Electronic Supporting Information

Cyclization-Carbonylation-Cyclization Coupling Reactions of γ-Propynyl-1,3-diketones with Palladium(II)-Bisoxazoline Catalyst

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General Information.

All melting points were measured on a Yanaco MP-3S micro melting point apparatus and are uncorrected. ^{1}H, ^{13}C NMR and HMBC spectra were recorded on JEOL AL 400 and JEOL Lambda 500 spectrometer spectrometers in $CDCl_3$ with Me_4Si as an internal reference. In the case of CD_3CN, solvent peaks were used as a reference (1.93ppm for ^{1}H, and 118.2ppm for ^{13}C). ^{13}C NMR spectra were recorded at 100 MHz. High-resolution mass spectra (HR-MS) were obtained with JEOL GC Mate II, JMS-SX102 and JEOL JMS 600H spectrometer. IR spectra were recorded with JASCO FT/IR-300 spectrometer. All reagents were purchased from commercial sources and used without purification. All evaporations were performed under reduced pressure. For column chromatography, silica gel (Kieselgel 60) was employed.

Preparation of substrates 1, 2 and 5.

The substrates **1**, **2** and **5** were prepared according to the literature.[1] The diketones **1** and **2** except **1a**, **1b**, **2a** and **5** are new compounds.[1,2]

Keto : enol = 7 : 3, Colorless powder, mp. 84-86°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.11 (3H, t, *J* = 7.6 Hz), 1.65-2.78 (9.3H, m), 3.39-3.50 (1.4H, m), 5.47 (0.3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$, major isomer) δ 12.4 (CH_2), 14.2 (CH_3), 19.1 (CH_2), 23.9 (CH_2), 39.8 (CH_2), 48.6 (CH), 58.2 (CH_2), 75.8 (C), 84.1 (C) , 203.3 (C), 203.9 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{11}H_{14}O_2$: 178.0994; found: 178.0993; IR (KBr): 2971, 2323, 1633, 1589, 1535, 1191 cm^{-1}.

Keto : enol = 7 : 3. Pale yellow powder, mp. 46-48°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.2 Hz), 1.25-1.49 (8H, m), 1.69-2.74 (9.3H, m), 3.39-3.49 (1.4H, m), 5.46 (0.3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$, major isomer) δ 14.0 (CH_3), 18.7 (CH_2), 19.1 (CH_2), 22.6 (CH_2), 23.9 (CH_2), 28.6 (CH_2), 28.9 (CH_2), 31.3 (CH_2), 39.8 (CH_2) , 48.7 (CH), 58.2 (CH_2), 76.5 (C), 82.8 (C), 203.3 (C), 203.9 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{15}H_{22}O_2$: 234.1620; found: 234.1618; IR (KBr): 2956, 2331, 1597, 1518, 1201 cm^{-1}.

Keto : enol = 6 : 4. Colorless powder, mp. 81-83°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 0.59-0.74 (4H, m), 1.17-1.23 (1H, m), 1.62-1.95 (1H, m), 2.19-2.79 (6H, m), 3.39-3.50 (1.2H, m), 5.45 (0.4H, s), 5.88 (0.4H, br-s); ^{13}C-NMR (100 MHz, $CDCl_3$, major isomer) δ -0.5 (CH), 8.1 (2C, CH_2), 19.1 (CH_2), 23.9 (CH_2), 39.8 (CH_2), 48.6 (CH), 58.2 (CH_2), 71.9 (C), 85.7 (C) , 203.3 (C), 203.9 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{12}H_{14}O_2$: 190.0994; found: 190.0992; IR (KBr): 2887, 2334, 1604, 1531, 1202 cm^{-1}.

Keto : enol = 1 : 1. Colorless powder, mp. 125-127°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.69-1.79 (0.5H, m), 1.94-2.03 (0.5H, m), 2.28-2.33 (0.5H, m), 2.54-2.68 (3.5H, m), 2.75-2.80 (1H, m), 2.93-2.99 (1H, m), 3.42-3.53 (1H, m), 7.25-7.30 (3H, m), 7.37-7.40 (2H, m), 9.88 (0.5H, br-s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 1.97 (0.5C, CH_2), 20.7 (0.5C, CH_2), 24.0 (0.5C, CH_2), 26.1 (0.5C, CH_2), 30.2 (0.5C, CH_2), 39.8 (0.5C, CH_2), 41.8 (0.5C, CH), 48.5 (0.5C, CH), 58.2 (0.5C, CH_2) , 82.4 (0.5C, CH), 82.7 (0.5C, CH), 86.5 (0.5C, CH), 87.4 (0.5C, CH), 104.3 (0.5C, CH), 123.2 (0.5C, C), 123.6 (0.5C, C), 127.8 (0.5C, CH), 128.0 (0.5C, CH), 128.2 (1C, CH), 128.3 (1C, CH), 131.6 (2C, CH), 188.0 (0.5C, C), 195.5 (0.5C, C), 202.9 (0.5C, C), 203.7 (0.5C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{15}H_{14}O_2$: 226.0994; found: 226.0994; IR (KBr): 2950, 2335, 1616, 1490, 1200, 753, 690 cm^{-1}.

Keto : enol = 4 : 1. Pale yellow powder, mp. 135-137°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.70-1.80 (0.8H, m), 1.96-2.01 (0.2H, m), 2.30-2.35 (0.2H, m), 2.48-2.68 (3.2H, m), 2.72-2.81 (1.6H, m), 2.93-2.98 (1H, m), 3.42-3.51 (1.6H, m), 3.79 (0.6H, s), 3.80 (2.4H, s), 5.50 (0.2H, s), 6.79-6.84 (2H, m), 7.31-7.33 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, major isomer) δ 19.7 (CH_2), 24.1 (CH_2), 39.9 (CH_2), 48.6 (CH_3), 55.3 (CH_3), 58.2 (CH_2), 82.5 (C), 84.9 (C), 113.9 (2C, CH) , 115.4 (C), 133.0 (CH), 159.4 (C), 203.0 (C), 203.6 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{16}H_{16}O_3$: 256.1100; found: 256.1103; IR (KBr): 2935, 1607, 1551, 1509, 1246, 1197, 1034, 832 cm^{-1}.

Keto : enol = 7 : 3. Pale yellow powder, mp. 152-154°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.75 (0.7H, qd, J = 13.2, 4.4 Hz), 1.98-2.01 (0.3H, m), 2.31-2.35 (0.3H, m), 2.46-2.81 (4.7H, m), 2.97-3.02 (1H, m), 3.43-3.55 (1.4H, m), 5.52 (0.3H, s), 7.48-7.56 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.7 (CH_2), 24.1 (CH_2), 39.9 (CH_2), 48.4 (CH), 58.2 (CH_2), 81.4 (C), 89.3 (C), 123.9 ($^{1}J_{C\text{-}F}$ = 270.9 Hz, C), 125.2 ($^{3}J_{C\text{-}F}$ = 3.3 Hz, CH) , 127.1 (C), 129.8 ($^{2}J_{C\text{-}F}$ = 32.1 Hz, C), 131.9 (CH), 202.5 (C), 203.3 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{16}H_{13}O_2F_3$: 294.0868; found: 294.0870; IR (KBr): 2221, 1619, 1594, 1529, 1325, 841 cm^{-1}.

Keto : enol = 3 : 1. Colorless powder, mp. 145-146°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.69-1.79 (0.75H, m), 1.93-2.03 (0.75H, m), 2.29-2.34 (0.25H, m), 2.47-2.99 (5.85H, m), 3.42-3.51 (1.5H, m), 5.50 (0.25H, s), 7.25-7.32 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, major isomer) δ 19.7 (CH_2), 24.1 (CH_2), 39.9 (CH_2), 48.4 (CH), 58.2 (CH_2), 81.6 (C), 87.6 (C), 121.7 (C), 128.6 (2C, CH) , 132.8 (2C, CH), 134.0 (C), 202.7 (C), 203.4 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{15}H_{13}O_2Cl$: 260.0604; found: 260.0601; IR (KBr): 2252, 1620, 1538, 1488, 1201, 1088 cm^{-1}.

diastereomeric mixture, ratio = 25 : 1. Yellow oil ; ^{1}H- NMR (400 MHz, $CDCl_3$, major isomer) δ 0.86 (3H, s), 1.27 (3H, s), 2.57-2.69 (3H, m), 2.85-2.88 (1H, m), 2.95-3.01 (1H, m), 3.43-5.34 (2H, m), 7.26-7.29 (3H, m), 7.35-7.38 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, major isomer) δ 15.1 (CH_2), 22.2 (CH_3), 29.0 (CH_3), 34.0 (C), 55.2 (CH_2), 58.1 (CH_2), 59.5 (CH), 81.8 (C), 88.1 (C) , 123.4 (C), 127.9 (CH), 128.3 (2C, CH), 131.5 (2C, CH), 202.6 (C), 202.7 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{17}H_{18}O_2$: 254.1307; found: 254.1305; IR (KBr): 2963, 2238, 1710, 1597, 757, 692 cm^{-1}.

Enol form. Pale yellow powder, mp. 80-82°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.07 (3H, t, *J* = 7.6 Hz), 2.08-2.15 (2H, m), 2.43-2.61 (3H, m), 2.70-2.76 (1H, m), 2.82-2.86 (1H, m), 5.31 (1H, s), 9.14-9.24 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 12.3 (CH_2), 14.2 (CH_3), 20.9 (CH_2), 37.1 (CH_2), 42.2 (CH), 74.8 (C), 83.9 (C), 105.7 (CH), 201.7 (C) , 203.2 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{10}H_{12}O_2$: 164.0837; found: 164.0830; IR (KBr): 2973, 1607, 1168, 819 cm^{-1}.

Enol form. Yellow oil; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 7.2 Hz), 1.23-1.35 (7H, m), 1.40-1.47 (2H, m), 2.08-2.12 (2H, m), 2.41-2.84 (5H, m), 5.30 (1H, s), 9.78 (1H, br-s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 18.7 (CH_2), 21.0 (CH_2), 22.6 (CH_2), 28.5 (CH_2), 28.9 (CH_2), 31.3 (CH_2), 37.1 (CH_2), 42.3 (CH) , 75.5 (C), 82.5 (C), 105.7 (CH), 201.5 (C), 203.2 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{14}H_{20}O_2$: 220.1463; found: 220.1461; IR (KBr): 2929, 2336, 1652, 1573, 1173, 833 cm^{-1}.

Enol form. Pale yellow powder, mp. 102-104°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 2.56-2.90 (5H, m), 5.35 (1H, s), 7.23-7.26 (3H, m), 7.32-7.34 (2H, m), 11.3 (1H, br-s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.5 (CH_2), 37.1 (CH_2), 42.0 (CH), 82.5 (C), 85.5 (C), 105.7 (CH), 123.2 (C), 128.0 (CH), 128.3 (2C, CH) , 131.7 (2C, CH), 201.6 (C), 203.1 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{14}H_{12}O_2$: 212.0837; found: 212.0838; IR (KBr): 2334, 1598, 1522, 1490, 1167, 756 cm^{-1}.

General procedure for the CCC-coupling reaction of 1 or 2

A 50 mL two-neck round-bottom flask containing a magnetic stirring bar, $Pd(tfa)_2$ (0.025 mmol or 0.05 mmol), ligand (0.038 mmol or 0.06 mmol), *p*-benzoquinone (1 mmol) and MeOH (4 mL) was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with carbon monoxide. The apparatus was purged with carbon monoxide by pump-filling via the three-way stopcock. A MeOH (or CH_2Cl_2) solution (1 mL) of substrate **1** or **2** (0.5 mmol) was added to the stirred solution via syringe at an appropriate temperature. The remaining substrate was washed in MeOH (or CH_2Cl_2) (1 mL) twice. In the case of **1g**-**1i**, CH_2Cl_2 was used instead of MeOH, because of their poor solubility in MeOH. After stirring for the period of time at the appropriate temperature, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with 3% NaOH (40 mL). The aqueous layer was extracted with CH_2Cl_2 (50 mL) twice and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel. The fraction eluted with hexane / acetone (4/1-2/1) afforded dimeric ketone **6** or **9**. The product **6** or **9** was then precipitated from the reaction mixture and the resulting precipitate collected by filtration and washed with cold MeOH (1 mL × 2). The filtrate was reprocessed via the above procedure to provide additional product after flash chromatography.

Diastereomeric mixture, ratio = 1:1. Pale yellow powder, mp. 219-222°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.76-1.87 (2H, m), 2.33-2.42 (4H, m), 2.55-2.66 (4H, m), 3.06-3.16 (2H, m), 3.79-3.88 (2H, m), 5.69 (2H, d, J = 2.4 Hz), 6.11-6.12 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.8 (2C, CH_2), 34.0 (1C, CH_2), 34.0 (1C, CH_2), 36.8 (2C, CH_2), 37.5 (1C, CH), 37.5 (1C, CH), 104.3 (2C, CH), 105.7 (1C, CH), 105.7 (1C, CH), 171.0 (1C, C), 171.1 (1C, C), 177.8 (1C, C), 177.8 (1C, C), 188.3 (1C, C), 198.3 (2C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{19}H_{18}O_5$: 326.1154; found: 326.1128; IR (KBr): 2948, 1654, 1607, 1359, 1161, 1065, 1033 cm^{-1}.

Diastereomeric mixture, ratio = 1:1. Colorless powder, mp. 205-208°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.73-1.85 (2H, m), 1.96-1.98 (6H, m), 2.33-2.58 (8H, m), 3.06-3.12 (2H, m), 3.12-3.21 (1H, m), 3.35-3.41 (1H, m), 5.69 (2H, d, J = 1.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 12.7 (1C, CH_3), 12.8 (1C, CH_3), 27.7 (1C, CH_2), 27.8 (1C, CH_2), 32.8 (1C, CH_2), 33.7 (1C, CH_2), 36.7 (1C, CH_2) , 36.7 (1C, CH_2), 38.2 (1C, CH), 38.3 (1C, CH), 103.6 (1C, CH), 103.7 (1C, CH), 113.4 (1C, C), 113.6 (1C, C), 160.8 (1C, C), 161.4 (1C, C), 178.3 (1C, C), 178.3 (1C, C), 197.5 (0.5C, C), 197.8 (0.5C, C), 198.5 (1C, C), 198.5 (1C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{21}H_{22}O_5$: 354.1467; found: 354.1470; IR (KBr): 2948, 1631, 1367, 1172, 1151 cm^{-1}.

Diastereomeric mixture, ratio = 1:1. Pale yellow powder, mp. 204-206°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.03-1.07 (6H, m), 1.73-1.83 (2H, m), 2.32-2.58 (12H, m), 3.05-3.17 (3H, m), 3.24-3.33 (1H, m), 5.68 (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.7 (1C, CH_3), 13.8 (1C, CH_3), 21.0 (1C, CH_2), 21.0 (1C, CH_2), 27.7 (1C, CH_2), 27.7 (1C, CH_2), 32.8 (1C, CH_2), 33.5 (1C, CH_2), 36.7 (1C, CH_2) , 36.7 (1C, CH_2), 38.2 (1C, CH), 38.2 (1C, CH), 103.6 (1C, CH), 103.6 (1C, CH), 120.6 (1C, C), 120.8 (1C, C), 159.6 (1C, C), 160.0 (1C, C), 178.2 (1C, C), 178.2 (1C, C), 197.7 (0.5C, C), 197.8 (0.5C, C), 198.4 (1C, C), 198.4 (1C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{23}H_{26}O_5$: 382.1780; found: 382.1783; IR (KBr): 2965, 1623, 1366, 1165 cm^{-1}.

Diastereomeric mixture, ratio = 1:1. Pale yellow oil ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 0.86-0.89 (6H, m), 1.27-1.42 (16H, m), 1.73-1.83 (2H, m), 2.29-2.57 (12H, m), 3.03-3.14 (3H, m), 3.26-3.32 (1H, m), 5.68 (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1 (2C, CH_3), 22.6 (1C, CH_2), 22.6 (1C, CH_2), 27.6 (1C, CH_2), 27.7 (2C, CH_2), 27.8 (1C, CH_2), 29.1 (1C, CH_2), 29.1 (1C, CH_2), 29.2 (1C, CH_2), 29.3 (1C, CH_2), 31.5 (1C, CH_2), 31.6 (1C, CH_2), 32.8 (1C, CH_2), 33.5 (1C, CH_2), 36.7 (1C, CH_2) , 36.7 (1C, CH_2), 38.2 (2C, CH), 103.6 (1C, CH), 103.6 (1C, CH), 119.5 (1C, C), 119.7 (1C, C), 159.8 (1C, C), 160.2 (1C, C), 178.2 (1C, C), 178.3 (1C, C), 198.1 (0.5C, C), 198.2 (0.5C, C), 198.4 (1C, C), 198.4 (1C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{31}H_{42}O_5$: 490.3032; found: 490.3031; IR (KBr): 2926, 1661, 1626, 1367, 1166 cm^{-1}.

Diastereomeric mixture, ratio = 1:1. Pale yellow powder, mp. 184-186°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 0.42-0.59 (4H, m), 0.75-0.95 (4H, m), 1.70-1.84 (2H, m), 2.32-2.58 (8H, m), 3.04-3.13 (2H, m), 3.17-3.23 (1H, m), 3.39-3.45 (1H, m), 5.71 (2H, d, J = 1.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 6.2 (1C, CH_2), 6.7 (1C, CH_2), 6.8 (1C, CH_2), 7.3 (1C, CH_2), 8.6 (1C, CH_3), 8.7 (1C, CH_3), 27.7 (1C, CH_2), 27.7 (1C, CH_2), 33.3 (1C, CH_2) , 34.1 (1C, CH_2), 36.7 (2C, CH_2), 37.9 (1C, CH) , 38.0 (1C, CH), 103.7 (1C, CH), 103.7 (1C, CH), 119.9 (1C, C), 120.0 (1C, C), 163.3 (1C, C), 163.8 (1C, C), 178.5 (1C, C), 178.6 (1C, C), 196.8 (0.5C, C), 197.0 (0.5C, C), 198.5 (2C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{25}H_{26}O_5$: 406.1780; found: 406.1775; IR (KBr): 3008, 1656, 1615, 1151, 1113 cm^{-1}.

Diastereomeric mixture, ratio = 1:1. Pale yellow powder, mp. 213-215°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.77-1.88 (2H, m), 2.32-2.43 (4H, m), 2.53-2.58 (2H, m), 2.71 (1H, dd, *J* = 11.2, 17.6 Hz), 2.86 (1H, dd, *J* = 11.2, 17.6 Hz), 3.11-3.25 (2H, m), 3.51 (1H, dd, *J* = 9.2, 17.2 Hz), 3.77 (1H, dd, *J* = 9.2, 17.2 Hz), 5.53 (2H, s), 6.67-6.71 (4H, m), 7.06-7.14 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.7 (2C, CH_2), 33.6 (1C, CH_2), 34.5 (1C, CH_2), 36.7 (1C, CH_2), 36.7 (1C, CH_2), 37.7 (1C, CH), 37.9 (1C, CH), 104.1 (1C, CH), 104.1 (1C, CH), 120.4 (1C, C), 120.4 (1C, C), 127.2 (1C, CH), 127.2 (1C, CH), 127.9 (4C, CH), 129.2 (4C, CH), 133.1 (1C, C), 133.1 (1C, C), 162.6 (1C, C), 163.1 (1C, C), 178.1 (1C, C), 178.2 (1C, C), 195.4 (0.5C, C), 195.5 (0.5C, C), 198.3 (1C, C), 198.3 (1C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{31}H_{26}O_5$: 478.1780; found: 478.1778; IR (KBr): 2951, 1660, 1617, 1148, 1125, 815 cm^{-1}.

Diastereomeric mixture, ratio = 1.5:1. Pale yellow needles, mp. 150-152°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.77-1.87 (2H, m), 2.33-2.42 (4H, m), 2.52-2.57 (2H, m), 2.67 (0.8H, dd, *J* = 11.2, 17.6 Hz), 2.82 (1.2H, dd, *J* = 11.2, 17.6 Hz), 3.13-3.19 (2H, m), 3.46 (1.2H, dd, *J* = 9.2, 17.2 Hz), 3.72 (0.8H, dd, *J* = 9.2, 17.2 Hz), 3.76-3.77 (6H, m), 5.54 (2H, s), 6.64-6.66 (8H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.7 (2C, CH_2), 33.5 (0.8C, CH_2), 34.4 (1.2C, CH_2), 36.7 (2C, CH_2), 37.8 (0.8C, CH), 38.0 (1.2C, CH), 55.3 (2C, CH_3), 104.0 (0.8C, CH), 104.1 (1.2C, CH), 113.4 (4C, CH), 120.0 (1.2C, C), 120.1 (0.8C, C), 125.5 (0.8C, CH), 125.5 (1.2C, CH), 130.3 (4C, CH), 158.8 (1.2C, C), 158.8 (0.8C, C), 161.9 (0.8C, C), 162.4 (1.2C, C), 178.3 (0.8C, C), 178.3 (1.2C, C), 195.9 (0.6C, C), 196.0 (0.4C, C), 198.3 (1.2C, C), 198.4 (0.8C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{33}H_{30}O_7$: 538.1992; found: 538.1991; IR (KBr): 2953, 1656, 1614, 1513, 1149, 1123, 814 cm^{-1}.

Diastereomeric mixture, ratio = 1.5:1. Pale yellow powder, mp. 215-217°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.81-1.90 (2H, m), 2.33-2.63 (6H, m), 2.77 (0.8H, dd, *J* = 11.0, 17.6 Hz), 2.93 (1.2H, dd, *J* = 11.0, 17.6 Hz), 3.19-3.24 (2H, m), 3.57 (1.2H, dd, *J* = 9.2, 17.6), 3.86 (0.8H, dd, *J* = 9.2, 17.6 Hz), 5.53-5.55 (2H, m), 6.76-6.79 (4H, m), 7.26-7.31 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.7 (2C, CH_2), 33.9 (0.8C, CH_2), 34.9 (1.2C, CH_2), 36.7 (1.2C, CH_2), 36.7 (0.8C, CH_2), 37.5 (0.8C, CH), 37.7 (1.2C, CH), 104.6 (0.8C, CH), 104.6 (1.2C, CH), 118.7 (1.2C, C), 118.7 (0.8C, C), 123.9 (2C, C, $^{1}J_{C\text{-}F}$ = 270.7 Hz), 124.8 (4C, C, $^{3}J_{C\text{-}F}$ = 4.1 Hz), 129.4 (1.2C, C, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 129.4 (0.8C, C, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 129.7 (1.6C, CH), 129.7 (2.4C, CH), 137.0 (2C, C), 165.0 (0.8C, C), 165.5 (1.2C, C), 177.5 (0.8C, C), 177.6 (1.2C, C), 193.2 (0.6C, C), 193.3 (0.4C, C), 198.0 (0.8C, C), 198.0 (1.2C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{33}H_{24}O_5F_6$: 614.1528; found: 614.1527; IR (KBr): 3006, 1656, 1609, 1326, 1122, 817, 754 cm^{-1}.

Diastereomeric mixture, ratio = 1.2:1. Pale yellow powder, mp. 233-235°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.78-1.88 (2H, m), 2.32-2.58 (6H, m), 2.71 (0.9H, dd, *J* = 11.2, 17.6 Hz), 2.86 (1.1H, dd, *J* = 11.2, 17.6 Hz), 3.15-3.21 (2H, m), 3.49 (1.1H, dd, *J* = 9.0, 17.2 Hz), 3.76 (0.9H, dd, *J* = 9.0, 17.2 Hz), 5.53-5.55 (2H, m), 6.62-6.66 (4H, m), 7.07-7.10 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.7 (2C, CH_2), 33.7 (0.9C, CH_2), 34.6 (1.1C, CH_2), 36.7 (2C, CH_2), 37.6 (0.9C, CH), 37.8 (1.1C, CH), 104.3 (0.9C, CH), 104.4 (1.1C, CH), 119.0 (1.1C, CH), 119.0 (0.9C, C), 128.2 (4C, CH), 130.5 (1.8C, CH), 130.6 (2.2C, CH), 131.6 (0.9C, C), 131.6 (1.1C, C), 133.4 (1.1C, C), 133.5 (0.9C, C), 163.6 (0.9C, C), 164.1 (1.1C, C), 177.7 (0.9C, C), 177.8 (1.1C, C), 194.2 (0.55C, C), 194.3 (0.45C, C), 198.1 (0.9C, C), 198.1 (1.1C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{31}H_{24}Cl_2O_5$: 546.1001; found: 546.0996; IR (KBr): 2952, 1656, 1614, 1149, 1123, 813 cm^{-1}.

Diastereomeric mixture, ratio = 1.5:1. Yellow powder, mp. 204-206°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.00, 1.01 (total 6H, s each, ratio = 1.5 : 1), 1.21, 1.21 (total 6H, s each, ratio = 1.5 : 1), 2.31, 2.32 (total 4H, s each, ratio = 1.5 : 1), 2.83-3.84 (6H, m), 5.53, 5.54 (total 2H, s each, ratio = 1.5 : 1), 6.66-6.71 (4H, m), 7.03-7.27 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.8 (1.2C, CH_3), 19.8 (0.8C, CH_3), 28.1 (1.2C, CH_2), 29.1 (0.8C, CH_2), 29.2 (2C, CH_3), 35.7 (1.2C, CH), 35.7 (0.8C, CH),47.9 (0.8C, CH), 48.1 (1.2H, CH), 52.4 (0.8H, CH_2), 52.5 (1.2C, CH_2), 103.3 (0.8C, CH), 103.4 (1.2C, CH), 120.4 (1.2C, C), 120.4 (0.8C, C), 127.1 (1.2C, CH), 127.2 (0.8C, CH), 127.8 (4C, CH), 129.2 (4C, CH), 133.1 (0.8C, C), 133.1 (1.2C, C), 162.7 (0.8C, C), 163.4 (1.2C, C), 176.1 (0.8C, C), 176.1 (1.2C, C), 195.7 (0.6C, C),195.8 (0.4C, C), 198.0 (2C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{35}H_{34}O_5$: 534.2406; found: 534.2411; IR (KBr): 2962, 1655, 1611, 1361, 1149, 818 cm^{-1}.

CCC-coupling reaction of 5

A 50 mL two-neck round-bottom flask containing a magnetic stirring bar, $Pd(tfa)_2$ (0.015 mmol), ligand (0.023 mmol), *p*-benzoquinone (0.6 mmol) and MeOH / CH_2Cl_2 = 1 / 1 (5 mL) was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with carbon monoxide. The apparatus was purged with carbon monoxide by pump-filling via the three-way stopcock. A MeOH / CH_2Cl_2 = 1 / 1 solution (1 mL) of substrate **5** (0.3 mmol) was added to the stirred solution via syringe at an appropriate temperature. The remaining substrate was washed in MeOH / CH_2Cl_2 = 1 / 1 (1 mL) twice. After stirring for the period of time at the appropriate temperature, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with 3% NaOH (40 mL). The aqueous layer was extracted with CH_2Cl_2 (50 mL) twice and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel. The fraction eluted with hexane / ethyl acetate (3/1- 0/1) afforded dimeric ketone **7** and **8**.

Pale yellow powder, mp. 180-182 ; °C ^{1}H- NMR (400 MHz, $CDCl_3$) δ 2.97-3.01 (4H, m), 3.25-3.29 (4H, m), 6.24 (4H, s), 7.43-7.55 (6H, m), 7.92 (4H, d, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.6 (2C, CH_2), 29.1 (2C, CH_2), 98.2 (2C, CH), 105.4 (2C, CH), 128.0 (4C, CH), 128.5 (4C, CH), 132.4 (2C, CH), 138.8 (2C, C), 166.8 (2C, C), 172.6 (2C, C), 187.6 (2C, C), 189.2 (1C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{27}H_{22}O_5$: 426.1467; found: 426.1467; IR (KBr): 3056, 1639, 1598, 1287, 1216, 1066, 941 cm^{-1}.

Pale yellow powder, mp. 122-124°C; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 3.27-3.32 (2H, m), 3.38-3.43 (2H, m), 3.73 (3H, s), 5.67-5.68 (1H, m), 6.80-6.81 (1H, m), 7.45-7.57 (3H, m), 7.91-7.93 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.5 (CH_2), 28.5 (CH_2), 51.3 (CH_3), 94.9 (CH), 98.8 (CH), 127.8 (CH) 128.6 (CH), 132.5 (CH), 138.9 (C), 167.5 (C), 172.2 (C), 174.0 (C), 190.1 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{15}H_{14}O_4$: 258.0892; found: 258.0889; IR (KBr): 2952, 1713, 1649, 1598, 1159, 1122, 703 cm^{-1}.

Diastereomeric mixture, ratio = 1.5:1. Pale yellow powder, mp. 183-184°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 2.09-2.22 (10H, m), 2.71-2.85 (4H, m),2.93-2.97 (2H, m), 5.60 (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 18.0 (1.2C, CH_3), 18.1 (0.8C, CH_3), 27.3 (1.2C, CH_2), 27.4 (0.8C, CH_2), 32.7 (1.2C, CH_3), 32.7 (0.8C, CH), 41.3 (0.8C, CH_2), 41.3 (1.2C, CH_2), 109.0 (0.8C, CH), 109.0 (1.2C, CH), 114.9 (0.8C, C), 115.0 (1.2C, C), 155.4 (1.2C, C), 156.1 (0.8C, C), 182.8 (1.2C, C), 182.9 (0.8C, C), 194.7 (0.4C, C), 195.1 (0.6C, C), 203.1 (0.8C, C), 203.1 (1.2C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{19}H_{18}O_5$: 326.1154; found: 326.1152; IR (KBr): 3101, 2913, 1704, 1618, 1359, 1222, 1156, 961, 839 cm^{-1}.

Diastereomeric mixture, ratio = 1.5:1. Pale yellow powder, mp. 116-118°C ; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 1.19 (3H, t, *J* = 7.6 Hz), 1.20 (3H, t, *J* = 7.6 Hz), 2.13-2.21 (4H, m), 2.47-2.59 (4H, m),2.67-2.85 (4H, m), 2.92-2.95 (2H, m), 5.61-5.62 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 11.9 (1.2C, CH_3), 11.9 (0.8C, CH_3), 24.9 (1.2C, CH_2), 24.9 (0.8C, CH_2), 27.5 (0.8C, CH_2), 27.5 (1.2C, CH_2) 32.7 (1.2C, CH_3), 32.8 (0.8C, CH), 41.3 (0.8C, CH_2), 41.3 (1.2C, CH_2), 108.9 (0.8C, CH), 109.0 (1.2C, CH), 114.1 (0.8C, C), 114.2 (1.2C, C), 159.8 (1.2C, C), 160.5 (0.8C, C), 183.1 (1.2C, C), 183.2 (0.8C, C), 194.7 (0.4C, C), 195.1 (0.6C, C), 203.2 (0.8C, C), 203.2 (1.2C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{21}H_{22}O_5$: 354.1467; found: 354.1461; IR (KBr): 2976, 2940, 1703, 1620, 1360, 1217, 1156, 835 cm^{-1}.

Diastereomeric mixture, ratio = 1.5:1. Yellow oil; ^{1}H- NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, t, *J* = 6.8 Hz), 1.23-1.33 (12H, m), 1.56-1.61 (4H, m), 2.09-2.21 (4H, m), 2.47-2.56 (4H, s), 2.64-2.93 (6H, m), 5.60 (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.0 (2C, CH_3), 22.5 (1.2C, CH_2), 22.5 (0.8C, CH_2), 27.2 (1.2C, CH_2), 27.3 (0.8C, CH_3), 27.6 (0.8C, CH_2) 27.6 (1.2C, CH_2), 28.9 (1.2C, CH_2), 29.0 (0.8C, CH_2), 31.4 (0.8C, CH_2), 31.4 (0.8C, CH_2), 31.4 (1.2C, CH_2), 31.5 (1.2C, CH_2), 32.8 (1.2C, CH), 32.8 (0.8C, CH), 108.9 (0.8C, CH), 108.9 (1.2C, CH), 114.7 (0.8C, C), 114.7 (1.2C, C), 158.9 (1.2C, C), 159.5 (0.8C, C), 183.1 (1.2C, C), 183.2 (0.8C, C), 194.8 (0.8C, C), 195.1 (1.2C, C), 203.2 (0.8C, C), 203.2 (1.2C, C); HRMS-EI:*m/z* [M^+] calcd for $C_{29}H_{38}O_5$: 466.2719; found: 466.2717; IR (KBr): 2955, 2929, 1708, 1657, 1615, 1362, 1216, 1158, 836 cm^{-1}.

Yellow oil, ^{1}H- NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 6.8 Hz), 1.29-1.39 (6H, m), 1.58-1.65 (2H, m), 2.04-2.11 (1H, m), 2.18 (1H, dd, *J* = 17.6, 3.2 Hz), 2.75-2.87 (4H, m), 2.99 (1H, dd, *J* = 16.4, 6.8 Hz), 3.76 (3H, s), 5.58 (1H, d, *J* = 1.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.5 (CH_2), 26.5 (CH_2), 27.4 (CH_2), 29.0 (CH_2), 31.5 (CH_2), 31.9 (CH_2), 32.5 (CH), 41.4 (CH_2), 51.8 (CH_3), 105.9 (C), 108.6 (CH), 164.0 (C), 166.9 (C), 183.6 (C), 203.7 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{16}H_{22}O_4$: 278.1518; found: 278.1519; IR (KBr): 2954, 2930, 1714, 1624, 1362, 1216, 1160 cm^{-1}.

Pale yellow powder, mp. 125-127°C ^{1}H- NMR (400 MHz, $CDCl_3$) δ 2.23-2.32 (2H, m), 2.87 (1H, dd, *J* = 17.8, 6.8 Hz), 3.02-3.10 (1H, m), 3.14 (1H, dd, *J* = 16.0, 7.2 Hz), 3.56 (3H, s), 5.65 (1H, d, *J* = 1.6 Hz), 7.42-7.46 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.4 (CH_2), 32.3 (CH), 41.5 (CH_2), 51.9 (CH_3), 107.9 (C), 109.3 (CH) 128.1 (CH), 128.6 (CH), 130.1 (CH), 133.5 (C), 157.9 (C), 167.2 (C), 183.2 (C), 203.4 (C); HRMS-EI:*m/z* [M^+] calcd for $C_{16}H_{14}O_4$: 270.0892; found: 270.0888; IR (KBr): 2986, 2945, 1701, 1626, 1226, 1165, 1054, 768 cm^{-1}.

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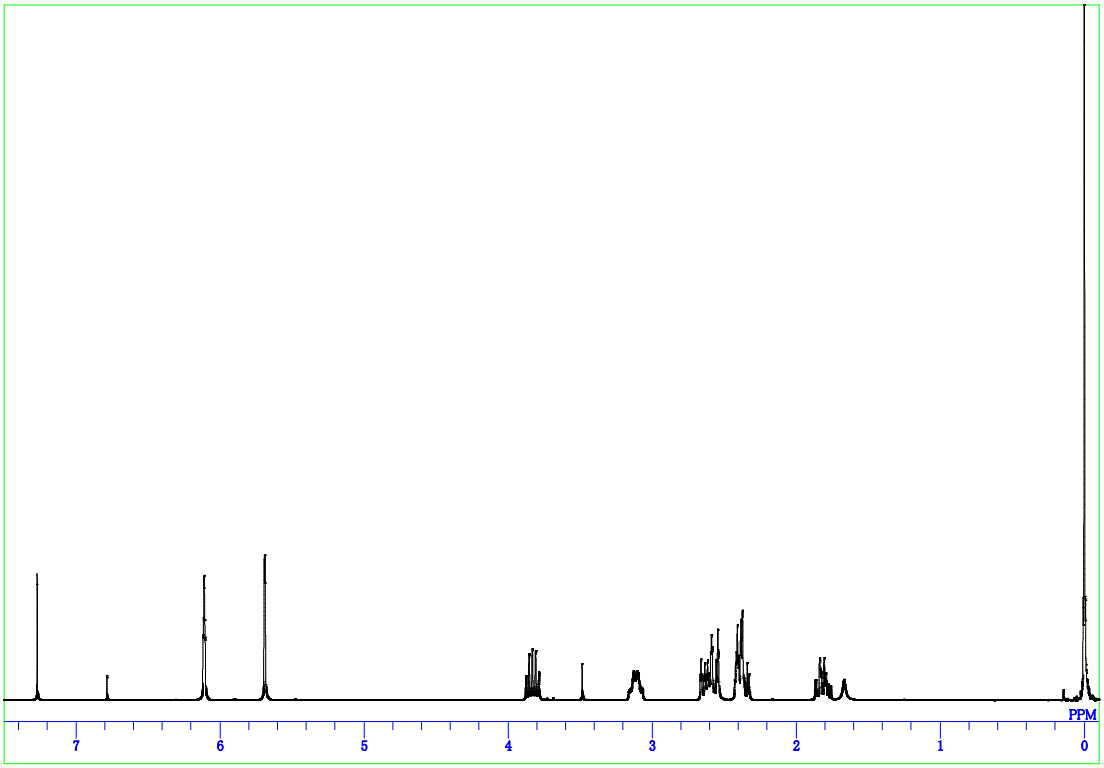
6a-1H



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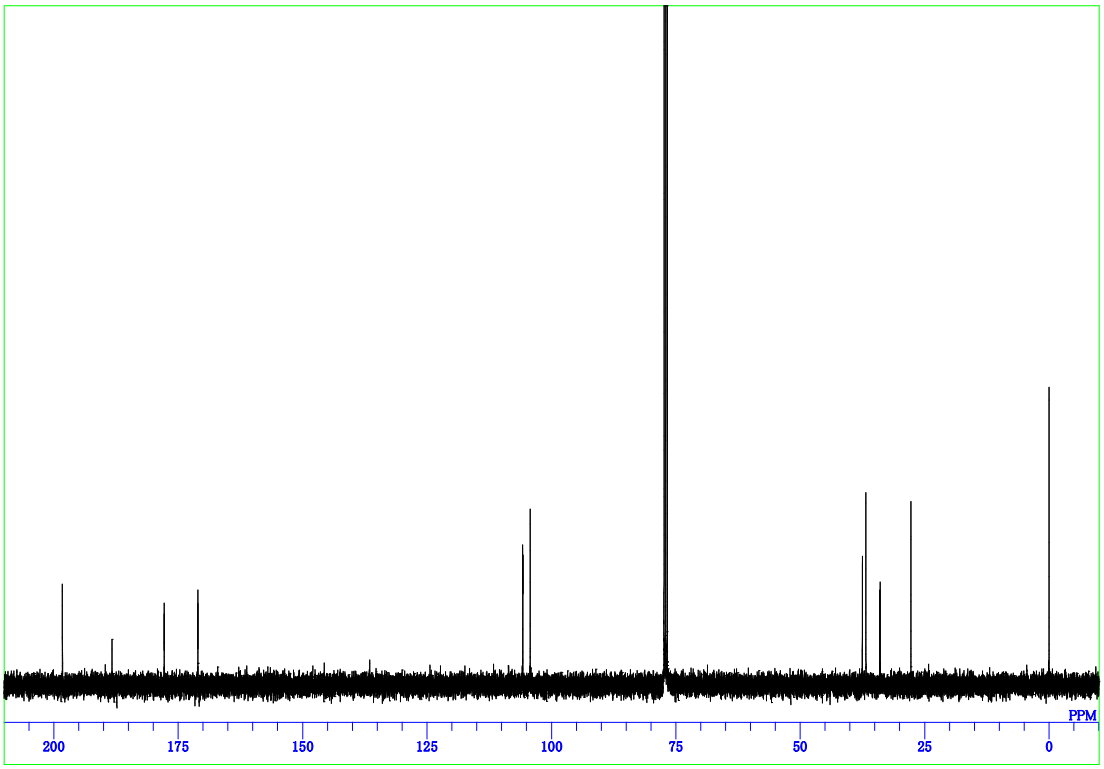

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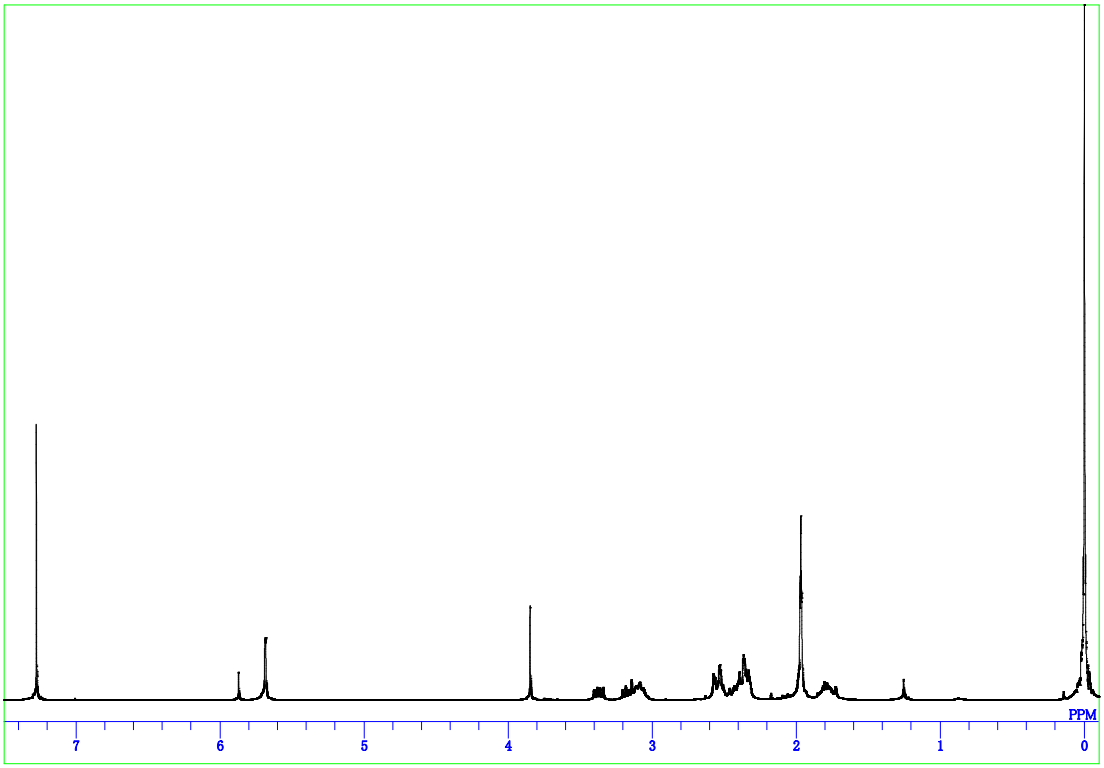

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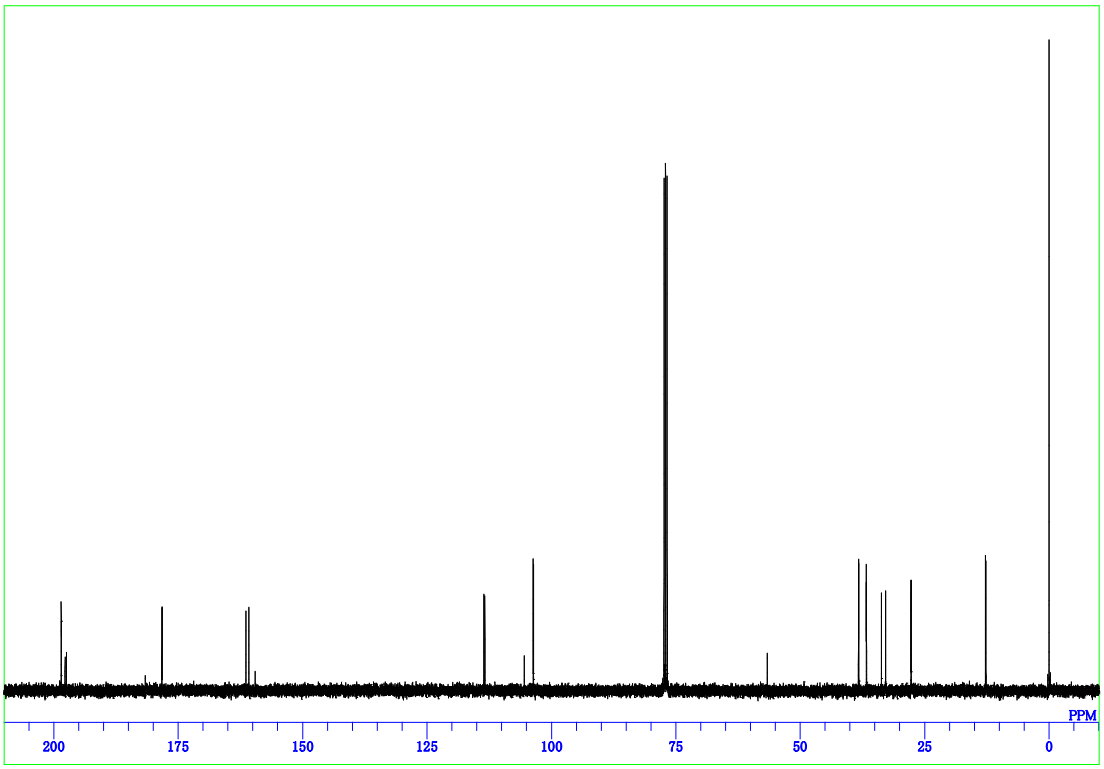

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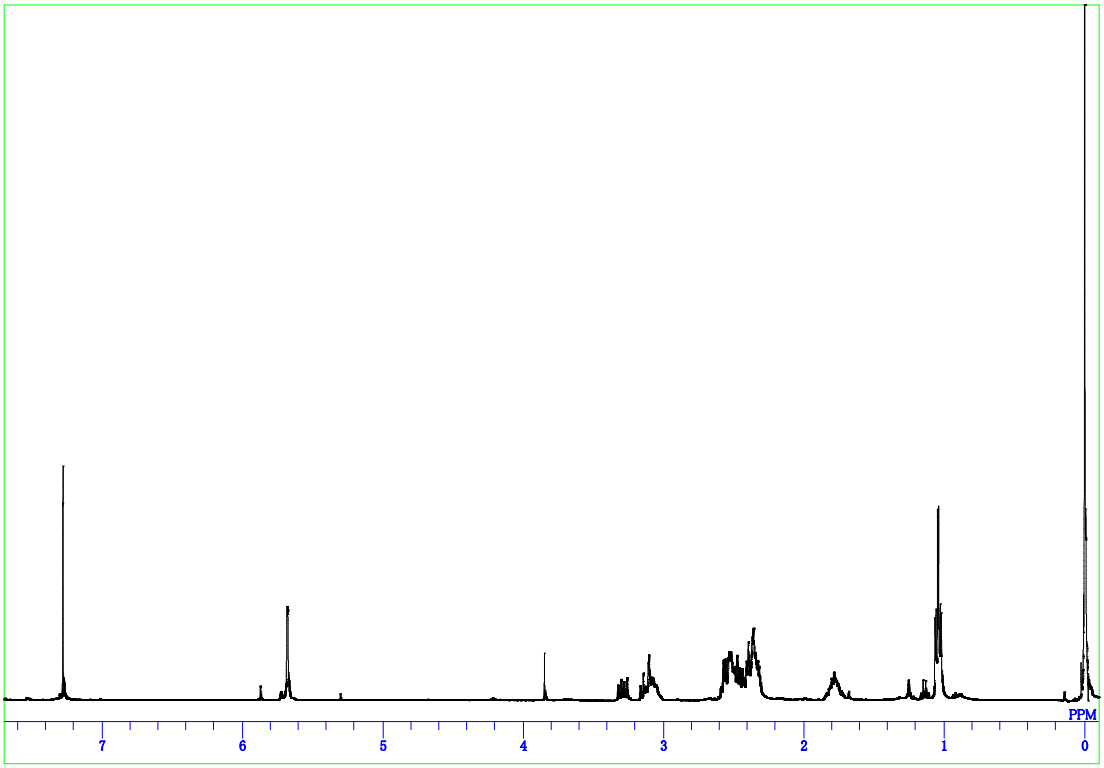

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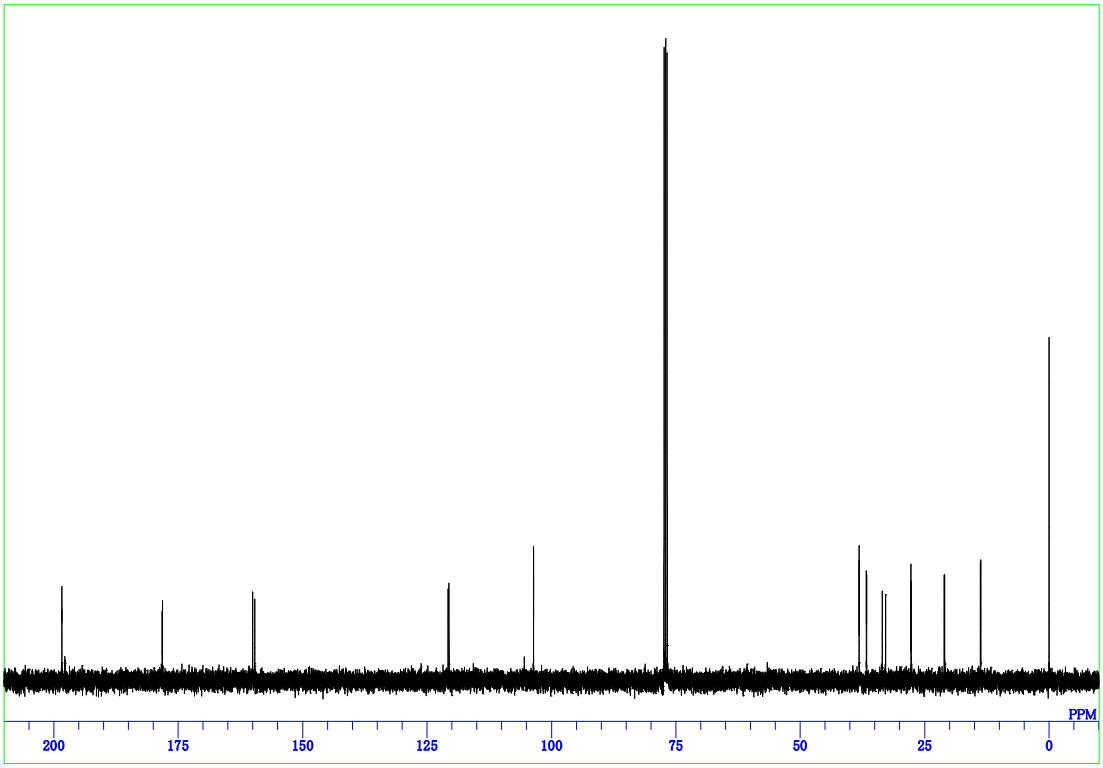

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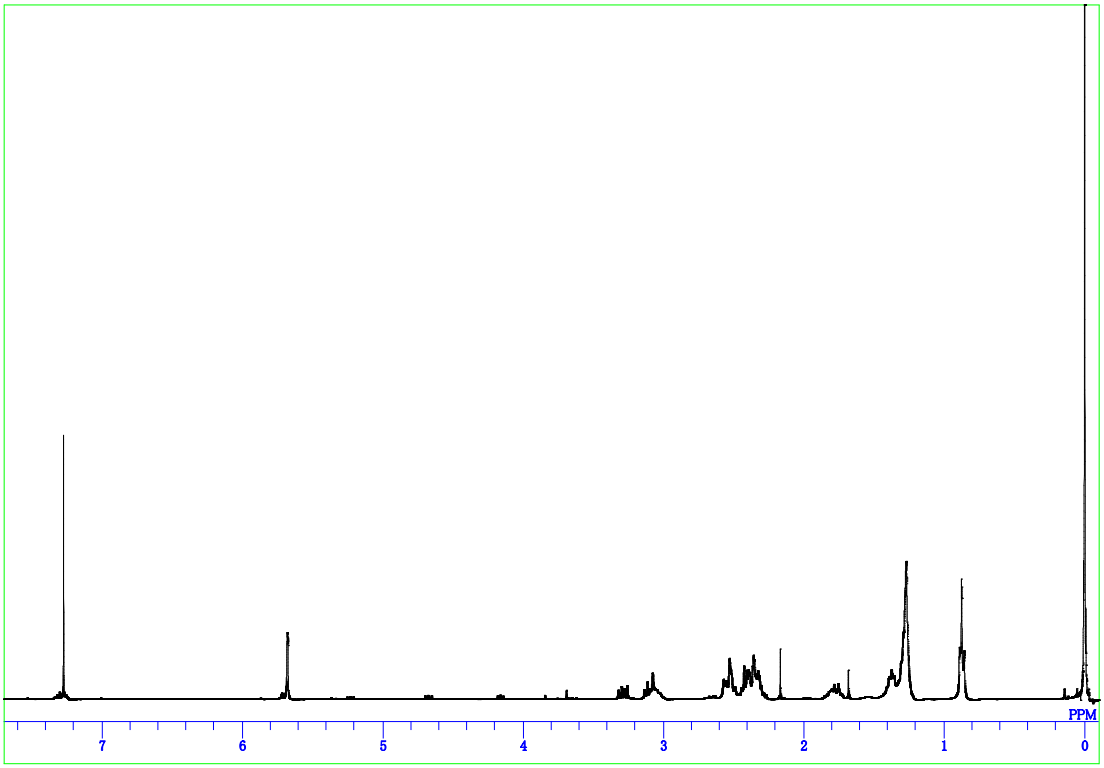

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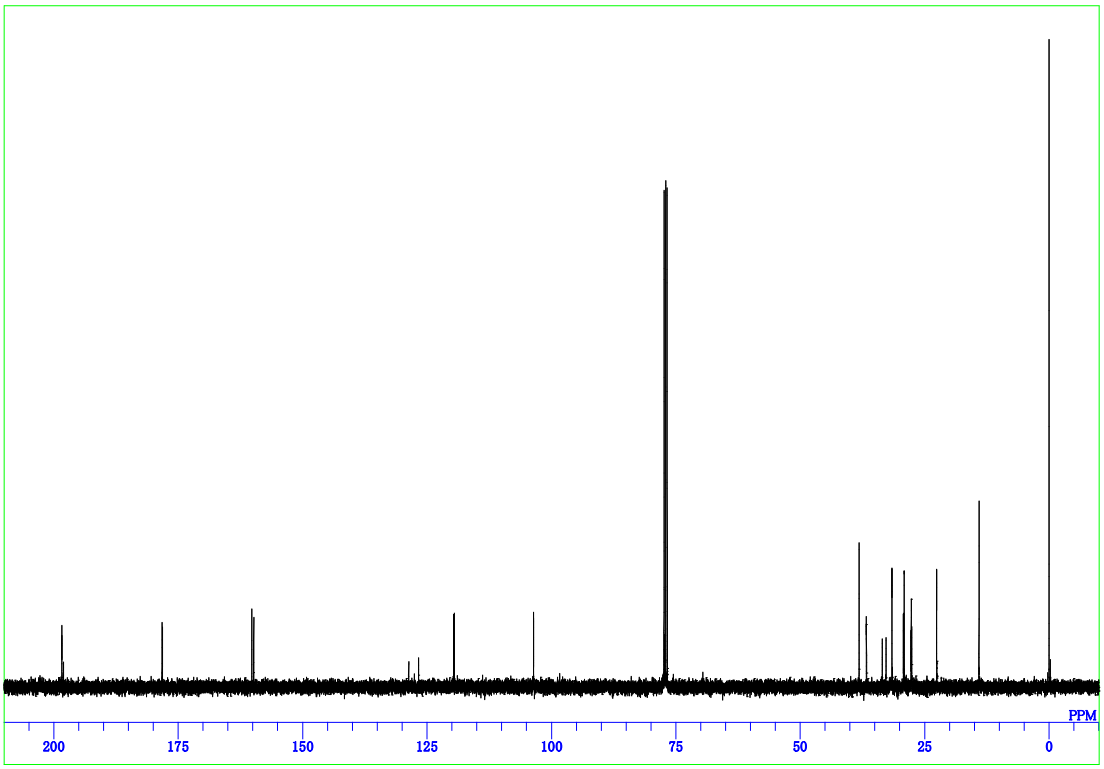

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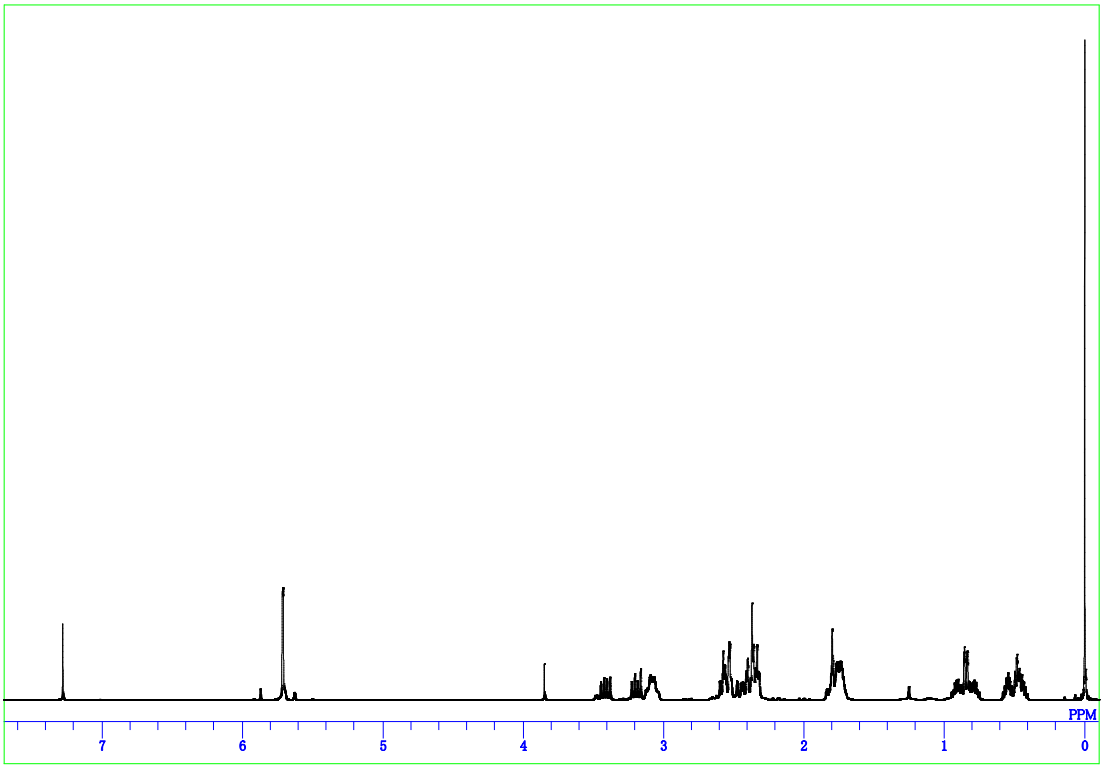

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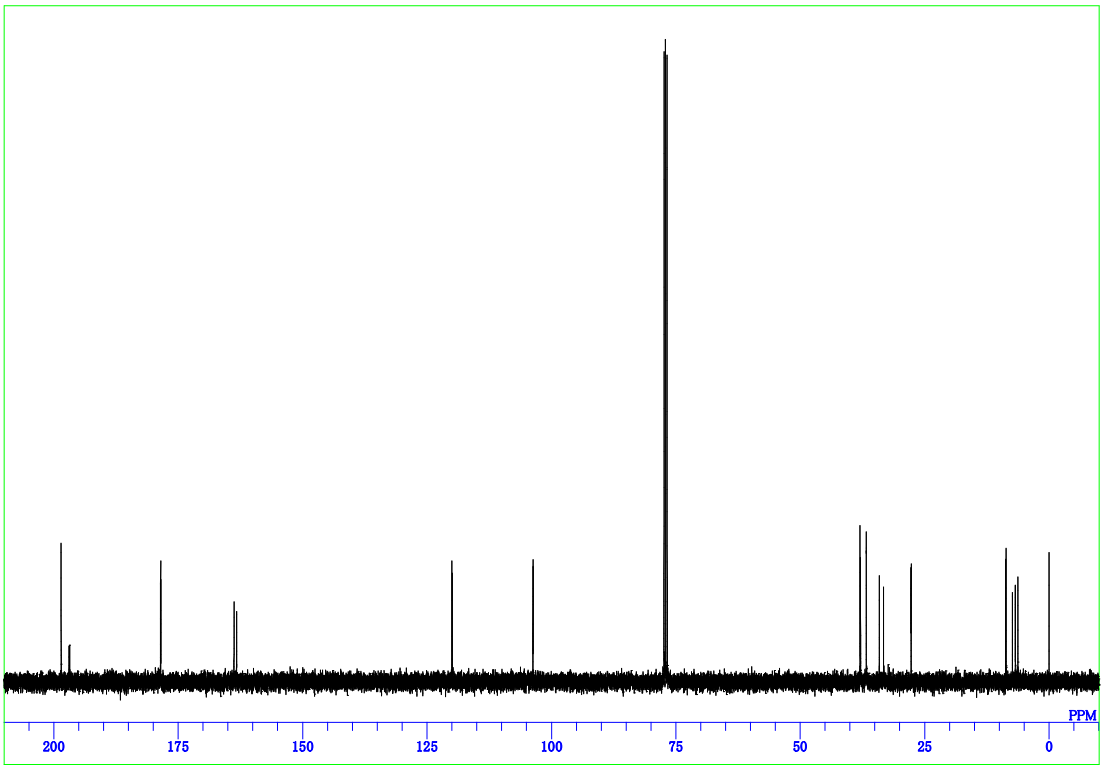

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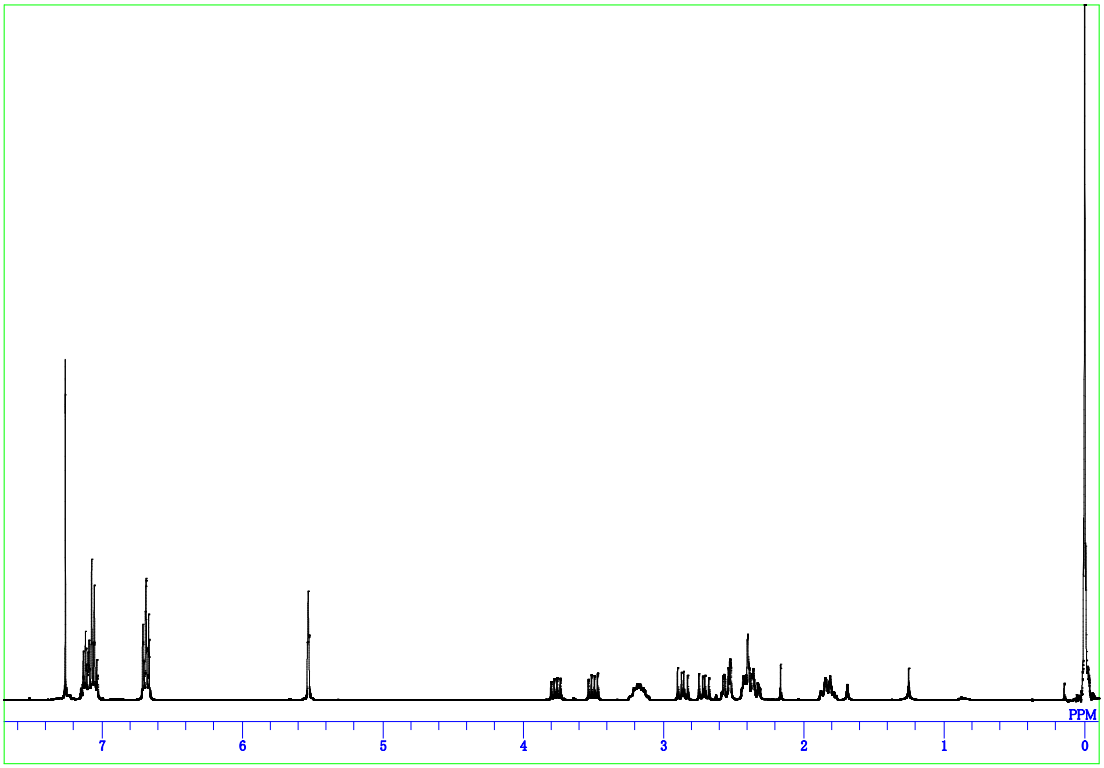

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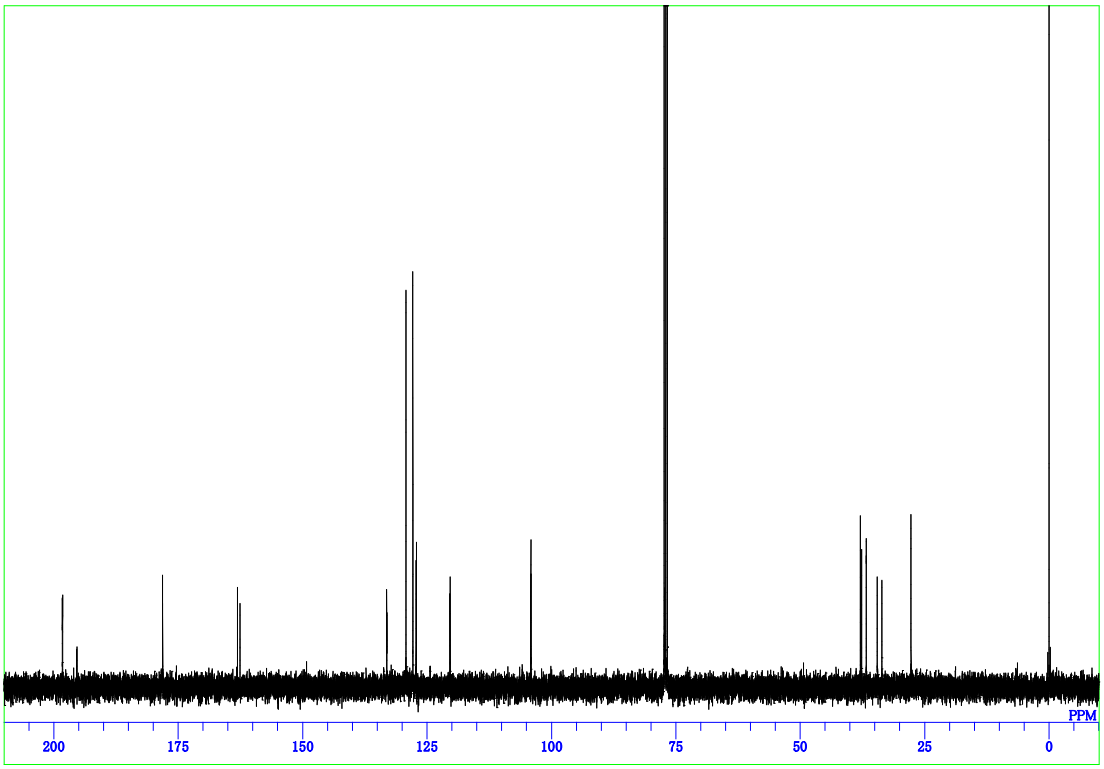

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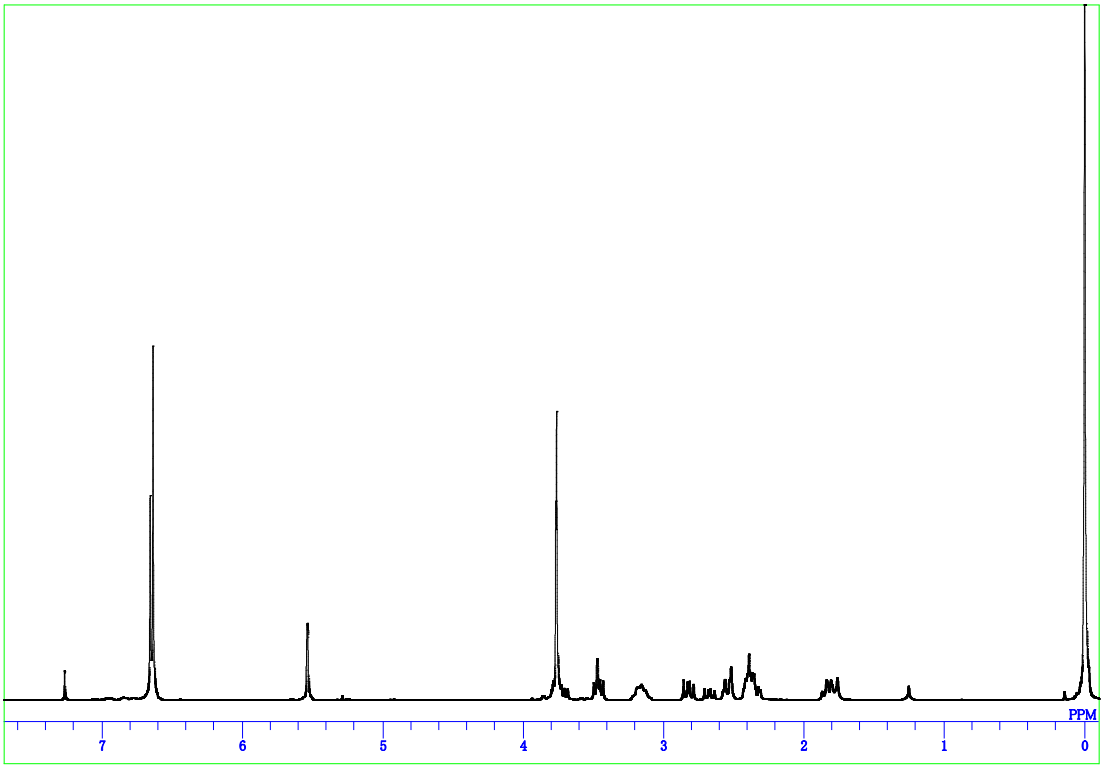

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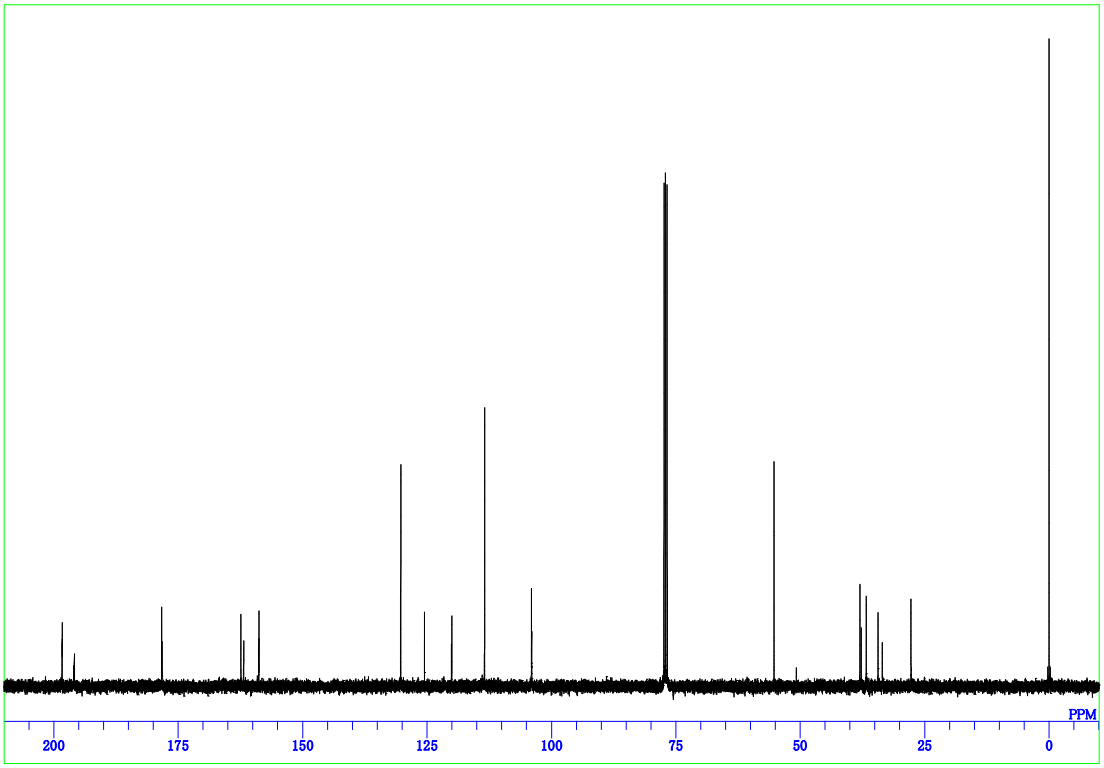

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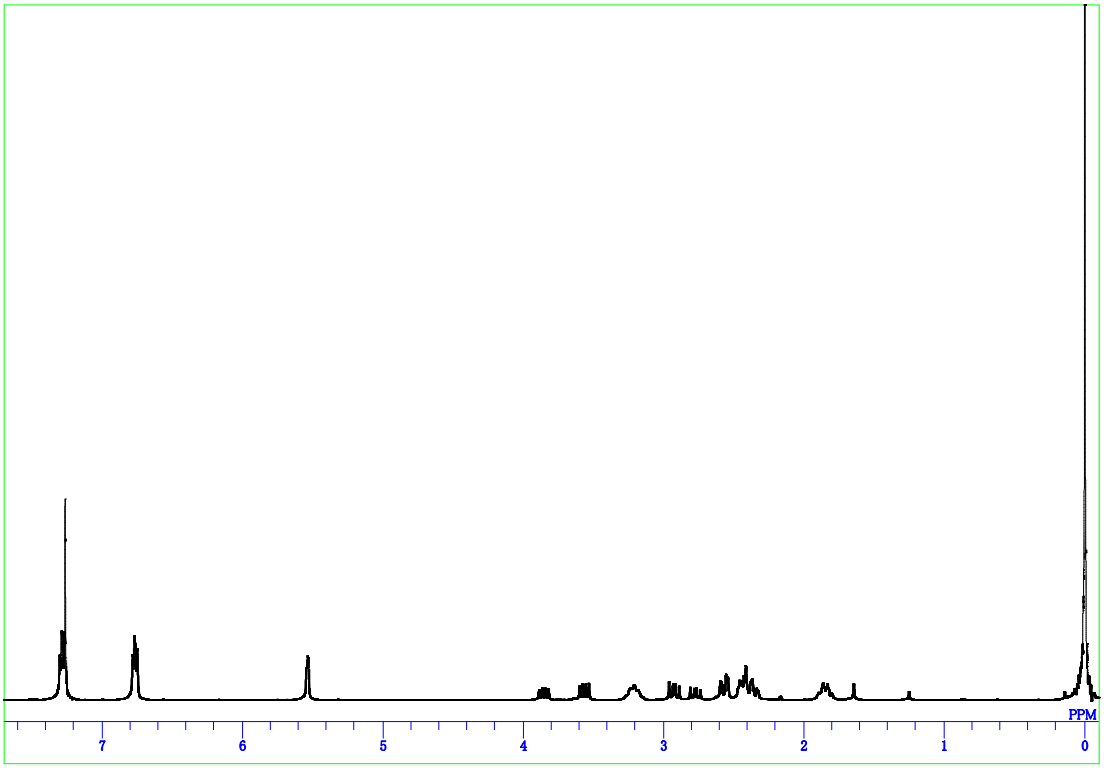

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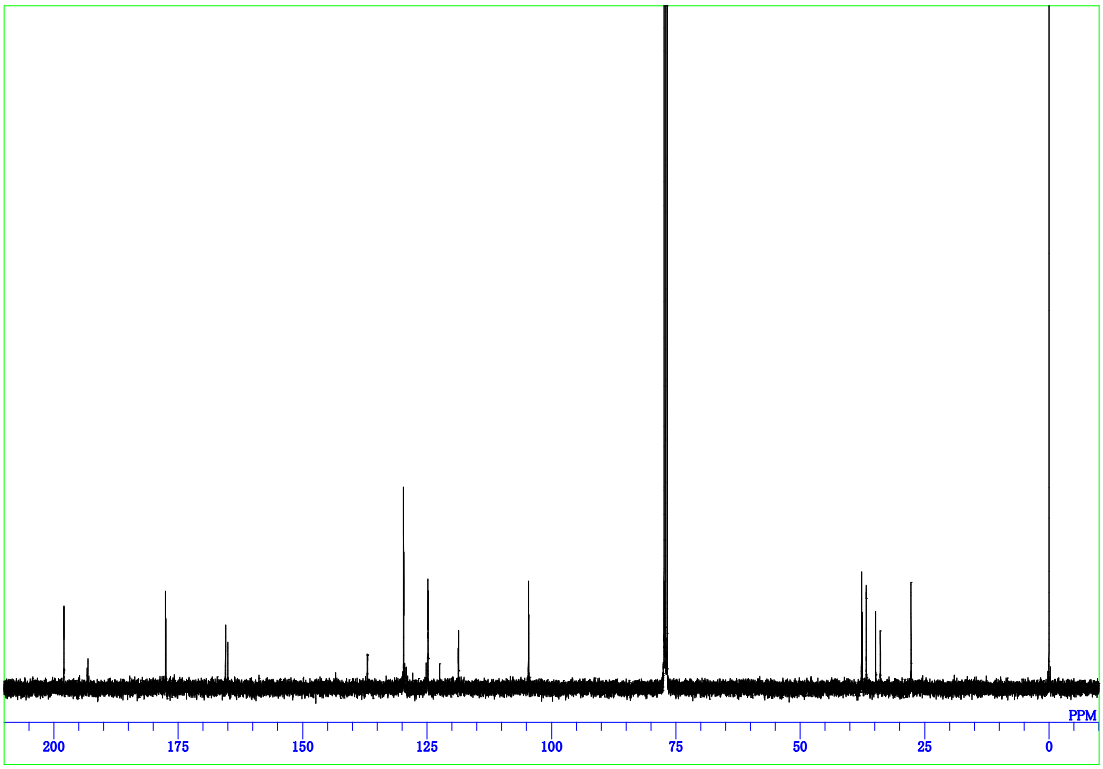

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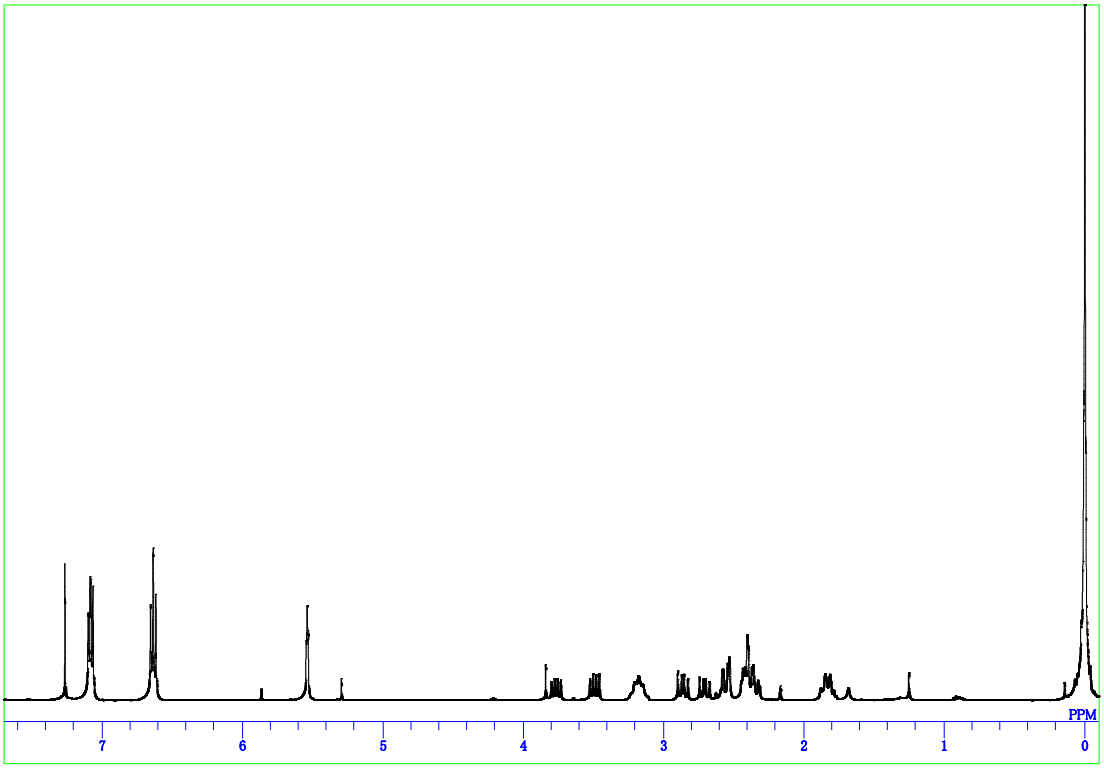

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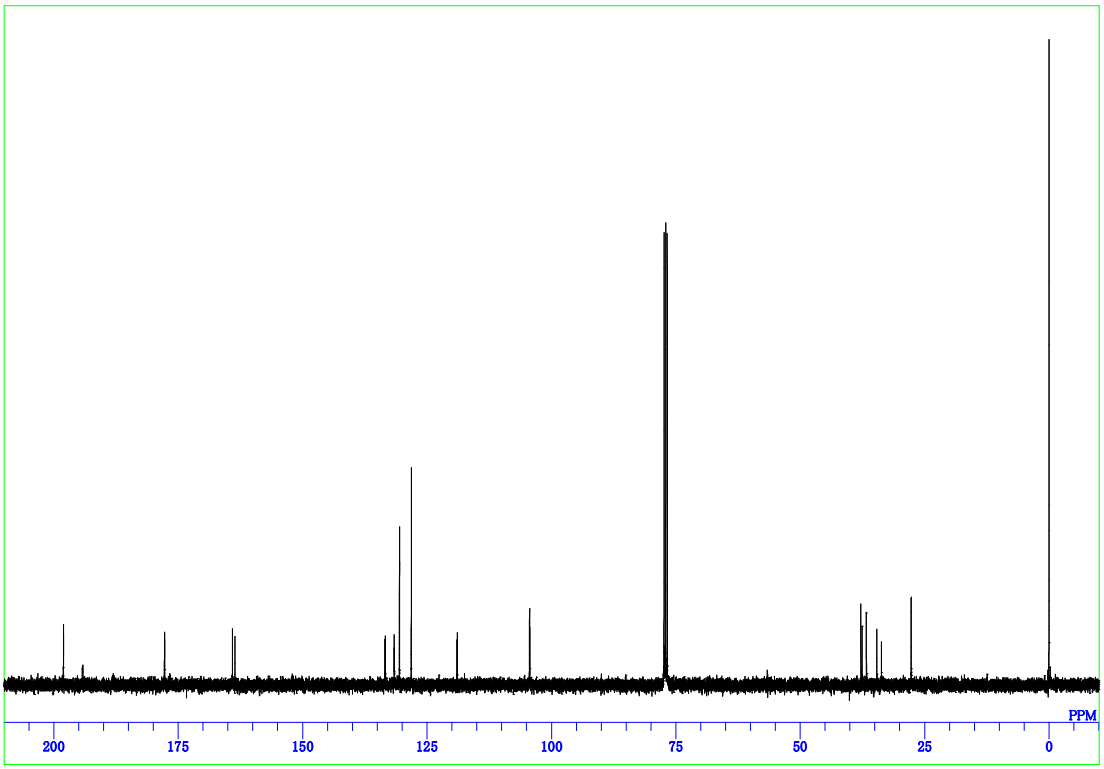

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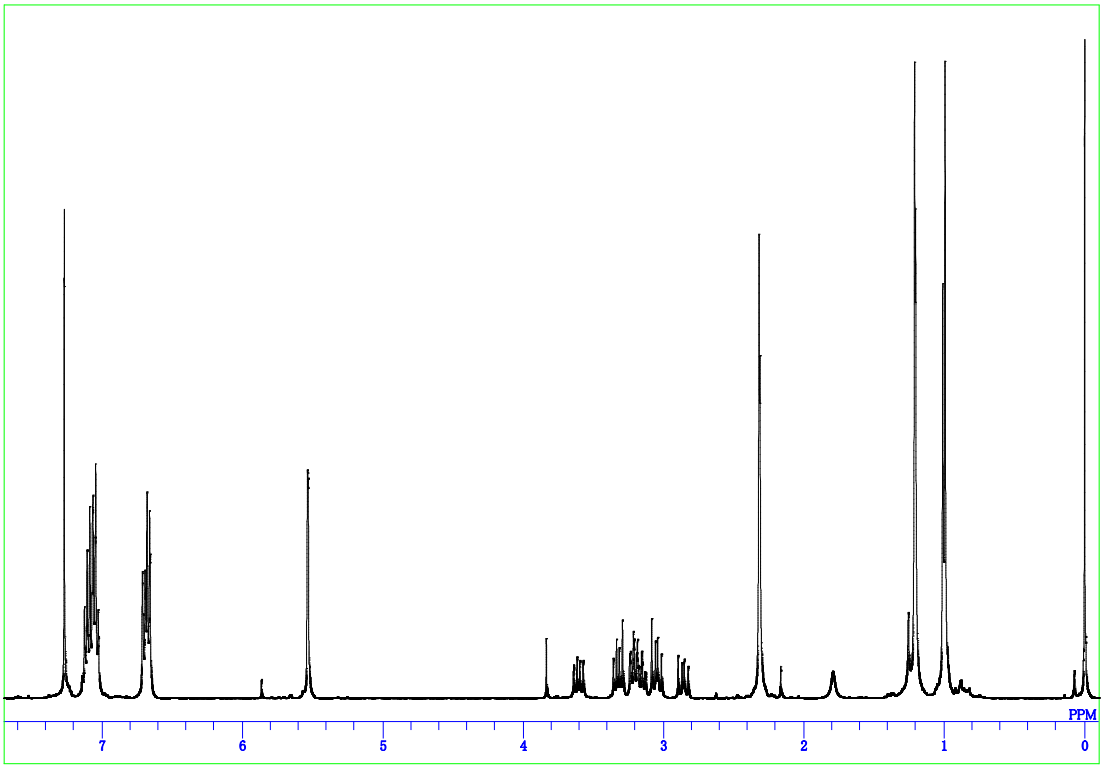

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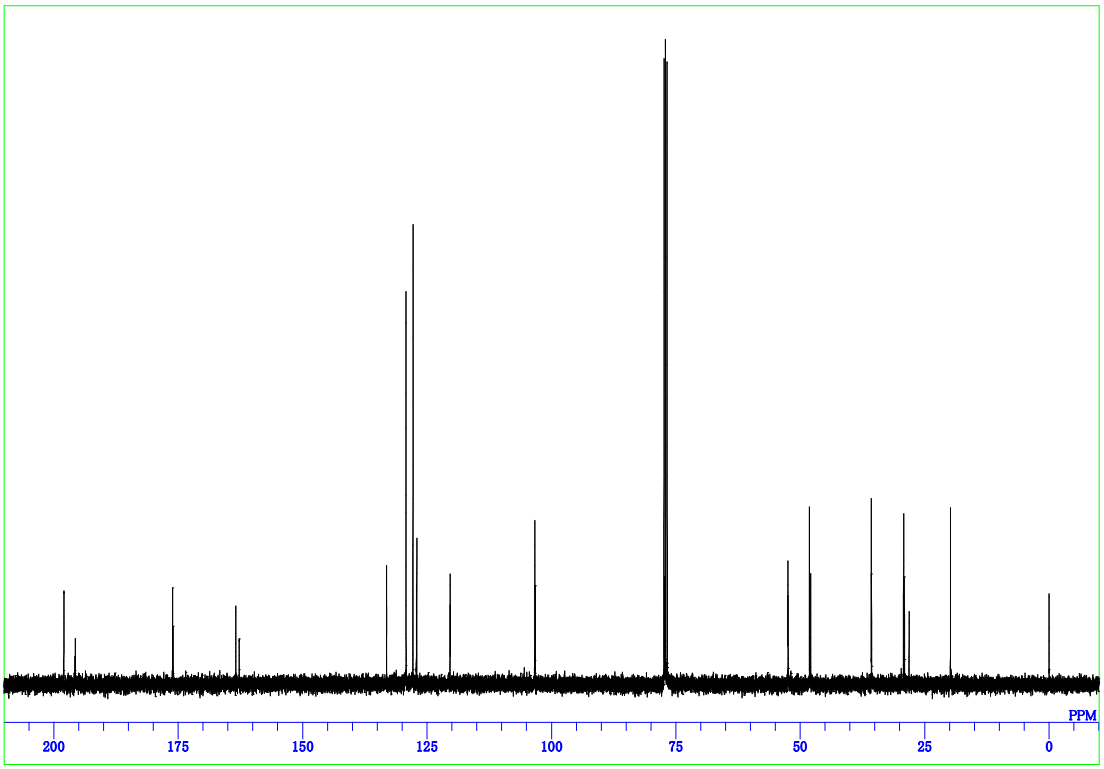
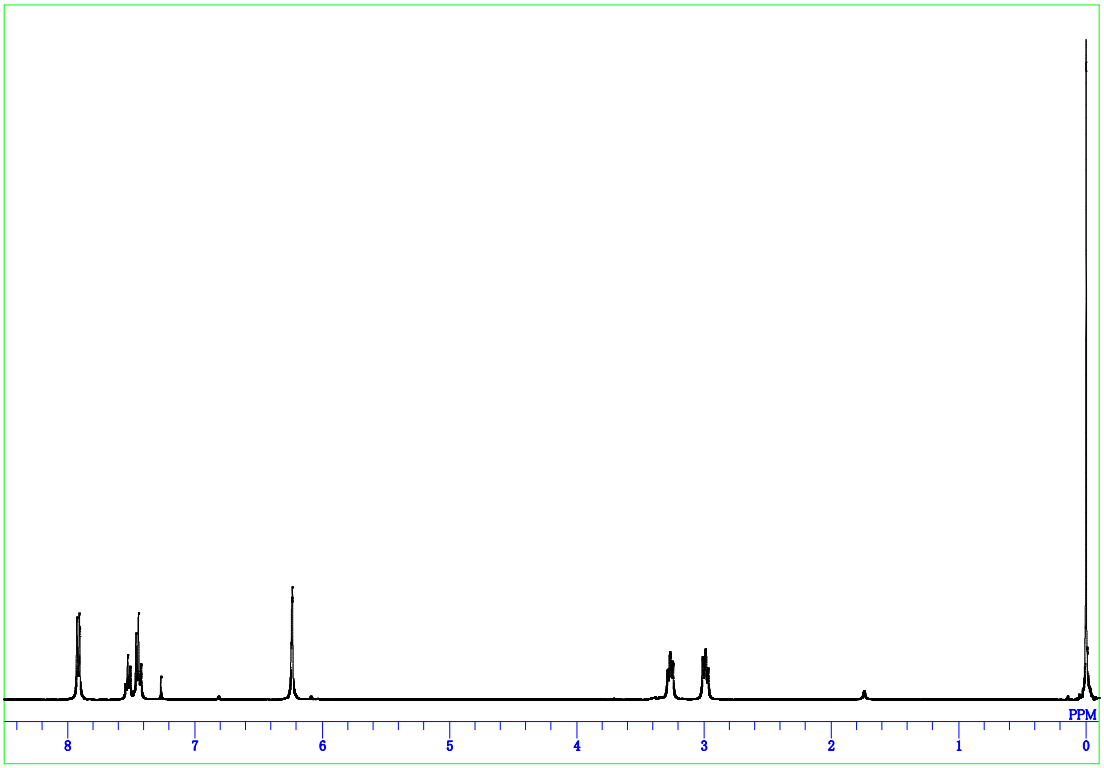
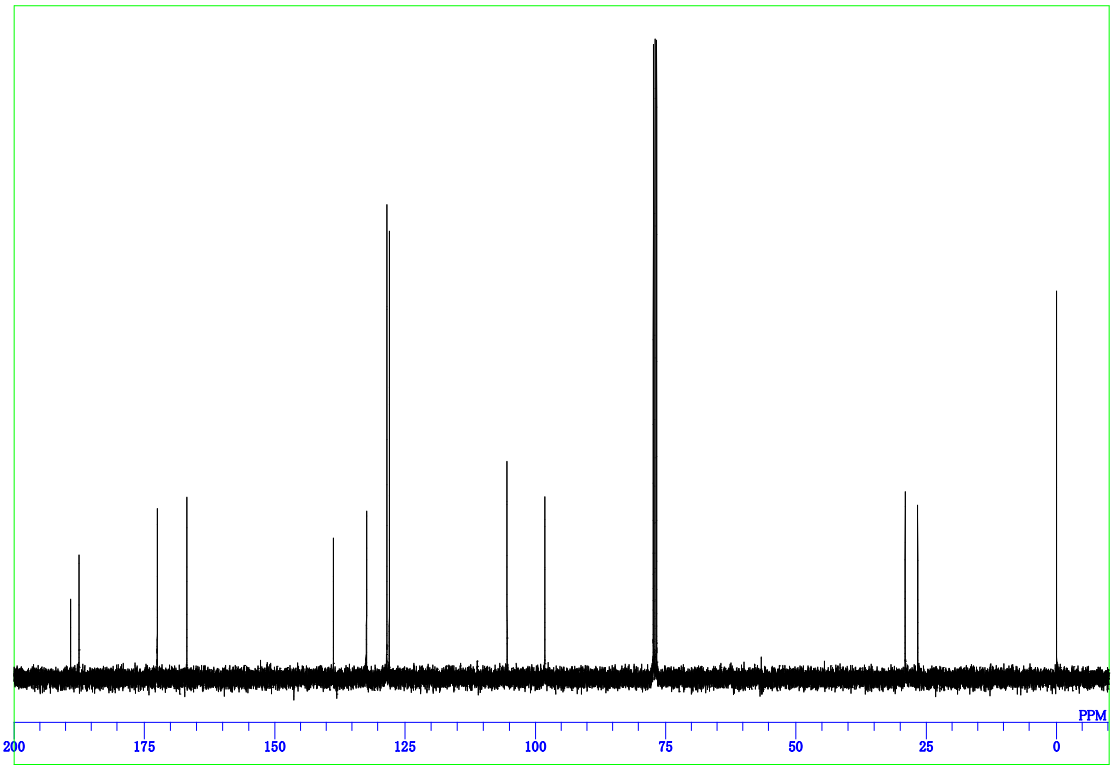


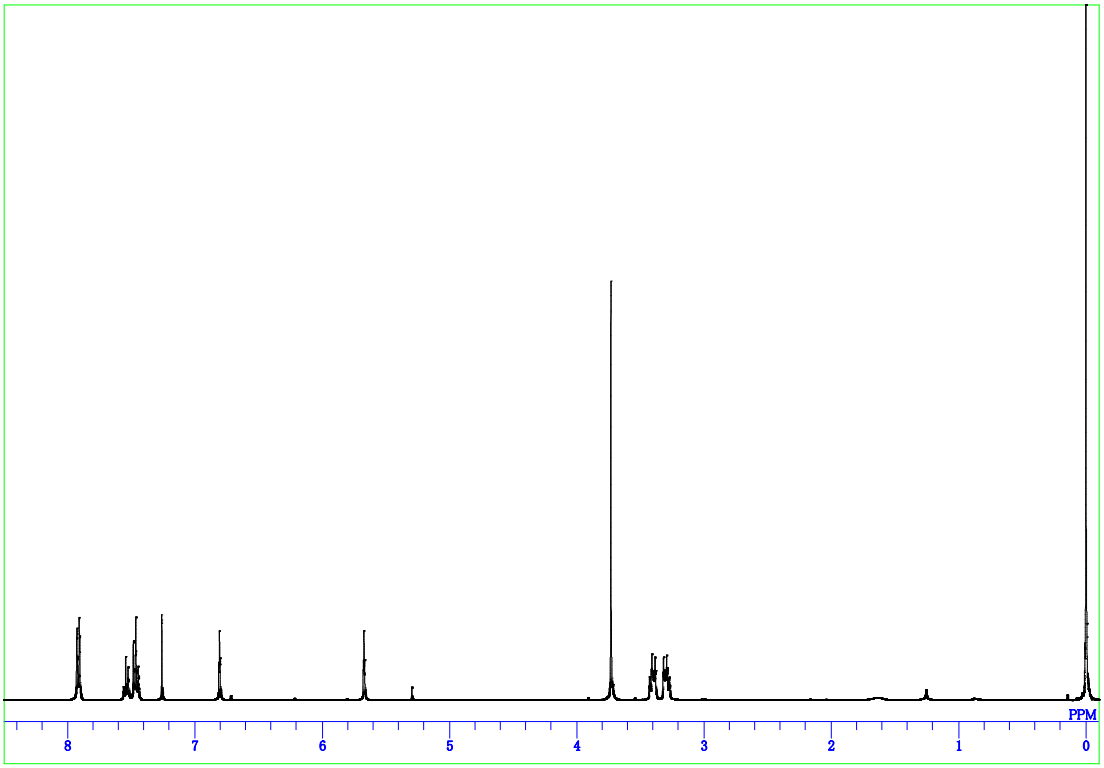
7-1H



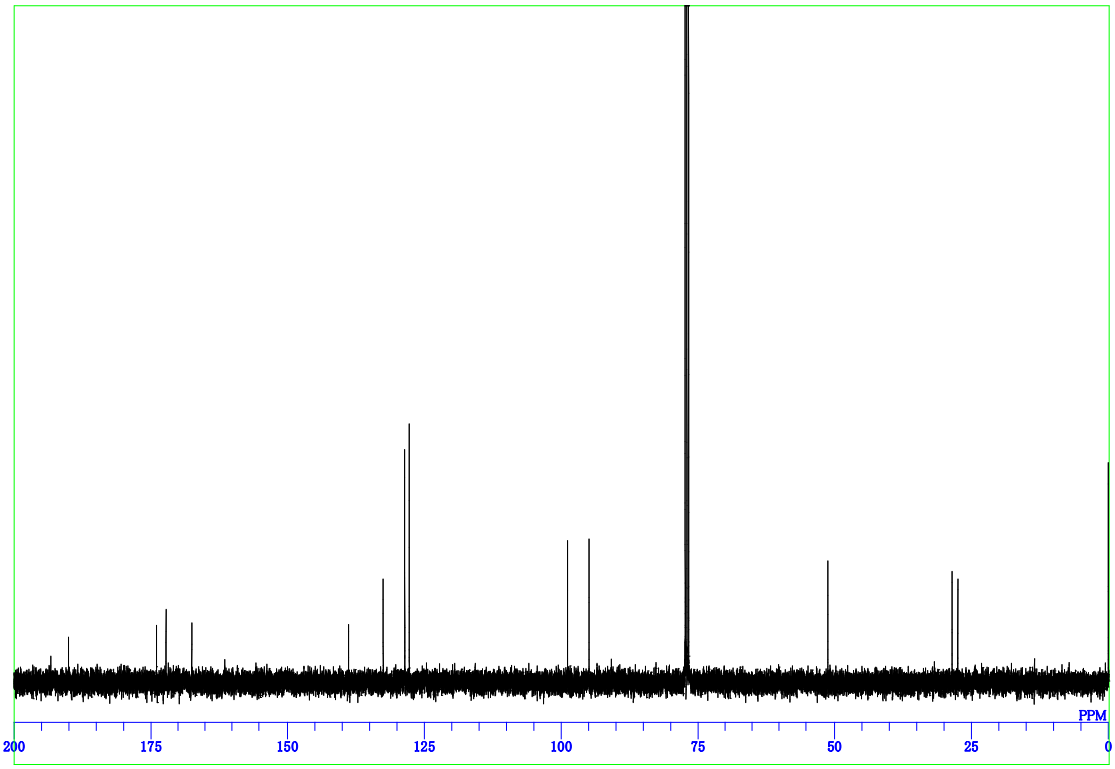
7-BCM



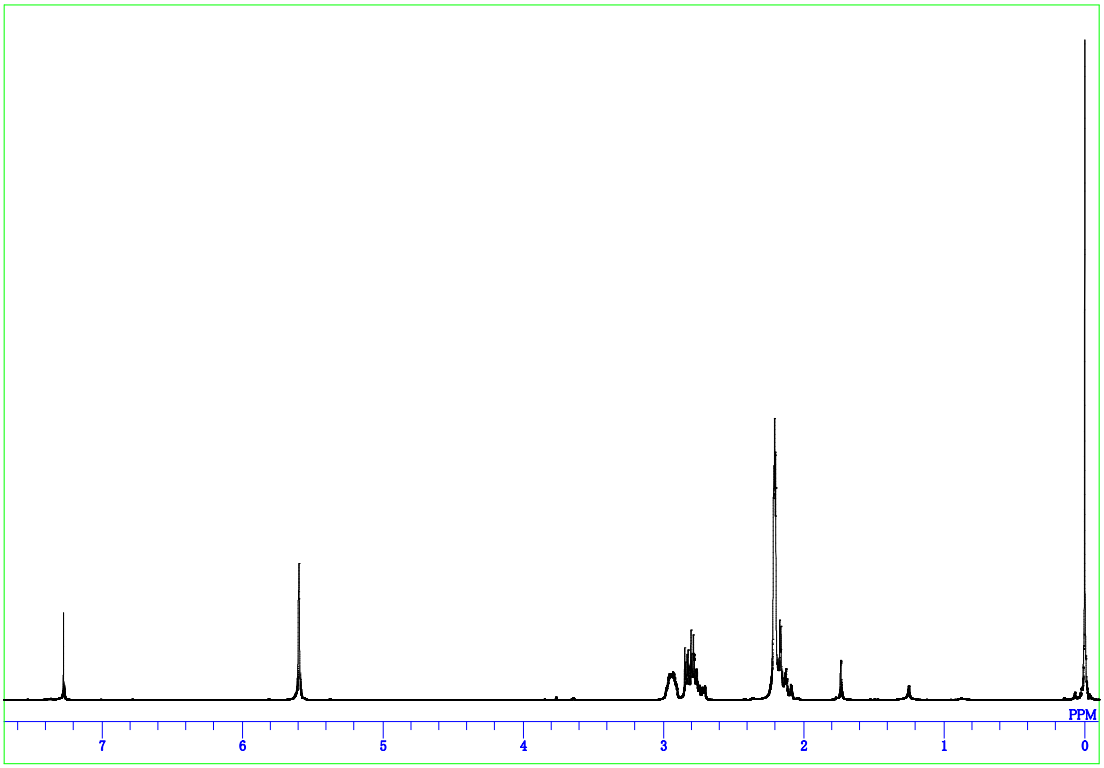
8-1H



8-BCM



9a-1H



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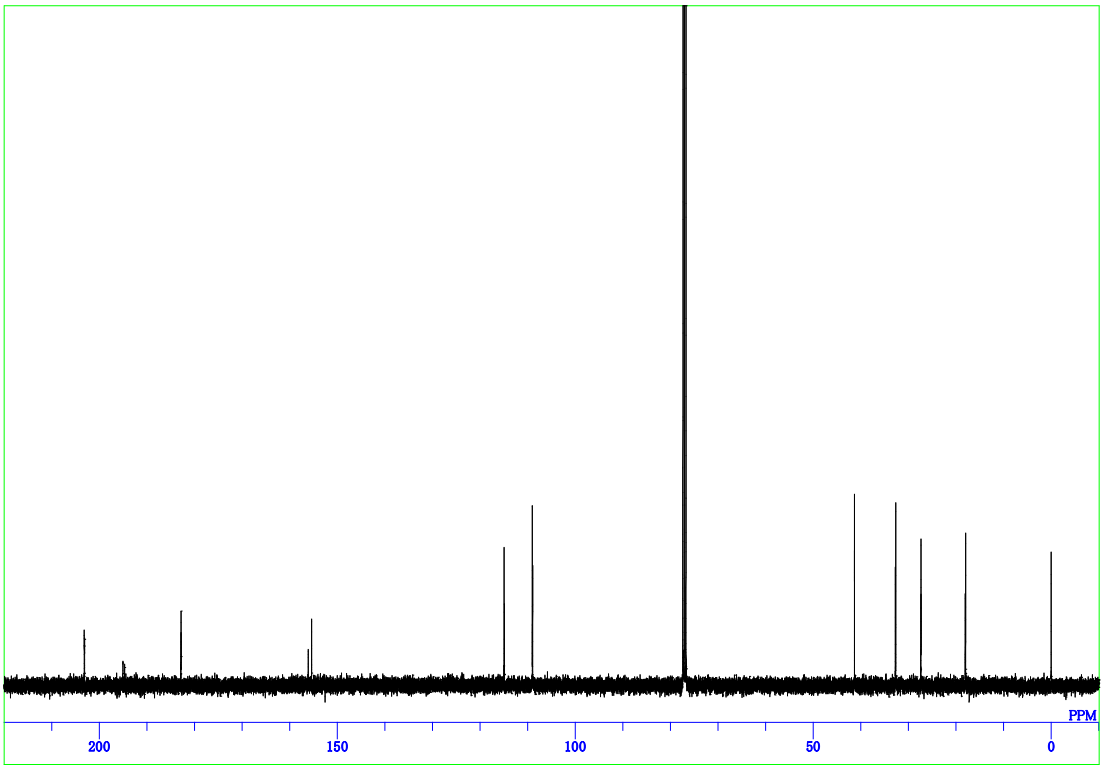

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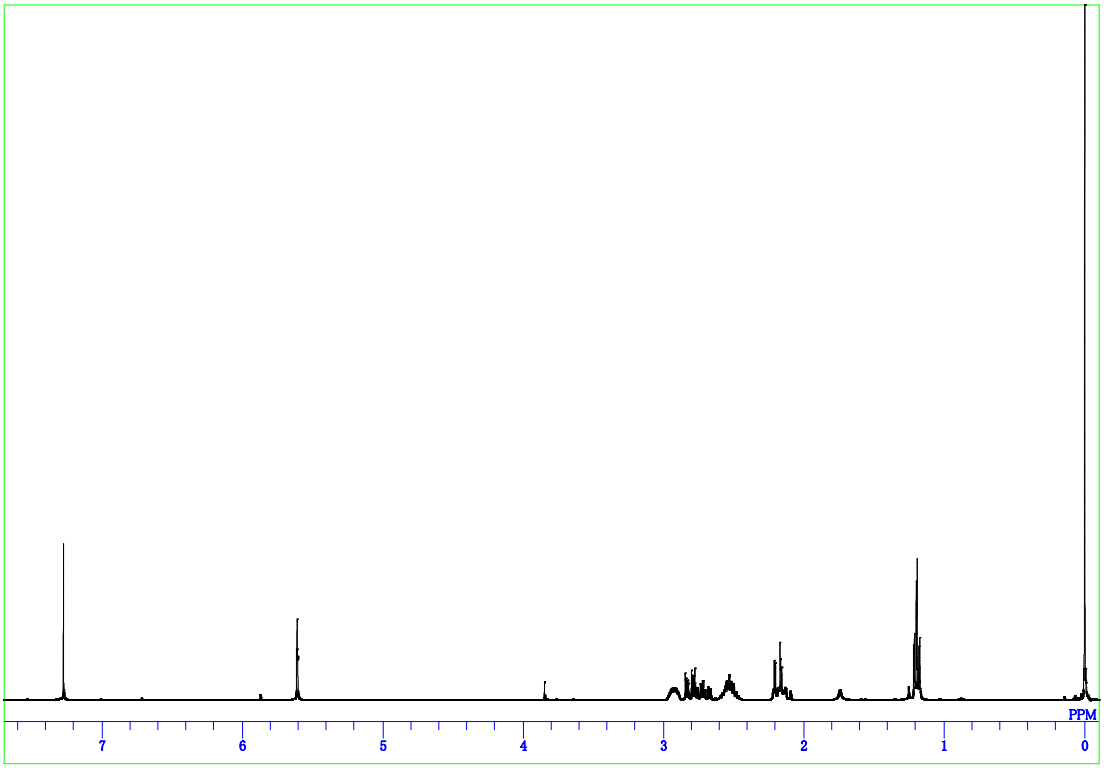

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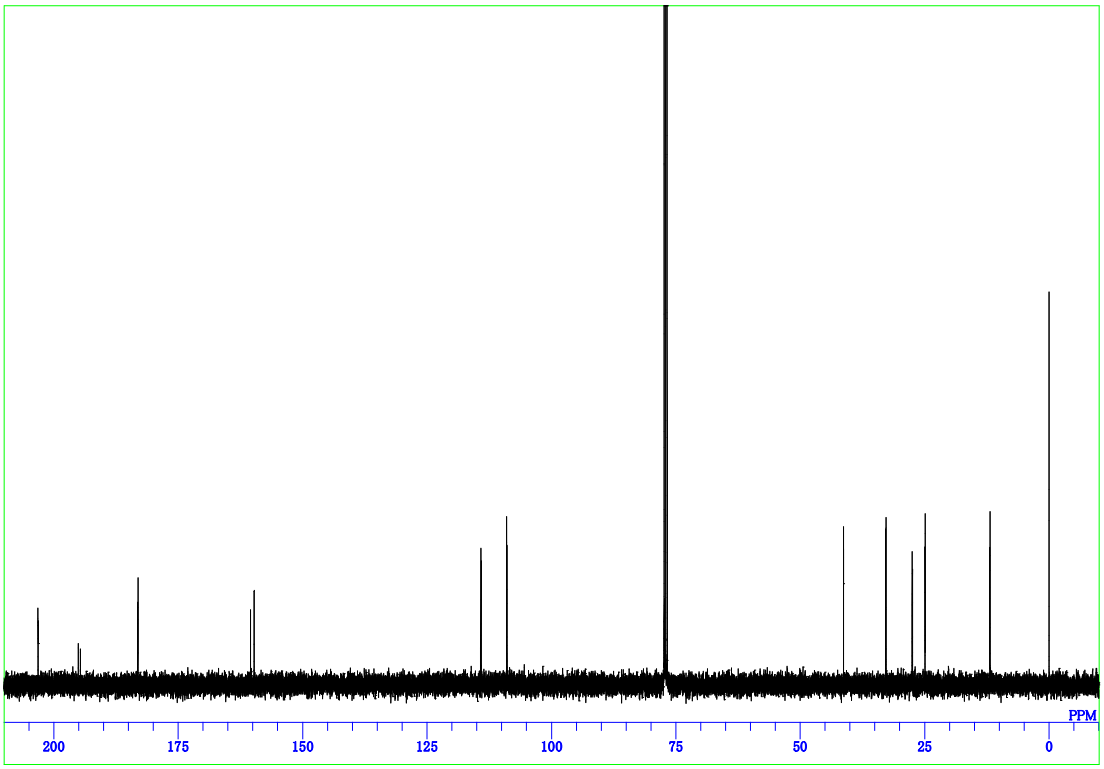

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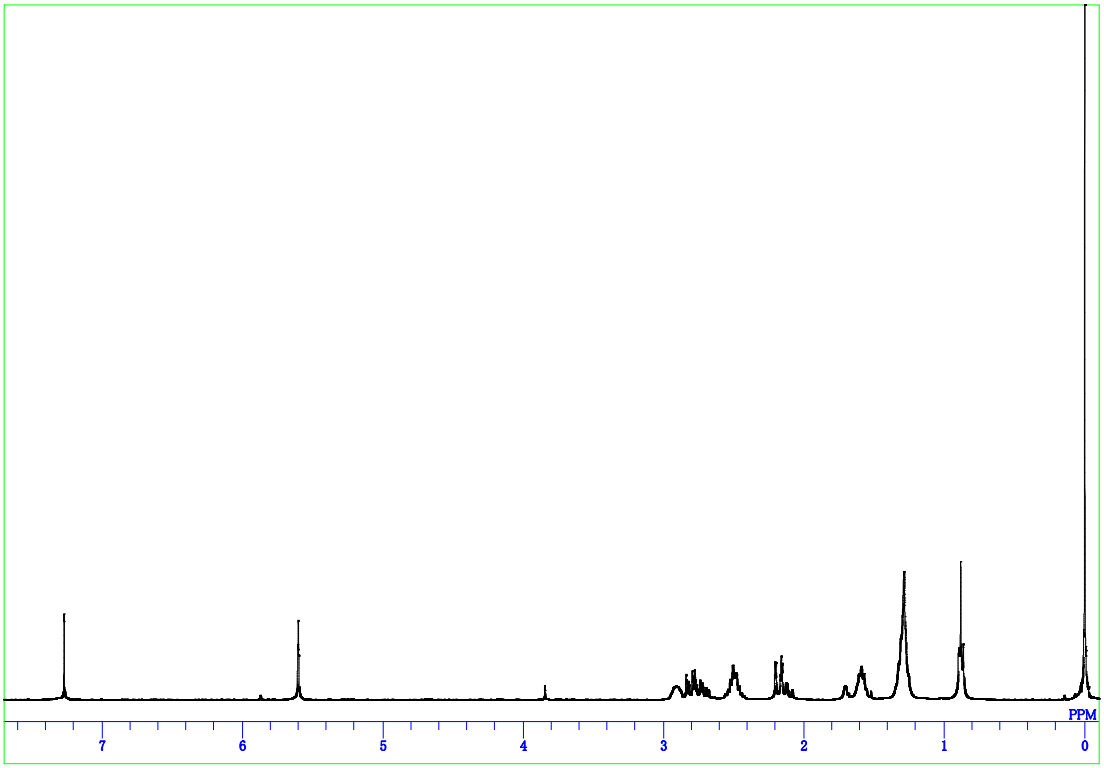

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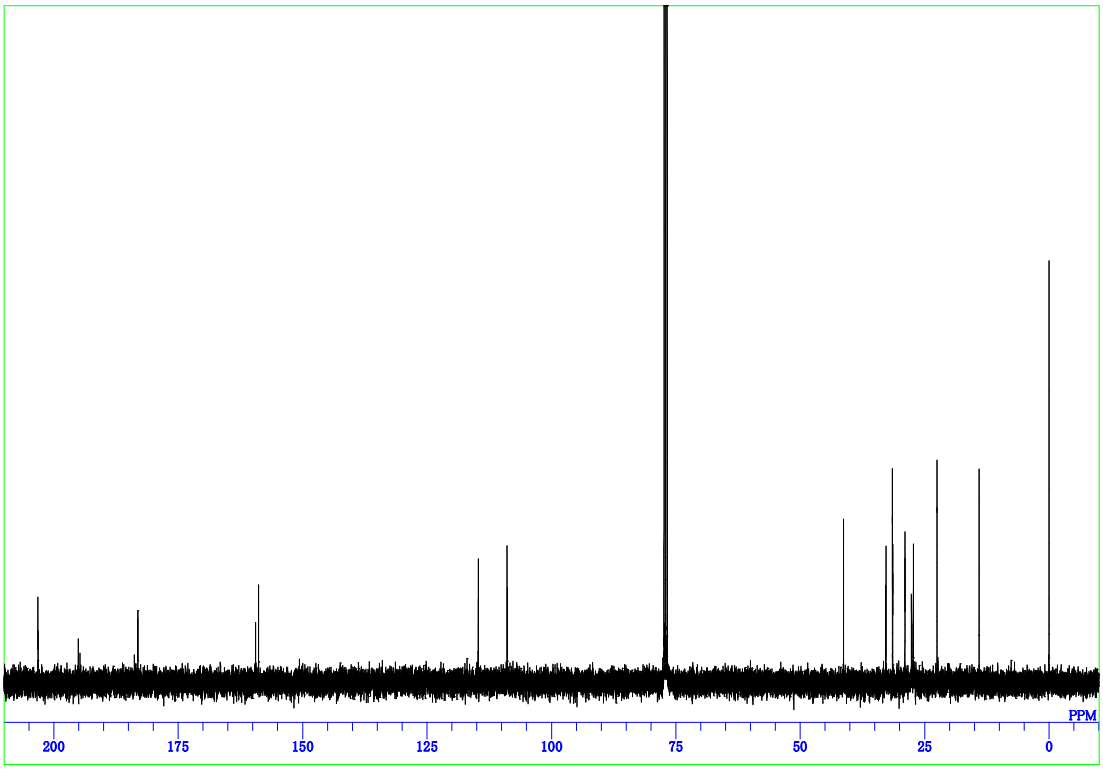

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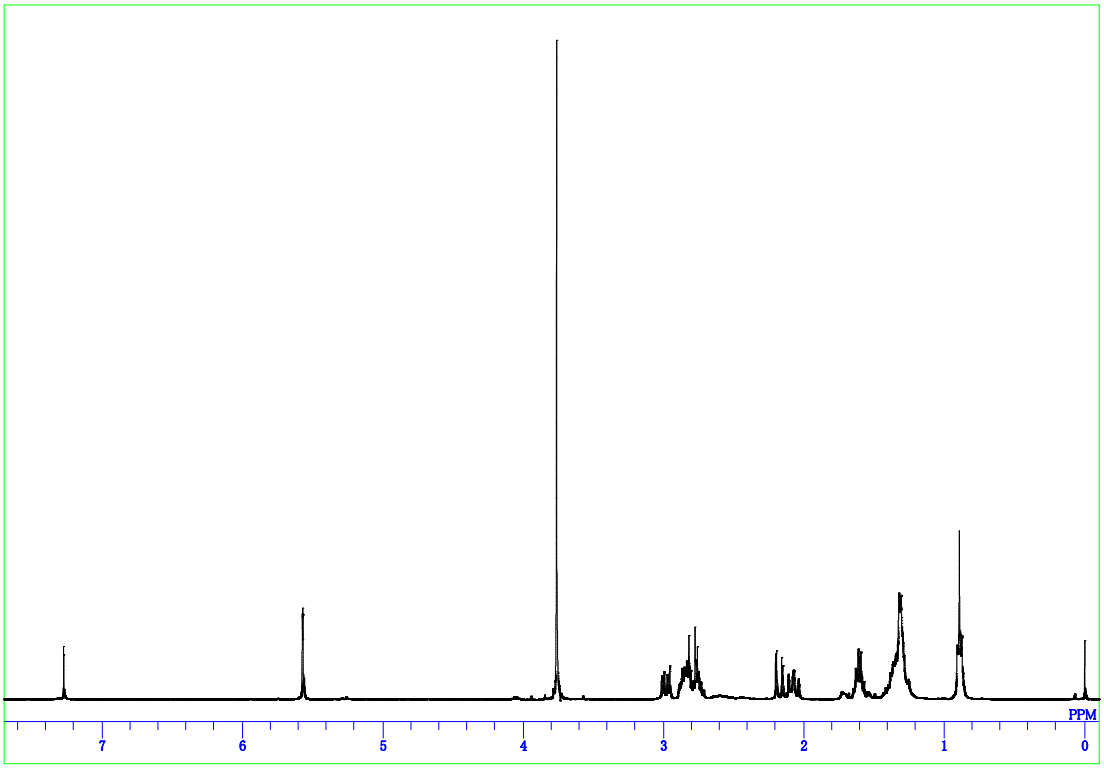

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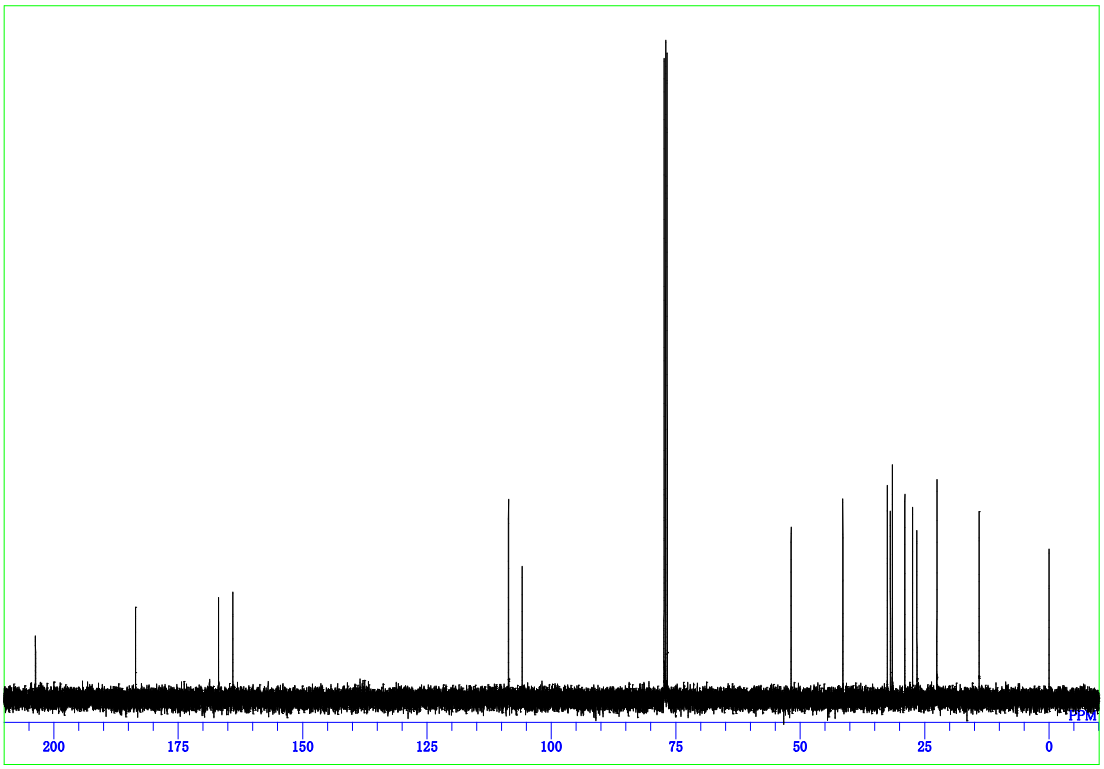

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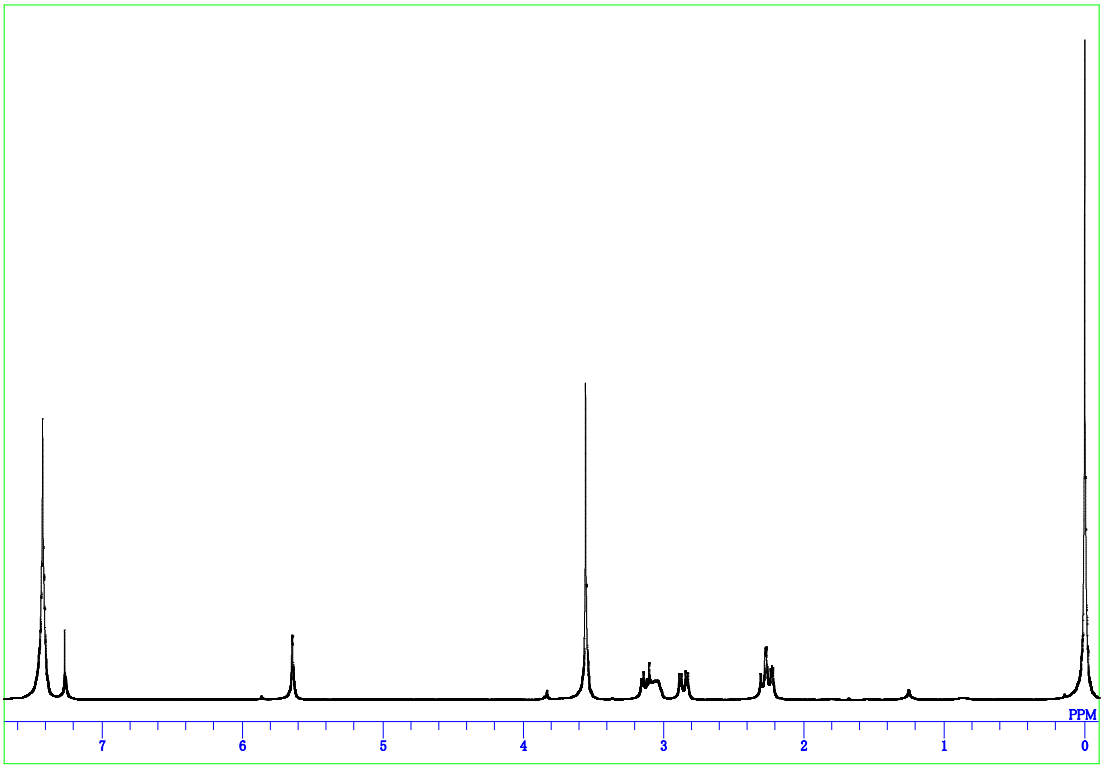

10d-BCM