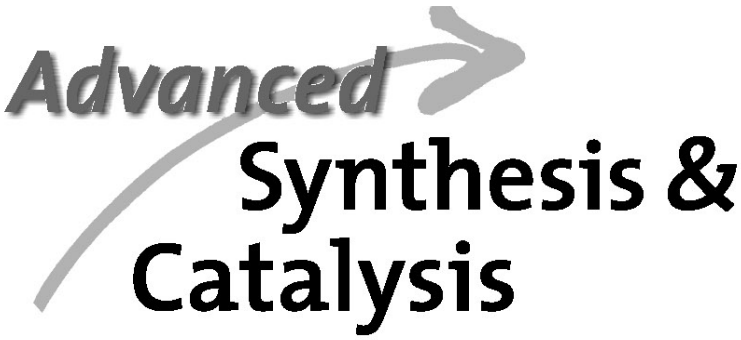

Supporting Information

Supporting Information

Palladium Nanoparticles Immobilized on Nano-Silica Triazine Dendritic Polymer (Pd_{np}-nSTDP): An Efficient and Reusable Catalyst for Suzuki-Miyaura Cross-Coupling and Heck Reactions

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General Remarks

1. General Remarks

The chemicals used in this work were purchased from Fluka and Merck chemical companies. Melting point were determined with a Stuart Scientific SMP2 apparatus. FT-IR spectra were recorded on a Nicolet-Impact 400D spectrophotometer. ^{1}H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ as solvent. Elemental analysis was performed on a LECO, CHNS-932 analyzer. Thermogravimetric analysis (TGA) was carried out on a Mettler TG50 instrument under air flow at a uniform heating rate of 5 $^oCmin^{-1}$ in the range 30-600 ^oC. The TGA instrument was re-calibrated at frequent intervals with

standards; the accuracy was always better than ±2.0%. The scanning electron microscope measurement was carried out on a Hitachi S-4700 field emission-scanning electron microscope (FE-SEM). The transmission electron microscopy (TEM) was carried out on a Philips CM10 Transmission Electron Microscope operating at 100 kV. The Pd content of the catalyst was determined by a Jarrell-Ash 1100 ICP analysis. The microwave system used in these experiments includes the following items: Micro-SYNTH labstation, equipped with a glass door, a dual magnetron system with pyramid shaped diffuser, 1000 W delivered power, exhaust system, magnetic stirrer, 'quality pressure' sensor for flammable organic solvents, and a ATCFO fiber optic system for automatic temperature control.

2. Synthesis of Triazine Dendritic Polymer Supported on Nano-Silica (nSTDP)

Activation of Nano-Silica

In a round-bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of nano-silica (10 g, 40-100 nm) and concentrated HCl (80 mL, 6 M) was heated in an oil-bath at 120 ^{o}C for 24 h. The mixture was filtered and the white powder was washed with distilled water until neutral pH. The solid was dried under vacuum at 120 ^{o}C.[1]

Preparation of Propylamine Functionalized Nano-Silica (AP-nSiO_2)

In a round-bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of activated nano-silica (3 g) and 3-aminopropyltrimethoxysilane (APTS) (8 mL) in 50 mL of anhydrous toluene was stirred under reflux conditions for 8 h. The reaction mixture was filtered and the solid material was washed with toluene in a continuous extraction apparatus (Soxhlet) to remove the unreacted starting material, and dried in a vacuum oven at 110 ^{o}C.[2]

Preparation of CC1-nSiO_2

The AP-nSiO_2 (2 g, 0.99 mmol/g) was added to a solution of cyanuric chloride (1.85 g, 10 mmol) and diisopropylethylamine (DIPEA) (10 mmol, 1.7 mL) in THF (10 mL). The reaction mixture was shaken overnight at room temperature. The solid material was separated by filtration, washed with hot THF for 12 h in Soxhlet to remove the unreacted starting materials and then dried in a vacuum oven at 50 ^{o}C.

Preparation of Nano-Silica Supported Triazine Dendritic Polymer (G1)

To a slurry of CC1-nSiO_2 (1 g) in DMF (12 mL) was added *bis*(3-aminopropyl)amine (8.11 mmol, 1 mL) and DIPEA (8.11 mmol, 1.4 mL). The reaction mixture was stirred at 80 ^{o}C for 16 h. The

solid material was filtered, washed with hot ethanol for 12 h in Soxhlet to remove the unreacted starting materials and then dried in a vacuum oven at 50 ^{o}C.

Preparation of CC2-nSiO_2

Nano-silica supported triazine dendritic polymer, G1 (1 g, 0.45 mmol) was added to a solution of cyanuric chloride (1.66 g, 9 mmol) and DIPEA (9 mmol, 1.56 mL) in THF (20 mL). The reaction mixture was agitated at room temperature for 16 h. The reaction mixture was filtered and the solid was washed with hot THF for 16 h in Soxhlet to remove the unreacted starting materials. Finally, the CC2-nSiO_2 was dried in a vacuum oven at 50 ^{o}C.

Preparation of Nano-Silica Supported Triazine Dendritic Polymer (G2 or nSTDP)

To a slurry of CC2-nSiO_2 (1 g, 0.36 mmol) in DMF (20 mL) was added *bis*(3-aminopropyl)amine (9.36 mmol, 1.14 mL) and DIPEA (9.36 mmol, 1.61 mL). The reaction mixture was agitated at 80 ^{o}C for 16 h and then filtered. The resulting nano-silica supported dendritic polymer (G2 or nSTDP) was washed with hot ethanol for 24 h in Soxhlet to remove unreacted starting materials and dried in a vacuum oven at 50 ^{o}C.

3. Preparation of Nano-Silica Triazine Dendritic Polymer Supported Palladium Nanoparticles (Pd$_{np}$-nSTDP)

A mixture of $PdCl_2$ (240 mg, 1.36 mmol) and NaCl (88 mg, 1.52 mmol) in methanol (8 mL) was stirred at room temperature for 24 h and then filtered. The filtrates were diluted with methanol (40 mL) and nSTDP (1 g, 0.21 mmol) was added to this solution. The resulting mixture was stirred at 60 ºC for 24 h. At the end of the reaction, the mixture was cooled to room temperature, sodium acetate (0.76 g, 9.28 mmol) was added and stirred at room temperature for 1 h. The solid was filtered, washed with methanol, water and acetone, to remove the unreacted starting materials and then dried in vacuum to afford Pd$_{np}$-nSTDP catalyst (1.07 g) as a light gray solid. Palladium analysis (ICP): 1.27%. Average particle diameter: 3.1 ± 0.5 nm (based on TEM and particle size analyzing).

4.General Procedure for Suzuki-Miyaura Cross-Coupling Catalyzed by Pd$_{np}$-nSTDP at Room Temperature and Under Microwave Irradiation

A mixture of aryl halide (1 mmol), arylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol) and Pd$_{np}$-nSTDP (0.006 mol% Pd) in 2 mL of DMF/H_2O (1:3) was stirred at room temperature or exposed to microwave irradiation (200 W, 70 ^{o}C) under air atmosphere for the period of time indicated in Table 4. The progress of the reaction was monitored by TLC (eluent: ether/ethyl acetate, 6:1). After completion of the reaction, ethyl acetate (15 mL) was added (in the case of the reaction under MW irradiation, the mixture was first cooled to room

temperature) and the catalyst was separated by centrifugation. The organic phase was washed with water (2×10 mL), dried over anhydrous $MgSO_4$ and evaporated. The residue was recrystallized from ethyl acetate and ether (1:3) to afford the pure product (Table 4).

5. General Procedure for Heck Reaction Catalyzed by Pd_{np}-nSTDP Under Thermal Conditions and Microwave Irradiation

In a round-bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of aryl halide (1 mmol), styrene (1.1 mmol), K_2CO_3 (1.5 mmol) and Pd_{np}-nSTDP (0.01 mol% Pd) in 2 mL of DMF/H_2O (1:3) was stirred at 85 ^oC or irradiated with MW (200 W, 70 ^oC) under air atmosphere for the desired time according to Table 6. The progress of the reaction was monitored by TLC (eluent: ether/ethyl acetate, 6:1). At the end of the reaction, the mixture was cooled to room temperature, ethyl acetate (15 mL) was added and the catalyst was separated by centrifugation. The organic layer was washed with water (2×10 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent and purification of the crude product by recrystallization from ethyl acetate and ether (1:3) afforded the pure product (Table 6).

6. General Procedure for Synthesis of Star- and Banana-Shaped Molecules Containing Benzene, Pyridine, Pyrimidine or 1,3,5-Triazine Central Cores via Suzuki-Miyaura Cross-Coupling Catalyzed by Pd_{np}-nSTDP

A mixture of 1,3,5-tribromobenzene, 2,6-dibromopyridine, 2,4,6-trichloropyrimidine or 2,4,6-trichlorotriazine (1 mmol), arylboronic acid (2.3-4.2 mmol), K_2CO_3 (3-4.5 mmol) and Pd_{np}-nSTDP (0.012-0.045 mol% Pd) in 8 mL of DMF/H_2O (1:3) was stirred at room temperature or exposed to MW irradiation (200 W, 70 ^oC) for the appropriate time according to Table 7. The work-up was performed as described for Suzuki Miyaura cross-coupling and the pure product was obtained by recrystallization of the crude product from ethyl acetate and ether (1:1).

7. Synthesis of S11 and S12 from S9 and S10 Catalyzed by Pd_{np}-nSTDP at Room Temperature and Under MW Irradiation (Scheme 4, Path a)

To a mixture of 1,3,5-tris(4-halophenyl)benzene (**S9 or S10**, prepared according to the previously reported method[3]) (1 mmol), arylboronic acid (4.5 mol) and K_2CO_3 (4.5 mmol) in 10 mL of DMF/H_2O (1:1), was added Pd_{np}-nSTDP (0.018 mol% Pd). The reaction mixture was stirred at room temperature or exposed to MW irradiation (270 W, 70 ^oC) for the time indicated in Scheme 4. The progress of the reaction was monitored by TLC (eluent: ether/EtOAc, 9:1). After completion of the reaction, ethyl acetate (15 mL) was added (in the case of the reaction under MW irradiation, the mixture was first cooled to room temperature) and the catalyst was separated by centrifugation. The organic phase was washed with water (2×10 mL), dried over anhydrous $MgSO_4$, and evaporated. The resulting crude material was purified by recrystallization from ethyl acetate and ether (1:1) to afford the pure product.

8. Synthesis of S11 and S12 by Suzuki-Miyaura Cross-Coupling and Subsequent Cyclotrimerization (Scheme 4, Path b)

In this manner, the reaction was performed in two steps. First, the desired 4-arylacetophenone was prepare by the reaction of 4-haloacetophenone with arylboronic acid according to the above mentioned general procedure for Suzuki-Miyaura cross-coupling catalyzed by Pd_{np}-nSTDP (Table 4, entries 3, 5, 10 and 11). Then, the cyclotrimerization of 4-arylacetophenone was carried out according to the reported procedure.[3] In this manner, a mixture of 4-arylacetophenone (1 mmol) and $H_3PW_{12}O_{40}$ (15 mol%) was subjected to MW irradiation (450 W, 90 ^oC) for the appropriate time according to Scheme 4. After completion of the reaction, monitored by TLC, hot ethyl acetate (10 mL) was added and the catalyst was separated by filtration. The solvent was evaporated and the resulting crude material was purified by recrystallization from ethyl acetate and ether (1:1) to afford the pure product.

9. Synthesis of 1,3,5-Tristyrylbenzenes (S15 and S16) via Heck Reaction Catalyzed by Pd_{np}-nSTDP Under Thermal Conditions and Microwave Irradiation

The 1,3,5-tribromobenzene (1 mmol), styrene (5.5 mmol), K_2CO_3 (4.5 mmol) and Pd_{np}-nSTDP (0.08 mol% Pd) were mixed in DMF/H_2O (1:1, 10 mL). The reaction mixture was stirred at 85 ^oC or irradiated with MW (300 W, 85 ^oC) for the appropriate time as mentioned in Scheme 6. The reaction progress was monitored by TLC (eluent: ethyl acetate/ether, 1:6). After completion of the reaction, the mixture was cooled to room temperature, ethyl acetate (15 mL) was added and the catalyst was separated by centrifugation. The organic phase was washed with water (2×10 mL), dried over anhydrous $MgSO_4$, and evaporated. The organic phase was evaporated and the residue was recrystallized from *n*-hexane to afford the pure product.

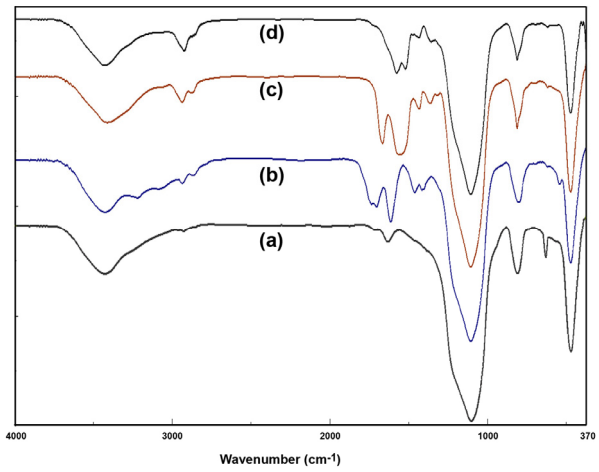


Figure 1. The FT-IR spectra of: a) AP-nSiO_2; b) CC1-nSiO_2; c) G1 and d) G2 (nSTDP).

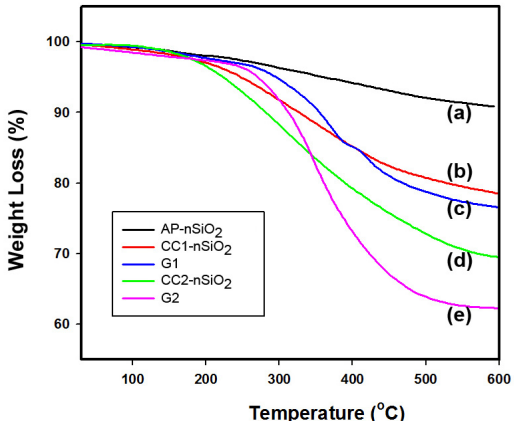


Figure 2. TGA spectra of: a) AP-nSiO_2; b) CC1-nSiO_2; c) G1; d) CC2-nSiO_2 and e) G2.

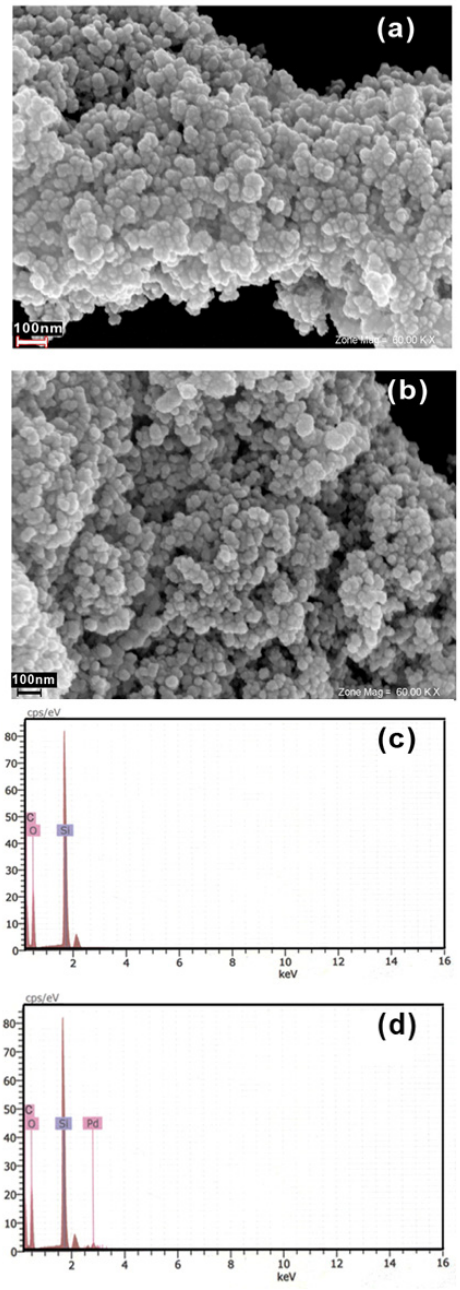


Figure 3. FE-SEM image of: a) nSTDP and b) Pd_{np}-nSTDP. SEM-EDX spectrum of: c) nSTDP and d) Pd_{np}-nSTDP.

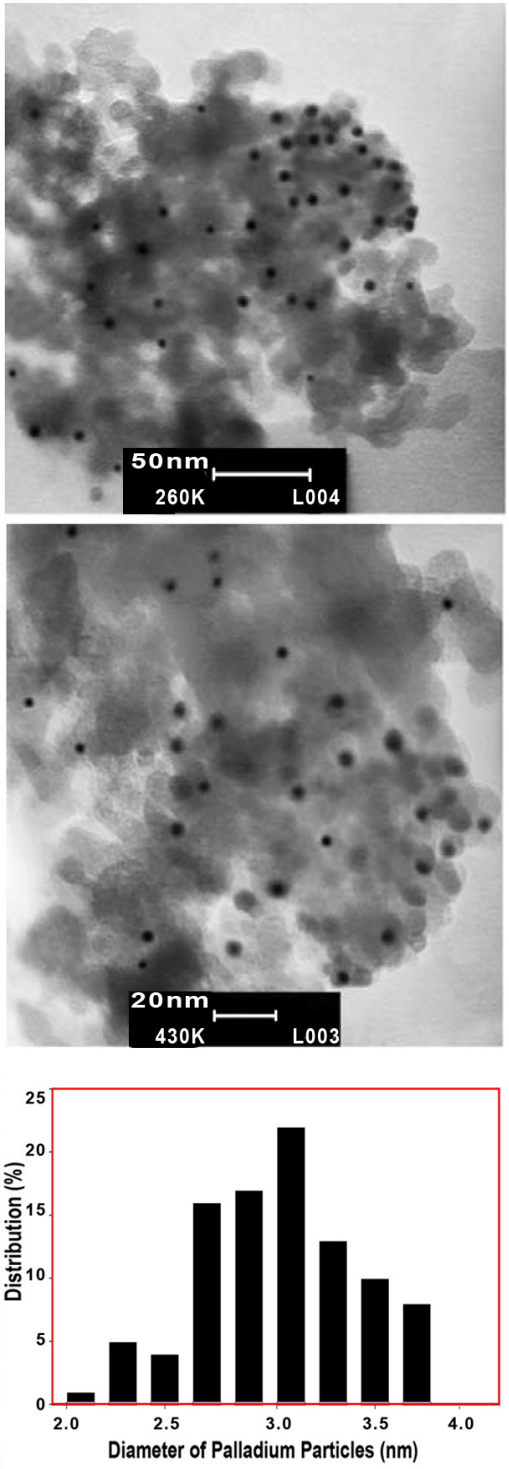


Figure 4. TEM image and particle size distribution results for Pd_{np}-nSTDP catalyst.

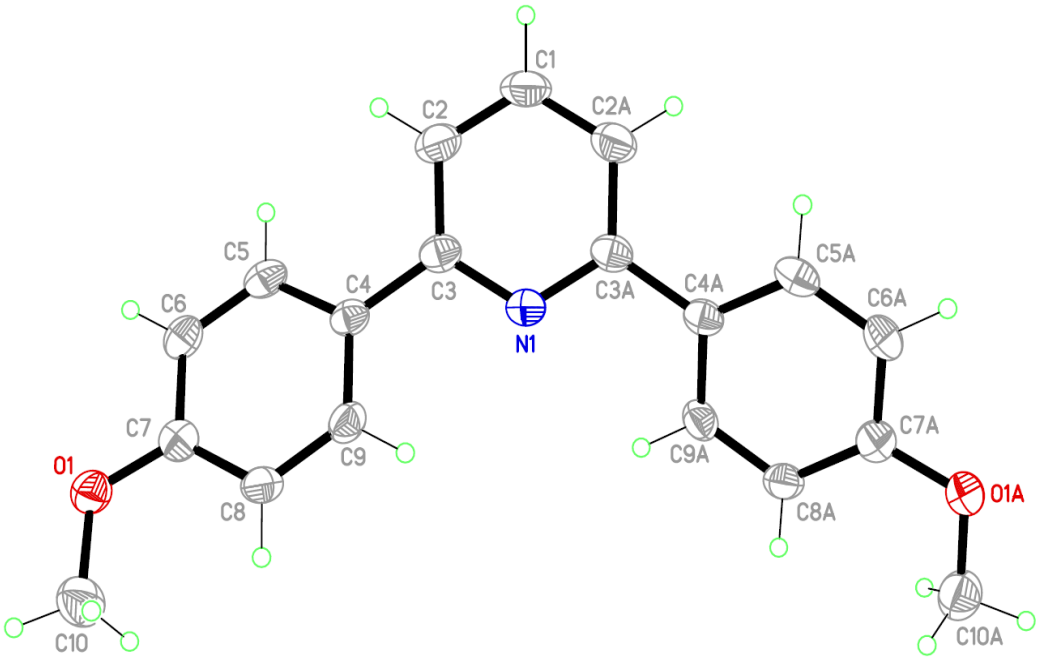
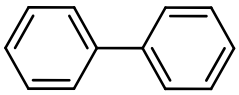


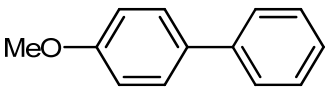
Figure 5. Crystal structure of compound **S2.**

15. Spectroscopic data of the products:



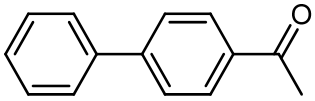
Biphenyl (Table 4, entry 1)

Mp 68-69 °C (Lit.[4] 70-72 °C). IR (KBr) ν = 2997, 1602, 1495, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d , J = 8.0 Hz, 4H), 7.39 (t, J = 8.0 Hz, 4H), 7.31-7.27 (m, 2H).



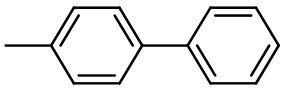
4-Methoxybiphenyl (Table 4, entry 2)

Mp 88-90 °C (Lit.[5] 88-89 °C). IR (KBr) ν = 2991, 1605, 1497, 1387, 1251, 876 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (t, J = 8.4 Hz, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 6.8 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H).



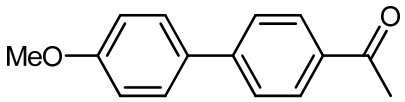
4-Phenylacetophenone (Table 4, entry 3)

Mp 117-118°C (Lit.[6] 122-123 °C). IR (KBr) ν = 2910, 1680, 1601, 1490, 1380, 860 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 6.8 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 6.8 Hz, 2H), 7.44 (t, J = 6.4 Hz, 1H), 2.66 (s, 3H).



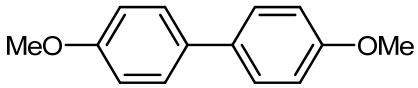
4-Methylbiphenyl (Table 4, entry 4)

Mp 61-62 °C (Lit.[7] 61-62 °C). IR (KBr) ν = 2925, 1605, 1490, 1380, 890 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H),7.47 (t, J = 7.2, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H).



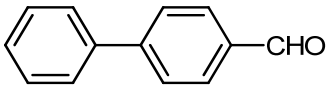
4(4'-Methoxyphenyl)acetophenone (Table 4, entry 5)

Mp 152-153 °C (Lit.[8] 156-157 °C). IR (KBr) ν = 2955, 1680, 1603,1495, 1389, 1240, 882 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H), 2.65 (s, 3H).



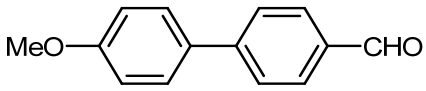
4,4'-Dimethoxybiphenyl (Table 4, entry 9)

Mp 172-173 °C (Lit.[9] 168-170 °C). IR (KBr) ν = 2938, 1680, 1601,1490,1378, 1253, 852 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.8 Hz, 4H), 7.50 (d, J = 8.8 Hz, 4H), 3.87 (s, 6H).



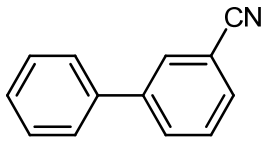
Biphenyl-4-carbaldehyde (Table 4, entry 12)

Mp 62-63 °C (Lit.[10] 62-65 °C). IR (KBr) ν = 2950, 2831, 1699, 1602, 1495, 890, 680. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H).



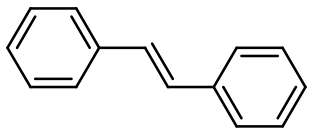
4'-Methoxybiphenyl-4-carbaldehyde (Table 4, entry 13)

Mp 109-110 ^{o}C (Lit.[10] 105-108 ^{o}C).). IR (KBr) ν = 2839, 1706, 1605 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H).



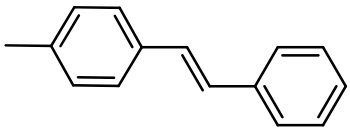
Biphenyl-3-carbonitrile (Table 4, entry 14)

Mp 48-49 ^{o}C (Lit.[11] 48 ^{o}C). IR (KBr) ν = 2967, 2192, 1601, 1492, 901, 710 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.80-7.77 (m, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H).



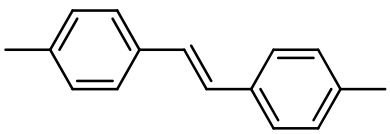
(*E*)-Stilbene (Table 6, entry 1)

Mp 120-122 ^{o}C (Lit.[12] 125 ^{o}C). IR (KBr) ν = 2992, 1602, 1495, 780 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.2 Hz, 4H), 7.39 (t, J = 7.6 Hz, 4H), 7.29 (t, J = 7.6 Hz, 2H), 7.16 (s, 2H).



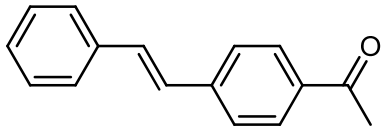
(*E*)-4-Methylstilbene (Table 6, entry 2)

M.p.:122-123 ^{o}C (Lit.[13] 119-122 ^{o}C). IR (KBr) ν = 2987, 1600, 1495, 1380, 885 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 2H), 6.95 (A of ABq, J = 16 Hz, 1H), 6.88 (B of ABq, J = 16 Hz, 1H), 2.30 (s, 3H).



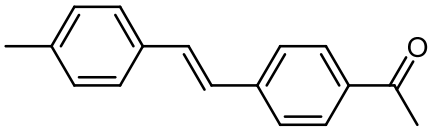
(E)-1,2-Di-*p*-tolylethene (Table 6, entry 3)

Mp 181-183 °C (Lit.[14]184-185 °C). IR (KBr) v = 2992, 1601, 1494, 1380, 880 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, J = 7.6 Hz, 4H), 7.08 (d, J = 7.6 Hz, 4H), 6.96 (s, 2H), 2.28 (s, 6H).



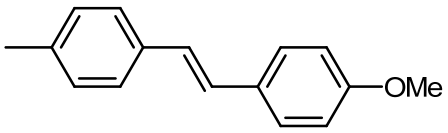
(E)-1-(Prop-1-en-2-yl)-4-styrylbenzene (Table 6, entry 4)

Mp142-144 °C (Lit.[15] 143-145 °C). IR (KBr) v = 2994, 1680, 1601, 1495, 1383, 880 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 7.25 (t, J = 7.2 Hz, 1H), 7.16 (A of ABq, J = 16 Hz, 1H), 7.06 (B of ABq, J = 16 Hz, 1H) 2.54 (3H, s).



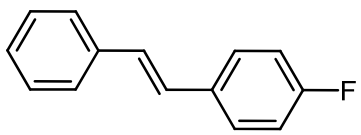
4(4-Methylstyrene)acetophenone (Table 6, entry 5)

Mp168-169 °C. IR (KBr) v =2989,1685, 1601,1480, 1387, 892 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J= 7.2 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.27 (d, J = 6.4 Hz, 2H), 7.11 (d, J = 6.4 Hz, 2H), 7.07 (A of ABq, J = 16.4 Hz, 1H), 6.98 (B of ABq, 6,98, J = 16.4 Hz, 1H), 2.50 (s, 3H), 2.28 (s, 3H).



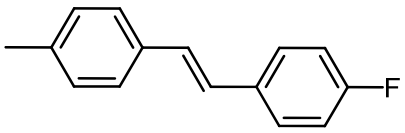
(E)-1-Methoxy-4-(4-methylstyryl)benzene (Table 6, entry 8)

Mp 145-147 °C (Lit.[14]142-144 °C). IR (KBr) v = 2969, 1602, 1495, 1378, 1253, 860 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 8.0 Hz, 2H), 6.95 (A ofABq, J = 16.4 Hz, 1H), 6.84 (B of ABq, J = 16.4 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 2.28 (s, 3H).



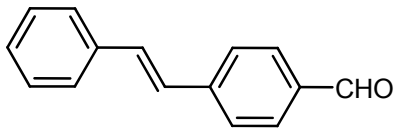
(E)-1-Fluoro-4-styrylbenzene (Table 6, entry 9)

Mp 113-115 °C (Lit.[14] 117-119 °C). IR (KBr) v = 2985,1605, 1499, 1153, 880 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.39 (m, 4H), 7.28 (t, J = 8.8 Hz, 2H), 7.21-717 (m, 1H), 7.02-6.94 (m, 4H).



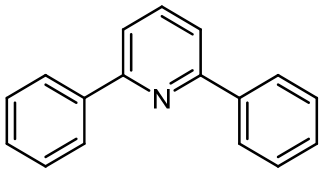
(E)-1-Fluoro-4-(4-methylstyryl)benzene (Table 6, entry 10)

Mp 125-126 ^{o}C (Lit.[16] 125-126 ^{o}C). IR (KBr) v =2990, 1600, 1495, 1375, 1175, 875 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.37 (m, 4H), 7.32 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.98- 6.93 (m, 2H), 2.28 (s, 3H)



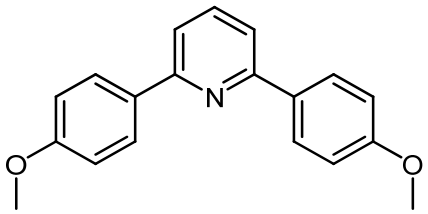
(E)-4-Styrylbenzaldehyde (Table 6, entry 14)

Mp 118-120 ^{o}C(Lit.[17] 115-116 ^{o}C). IR (KBr) v = 2995, 2851, 1701, 1603, 1499, 910, 845 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.92 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 6.4 Hz, 2H), 7.24 (t, J = 7.2 Hz. 1H), 7.21 (A of ABq, J = 16.4 Hz, 1H), 7.07(B of ABq, J = 16 Hz, 1H).



2,6-Diphenylprydine (S1, Table 7, entry 1)

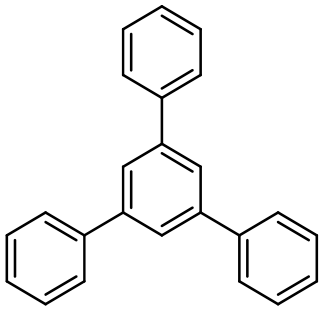
Mp 77-79 ^{o}C (Lit.[18] 80-81 ^{o}C) IR (KBr) v = 2986, 1593, 1577, 1492, 1018, 910, 780 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78-7.72 (m, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.47-7.42 (m, 4H), 739 (t, J = 6.4 Hz, 4H), 7.32 (t, J = 7.2 Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.8, 139.5, 137.5, 129.0, 128.7, 127.0, 118.6.



2,6-Bis(4-methoxyphenyl)pyridine (S2, Table 7, entry 2)

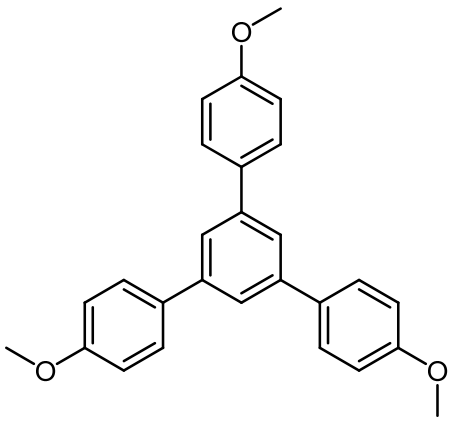
Mp 195-196 ^{o}C (Lit.[19] 197.7-198.4 ^{o}C). IR (KBr) v = 2910, 1606, 1578, 1513, 1376, 1248, 1020, 880cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 6.0 Hz, 4H), 7.66 (t, J = 8.0 Hz, 1H), 7.49

(d, J = 8.0 Hz, 2H), 6.93 (d, J = 6.0 Hz, 4H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.7, 156.4, 137.3, 135.0, 127.7, 114.1, 113.4, 55.3.



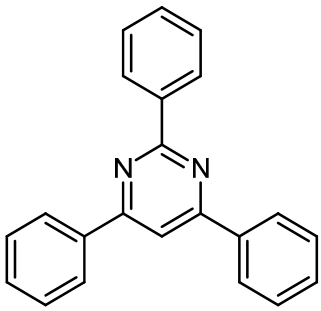
1,3,5-Triphenylbenzene (S3, Table 7, entry 3)

Mp 175-176 °C (Lit.[20a] 175-176 °C). IR (KBr) v = 2994, 1601, 1490, 850, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 3H), 7.63 (d, J = 7.2 Hz, 6H), 7.42 (t, J = 8.0 Hz, 6H), 7. 31 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 140.1, 128.9, 127.7, 127.2, 124.4.



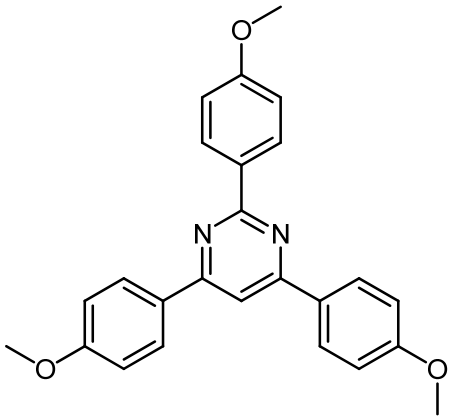
1,3,5-Tri(4-methoxyphenyl)benzene (S4, Table 7, entry 4)

Mp 141-143^{o}C (Lit.[20b] 140-142 ^{o}C). IR (KBr) v = 2910, 1605, 1499, 1380, 1253, 870, 711 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 3H), 7.65 (d, J = 8.8 Hz, 6H), 7.04 (t, J = 8.8 Hz, 6H), 3.89 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 141.4, 134.0, 128.3, 122.7, 114.2, 55.2.



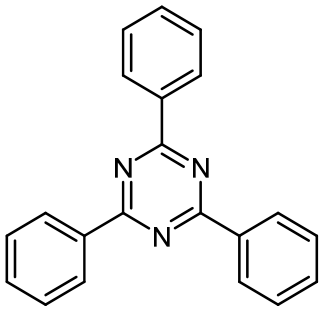
2,4,6-Triphenylprimidine (S5, Table 7, entry 5)

Mp 176-178 (Lit.[21a] 174-175 °C) IR (KBr) ν = 2945, 1604, 1514, 1364, 1250, 1182, 1021, 810 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.77-8.751 (m, 2H), 8.34- 8.31 (m, 4H), 8.05 (s, 1H), 7.61 -7.55 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.81, 164.5, 138.2, 10.3, 137.6, 130.8, 130.6, 128.9, 128.6, 128.5, 127.3.



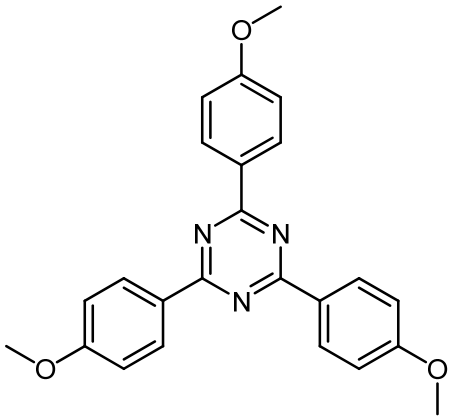
2,4,6-Tris(4-methoxyphenyl)pyrimidine (S6, Table 7, entry 6)

Mp 175-177 °C (Lit.[21b] 174 °C). IR (KBr) ν = 2936, 1606, 1510, 1364, 1242, 1175, 1021, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 8.8 Hz, 4H), 7.99 (d, J = 8.8 Hz, 2H), 7.73 (s, 1H), 6.96 (d, J = 8.8 Hz, 4H), 3.81 (s, 3H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 162.1, 16.0, 131.6, 130.5, 130.0, 129.2, 114.6, 107.8, 55.3.



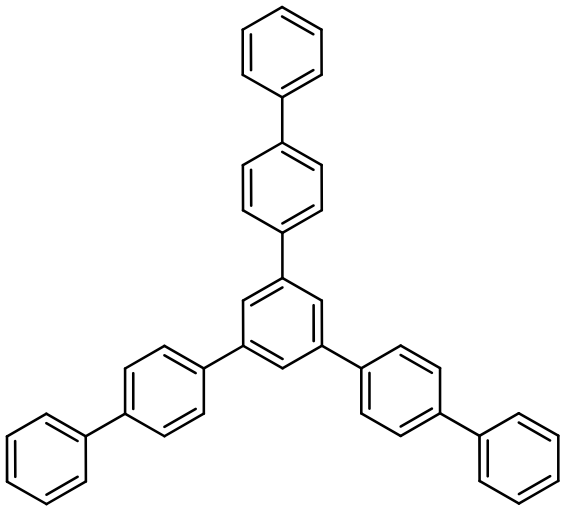
2,4,6-Triphenyltriazine (S7, Table 7, entry 7)

Mp 231-232°C (Lit.[22a] 231-232 °C]. IR (KBr) ν = 2988, 1595, 1520, 1480, 860, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54-7. 51 (m, 6H), 7.37 (t, J = 8.0 Hz, 6H), 7.28 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0, 136.6, 132.9, 129.4, 128.1.



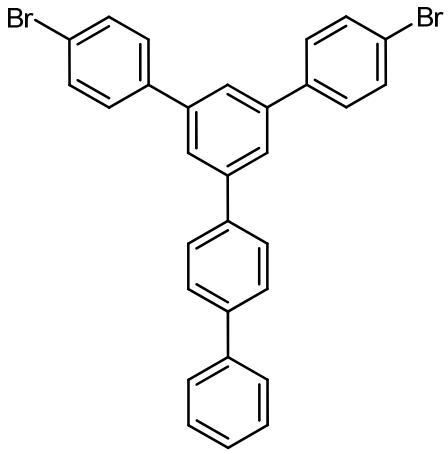
2,4,6-Tris(4-methoxyphenyl)triazine (S8, Table 7, entry 8)

Mp 219-220 ^{o}C (Lit.[22b] 214-216 ^{o}C), IR (KBr) ν = 2996, 1609, 1568, 1510, 1363, 1245, 1170, 827 cm^{-1}. H NMR (400 MHz, $CDCl_3$): δ = 8.1 (d, J = 8.4 Hz, 6H), 6.94 (d, J = 8.4 Hz, 6H), 3.82 (s, 9H). ^{13}C NMR(100 MHz, $CDCl_3$): δ = 163.7, 152.5, 129.1, 125.3, 114.0, 55.8.



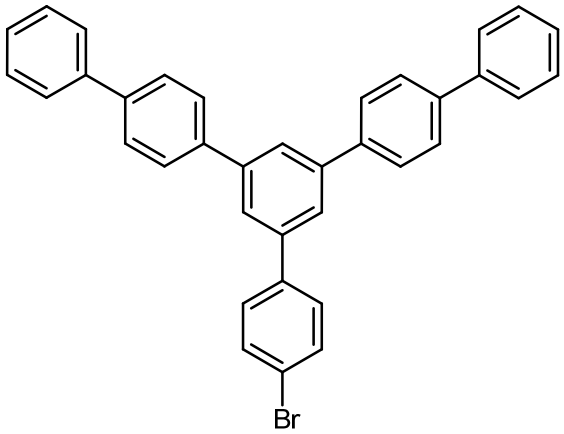
1,3,5-Tris(4-phenylphenyl)benzene (S11)

Mp 232-234 ^{o}C (Lit.[22c] 230 ^{o}C). IR (KBr) ν = 2979, 1590, 1486, 1380, 1217, 1005, 862 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 3H), 7.83 (d, J = 7.2 Hz, 6H), 7.72 (d, J = 7.6 Hz, 6H), 7.63 (d, J = 8.4 Hz, 6H), 7.41 (t, J = 8.0 Hz, 6H), 7.32 (t, J = 8.0 Hz, 3H). ^{13}C NMR(100 MHz, $CDCl_3$): δ = 142.0, 141.7, 141.1, 140.8, 129.5, 128.8, 128.0, 127.8, 127.0, 125.0.



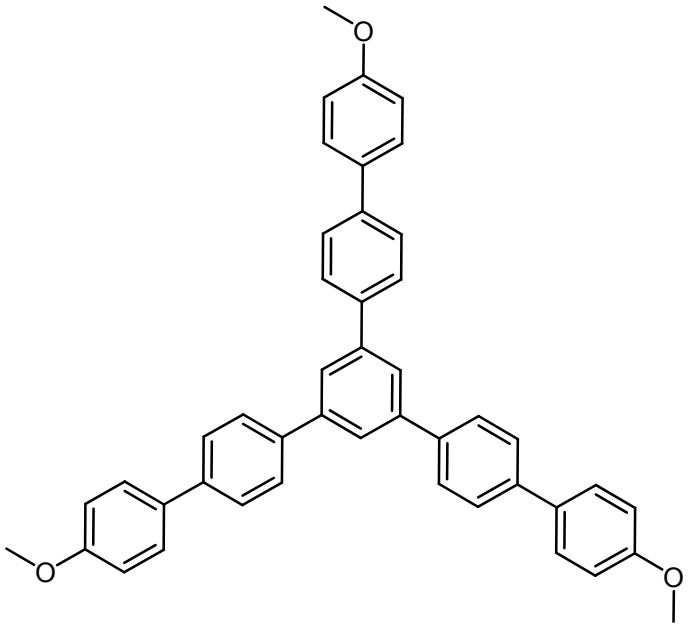
1-(4'-Phenylphenyl)-3,5-di(4-bromophenyl) benzene (S13)

Mp 211-213 ^{o}C. IR (KBr) ν = 2980, 1593, 1485, 1376, 809 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.89 (s, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 4H), 7.62 (d, J = 8.0 Hz, 4H), 7.57 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H) 7.38 (t, J = 7.2 Hz, 1H). ^{13}C NMR(100 MHz, $CDCl_3$): δ = δ = 146.4, 146.2, 139.0, 137.4, 130.0, 129.2, 128.6, 128.3, 127.4, 127.0, 126.7, 126.3, 126.1, 125.83. Anal. Cald. for $C_{30}H_{20}Br_2$: C, 66.69; H, 3.73. Foumd: C, 67.21; H, 3.80.



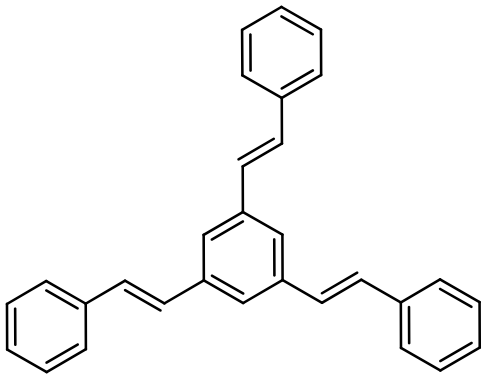
1,3-Di(4'-phenylphenyl)-5-(4-bromophenyl) benzene; (S14)

Mp 189-190 ^{o}C. IR (KBr) ν = 2970, 1598, 1486, 1380, 829. 766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 2H), 7.89 (s, 1H), 7.83 (d, J = 8.0 Hz, 4H), 7.75 (d, J = 8.0 Hz, 4H), 7.68 (d, J = 8.0 Hz, 2H),7.62 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 4H), 7.49 (t, J = 7.2 Hz, 4H) 7.39 (t, J = 7.2 Hz, 2H). ^{13}C NMR(100 MHz, $CDCl_3$): δ = 146.4, 146.0, 139.2, 137.5, 130.0, 129.4, 128.6, 128.2, 127.7, 127.2, 126.6, 126.3, 126.0, 125.1. Anal. Cald for $C_{36}H_{25}Br$: C, 80.45; H, 4.69. Found: C, 80.38; H, 4.72.



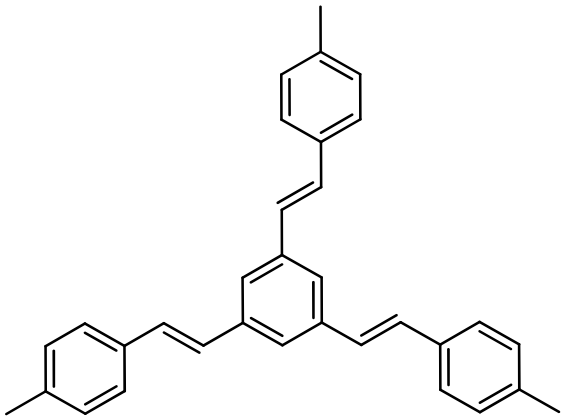
1,3,5-Tris[4-(4'-methoxyphenyl)phenyl]benzene (S12)

Mp 186-187 °C (Lit.[23a] 182-184 °C). IR (KBr) v = 2991, 1602, 1490, 1396, 1245, 1170, 869 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 3H), 7.72 (d, J = 8.4 Hz, 6H), 7.63 (d, J = 8.4 Hz, 6H), 7.41 (d, J = 8.4 Hz, 6H), 6.89 (d, J = 8.4 Hz, 6H), 3.78 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 141.9, 140.0, 139.3, 133.1, 128.1, 127.6, 127.1, 124.8, 114.2, 55.3.



1,3,5-Tristyrylbenzene (S15)

Mp 190-193 °C. IR (KBr) v = 2986, 1605, 1492, 1350, 850 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.59 (m, 9H), 7.42 (t, J = 7.2 Hz, 6H), 7.32 (t, J = 7.2 Hz, 3H), 7.25 (A of ABq, J = 16 Hz, 3H), 7.19 (B of ABq, J = 16 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 137.2, 130.0, 129.3, 128.3, 127.8, 126.6, 123.9. MS: *m/z* (%): 385 (M^++1 ,21.1), 354 (M^+, 56.7), 292 (10.7), 278 (10.7), 202 (23.0), 91 (100.0). Anal. Calcd for $C_{30}H_{24}$: C 93.71.64; H 6.29. Found: C 93.65; H 6.35.

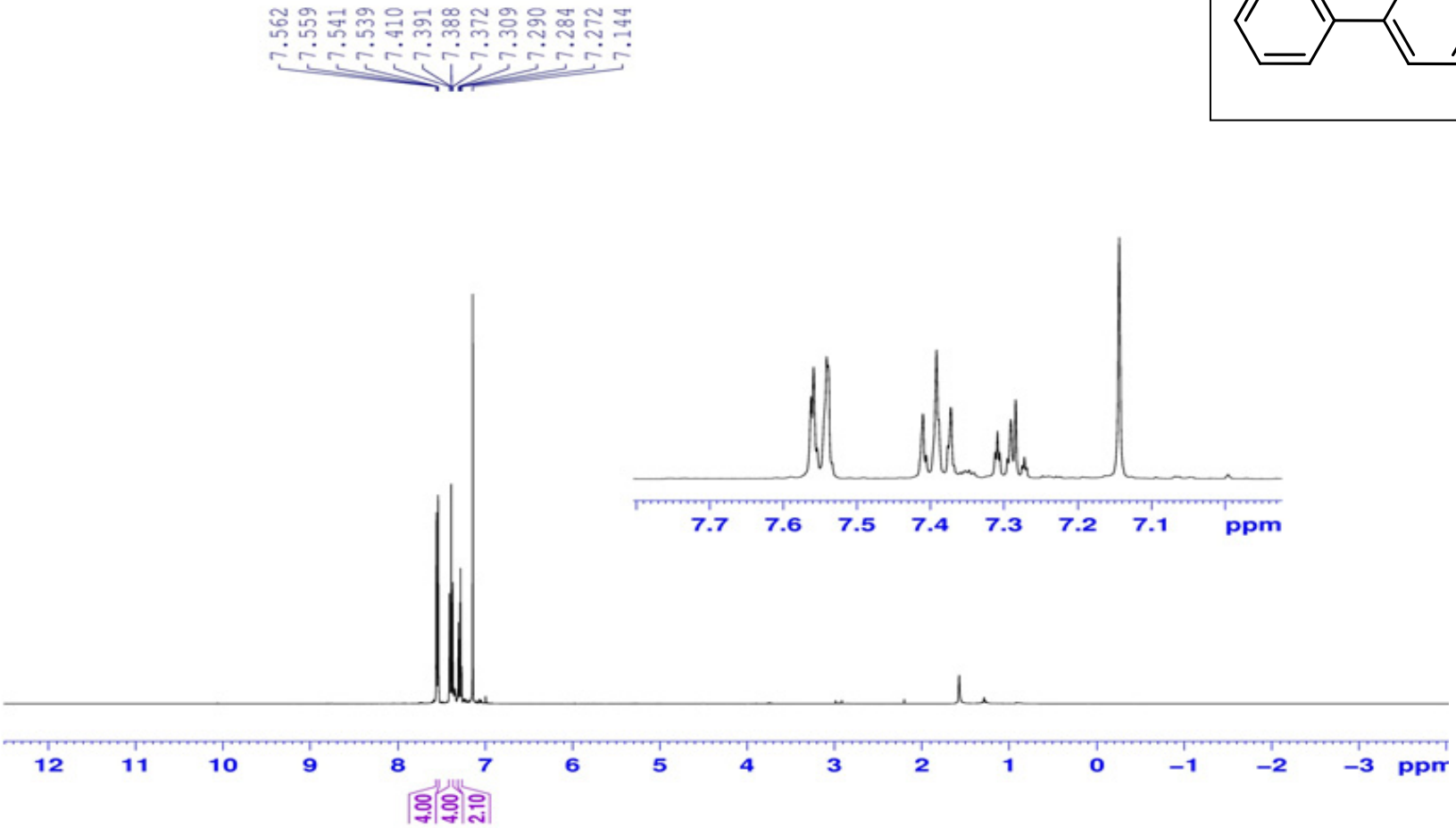


1,3,5-Tris(*p*-methylstyryl)benzene (S16)

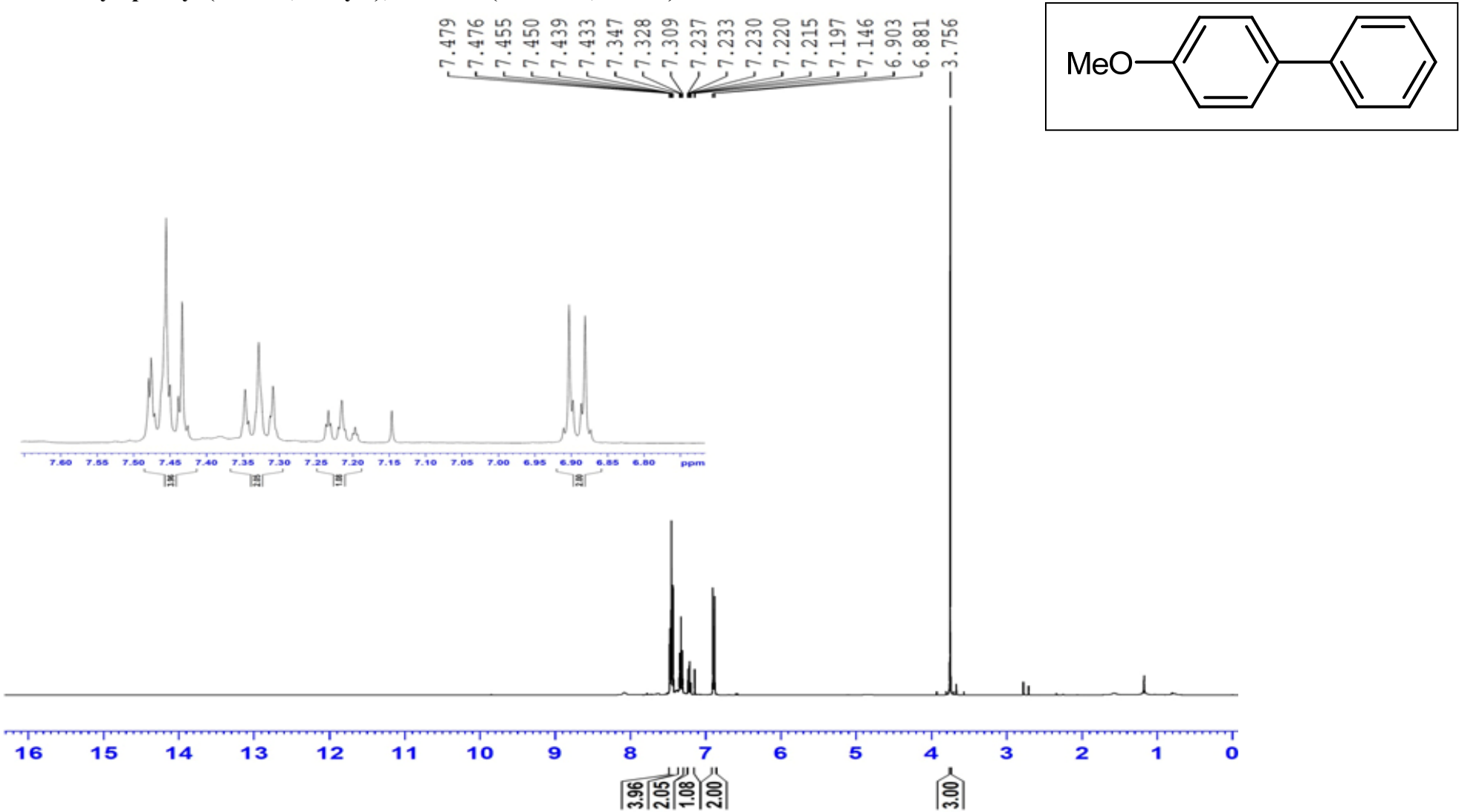
Mp 210-211 ºC (Lit.[23b] 213-217 ºC)**.** IR (KBr) ν = 2980, 1605, 1490, 1370, 890, 730 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 3H), 7.45 (d, J = 8.4 Hz, 6H), 7.24 (d, J = 8.4, 6H), 7.26-7.04 (m 12H), 2.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 137.6, 134.5, 129.4, 129.1, 127.4, 126.5, 123.6, 21.3.

16. ^{1}H NMR Spectra of coupling products

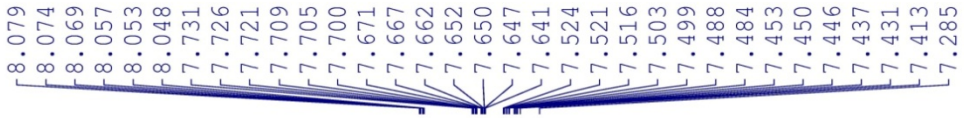
Biphenyl (Table 4, entry 1); ^{1}H NMR (400 MHz, $CDCl_3$)

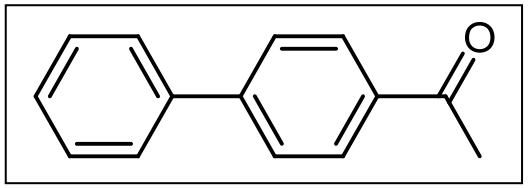


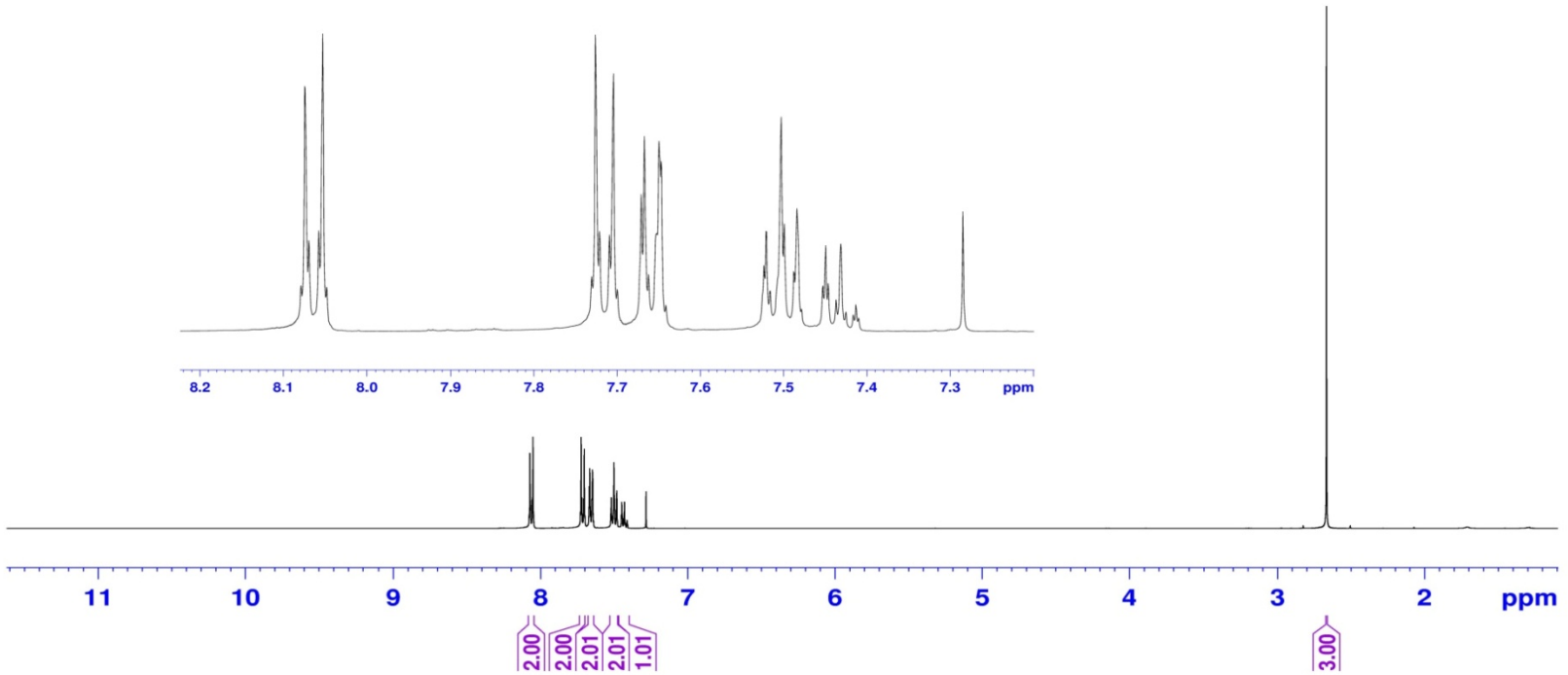
4-Methoxybiphenyl (Table 4, entry 2); ^{1}H NMR (400 MHz, $CDCl_3$)



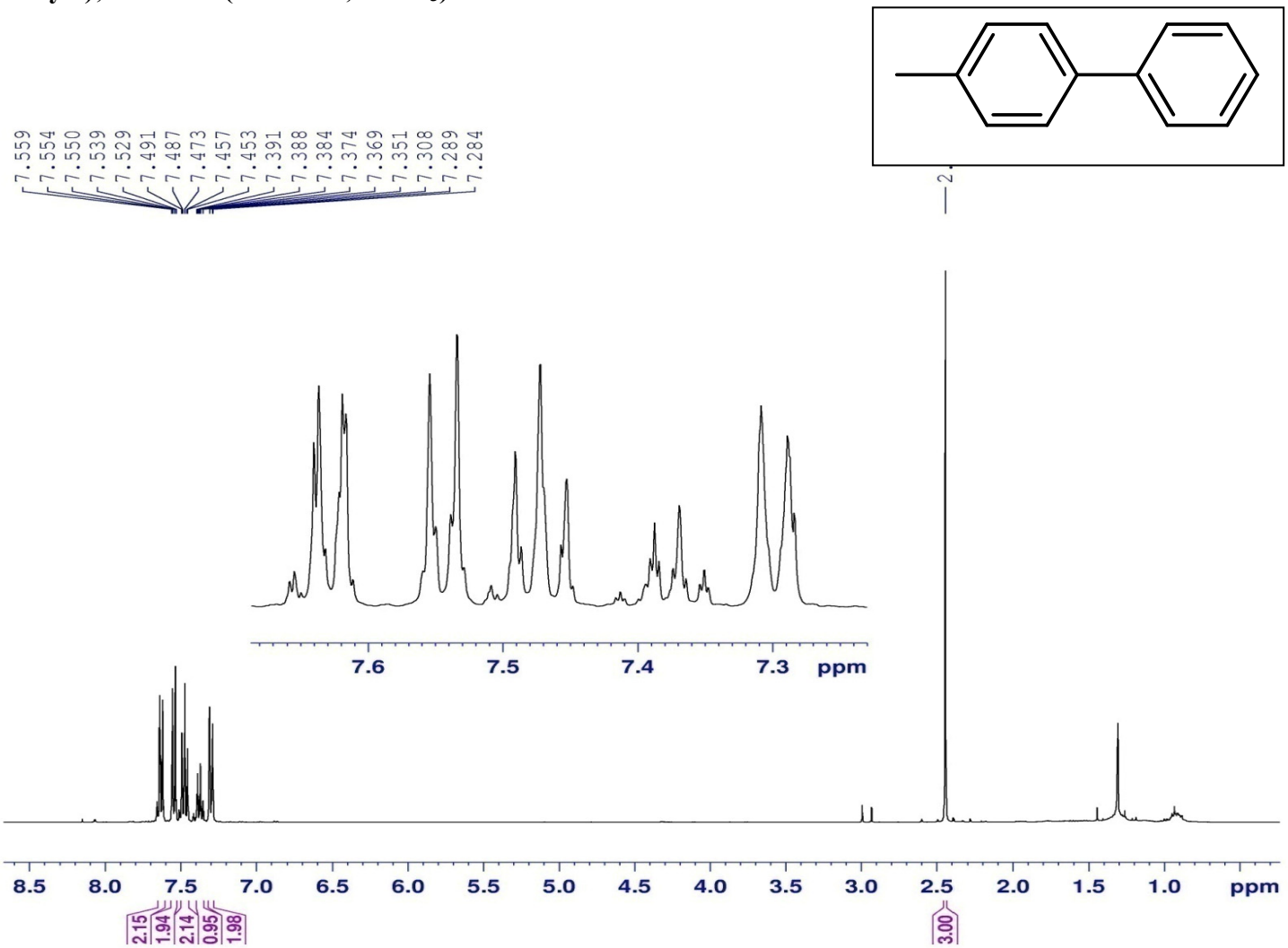
Phenylacetophenone (Table 4, entry 3); ^{1}H NMR (400 MHz, $CDCl_3$)



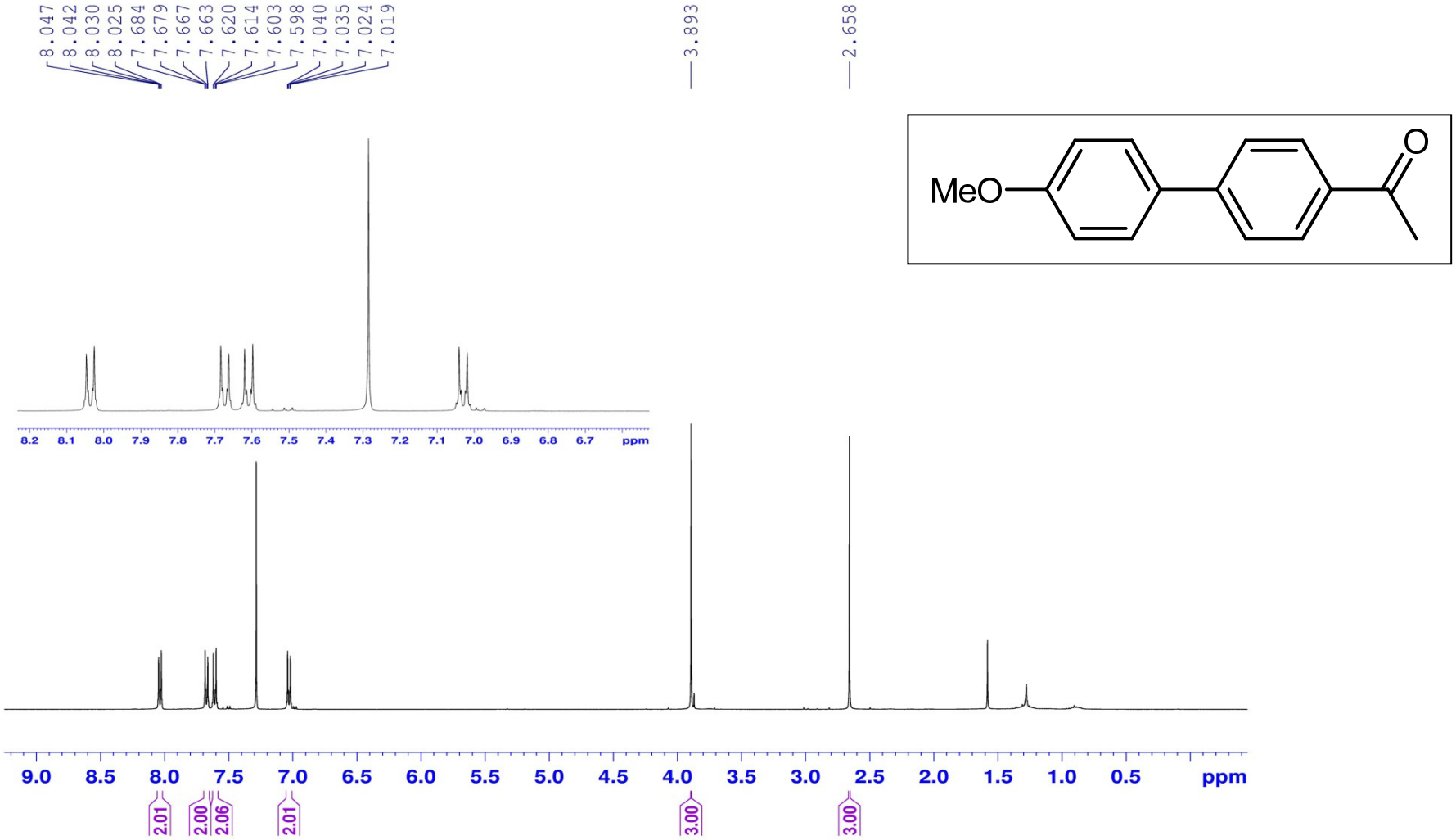




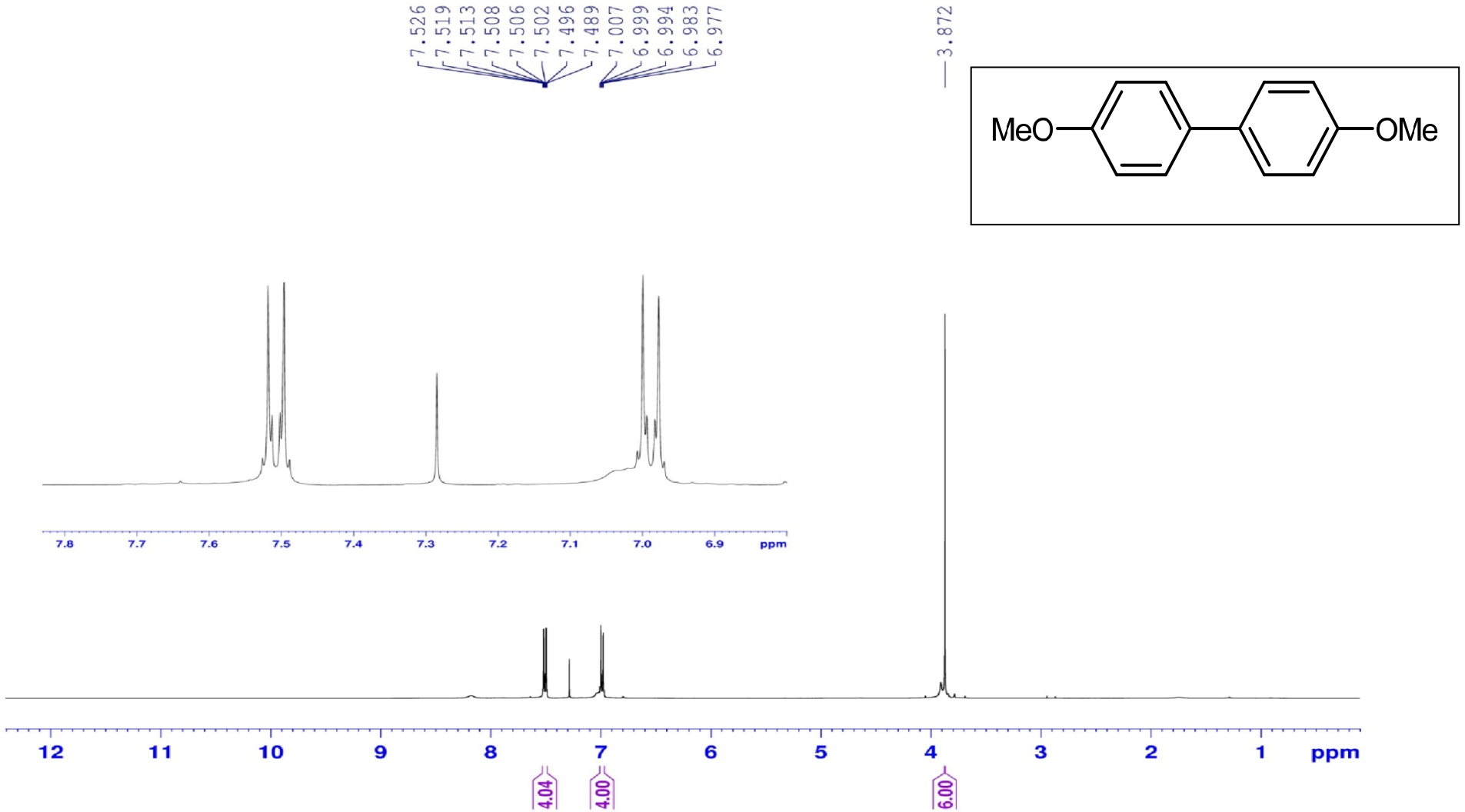
4-Methylbiphenyl (Table 4, entry 4); ^{1}H NMR (400 MHz, $CDCl_3$)



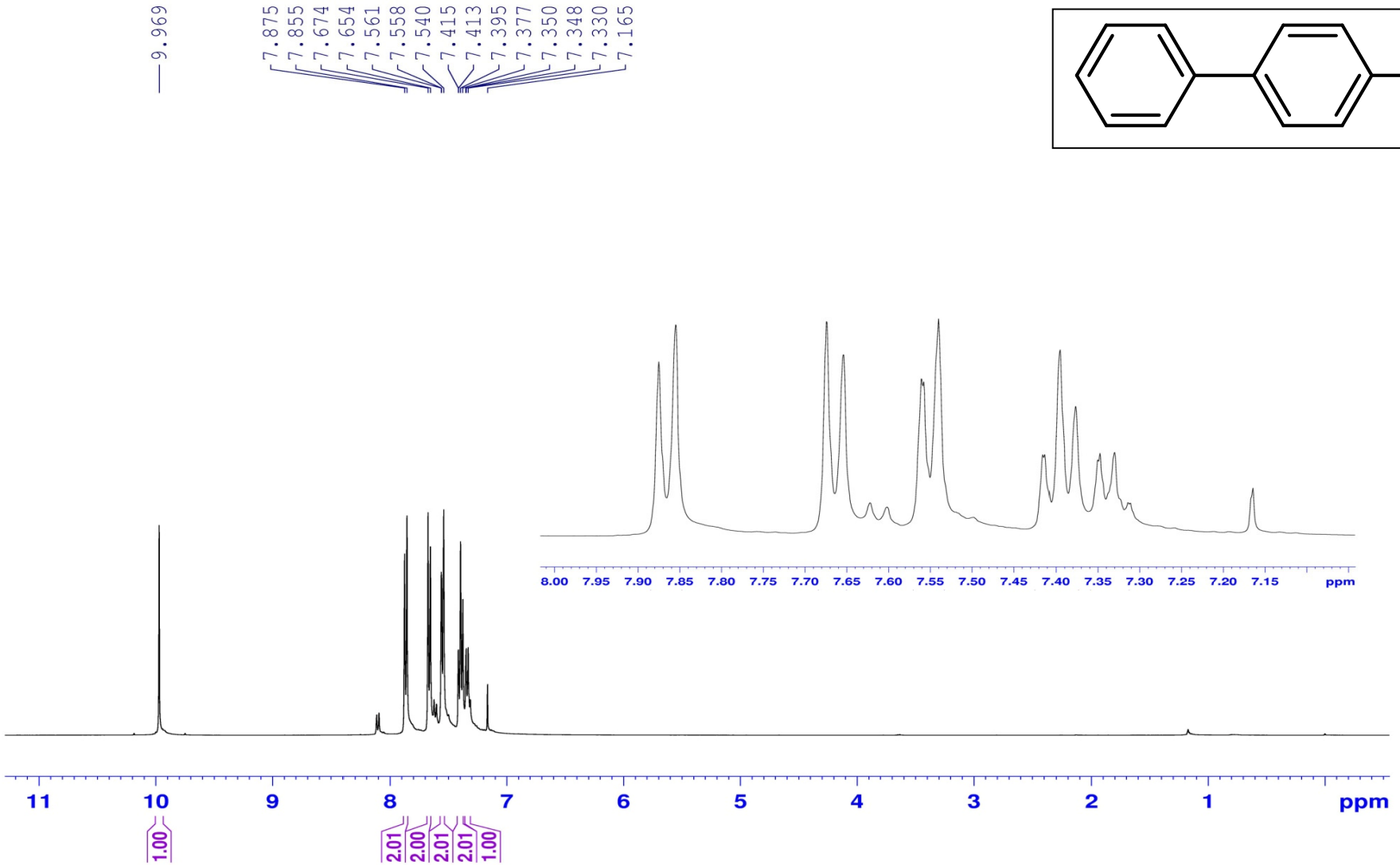
4(4'-Methoxyphenyl)acetophenone (Table 4, entry 5); ^{1}H NMR (400 MHz, $CDCl_3$)



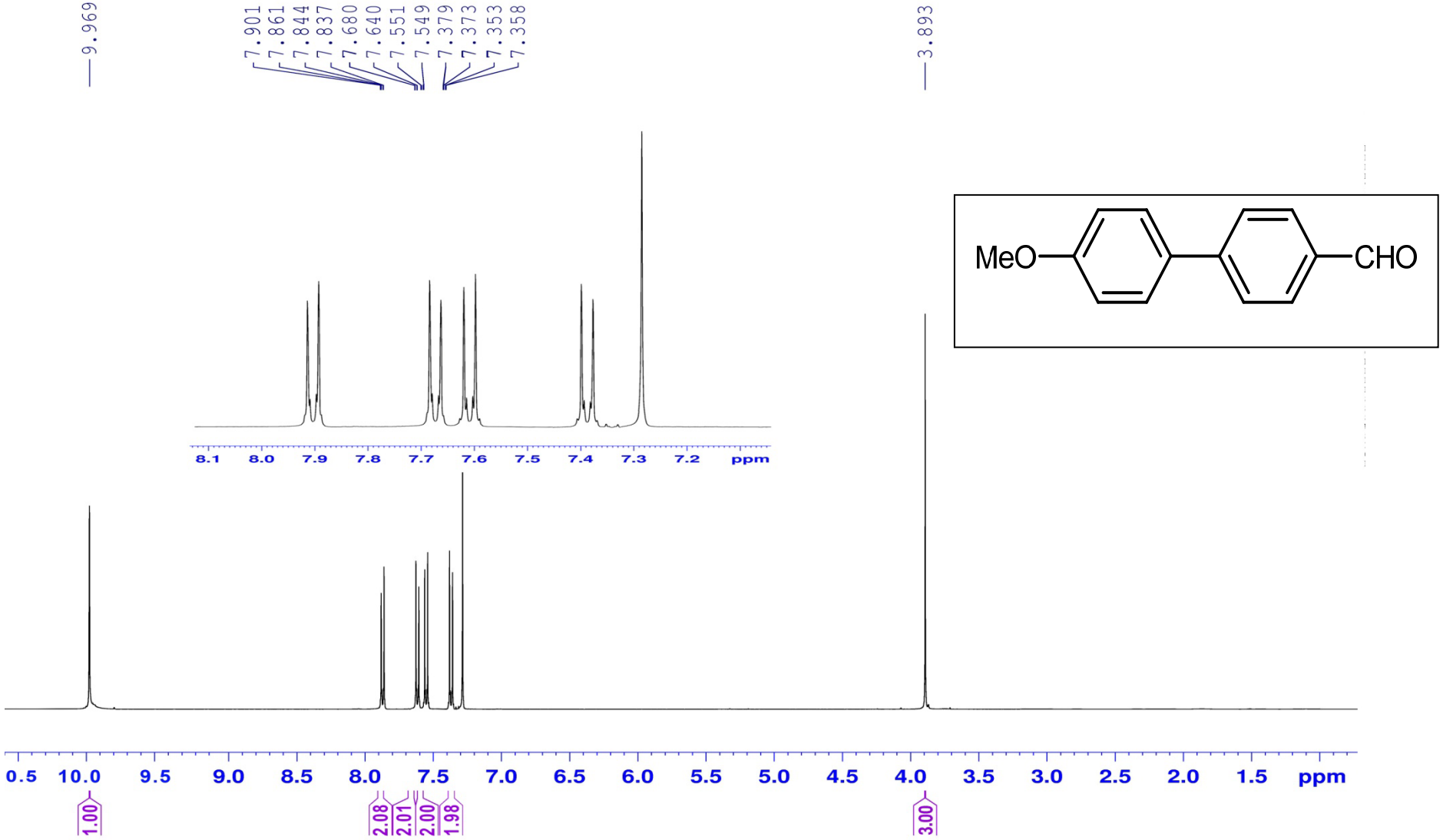
4,4'-Dimethoxybiphenyl (Table 4, entry 9); ^{1}H NMR(400 MHz, $CDCl_3$)



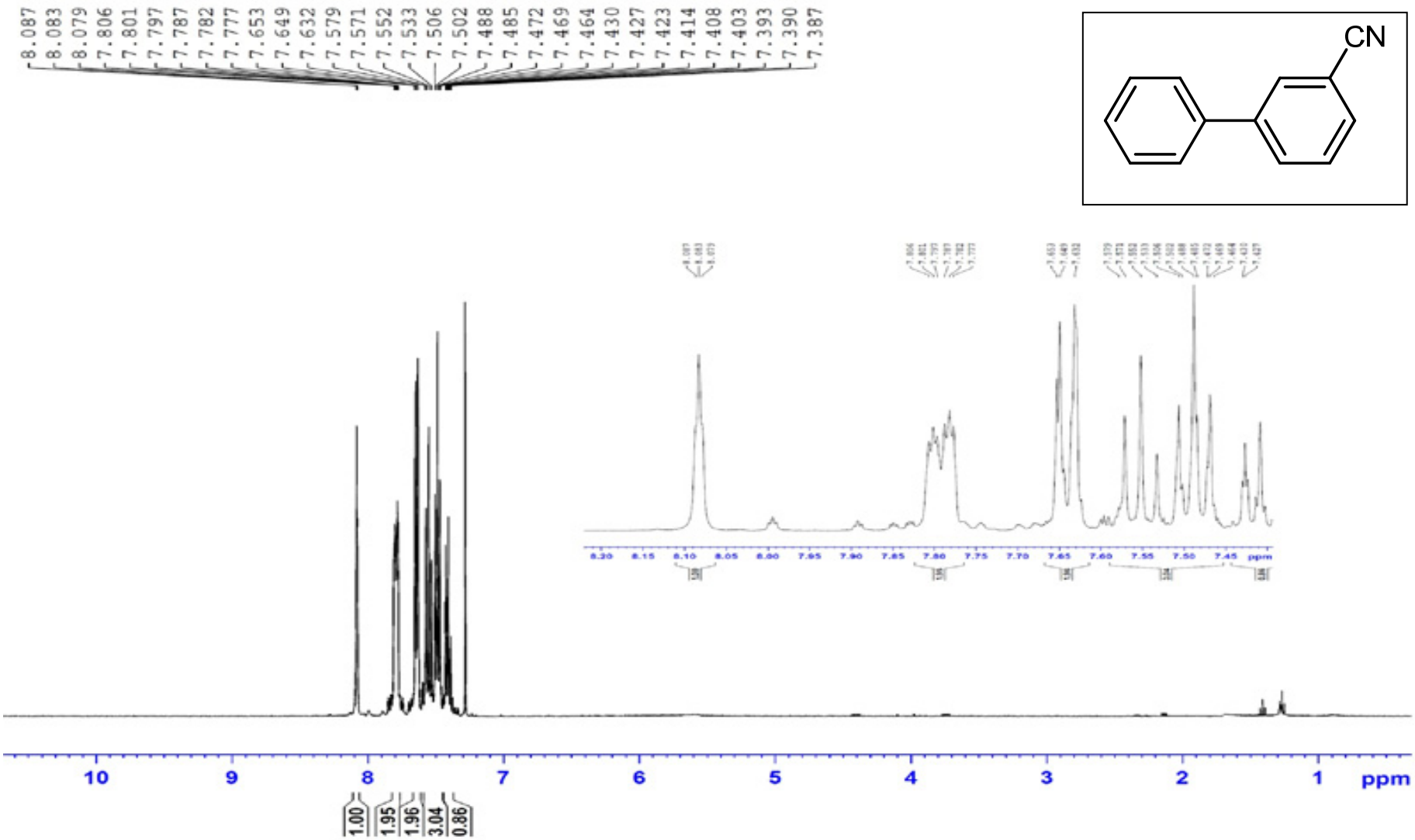
Biphenyl-4-carbaldehyde (Table 4, entry12); ^{1}H NMR (400 MHz, $CDCl_3$)



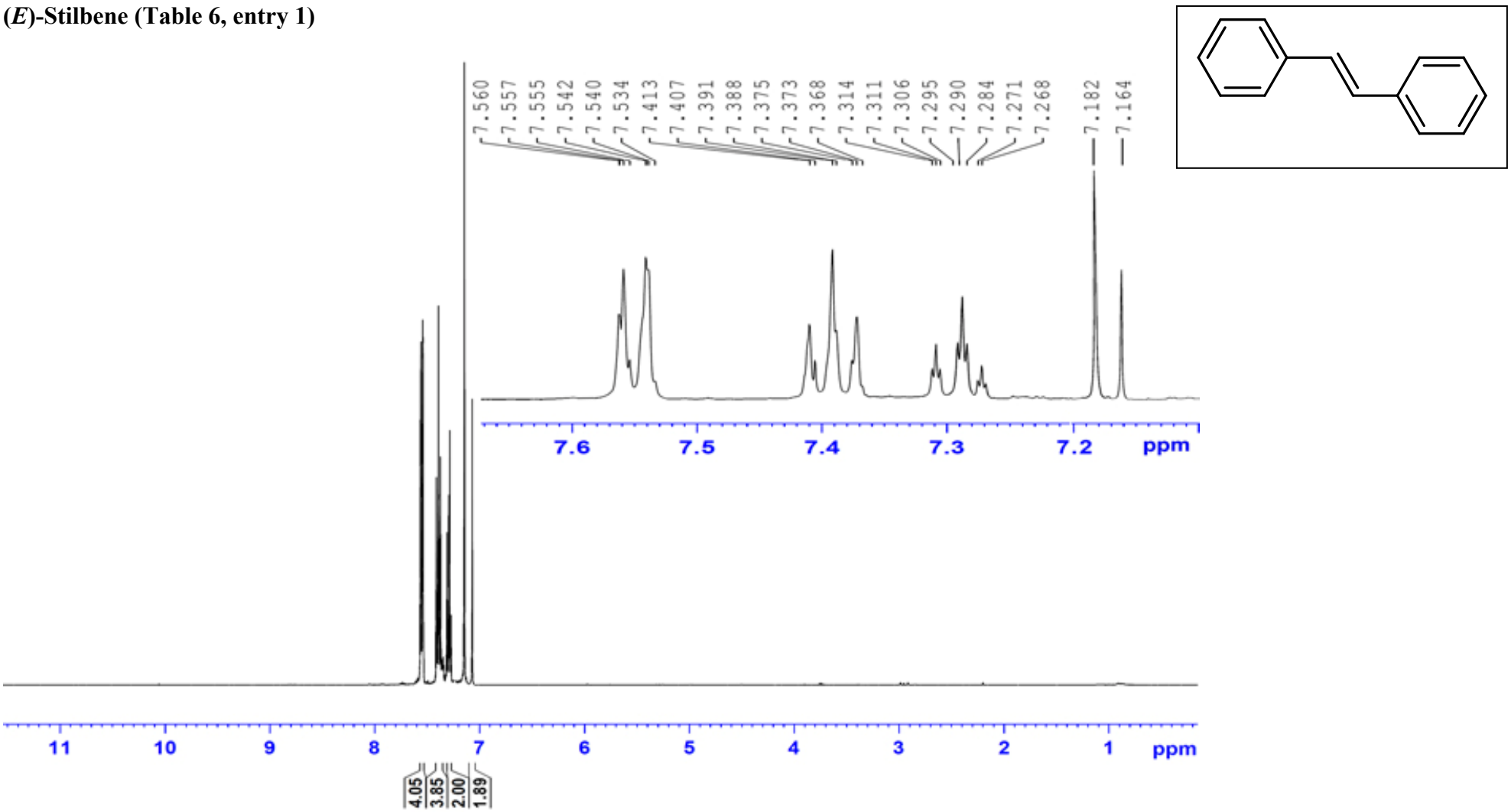
4'-Methoxybiphenyl-4-carbaldehyde (Table 4, entry 13); ^{1}H NMR (400 MHz, $CDCl_3$)



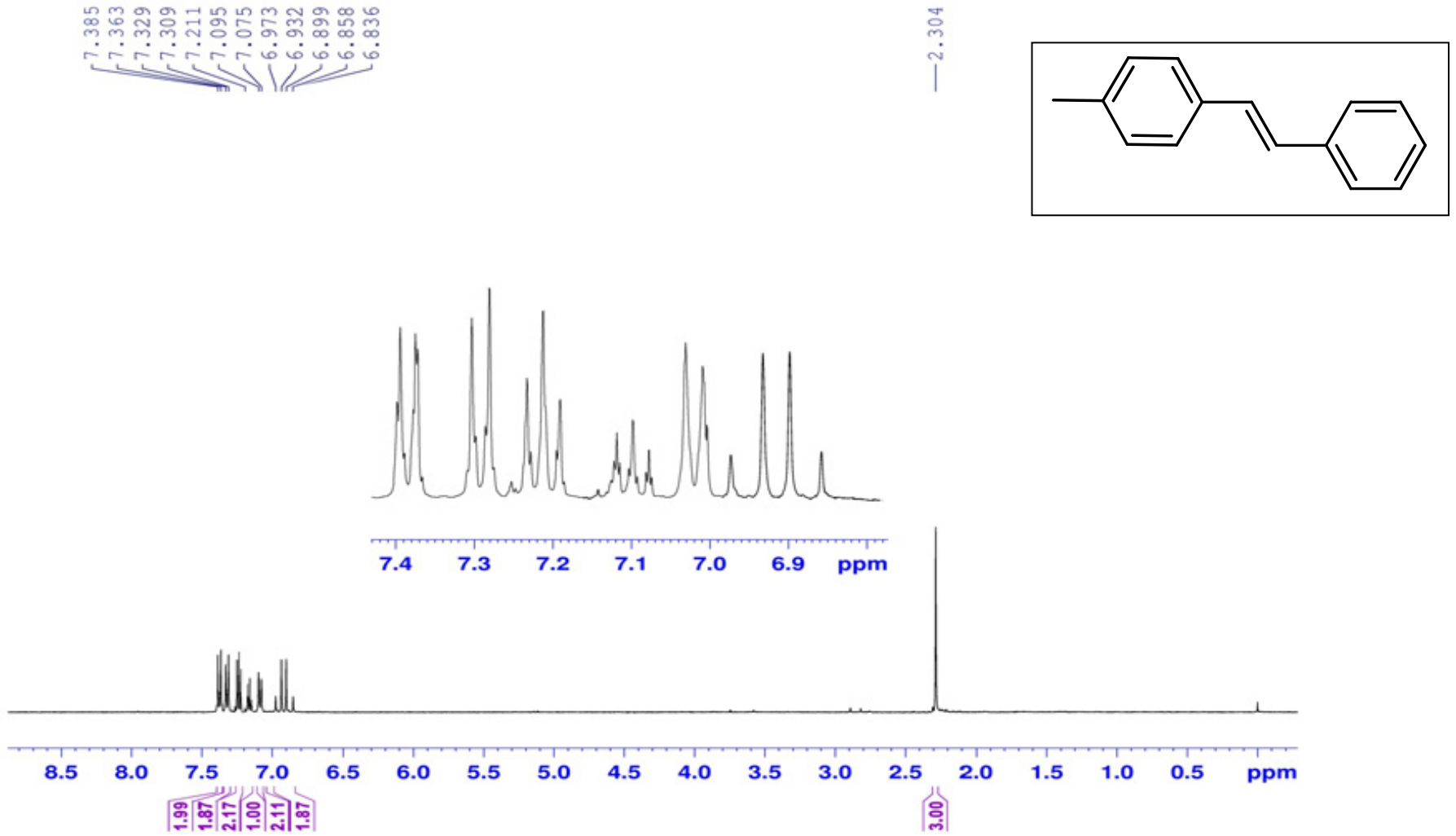
Biphenyl-3-carbonitrile (Table 4, entry 14); ^{1}H NMR (400 MHz, $CDCl_3$)



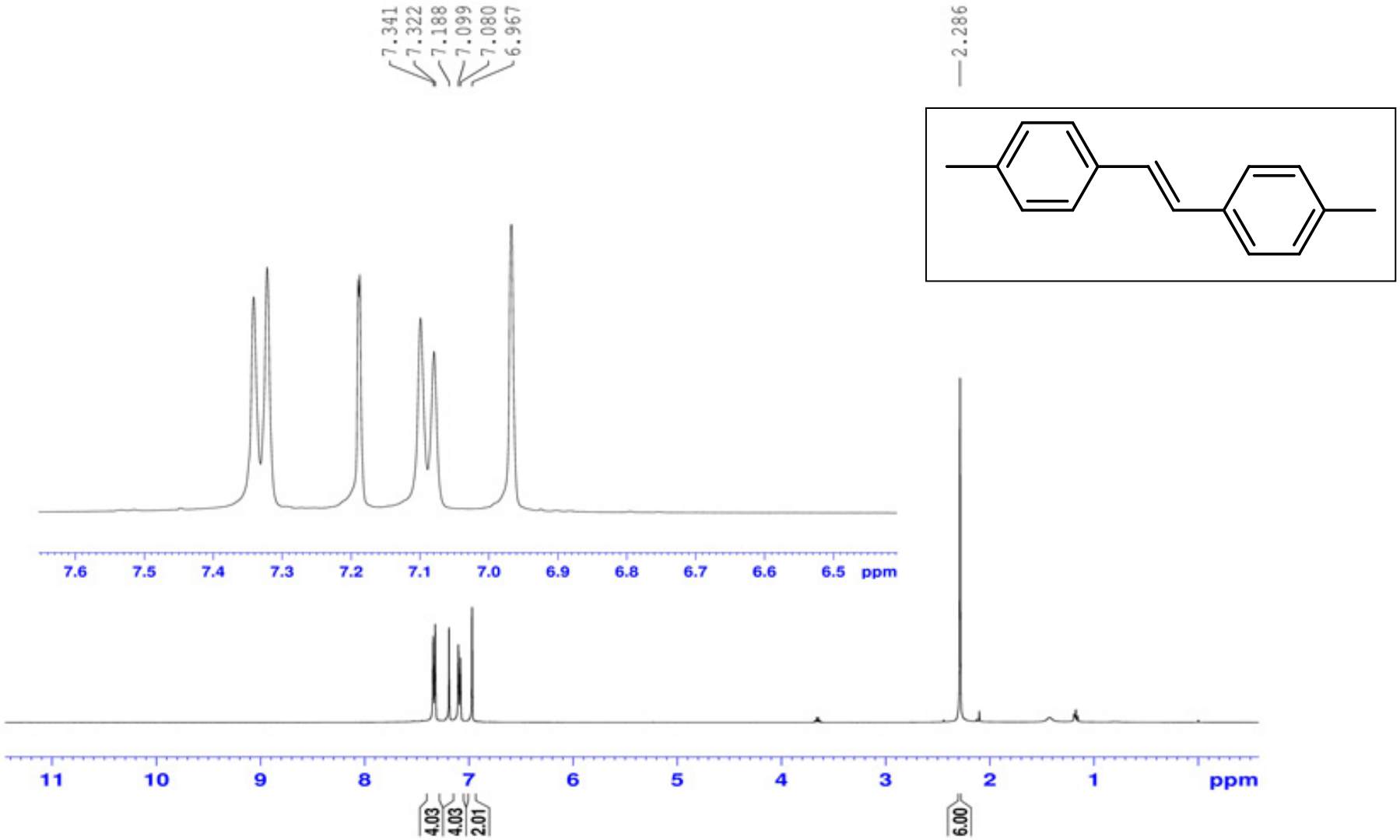
(*E*)-Stilbene (Table 6, entry 1)



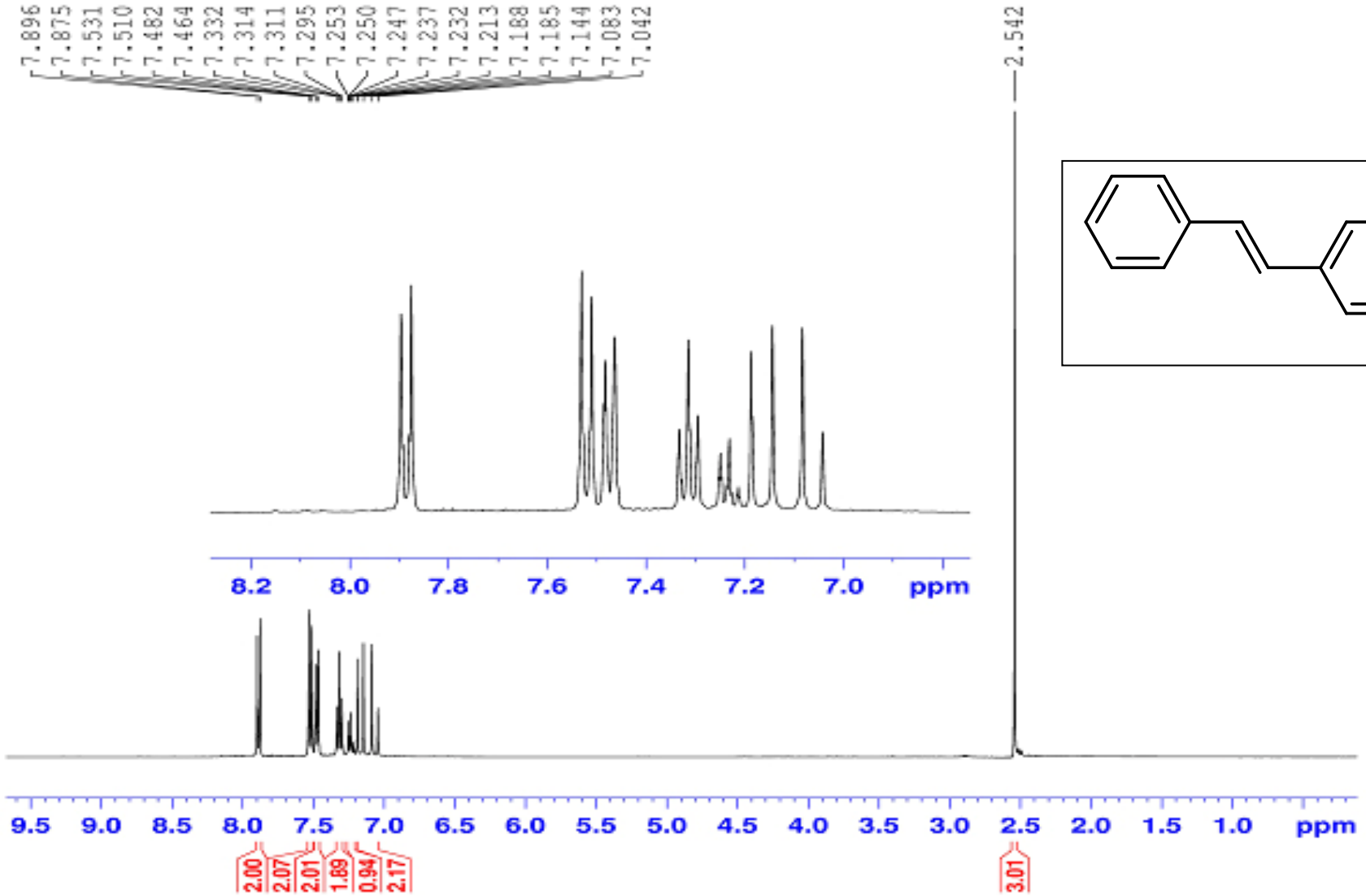
(*E*)-4-Methylstilbene (Table 6, entry 2)



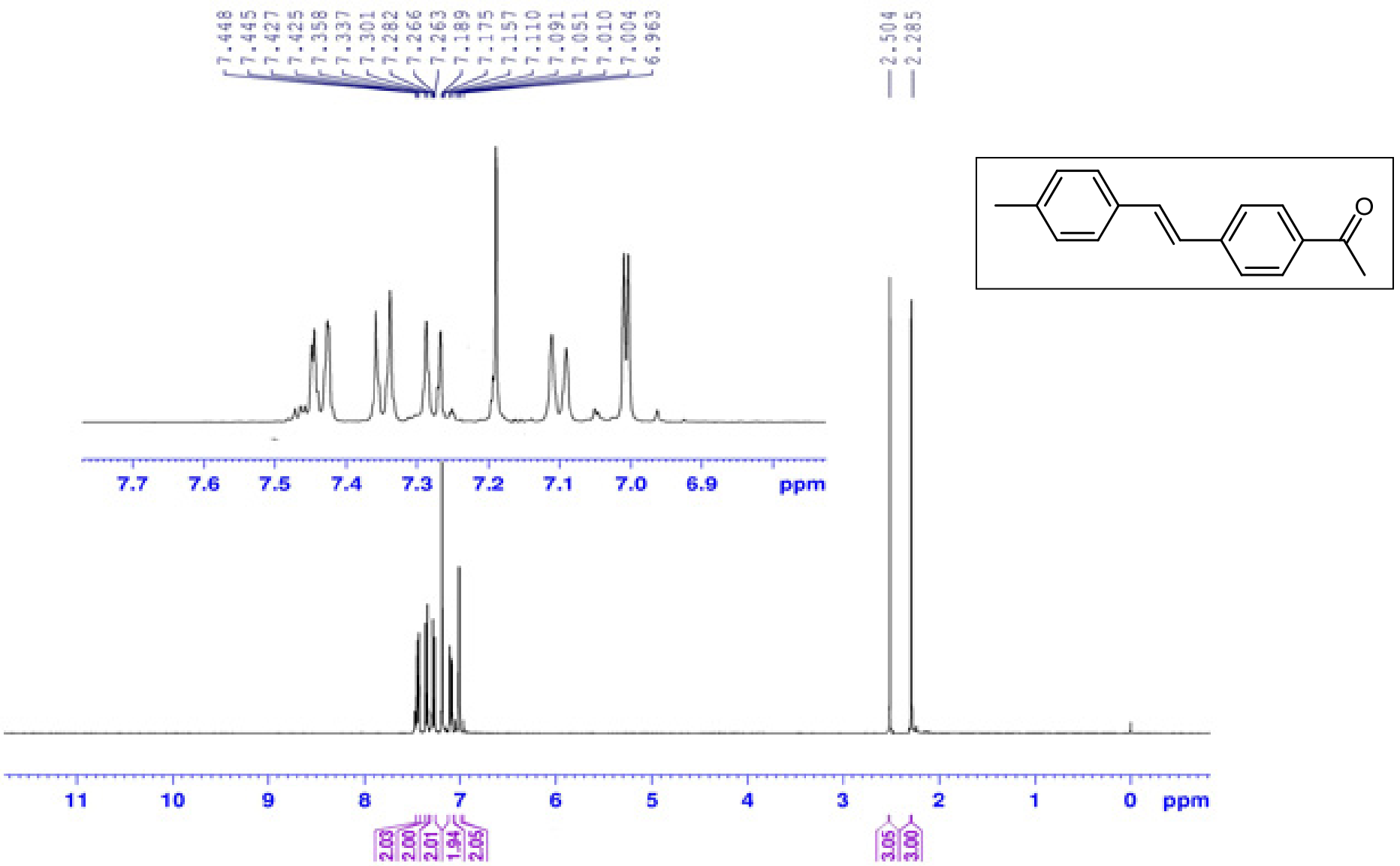
(E)-1,2-Di-*p*-tolylethene (Table 6, entry 3); ^{1}H NMR (400 MHz, $CDCl_3$)



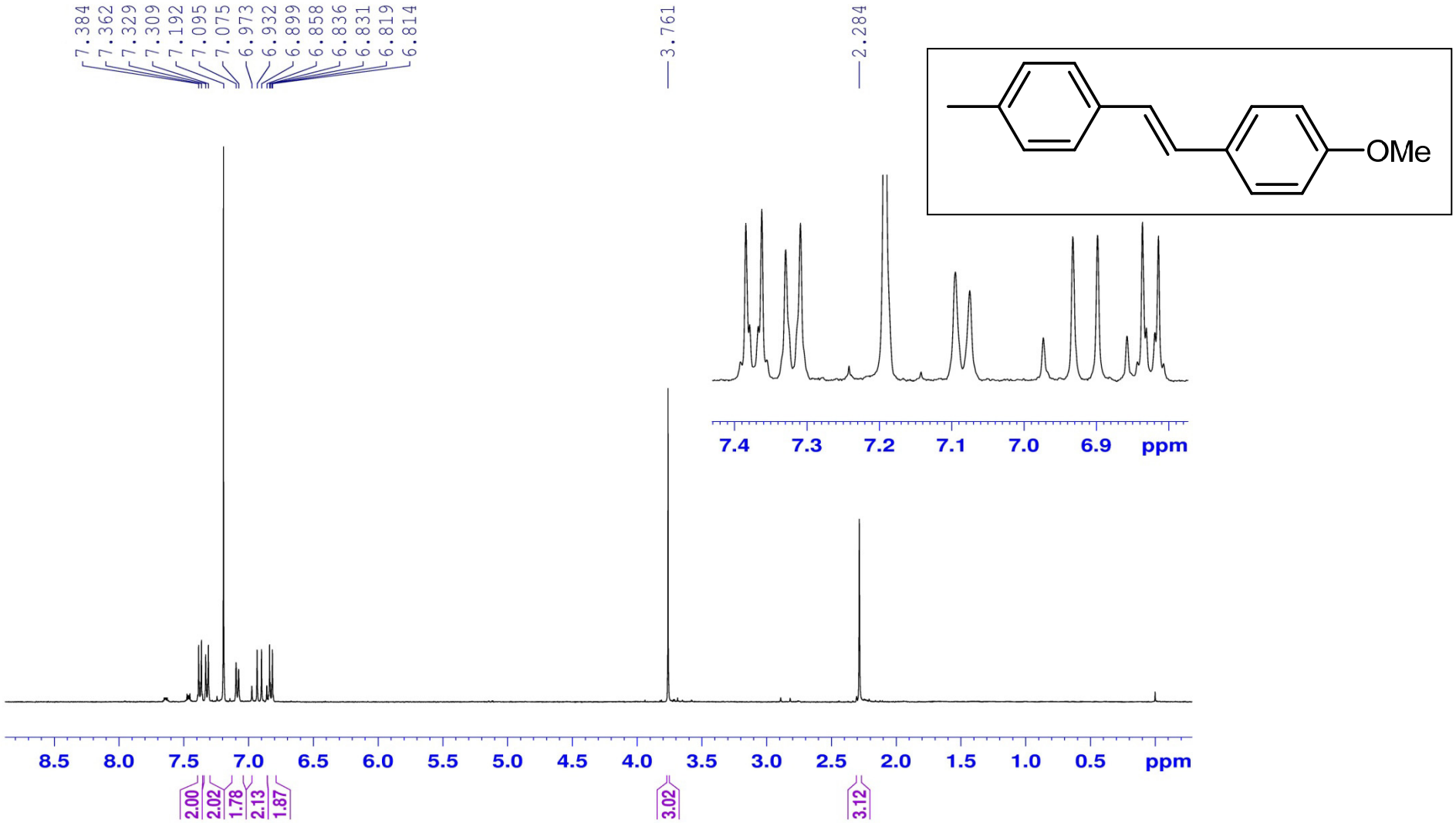
(E)-1-(Prop-1-en-2-yl)-4-styrylbenzene (Table 6, entry 4); ^{1}H NMR (400 MHz, $CDCl_3$)



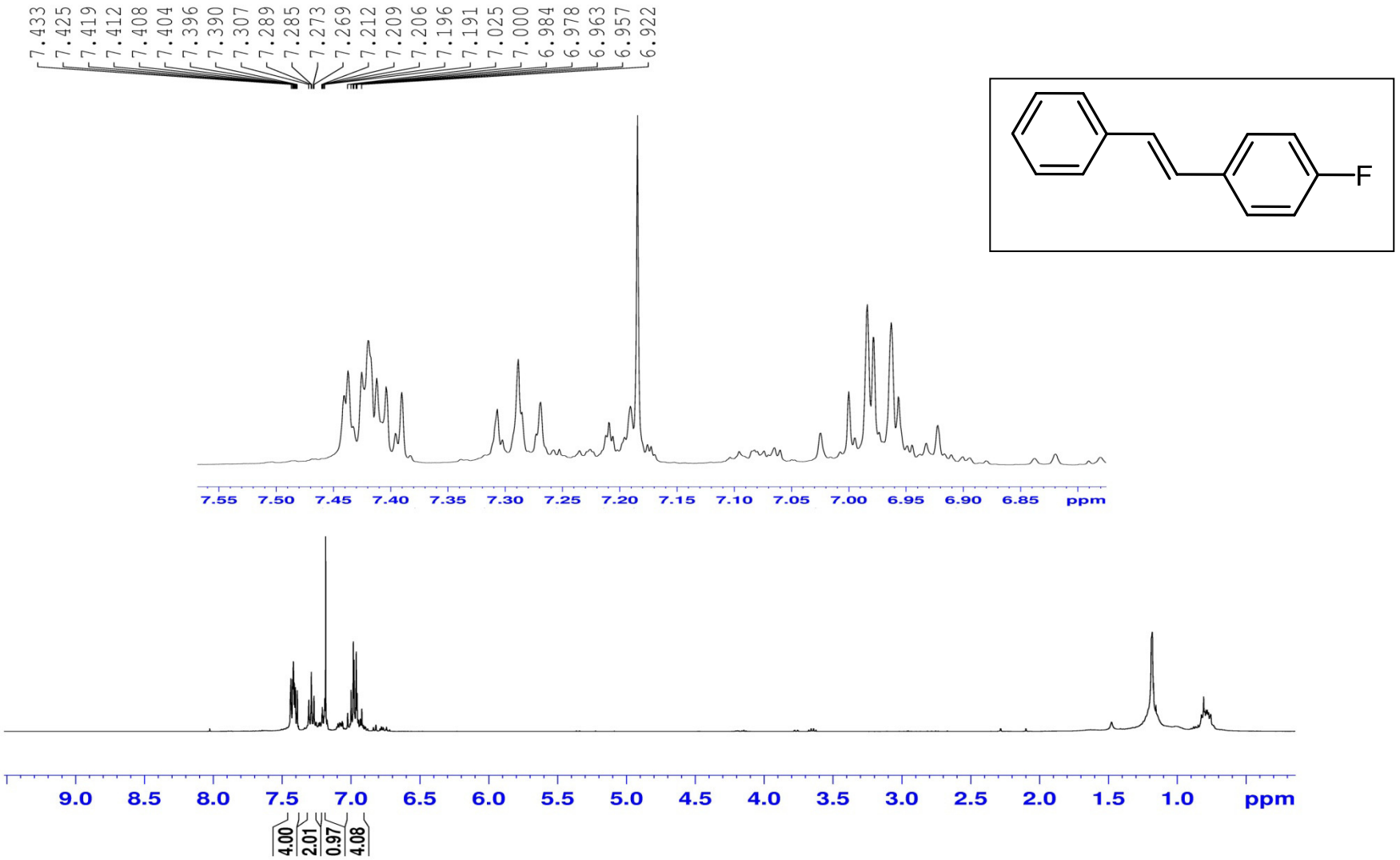
4(4-Methylstyrene)acetophenone (Table 6, entry 5); ^{1}H NMR (400 MHz, $CDCl_3$)



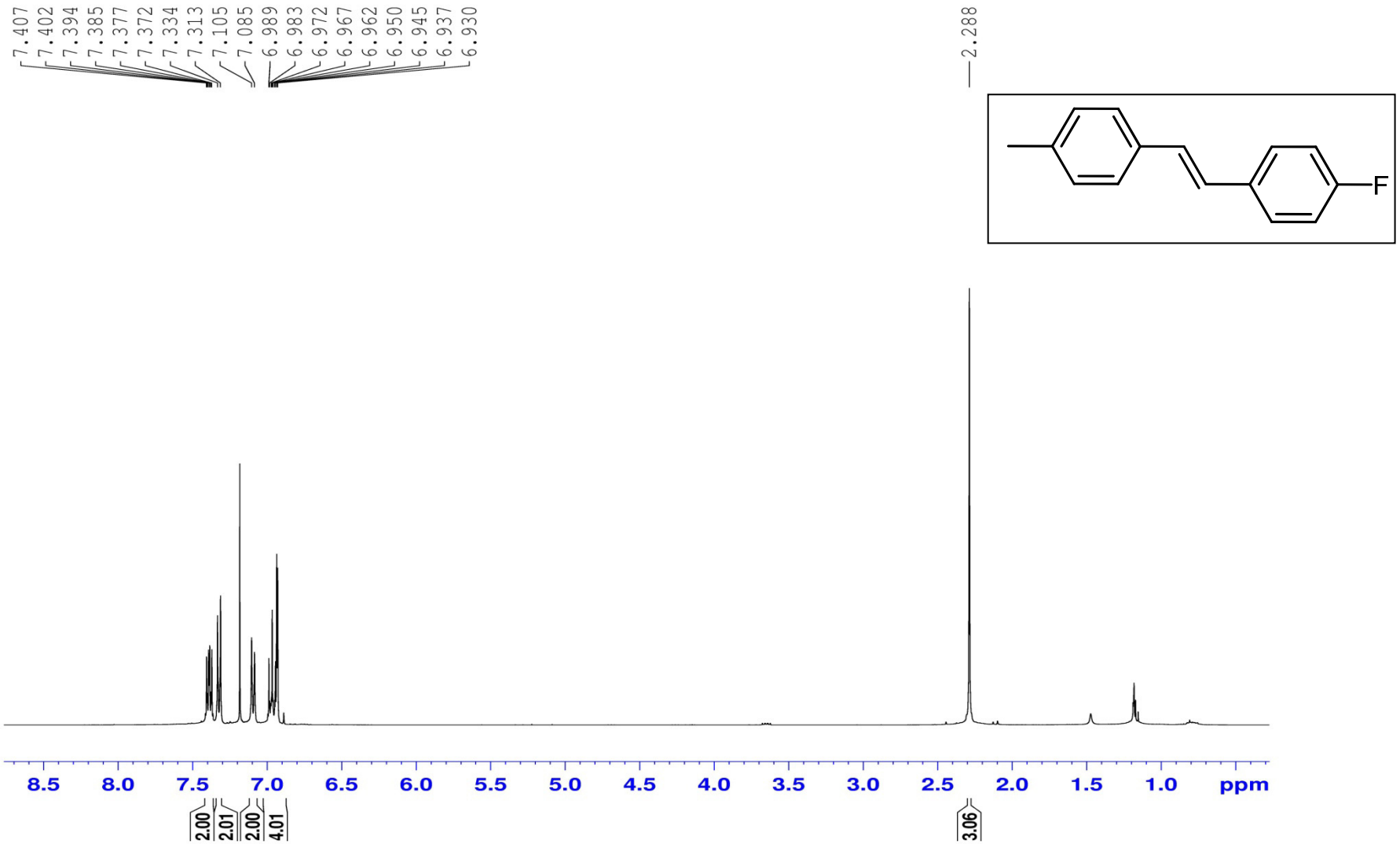
(E)-1-Methoxy-4-(4-methylstyryl)benzene (Table 6, entry 7); ^{1}H NMR (400 MHz, $CDCl_3$)



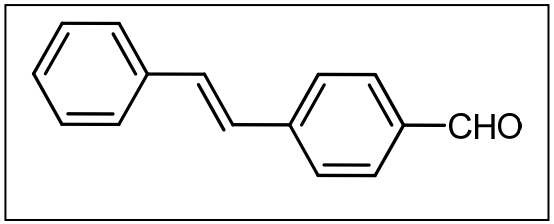
(E)-1-Fluoro-4-styrylbenzene (Table 6, entry 8); ^{1}H NMR (400 MHz, $CDCl_3$)

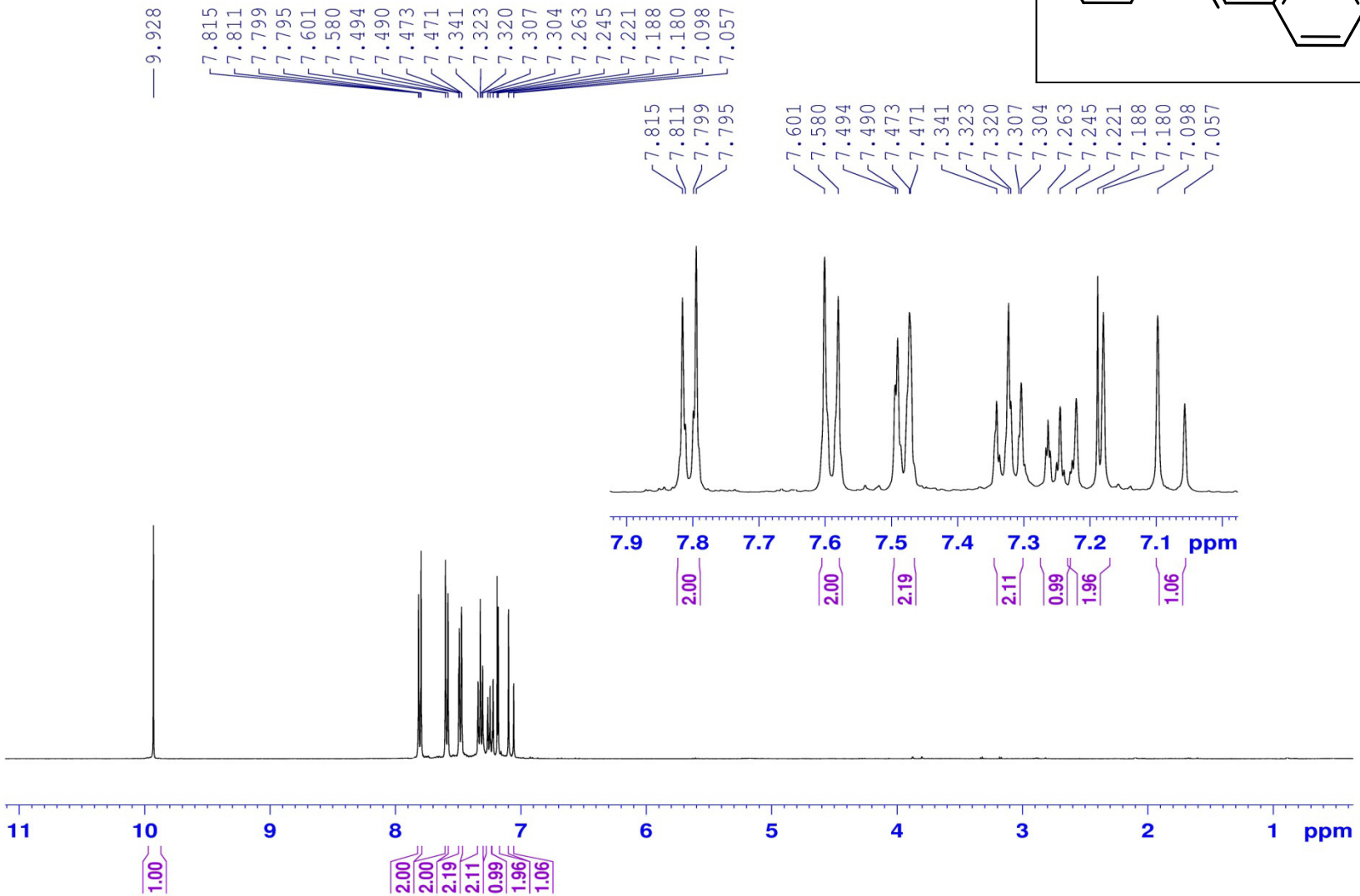


(E)-1-Fluoro-4-(4-methylstyryl)benzene (Table 6, entry 9); ^{1}H NMR (400 MHz, $CDCl_3$)



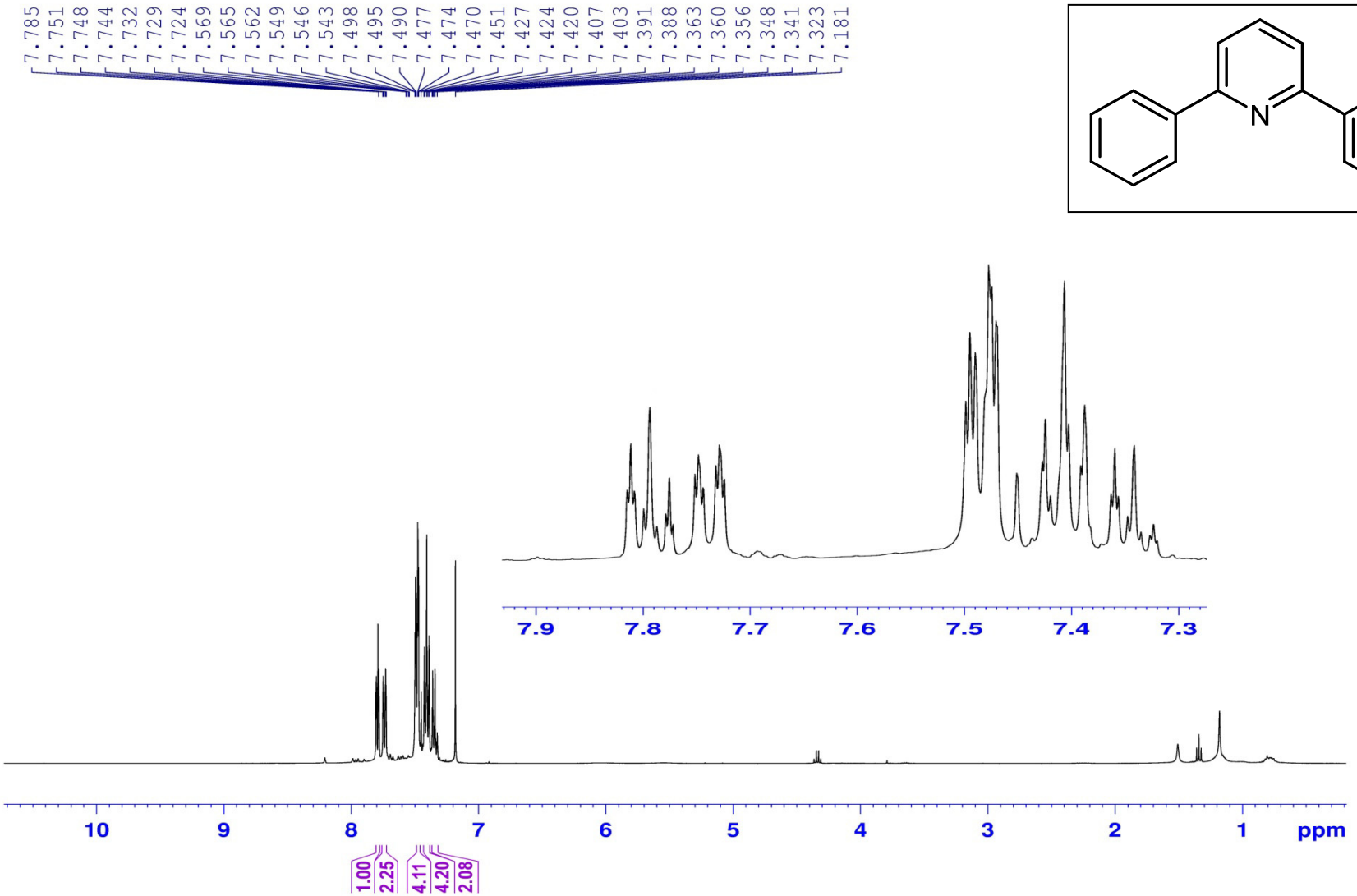
(E)-4-Styrylbenzaldehyde (Table 6, entry 16); ^{1}H NMR (400 MHz, $CDCl_3$)



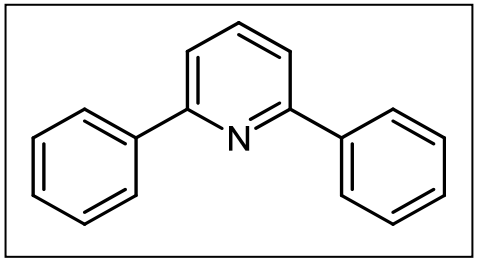


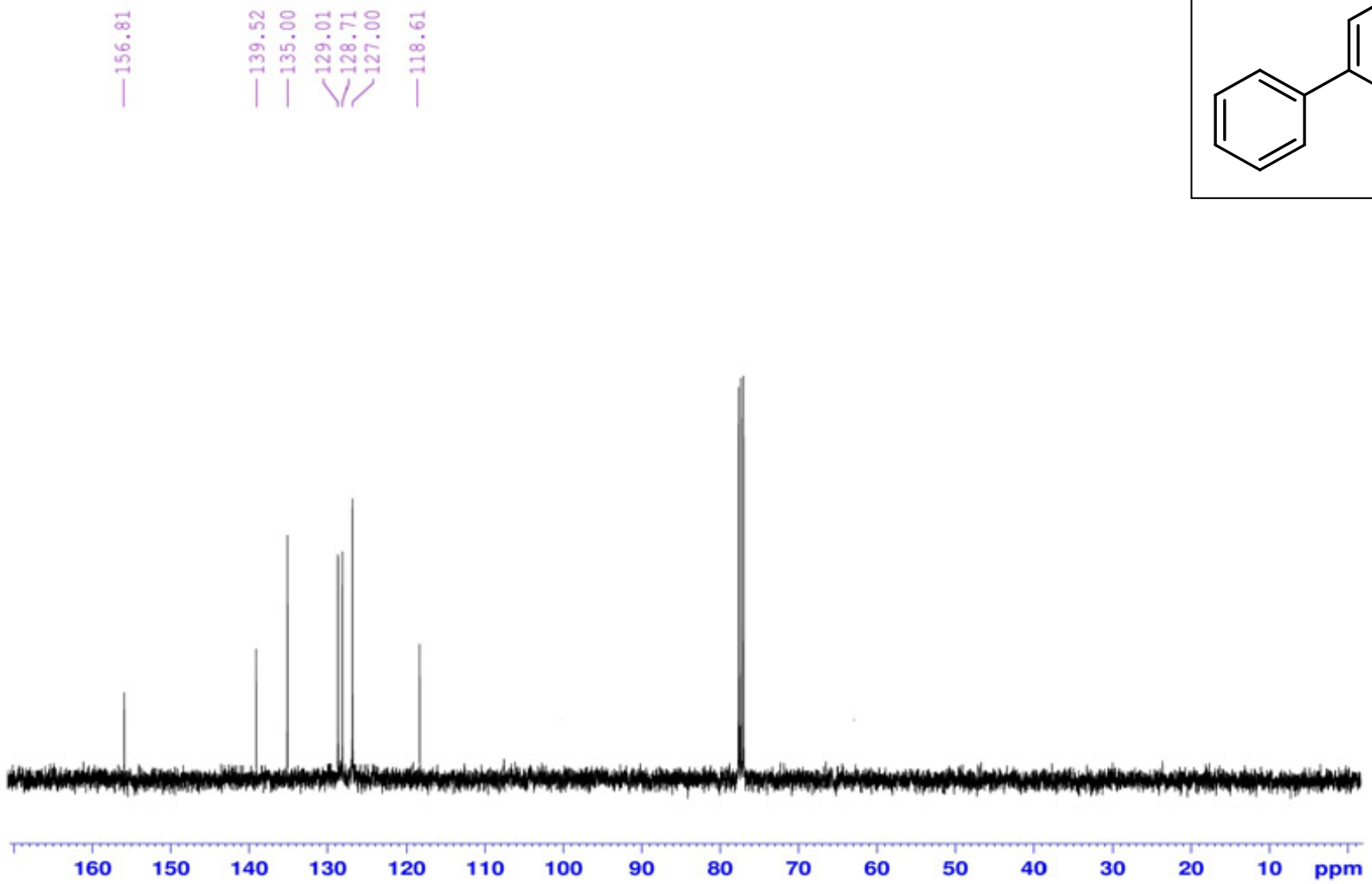
17. ^{1}H and ^{13}C NMR Spectra of star- and banana-shaped compounds

2,6-Diphenylprydine (S1, Table 7, entry 1); ^{1}H NMR (400 MHz, $CDCl_3$)

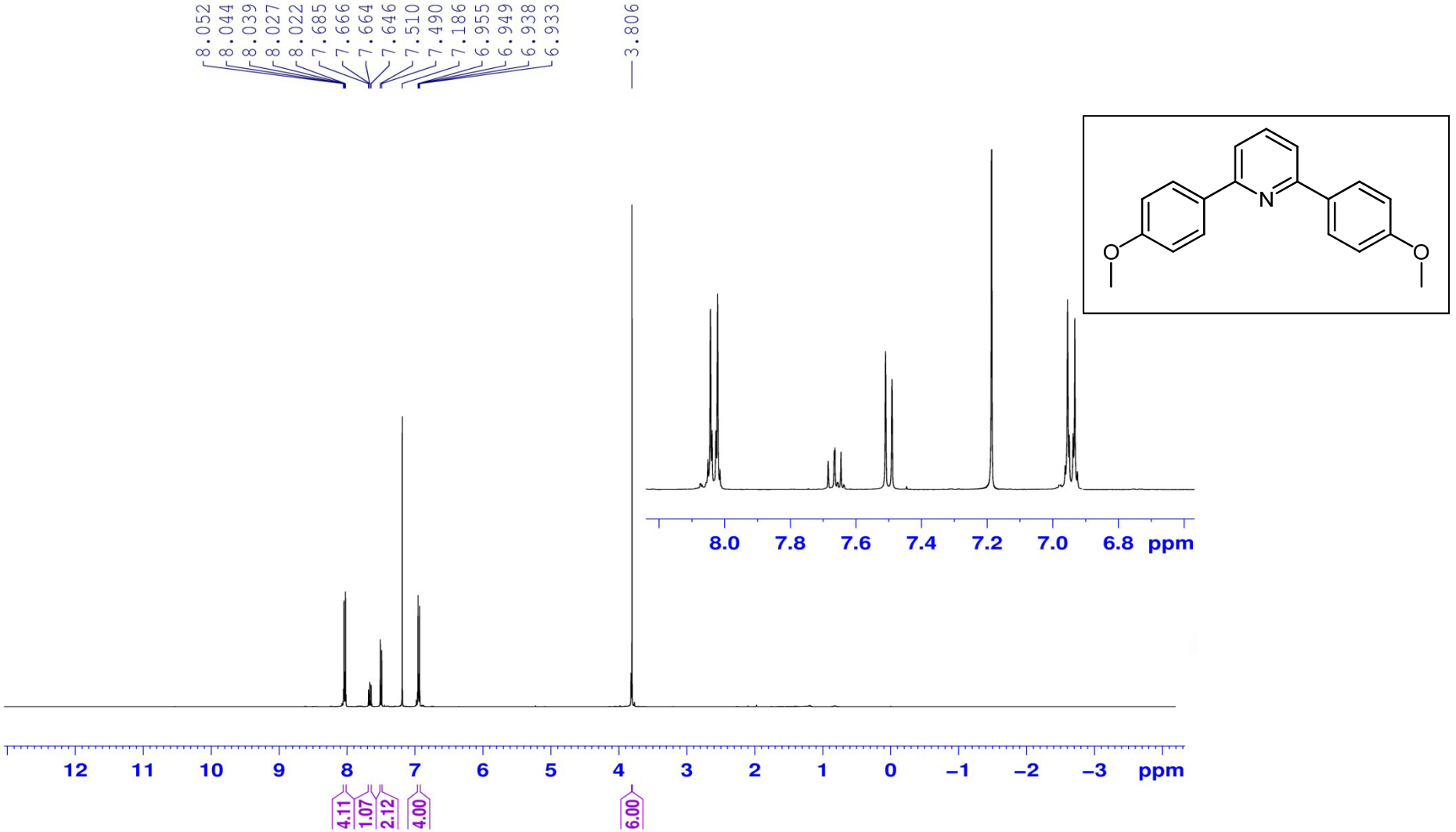


2,6-Diphenylprydine (S1, Table 7, entry 1); ^{13}C NMR (100 MHz, $CDCl_3$)

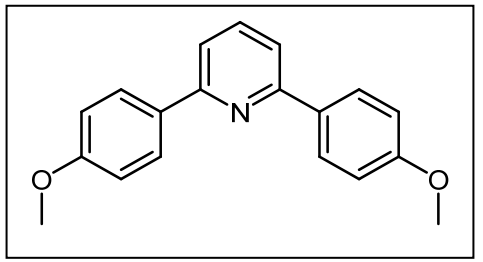


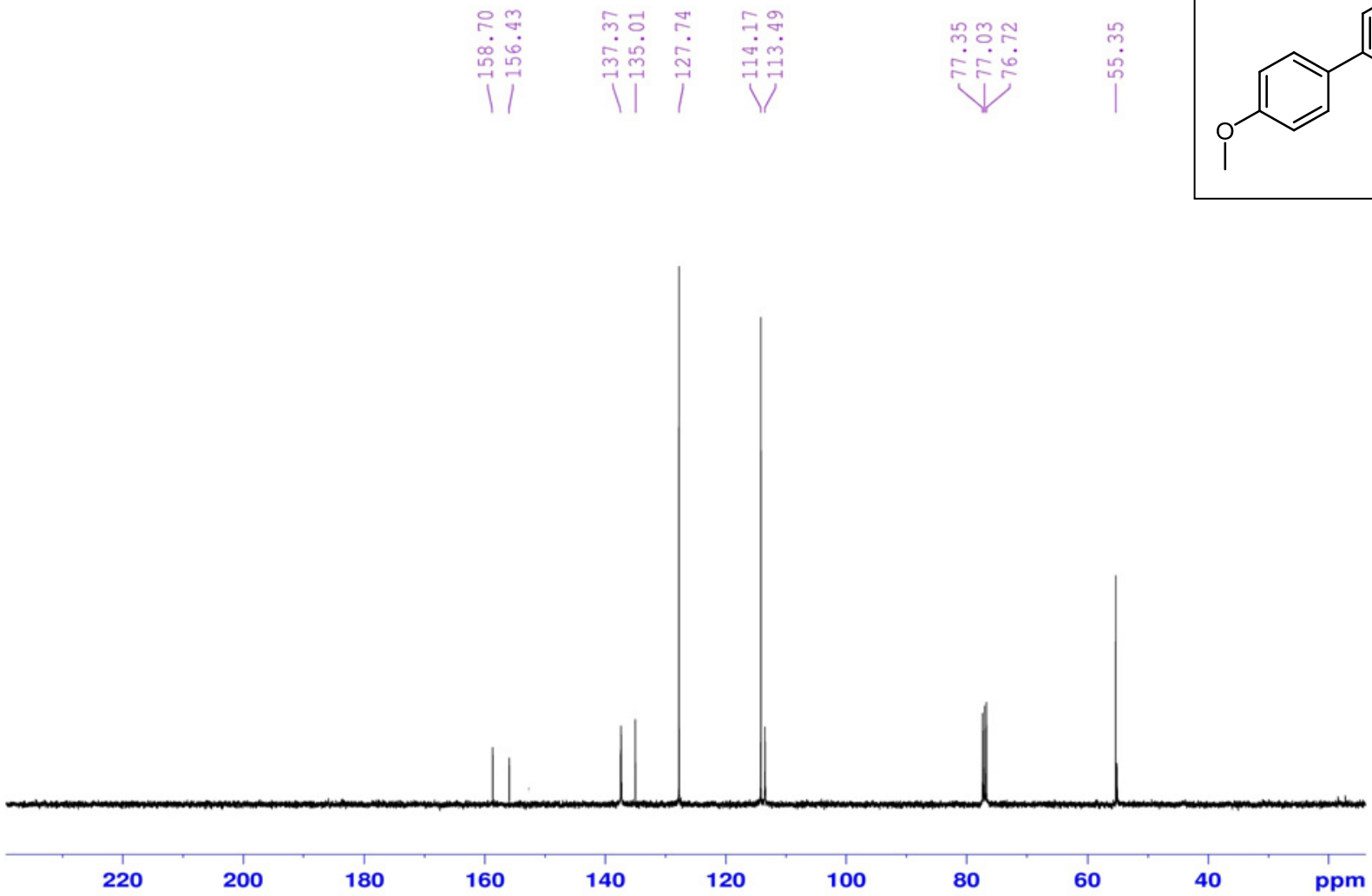


2,6-Bis(4-methoxyphenyl)pyridine (S2, Table 7, entry 2); ^{1}H NMR (400 MHz, $CDCl_3$)

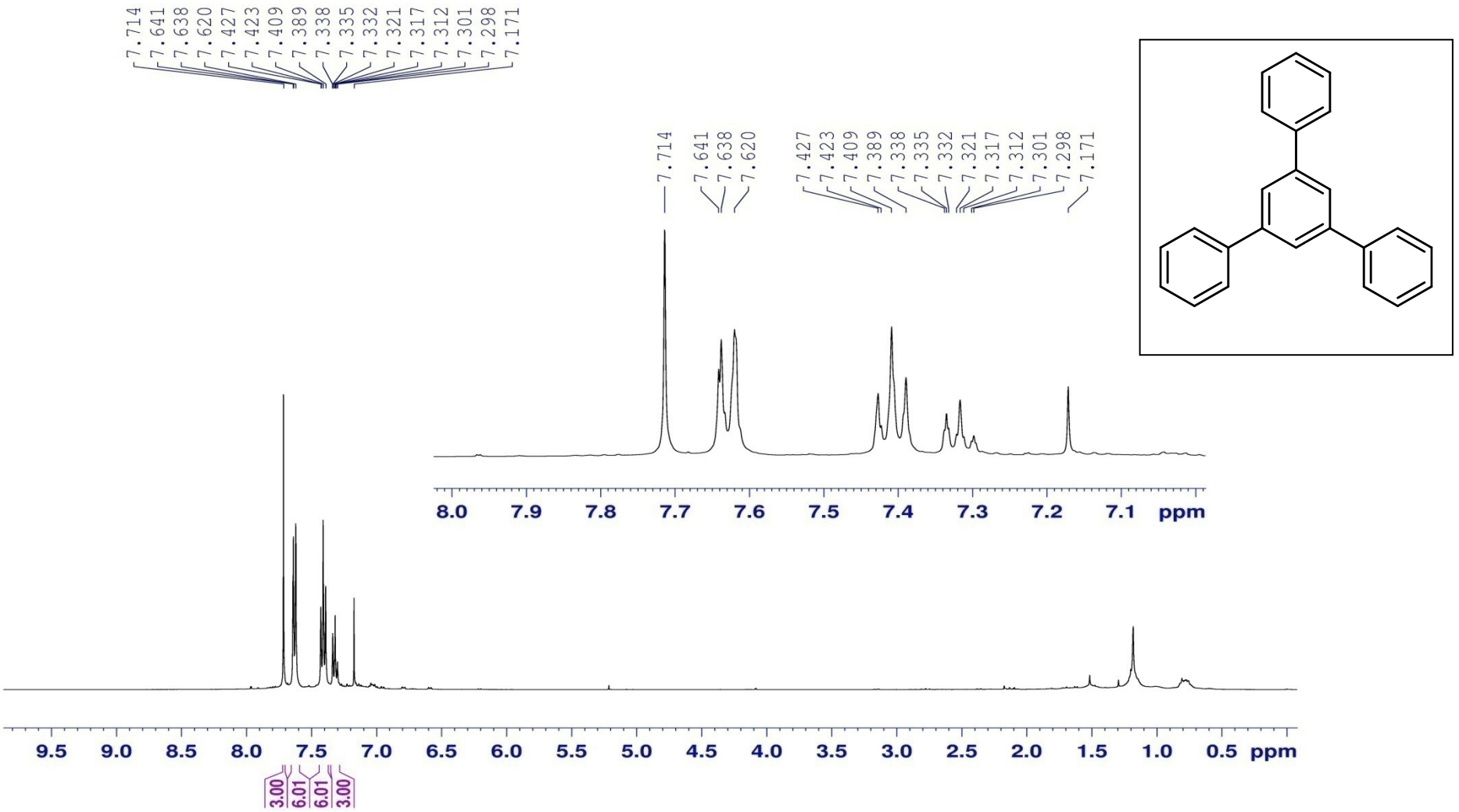


2,6-Bis(4-methoxyphenyl)pyridine (S2, Table 7, entry 2); ^{13} C NMR (100 MHz, $CDCl_3$)

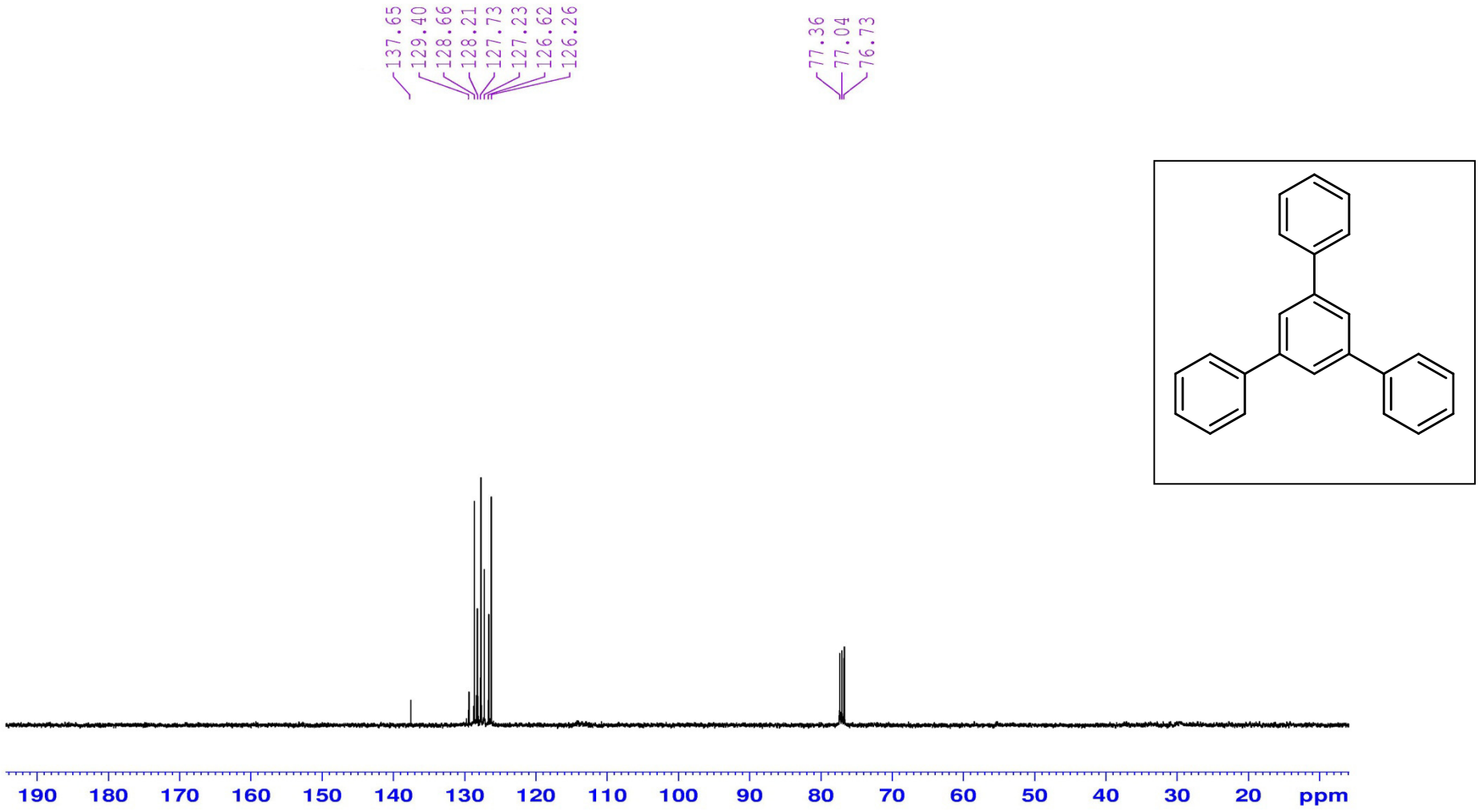




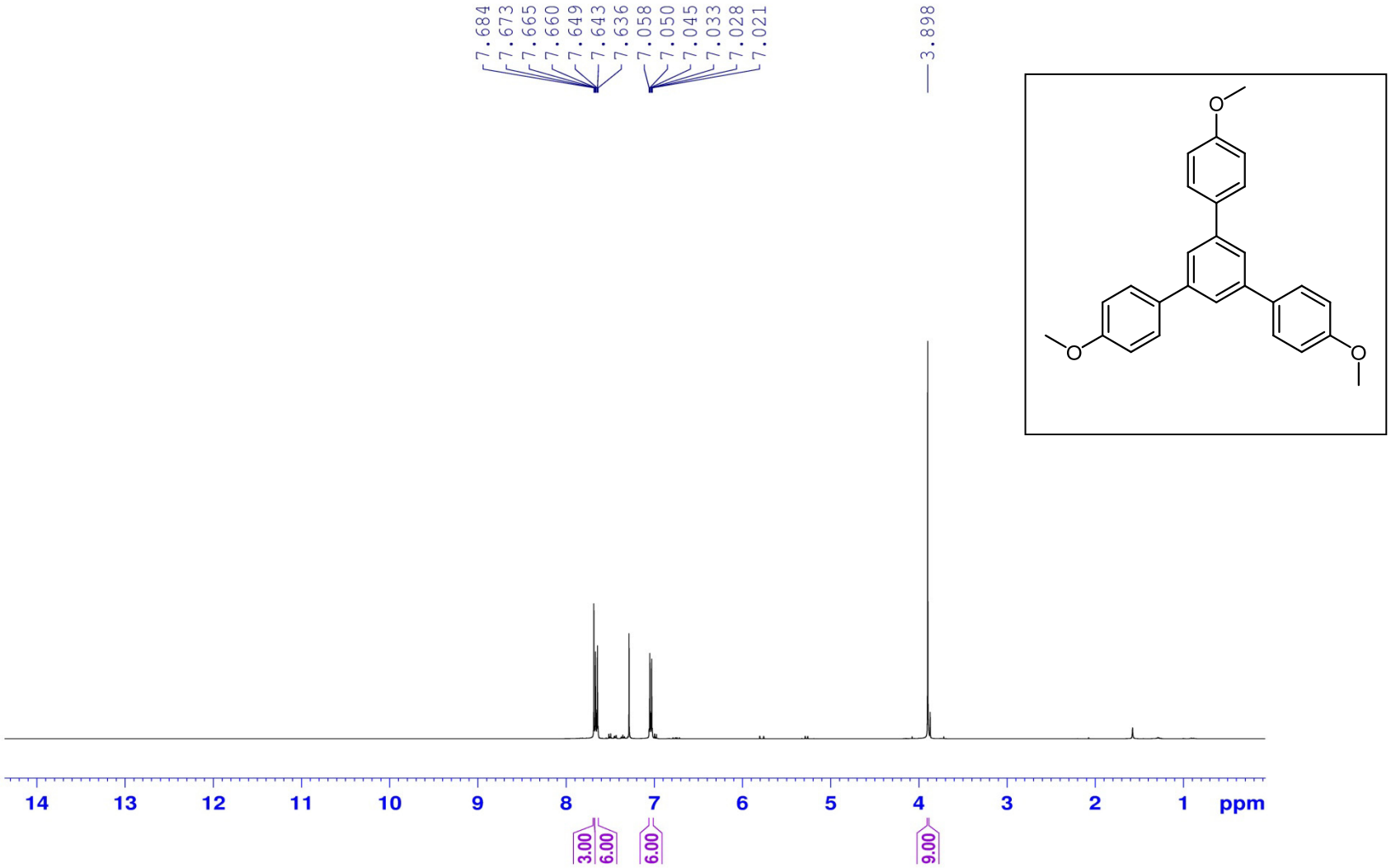
1,3,5-1,3,5-Triphenylbenzene (S3, Table 7, entry 3); ^{1}H NMR (400 MHz, $CDCl_3$)



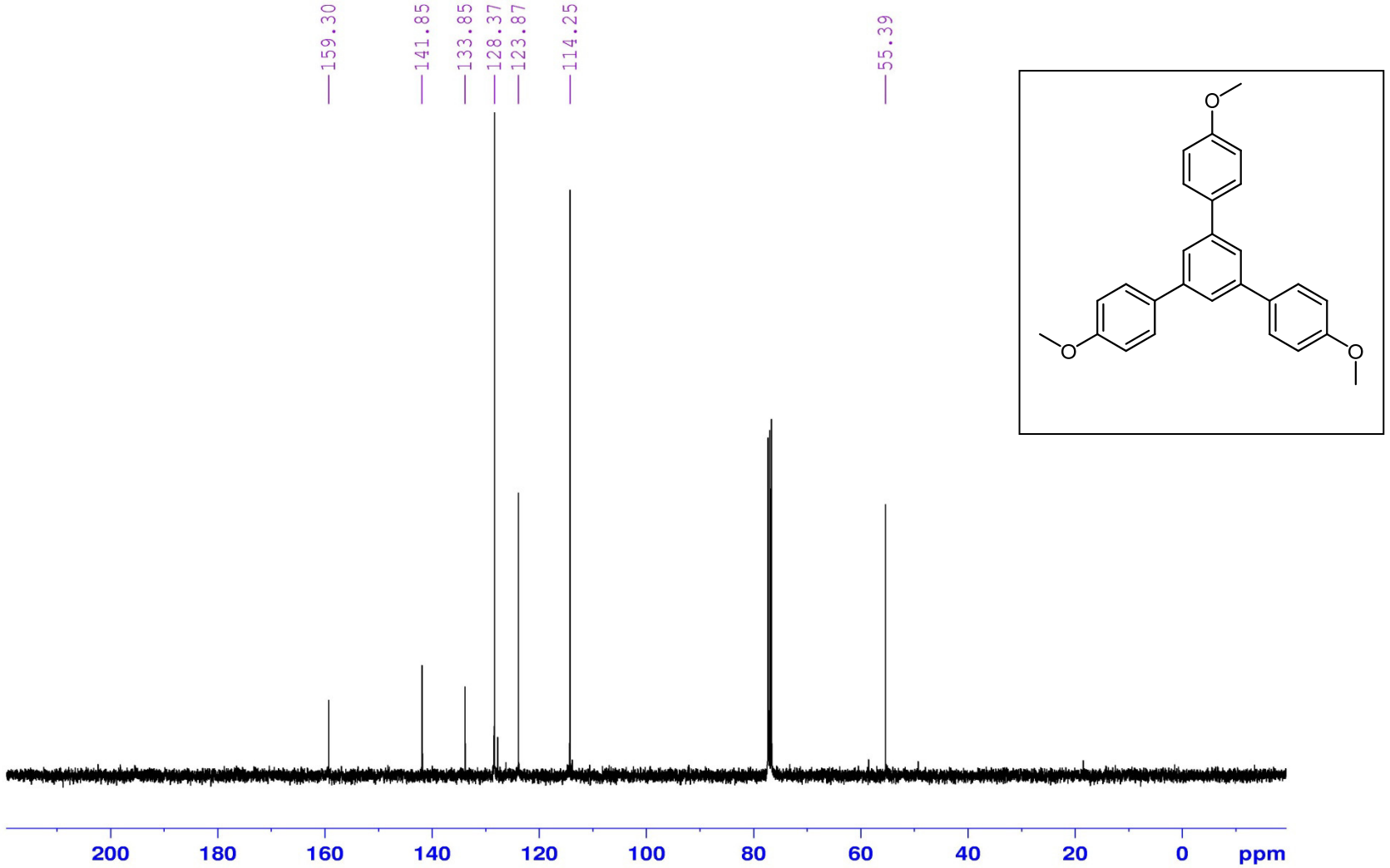
1,3,5-Triphenylbenzene (S3, Table 7, entry 3); ^{13}C NMR (100 MHz, $CDCl_3$)



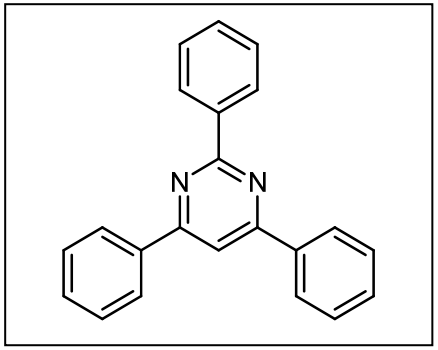
1,3,5-Tri(4-methoxyphenyl)benzene (S4, Table 7, entry 4); ^{1}H NMR (400 MHz, $CDCl_3$)

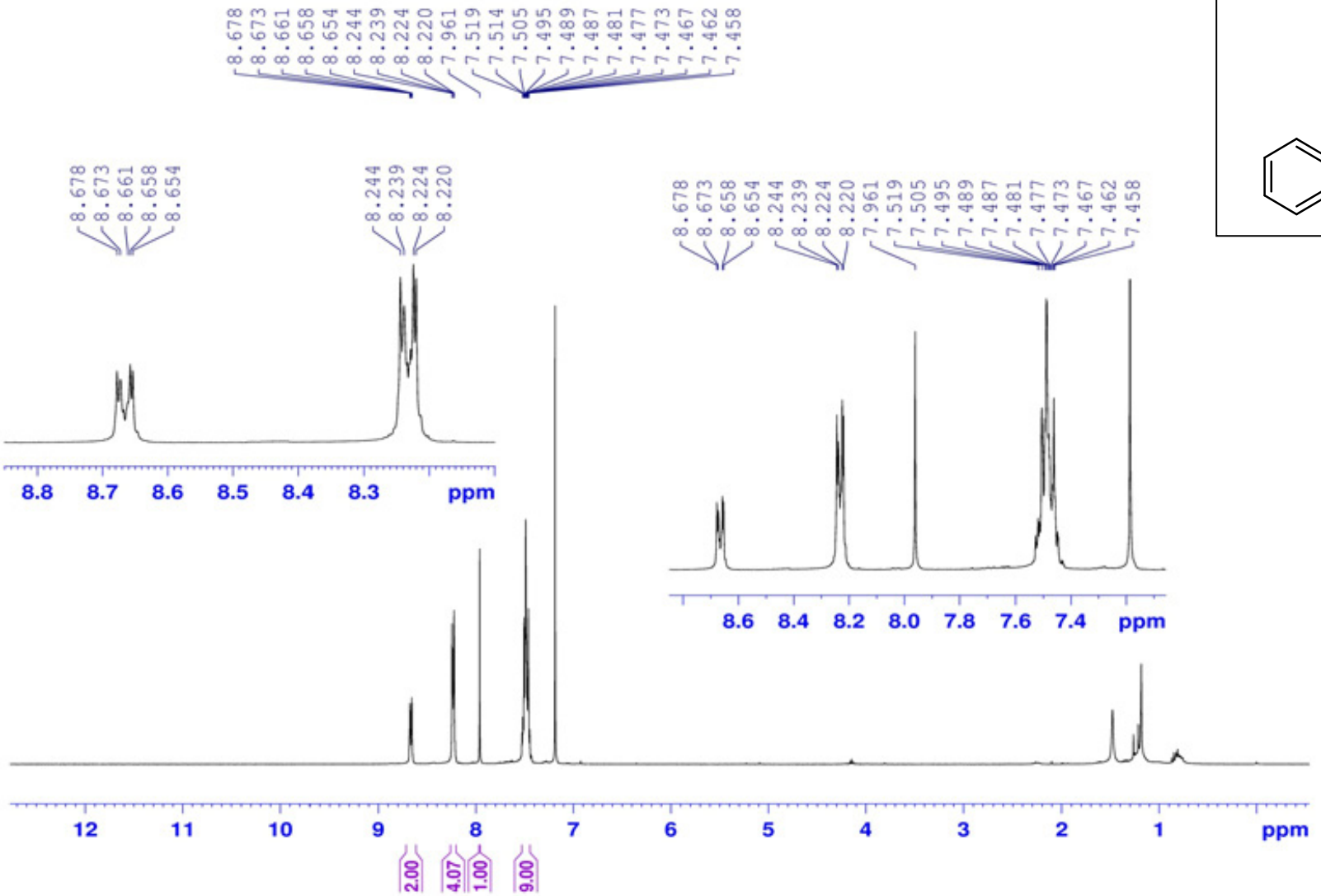


1,3,5-Tri(4-methoxyphenyl)benzene (S4, Table 7, entry 4); ^{13}C NMR (100 MHz, $CDCl_3$)

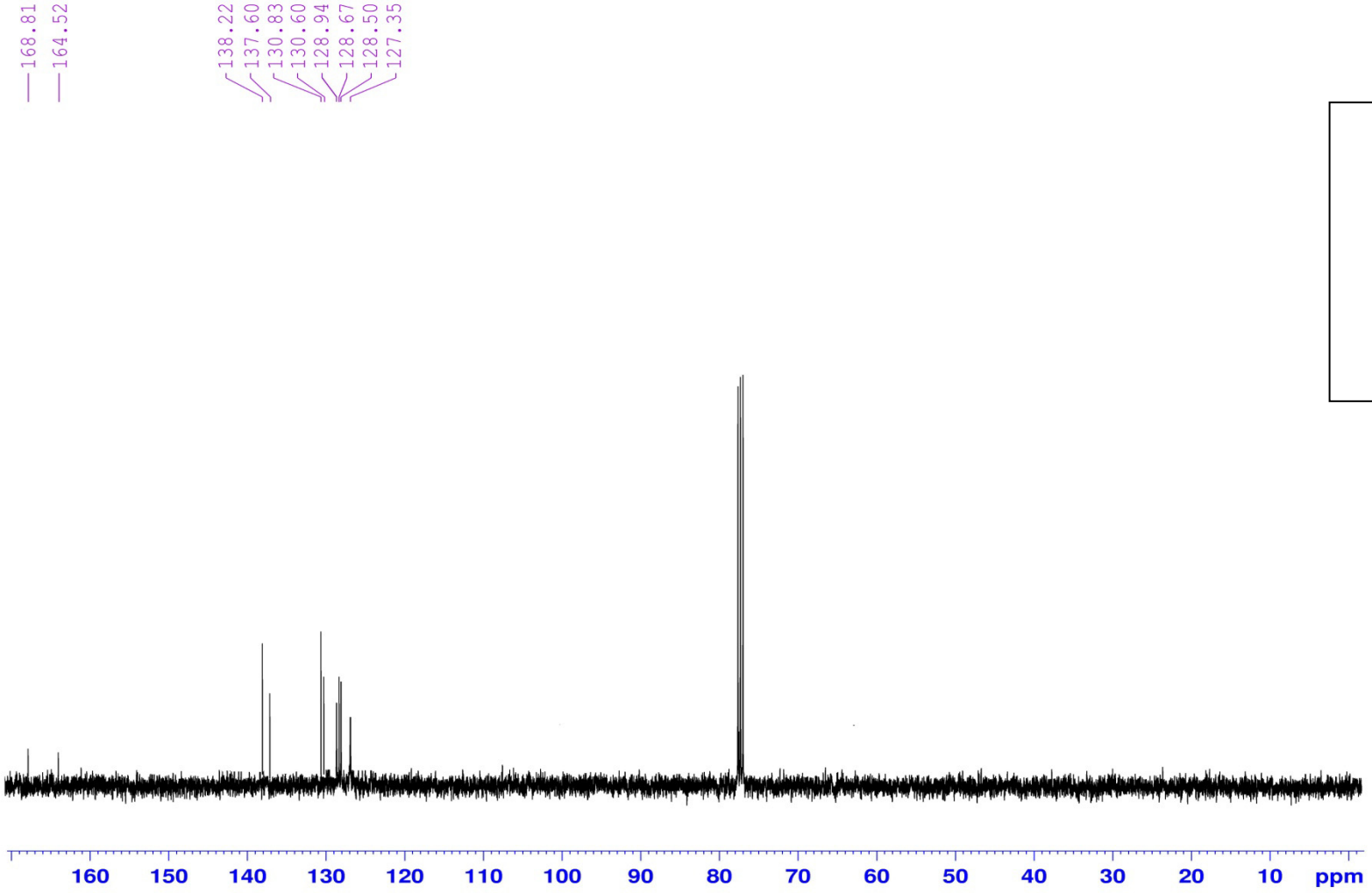


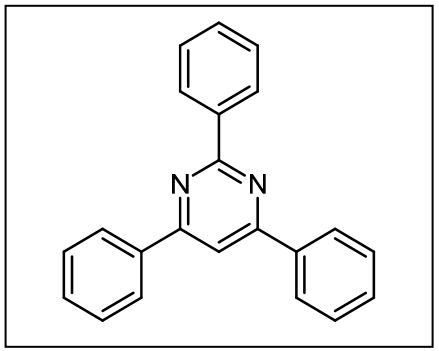
2,4,6-Triphenylprimidine (S5, Table 7, entry 5); ^{1}H NMR (400 MHz, $CDCl_3$)



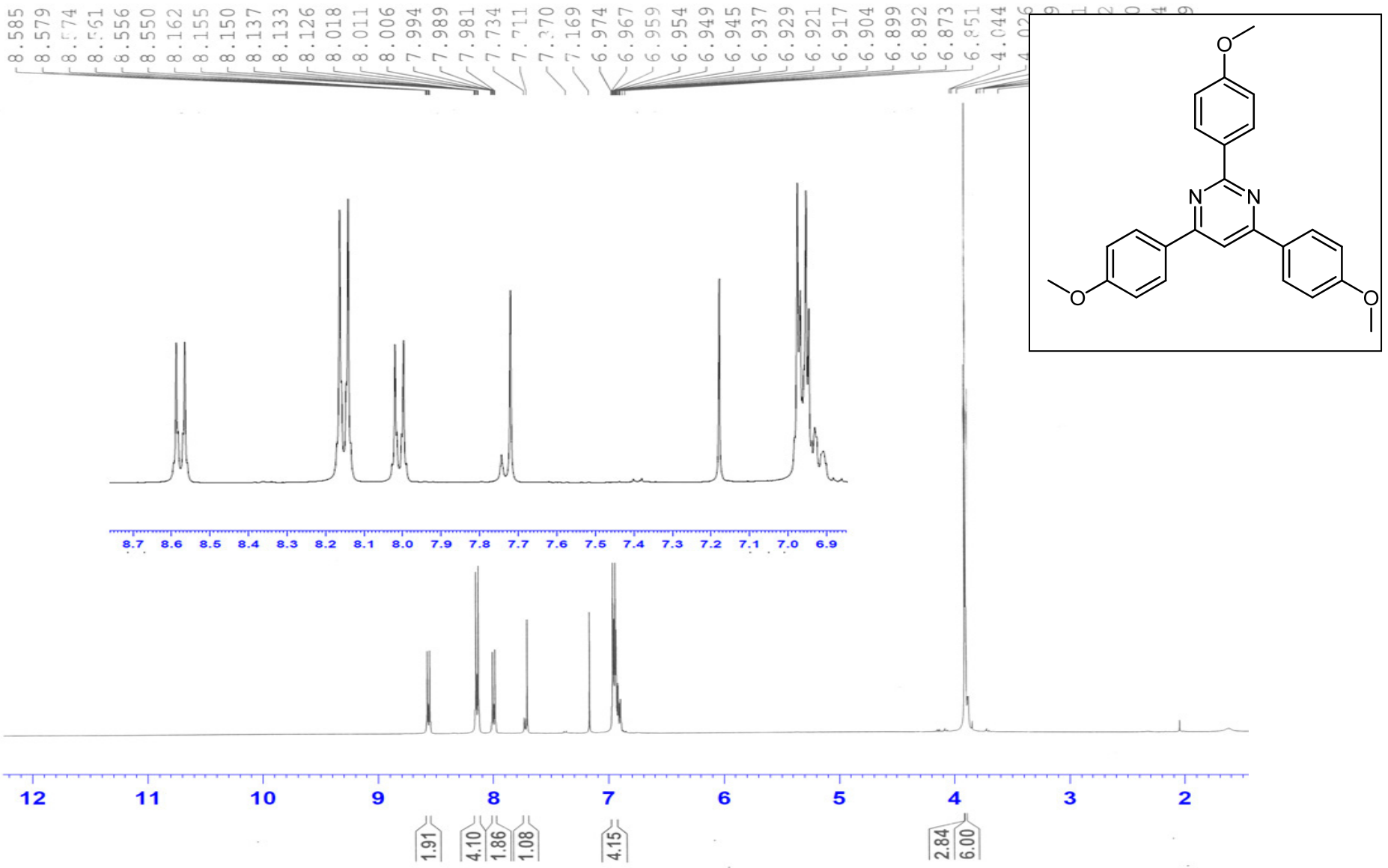


2,4,6-Triphenylprimidine (S5, Table 7, entry 5); ^{13}C NMR (100 MHz, $CDCl_3$)

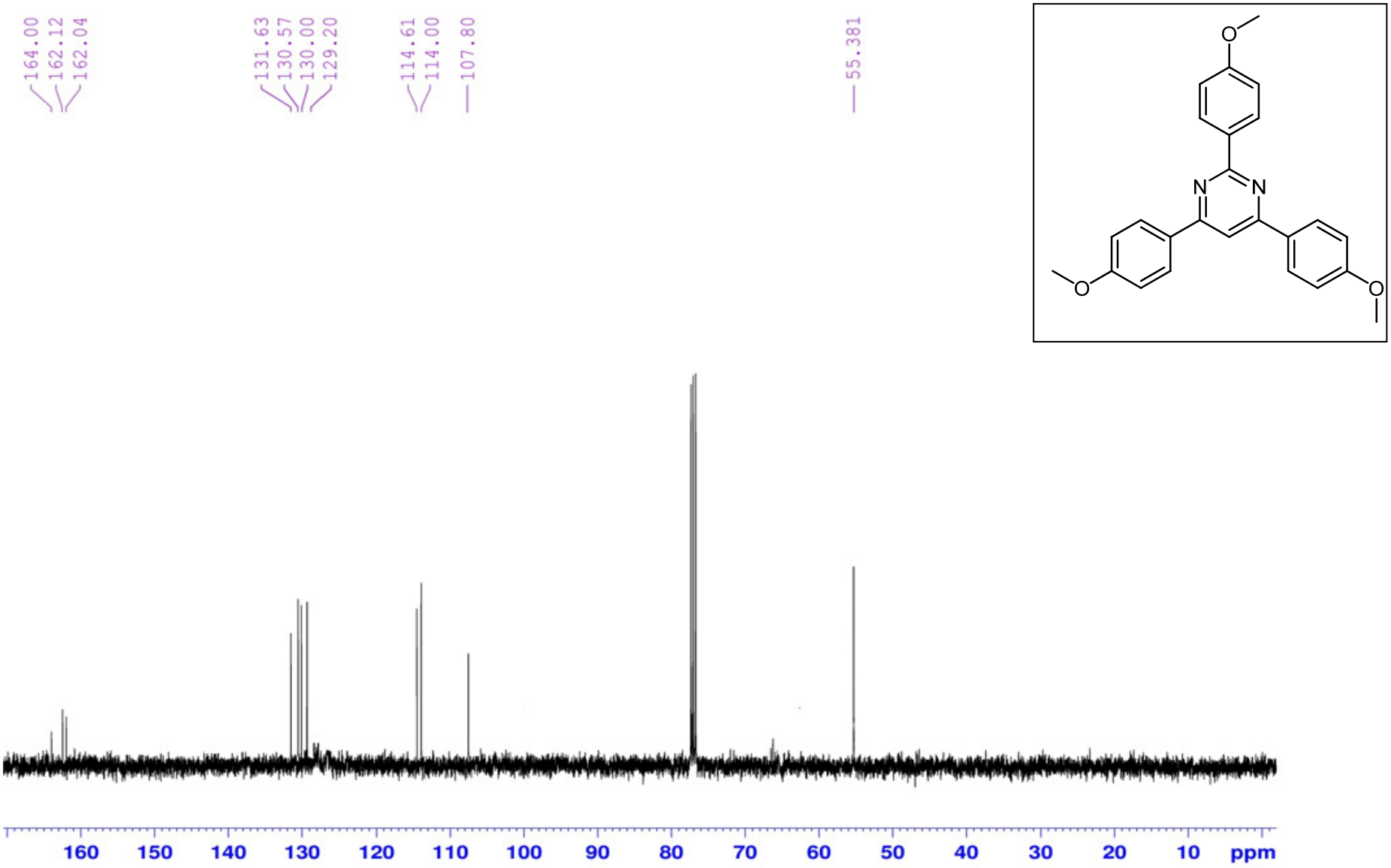




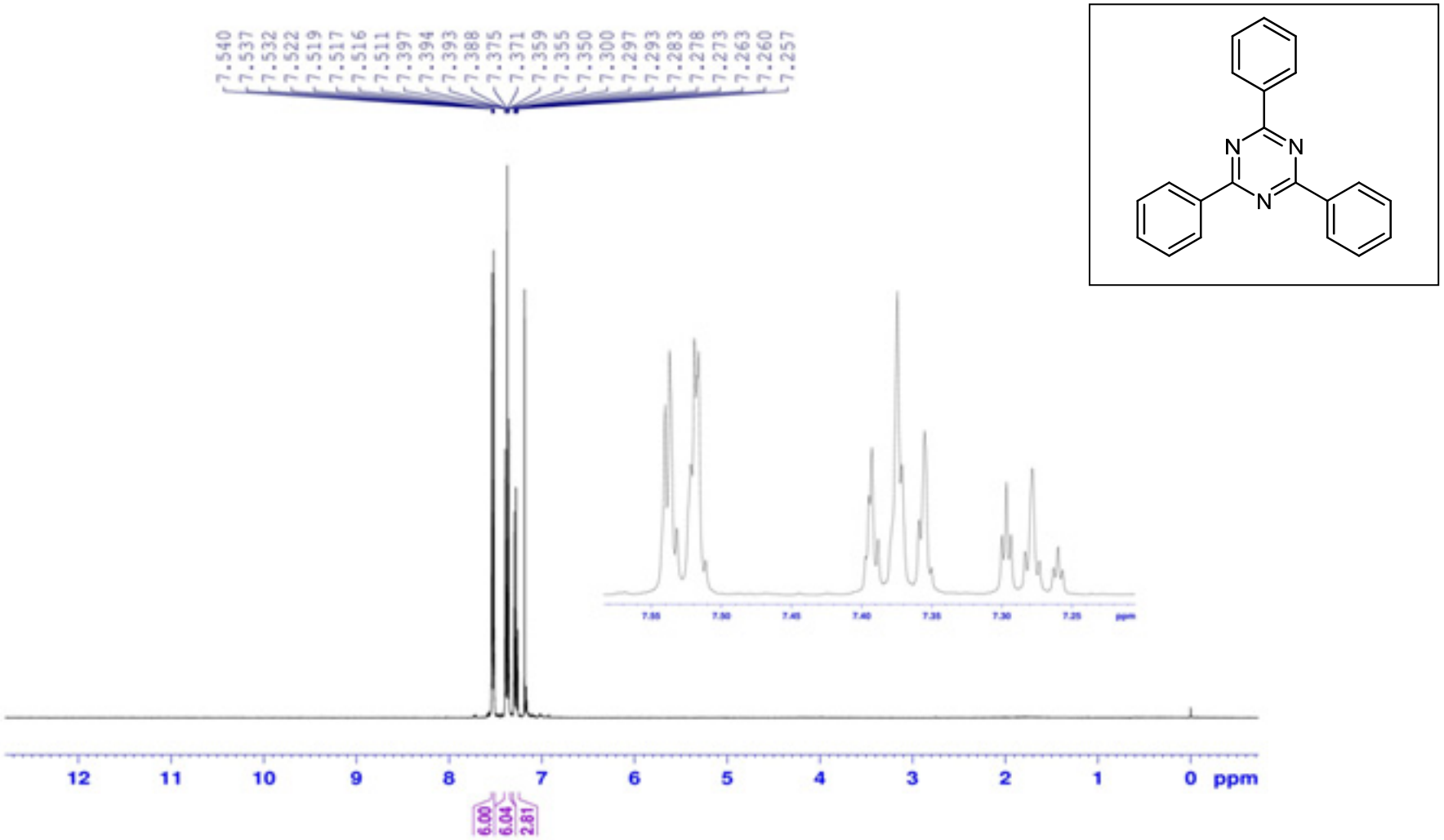
2,4,6-Tris(4-methoxyphenyl)pyrimidine (S6, Table 7, entry 6); ^{1}H NMR (400 MHz, $CDCl_3$)



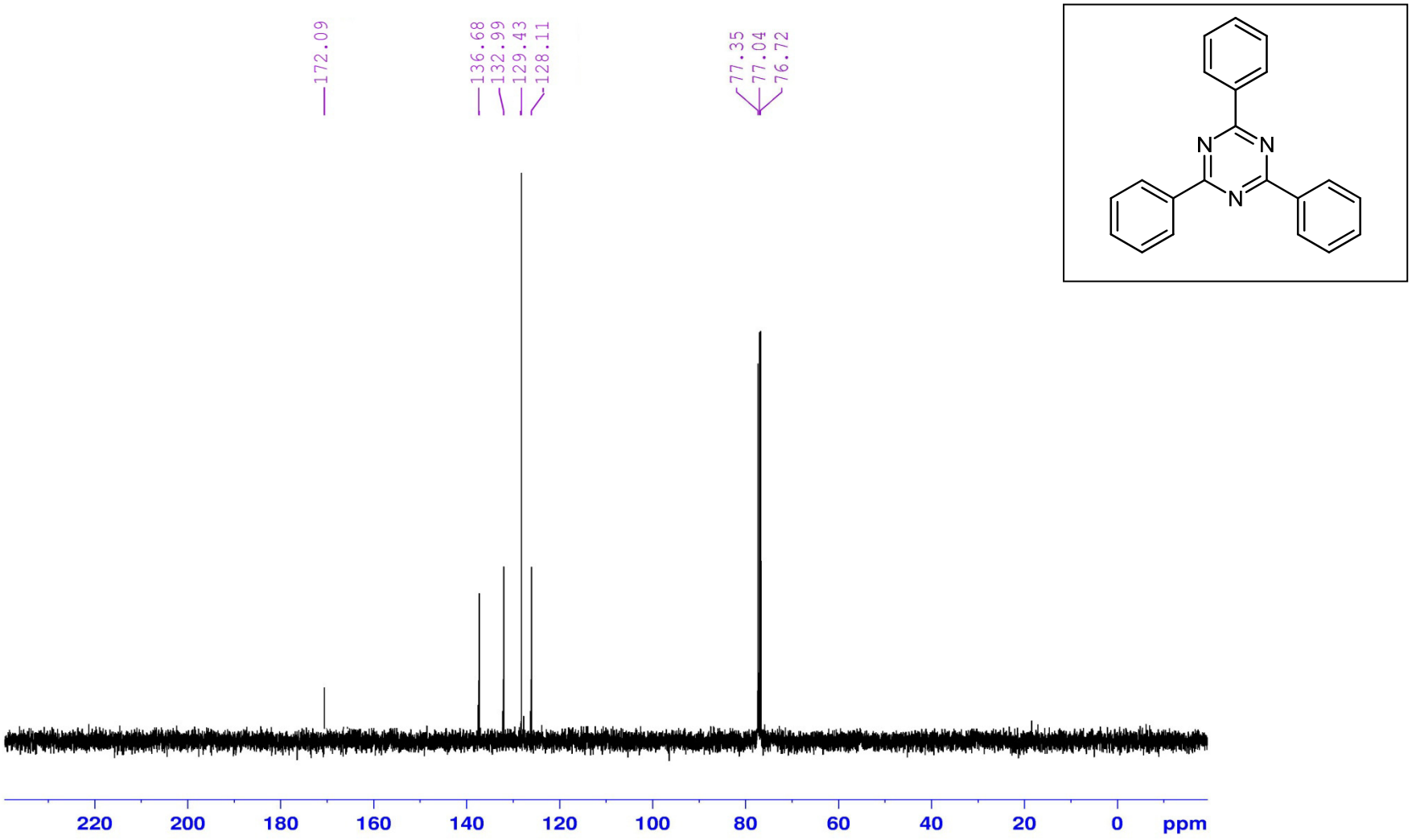
2,4,6-Tris(4-methoxyphenyl)pyrimidine (S6, Table 7, entry 6); ^{13}C NMR (100 MHz, $CDCl_3$)



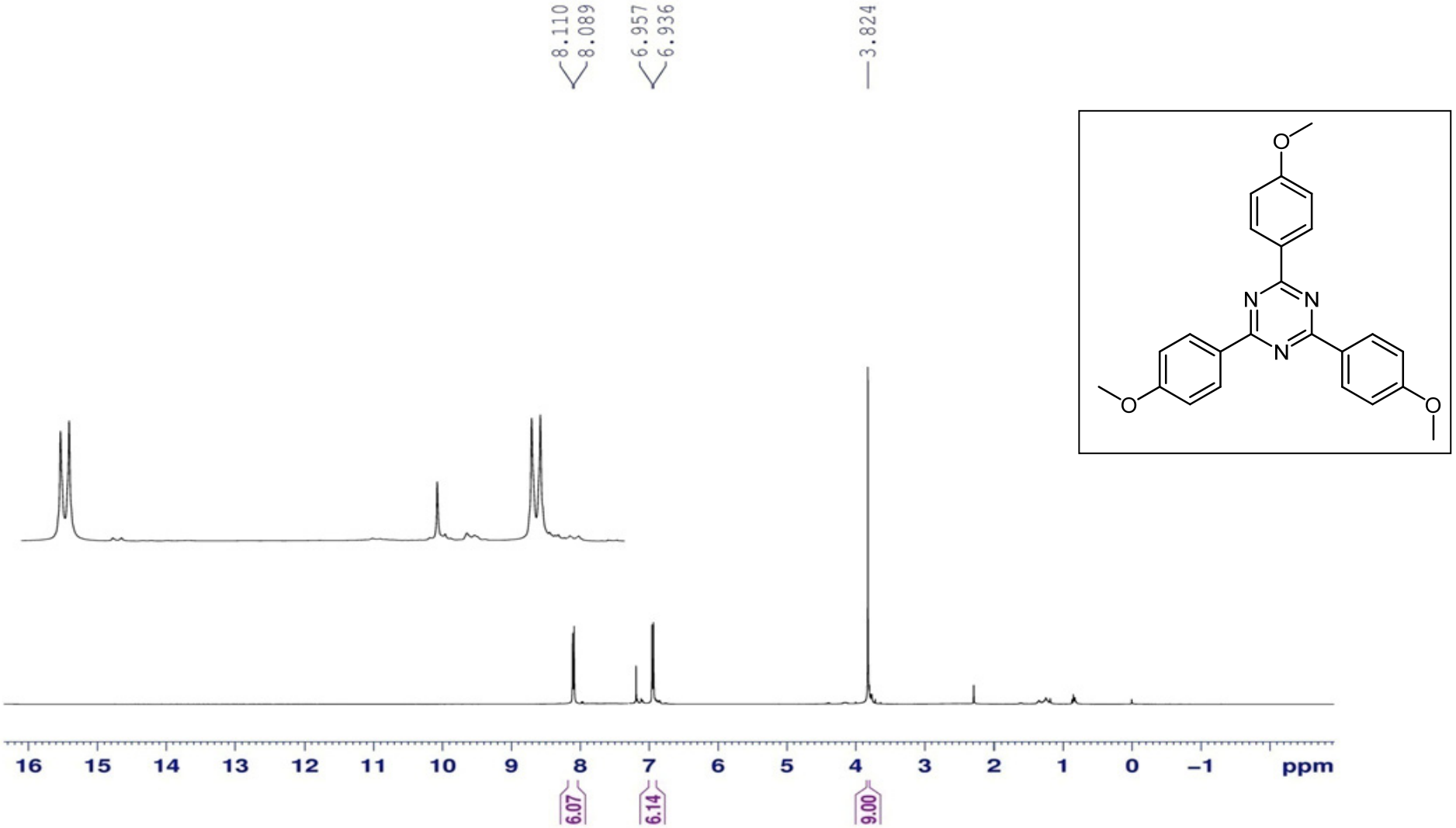
2,4,6-Triphenyltriazine (S7, Table 7, entry 7); ^{1}H NMR (400 MHz, $CDCl_3$)



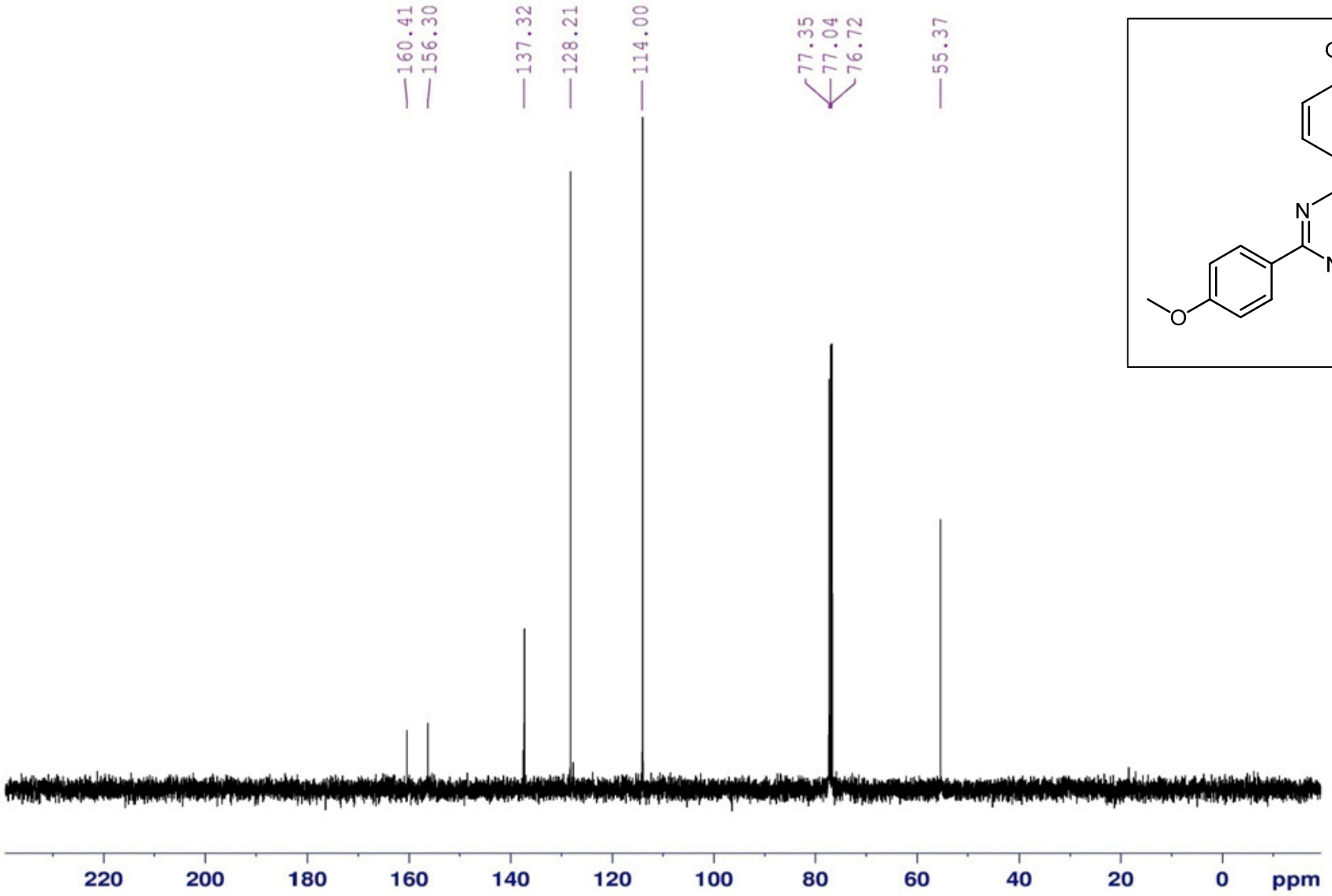
2,4,6-Triphenyltriazine (S7, Table 7, entry 7); ^{13}C NMR (100 MHz, $CDCl_3$)



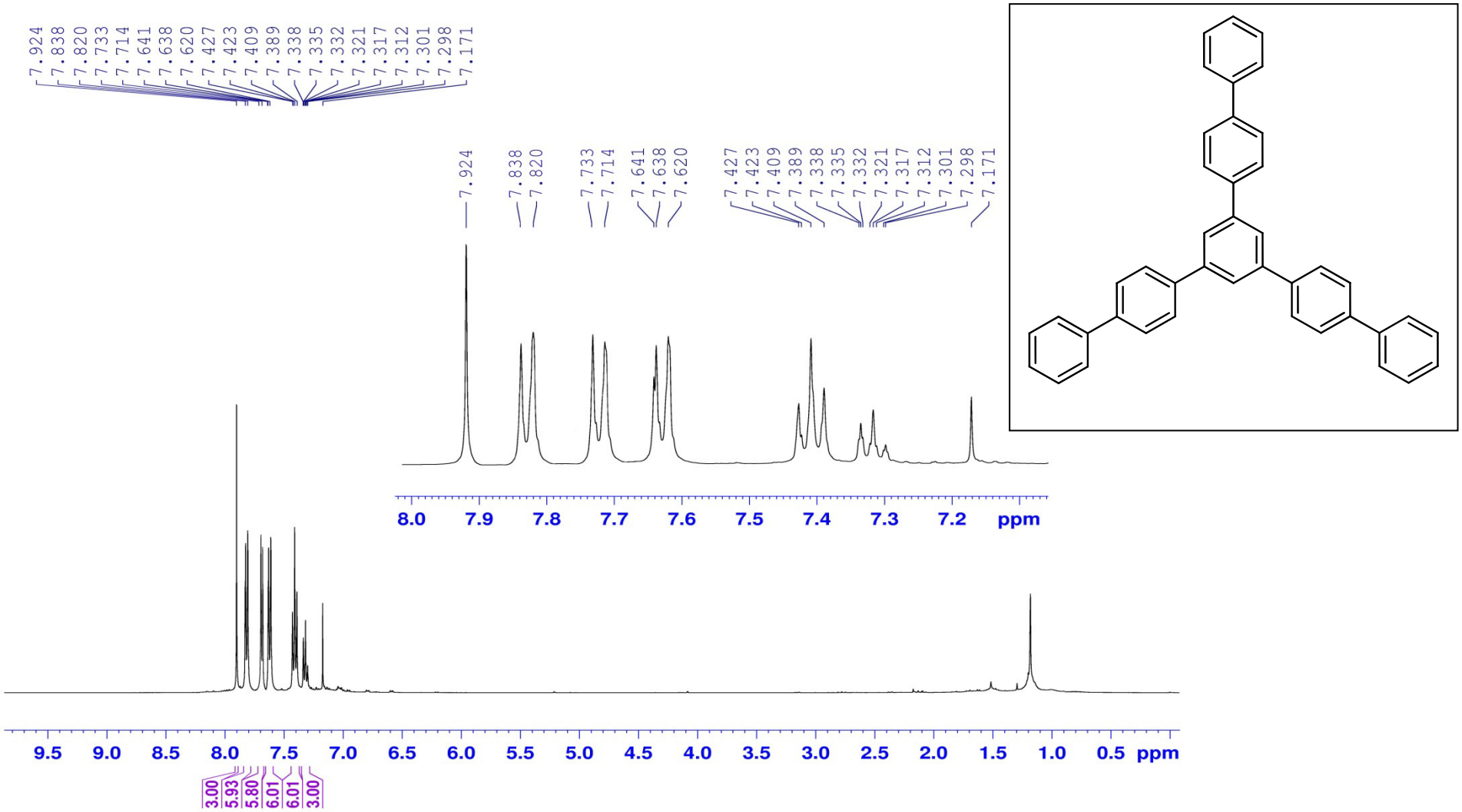
2,4,6-Tris(4-methoxyphenyl)triazine (S8, Table 7, entry 8); ^{1}H NMR (400 MHz, $CDCl_3$)



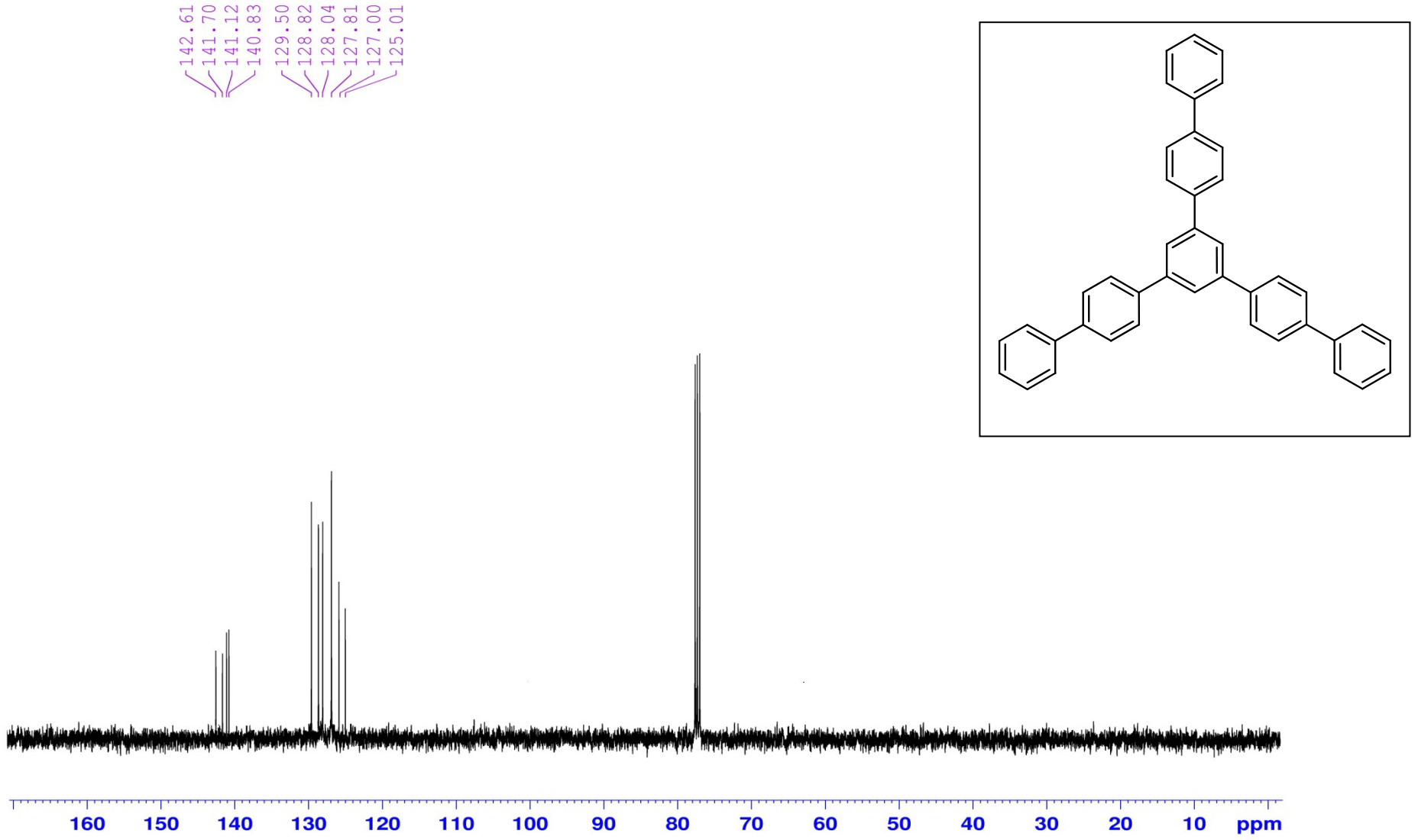
2,4,6-Tris(4-methoxyphenyl)triazine (S8, Table 7, entry 8); ^{13}C NMR (100 Mhz, $CDCl_3$)



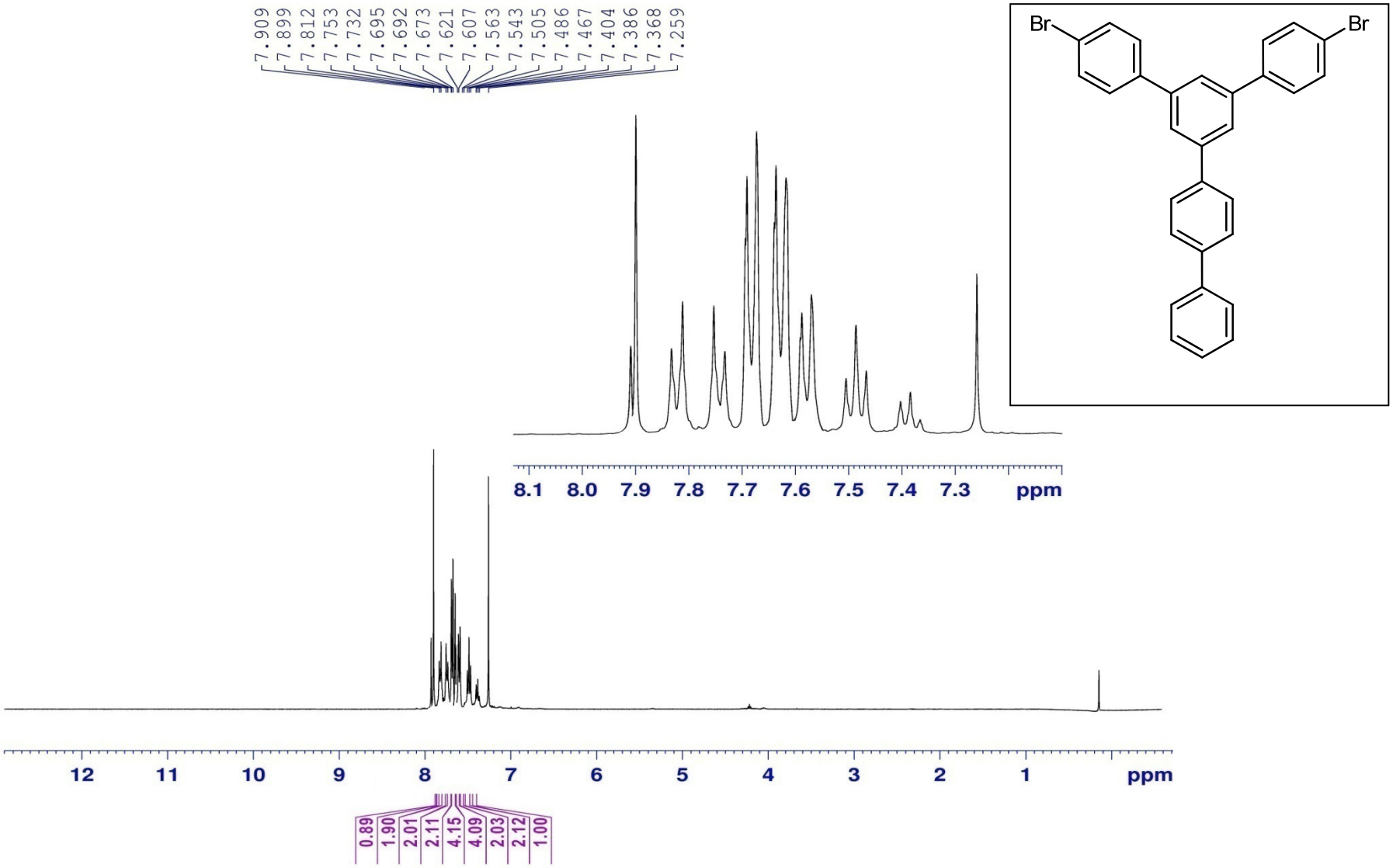
1,3,5-Tris(4-phenylphenyl)benzene (S11); ^{1}H NMR (400 MHz, $CDCl_3$)



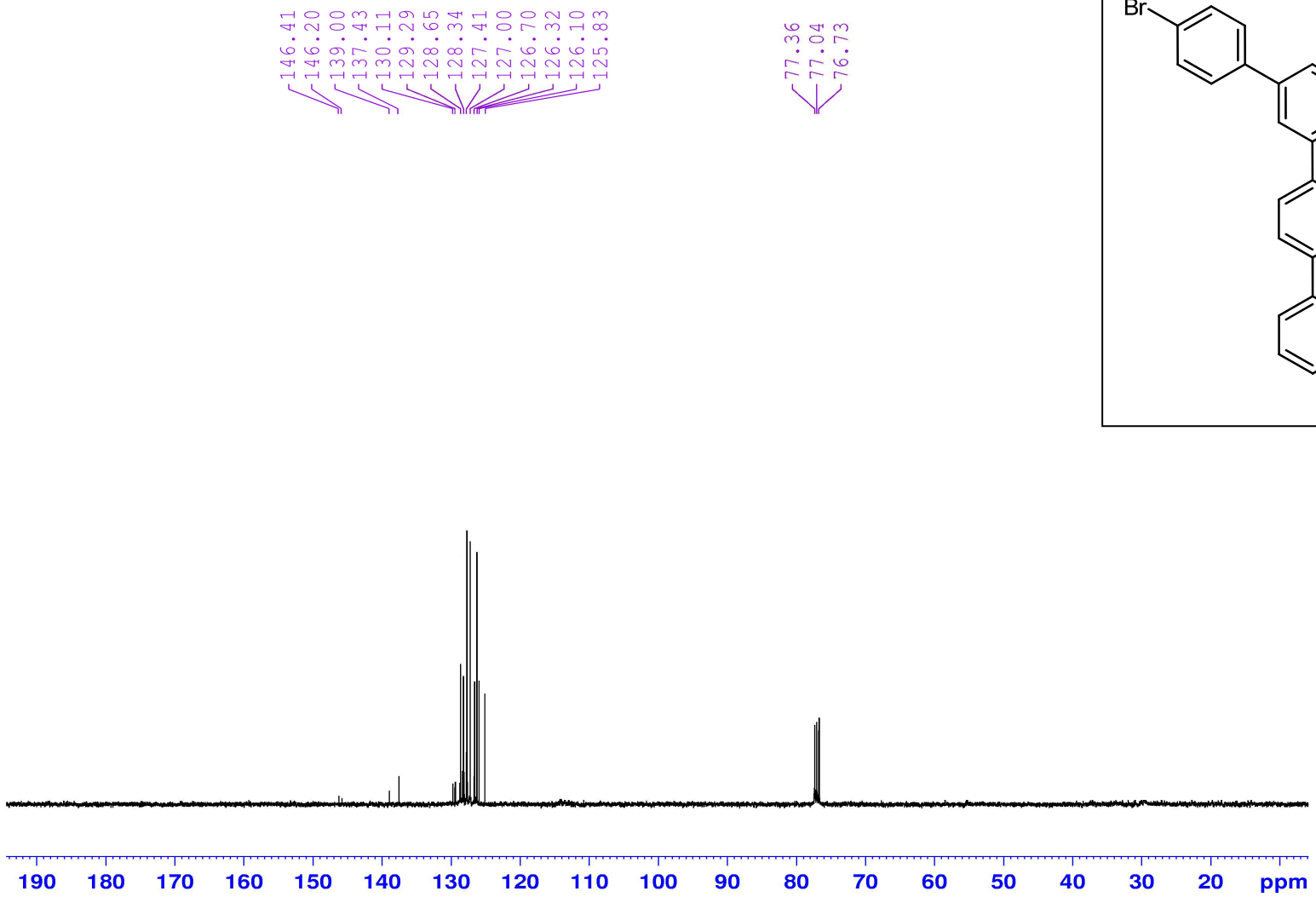
1,3,5-Tris(4-phenylphenyl)benzene (S11); ^{13}C NMR (100 MHz, $CDCl_3$)



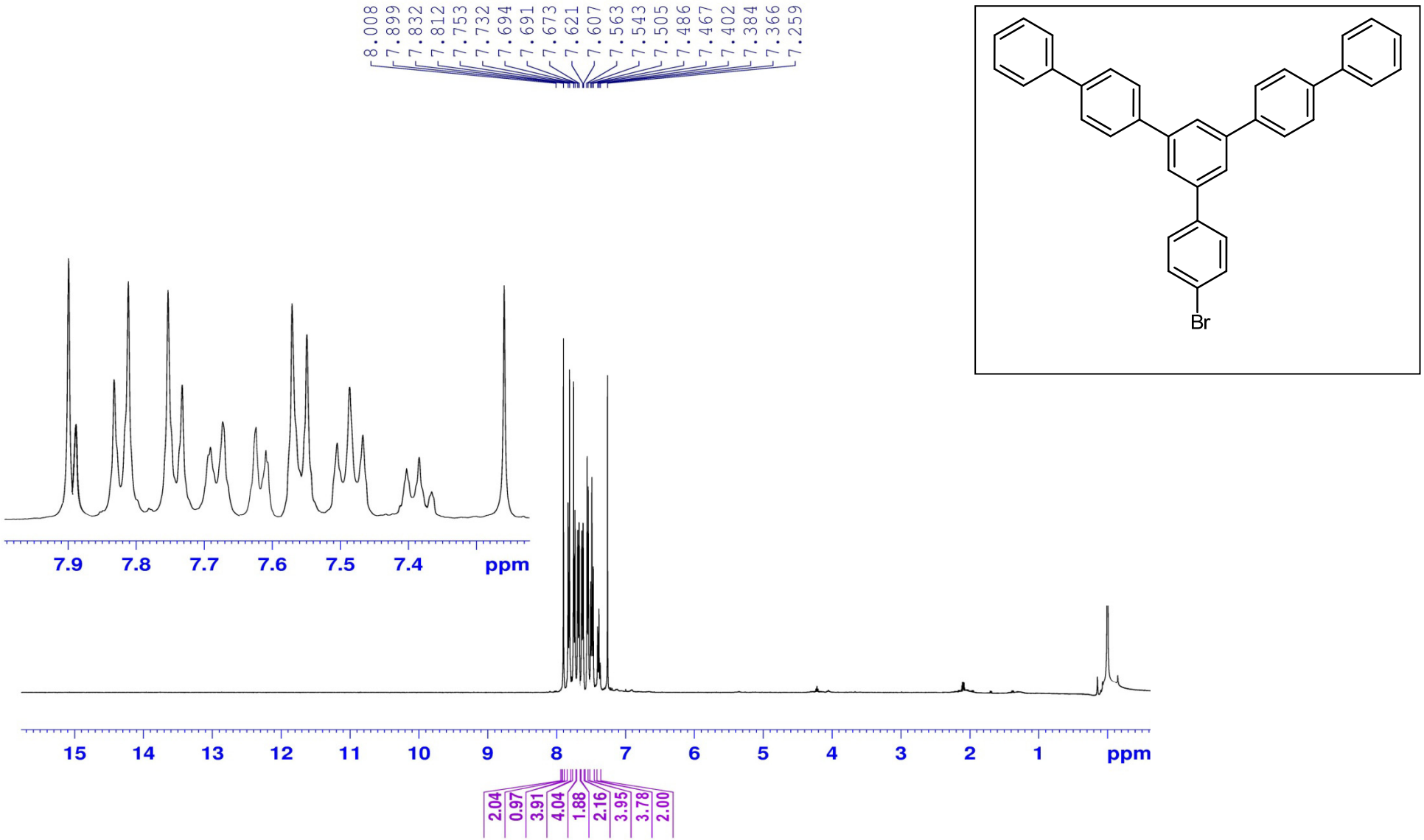
1-(4'-Phenylphenyl)-3,5-di(4-bromophenyl) benzene (S13); ^{1}H NMR (400MHz, $CDCl_3$)



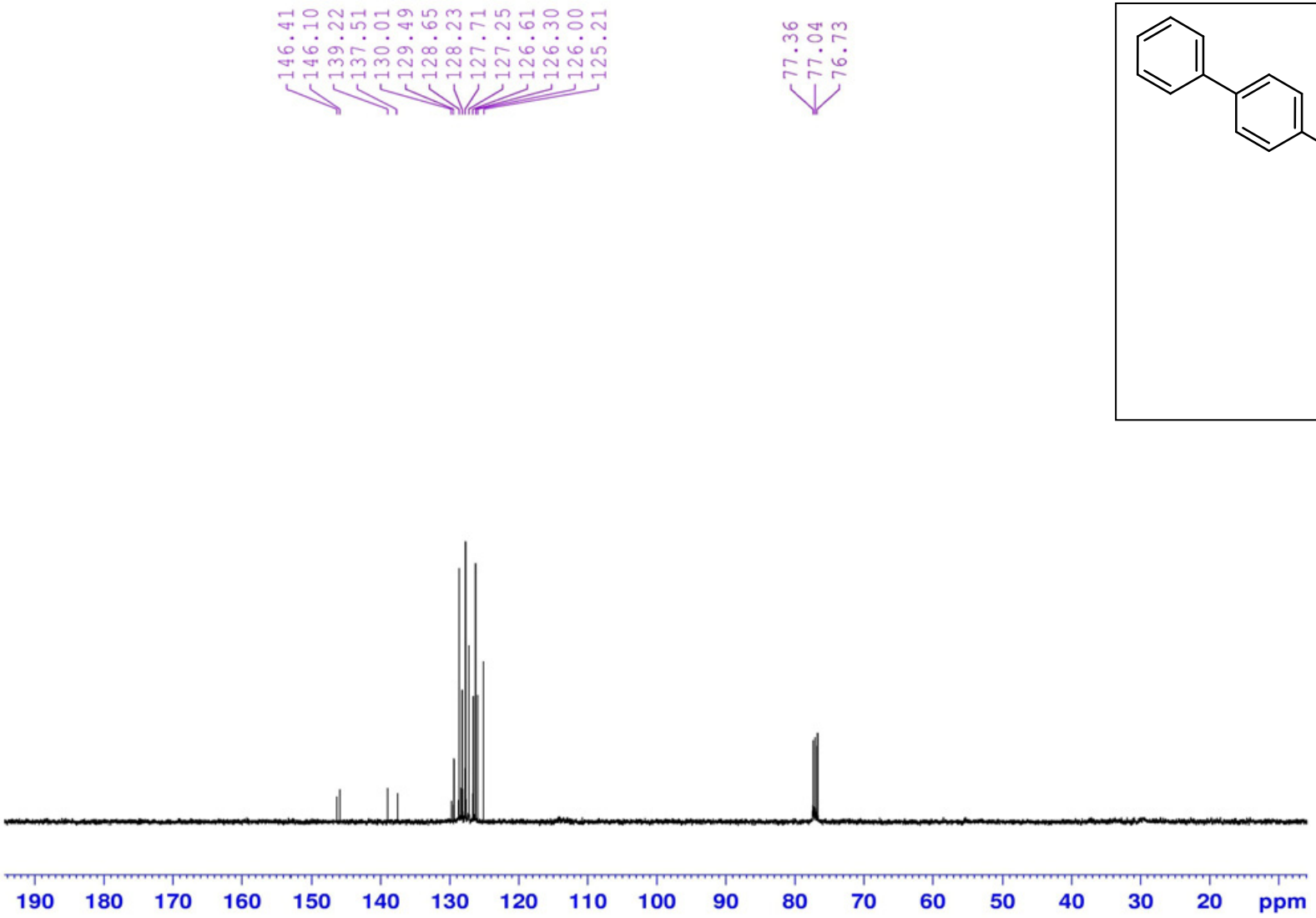
1-(4'-Phenylphenyl)-3,5-di(4-bromophenyl) benzene (S13); ^{13}C NMR (100MHz, $CDCl_3$)



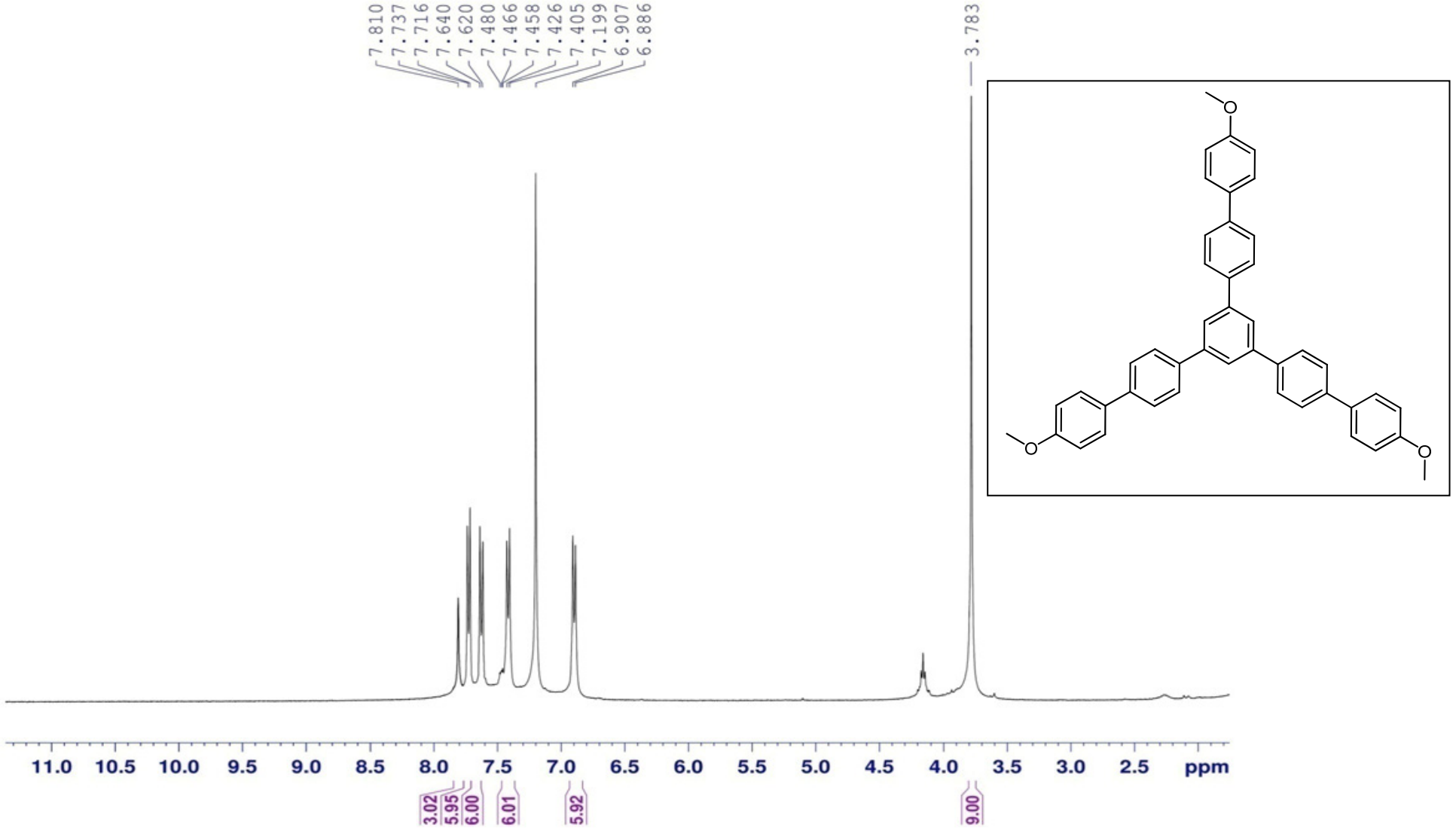
1,3-Di(4'-phenylphenyl)-5-(4-bromophenyl) benzene; (S14); ^{1}H NMR (400 MHz, $CDCl_3$)



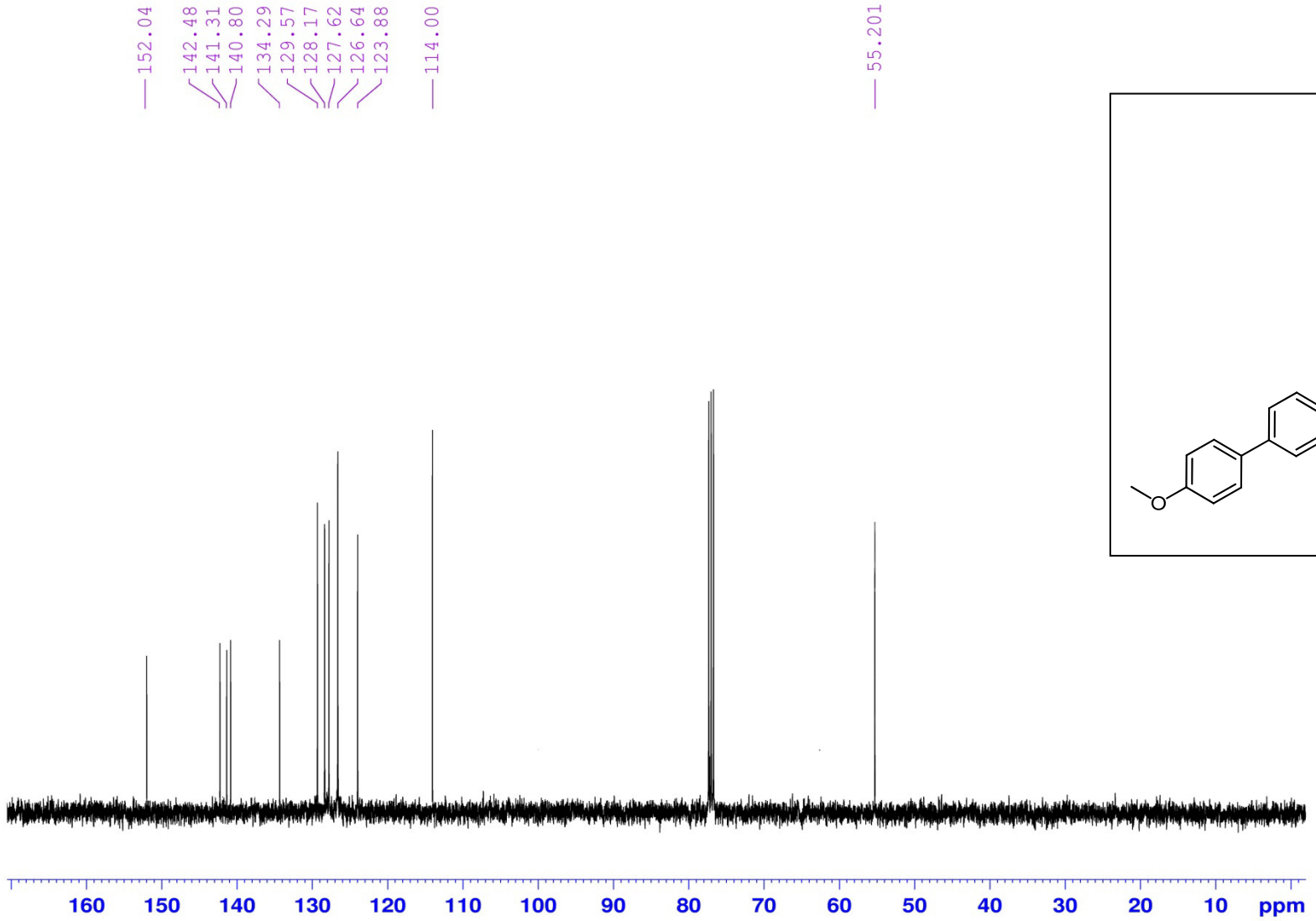
1,3-Di(4'-phenylphenyl)-5-(4-bromophenyl) benzene; (S14); ^{13}C NMR (100 MHz, $CDCl_3$)

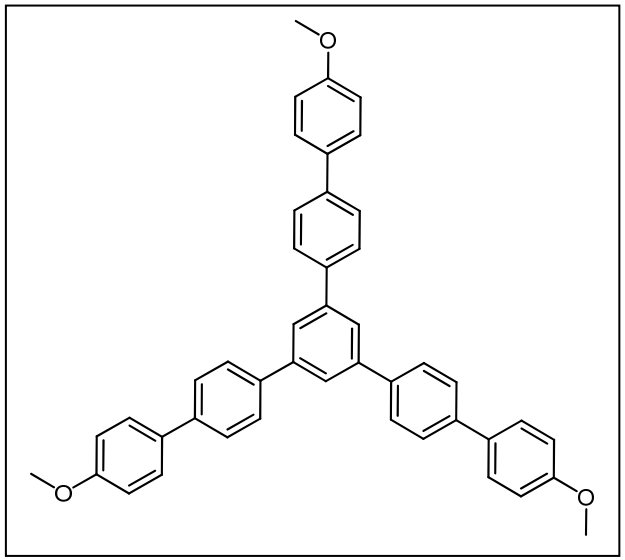


1,3,5-Tris[4-(4'-methoxyphenyl)phenyl]benzene (S12); ^{1}H NMR (400 MHz, $CDCl_3$)

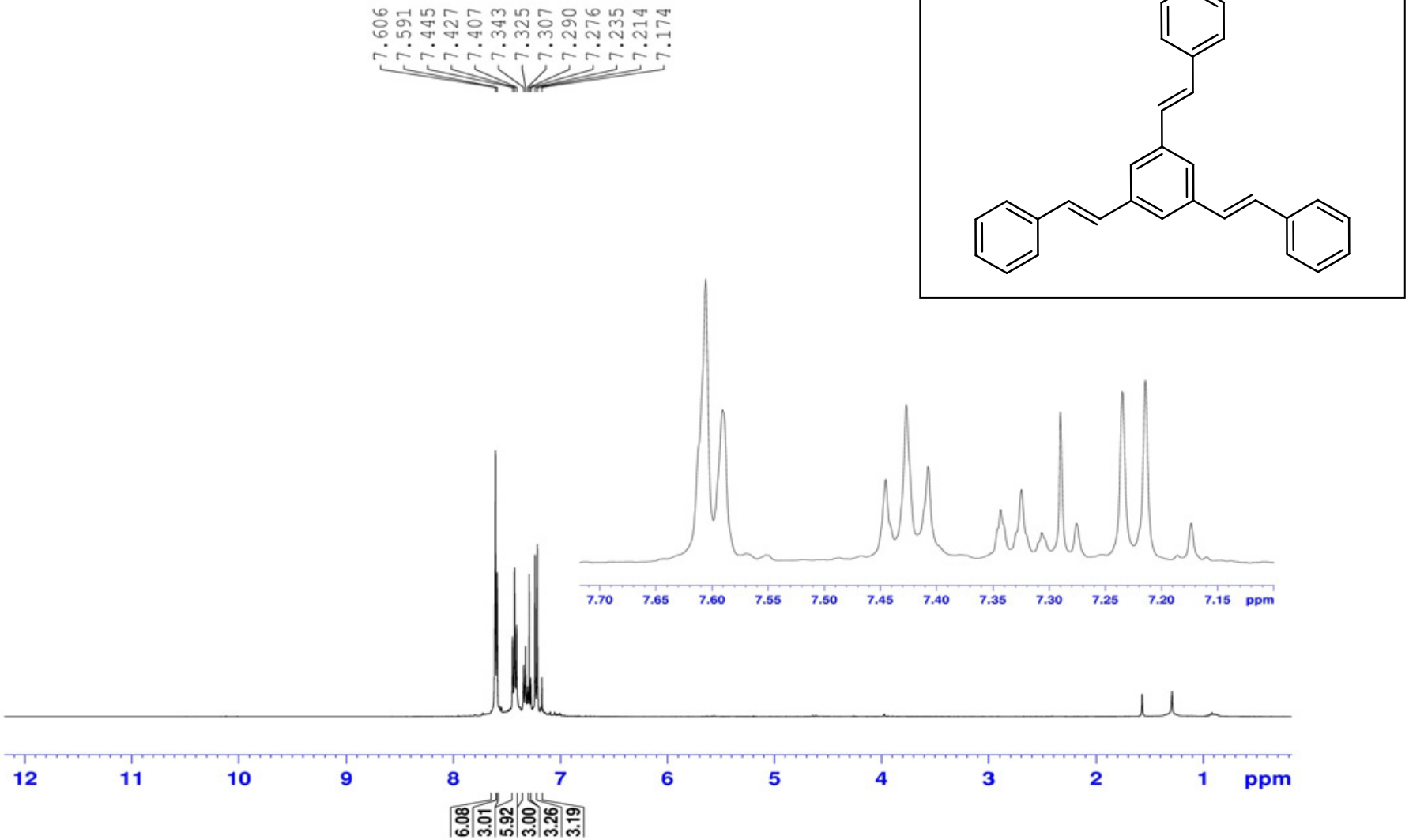


1,3,5-Tris[4-(4'-methoxyphenyl)phenyl]benzene (S12); ^{13}C NMR (100 MHz, $CDCl_3$)

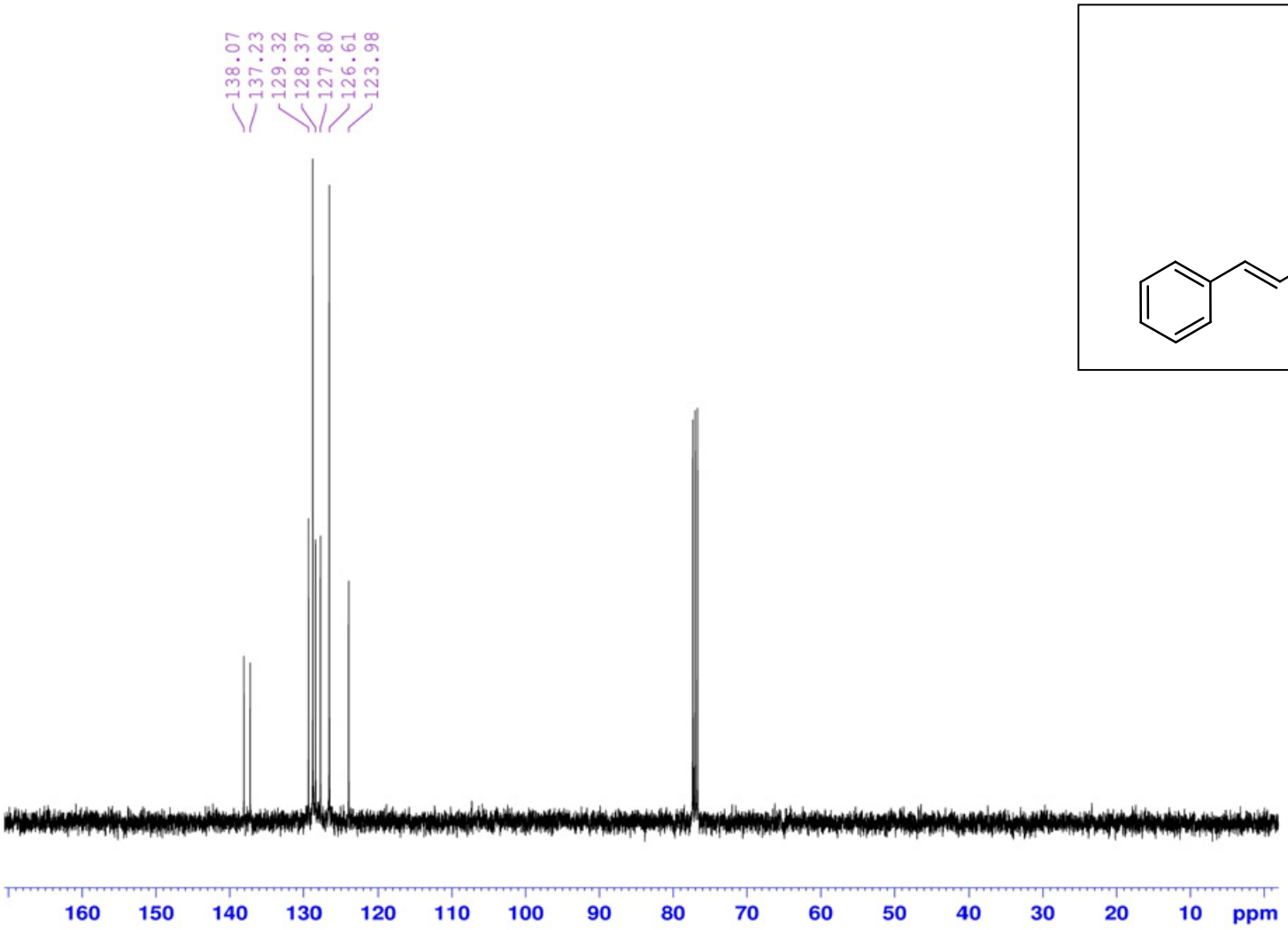




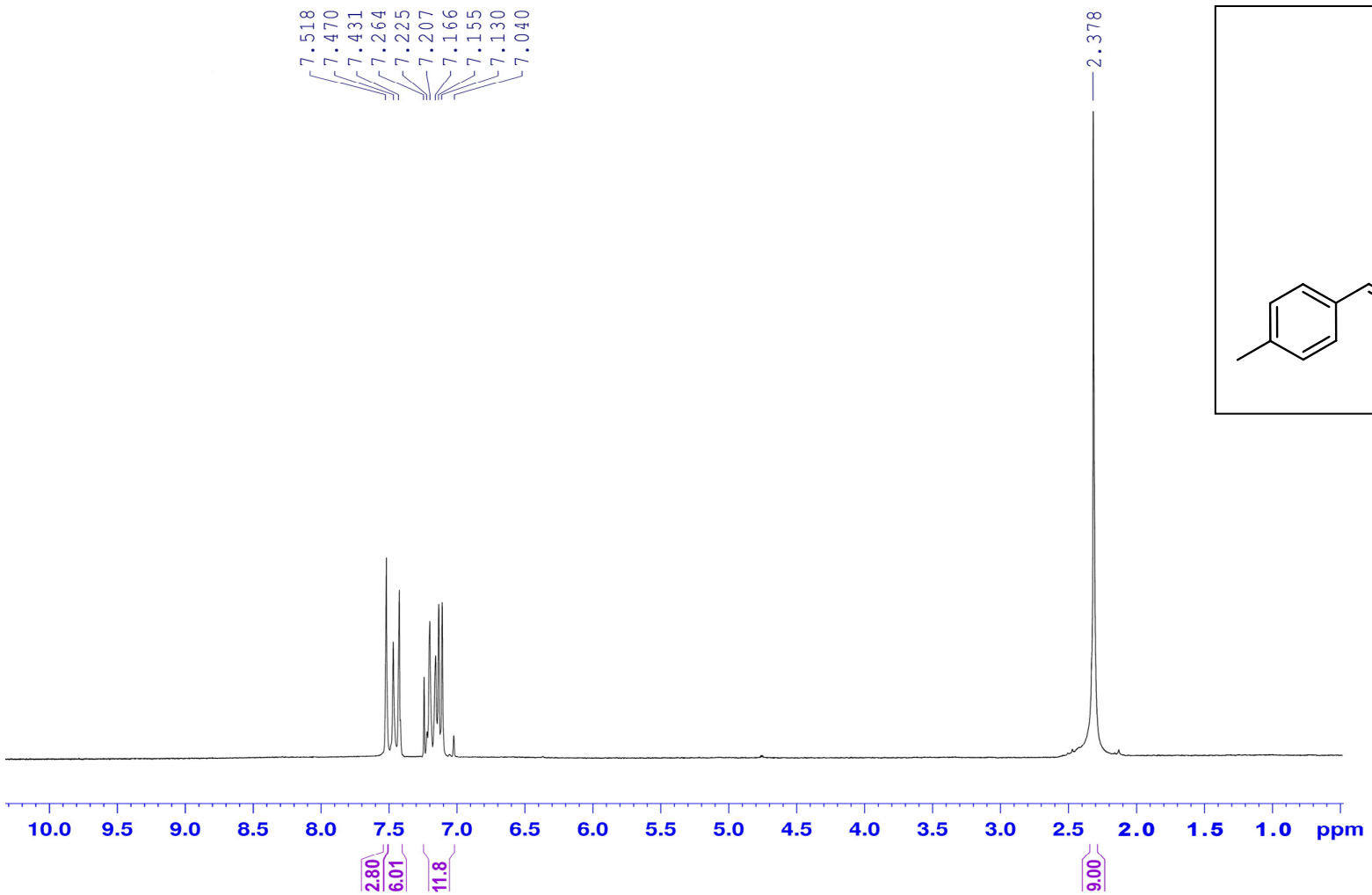
1,3,5-Tristyrylbenzene (S15); ^{1}H NMR (400 MHz, $CDCl_3$)

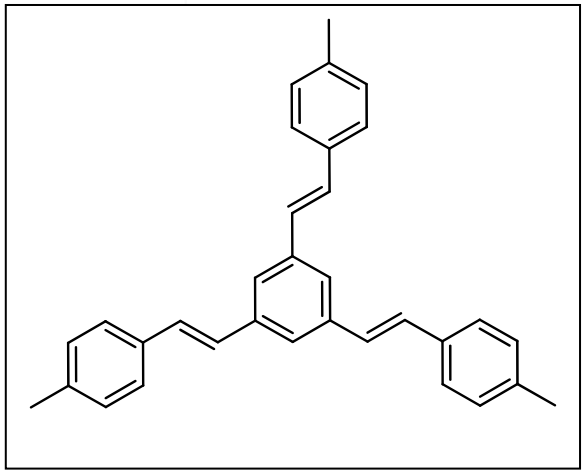


1,3,5-Tristyrylbenzene (S15); ^{13}C NMR (100 MHz, $CDCl_3$)

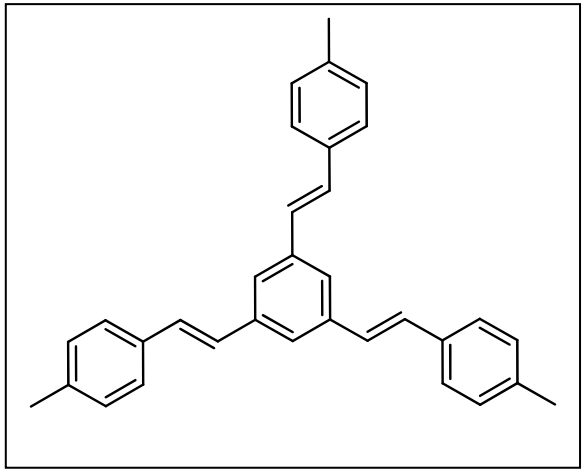


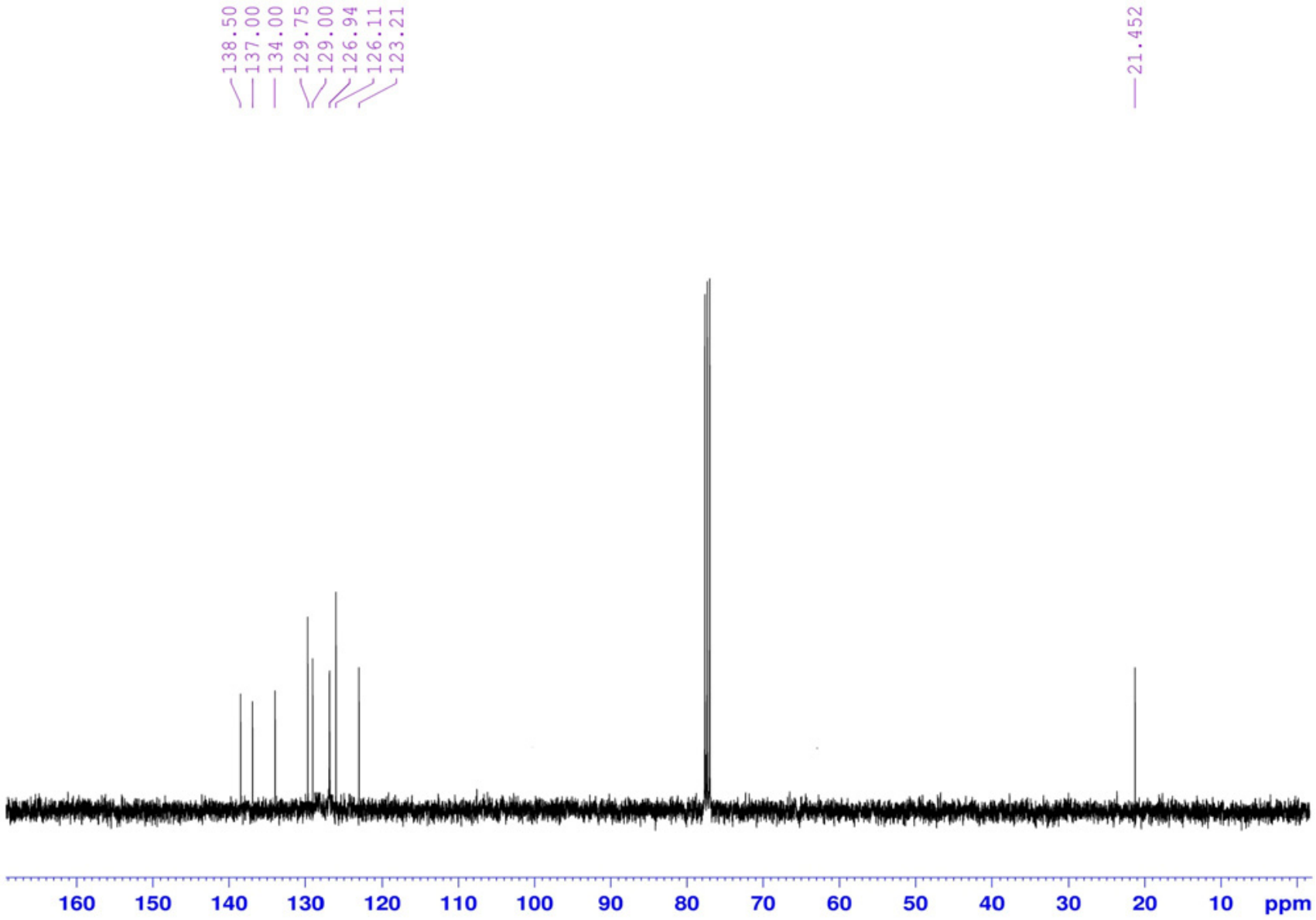
1,3,5-Tris(*p*-methylstyryl)benzene (S16); ^{1}H NMR (400 MHz, $CDCl_3$)





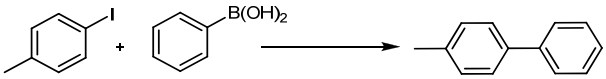
1,3,5-Tris(*p*-methylstyryl)benzene (S16); ^{13}C NMR (100 MHz, $CDCl_3$)



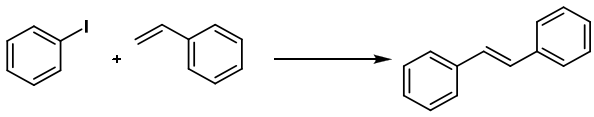

138.50
137.00
134.00
129.75
129.00
126.94
126.11
123.21
21.452
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

18.

Table S1. Comparison of some of the results obtained from Pd_{np}-nSTDP and some of those reported with other Pd-supported catalysts.



Entry	Catalyst	Mol% Pd	Condition	Time [h]	Yield [%][a]	TOF [h^{-1}]	Ref.
1	Pd_{np}-nSTDP	0.006	K_2CO_3, DMF/H_2O, RT	2	95	7916.7	Present work
2	Amphiphilic dendritic phosphine-Pd (G3[CO_2K])	0.5	K_2CO_3, H_2O, 50 °C	20	93	9.3	[24a]
3	Silica supported palladium-phosphin complex	0.5	K_2CO_3, MeOH/H_2O, RT,	4	91	45.5	[24b]
4	Polyaniline (PANI)-Pd	1.0	K_3PO_4, 1,4-dioxane, 100 °C	15	85	5.7	[24c]
5	Silicadiphenylphosphinite Pd (SDPP)-Pd	1.5	NaOH, EtOH, 80 °C	3	93	20.7	[24d]
6	Pd–$CoFe_2O_4$ MNPs	1.6	Na_2CO_3, EtOH, reflux	6	88	9.2	[24e]
7	Fluorapatite-supported palladium, FAP-Pd	0.11	Na_2CO_3, MeOH, RT	4	92	209.1	[24f]
8	Pd-amphiphilic carbon spheres (CSP)	0.2	K_2CO_3, DMF/H_2O, 90 °C	1.5	93	310.0	[24g]



9	Pd_{np}-nSTDP	0.01	K_2CO_3, DMF/H_2O, 85 °C	9	95	1055.6	Present work
10	Polyaniline (PANI)-Pd	5.0	*n*-Pr_3N, DMF, 130 °C	30	65	0.4	[24c]
11	Silica hybride Pd-NHC complex	0.9	Et_3N, DMF, reflux	12	77	7.1	[25a]
12	Pd–phosphine complexes modified poly(etherimine) dendrimer	0.1	K_2CO_3, Toluene, 140 °C	20	65	32.5	[25b]
13	Polymer-supported macrocyclic Schiff base palladium complex	0.5	K_2CO_3, DMF, 100 °C	2	97	97.0	[25c]
14	Aminopropyl-modified silica (SBA-15-NH_2)-Pd	1.0	NaOAc, DMF, 120 °C	15	96	6.4	[25d]
15	Pd/$CaCO_3$, α-hydroxypropylated cyclodextrin (α-HPCD)	1.0	K_2CO_3, DMF/H_2O, reflux	24	80	3.3	[25e]
16	Diarylphosphinopolystyrene-Pd	0.3	Et_3N, MeCN, 80 °C	20	98	16.3	[25f]
17	SiO_2@Fe_3O_4–Pd	1.0	K_2CO_3, DMF, 100 °C	8	95	11.9	[25g]

19.

Crystal data and structure refinement for S2.[a]

Empirical formula	$C_{19}H_{17}NO_2$	
Formula weight	291.34	
Temperature	291(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P 43212	
Unit cell dimensions	a = 7.9181(11) Å	α = 90°.
	b = 7.9181(11) Å	β = 90°.
	c = 24.418(5) Å	γ = 90°.
Volume	1530.9(4) $Å^3$	
Z	4	
Density (calculated)	1.264 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	616	
Crystal size	0.24 x 0.24 x 0.24 mm^3	
Theta range for data collection	2.70 to 29.25°.	
Index ranges	-9<=h<=10, -10<=k<=9, -33<=l<=33	
Reflections collected	6592	
Independent reflections	1185 [R(int) = 0.0721]	
Completeness to theta = 29.25°	91.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.977	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1185 / 0 / 102	
Goodness-of-fit on F^2	0.580	
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0415	
R indices (all data)	R1 = 0.1198, wR2 = 0.0501	
Largest diff. peak and hole	0.068 and -0.121 $e.Å^3$	

[a] CCDC-854353 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk).

20.
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