

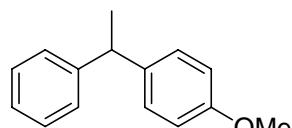
An Efficient Metal-Catalyzed Hydroarylation of Styrenes

Magnus Rueping,^{*} Boris J. Nachtsheim, Thomas Scheidt

Supporting Information

General: Unless otherwise noted, all materials were obtained from commercial suppliers and were used without further purification. Solvents for extraction and chromatography were technical grade and distilled prior to use. For thin-layer chromatography (TLC), silica gel plates coated aluminium plates (Merck, silica gel 60 F₂₅₄) were used and chromatograms were visualised by irradiation with UV light at 254 nm. Column chromatography was performed using Merck silica gel 60 (particle size 0.040-0.063 mm). Solvents mixtures are understood as volume/volume.

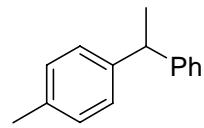
¹H-NMR and ¹³C-NMR were recorded on a Bruker AM 250 spectrometer in CDCl₃. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated (bs (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)); coupling constants (J) are in Hertz (Hz). MALDI-TOF mass spectra were obtained on a VG-TofSpec spectrometer. ESI mass spectra were obtained on a VG-Platform II (Fisons instruments). Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer and are reported in terms of frequency of absorption (cm⁻¹).



Preparation of 1-methoxy-4-(1-phenylethyl)benzene^[1] - General Procedure for the FC-arylation of styrenes: In a typical experiment Bi(OTf)₃(H₂O)₄ (0.005 mmol; 0.5 mol%) ¹ and anisole (4 mmol; 4 eq.) were dissolved in 4 ml of cyclohexane and styrene (1 mmol, 1 eq) was added. The solution was heated to reflux for 3 h, cooled down and gently evaporated under vacuo. The resulting crude mixture was purified by column chromatography on silica gel (Gradient hexane to hexane/ethyl acetate 100:1) to afford 178 mg (84 %) of a colorless oil.

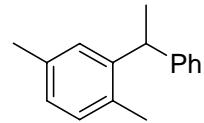
¹H-NMR (250 MHz, CDCl₃): δ = 7.42 - 7.27 (m, 7H), 6.97 (m, 2H), 4.25 (q, J = 7.2 Hz, 1H), 3.89 (s, 3H), 1.76, (d, J = 7.2 Hz, 3H)

¹ The water content of the catalyst was determined by elemental analysis



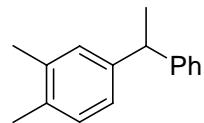
1-methyl-4-(1-phenylethyl)benzene (Table 2 - Entry 1)^[2]

H-NMR (250 MHz, CDCl₃): δ = 7.47 - 7.15 (m, 9H), 4.21 (q, *J* = 7.2 Hz, 1H), 2.40 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H)



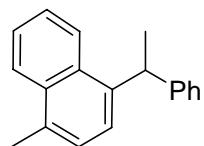
1,4-dimethyl-2-(1-phenylethyl)benzene (Table 2 - Entry 2)^[3]

1H-NMR (250 MHz, CDCl₃): δ = 7.28 - 6.82 (m, 8H), 4.19 (q, *J* = 7.2 Hz, 1H), 2.22 (s, 3H), 2.09 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H)



1,2-dimethyl-4-(1-phenylethyl)benzene (Table 2 - Entry 3)^[4]

1H-NMR (250 MHz, CDCl₃): δ = 7.34 - 7.13 (m, 8H), 4.18 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 6H), 1.71 (d, *J* = 7.2 Hz, 3H)



1-methyl-4-(1-phenylethyl)naphthalene (Table 2 - Entry 4)

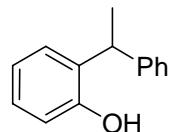
1H-NMR (CDCl₃): δ = 7.98 - 7.90 (m, 2H), 7.41 - 7.29 (m, 2H), 7.22 (s, 2H), 7.20 - 7.02 (m, 7H), 4.81 (q, *J* = 7.13, 1H), 2.59 (s, 3H), 1.66 (d, *J* = 7.14, 3H)

13C-NMR (CDCl₃): δ = 147.0, 139.8, 133.1, 132.9, 131.8, 128.5, 127.7, 126.3, 126.0, 125.6, 125.2, 124.9, 124.6, 124.1, 40.5, 22.7, 19.6

IR (neat): ν = 3060, 3025, 2966, 2931, 2871, 1947, 1871, 1806, 1600, 1514, 1492, 1450, 1423, 1390, 1372, 1335, 1257, 1163, 1075, 1029, 1011, 978, 908, 833, 786, 756, 726, 700, 561 cm⁻¹

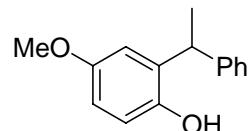
MS (ESI): *m/z* = 247.0 ([M+H]⁺)

EA: calcd. for C₁₉H₁₈: C 92.64, H 7.36; found: C 92.39, H 7.43



2-(1-phenylethyl)phenol (Table 2 - Entry 6)^[5]

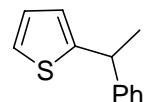
¹H-NMR (250 MHz, CDCl₃): δ = 7.24-7.08 (m, 6H), 7.02 (td, J₁ = 7.7 Hz, J₂ = 1.8 Hz, 1H), 6.96 (td, J₁ = 7.5 Hz, J₂ = 1.2 Hz, 1H), 6.66 (dd, J₁ = 7.9 Hz, J₂ = 1.3 Hz, 1H), 4.59 (s, 1H), 4.28 (q, J = 7.2 Hz, 1H), 1.54 (d, J = 7.2 Hz, 3H)



4-methoxy-2-(1-phenylethyl)phenol (Table 2 - Entry 7)^[6]

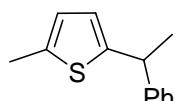
¹H-NMR (250 MHz, CDCl₃): δ = 7.19 - 7.01 (m, 5H), 6.74 - 6.73 (m, 1H), 6.56 - 6.55 (m, 2H), 4.49 (s, 1H), 4.26 (q, J = 7.2 Hz, 1H), 3.66 (s, 3H), 1.51 (d, J = 7.2 Hz, 3H)

¹³C-NMR (63 MHz, CDCl₃): δ = 153.8, 147.3, 145.2, 133.4, 128.8, 127.6, 126.5, 116.7, 114.4, 111.6, 55.8, 39.0, 21.0



2-(1-phenylethyl)thiophene (Table 2 - Entry 8)^[7]

¹H-NMR (250 MHz, CDCl₃): δ = 7.22 - 7.10 (m, 5H), 7.05 (dd, J₁ = 5.1 Hz, J₂ = 1.2 Hz, 1H), 6.85 - 6.81 (m, 1H), 6.73 - 6.70 (m, 1H), 4.26 (q, J = 7.2 Hz, 1H), 1.62 (d, J = 7.2 Hz, 3H)



2-methyl-5-(1-phenylethyl)thiophene (Table 2 - Entry 9)

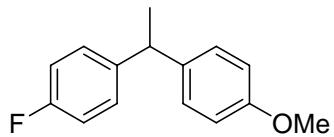
¹H-NMR (250 MHz, CDCl₃): δ = 7.23 - 7.05 (m, 5H), 6.48-6.43 (m, 2H), 4.15 (q, J = 7.1 Hz, 1H), 2.29 (s, 3H), 1.56 (d, J = 7.1 Hz, 3H)

¹³C-NMR (63 MHz, CDCl₃): δ = 148.5, 146.3, 138.1, 128.6, 127.4, 126.6, 124.6, 123.3, 41.0, 23.3, 15.4

IR (neat): ν = 3060, 3025, 2967, 2918, 2872, 1600, 1492, 1451, 1373, 1230, 1048, 800, 699, 447 cm⁻¹

MS (ESI): m/z = 202.6 ([M+H]⁺)

EA: calcd. for C₁₃H₁₄S: C 77.18, H 6.97; found: C 77.16, H 6.98



1-fluoro-4-(1-(4-methoxyphenyl)ethyl)benzene (Table 3 - Entry 2)

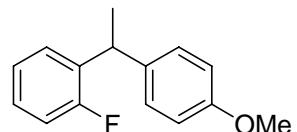
colorless oil

¹H-NMR (CDCl₃): δ = 7.24 - 7.15 (m, 4H), 7.04 - 6.98 (m, 2H), 6.91 - 6.87 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 1.65 (d, *J* = 7.2 Hz)

¹³C-NMR (CDCl₃): δ = 163.2, 159.3, 158.0, 142.5, 142.5, 138.4, 138.4, 129.0, 128.9, 128.5, 115.3, 114.9, 113.8, 55.3, 43.3, 22.3

IR (neat): ν = 3035, 2965, 2932, 2834, 2058, 1885, 1605, 1583, 1508, 1461, 1302, 1245, 1179, 1159, 1034, 1014, 830, 753 cm⁻¹

MS (MALDI-TOF): m/z = 230.2 (100) [M]



1-fluoro-2-(1-(4-methoxyphenyl)ethyl)benzene (Table 3 - Entry 3)

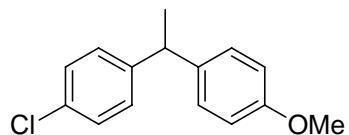
colorless oil

¹H-NMR (CDCl₃): δ = 7.26 - 7.03 (m, 7H), 6.93 - 6.89 (m, 2H), 4.51 (q, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 1.68 (d, *J* = 7.3 Hz, 3H)

¹³C-NMR (CDCl₃): δ = 162.5, 158.7, 158.0, 137.2, 133.8, 133.6, 128.5, 128.4, 127.7, 127.5, 124.1, 124.1, 115.6, 115.2, 113.8, 55.3, 36.9, 36.8, 21.0, 20.9

IR (neat): ν = 3035, 2968, 2933, 2875, 2835, 2058, 1880, 1611, 1583, 1511, 1488, 1453, 1247, 1227, 1179, 1118, 1035, 831, 810, 758 cm⁻¹

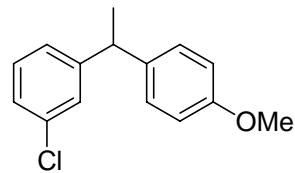
MS (MALDI-TOF): m/z = 231.4 (100) [M+H⁺]



1-chloro-4-(1-(4-methoxyphenyl)ethyl)benzene (Table 4 - Entry 4)^[4]

colorless oil

¹H-NMR (CDCl₃): δ = 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 - 7.03 (m, 4H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 1.66 (d, *J* = 7.2 Hz)



1-chloro-3-(1-(4-methoxyphenyl)ethyl)benzene (Table 4 - Entry 5)

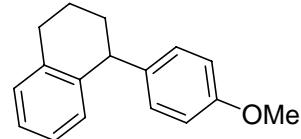
colorless oil

¹H-NMR (CDCl_3): $\delta = 7.25 - 7.11$ (m, 7H), 6.90 - 6.87 (m, 2H), 4.12 (q, $J = 7.2$ Hz, 1H), 3.83 (s, 3H), 1.64 (d, $J = 7.2$ Hz, 3H)

¹³C-NMR (CDCl_3): $\delta = 158.1, 148.9, 137.7, 134.2, 129.6, 128.5, 127.7, 126.2, 125.8, 113.9, 55.3, 43.8, 21.9$ cm^{-1}

IR (neat): $\nu = 2965, 2932, 2833, 1879, 1611, 1594, 1572, 1510, 1462, 1303, 1248, 1179, 1080, 1035, 881, 831, 805, 787, 742, 695$

MS (MALDI-TOF): m/z = 246.29 [M]



1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (Table 3 - Entry 6)

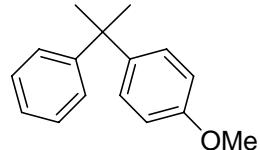
pale yellow oil

¹H-NMR (CDCl_3): $\delta = 7.04 - 7.03$ (m, 2H), 6.99 - 6.92 (m, 3H), 6.78 - 6.72 (m, 3H), 3.99 (t, $J = 6.9$ Hz, 1H), 3.70 (s, 3H), 2.87 - 2.75 (m, 2H), 2.08 - 2.00 (m, 1H), 1.83 - 1.66 (m, 4H)

¹³C-NMR (CDCl_3): $\delta = 157.8, 139.8, 139.7, 137.5, 130.1, 129.7, 129.0, 125.8, 125.6, 113.6, 55.3, 44.8, 33.4, 29.8, 21.0$

IR (neat): $\nu = 3057, 3014, 2930, 2857, 2834, 1610, 1583, 1510, 1491, 1449, 1302, 1244, 1176, 1107, 1037, 827, 778, 741$ cm^{-1}

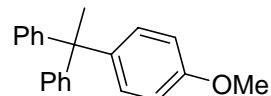
MS (MALDI-TOF): m/z = 239.4 [M+H⁺]



1-(2-(4-methoxyphenyl)propan-2-yl)benzene (Table 3 - Entry 7)^[8]

pale yellow oil

¹H-NMR (CDCl_3): $\delta = 7.34 - 7.24$ (m, 5H), 7.22 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H), 1.73 (s, 6H)



1-(1,1-diphenylethyl)-4-methoxybenzene (Table 3 - Entry 8)

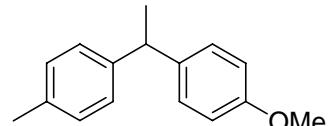
pale yellow oil

¹H-NMR (CDCl_3): $\delta = 7.22 - 7.12$ (m, 6H), $7.03 - 7.01$ (m, 4H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.73 (d, $J = 8.8$ Hz, 2H), 3.72 (s, 3H), 2.09 (s, 3H)

¹³C-NMR (CDCl_3): 157.6, 149.4, 141.2, 129.7, 128.7, 127.8, 125.9, 113.1, 55.2, 51.9, 30.612

IR (neat): $\nu = 3081, 3056, 3021, 2978, 2834, 1951, 1888, 1808, 1759, 1598, 1580, 1510, 1492, 1463, 1443, 1374, 1297, 1250, 1183, 1030, 911, 851, 822, 790, 761, 700, 585, 571 \text{ cm}^{-1}$

MS (MALDI-TOF): m/z = 287.98 [M]



1-(1-(4-methoxyphenyl)ethyl)-4-methylbenzene (Table 3 - Entry 9)

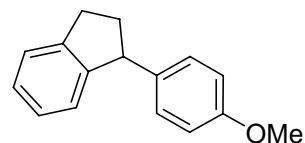
colorless oil

¹H-NMR (CDCl_3): $\delta = 7.06 - 6.97$ (m, 6H), $6.74 - 6.71$ (m, 2H), 3.98 (q, $J = 7.2$ Hz, 1H), 3.67 (s, 3H), 2.22 (s, 3H), 1.51 (d, $J = 7.2$ Hz, 3H)

¹³C-NMR (CDCl_3): 157.8, 143.9, 138.8, 135.4, 129.1, 128.5, 127.4, 113.8, 55.3, 43.6, 22.2, 21.2

IR (neat): $\nu = 2963, 2834, 1898, 1610, 1582, 1510, 1459, 1246, 1177, 1120, 1036, 816, 745$

MS (MALDI-TOF): m/z = 249.36 [M+Na]



1-(4-methoxyphenyl)-2,3-dihydro-1H-indene (Table 3 - Entry 10)

pale yellow oil

¹H-NMR (CDCl_3): $\delta = 7.19 - 7.16$ (m, 1H), $7.08 - 6.99$ (m, 4H), $6.84 - 6.87$ (m, 1H), $6.76 - 6.73$ (m, 2H), 4.18 (t, $J = 8.4$ Hz, 1H), 3.68 (s, 3H), $2.93 - 2.82$ (m, 2H), $2.48 - 2.41$ (m, 1H), $1.96 - 1.87$ (m, 1H)

¹³C-NMR (CDCl_3): 158.2, 147.2, 144.3, 137.6, 129.1, 126.5, 126.4, 124.9, 124.4, 113.9, 77.6, 77.1, 76.6, 55.3, 50.9, 36.8, 31.9

IR (neat): $\nu = 3065, 3019, 2951, 2835, 2061, 1878, 1611, 1584, 1512, 1477, 1457, 1440, 1344, 1302, 1244, 1177, 1107, 1038, 828, 763,$

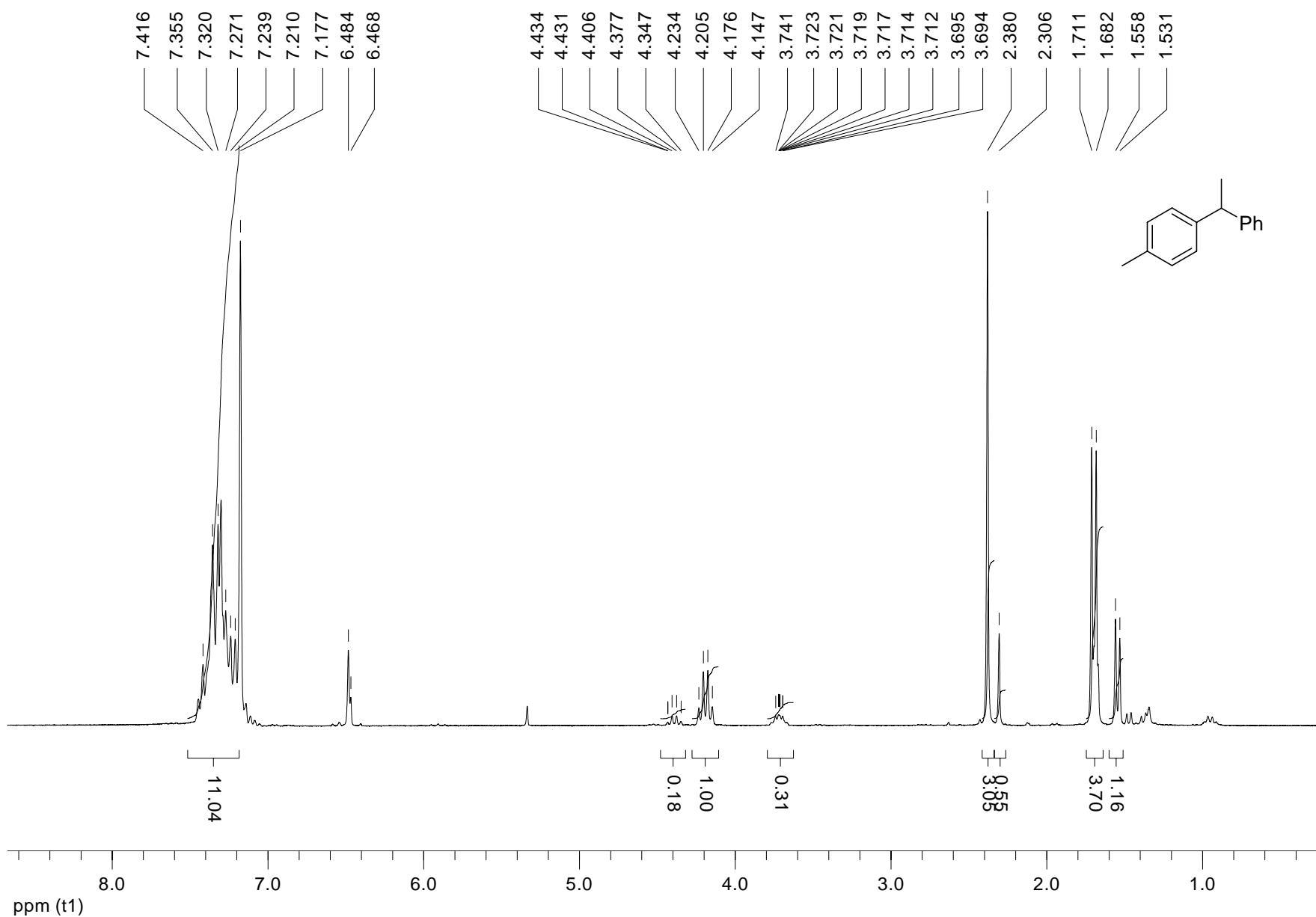
MS (MALDI-TOF): m/z = 223.67 [M-H⁺]

References of the known products:

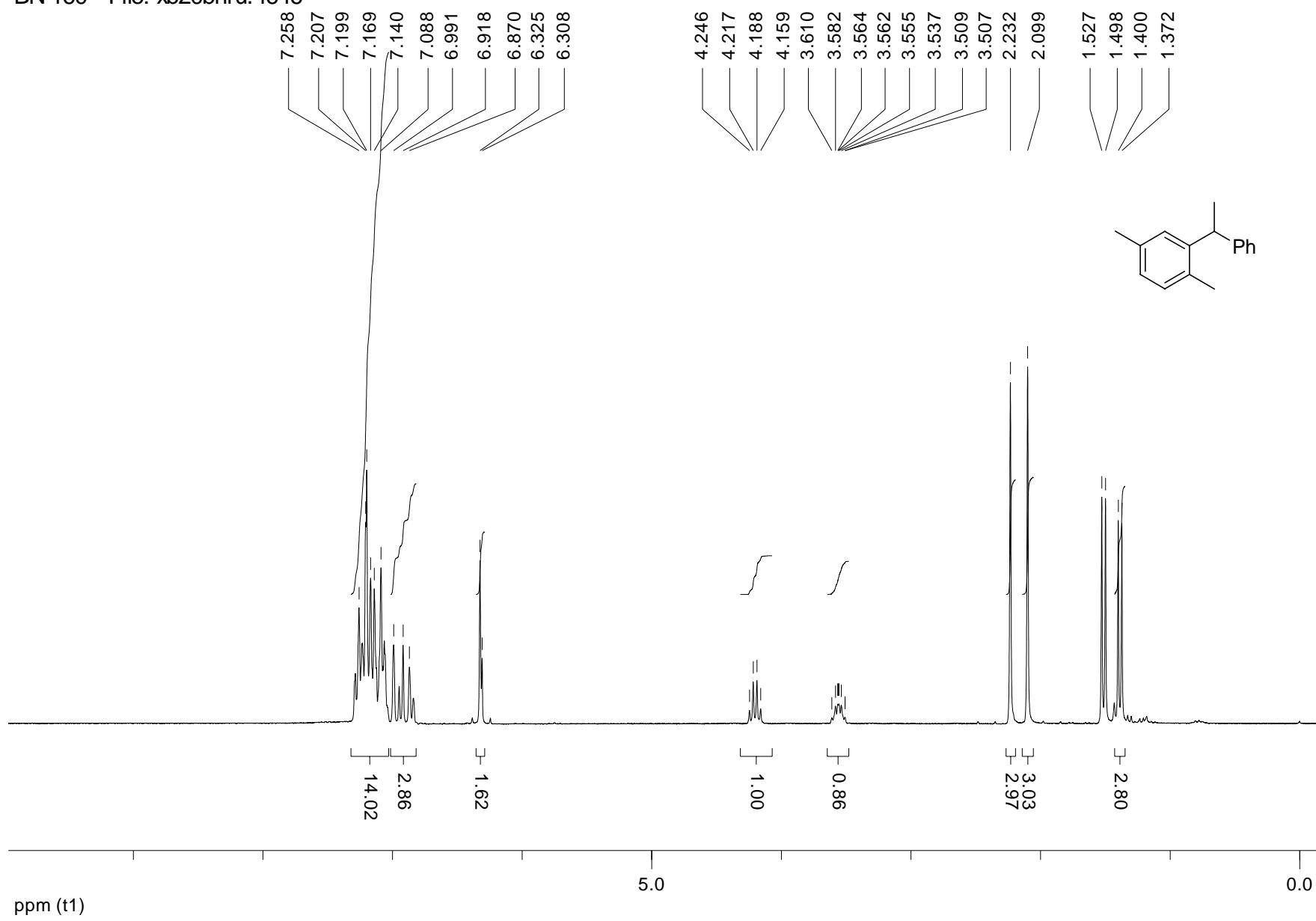
- [1] K. H. Y.Yamaushi, S.Uemura, *Bull. Chem. Soc. Jap.* **1986**, 59, 3617
- [2] T. Miyai, Y. Onishi, A. Baba, *Tetrahedron* **1999**, 55, 1017.
- [3] G. Montaudo, Finocchi.P, *J. Am. Chem. Soc.* **1972**, 94, 6745.
- [4] J. Kischel, I. Jovel, K.Mertins, A.Zapf, M.Beller, *Org.Lett*, **2006**, 8, 19-22.
- [5] R. M. Jones, R. W. Van de Water, C. C. Lindsey, C. Hoarau, T. Ung, T. R. R. Pettus, *J. Org. Chem.* **2001**, 66, 3435.
- [6] K. R. B.Hunter, A.Zaghloul, *Can. J. Chem.* **1983**, 62, 124.
- [7] S. F. S.Hall, *J. Heterocycl. Chem* **1987**, 24, 1205.
- [8] C. A. Van Walree, M. R. Roest, W. Schuddeboom, L. W. Jenneskens, J. W. Verhoeven, J.M. Warman, H. Kooijman, A. L. Spek, *J. Am. Chem. Soc*, 1996, 118, 8395-8407

^1H -NMR-Spectra of the known compounds

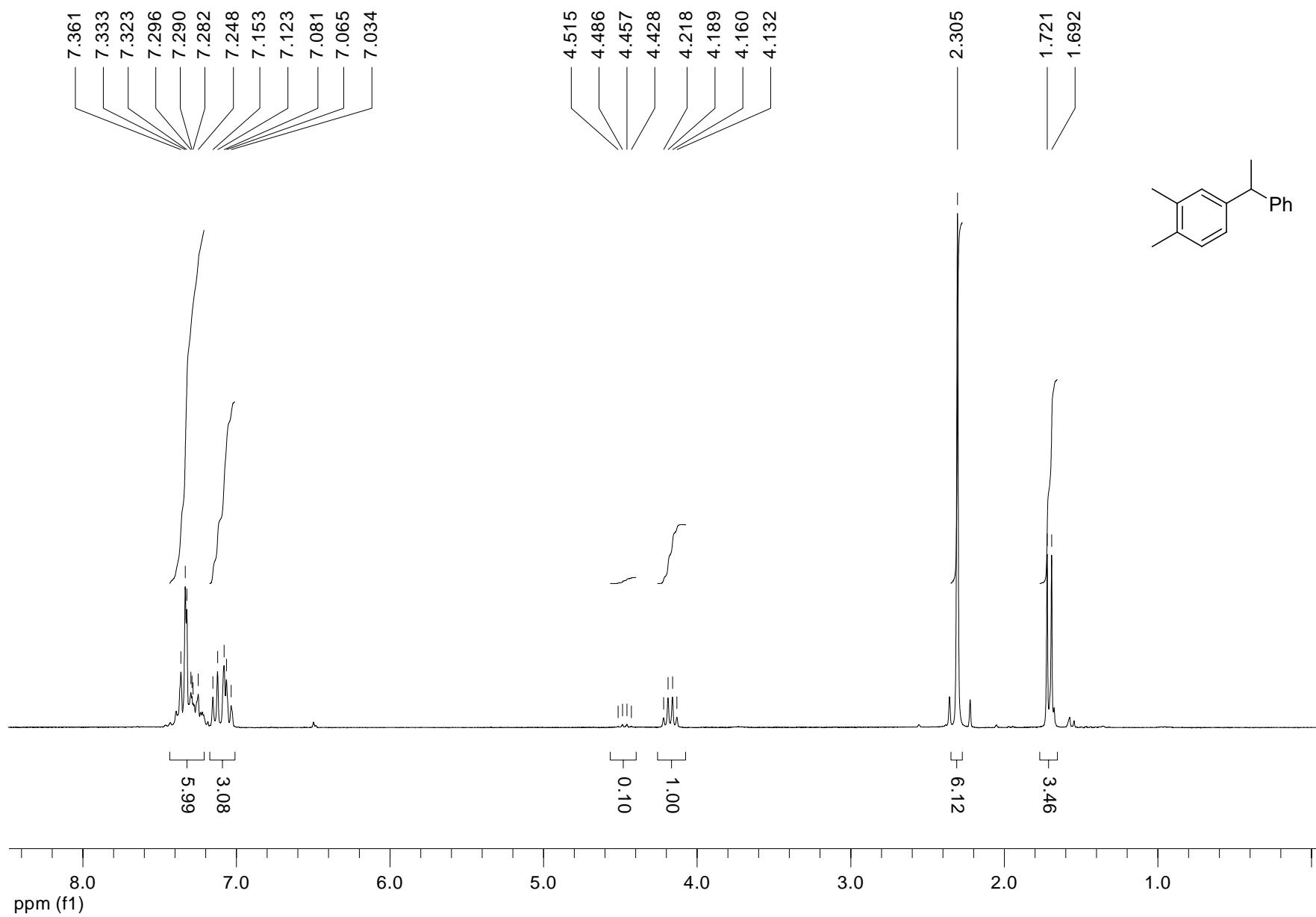
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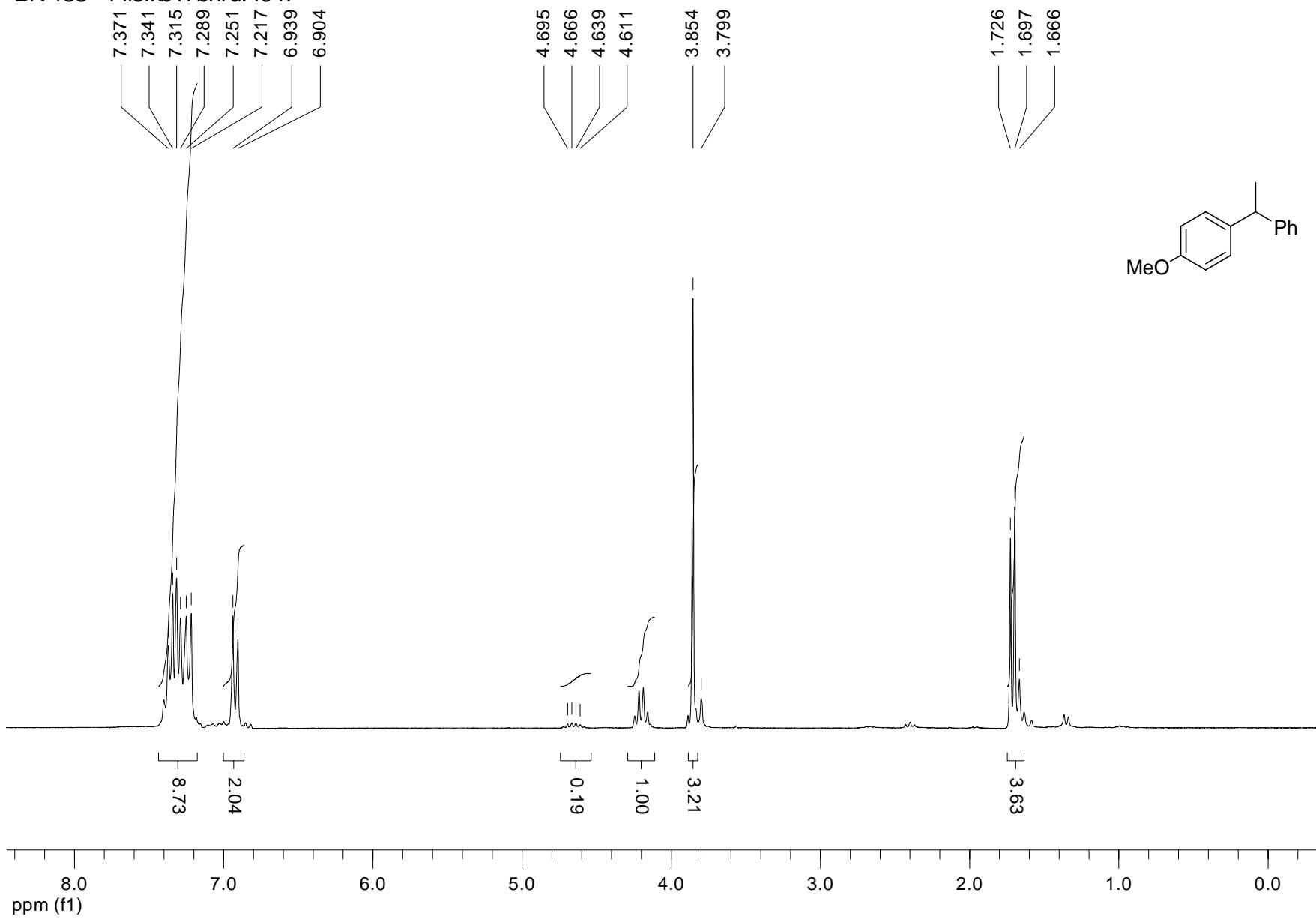
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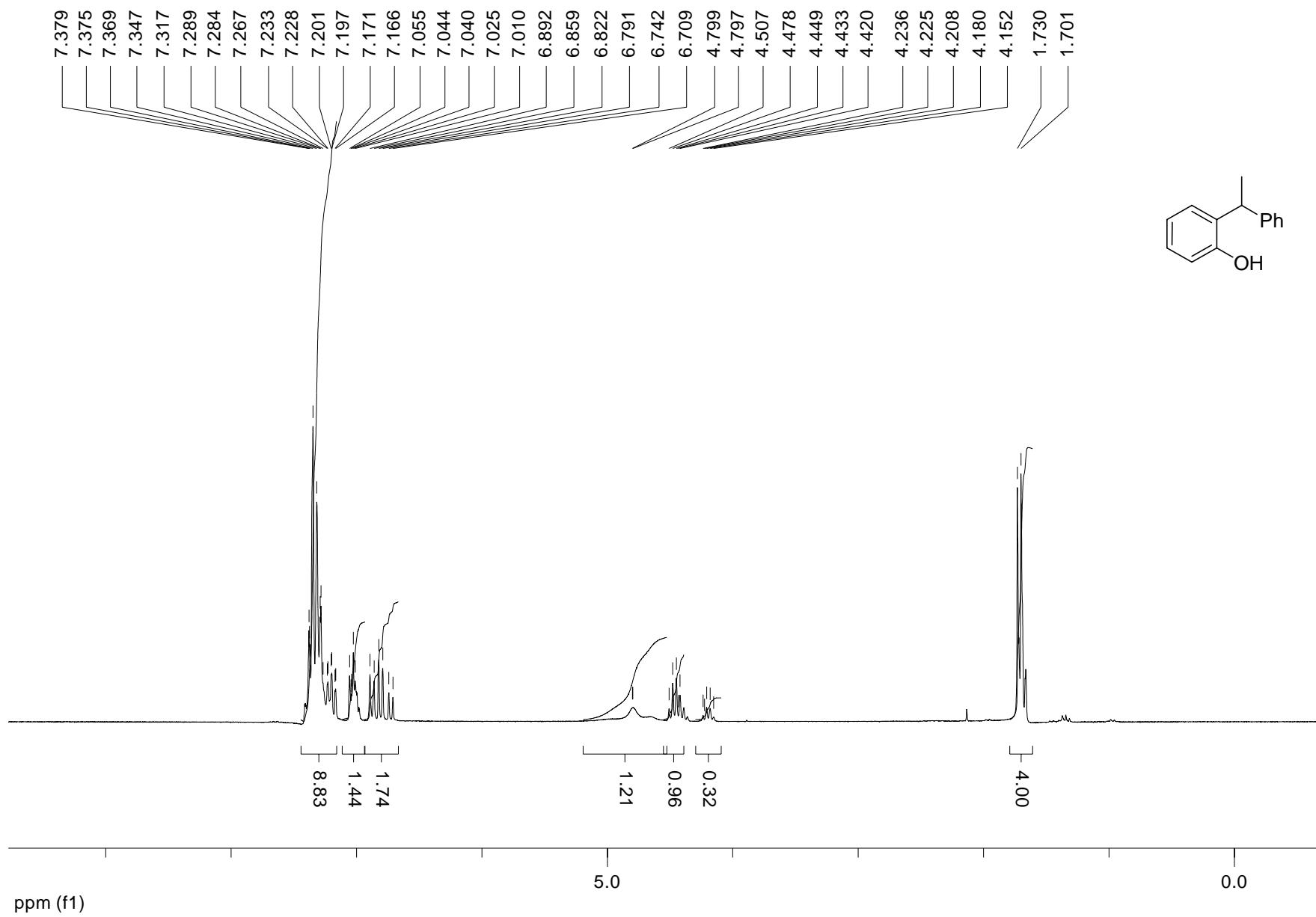
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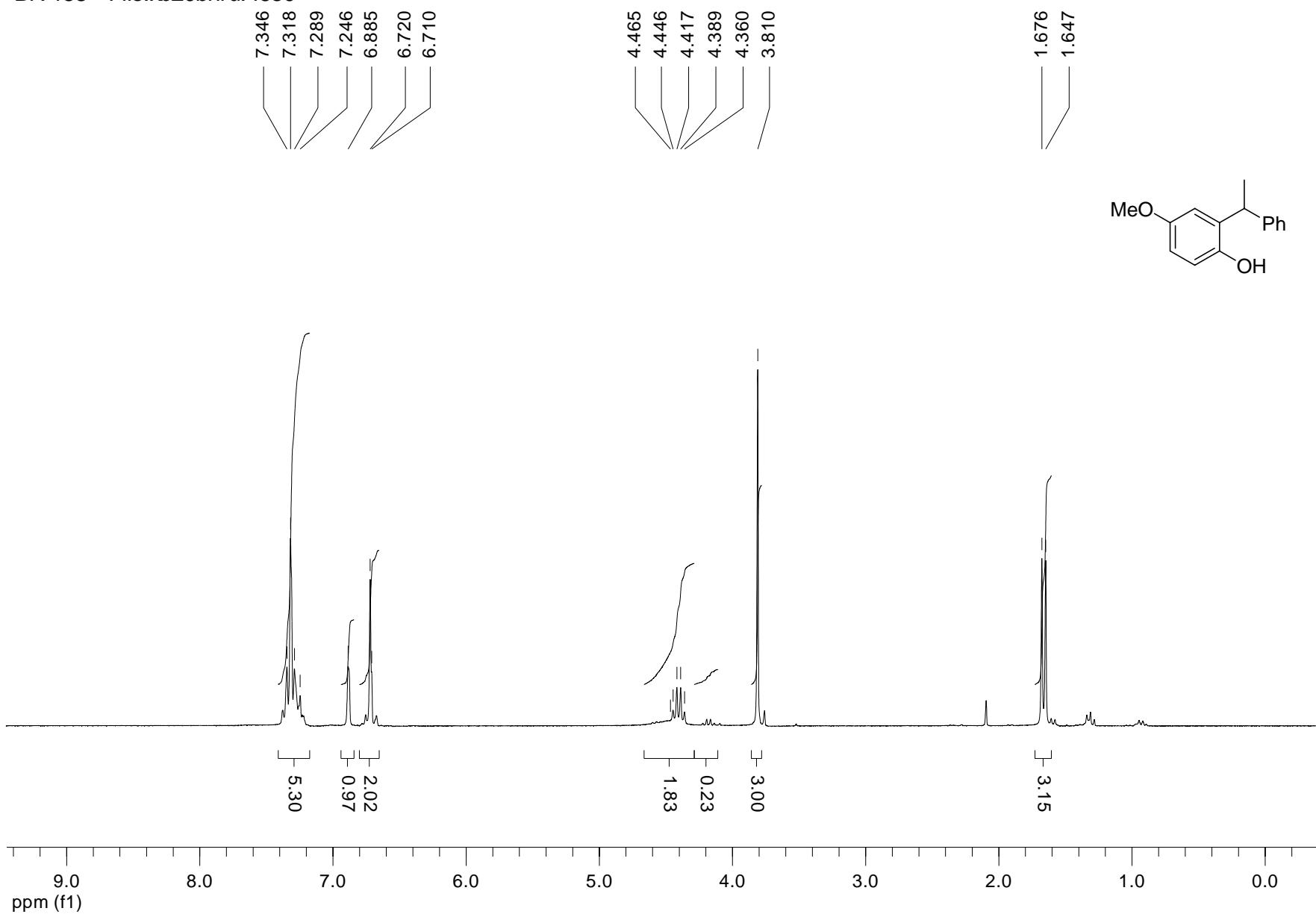
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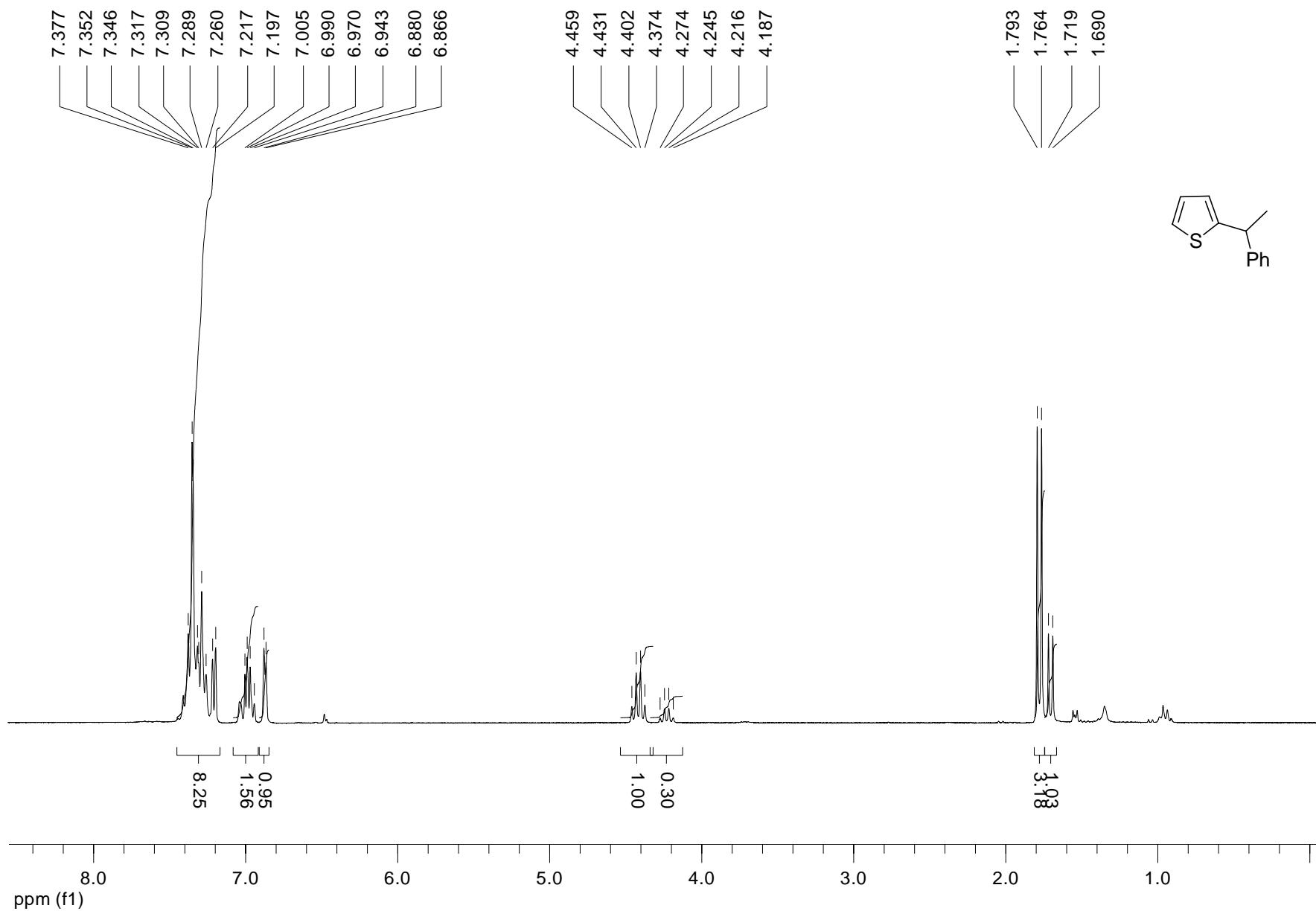
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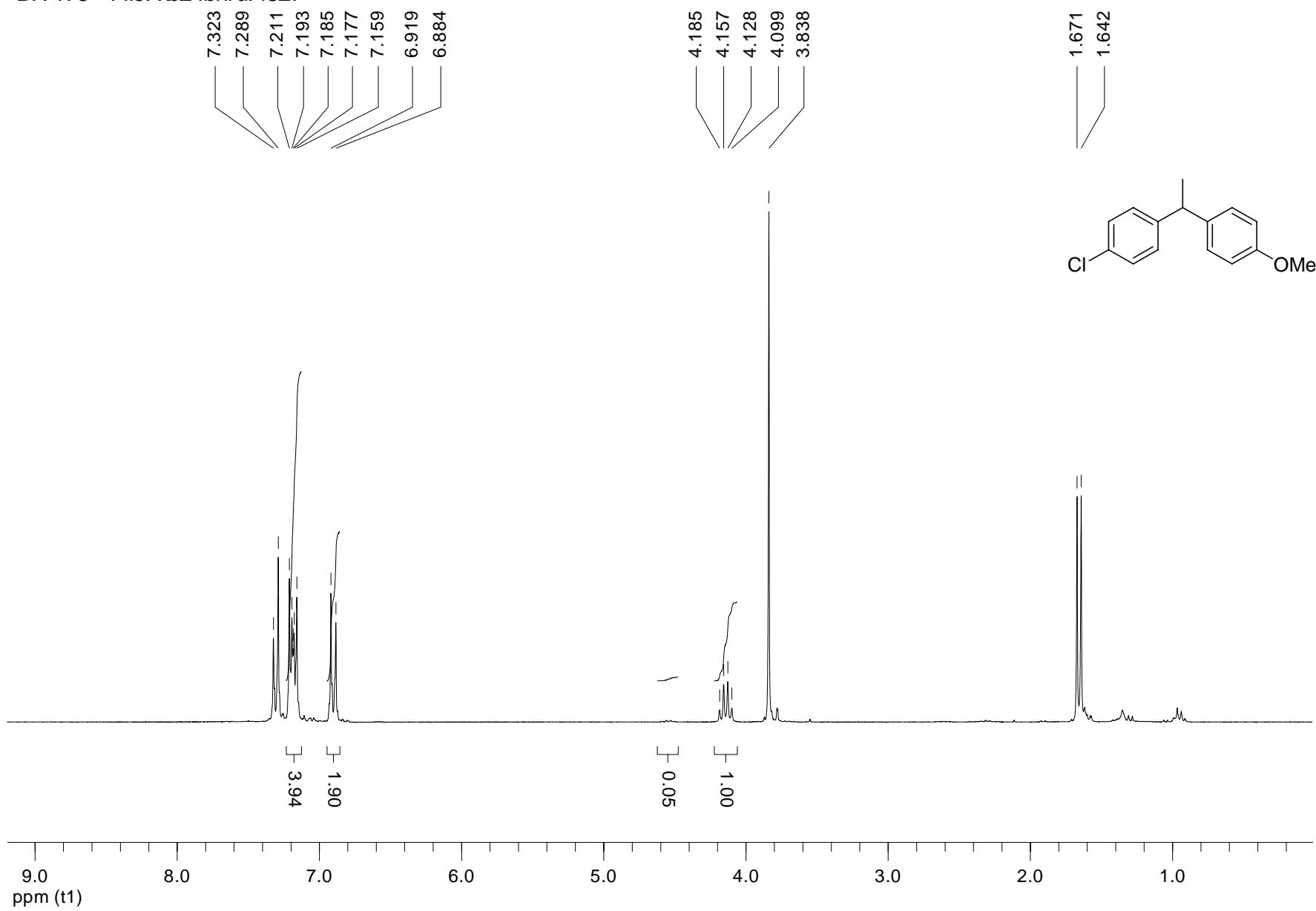
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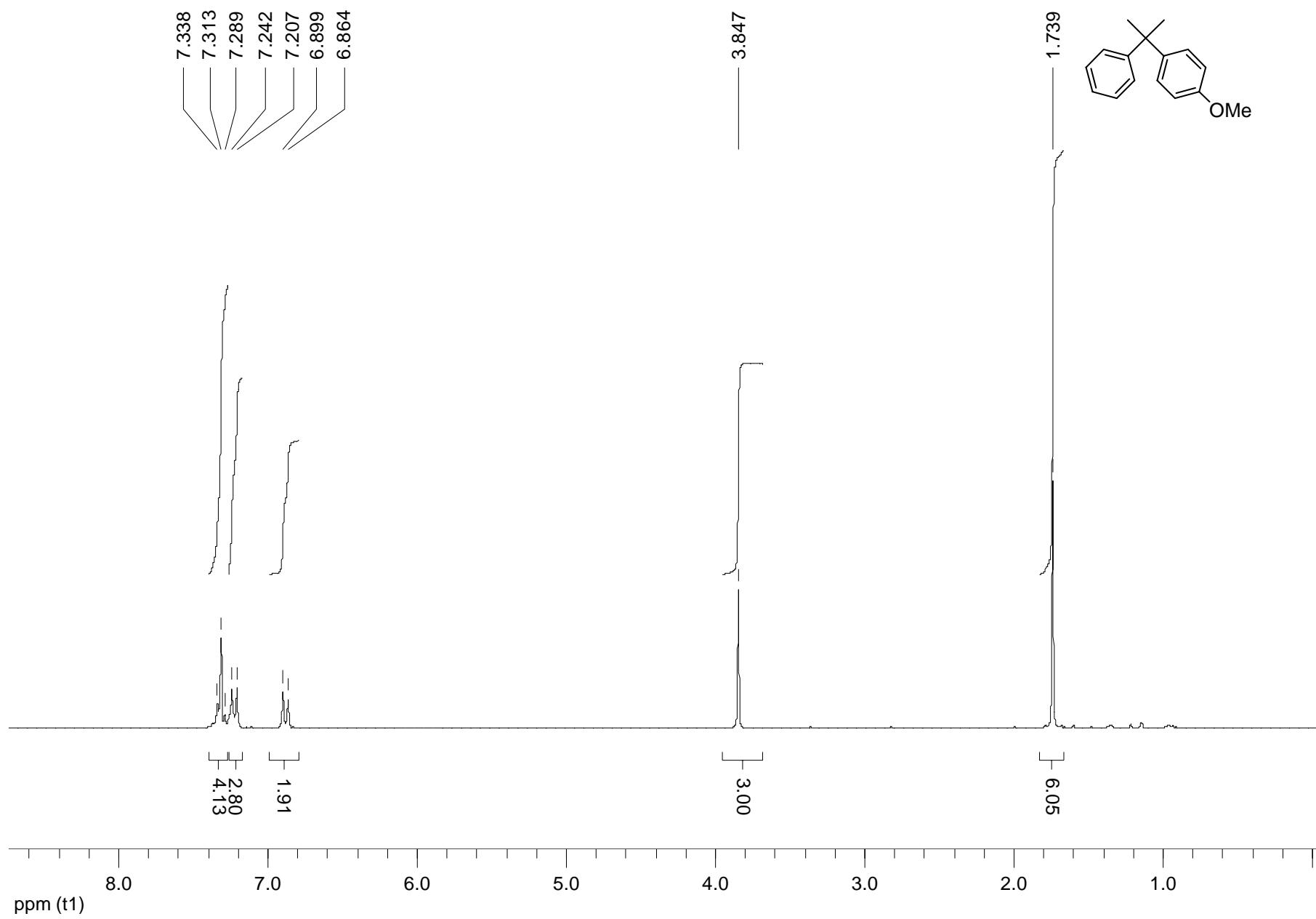
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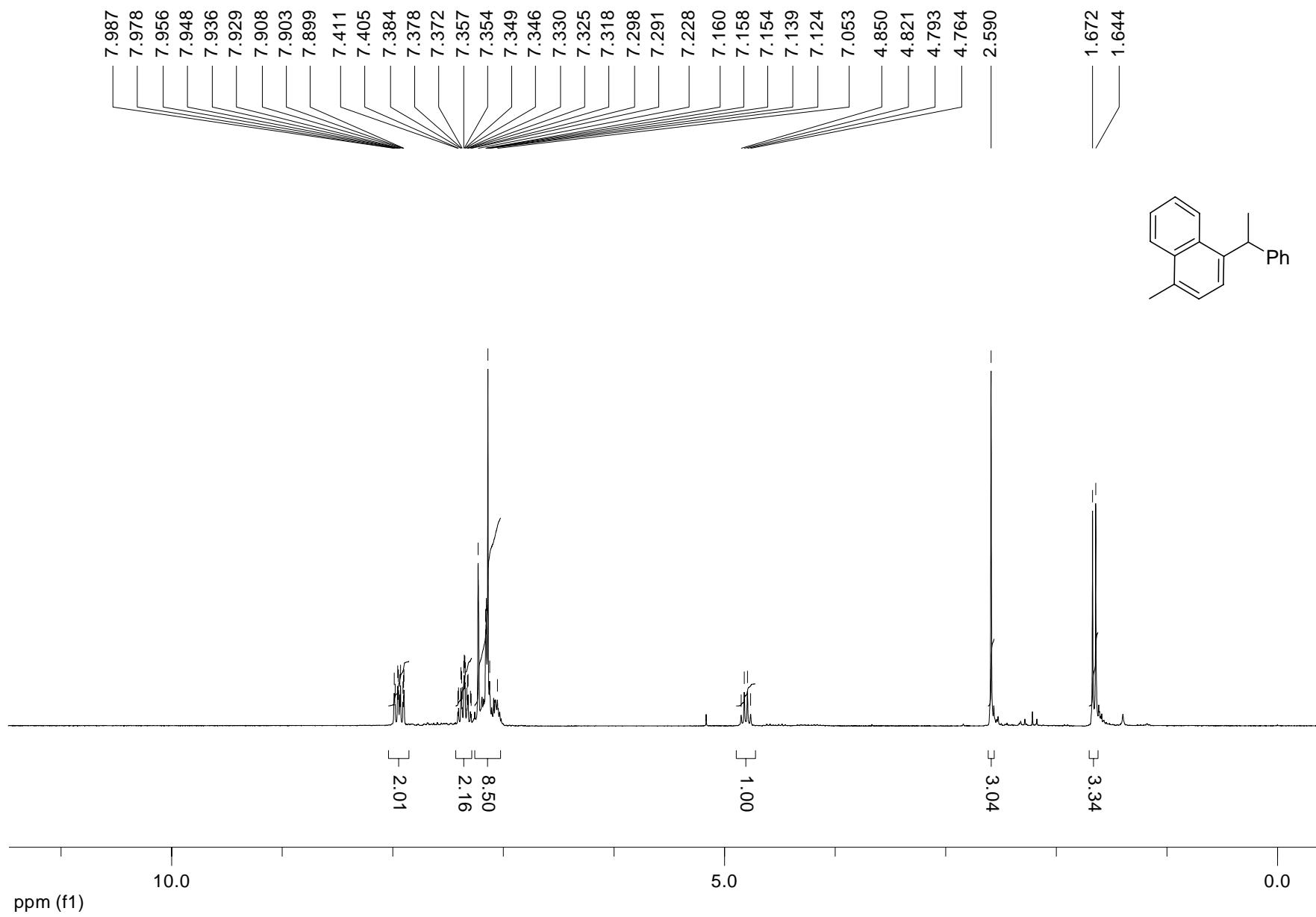


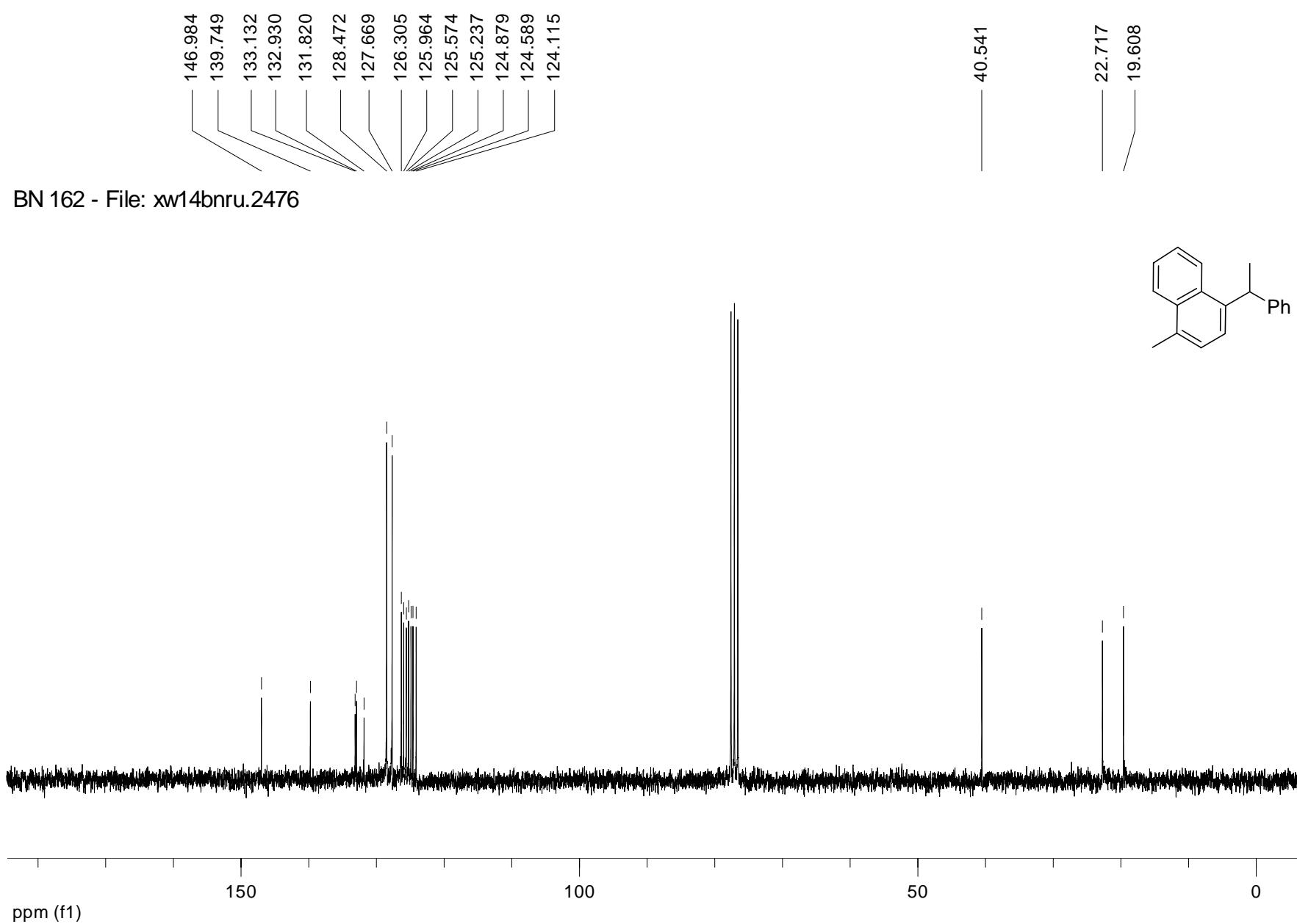
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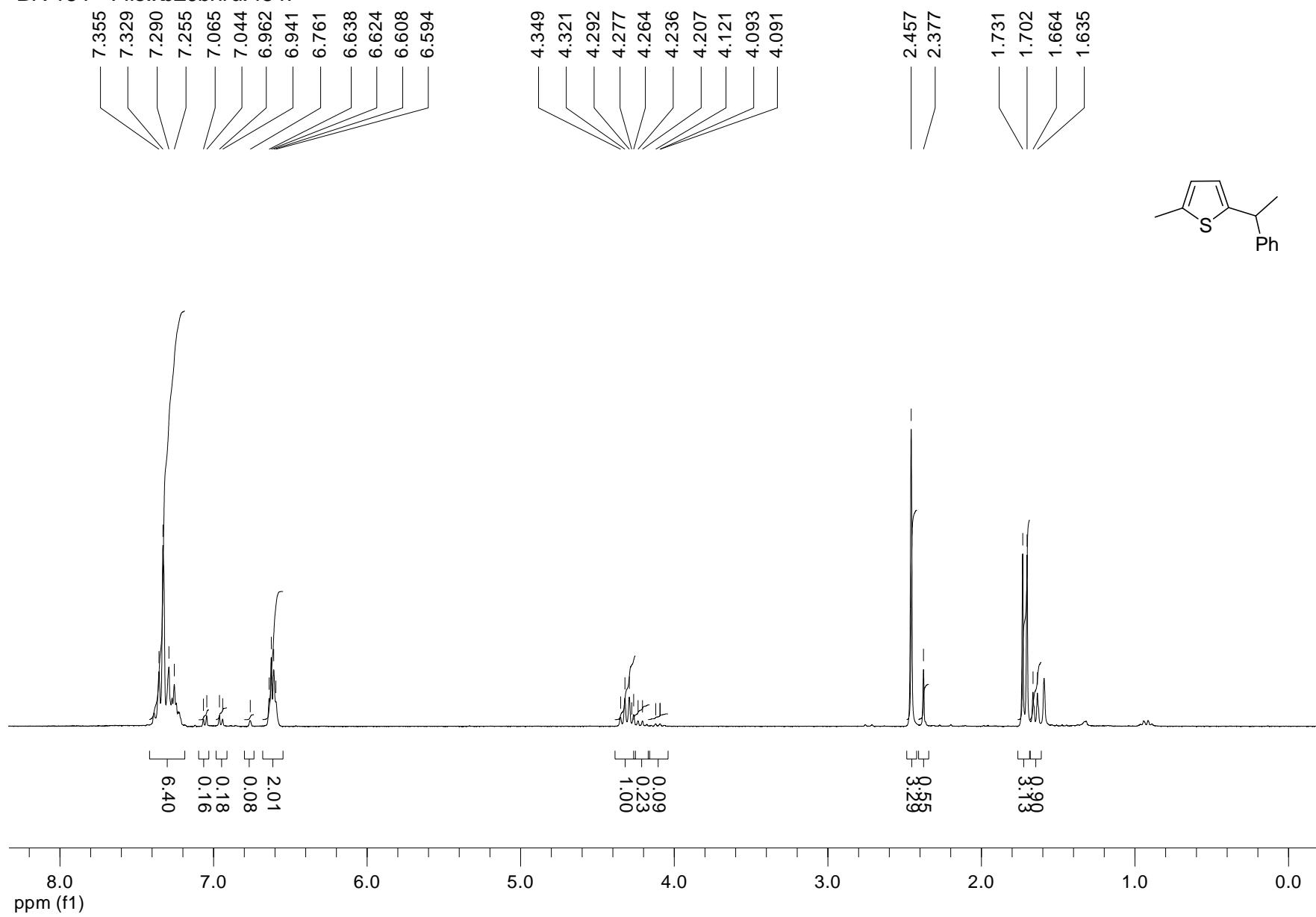
^1H - and ^{13}C -NMR-Spectra of the
unknown or previously not well
described compounds

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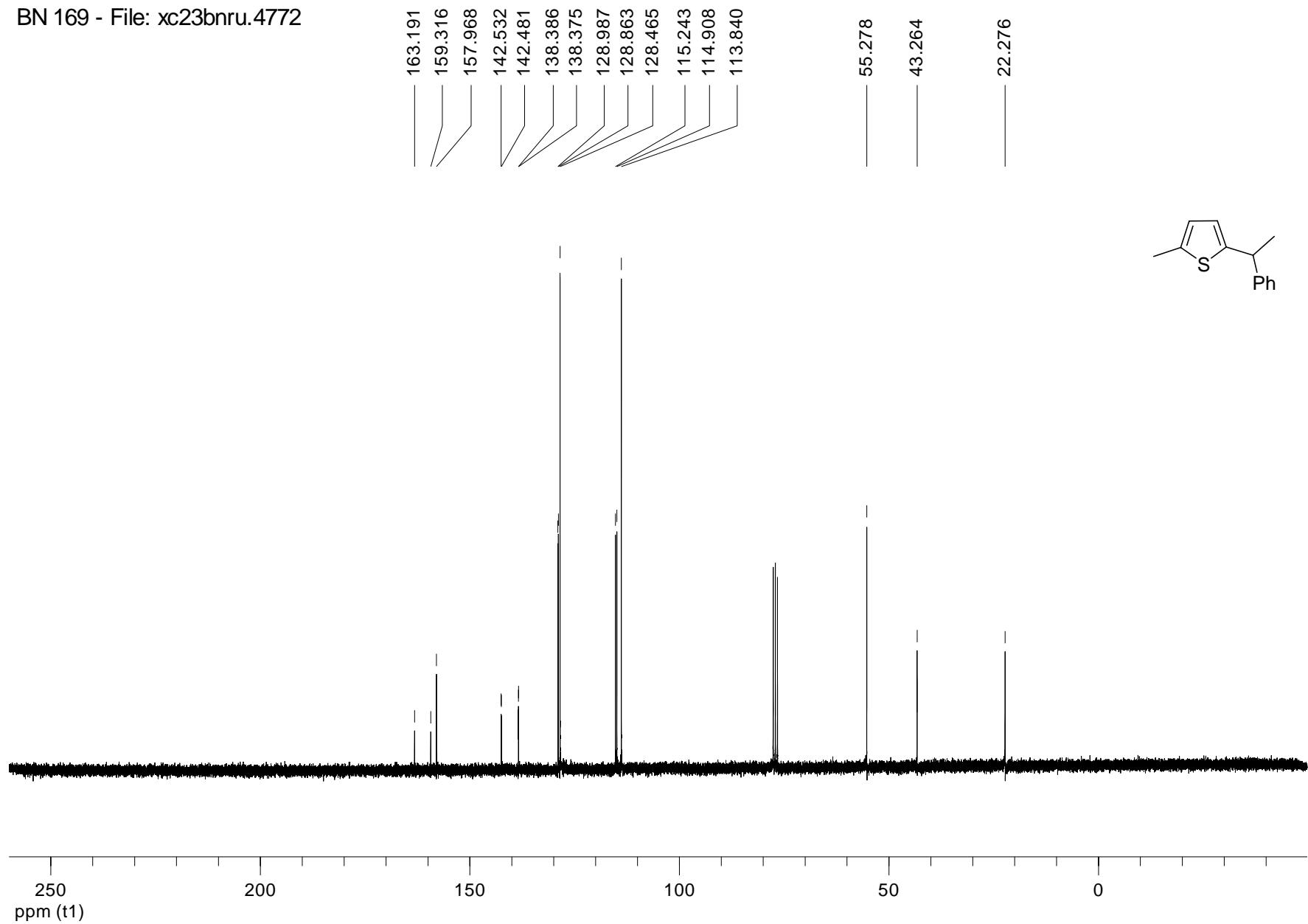




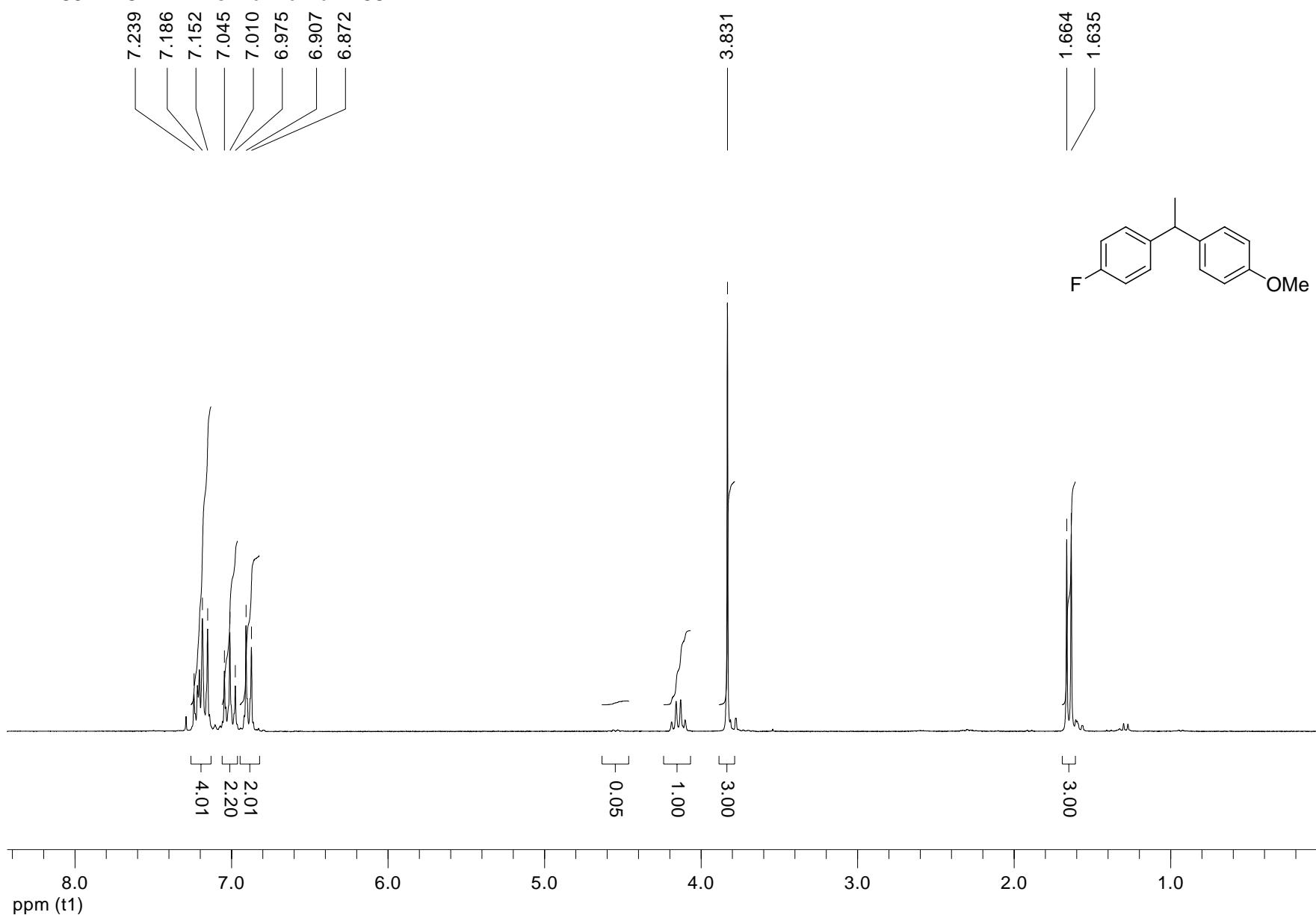
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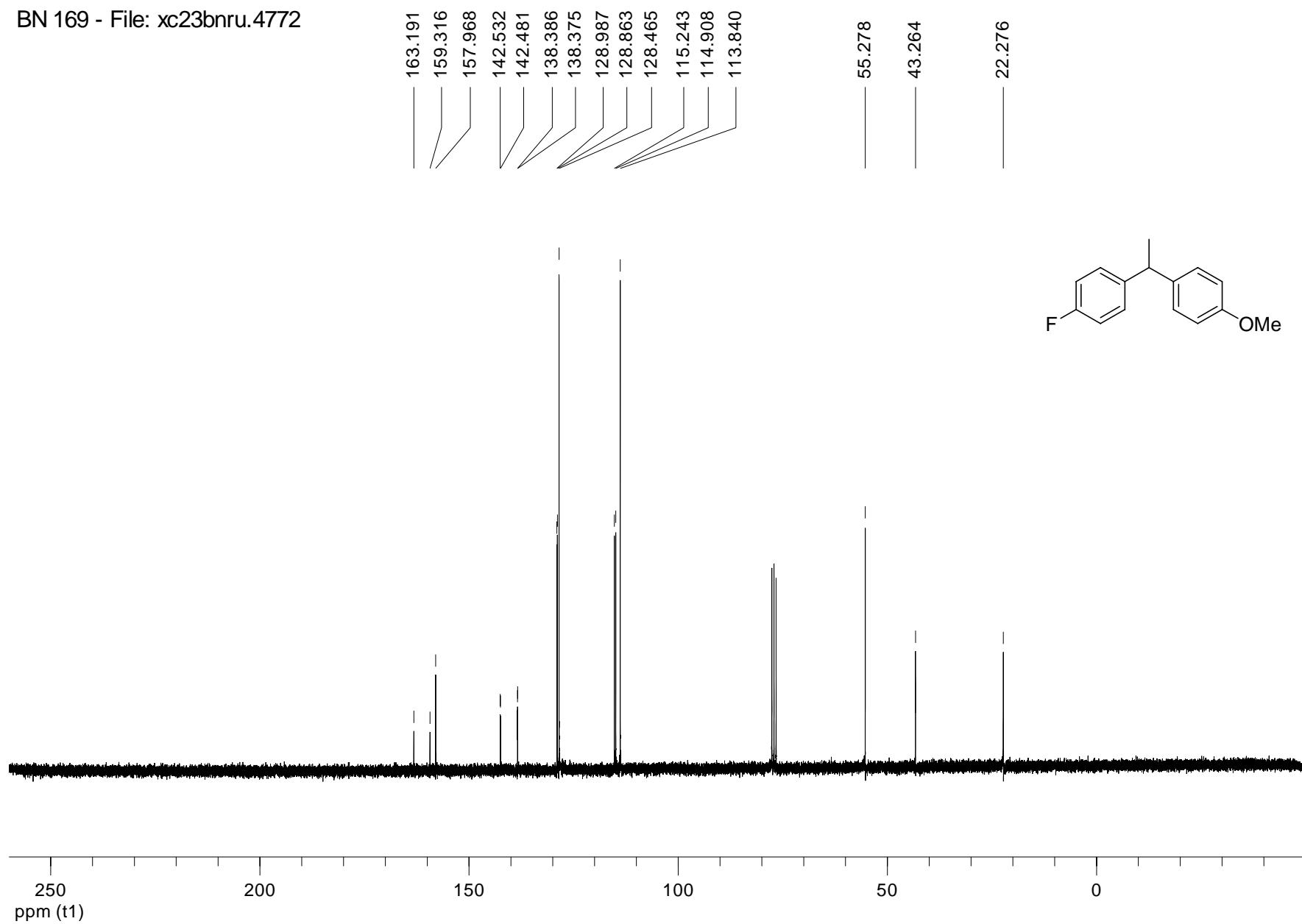
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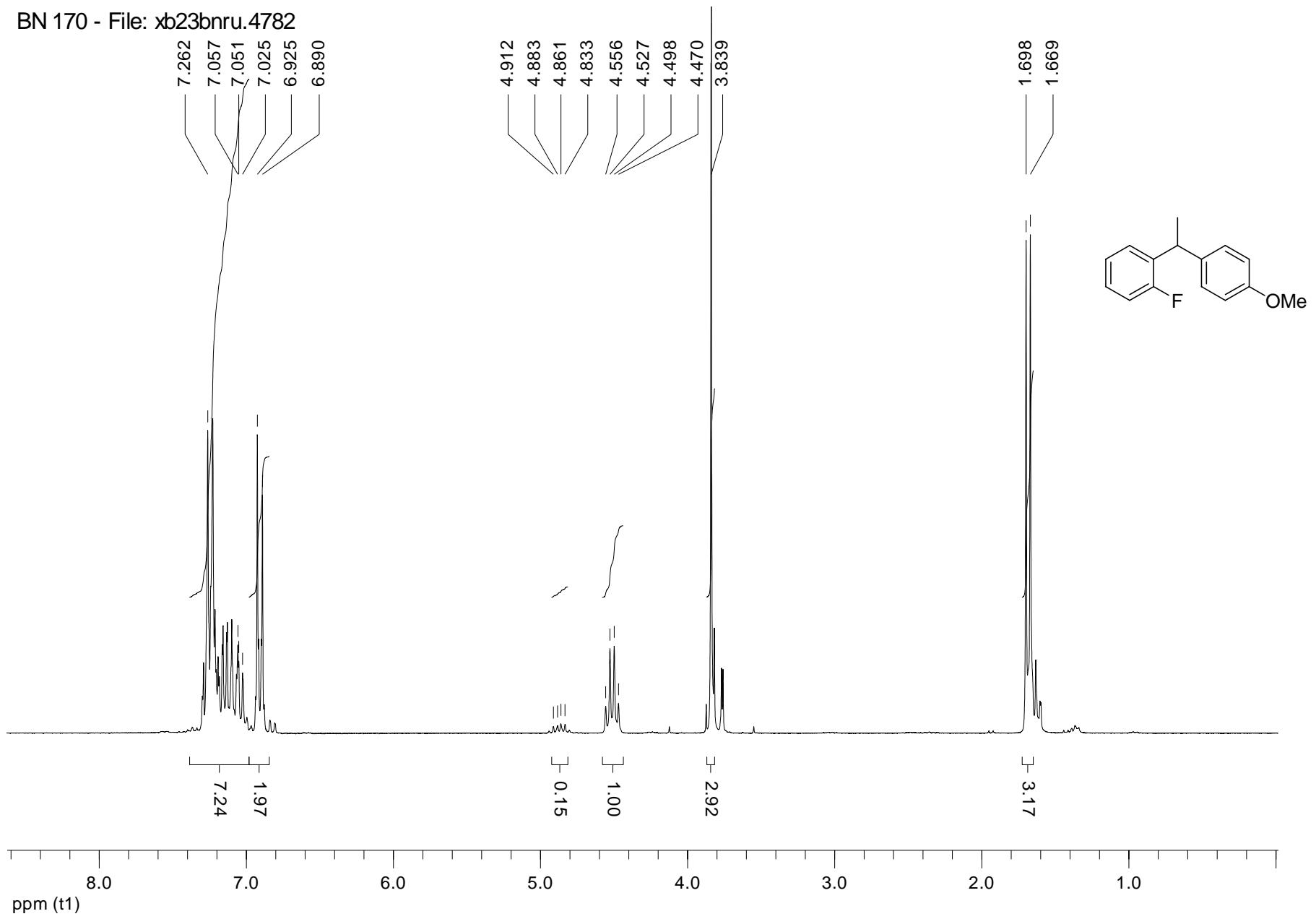
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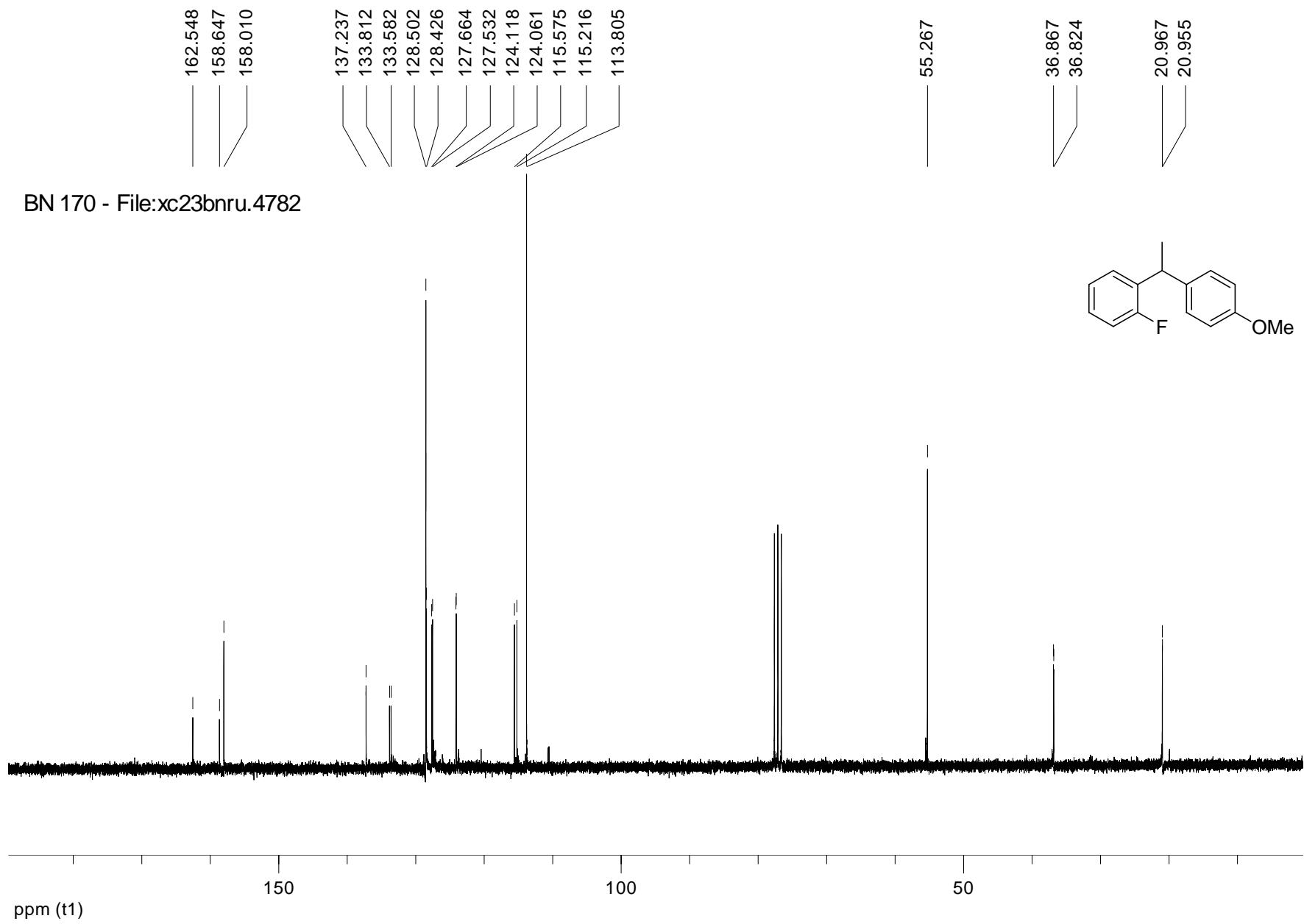


BN 169 - File: xc23bnru.4772

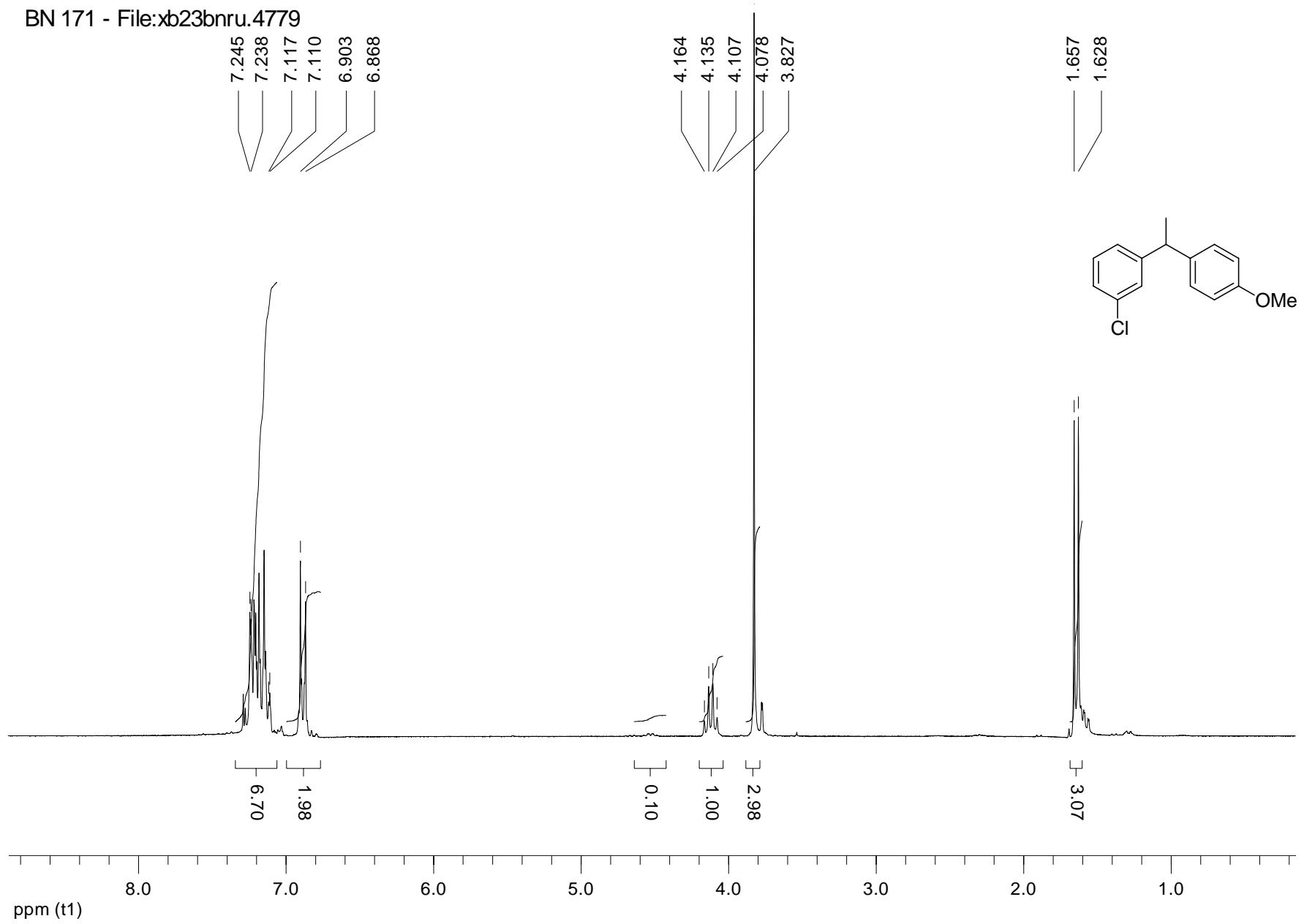


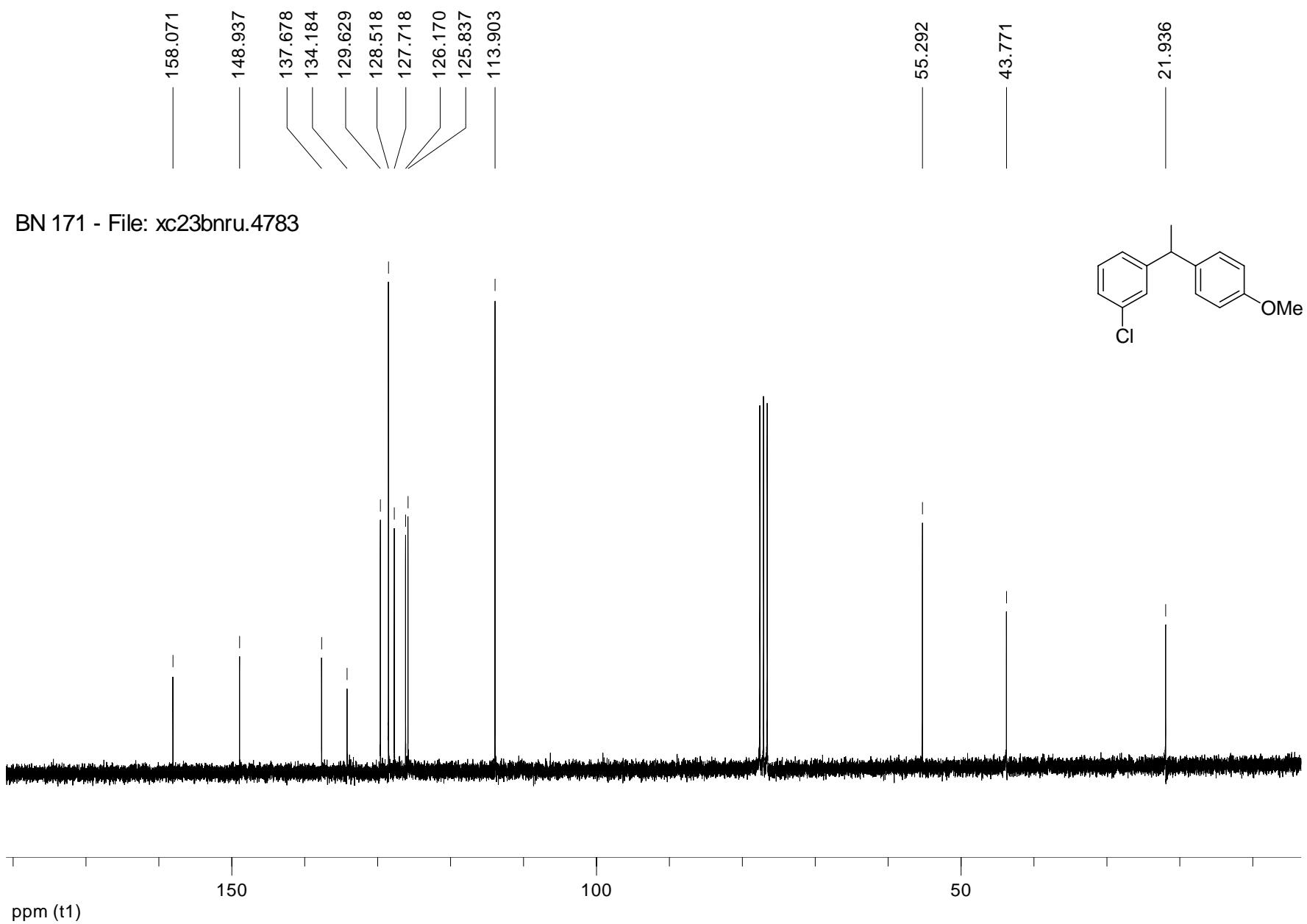
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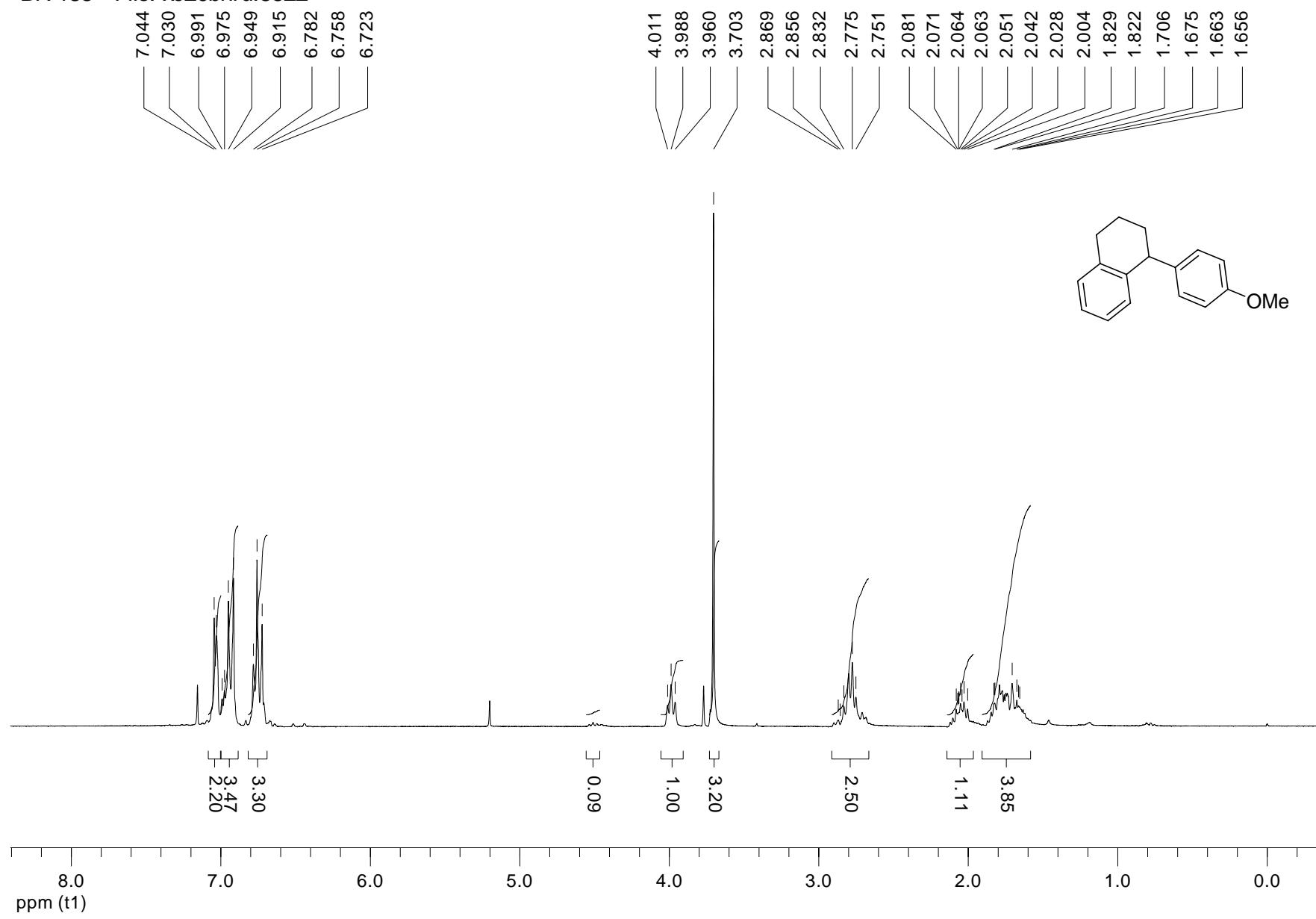


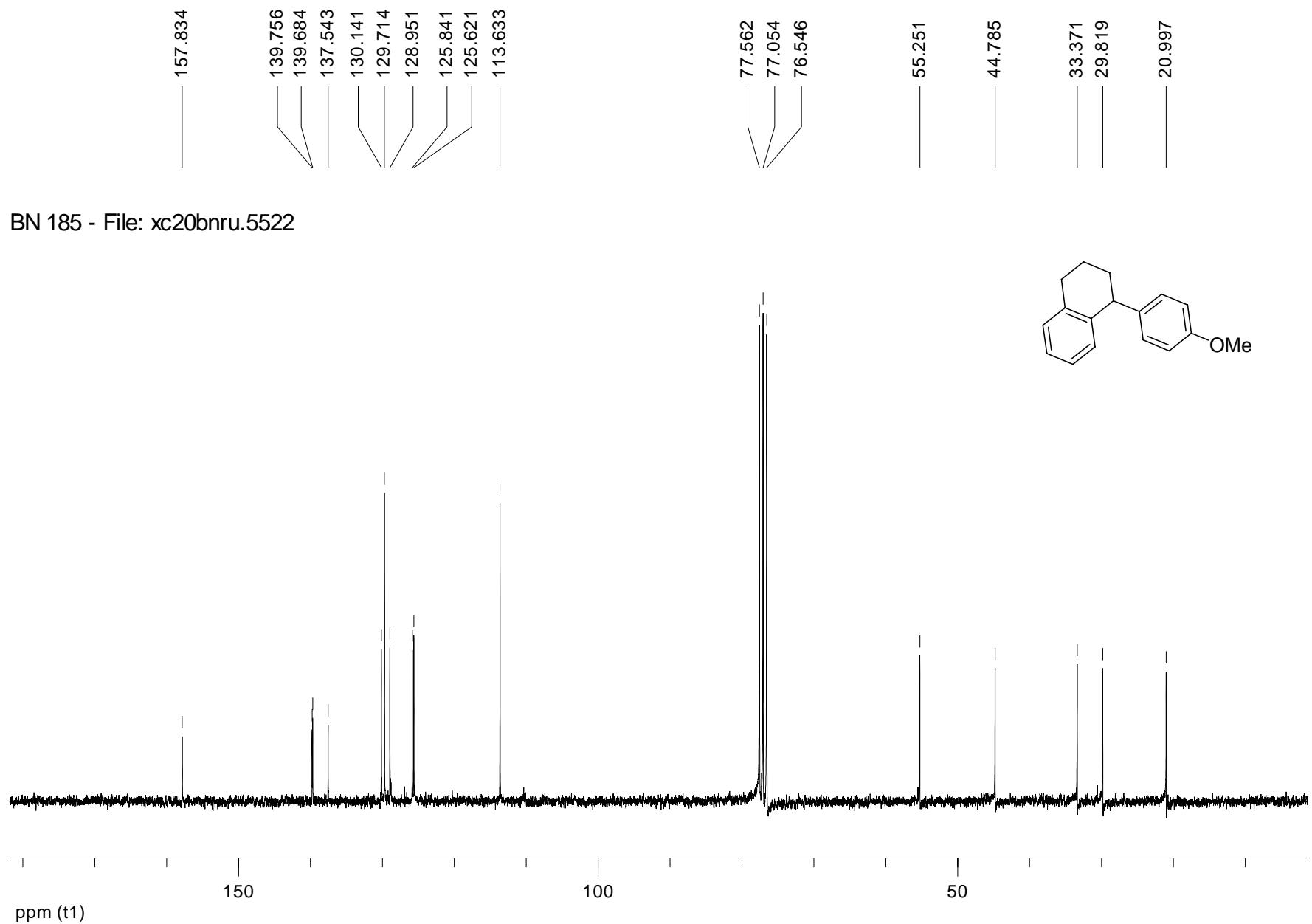
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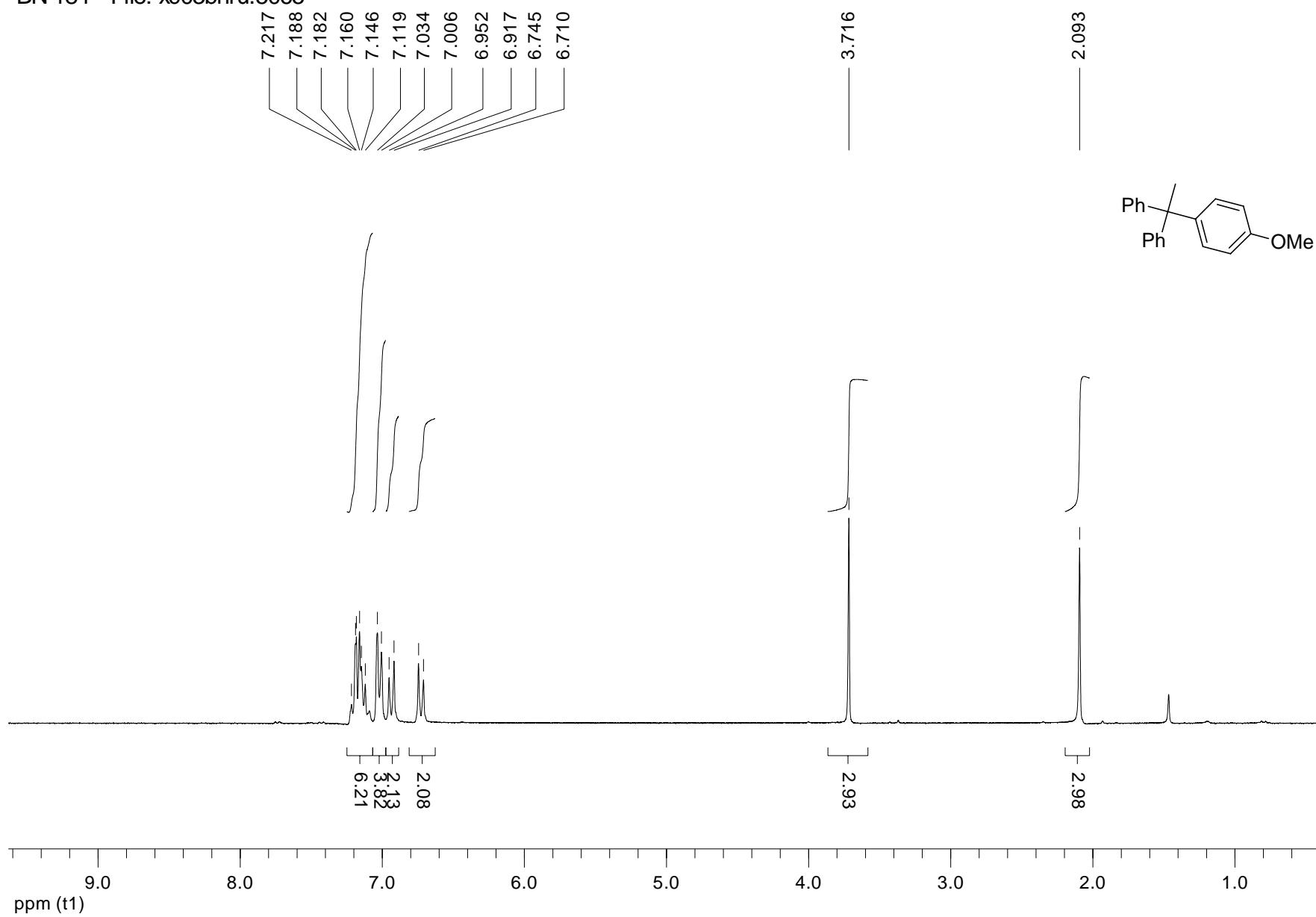


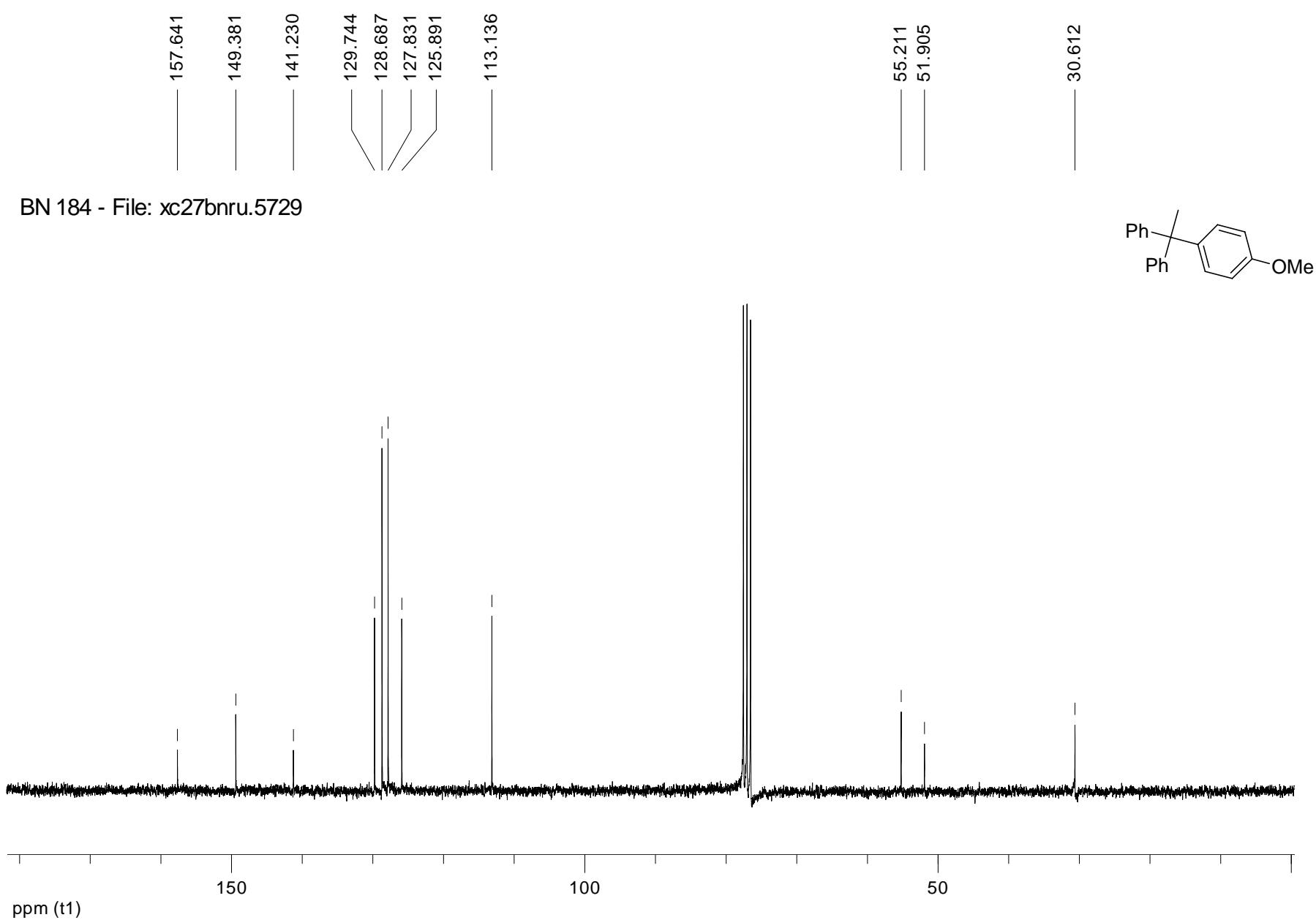
BN 185 - File: xc20bnru.5522



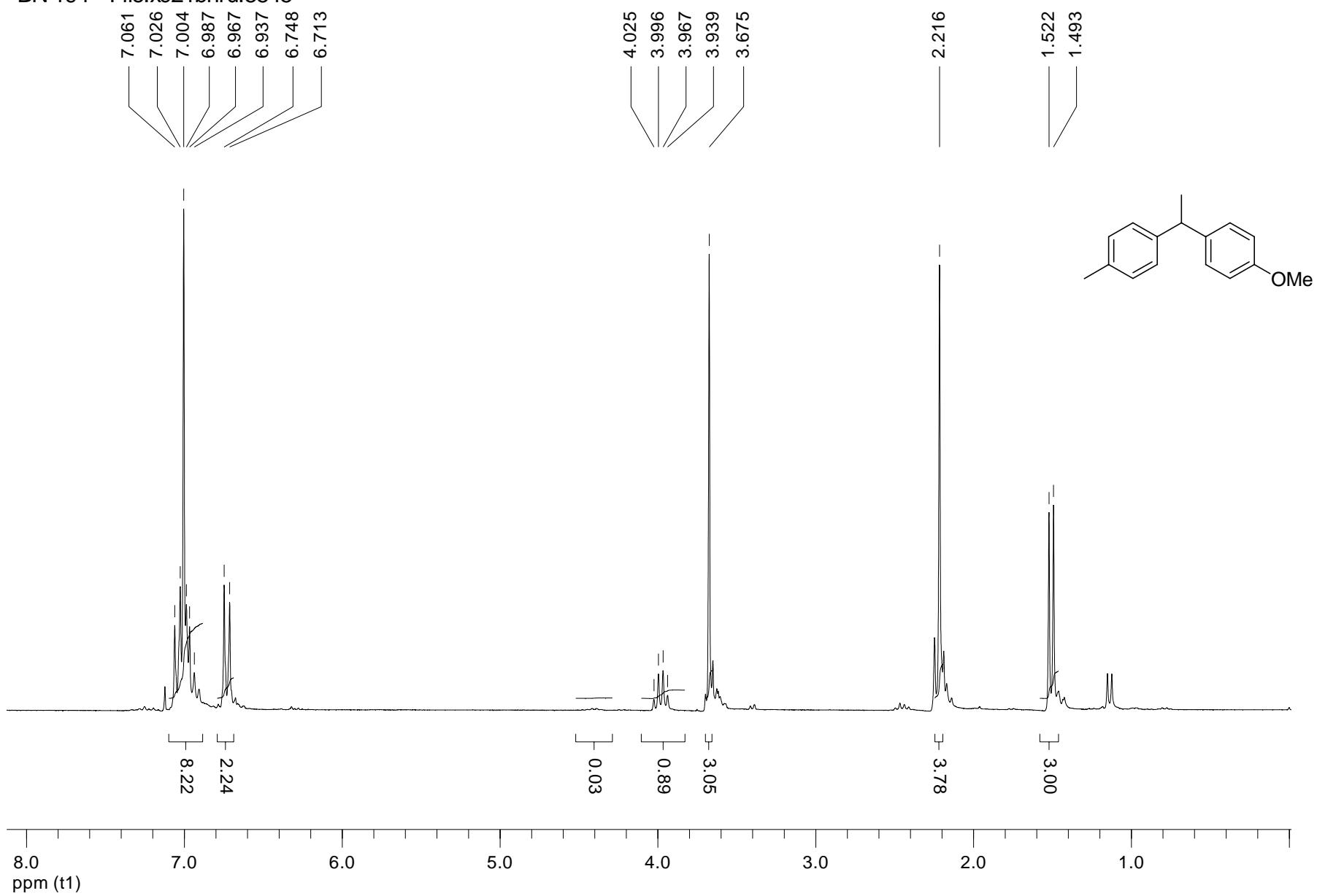


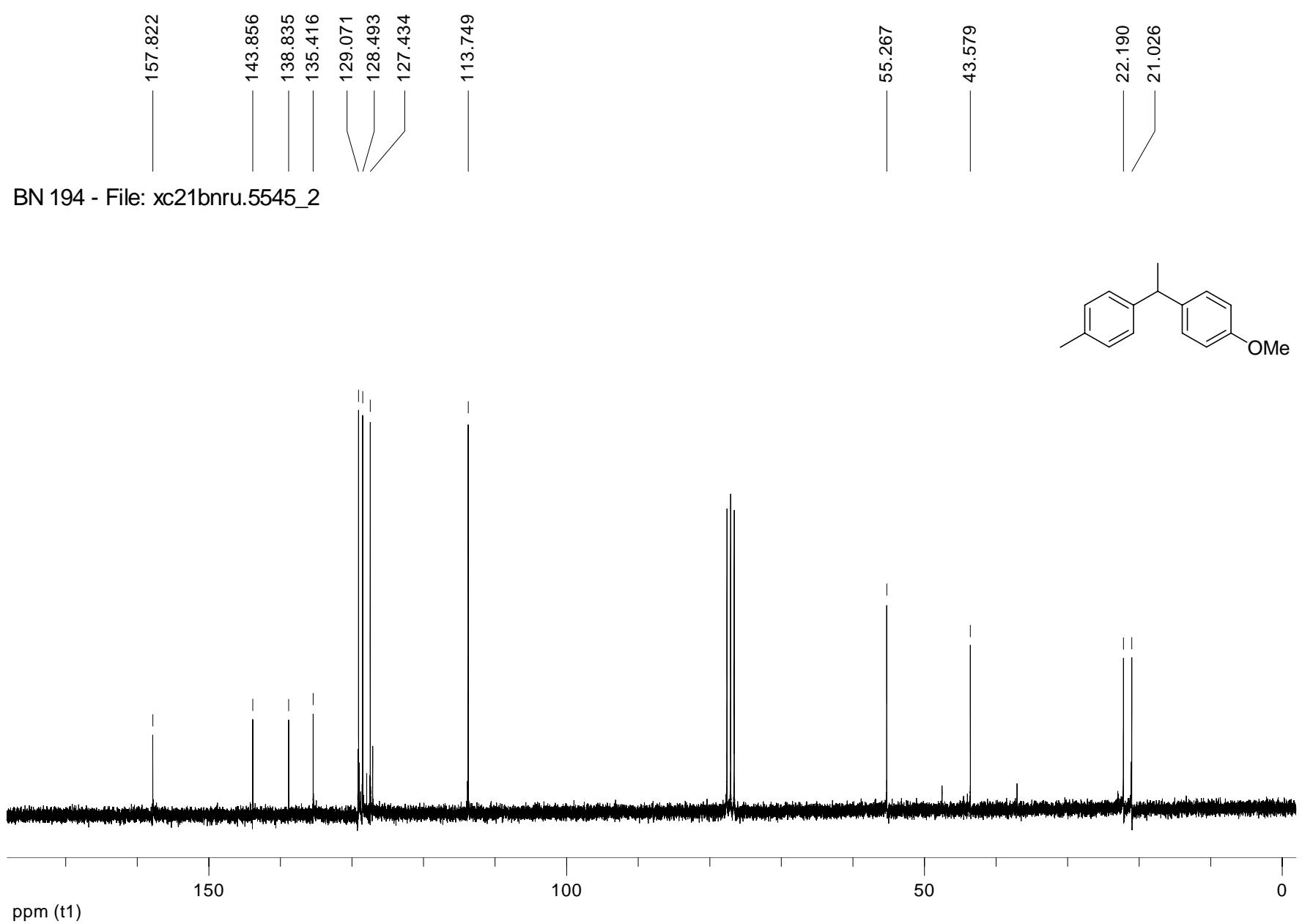
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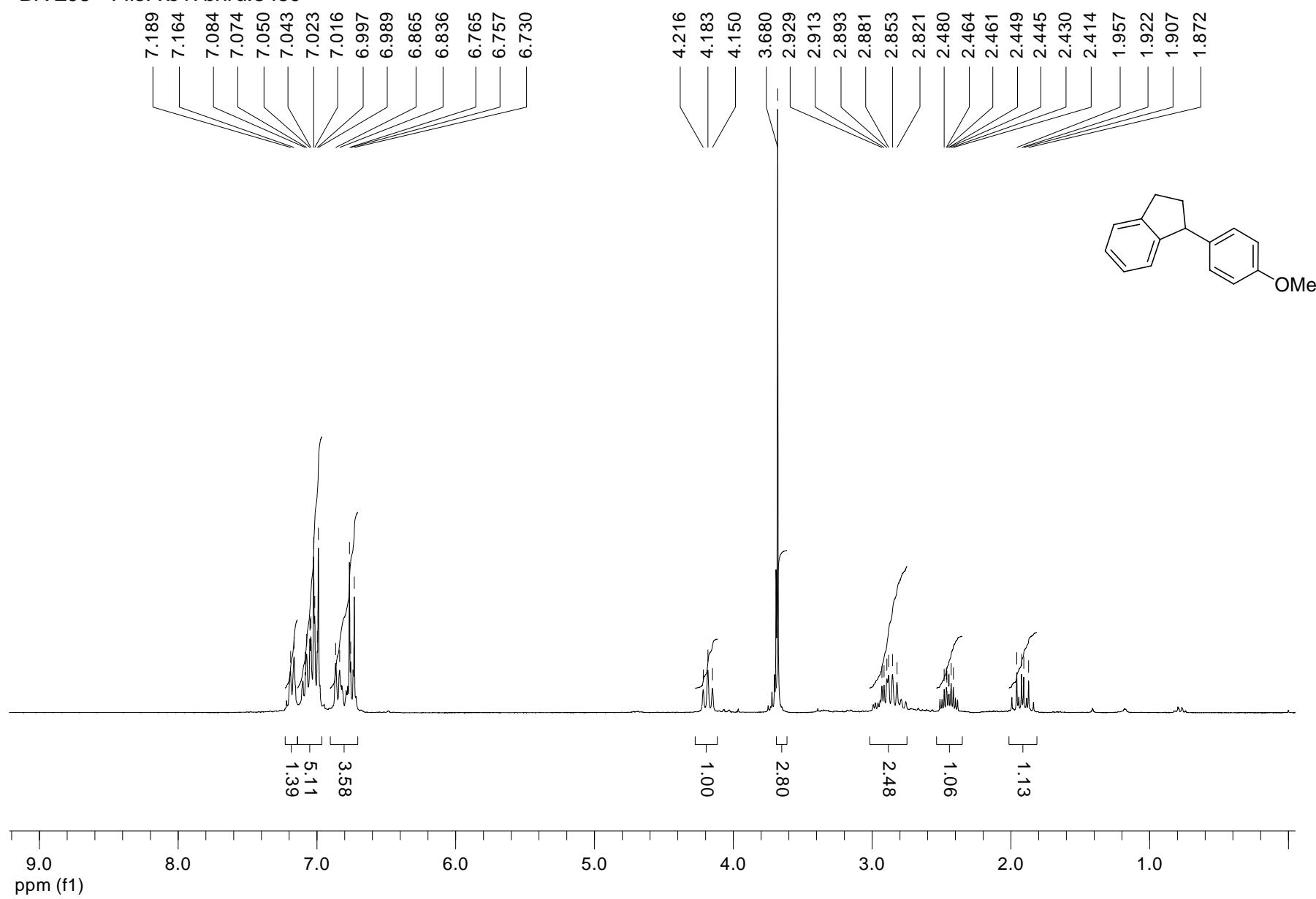


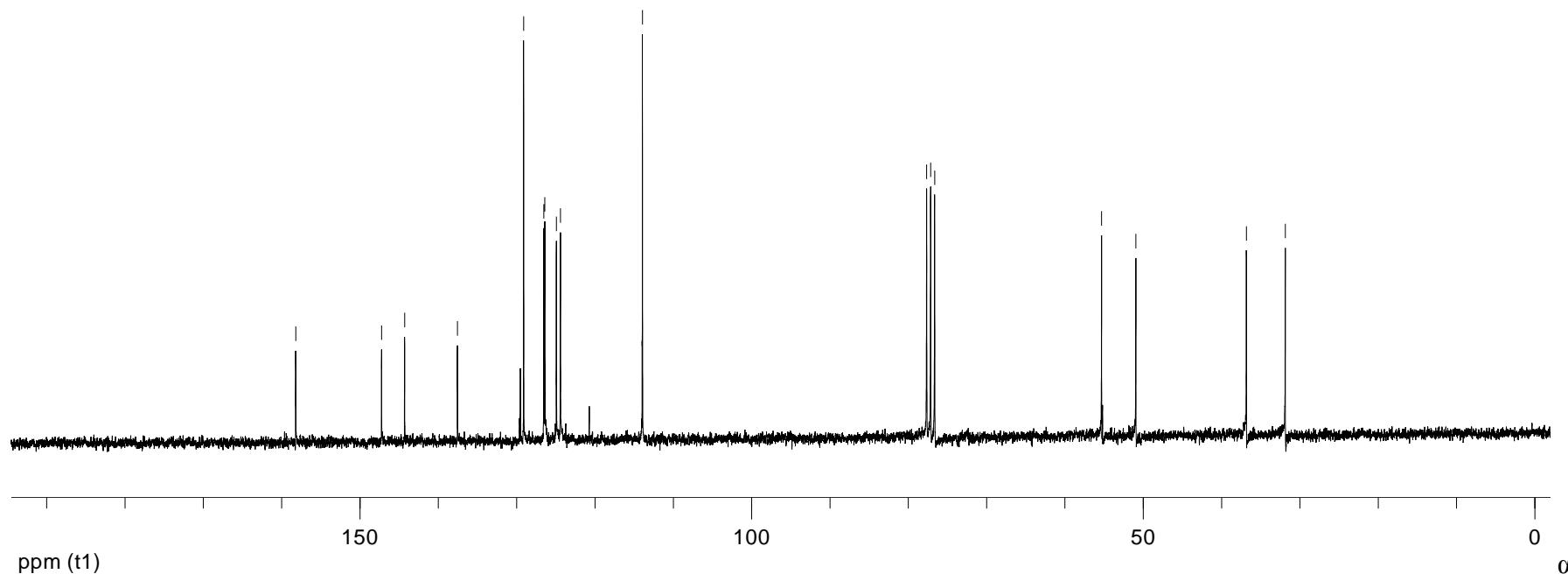
BN 194 - File:xc21bnru.5545





BN 206 - File: xc17bnru.5460





BN 206 - File:xc17bnru.5460

