Supporting Information

Practical Method for Asymmetric Addition of Arylboronic Acids to α,β-Unsaturated Carbonyl Compounds Utilizing an in situ Prepared Rhodium Catalyst

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General Information.

Dioxane solvent was sparged with nitrogen for 30 min prior to the reactions. All reactions were conducted under nitrogen atmosphere.

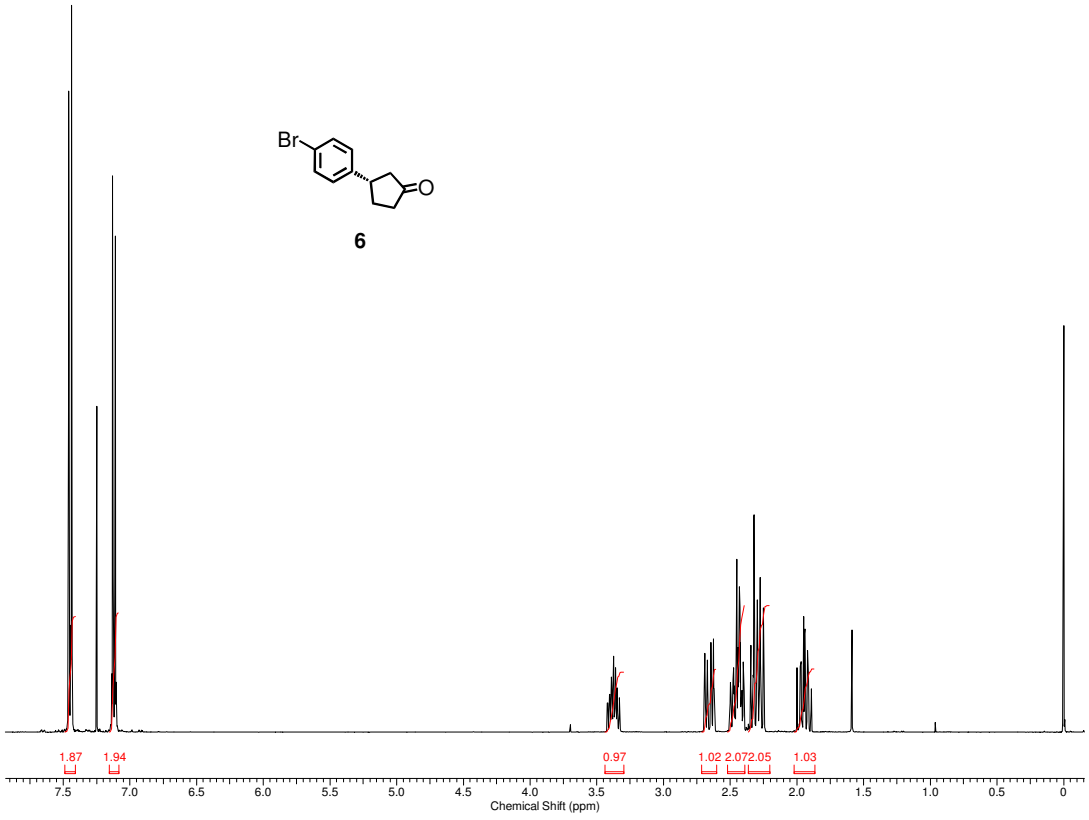
The reaction yields were determined by HPLC method using isolated reference material. The reference materials were obtained from the crude isolated products by column chromatography (silica; ethyl acetate hexane). Crude isolated products typically had purity > 90 % (as determined by HPLC and ^{1}H NMR)

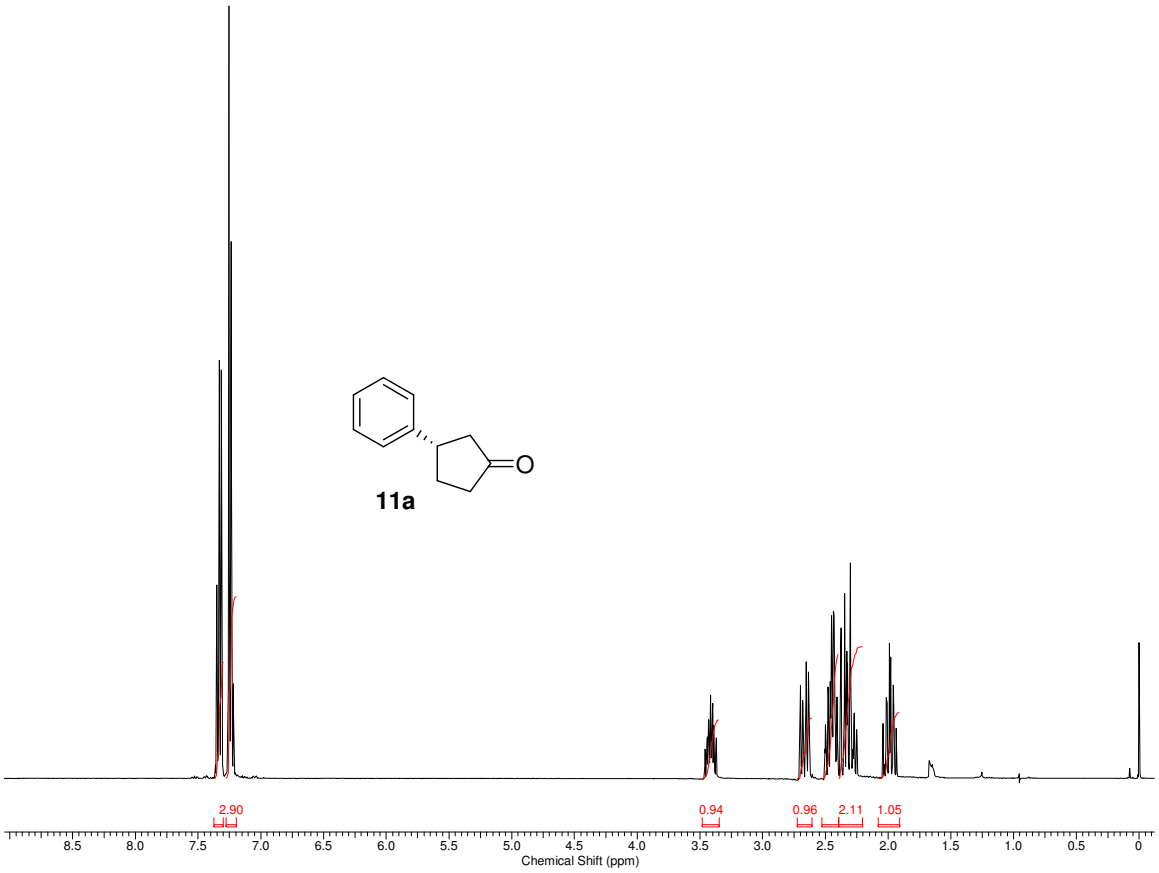
^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$.

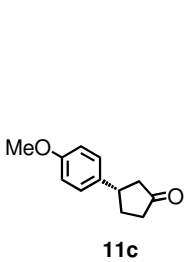
Analytical methods for the determination of chiral purity of compounds 6, 11-14.

Chiral purities of compounds **11d**, **12a** and **12b** were determined by HPLC method using a Chiralpak, AD-H column (250 mm x 4.6 mm, 5μm) at room temperature with UV detection at 230 nm. The flow rate was 0.8 mL/min with the eluent consisting of a mixture of heptane-isopropyl alcohol in 95:5 ratio. Chiral purities of compounds **6** and **11c** were determined by HPLC using the above method, except the eluent was a mixture of heptane-methanol-ethanol-diethylamine in 90:5:5:0.05 ratio.

Chiral purities of compounds **11a**, **13** and **14** were determined using supercritical fluid chromatography and Chirapak, AD-H column (250 mm x 4.6 mm, 5 μm) for **11a,** and Chirapak OD-H (250 mm x 4.6 mm, 5 μm) for **13** and **14**. The mobile phase was a mixture of carbon dioxide with 2% isopropyl alcohol as a modifier containing 0.1 % diethylamine additive at 35°C. The flow rate of carbon dioxide was 2 mL/min and a back pressure of 100 bar was maintained.

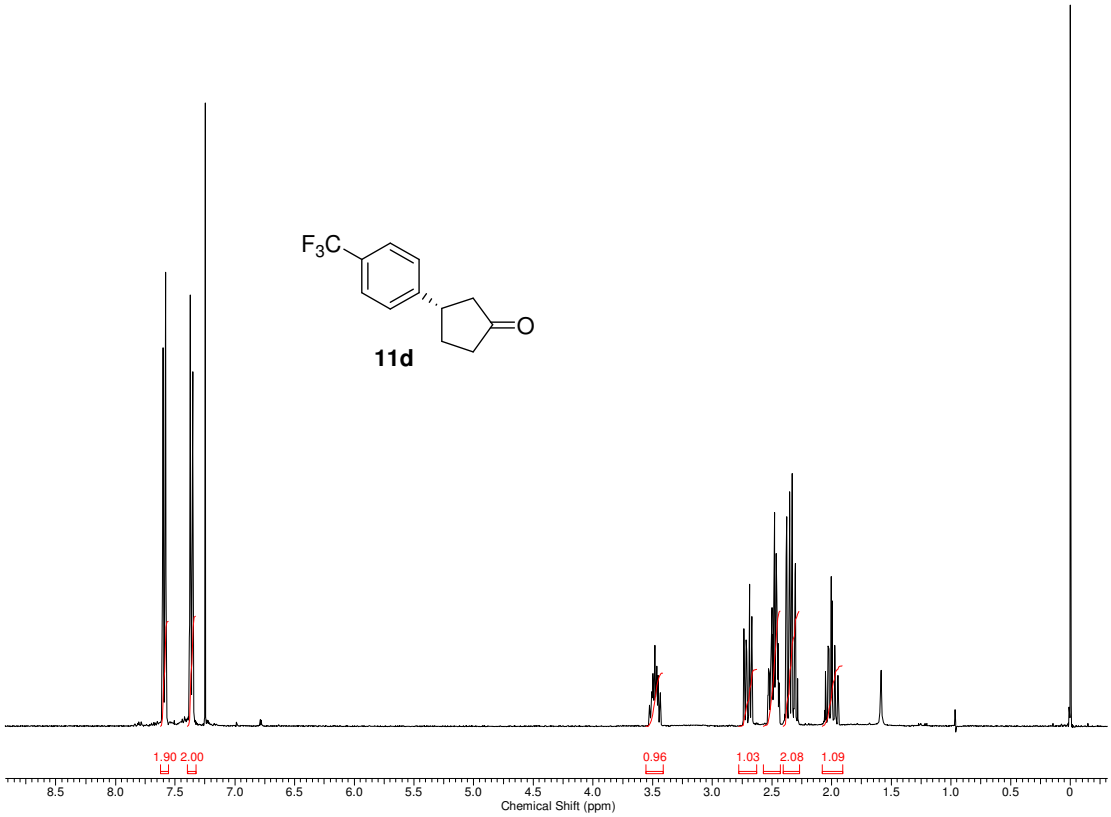

Br
O
6
1.87
1.94
0.97
1.02
2.07
2.05
1.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

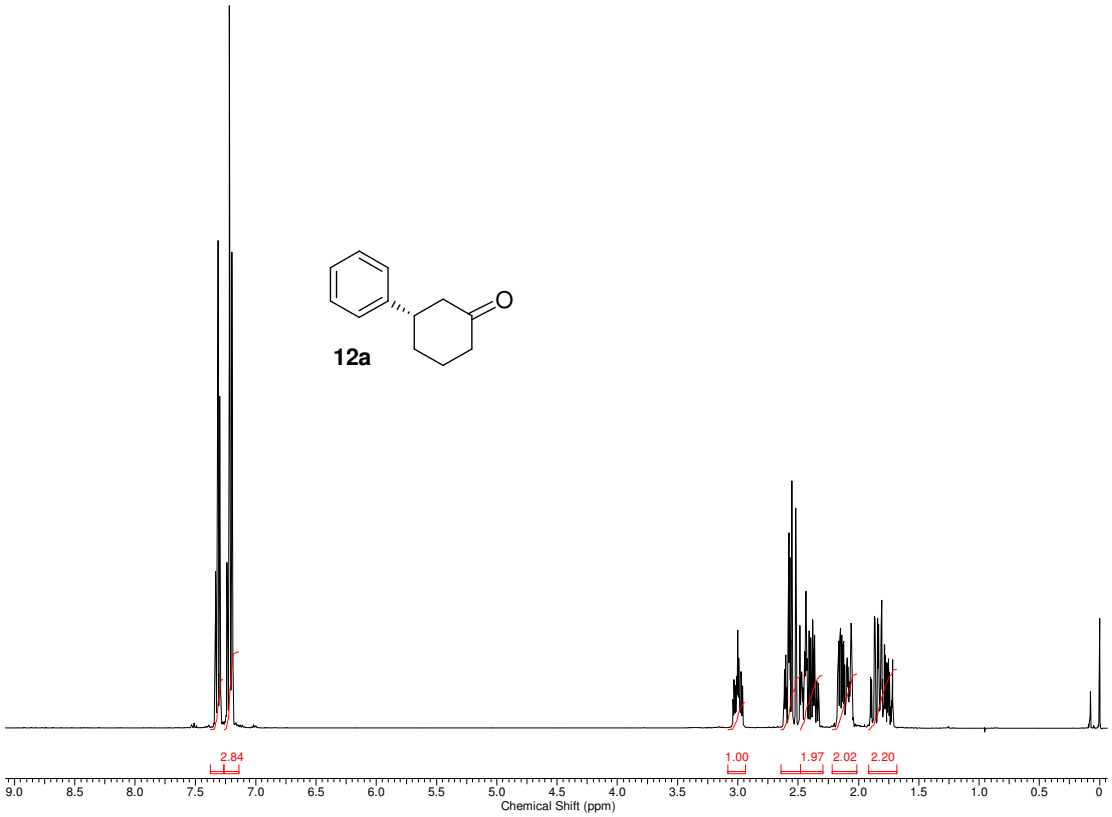

O
11a
2.90
0.94
0.96
2.11
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

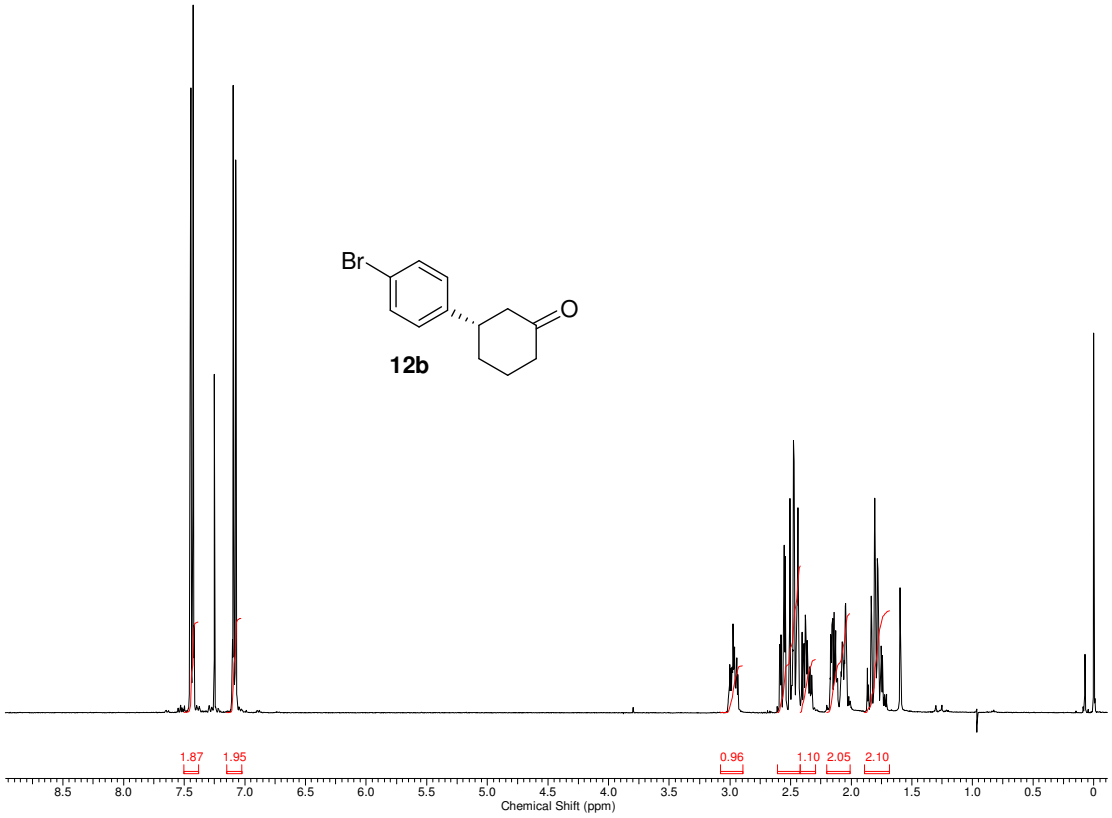

MeO
O

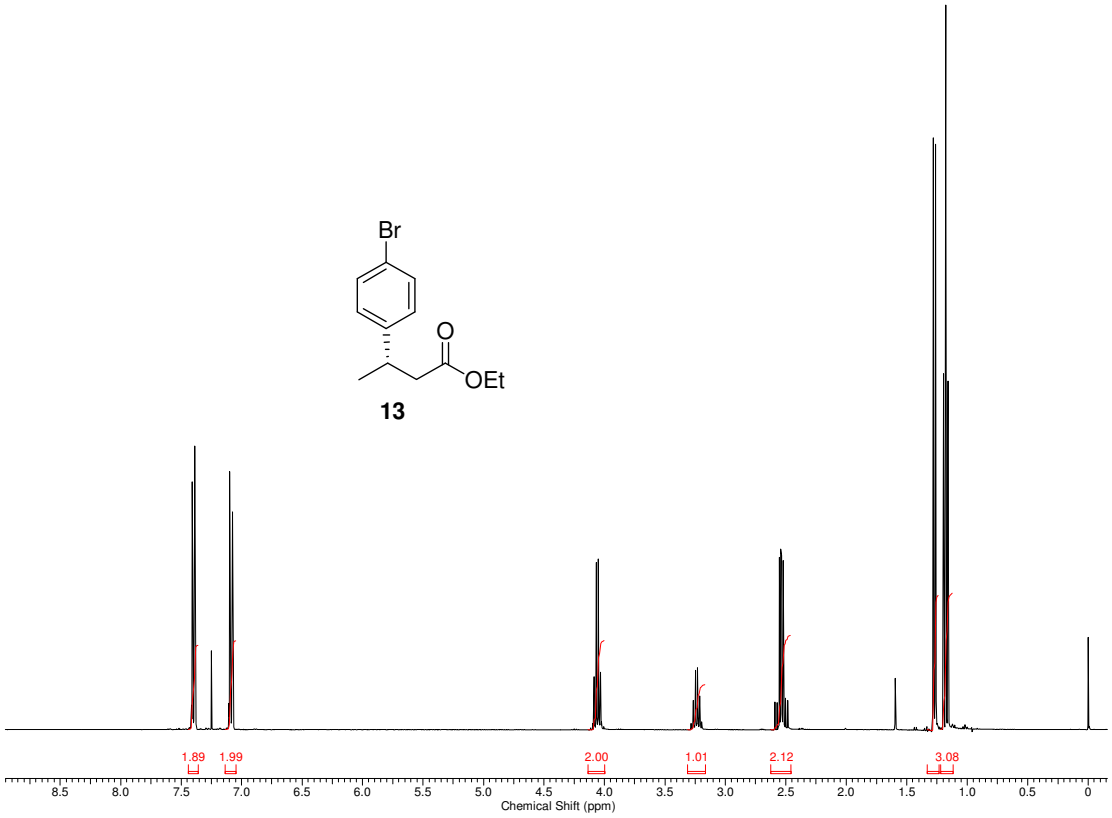
11c

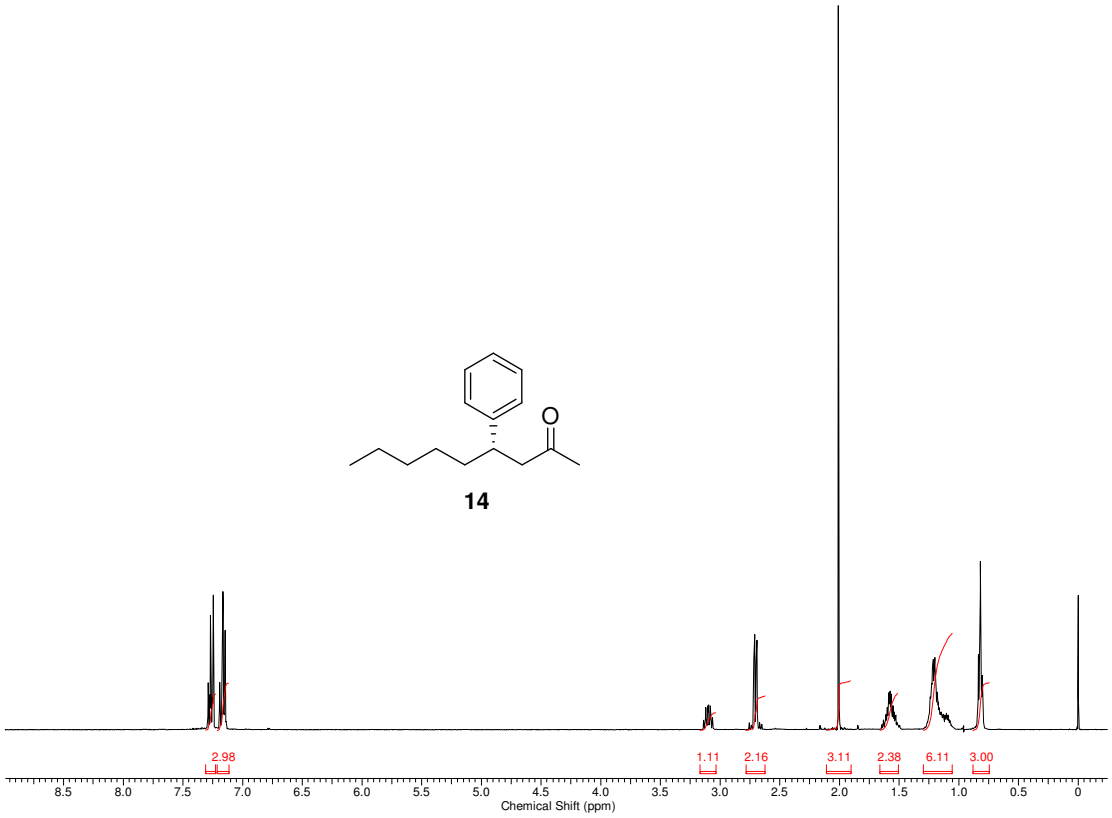
1.95
1.91
3.06
1.03
1.06
2.05
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


F3C
O
11d
1.90
2.00
0.96
1.03
2.08
1.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


O
12a
2.84
1.00
1.97
2.02
2.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Br
O
12b
1.87
1.95
0.96
1.10
2.05
2.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Br
O
OEt
13
1.89
1.99
2.00
1.01
2.12
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


O
14
2.98
1.11
2.16
3.11
2.38
6.11
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)