Electronic Supplemental Information (ESI)

Eco-friendly Suzuki-Miyaura coupling of Arylboronic acids to Aromatic Ketones Catalyzed by Oxime-Palladacycle in Biosolvent 2-MeTHF

Manoj Mondal[a] and Utpal Bora*[a,b]

[a] *Department of Chemistry, Dibrugarh University, Dibrugarh 786004, Assam, India*

[b] *Department of Chemical Sciences, Tezpur University, Tezpur 784028, Assam, India*

E-mail: utbora@yahoo.co.in; ubora@tezu.ernet.in

Table of Contents

1. General Information

Instrumentation and Chemicals

All chemicals were obtained commercially and used as received. Solvents were used as received. The acetophenone oxime-palladacycle was synthesized according to the reported literature.[1] All reactions were carried out on a Process Station Personal Synthesizer (Eyela, Tokyo Rikakikai Co. Ltd., Japan). FT-IR spectra (4000-250 cm^{-1}) were recorded in $CHCl_3$ or KBr on a Shimadzu Prestige-21 FT-IR spectrophotometer. Melting points was determined using a Buchi B450 melting point apparatus. GC-MS analysis was performed on an Agilent Technologies GC system 7820A coupled with a mass detector 5975 and SHRXI-5MS column (15 m, 0.25 mm inner diameter, 0.25 micron film thickness). ^1H NMR spectra were recorded on 400 MHz spectrometers using $CDCl_3$ as solvent referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm) on a JEOL, JNM ECS NMR spectrometer. ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ using $CDCl_3$ (77.0 ppm) as standard. Products are known compounds and were identified by ^1H and ^{13}C NMR spectra and confirmed by comparing with those reported in the literature. The following abbreviations are used for the description of signals: s (singlet), d (doublet), t (triplet), m (multiplet). Coupling constants (*J*) were measured in Hz. Analytical thin layer chromatography was carried out on Merck silica gel $60F_{254}$ plates using short wave (254 nm) UV light and I_2 or $KMnO_4$ to visualize components. Silica gel (60-120 mesh) was used for column chromatography.

2. Experimental Section:

Typical Experimental Procedure for Acylation of Arylboronic acid (3a)

A 50 mL branched test tube was charged with a mixture of K_2CO_3 (138 mg, 1.0 mmol), complex **1** (0.4 mol%Pd), 2-MeTHF (4 mL) under open air. The solution was heated to 80 °C on a *Process Station Personal Synthesizer* with continuous stirring, and added with arylboronic acid (0.55 mmol) and acid chloride (0.5 mmol). The mixture was stirred at 80 °C for the required time and progress of the reaction was monitored using TLC. After completion of the reaction, the resulting mixture was added with saturated solution of brine (4 mL). The resulting water-organic phases were separated and the organic phase (in 2-MeTHF) was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The resultant residue was subjected to silica gel column chromatography (eluent, 10-15%: ethyl acetate/hexane) to afford the desired product.

3. TEM images of the Pd-nanoparticles:

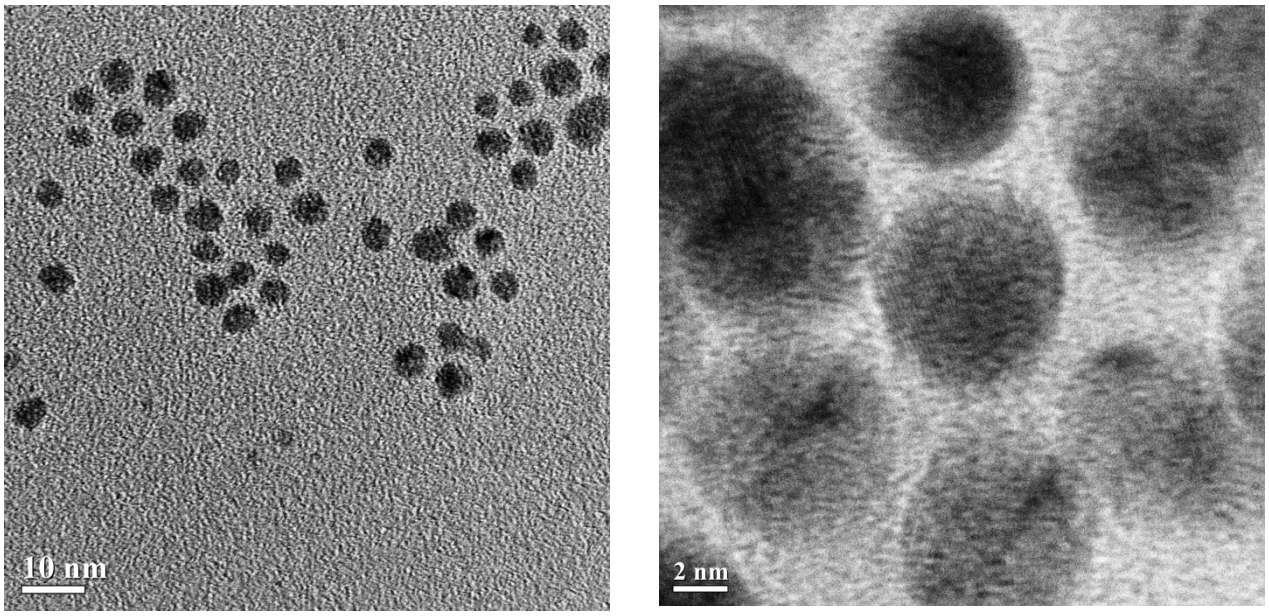
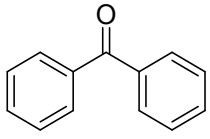


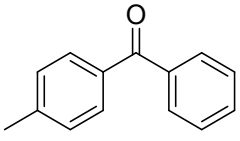
Figure S1. TEM analysis of oxime-palladacycle Catalyst 1 formed during the cross-coupling reaction

3. Spectroscopic data for the products:



Benzophenone

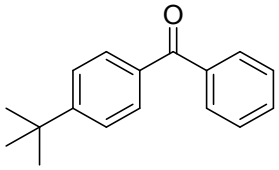
Benzophenone (**4aa**):[2] White solid, Yield: 97%, 88.2 mg; m.p. 48-49 °C (literature,[3] 47-48.5 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.81-7.79 (m, 4H), 7.57 (t, *J*=7.7 Hz, 2H), 7.48 (t, *J*=7.7 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 196.9, 137.6, 132.5, 130.1, 128.3; FT-IR (KBr, cm^{-1}): 1659 ($\nu_{C=O}$); GC-MS m/z: 182.1 (M^+, 100).



Phenyl(p-tolyl)methanone

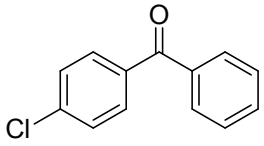
Phenyl(*p*-tolyl)methanone (**4ab**):[2] Colorless liquid, Yield: 96%, 94 mg; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.76 (d, *J*= 6.88 Hz, 2H), 7.71 (d, J= 7.76 Hz, 2H), 7.56 (t, *J*= 7.6 Hz, 1H), 7.45 (t, *J*=7.6 Hz, 2H), 7.27-7.25 (m, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 196.7, 143.3, 138, 134.9, 132.3, 130.4, 130.2, 129, 128.5, 128.3, 21.7; FT-IR ($CHCl_3$, cm^{-1}): 1657 ($\nu_{C=O}$). GC-MS

m/z: 196.1 (M^+, 100).



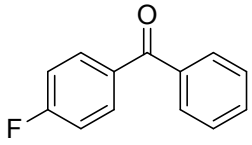
(4-(tert-butyl)phenyl)(phenyl)methanone

(4-(*tert*-butyl)phenyl)(phenyl)methanone (**4ac**):[2] White solid, Yield: 93%, 110.6 mg; m.p. 39-40 °C (literature[2] 38-40 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.8-7.74 (m, 4H), 7.58-7.54 (m, 1H), 7.49-7.45 (m, 4H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 196.5, 156.2, 138, 134.9, 132.2, 130.2, 130, 128.6, 128.2, 125.3, 31.5, 31.2; FT-IR (KBr, cm^{-1}): 1658 ($\nu_{C=O}$). GC-MS m/z: 238.0 (M^+, 100).



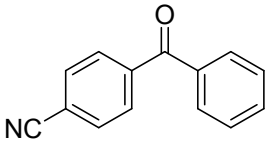
(4-Chlorophenyl)(phenyl)methanone

(4-Chlorophenyl)(phenyl)methanone (**4ad/4ca**):[2] White solid, Yield: 91%, 98.3 mg; m.p. 73-74 °C (literature[3] 73.5-75 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.78-7.74 (m, 4H), 7.59 (t, *J*= 7.4 Hz, 1H), 7.48-7.44 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 195.5, 138.7, 137.4, 135, 132.7, 131.5, 129.9, 128.7, 128.4,; FT-IR (KBr, cm^{-1}): 1648 ($\nu_{C=O}$). GC-MS m/z: 216.0 (M^+, 100).



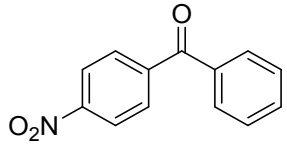
(4-Fluorophenyl)(phenyl)methanone

(4-Fluorophenyl)(phenyl)methanone (**4ae**):[2] White solid, Yield: 90%, 90 mg; m.p. 47-48 °C (literature[2] 48-49 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.85-7.83 (m, 2H), 7.78-7.76 (m, 2H), 7.61-7.59 (m, 1H), 7.51-7.49 (m, 2H), 7.20-7.16 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 195.3, 195.3, 166.7, 137.5, 133.8, 132.7, 132.6, 132.5, 129.9, 128.4, 115.6 (d, *J*= 21.93 Hz); FT-IR (KBr, cm^{-1}): 1660 ($\nu_{C=O}$). GC-MS m/z: 200.2 (M^+, 100).



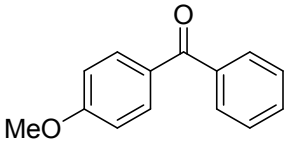
4-Benzoylbenzonitrile

4-Benzoylbenzonitrile (**4af**):[4] White solid, Yield: 94%, 97.3 mg; m.p. 111-112 °C (literature[5] 113-114 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.82-7.79 (m, 2H), 7.59-7.57 (m, 2H), 7.51-7.46 (m, 3H), 7.45-7.38 (m, 2H); FT-IR (KBr, cm^{-1}): 1648 ($\nu_{C=O}$). GC-MS m/z: 207.1 (M^+, 100).



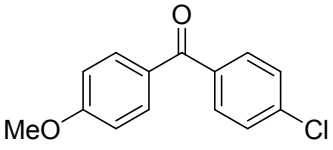
(4-Nitrophenyl)(phenyl)methanone

(4-Nitrophenyl)(phenyl)methanone (**4ba**):[4] Yellow solid, Yield: 87%, 98.7 mg; m.p. 137-138 °C (literature[3] 138-139 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 8.32-8.30 (d, *J*= 4.12, 2H), 7.92-7.90 (d, *J*= 4.12 Hz, 2H), 7.77 (d, *J*= 3.68 Hz, 2H), 7.63 (t, *J*= 7.8 Hz, 1H), 7.50 (t, *J*= 7.8, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 194.8, 149.9, 142.9, 136.4, 133.5, 130.7, 130.1, 128.7, 123.5; FT-IR (KBr, cm^{-1}): 1659 ($\nu_{C=O}$). GC-MS m/z: 227.0 (M^+, 100).



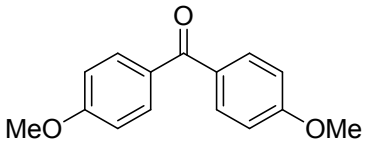
(4-Methoxyphenyl)(phenyl)methanone

(4-Methoxyphenyl)(phenyl)methanone (**4da**):[6] White solid, Yield: 95%, 100 mg; m.p. 61-62 °C (literature[3] 61-61.5 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.82-7.8 (m, 2H), 7.74-7.72 (m, 2H), 7.57-7.55 (m, 1H), 7.44-7.45 (m, 2H), 6.95-6.93 (d, *J*= 8.68 Hz, 2H), 3.8 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 194.5, 162.2, 137.2, 131.5, 130.8, 129.1, 128.6, 127.1, 112.5, 54.47; FT-IR (KBr, cm^{-1}): 1661 ($\nu_{C=O}$). GC-MS m/z: 212.1 (M^+, 100).



(4-Chlorophenyl)(4-methoxyphenyl)methanone

(4-Chlorophenyl)(4-methoxyphenyl)methanone (**4dd/4cg**):[7] White solid, Yield: 89%, 109 mg; m.p. 123-124 °C (literature[5] 119-120 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.80-7.78 (m, 2H), 7.71-7.69 (m, 2H), 7.46-7.44 (t, *J*= 8.7 Hz, 2H), 6.95-6.98 (d, *J*= 8.7 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 194.3, 163.4, 138.3, 136.6, 132.5, 131.2, 129.8, 128.6, 113.7, 55.6; FT-IR (KBr, cm^{-1}): 1641 ($\nu_{C=O}$). GC-MS m/z: 246.1 (M^+, 100).



bis(4-methoxyphenyl)methanone

bis(4-methoxyphenyl)methanone (4dg):[7] White solid, Yield: 94%, 112 mg, m.p. 143-144 °C (literature[5] 138-139 °C), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.78 (d, *J*= 7.2 Hz, 4H), 6.97 (d, *J*= 7.2 Hz, 4H), 3.89 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 194.6, 162.89, 132.3, 130.78, 113.5, 55.5; FT-IR (KBr, cm^{-1}): 1639 ($\nu_{C=O}$). GC-MS m/z: 242.1 (M^+, 100).

References:

1 H. Onoue, K. Minami and K. Nakagawa, *Bull. Chem. Soc. Jpn*., 1970, **43**, 3480.

2 A. Yu, L. Shen, X. Cui, D. Peng and Y. Wu, *Tetrahedron*, 2012, **68**, 2283.

3 S. S. Kulp and M. J. McGee, *J. Org. Chem*., 1983, **48**, 4097.

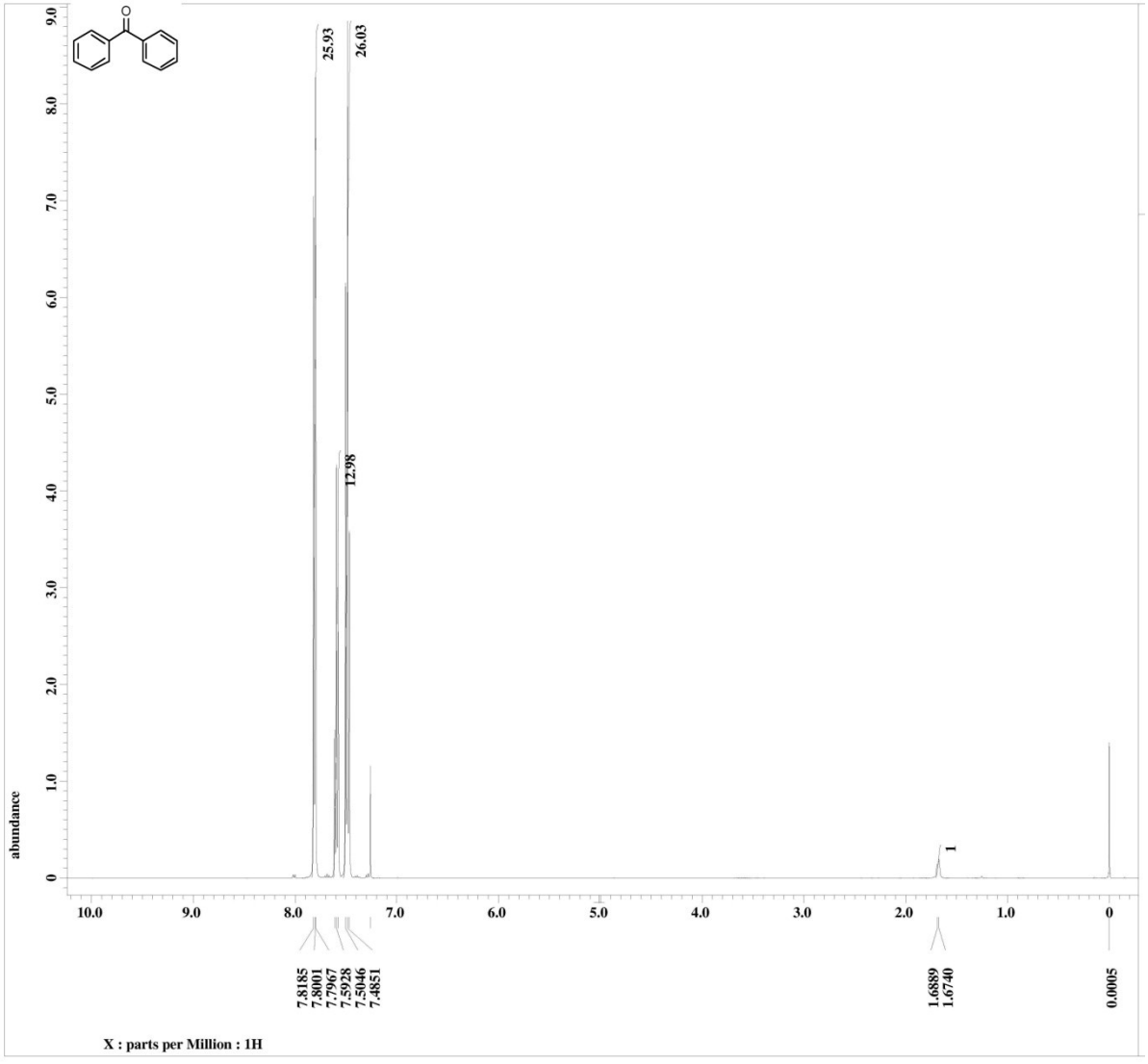
4 B. Xin, Y. Zhang and K. Cheng, *Synthesis*, 2007, 1970.

5 C. Duplais, F. Bures, I. Sapountzis, T. J. Korn, G. Cahiez and P. Knochel, *Angew. Chem*., *Int. Ed*., 2004, **43**, 2968.

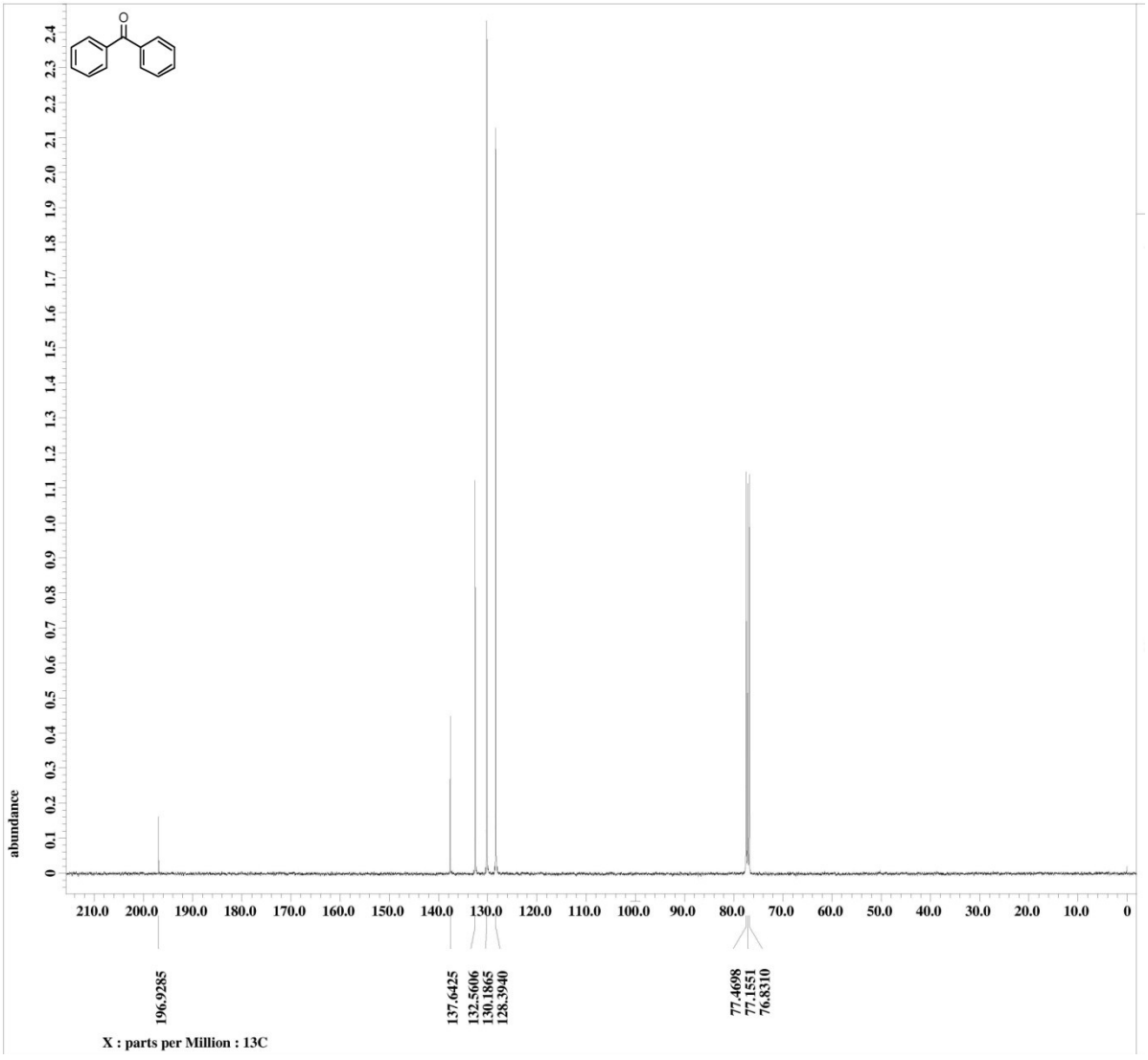
6 L. Gu, C. Jin, H. Zhang and L. Zhang, *J. Org. Chem*., 2014, **79**, 8453.

7 Y.-X. Liao and Q.-S. Hu, *J. Org. Chem*., 2010, **75**, 6986.

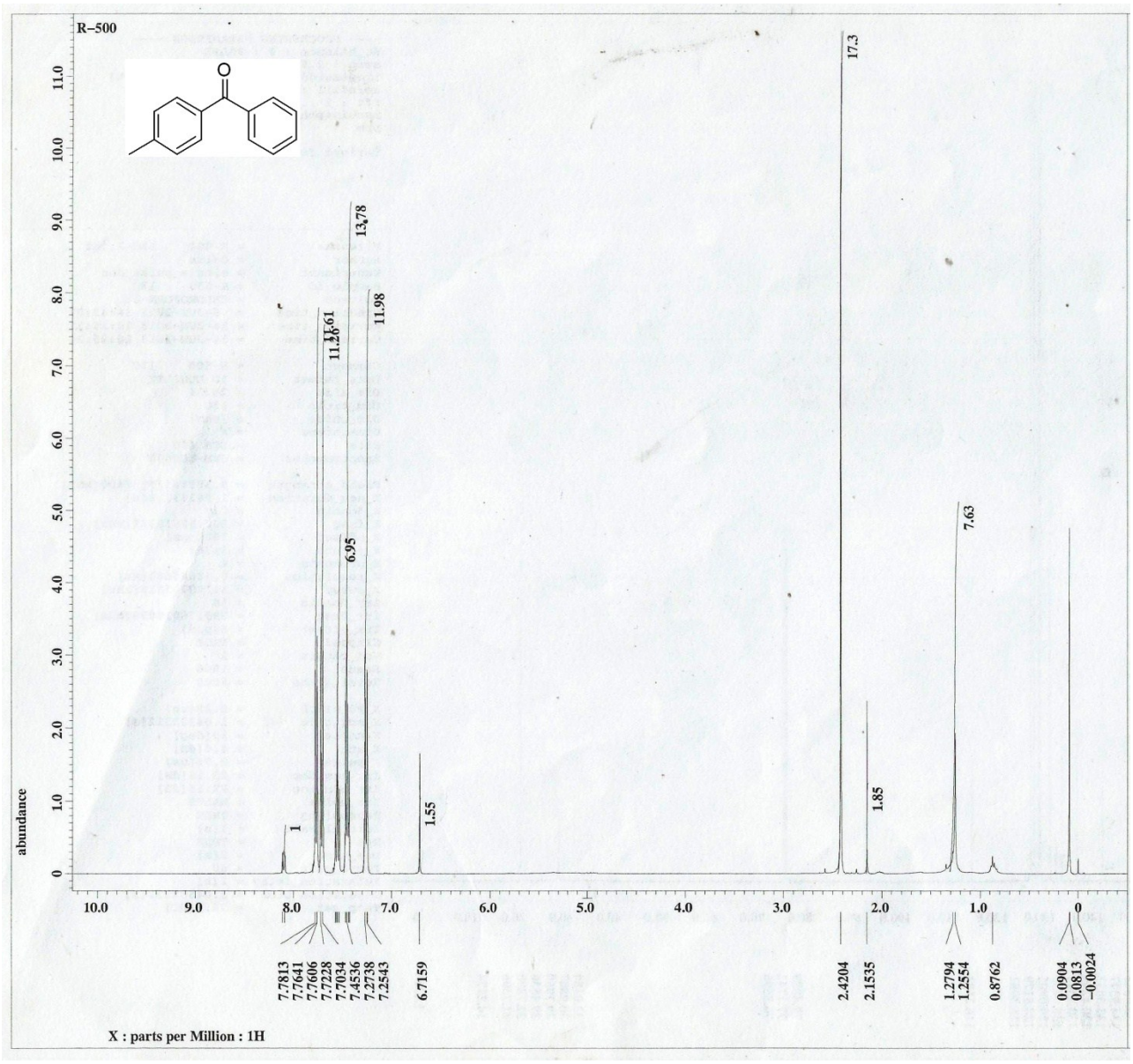
NMR Spectra



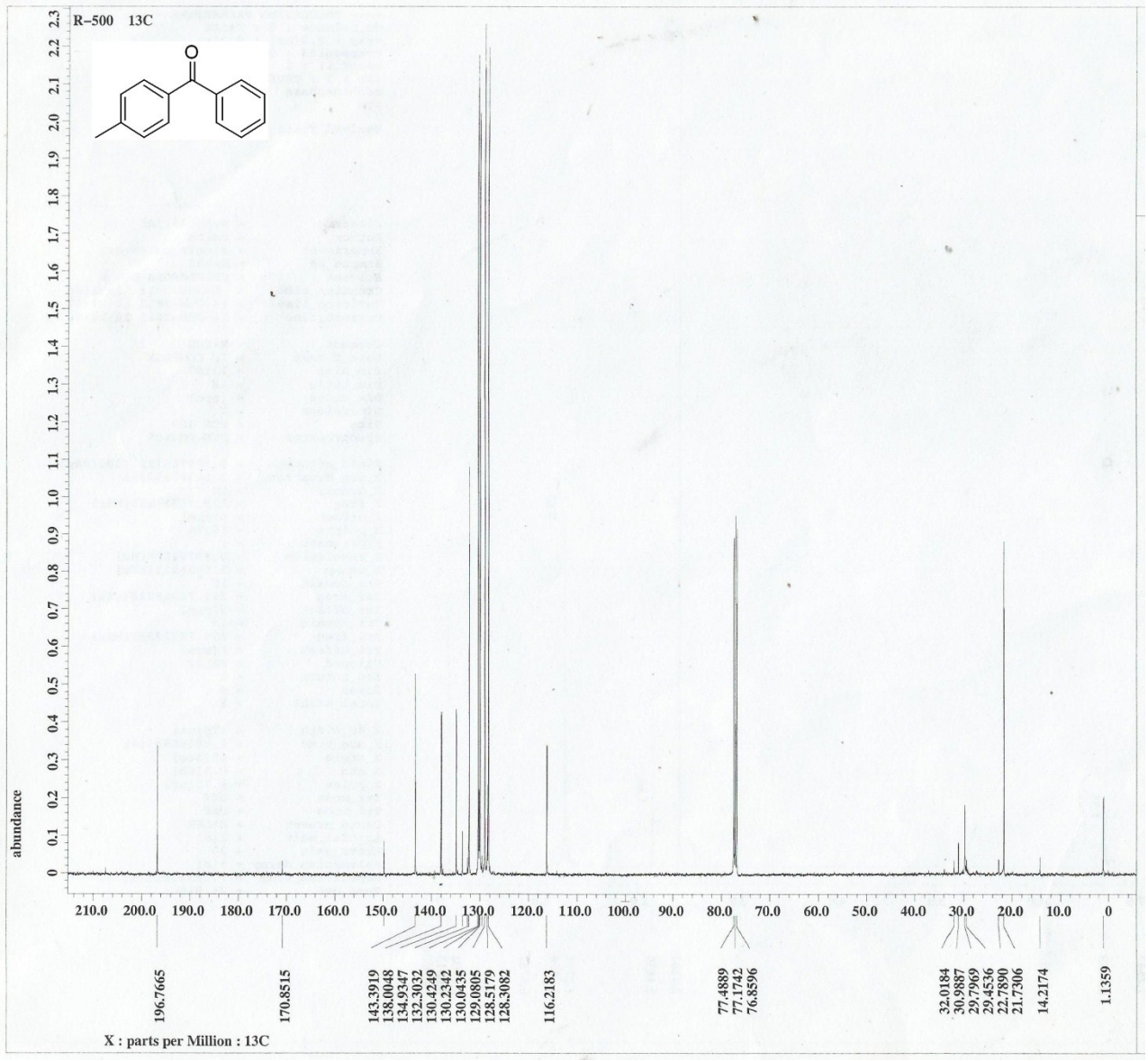
^{1}H NMR of Compound 4aa



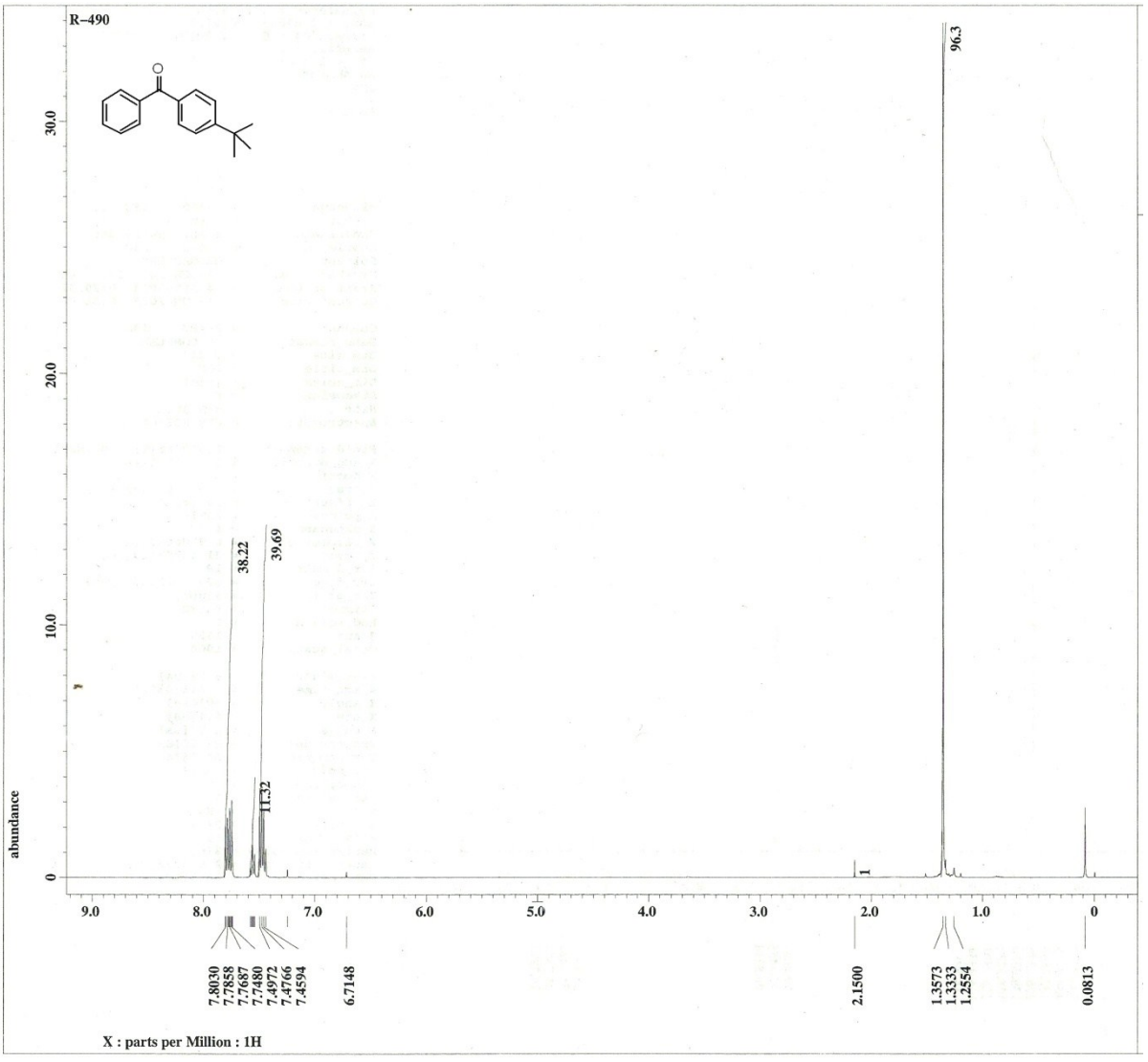
^{13}C NMR of Compound 4aa



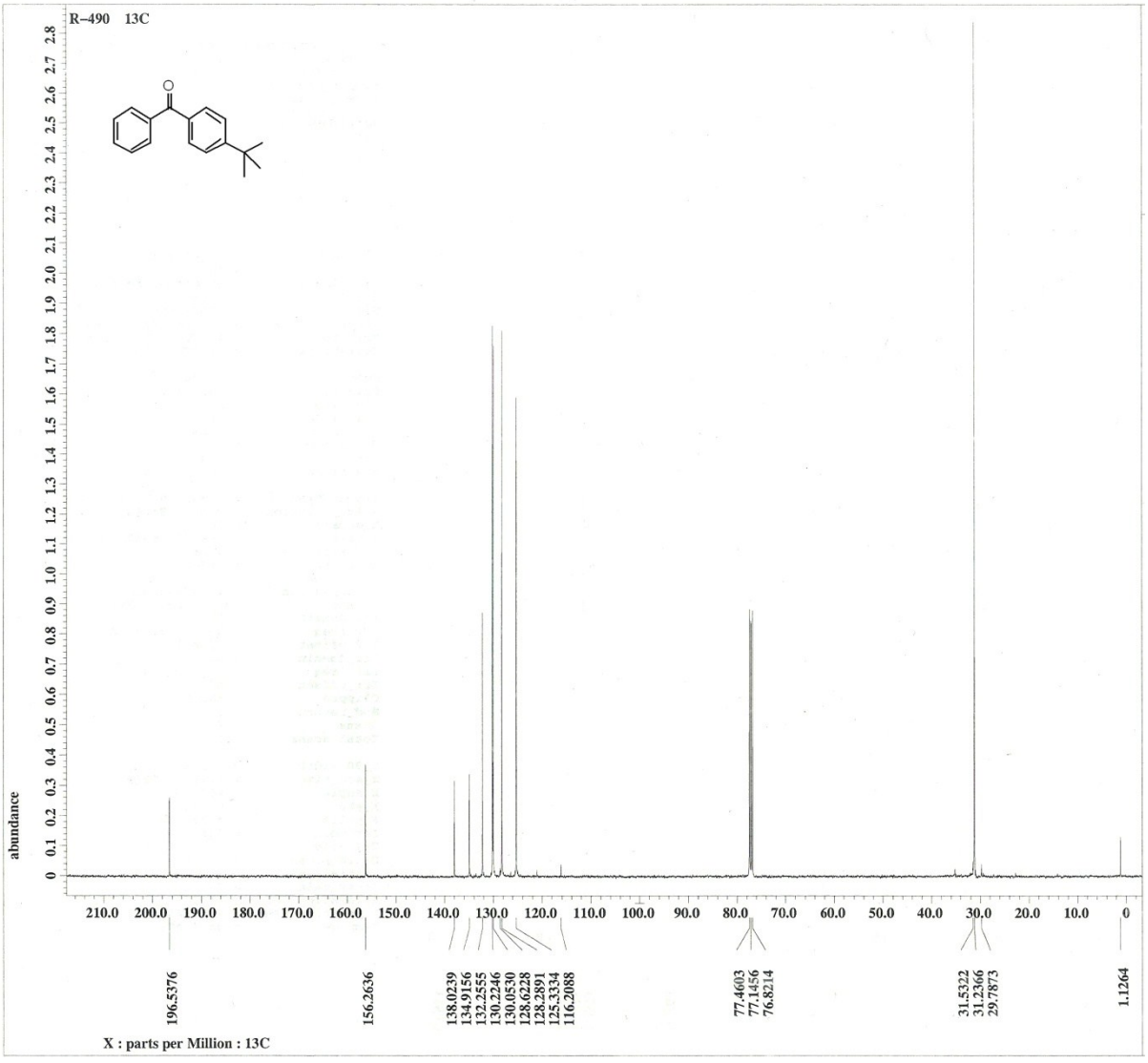
^{1}H NMR of Compound 4ab



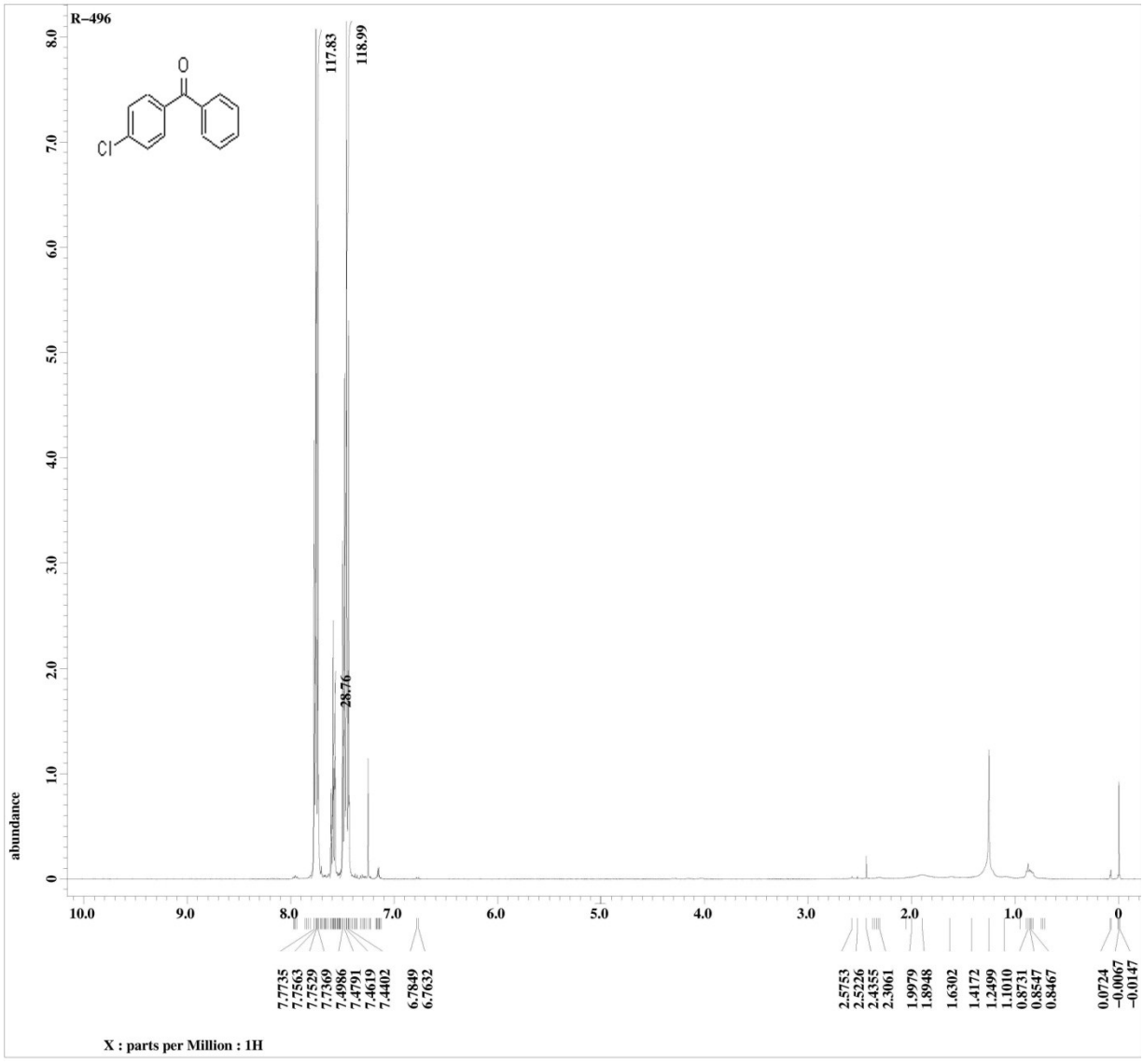
^{13}C NMR of Compound 4ab



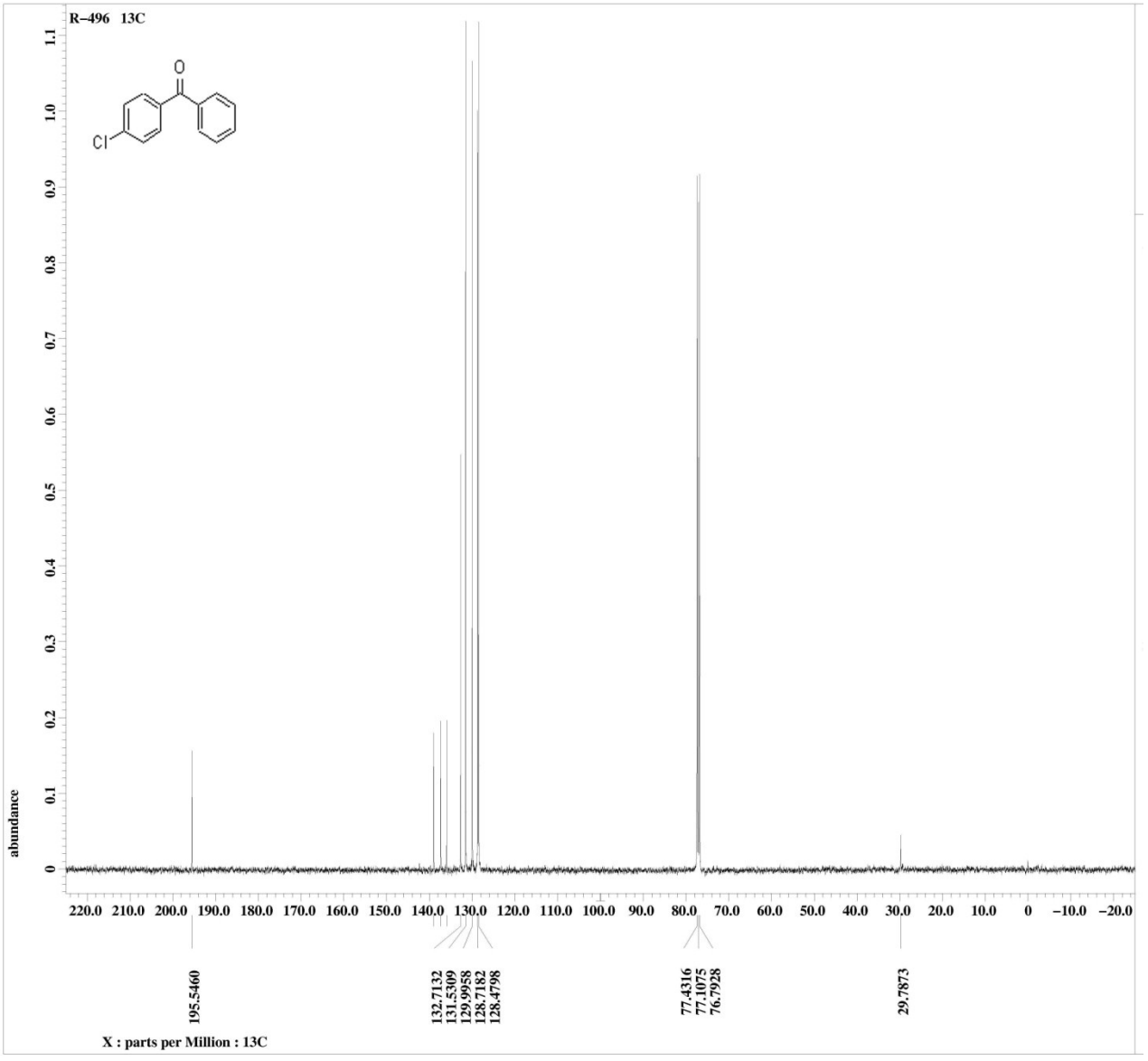
^{1}H NMR of Compound 4ac



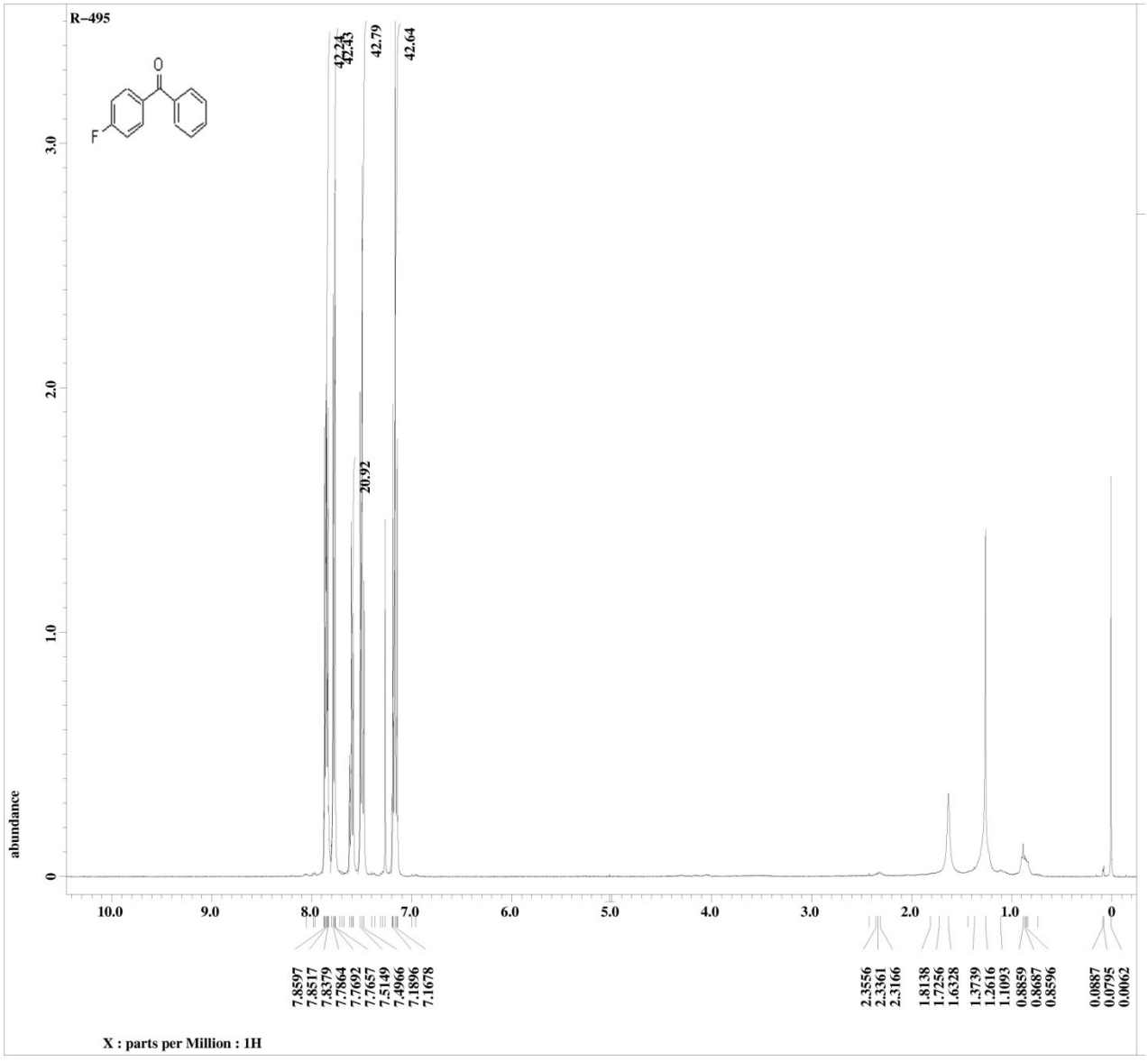
^{13}C NMR of Compound 4ac



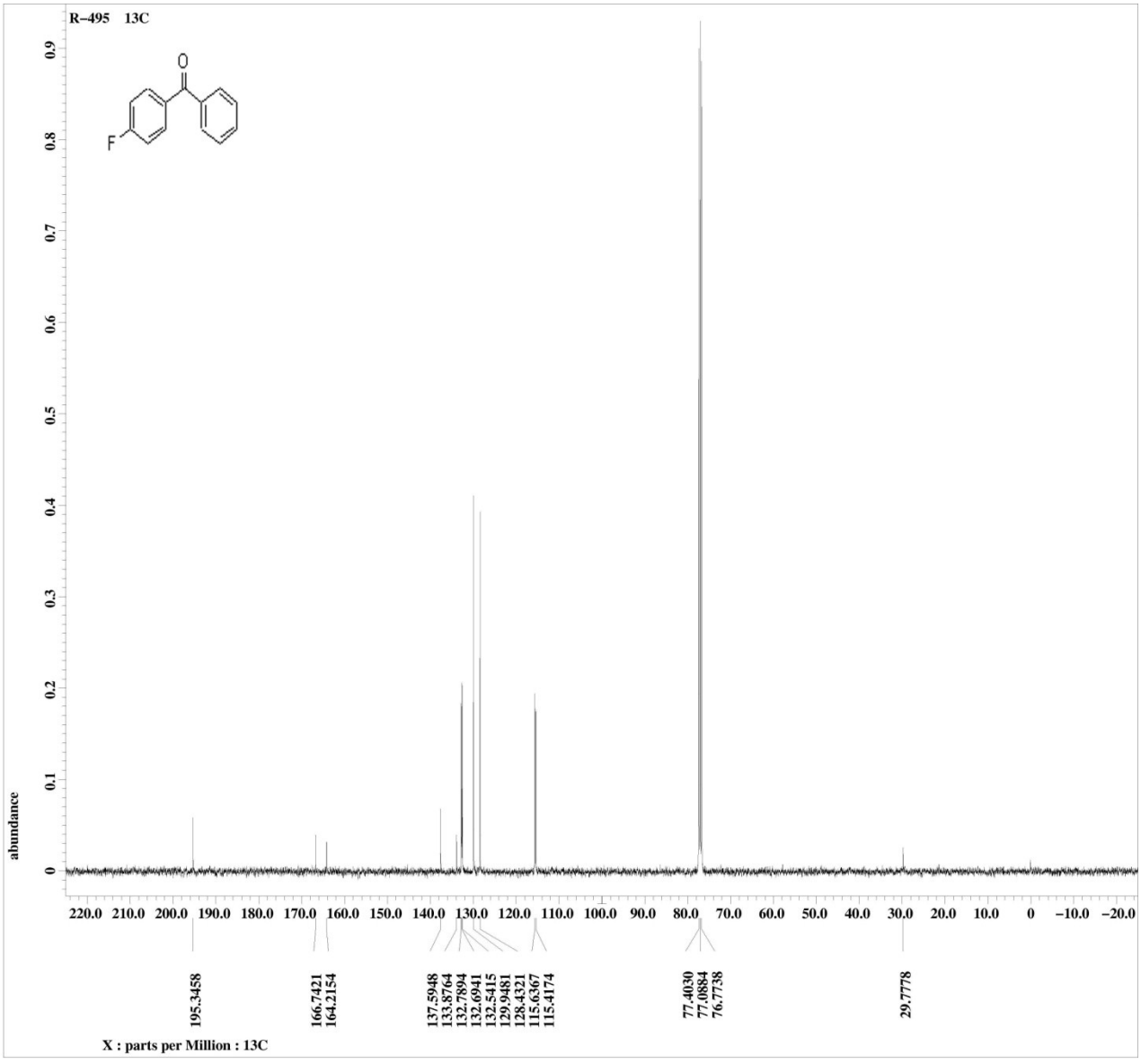
^{1}H NMR of Compound 4ad



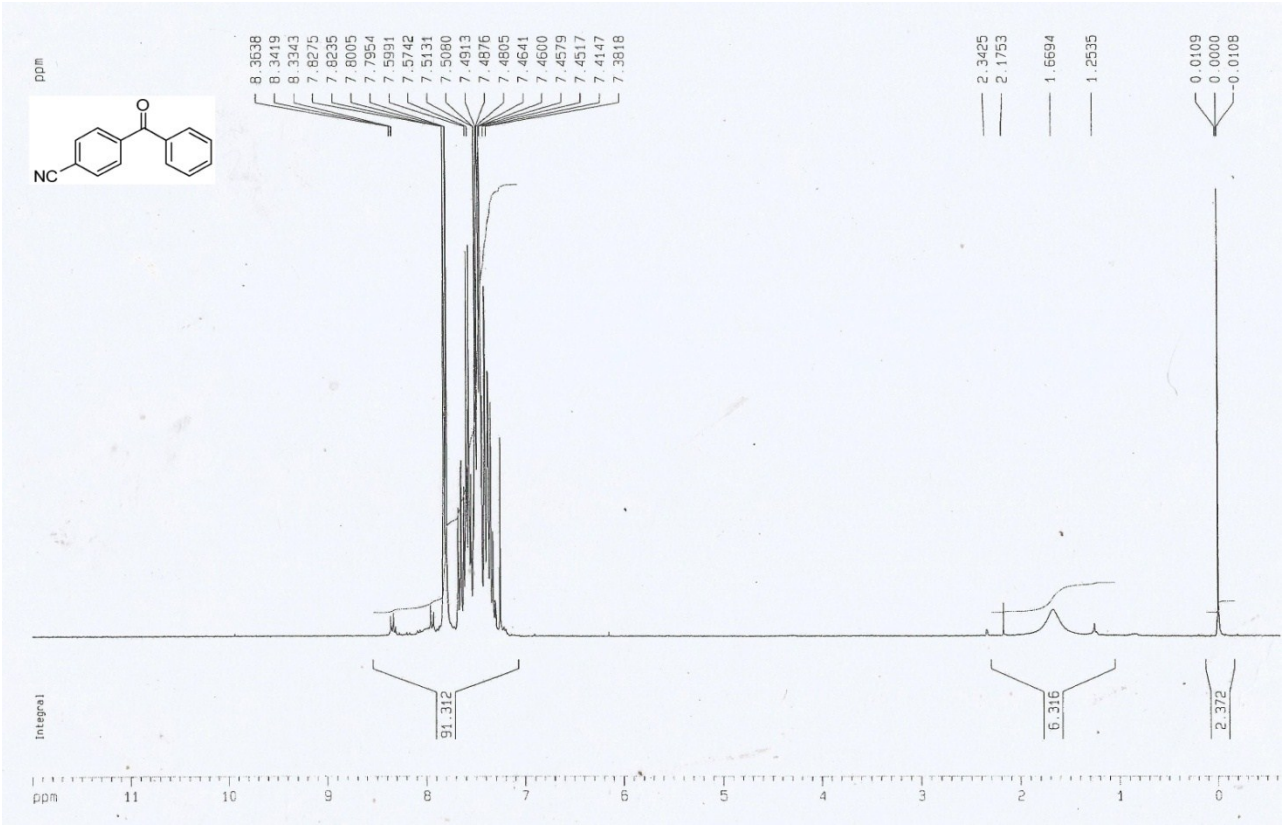
^{13}C NMR of Compound 4ad



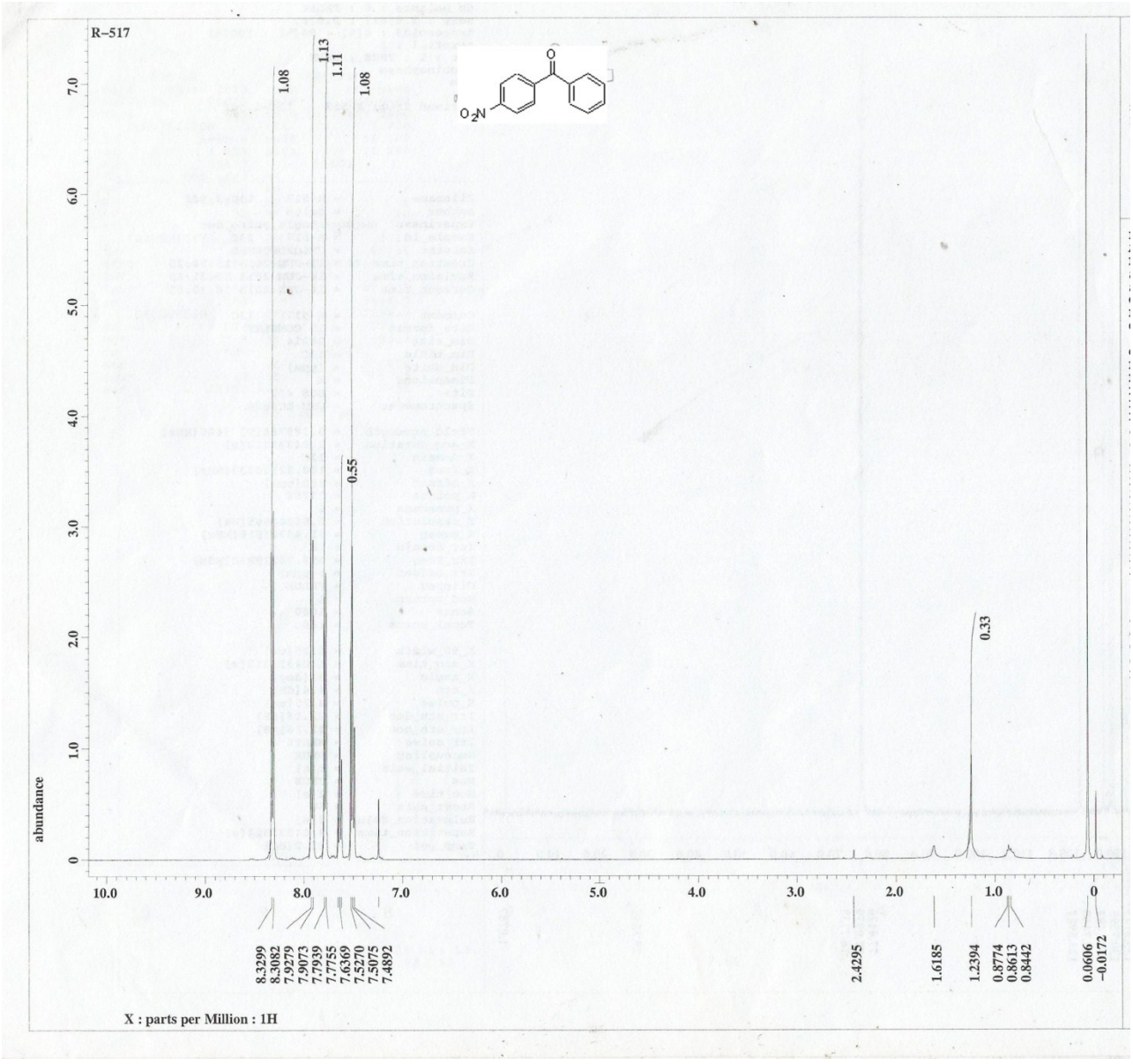
^{1}H NMR of Compound 4ae



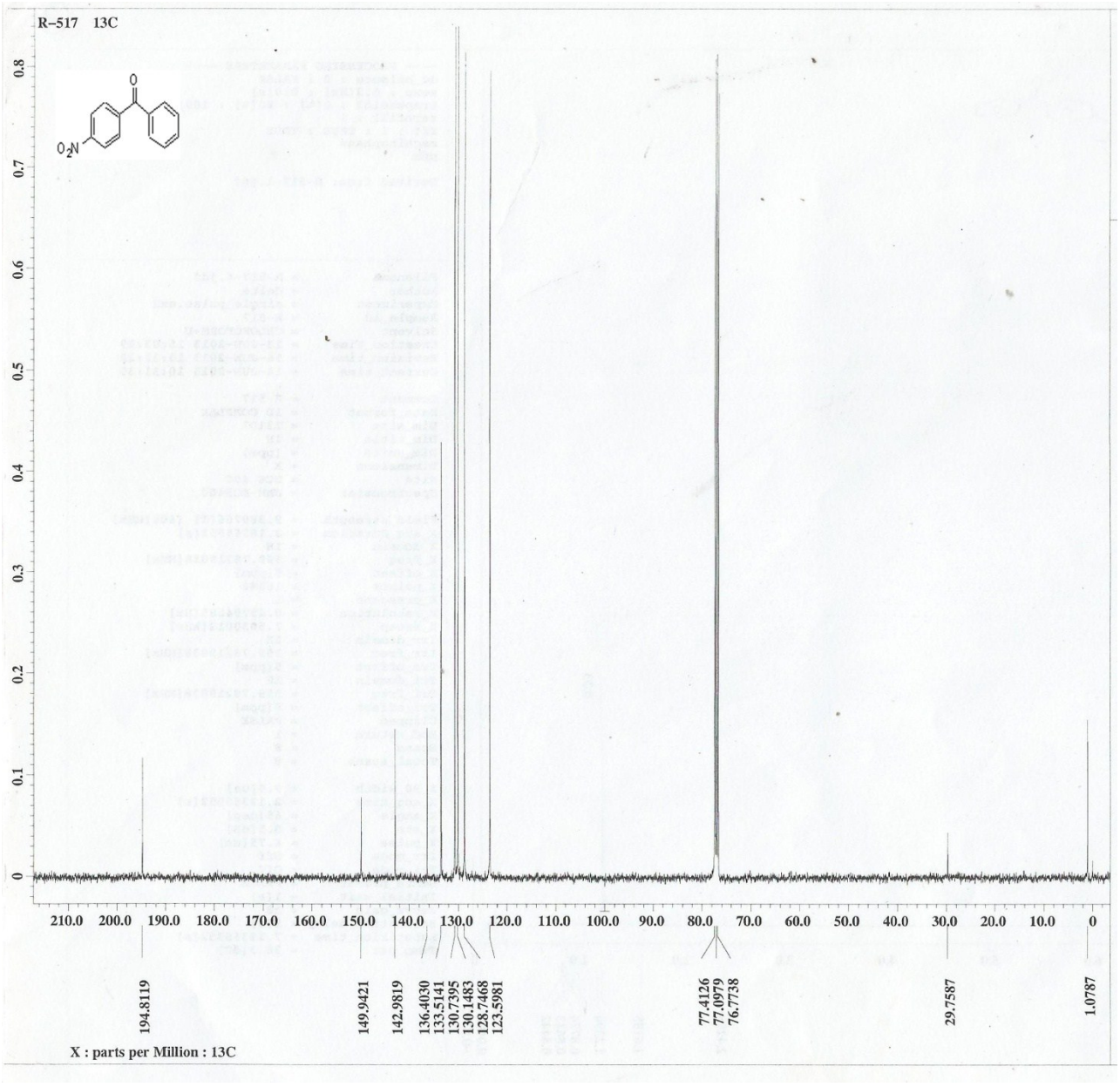
^{13}C NMR of Compound 4ae



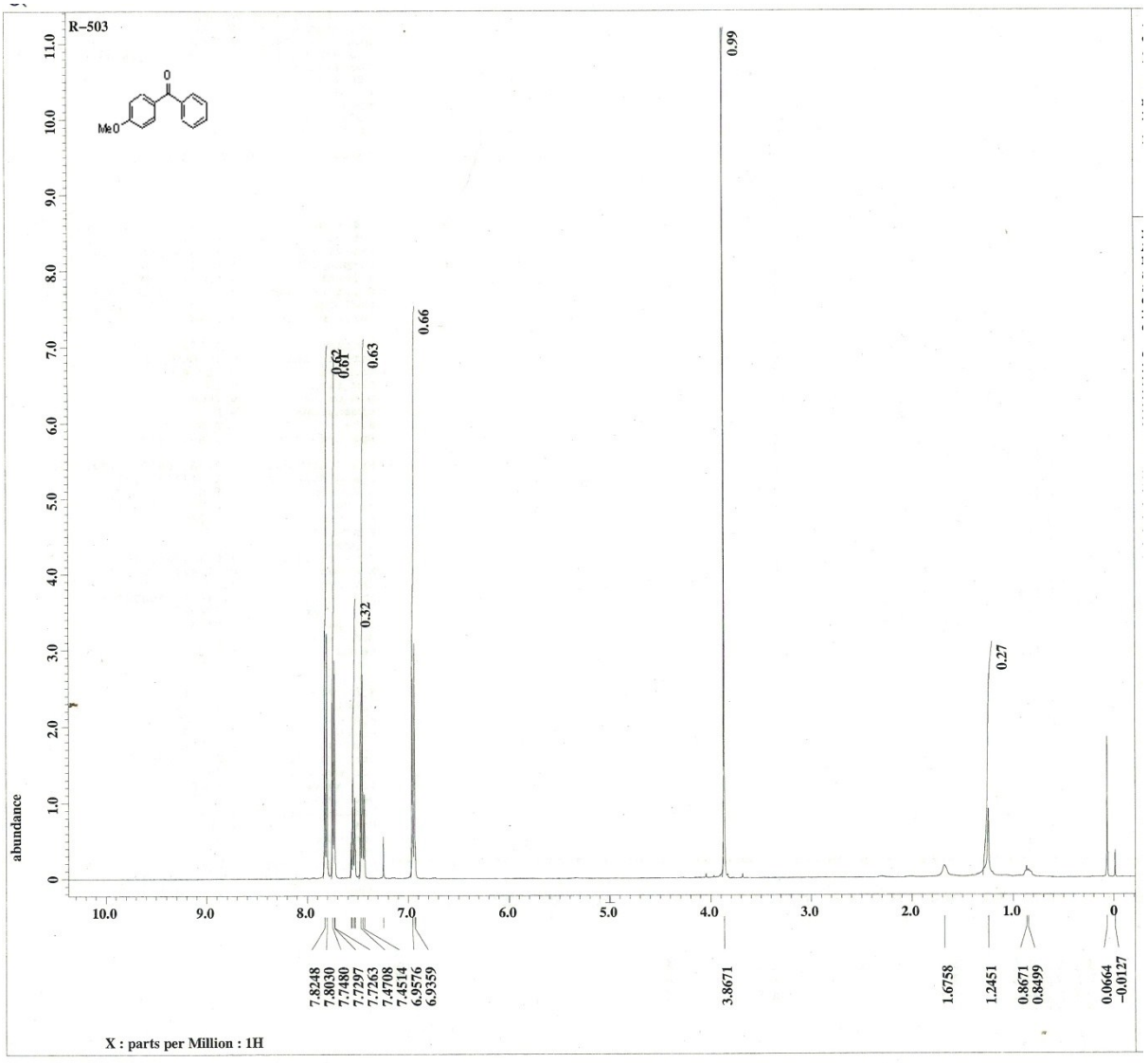
^{1}H NMR of Compound 4af



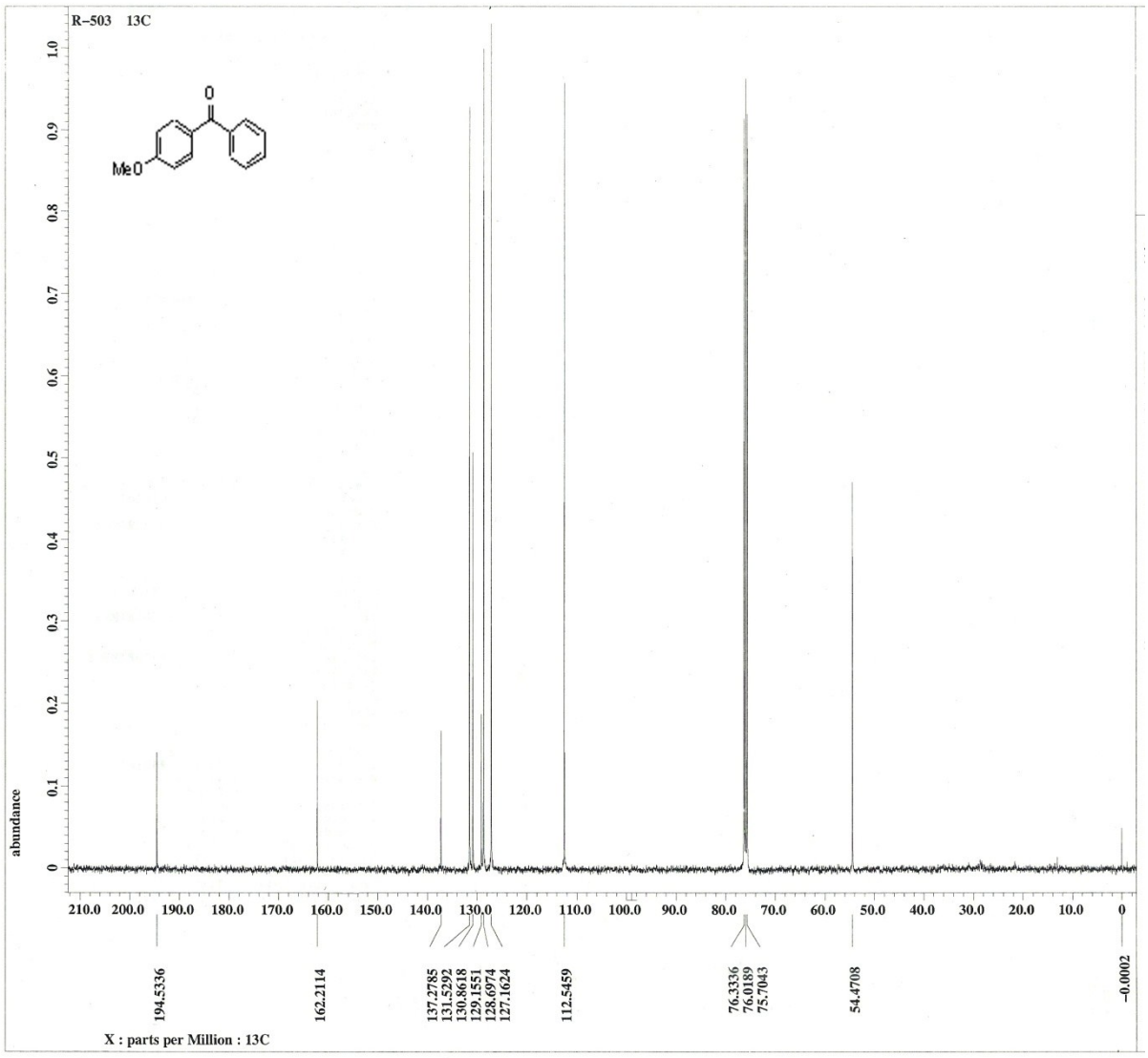
^{1}H NMR of Compound 4ba



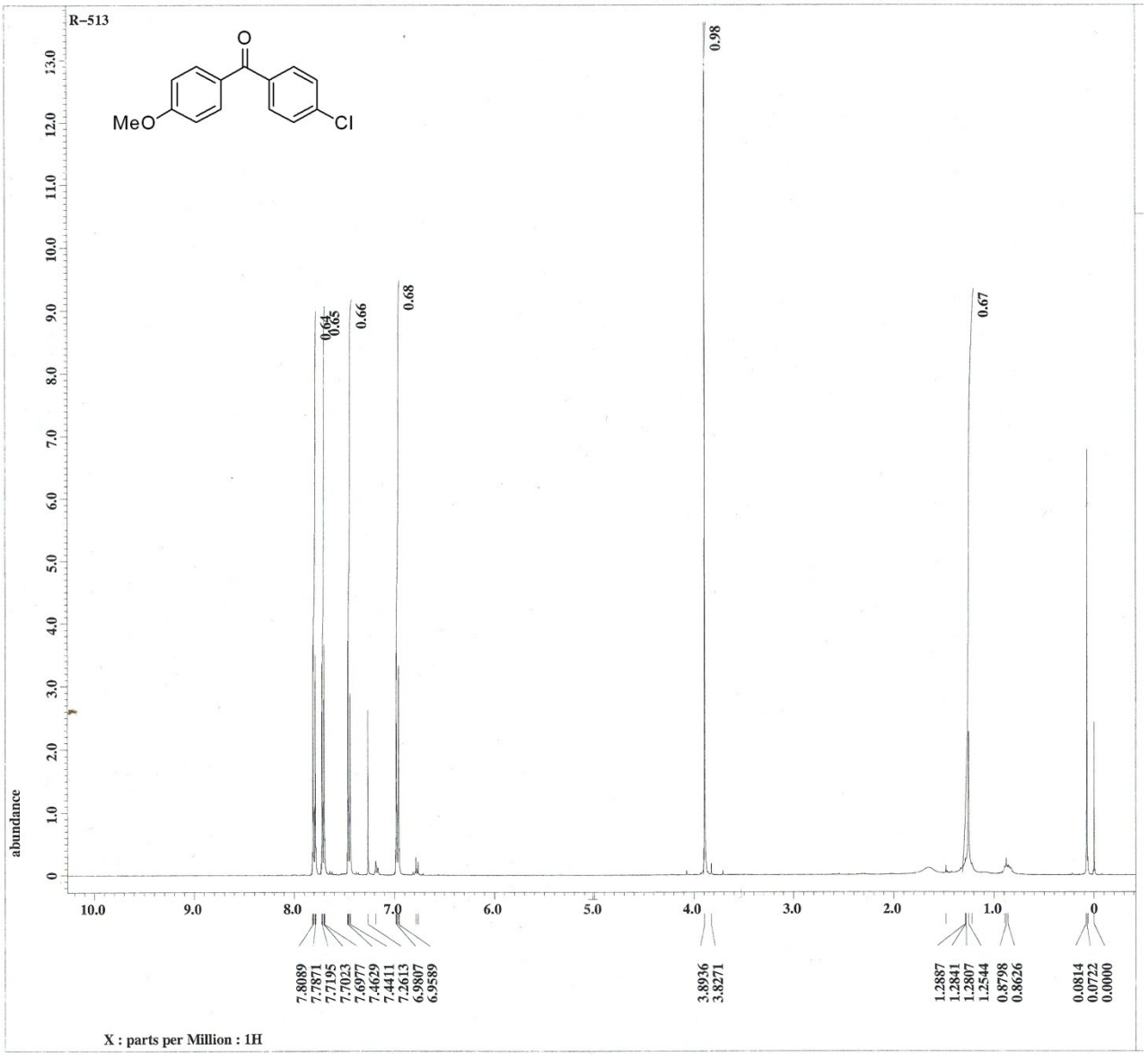
^{13}C NMR of Compound 4ba



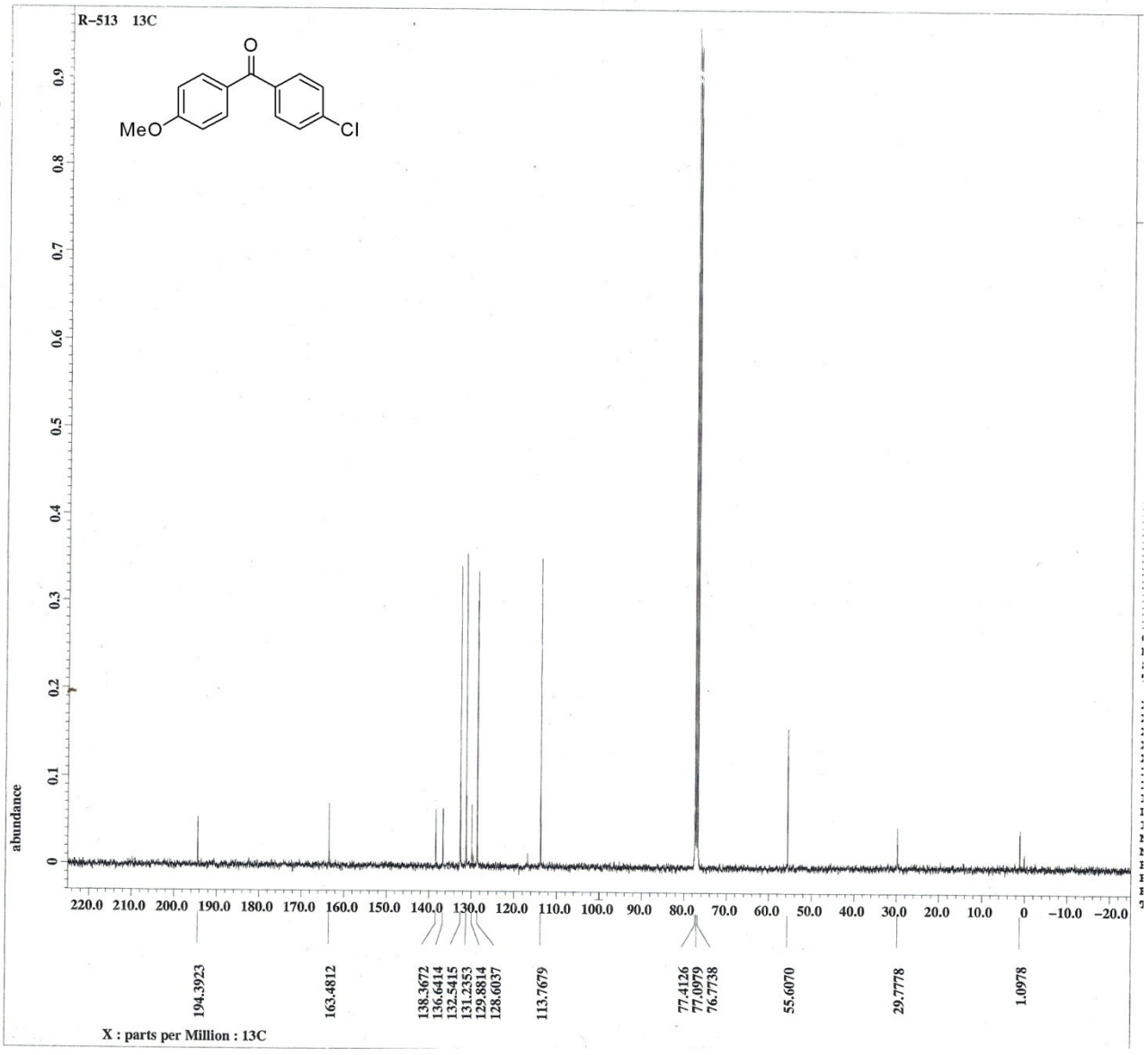
^{1}H NMR of Compound 4da



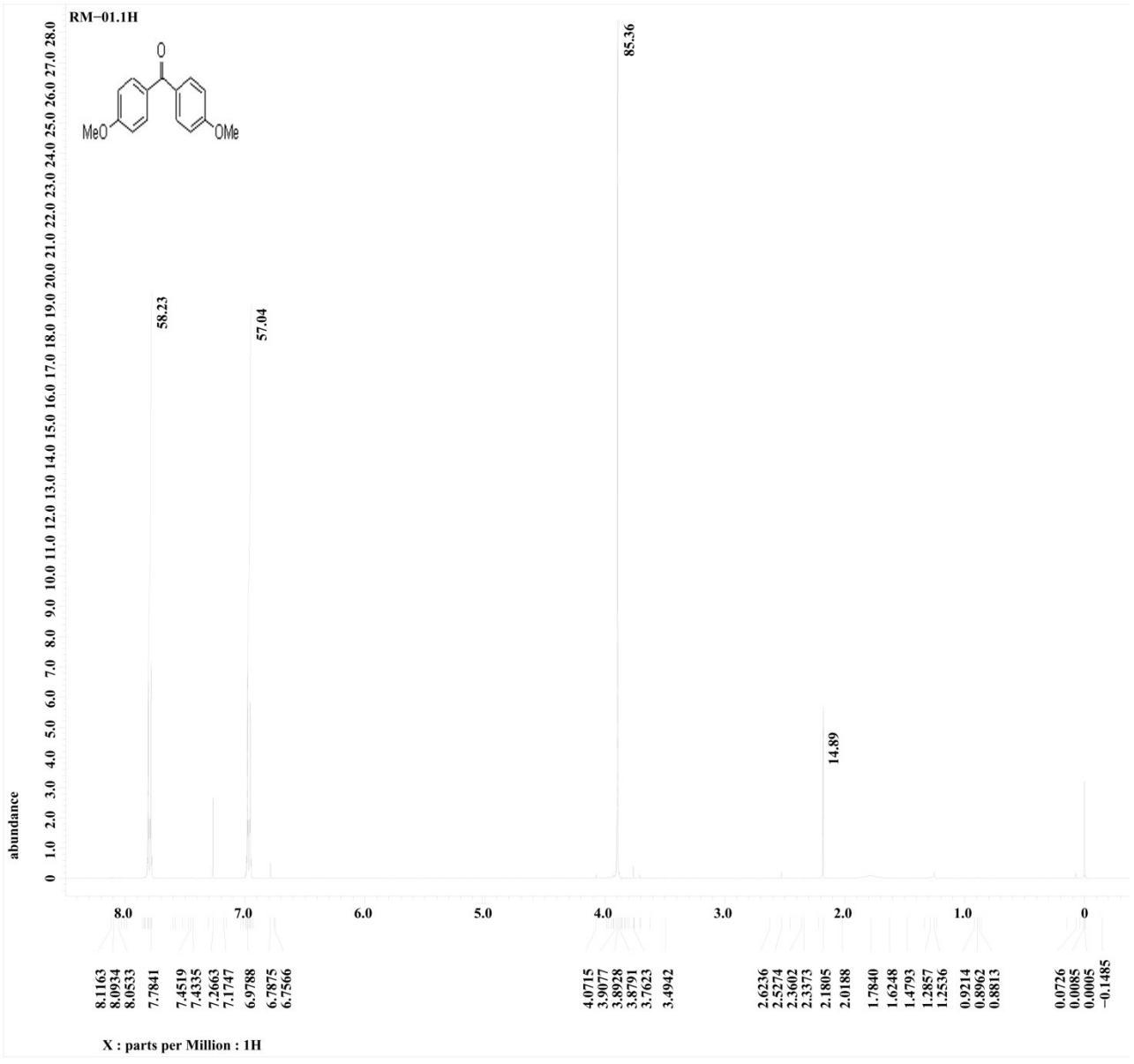
^{13}C NMR of Compound 4da



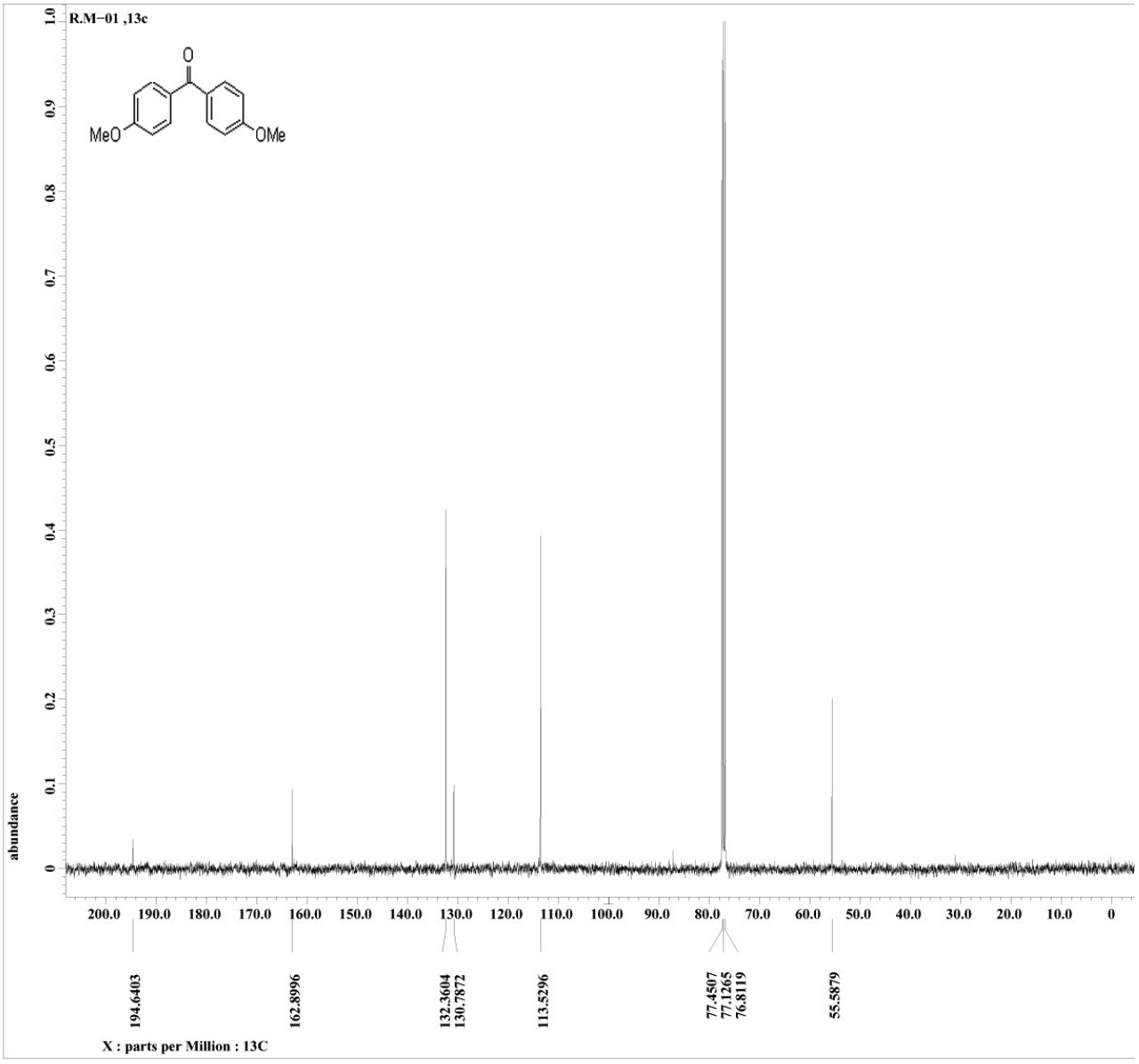
^{1}H NMR of Compound 4dd



^{13}C NMR of Compound 4dd



^{1}H NMR of Compound 4dg



^{13}C NMR of Compound 4dg