Supporting Information

Construction of 2,3-disubstituted benzo[*b*]thieno[2,3-*d*]thiophenes and benzo[4,5]selenopheno[3,2-*b*]thiophenes using the Fiesselmann thiophene synthesis

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Table of content

Experimental section

Instruments and measurements

Analytical studies were carried out using equipment of the Center for Joint Use "Spectroscopy and Analysis of Organic Compounds" at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Division). Melting points were determined on combined heating stages and are uncorrected. Mass spectrometry was performed using a high resolution Q-TOF LC-MS/MS spectrometer. NMR measurements were performed on NMR spectrometers at 400 MHz, 500 MHz and 600 Hz for ^{1}H, and 126 MHz for ^{13}C spectra in DMSO-d_6 or $CDCl_3$ with tetramethylsilane as an internal standard. ^{19}F NMR was recorded at 471 MHz in DMSO-d_6 or $CDCl_3$ with hexafluorobenzene as an internal standard. X-ray diffraction analysis was performed on an automated X-ray diffractometer on standard procedure.

Materials

All solvents used were dried and distilled per standard procedures. All reagents were purchased from commercial sources and used without further purification, except for acyl chlorides **5a-b,d**,[1] **5c**,[2] **5e**[3] as well as ethyl 3-bromobenzo[*b*]selenophene-2-carboxylate,[4] which were prepared in accordance with the reported procedures.

1. General procedure for the synthesis of (3-chlorobenzo[*b*]thiophen-2-yl)((het)aryl)methanones (6a-m)

Acyl chloride **5a-e** (10.0 mmol) was dissolved in anhydrous CH_2Cl_2 (100 ml) (or in benzene for synthesis of compound **6f**), then grinded $AlCl_3$ (1.7 g, 13.0 mmol) was added, and the resulting mixture was stirred for 30 minutes until complete homogenization. After that the solution was cooled down to 0 °C with ice bath, and the appropriate (het)arene (12.0 mmol) was added dropwise (in the case of compound **6f** this step was skipped). The obtained reaction mixture was kept overnight at room temperature, and then quenched with water (100 ml). The organic layer was separated, washed with aqueous solution of Na_2CO_3 (100 ml, 0.1 M) and dried with anhydrous $CaCl_2$. The solvent was distilled under reduced pressure, and the residue was recrystallized from ethanol, thus giving desired compounds **6a-m**.

1.1 (3-Chlorobenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6a)

White crystals (2.9 g, 86%), m.p. (105-106 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 – 8.14 (m, 1H), 8.01 – 7.93 (m, 1H), 7.70 – 7.61 (m, 2H), 7.53 (dd, J = 8.3, 2.1 Hz, 1H), 7.48 (d, J = 2.1 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ

187.3, 153.8, 149.0, 138.3, 136.6, 134.0, 130.0, 127.4, 125.7, 125.5, 123.3, 123.0, 122.6, 111.5, 109.9, 56.1, 56.0. HRMS (+ESI): Calcd. for $C_{17}H_{13}ClLiO_3S$ m/z 339.0428 $[M+Li]^+$, found m/z 339.0423 $[M+ Li]^+$.

1.2 3-Chlorobenzo[*b*]thiophen-2-yl)(4-methoxyphenyl)methanone (6b)

White crystals (2.6 g, 87%), m.p. (80-81 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.90 (m, 3H), 7.94 – 7.83 (m, 1H), 7.57 – 7.48 (m, 2H), 7.01 – 6.94 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 164.0, 138.3, 136.6, 134.2, 132.5, 130.0, 127.4, 125.5, 123.3, 122.9, 122.7, 113.7, 55.5. HRMS (+ESI): Calcd. for $C_{16}H_{11}ClLiO_2S$ m/z 309.0323 $[M+Li]^+$, found m/z 309.0321 $[M+ Li]^+$.

1.3 (3-Chlorobenzo[*b*]thiophen-2-yl)(4-ethoxyphenyl)methanone (6c)

Pale yellow crystals (2.2 g, 70%), m.p. (95-96 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 – 7.94 (m, 1H), 7.94 – 7.91 (m, 2H), 7.90 – 7.83 (m, 1H), 7.57 – 7.50 (m, 2H), 7.01 – 6.92 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 3H), 1.46 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 163.5, 138.3, 136.6, 134.3, 132.5, 129.8, 127.4, 125.5, 123.3, 122.9, 122.7, 114.1, 63.8, 14.6. HRMS (+ESI): Calcd. for $C_{17}H_{13}ClLiO_2S$ m/z 323.0479 $[M+Li]^+$, found m/z 323.0478 $[M+ Li]^+$.

1.4 (3-Chlorobenzo[*b*]thiophen-2-yl)(2,5-dimethoxyphenyl)methanone (6d)

Yellow solid (1.9 g, 56%), m.p. (57-58 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (m, 1H), 7.89 – 7.79 (m, 1H), 7.60 – 7.41 (m, 2H), 7.05 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.99 (d, *J* = 3.1 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.3, 153.5, 151.7, 139.1, 137.3, 136.5, 129.5, 128.1, 125.3, 125.3, 124.0, 122.8, 118.3, 113.8, 112.7, 56.3, 55.8. HRMS (+ESI): Calcd. for $C_{17}H_{13}ClLiO_3S$ m/z 339.0428 $[M+Li]^+$, found m/z 339.0434 $[M+ Li]^+$.

1.5 (3-Chlorobenzo[*b*]thiophen-2-yl)(4-(dimethylamino)phenyl)methanone (6e)

Dark yellow crystals (1.5 g, 49%), m.p. (124-125 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.18 – 8.12 (m, 1H), 7.96 – 7.89 (m, 1H), 7.78 – 7.71 (m, 2H), 7.66 – 7.59 (m, 2H), 6.82 – 6.75 (m, 2H), 3.07 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.3, 153.9, 138.0, 136.5, 135.0, 132.7, 126.8, 125.3, 124.3, 123.0, 122.6, 121.3, 110.5, 39.9. HRMS (+ESI): Calcd. for $C_{17}H_{14}ClLiNOS$ m/z 322.0639 $[M+Li]^+$, found m/z 322.0639 $[M+ Li]^+$.

1.6 (3-Chlorobenzo[*b*]thiophen-2-yl)(phenyl)methanone (6f)

Beige solid (1.7 g, 61%), m.p. (75-76 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19 (m, 1H), 8.04 – 7.96 (m, 1H), 7.92 – 7.85 (m, 2H), 7.74 (m, 1H), 7.72 – 7.61 (m, 2H), 7.60 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 189.0, 138.6, 137.5, 136.7, 133.9, 133.2, 129.6, 128.3, 127.8, 125.5, 124.2, 123.6, 122.7. HRMS (+ESI): Calcd. for $C_{15}H_9ClLiOS$ m/z 279.0217 $[M+Li]^+$, found m/z 279.0217 $[M+ Li]^+$.

1.7 (3-Chlorobenzo[*b*]thiophen-2-yl)(thiophen-2-yl)methanone (6g)

Pale yellow solid (0.8 g, 28%), m.p. (70-71 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.93 (m, 1H), 7.92 – 7.85 (m, 2H), 7.79 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.19 (dd, *J* = 4.9, 3.9 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.7, 143.6, 138.1, 136.6, 135.6, 135.4, 132.3, 128.2, 127.7, 125.7, 124.0, 123.6, 122.6. HRMS (+ESI): Calcd. for $C_{13}H_7ClLiOS_2$ m/z 284.9781 $[M+Li]^+$, found m/z 284.9780 $[M+ Li]^+$.

1.8 (3-Chlorobenzo[*b*]thiophen-2-yl)(5-methylthiophen-2-yl)methanone (6h)

Beige solid (1.1 g, 38%), m.p. (89-90 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.94 (m, 1H), 7.89 – 7.82 (m, 1H), 7.70 (d, *J* = 3.8 Hz, 1H), 7.58 – 7.50 (m, 2H), 6.86 (dd, *J* = 3.8, 1.1 Hz, 1H), 2.59 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.2, 152.1, 141.3, 138.0, 136.6, 132.4, 127.5, 127.05, 127.04, 125.6, 123.44, 123.38, 122.6, 16.2. HRMS (+ESI): Calcd. for $C_{14}H_{10}ClLiOS_2$ m/z 292.9856 $[M+H]^+$, found m/z 292.9852 $[M+ H]^+$.

1.9 (5-Bromothiophen-2-yl)(3-chlorobenzo[*b*]thiophen-2-yl)methanone (6i)

Red solid (2.8 g, 78%), m.p. (130-131 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25 – 8.16 (m, 1H), 8.04 – 7.98 (m, 1H), 7.85 (d, *J* = 4.1 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.49 (d, *J* = 4.1 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.4, 144.9, 138.1, 136.6, 135.7, 131.4, 131.3, 127.9, 125.8, 124.7, 124.4, 123.6, 122.7. HRMS (+ESI): Calcd. for $C_{13}H_6BrClLiOS_2$ m/z 362.8887 $[M+Li]^+$, found m/z 362.8882 $[M+ Li]^+$.

1.10 (3-Chloro-6-methoxybenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6j)

Orange solid (2.9 g, 80%), m.p. (174-175 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.56 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.1, 159.9, 153.5, 148.8, 140.4, 131.5, 130.7, 130.3, 125.3, 124.4, 123.6, 116.3, 111.6, 109.9, 104.2, 56.0, 56.0, 55.6. HRMS (+ESI): Calcd. for $C_{18}H_{15}ClLiO_4S$ m/z 369.0534 $[M+Li]^+$, found m/z 369.0539 $[M+ Li]^+$.

1.11 (3,7-Dichloro-6-methoxybenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6k)

Orange solid (2.8 g, 71%), m.p. (167-168 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H), 3.98 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.8, 154.5, 153.8, 149.0, 139.5, 133.0, 131.3, 130.0, 125.5, 123.5, 122.6, 114.8, 111.9, 111.5, 109.9, 56.9, 56.1, 56.0. HRMS (+ESI): Calcd. for $C_{18}H_{15}Cl_2O_4S$ m/z 397.0063 $[M+H]^+$, found m/z 397.0061 $[M+ H]^+$.

1.12 (6-Bromo-3-chlorobenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6l)

Pale yellow solid (3.5 g, 85%), m.p. (153-154 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 1.7 Hz, 1H), 7.81 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.63 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.58 – 7.50 (m, 2H), 6.92 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.8, 154.0, 149.1, 139.5, 135.4, 134.4, 129.7, 129.2, 125.8, 125.2, 124.5, 122.9, 121.8, 111.5, 109.9, 56.1, 56.0. HRMS (+ESI): Calcd. for $C_{17}H_{12}BrClLiO_3S$ m/z 416.9534 $[M+Li]^+$, found m/z 416.9526 $[M+ Li]^+$.

1.13 (1-Chloronaphtho[2,1-*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6m)

Pale orange solid (2.5 g, 64%), m.p. (155-156 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.50 (d, *J* = 8.2 Hz, 1H), 7.98 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.65 – 7.60 (m, 1H), 7.59 – 7.54 (m, 2H), 6.93 – 6.90 (m, 1H), 3.98 (s, 3H), 3.96 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 153.8, 149.0, 138.3, 133.8, 132.0, 130.3, 129.7, 129.0, 128.7, 126.9, 126.1, 125.8, 124.1, 122.9, 120.2, 111.5, 109.9, 56.05, 55.99. (One signal was not found due to overlapping peaks). HRMS (+ESI): Calcd. for $C_{21}H_{15}ClNaO_3S$ m/z 405.0323 $[M+Na]^+$, found m/z 405.0326 $[M+Na]^+$.

2. General procedure for the synthesis of methyl 3-(het)arylbenzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylates (7b-m) and methyl 3-(3,4-dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophene-2-carboxylate (15)

Compound **6b-m** or **14** (1.0 mmol) was dissolved in THF-MeOH (9:1, v/v, 10 ml) under an argon atmosphere, then methyl thioglycolate (135 μl, 1.5 mmol), DBU (75 μl, 0.5 mmol) and CaO (280.0 mg, 5.0 mmol) were added. The resulted reaction mixture was stirred for 15 h at room temperature, after that the precipitate of CaO was filtered off and washed with THF (2×10 ml). The combined

filtrates were evaporated under reduced pressure, and the residue was recrystallized from MeOH-toluene (5:1, v/v) to afford analytically pure products **7b-m** or **15**, respectively.

Large-scale procedure for the synthesis of compound 7a

Compound **6a** (1.7 g, 5.0 mmol) was dissolved in THF-MeOH (9:1, v/v, 50 ml) under an argon atmosphere, then methyl thioglycolate (0.7 ml, 7.5 mmol), DBU (0.4 ml, 2.5 mmol) and CaO (1.4 g, 25.0 mmol) were added. The resulted reaction mixture was stirred for 15 h at room temperature, after that the precipitate of CaO was filtered off and washed with THF (2×50 ml). The combined filtrates were evaporated under reduced pressure, and the residue was recrystallized from MeOH-toluene (5:1, v/v) to afford product **7a** (1.78 g, 91%).

2.1 Methyl 3-(3,4-dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7a)

White solid, m.p. (162-163 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19 – 8.12 (m, 1H), 8.14 – 8.06 (m, 1H), 7.58 – 7.49 (m, 2H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.4, 149.3, 148.4, 143.1, 141.2, 140.6, 136.8, 132.3, 127.1, 126.4, 125.9, 124.9, 123.8, 121.9, 121.7, 112.4, 110.7, 55.9, 55.8, 52.0. HRMS (+ESI): Calcd. for $C_{20}H_{16}LiO_4S_2$ m/z 391.0645 $[M+Li]^+$, found m/z 391.0646 $[M+Li]^+$.

2.2 Methyl 3-(4-methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7b)

White solid (315.0 mg, 89%), m.p. (135-136 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 – 8.12 (m, 1H), 8.12 – 8.03 (m, 1H), 7.63 – 7.55 (m, 2H), 7.55 – 7.49 (m, 2H), 7.12 – 7.04 (m, 2H), 3.85 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.5, 159.8, 143.2, 141.3, 140.6, 136.8, 132.3, 130.4, 127.0, 126.2, 125.9, 124.9, 123.9, 121.7, 113.6, 55.2, 52.0. HRMS (+ESI): Calcd. for $C_{19}H_{14}LiO_3S_2$ m/z 361.0539 $[M+Li]^+$, found m/z 361.0543 $[M+Li]^+$.

2.3 Methyl 3-(4-ethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7c)

Pale yellow crystals (313.0 mg, 85%), m.p. (137-138 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19 – 8.12 (m, 1H), 8.13 – 8.05 (m, 1H), 7.60 – 7.49 (m, 4H), 7.11 – 7.02 (m, 2H), 4.12 (q, *J* = 6.9 Hz, 2H), 3.76 (s, 3H), 1.38 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.6, 159.3, 143.2, 141.4, 140.6, 136.8, 132.3, 130.4, 127.0, 126.1, 125.9, 124.9, 123.9, 121.7, 114.1, 63.4, 52.0, 14.8. HRMS (+ESI): Calcd. for $C_{20}H_{16}LiO_3S_2$ m/z 375.0695 $[M+Li]^+$, found m/z 375.0694 $[M+Li]^+$.

2.4 Methyl 3-(2,5-dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7d)

Beige crystals (250.0 mg, 65%), m.p. (149-150 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 – 8.10 (m, 1H), 8.12 – 8.02 (m, 1H), 7.58 – 7.46 (m, 2H), 7.10 (dd, *J* = 8.9, 0.6 Hz, 1H), 7.06 – 6.99 (m, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 152.9, 150.5, 142.8, 140.2, 136.5, 136.1, 131.9, 129.2, 125.3, 124.4, 123.5, 123.4, 121.2, 115.3, 114.5, 111.9, 55.7, 55.3, 51.6. HRMS (+ESI): Calcd. for $C_{20}H_{16}LiO_4S_2$ m/z 391.0645 $[M+Li]^+$, found m/z 391.0644 $[M+Li]^+$.

2.5 Methyl 3-(4-(dimethylamino)phenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7e)

Yellow crystals (202.0 mg, 55%), m.p. (202-203 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 1H), 7.85 (m, 1H), 7.61 – 7.54 (m, 2H), 7.48 – 7.37 (m, 2H), 6.85 – 6.78 (m, 2H), 3.84 (s, 3H), 3.05 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.7, 150.5, 143.3, 142.3, 140.6, 136.6, 132.4, 130.2, 125.75, 125.70, 124.8, 123.8, 121.7, 121.3, 111.5, 52.0, 40.2. HRMS (+ESI): Calcd. for $C_{20}H_{17}LiNO_2S_2$ m/z 374.0655 $[M+Li]^+$, found m/z 374.0854 $[M+Li]^+$.

2.6 Methyl 3-phenylbenzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7f)

Pale orange crystals (266.0 mg, 82%), m.p. (142-143 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.21 – 8.14 (m, 1H), 8.13 – 8.05 (m, 1H), 7.66 – 7.59 (m, 2H), 7.59 – 7.46 (m, 5H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.4, 143.2, 141.4, 140.5, 136.9, 134.1, 132.2, 129.0, 128.6, 128.2, 127.8, 125.9, 124.9, 123.9, 121.7, 52.0. HRMS (+ESI): Calcd. for $C_{18}H_{12}LiO_2S_2$ m/z 331.0433 $[M+Li]^+$, found m/z 331.0433 $[M+Li]^+$.

2.7 Methyl 3-(thiophen-2-yl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7g)

Pale yellow crystals (267.0 mg, 81%), m.p. (130-132 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 – 8.15 (m, 1H), 8.14 – 8.09 (m, 1H), 7.84 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.69 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.27 (dd, *J* = 5.1, 3.6 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.2, 143.1, 140.4, 136.8, 134.2, 133.7, 132.0, 129.6, 127.3, 127.2, 127.0, 126.1, 125.0, 123.8, 121.7, 52.2. HRMS (+ESI): Calcd. for $C_{16}H_{10}LiO_2S_3$ m/z 339.9997 $[M+Li]^+$, found m/z 339.9995 $[M+Li]^+$.

2.8 Methyl 3-(5-methylthiophen-2-yl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7h)

Yellow solid (258.0 mg, 75%), m.p. (69-70 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 – 8.07 (m, 2H), 7.59 – 7.51 (m, 2H), 7.50 (d, *J* = 3.6 Hz, 1H), 6.95 (dd, *J* = 3.6, 1.1 Hz, 1H), 3.83 (s, 3H), 2.55 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.3, 143.16, 143.15, 142.1,

140.2, 136.7, 134.1, 132.0, 131.8, 129.9, 126.0, 125.4, 124.9, 123.7, 121.6, 52.1, 15.3. HRMS (+ESI): Calcd. for $C_{17}H_{12}LiO_2S_3$ m/z 351.0154 $[M+Li]^+$, found m/z 351.0154 $[M+Li]^+$.

2.9 Methyl 3-(5-bromothiophen-2-yl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7i)

Orange solid (217.0 mg, 53%), m.p. (171-173 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 – 8.16 (m, 1H), 8.16 – 8.12 (m, 1H), 7.60 – 7.53 (m, 2H), 7.51 (d, *J* = 3.9 Hz, 1H), 7.40 (d, *J* = 3.9 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1, 143.0, 139.9, 137.0, 135.7, 132.6, 131.9, 129.9, 129.8, 127.4, 126.3, 125.1, 123.8, 121.7, 114.7, 52.3. HRMS (+ESI): Calcd. for $C_{16}H_9BrLiO_2S_3$ m/z 414.9103 $[M+Li]^+$, found m/z 414.9106 $[M+Li]^+$.

2.10 Methyl 3-(3,4-dimethoxyphenyl)-6-methoxybenzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7j)

White solid (273.0 mg, 66%), m.p. (170-171 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.01 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.16 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.11 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.5, 158.5, 149.2, 148.4, 145.1, 141.3, 138.8, 136.9, 126.5, 126.0, 125.6, 122.4, 121.9, 114.4, 112.5, 110.7, 106.5, 55.9, 55.8, 55.5, 51.9. HRMS (+ESI): Calcd. for $C_{21}H_{18}LiO_5S_2$ m/z 421.0750 $[M+Li]^+$, found m/z 421.0755 $[M+Li]^+$.

2.11 Methyl 5-chloro-3-(3,4-dimethoxyphenyl)-6-methoxybenzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7k)

White solid (228.0 mg, 51%), m.p. (235-236 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 4.01 (s, 3H), 3.96 (s, 3H), 3.94 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.5, 153.5, 149.4, 148.6, 144.6, 141.5, 139.7, 137.0, 127.1, 126.5, 126.2, 121.9, 120.6, 116.2, 112.5, 110.84, 110.77, 56.9, 56.0, 55.9, 52.1. HRMS (+ESI): Calcd. for $C_{21}H_{18}ClO_5S_2$ m/z 449.0279 $[M+H]^+$, found m/z 449.0278 $[M+H]^+$.

2.12 Methyl 6-bromo-3-(3,4-dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7l)

White solid (278.0 mg, 60%), m.p. (197-198 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.43 (d, *J* = 1.8 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.20 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3, 149.4, 148.5, 144.5, 141.1, 140.8, 136.1, 131.1, 128.4,

127.6, 126.3, 126.1, 122.6, 121.8, 119.7, 112.4, 110.8, 55.9, 55.8, 52.1. HRMS (+ESI): Calcd. for $C_{20}H_{15}BrLiO_4S_2$ m/z 468.9750 $[M+Li]^+$, found m/z 468.9753 $[M+Li]^+$.

2.13 Methyl 8-(3,4-dimethoxyphenyl)naphtho[2,1-*b*]thieno[2,3-*d*]thiophene-9-carboxylate (7m)

White solid (291.0 mg, 67%), m.p. (237-238 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.50 (d, *J* = 8.2 Hz, 1H), 7.98 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.65 – 7.59 (m, 1H), 7.60 – 7.55 (m, 2H), 6.97 – 6.83 (m, 1H), 3.98 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 153.8, 149.0, 138.3, 133.8, 132.0, 130.3, 129.7, 129.0, 128.7, 126.9, 126.1, 125.8, 124.10, 124.09, 122.9, 120.2, 111.5, 109.9, 56.05, 55.99, 55.98. (Two signals were not found due to overlapping peaks). HRMS (+ESI): Calcd. for $C_{24}H_{18}LiO_4S_2$ m/z 441.0801 $[M+Li]^+$, found m/z 441.0801 $[M+Li]^+$.

2.14 Methyl 3-(3,4-dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophene-2-carboxylate (15)

White solid (272.0 mg, 63%), m.p. (166-167 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 2H), 7.50 – 7.43 (m, 1H), 7.36 (m, 1H), 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.4, 149.3, 148.5, 143.9, 143.0, 139.35, 139.34, 139.1, 134.6, 127.4, 126.9, 126.1, 125.5, 123.2, 121.7, 112.2, 110.8, 56.0, 55.9, 52.1. HRMS (+ESI): Calcd. for $C_{20}H_{17}O_4SSe$ m/z 433.0007 $[M+H]^+$, found m/z 433.0011 $[M+H]^+$.

3. General procedure for the synthesis of 2-substituted 3-arylbenzo[*b*]thieno[2,3-*d*]thiophenes (8a-d, 9a-d, 10a-c), and 3-(3,4-dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophenes (16, 17a,b, 18).

$Na_2S·9H_2O$ (264.0 mg, 1.1 mmol) was suspended in DMF (10 ml) under an argon atmosphere. Then the substrate **6a**,**b**,**f**,**i** or **14** (1.0 mmol) was added, and the reaction mixture was heated at 60 °C for 45 min. The solution turned dark red. After cooling, the appropriate alkylating agent was added to the reaction mixture, namely chloroacetonitrile (70 µl, 1.1 mmol) for products **8a-d** and **16**, 2-chloro-acetophenone (171.0 mg, 1.1 mmol) or 2-chloro-4'-fluoroacetophenone (190.0 mg, 1.1 mmol) for products **9a-d** and **17a,b**, and chloroacetone (88 µl, 1.1 mmol) for products **10a-c** and **18**. The dark color immediately disappeared. The reaction mixture was stirred for 15 min, followed by addition of CaO (840.0 mg, 15.0 mmol) and DBU (75 µl, 0.5 mmol), and then kept at room temperature for another 15 h. After that the resulting mixture was diluted with hydrochloric acid solution (50 ml, 1 M), and the formed precipitate was filtered off, washed with

water (2×10 ml), dried, and recrystallized from acetonitrile, thus giving desired products **8a-d**, **9a-d**, **10a-c** or **16**, **17a-b**, **18**.

3.1 3-(3,4-Dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitrile (8a)

White solid (270.0 mg, 77%), m.p. (193-194 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.86 (m, 2H), 7.55 – 7.46 (m, 3H), 7.44 (d, *J* = 2.2 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 4.00 (s, 3H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 149.3, 144.2, 143.5, 137.8, 136.8, 131.5, 126.5, 125.3, 124.5, 123.9, 121.7, 120.7, 115.3, 111.4, 110.7, 103.5, 56.0, 55.9. HRMS (+ESI): Calcd. for $C_{19}H_{13}LiNO_2S_2$ m/z 358.0542 $[M+Li]^+$, found m/z 358.0542 $[M+Li]^+$.

3.2 3-(4-Methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitrile (8b)

White solid (254.0 mg, 79%), m.p. (199-200 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.85 (m, 2H), 7.88 – 7.79 (m, 2H), 7.54 – 7.42 (m, 2H), 7.13 – 7.04 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.7, 144.3, 143.6, 138.1, 137.9, 137.0, 131.7, 129.3, 126.5, 125.3, 124.4, 124.0, 121.7, 115.3, 114.7, 55.4. HRMS (+ESI): Calcd. for $C_{18}H_{11}LiNOS_2$ m/z 328.0437 $[M+Li]^+$, found m/z 328.0436 $[M+Li]^+$.

3.3 3-Phenylbenzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitrile (8c)

White solid (175.0 mg, 60%), m.p. (215-216 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.84 (m, 4H), 7.63 – 7.44 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.5, 143.7, 137.2, 132.0, 131.6, 129.9, 129.4, 127.9, 126.6, 125.4, 124.0, 121.8, 115.0, 105.0, 90.0. HRMS (+ESI): Calcd. for $C_{17}H_9LiNS_2$ m/z 298.0331 $[M+Li]^+$, found m/z 298.0328 $[M+Li]^+$.

3.4 3-(5-Bromothiophen-2-yl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitrile (8d)

Orange solid (173.0 mg, 46%), m.p. (203-204 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 2H), 7.59 (d, *J* = 4.0 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.19 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.6, 138.3, 136.1, 135.8, 135.2, 131.3, 131.0, 128.4, 126.9, 125.6, 124.1, 121.8, 115.5, 114.9, 103.1. HRMS (+ESI): Calcd. for $C_{15}H_6BrLiNS_3$ m/z 381.9000 $[M+Li]^+$, found m/z 381.9005 $[M+Li]^+$.

3.5 (3-(3,4-Dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)(phenyl)methanone (9a)

Pale yellow crystals (344.0 mg, 80%), m.p. (151-152 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 1H), 7.92 – 7.85 (m, 1H), 7.69 – 7.63 (m, 2H), 7.52 – 7.42 (m, 2H), 7.39 – 7.30 (m, 1H), 7.23 – 7.16 (m, 2H), 7.05 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* =

8.3 Hz, 1H), 3.85 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.1, 149.1, 148.6, 143.1, 139.9, 139.6, 137.9, 137.8, 137.5, 132.4, 132.3, 129.6, 127.8, 127.0, 126.1, 125.1, 123.9, 122.0, 121.8, 112.7, 111.0, 55.9, 55.7. HRMS (+ESI): Calcd. for $C_{25}H_{19}O_3S_2$ m/z 431.0770 $[M+H]^+$, found m/z 431.0773 $[M+H]^+$.

3.6 (3-(4-Methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)(phenyl)methanone (9b)

Pale yellow crystals (212.0 mg, 53%), m.p. (111-112 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 – 8.17 (m, 1H), 8.16 – 8.09 (m, 1H), 7.64 – 7.58 (m, 2H), 7.57 – 7.50 (m, 2H), 7.50 – 7.40 (m, 1H), 7.37 – 7.31 (m, 2H), 7.32 – 7.23 (m, 2H), 6.87 – 6.79 (m, 2H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.0, 159.5, 143.1, 139.9, 139.7, 137.7, 137.6, 137.4, 132.4, 132.1, 130.5, 129.6, 127.8, 126.6, 125.9, 125.0, 123.9, 121.9, 113.8, 55.2. HRMS (+ESI): Calcd. for $C_{24}H_{16}LiO_2S_2$ m/z 407.0746 $[M+Li]^+$, found m/z 407.0749 $[M+Li]^+$.

3.7 Phenyl(3-phenylbenzo[*b*]thieno[2,3-*d*]thiophen-2-yl)methanone (9c)

Pale yellow solid (222.0 mg, 60%), m.p. (113-114 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 1H), 7.91 – 7.85 (m, 1H), 7.67 – 7.61 (m, 2H), 7.52 – 7.43 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.29 (m, 1H), 7.25 – 7.14 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.0, 143.2, 140.0, 139.9, 138.5, 137.8, 137.4, 134.3, 132.4, 132.2, 129.7, 129.2, 128.4, 128.3, 127.8, 126.1, 125.1, 123.9, 121.9. HRMS (+ESI): Calcd. for $C_{23}H_{15}OS_2$ m/z 371.0559 $[M+H]^+$, found m/z 371.0561 $[M+H]^+$.

3.8 (4-Fluorophenyl)(3-(4-methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)methanone (9d)

Yellow crystals (314.0 mg, 75%), m.p. (143-144 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 – 8.19 (m, 1H), 8.17 – 8.05 (m, 1H), 7.71 – 7.63 (m, 2H), 7.60 – 7.47 (m, 2H), 7.37 – 7.30 (m, 2H), 7.12 – 7.03 (m, 2H), 6.89 – 6.82 (m, 2H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.5, 159.7, 143.1, 139.8, 139.5, 137.7, 137.4, 132.3, 132.2, 132.1, 130.5, 126.5, 126.0, 125.0, 123.9, 121.9, 115.0, 114.8, 113.9, 55.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 56.18 – 55.17 (m). HRMS (+ESI): Calcd. for $C_{24}H_{15}FNaO_2S_2$ m/z 441.0390 $[M+Na]^+$, found m/z 441.0389 $[M+Na]^+$.

3.9 1-(3-(3,4-Dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)ethan-1-one (10a)

Beige crystals (254.0 mg, 69%), m.p. (166-167 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 1H), 7.88 – 7.78 (m, 1H), 7.51 – 7.38 (m, 2H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.3, 149.7, 149.2, 143.4, 141.4, 141.0, 139.7, 137.6, 132.4, 126.9, 126.1,

125.1, 123.9, 122.2, 121.9, 112.0, 111.3, 56.1, 55.9, 28.9. HRMS (+ESI): Calcd. for $C_{20}H_{17}O_3S_2$ m/z 369.0614 $[M+H]^+$, found m/z 369.0615 $[M+H]^+$.

3.10 1-(3-(4-Methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)ethan-1-one (10b)

Orange crystals (195.0 mg, 57%), m.p. (157-158 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 1H), 7.83 (m, 1H), 7.51 – 7.38 (m, 4H), 7.10 – 7.02 (m, 2H), 3.91 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.3, 160.2, 143.4, 141.4, 140.9, 139.8, 137.6, 132.4, 130.3, 126.7, 126.1, 125.0, 123.9, 122.1, 114.4, 55.3, 28.9. HRMS (+ESI): Calcd. for $C_{19}H_{15}O_2S_2$ m/z 339.0508 $[M+H]^+$, found m/z 339.0508 $[M+H]^+$.

3.11 1-(3-Phenylbenzo[*b*]thieno[2,3-*d*]thiophen-2-yl)ethan-1-one (10c)

Brown crystals (129.0 mg, 42%), m.p. (145-146 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.92 (m, 1H), 7.87 – 7.79 (m, 1H), 7.58 – 7.50 (m, 5H), 7.48 – 7.40 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.1, 143.5, 141.4, 141.2, 139.8, 137.8, 134.7, 132.4, 129.1, 129.02, 128.96, 126.1, 125.1, 123.9, 122.2, 28.9. HRMS (+ESI): Calcd. for $C_{18}H_{13}OS_2$ m/z 309.0402 $[M+H]^+$, found m/z 309.0407 $[M+H]^+$.

3.12 3-(3,4-Dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophene-2-carbonitrile (16)

White solid (239.0 mg, 60%), m.p. (219-220 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.88 (m, 2H), 7.53 – 7.45 (m, 1H), 7.47 – 7.37 (m, 3H), 7.04 (d, *J* = 8.3 Hz, 1H), 3.99 (s, 6H), 3.97 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.3, 149.4, 147.0, 143.4, 140.5, 133.9, 126.9, 126.7, 125.8, 125.4, 123.1, 120.5, 115.2, 111.6, 110.6, 102.8, 56.1, 56.0. HRMS (+ESI): Calcd. for $C_{19}H_{14}NO_2SSe$ m/z 399.9905 $[M+H]^+$, found m/z 399.9907 $[M+H]^+$.

3.13 (3-(3,4-Dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophen-2-yl)(phenyl)methanone (17a)

Yellow crystals (281.0 mg, 59%), m.p. (171-172 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 1H), 7.93 – 7.89 (m, 1H), 7.69 – 7.63 (m, 2H), 7.51 – 7.44 (m, 1H), 7.41 – 7.31 (m, 2H), 7.22 – 7.15 (m, 2H), 7.03 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 189.9, 149.2, 148.8, 142.9, 142.3, 140.4, 138.4, 137.5, 136.9, 134.7, 132.3, 129.6, 127.9, 127.9, 126.9, 126.2, 125.6, 123.4, 121.4, 112.6, 111.2, 55.9, 55.8. HRMS (+ESI): Calcd. for $C_{25}H_{19}O_3SSe$ m/z 479.0215 $[M+H]^+$, found m/z 479.0212 $[M+H]^+$.

3.14 (3-(3,4-Dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophen-2-yl)(4-fluorophenyl)methanone (17b)

Yellow crystals (303.0 mg, 61%), m.p. (178-179 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.90 (m, 2H), 7.73 – 7.65 (m, 2H), 7.52 – 7.45 (m, 1H), 7.43 – 7.35 (m, 1H), 7.00 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.91 – 6.83 (m, 3H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.3, 166.1, 149.3, 148.8, 142.9, 142.1, 140.3, 138.3, 136.5, 134.6, 133.7, 132.2, 127.7, 126.9, 126.2, 125.6, 123.3, 121.5, 115.1, 112.3, 111.2, 55.9, 55.8. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 56.50 – 54.96 (m). HRMS (+ESI): Calcd. for $C_{25}H_{19}O_3SSe$ m/z 479.0120 $[M+H]^+$, found m/z 479.0116 $[M+H]^+$.

3.15 -(3,4-Dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophen-2-yl)ethan-1-one (18)

Pale yellow solid (175.0 mg, 42%), m.p. (185-186°C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 1H), 7.91 – 7.86 (m, 1H), 7.50 – 7.43 (m, 1H), 7.40 – 7.33 (m, 1H), 7.11 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.0, 149.6, 149.1, 143.2, 142.3, 140.2, 139.86, 139.85, 134.7, 127.9, 126.9, 126.2, 125.5, 123.5, 121.6, 111.7, 111.3, 56.0, 55.9, 28.8. HRMS (+ESI): Calcd. for $C_{20}H_{17}O_3SSe$ m/z 417.0058 $[M+H]^+$, found m/z 417.0059 $[M+H]^+$.

4. Procedure for the synthesis of bis(3-(3,4-dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)methanone (11)

$Na_2S·9H_2O$ (528.0 mg, 2.2 mmol) was dissolved in DMF (10 ml) under an argon atmosphere. Then the compound **6a** (664.0 mg, 2.0 mmol) was added, and the reaction mixture was heated at 60 °C for 45 min. The solution turned dark red. After cooling, 1,3-dichloroacetone (101 μl, 1.1 mmol). The dark color immediately disappeared. The reaction mixture was stirred for 15 min, followed by addition of CaO (1.7 g, 30.0 mmol) and DBU (150 μl, 1.0 mmol), and then kept at room temperature for another 15 h. After that the resulting mixture was diluted with hydrochloric acid solution (100 ml, 1 M), and the formed precipitate was filtered off, washed with water (2 × 10 ml), dried, and recrystallized from ethyl acetate to afford product **11** in 71 % yield.

Yellow crystals (481.0 mg), m.p. (138-139 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.89 (m, 1H), 7.84 – 7.78 (m, 1H), 7.50 – 7.39 (m, 2H), 6.81 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 183.1, 149.1, 148.3, 142.9, 139.3, 139.1, 137.6, 137.4, 132.2, 126.03, 126.02, 125.1, 123.8, 122.2, 121.8, 112.4, 110.4, 55.9, 55.8. HRMS (+ESI): Calcd. for $C_{37}H_{27}O_5S_4$ m/z 679.0736 $[M+H]^+$, found m/z 679.0729 $[M+H]^+$.

5. General procedure for the synthesis of 3-arylbenzo[*b*]thieno[2,3-*d*]thiophene-2-carbaldehydes (12a,b)

The suspension of $LiAlH_4$ (102.0 mg, 3.0 mmol) in dry THF (15 ml) was cooled down to 0 °C with ice bath, and ester **7a** or **7b** (1.0 mmol) was added in small portions. Then, the reaction mixture was stirred for 3 h at room temperature and quenched by a sequential addition of ethyl acetate (100 μl), 10% aqueous solution of NaOH (100 μl), water (300 μl) and ethanol (5 ml). The formed precipitate was filtered off, washed with THF (2×10 ml). The obtained filtrate was evaporated under reduced pressure to give the crude carbinol, which was used further without isolation. The latter residue was dissolved in CH_2Cl_2 (10 ml), MnO_2 (435.0 mg, 5.0 mmol) was added, and the resulted suspension was stirred for 5 h at room temperature. The precipitate of MnO_2 was filtered off, washed with dichloromethane (2×10 ml), and the solvent was distilled off to afford desired products **12a,b**.

5.1 3-(3,4-Dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbaldehyde (12a)

Pale yellow solid (159.0 mg, 45%), m.p. (192-193 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.95 (s, 1H), 8.22 (dt, *J* = 7.4, 3.7 Hz, 1H), 8.15 (dd, *J* = 6.1, 3.2 Hz, 1H), 7.57 (dd, *J* = 6.1, 3.1 Hz, 2H), 7.42 (d, *J* = 2.1 Hz, 2H), 7.38 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 3.87 (d, *J* = 1.4 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 184.4, 150.2, 149.4, 144.3, 143.9, 140.3, 139.3, 139.1, 132.2, 126.7, 125.3, 125.0, 124.0, 122.7, 122.4, 112.1, 111.5, 56.1, 56.0. HRMS (+ESI): Calcd. for $C_{19}H_{14}LiO_3S_2$ m/z 361.0539 $[M+Li]^+$, found m/z 361.0543 $[M+Li]^+$.

5.2 3-(4-Methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbaldehyde (12b)

Pale yellow solid (136.0 mg, 42%), m.p. (198-199 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.88 (s, 1H), 8.25 – 8.18 (m, 1H), 8.19 – 8.12 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 184.4, 160.7, 144.3, 143.9, 140.3, 139.3, 139.0, 132.2, 130.8, 126.6, 125.2, 124.8, 124.0, 122.4, 114.7, 55.4. HRMS (+ESI): Calcd. for $C_{18}H_{12}LiO_2S_2$ m/z 331.0433 $[M+Li]^+$, found m/z 331.0433 $[M+Li]^+$.

6. Procedure for the synthesis of 3-bromobenzo[*b*]selenophene-2-carboxylic acid (13)

Ethyl 3-bromobenzo[*b*]selenophene-2-carboxylate (3.3 g, 10 mmol) was immersed into mixture of 15% aqueous solution of NaOH (25 ml) and ethanol (25 ml), and the resulting mixture was refluxed for 4 h, then cooled and quenched with hydrochloric acid (12 ml). Ethanol was distilled off, and the formed orange precipitate was filtered off, washed with water (2 × 10 ml) and dried, thus giving the product **13** in 95% yield.

Orange solid (2.9 g), m.p. (283-284 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.79 (s, 1H), 8.20 (m, 1H), 8.00 (m, 1H), 7.63 – 7.52 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.3, 140.2, 140.0, 131.9, 128.1, 126.9, 126.6, 126.2, 114.2. HRMS (+ESI): Calcd. for $C_9H_6BrO_2Se$ m/z 304.8711 $[M+H]^+$, found m/z 304.8708 $[M+H]^+$.

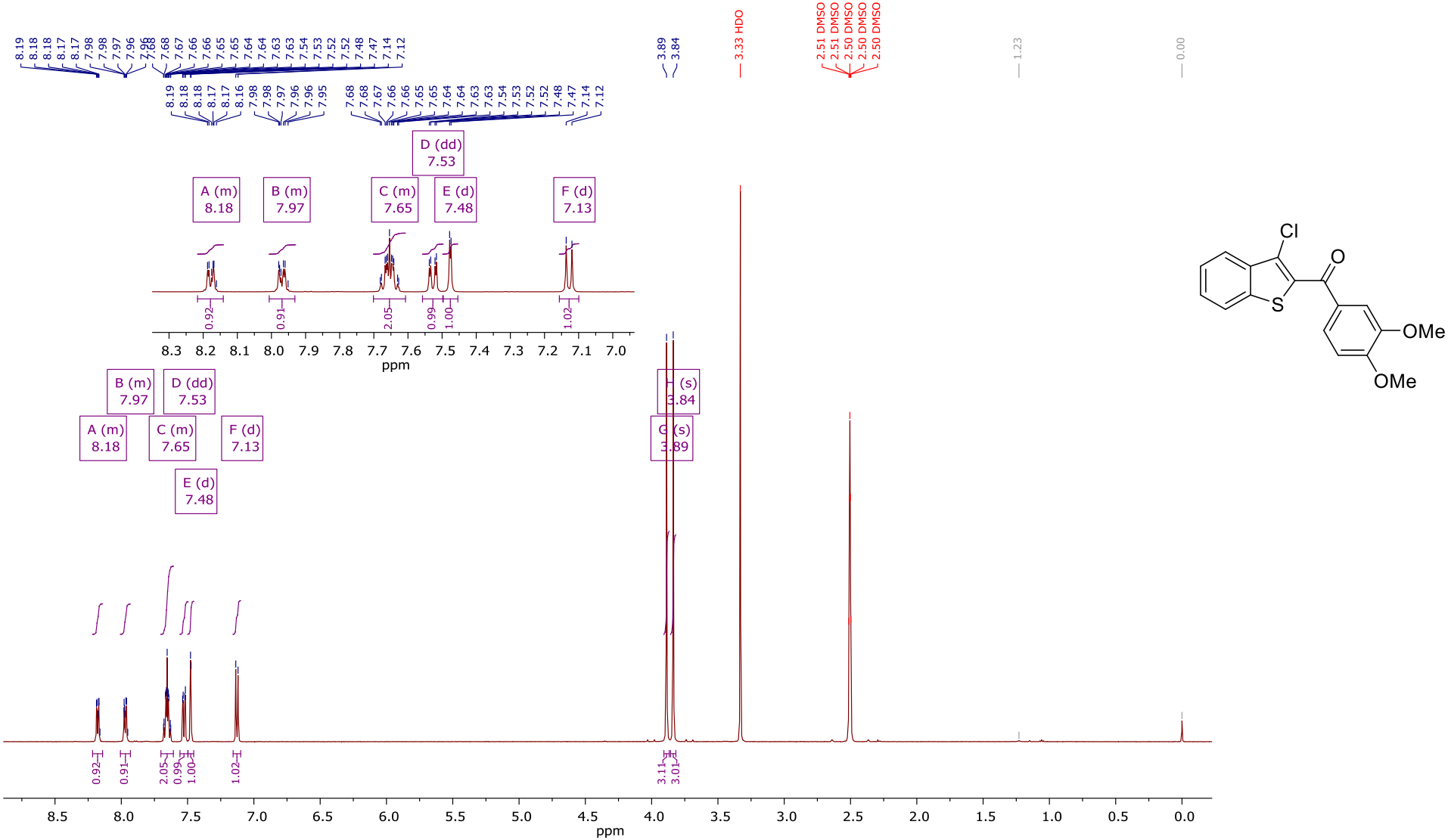
7. Procedure for the synthesis of (3-bromobenzo[*b*]selenophen-2-yl)(3,4-dimethoxyphenyl)methanone (14)

Thionyl chloride (435 μl, 6 mmol) and the catalytic amount of DMF (10 μl) were added to solution of carboxylic acid **13** (1.5 g, 5 mmol) in $CHCl_3$ (50 ml). The reaction mixture was refluxed for 4 h, and then the solvent was removed under reduced pressure. The residue of acyl chloride was dissolved in anhydrous CH_2Cl_2 (50 ml), then grinded $AlCl_3$ (0.9 g, 6.5 mmol) was added, and the resulting mixture was stirred for 0.5 h until complete homogenization. After that the solution was cooled down to 0 °C with ice bath, and veratrole (6.0 mmol) was added dropwise. The obtained reaction mixture was kept overnight at room temperature, and then quenched with water (50 ml). The organic layer was separated and washed with aqueous solution of Na_2CO_3 (50 ml, 0.1 M). The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to afford compound **14** in 83% yield.

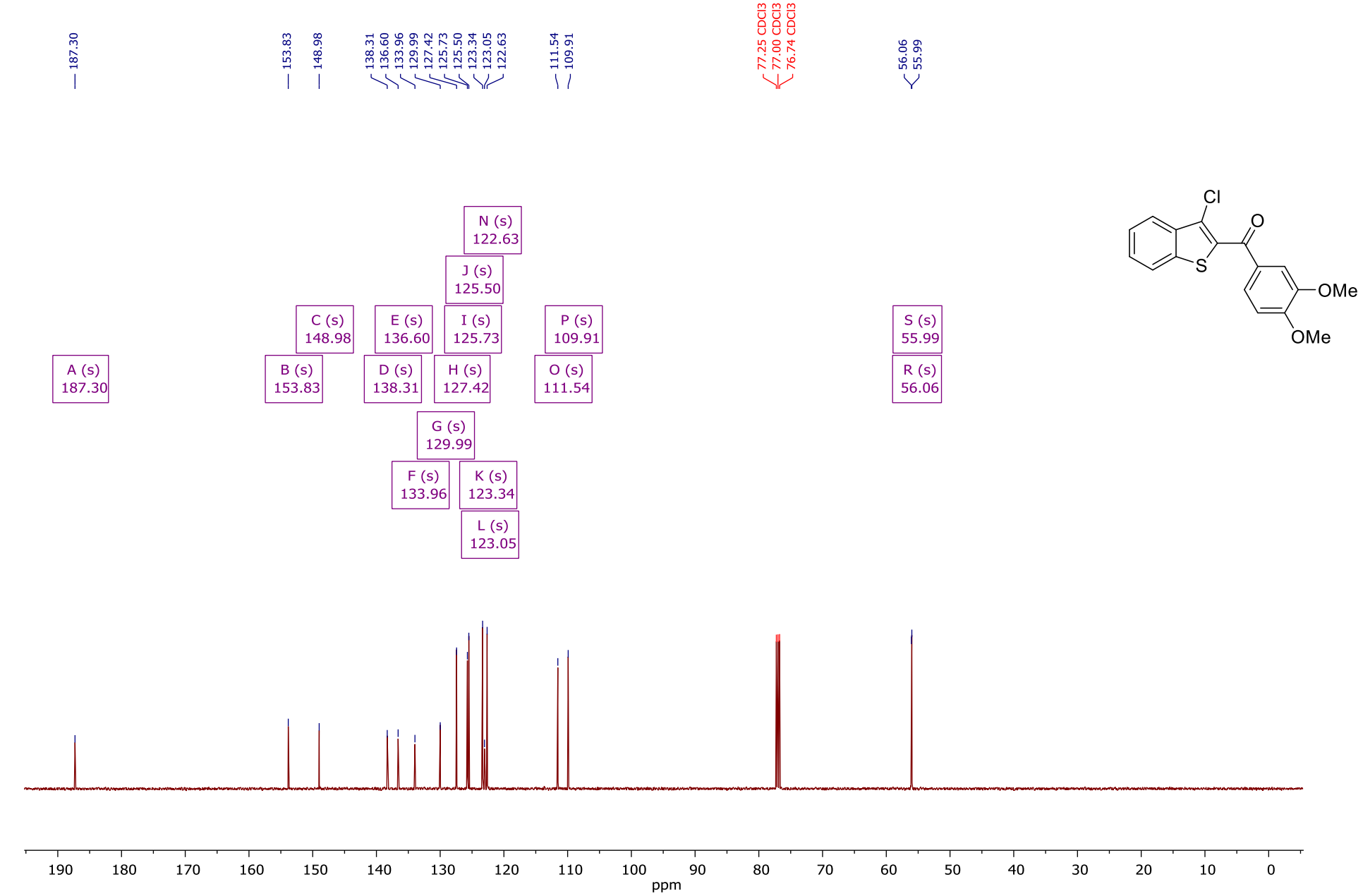
Pale yellow solid (1.8 g), m.p. (155-156 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.27 (m, 1H), 7.97 – 7.91 (m, 1H), 7.63 (m, 1H), 7.55 (m, 1H), 7.50 – 7.44 (m, 2H), 7.14 – 7.08 (m, 1H), 3.87 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 189.0, 154.0, 148.8, 139.7, 139.0, 138.5, 128.8, 127.2, 126.5, 126.3, 126.0, 125.9, 111.0, 110.9, 109.7, 55.9, 55.6. HRMS (+ESI): Calcd. for $C_9H_6BrO_2Se$ m/z 304.8711 $[M+H]^+$, found m/z 304.8708 $[M+H]^+$.

Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of new compounds

(3-Chlorobenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6a)

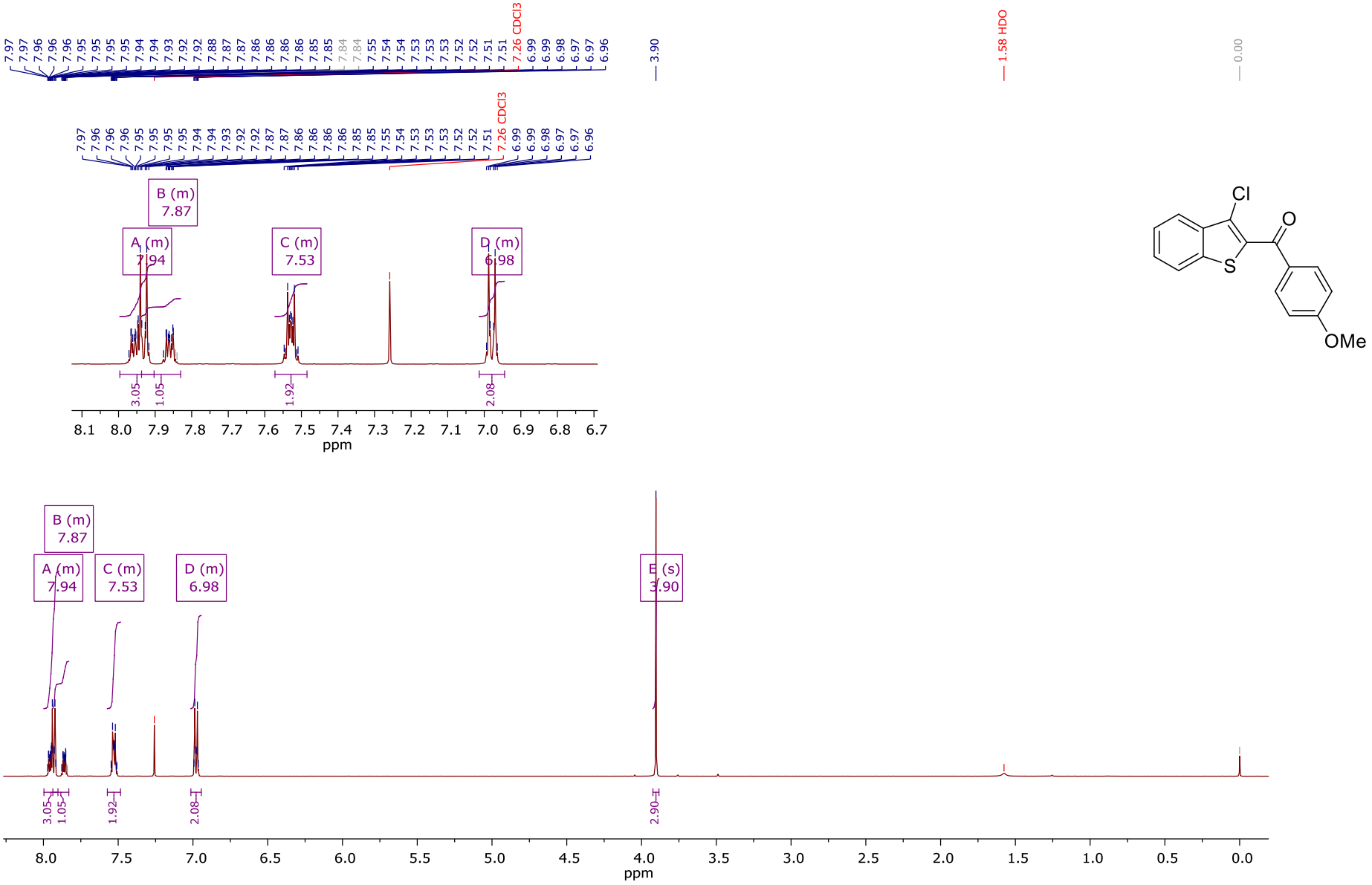


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 – 8.14 (m, 1H), 8.01 – 7.93 (m, 1H), 7.70 – 7.61 (m, 2H), 7.53 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H).

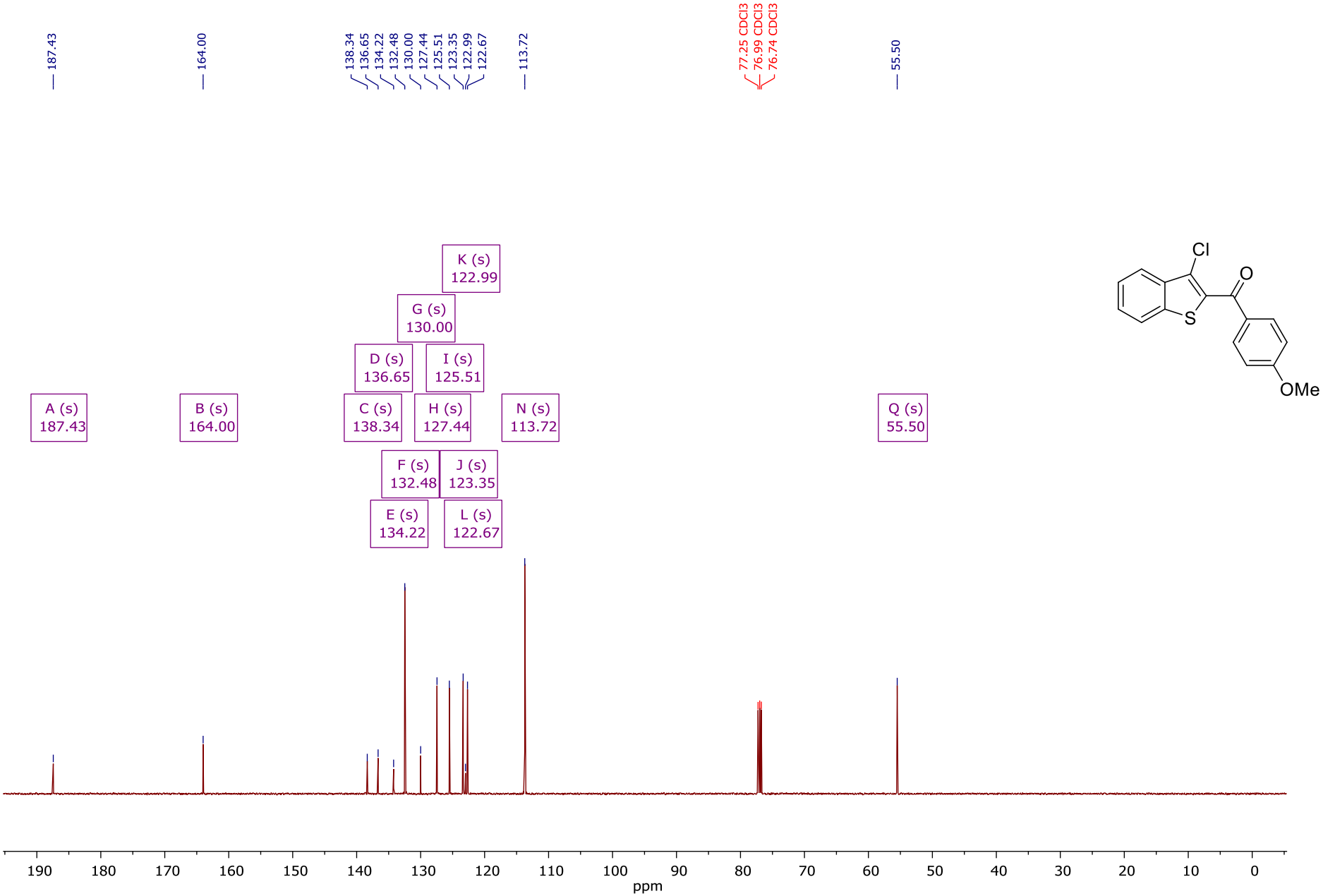


^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.3, 153.8, 149.0, 138.3, 136.6, 134.0, 130.0, 127.4, 125.7, 125.5, 123.3, 123.0, 122.6, 111.5, 109.9, 56.1, 56.0.

3-Chlorobenzo[*b*]thiophen-2-yl)(4-methoxyphenyl)methanone (6b)

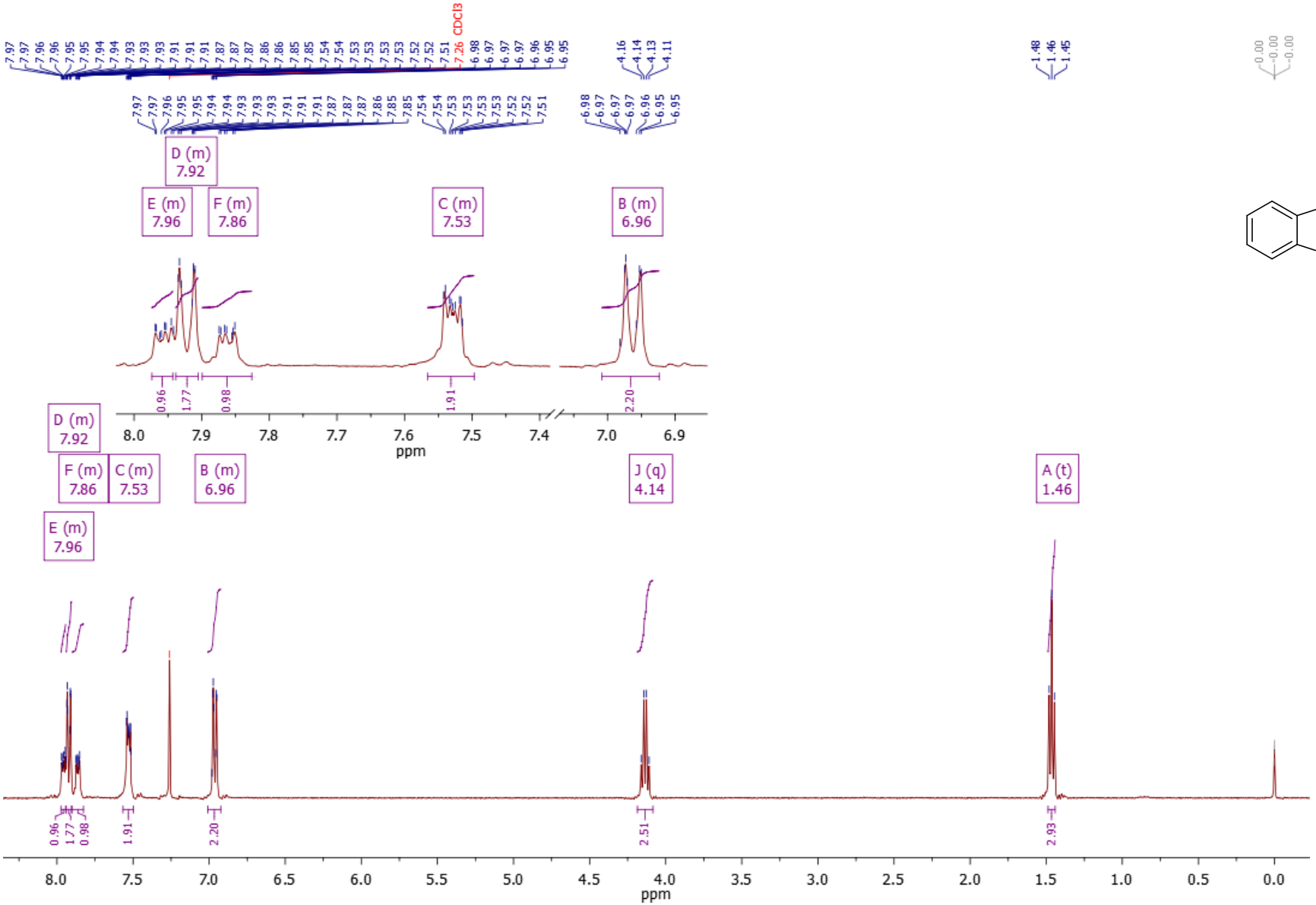


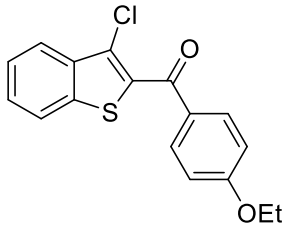
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.90 (m, 3H), 7.94 – 7.83 (m, 1H), 7.57 – 7.48 (m, 2H), 7.01 – 6.94 (m, 2H), 3.90 (s, 3H).



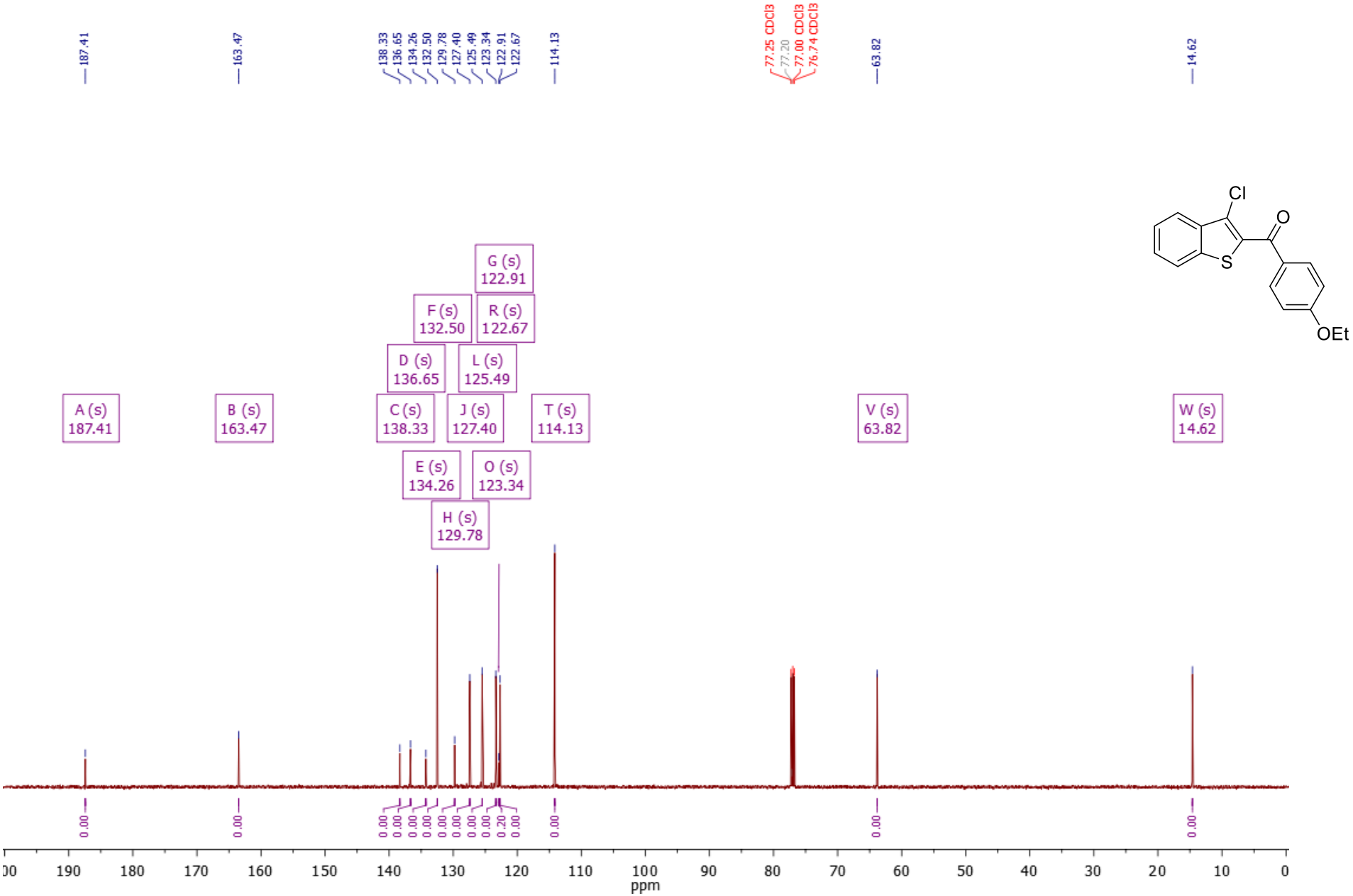
^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 164.0, 138.3, 136.6, 134.2, 132.5, 130.0, 127.4, 125.5, 123.3, 122.9, 122.7, 113.7, 55.5.

(3-Chlorobenzo[*b*]thiophen-2-yl)(4-ethoxyphenyl)methanone (6c)



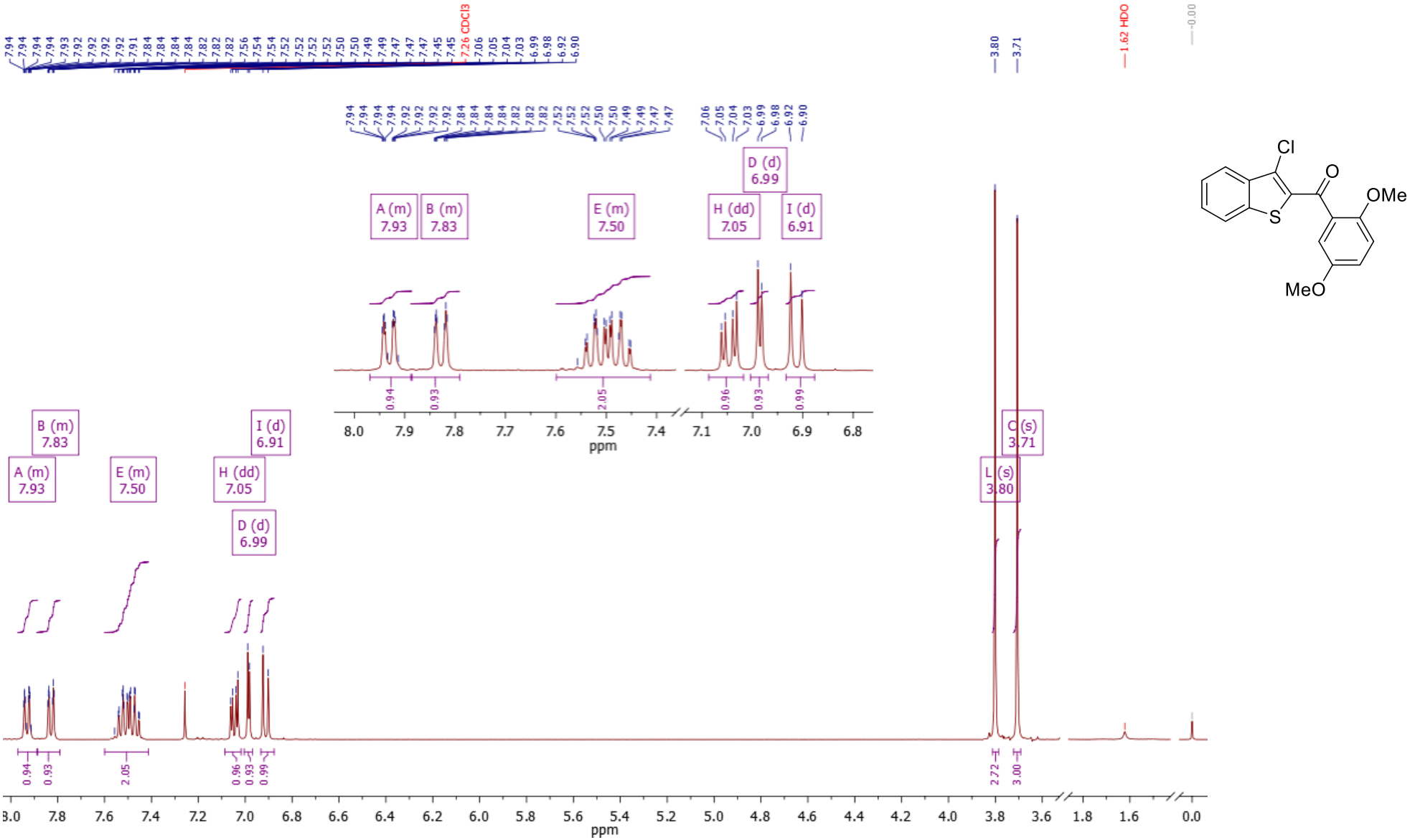


^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 – 7.94 (m, 1H), 7.94 – 7.91 (m, 2H), 7.90 – 7.83 (m, 1H), 7.57 – 7.50 (m, 2H), 7.01 – 6.92 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 3H), 1.46 (t, *J* = 7.0 Hz, 3H).

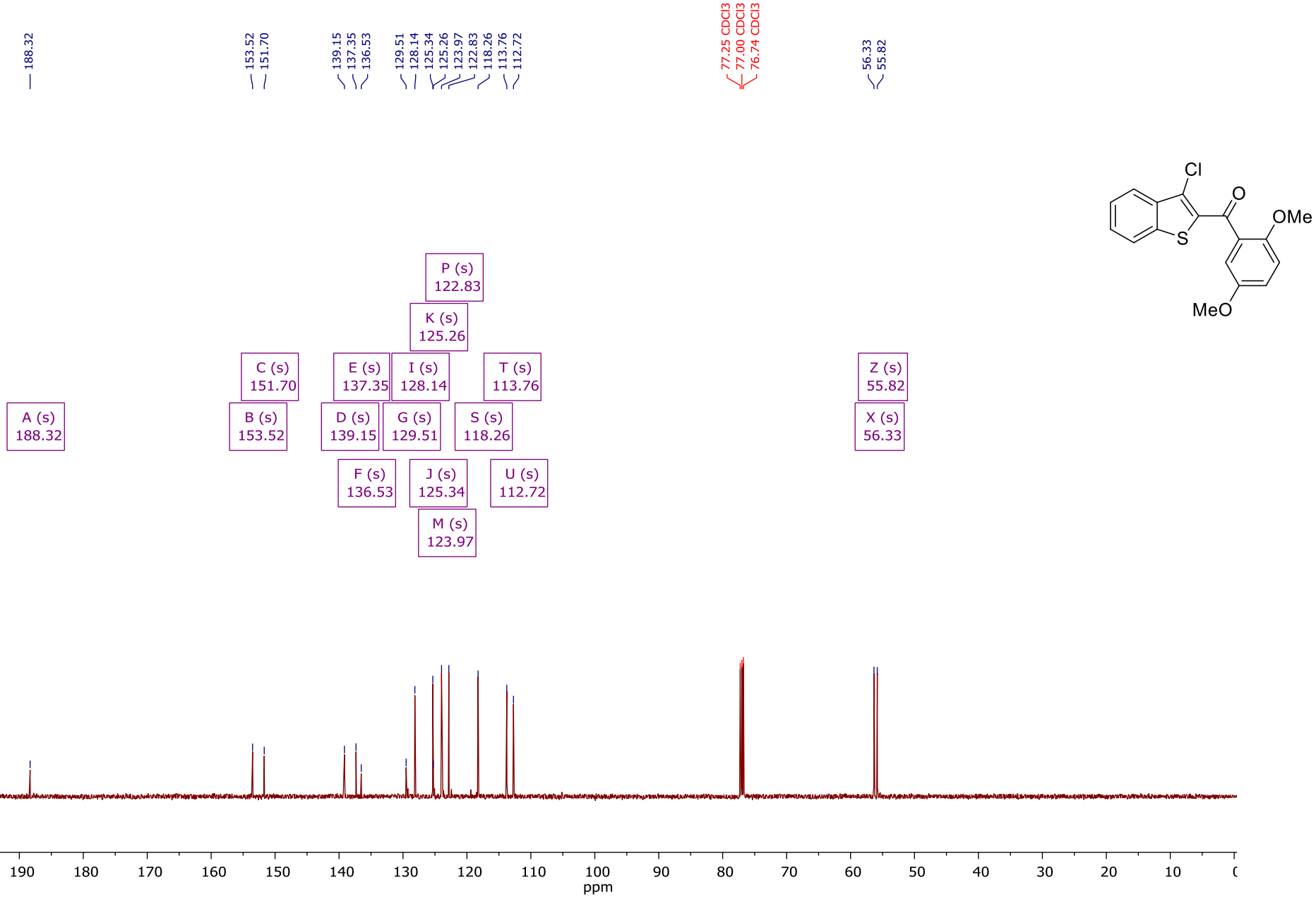


^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 163.5, 138.3, 136.6, 134.3, 132.5, 129.8, 127.4, 125.5, 123.3, 122.9, 122.7, 114.1, 63.8, 14.6.

(3-Chlorobenzo[*b*]thiophen-2-yl)(2,5-dimethoxyphenyl)methanone (6d)

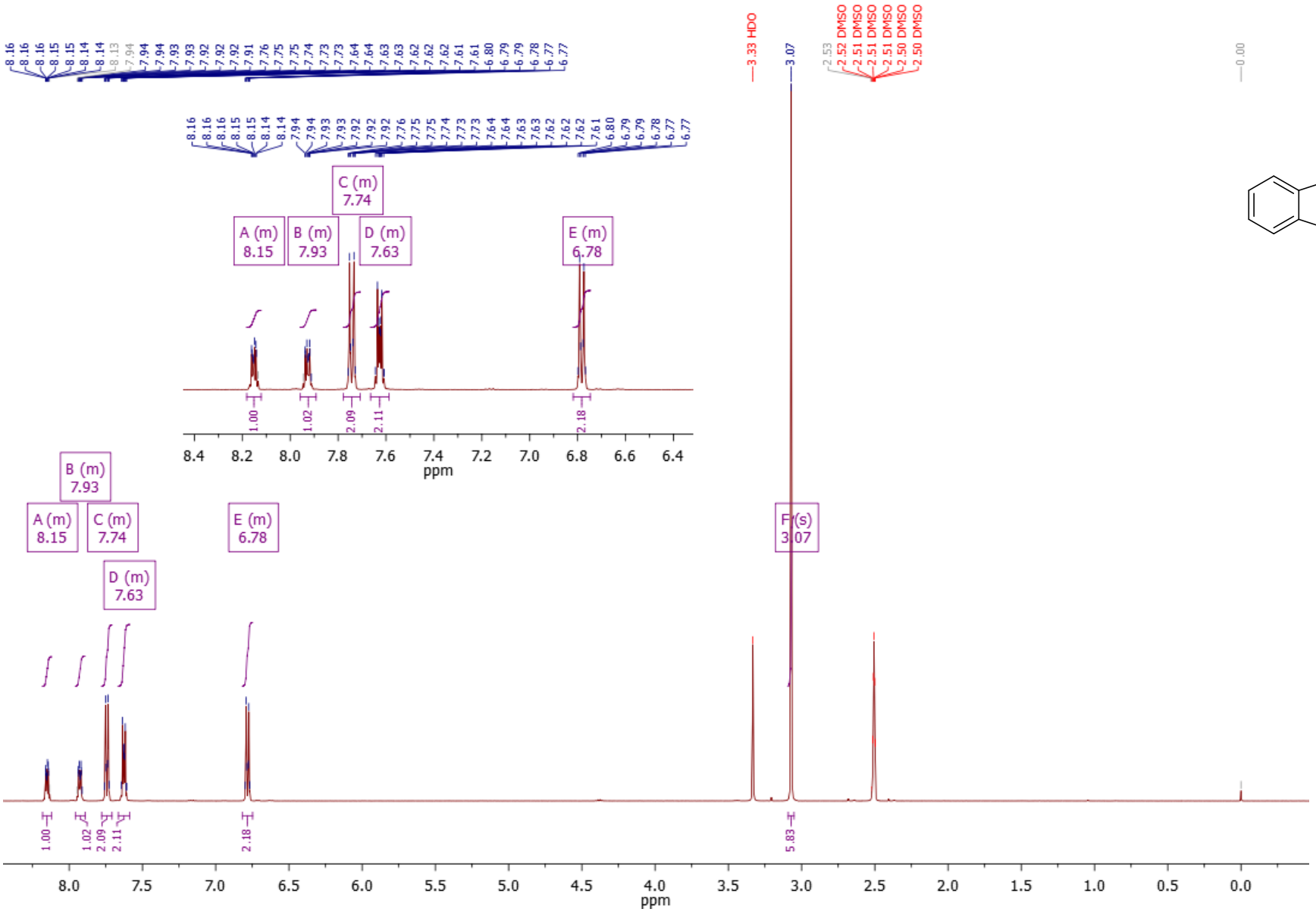


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (m, 1H), 7.89 – 7.79 (m, 1H), 7.60 – 7.41 (m, 2H), 7.05 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.99 (d, *J* = 3.1 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H).

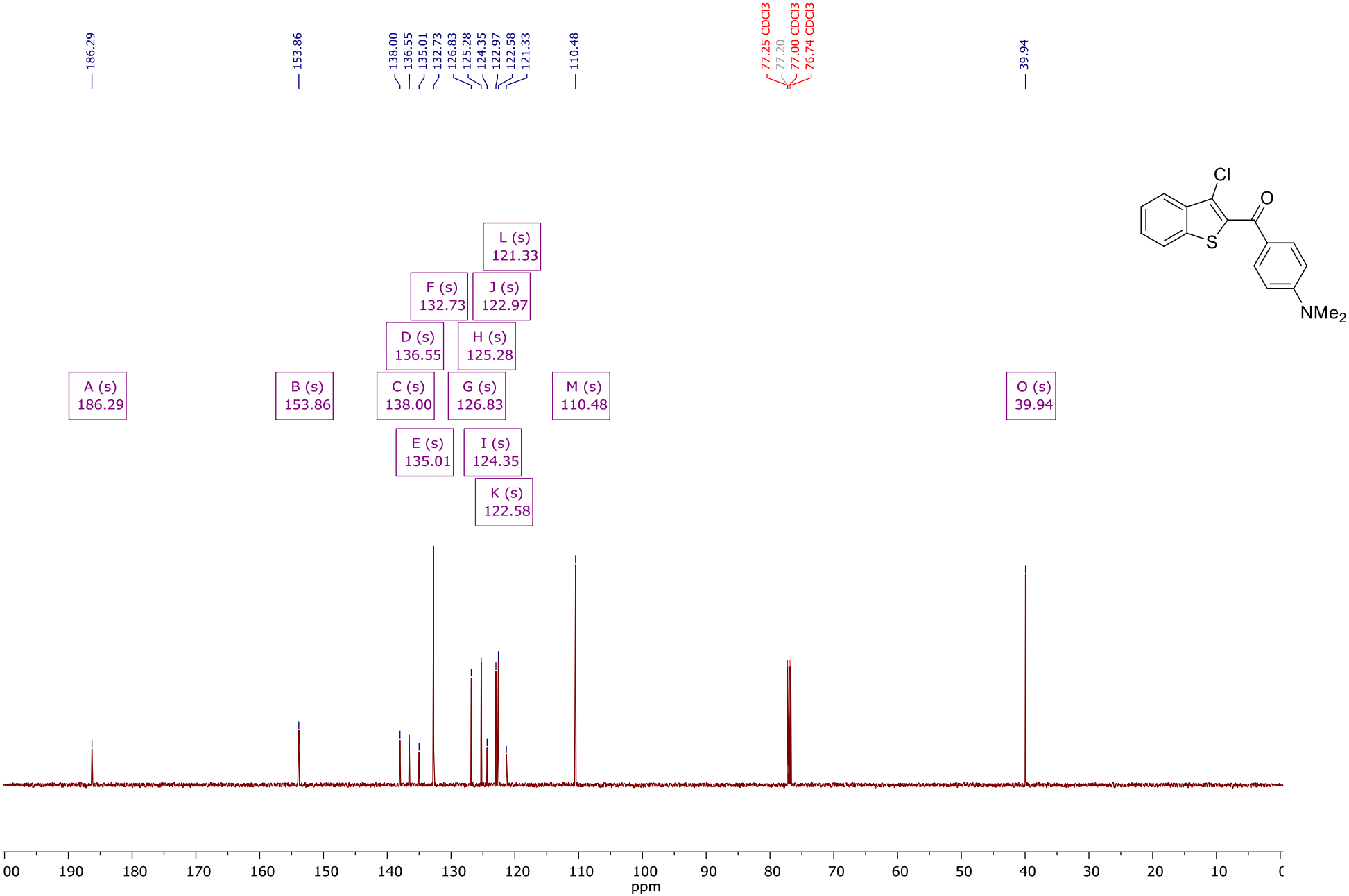


^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.3, 153.5, 151.7, 139.1, 137.3, 136.5, 129.5, 128.1, 125.3, 125.3, 124.0, 122.8, 118.3, 113.8, 112.7, 56.3, 55.8.

(3-Chlorobenzo[*b*]thiophen-2-yl)(4-(dimethylamino)phenyl)methanone (6e)

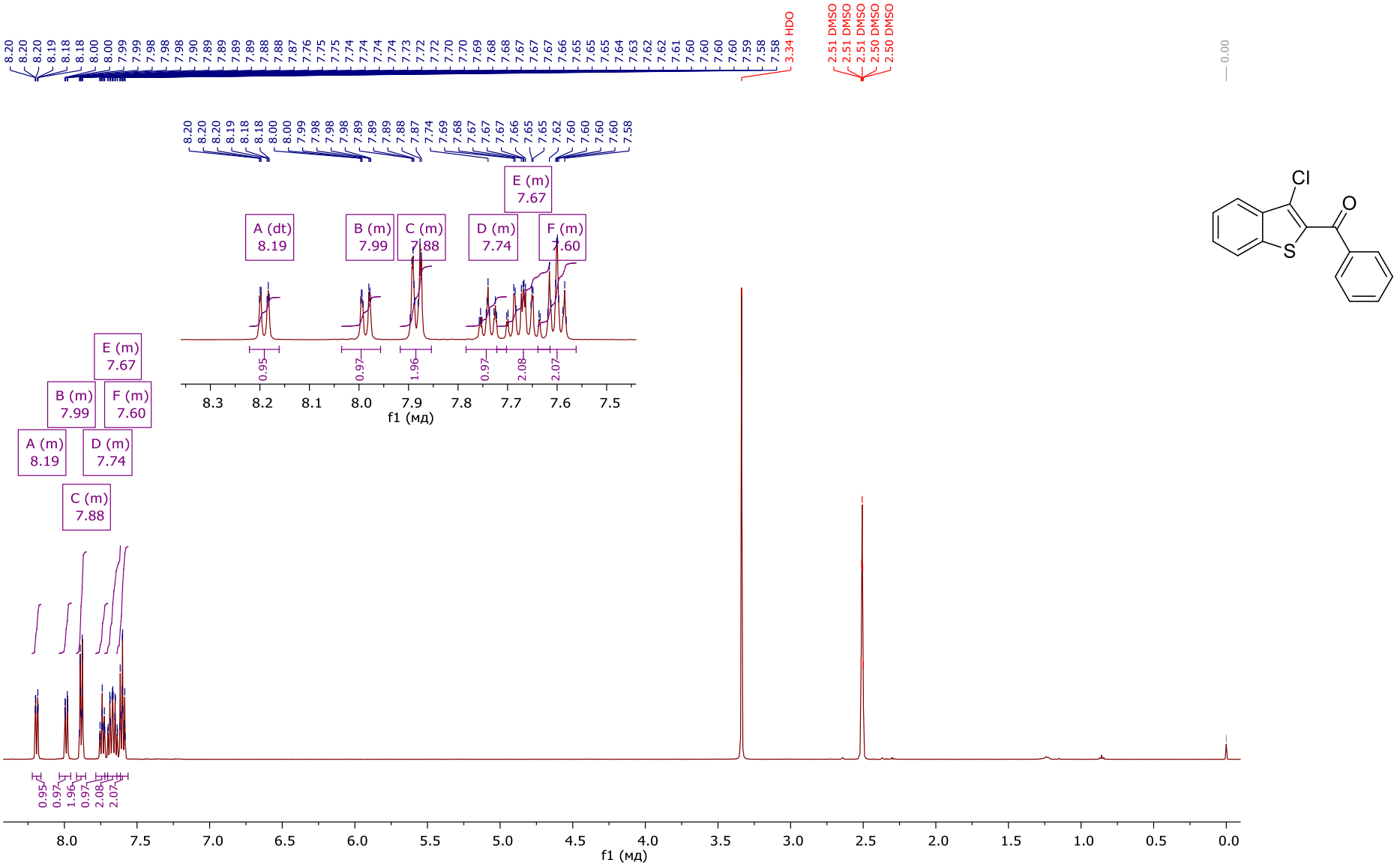


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.18 – 8.12 (m, 1H), 7.96 – 7.89 (m, 1H), 7.78 – 7.71 (m, 2H), 7.66 – 7.59 (m, 2H), 6.82 – 6.75 (m, 2H), 3.07 (s, 6H).

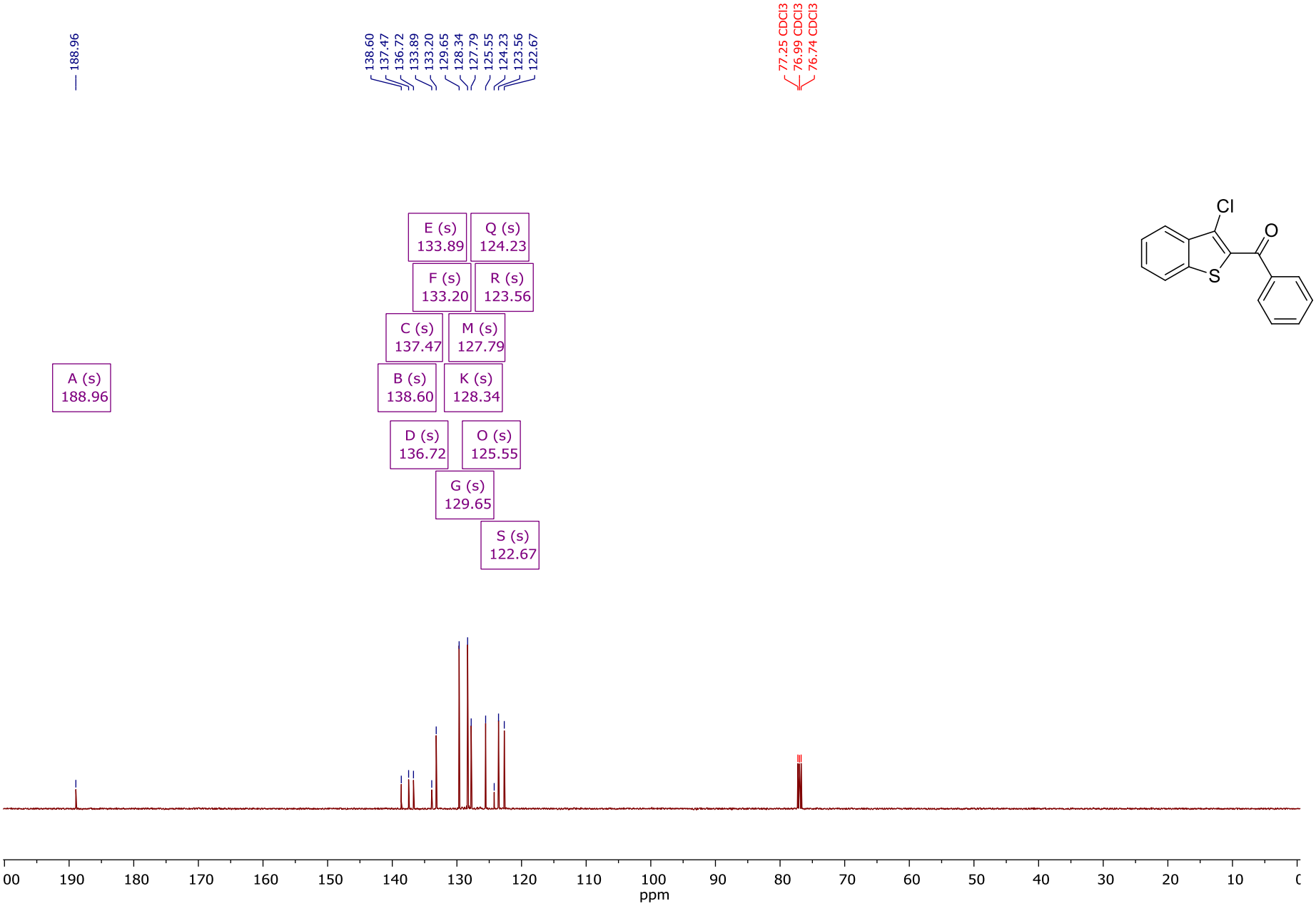


^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.3, 153.9, 138.0, 136.5, 135.0, 132.7, 126.8, 125.3, 124.3, 123.0, 122.6, 121.3, 110.5, 39.9.

(3-Chlorobenzo[*b*]thiophen-2-yl)(phenyl)methanone (6f)

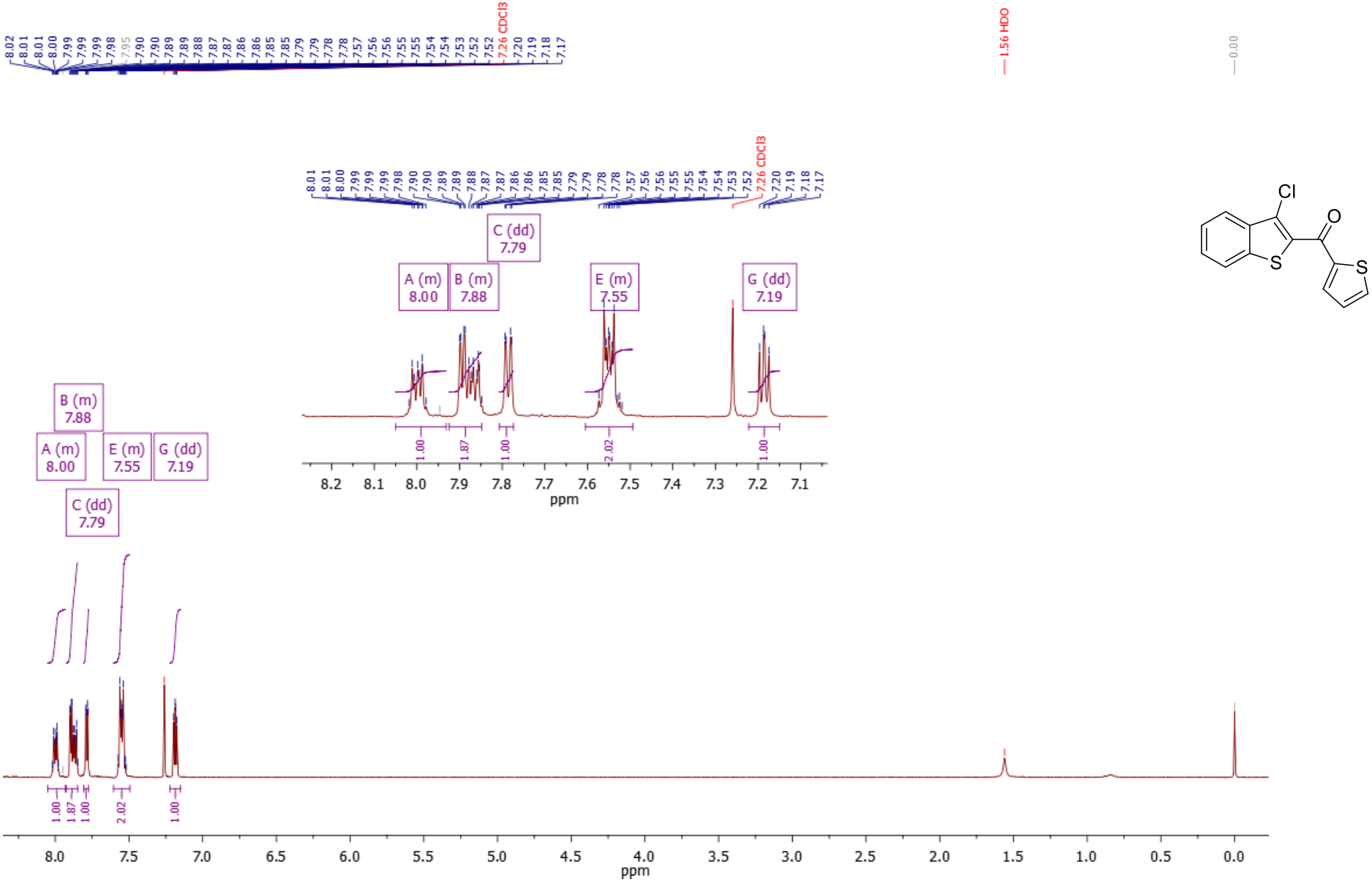


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19 (m, 1H), 8.04 – 7.96 (m, 1H), 7.92 – 7.85 (m, 2H), 7.74 (m, 1H), 7.72 – 7.61 (m, 2H), 7.60 (m, 2H).

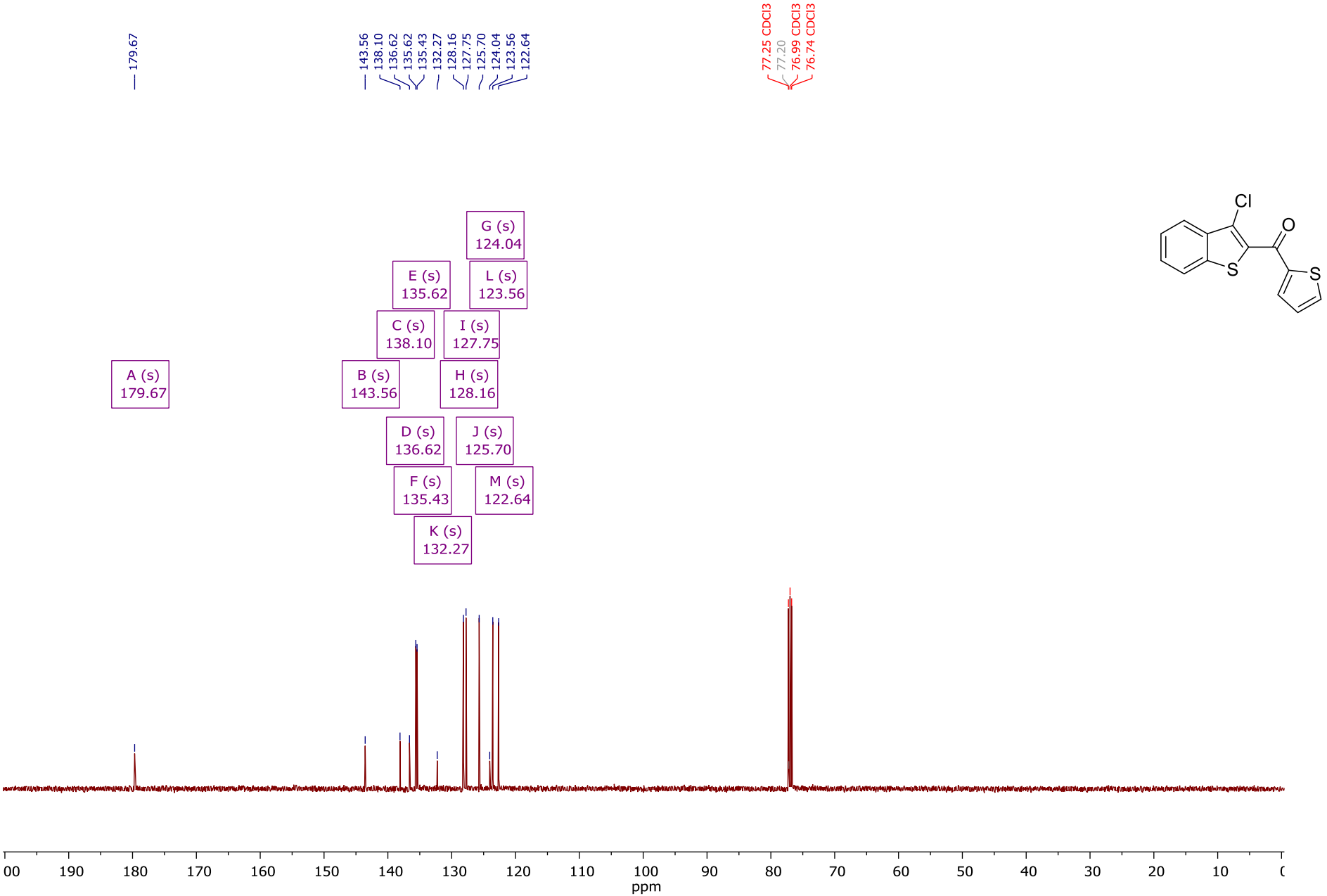


^{13}C NMR (126 MHz, Chloroform-*d*) δ 189.0, 138.6, 137.5, 136.7, 133.9, 133.2, 129.6, 128.3, 127.8, 125.5, 124.2, 123.6, 122.7.

(3-Chlorobenzo[*b*]thiophen-2-yl)(thiophen-2-yl)methanone (6g)

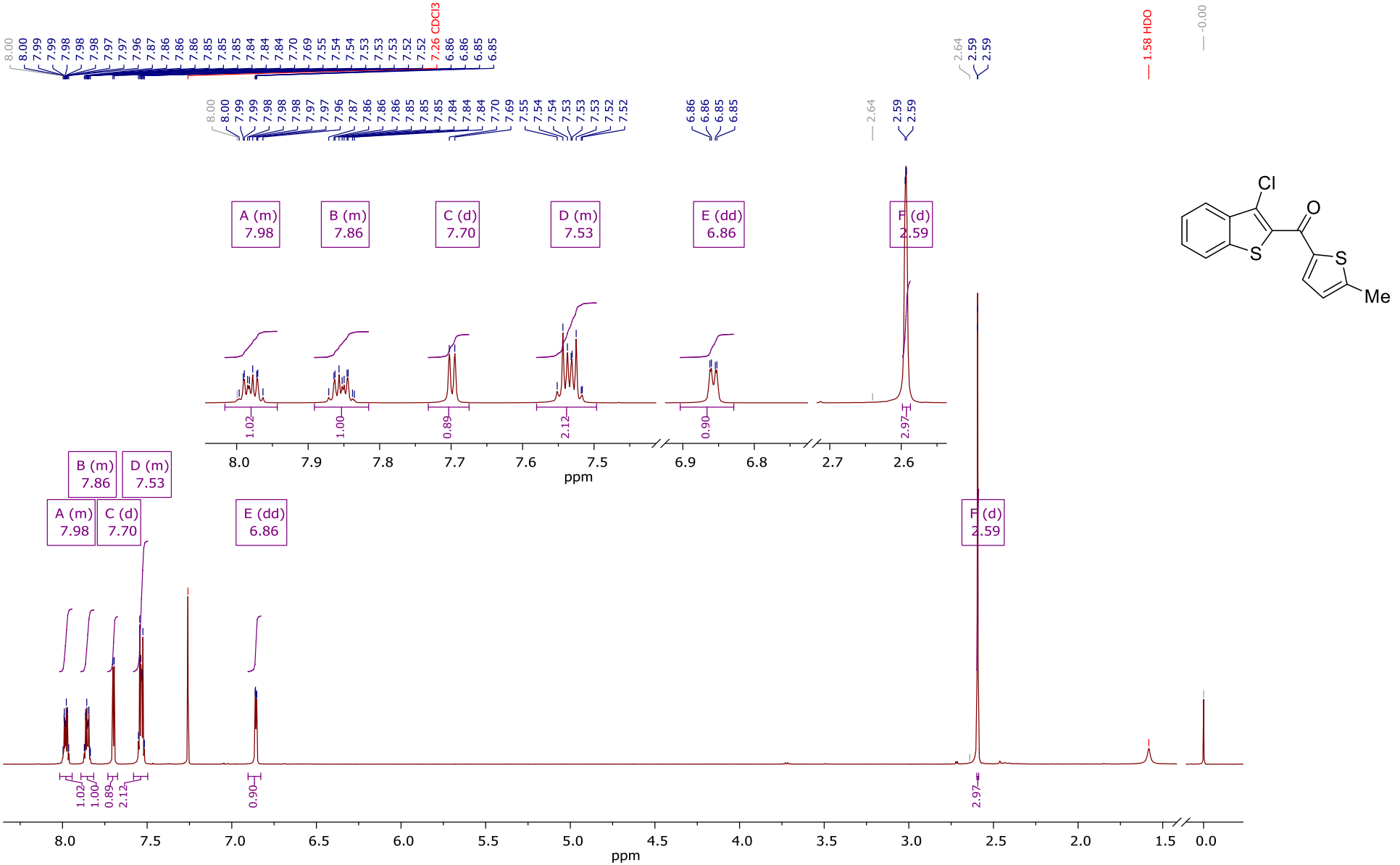


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.93 (m, 1H), 7.92 – 7.85 (m, 2H), 7.79 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.19 (dd, *J* = 4.9, 3.9 Hz, 1H).



^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.7, 143.6, 138.1, 136.6, 135.6, 135.4, 132.3, 128.2, 127.7, 125.7, 124.0, 123.6, 122.6.

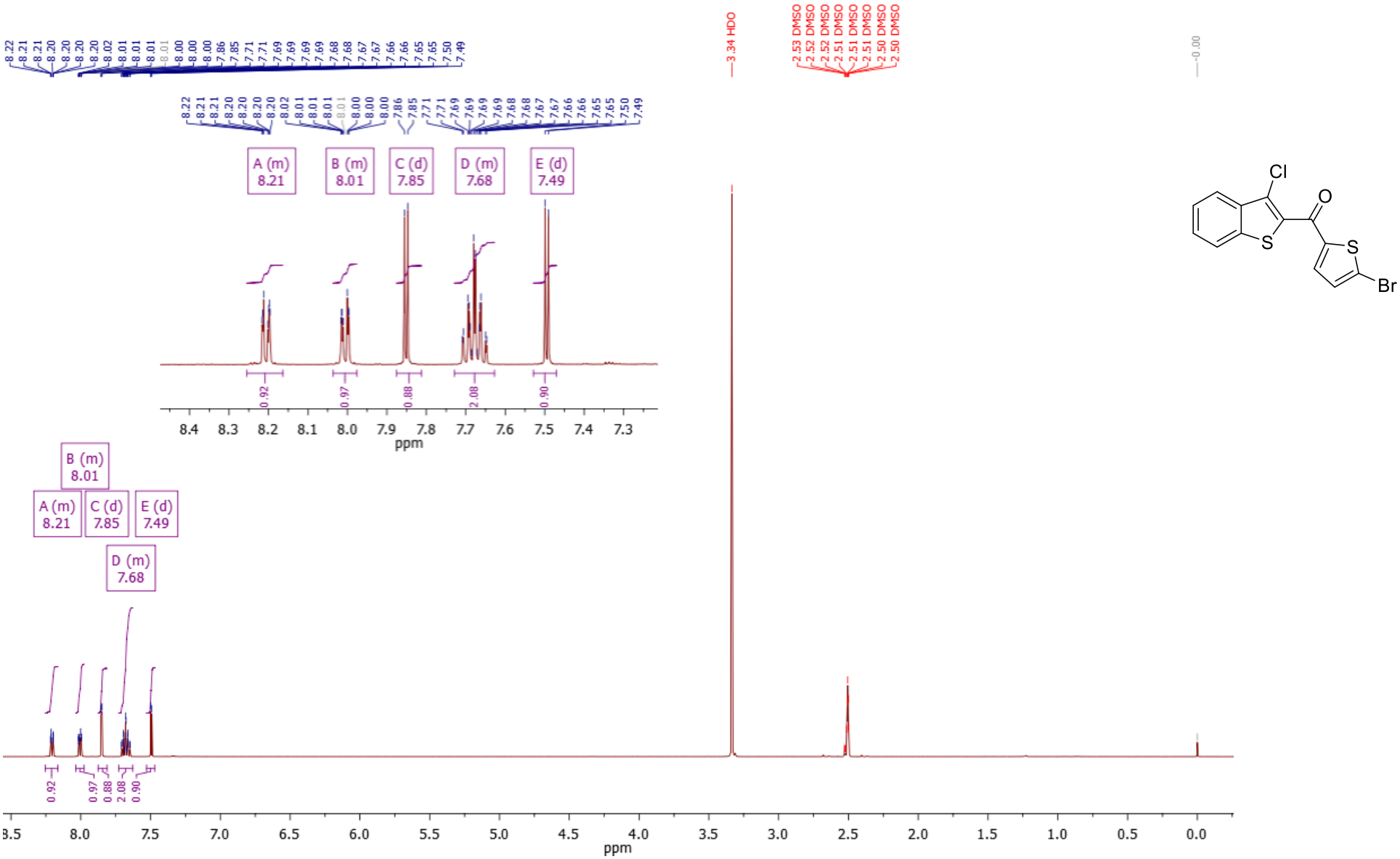
(3-Chlorobenzo[*b*]thiophen-2-yl)(5-methylthiophen-2-yl)methanone (6h)



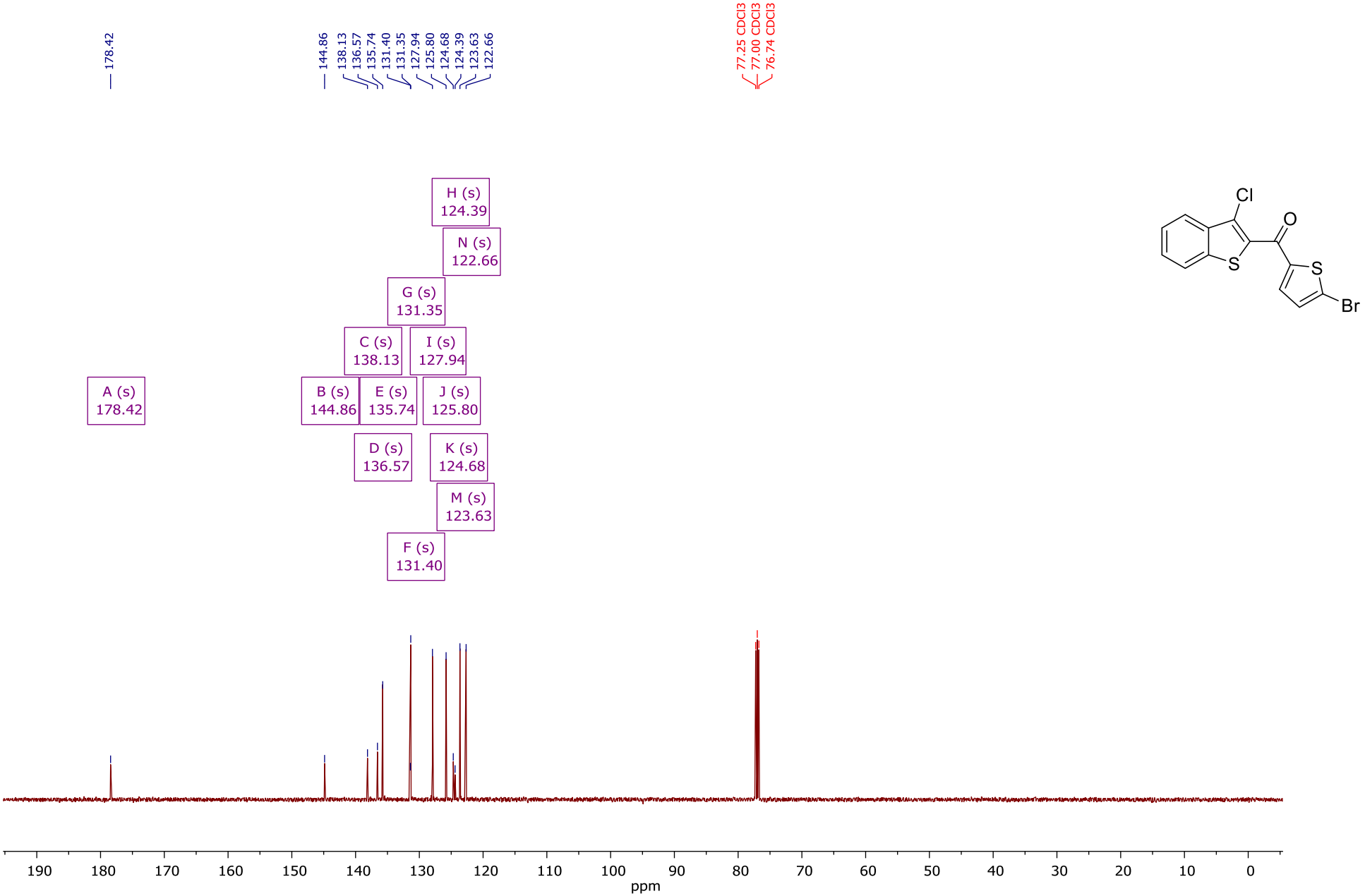
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.94 (m, 1H), 7.89 – 7.82 (m, 1H), 7.70 (d, *J* = 3.8 Hz, 1H), 7.58 – 7.50 (m, 2H), 6.86 (dd, *J* = 3.8, 1.1 Hz, 1H), 2.59 (d, *J* = 0.9 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.2, 152.1, 141.3, 138.0, 136.6, 132.4, 127.5, 127.05, 127.04, 125.6, 123.44, 123.38, 122.6, 16.2.

(5-Bromothiophen-2-yl)(3-chlorobenzo[*b*]thiophen-2-yl)methanone (6i)

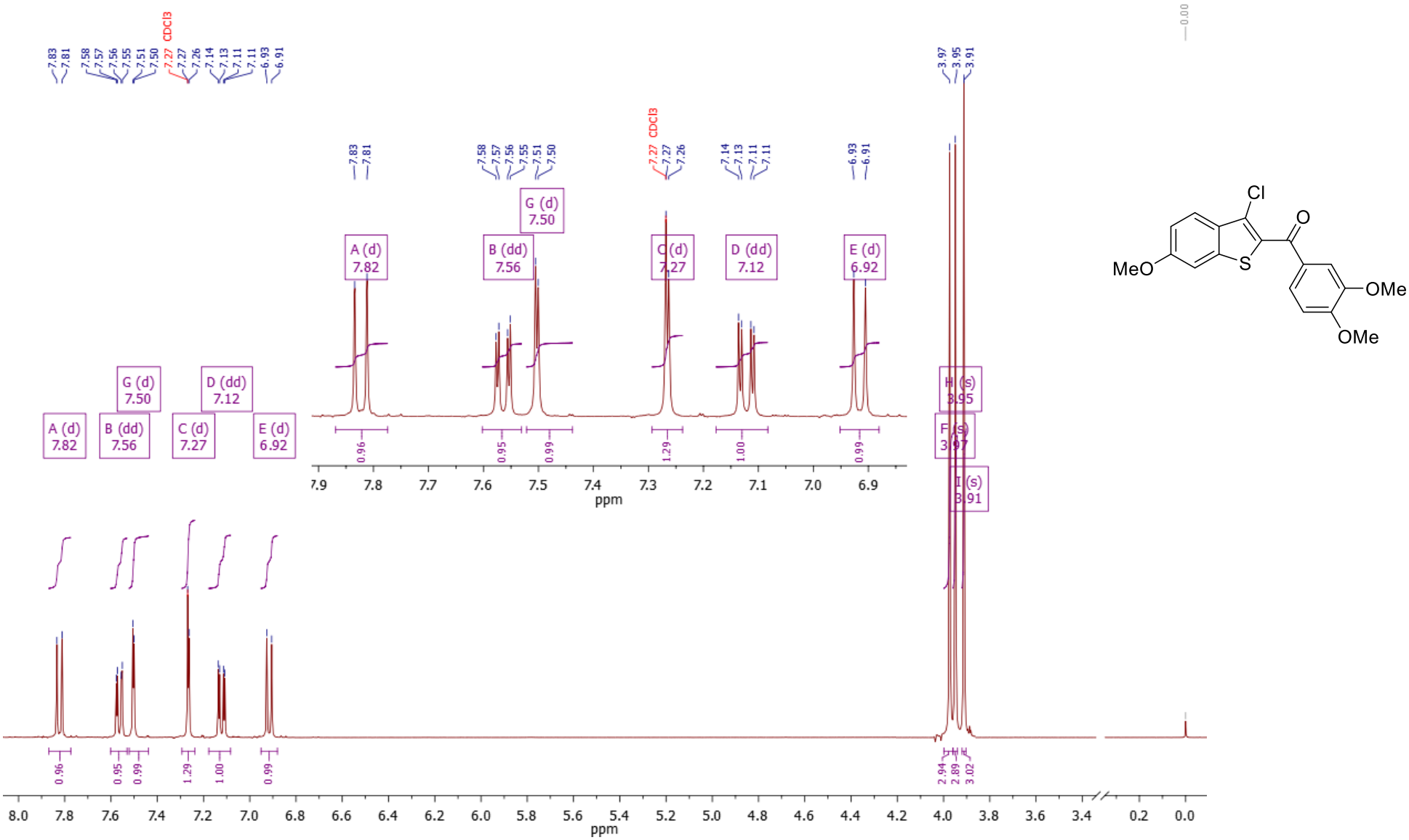


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25 – 8.16 (m, 1H), 8.04 – 7.98 (m, 1H), 7.85 (d, *J* = 4.1 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.49 (d, *J* = 4.1 Hz, 1H).

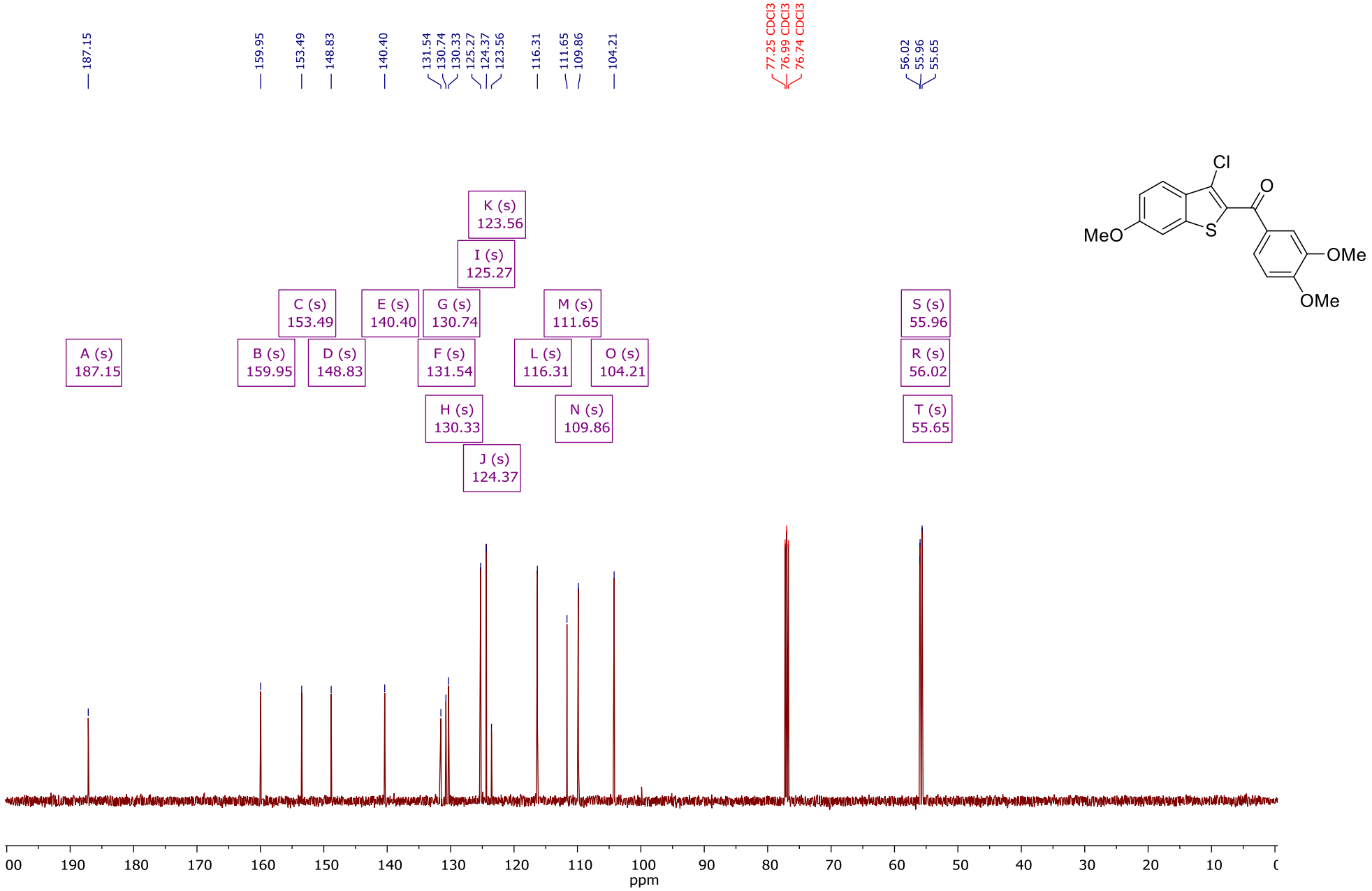


^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.4, 144.9, 138.1, 136.6, 135.7, 131.4, 131.3, 127.9, 125.8, 124.7, 124.4, 123.6, 122.7.

(3-Chloro-6-methoxybenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6j)

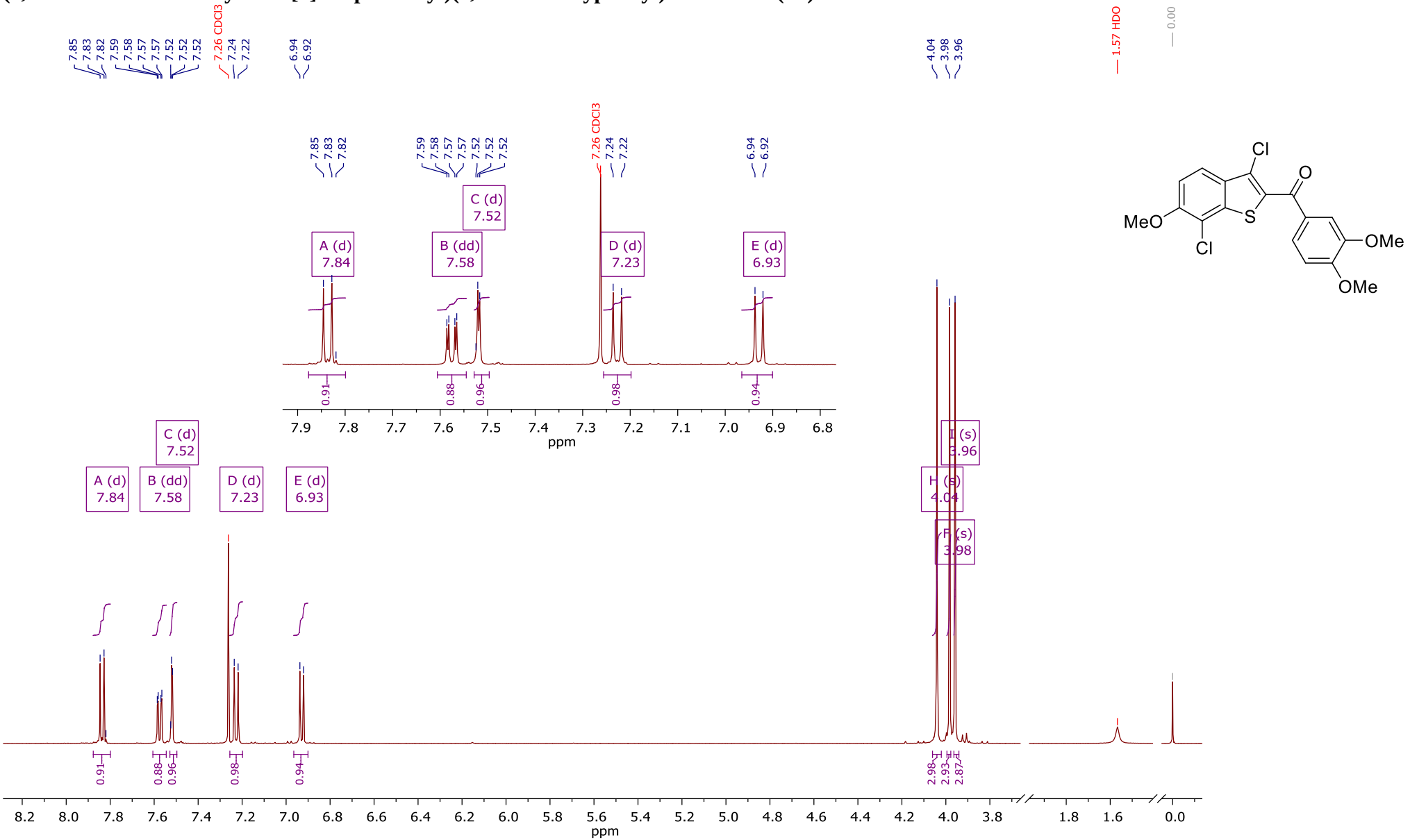


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.56 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.91 (s, 3H).

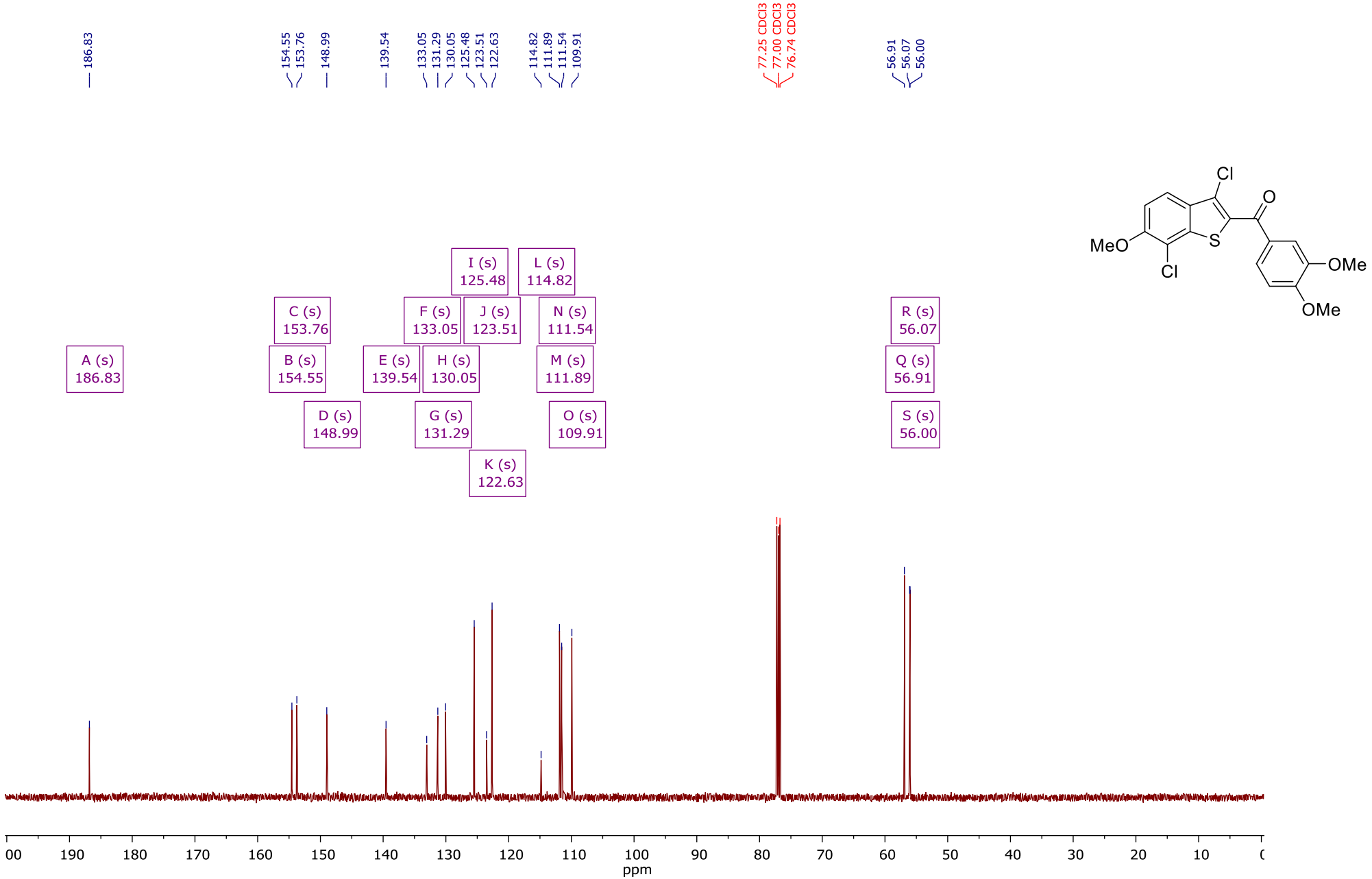


^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.1, 159.9, 153.5, 148.8, 140.4, 131.5, 130.7, 130.3, 125.3, 124.4, 123.6, 116.3, 111.6, 109.9, 104.2, 56.0, 56.0, 55.6.

(3,7-Dichloro-6-methoxybenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6k)

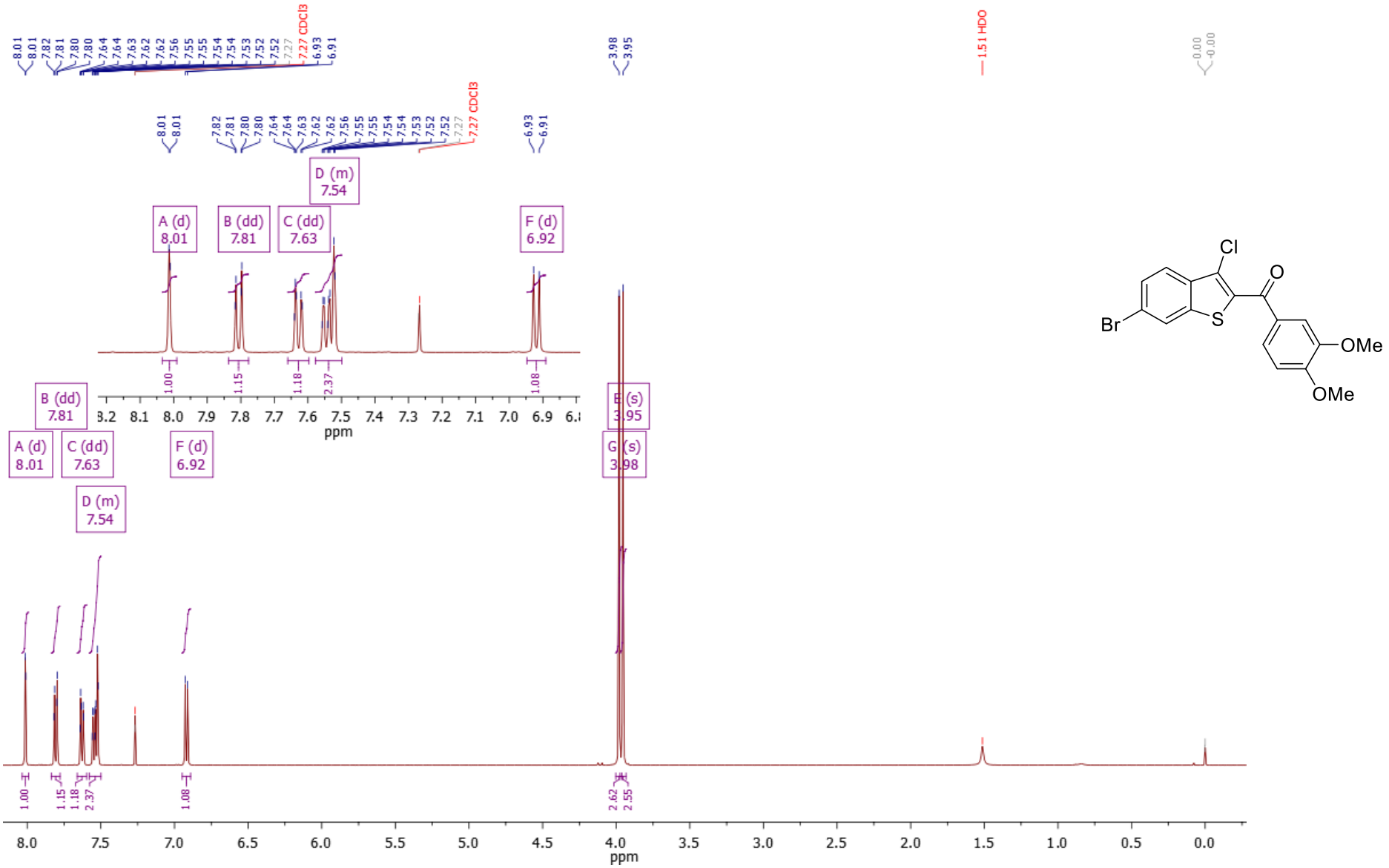


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H), 3.98 (s, 3H), 3.96 (s, 3H).

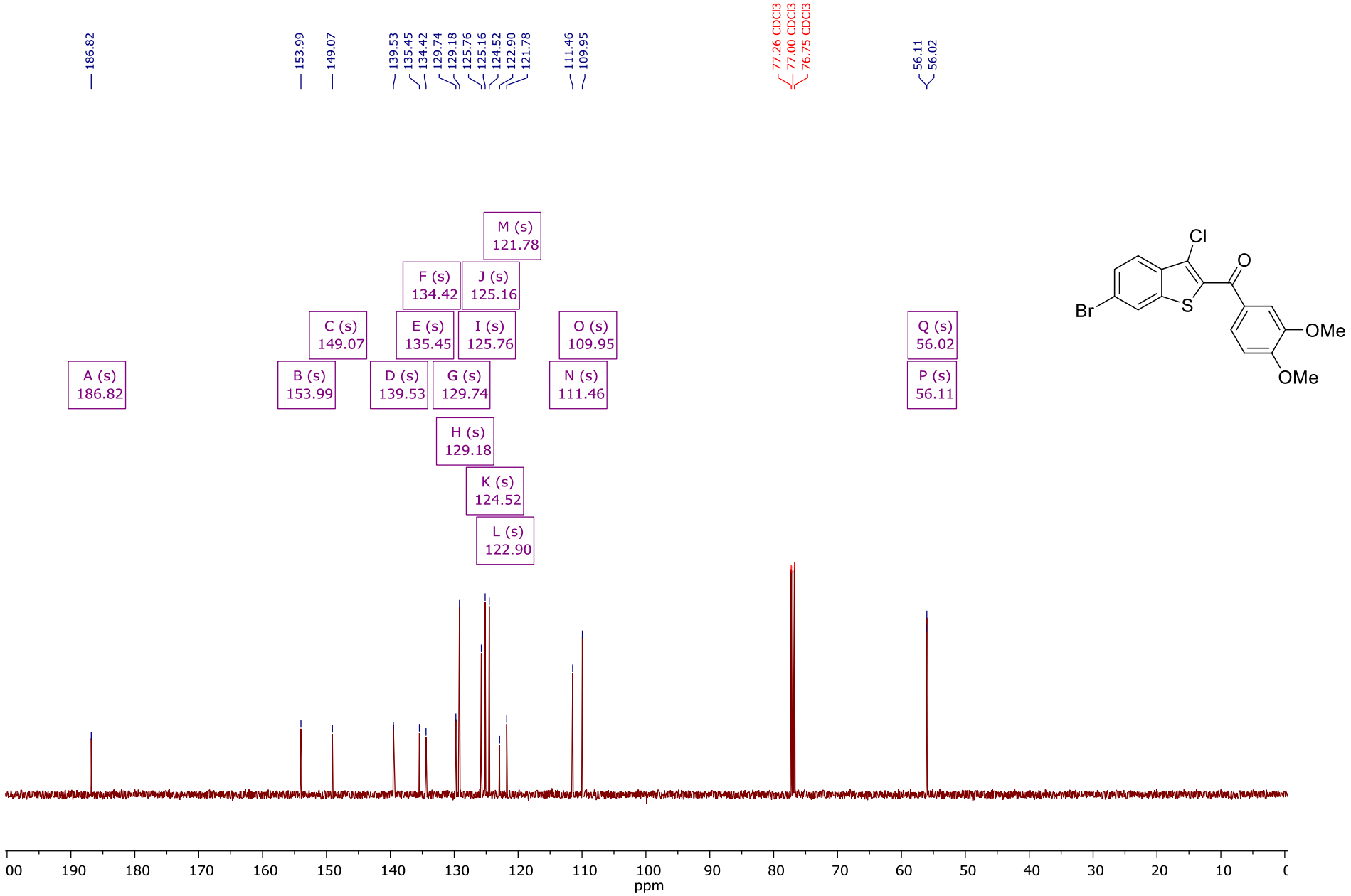


^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.8, 154.5, 153.8, 149.0, 139.5, 133.0, 131.3, 130.0, 125.5, 123.5, 122.6, 114.8, 111.9, 111.5, 109.9, 56.9, 56.1, 56.0.

(6-Bromo-3-chlorobenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6l)

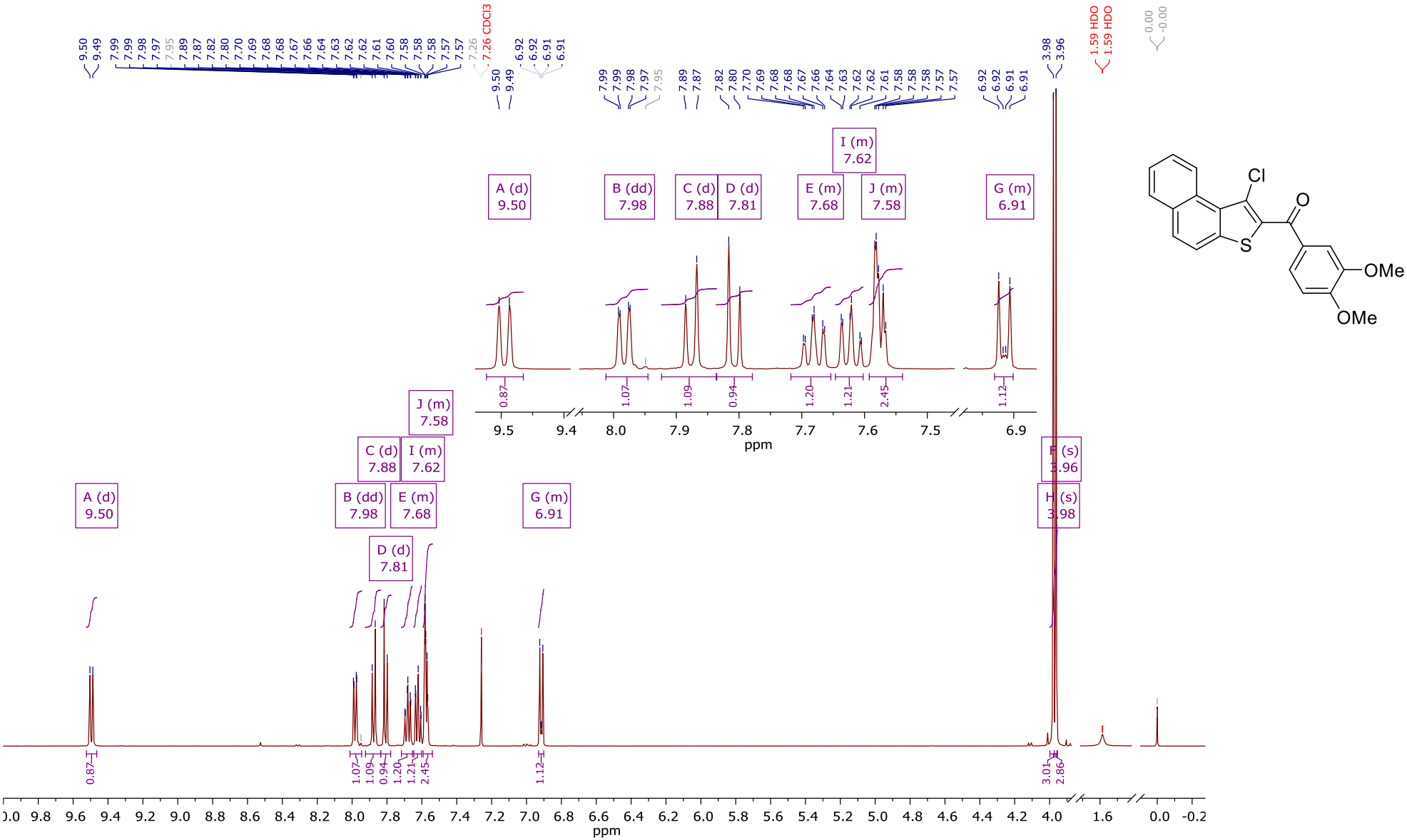


^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 1.7 Hz, 1H), 7.81 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.63 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.58 – 7.50 (m, 2H), 6.92 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H).

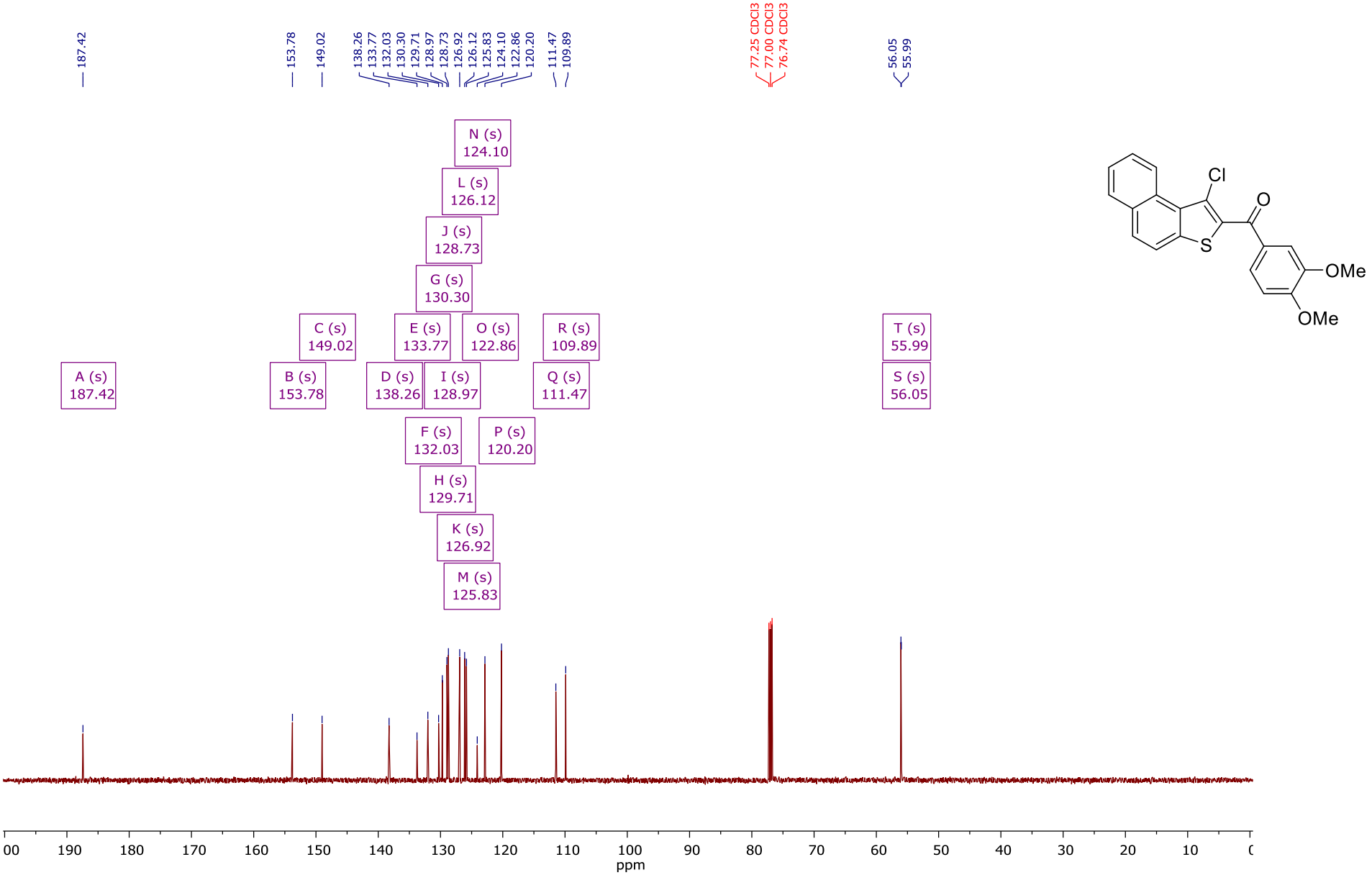


^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.8, 154.0, 149.1, 139.5, 135.4, 134.4, 129.7, 129.2, 125.8, 125.2, 124.5, 122.9, 121.8, 111.5, 109.9, 56.1, 56.0.

(1-Chloronaphtho[2,1-*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (6m)

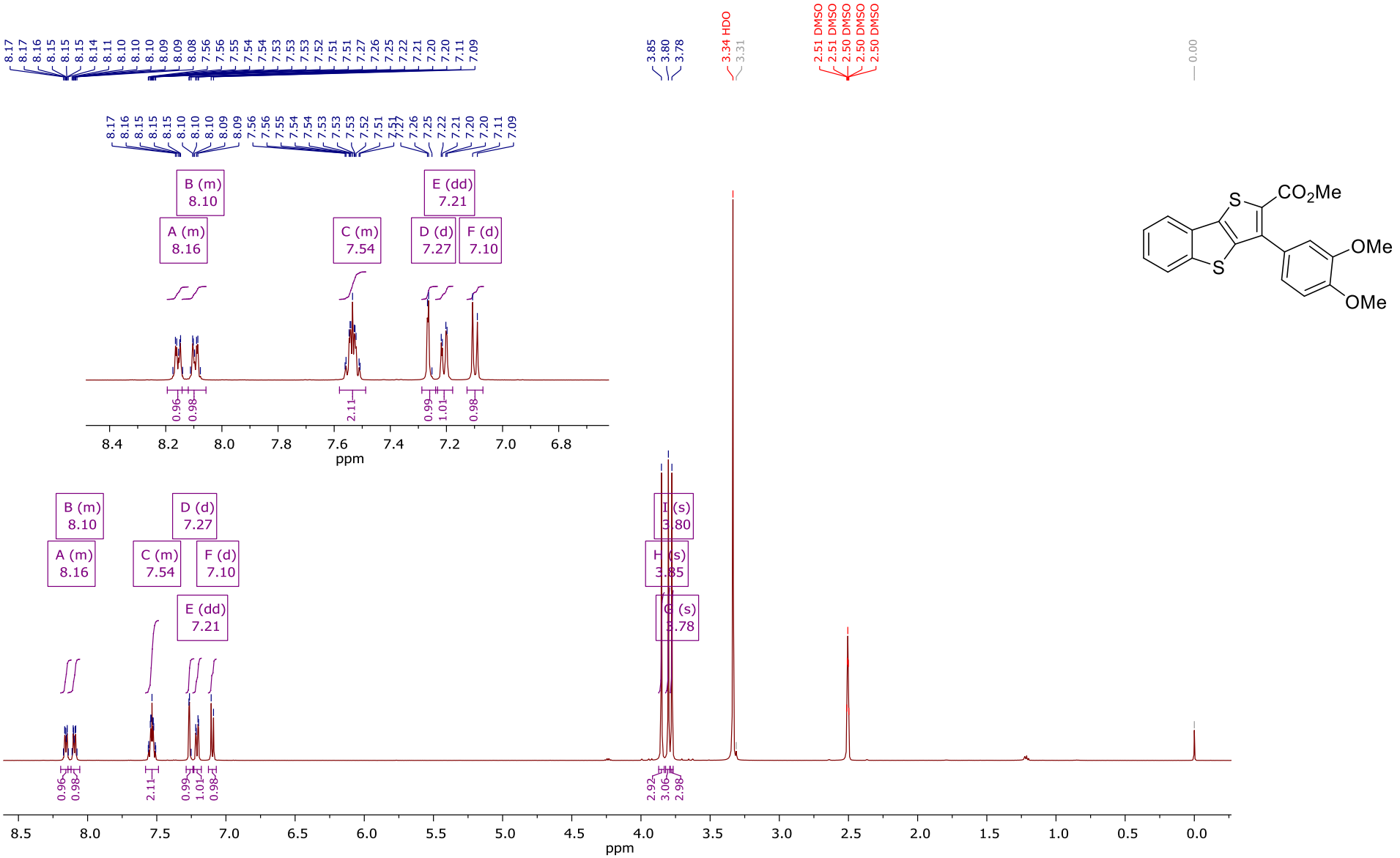


^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.50 (d, *J* = 8.2 Hz, 1H), 7.98 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.65 – 7.60 (m, 1H), 7.59 – 7.54 (m, 2H), 6.93 – 6.90 (m, 1H), 3.98 (s, 3H), 3.96 (s, 3H).

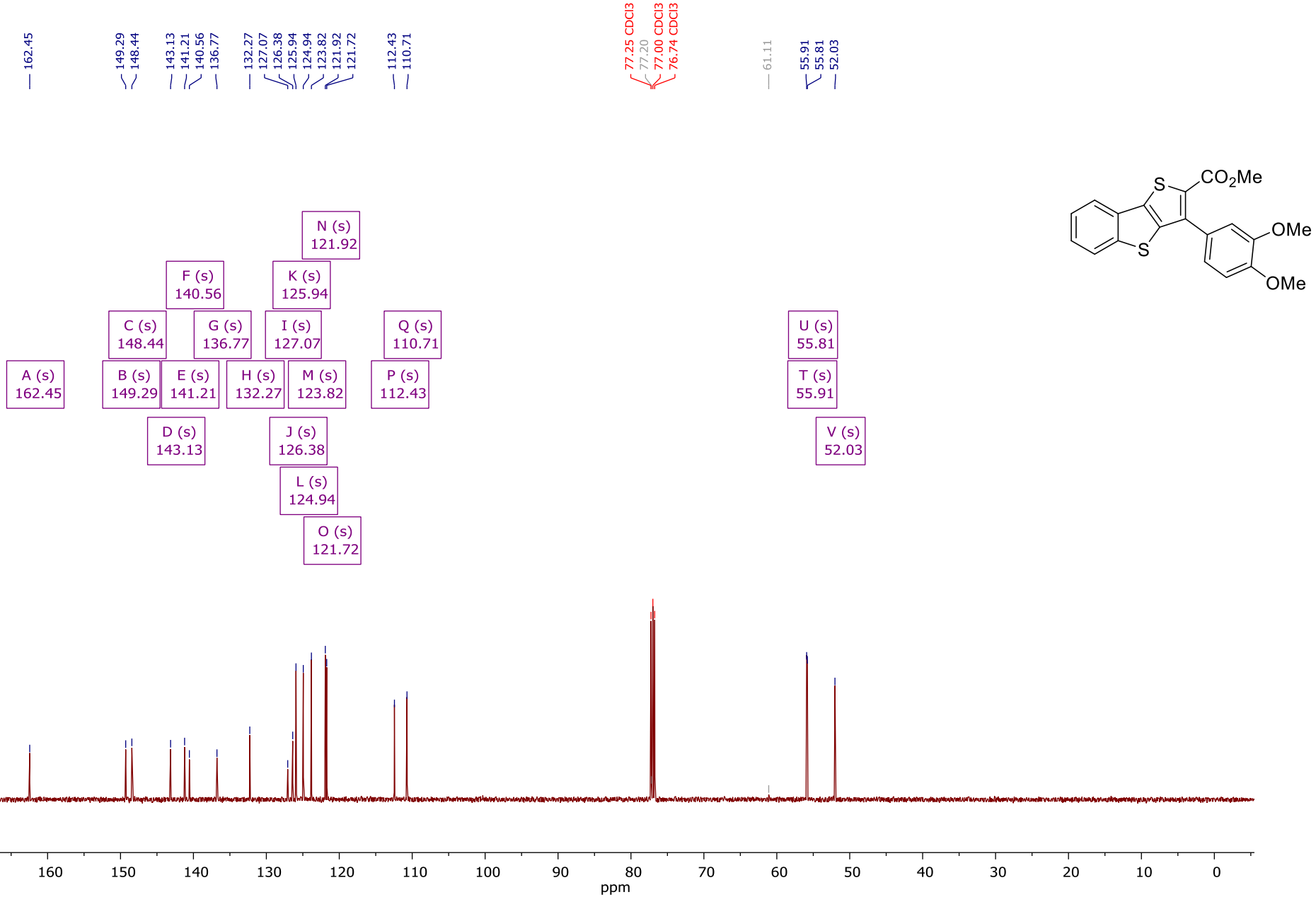


^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 153.8, 149.0, 138.3, 133.8, 132.0, 130.3, 129.7, 129.0, 128.7, 126.9, 126.1, 125.8, 124.1, 122.9, 120.2, 111.5, 109.9, 56.05, 55.99. (One signal was not found due to overlapping peaks).

Methyl 3-(3,4-dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7a)

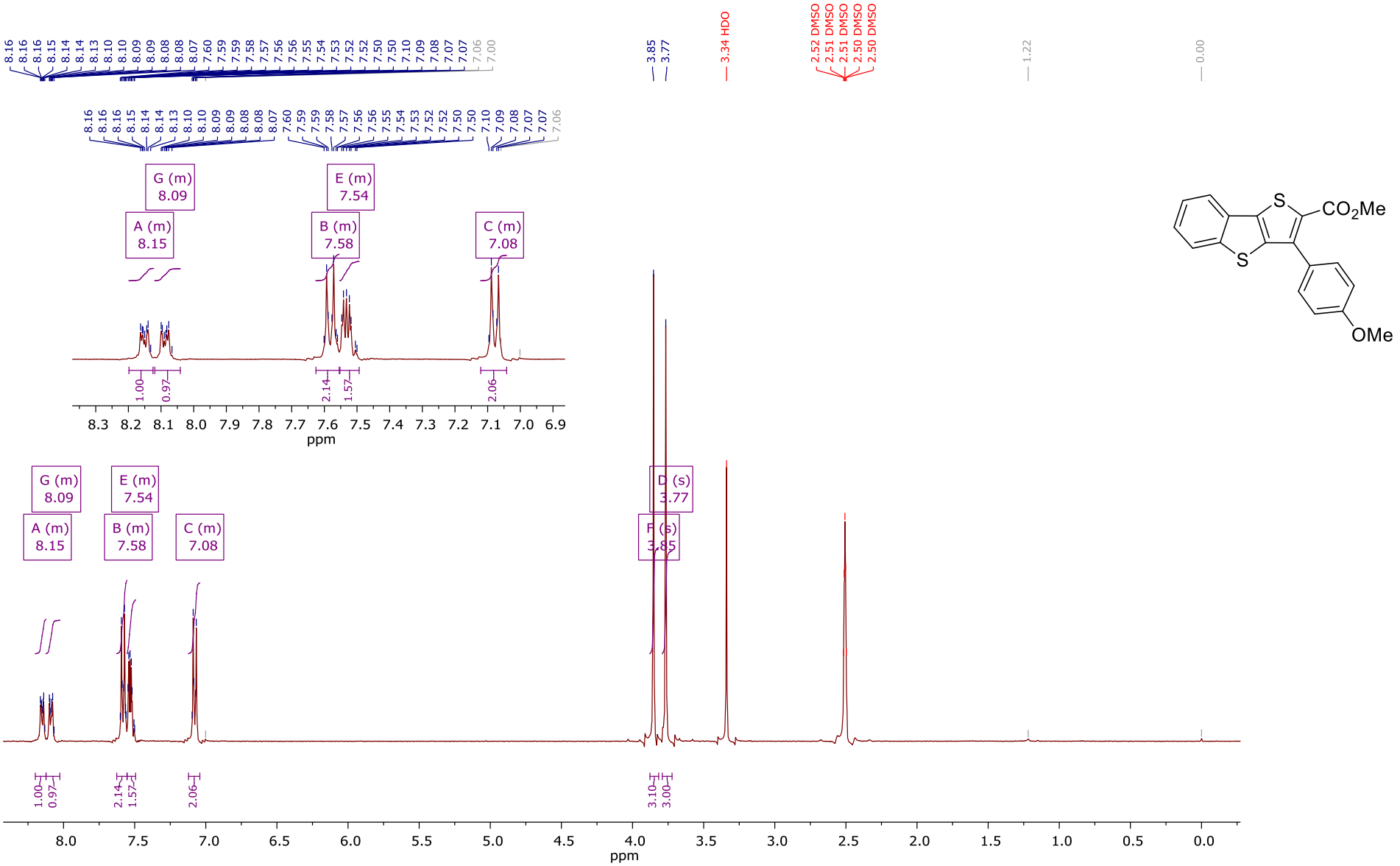


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19 – 8.12 (m, 1H), 8.14 – 8.06 (m, 1H), 7.58 – 7.49 (m, 2H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H).

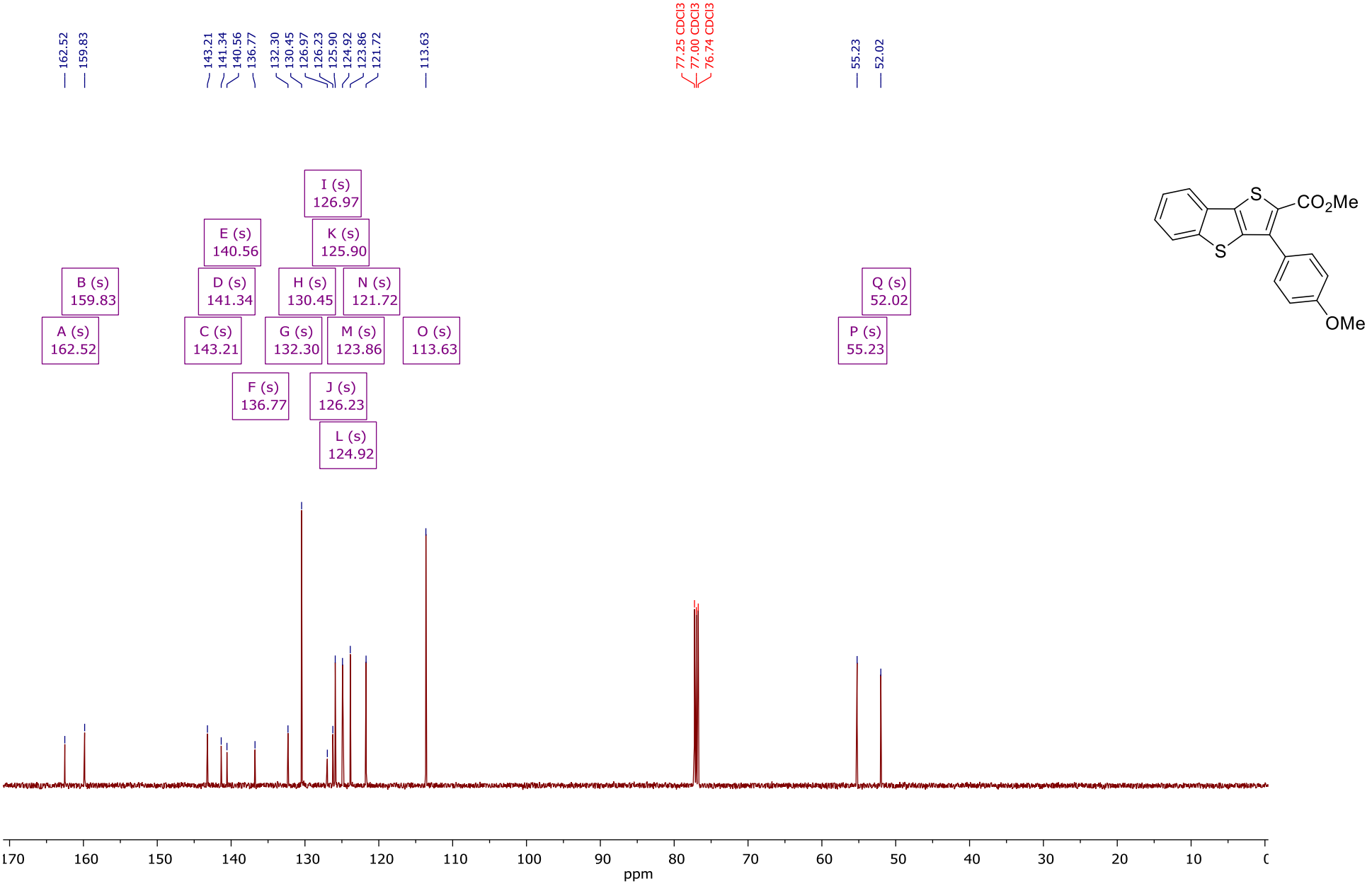


^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.4, 149.3, 148.4, 143.1, 141.2, 140.6, 136.8, 132.3, 127.1, 126.4, 125.9, 124.9, 123.8, 121.9, 121.7, 112.4, 110.7, 55.9, 55.8, 52.0.

Methyl 3-(4-methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7b)

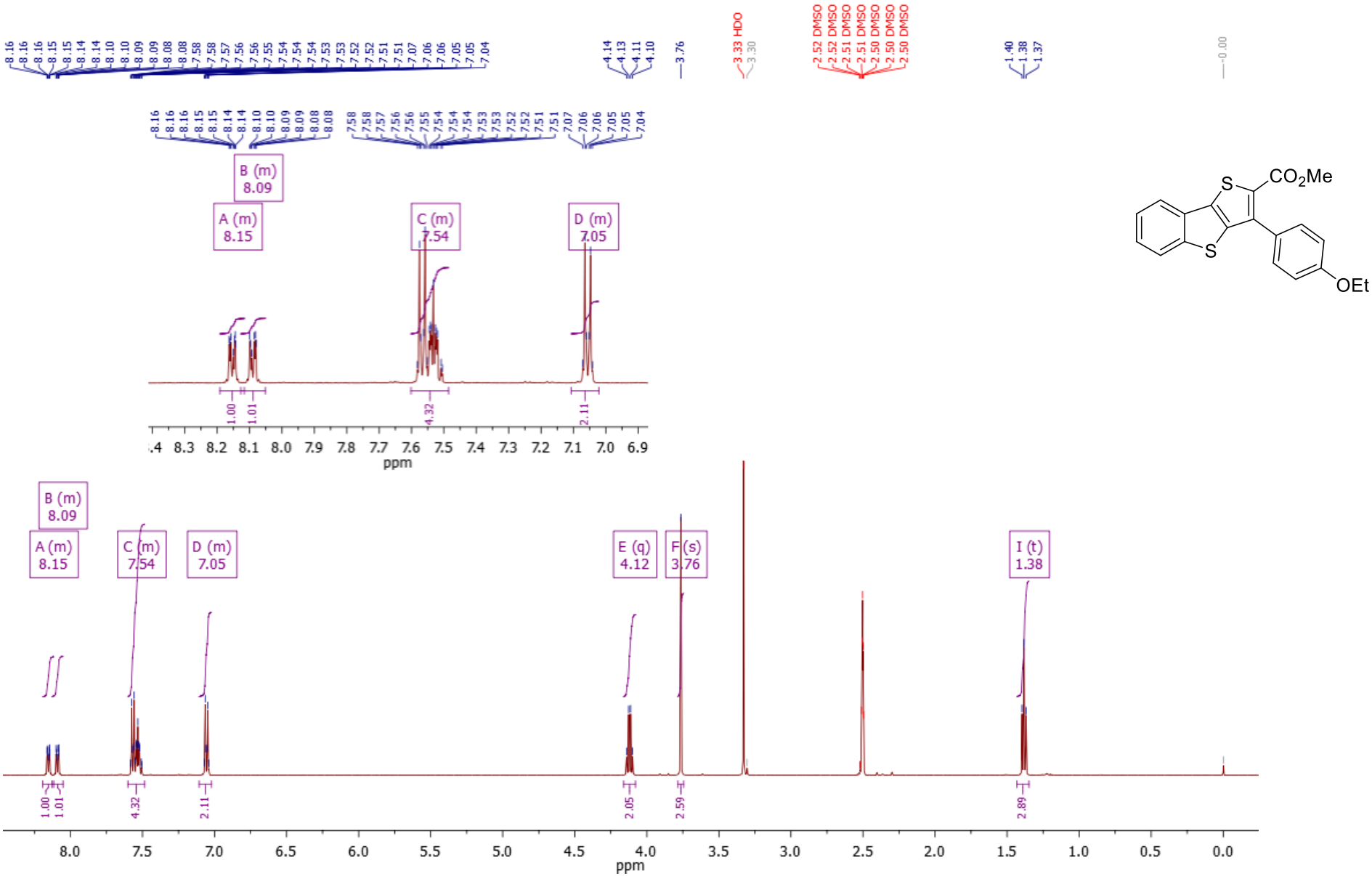


^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 – 8.12 (m, 1H), 8.12 – 8.03 (m, 1H), 7.63 – 7.55 (m, 2H), 7.55 – 7.49 (m, 2H), 7.12 – 7.04 (m, 2H), 3.85 (s, 3H), 3.77 (s, 3H).

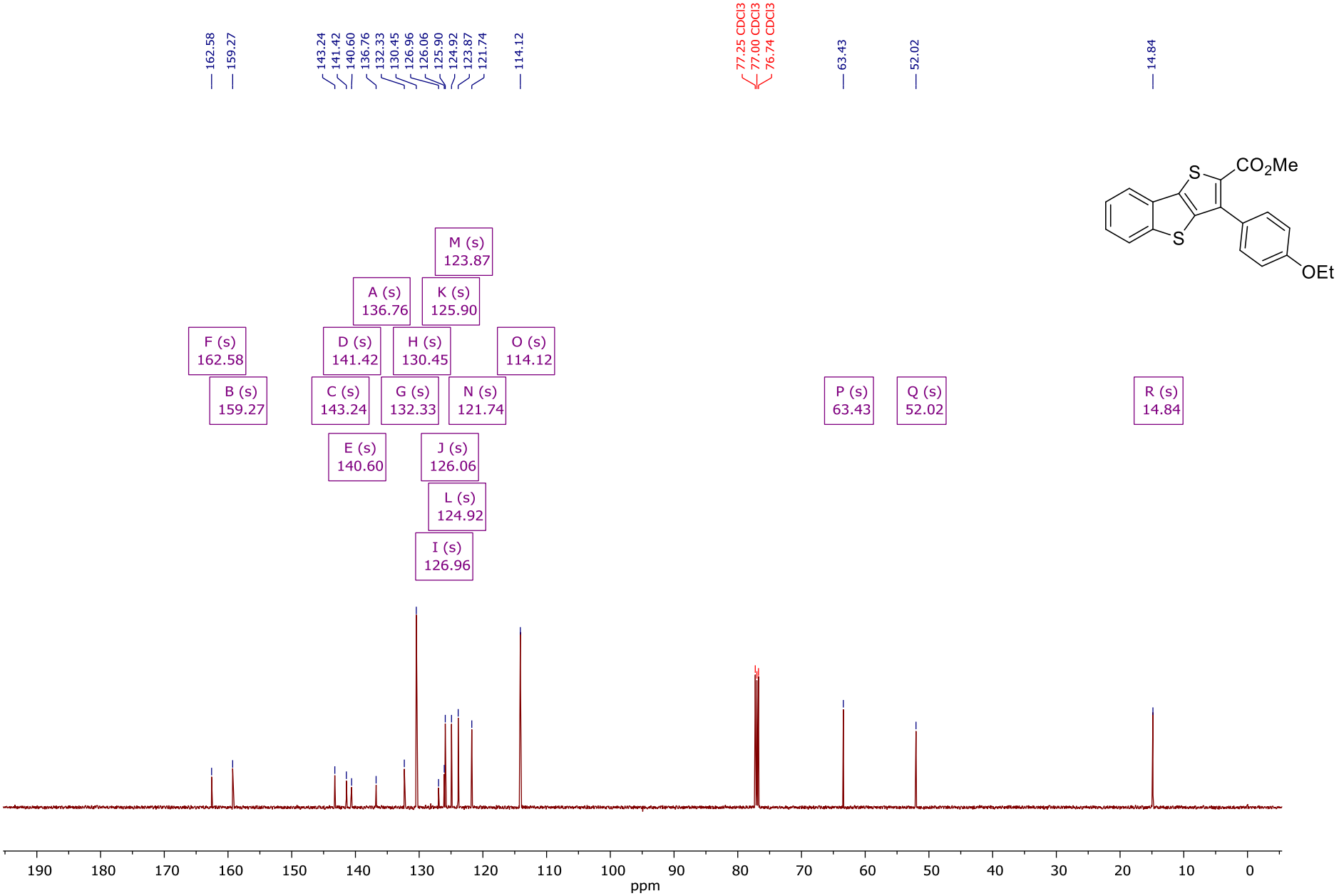


^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.5, 159.8, 143.2, 141.3, 140.6, 136.8, 132.3, 130.4, 127.0, 126.2, 125.9, 124.9, 123.9, 121.7, 113.6, 55.2, 52.0.

Methyl 3-(4-ethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7c)

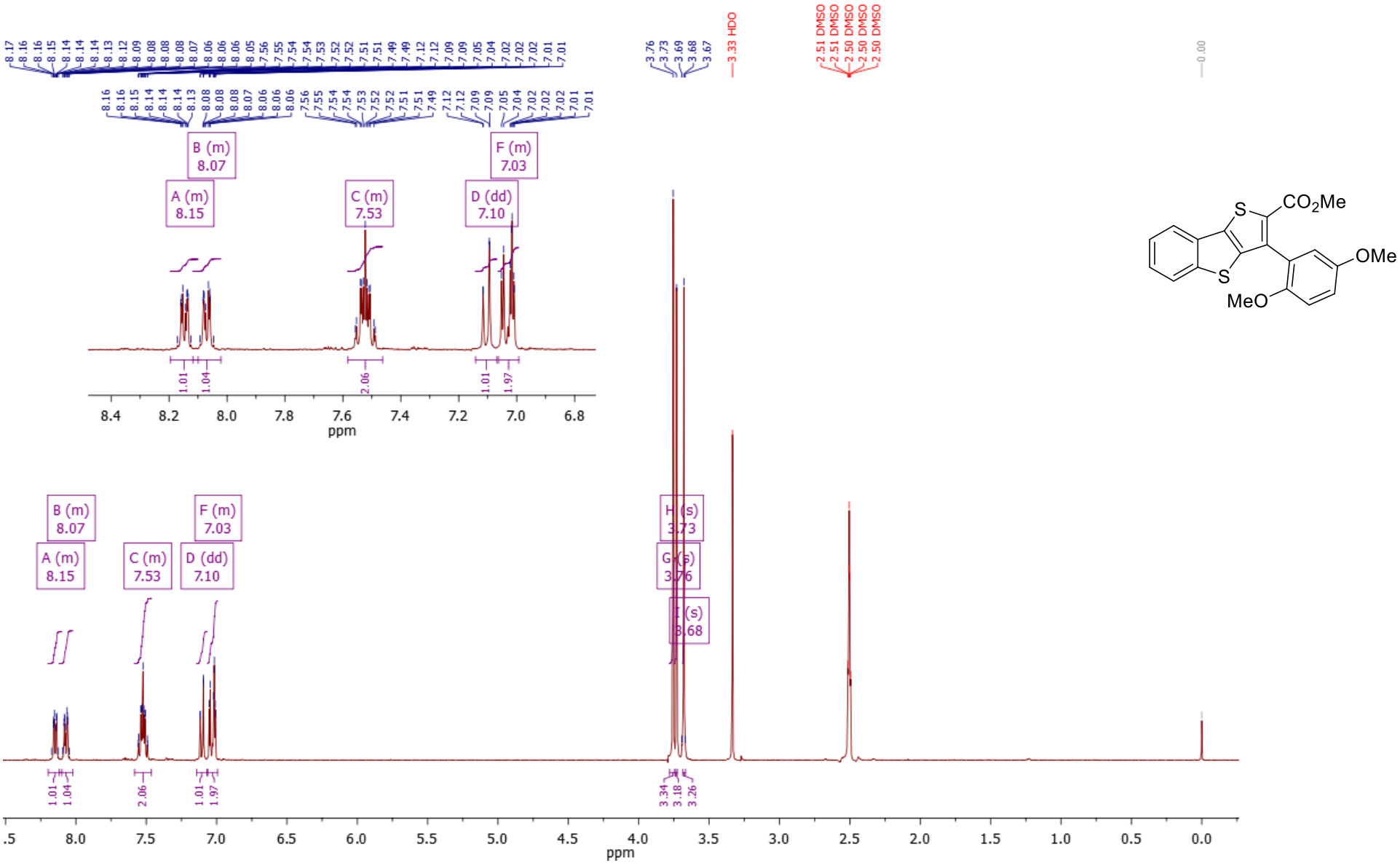


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19 – 8.12 (m, 1H), 8.13 – 8.05 (m, 1H), 7.60 – 7.49 (m, 4H), 7.11 – 7.02 (m, 2H), 4.12 (q, J = 6.9 Hz, 2H), 3.76 (s, 3H), 1.38 (t, J = 6.9 Hz, 3H).



^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.6, 159.3, 143.2, 141.4, 140.6, 136.8, 132.3, 130.4, 127.0, 126.1, 125.9, 124.9, 123.9, 121.7, 114.1, 63.4, 52.0, 14.8.

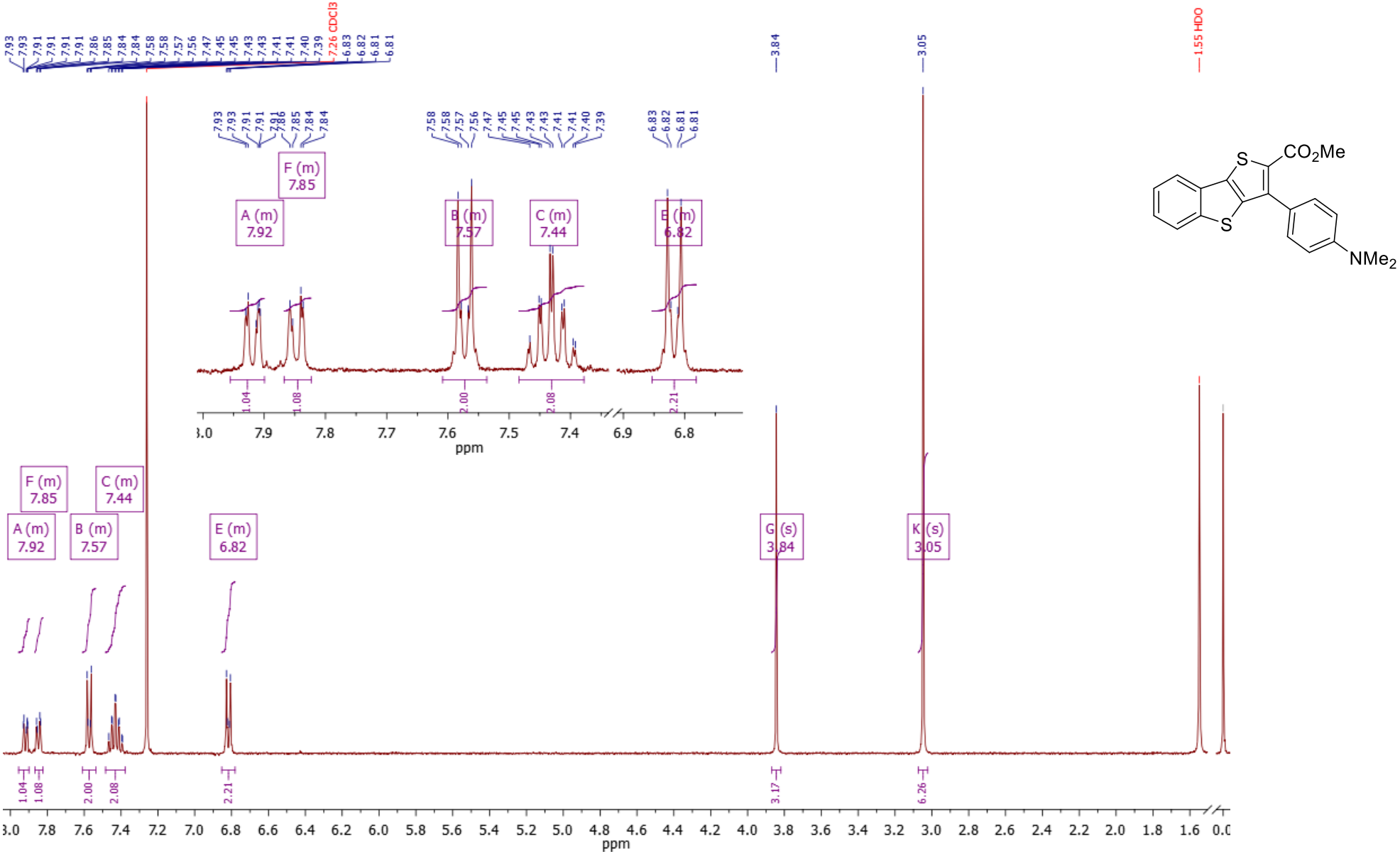
Methyl 3-(2,5-dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7d)



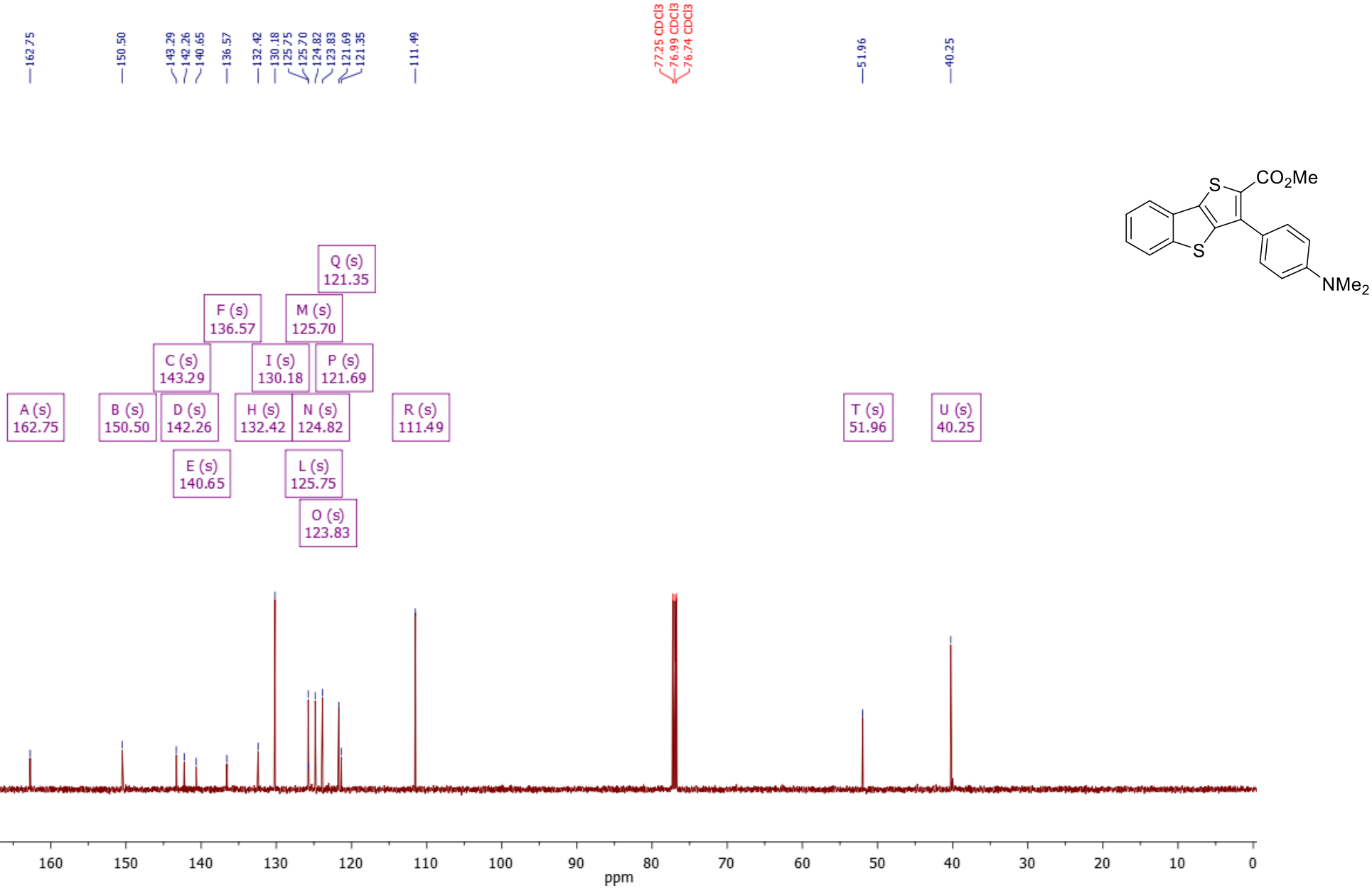
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 – 8.10 (m, 1H), 8.12 – 8.02 (m, 1H), 7.58 – 7.46 (m, 2H), 7.10 (dd, *J* = 8.9, 0.6 Hz, 1H), 7.06 – 6.99 (m, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 152.9, 150.5, 142.8, 140.2, 136.5, 136.1, 131.9, 129.2, 125.3, 124.4, 123.5, 123.4, 121.2, 115.3, 114.5, 111.9, 55.7, 55.3, 51.6.

Methyl 3-(4-(dimethylamino)phenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7e)

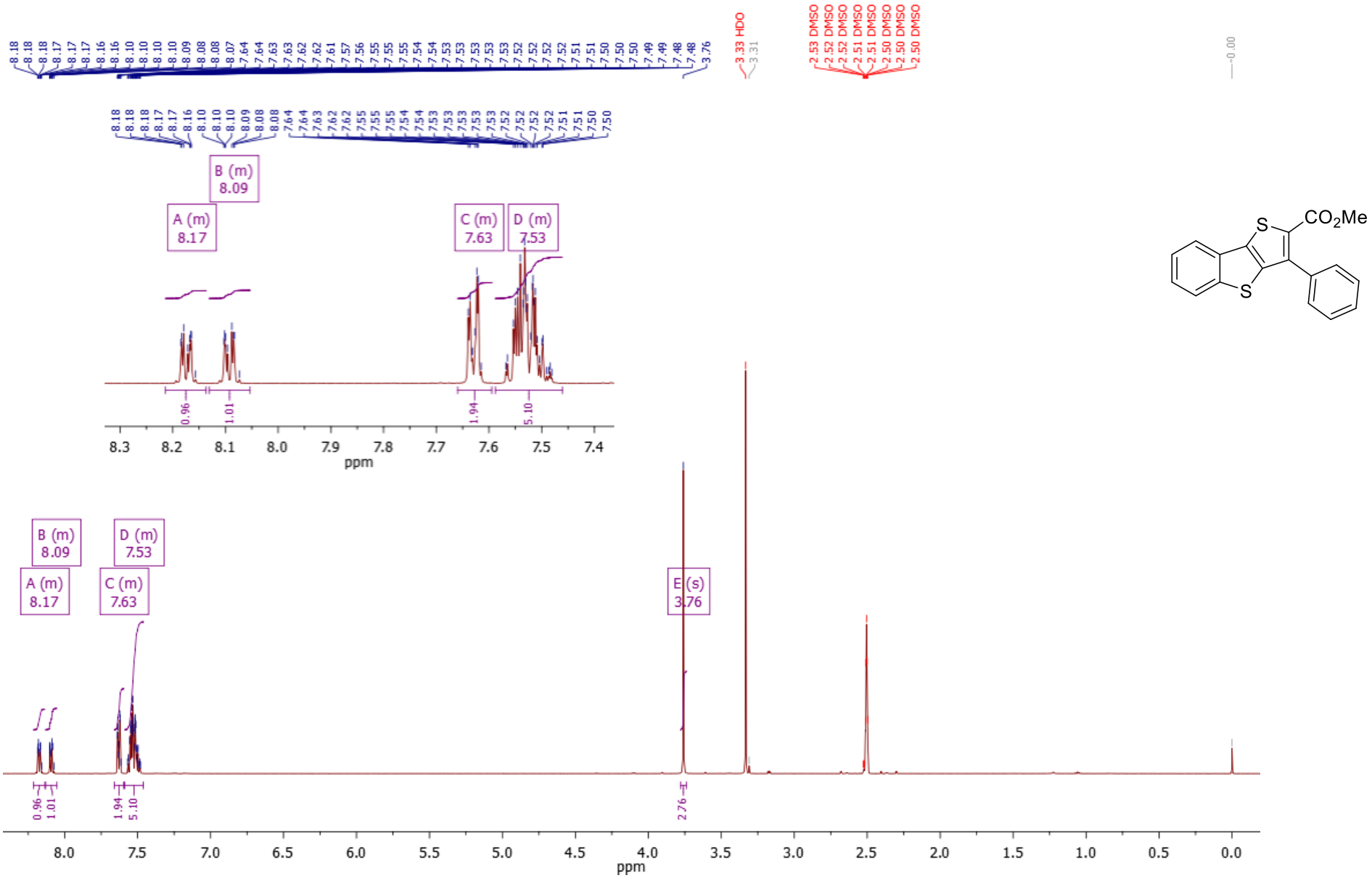


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 1H), 7.85 (m, 1H), 7.61 – 7.54 (m, 2H), 7.48 – 7.37 (m, 2H), 6.85 – 6.78 (m, 2H), 3.84 (s, 3H), 3.05 (s, 6H).

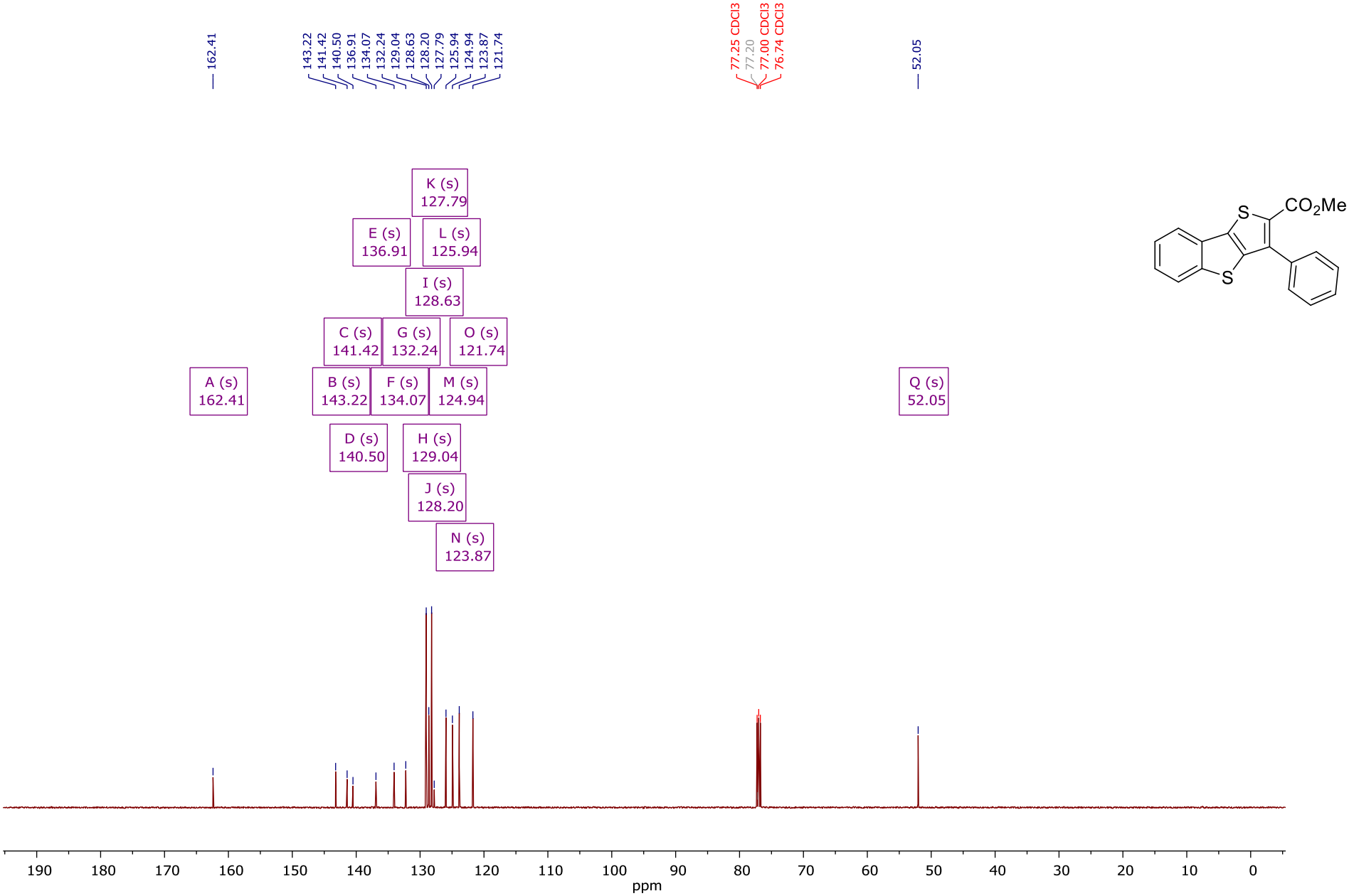


^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.7, 150.5, 143.3, 142.3, 140.6, 136.6, 132.4, 130.2, 125.75, 125.70, 124.8, 123.8, 121.7, 121.3, 111.5, 52.0, 40.2.

Methyl 3-phenylbenzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7f)

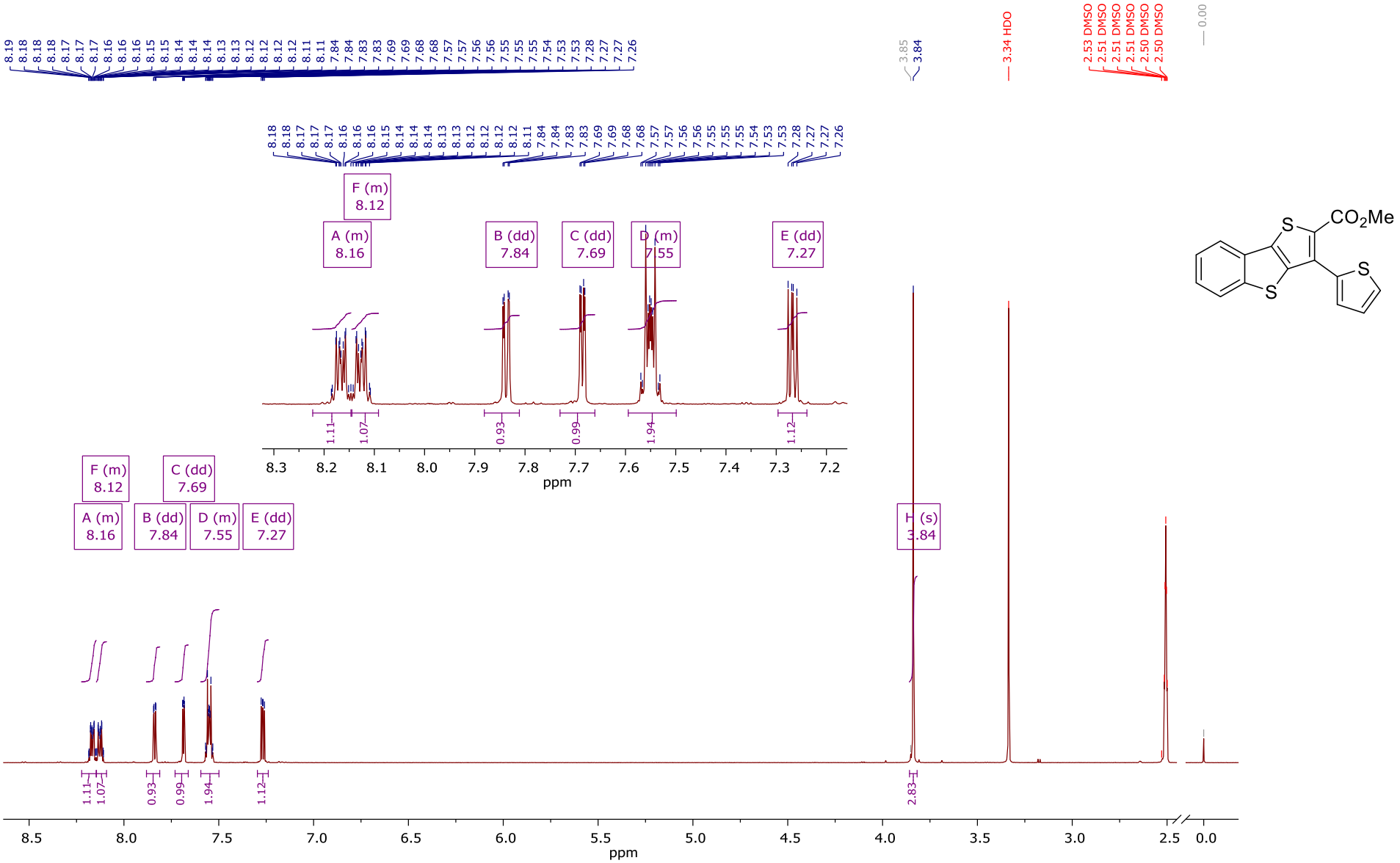


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.21 – 8.14 (m, 1H), 8.13 – 8.05 (m, 1H), 7.66 – 7.59 (m, 2H), 7.59 – 7.46 (m, 5H), 3.76 (s, 3H).

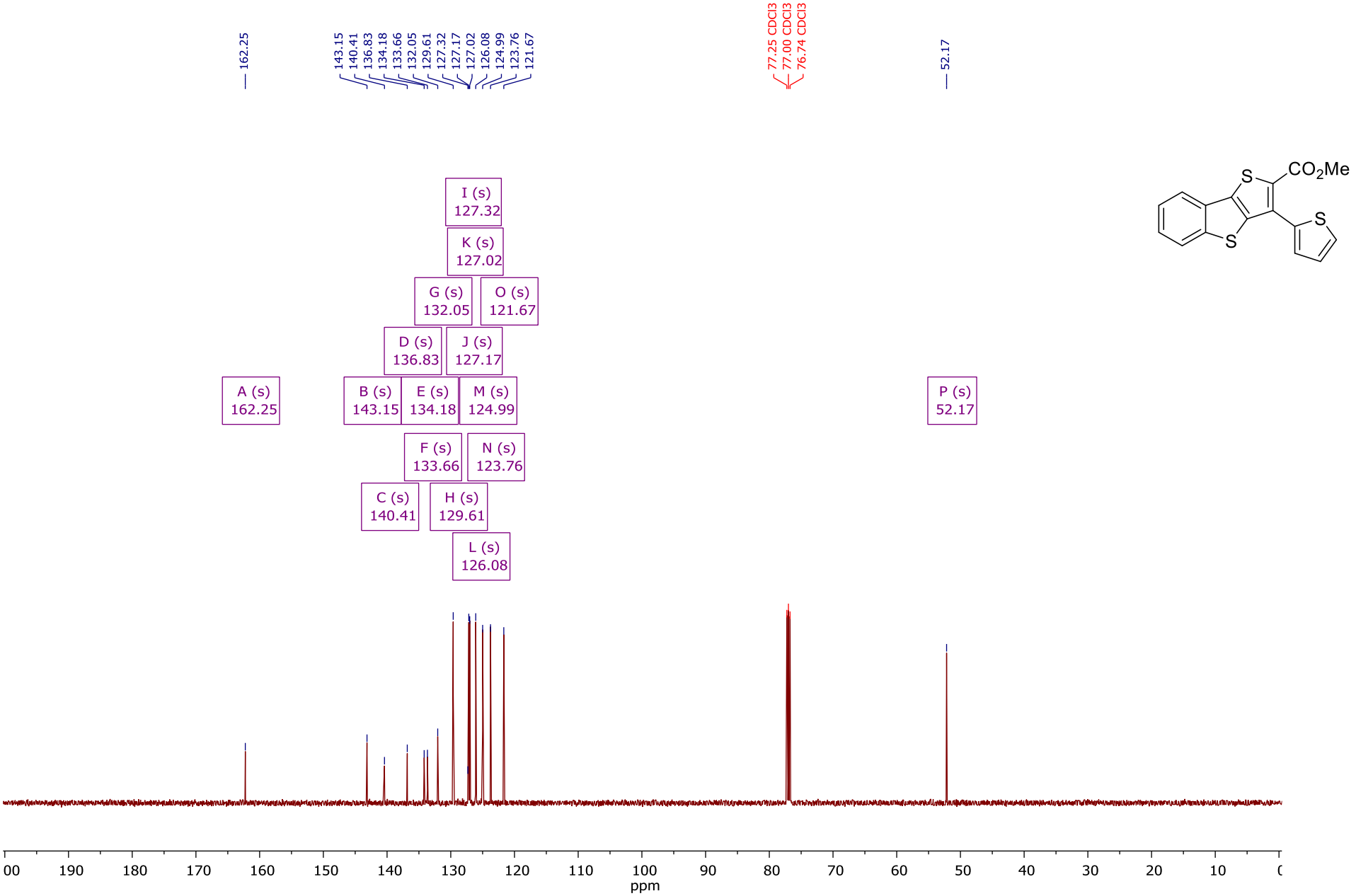


^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.4, 143.2, 141.4, 140.5, 136.9, 134.1, 132.2, 129.0, 128.6, 128.2, 127.8, 125.9, 124.9, 123.9, 121.7, 52.0.

Methyl 3-(thiophen-2-yl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7g)

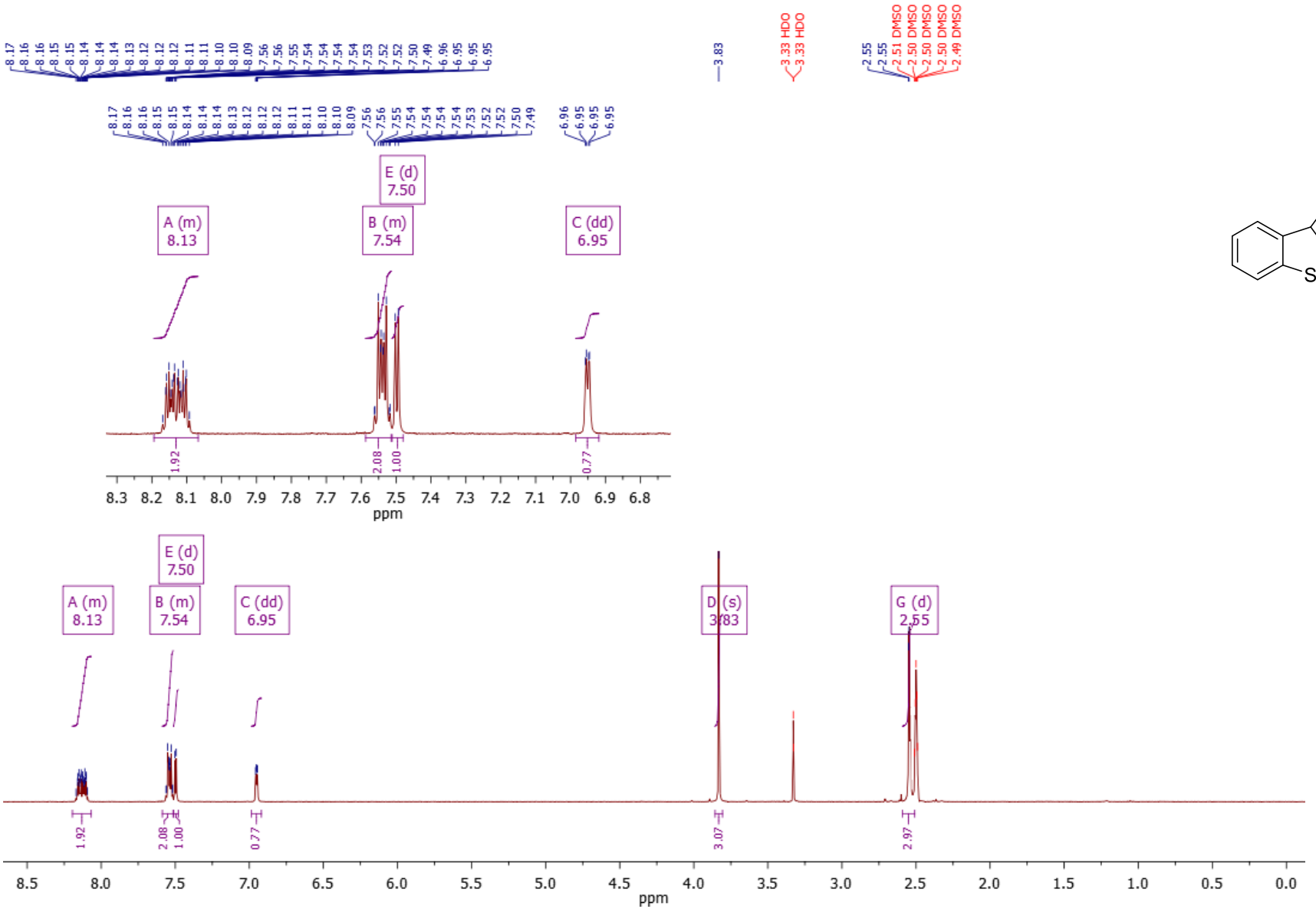


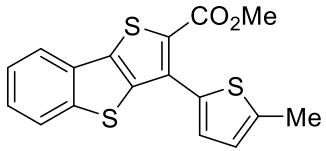
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 – 8.15 (m, 1H), 8.14 – 8.09 (m, 1H), 7.84 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.69 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.27 (dd, *J* = 5.1, 3.6 Hz, 1H), 3.84 (s, 3H).



^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.2, 143.1, 140.4, 136.8, 134.2, 133.7, 132.0, 129.6, 127.3, 127.2, 127.0, 126.1, 125.0, 123.8, 121.7, 52.2.

Methyl 3-(5-methylthiophen-2-yl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7h)

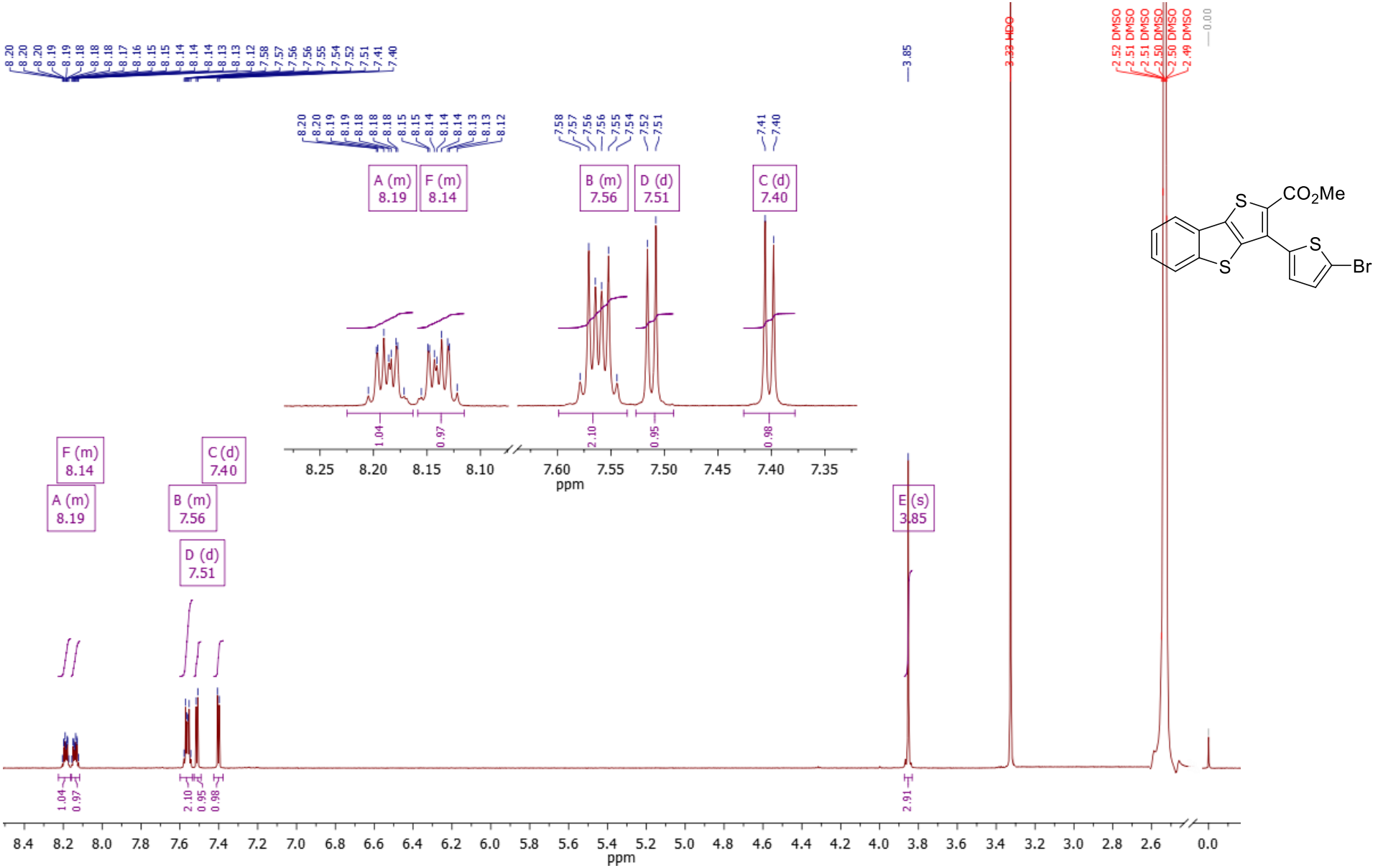




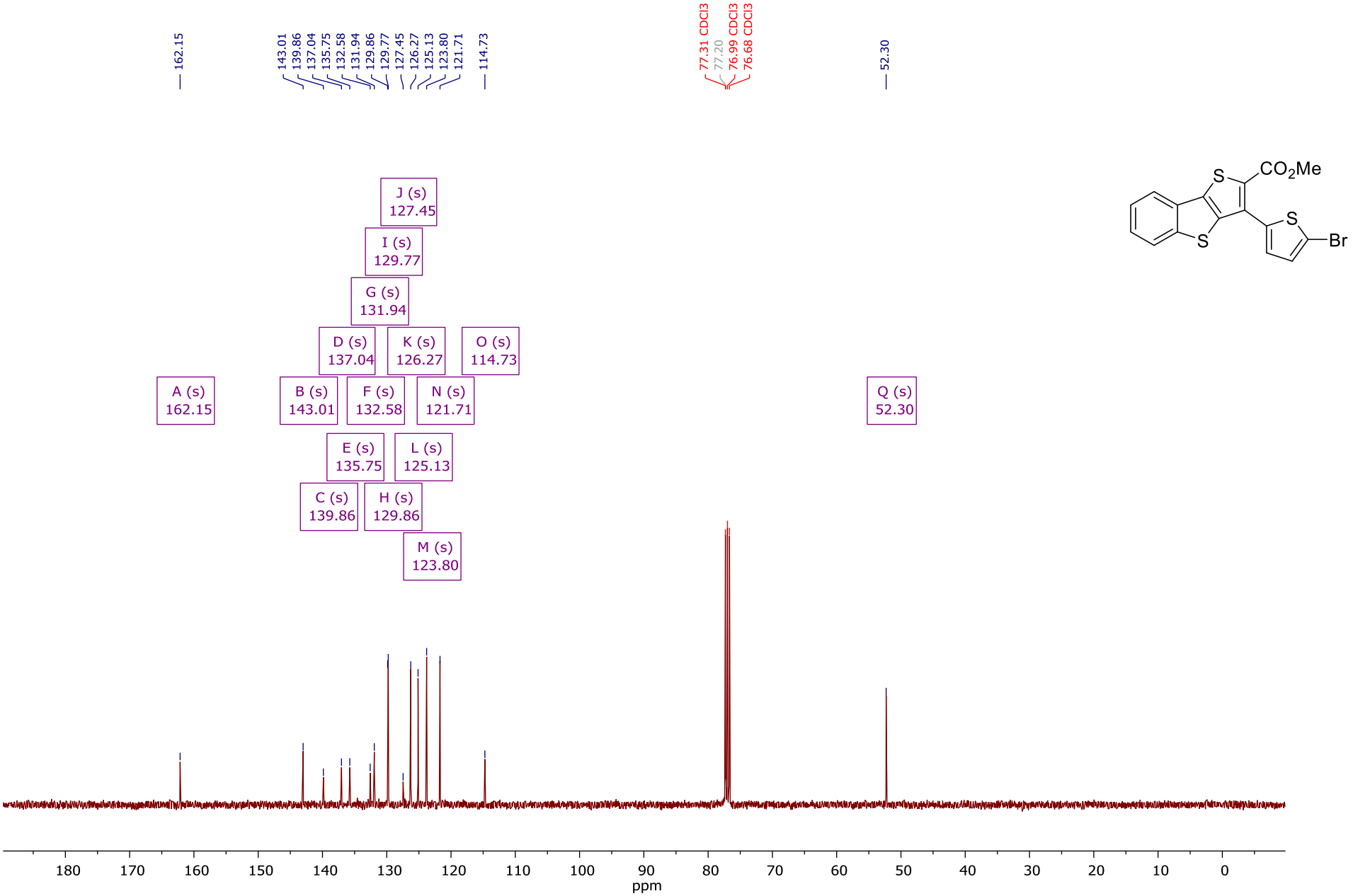
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 – 8.07 (m, 2H), 7.59 – 7.51 (m, 2H), 7.50 (d, J = 3.6 Hz, 1H), 6.95 (dd, J = 3.6, 1.1 Hz, 1H), 3.83 (s, 3H), 2.55 (d, J = 1.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.3, 143.16, 143.15, 142.1, 140.2, 136.7, 134.1, 132.0, 131.8, 129.9, 126.0, 125.4, 124.9, 123.7, 121.6, 52.1, 15.3.

Methyl 3-(5-bromothiophen-2-yl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7i)

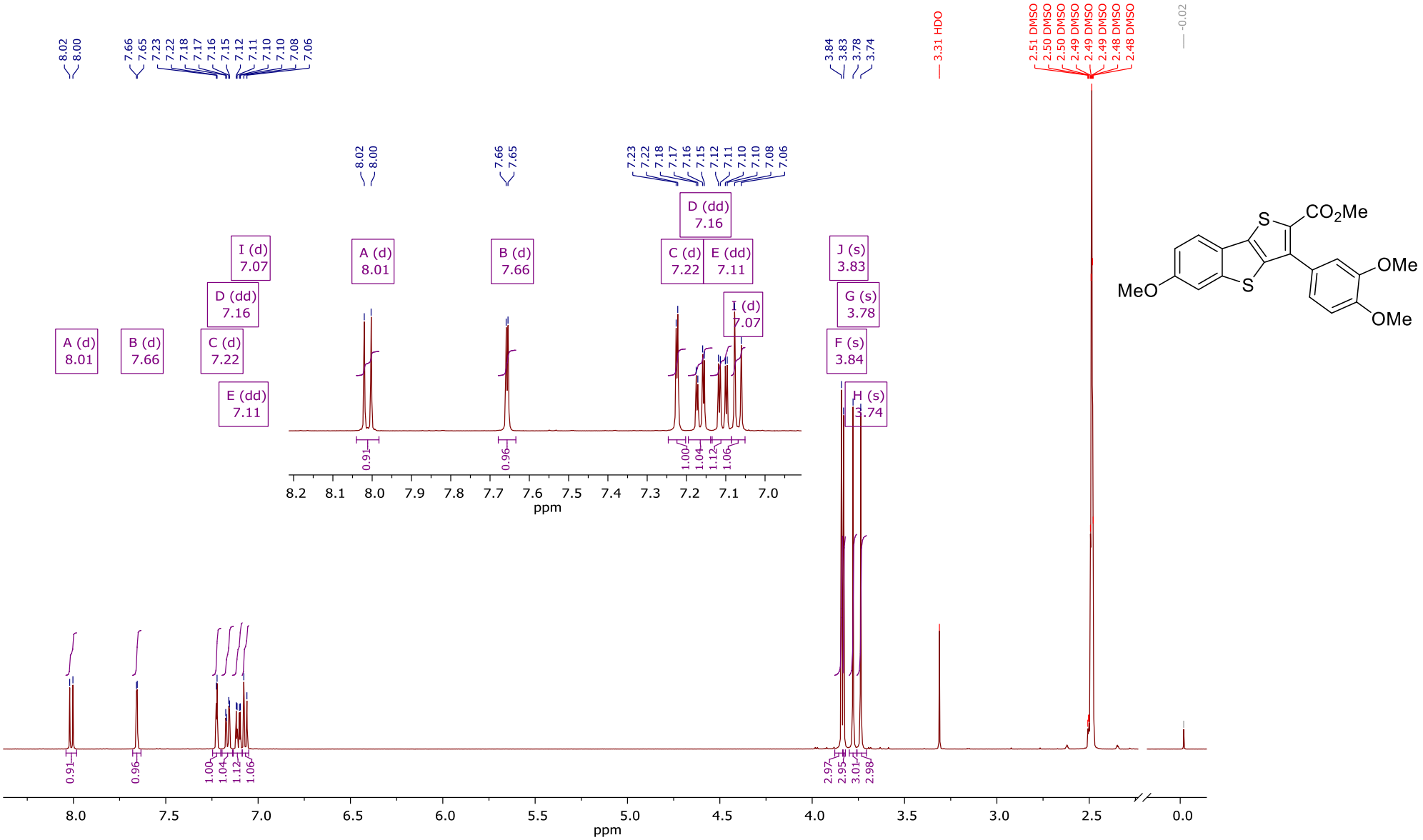


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 – 8.16 (m, 1H), 8.16 – 8.12 (m, 1H), 7.60 – 7.53 (m, 2H), 7.51 (d, *J* = 3.9 Hz, 1H), 7.40 (d, *J* = 3.9 Hz, 1H), 3.85 (s, 3H).

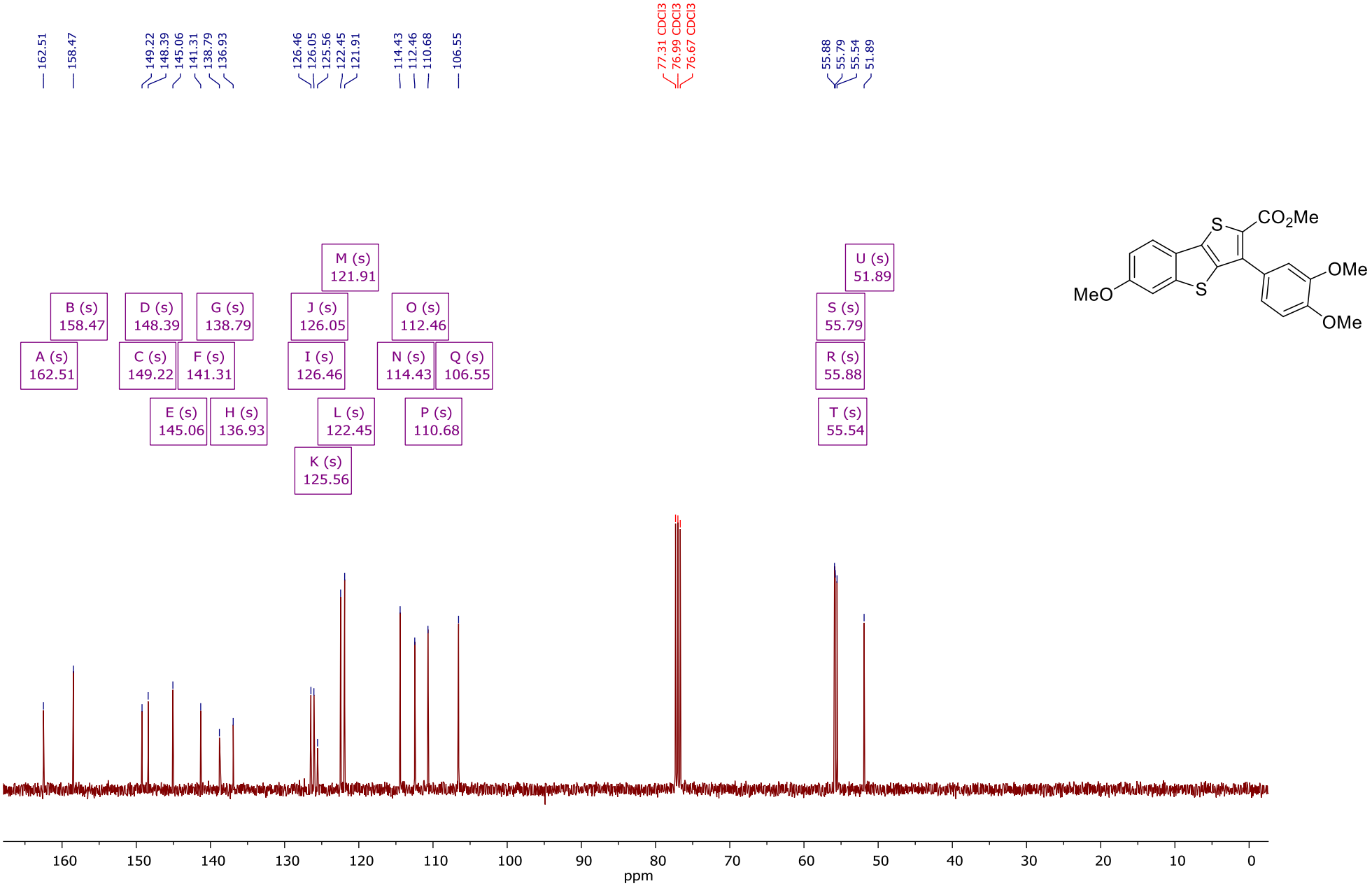


^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1, 143.0, 139.9, 137.0, 135.7, 132.6, 131.9, 129.9, 129.8, 127.4, 126.3, 125.1, 123.8, 121.7, 114.7, 52.3.

Methyl 3-(3,4-dimethoxyphenyl)-6-methoxybenzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7j)

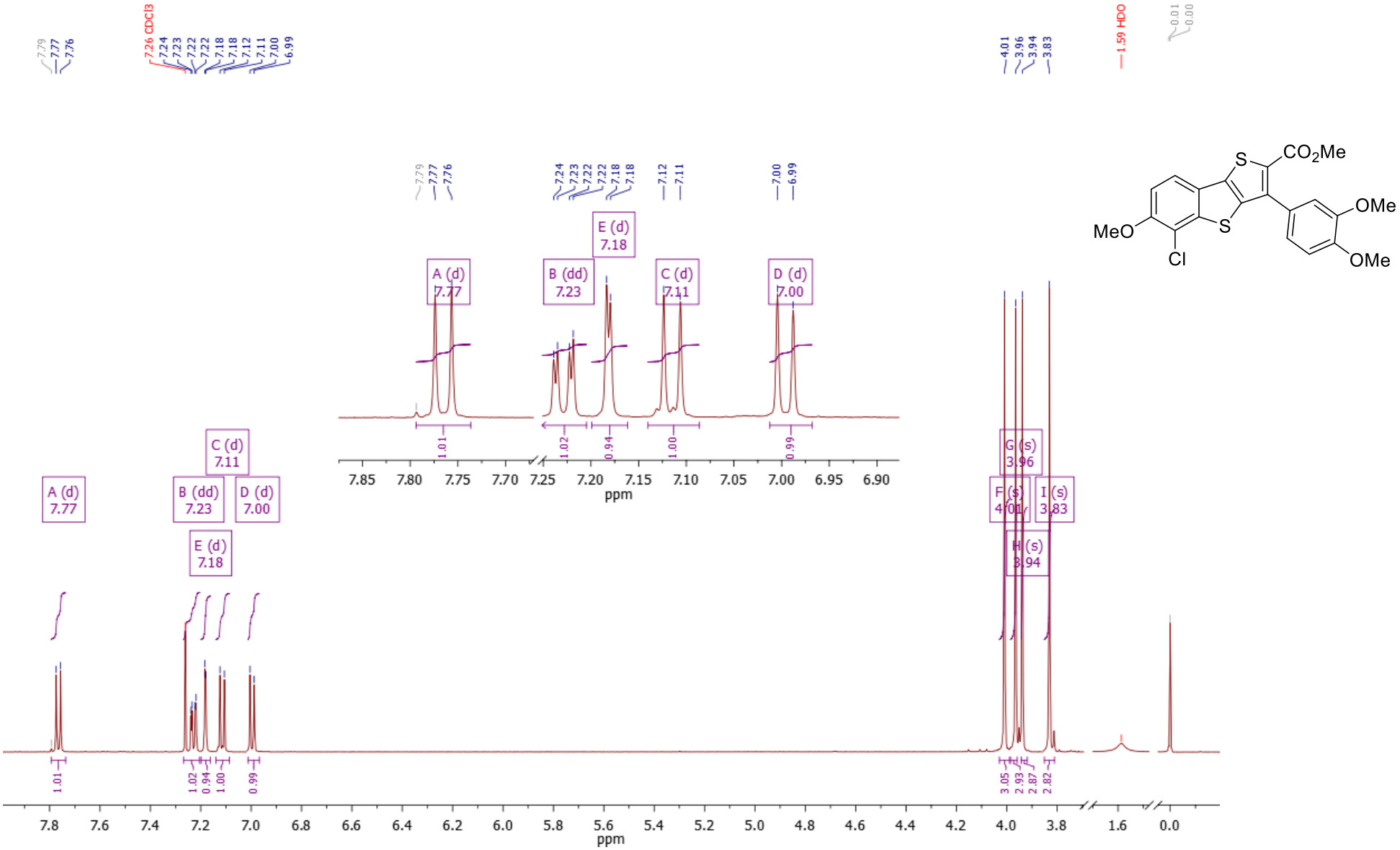


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.01 (d, J = 8.7 Hz, 1H), 7.66 (d, J = 2.4 Hz, 1H), 7.22 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 8.2, 2.1 Hz, 1H), 7.11 (dd, J = 8.8, 2.4 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H).

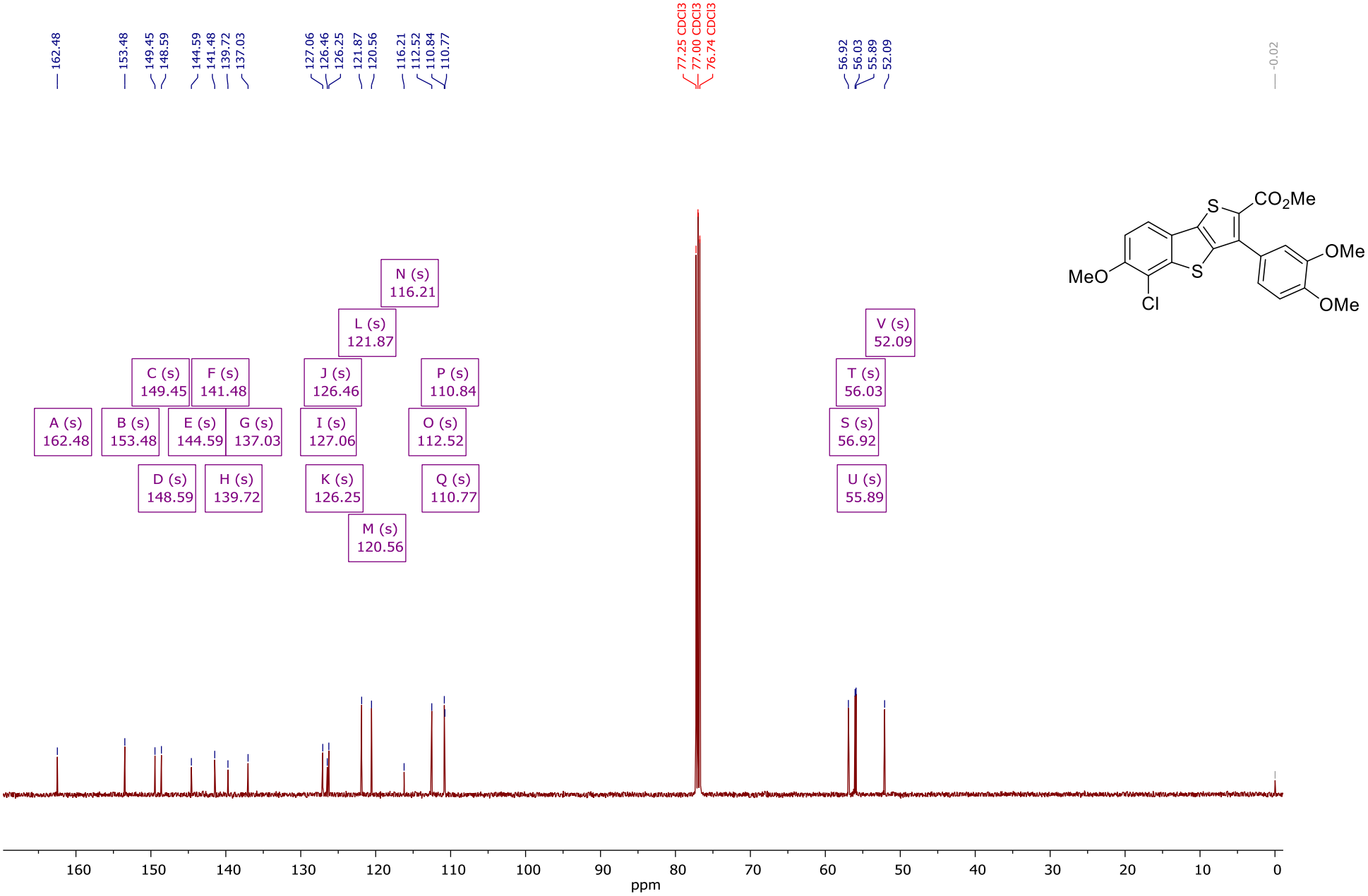


^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.5, 158.5, 149.2, 148.4, 145.1, 141.3, 138.8, 136.9, 126.5, 126.0, 125.6, 122.4, 121.9, 114.4, 112.5, 110.7, 106.5, 55.9, 55.8, 55.5, 51.9.

Methyl 5-chloro-3-(3,4-dimethoxyphenyl)-6-methoxybenzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7k)

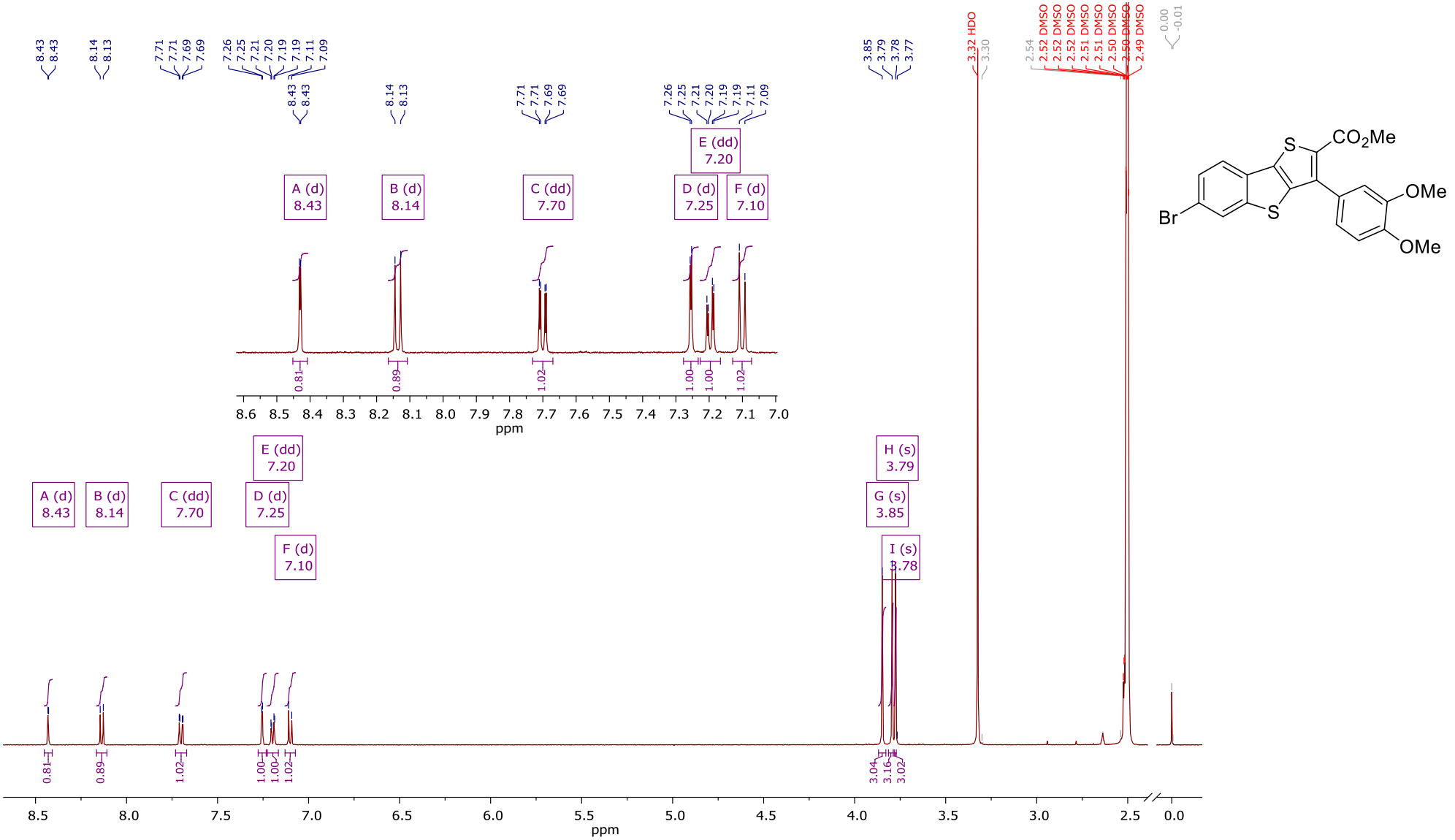


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 4.01 (s, 3H), 3.96 (s, 3H), 3.94 (s, 3H), 3.83 (s, 3H).

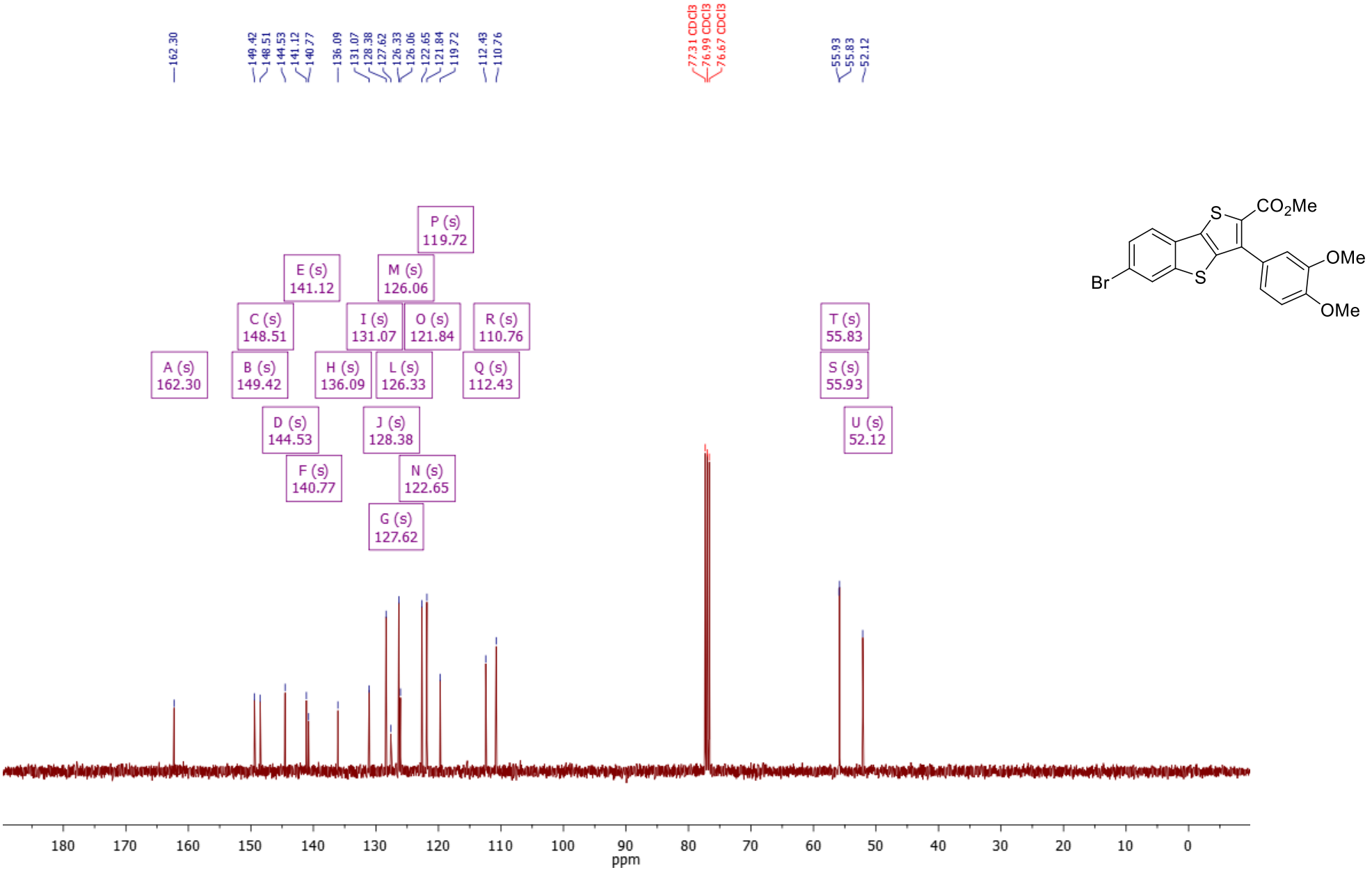


^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.5, 153.5, 149.4, 148.6, 144.6, 141.5, 139.7, 137.0, 127.1, 126.5, 126.2, 121.9, 120.6, 116.2, 112.5, 110.84, 110.77, 56.9, 56.0, 55.9, 52.1.

Methyl 6-bromo-3-(3,4-dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylate (7l)

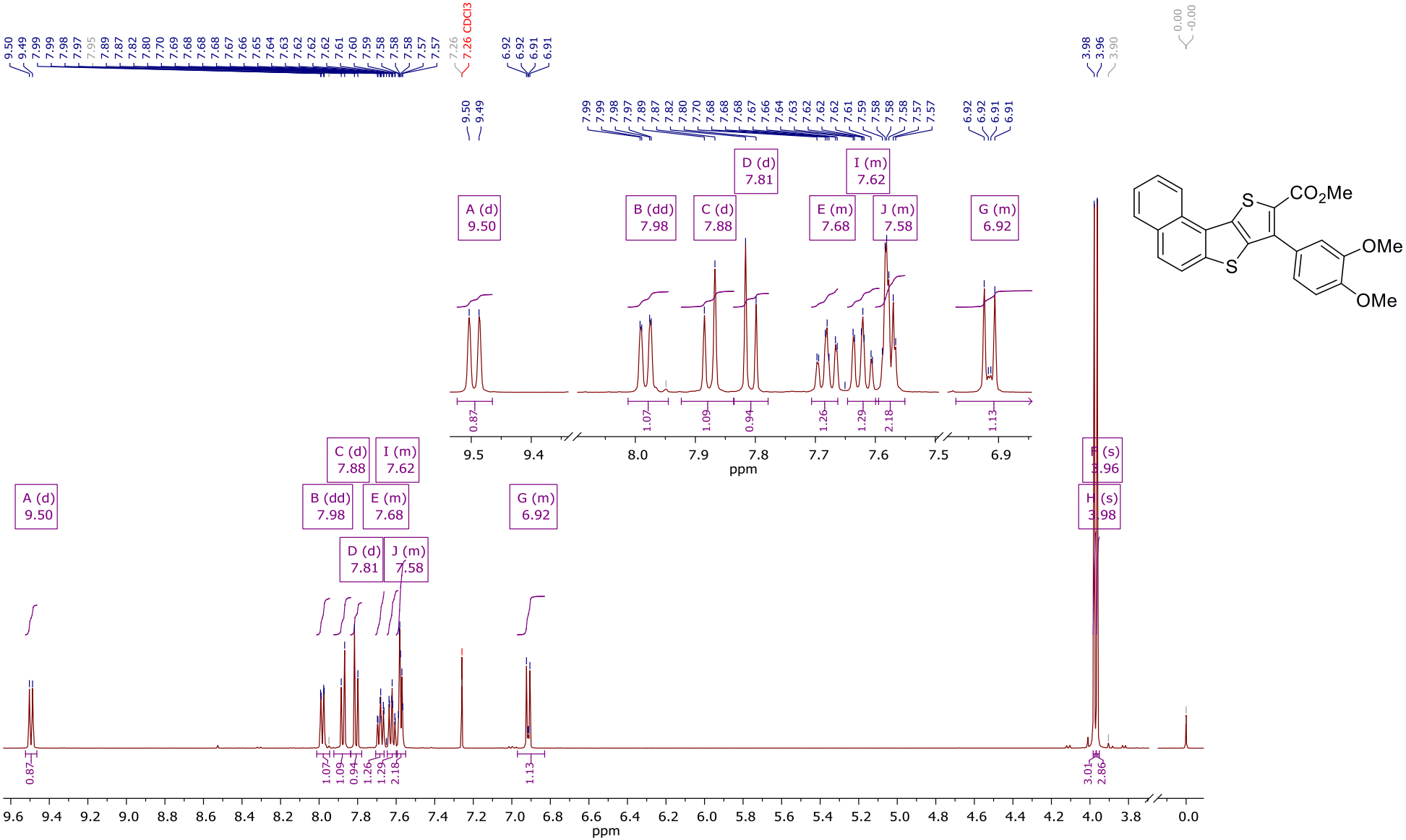


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.43 (d, J = 1.8 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.70 (dd, J = 8.5, 1.8 Hz, 1H), 7.25 (d, J = 2.1 Hz, 1H), 7.20 (dd, J = 8.2, 2.1 Hz, 1H), 7.10 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H).

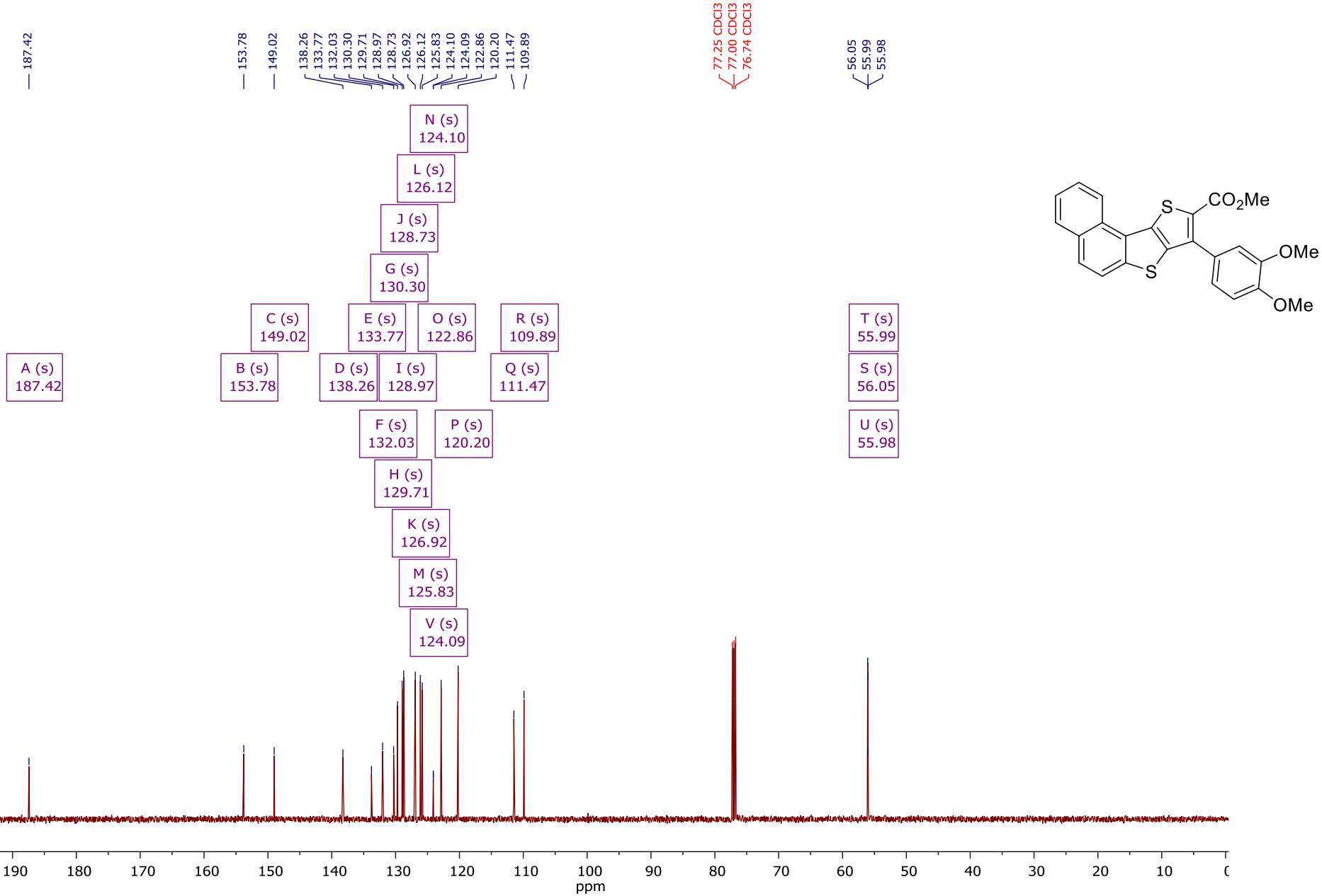


^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3, 149.4, 148.5, 144.5, 141.1, 140.8, 136.1, 131.1, 128.4, 127.6, 126.3, 126.1, 122.6, 121.8, 119.7, 112.4, 110.8, 55.9, 55.8, 52.1.

Methyl 8-(3,4-dimethoxyphenyl)naphtho[2,1-*b*]thieno[2,3-*d*]thiophene-9-carboxylate (7m)

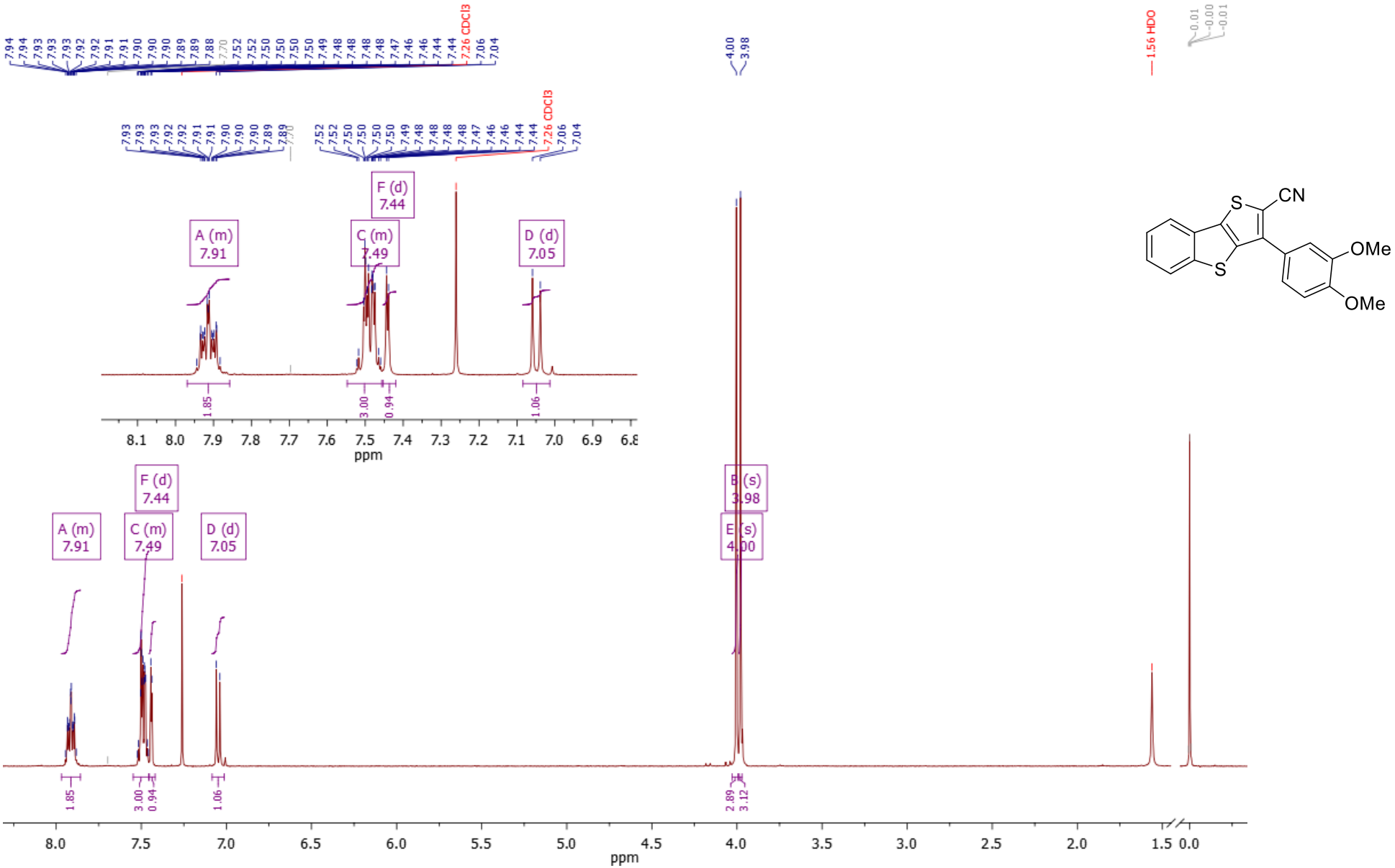


^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.50 (d, *J* = 8.2 Hz, 1H), 7.98 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.65 – 7.59 (m, 1H), 7.60 – 7.55 (m, 2H), 6.97 – 6.83 (m, 1H), 3.98 (s, 3H), 3.96 (s, 3H).

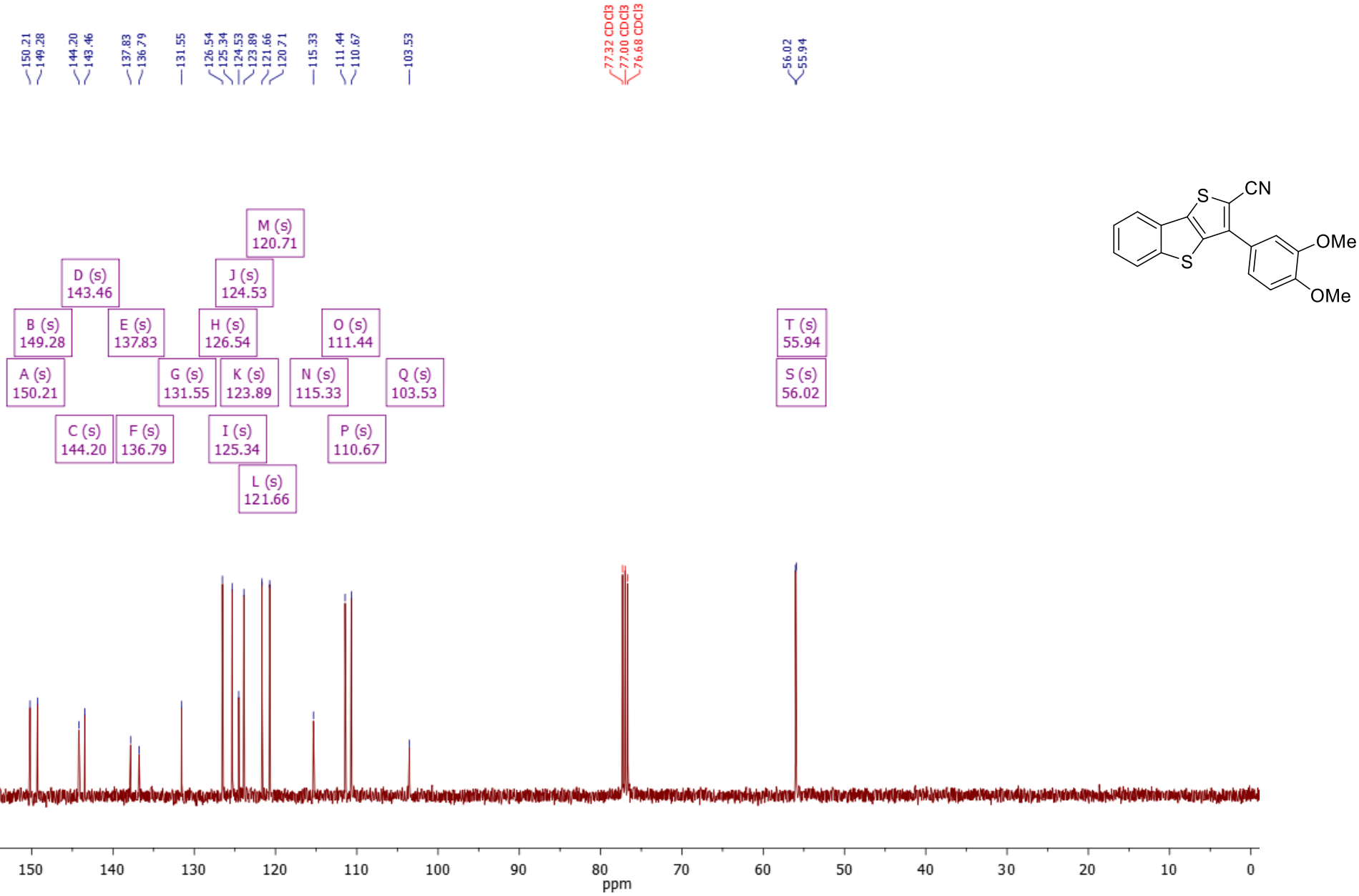


^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 153.8, 149.0, 138.3, 133.8, 132.0, 130.3, 129.7, 129.0, 128.7, 126.9, 126.1, 125.8, 124.10, 124.09, 122.9, 120.2, 111.5, 109.9, 56.05, 55.99, 55.98. (Two signals were not found due to overlapping peaks).

3-(3,4-Dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitrile (8a)

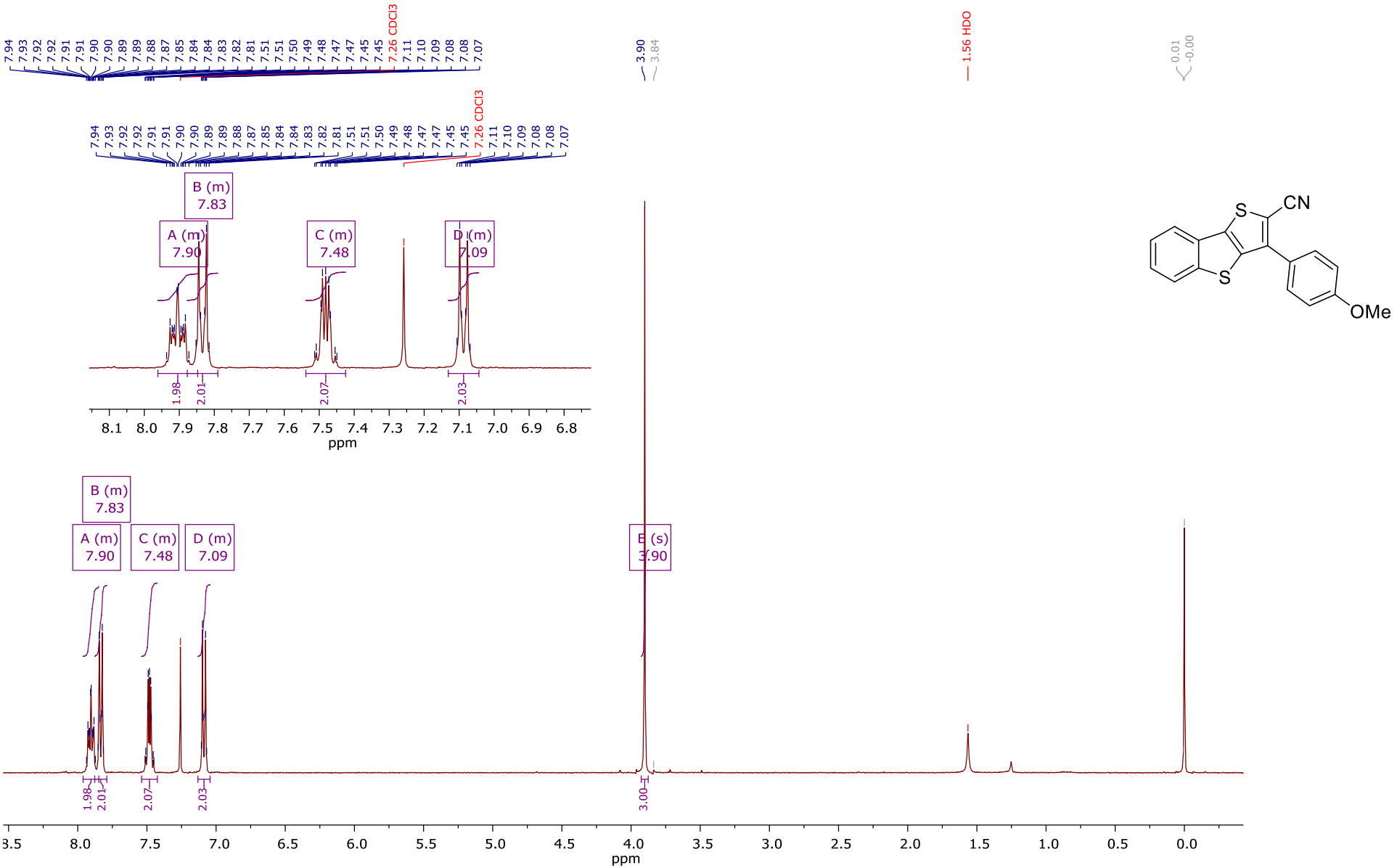


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.86 (m, 2H), 7.55 – 7.46 (m, 3H), 7.44 (d, *J* = 2.2 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 4.00 (s, 3H), 3.98 (s, 3H).

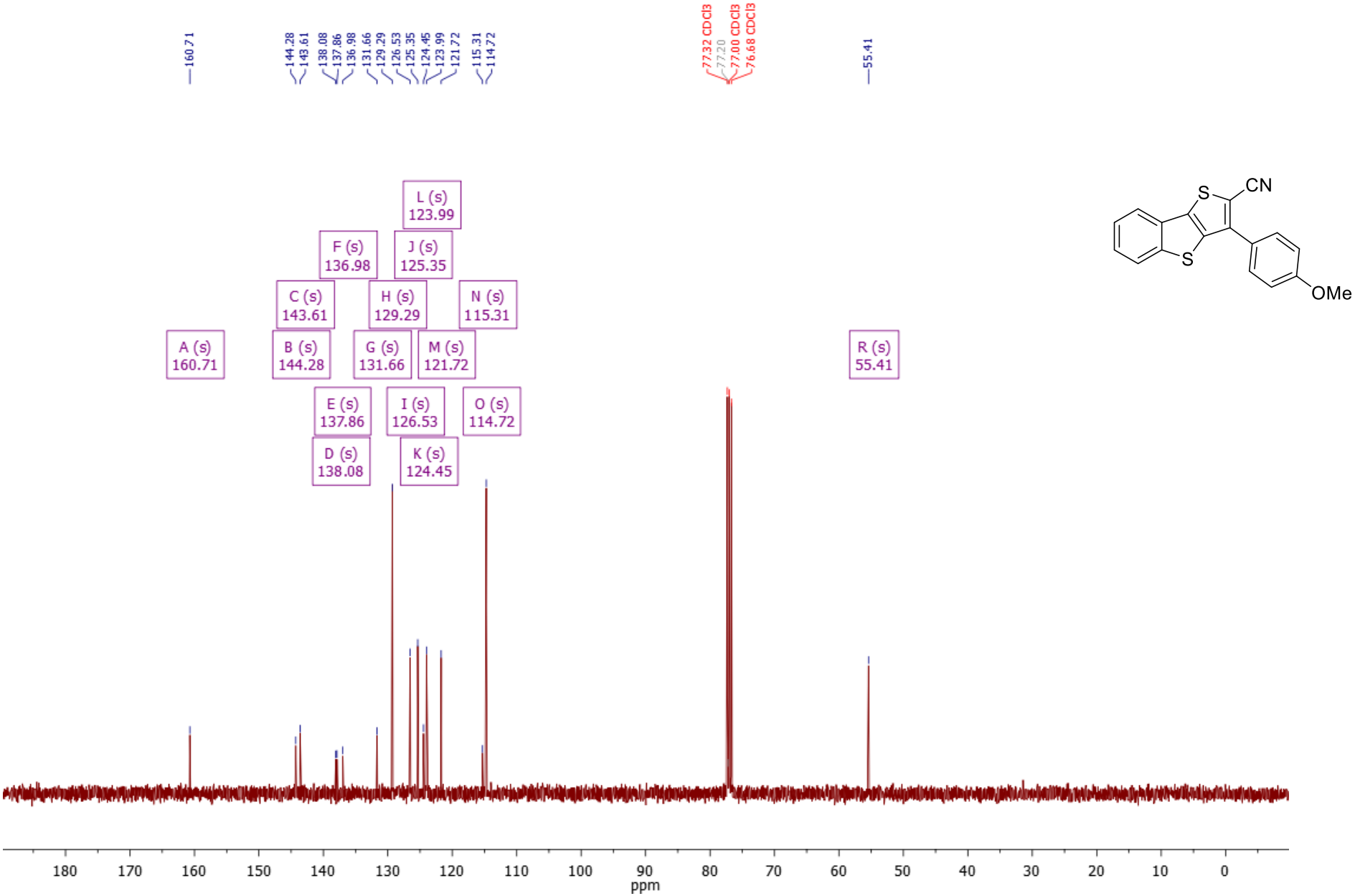


^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 149.3, 144.2, 143.5, 137.8, 136.8, 131.5, 126.5, 125.3, 124.5, 123.9, 121.7, 120.7, 115.3, 111.4, 110.7, 103.5, 56.0, 55.9.

3-(4-Methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitrile (8b)

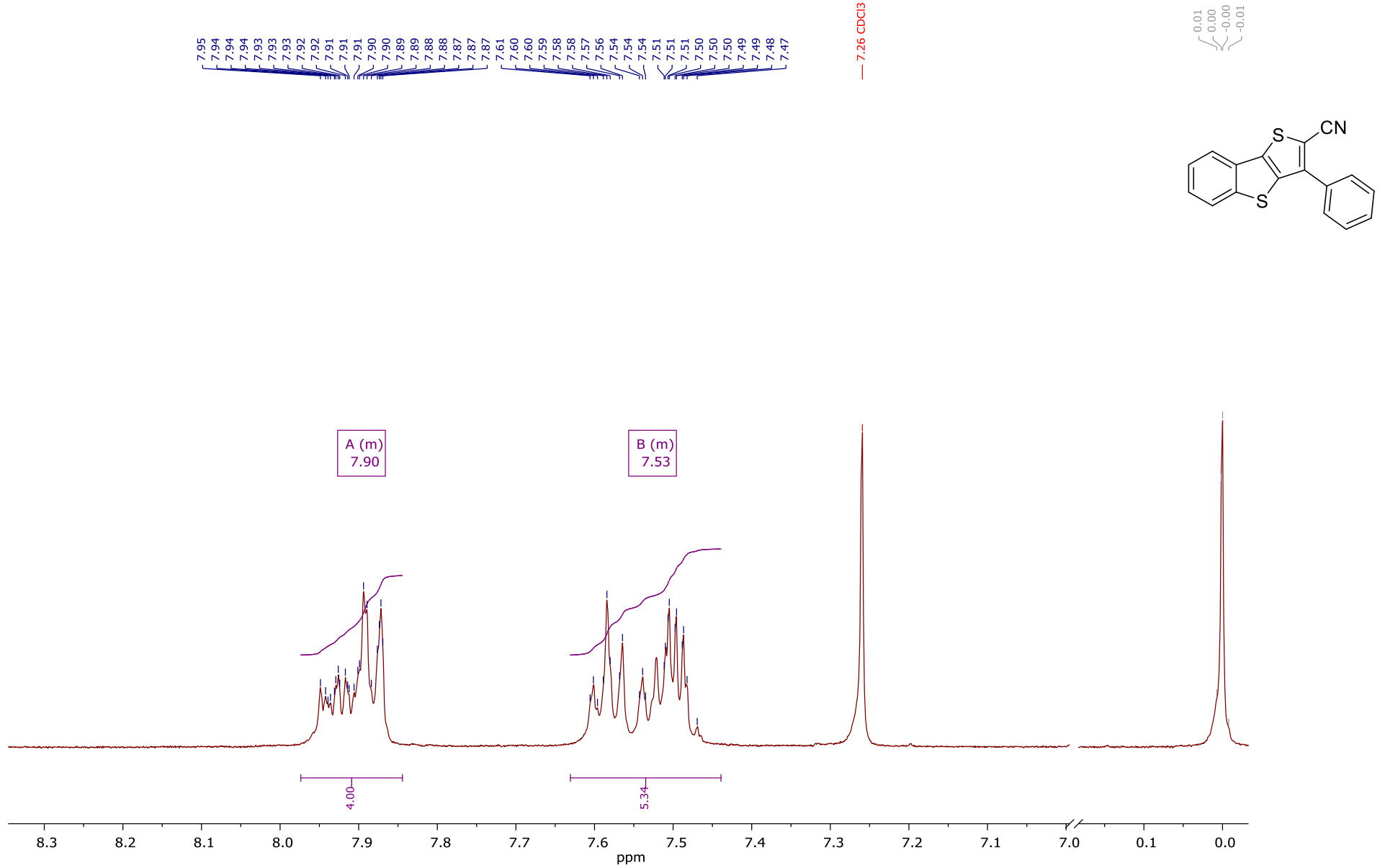


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.85 (m, 2H), 7.88 – 7.79 (m, 2H), 7.54 – 7.42 (m, 2H), 7.13 – 7.04 (m, 2H), 3.90 (s, 3H).

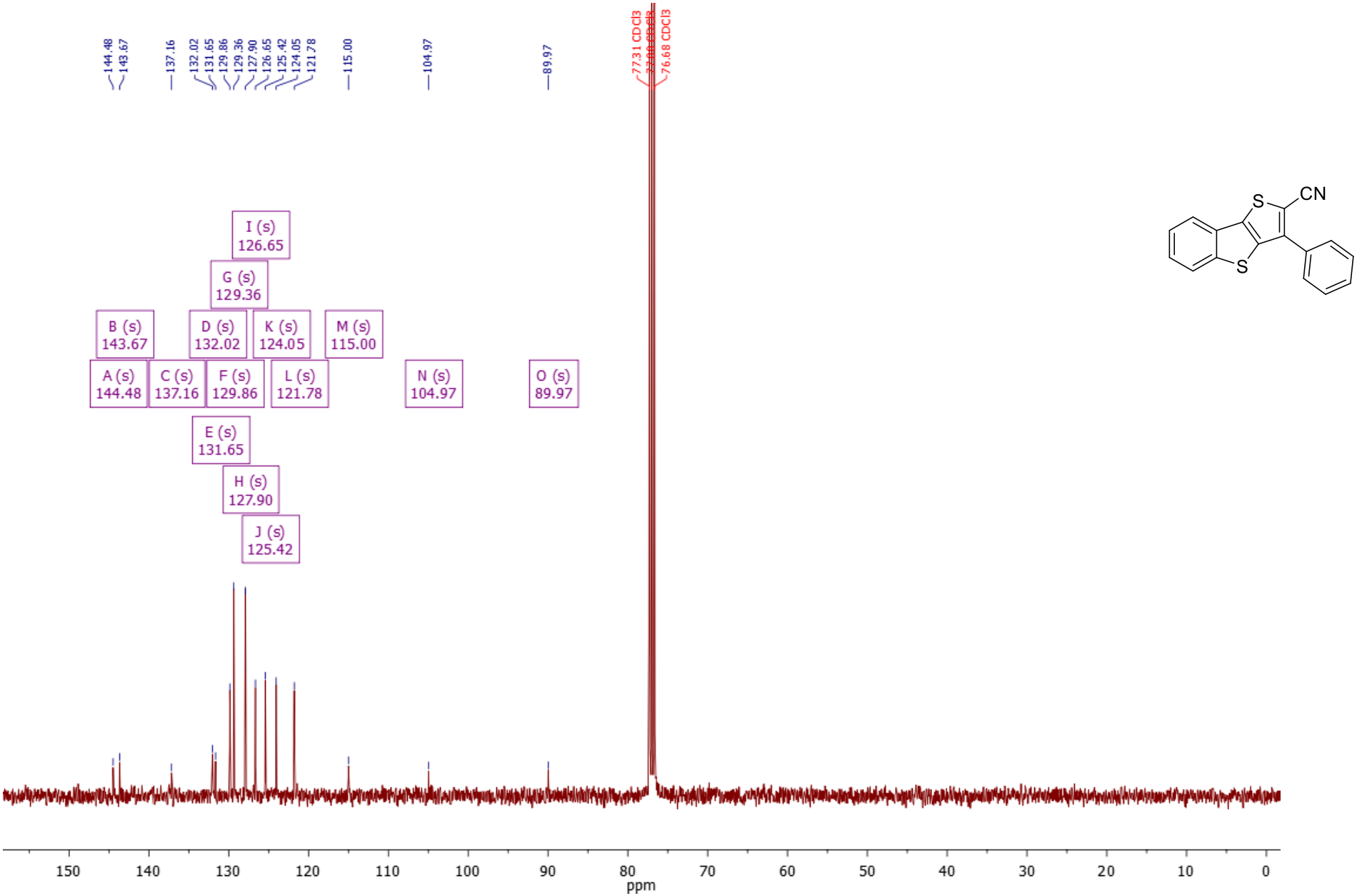


^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.7, 144.3, 143.6, 138.1, 137.9, 137.0, 131.7, 129.3, 126.5, 125.3, 124.4, 124.0, 121.7, 115.3, 114.7, 55.4.

3-Phenylbenzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitrile (8c)

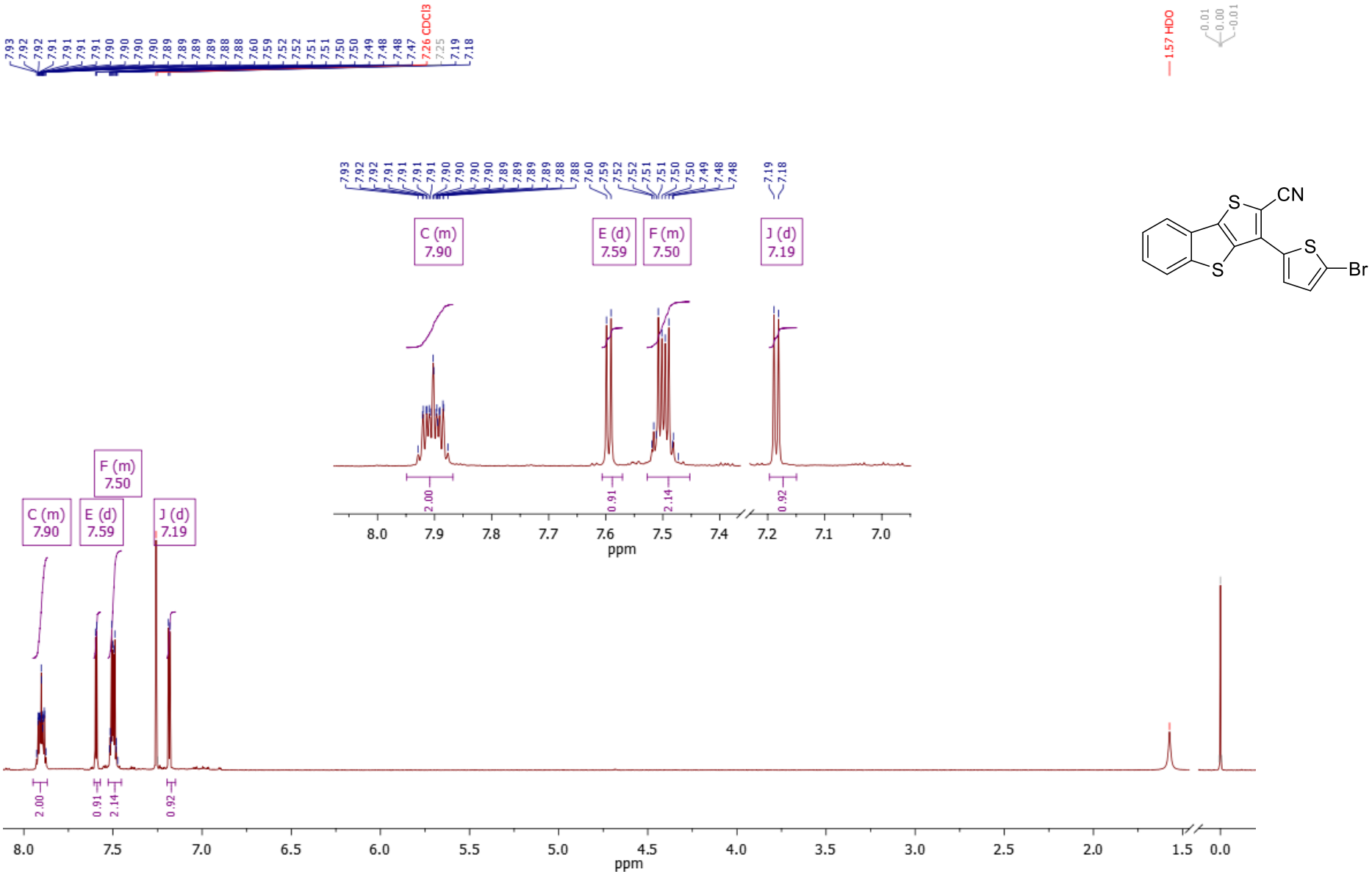


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.84 (m, 4H), 7.63 – 7.44 (m, 5H).

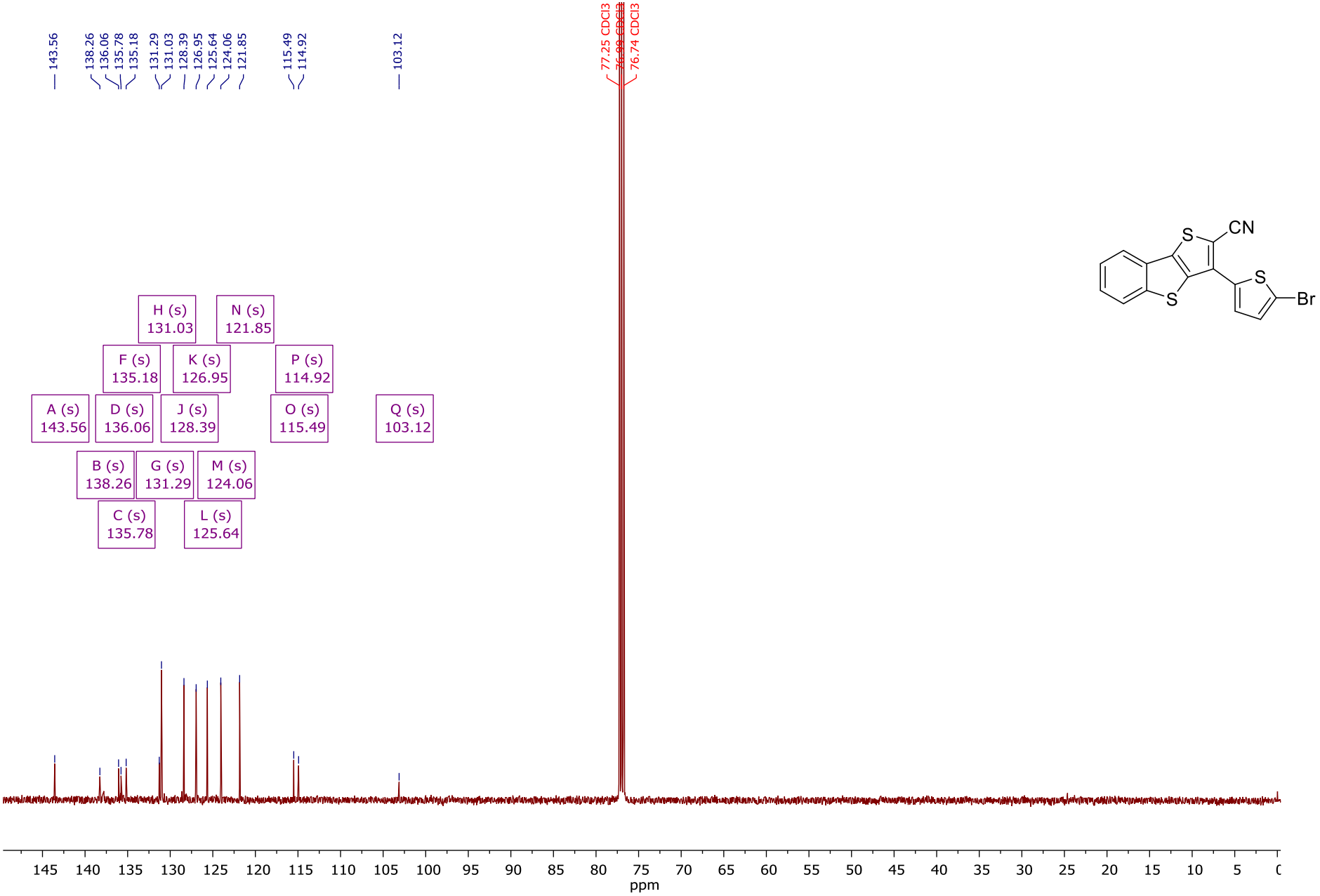


^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.5, 143.7, 137.2, 132.0, 131.6, 129.9, 129.4, 127.9, 126.6, 125.4, 124.0, 121.8, 115.0, 105.0, 90.0.

3-(5-Bromothiophen-2-yl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitrile (8d)

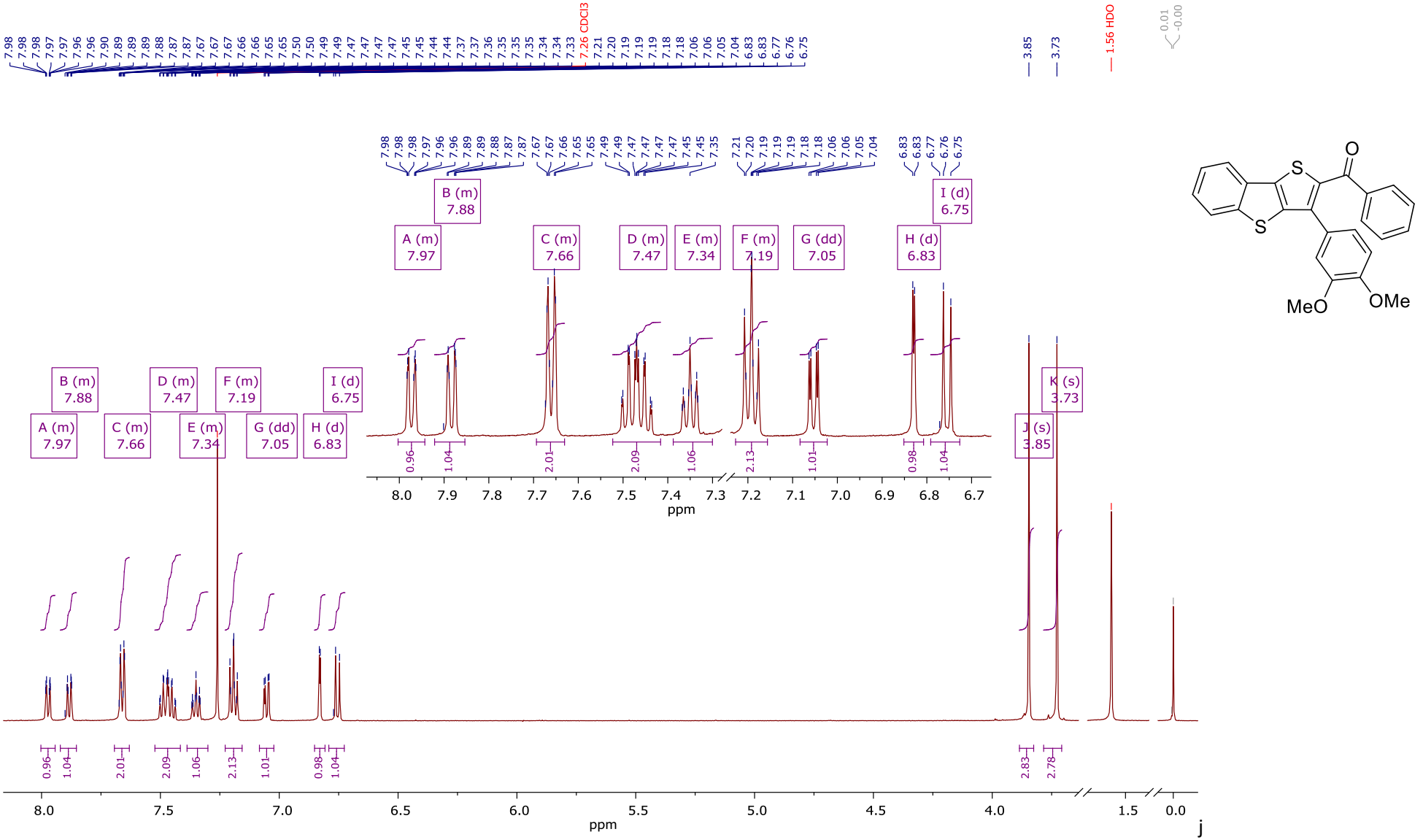


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 2H), 7.59 (d, *J* = 4.0 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.19 (d, *J* = 4.0 Hz, 1H).

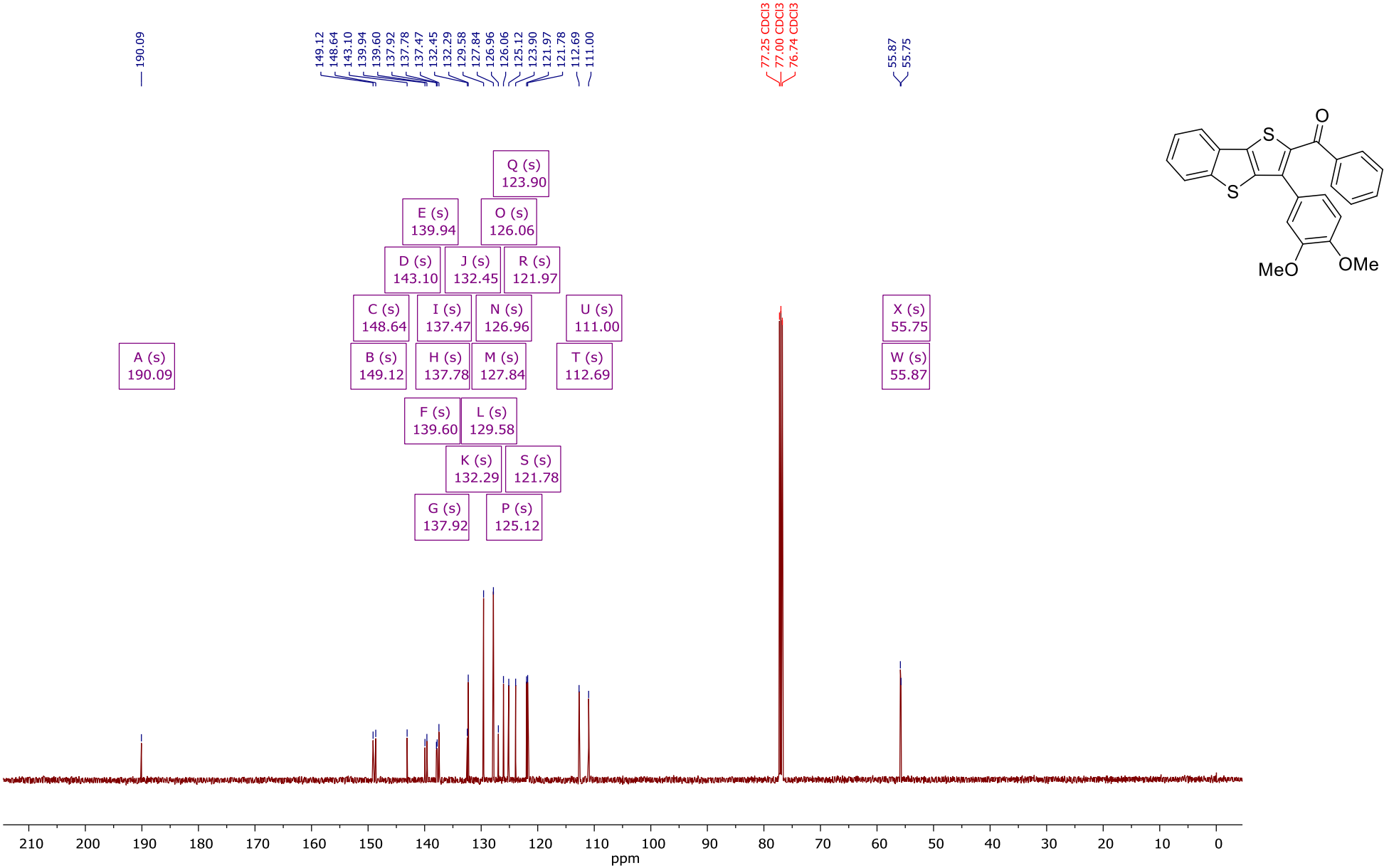


^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.6, 138.3, 136.1, 135.8, 135.2, 131.3, 131.0, 128.4, 126.9, 125.6, 124.1, 121.8, 115.5, 114.9, 103.1.

(3-(3,4-Dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)(phenyl)methanone (9a)

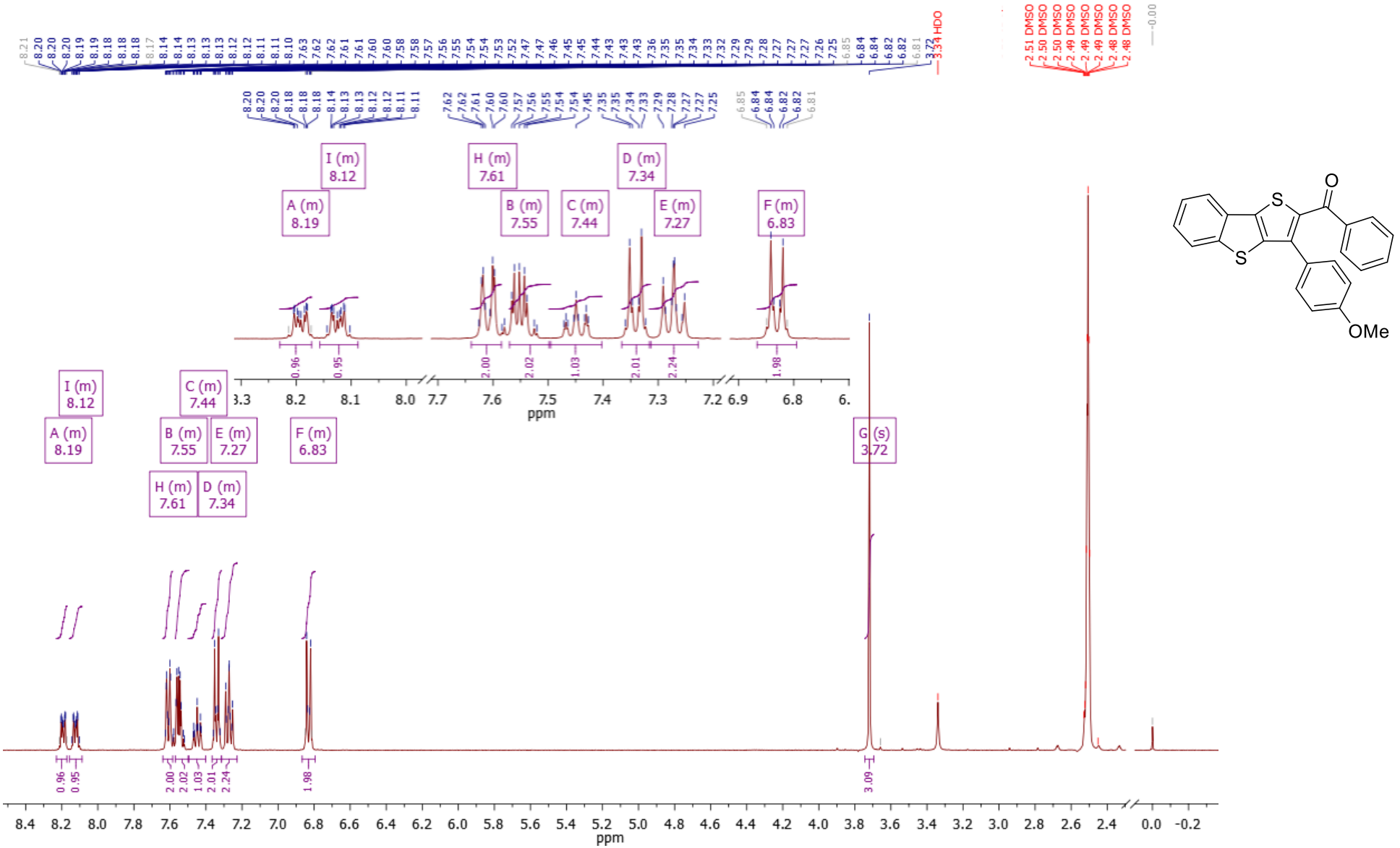


^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 1H), 7.92 – 7.85 (m, 1H), 7.69 – 7.63 (m, 2H), 7.52 – 7.42 (m, 2H), 7.39 – 7.30 (m, 1H), 7.23 – 7.16 (m, 2H), 7.05 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 3.73 (s, 3H).

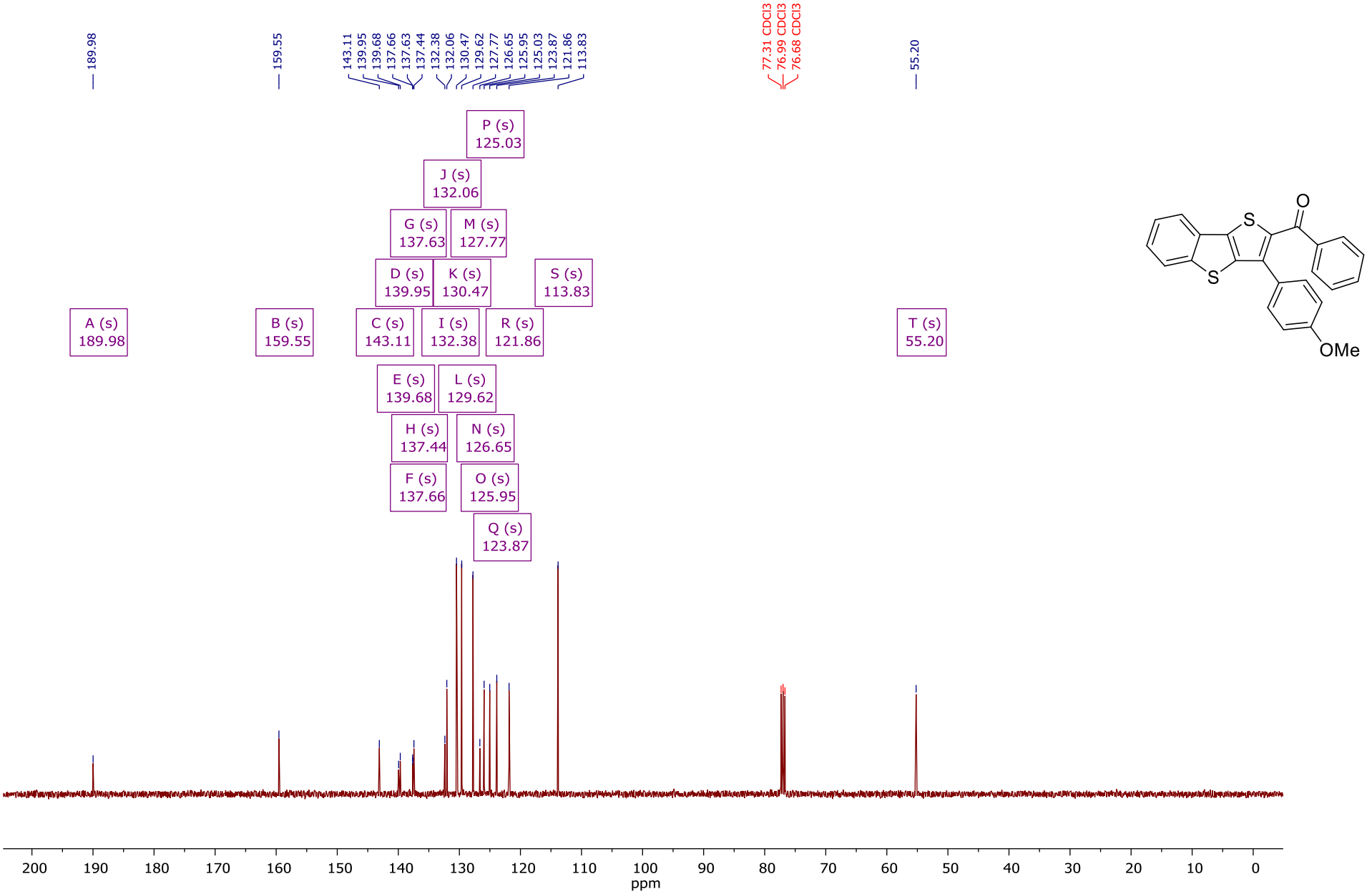


^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.1, 149.1, 148.6, 143.1, 139.9, 139.6, 137.9, 137.8, 137.5, 132.4, 132.3, 129.6, 127.8, 127.0, 126.1, 125.1, 123.9, 122.0, 121.8, 112.7, 111.0, 55.9, 55.7.

(3-(4-Methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)(phenyl)methanone (9b)

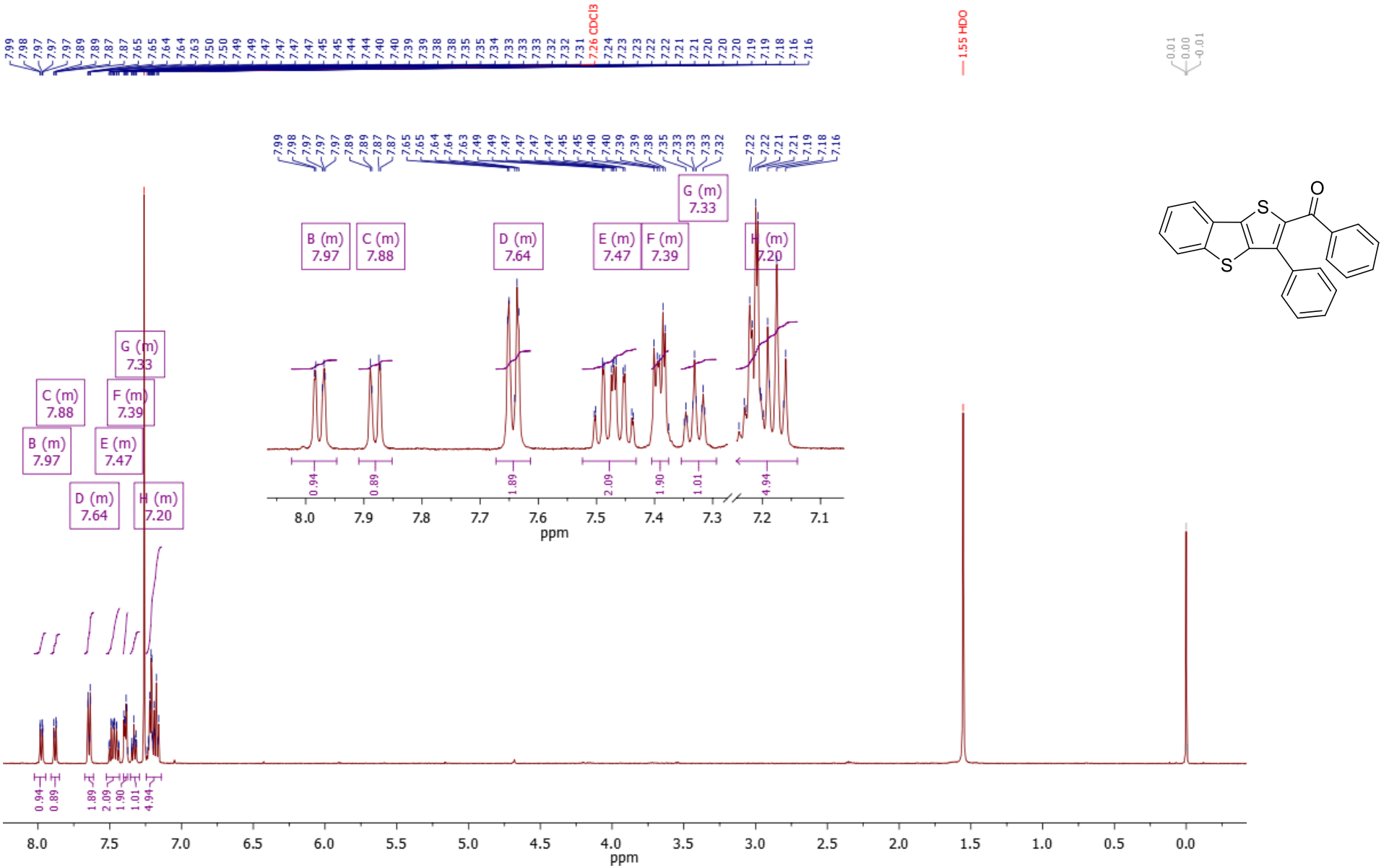


^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 – 8.17 (m, 1H), 8.16 – 8.09 (m, 1H), 7.64 – 7.58 (m, 2H), 7.57 – 7.50 (m, 2H), 7.50 – 7.40 (m, 1H), 7.37 – 7.31 (m, 2H), 7.32 – 7.23 (m, 2H), 6.87 – 6.79 (m, 2H), 3.72 (s, 3H).

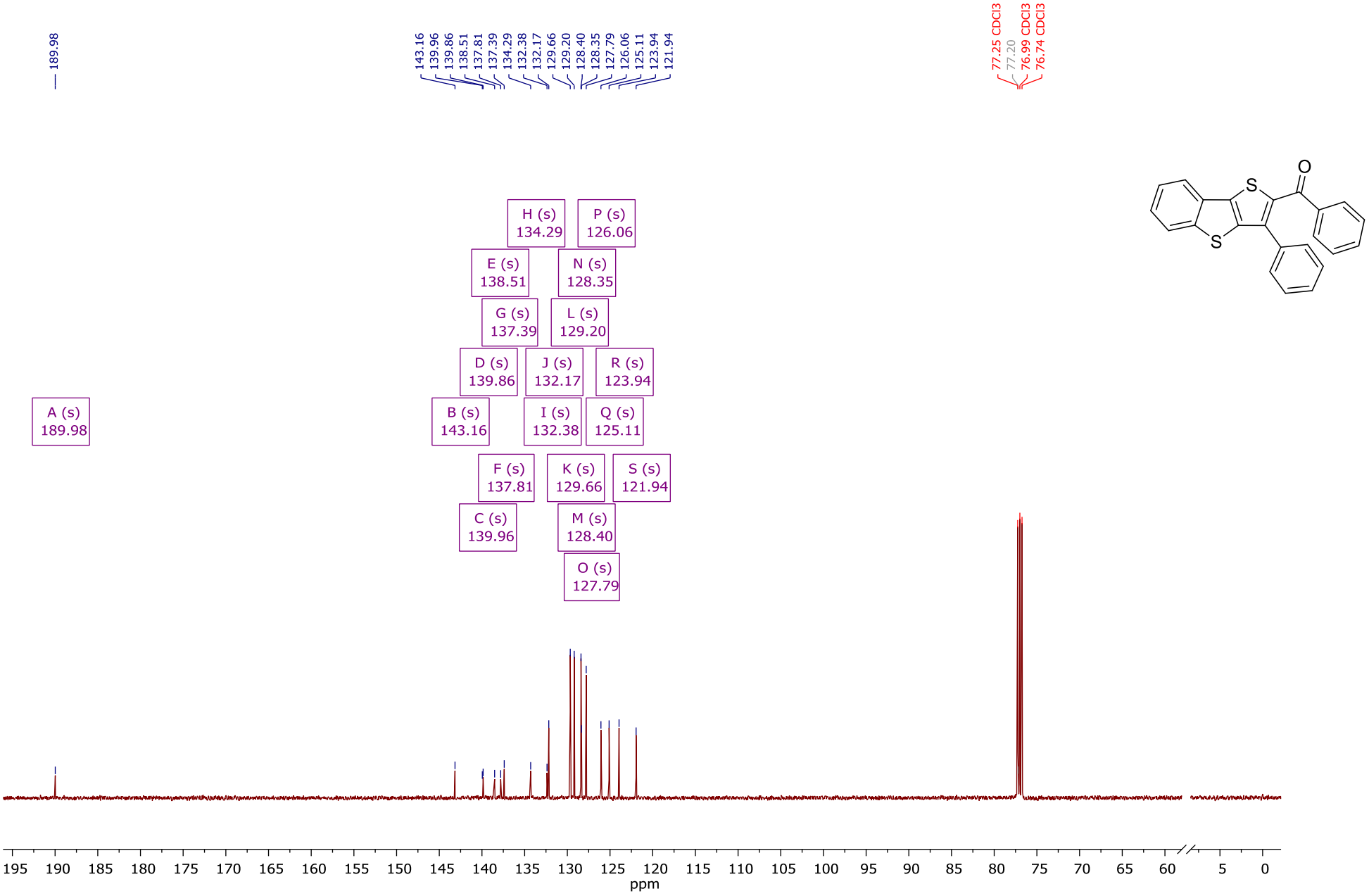


^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.0, 159.5, 143.1, 139.9, 139.7, 137.7, 137.6, 137.4, 132.4, 132.1, 130.5, 129.6, 127.8, 126.6, 125.9, 125.0, 123.9, 121.9, 113.8, 55.2.

Phenyl(3-phenylbenzo[*b*]thieno[2,3-*d*]thiophen-2-yl)methanone (9c)

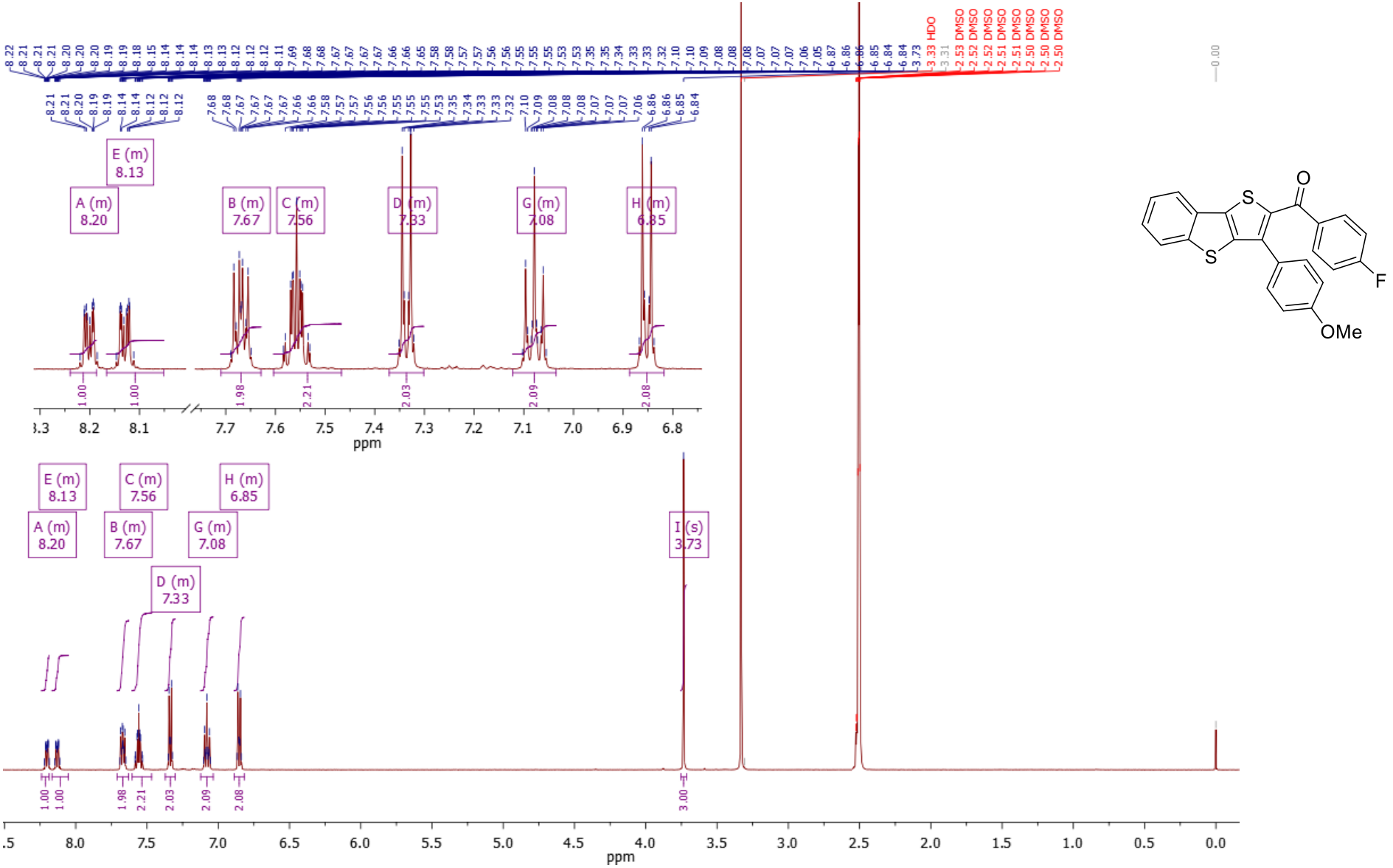


^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 1H), 7.91 – 7.85 (m, 1H), 7.67 – 7.61 (m, 2H), 7.52 – 7.43 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.29 (m, 1H), 7.25 – 7.14 (m, 5H).

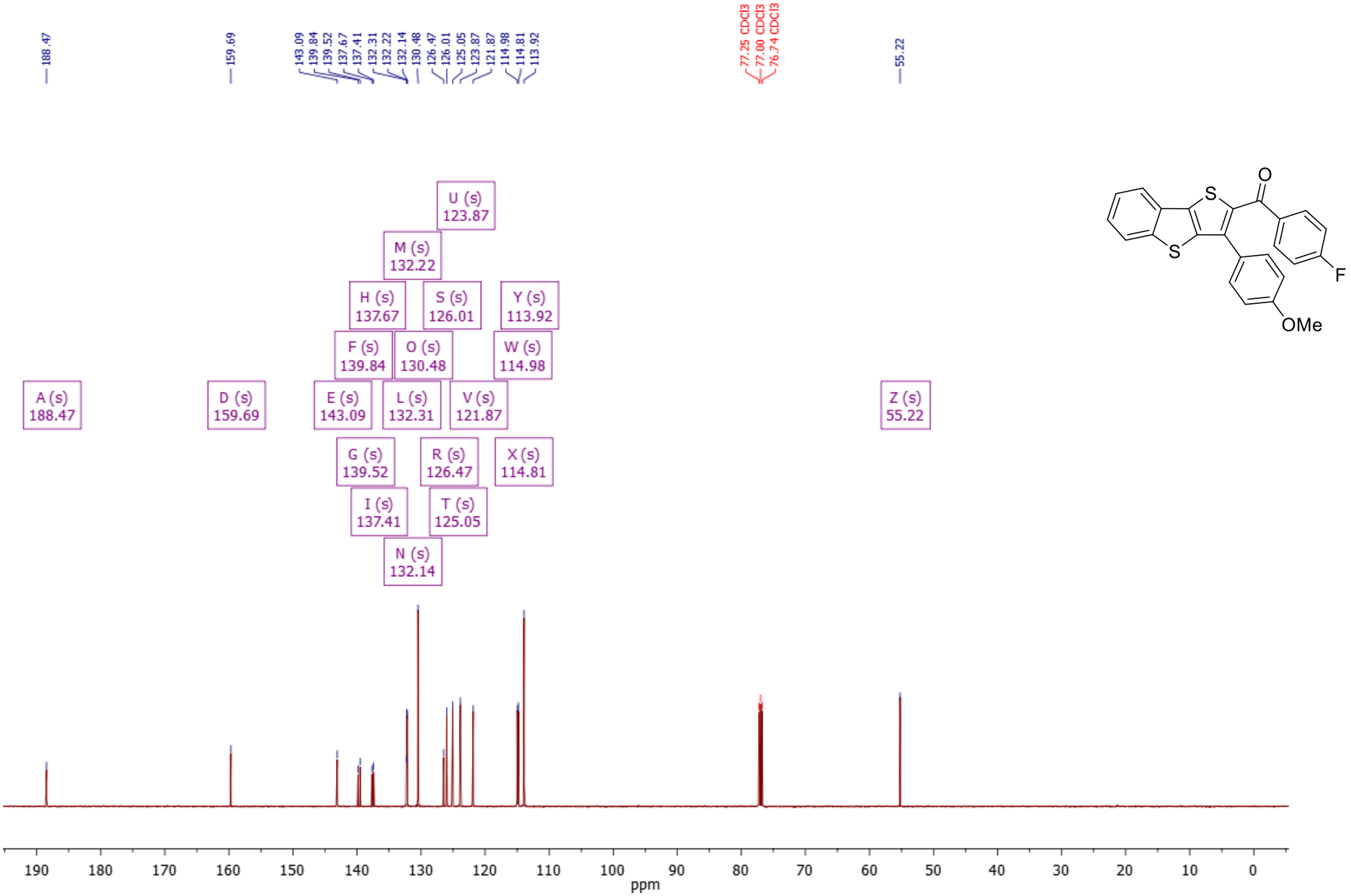


^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.0, 143.2, 140.0, 139.9, 138.5, 137.8, 137.4, 134.3, 132.4, 132.2, 129.7, 129.2, 128.4, 128.3, 127.8, 126.1, 125.1, 123.9, 121.9.

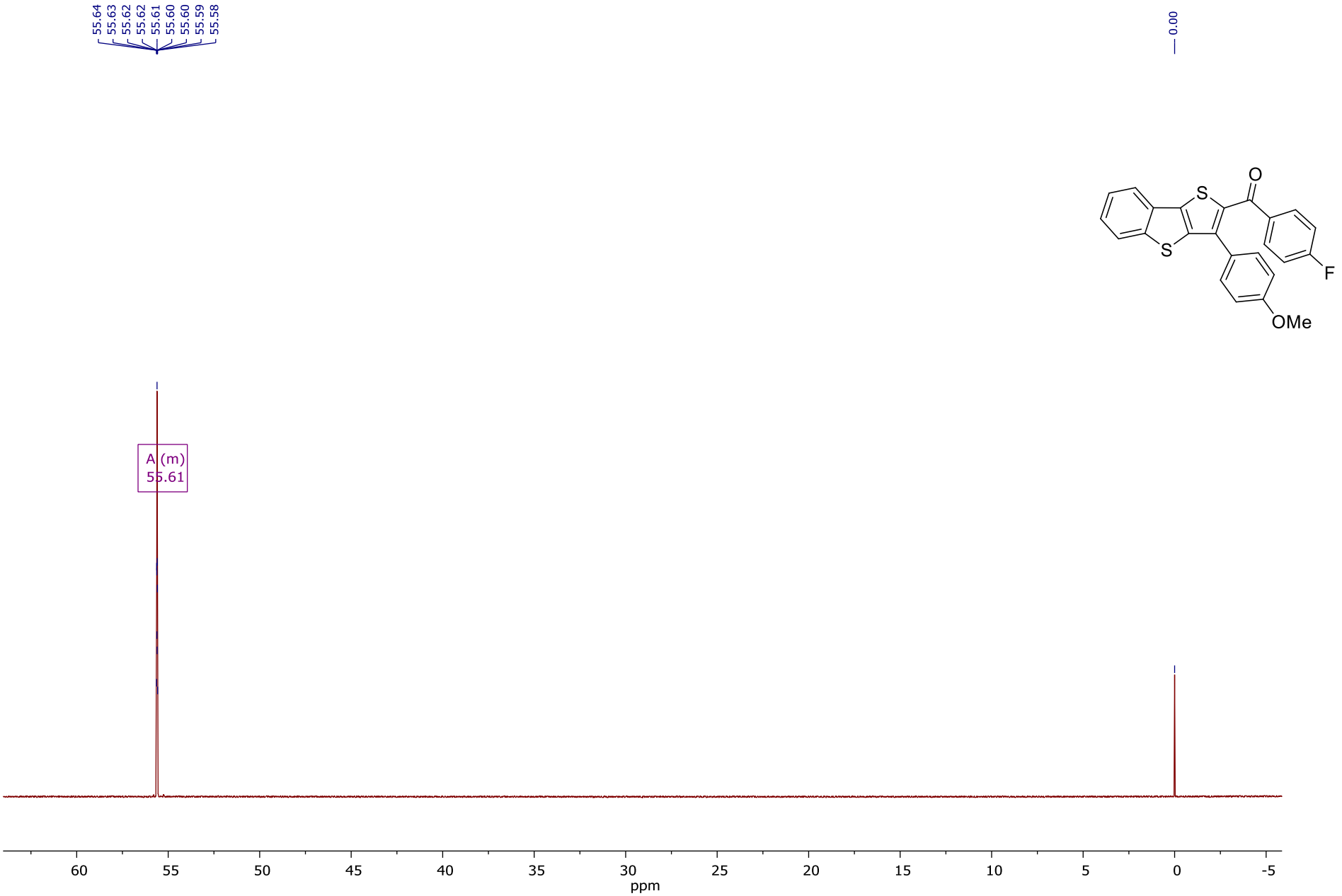
(4-Fluorophenyl)(3-(4-methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)methanone (9d)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 – 8.19 (m, 1H), 8.17 – 8.05 (m, 1H), 7.71 – 7.63 (m, 2H), 7.60 – 7.47 (m, 2H), 7.37 – 7.30 (m, 2H), 7.12 – 7.03 (m, 2H), 6.89 – 6.82 (m, 2H), 3.73 (s, 3H).

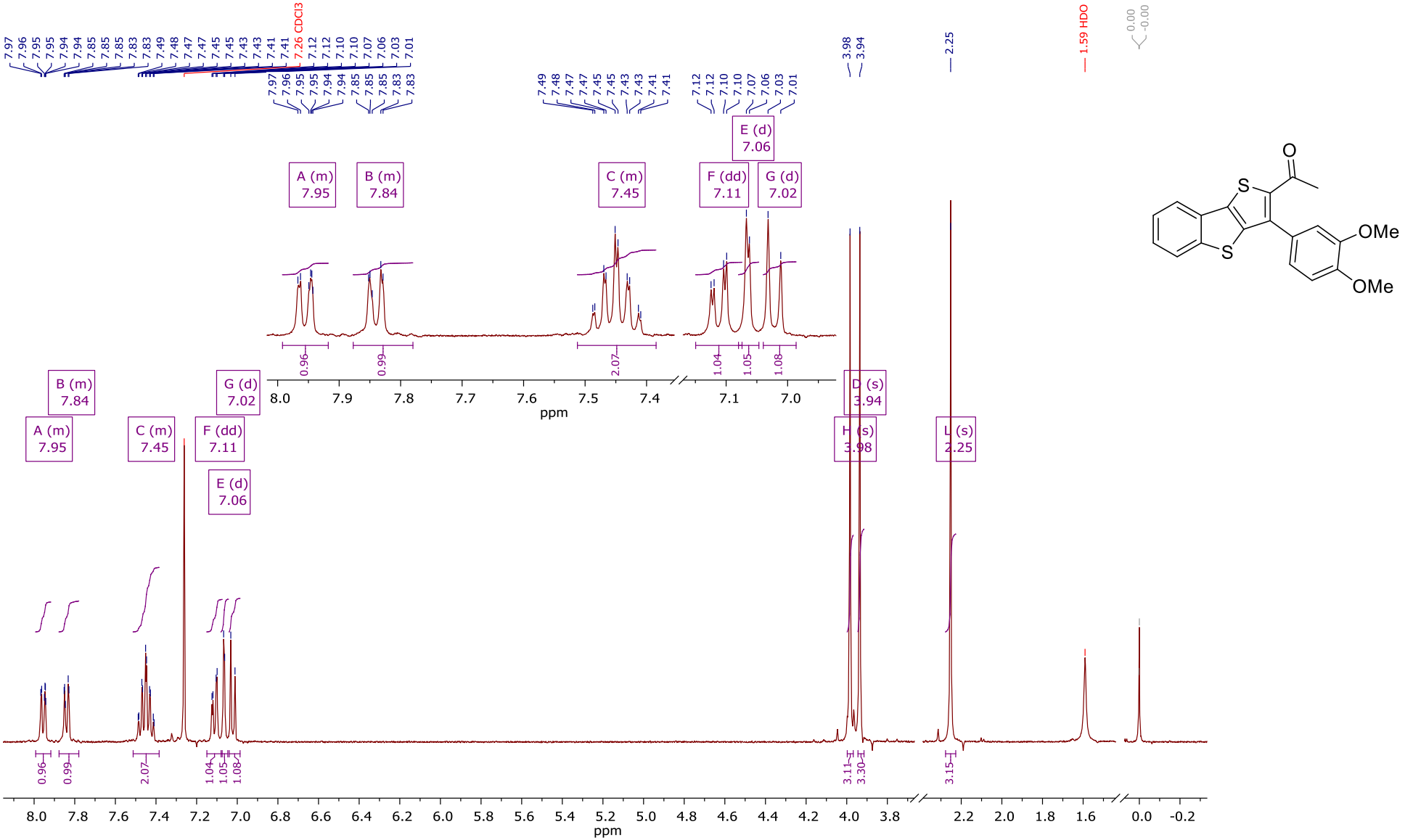


^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.5, 159.7, 143.1, 139.8, 139.5, 137.7, 137.4, 132.3, 132.2, 132.1, 130.5, 126.5, 126.0, 125.0, 123.9, 121.9, 115.0, 114.8, 113.9, 55.2.

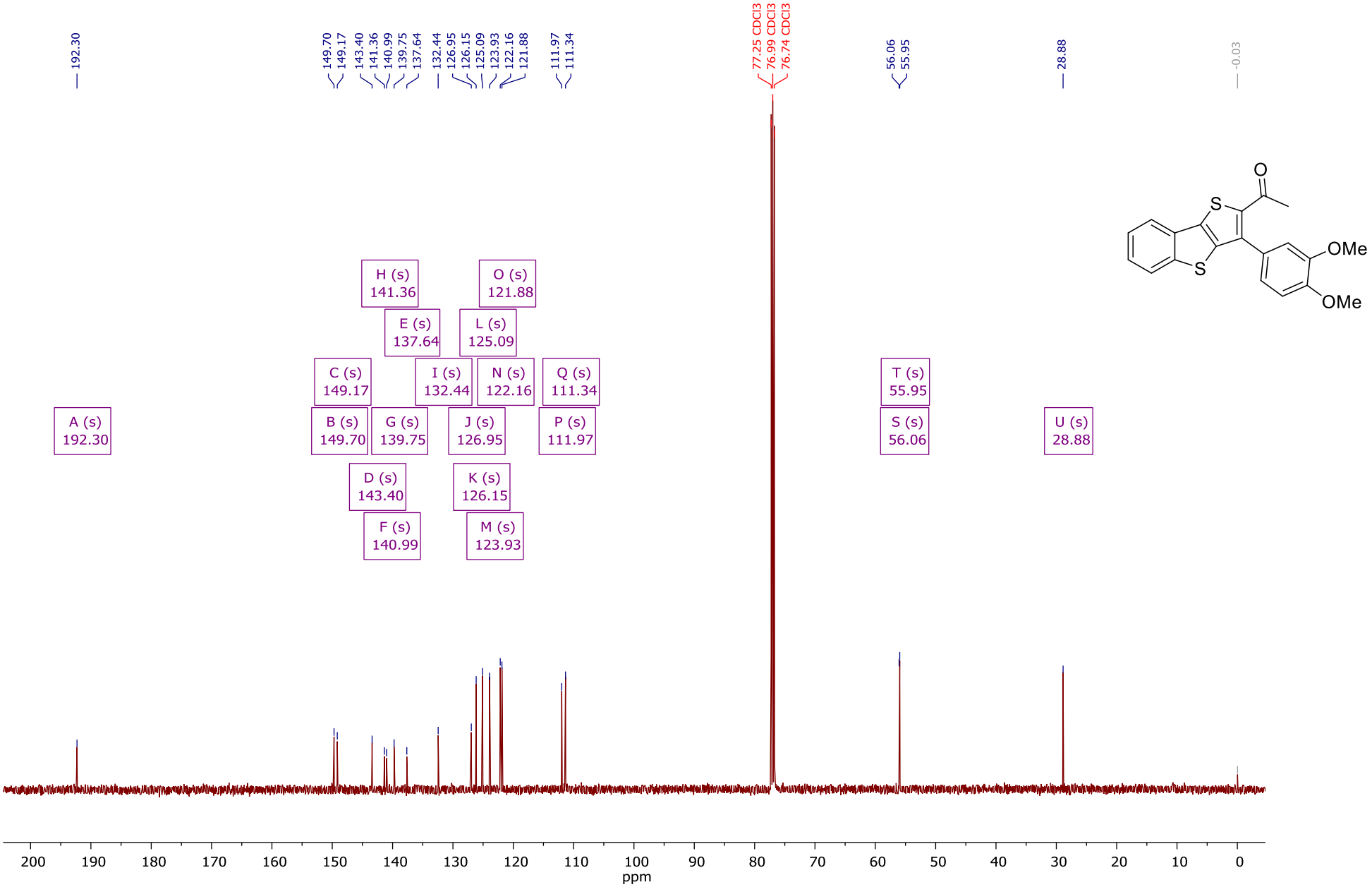


^{19}F NMR (471 MHz, Chloroform-*d*) δ 56.18 – 55.17 (m).

1-(3-(3,4-Dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)ethan-1-one (10a)

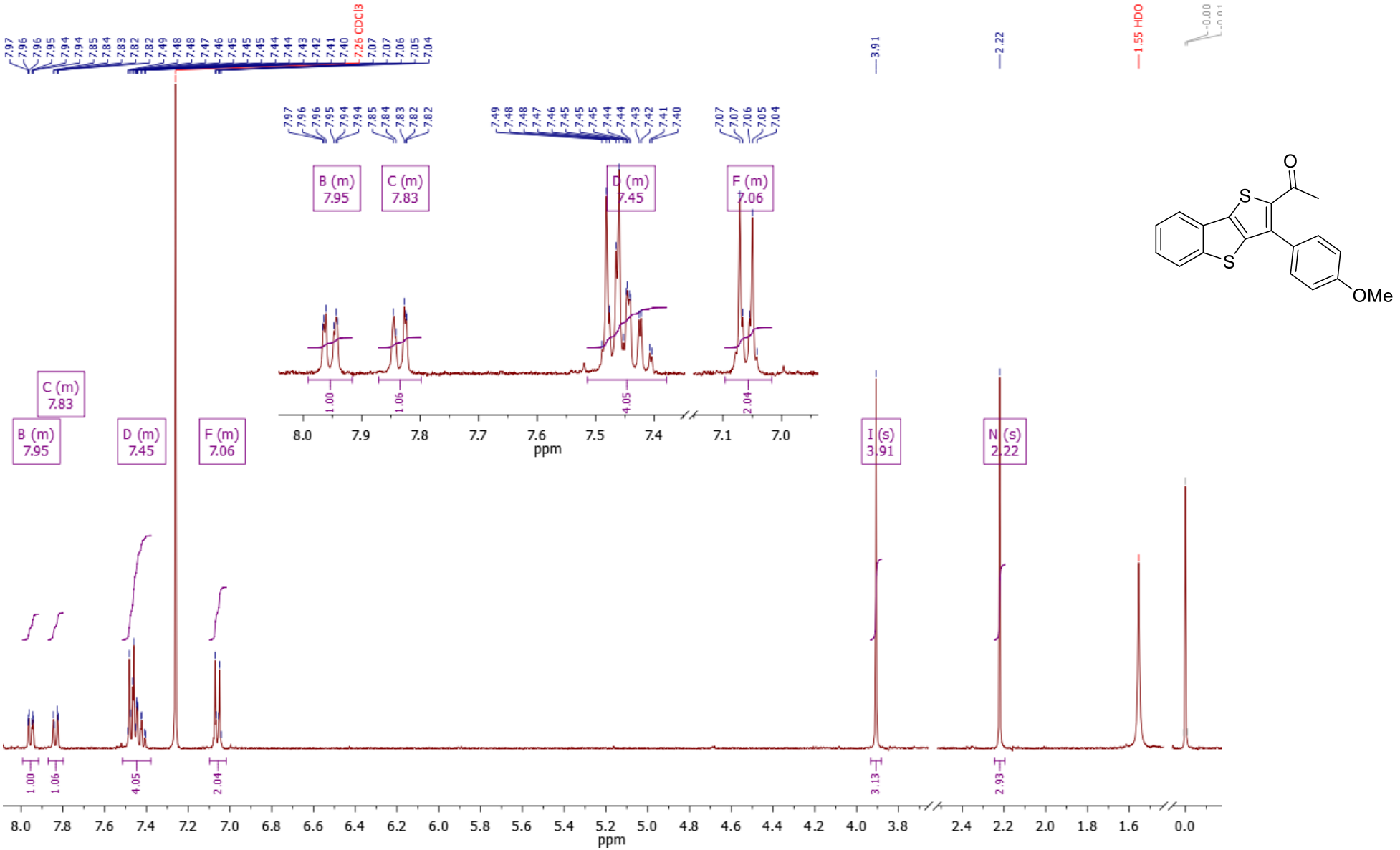


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 1H), 7.88 – 7.78 (m, 1H), 7.51 – 7.38 (m, 2H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 2.25 (s, 3H).

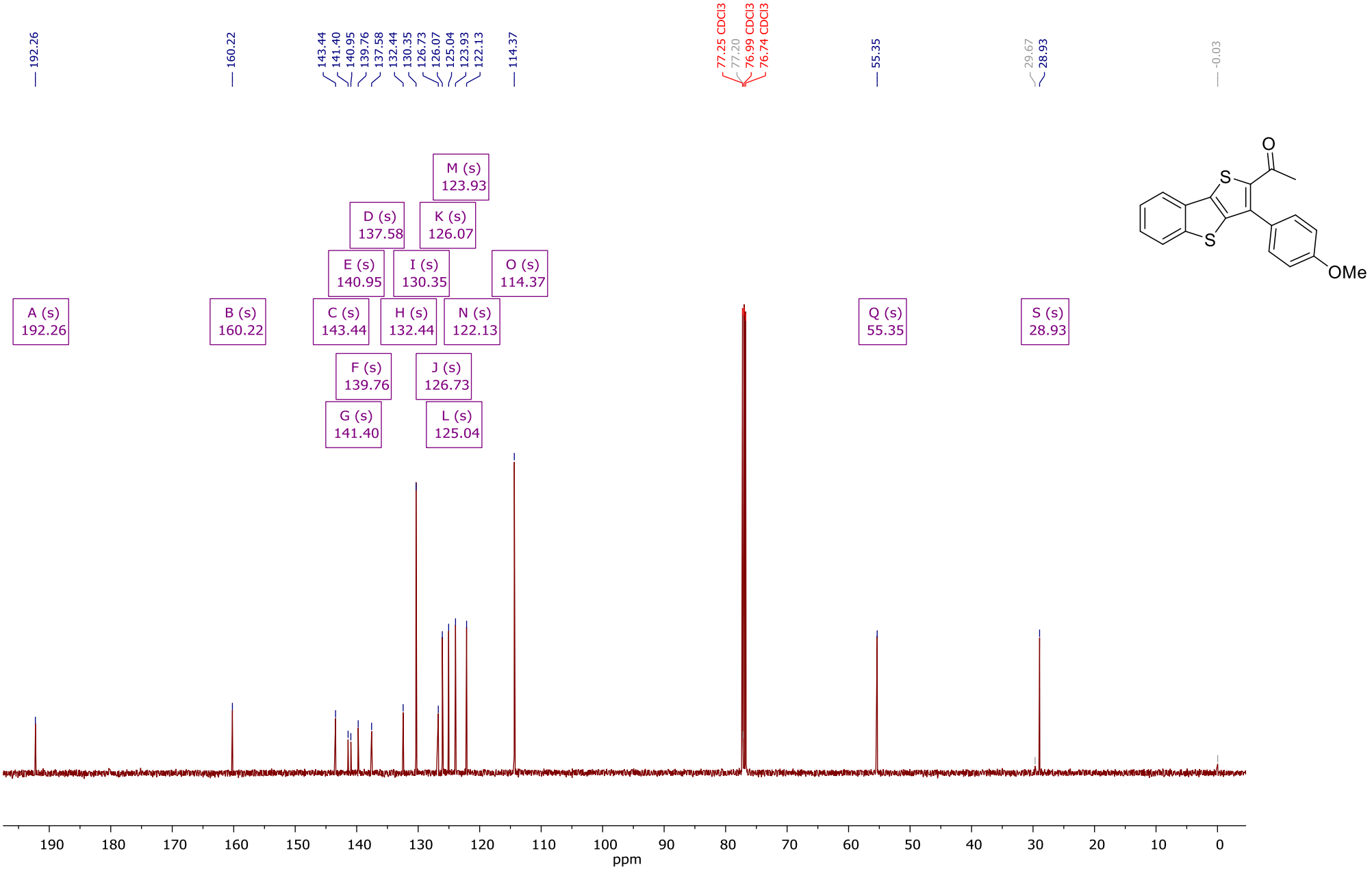


^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.3, 149.7, 149.2, 143.4, 141.4, 141.0, 139.7, 137.6, 132.4, 126.9, 126.1, 125.1, 123.9, 122.2, 121.9, 112.0, 111.3, 56.1, 55.9, 28.9.

1-(3-(4-Methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)ethan-1-one (10b)

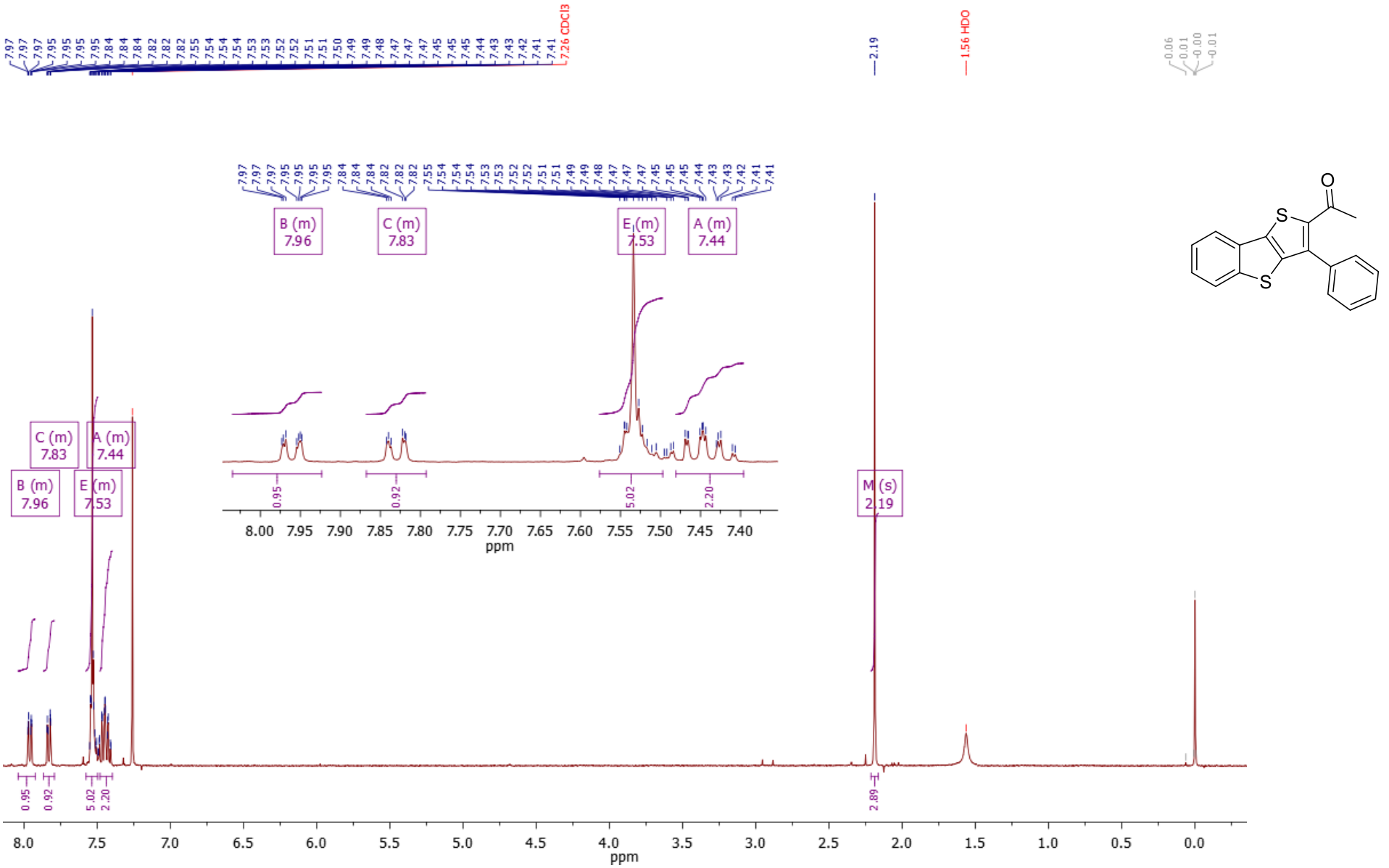


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 1H), 7.83 (m, 1H), 7.51 – 7.38 (m, 4H), 7.10 – 7.02 (m, 2H), 3.91 (s, 3H), 2.22 (s, 3H).

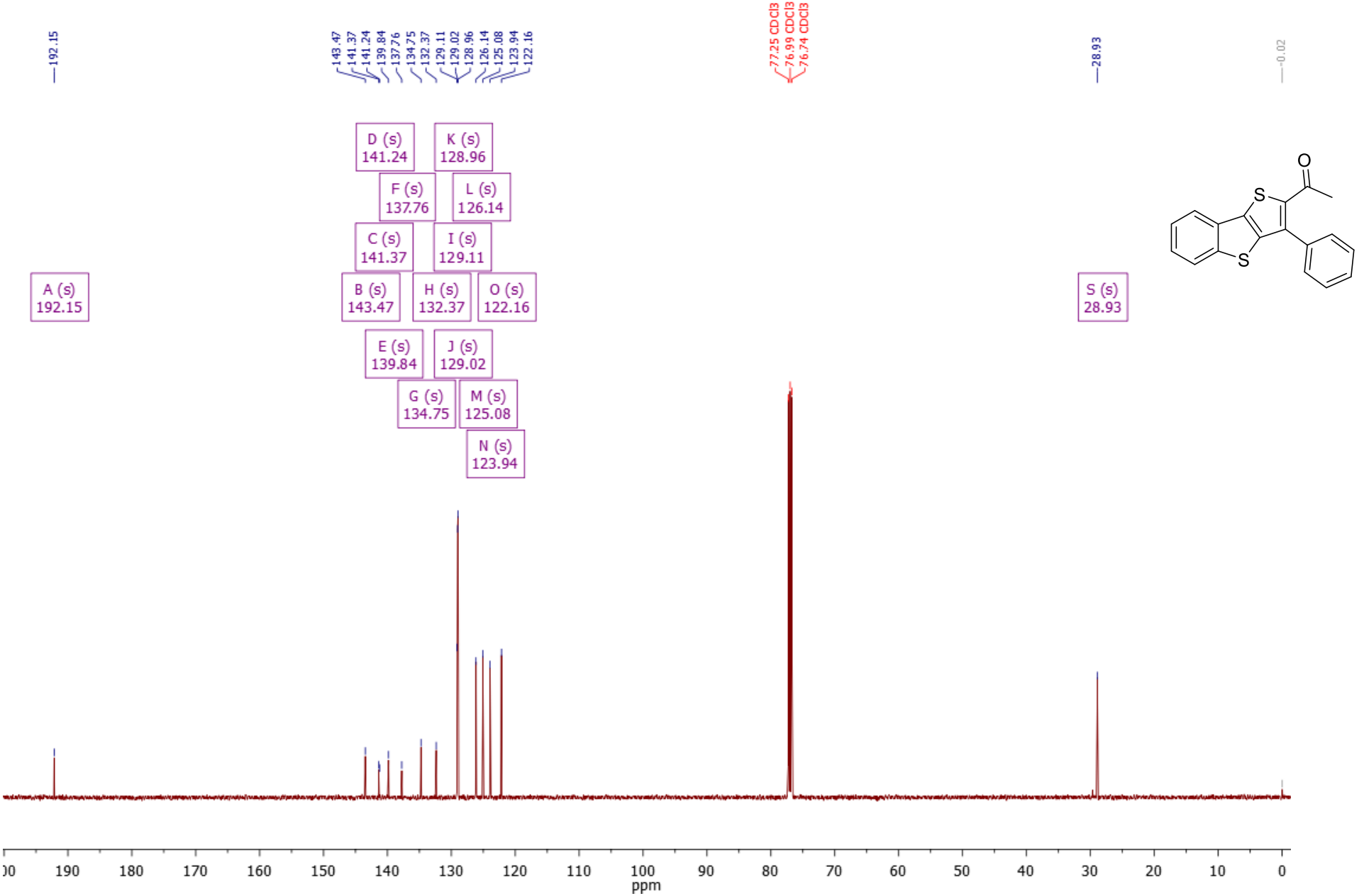


^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.3, 160.2, 143.4, 141.4, 140.9, 139.8, 137.6, 132.4, 130.3, 126.7, 126.1, 125.0, 123.9, 122.1, 114.4, 55.3, 28.9.

1-(3-Phenylbenzo[*b*]thieno[2,3-*d*]thiophen-2-yl)ethan-1-one (10c)

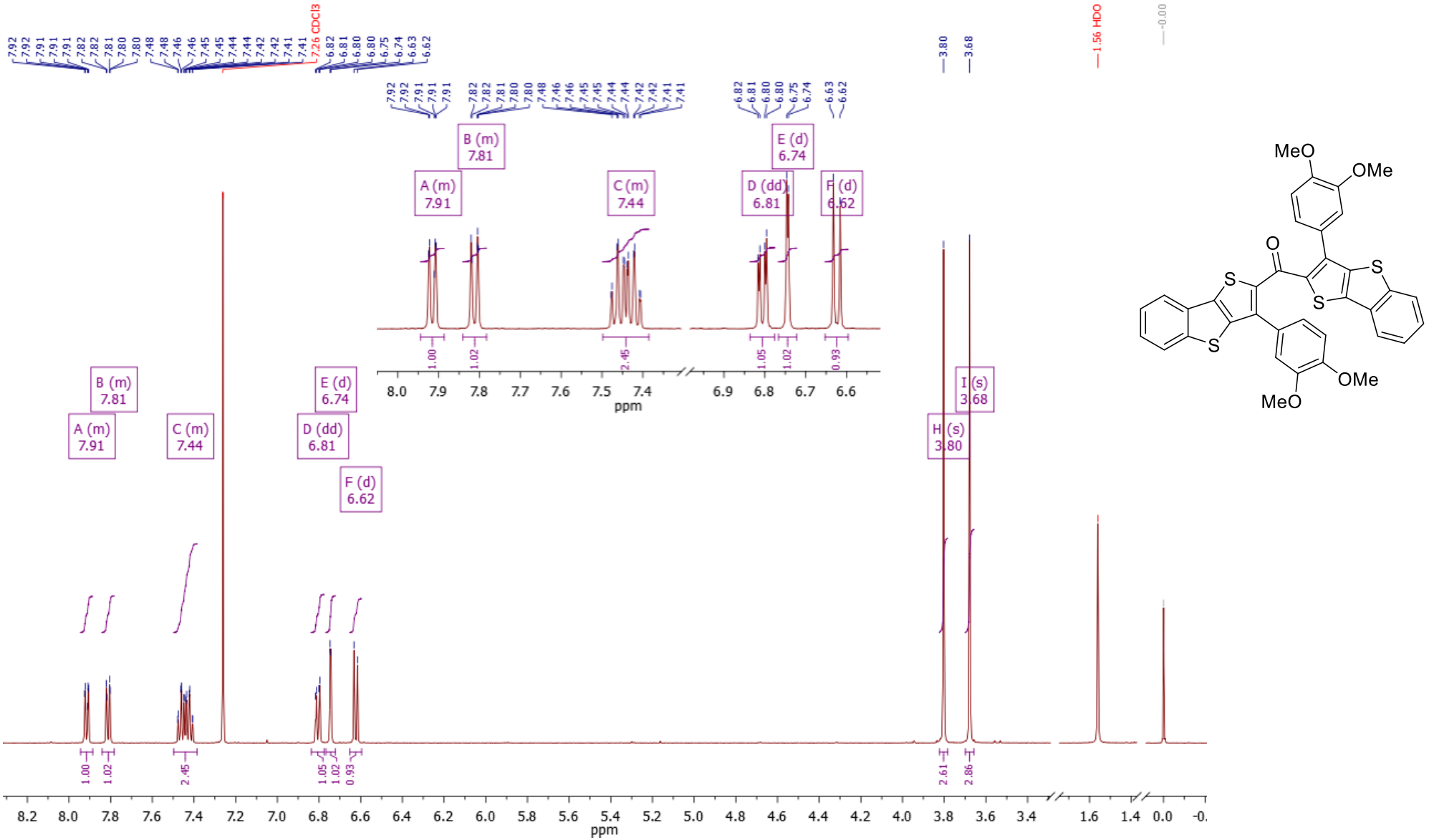


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.92 (m, 1H), 7.87 – 7.79 (m, 1H), 7.58 – 7.50 (m, 5H), 7.48 – 7.40 (m, 2H), 2.19 (s, 3H).

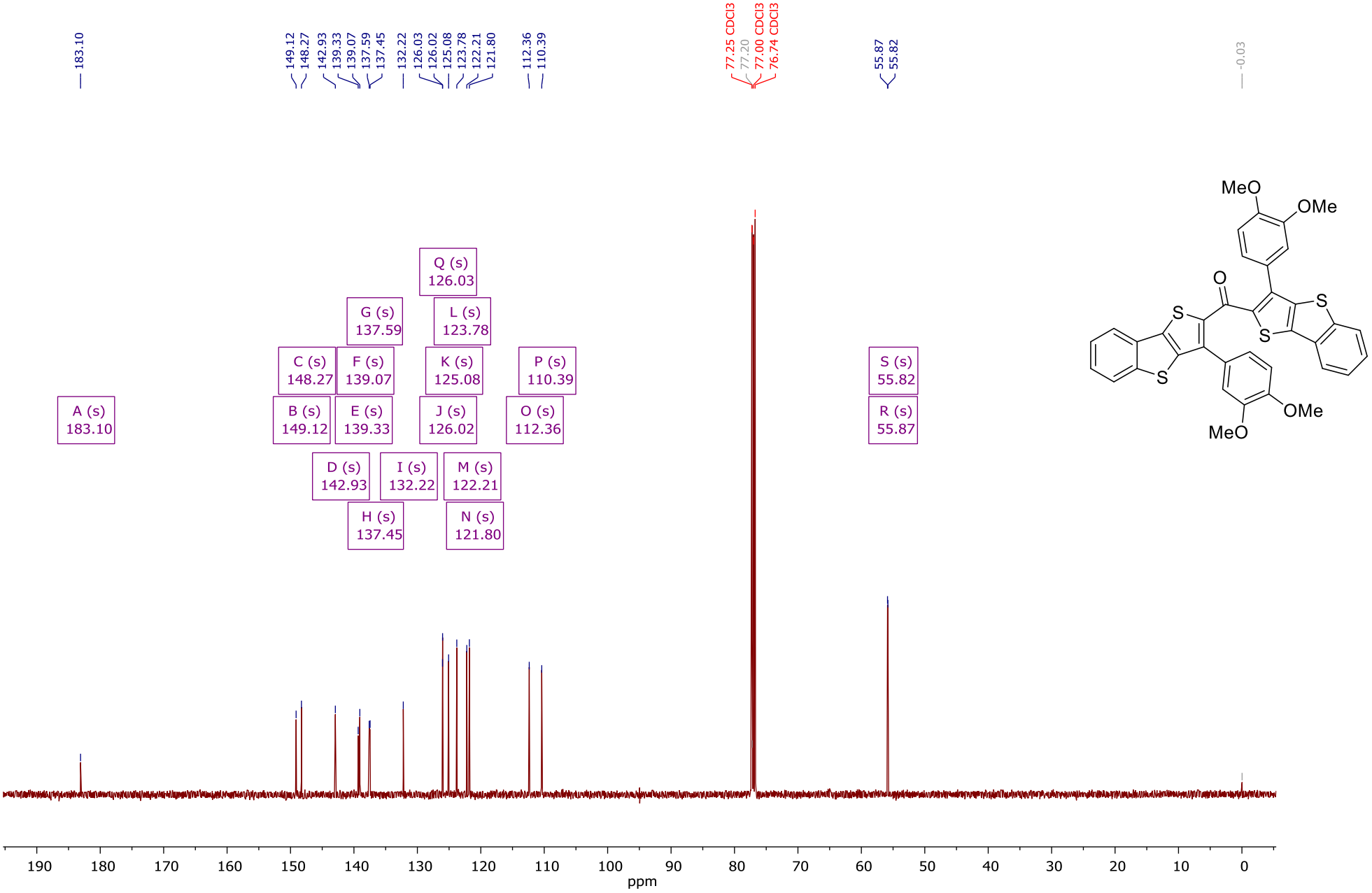


^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.1, 143.5, 141.4, 141.2, 139.8, 137.8, 134.7, 132.4, 129.1, 129.02, 128.96, 126.1, 125.1, 123.9, 122.2, 28.9.

Bis(3-(3,4-dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophen-2-yl)methanone (11)

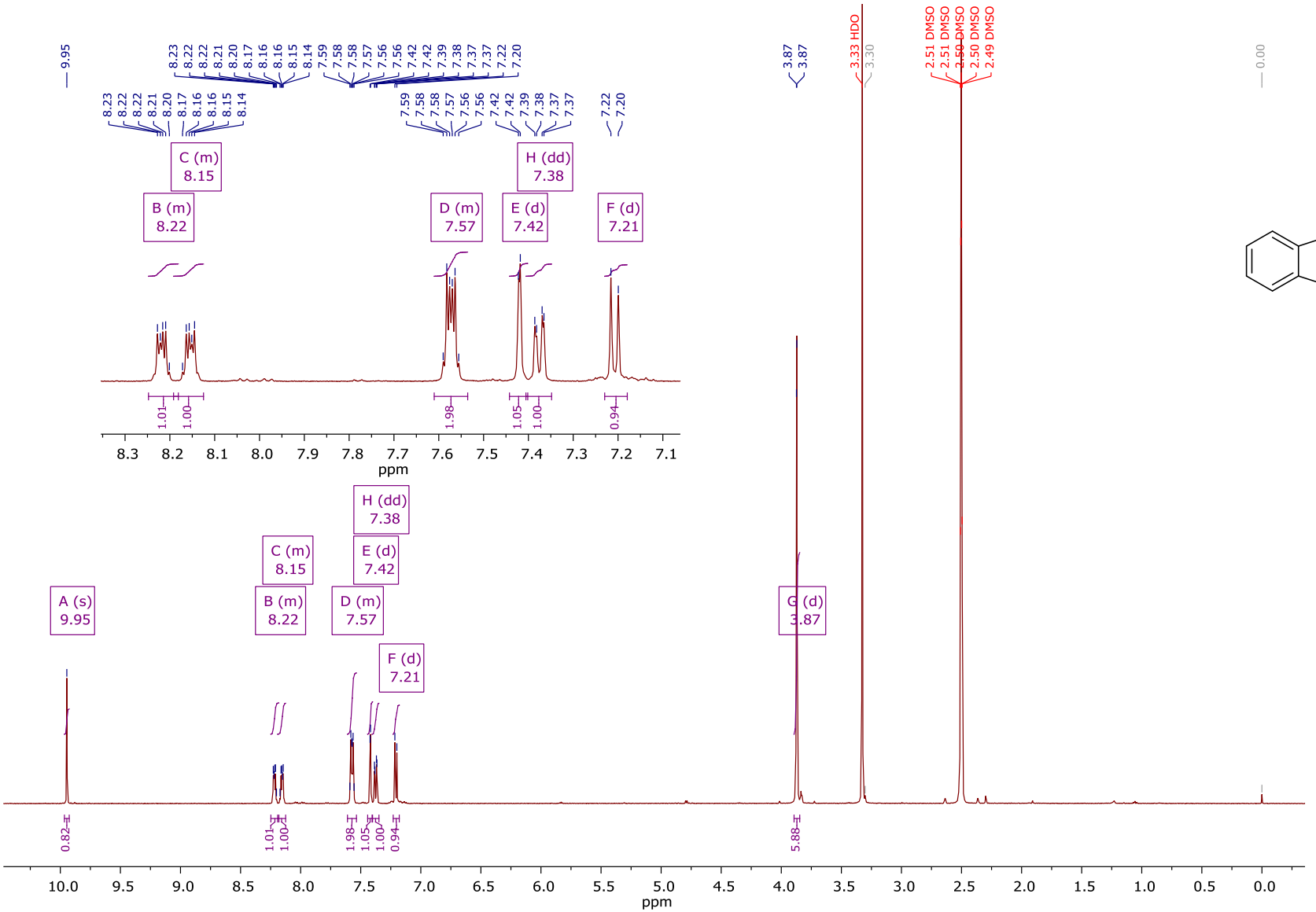


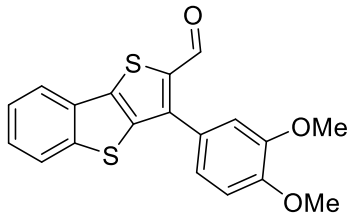
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.89 (m, 1H), 7.84 – 7.78 (m, 1H), 7.50 – 7.39 (m, 2H), 6.81 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 3H).



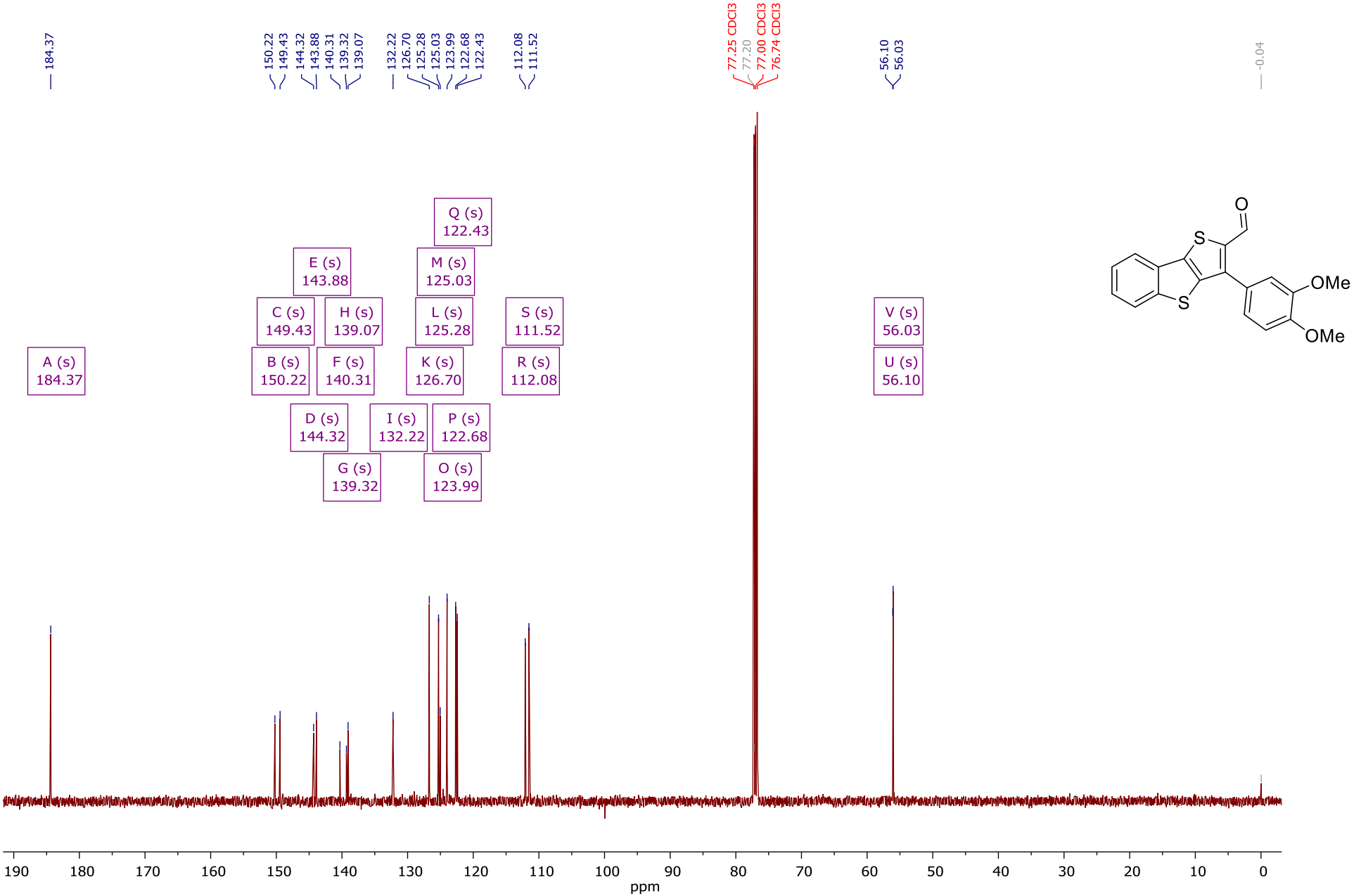
^{13}C NMR (126 MHz, Chloroform-*d*) δ 183.1, 149.1, 148.3, 142.9, 139.3, 139.1, 137.6, 137.4, 132.2, 126.03, 126.02, 125.1, 123.8, 122.2, 121.8, 112.4, 110.4, 55.9, 55.8.

3-(3,4-Dimethoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbaldehyde (12a)



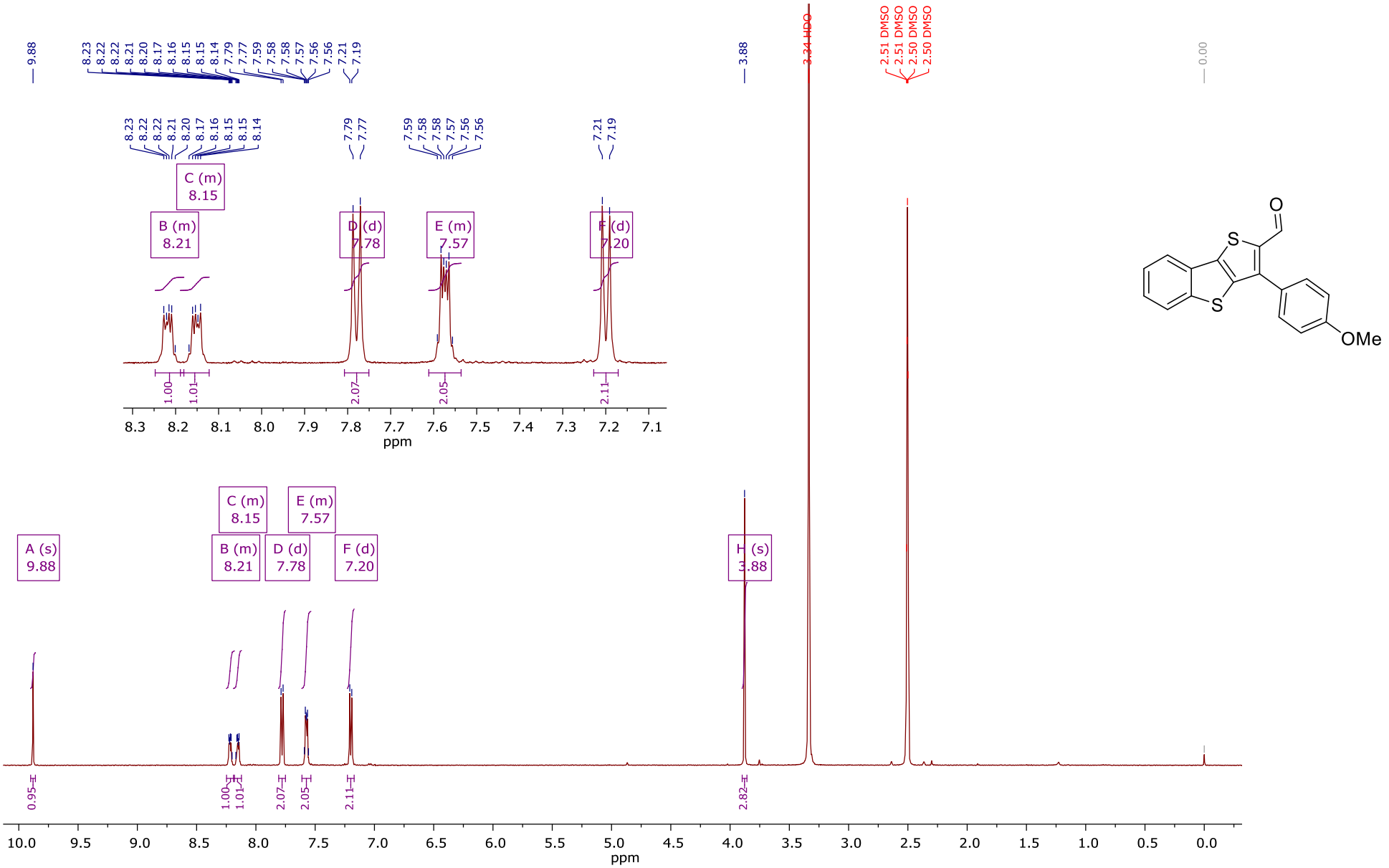


^{1}H NMR (500 MHz, DMSO-d_6) δ 9.95 (s, 1H), 8.22 (dt, J = 7.4, 3.7 Hz, 1H), 8.15 (dd, J = 6.1, 3.2 Hz, 1H), 7.57 (dd, J = 6.1, 3.1 Hz, 2H), 7.42 (d, J = 2.1 Hz, 2H), 7.38 (dd, J = 8.2, 2.0 Hz, 1H), 7.21 (d, J = 8.2 Hz, 1H), 3.87 (d, J = 1.4 Hz, 6H).

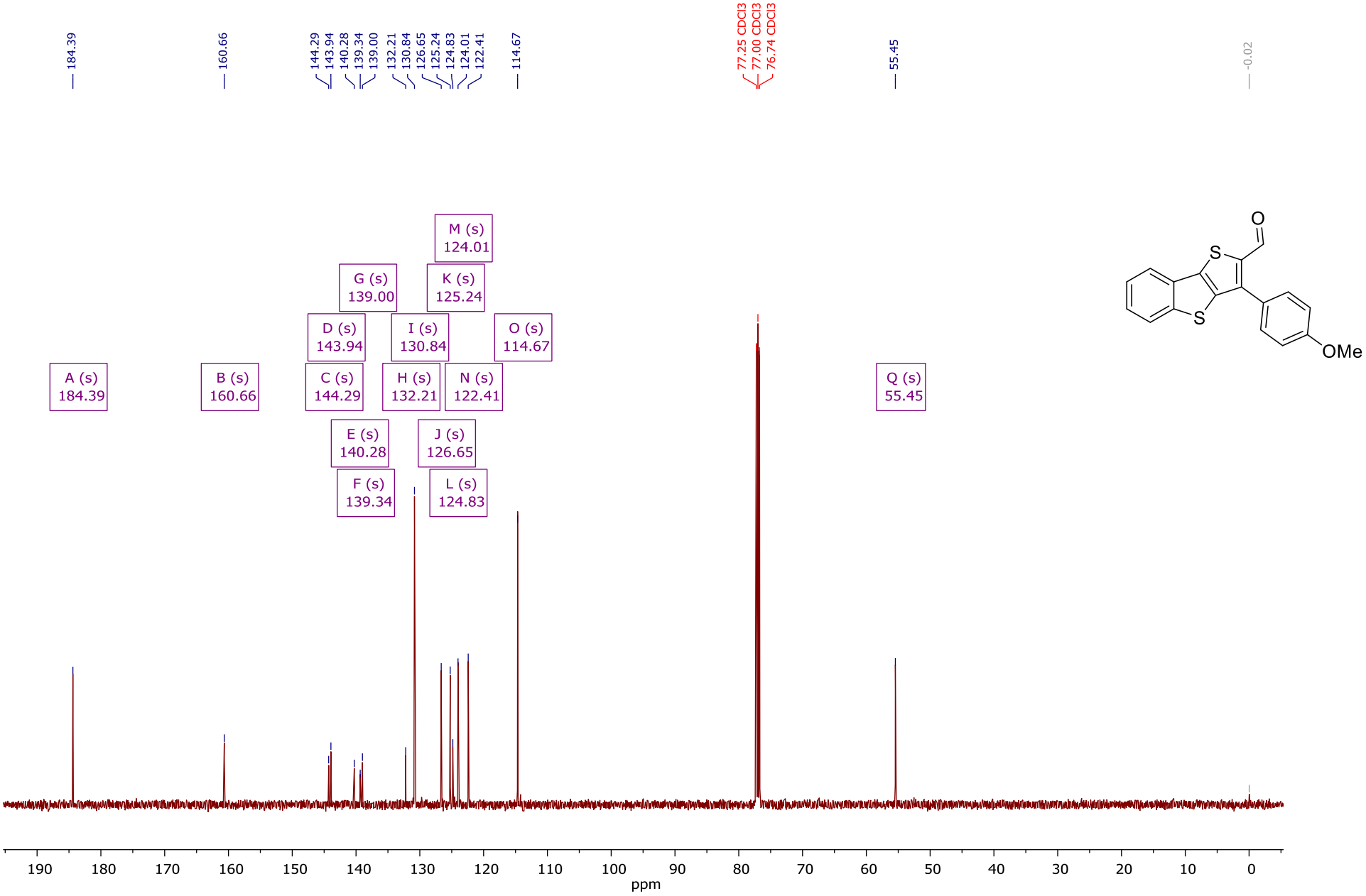


^{13}C NMR (126 MHz, Chloroform-*d*) δ 184.4, 150.2, 149.4, 144.3, 143.9, 140.3, 139.3, 139.1, 132.2, 126.7, 125.3, 125.0, 124.0, 122.7, 122.4, 112.1, 111.5, 56.1, 56.0.

3-(4-Methoxyphenyl)benzo[*b*]thieno[2,3-*d*]thiophene-2-carbaldehyde (12b)

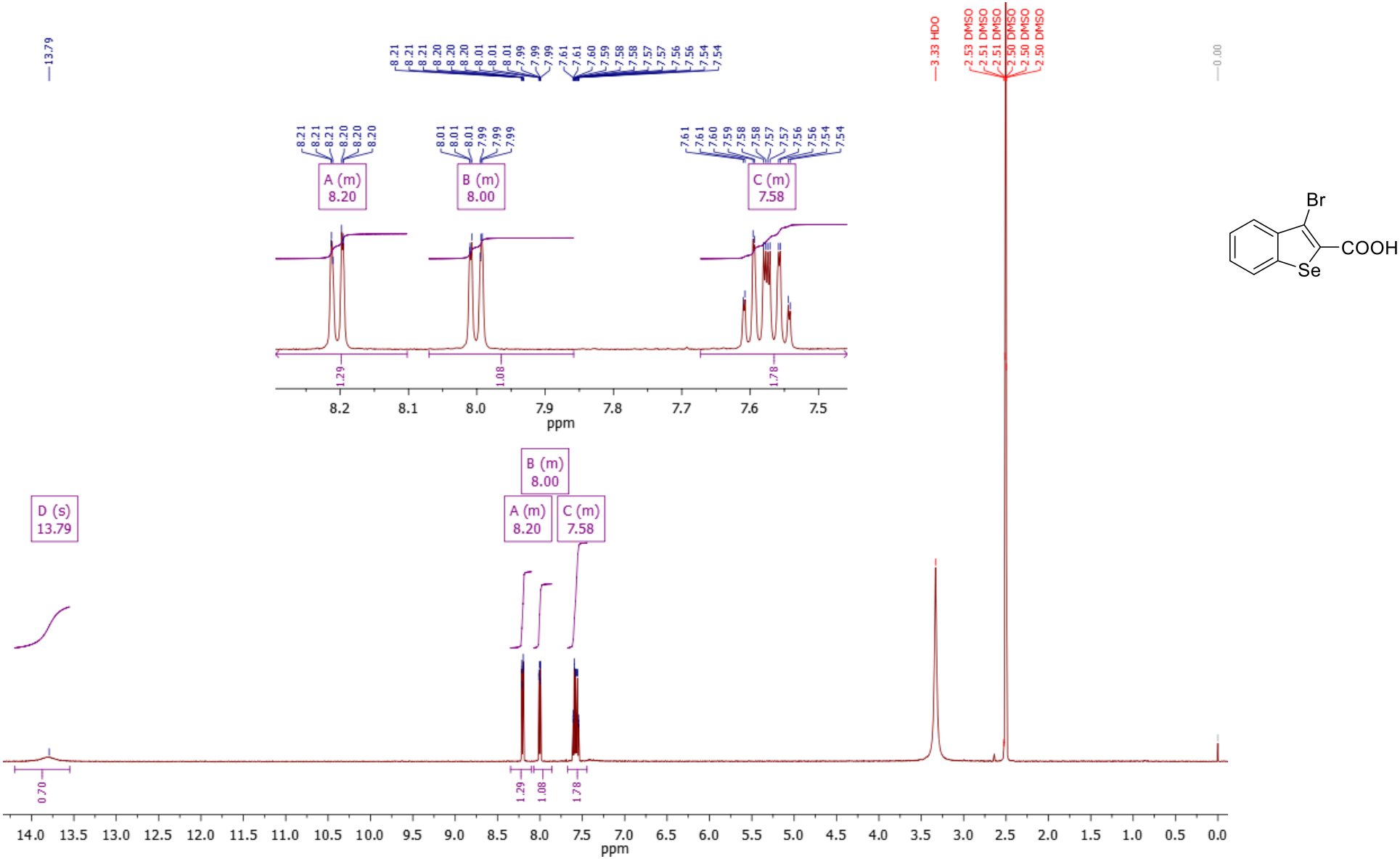


^{1}H NMR (500 MHz, DMSO-d_6) δ 9.88 (s, 1H), 8.25 – 8.18 (m, 1H), 8.19 – 8.12 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H).

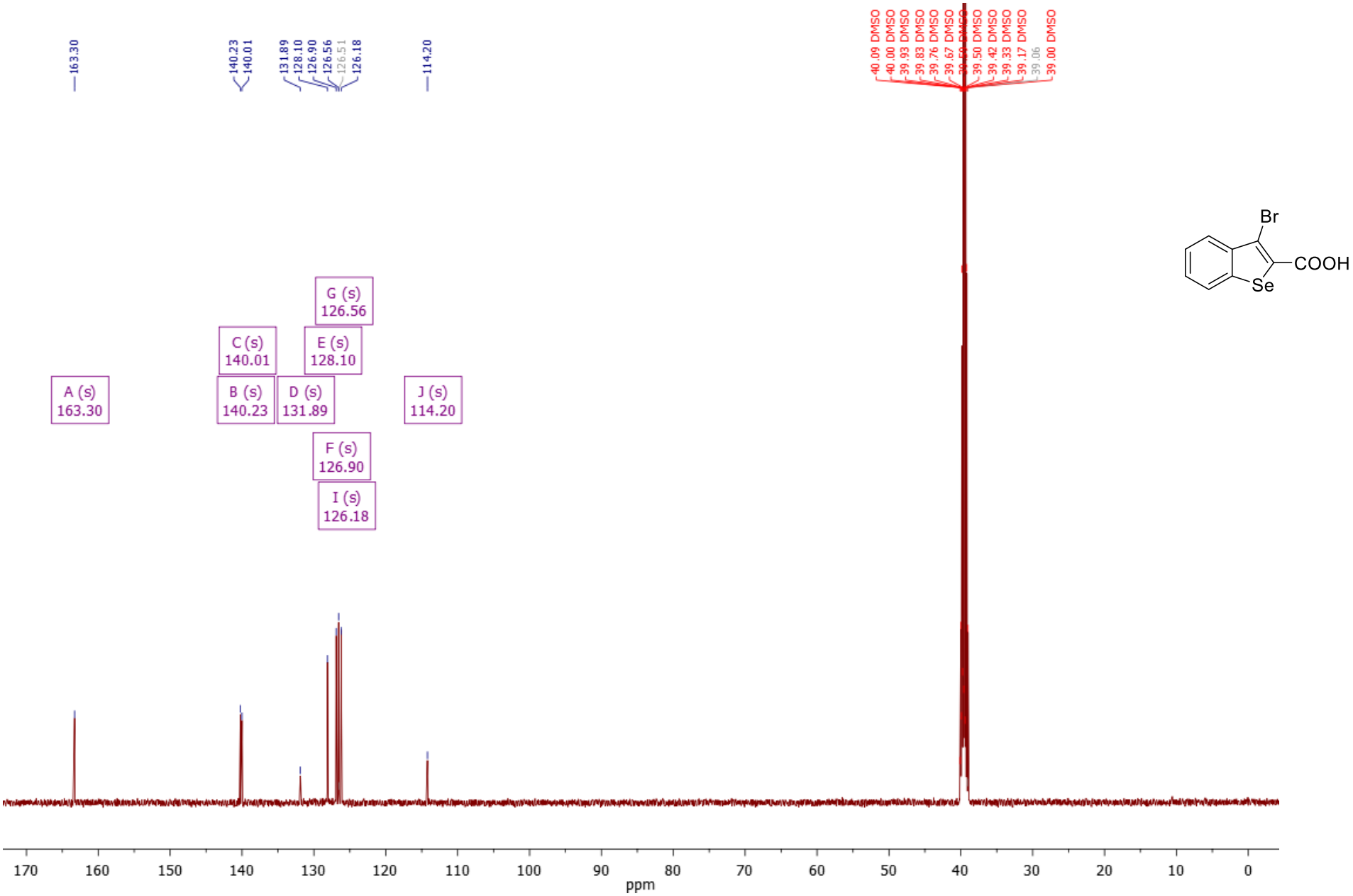


^{13}C NMR (126 MHz, Chloroform-*d*) δ 184.4, 160.7, 144.3, 143.9, 140.3, 139.3, 139.0, 132.2, 130.8, 126.6, 125.2, 124.8, 124.0, 122.4, 114.7, 55.4.

3-Bromobenzo[*b*]selenophene-2-carboxylic acid (13)

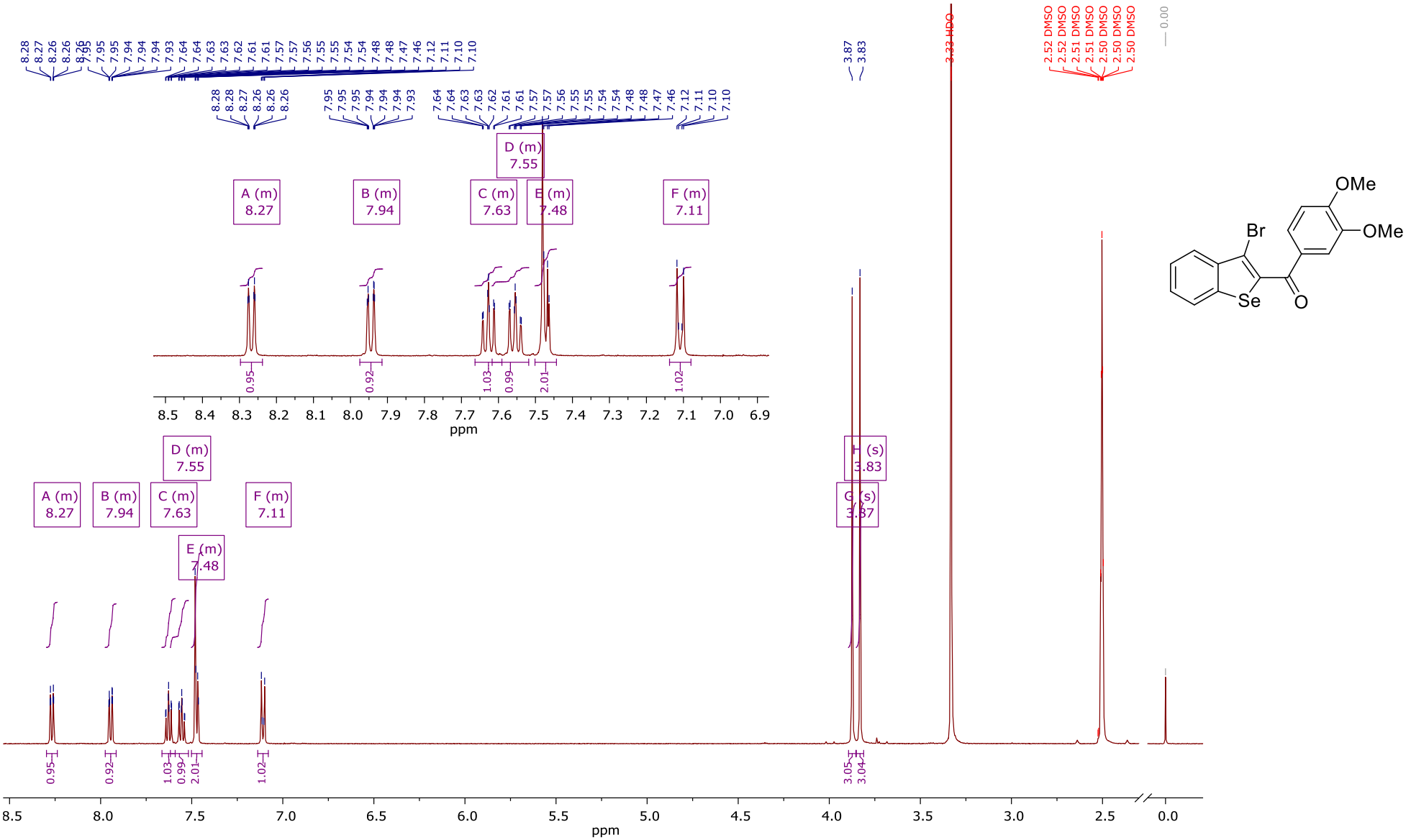


^{1}H NMR (500 MHz, DMSO-d_6) δ 13.79 (s, 1H), 8.35 – 8.10 (m, 1H), 8.07 – 7.86 (m, 1H), 7.67 – 7.44 (m, 2H).

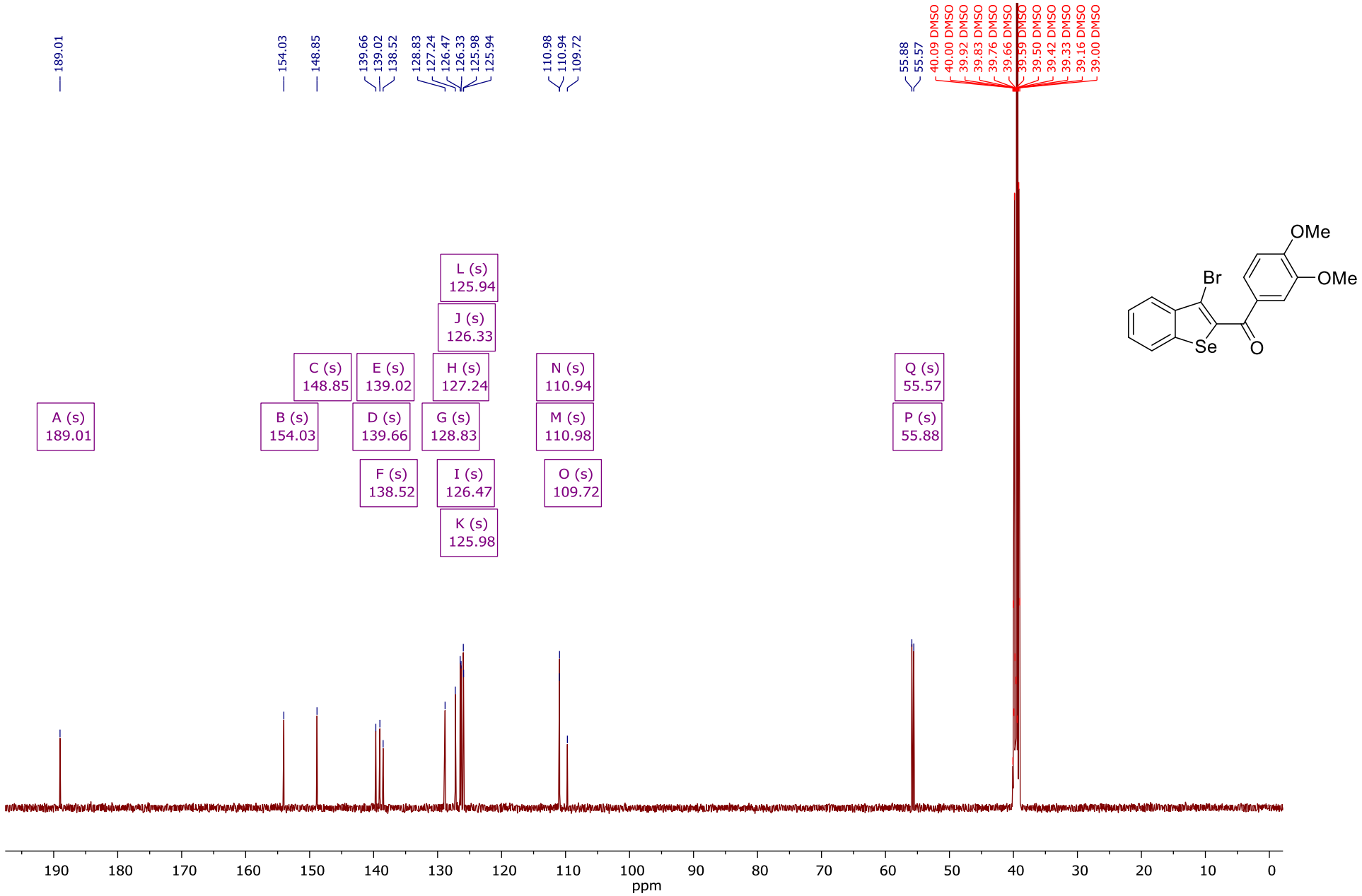


^{13}C NMR (126 MHz, DMSO-d_6) δ 163.3, 140.2, 140.0, 131.9, 128.1, 126.9, 126.6, 126.2, 114.2.

(3-Bromobenzo[*b*]selenophen-2-yl)(3,4-dimethoxyphenyl)methanone (14)

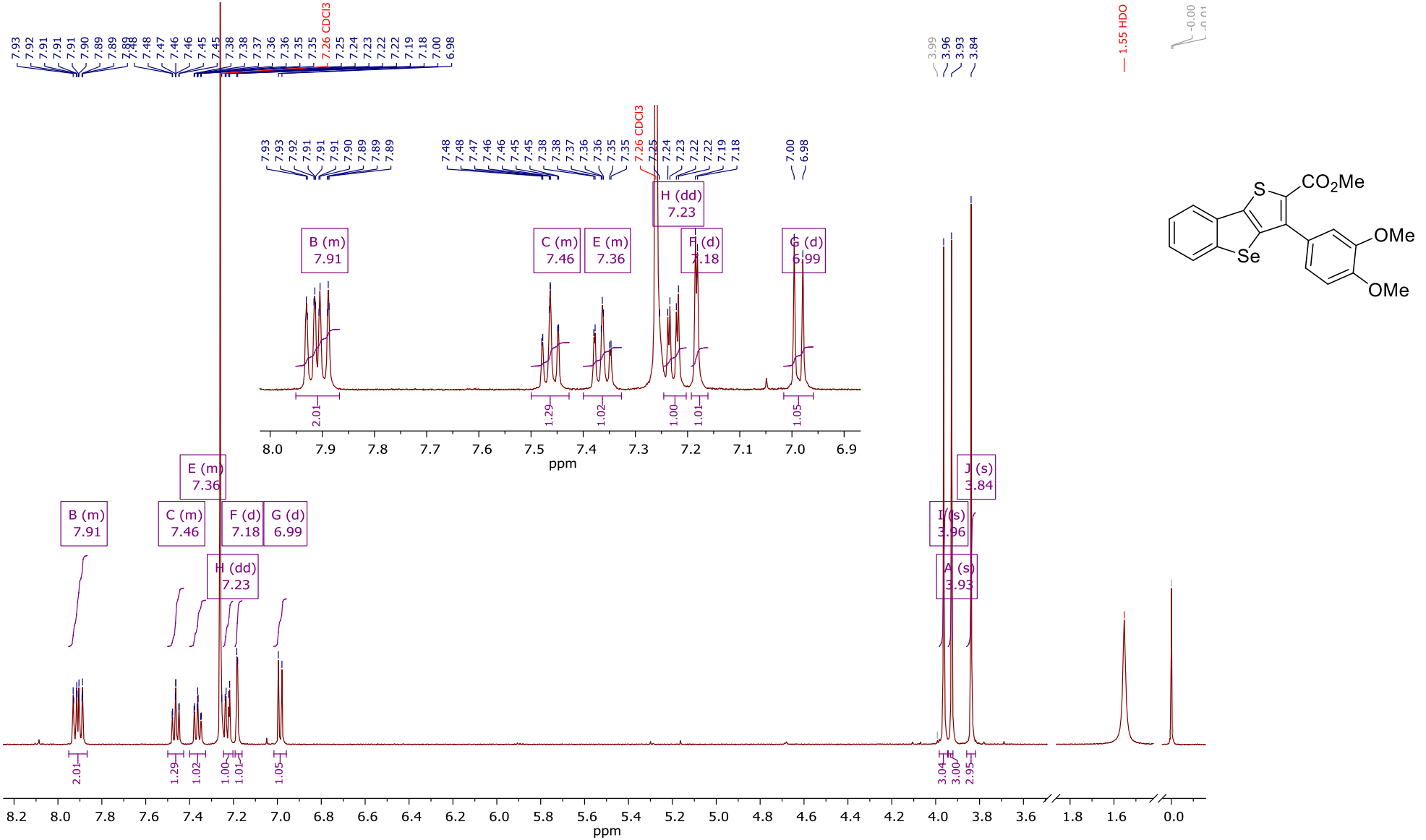


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.27 (m, 1H), 7.97 – 7.91 (m, 1H), 7.63 (m, 1H), 7.55 (m, 1H), 7.50 – 7.44 (m, 2H), 7.14 – 7.08 (m, 1H), 3.87 (s, 3H), 3.83 (s, 3H).

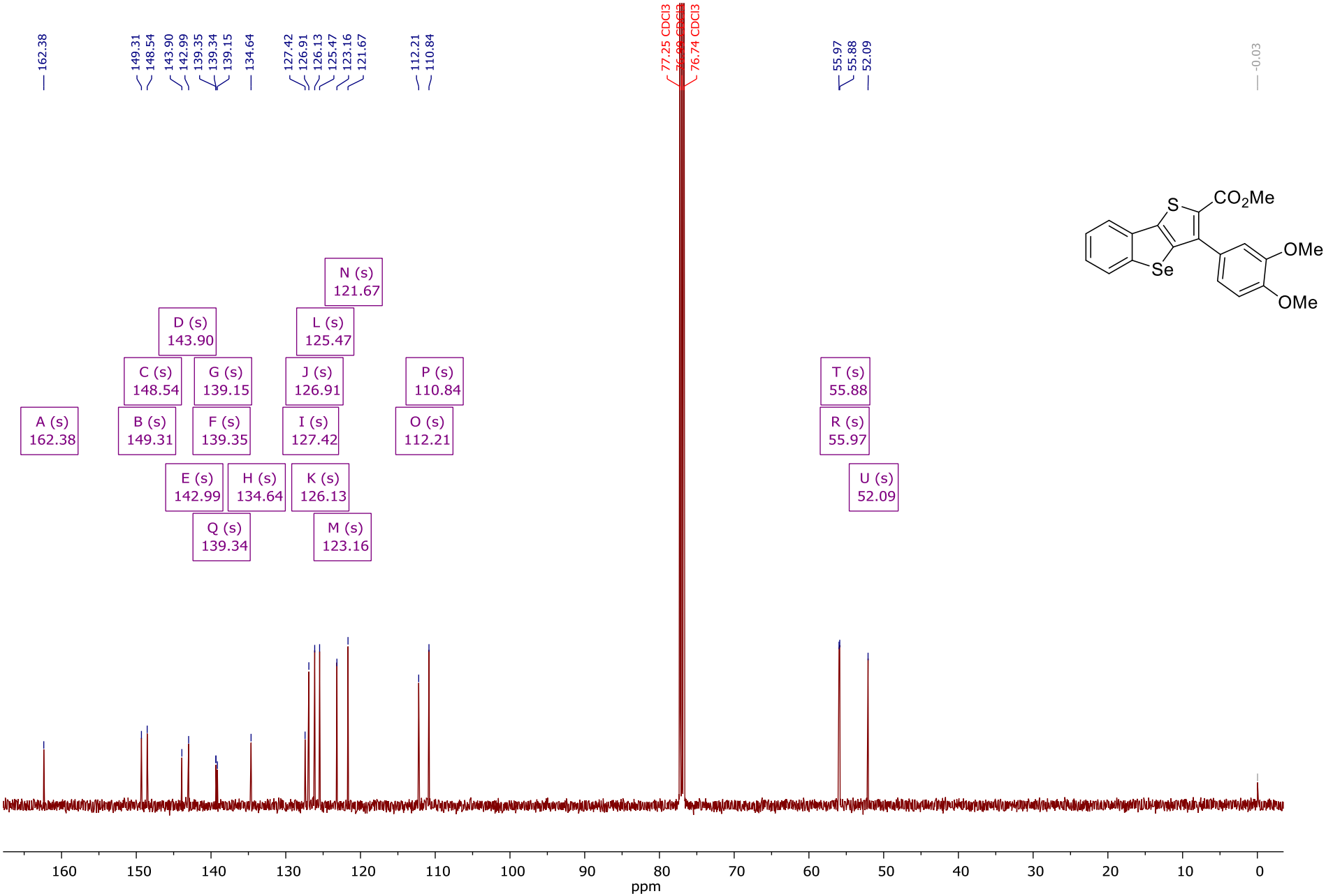


^{13}C NMR (126 MHz, DMSO-d_6) δ 189.0, 154.0, 148.8, 139.7, 139.0, 138.5, 128.8, 127.2, 126.5, 126.3, 126.0, 125.9, 111.0, 110.9, 109.7, 55.9, 55.6.

Methyl 3-(3,4-dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophene-2-carboxylate (15)

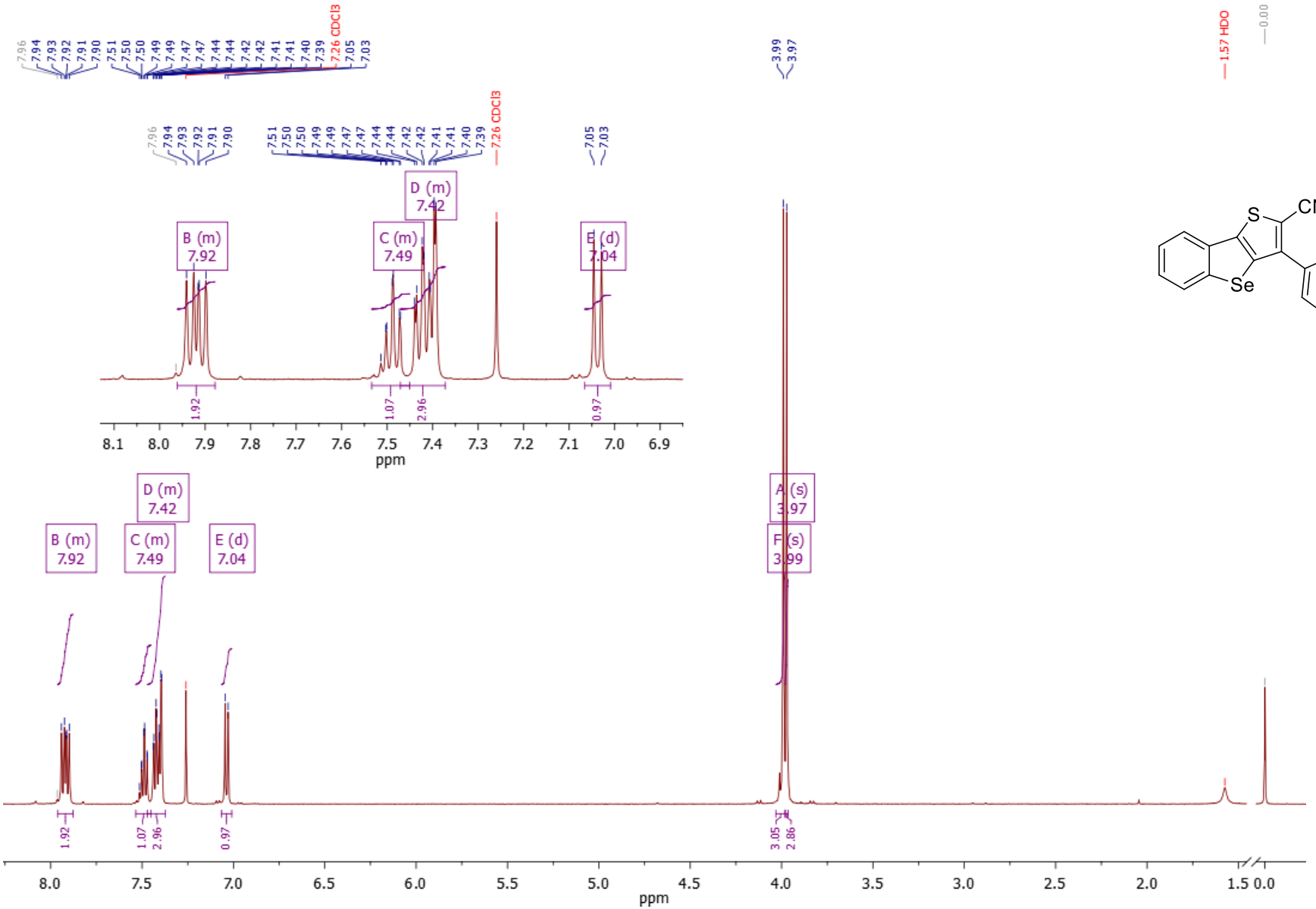


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 2H), 7.50 – 7.43 (m, 1H), 7.36 (m, 1H), 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.84 (s, 3H).

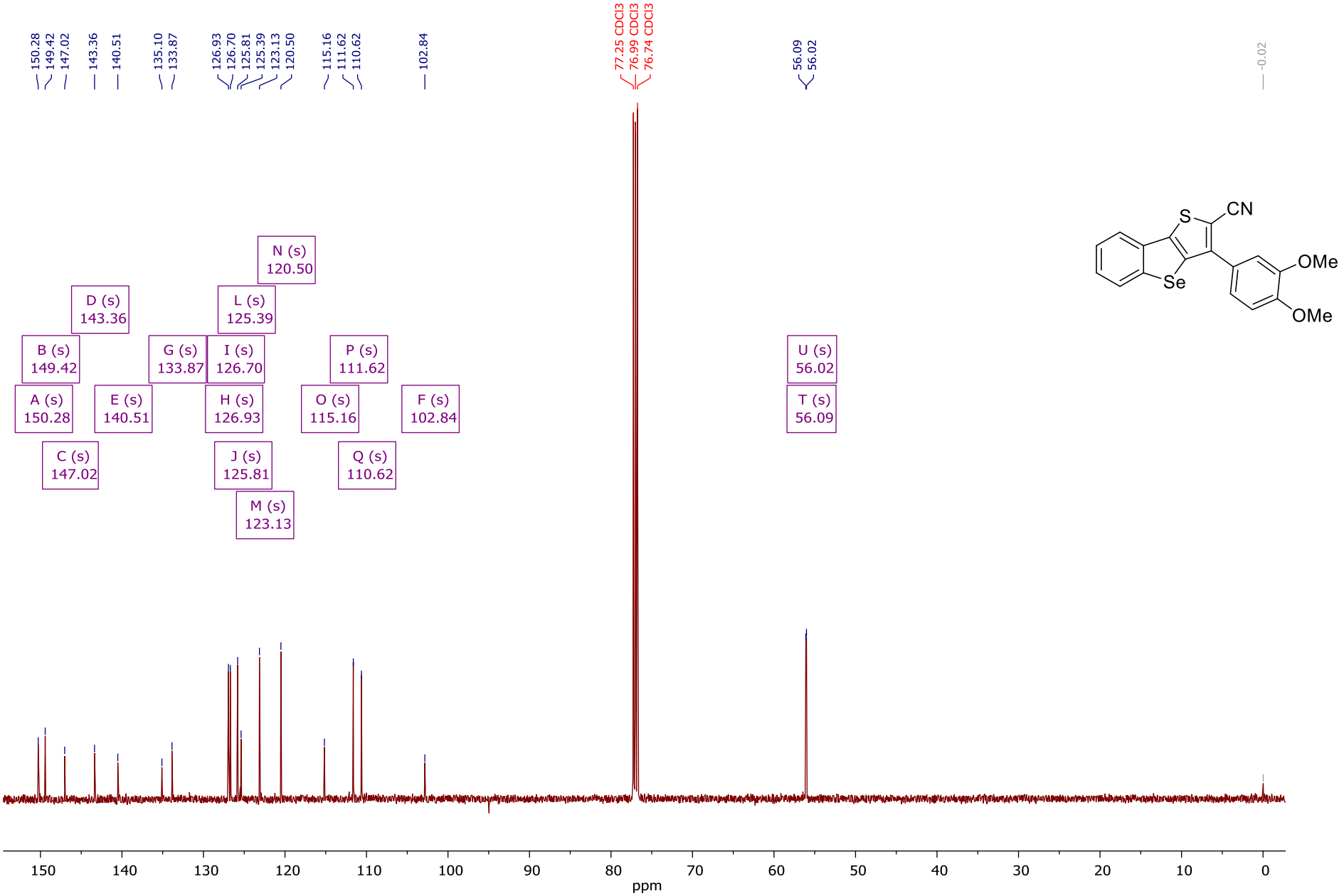


^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.4, 149.3, 148.5, 143.9, 143.0, 139.35, 139.34, 139.1, 134.6, 127.4, 126.9, 126.1, 125.5, 123.2, 121.7, 112.2, 110.8, 56.0, 55.9, 52.1.

3-(3,4-Dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophene-2-carbonitrile (16)

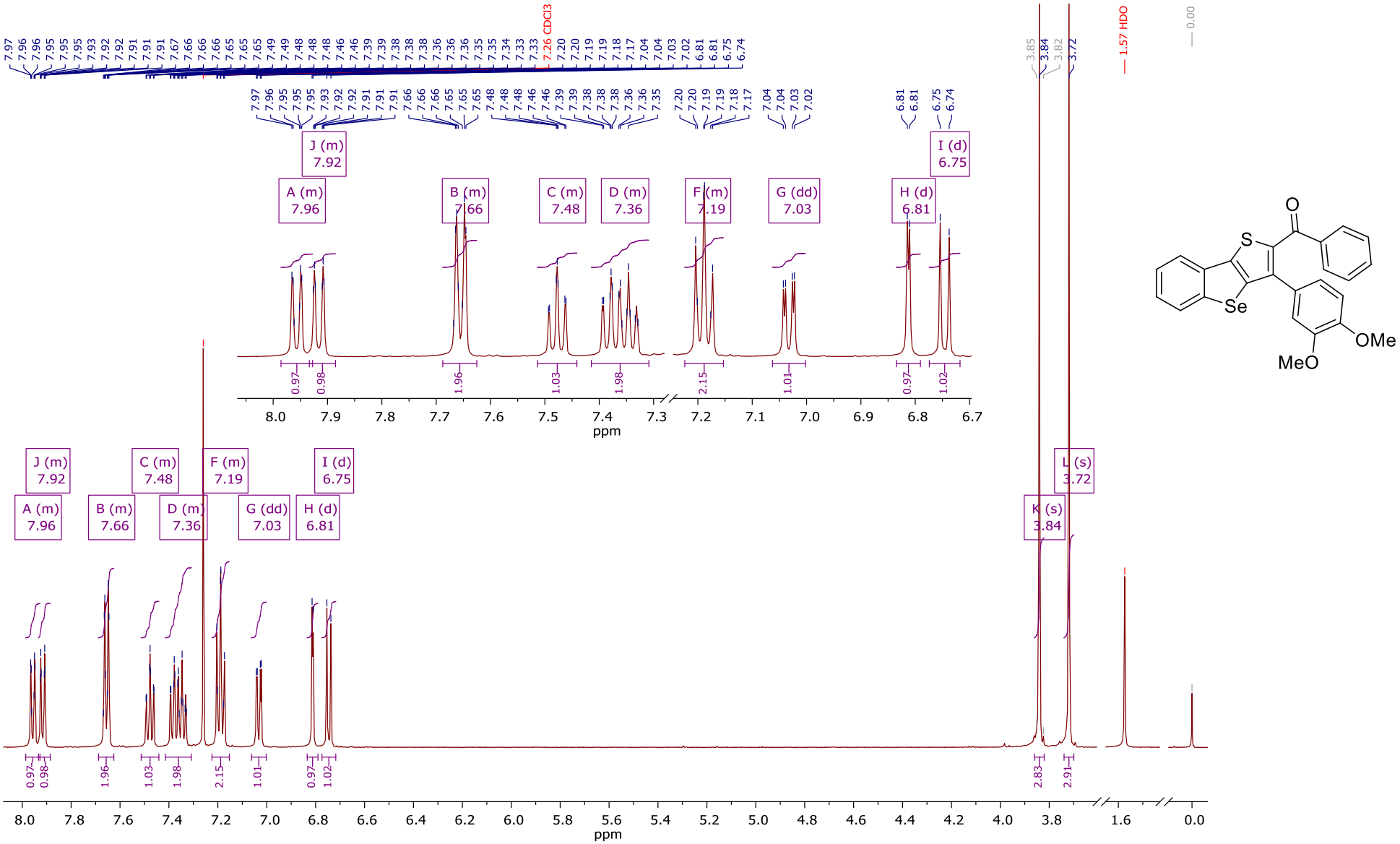


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.88 (m, 2H), 7.53 – 7.45 (m, 1H), 7.47 – 7.37 (m, 3H), 7.04 (d, *J* = 8.3 Hz, 1H), 3.99 (s, 6H), 3.97 (s, 3H).

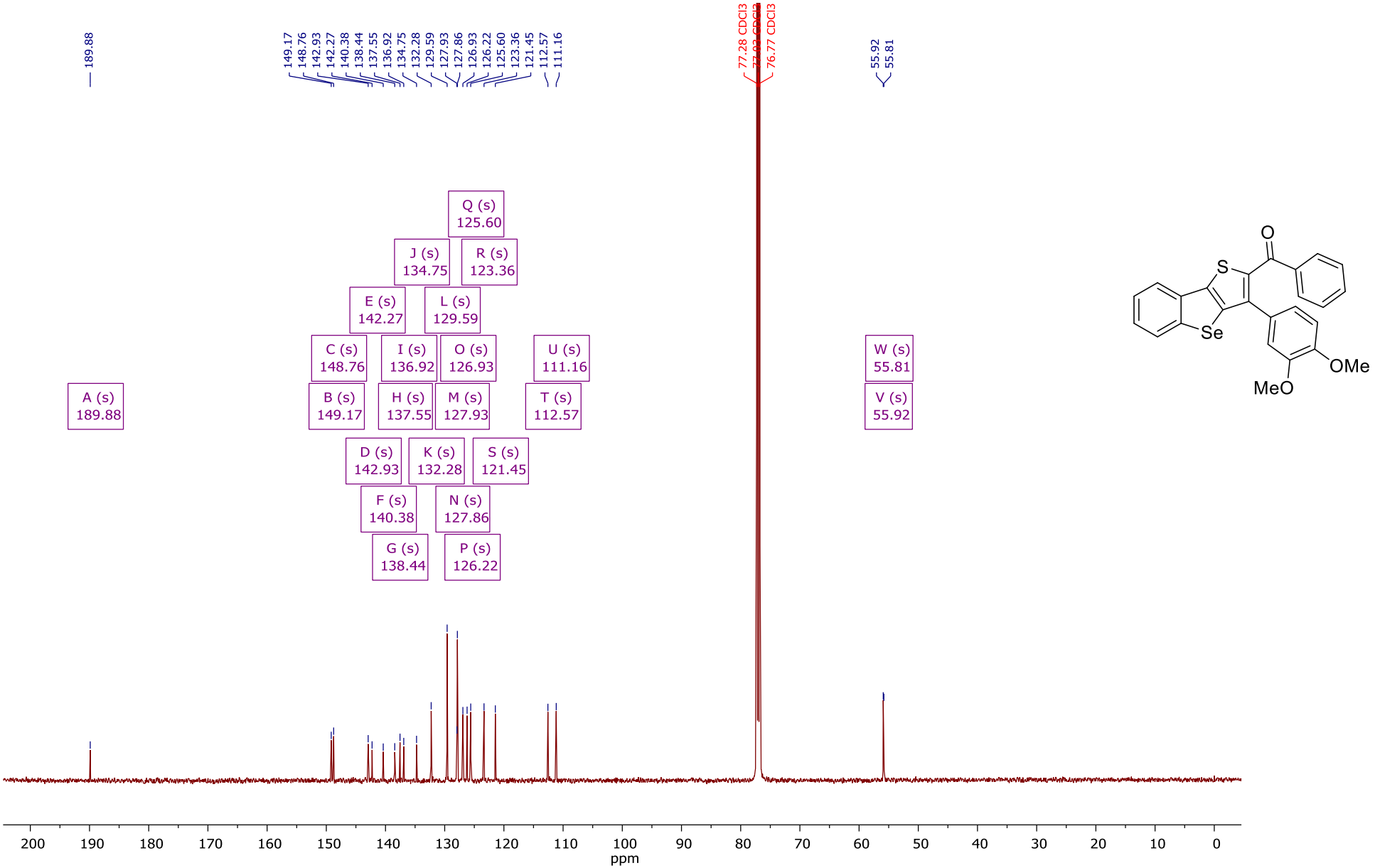


^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.3, 149.4, 147.0, 143.4, 140.5, 133.9, 126.9, 126.7, 125.8, 125.4, 123.1, 120.5, 115.2, 111.6, 110.6, 102.8, 56.1, 56.0.

(3-(3,4-Dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophen-2-yl)(phenyl)methanone (17a)

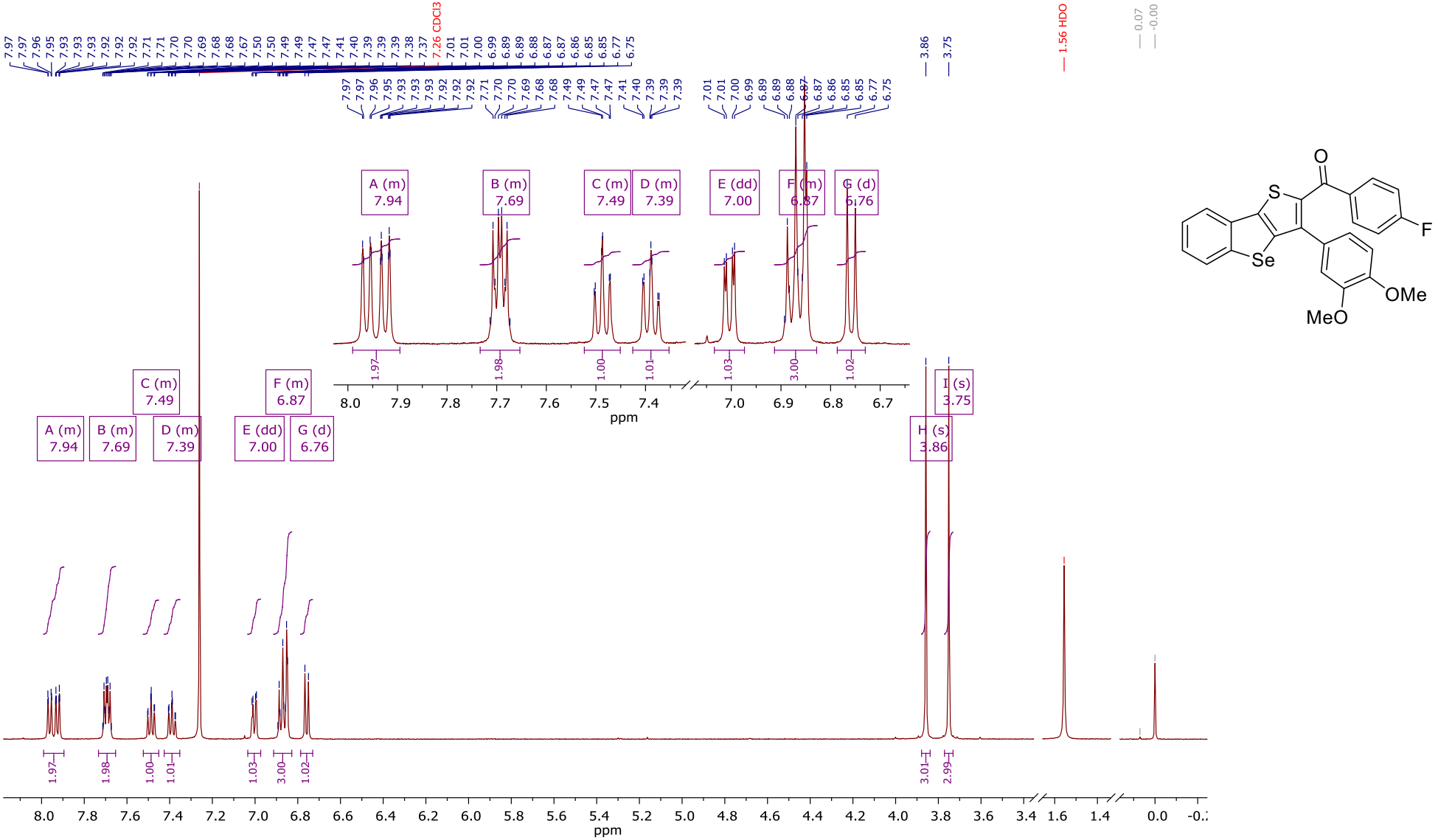


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 1H), 7.93 – 7.89 (m, 1H), 7.69 – 7.63 (m, 2H), 7.51 – 7.44 (m, 1H), 7.41 – 7.31 (m, 2H), 7.22 – 7.15 (m, 2H), 7.03 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H).

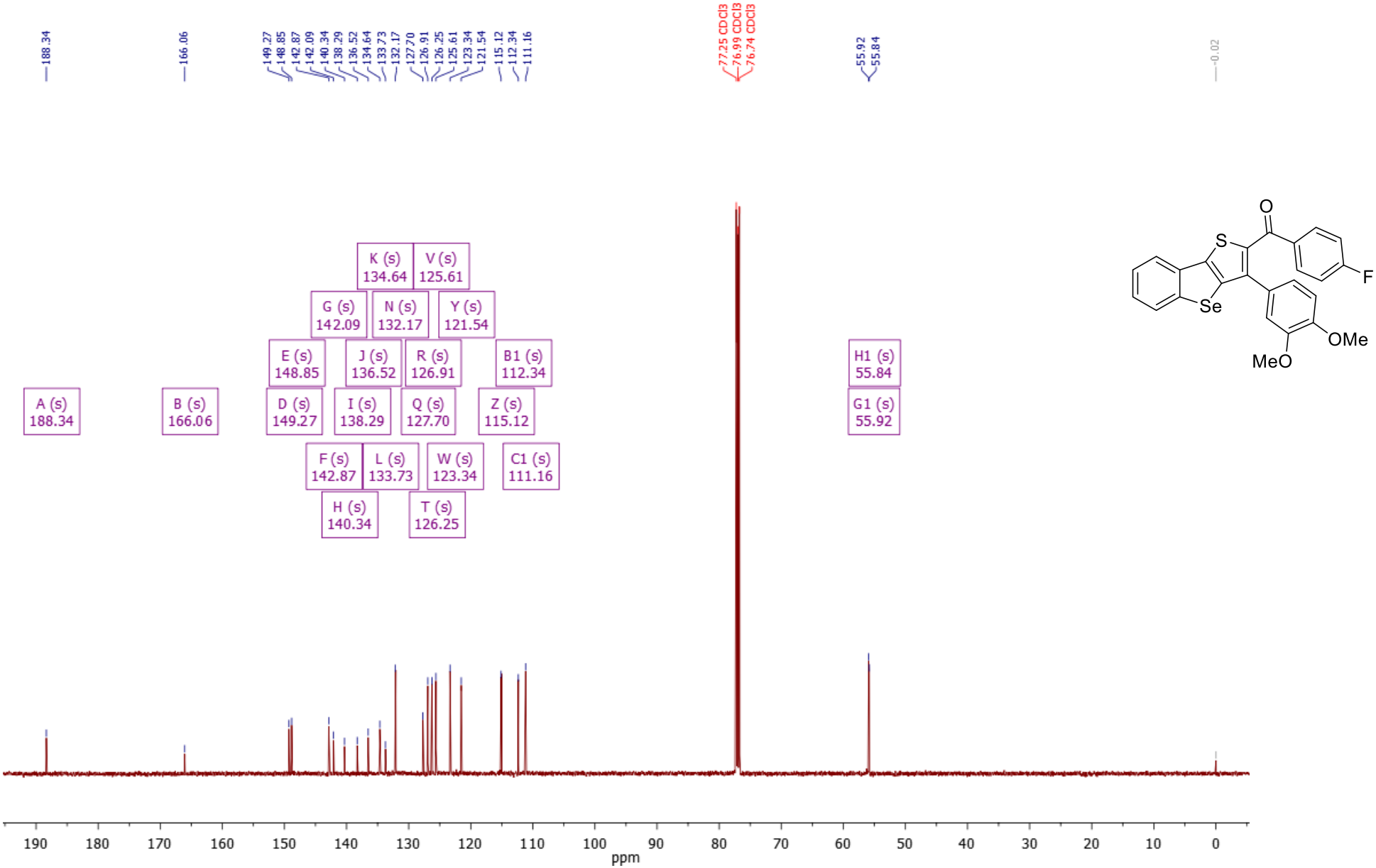


^{13}C NMR (126 MHz, Chloroform-*d*) δ 189.9, 149.2, 148.8, 142.9, 142.3, 140.4, 138.4, 137.5, 136.9, 134.7, 132.3, 129.6, 127.9, 127.9, 126.9, 126.2, 125.6, 123.4, 121.4, 112.6, 111.2, 55.9, 55.8.

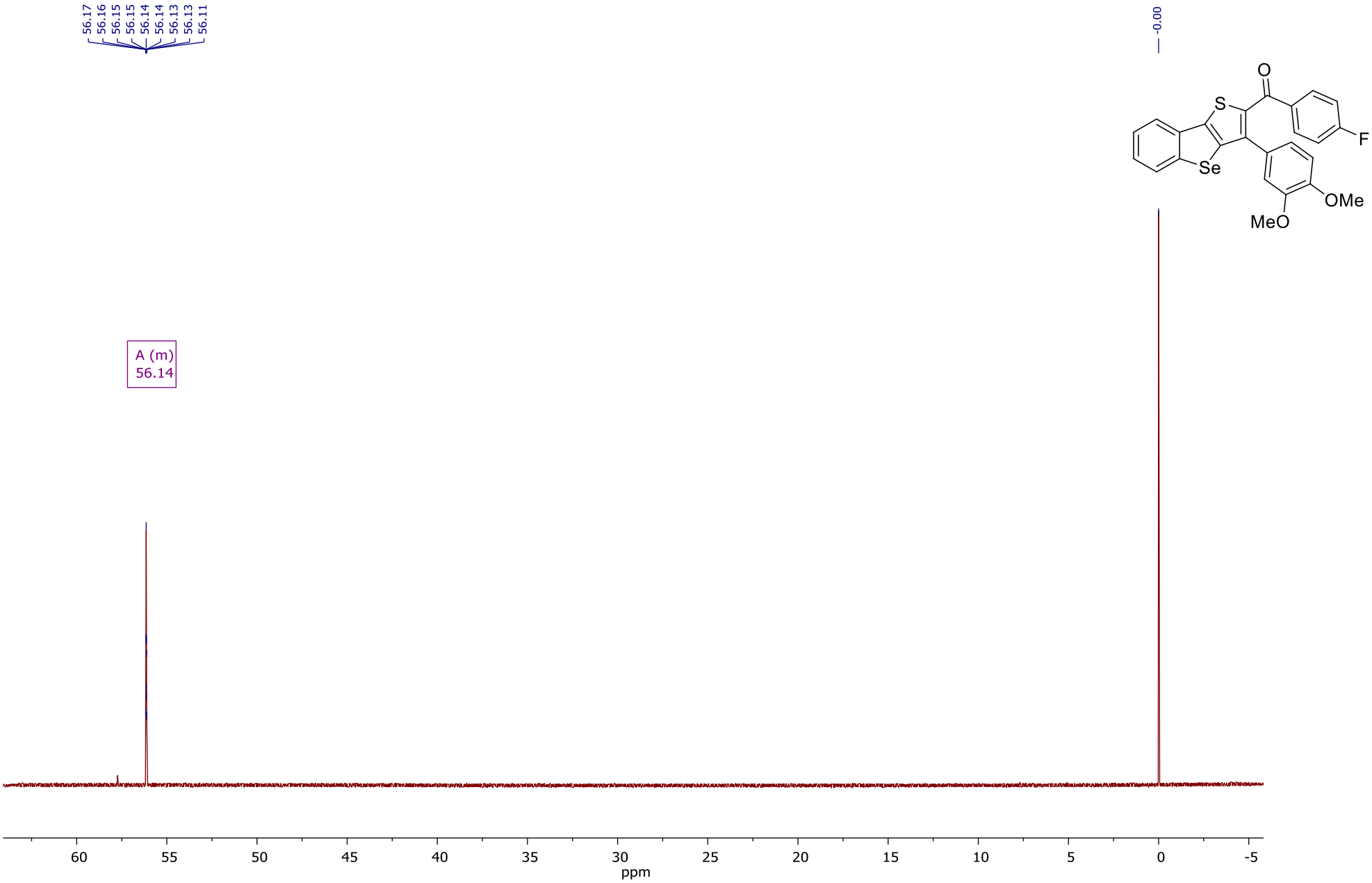
(3-(3,4-Dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophen-2-yl)(4-fluorophenyl)methanone (17b)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.90 (m, 2H), 7.73 – 7.65 (m, 2H), 7.52 – 7.45 (m, 1H), 7.43 – 7.35 (m, 1H), 7.00 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.91 – 6.83 (m, 3H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 3.75 (s, 3H).

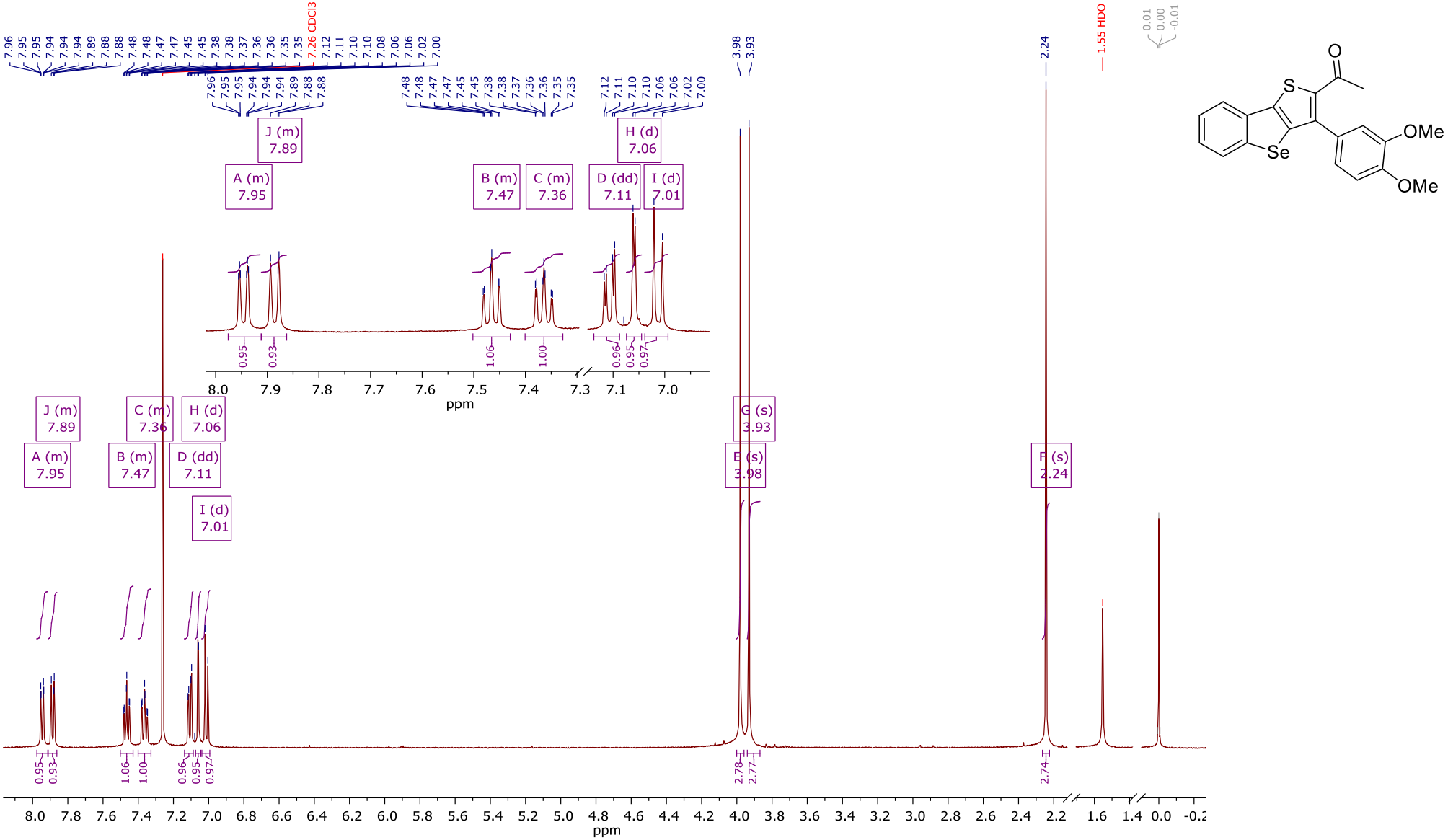


^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.3, 166.1, 149.3, 148.8, 142.9, 142.1, 140.3, 138.3, 136.5, 134.6, 133.7, 132.2, 127.7, 126.9, 126.2, 125.6, 123.3, 121.5, 115.1, 112.3, 111.2, 55.9, 55.8.

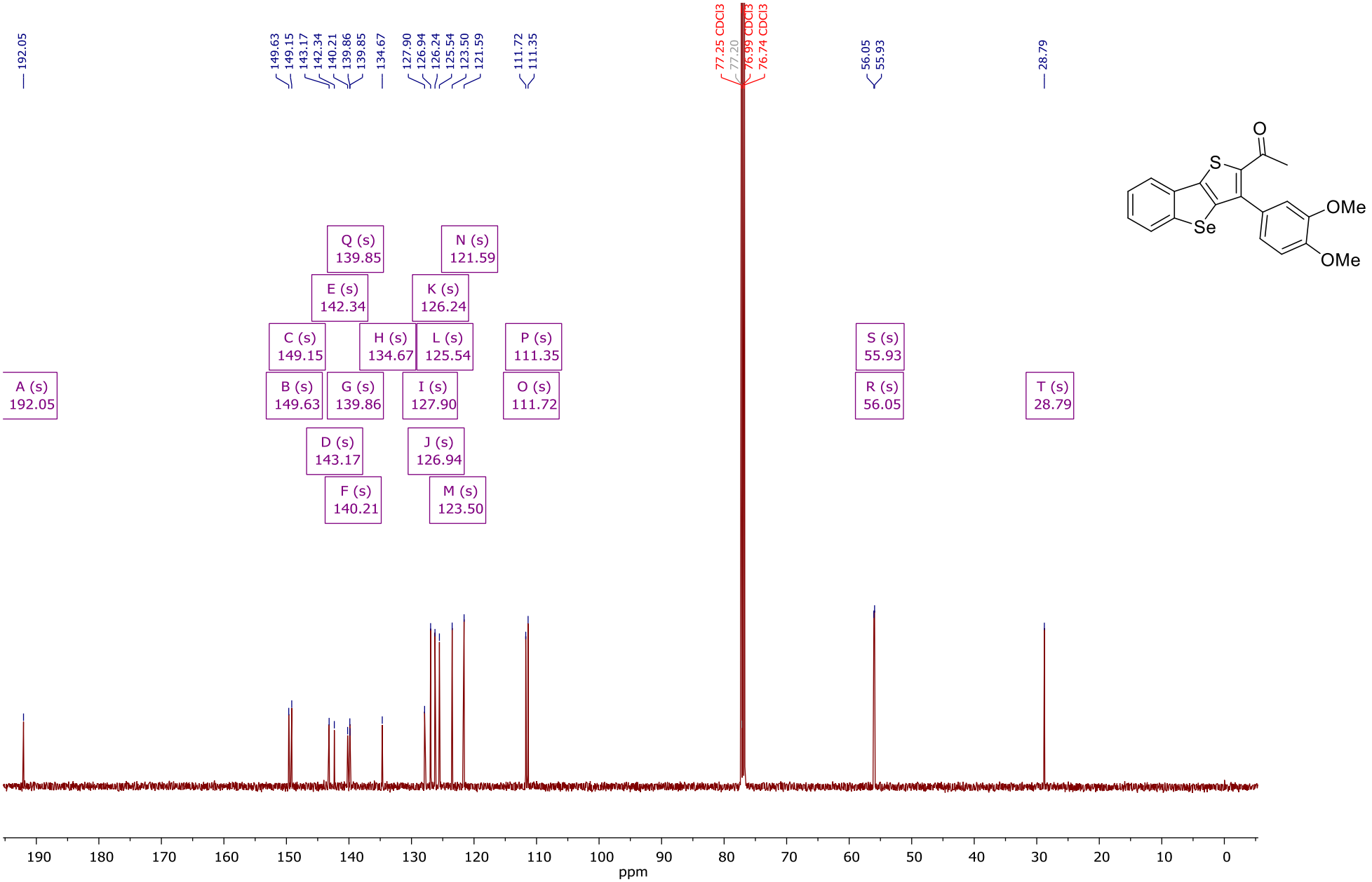


^{19}F NMR (471 MHz, Chloroform-*d*) δ 56.50 – 54.96 (m).

1-(3-(3,4-Dimethoxyphenyl)benzo[4,5]selenopheno[3,2-*b*]thiophen-2-yl)ethan-1-one (18)



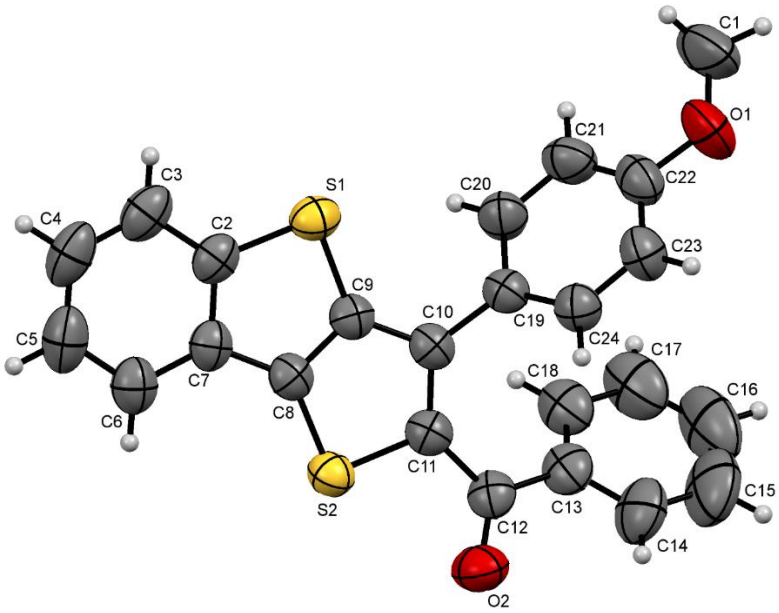
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 1H), 7.91 – 7.86 (m, 1H), 7.50 – 7.43 (m, 1H), 7.40 – 7.33 (m, 1H), 7.11 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 2.24 (s, 3H).



^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.0, 149.6, 149.1, 143.2, 142.3, 140.2, 139.86, 139.85, 134.7, 127.9, 126.9, 126.2, 125.5, 123.5, 121.6, 111.7, 111.3, 56.0, 55.9, 28.8.

Crystallographic data for compounds 9d, 11 and 17a

1. Crystallographic data and results of refinement for the structure 9d in the XRD experiment



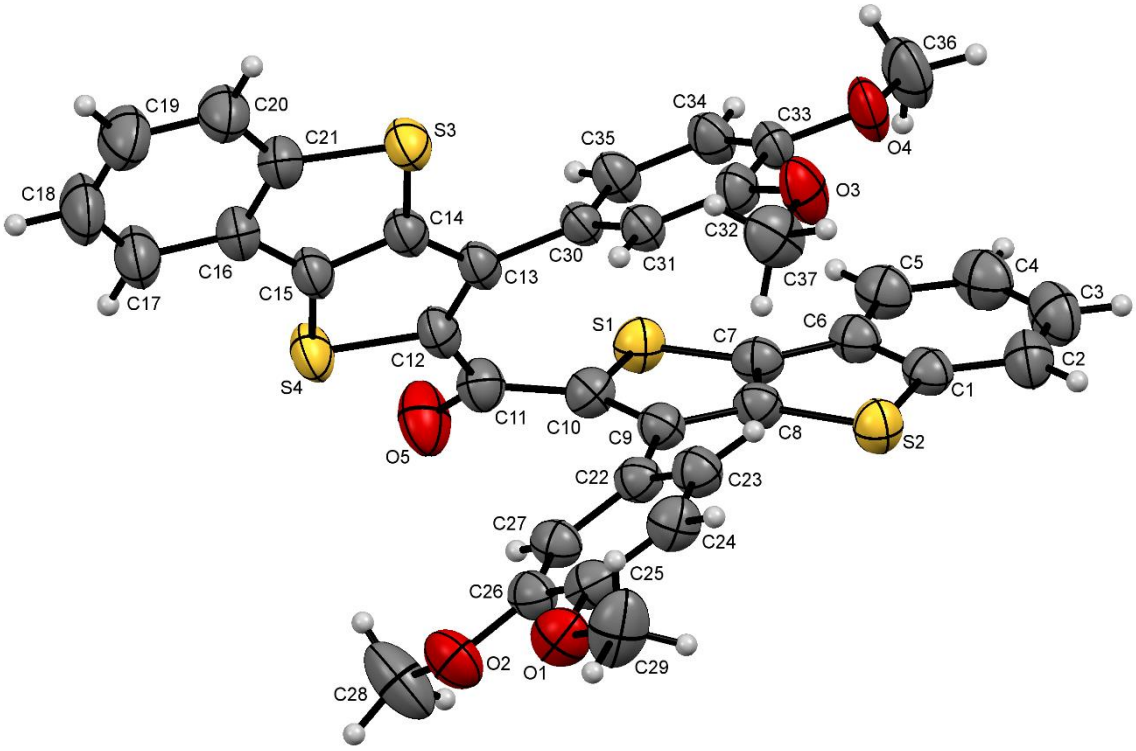
Compound **9d** in according XRD data. Thermal ellipsoids are shown at 50% probability level.

Compound **9d**

Empirical formula	$C_{24}H_{16}O_2S_2$	ρ_{calc} mg/mm^3	1.330
Formula weight	400.49	m/mm^{-1}	0.283
Temperature/K	295(2)	F(000)	1664
Crystal system	monoclinic	Crystal size/mm^3	0.43 × 0.35 × 0.28
Space group	P2(1)/c	2Θ range for data collection	3.52 < Θ < 30.95°
a/Å	18.5085(13)	Index ranges	-16 < h < 25, -14 < k < 13, -28 < l < 24
b/Å	10.2845(7)	Reflections collected	24153
c/Å	21.0481(13)	Independent reflections	10789 [R(int) = 0.0440]
α/°	90.00	Data/restraints/parameters	10789 / 0 / 508
β/°	93.372(7)	Goodness-of-fit on F^2	1.003
γ/°	90.00	Final R indexes [I>2σ (I)]	R_1 = 0.0551, wR_2 = 0.1332
Volume/Å^3	3999.6(5)	Final R indexes [all data]	R_1 = 0.1301, wR_2 = 0.1922
Z	8	Largest diff. peak/hole / e Å^{-3}	0.265 / -0.351

Deposition number CCDC 1981665 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Crystallographic data and results of refinement for the structure 11 in the XRD experiment



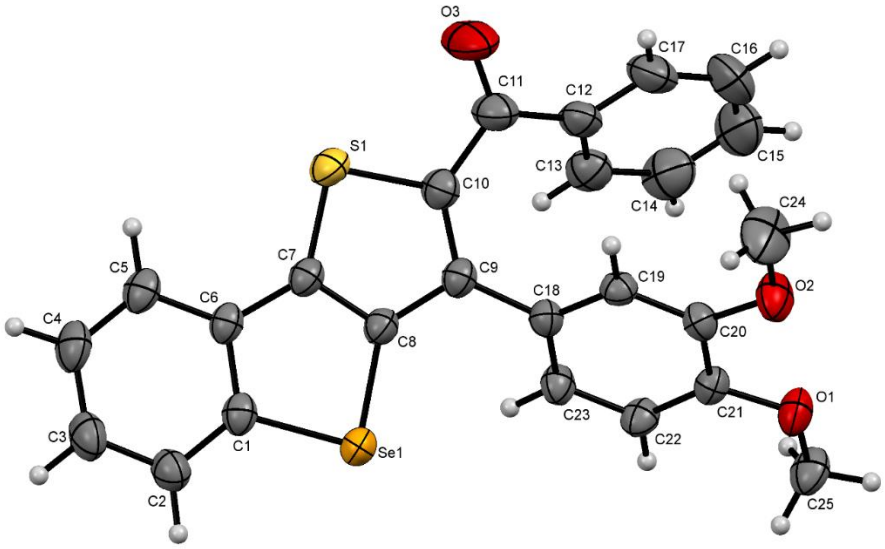
Compound **11** in according XRD data. Thermal ellipsoids are shown at 50% probability level.

Compound **11**

Empirical formula	$C_{41}H_{34}O_7S_4$	ρ_{calc} mg/mm^3	1.359
Formula weight	766.92	m/mm^{-1}	0.304
Temperature/K	295(2)	F(000)	800
Crystal system	triclinic	Crystal size/mm^3	0.44 × 0.37 × 0.18
Space group	P-1	2Θ range for data collection	3.58 < Θ < 30.49°
a/Å	11.9138(8)	Index ranges	-16 < h < 15, -16 < k < 13, -11 < l < 19
b/Å	12.2695(7)	Reflections collected	18236
c/Å	13.3791(8)	Independent reflections	10029 [R(int) = 0.0483]
α/°	97.497(5)	Data/restraints/parameters	10029 / 0 / 475
β/°	92.616(5)	Goodness-of-fit on F^2	1.005
γ/°	104.106(5)	Final R indexes [I>2σ (I)]	R_1 = 0.0594, wR_2 = 0.1317
Volume/Å^3	1874.4(2)	Final R indexes [all data]	R_1 = 0.1282, wR_2 = 0.1887
Z	2	Largest diff. peak/hole / e Å^{-3}	0.328 / -0.427

Deposition number CCDC 1981668 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Crystallographic data and results of refinement for the structure 17a in the XRD experiment



Compound **17a** in according XRD data. Thermal ellipsoids are shown at 50% probability level.

Compound **17a**

Empirical formula	$C_{25}H_{18}O_3SSe$	ρ_{calc} mg/mm^3	1.526
Formula weight	477.41	m/mm^{-1}	1.933
Temperature/K	295(2)	F(000)	968
Crystal system	monoclinic	Crystal size/mm^3	0.46 × 0.38 × 0.31
Space group	P2(1)/c	2Θ range for data collection	3.55 < Θ < 31°
a/Å	18.5085(13)	Index ranges	-13 < h < 15, -31 < k < 28, -11 < l < 11
b/Å	21.6499(12)	Reflections collected	14525
c/Å	8.7289(5)	Independent reflections	5660 [R(int) = 0.0388]
α/°	90.00	Data/restraints/parameters	5660 / 0 / 290
β/°	91.177(5)	Goodness-of-fit on F^2	1.003
γ/°	90.00	Final R indexes [I>2σ (I)]	R_1 = 0.0419, wR_2 = 0.0849
Volume/Å^3	2077.5(2)	Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1025
Z	4	Largest diff. peak/hole / e Å^{-3}	0.658 / -0.627

Deposition number CCDC 1981666 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

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3 H. Kudo, R. N. Castle and M. L. Lee, *J. Heterocycl. Chem.*, 1984, **21**, 1761–1764.

4 E. Paegle, S. Belyakov and P. Arsenyan, *European J. Org. Chem.*, 2014, **2014**, 3831–3840.