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Supporting Information

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COMMUNICATION

Copper or Iron Catalysed Arylation of Phenols from respectively Aryl Chlorides and Aryl Iodides

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Supporting Information

General Experimental Procedures

All reactions were carried out in 35 mL Schlenk tubes or in Carousel “reaction stations RR98030” Radley tubes, under a pure and dry nitrogen atmosphere. DMF was distilled from CaH_2 and was stored on 4 Å activated molecular sieves under a nitrogen atmosphere. Cesium carbonate (Alfa Aesar), CuBr (Acros) and $FeCl_3$ (Acros) and all other solid materials were stored in the presence of P_4O_{10} in a bench-top desiccator under vacuum at room temperature and weighed in the air. 2,2,6,6-tetramethyl-heptanedione was purchased from Alfa Aesar. Aryl iodides, aryl bromides and aryl chlorides were purchased from commercial sources (Aldrich, Acros, Avocado, Fluka, Lancaster), If solids, they were recrystallized in an appropriate solvent.[1] If liquids, they were distilled under vacuum and stored under an atmosphere of nitrogen. Column chromatography was performed with SDS 60 A C.C silica gel (35-70 µm). Thin layer chromatography was carried out using Merck silica gel 60 F_{254} plates. All products were characterized by their NMR, GC/MS. NMR spectra were recorded at 20°C on a Bruker AC 400 MHz or on a DRX-250 spectrometer working respectively at 400 MHz for ^1H, at 100 MHz for ^{13}C. Chemical shifts are reported in ppm/TMS for ^1H and $\{^1H\}^{13}C$ (δ 77.00 for $\underline{C}DCl_3$ signal). The first-order peak patterns are indicated as s (singulet), d (doublet), t (triplet), q (quadruplet). Complex non-first-order signals are indicated as m (multiplet). Gas chromatography - mass spectra (GC/MS) were recorded on an Agilent Technologies 6890 N instrument with an Agilent 5973 N mass detector (EI) and a HP5-MS 30 m x 0.25 mm capillary apolar column (Stationary phase: 5 % diphenyldimethylpolysiloxane film, 0.25 µm). GC/MS method: Initial temperature: 45°C; Initial time: 2 min; Ramp: 2°C/min until 50°C then 10 °C/min; Final temperature: 250°C; Final time: 10 min. IR spectra were recorded on a Nicolet 210 FT-IR instrument (neat, thin film for liquid products and KBr pellet or in carbon tetrachloride solution for solid products). FAB+ mass spectra and HRMS were recorded on a JEOL JMS-DX300 spectrometer (3 keV, xenon) in a *m*-nitrobenzylalcohol matrix. Melting points were determined using a Büchi B-540 apparatus and are uncorrected.

General Procedure A for Copper catalyzed Arylation of Phenol (1.5 mmol scale)

After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube (Carousel “reaction stations RR98030”) equipped with a magnetic stirring bar was charged with CuBr (0.1 eq.), the phenol (1 eq.), Cs_2CO_3 (2.5 eq.) and the aryl chloride (1.5 eq.), if a solid. The tube was evacuated, back-filled with nitrogen. If a liquid, aryl halide was added under a stream of nitrogen by syringe at room temperature, followed by 2,2,6,6-tetramethyl-heptanedione (0.8 eq.) and anhydrous and degassed DMF (2.0 mL). The tube was sealed under a positive pressure of nitrogen, stirred and heated to 135°C for the required time period. After cooling to room temperature, the mixture was diluted with dichloromethane (~ 20 mL) and filtered through a plug of celite®, the filter cake being further washed with dichloromethane (~ 5 mL). The filtrate was washed twice with water (~ 10 mL x 2). Gathered aqueous phases were twice extracted with dichloromethane (~ 10 mL). Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product obtained was purified by silica gel chromatography with an eluent of cyclohexanes and dichloromethane. The products were characterized by NMR, mass spectra with those of authentic samples.

General Procedure B for Iron catalyzed Arylation of Phenol (1.5 mmol scale)

After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube (Carousel “reaction stations RR98030”) equipped with a magnetic stirring bar was charged with $FeCl_3$ (0.1 eq.), the phenol (1 eq.), Cs_2CO_3 (2.5 eq.) and the aryl iodide (1.5 eq.), if a solid. The tube was evacuated, back-filled with nitrogen. If a liquid, aryl halide was added under a stream of nitrogen by syringe at room temperature, followed by 2,2,6,6-tetramethyl-heptanedione (0.8 eq.) and anhydrous and degassed DMF (2.0 mL). The tube was sealed under a positive pressure of nitrogen, stirred and heated to 135°C for the required time period. After cooling to room temperature, the mixture was diluted with dichloromethane (~ 20 mL) and filtered through a plug of celite®, the filter cake being further washed with dichloromethane (~ 5 mL). The filtrate was washed twice with water (~ 10 mL x 2). Gathered aqueous phases were twice extracted with dichloromethane (~ 10 mL). Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product obtained was purified by silica gel chromatography with an eluent of cyclohexanes and dichloromethane. The products were characterized by NMR, mass spectra with those of authentic samples.

General Procedure C for SNAr Arylation of Phenol (1.5 mmol scale)

After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube (Carousel “reaction stations RR98030”) equipped with a magnetic stirring bar was charged with the phenol (1 eq.), Cs_2CO_3 (2.5 eq.) and the aryl halide (1.5 eq.), if a solid. The tube was evacuated, back-filled with nitrogen. If a liquid, aryl halide was added under a stream of nitrogen by syringe at room temperature, followed by anhydrous and degassed DMF (2.0 mL). The tube was sealed under a positive pressure of nitrogen, stirred and heated to 80-120°C for the required time period. After cooling to room temperature, the mixture was diluted with dichloromethane (~ 20 mL) and filtered through a plug of celite®, the filter cake being further washed with dichloromethane (~ 5 mL). The filtrate was washed twice with water (~ 10 mL x 2). Gathered aqueous phases were twice extracted with dichloromethane (~ 10 mL). Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product obtained was purified by silica gel chromatography with an eluent of cyclohexanes and dichloromethane. The products were characterized by NMR, mass spectra with those of authentic samples.

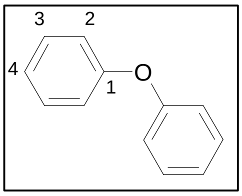
Experimental procedures and characterization data

Diphenyl ether 2a [2]

Experimental procedure

Following the general procedure A (135°C, 36 hours), phenol (1.5 mmol) was coupled with chlorobenzene (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 81 % yield of the desired product as a crystal.

Identification



^1H NMR (400 MHz, $CDCl_3$): δ 7.21-7.26 (m, 4H, H_3), 6.99-7.02 (t, 2H, H_4), 6.91-6.93 (d, 4H, H_2).
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.29 (C_1), 129.79 (C_3), 123.26 (C_4), 118.94 (C_2).
GC/MS: rt = 38.97 min, M/Z = 170.
Mp: 28°C.

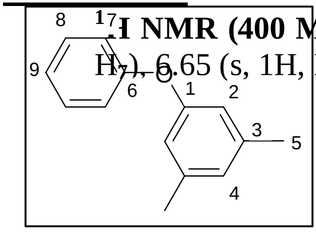
1, 3-dimethyl-5-phenoxybenzene 2f[2]

Experimental procedure

Following the general procedure A (135°C, 36 hours), 3, 5-dimethylphenol (1.5 mmol) was coupled with chlorobenzene (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent: cyclohexane) to provide 82 % yield of the desired product as an oil.

Identification

^1H NMR (400 MHz, $CDCl_3$): δ 7.20-7.24 (m, 2H, H_8), 6.97-7.00 (t, 1H, H_9), 6.90-6.92 (t, 2H, H_7), 6.65 (s, 1H, H_4), 6.54 (s, 2H, H_2), 2.19 (s, 6H, H_5).



^{13}C NMR (100 MHz, CDCl$_3$): δ 157.49 (C_6), 157.20 (C_1), 139.62 (C_3), 129.70 (C_8), 125.05 (C_4), 123.02(C_9), 118.89(C_7), 116.66 (C_2), 21.36 (C_5).
GC/MS: rt = 45.14 min, M/Z = 198.

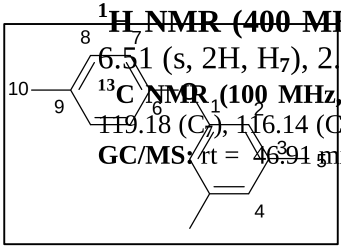
1,3-dimethyl-5-(p-tolyloxy)benzene 2g[2]

Experimental procedure

Following the general procedure A (135°C, 36 hours), 3, 5-dimethylphenol (1.5 mmol) was coupled with 4-chlorotoluene (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent: cyclohexane) to provide 91 % yield of the desired product as an oil.

Identification

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.00-7.03 (t, 2H, H_8), 6.79-6.82 (t, 2H, H_2), 6.60 (s, 1H, H_4), 6.51 (s, 2H, H_7), 2.22 (s, 3H, H_{10}), 2.16 (s, 6H, H_5).
^{13}C NMR (100 MHz, CDCl$_3$): δ 157.84 (C_1), 154.97 (C_6), 139.54 (C_3), 132.70 (C_9), 130.24 (C_8), 124.65 (C_4), 119.18 (C_7), 116.14 (C_2), 21.38 (C_5), 20.78 (C_{10}).
GC/MS: rt = 46.91 min, M/Z = 212.



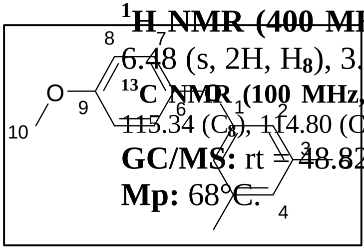
1-(4-methoxyphenoxy)-3,5-dimethylbenzene 2i[2]

Experimental procedure

Following the general procedure A (135°C, 36 hours), 3, 5-dimethylphenol (1.5 mmol) was coupled with 4-chloroanisole (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 81 % yield of the desired product as a solid.

Identification

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.87-6.89 (t, 2H, H_7), 6.77-6.80 (t, 2H, H_2), 6.60 (s, 1H, H_4), 6.48 (s, 2H, H_8), 3.71 (s, 3H, H_{10}), 2.17 (s, 6H, H_5).
^{13}C NMR (100 MHz, CDCl$_3$): δ 158.53 (C_1), 155.78 (C_9), 150.31 (C_6), 139.48 (C_3), 124.24 (C_4), 120.86 (C_7), 115.34 (C_8), 114.80 (C_2), 55.65 (C_{10}), 21.37 (C_5).
GC/MS: rt = 48.82 min, M/Z = 228.
Mp: 68°C.

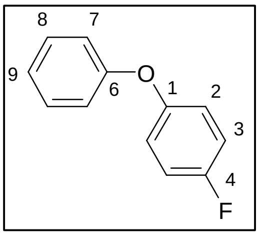


1-fluoro-4-phenoxybenzene 2e[3]

Experimental procedure

Following the general procedure B (135°C, 24 hours), 4-fluorophenol (1.5 mmol) was coupled with iodobenzene (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 80 % yield of the desired product as an oil.

Identification



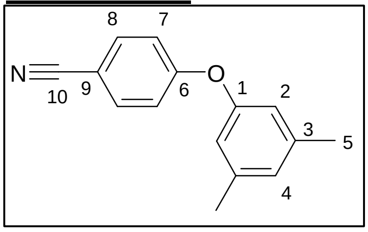
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.22-7.26 (m, 2H, H_2), 6.98-7.02 (m, 1H, H_9), 6.87-6.96 (m, 6H, $H_{3,7,8}$).
^{13}C NMR (100 MHz, CDCl$_3$): δ 160.05 (C_6), 157.73 (C_4), 152.93 (C_1), 129.81 (C_8), 123.16 (C_9), 120.61 (C_2), 118.30 (C_7), 116.43 (C_3).
GC/MS: rt = 38.95 min, M/Z = 188.

4-(3,5-dimethylphenoxy)benzonitrile 2l[2]

Experimental procedure

Following the general procedure C (90°C, 24 hours), 3, 5-dimethylphenol (1.5 mmol) was coupled with 4-chlorobenzonitrile (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane/dichloromethane 1/1) to provide 98 % yield of the desired product as a solid.

Identification



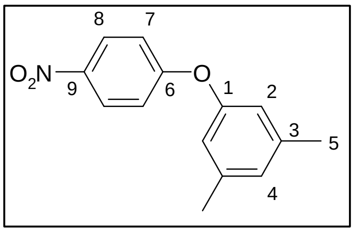
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.52 (m, 2H, H_8), 6.90-6.92 (m, 2H, H_7), 6.79 (t, 1H, H_4), 6.60 (m, 2H, H_2), 2.24 (s, 6H, H_5).
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.92 (C_6), 154.71 (C_1), 140.18 (C_3), 134.07 (C_8), 126.84 (C_4), 118.97 (C_{10}), 118.01 (C_7), 117.85 (C_2), 105.49 (C_9), 21.28 (C_5).
GC/MS: rt = 49.69 min, M/Z = 223.
Mp: 58 °C

3’,5’-dimethyl-4-nitrodiphenylether 2k[2]

Experimental procedure

Following the general procedure C (90°C, 24 hours), 3, 5-dimethylphenol (1.5 mmol) was coupled with 1-chloro-4-nitrobenzene (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 91 % yield of the desired product as a solid.

Identification



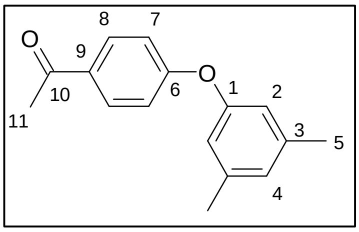
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.11 (m, 2H, H_8), 6.90-6.92 (m, 2H, H_7), 6.80 (s, 1H, H_4), 6.62 (s, 2H, H_2), 2.25 (s, 6H, H_5).
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.65 (C_6), 154.63 (C_1), 142.45 (C_9), 140.29 (C_3), 127.10 (C_4), 125.89 (C_8), 118.12 (C_7), 117.03 (C_2), 21.29 (C_5).
GC/MS: rt = 51.06 min, M/Z = 243.
Mp: 59 °C

3’,5’-dimethyl-4-acetodiphenylether 2j[4]

Experimental procedure

Following the general procedure C (120°C, 24 hours), 3, 5-dimethylphenol (1.5 mmol) was coupled with 4'-iodoacetophenone (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane / dichloromethane= 75 / 15) to provide 63 % yield of the desired product as an oil.

Identification



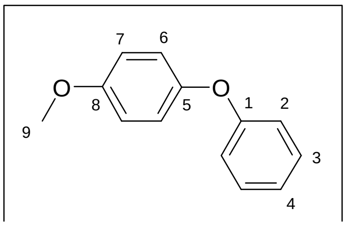
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.98 (t, 2H, H_8), 7.01-7.03 (t, 2H, H_7), 6.87 (s, 1H, H_4), 6.72 (s, 2H, H_2), 2.60 (s, 3H, H_{11}), 2.34 (s, 6H, H_5).
^{13}C NMR (100 MHz, $CDCl_3$): δ 197.10 (C_{11}), 162.33 (C_6), 155.36 (C_1), 139.99 (C_3), 131.60 (C_9), 130.63 (C_8), 126.39 (C_4), 117.85 (C_7), 117.24 (C_2), 26.47 (C_{11}), 21.32 (C_5).
GC/MS: rt = 50.75 min, M/Z = 240.

1-methoxy-4-phenoxybenzene 2c[4]

Experimental procedure

Following the general procedure A (135°C, 36 hours), 4-methoxyphenol (1.5 mmol) was coupled with 4-chlorobenzene (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 91 % yield of the desired product as an oil.

Identification



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.24 (q, 2H, H_3), 6.94-6.98 (t, 1H, H_4), 6.85-6.92 (m, 4H, $H_{2,6}$), 6.79-6.82 (d, 2H, H_7), 3.72 (s, 3H, H_9).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.53 (C_1), 155.90 (C_8), 150.11 (C_5), 129.63 (C_3), 122.43 (C_4), 120.86 (C_6), 117.58 (C_2), 114.86 (C_7), 55.66 (C_9).

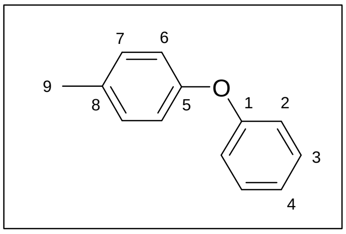
GC/MS: rt = 46.52 min, M/Z = 200.

1-methyl-4-phenoxybenzene 2b[5]

Experimental procedure

Following the general procedure A (135°C, 36 hours), 4-cresol (1.5 mmol) was coupled with 4-chlorobenzene (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 80 % yield of the desired product as an oil.

Identification



^1H NMR (400 MHz, $CDCl_3$): δ 7.20-7.22 (d, 2H, H_3), 7.03-7.05 (d, 2H, H_7), 6.97 (s, 1H, H_4), 6.88-6.90 (d, 2H, H_2), 6.82-6.84 (d, 2H, H_6), 2.24 (s, 3H, H_9).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.88 (C_1), 154.76 (C_5), 132.95 (C_8), 130.31 (C_7), 129.72 (C_3), 122.86 (C_4), 119.20 (C_2), 118.40 (C_6), 20.78 (C_9).

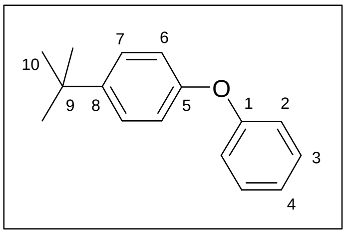
GC/MS: rt = 43.51 min, M/Z = 184.

1-tert-butyl-4-phenoxybenzene 2d[5]

Experimental procedure

Following the general procedure A (135°C, 36 hours), 4-tert-butylphenol (1.5 mmol) was coupled with 4-chloroanisole (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 87 % yield of the desired product as an oil.

Identification



^1H NMR (400 MHz, $CDCl_3$): δ 7.20-7.26 (m, 4H, $H_{3,7}$), 6.92 (s, 1H, H_4), 6.90 (s, 2H, H_6), 6.84-6.86 (d, 2H, H_2), 1.23 (s, 9H, H_{10}).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.63 (C_1), 154.75 (C_5), 146.15 (C_8), 129.70 (C_3), 126.59 (C_7), 122.96 (C_4), 118.67 (C_2), 118.51 (C_6), 34.36 (C_9), 31.56 (C_{10}).

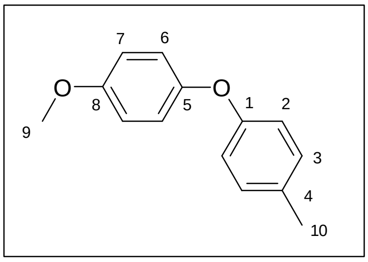
GC/MS: rt = 47.37 min, M/Z = 226.

1-tert-butyl-4-(p-tolyloxy)benzene 2h[6]

Experimental procedure

Following the general procedure A (135°C, 36 hours), 4-methoxyphenol (1.5 mmol) was coupled with 4-chlorotoluene (2.25 mmol). The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 81 % yield of the desired product as an oil.

Identification



^1H NMR (400 MHz, $CDCl_3$): δ 7.00-7.03 (d, 2H, H_6), 6.87-6.89 (d, 2H, H_3), 6.76-6.80 (m, 4H, $H_{2,7}$), 3.72 (s, 3H, H_9), 2.23 (s, 3H, H_{10}).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.10 (C_1), 155.62 (C_8), 150.74 (C_5), 132.03 (C_4), 130.11 (C_3), 120.35 (C_6), 117.81 (C_2), 114.78 (C_7), 55.66 (C_9), 20.65 (C_{10}).

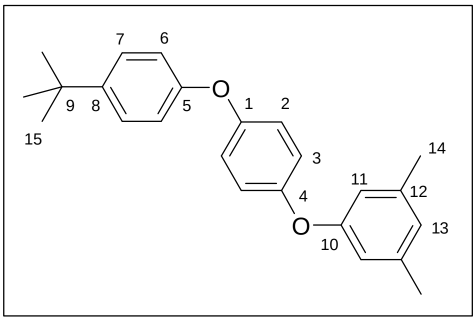
GC/MS: rt = 47.86 min, M/Z = 214.

1-(4-(4-tert-butylphenoxy)phenoxy)-3,5-dimethylbenzene 3

Experimental procedure

Following the general procedure B (135°C, 24 hours), 4-tert-butylphenol (1.5 mmol) was coupled with 4-chloroiodo benzene (1.5 mmol). Then 0.1 eq. CuBr, 0.8 eq. ligand, 2.5eq. Cs_2CO_3 and 1.5 mmol 3, 5-dimethylphenol were added under N_2, and reaction was sealed and heated at 140°C for 36 hours. The crude brown oil was purified by flash chromatography on silica gel (eluent : cyclohexane) to provide 80 % yield of the desired product as an oil.

Identification



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.25 (d, 2H, H_7), 6.85-6.87 (m, 4H, $H_{2,3}$), 6.83 (s, 2H, H_6), 6.62 (s, 1H, H_{13}), 6.52 (s, 2H, H_{11}), 2.19 (s, 6H, H_{14}), 1.22 (s, 9H, H_9).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.84 (C_{10}), 155.39 (C_5), 152.95 (C_4), 152.66 (C_1), 145.89 (C_8), 139.62 (C_{12}), 126.60 (C_7), 124.78 (C_{13}), 120.45 (C_2), 120.19 (C_3), 117.94 (C_6), 116.02 (C_{11}), 34.35 (C_9), 31.59 (C_{15}), 21.42 (C_{14}).

GC/MS: rt = 59.85 min, M/Z = 346.

References

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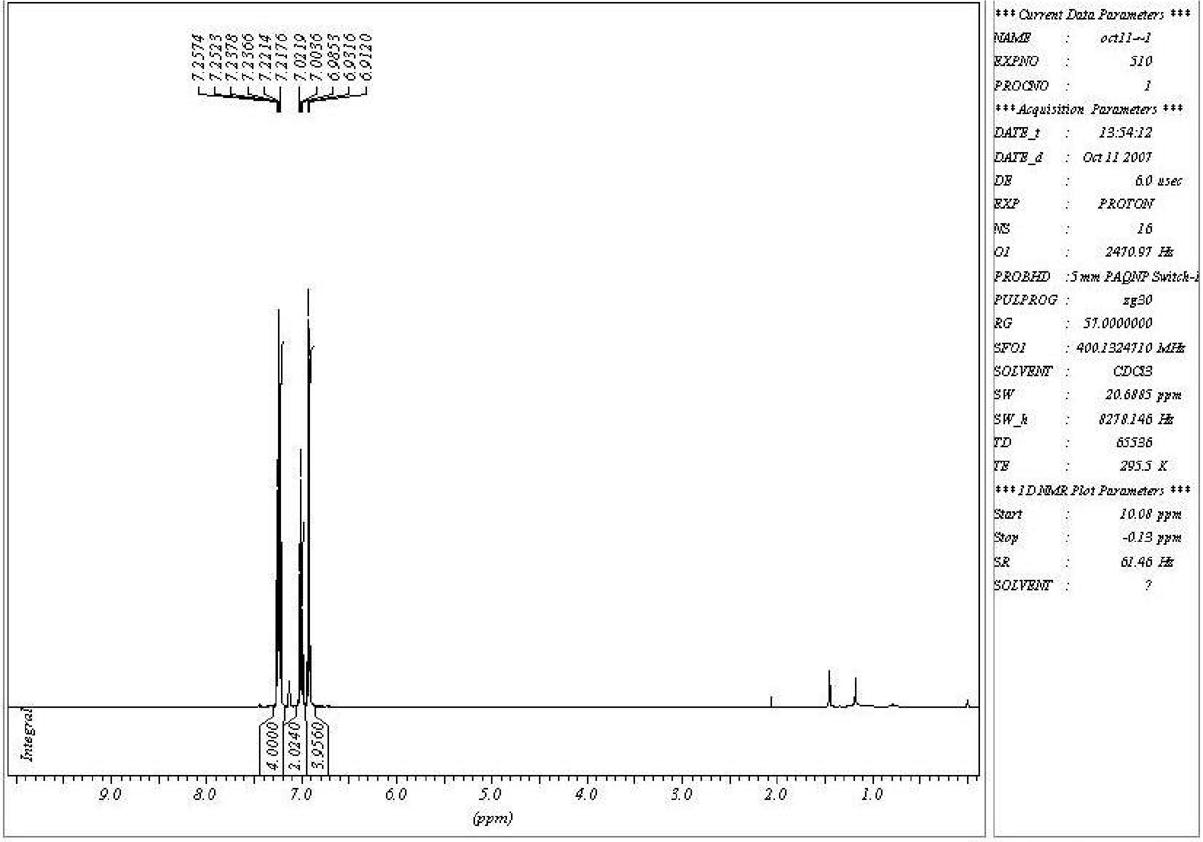
Selected specters of cross-coupling products

Diphenyl ether



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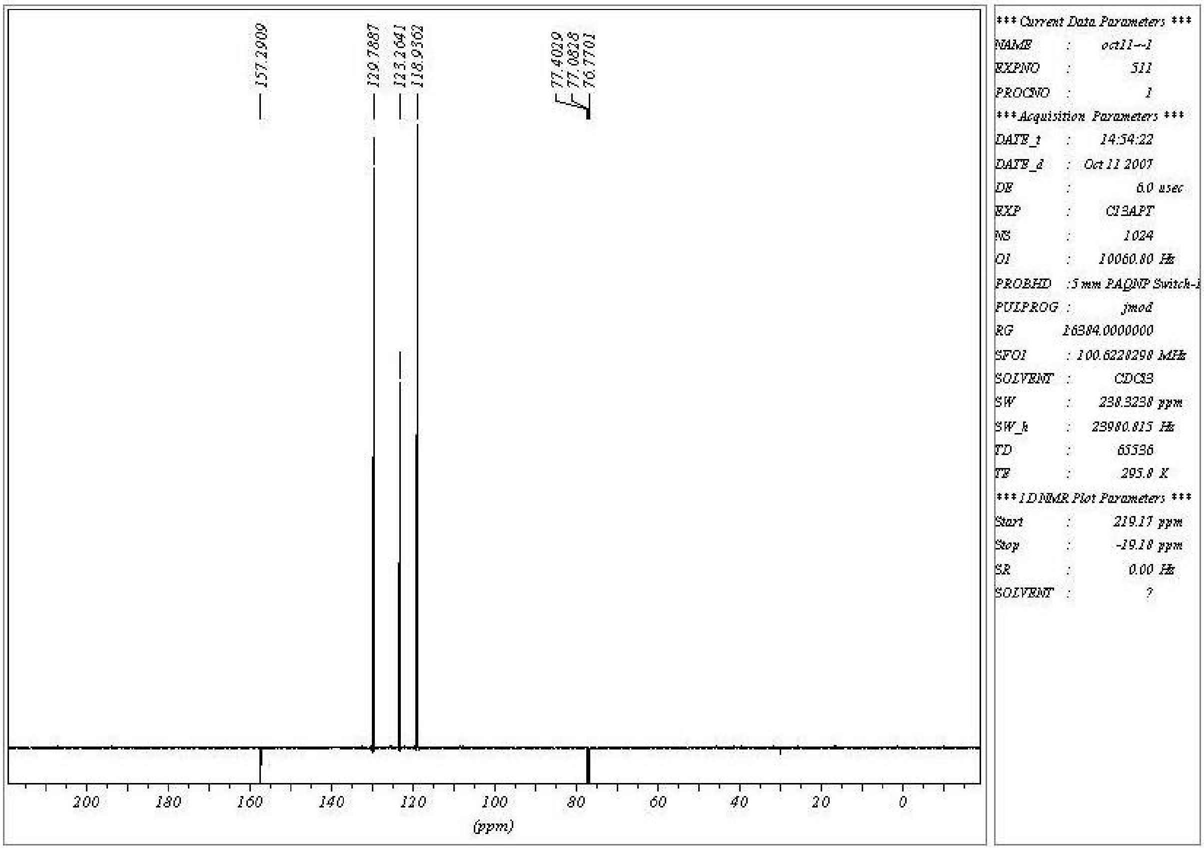

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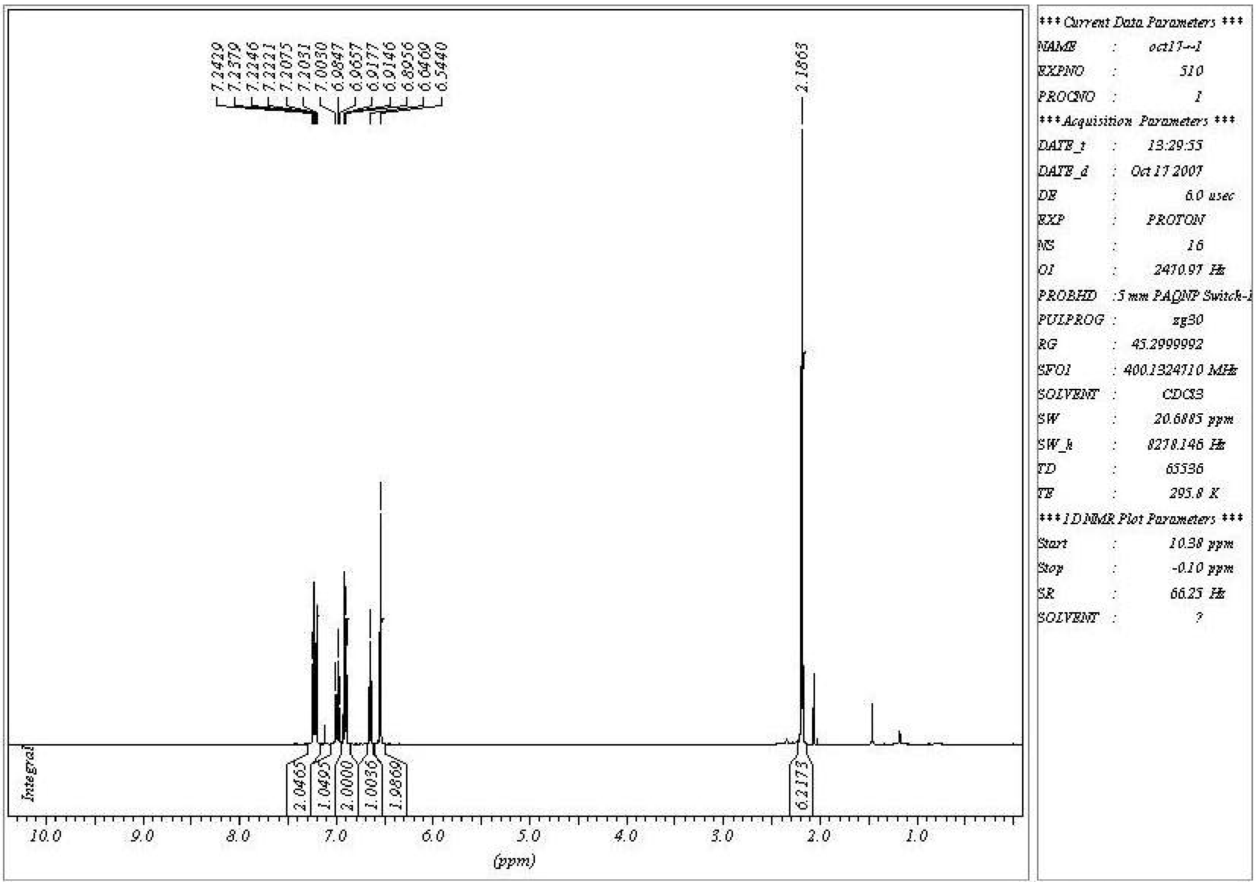
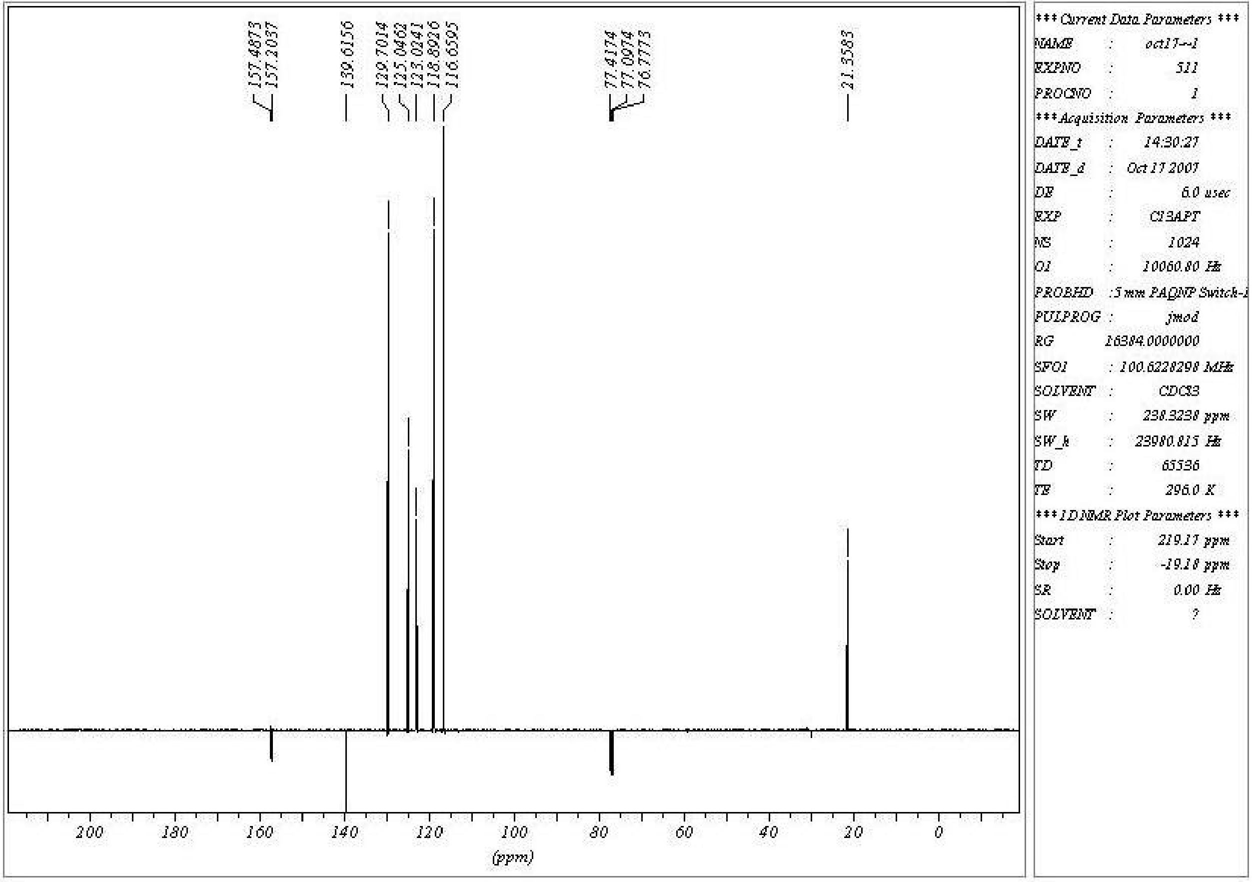
DATE_t    :     14:54:22
DATE_d    :  Oct 11 2007
DE        :          6.0 usec
EXP       :       C13APT
NS        :         1024
O1        :     10060.80 Hz
PROBHD    :5 mm PAQNP Switch-
PULPROG   :         jmod
RG         16384.0000000
SFO1      : 100.6228298 MHz
SOLVENT   :        CDCl3
SW        :     238.3238 ppm
SW_h      :    23980.815 Hz
TD        :        65536
TE        :        295.8 K
*** 1D NMR Plot Parameters ***
Start     :       219.17 ppm
Stop      :       -19.18 ppm
SR        :         0.00 Hz
SOLVENT   :            ?
```

1,3-dimethyl-5-phenoxybenzene

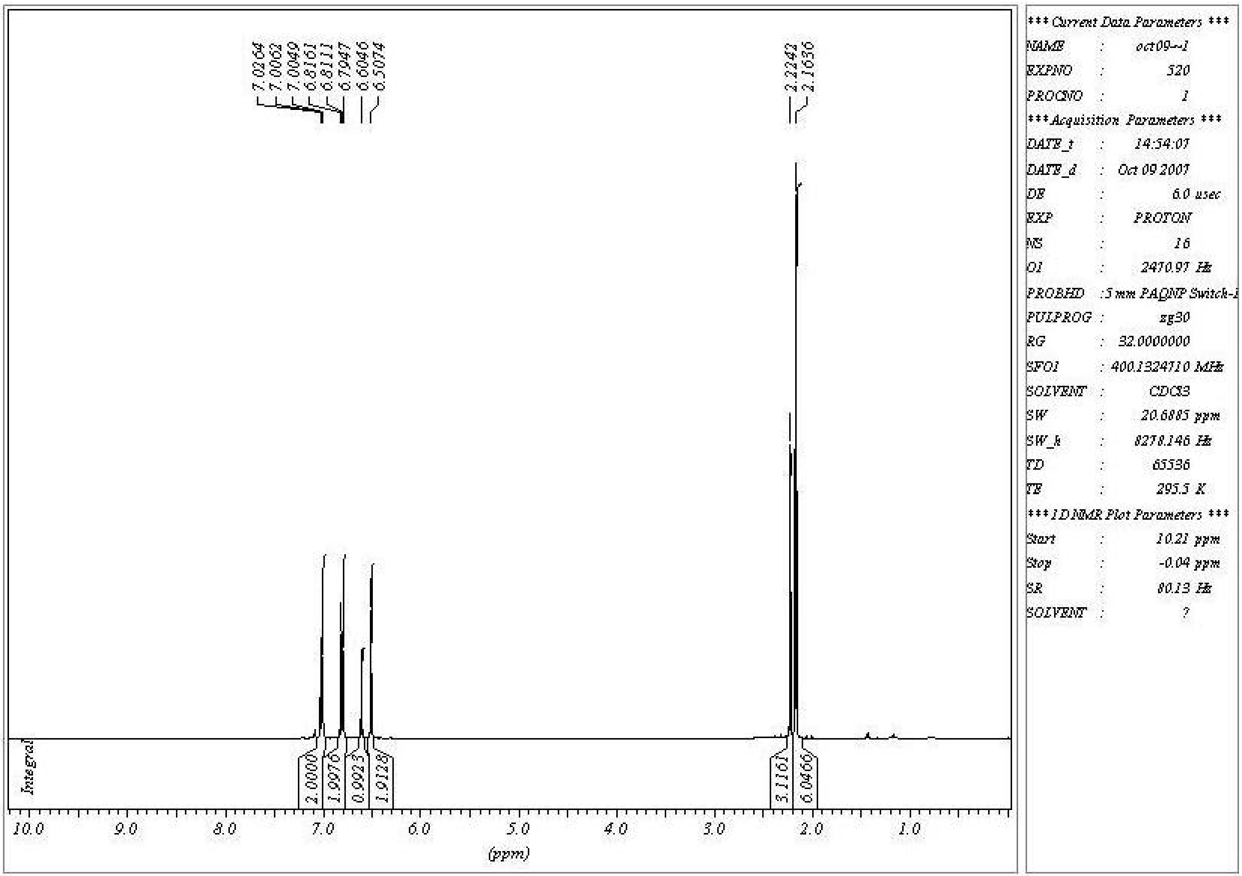


*** Current Data Parameters ***
NAME : oct17--1
EXPNO : 510
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 13:29:55
DATE_d : Oct 17 2007
DE : 6.0 usec
EXP : PROTON
NS : 16
O1 : 2470.97 Hz
PROBHD : 5 mm PAQNP Switch-
PULPROG : zg30
RG : 45.2999992
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.6885 ppm
SW_h : 8278.146 Hz
TD : 65536
TE : 295.8 K
*** 1D NMR Plot Parameters ***
Start : 10.38 ppm
Stop : -0.10 ppm
SR : 66.25 Hz
SOLVENT : ?

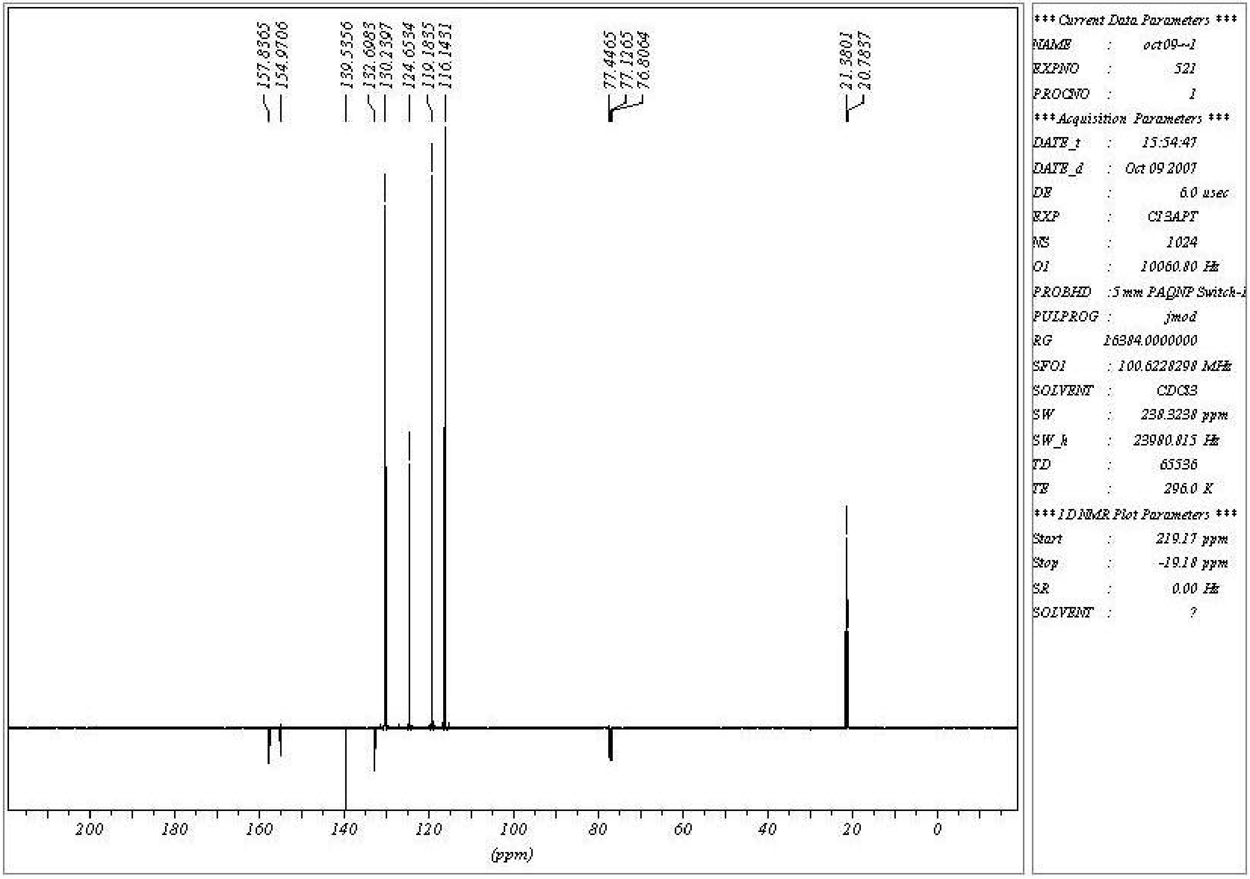


*** Current Data Parameters ***
NAME : oct17--1
EXPNO : 511
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 14:30:27
DATE_d : Oct 17 2007
DE : 6.0 usec
EXP : C13APT
NS : 1024
O1 : 10060.80 Hz
PROBHD : 5 mm PAQNP Switch-
PULPROG : jmod
RG 16384.0000000
SFO1 : 100.6228298 MHz
SOLVENT : CDCl3
SW : 238.3238 ppm
SW_h : 23980.815 Hz
TD : 65536
TE : 296.0 K
*** 1D NMR Plot Parameters ***
Start : 219.17 ppm
Stop : -19.18 ppm
SR : 0.00 Hz
SOLVENT : ?

1,3-dimethyl-5-(p-tolyloxy)benzene

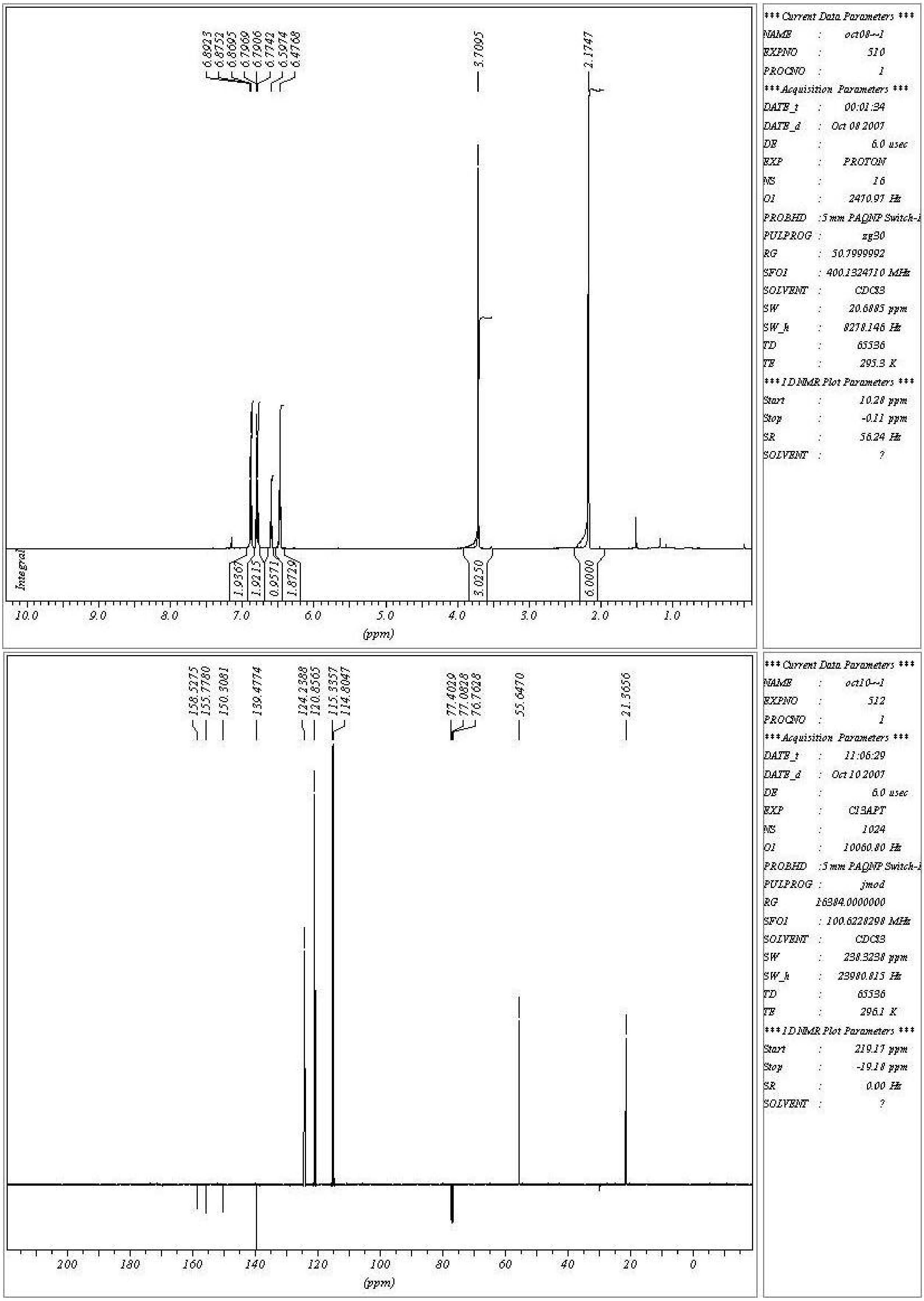


*** Current Data Parameters ***
NAME : oct09--1
EXPNO : 520
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 14:54:07
DATE_d : Oct 09 2007
DE : 6.0 usec
EXP : PROTON
NS : 16
O1 : 2470.97 Hz
PROBHD : 5 mm PAQNP Switch-
PULPROG : zg30
RG : 32.0000000
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.6885 ppm
SW_h : 8278.146 Hz
TD : 65536
TE : 295.5 K
*** 1D NMR Plot Parameters ***
Start : 10.21 ppm
Stop : -0.04 ppm
SR : 80.13 Hz
SOLVENT : ?



*** Current Data Parameters ***
NAME : oct09--1
EXPNO : 521
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 15:54:47
DATE_d : Oct 09 2007
DE : 6.0 usec
EXP : C13APT
NS : 1024
O1 : 10060.80 Hz
PROBHD : 5 mm PAQNP Switch-
PULPROG : jmod
RG 16384.0000000
SFO1 : 100.6228298 MHz
SOLVENT : CDCl3
SW : 238.3238 ppm
SW_h : 23980.815 Hz
TD : 65536
TE : 296.0 K
*** 1D NMR Plot Parameters ***
Start : 219.17 ppm
Stop : -19.18 ppm
SR : 0.00 Hz
SOLVENT : ?

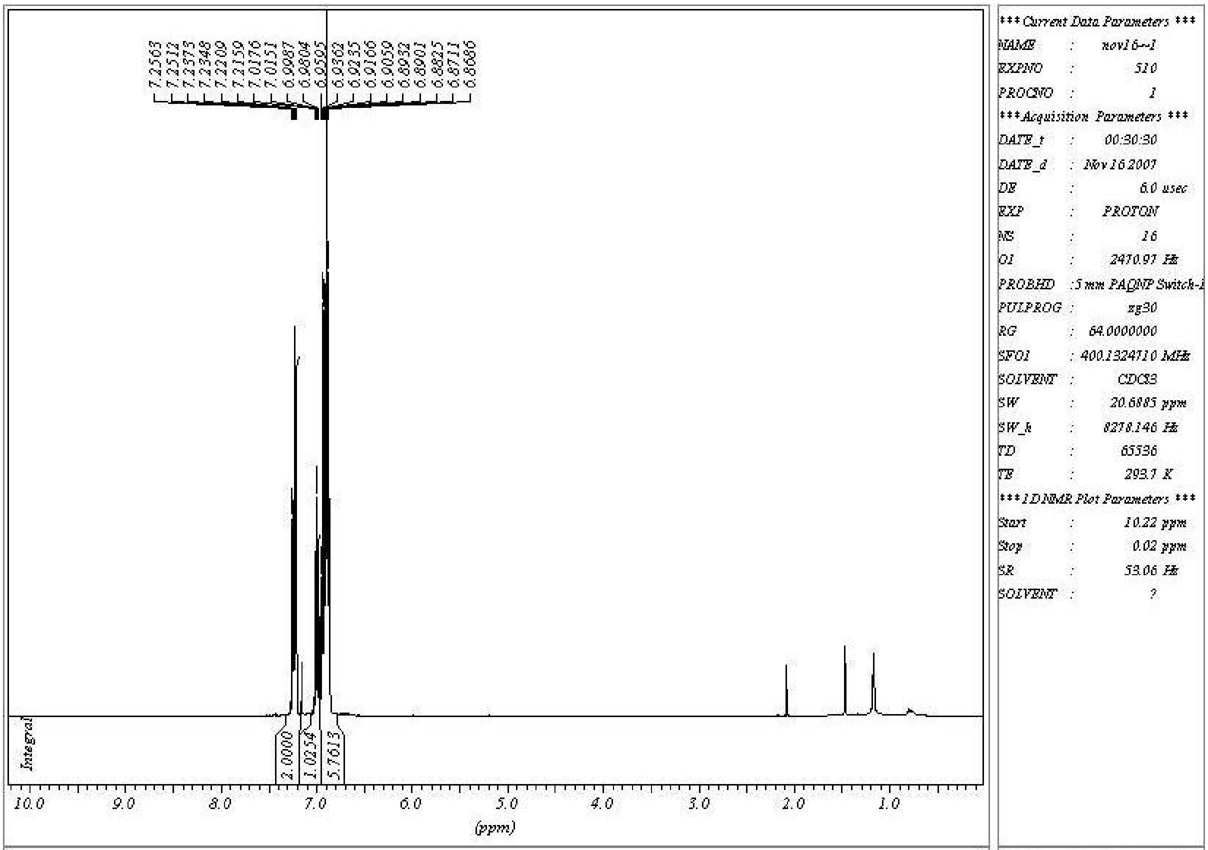
1-(4-methoxyphenoxy)-3,5-dimethylbenzene



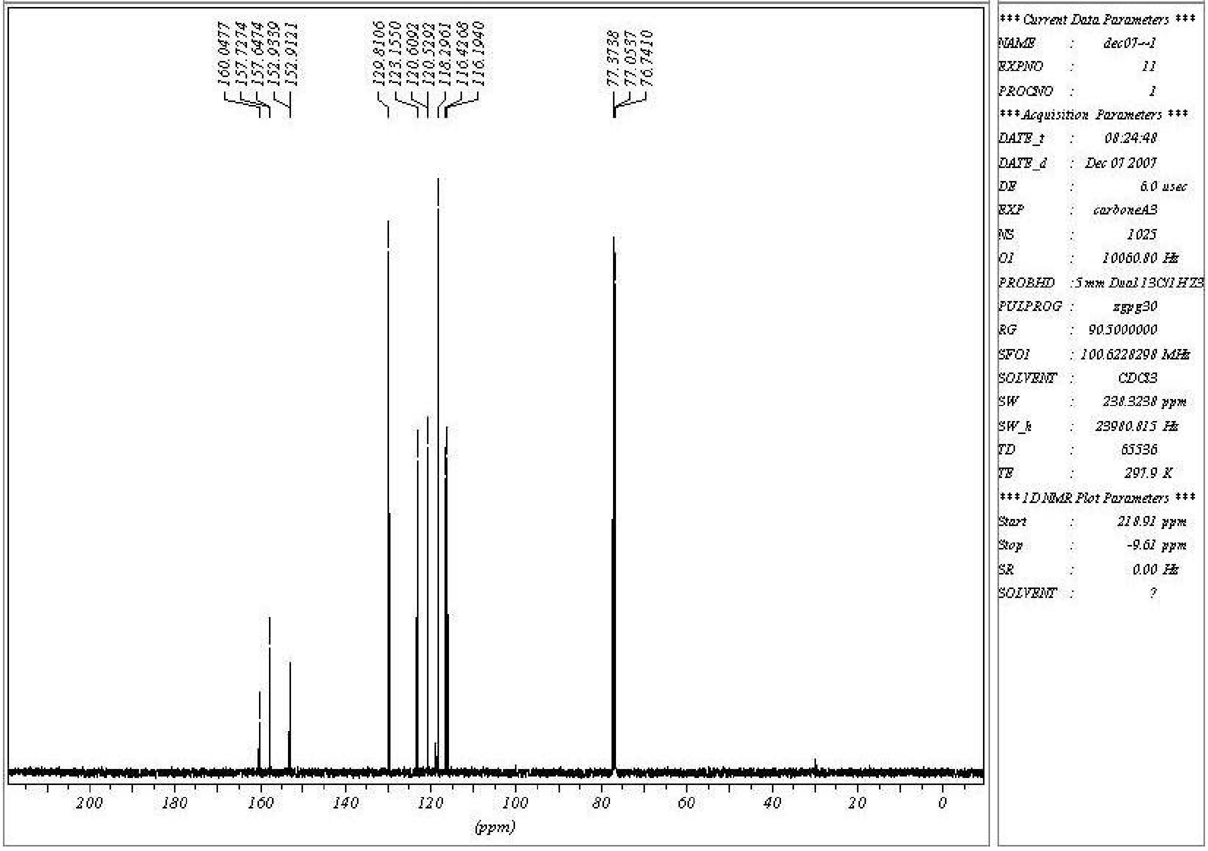
*** Current Data Parameters ***
NAME : oct08--1
EXPNO : 510
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 00:01:34
DATE_d : Oct 08 2007
DE : 6.0 usec
EXP : PROTON
NS : 16
O1 : 2470.97 Hz
PROBHD : 5 mm PAQNP Switch-
PULPROG : zg30
RG : 50.7999992
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.6885 ppm
SW_h : 8278.146 Hz
TD : 65536
TE : 295.3 K
*** 1D NMR Plot Parameters ***
Start : 10.28 ppm
Stop : -0.11 ppm
SR : 56.24 Hz
SOLVENT : ?

*** Current Data Parameters ***
NAME : oct10--1
EXPNO : 512
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 11:06:29
DATE_d : Oct 10 2007
DE : 6.0 usec
EXP : C13APT
NS : 1024
O1 : 10060.80 Hz
PROBHD : 5 mm PAQNP Switch-
PULPROG : jmod
RG 16384.0000000
SFO1 : 100.6228298 MHz
SOLVENT : CDCl3
SW : 238.3238 ppm
SW_h : 23980.815 Hz
TD : 65536
TE : 296.1 K
*** 1D NMR Plot Parameters ***
Start : 219.17 ppm
Stop : -19.18 ppm
SR : 0.00 Hz
SOLVENT : ?

1-fluoro-4-phenoxybenzene

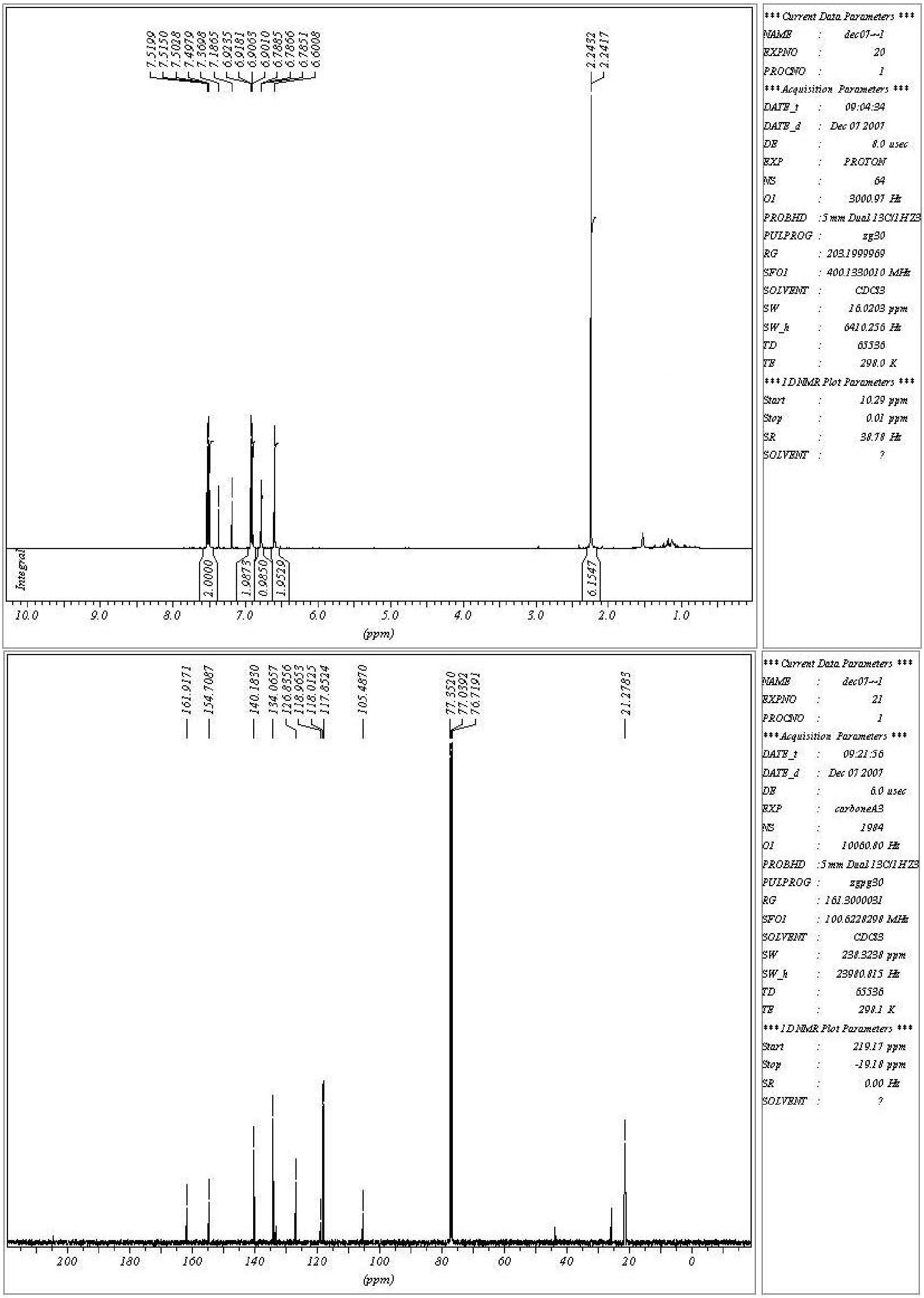


```
*** Current Data Parameters ***
NAME      :     nov16~~1
EXPNO     :          510
PROCNO    :            1
***Acquisition  Parameters ***
DATE_t    :     00:30:30
DATE_d    :  Nov 16 2007
DE        :          6.0 usec
EXP       :       PROTON
NS        :           16
O1        :      2410.97 Hz
PROBHD    :5 mm PAQNP Switch-
PULPROG   :         zg30
RG        :   64.0000000
SFO1      :  400.1324710 MHz
SOLVENT   :        CDCl3
SW        :      20.6885 ppm
SW_h      :     8278.146 Hz
TD        :        65536
TE        :        293.1 K
***1D NMR Plot Parameters ***
Start     :        10.22 ppm
Stop      :         0.02 ppm
SR        :        53.06 Hz
SOLVENT   :            ?
```



```
*** Current Data Parameters ***
NAME      :     dec07~~1
EXPNO     :           11
PROCNO    :            1
***Acquisition  Parameters ***
DATE_t    :     08:24:48
DATE_d    :  Dec 07 2007
DE        :          6.0 usec
EXP       :     carboneA3
NS        :         1025
O1        :     10060.80 Hz
PROBHD    :5 mm Dual 13C/1H Z3
PULPROG   :       zgpg30
RG        :   90.5000000
SFO1      :  100.6228298 MHz
SOLVENT   :        CDCl3
SW        :     238.3238 ppm
SW_h      :    23980.815 Hz
TD        :        65536
TE        :        297.9 K
***1D NMR Plot Parameters ***
Start     :       218.91 ppm
Stop      :        -9.61 ppm
SR        :         0.00 Hz
SOLVENT   :            ?
```

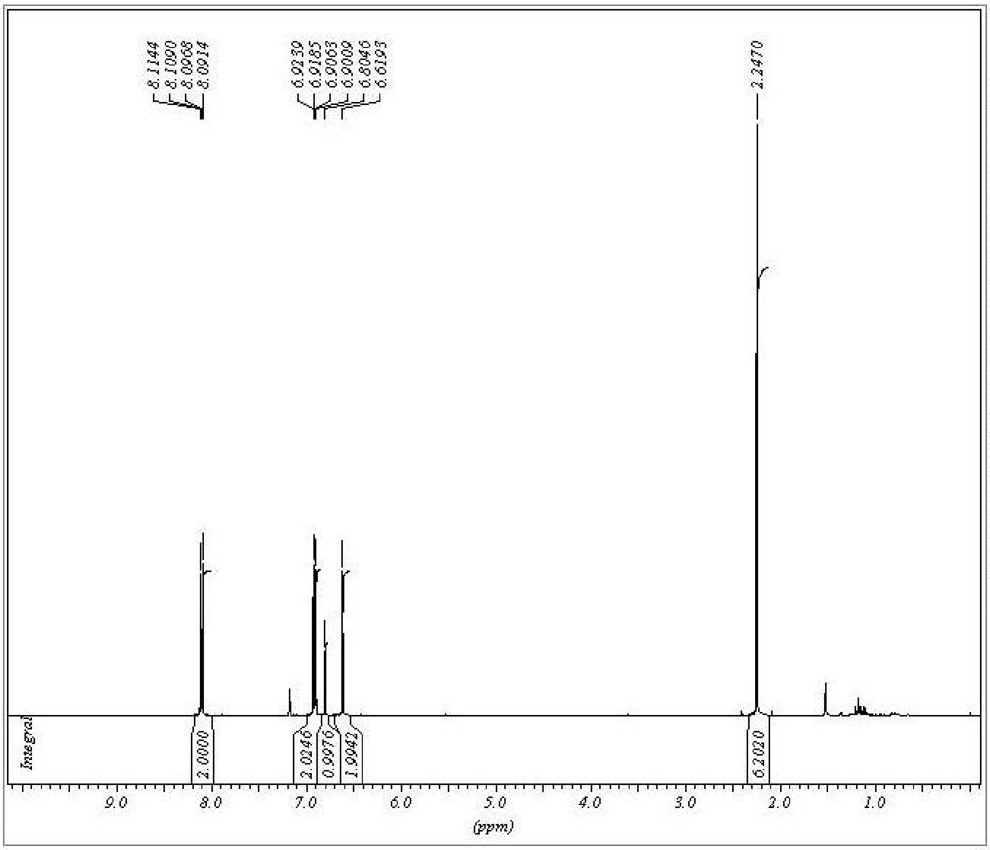
4-(3,5-dimethylphenoxy)benzonitrile



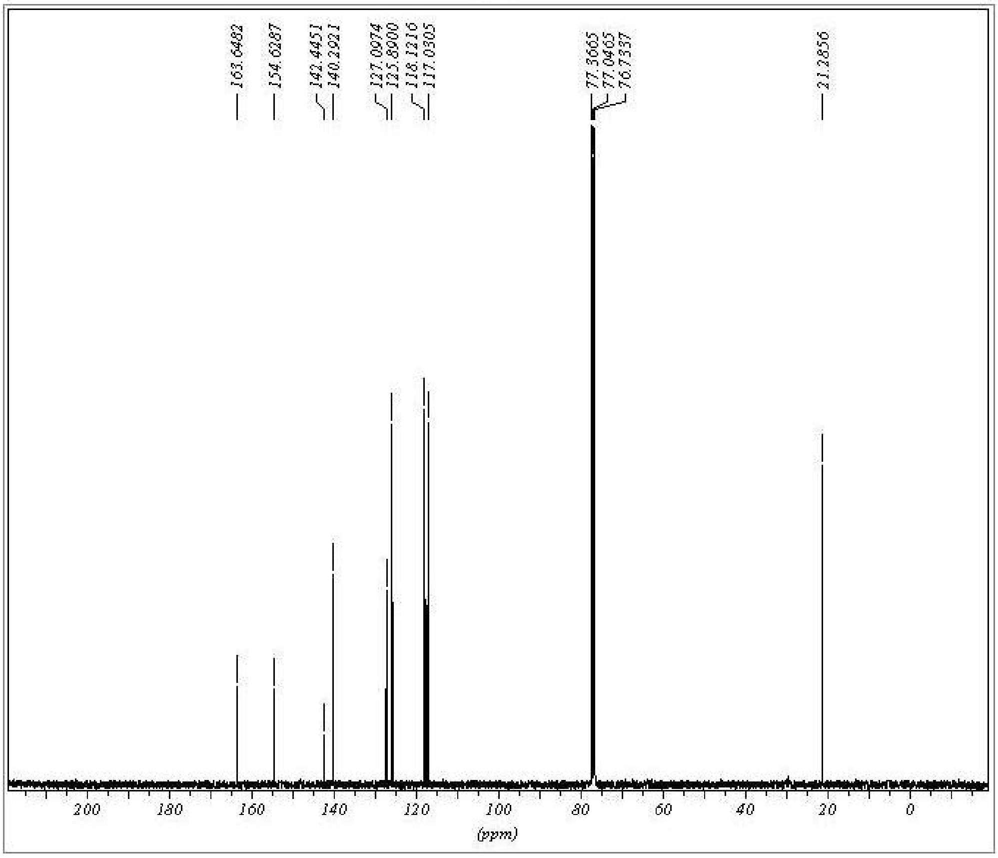
*** Current Data Parameters ***
NAME : dec07--1
EXPNO : 20
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:04:34
DATE_d : Dec 07 2007
DE : 8.0 usec
EXP : PROTON
NS : 64
O1 : 3000.97 Hz
PROBHD : 5 mm Dual 13C/1H Z3
PULPROG : zg30
RG : 203.1999969
SFO1 : 400.1330010 MHz
SOLVENT : CDCl3
SW : 16.0203 ppm
SW_h : 6410.256 Hz
TD : 65536
TE : 298.0 K
*** 1D NMR Plot Parameters ***
Start : 10.29 ppm
Stop : 0.01 ppm
SR : 38.78 Hz
SOLVENT : ?

*** Current Data Parameters ***
NAME : dec07--1
EXPNO : 21
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:21:56
DATE_d : Dec 07 2007
DE : 6.0 usec
EXP : carboneA3
NS : 1984
O1 : 10060.80 Hz
PROBHD : 5 mm Dual 13C/1H Z3
PULPROG : zgpg30
RG : 161.3000031
SFO1 : 100.6228298 MHz
SOLVENT : CDCl3
SW : 238.3238 ppm
SW_h : 23980.815 Hz
TD : 65536
TE : 298.1 K
*** 1D NMR Plot Parameters ***
Start : 219.17 ppm
Stop : -19.18 ppm
SR : 0.00 Hz
SOLVENT : ?

3’,5’-dimethyl-4-nitrodiphenylether

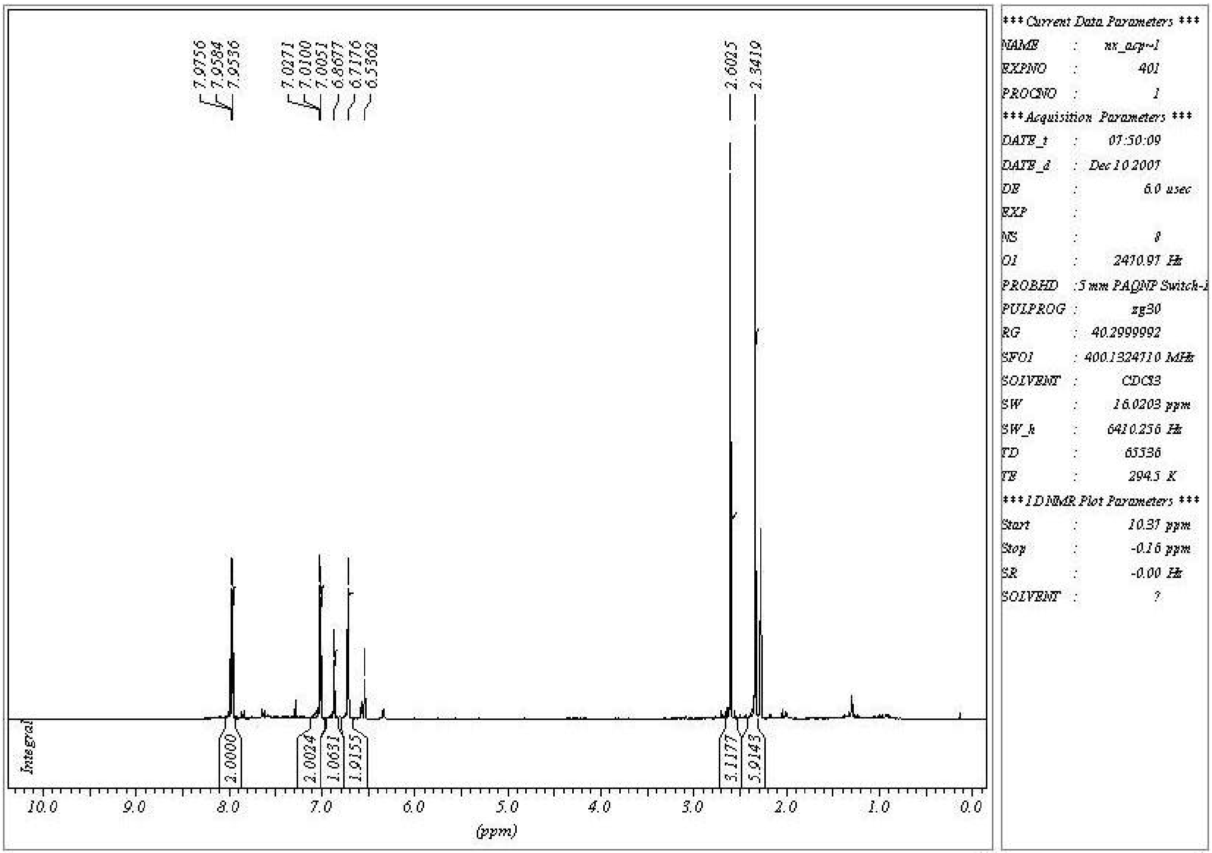


```
*** Current Data Parameters ***
NAME      :      dec07~-1
EXPNO     :            30
PROCNO    :             1
*** Acquisition Parameters ***
DATE_t    :      10:38:34
DATE_d    :   Dec 07 2007
DE        :        8.0 usec
EXP       :        PROTON
NS        :            64
O1        :     3000.97 Hz
PROBHD    :5 mm Dual 13C/1H Z3
PULPROG   :          zg30
RG        :   114.0000000
SFO1      : 400.1330010 MHz
SOLVENT   :         CDCl3
SW        :    16.0203 ppm
SW_h      :    6410.256 Hz
TD        :         65536
TE        :        298.0 K
*** 1D NMR Plot Parameters ***
Start     :      10.14 ppm
Stop      :      -0.12 ppm
SR        :       42.32 Hz
SOLVENT   :             ?
```

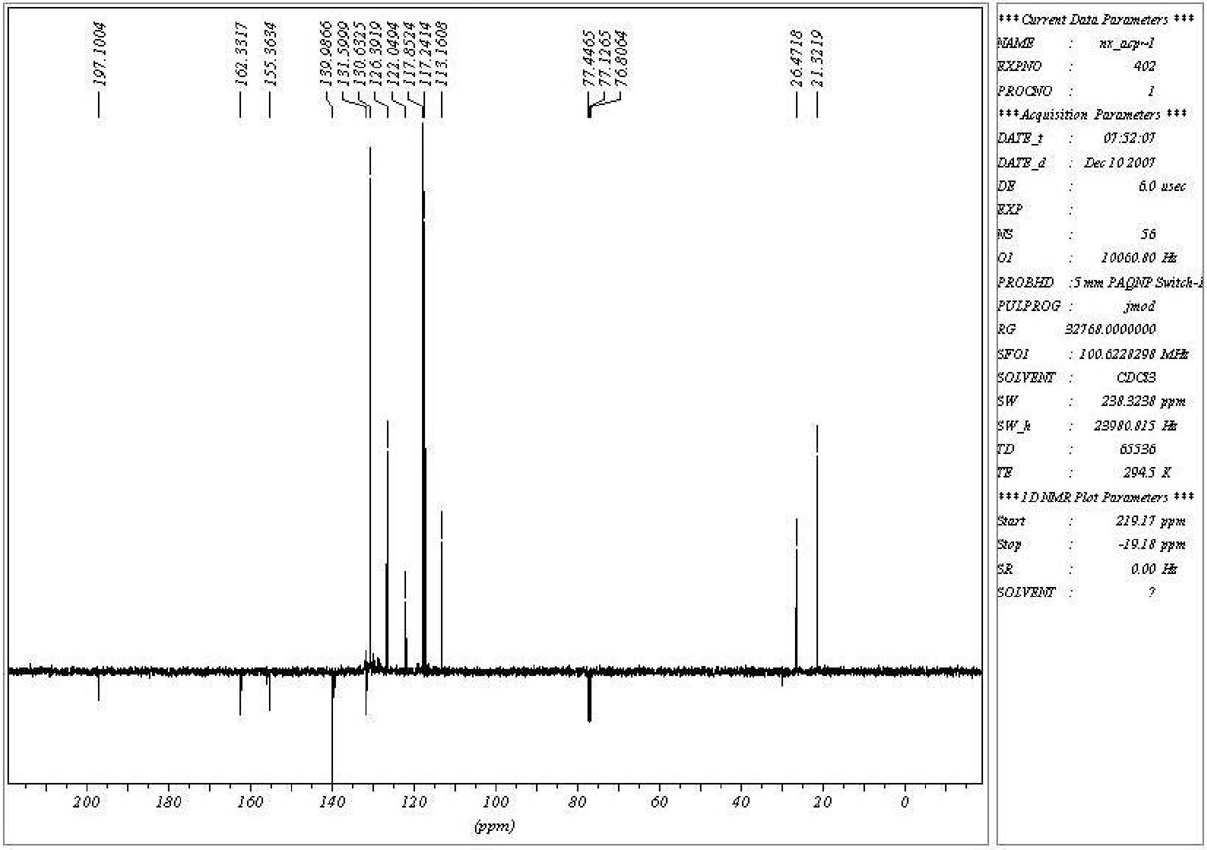


```
*** Current Data Parameters ***
NAME      :      dec07~-1
EXPNO     :            31
PROCNO    :             1
*** Acquisition Parameters ***
DATE_t    :      12:02:08
DATE_d    :   Dec 07 2007
DE        :        6.0 usec
EXP       :     carboneA3
NS        :          2048
O1        :    10060.80 Hz
PROBHD    :5 mm Dual 13C/1H Z3
PULPROG   :        zgpg30
RG        :    90.5000000
SFO1      : 100.6228298 MHz
SOLVENT   :         CDCl3
SW        :   238.3238 ppm
SW_h      :   23980.815 Hz
TD        :         65536
TE        :        298.0 K
*** 1D NMR Plot Parameters ***
Start     :     219.17 ppm
Stop      :     -19.18 ppm
SR        :        0.00 Hz
SOLVENT   :             ?
```

3’,5’-dimethyl-4-acetodiphenylether

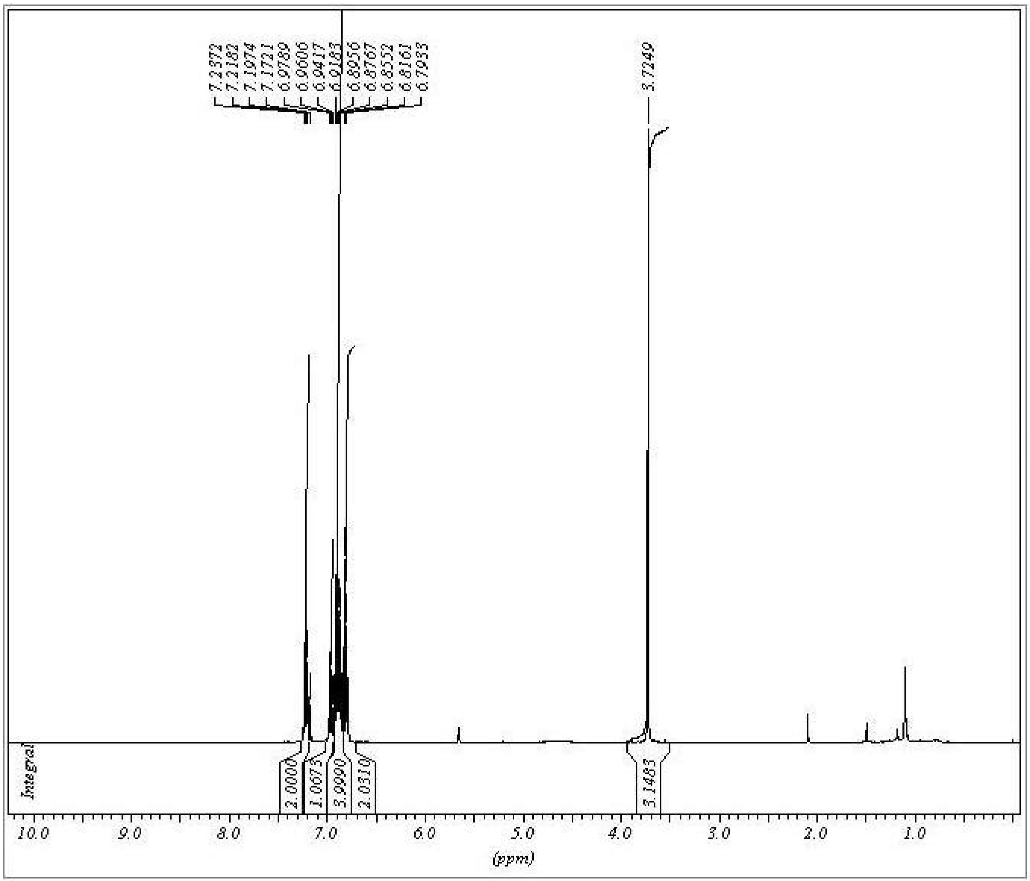


```
*** Current Data Parameters ***
NAME       :    nx_acp~1
EXPNO      :         401
PROCNO     :           1
*** Acquisition Parameters ***
DATE_t     :    07:50:09
DATE_d     : Dec 10 2007
DE         :          6.0 usec
EXP        :
NS         :           8
O1         :     2470.97 Hz
PROBHD     :5 mm PAQNP Switch-
PULPROG    :        zg30
RG         :  40.2999992
SFO1       : 400.1324710 MHz
SOLVENT    :       CDCl3
SW         :     16.0203 ppm
SW_h       :    6410.256 Hz
TD         :       65536
TE         :       294.5 K
*** 1D NMR Plot Parameters ***
Start      :       10.37 ppm
Stop       :       -0.16 ppm
SR         :       -0.00 Hz
SOLVENT    :           ?
```

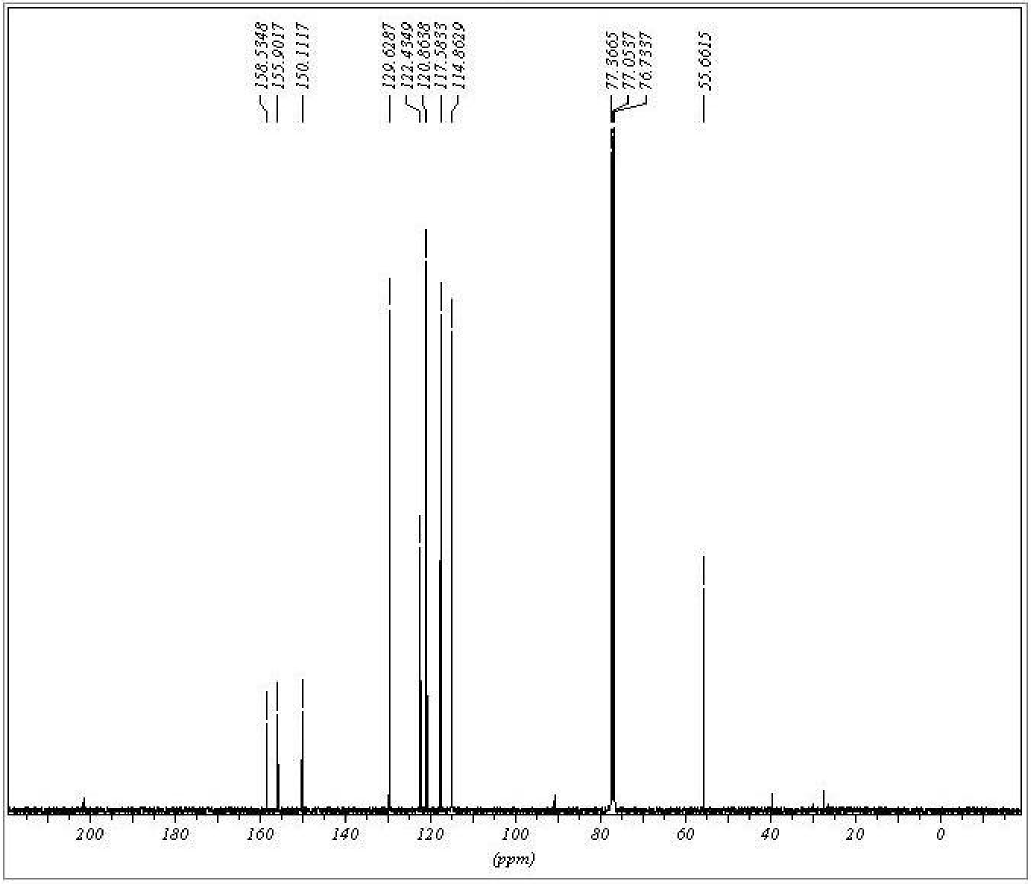


```
*** Current Data Parameters ***
NAME       :    nx_acp~1
EXPNO      :         402
PROCNO     :           1
*** Acquisition Parameters ***
DATE_t     :    07:52:07
DATE_d     : Dec 10 2007
DE         :          6.0 usec
EXP        :
NS         :          56
O1         :    10060.80 Hz
PROBHD     :5 mm PAQNP Switch-
PULPROG    :        jmod
RG           32768.0000000
SFO1       : 100.6228298 MHz
SOLVENT    :       CDCl3
SW         :    238.3238 ppm
SW_h       :   23980.815 Hz
TD         :       65536
TE         :       294.5 K
*** 1D NMR Plot Parameters ***
Start      :      219.17 ppm
Stop       :      -19.18 ppm
SR         :        0.00 Hz
SOLVENT    :           ?
```

1-methoxy-4-phenoxybenzene

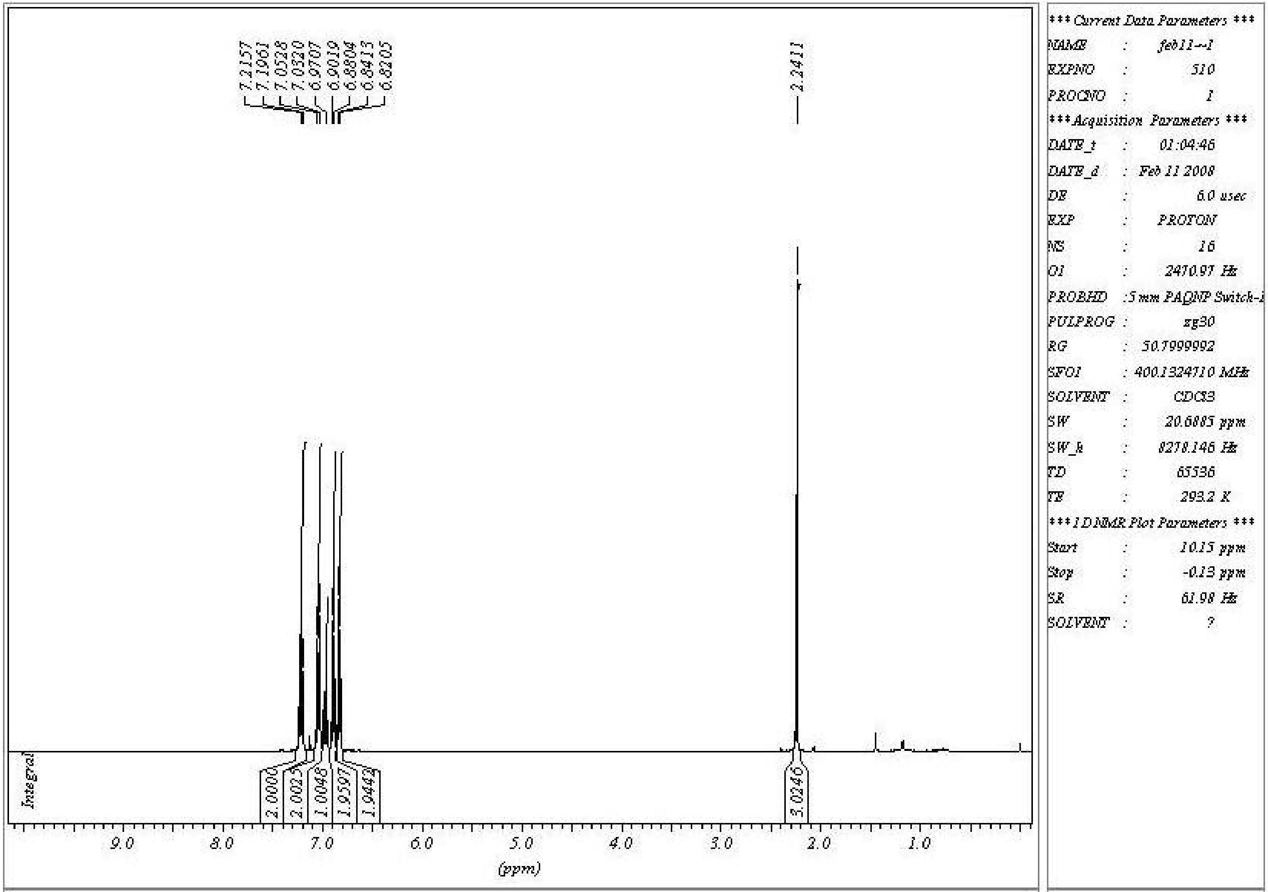


*** Current Data Parameters ***
NAME : feb02~~1
EXPNO : 510
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 12:16:57
DATE_d : Feb 02 2008
DE : 6.0 usec
EXP : PROTON
NS : 16
O1 : 2470.97 Hz
PROBHD : 5 mm PAQNP Switch-
PULPROG : zg30
RG : 80.5999985
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.6885 ppm
SW_h : 8278.146 Hz
TD : 65536
TE : 294.6 K
*** 1D NMR Plot Parameters ***
Start : 10.25 ppm
Stop : -0.08 ppm
SR : 44.79 Hz
SOLVENT : ?

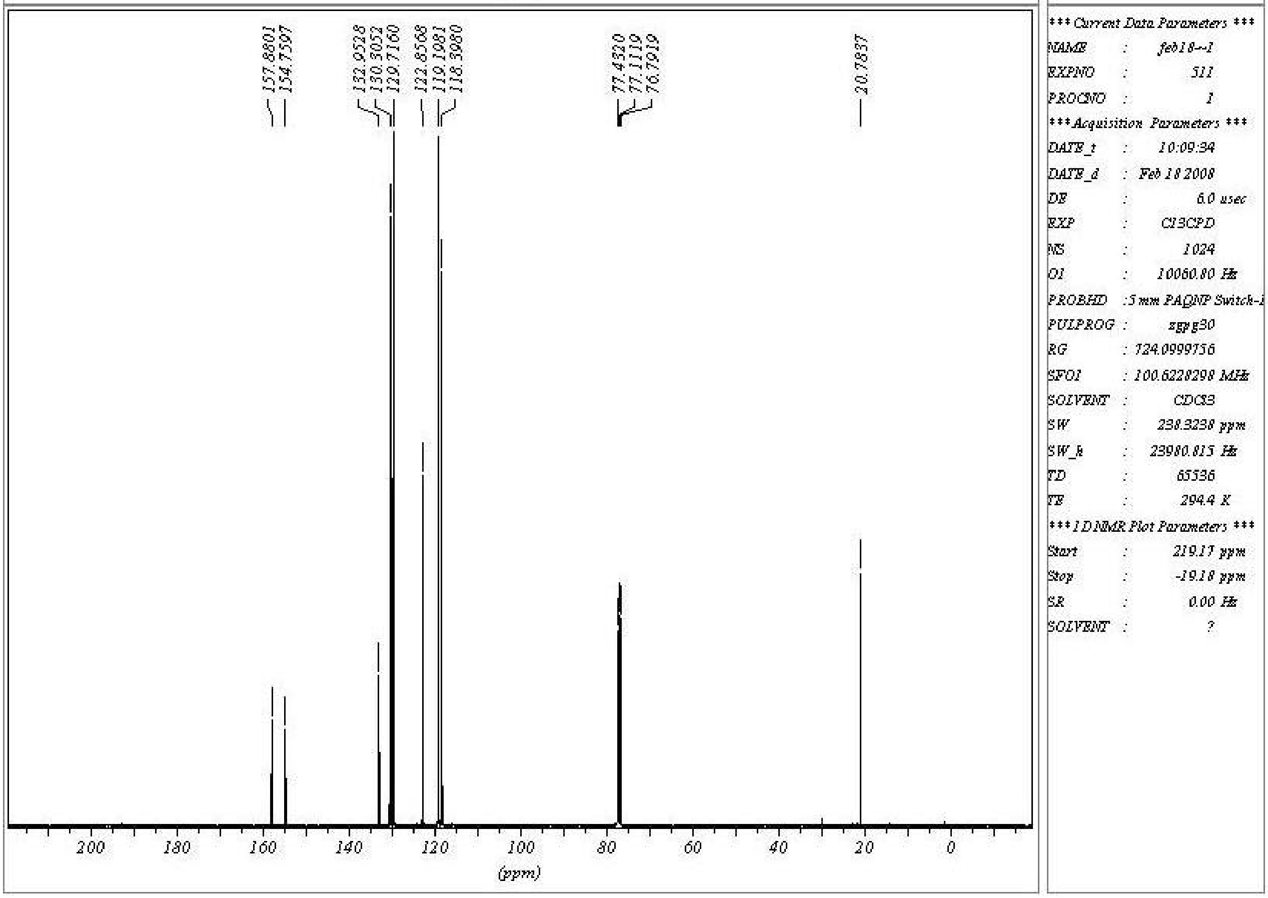


*** Current Data Parameters ***
NAME : feb02~~1
EXPNO : 511
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 13:18:06
DATE_d : Feb 02 2008
DE : 6.0 usec
EXP : C13CPD
NS : 1024
O1 : 10060.80 Hz
PROBHD : 5 mm PAQNP Switch-
PULPROG : zgpg30
RG : 456.1000061
SFO1 : 100.6228298 MHz
SOLVENT : CDCl3
SW : 238.3238 ppm
SW_h : 23980.815 Hz
TD : 65536
TE : 295.0 K
*** 1D NMR Plot Parameters ***
Start : 219.17 ppm
Stop : -19.18 ppm
SR : 0.00 Hz
SOLVENT : ?

1-methyl-4-phenoxybenzene

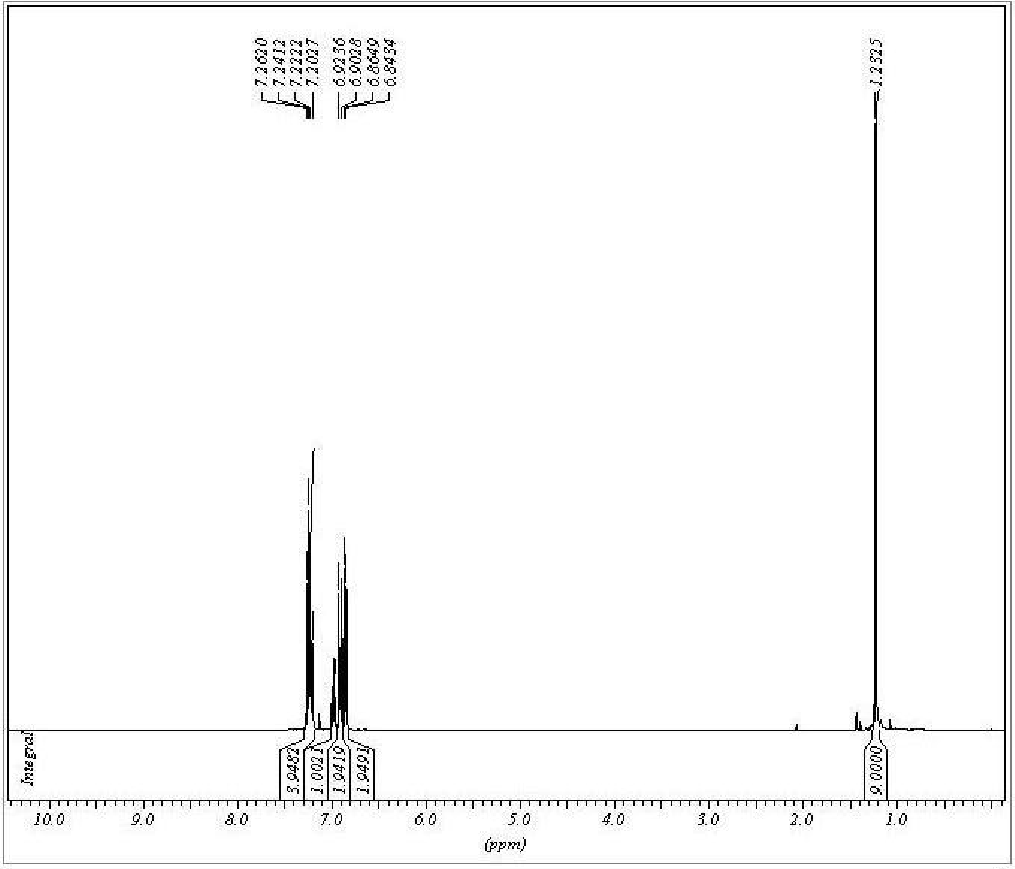


```
*** Current Data Parameters ***
NAME      :     feb11--1
EXPNO     :          510
PROCNO    :            1
*** Acquisition  Parameters ***
DATE_t    :     01:04:46
DATE_d    :  Feb 11 2008
DE        :     6.0 usec
EXP       :       PROTON
NS        :           16
O1        :   2470.97 Hz
PROBHD    :5 mm PAQNP Switch-
PULPROG   :         zg30
RG        :   50.7999992
SFO1      : 400.1324710 MHz
SOLVENT   :        CDCl3
SW        :  20.6885 ppm
SW_h      :  8278.146 Hz
TD        :        65536
TE        :      293.2 K
*** 1D NMR Plot Parameters ***
Start     :    10.15 ppm
Stop      :    -0.13 ppm
SR        :     61.98 Hz
SOLVENT   :            ?
```

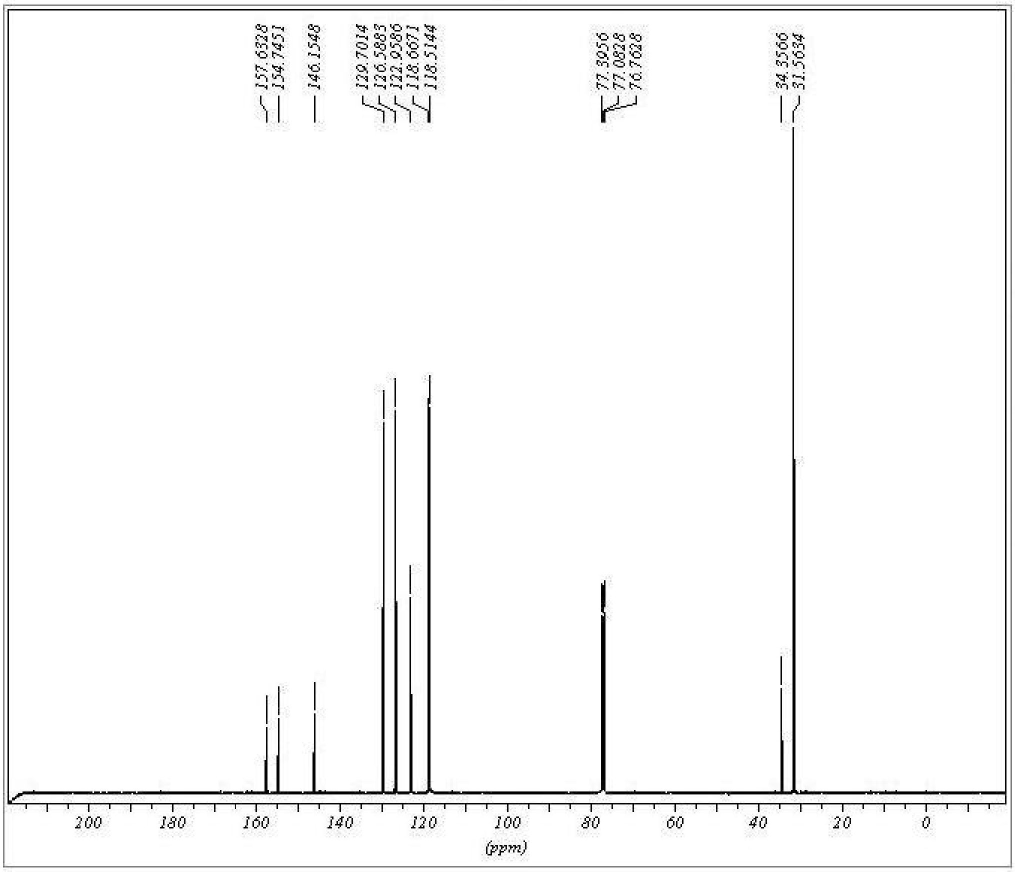


```
*** Current Data Parameters ***
NAME      :     feb18--1
EXPNO     :          511
PROCNO    :            1
*** Acquisition  Parameters ***
DATE_t    :     10:09:34
DATE_d    :  Feb 18 2008
DE        :     6.0 usec
EXP       :       C13CPD
NS        :         1024
O1        :  10060.80 Hz
PROBHD    :5 mm PAQNP Switch-
PULPROG   :       zgpg30
RG        :  724.0999756
SFO1      : 100.6228298 MHz
SOLVENT   :        CDCl3
SW        : 238.3238 ppm
SW_h      : 23980.815 Hz
TD        :        65536
TE        :      294.4 K
*** 1D NMR Plot Parameters ***
Start     :   219.17 ppm
Stop      :   -19.18 ppm
SR        :      0.00 Hz
SOLVENT   :            ?
```

1-tert-butyl-4-phenoxybenzene

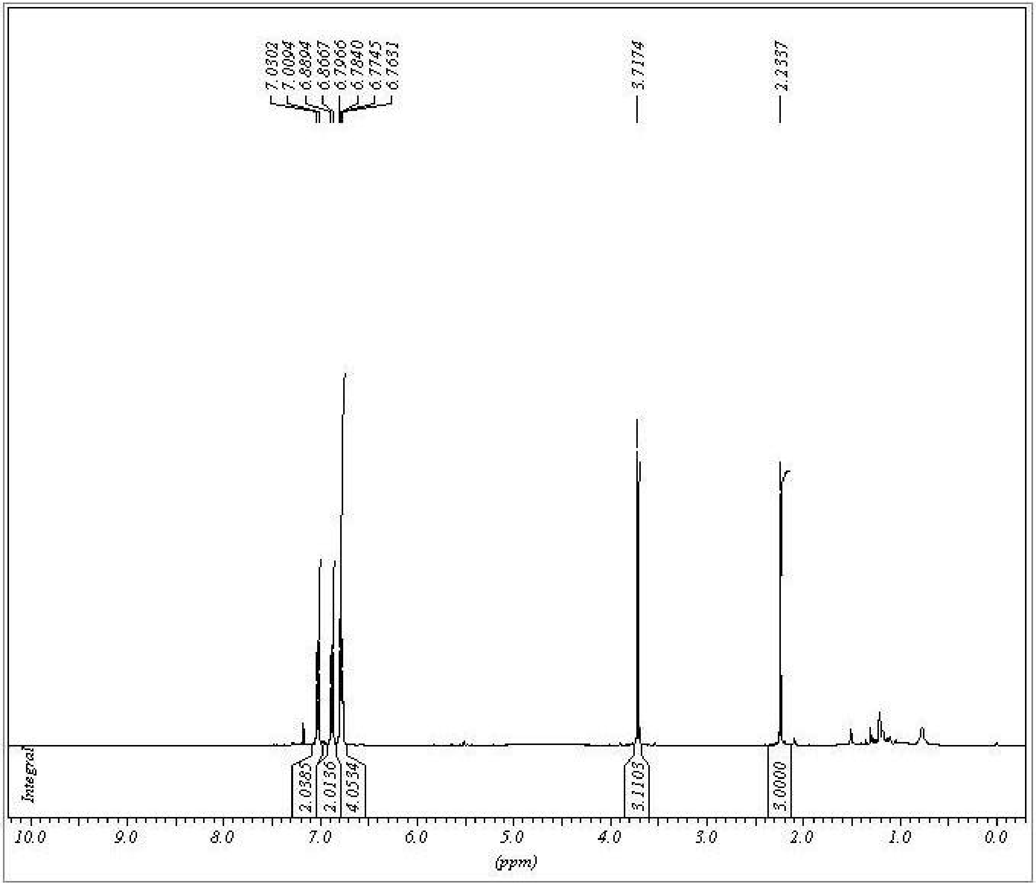


*** Current Data Parameters ***
NAME : feb07--1
EXPNO : 510
PROCNO : 1
***Acquisition Parameters ***
DATE_t : 16:21:21
DATE_d : Feb 07 2008
DE : 6.0 usec
EXP : PROTON
NS : 16
O1 : 2410.97 Hz
PROBHD :5 mm PAQNP Switch-
PULPROG : zg30
RG : 40.2999992
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.6885 ppm
SW_h : 8278.146 Hz
TD : 65536
TE : 294.4 K
*** 1D NMR Plot Parameters ***
Start : 10.43 ppm
Stop : -0.15 ppm
SR : 61.63 Hz
SOLVENT : ?

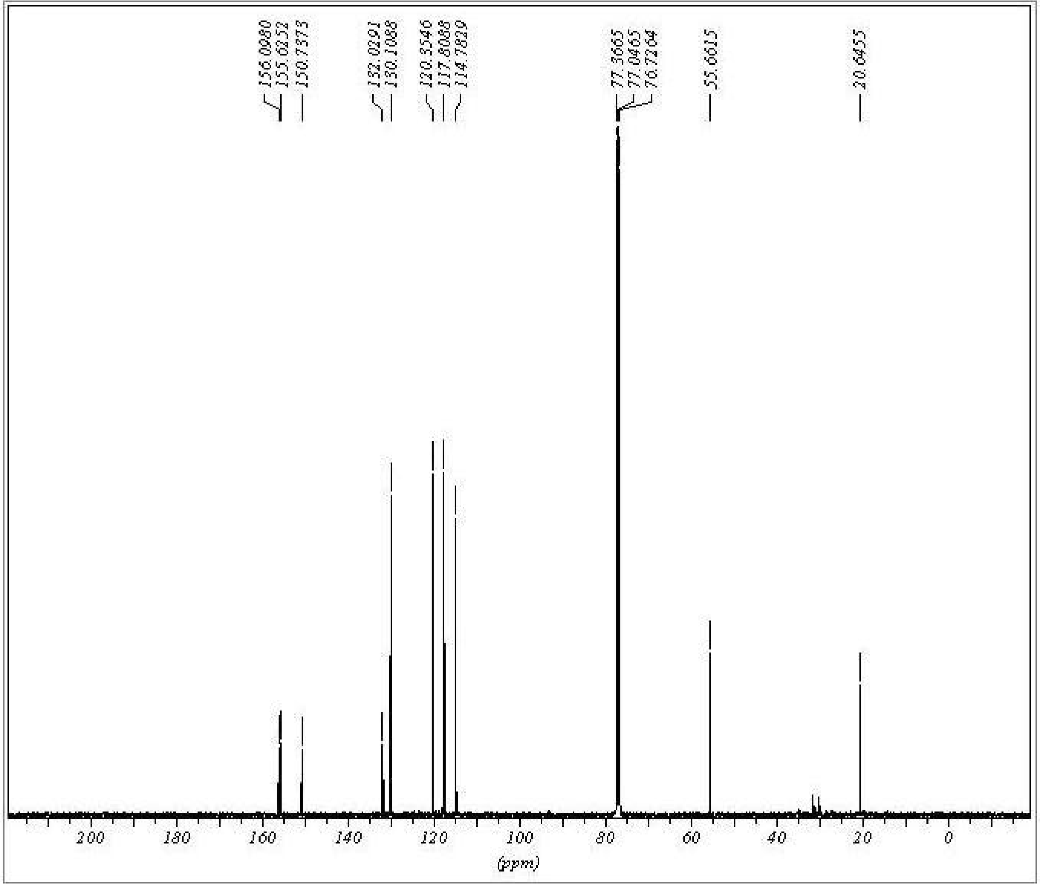


*** Current Data Parameters ***
NAME : feb07--1
EXPNO : 511
PROCNO : 1
***Acquisition Parameters ***
DATE_t : 17:21:59
DATE_d : Feb 07 2008
DE : 6.0 usec
EXP : C13CPD
NS : 1024
O1 : 10060.80 Hz
PROBHD :5 mm PAQNP Switch-
PULPROG : zgpg30
RG : 724.0999756
SFO1 : 100.6228298 MHz
SOLVENT : CDCl3
SW : 238.3238 ppm
SW_h : 23980.815 Hz
TD : 65536
TE : 294.8 K
*** 1D NMR Plot Parameters ***
Start : 219.17 ppm
Stop : -19.18 ppm
SR : 0.00 Hz
SOLVENT : ?

1-tert-butyl-4-(p-tolyloxy) benzene

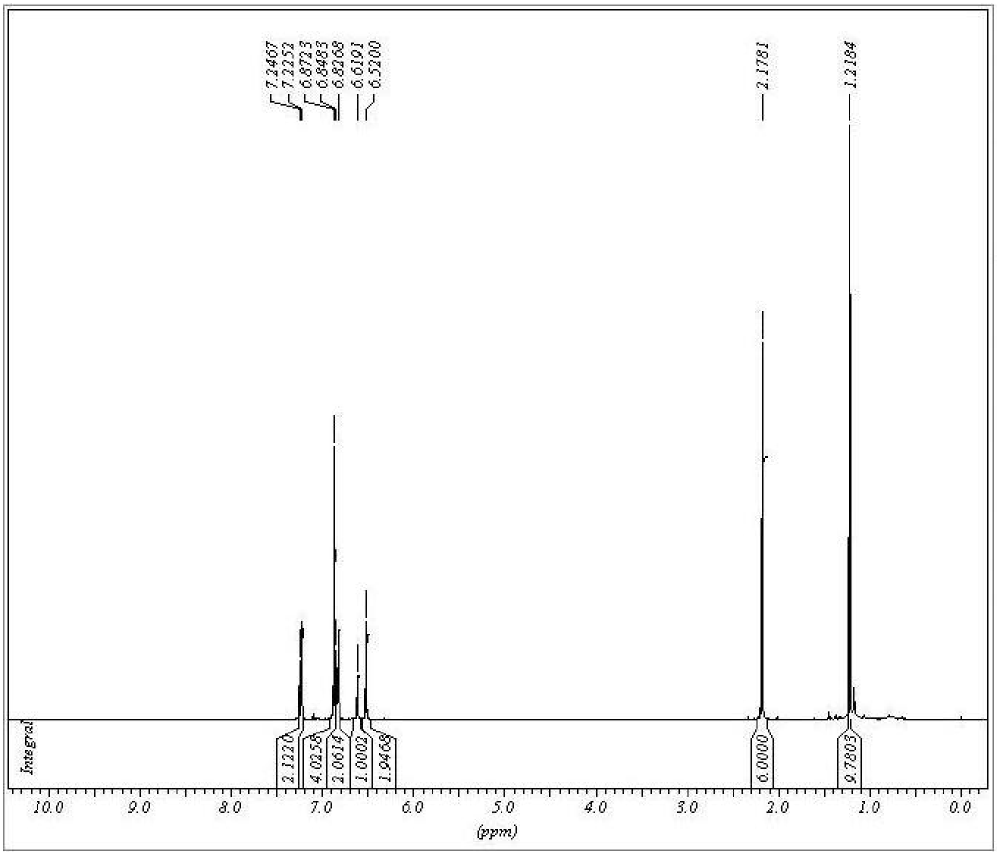


```
*** Current Data Parameters ***
NAME      :    feb06--1
EXPNO     :         510
PROCNO    :           1
*** Acquisition Parameters ***
DATE_t    :    02:46:50
DATE_d    :  Feb 06 2008
DE        :          6.0 usec
EXP       :      PROTON
NS        :          16
O1        :     2470.97 Hz
PROBHD    : 5 mm PAQNP Switch-
PULPROG   :        zg30
RG        :  71.8000031
SFO1      : 400.1324710 MHz
SOLVENT   :       CDCl3
SW        :     20.6885 ppm
SW_h      :    8278.146 Hz
TD        :       65536
TE        :       293.2 K
*** 1D NMR Plot Parameters ***
Start     :       10.22 ppm
Stop      :       -0.31 ppm
SR        :       44.74 Hz
SOLVENT   :           ?
```

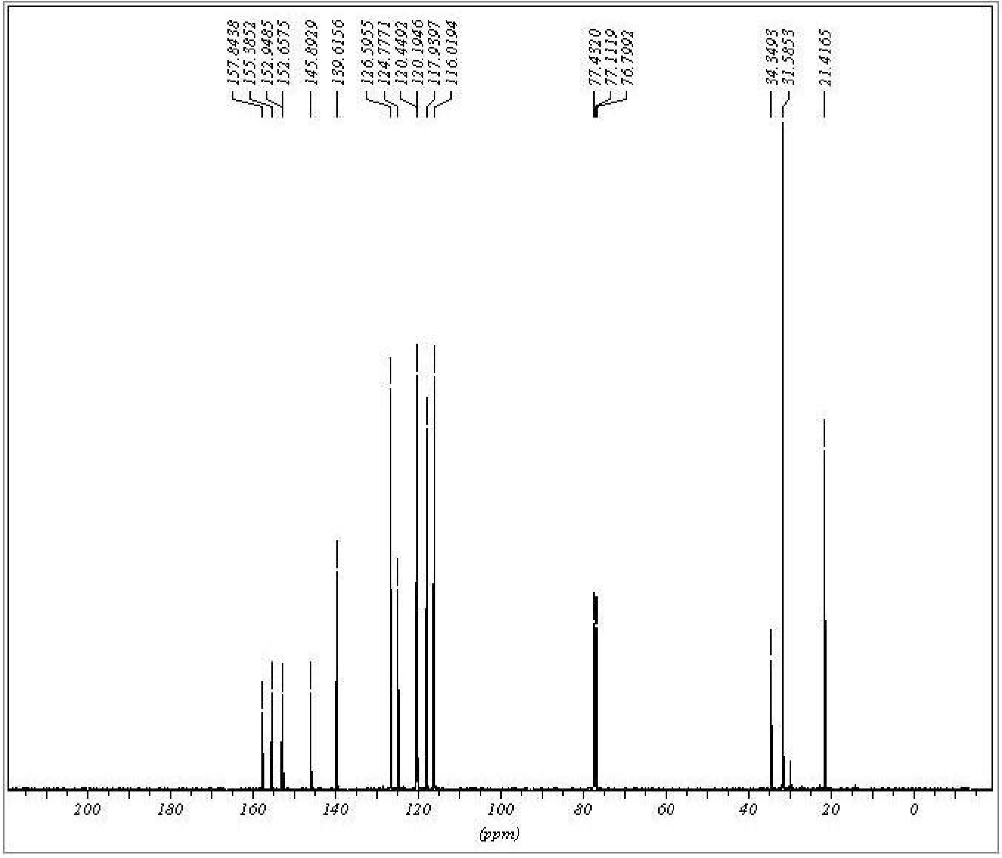


```
*** Current Data Parameters ***
NAME      :    feb06--1
EXPNO     :         511
PROCNO    :           1
*** Acquisition Parameters ***
DATE_t    :    16:20:25
DATE_d    :  Feb 06 2008
DE        :          6.0 usec
EXP       :      C13CPD
NS        :        1024
O1        :    10060.80 Hz
PROBHD    : 5 mm PAQNP Switch-
PULPROG   :      zgpg30
RG        : 724.0999756
SFO1      : 100.6228298 MHz
SOLVENT   :       CDCl3
SW        :    238.3238 ppm
SW_h      :   23980.815 Hz
TD        :       65536
TE        :       294.9 K
*** 1D NMR Plot Parameters ***
Start     :      219.17 ppm
Stop      :      -19.18 ppm
SR        :        0.00 Hz
SOLVENT   :           ?
```

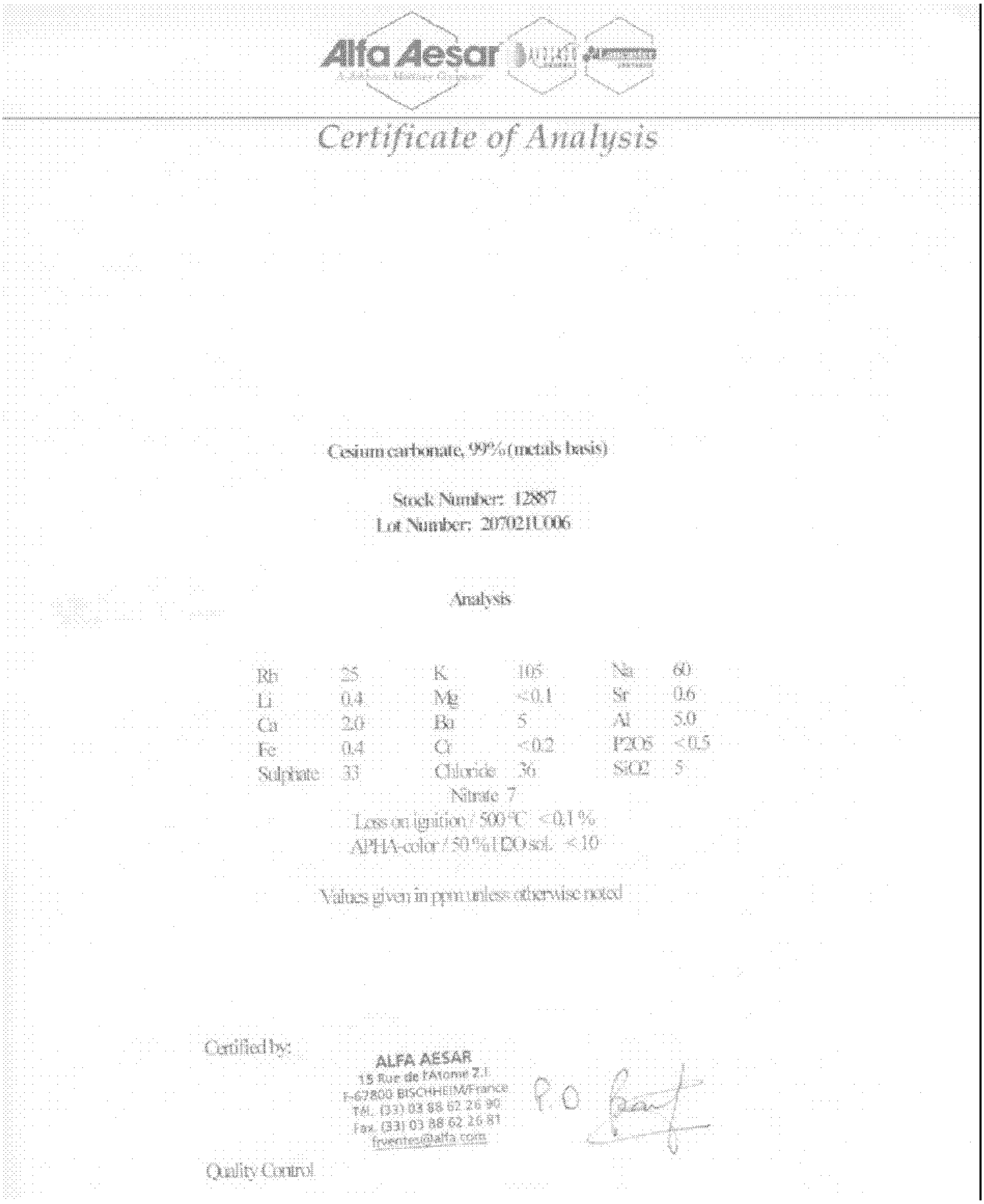
1-(4-(4-tert-butylphenoxy)phenoxy)-3,5-dimethylbenzene



```
*** Current Data Parameters ***
NAME      :      feb14--1
EXPNO     :           520
PROCNO    :             1
*** Acquisition  Parameters ***
DATE_t    :      03:25:46
DATE_d    :   Feb 14 2008
DE        :      6.0 usec
EXP       :        PROTON
NS        :            16
O1        :    2470.97 Hz
PROBHD    :5 mm PAQNP Switch-1
PULPROG   :          zg30
RG        :    28.5000000
SFO1      : 400.1324710 MHz
SOLVENT   :         CDCl3
SW        :   20.6885 ppm
SW_h      :   8278.146 Hz
TD        :         65536
TE        :       293.4 K
*** 1D NMR Plot Parameters ***
Start     :     10.44 ppm
Stop      :     -0.30 ppm
SR        :      72.57 Hz
SOLVENT   :             ?
```



```
*** Current Data Parameters ***
NAME      :      feb18--1
EXPNO     :           521
PROCNO    :             1
*** Acquisition  Parameters ***
DATE_t    :      11:14:21
DATE_d    :   Feb 18 2008
DE        :      6.0 usec
EXP       :        C13CPD
NS        :          1024
O1        :   10060.80 Hz
PROBHD    :5 mm PAQNP Switch-1
PULPROG   :        zgpg30
RG        :   724.0999756
SFO1      : 100.6228298 MHz
SOLVENT   :         CDCl3
SW        :  238.3238 ppm
SW_h      :  23980.815 Hz
TD        :         65536
TE        :       294.4 K
*** 1D NMR Plot Parameters ***
Start     :    219.17 ppm
Stop      :    -19.18 ppm
SR        :       0.00 Hz
SOLVENT   :             ?
```



Alfa Aesar

A Johnson Matthey Company

Certificate of Analysis

Cesium carbonate, 99% (metals basis)

Stock Number: 12887
Lot Number: 20702IU006

Analysis

Rb	25	K	105	Na	60
Li	0.4	Mg	<0.1	Sr	0.6
Ca	2.0	Ba	5	Al	5.0
Fe	0.4	Cr	<0.2	P_2O_5	<0.5
Sulphate	33	Chloride	36	SiO_2	5

Nitrate 7

Loss on ignition / 500 °C <0.1 %

APHA-color / 50 % H_2O sol. <10

Values given in ppm unless otherwise noted

Certified by:

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P. O

Quality Control