

One-Pot Synthesis of Symmetrical and Unsymmetrical Diarylmethanes via Diborylmethane

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1. General Instruments and Chemicals

General: All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator. Thin layer chromatography plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating. Organic solutions were concentrated by rotary evaporation at c.a. 30 mmHg. Flash column chromatography was performed on silica gel as described by Still *et al.*¹

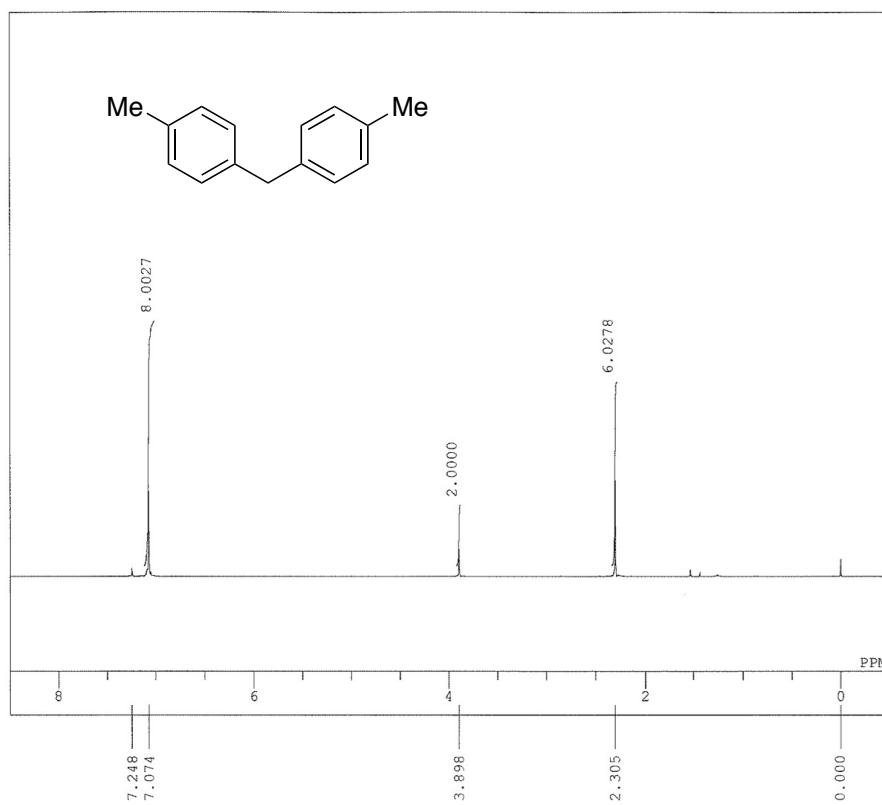
Instrumentation: NMR spectra were measured for ¹H and ¹³C NMR, and ¹⁹F NMR using tetramethylsilane as an internal reference, and trifluoroacetic acid as external references and CDCl₃ as a solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of CDCl₃ (δ 7.26). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 100 MHz: chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of CDCl₃ (δ 77.0). Fluorine nuclear magnetic resonance spectra (¹⁹F NMR) were recorded at 470 MHz: chemical shifts for fluorine are reported in parts per million (ppm, δ scale) referenced to the fluorine resonance of trifluoroacetic acid (δ -76.5). Phosphorous nuclear magnetic resonance spectra (³¹P NMR) were recorded at 202 MHz: chemical shifts for phosphorous are reported in parts per million (ppm, δ scale) referenced to the phosphorous resonance of phosphoric acid (δ 0). Data are presented as following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers, assignment (*italic*). Mass spectra were measured with a FAB-MS (Double-Focusing) or ESI-TOF-MS.

Chemicals: All reagents were purchased as commercially available source unless otherwise noted. Diborylmethane **1** was prepared according to the literature known procedure.²

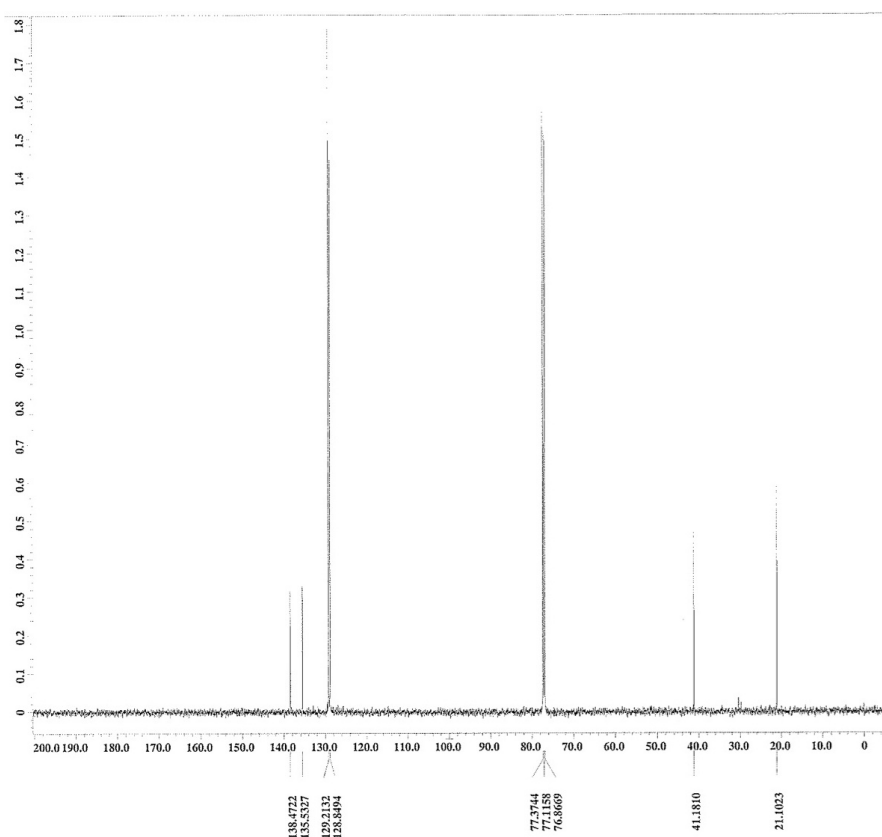
¹ W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

² (a) Castle, R. B.; Matteson, D. S. *J. Organometal. Chem.* **1969**, *20*, 19. (b) Matteson, D. S. *Synthesis* **1975**, 147.

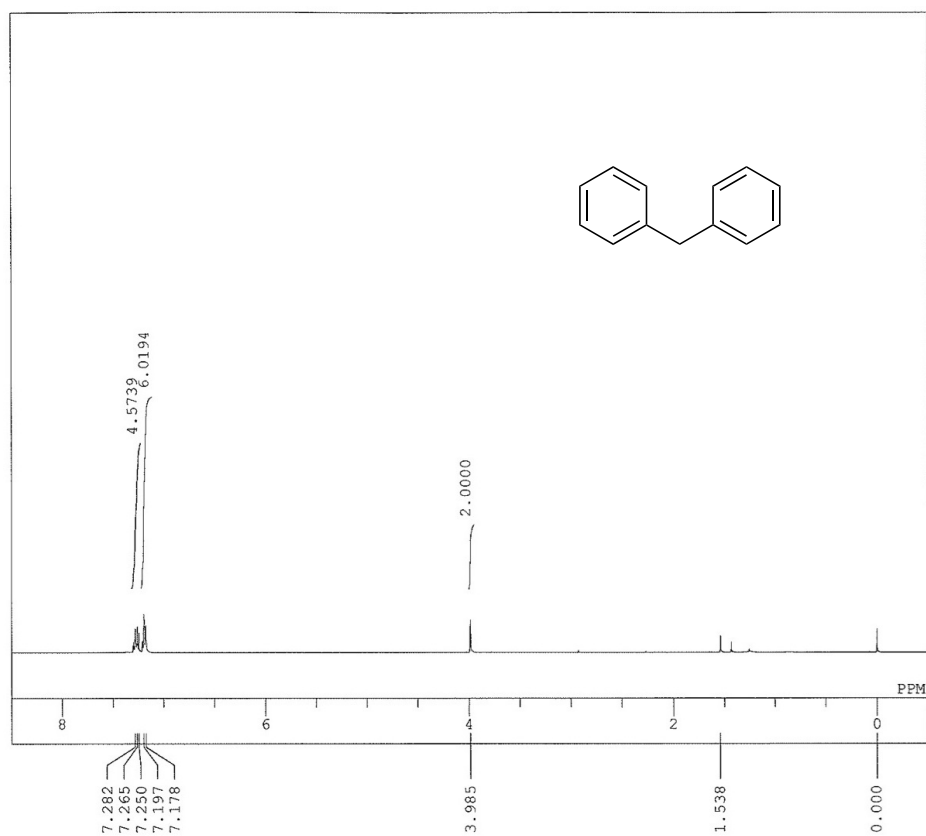
^1H NMR (CDCl_3 , 400 MHz) **4a**



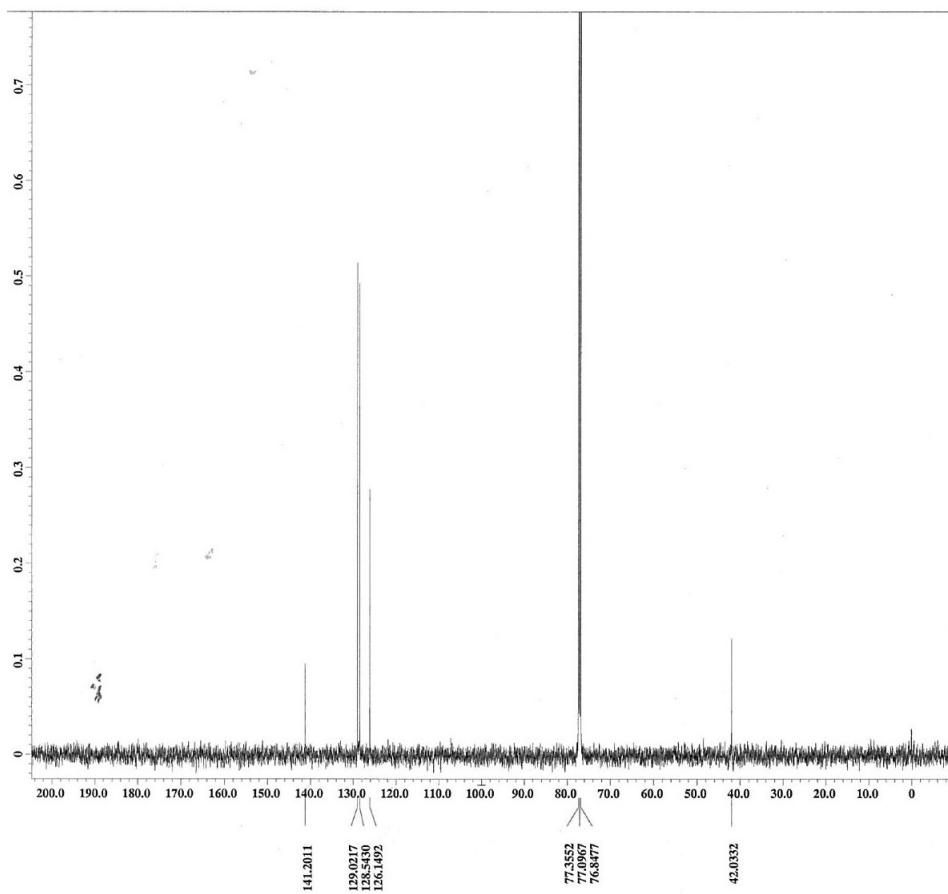
^{13}C NMR (CDCl_3 , 125 MHz) **4a**



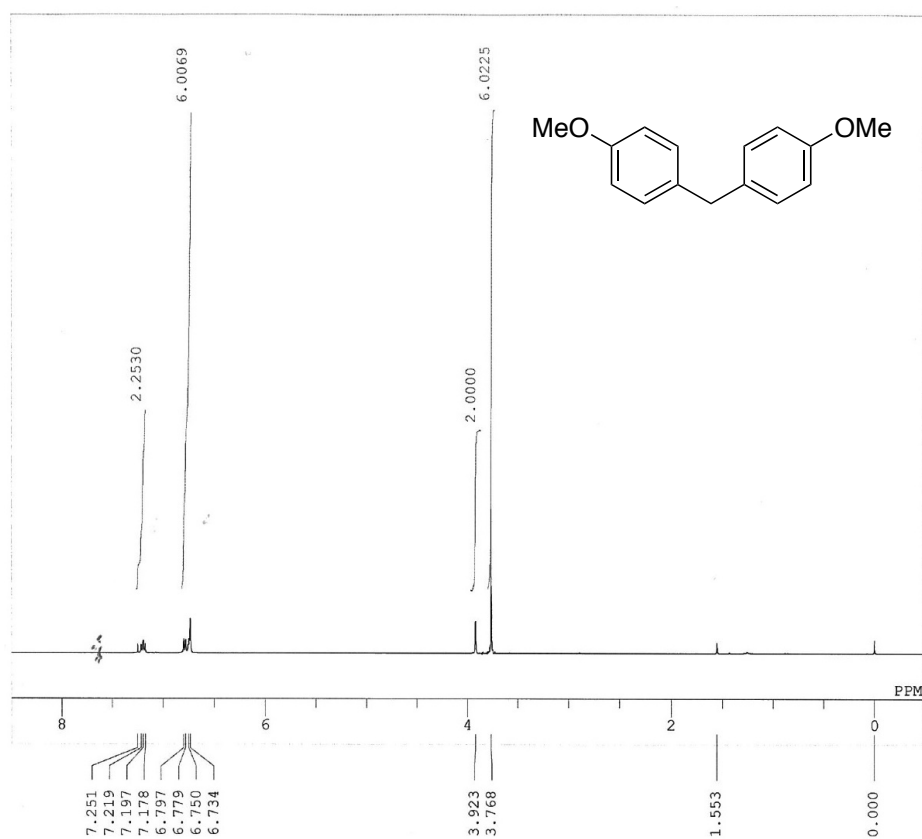
^1H NMR (CDCl_3 , 400 MHz) **4b**



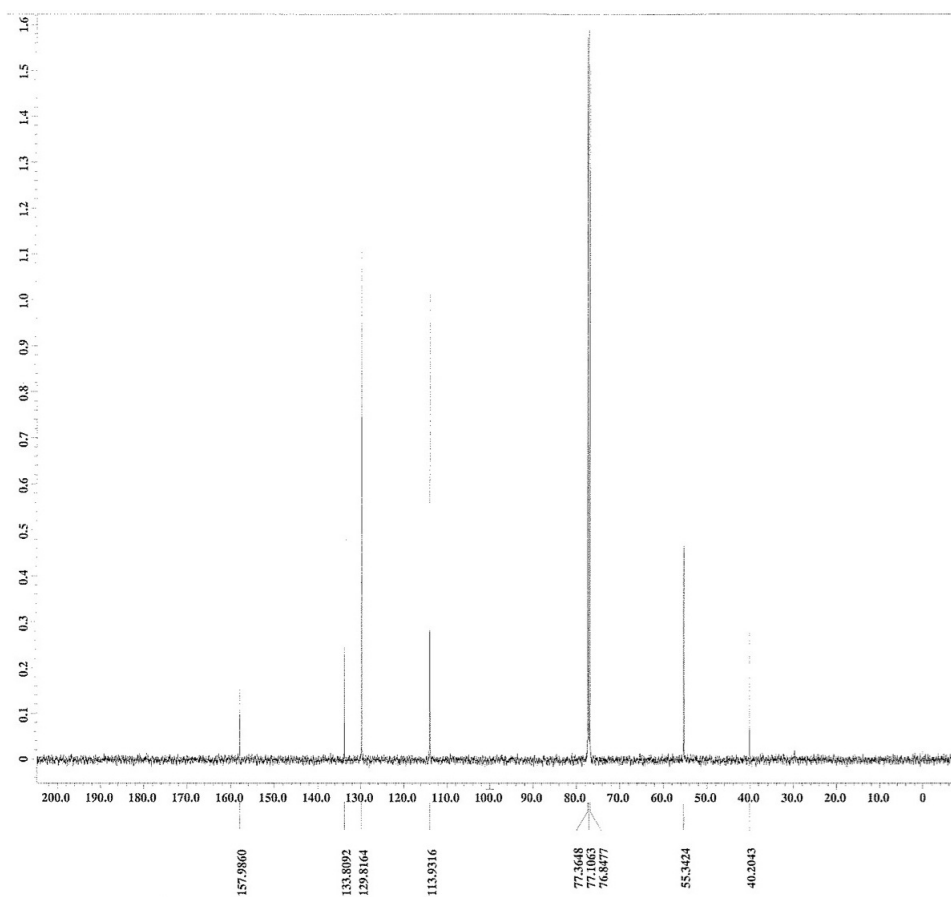
^{13}C NMR (CDCl_3 , 125 MHz) **4b**



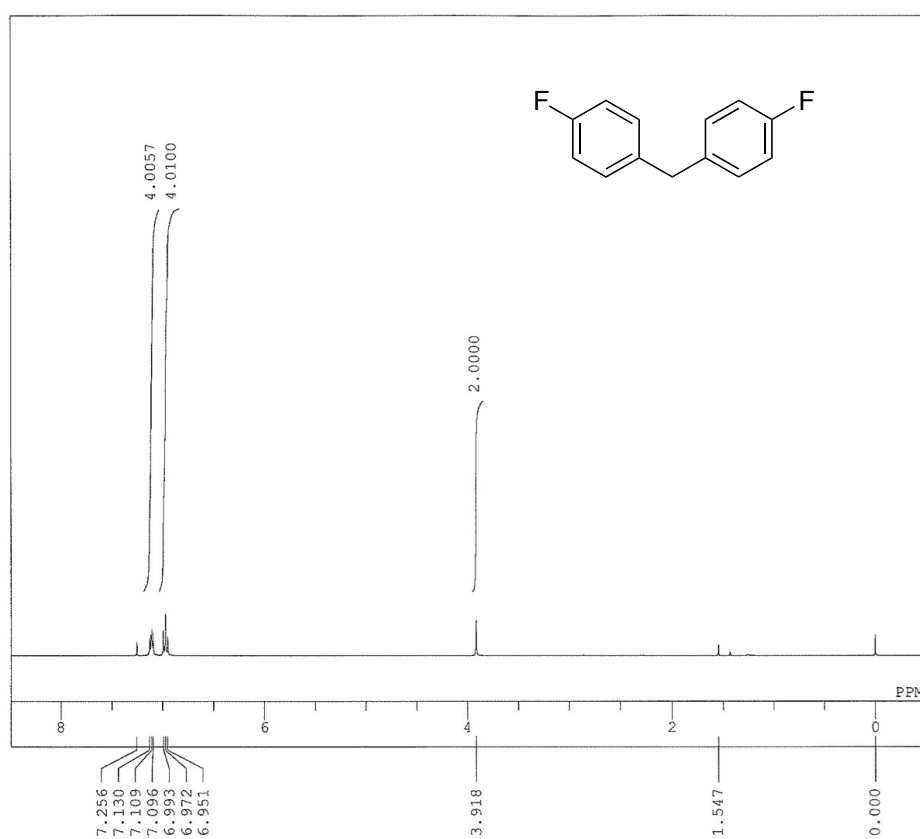
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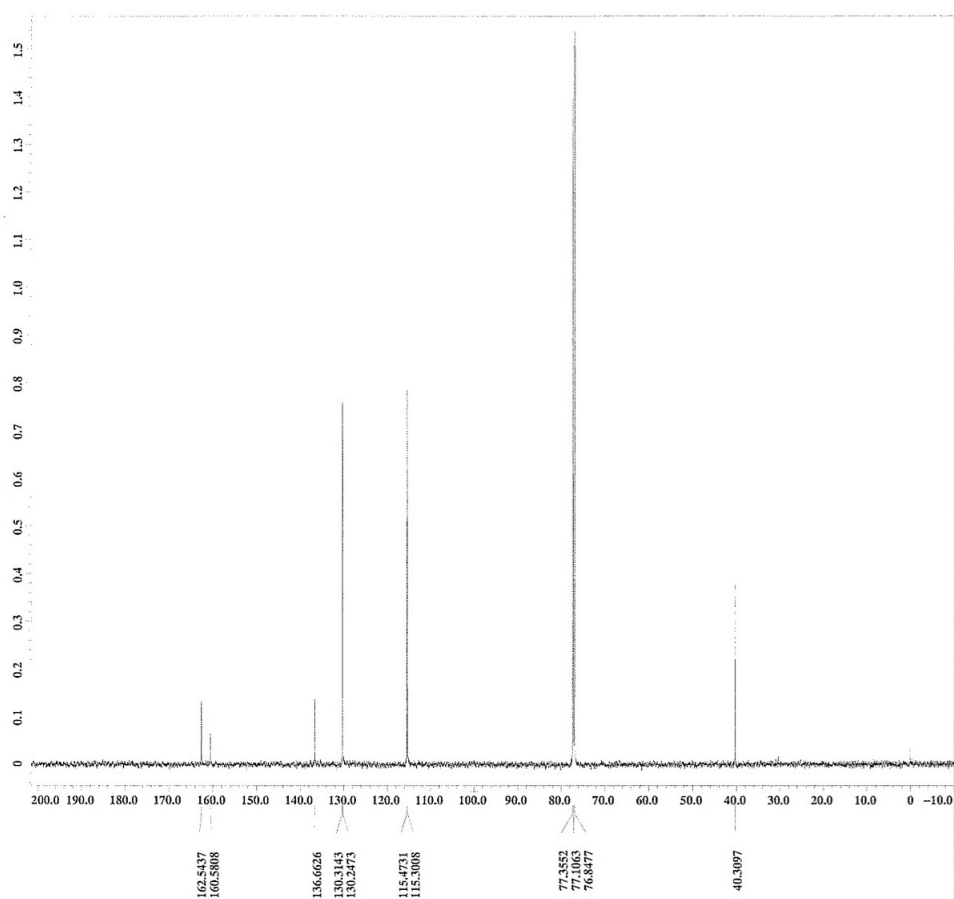
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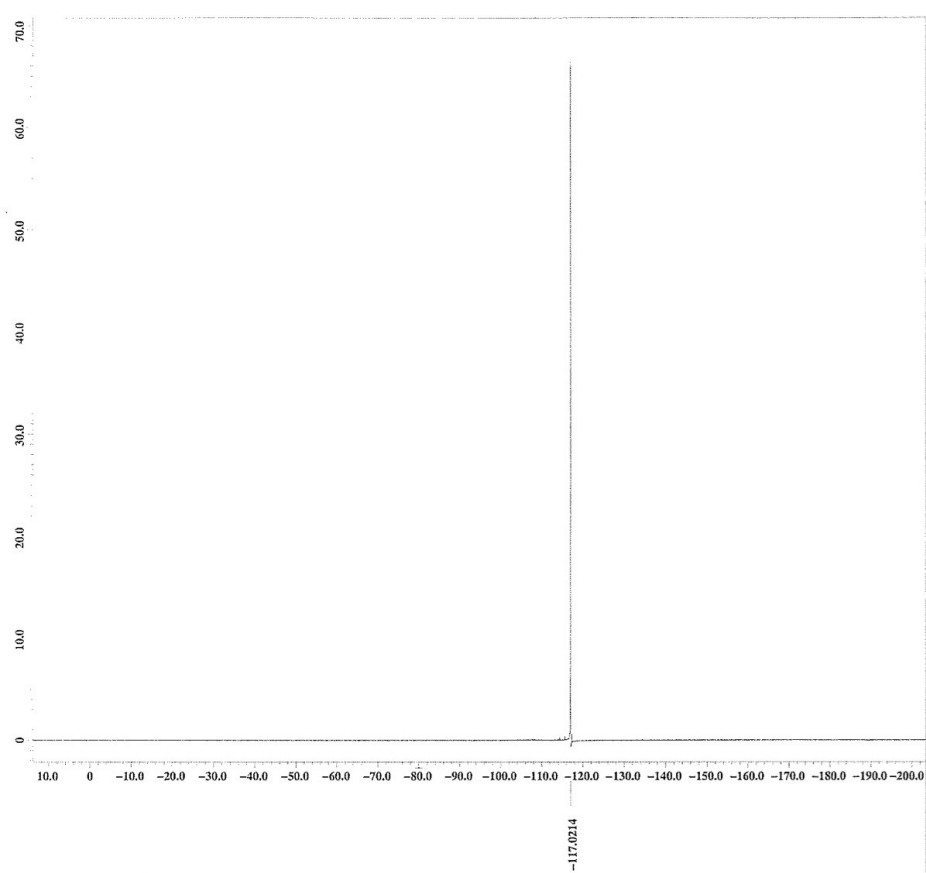
^1H NMR (CDCl_3 , 400 MHz) **4d**



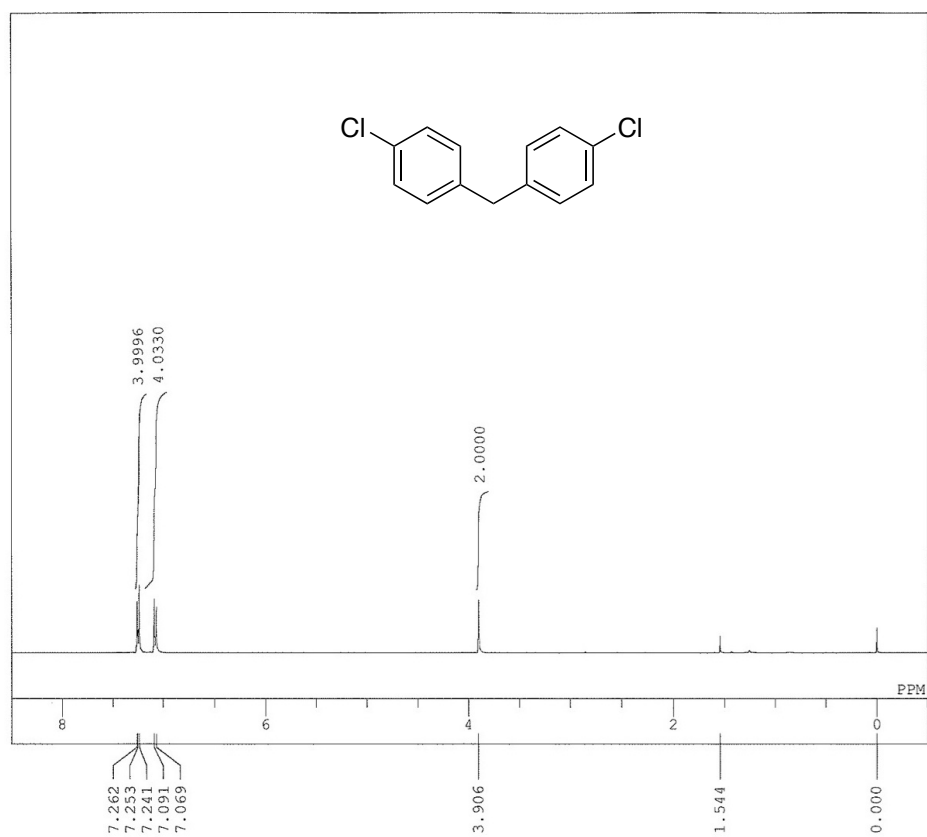
^{13}C NMR (CDCl_3 , 125 MHz) **4d**



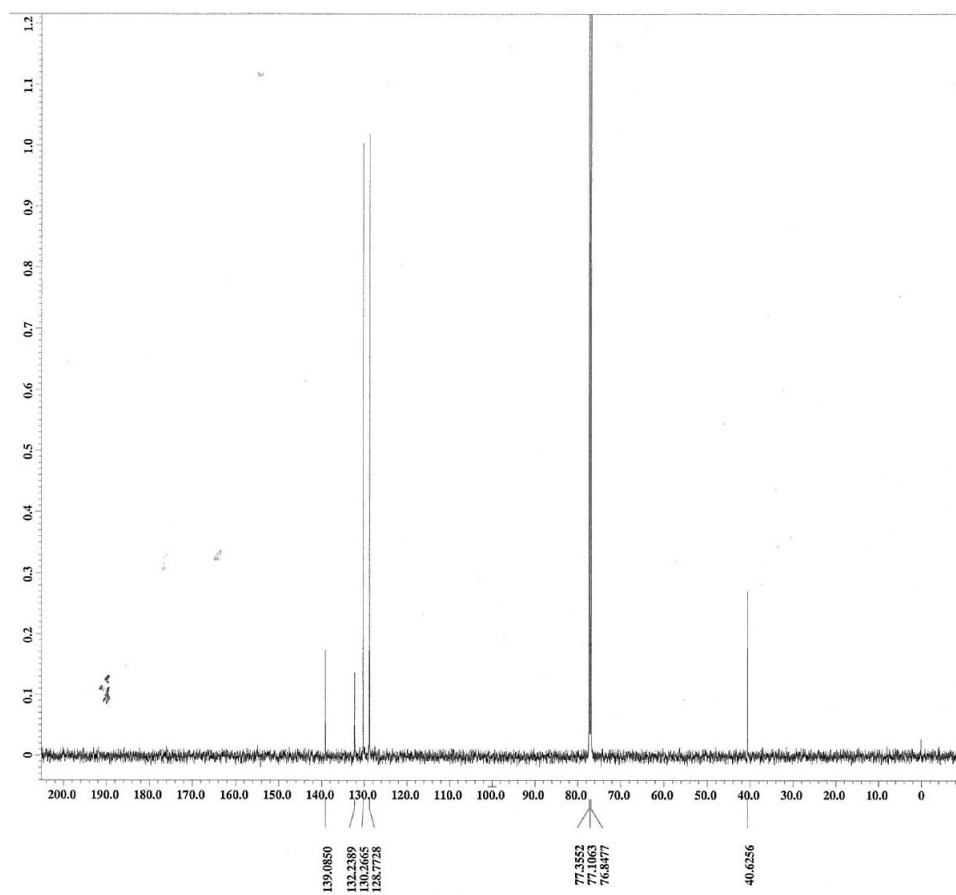
^{19}F NMR (CDCl_3 , 466 MHz) **4d**



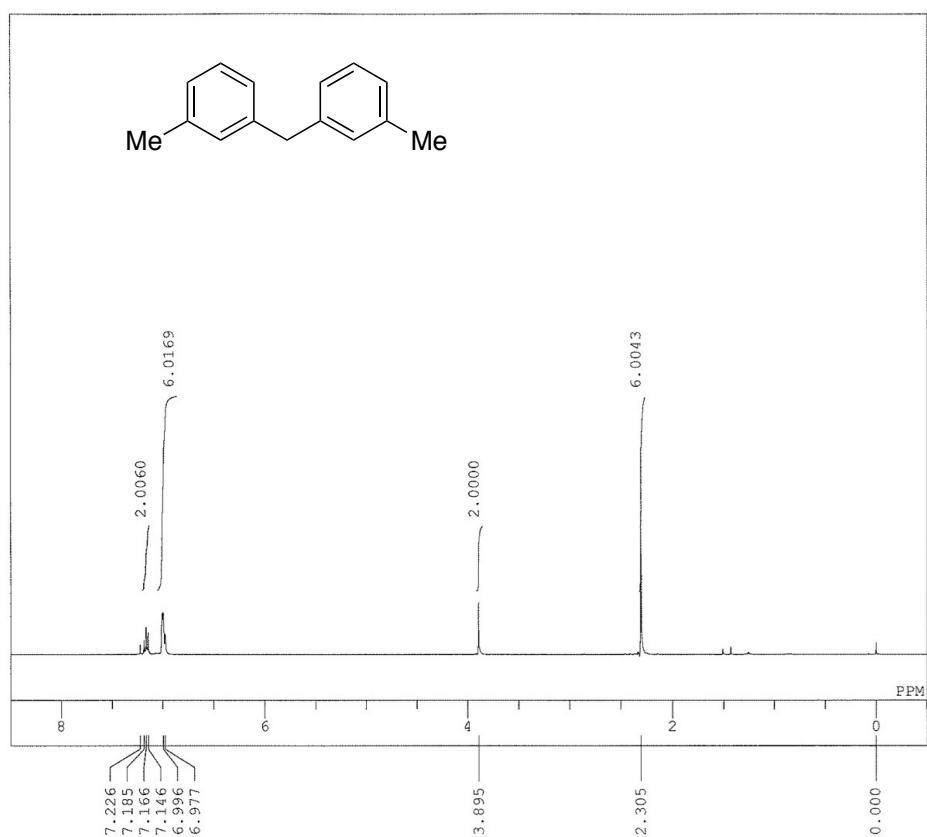
^1H NMR (CDCl_3 , 400 MHz) **4e**



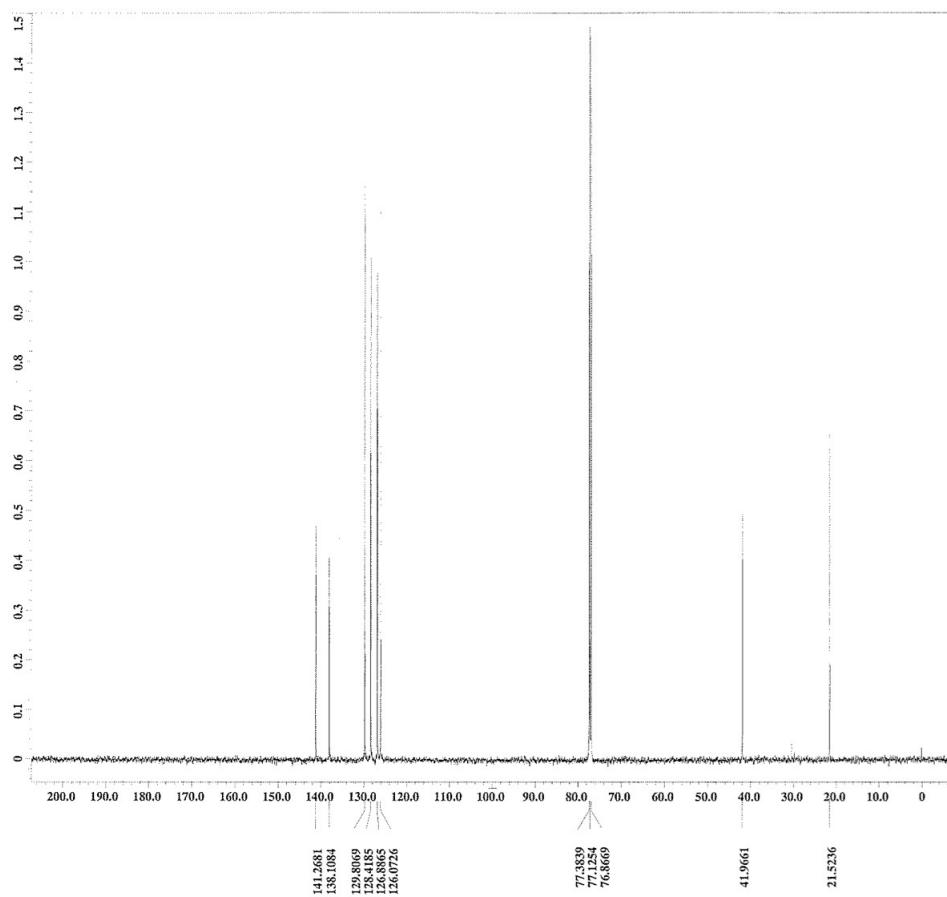
^{13}C NMR (CDCl_3 , 125 MHz) **4e**



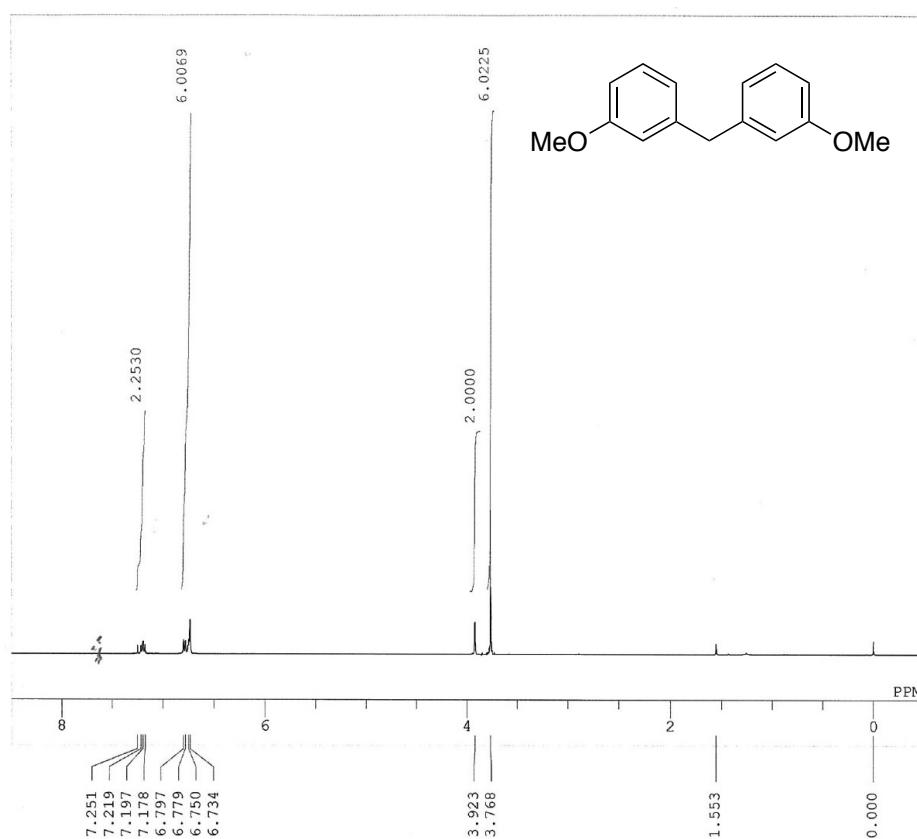
^1H NMR (CDCl_3 , 400 MHz) **4f**



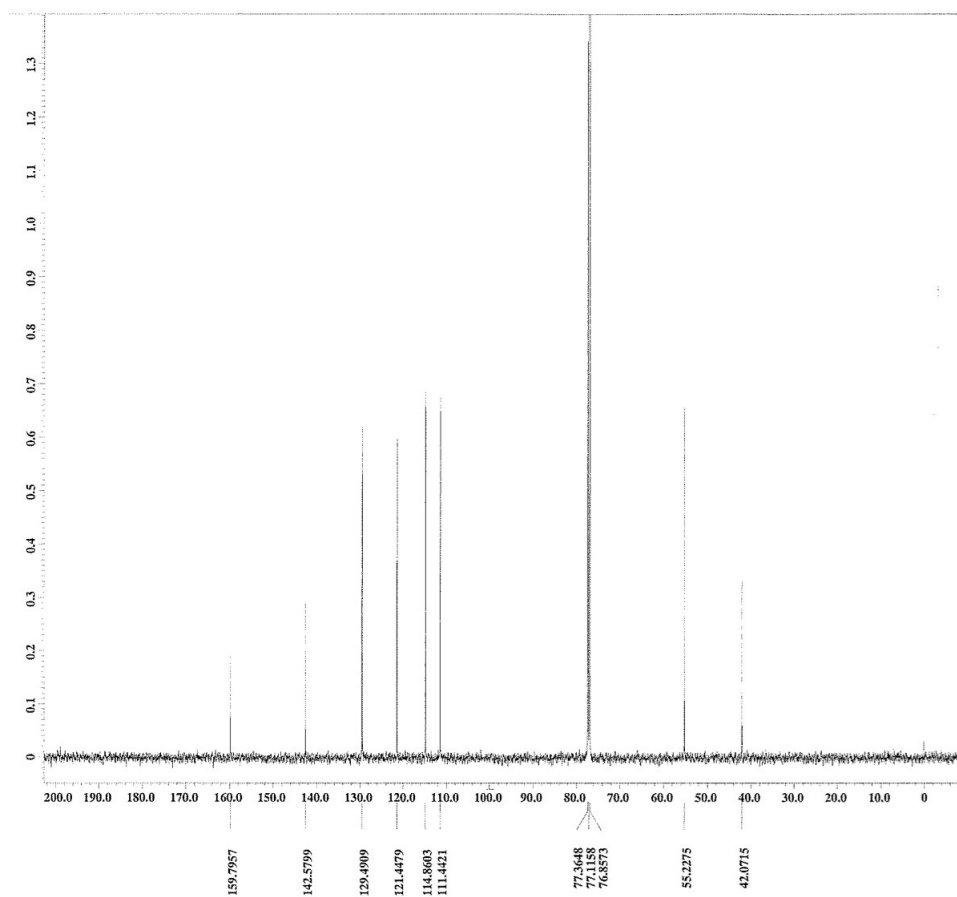
^{13}C NMR (CDCl_3 , 125 MHz) **4f**



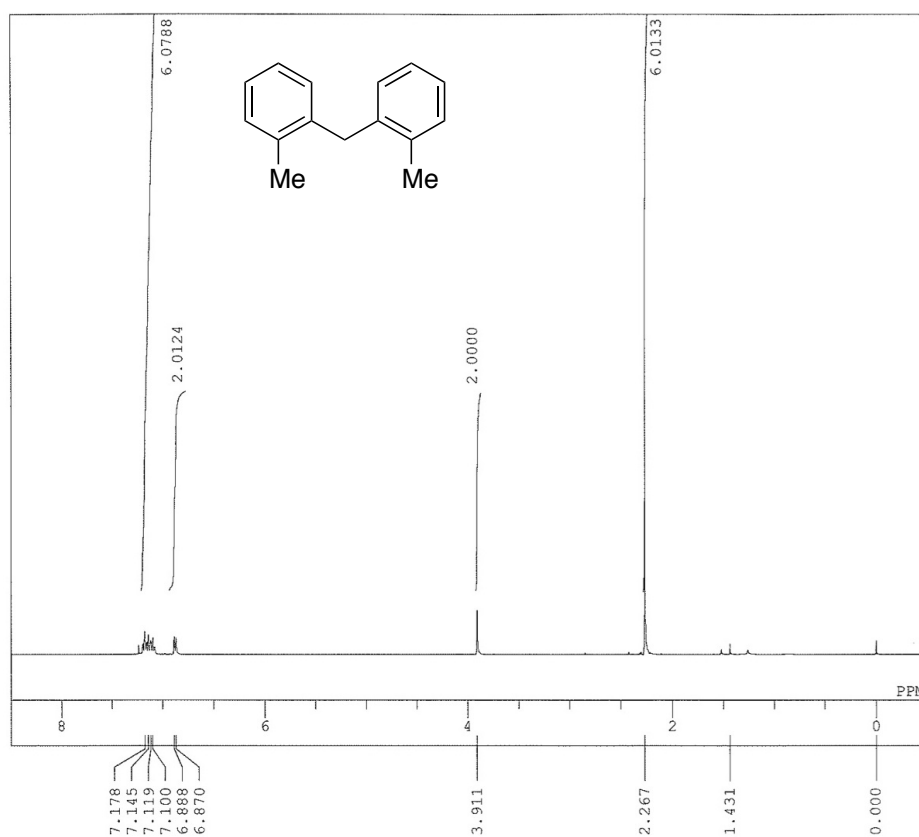
^1H NMR (CDCl_3 , 400 MHz) **4g**



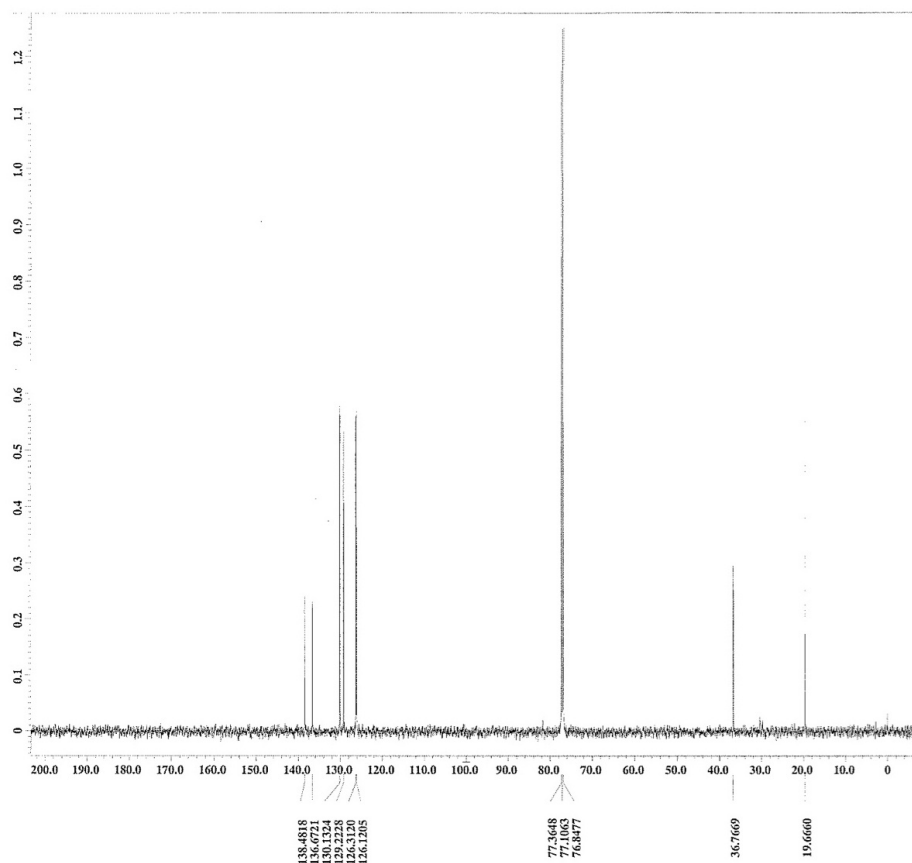
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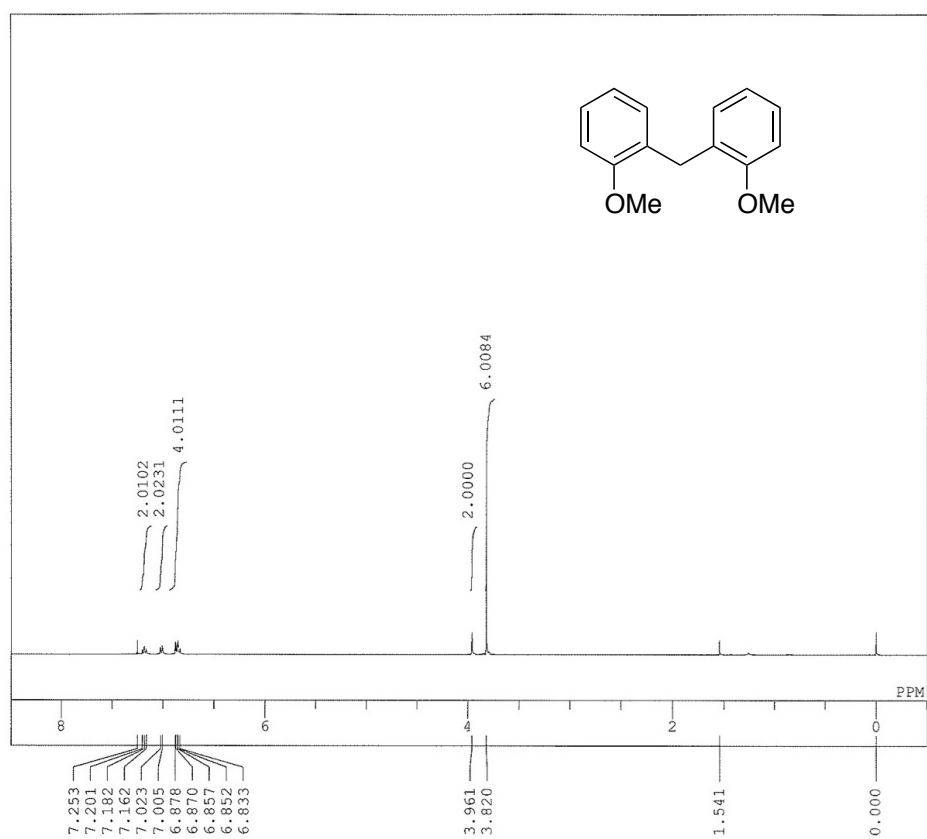
^1H NMR (CDCl_3 , 400 MHz) **4h**



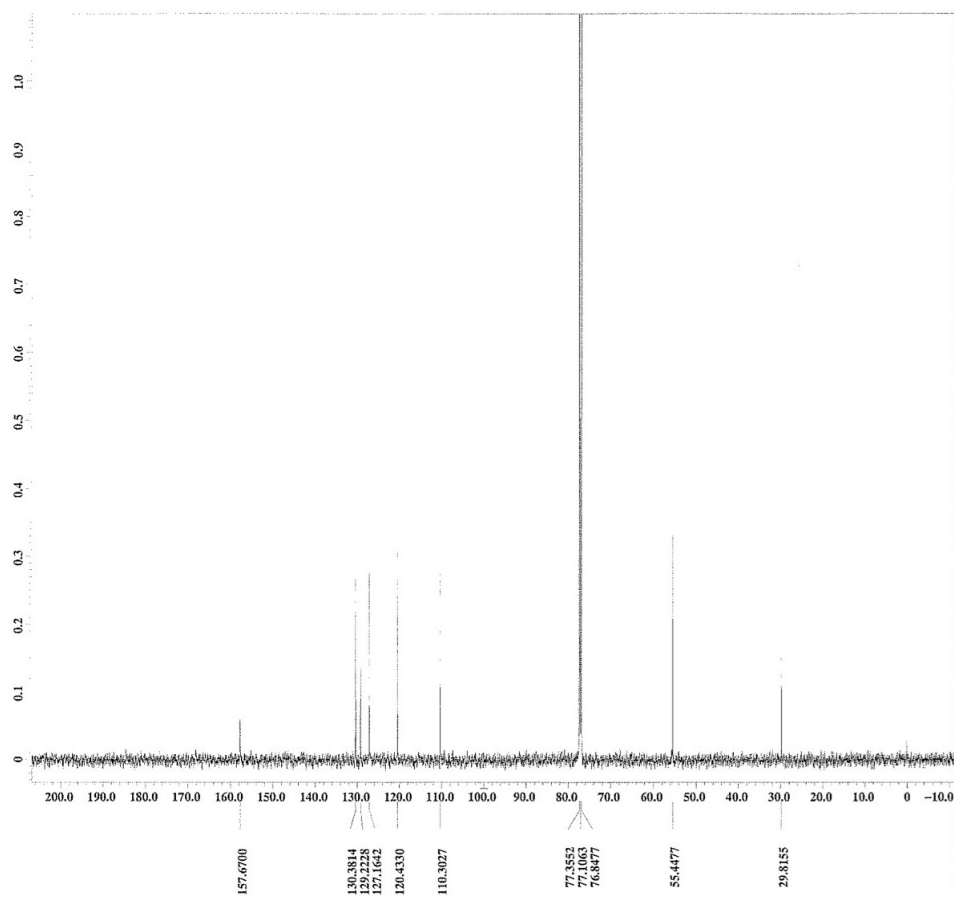
^{13}C NMR (CDCl_3 , 125 MHz) **4h**



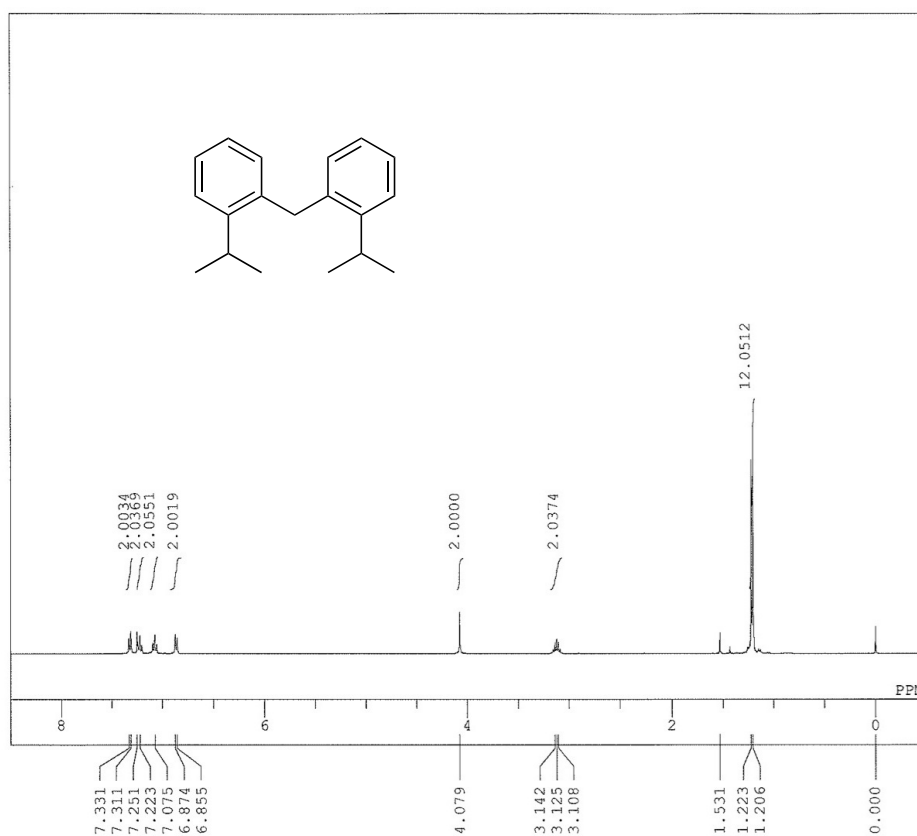
^1H NMR (CDCl_3 , 400 MHz) **4i**



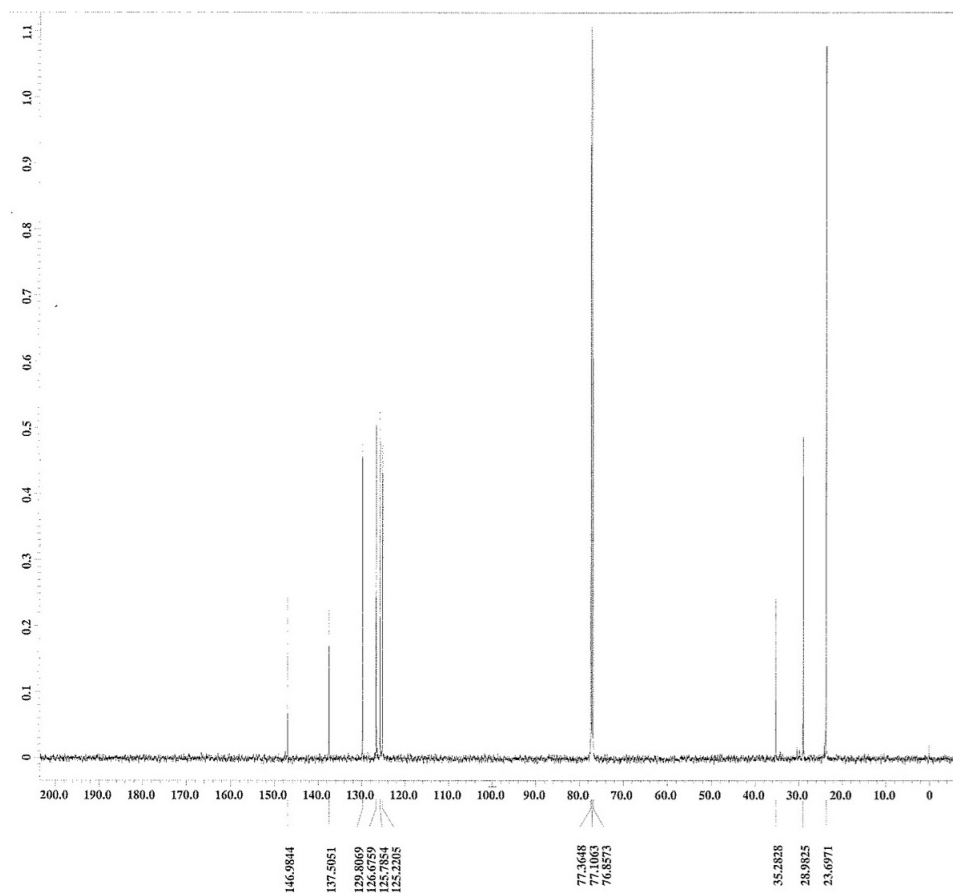
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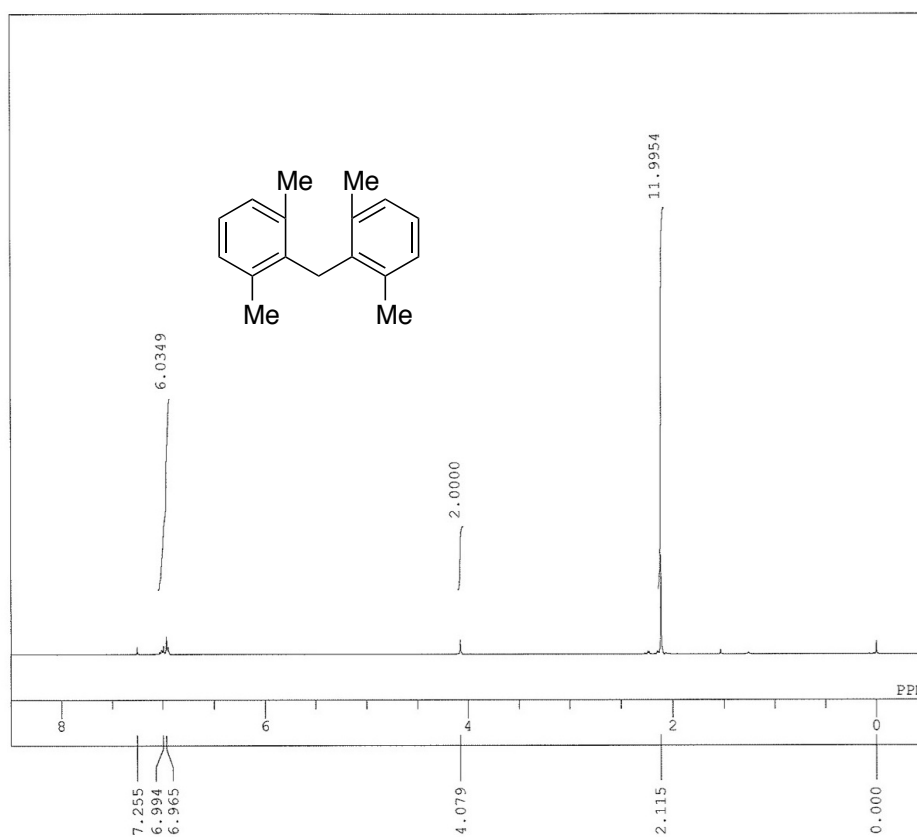
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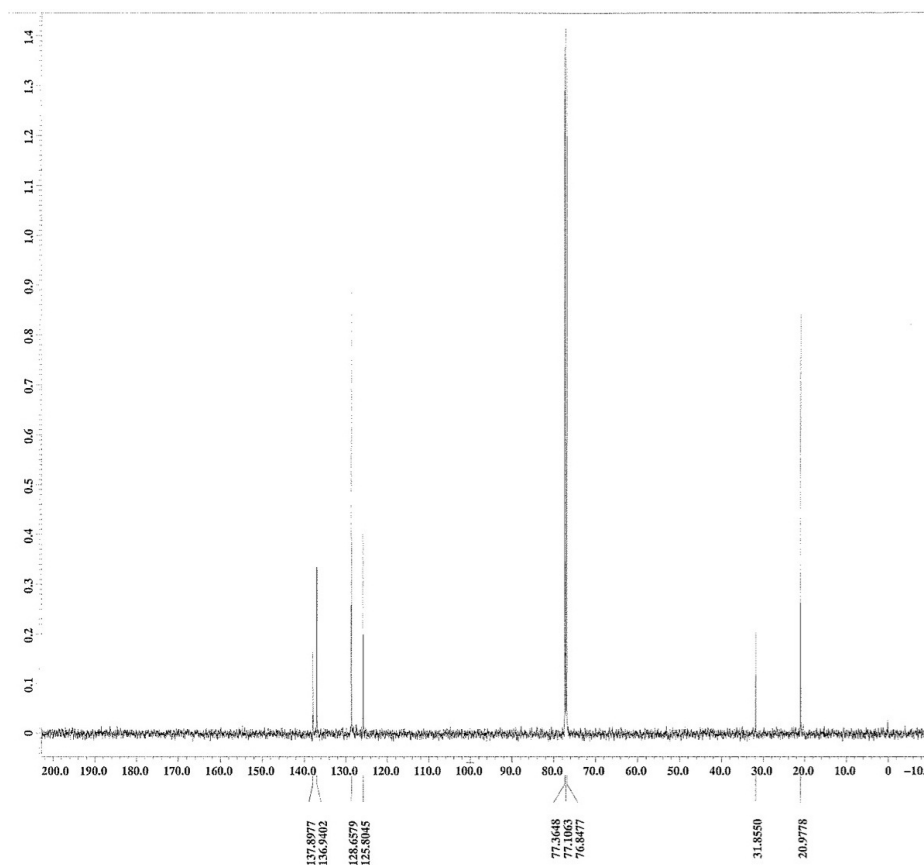
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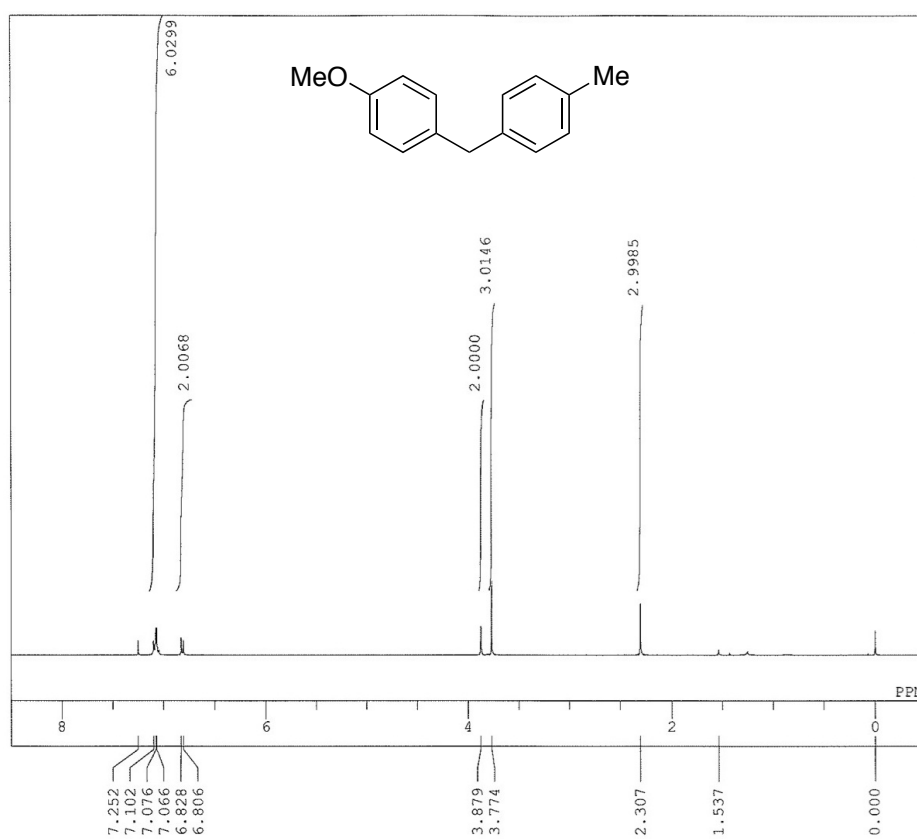
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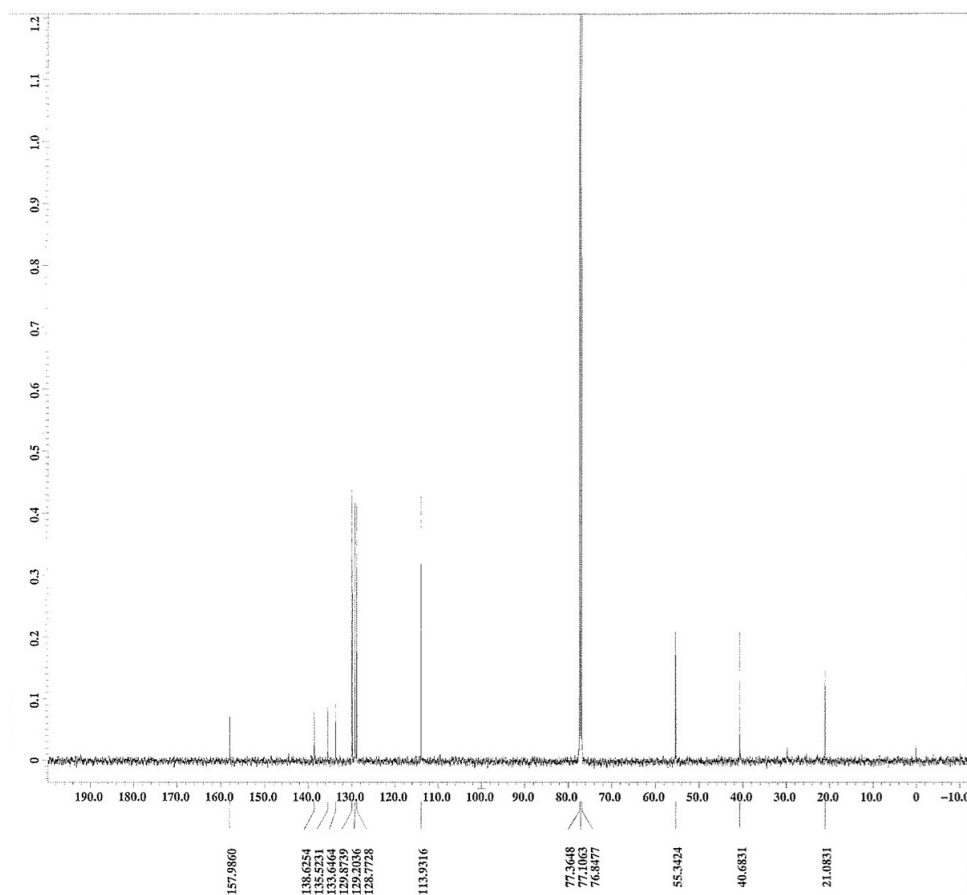
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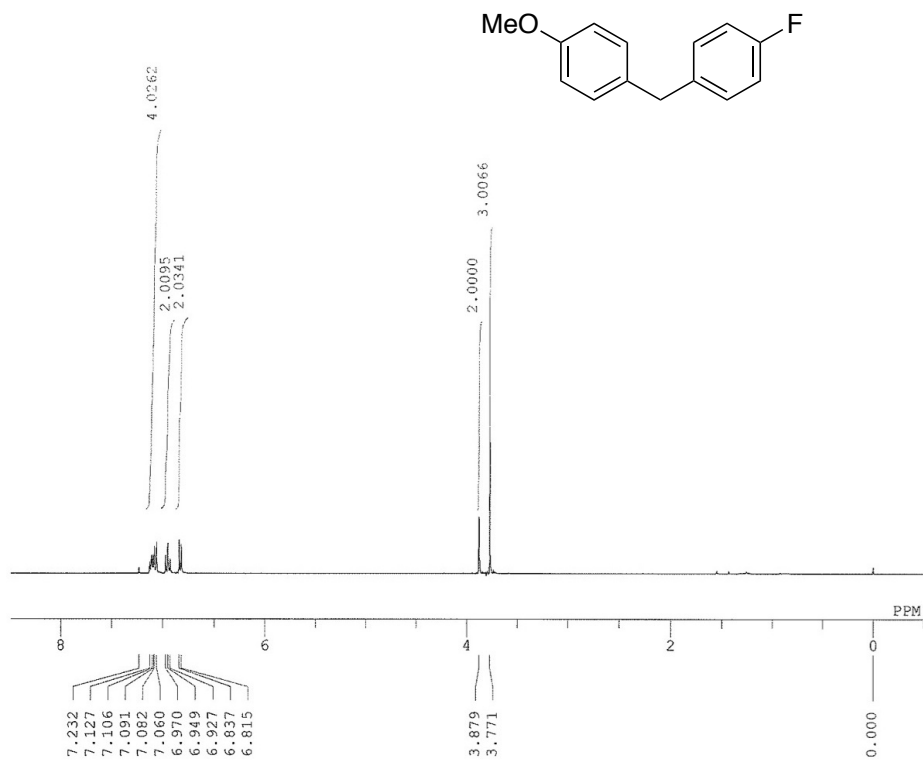
^1H NMR (CDCl_3 , 400 MHz) **5a**



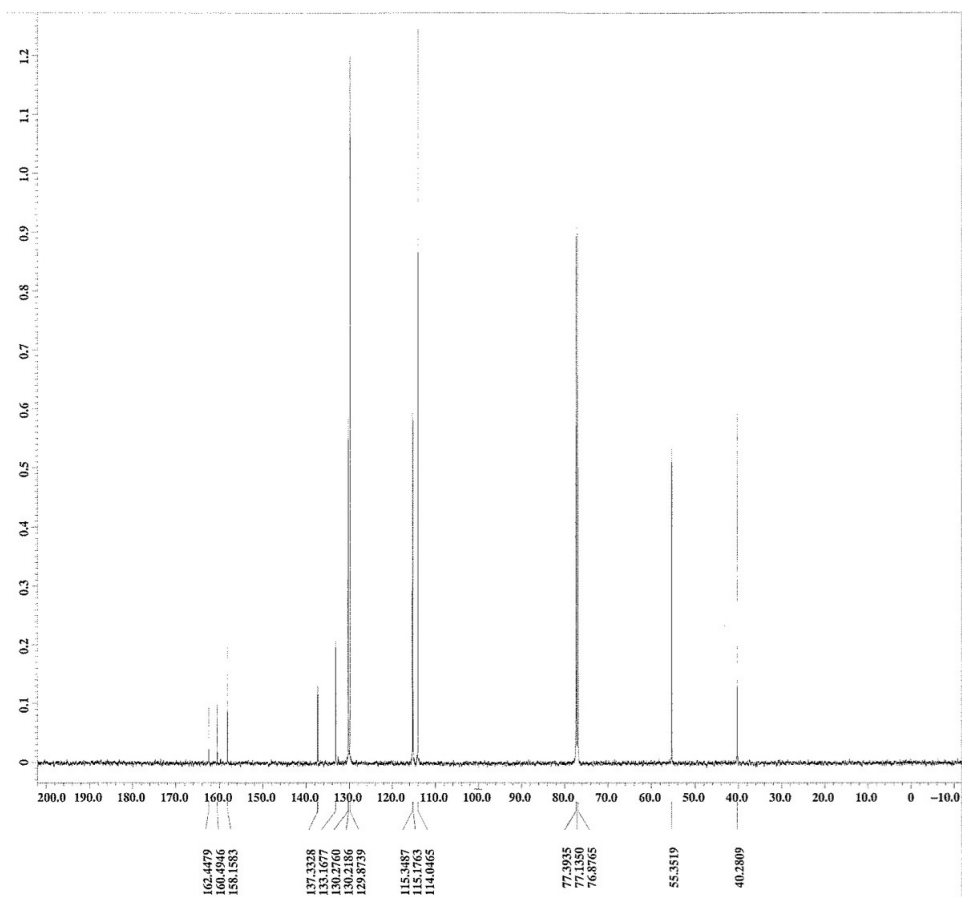
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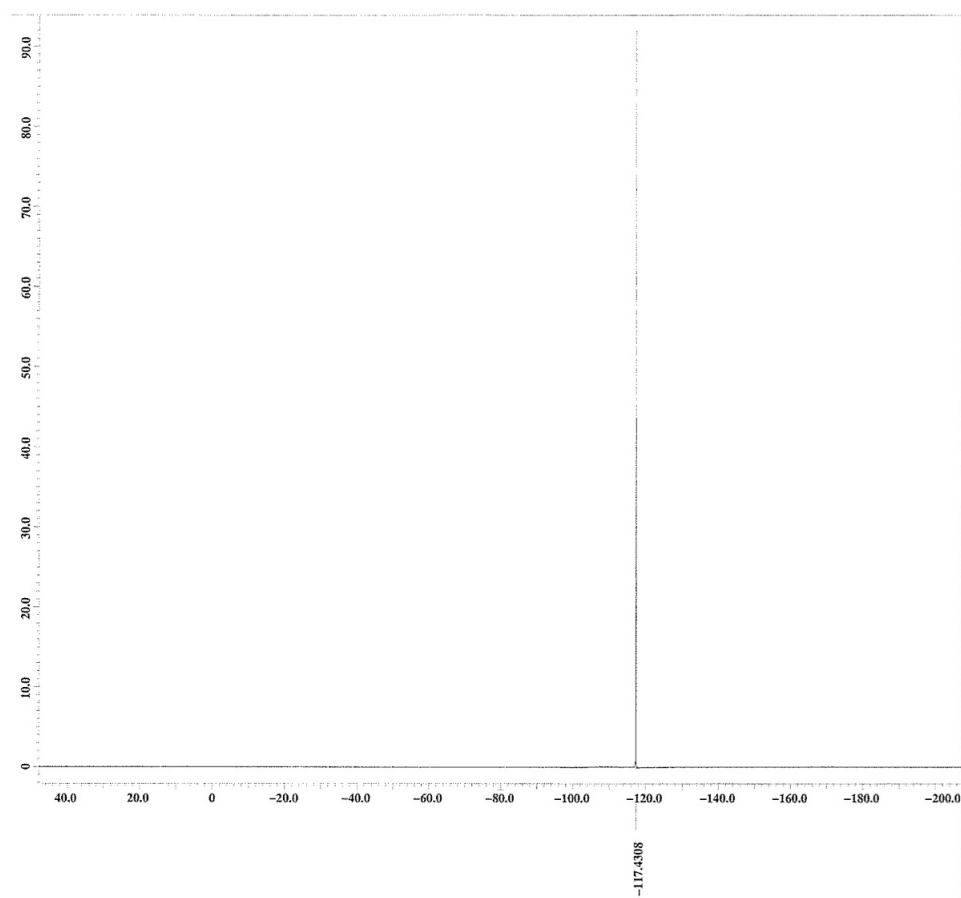
^1H NMR (CDCl_3 , 400 MHz) **5b**



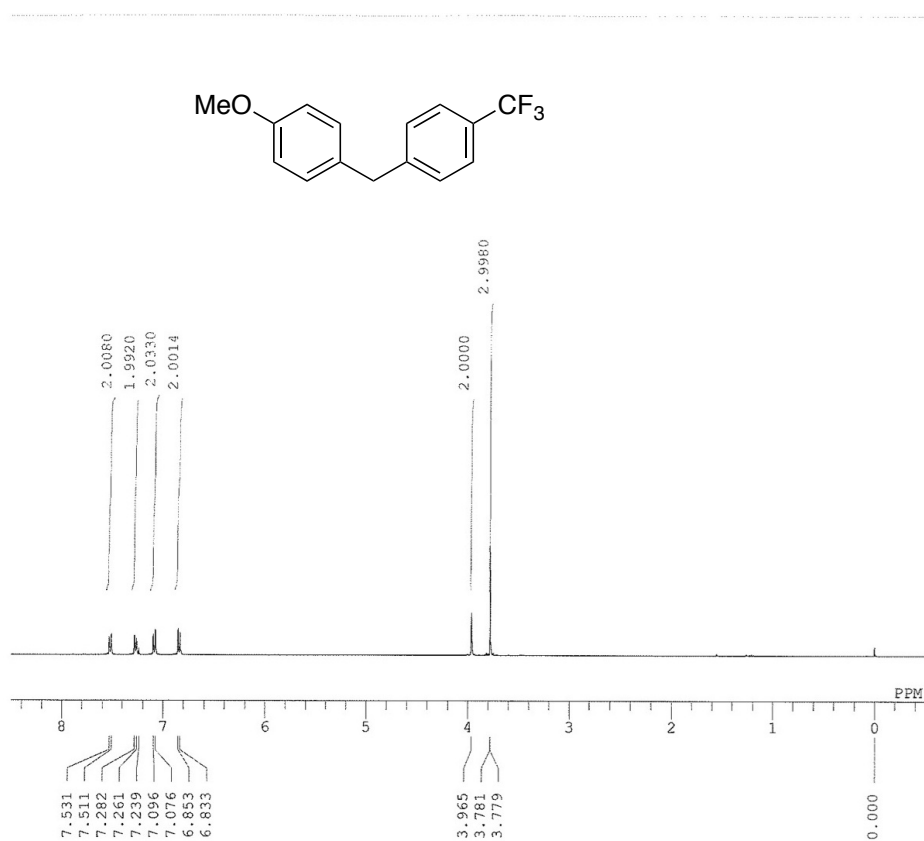
^{13}C NMR (CDCl_3 , 125 MHz) **5b**



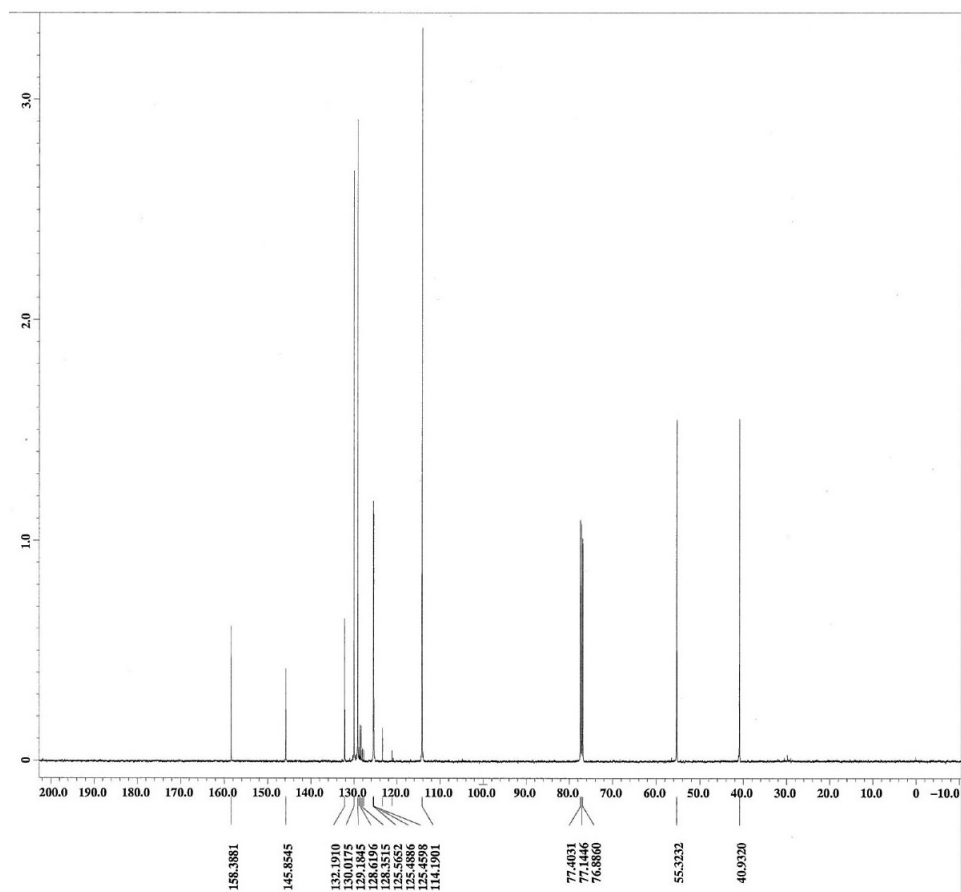
^{19}F NMR (CDCl_3 , 466 MHz) **5b**



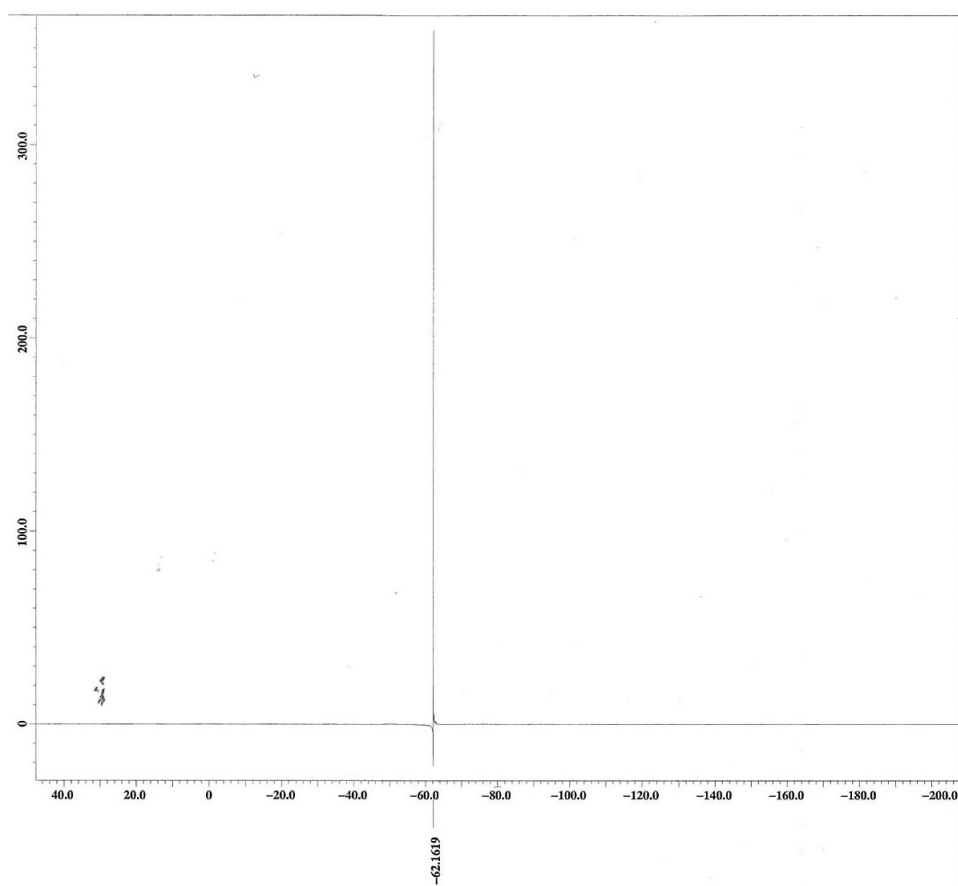
^1H NMR (CDCl_3 , 400 MHz) **5c**



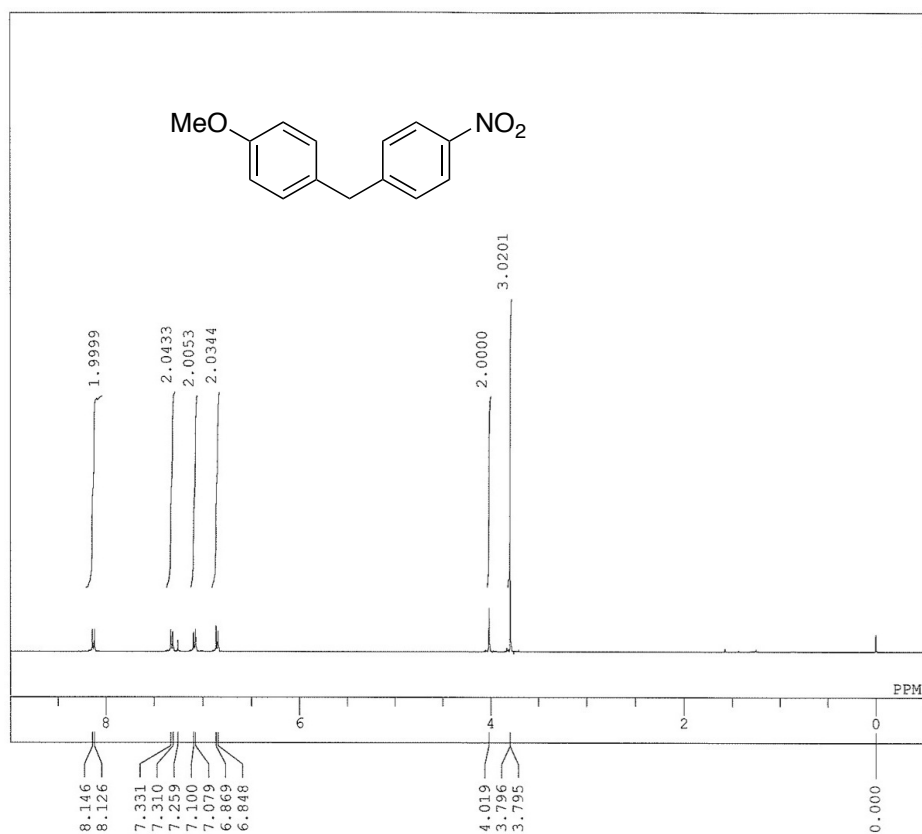
^{13}C NMR (CDCl_3 , 125 MHz) **5c**



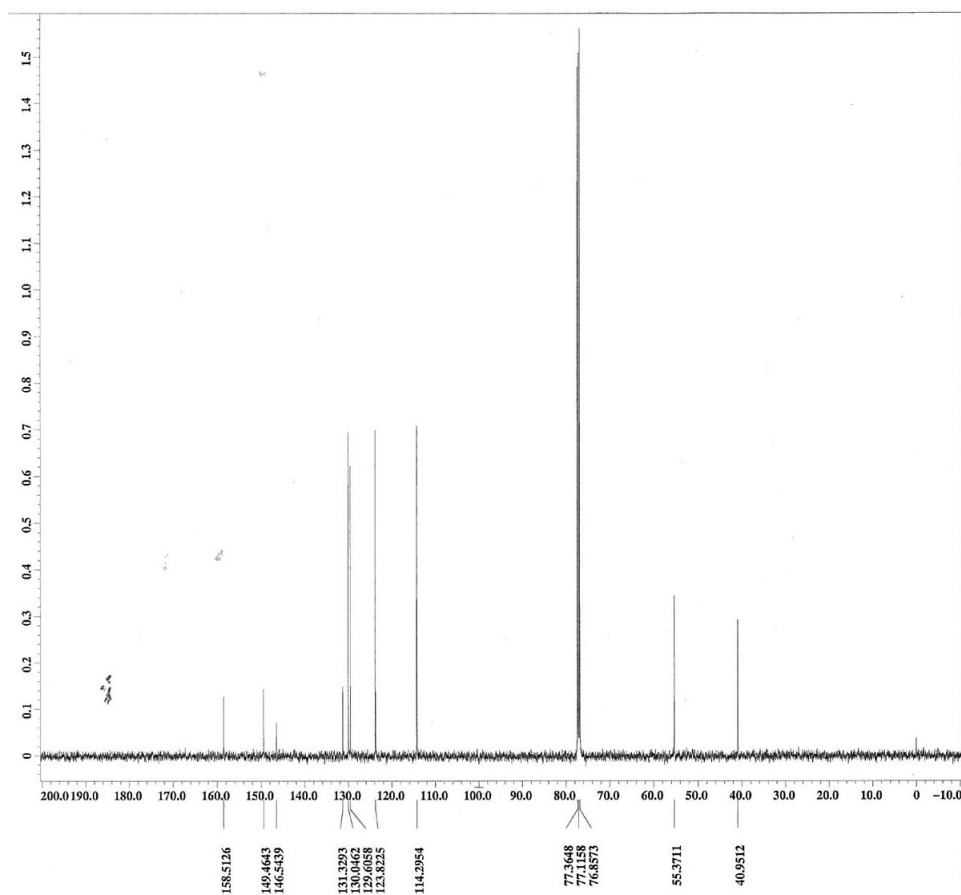
^{19}F NMR (CDCl_3 , 466 MHz) **5c**



^1H NMR (CDCl_3 , 400 MHz) **5d**



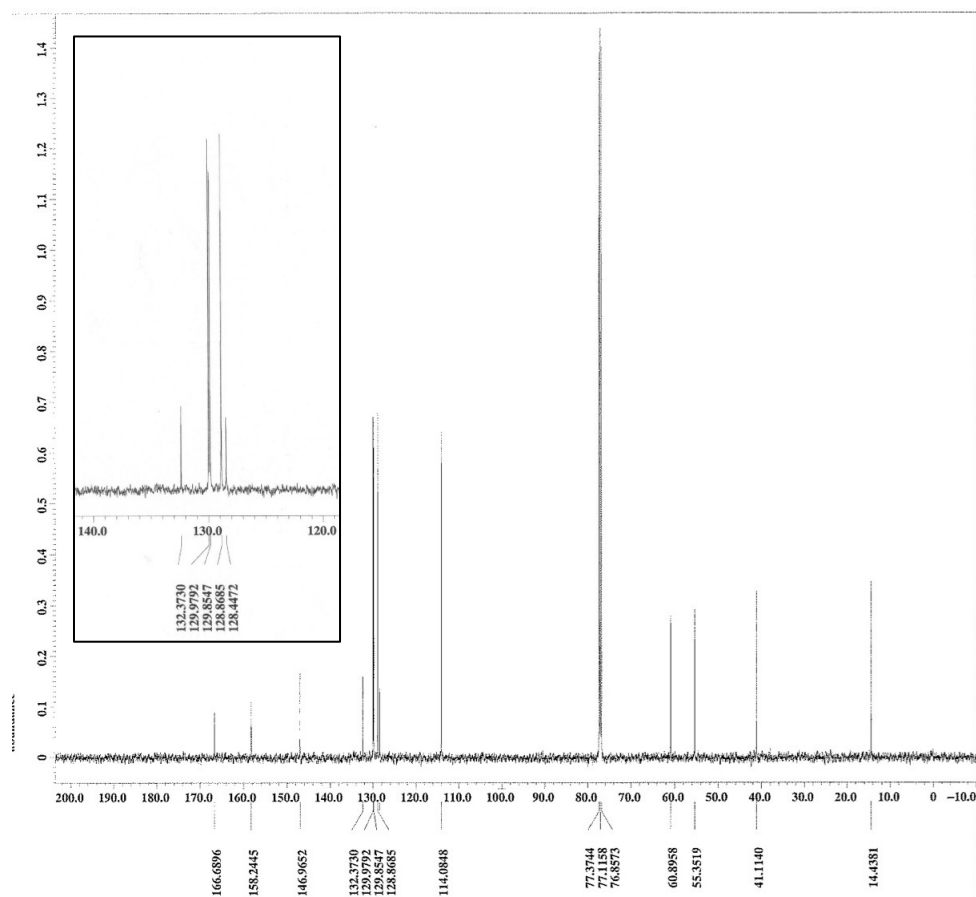
^{13}C NMR (CDCl_3 , 125 MHz) **5d**



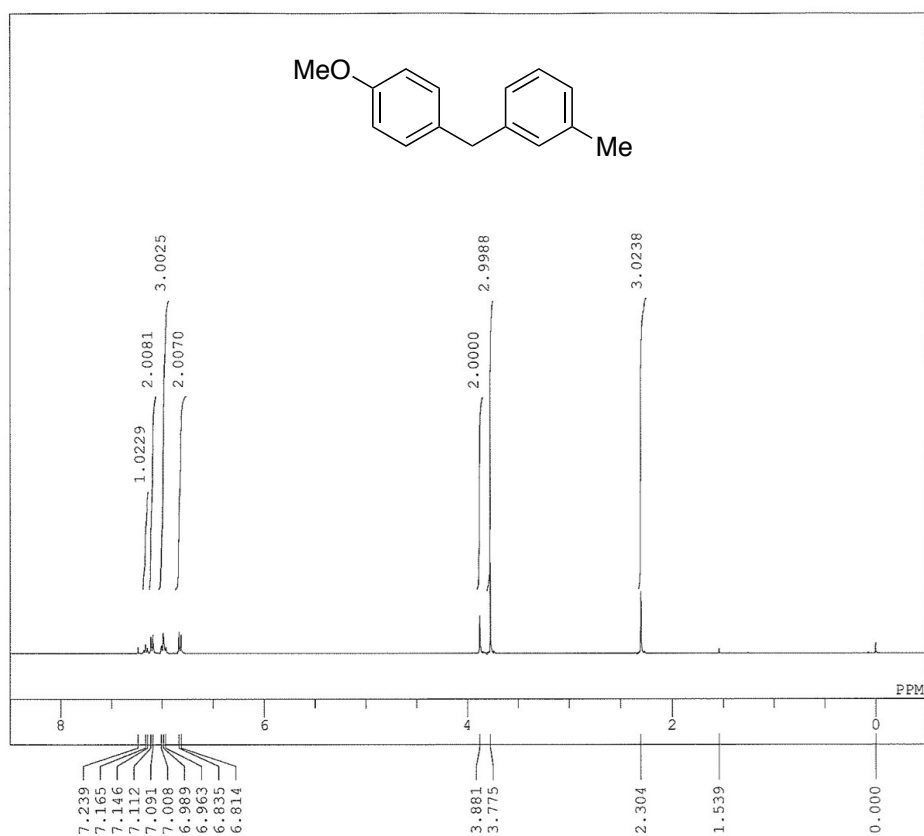
^1H NMR (CDCl_3 , 400 MHz) **5e**



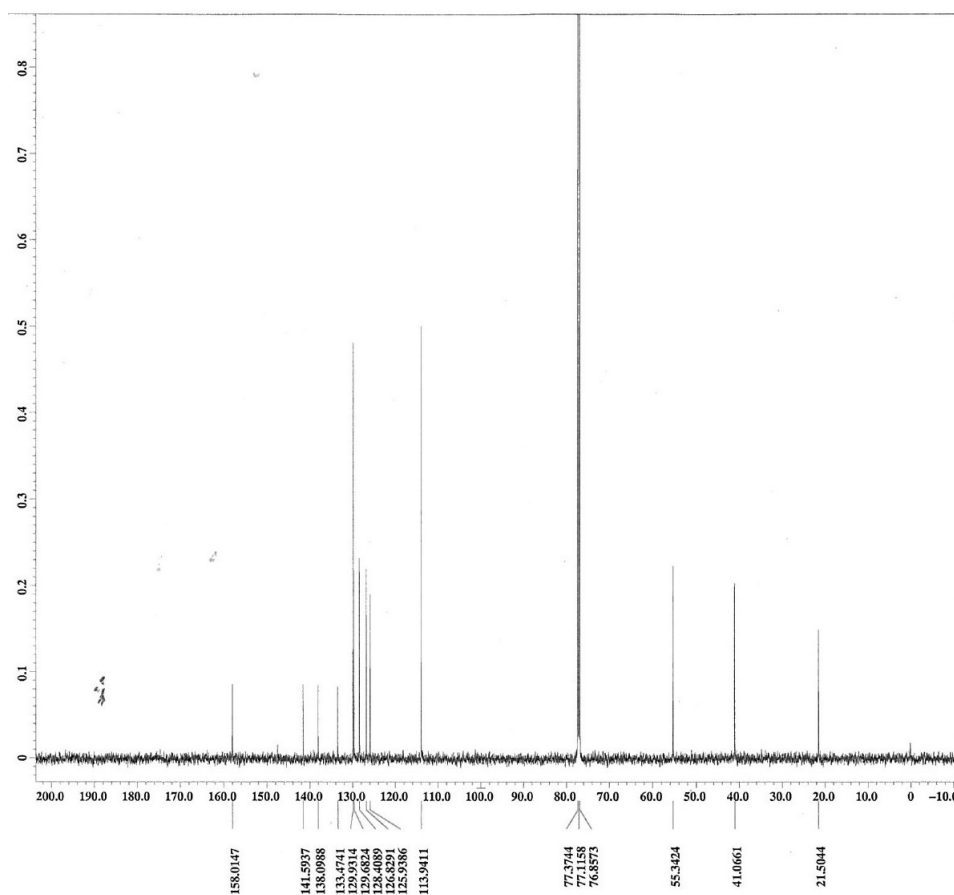
^{13}C NMR (CDCl_3 , 125 MHz) **5e**



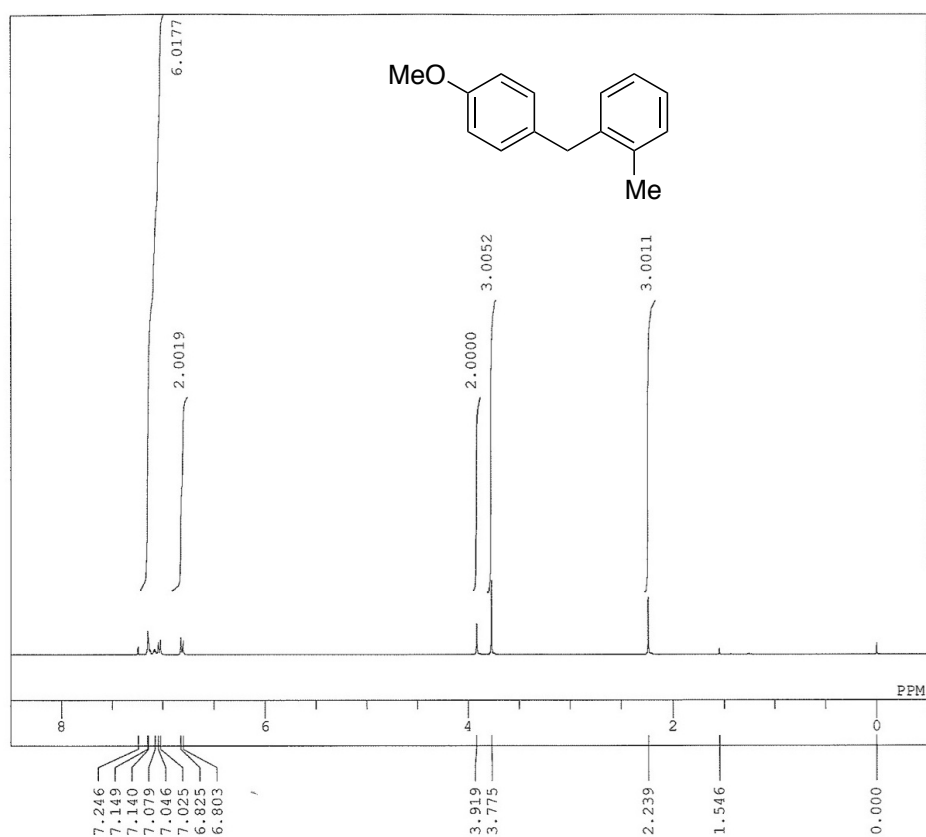
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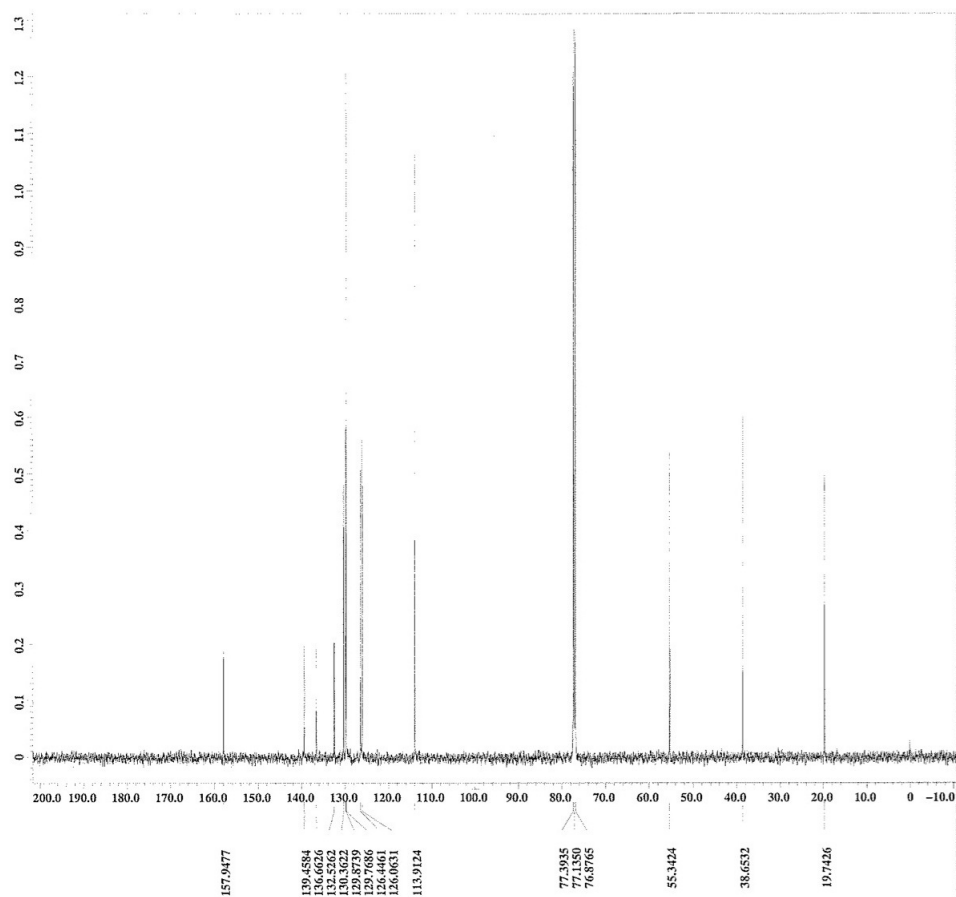
^{13}C NMR (CDCl_3 , 125 MHz) **5f**



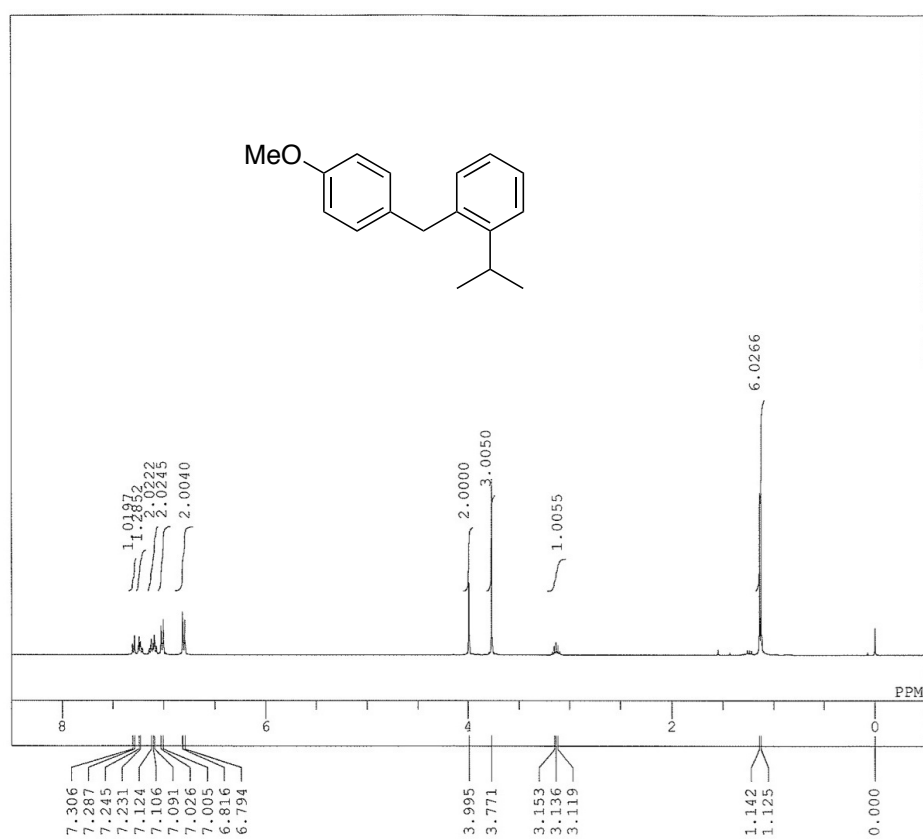
^1H NMR (CDCl_3 , 400 MHz) **5g**



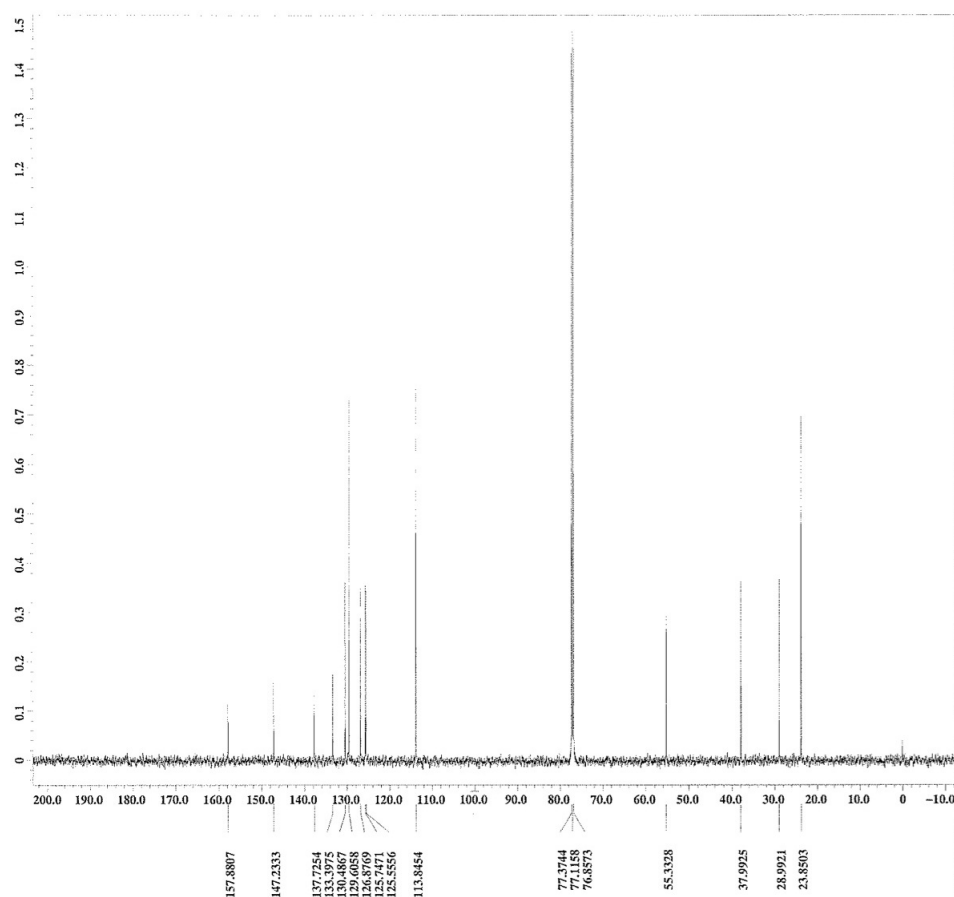
^{13}C NMR (CDCl_3 , 125 MHz) **5g**



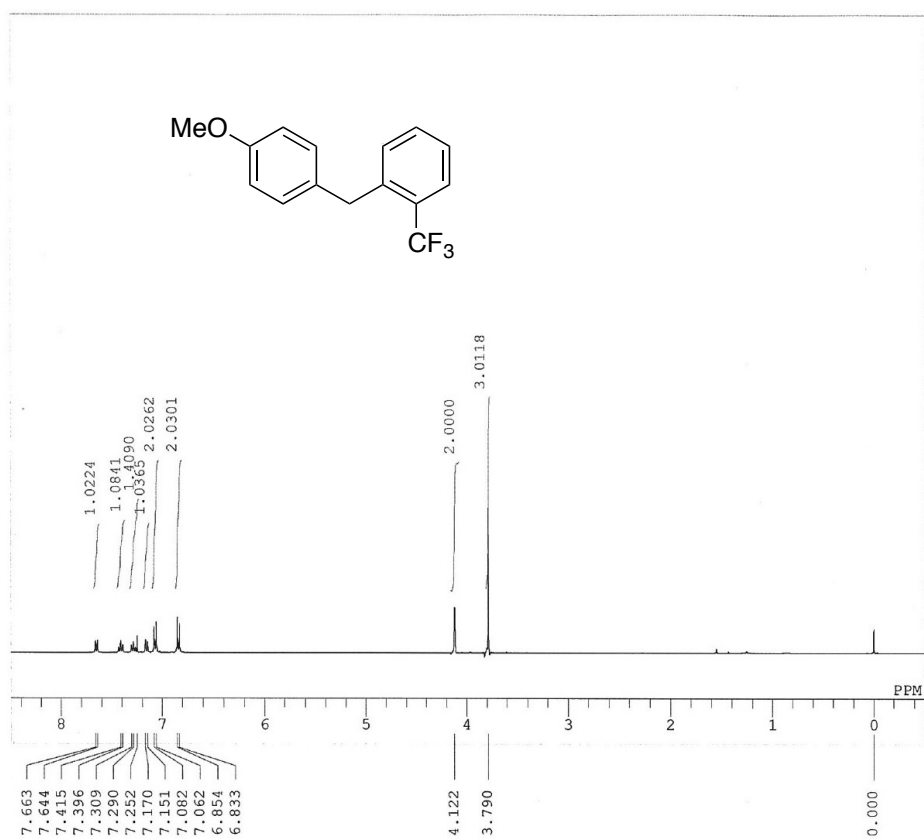
^1H NMR (CDCl_3 , 400 MHz) **5h**



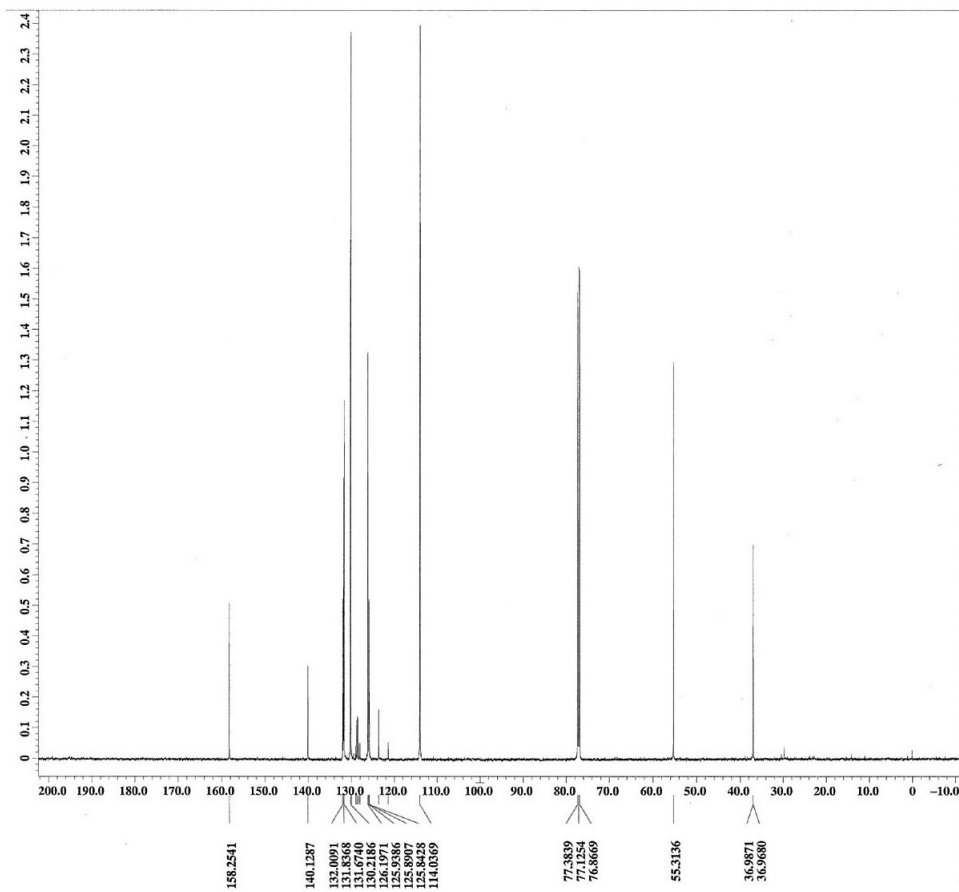
^{13}C NMR (CDCl_3 , 125 MHz) **5h**



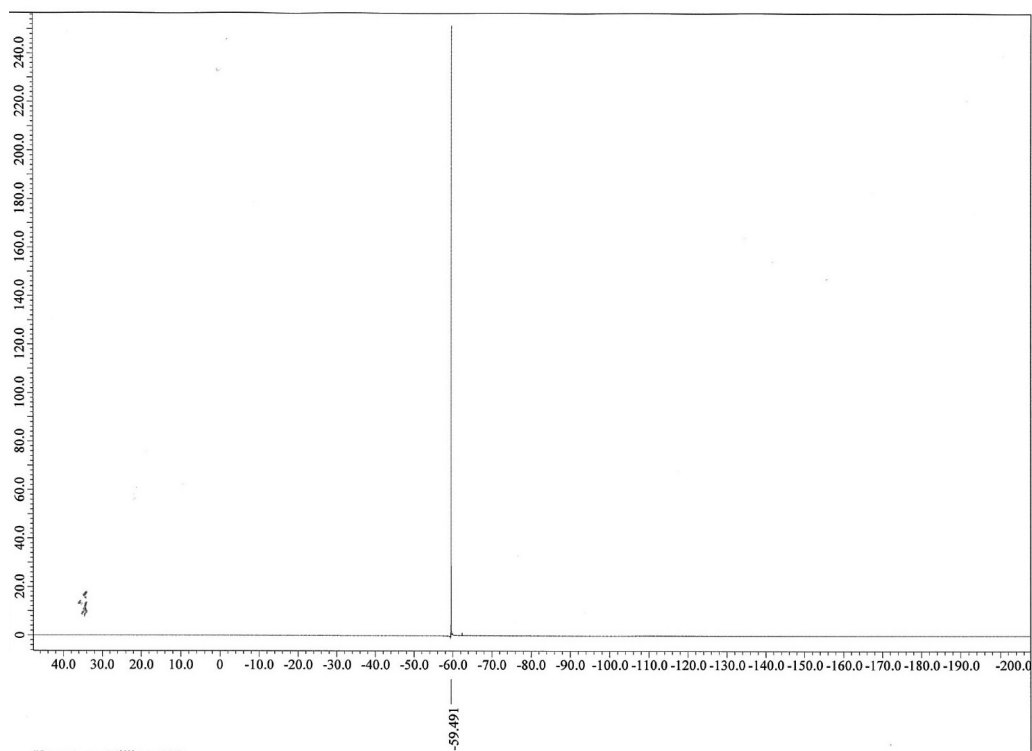
^1H NMR (CDCl_3 , 400 MHz) **5i**



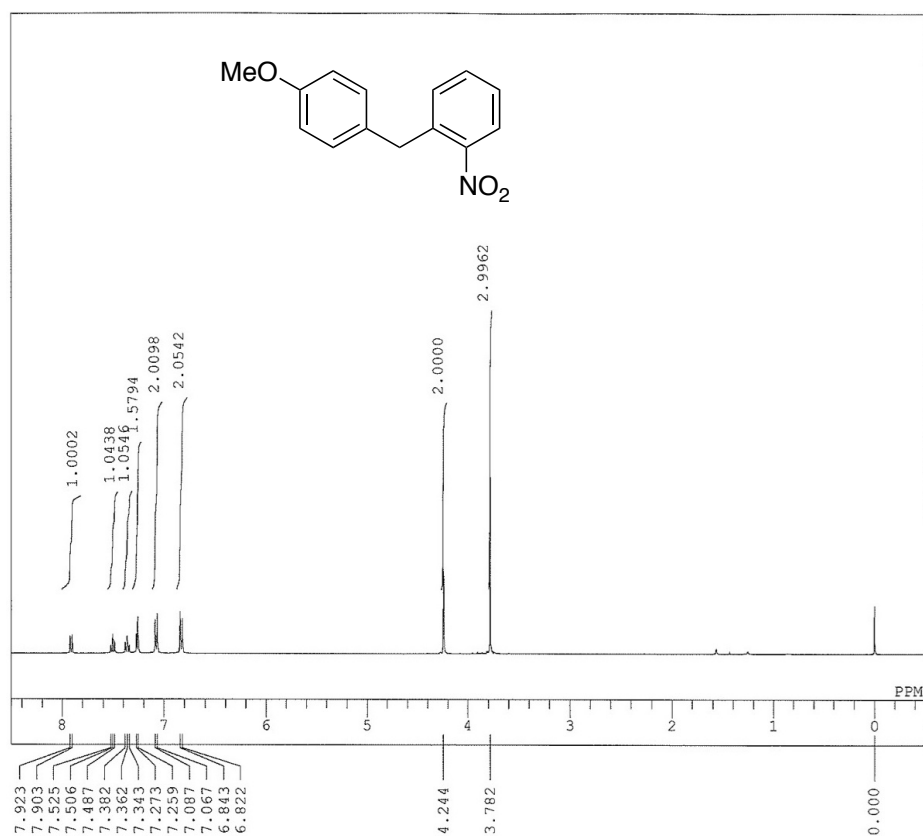
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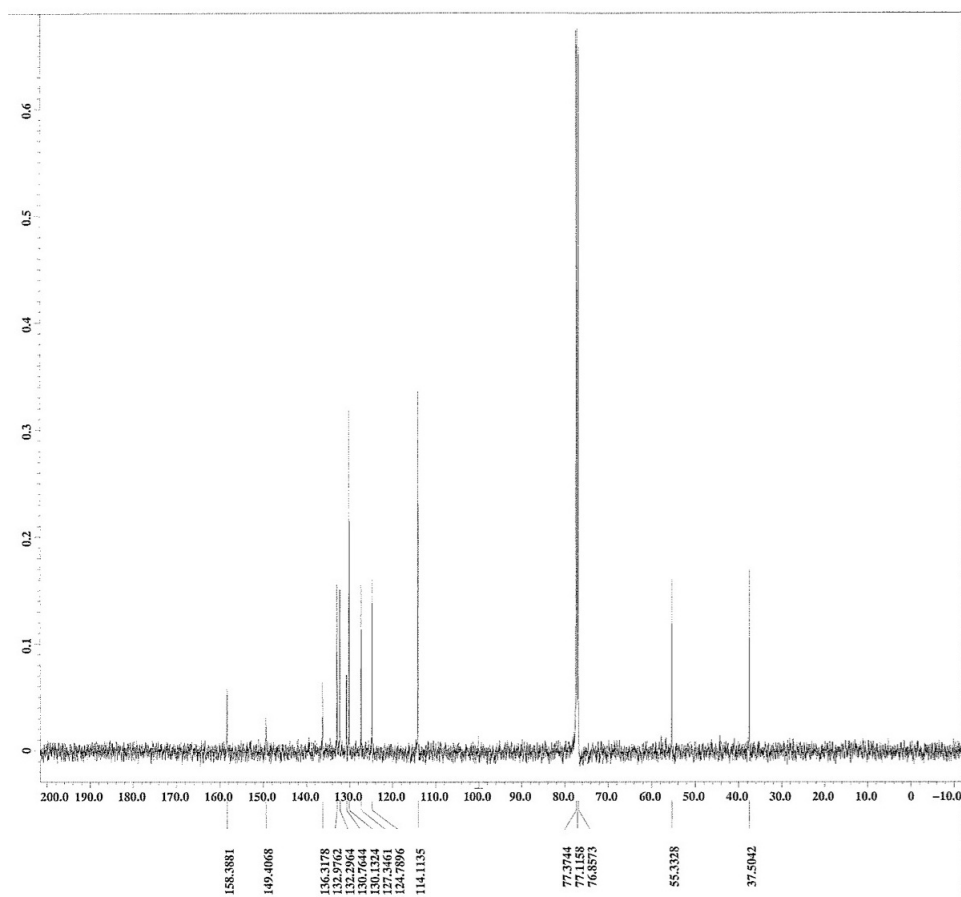
^{19}F NMR (CDCl_3 , 466 MHz) **5i**



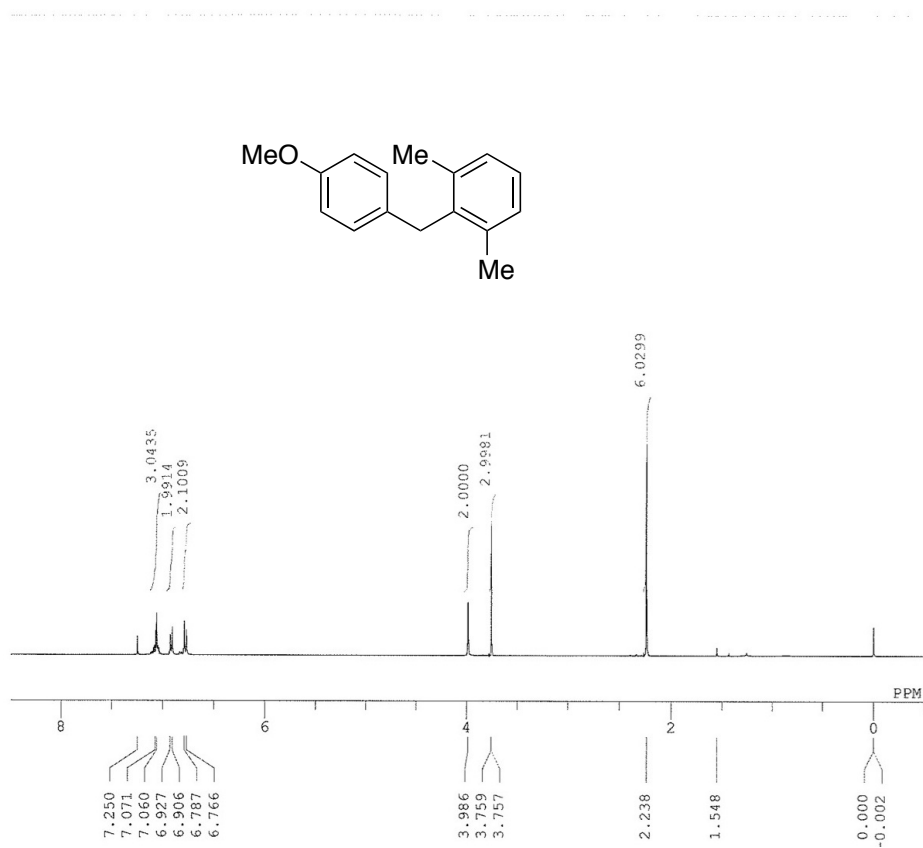
^1H NMR (CDCl_3 , 400 MHz) **5j**



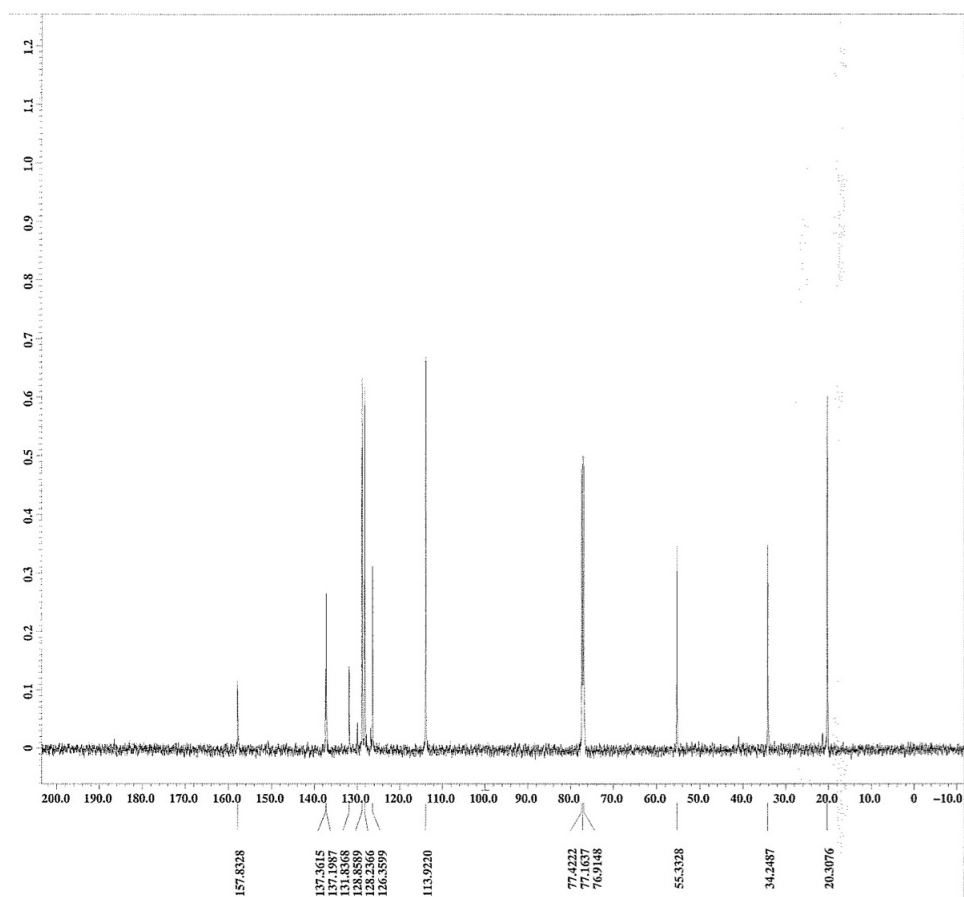
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^1H NMR (CDCl_3 , 400 MHz) **5k**



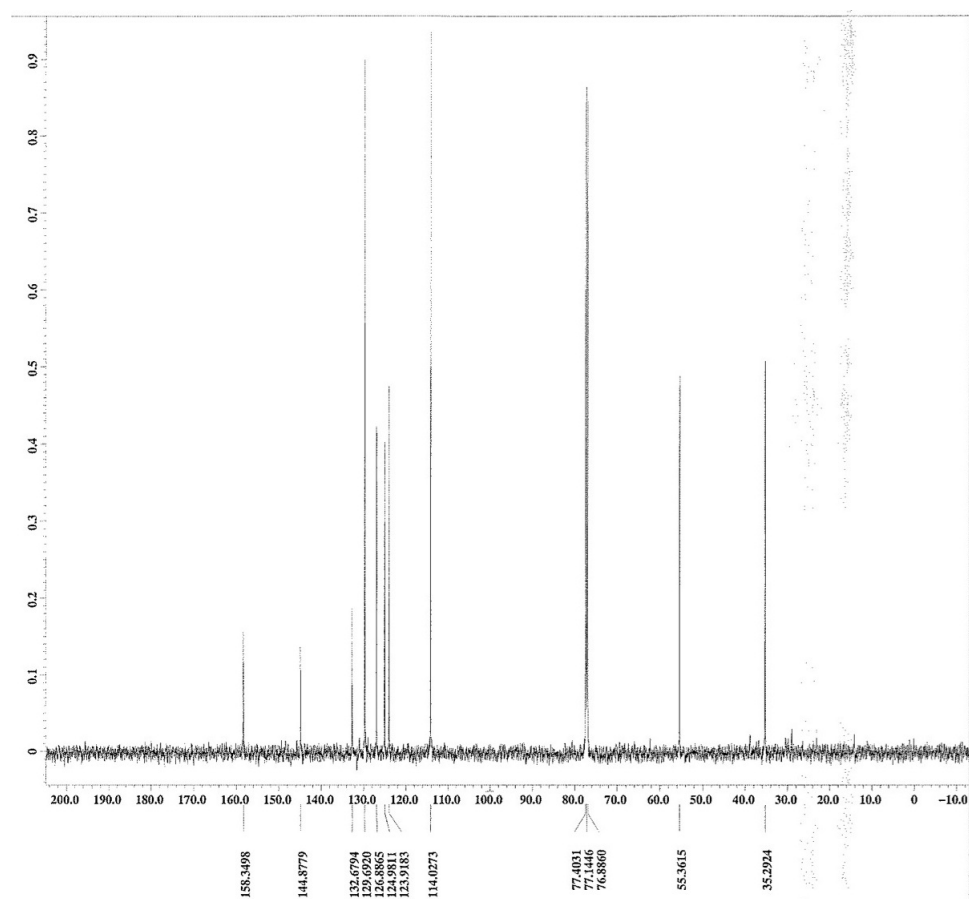
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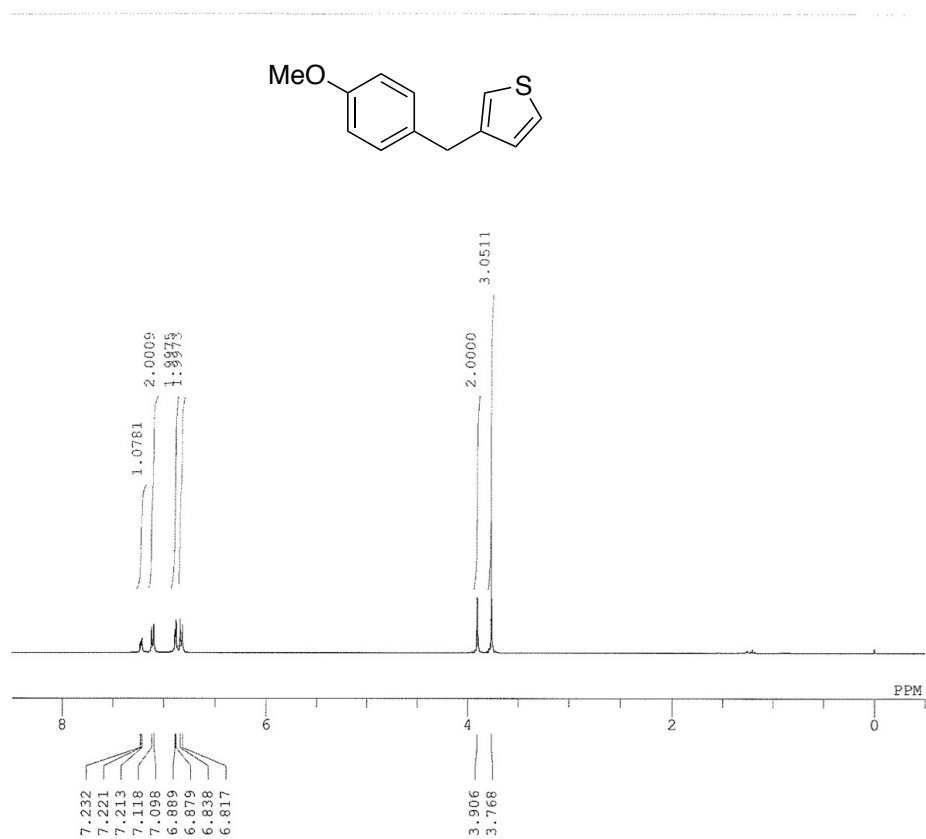
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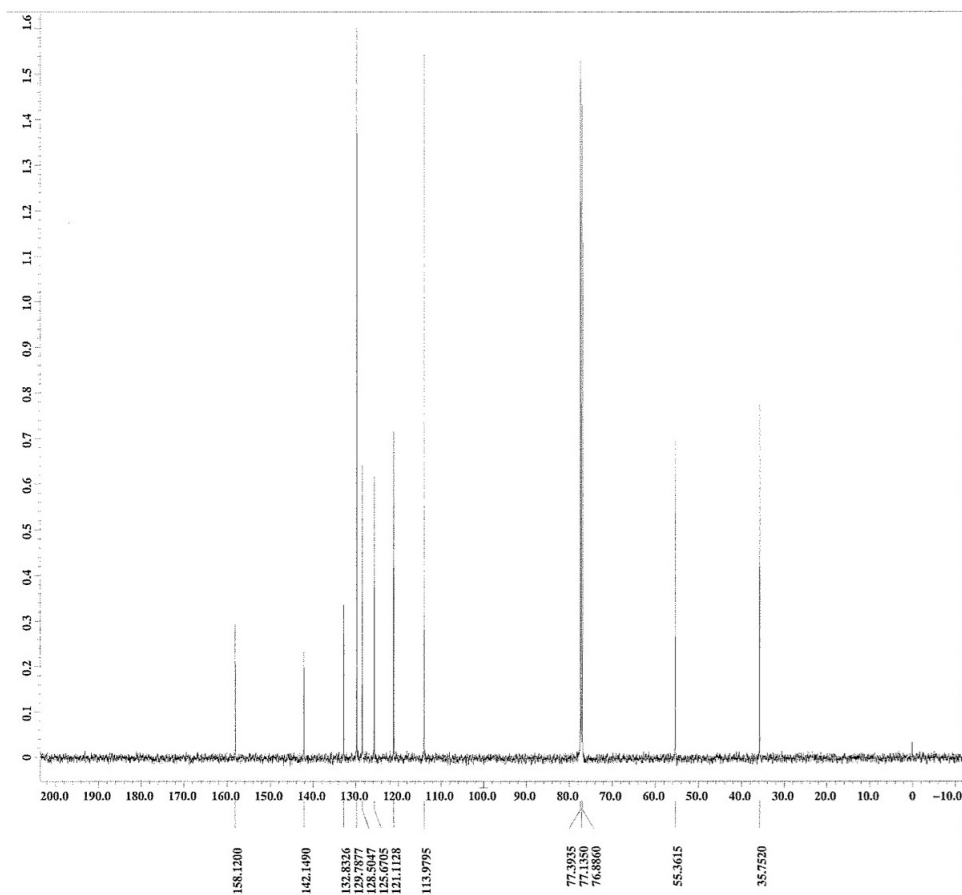
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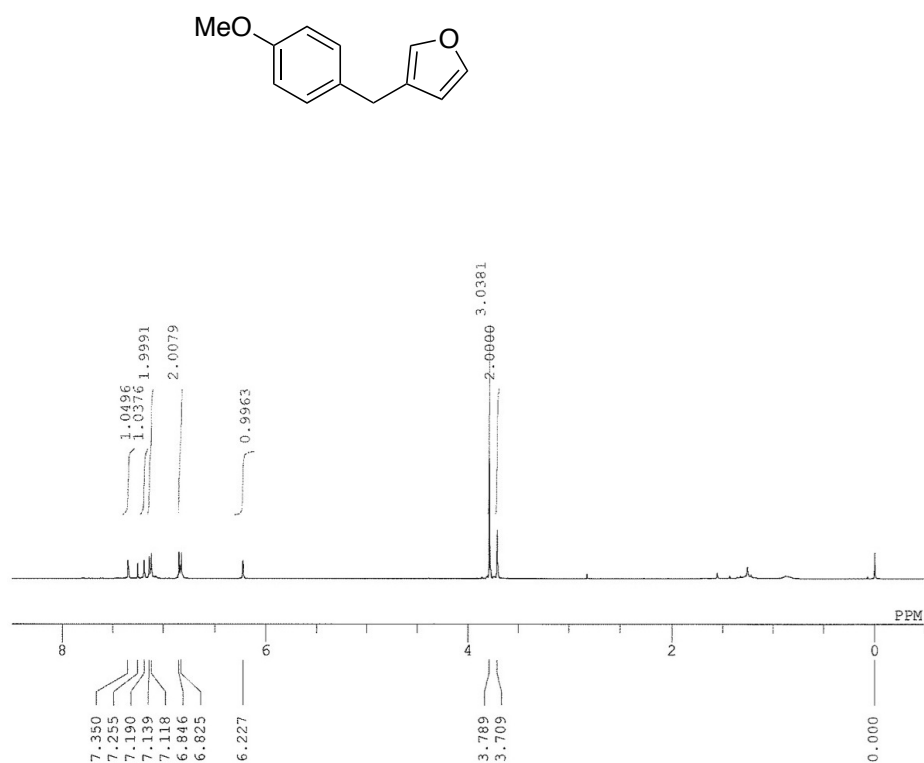
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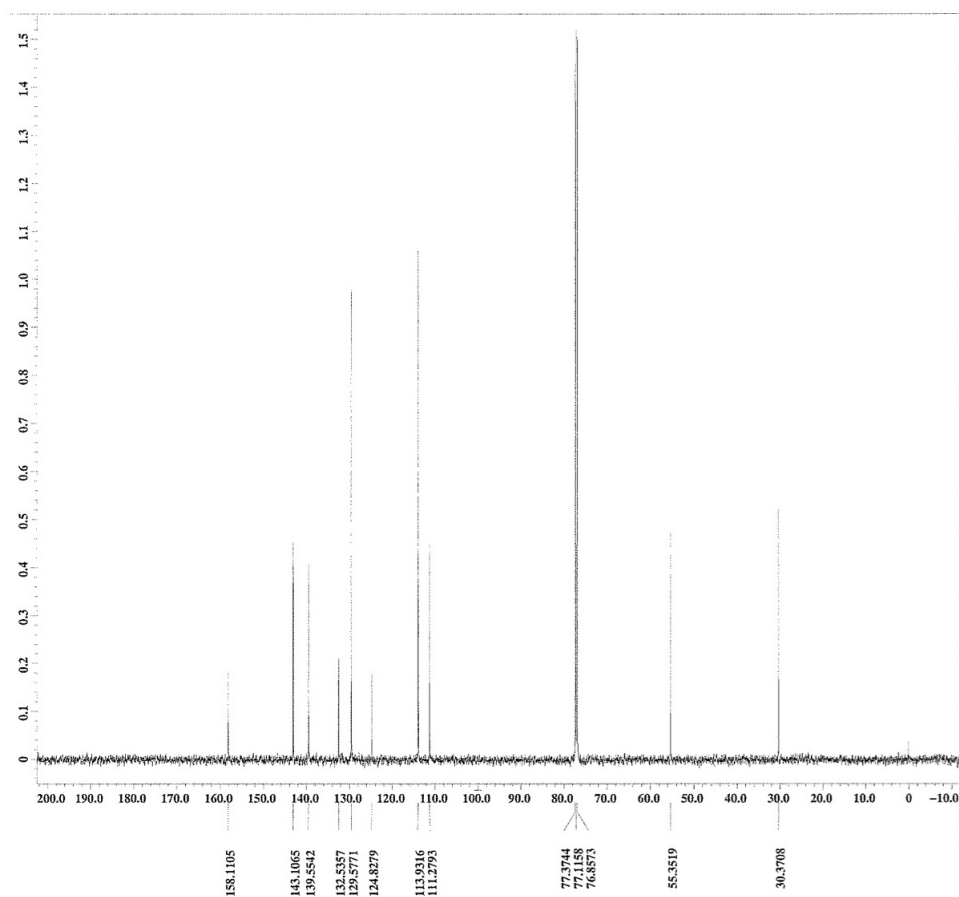
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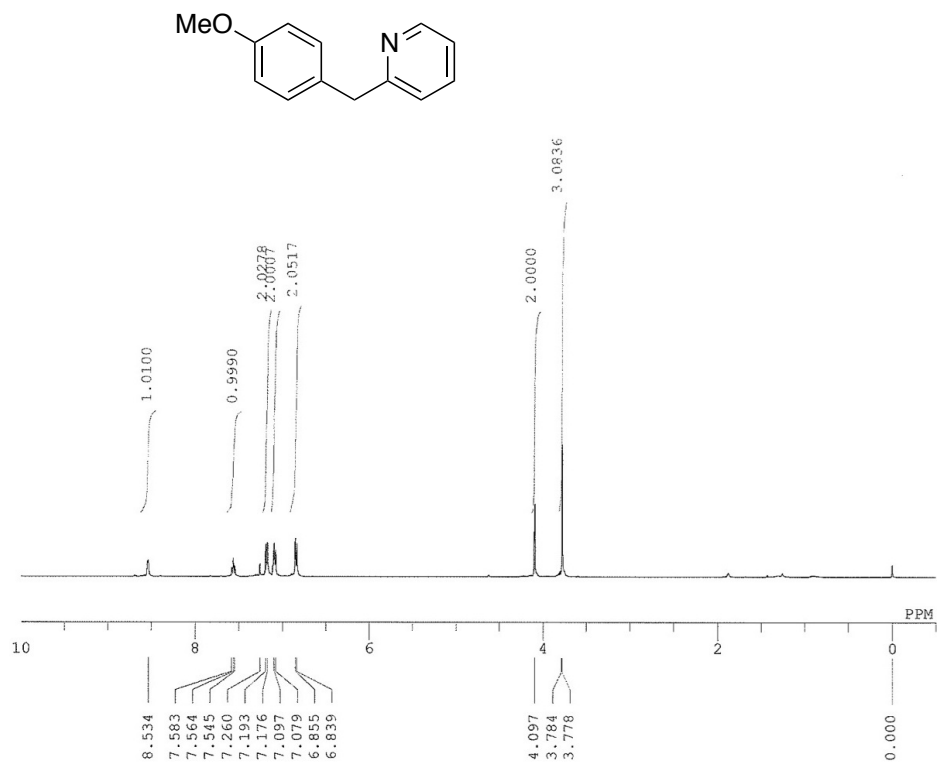
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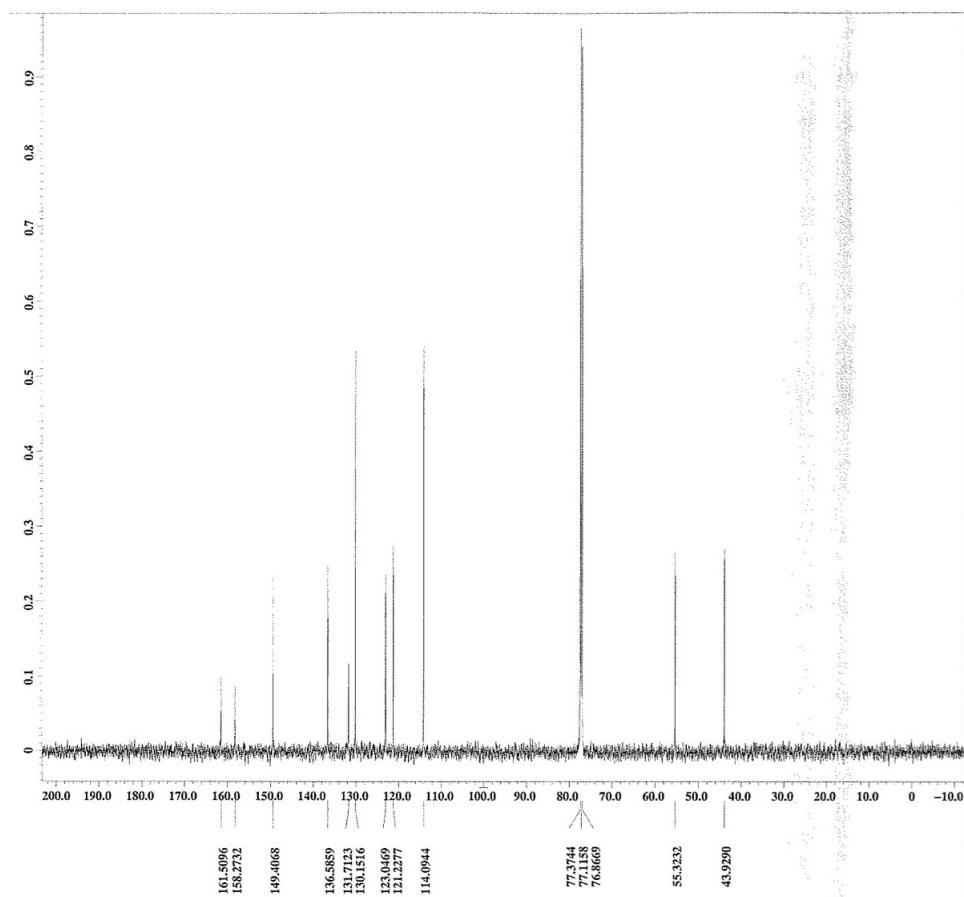
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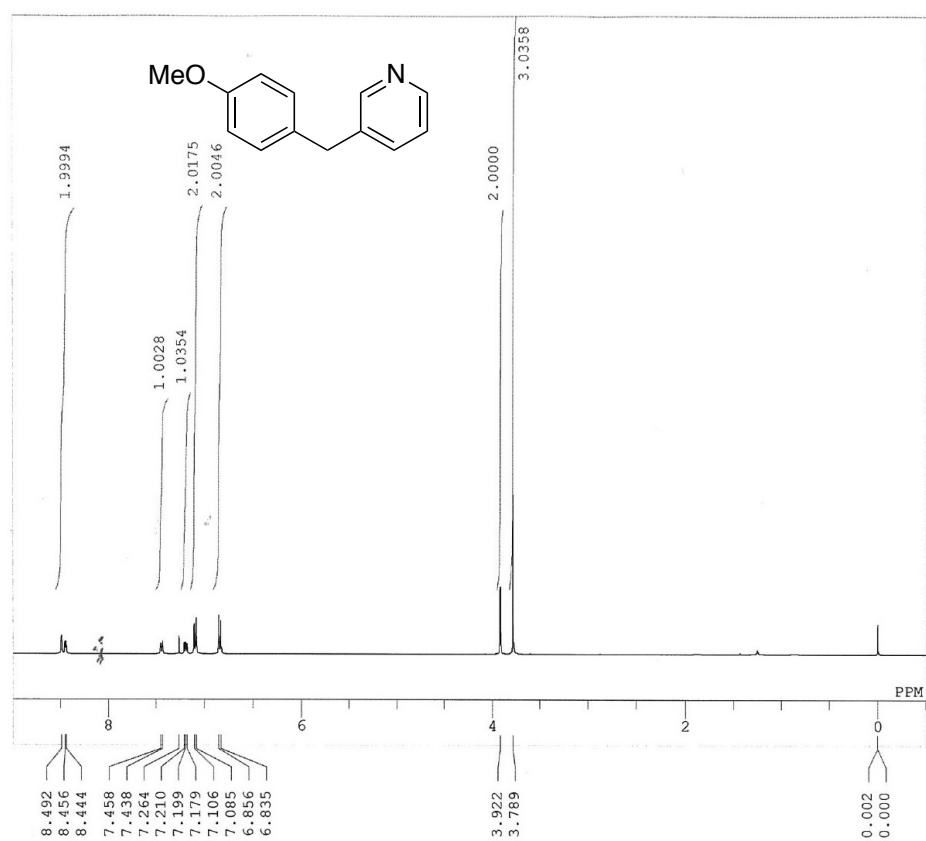
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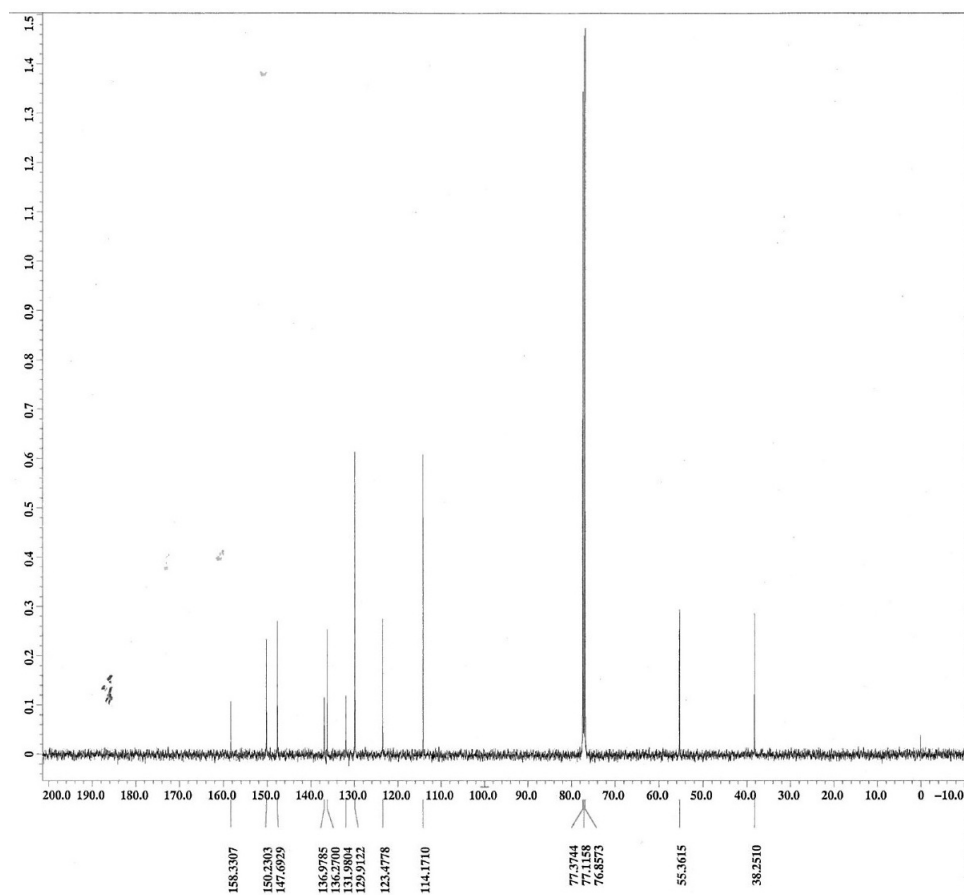
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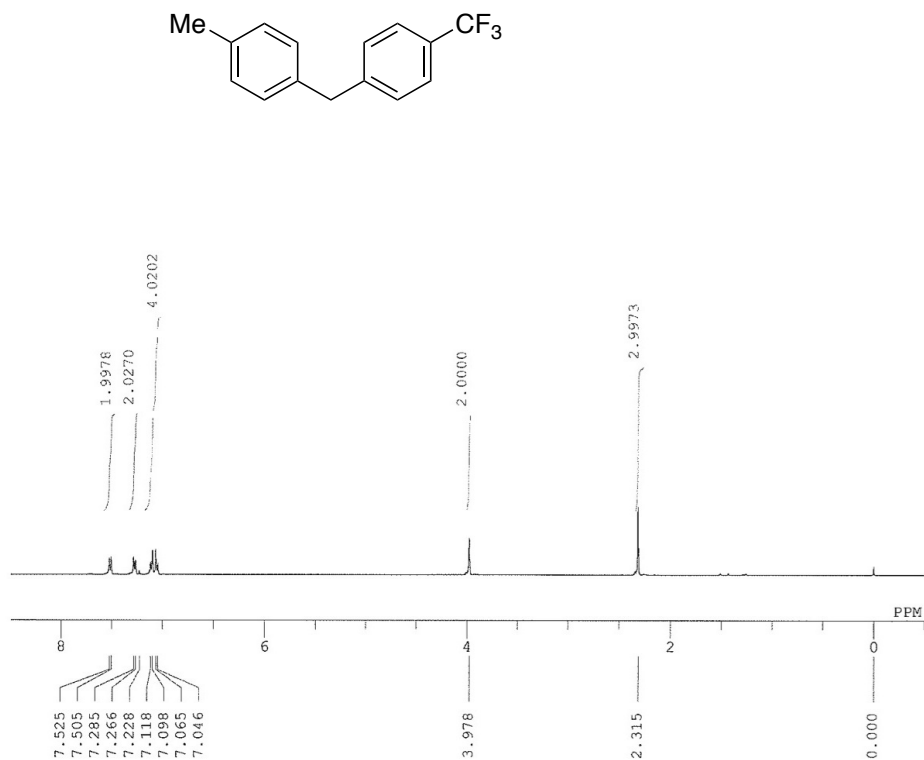
^1H NMR (CDCl_3 , 400 MHz) **5p**



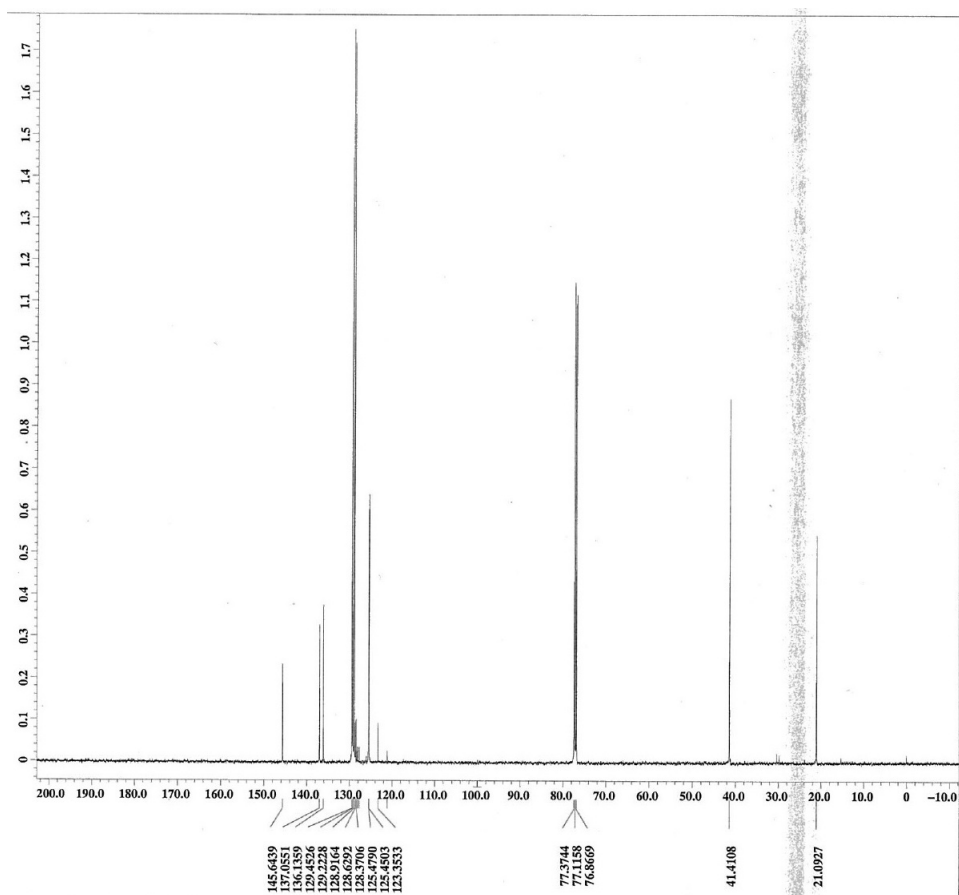
^{13}C NMR (CDCl_3 , 125 MHz) **5p**



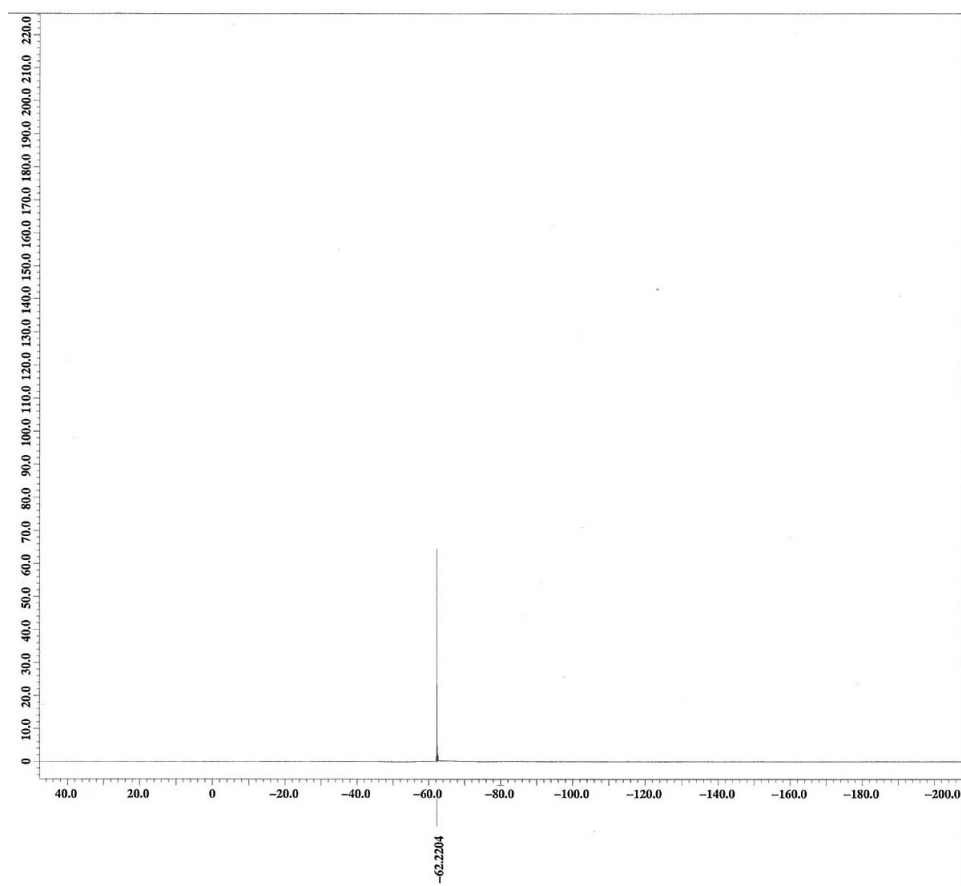
^1H NMR (CDCl_3 , 400 MHz) **5q**



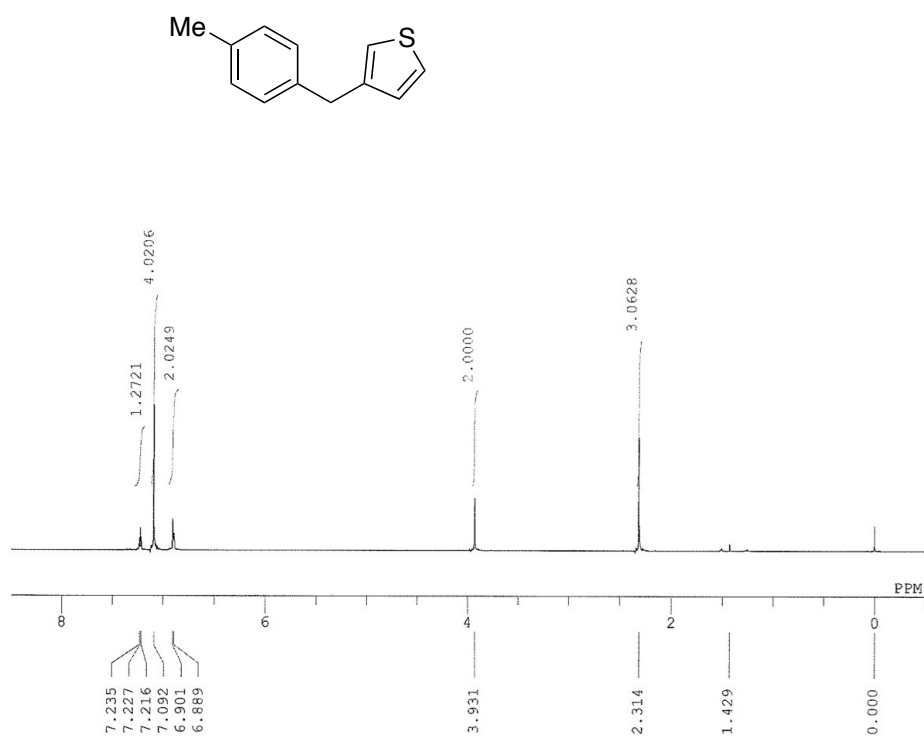
^{13}C NMR (CDCl_3 , 125 MHz) **5q**



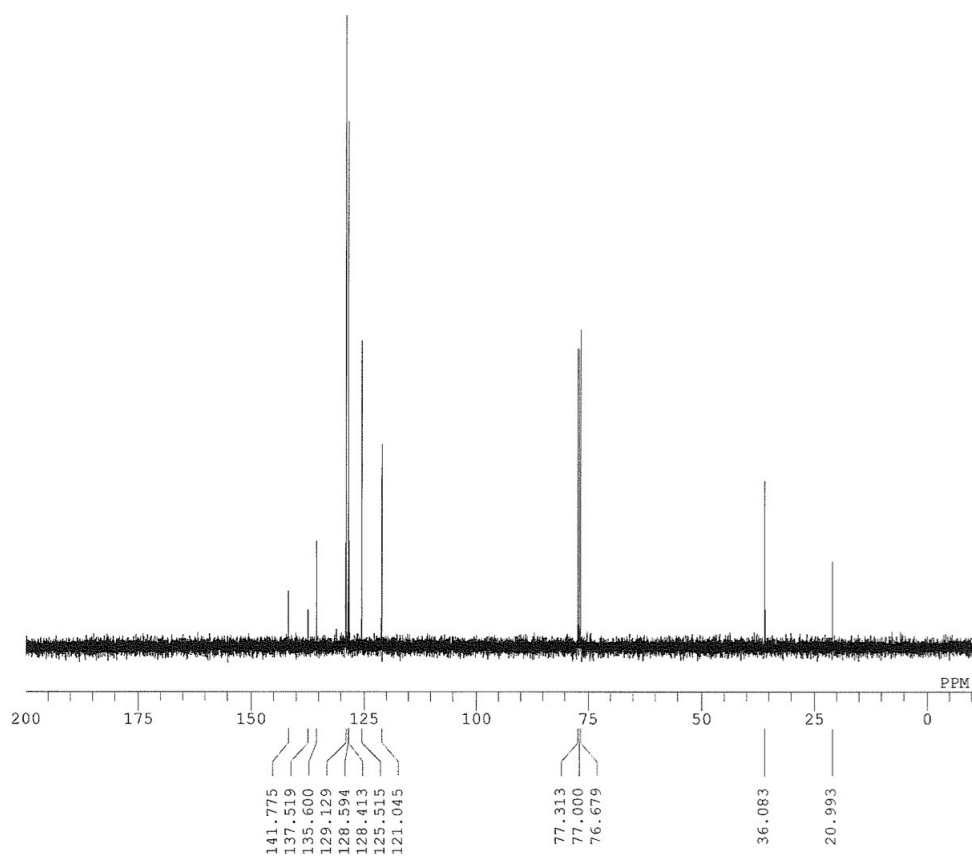
^{19}F NMR (CDCl_3 , 466 MHz) **5q**



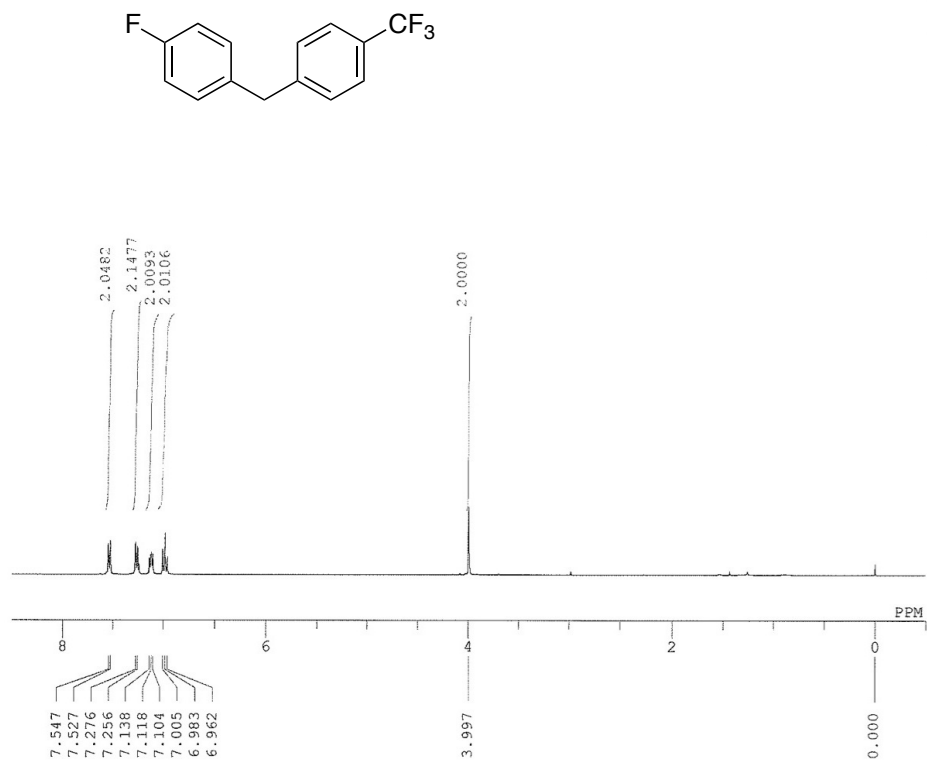
^1H NMR (CDCl_3 , 400 MHz) **5r**



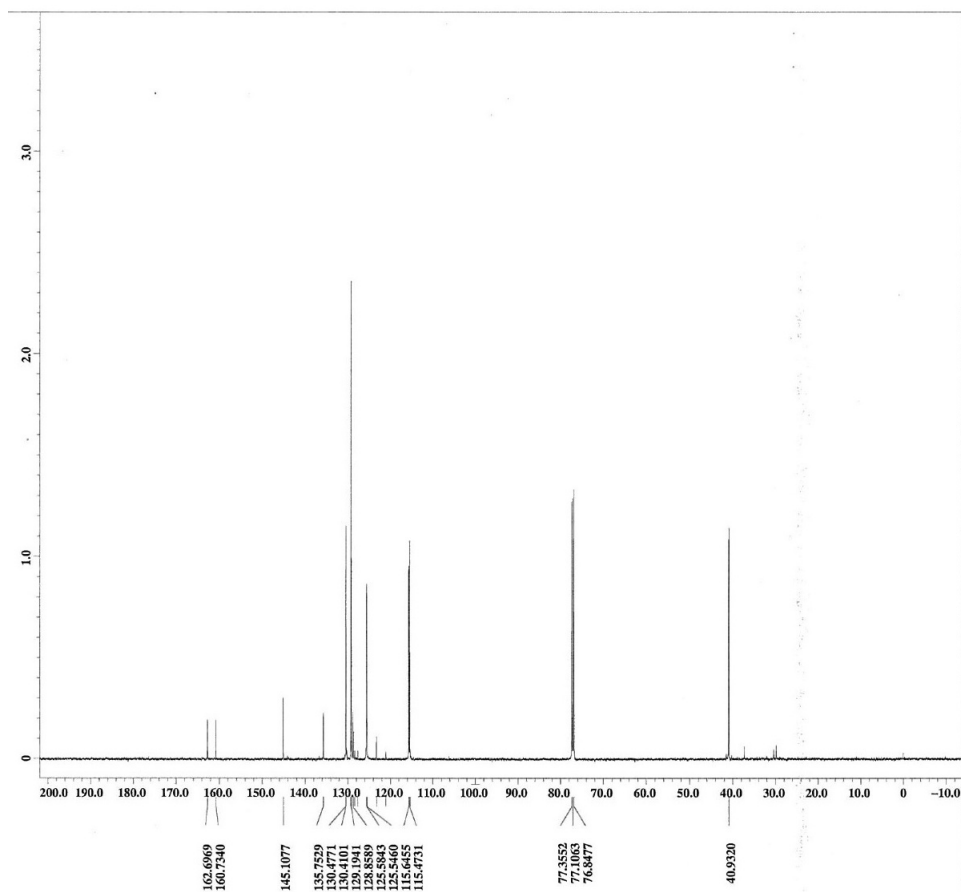
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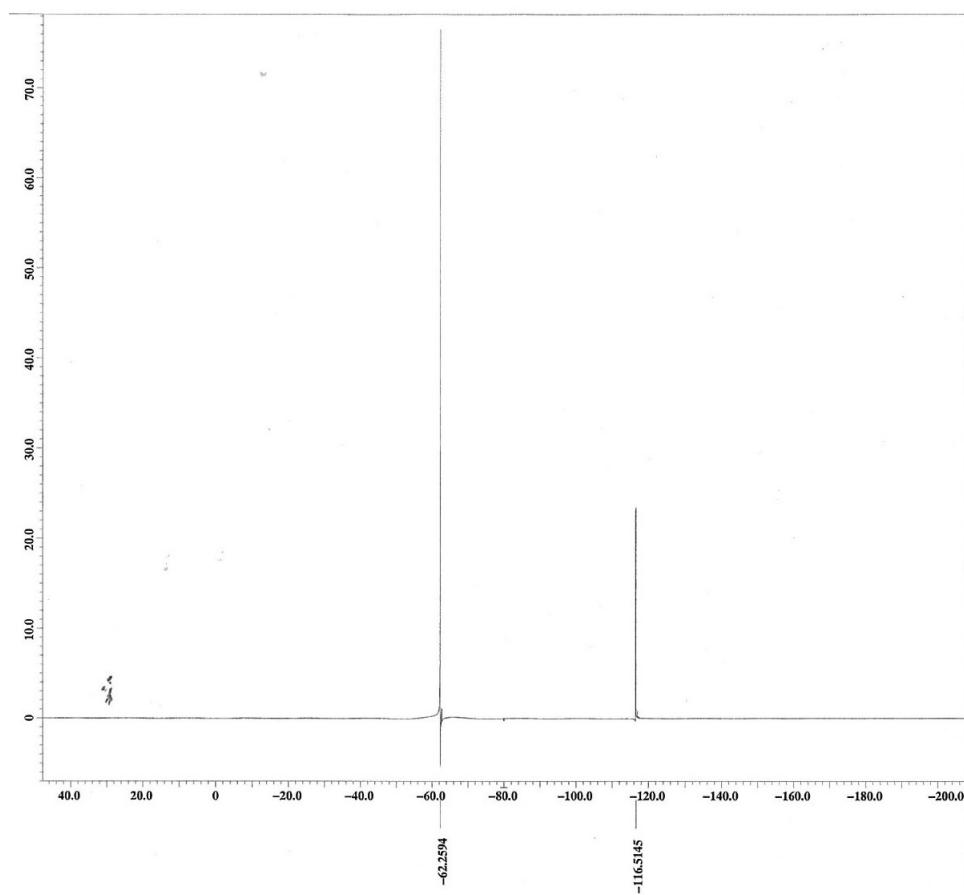
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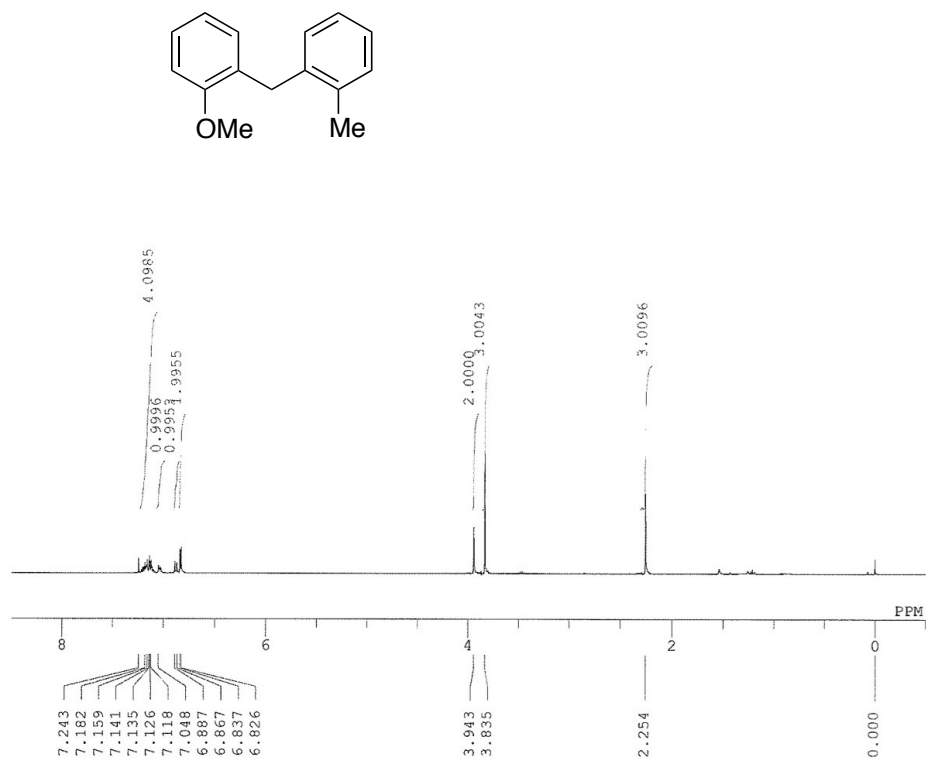
^{13}C NMR (CDCl_3 , 125 MHz) **5s**



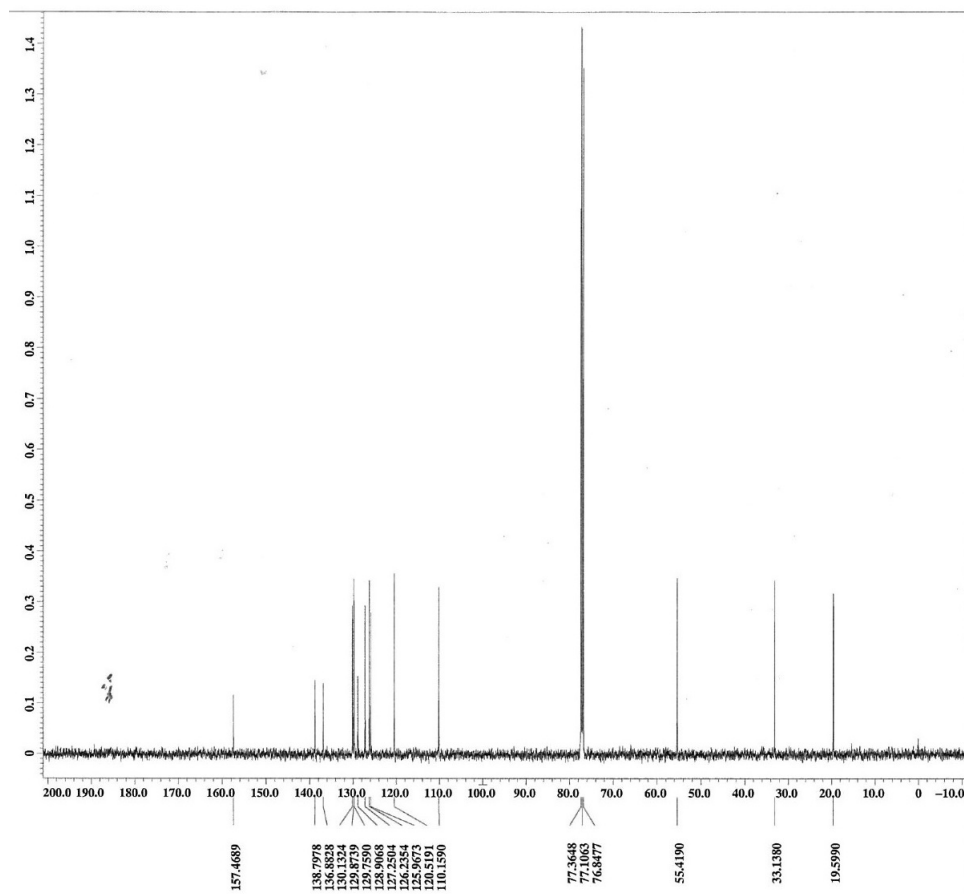
^{19}F NMR (CDCl_3 , 466 MHz) **5s**



^1H NMR (CDCl_3 , 400 MHz) **5t**



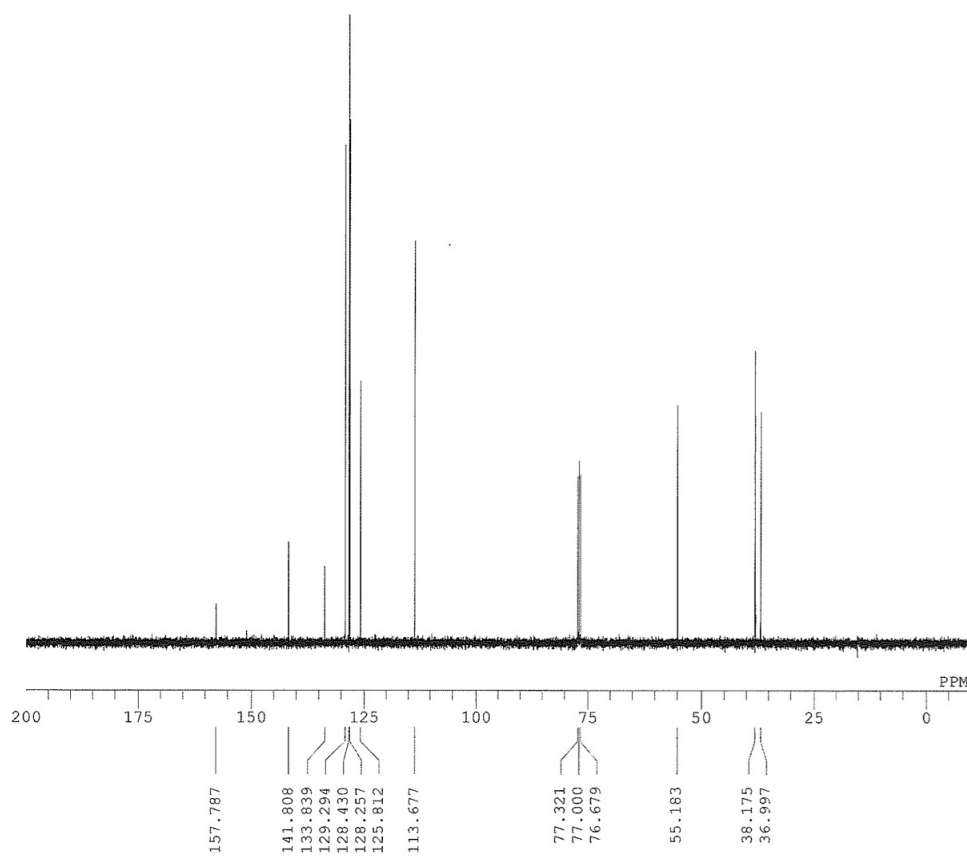
^{13}C NMR (CDCl_3 , 125 MHz) **5t**



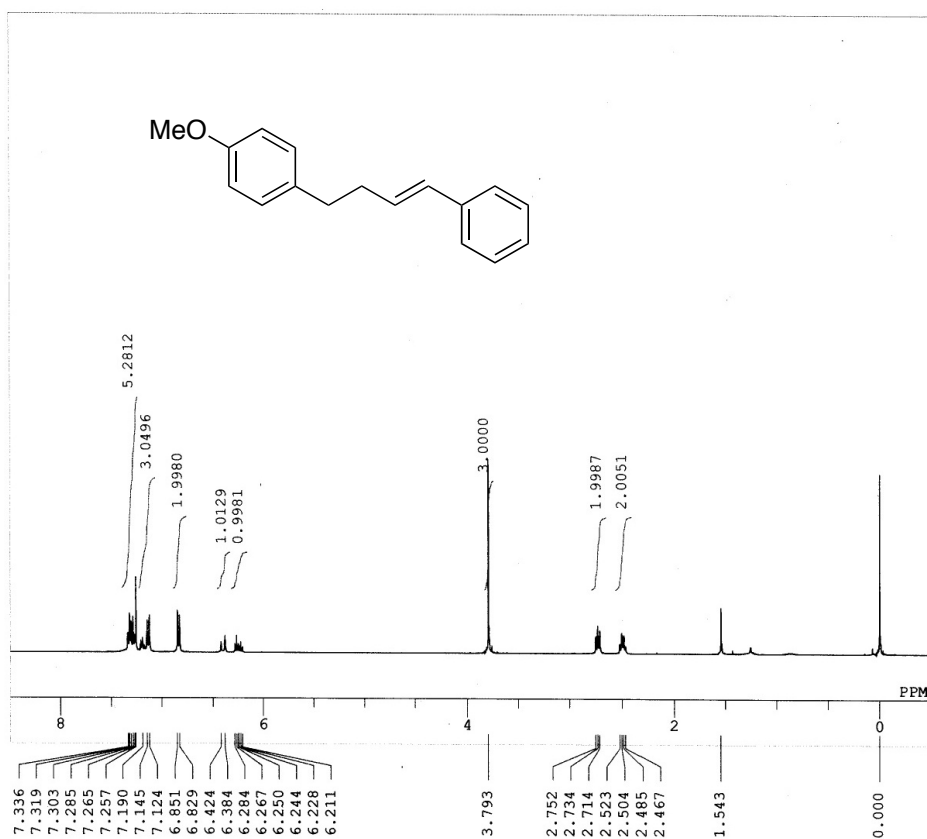
¹H NMR (CDCl₃, 400 MHz) **7a**



¹³C NMR (CDCl₃, 100 MHz) **7a**



^1H NMR (CDCl_3 , 400 MHz) **7b**



^{13}C NMR (CDCl_3 , 100 MHz) **7b**

