Carbonylative Coupling of Aryl Tosylates/triflates with Arylboronic Acids under CO Atmosphere

Cheng Yi Hao, Dan Wang, Ya Wei Li, Lin Lin Dong, Ying Jin, Xiu Rong Zhang, Sheng Chang, Zhu, Heyun *

College of Pharmacy, JiLin Medical University, JiLin 132013, JiLin, PR China

Corresponding author. Tel.: +86 432 6456 0532.
E-mail address: jmu_changsheng@126.com

Supporting Materials

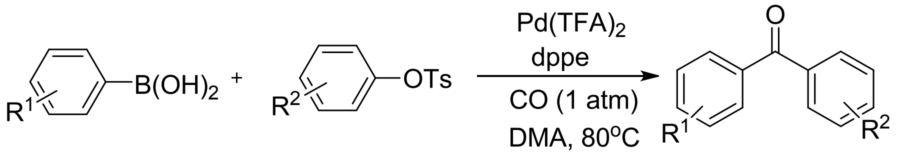
Content

General

Starting materials were purchased from common commercial sources and all solvents were purified and dried according to standard methods prior to use. ^{1}H NMR spectra were recorded on a 400 M Hz spectrometer using tetramethylsilane (TMS) as internal standard. Proton chemical shifts are reported in parts per million (ppm) relative to TMS. Multiplicities are reported as: singlet (s), doublet (d), triplet (t) and multiplet (m). ^{13}C NMR spectra were recorded at 100 MHz using TMS as internal standard. HRMS (EI) data were collected on High Resolution mass spectrometer (ion trap). Other substrates and catalysts were commercially available and used without additional purification.

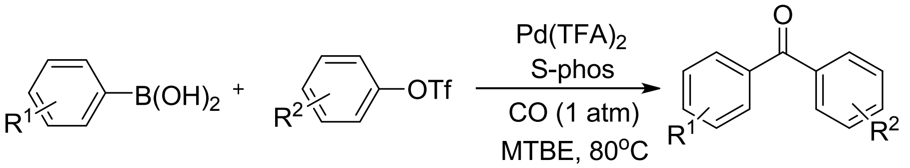
Typical procedure for the product

Typical procedure for carbonylative coupling with aryl tosylates



A mixture of arylboronic acids (0.6 mmol), aryl tosylates (0.5 mmol), Pd(TFA)$_2$ (5 mol%), and dppe (10 mol%) was stirred at 80°C for 6 h in DMA (1 mL) under CO (1 atm). Afterwards, 1 mL water was added to the reaction solution and then filtered through a filter paper and the solution was extracted by Et$_2$O (2 mL) for three times. The organic phase was combined and evaporated under reduced pressure. The residue was purified on a SiO$_2$ column to afford the desired product(ethyl acetate/hexane).

Typical procedure for carbonylative coupling with aryl triflates



A mixture of arylboronic acids (0.6 mmol), aryl triflates (0.5 mmol), Pd(TFA)$_2$ (5 mol%), and S-phos (10 mol%) was stirred at 80°C for 6 h in MTBE (1 mL) under CO (1 atm). Afterwards, the solution was filtered through a filter paper and the organic phase was evaporated under reduced pressure. The residue was purified on a SiO$_2$ column to afford the desired product(ethyl acetate/hexane).

Typical procedure for the synthesis of Oxybenzone with aryl tosylates

A mixture of 2,4-dimethoxy-phenylboronic acids (0.6 mmol), phenyl 4-methylbenzenesulfonate (0.5 mmol), Pd(TFA)$_2$ (5 mol%), and dppe (10 mol%) was stirred at 80°C for 6 h in DMA (1 mL) under CO (1 atm). Afterwards, 1 mL water was added to the reaction solution and then filtered through a filter paper and the solution was extracted by Et$_2$O (2 mL) for three times. The organic phase was combined and evaporated under reduced pressure. The residue was purified on a SiO$_2$ column to afford the coupling product (93%). The purificative product was then treated by the the solution of AlCl$_3$ (1 mmol) in CH$_2$Cl$_2$ (2 mL), and the mixture was stirred at room temperature for 12h. The reaction residue was then washed by HCl (1 mol/L), NaCl saturation and dried by anhydrous Na$_2$SO$_4$. The organic phase was combined and evaporated under reduced pressure, and the residue was purified on a SiO$_2$ column to afford Oxybenzone (87%).

Typical procedure for the synthesis of Oxybenzone with aryl triflates

A mixture of 2,4-dimethoxy-phenylboronic acids (0.6 mmol), phenyl trifluoromethanesulfonate (0.5 mmol), Pd(TFA)$_2$ (5 mol%), and S-phos (10 mol%) was stirred at 80°C for 6 h in MTBE (1 mL) under CO (1 atm). Afterwards, the solution was filtered through a filter paper and the organic phase was evaporated under reduced pressure. The residue was purified on a SiO_2 column to afford the desired product (95%). The purificative product was then treated by the the solution of $AlCl_3$ (1 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred at room temperature for 12h. The reaction residue was then washed by HCl (1 mol/L), NaCl saturation and dried by anhydrous Na_2SO_4. The organic phase was combined and evaporated under reduced pressure, and the residue was purified on a SiO_2 column to afford Oxybenzone (88%).

Typical procedure for the synthesis of Ketoprofen with aryl tosylates

A mixture of 2-(3-boronophenyl)propanoic acid (0.6 mmol), phenyl 4-methylbenzenesulfonate (0.5 mmol), $Pd(TFA)_2$ (5 mol%), and dppe (10 mol%) was stirred at 80^oC for 6 h in DMA (1 mL) under CO (1 atm). Afterwards, 1 mL water was added to the reaction solution and then filtered through a filter paper and the solution was extracted by Et_2O (2 mL) for three times. The organic phase was combined and evaporated under reduced pressure. The residue was purified on a SiO_2 column to afford Ketoprofen (83%).

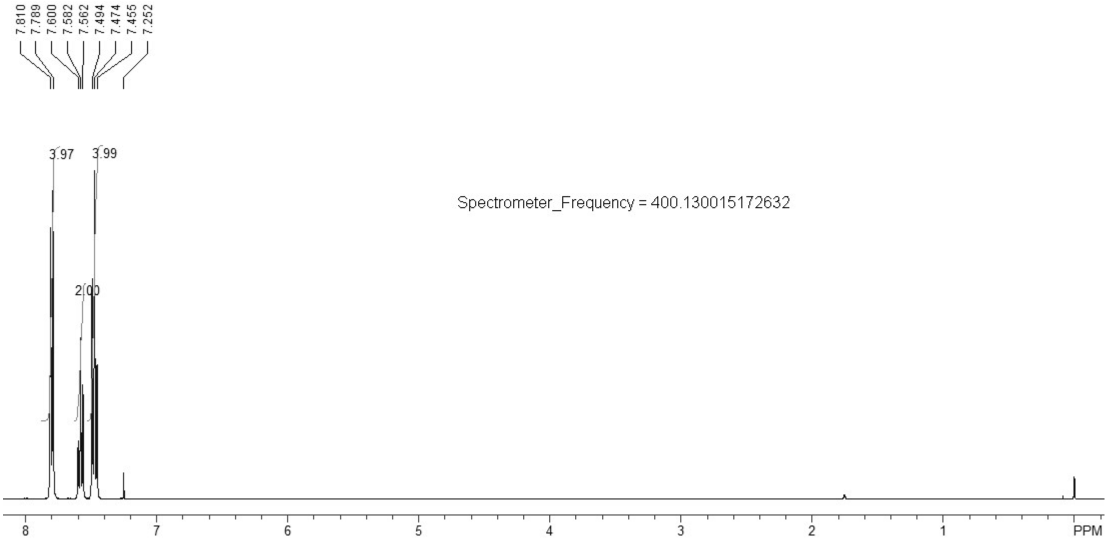
Typical procedure for the synthesis of Ketoprofen with aryl triflates

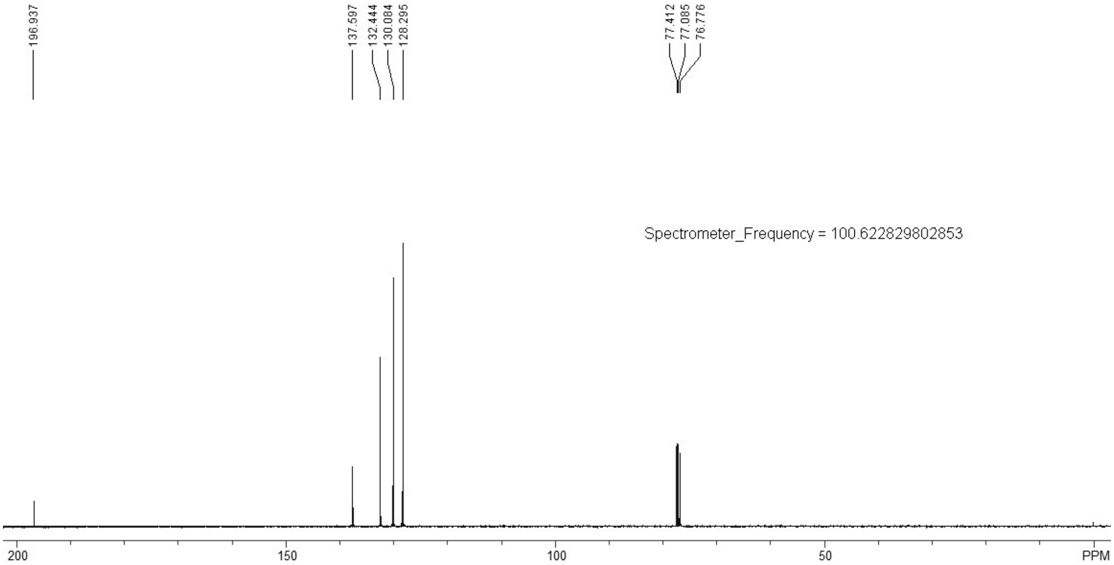
A mixture of 2-(3-boronophenyl)propanoic acid (0.6 mmol), phenyl trifluoromethanesulfonate (0.5 mmol), $Pd(TFA)_2$ (5 mol%), and S-phos (10 mol%) was stirred at 80^oC for 6 h in MTBE (1 mL) under CO (1 atm). Afterwards, the solution was filtered through a filter paper and the organic phase was evaporated under reduced pressure. The residue was purified on a SiO_2 column to afford Ketoprofen (86%).

Characterization data of the product

(1) benzophenone

m.p. 48.7-49.2 ^{o}C (lit.[2] mp 47–48 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, *J* = 8.0 Hz, 4 H), 7.59 (t, *J* = 8.0 Hz, 2 H), 7.46 (t, *J* = 7.6 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 137.7, 132.5, 130.2, 128.4. HRMS (EI) Calcd for $C_{13}H_{10}O$ (M^+) 182.0732, Found 182.0731.

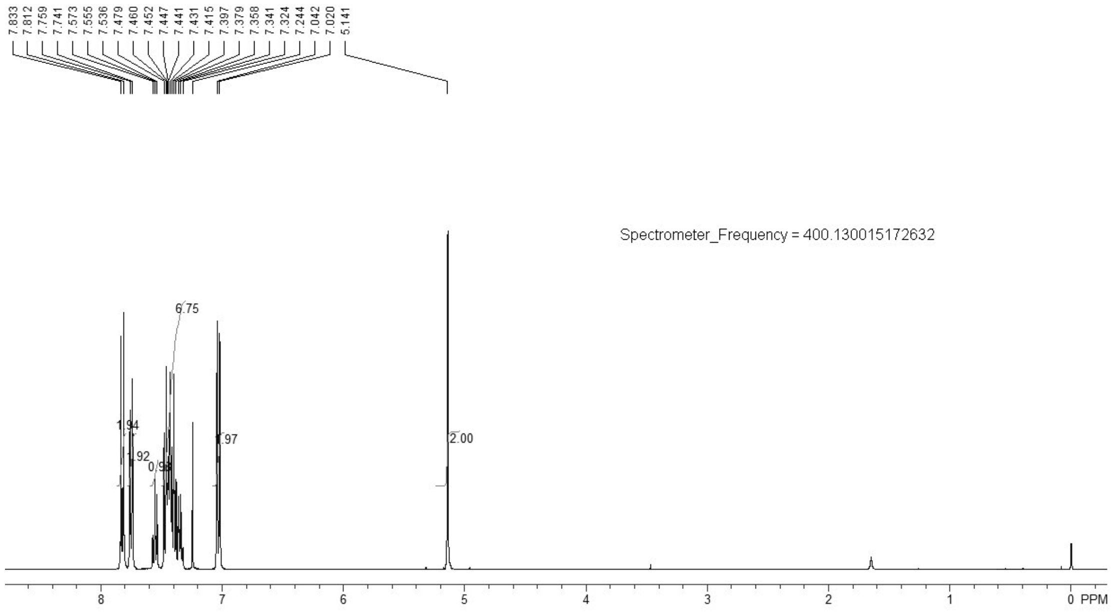


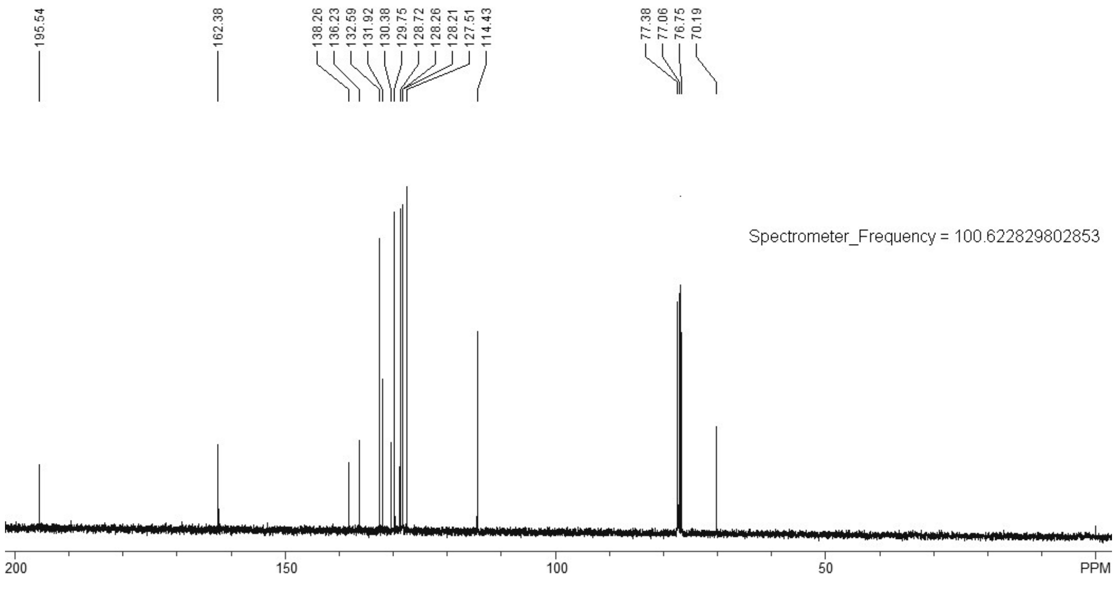


(2) 4-benzyloxy-benzophenone (T5-1)

m.p. 83.5–84.7 ^{o}C (lit.[1] mp 82–85 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.84 (d, *J* = 8.0

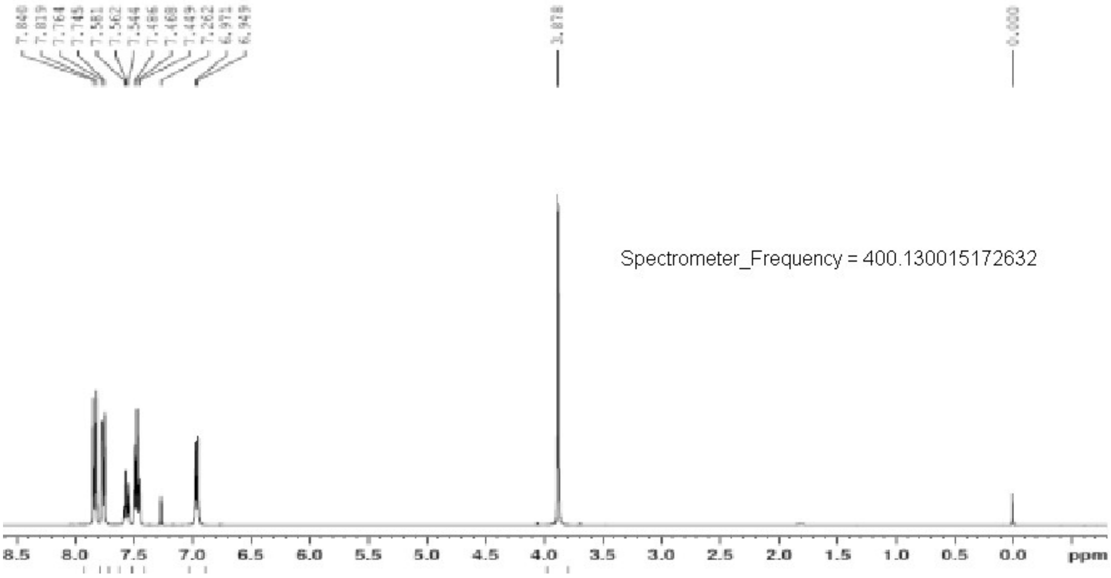
Hz, 2 H), 7.77 (t, J = 7.6 Hz, 2 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.32-7.47 (m, 7 H), 7.04 (d, J = 8.4 Hz, 2 H), 5.15 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 162.2, 138.1, 136.2, 132.4, 131.8, 130.4, 129.8, 128.7, 128.3, 128.2, 127.4, 114.3, 70.2. HRMS (EI) Calcd for $C_{20}H_{16}O_2$ (M^+) 288.1150, Found 288.1163.

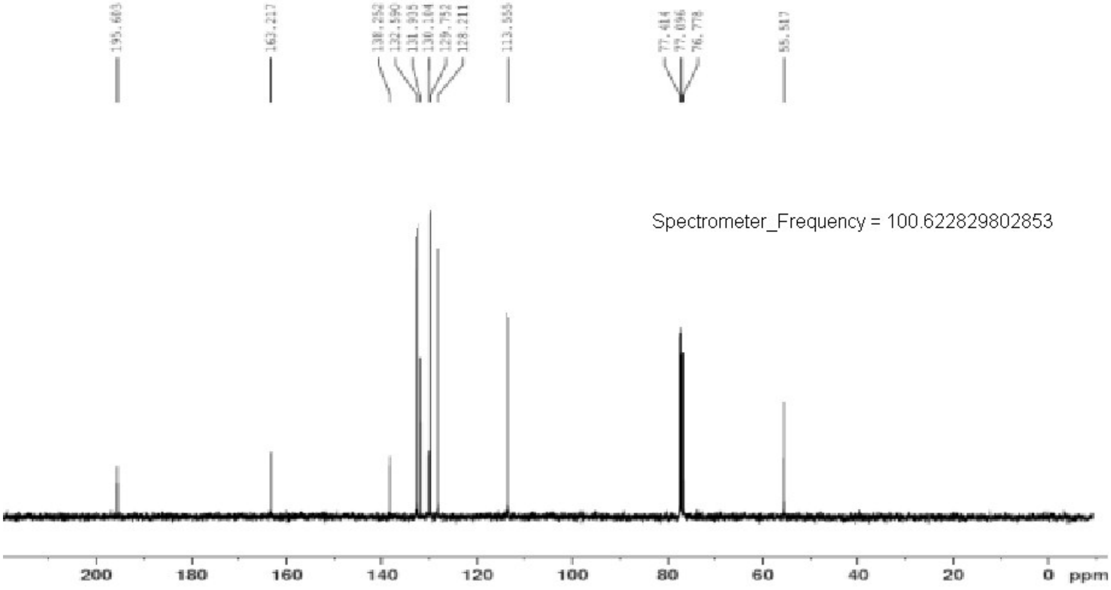




(3) 4-methoxy-benzophenone (T5-2)

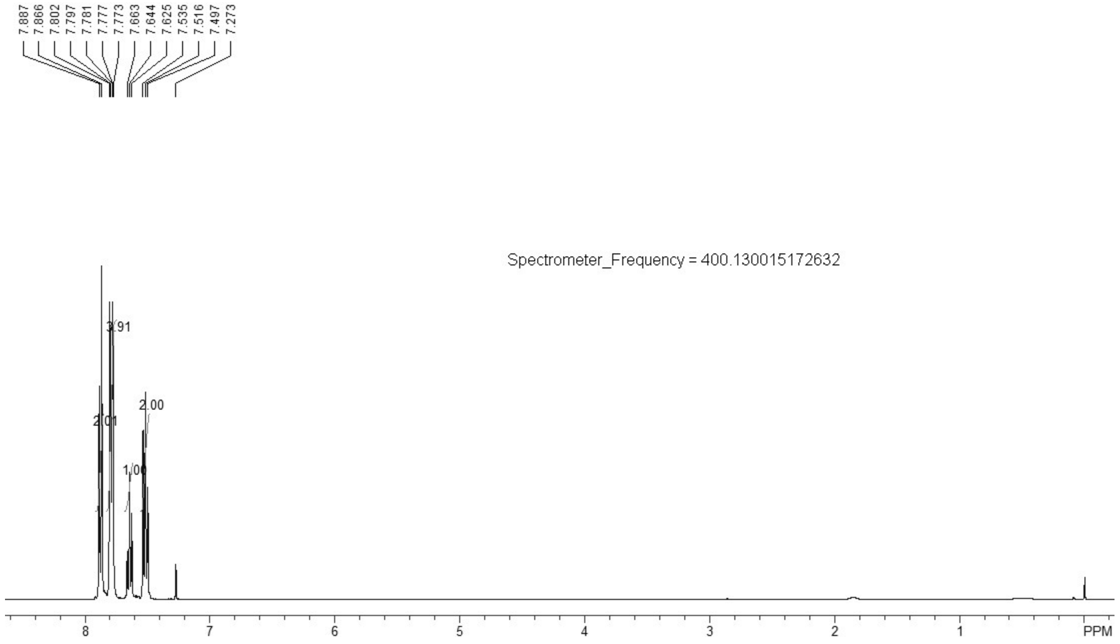
m.p. 132.2–133.7 °C (lit.[4] mp 133–134 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.83 (d, J = 8.4 Hz, 2 H), 7.74 (t, J = 8.0 Hz, 2 H), 7.57 (t, J = 7.6 Hz, 1 H), 7.45 (t, J = 7.6 Hz, 2 H), 6.97 (d, J = 8.4 Hz, 2 H), 3.87 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.5, 163.1, 138.3, 132.4, 131.9, 130.2, 129.7, 128.3, 113.4, 55.6. HRMS (EI) Calcd for $C_{14}H_{12}O_2$ (M^+) 212.0837, Found 212.0844.

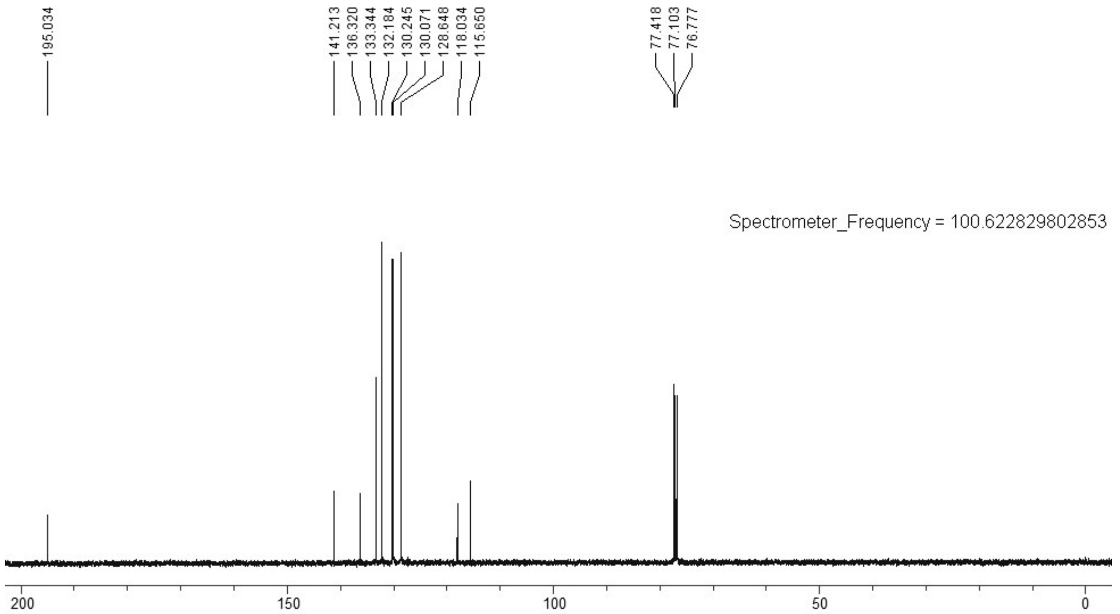




(4) 4-benzoylbenzonitrile (T5-3)

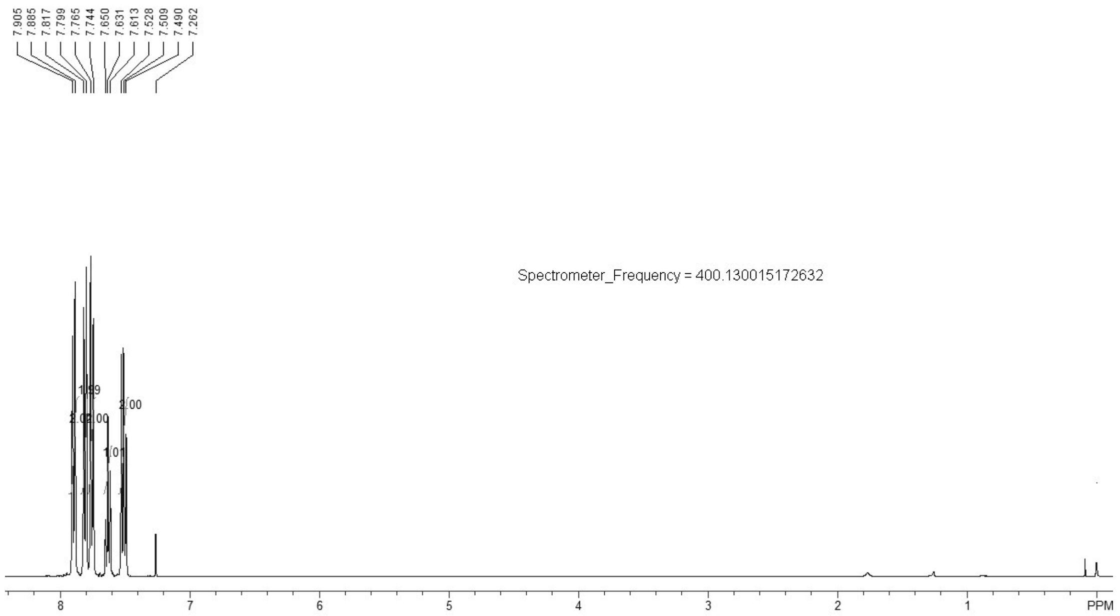
m.p. 113.2–114.4 ^{o}C (lit.^{2} mp 114–116 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.89 (t, *J* = 8.4 Hz, 2 H), 7.77-7.81 (m, 4 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.2, 141.3, 136.3, 133.4, 132.2, 130.4, 130.1, 128.7, 118.1, 115.7. HRMS (EI) Calcd for $C_{14}H_9NO$ (M^+) 207.0684, Found 207.0689.

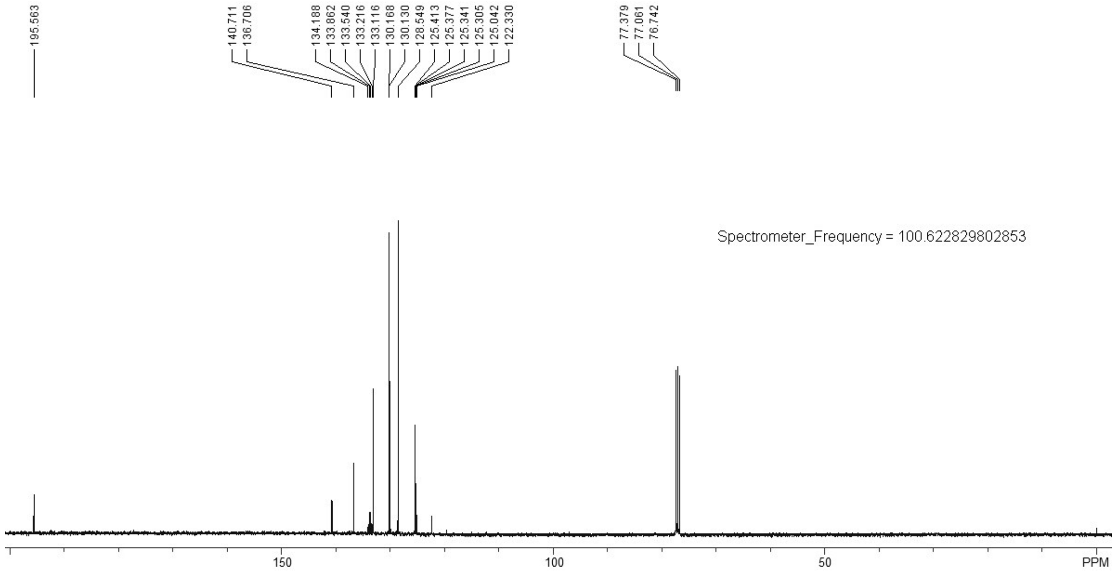




(5) 4-trifluoromethyl-benzophenone (T5-4)

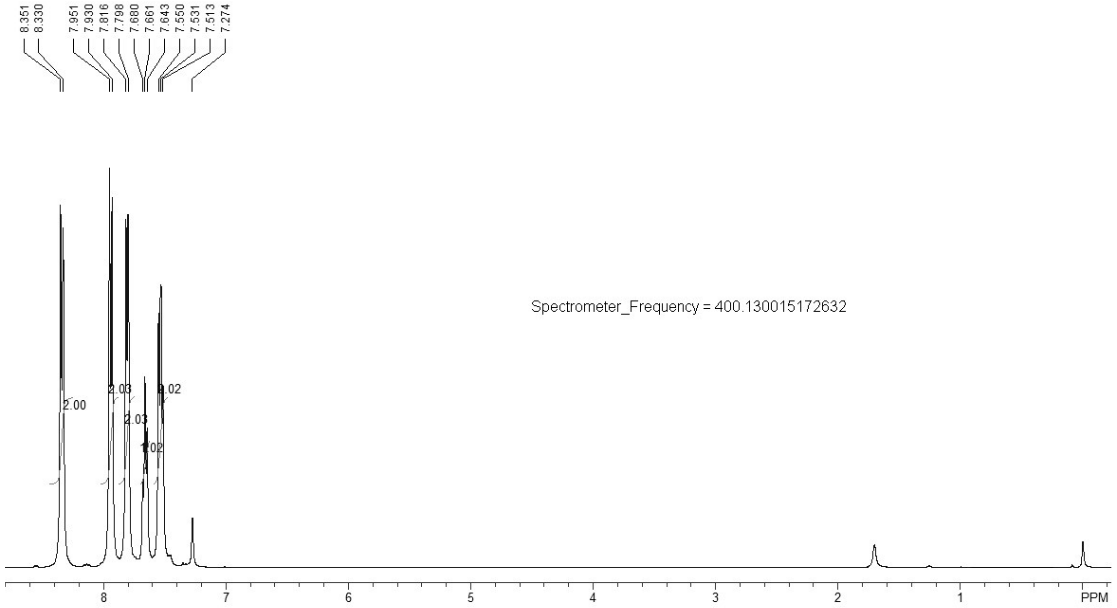
m.p. 117.3–118.9 ^{o}C (lit.[1] mp 116–117 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.91 (d, J = 8.0 Hz, 2 H), 7.82 (d, J = 7.6 Hz, 2 H), 7.76 (d, J = 8.0 Hz, 2 H), 7.62 (t, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.6, 140.8, 136.8, 133.7 (dd, J_1 = 64.2 Hz, J_2 = 32.2 Hz), 133.2, 130.2 (d, J = 3.9 Hz), 128.6, 125.4 (dd, J_1 = 7.2 Hz, J_2 = 3.6 Hz), 123.8 (d, J = 271.7 Hz). HRMS (EI) Calcd for $C_{14}H_9F_3O$ (M^+) 250.0605, Found 250.0613.

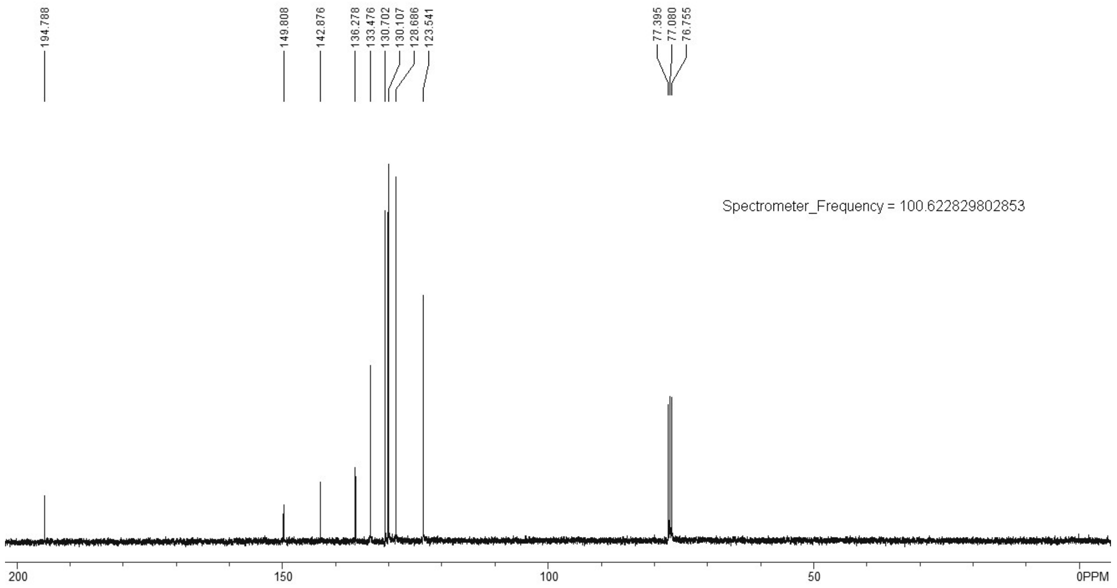




(6) 4-nitrobenzophenone (T5-5)

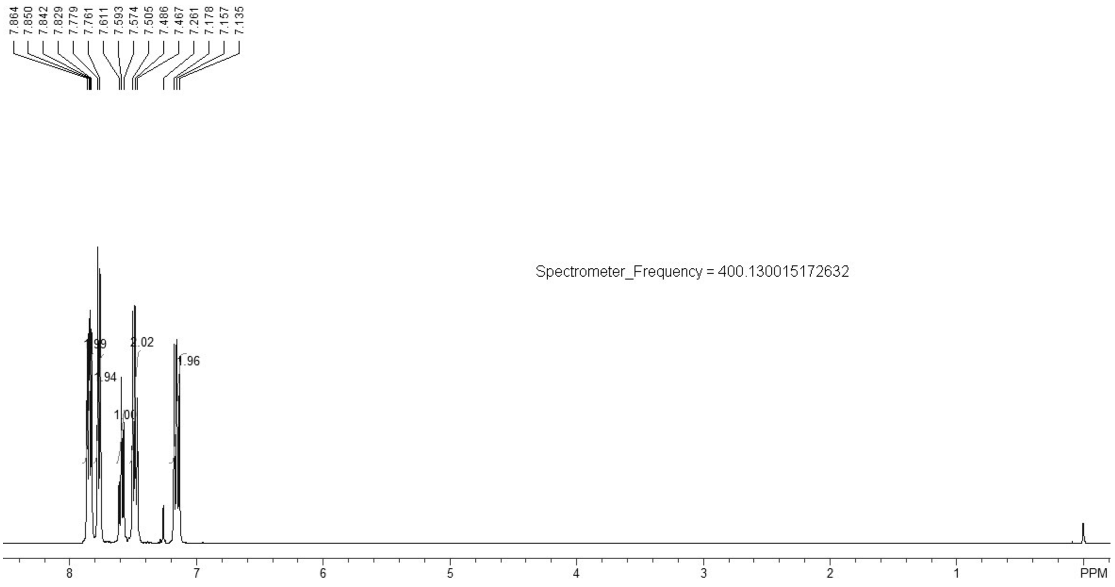
m.p. 139.5–141.6 ^{o}C (lit.[1] mp 140–142 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 8.35 (d, J = 7.6 Hz, 2 H), 7.94 (d, J = 7.6 Hz, 2 H), 7.82 (d, J = 7.6 Hz, 2 H), 7.65 (t, J = 7.6 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.8, 149.9, 142.9, 136.3, 133.5, 130.8, 130.2, 128.7, 123.6. HRMS (EI) Calcd for $C_{13}H_9NO_3$ (M$^+$) 227.0582, Found 227.0580.

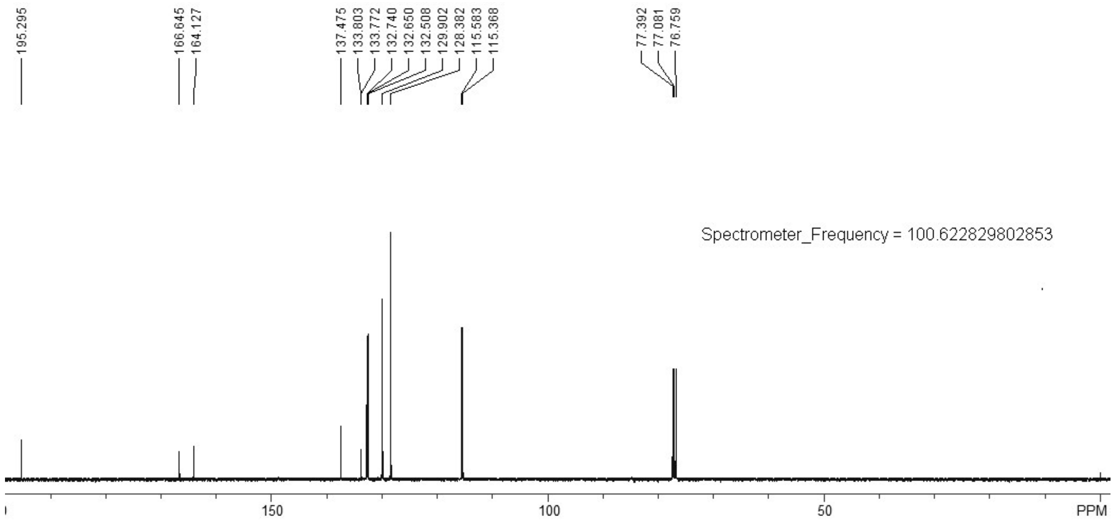




(7) 4-fluorobenzophenone (T5-6)

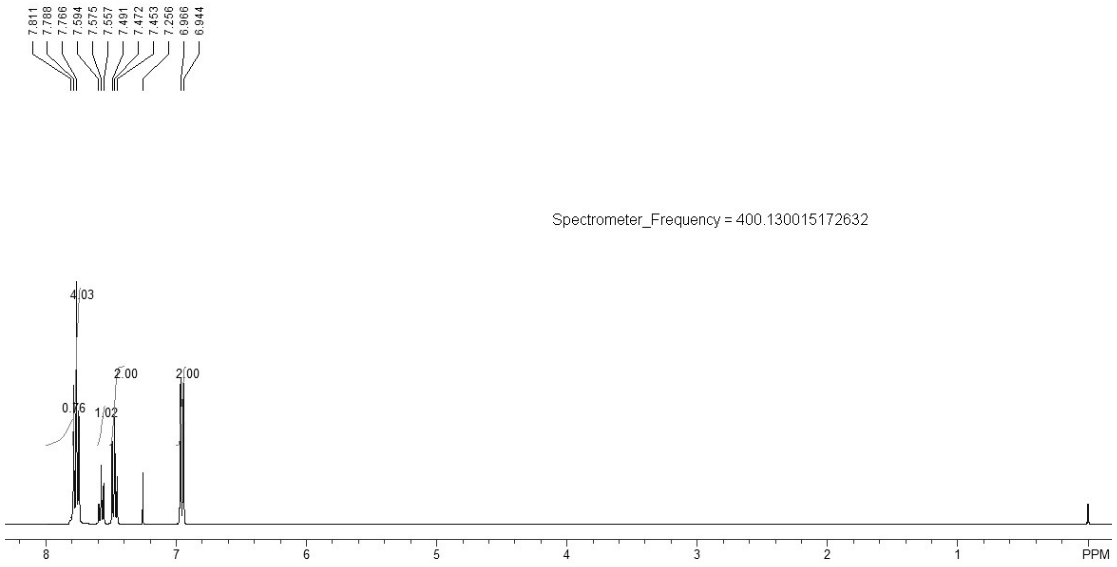
m.p. 43.4–44.8 °C (lit.[3] mp 45–47 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (dd, J_1 = 8.2 Hz, J_2 = 5.2 Hz, 2 H), 7.76 (d, J = 7.6 Hz, 2 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.17 (t, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 166.7 (d, J = 248 Hz), 137.5, 133.8, 132.8(d, J = 9.2 Hz), 132.6, 129.9, 128.4, 115.6 (d, J = 20 Hz). HRMS (EI) Calcd for $C_{13}H_9FO$ (M^+) 200.0637, Found 200.0630.

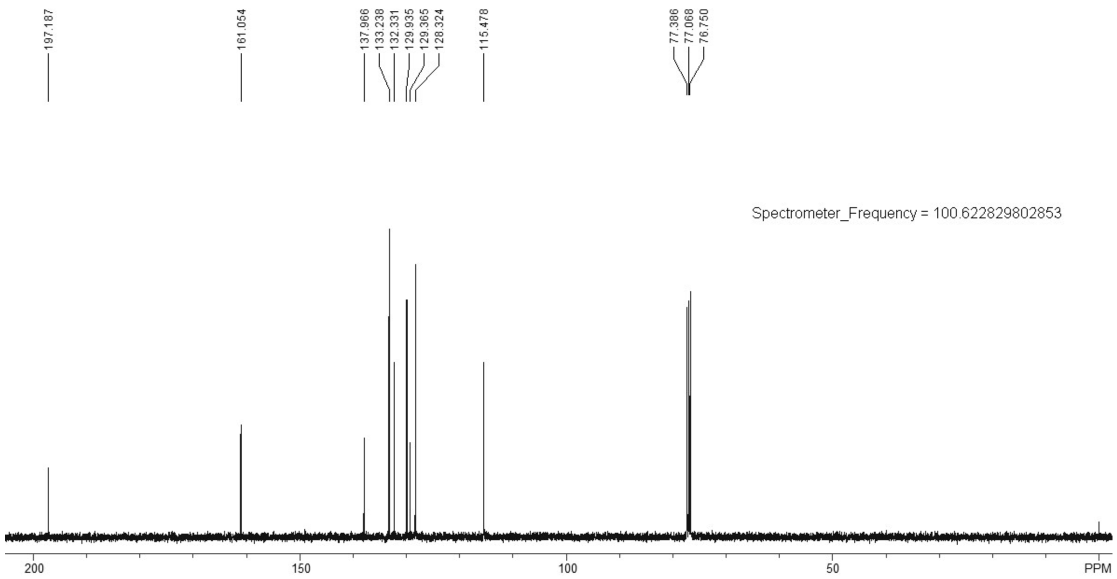




(8) 4-chloro-benzophenone (T5-7)

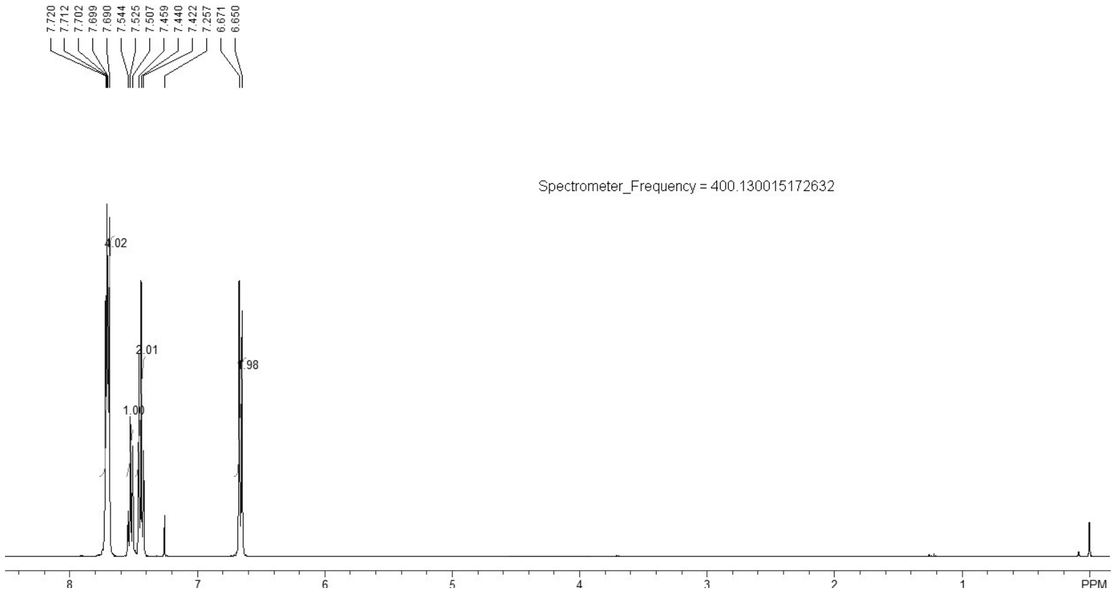
m.p. 73.7–74.6 °C (lit.[2] mp 74–75 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.78 (d, J = 8.4 Hz, 4 H), 7.59 (t, J = 7.6 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 6.95 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 161.1, 137.9, 133.4, 132.3, 129.9, 129.4, 128.4, 115.5. HRMS (EI) Calcd for $C_{13}H_9ClO$ (M^+) 216.0342, Found 216.0349.

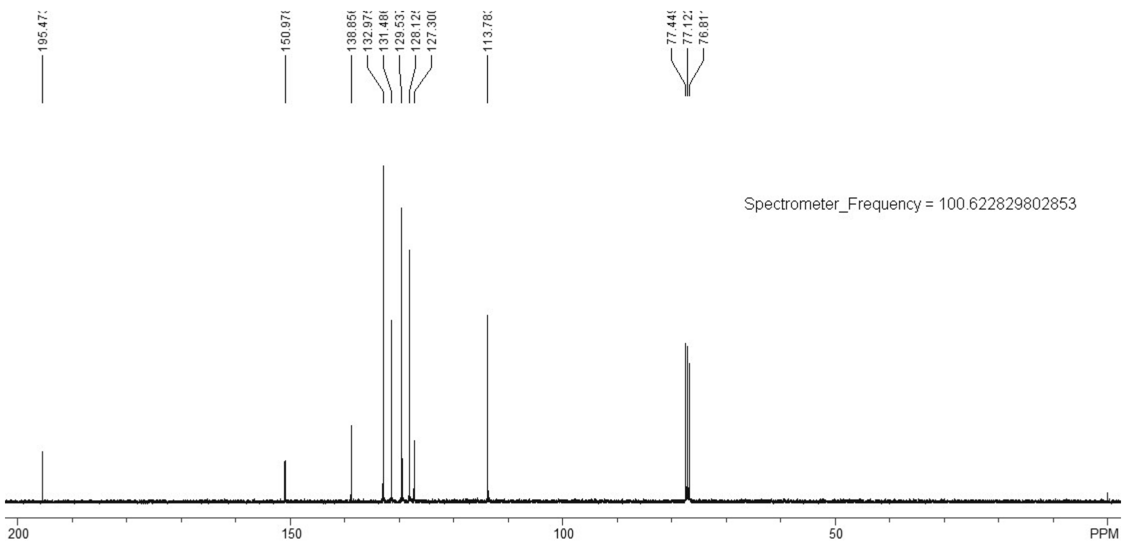




(9) 4-bromobenzophenone (T5-8)

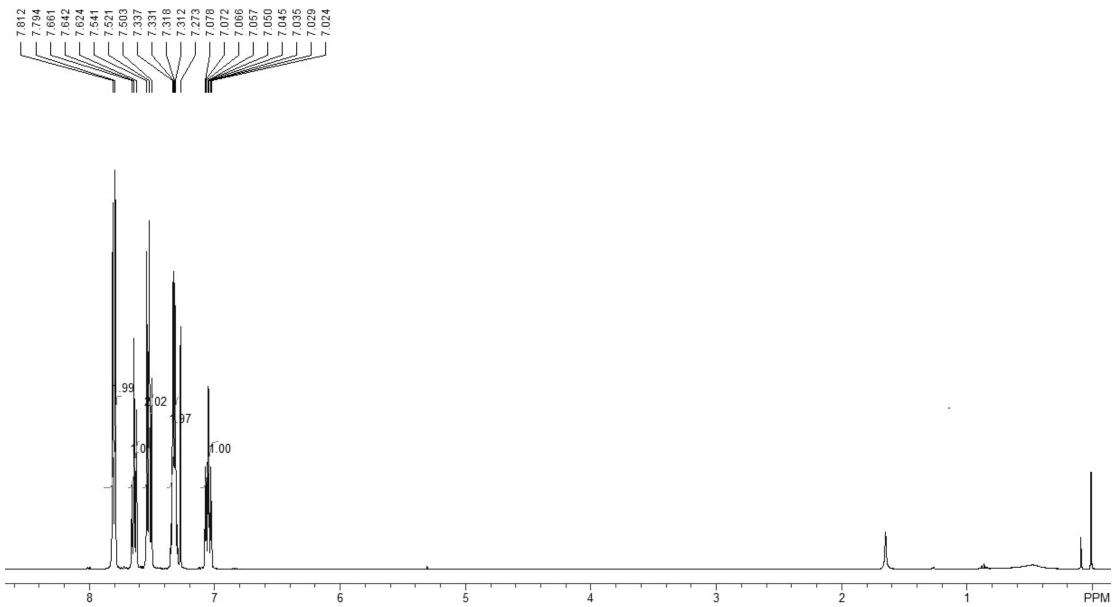
m.p. 80.1–81.4 ^{o}C (lit.[4] mp 81–83 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.69-7.73 (m, 4 H), 7.54 (t, J = 7.2 Hz, 1 H), 7.43 (t, J = 7.2 Hz, 2 H), 6.66 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.5, 151.0, 138.9, 132.9, 131.5, 129.6, 128.2, 127.4, 112.8. HRMS (EI) Calcd for $C_{13}H_9BrO$ (M$^+$) 259.9837, Found 259.9831.

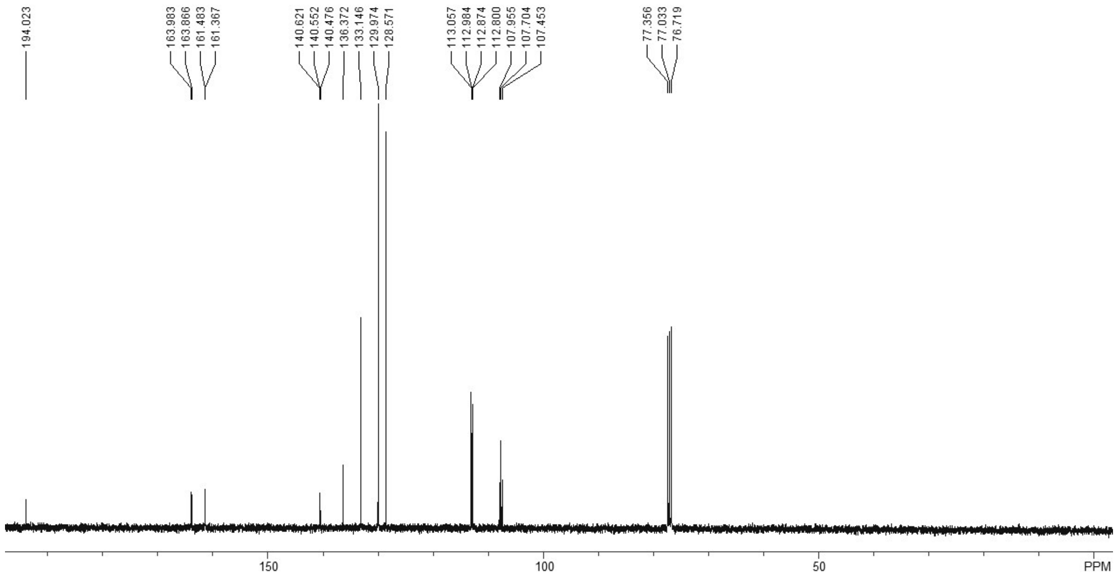




(10) 3,5-difluorobenzophenone (T5-9)

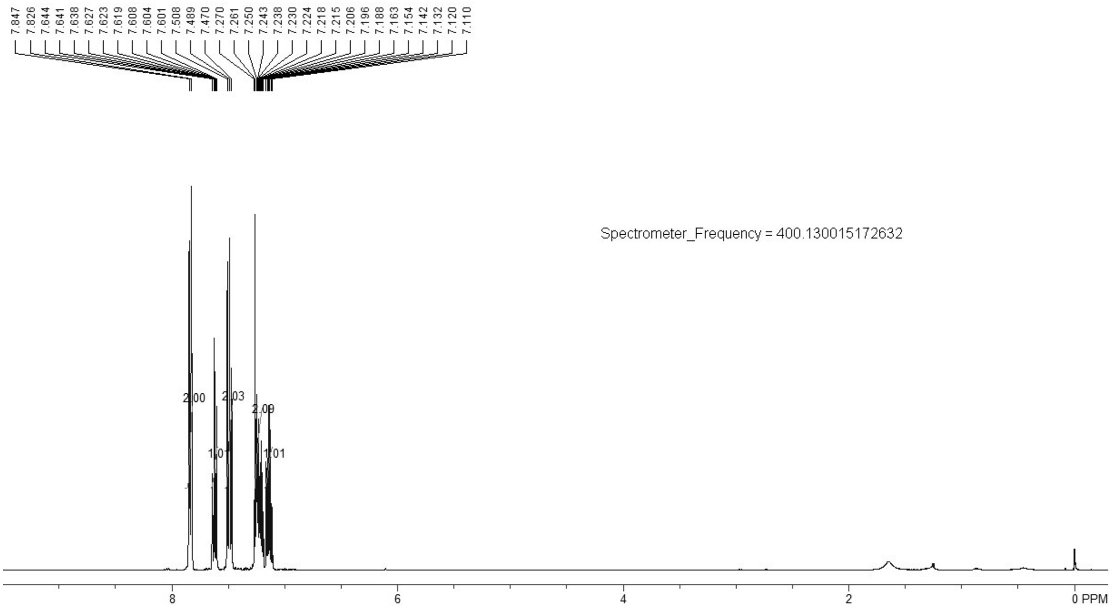
m.p. 58.8–59.7 ^{o}C (lit.[3] mp 57–59 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, J = 7.2 Hz, 2 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H), 7.32 (dd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 2 H), 7.05 (tt, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.02, 163.92 (dd, J_1 = 250 Hz, J_2 = 11.7 Hz), 140.55 (t, J = 7.2 Hz), 136.37, 133.15, 129.97, 128.57, 112.93 (dd, J_1 = 18.3 Hz, J_2 = 7.3 Hz), 107.70 (t, J = 25.1 Hz). HRMS (EI) Calcd for $C_{13}H_8F_2O$ (M^+) 218.0543, Found 218.0547.

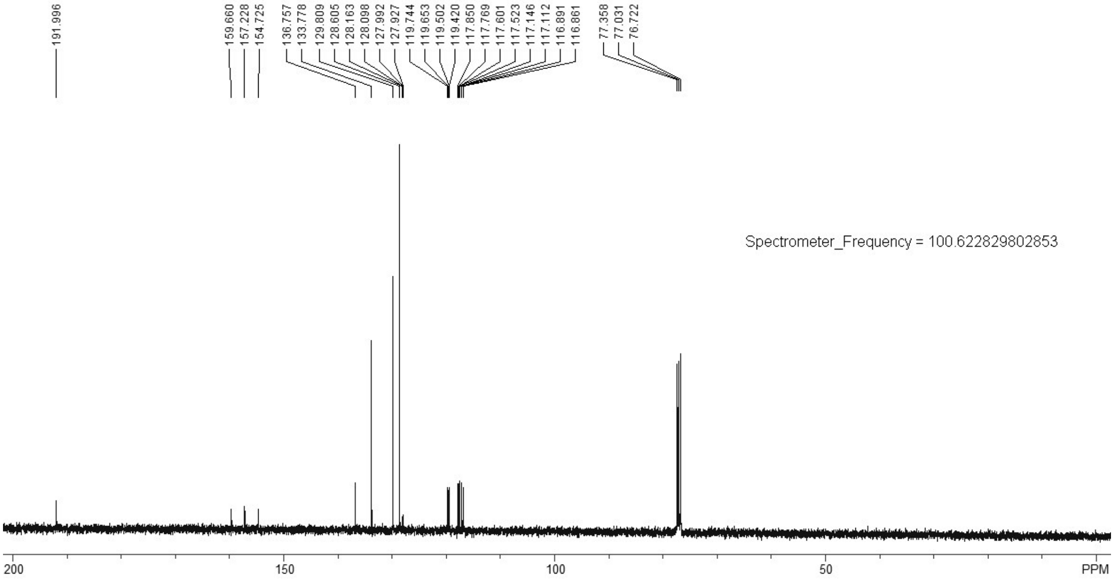




(11) 2,5-difluorobenzophenone (T5-10)

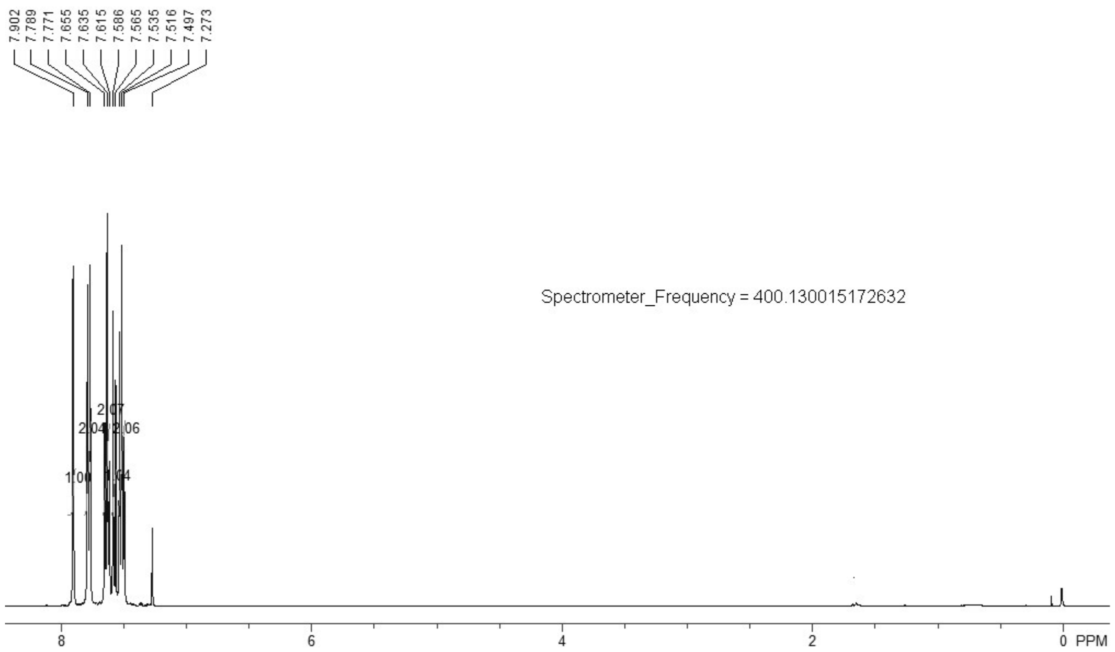
m.p. 87.1–88.6 ^{o}C (lit.[3] mp 87–89 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83 (d, J = 8.4 Hz, 2 H), 7.63 (tt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1 H), 7.49 (d, J = 7.6 Hz, 2 H), 7.19-7.28 (m, 2 H), 7.10-7.16 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 159.7, 157.3 (d, J = 253 Hz), 136.8, 133.8, 129.9, 128.7, 128.2 (dd, J_1 = 16.8 Hz, J_2 = 6.4 Hz), 119.6 (dd, J_1 = 23.2 Hz, J_2 = 8.6 Hz), 117.7 (dd, J_1 = 24.0 Hz, J_2 = 8.0 Hz), 117.1 (dd, J_1 = 18.2 Hz, J_2 = 7.2 Hz), 112.9 (dd, J_1 = 25.2 Hz, J_2 = 3.2 Hz). HRMS (EI) Calcd for $C_{13}H_8F_2O$ (M^+) 218.0543, Found 218.0534.

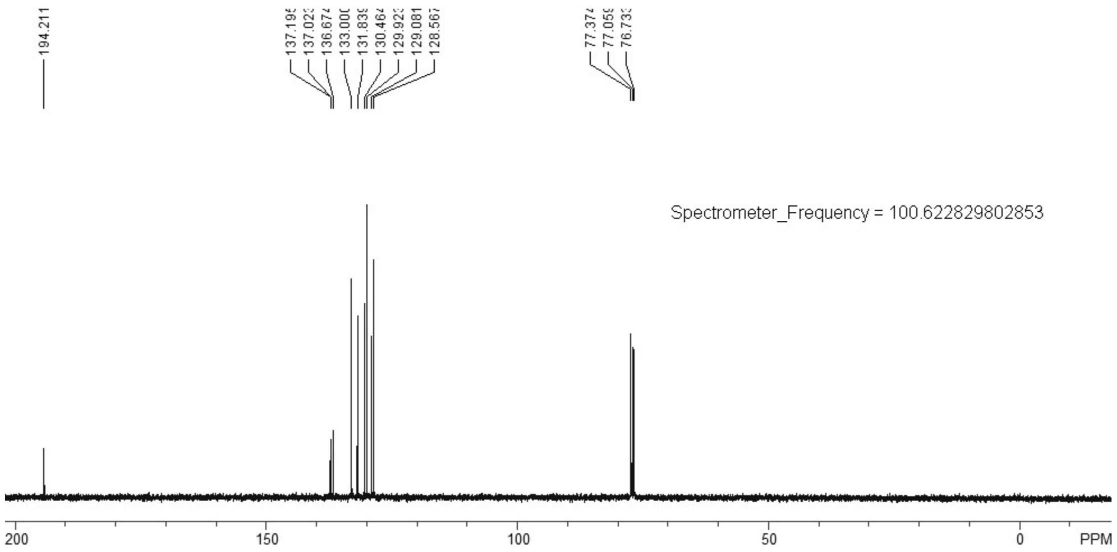




(12) 3,4-dichlorobenzophenone (T5-11)

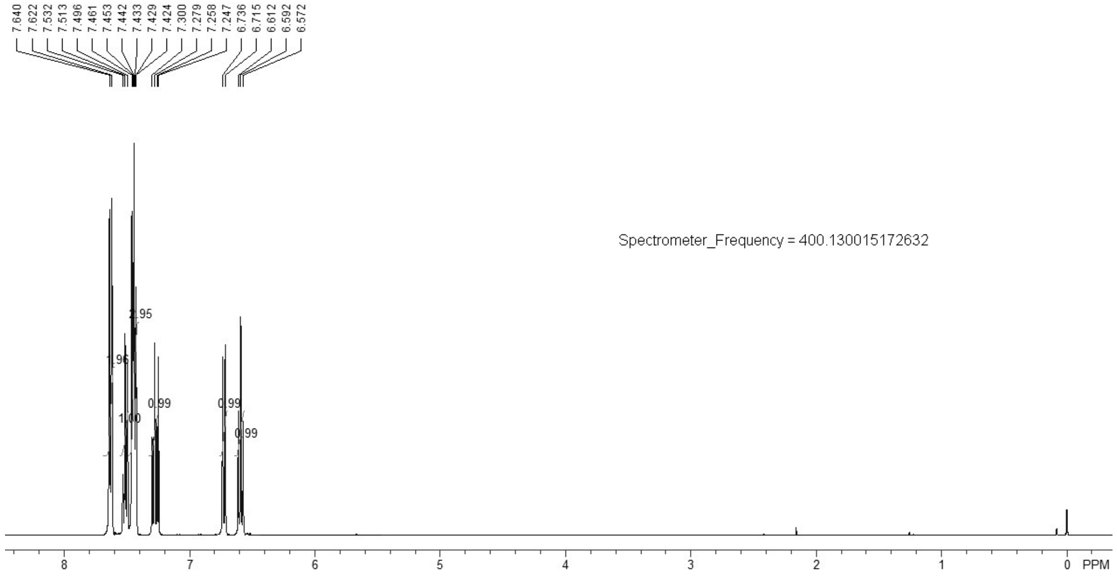
m.p. 100.8–102.2 ^{o}C (lit.^{4} mp 102–103 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.91 (s, 1 H), 7.77 (d, J = 7.6 Hz, 2 H), 7.64 (t, J = 8.0 Hz, 2 H), 7.59 (d, J = 8.4 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 137.3, 137.1, 136.7, 133.1, 131.9, 130.5, 129.9, 129.1, 128.6. HRMS (EI) Calcd for $C_{13}H_8Cl_2O$ (M^+) 249.9952, Found 249.9958.

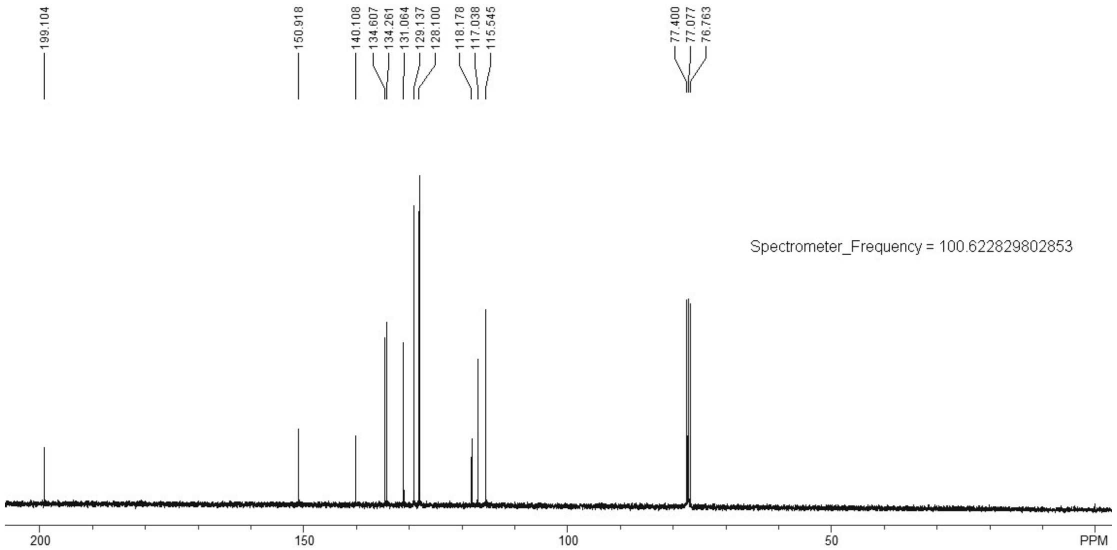




(13) 2-bromo-benzophenone (T5-12)

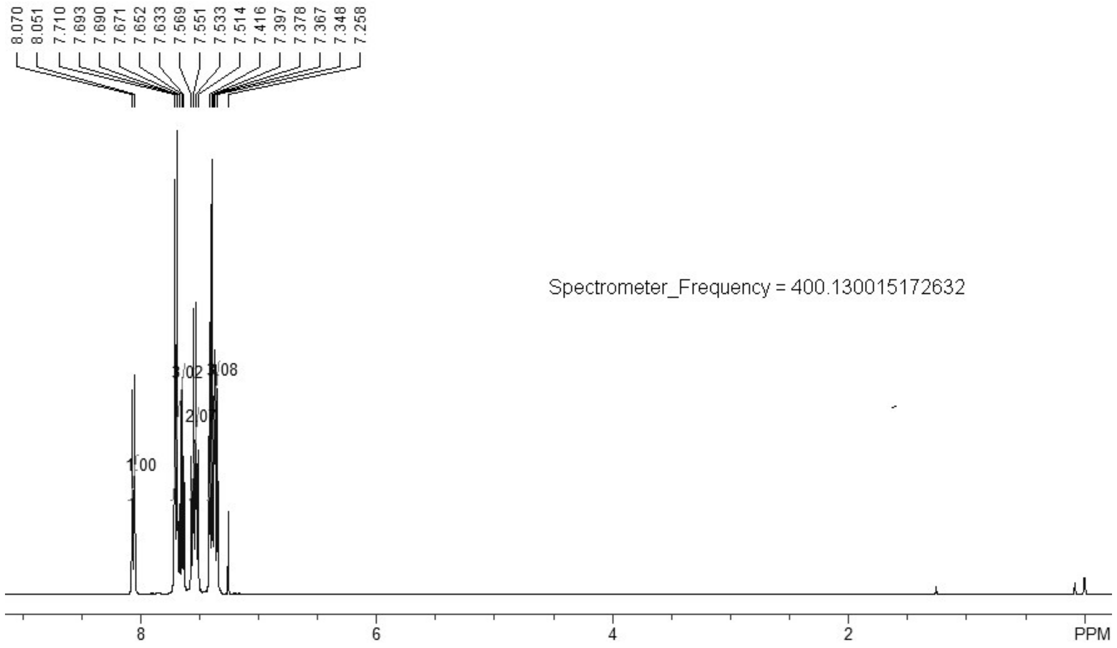
m.p. 42.9–44.3 °C (lit. mp 42 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, J = 7.2 Hz, 2 H), 7.51 (t, J = 7.2 Hz, 1 H), 7.42-7.46 (m, 3 H), 7.28 (t, J = 8.4 Hz, 1 H), 6.72 (d, J = 8.4 Hz, 1 H), 6.59 (t, J = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 150.9, 140.2, 134.7, 134.3, 131.1, 129.2, 128.2, 118.2, 117.1, 115.6. HRMS (EI) Calcd for $C_{13}H_9BrO$ (M^+) 259.9837, Found 259.9839.

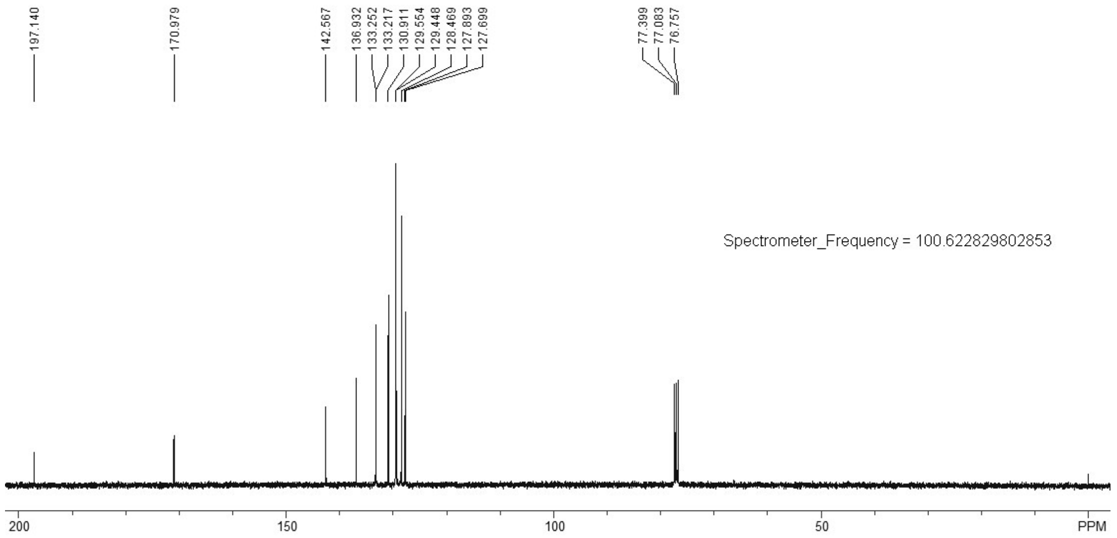




(14) 2-benzoylbenzonitrile (T5-13)

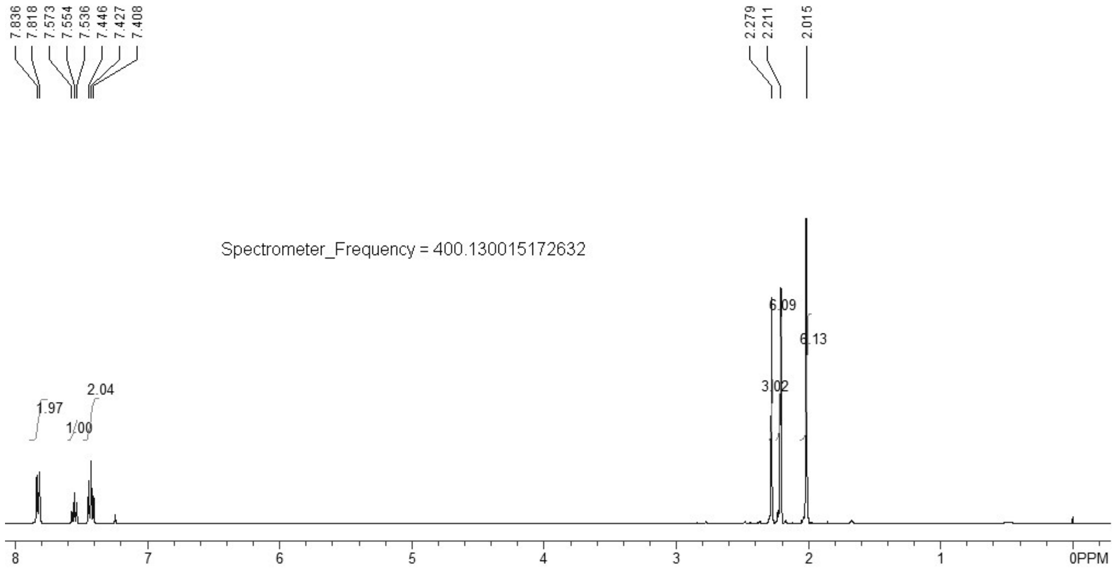
m.p. 82.5–84.4 ^{o}C (lit. mp 83–84 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ8.06 (d, *J* = 7.6 Hz, 1 H), 7.63-7.72 (m, 3 H), 7.54 (dd, J_1 = 14.0 Hz, J_2 = 7.2 Hz, 2 H), 7.34-7.42 (m, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.2, 170.9, 142.6, 136.9, 133.3, 133.2, 130.9, 129.6, 129.5, 128.5, 127.9, 127.8. HRMS (EI) Calcd for $C_{14}H_9NO$ (M^+) 226.0684, Found 226.0680.

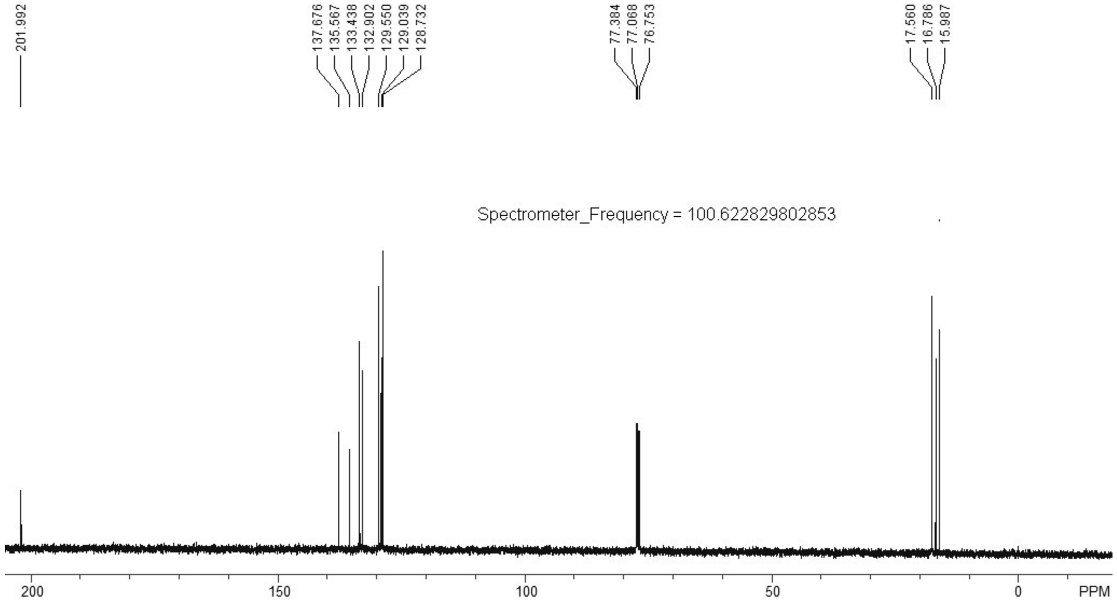




(15) 2,3,4,5,6-pentamethyl-benzophenone (T5-14)

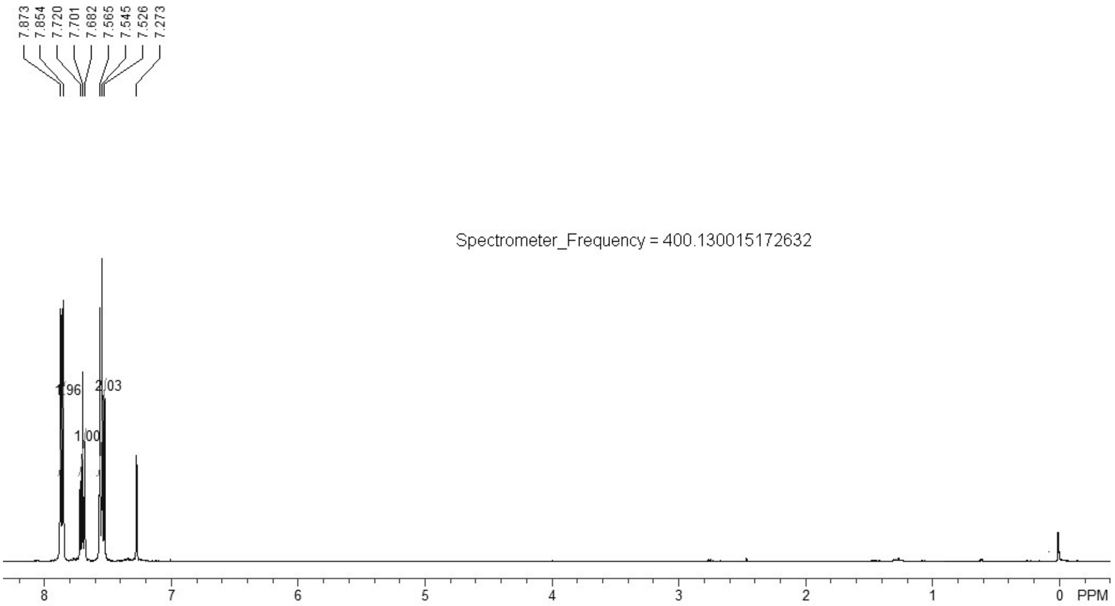
m.p. 134.2–135.6 ^{o}C (lit.[7] mp 135–136 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83 (d, *J* = 7.2 Hz, 2 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 2.27 (s, 3 H), 2.22 (s, 6 H), 2.02 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 137.7, 135.6, 133.5, 132.9, 129.6, 129.1, 128.8, 17.6, 16.7, 15.8. HRMS (EI) Calcd for $C_{18}H_{20}O$ (M^+) 252.1514, Found 252.1508.

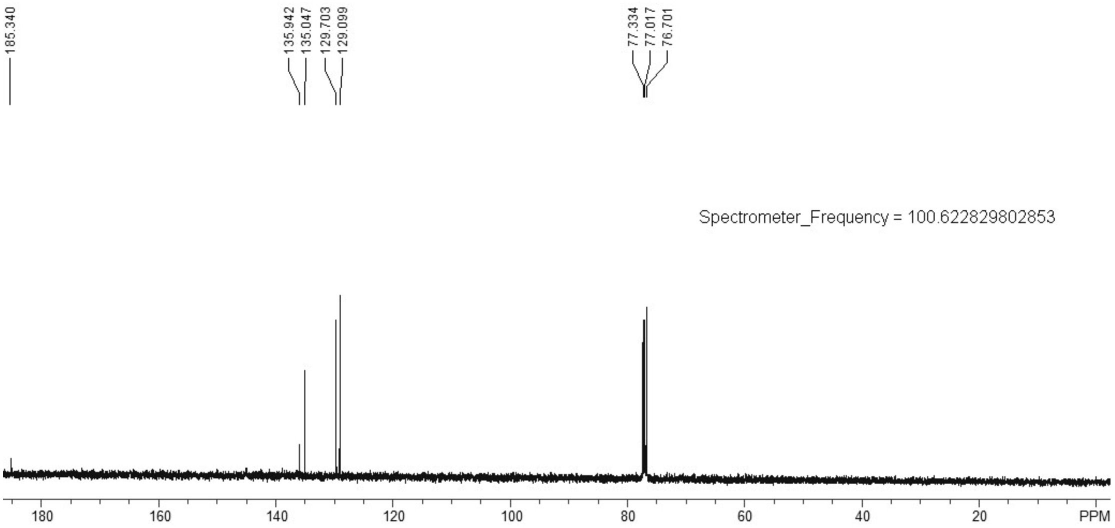




(16) 2,3,4,5,6-perfluoro-benzophenone (T5-15)

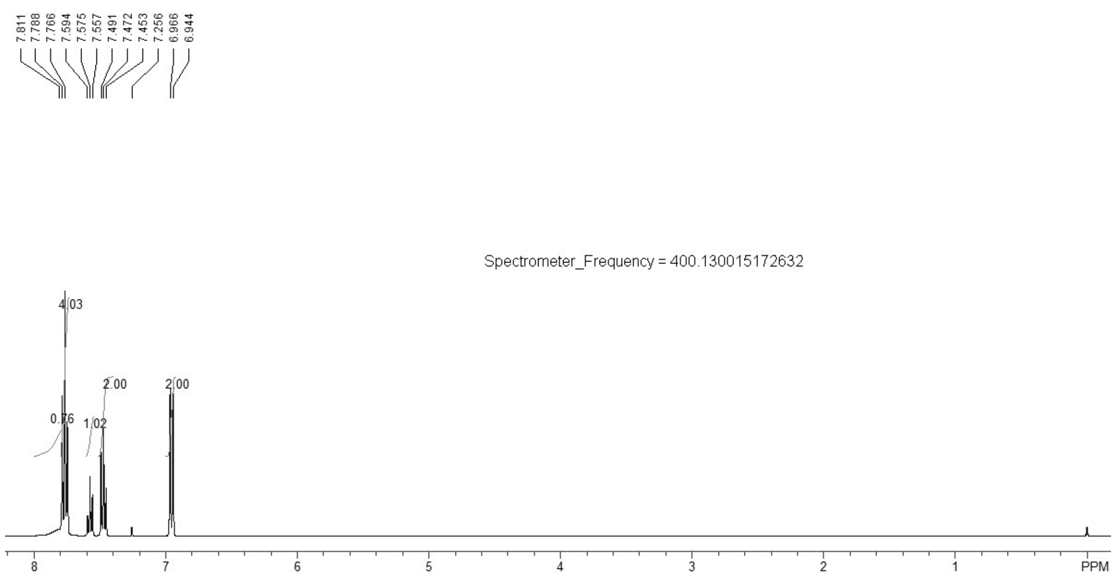
m.p. 34.4–36.1 ^{o}C (lit.[8] mp 33–34 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.87 (d, *J* = 7.6 Hz, 2 H), 7.71 (t, *J* = 7.6 Hz, 1 H), 7.56 (t, *J* = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 135.9, 135.1, 129.8, 129.2. HRMS (EI) Calcd for $C_{13}H_5F_5O$ (M^+) 272.0261, Found 272.0263.

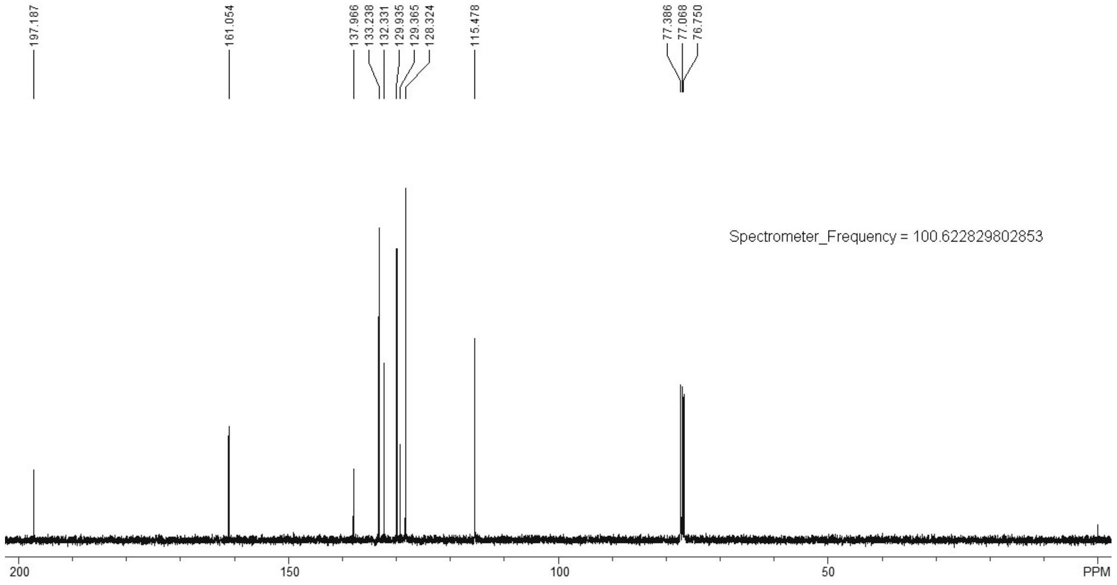




(17) 4-benzoylpyridine (T5-16)

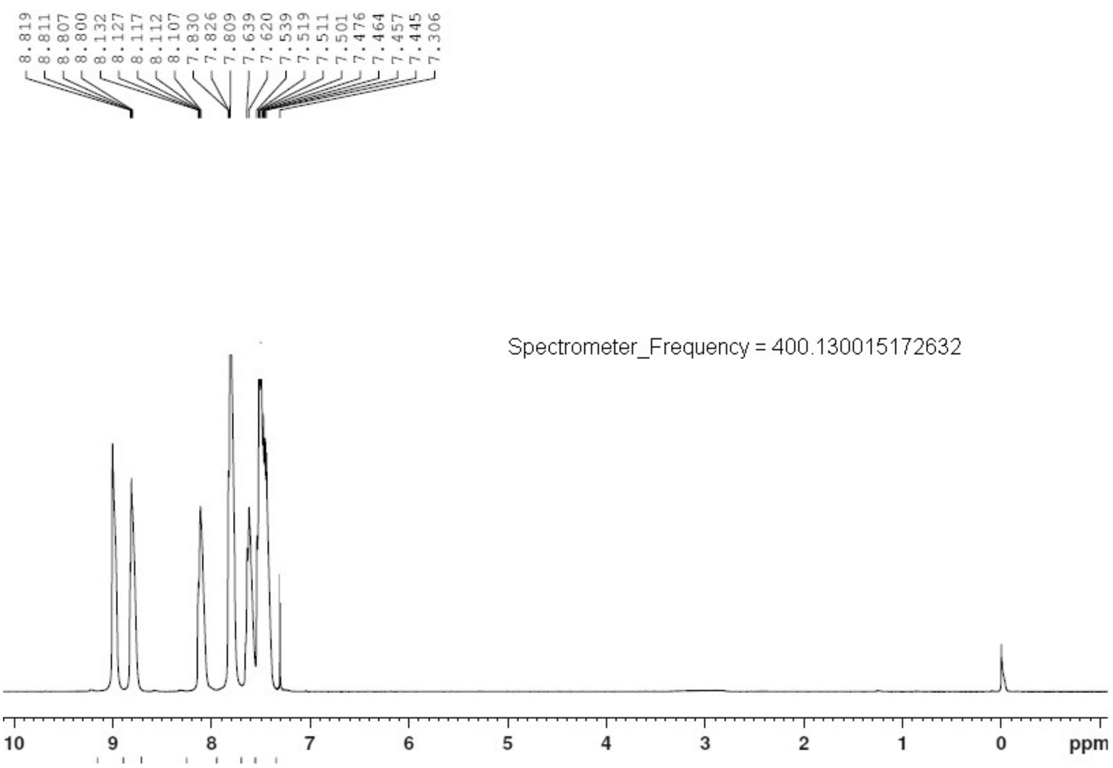
m.p. 71.2–72.7 ^{o}C (lit.[9] mp 71–72 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.78 (d, J = 8.4 Hz, 4 H), 7.57 (t, J = 7.6 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 6.88 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 161.0, 137.9, 133.2, 132.3, 129.9, 129.3, 128.3, 115.5. HRMS (EI) Calcd for $C_{12}H_9NO$ (M^+) 183.0684, Found 183.0682.

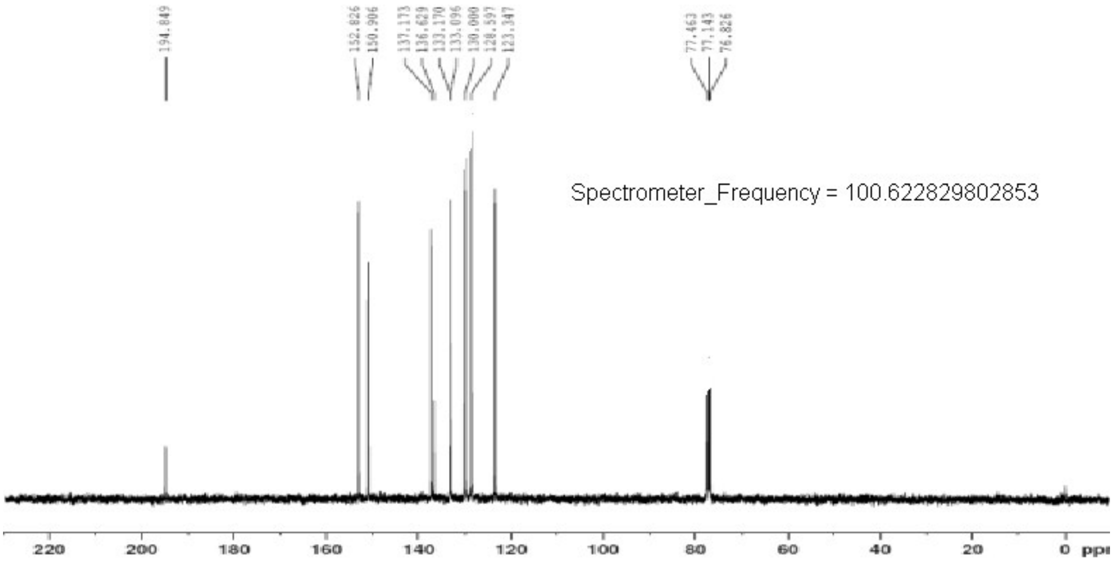




(18) 3-Benzoylpyridine (T5-17)

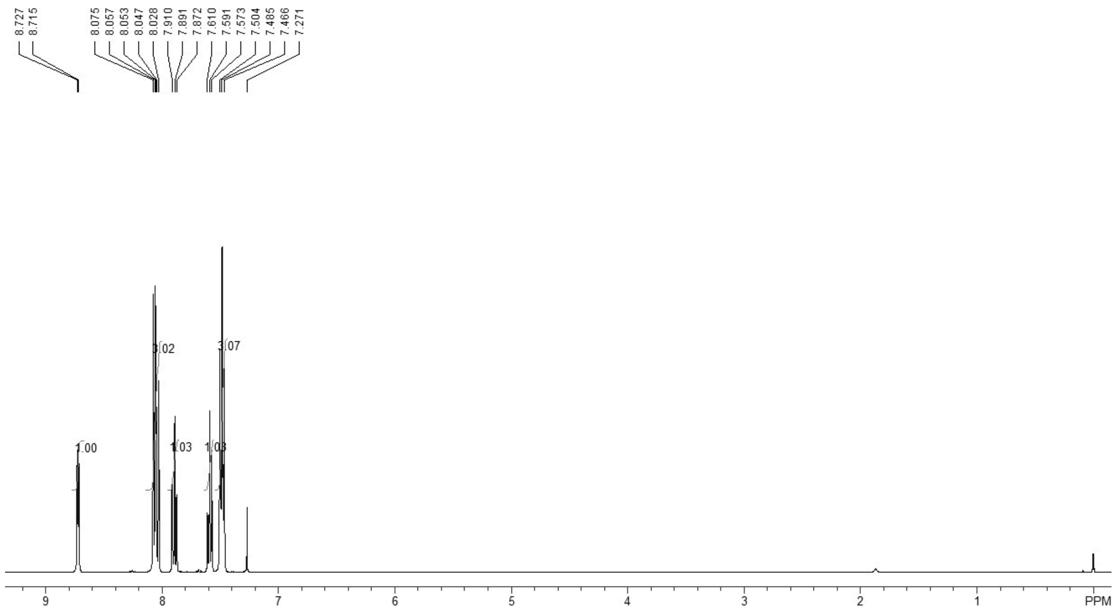
m.p. 37.2–38.3 ^{o}C (lit.[11] mp 38-40 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.98 (s, 1 H), 8.80 (d, J = 5.2 Hz, 1 H), 8.12 (d, J = 8.0 Hz, 1 H), 7.44-7.81 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 152.8, 150.8, 137.1, 136.5, 133.1, 133.0, 130.0, 128.5, 123.2. HRMS (EI) Calcd for $C_{12}H_9NO$ (M^+) 183.0684, Found 183.0681.

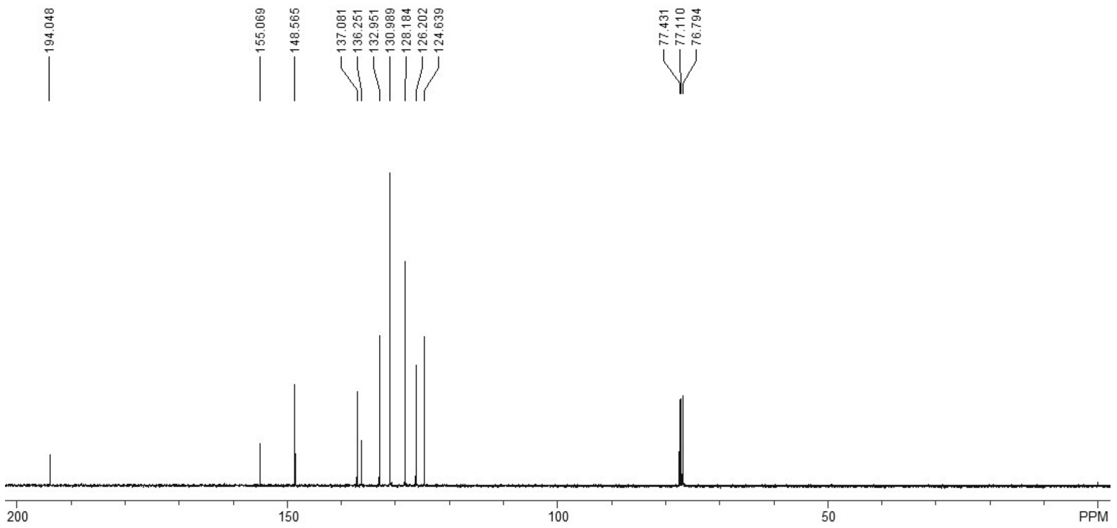




(19) 2-benzoylpyridine (T5-18)

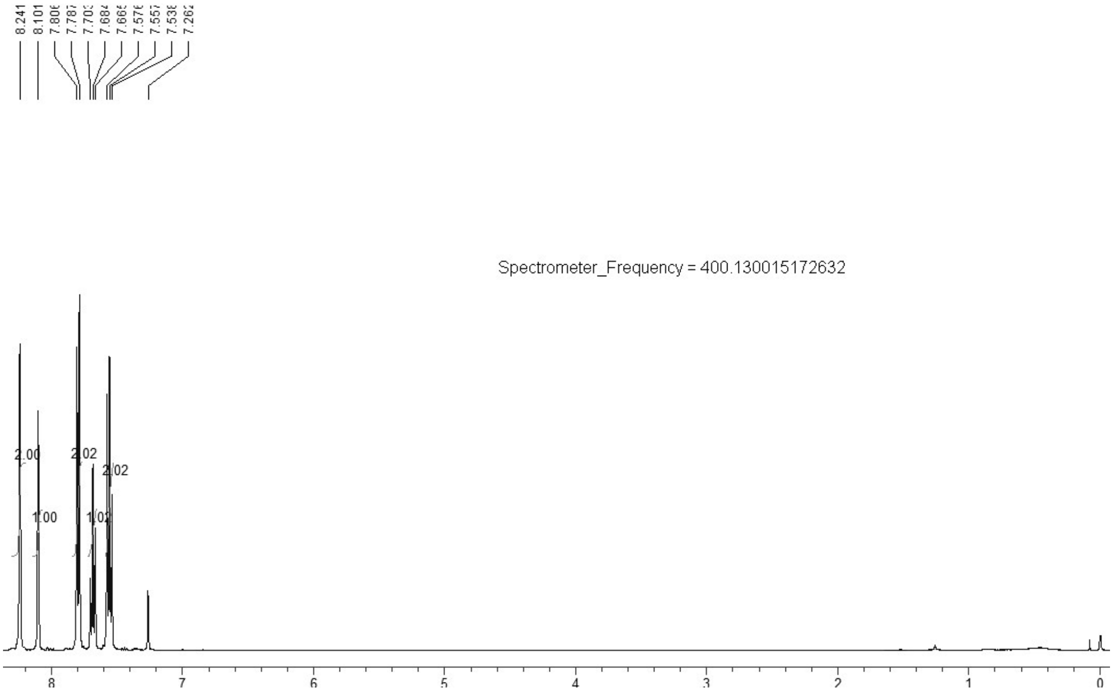
m.p. 40.4–41.9 ^{o}C (lit.[9] mp 42 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.72 (d, J = 4.8 Hz, 1 H), 8.03-8.08 (m, 3 H), 7.89 (t, J = 7.6 Hz, 1 H), 7.59 (d, J = 7.6 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.05, 155.07, 148.57, 137.08, 136.25, 132.95, 130.99, 128.18, 126.20, 124.64. HRMS (EI) Calcd for $C_{12}H_9NO$ (M^+) 183.0684, Found 183.0689.

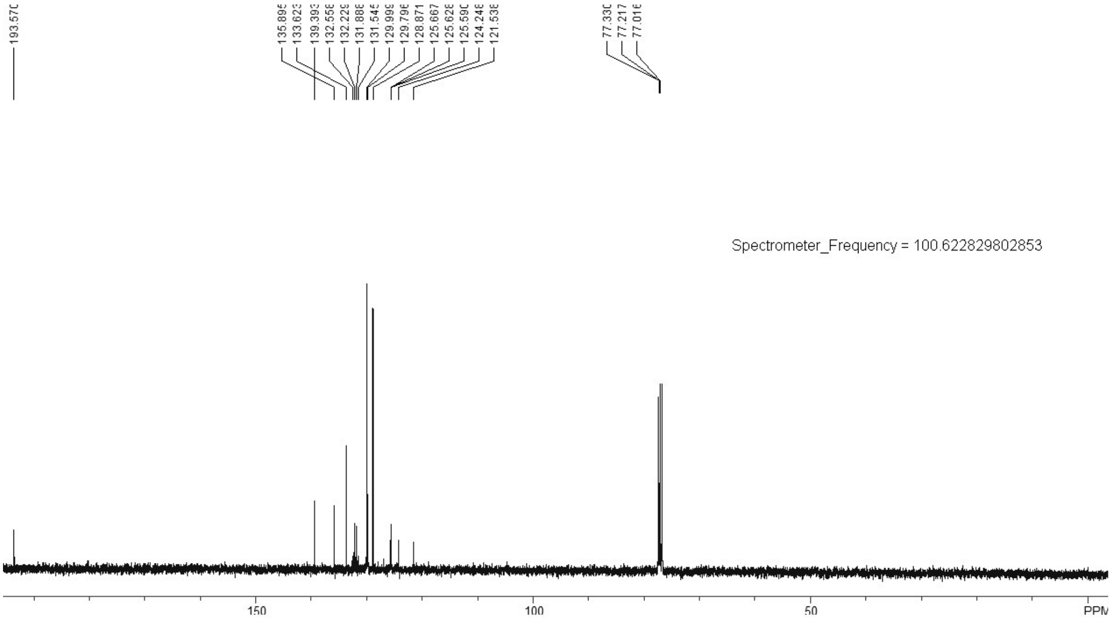




(20) 3,5-bis(trifluoromethyl)benzophenone (T6-5)

m.p. 109.5–110.7 ^{o}C (lit.[14] mp 109–111 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.24 (s, 2 H), 8.11 (s, 1 H), 7.81 (d, J = 7.6 Hz, 2 H), 7.68 (t, J = 8.0 Hz, 1 H), 7.54 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 139.4, 136.0, 133.7, 132.1 (dd, J_1 = 65.2 Hz, J_2 = 32.6 Hz), 130.0, 129.9, 128.9, 125.7 (t, J = 4.0 Hz), 124.3, 121.6 (q, J = 269 Hz). HRMS (EI) Calcd for $C_{15}H_8F_6O$ (M^+) 318.0479, Found 318.0471.

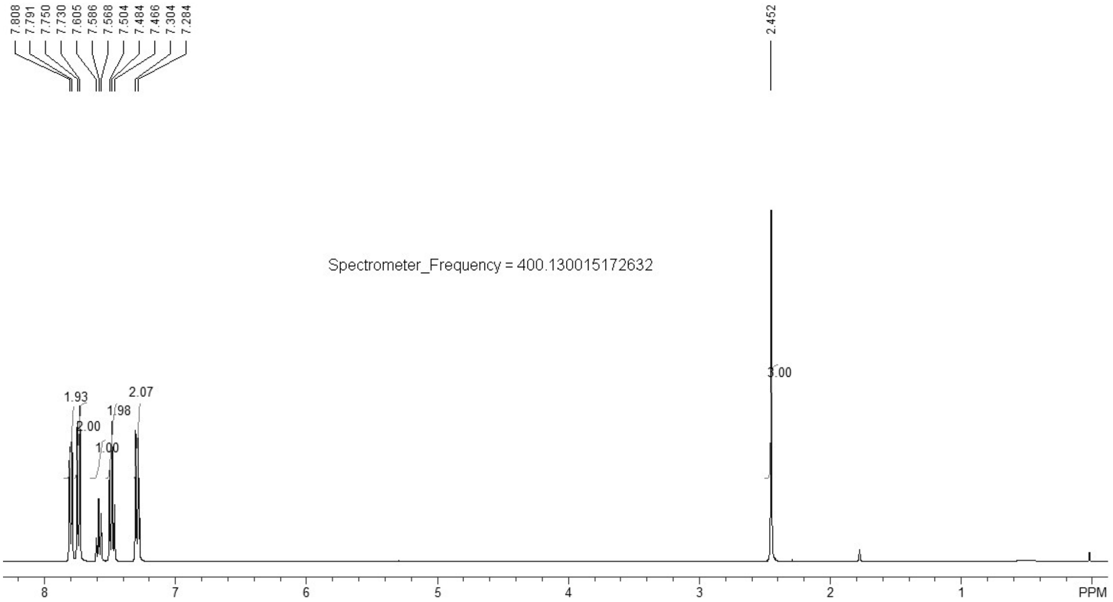


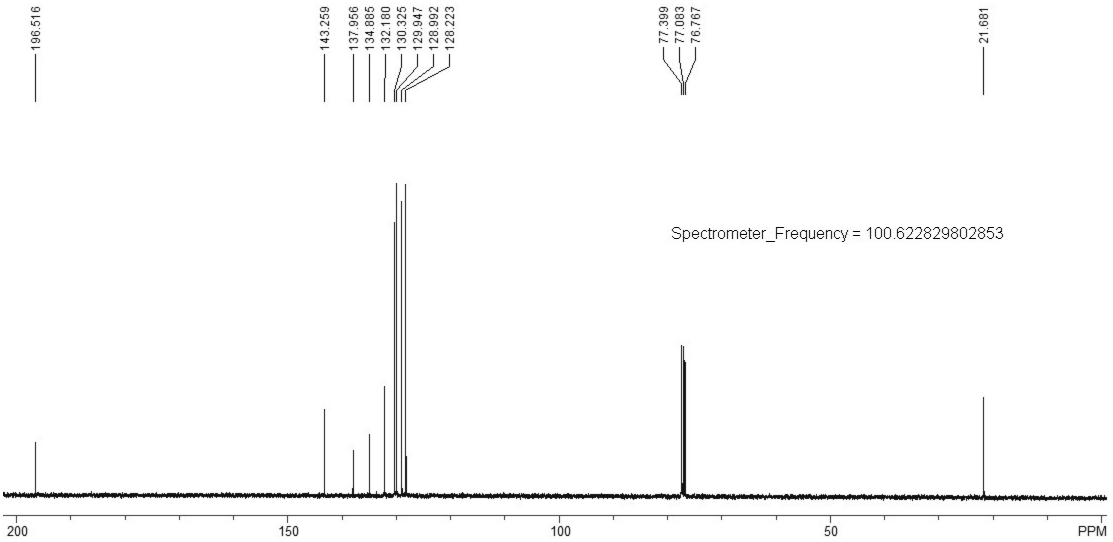


(21) 4-methylbenzophenone (T6-6)

m.p. 56.2–57.4 ^{o}C (lit.^{1} mp 56–58 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.80 (d, *J* = 6.8 Hz, 2 H), 7.74 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 2.47 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.6, 143.3, 137.9, 134.9, 132.2, 130.4, 129.9, 129.0, 128.3, 21.7. HRMS (EI) Calcd for $C_{14}H_{12}O$ (M^{+}) 196.0888, Found

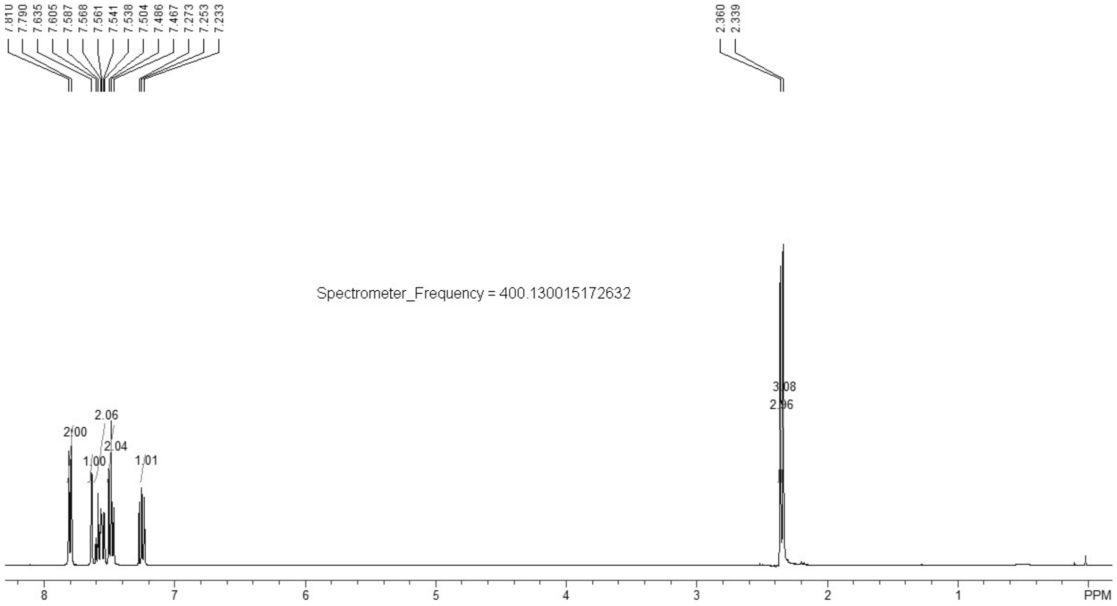
196.0883.

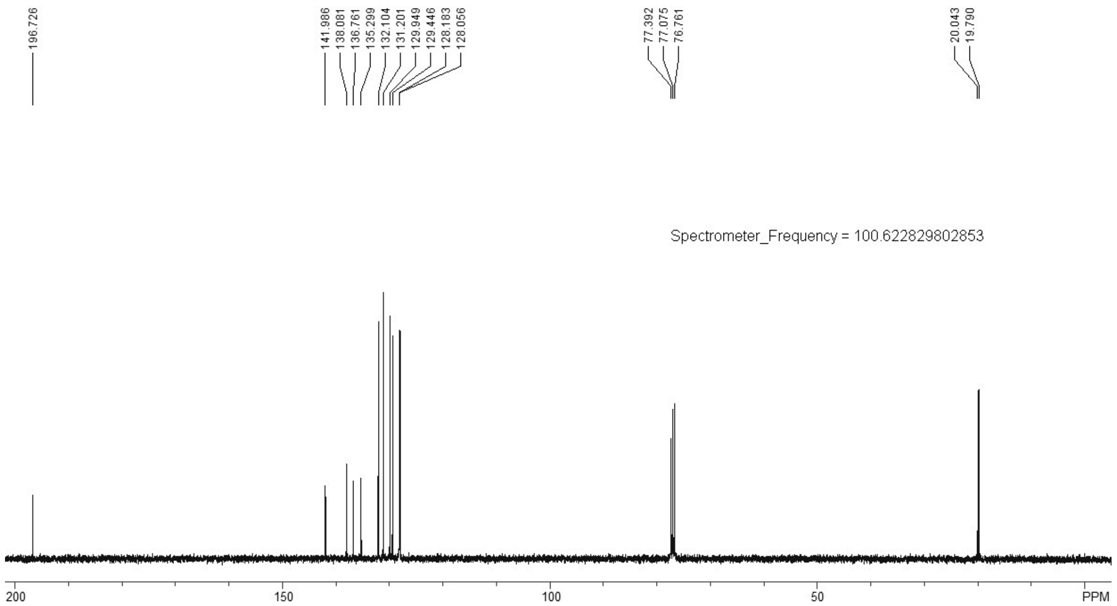




(22) 3,4-dimethylbenzophenone (T6-7)

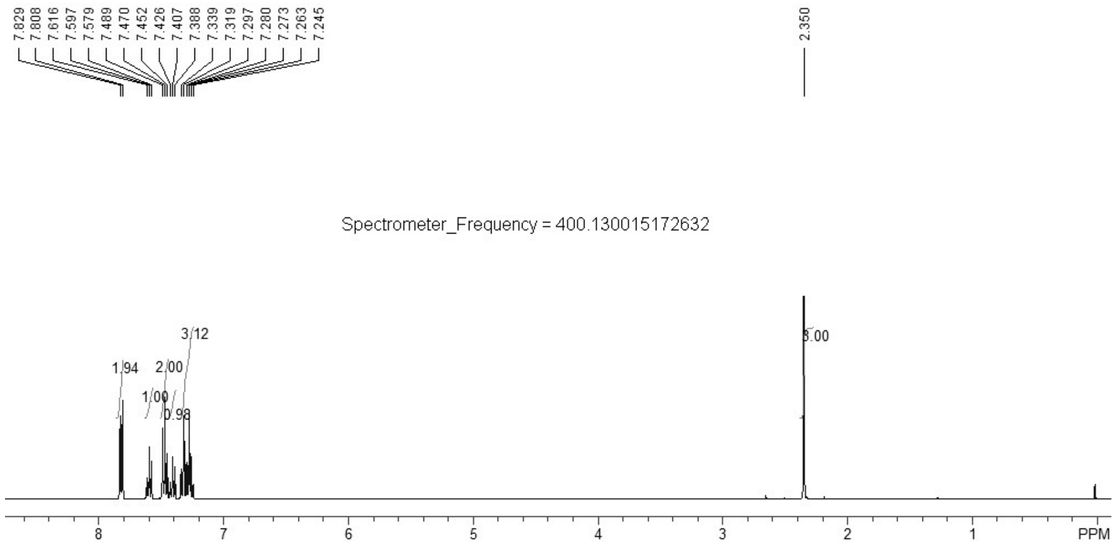
m.p. 46.6–47.4 °C (lit.[4] mp 47–49 °C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.81 (d, J = 8.0 Hz, 2 H), 7.65 (s, 1 H), 7.54-7.61 (m, 2 H), 7.48 (t, J = 7.6 Hz, 2 H), 7.24 (t, J = 8.0 Hz, 1 H), 2.37 (s, 3 H), 2.34 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 141.9, 138.2, 136.7, 135.3, 132.2, 131.4, 129.9, 129.4, 128.2, 128.0, 20.1, 19.8. HRMS (EI) Calcd for $C_{15}H_{14}O$ (M$^+$) 210.1045, Found 210.1052.

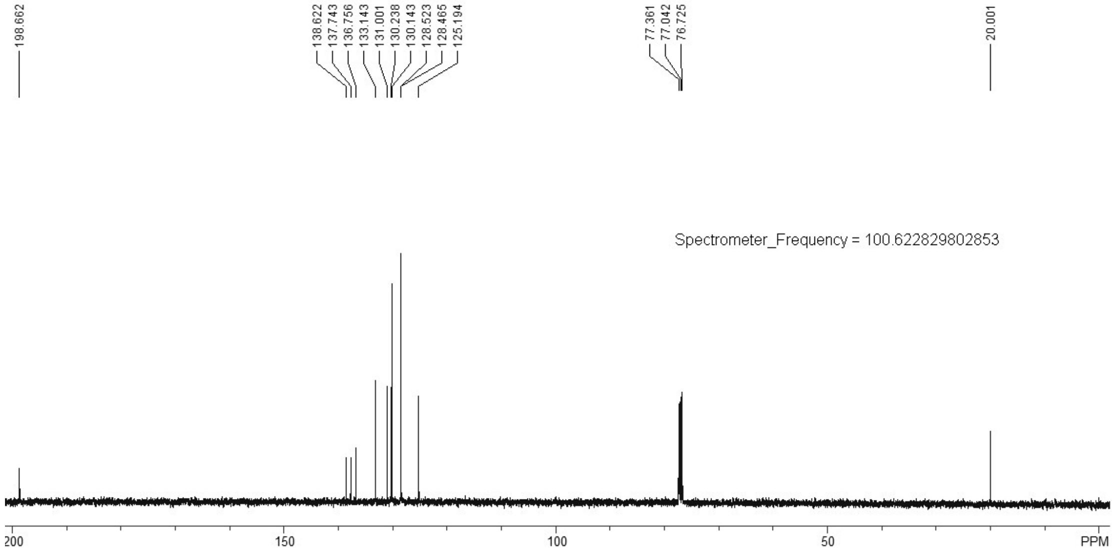




(23) 2-methylbenzophenone (T6-8)

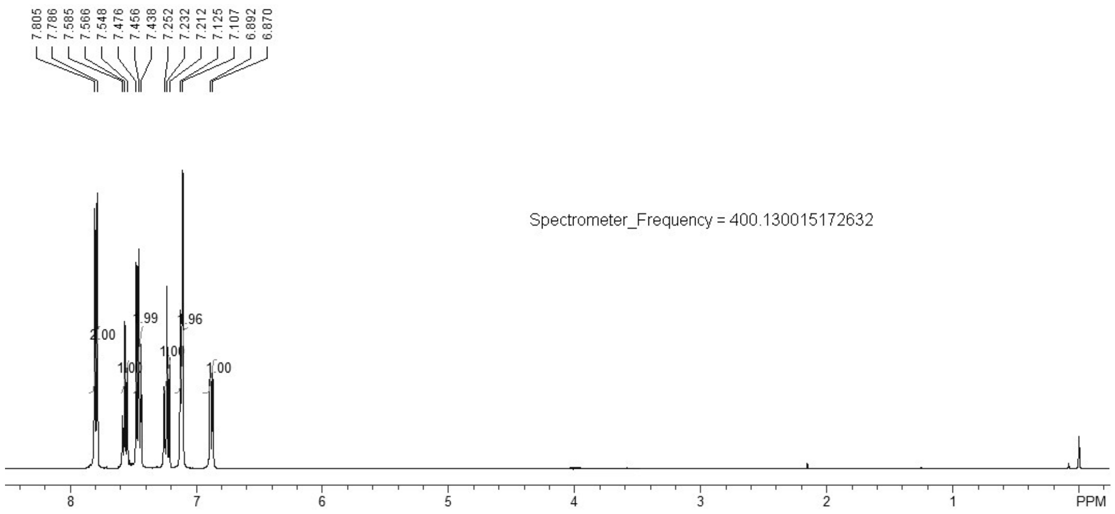
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (d, J = 8.0 Hz, 2 H), 7.60 (t, J = 7.6 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 2 H), 7.42 (t, J = 7.6 Hz, 1 H), 7.25-7.34 (m, 3 H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 138.7, 137.8, 136.8, 133.2, 131.0, 130.3, 130.2, 128.5, 128.4, 125.2, 20.0. HRMS (EI) Calcd for $C_{14}H_{12}O$ (M^+) 196.0888, Found 196.0881.

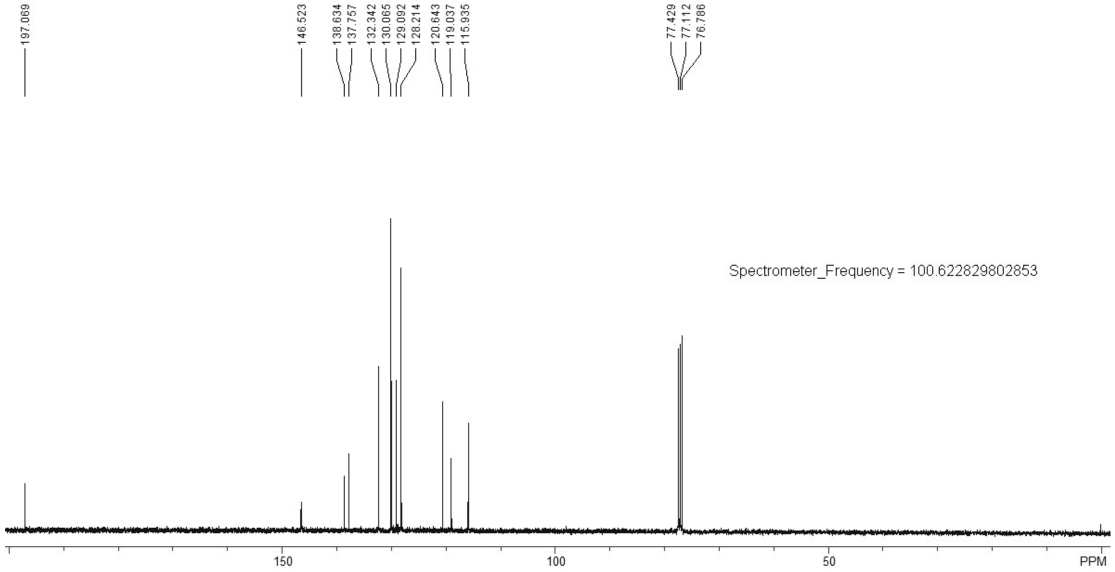




(24) 3-chloro-benzophenone (T6-10)

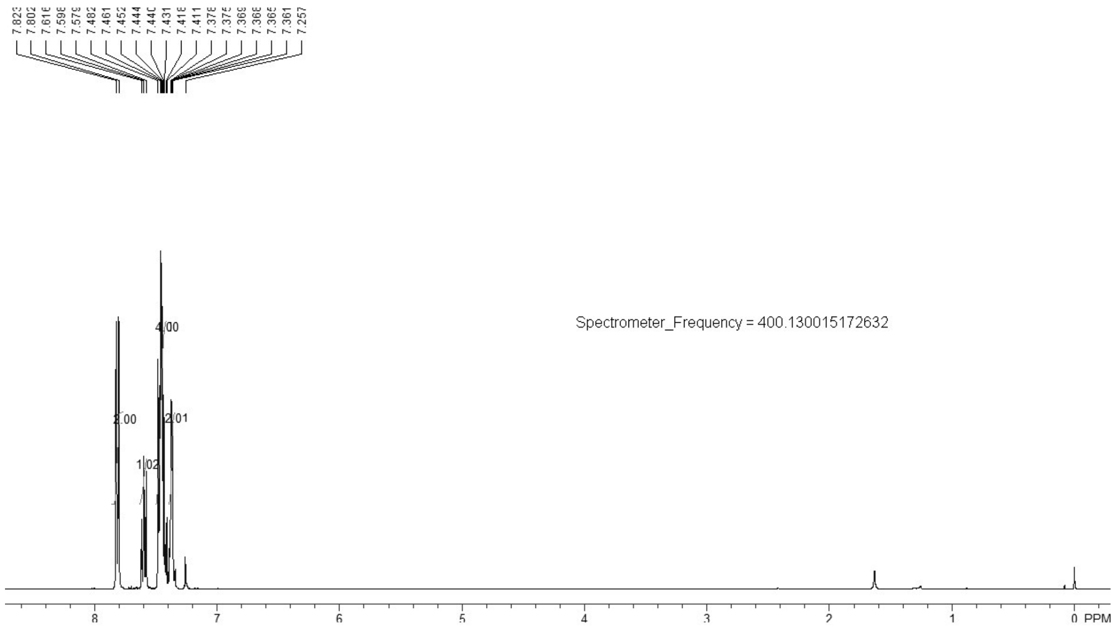
m.p. 83.4–84.5 °C (lit.[5] mp 84 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ7.81 (d, J = 7.6 Hz, 2 H), 7.57 (t, J = 7.6 Hz, 1 H), 7.45 (t, J = 7.6 Hz, 2 H), 7.24 (t, J = 8.0 Hz, 1 H), 7.13 (d, J = 7.2 Hz, 2 H), 6.88 (d, J = 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.1, 146.6, 138.7, 137.8, 132.4, 130.1, 129.1, 128.3, 120.7, 119.1, 115.9. HRMS (EI) Calcd for $C_{13}H_9ClO$ (M^+) 216.0342, Found 216.0349.

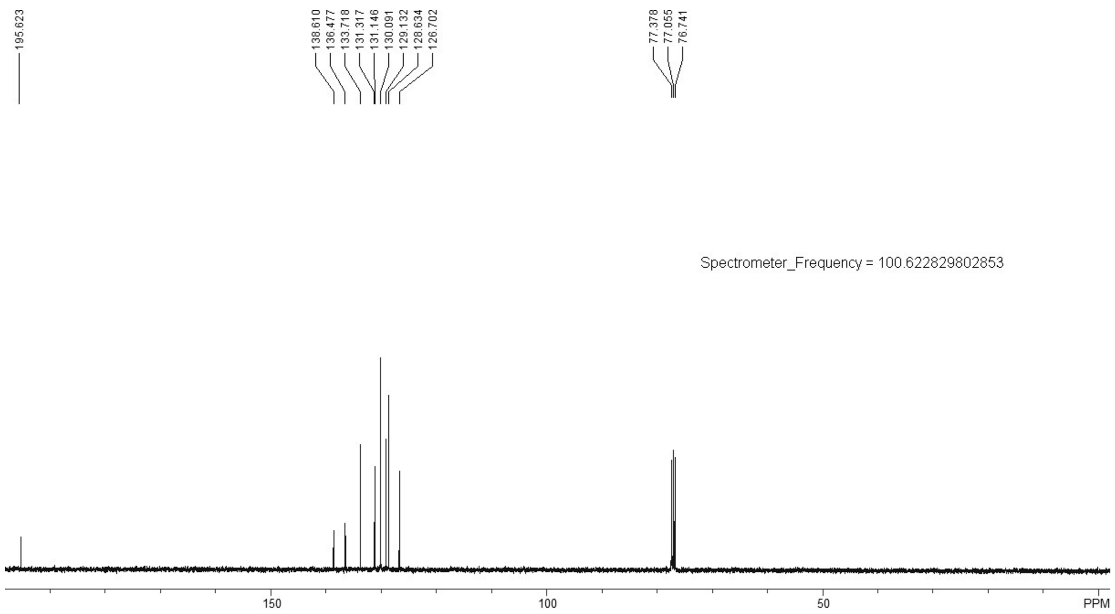




(25) 2-chlorobenzophenone (T6-11)

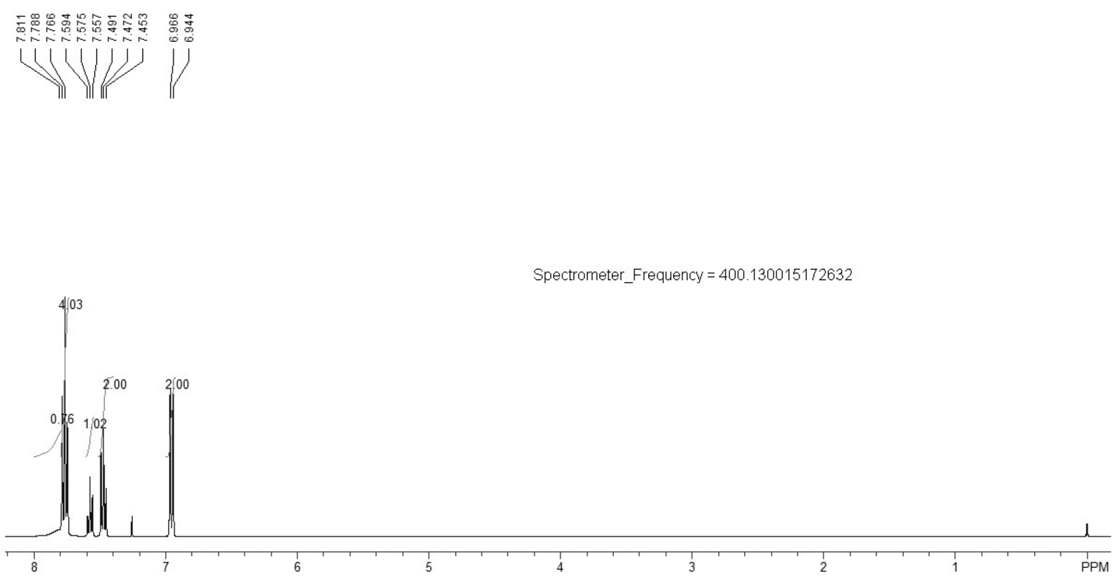
m.p. 42.4–43.9 ^{o}C (lit.^{2} mp 43–45 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.81 (d, J = 8.4 Hz, 2 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.41-7.48 (m, 4 H), 7.35-7.38 (m, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.7, 138.7, 136.5, 133.7, 131.4, 131.2, 130.1, 129.2, 128.7, 126.8. HRMS (EI) Calcd for $C_{13}H_9ClO$ (M^+) 216.0342, Found 216.0347.

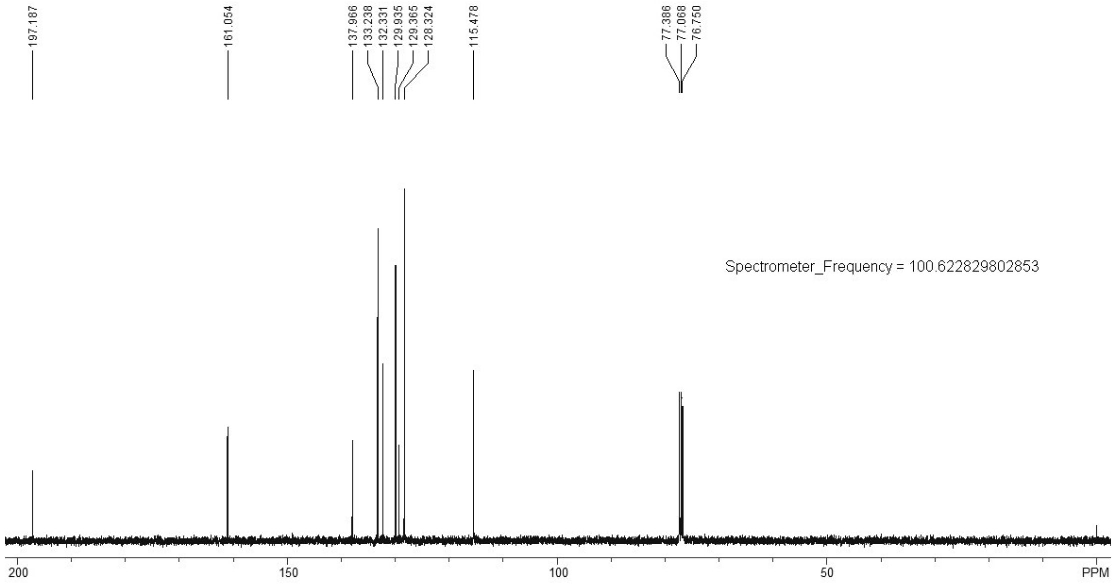




(26) 4-hydroxy-benzophenone (T6-12)

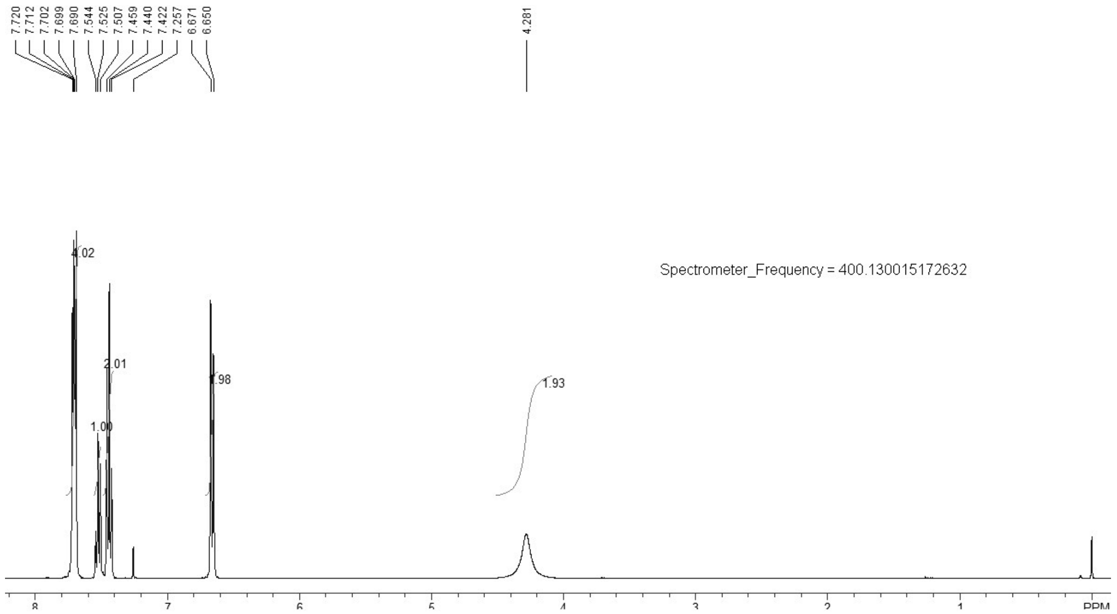
m.p. 132.1–134.3 °C (lit.[9] mp 133–134 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (br, 1 H), 7.78 (d, J = 8.4 Hz, 4 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.47 (t, J = 7.2 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 161.0, 137.9, 133.3, 132.2, 129.9, 129.3, 128.4, 115.4. HRMS (EI) Calcd for $C_{13}H_{10}O_2$ (M^+) 198.0681, Found 198.0678.

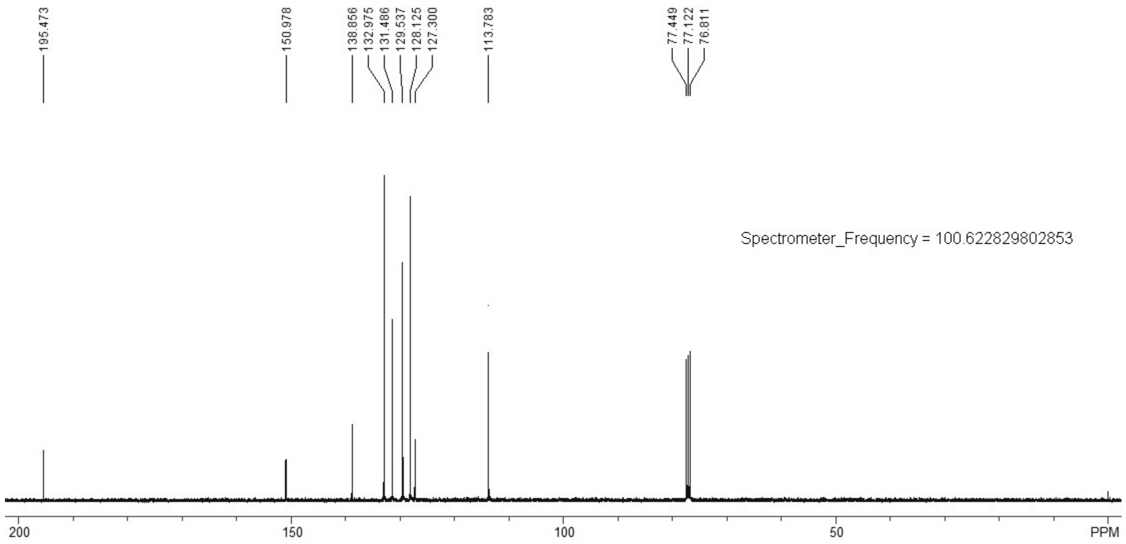




(27) 4-aminobenzophenone (T6-13)

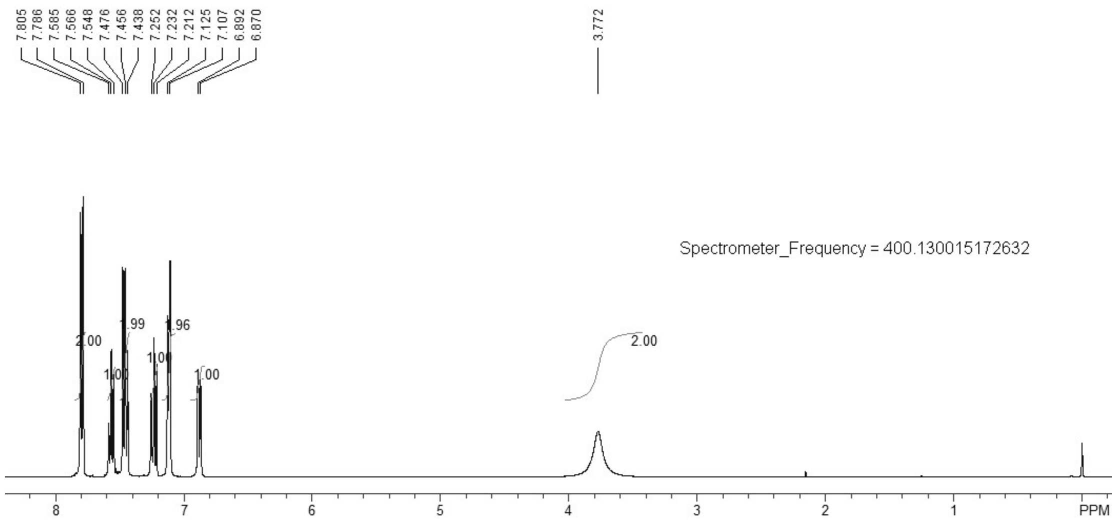
m.p. 120.8–122.4 ºC (lit.[5] mp 120–121 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68-7.72 (m, 4 H), 7.53 (t, J = 7.2 Hz, 1 H), 7.45 (t, J = 7.2 Hz, 2 H), 6.67 (d, J = 8.0 Hz, 2 H), 4.28 (br, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 150.9, 138.9, 132.8, 131.5, 129.6, 128.2, 127.4, 112.8. HRMS (EI) Calcd for $C_{13}H_{11}NO$ (M^+) 197.0841, Found 197.0837.

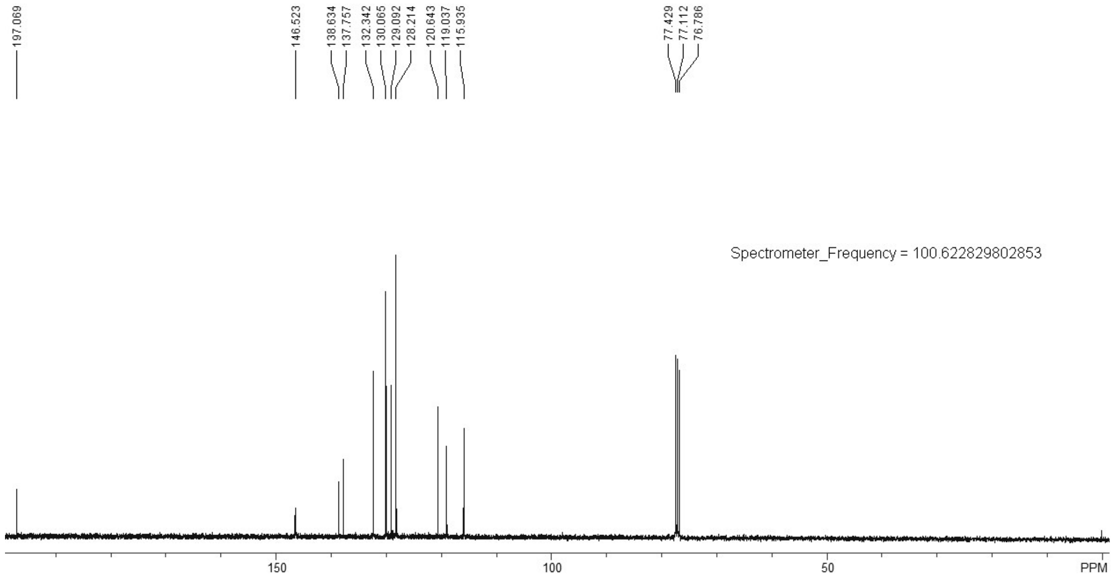




(28) 3-aminobenzophenone (T6-14)

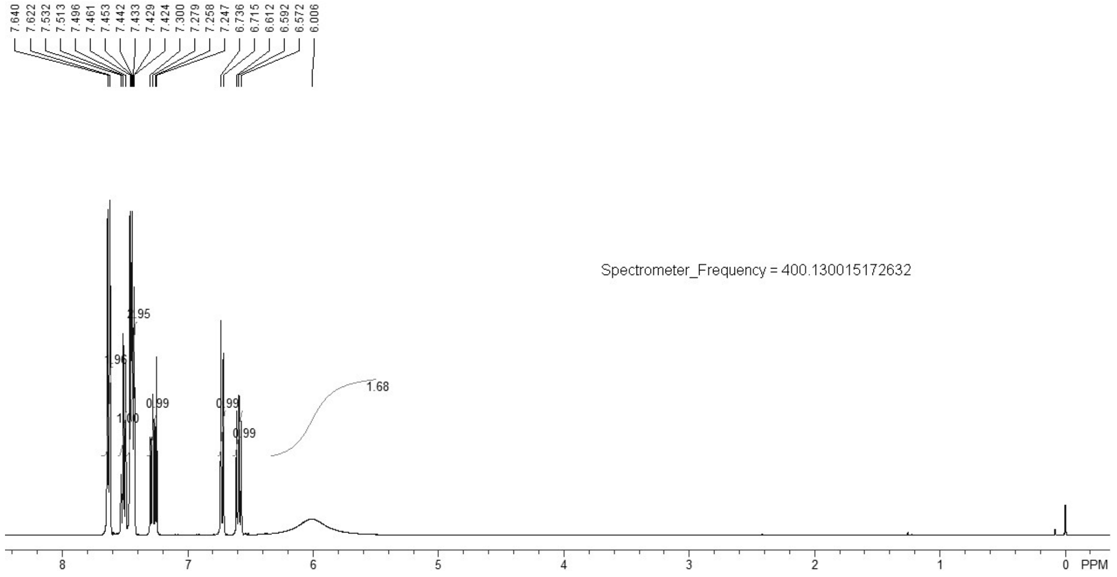
m.p. 83.6–85.2 ^{o}C (lit.[10] mp 84–86 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.79 (d, J = 7.6 Hz, 2 H), 7.58 (t, J = 7.6 Hz, 1 H), 7.46 (t, J = 7.6 Hz, 2 H), 7.22 (t, J = 8.0 Hz, 1 H), 7.13 (d, J = 7.2 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 1 H), 3.75 (br, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 146.6, 138.7, 137.8, 132.4, 130.1, 129.1, 128.3, 120.6, 119.1, 115.7. HRMS (EI) Calcd for $C_{13}H_{11}NO$ (M^+) 197.0841, Found 197.0835.

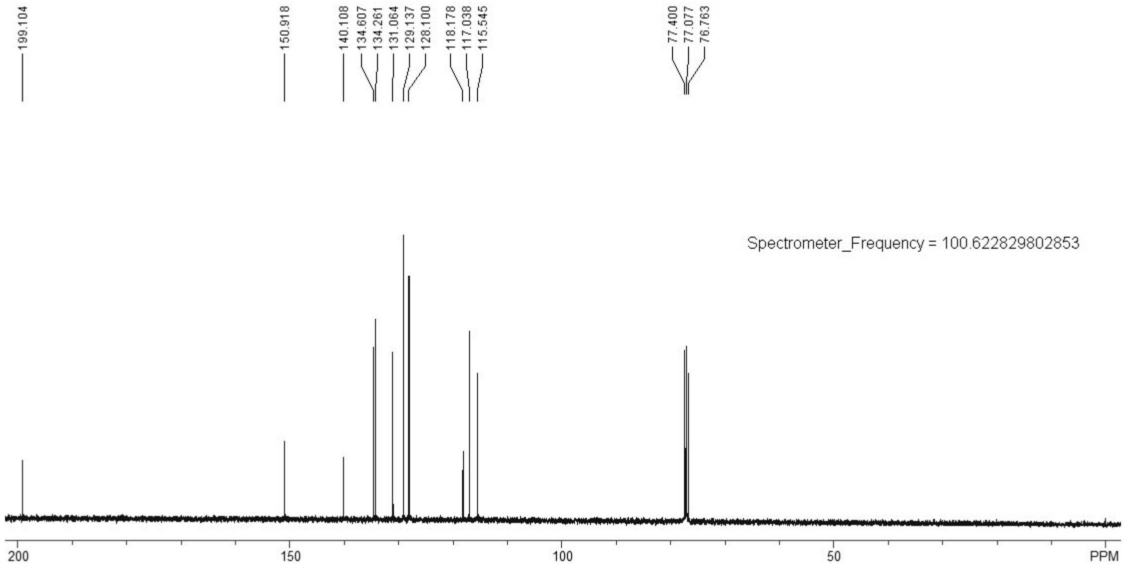




(29) 2-aminobenzophenone (T6-15)

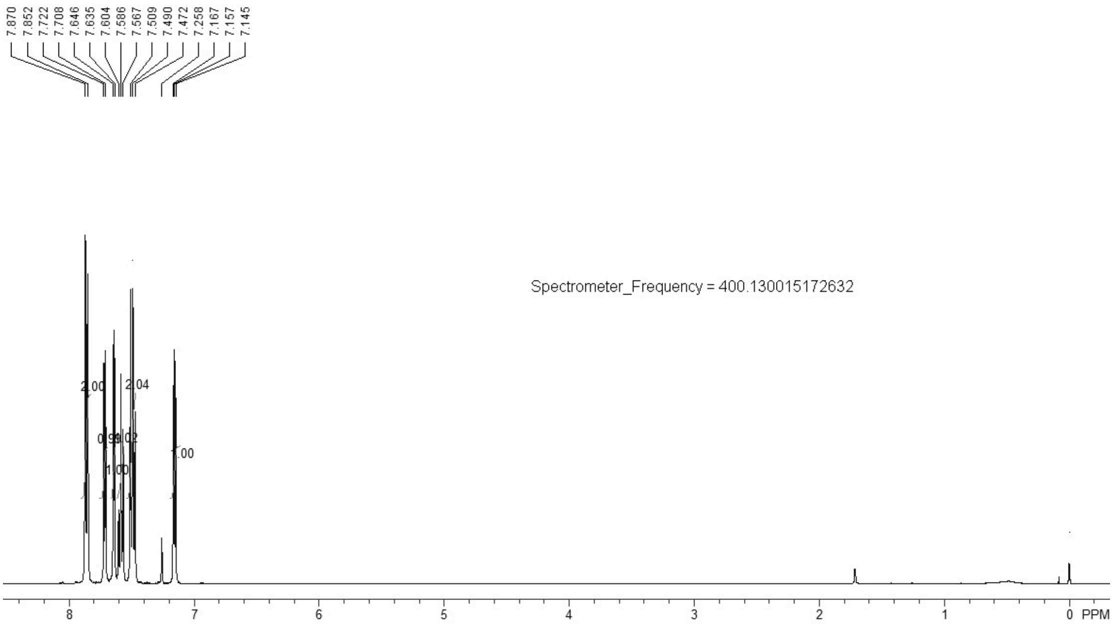
m.p. 102.4–103.7 ^{o}C (lit.[11] mp 103–104 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, J = 7.2 Hz, 2 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.42-7.46 (m, 3 H), 7.27 (t, J = 8.4 Hz, 1 H), 6.72 (d, J = 8.4 Hz, 1 H), 6.58 (t, J = 8.0 Hz, 1 H), 6.01 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 150.9, 140.2, 134.7, 134.3, 131.1, 129.2, 128.2, 118.2, 117.1, 115.6. HRMS (EI) Calcd for $C_{13}H_{11}NO$ (M^+) 197.0841, Found 197.0840.

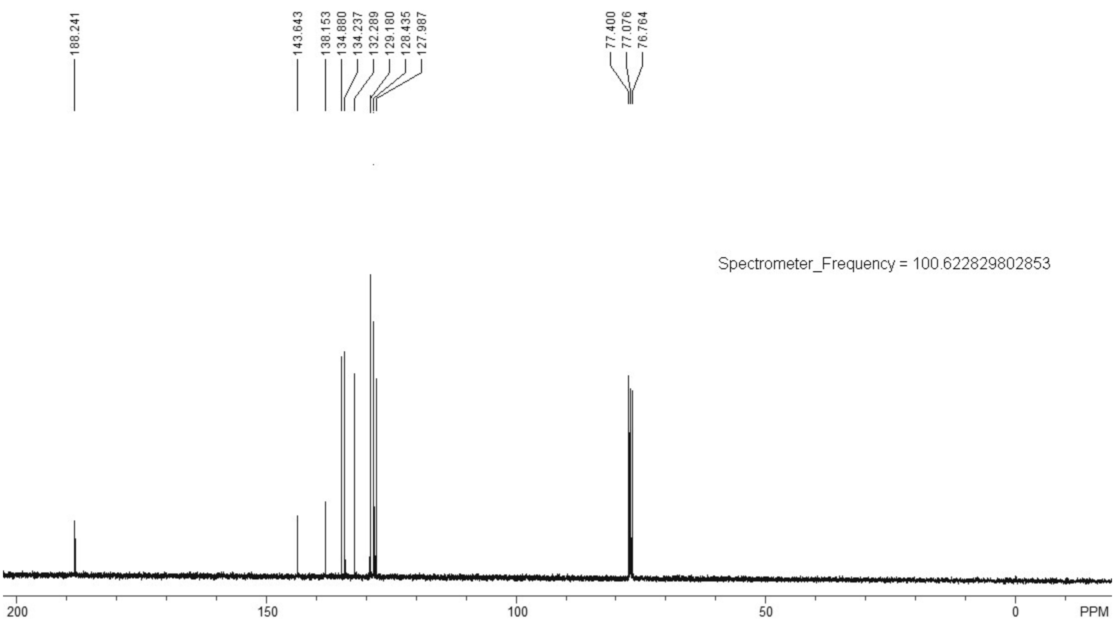




(30) 2-benzoylthiophene (T6-17)

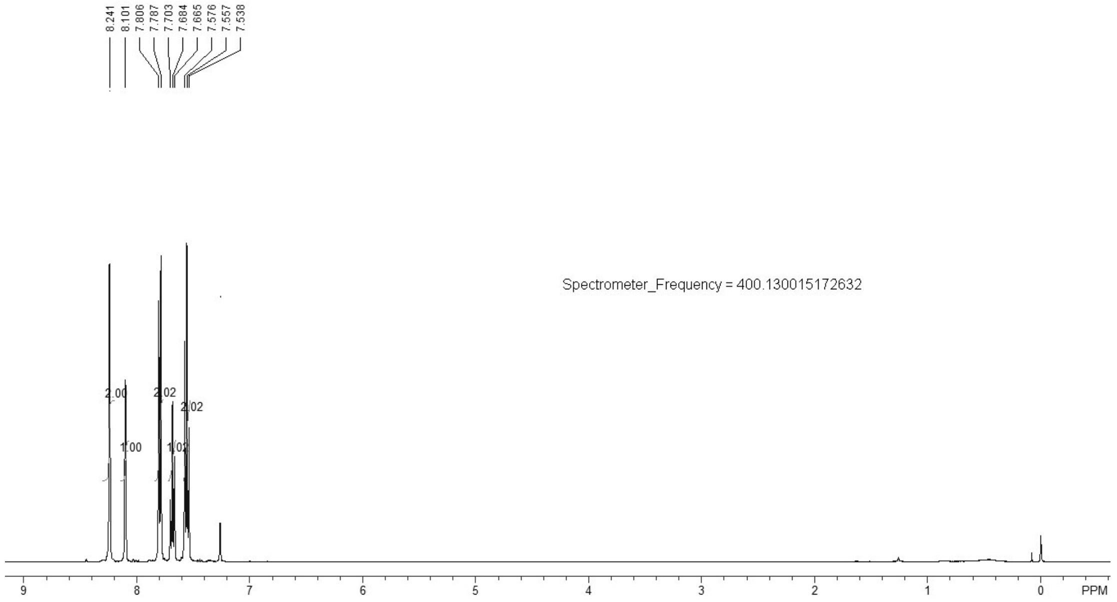
m.p. 53.4–54.9 ^{o}C (lit.[11] mp 54–55 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (t, J = 7.6 Hz, 2 H), 7.72 (d, J = 5.6 Hz, 1 H), 7.65 (d, J = 4.8 Hz, 1 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.49 (t, J = 7.2 Hz, 2 H), 7.15 (t, J = 4.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 143.6, 138.2, 134.9, 134.3, 132.3, 129.2, 128.5, 128.0. HRMS (EI) Calcd for $C_{11}H_8OS$ (M^+) 188.0296, Found 188.0299.

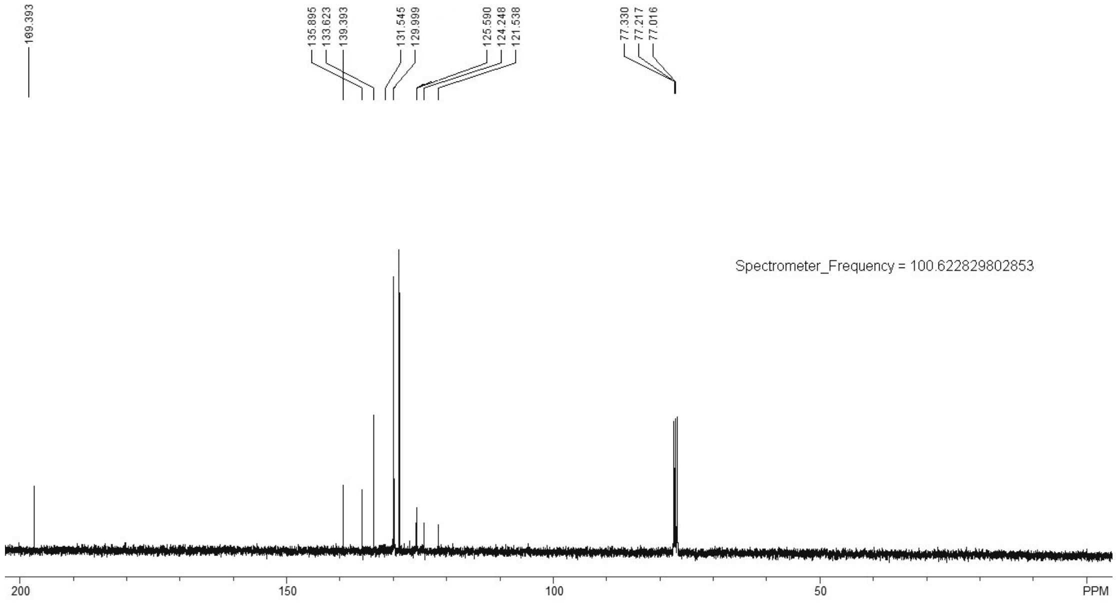




(31) Phenyl(pyrimidin-5-yl)methanone (T6-18)

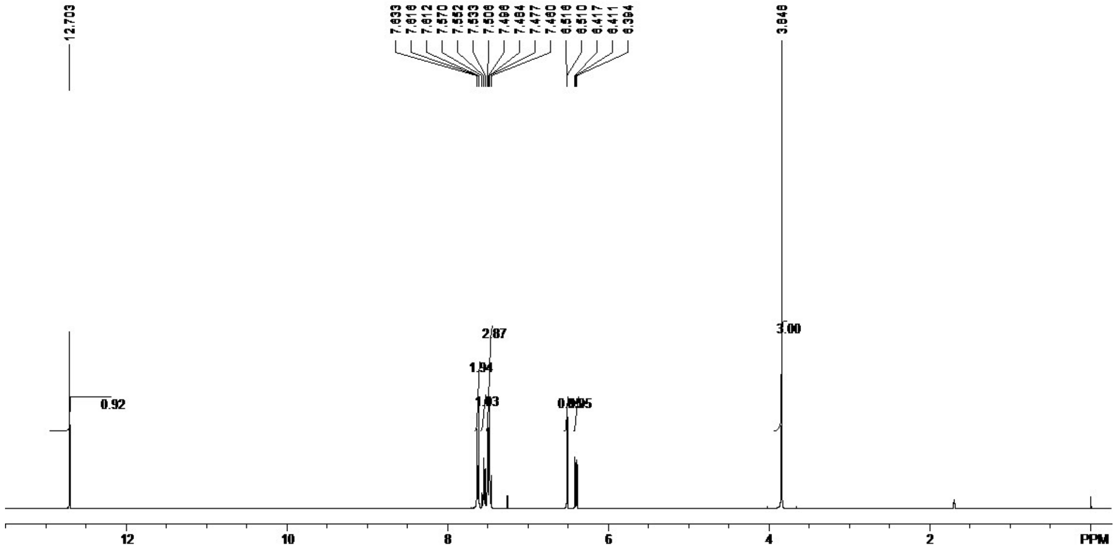
m.p. 88.8–91.1 ^{o}C (lit.^{10} mp 88–90 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 8.24 (s, 2 H), 8.11 (s, 1 H), 7.80 (d, *J* = 7.6 Hz, 2 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.56 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.7, 139.5, 135.8, 133.7, 131.6, 130.1, 125.6, 124.0, 121.5. HRMS (EI) Calcd for $C_{11}H_8N_2O$ (M^+) 184.0637, Found 184.0632.

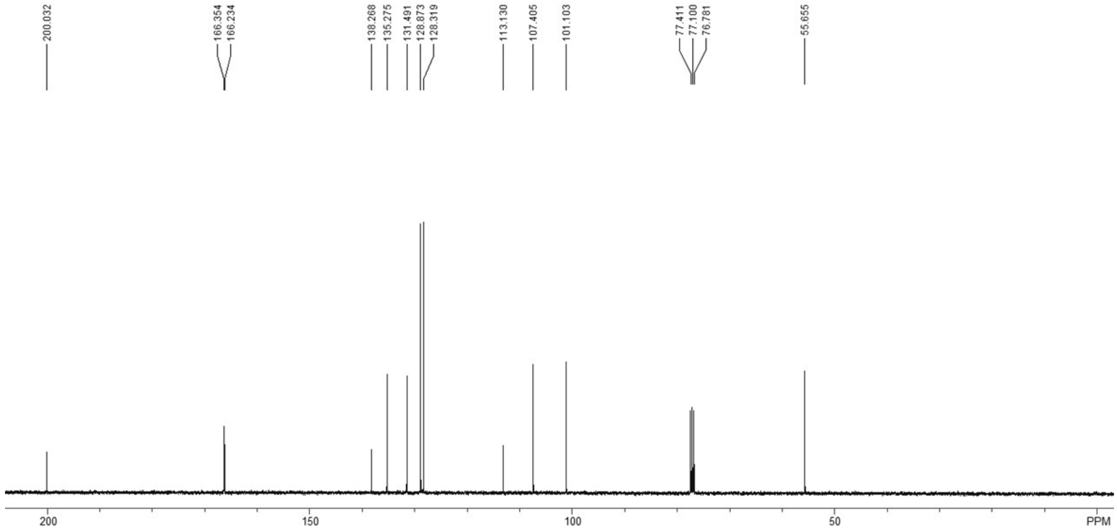




(32) Oxybenzone

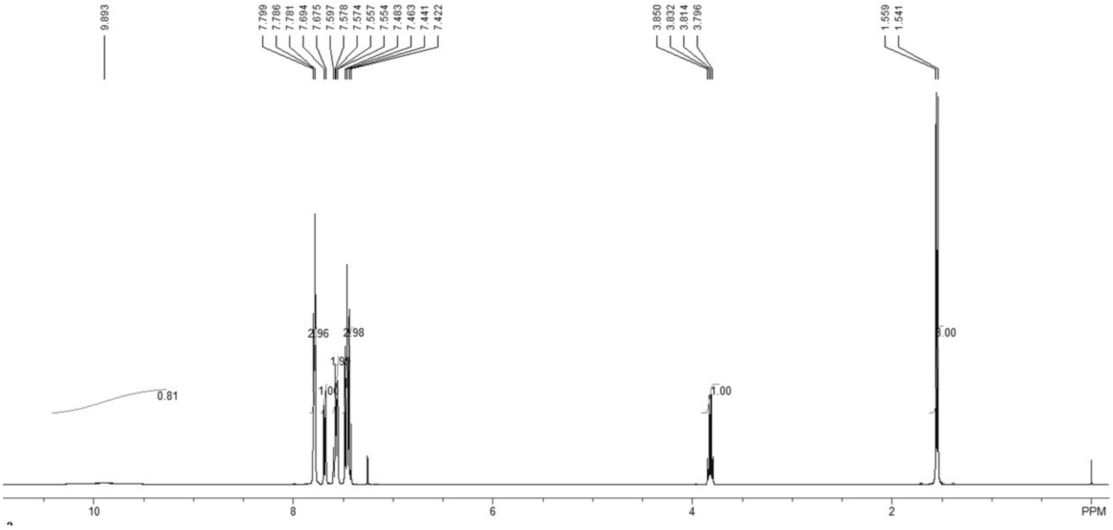
m.p. 65.2–66.4 °C (lit.[12] mp 66 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 12.71 (s, 1 H), 7.61-7.64 (m, 2 H), 7.65 (t, *J* = 7.2 Hz, 1 H), 7.46-7.51 (m, 3 H), 6.51 (d, *J* = 2.4 Hz, 1 H), 6.40 (dd, *J* = 9.2 Hz, 2.4 Hz, 1 H), 3.85 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.0, 166.4, 166.2, 138.3, 135.3, 131.5, 128.9, 128.3, 113.1, 107.4, 101.4, 55.7. HRMS (EI) Calcd for $C_{14}H_{12}O_3$ (M^+) 228.0786, Found 228.0769.

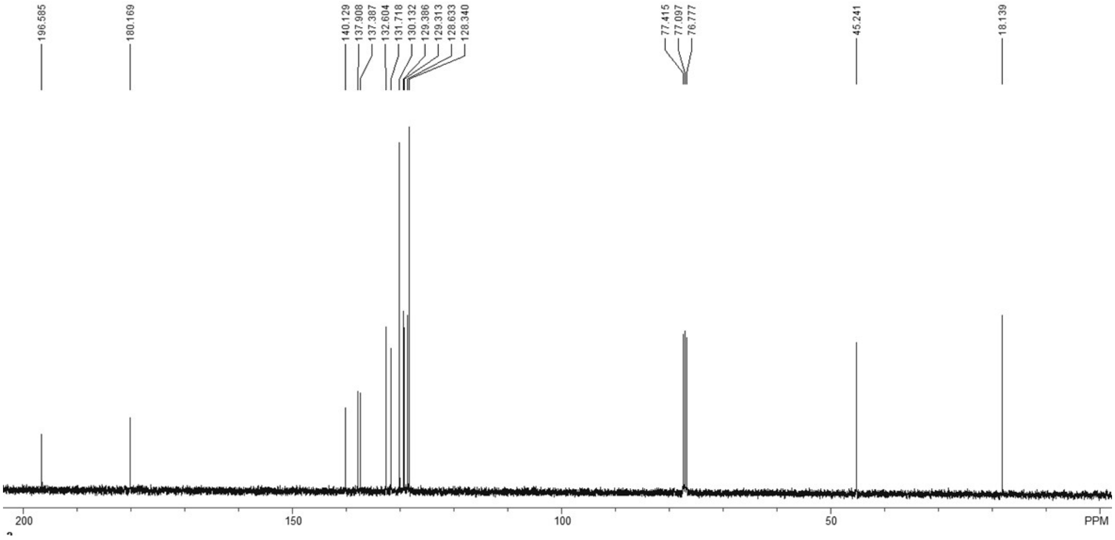




(33) Ketoprofen

m.p. 93–94 ^{o}C (lit.[13] mp 94°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.89 (s, 1 H), 7.78-7.80 (m, 3 H), 7.68 (d, J = 7.6 Hz, 1 H), 7.55-7.60 (m, 2 H), 7.42-7.48 (m, 3 H), 3.82 (q, J = 7.2 Hz, 1 H), 1.55 (d, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 180.2, 140.1, 137.9, 137.4, 132.6, 131.7, 130.1, 129.4, 129.3, 128.6, 128.3, 45.2, 18.1. HRMS (EI) Calcd for $C_{16}H_{14}O_3$ (M^+) 254.0943, Found 254.0932.





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