Silver-catalyzed Decarbonylative Acylation of Arylglyoxylic Acids with Arylboronic Acids

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Supporting Materials

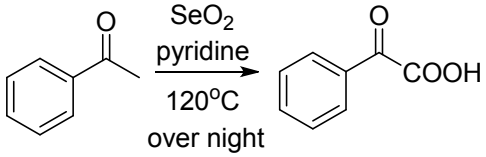
Content

General

Starting materials were purchased from common commercial sources and all solvents were purified and dried according to standard methods prior to use. Arylglyoxylic acids were prepared from corresponding aryl methyl ketone. ^{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). Element analysis data were collected on elemental analyser (EuroVector, Italy, EA3000). Other substrates and catalysts were commercially available and used without additional purification.

Preparation and Characterization of Starting Materials:

Preparation of arylglyoxylic acids by the method of literature: [1]

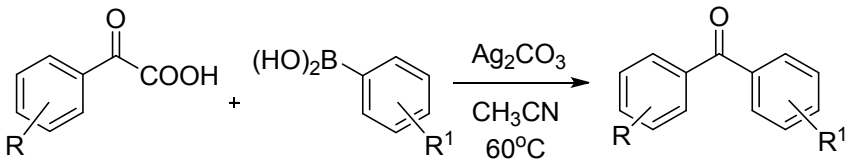


A mixture of aryl methyl ketone (10.0 mmol) and selenium dioxide (20.0 mmol) in dry pyridine (5 mL) was stirred at 120°C under nitrogen for 18 h. After the disappearance of acetophenone detected by TLC, the mixture was filtrated and removing the organic solvent by evaporation. Then 2 M sodium hydroxide solution was added to the residue and some ethyl acetate followed. Subsequently 37% concentrated hydrochloric acid was put into the mixture dropwise and arylglyoxylic acids was separated out.

[1] Zhuang, J.; Wang, C.; Xie, F.; Zhang, W. *Tetrahedron* **2009**, *65*,9797-9800.

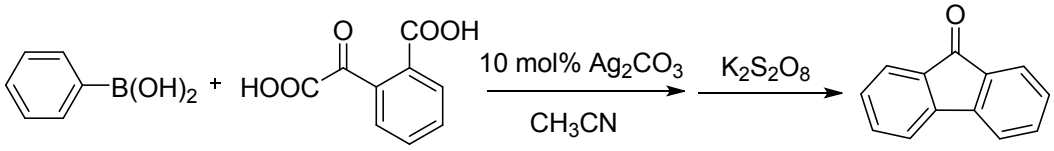
Typical procedure for the product

Typical procedure for decarbonylative acylation:



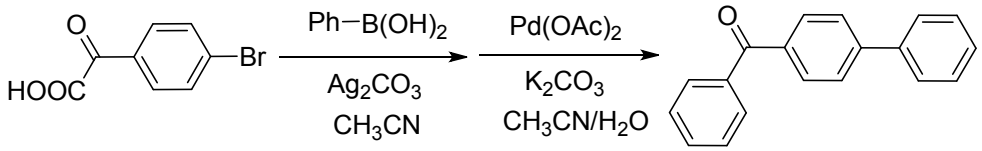
A mixture of arylglyoxylic acids (5.5 mmol), arylboronic acids (5 mmol), Ag_2CO_3 (0.5 mmol) was stirred at 60°C for 60 min in CH_3CN (5 mL). Afterward, the mixture was filtered through a pad of celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

Typical procedure for "One-pot" synthesis of fluorenone



A mixture of 2-(carboxycarbonyl)benzoic acid (1.0 mmol), phenylboronic acid (1.1 mmol), Ag_2CO_3 (10 mol%) was stirred at 60°C for 60 min in CH_3CN (2 mL). Then potassium persulfate (2.0 mmol) was added to the mixture and the temperature was raised to 120 °C for 12h. Afterward, the mixture was filtered through a pad of celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

Typical procedure for "One-pot" synthesis of 4-biphenylyl-benzophenone

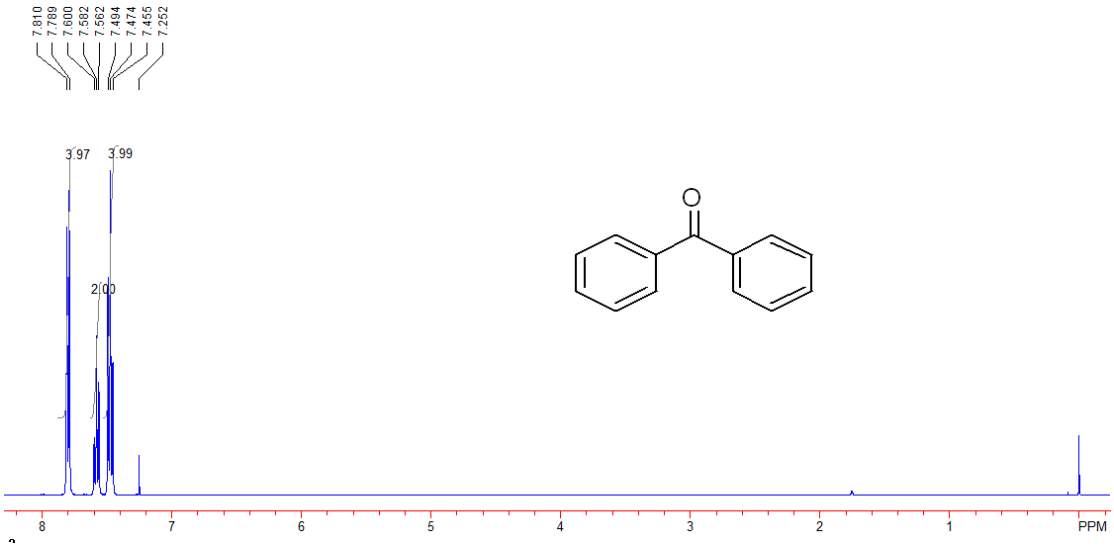


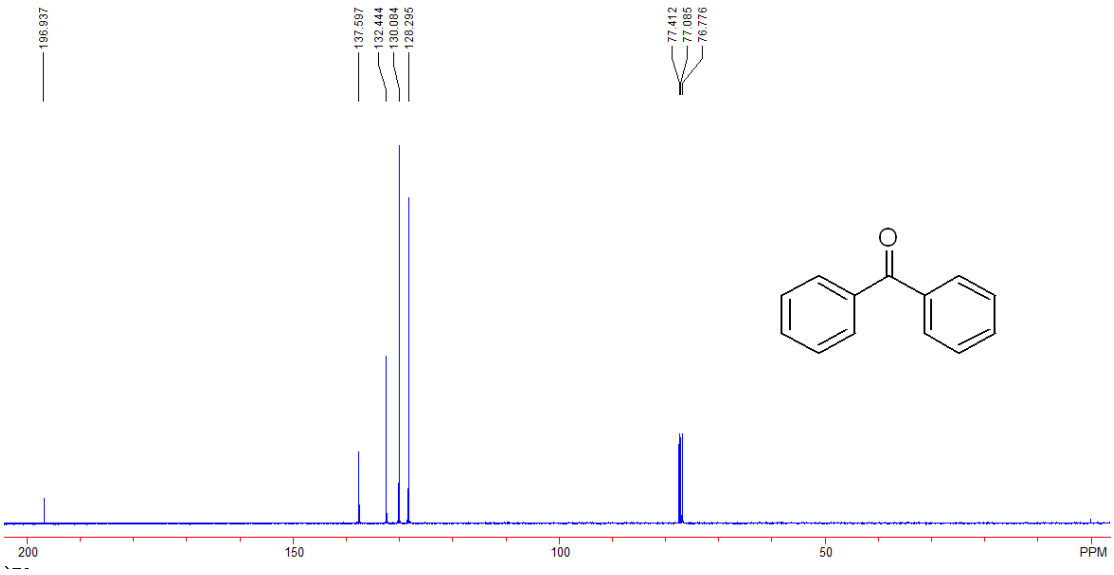
A mixture of 4-bromo-phenylglyoxylic acids (1.0 mmol), phenylboronic acid (2.5 mmol), Ag_2CO_3 (10 mol%) was stirred at 60°C for 60 min in CH_3CN (2 mL). Then $Pd(OAc)_2$ (5 mol%), K_2CO_3 (2.0 mmol) and water (0.5 mL) were added to the mixture for 6h. Afterward, the mixture was filtered through a pad of celite and the solution was extracted by Et_2O (2 mL) for three times. The organic phase was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

Characterization data of the product

(1) benzophenone (1a)

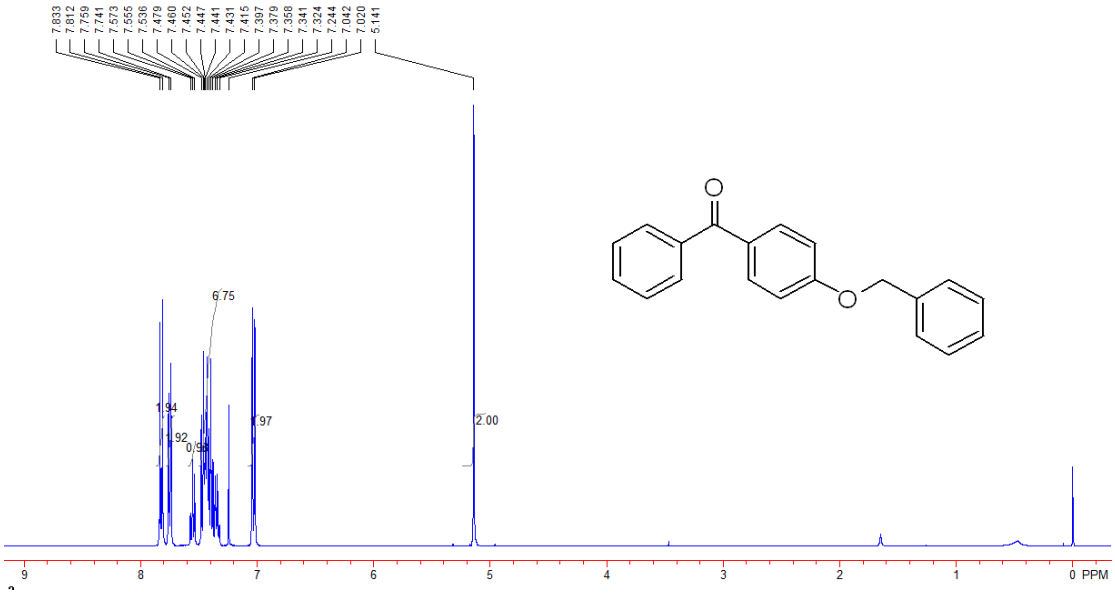
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (837mg). m.p. 47–48 °C (lit.[1] mp 47–48 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, J = 8.4 Hz, 4 H), 7.58 (t, J = 7.6 Hz, 2 H), 7.47 (t, J = 7.6 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.94, 137.60, 132.44, 130.08, 128.30. HRMS (EI) Calcd for $C_{13}H_{10}O$ (M^+) 182.0732, Found 182.0734. Elemental Analysis: C, 85.69; H, 5.53; O, 8.78 (Calcd. C, 85.69; H, 5.53; O, 8.78).

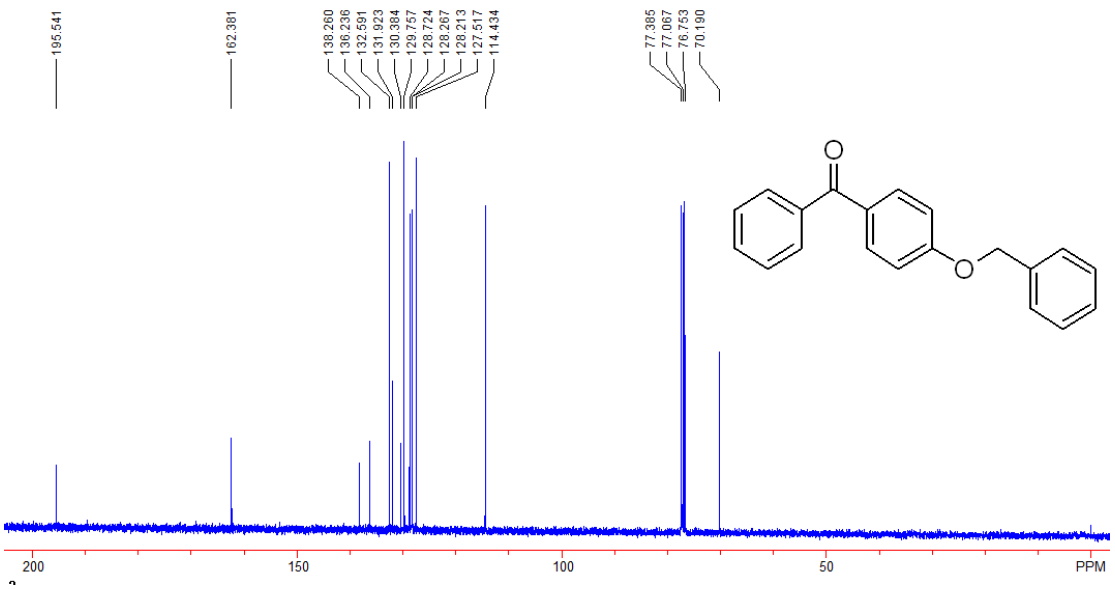




(2) 4-benzyloxy-benzophenone (2a, 3a)

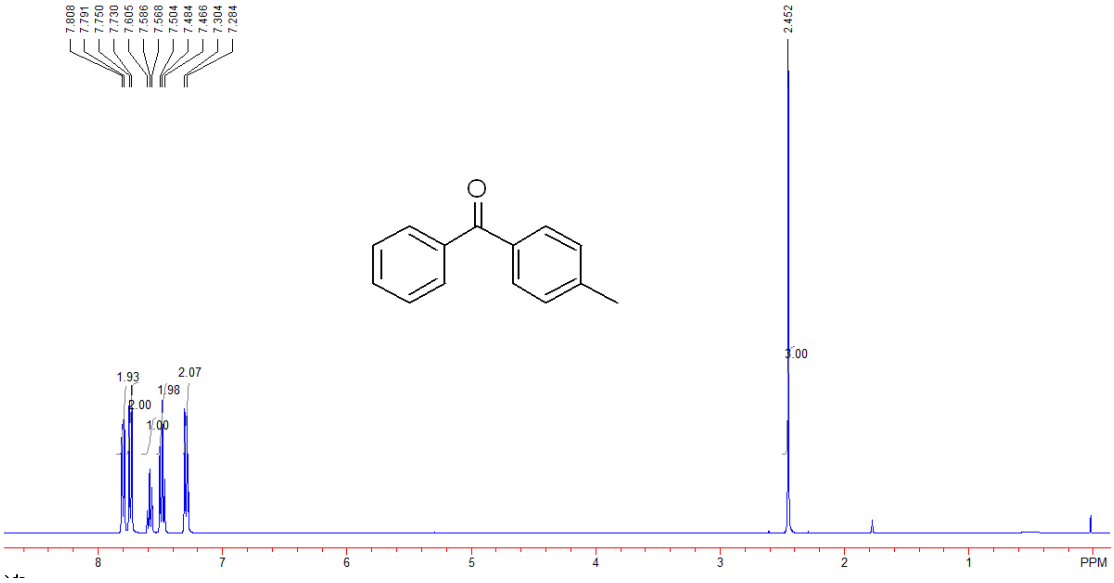
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a white solid (1339mg). m.p. 83–84 ^{o}C (lit.[1] mp 82–85 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.82 (d, *J* = 8.4 Hz, 2 H), 7.75 (t, *J* = 7.2 Hz, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.32-7.48 (m, 7 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 5.14 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.54, 162.38, 138.26, 136.24, 132.59, 131.92, 130.38, 129.76, 128.72, 128.27, 128.21, 127.52, 114.43, 70.19. HRMS (EI) Calcd for $C_{20}H_{16}O_2$ (M^+) 288.1150, Found 288.1148. Elemental Analysis: C, 83.31; H, 5.59; O, 11.10 (Calcd. C, 83.31; H, 5.59; O, 11.10).

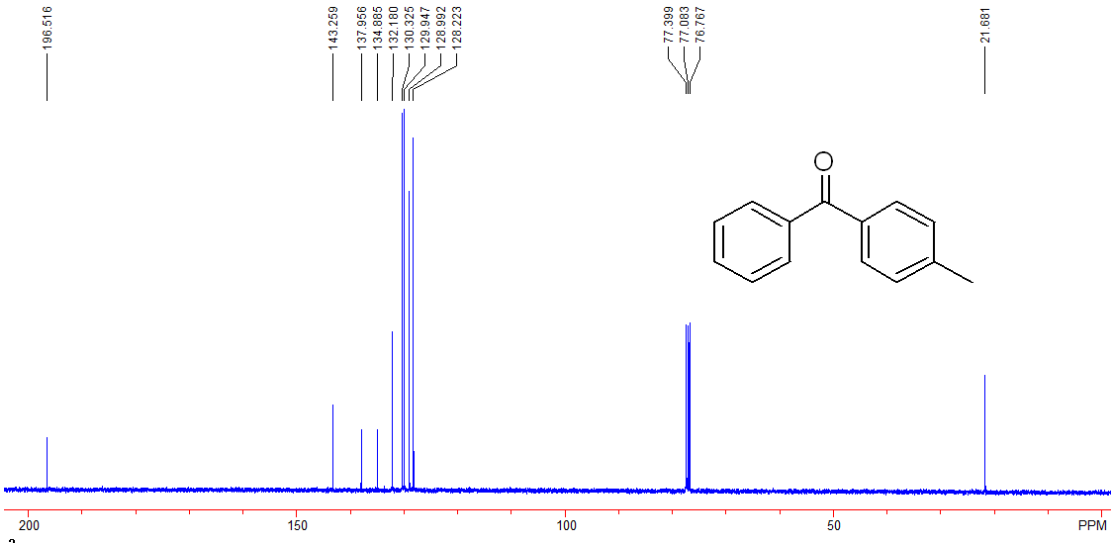




(3) 4-methylbenzophenone (2b, 3b)

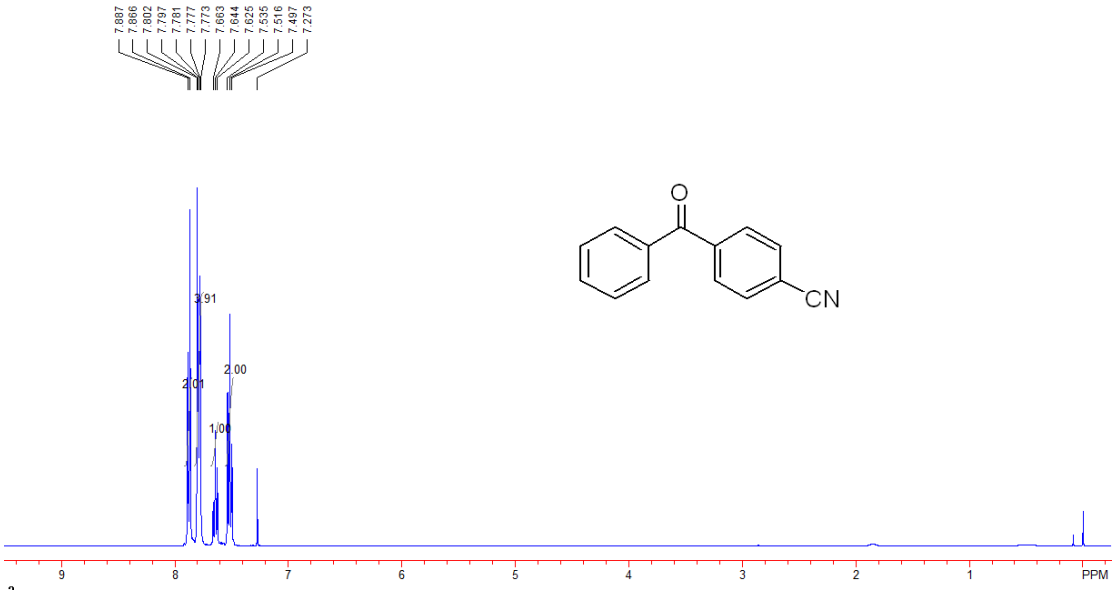
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (931mg). m.p. 57–58 ºC (lit.[2] mp 56–58 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, *J* = 6.8 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 2.45 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.52, 143.26, 137.96, 134.89, 132.18, 130.33, 129.95, 128.99, 128.22, 21.68. HRMS (EI) Calcd for $C_{14}H_{12}O$ (M^+) 196.0888, Found 196.0890. Elemental Analysis: C, 85.68; H, 6.16; O, 8.15 (Calcd. C, 85.68; H, 6.16; O, 8.15).

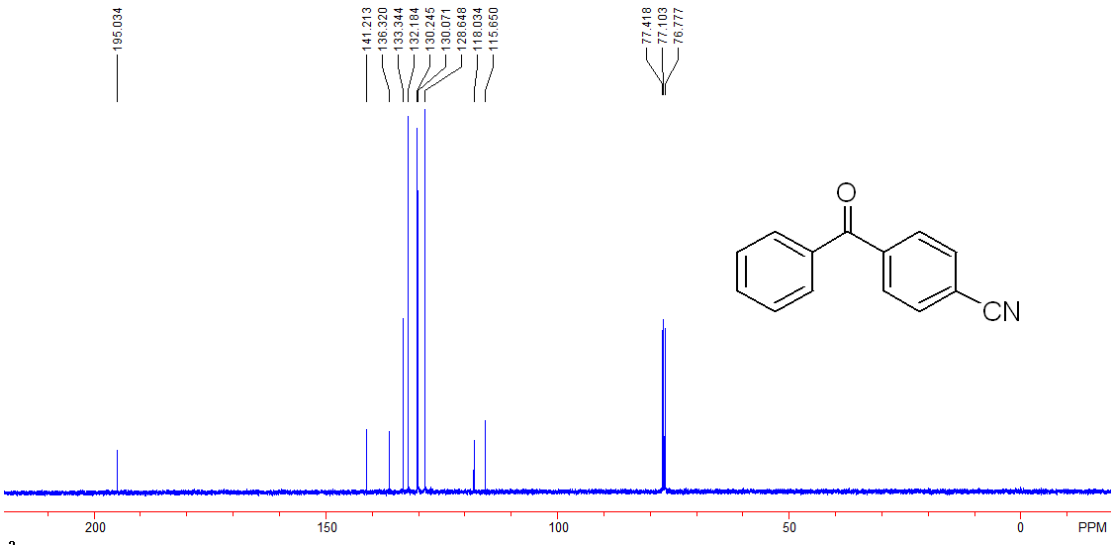




(4) 4-benzoylbenzonitrile (2c, 3d)

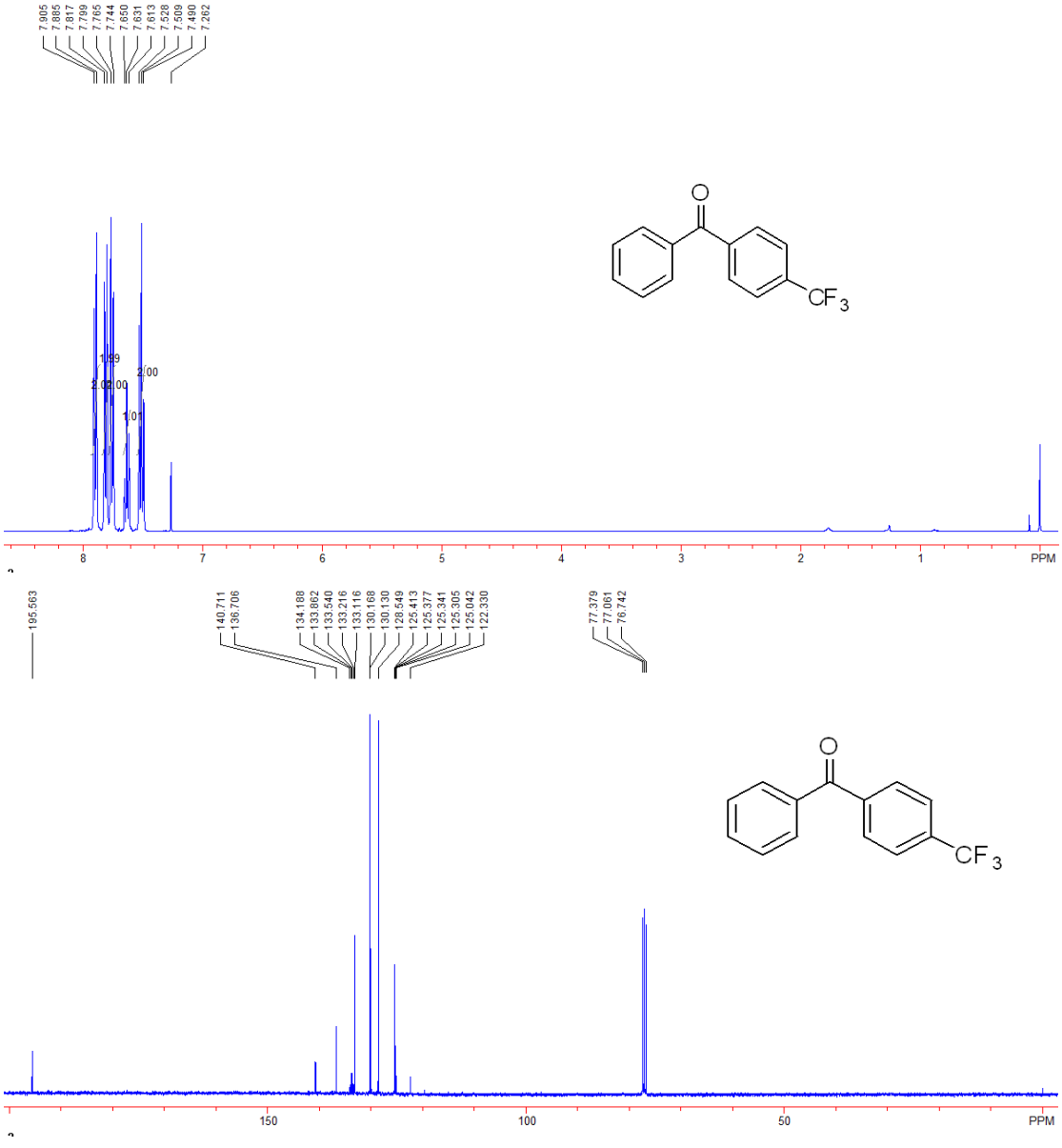
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/3, v/v) afforded as a white solid (911mg). m.p. 114–115 ^{o}C (lit.[2] mp 114–116 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.88 (t, *J* = 8.4 Hz, 2 H), 7.77-7.80 (m, 4 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.03, 141.21, 136.32, 133.34, 132.18, 130.25, 130.07, 128.65, 118.03, 115.65. HRMS (EI) Calcd for $C_{14}H_9NO$ (M^+) 207.0684, Found 207.0681. Elemental Analysis: C, 81.14; H, 4.39; N, 6.75; O, 7.72 (Calcd. C, 81.14; H, 4.38; N, 6.76; O, 7.72).





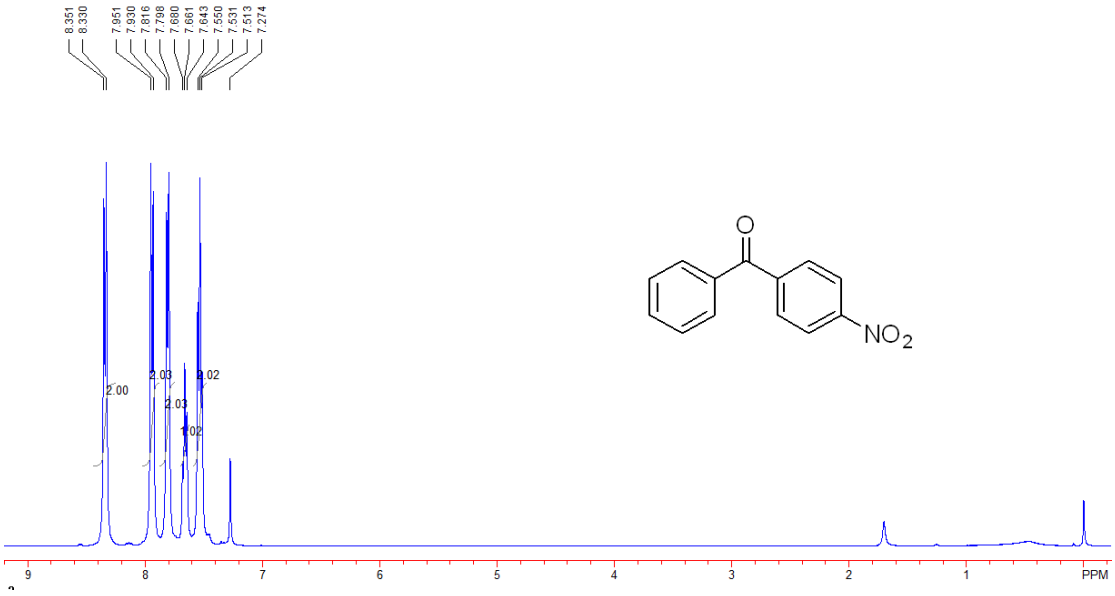
(5) 4-trifluoromethyl-benzophenone (2d)

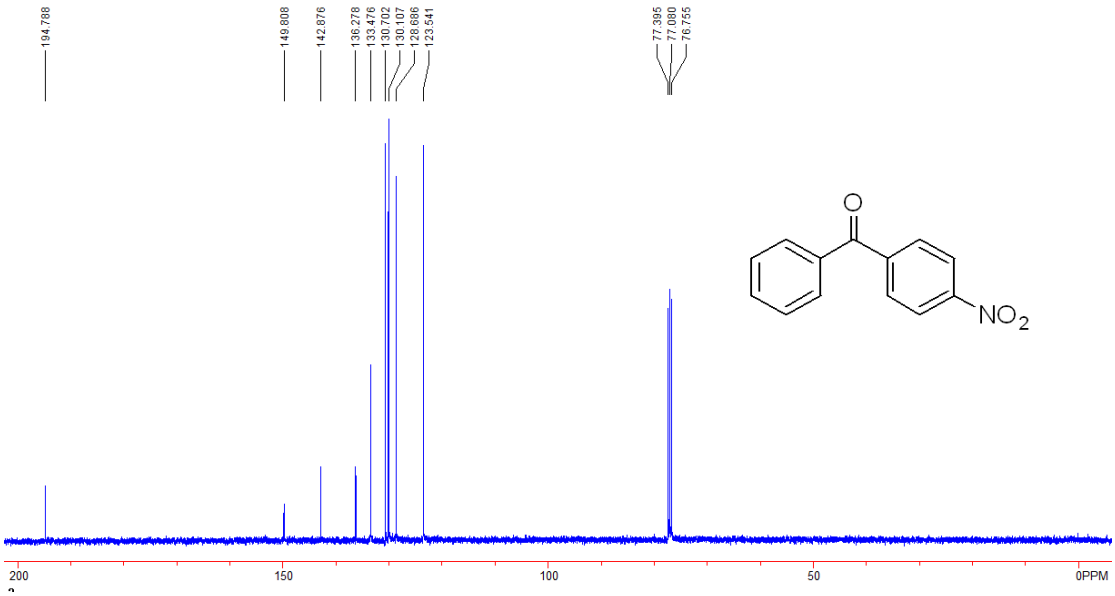
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/3, v/v) afforded as a yellow solid (1075mg). m.p. 115–116 °C (lit.[2] mp 116–117 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90 (d, J = 8.0 Hz, 2 H), 7.81 (d, J = 7.2 Hz, 2 H), 7.76 (d, J = 8.4 Hz, 2 H), 7.63 (t, J = 7.2 Hz, 1 H), 7.51 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.56, 140.71, 136.71, 133.70 (dd, J_1 = 64.7 Hz, J_2 = 32.5 Hz), 133.12, 130.15 (d, J = 3.8 Hz), 128.55, 125.36(dd, J_1 = 7.2 Hz, J_2 = 3.6 Hz), 123.70(d, J = 271.3 Hz). HRMS (EI) Calcd for $C_{14}H_9F_3O$ (M^+) 250.0605, Found 250.0607. Elemental Analysis: C, 67.20; H, 3.63; F, 22.78; O, 6.39 (Calcd. C, 67.20; H, 3.63; F, 22.78; O, 6.39).



(6) 4-nitrobenzophenone (2e, 3e)

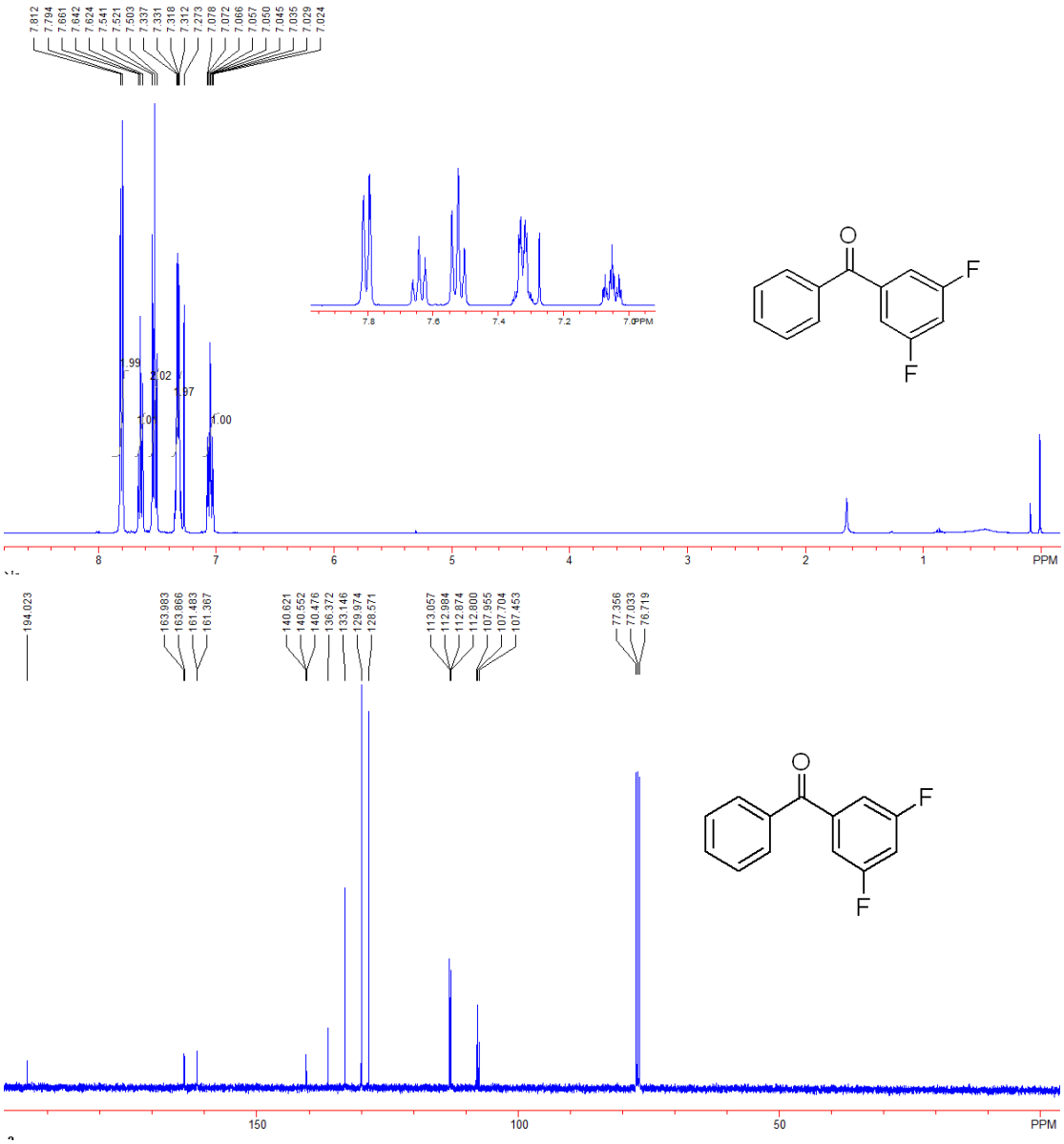
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/3, v/v) afforded as a yellow solid (1010mg). m.p. 141–142 °C (lit.[2] mp 140–142 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.34 (d, *J* = 7.6 Hz, 2 H), 7.94 (d, *J* = 7.6 Hz, 2 H), 7.81 (d, *J* = 7.2 Hz, 2 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.79, 149.81, 142.88, 136.28, 133.48, 130.70, 130.11, 128.69, 123.54. HRMS (EI) Calcd for $C_{13}H_9NO_3$ (M^+) 227.0582, Found 227.0584. Elemental Analysis: C, 68.72; H, 3.99; N, 6.16; O, 21.12. (Calcd. C, 68.72; H, 3.99; N, 6.16; O, 21.12).





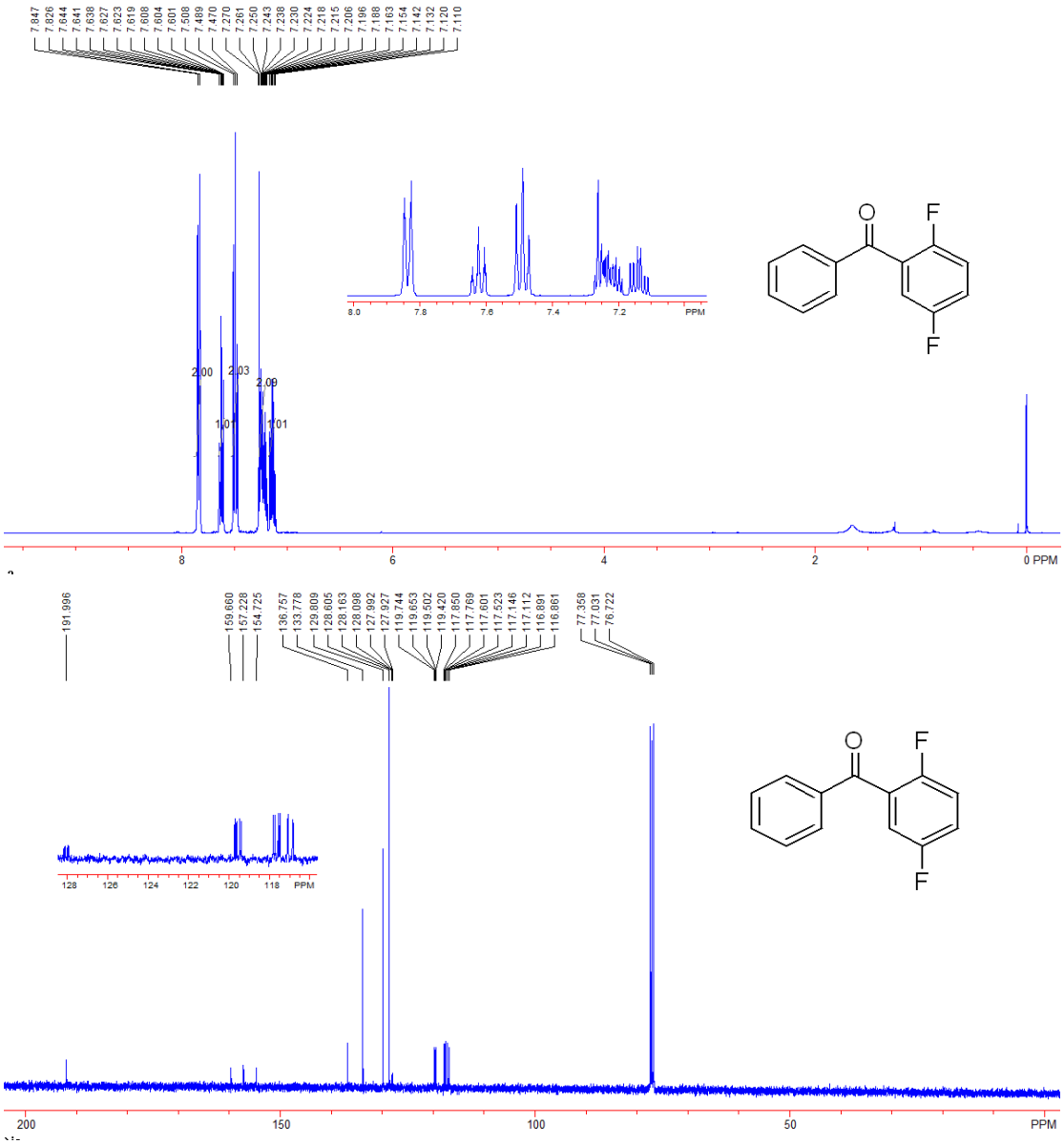
(7) 3,5-difluorobenzophenone (2f)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (981mg). m.p. 59–60 °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. Elemental Analysis: C, 71.56; H, 3.70; F, 17.41; O, 7.33. (Calcd. C, 71.56; H, 3.70; F, 17.41; O, 7.33).



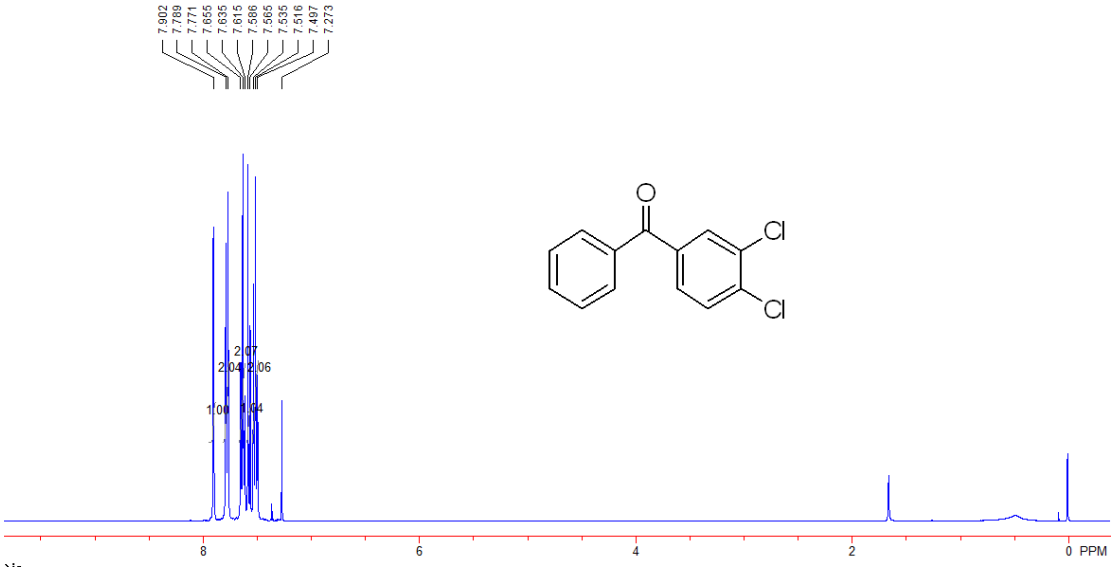
(8) 2,5-difluorobenzophenone (2g)

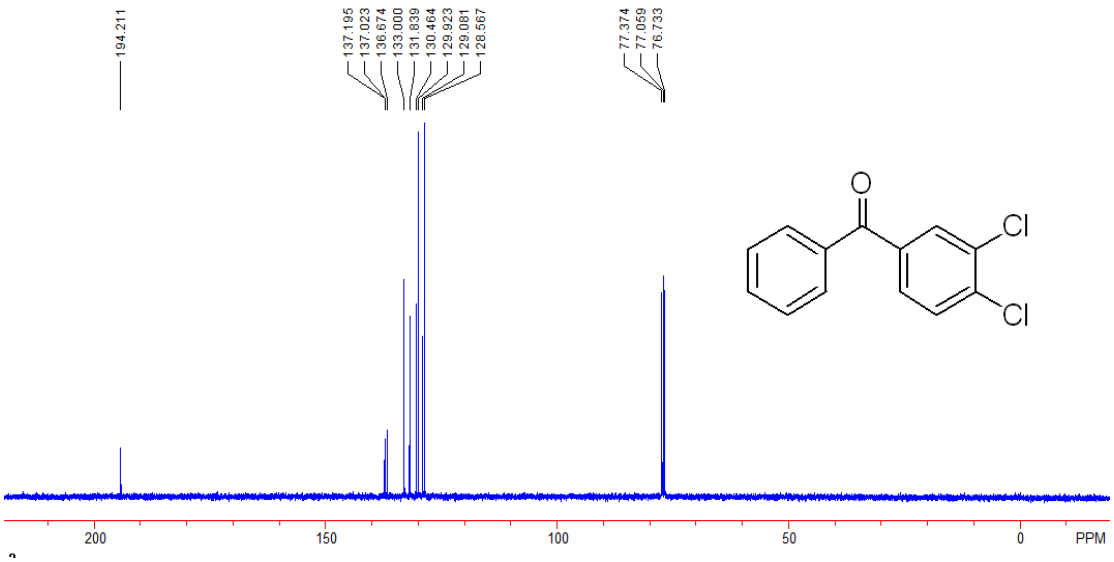
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a yellow oil (959mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.84 (d, J = 8.4 Hz, 2 H), 7.62 (tt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1 H), 7.49 (d, J = 7.6 Hz, 2 H), 7.19-7.27 (m, 2 H), 7.11-7.16 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.00, 159.66, 157.23(d, J = 250 Hz), 136.76, 133.78, 129.81, 128.61, 128.05 (dd, J_1 = 17.1 Hz, J_2 = 6.5 Hz), 119.58 (dd, J_1 = 23.7 Hz, J_2 = 8.6 Hz), 117.69 (dd, J_1 = 24.7 Hz, J_2 = 8.0 Hz), 117.01 (dd, J_1 = 18.3 Hz, J_2 = 7.3 Hz), 112.93 (dd, J_1 = 25.3 Hz, J_2 = 3.2 Hz). HRMS (EI) Calcd for $C_{13}H_8F_2O$ (M^+) 218.0543, Found 218.0540. Elemental Analysis: C, 71.55; H, 3.70; F, 17.41; O, 7.34. (Calcd. C, 71.56; H, 3.70; F, 17.41; O, 7.33).



(9) 3,4-dichlorobenzophenone (2h, 3g)

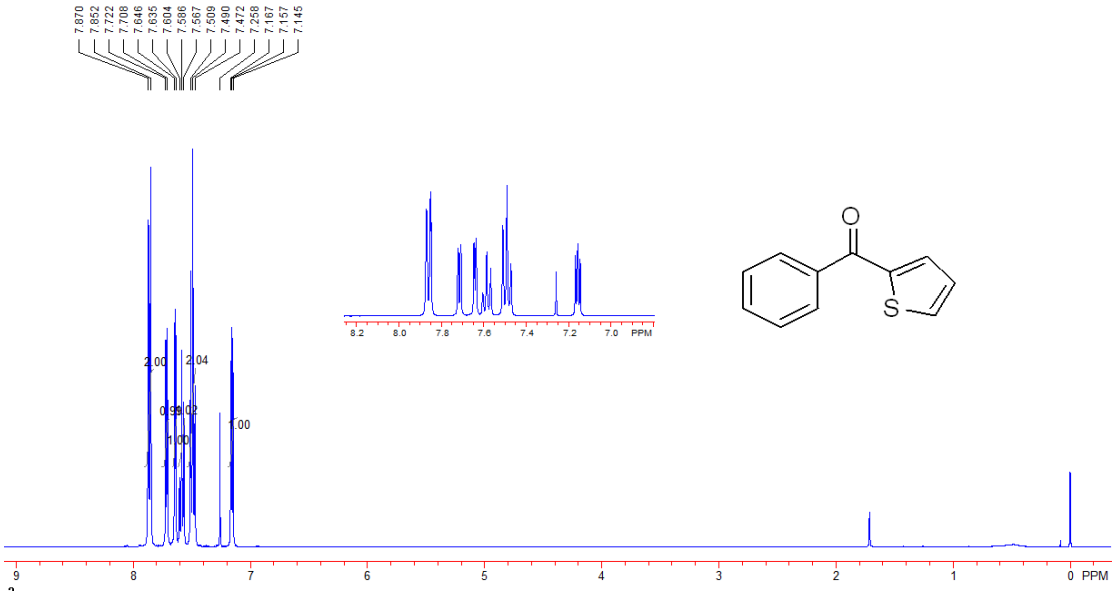
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (1154mg). m.p. 102–103 °C (lit.[4] mp 102–103 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90 (s, 1 H), 7.78 (d, J = 7.2 Hz, 2 H), 7.64 (t, J = 8.0 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.21, 137.20, 137.02, 136.67, 133.00, 131.84, 130.46, 129.92, 129.08, 128.57. HRMS (EI) Calcd for $C_{13}H_8Cl_2O$ (M^+) 249.9952, Found 249.9950. Elemental Analysis: C, 62.18; H, 3.21; Cl, 28.24; O, 6.37. (Calcd. C, 62.18; H, 3.21; Cl, 28.24; O, 6.37).

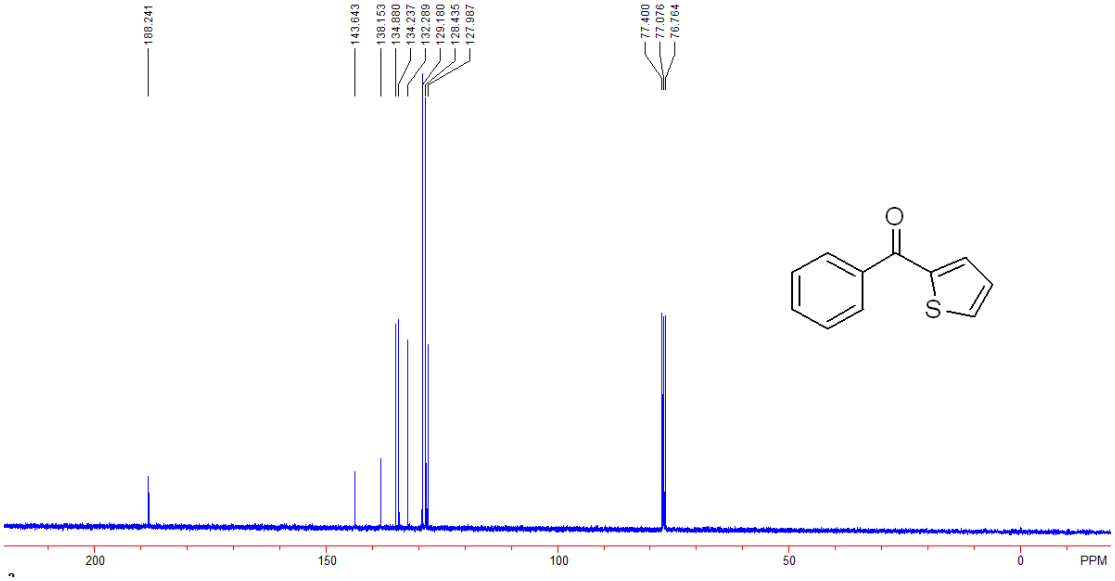




(10) 2-benzoylthiophene (2i, 3k)

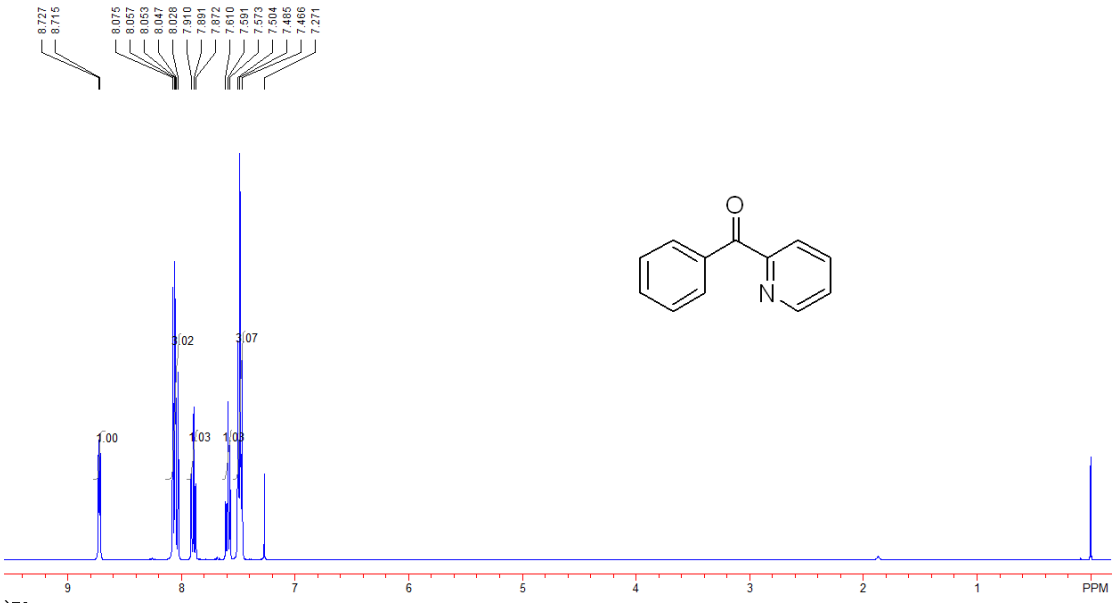
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (865mg). m.p. 53–55 ^{o}C (lit.[5] mp 54–55 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.86 (t, *J* = 7.2 Hz, 2 H), 7.72 (d, *J* = 5.6 Hz, 1 H), 7.64 (d, *J* = 4.4 Hz, 1 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.49 (t, *J* = 7.2 Hz, 2 H), 7.16 (t, *J* = 4.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.24, 143.64, 138.15, 134.88, 134.24, 132.29, 129.18, 128.44, 127.99. HRMS (EI) Calcd for $C_{11}H_8OS$ (M^+) 188.0296, Found 188.0299. Elemental Analysis: C, 70.18; H, 4.27; O, 8.50; S, 17.04. (Calcd.C, 70.18; H, 4.28; O, 8.50; S, 17.03).

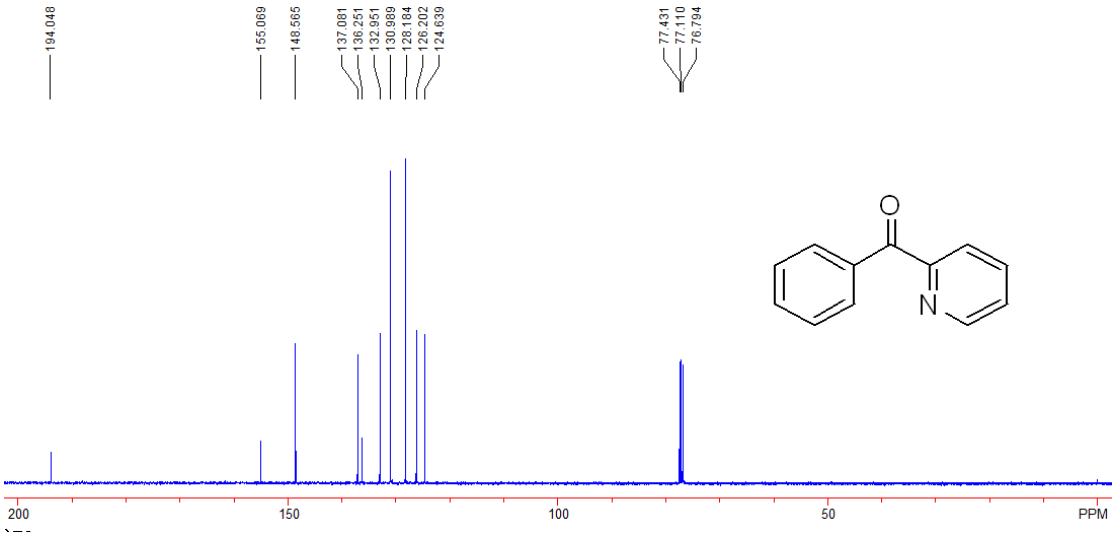




(11) 2-benzoylpyridine (2j, 3l)

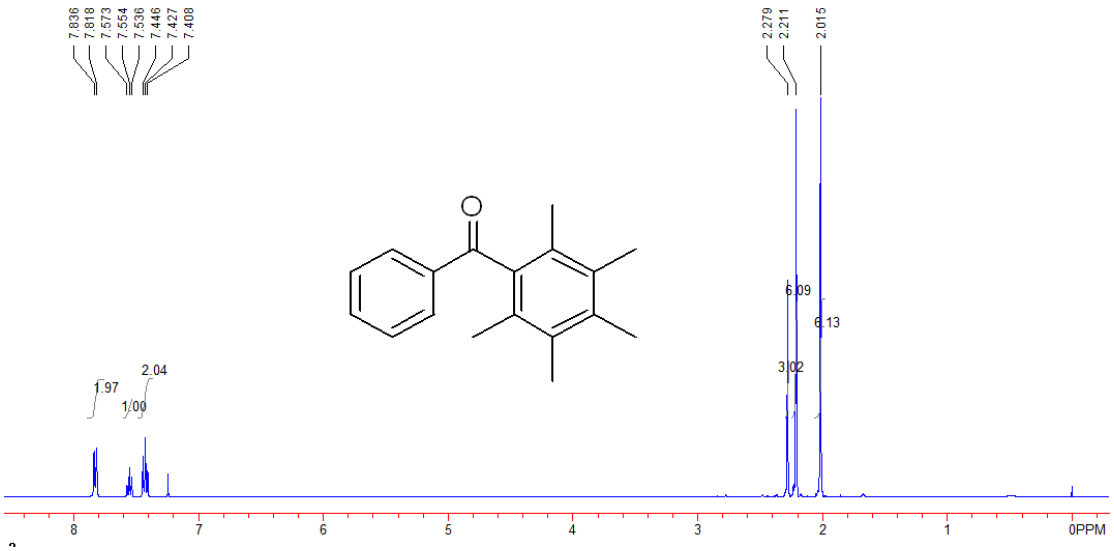
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a yellow solid (778mg). m.p. 41–42 °C (lit.[6] mp 42 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.72 (d, *J* = 4.8 Hz, 1 H), 8.03-8.08 (m, 3 H), 7.89 (t, *J* = 7.6 Hz, 1 H), 7.59 (d, *J* = 7.6 Hz, 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 183.0683. Elemental Analysis: C, 78.67; H, 4.95; N, 7.65; O, 8.73. (Calcd. C, 78.67; H, 4.95; N, 7.65; O, 8.73).

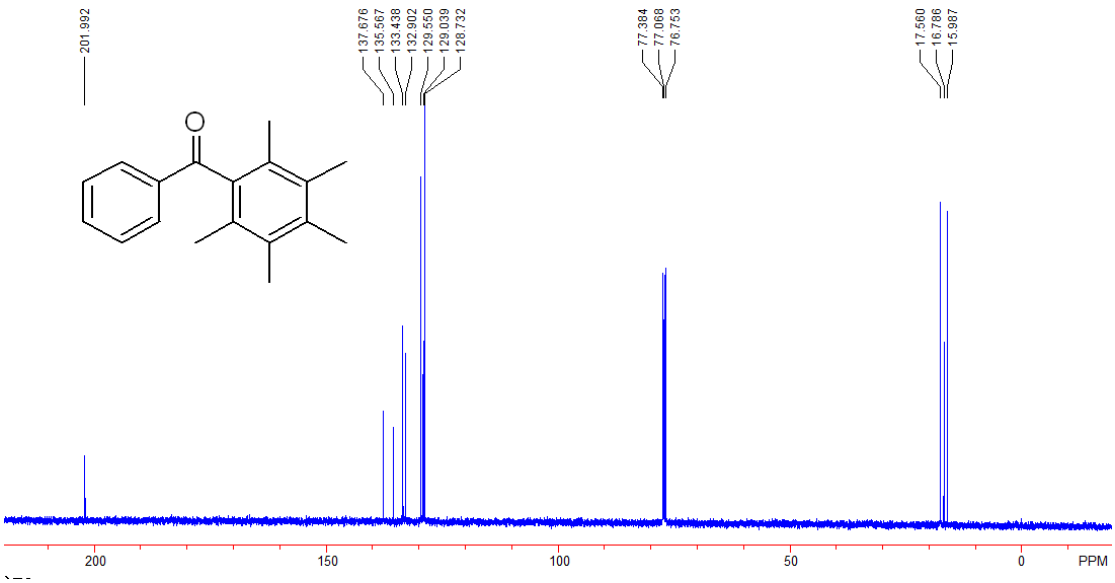




(12) 2,3,4,5,6-pentamethyl-benzophenone (2k)

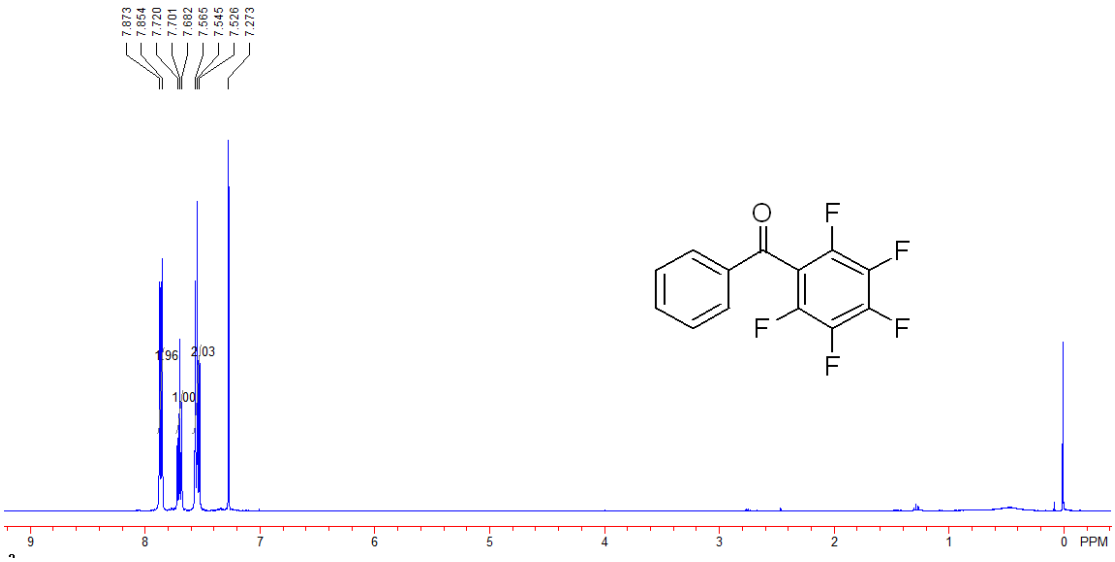
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (1046mg). m.p. 135–137 °C (lit.[7] mp 135–136 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (d, J = 7.2 Hz, 2 H), 7.55 (t, J = 7.2 Hz, 1 H), 7.43 (t, J = 7.6 Hz, 2 H), 2.28 (s, 3 H), 2.21 (s, 6 H), 2.02 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.99, 137.68, 135.57, 133.44, 132.90, 129.55, 129.04, 128.73, 17.56, 16.79, 15.99. HRMS (EI) Calcd for $C_{18}H_{20}O$ (M^+) 252.1514, Found 252.1517. Elemental Analysis: C, 85.67; H, 7.99; O, 6.34. (Calcd. C, 85.67; H, 7.99; O, 6.34).

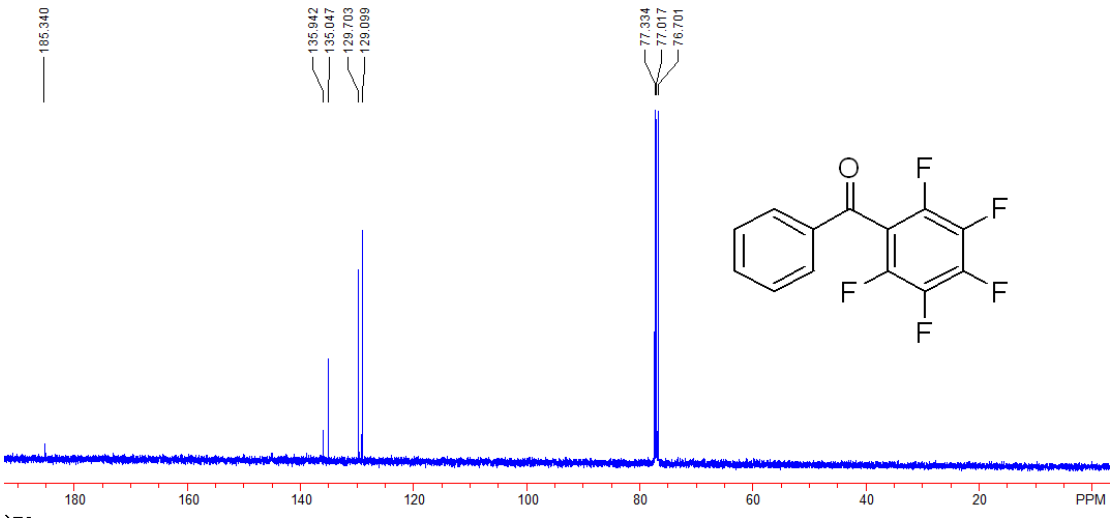




(13) 2,3,4,5,6-perfluoro-benzophenone (2l)

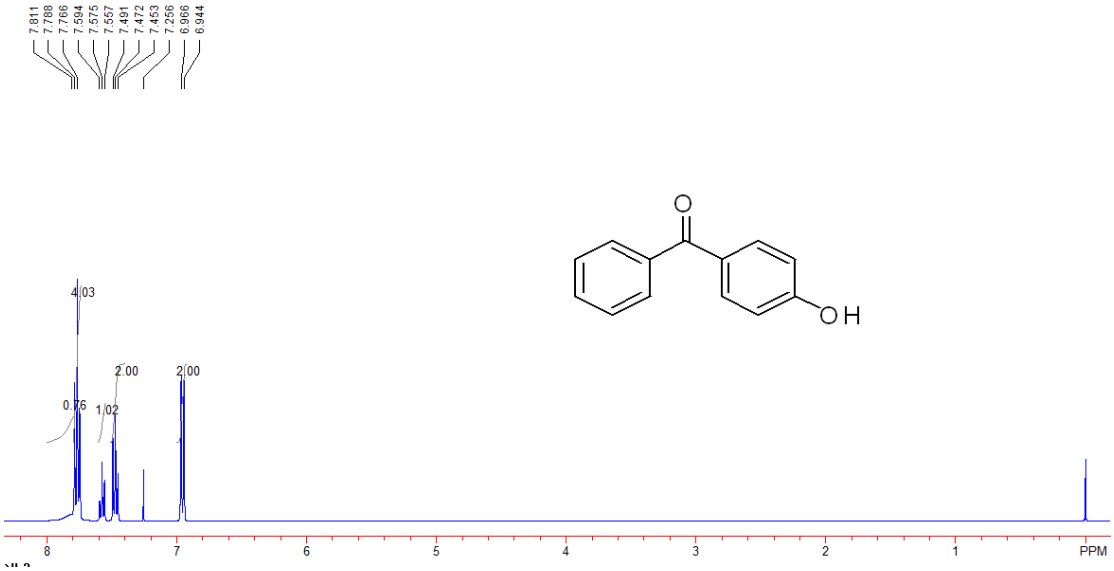
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a white solid (1156mg). m.p. 35–36 ^{o}C (lit.[8] mp 33–34 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.86 (d, J = 7.6 Hz, 2 H), 7.70 (t, J = 7.6 Hz, 1 H), 7.55 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.34, 135.94, 135.05, 129.70, 129.10. HRMS (EI) Calcd for $C_{13}H_5F_5O$ (M^+) 272.0261, Found 272.0263. Elemental Analysis: C, 57.37; H, 1.85; F, 34.90; O, 5.88. (Calcd. C, 57.37; H, 1.85; F, 34.90; O, 5.88).

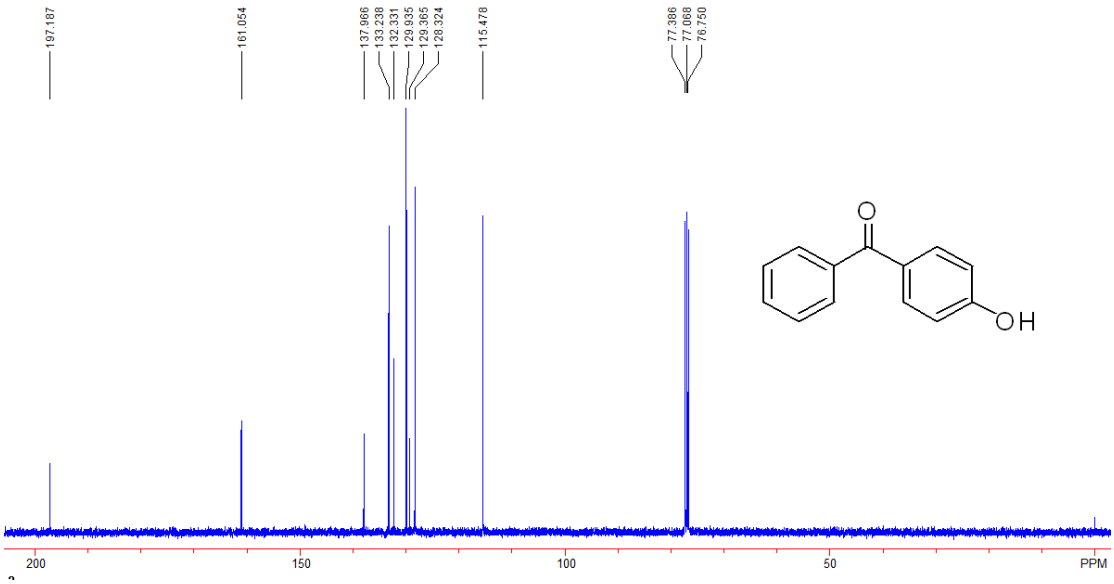




(14) 4-hydroxy-benzophenone (2m, 3m)

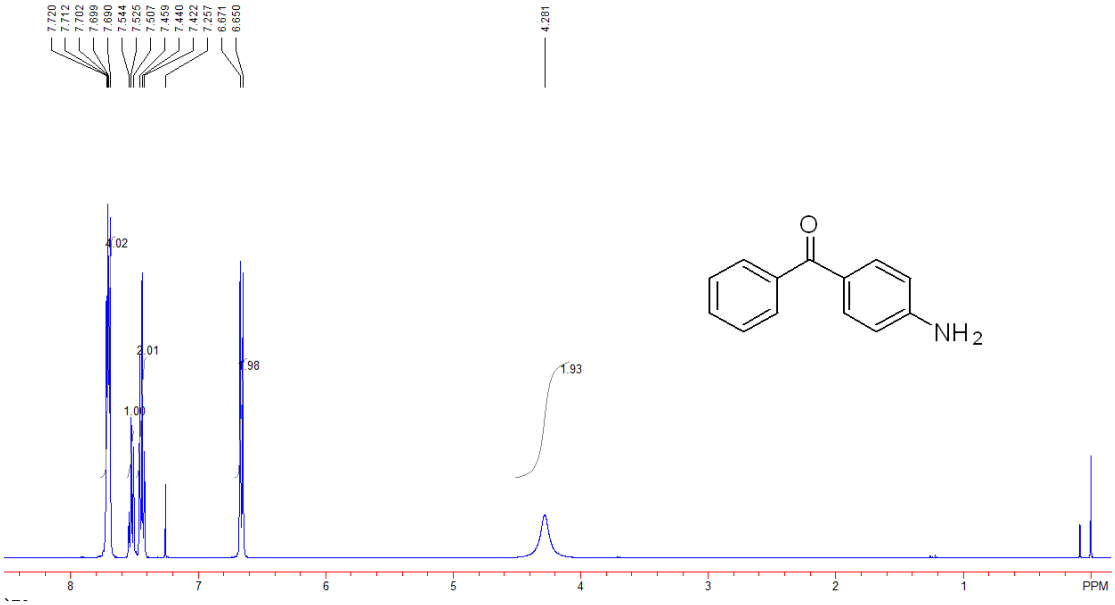
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 1/15/0.08, v/v/v) afforded as a white solid (772mg). m.p. 133–135 ºC (lit.[9] mp 133–134 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (br, 1 H), 7.78 (d, *J* = 8.8 Hz, 4 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.19, 161.05, 137.97, 133.24, 132.33, 129.94, 129.37, 128.32, 115.48. HRMS (EI) Calcd for $C_{13}H_{10}O_2$ (M^+) 198.0681, Found 198.0677. Elemental Analysis: C, 78.77; H, 5.09; O, 16.14. (Calcd. C, 78.77; H, 5.09; O, 16.14).

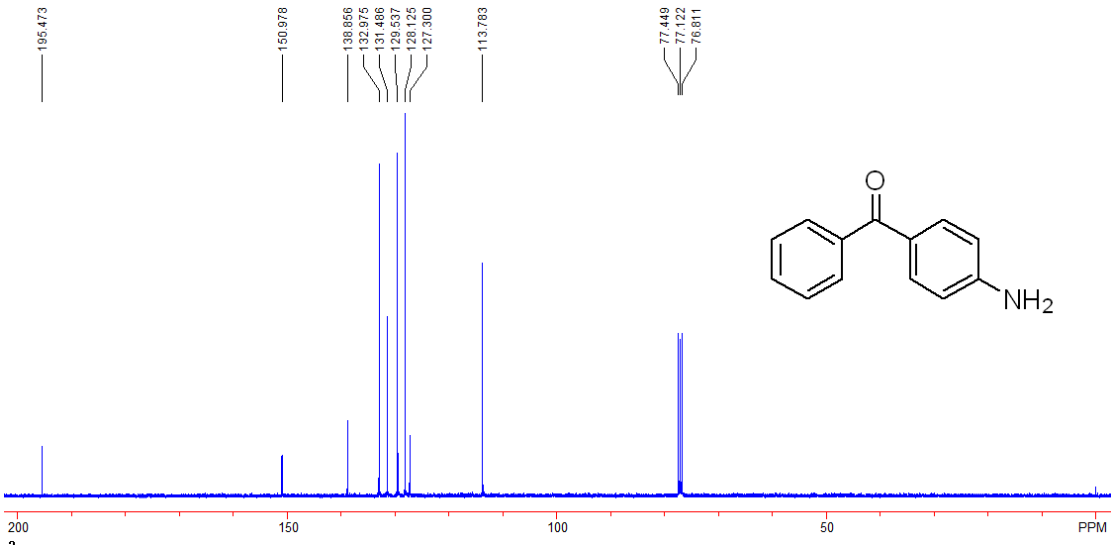




(15) 4-aminobenzophenone (2n, 3n)

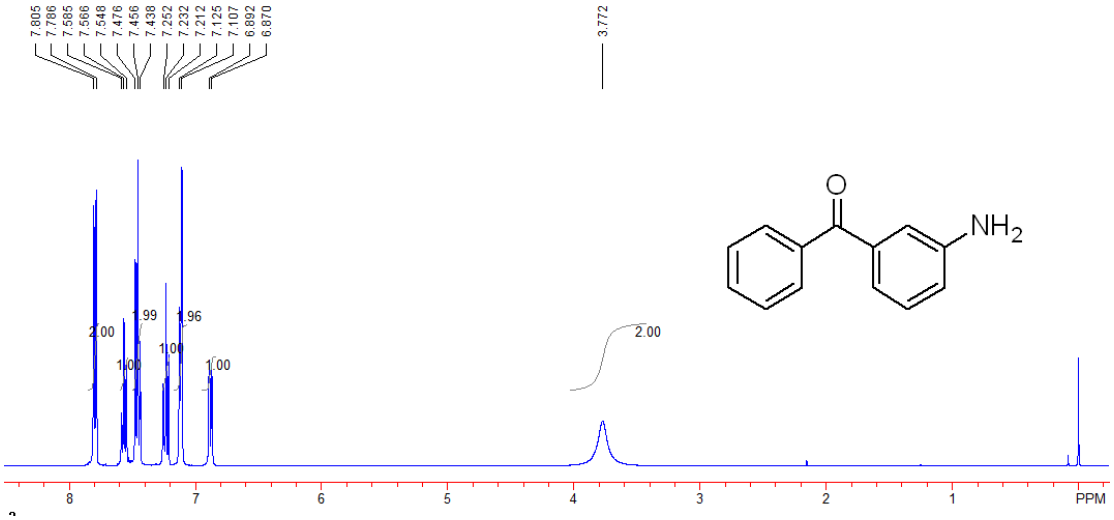
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 1/10/0.05, v/v/v) afforded as a yellow solid (719mg). m.p. 121–122 °C (lit.[5] mp 120–121 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.69-7.72 (m, 4 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 6.67 (d, *J* = 8.4 Hz, 2 H), 4.28 (br, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.47, 150.98, 138.86, 132.98, 131.49, 129.54, 128.13, 127.30, 112.78. HRMS (EI) Calcd for $C_{13}H_{11}NO$ (M^+) 197.0841, Found 197.0839. Elemental Analysis: C, 79.16; H, 5.63; N, 7.10; O, 8.11. (Calcd. C, 79.16; H, 5.62; N, 7.10; O, 8.11).

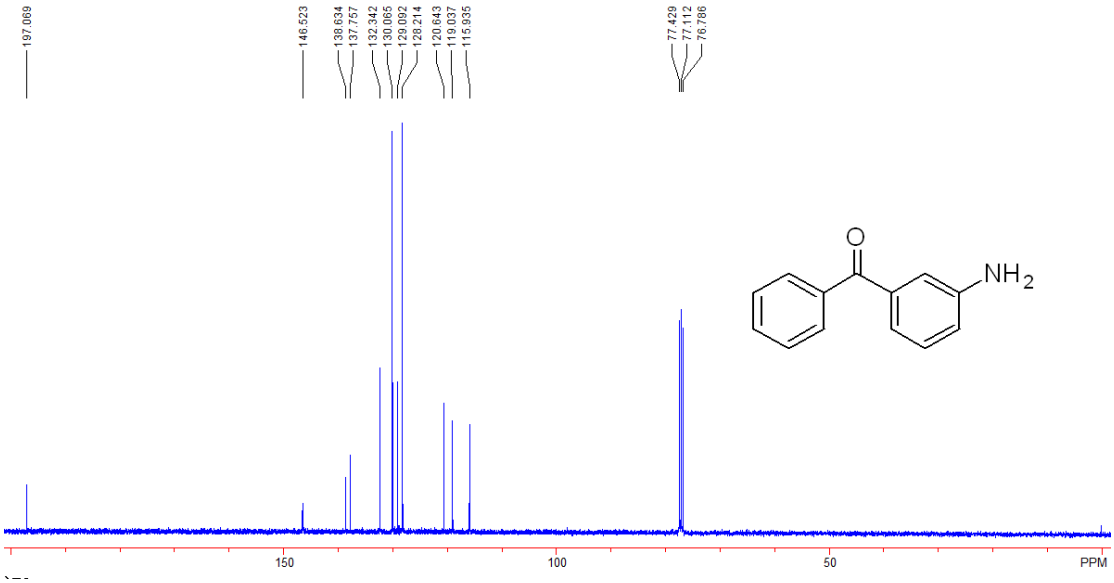




(16) 3-aminobenzophenone (2o, 3o)

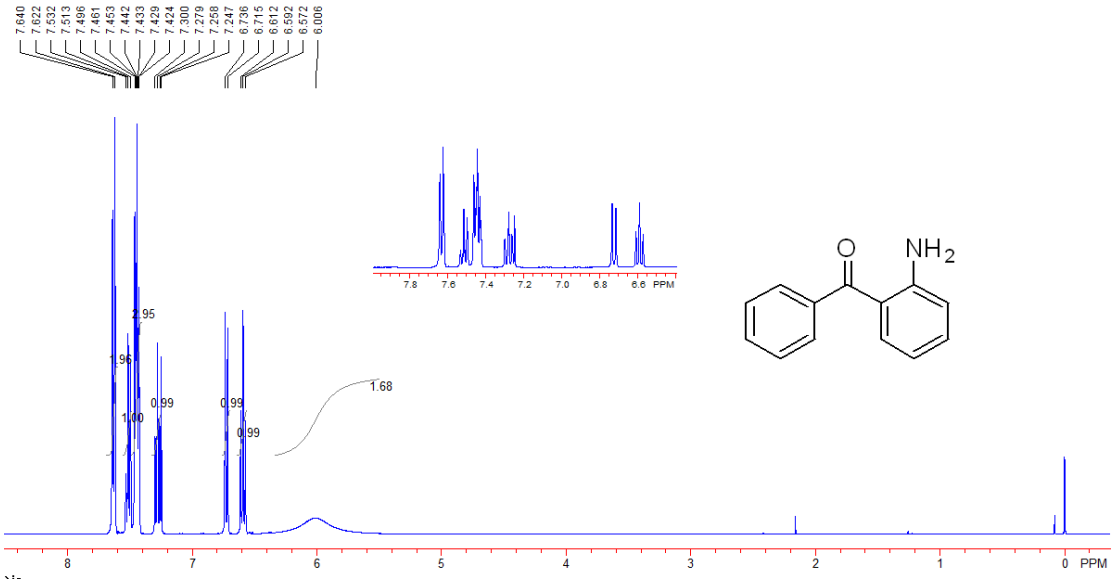
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 1/10/0.05, v/v/v) afforded as a yellow solid (778mg). m.p. 84–85 °C (lit.[10] mp 84–86 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.80 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 7.12 (d, *J* = 7.2 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 1 H), 3.77 (br, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.07, 146.52, 138.63, 137.76, 132.34, 130.07, 129.09, 128.21, 120.64, 119.04, 115.94. HRMS (EI) Calcd for $C_{13}H_{11}NO$ (M^+) 197.0841, Found 197.0844. Elemental Analysis: C, 79.16; H, 5.63; N, 7.11; O, 8.10. (Calcd. C, 79.16; H, 5.62; N, 7.10; O, 8.11).

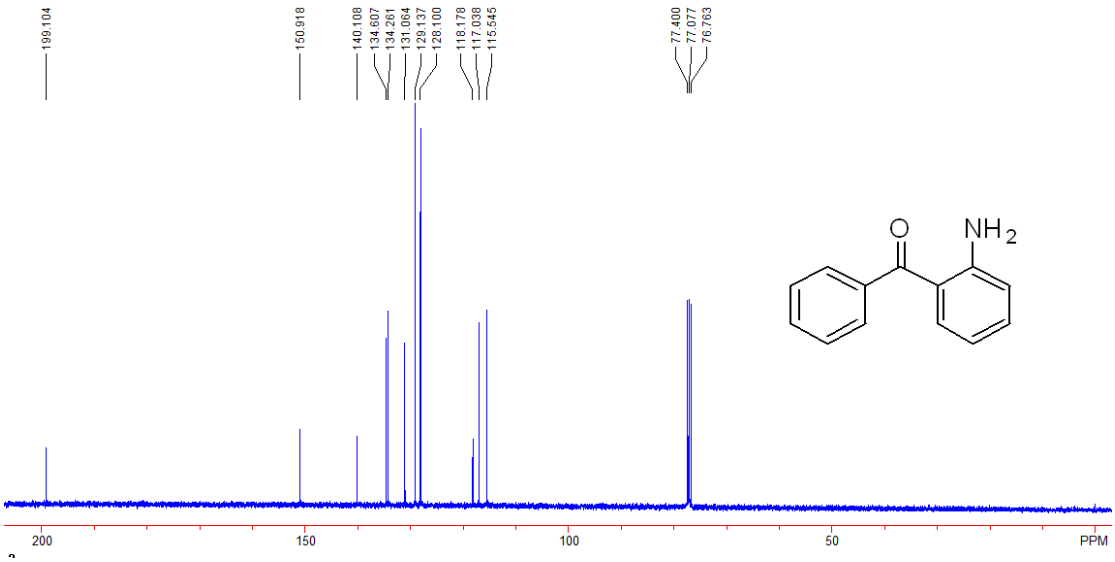




(17) 2-aminobenzophenone (2p, 3p)

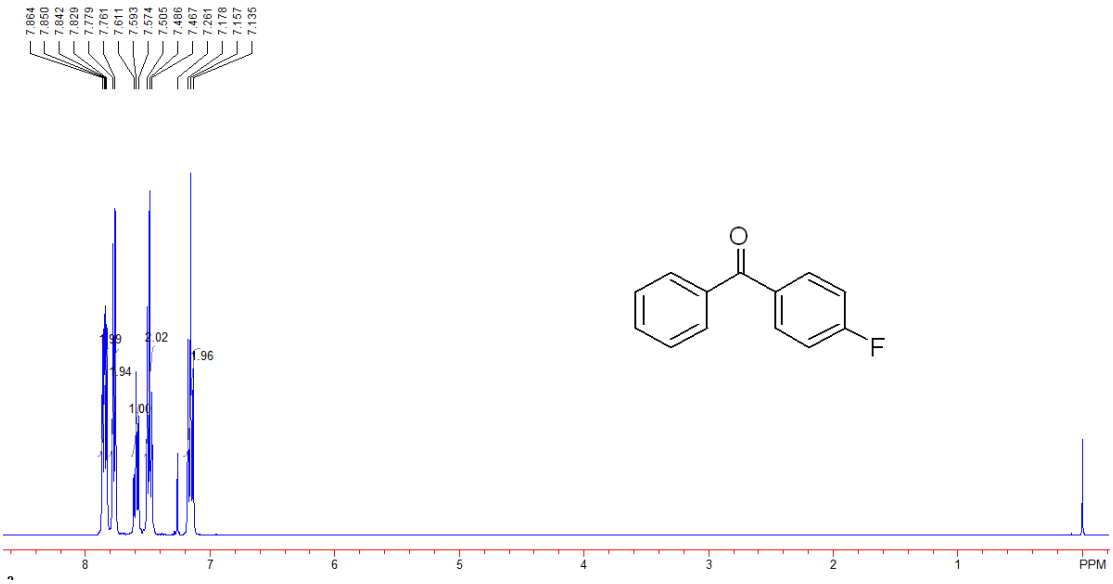
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 1/10/0.05, v/v/v) afforded as a yellow solid (788mg). m.p. 104–105 °C (lit.[11] mp 103–104 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, *J* = 7.2 Hz, 2 H), 7.51 (t, *J* = 7.2 Hz, 1 H), 7.42-7.46 (m, 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), 6.00 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.10, 150.92, 140.11, 134.61, 134.26, 131.06, 129.14, 128.10, 118.18, 117.04, 115.55. HRMS (EI) Calcd for $C_{13}H_{11}NO$ (M^+) 197.0841, Found 197.0845. Elemental Analysis: C, 79.16; H, 5.63; N, 7.10; O, 8.11. (Calcd. C, 79.16; H, 5.62; N, 7.10; O, 8.11).

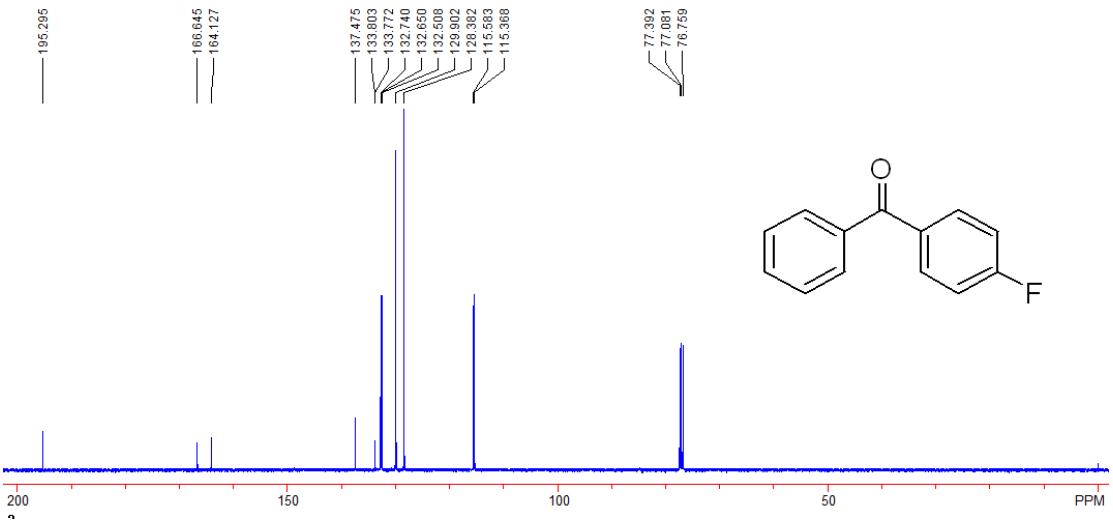




(18) 4-fluorobenzophenone (3c)

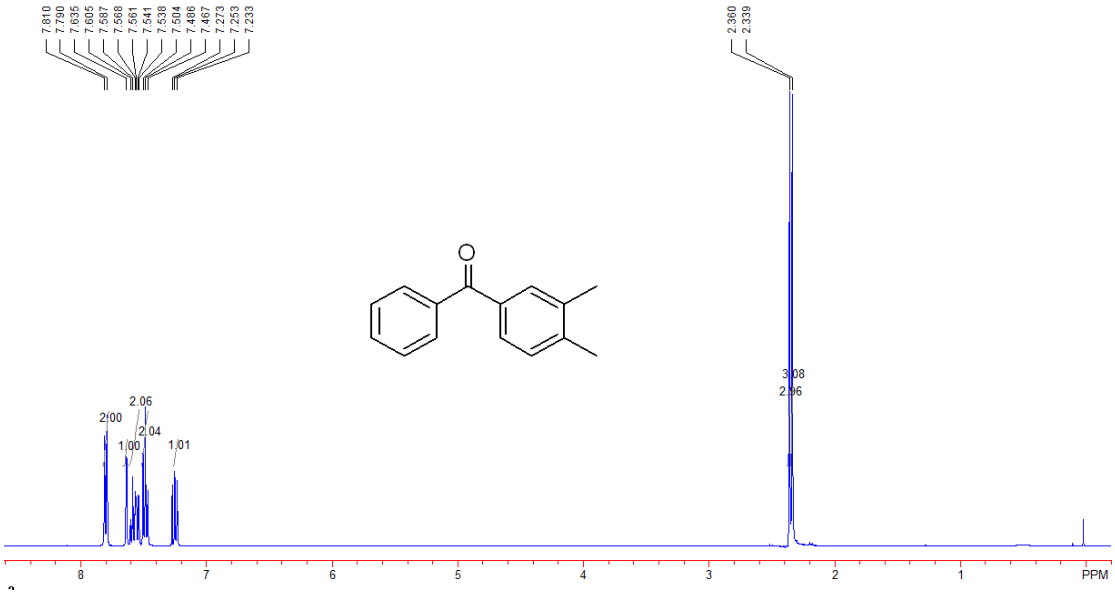
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (890mg). m.p. 45–46 ºC (lit.[12] mp 45–47 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (dd, J_1 = 8.4 Hz, J_2 = 5.2 Hz, 2 H), 7.77 (d, J = 7.2 Hz, 2 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.16 (t, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.30, 166.65 (d, J = 252 Hz), 137.48, 133.78, 132.74(d, J = 9.0 Hz), 132.51, 129.90, 128.38, 115.58 (d, J = 21 Hz). HRMS (EI) Calcd for $C_{13}H_9FO$ (M^+) 200.0637, Found 200.0639. Elemental Analysis: C, 77.99; H, 4.53; F, 9.49; O, 7.99. (Calcd. C, 77.99; H, 4.53; F, 9.49; O, 7.99).

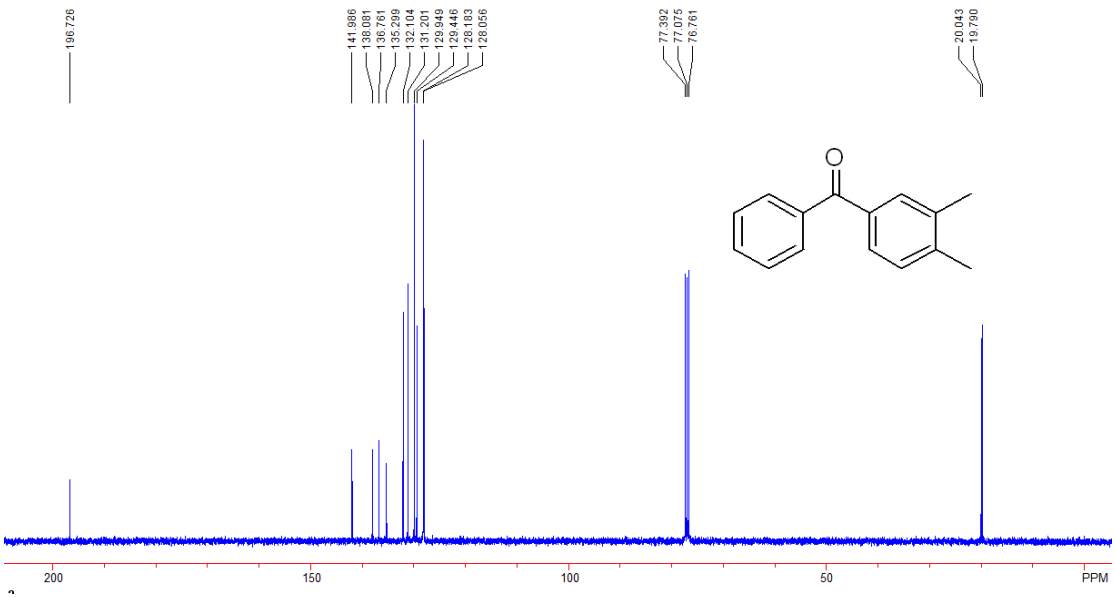




(19) 3,4-dimethylbenzophenone (3f)

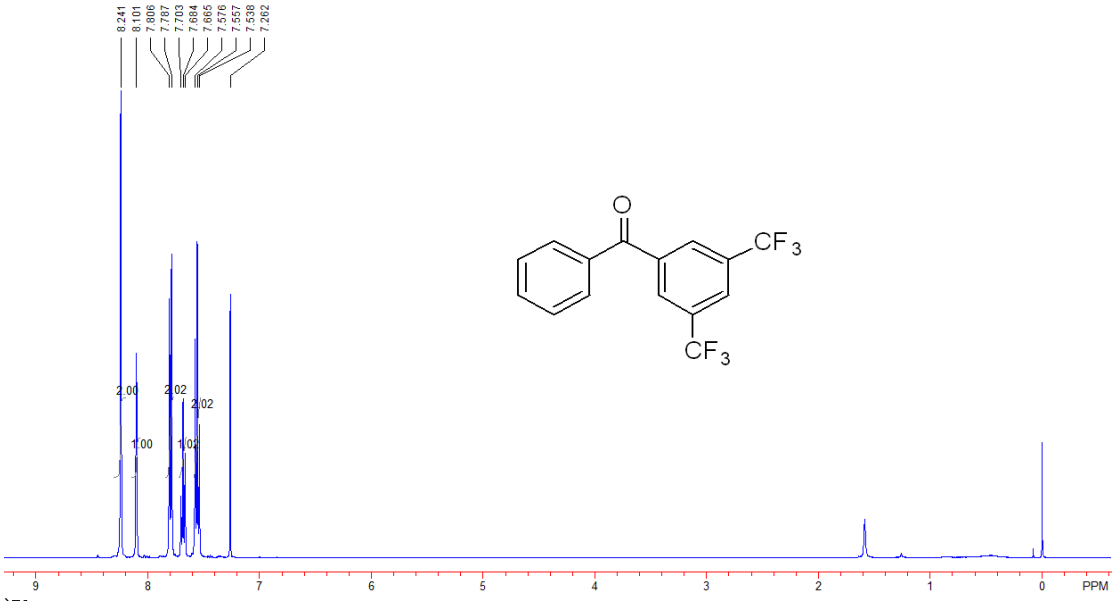
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (966mg). m.p. 48–49 ºC (lit.[13] mp 47–49 °C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.81 (d, *J* = 8.0 Hz, 2 H), 7.64 (s, 1 H), 7.54-7.61 (m, 2 H), 7.49 (t, *J* = 7.2 Hz, 2 H), 7.25 (t, *J* = 8.0 Hz, 1 H), 2.36 (s, 3 H), 2.34 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.73, 141.99, 138.08, 136.76, 135.30, 132.10, 131.20, 129.95, 129.45, 128.18, 128.06, 20.04, 19.79. HRMS (EI) Calcd for $C_{15}H_{14}O$ (M^+) 210.1045, Found 210.1044. Elemental Analysis: C, 85.68; H, 6.71; O, 7.61. (Calcd. C, 85.68; H, 6.71; O, 7.61).

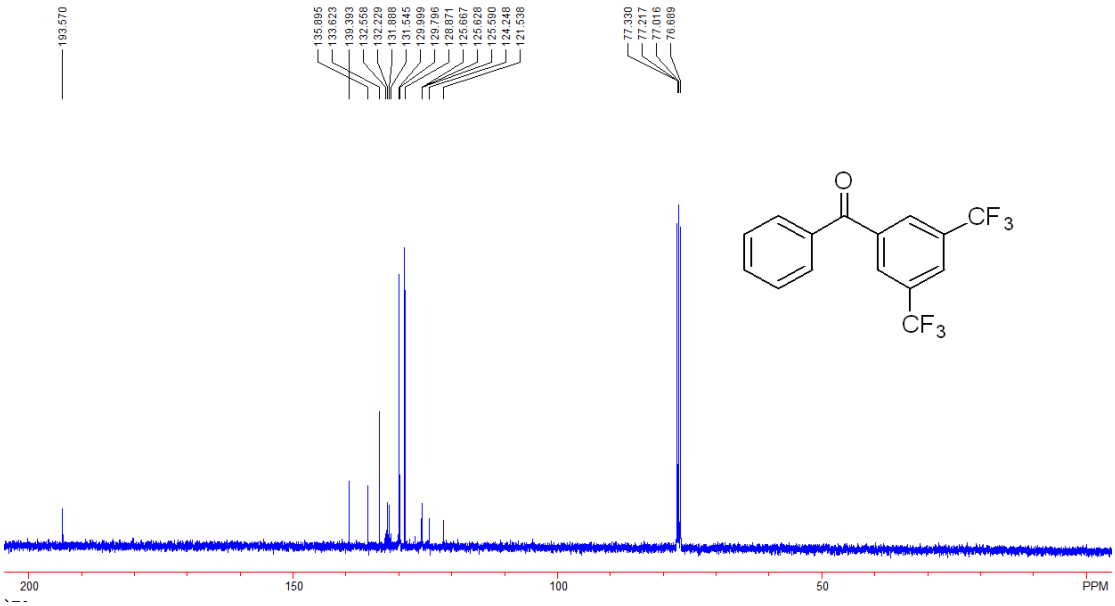




(20) 3,5-bis(trifluoromethyl)benzophenone (3h)

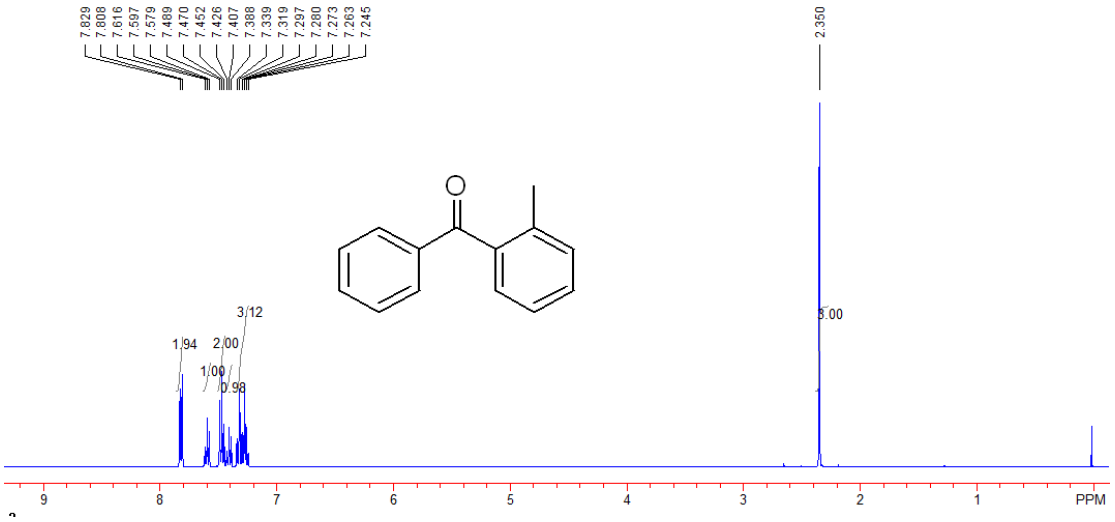
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a white solid (1288mg). m.p. 109–110 °C (lit.[14] mp 109–111 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.24 (s, 2 H), 8.10 (s, 1 H), 7.80 (d, J = 7.6 Hz, 2 H), 7.68 (t, J = 7.6 Hz, 1 H), 7.56 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.57, 139.39, 135.90, 133.62, 132.00 (dd, J_1 = 67.2 Hz, J_2 = 33.6 Hz), 130.00, 129.80, 128.87, 125.63 (t, J = 3.9 Hz), 124.25, 121.54(q, J = 271 Hz). HRMS (EI) Calcd for $C_{15}H_8F_6O$ (M^+) 318.0479, Found 318.0481. Elemental Analysis: C, 56.62; H, 2.53; F, 35.82; O, 5.03. (Calcd. C, 56.62; H, 2.53; F, 35.82; O, 5.03).

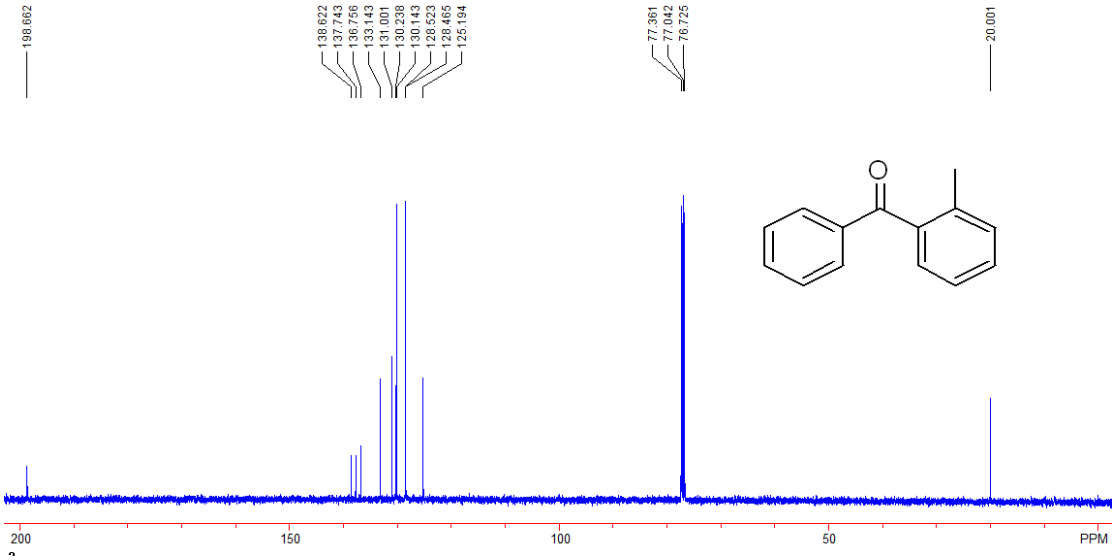




(21) 2-methylbenzophenone (3i)

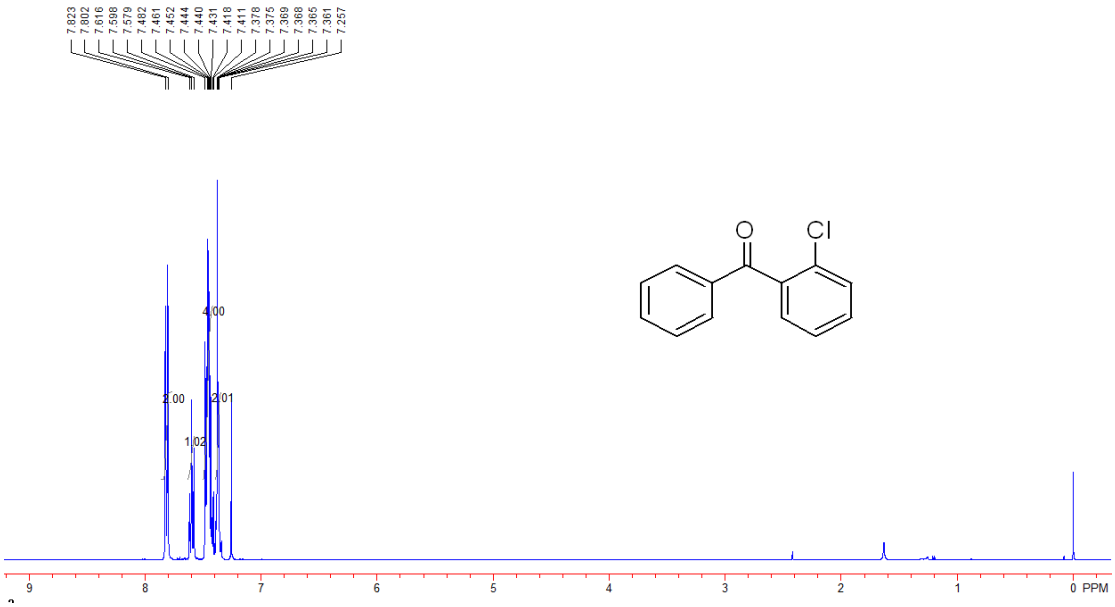
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a colorless oil (813mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (d, J = 8.4 Hz, 2 H), 7.60 (t, J = 7.6 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 7.41 (t, J = 7.6 Hz, 1 H),7.24-7.34 (m, 3 H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.66, 138.62, 137.74, 136.76, 133.14, 131.00, 130.24, 130.14, 128.52, 128.47, 125.19, 20.00. HRMS (EI) Calcd for $C_{14}H_{12}O$ (M^+) 196.0888, Found 196.0884. Elemental Analysis: C, 85.68; H, 6.17; O, 8.15. (Calcd. C, 85.68; H, 6.16; O, 8.15).

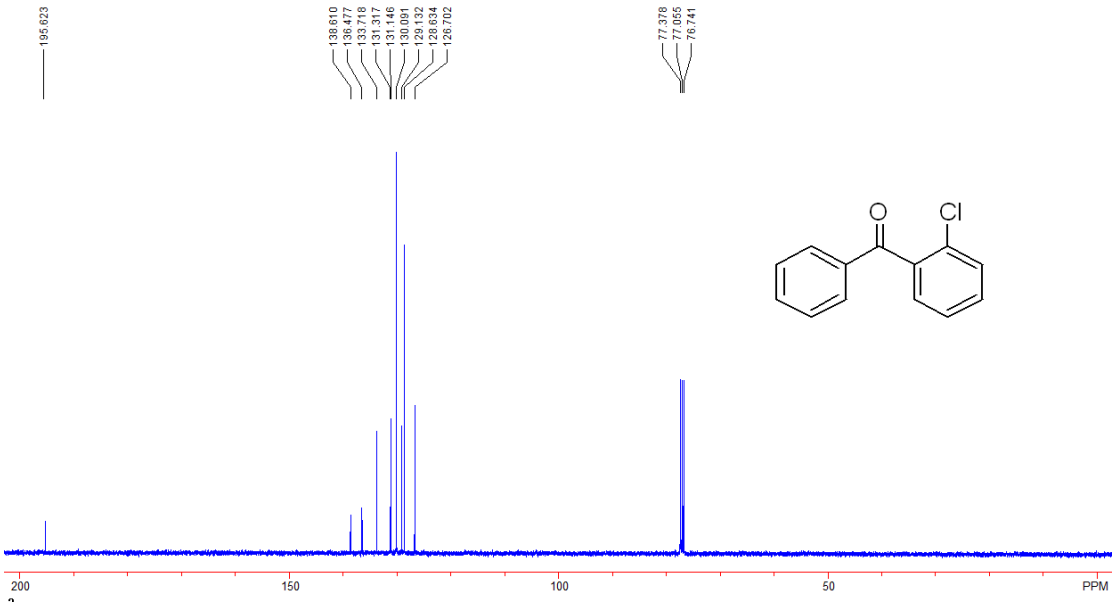




(22) 2-chlorobenzophenone (3j)

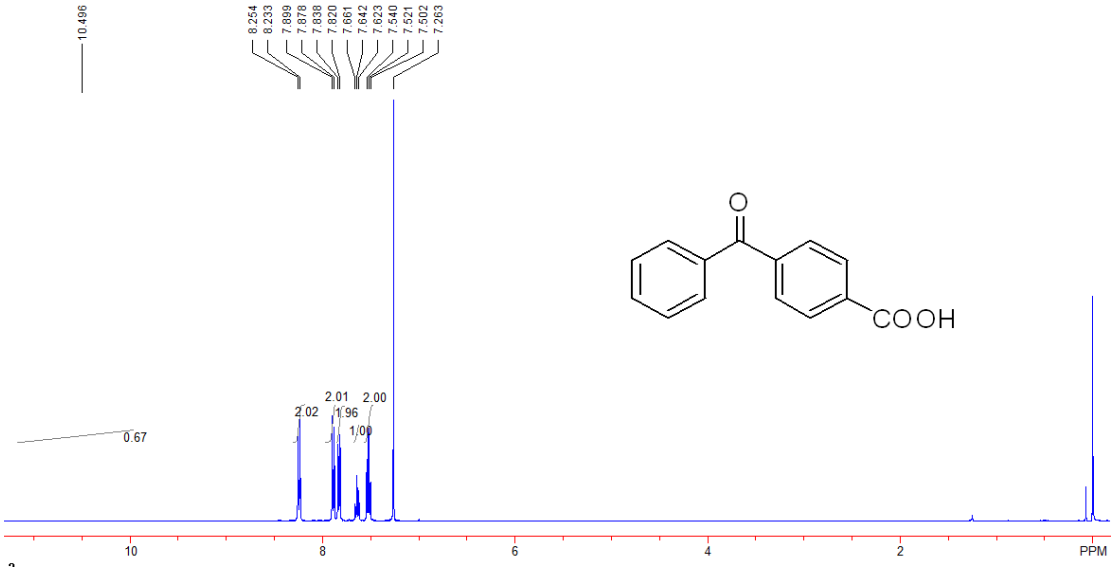
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (942mg). m.p. 45–46 ºC (lit.[1] mp 43–45 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.4 Hz, 2 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.41-7.48 (m, 4 H), 7.36-7.38 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.62, 138.61, 136.48, 133.72, 131.32, 131.15, 130.09, 129.13, 128.63, 126.70. HRMS (EI) Calcd for $C_{13}H_9ClO$ (M^+) 216.0342, Found 216.0343. Elemental Analysis: C, 72.07; H, 4.19; Cl, 16.36; O, 7.38. (Calcd. C, 72.07; H, 4.19; Cl, 16.36; O, 7.38).

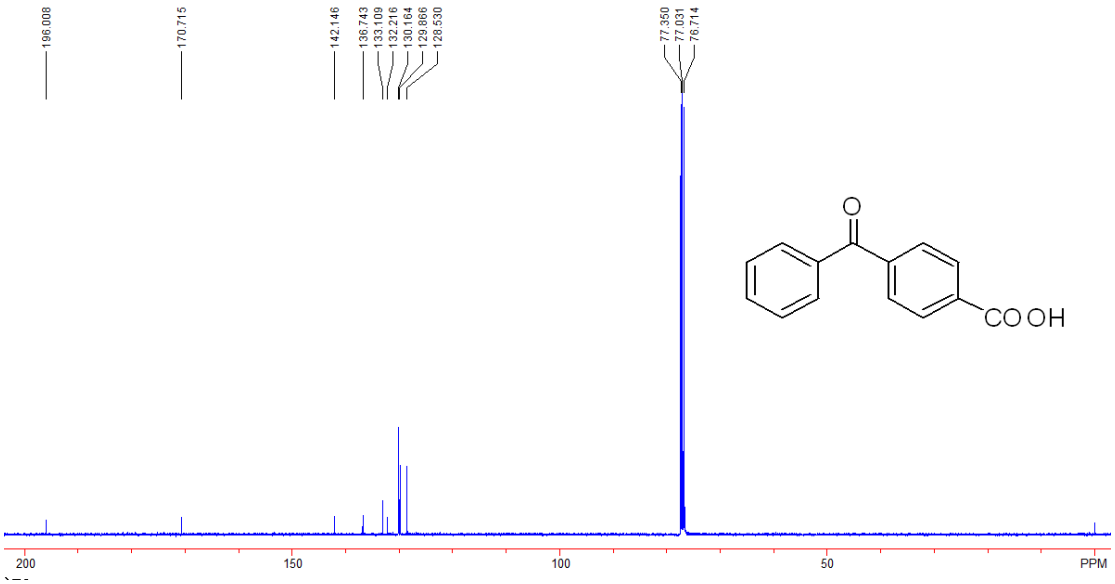




(23) 4-benzoylbenzoic acid (4a)

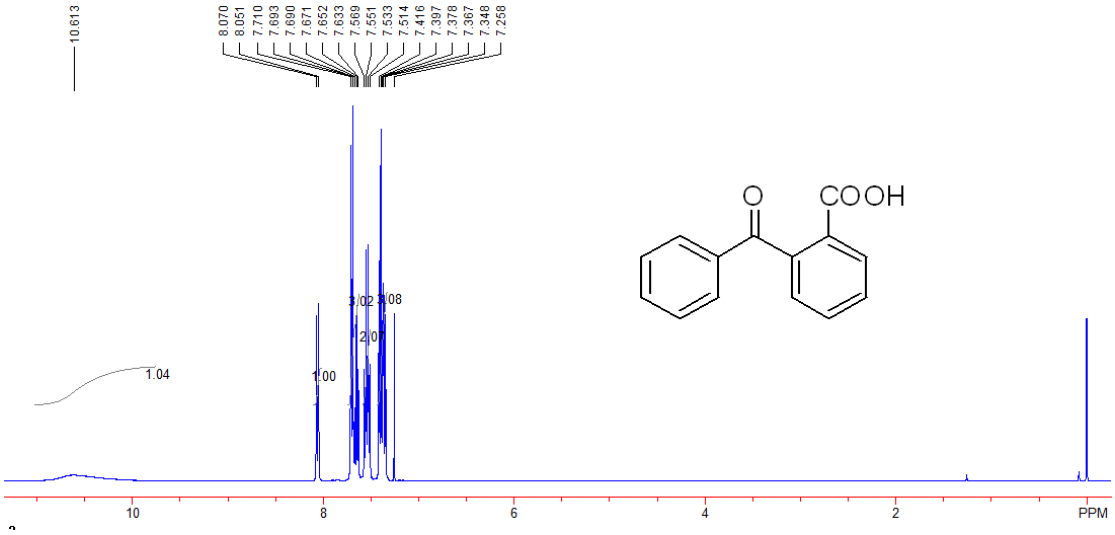
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 4/1/0.025, v/v/v) afforded as a white solid (169mg). m.p. 197–199 °C (lit.[15] mp 198–200 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.50 (br, 1 H), 8.24 (d, *J* = 8.4 Hz, 2 H), 7.89 (d *J* = 8.4 Hz, 2 H), 7.83 (d, *J* = 7.2 Hz, 2 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.01, 170.72, 142.15, 136.74, 133.11, 132.22, 130.16, 129.87, 128.53. HRMS (EI) Calcd for $C_{14}H_{10}O_3$ (M^+) 226.0630, Found 226.0628. Elemental Analysis: C, 74.32; H, 4.46; O, 21.22. (Calcd. C, 74.33; H, 4.46; O, 21.22).

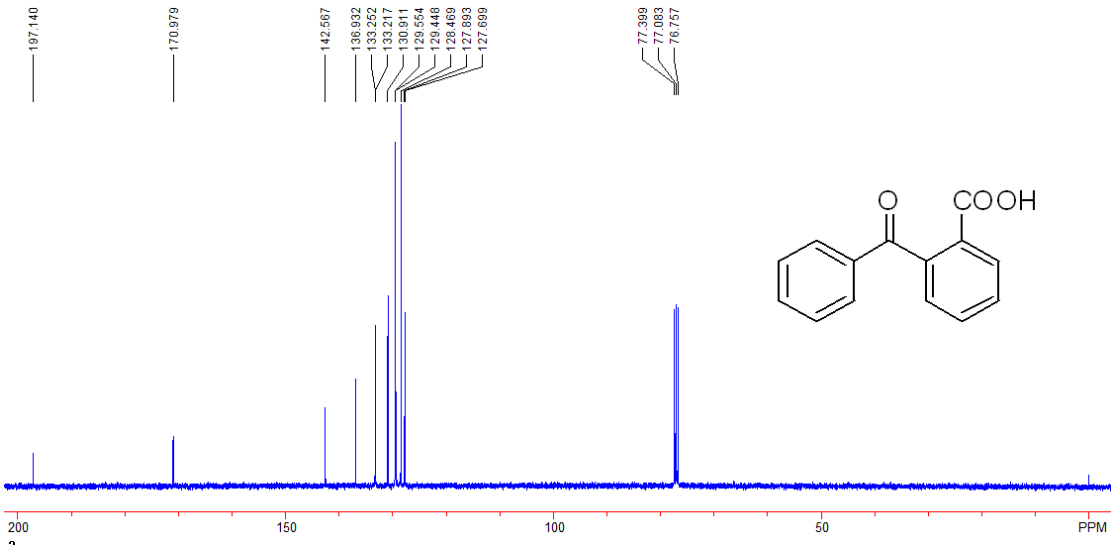




(24) 2-benzoylbenzoic acid (4b)

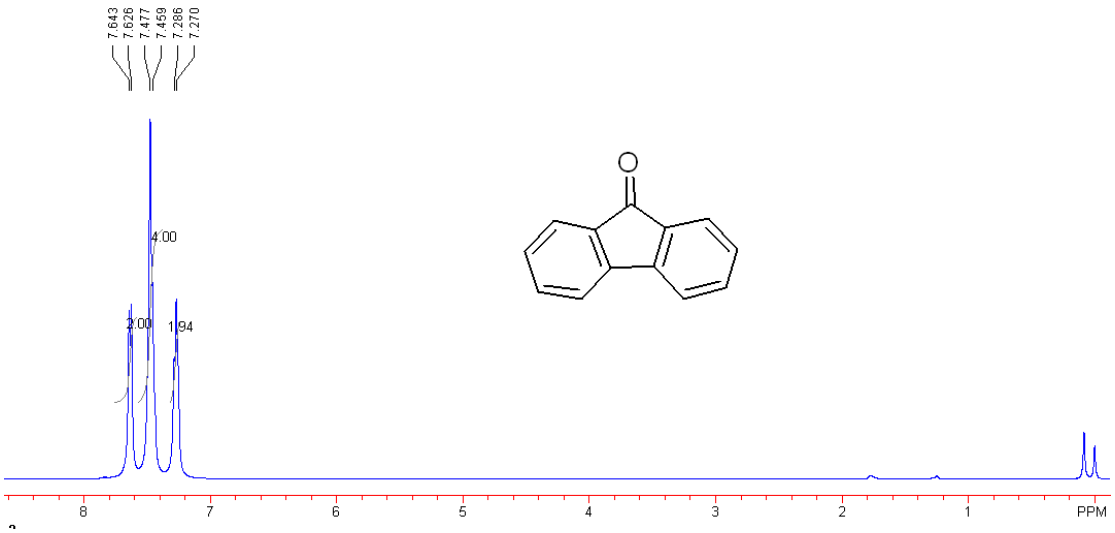
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 4/1/0.025, v/v/v) afforded as a white solid (160mg). m.p. 123–125 °C (lit.[16] mp 124–125 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ10.61 (br, 1 H), 8.06 (d, J = 7.6 Hz, 1 H), 7.63-7.71 (m, 3 H), 7.54 (dd, J_1 = 14.4 Hz, J_2 = 7.2 Hz, 2 H), 7.35-7.42 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.14, 170.98, 142.57, 136.93, 133.25, 133.22, 130.91, 129.55, 129.45, 128.47, 127.89, 127.70. HRMS (EI) Calcd for $C_{14}H_{10}O_3$ (M^+) 226.0630, Found 226.0634. Elemental Analysis: C, 74.33; H, 4.45; O, 21.22. (Calcd. C, 74.33; H, 4.46; O, 21.22).

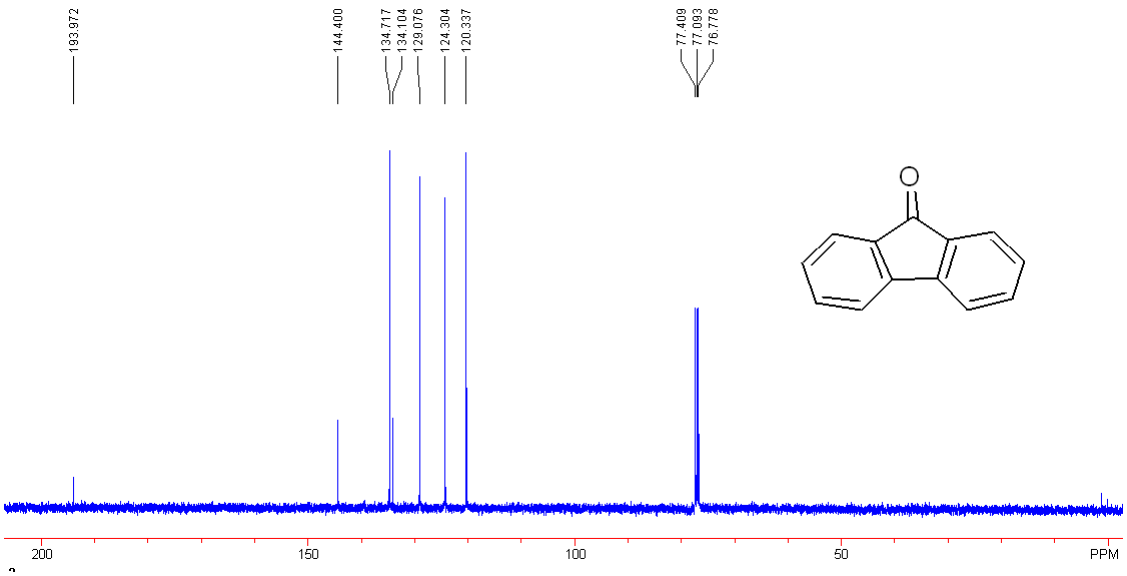




(25) 9-Fluorenone (4c)

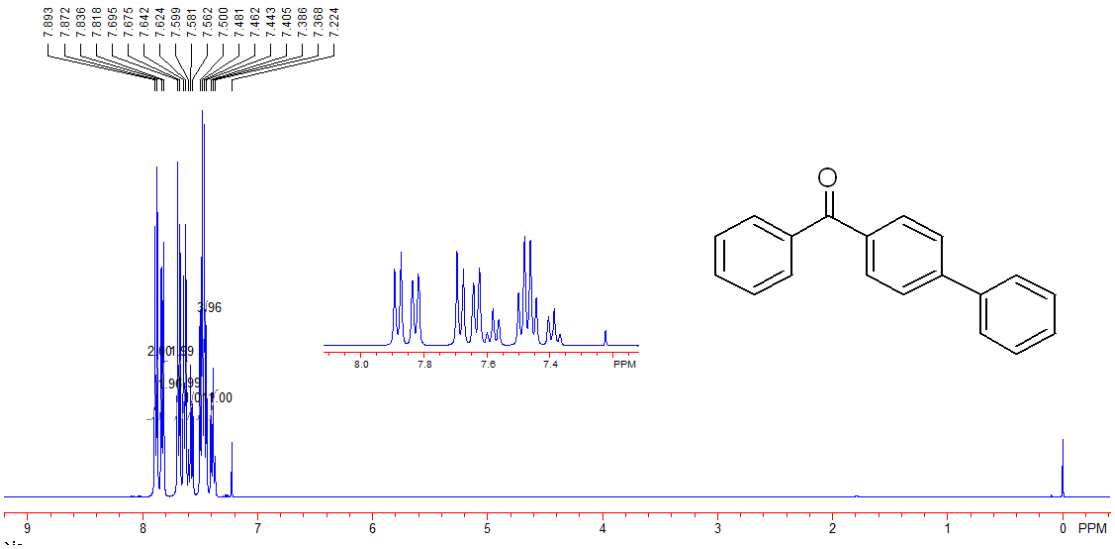
Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a yellow solid (112mg). m.p. 75–76 ºC (lit.[4] mp 75–76 °C);[1]H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, *J* = 6.8 Hz, 2 H), 7.47 (d, *J* = 7.2 Hz, 4 H), 7.28 (d, *J* = 6.4 Hz, 2 H). [13]C NMR (100 MHz, $CDCl_3$) δ 193.97, 144.40, 134.72, 134.10, 129.08, 124.30, 120.34. HRMS (EI) Calcd for $C_{13}H_8O$ (M^+) 180.0575, Found 180.0573. Elemental Analysis: C, 86.65; H, 4.47; O, 8.88. (Calcd. C, 86.65; H, 4.47; O, 8.88).

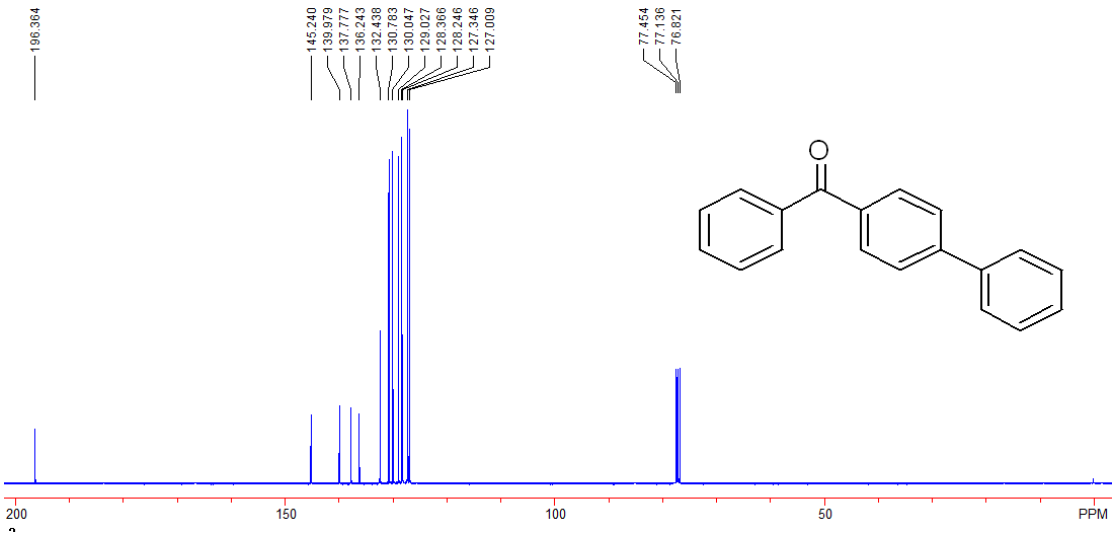




(26) 4-biphenylyl-benzophenone (5a)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (224mg). m.p. 100–102 ^{o}C (lit.[17] mp 101–102 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.88 (d, J = 8.4 Hz, 2 H), 7.83 (d, J = 7.2 Hz, 2 H), 7.69 (d, J = 8.0 Hz, 2 H), 7.63 (d, J = 7.2 Hz, 2 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.47 (dd, J_1 = 15.2 Hz, J_2 = 7.6 Hz, 4 H), 7.39 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.36, 145.24, 139.98, 137.78, 136.24, 132.44, 130.78, 130.05, 129.03, 128.37, 128.25, 127.35, 127.01. HRMS (EI) Calcd for $C_{19}H_{14}O$ (M^+) 258.1045, Found 258.1042. Elemental Analysis: C, 88.34; H, 5.46; O, 6.19. (Calcd. C, 88.34; H, 5.46; O, 6.19).





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