# Methylation of Arenes via Ni-Catalyzed Aryl C-O/F Activation

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# Experimental Section

**General**: All reactions were carried out under $N_2$ atmosphere. All the metal reagents were purchased from Alfa Aesar and Acros Chemical and used without further purification. $NiCl_2(PCy_3)_2$ was synthesized according to literature method. [1] The solvent was freshly distilled over sodium with the use of diphenyl ketone as an indicator. $^1$HNMR (300 MHz) and $^{13}$CNMR (75.4 MHz) were registered on 300M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in units (ppm) by assigning TMS resonance in the $^1$H spectrum as 0.00 ppm and $CDCl_3$ resonance in the $^{13}$C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. GC, HPLC, MS, and HRMS were performed by the Analytical Center in Peking University.

## General procedure for the synthesis of aryl ethers.

Aryl ethers were made from the aryl phenol and organic halide in DMF at 80□ using potassium carbonate as base.

**6-methoxynaphthalen-2-ol (1z)** was prepared according to literature methods.[2]

**2-phenoxynaphthalene (1h)** was prepared according to literature methods.[3]

**2-methoxy-6-phenylnaphthalene (1l)** was prepared from 1s according to literature methods.[4]

**2-methoxy-6-styrylnaphthalene (1m)** and **1-methoxy-4-styryl-benzene (1n)** were prepared from 1s according to literature methods.[5]

**2-methoxy-6-(4-methoxyphenyl)naphthalene (1y)** was prepared according to literature methods.[6]

**2-tert-butoxynaphthalene (1e), 4-tert-butoxybiphenyl (1o) and 2-tert-butoxy-6-methoxynaphthalene (1w)** were prepared according to literature methods. [7]

**2-methoxy-6-phenoxynaphthalene (1x)** was prepared according to literature methods.[8]

## Typical experiment for the Methylation reaction of Aromatic Rings

$[NiCl_2(PCy_3)_2]$ (17.0 mg, 0.025 mmol), 2-methoxynaphthalene (79.0 mg, 0.5 mmol), and 4 mL of freshly distilled toluene were added into a dry Schlenck tube under a nitrogen atmosphere, and then the methyl magnesium bromide (0.20mL, 3M in ether) was added at room temperature. The reaction mixture was heated to appointed temperature and stirred until the complete convention of the starting material or no more product could be detected by TLC. The solution was cooled to room temperature and the mixture was filtrated through a thin layer of silica. The solvent was removed and the product was obtained by flash column chromatography with PE as eluant.

**2-methylnaphthalene (3a).** The Methylation reaction was effected following the general procedure and the title compound was got as a white solid. $^1$H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 3H), 7.23-7.47 (m, 3H), 7.61 (s, 1H), 7.73-7.80 (m, 3H). $^{13}$C NMR (75.4 MHz, CDCl3): 21.7, 124.9, 128.8, 126.8, 127.2, 127.6, 127.7, 128.1, 131.7, 133.6, 135.4. *m/z* (EI)：142 (M+, 100%), 115 (27%). IR (KBr), ν ($cm^{-1}$): 3050, 2925, 2855, 1601, 1509, 1458, 945, 849, 883, 810, 764, 677.

**1-methylnaphthalene (3b).** The Methylation reaction was effected following the general procedure and the title compound was got as a colorless oil.$^1$H NMR (300 MHz, $CDCl_3$): δ 2.67 (s, 3H), 7.29-7.44 (m, 2H), 7.46-7.53 (m, 2H), 7.68-7.71 (m, 1H), 7.82-7.85 (m, 1H), 7.97-8.00 (m, 1H). $^{13}$C NMR (75.4 MHz, CDCl3): 19.4, 124.1, 125.5, 125.6, 125.7, 126.3, 126.5, 128.5, 132.6, 133.5, 134.2. *m/z* (EI)：142 (M+, 100%), 115 (29%). IR (KBr), ν ($cm^{-1}$): 2294, 2853, 2359, 1462, 1398, 1378, 1021, 790, 771.

**2-methyl-6-phenylnaphthalene (3c).** The Methylation reaction was effected following the general procedure and the title compound was got as a white solid. $^1$H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 3H), 7.28-7.36 (m, 2H), 7.42-7.47 (m, 2H), 7.59 (m, 1 H), 7.66-7.70 (m, 3H), 7.74-7.80 (m, 2H), 8.00 (s, 1H). $^{13}$C NMR (75.4 MHz, CDCl3): 21.7, 125.5, 125.6, 126.6, 127.2, 127.3, 127.8, 128.0, 128.6, 128.8, 131.9, 132.8, 135.6, 137.7, 141.2. *m/z* (EI)：218 (M+, 100%), 202(21%), 189(5%), 176 (2%), 141 (4%), 109 (5%), 95 (4%). IR (KBr), ν ($cm^{-1}$): 3051, 2914, 1601, 1497, 1448, 1378, 911, 888, 825, 805, 770, 753, 741, 693.

**2-methyl-6-styrylnaphthalene (3d).** The Methylation reaction was effected following the general procedure and the title compound was got as a white solid. $^1$H NMR (300 MHz, $CDCl_3$): δ 2.51 (s, 3H), 7.22-7.40 (m, 6H), 7.54-7.58 (m, 3H), 7.71-7.81 (m, 4H). $^{13}$C NMR (75.4 MHz, CDCl3): 21.7, 123.6, 126.4, 126.5, 126.8, 127.6, 127.7, 127.8, 128.5, 128.6, 128.7, 128.9, 131.9, 133.3, 134.0, 135.7, 137.5. *m/z* (EI)：244 (M+, 100%), 228 (60%), 207 (20%), 114 (3%). IR (KBr), ν

($cm^{-1}$): 2911, 1598, 1500, 1446, 1156, 965, 895, 823, 746, 691.

**1-methyl-4-styrylbenzene (3e).** The Methylation reaction was effected following the general procedure and the title compound was got as a white solid. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H), 7.07-7.08 (m, 2H), 7.15-7.25 (m, 3H), 7.32-7.43 (m, 4H), 7.49-7.52 (m, 2H). $^{13}C$ NMR (75.4 MHz, CDCl3): 21.2, 126.3, 126.4, 127.4, 127.7, 128.6, 129.4, 134.5, 137.5. *m/z* (EI):194 (M+, 100%), 179 (100%), 165 (13%), 152 (8%), 139 (3%), 128 (3%), 115 (15%), 102 (3%), 89 (8%). IR (KBr), ν ($cm^{-1}$): 3029, 1511, 964, 907, 807, 730, 708, 690.

**4-methylbiphenyl (3f).** The Methylation reaction was effected following the general procedure and the title compound was got as a white solid. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 7.23-7.29 (m, 2H), 7.32-7.35 (m, 1H), 7.40-7.45 (m, 2H), 7.48-7.52 (m, 2H), 7.56-7.60 (m, 2H). $^{13}C$ NMR (75.4 MHz, CDCl3): 21.1, 126.94, 126.96, 128.68, 128.72, 129.5, 137.0, 138.3, 141.1. *m/z* (EI): 168 (M+, 100%), 152 (20%), 139 (5%), 128 (4%), 115 (7%), 91 (5%), 83 (6%). IR (KBr), ν ($cm^{-1}$): 2923, 2855, 1488, 1455, 1008,821, 756, 696.

**2,6-dimethylnaphthalene (3g).** The Methylation reaction was effected following the general procedure and the title compound was got as a white solid. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.22-7.28 (m, 2H), 7.56-7.66 (m, 4H). $^{13}C$ NMR (75.4 MHz, CDCl3): 21.6, 126.6, 127.0, 128.1, 134.4. *m/z* (EI): 156 (M+, 100%), 141 (62%), 128 (11%), 115 (11%), 77 (7%). IR (KBr), ν ($cm^{-1}$): 2900, 906, 875, 813, 731.

**2-(4-methoxyphenyl)-6-methylnaphthalene (3h).** The Methylation reaction was effected following the general procedure and the title compound was got as a white solid. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 2.51 (s, 3H), 3.85 (s, 3H), 7.00 (d, J = 4.2 Hz, 2H), 7.30-7.33 (m, 1H), 7.61-7.69 (m, 4H), 7.75-7.81 (m, 2H), 7.94 (s, 1H). $^{13}C$ NMR (75.4 MHz, CDCl3): 21.7, 55.3, 114.2, 124.8, 125.4, 126.4, 127.7, 127.8, 128.3, 128.5, 131.9, 132.5, 133.7, 135.3, 137.2, 159.1. *m/z* (EI): 248 (M+, 100%), 233 (50%), 205 (15%), 189 (15%), 165 (3%), 152 (2%), 139 (2%), 124 (6%), 101 (4%). IR (KBr), ν ($cm^{-1}$): 2905, 1604, 1521, 1284, 1255, 1185, 1037, 889, 841, 830, 815, 720, 711.

**6-methylnaphthalen-2-ol (3i).** The Methylation reaction was effected following the general procedure and the title compound was obtained by flash column chromatography (PE/EA = 10:1) as a white solid. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.03-7.10 (m, 2H), 7.24-7.27 (m, 1 H), 7.53-7.66 (m, 3H). $^{13}C$ NMR (75.4 MHz, CDCl3): 21.5, 109.3, 117.7, 126.2 126.7, 128.8, 129.1, 132.7, 133.0, 152.7. *m/z* (EI): 158 (M+, 100%), 141 (4%), 128 (9%). IR (KBr), ν ($cm^{-1}$): 3367, 3047, 2917, 2849, 1636, 1606, 1576, 1513, 1482, 1430, 1219, 1176, 928, 863, 840, 812, 757, 680.

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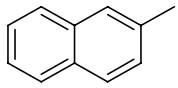

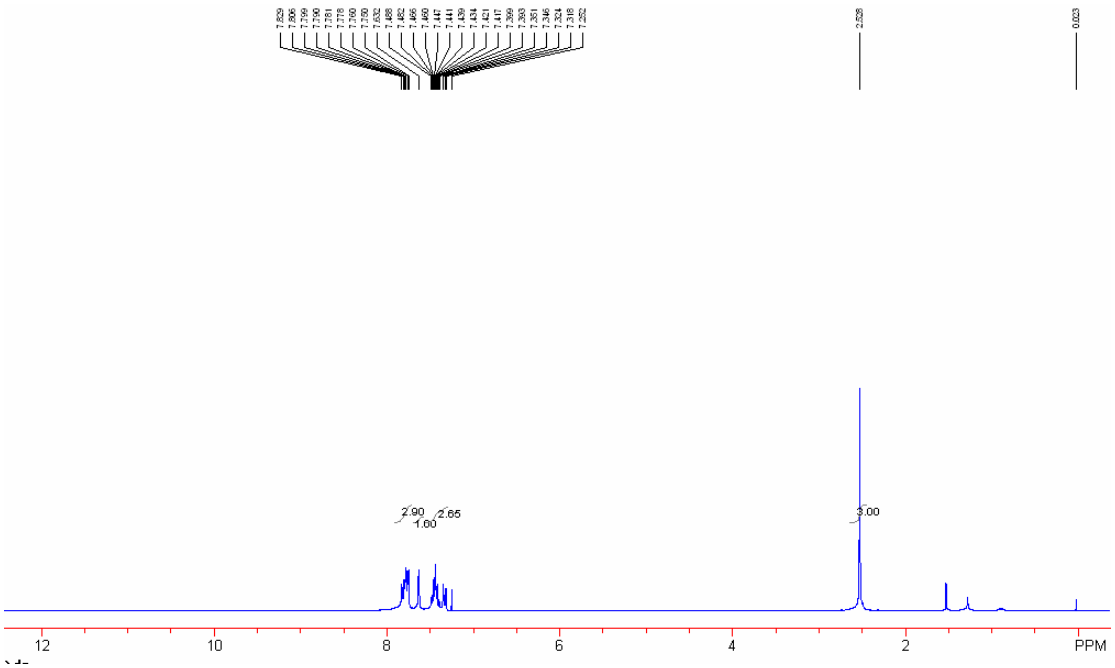


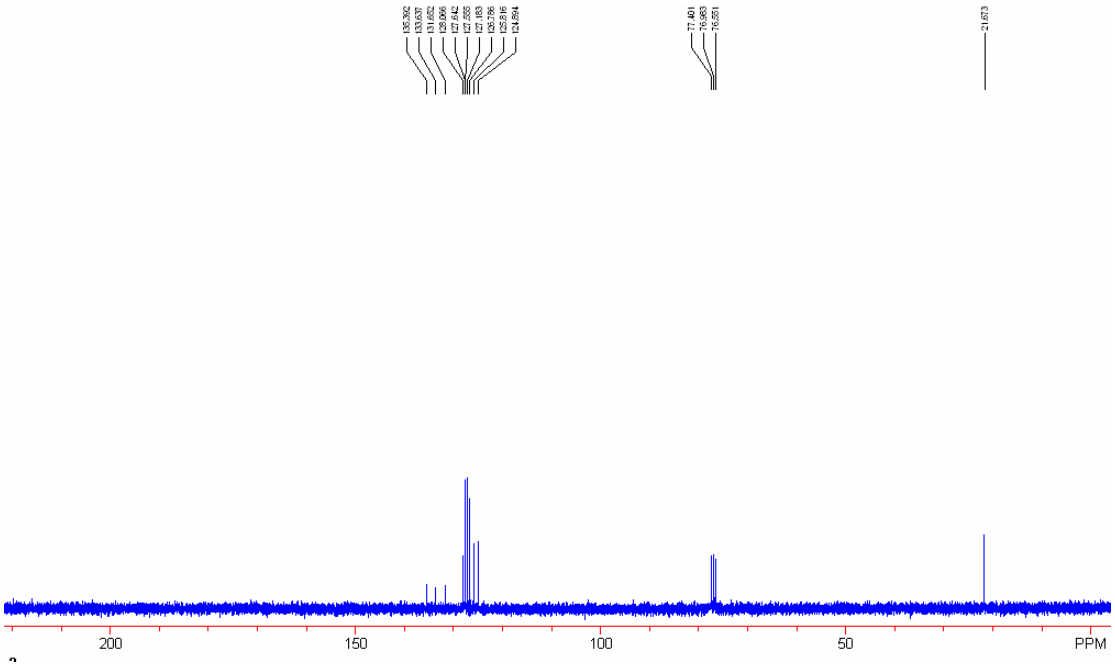

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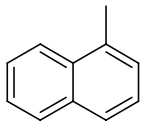

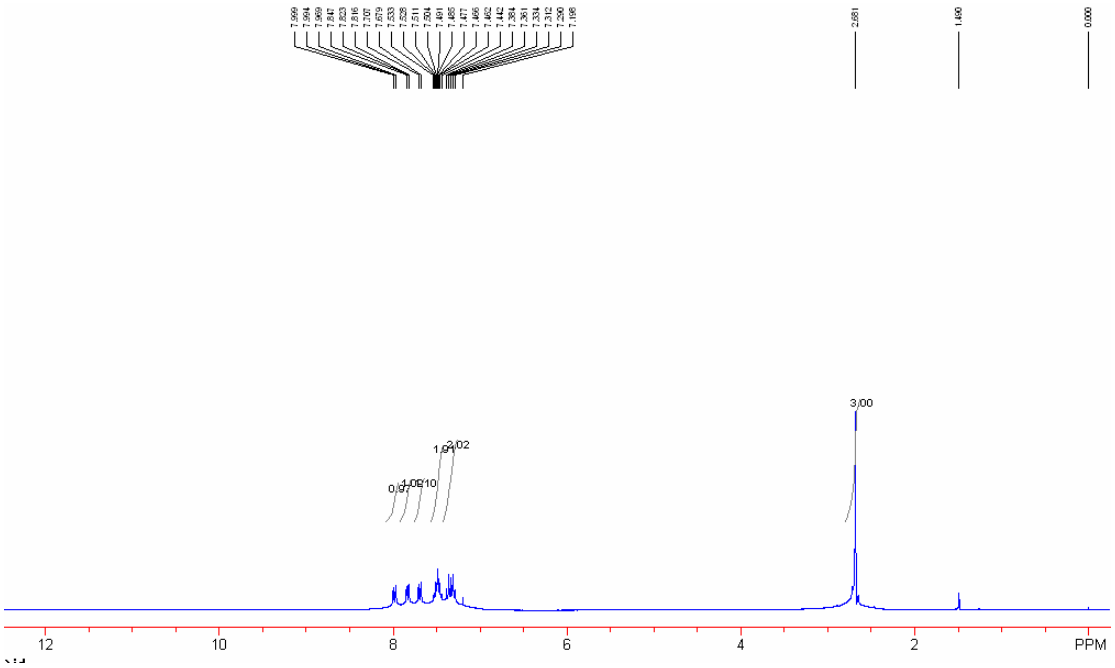
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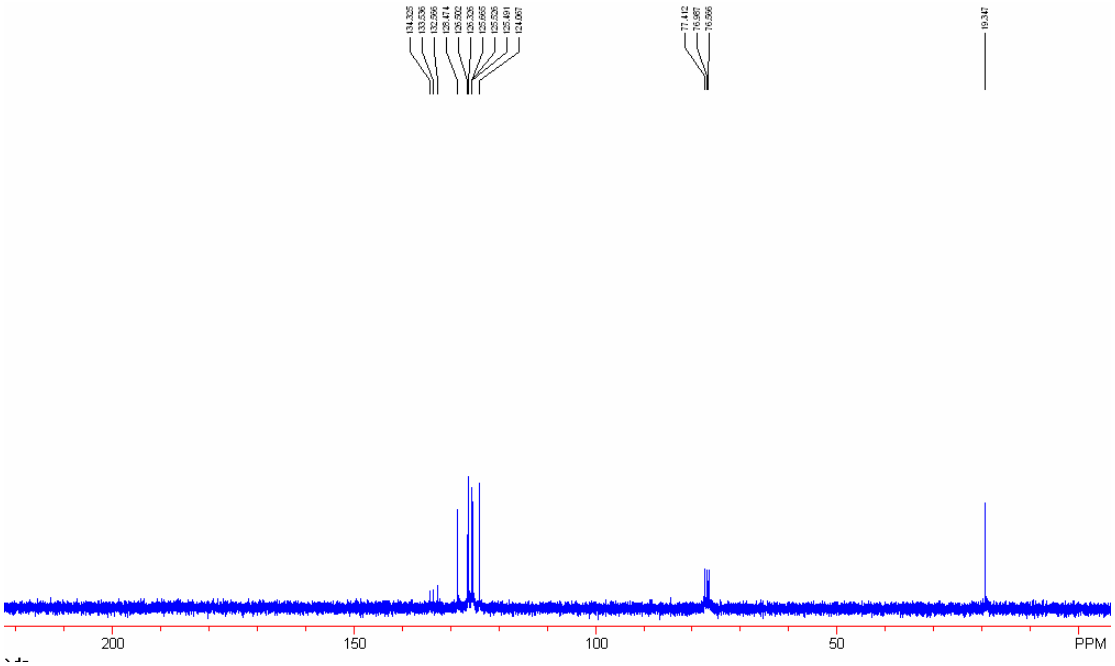
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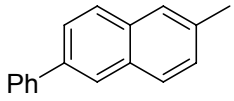


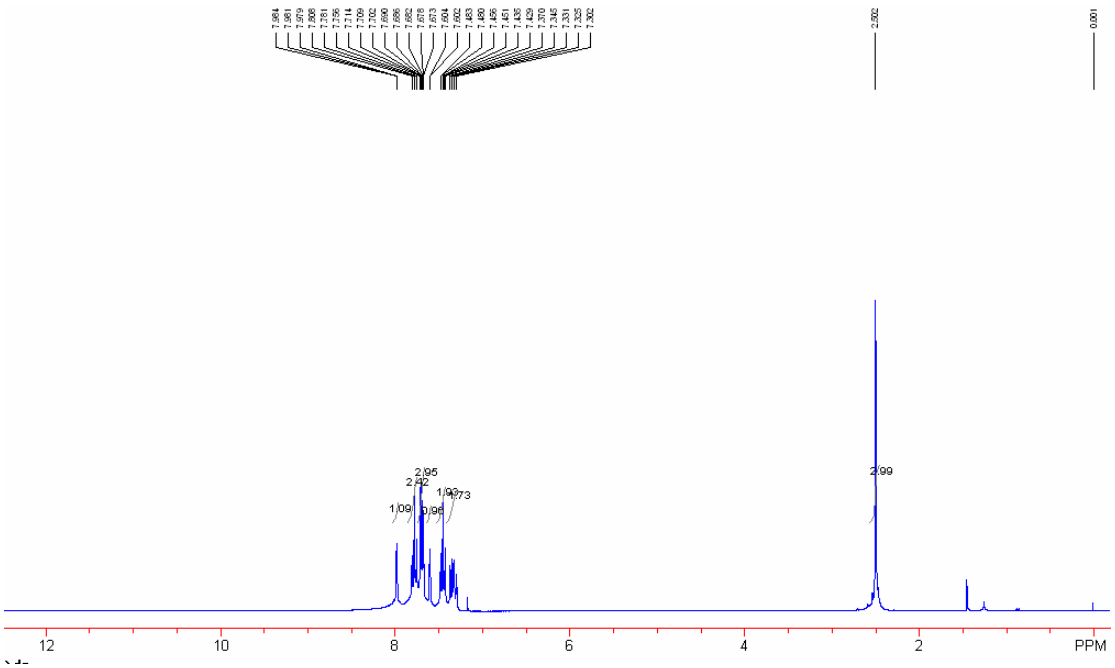


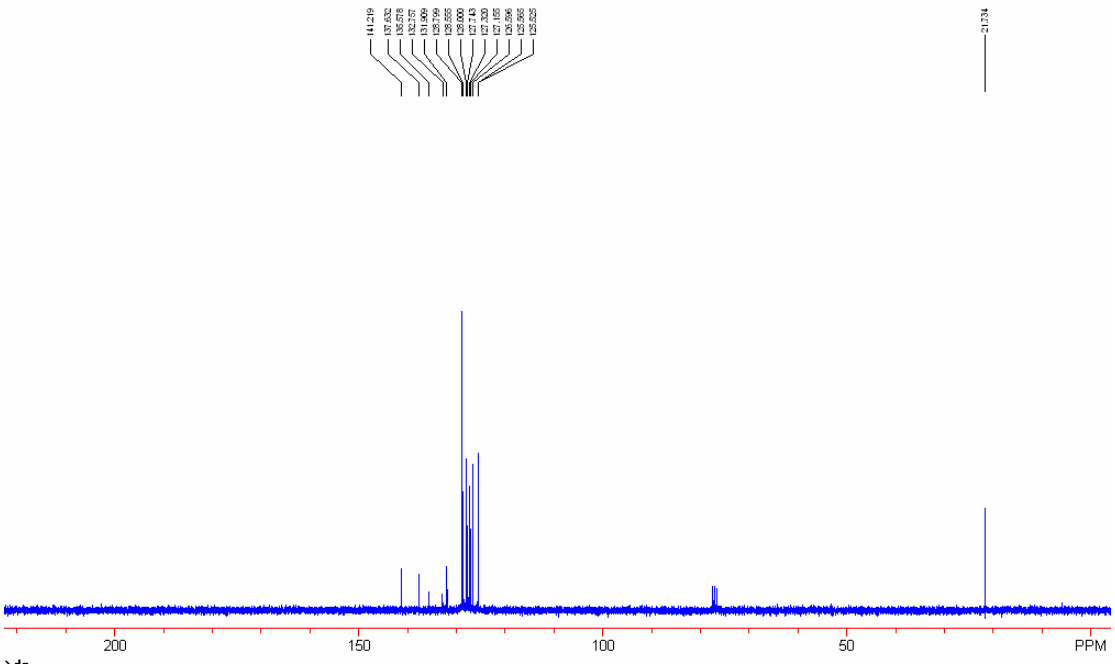

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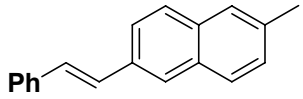


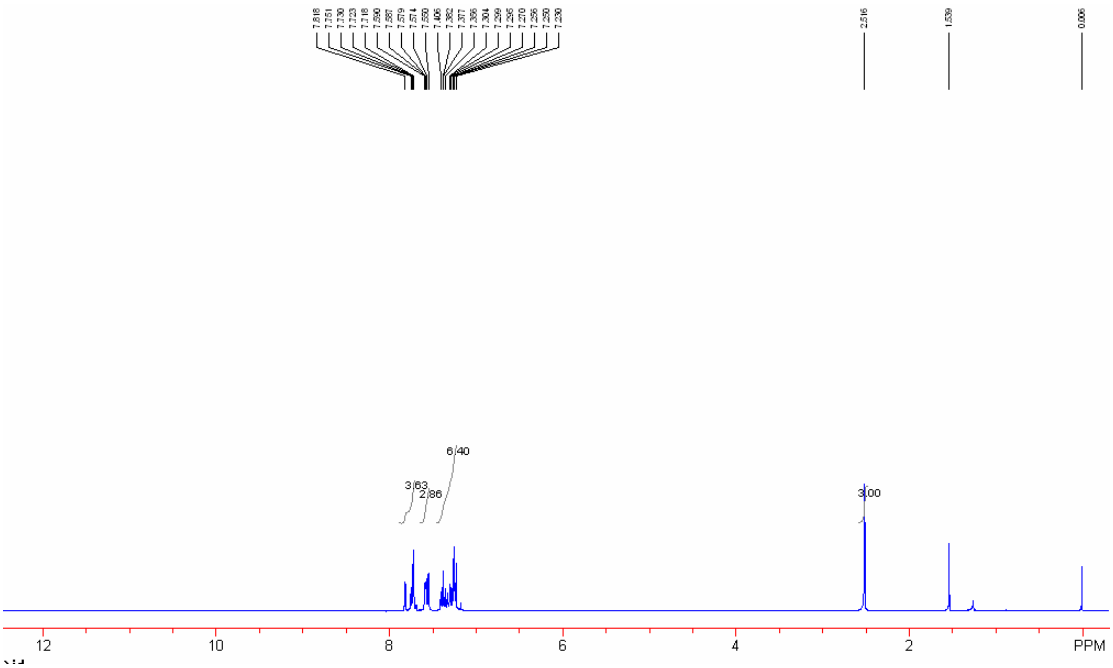


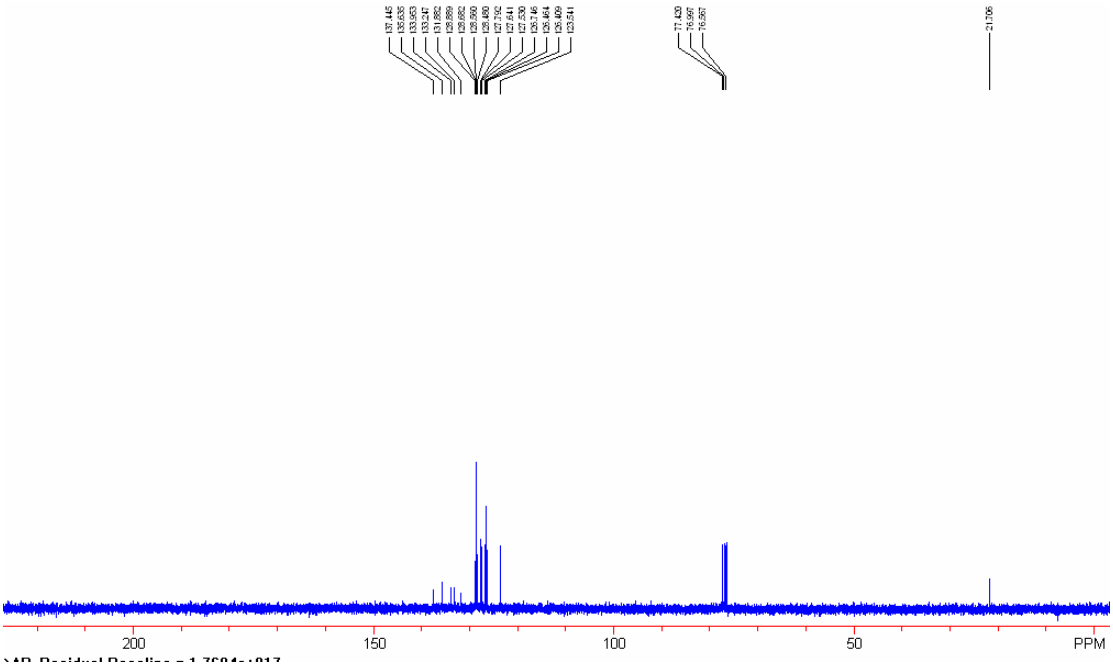

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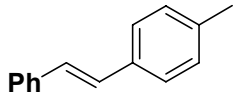


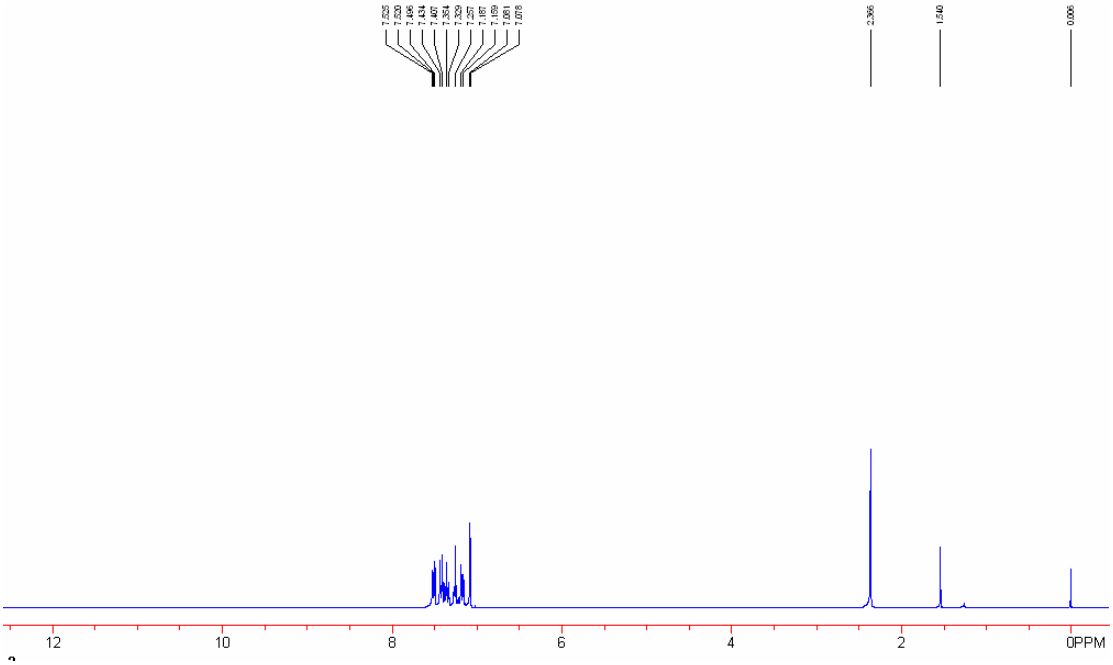


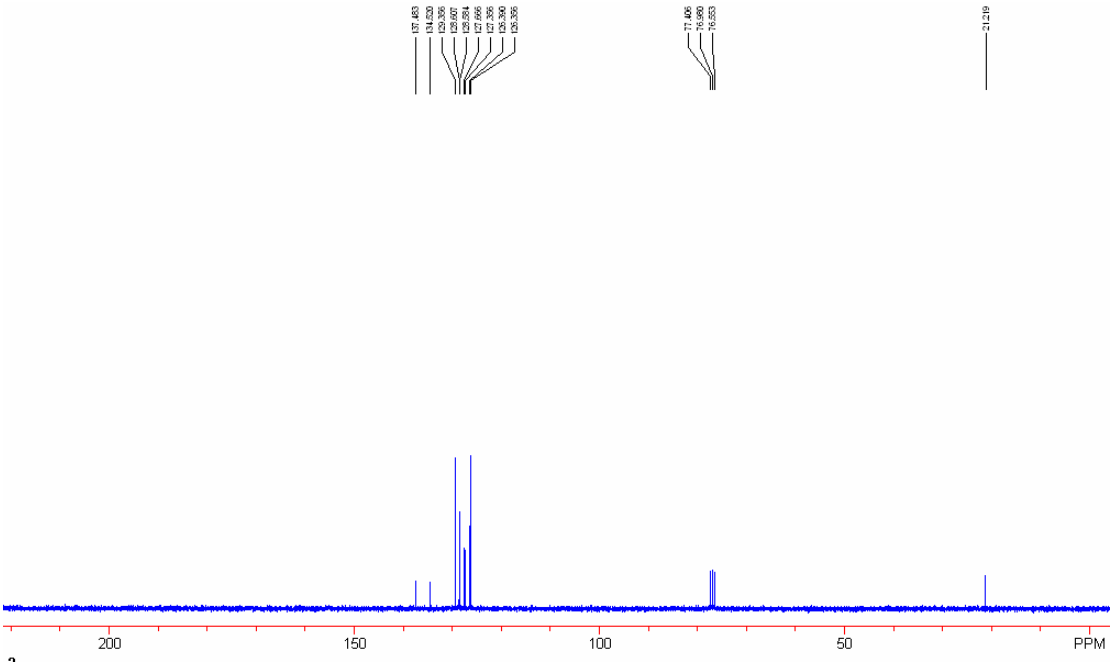

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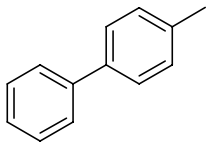

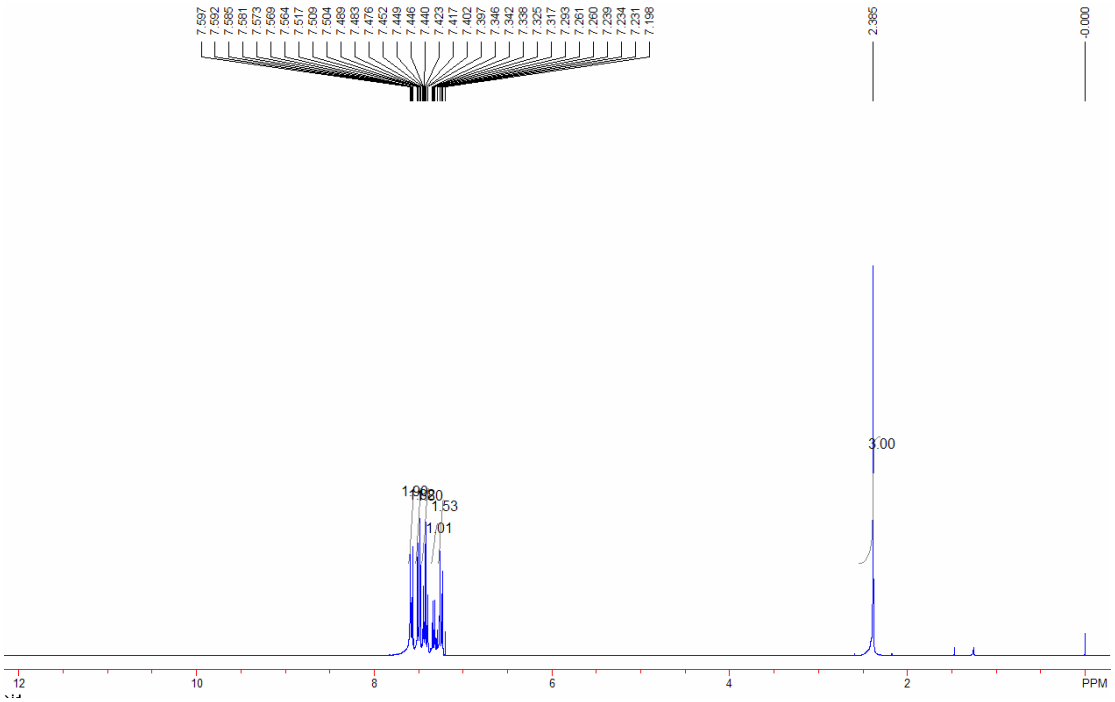
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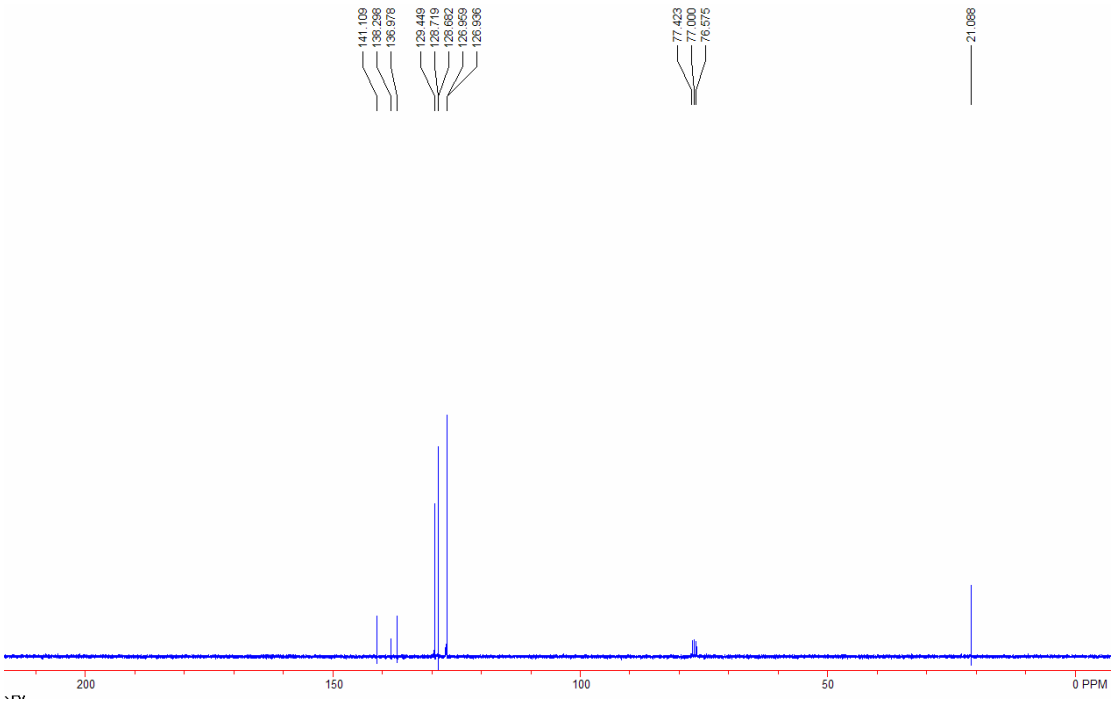
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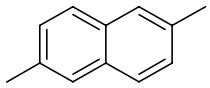

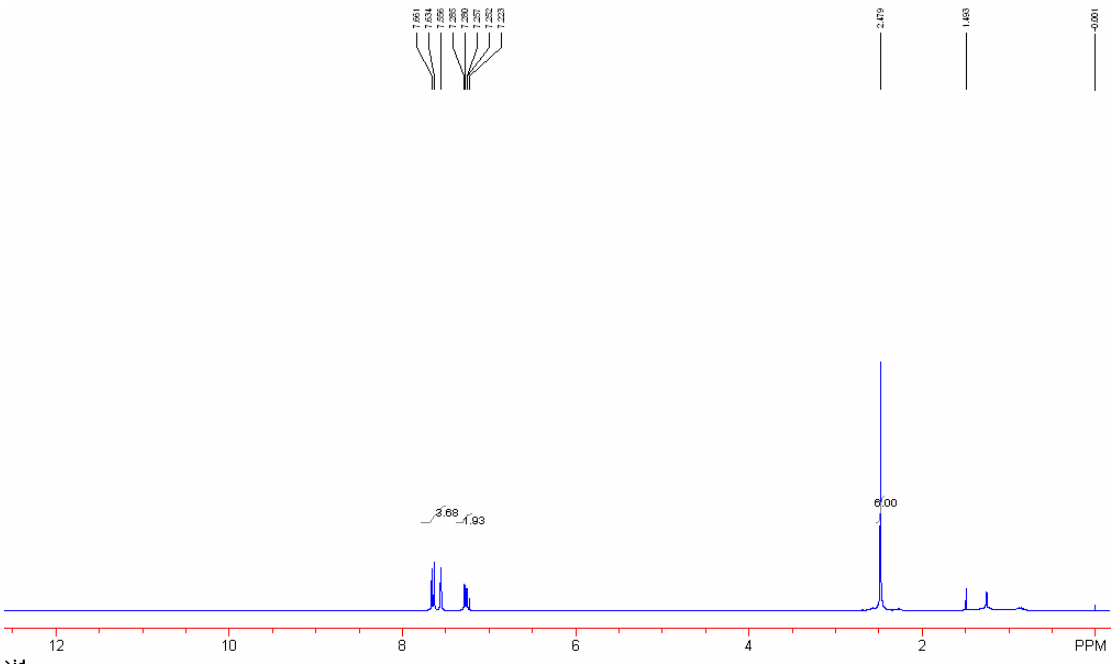
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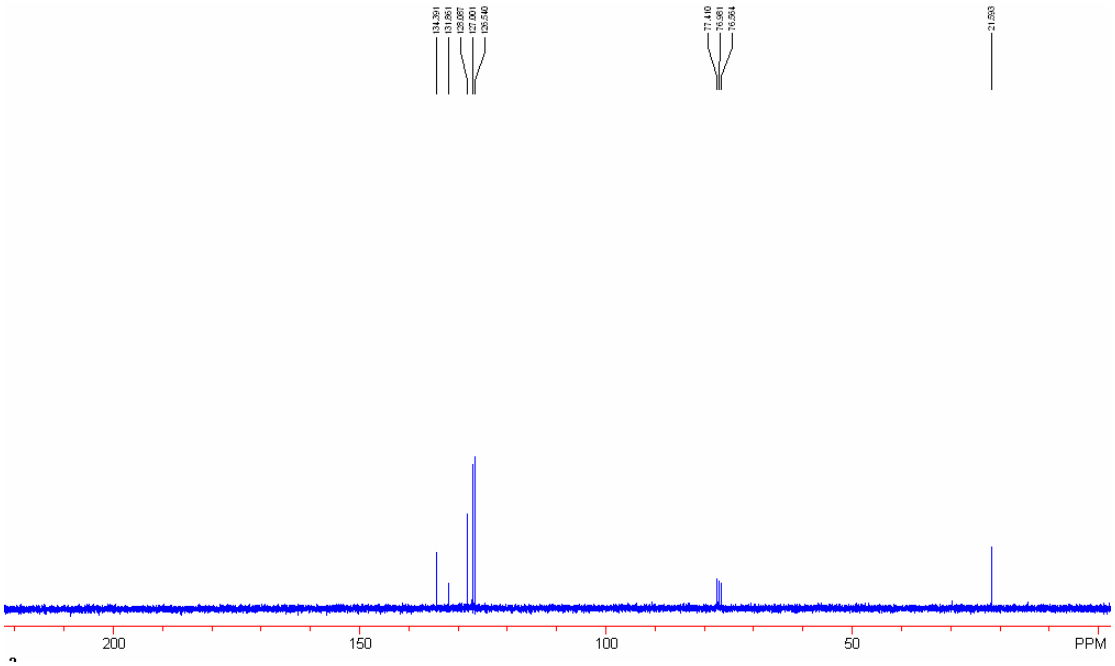
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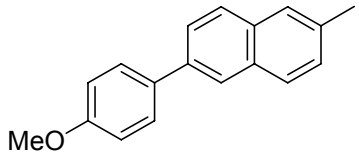
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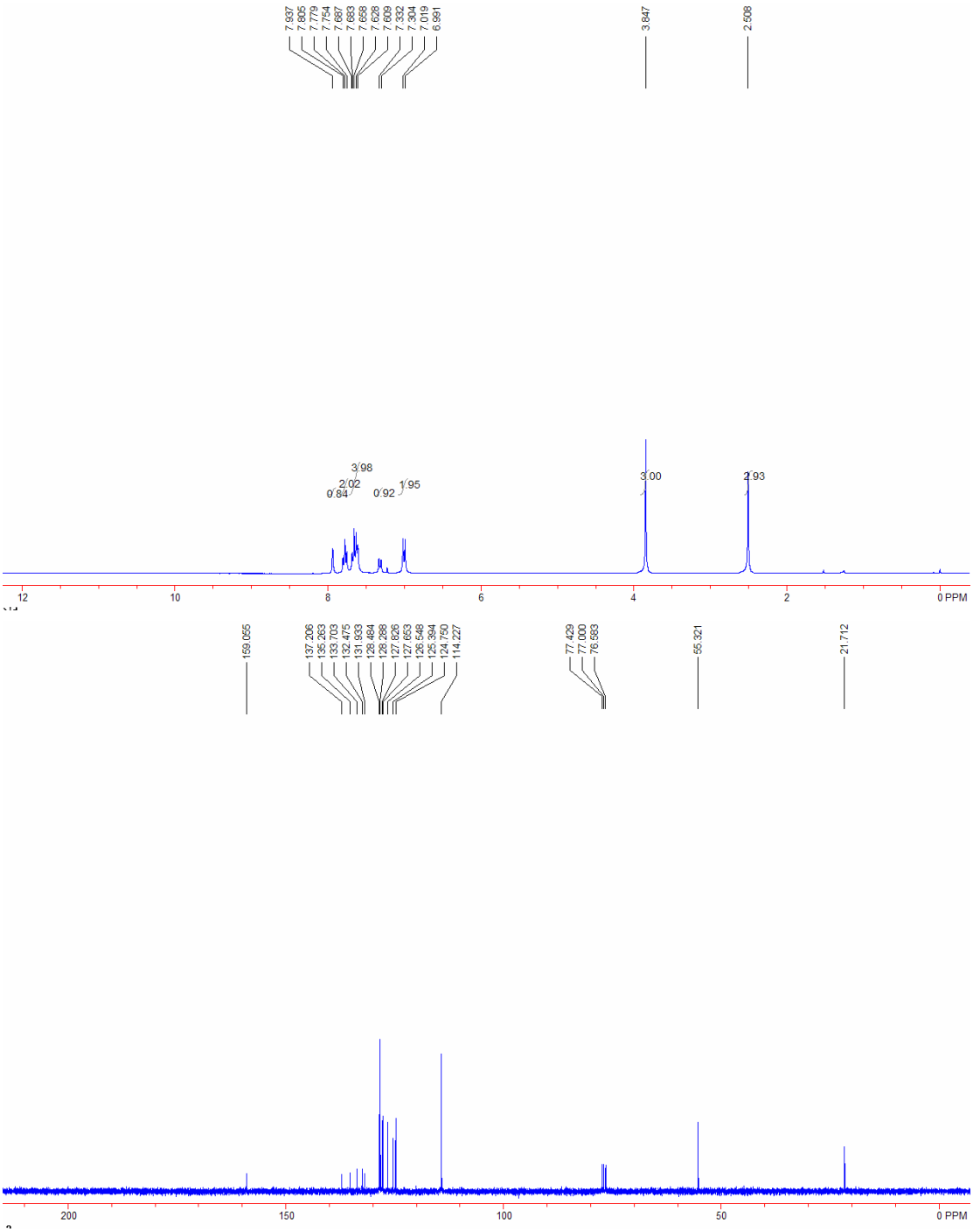
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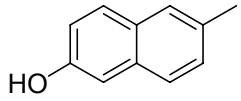
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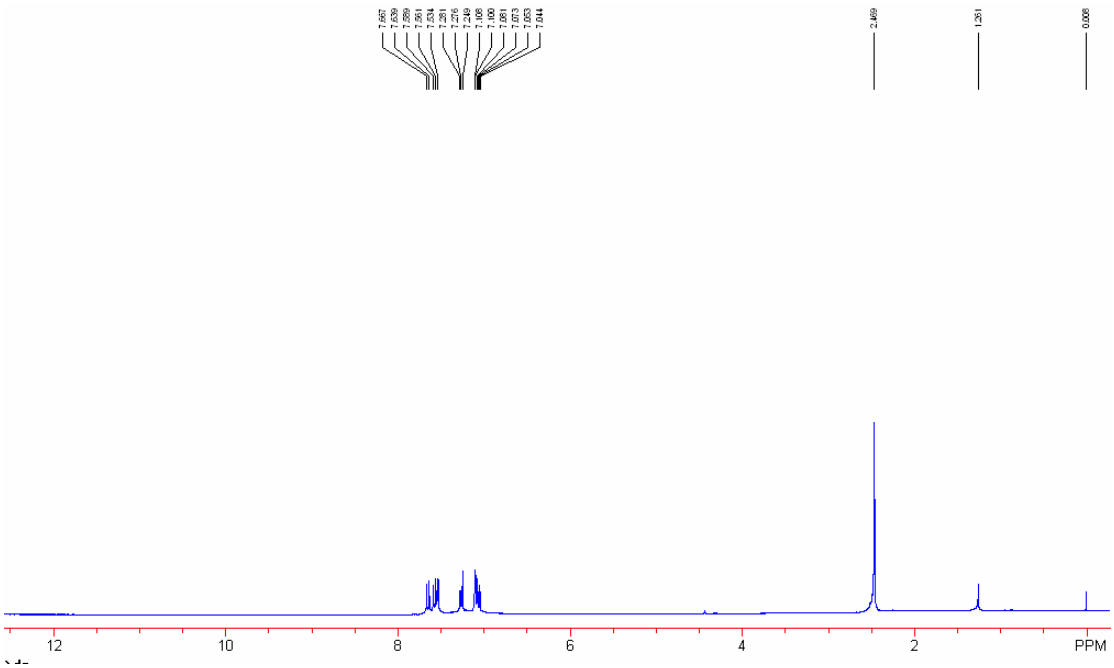
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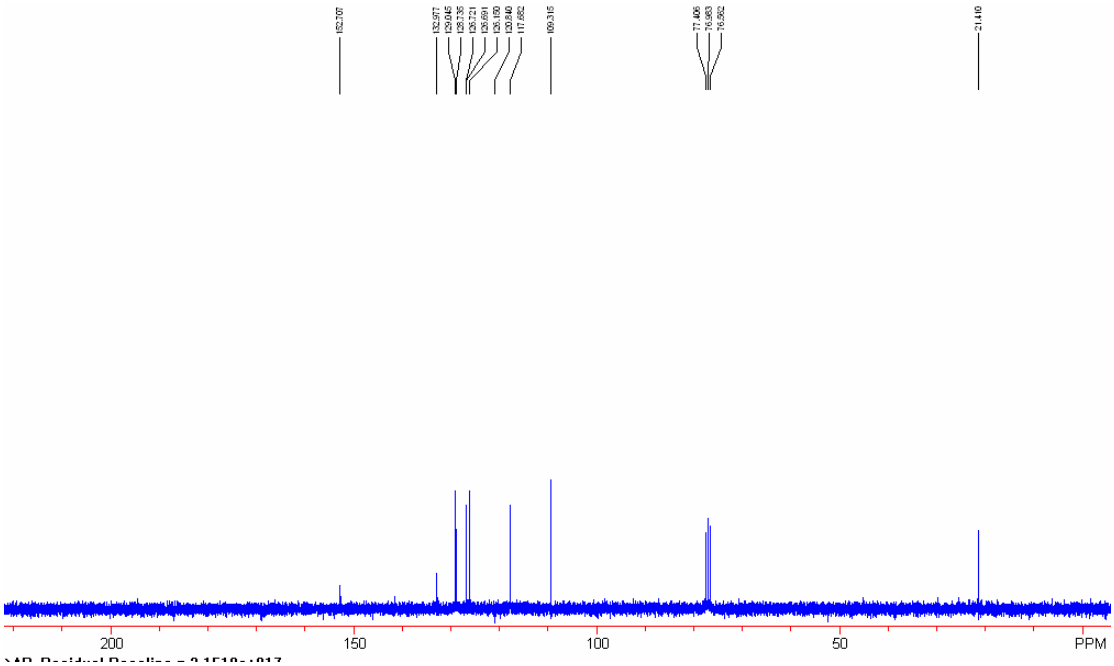
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