

Supporting Information

Microwave-Assisted Synthesis of 3-Aminobenzo[*b*]thiophene Scaffolds for the Preparation of Kinase Inhibitors

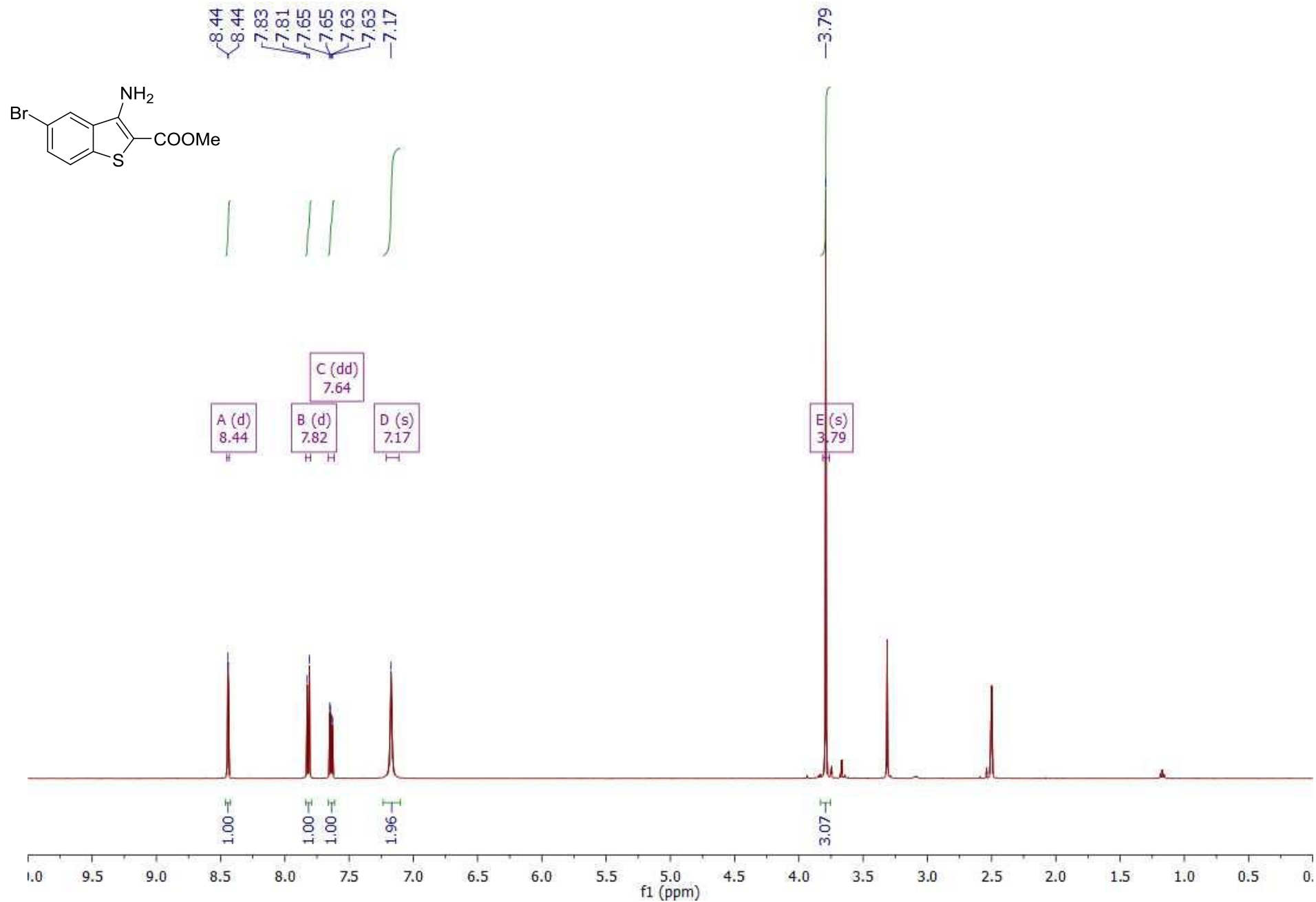
Mark C. Bagley,^{*,a} Jessica E. Dwyer,^a Maria D. Beltran Molina,^b Alexander W. Rand,^a
Hayley L. Rand,^a and Nicholas C. O. Tomkinson^b

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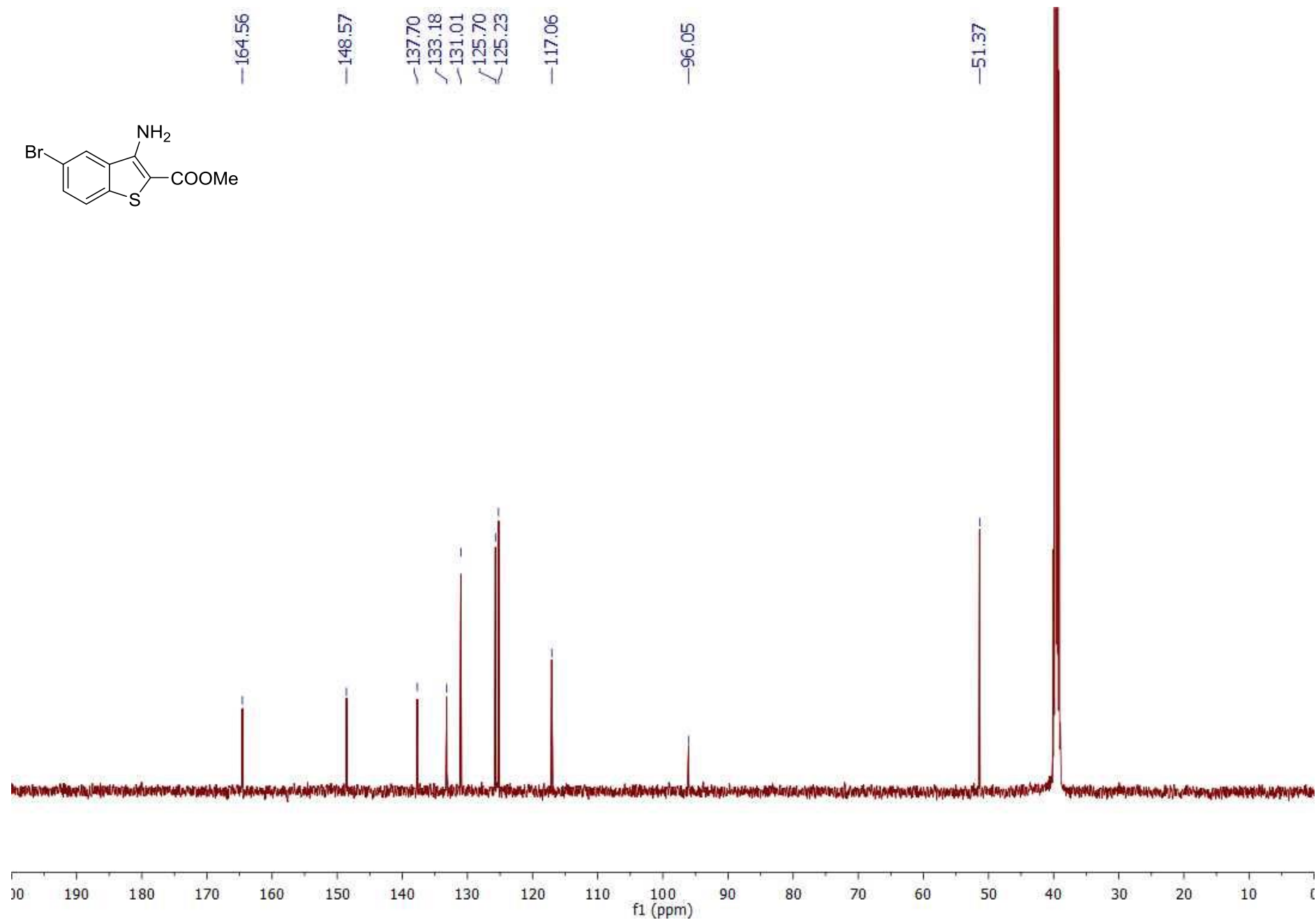
S3	¹ H NMR spectrum for methyl 3-amino-5-bromobenzo[<i>b</i>]thiophene-2-carboxylate (5a)
S4	¹³ C NMR spectrum for methyl 3-amino-5-bromobenzo[<i>b</i>]thiophene-2-carboxylate (5a)
S5	¹ H NMR spectrum for methyl 3-amino-5-nitrobenzo[<i>b</i>]thiophene-2-carboxylate (5b)
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S7	¹ H NMR spectrum for methyl 3-amino-5-chlorobenzo[<i>b</i>]thiophene-2-carboxylate (5c)
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S13	¹ H NMR spectrum for methyl 3-amino-5-phenylbenzo[<i>b</i>]thiophene-2-carboxylate (5f)
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S15	¹ H NMR spectrum for methyl 3-aminobenzo[<i>b</i>]thiophene-2-carboxylate (5g)
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S17	¹ H NMR spectrum for methyl 3-amino-5-(trifluoromethyl)benzo[<i>b</i>]thiophene-2-carboxylate (5h)
S18	¹³ C NMR spectrum for methyl 3-amino-5-(trifluoromethyl)benzo[<i>b</i>]thiophene-2-carboxylate (5h)
S19	¹ H NMR spectrum for methyl (<i>E</i>)-3-amino-5-(2-cyclopropylvinyl)benzo[<i>b</i>]thiophene-2-carboxylate (5i)
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S21	¹ H NMR spectrum for (3 <i>R</i>)-3-methyl-9-nitro-1,2,3,4-tetrahydro-5 <i>H</i> -[1]benzothieno[3,2- <i>e</i>][1,4]diazepin-5-one (6b)
S22	¹³ C NMR spectrum for (3 <i>R</i>)-3-methyl-9-nitro-1,2,3,4-tetrahydro-5 <i>H</i> -[1]benzothieno[3,2- <i>e</i>][1,4]diazepin-5-one (6b)
S23	¹ H NMR spectrum for methyl 5-nitrobenzo[<i>b</i>]thiophene-2-carboxylate (10)
S24	¹³ C NMR spectrum for methyl 5-nitrobenzo[<i>b</i>]thiophene-2-carboxylate (10)
S25	¹ H NMR spectrum for 5-nitrobenzo[<i>b</i>]thiophene-2-carboxylic acid (11)
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S32	¹ H NMR spectrum for methyl 3-aminothieno[2,3- <i>b</i>]pyridine-2-carboxylate (16)

- S33 ¹³C NMR spectrum for methyl 3-aminothieno[2,3-*b*]pyridine-2-carboxylate (**16**)
- S34 ¹H NMR spectrum for *tert*-butyl [(2*R*)-1-aminopropan-2-yl]carbamate (**17**)
- S35 ¹³C NMR spectrum for *tert*-butyl [(2*R*)-1-aminopropan-2-yl]carbamate (**17**)
- S36 ¹H NMR spectrum for (*R*)-methyl 3-((2-((*tert*-butoxycarbonyl)amino)propyl)amino)-5-nitrobenzo[*b*]thiophene-2-carboxylate (**18**)
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- S38 ¹H NMR spectrum for methyl 3-(((*E*)-1-amino-2-chloroethylidene)amino)-5-((*E*)-2-cyclopropylvinyl)benzo[*b*]thiophene-2-carboxylate hydrochloride (**19**)
- S39 ¹³C NMR spectrum for methyl 3-(((*E*)-1-amino-2-chloroethylidene)amino)-5-((*E*)-2-cyclopropylvinyl)benzo[*b*]thiophene-2-carboxylate hydrochloride (**19**)
- S40 ¹H NMR spectrum for (*E*)-8-(2-cyclopropylvinyl)-2-((dimethylamino)methyl)benzo[4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (**20**)
- S41 ¹³C NMR spectrum for (*E*)-8-(2-cyclopropylvinyl)-2-((dimethylamino)methyl)benzo[4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (**20**)

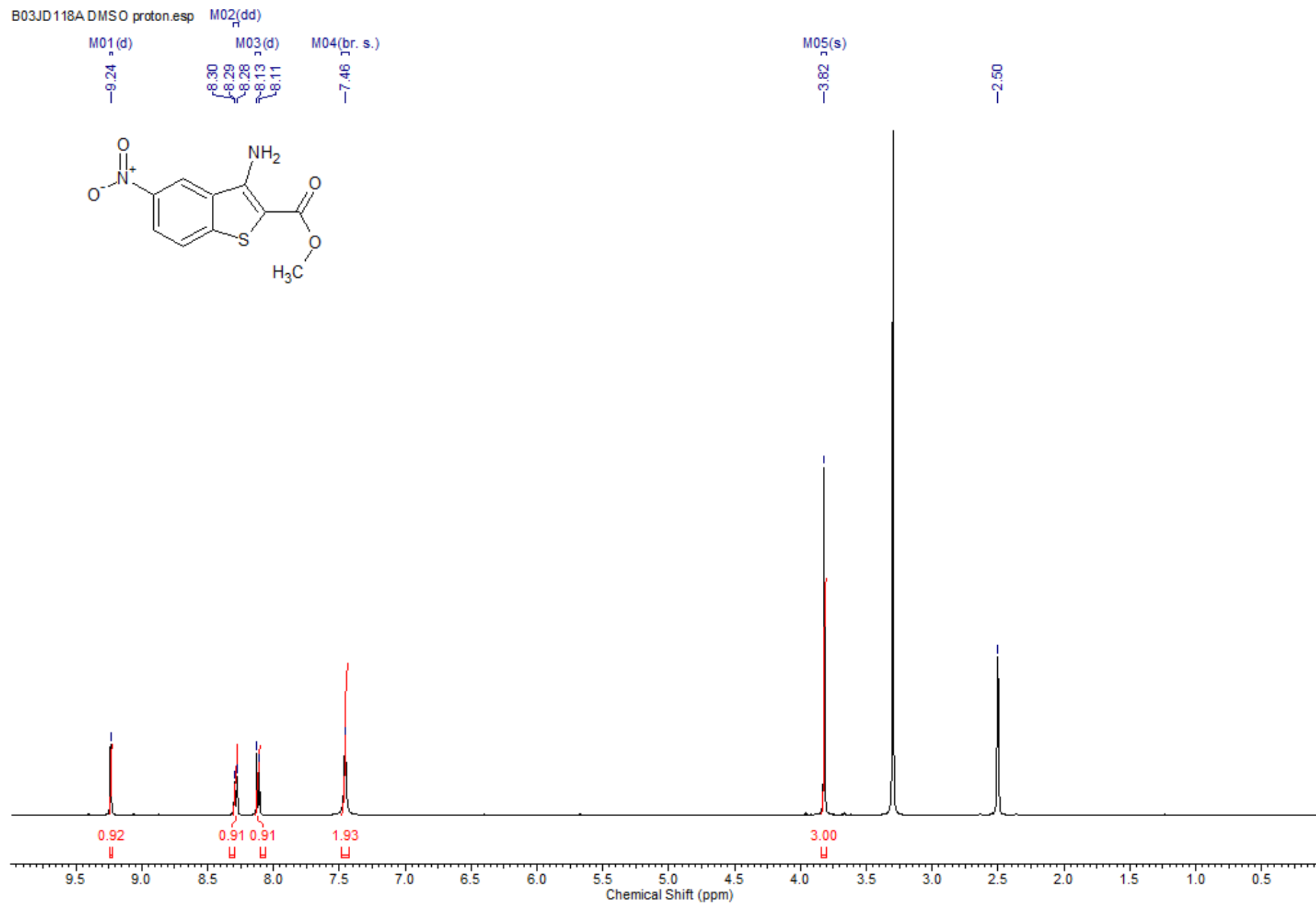
^1H NMR spectrum (500 MHz, d_6 -DMSO) for methyl 3-amino-5-bromobenzo[*b*]thiophene-2-carboxylate (**5a**)



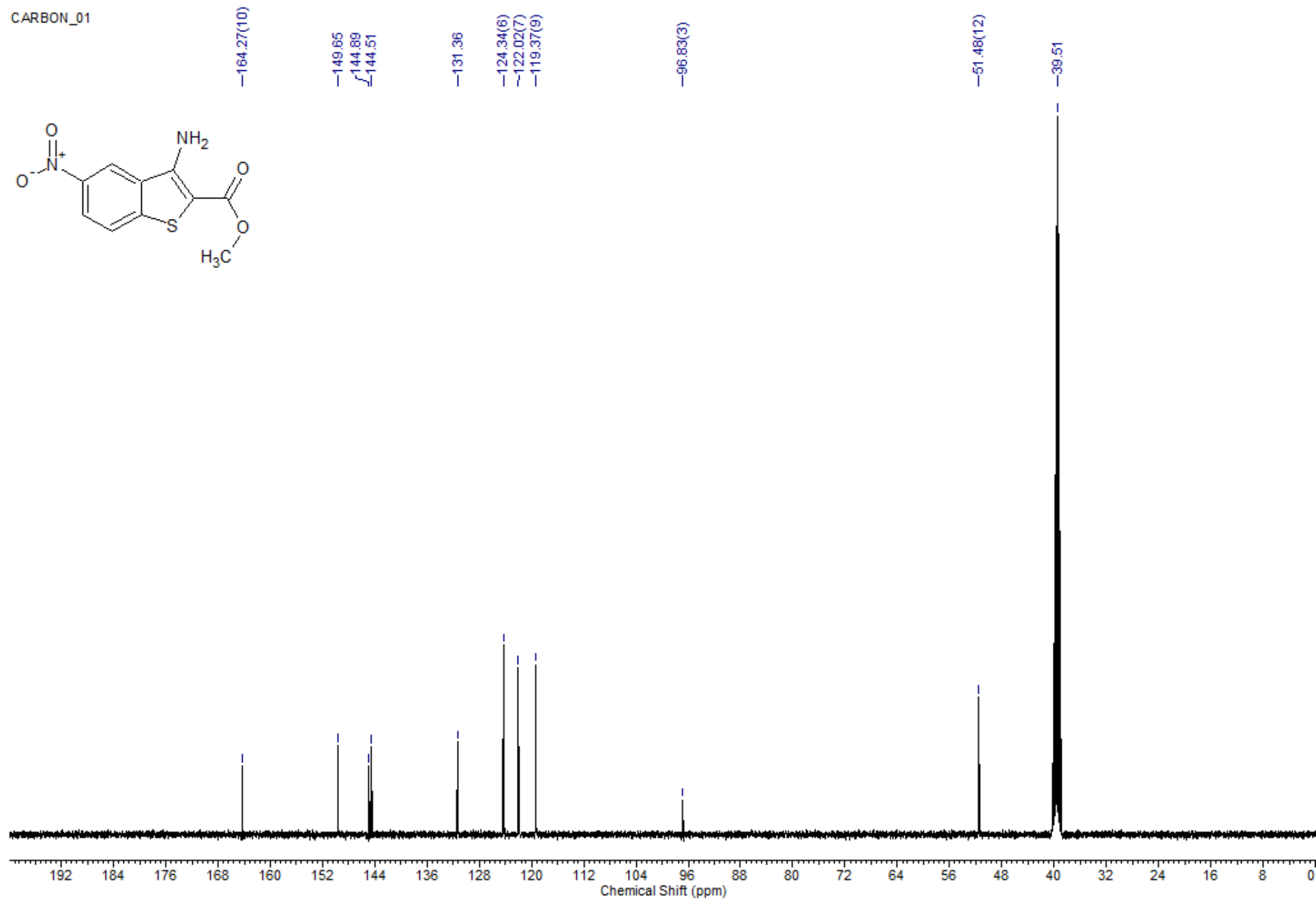
^{13}C NMR spectrum (126 MHz, d_6 -DMSO) for methyl 3-amino-5-bromobenzo[*b*]thiophene-2-carboxylate (**5a**)



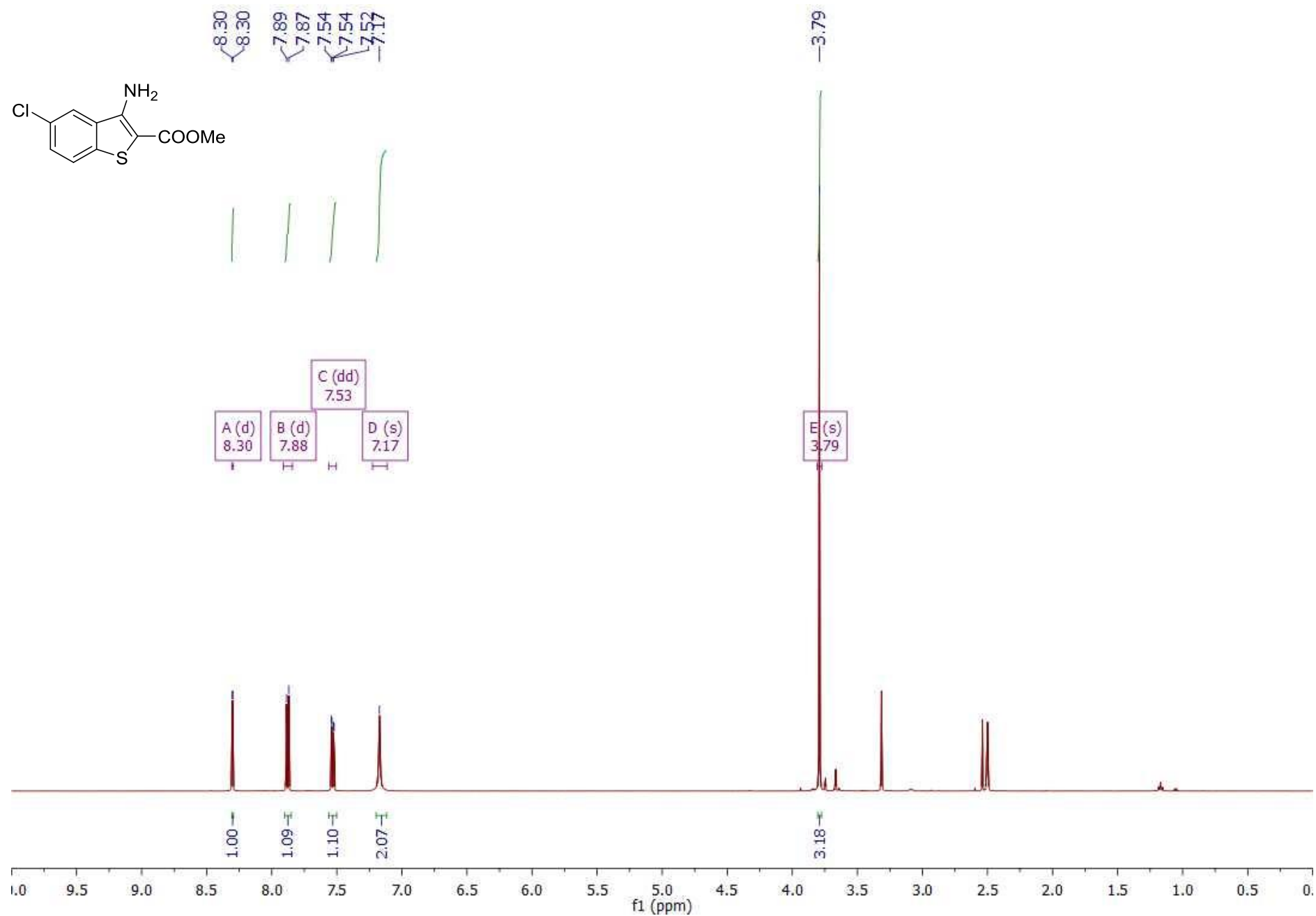
¹H NMR spectrum (500 MHz, *d*₆-DMSO) for methyl 3-amino-5-nitrobenzo[*b*]thiophene-2-carboxylate (**5b**)



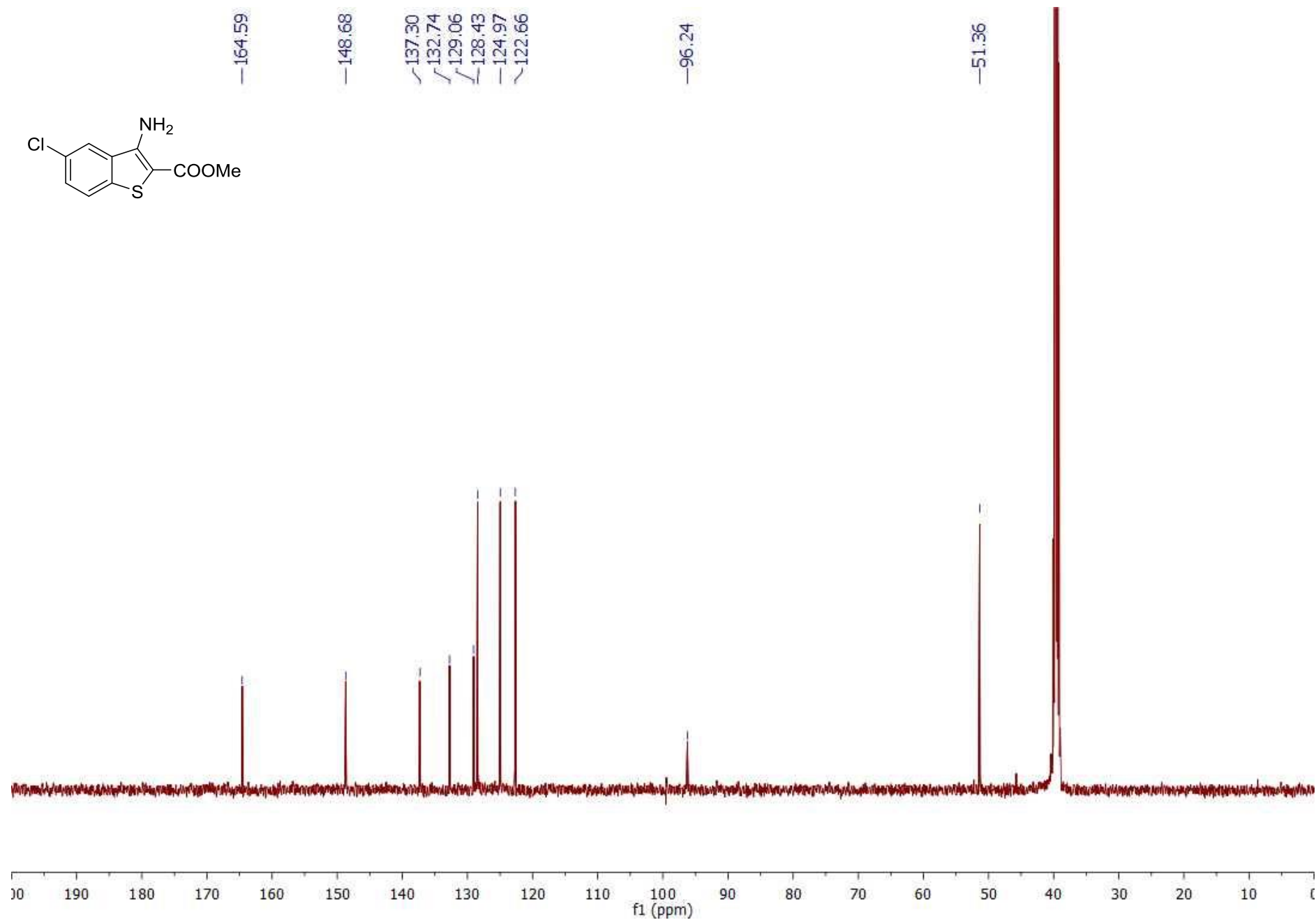
^{13}C NMR spectrum (100 MHz, d_6 -DMSO) for methyl 3-amino-5-nitrobenzo[*b*]thiophene-2-carboxylate (**5b**)



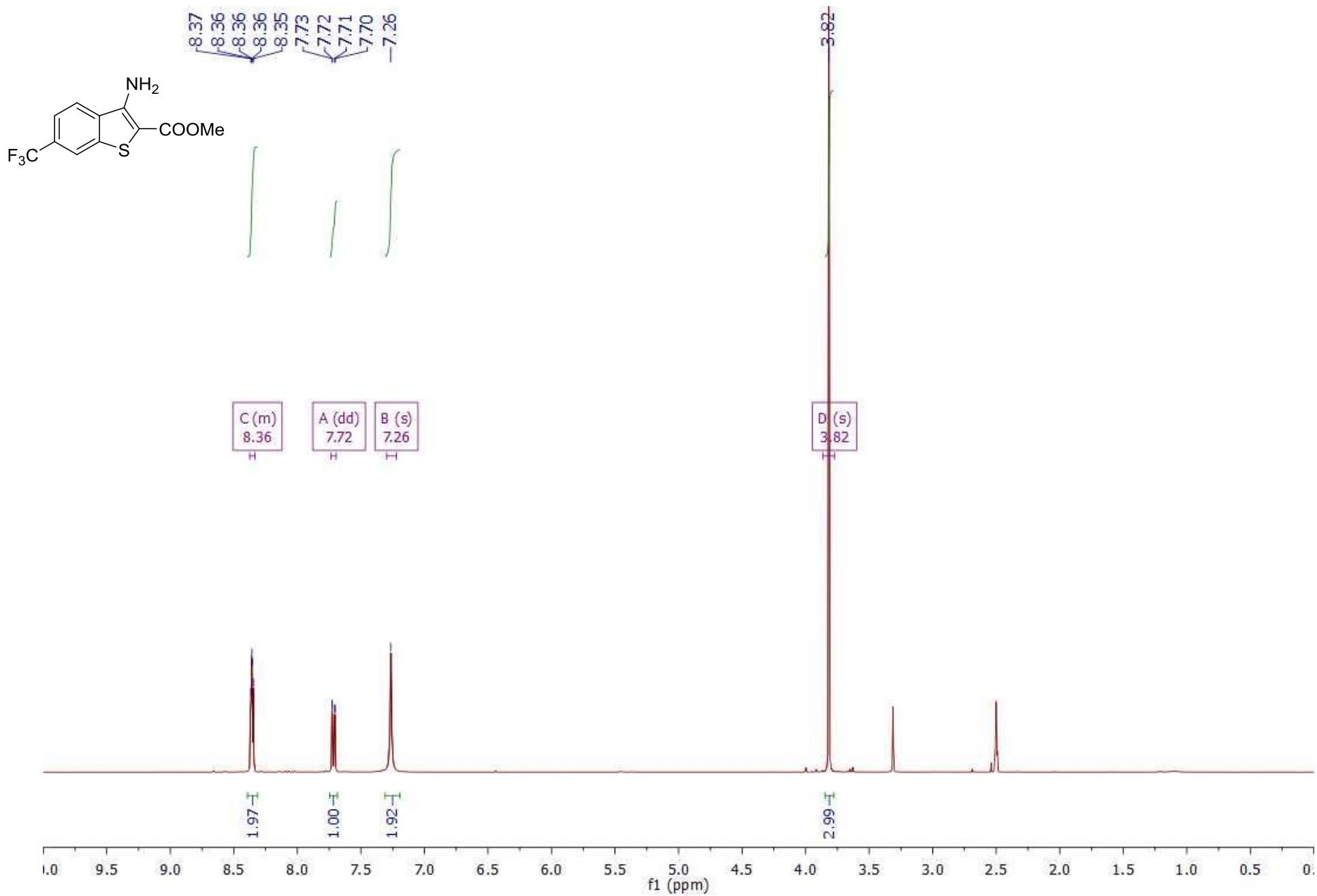
^1H NMR spectrum (500 MHz, d_6 -DMSO) for methyl 3-amino-5-chlorobenzo[*b*]thiophene-2-carboxylate (**5c**)



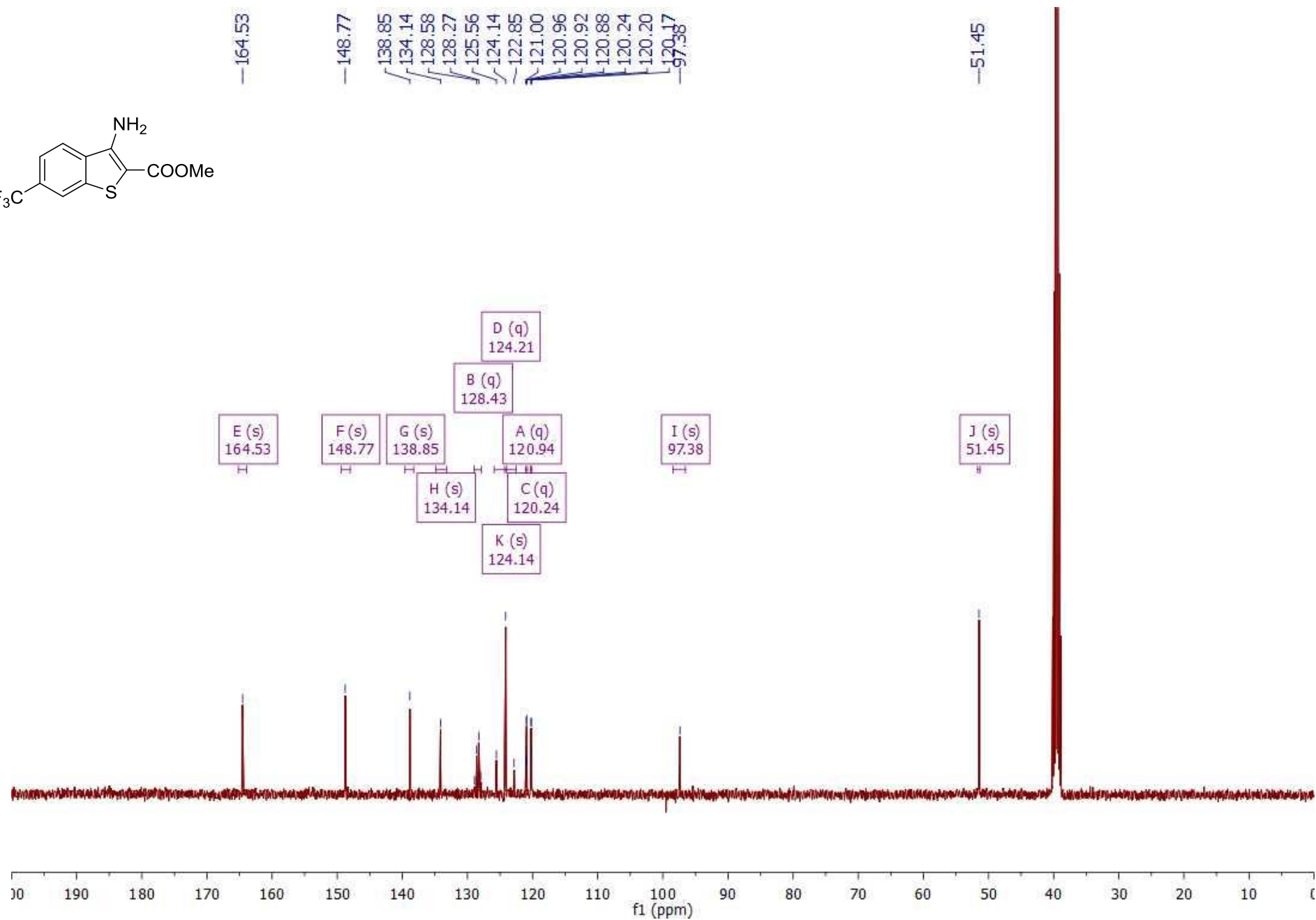
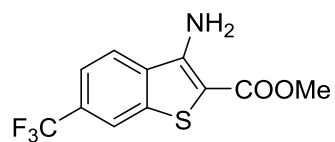
^{13}C NMR spectrum (126 MHz, d_6 -DMSO) for methyl 3-amino-5-chlorobenzo[*b*]thiophene-2-carboxylate (5c)



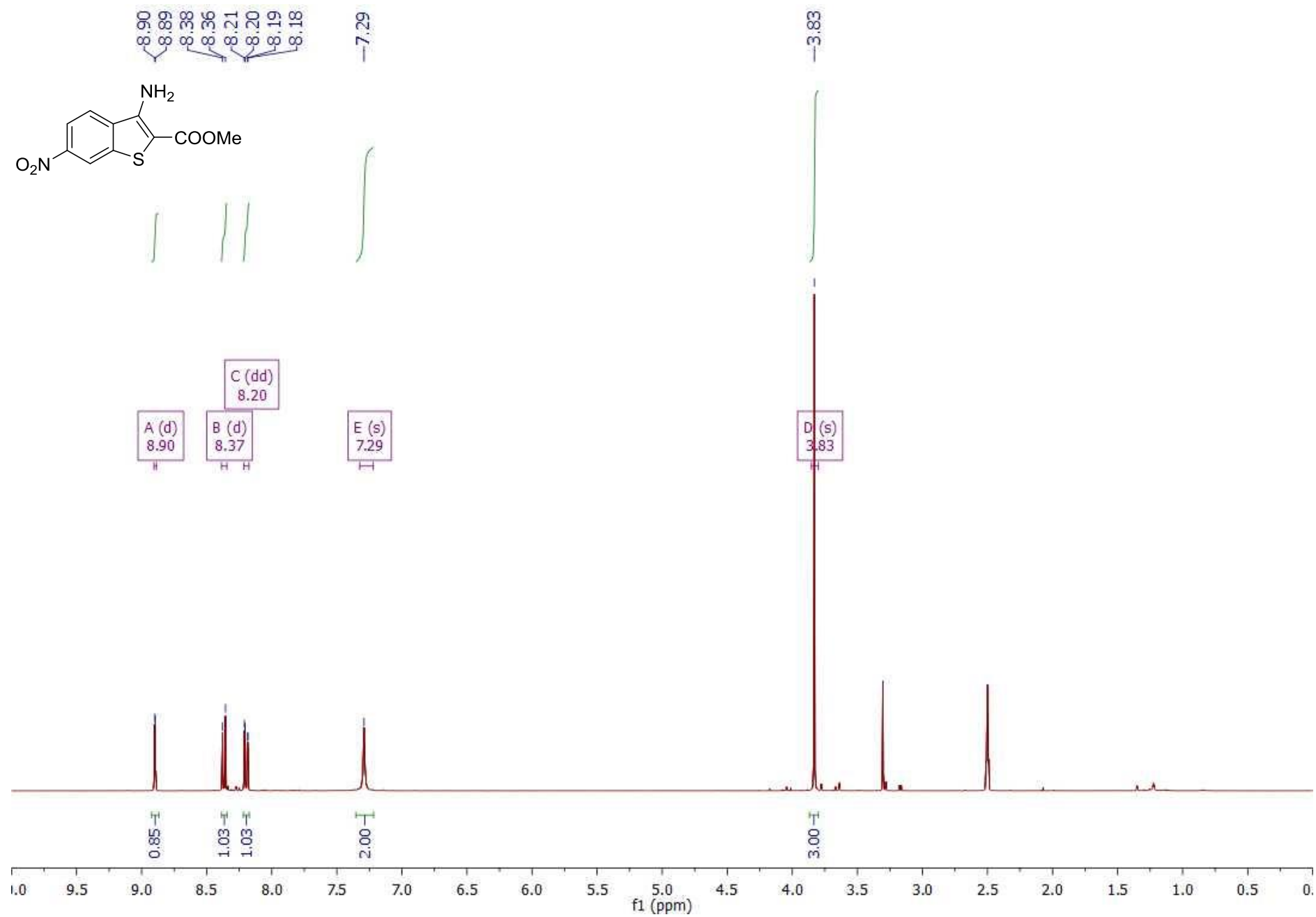
^1H NMR spectrum (400 MHz, d_6 -DMSO) for methyl 3-amino-6-(trifluoromethyl)benzo[*b*]thiophene-2-carboxylate (**5d**)



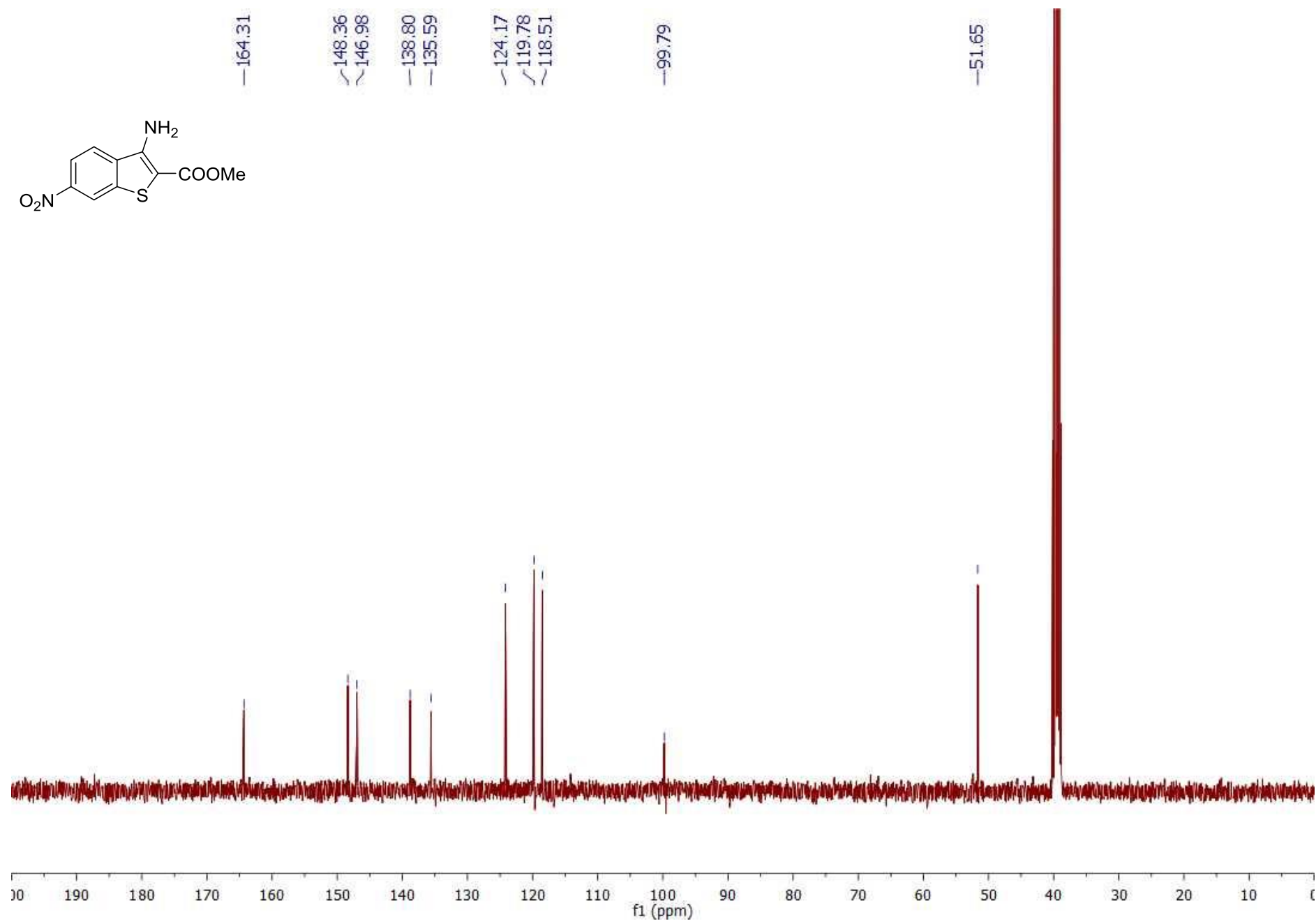
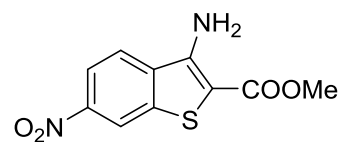
^{13}C NMR spectrum (101 MHz, d_6 -DMSO) for methyl 3-amino-6-(trifluoromethyl)benzo[*b*]thiophene-2-carboxylate (**5d**)



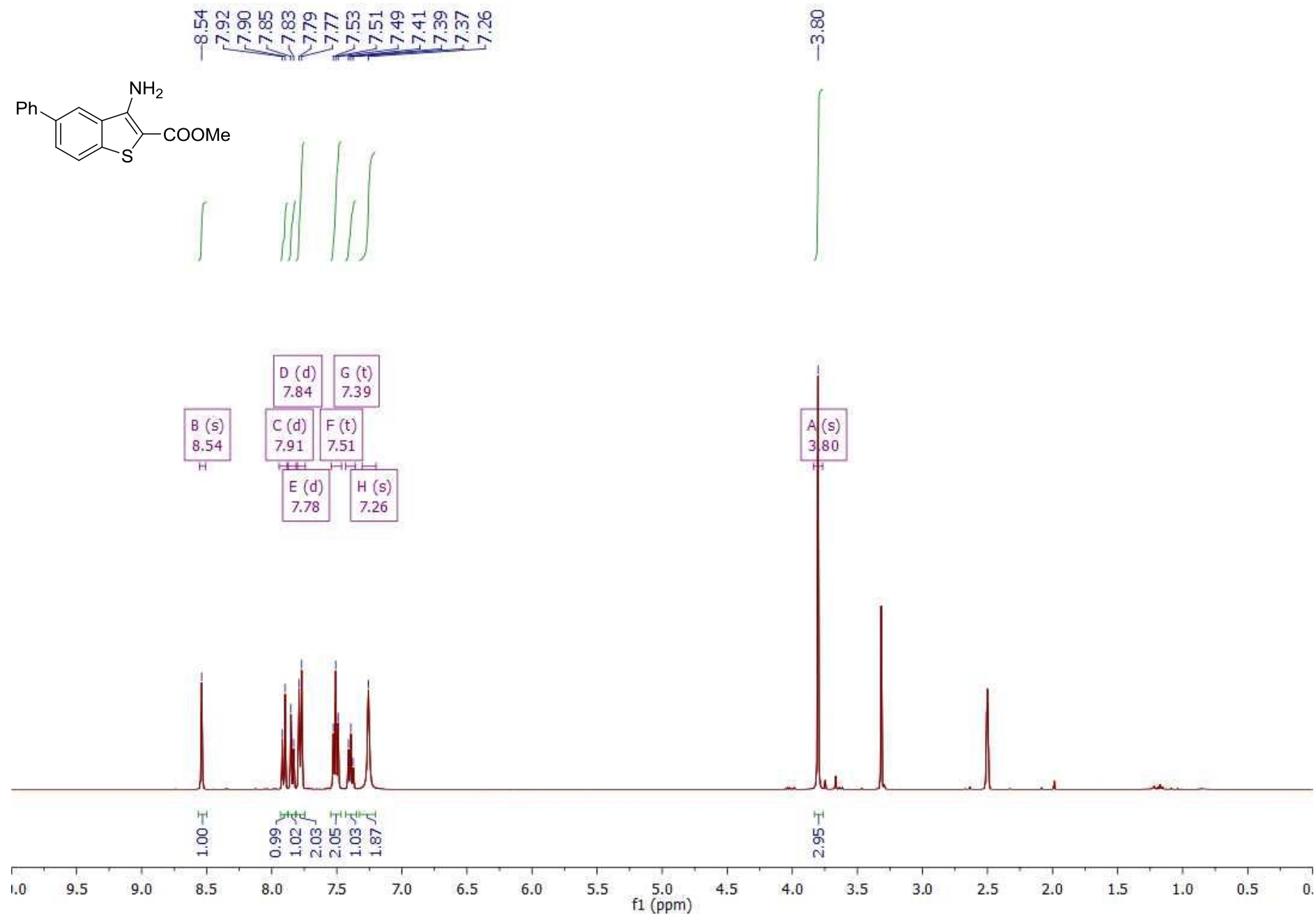
^1H NMR spectrum (400 MHz, d_6 -DMSO) for methyl 3-amino-6-nitrobenzo[*b*]thiophene-2-carboxylate (**5e**)



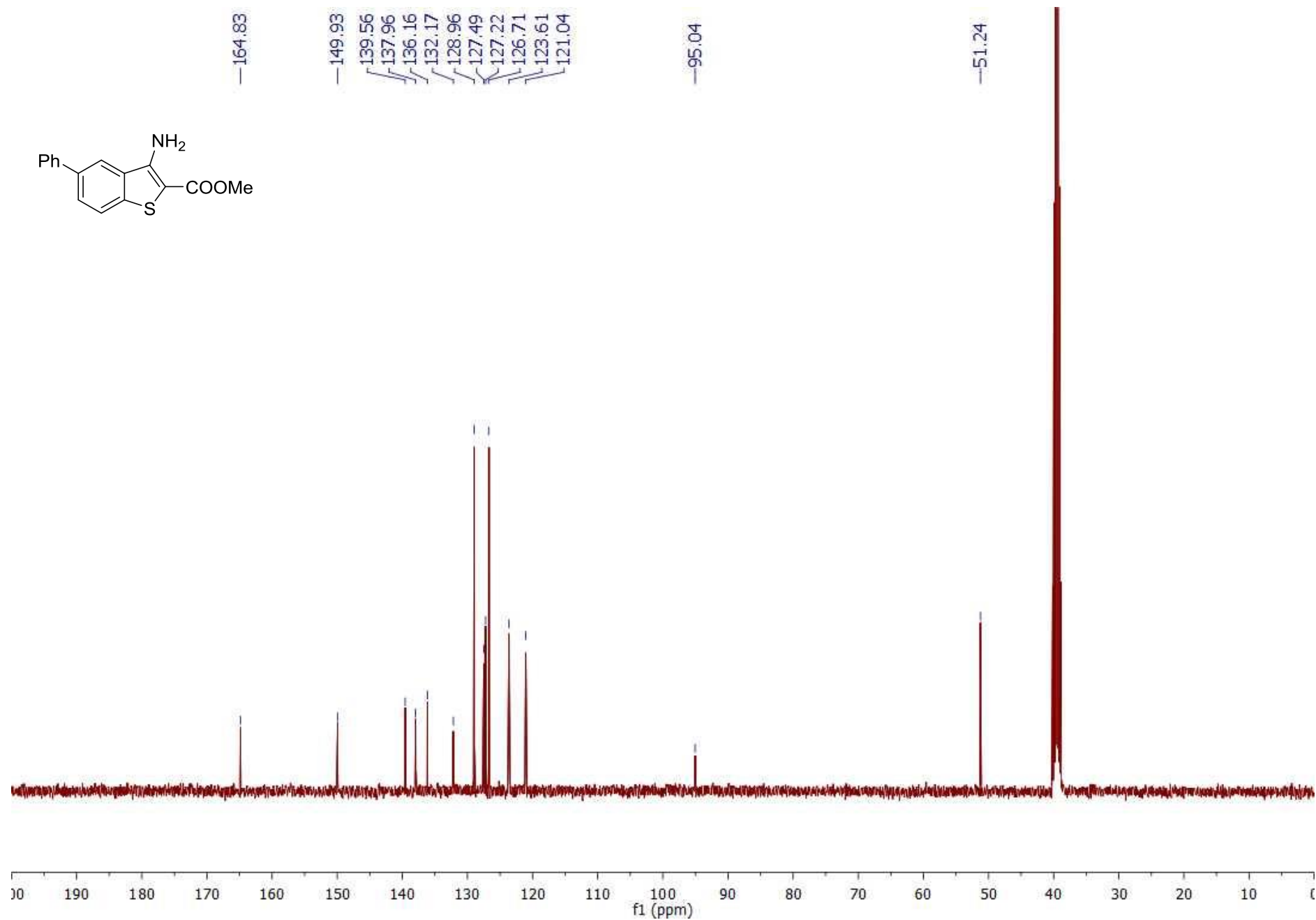
^{13}C NMR spectrum (101 MHz, d_6 -DMSO) for methyl 3-amino-6-nitrobenzo[*b*]thiophene-2-carboxylate (**5e**)



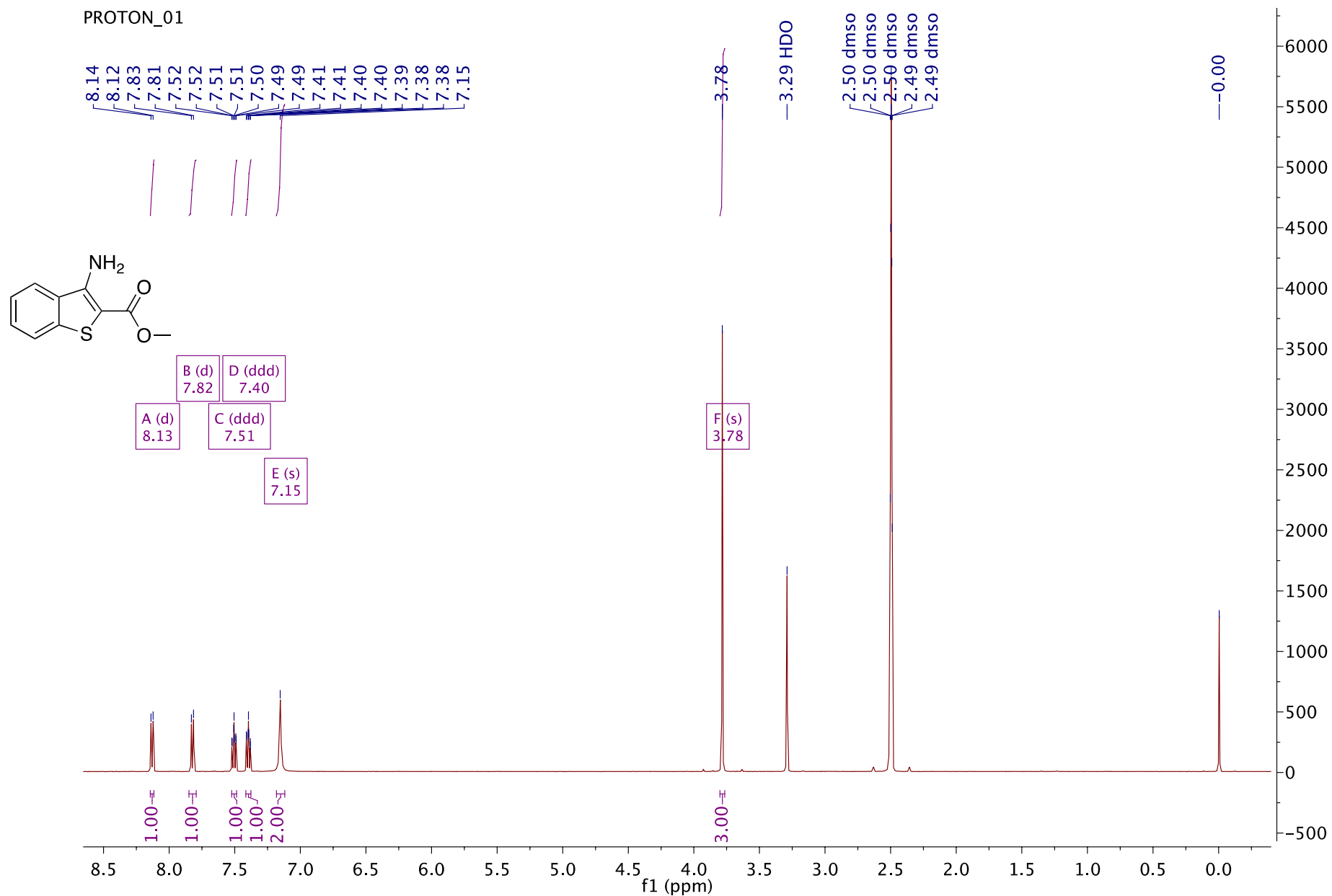
^1H NMR spectrum (400 MHz, d_6 -DMSO) for methyl 3-amino-5-phenylbenzo[*b*]thiophene-2-carboxylate (**5f**)



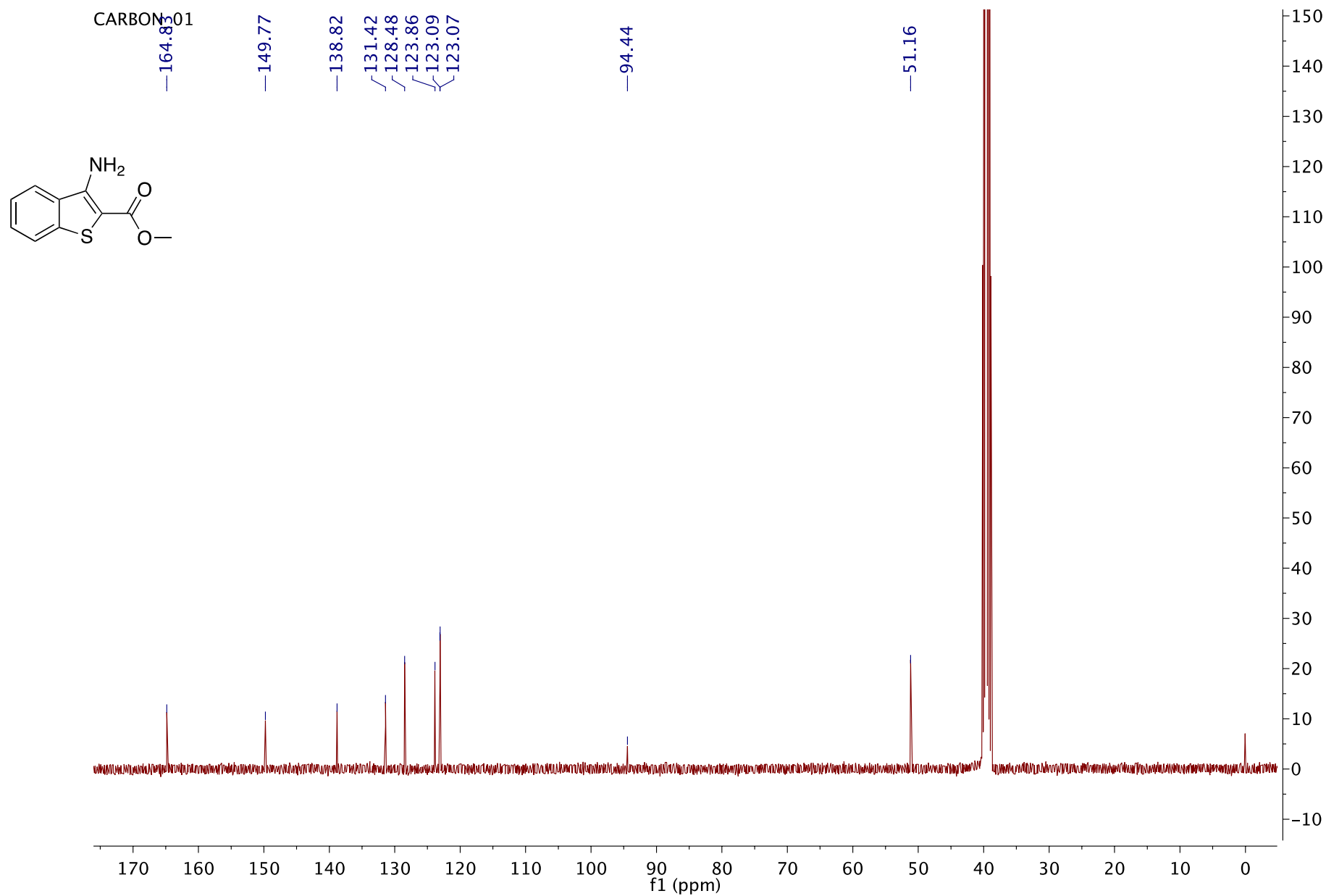
^{13}C NMR spectrum (101 MHz, d_6 -DMSO) for methyl 3-amino-5-phenylbenzo[*b*]thiophene-2-carboxylate (**5f**)



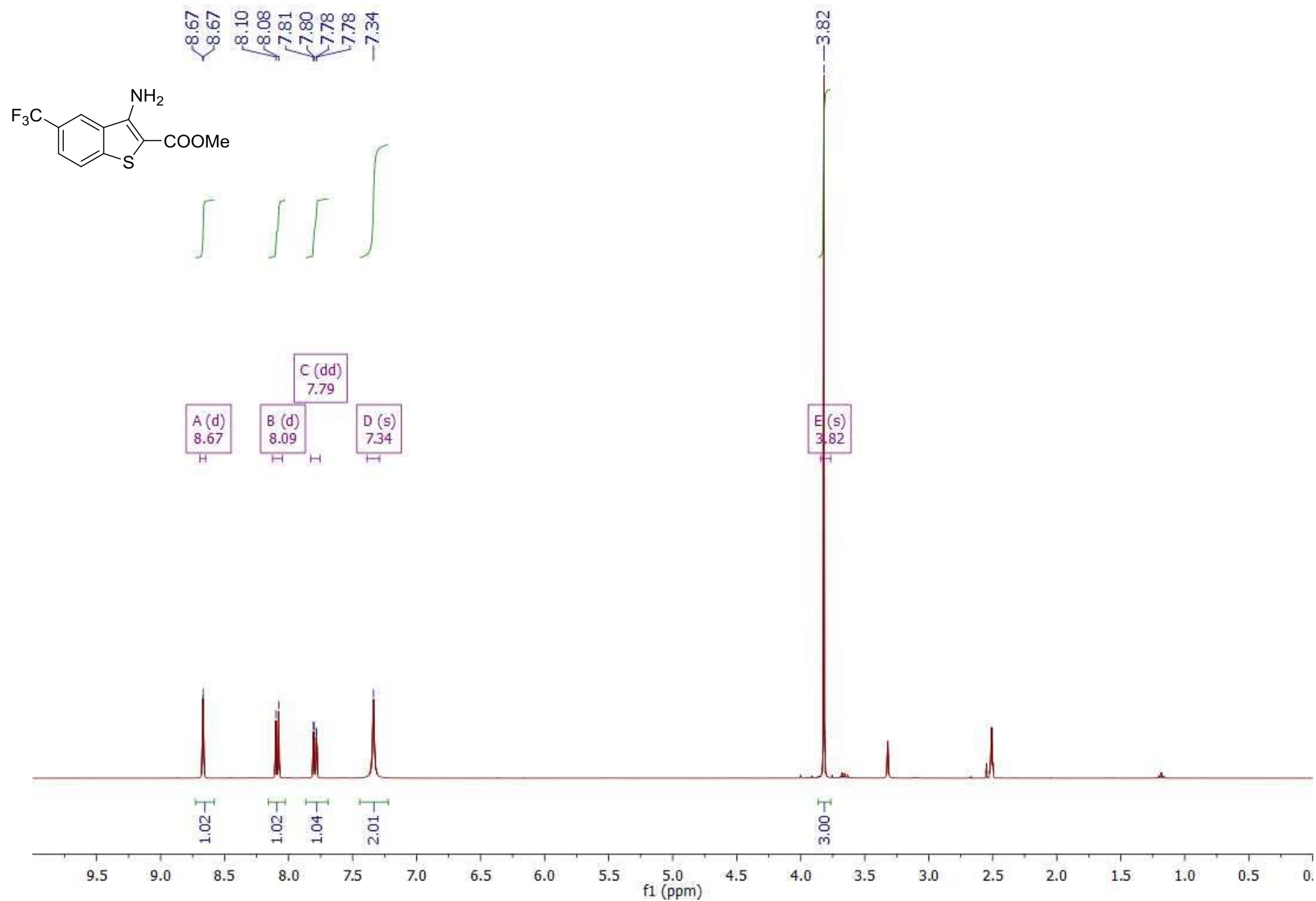
¹H NMR spectrum (500 MHz, *d*₆-DMSO) for methyl 3-aminobenzo[*b*]thiophene-2-carboxylate (**5g**)



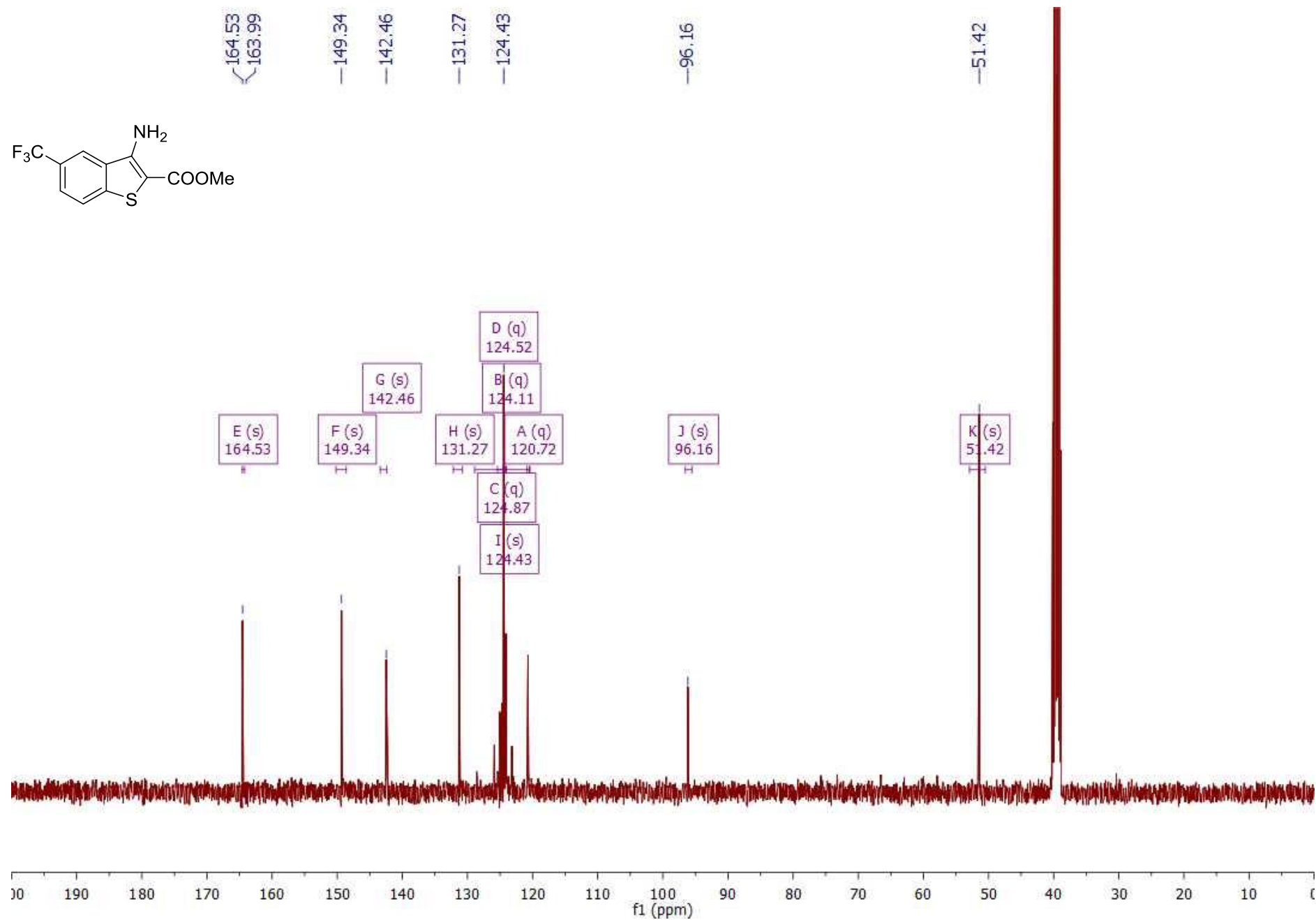
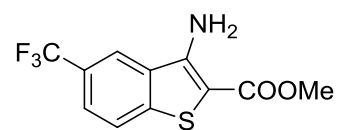
^{13}C NMR spectrum (101 MHz, d_6 -DMSO) for methyl 3-aminobenzo[*b*]thiophene-2-carboxylate (**5g**)



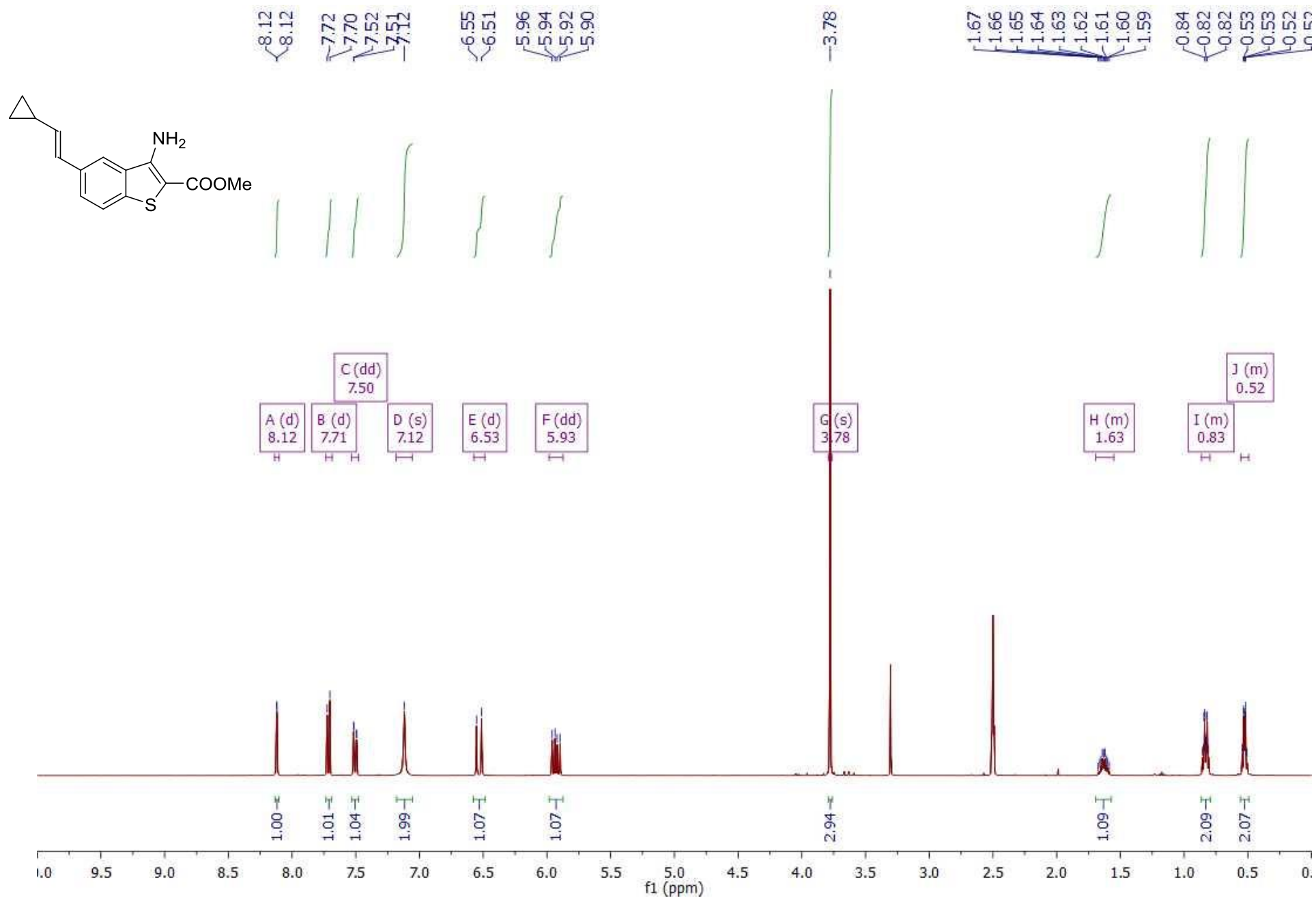
^1H NMR spectrum (400 MHz, d_6 -DMSO) for methyl 3-amino-5-(trifluoromethyl)benzo[*b*]thiophene-2-carboxylate (**5h**)



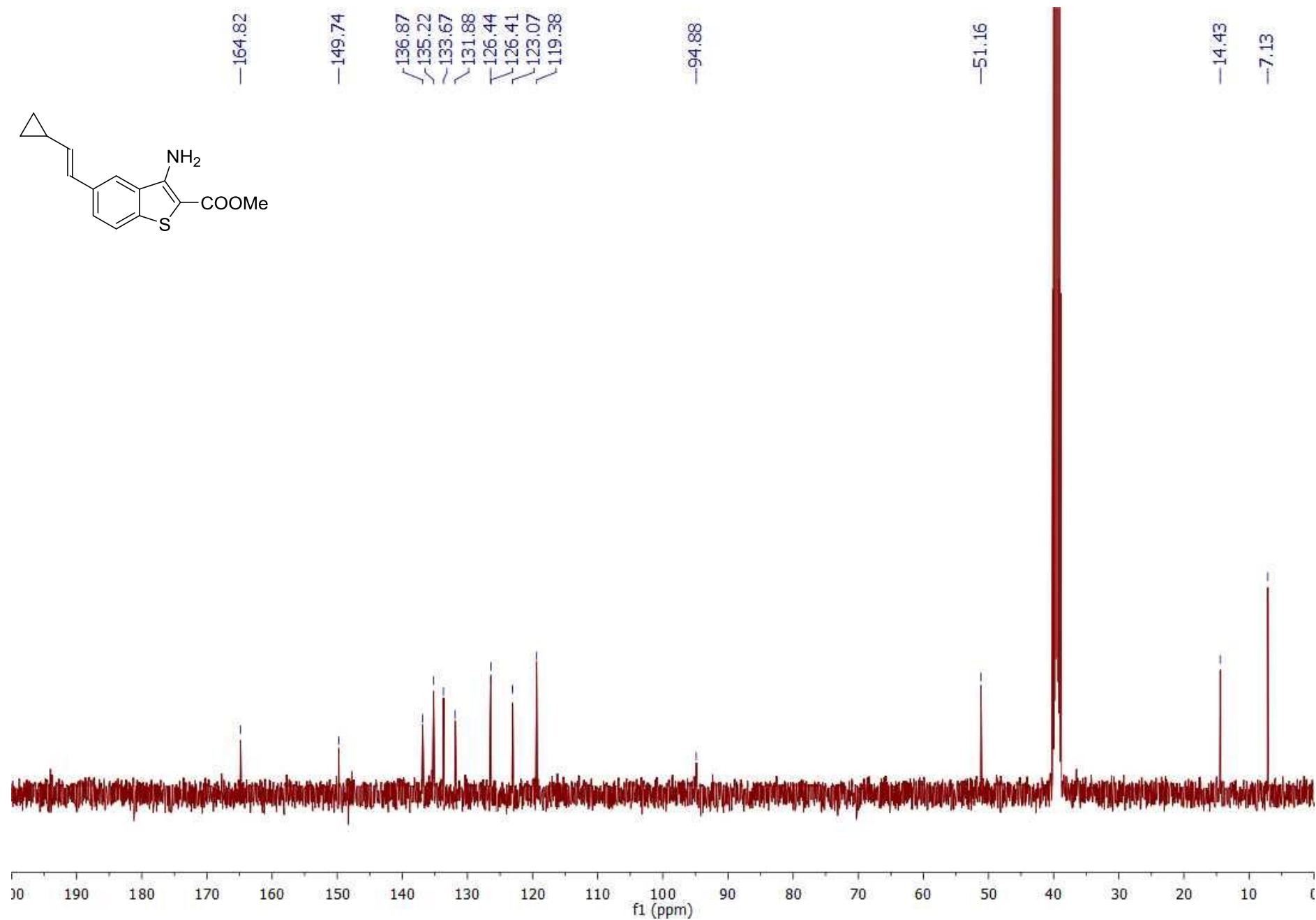
^{13}C NMR spectrum (101 MHz, d_6 -DMSO) for methyl 3-amino-5-(trifluoromethyl)benzo[*b*]thiophene-2-carboxylate (**5h**)



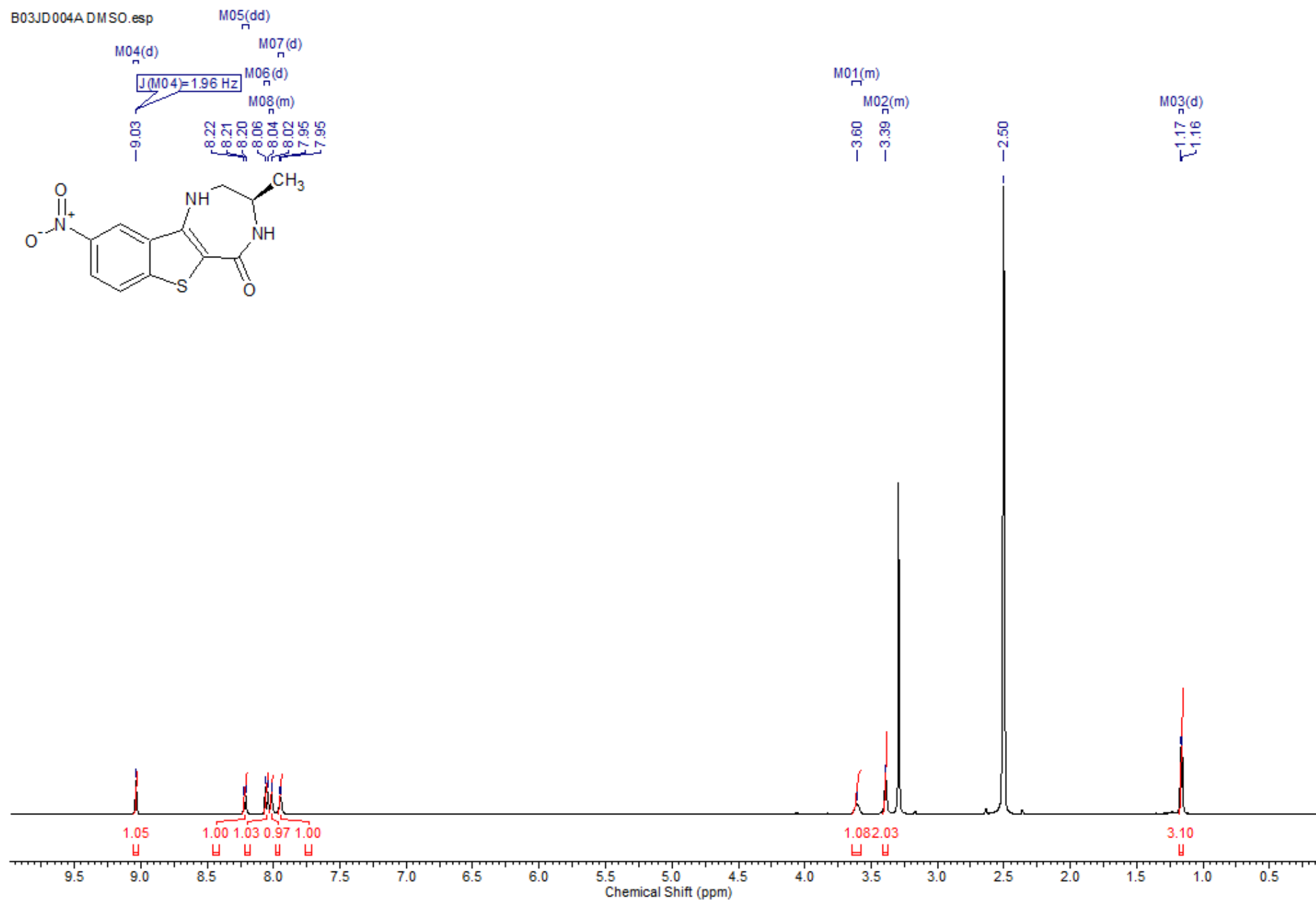
^1H NMR spectrum (500 MHz, d_6 -DMSO) for methyl (*E*)-3-amino-5-(2-cyclopropylvinyl)benzo[*b*]thiophene-2-carboxylate (**5i**)



^{13}C NMR spectrum (101 MHz, d_6 -DMSO) for methyl (*E*)-3-amino-5-(2-cyclopropylvinyl)benzo[*b*]thiophene-2-carboxylate (**5i**)

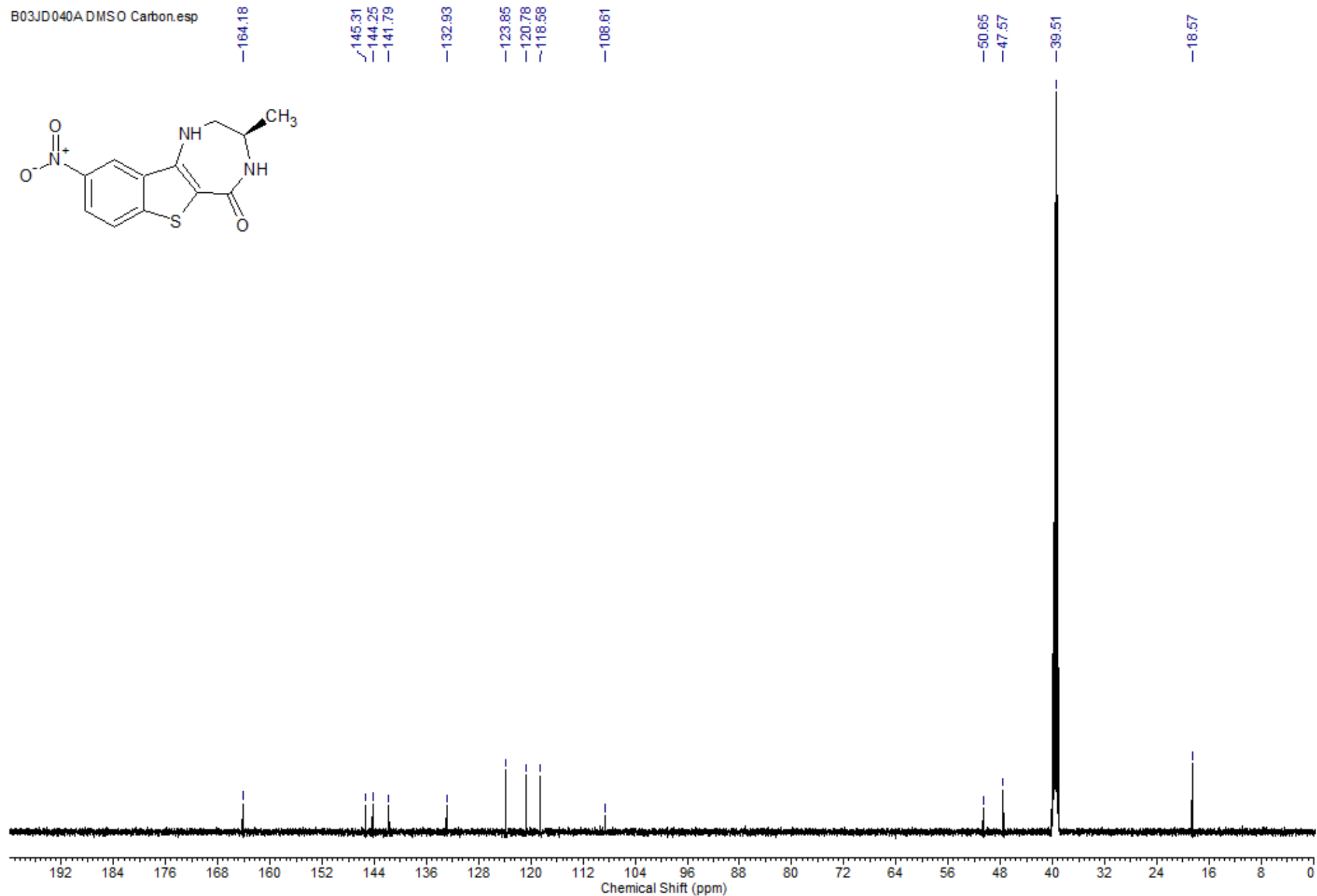
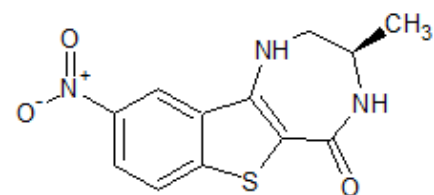


^1H NMR spectrum (500 MHz, d_6 -DMSO) for (3*R*)-3-methyl-9-nitro-1,2,3,4-tetrahydro-5*H*-[1]benzothieno[3,2-*e*][1,4]diazepin-5-one (**6b**)

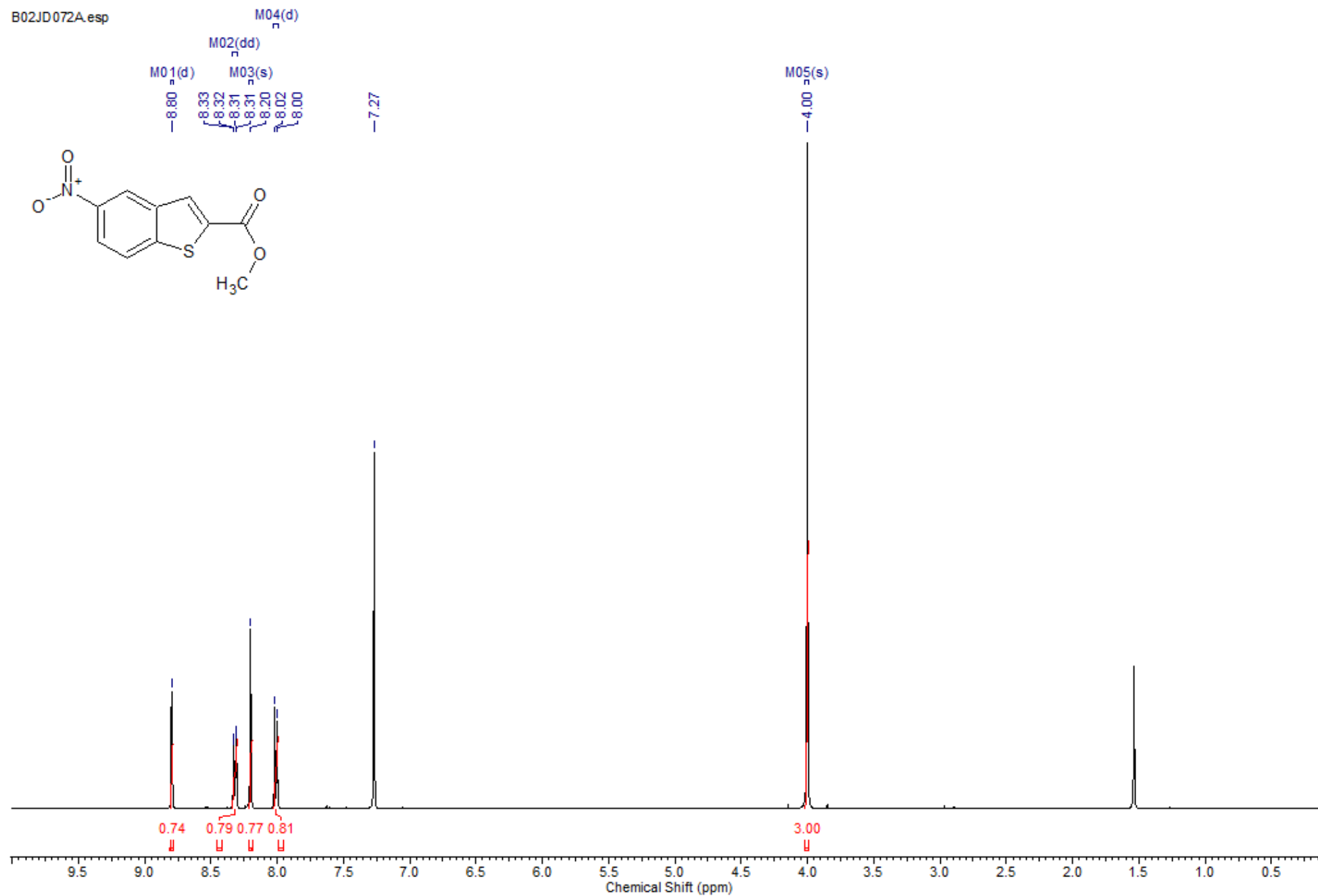


^{13}C NMR spectrum (125 MHz, d_6 -DMSO) for (3*R*)-3-methyl-9-nitro-1,2,3,4-tetrahydro-5*H*-[1]benzothieno[3,2-*e*][1,4]diazepin-5-one (**6b**)

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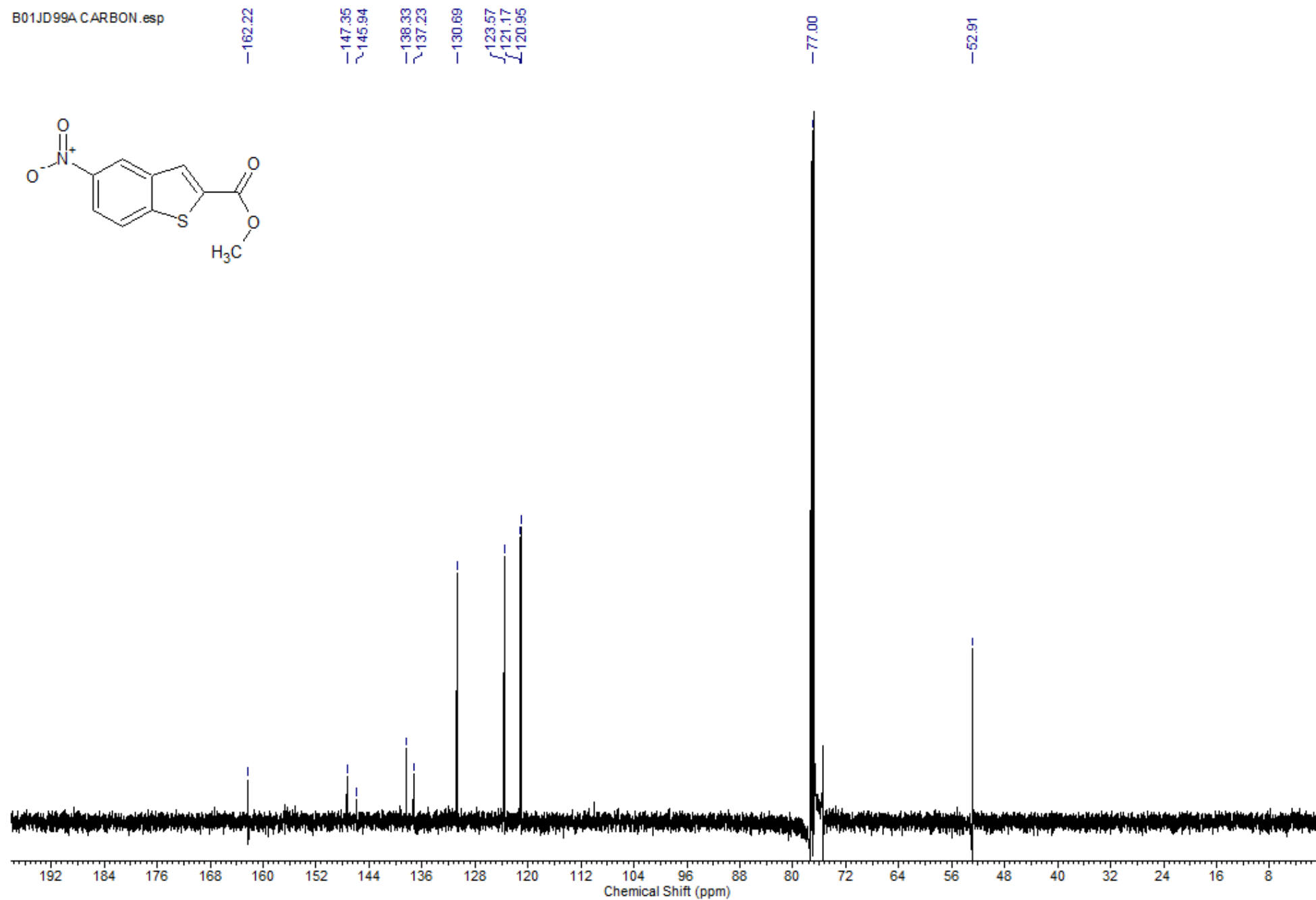


^1H NMR spectrum (500 MHz, CDCl_3) for methyl 5-nitrobenzo[*b*]thiophene-2-carboxylate (**10**)

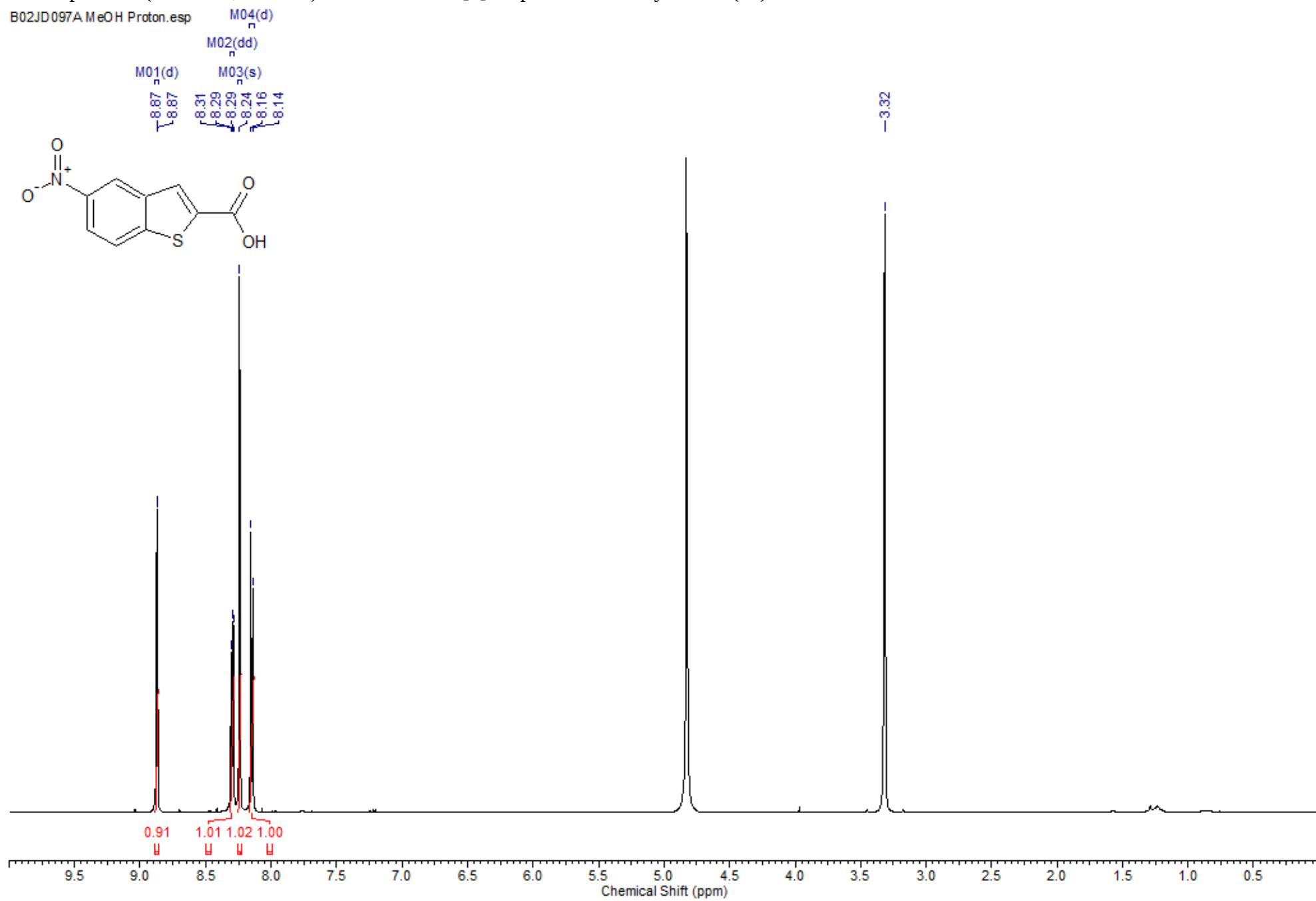


^{13}C NMR spectrum (125 MHz, CDCl_3) for methyl 5-nitrobenzo[*b*]thiophene-2-carboxylate (**10**)

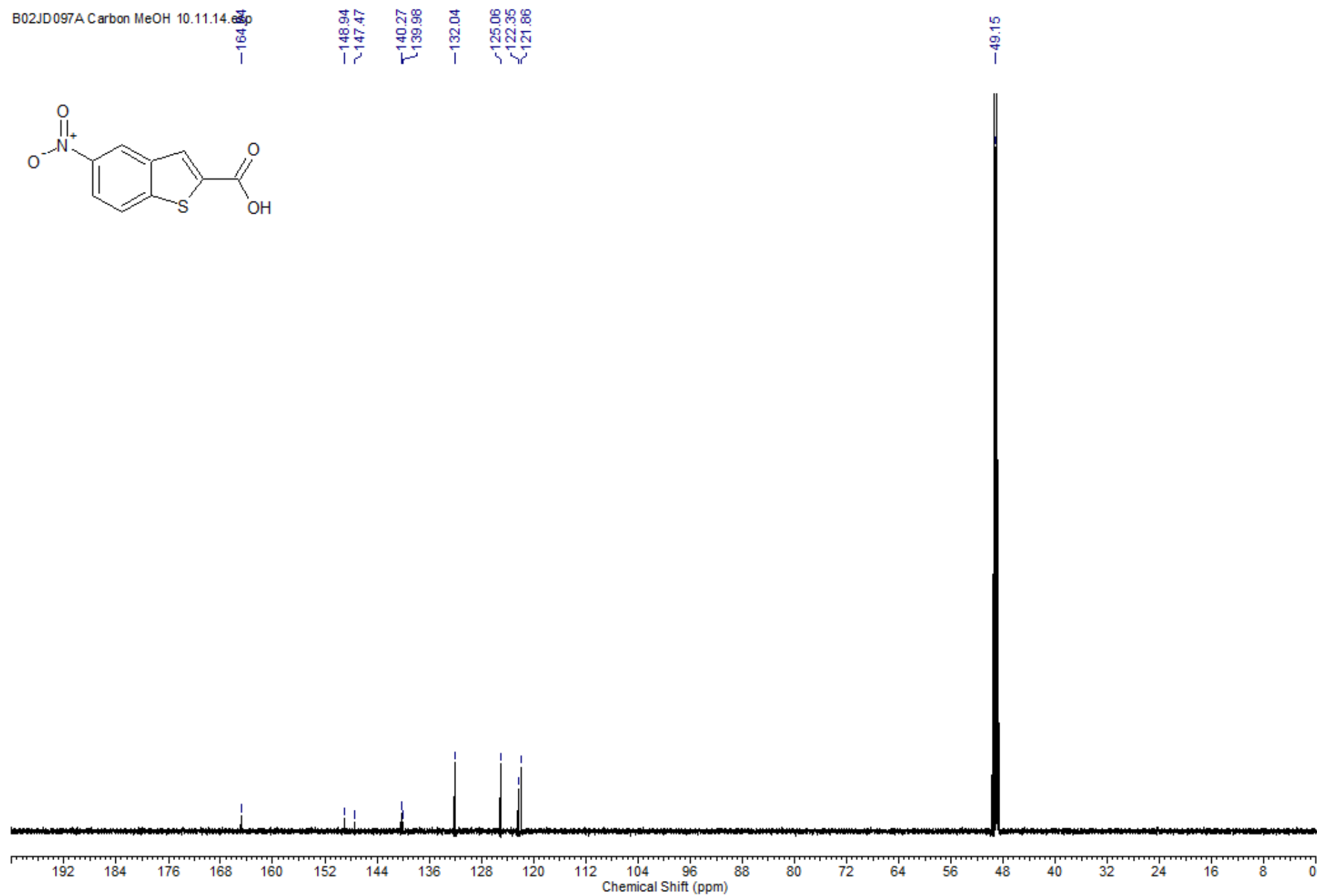
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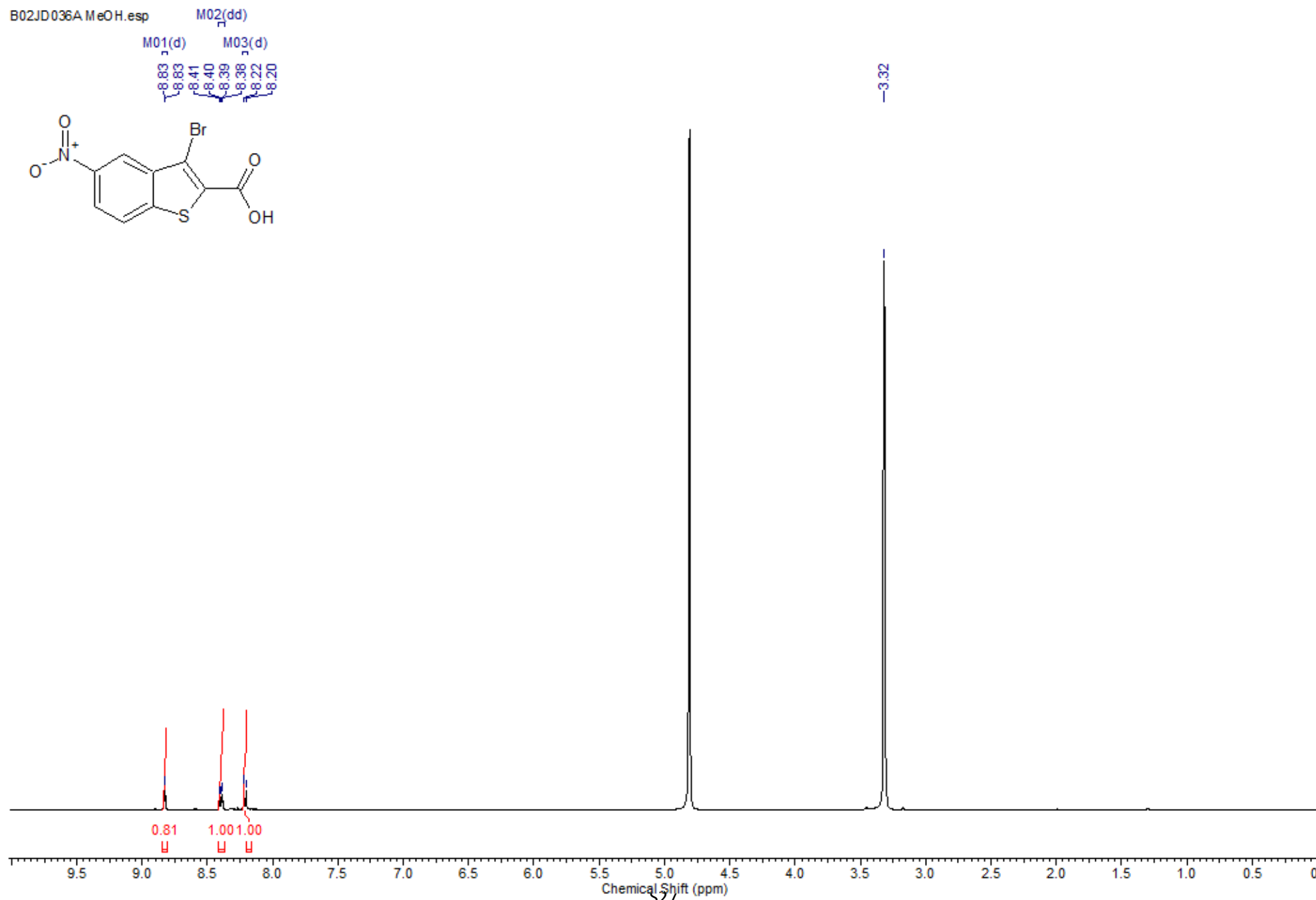
¹H NMR spectrum (500 MHz, CD₃OD) for 5-nitrobenzo[*b*]thiophene-2-carboxylic acid (**11**)



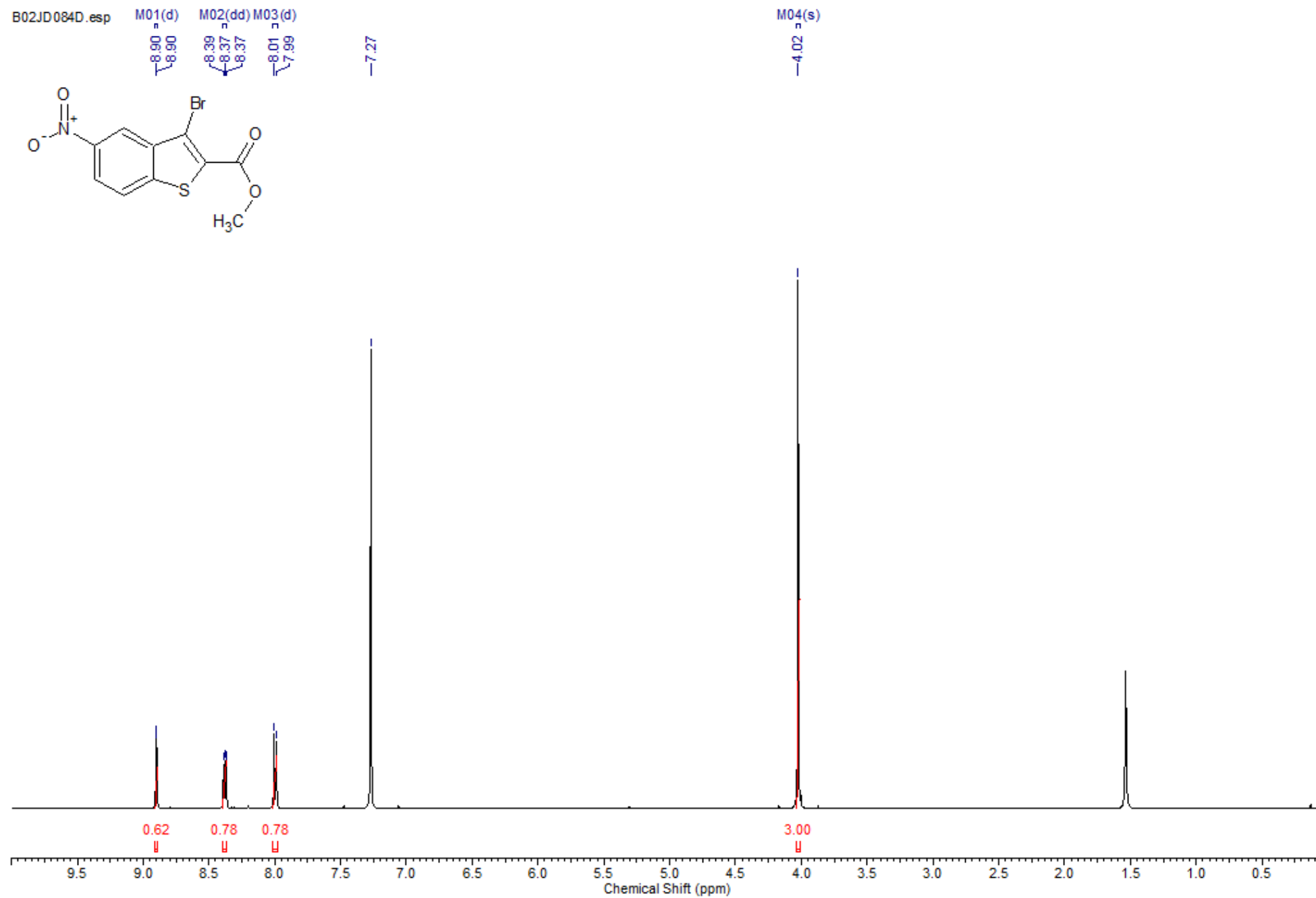
^{13}C NMR spectrum (125 MHz, CD_3OD) for 5-nitrobenzo[*b*]thiophene-2-carboxylic acid (**11**)



^1H NMR spectrum (500 MHz, CD_3OD) for 3-bromo-5-nitrobenzo[*b*]thiophene-2-carboxylic acid (**12**)

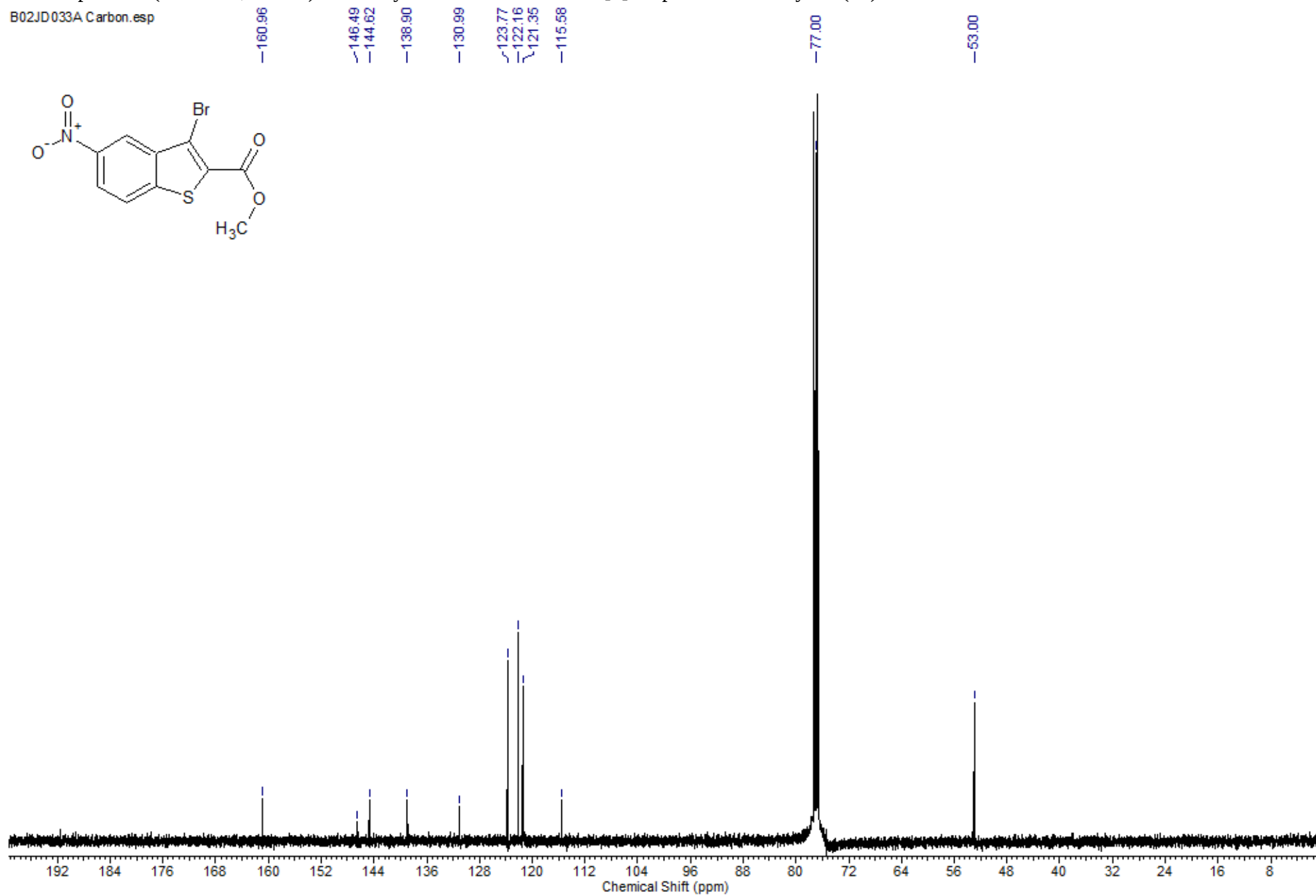


¹H NMR spectrum (500 MHz, CDCl₃) for methyl 3-bromo-5-nitrobenzo[*b*]thiophene-2-carboxylate (**13**)

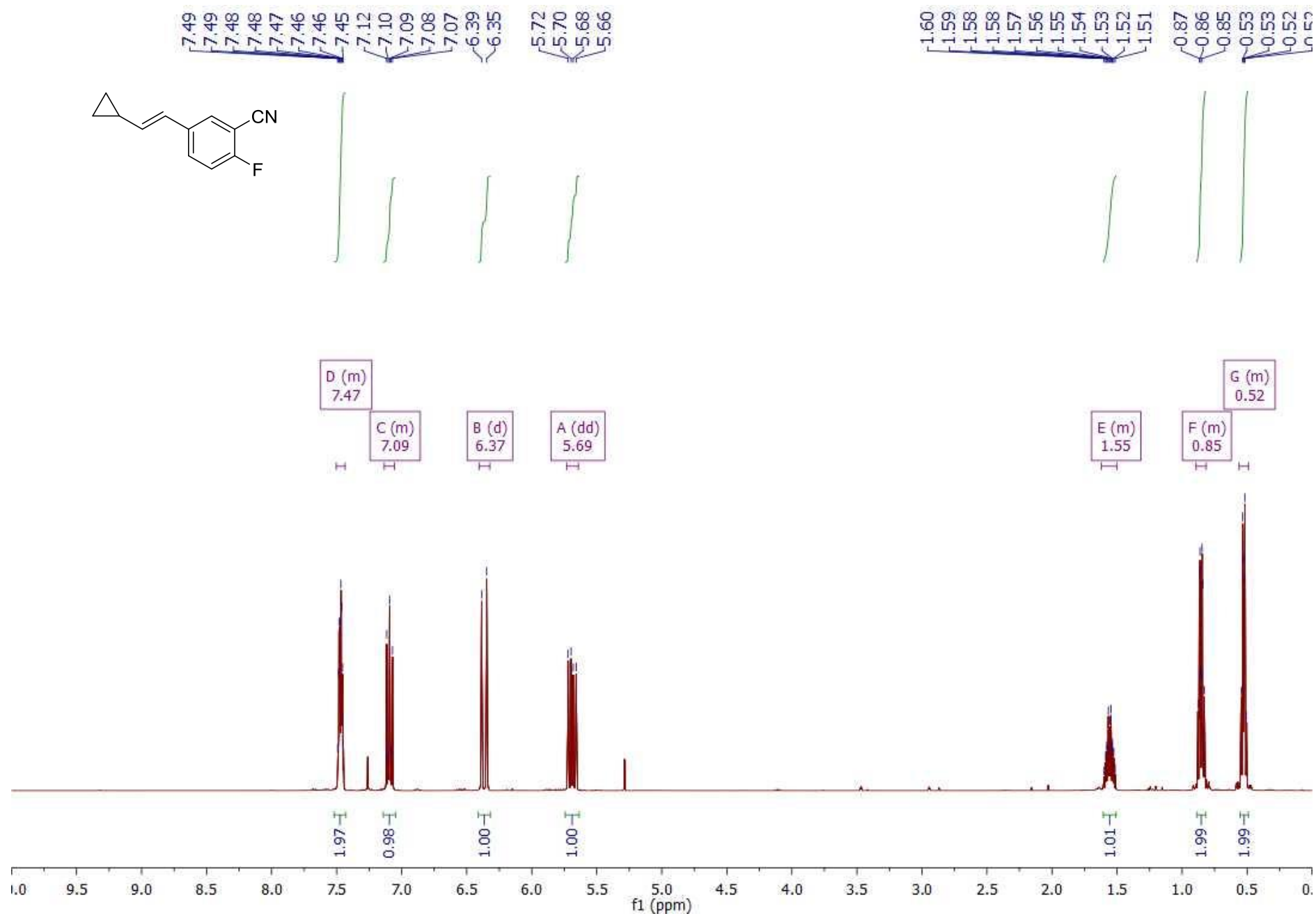


^{13}C NMR spectrum (125 MHz, CDCl_3) for methyl 3-bromo-5-nitrobenzo[*b*]thiophene-2-carboxylate (**13**)

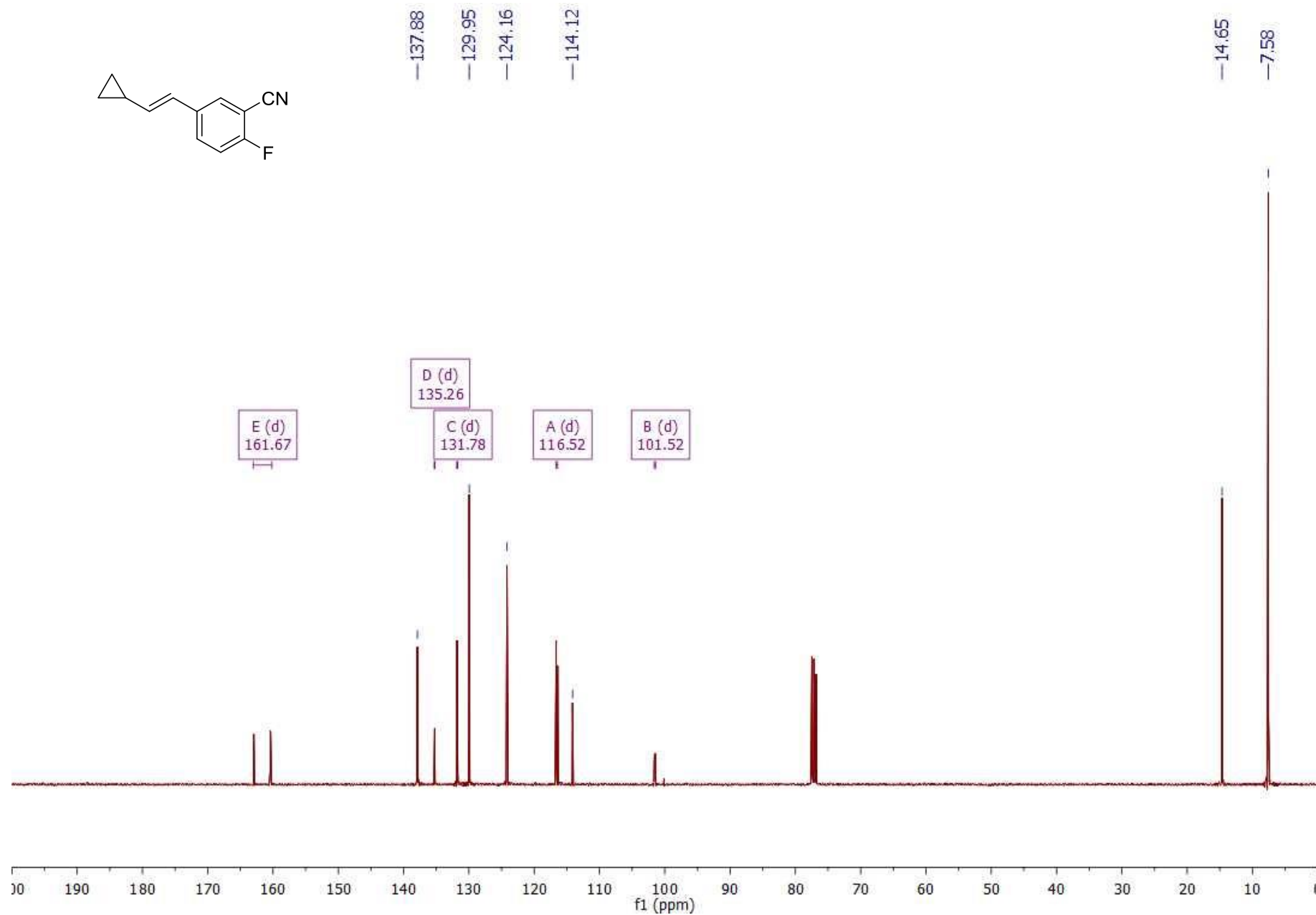
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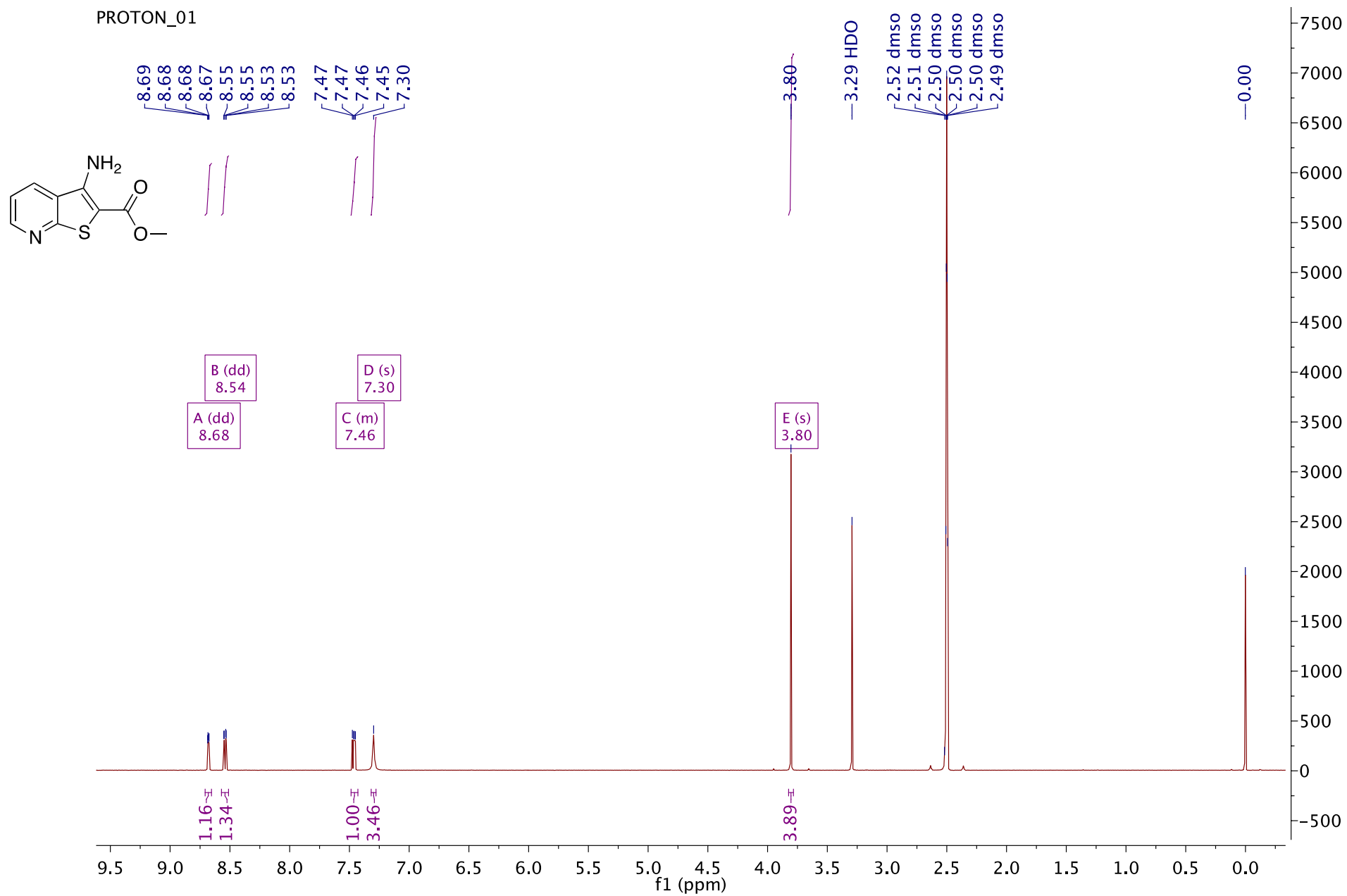
^1H NMR spectrum (400 MHz, CDCl_3) for (*E*)-5-(2-cyclopropylvinyl)-2-fluorobenzonitrile (**14i**)



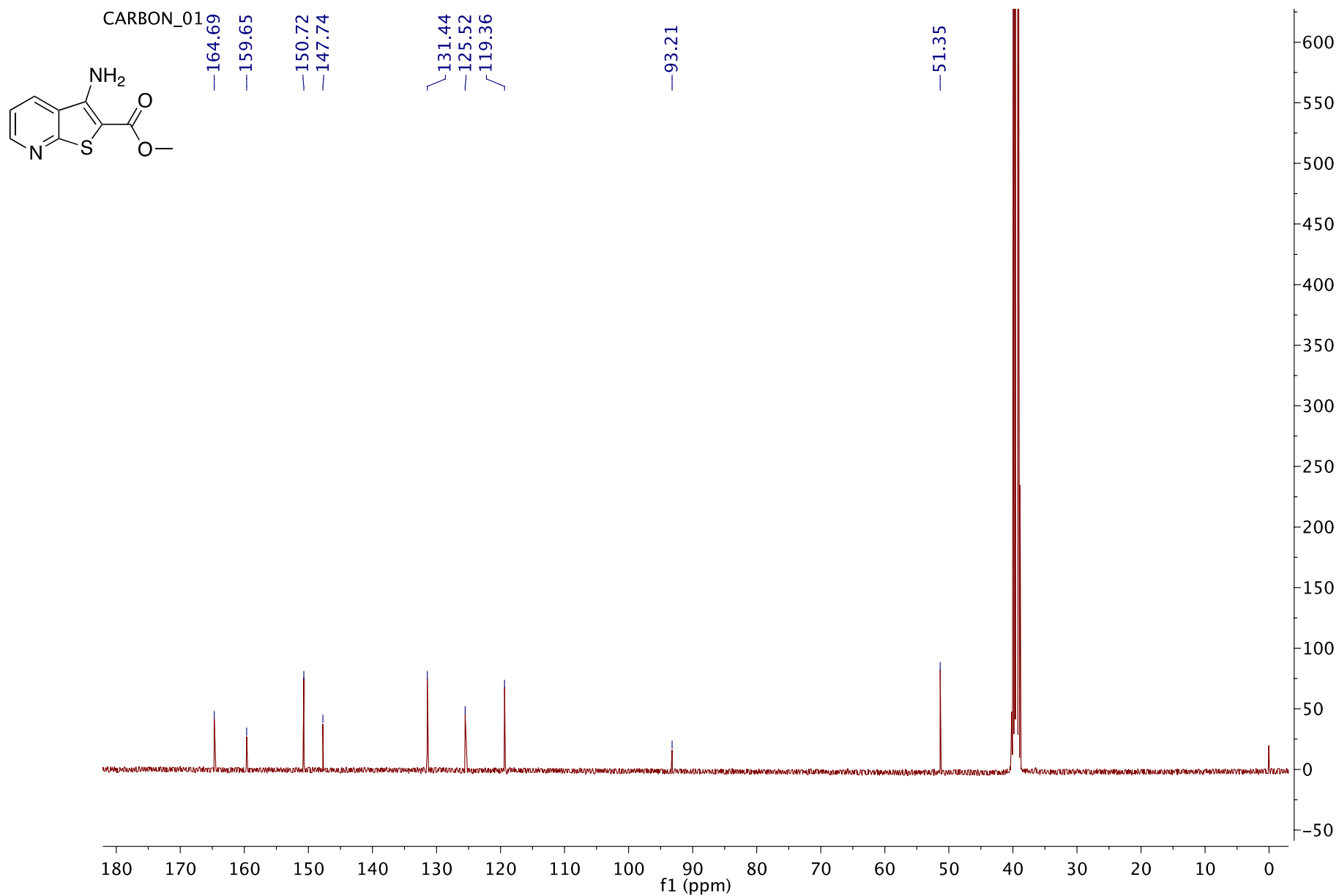
^{13}C NMR spectrum (101 MHz, CDCl_3) for (*E*)-5-(2-cyclopropylvinyl)-2-fluorobenzonitrile (**14i**)



¹H NMR spectrum (500 MHz, *d*₆-DMSO) for methyl 3-aminothieno[2,3-*b*]pyridine-2-carboxylate (**16**)

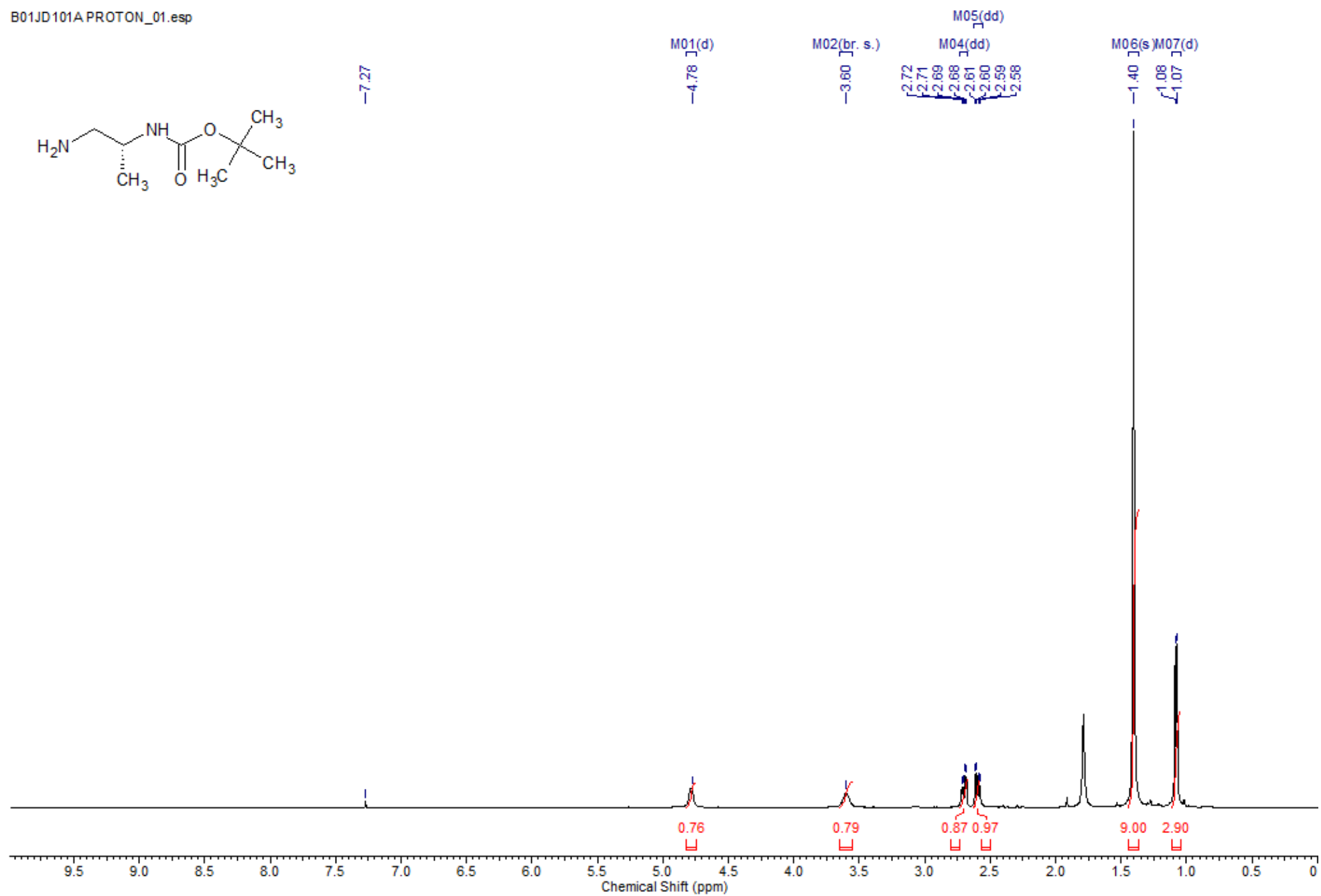


^{13}C NMR spectrum (125 MHz, d_6 -DMSO) for methyl 3-aminothieno[2,3-*b*]pyridine-2-carboxylate (**16**)



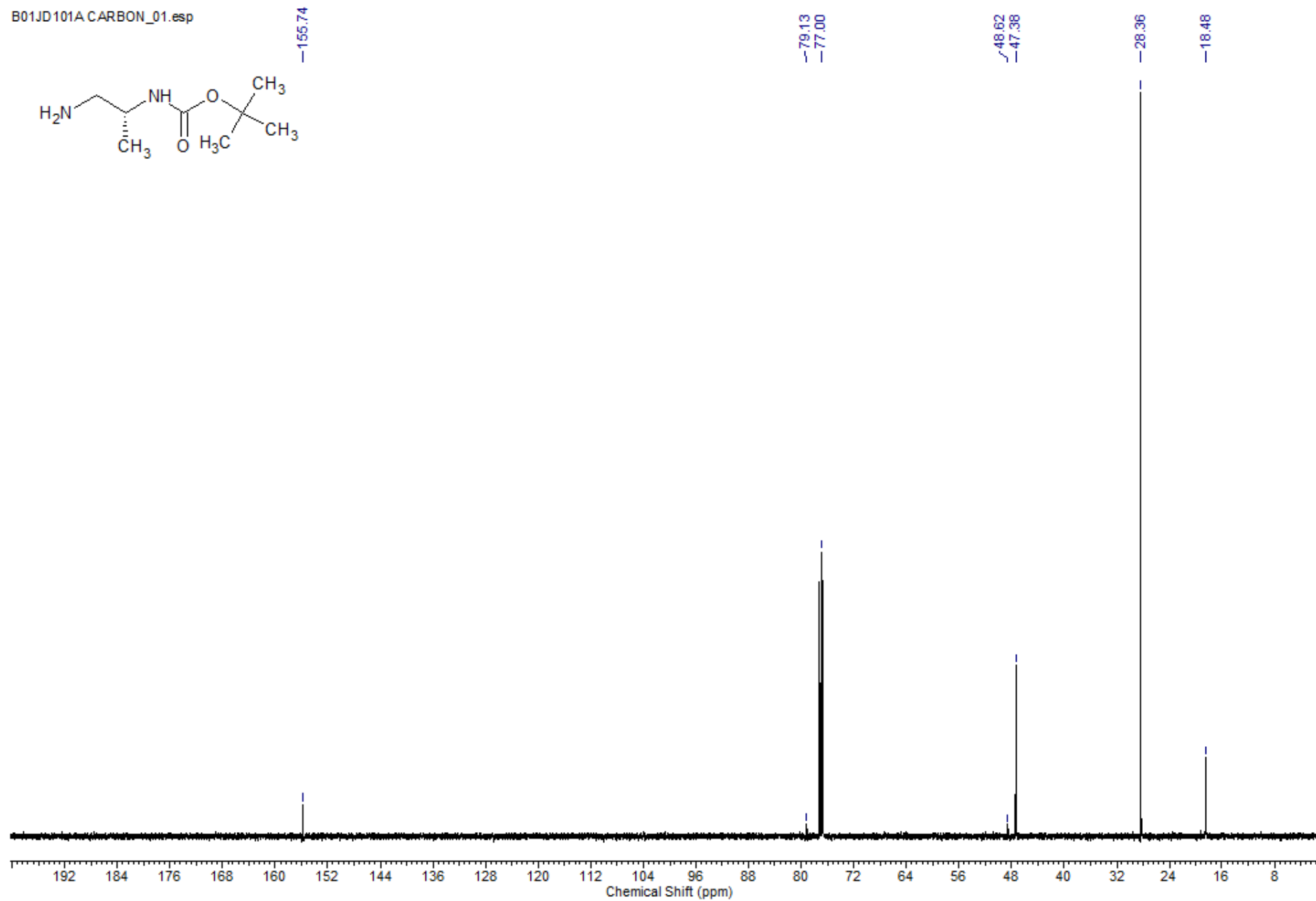
¹H NMR spectrum (500 MHz, CDCl₃) for *tert*-butyl [(2*R*)-1-aminopropan-2-yl]carbamate (**17**)

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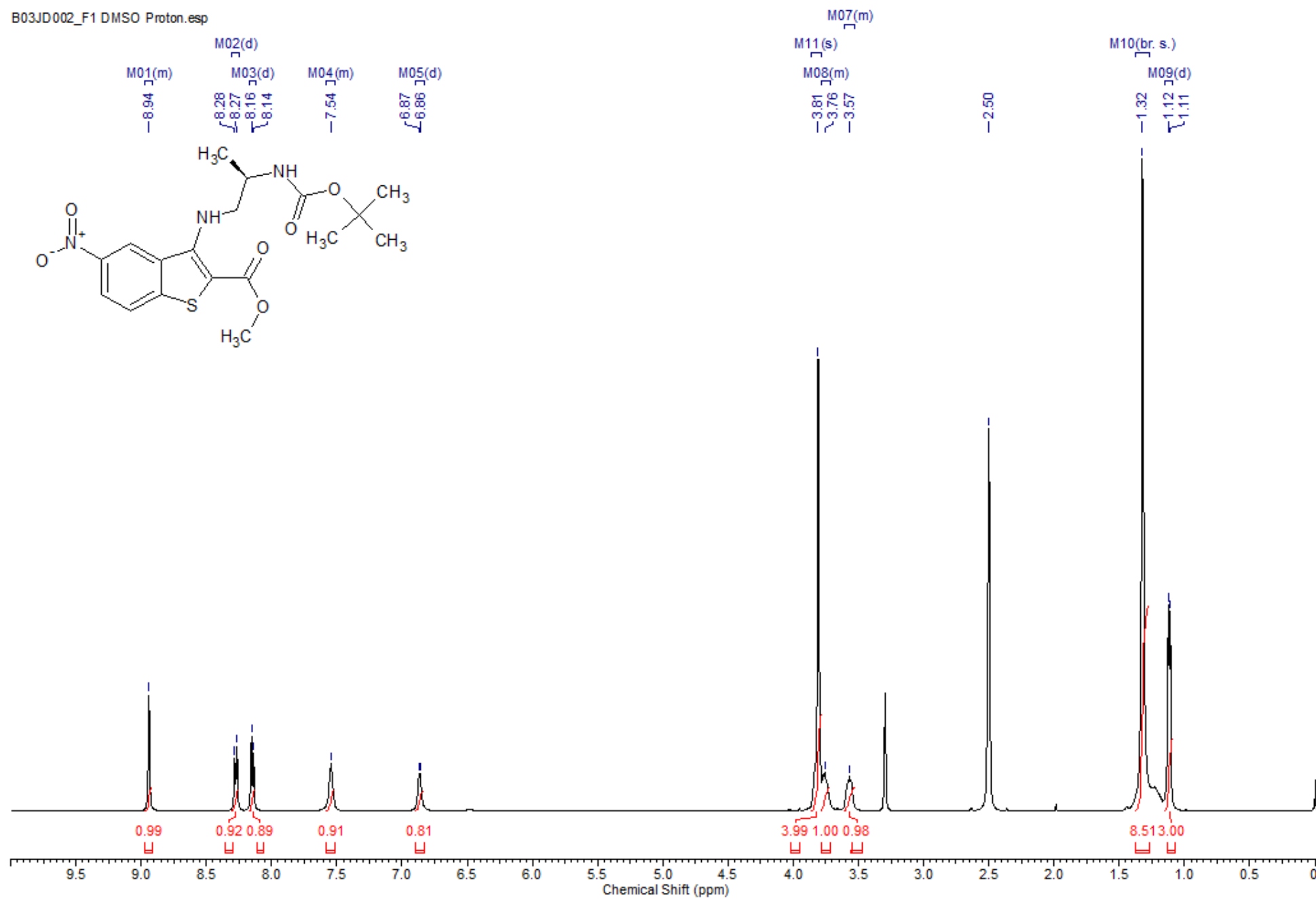
^{13}C NMR spectrum (125 MHz, CDCl_3) for *tert*-butyl [(2*R*)-1-aminopropan-2-yl]carbamate (**17**)

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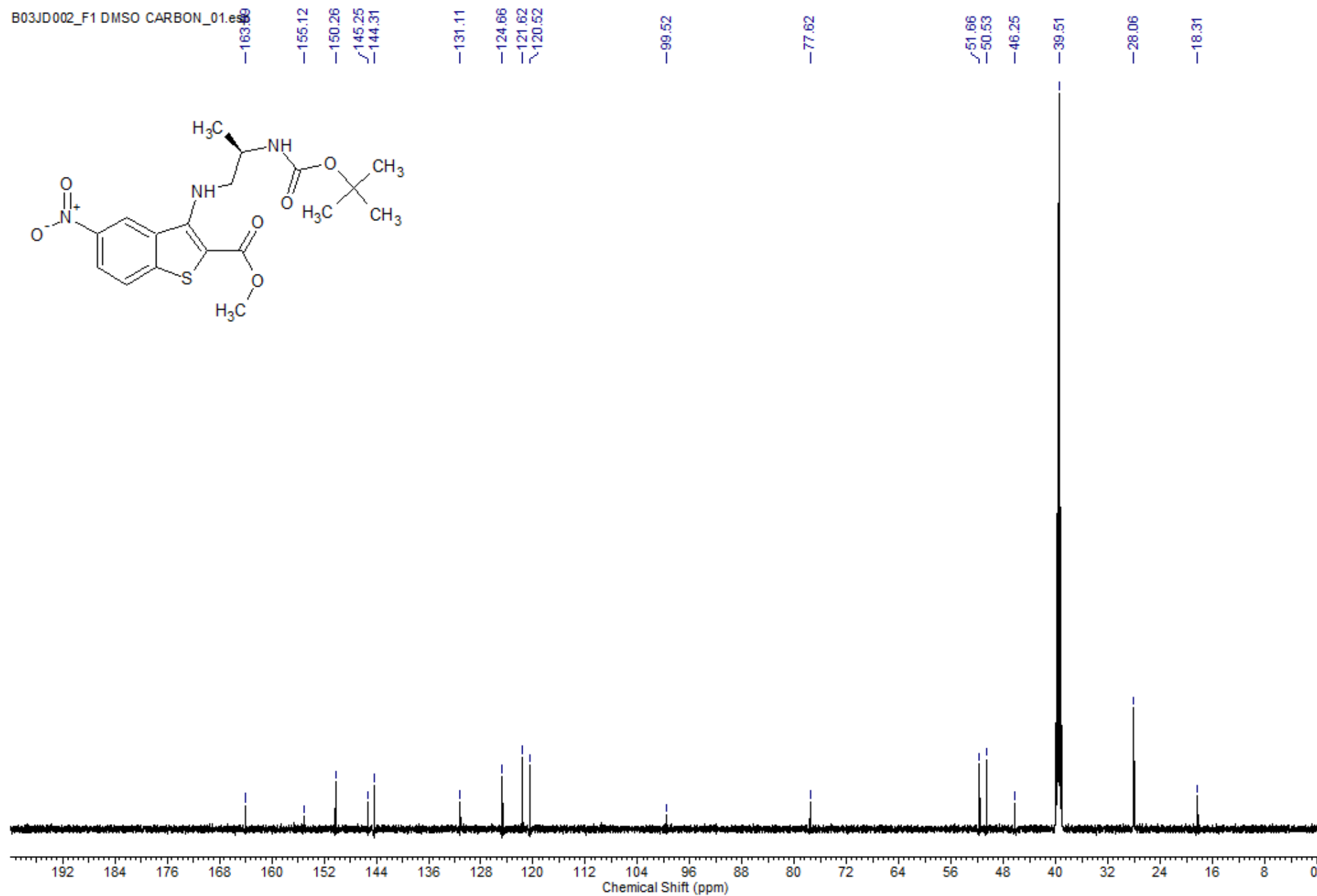


^1H NMR spectrum (500 MHz, d_6 -DMSO) for (*R*)-methyl 3-((2-((*tert*-butoxycarbonyl)amino)propyl)amino)-5-nitrobenzo[*b*]thiophene-2-carboxylate (**18**)

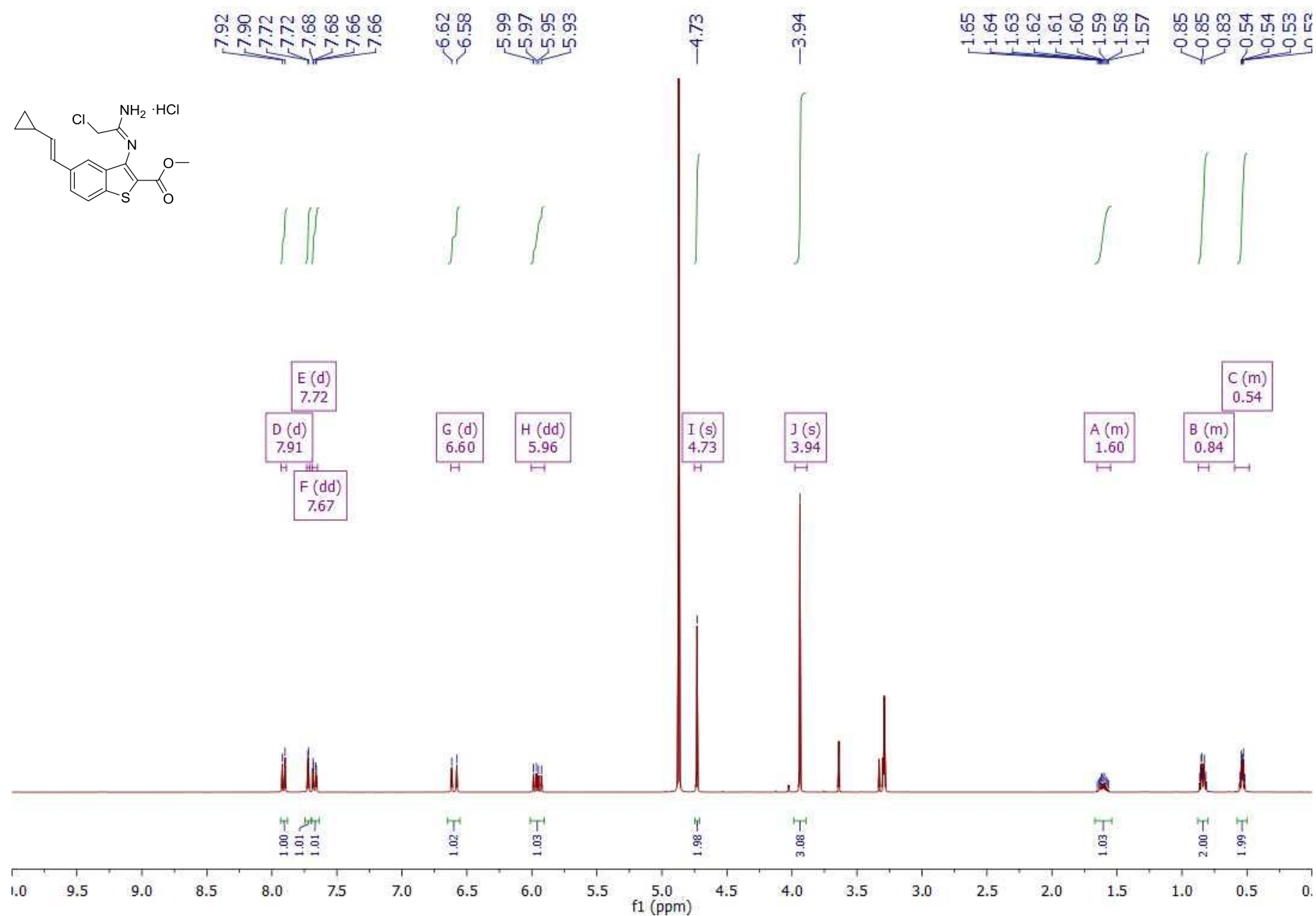
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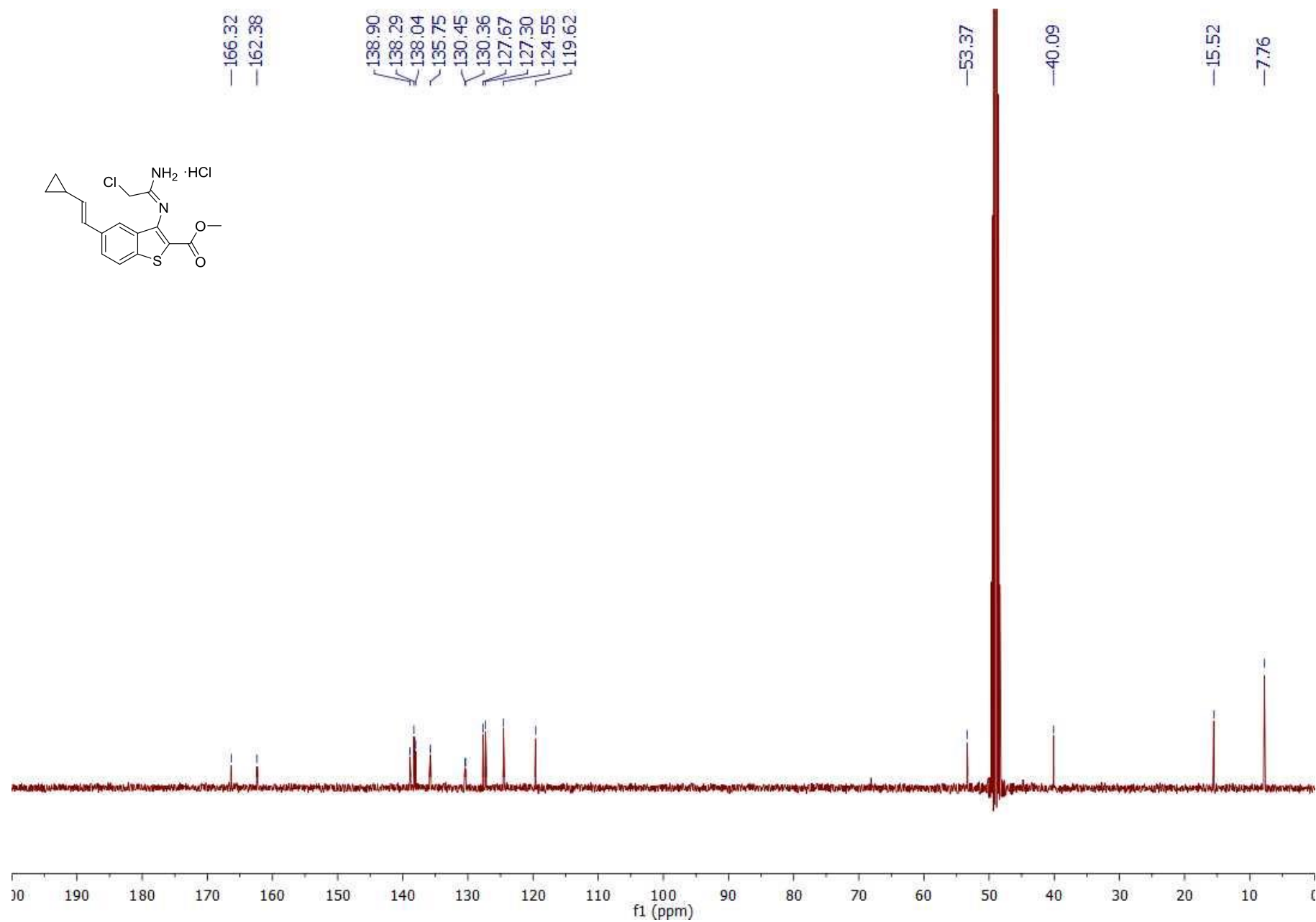
^{13}C NMR spectrum (125 MHz, d_6 -DMSO) for (*R*)-methyl 3-((2-((*tert*-butoxycarbonyl)amino)propyl)amino)-5-nitrobenzo[*b*]thiophene-2-carboxylate (**18**)



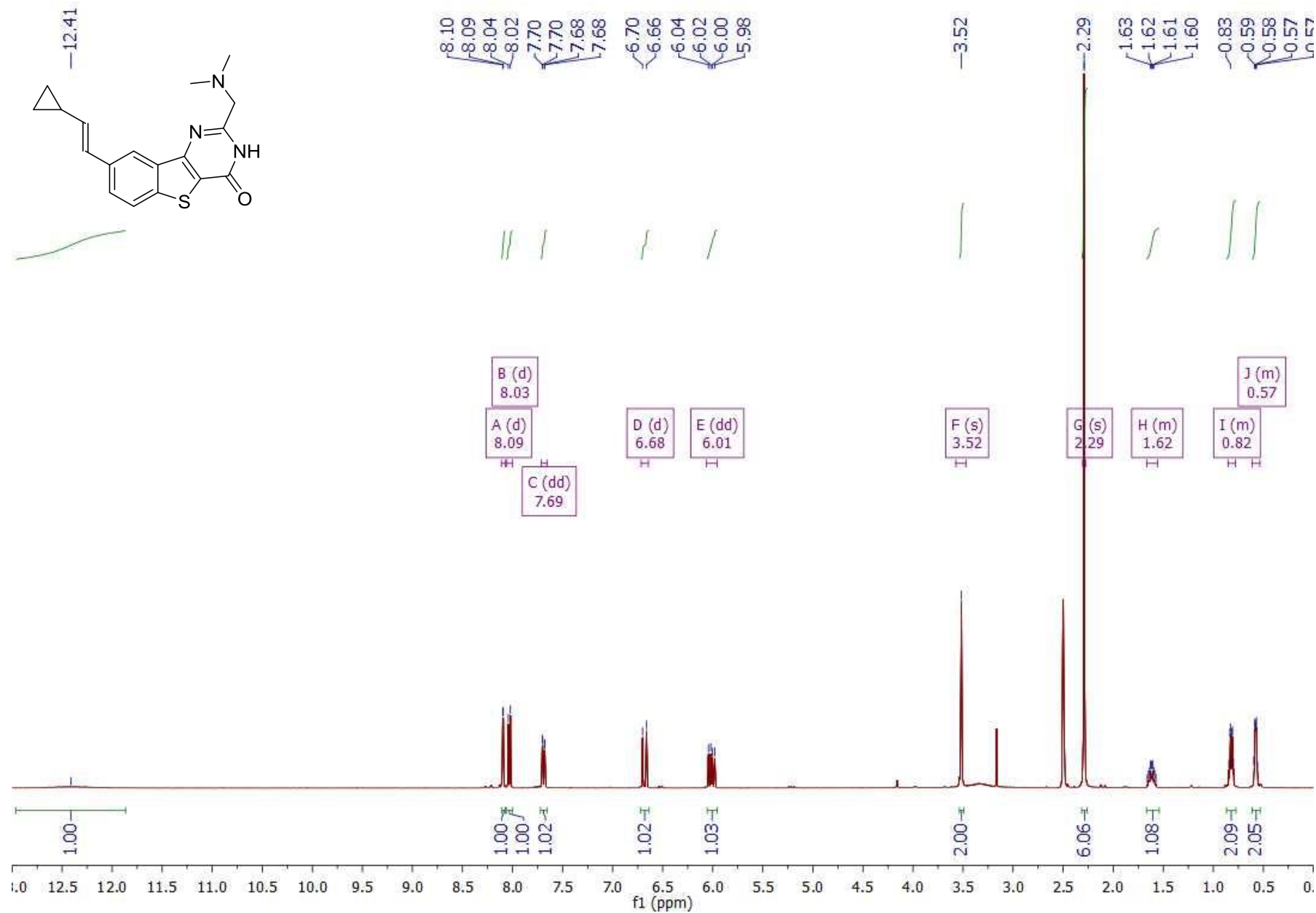
^1H NMR spectrum (400 MHz, CD_3OD) for methyl 3-(((*E*)-1-amino-2-chloroethylidene)amino)-5-((*E*)-2-cyclopropylvinyl)benzo[*b*]thiophene-2-carboxylate hydrochloride (**19**)



^{13}C NMR spectrum (101 MHz, CD_3OD) for methyl 3-(((*E*)-1-amino-2-chloroethylidene)amino)-5-((*E*)-2-cyclopropylvinyl)benzo[*b*]thiophene-2-carboxylate hydrochloride (**19**)



^1H NMR spectrum (400 MHz, d_6 -DMSO) for (*E*)-8-(2-cyclopropylvinyl)-2-((dimethylamino)methyl)benzo[4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (**20**)



^{13}C NMR spectrum (101 MHz, d_6 -DMSO) for (*E*)-8-(2-cyclopropylvinyl)-2-((dimethylamino)methyl)benzo[4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (**20**)

