Biaryl Synthesis via Direct Arylation: Establishment of an Efficient Catalyst for Intramolecular Processes

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Supporting Information

General Methods. All experiments were carried out under an atmosphere of nitrogen. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ solutions using a Bruker AVANCE 300 spectrometer with Me_4Si as an internal standard. High-resolution mass spectra were obtained on a Kratos Concept IIH. Infra-Red analysis was performed with a Bruker EQUINOX 55. Unless otherwise specified, all reagents and solvents were used as is from commercial sources.

Bromo ethers 7 and 15[1], 11[2], 3[3] were prepared according to the general procedure and exhibited spectral data identical to literature values[1-3] Cyclization precursors 21[4] and 19[5] were prepared according, and exhibited spectral data identical, to literature.[4-5]

General procedure for the synthesis of bromo ethers 3, 7, 9, 11, 13, 15, 17:

To a mixture of K_2CO_3 (4.4g, 32mmol, 2eq.) and 4-chloro phenol (6.2g, 48mmol, 3eq.) was added 30mL of acetone in a 100mL round bottom flask equipped with a mechanical stir bar. To the stirring mixture was added 2-bromobenzyl bromide (4g, 16mmol, 1eq.) followed by heating to 50^0C overnight. The reaction mixture was then poured into a NaOH (2N) solution and extracted with ethyl acetate. The organic extracts were dried over $MgSO_4$, and concentrated under reduced pressure. Purification was done by flash chromatography using 15% ethyl acetate in hexanes to afford (2-Bromo phenyl)methyl 4-chlorophenyl ether **15**[1], as a clear oil in 90% yield (4.27g).

1-(2-Bromo-benzyloxy)-*p*-toluene (9)

R_f = 0.64 on silica gel (5% EtOAc:Hexanes); IR (ν_{max} /cm^{-1}) 3029 (weak), 1510, 1237, 1024, 816, 745 ; ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 2.26 (3H, s), 5.06 (2H, s), 6.85 (2H, m), 7.10 (3H, m), 7.27 (1H, td, *J*=8Hz & *J*=1Hz), 7.52 (2H, m); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 20.47, 69.37, 114.65, 122.17, 127.46, 128.78, 129.04, 129.93, 130.32, 132.49, 136.49, 156.29; HRMS calculated for $C_{14}H_{13}BrO$ (M+) 276.0163; Found : 276.0150

1-(2-Bromo-benzyloxy)-α,α,α-trifluorotoluene (13)

R_f = 0.62 on silica gel (5% EtOAc:Hexanes); IR (ν_{max} /cm^{-1}) 2925 (weak), 1320, 1248, 1108, 841, 750 ; ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 5.14 (2 H, s), 7.02 (2 H, d, *J*=9Hz), 7.17 (1 H, t, *J*=8Hz), 7.31 (1 H, d, *J*=7Hz), 7.52 (4 H, m);

^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS): 69.51, 114.85, 122.39, 123.34 (q, *J*=33Hz), 124.28 (q, *J*=271Hz), 126.98 (q, *J*=3Hz), 127.68, 128.87, 129.56, 132.77, 135.46. 160.82; HRMS calculated for $C_{14}H_{11}BrF_3O$ (M+) 329.9853; Found: 329.9867

1-(2-Bromo-benzyloxy)-naphthalene (17)
R_f = 0.55 on silica gel (5% EtOAc:Hexanes); IR (*ν_{max}* /cm^{-1}) 3053 (weak), 1364, 1246, 1096, 758 ; ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 5.33 (2H, s), 6.89 (1H, d, *J*=8Hz), 7.24 (1H, d, *J*=3Hz), 7.38 (2H, m), 7.49 (3H, m), 7.62 (1H, d, *J*=8Hz), 7.69 (1H, d, *J*=8Hz), 7.82 (1H, m), 8.38 (1H, m); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 69.46, 105.35, 120.75, 122.25, 125.34, 125.66, 125.83, 126.49, 127.53, 127.60, 128.72, 129.21, 132.64, 134.56, 136.38, 154.03; HRMS calculated for $C_{17}H_{13}BrO$ (M+) 312.0046; Found: 312.0150

1-Bromo-2-(2-phenoxy-ethyl)-benzene (23)
R_f = 0.50 on silica gel (5% EtOAc:Hexanes); IR (*ν_{max}* /cm^{-1}) 2938 (weak), 1240, 1036, 747 ; ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 3.22 (2H, t, J=7Hz), 4.17 (2H, t, *J*=7Hz), 6.91 (3H, m), 7.08 (1H, m), 7.26 (4H, m), 7.53 (1H, dd, *J*=9Hz & 1Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 35.99, 66.59, 114.47, 120.72, 124.63, 127.45, 128.26, 129.42, 131.29, 123.80, 137.49, 158.60; HRMS calculated for $C_{14}H_{13}BrO$ (M+) 276.0135; Found: 276.0150

***6H*-benzo[*c*]chromenes 8[1] and 16[1], 10[1], 4[3] were prepared according to the general procedure and exhibited spectral data identical to literature values.[1, 3] Cyclization product 22[6] and 20[5] as well as by product 5[3] exhibited spectral data identical to literature values.[3, 4, 6]**

General procedure for cyclization:

To a mixture of *crushed* K_2CO_3 (169mg, 1.22mmol) and bromo ether **15** (169mg, 0.61mmol) under nitrogen atmosphere was added 3mL of *N,N*-Dimethylacetamide (DMA) in a 10mL round bottom flask equipped with a mechanical stir bar. To the stirring reaction mixture was added 50µL of a $Pd(OAc)_2$ and Ligand[7] stock solution containing 7mg/mL $Pd(OAc)_2$ and 36mg/mL Ligand[7]. (Similar results are obtained if the palladium and ligand are weighed out exactly and placed in the reaction mixture prior to addition the solvent). The reaction mixture is then heated overnight at 125^{0}C. After the reaction was judged complete by TLC or GC/MS analysis, the heat source was removed and the reaction mixture was allowed to cool. The crude mixture was then loaded onto a silica gel flash chromatography column 10% ethyl acetate in hexanes as the eluent to afford 2-Chloro-*6H*-benzo[*c*]chromene **16**[1] in 92% yield (110mg).

4-Methyl-*6H*-benzo[*c*]chromene (12)
R_f = 0.43 on silica gel (5% EtOAc:Hexanes); IR (*ν_{max}* /cm^{-1}) 2921 (weak), 1421, 1249, 1195, 1020, 752; ^{1}NMR (300MHz, $CDCl_3$, 293K, TMS): 2.26 (3H, s), 5.08 (2H, s), 6.93 (1H, t, *J*=7Hz), 7.09 (2H, t, *J*=7Hz), 7.23 (1H, t, *J*=7Hz), 7.32 (1H, t, *J*=3Hz), 7.55 (1H, d, *J*=8Hz), 7.64 (1H, d, *J*=8Hz); ^{13}C NMR (75MHz, $CDCl_3$,

293K, TMS): 15.93, 68.33, 120.93, 121.41, 122.18, 122.41, 124.48, 126.64, 127.40, 128.32, 130.46, 130.77, 131.37, 152.91; HRMS calculated for $C_{14}H_{12}O$ (M+) 196.0869; Found: 196.0888

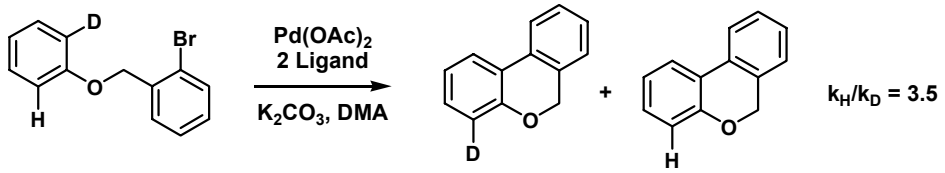
2-Trifluoromethyl-*6H*-benzo[*c*]chromene (14)
R_f = 0.43 on silica gel (5% EtOAc:Hexanes); IR (ν_{max} /cm^{-1}) 2850 (weak), 1315, 1250, 1112, 752 ^{1}NMR (300MHz, $CDCl_3$, 293K, TMS): 5.12 (2H, s), 7.01 (1H, d, *J*=8Hz), 7.11 (1H, m), 7.33 (2H, m), 7.44 (1H, m), 7.66 (1H, d, *J*=7Hz), 7.93 (1H, s); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS): 68.50, 117.84, 120.61 (q, *J*=4Hz), 122.17, 123.07, 124.32 (q, *J*=33Hz), 124.46 (q, *J*=272Hz), 124.77, 126.30 (q, *J=4*Hz), 128.56, 128.73, 130.98, 157.22; HRMS calculated for $C_{14}H_9F_3O$ (M+) 250.0601; Found: 250.0605

***6H*-Dibenzo[*c,h*]chromene (18)**
R_f = 0.47 on silica gel (5% EtOAc:Hexanes); IR (ν_{max} /cm^{-1}) 2870 (weak), 1395, 1351, 1096, 758; ^{1}NMR (300MHz, $CDCl_3$, 293K, TMS): 5.23 (2H, s), 7.11 (1H, d, *J*=7Hz), 7.22 (1H, t, *J*=2Hz), 7.33 (1H, t, *J*=3Hz), 7.45 (3H, m), 7.65 (1H, d, *J*=3Hz), 7.75 (2H, m), 8.25 (1H, m); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS): 68.73, 117.07, 120.90, 121.48, 121.85, 122.19, 124.52, 125.28, 125.71, 126.55, 127.29, 127.57, 128.45, 130.56, 130.62, 134.29, 150.23; HRMS calculated for $C_{17}H_{12}O$ (M+) 232.0871; Found: 232.0888

Dibenzoxapine (24)
R_f = 0.36 on silica gel (5% EtOAc:Hexanes); IR (ν_{max} /cm^{-1}) 2870 (weak), 1309, 1252, 1030, 758; ; ^{1}NMR (300MHz, $CDCl_3$, 293K, TMS): 2.82 (2H, t, *J*=6Hz), 4.57 (2H, t, *J*=6Hz), 7.14 (1H, d, *J*=8Hz), 7.29 (4H, m), 7.41 (3H, m); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS): 33.39, 78.42, 122.31, 124.55, 127.35, 127.71, 128.03, 128.13, 129.02, 129.21, 135.24, 137.37, 138.86, 154.33; HRMS calculated for $C_{14}H_{12}O$ (M+) 196.0893; Found: 196.0888

(1,1'-Biphenyl-2-yl)di(4-trifluoromethylphenyl)phosphine (27)
R_f = 0.52 on silica gel (5% EtOAc:Hexanes); IR (ν_{max} /cm^{-1}) 2922 (medium), 2860, 1610, 1318, 1107, 1064, 1011, 825, 748, 700 ; ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 7.01-7.06 (1H, m), 7.15-7.19 (2H, m), 7.28-7.47 (10H, m), 7.53-7.57 (4H, m); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : Complex peak patterns due to fluorine and phosphorous coupling; 118.59, 122.20, 125.14, 125.18, 125.23, 125.27, 125.32, 125.36, 125.48, 125.55, 125.81, 127.55, 127.63, 127.81, 127.84, 129.42, 129.59, 129.65, 129.78, 129.80, 130.17, 130.41, 130.48, 130.60, 131.03, 131.46, 133.67, 133.83, 134.04, 134.10, 134.22, 134.30, 134.39, 134.47, 141.19, 141.28, 141.92, 142.13, 148.50, 148.89; ^{19}F NMR (282.2MHz, $CDCl_3$, 293K, TFA): 12.86 ; ^{31}P NMR (121.4MHz, $CDCl_3$, 293K, HMPA): -13.50; HRMS calculated for $C_{26}H_{17}PF_6$ (M+) 474.0972; Found : 474.0943; MP: 137-138ºC (Hex)

Intramolecular Kinetic Isotope Effect Experiment



(2-bromobenzyloxy)-2-*d*-benzene (A)

R_f = 0.64 on silica gel (5% EtOAc:Hexanes); IR (ν_{max} /cm^{-1}) 3030 (weak), 1515, 1240, 1028, 819, 735 ; ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 5.14 (2H, s), 6.98 (2H, m), 7.18 (1H, td, *J*=7.6 et *J*=1.6), 7.31 (3H, m), 7.57 (2H, m); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS): 69.27, 114.87, 121.16, 122.23, 127.56, 128.84, 129.18, 129.43, 129.53, 132.59, 136.33, 158.36; HRMS calculated for $C_{10}H_{13}DBrO$ (M+) 263.0055; Found 263.0066;

Crude NMR of the experiment shown at the end of experimental data.

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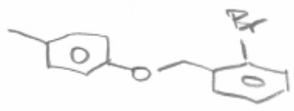
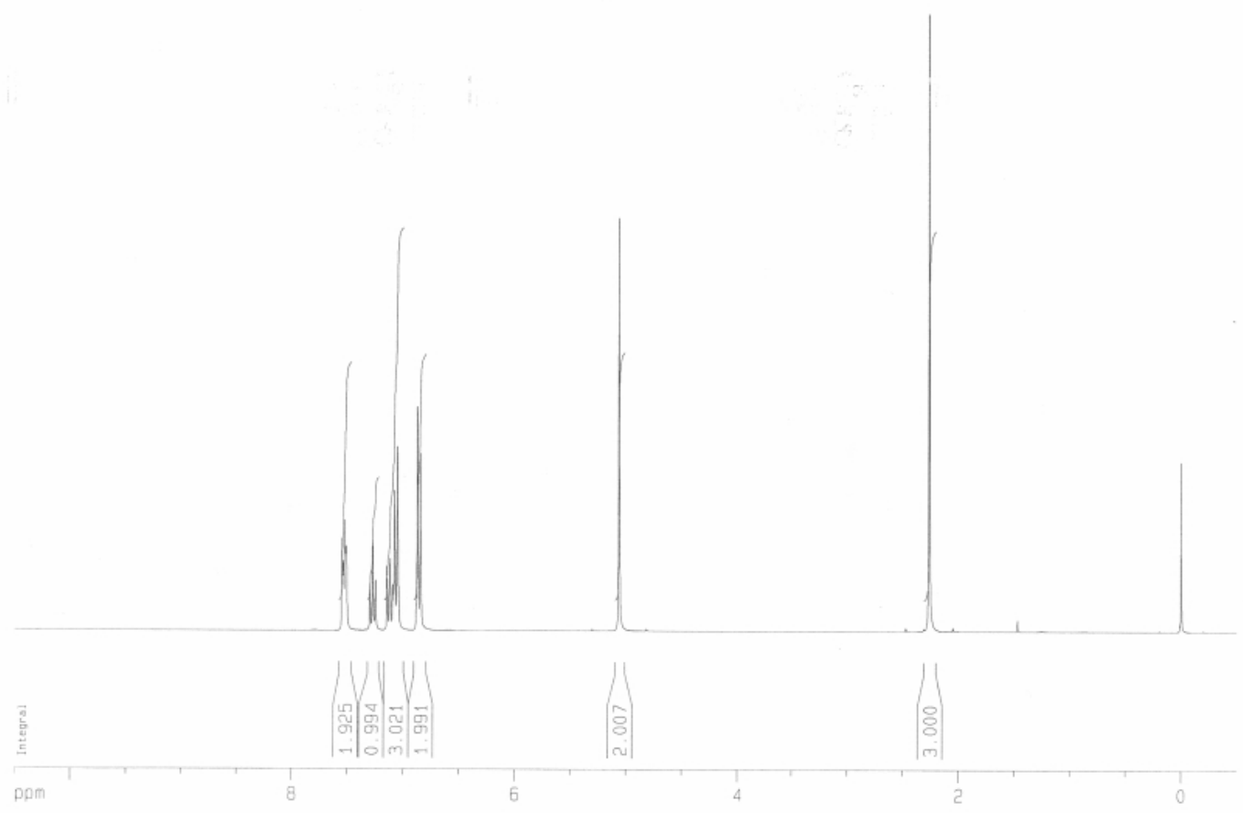
[1] Bowman, R., Mann, E., Parr, J., *J. Chem. Soc., Perkin Trans. 1,* **2000**, 2991-2999
[2] Rossi, R., Carpita, A., Pazzi, P., Mannina, L., Valensin, D. *Tetrahedron,* **1999**, *55*, 11343-11364
[3] Ames, D.E.., Opalko, A., *Tetrahedron,* **1984**, 40, 1919-1925
[4] Parham, W.E., Jones, L.D., Sayed, Y.A., *J. Org. Chem.* **1976**, *41*,1184
[5] Harayama, T., Akiyama, T.,Akamatsu, H., Kazuko., Abe, H., Takeuchi, Y., *Synthesis*, **2001**, *3*, 444-450
[6] Cas No : 776-35-2
[7] 2-(Diphenylphosphino)-2'-(N,N-dimethyl-amino)byphenyl is the ligand used for all cyclization reactions



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FIDRES          0.165407 Hz
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RG                  45.3
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TE                300.0 K
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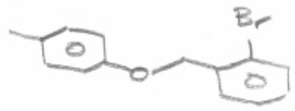
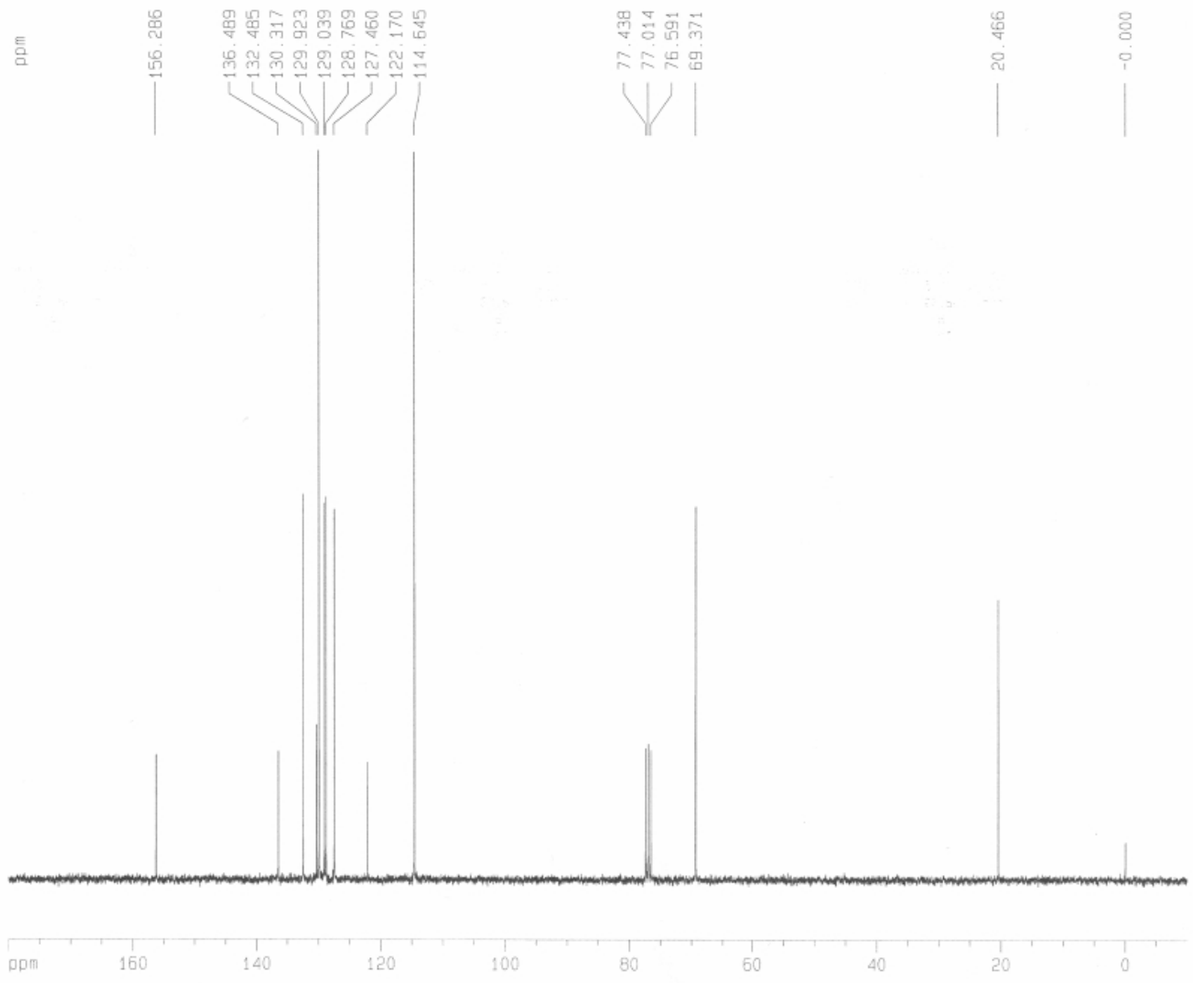


13C with proton decoupling

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FIDRES        0.548877 Hz
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d12           0.00002000 sec

========== CHANNEL f1 ============
NUC1                13C
P1                 5.00 usec
PL1               -6.00 dB
SFO1         75.4752653 MHz

========== CHANNEL f2 ============
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NUC2                1H
PCPD2             70.00 usec
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PL12              13.48 dB
PL13              15.63 dB
SFO2        300.1314860 MHz

F2 - Processing parameters
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1D NMR plot parameters
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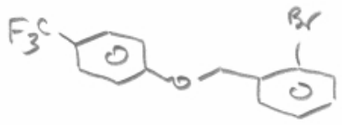

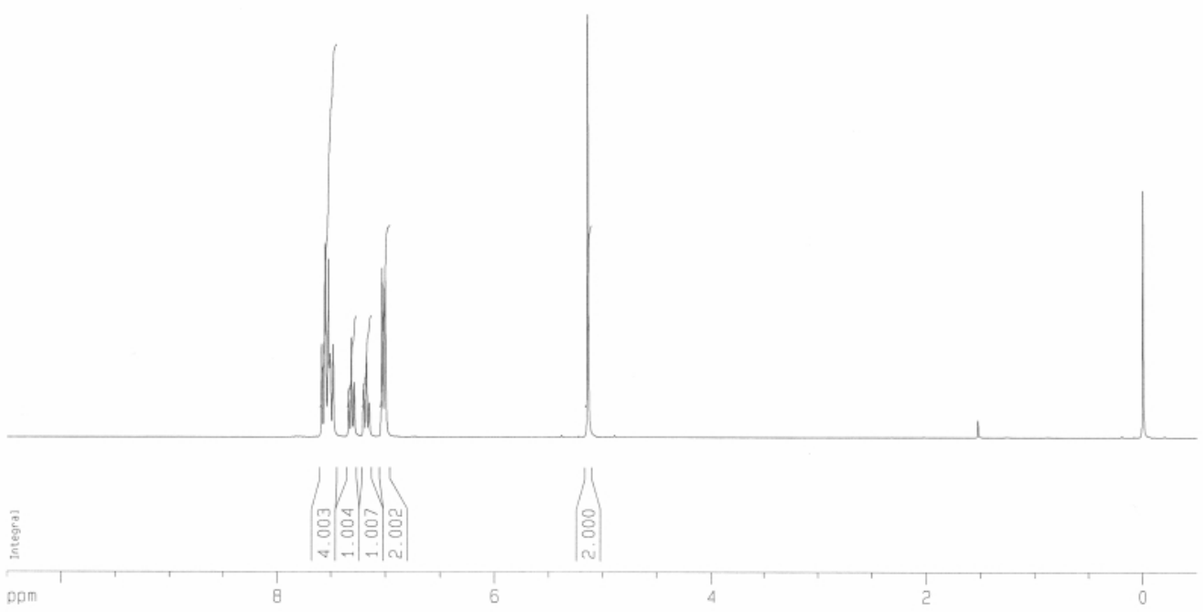


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F2 - Processing parameters
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1D NMR plot parameters
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F2P              -0.500 ppm
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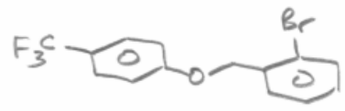
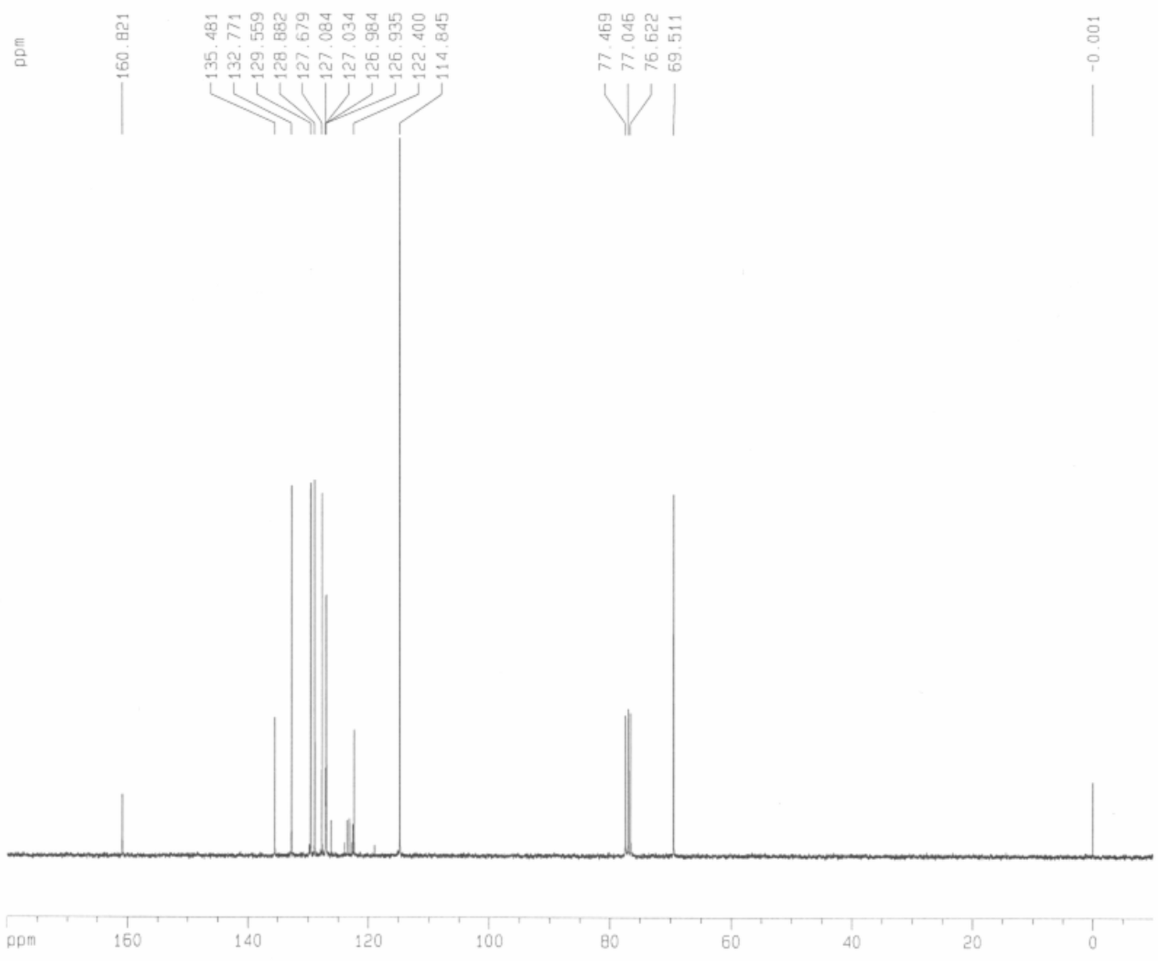


13C with proton decoupling

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FIDRES        0.548877 Hz
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============ CHANNEL f1 =============
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PL1              -6.00 dB
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============ CHANNEL f2 =============
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NUC2               1H
PCPD2            70.00 usec
PL2              -3.00 dB
PL12             13.48 dB
PL13             15.63 dB
SF02        300.1314860 MHz

F2 - Processing parameters
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SF           75.4677484 MHz
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SSB                   0
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1D NMR plot parameters
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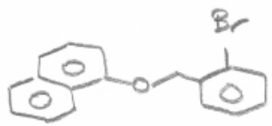

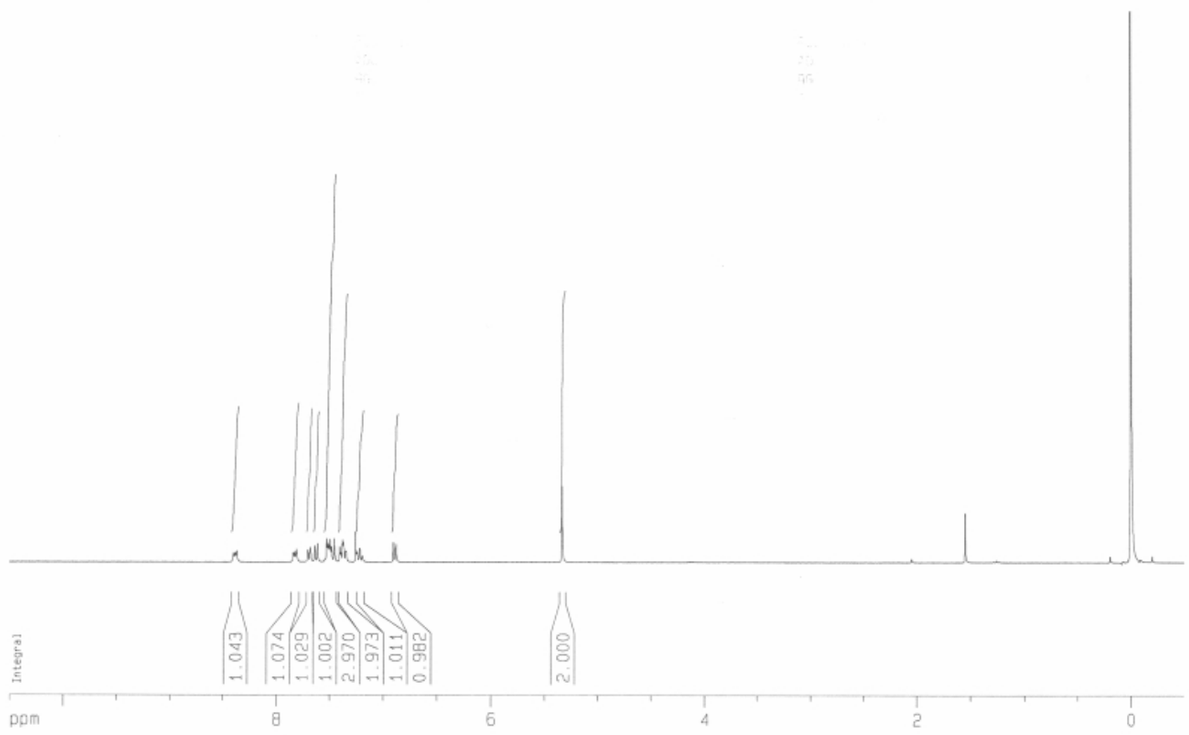


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FIDRES        0.165407 Hz
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RG               406.4
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TE              300.0 K
D1           1.00000000 sec

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F2 - Processing parameters
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1D NMR plot parameters
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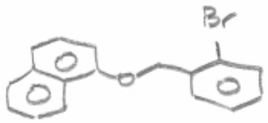
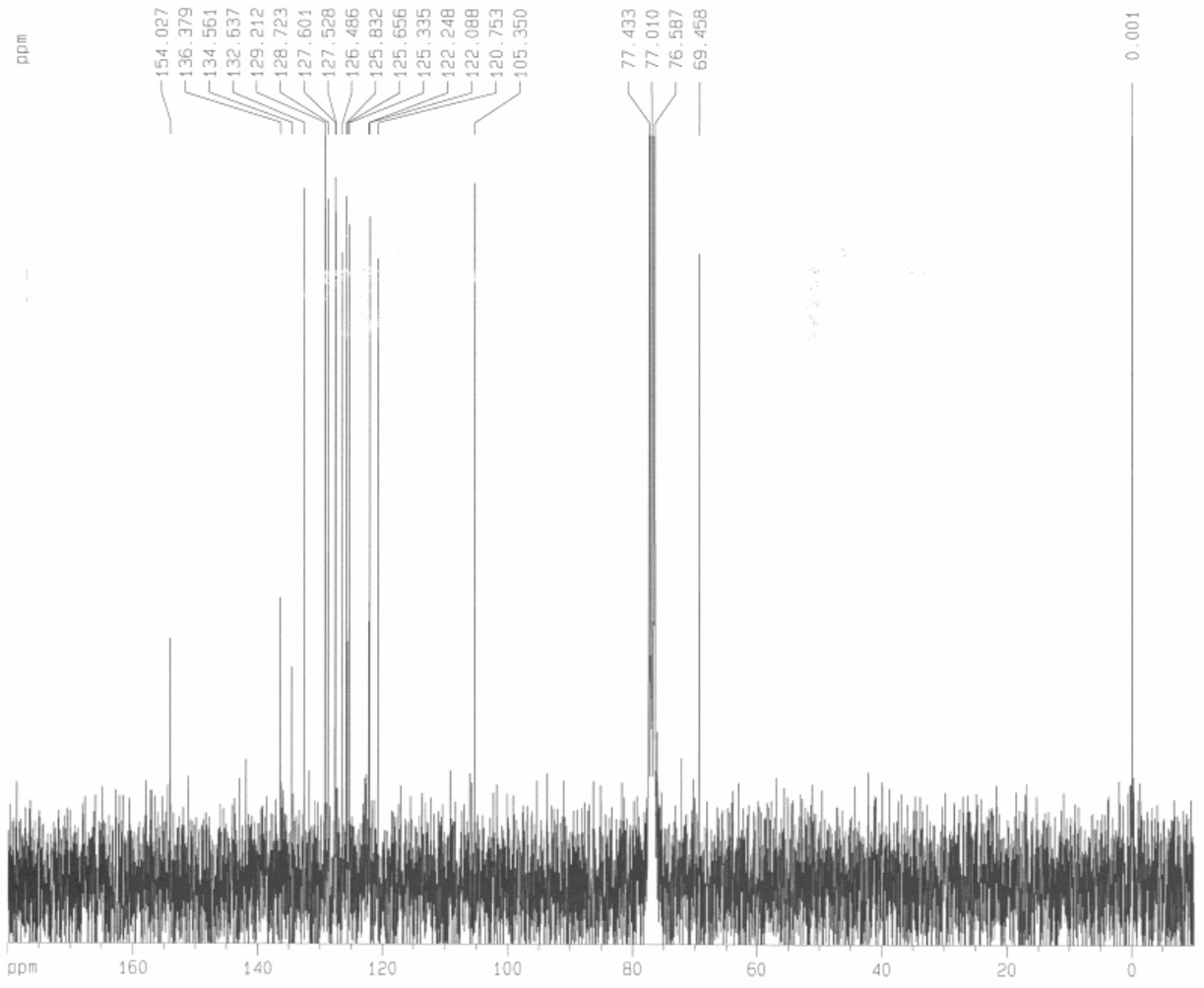


13C with proton decoupling



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FIDRES	0.548877 Hz
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DW	27.800 usec
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D1	1.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	5.00 usec
PL1	-6.00 dB
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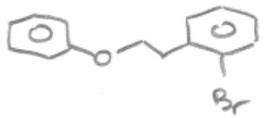
CPDPRG2	waltz16
NUC2	1H
PCPD2	70.00 usec
PL2	-3.00 dB
PL12	13.48 dB
PL13	15.63 dB
SF02	300.1314860 MHz

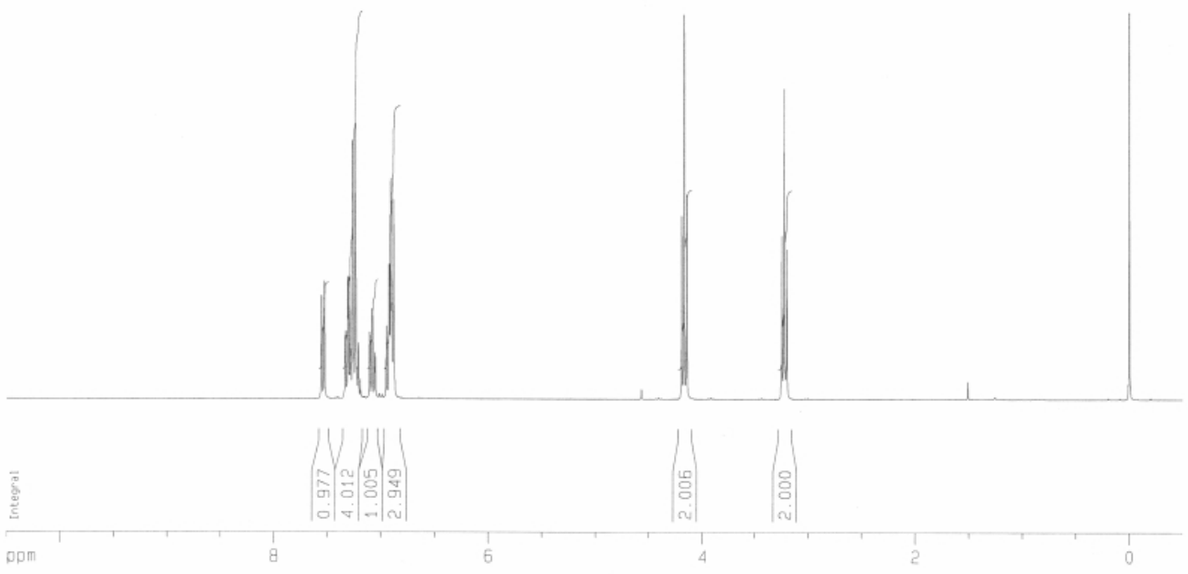
F2 - Processing parameters

SI	65536
SF	75.4677473 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

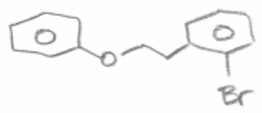
1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	180.000 ppm
F1	13584.20 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.50000 ppm/cm
HZCM	716.94360 Hz/cm

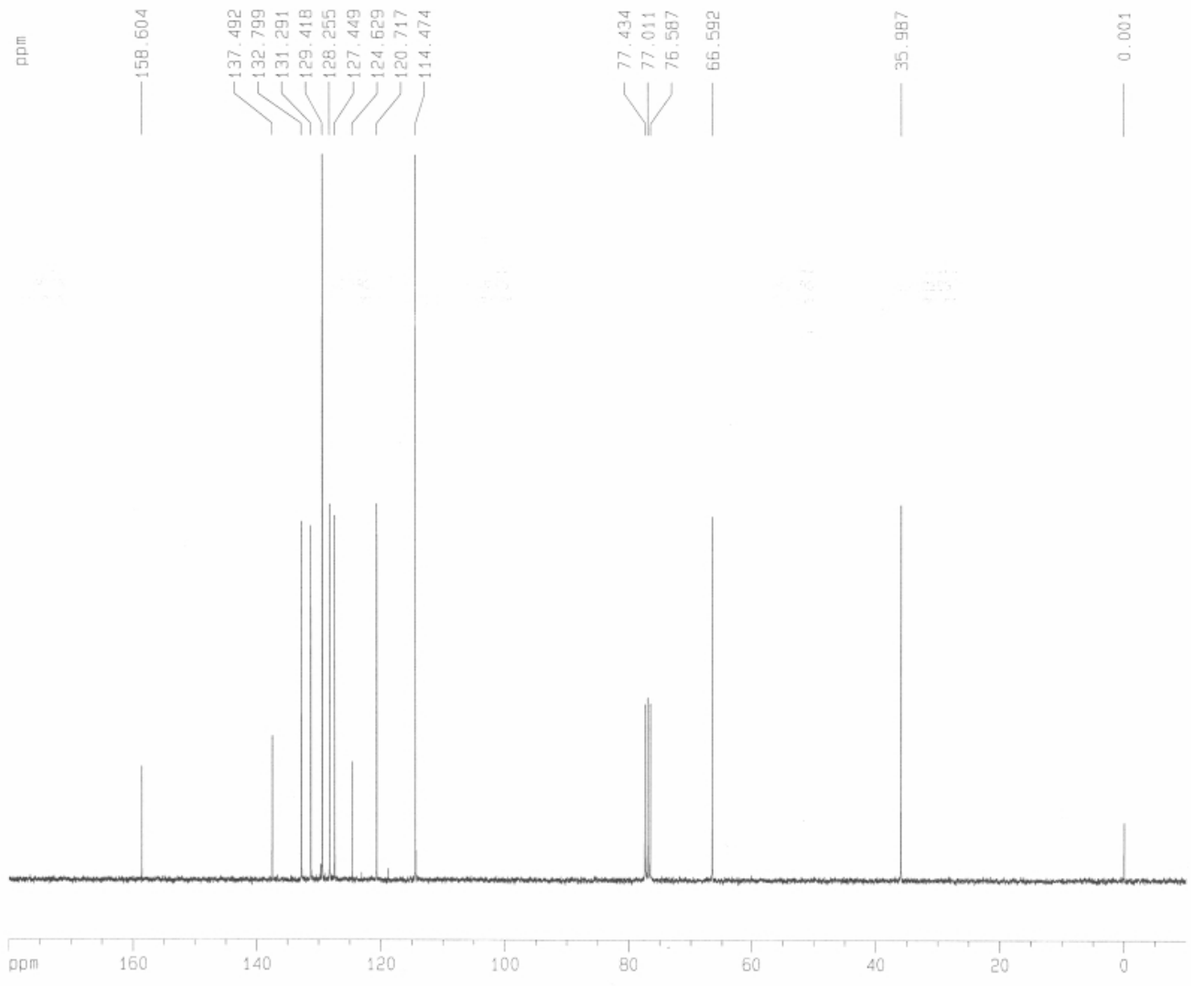




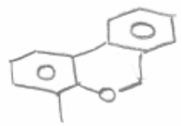

```
Current Data Parameters
NAME                  LCC7mbr
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20031215
Time                   11.02
INSTRUM                av300
PROBHD   5 mm QNP  1H/1
PULPROG                zg30
TD                     30720
SOLVENT                CDCl3
NS                        16
DS                         0
SWH                5081.301 Hz
FIDRES             0.165407 Hz
AQ                 3.0228980 sec
RG                      71.8
DW                    98.400 usec
DE                     6.00 usec
TE                    300.0 K
D1                1.00000000 sec

============ CHANNEL f1 =============
NUC1                       1H
P1                      10.50 usec
PL1                     -3.00 dB
SFO1              300.1319477 MHz

F2 - Processing parameters
SI                         65536
SF                300.1300152 MHz
WDW                        EM
SSB                         0
LB                      0.10 Hz
GB                          0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                      6.50 cm
F1P                   10.500 ppm
F1                   3151.36 Hz
F2P                   -0.500 ppm
F2                   -150.06 Hz
PPMCM                 0.55000 ppm/cm
HZCM                165.07150 Hz/cm
```

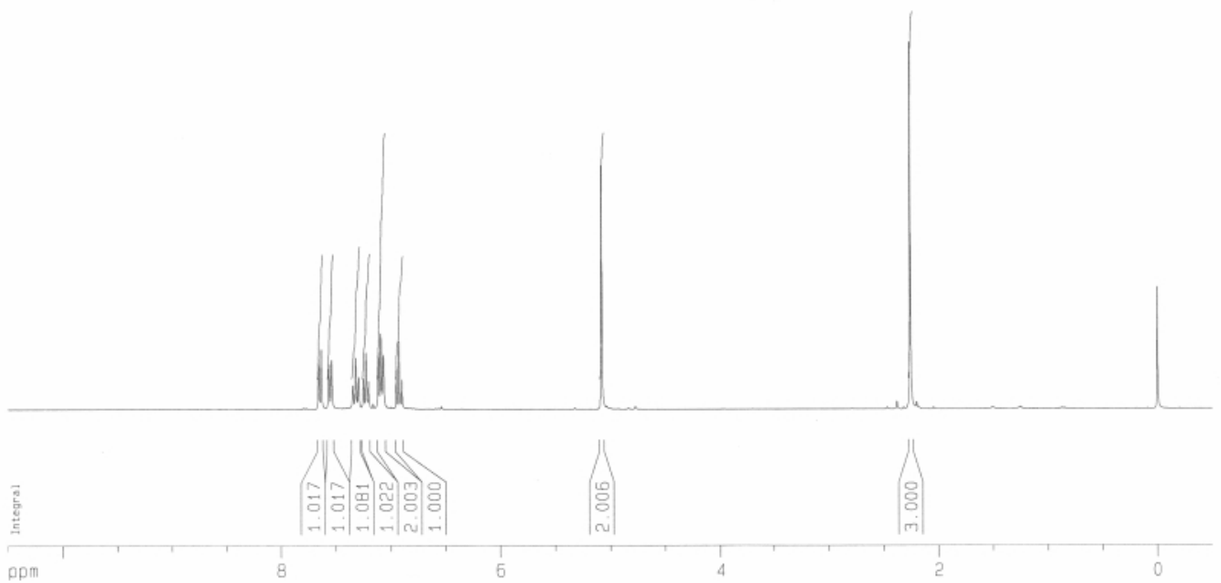


13C with proton decoupling

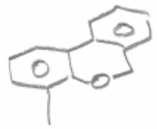



```
Current Data Parameters
NAME                LCC7mbr
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20031215
Time                  11.12
INSTRUM                av300
PROBHD   5 mm QNP  1H/1
PULPROG               zgpg30
TD                     32768
SOLVENT                CDCl3
NS                       270
DS                         0
SWH                17985.611 Hz
FIDRES             0.548877 Hz
AQ                 0.9110004 sec
RG                    2298.8
DW                    27.800 usec
DE                     6.00 usec
TE                    300.0 K
D1                 1.00000000 sec
d11                0.03000000 sec
d12                0.00002000 sec

============ CHANNEL f1 =============
NUC1                     13C
P1                      5.00 usec
PL1                    -6.00 dB
SF01               75.4752653 MHz

============ CHANNEL f2 =============
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                    -3.00 dB
PL12                   13.48 dB
PL13                   15.63 dB
SF02              300.1314860 MHz

F2 - Processing parameters
SI                       65536
SF                 75.4677553 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
CY                       12.50 cm
F1P                     180.000 ppm
F1                    13584.20 Hz
F2P                    -10.000 ppm
F2                     -754.68 Hz
PPMCM                  9.50000 ppm/cm
HZCM                 716.94373 Hz/cm
```

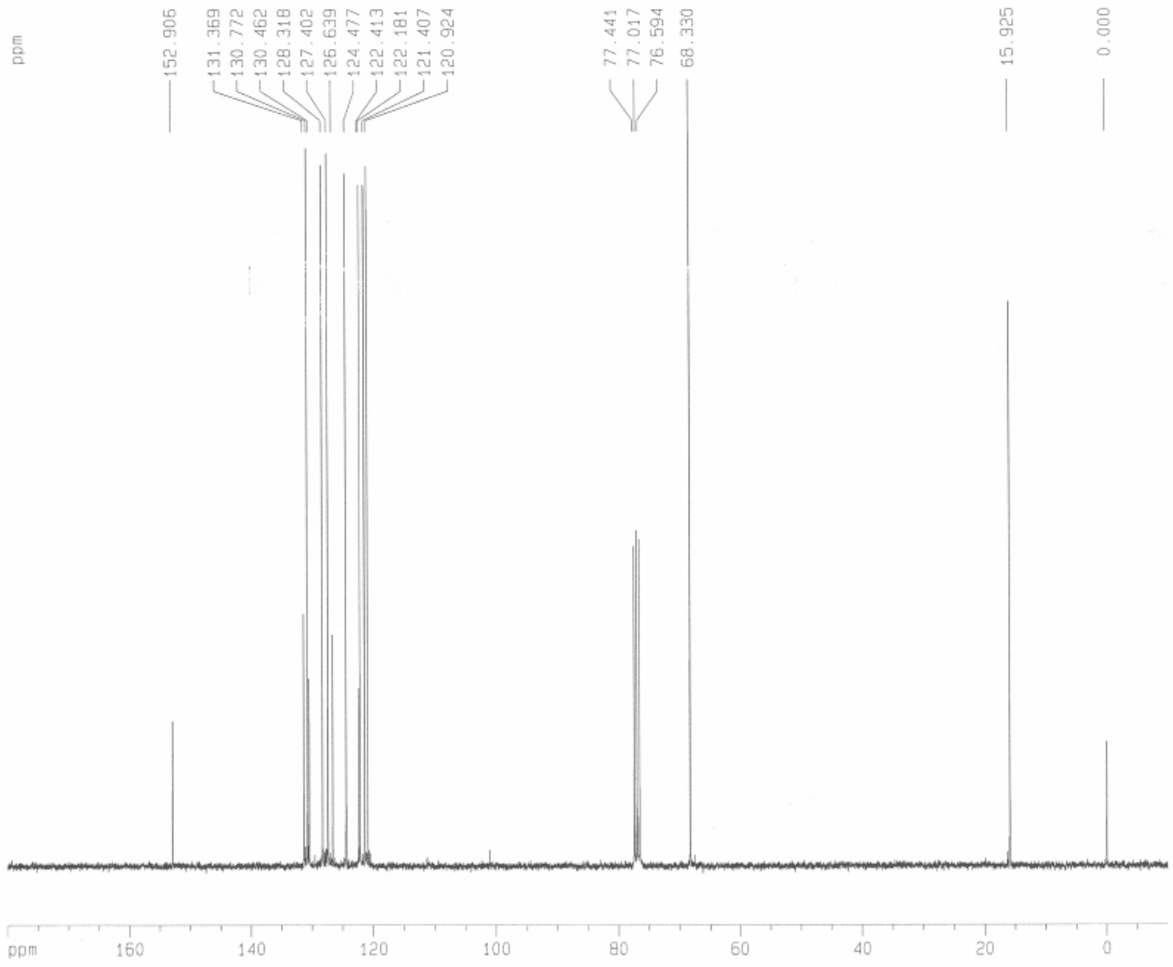




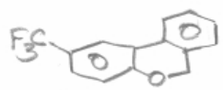

```
Current Data Parameters
NAME            LCC-II-10
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20031020
Time                19.05
INSTRUM             av300
PROBHD   5 mm QNP  1H/1
PULPROG              zg30
TD                  30720
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              5081.301 Hz
FIDRES           0.165407 Hz
AQ               3.0228980 sec
RG                     64
DW                98.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                   1H
P1                 10.50 usec
PL1                -3.00 dB
SFO1         300.1319477 MHz

F2 - Processing parameters
SI                  65536
SF           300.1300232 MHz
WDW                    EM
SSB                     0
LB                 0.10 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  6.00 cm
F1P               10.500 ppm
F1                3151.37 Hz
F2P                -0.500 ppm
F2                -150.06 Hz
PPMCM             0.55000 ppm/cm
HZCM            165.07152 Hz/cm
```

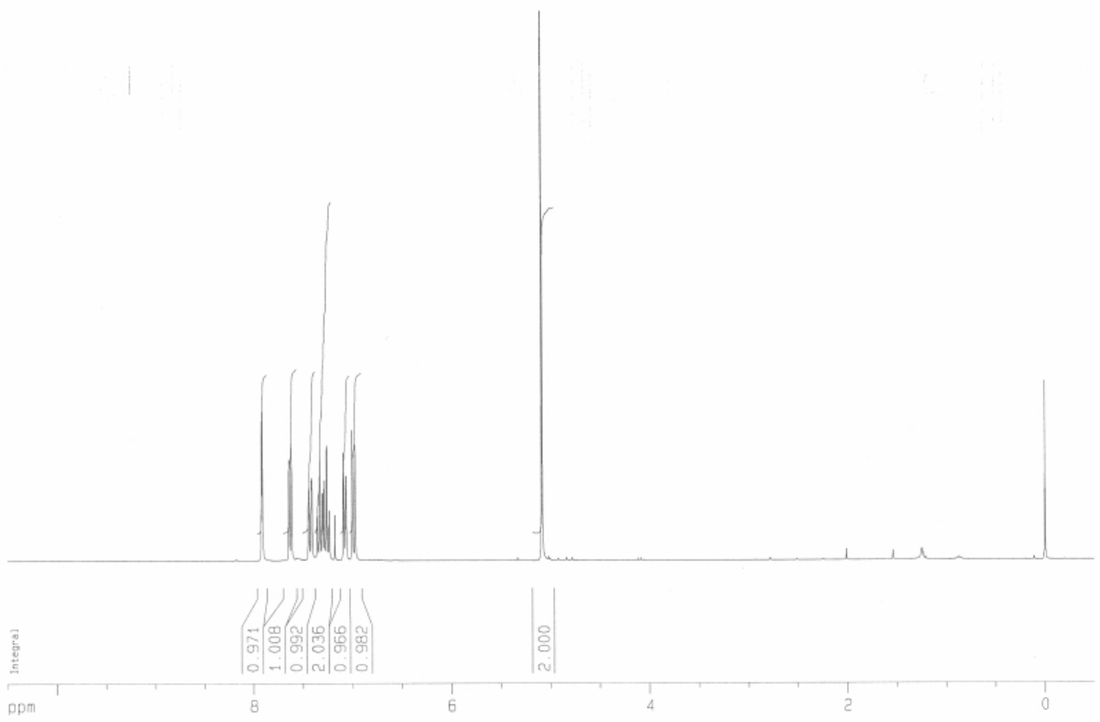


13C with proton decoupling

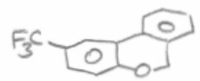



```
Current Data Parameters
NAME            LCC-II-10
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20031020
Time                19.25
INSTRUM             av300
PROBHD   5 mm GNP  1H/1
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                     638
DS                       0
SWH              17985.611 Hz
FIDRES           0.548877 Hz
AQ               0.9110004 sec
RG                  3649.1
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1               1.00000000 sec
d11              0.03000000 sec
d12              0.00002000 sec

============ CHANNEL f1 =============
NUC1                   13C
P1                    5.00 usec
PL1                  -6.00 dB
SFO1            75.4752653 MHz

============ CHANNEL f2 =============
CPDPRG2             waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -3.00 dB
PL12                 13.48 dB
PL13                 15.63 dB
SFO2           300.1314860 MHz

F2 - Processing parameters
SI                     65536
SF              75.4677561 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                     1.40

1D NMR plot parameters
CX                   20.00 cm
CY                   12.50 cm
F1P                180.000 ppm
F1                13584.20 Hz
F2P                -10.000 ppm
F2                 -754.68 Hz
PPMCM              9.50000 ppm/cm
HZCM              716.94373 Hz/cm
```

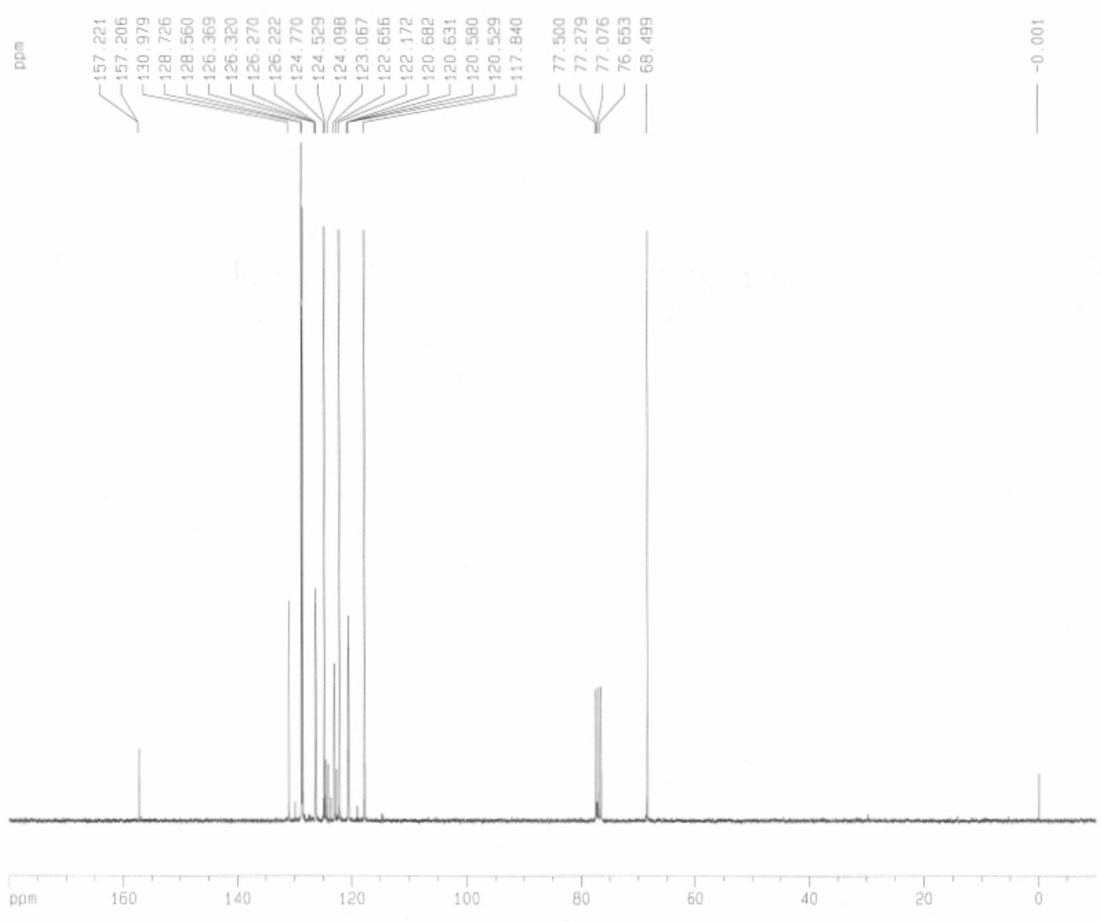




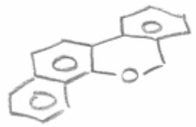

```
Current Data Parameters
NAME          LCC-III-69
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20040212
Time               15.38
INSTRUM            av300
PROBHD   5 mm QNP  1H/1
PULPROG            zg30
TD                30720
SOLVENT           CDCl3
NS                   16
DS                    0
SWH           5081.301 Hz
FIDRES        0.165407 Hz
AQ            3.0228980 sec
RG                 45.3
DW               98.400 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                10.50 usec
PL1               -3.00 dB
SFO1         300.1319477 MHz

F2 - Processing parameters
SI                 65536
SF          300.1300176 MHz
WDW                   EM
SSB                   0
LB                 0.10 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                10.00 cm
F1P              10.500 ppm
F1              3151.36 Hz
F2P              -0.500 ppm
F2               -150.06 Hz
PPMCM          0.55000 ppm/cm
HZCM         165.07150 Hz/cm
```

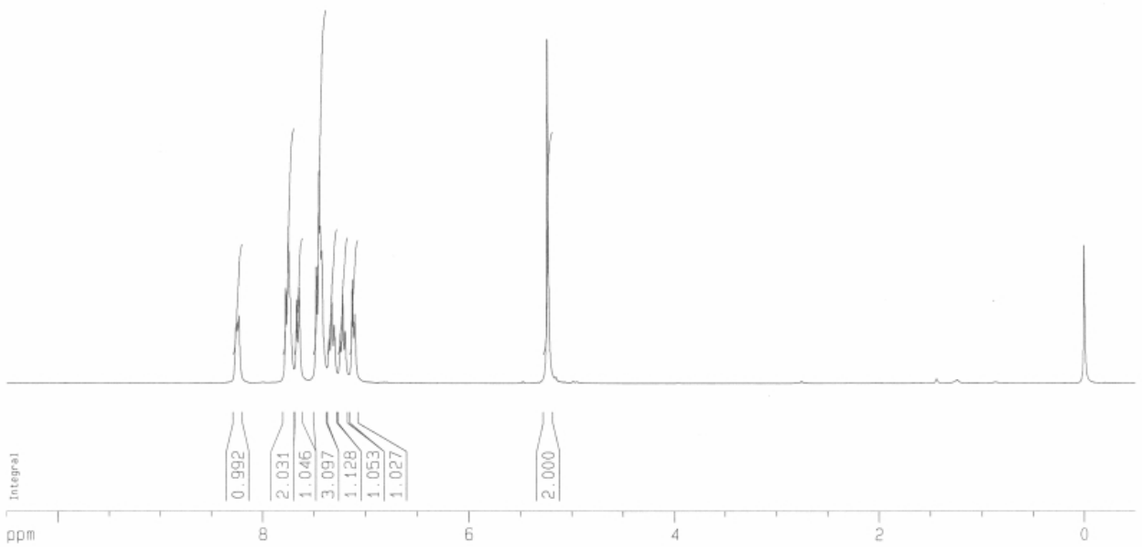


13C with proton decoupling

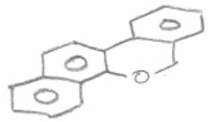


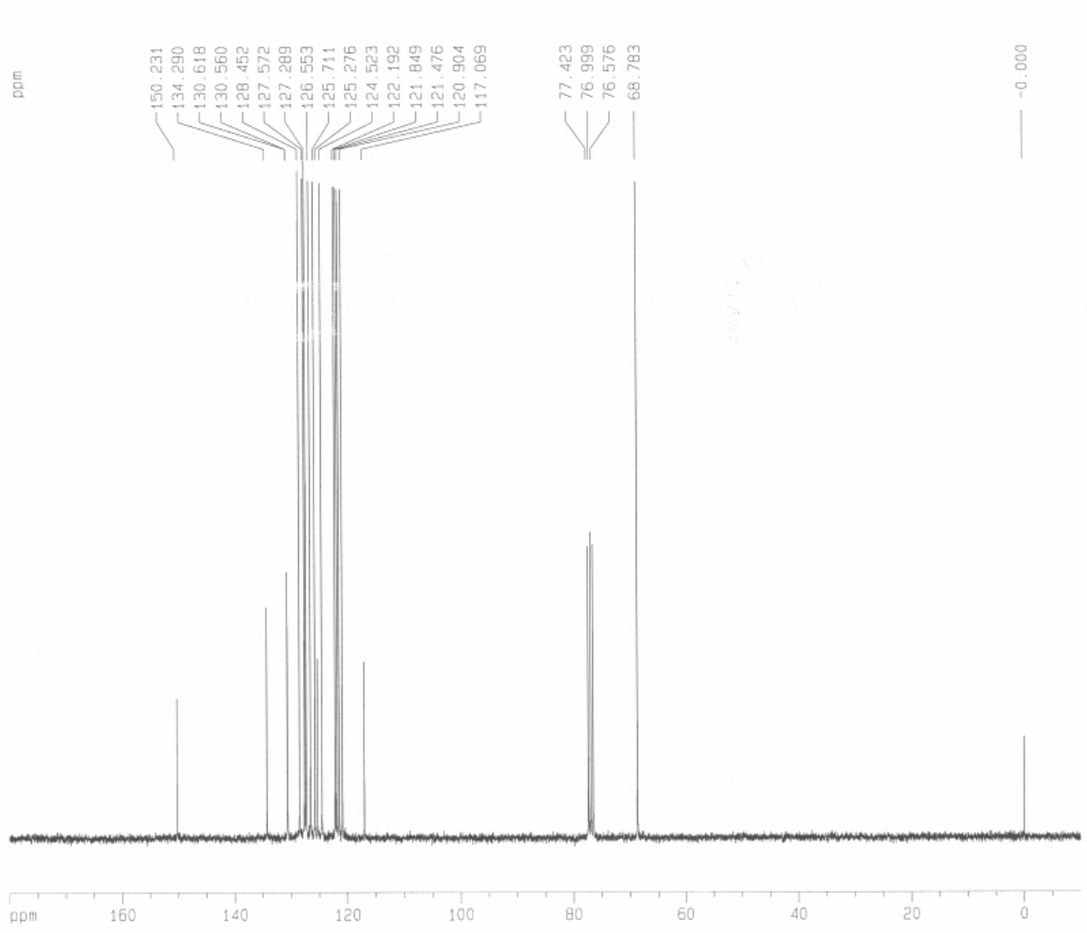

```
Current Data Parameters
NAME          LCC-III-69
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20040212
Time               15.49
INSTRUM            av300
PROBHD   5 mm GNP 1H/1
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  335
DS                    0
SWH           17985.611 Hz
FIDRES         0.548877 Hz
AQ             0.9110004 sec
RG                3649.1
DW                27.800 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 5.00 usec
PL1               -6.00 dB
SFO1          75.4752653 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2             70.00 usec
PL2               -3.00 dB
PL12              13.48 dB
PL13              15.63 dB
SFO2         300.1314860 MHz

F2 - Processing parameters
SI                 65536
SF            75.4677468 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P              180.000 ppm
F1             13584.20 Hz
F2P              -10.000 ppm
F2              -754.68 Hz
PPMCM             9.50000 ppm/cm
HZCM            716.94360 Hz/cm
```






```
Current Data Parameters
NAME          LCC-II-29
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20031024
Time              17.18
INSTRUM           av300
PROBHD   5 mm QNP 1H/1
PULPROG             zg30
TD                30720
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            5081.301 Hz
FIDRES         0.165407 Hz
AQ             3.0228980 sec
RG                   64
DW               98.400 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                 1H
P1                10.50 usec
PL1               -3.00 dB
SF01        300.1319477 MHz

F2 - Processing parameters
SI                65536
SF          300.1300339 MHz
WDW                  EM
SSB                   0
LB                0.10 Hz
GB                    0
PC                1.00

1D NMR plot parameters
CX               20.00 cm
CY                6.00 cm
F1P              10.500 ppm
F1             3151.37 Hz
F2P              -0.500 ppm
F2             -150.06 Hz
PPMCM          0.55000 ppm/cm
HZCM         165.07152 Hz/cm
```





Current Data Parameters
NAME LCC-II-29
EXPNO 2
PROCNO 1

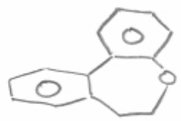
F2 - Acquisition Parameters
Date_ 20031024
Time 17.46
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 528
DS 0
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 6502
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

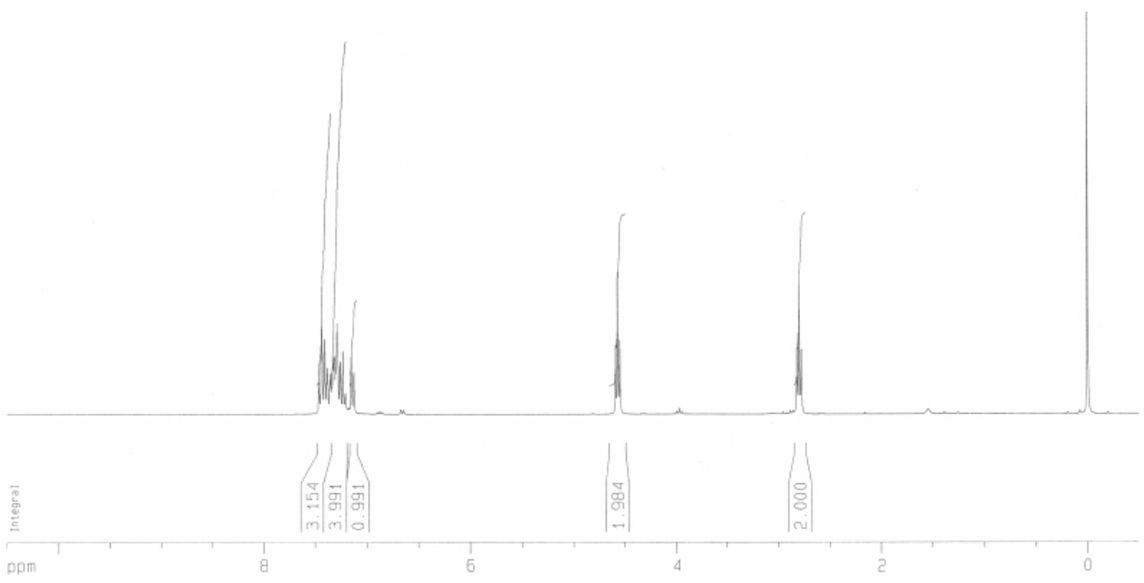
========== CHANNEL f1 ==========
NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SFO1 75.4752653 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 13.48 dB
PL13 15.63 dB
SFO2 300.1314860 MHz

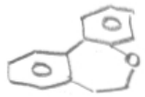
F2 - Processing parameters
SI 65536
SF 75.4677608 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 180.000 ppm
F1 13584.20 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.50000 ppm/cm
HZCM 716.94373 Hz/cm

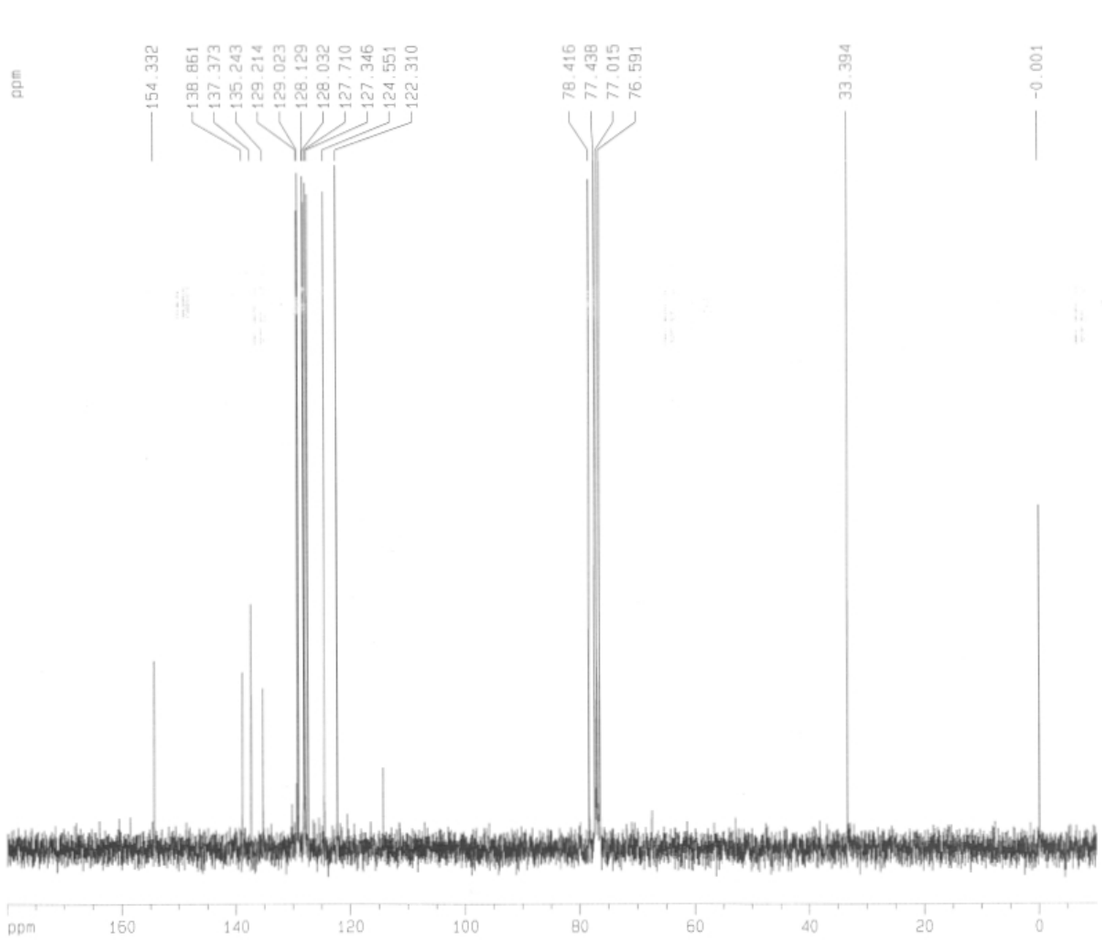




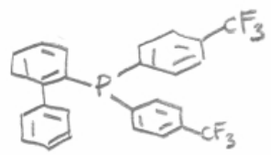

```
Current Data Parameters
NAME          LCC-III-20
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20040212
Time               15.54
INSTRUM            av300
PROBHD   5 mm QNP  1H/1
PULPROG            zg30
TD                30720
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            5081.301 Hz
FIDRES        0.165407 Hz
AQ            3.0228980 sec
RG                  181
DW               98.400 usec
DE                6.00 usec
TE               300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                1H
P1                10.50 usec
PL1               -3.00 dB
SFO1        300.1319477 MHz

F2 - Processing parameters
SI                 65536
SF          300.1300019 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                20.00 cm
CY                 7.00 cm
F1P              10.500 ppm
F1               3151.36 Hz
F2P               -0.500 ppm
F2               -150.06 Hz
PPMCM          0.55000 ppm/cm
HZCM         165.07150 Hz/cm
```

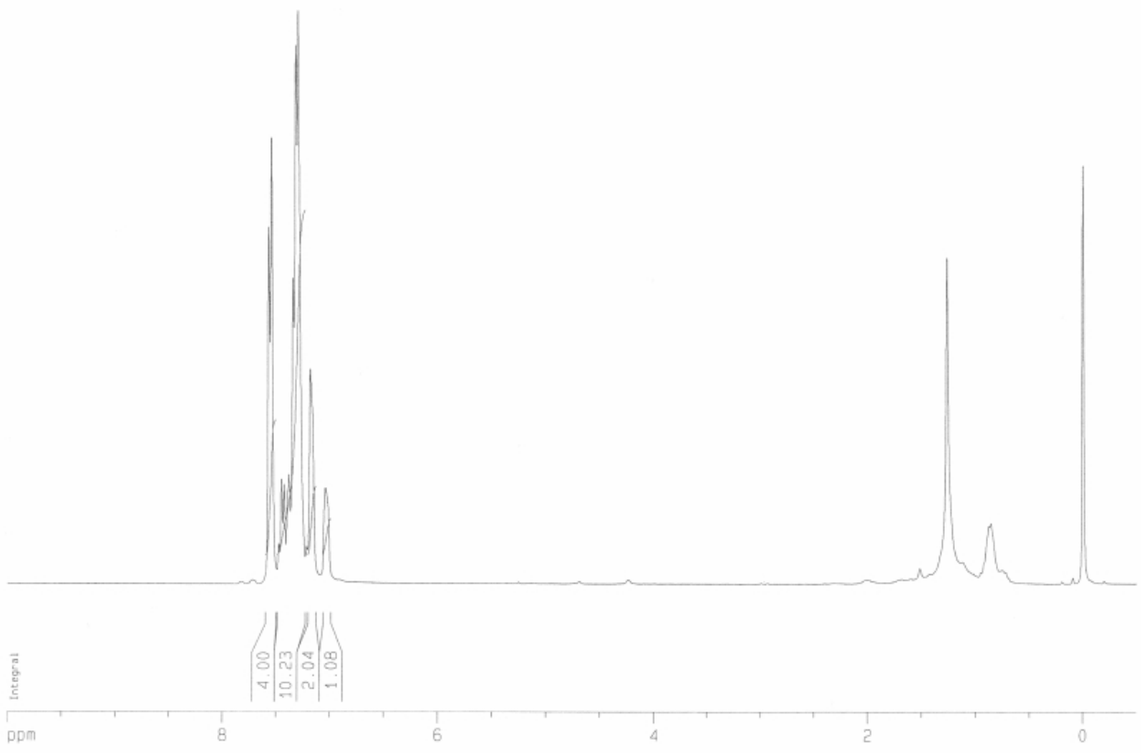


13C with proton decoupling

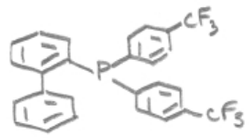



```
Current Data Parameters
NAME          LCC-III-20
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20040212
Time               15.58
INSTRUM            av300
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  276
DS                    0
SWH           17985.611 Hz
FIDRES        0.548877 Hz
AQ            0.9110004 sec
RG               3649.1
DW               27.800 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 5.00 usec
PL1               -6.00 dB
SF01          75.4752653 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2             70.00 usec
PL2               -3.00 dB
PL12              13.48 dB
PL13              15.63 dB
SF02         300.1314860 MHz

F2 - Processing parameters
SI                 65536
SF            75.4677492 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P              180.000 ppm
F1             13584.20 Hz
F2P              -10.000 ppm
F2              -754.68 Hz
PPMCM             9.50000 ppm/cm
HZCM            716.94360 Hz/cm
```

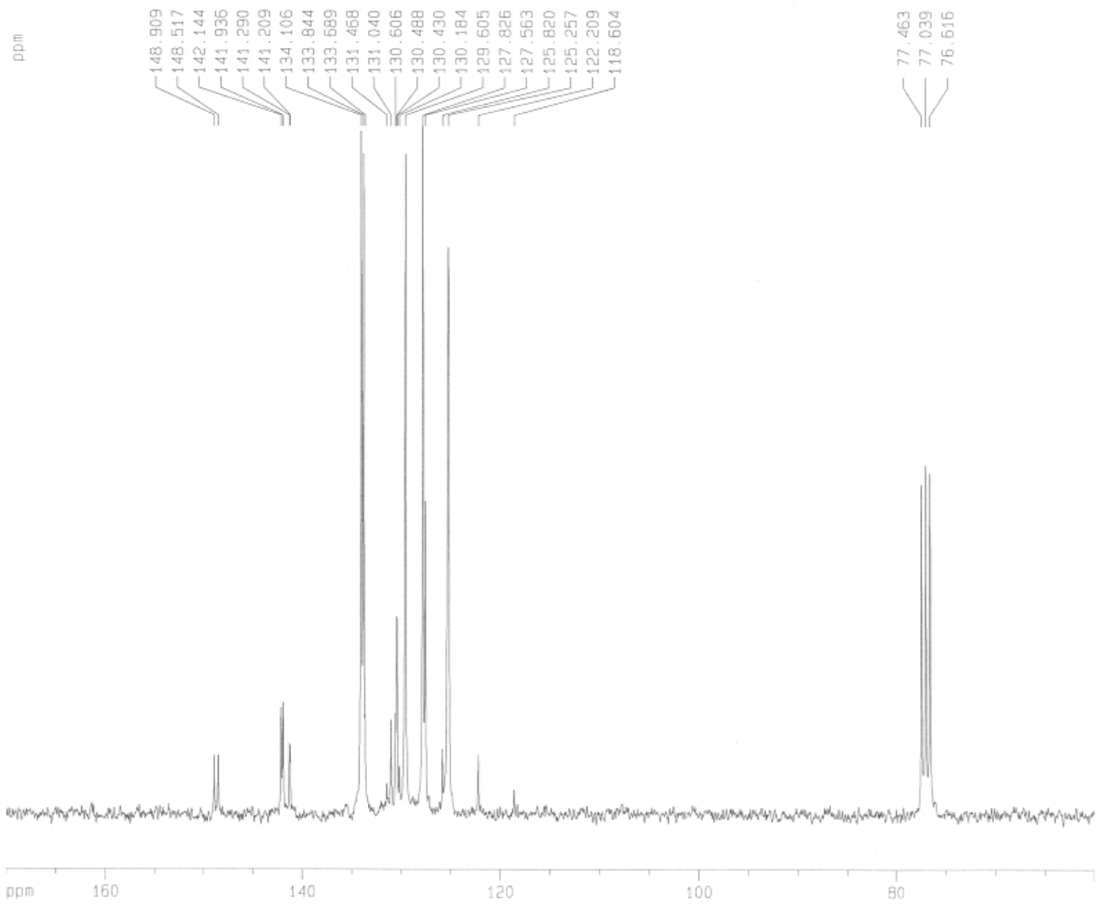




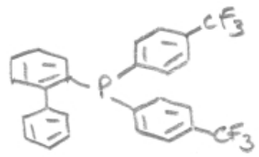

```
Current Data Parameters
NAME         Mat-1-Final
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20040426
Time                8.41
INSTRUM            av300
PROBHD   5 mm QNP  1H/1
PULPROG             zg30
TD                 30720
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            5081.301 Hz
FIDRES         0.165407 Hz
AQ             3.0228980 sec
RG                  71.8
DW                98.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

========== CHANNEL f1 ============
NUC1                  1H
P1                 10.50 usec
PL1                -3.00 dB
SF01         300.1319477 MHz

F2 - Processing parameters
SI                 65536
SF           300.1300070 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 10.00 cm
F1P               10.000 ppm
F1               3001.30 Hz
F2P               -0.500 ppm
F2               -150.06 Hz
PPMCM          0.52500 ppm/cm
HZCM         157.56824 Hz/cm
```

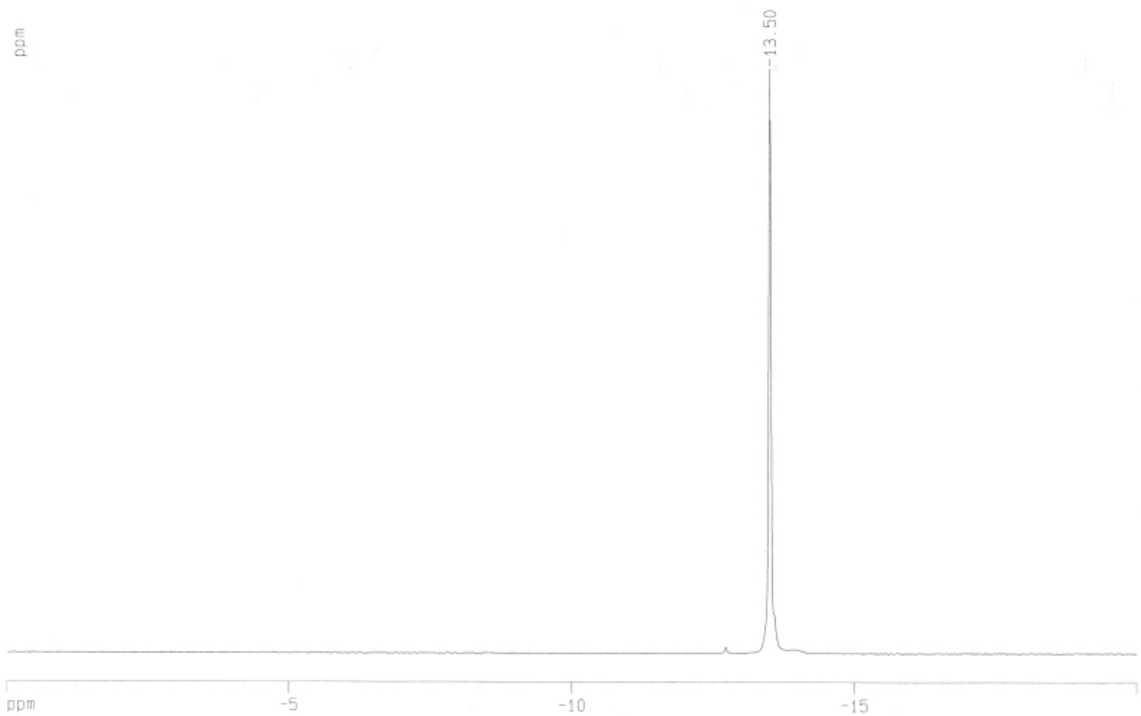


13C with proton decoupling

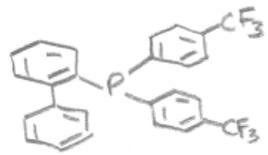



```
Current Data Parameters
NAME         Mat-1-Final
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20040426
Time                8.46
INSTRUM            av300
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                32768
SOLVENT            CDCl3
NS                   255
DS                     0
SWH           17985.611 Hz
FIDRES         0.548877 Hz
AQ             0.9110004 sec
RG                2298.8
DW                27.800 usec
DE                 6.00 usec
TE                300.0 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 5.00 usec
PL1                -6.00 dB
SFO1          75.4752653 MHz

============ CHANNEL f2 =============
CPDPRG2          waltz16
NUC2                1H
PCPD2             70.00 usec
PL2                -3.00 dB
PL12               13.48 dB
PL13               15.63 dB
SFO2         300.1314860 MHz

F2 - Processing parameters
SI                 65536
SF          75.4677470 MHz
WDW                   EM
SSB                    0
LB                  5.00 Hz
GB                     0
PC                  0.10

1D NMR plot parameters
CX                 20.00 cm
CY                 14.00 cm
F1P               170.000 ppm
F1                12829.52 Hz
F2P                60.000 ppm
F2                 4528.06 Hz
PPMCM              5.50000 ppm/cm
HZCM             415.07260 Hz/cm
```

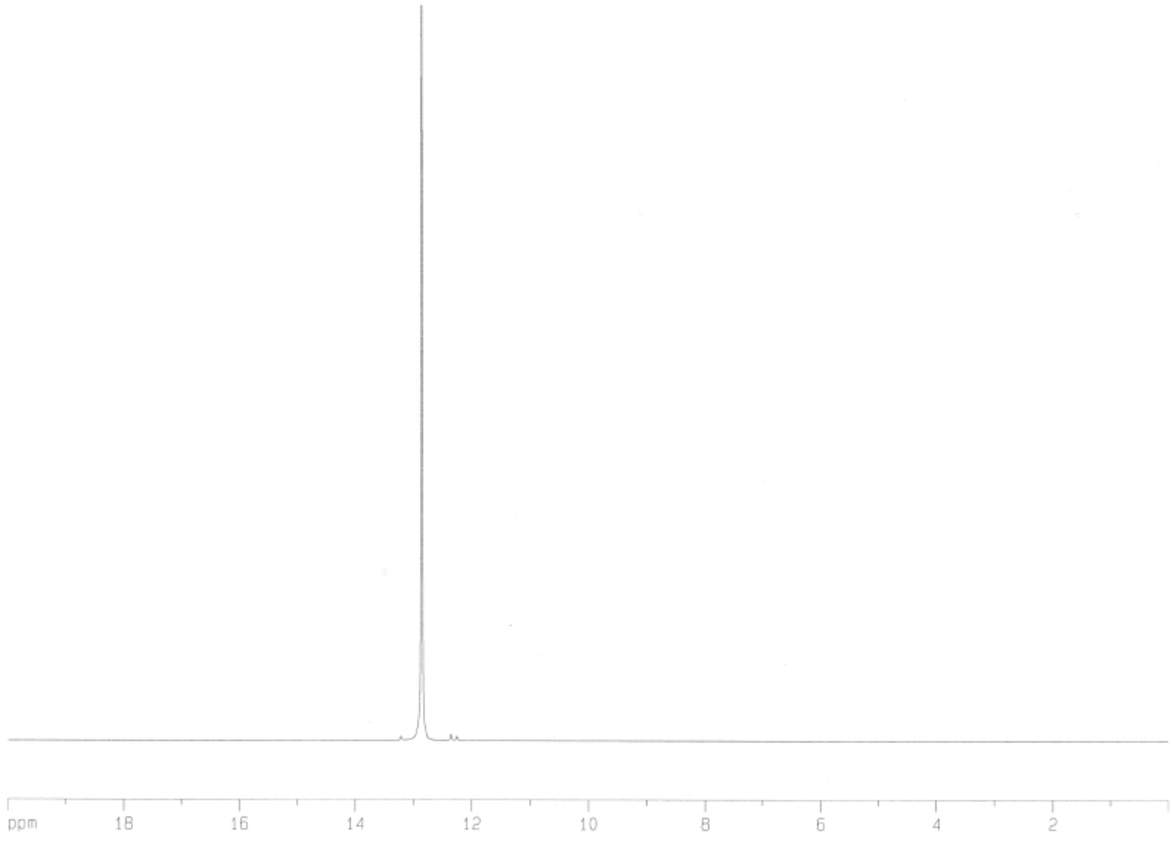




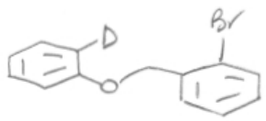

```
Current Data Parameters
NAME        Mat-1-Final
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20040426
Time               8.54
INSTRUM            av300
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           36496.352 Hz
FIDRES        0.556890 Hz
AQ            0.8978932 sec
RG               9195.2
DW               13.700 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                31P
P1                12.00 usec
PL1               -4.00 dB
SFO1        121.4946820 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2             70.00 usec
PL2               -3.00 dB
PL12              13.48 dB
PL13              15.63 dB
SFO2        300.1315007 MHz

F2 - Processing parameters
SI                32768
SF          121.4948364 MHz
WDW                EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                10.00 cm
F1P               0.000 ppm
F1                 0.00 Hz
F2P             -20.000 ppm
F2             -2429.90 Hz
PPMCM          1.00000 ppm/cm
HZCM         121.49483 Hz/cm
```



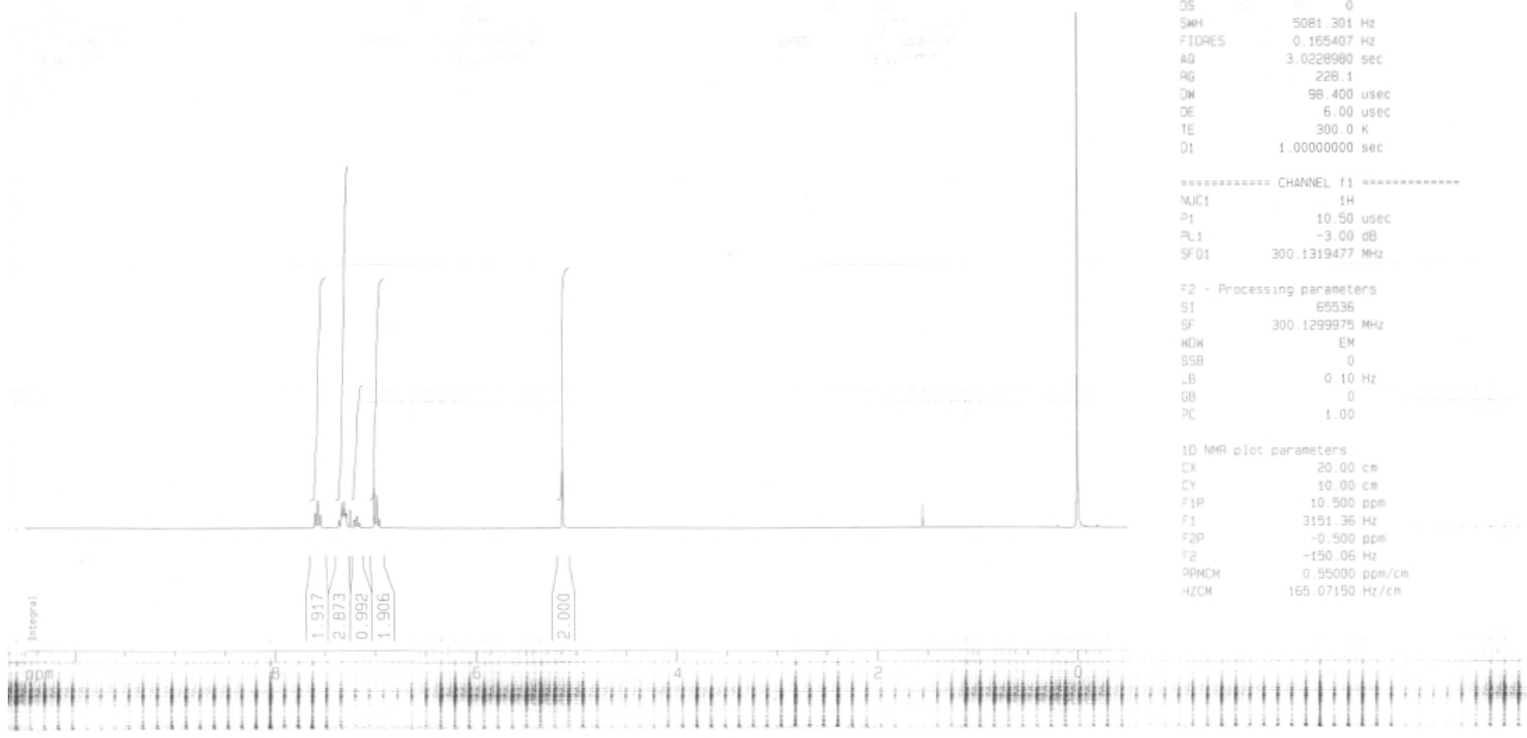
19F with proton decoupling



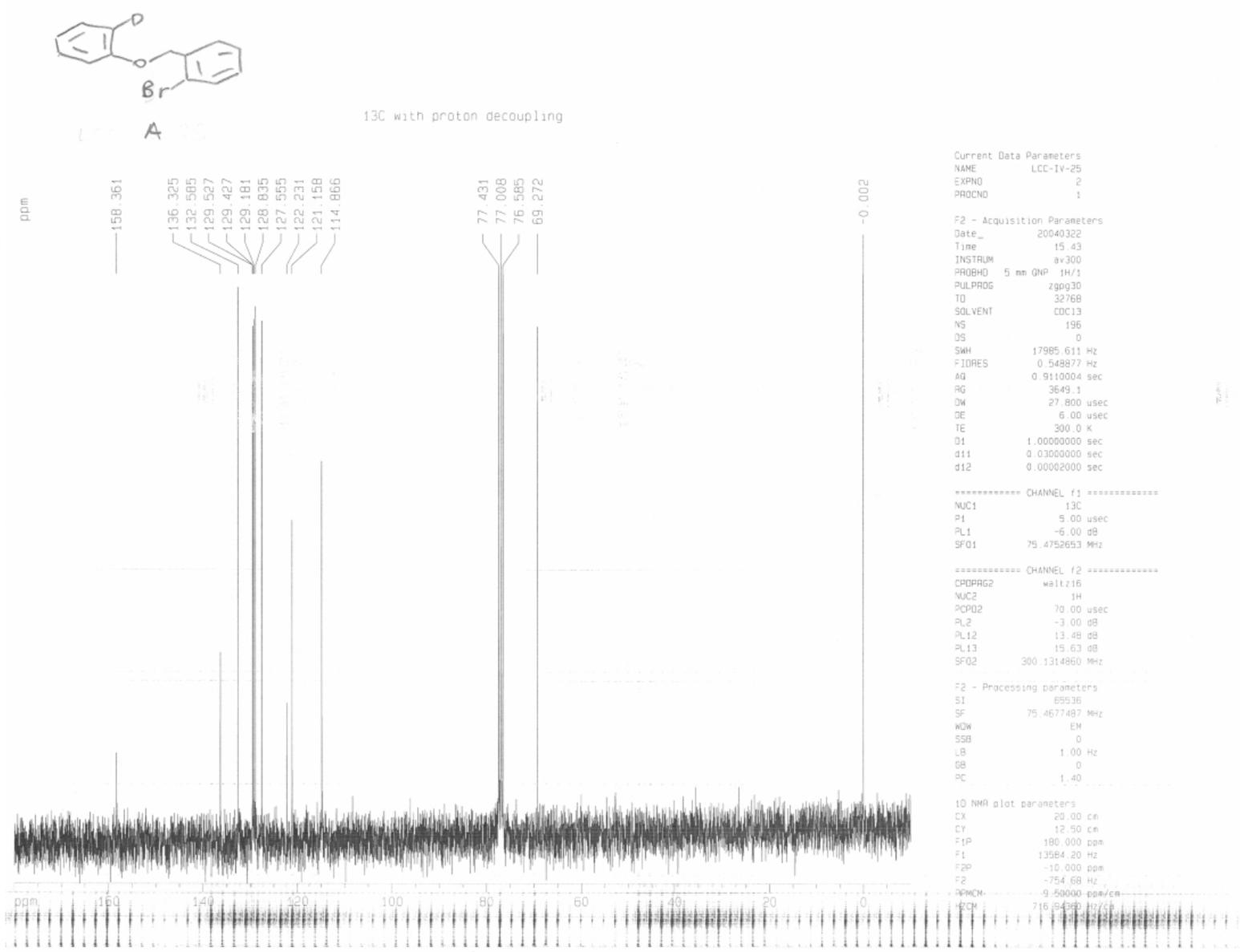

```
Current Data Parameters
NAME          Mat-1-Final
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20040426
Time                9.00
INSTRUM            av300
PROBHD   5 mm QNP  1H/1
PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            75179.281 Hz
FIDRES          2.294290 Hz
AQ             0.2179824 sec
RG                   362
DW                 6.651 usec
DE                 9.50 usec
TE                300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                  19F
P1                   7.90 usec
PL1                 -3.00 dB
SF01         282.3540472 MHz

F2 - Processing parameters
SI                 65536
SF           282.3829598 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 13.50 cm
F1P              20.000 ppm
F1               5647.66 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM           1.00000 ppm/cm
HZCM          282.38297 Hz/cm
```

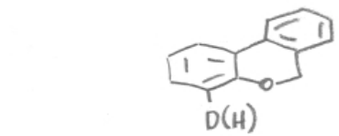


A




```
Current Data Parameters
NAME                  LCC-IV-25
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20040322
Time                      15.39
INSTRUM                   av300
PROBHD   5 mm QNP  1H/1
PULPROG                    zg30
TD                        30720
SOLVENT                   CDCl3
NS                           16
DS                            0
SWH                    5081.301 Hz
FIDRES                 0.165407 Hz
AQ                     3.0228980 sec
RG                         228.1
DW                        98.400 usec
DE                         6.00 usec
TE                        300.0 K
D1                     1.00000000 sec

============ CHANNEL f1 =============
NUC1                          1H
P1                        10.50 usec
PL1                       -3.00 dB
SFO1                300.1319477 MHz

F2 - Processing parameters
SI                         65536
SF                  300.1299975 MHz
WDW                           EM
SSB                           0
LB                         0.10 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
CY                        10.00 cm
F1P                       10.500 ppm
F1                      3151.36 Hz
F2P                       -0.500 ppm
F2                      -150.06 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 165.07150 Hz/cm
```

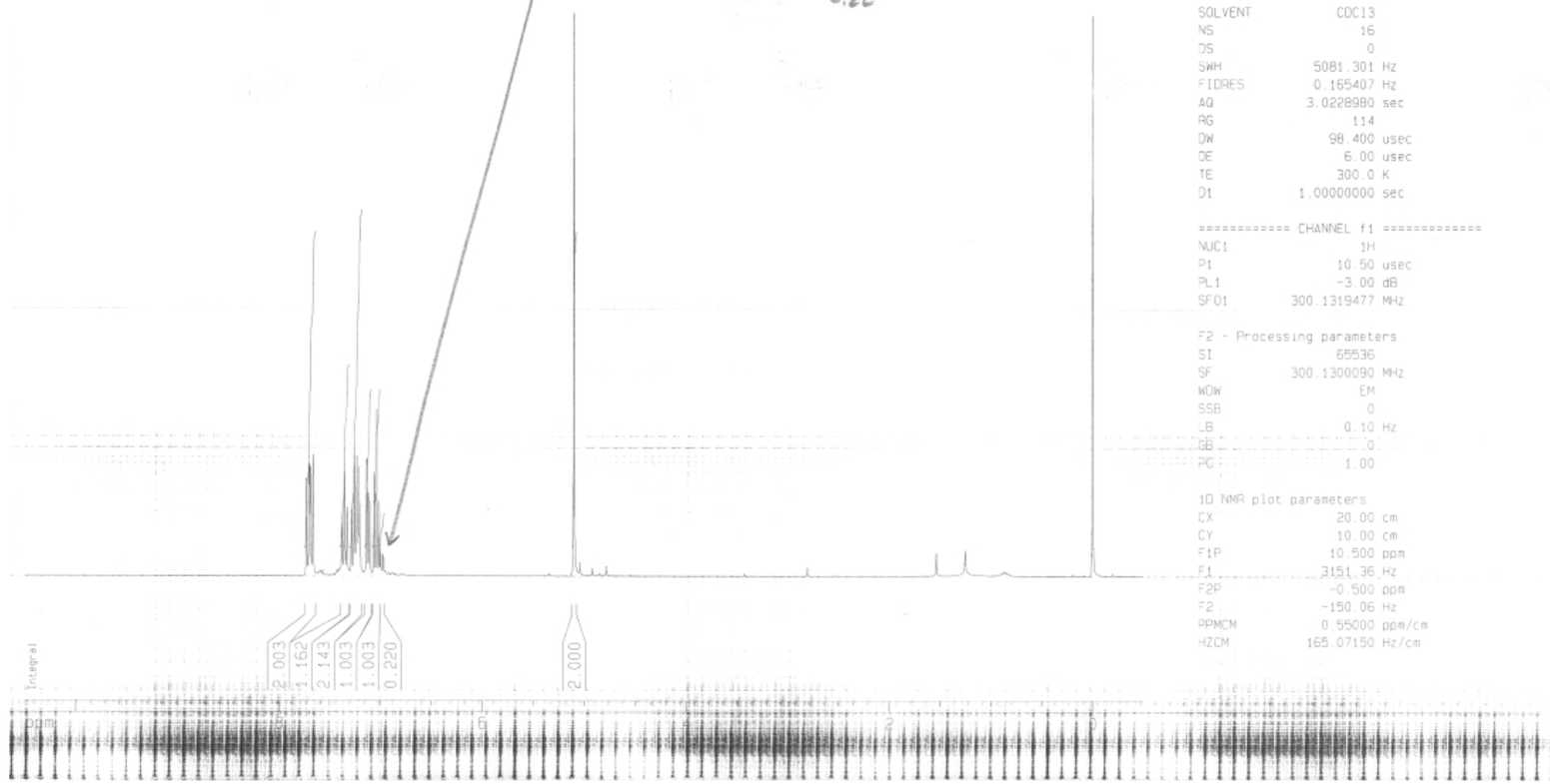

A
13C with proton decoupling
ppm
158.361
136.325
132.585
129.527
129.427
129.181
128.835
127.555
122.231
121.158
114.866
77.431
77.008
76.585
69.272
-0.002
Current Data Parameters
NAME LCC-IV-25
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040322
Time 15.43
INSTRUM av300
PROBHD 5 mm GNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 196
DS 0
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 3649.1
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SFO1 75.4752653 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 13.48 dB
PL13 15.63 dB
SFO2 300.1314860 MHz
F2 - Processing parameters
SI 65536
SF 75.4677487 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 180.000 ppm
F1 13584.20 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.50000 ppm/cm
HZCM 716.94360 Hz/cm
ppm
160
140
120
100
80
60
40
20
0



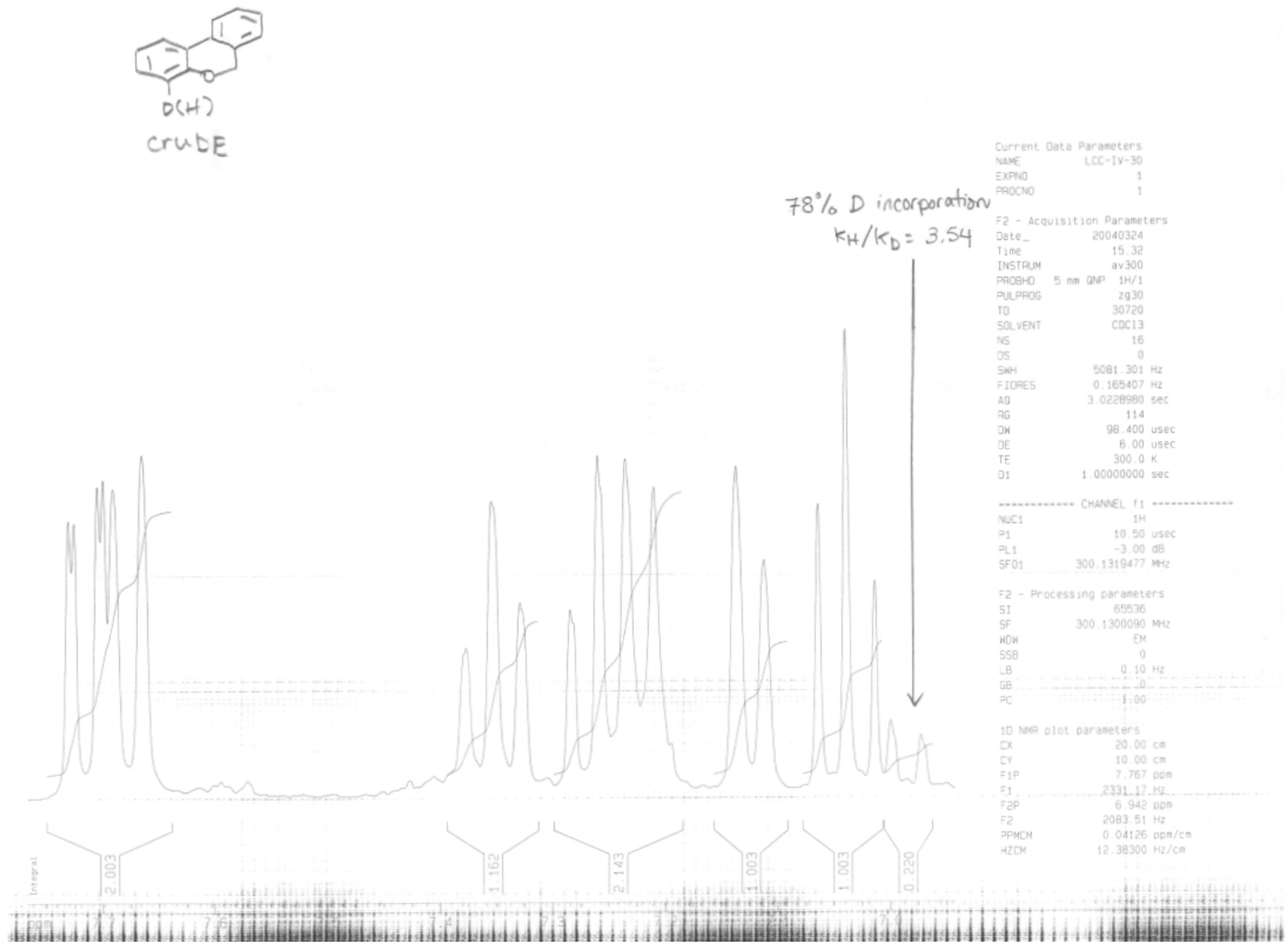
CRUDE

78% D incorporation

$k_H / k_D = \frac{0.78}{0.22} = 3.54$




```
Current Data Parameters
NAME            LCC-IV-30
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20040324
Time                15.32
INSTRUM             av300
PROBHD   5 mm QNP  1H/1
PULPROG             zg30
TD                 30720
SOLVENT            CDCl3
NS                    16
DS                     0
SWH              5081.301 Hz
FIDRES           0.165407 Hz
AQ               3.0228980 sec
RG                   114
DW                98.400 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 =============
NUC1                   1H
P1                 10.50 usec
PL1                -3.00 dB
SFO1          300.1319477 MHz

F2 - Processing parameters
SI                  65536
SF            300.1300090 MHz
WDW                    EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 10.00 cm
F1P                10.500 ppm
F1               3151.36 Hz
F2P                -0.500 ppm
F2               -150.06 Hz
PPMCM              0.55000 ppm/cm
HZCM             165.07150 Hz/cm
```


D(H)
crude
78% D incorporation
k_H/k_D = 3.54
Integral
2.003
1.162
2.143
1.003
1.003
0.220
Current Data Parameters
NAME LCC-1V-30
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040324
Time 15.32
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDCl3
NS 16
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 114
DW 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SF01 300.1319477 MHz
F2 - Processing parameters
SI 65536
SF 300.1300090 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 7.767 ppm
F1 2331.17 Hz
F2P 6.942 ppm
F2 2083.51 Hz
PPMCM 0.04126 ppm/cm
HZCM 12.38300 Hz/cm