

**Palladium Nanoparticle Catalysis: Borylation of Aryl and Benzyl Halides and
One-Pot Biphenyl Synthesis *via* Sequential Borylation-Suzuki-Miyaura Coupling**

Ansuman Bej, Dipankar Srimani, and Amitabha Sarkar*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Kolkata

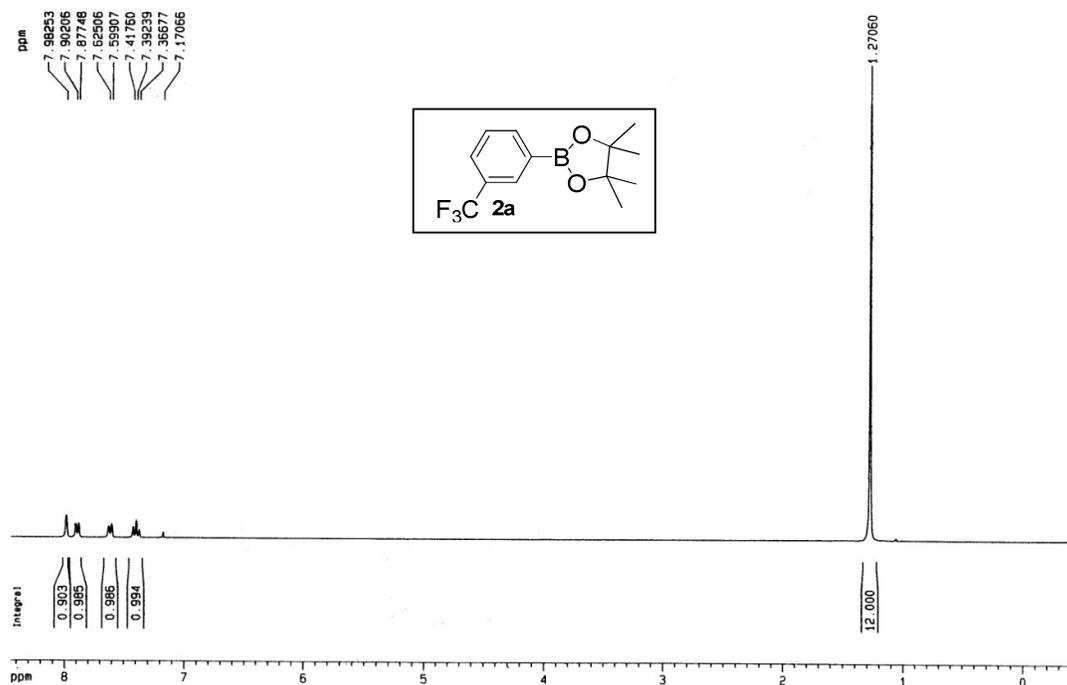
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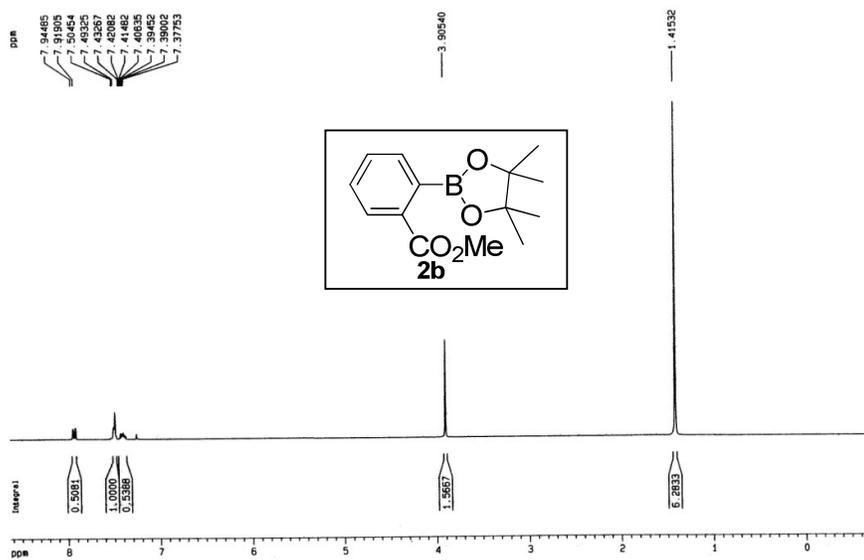
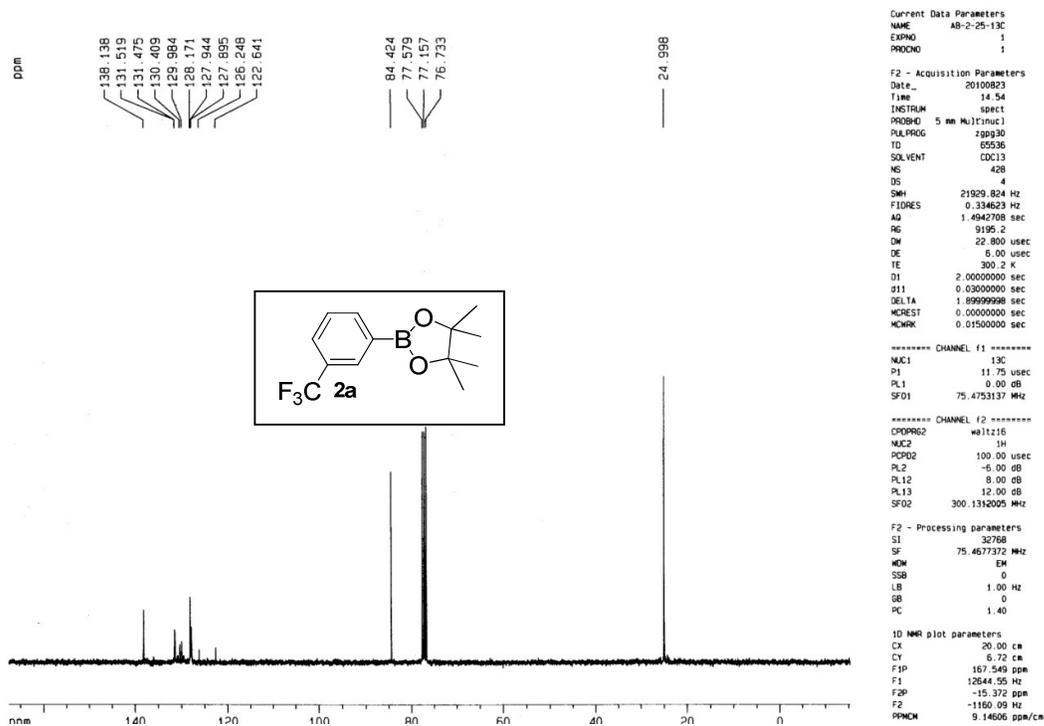
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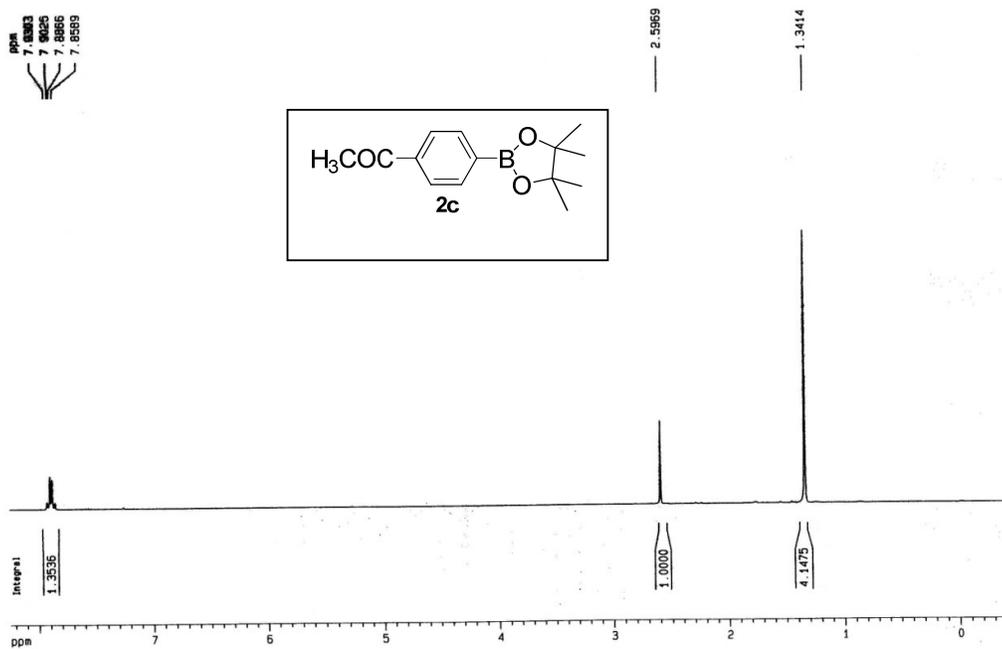
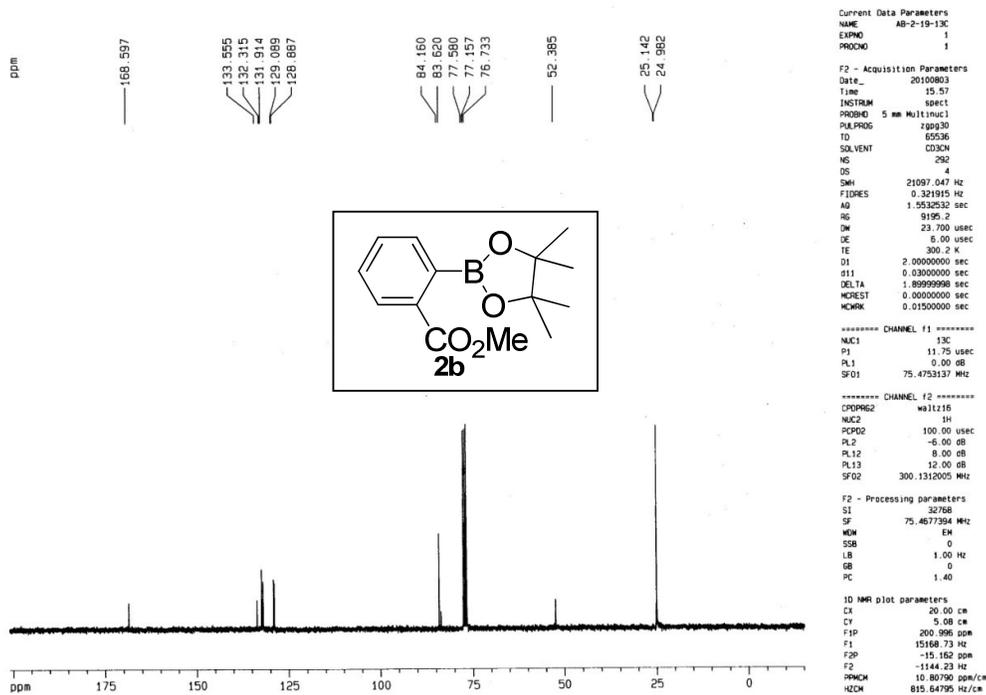
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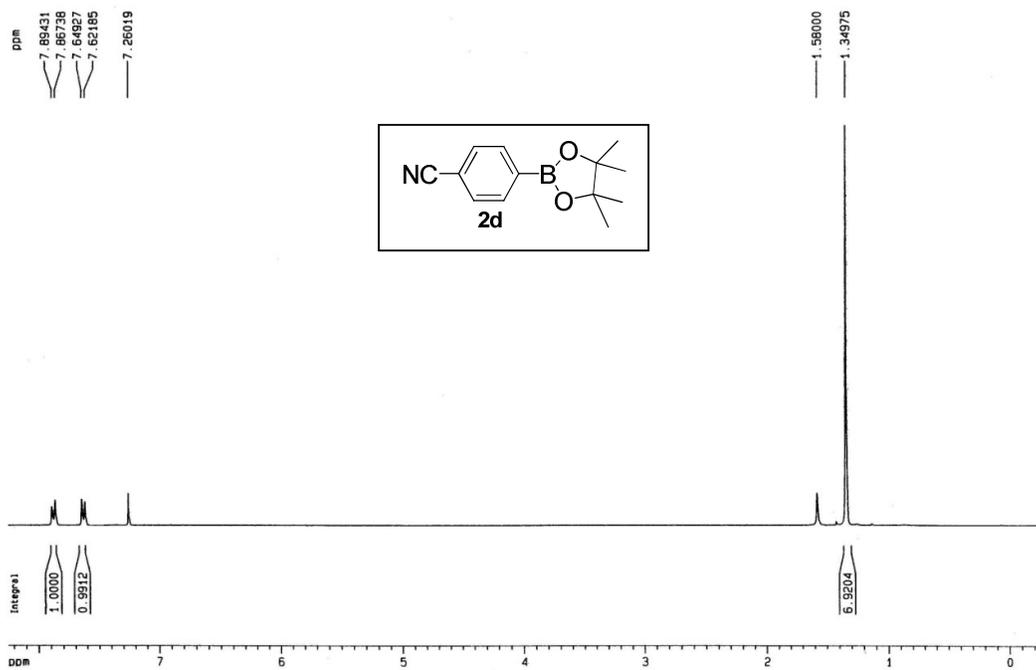
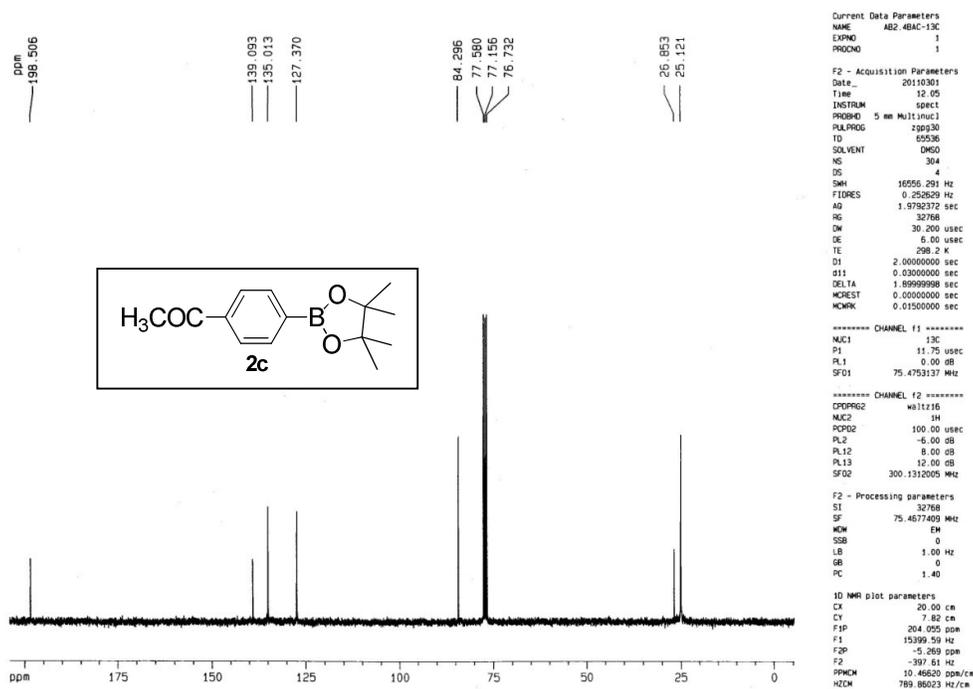
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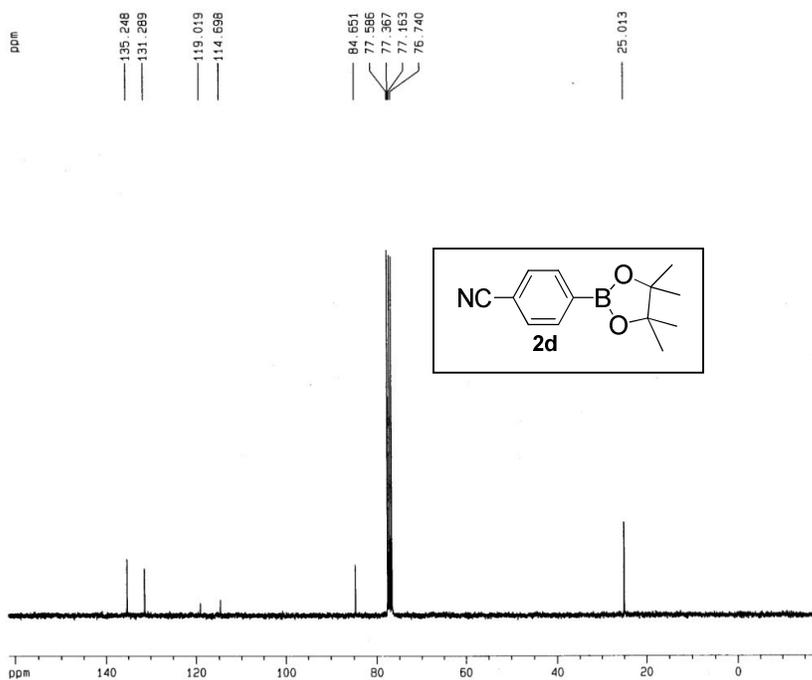
Figures reproducing ^1H and ^{13}C NMR spectra











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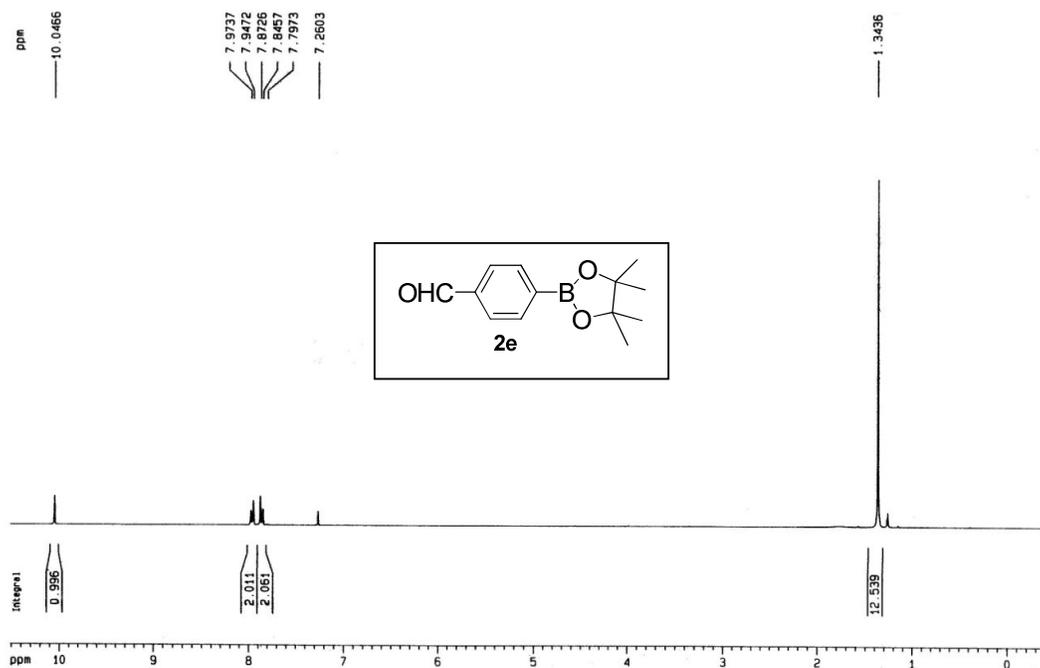
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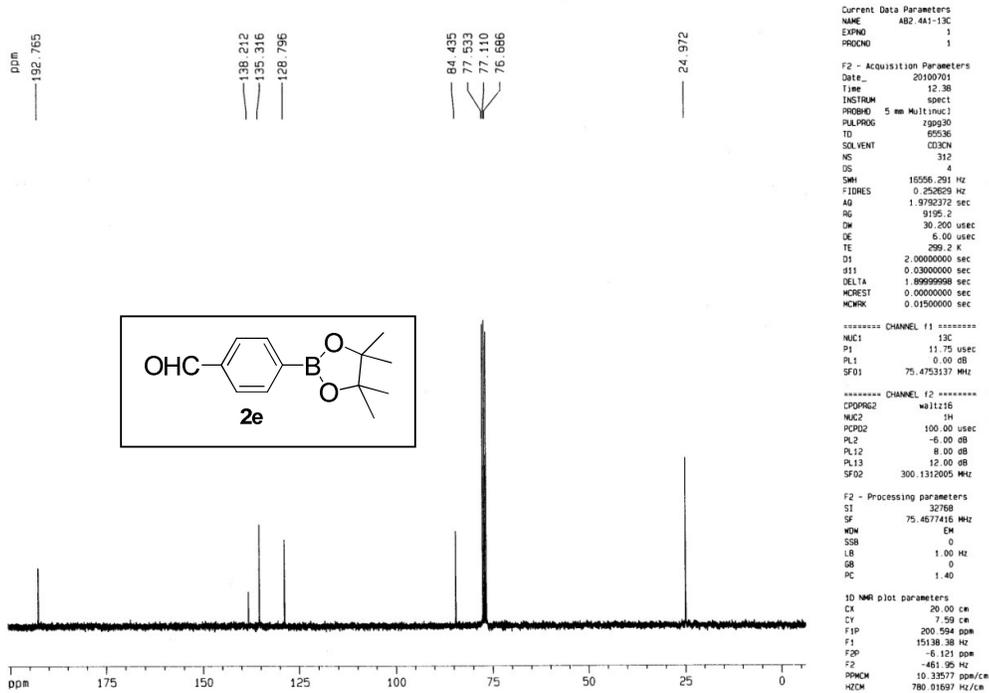
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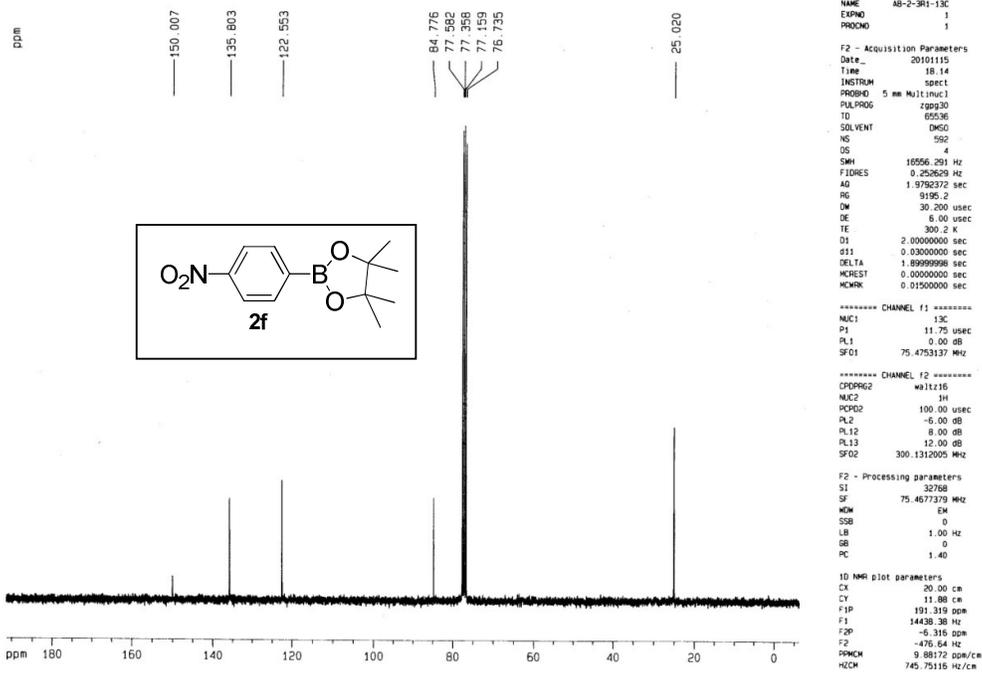
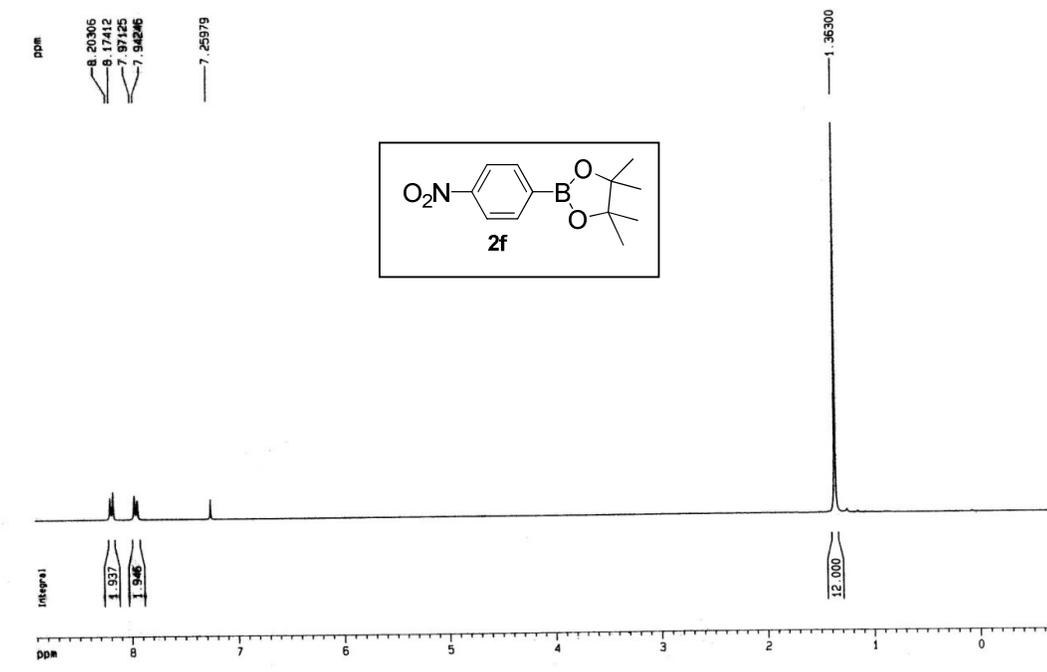
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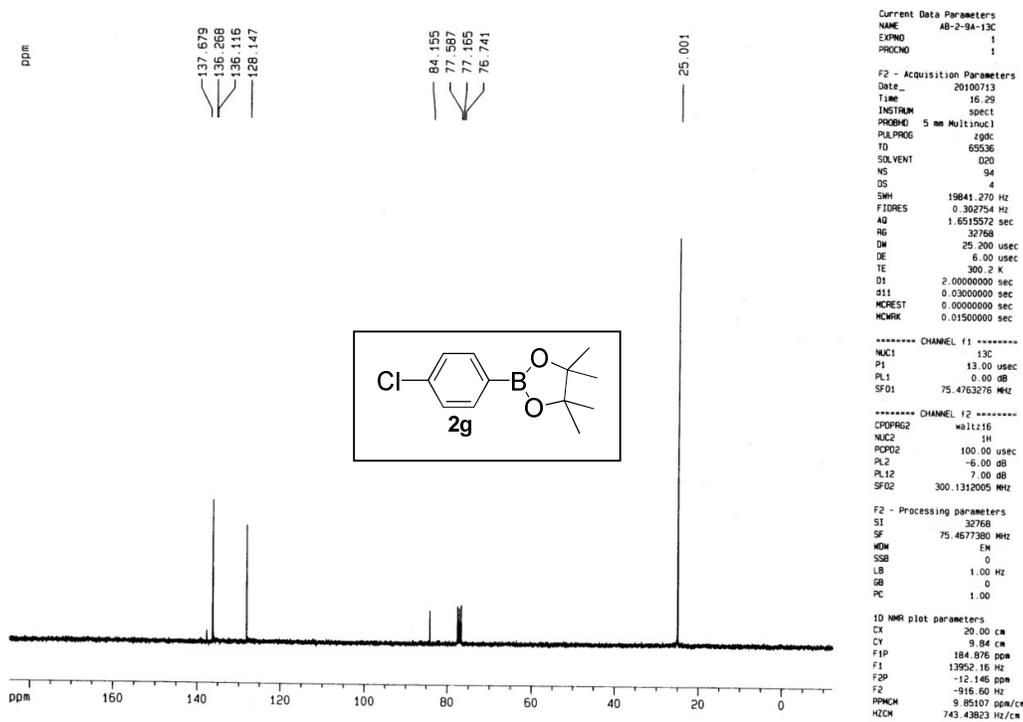
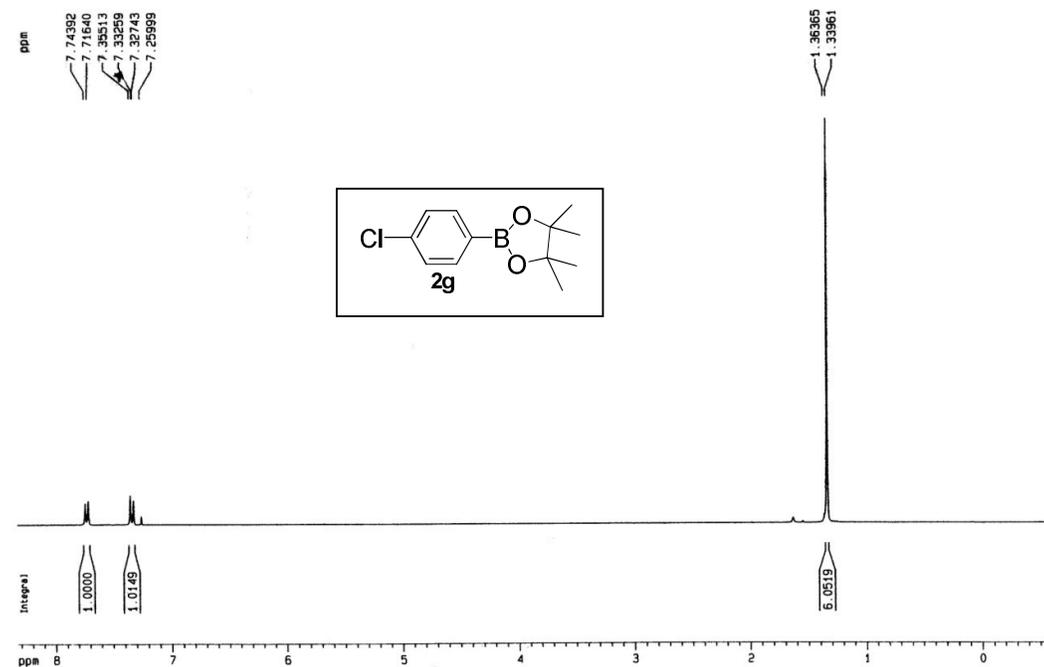
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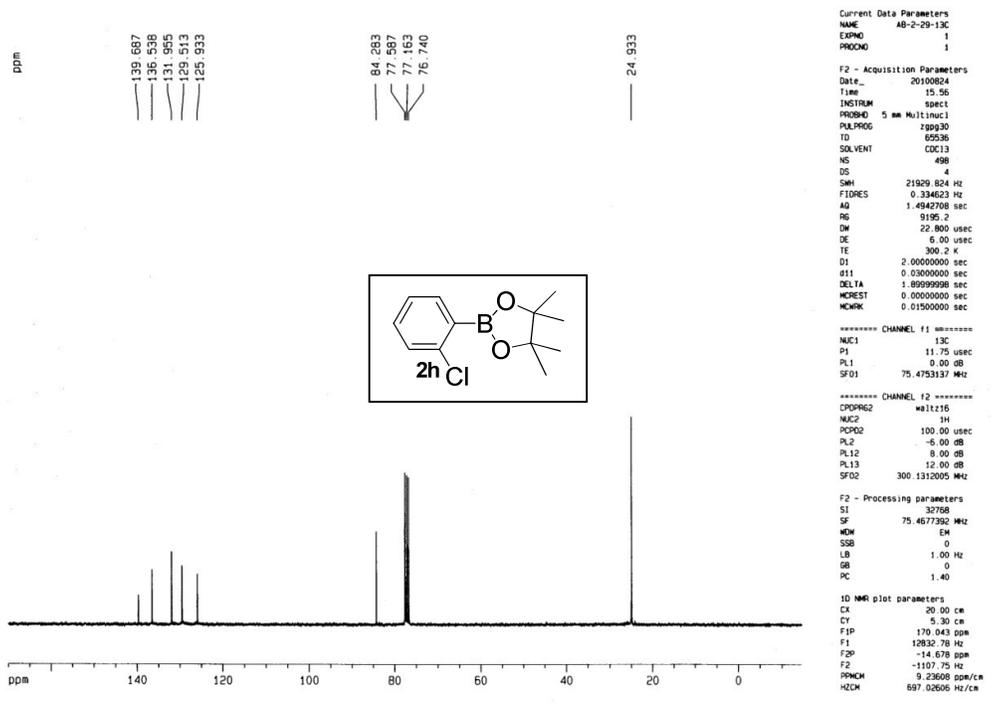
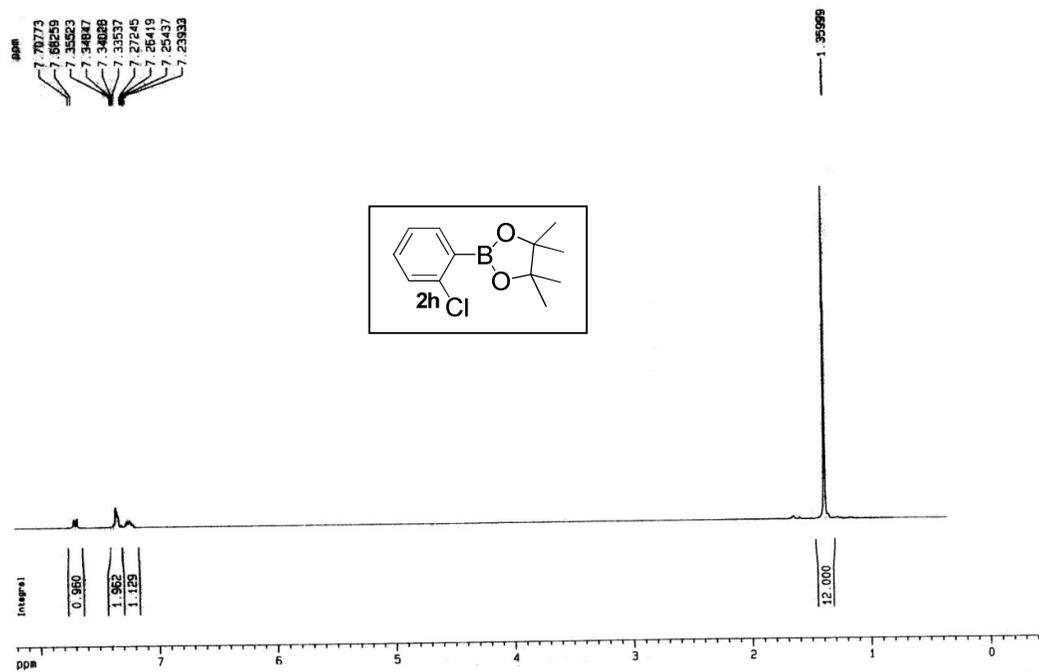
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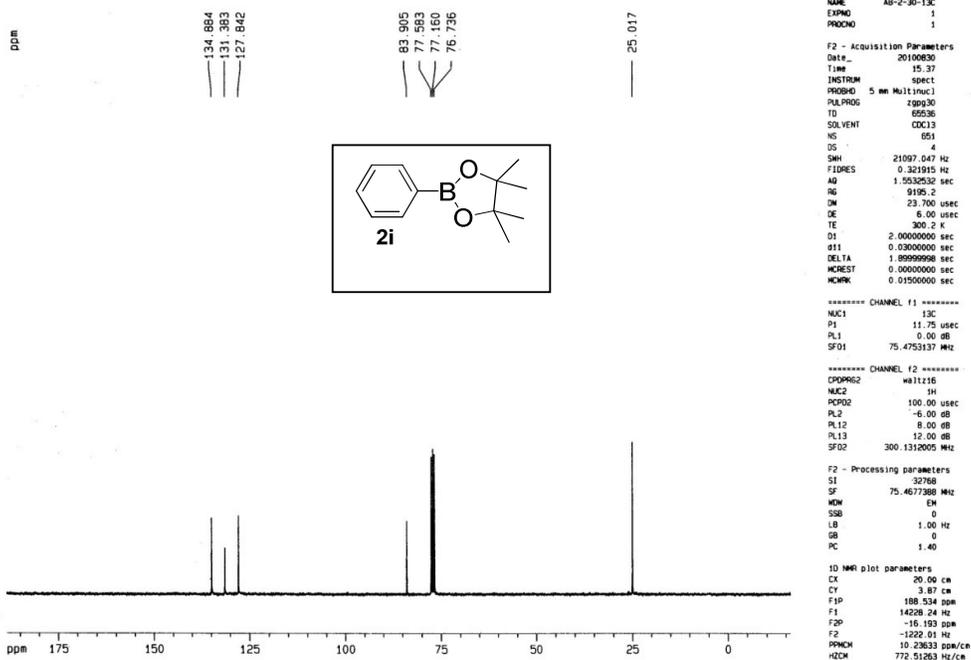
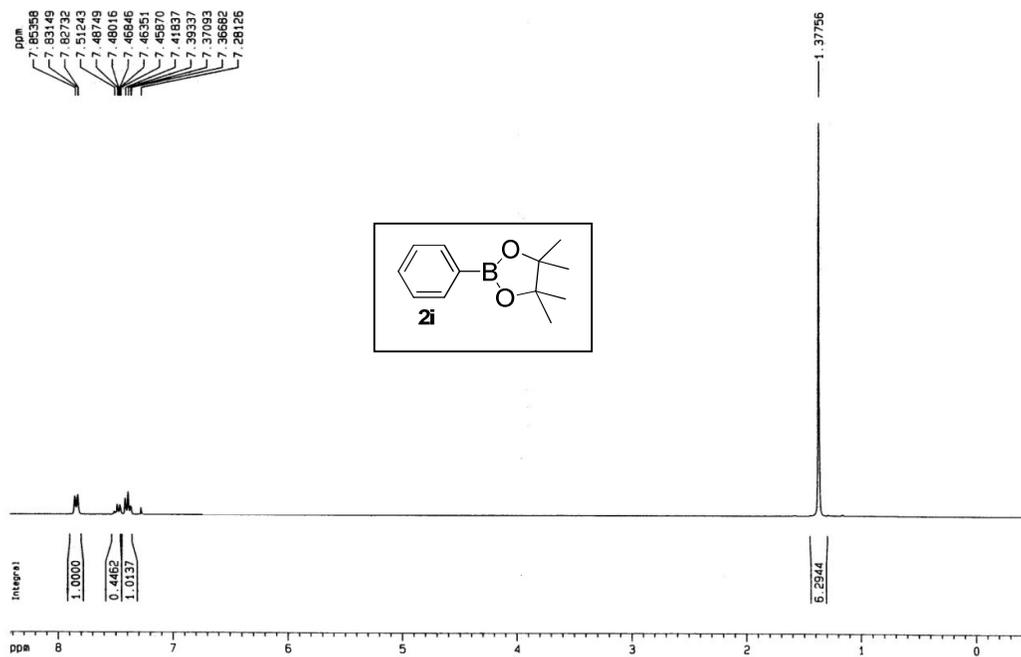


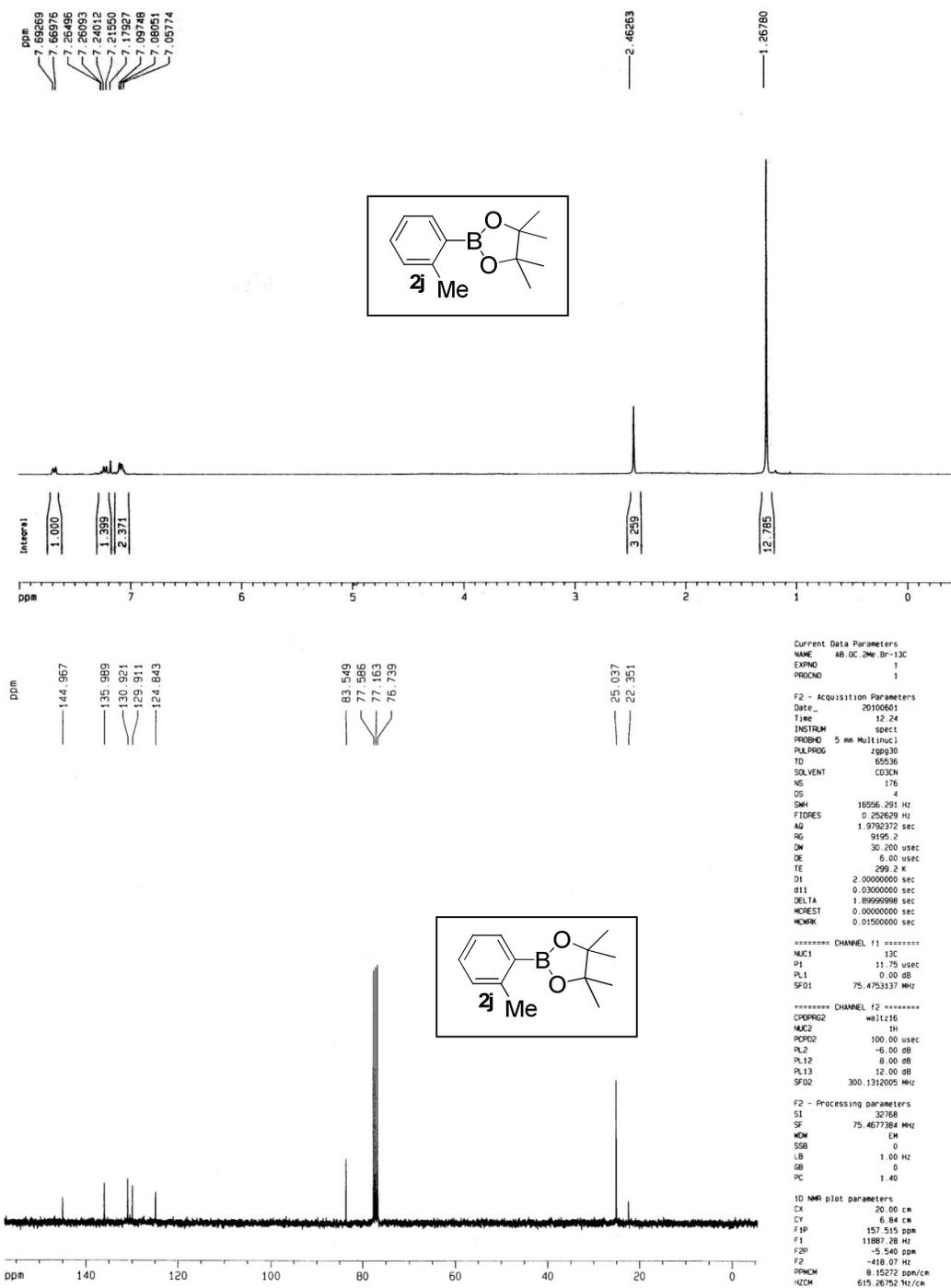


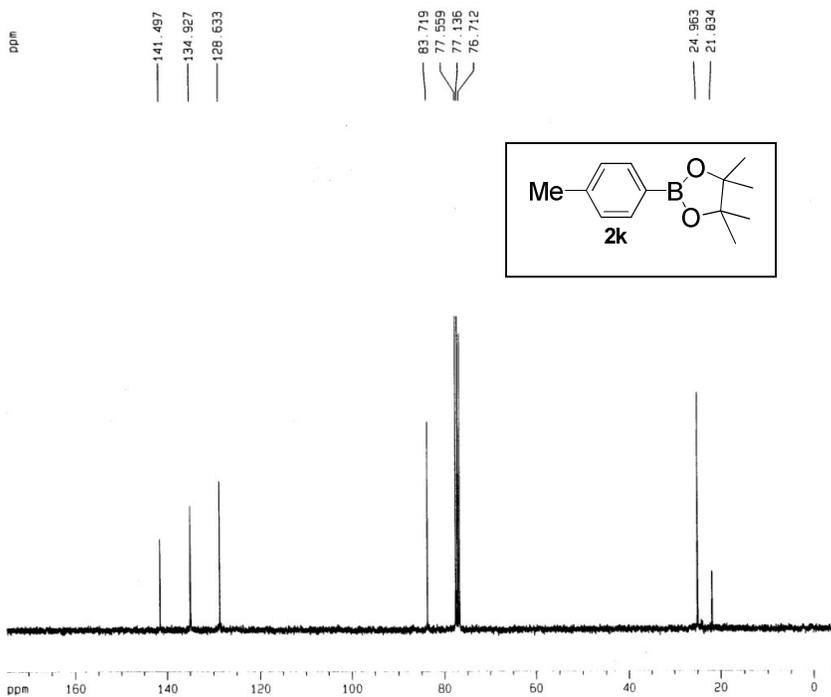
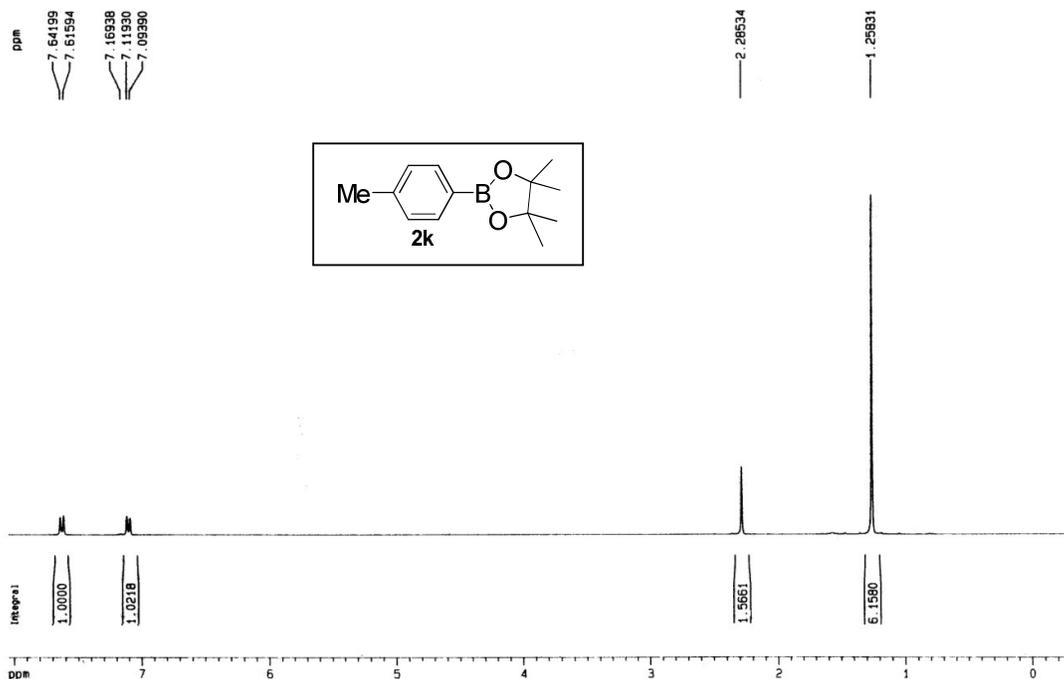












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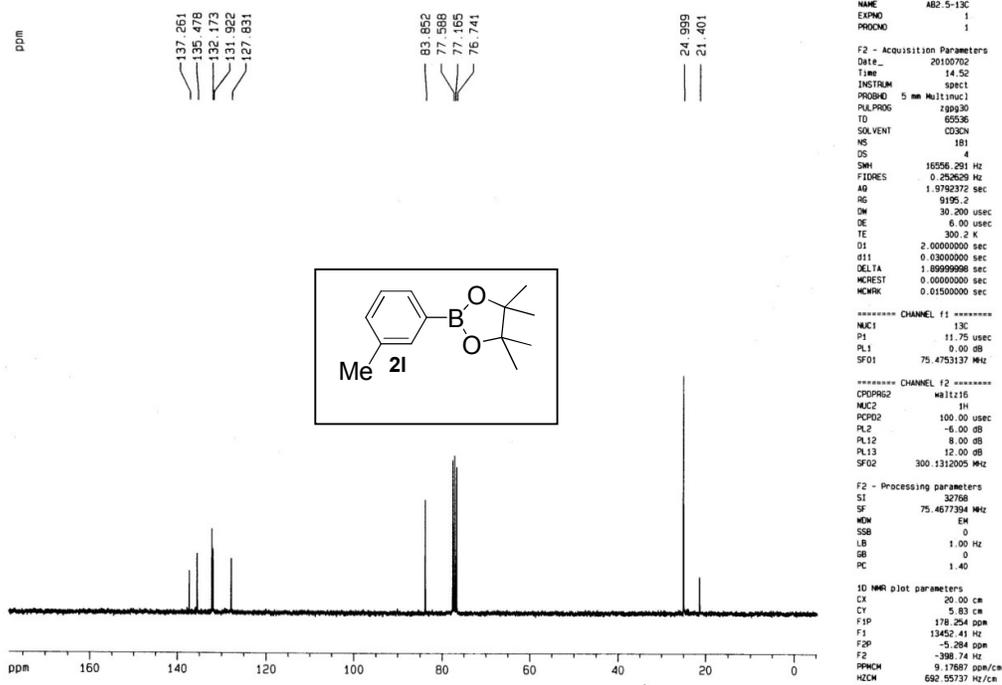
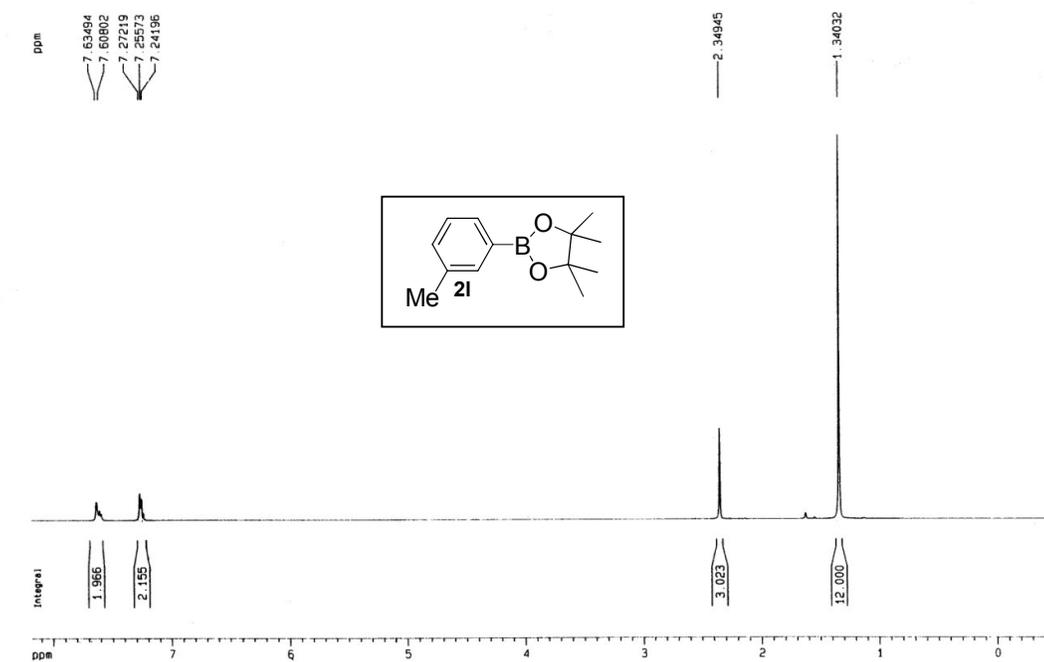
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AQ       1.9792372 sec
RG       32768
DM       30.290 usec
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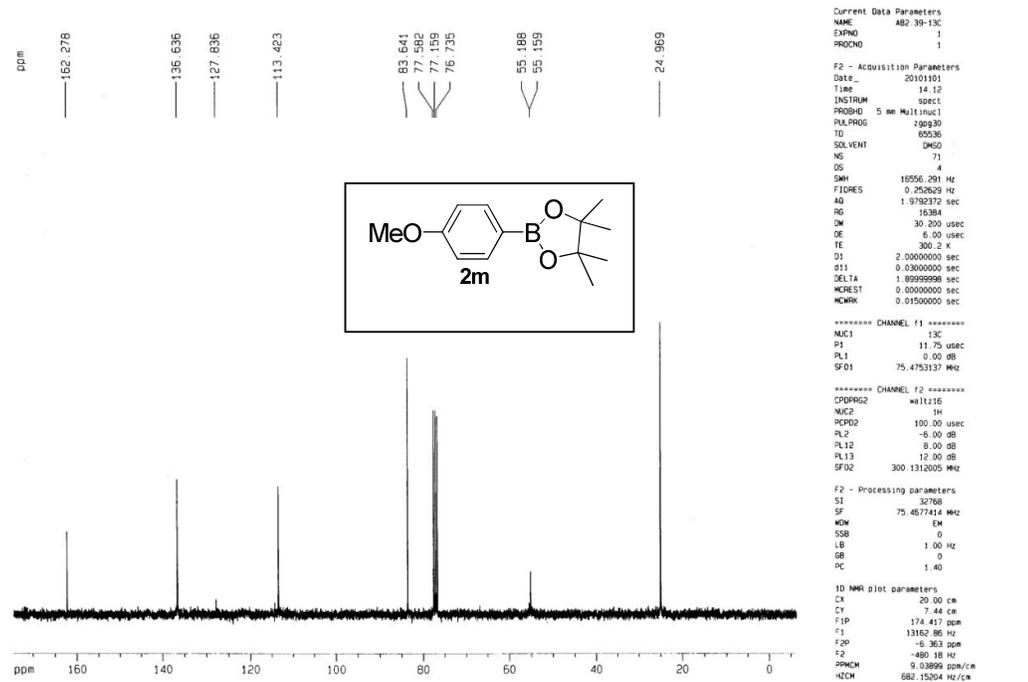
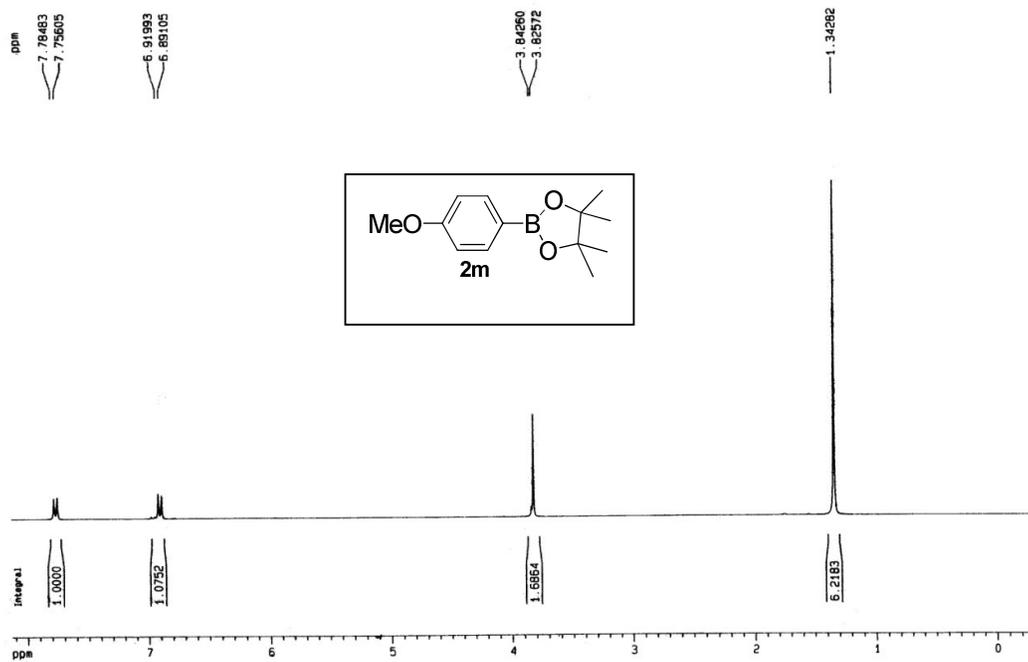
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NUC2      1H
PCPRG2   100.00 usec
PL2       -6.00 dB
PL12      8.00 dB
PL13     12.00 dB
SFO2     300.1312005 MHz

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GB        0
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1D NMR plot parameters
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CY        7.50 cm
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F1        13183.20 Hz
c2p       -6.365 ppm
F2        -480.36 Hz
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Current Data Parameters
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EXPNO    1
PROCNO   1

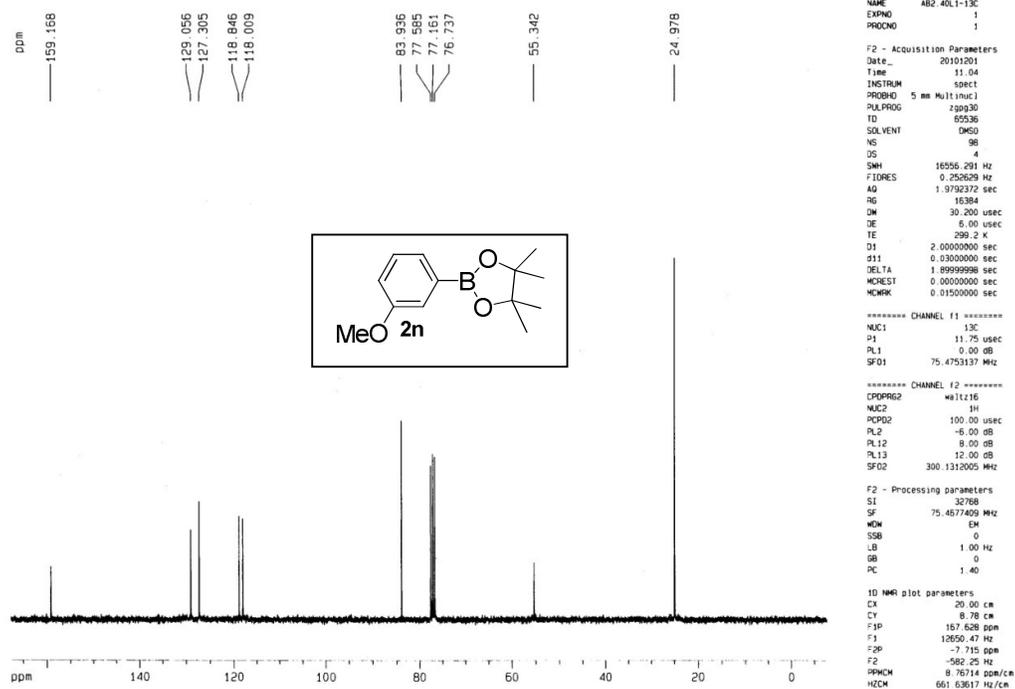
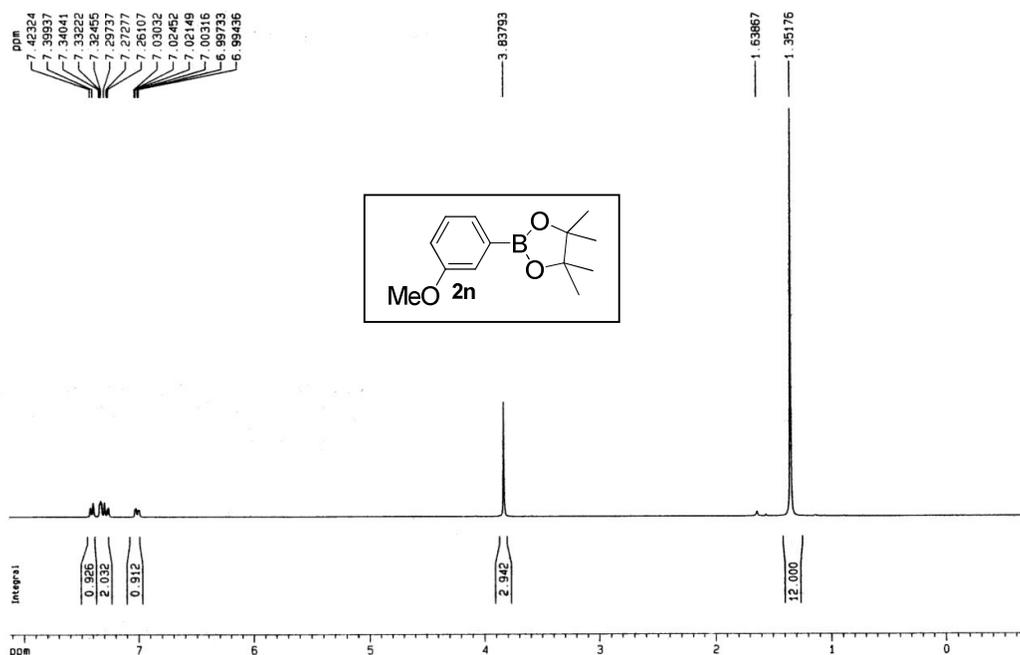
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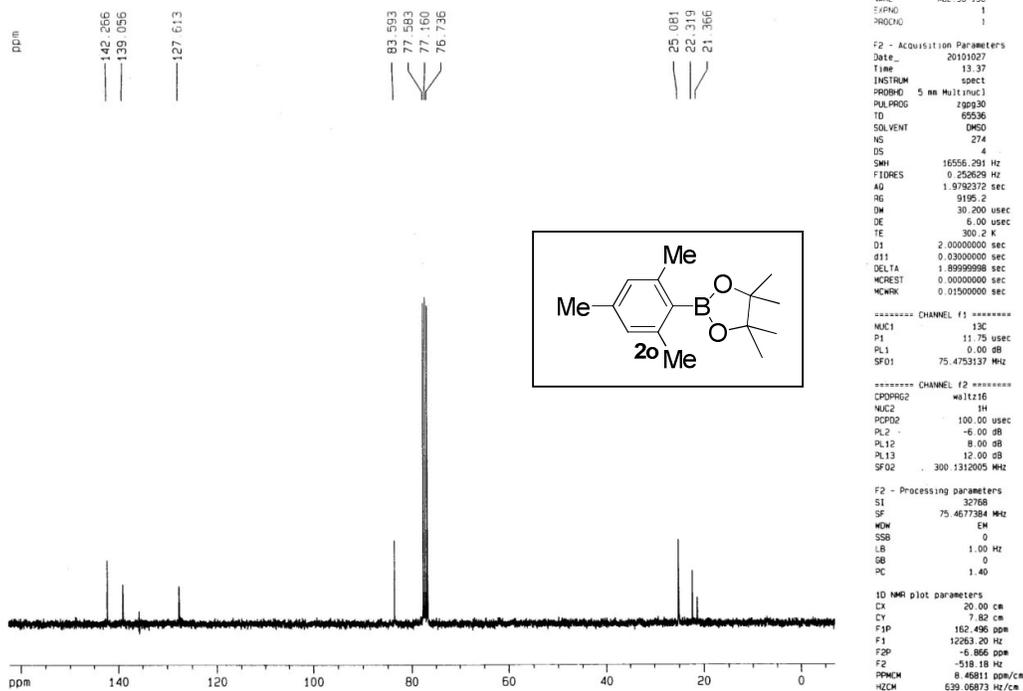
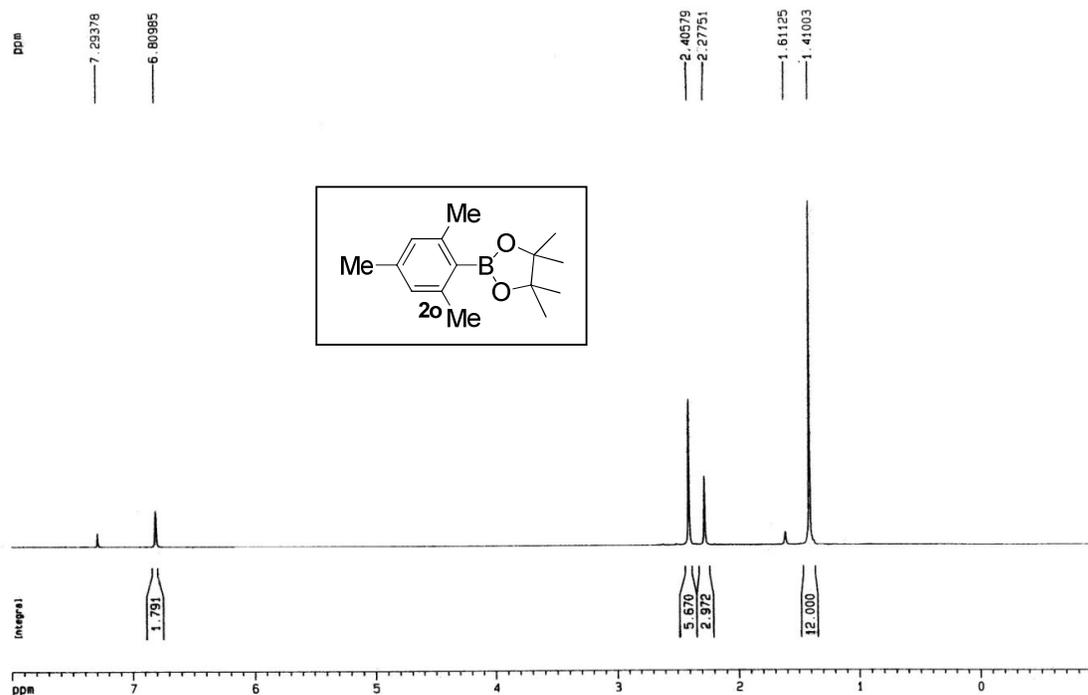
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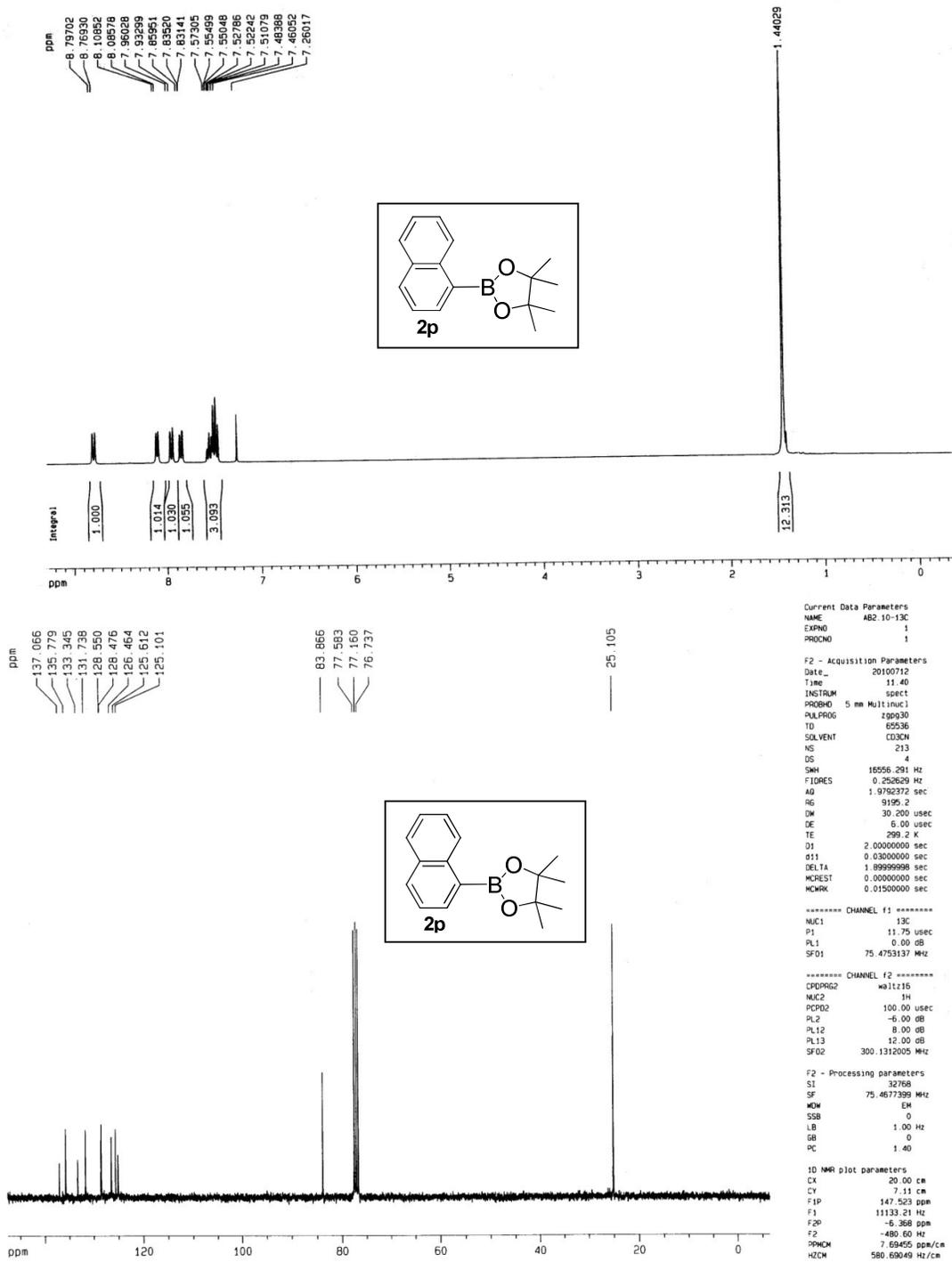
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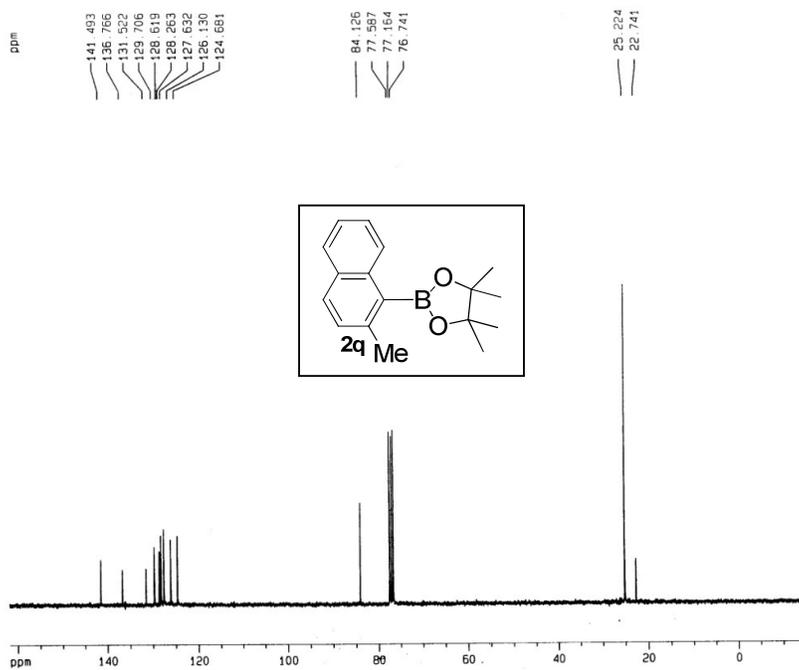
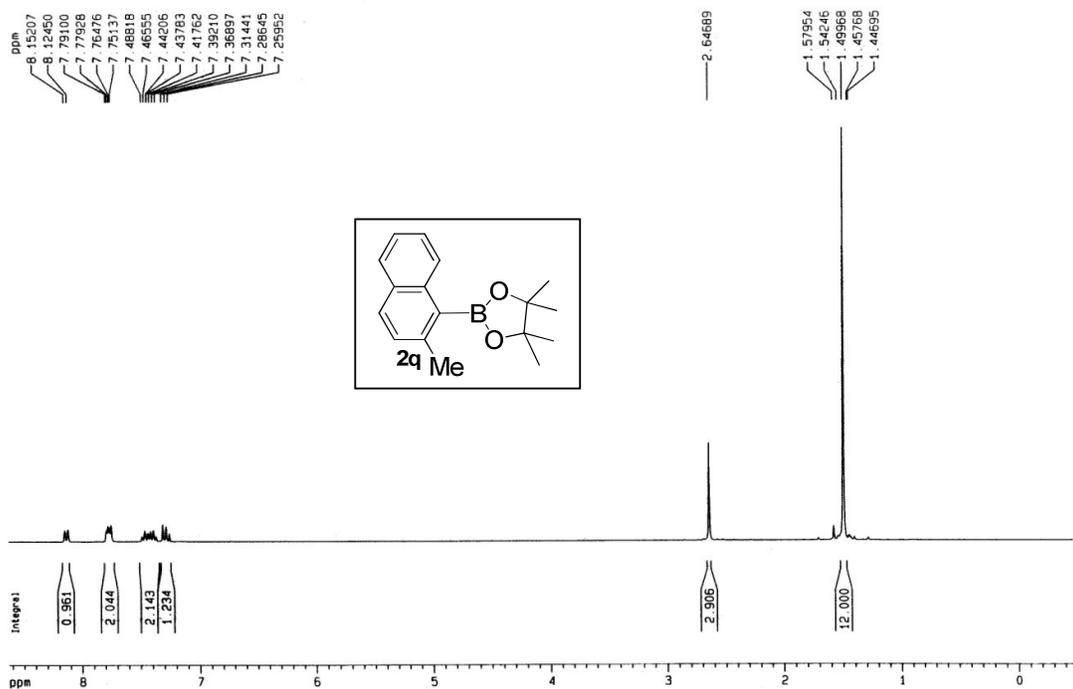
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CY       7.44 cm
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F1       13162.86 Hz
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F2       -480.18 Hz
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Current Data Parameters
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 PROCNO 1

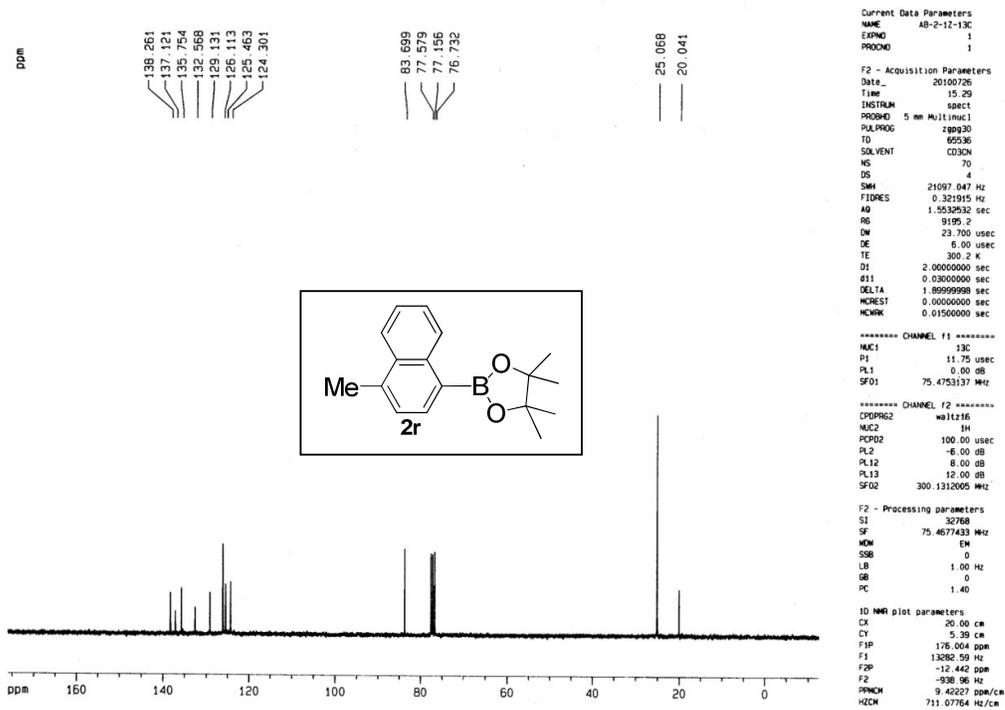
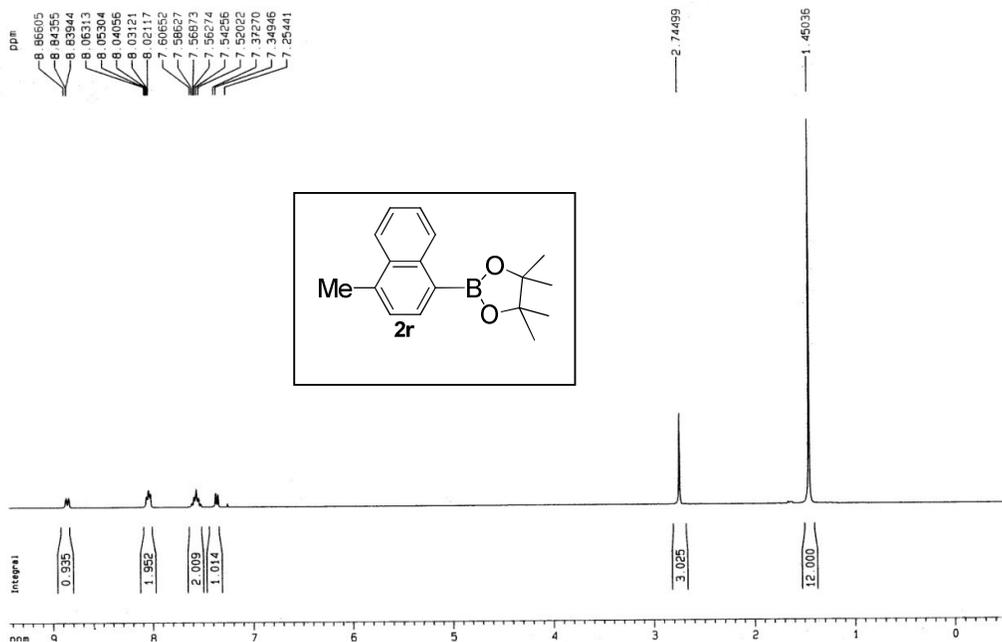
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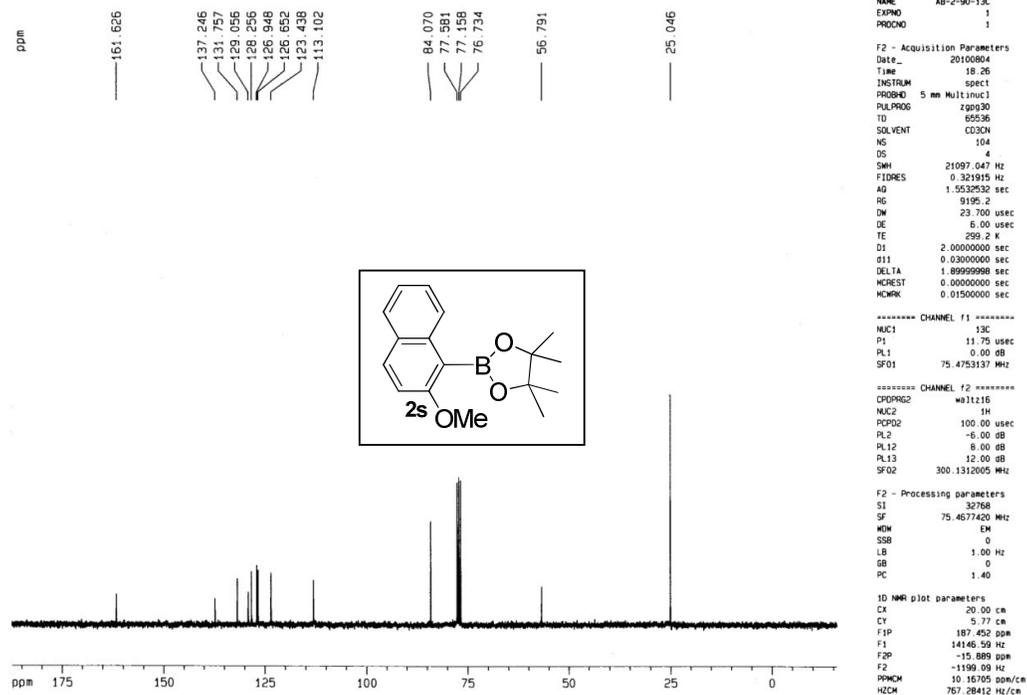
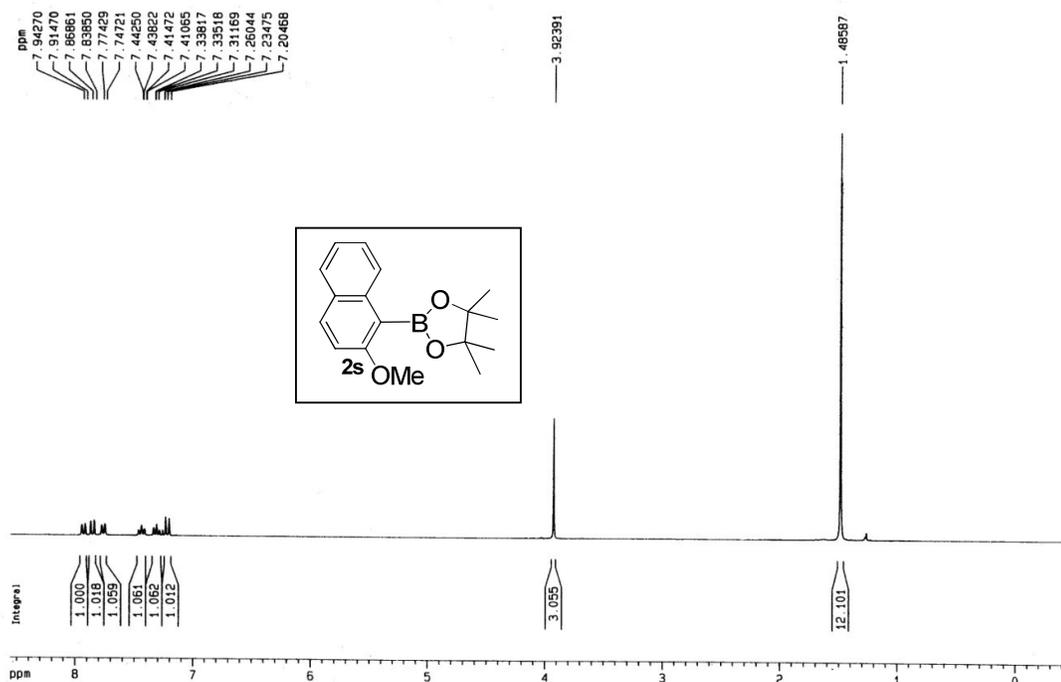
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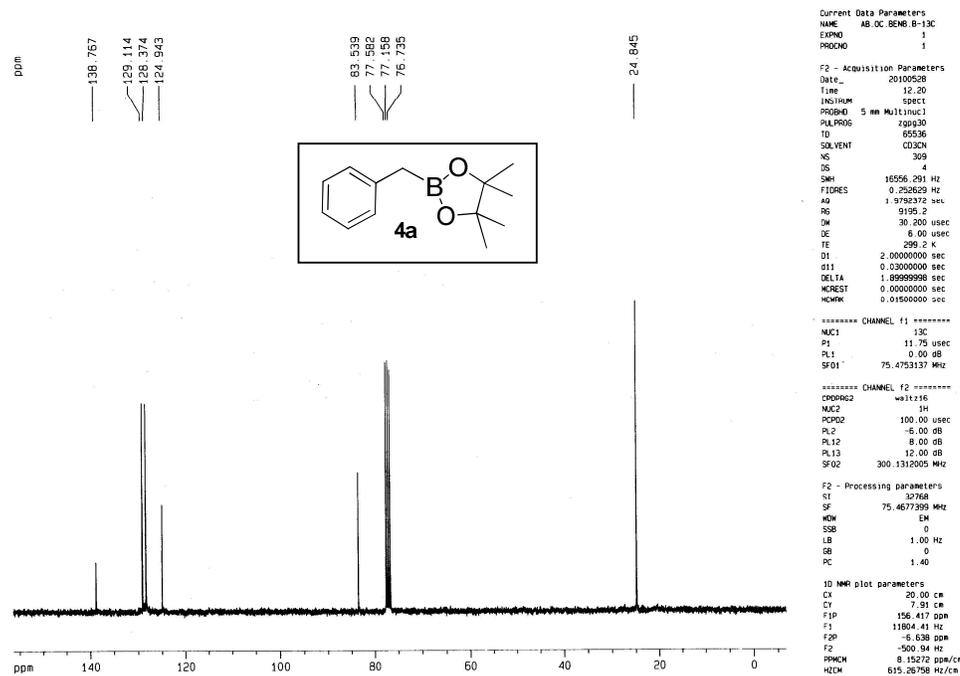
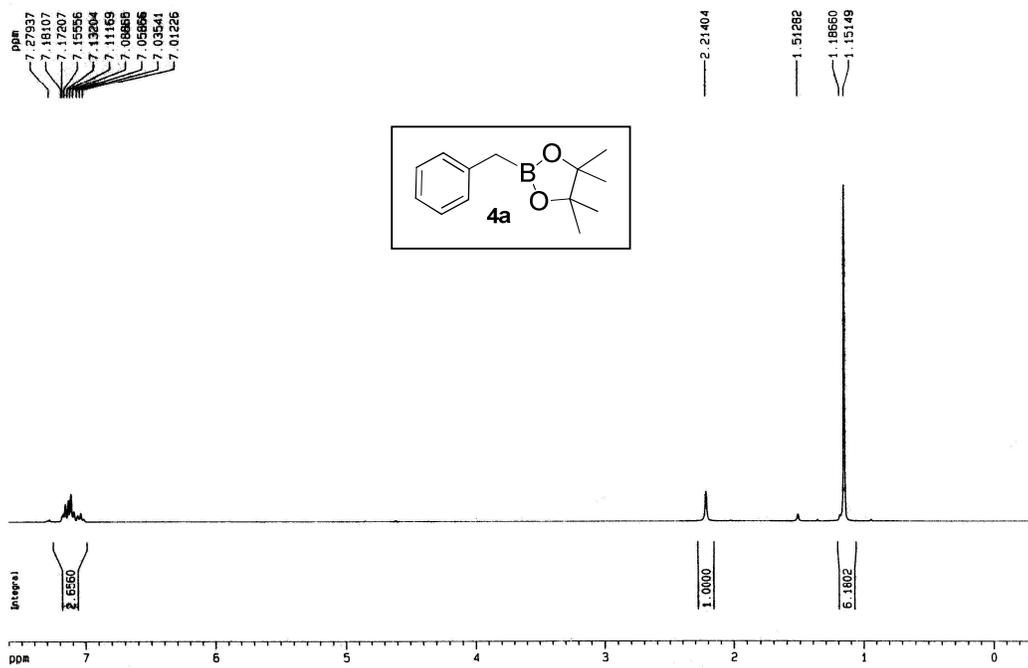
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F2 - Processing parameters
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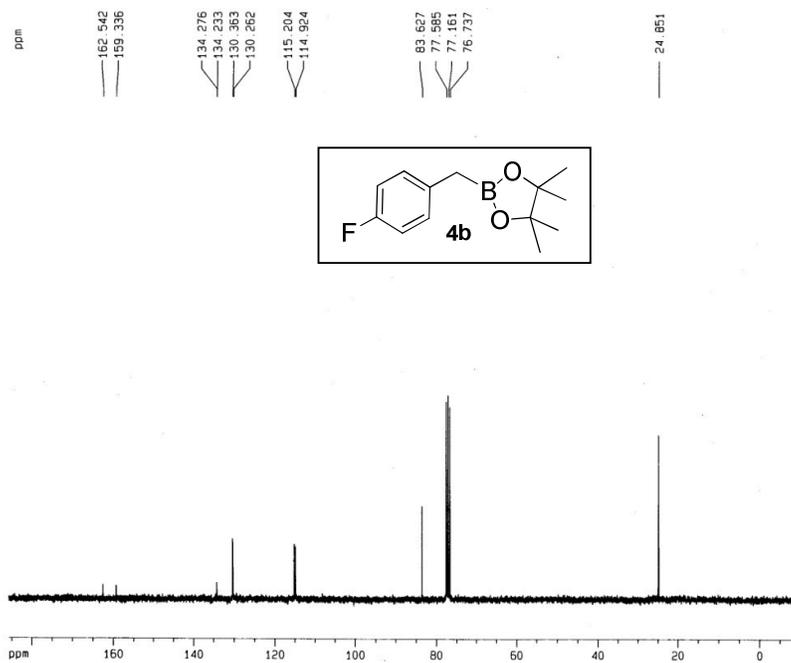
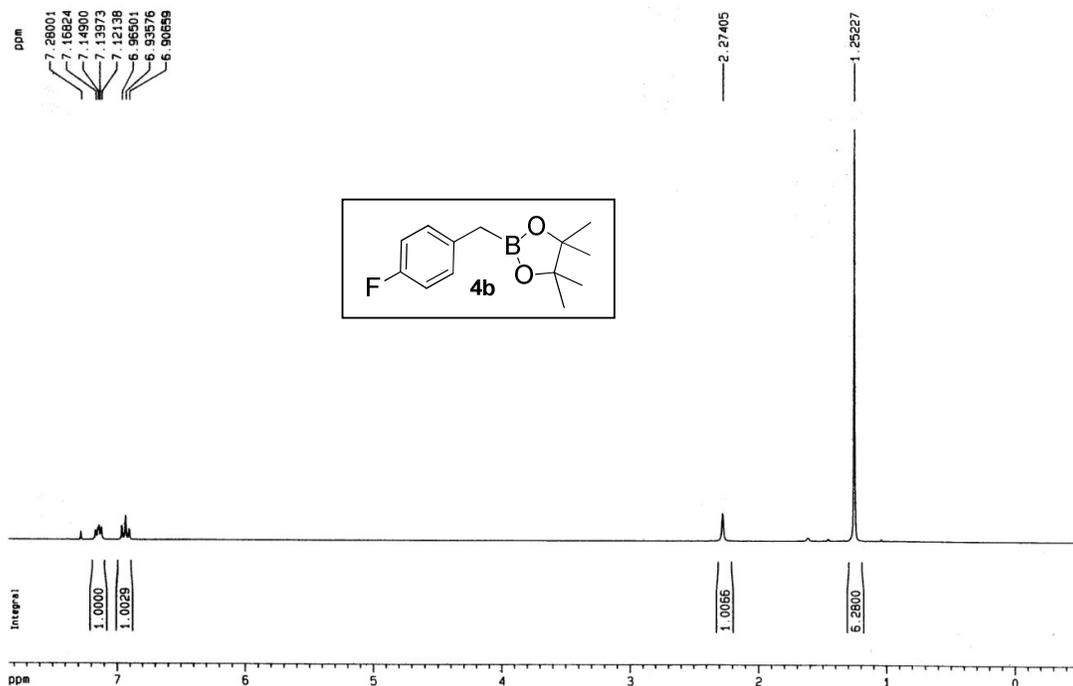
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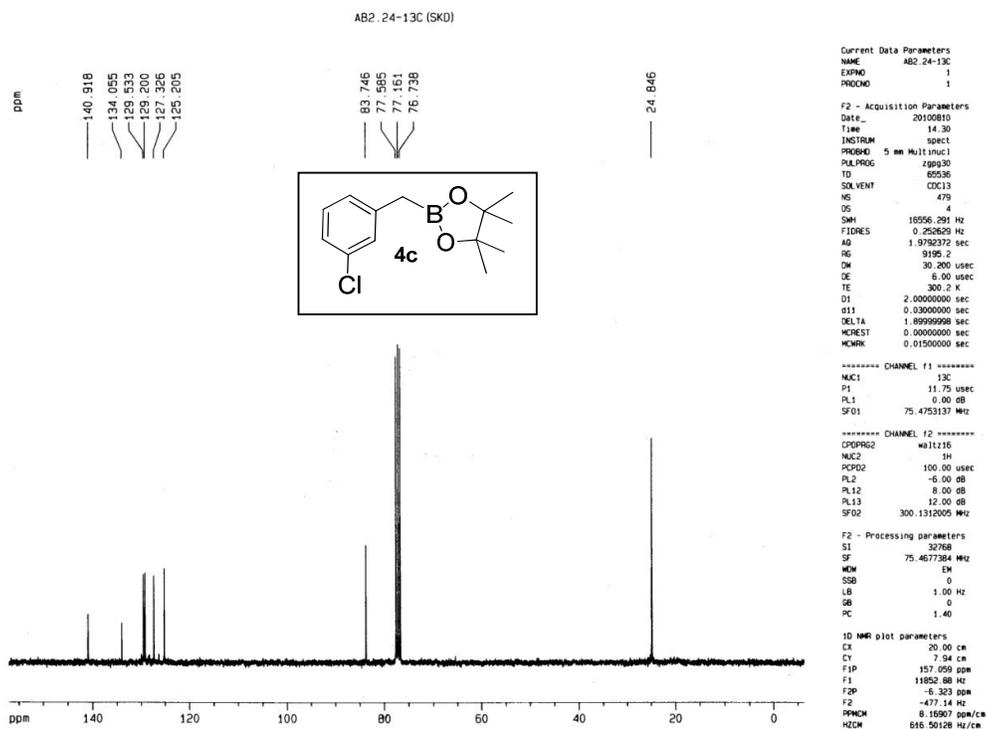
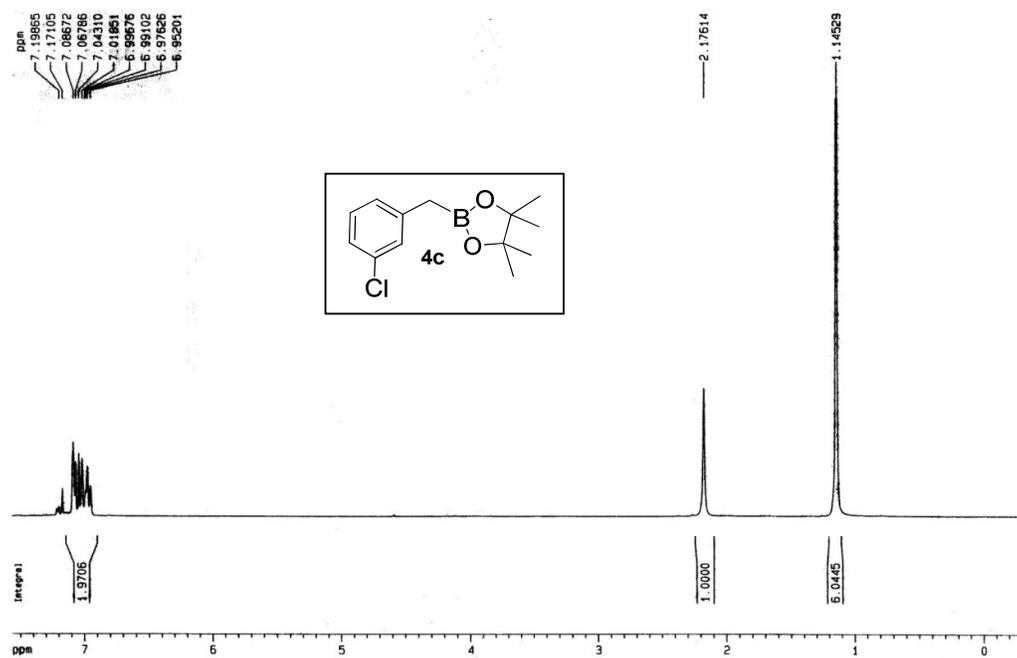
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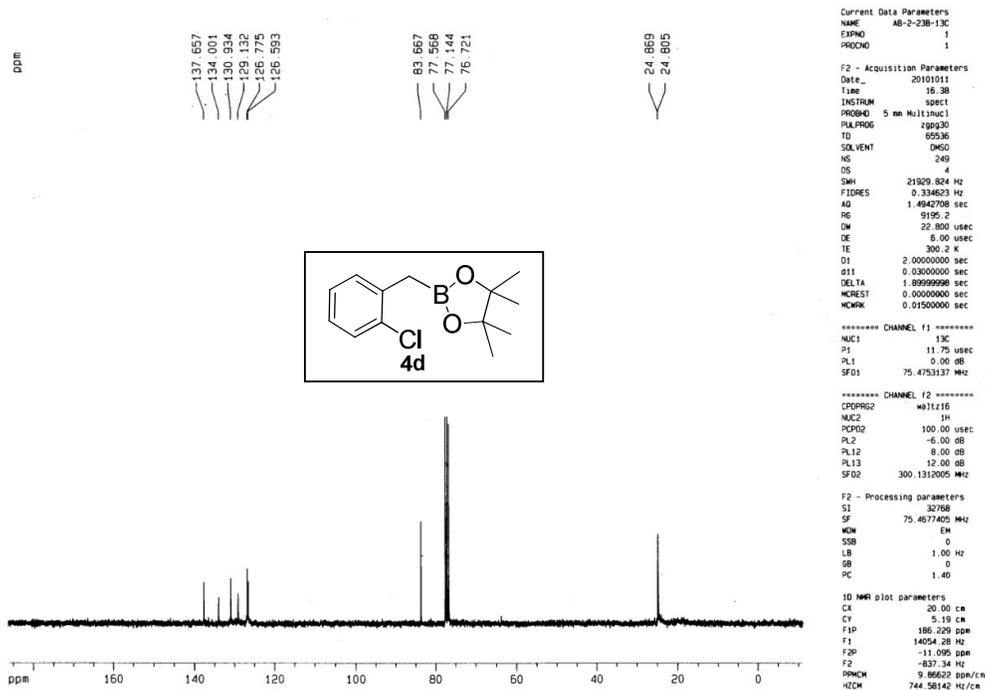
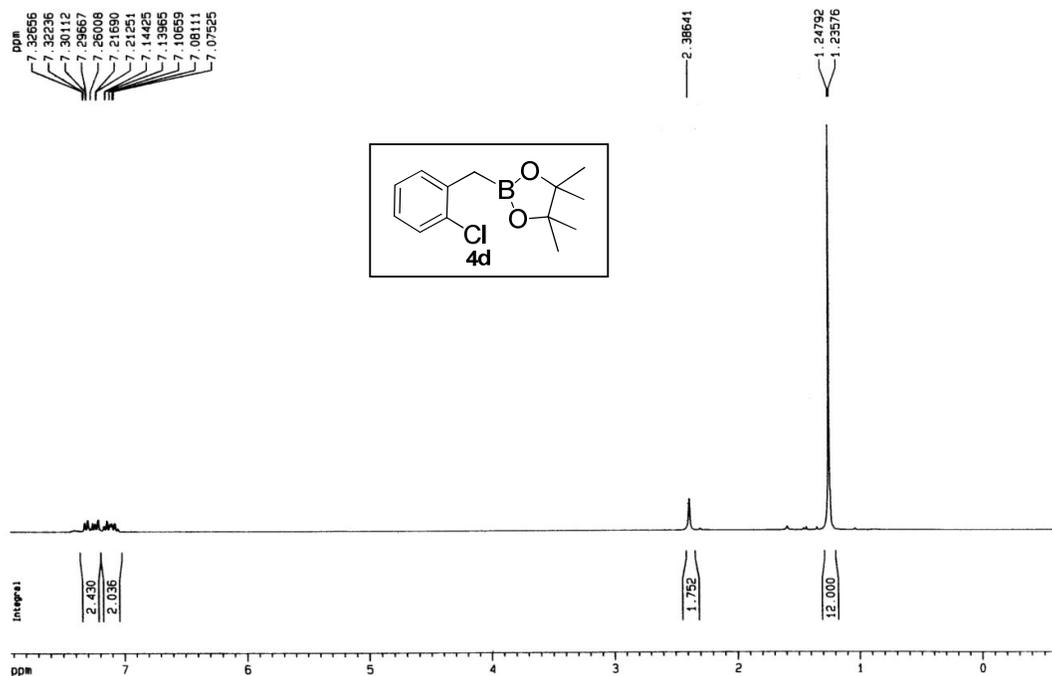
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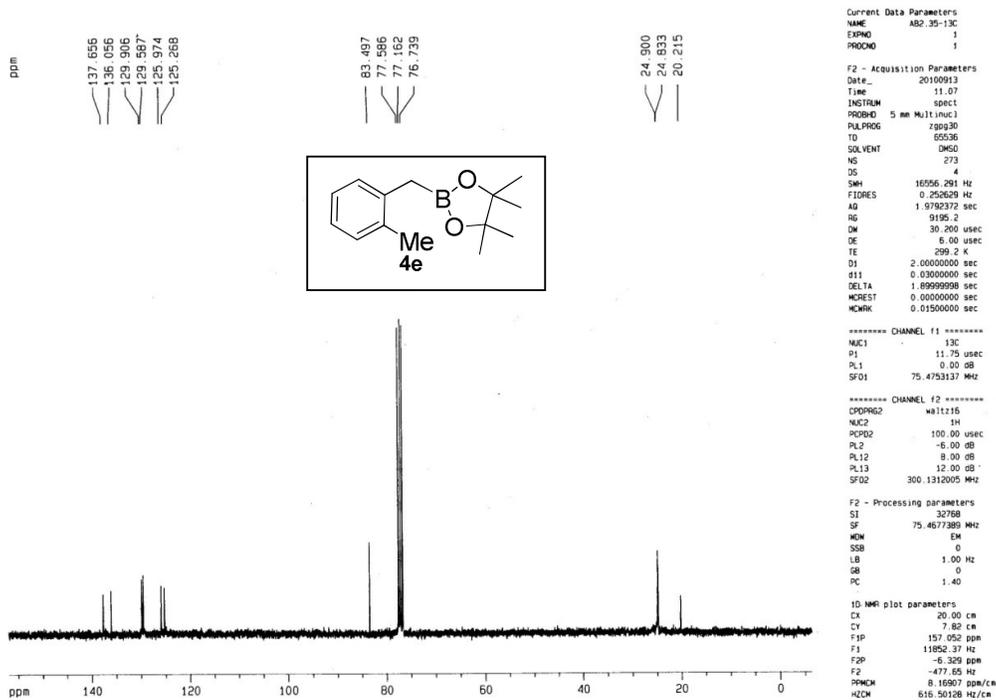
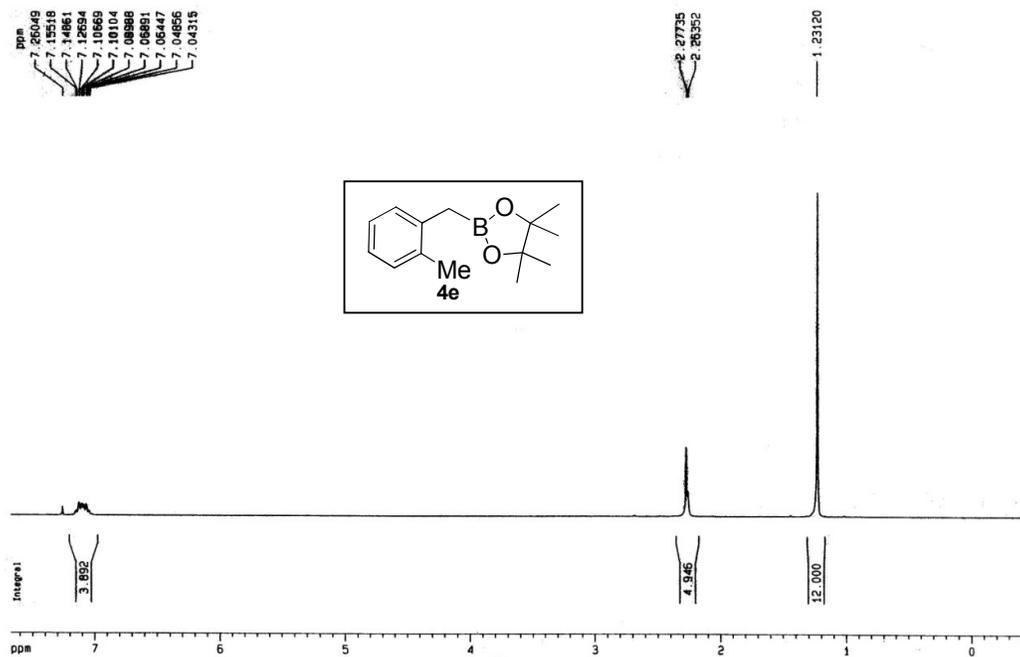
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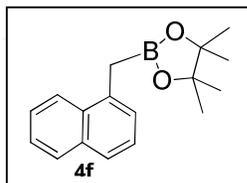
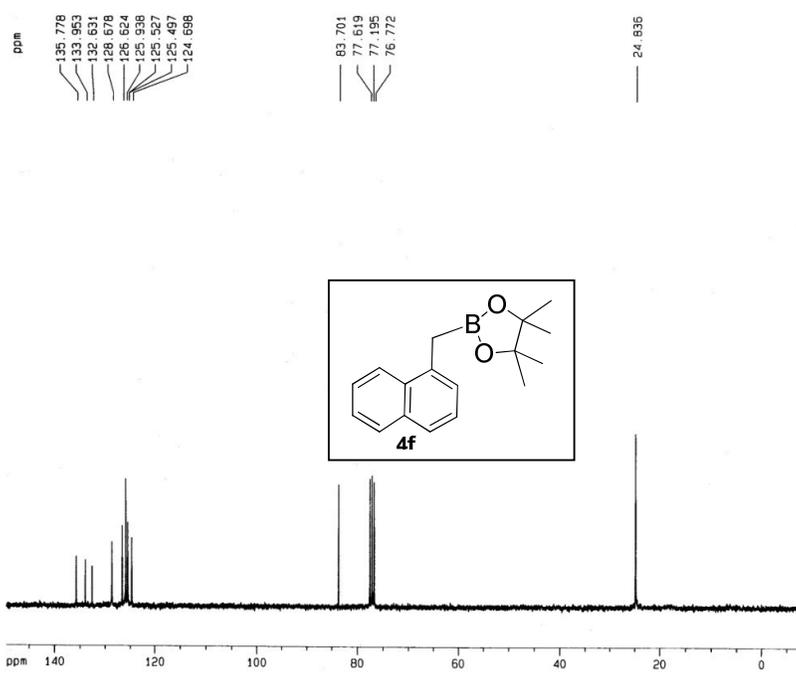
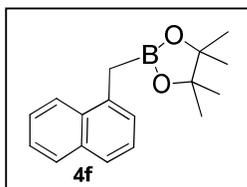
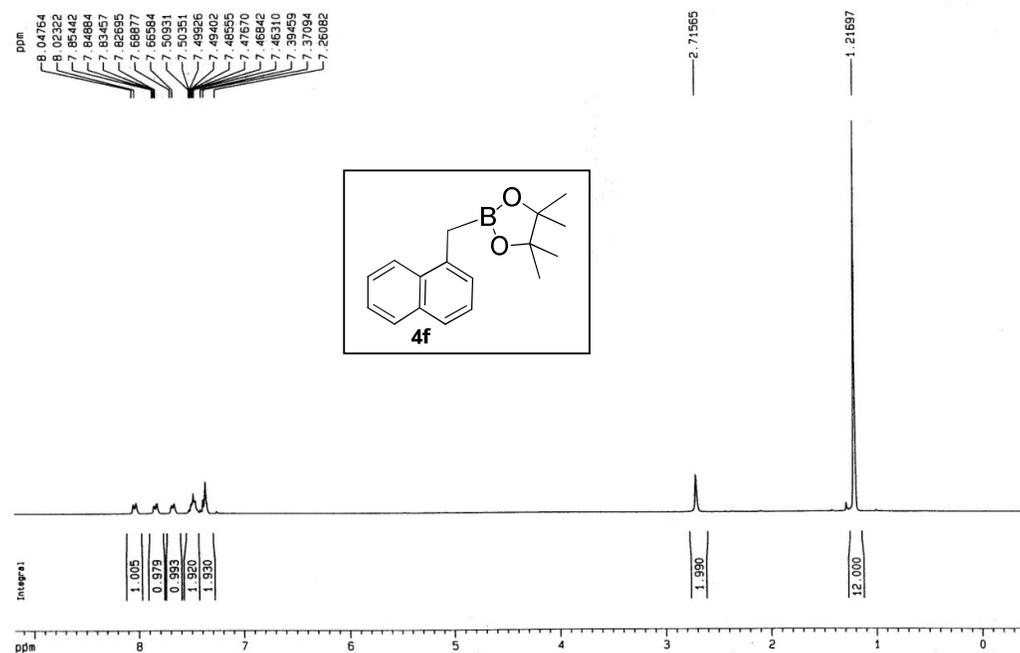
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ID NMR plot parameters
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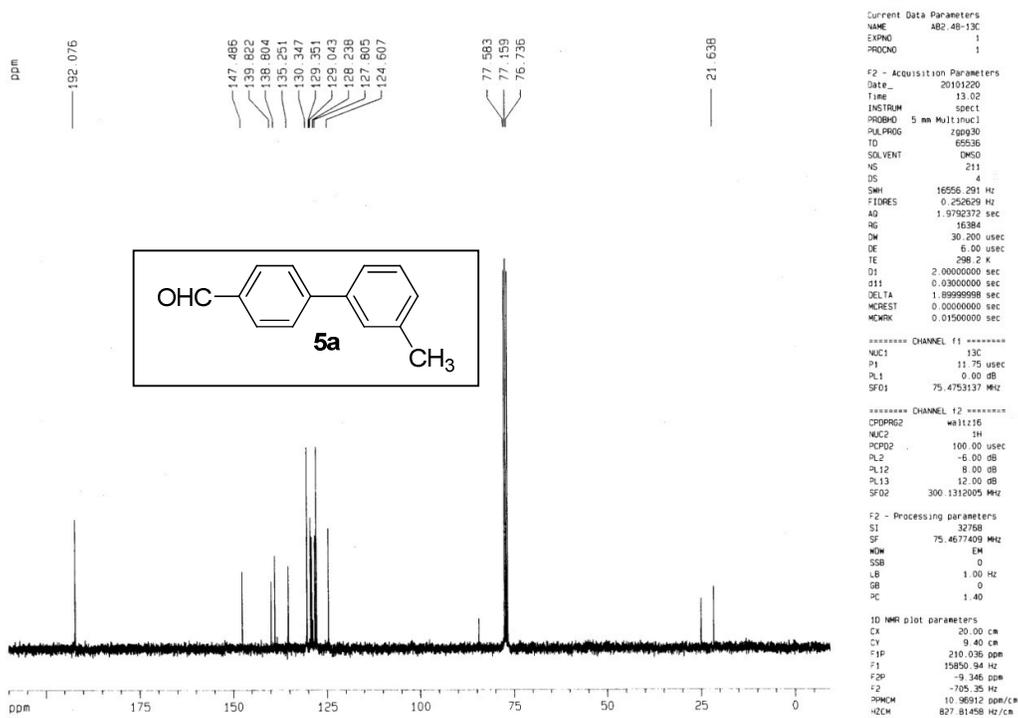
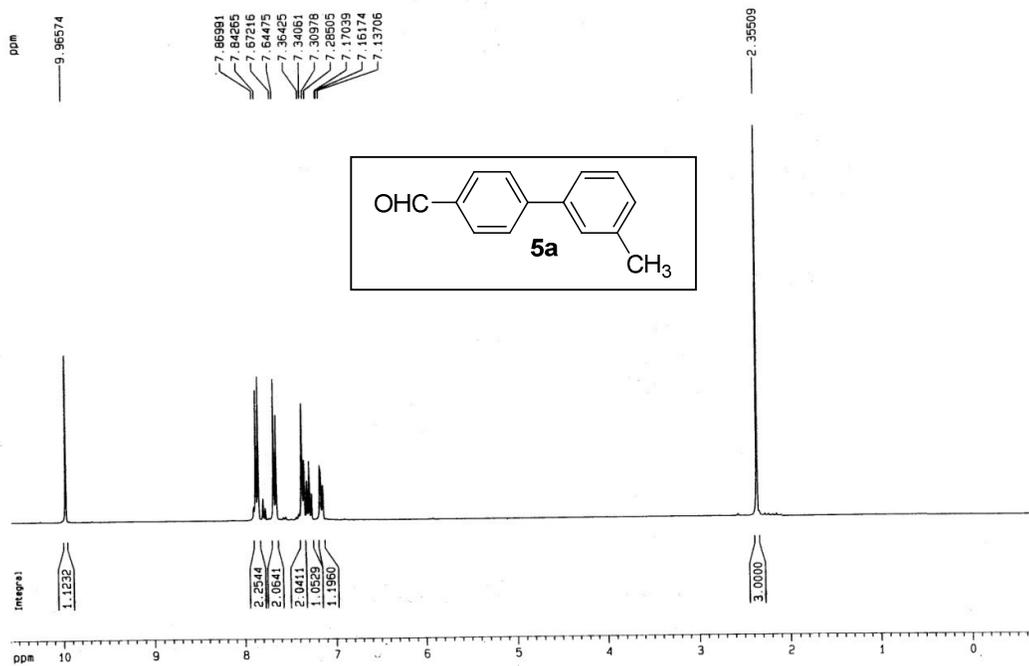
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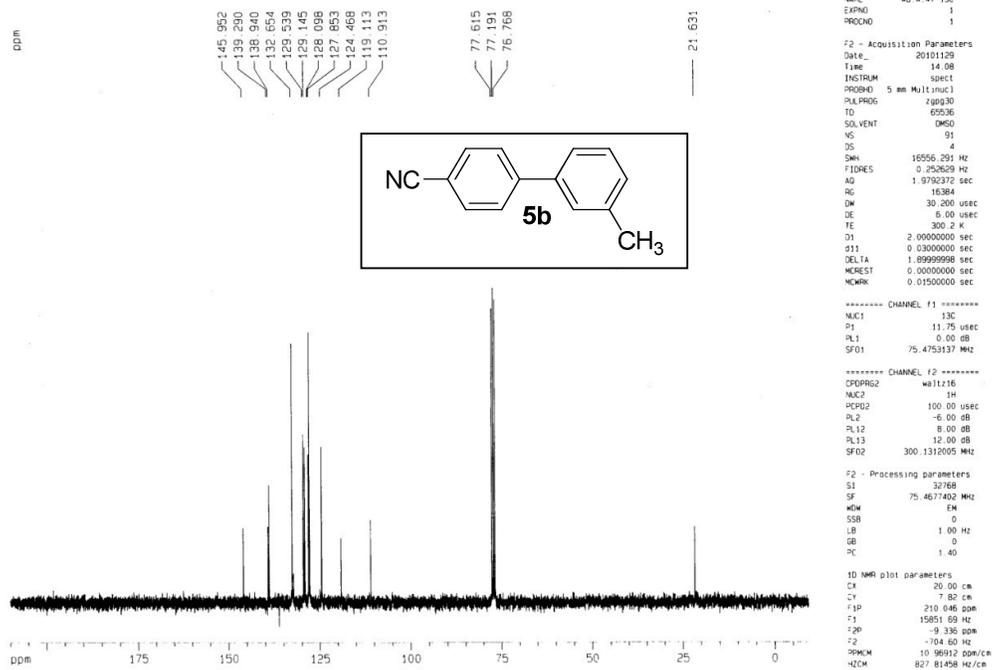
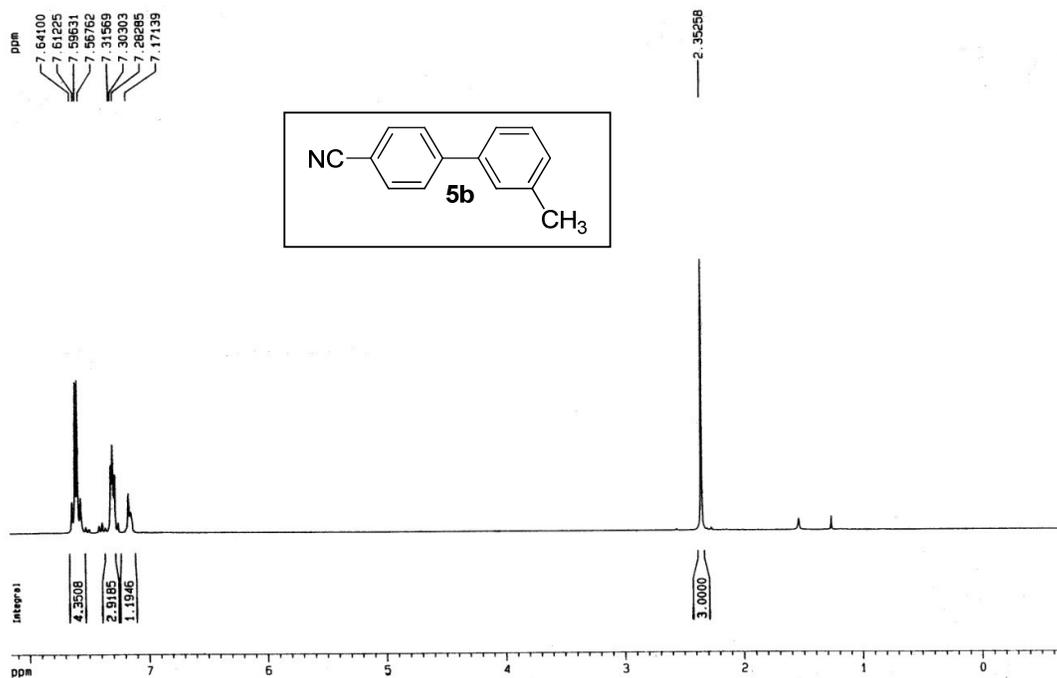
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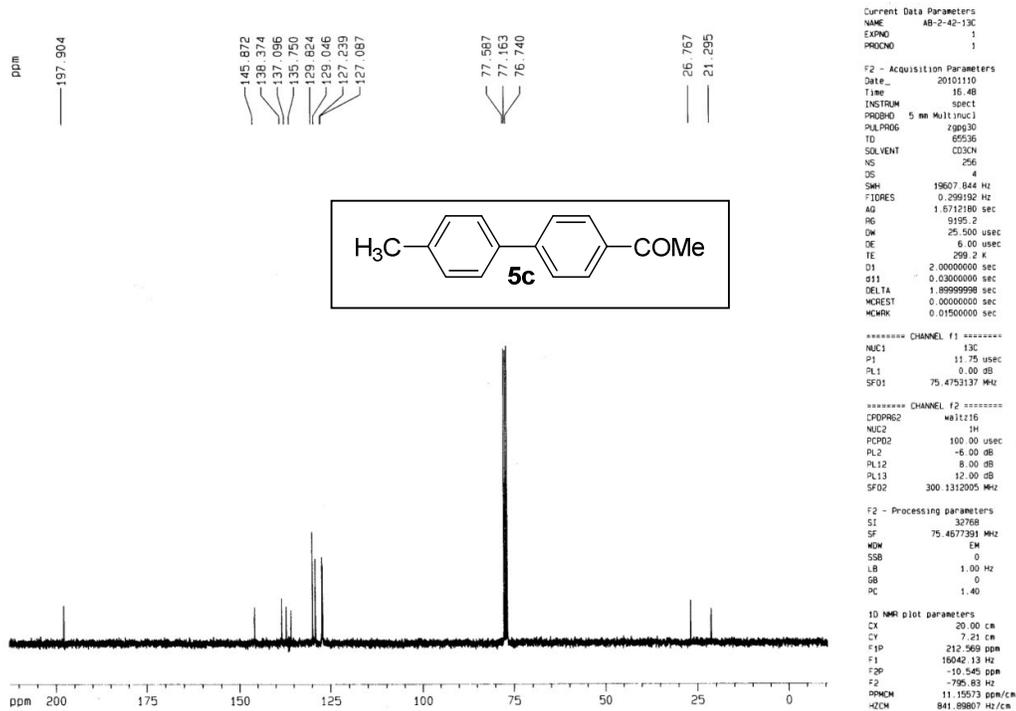
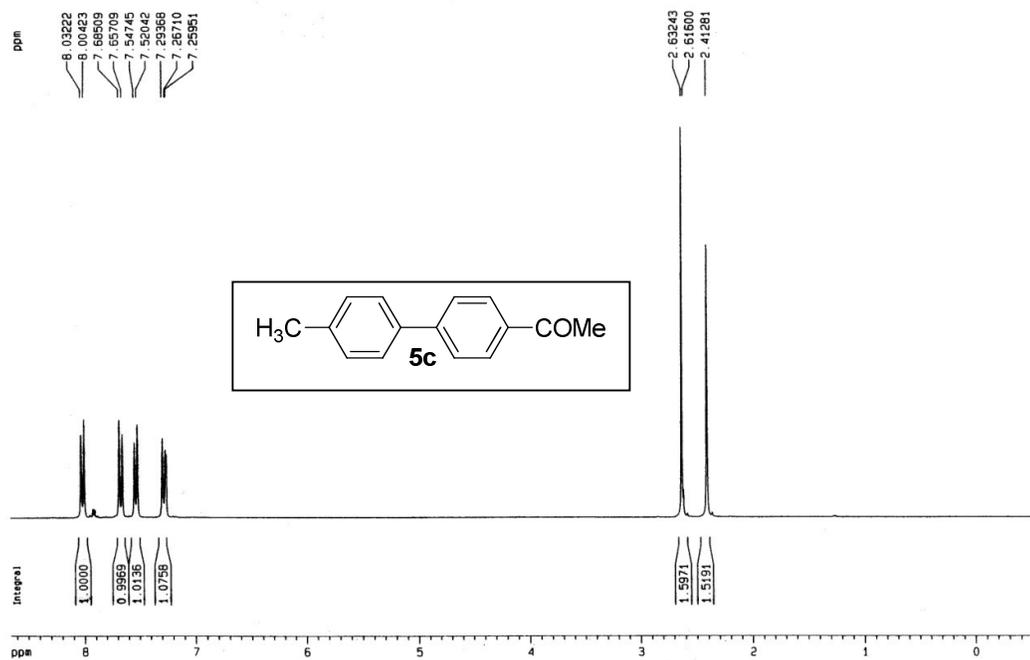
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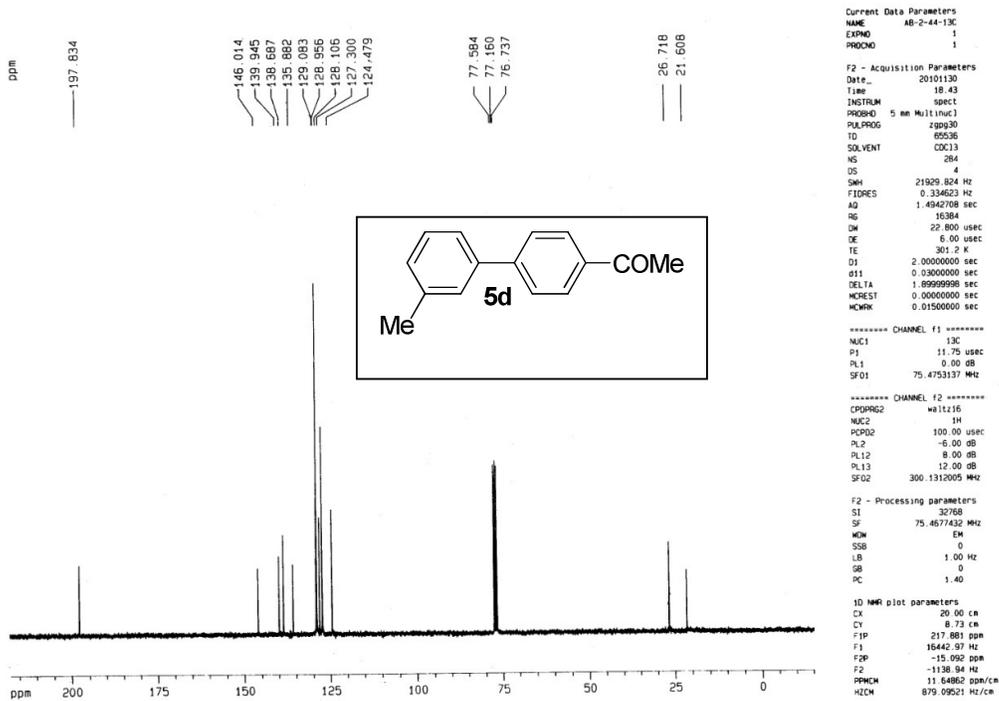
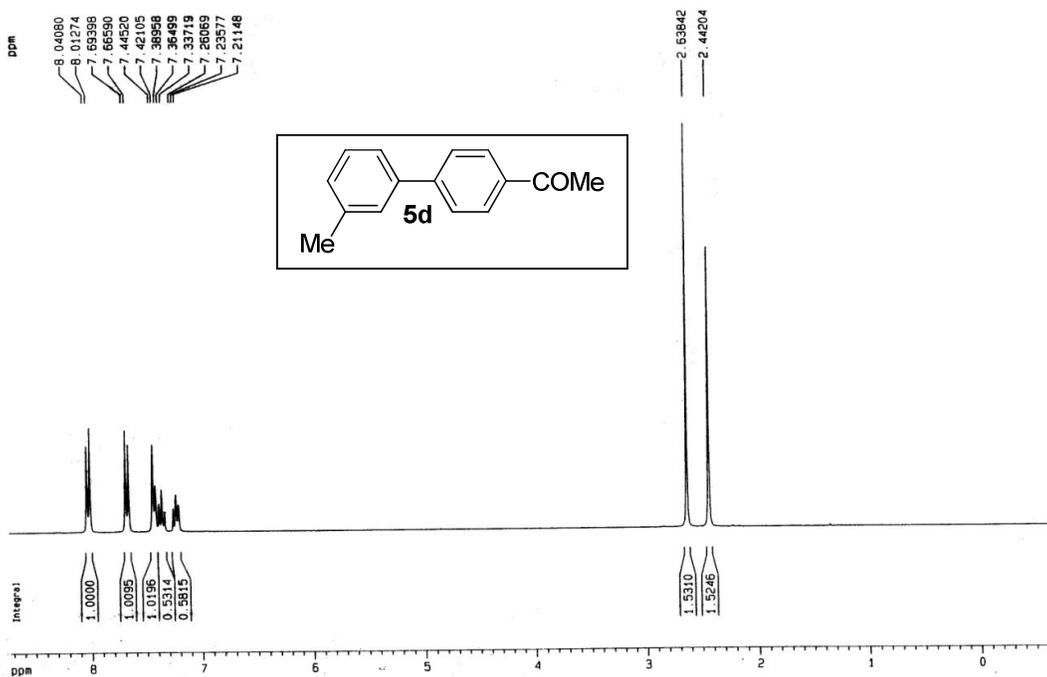
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 SF 75.4677375 MHz
 MHZ 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

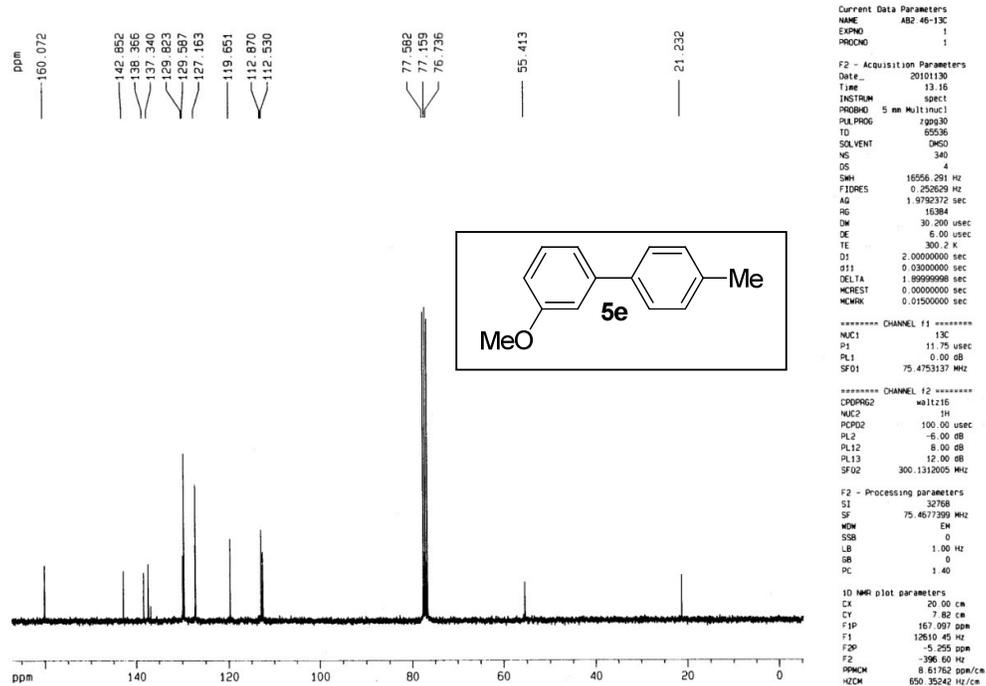
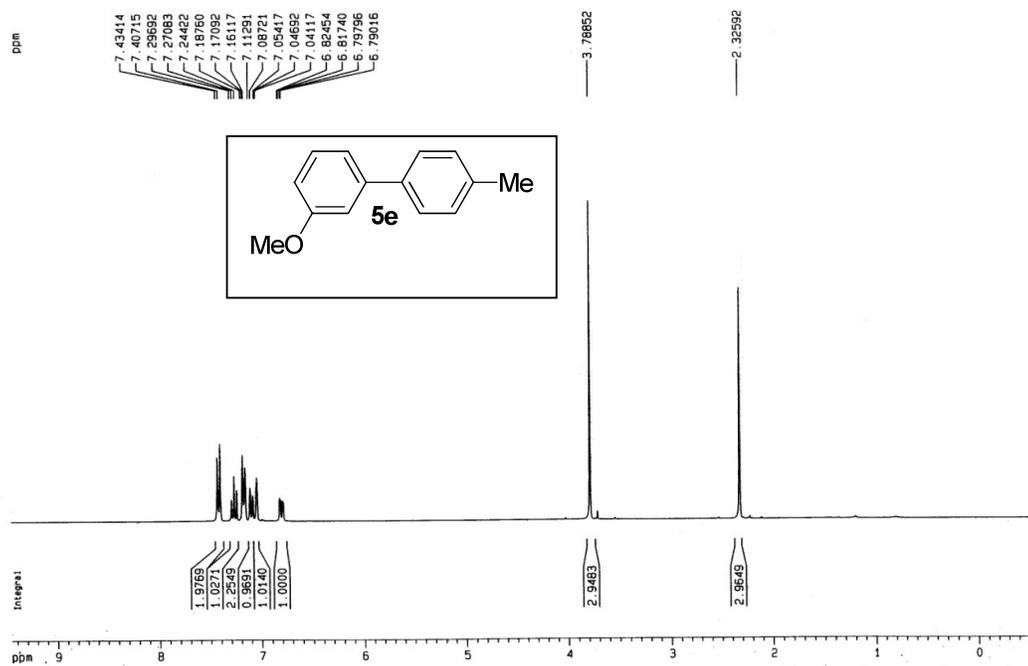
1D NMR plot parameters
 CX 20.00 cm
 CY 4.35 cm
 F1P 149.435 ppm
 F1 11277.48 Hz
 F2P -8.323 ppm
 F2 -628.10 Hz
 FWHM 7.88787 ppm/cm
 HZCM 595.27936 Hz/cm

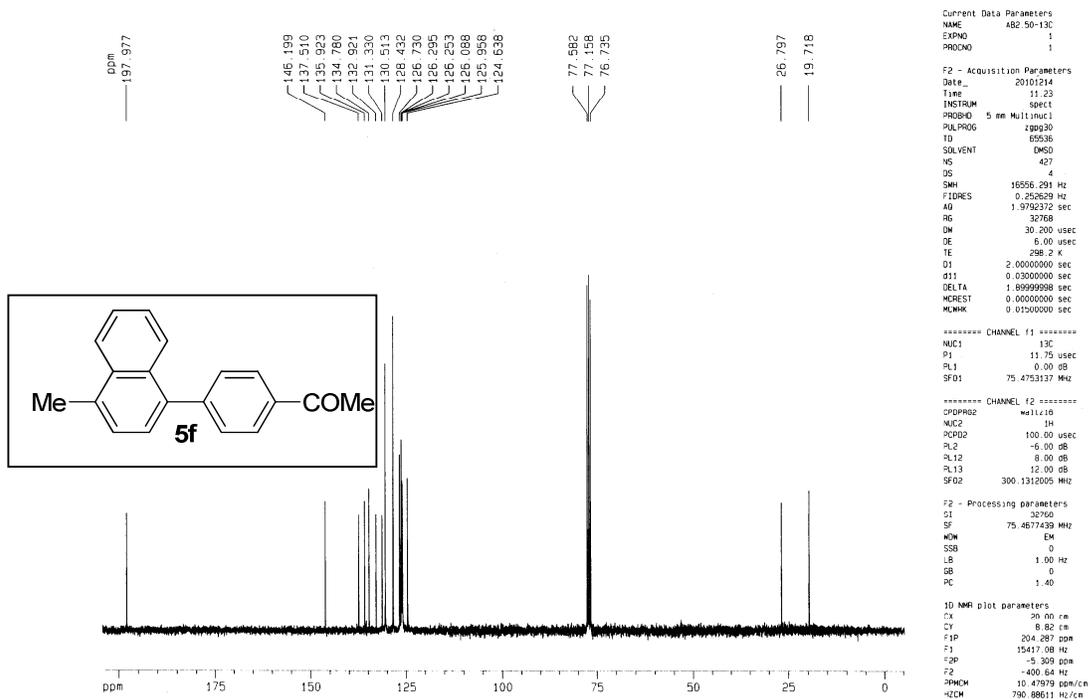
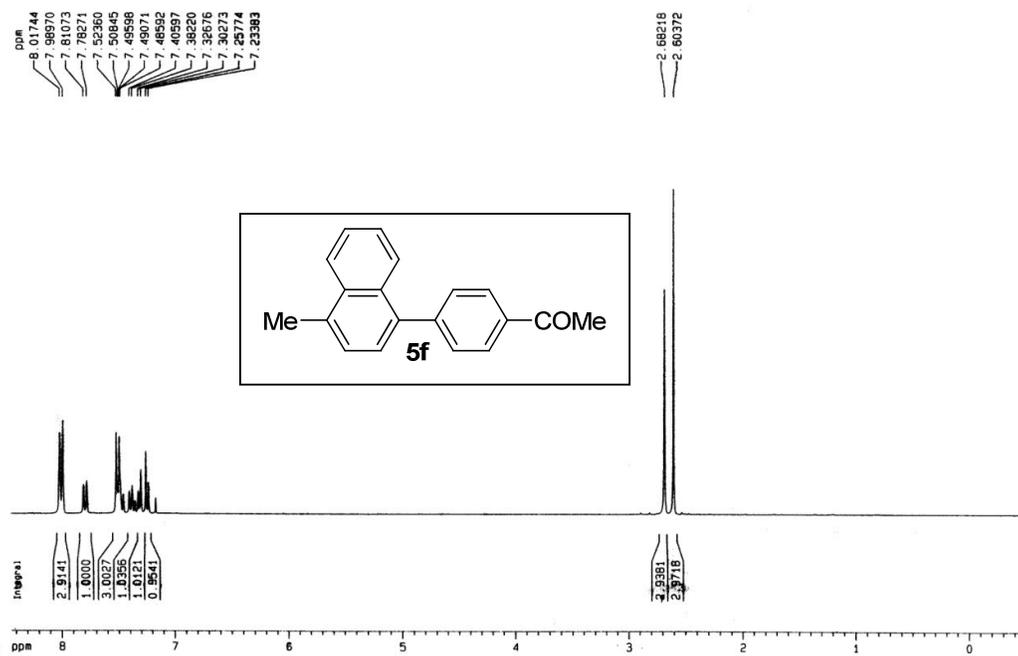


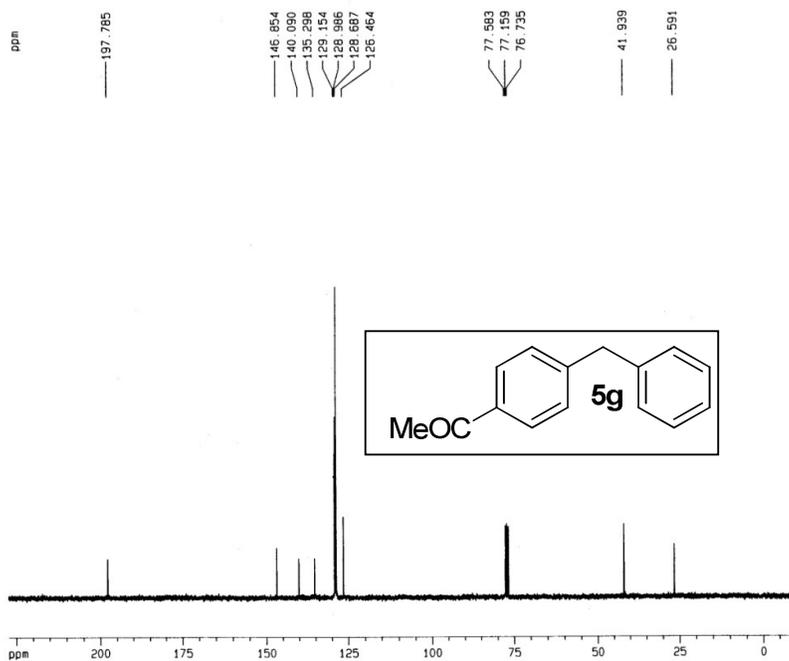
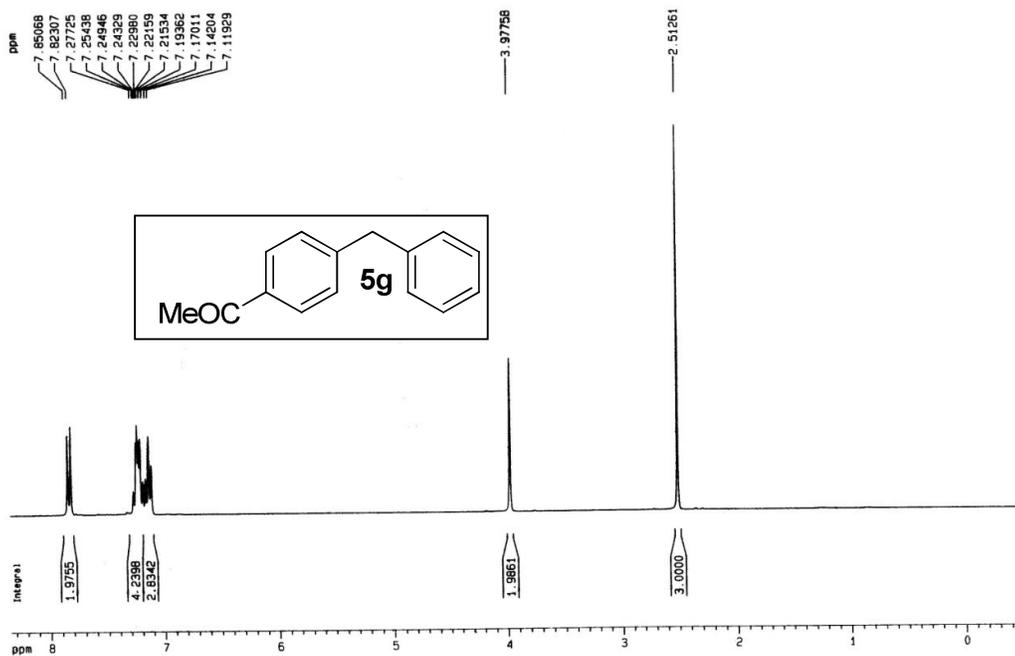












Current Data Parameters
 NAME DKSI.CO-13C
 EXPNO 1
 PROCNO 1

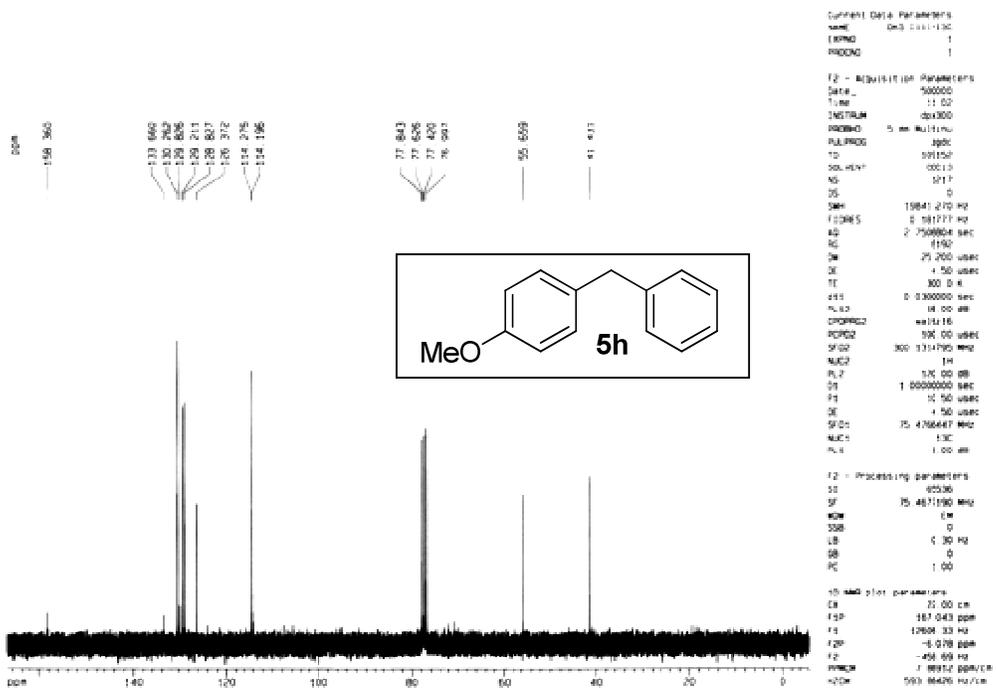
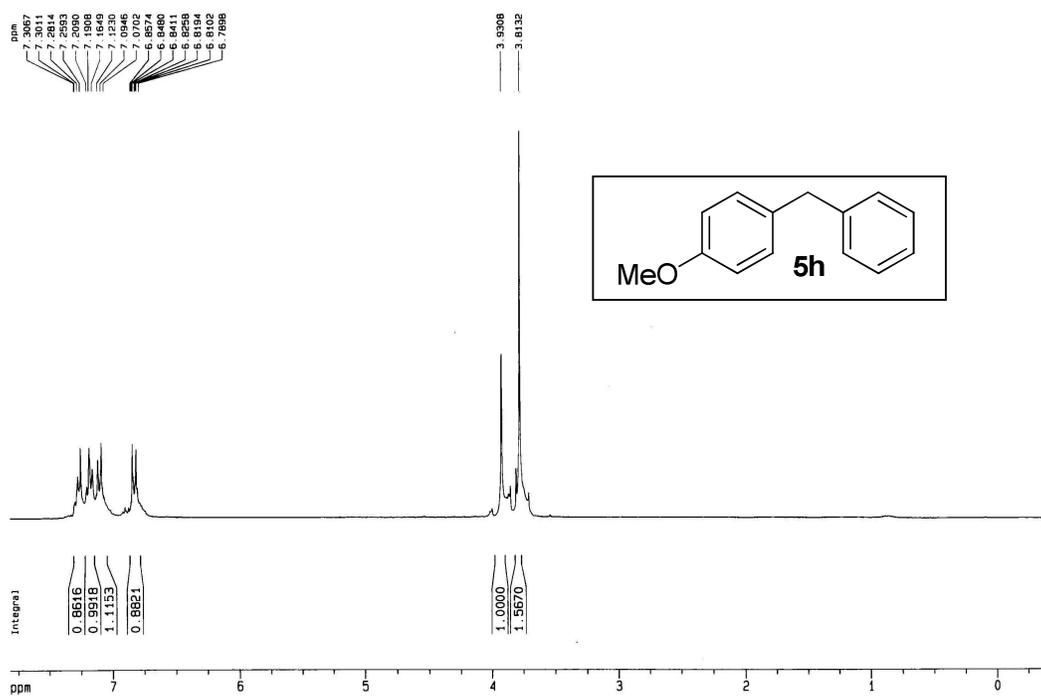
F2 - Acquisition Parameters
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 Time 12:15
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 65536
 ID 65536
 SOLVENT CDCl3
 NS 33
 DS 4
 SMH 18939.395 Hz
 FIDRES 0.288992 Hz
 AQ 1.732004 sec
 RG 9195.2
 DW 26.400 usec
 DE 6.00 usec
 TE 298.2 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999999 sec
 WREST 0.00000000 sec
 WCMR 0.01500000 sec

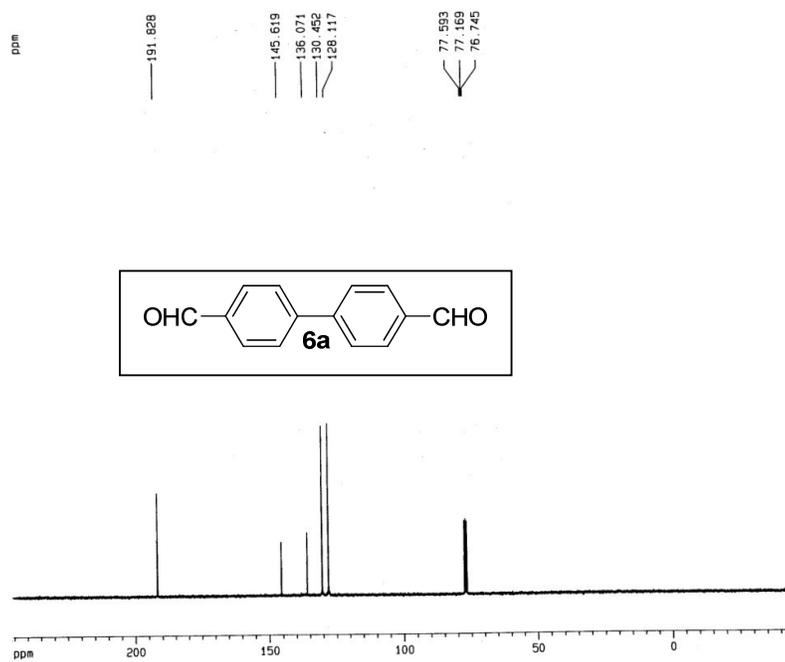
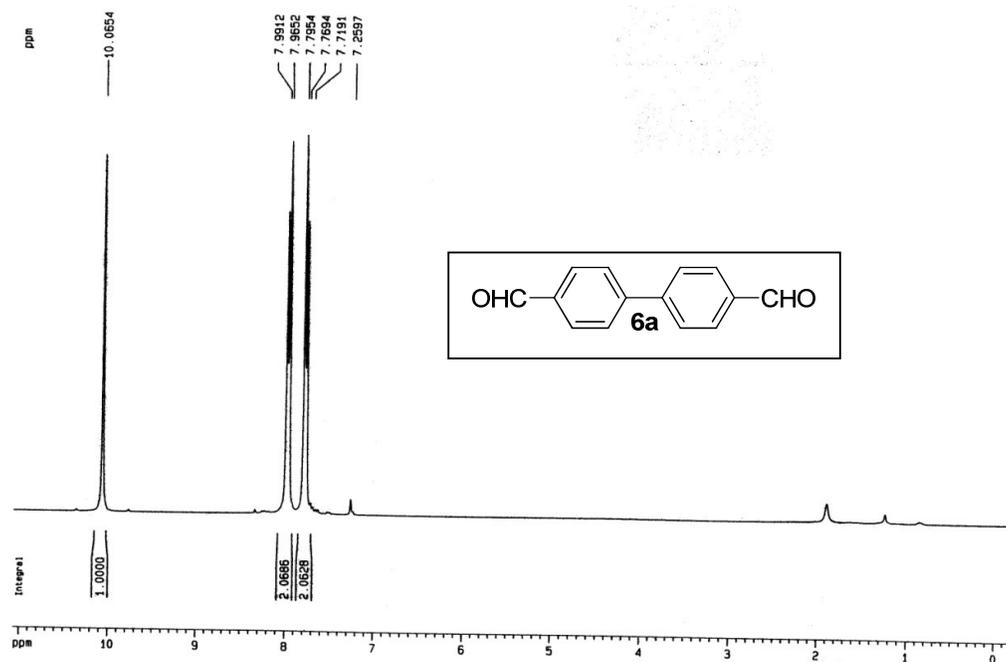
***** CHANNEL f1 *****
 NUC1 13C
 P1 11.75 usec
 PL1 0.00 dB
 SFO1 75.4763276 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 PL2 -8.00 dB
 PL12 8.00 dB
 PL13 12.00 dB
 SFO2 300.1332000 MHz

F2 - Processing parameters
 SI 32768
 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 7.63 cm
 F1P 227.541 ppm
 F1 17172.01 Hz
 F2P -10.581 ppm
 F2 -798.50 Hz
 PPMCH 11.90609 ppm/cm
 HZCH 898.52545 Hz/cm





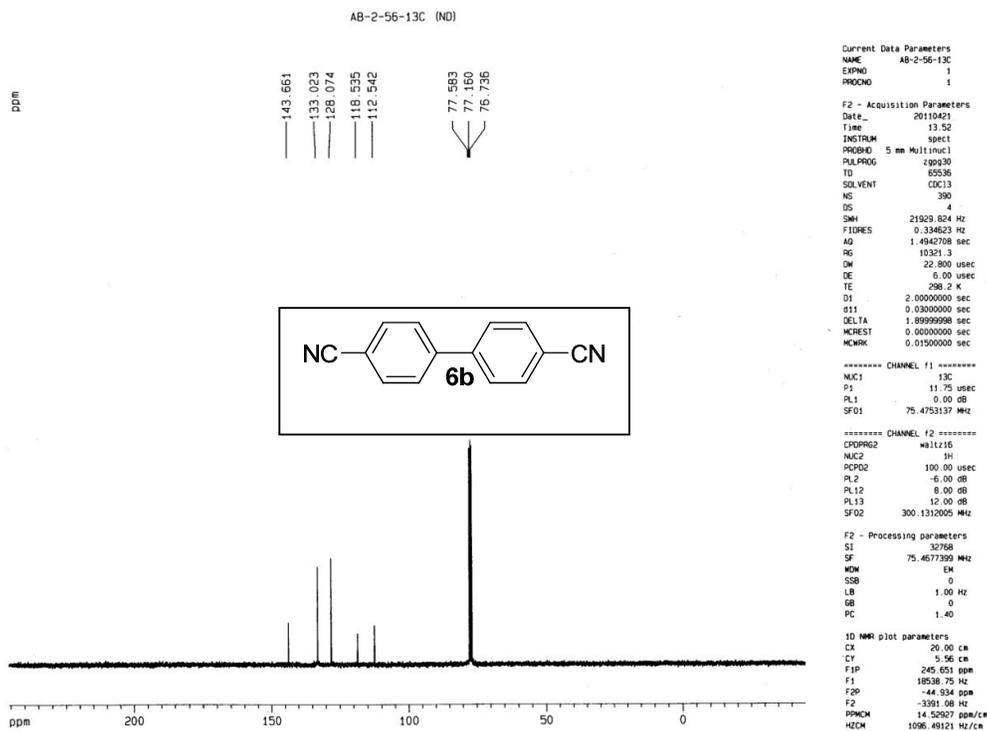
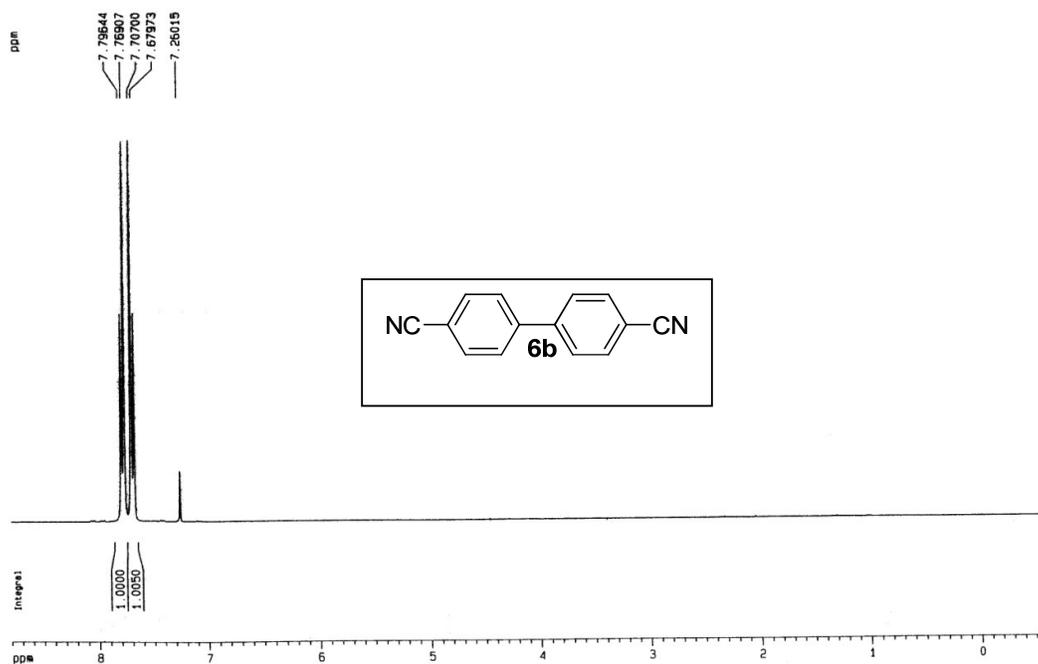
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 PROCNO 1
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 Time 15.28
 INSTRUM spect
 PROBR0 5 mm Multinucl
 PULPROG zgpg30
 TD 65535
 SOLVENT CDCl3
 NS 253
 DS 4
 SWH 21929.824 Hz
 FIDRES 0.334623 Hz
 AQ 1.4942708 sec
 RG 10321.3
 DW 22.800 usec
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 WCHR 0.0150000 sec

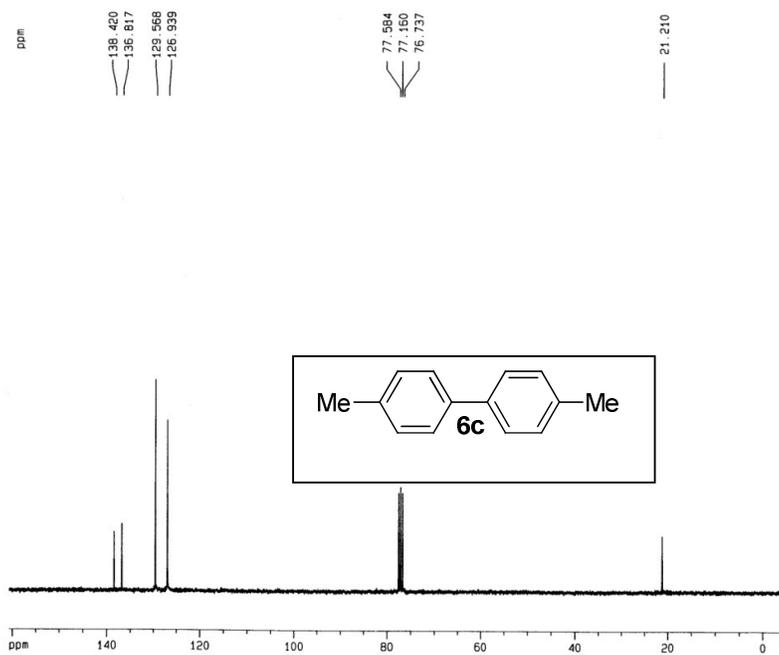
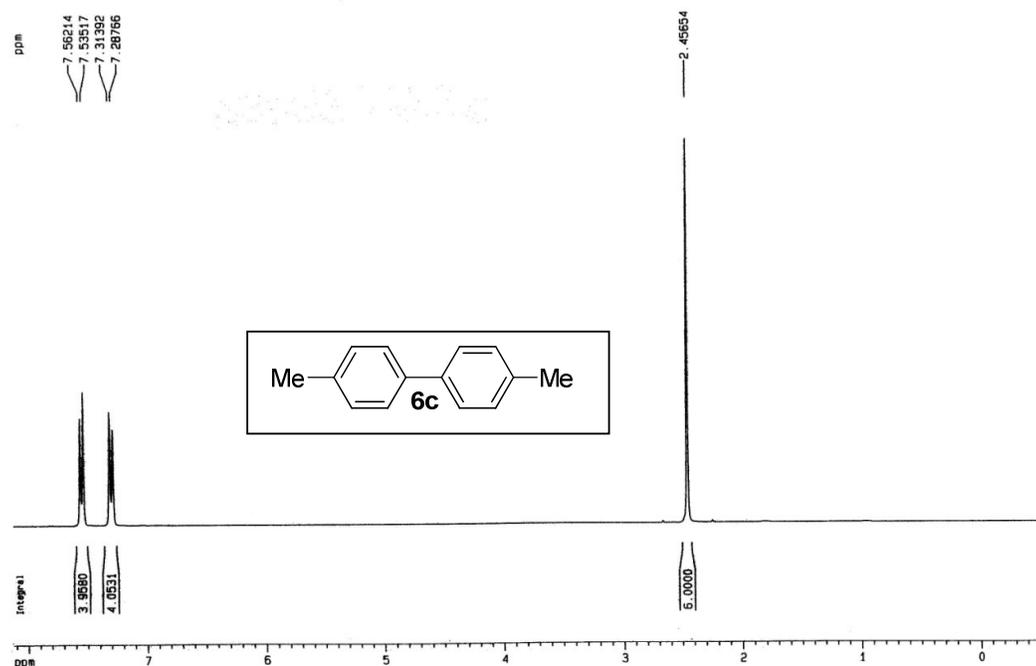
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 P1 11.75 usec
 PL1 0.00 dB
 SFO1 75.473137 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 -5.00 dB
 PL12 8.00 dB
 PL13 12.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 S1 32708
 SF 75.4677419 MHz
 WM EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

ID NMR plot parameters
 CX 20.00 cm
 CY 4.44 cm
 F1P 245.620 ppm
 F1 18536.74 Hz
 F2 -44.961 ppm
 F2 -3393.09 Hz
 PPMCM 14.52927 ppm/cm
 HZCM 1096.49121 Hz/cm





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Current Data Parameters
NAME      AB-2-5AA-13C
EXPNO     2
PROCNO    1

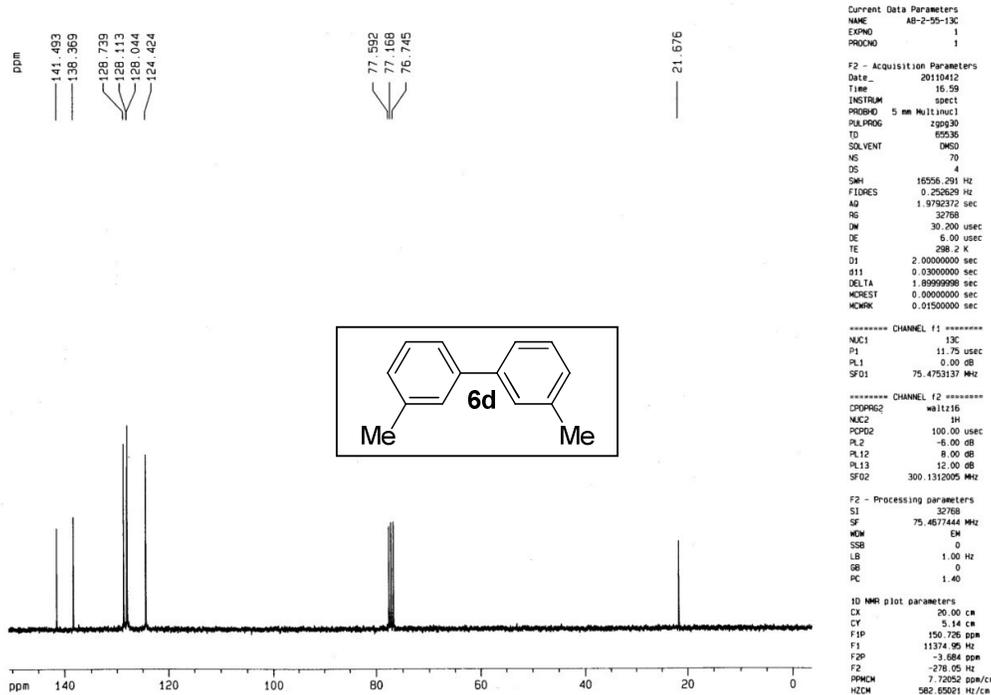
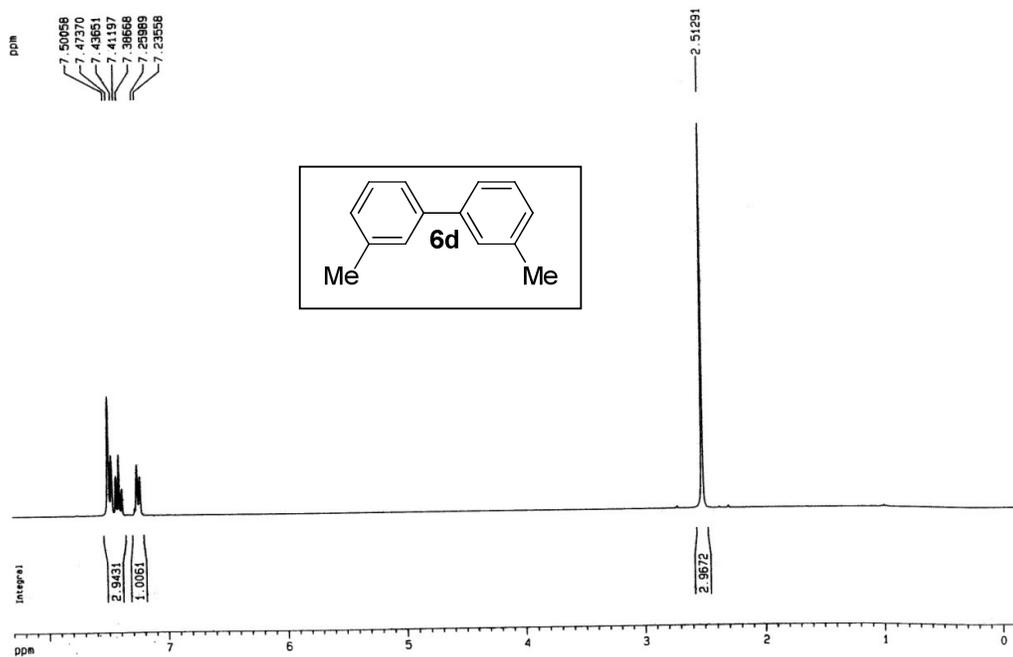
F2 - Acquisition Parameters
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PROBHD    5 mm Multinucl
PULPROG   zgpg30
ID        60536
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NS         105
DS         4
SWH        21829.824 Hz
FIDRES     0.334823 Hz
AQ         1.4942708 sec
RG          9125.2
DM         22.800 usec
DE         6.00 usec
TE         298.2 K
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d11        0.03000000 sec
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MORSE1    0.00000000 sec
MORSE2    0.01500000 sec

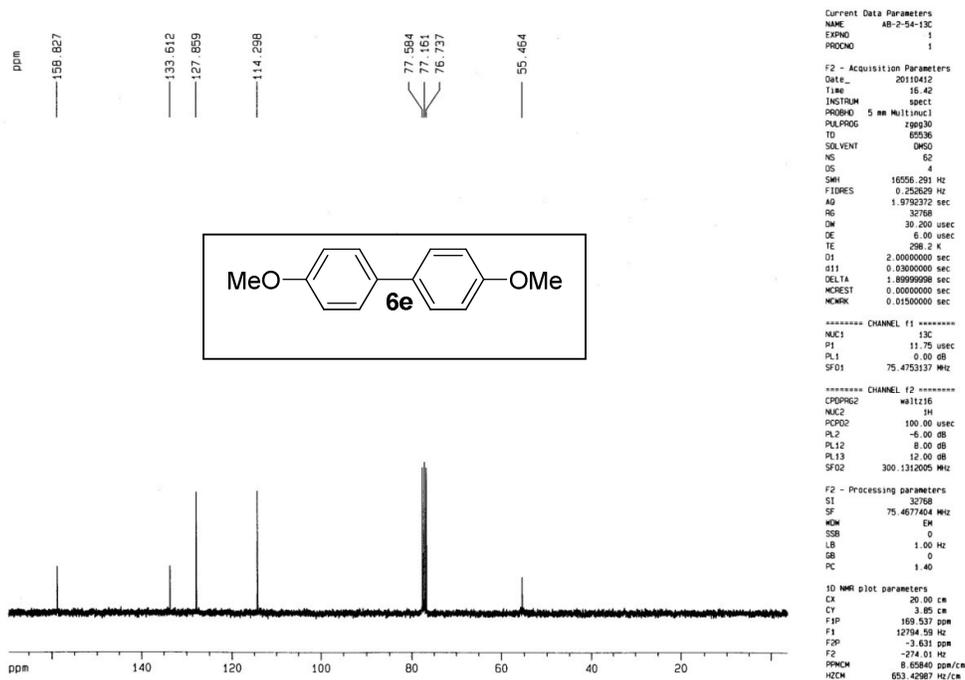
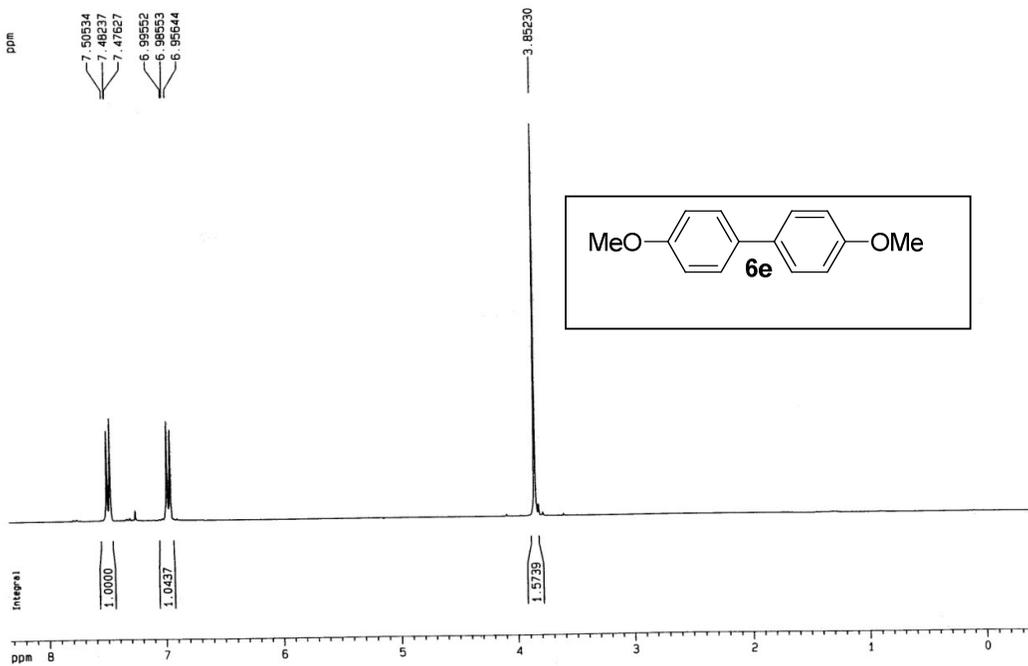
***** CHANNEL f1 *****
NUC1       13C
P1         11.75 usec
PL1        0.00 dB
SF01       75.4753137 MHz

***** CHANNEL f2 *****
CPDPRG2   mlti215
NUC2       1H
P2         100.00 usec
PL2        -5.00 dB
PL12       8.00 dB
PL13       12.00 dB
SF02       300.1312005 MHz

F2 - Processing parameters
SI         32768
SF         75.4677425 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         0.30

ID NMR plot parameters
CX         20.00 cm
CY         5.41 cm
F1P        160.733 ppm
F1         12130.18 Hz
F2P        -5.267 ppm
F2         -397.45 Hz
PRNCH      8.29999 ppm/cm
H2CH       626.38184 Hz/cm
    
```





5. TEM image of nanoparticle:

The nanoparticle formed is characterized by Transmission electron microscopy (TEM). The average size of the nanoparticle formed was 6 nm. The selected area electron diffraction (SAED) pattern shows four diffused rings corresponds to (200), (220) and (311) reflections of *fcc* Pd (Figure-1)

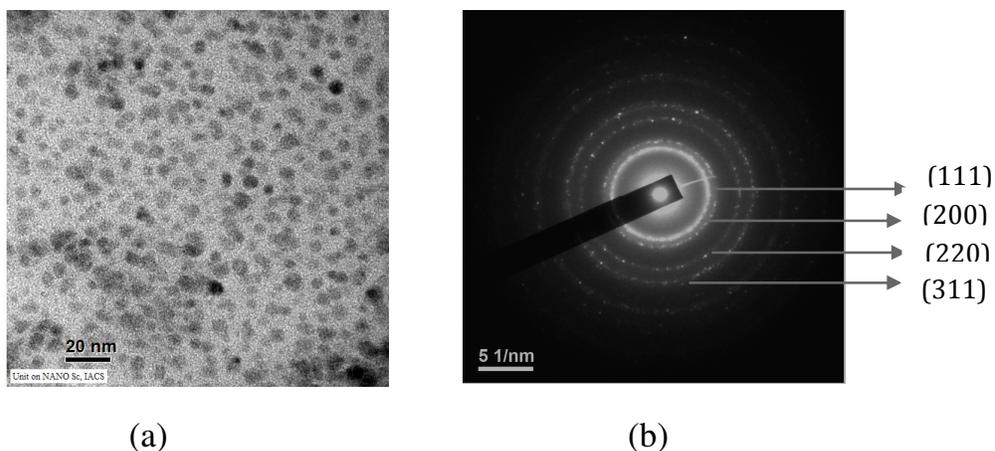


Figure 1: (a) TEM image of palladium nanoparticle and (b) selected area electron diffraction (SAED) image.

6. Recycling study:

The organic product was extracted five times with ether after each run and the reaction was continued with a fresh batch of substrate (3-bromotoluene, 1 mmol scale) added to the separated nanoparticle suspension.

