

EFFICIENT DESULFINATIVE CROSS-COUPPLING OF HETEROAROMATIC SULFINATES WITH ARYL TRIFLATE IN ENVIRONMENTALLY FRIENDLY PROTIC SOLVENTS

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Table of Contents

Procedure for the synthesis of 1,1,1-trifluoro-N-(pyridin-2-yl)-N-((trifluoromethyl)sulfonyl) methanesulfonamide (2a)	S2
General Procedure for the Formation of Aryl Triflates (D).....	S2
References	S2
¹ H and ¹³ C NMR Spectra of Compounds 2b to 3l	S3

1,1,1-trifluoro-N-(pyridin-2-yl)-N-((trifluoromethyl)sulfonyl)methanesulfonamide (2a).¹

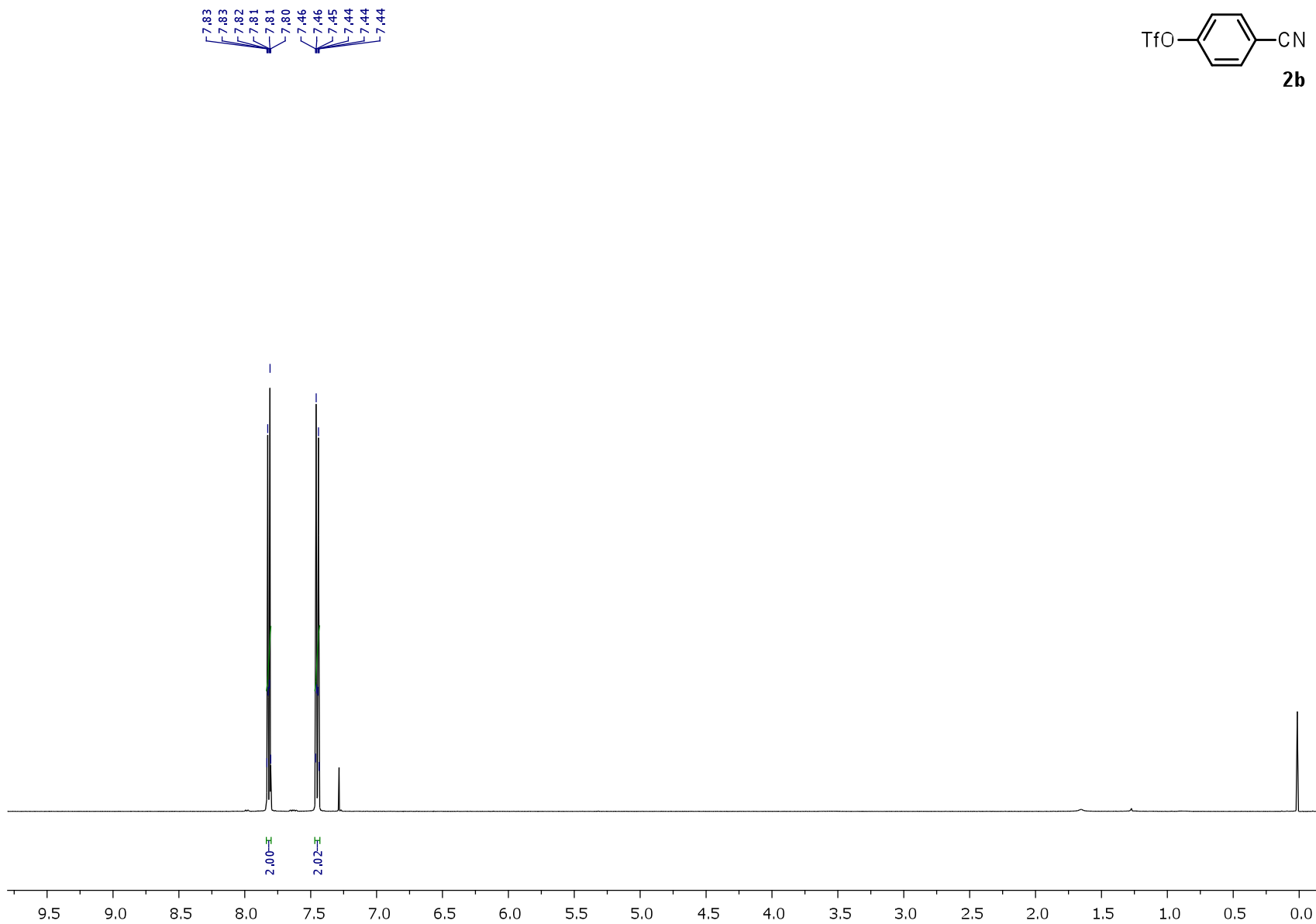
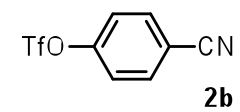
To flame-dry three-neck round-bottomed flask equipped with addition funnel and magnetic stir bar was added 2-aminopyridine (4.17 g, 44.3 mmol) in dry CH₂Cl₂ (177 mL) under argon atmosphere. Pyridine (7.15 mL, 88.6 mmol) was added to the solution and the reaction media was cooled to – 78 °C. A solution of trifluoromethane sulfonic anhydride (14.5 mL, 88.6 mmol) in dry CH₂Cl₂ (33.0 mL) was added dropwise to the reaction *via* a flame-dried addition funnel for 3.5 h. The reaction mixture was stirred for 2 h at – 78 °C, and was then stirred for 19 h at room temperature. The reaction media was quenched with ice-water mix (100 mL), and extracted with CH₂Cl₂ (4 x 100 mL). Combined organic phases were washed with a 10 % (w/v) solution of NaOH (180 mL), followed by ice-water (1 x 180 mL), and a saturated solution of NaCl (1 x 180 mL). Organic phases were dried with Na₂SO₄, filtered and evaporated to obtain a brown oil. Purification by vacuum micro-distillation afforded the desired compound in 86% yield (13.59 g) as a white solid.

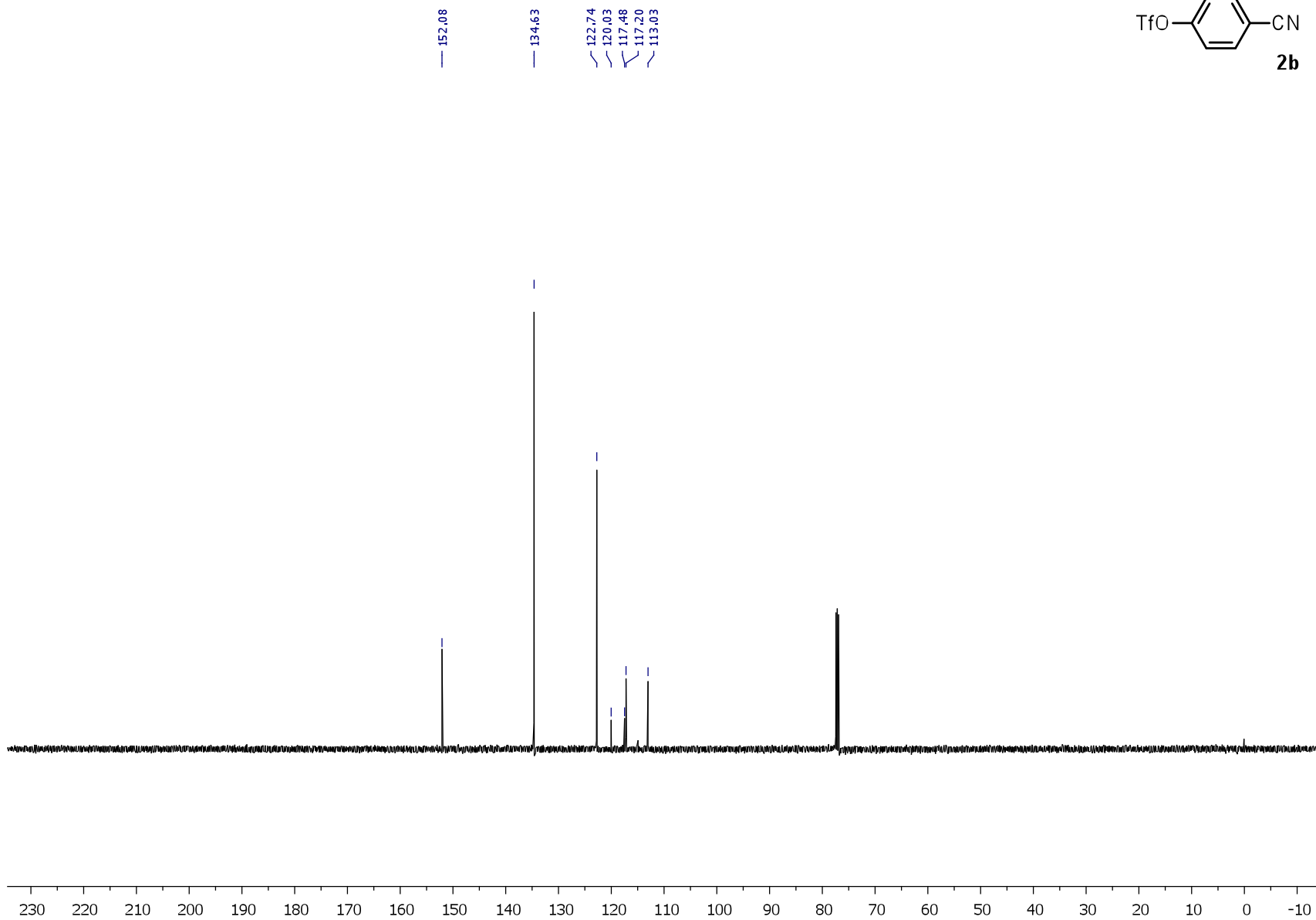
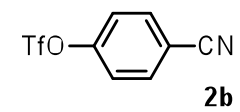
General procedure for the formation of aryl triflates (D).²

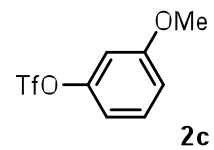
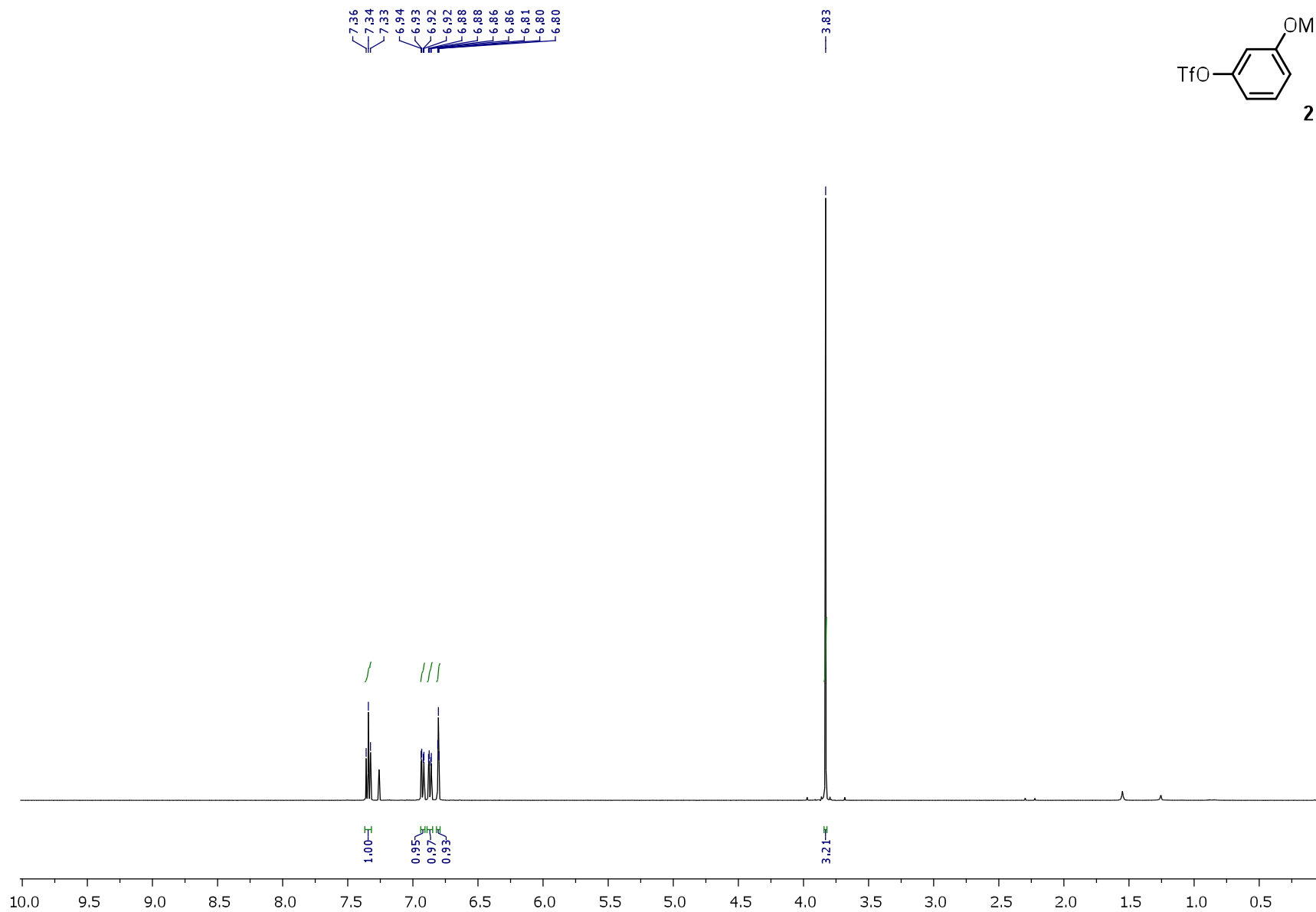
To a flame-dried round-bottomed flask equipped with a magnetic stir bar was added phenol (3.12 mmol, 1.0 equiv.) and NEt₃ (9.36 mmol, 3.0 equiv.) in dry CH₂Cl₂ (31 mL) under argon atmosphere. The reaction media was cooled to 0 °C, and the triflating agent **2a** was added. The reaction was warmed to room temperature and stirred for 2 h. Et₂O (45 mL) and water (30 mL) were added to the reaction media, and the two phases were separated. Aqueous phase was washed with Et₂O (3 x 30 mL). Combined organic phases were washed with a saturated solution of NaHCO₃ (1 x 30 mL), and a saturated solution of NaCl (2 x 30 mL), dried with Na₂SO₄, filtered and evaporated to obtain an oil. Purification by flash chromatography afforded the expected product. All NMR spectra were in agreement with spectra reported in reference 2.

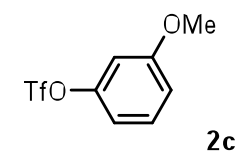
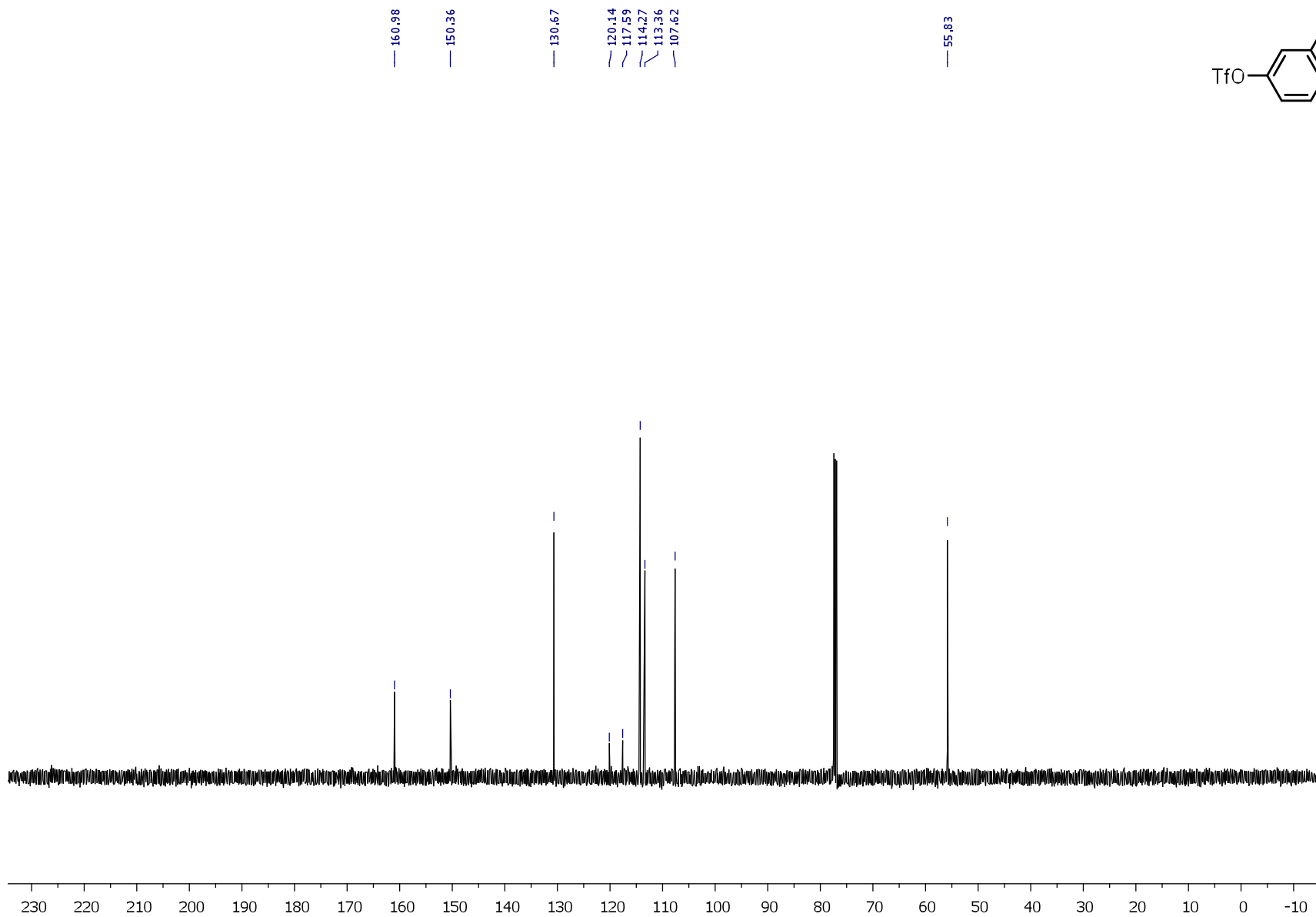
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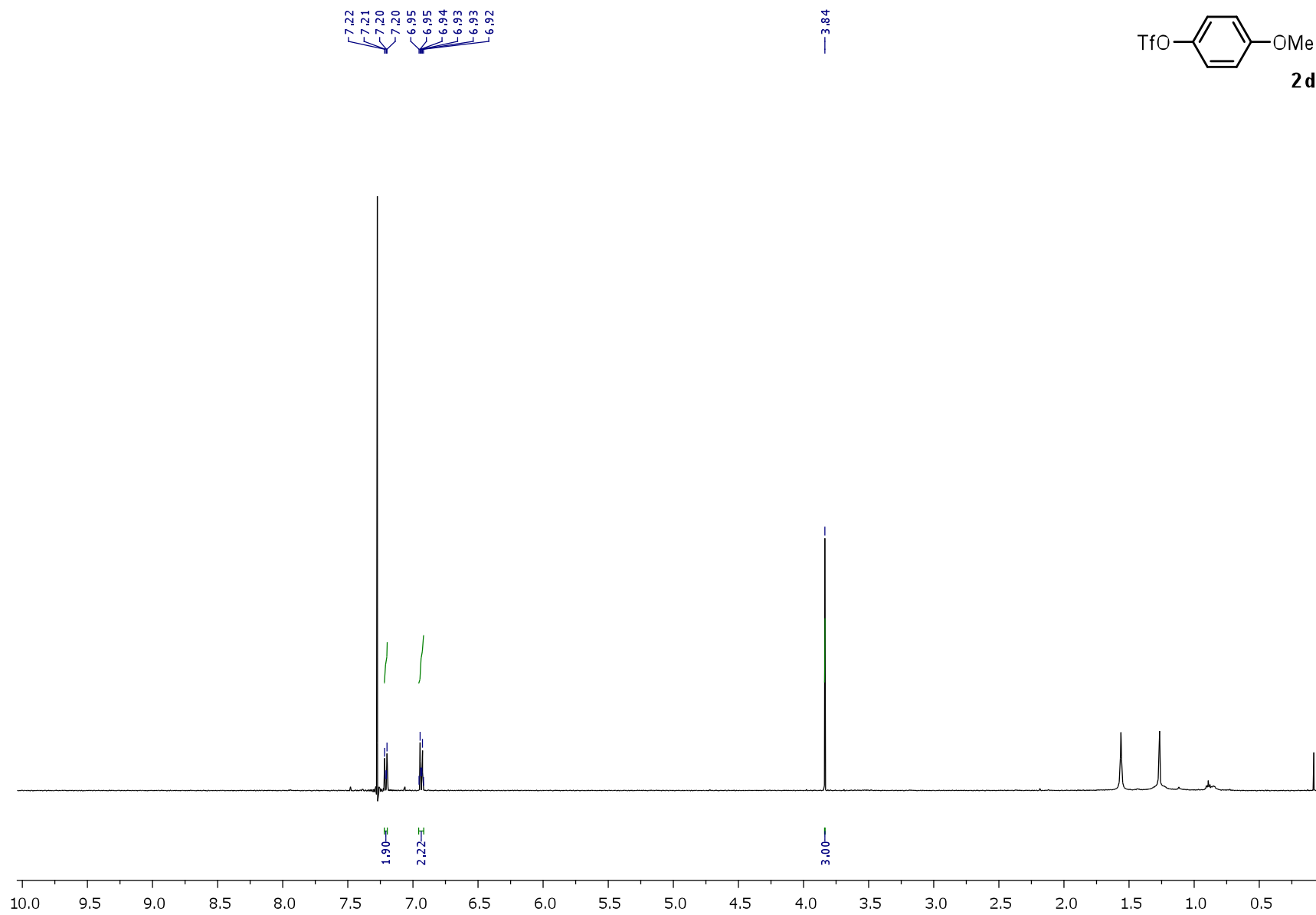
- (1) Comins, D. L. and Dehghani, A. *Tetrahedron Lett.*, 1992, **33**, 6299.
- (2) J. R. Vyvyan, J. A. Dell Nee Meyer, T. J. Ligon, K. K. Motanic and H. S. Wall *Synthesis*, **2010**, 3637.

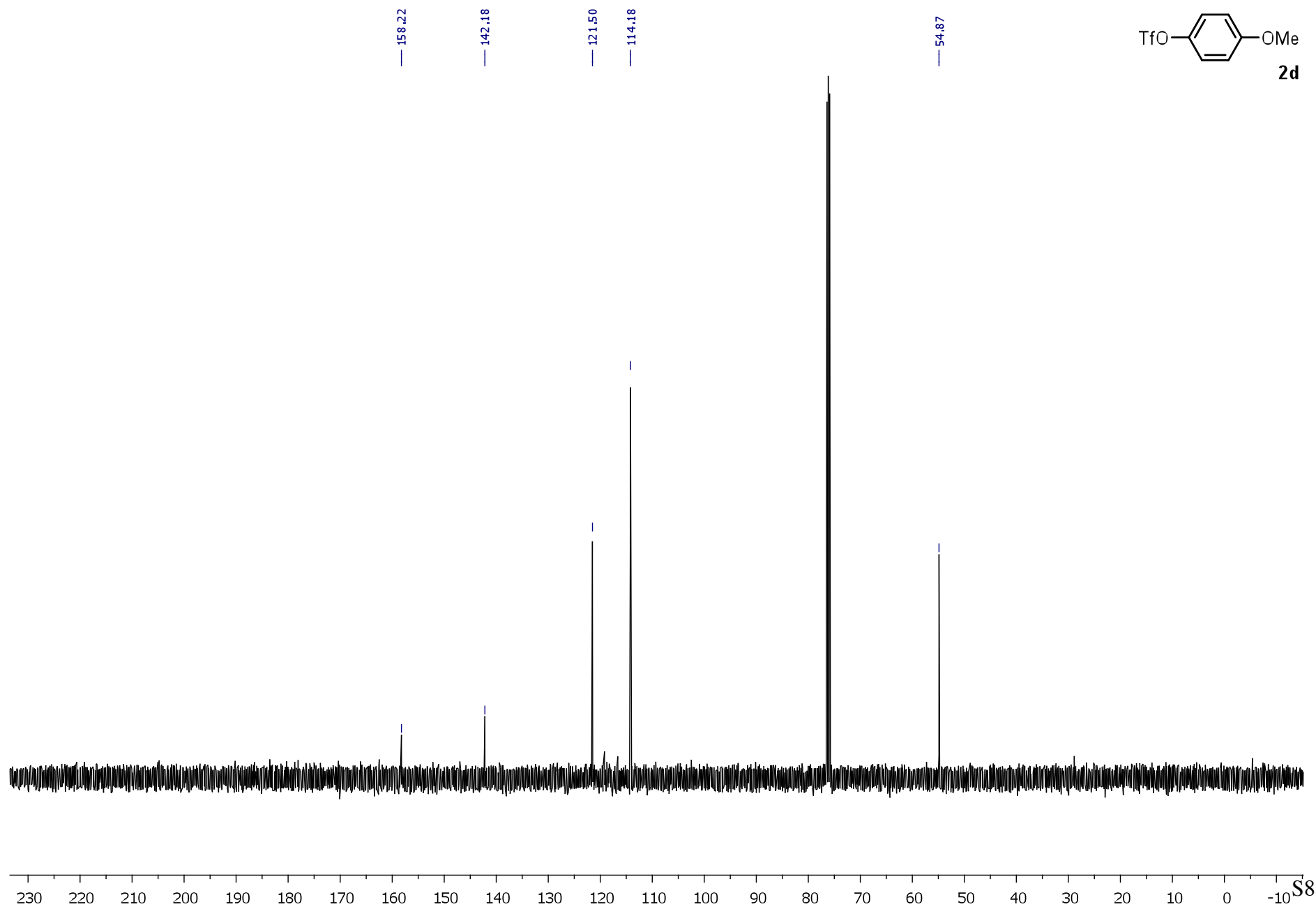
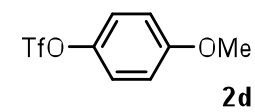


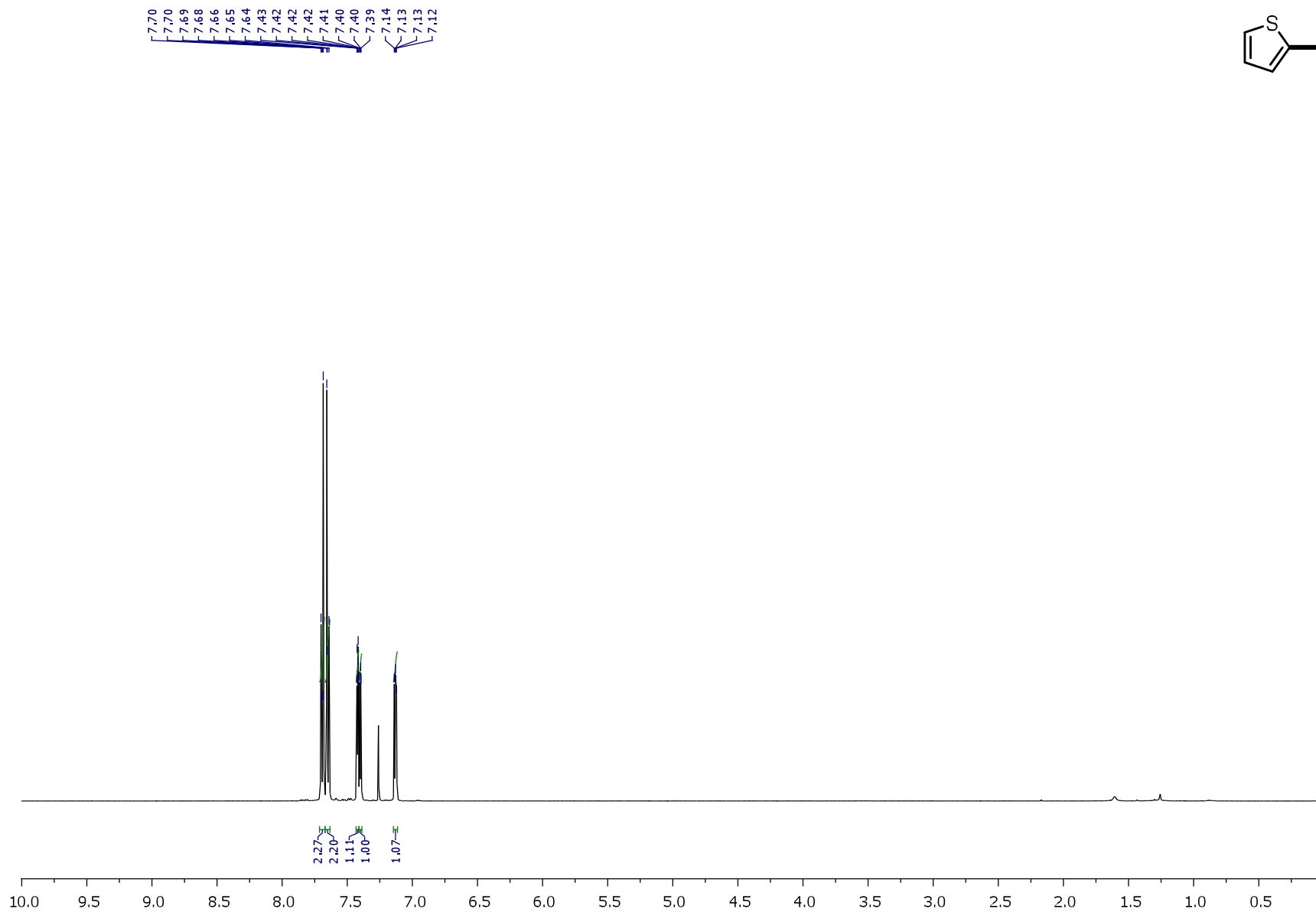
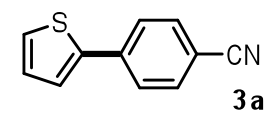


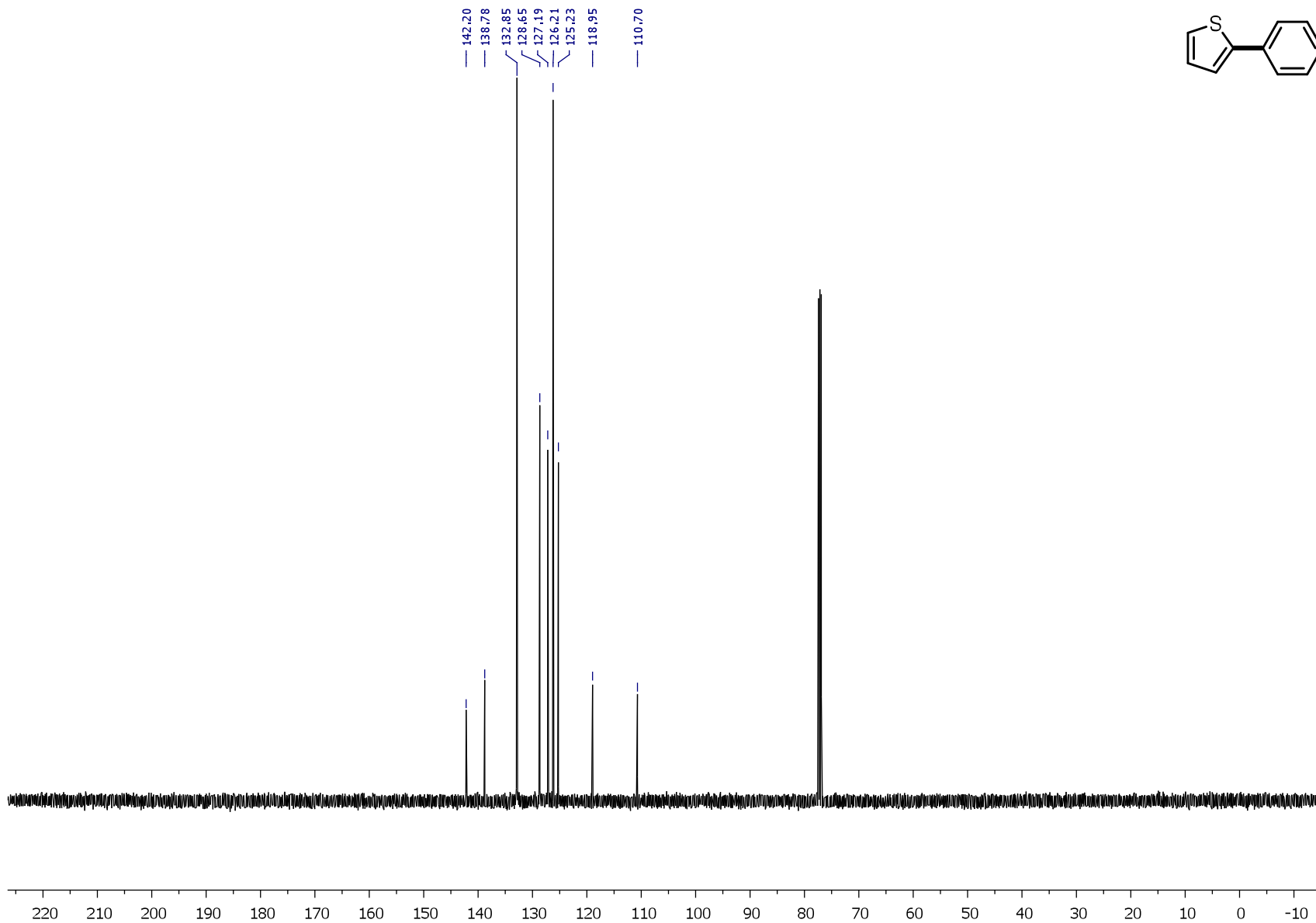
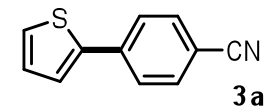


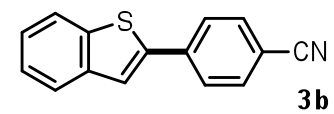
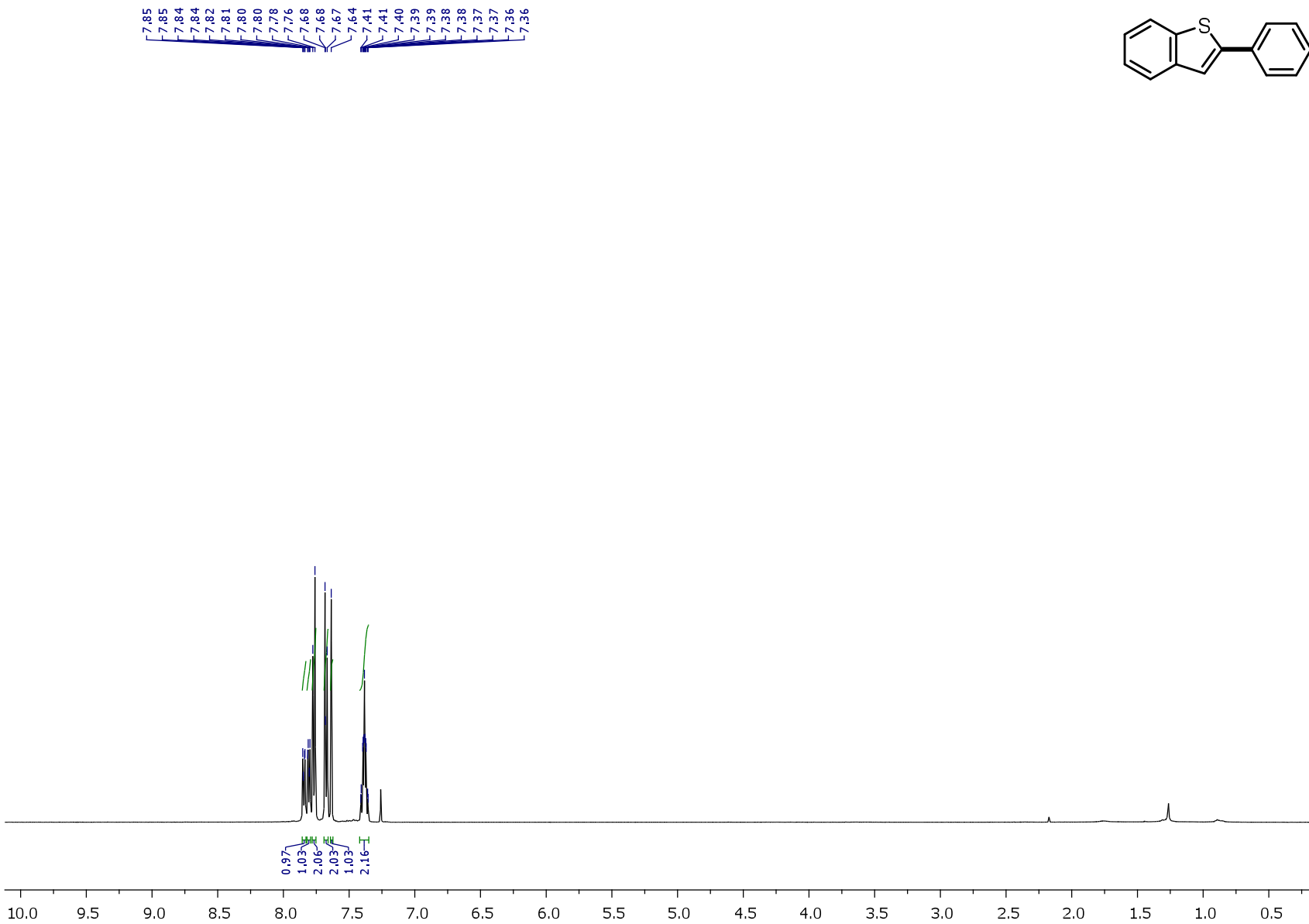


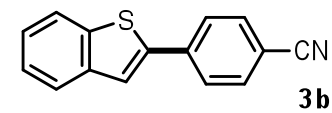
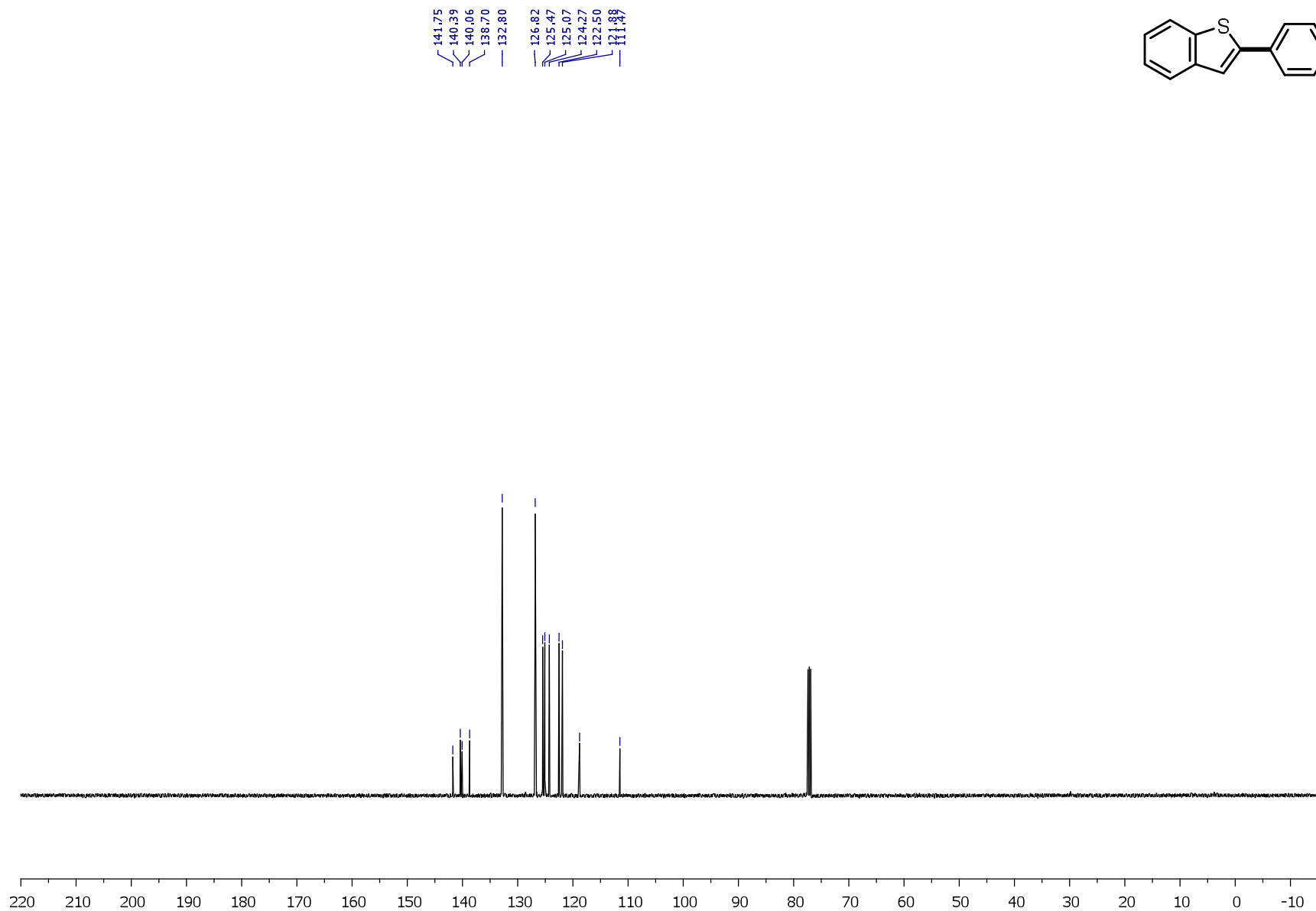


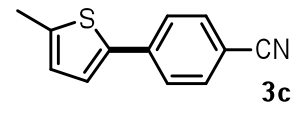
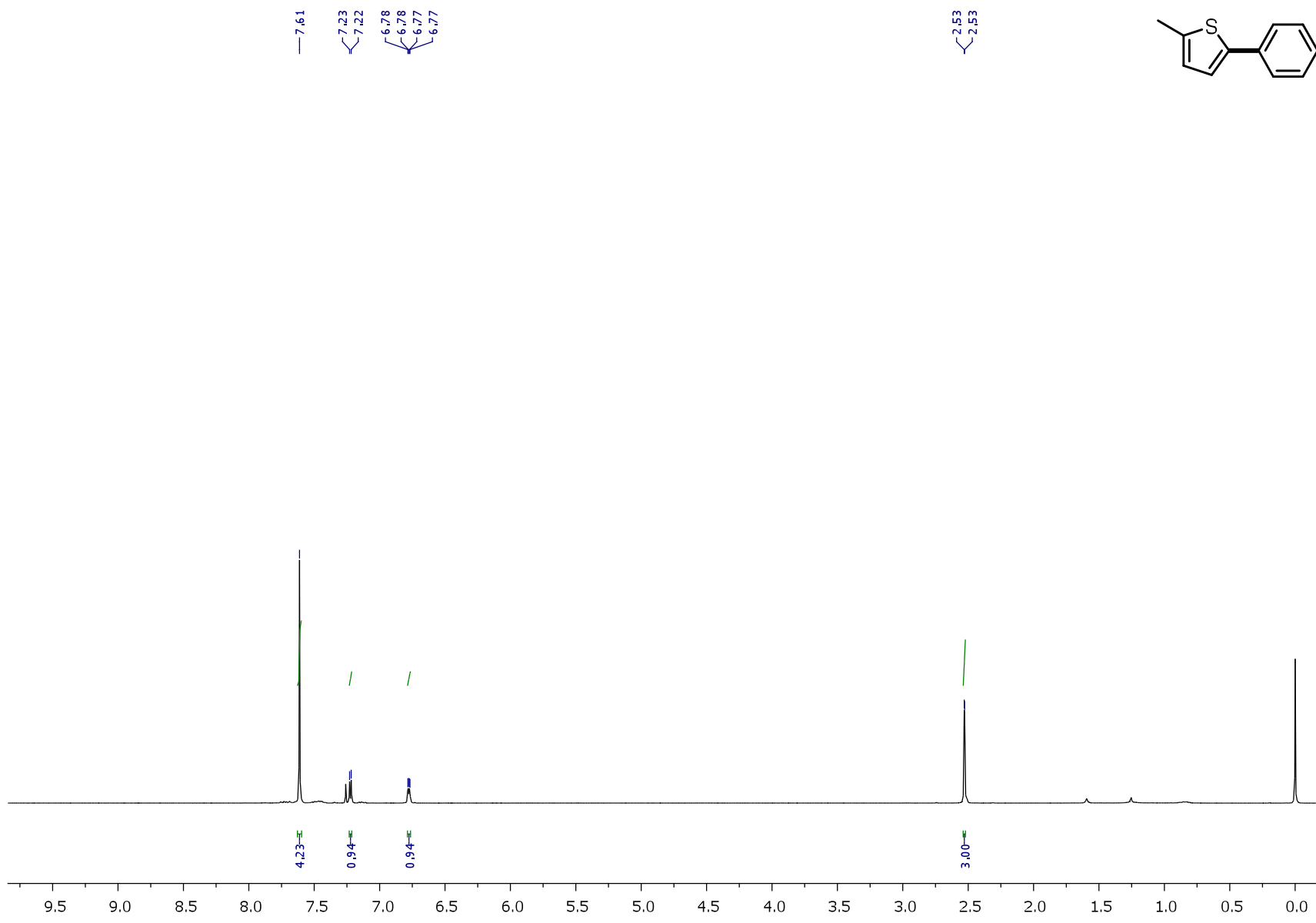


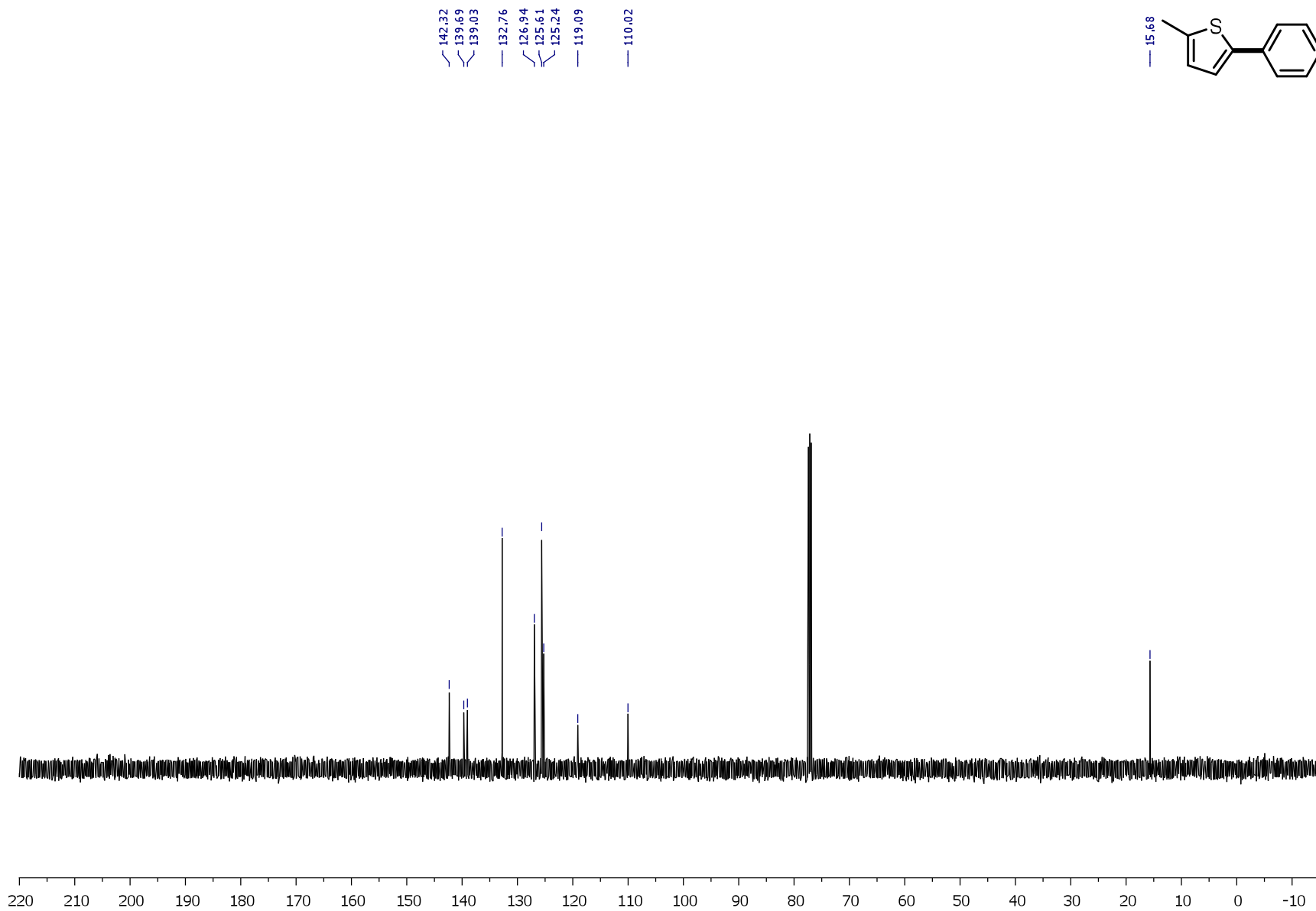


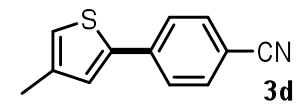
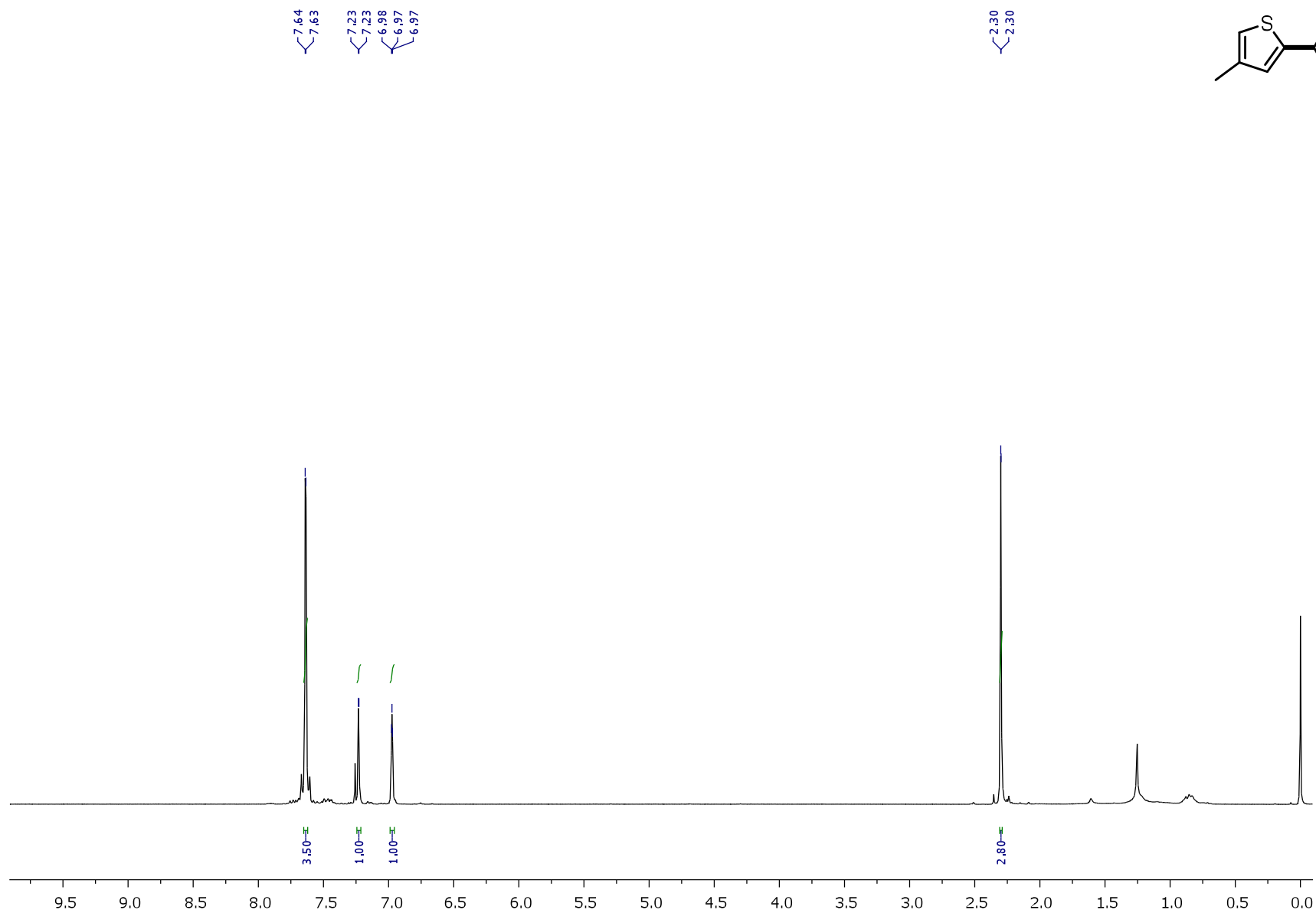


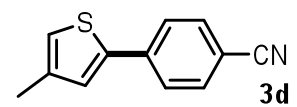
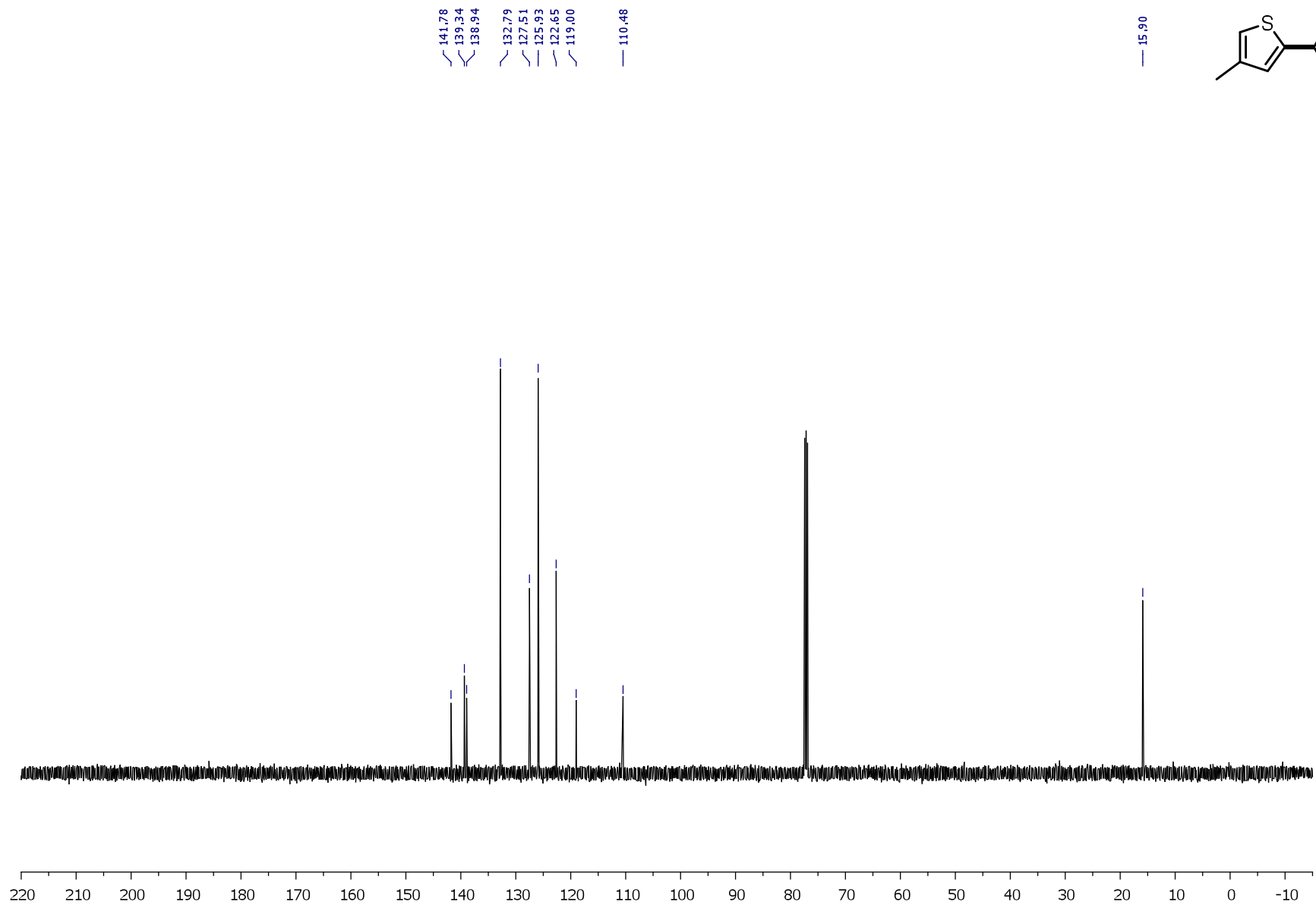


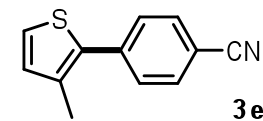
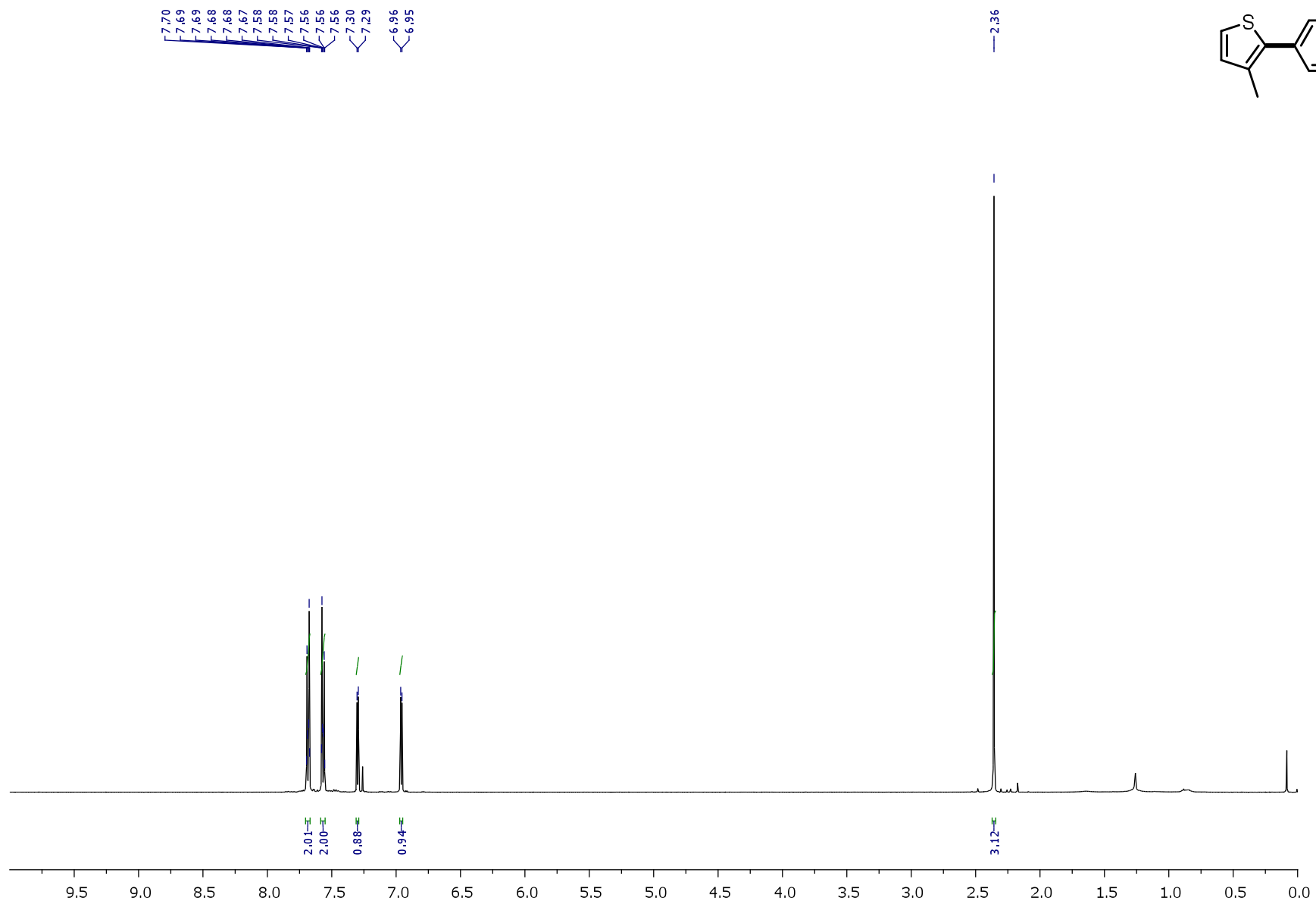


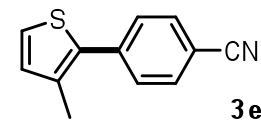
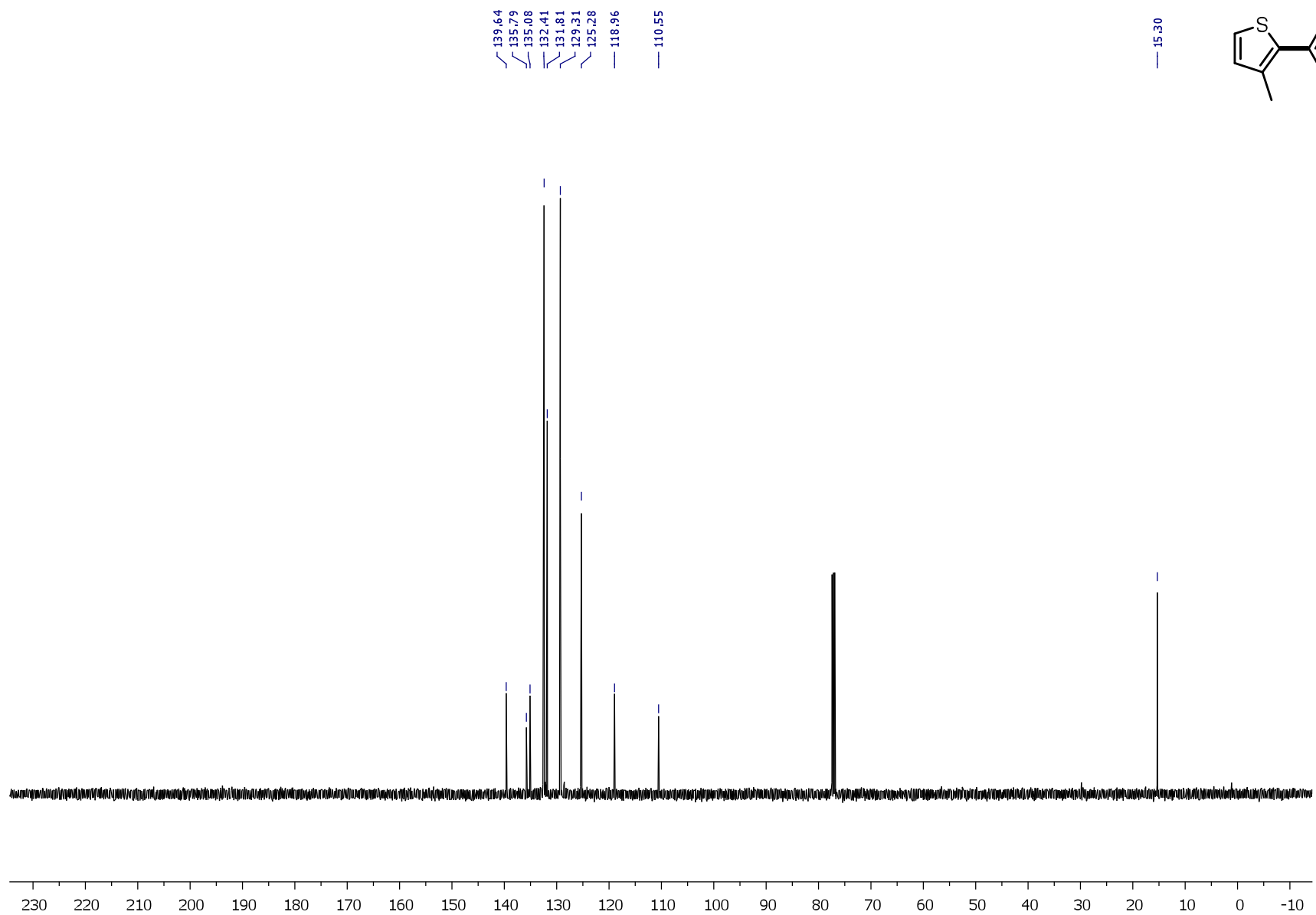


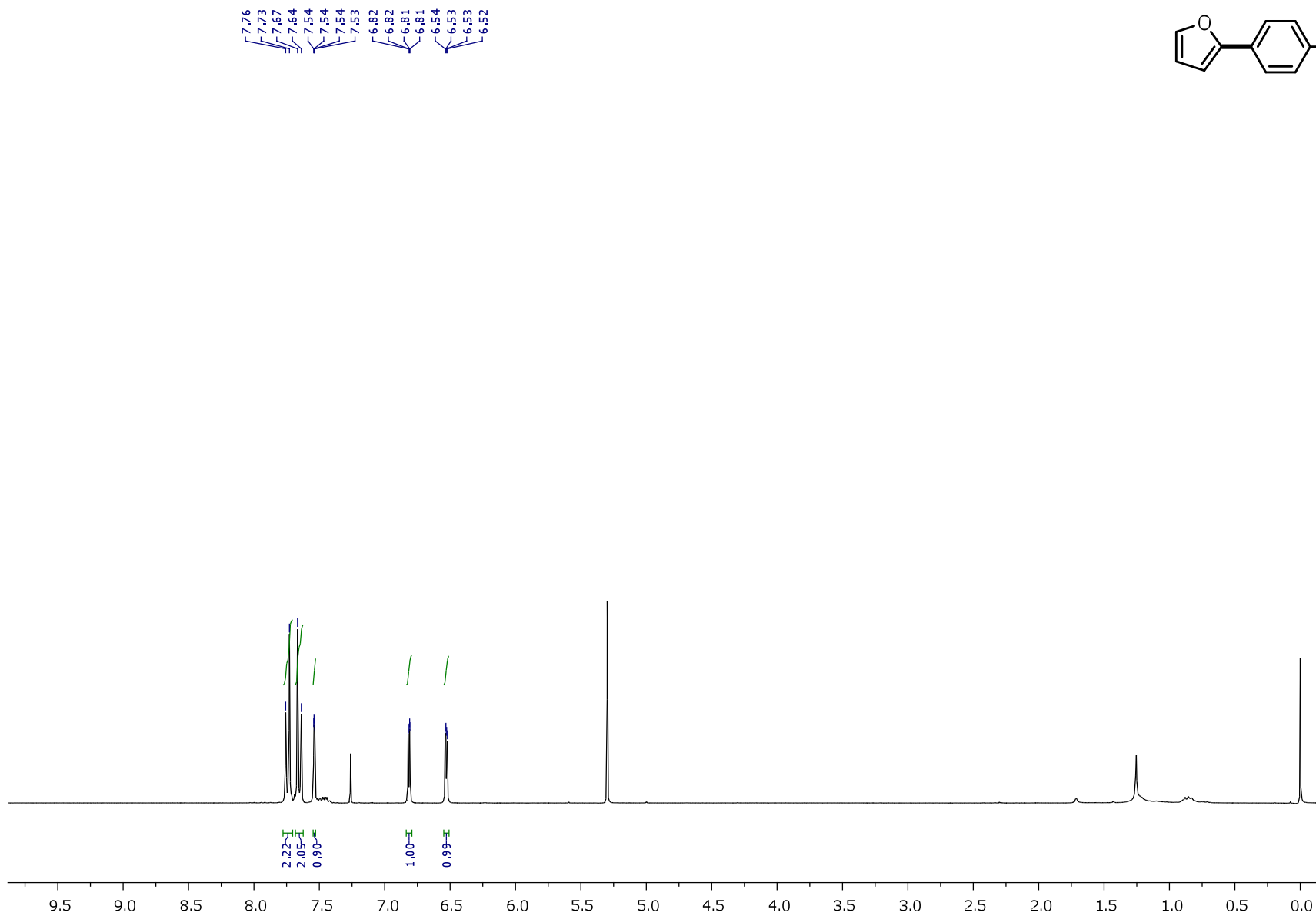
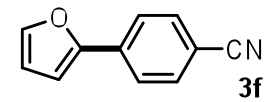


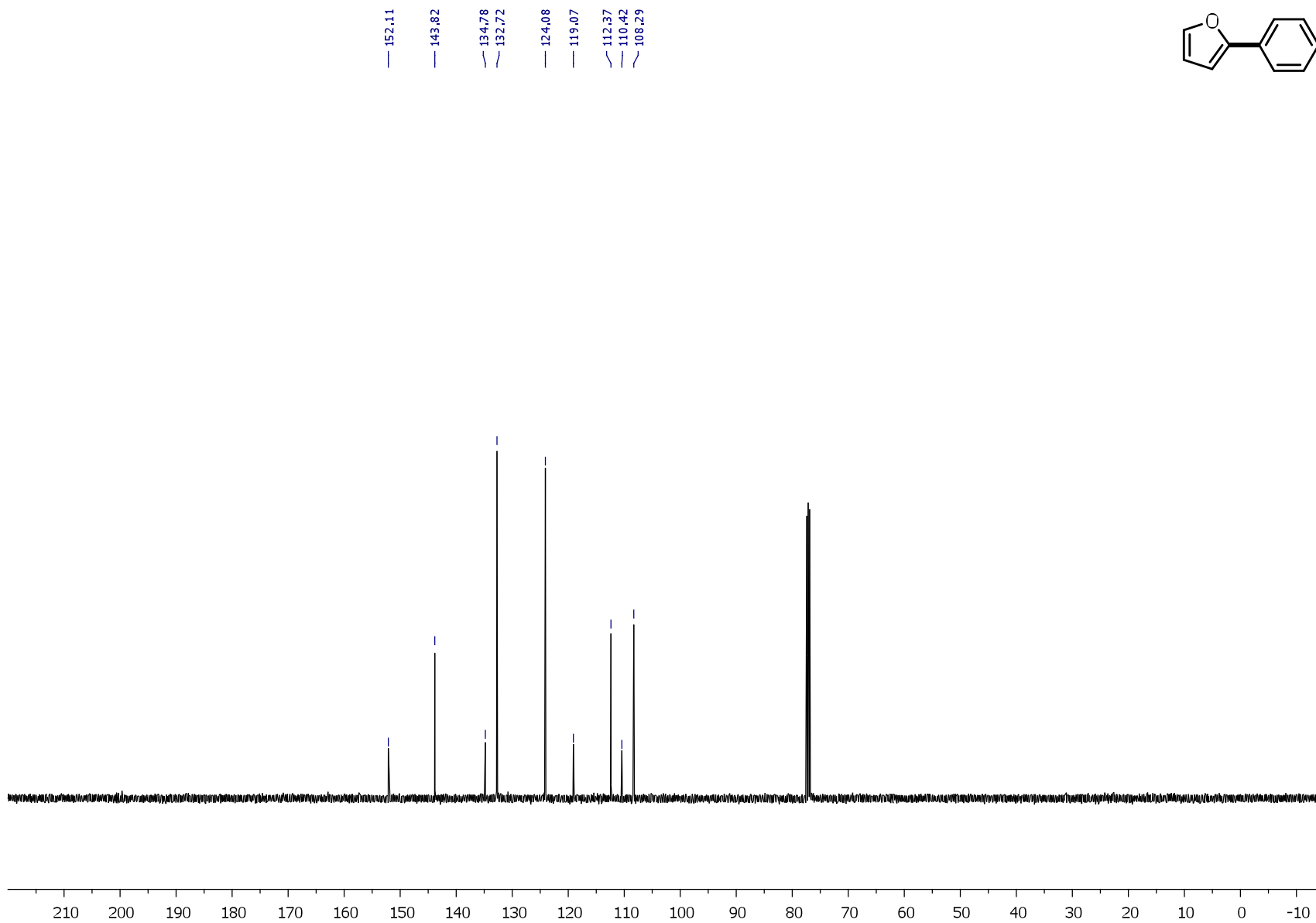
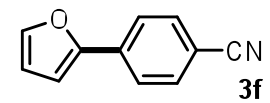


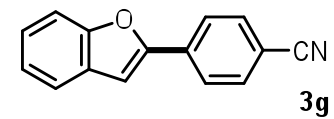
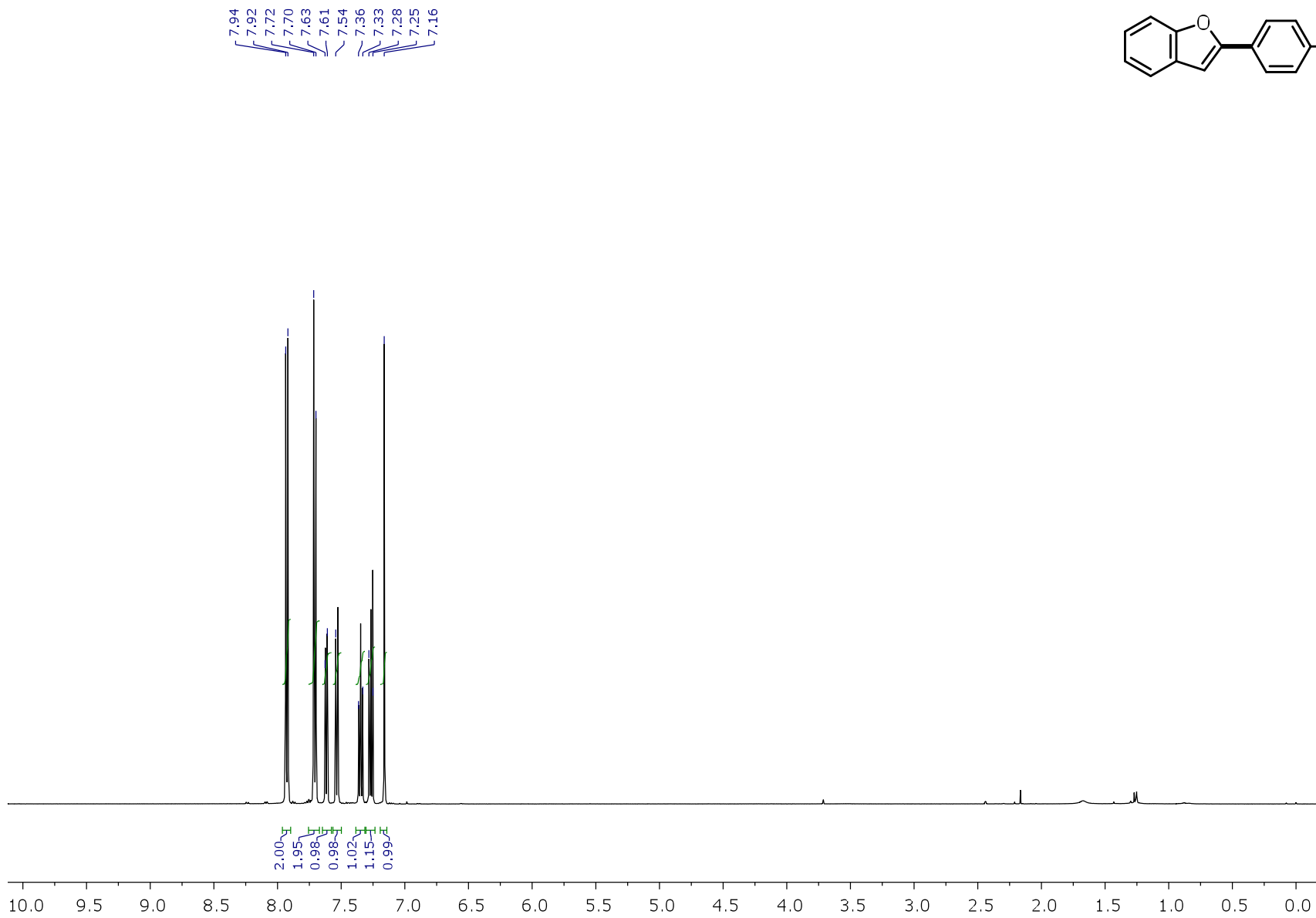


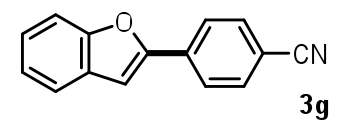
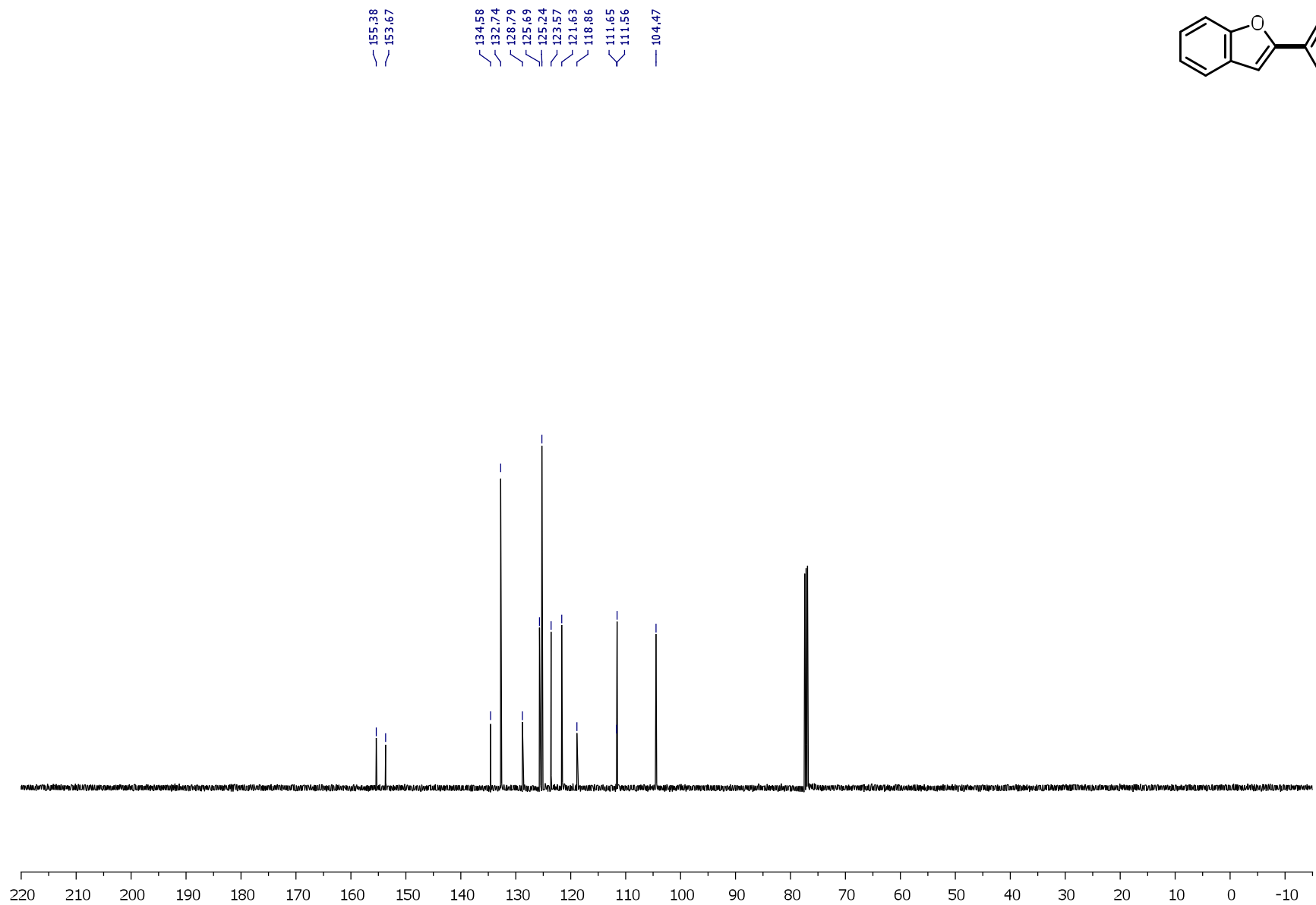


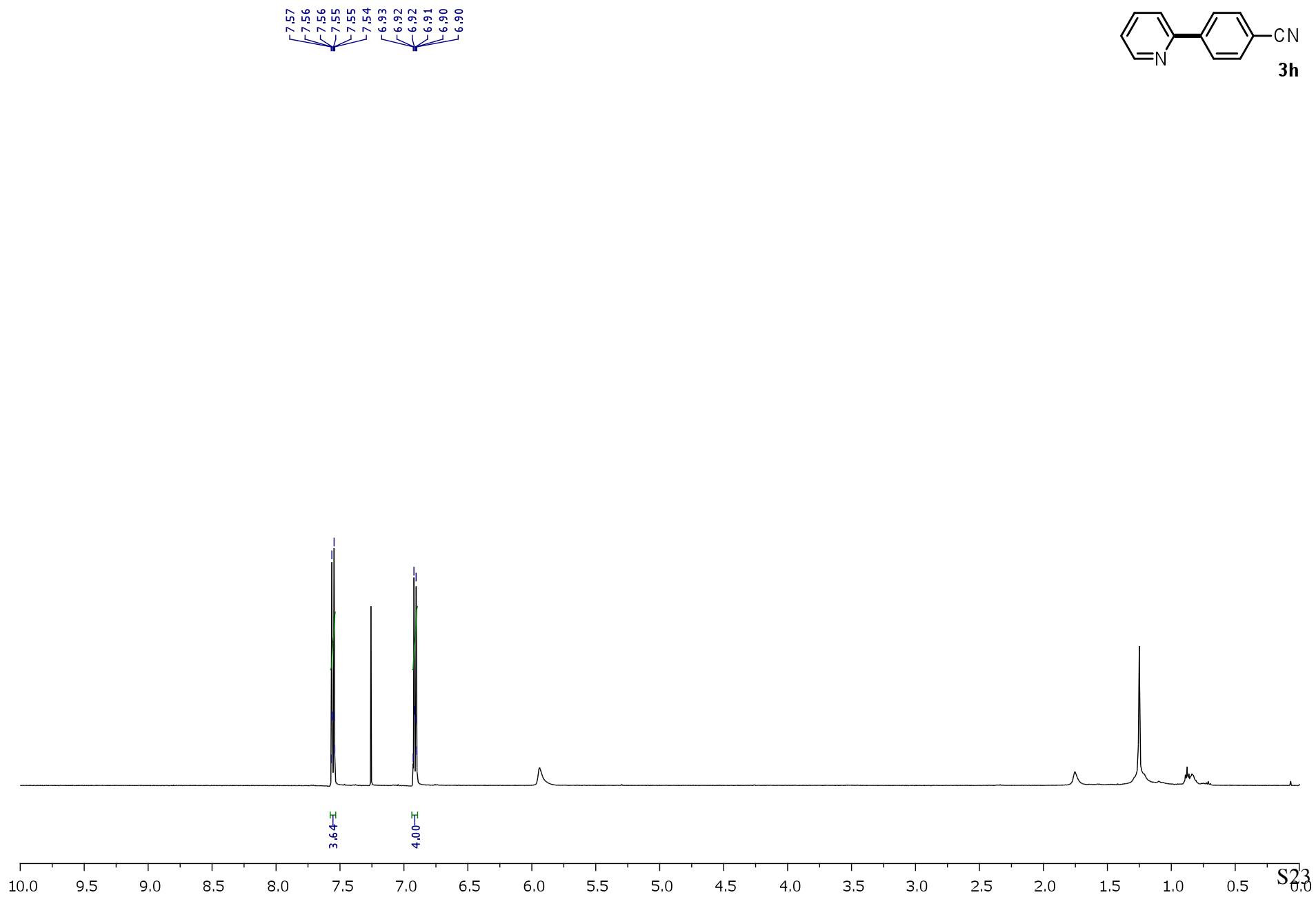
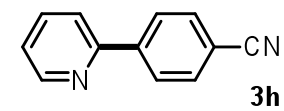


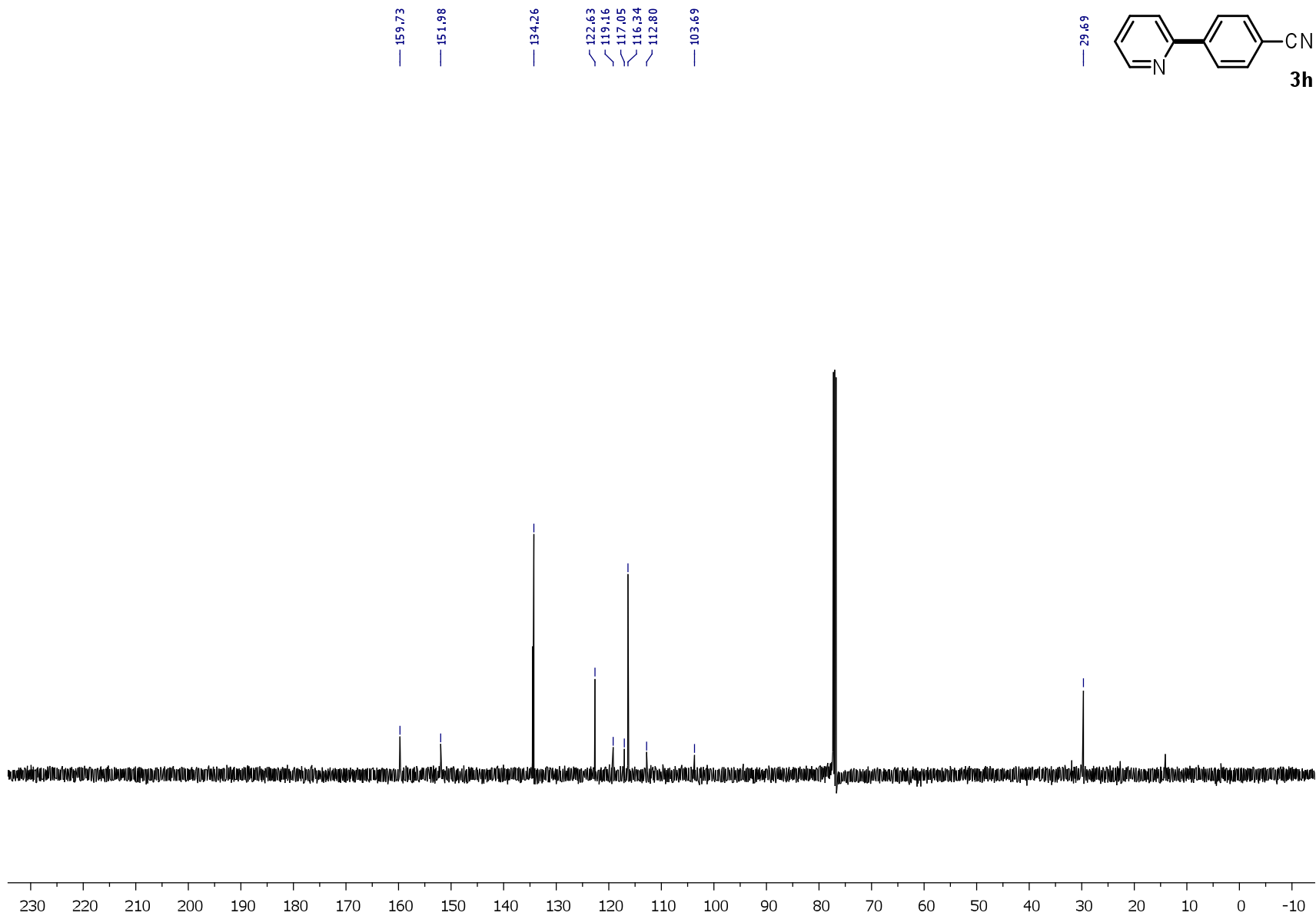


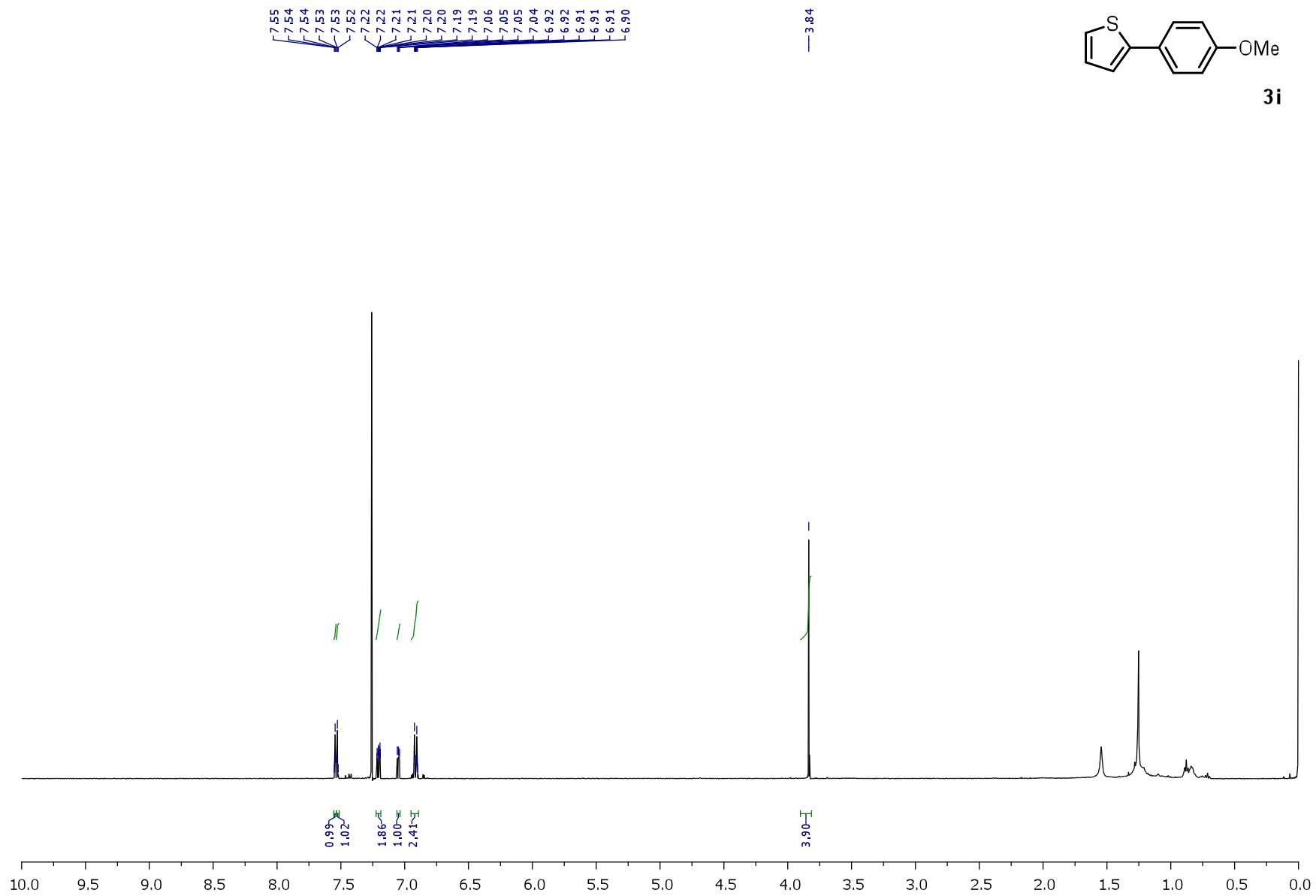


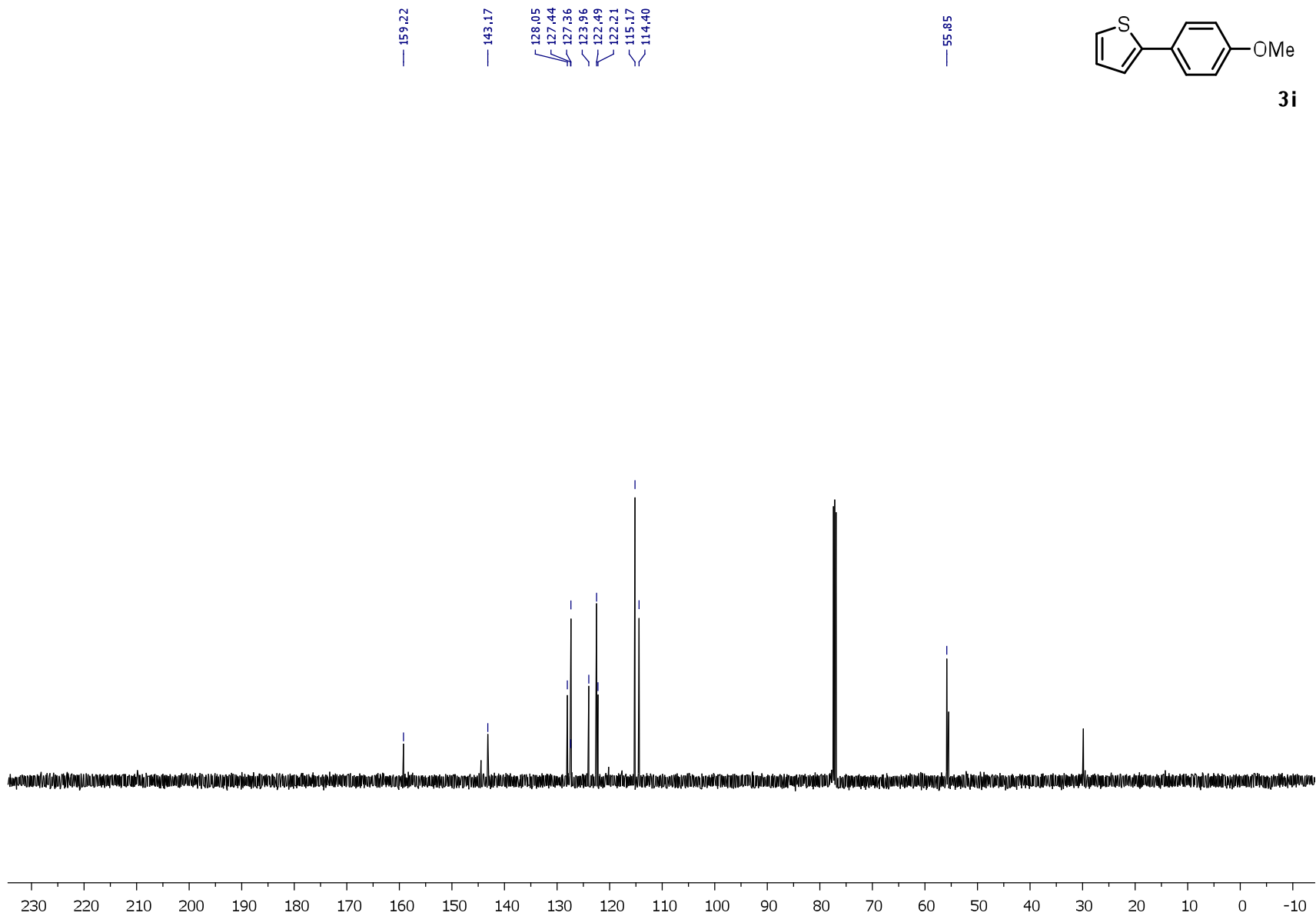


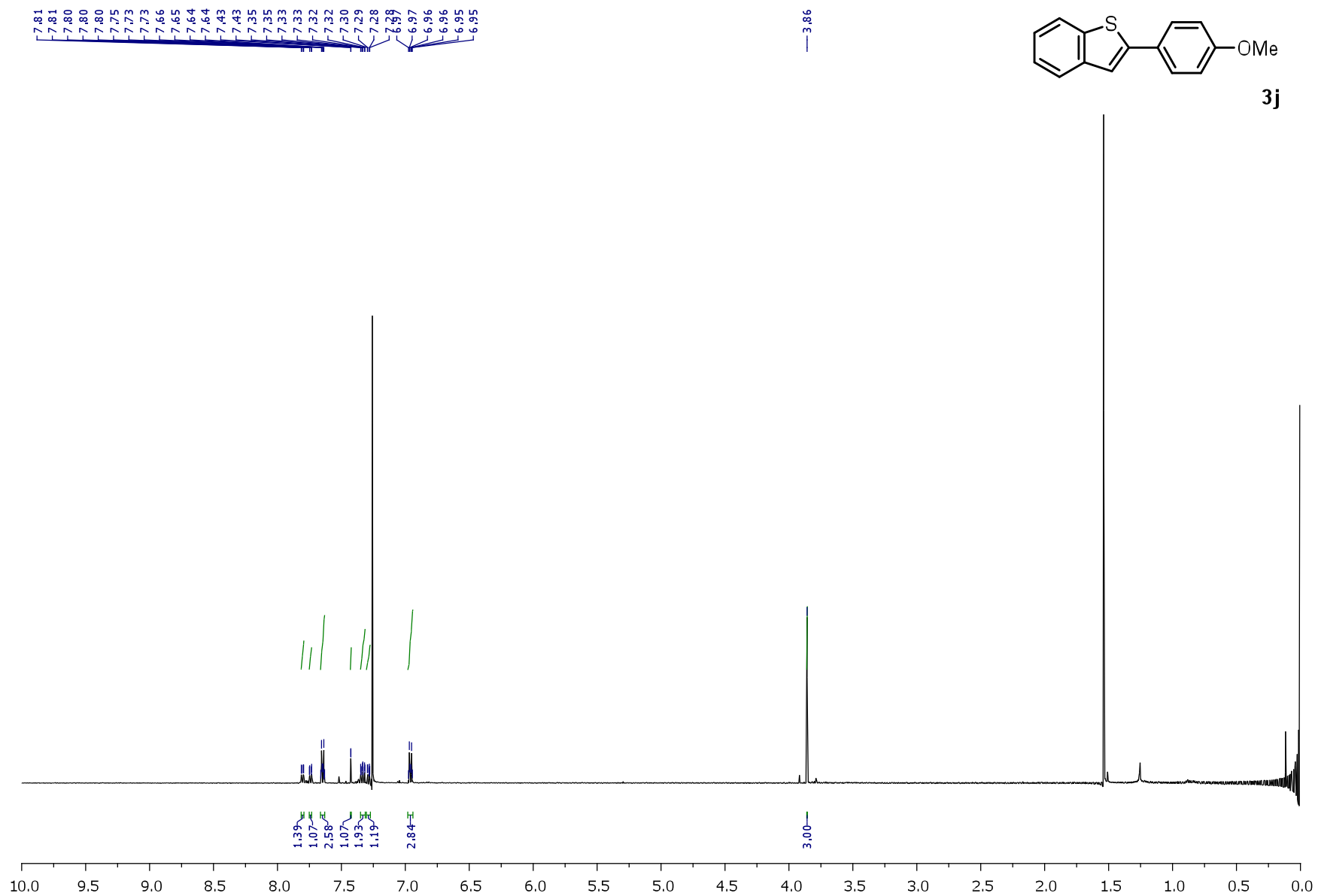


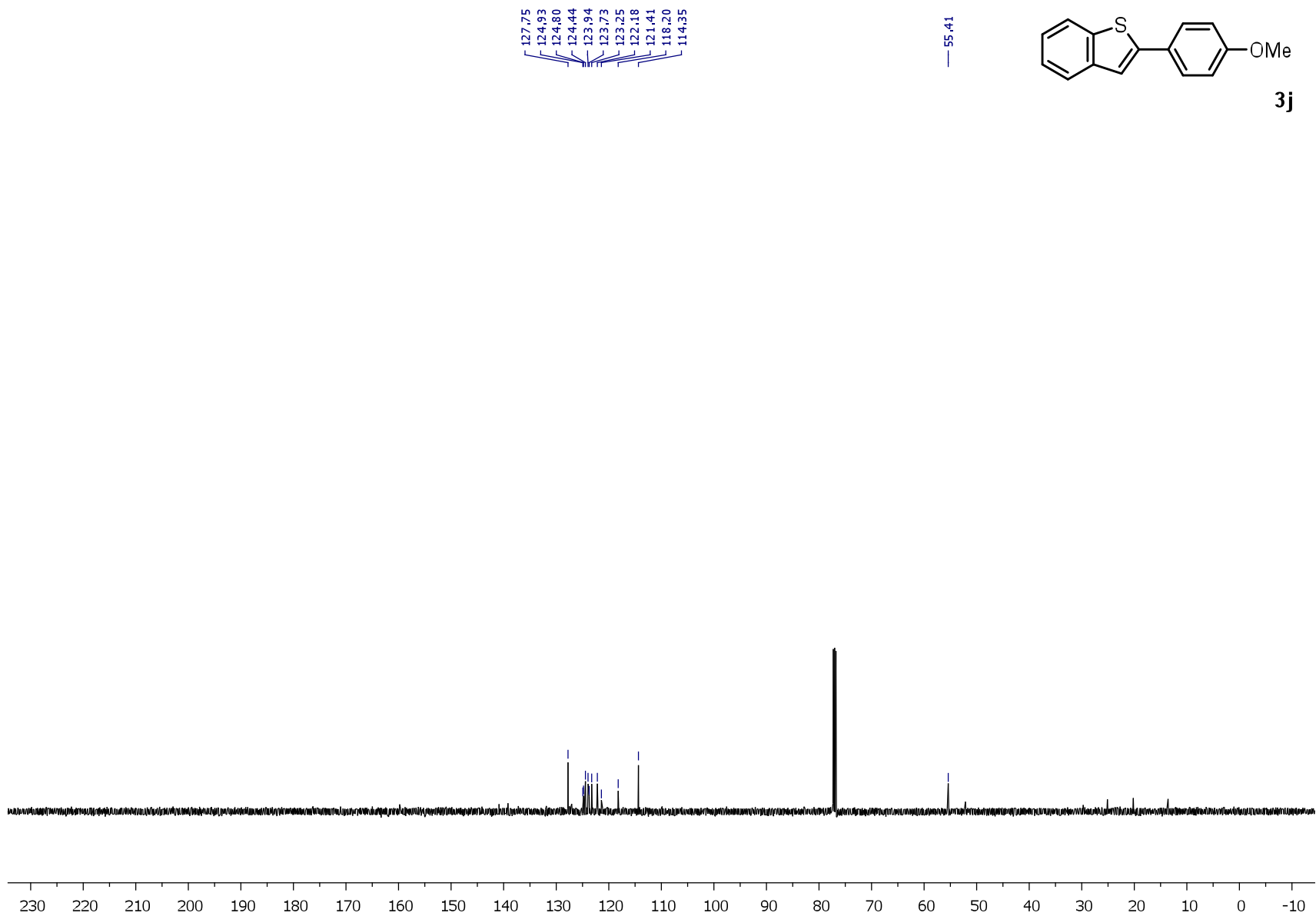


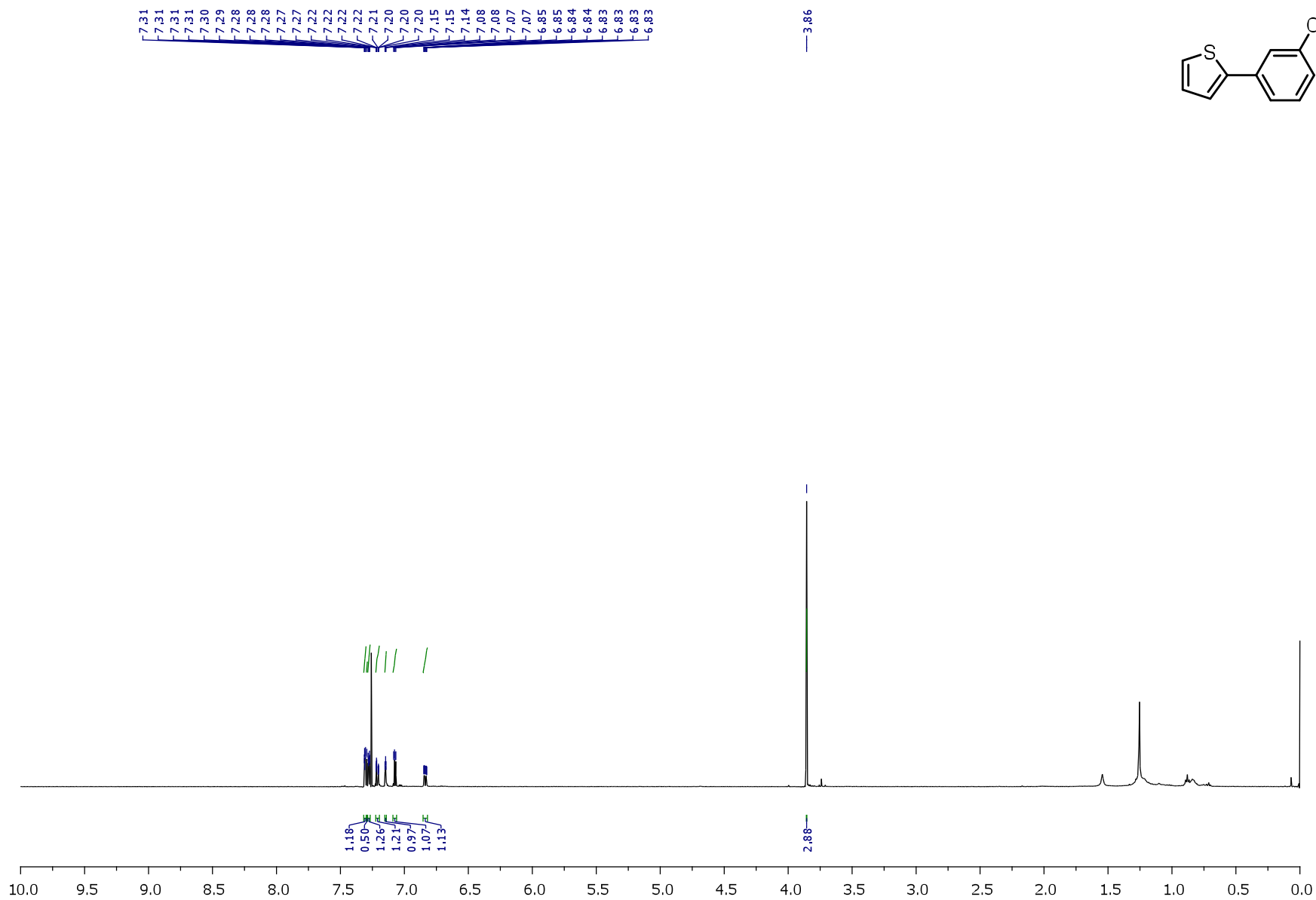


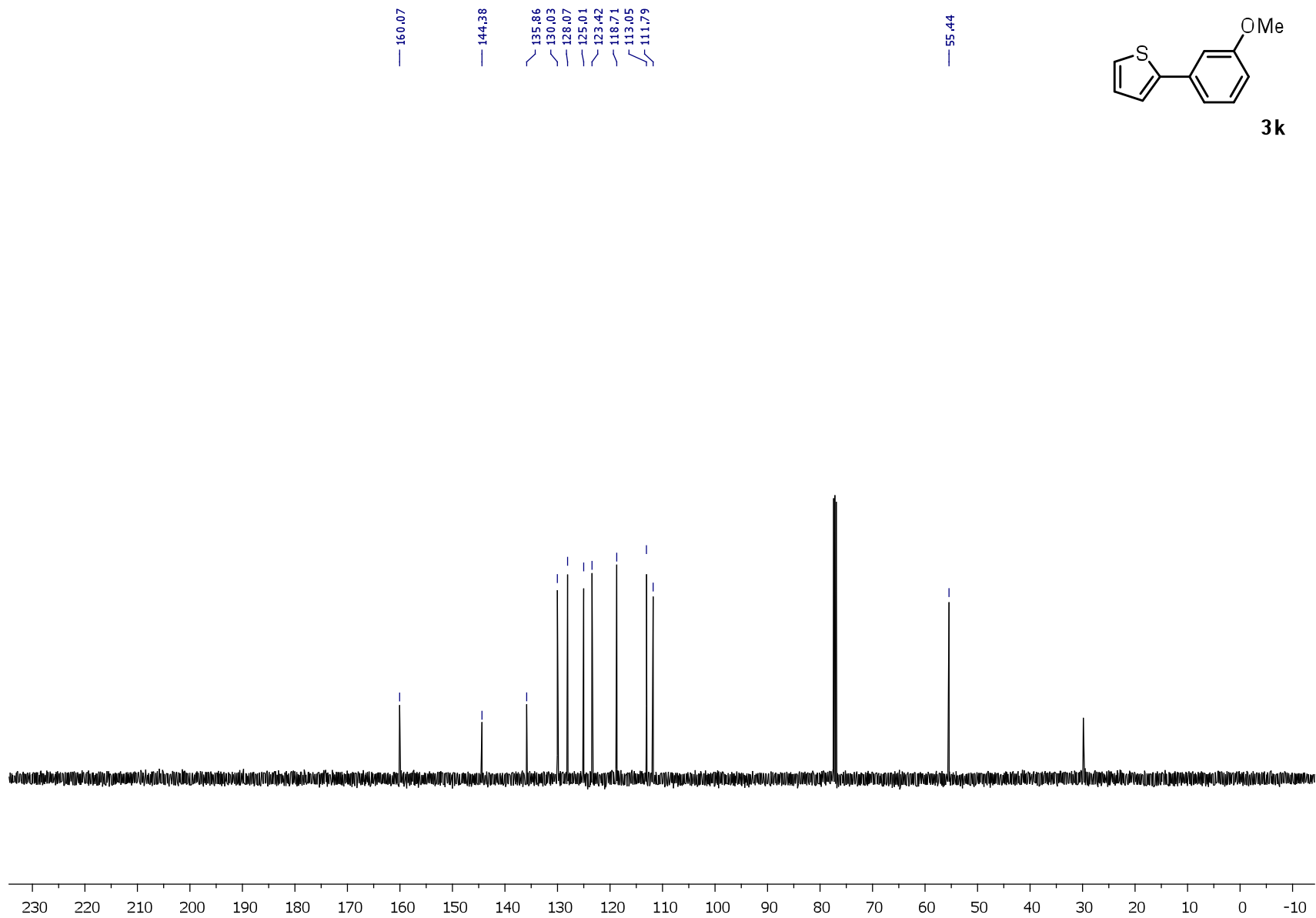


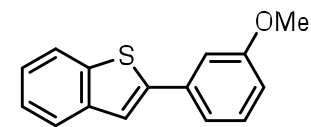
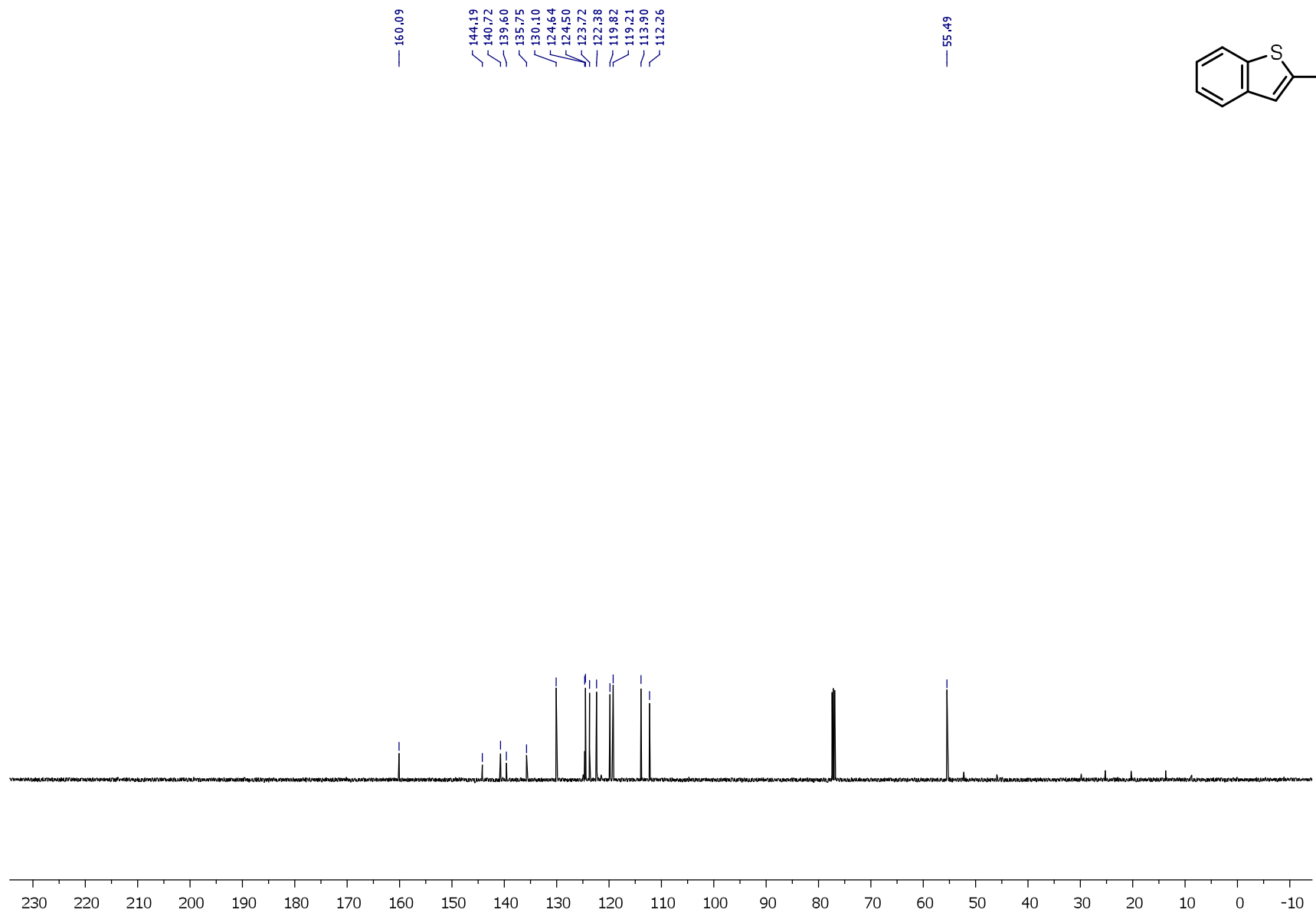












31