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Mono- and multifold C-C coupling reactions catalyzed by a palladium complex encapsulated in MIL–Cr as a three dimensional nano reactor

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Experimental Section

EXPERIMENTAL SECTION

General Remarks

All materials were commercial reagent grade. Compounds were obtained from Merck or Fluka chemical companies. FT–IR spectra were recorded from potassium bromide pellets in a special range of 400–4000 cm^{-1} using a JASCO 6300D spectrophotometer. The scanning electron micrographs were taken on a Hitachi S–4700 field emission–scanning electron microscope (FE–SEM). The XRD analysis was carried out a D8 Advanced Bruker anode X–ray Diffractometer with Cu Kα (λ=1.5406Å) radiation. Substances were identified and quantified by gas chromatography (GC) on an Agilent GC 6890 equipped with a 19096C006 80/100 WHP packed column and a flame ionization detector (FID). In GC experiments anisole was used as internal standard. The X–ray photo–electron spectroscopy (XPS) measurements were performed using a Gammadata–scienta ESCA200 hemispherical analyzer equipped with an Al (Kα=1486.6 eV) X–ray source. X–ray data for Pd(II) complex was collected on a STOE IPDS–II diffractometer with graphite monochromated Mo Kα radiation. Specific surface area was measured by adsorption–desorption of N_2 gas at 77 K with ASAP 2000 Micromeritics instrument. 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.

Catalyst Preparation

Synthesis of MIL-Cr

The MOF was synthesized and purified according to a procedure reported by Férey and coworkers.[46] For MIL-Cr, chromium(III) nitrate $Cr(NO_3)_3 \cdot 9H_2O$ (400 mg, 1 mmol (Aldrich, 99%)), CrO_3 (35 mg, 0.35 mmol) and terephthalic acid (58 mg, 0.35 mmol) were dissolved in 4.8 ml H_2O (4 mL) and the mixture was stirred at room temperature. The obtained mixture

was placed in a Teflon-lined stainless steel autoclave and heated at 220 °C for 8 h. The solid MOFs were washed with fresh DMF, chloroform and methanol three times every 12 hours. Then it was activated at 150 °C under vacuum for 6 hours.

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Synthesis of Pd(II) complex

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. The mixture was filtered and $Na_2[PdCl_4]$ solution was formed. Then, the solution of $Na_2[PdCl_4]$ (5 ml) was added to 4–iodoaniline (0.132 g) in methanol (5 ml) and stirred at room temperature for 2 h. The desired palladium complex was collected by filtration and purified by recrystallization. The yield of yellow product was 87%.

Synthesis of palladium complex encapsulated in MIL (Palladium complex@MIL–Cr)

In a round–bottomed flask equipped with a condenser and a mag) netic stirrer, a mixture of MIL–Cr (0.3 g) and Pd(II) complex (0.03 g) in DMF (12 mlwas stirred at 100 °C under N_2 atmosphere for 24 h. The reaction mixture was filtered and the resulting solid was washed with DMF several times for removing excess Pd(II) complex.

General procedure for Suzuki cross–coupling reaction catalyzed by Pd complex@MIL–Cr

Typically, a mixture of aryl halide (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol) and the Pd complex@MIL–Cr catalyst (0.06 mol% Pd) in a 2:1 solution of $EtOH/H_2O$ (2 mL) was stirred at room temperature under air atmosphere. The progress of the reaction was monitored by GC. After completion of the reaction, the catalyst was separated by filtration and the desired products were extracted with ethyl acetate (3×10 mL). The organic phase was collected and dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was recrystallized from ethyl acetate and ether (1: 3) to afford the pure product.

Genera Procedure for Synthesis of C_3-Symmetric Molecules via Suzuki-Miyaura Cross-Coupling Catalyzed by Pd complex@MIL-Cr

A mixture of 1,3,5-tribromobenzene, 2,4,6-trichloropyrimidine or 2,4,6-trichlorotriazine (1 mmol), arylboronic acid (4 mmol), K_2CO_3 (3 mmol) and Pd complex@MIL-Cr (0.1 mol% Pd) in 6 mL of EtOH/H_2O (2:1, 6 ml) was stirred at room temperature for the appropriate time according to Scheme 3. 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).

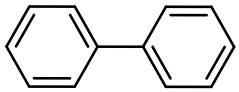
General Procedure for Heck Reaction Catalyzed by Pd complex@MIL–Cr

Typically, a mixture of aryl halide (1 mmol), styrene (1.5 mmol), K_2CO_3 (1.5 mmol) and the Pd complex@MIL–Cr catalyst (0.5 mol% Pd) in a 2:1 solution of DMF/H_2O (2 mL) was stirred at 80 °C under air atmosphere. The reaction progress was monitored by GC. After completion of the reaction, the catalyst was separated by filtration and washed with DMF, and reused for next cycle.

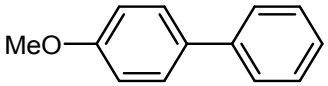
Synthesis of 1,3,5-Tristyrylbenzenes (*C_3*f and *C_3*g) via Heck Reaction Catalyzed by Pd Complex@MIL-Cr

The 1,3,5-tribromobenzene (1 mmol), styrene (4 mmol), K_2CO_3 (3.5 mmol) and Pd complex@MIL-Cr (1.2 mol% Pd) were mixed in DMF/H_2O (2:1, 6 mL). The reaction mixture was stirred at 80 °C for the appropriate time as mentioned in Scheme 4. 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.

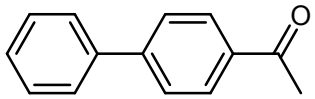
Spectroscopic data of the products:



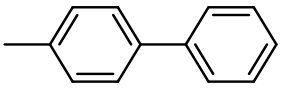
Biphenyl (Table 2, entry 1)
Mp 68-69 °C (Lit.[1] 70-72 °C). IR (KBr) v = 2997, 1602, 1495, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d , J = 8.0 Hz, 4H), 7.39 (t, J = 8.0 Hz, 4H), 7.31-7.27 (m, 2H).



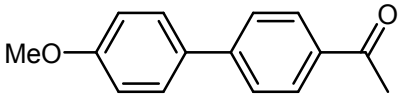
4-Methoxybiphenyl (Table 2, entry 2)
Mp 88-90 °C (Lit.[2] 88-89 °C). IR (KBr) v = 2991, 1605, 1497, 1387, 1251, 876 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (t, J = 8.4 Hz, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 6.8 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H).



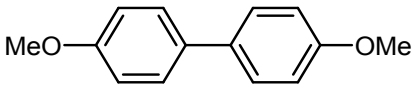
4-Phenylacetophenone (Table 2, entry 3)
Mp 117-118°C (Lit.[3] 122-123 °C). IR (KBr) v = 2910, 1680, 1601, 1490, 1380, 860 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 6.8 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 6.8 Hz, 2H), 7.44 (t, J = 6.4 Hz, 1H), 2.66 (s,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



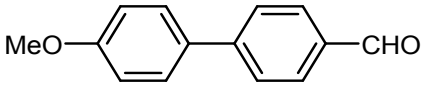
4-Methylbiphenyl (Table 2, entry 4)
Mp 61-62 °C (Lit.[4] 61-62 °C). IR (KBr) v = 2925, 1605, 1490, 1380, 890 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H),7.47 (t, J = 7.2, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H).



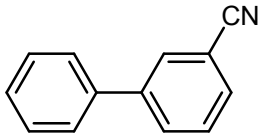
4(4'-Methoxyphenyl)acetophenone (Table 2, entry 5)
Mp 152-153 °C (Lit. [5] 156-157 °C). IR (KBr) v = 2955, 1680, 1603,1495, 1389, 1240, 882 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H), 2.65 (s, 3H).



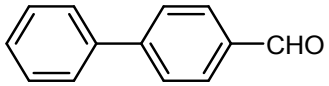
4,4'-Dimethoxybiphenyl (Table 2, entry 8)
Mp 172-173 °C (Lit. [6] 168-170 °C). IR (KBr) v = 2938, 1680, 1601,1490,1378, 1253, 852 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.8 Hz, 4H), 7.50 (d, J = 8.8 Hz, 4H), 3.87 (s, 6H).



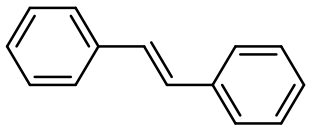
4'-Methoxybiphenyl-4-carbaldehyde (Table 2, entry 10)
Mp 109-110 °C (Lit. [7] 105-108 °C).). IR (KBr) ν = 2839, 1706, 1605 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H).



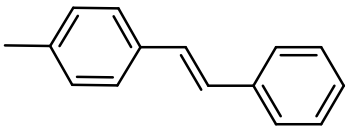
Biphenyl-3-carbonitrile (Table 2, entry 11)
Mp 48-49 °C (Lit. [8] 48 °C). IR (KBr) ν = 2967, 2192, 1601, 1492, 901, 710 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.80-7.77 (m, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H).



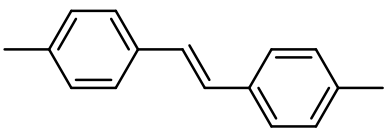
Biphenyl-4-carbaldehyde (Table 2, entry 16)
Mp 62-63 °C (Lit. [7] 62-65 °C). IR (KBr) ν = 2950, 2831, 1699, 1602, 1495, 890, 680. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H).



(*E*)-Stilbene (Table 4, entry 1)
Mp 120-122 °C (Lit. [9] 125 °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).

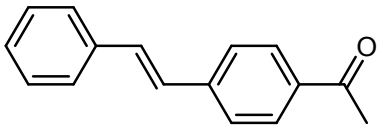


(*E*)-4-Methylstilbene (Table 4, entry 2)
M.p.:122-123 °C (Lit. [10] 119-122 °C). IR (KBr) ν = 2987, 1600, 1495, 1380, 885 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 2H), 6.95 (A of ABq, J = 16 Hz, 1H), 6.88 (B of ABq, J = 16 Hz, 1H), 2.30 (s, 3H).



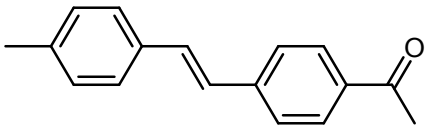
(E)-1,2-Di-*p*-tolylethene (Table 4, entry 3)

Mp 181-183 °C (Lit. [11]184-185 °C). IR (KBr) ν = 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).



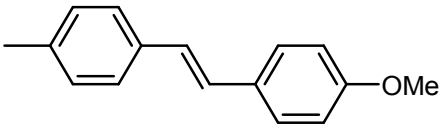
(E)-1-(Prop-1-en-2-yl)-4-styrylbenzene (Table 4, entry 4)

Mp142-144 °C (Lit. [12] 143-145 °C). IR (KBr) ν = 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).



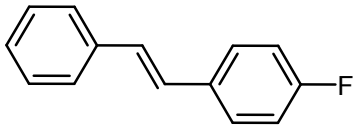
4(4-Methylstyrene)acetophenone (Table 4, entry 5)

Mp168-169 °C. IR (KBr) ν =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).



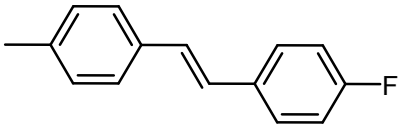
(E)-1-Methoxy-4-(4-methylstyryl)benzene (Table 4, entry 8)

Mp 145-147 °C (Lit. [11] 142-144 °C). IR (KBr) ν = 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).



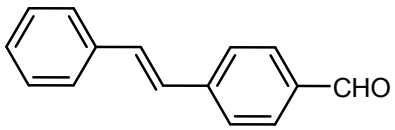
(E)-1-Fluoro-4-styrylbenzene (Table 4, entry 9)

Mp 113-115 °C (Lit. [11] 117-119 °C). IR (KBr) ν = 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).



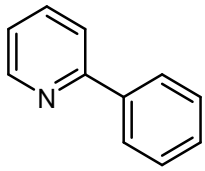
(E)-1-Fluoro-4-(4-methylstyryl)benzene (Table 4, entry 10)

Mp 125-126 °C (Lit. [13] 125-126 °C). IR (KBr) ν =2990, 1600, 1495, 1375, 1175, 875 cm^{-1}. ^1H 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)



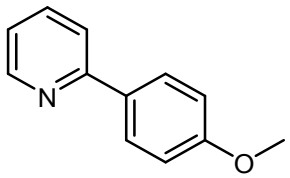
(E)-4-Styrylbenzaldehyde (Table 4, entry 14)

Mp 118-120 °C(Lit. [14] 115-116 °C). IR (KBr) ν = 2995, 2851, 1701, 1603, 1499, 910, 845 cm^{-1}. ^1H 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).



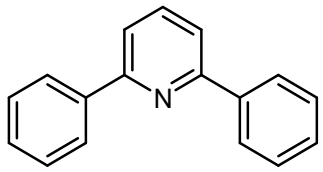
2-Phenylpyridine (Scheme 3, *P*a)

IR (KBr) ν = 3012, 2983, 1612, 1562, 1485, 975, 862 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, J = 4.4 Hz, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.75 (m, 2H), 7.49-7.39 (m, 3H), 7.25 - 7.21 (m, 1H), ppm.



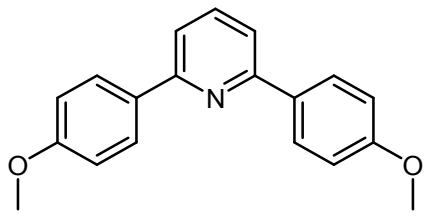
2-(4-Methoxyphenyl)pyridine (Scheme 3, *P*b)

Mp. 55-56 °C. IR (KBr) ν = 2996, 2875, 1612, 1584, 1401, 1224, 962, 846 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, J = 4.4 Hz, 1H), 7.95 (d, J = 8.8 Hz, 2H), 7.65-7.73 (m, 2H), 7.17 (t, J = 6.0 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H).



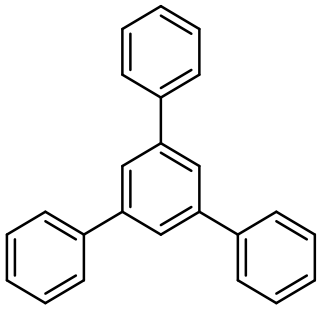
2,6-Diphenylprydine (Scheme 3, *P*c)

Mp 77-79 °C (Lit. [15] 80-81 °C) IR (KBr) ν = 2986, 1593, 1577, 1492, 1018, 910, 780 cm^{-1}. ^1H 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.

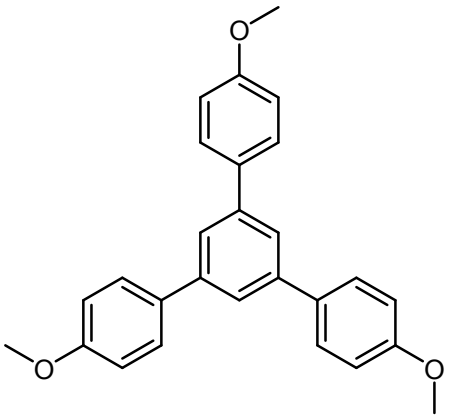


2,6-Bis(4-methoxyphenyl)pyridine (Scheme 3, *P*d)

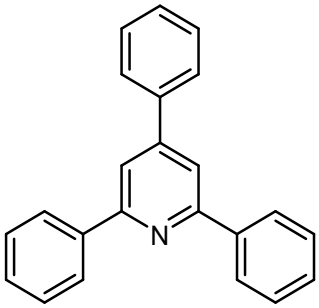
Mp 195-196 °C (Lit. [16] 197.7-198.4 °C). IR (KBr) ν = 2910, 1606, 1578, 1513, 1376, 1248, 1020, 880cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 6.0 Hz, 4H), 7.66 (t, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 6.0 Hz, 4H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.7, 156.4, 137.3, 135.0, 127.7, 114.1, 113.4, 55.3.



1,3,5-Triphenylbenzene (Scheme 4, C_3a)
Mp 175-176 °C (Lit. [17a] 175-176 °C). IR (KBr) ν = 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.

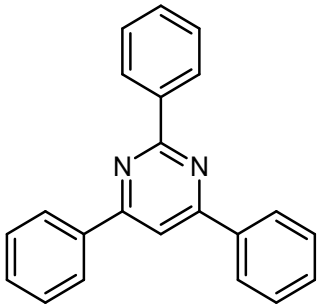


1,3,5-Tri(4-methoxyphenyl)benzene (Scheme 4, C_3b)
Mp 141-143°C (Lit. [18] 140-142 °C). IR (KBr) ν = 2910, 1605, 1499, 1380, 1253, 870, 711 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 3H), 7.65 (d, J = 8.8 Hz, 6H), 7.04 (t, J = 8.8 Hz, 6H), 3.89 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 141.4, 134.0, 128.3, 122.7, 114.2, 55.2.

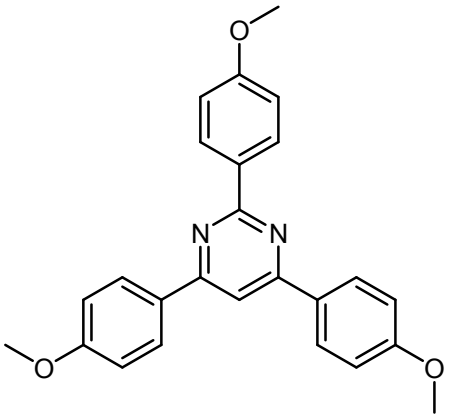


2,4,6-Triphenylpyridine (Scheme 4, C_3c)
Mp 134-135 °C (Lit. [19] 136-137 °C). IR (KBr) ν = 2998, 1614, 1573, 1495, 872, 705 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 7.2 Hz, 6H), 7.83 (s, 2H), 7.63 (t, J = 6.8 Hz, 3H),

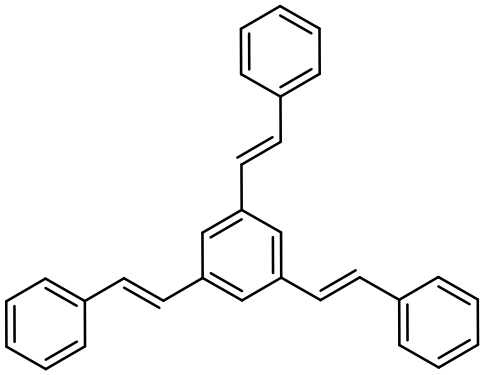
7.51-7.42 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 150.7, 140.6,139.7, 130.3, 130.1, 129.7, 129.3, 128.5, 127.6, 118.3.



2,4,6-Triphenylprimidine (Scheme 4, C_3d)
Mp 176-178 (Lit. [20] 174-175 ^{o}C) IR (KBr) v = 2945, 1604, 1514, 1364, 1250, 1182, 1021, 810 cm^{-1}. ^{1}H 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.

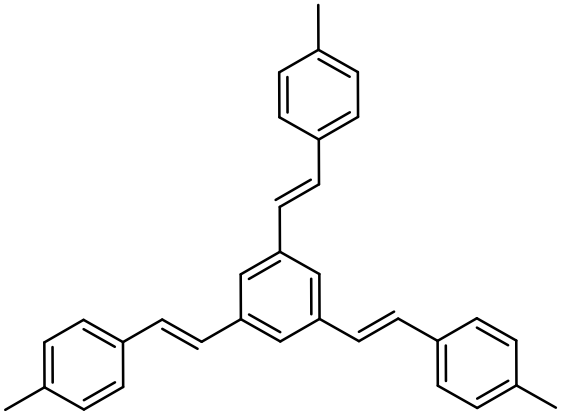


2,4,6-Tris(4-methoxyphenyl)pyrimidine (Scheme 4, C_3e)
Mp 175-177 °C (Lit. [21] 174 °C). IR (KBr) v = 2936, 1606, 1510, 1364, 1242, 1175, 1021, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 8.8 Hz, 4H), 7.99 (d, J = 8.8 Hz, 2H), 7.73 (s, 1H), 6.96 (d, J = 8.8 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.



1,3,5-Tristyrylbenzene (Scheme 4, C_3f)
Mp 190-193 ^{o}C. IR (KBr) v = 2986, 1605, 1492, 1350, 850 cm^{-1}. ^{1}H 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 (Scheme 4, C_3g)
Mp 210-211 ºC (Lit. [22] 213-217 ºC)**.** IR (KBr) ν = 2980, 1605, 1490, 1370, 890, 730 cm^{-1}. ^1H 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.

Figure S1. Biphenyl; ^{1}H NMR (400 MHz, $CDCl_3$)

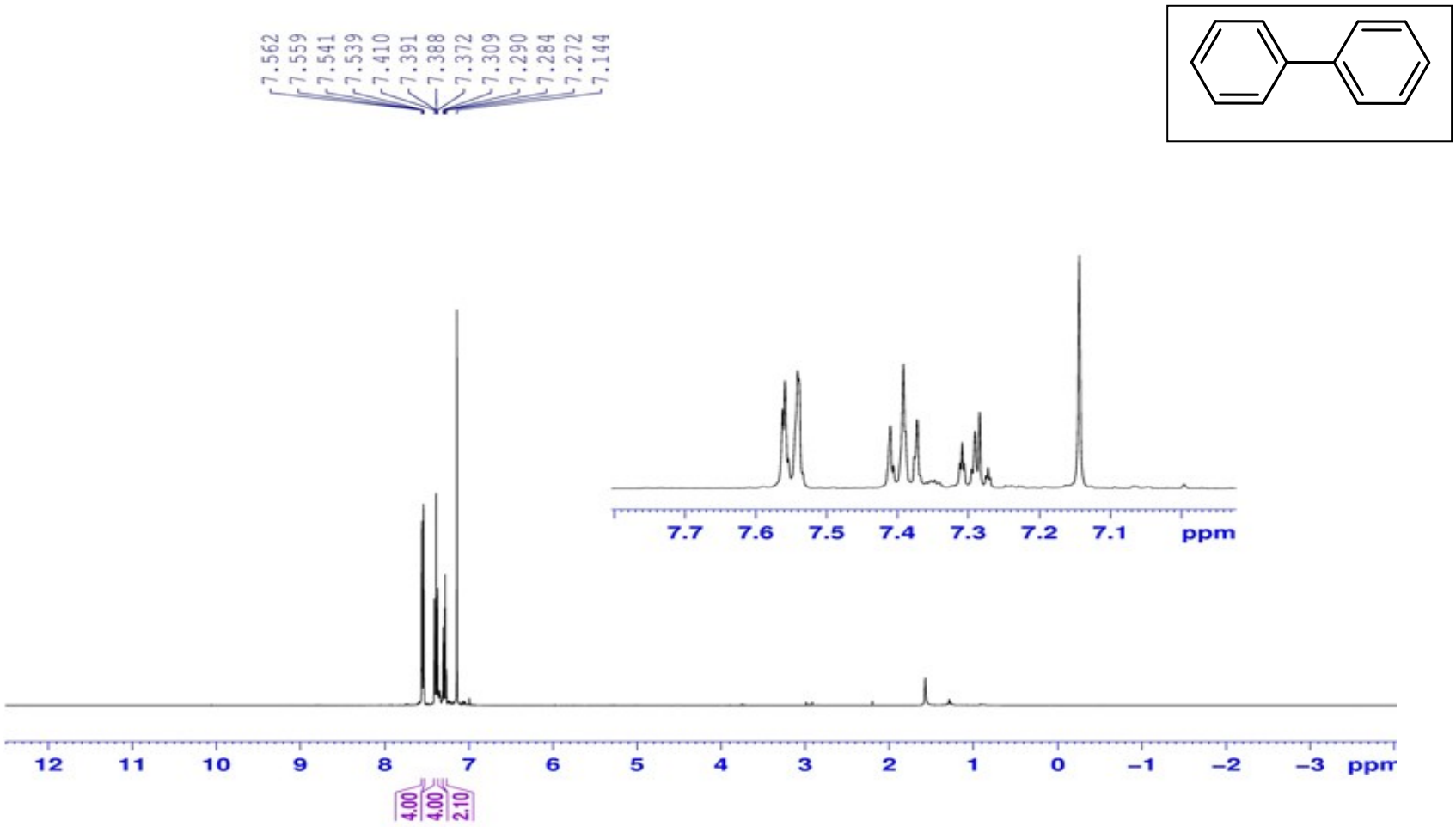


Figure S2. 4-Methoxybiphenyl (Table 2, entry 2); ^{1}H NMR (400 MHz, $CDCl_3$)

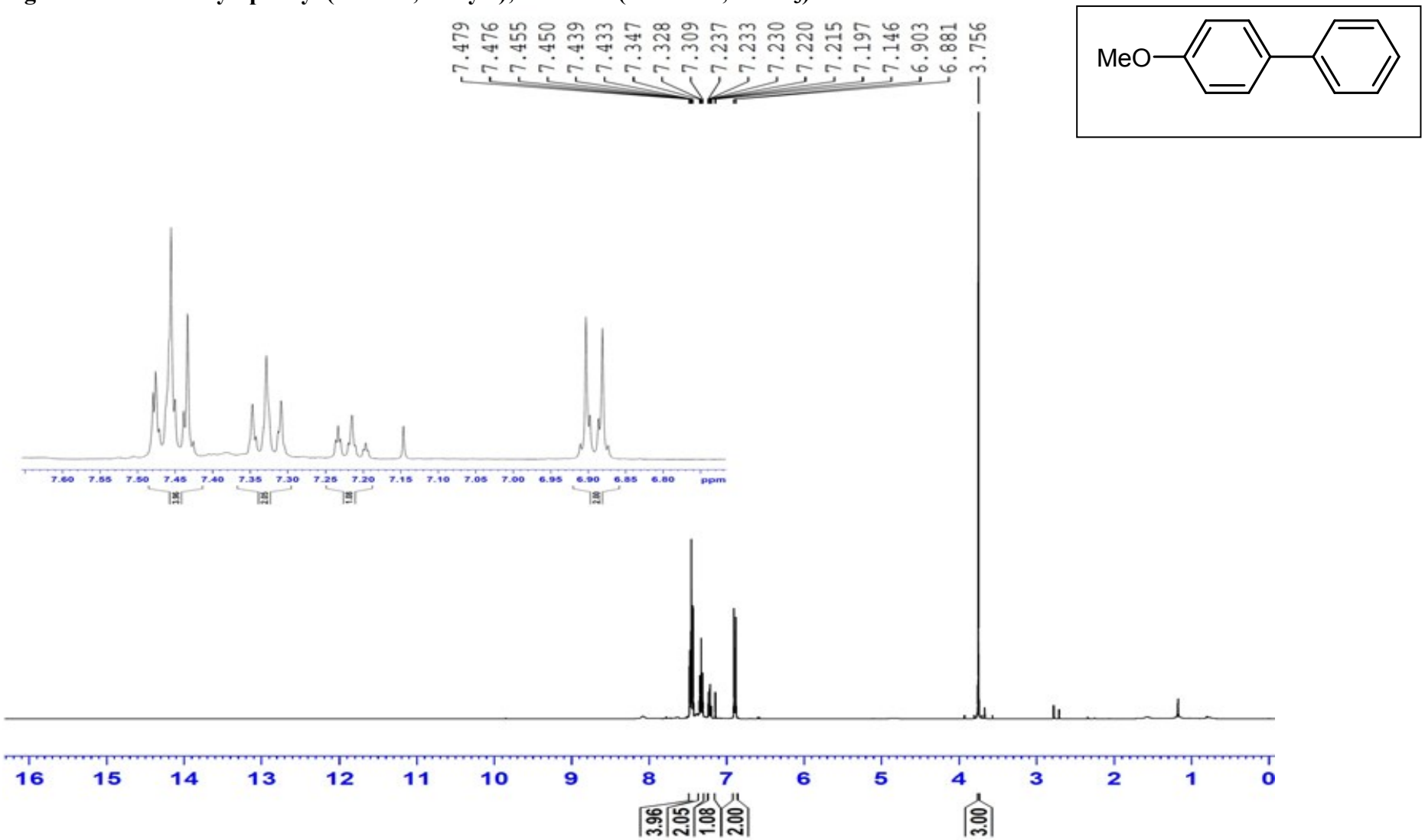


Figure S3. Phenylacetophenone; ^{1}H NMR (400 MHz, $CDCl_3$)

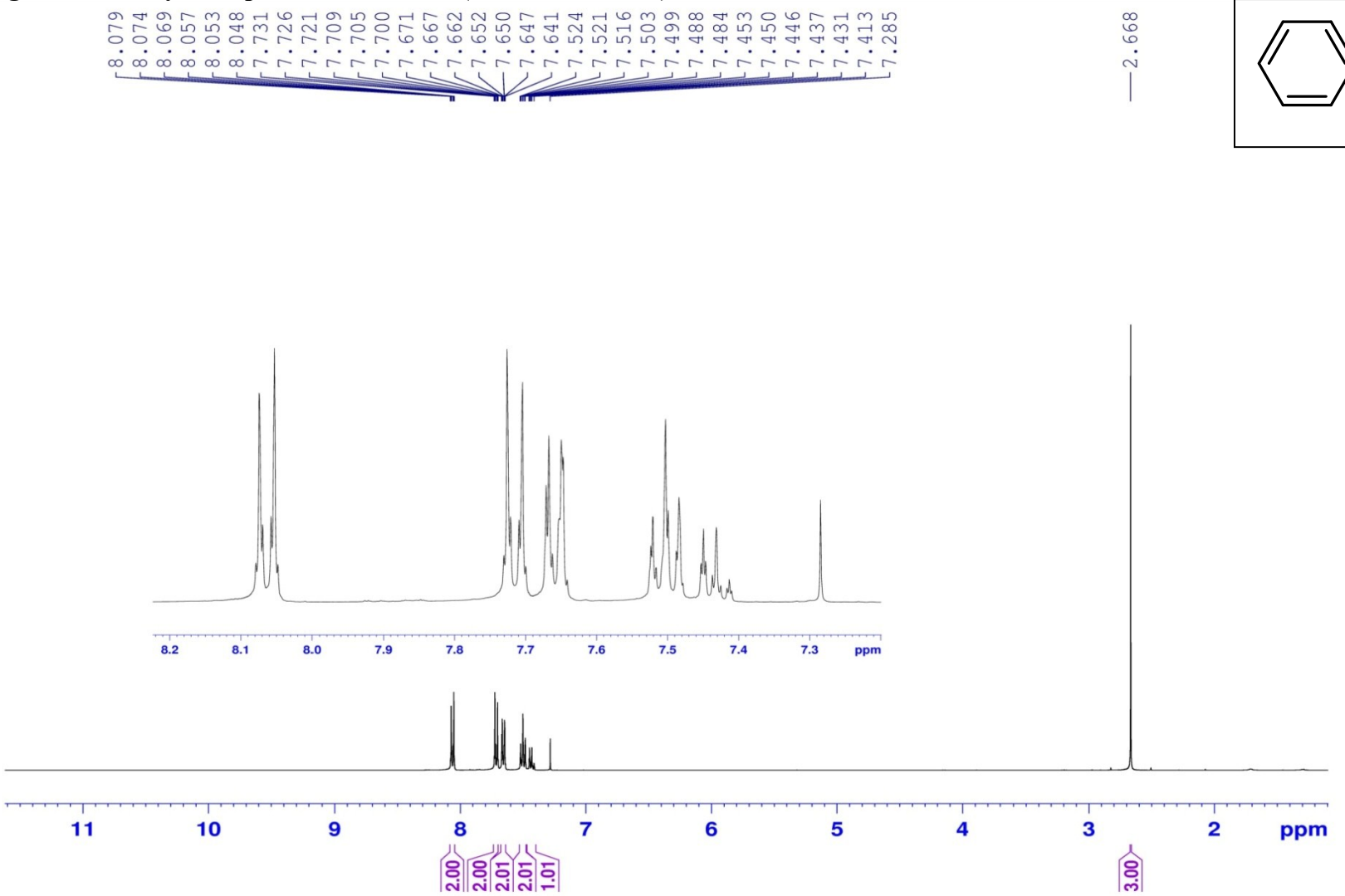


Figure S4. 4-Methylbiphenyl; ^{1}H NMR (400 MHz, $CDCl_3$)

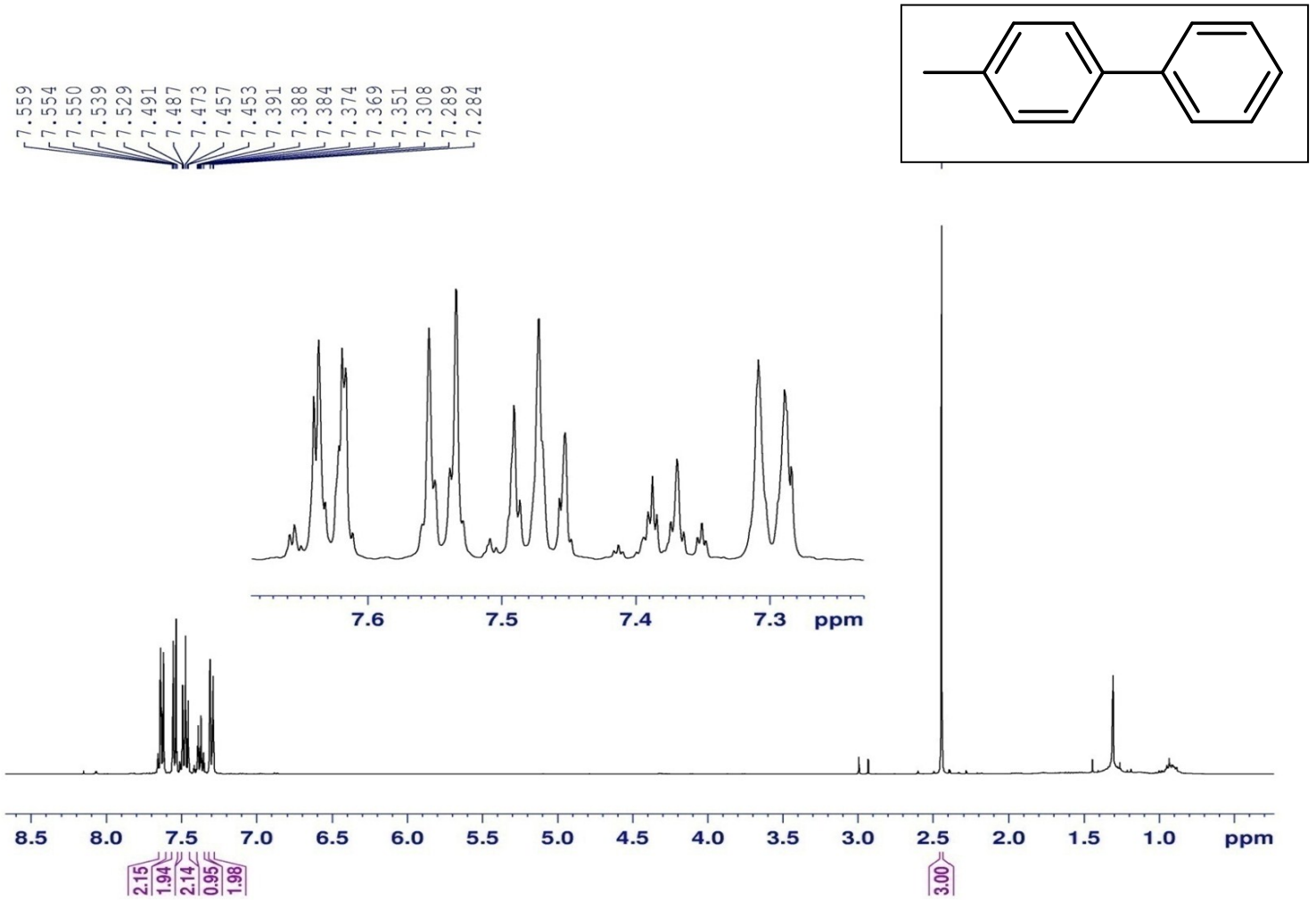


Figure S5. 4(4'-Methoxyphenyl)acetophenone; ^{1}H NMR (400 MHz, $CDCl_3$)

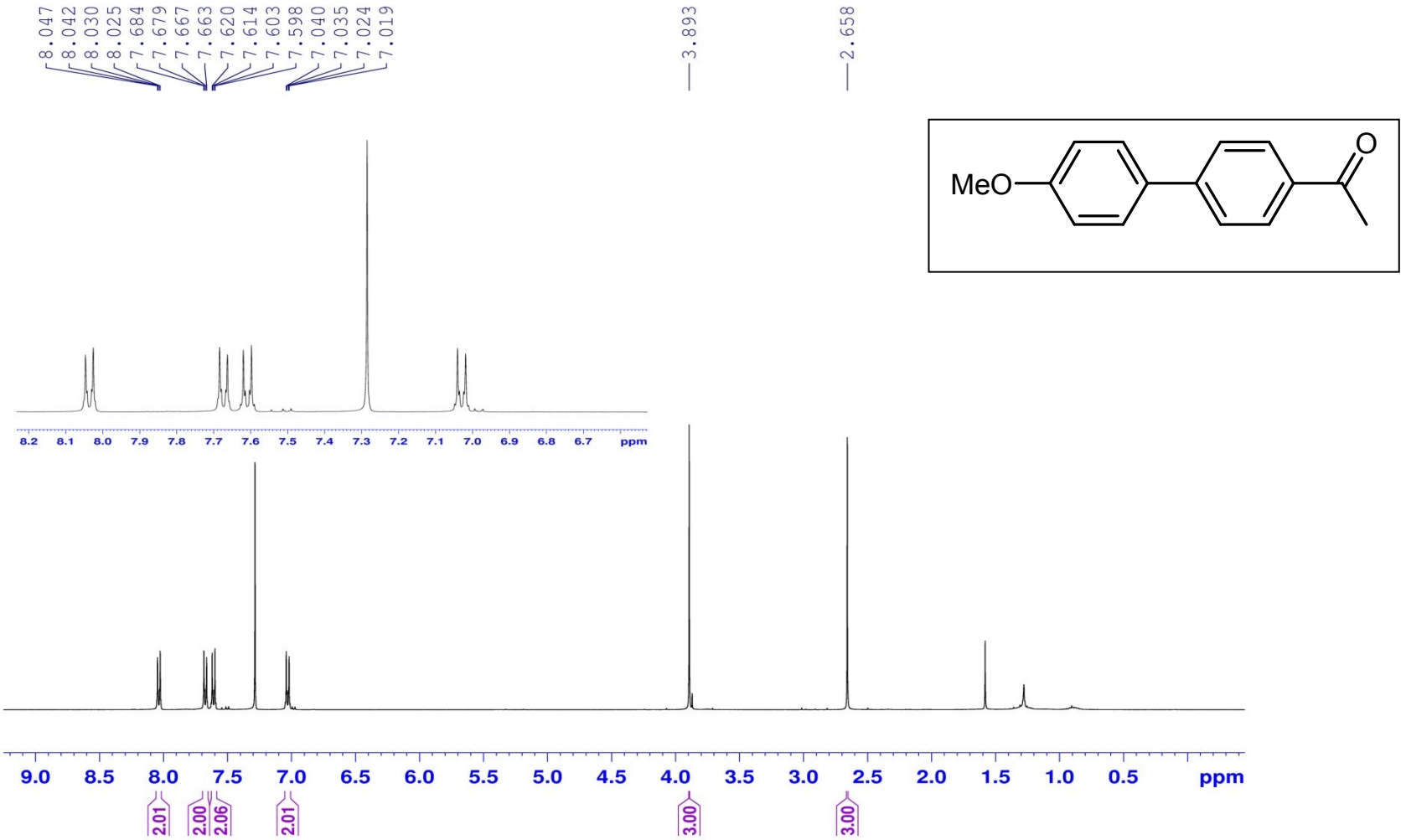


Figure S6. 4,4'-Dimethoxybiphenyl; ^{1}H NMR(400 MHz, $CDCl_3$)

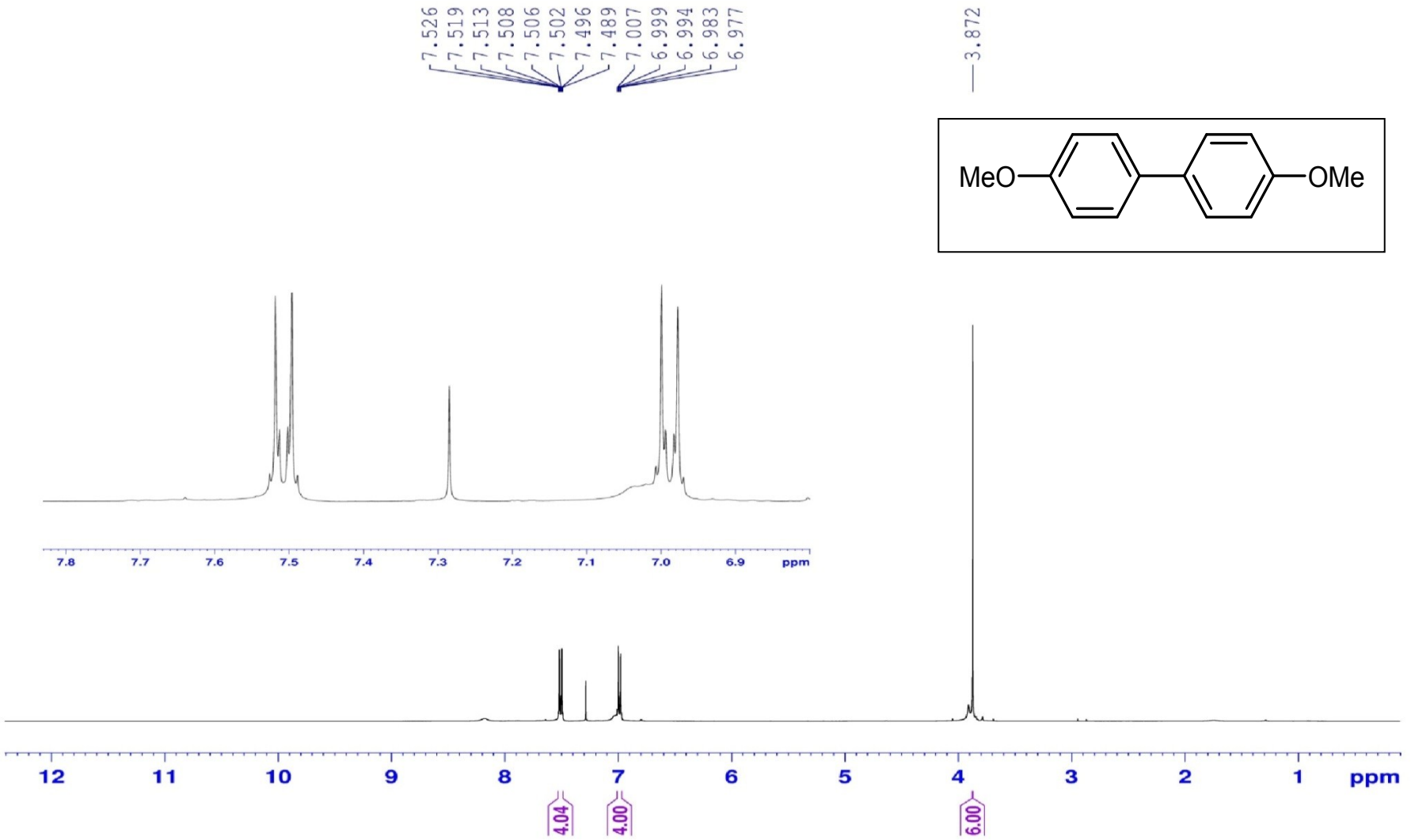


Figure S7. Biphenyl-4-carbaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$)

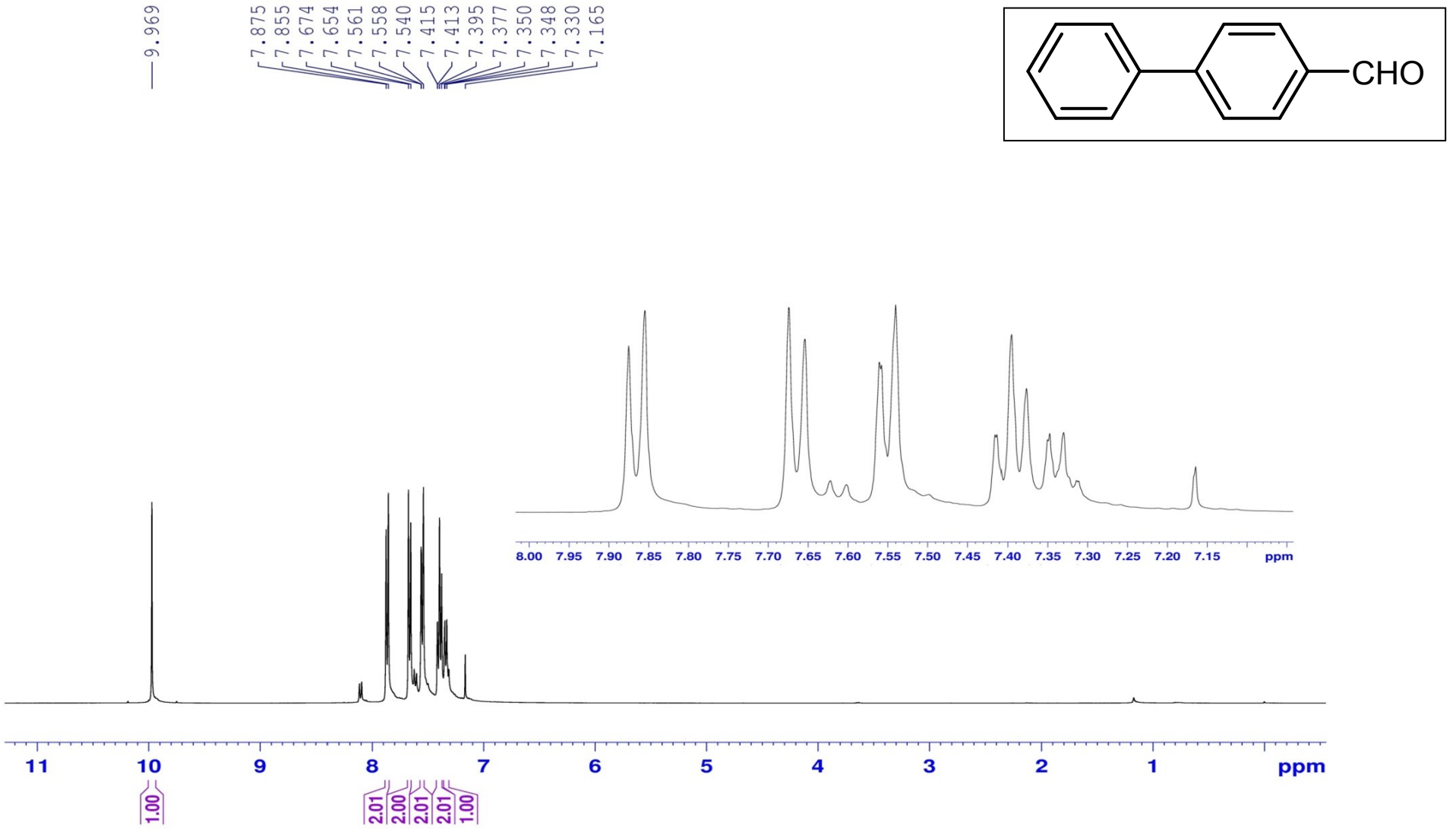


Figure S8. 4'-Methoxybiphenyl-4-carbaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$)

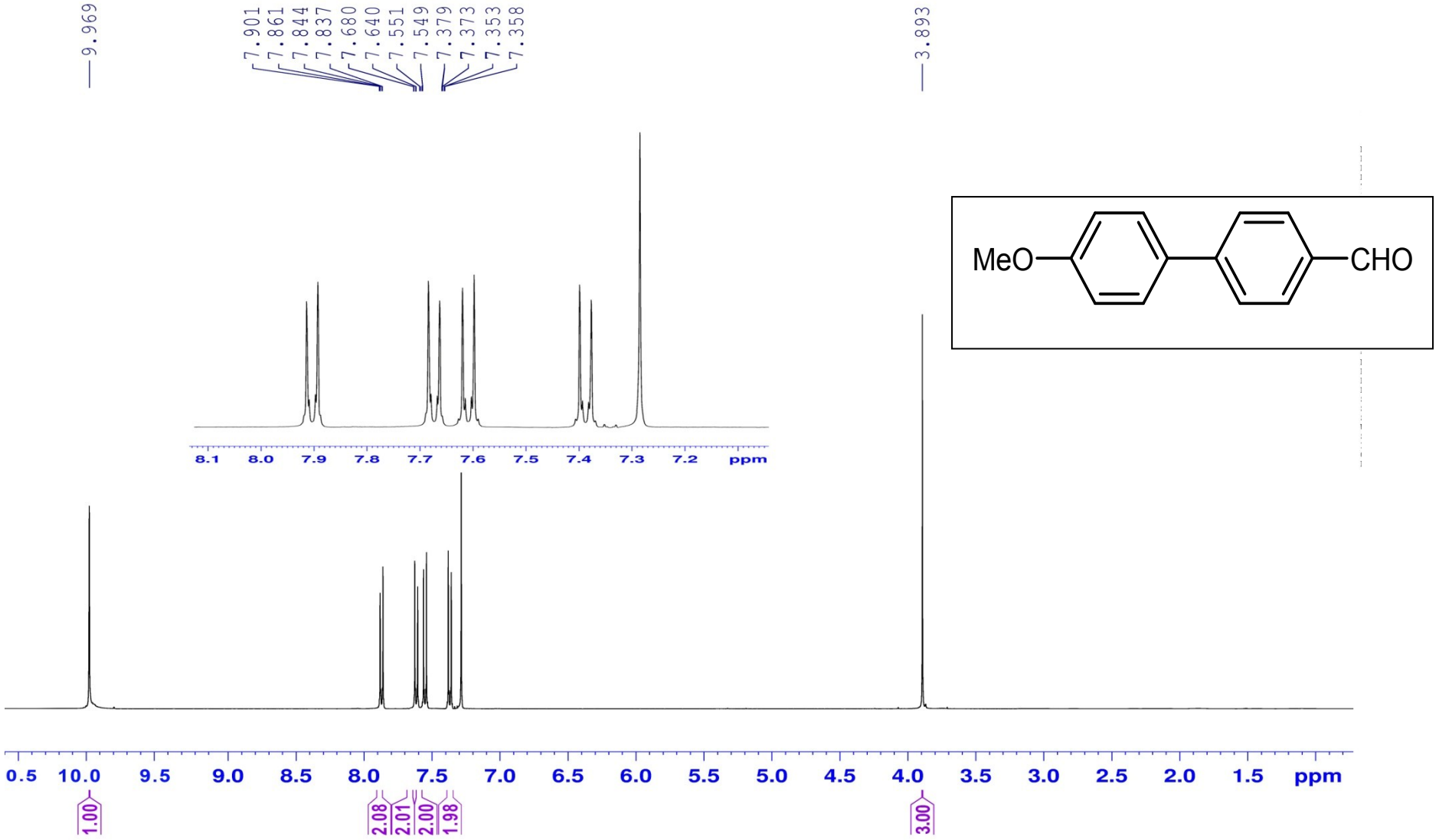


Figure S9. Biphenyl-3-carbonitrile; ^{1}H NMR (400 MHz, $CDCl_3$)

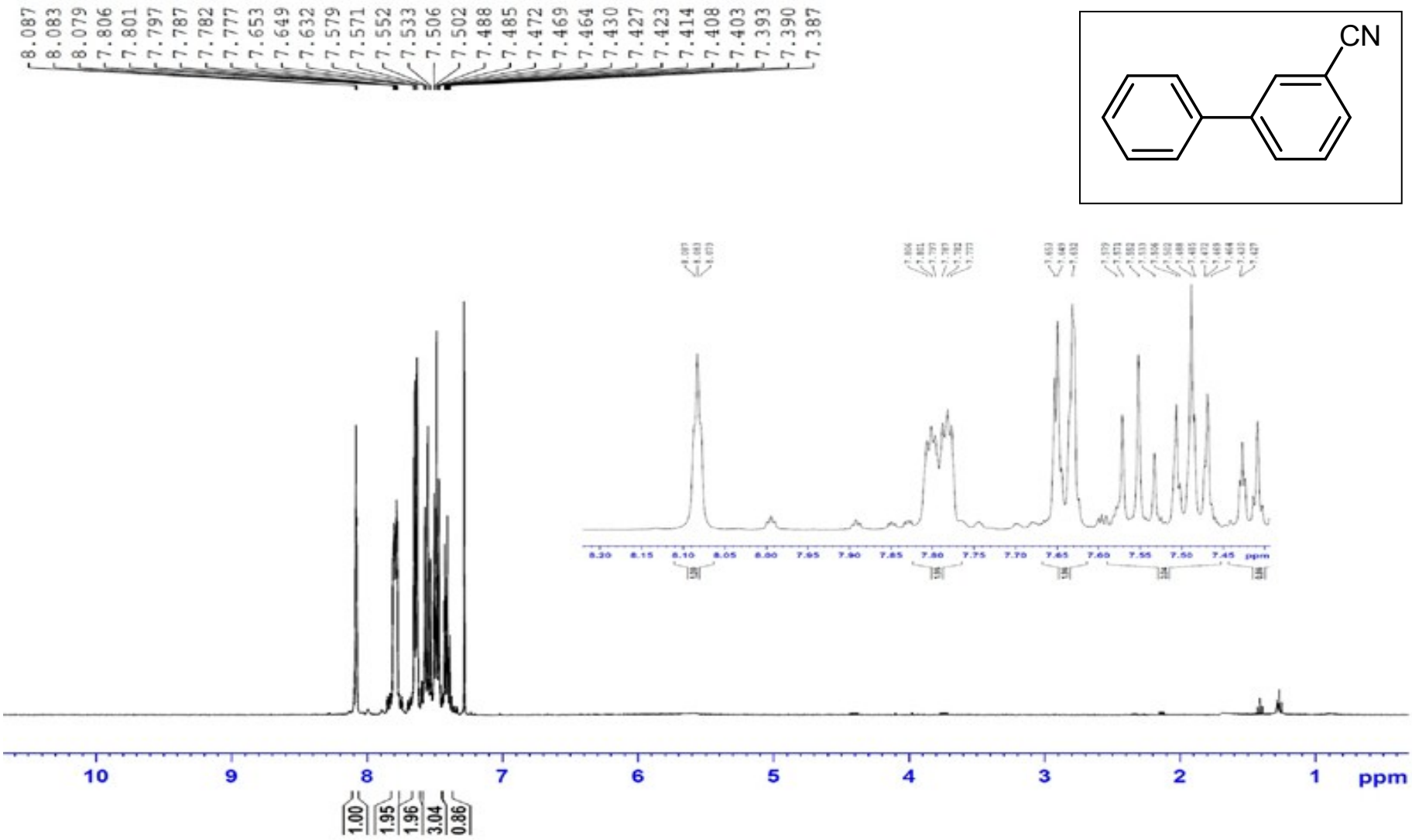


Figure S10. (*E*)-Stilbene, ^{1}H NMR (400 MHz, $CDCl_3$)

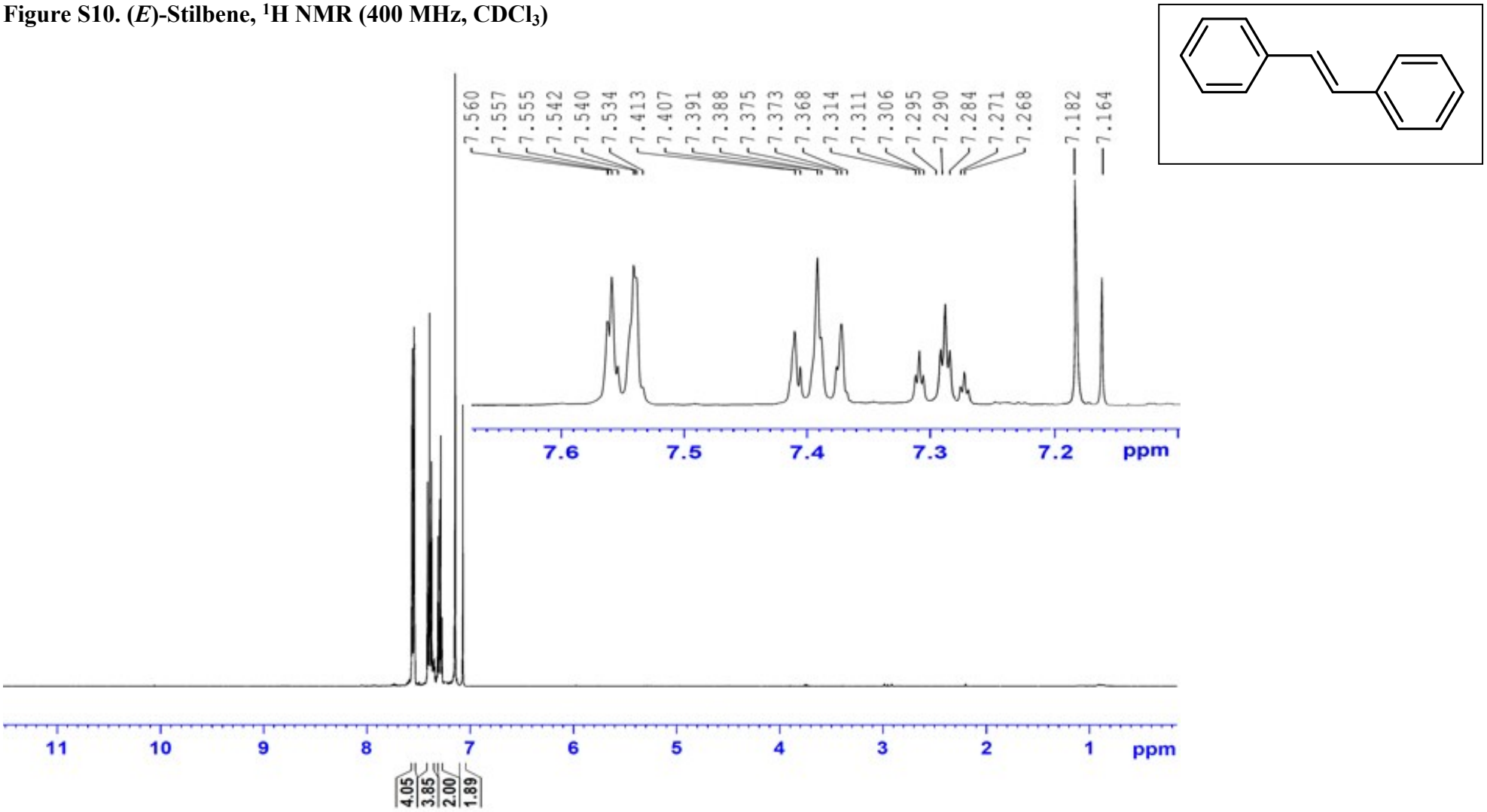


Figure S11. (*E*)-4-Methylstilbene, ^{1}H NMR (400 MHz, $CDCl_3$)

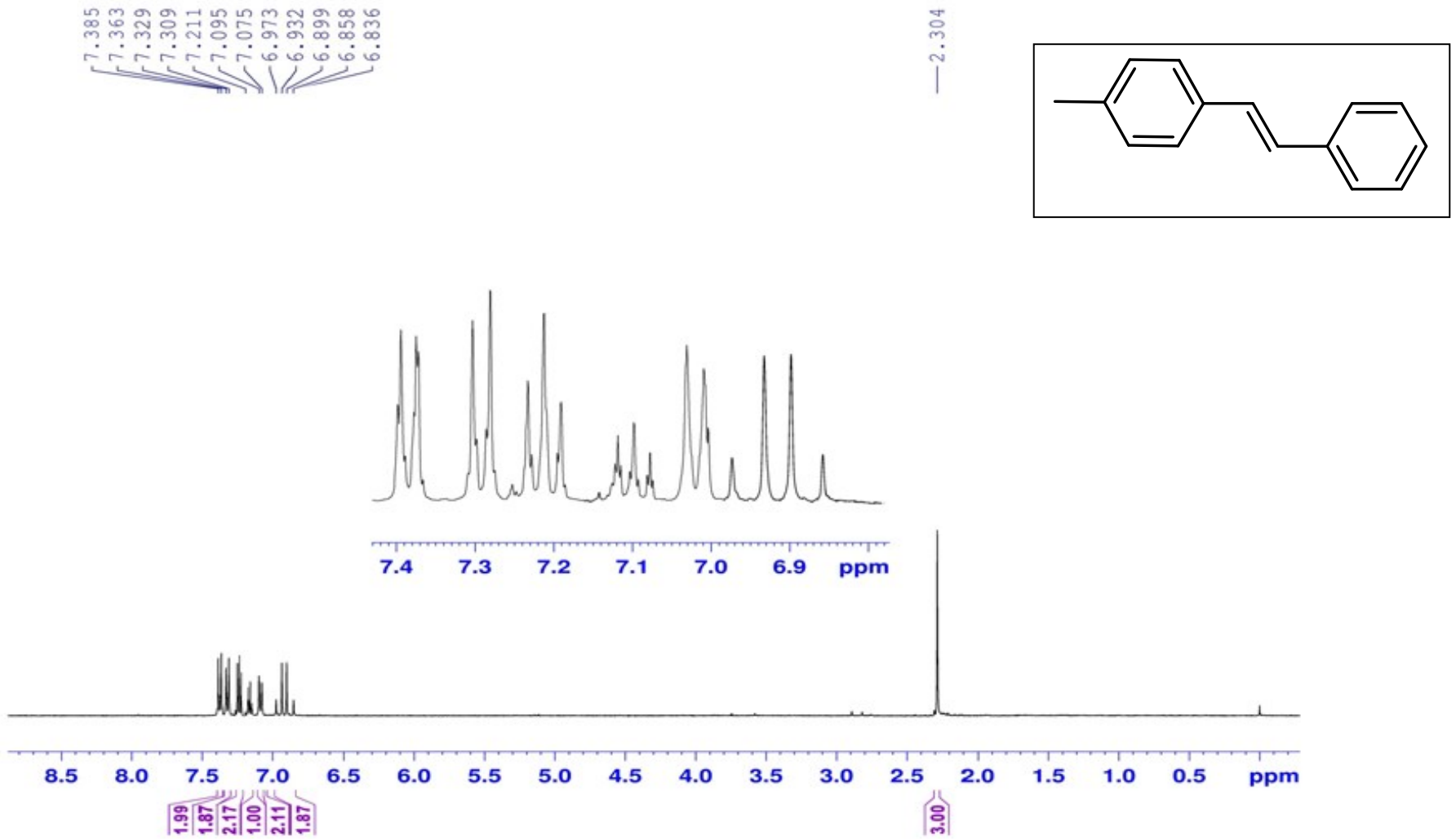


Figure S12. (E)-1,2-Di-*p*-tolylethene; ^{1}H NMR (400 MHz, $CDCl_3$)

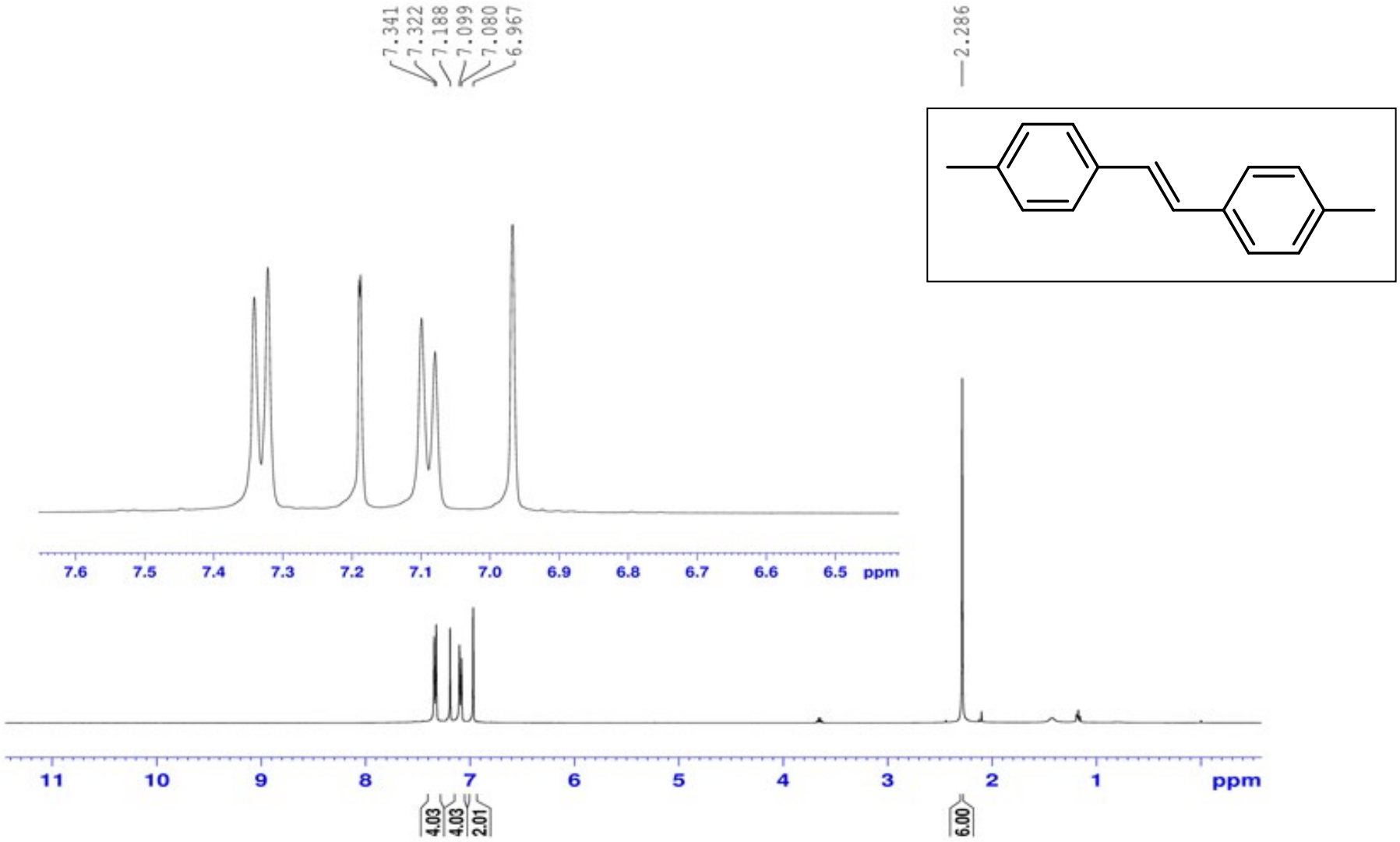


Figure S13. (*E*)-1-(Prop-1-en-2-yl)-4-styrylbenzene; ^{1}H NMR (400 MHz, $CDCl_3$)

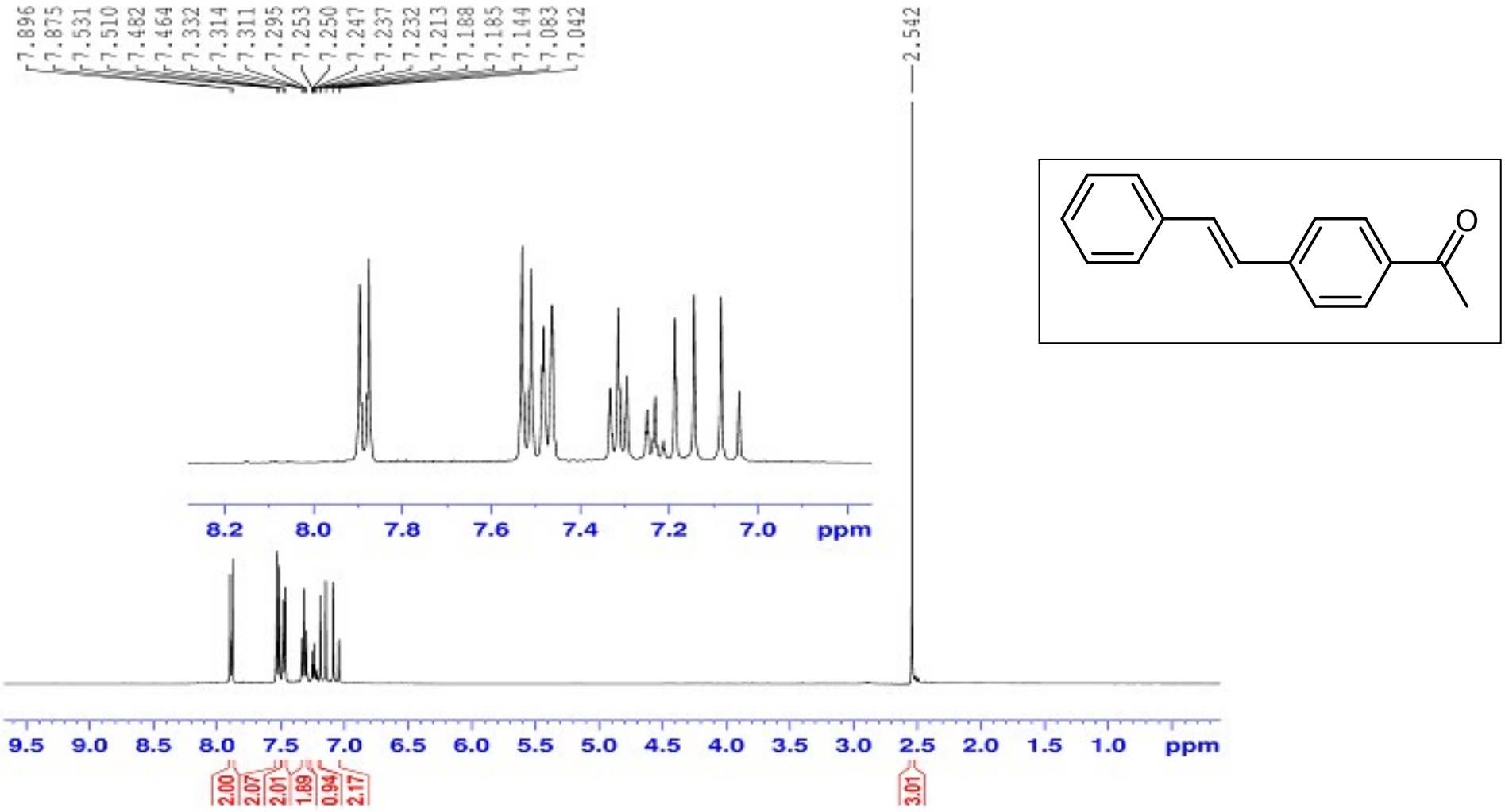


Figure S14. 4(4-Methylstyrene)acetophenone; ^{1}H NMR (400 MHz, $CDCl_3$)

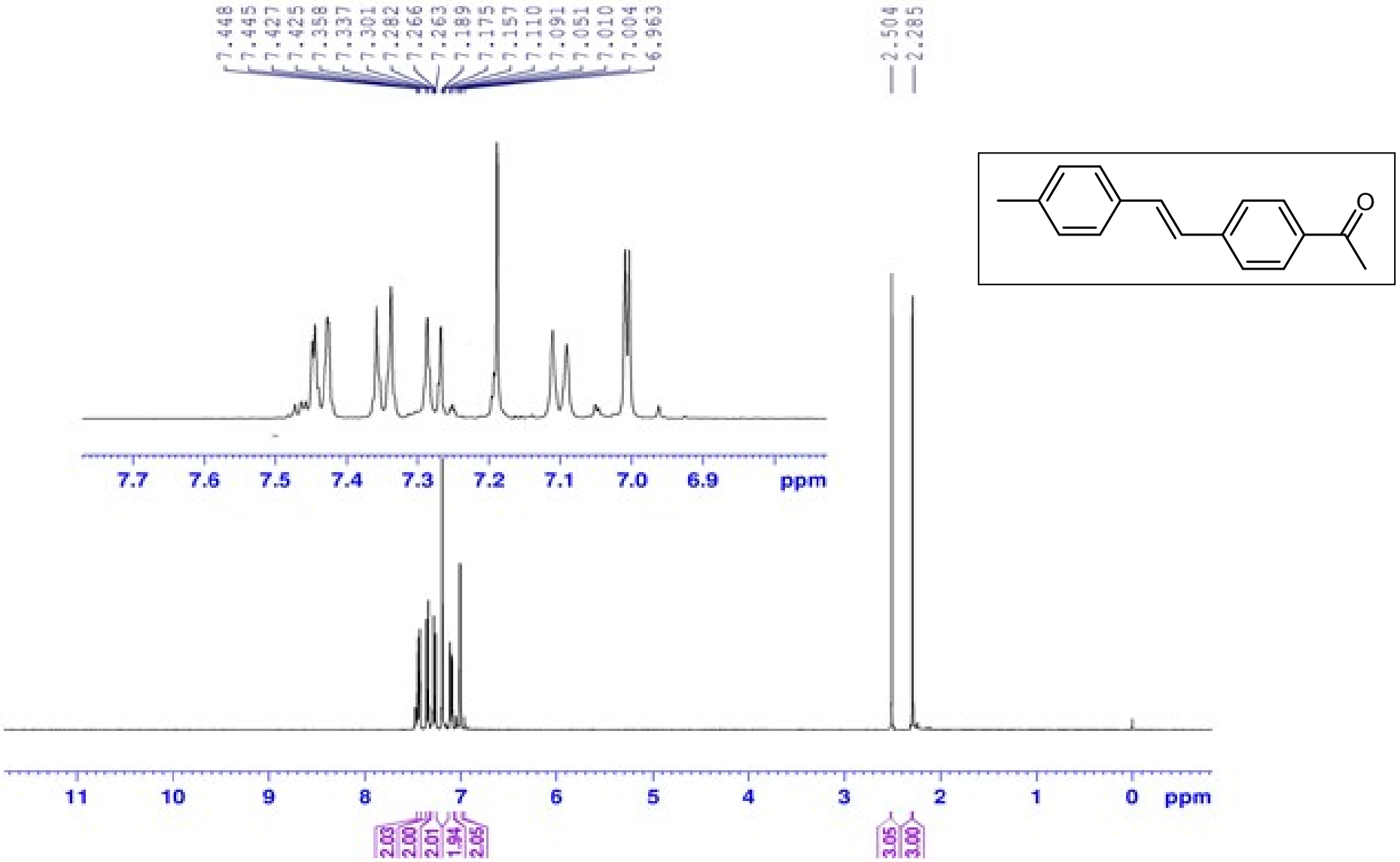


Figure S15. (*E*)-1-Methoxy-4-(4-methylstyryl)benzene; ^{1}H NMR (400 MHz, $CDCl_3$)

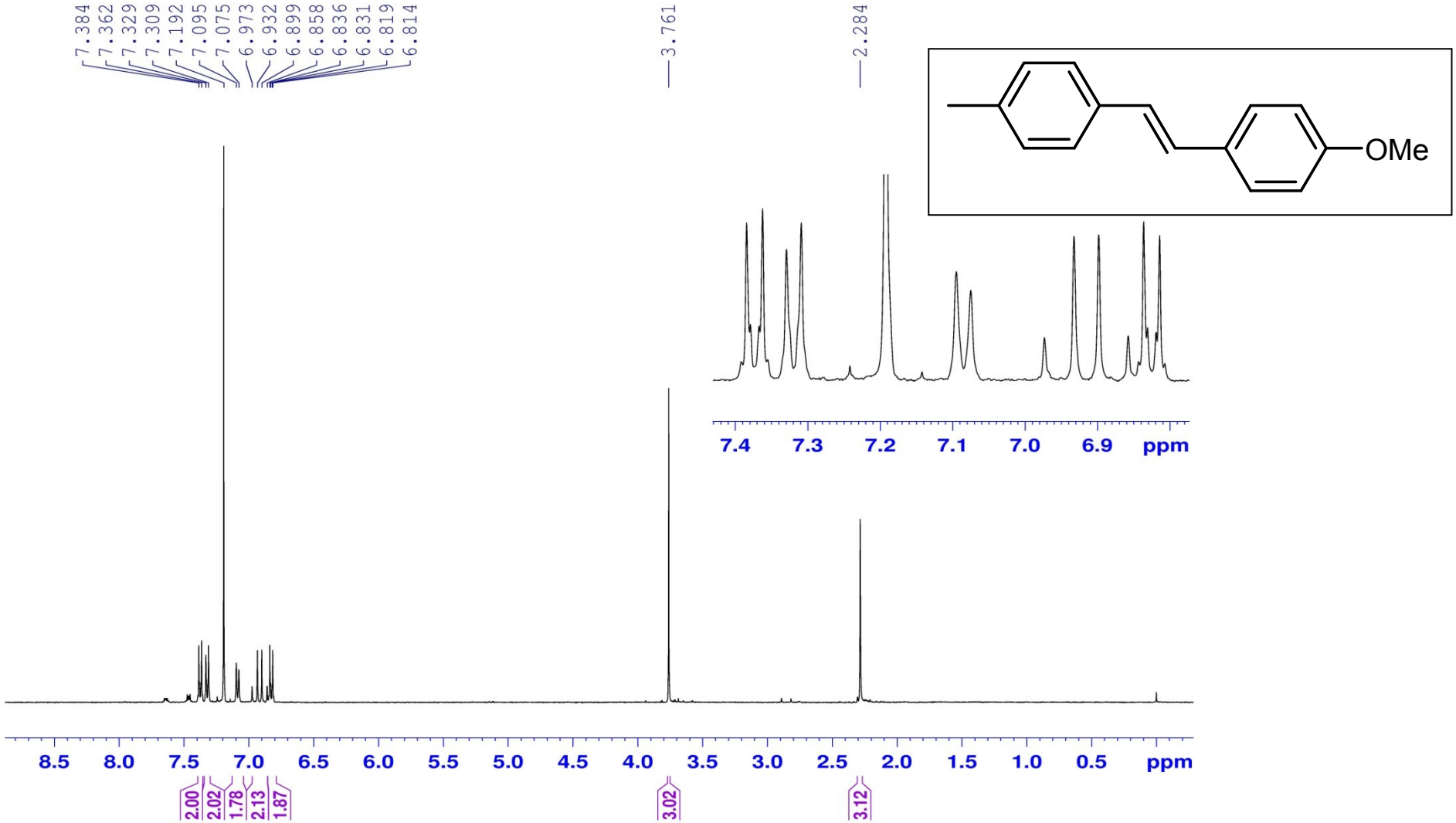


Figure S16. (*E*)-1-Fluoro-4-styrylbenzene; ^{1}H NMR (400 MHz, $CDCl_3$)

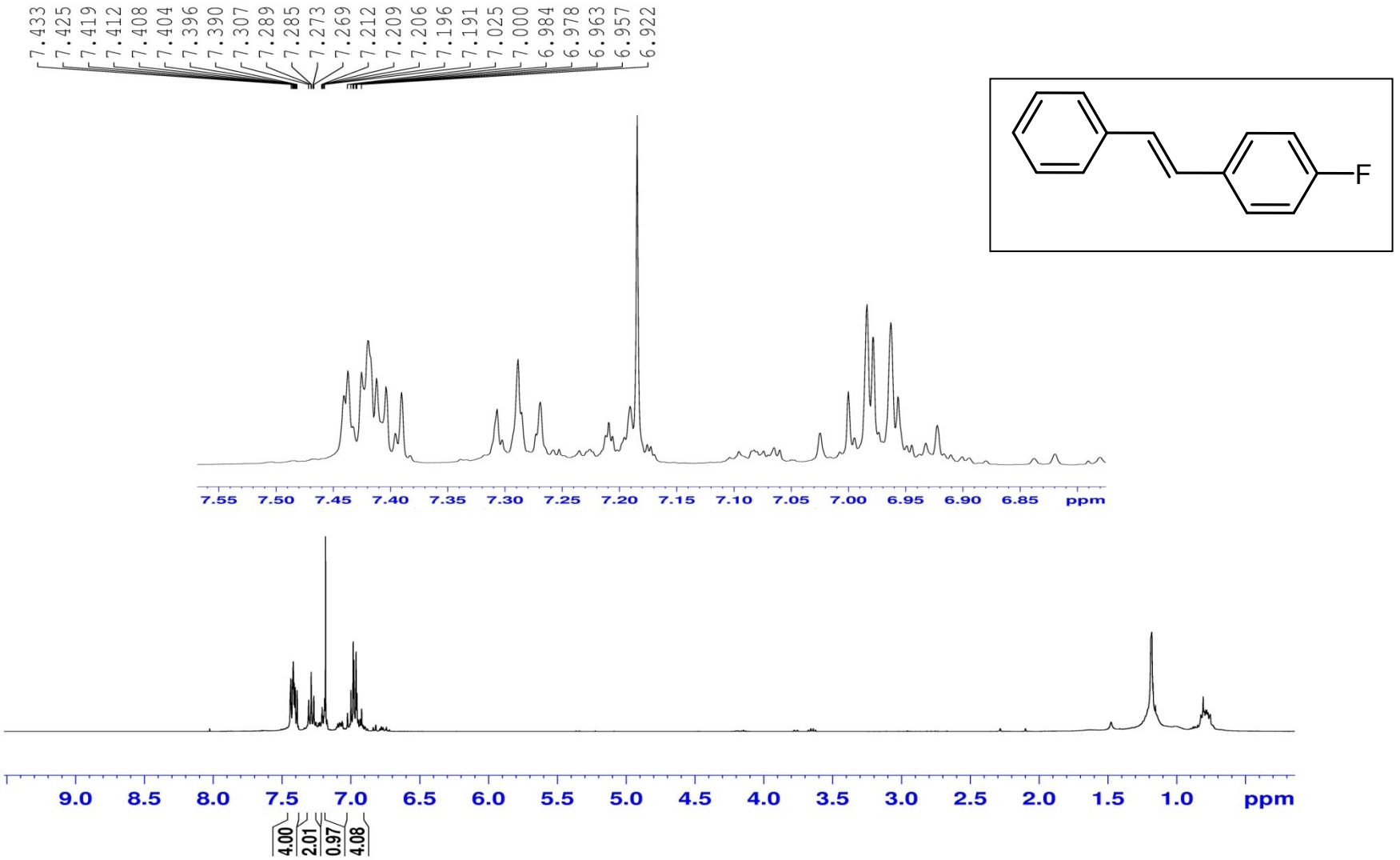


Figure S17. (E)-1-Fluoro-4-(4-methylstyryl)benzene; ^{1}H NMR (400 MHz, $CDCl_3$)

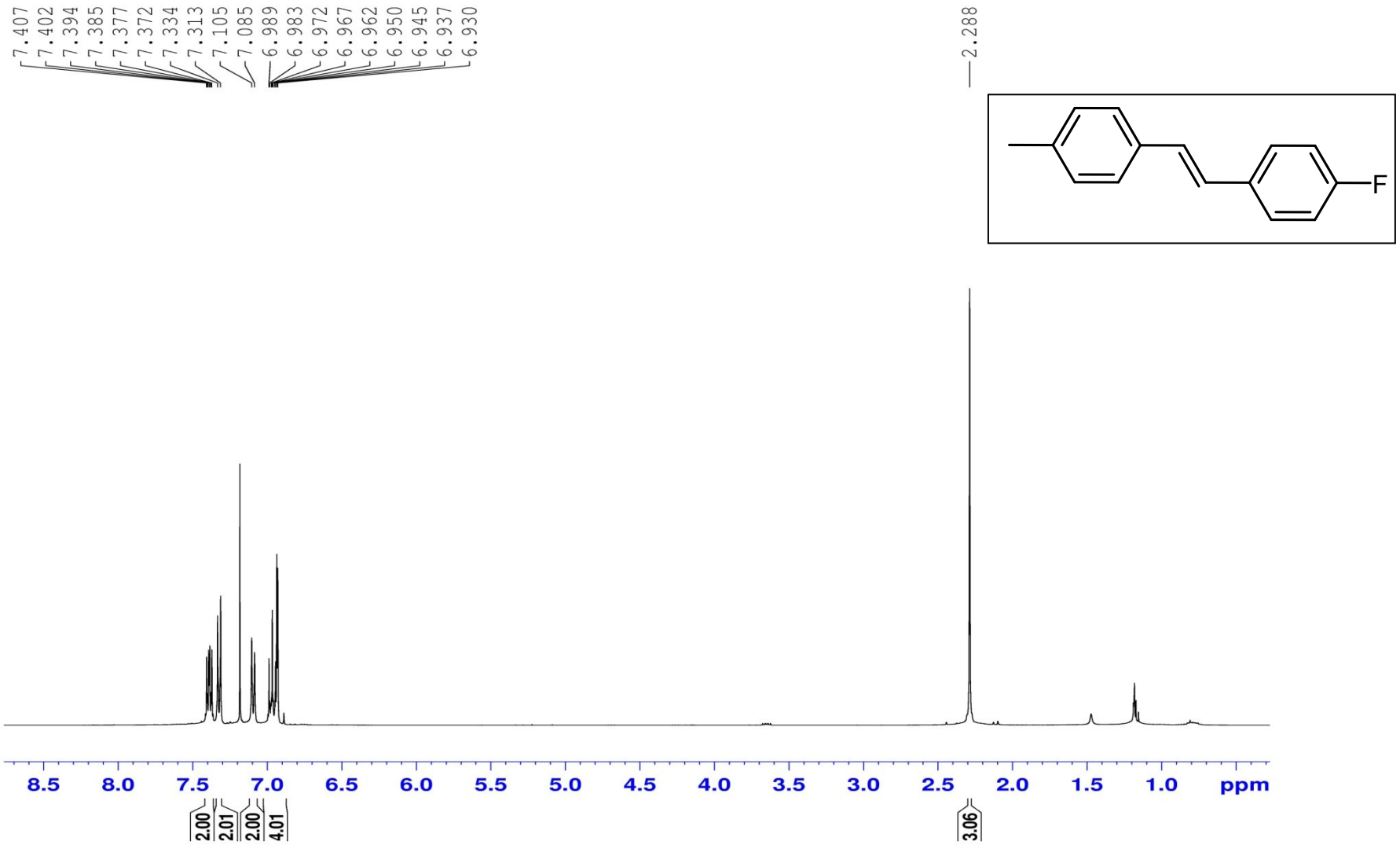


Figure S18. (E)-4-Styrylbenzaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$)

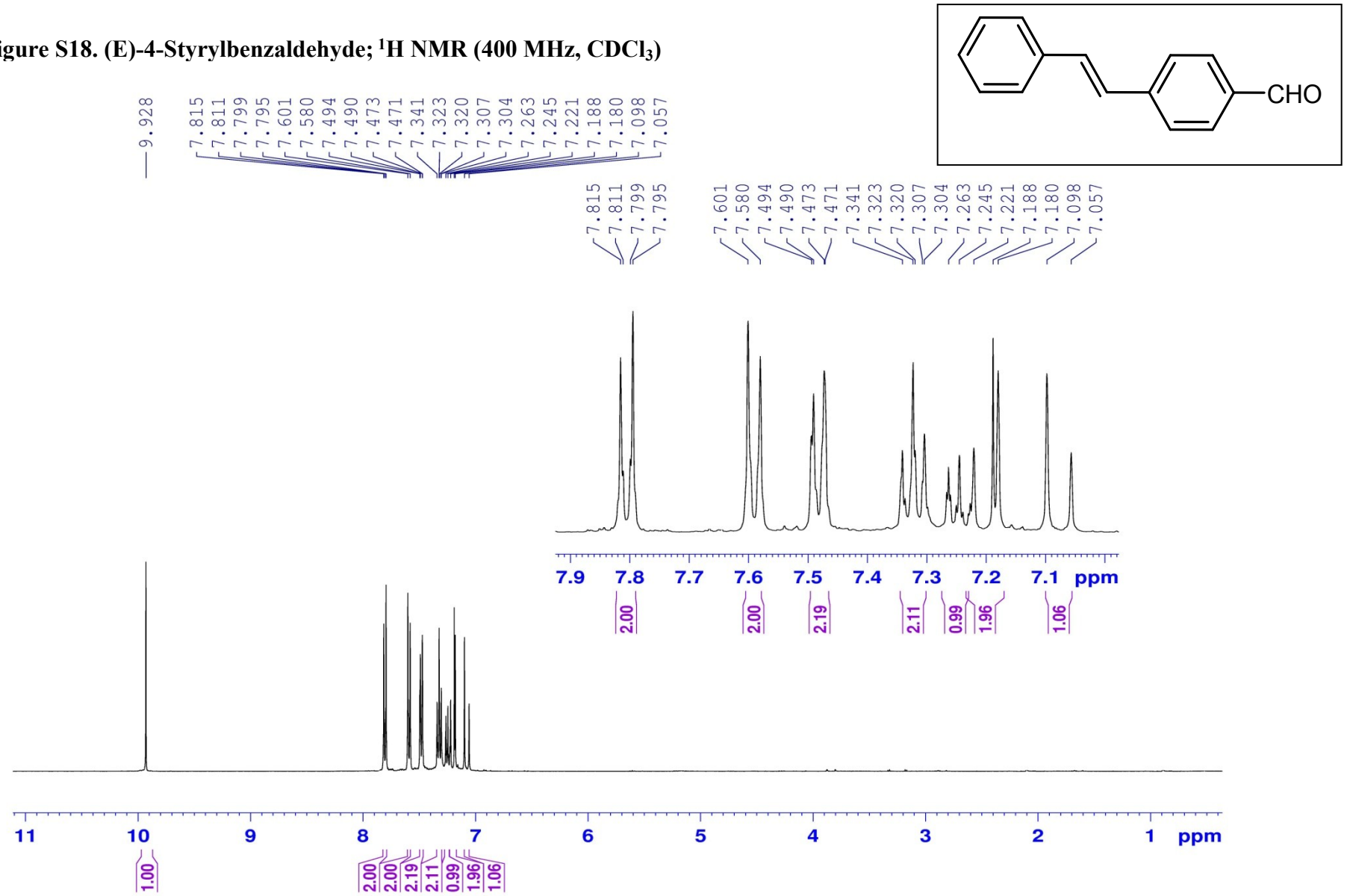


Figure S19. 2-Phenylpyridine, ^{1}H NMR (400 MHz, $CDCl_3$)

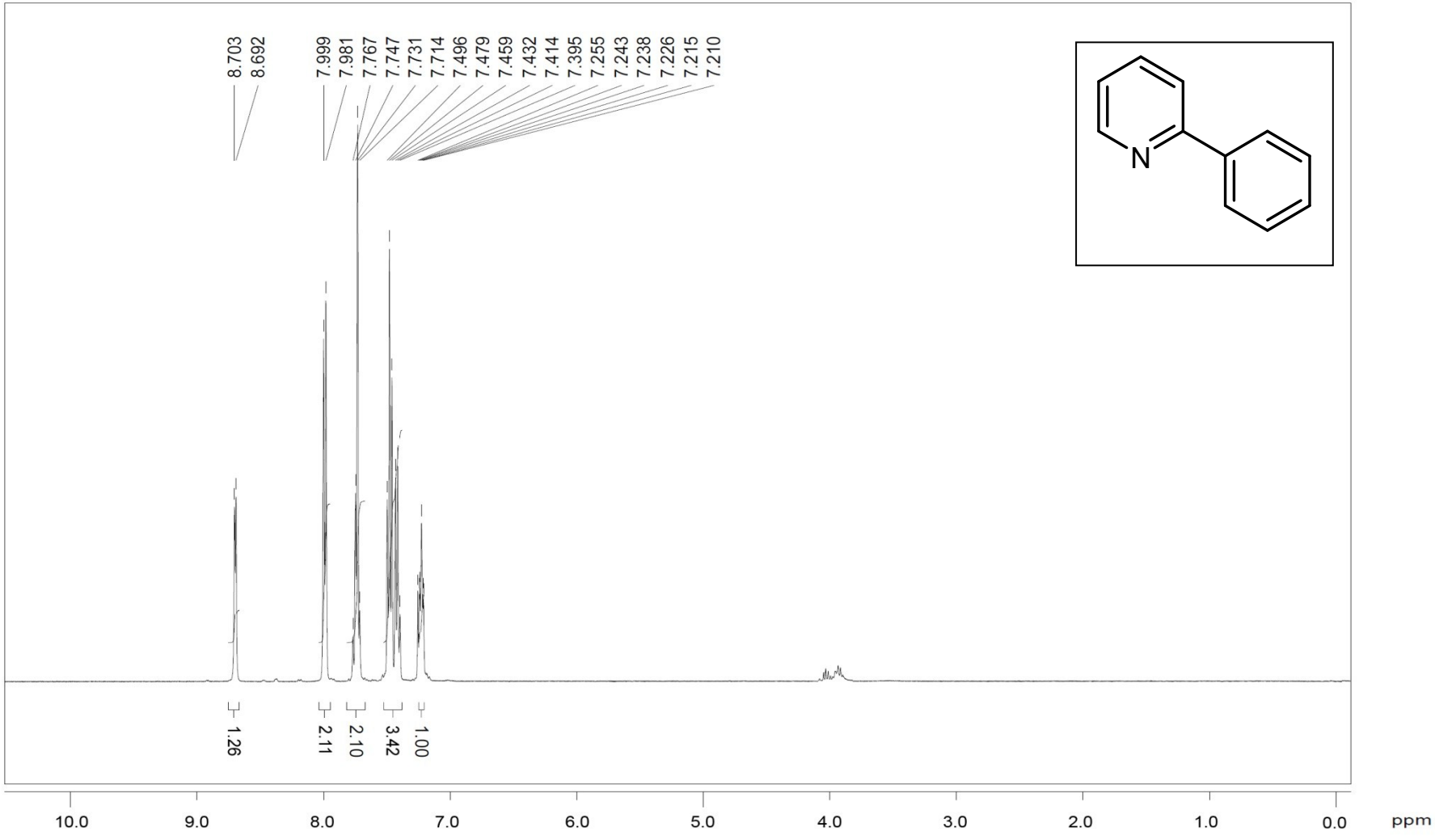


Figure S20. 2-(4-Methoxyphenyl)pyridine, ^{1}H NMR (400 MHz, $CDCl_3$)

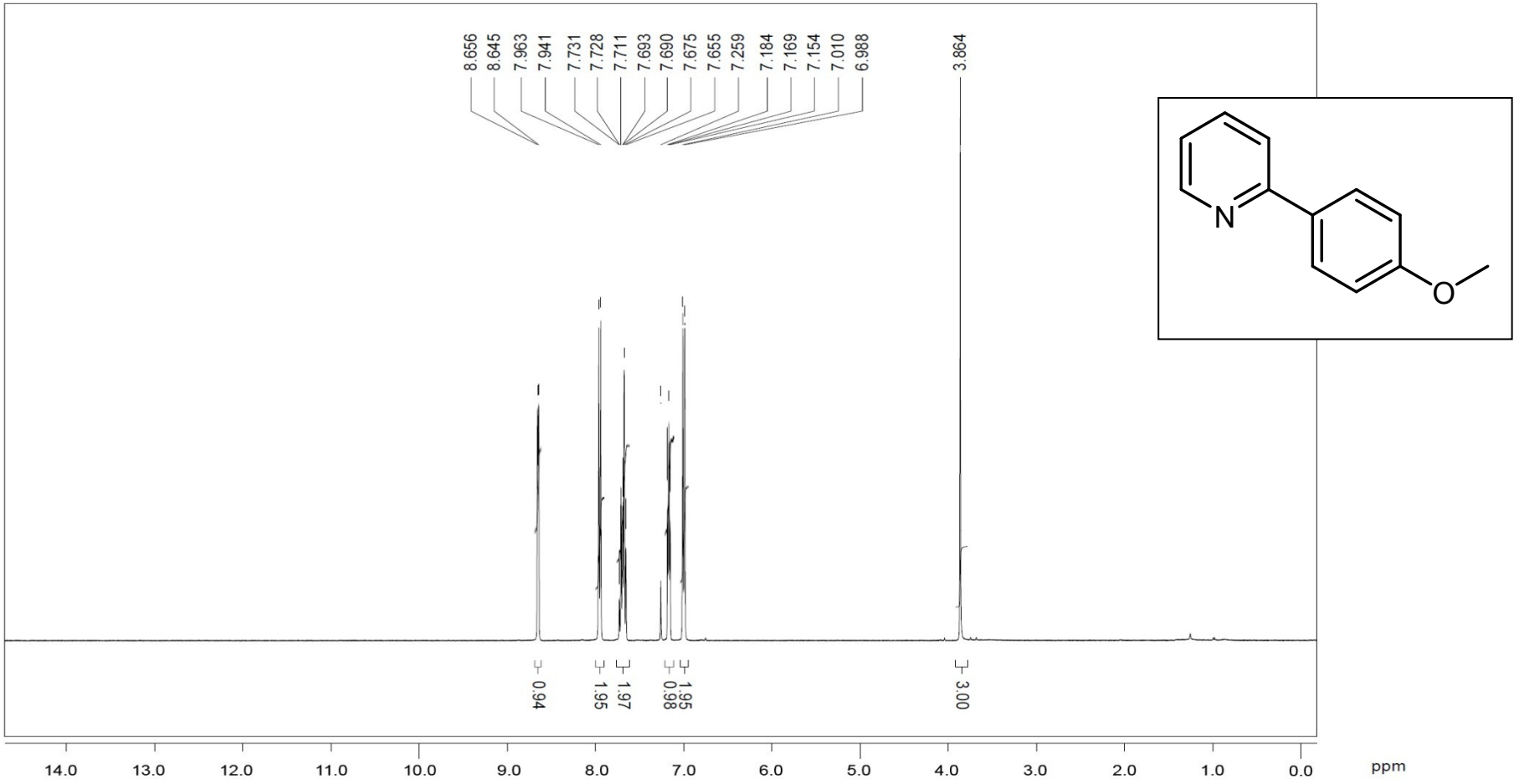


Figure S21. 2,6-Diphenylprydine; ^{1}H NMR (400 MHz, $CDCl_3$)

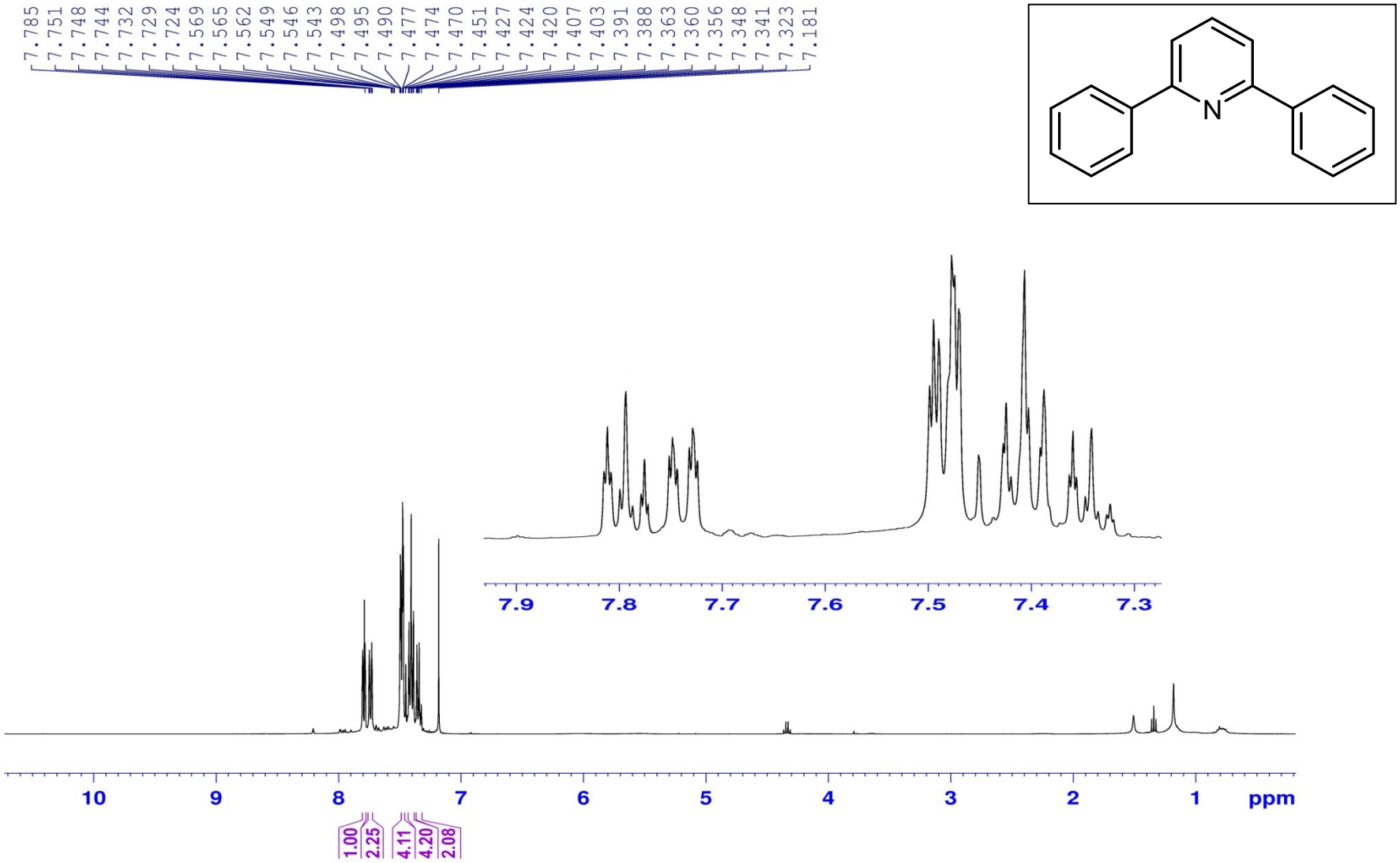
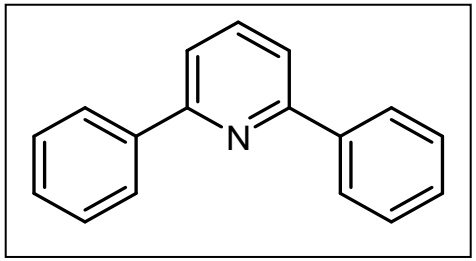


Figure S22. 2,6-Diphenylprydine; ^{13}C NMR (100 MHz, $CDCl_3$)



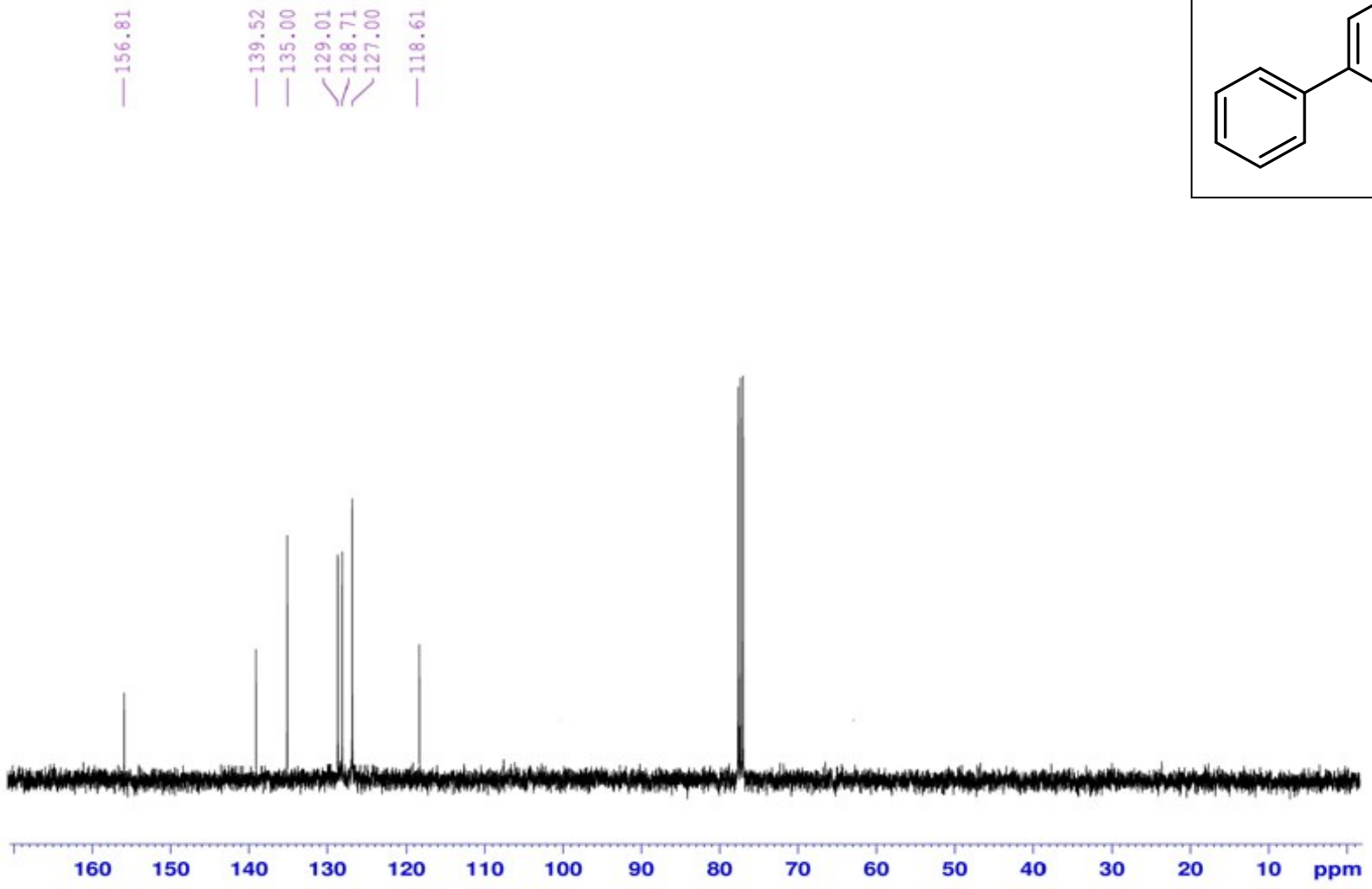


Figure S23. 2,6-Bis(4-methoxyphenyl)pyridine; ^{1}H NMR (400 MHz, $CDCl_3$)

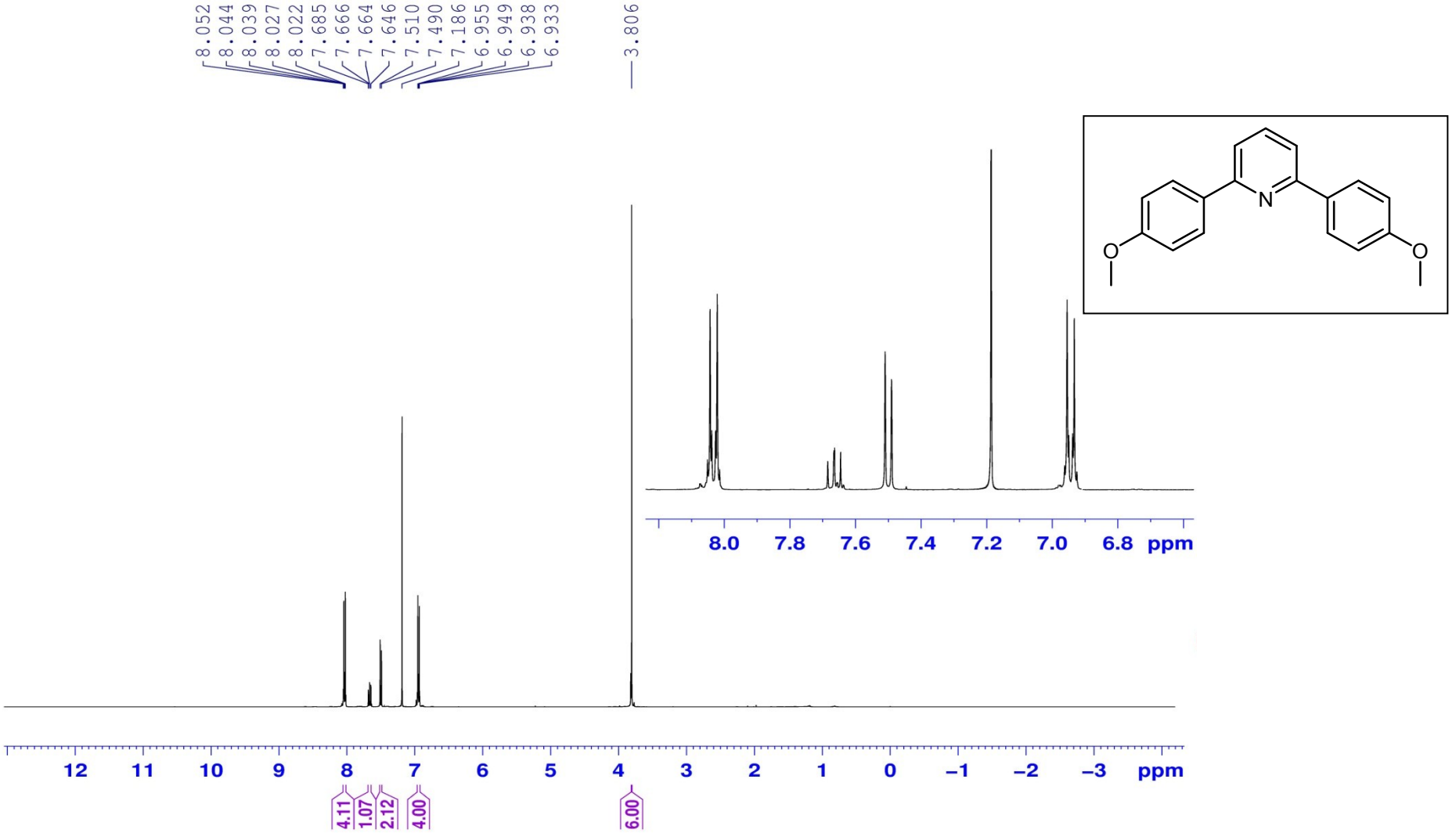


Figure S24. 2,6-Bis(4-methoxyphenyl)pyridine; ^{13} C NMR (100 MHz, $CDCl_3$)

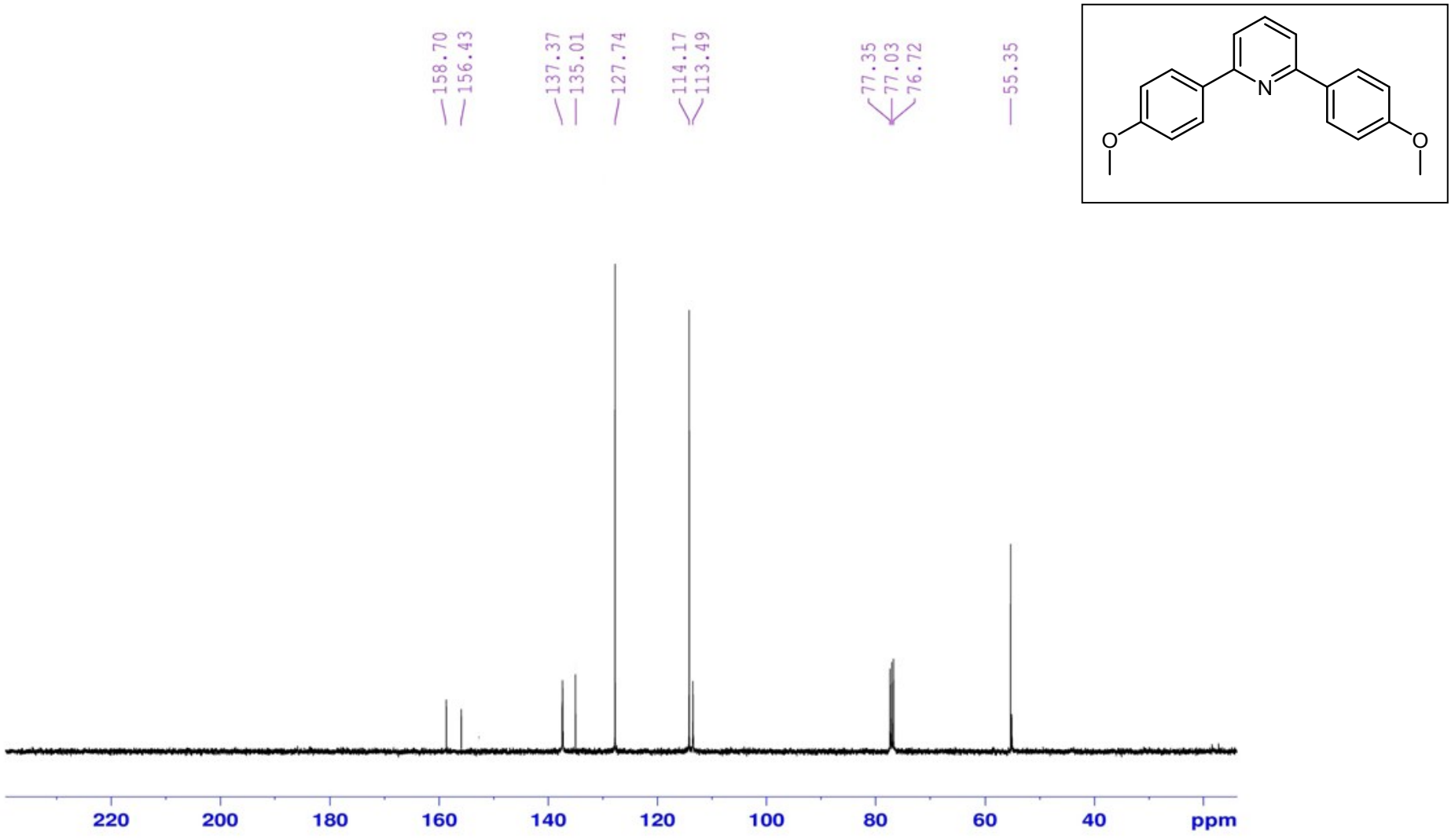


Figure S25. -1,3,5-Triphenylbenzene; ^{1}H NMR (400 MHz, $CDCl_3$)

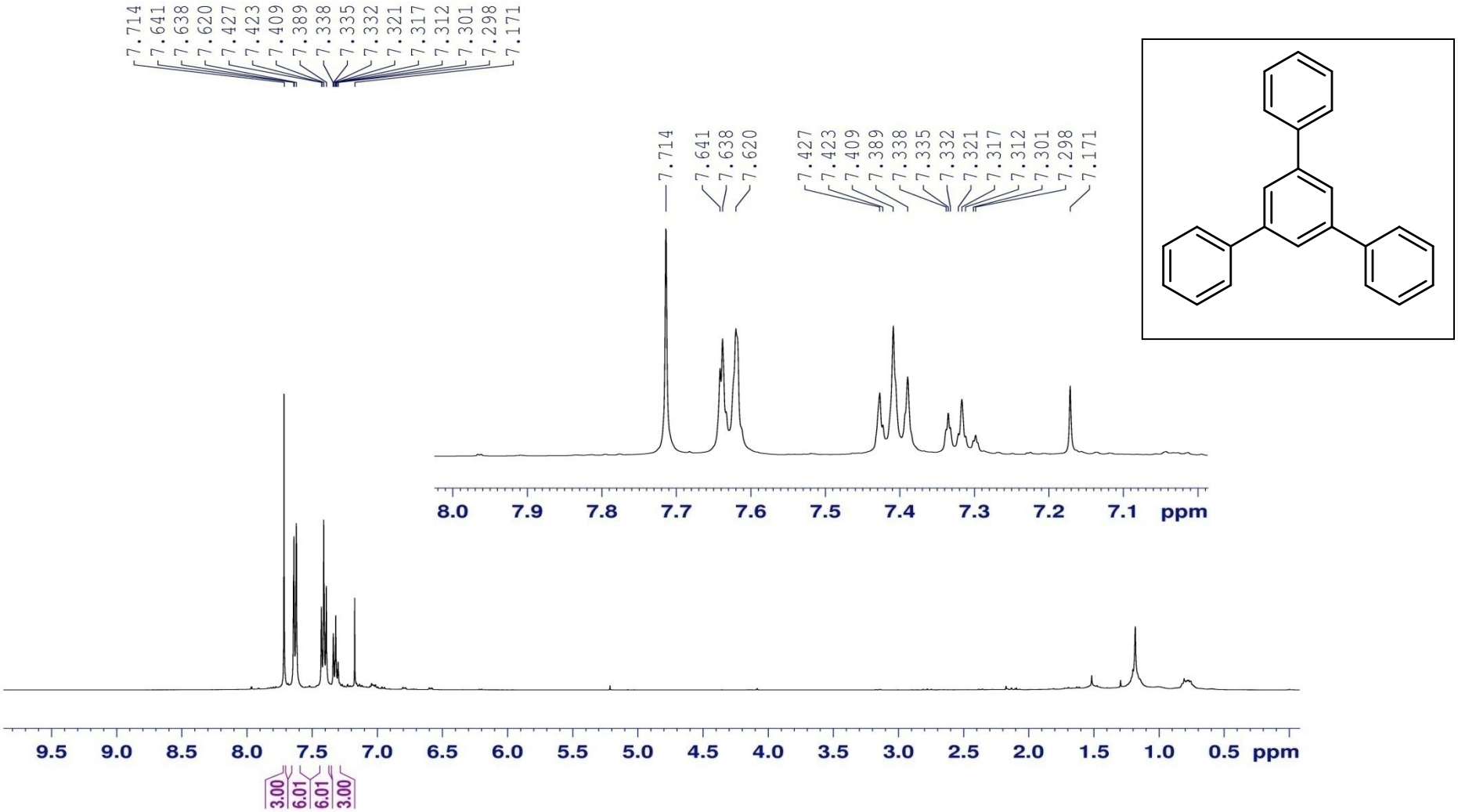


Figure S26. 1,3,5-Triphenylbenzene; ^{13}C NMR (100 MHz, $CDCl_3$)

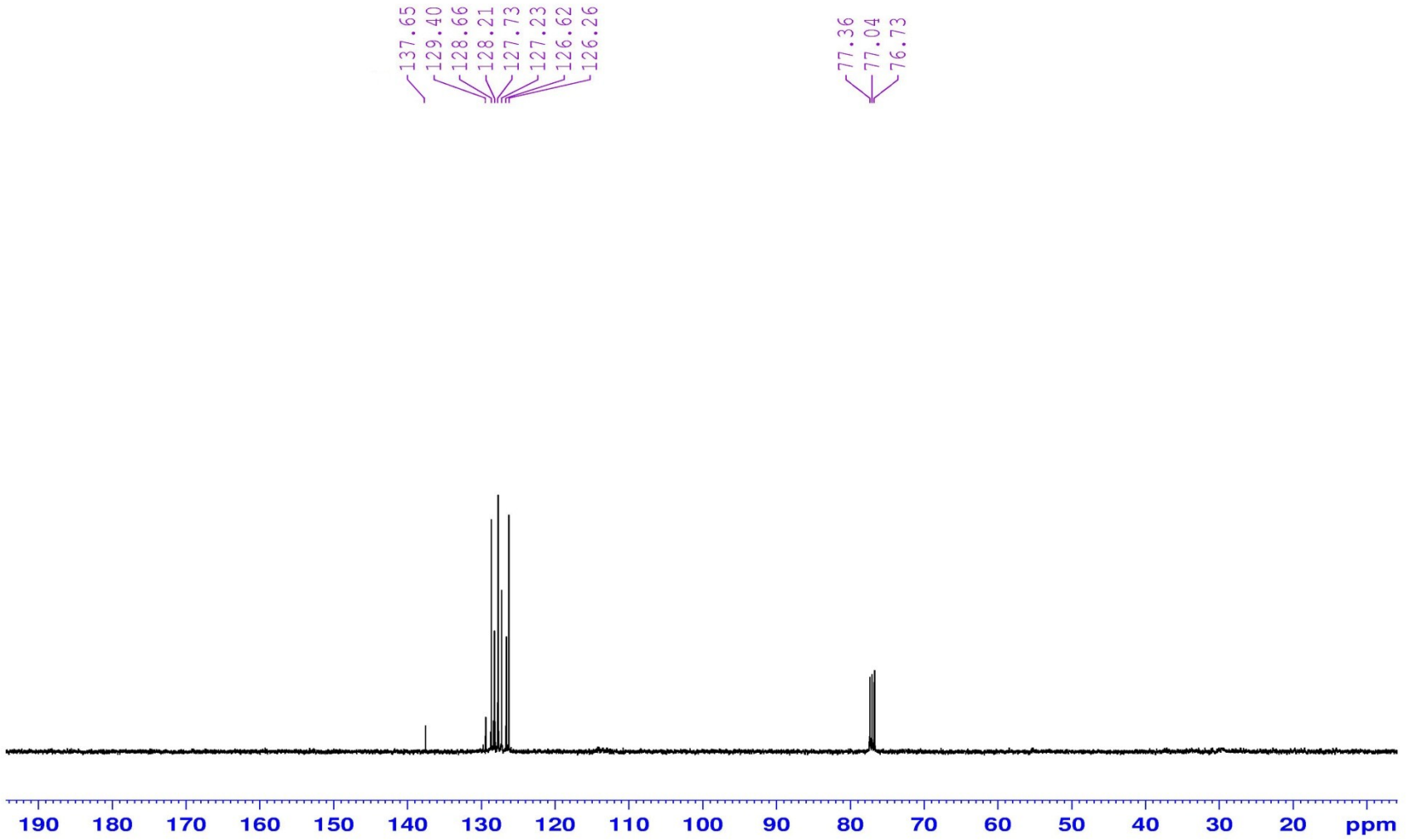


Figure S27. 1,3,5-Tri(4-methoxyphenyl)benzene; ^{1}H NMR (400 MHz, $CDCl_3$)

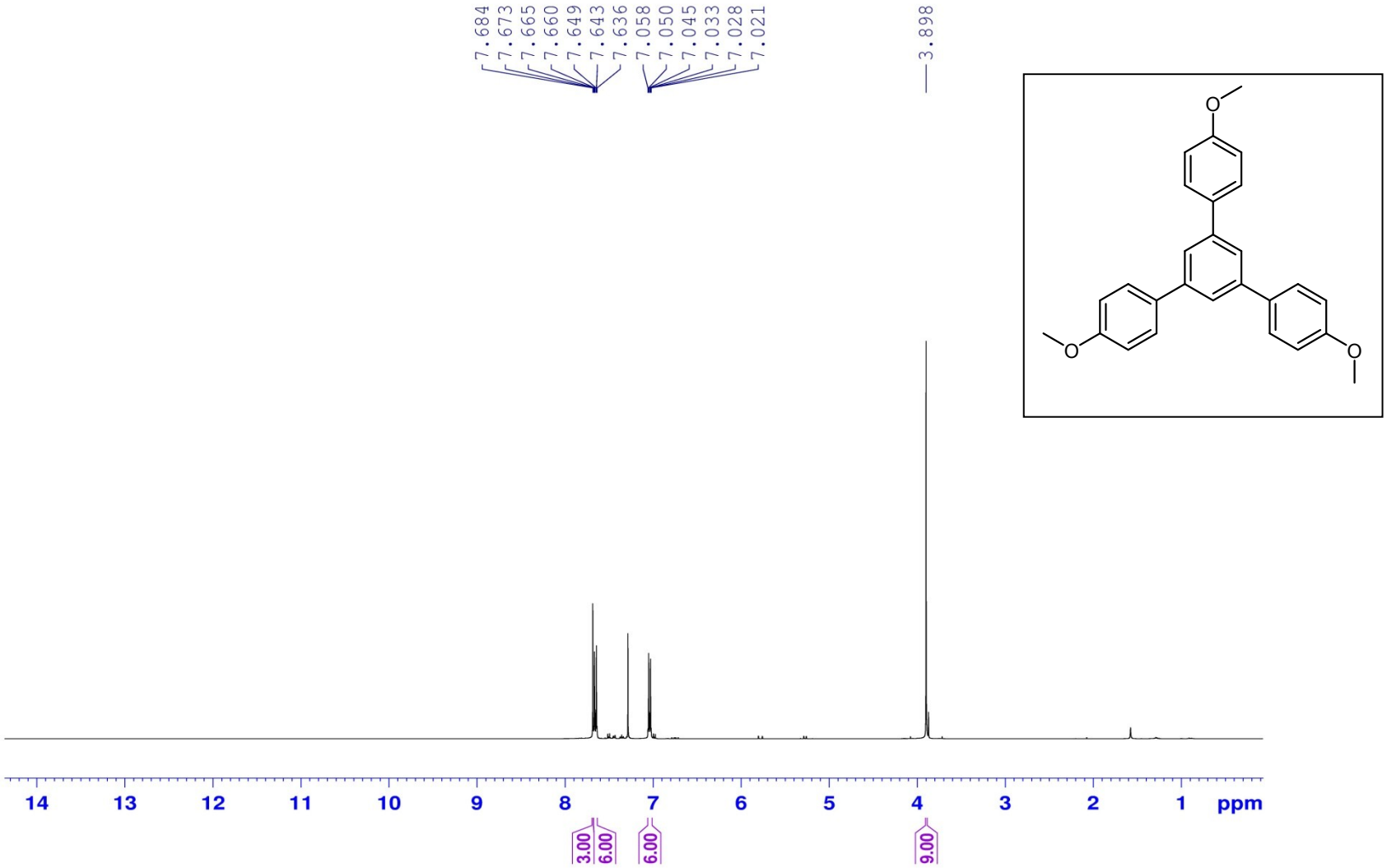


Figure S28. 1,3,5-Tri(4-methoxyphenyl)benzene, ^{13}C NMR (100 MHz, $CDCl_3$)

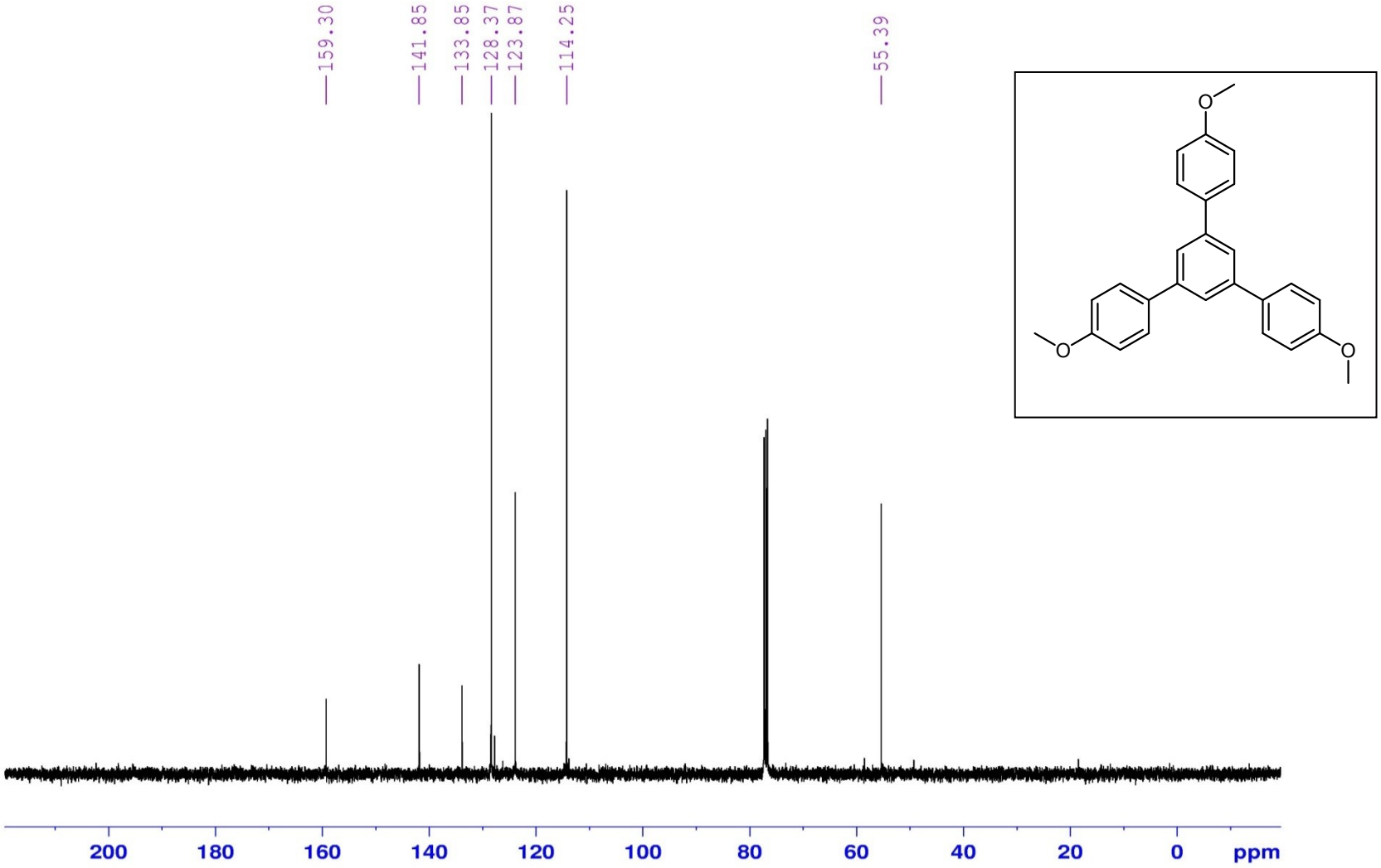
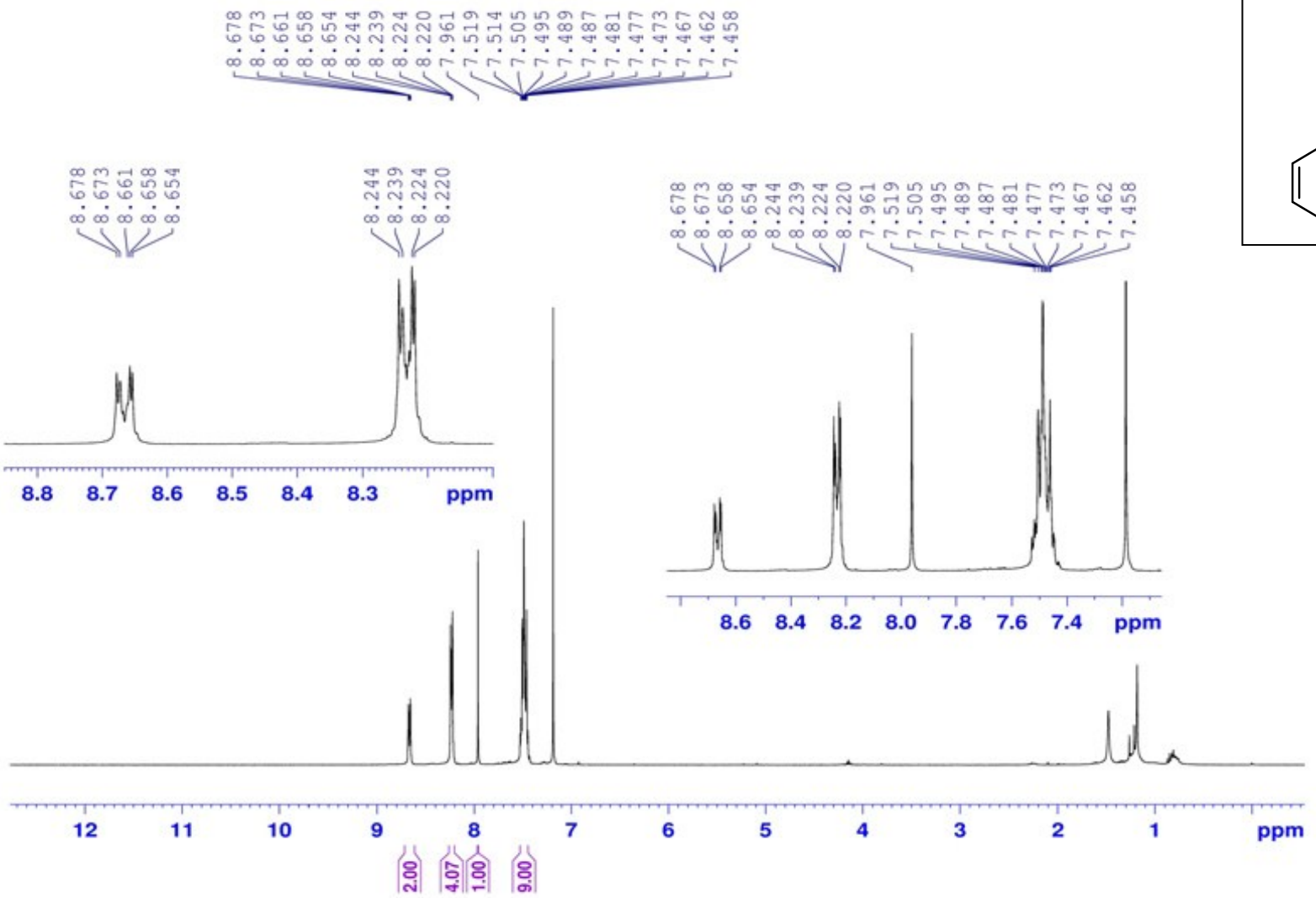


Figure S29. 2,4,6-Triphenylprimidine; ^{1}H NMR (400 MHz, $CDCl_3$)



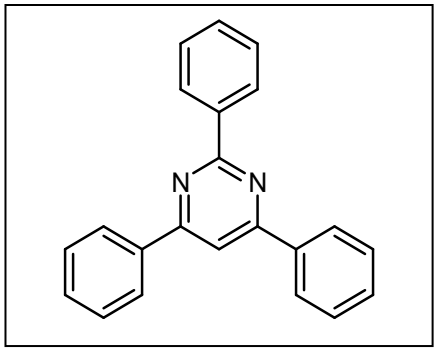


Figure S30. 2,4,6-Triphenylprimidine; ^{13}C NMR (100 MHz, $CDCl_3$)

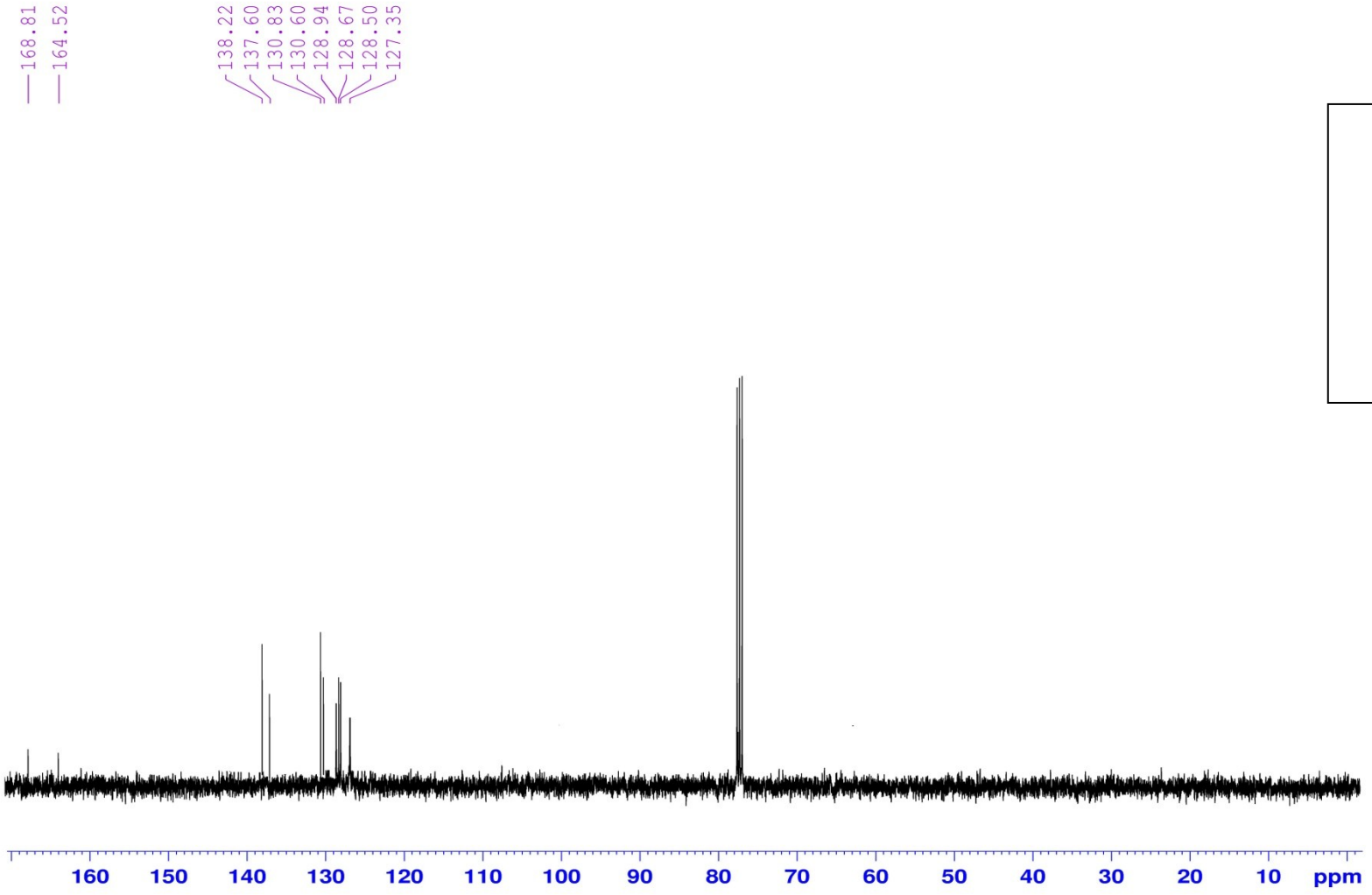


Figure S31. 2,4,6-Tris(4-methoxyphenyl)pyrimidine; ^{1}H NMR (400 MHz, $CDCl_3$)

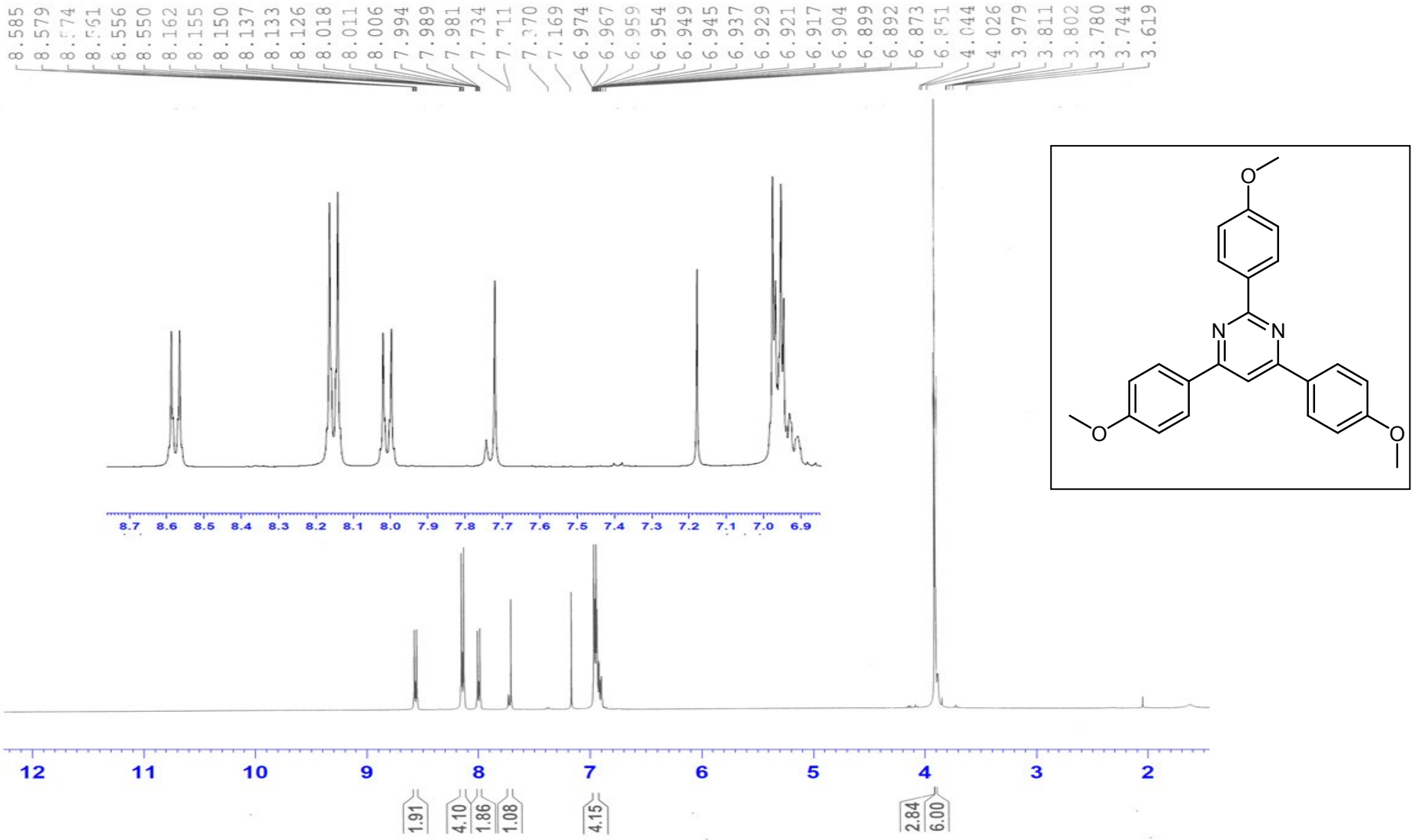


Figure S32. 2,4,6-Tris(4-methoxyphenyl)pyrimidine; ^{13}C NMR (100 MHz, $CDCl_3$)

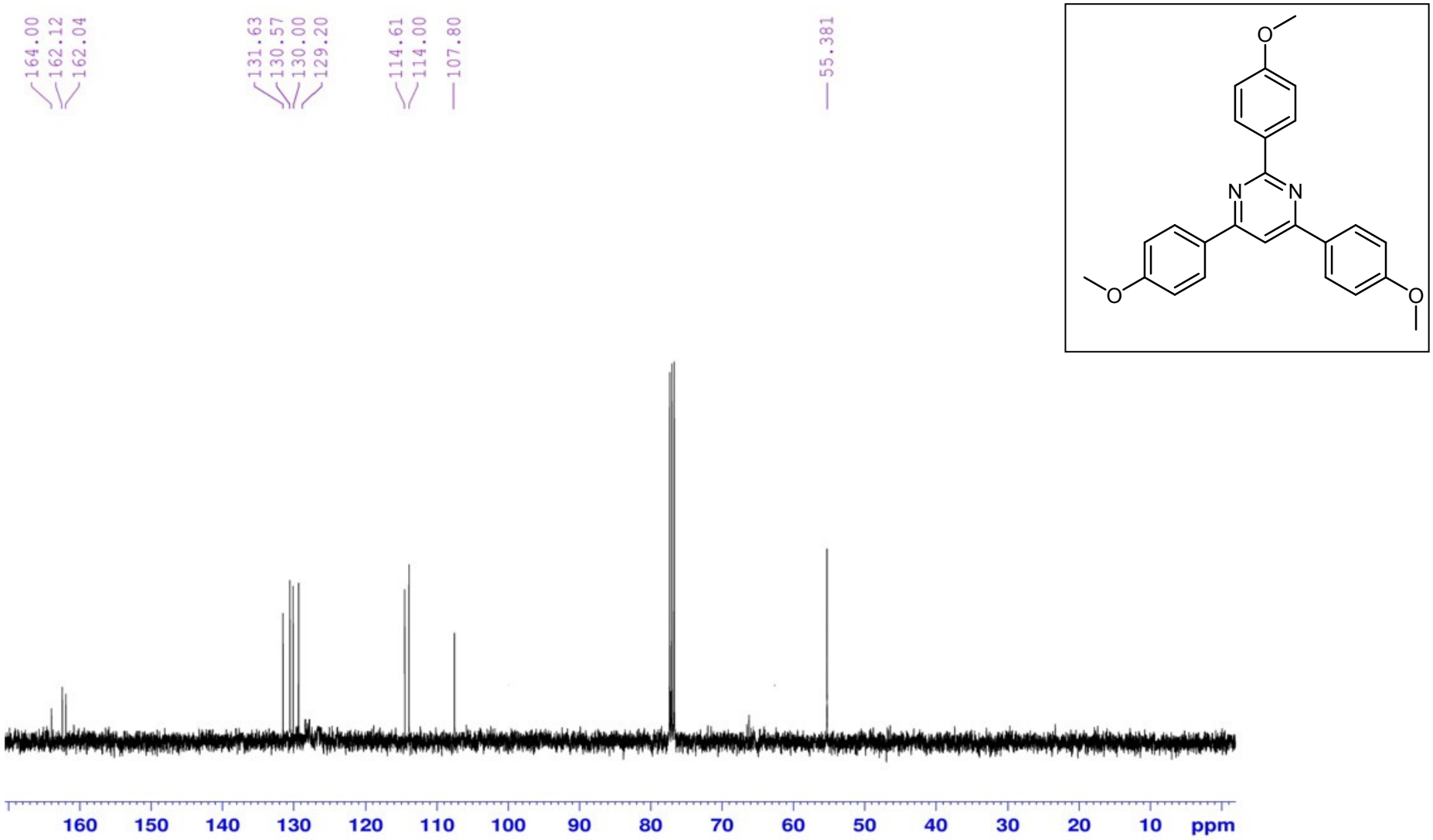


Figure S33. 1,3,5-Tristyrylbenzene; ^{1}H NMR (400 MHz, $CDCl_3$)

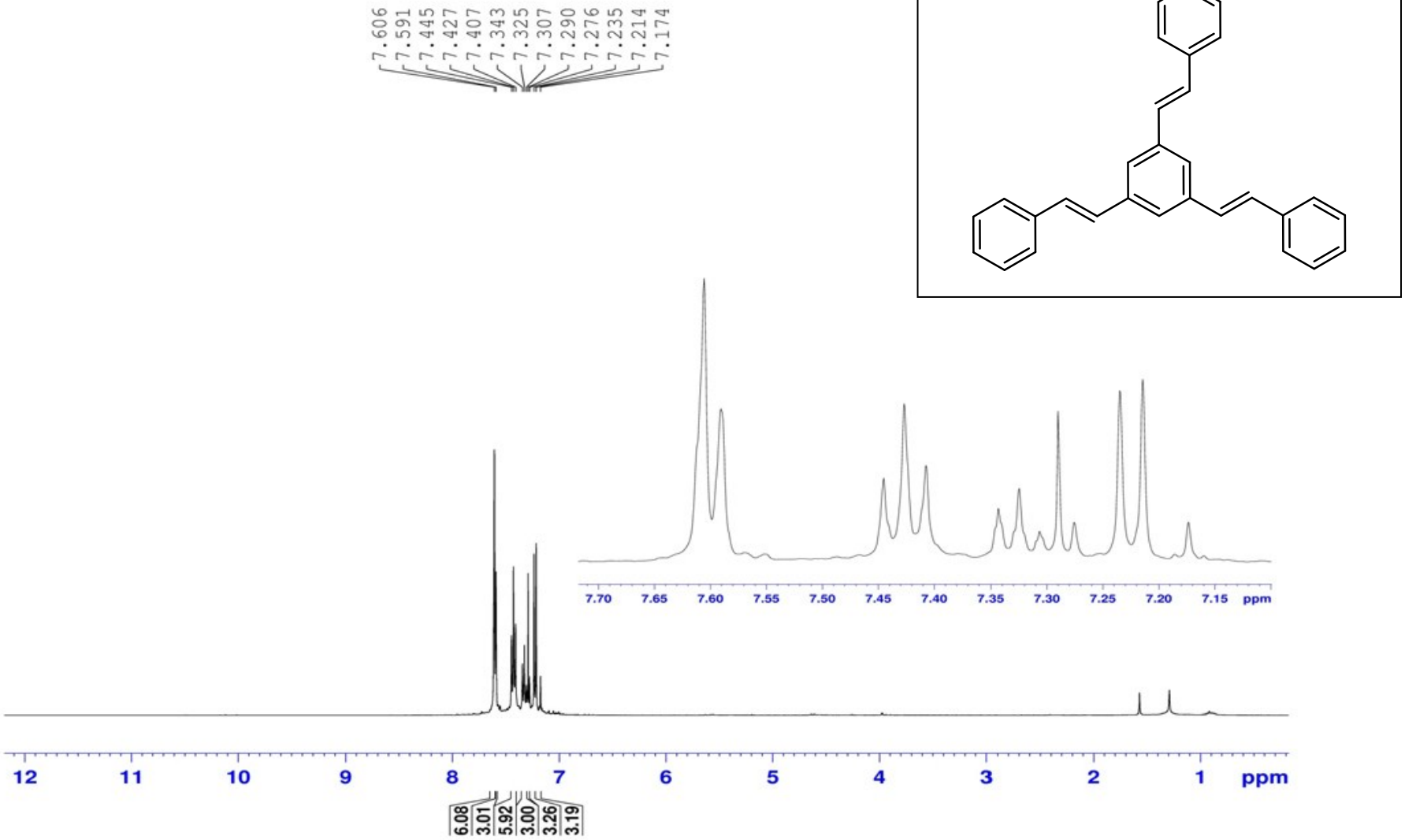


Figure S34. 1,3,5-Tristyrylbenzene; ^{13}C NMR (100 MHz, $CDCl_3$)

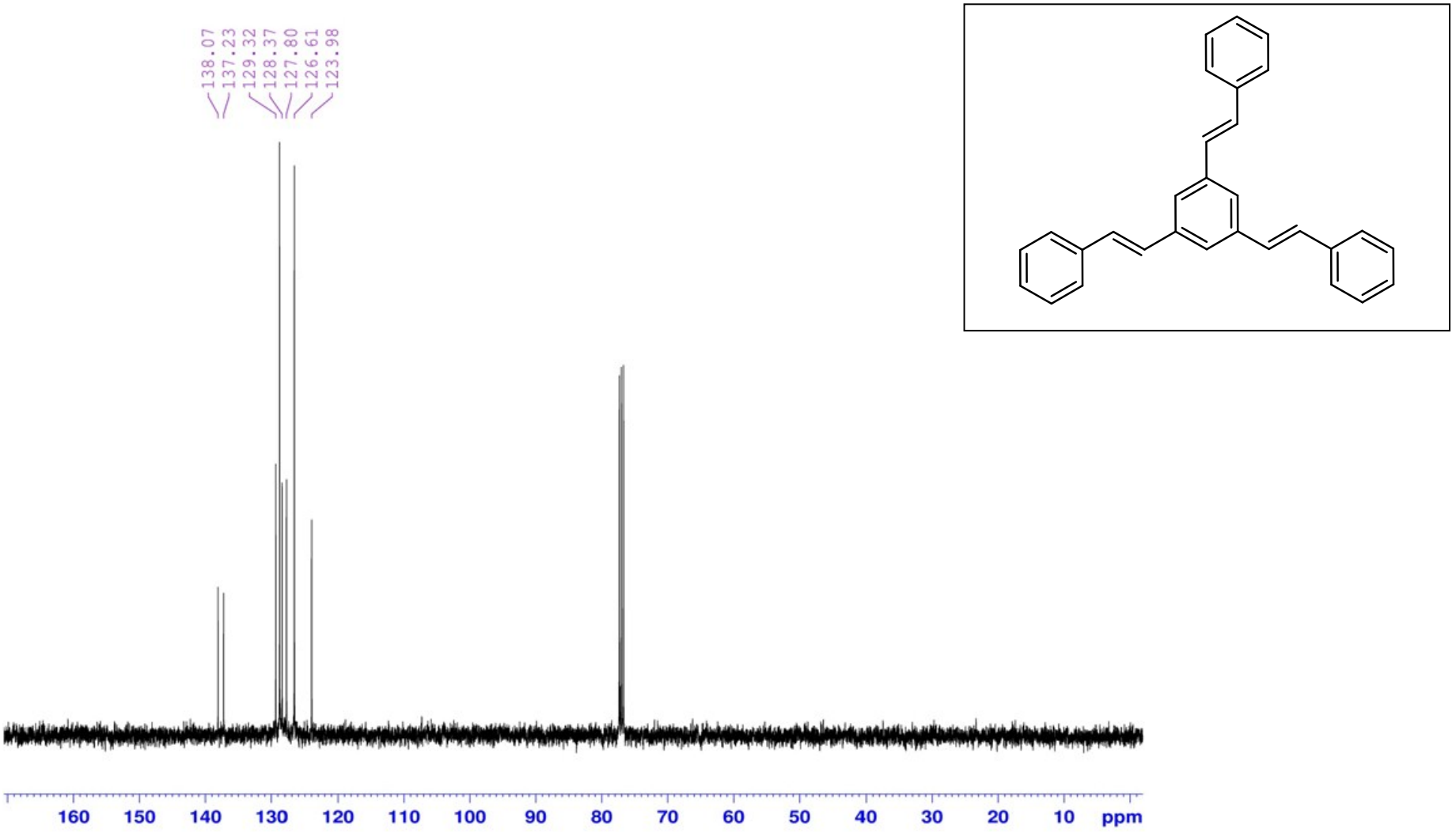


Figure S35. 1,3,5-Tris(*p*-methylstyryl)benzene; ^{1}H NMR (400 MHz, $CDCl_3$)

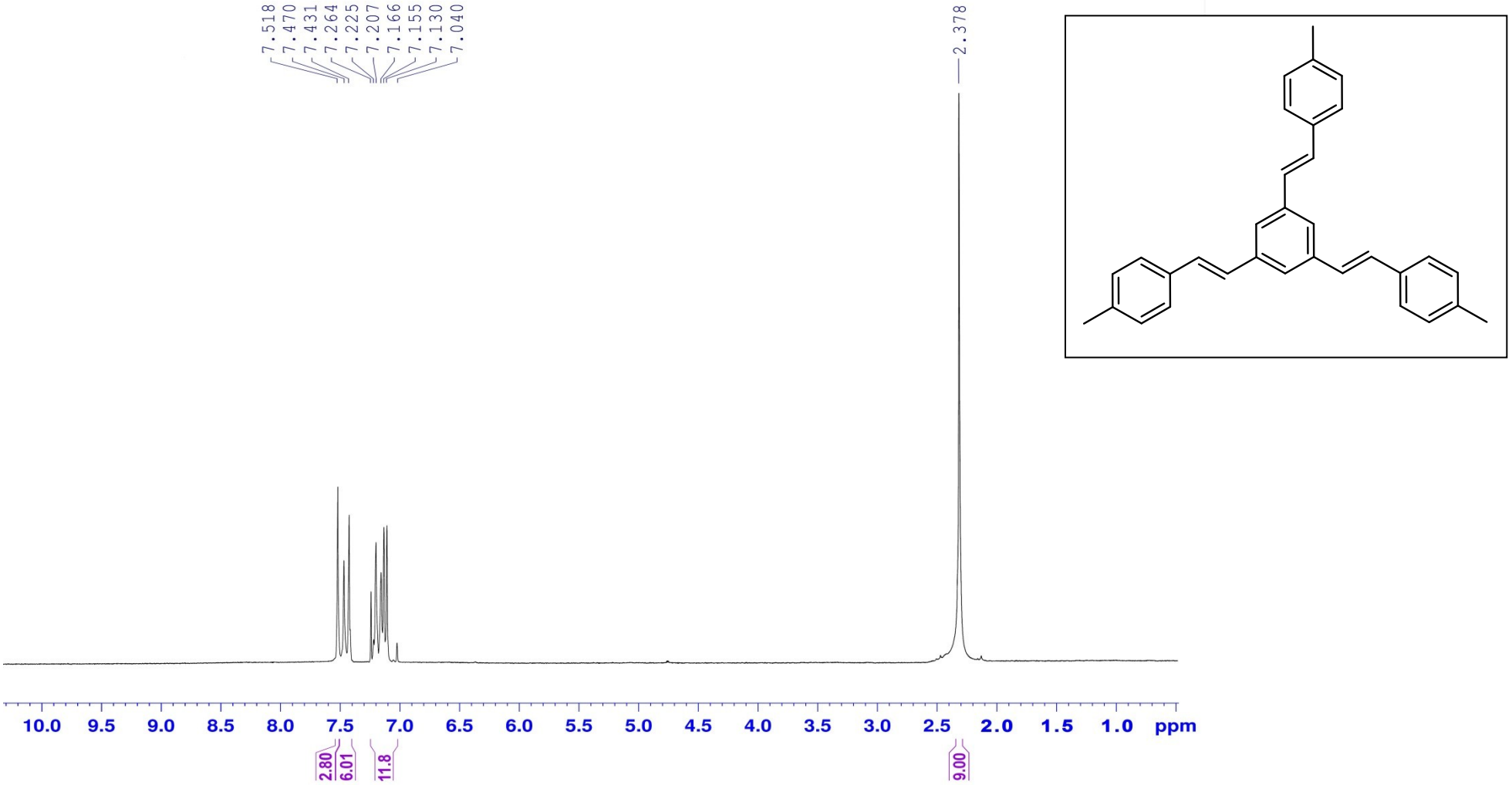
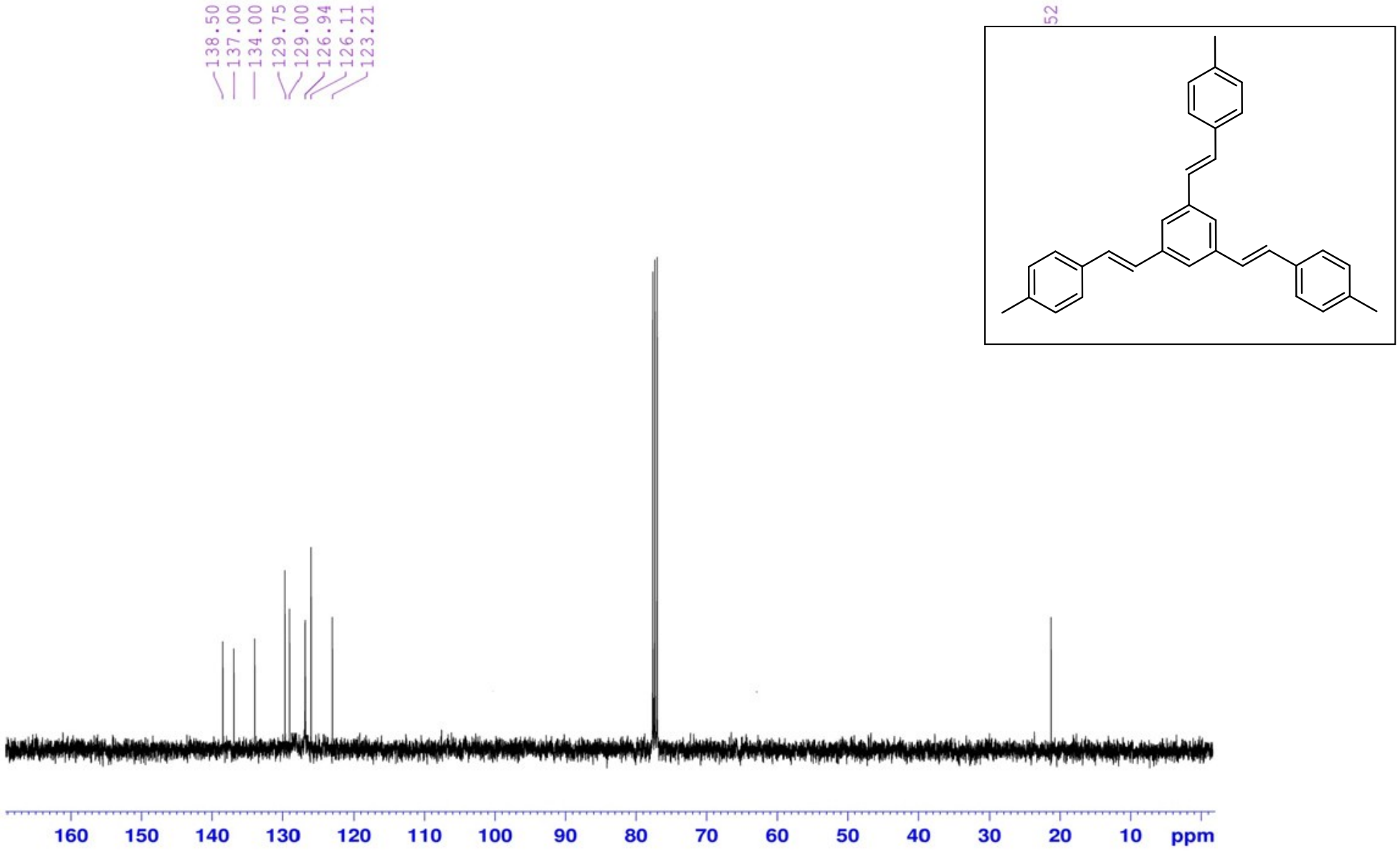


Figure S36. 1,3,5-Tris(*p*-methylstyryl)benzene; ^{13}C NMR (100 MHz, $CDCl_3$)



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