

The Intramolecular Allenolate Rauhut-Currier Reaction

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General Experimental

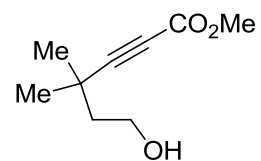
Unless otherwise specified, solvents were degassed by purging with nitrogen and dried over activated alumina. Triethylamine (NEt₃) and benzene (C₆H₆) were distilled from CaH₂. Organolithium reagents were titrated prior to use either with diphenylacetic acid or 1,10-phenanthroline/*iso*-butyl alcohol in the reaction solvent. **3a** and **3c** were commercially available. **3b**,¹ **4a**,² **4c**,² **5**,³ **6b**³ were readily available from known procedures. All reactions were performed in flame or oven-dried glassware under a nitrogen atmosphere.

Solvents used in reactions involving phosphines were degassed either by refluxing and distillation under N₂, purging with N₂ for 30 min, or via three freeze/pump/thaw cycles. In addition, distillation of TMSCN (bulb-to-bulb) and CH₃CN (over CaH) immediately prior to cyclization reactions produced the best results. For all cyclization reactions, no other products were isolated but the formation of immobile highly polar bands on TLC alluded to the formation of oligomeric byproducts.

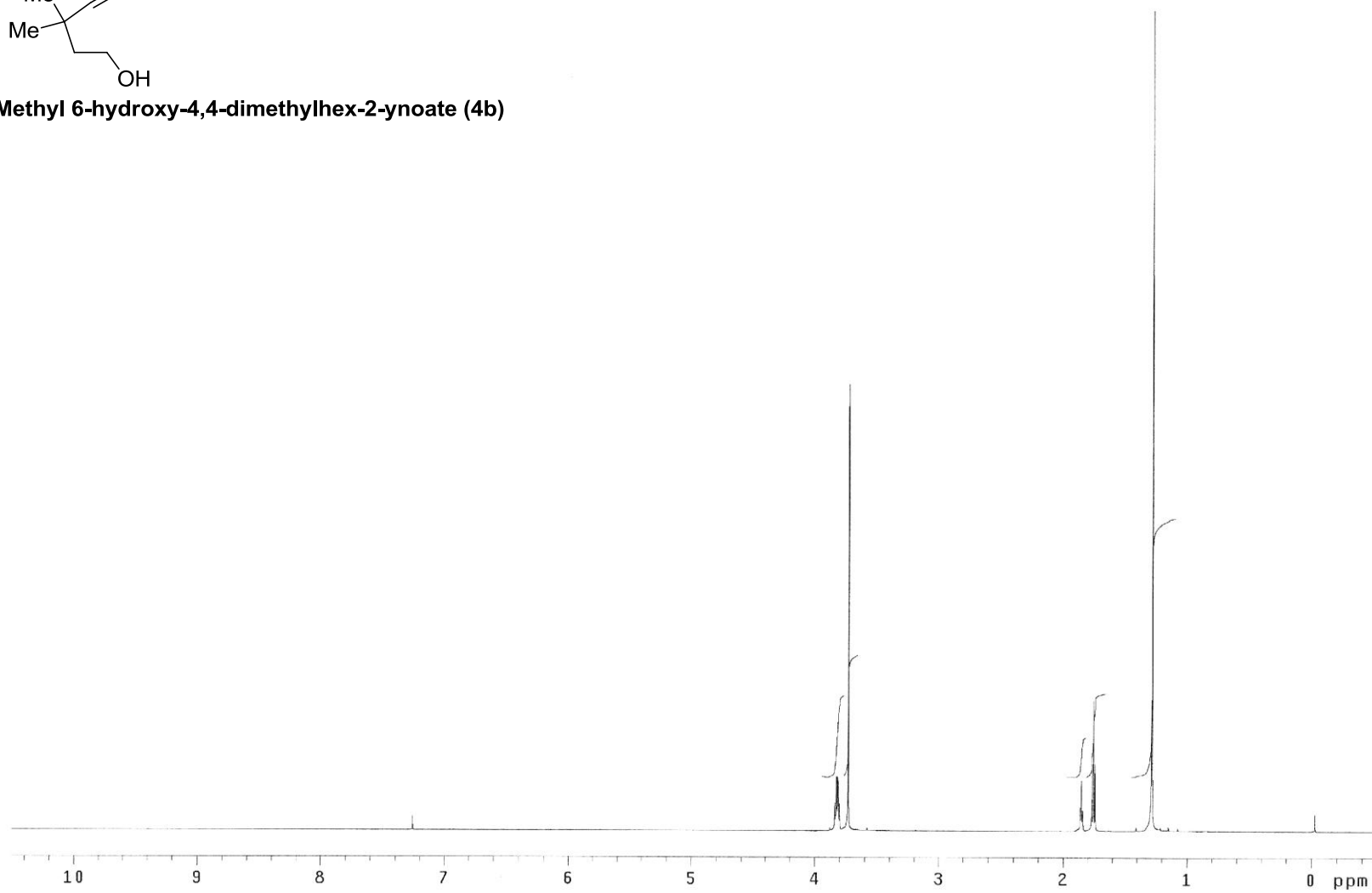
Analytical thin-layer chromatography (tlc) was run on Whatman 0.25 mm K6F silica gel 60Å plates and visualized with the aid of UV light, iodine vapor, KMnO₄ or PMA stain. Manual flash chromatography was run using Whatman Silica Gel; Purasil 60 Å (230-400 mesh) or in automation using Silica RediSepR_f High Performance Gold disposable columns and a hexanes/ethyl acetate eluent. Mass spectra were obtained using positive electrospray ionization and FTICR mass analyzer.

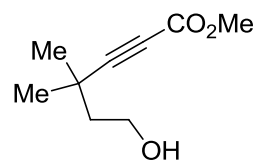
Additional References for SI

1. Rank, E.; Bruckner, R. *Eur. J. Org. Chem.* **1998**, 1045.
2. Marino, J. P.; Nguyen, H. N. *J. Org. Chem.* **2002**, 67, 6291.
3. Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, 52, 1483.

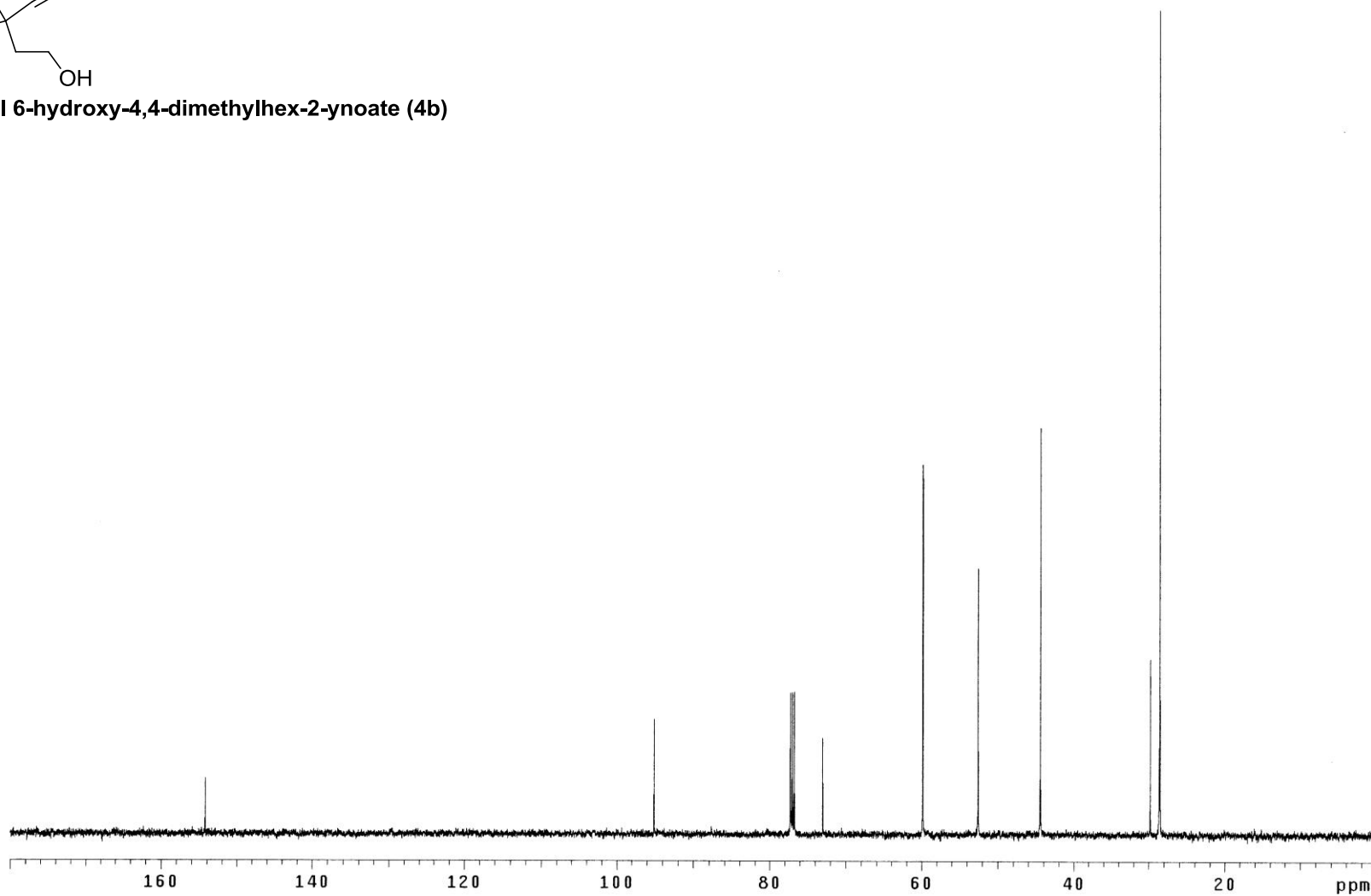


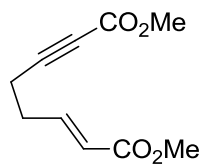
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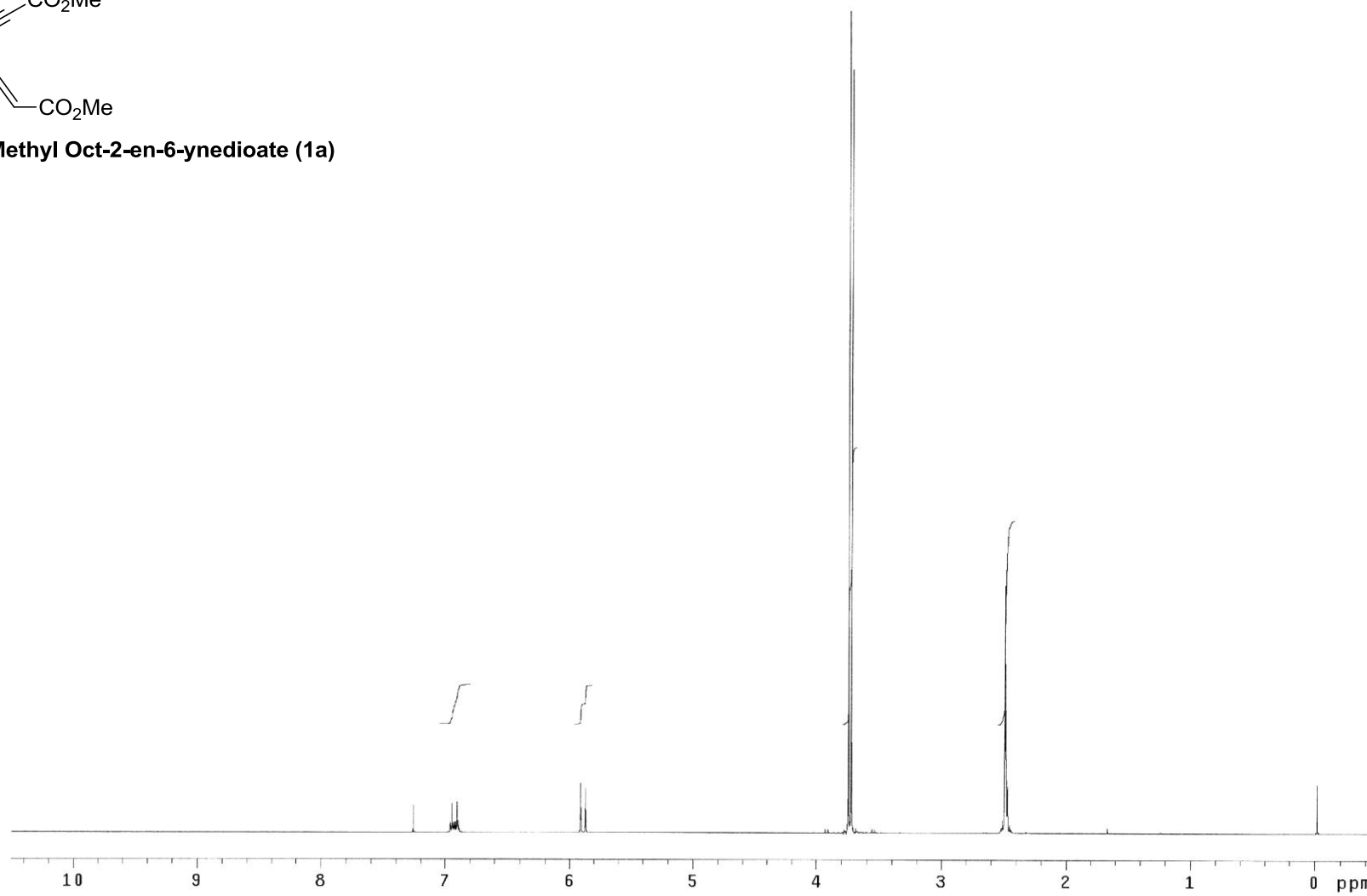


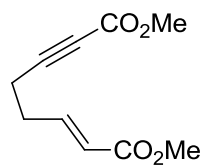
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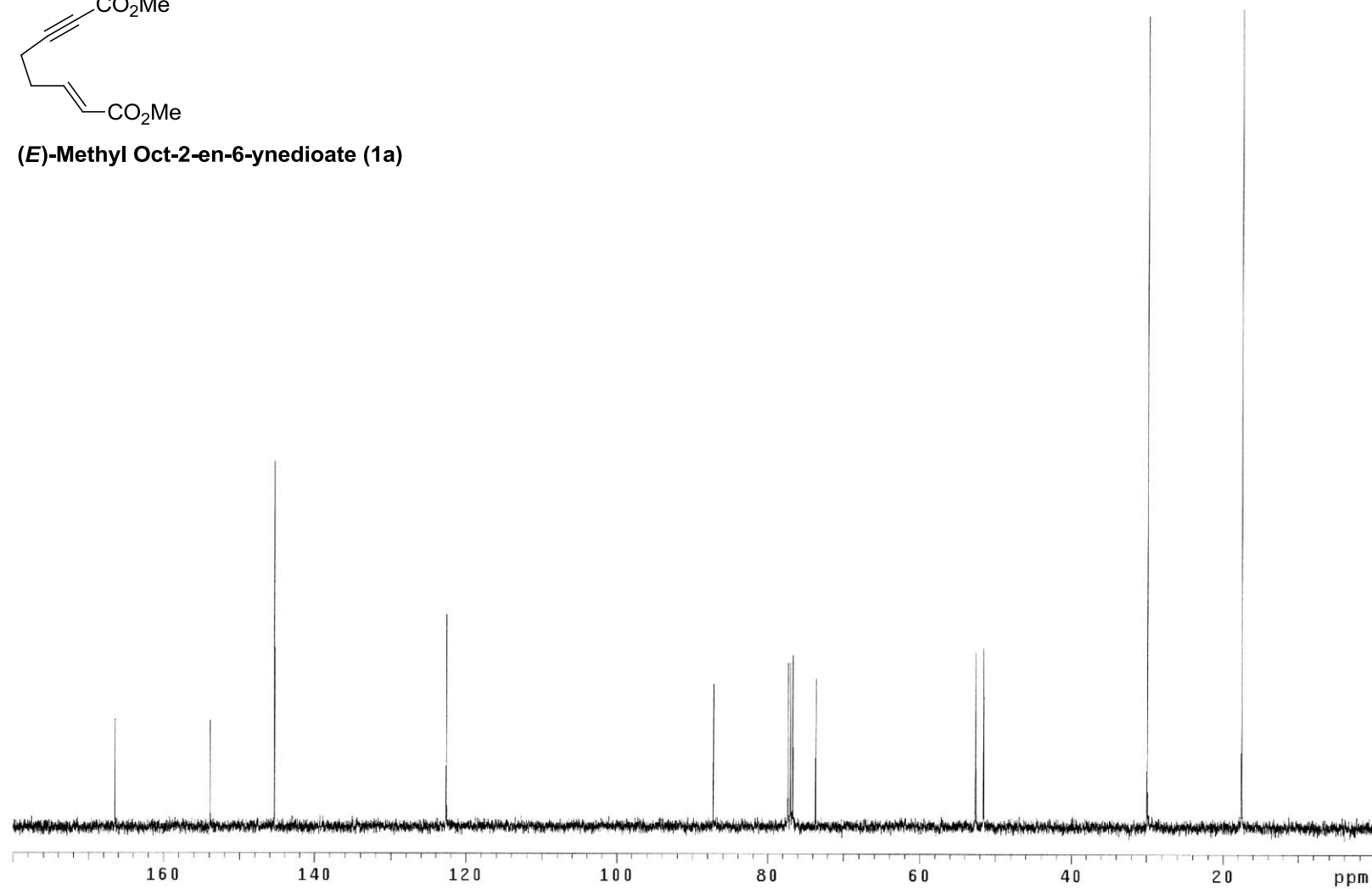


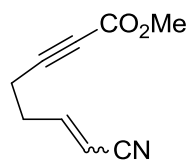
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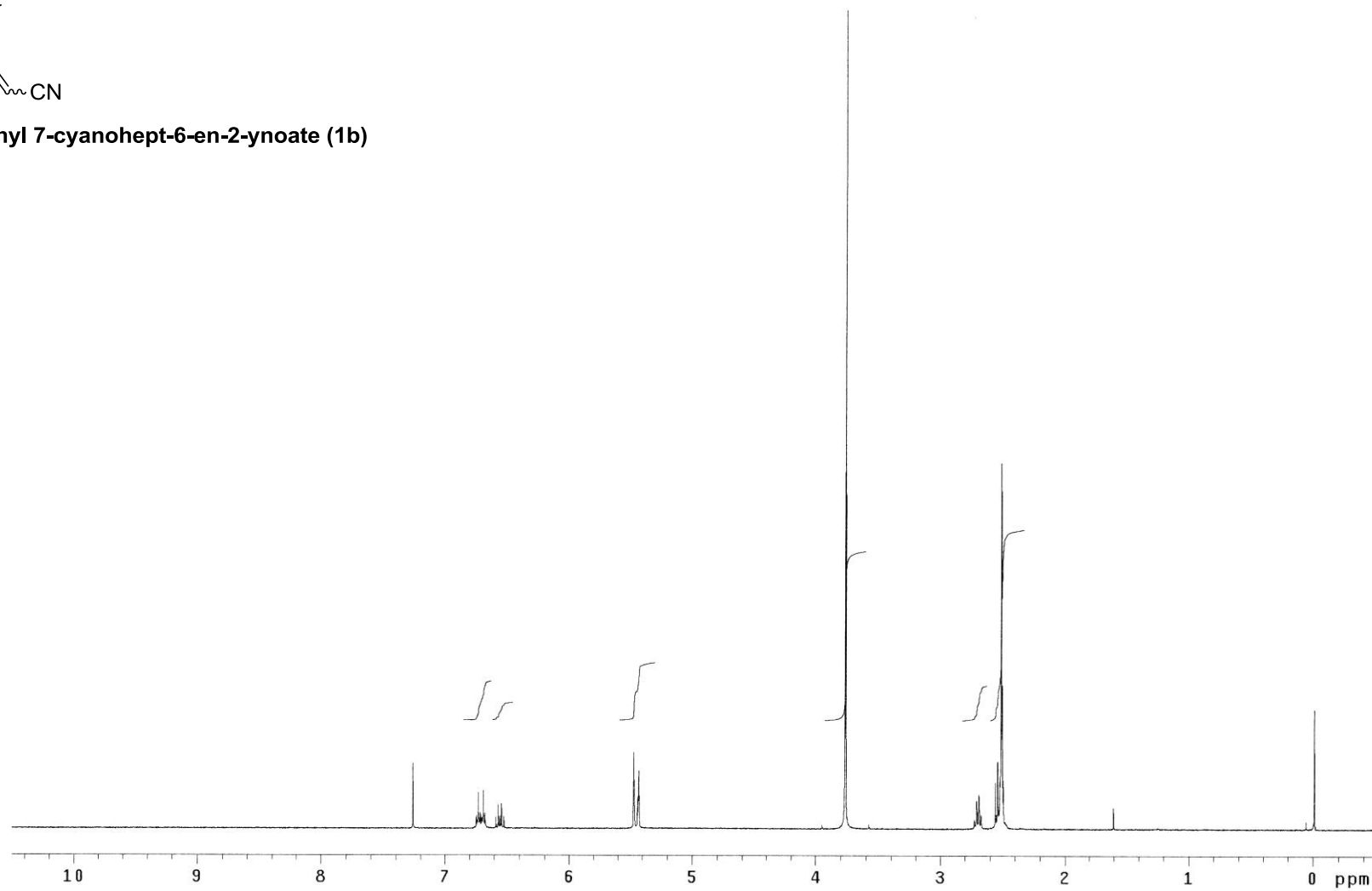


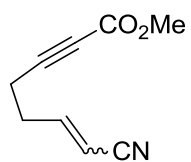
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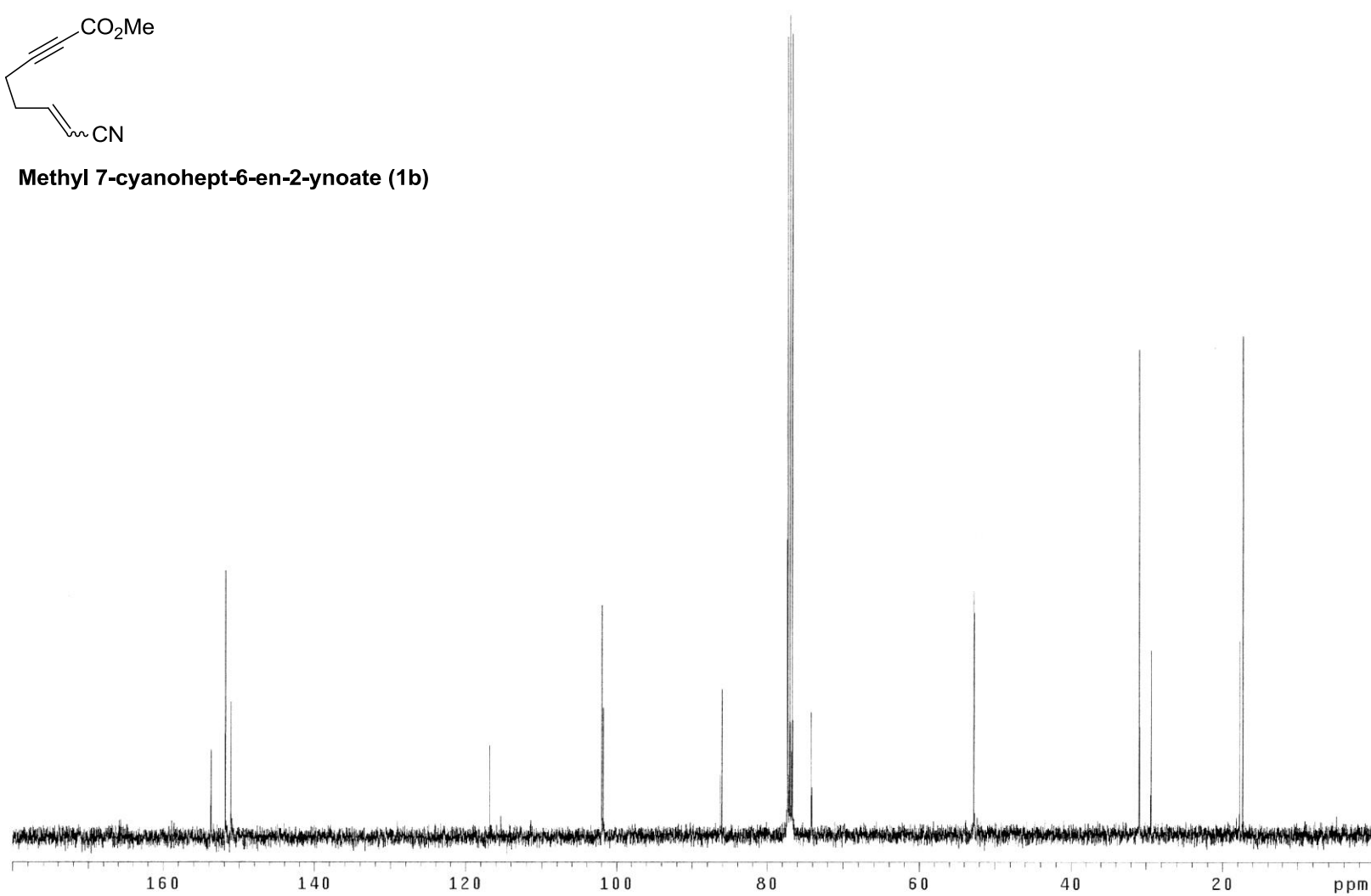


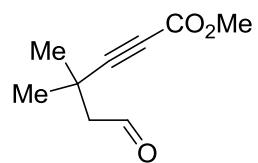
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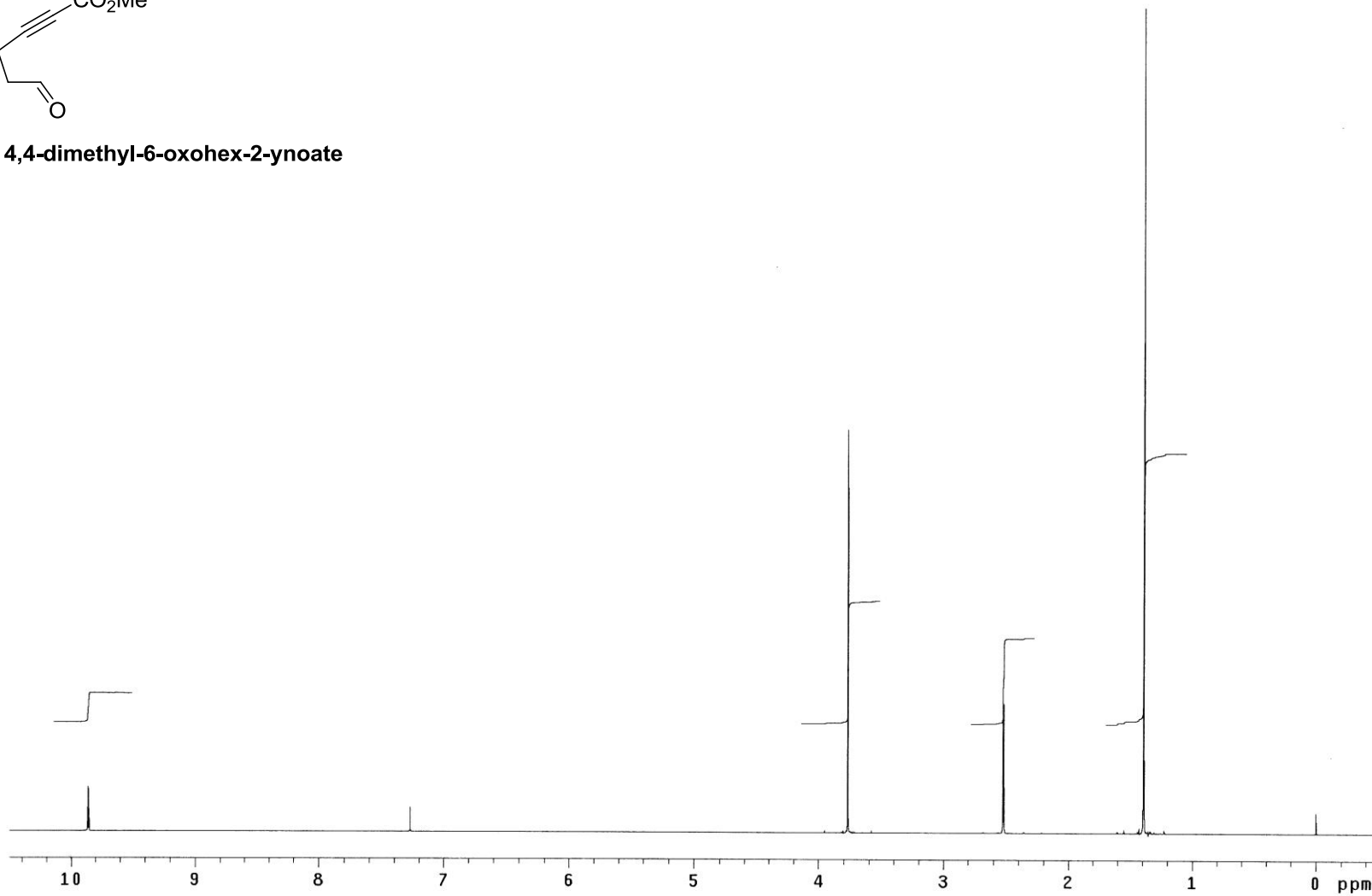


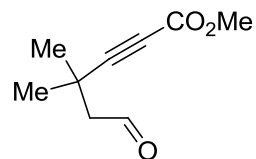
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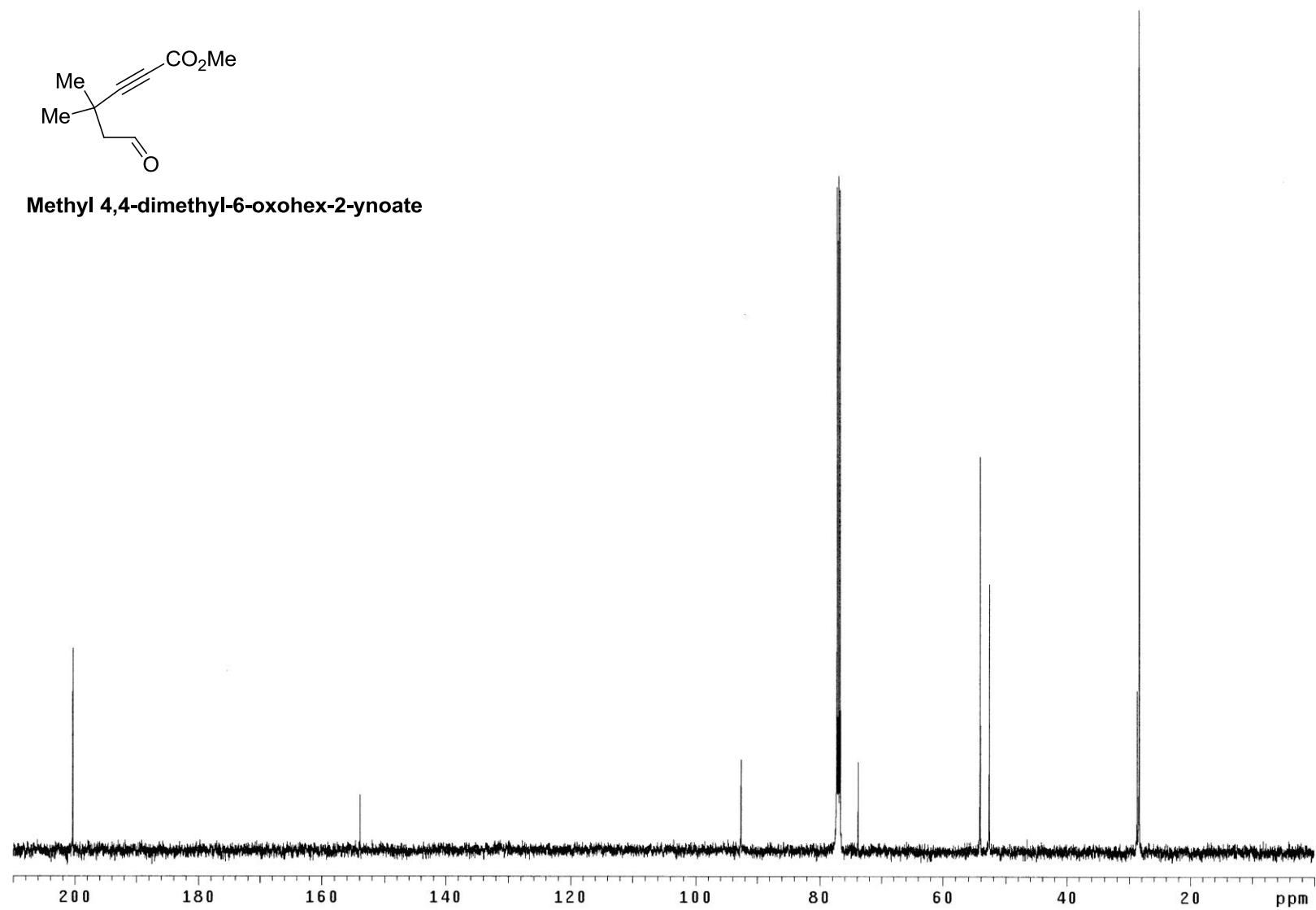


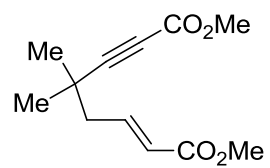
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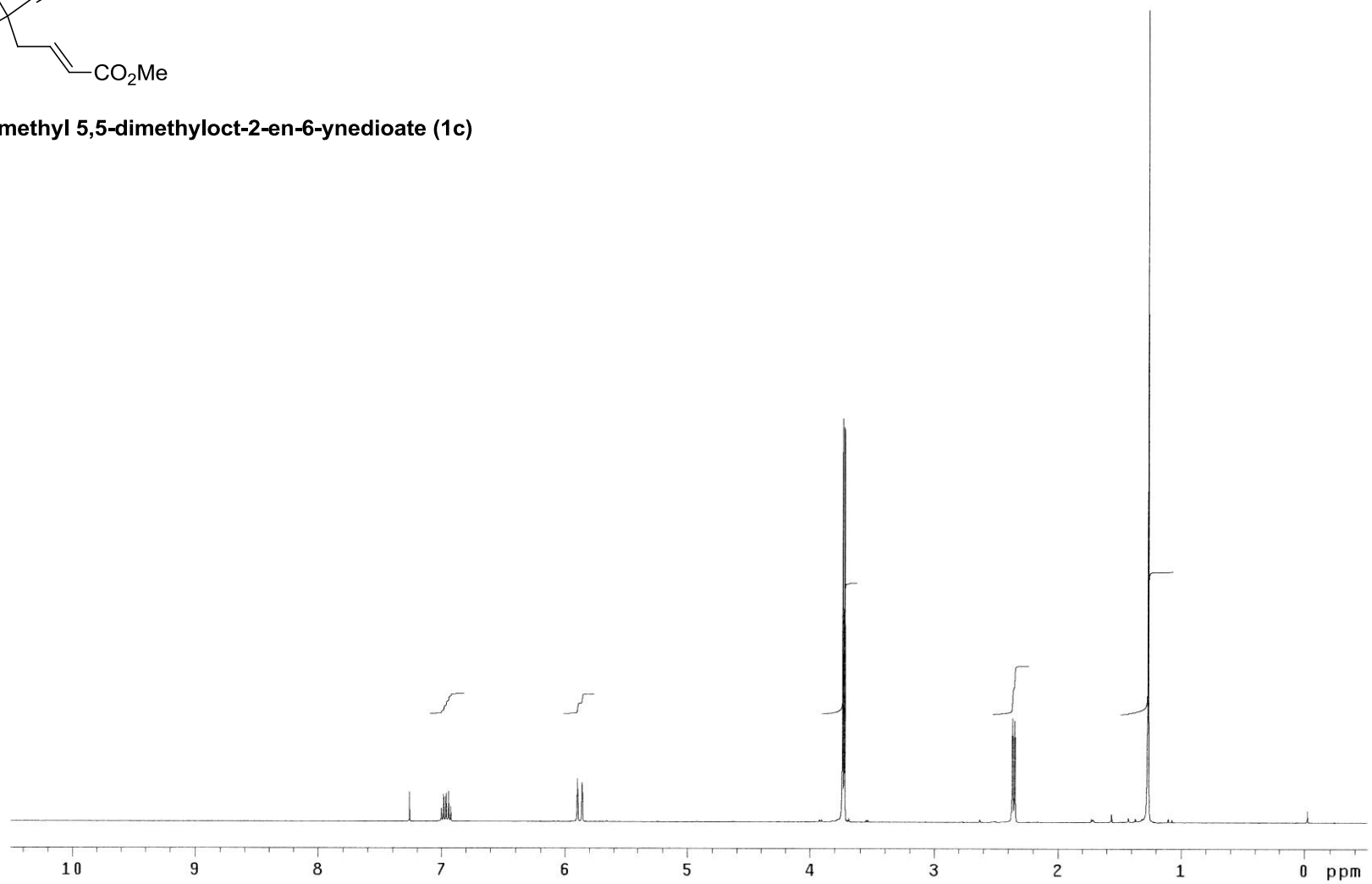


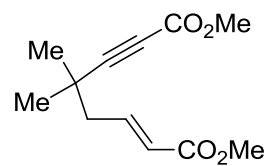
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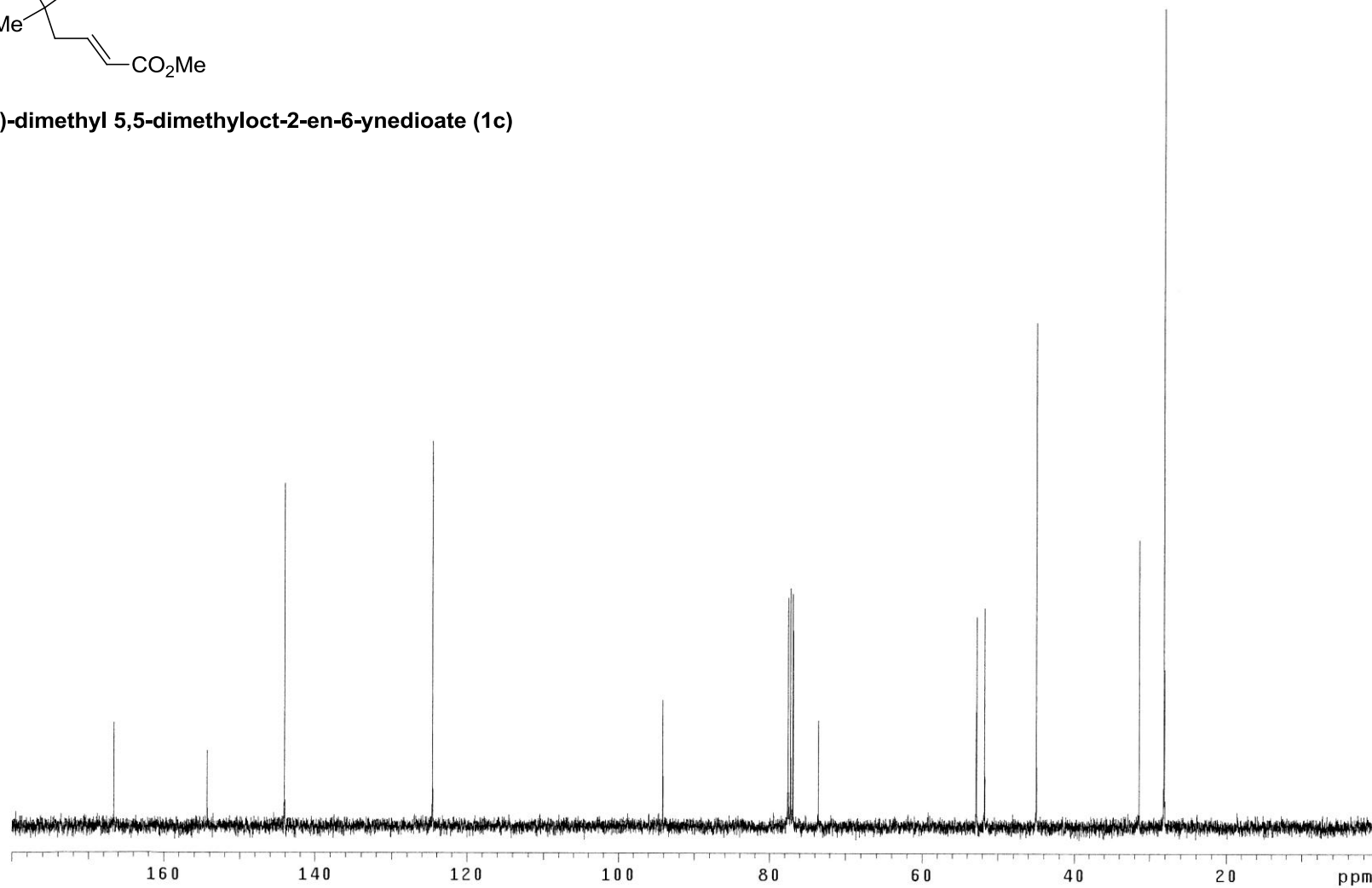


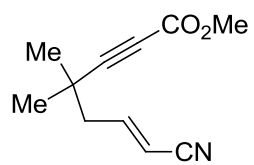
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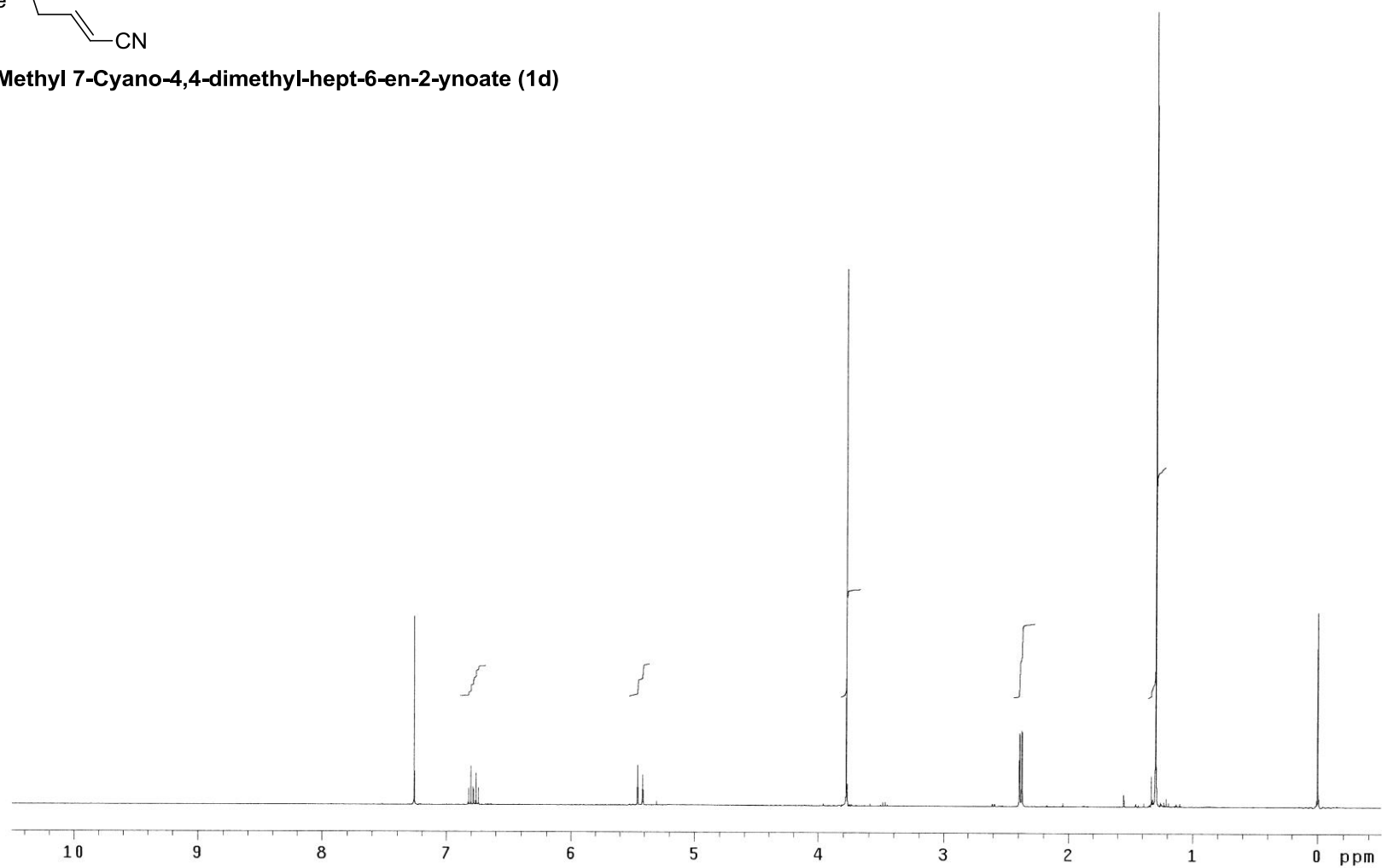


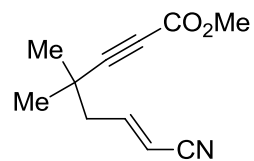
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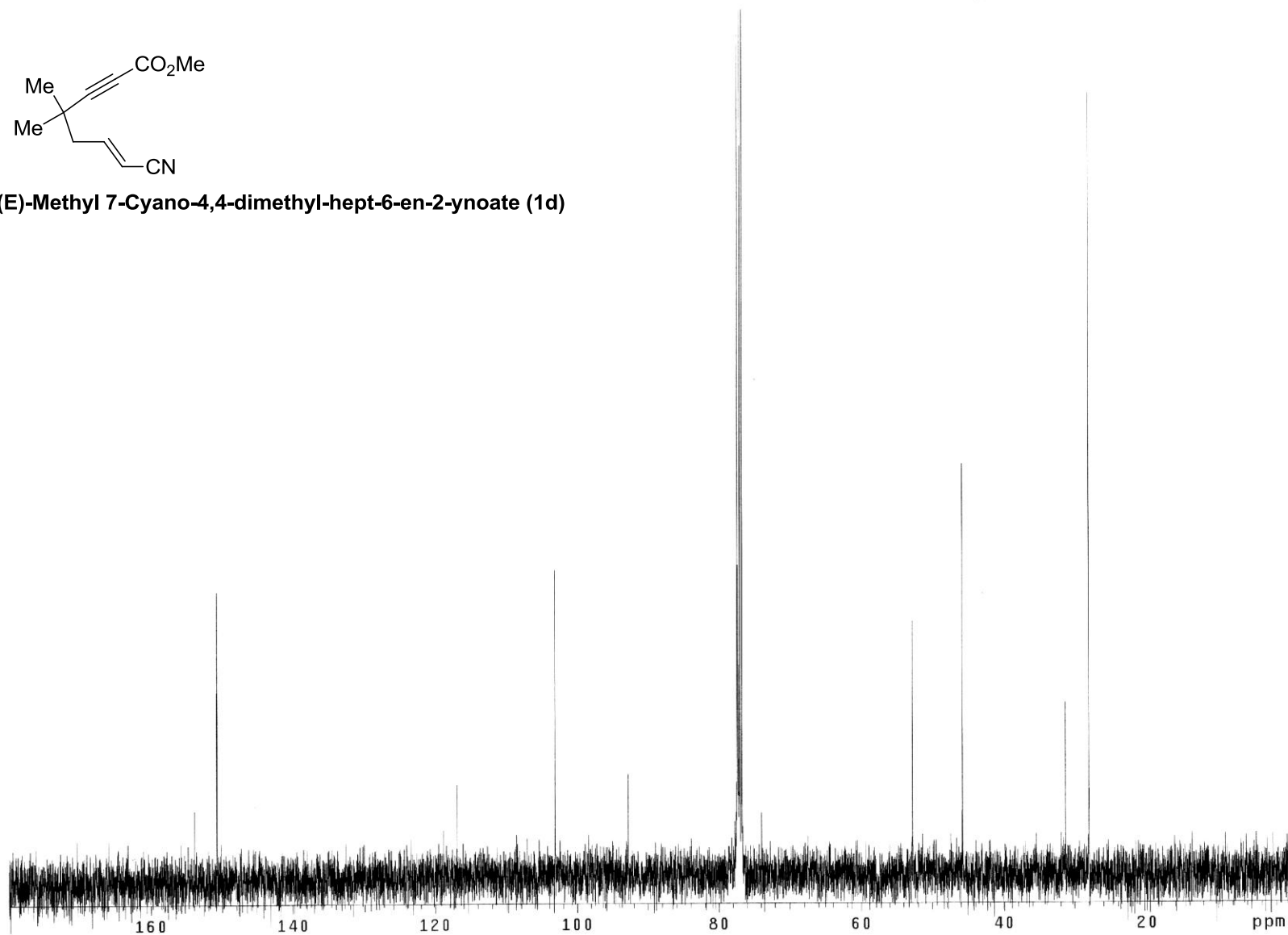


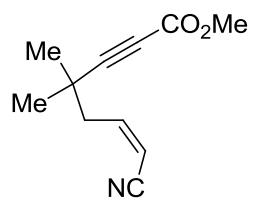
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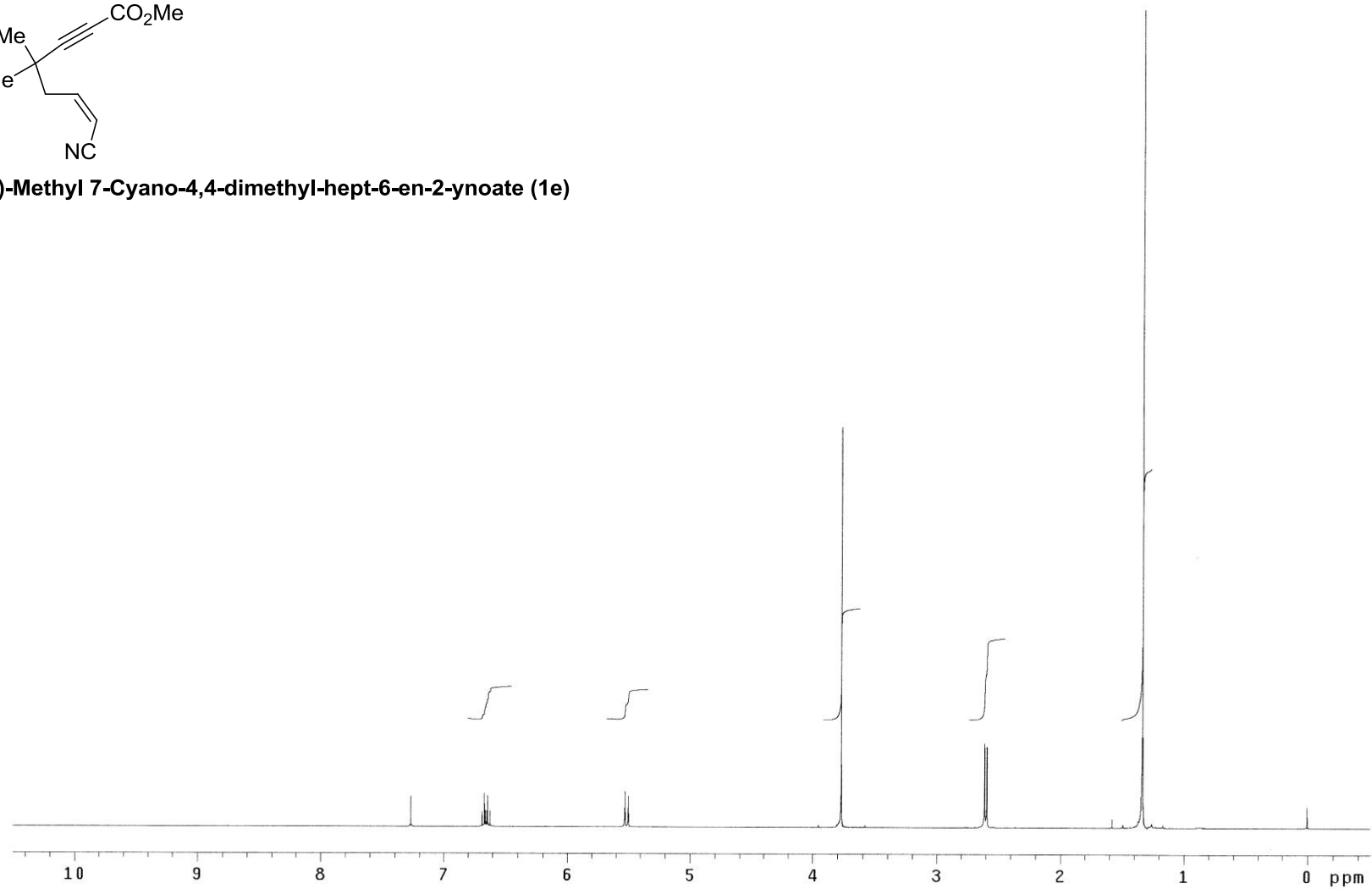


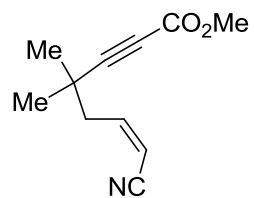
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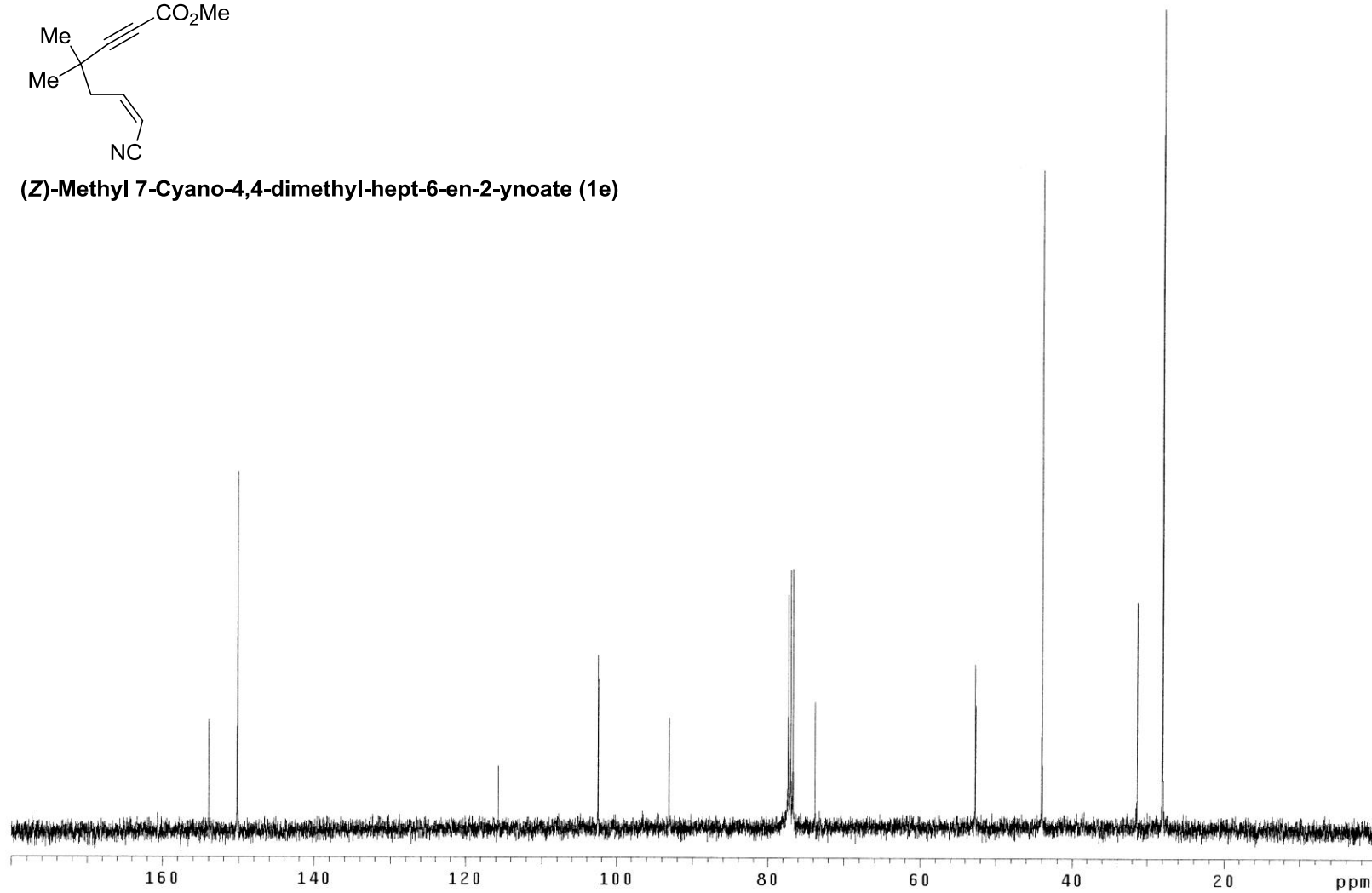


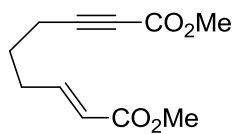
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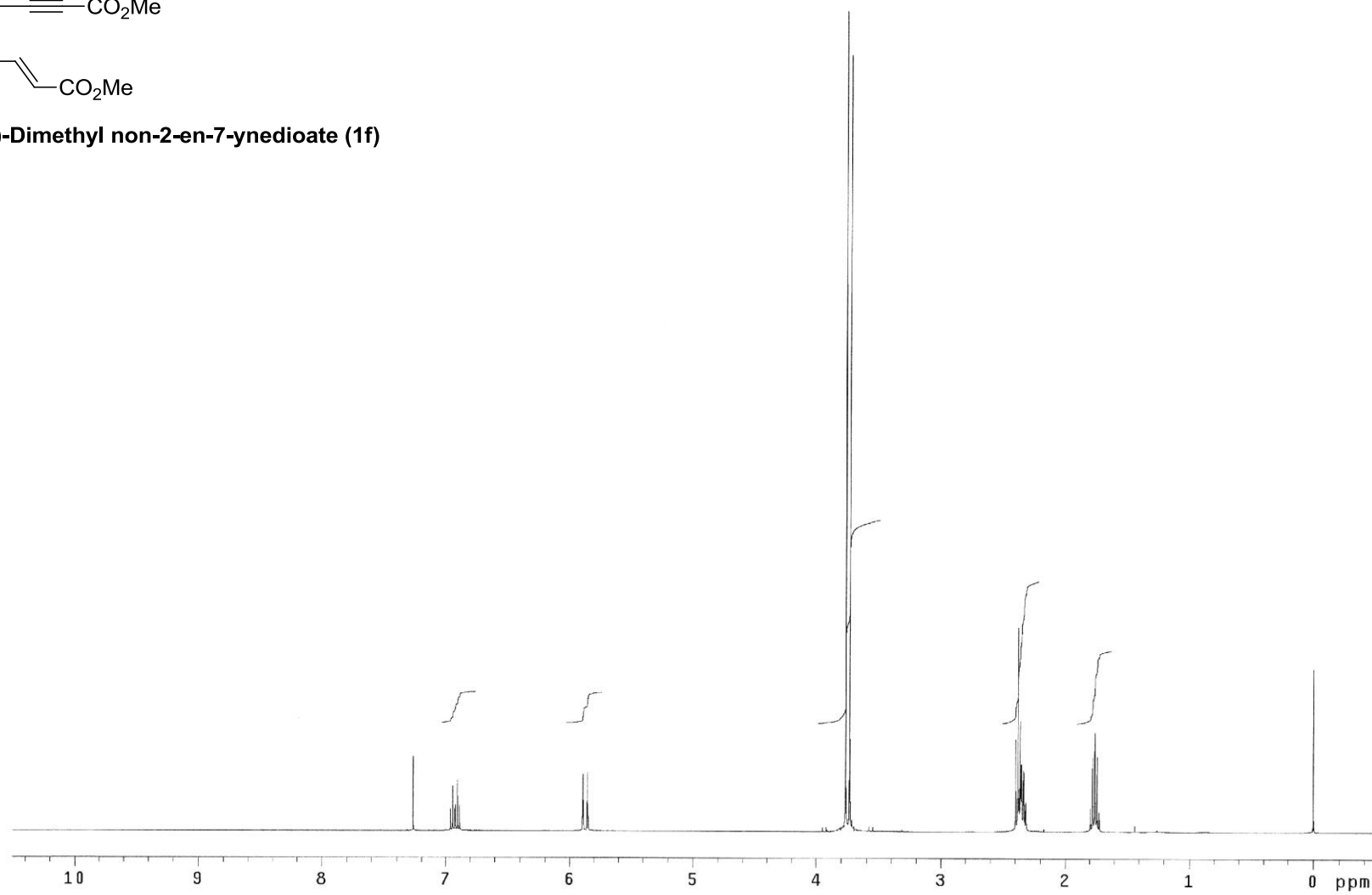


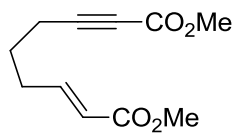
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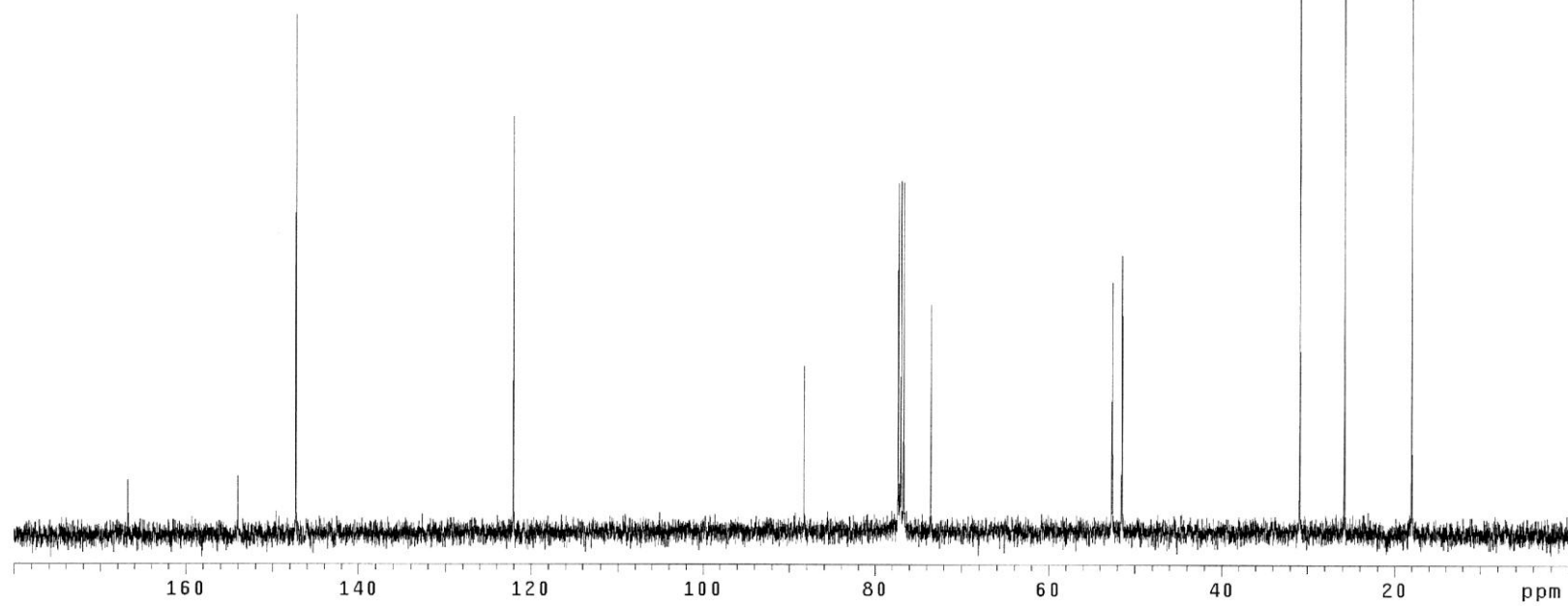


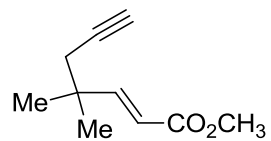
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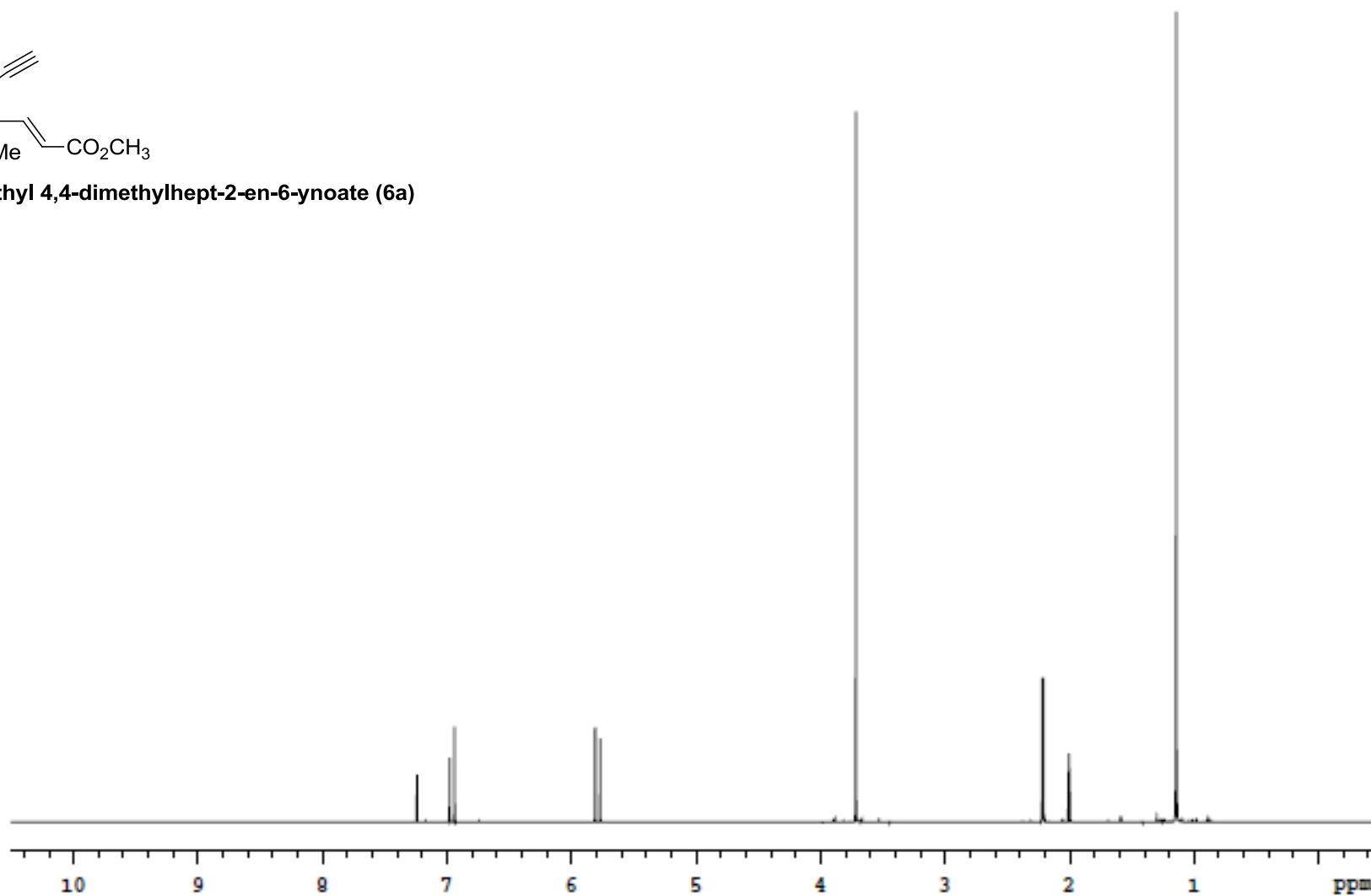


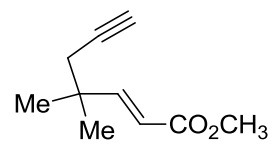
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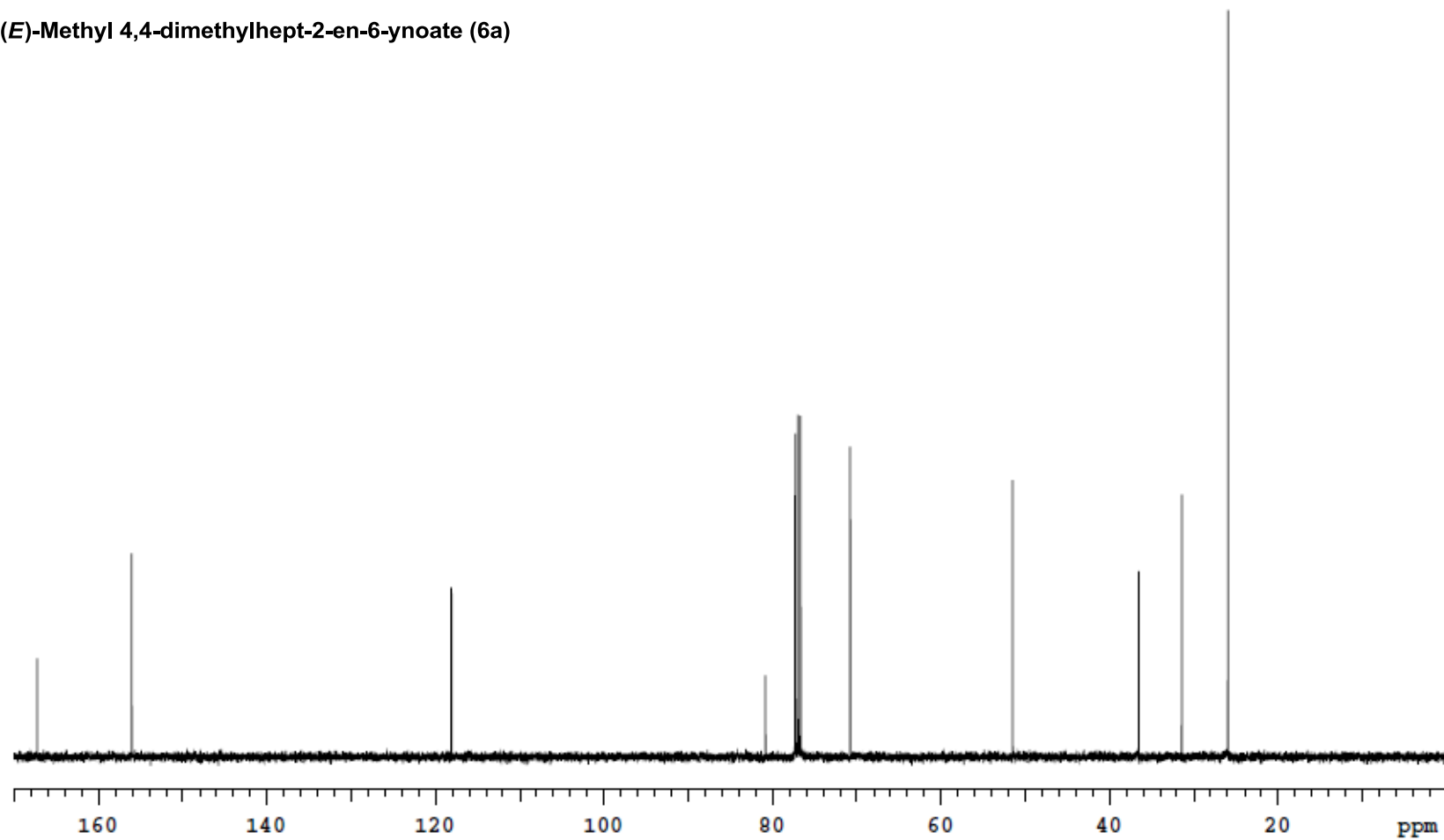


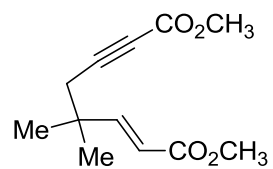
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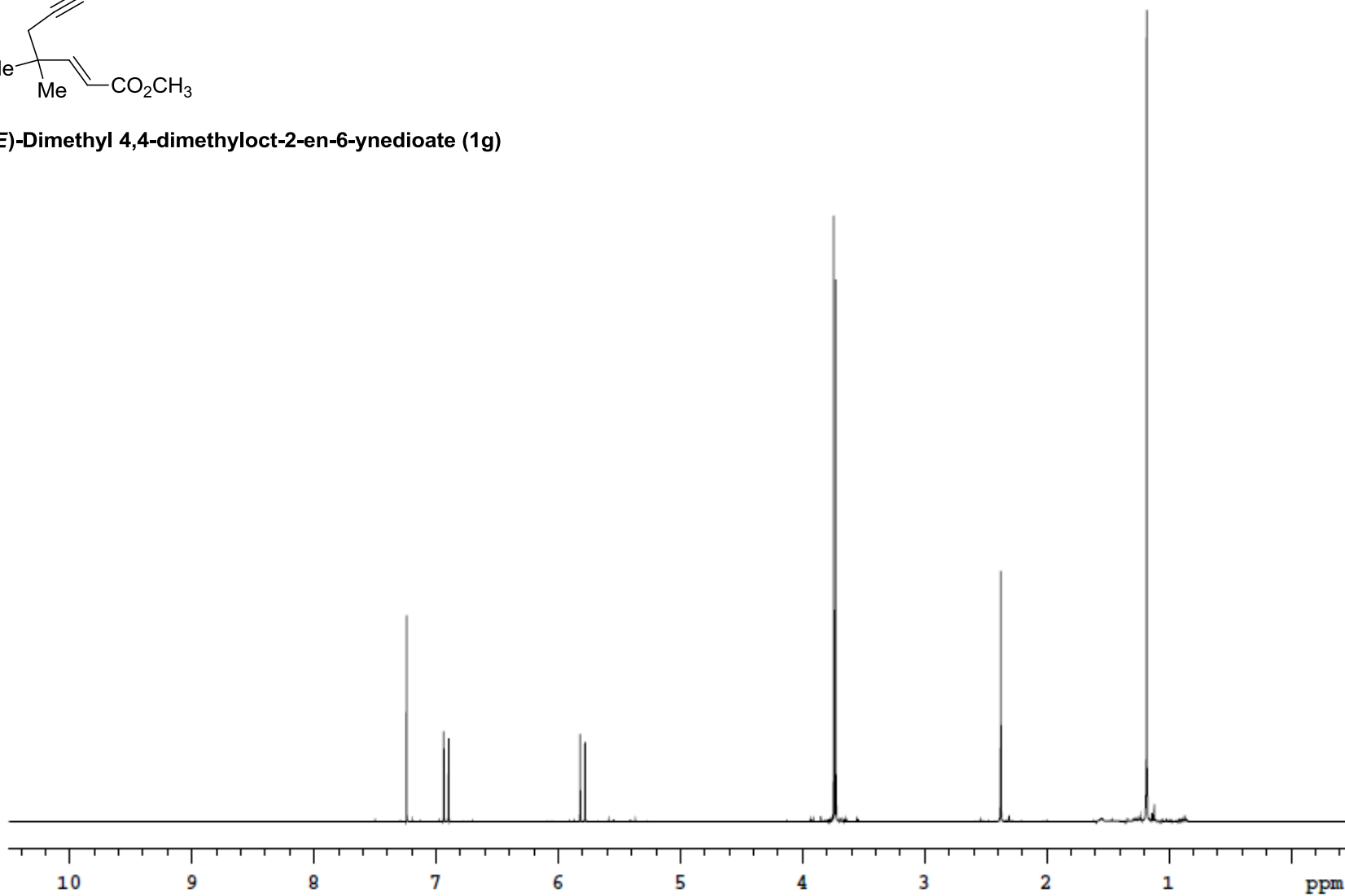


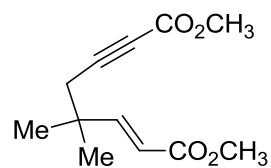
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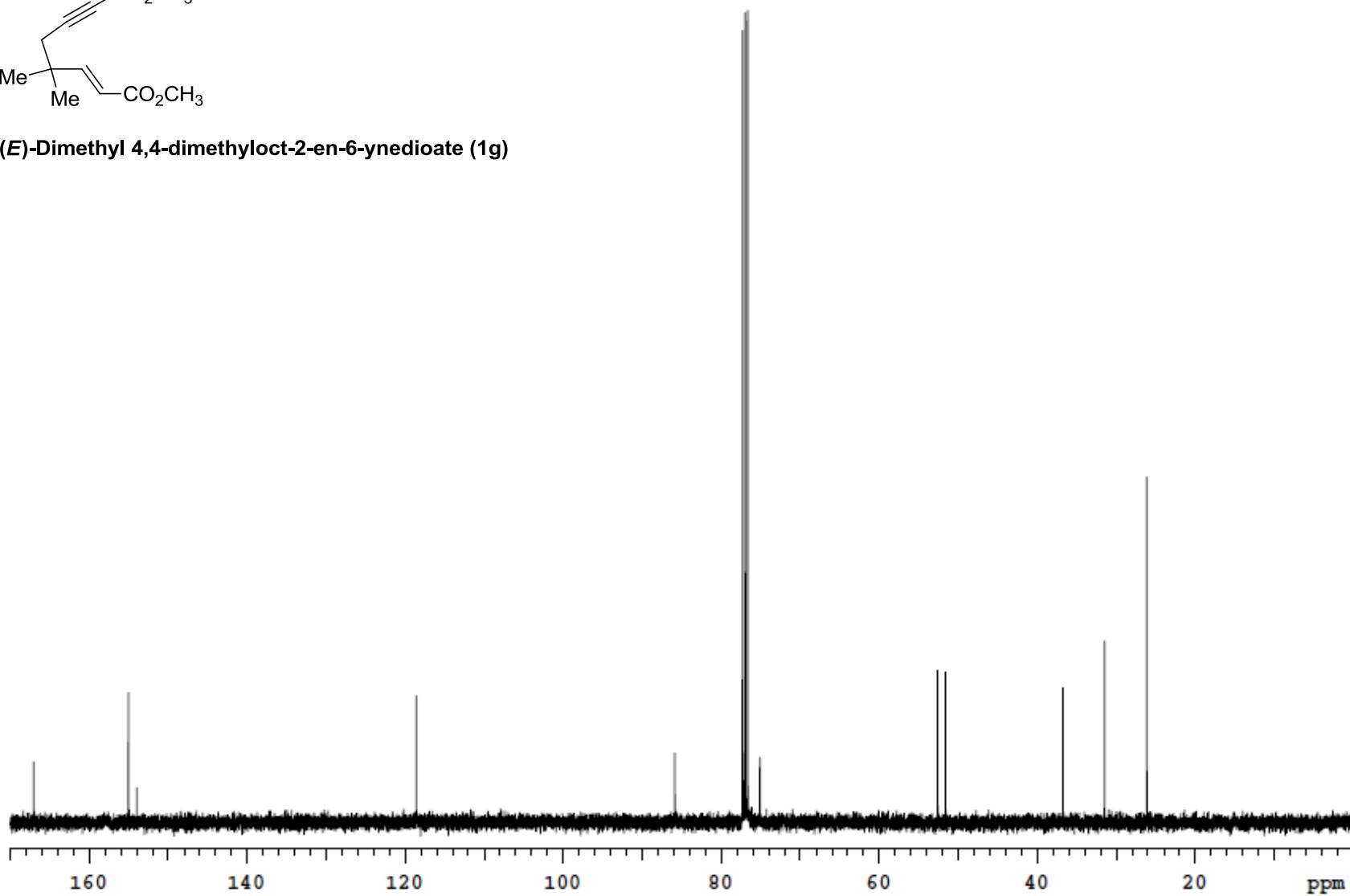


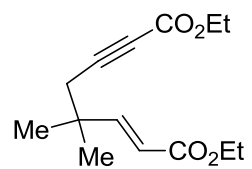
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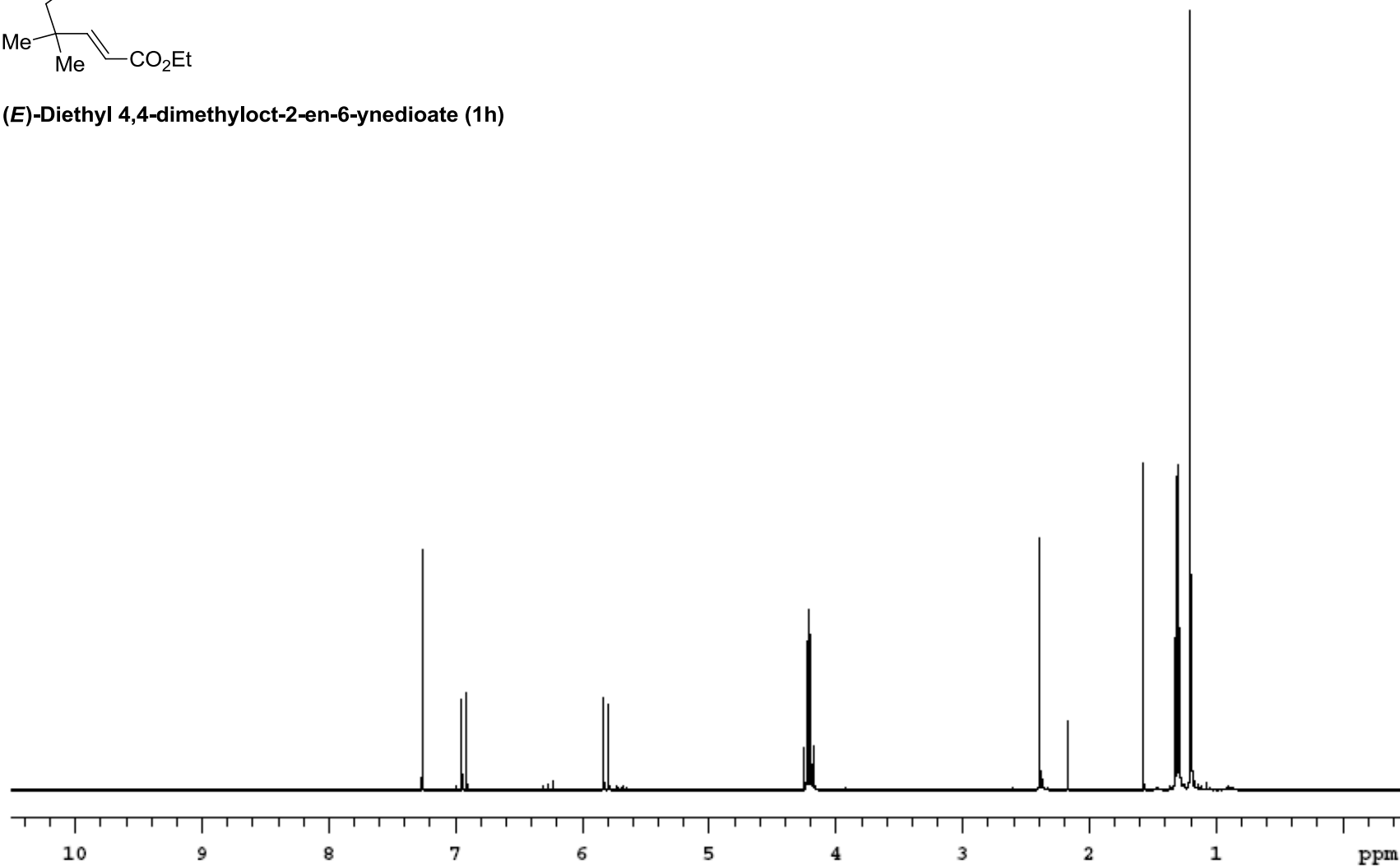


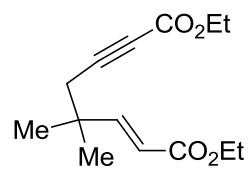
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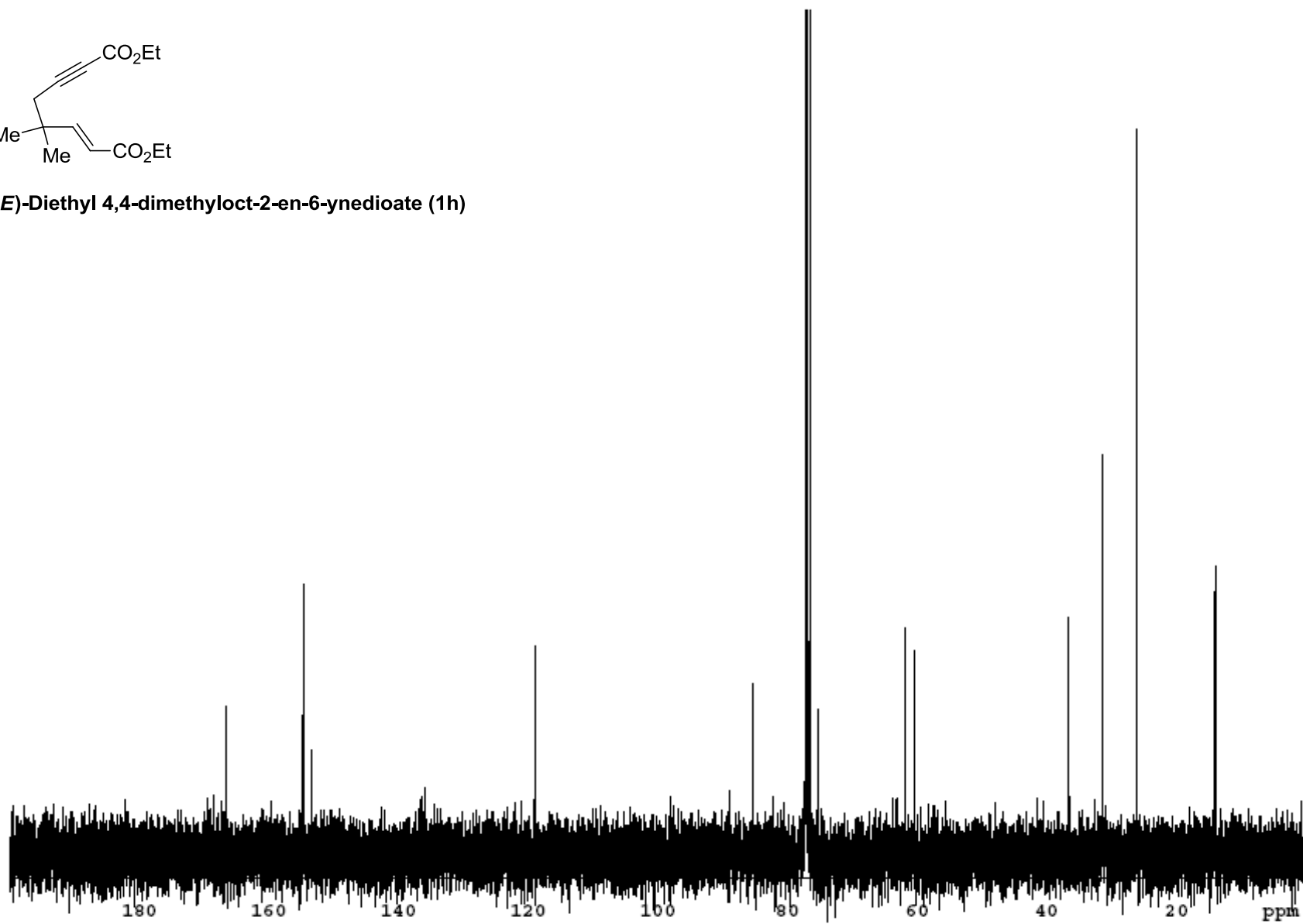


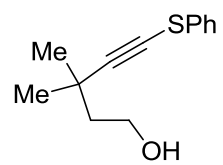
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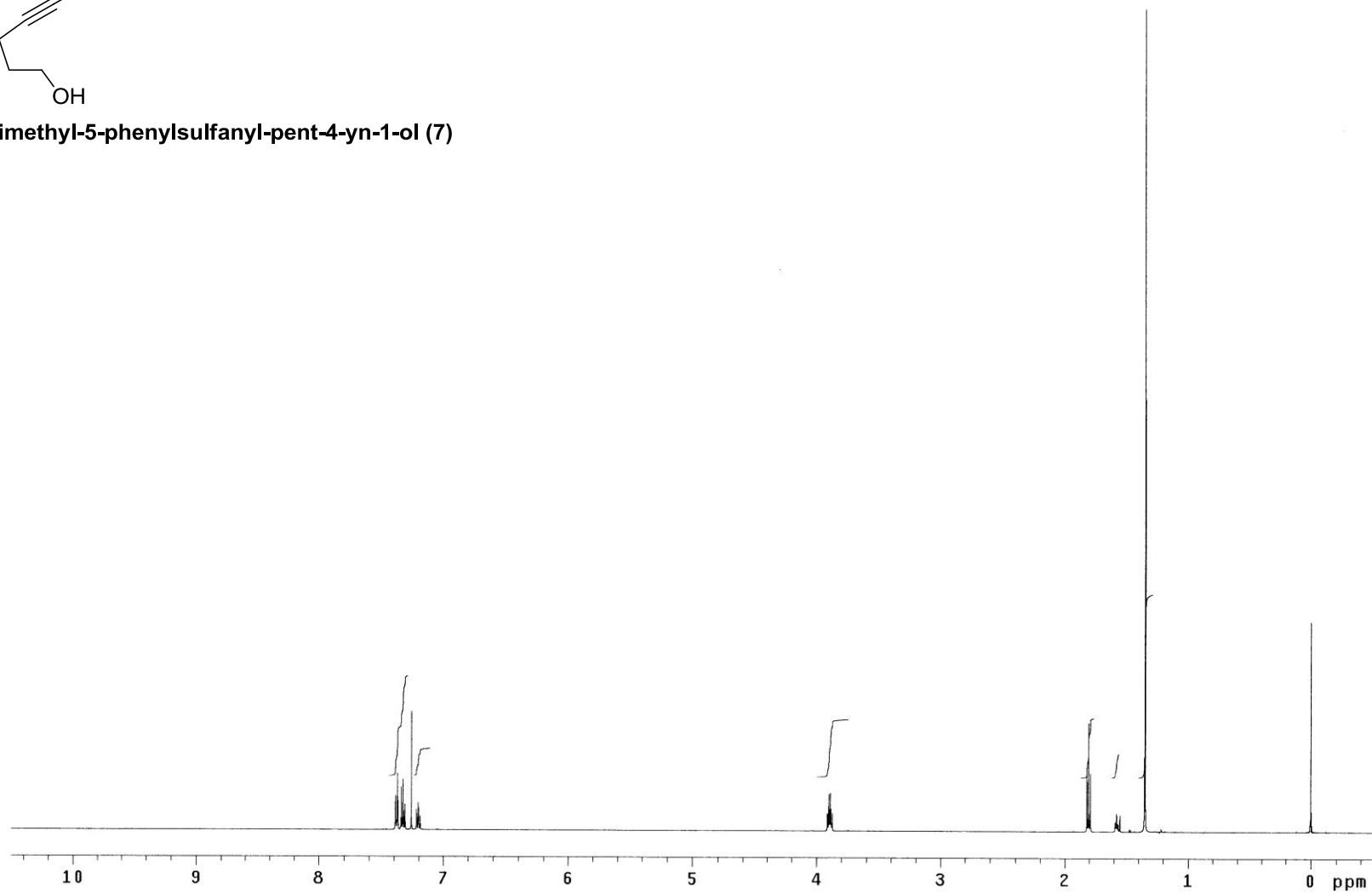


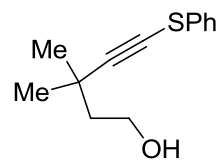
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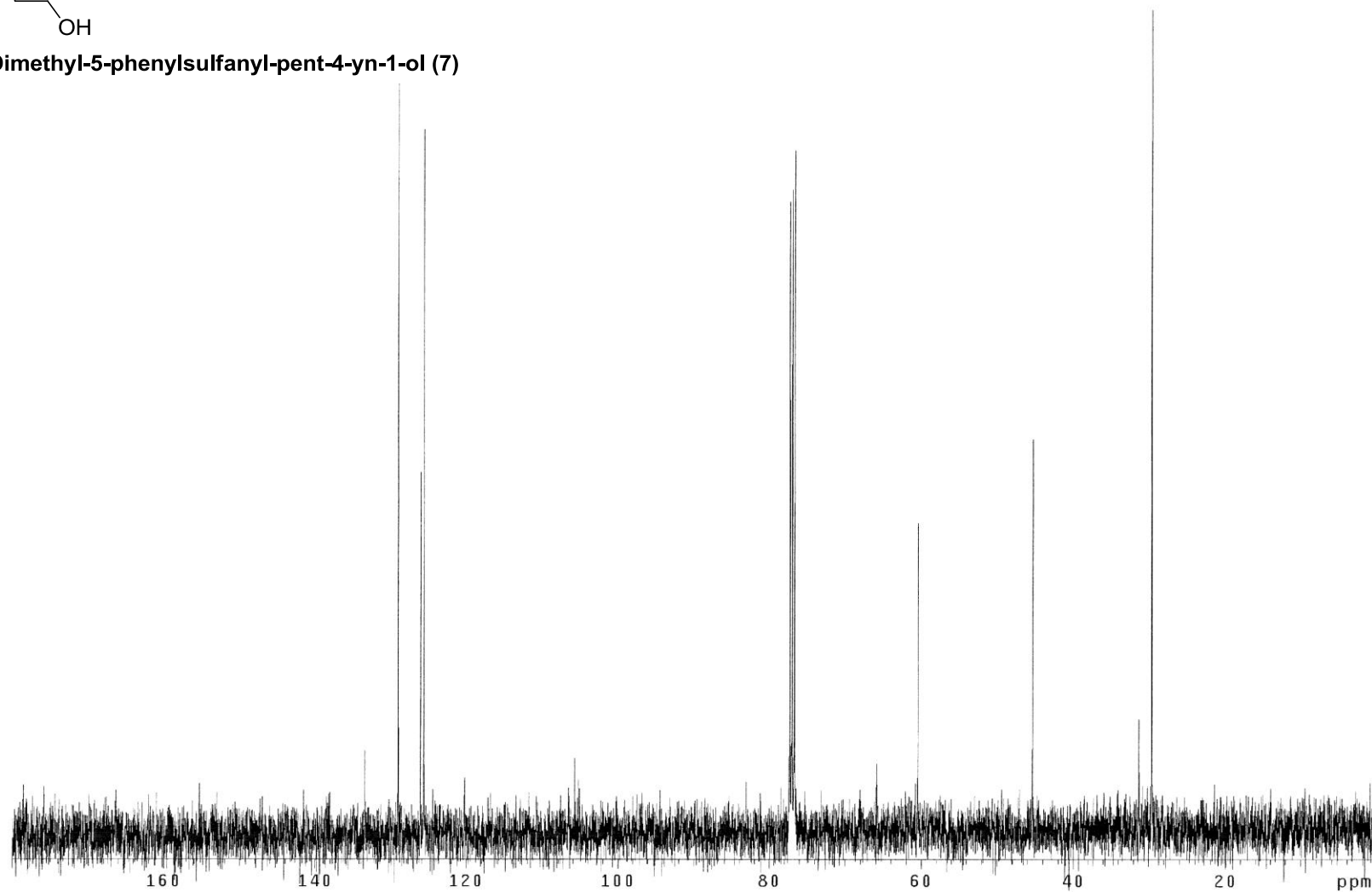


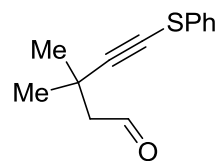
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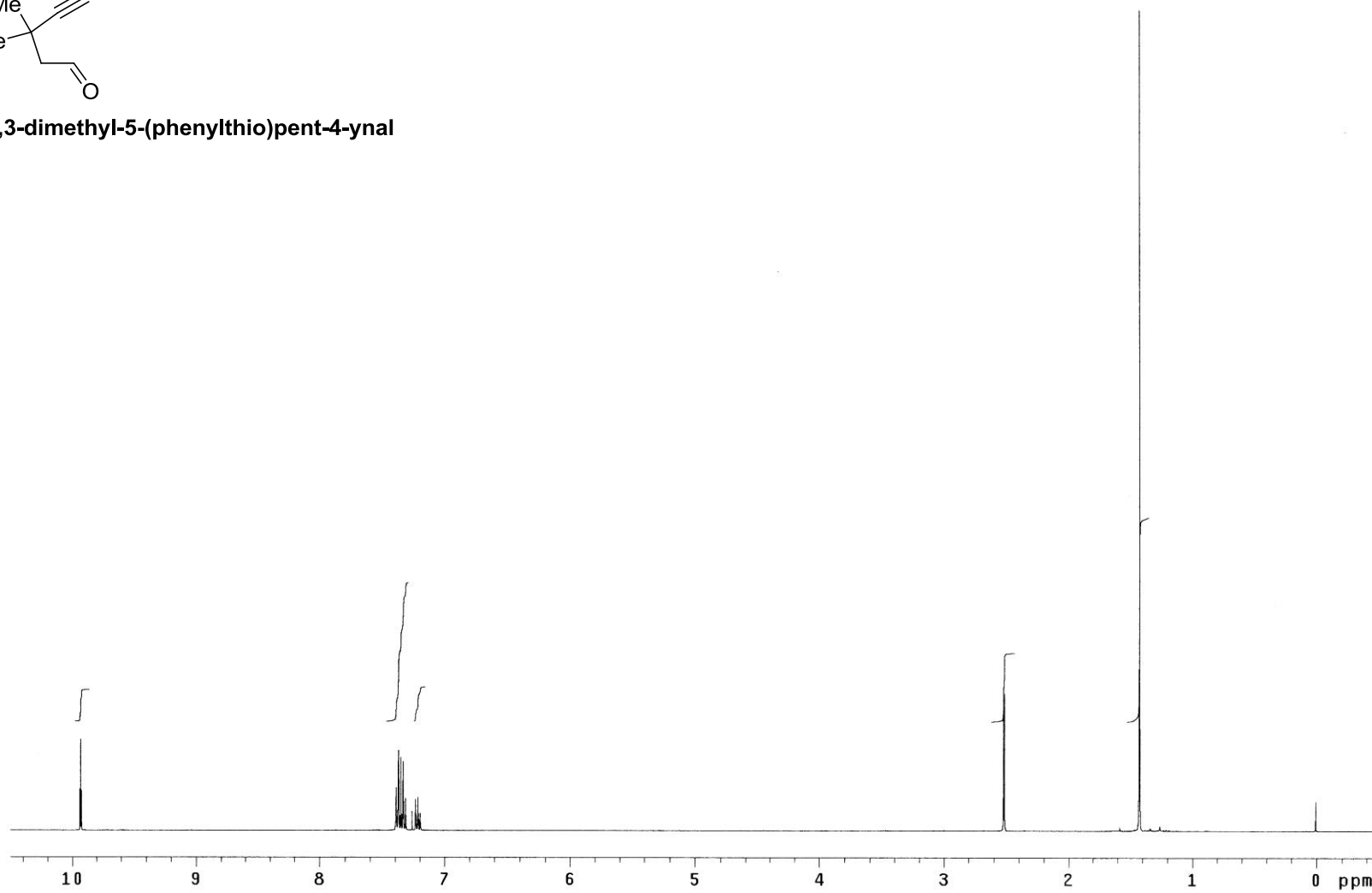


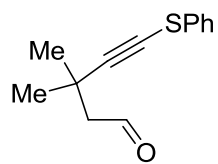
3,3-Dimethyl-5-phenylsulfanyl-pent-4-yn-1-ol (7)



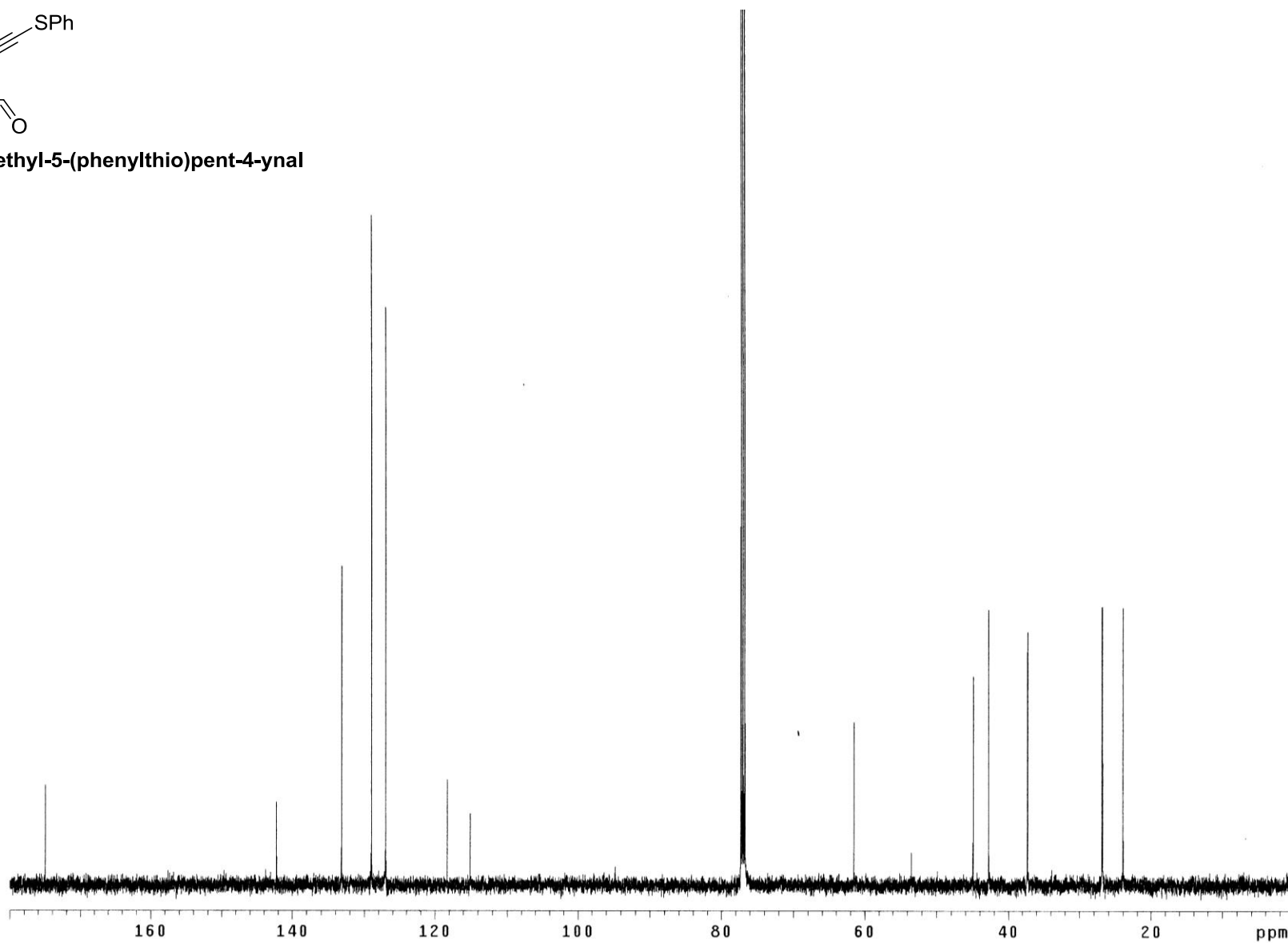


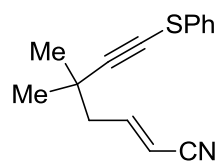
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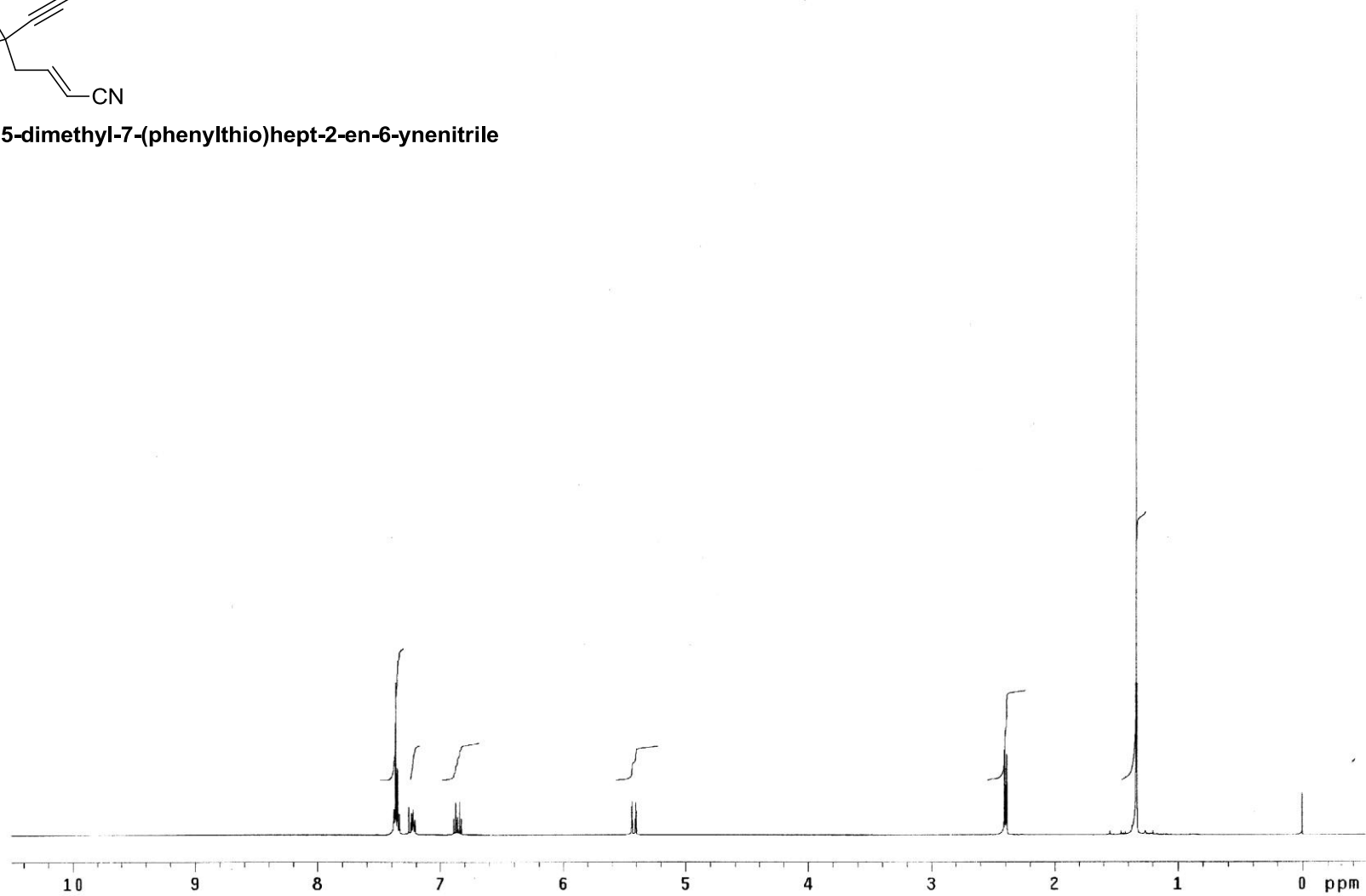


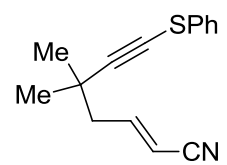
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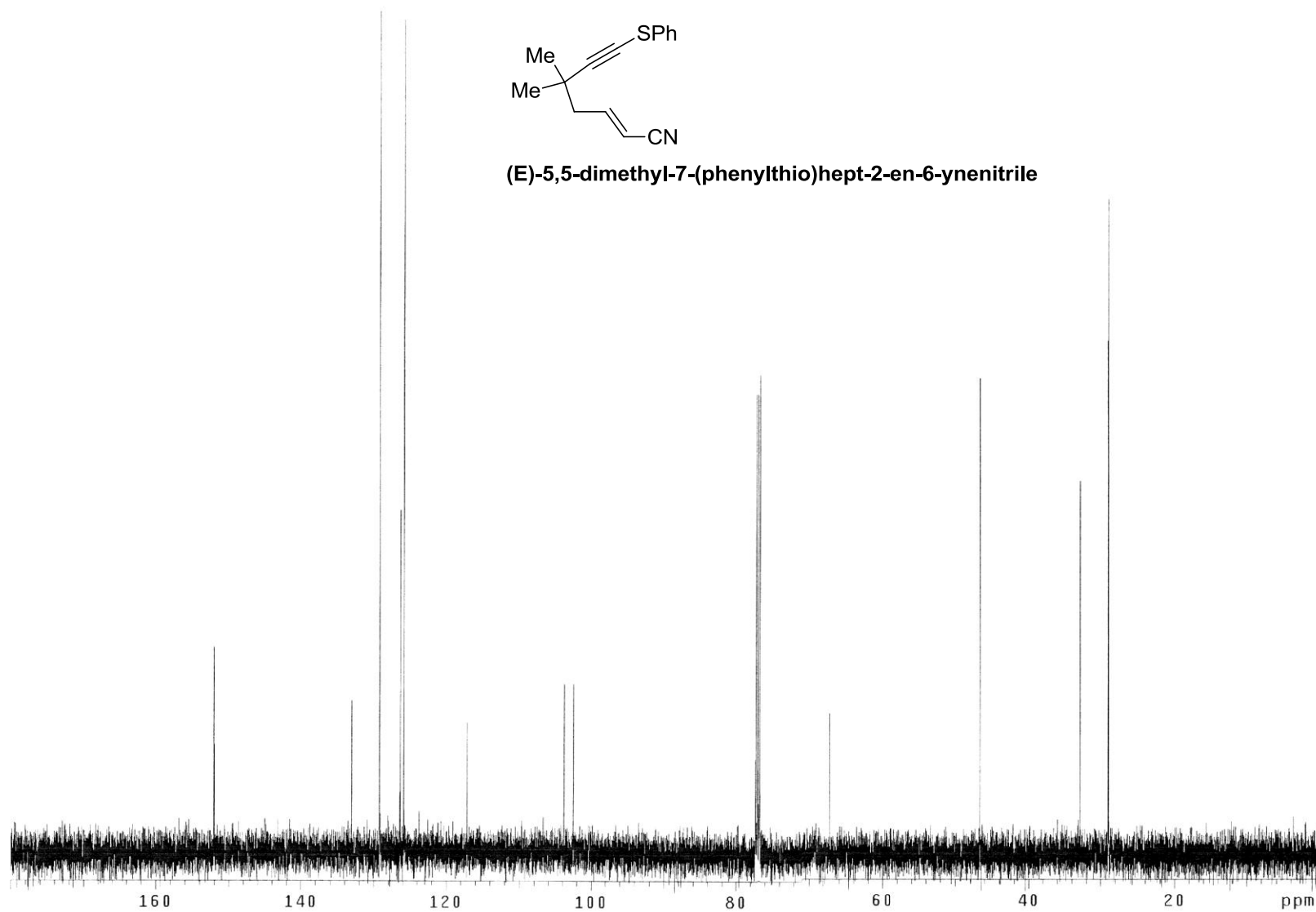


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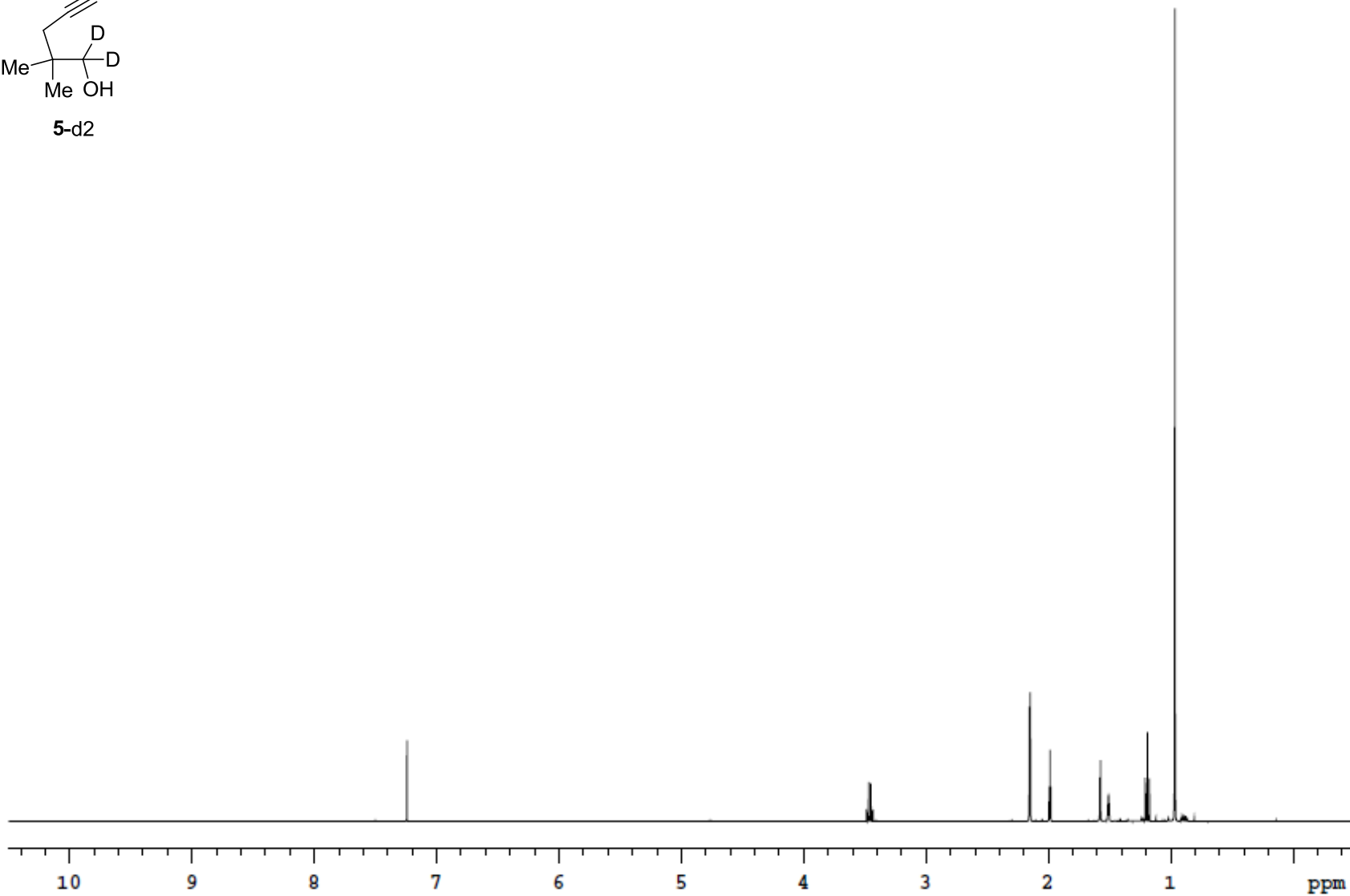
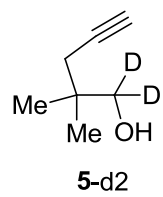


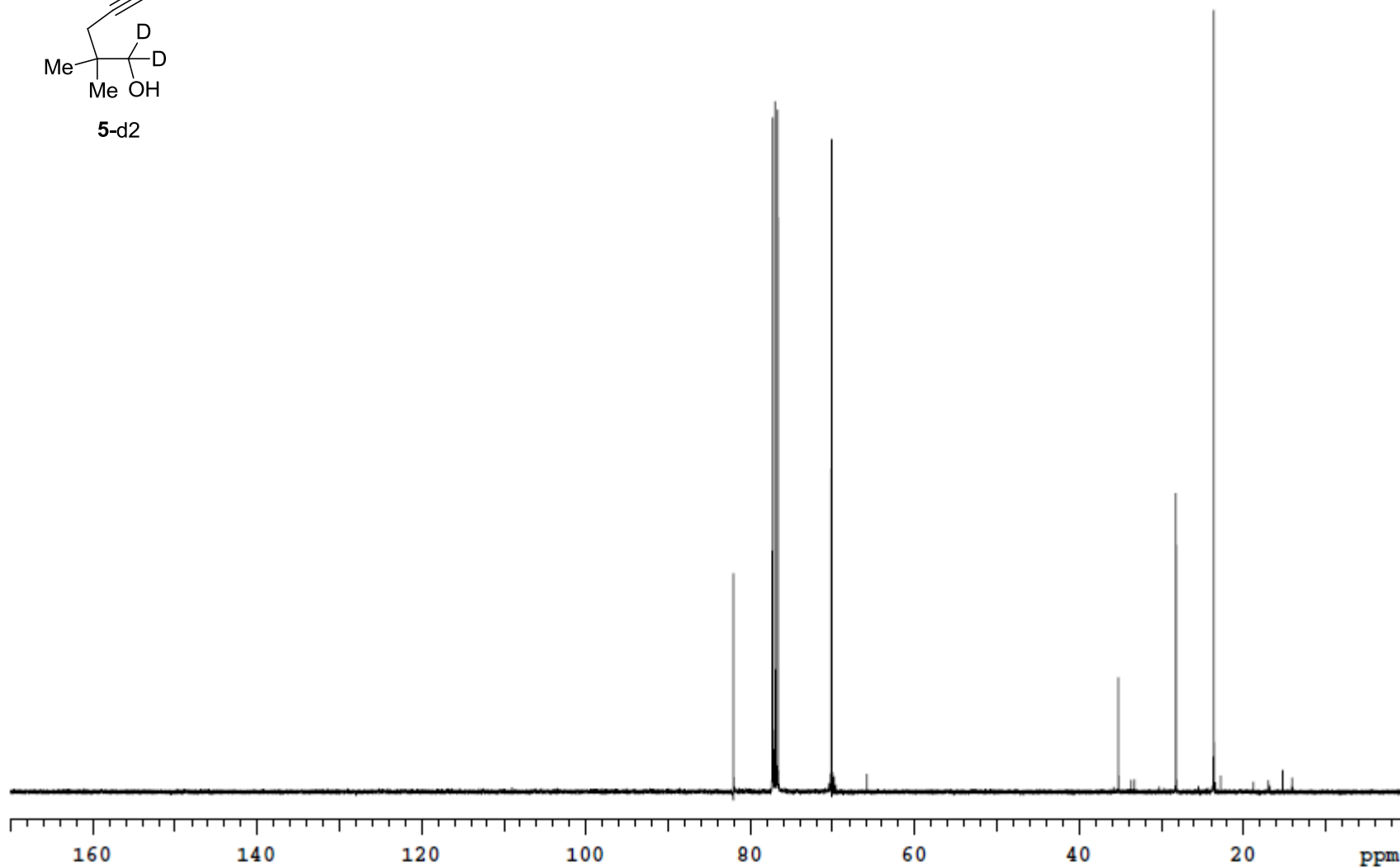
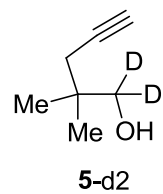
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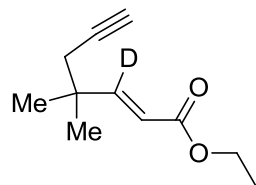




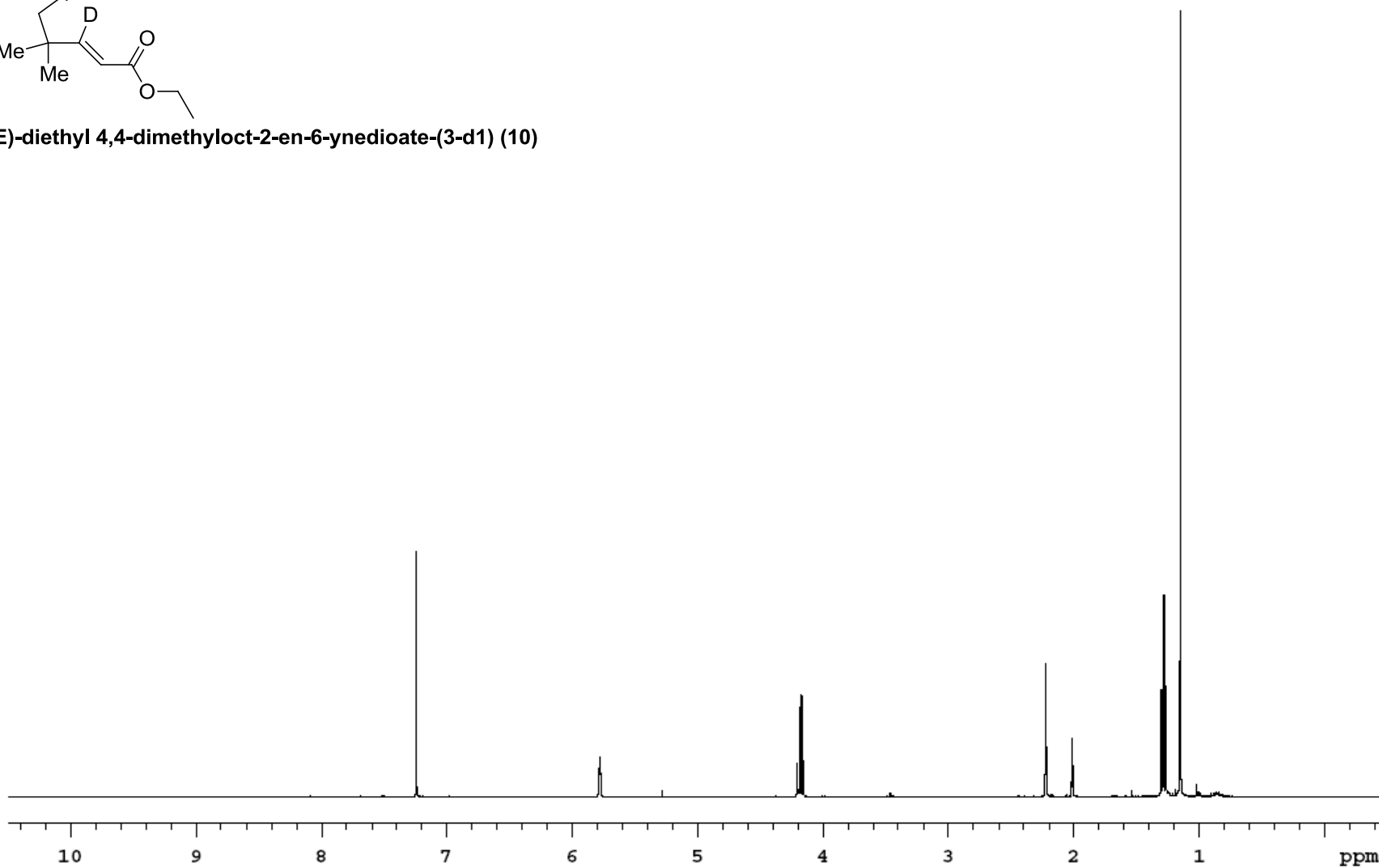


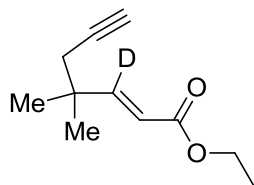




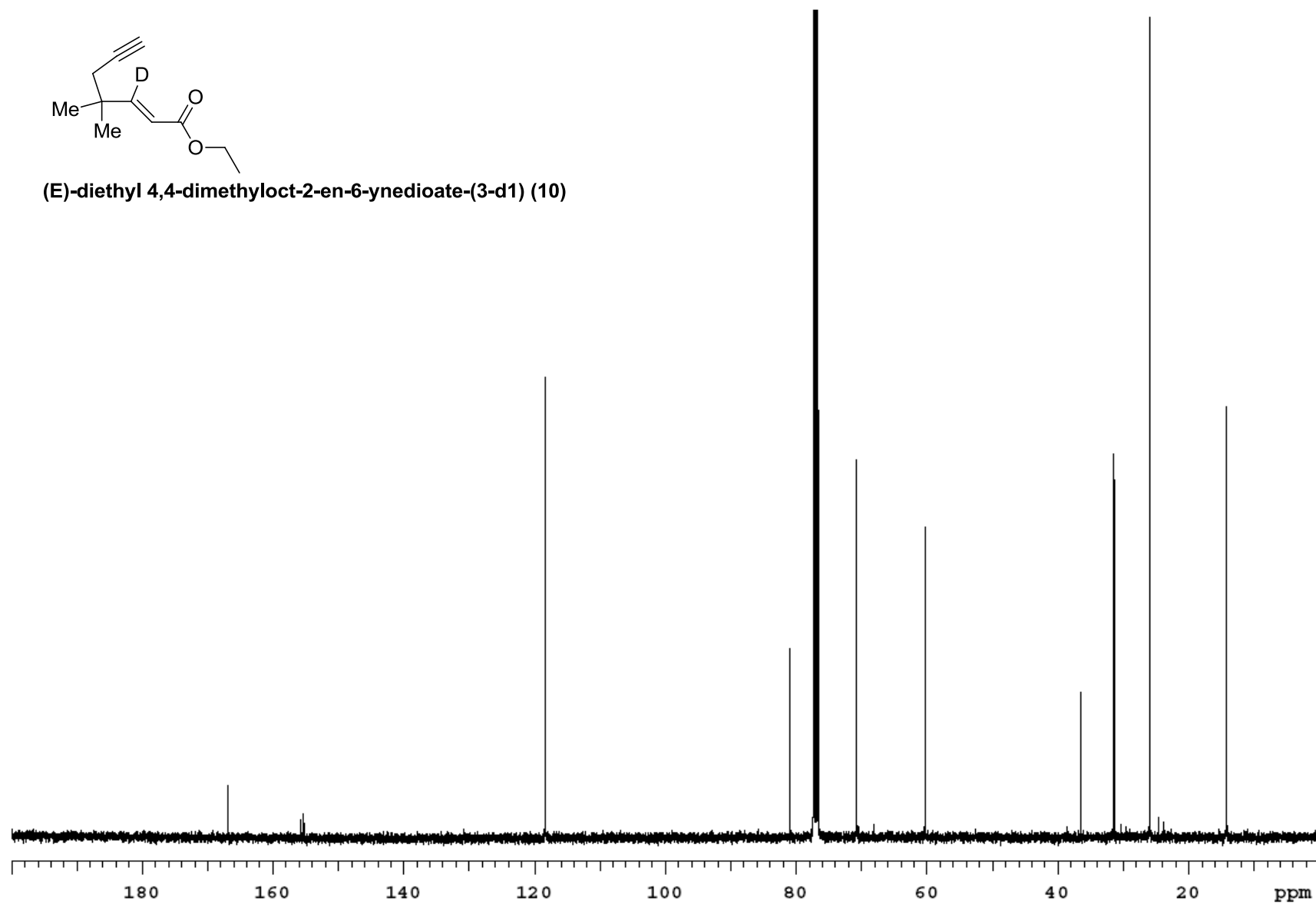


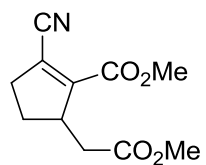
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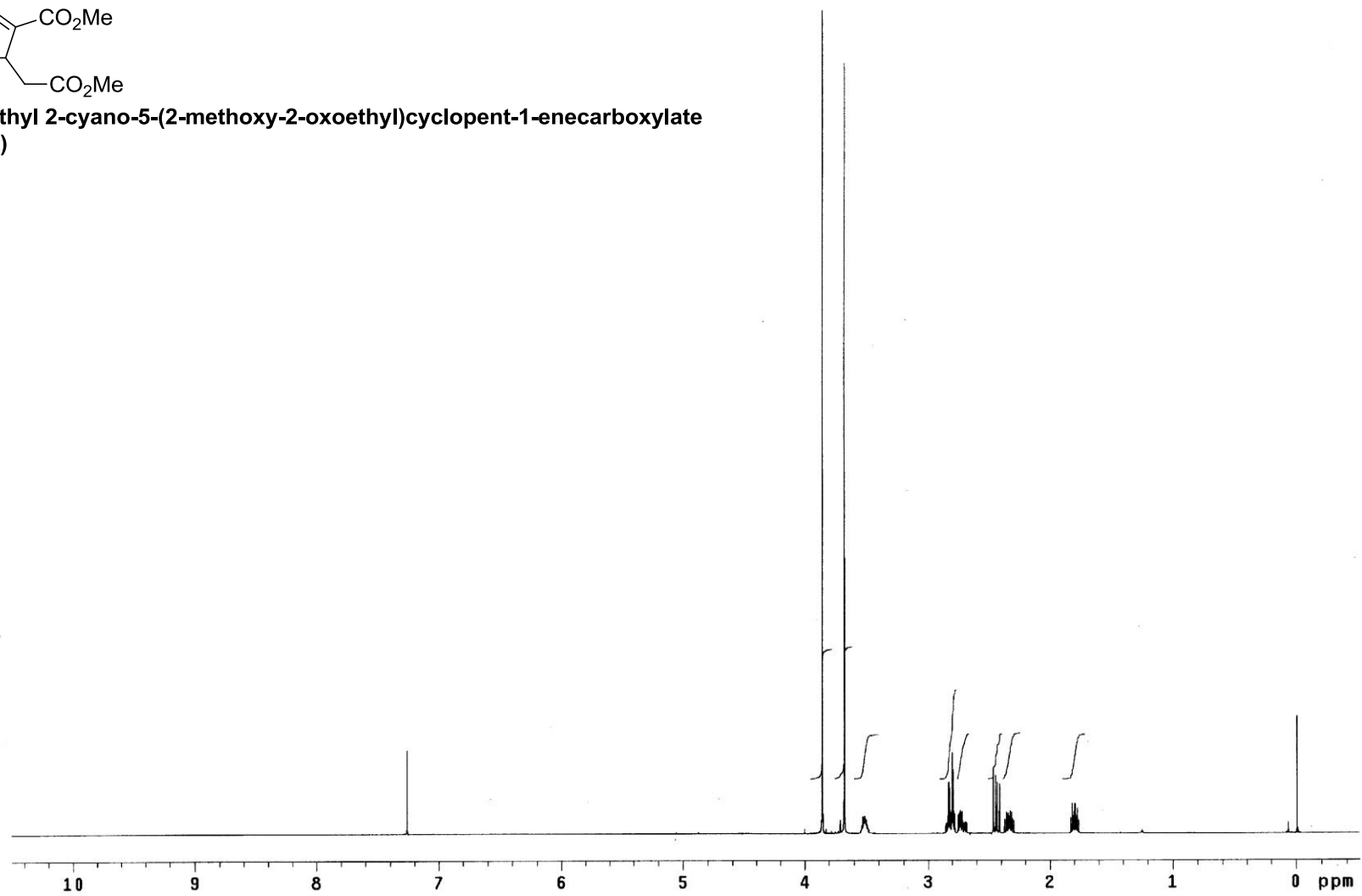


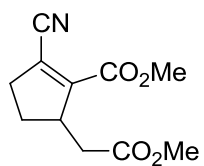
(E)-diethyl 4,4-dimethyloct-2-en-6-ynedioate-(3-d1) (10)



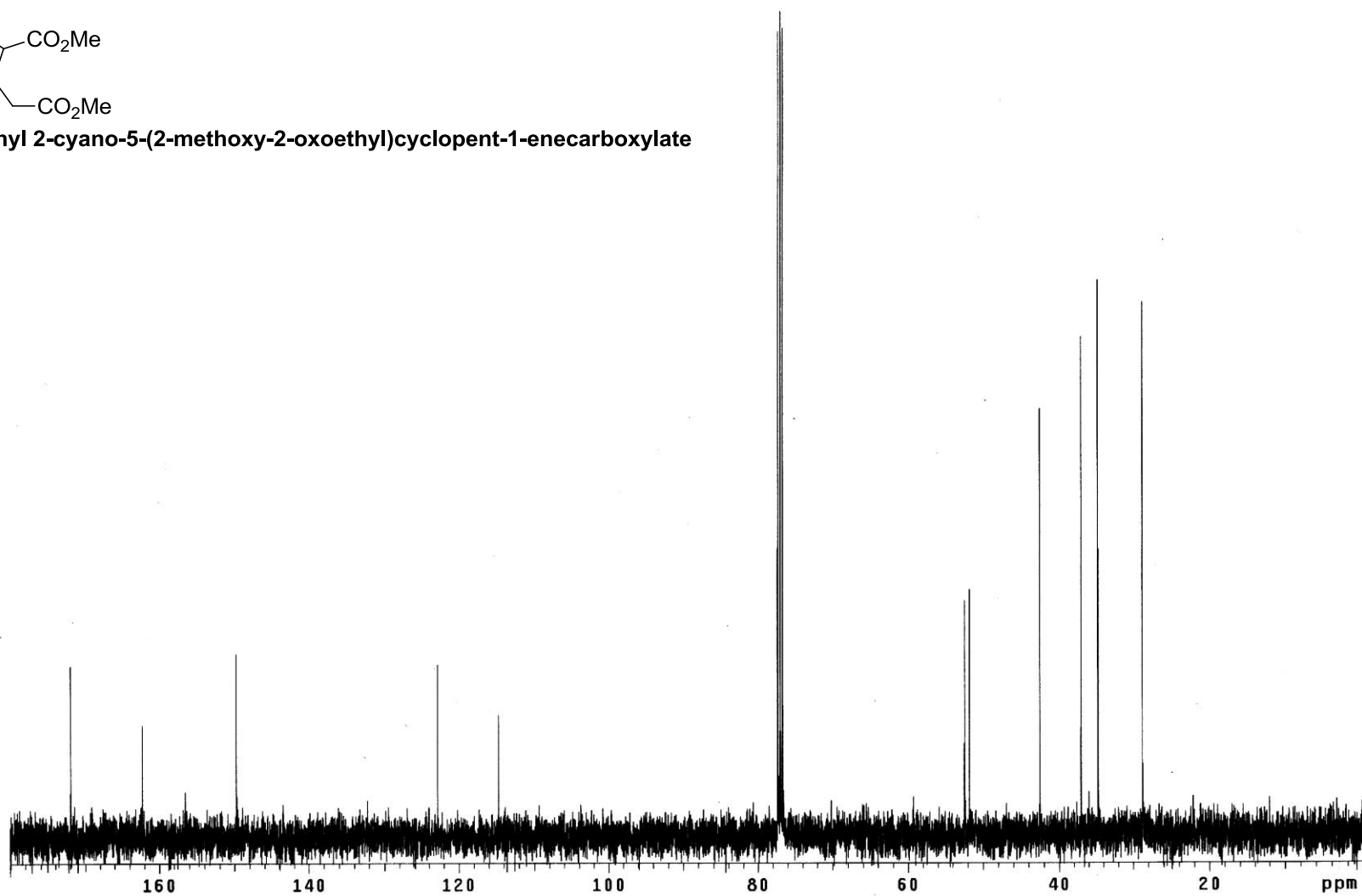


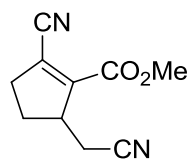
**Methyl 2-cyano-5-(2-methoxy-2-oxoethyl)cyclopent-1-enecarboxylate
(2a)**



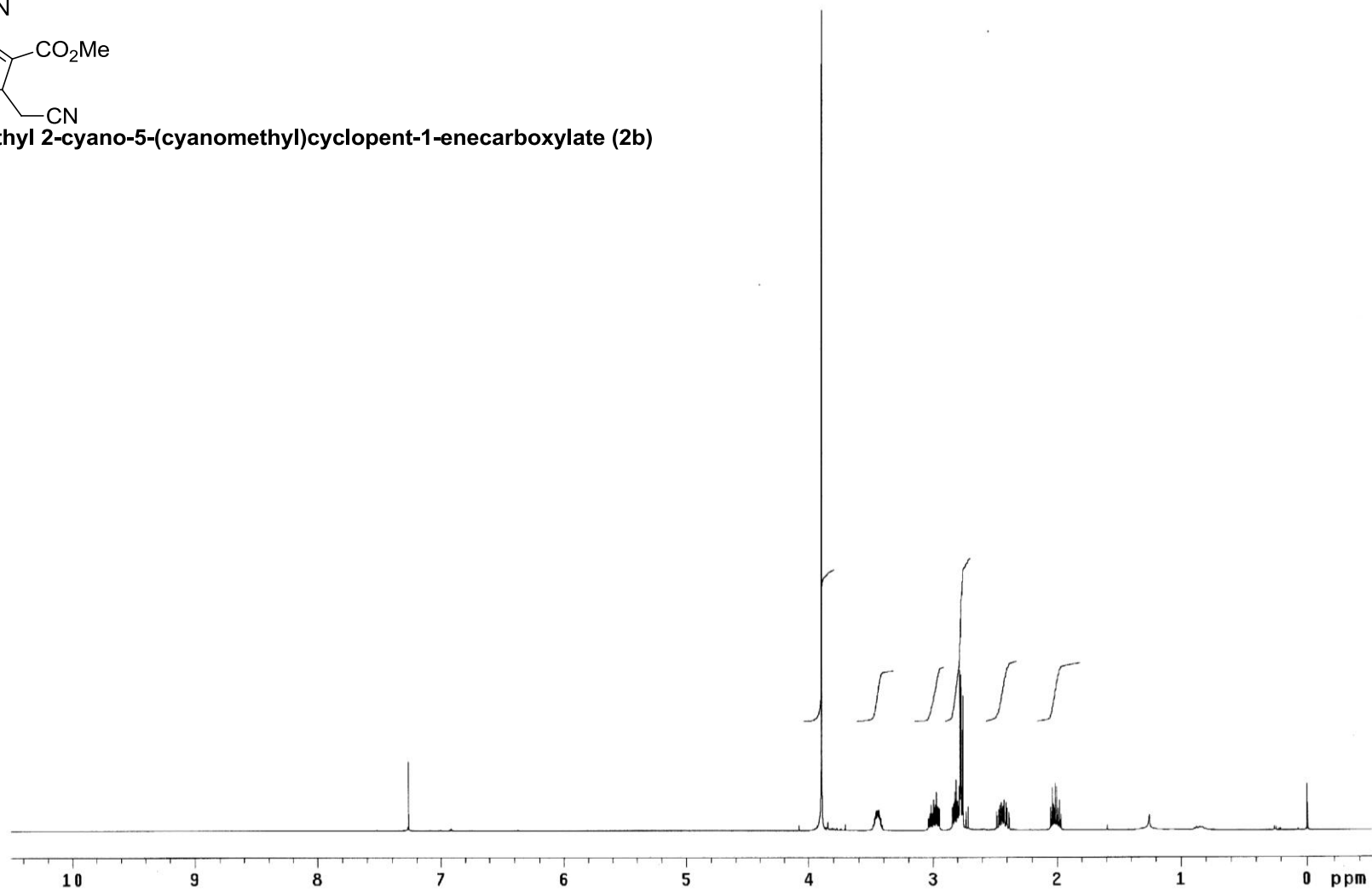


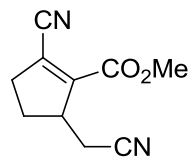
Methyl 2-cyano-5-(2-methoxy-2-oxoethyl)cyclopent-1-enecarboxylate (2a)



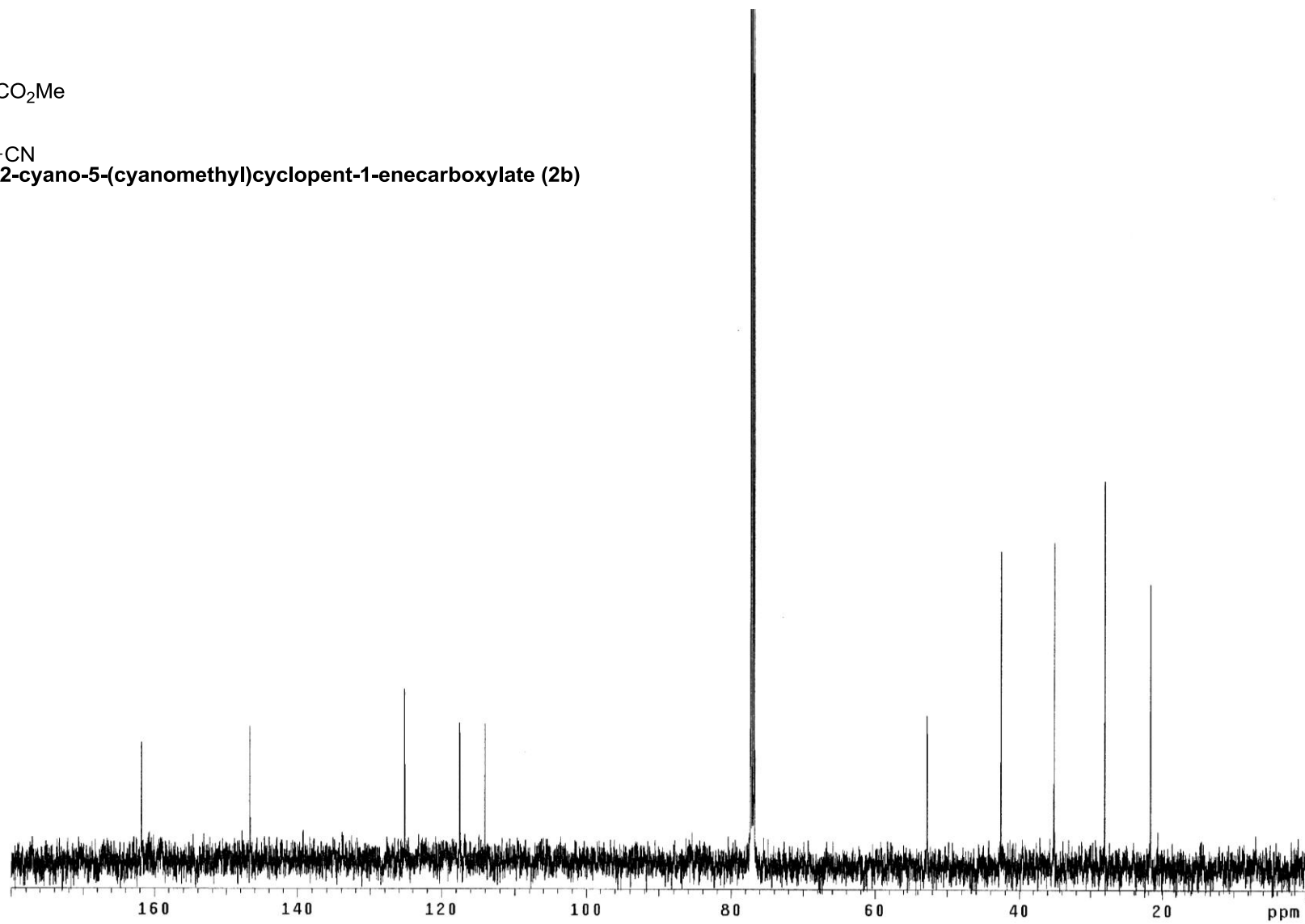


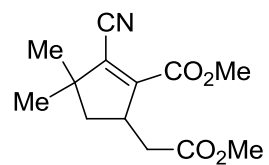
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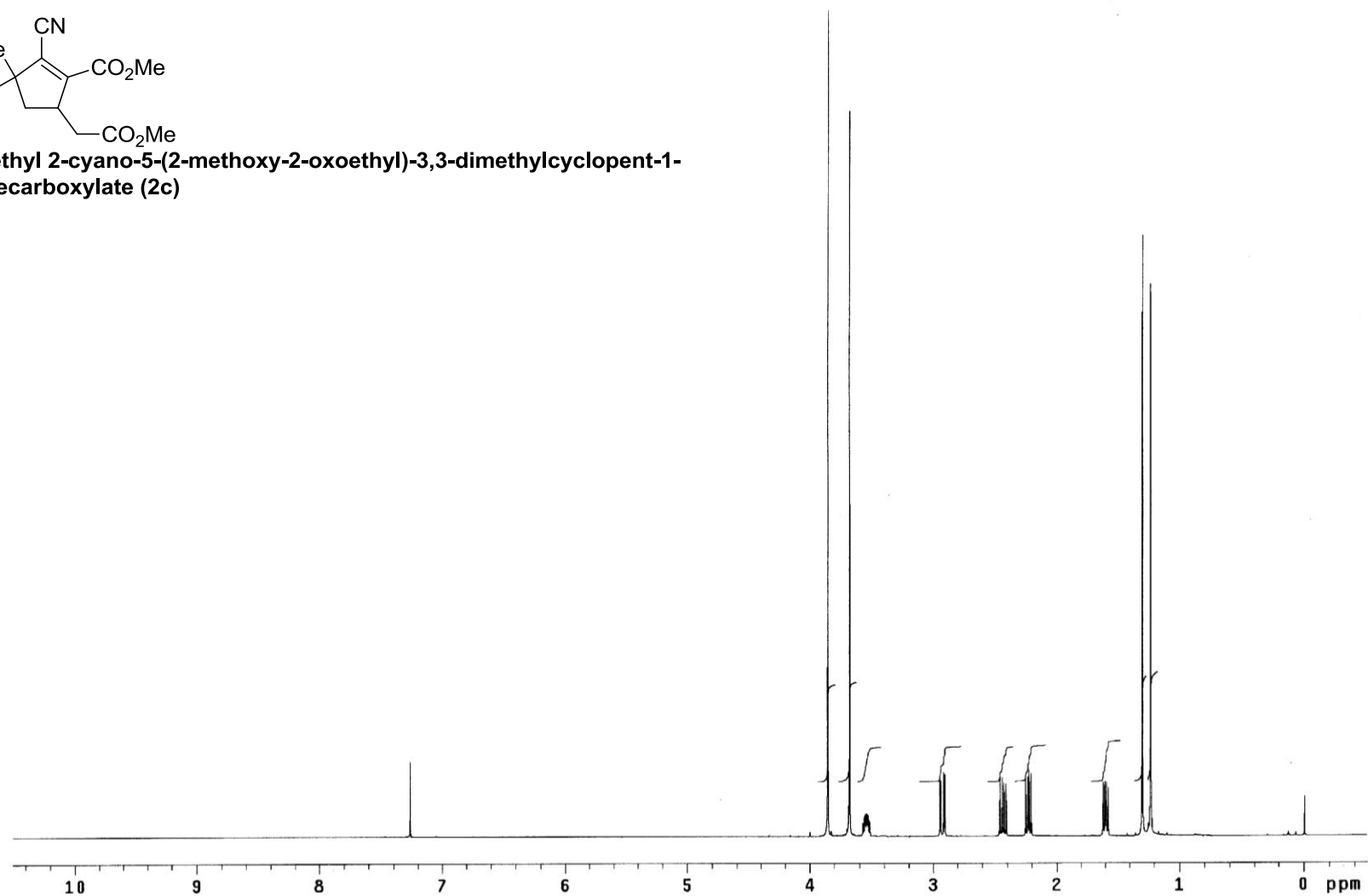


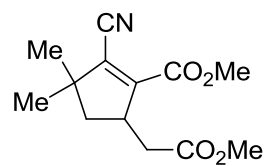
methyl 2-cyano-5-(cyanomethyl)cyclopent-1-enecarboxylate (2b)



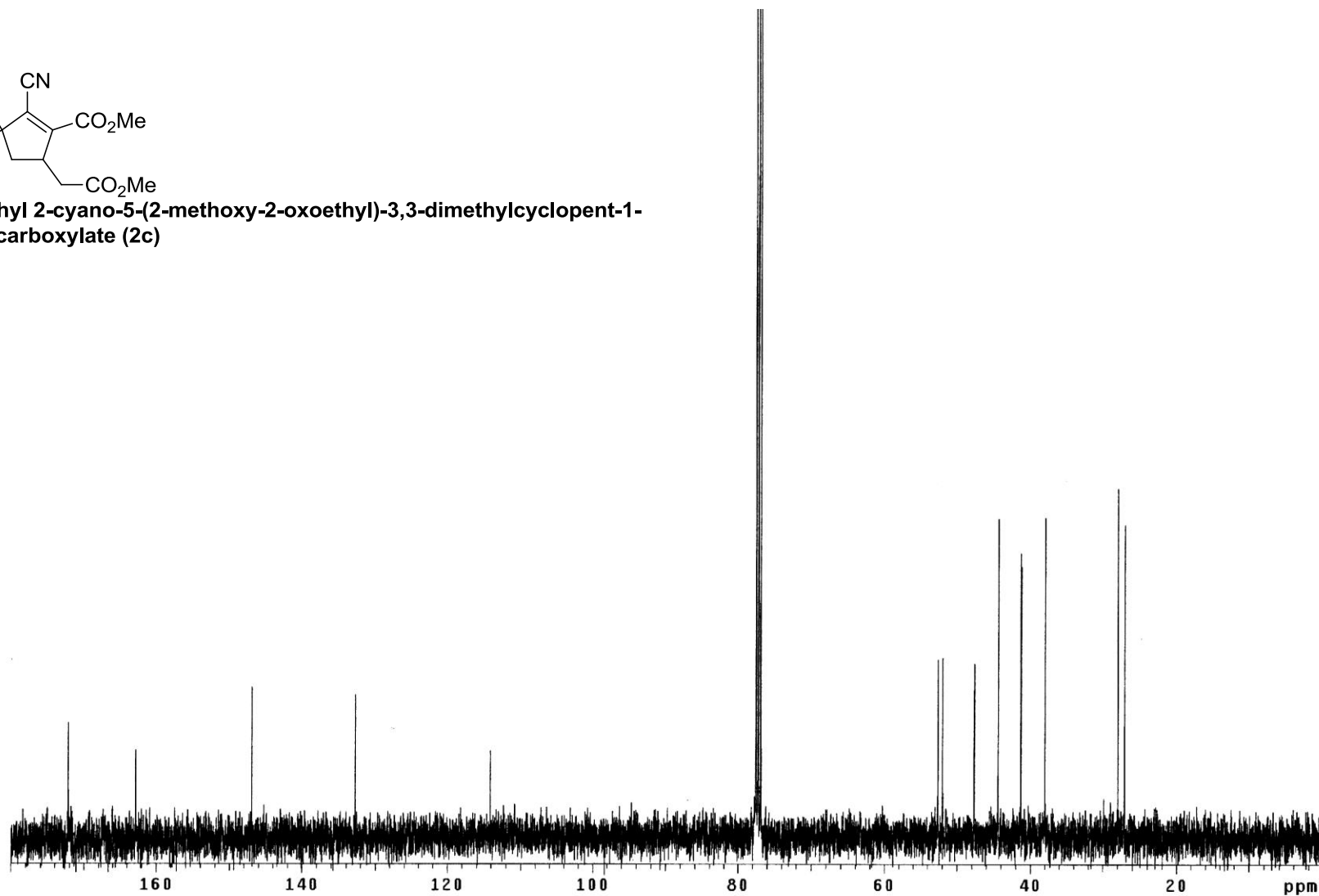


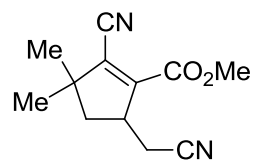
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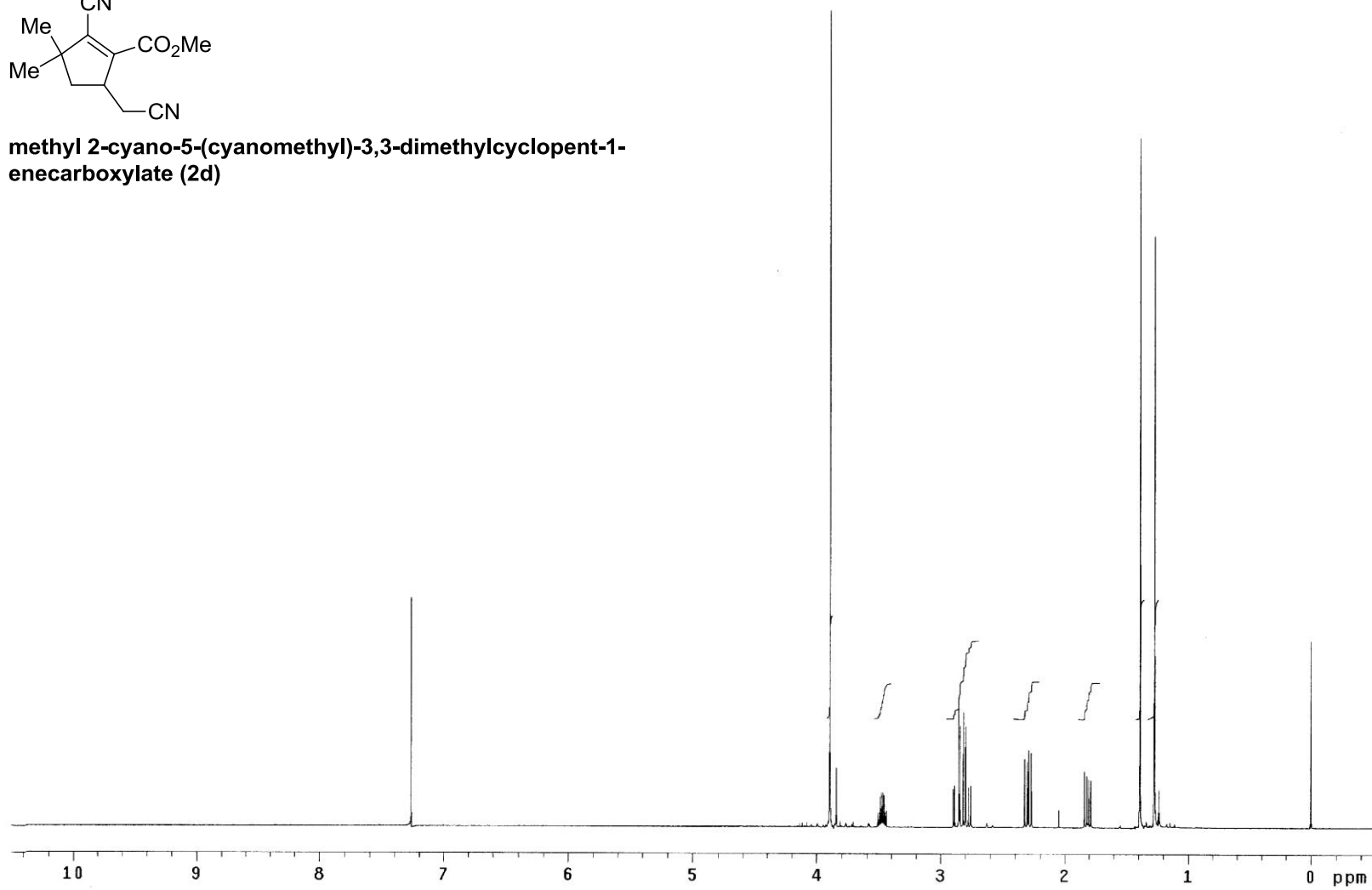


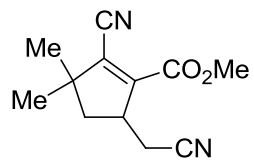
methyl 2-cyano-5-(2-methoxy-2-oxoethyl)-3,3-dimethylcyclopent-1-enecarboxylate (2c)



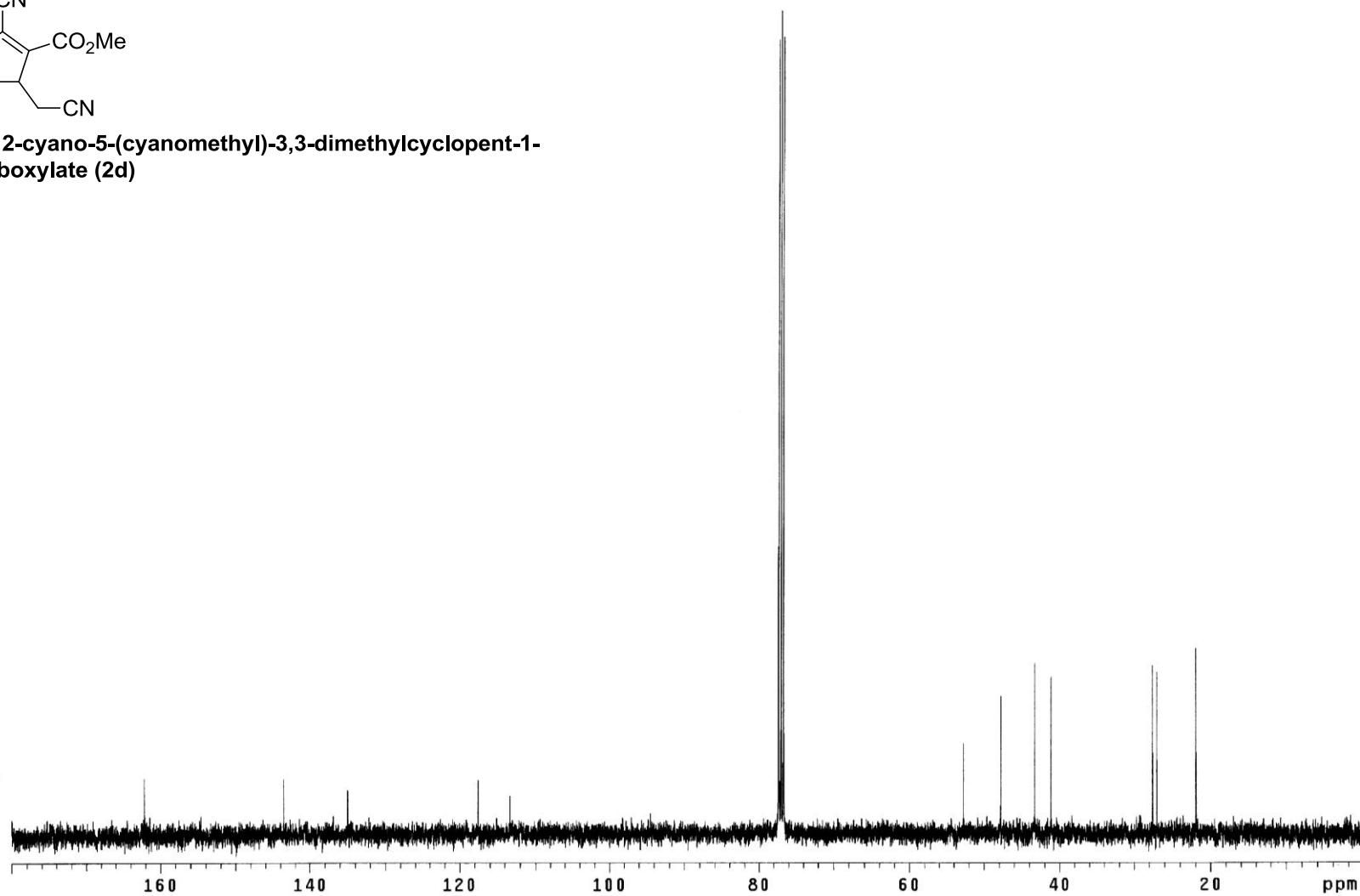


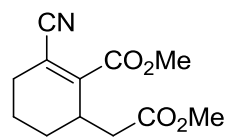
methyl 2-cyano-5-(cyanomethyl)-3,3-dimethylcyclopent-1-enecarboxylate (2d)



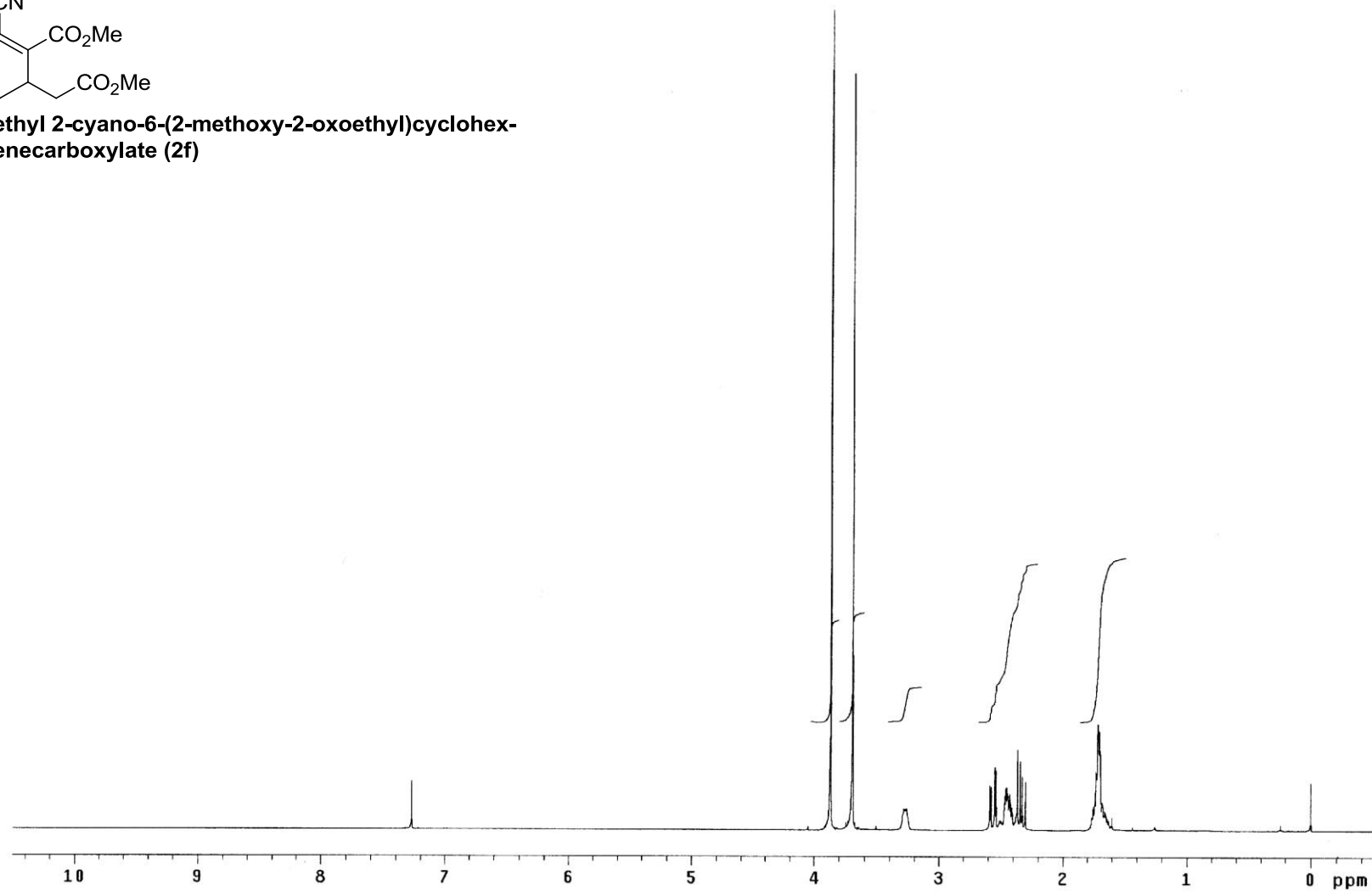


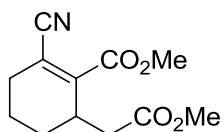
methyl 2-cyano-5-(cyanomethyl)-3,3-dimethylcyclopent-1-enecarboxylate (2d)



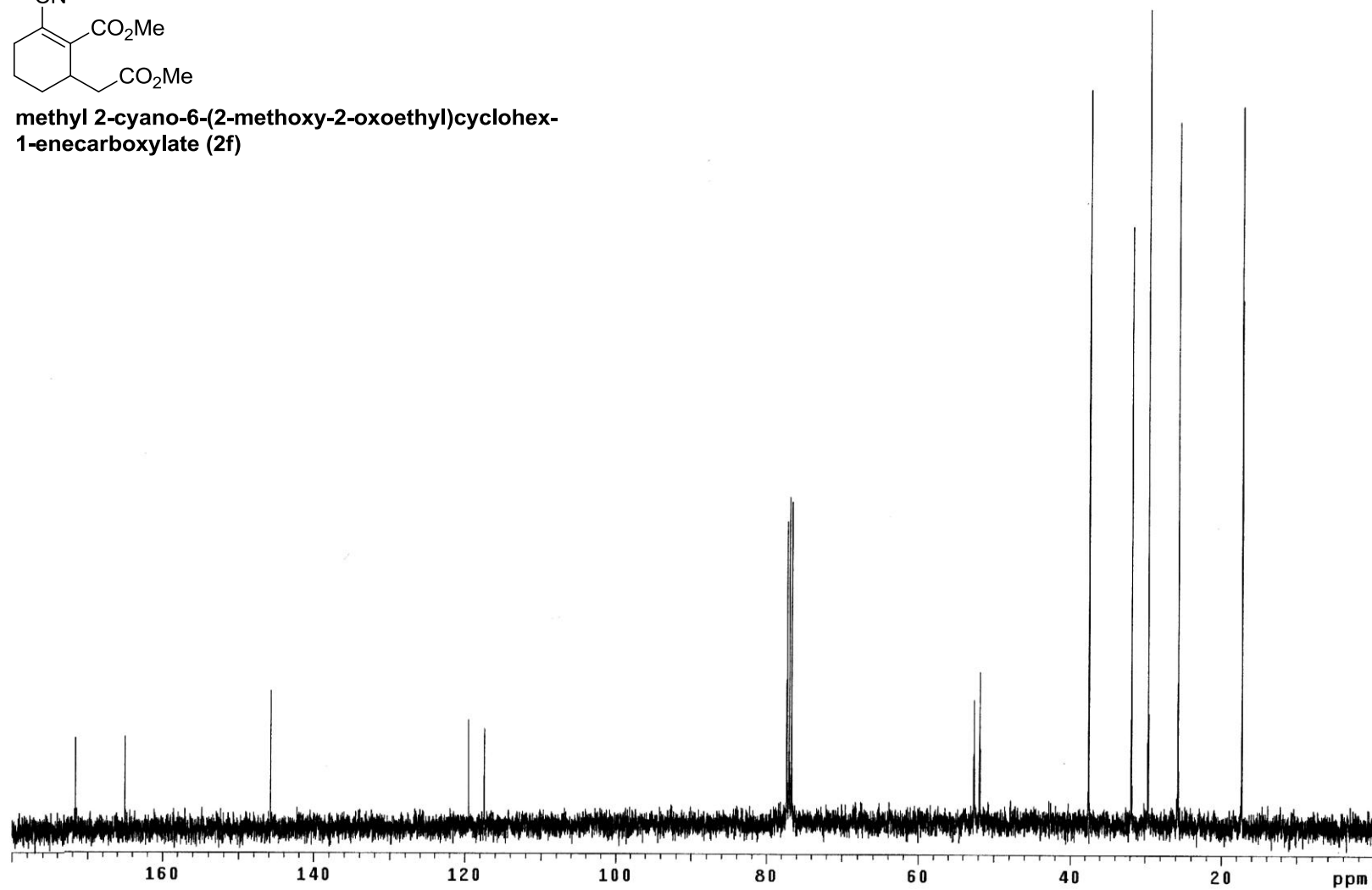


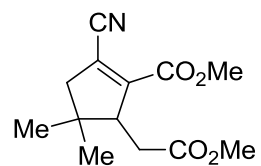
methyl 2-cyano-6-(2-methoxy-2-oxoethyl)cyclohex-1-enecarboxylate (2f)



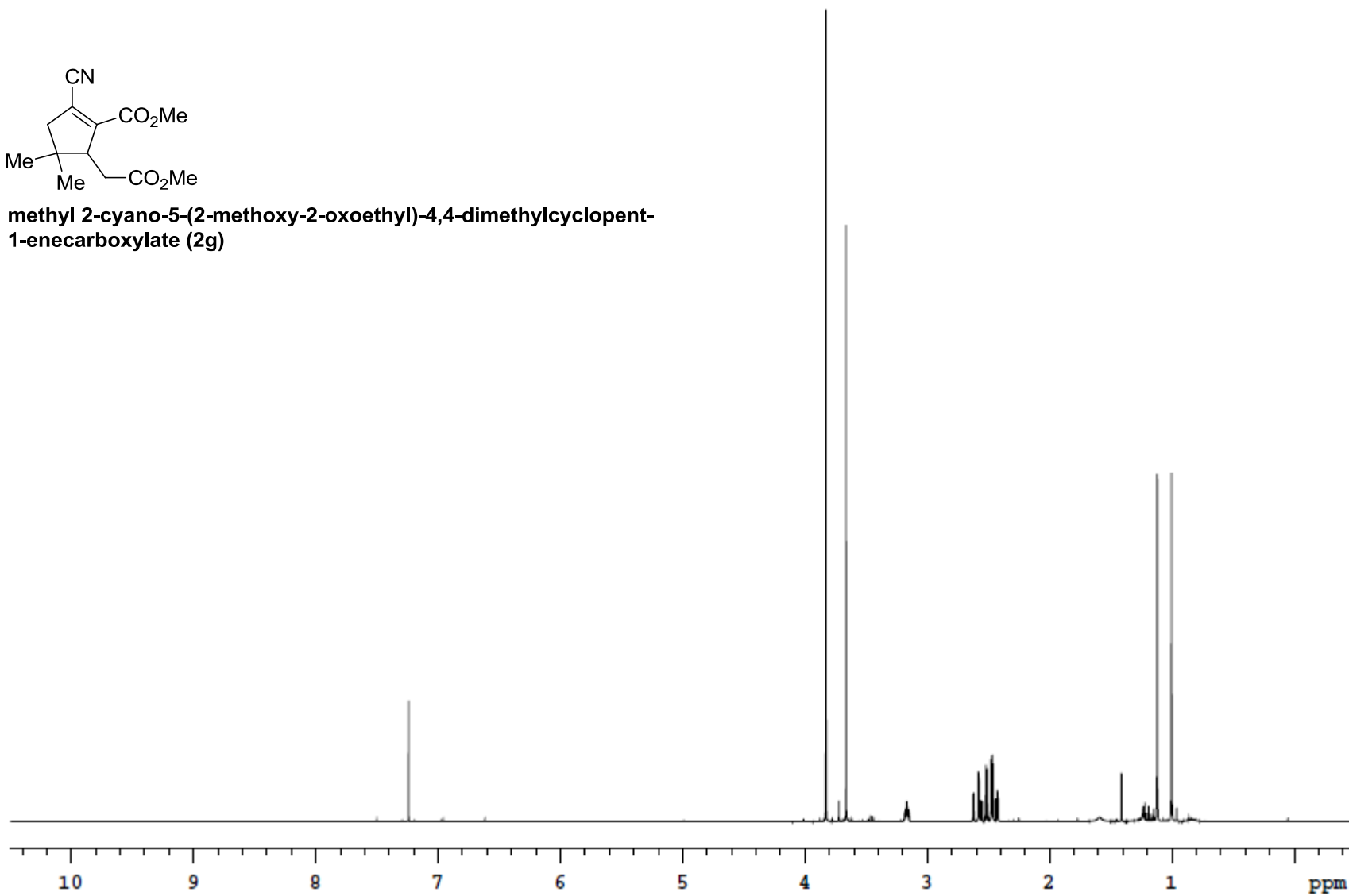


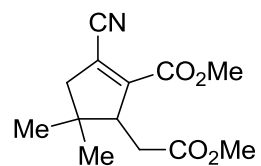
methyl 2-cyano-6-(2-methoxy-2-oxoethyl)cyclohex-1-enecarboxylate (2f)



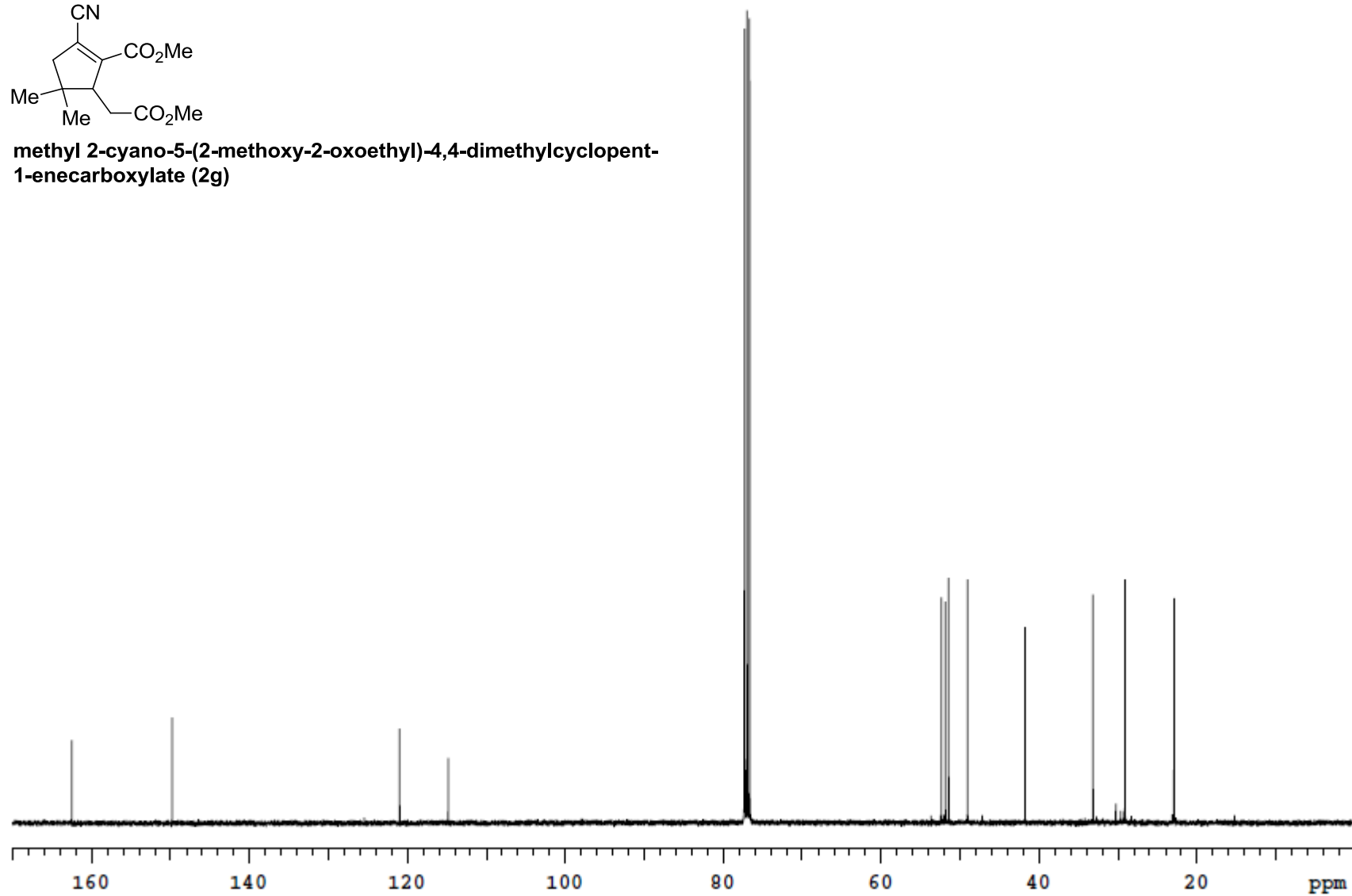


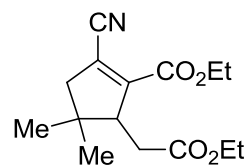
methyl 2-cyano-5-(2-methoxy-2-oxoethyl)-4,4-dimethylcyclopent-1-enecarboxylate (2g)



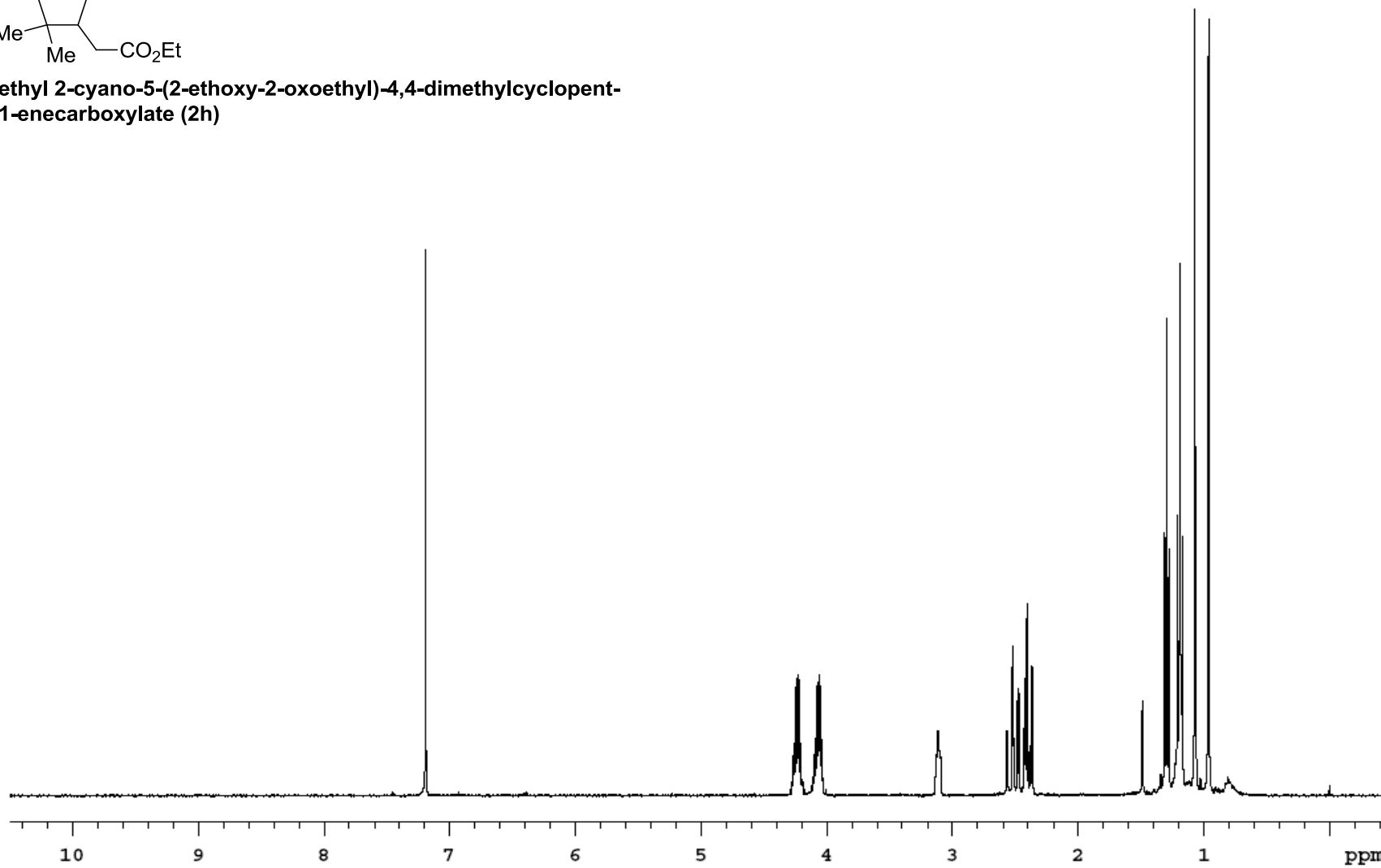


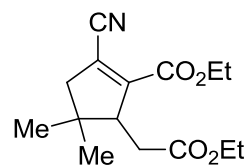
methyl 2-cyano-5-(2-methoxy-2-oxoethyl)-4,4-dimethylcyclopent-1-enecarboxylate (2g)



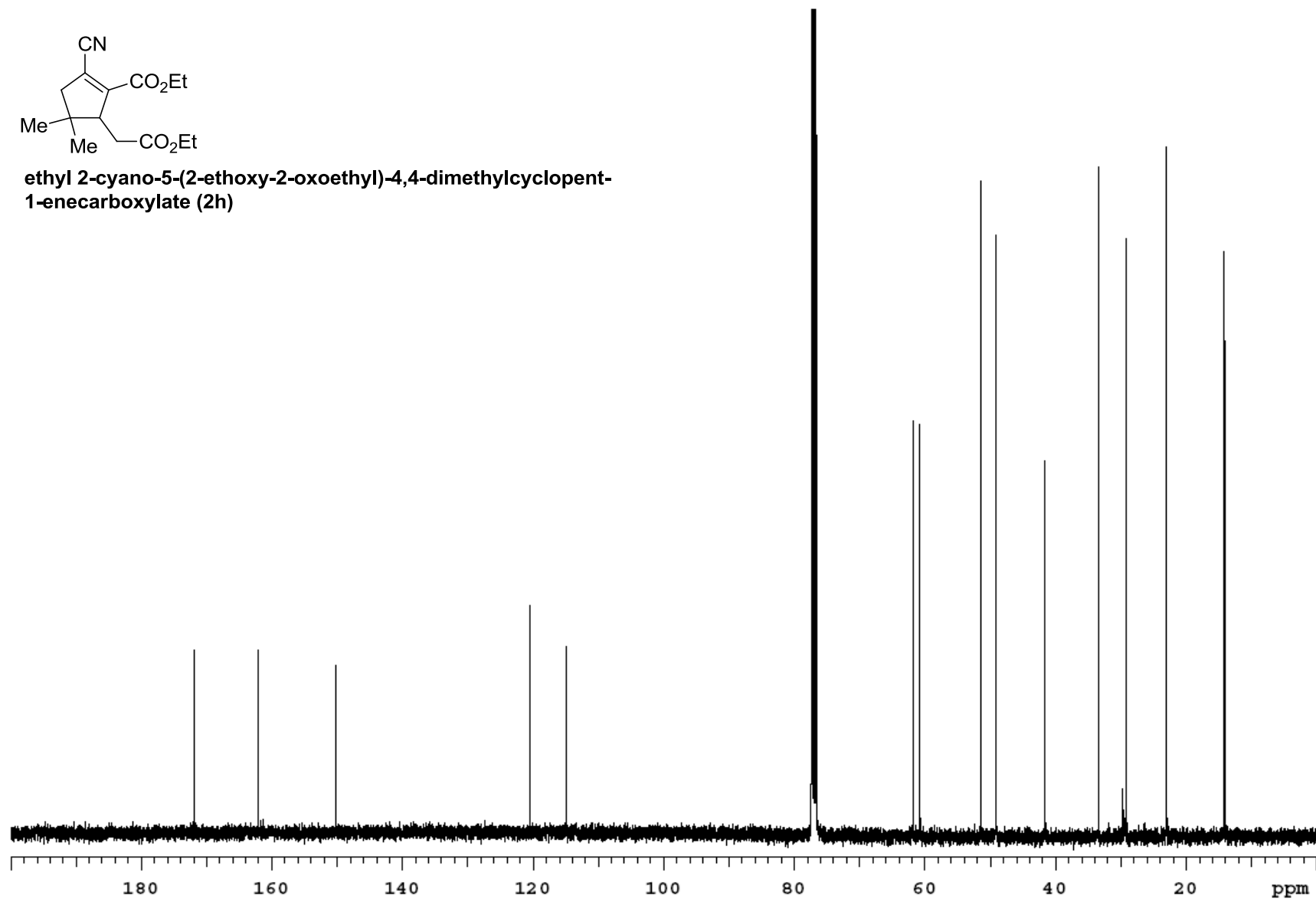


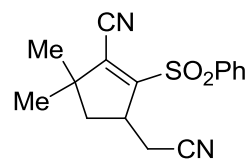
ethyl 2-cyano-5-(2-ethoxy-2-oxoethyl)-4,4-dimethylcyclopent-1-enecarboxylate (2h)



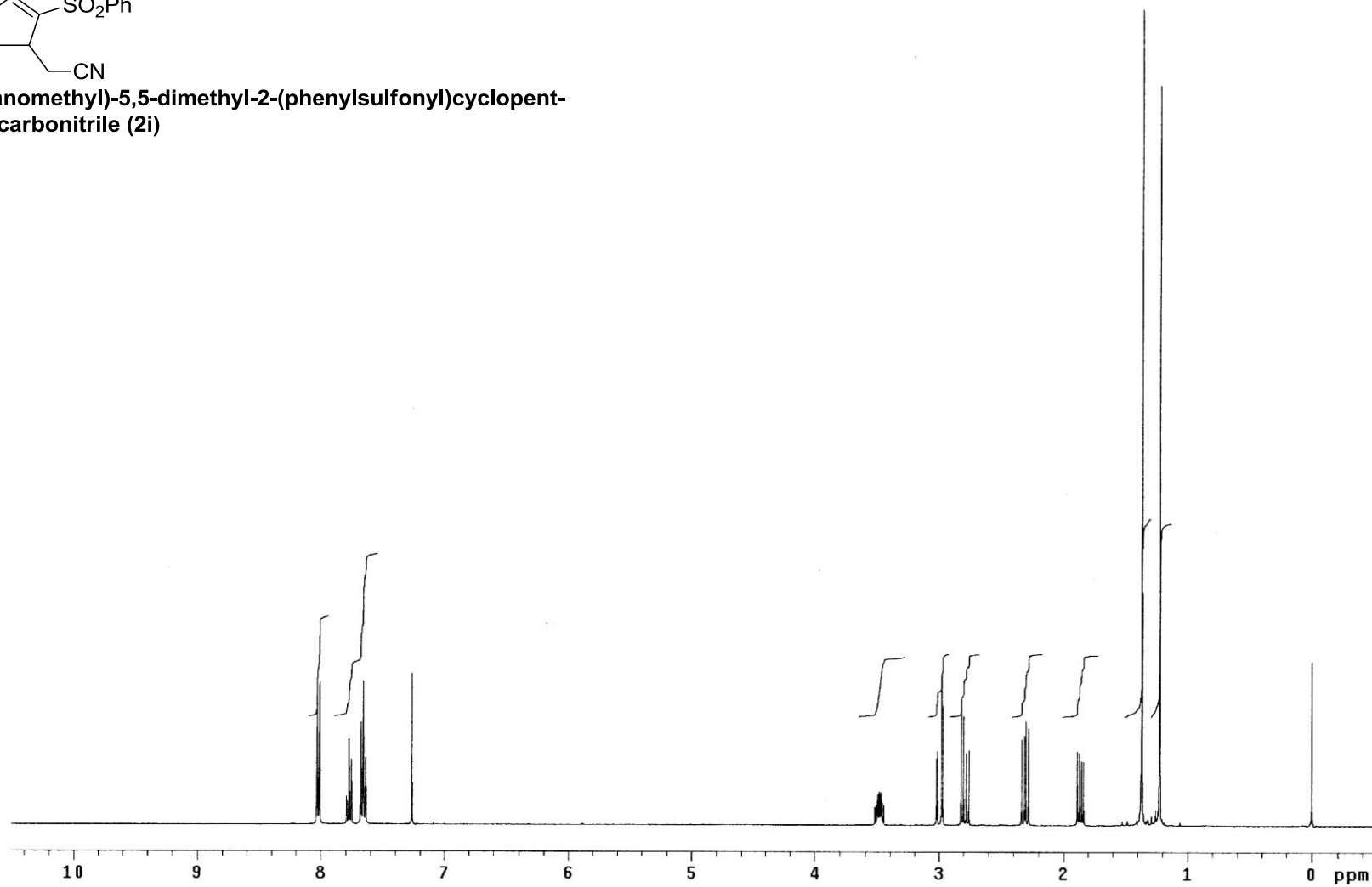


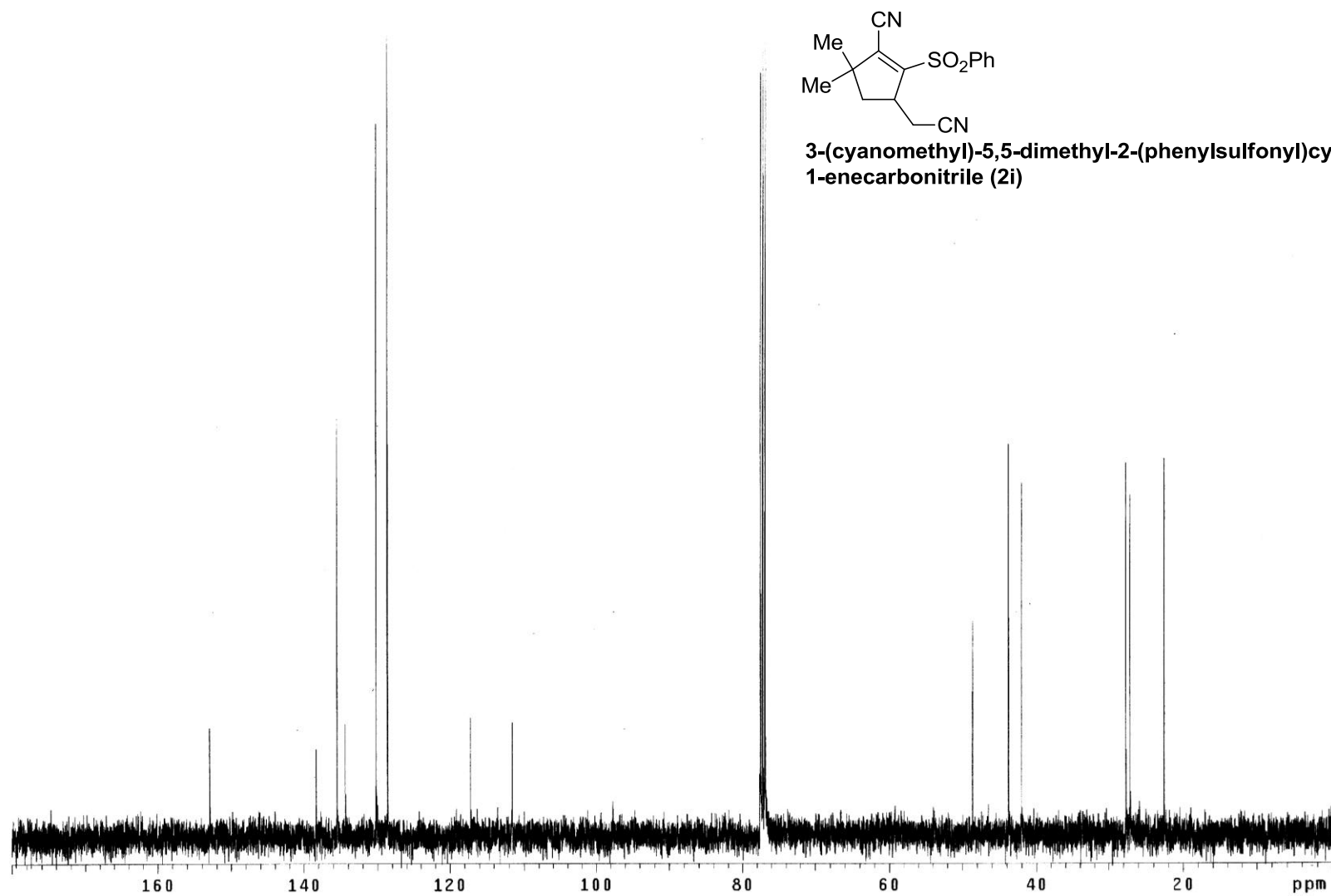
ethyl 2-cyano-5-(2-ethoxy-2-oxoethyl)-4,4-dimethylcyclopent-1-enecarboxylate (2h)

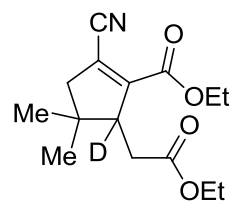




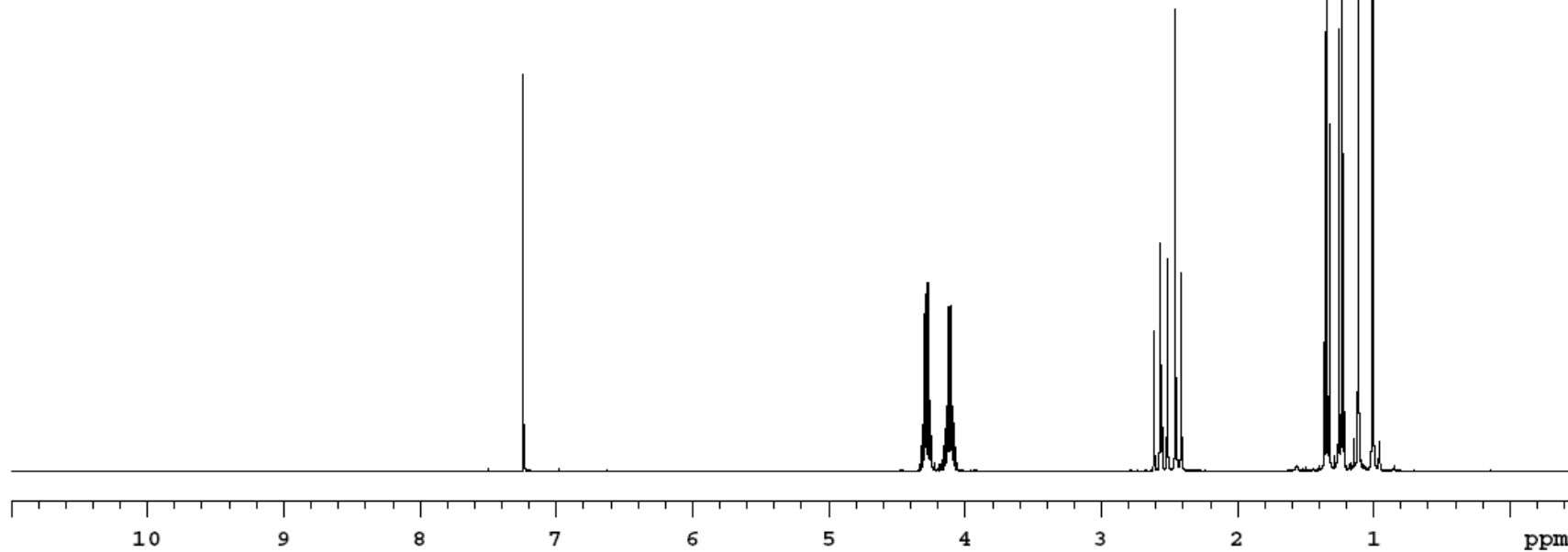
3-(cyanomethyl)-5,5-dimethyl-2-(phenylsulfonyl)cyclopent-1-enecarbonitrile (2i)

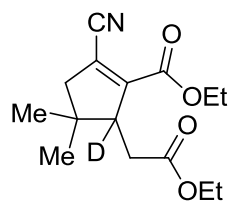




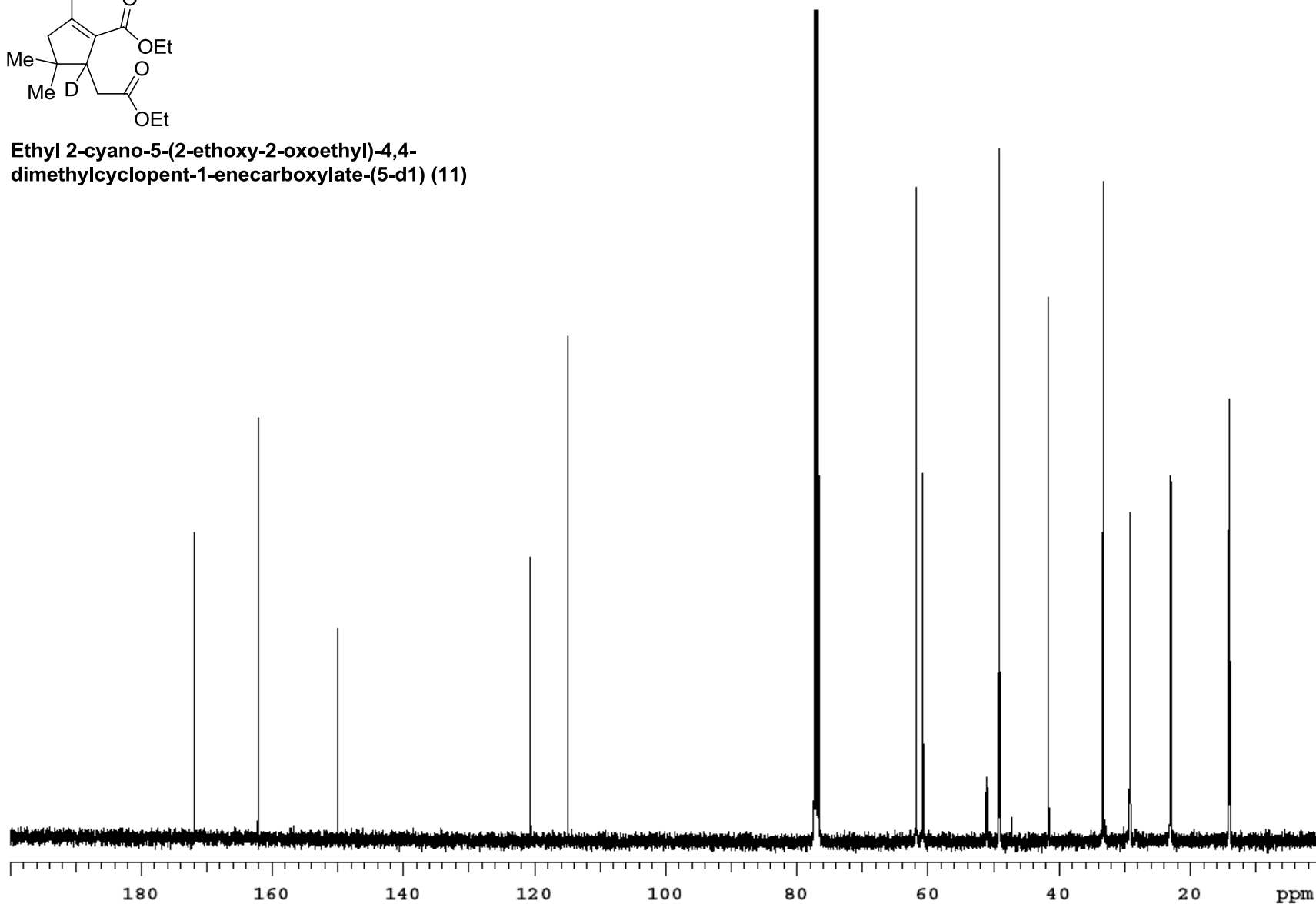


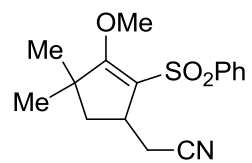
Ethyl 2-cyano-5-(2-ethoxy-2-oxoethyl)-4,4-dimethylcyclopent-1-enecarboxylate-(5-d1) (11)



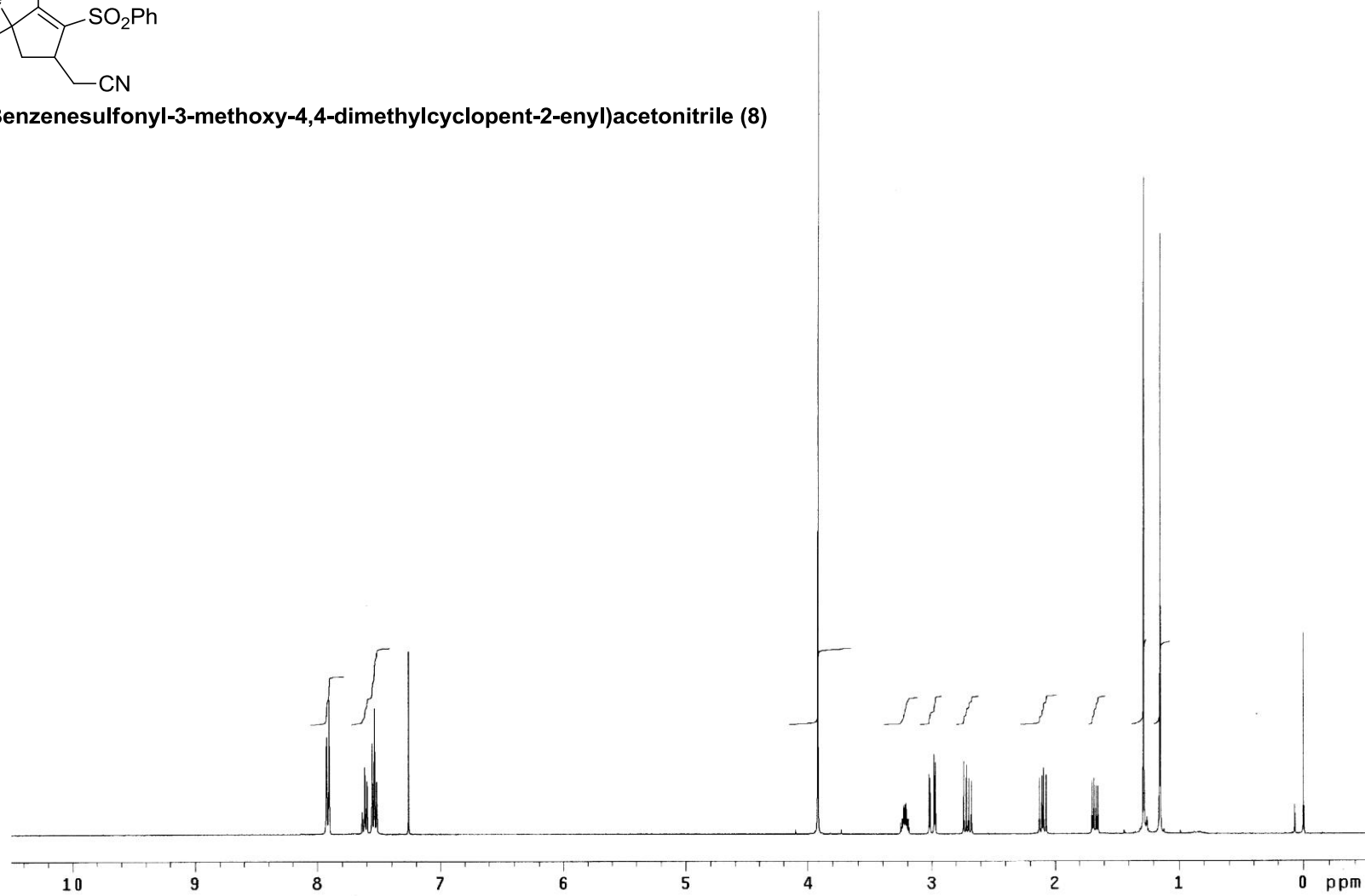


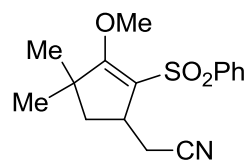
Ethyl 2-cyano-5-(2-ethoxy-2-oxoethyl)-4,4-dimethylcyclopent-1-enecarboxylate-(5-d1) (11)



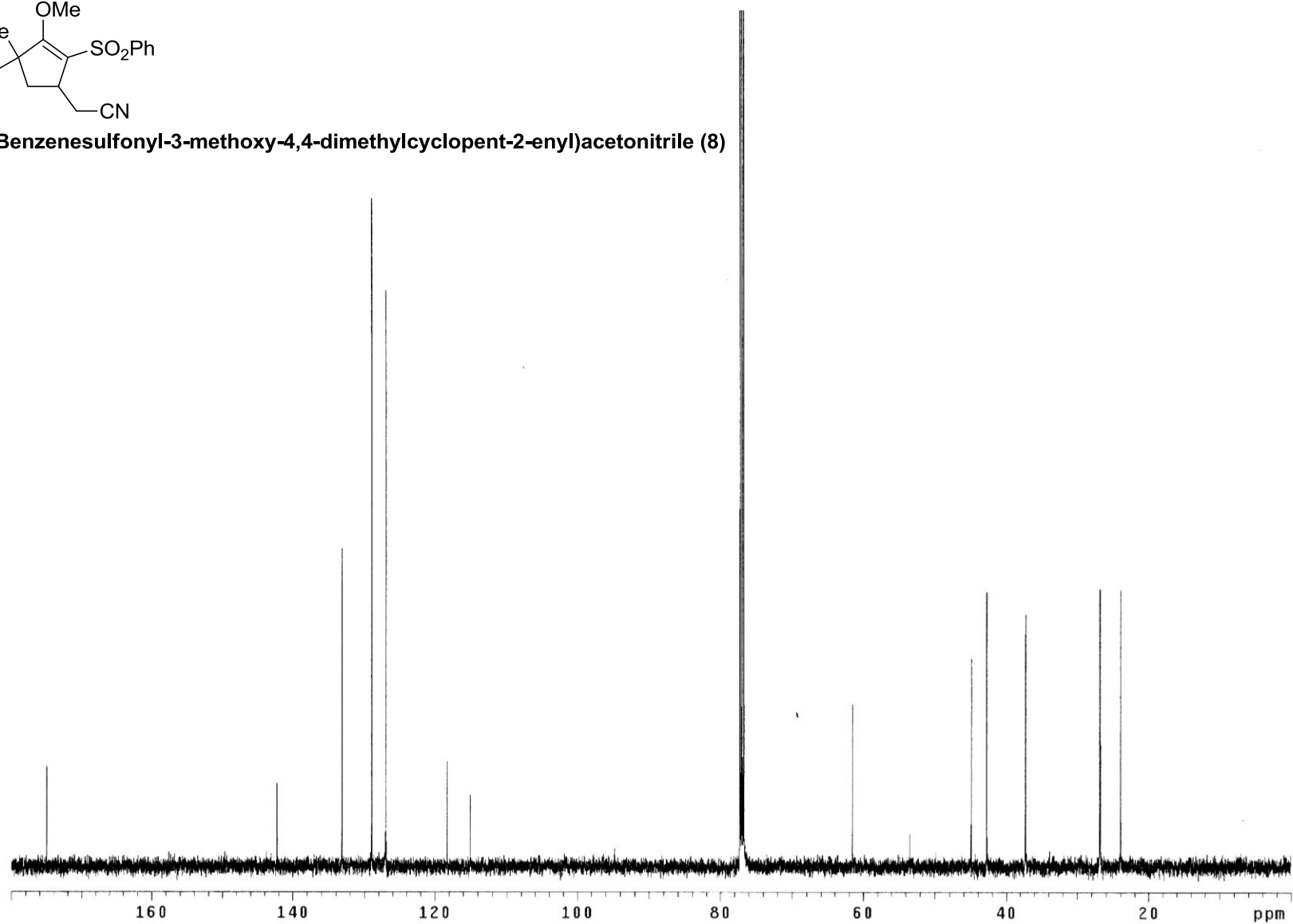


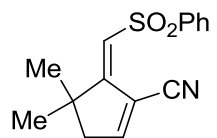
(2-Benzenesulfonyl-3-methoxy-4,4-dimethylcyclopent-2-enyl)acetonitrile (8)



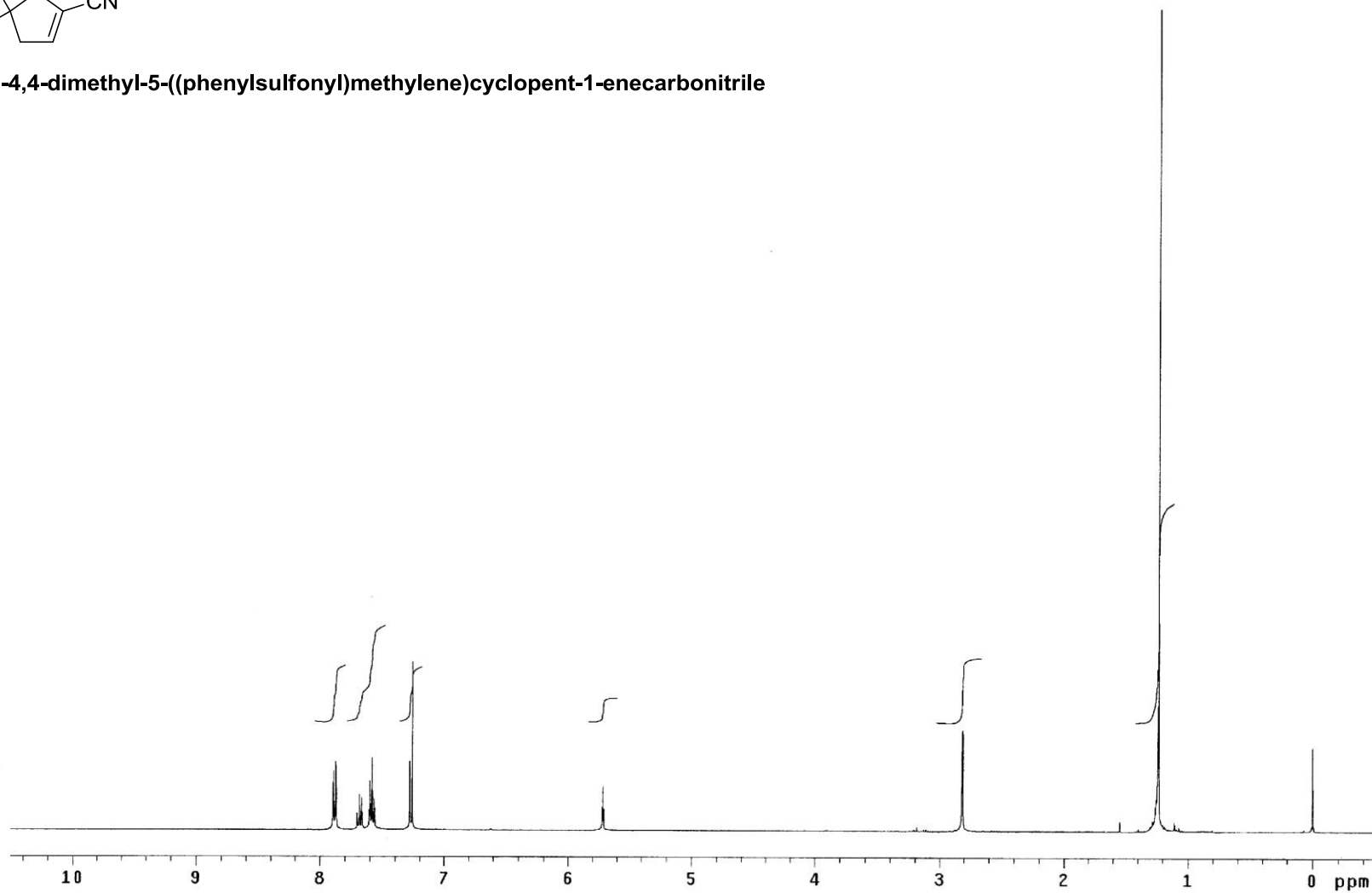


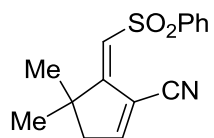
(2-Benzenesulfonyl-3-methoxy-4,4-dimethylcyclopent-2-enyl)acetonitrile (8)





(Z)-4,4-dimethyl-5-((phenylsulfonyl)methylene)cyclopent-1-enecarbonitrile





(Z)-4,4-dimethyl-5-((phenylsulfonyl)methylene)cyclopent-1-enecarbonitrile

