Supporting Information for

Enhanced Reactivity Results in Reduced Catalytic Performance. Unexpected Ligand Reactivity of a Bis(*N*-2,6-diisopropylphenylperflourophenyl-amidate)titanium-bis(diethylamido) Hydroamination Precatalyst.

Jason A. Bexrud, Chunyu Li and Laurel L. Schafer*

Department of Chemistry, University of British Columbia, 6174 University Boulevard, Vancouver, B.C., Canada, V6T 1Z1.

Crystallographic data for **3**

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
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 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
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C5 C -0.20175(6) 0.11403(15) 0.06546(7) 0.0364(3) Uani 1 1 d . . .
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C103 C 0.08623(15) 0.4044(3) 0.53862(13) 0.0990(10) Uani 1 1 d . . .
H103 H 0.0791 0.4879 0.5305 0.119 Uiso 1 1 calc R . .
C10 C -0.13424(6) 0.33867(15) 0.13898(8) 0.0419(4) Uani 1 1 d . . .
H10A H -0.1287 0.4094 0.1666 0.063 Uiso 1 1 calc R . .
H10B H -0.1606 0.3565 0.0967 0.063 Uiso 1 1 calc R . .
H10C H -0.1036 0.3190 0.1350 0.063 Uiso 1 1 calc R . .
C9 C -0.15000(5) 0.22855(14) 0.16870(7) 0.0315(3) Uani 1 1 d . . .
H9 H -0.1220 0.2095 0.2108 0.038 Uiso 1 1 calc R . .
C12 C -0.09334(6) -0.18178(15) 0.10323(8) 0.0363(3) Uani 1 1 d . . .
H12 H -0.0657 -0.1744 0.1469 0.044 Uiso 1 1 calc R . .
C025 C 0.01636(6) 0.15767(14) 0.38259(7) 0.0329(3) Uani 1 1 d . . .
H02A H 0.0400 0.2177 0.4113 0.040 Uiso 1 1 calc R . .
H02B H 0.0346 0.0809 0.3869 0.040 Uiso 1 1 calc R . .
C026 C -0.02740(6) 0.32260(14) 0.30363(7) 0.0344(3) Uani 1 1 d . . .
H02C H -0.0579 0.3142 0.3103 0.041 Uiso 1 1 calc R . .
H02D H -0.0376 0.3458 0.2585 0.041 Uiso 1 1 calc R . .
C7 C -0.17421(6) -0.07258(16) 0.03436(7) 0.0385(4) Uani 1 1 d . . .
H7 H -0.1795 -0.1344 0.0038 0.046 Uiso 1 1 calc R . .
C6 C -0.20975(6) 0.02036(16) 0.02071(8) 0.0421(4) Uani 1 1 d . . .
H6 H -0.2388 0.0199 -0.0183 0.051 Uiso 1 1 calc R . .
C029 C -0.02587(7) 0.13676(18) 0.40444(8) 0.0473(4) Uani 1 1 d . . .
H02E H -0.0115 0.1081 0.4486 0.071 Uiso 1 1 calc R . .
H02F H -0.0491 0.0762 0.3769 0.071 Uiso 1 1 calc R . .
H02G H -0.0435 0.2129 0.4015 0.071 Uiso 1 1 calc R . .
C106 C 0.10506(10) 0.1586(3) 0.56221(11) 0.0851(8) Uani 1 1 d . . .
H106 H 0.1112 0.0748 0.5704 0.102 Uiso 1 1 calc R . .
C14 C -0.11895(7) -0.30802(16) 0.09796(9) 0.0466(4) Uani 1 1 d . . .
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H14B H -0.1464 -0.3164 0.0555 0.070 Uiso 1 1 calc R . .
H14C H -0.1317 -0.3139 0.1305 0.070 Uiso 1 1 calc R . .
C11 C -0.19641(6) 0.26351(16) 0.18057(9) 0.0434(4) Uani 1 1 d . . .
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H11B H -0.2055 0.1954 0.2005 0.065 Uiso 1 1 calc R . .
H11C H -0.2243 0.2830 0.1398 0.065 Uiso 1 1 calc R . .
C109 C 0.74947(8) 0.6694(2) 0.12608(9) 0.0630(6) Uani 1 1 d . . .
H109 H 0.7744 0.6165 0.1257 0.076 Uiso 1 1 calc R . .
C102 C 0.05789(9) 0.3334(3) 0.55957(11) 0.0759(7) Uani 1 1 d . . .
H102 H 0.0315 0.3693 0.5662 0.091 Uiso 1 1 calc R . .
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H13B H -0.0532 -0.0986 0.0579 0.082 Uiso 1 1 calc R . .
H13C H -0.0974 -0.1814 0.0101 0.082 Uiso 1 1 calc R . .
C108 C 0.71173(10) 0.6253(2) 0.14176(10) 0.0678(6) Uani 1 1 d . . .
H108 H 0.7113 0.5424 0.1521 0.081 Uiso 1 1 calc R . .
C101 C 0.06711(8) 0.2127(3) 0.57088(10) 0.0671(6) Uani 1 1 d . . .
H101 H 0.0470 0.1658 0.5849 0.081 Uiso 1 1 calc R . .
C105 C 0.13492(11) 0.2268(5) 0.54124(15) 0.1232(16) Uani 1 1 d . . .
H105 H 0.1612 0.1894 0.5350 0.148 Uiso 1 1 calc R . .
C107 C 0.67482(9) 0.7036(3) 0.14207(10) 0.0724(7) Uani 1 1 d . . .
H107 H 0.6492 0.6735 0.1522 0.087 Uiso 1 1 calc R . .
C110 C 0.75003(9) 0.7921(2) 0.11102(10) 0.0686(6) Uani 1 1 d . . .
H110 H 0.7753 0.8223 0.1003 0.082 Uiso 1 1 calc R . .
C111 C 0.71336(10) 0.8694(2) 0.11190(11) 0.0753(7) Uani 1 1 d . . .
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C112 C 0.67561(9) 0.8256(2) 0.12748(11) 0.0735(6) Uani 1 1 d . . .
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C104 C 0.12549(16) 0.3517(5) 0.52950(14) 0.1270(17) Uani 1 1 d . . .
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C11 0.0383(9) 0.0457(10) 0.0529(10) 0.0015(8) 0.0258(8) 0.0113(7)
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C105 0.0569(16) 0.237(5) 0.0703(19) -0.073(3) 0.0223(14) 0.001(3)
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C110 0.0584(13) 0.0928(18) 0.0458(11) 0.0020(11) 0.0138(10) -0.0272(13)
C111 0.0834(17) 0.0590(14) 0.0653(14) 0.0112(11) 0.0140(13) -0.0169(13)
C112 0.0702(15) 0.0837(18) 0.0600(13) -0.0001(12) 0.0215(12) 0.0036(13)
C104 0.120(3) 0.214(5) 0.0549(16) -0.043(2) 0.0439(19) -0.098(3)
C051 0.0456(10) 0.0334(9) 0.0573(11) -0.0102(8) 0.0114(8) 0.0049(7)

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 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
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F4 C19 C20 C15 179.13(13) . . . . ?
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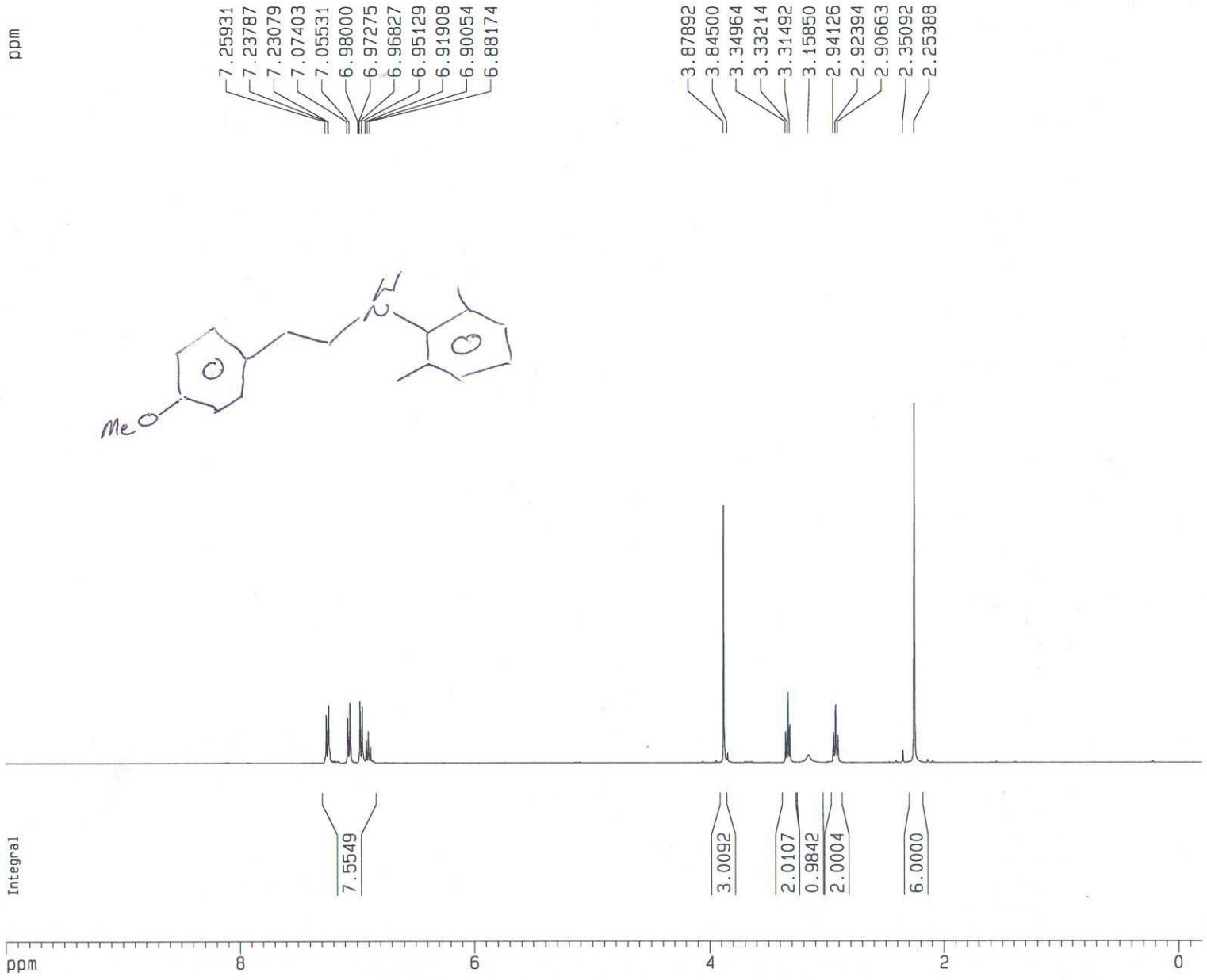
JOB NO: III-39-JB (C) CDCl3
1H spectrum ref. to CDCl3 at 7.27 ppm



Current Data Parameters

NAME	JAB126
EXPNO	1
PROCNO	1

F2 - Acquisition Parameter

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PULPROG	zg30
TD	16384
SOLVENT	CDCl3
NS	29
DS	2
SWH	4990.020 Hz
FIDRES	0.304567 Hz
AQ	1.6417269 se
RG	80.6
DW	100.200 us
DE	6.00 us
TE	300.0 K
D1	1.00000000 se

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

NUC1	1H
P1	5.30 us
PL1	4.00 dB
SFO1	400.1324008 MH

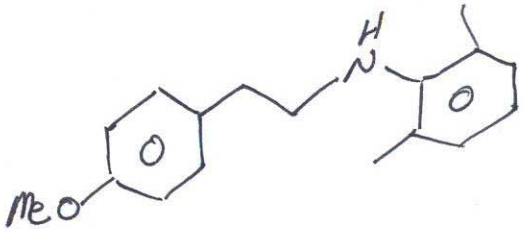
F2 - Processing parameters

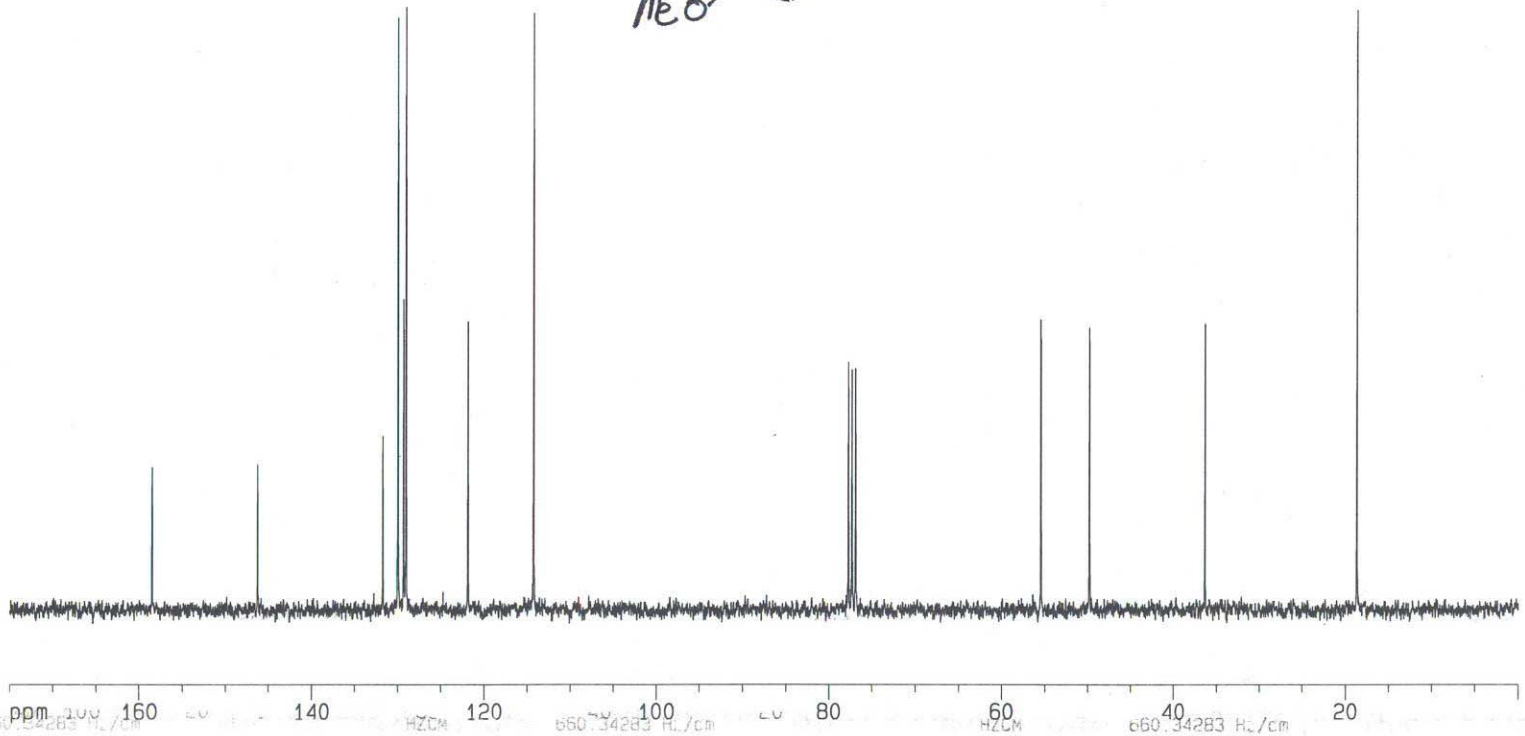
SI	32768
SF	400.1300051 MH
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	0.50

1D NMR plot parameters

CX	20.00 cm
CY	6.00 cm
F1P	10.000 pp
F1	4001.30 Hz
F2P	-0.200 pp
F2	-80.03 Hz
PPMCM	0.51000 pp
HZCM	204.06630 Hz

III-39-JB (C) CDCl3 13C BB EXPT ref. to CDCl3 at 77.23 ppm





Current Data Parameters

NAME	JB406
EXPNO	1
PROCNO	1

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PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	24
DS	4
SWH	18832.393 Hz
FIDRES	0.287360 Hz
AQ	1.7400308 sec
RG	16384
DW	26.550 usec
DE	37.93 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

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

NUC1	13C
P1	11.00 usec
PL1	0.00 dB
SFO1	75.4755190 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.97 dB
PL13	19.00 dB
SFO2	300.1316000 MHz

F2 - Processing parameters

SI	32768
SF	75.4677395 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY	8.00 cm
F1P	175.000 ppm
F1	13206.86 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	8.75000 ppm/cm
HZCM	660.34283 Hz/cm

I-75-JB CDCl3

Current Data Parameters

NAME	JB87
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20040715
Time	14.26
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PROBHD	5 mm QNP 1H/
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6313.131 Hz
FIDRES	0.192661 Hz
AQ	2.5952756 sec
RG	35.9
DW	79.200 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

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

NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	300.1316000 MHz

F2 - Processing parameters

SI	32768
SF	300.1300112 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-1.000 ppm
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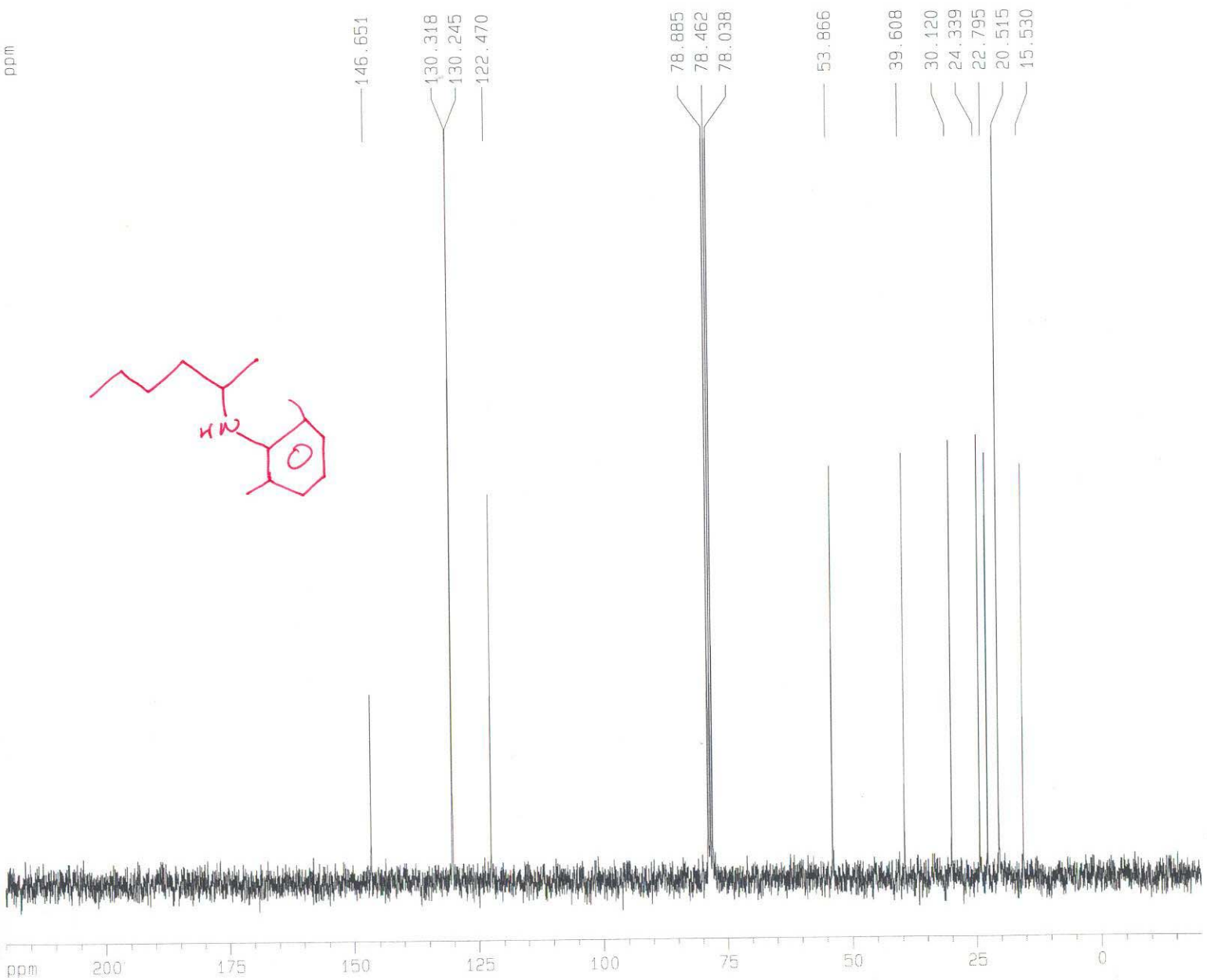
13C BB EXPT I-75-JB CDCl3



Current Data Parameters

NAME	JB88.
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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SOLVENT	CDCl3
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DS	4
SWH	18832.393 Hz
FIDRES	0.287360 Hz
AQ	1.7400308 sec
RG	18390.4
DW	26.550 usec
DE	37.93 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

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

NUC1	13C
P1	6.00 usec
PL1	0.00 dB
SFO1	75.4755190 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	120.00 dB
PL12	18.00 dB
PL13	18.00 dB
SFO2	300.1316000 MHz

F2 - Processing parameters

SI	32768
SF	75.4676423 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	220.000 ppm
F1	16602.88 Hz
F2P	-20.000 ppm
F2	-1509.35 Hz
PPMCM	12.00000 ppm/cm
HZCM	905.61176 Hz/cm