Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

An efficient synthesis of amides from alcohols and azides catalyzed by a bifunctional catalyst Au/DNA under mild conditions

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Contents:

General Remarks

All substrates were purchased commercially without further purification. CeO_2 (CAS: 1306-38-3), Polyvinyl pyrrolidone (PVP K-30, CAS: 9003-39-8), polyethylene glycol (PEG-600, CAS: 25322-68-3) were purchased from Sinopharm Chemical Reagent Co., Ltd. Au/TiO_2 (CAS: 7440-57-5) was purchased from Strem Chemicals co., Ltd. The morphology and size of the nanoparticles were characterized on transmission electron microscopy (TEM) (JEOL–2010 and Hitachi H7650). The as-synthesized heterogenous catalysts dispersed with ethanol were used as samples directly and dried on the carbon-coated Cu grids. The accurate metal loading was directly determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) using Perkin Elmer Optima 7300 DV. ^{1}H NMR, ^{13}C NMR were recorded on a Bruker AC-400 FT (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) using TMS as internal reference. Infrared samples were recorded on a Bruker EQUINOX 55 spectrometer. HRMS were recorded on a MicroMass UK LTD GCT TOF-MS. GC-MS samples were recorded on a Shimadzu QP-5050 GC-MS system. And the yields were determined using 1,3,5-trimethylbenzene as an internal standard.

General procedures for the synthesis of heterogeneous catalysts

Preparation of M/DNA

M/DNA nanohybrids (M = Au, Pd, Pt, Ag) were synthesized as follow: 0.1 mmol of the corresponding metal salt (K_2PdCl_4, $KAuCl_4$, $AgNO_3$, K_2PtCl_6) and 10 mg of fish sperm DNA were dissolved in 10 mL Tris buffer (10mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion (Pd^{2+}, Ag^+, Au^{3+}, Pt^{4+}) thoroughly bind to DNA. After this aging process, 0.5 mmol of freshly dissolved $NaBH_4$ in 10 mL Tris buffer was added dropwise under N_2 atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N_2 from 0 °C to room temperature to obtain the resulting M/DNA nanohybrids (c.a. 5 mM in Tris).

Preparation of Au/PVP

Au/PVP: 0.05 mmol of $KAuCl_4$ and 50 mg of polyvinyl pyrrolidone were dissolved in 5 mL H_2O. The combined solution was stirred for 4 h. After this aging process, 0.25 mmol of freshly dissolved $NaBH_4$ in 5 mL H_2O was added dropwise under N_2 atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N_2 from 0 °C to room temperature to obtain the resulting Au-PVP (c.a. 5 mM in H_2O).

Preparation of Au/PEG

Au/PEG: 0.05 mmol of $KAuCl_4$ and 50 mg of polyethylene glycol were dissolved in 5 mL H_2O. The combined solution was stirred for 4 h. After this aging process, 0.25 mmol of freshly dissolved $NaBH_4$ in 5 mL H_2O was added dropwise under N_2 atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N_2 from 0 °C to room temperature to obtain the resulting Au/PEG (c.a. 5 mM in H_2O).

Preparation of Au/CeO_2

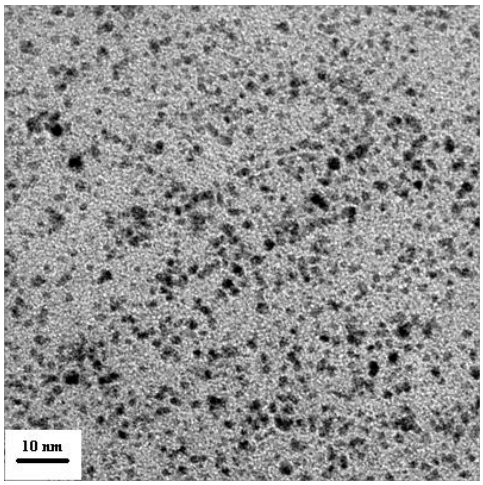
Au/CeO_2 catalyst was prepared via deposition-precipitation (DP) procedure. 1 g CeO_2 was dispersed in 20 mL of deionized water. An appropriate volume of 2.5 mM $HAuCl_4$ solution was added, and the pH value raised to 8 using 0.2 M NaOH. During the aging step, the slurry pH was maintained overnight at 298 K under constant stirring. Au/CeO_2 solid was then filtered and exhaustively washed with deionized water until no traces of chlorides were detected by the $AgNO_3$. The catalyst was dried at room temperature under vacuum before calcination at 200 °C for 4 h.

General procedure of the amidation catalyzed by Au/DNA

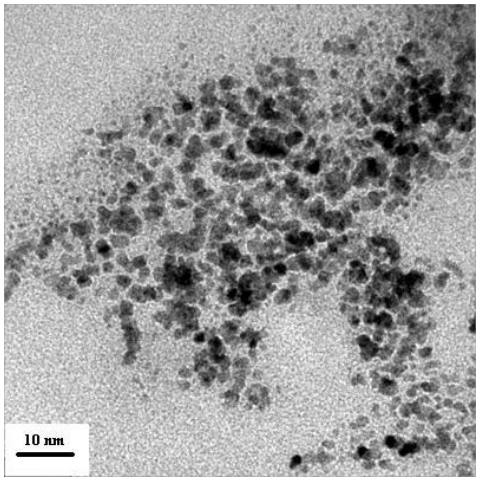
To 2 mL of as-synthesized Au/DNA excess EtOH (2-3 volumes) were added and the solutions were placed still for precipitation in 1-2 h. With the aid of centrifugation at 6500 r/min for 3 minutes, then the decantate were poured out. The residues were dried by N_2 flow and redispersed in 1 mL of water solution containing KOH or other bases. The solutions were placed in a glass tube with a magnetic stirring bar. Alcohol and azide were then added. The air in the reaction mixture was removed in vacuum and refilled with O_2. This procedure was repeated for three times. Then the reaction mixture was stirred under O_2 balloon at 50 °C for 12 hours. After the reaction was finished, to the reaction mixture 3 volumes of EtOH and 5 volumes of EtOAc were added. This reaction mixture was placed still for 2 h for precipitation and then centrifuged at 6500 r/min for 3 minutes. The decantate was poured out and the residue solid was dried by N_2 flow and redispersed in 1 mL of water solution containing KOH directly as the catalyst for the next round. The decantate was evaporated with a rotavapor. The obtained residue was purified with column chromatography over silica gel. The resulting products were characterized by ^1H NMR and ^{13}C NMR.

Characterization of Au/DNA

TEM analysis of Au/DNA



Au/DNA before reaction



Au/DNA after the fifth round

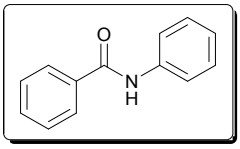
ICP analysis of Au/DNA

For the as-synthesized Au-DNA nanohybrids (2 mL), we redissolved it in water (1 mL) and measured the accurate gold concentration with ICP-OES to give a 9.6 mM

value. After five cycles the Au-DNA was recovered and redissolved in the same volume of water (1 mL). It was found that the corresponding Au concentration was decreased to 7.3 mM.

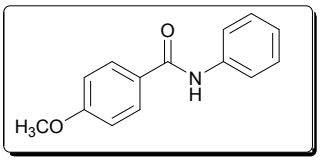
Characterization data of products

N-Phenyl-benzamide **(3aa)**



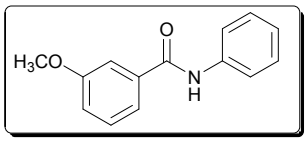
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.26 (s, 1H), 8.04 – 7.88 (m, 2H), 7.79 (m, 2H), 7.65 – 7.47 (m, 3H), 7.41 – 7.28 (m, 2H), 7.19 – 7.02 (m, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.0, 139.6, 135.5, 132.0, 129.1, 128.9, 128.1, 124.1, 120.8; IR (film, cm^{-1}): 3344, 2922, 1656, 1599, 1530, 1440, 750, 716; HRMS [M+H]$^+$ calcd for $C_{13}H_{12}NO$: 198.0919, found 198.0917. This compound was known.[1]

4-Methoxy-N-phenyl-benzamide (**3ba**)



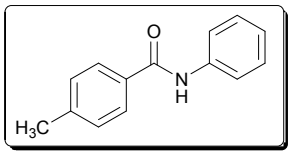
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.06 (s, 1H), 8.03 – 7.88 (m, 2H), 7.82 – 7.69 (m, 2H), 7.40 – 7.25 (m, 2H), 7.13 – 6.95 (m, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 164.9, 161.9, 139.3, 129.6, 128.5, 126.9, 123.4, 120.3, 113.6, 55.4; IR (film, cm^{-1}): 3291, 2960, 1658, 1450, 1376, 1260, 1092, 836, 750; HRMS [M+H]$^+$ calcd for $C_{14}H_{14}NO_2$: 228.1025, found 228.1030. This compound was known.[1]

3-Methoxy-N-phenyl-benzamide (**3ca**)



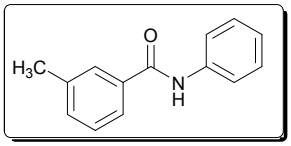
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.21 (s, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.47 (m, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.14 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 165.7, 159.7, 139.6, 136.9, 130.0, 129.1, 124.2, 121.0, 120.3, 117.8, 113.4, 55.8; IR (film, cm^{-1}): 3293, 2961, 1658, 1455, 1375, 1268, 1100, 859, 753; HRMS [M+H]$^+$ calcd for $C_{14}H_{14}NO_2$: 228.1025, found 228.1031. This compound was known.[2]

4-Methyl-N-phenyl-benzamide (**3da**)



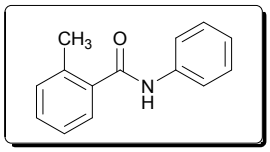
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.14 (s, 1H), 7.88 (d, J = 8.2 Hz, 2H), 7.78 (m, 2H), 7.35 (m, 4H), 7.14 – 7.04 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 165.3, 141.5, 139.2, 132.1, 128.9, 128.5, 127.7, 123.5, 120.3, 20.9; IR (film, cm^{-1}): 3350, 2973, 1661, 1438, 1389, 1095, 1053, 882, 748; HRMS [M+H]$^+$ calcd for $C_{14}H_{14}NO$: 212.1075, found 212.1075. This compound was known.[1]

3-Methyl-N-phenyl-benzamide (**3ea**)



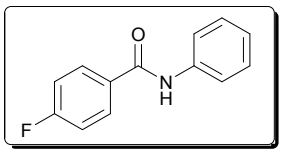
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.27 (s, 1H), 7.74 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 7.6 Hz, 1H), 7.42 – 7.25 (m, 5H), 7.09 (t, J = 7.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 167.8, 139.3, 137.3, 135.1, 130.5, 129.5, 128.6, 127.1, 125.6, 123.5, 119.6, 19.3; IR (film, cm^{-1}): 3357, 2922, 1648, 1600, 1535, 1324, 859, 753; HRMS [M+H]$^+$ calcd for $C_{14}H_{14}NO_2$: 212.1075, found 212.1075.This compound was known.[1]

2-Methyl-N-phenyl-benzamide (**3fa**)



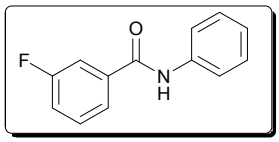
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.18 (s, 1H), 7.85 – 7.70 (m, 4H), 7.41 (m, 2H), 7.38 – 7.30 (m, 2H), 7.17 – 7.00 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 165.6, 139.2, 137.6, 135.0, 132.1, 128.5, 128.2, 128.1, 124.8, 123.6, 120.3, 20.9; IR (film, cm^{-1}): 3286, 2922, 1652, 1535, 1440, 1321, 837, 753; HRMS [M+H]$^+$ calcd for $C_{14}H_{14}NO_2$: 212.1075, found 212.1075. This compound was known.[1]

4-Fluoro-N-phenyl-benzamide (**3ga**)



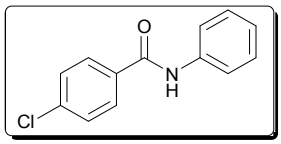
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.29 (s, 1H), 8.13 – 7.97 (m, 2H), 7.84 – 7.75 (m, 2H), 7.45 – 7.32 (m, 4H), 7.16 – 7.07 (m, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 165.8, 164.9, 163.3, 139.5, 131.9, 131.8, 130.9, 130.8, 129.4, 129.1, 124.2, 120.9, 115.9, 115.7; IR (film, cm^{-1}): 3349, 2920, 1655, 1529, 1440, 1260, 847, 752; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}FNO$: 216.0825, found 216.0823.This compound was known.[1]

3-Fluoro-N-phenyl-benzamide (**3ha**)



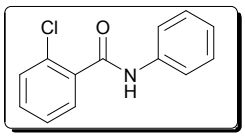
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.30 (s, 1H), 7.86 – 7.70 (m, 4H), 7.59 (m, 1H), 7.51 – 7.40 (m, 1H), 7.40 – 7.30 (m, 2H), 7.17 – 7.04 (m, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 164.1, 164.1, 163.1, 160.7, 138.9, 137.3, 137.2, 130.6, 130.5, 128.6, 123.9, 123.9, 123.8, 120.5, 118.5, 118.3, 114.6, 114.3; IR (film, cm^{-1}): 3351, 2921, 1655, 1530, 1444, 1260, 858, 752; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}FNO$: 216.0825, found 216.0827. This compound was known.[3]

4-Chloro-N-phenyl-benzamide (**3ia**)



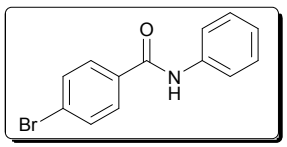
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.31 (s, 1H), 8.05 – 7.90 (m, 2H), 7.77 (d, J = 7.6 Hz, 2H), 7.69 – 7.54 (m, 2H), 7.36 (m, 2H), 7.11 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 164.9, 139.4, 136.8, 134.1, 130.1, 129.1, 128.9, 124.3, 120.9; IR (film, cm^{-1}): 3348, 2920, 1653, 1598, 1440, 1285, 847, 755; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}ClNO$: 232.0529, found 232.0537. This compound was known.[1]

2-chloro-N-phenylbenzamide (**3ja**)



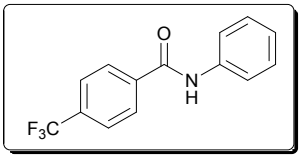
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.51 (s, 1H), 7.78 – 7.68 (m, 2H), 7.62 – 7.41 (m, 4H), 7.35 (t, J = 7.9 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 165.4, 139.4, 137.5, 131.5, 130.4, 130.1, 129.4, 129.3, 127.7, 124.3, 120.0; IR (film, cm^{-1}): 3360, 2924, 1661, 1451, 1376, 1260, 1040, 836, 801; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}ClNO$: 232.0529, found 232.0519. This compound was known.[1]

4-Bromo-N-phenyl-benzamide (**3ka**)



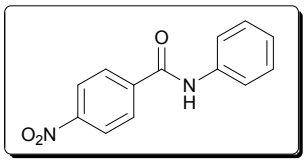
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.30 (s, 1H), 7.95 – 7.83 (m, 2H), 7.82 – 7.65 (m, 4H), 7.36 (m, 2H), 7.11 (m, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 164.5, 138.9, 134.0, 131.4, 129.8, 128.6, 125.3, 123.8, 120.4; IR (film, cm^{-1}): 3345, 2920, 1655, 1599, 1531, 1463, 1441, 845, 753; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}BrNO$: 276.0024, found 276.0019. This compound was known.[1]

N-phenyl-4-(trifluoromethyl)benzamide (**3la**)



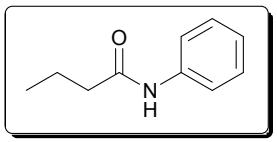
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.48 (s, 1H), 8.15 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.38 (m, 2H), 7.14 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 164.9, 139.3, 132.3, 131.9, 131.6, 129.2, 129.1, 125.8, 125.8, 125.8, 125.7, 124.5, 123.0, 120.9,119.4; IR (film, cm^{-1}): 3347, 2922, 1657, 1535, 1447, 1260, 1114, 859, 754; HRMS [M+H]$^+$ calcd for $C_{14}H_{11}F_3NO$: 266.0793, found 266.0793. This compound was known.[1]

4-nitro-N-phenylbenzamide (**3ma**)



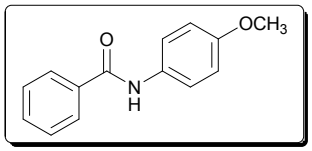
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.57 (s, 1H), 8.38 (d, J = 8.9 Hz, 2H), 8.19 (d, J = 8.9 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 164.4, 149.6, 141.1, 139.2, 129.7, 129.2, 124.7, 124.0, 121.0; IR (film, cm^{-1}): 3322, 2929, 2675, 1792, 1656, 1600, 1532, 1348, 1321, 853, 758; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}N_2O_3$: 243.0770, found 243.0776. This compound was known.[1]

N-phenylbutyramide (**3na**)



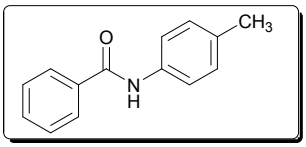
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 9.84 (s, 1H), 7.58 (d, J = 7.6 Hz, 2H), 7.28 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 2.27 (t, J = 7.3 Hz, 2H), 1.61 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 171.6, 139.8, 129.0, 123.3, 119.5, 38.8, 19.0, 14.1; IR (film, cm^{-1}): 3287, 2959, 1658, 1600, 1546, 1442, 1249, 757; HRMS [M+H]$^+$ calcd for $C_{10}H_{14}NO$: 164.1075, found 164.1074. This compound was known.[4]

N-(4-Methoxy-phenyl)-benzamide (**3ab**)



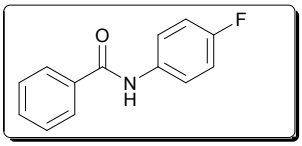
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.13 (s, 1H), 7.99 – 7.90 (m, 2H), 7.68 (d, J = 9.0 Hz, 2H), 7.63 – 7.45 (m, 3H), 6.99 – 6.83 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 165.6, 156.1, 135.5, 132.7, 131.8, 128.8, 128.0, 122.4, 114.2, 55.6; IR (film, cm^{-1}): 3330, 2926, 1647, 1515, 1448, 1376, 1249, 1031, 822, 715; HRMS [M+H]$^+$ calcd for $C_{14}H_{14}NO_2$: 228.1025, found 228.1031. This compound was known.[1]

N-p-Tolyl-benzamide (**3ac**)



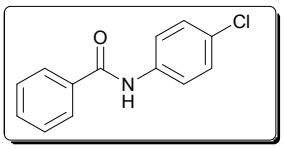
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.17 (s, 1H), 7.98 – 7.91 (m, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.63 – 7.47 (m, 3H), 7.15 (d, J = 8.3 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 165.8, 137.1, 135.5, 133.1, 131.9, 129.5, 128.8, 128.0, 120.8, 21.0; IR (film, cm^{-1}): 3309, 2920, 1646, 1597, 1527, 1404, 1318, 812, 712; HRMS [M+H]$^+$ calcd for $C_{14}H_{14}NO$: 212.1075, found 212.1076. This compound was known.[1]

N-(4-Fluoro-phenyl)-benzamide (**3ad**)



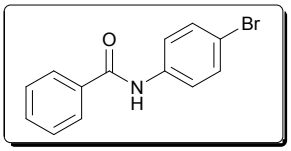
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.31 (s, 1H), 7.98 – 7.91 (m, 2H), 7.79 (m, 2H), 7.64 – 7.48 (m, 3H), 7.28 – 7.15 (m, 2H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 165.9, 159.9, 157.6, 136.0, 136.0, 135.3, 132.1, 128.8, 128.1, 122.7, 122.6, 115.8, 115.5; IR (film, cm^{-1}): 3350, 2922, 1656, 1600, 1510, 1400, 817, 715; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}FNO$: 216.0825, found 216.0827. This compound was known.[3]

N-(4-Chloro-phenyl)-benzamide (**3ae**)



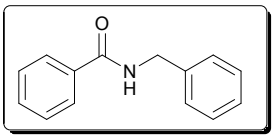
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.40 (s, 1H), 8.19 – 7.90 (m, 2H), 7.90 – 7.76 (m, 2H), 7.66 – 7.50 (m, 3H), 7.50 – 7.26 (m, 2H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.1, 138.6, 135.2, 132.2, 129.0, 128.9, 128.1, 127.7, 122.3; IR (film, cm^{-1}): 3346, 2924, 1653, 1595, 1519, 1398, 823, 718; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}ClNO$: 232.0529, found 232.0529. This compound was known.[1]

N-(4-Bromo-phenyl)-benzamide (**3af**)



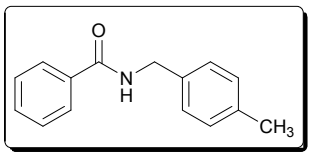
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 10.39 (s, 1H), 7.99 – 7.92 (m, 2H), 7.86 – 7.69 (m, 2H), 7.66 – 7.49 (m, 5H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.1, 139.0, 135.1, 132.2, 131.9, 128.9, 128.1, 122.7, 115.8; IR (film, cm^{-1}): 3332, 2922, 1649, 1593, 1523, 1393, 820, 718; HRMS [M+H]$^+$ calcd for $C_{13}H_{11}BrNO$: 276.0024, found 276.0019. This compound was known.[5]

N-benzylbenzamide (**3ag**)



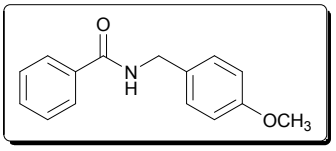
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 9.06 (t, J = 5.8 Hz, 1H), 7.89 (m, 2H), 7.61 – 7.40 (m, 3H), 7.41 – 7.17 (m, 5H), 4.48 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.6, 140.2, 134.8, 131.7, 128.8, 128.8, 127.7, 127.6, 127.2, 43.0; IR (film, cm^{-1}): 3326, 2923, 1641, 1540, 1451, 1376, 1259, 802, 727, 694; HRMS [M+H]$^+$ calcd for $C_{14}H_{14}NO$: 212.1075, found 212.1074. This compound was known[6].

N-(4-methylbenzyl)benzamide (**3ah**)



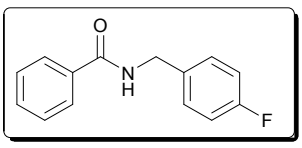
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 9.01 (t, J = 5.9 Hz, 1H), 7.88 (m, 2H), 7.58 – 7.42 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 4.43 (d, J = 6.0 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.6, 137.1, 136.2, 134.8, 131.7, 129.3, 128.8, 127.7, 127.7, 42.8, 21.1; IR (film, cm^{-1}): 3306, 2920, 1632, 1552, 1450, 785, 694; HRMS [M+H]$^+$ calcd for $C_{15}H_{16}NO$: 226.1232, found 226.1240. This compound was known[7].

N-(4-methoxybenzyl)benzamide (**3ai**)



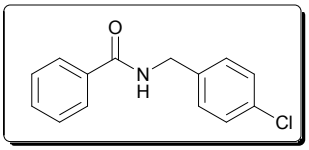
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 9.00 (t, J = 5.9 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.58 – 7.42 (m, 3H), 7.25 (t, J = 5.7 Hz, 2H), 6.94 – 6.83 (m, 2H), 4.42 (d, J = 6.0 Hz, 2H), 3.73 (d, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.5, 158.6, 134.9, 132.1, 131.6, 129.1, 128.7, 127.7, 114.1, 55.5, 42.5; IR (film, cm^{-1}): 3354, 2923, 1662, 1451, 1376, 1260, 836, 574; HRMS [M+H]$^+$ calcd for $C_{15}H_{16}NO_2$: 242.1181, found 242.1179. This compound was known[8].

N-(4-fluorobenzyl)benzamide (**3aj**)



^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 9.07 (t, J = 5.9 Hz, 1H), 7.96 – 7.86 (m, 2H), 7.59 – 7.43 (m, 3H), 7.41 – 7.27 (m, 2H), 7.16 (m, 2H), 4.46 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.6, 162.8, 160.4, 136.4, 136.3, 134.7, 131.8, 129.7, 129.6, 128.8, 127.7, 115.6, 115.4, 42.4; IR (film, cm^{-1}): 3344, 2924, 1657, 1601, 1535, 1444, 1329, 1171, 1115, 858, 754, 691; HRMS [M+H]$^+$ calcd for $C_{14}H_{13}FNO$: 230.0981, found 230.0977. This compound was known[9].

N-(4-chlorobenzyl)benzamide (**3ak**)



^{1}H NMR (400 MHz, d^{6}-DMSO): δ [ppm] = 9.09 (t, J = 5.9 Hz, 1H), 7.89 (m, 2H), 7.59 – 7.43 (m, 3H), 7.43 – 7.29 (m, 4H), 4.47 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, d^{6}-DMSO): δ [ppm] = 166.7, 139.2, 134.6, 131.8, 131.7, 129.6, 128.8, 128.7, 127.7, 42.5; IR (film, cm^{-1}): 3311, 2922, 1638, 1541, 1449, 1376, 1257, 837, 794, 692; HRMS $[M+H]^{+}$ calcd for $C_{14}H_{13}ClNO$: 246.0686, found 246.0684. This compound was known[2].

References:

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4. L. Zhang, W. Wang, A. Wang, Y. Cui, X. Yang, Y. Huang, X. Liu, W. Liu, J. Son, H. Oji and T. Zhang, *Green Chem*., 2013, **15**, 2680.

5. L. Kumar**,** T. Mahajan and D. D. Agarwal, *Green Chem.*, 2011, **13**, 2187.

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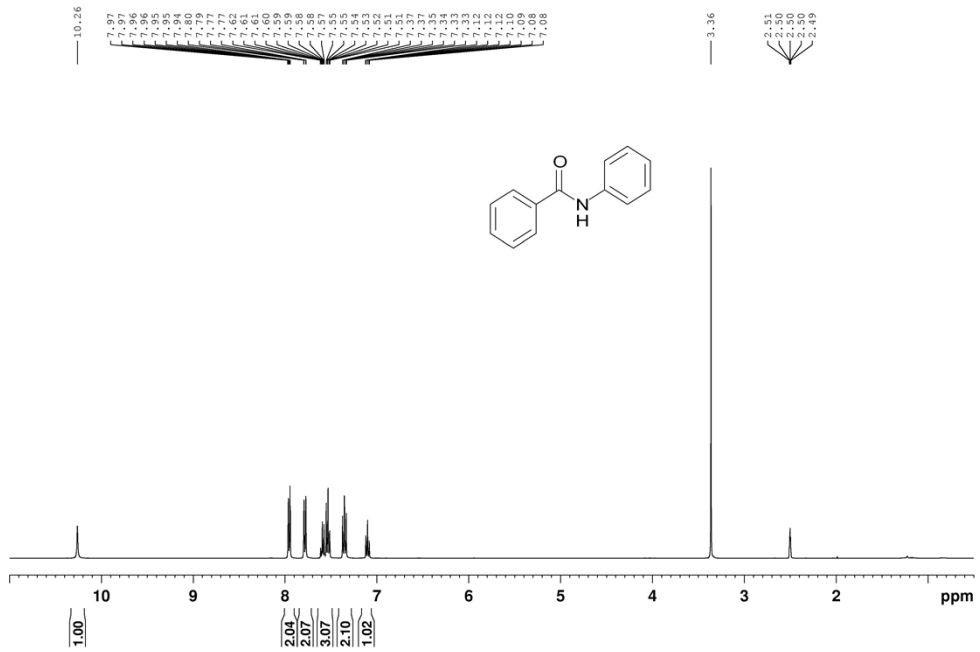
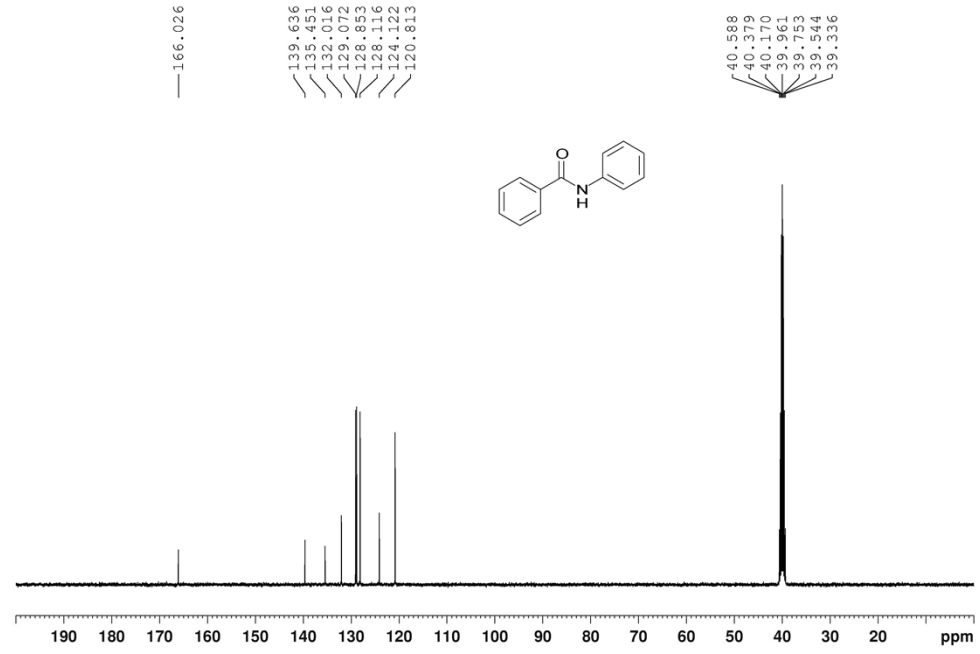
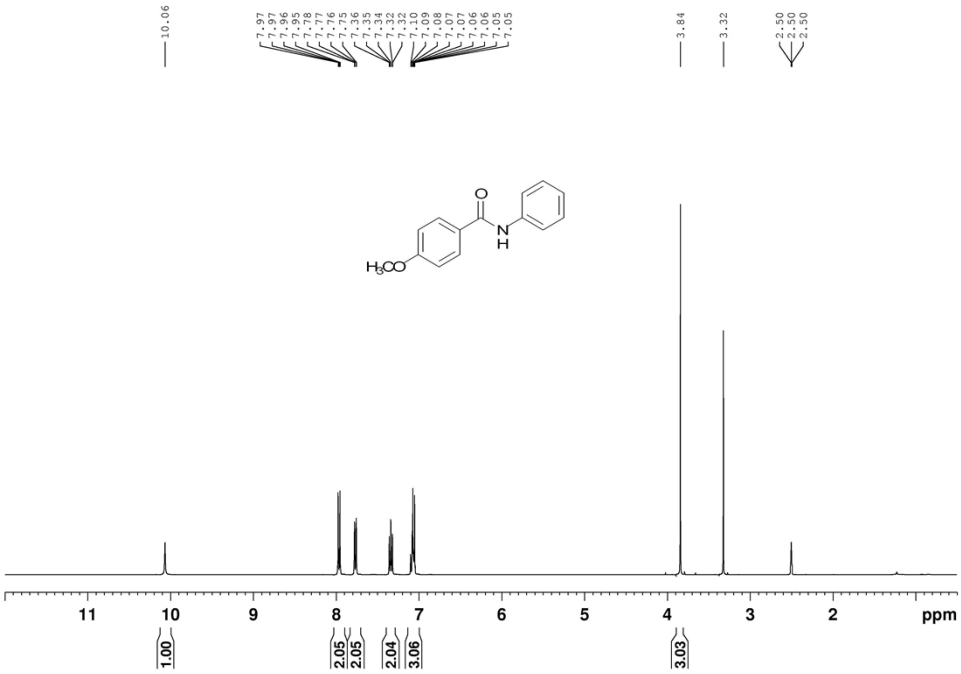
NMR Spectra of products



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7.76
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7.33
7.32
7.10
7.09
7.08
7.07
7.07
7.06
7.06
7.05
7.05
3.84
3.32
2.50
2.50
2.50
O
N
H
H3CO
11
10
9
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7
6
5
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3
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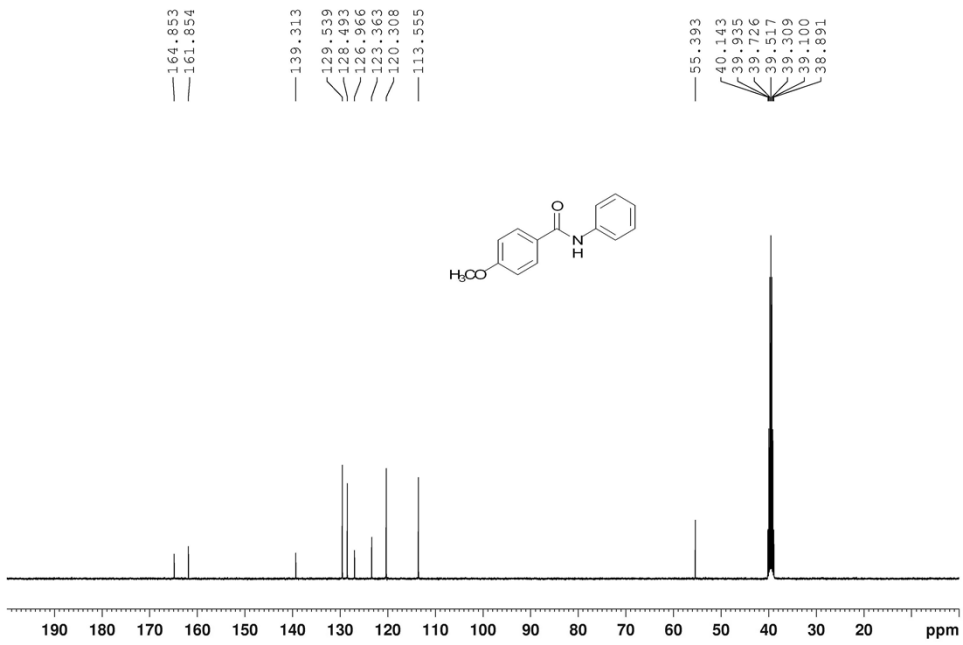
2.05
2.05
2.04
3.06
3.03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N
H
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150
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120
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40
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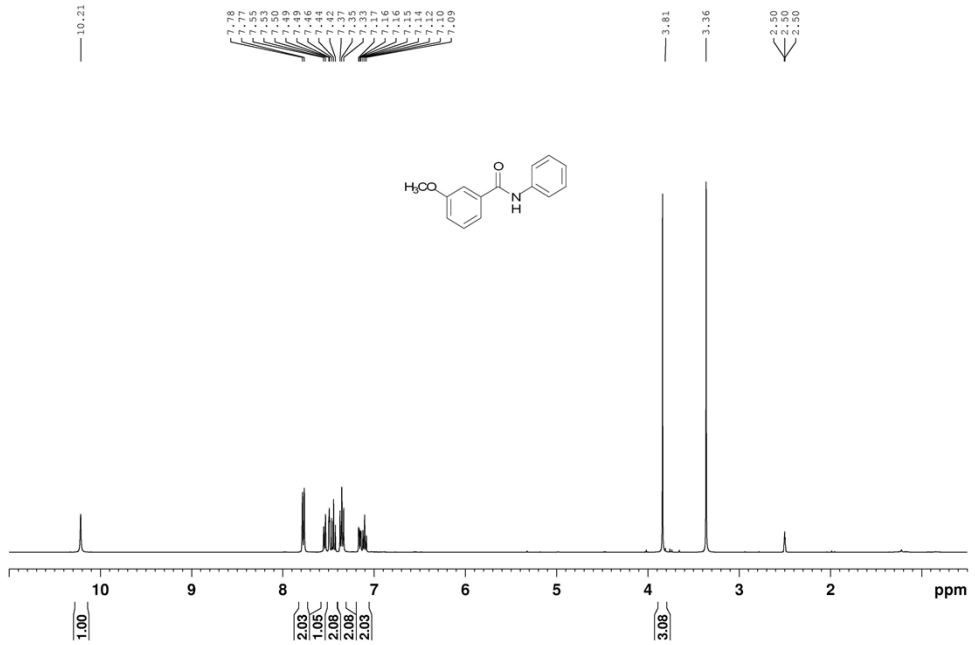
20
ppm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7.15
7.14
7.12
7.10
7.09
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2.50
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O
N
H
10
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4
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1.05
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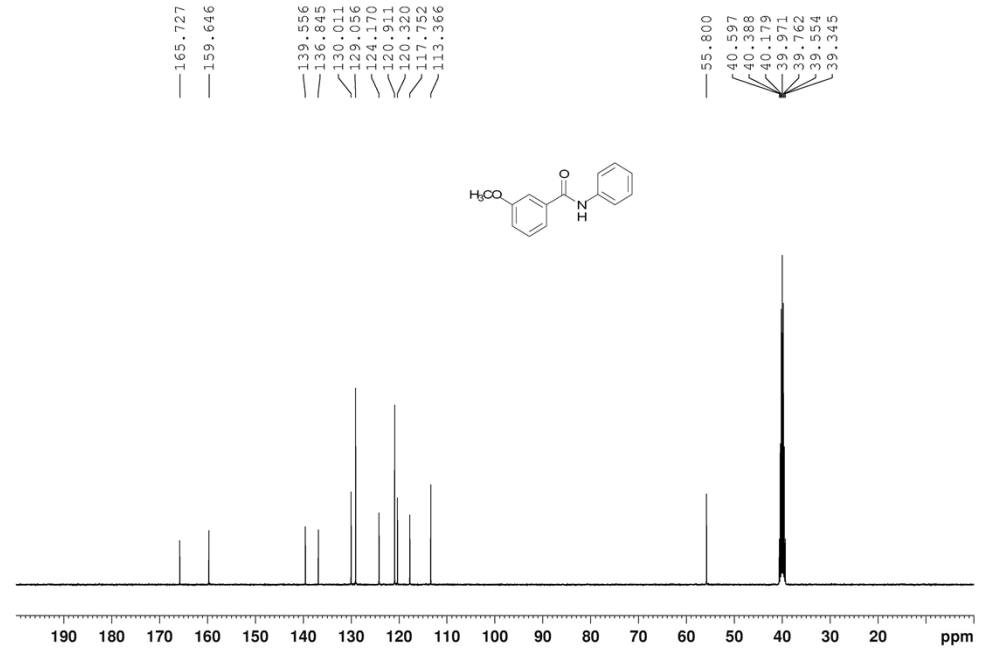
2.08
2.03
3.08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150
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130
120
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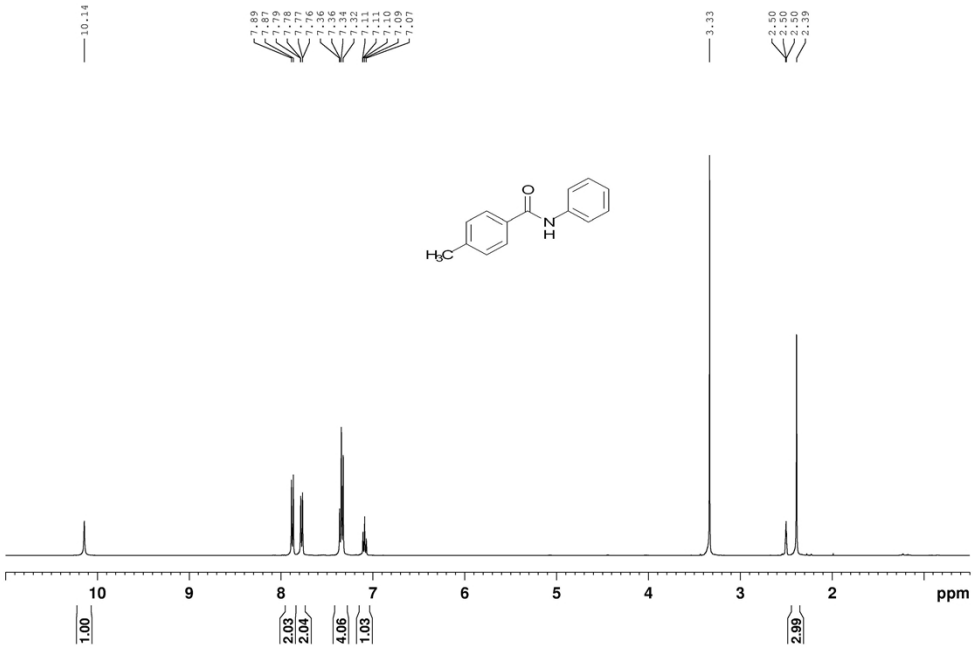
40
30
20
ppm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7.10
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7.07
3.33
2.50
2.50
2.50
2.39
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N
H
H3C
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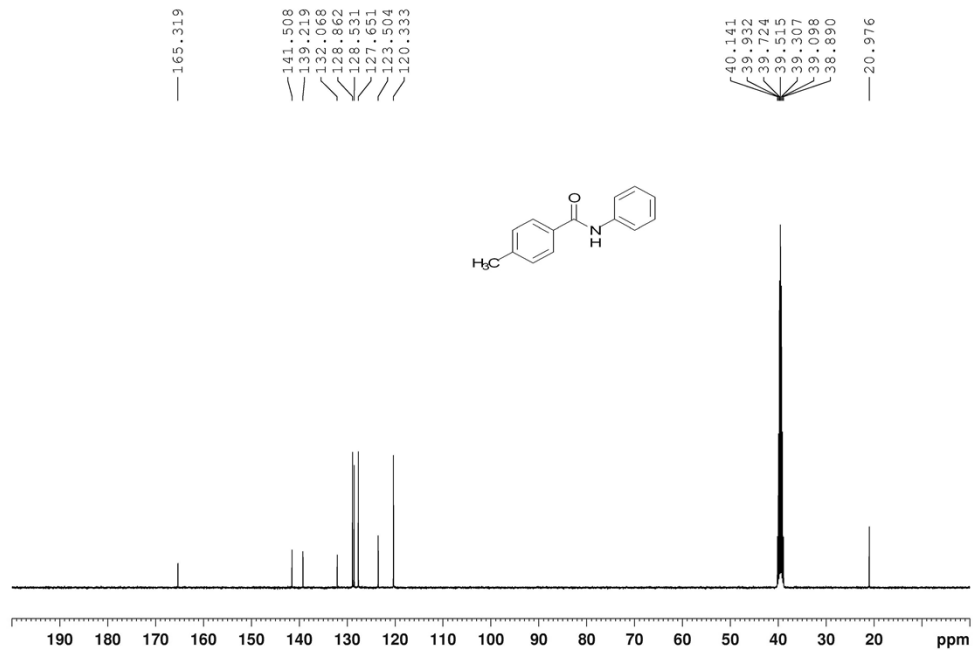
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N
H
H3C
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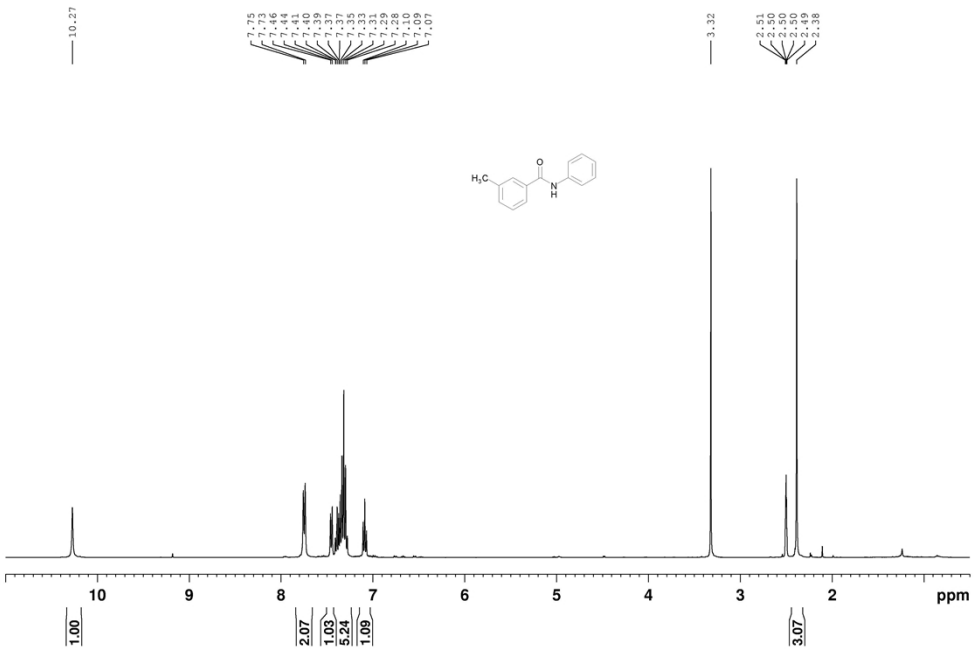
20
ppm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7.29
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7.10
7.09
7.07
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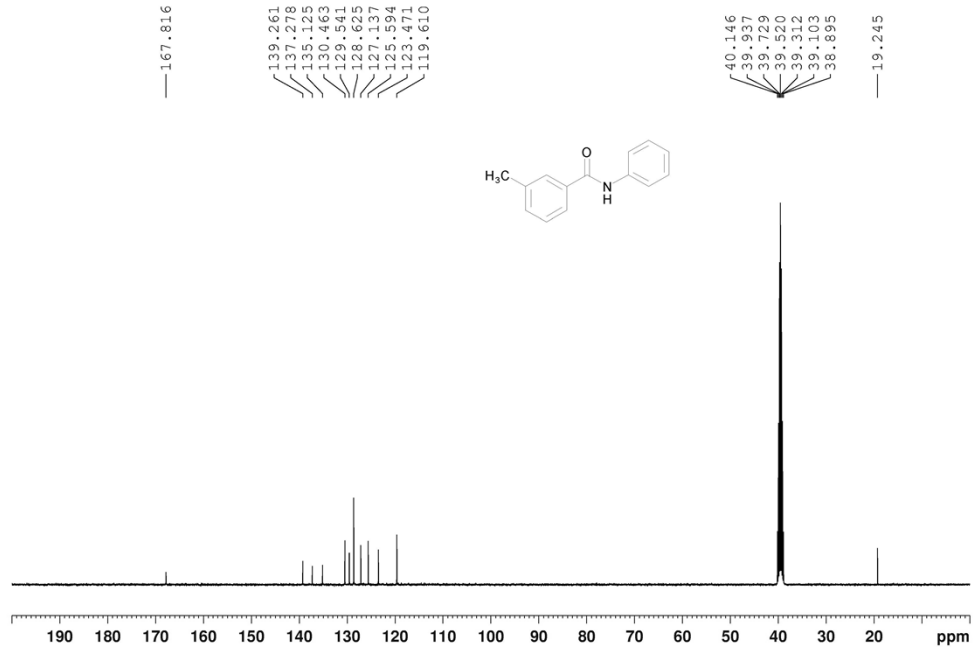
3.07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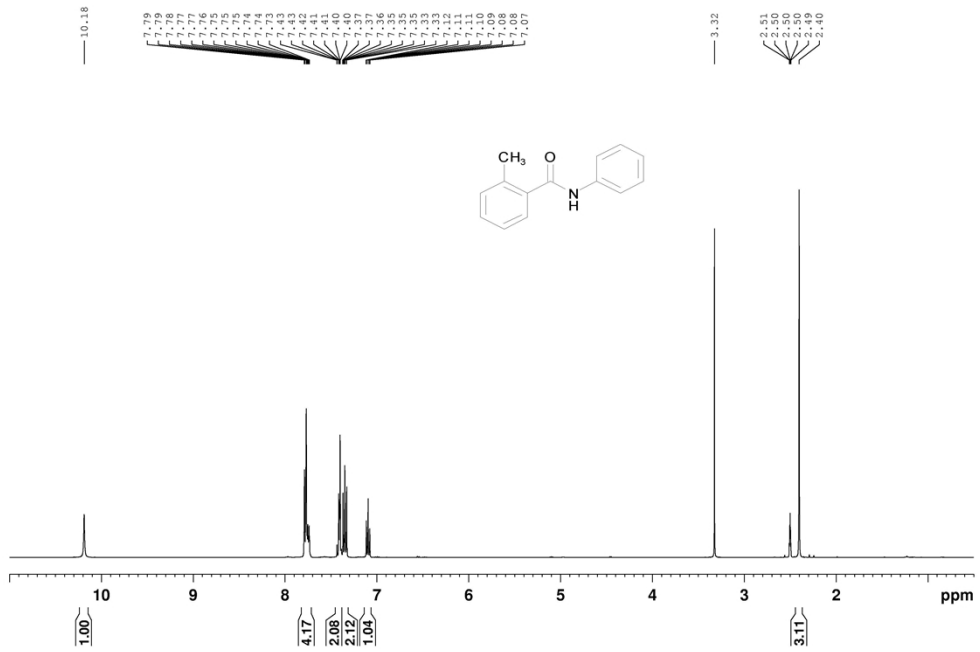
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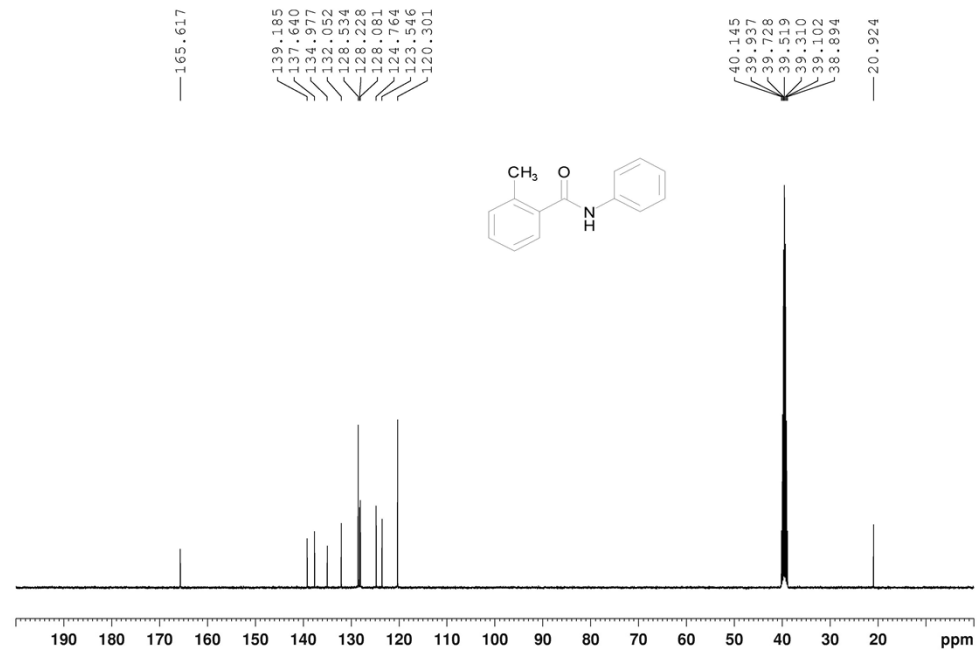
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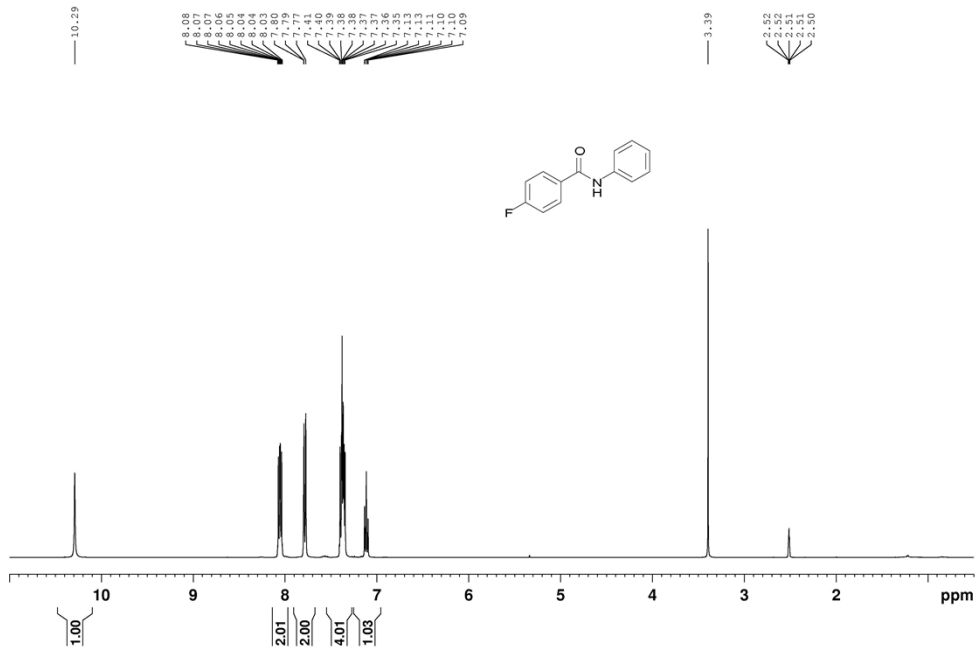
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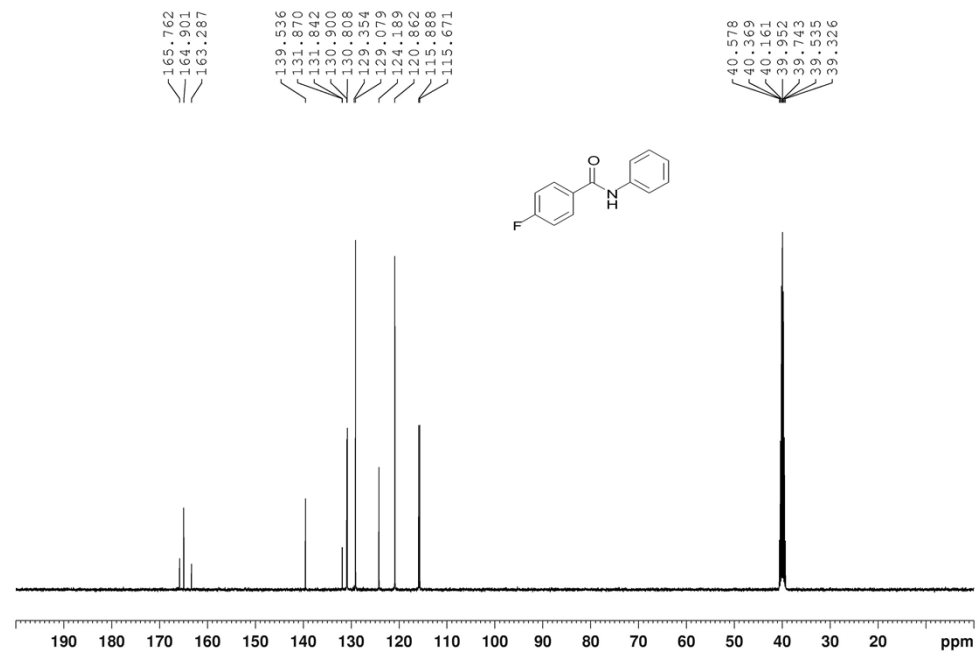
1.03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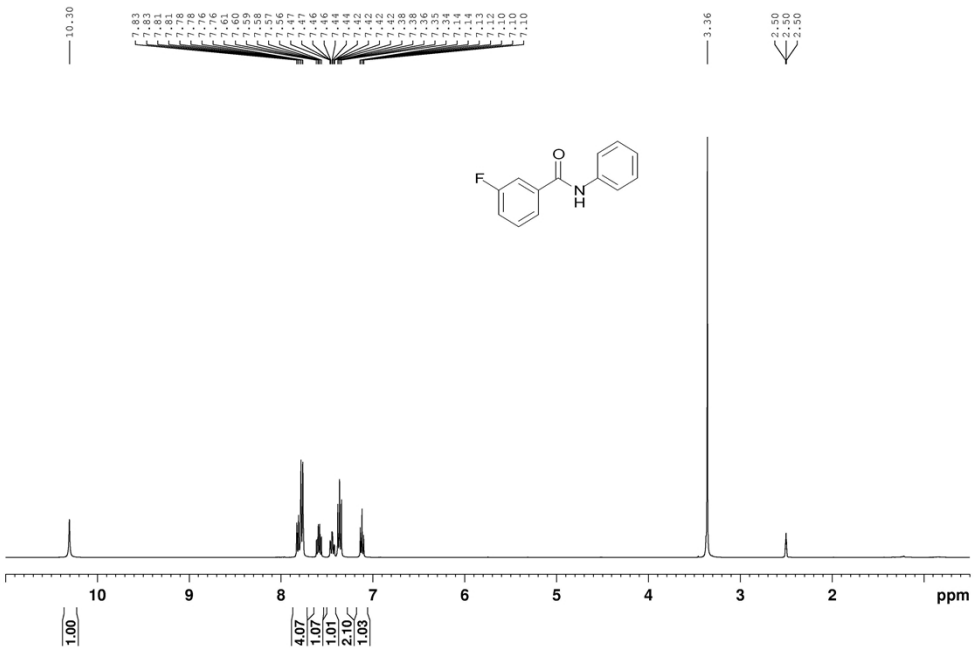
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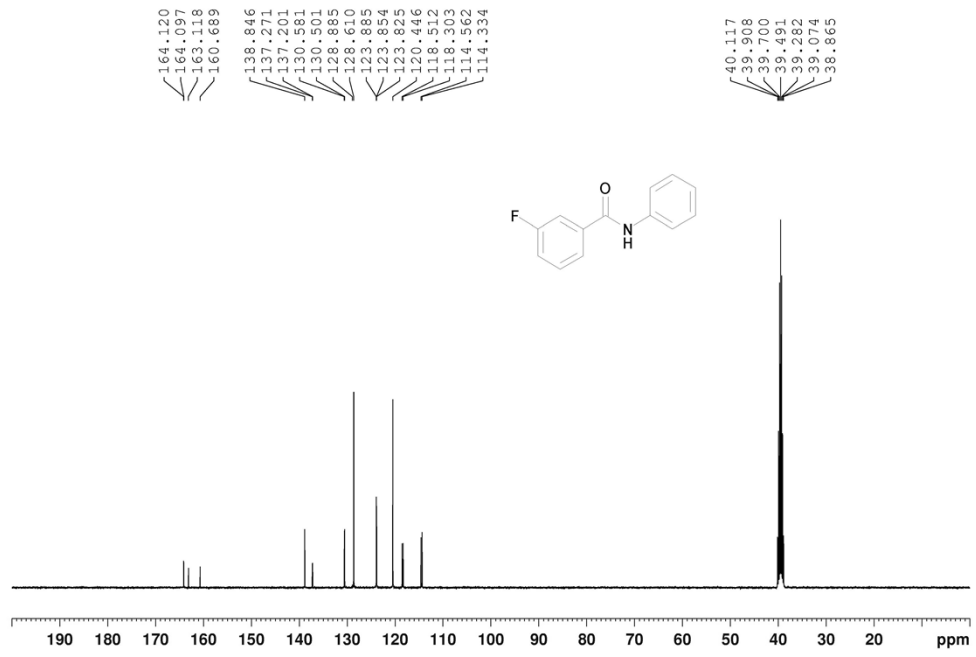
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114.562
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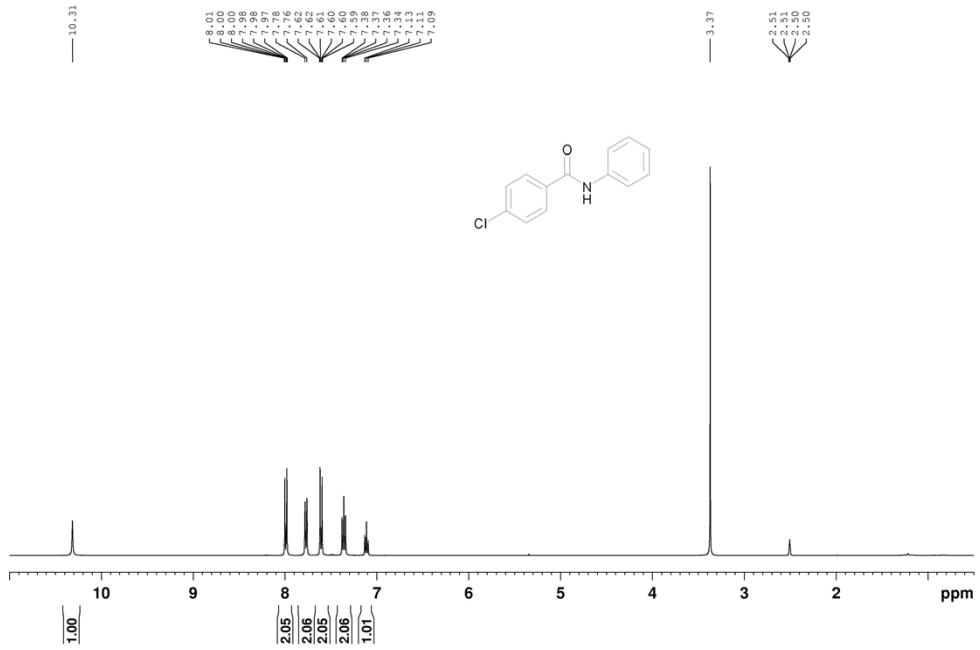
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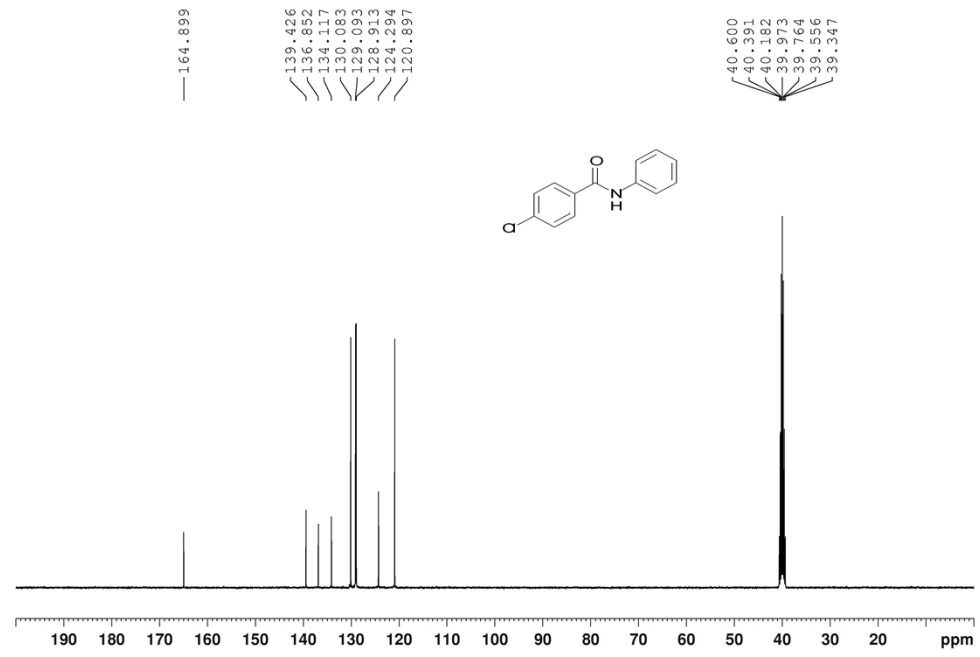
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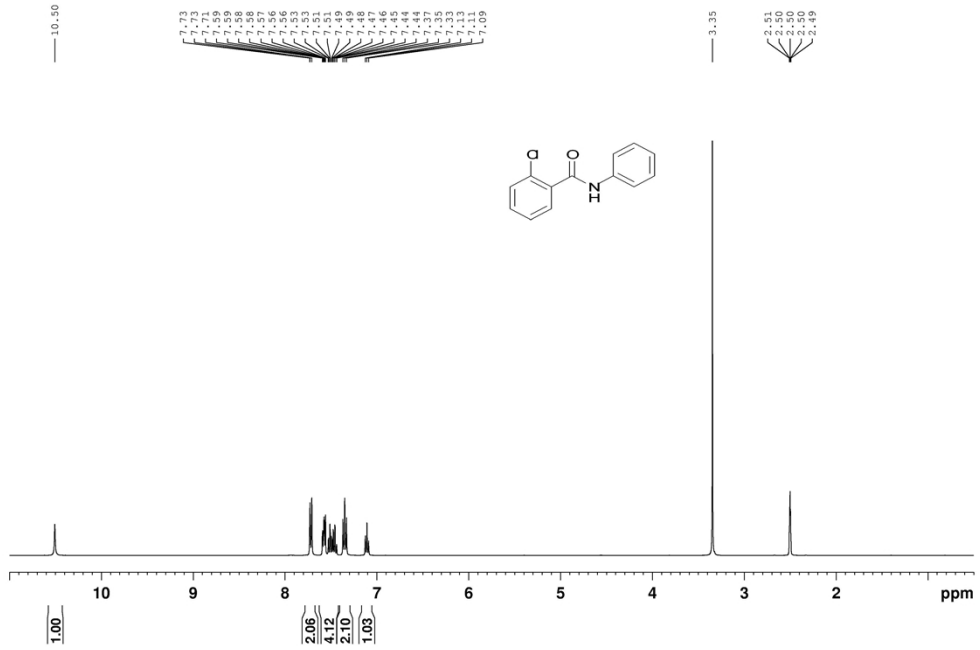
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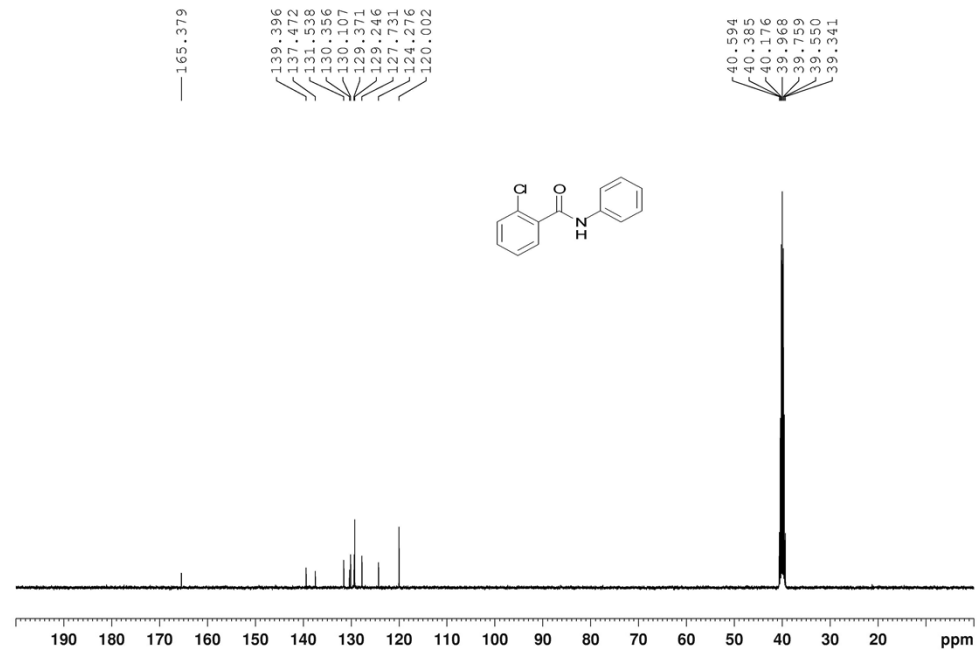
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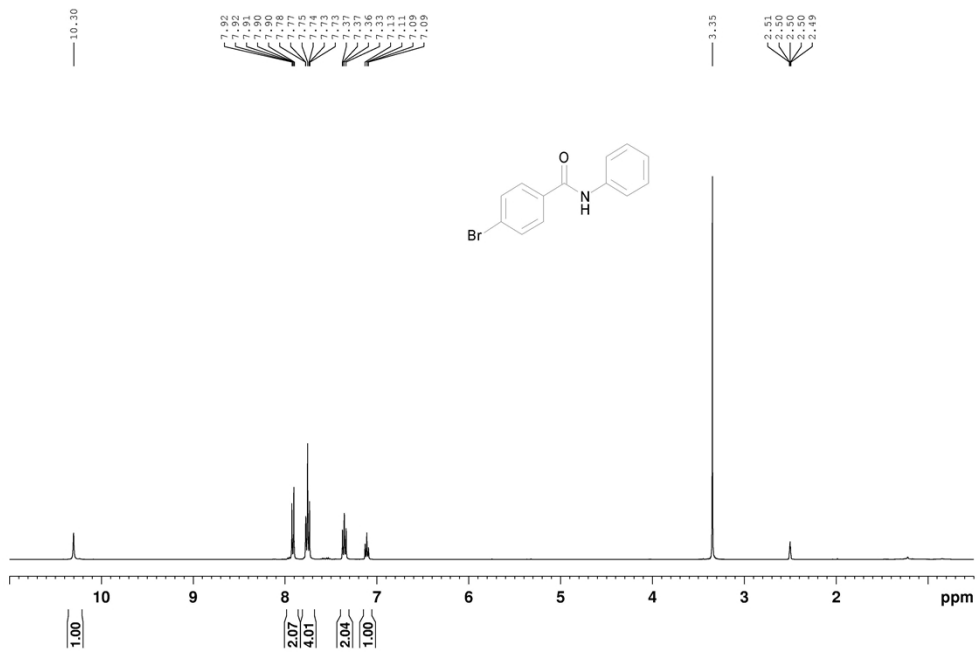
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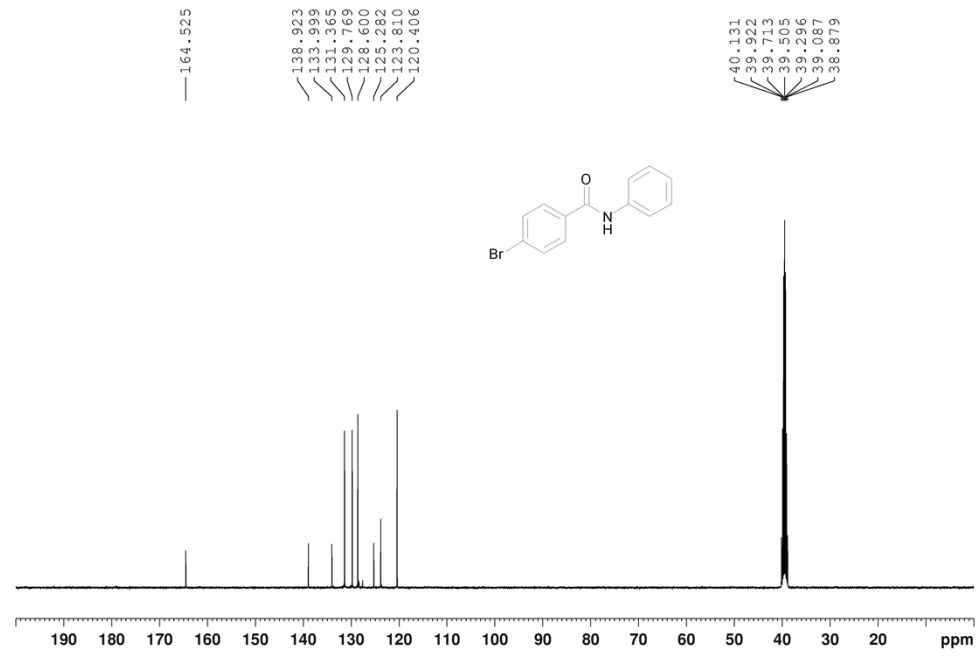
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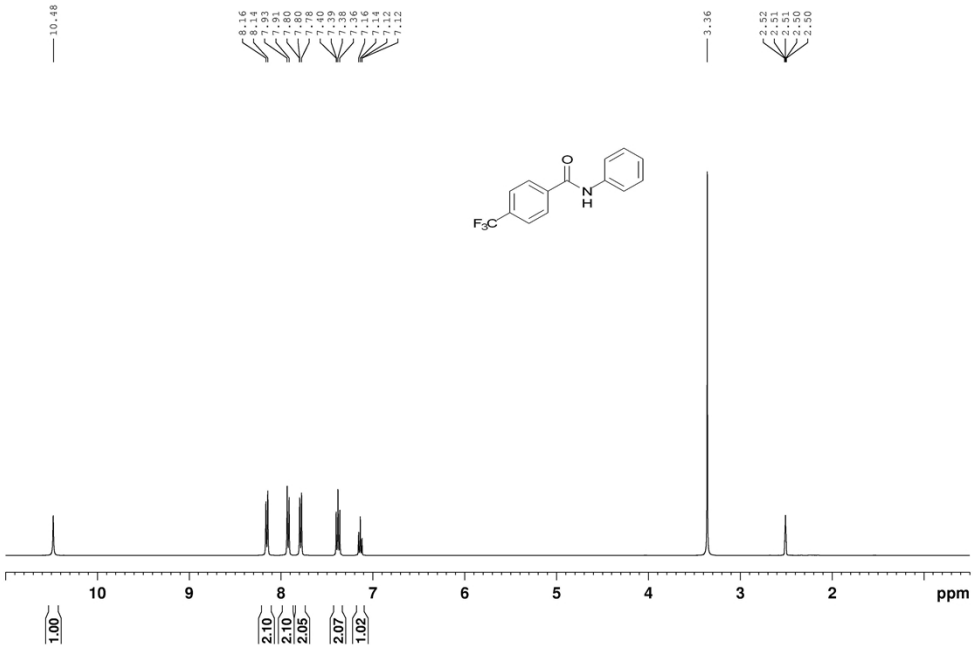
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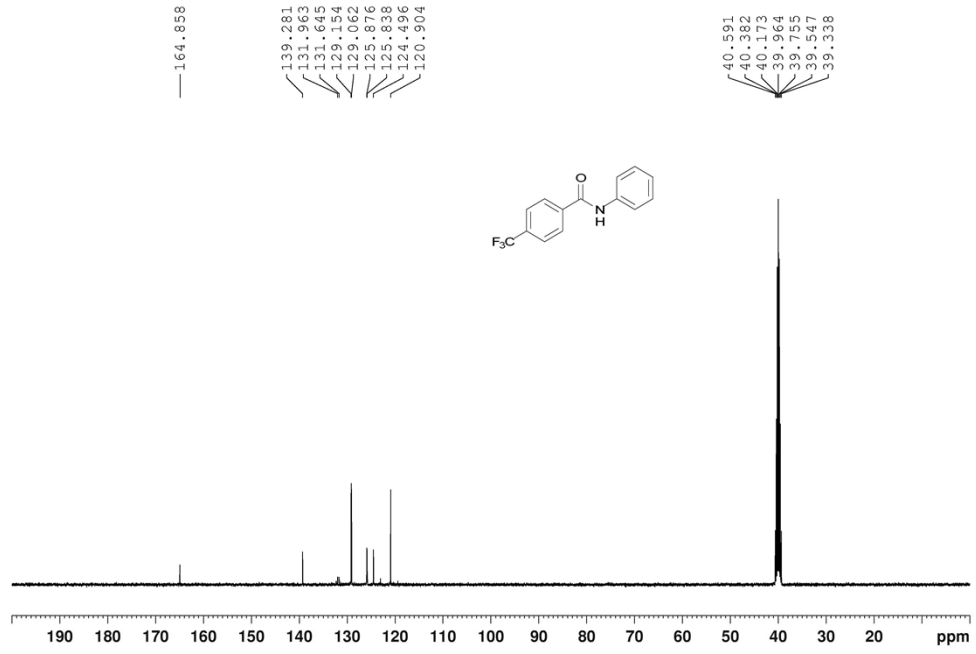
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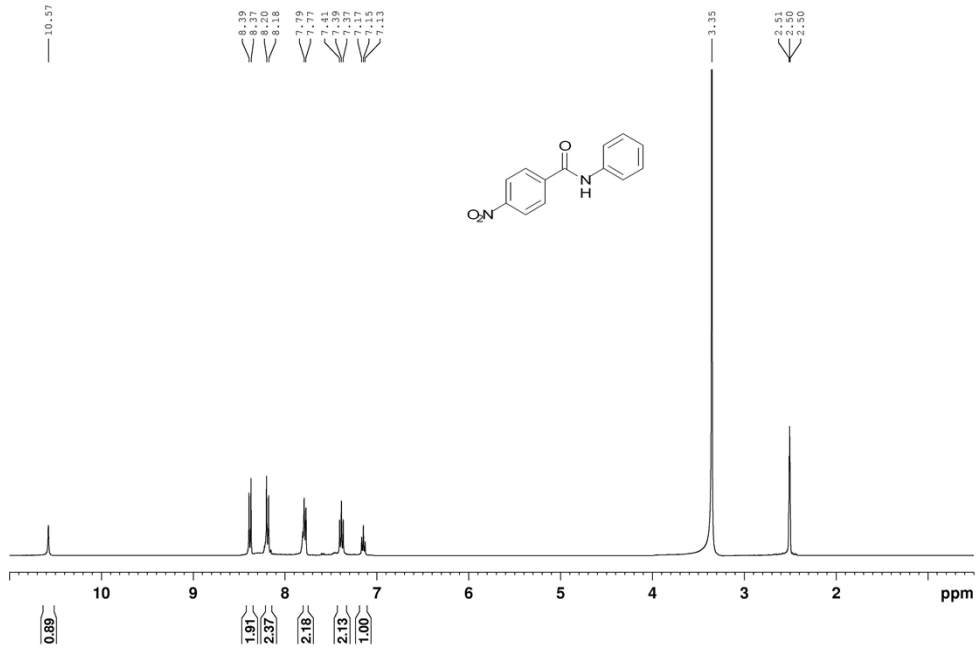
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N
H
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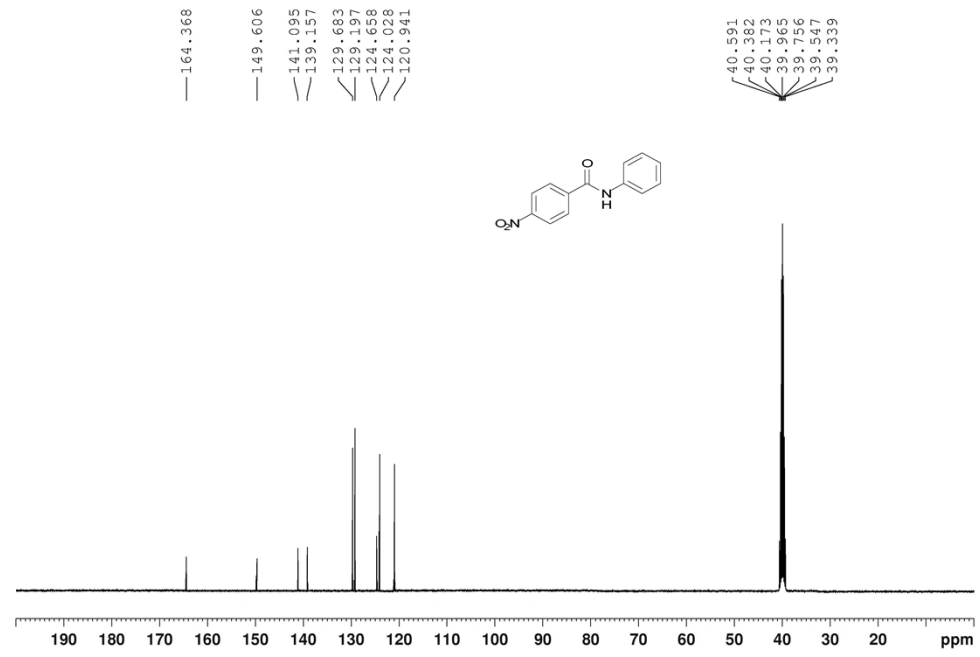
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N
H
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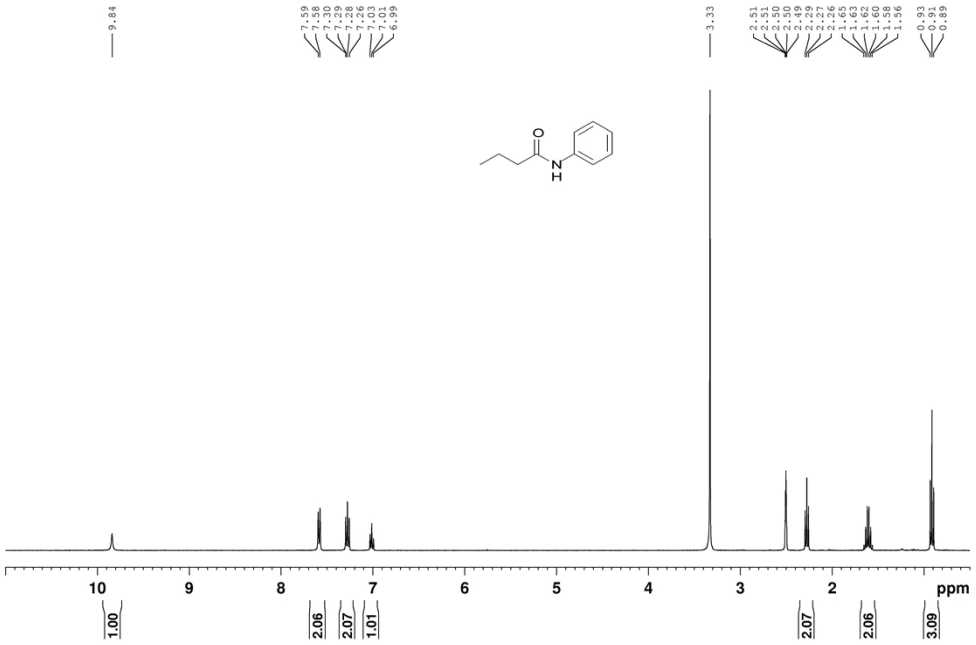
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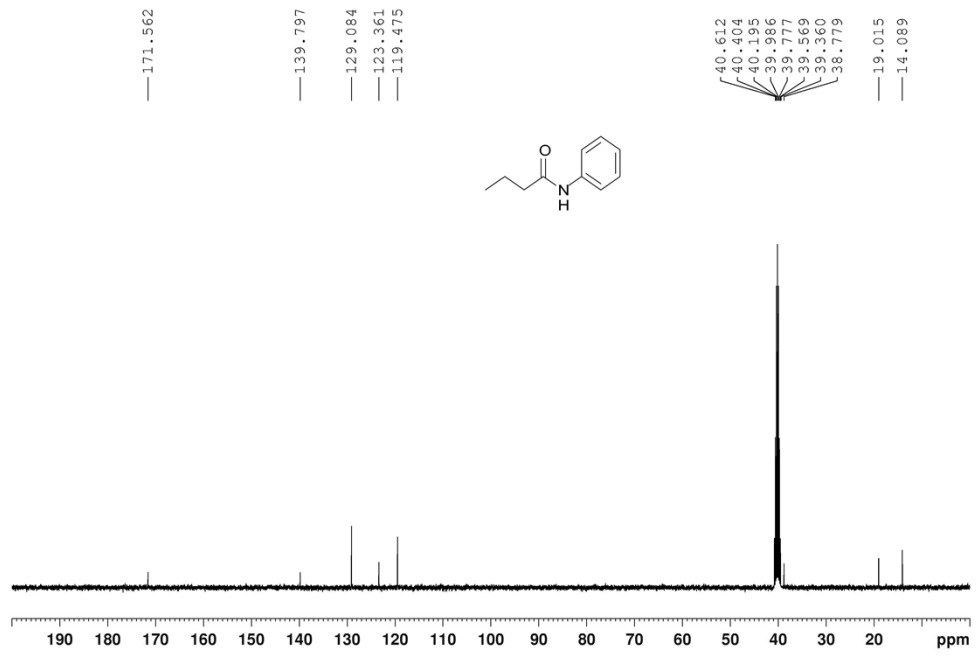
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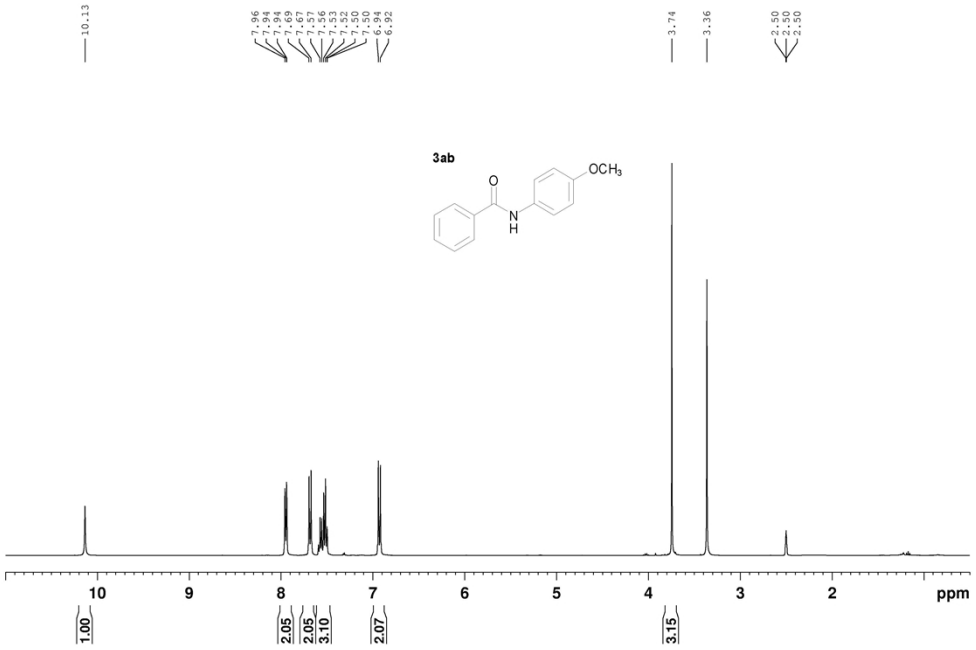
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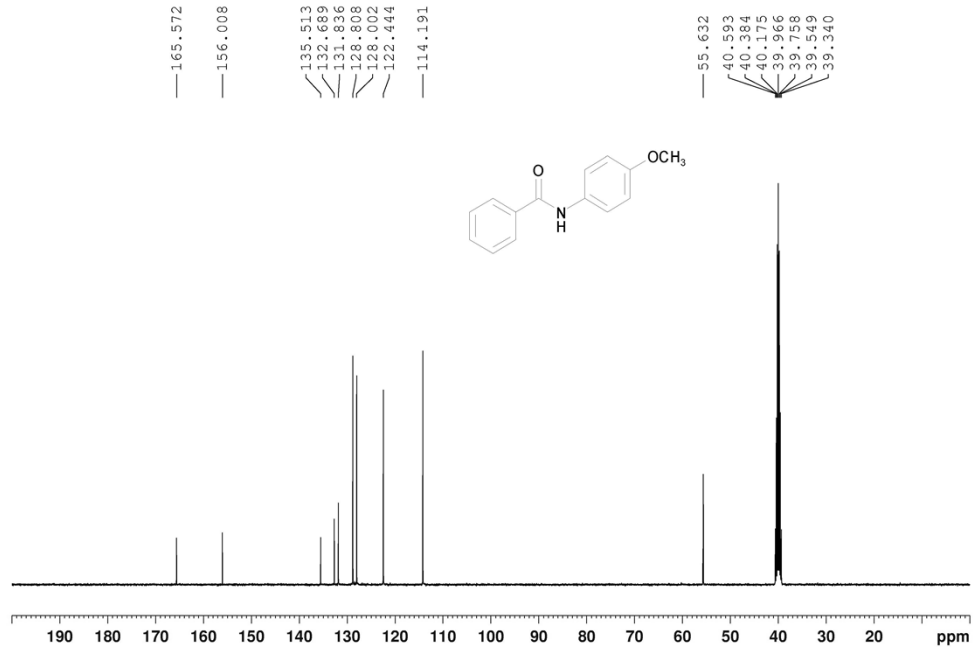
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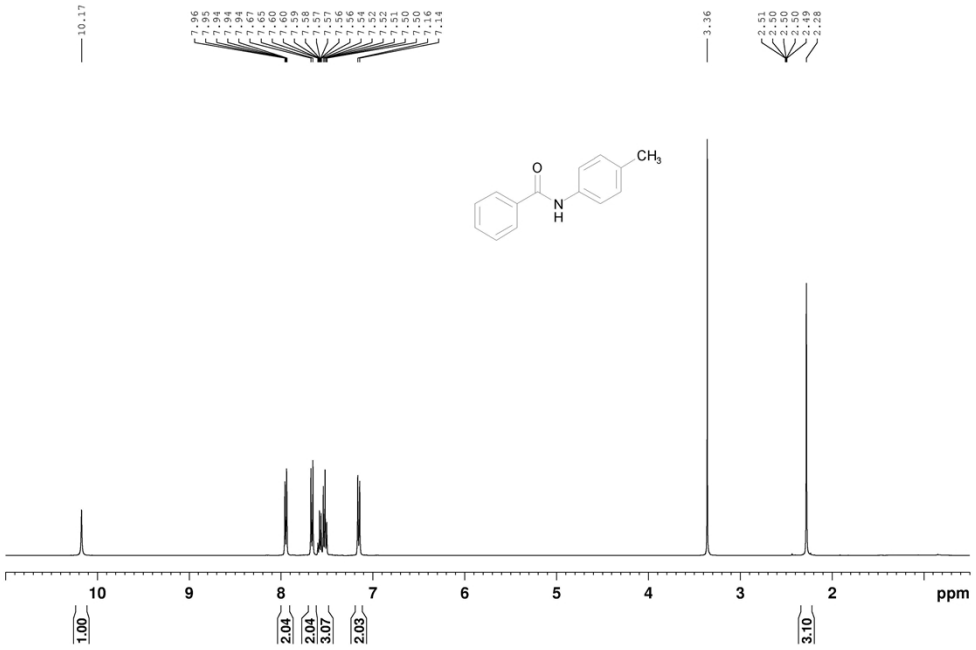
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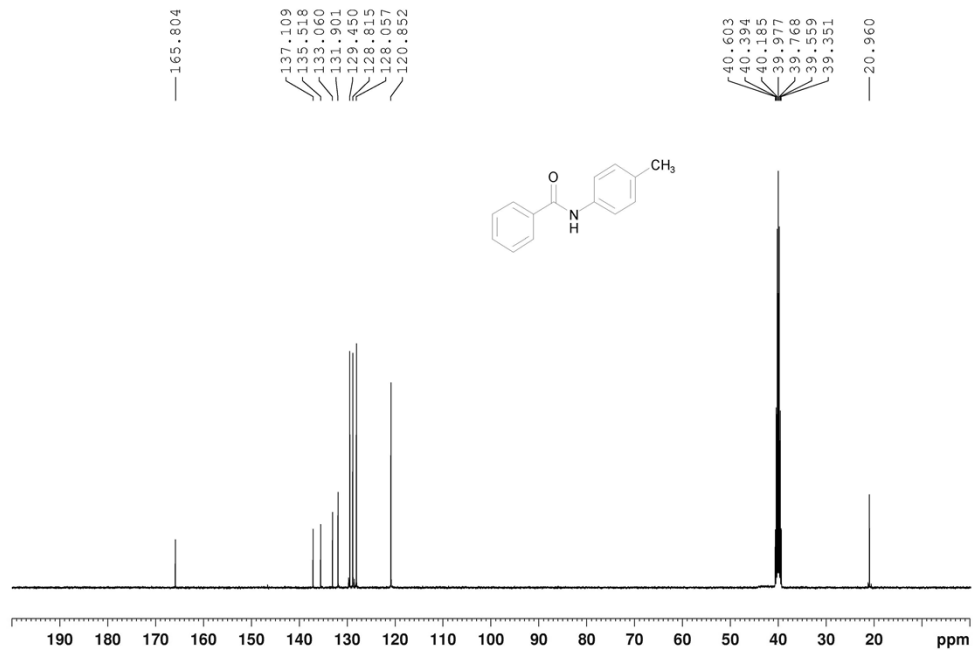
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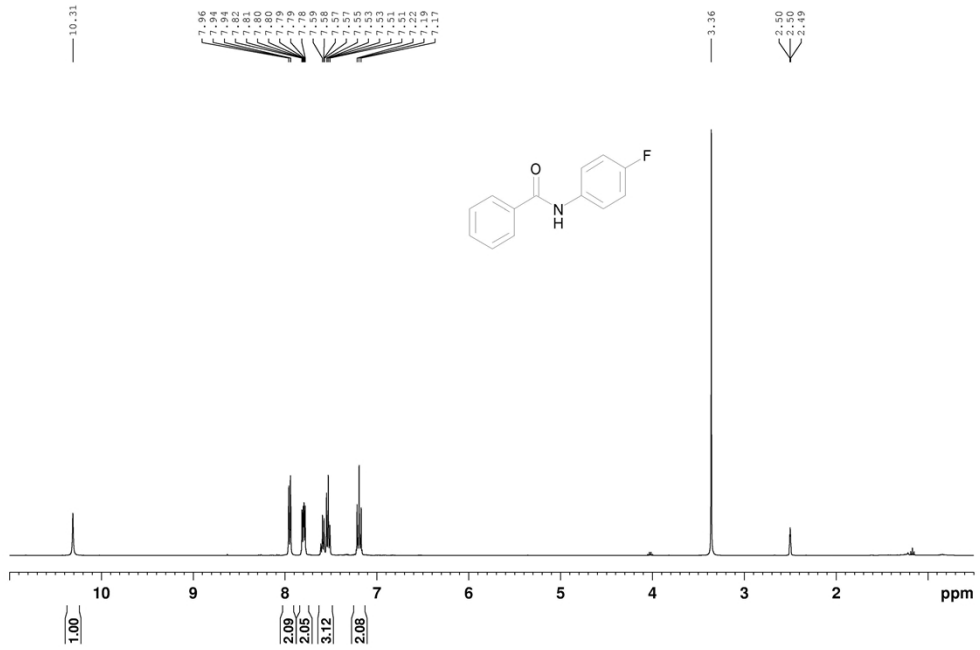
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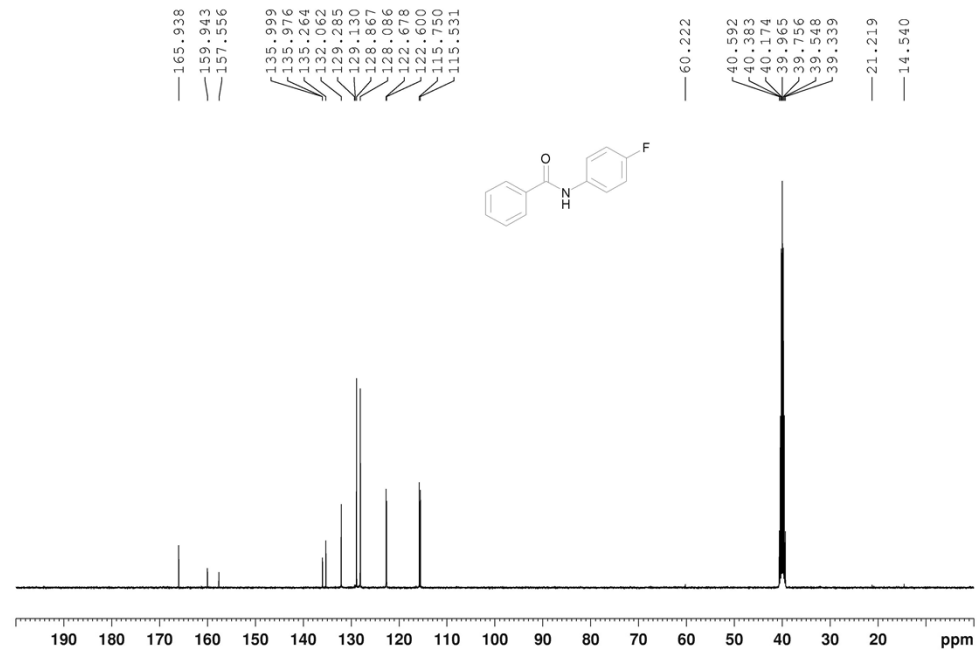
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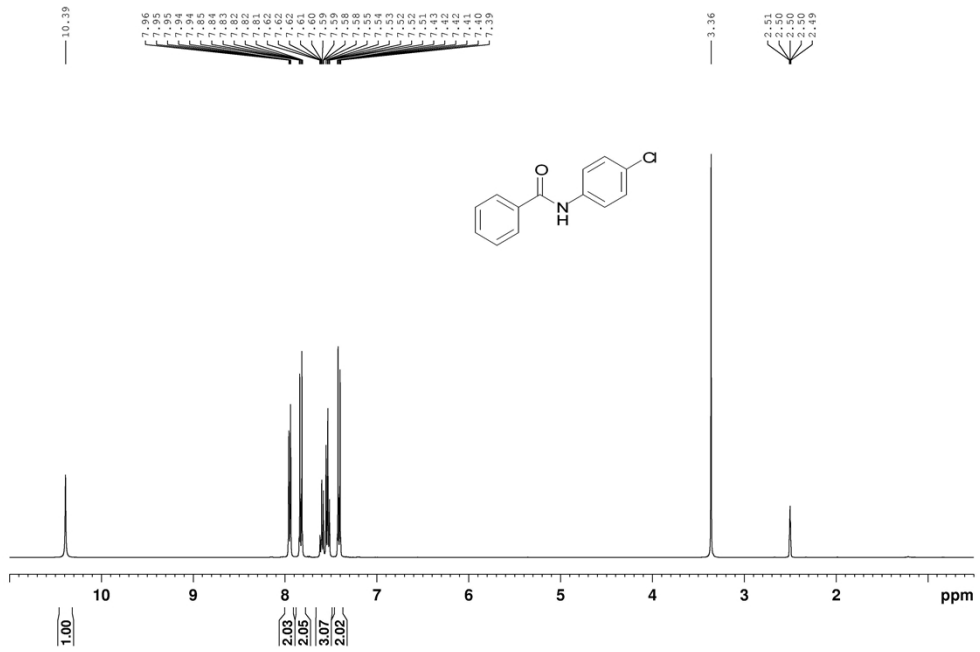
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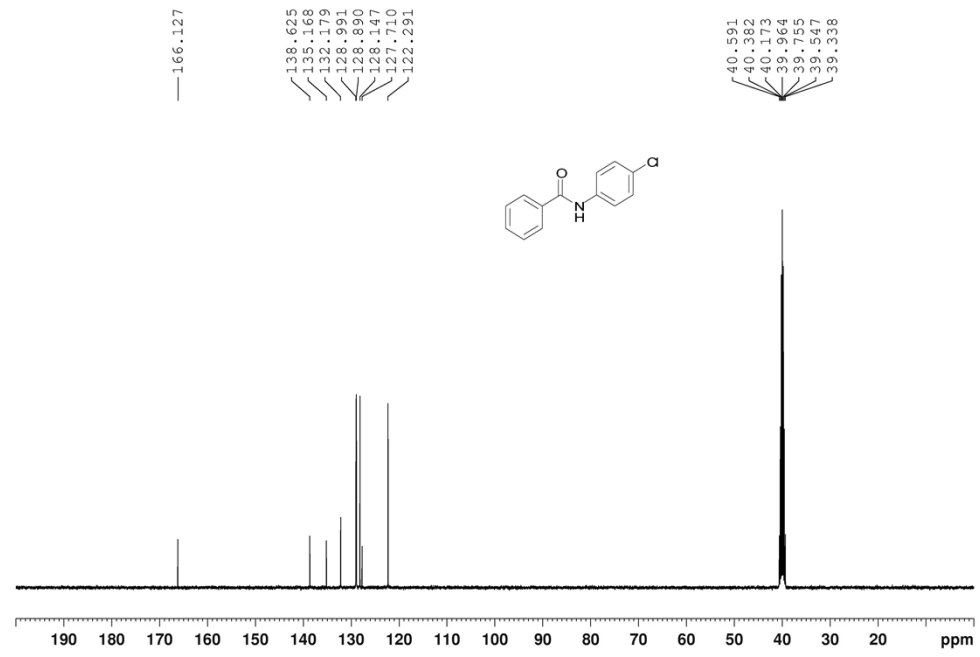
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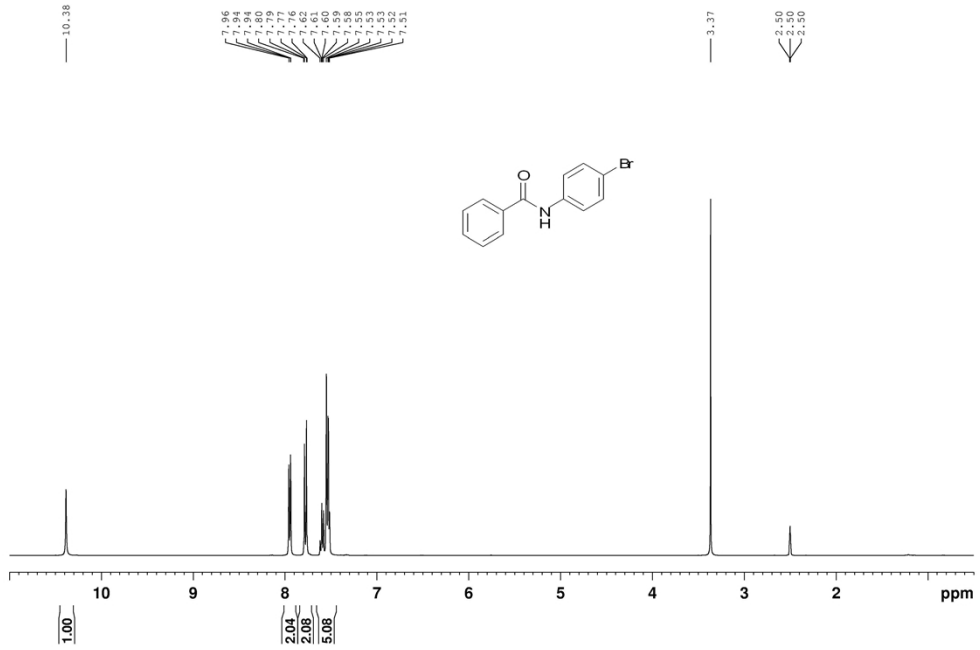
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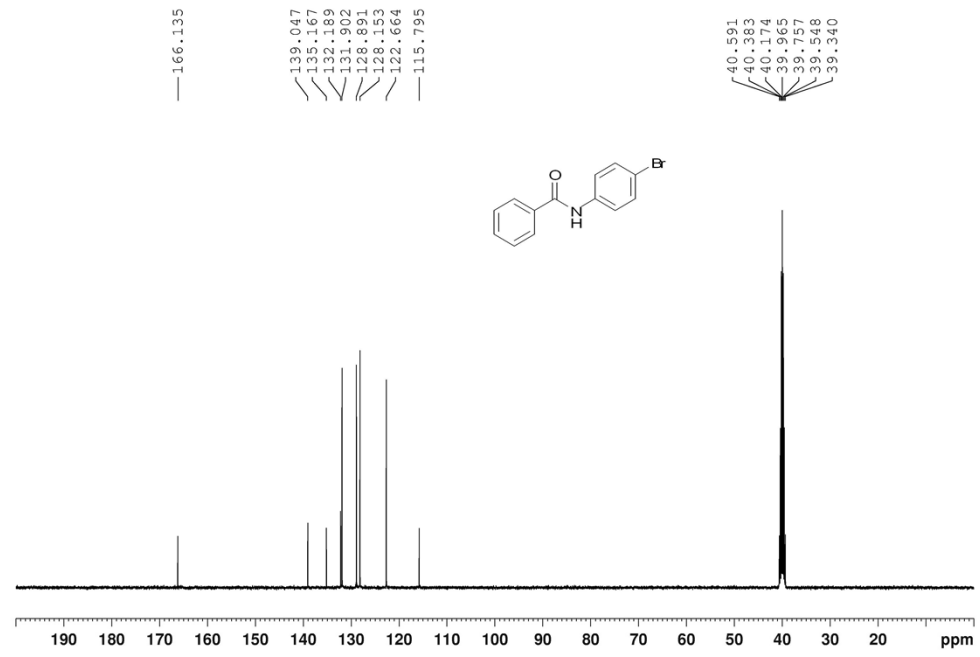
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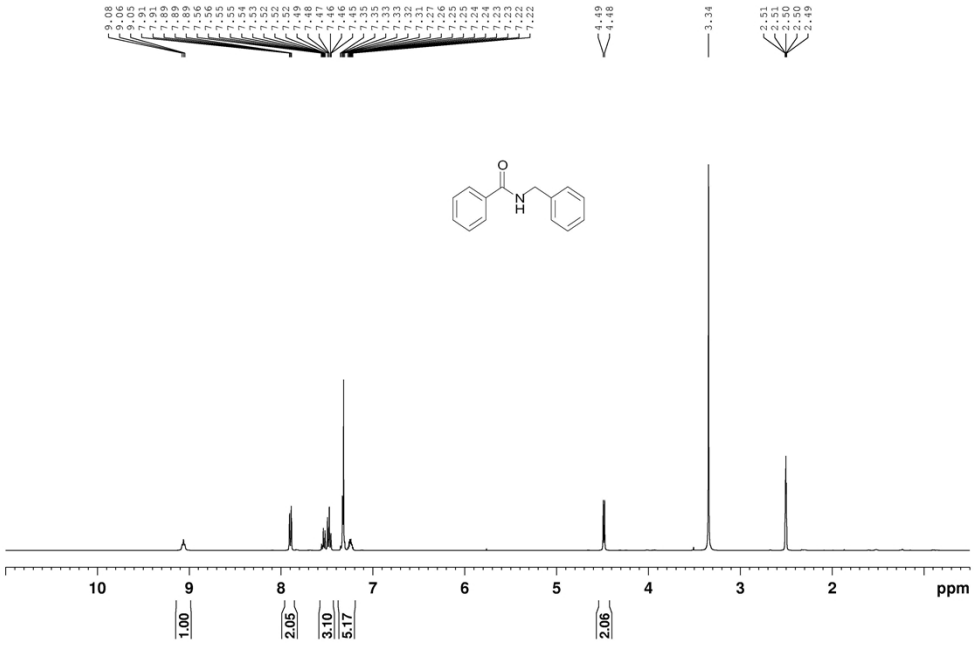
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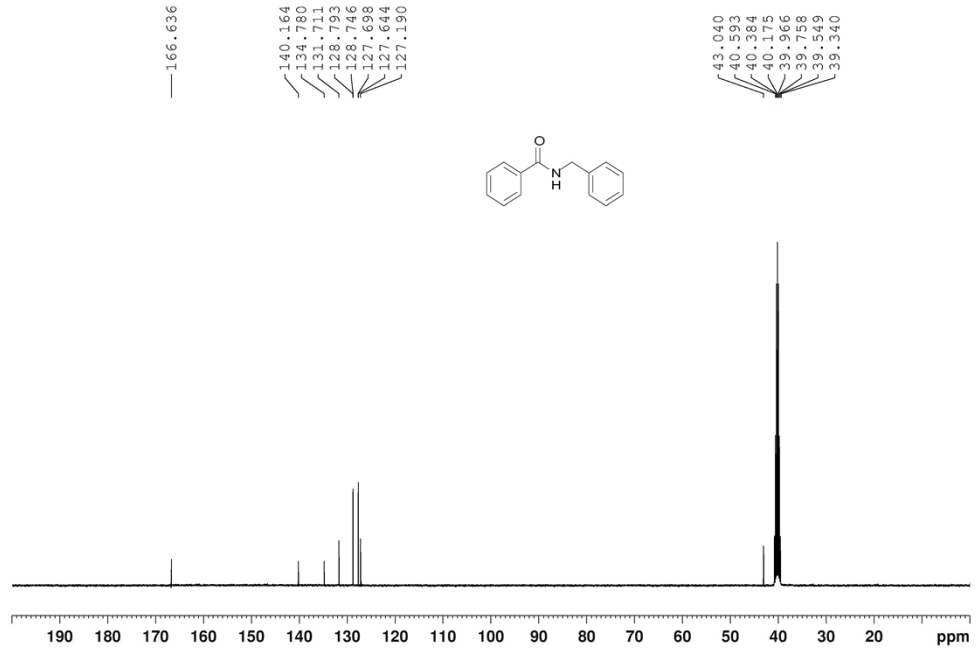
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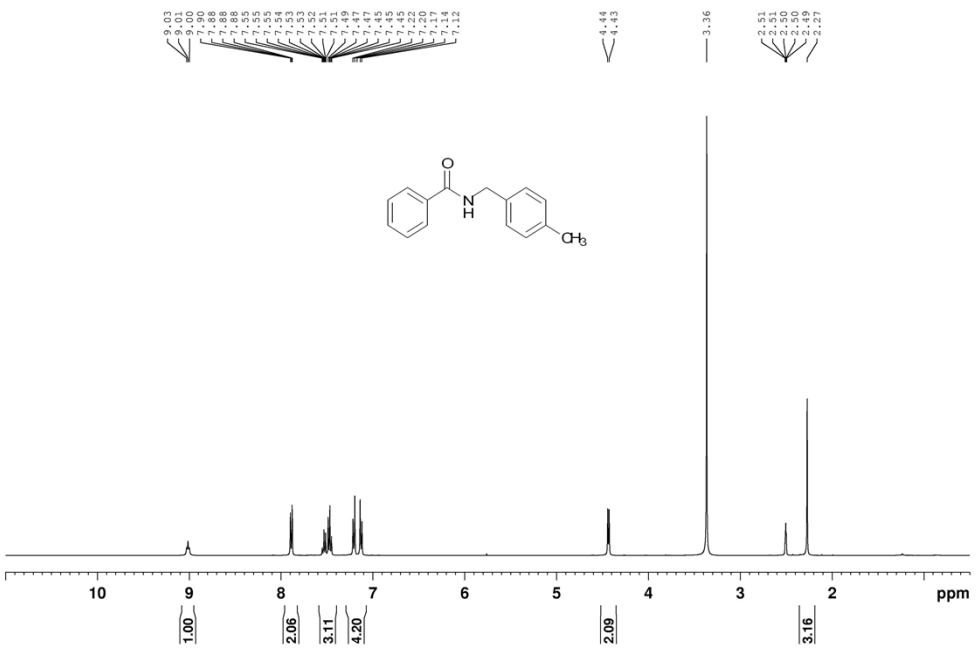
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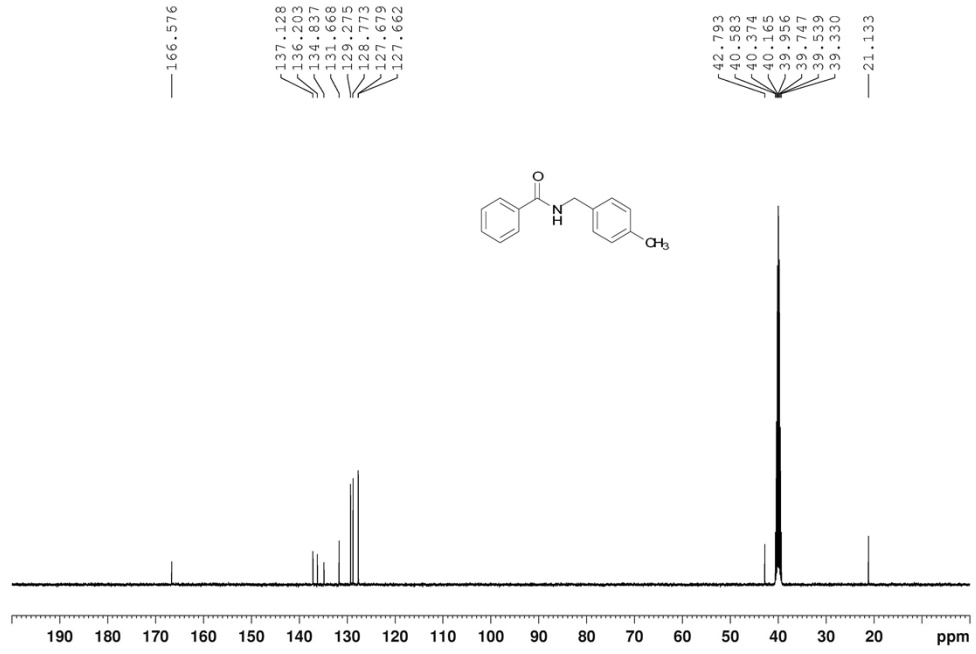
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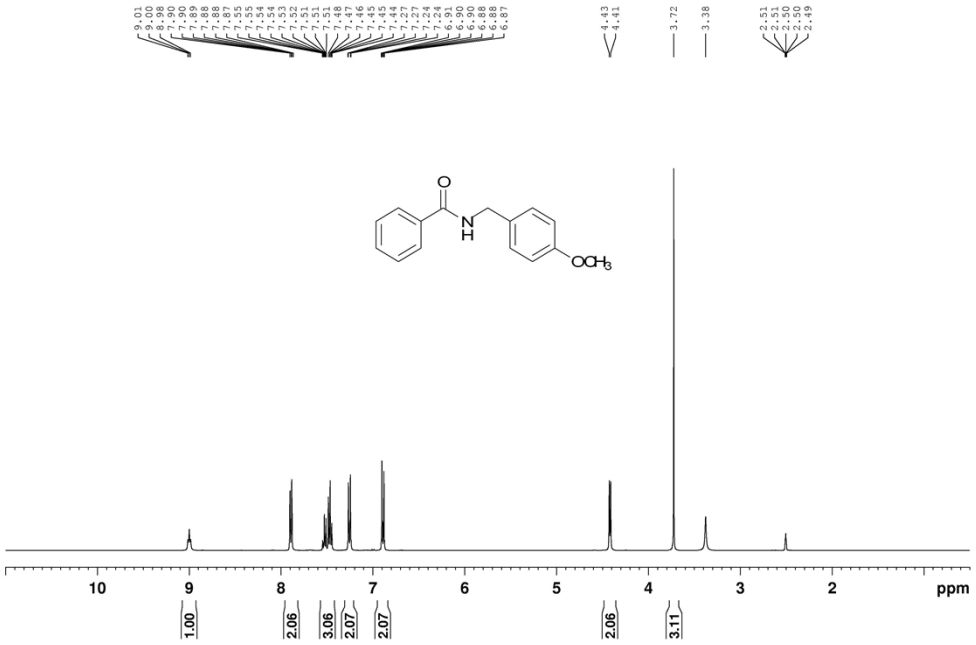
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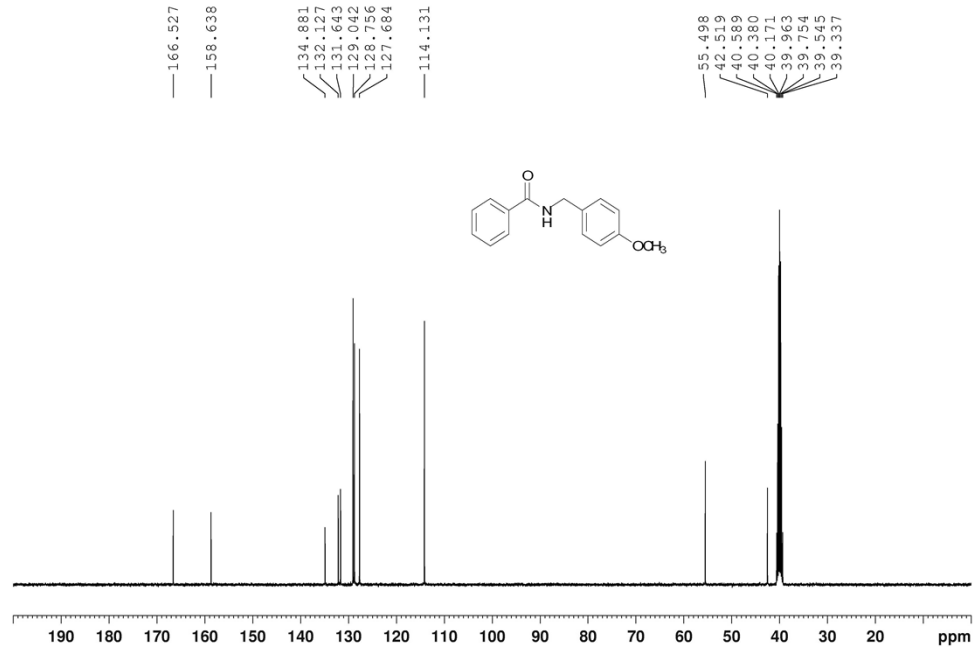
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N
H
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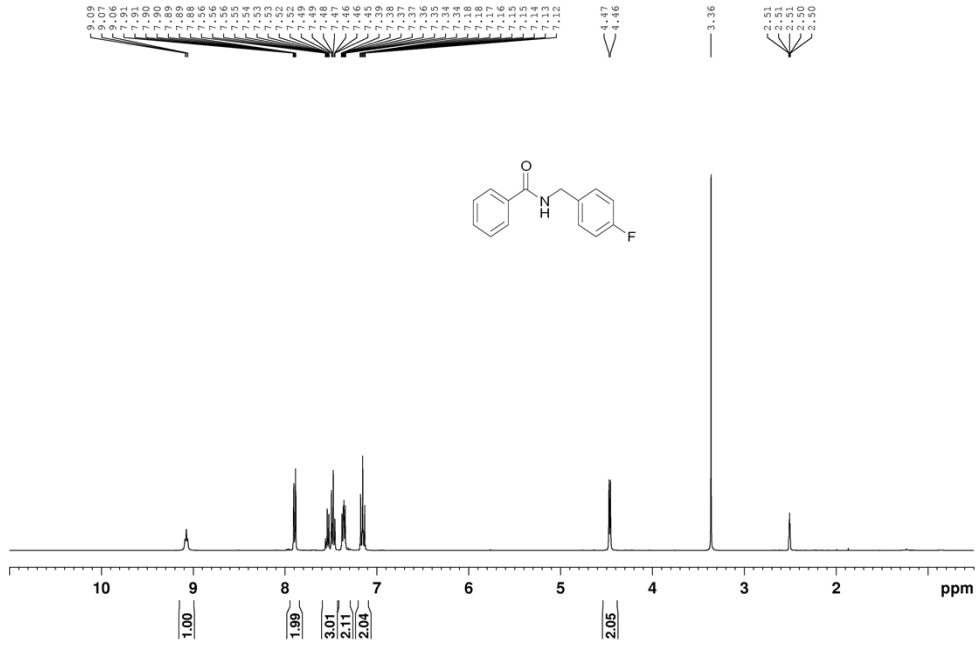
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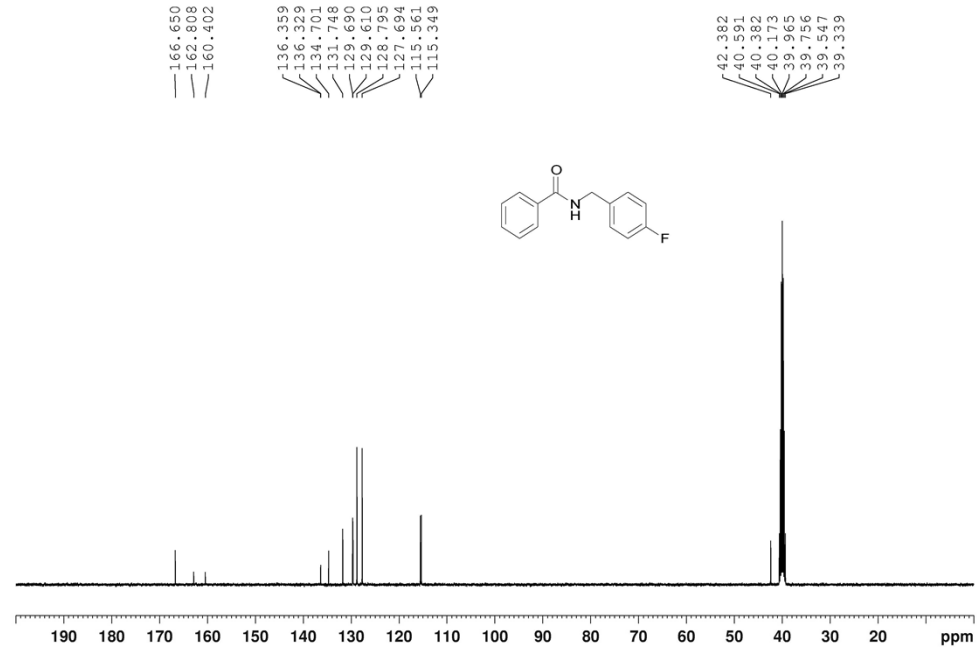
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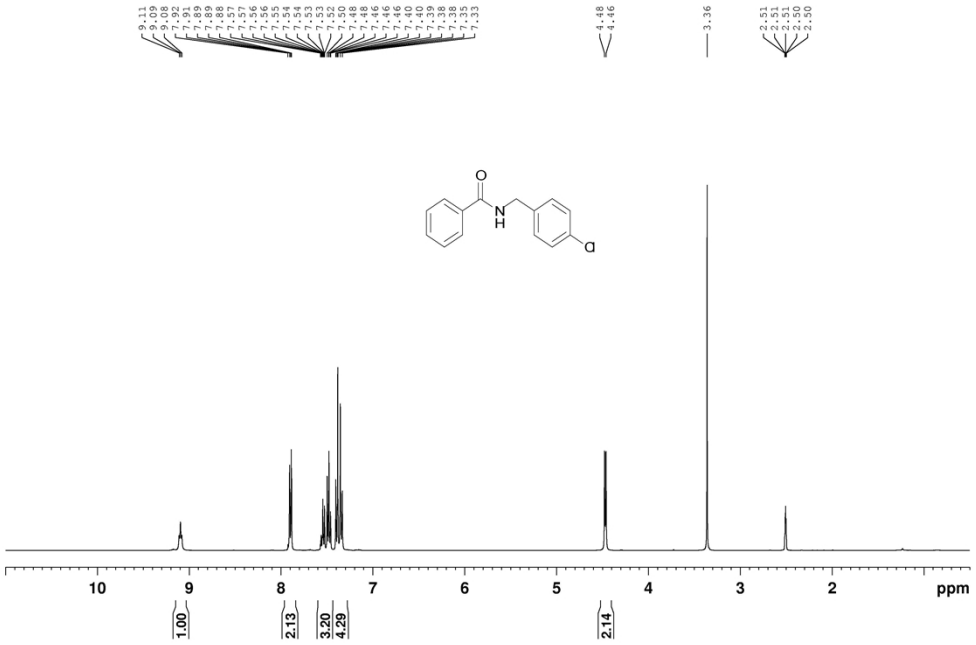
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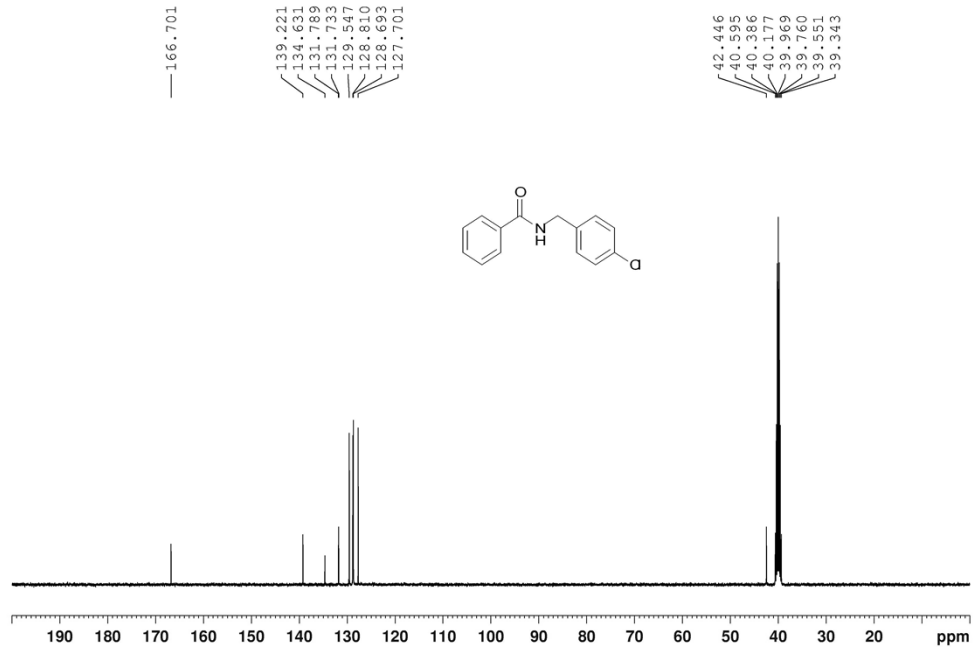
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30
20
ppm