Supplemental Information
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Experimental

All NMR spectra were recorded on a Bruker Avance 400 spectrometer. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover MA, and used without further purification. *p*-Bromobenzyl bromide, cesium floride, cyclohexanone, lithium hexamethyldisilazide, lithium hydroxide, 2-methyl-cyclohexanone, potassium carbonate, potassium hydroxide, sodium hydroxide and sodium hydride were purchased from Acros Organics and used without further purification. 18-crown-6 was purchased from Sigma-Aldrich and used without further purification. Ball milling was carried out in a 8000M SpexCertiprep mixer/mill. Ball bearings were purchased from Small Parts Incorporated. Custom made vials were made by the machine shop at the University of Cincinnati with metal rods purchased from ESPICorp Inc.

Procedure

2-(*p*-bromobenzyl)-cyclohexanone with KOH. Cyclohexanone (0.25 mL, 2.42 mmol), 4-bromobenzyl bromide (603 mg, 2.42 mmol), and potassium hydroxide (135 mg, 2.42 mmol) were added to a custom-made 2” by 1/2” screw capped stainless steel vial along with a 1/8” stainless steel ball bearing. The vial was placed in a 8000M Spex Certiprep mixer/mill and the contents were ball milled for 17 hours. The resulting mixture was dissolved in ethyl acetate (15 mL) and washed with 10% HCl (15 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The mixture was separated on a *CombiFlash Companion* from *Teledyne Isco* using a gradient of cyclohexane and methylene chloride. This afforded 2-(*p*-bromobenzyl)-cyclohexanone in a 29% yield.

2-(*p*-bromobenzyl)-cyclohexanone with LiHMDS. Cyclohexanone (0.25 mL, 2.42 mmol), 4-bromobenzyl bromide (603 mg, 2.42 mmol), and lithium hexamethyldisilazide (403 mg, 2.42 mmol) were added to a custom-made 2” by 1/2” screw capped stainless steel vial along with a 1/8” stainless steel ball bearing under an argon atmosphere. The vial was placed in a 8000M Spex Certiprep mixer/mill and the contents were ball milled for 17 hours. The resulting mixture was dissolved in ethyl acetate (15 mL) and washed with 10% HCl (15 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The mixture was separated on a *CombiFlash Companion* from *Teledyne Isco* using a gradient of cyclohexane and methylene chloride. This afforded 2-(*p*-bromobenzyl)-cyclohexanone in a 64% yield.

di-(*p*-bromobenzyl)-carbonate. Cyclohexanone (0.25 mL, 2.42 mmol), 4-bromobenzyl bromide (603 mg, 2.42 mmol), potassium carbonate (331 mg, 2.42 mmol), and 18-crown-6 (673 mg, 2.42 mmol) were added to a custom-made 2” by 1/2” screw capped stainless steel vial along with a 1/8” stainless steel ball bearing. The vial was placed in a 8000M Spex Certiprep mixer/mill and the contents were ball milled for 17 hours. The resulting mixture was dissolved in ethyl acetate (15 mL) and washed with 10% HCl (15 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The mixture was separated on a *CombiFlash Companion* from

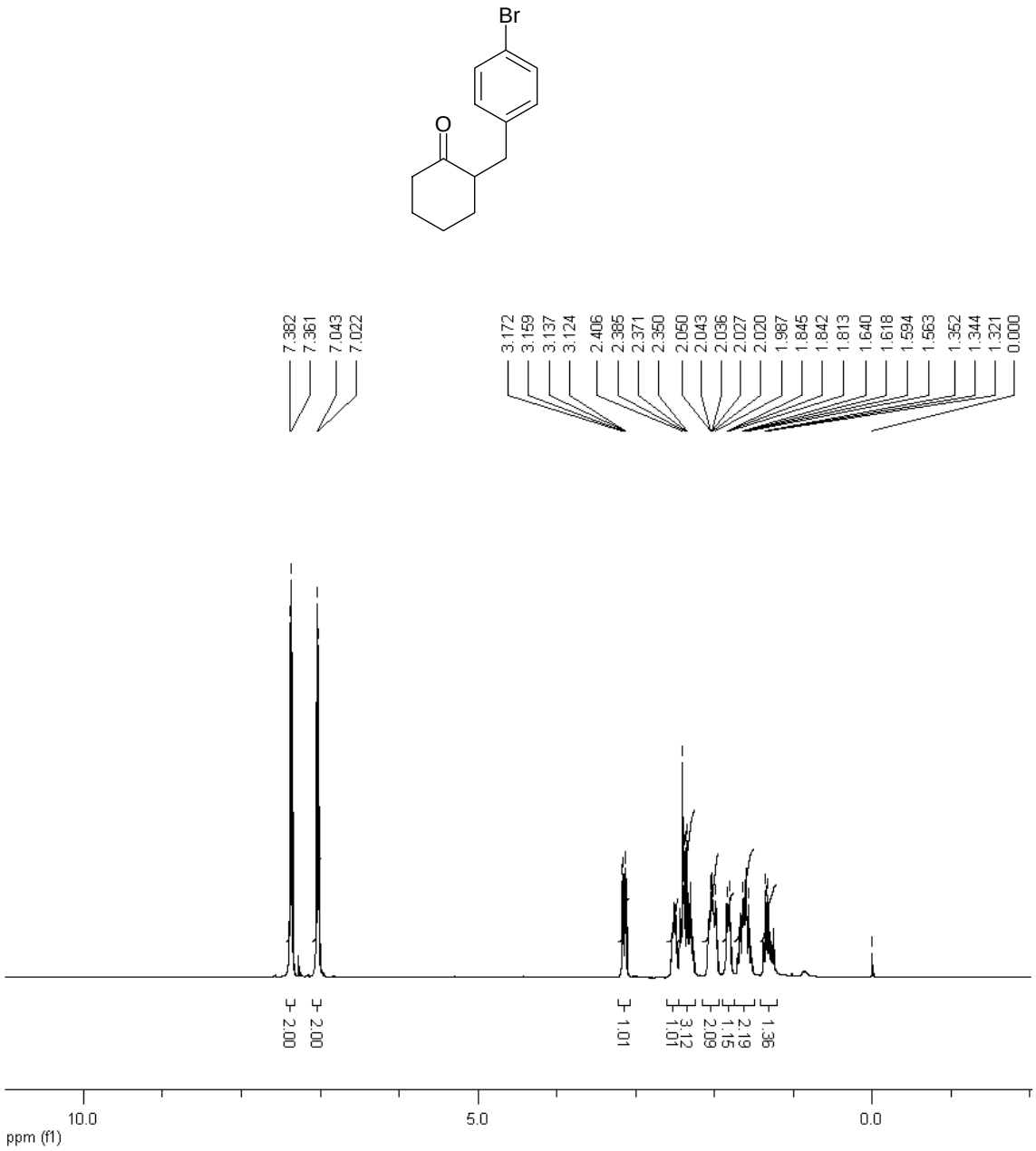
Teledyne Isco using a gradient of cyclohexane and methylene chloride. This afforded di-(*p*-bromobenzyl)-carbonate in a 45% yield.

Thermodynamic and Kinetic Products of 2-methyl-cyclohexanone

2-(*p*-bromobenzyl)-2-methyl-cyclohexanone. 2-methyl-cyclohexanone (224 mg, 2.00 mmol), 4-bromobenzyl bromide (500 mg, 2.00 mmol), and sodium hydroxide (80 mg, 2.00 mmol) were added to a custom-made 2" by 1/2" screw capped stainless steel vial along with a 1/8" stainless steel ball bearing. The vial was placed in a 8000M Spex Certiprep mixer/mill and the contents were ball milled for 17 hours. The resulting mixture was dissolved in ethyl acetate (15 mL) and washed with 10% HCl (15 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The mixture was separated on a *CombiFlash Companion* from *Teledyne Isco* using a gradient of cyclohexane and methylene chloride. This afforded 2-(*p*-bromobenzyl)-2-methyl-cyclohexanone in a 76% yield.

2-(*p*-bromobenzyl)-6-methyl-cyclohexanone. 2-methyl-cyclohexanone (224 mg, 2.00 mmol), 4-bromobenzyl bromide (500 mg, 2.00 mmol), and lithium hexamethyldisilazide (334 mg, 2.00 mmol) were added to a custom-made 2" by 1/2" screw capped stainless steel vial along with a 1/8" stainless steel ball bearing under an argon atomosphere. The vial was placed in a 8000M Spex Certiprep mixer/mill and the contents were ball milled for 17 hours. The resulting mixture was dissolved in ethyl acetate (15 mL) and washed with 10% HCl (15 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The mixture was separated on a *CombiFlash Companion* from *Teledyne Isco* using a gradient of cyclohexane and methylene chloride. This afforded 2-(*p*-bromobenzyl)-2-methyl-cyclohexanone in a 45% yield.

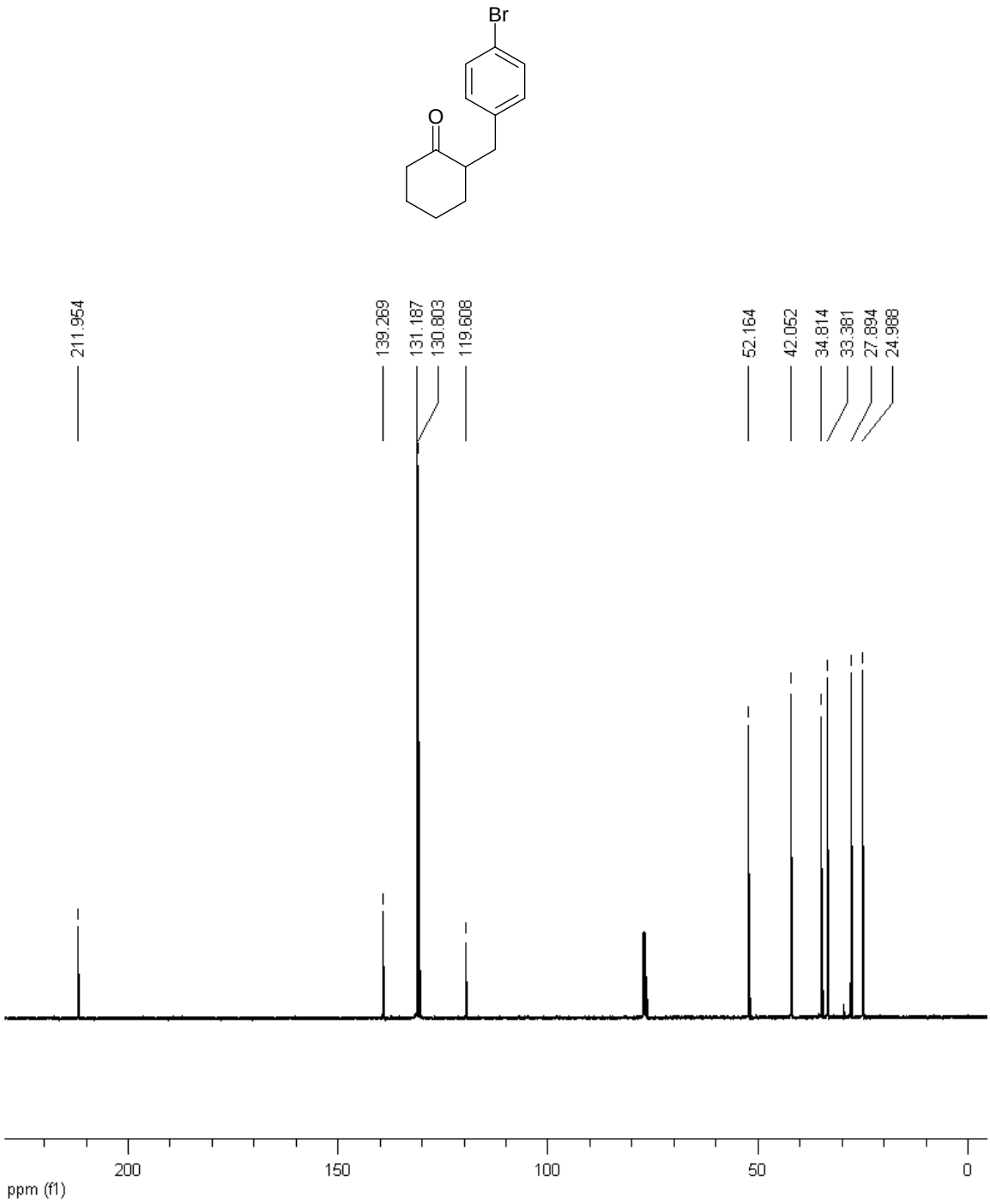
2-(*p*-bromobenzyl)-cyclohexanone



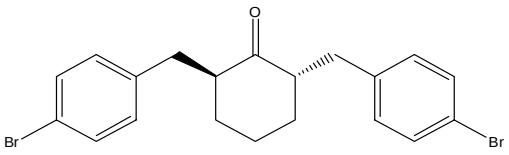
ESI-HRMS:

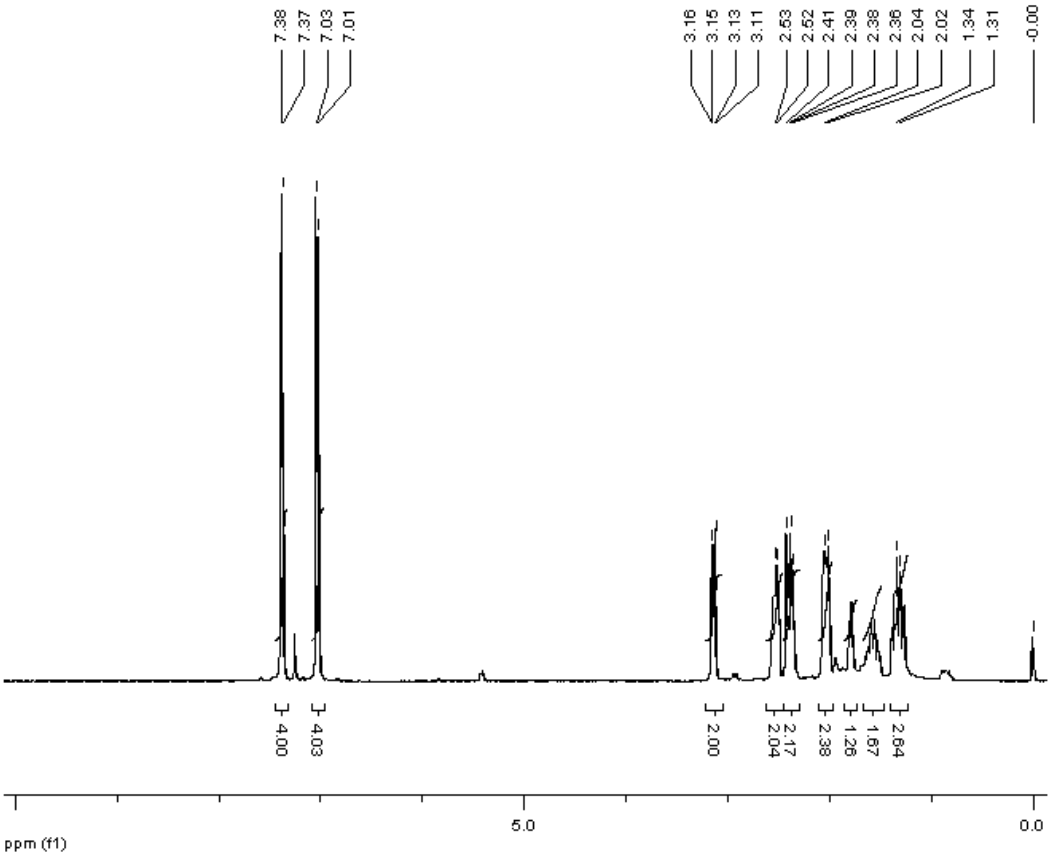
Calculated: 289.0204 [M+Na^+], 291.0185 [M+Na^++2]
Sample: 289.0206 [M+Na^+], 291.0186 [M+Na^++2]

2-(*p*-bromobenzyl)-cyclohexanone

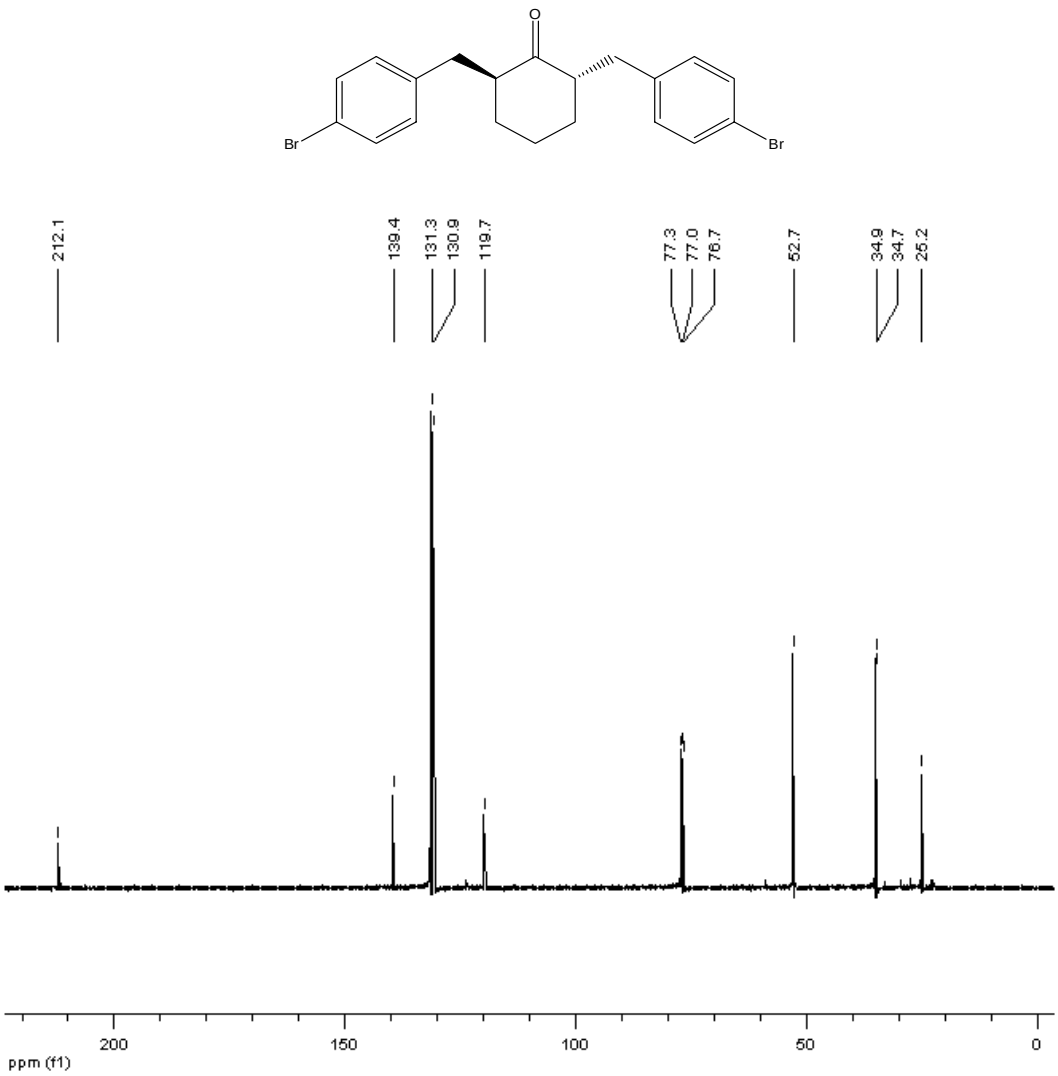


trans-2,6-di-(_p_-bromobenzyl)-cyclohexanone

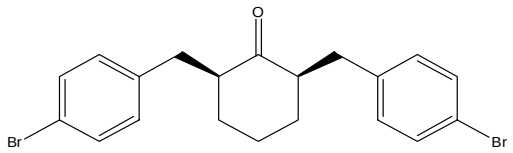


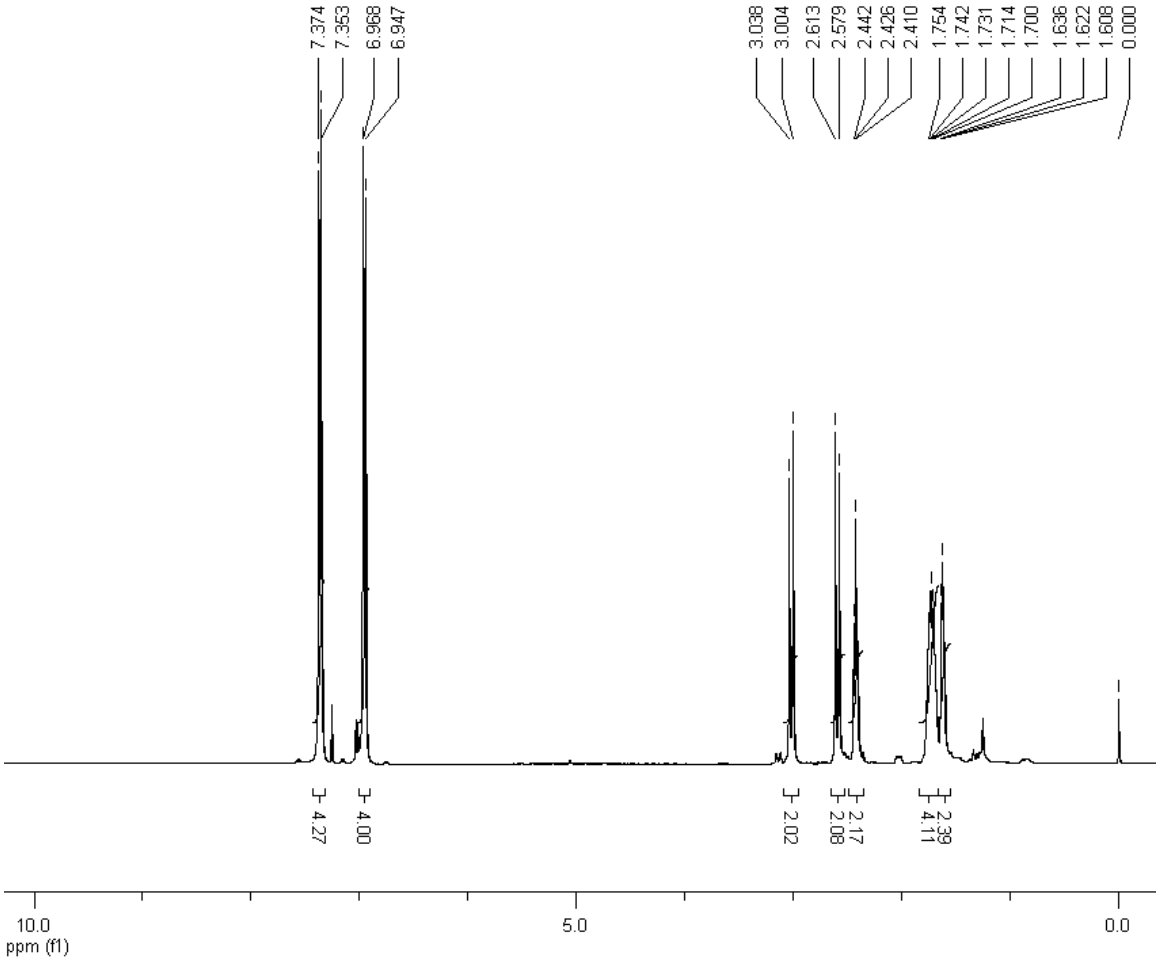


trans-2,6-di-(_p_-bromobenzyl)-cyclohexanone



***cis*-2,6-di-(*p*-bromobenzyl)-cyclohexanone**

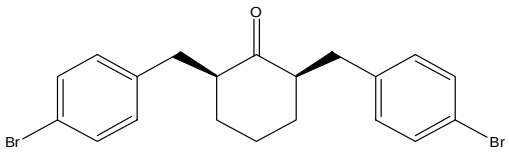


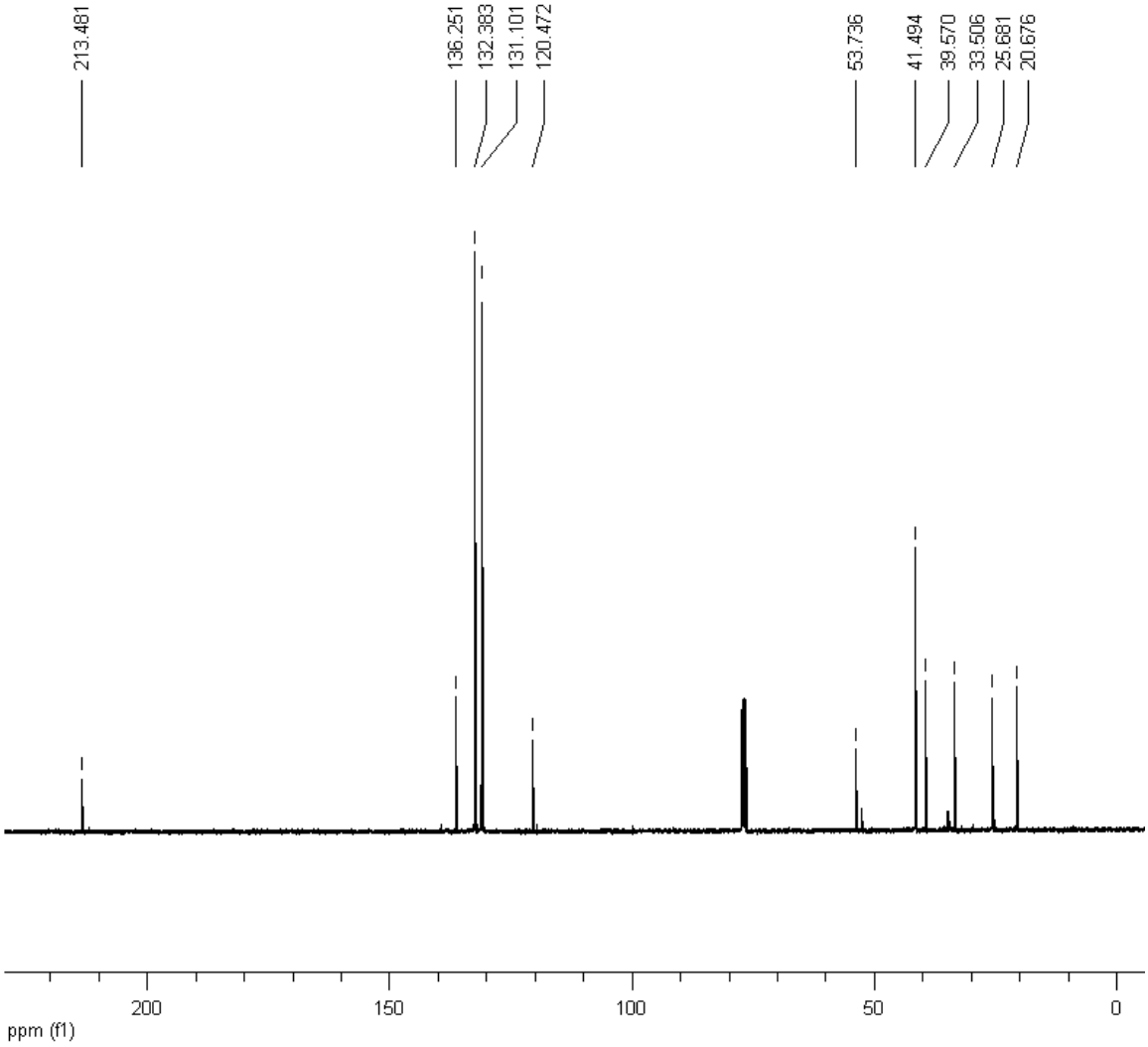


ESI-HRMS:

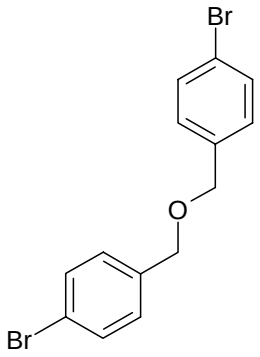
Calculated: 456.9778 [M+Na^+], 458.9759 [M+Na^++2], 460.9742 [M+Na^++4]
Sample: 456.9782 [M+Na^+], 458.9718 [M+Na^++2], 460.9754 [M+Na^++4]

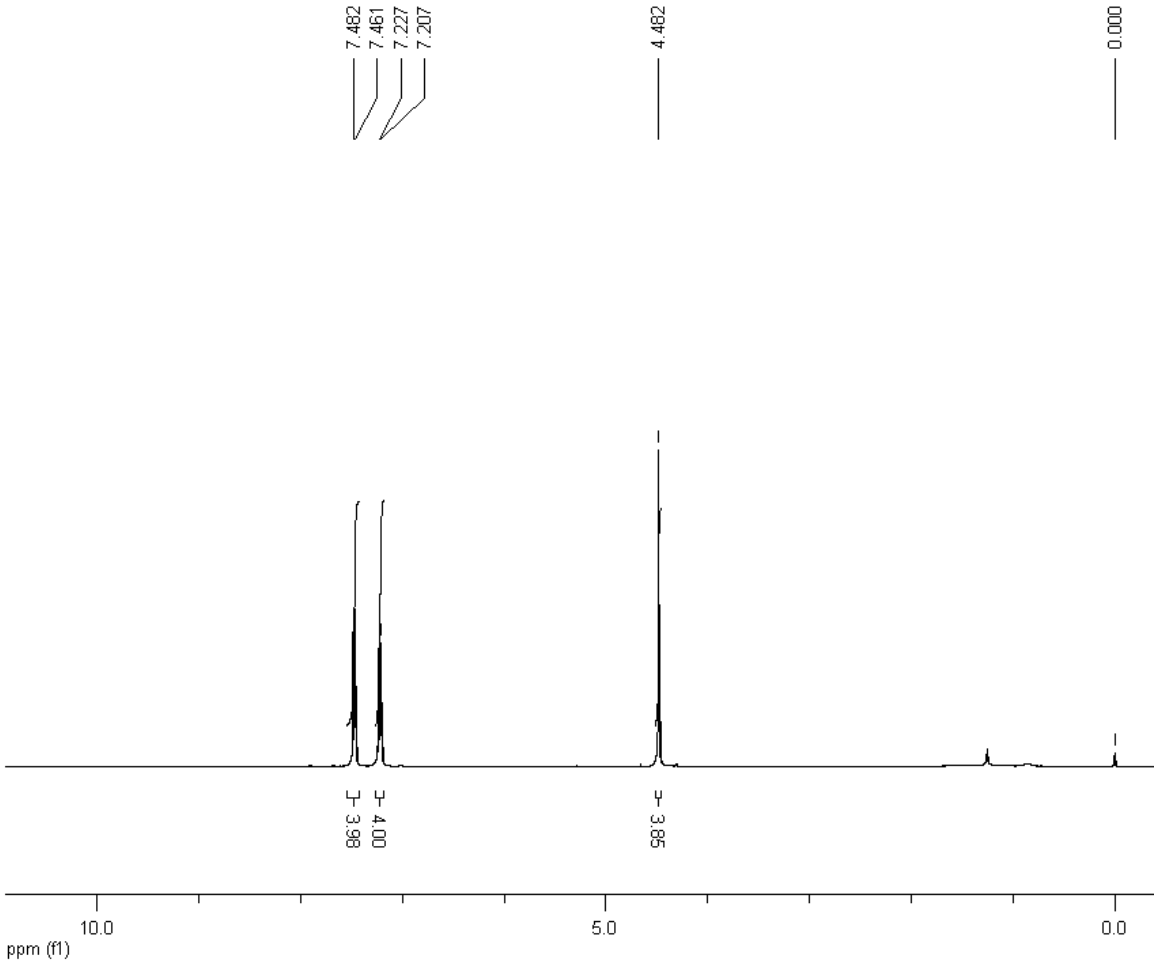
cis-2,6-di-(_p_-bromobenzyl)-cyclohexanone





di-(*p*-bromobenzyl)-ether

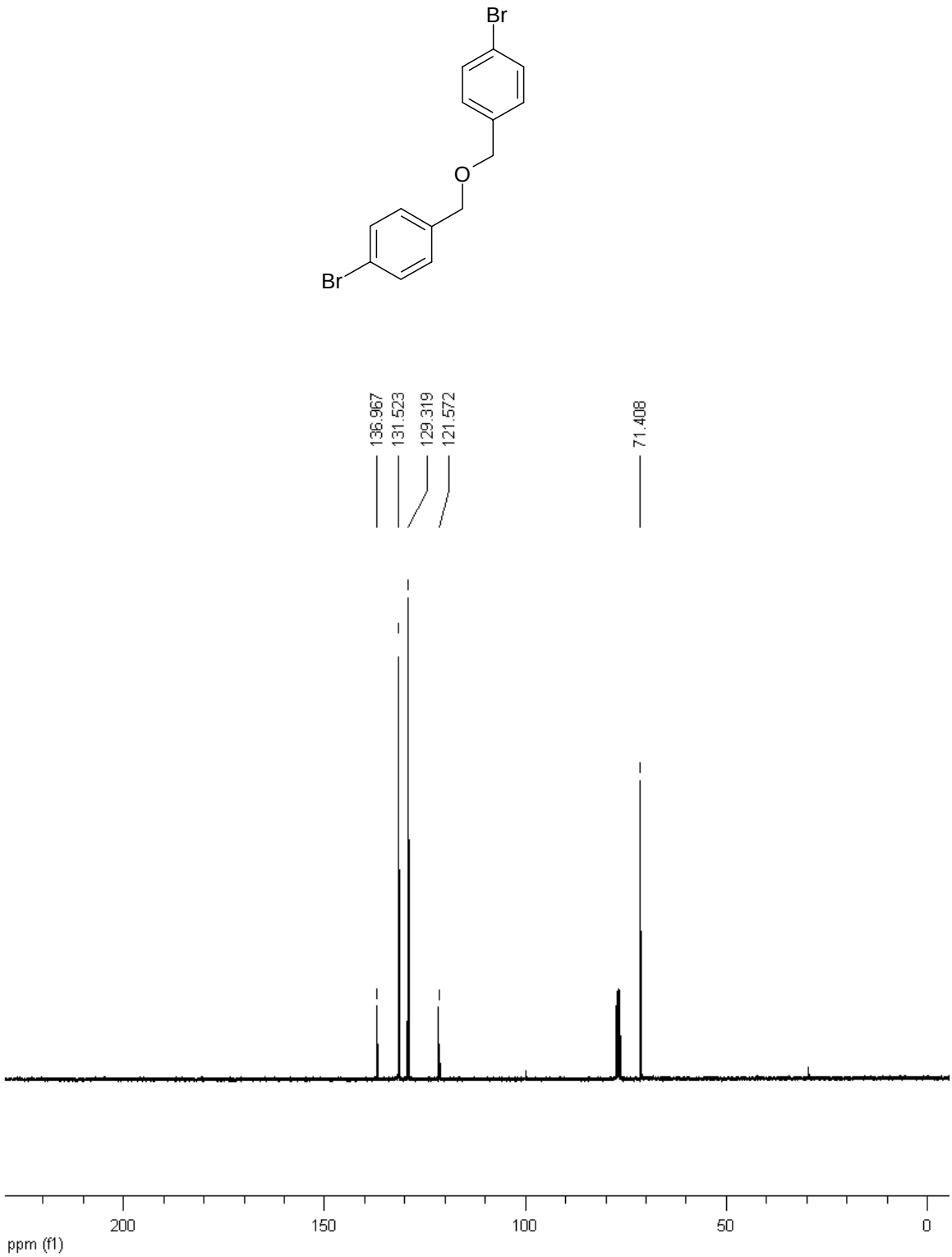




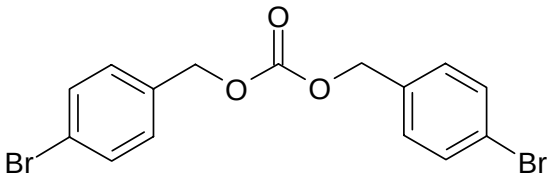
ESI-HRMS:

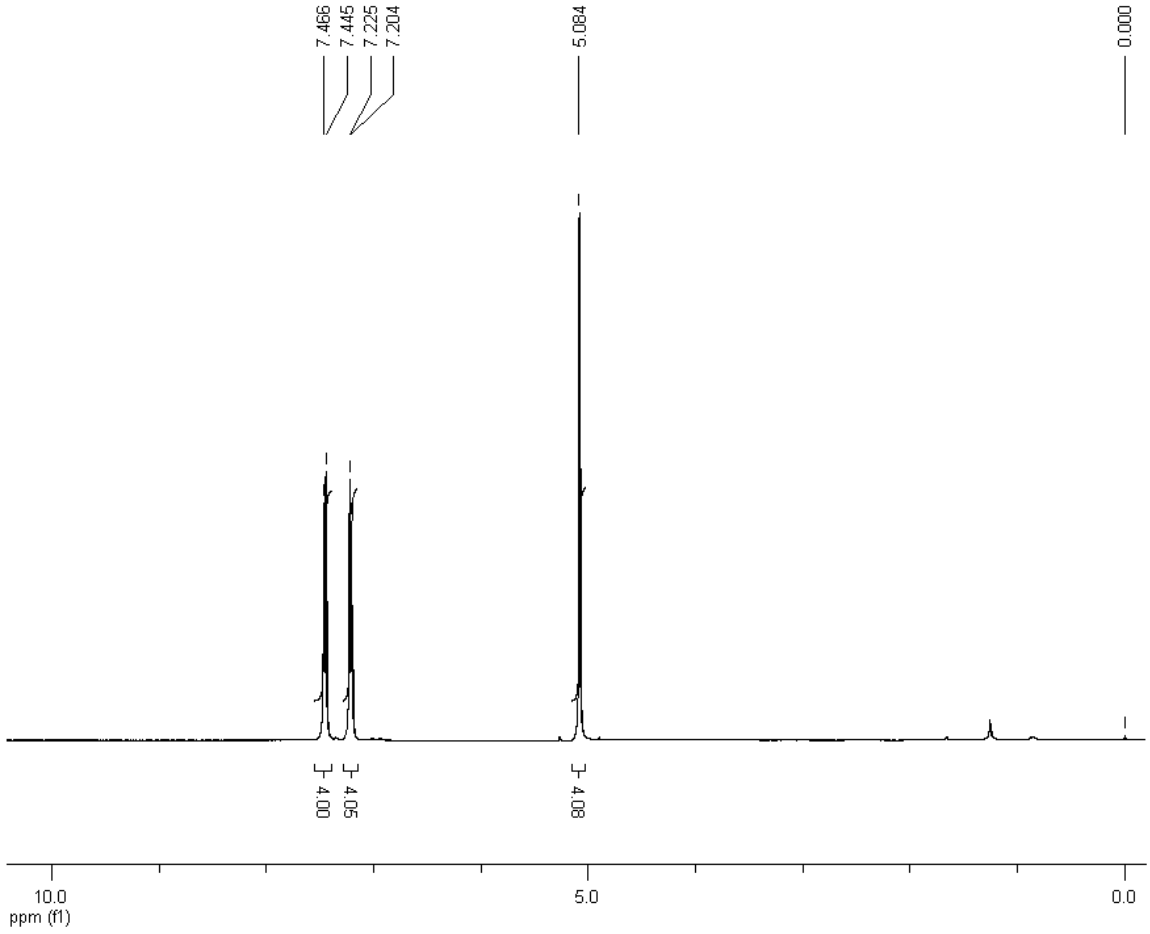
Calculated: 376.9153 [M+Na^+], 378.9133 [M+Na^++2], 380.9114 [M+Na^++4]
Sample: 376.9155 [M+Na^+], 378.9109 [M+Na^++2], 380.9101 [M+Na^++4]

di-(*p*-bromobenzyl)-ether



di-(*p*-bromobenzyl)-carbonate

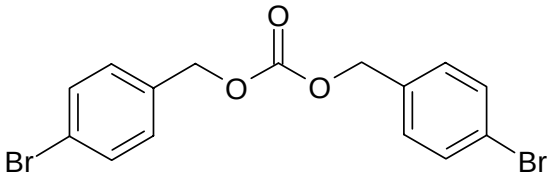


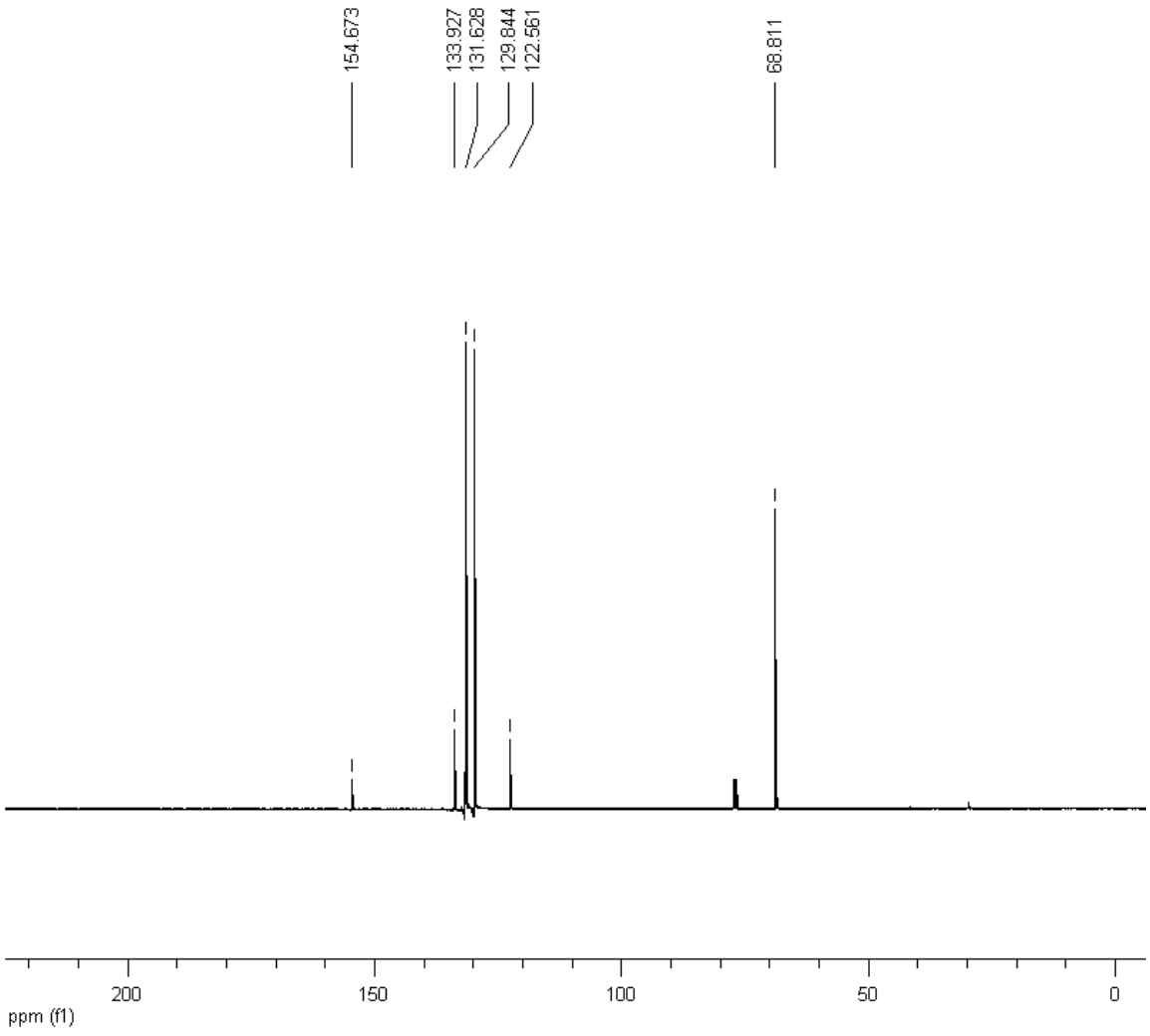


ESI-HRMS:

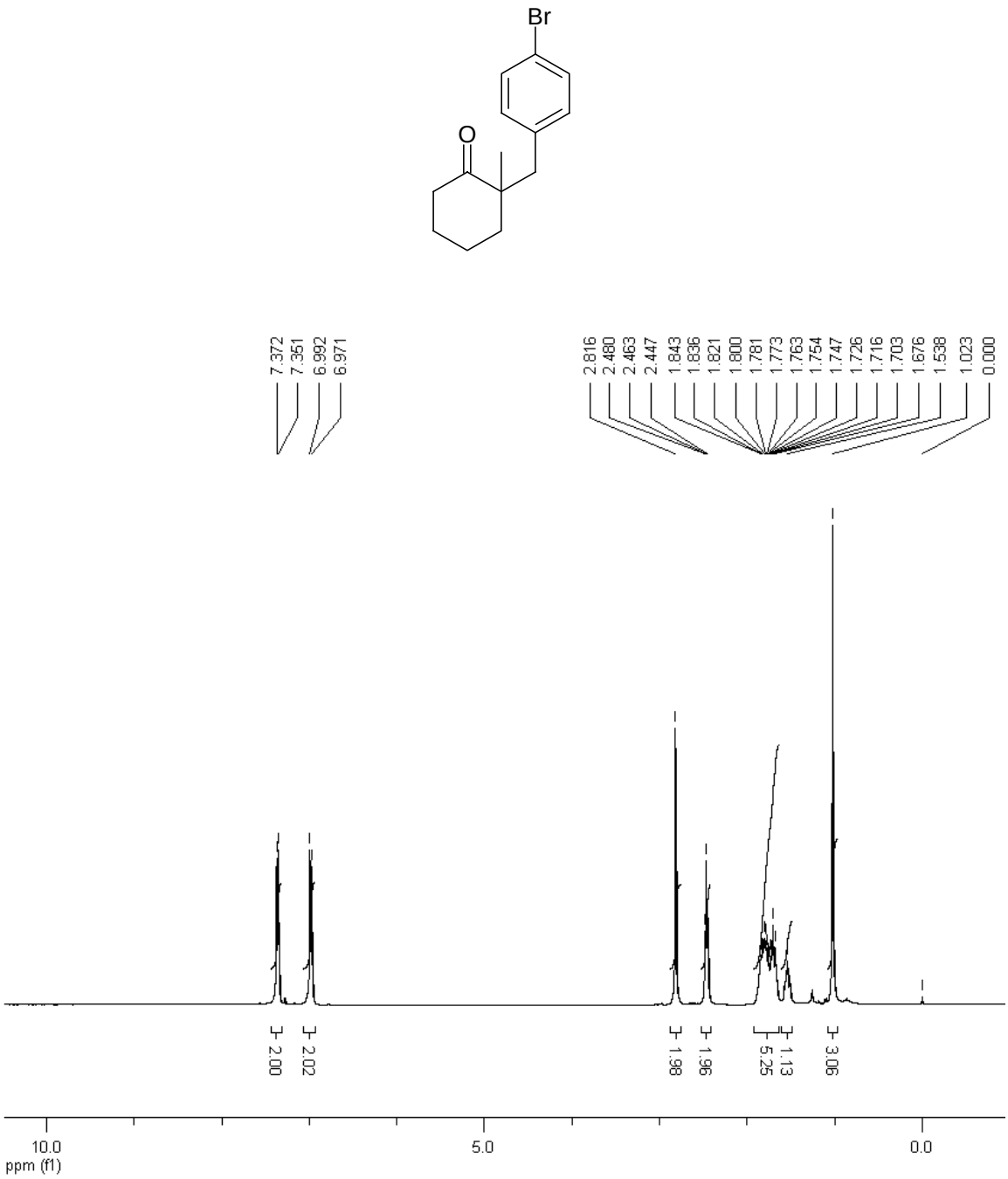
Calculated: 420.9051 [M+Na^+], 422.9031 [M+Na^++2], 424.9013 [M+Na^++4]
Sample: 420.9065 [M+Na^+], 422.9027 [M+Na^++2], 424.9054 [M+Na^++4]

di-(*p*-bromobenzyl)-carbonate





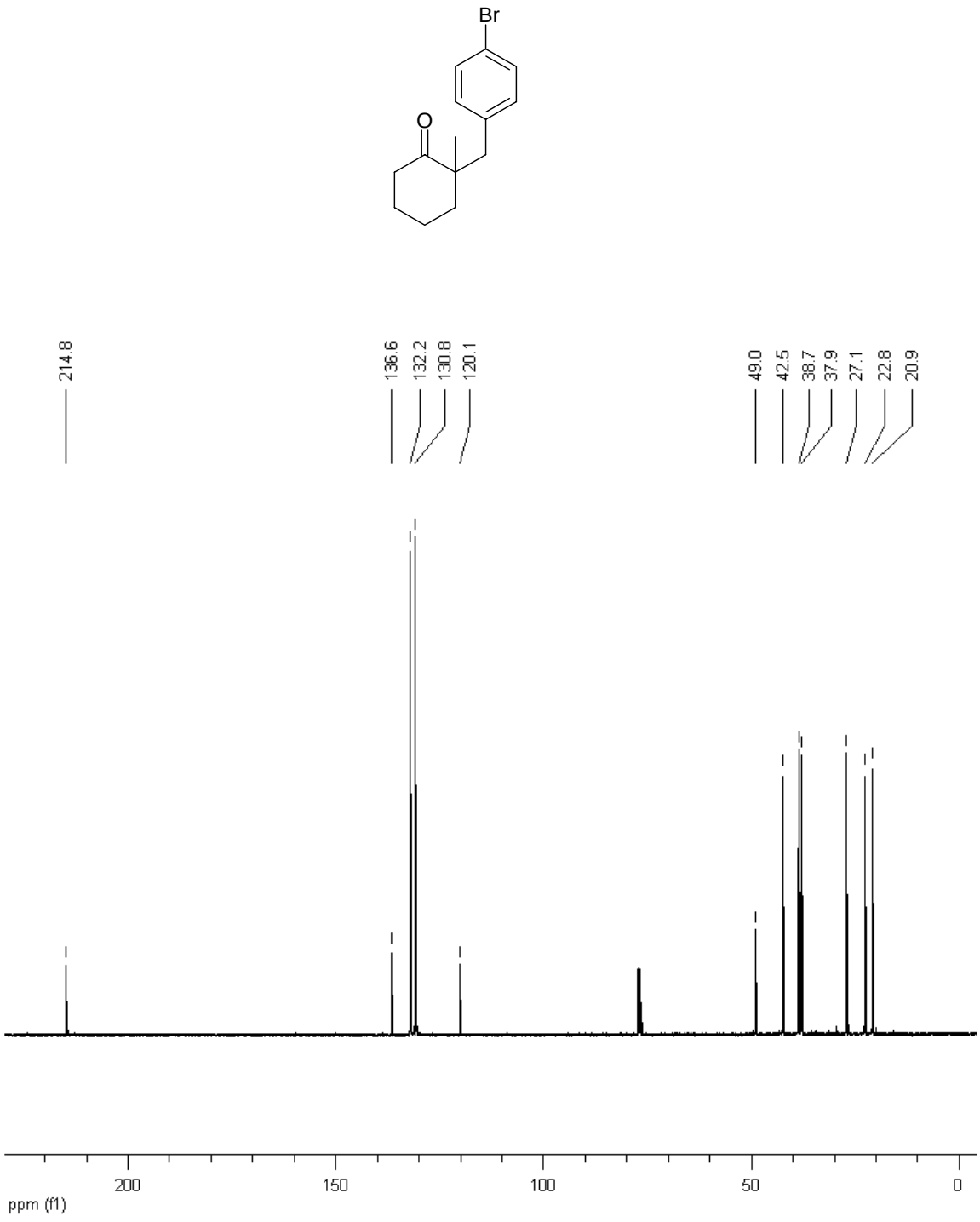
2-(*p*-bromobenzyl)-2-methyl-cyclohexanone



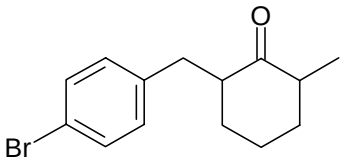
ESI-HRMS:

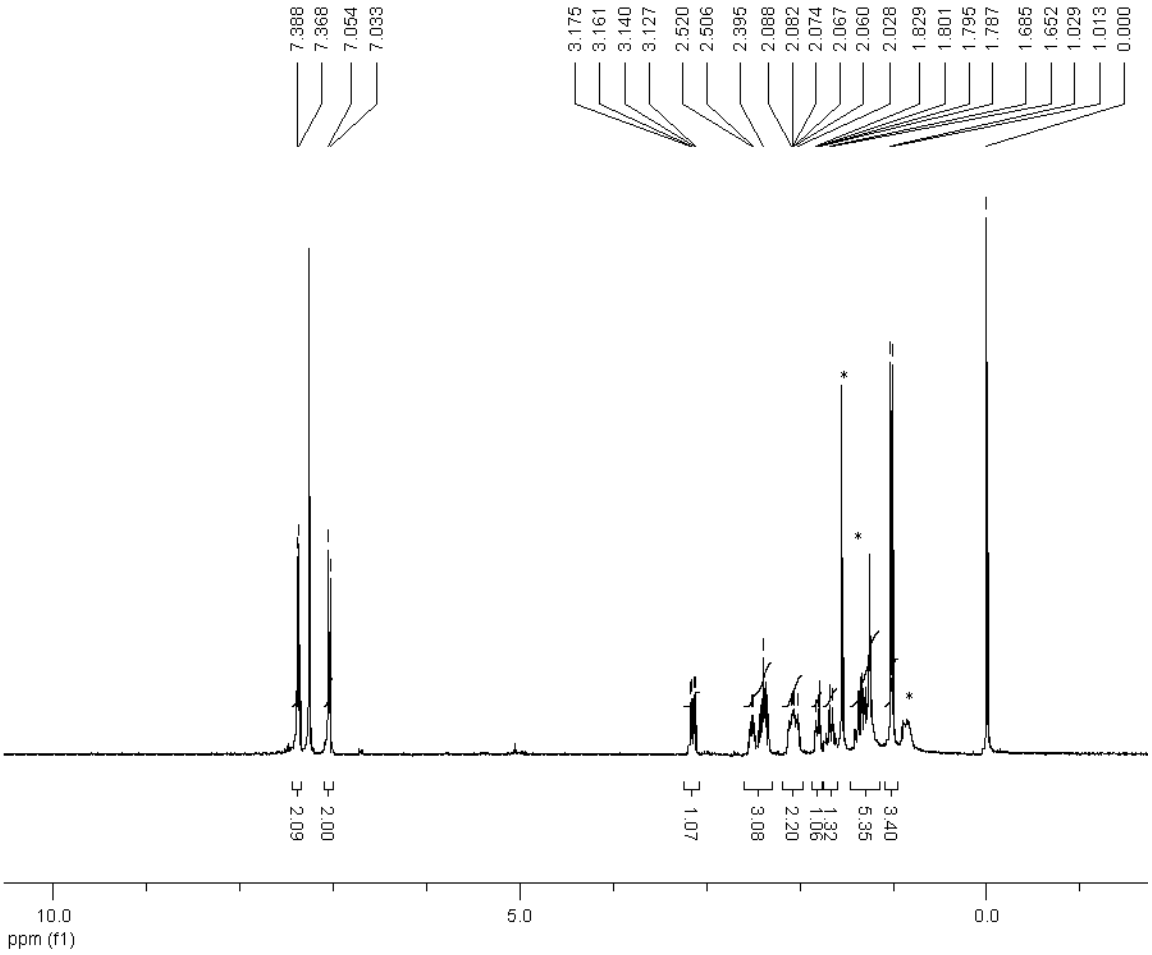
Calculated: 303.0360 [M+Na^+], 305.0341 [M+Na^++2]
Sample: 303.0356 [M+Na^+], 305.0340 [M+Na^++2]

2-(*p*-bromobenzyl)-2-methyl-cyclohexanone



2-(*p*-bromobenzyl)-6-methyl-cyclohexanone





*Impurity

ESI-HRMS:

Calculated: 303.0360 [M+Na^+], 305.0341 [M+Na^++2]
Sample: 303.0357 [M+Na^+], 305.0347 [M+Na^++2]

2-(*p*-bromobenzyl)-6-methyl-cyclohexanone