 0.65-0.69 (m, 2H), 1.22 (t, *J* = 6.8 Hz, 9H), 1.68-1.74 (m, 2H), 3.26 (t, *J* = 7.0 Hz, 2H), 3.80-3.84 (q, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 5.0, 15.7, 20.1, 51.2, 55.9. FT-IR (KBr, cm⁻¹): 2976, 2929, 2887, 2737, 2098, 1444, 1390, 1344, 1104, 958, 789, 490. The resulting 3-azidopropyltriethoxysilane (0.742 g, 3.0 mmol) was allowed to react with SBA-15 (6.0 g) in refluxing dry toluene (200.0 mL) under nitrogen for 24 h. After the mixture was cool to ambient temperature, it was filtered off, washed thoroughly with toluene and acetone and dry at 60 °C under vacuum. Yield: 6.285 g. The loading of azide group determined by Elemental Analysis (EA) was 0.239 mmol/g. According to FT-IR spectra, the absorption band at 2112 cm⁻¹ clearly indicates the successful attachment of azide group onto the surface of SBA-15 (Figure S1).

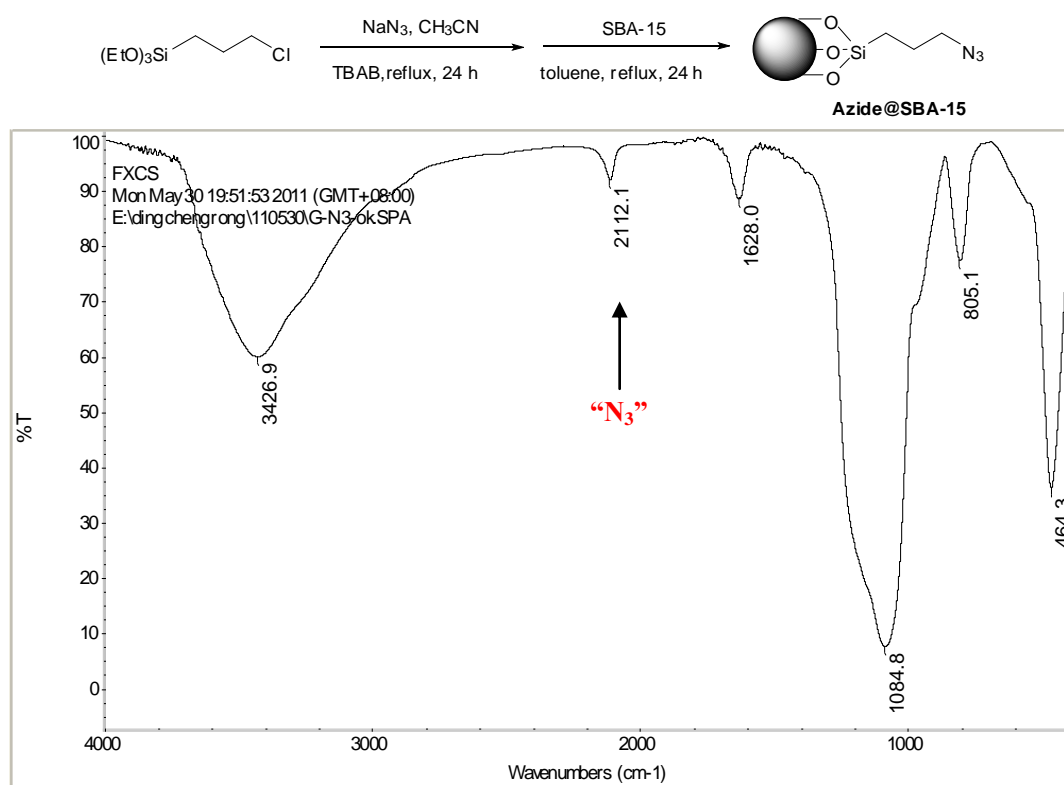


Fig. S1 FT-IR spectra of Azide@SBA-15.

Synthesis of PdL_n@SBA-15:⁴ A mixture of CuSO₄·5H₂O (0.013 g, 0.05 mmol), NaAsc (0.033 g, 0.17 mmol), 2-ethynylpyridine (0.103 g, 1.0 mmol), Azide@SBA-15 (3.000 g), 80.0 mL methanol and 80.0 mL water were placed in a 250 mL round-bottom flask. The mixture was stirred at room temperature for 72 h. After completion, the residue was filtered, washed twice with methanol, water, disodium edetate ehydrate (10 wt% solution in water), water and acetone. The solid was obtained after dried at 60 °C under vacuum. Notably, the absorption band at 2112 cm⁻¹ was disappeared which implied that the “click” process was completed and the “2,2’-bipyridine analogue” ligand has anchored onto the SBA-15 (Figure S2). The loading of “2,2’-bipyridine analogue” group determined by Elemental Analysis (EA) was 0.22 mmol/g. The catalyst was prepared by stirring a mixture of L_n@SBA-15 (2.000 g) and palladium acetate (0.3 mmol, 0.068 g) in toluene (80.0 mL) at room temperature for 2 h. The supernant of the mixture was clear after the coordination, indicating that the palladium has completely grafted on SBA-15. The solid was filtered, washed thoroughly with large volume of toluene, acetone in order to remove any adsorbed palladium on the surface and finally dried at 60 °C under vacuum. Yield: 2.024 g. The amount of palladium in the catalyst analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-MS) was 0.138 mmol/g.

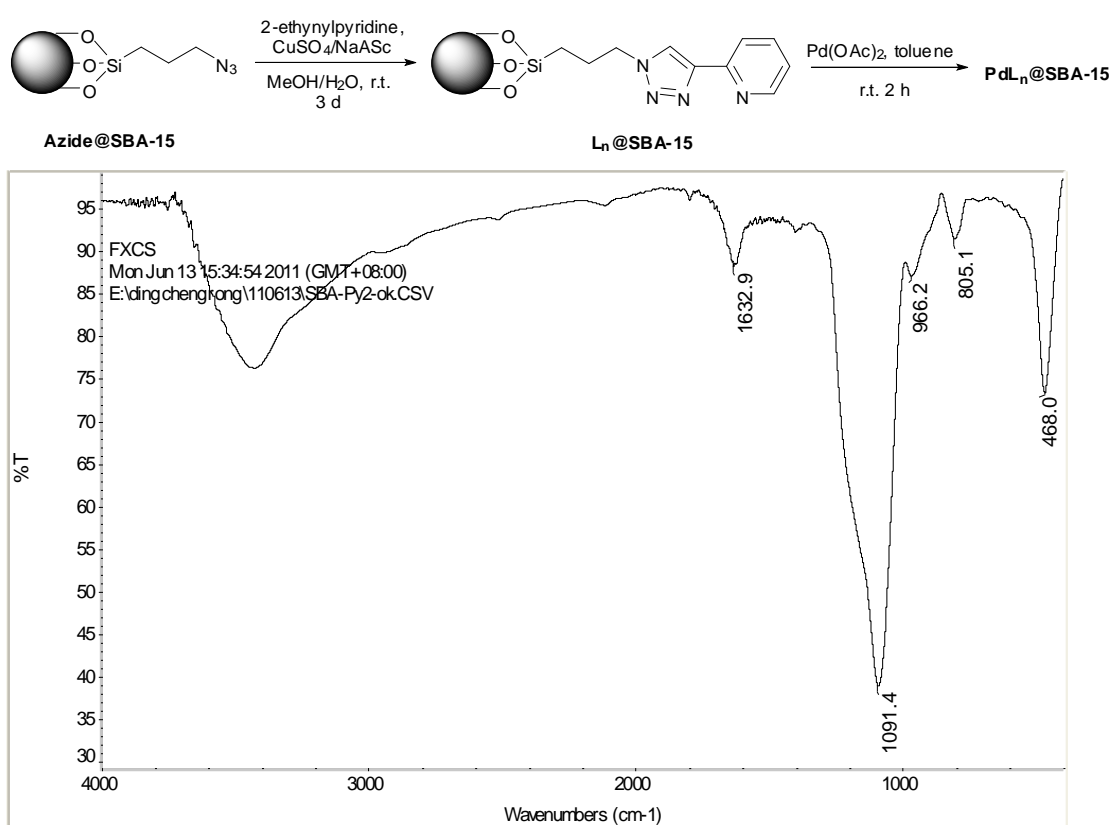


Fig. S2 FT-IR spectra of Ln@SBA-15

b) Synthesis and characterization of 1-methyl-4-(2'-pyridyl)-1,2,3-triazole (L'_n) and corresponding $PdL'_n(OAc)_2$

Synthesis of 1-methyl-4-(2'-pyridyl)-1,2,3-triazole (L'_n):⁵ Into a flame-dried 100 mL three-necked round-bottom flask, NaN_3 (0.198 g, 3 mmol) was added together with deoxygenated dry DMF (30.0 mL). Then CH_3I (0.3 mL, 4.8 mmol) in 10.0 mL DMF was added dropwise and the solution was stirred in the dark overnight. Considering of the highly explosive methyl-azide, the intermediate was not isolated. So after the reaction, the 2-ethynylpyridine (0.412 g, 4 mmol) was added under N_2 flow, followed by 8 mL copper catalyst solution, which was prepared by dissolving CuI (0.571 g, 3.0 mmol) and $PMDTA$ (0.7 mL, 3.3 mmol) in oxygen-free dry DMF (10.0 mL), bubbling nitrogen through the solution for 30 min to prevent oxidation of $Cu(I)$. The 'clicking' process was taken in the dark at room temperature under nitrogen atmosphere for 48 hours to ensure the completed consumption of CH_3N_3 . After the reaction, the obtained mixture was diluted in ice-water (400.0 mL) and extracted with CH_2Cl_2 for 3 times. The combined organic phase was washed with brine, dried over anhydrate Na_2SO_4 and concentrated to give the crude product, which was further purified by column chromatography ($Et_2O/Hexane$ 4/1) to give the product L'_n as a white solid (0.327 g, 68%). 1H NMR (500 MHz, d^6 -DMSO): δ 4.12 (s, 3H), 7.33-7.35 (m, 1H), 7.87-7.91 (m, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 8.85 (s, 1H), 8.59-8.61 (m, 1H). ^{13}C NMR (125 MHz, d^6 -DMSO): δ 36.2, 119.3, 122.8, 124.0, 137.2, 147.2, 149.6, 150.0.

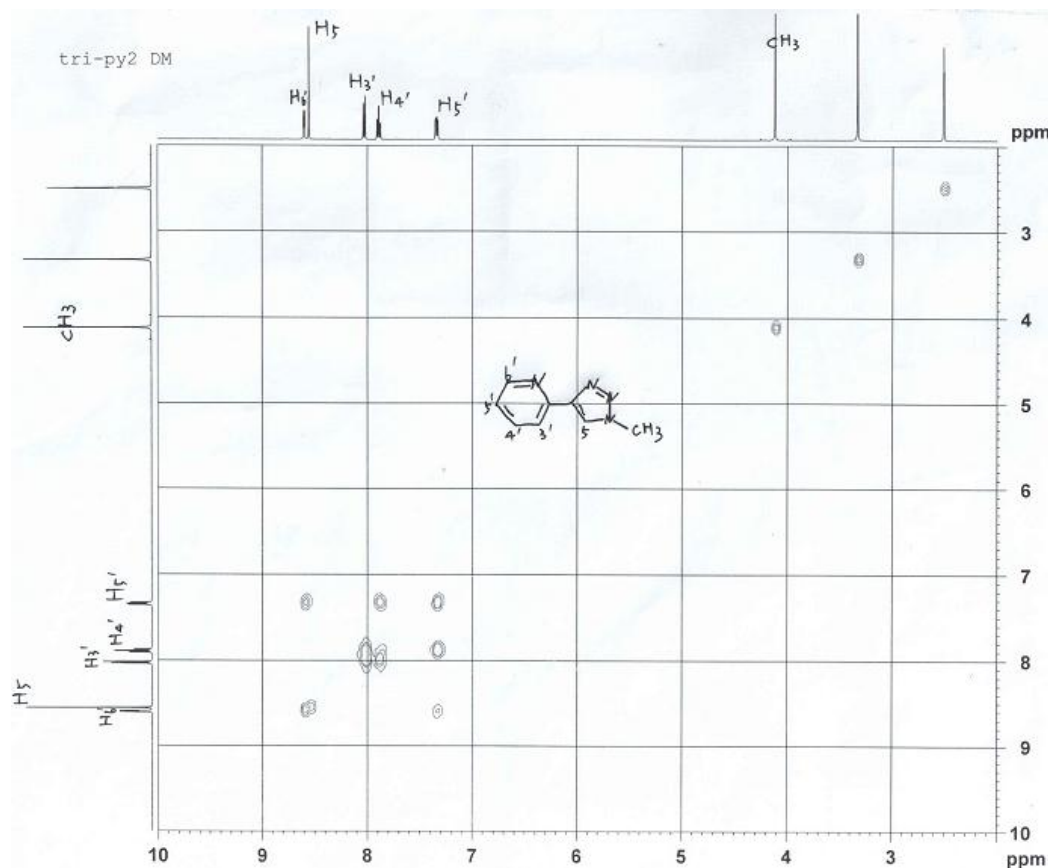


Fig. S3 H,H-COSY NMR spectrum of L'_n (500 MHz, d^6 -DMSO, 298K)

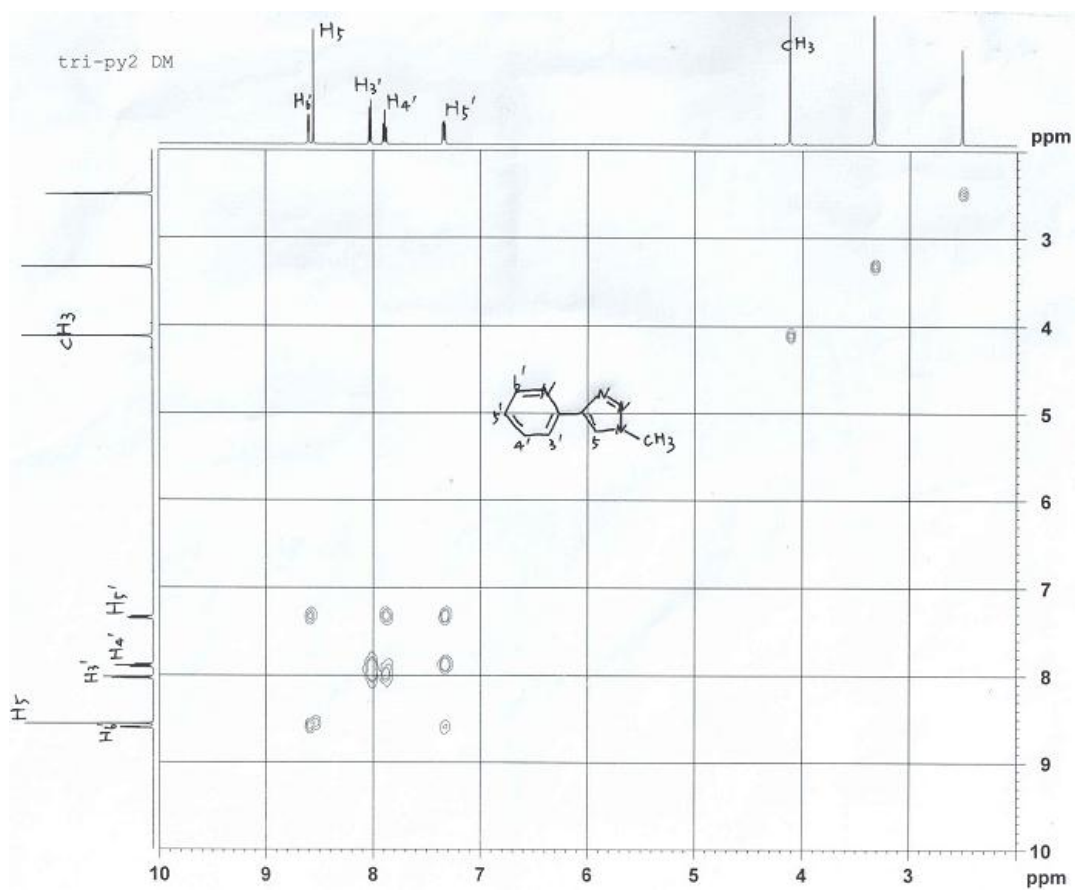


Fig. S4 H,C-COSY NMR spectrum of L'n (^1H , 500 MHz; ^{13}C , 125 MHz, $\text{d}^6\text{-DMSO}$, 298K)

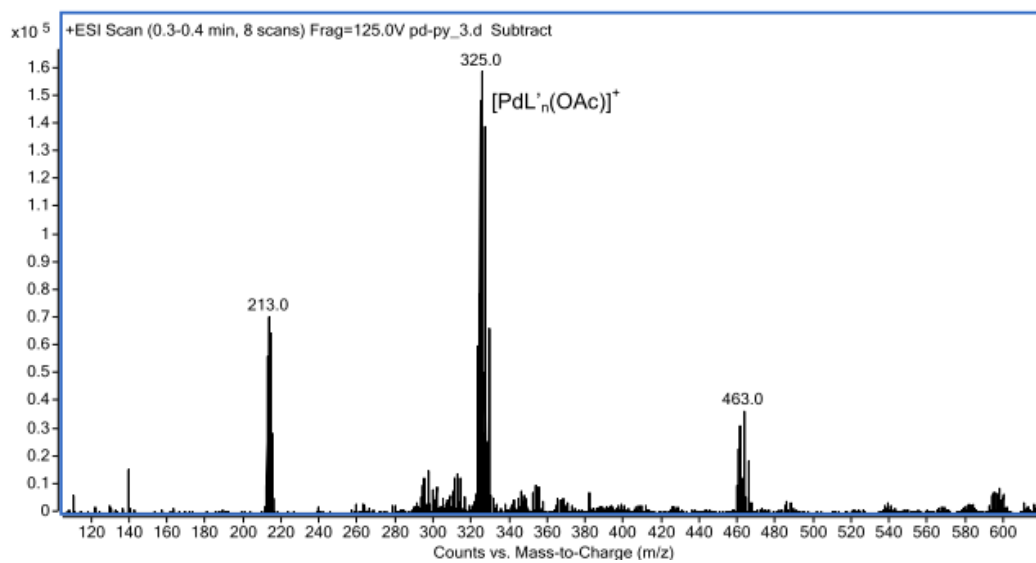


Fig. S7 ESI-MS analysis of PdL'_n(OAc)₂ and the sample was diluted with DMF

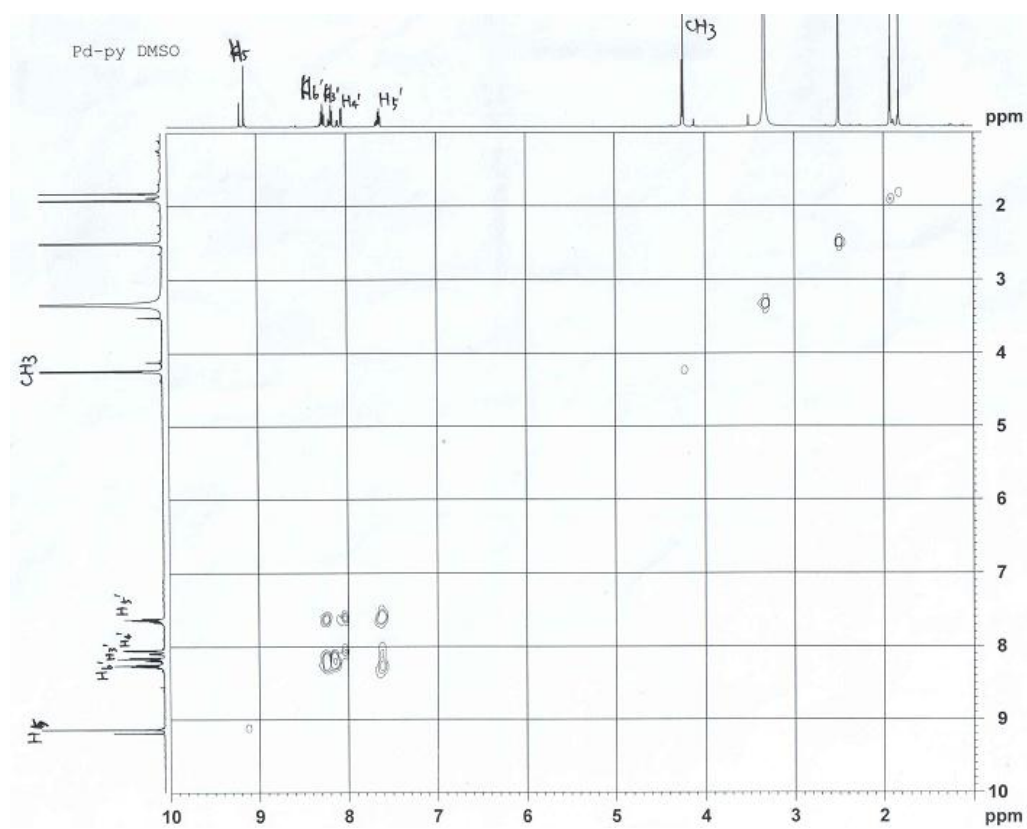


Fig. S8 H,H-COSY NMR spectrum of PdL'_n(OAc)₂ (500 MHz, d⁶-DMSO, 298K)

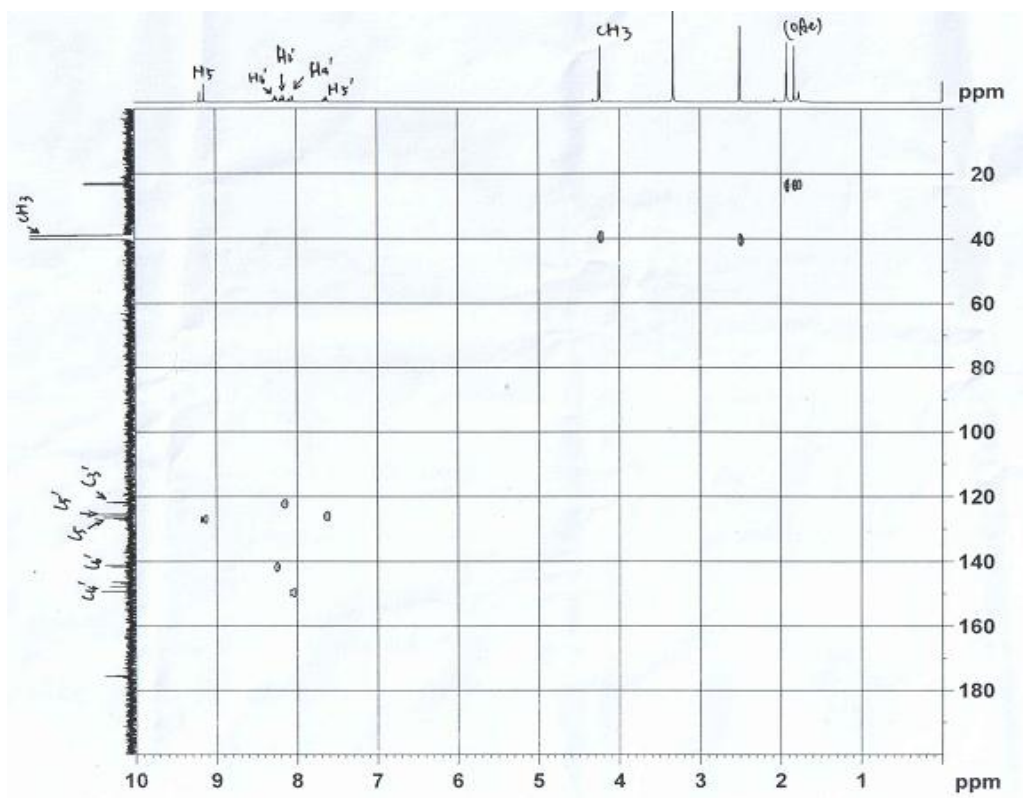


Fig. S9 H,C-COSY NMR spectrum of PdL_n(OAc)₂ (¹H, 500 MHz; ¹³C, 125 MHz, d⁶-DMSO, 298K)

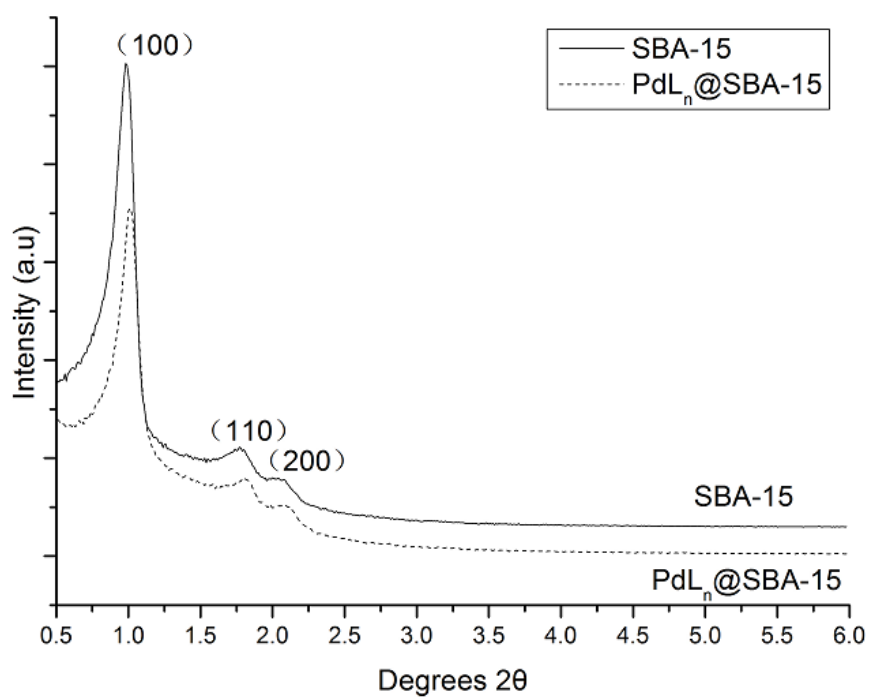


Fig. S10 Small-angle XRD patterns of the SBA-15 and the PdL_n@SBA-15

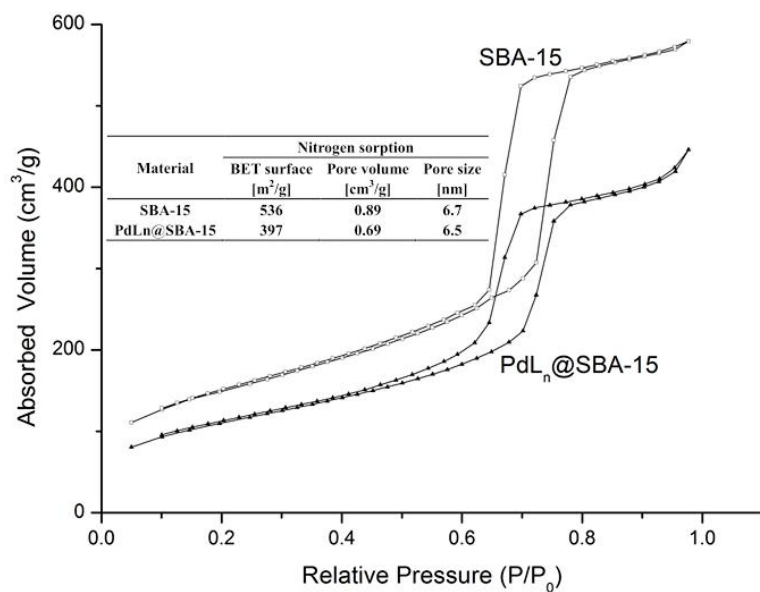


Fig. S11 Nitrogen absorption-desorption isotherms of the materials SBA-15 (\square) and PdL_n@SBA-15 (\blacktriangle)

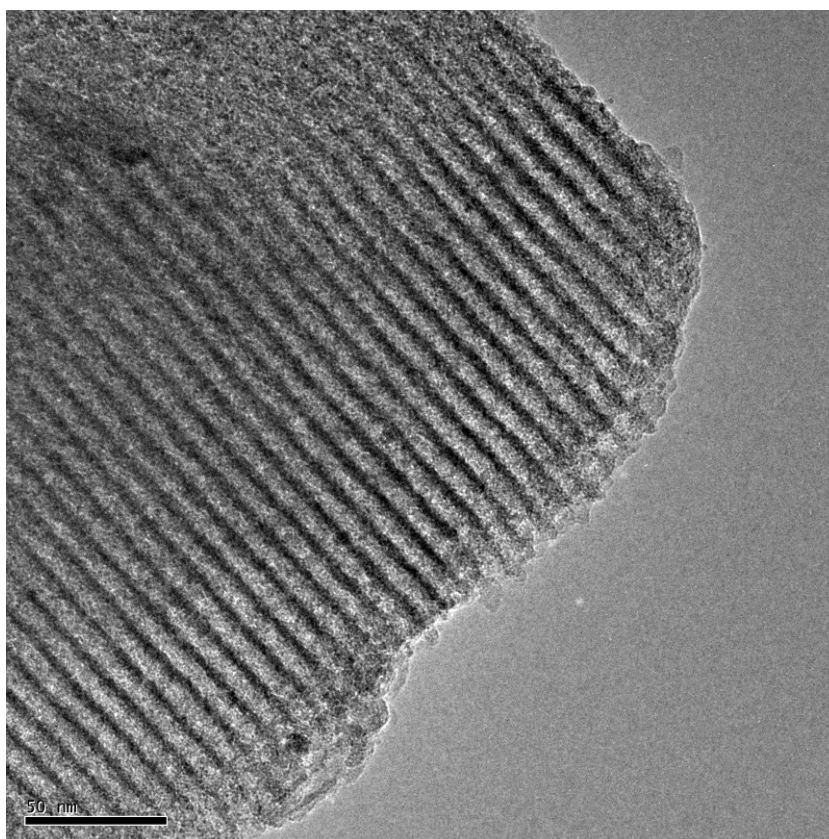


Fig. S12a TEM image of PdL_n@SBA-15 (scale bar: 50 nm)

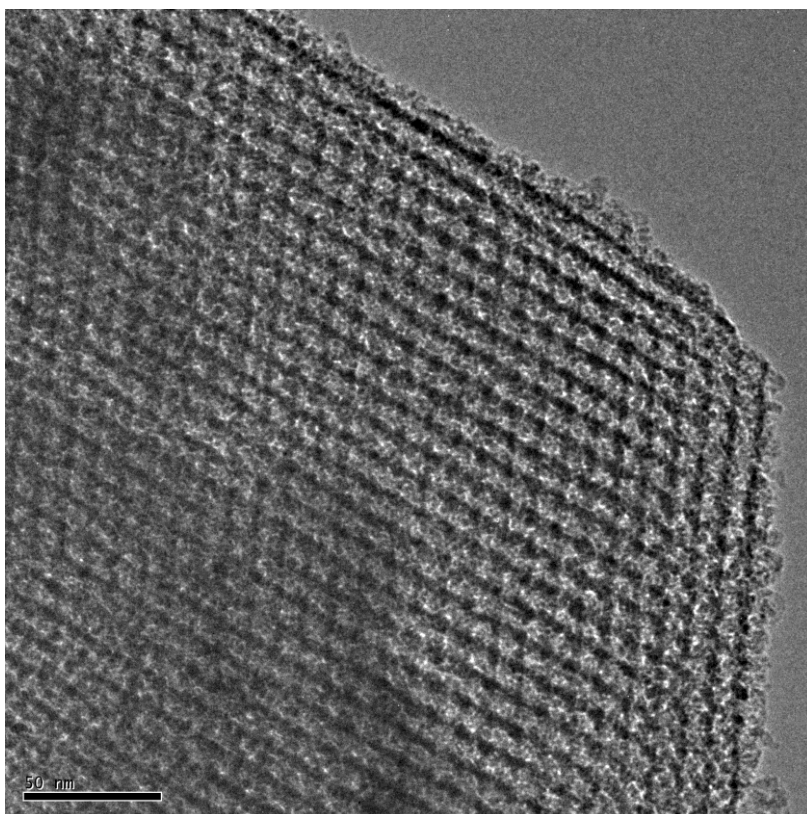


Fig. S12b TEM image of PdLn@SBA-15 (scale bar: 50 nm)

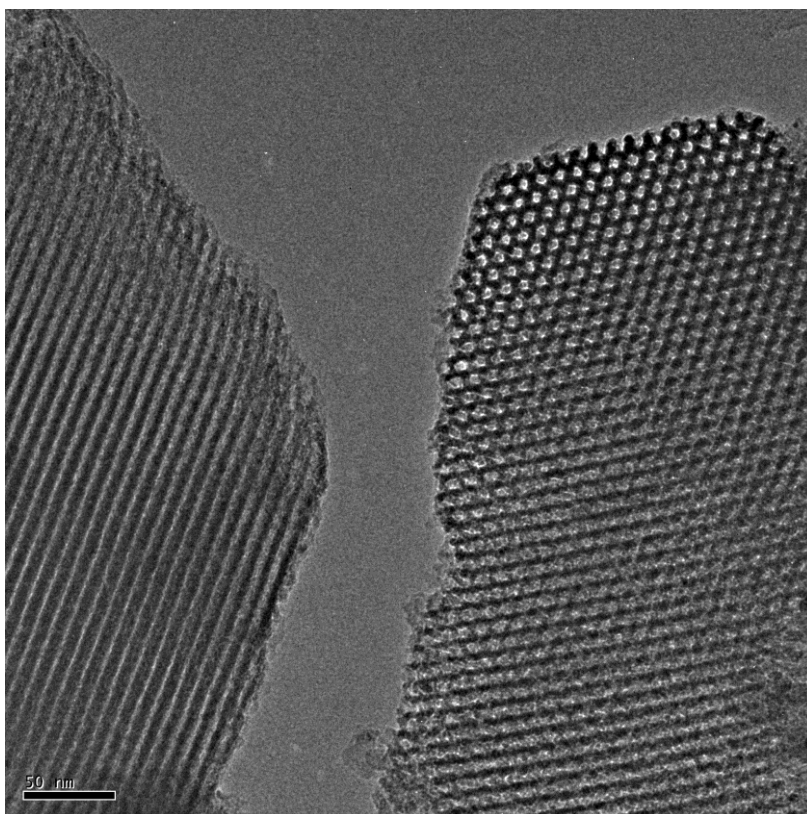


Fig. S12c TEM image of PdLn@SBA-15 (scale bar: 50 nm)

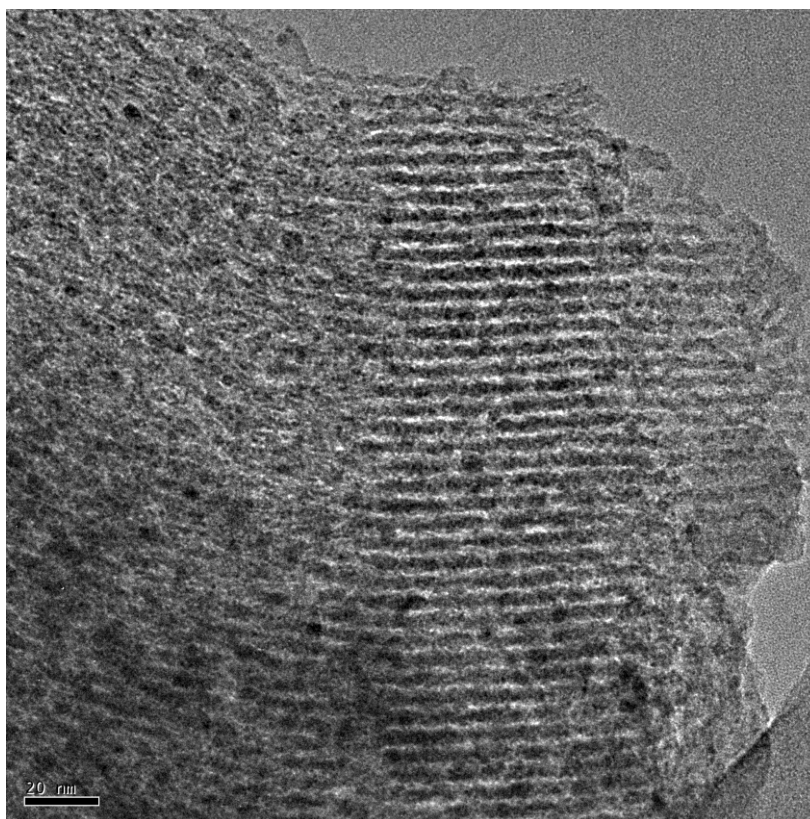


Fig. S12d TEM image of Pd_n@SBA-15 after first oxidative reaction cycle. (scale bar: 20 nm)

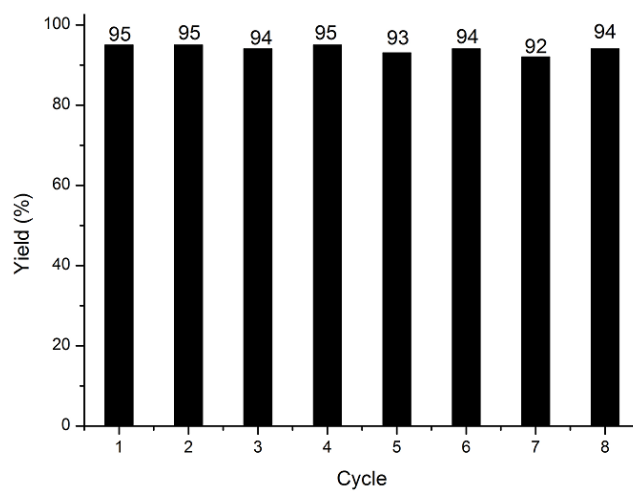


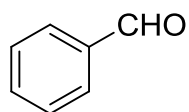
Fig. S13 Recycling test of Pd_n@SBA-15

b) General procedure for the aerobic oxidation of alcohols

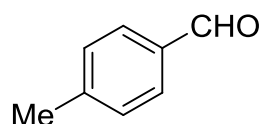
A mixture of K_2CO_3 (0.138 g, 1.0 mmol) and $PdL_n@SBA-15$ (0.005 mmol) in toluene (2.0 mL) was placed into a two-necked flask equipped with a magnetic stirrer. The flask was evacuated and refilled with pure oxygen (balloon filled) for 4 times. Then the benzyl alcohol (0.108 g, 1.0 mmol) in toluene (1.0 mL) was added into the solution with a syringe. And the resulting mixture was vigorously stirred at 100 °C under O_2 atmosphere for 4 h. After the reaction, the residue was filtered off and the catalyst was washed twice with CH_2Cl_2 (6.0 mL). Then the organic phase was combined and removed the solvent under vacuum to give the pure benzaldehyde. Yield: 0.101 g, 95%; 1H NMR (500 MHz, $CDCl_3$): δ 7.55(t, $J = 7.8$ Hz, 2H), 7.62-7.65(m, 1H), 7.88-7.90(q, 2H), 10.02(s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 129.0, 129.7, 134.4, 136.5, 192.3.

NMR Characterization Data and Figures

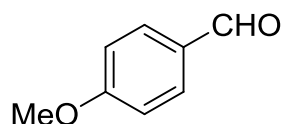
a) Characterization data for alcohol oxidation products



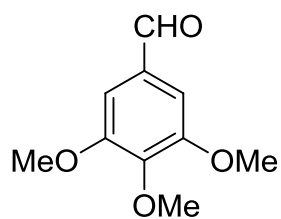
Benzaldehyde (Table 1, entry 1) ^1H NMR (500 MHz, CDCl_3): δ 7.55(t, $J = 7.8$ Hz, 2H), 7.62-7.65(m, 1H), 7.88-7.90(q, 2H), 10.02(s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 129.0, 129.7, 134.4, 136.5, 192.3.



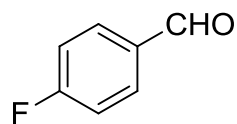
4-Methylbenzaldehyde (Table 1, entry 4) ^1H NMR (500 MHz, CDCl_3): δ 2.45(s, 3H), 7.34(d, $J = 8.0$ Hz, 2H), 7.78(d, $J = 7.5$ Hz, 2H), 9.97(s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 21.8, 129.7, 129.9, 134.2, 145.6, 192.0.



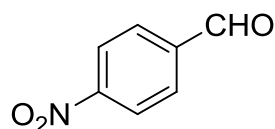
4-Methoxybenzaldehyde (Table 1, entry 5) ^1H NMR (500 MHz, CDCl_3): δ 3.90(s, 3H), 7.00-7.03(m, 2H), 7.84-7.86(m, 2H), 9.89(s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 55.6, 114.3, 130.0, 132.0, 164.6, 190.8.



3,4,5-trimethoxybenzaldehyde (Table 1, entry 6) ^1H NMR (500 MHz, CDCl_3): δ 3.95(s, 9H), 7.14(s, 2H), 9.88(s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 56.3, 61.0, 106.8, 131.8, 143.7, 153.7, 191.0.

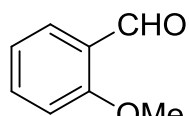


4-Fluorobenzaldehyde (Table 1, entry 7) ^1H NMR (500 MHz, CDCl_3): δ 7.16-7.21(m, 2H), 7.87-7.91(m, 2H), 9.94(s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 116.3, 132.3, 133.1, 164.7, 191.6.

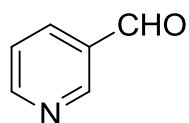


4-Nitrobenzaldehyde (Table 1, entry 8) ^1H NMR (500 MHz,

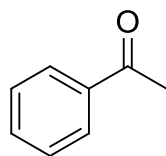
CDCl_3): δ 8.08-8.10(m, 2H), 8.40-8.42(m, 2H), 10.18(s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 124.3, 130.5, 140.1, 151.2, 190.3.



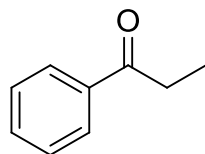
2-Methoxybenzaldehyde (Table 1, entry 9) ^1H NMR (500 MHz, CDCl_3): δ 3.95(s, 3H), 7.00-7.06(m, 2H), 7.56-7.59(m, 1H), 7.84-7.86(q, 1H), 10.50(s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 55.6, 111.6, 120.7, 125.0, 128.6, 136.0, 161.9, 189.8.



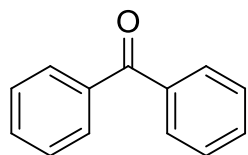
3-Nicotinaldehyde (Table 1, entry 10) ^1H NMR (500 MHz, CDCl_3): δ 7.47-7.49(q, 1H), 8.15-8.18(q, 1H), 8.83-8.84(q, 1H), 9.07(d, $J = 2.0$ Hz, 1H), 10.11(s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 124.0, 131.4, 135.8, 152.0, 154.7, 190.7.



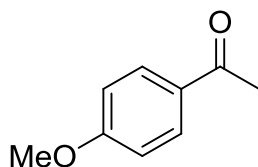
Acetophenone (Table 1, entry 11) ^1H NMR (500 MHz, CDCl_3): δ 2.62(s, 3H), 7.47(t, $J = 7.5$ Hz, 2H), 7.58(t, $J = 7.0$ Hz, 1H), 7.97(t, $J = 4.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 26.5, 128.2, 128.5, 133.0, 137.1, 198.1.



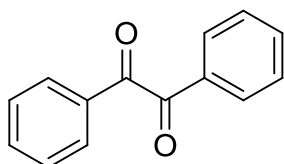
Propiophenone (Table 1, entry 12) ^1H NMR (500 MHz, CDCl_3): δ 1.24(t, $J = 7.3$ Hz, 3H), 3.01-3.05(q, 2H), 7.47(t, $J = 7.5$ Hz, 2H), 7.56(d, $J = 7.0$ Hz, 1H), 7.98(t, $J = 2.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 8.2, 31.8, 128.0, 128.6, 132.9, 137.0, 200.8.



Benzophenone (Table 1, entry 13) ^1H NMR (500 MHz, CDCl_3): δ 7.50(t, $J = 8.0$ Hz, 4H), 7.61(t, $J = 7.3$ Hz, 2H), 7.82(d, $J = 7.5$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 128.3, 130.0, 132.4, 137.6, 196.8.



4-Methoxyacetophenone (Table 1, entry 14) ^1H NMR (500 MHz, CDCl_3): δ 2.57(s, 3H), 3.89(s, 3H), 6.95(d, $J = 9.0$ Hz, 2H), 7.95 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 26.3, 55.5, 113.7, 130.4, 130.6, 163.5, 196.8.



Benzil (Table 1, entry 15) ^1H NMR (500 MHz, CDCl_3): δ 7.54(t, $J = 7.8$ Hz, 4H), 7.68(t, $J = 7.0$ Hz, 2H), 7.98-8.00(q, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 129.1, 129.9, 133.1, 135.0, 194.6.

Figure 1. ^1H NMR and ^{13}C NMR spectrum of 3-azidopropyltriethoxysilane.

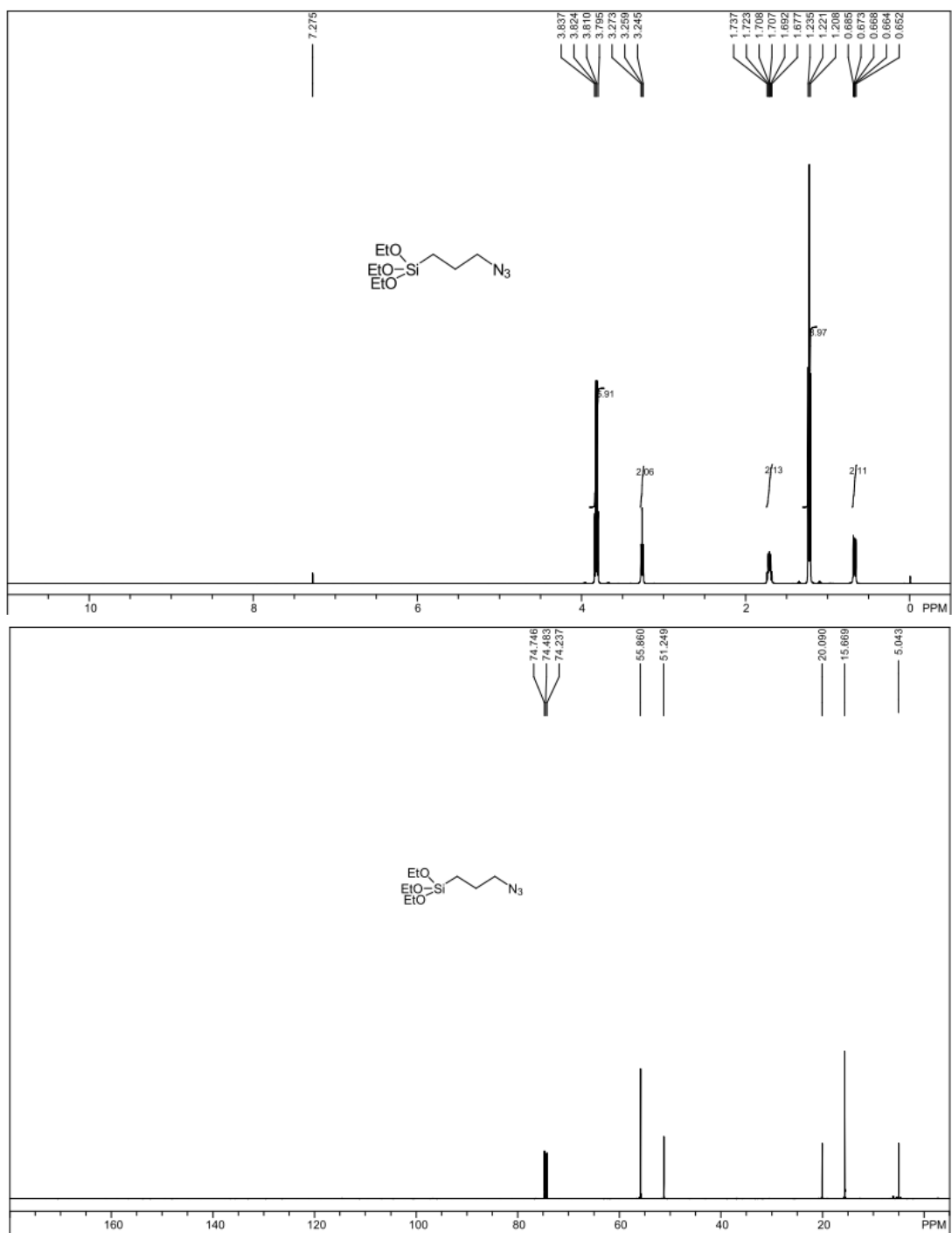


Figure 2. ^1H NMR, ^{13}C NMR spectrum of 1-methyl-4-(2'-pyridyl)-1,2,3-triazole.

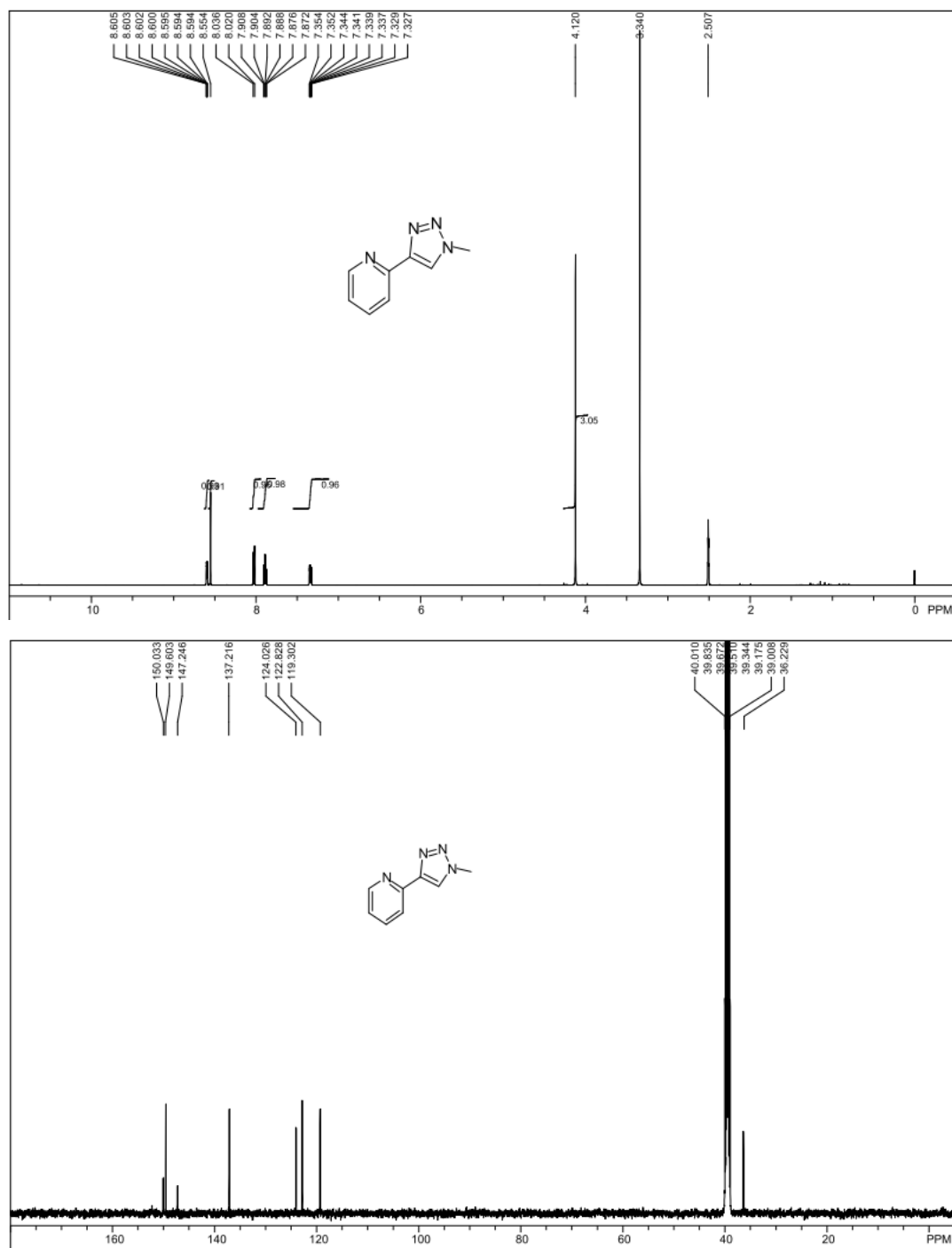


Figure 3. ^1H NMR and ^{13}C NMR spectra of benzaldehyde.

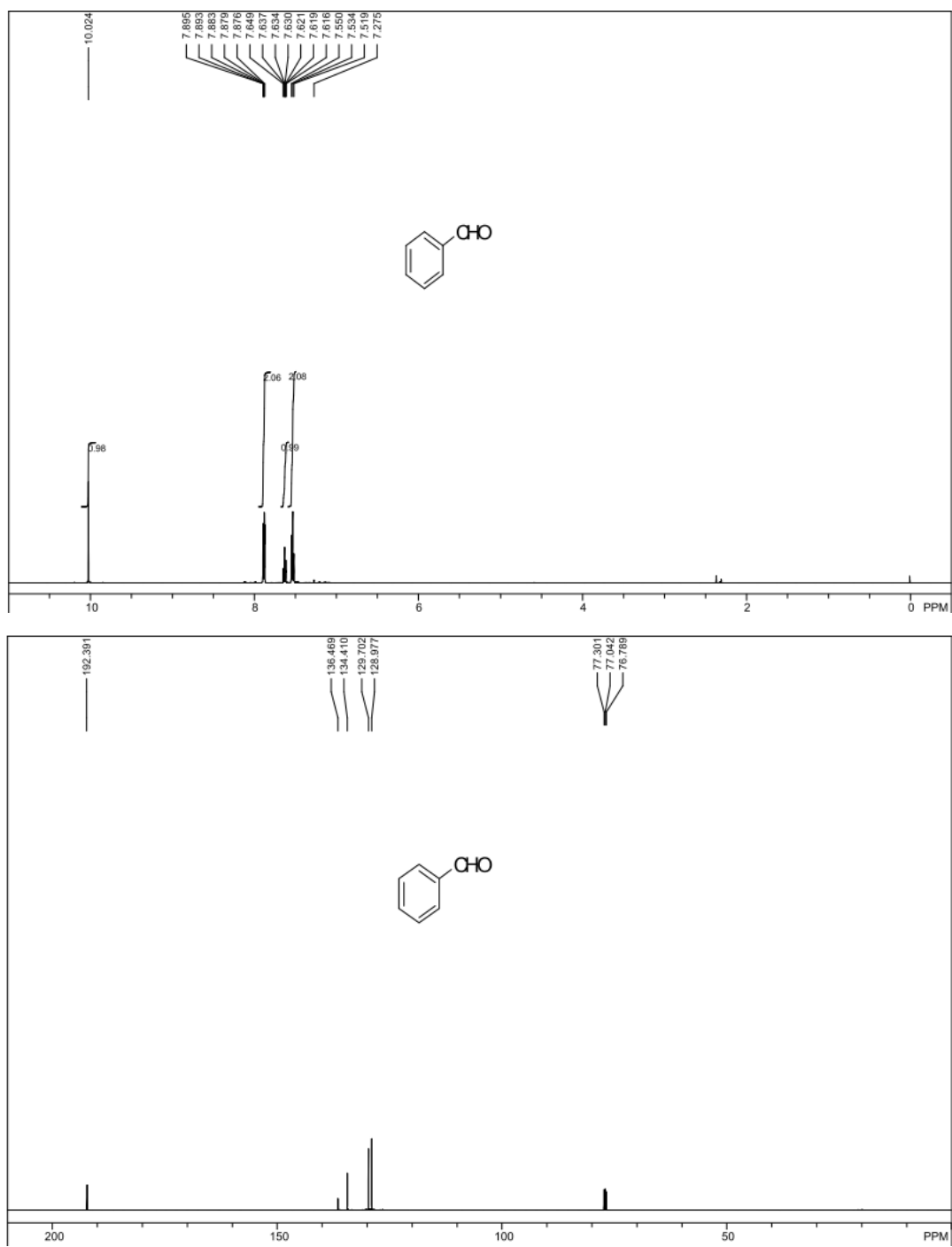


Figure 4. ^1H NMR and ^{13}C NMR spectra of 4-methylbenzaldehyde.

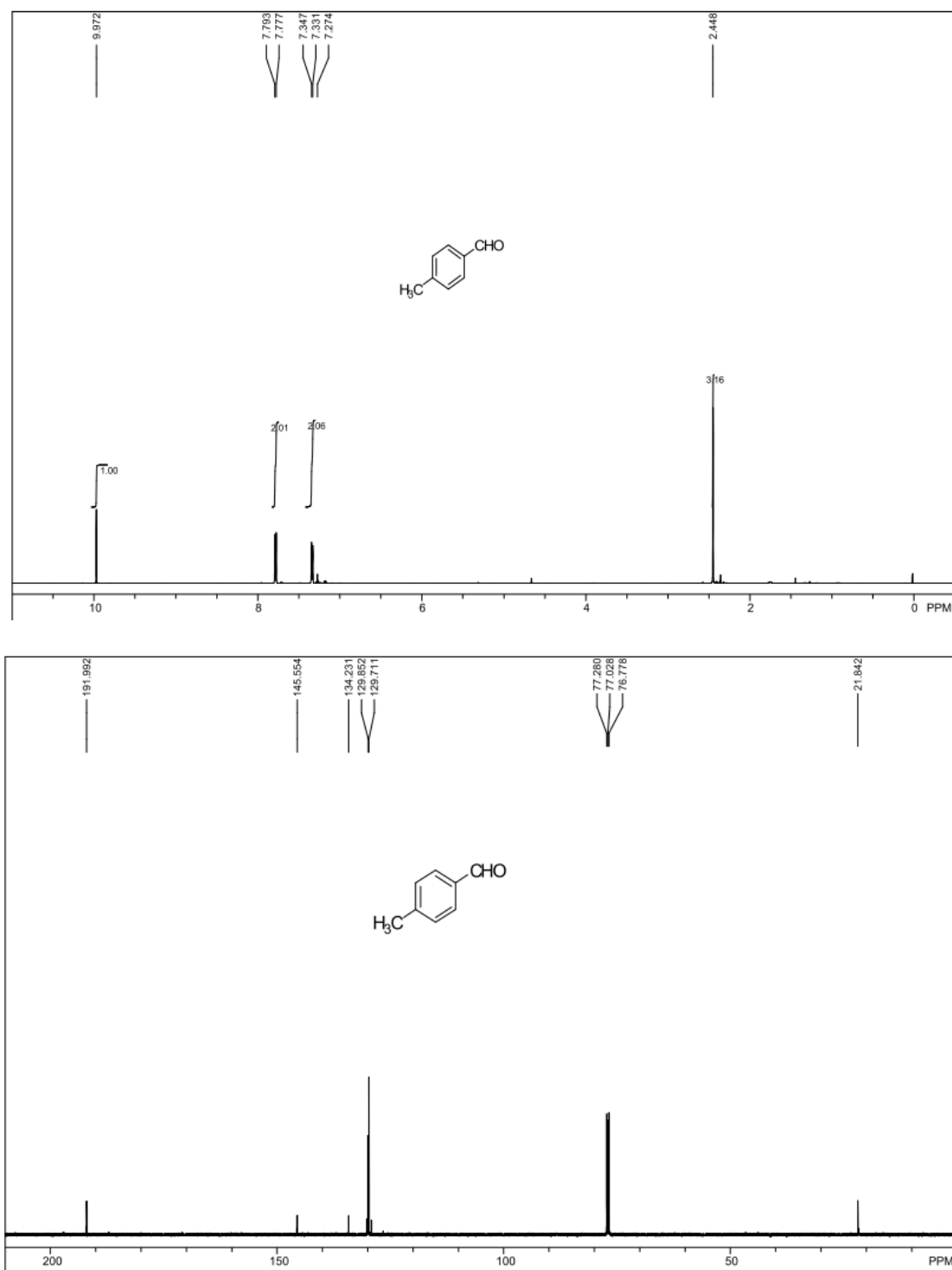


Figure 5. ^1H NMR and ^{13}C NMR spectra of 4-methoxybenzaldehyde.

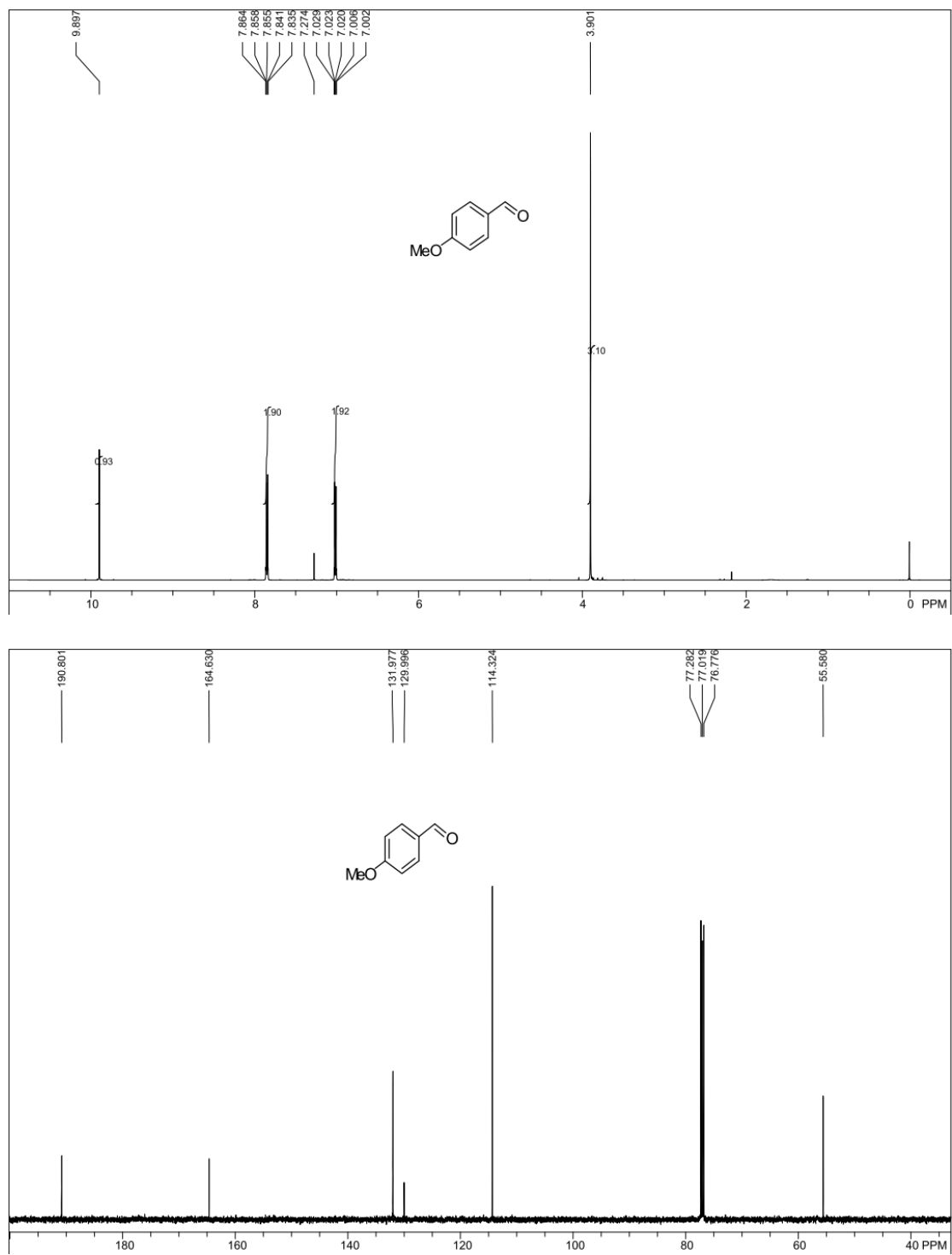


Figure 6. ^1H NMR and ^{13}C NMR spectra of 3,4,5-trimethoxybenzaldehyde

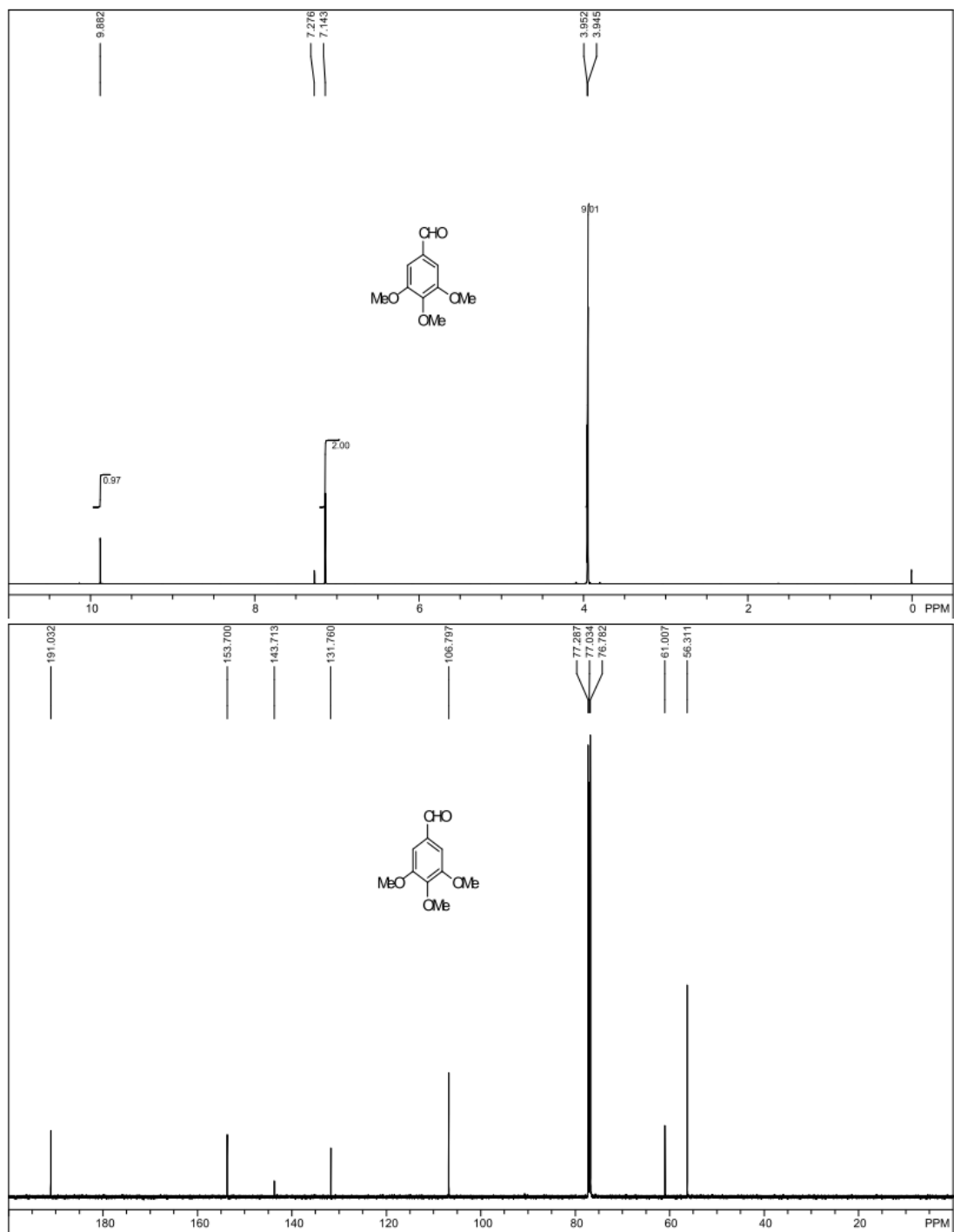


Figure 7. ^1H NMR and ^{13}C NMR spectra of 4-fluorobenzaldehyde.

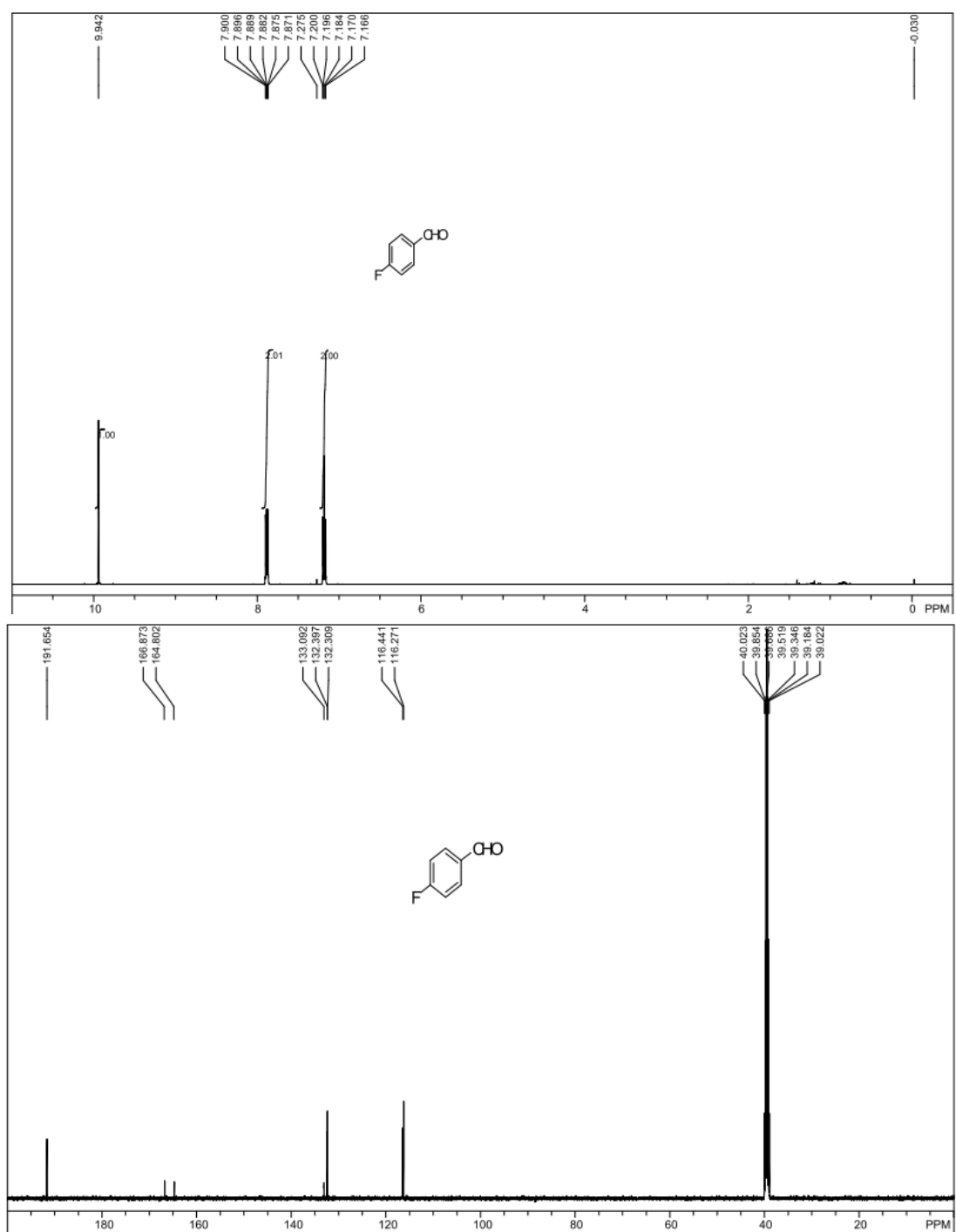


Figure 8. ^1H NMR and ^{13}C NMR spectra of 4-nitrobenzaldehyde.

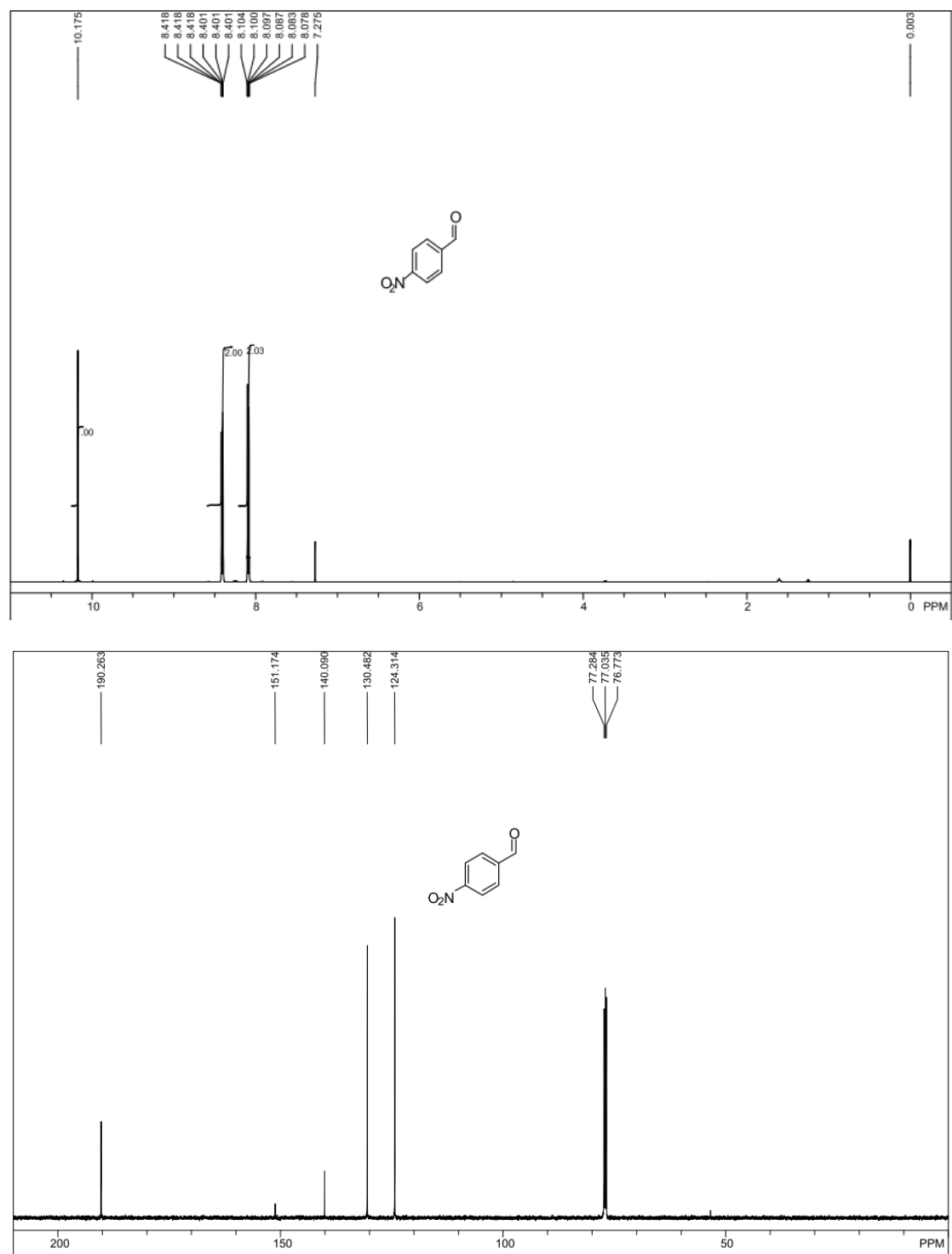


Figure 9. ^1H NMR and ^{13}C NMR spectra of 2-methoxybenzaldehyde.

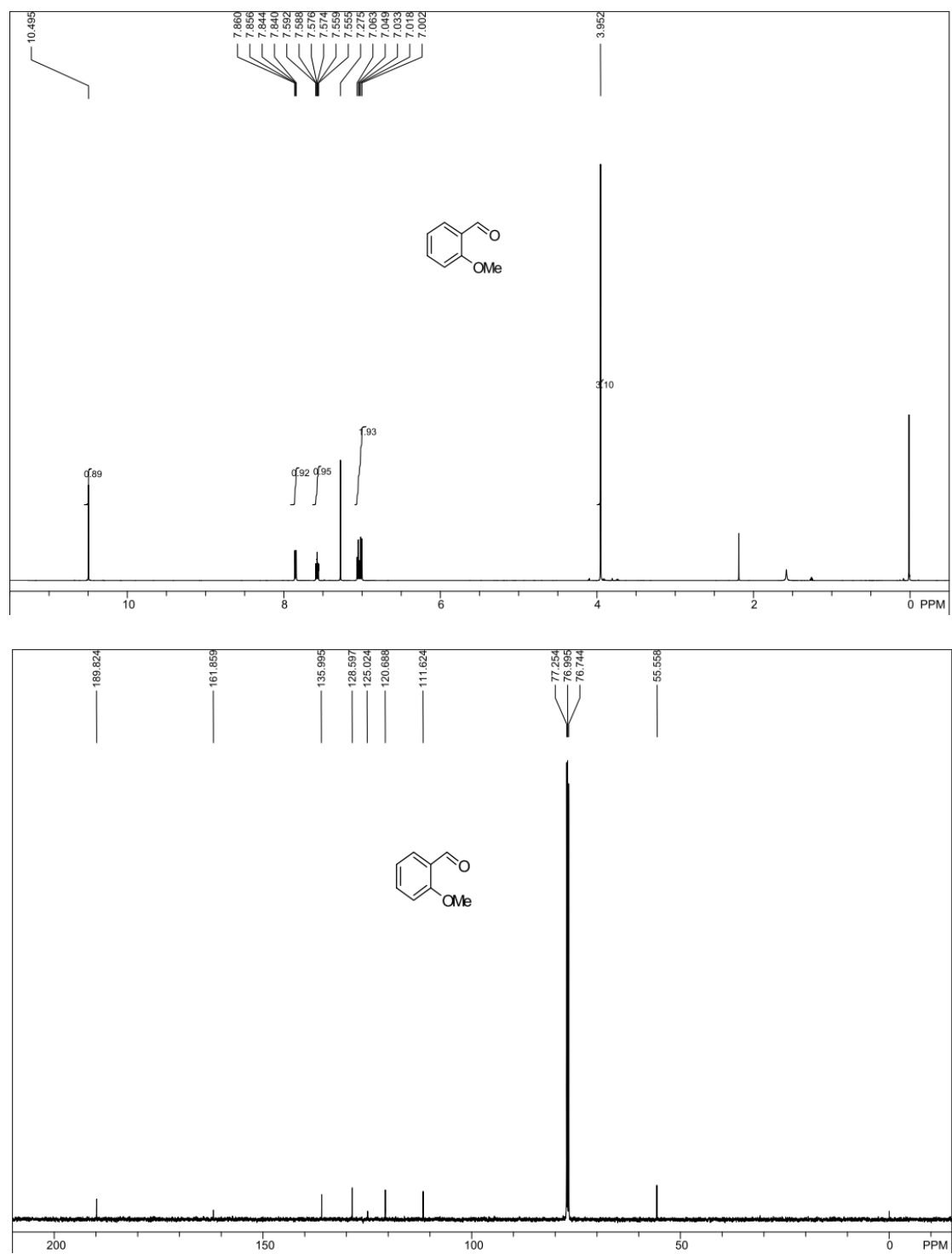


Figure 10. ^1H NMR and ^{13}C NMR spectra of 3-nicotinaldehyde.

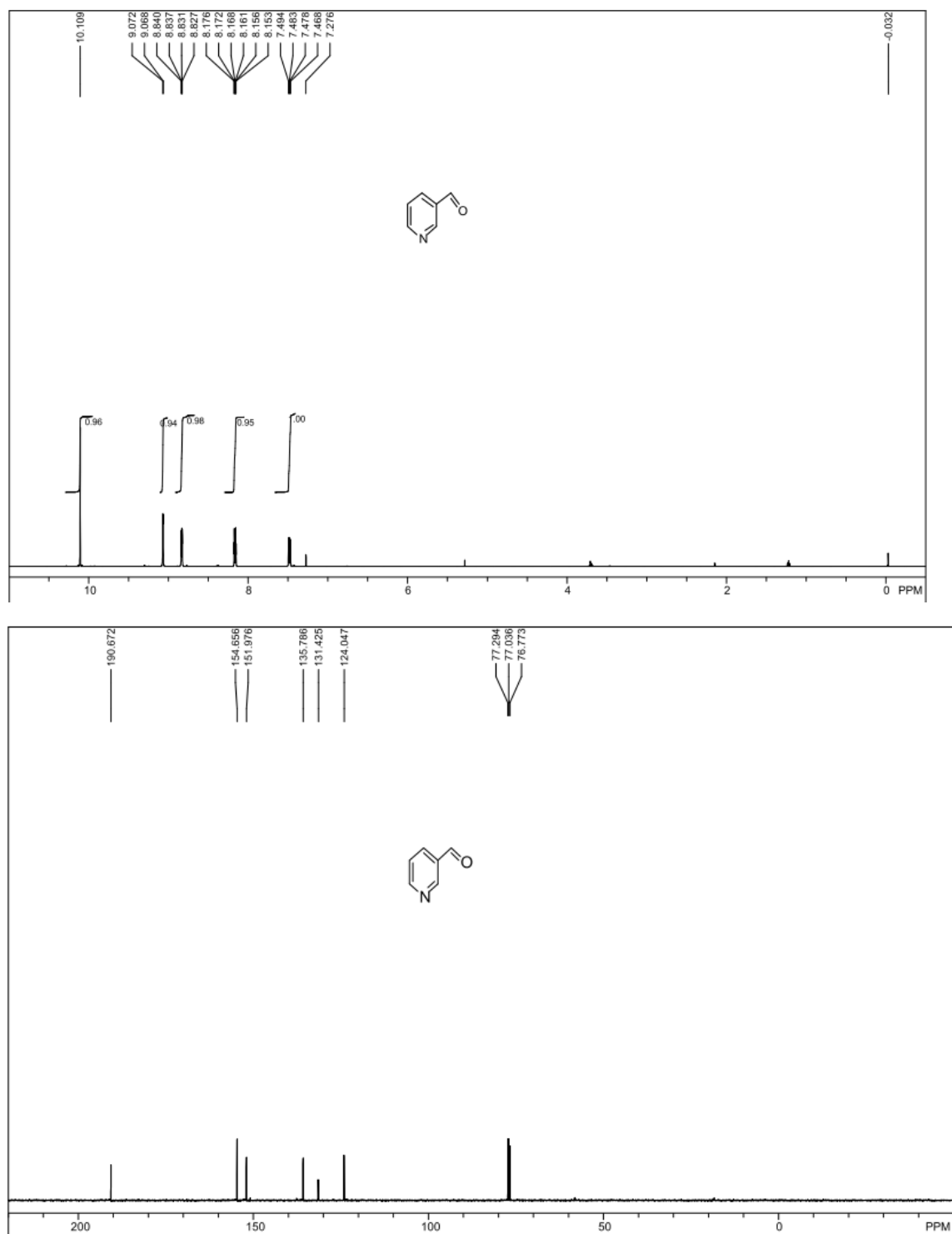


Figure 11. ^1H NMR and ^{13}C NMR spectra of acetophenone.

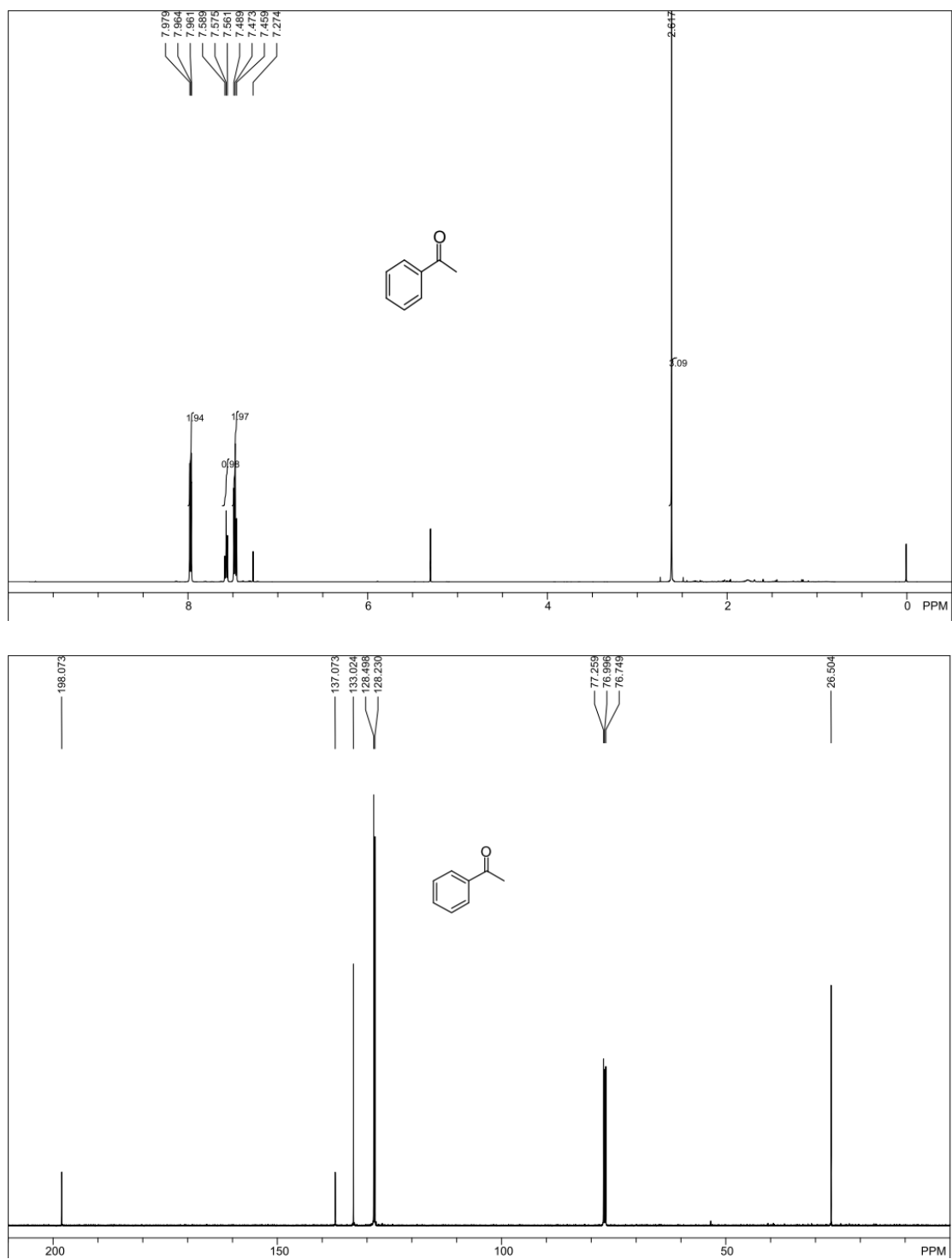


Figure 12. ^1H NMR and ^{13}C NMR spectra of propiophenone.

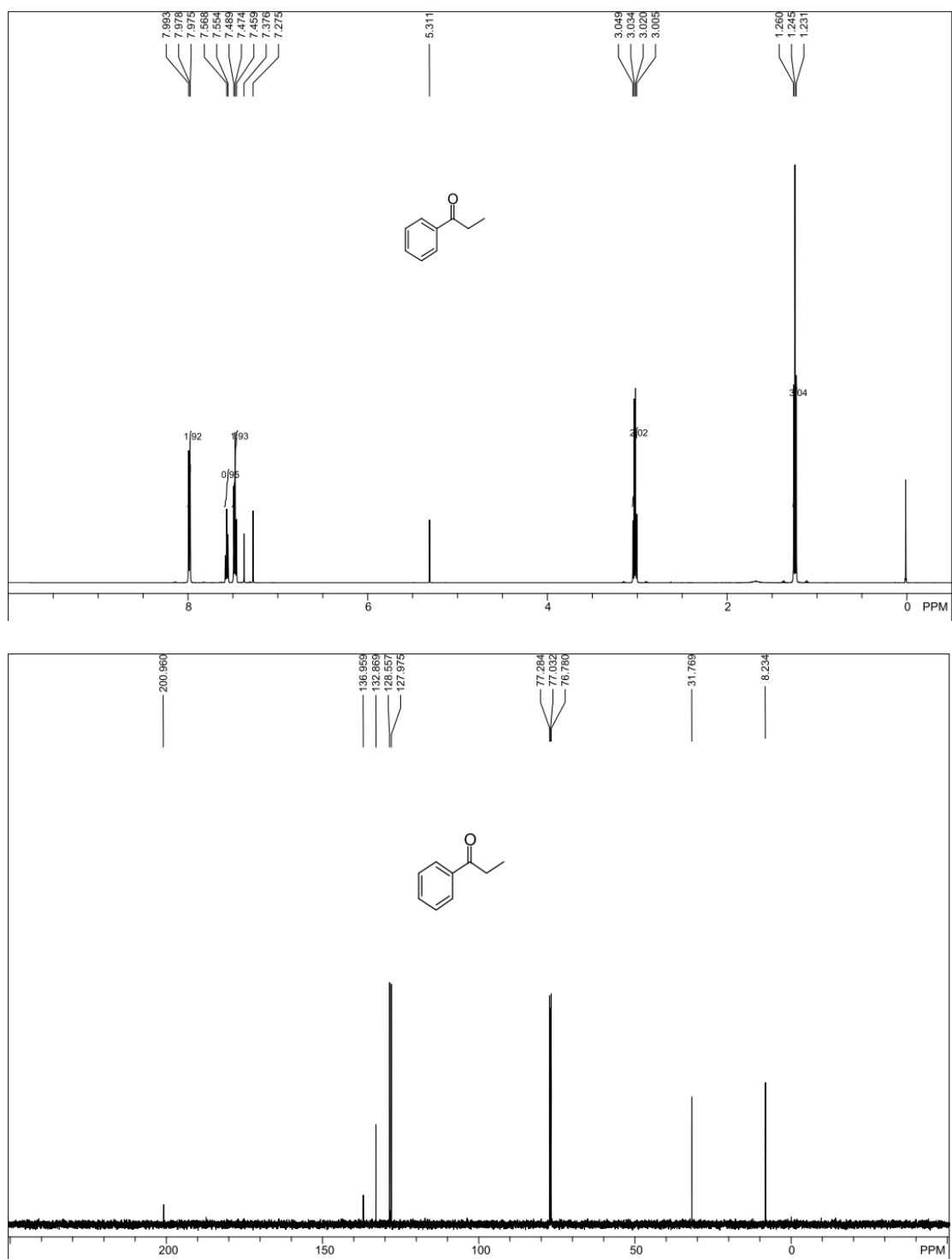


Figure 13. ^1H NMR and ^{13}C NMR spectra of benzophenone.

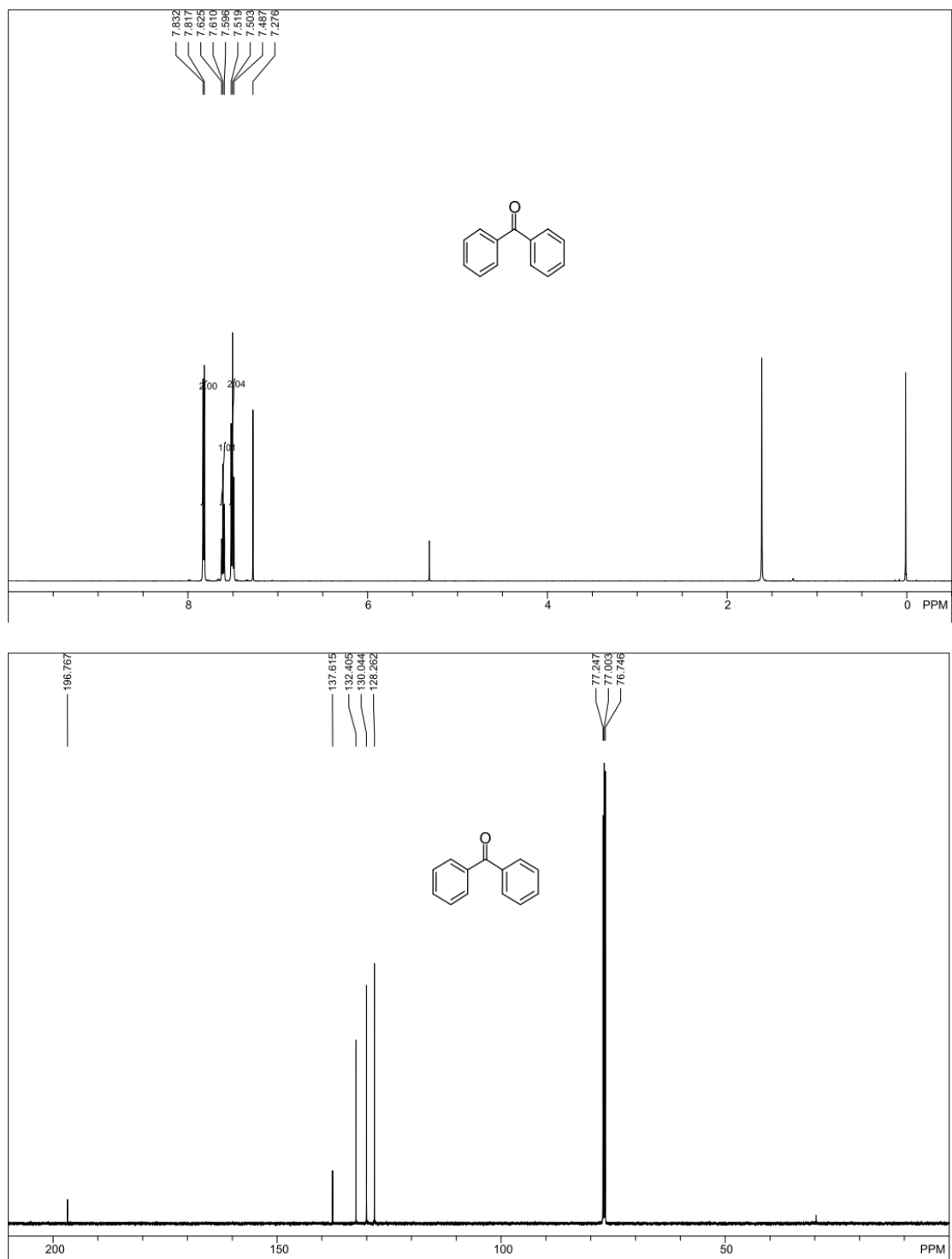
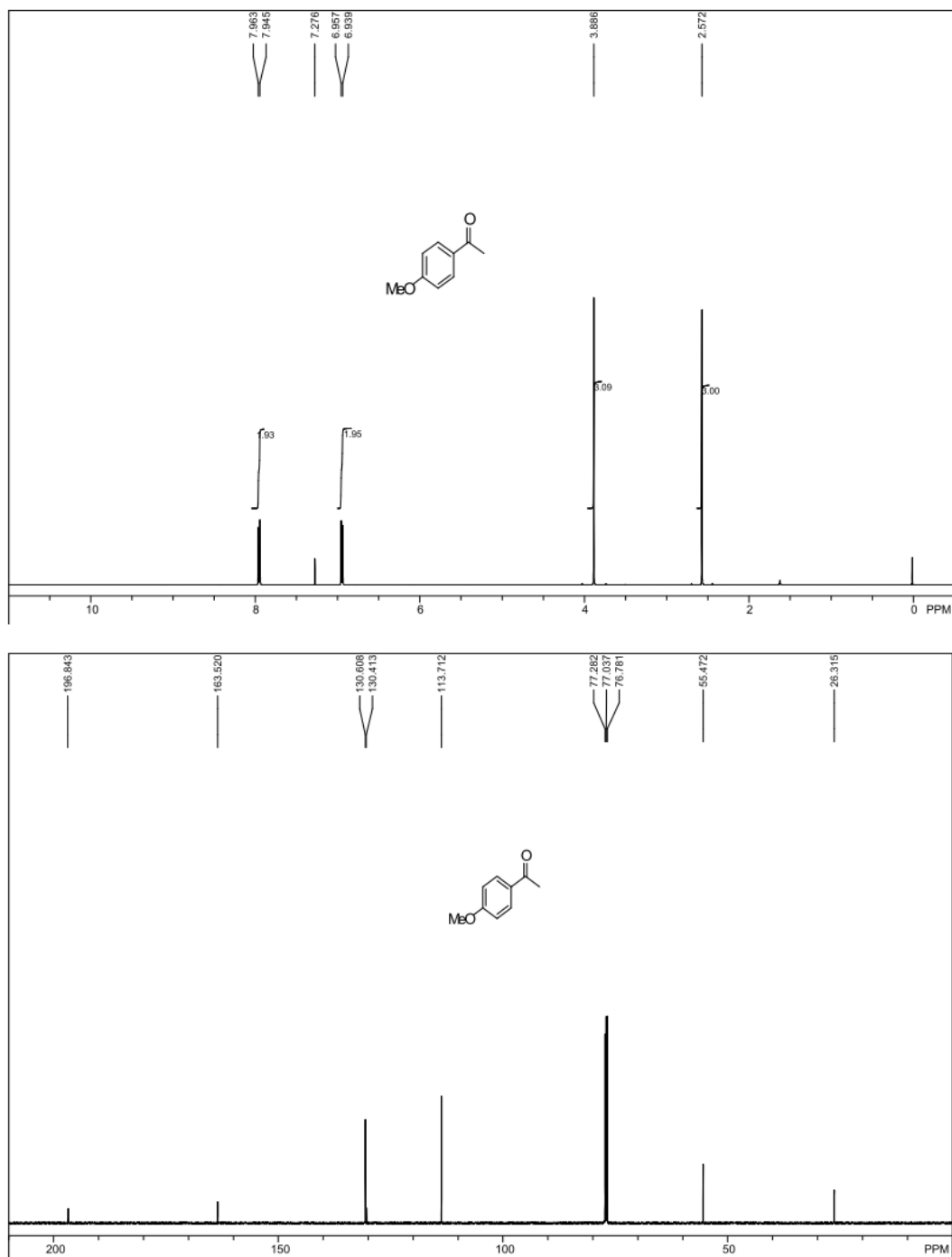


Figure 14. ^1H NMR and ^{13}C NMR spectra of 4-methoxyacetophenone.



References

- 1 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
- 2 A B. Malvi, B. R. Sarkar, D. Pati, R. Mathew, T. G. Ajithkumar and S. S. Gupta, *J. Mater. Chem.*, 2009, **19**, 1409.
- 3 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596.
- 4 (a) O. Fleischel, N. Wu and A. Petitjean, *Chem. Commun.*, 2010, 8454; (b) M. Felici, P. Contreras-Carballada, Y. Vida, J. M. M. Smits, R. J. M. Nolte, L. De Cola, R. M. Williams and M.C. Feiters, *Chem. Eur. J.*, 2009, **15**, 13124.