

**Synthesis of functionalized 2-(2-pyrrolyl)dihydropyridines
and 3(4)-amino-3-pyrrolylalkenoates from pyrrolylpropynoates
and aminomalonate**

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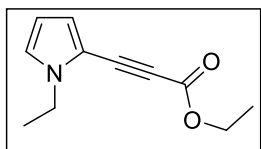
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General information

NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 MHz for ^1H , 100.6 MHz for ^{13}C) in CDCl_3 and DMSO-d_6 . The internal standards were HMDS (for ^1H) and the residual solvent signals (for ^{13}C). Resonance signals of carbon atoms were assigned based on ^1H – ^{13}C HSQC and ^1H – ^{13}C HMBC experiments. Coupling constants (J) were measured from one-dimensional spectra, and multiplicities were abbreviated as follows: s (singlet), d (doublet), dd (doublet of doublets), q (quartet), t (triplet), m (multiplet). IR spectra were recorded on a two-beam Bruker Vertex 70 spectrometer, in a microlayer from chloroform. The C, H, N microanalyses were performed on a Flash EA 1112 CHNS-O/MAS analyzer.

Commercial samples of diethyl aminomalonate hydrochloride **2**, MeCN, Cs_2CO_3 , were used. Pyrrolylpropynoates **1a-g** were obtained as reported [B. A. Trofimov, L. N. Sobenina, Z. V. Stepanova, O. V. Petrova, I. A. Ushakov, A. I. Mikhaleva, *Tetrahedron Lett.*, 2008, **459**, 3946].

Ethyl 3-(1-ethyl-1H-pyrrol-2-yl)propynoate (1b)

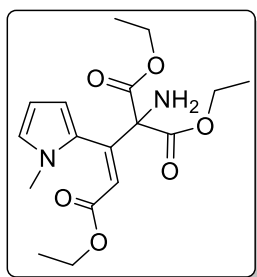


Yield 134 mg (70%); yellow oil. Calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_2$: C, 69.09; H, 6.85; N, 7.32%. Found: C, 69.27; H, 6.96; N, 7.48%. ν_{max} (film), cm^{-1} : 2982, 2936, 2873, 2855, 2199, 1700, 1530, 1476, 1461, 1444, 1388, 1366, 1324, 1241, 1173, 1064, 1034, 860, 798, 744, 732, 660, 609. ^1H NMR (400 MHz, CDCl_3) δ 6.83–6.81 (m, 1H of H5-pyrrole), 6.72–6.70 (m, 1H of H3-pyrrole), 6.14–6.13 (m, 1H of H4-pyrrole), 4.28 (d, J = 7.0 Hz, 2H, CH_2CH_3), 4.07 (d, J = 7.3 Hz, 2H, OCH_2CH_3), 1.43 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.34 (t, J = 7.1 Hz, 3H, OCH_2CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ 154.6, 125.0, 120.5, 111.6, 109.3, 87.2, 80.1, 61.9, 43.1, 16.6, 14.3.

The synthesis of C-adducts 3a-g (typical procedure)

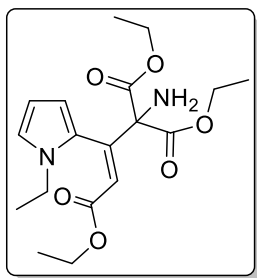
A suspension of diethyl aminomalonate hydrochloride **2** (211 mg, 1 mmol) and Cs_2CO_3 (648 mg, 2 mmol) in MeCN (50 mL) was stirred at 20-25 °C for 30 min. Then solution of pyrrolylpropynoates **1a-g** (1 mmol) in acetonitrile (50 mL) was added dropwise within 10 min. The reaction mixture was stirred at 80 °C for 6 h. The reaction was monitored using ^1H NMR (until the signals of the starting propynoates **1a-g** completely disappeared). After the reaction completion, the mixture was diluted with water (150 mL) and extracted with diethyl ether (4 x 30 mL). The ethereal extracts were washed with water (3 x 20 mL) and dried over CaCl_2 . The residue, after removing solvent, was fractionated by column chromatography (SiO_2 , *n*-hexane: diethyl ether, 1 : 1) to afford pure products **3a-g**.

Triethyl (Z)-1-amino-2-(1-methyl-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3a**)



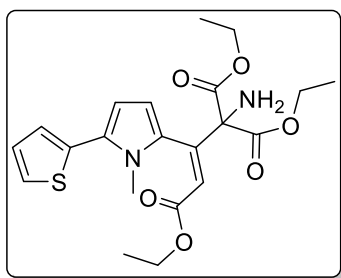
Yield 194 mg (55%); yellow oil. Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_6$: C, 57.94; H, 6.87; N, 7.95%. Found: C, 58.1; H, 7.02; N, 8.05%. ν_{max} (film), cm^{-1} : 3630, 3392, 3321, 3104, 2983, 2942, 2361, 2202, 1959, 1732, 1633, 1594, 1532, 1470, 1447, 1368, 1254, 1157, 1095, 1030, 906, 859, 791, 719, 650, 606. ^1H NMR (400 MHz, CDCl_3) δ 6.67-6.65 (m, 1H of H5-pyrrole), 6.52 (s, 1H of =CH), 6.10-6.08 (m, 1H of H3-pyrrole), 6.03-6.02 (m, 1H of H4-pyrrole), 4.29-4.20 (m, 4H of $2\text{CH}_2\text{CH}_3$), 3.72 (d, $J = 7.0$ Hz, 4H, $2\text{CH}_2\text{CH}_3$), 4.05 (d, $J = 7.2$ Hz, 2H, CH_2CH_3), 3.44 (s, 3H of N- CH_3), 1.86 (br.s, 2H of NH_2), 1.24 (t, 6H of $2\text{CH}_2\text{CH}_3$), 1.14 (t, 3H of CH_2CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 165.1 (2C), 145.9, 126.6, 125.4, 123.4, 120.4, 109.0, 107.7, 62.6 (2C), 60.5, 34.3, 14.2, 14.1 (2C).

Triethyl (Z)-1-amino-2-(1-ethyl-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3b**)



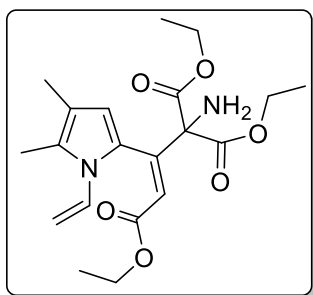
Yield 191 mg (52%); yellow oil. Calcd for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_6$: C, 59.00; H, 7.15; N, 7.65%. Found: C, 59.20; H, 7.31; N, 7.76%. ν_{max} (film), cm^{-1} : 3393, 3313, 2983, 2925, 1734, 1628, 1465, 1395, 1368, 1339, 1222, 1157, 1095, 1067, 1026, 906, 859, 798, 776, 616. ^1H NMR (400 MHz, CDCl_3) δ 6.78-6.77 (m, 1H of H5-pyrrole), 6.51 (s, 1H of =CH), 6.15-6.13 (m, 1H of H3-pyrrole), 5.95-5.93 (m, 1H of H4-pyrrole), 4.31-4.16 (m, 4H, $2\text{COOCH}_2\text{CH}_3$), 4.03 (q, $J = 7.1$ Hz, 2H, $=\text{CCOOCH}_2\text{CH}_3$), 3.78-3.71 (m, 2H of N- CH_2CH_3), 2.20 (br.s, 2H of NH_2), 1.35 (t, $J = 7.3$ Hz, 3H, N- CH_2CH_3), 1.28-1.21 (m, 6H, $2\text{COOCH}_2\text{CH}_3$), 1.12 (t, $J = 7.1$ Hz, 3H, $=\text{CCOOCH}_2\text{CH}_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 170.3, 169.7, 164.8 (2C), 145.5, 125.9, 125.8, 120.4, 108.3, 107.9, 62.5 (2C), 60.3, 41.2, 15.6, 14.0, 13.9 (2C).

Triethyl (Z)-1-amino-2-(1-methyl-5-(thiophen-2-yl)-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (3c)



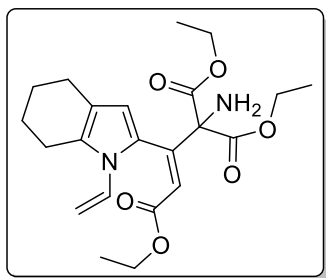
Yield 282 mg (65%); yellow oil. Calcd for $C_{21}H_{26}N_2O_6S$: C, 58.05; H, 6.03; N, 6.45; S, 7.38%. Found: C, 58.2; H, 6.18; N, 6.65; S, 7.21%. $\nu_{\max}$ (film), cm^{-1} : 3390, 3318, 3107, 2980, 2928, 1731, 1633, 1574, 1445, 1368, 1260, 1096, 1029, 845, 801, 701. 1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.26 (m, 1H of thiophene), 7.08-7.03 (m, 2H of thiophene), 6.59 (s, 1H of =CH), 6.31 (d, $J = 3.8$ Hz, 1H of pyrrole), 6.11 (d, $J = 3.8$ Hz, 1H of pyrrole), 4.25-4.22 (m, 4H of $2CH_2CH_3$), 4.07 (q, $J = 7.0$ Hz, 2H CH_2CH_3), 3.51 (s, 3H of N- CH_3), 2.27 (br.s. 2H of NH_2), 1.28-1.24 (m, 6H of $2CH_2CH_3$), 1.13 (t, $J = 7.1$ Hz, 3H of CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 165.0 (2C), 147.1, 145.0, 135.3, 128.8, 128.5, 127.3, 125.9, 125.1, 124.6, 109.6, 108.9, 62.6, 60.5 (2C), 32.8, 14.0, 13.9 (2C).

Triethyl (Z)-1-amino-2-(4,5-dimethyl-1-vinyl-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (3d).



Yield 267 mg (68%); brown oil. Anal. Calcd for $C_{20}H_{28}N_2O_6$: C, 61.21; H, 7.19; N, 7.14%. Found: C, 61.03; H, 7.02; N, 7.10%. $\nu_{\max}$ (film), cm^{-1} : 3389, 3322, 3113, 2981, 2924, 1732, 1644, 1465, 1446, 1423, 1378, 1368, 1300, 1256, 1185, 1158, 1102, 1096, 1031, 969, 865, 810, 630. 1H NMR (400.13 MHz, $CDCl_3$): δ 6.65 (dd, $J = 16.0$, 9.1 Hz, 1H, H_x), 6.31 (m, 1H, H-3, pyrrole), 5.92 (s, 1H, =CH), 5.06 (d, $J = 16.0$ Hz, 1H, H_a), 4.77 (d, $J = 9.1$ Hz, 1H, H_b), 4.26-4.18 (m, 4H, $2OCH_2$), 4.01 (q, $J = 7.1$ Hz, 2H, =CC(O)OCH₂), 2.25 (br. s., 2H, NH_2), 2.20 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.25-1.22 (m, 6H, CH_3), 1.11 (t, $J = 7.1$ Hz, 3H, =CC(O)CH₂CH₃). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 160.0, 165.1 (2C), 145.3, 131.5, 127.0, 124.8, 124.5, 116.6, 111.9 (2C), 105.0, 62.6 (2C), 60.4, 14.1 (2C), 14.0, 11.7, 11.4.

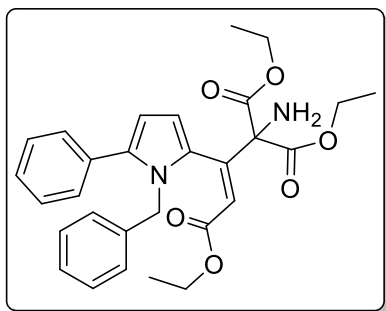
Triethyl (Z)-1-amino-2-(1-vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)prop-2-ene-1,1,3-tricarboxylate (3e).



Yield 305 mg (73%); brown oil. Anal. Calcd for $C_{22}H_{30}N_2O_6$: C, 63.14; H, 7.23; N, 6.69%. Found: C, 63.29; H, 7.37; N, 6.87%. $\nu_{\max}$ (film), cm^{-1} : 3392, 3321, 2939, 2934, 2851, 1732, 1710, 1643, 1582, 1466, 1437, 1385, 1368, 1253, 1209, 1185, 1156, 1096, 1032, 969, 863, 810, 637. 1H NMR (400.13 MHz, $CDCl_3$): 6.66 (dd, $J = 16.1$, 9.3 Hz, 1H, H_x), 6.36 (s, 1H, H-3, pyrrole), 5.92 (s, 1H, =CH), 4.97 (d, $J = 16.1$ Hz, 1H, H_a), 4.67 (d, $J = 9.3$ Hz, 1H, H_b), 4.27-4.22 (m, 4H, OCH₂), 4.01 (q, $J = 7.1$

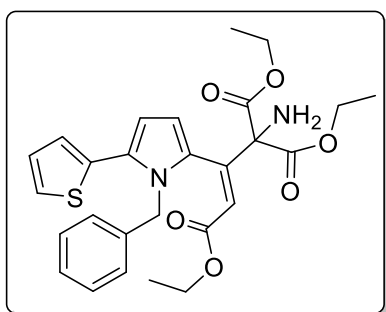
Hz, 2H, =CC(O)OCH₂), 2.73-2.62 (m, 2H, CH₂-7), 2.54-2.43 (m, 2H, CH₂-4), 2.35-2.20 (m, 2H, CH₂-6), 1.92-1.77 (m, 2H, CH₂-5), 1.70 (br. s, 2H, NH₂), 1.25-1.21 (m, 6H, CH₃), 1.10 (t, *J* = 7.1 Hz, 3H, =CC(O)OCH₂CH₃). ¹³C NMR (100.6 MHz, DMSO-d₆): δ 169.4 (2C), 164.3, 145.0, 130.9, 128.6, 125.6, 123.9, 118.1, 109.2, 102.0, 71.4, 61.7 (2C), 59.8, 24.0, 23.3, 22.8 (2C), 13.7, 13.5 (2C).

Triethyl (Z)-1-amino-2-(1-benzyl-5-phenyl-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (3f).



Yield 328 mg (65%); yellow oil. Anal. Calcd for C₂₉H₃₂N₂O₆: C, 69.03; H, 6.39; N, 5.55%. Found: C, 69.19; H, 6.49; N, 5.72%. *v*_{max} (film), cm⁻¹: 3390, 3322, 2924, 2854, 2249, 1959, 1732, 1603, 1454, 1368, 1194, 1096, 1029, 859, 757, 700. ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.27 (m, 6H of phenyl), 7.14-7.12 (m, 2H of phenyl), 6.87-6.85 (m, 2H of phenyl), 6.3jjj4 (m, 1H =CH), 6.30 (d, *J* = 3.7 Hz, 1H of pyrrole), 6.12 (d, *J* = 3.7 Hz, 1H of pyrrole), 5.11 (dd, *J* = 52.0, 16.0 Hz, 2H of CH₂Ph), 4.27-4.17 (m, 4H of 2CH₂CH₃), 4.08 (q, *J* = 7.1 Hz, 2H of CH₂CH₃), 1.72 (br.s, 2H of NH₂), 1.21-1.17 (m, 6H of 2CH₂CH₃), 0.88-0.84 (m, 3H of CH₂CH₃). ¹³C NMR (100.6 MHz, CDCl₃): δ 169.0, 164.9 (2C), 152.7, 142.2, 138.7, 137.7, 133.7, 129.4 (2C), 129.0, 128.5 (2C), 128.3 (2C), 127.3, 127.3 (2C), 127.1, 126.1, 110.8, 109.8, 62.8, 60.7 (2C), 48.9, 14.2, 14.0 (2C).

Triethyl (Z)-1-amino-2-(1-benzyl-5-(thiophen-2-yl)-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (3g).

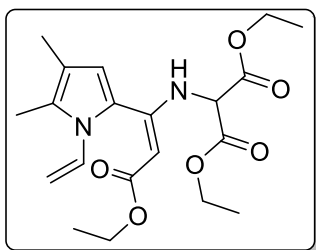


Yield 332 mg (65%); yellow oil. Anal. Calcd for C₂₇H₃₀N₂O₆S: C, 63.51; H, 5.92; N, 5.49; S, 6.28%. Found: C, 63.69; H, 6.09; N, 5.68; S, 6.09%. *v*_{max} (film), cm⁻¹: 3390, 3321, 3107, 2982, 2934, 1732, 1606, 1446, 1368, 1196, 1096, 1029, 845, 696. ¹H NMR (400 MHz, CDCl₃) δ 7.21-7.14 (m, 4H, 1H of phenyl, 3H of thiophene), 6.98-6.94 (m, 2H of phenyl), 6.92-6.88 (m, 2H, of phenyl), 6.41 (d, *J* = 3.8 Hz, 1H of pyrrole), 6.39 (s, 1H of =CH), 6.09 (d, *J* = 3.8 Hz, 1H of pyrrole), 5.17 (dd, *J* = 48.0, 20.0 Hz, 2H of CH₂Ph), 4.21-4.10 (m, 4H of 2CH₂CH₃), 4.00-3.96 (m, 2H of CH₂CH₃), 2.22 (br.s, 2H of NH₂), 1.26-1.21 (m, 6H of 2CH₂CH₃), 1.11 (t, *J* = 7.1 Hz, 3H of CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 169.6, 164.8 (2C), 160.1, 144.6, 138.4, 134.9, 129.2, 128.4 (2C), 128.2, 127.3, 127.1, 127.0 (3C), 125.8, 125.2, 111.0, 110.3, 62.76 (d, *J* = 17.0 Hz of CH₂Ph), 60.6 (2C), 48.8, 14.1 (2C), 14.0.

The synthesis of N-adduct: diethyl (*E*)-2-((1-(4,5-dimethyl-1-vinyl-1*H*-pyrrol-2-yl)-3-ethoxy-3-oxoprop-1-en-1-yl)amino)malonate (4**) (typical procedure)**

A suspension of diethyl aminomalonate hydrochloride **2** (423 mg, 2 mmol) and Cs₂CO₃ (650 mg, 2 mmol) in acetonitrile (50 mL) was stirred at 20-25 °C for 30 min. Then a solution of ethyl 3-(4,5-dimethyl-1-vinyl-1*H*-pyrrol-2-yl)propynoate **1d** (217 mg, 1 mmol) in acetonitrile (50 mL) was added dropwise within 10 min. The mixture was stirred at 80 °C for 6 h. The reaction was monitored using ¹H NMR (until the signals of the starting propiolate **1d** completely disappeared). After the reaction completion, the mixture was diluted with water (150 mL) and extracted with diethyl ether (4 x 30 mL). The ethereal extracts were washed with water (3 x 20 mL) and dried over CaCl₂. The residue, after removing the solvent, was fractionated by column chromatography (SiO₂, *n*-hexane: diethyl ether, 1 : 1) to afford the title compound **4**.

Diethyl (*E*)-2-((1-(4,5-dimethyl-1-vinyl-1*H*-pyrrol-2-yl)-3-ethoxy-3-oxoprop-1-en-1-yl)amino)malonate (4**).**

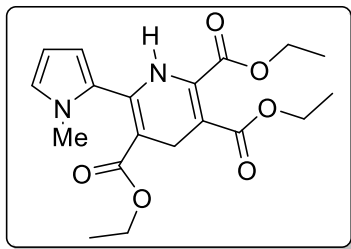


Yield 283 mg (72%); brown oil. Anal. Calcd for C₂₀H₂₈N₂O₆: C, 61.21; H, 7.19; N, 7.14%. Found: C, 61.04; H, 7.00; N, 7.06%. $\nu_{\max}$ (film), cm⁻¹: 3366, 3274, 2931, 2926, 2871, 1761, 1739, 1631, 1613, 1587, 1516, 1467, 1396, 1369, 1302, 1255, 1151, 1096, 1029, 966, 891, 861, 796, 734, 706, 633, 496. ¹H NMR (400.13 MHz, CDCl₃): δ 9.03 (d, *J* = 8.00 Hz, 1H, NH), 6.70 (dd, *J* = 15.9, 9.1 Hz, 1H, H_x), 6.04 (s, 1H, H-3, pyrrole), 5.08 (d, *J* = 15.9 Hz, 1H, H_a), 4.86-4.84 (m, 2H, =CH, NCH), 4.56 (d, *J* = 9.3 Hz, 1H, H_b), 4.20-4.14 (m, 6H, OCH₂), 2.18 (s, 3H, CH₃), 1.96 (s, 3H, CH₃), 1.29-1.21 (m, 9H, CH₃). ¹³C NMR (100.6 MHz, CDCl₃): δ 169.8 (2C), 166.8, 153.4, 130.3, 128.5, 124.3, 116.8, 115.3, 105.8, 90.5, 62.3 (2C), 61.1, 59.2, 14.6, 14.1 (2C), 11.2, 11.1.

The synthesis of pyrrolyl-1,4-dihydropyridines **6a,b (typical procedure)**

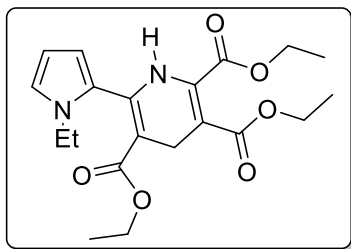
A suspension of diethyl aminomalonate hydrochloride **2** (211 mg, 1 mmol) and Cs₂CO₃ (650 mg, 2 mmol) in acetonitrile (50 mL) was stirred at 20-25 °C for 30 min. Then solution of pyrrolylpropynoates **1a,b** (1 mmol) in acetonitrile (50 mL) was added dropwise within 10 min. In the course of the addition, ethyl 3-bromopropiolate **5** (177 mg, 1 mmol) was also added. The reaction mixture was stirred at 80 °C for 6 h. The reaction was monitored using ¹H NMR (until the signals of the starting propynoate **1a,b** completely disappeared). After the reaction completion, the mixture was diluted with water (150 mL) and extracted with diethyl ether (4 x 30 mL). the ethereal extracts were washed with water (3 x 20 mL) and dried over CaCl₂. The residue, after removing solvent, was fractionated by column chromatography (SiO₂, *n*-hexane: diethyl ether, 1 : 1) to afford of correspondently pyrrolyldihydropyridines **6a,b**.

Triethyl 6-(1-methyl-1H-pyrrol-2-yl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6a).



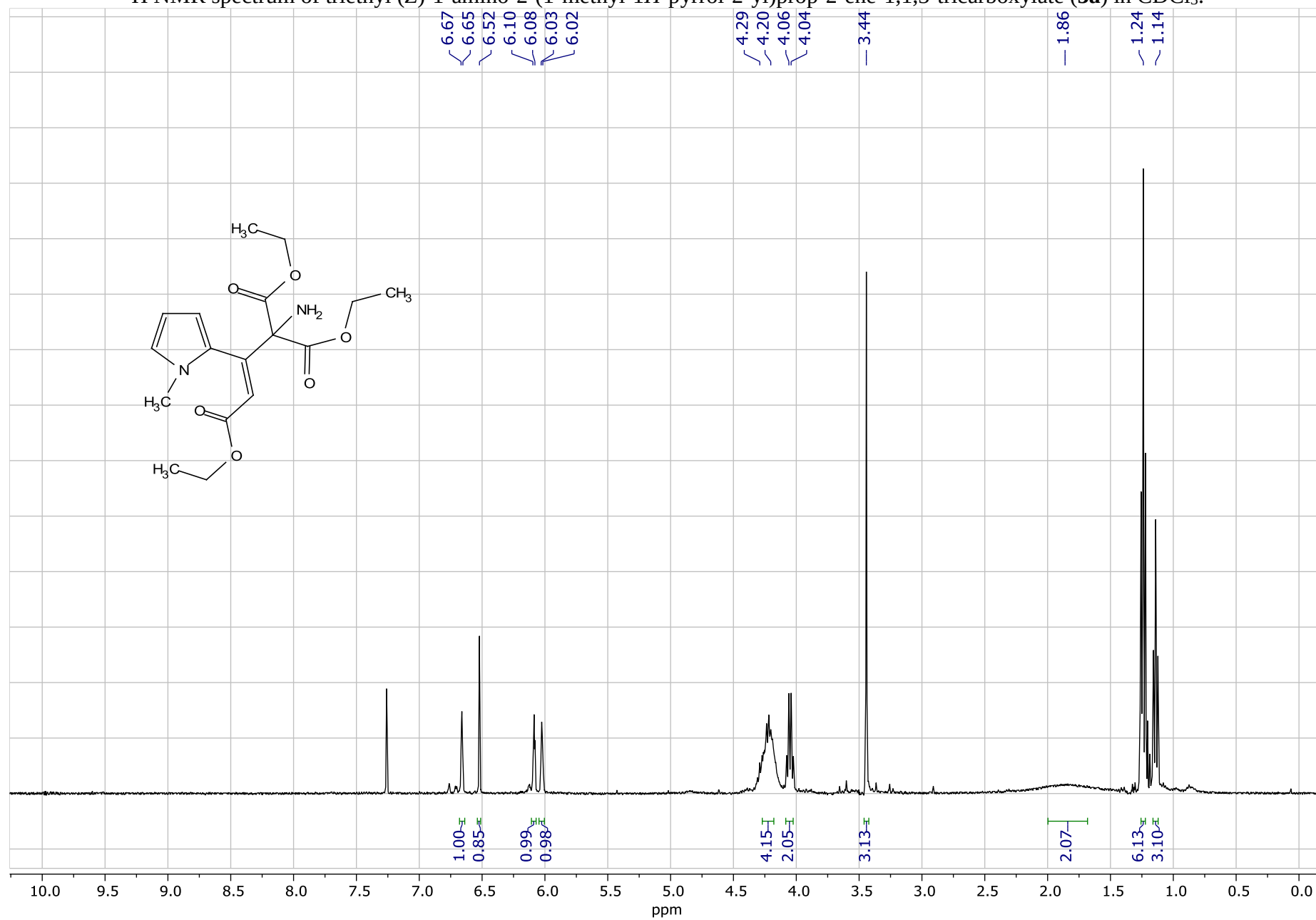
Yield 263 mg (70%); brown oil. Anal. Calcd for $C_{19}H_{24}N_2O_6$: C, 60.63; H, 6.43; N, 7.44 %. Found: C, 60.41; H, 6.26; N, 7.29%. $\nu_{\max}$ (film), cm^{-1} : 3274, 2925, 2857, 1730, 1705, 1558, 1507, 1460, 1369, 1232, 1177, 1054, 1035, 881, 856, 726, 589. ^1H NMR (400.13 MHz, CDCl_3): δ 9.10 (s, 1H, NH), 6.80-6.76 (m, 1H, H-3, pyrrole), 6.28-6.27 (m, 1H, H-5, pyrrole), 6.19-6.18 (m, 1H, H-4, pyrrole), 4.35-4.31 (m, 2H, 2-OCH₂), 4.28 (s, 2H, CH₂), 4.20-4.13 (m, 4H, 3,5-OCH₂), 3.50 (s, 3H, N-CH₃), 1.35 (t, $J = 7.1$ Hz, 3H, 2-CH₃), 1.27 (t, $J = 6.8$ Hz, 3H, 3-CH₃), 1.15 (t, $J = 7.1$ Hz, 3H, 5-CH₃). ^{13}C NMR (100.6 MHz, CDCl_3): δ 171.6, 164.0, 160.7, 131.7, 126.2, 124.2, 123.8, 120.8, 116.2, 111.0, 107.9, 60.9, 60.7, 60.0, 34.7, 31.7, 14.5, 14.4, 14.1.

Triethyl 6-(1-ethyl-1H-pyrrol-2-yl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6b).

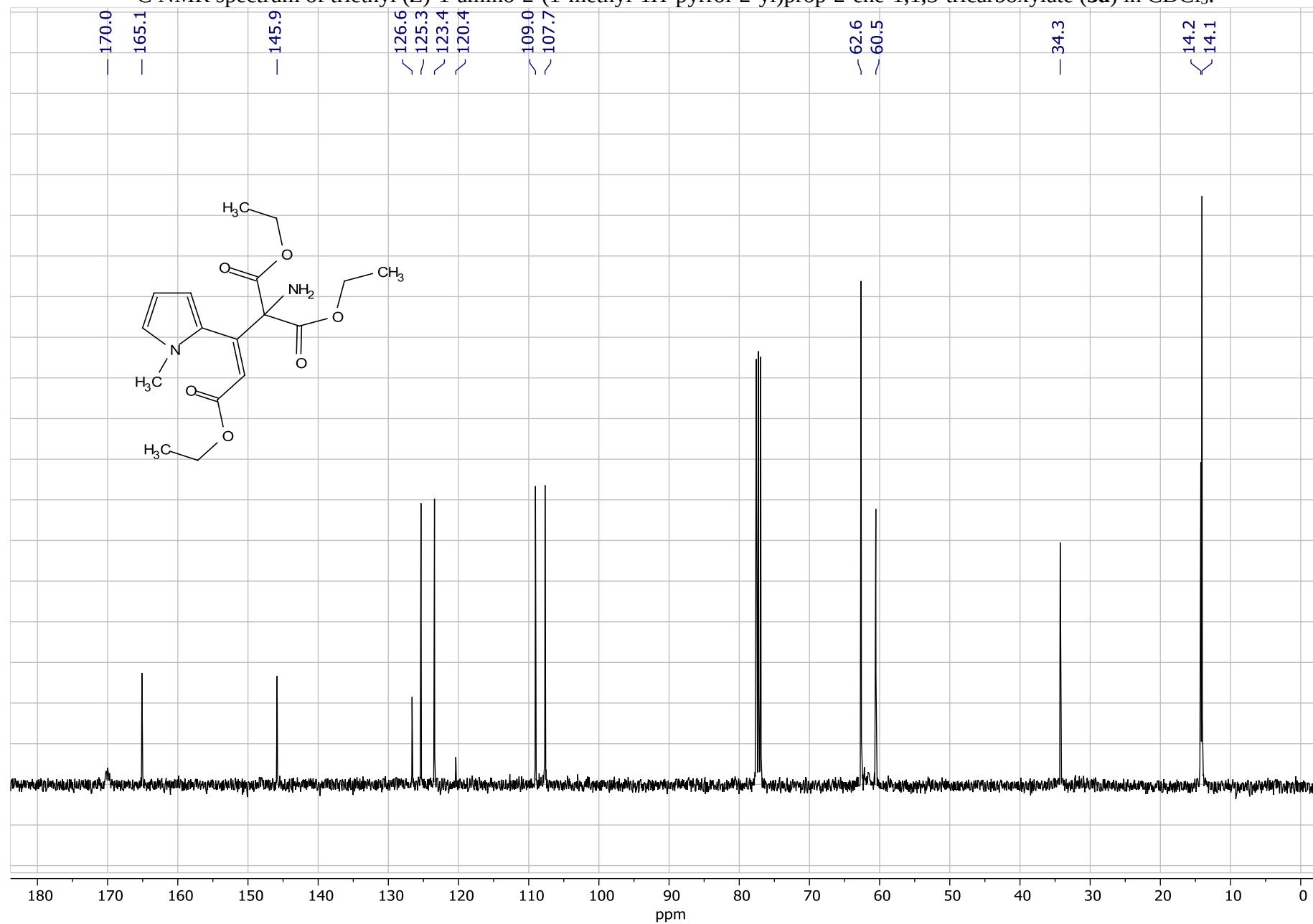


Yield 289 mg (74%); brown oil. Anal. Calcd for $C_{20}H_{26}N_2O_6$: C, 61.53; H, 6.71; N, 7.18%. Found: C, 61.37; H, 6.48; N, 7.02%. $\nu_{\max}$ (film), cm^{-1} : 3276, 2982, 2938, 2905, 1737, 1712, 1555, 1467, 1407, 1368, 1337, 1301, 1267, 1180, 1040, 861, 719, 614. ^1H NMR (400.13 MHz, CDCl_3): δ 9.11 (s, 1H, NH), 6.84-6.83 (m, 1H, H-3, pyrrole), 6.25-6.24 (m, 1H, H-5, pyrrole), 6.21-6.20 (m, 1H, H-4, pyrrole), 4.32 (q, $J = 7.1$ Hz, 2H, 2-OCH₂), 4.29 (s, 2H, CH₂), 4.25-4.09 (m, 4H, 3,5-OCH₂), 3.82 (q, $J = 7.3$ Hz, 2H, N-CH₂), 1.37-1.22 (m, 9H, CH₃), 1.12 (t, $J = 7.1$ Hz, 3H, CH₃). ^{13}C NMR (100.6 MHz, CDCl_3): δ 171.6, 164.0, 160.8, 131.9, 126.1, 122.8, 121.7, 120.8, 116.2, 111.1, 107.9, 60.9, 60.6, 59.8, 42.3, 31.7, 16.4, 14.4, 14.3, 14.1.

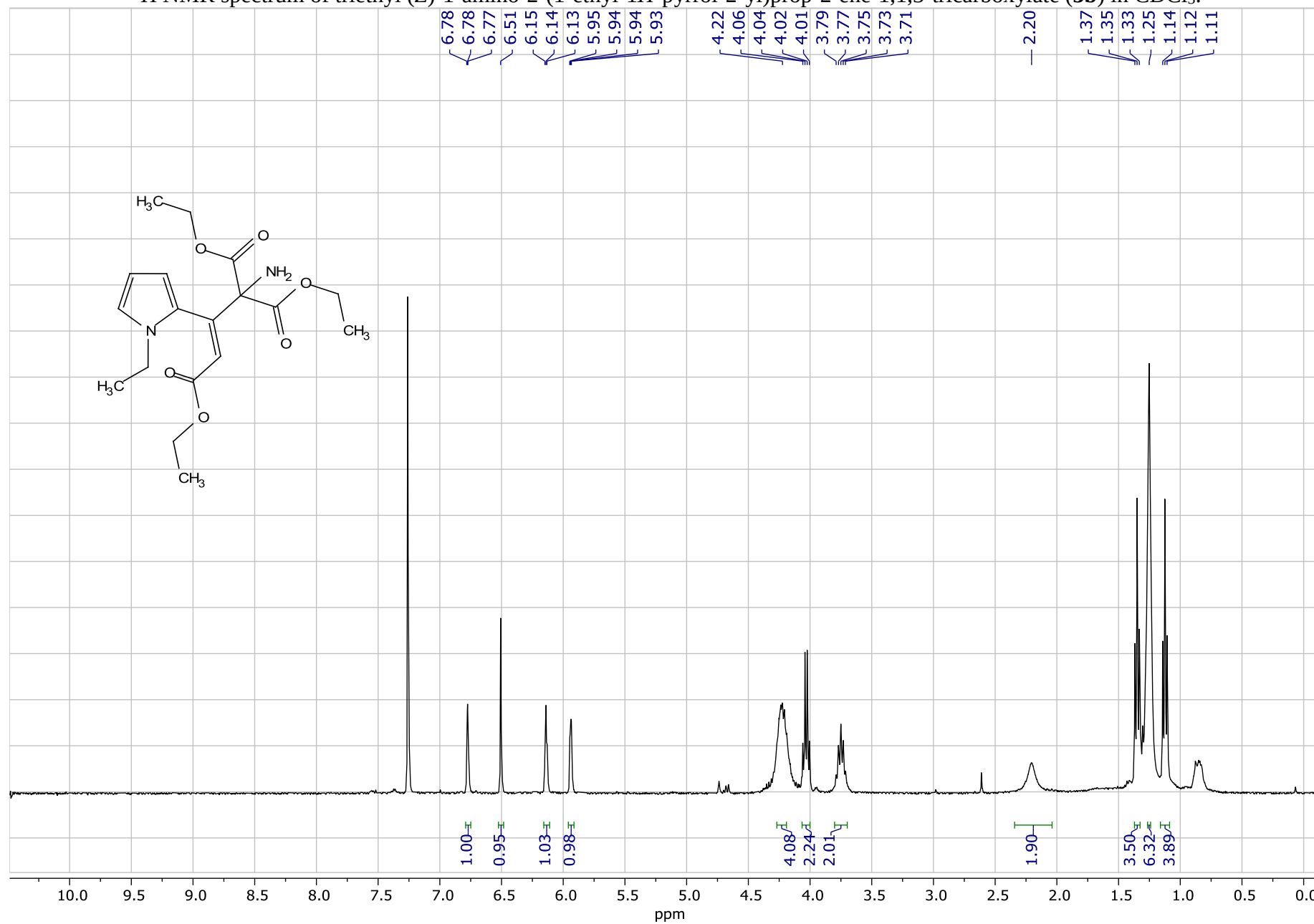
¹H NMR spectrum of triethyl (Z)-1-amino-2-(1-methyl-1*H*-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3a**) in CDCl₃.



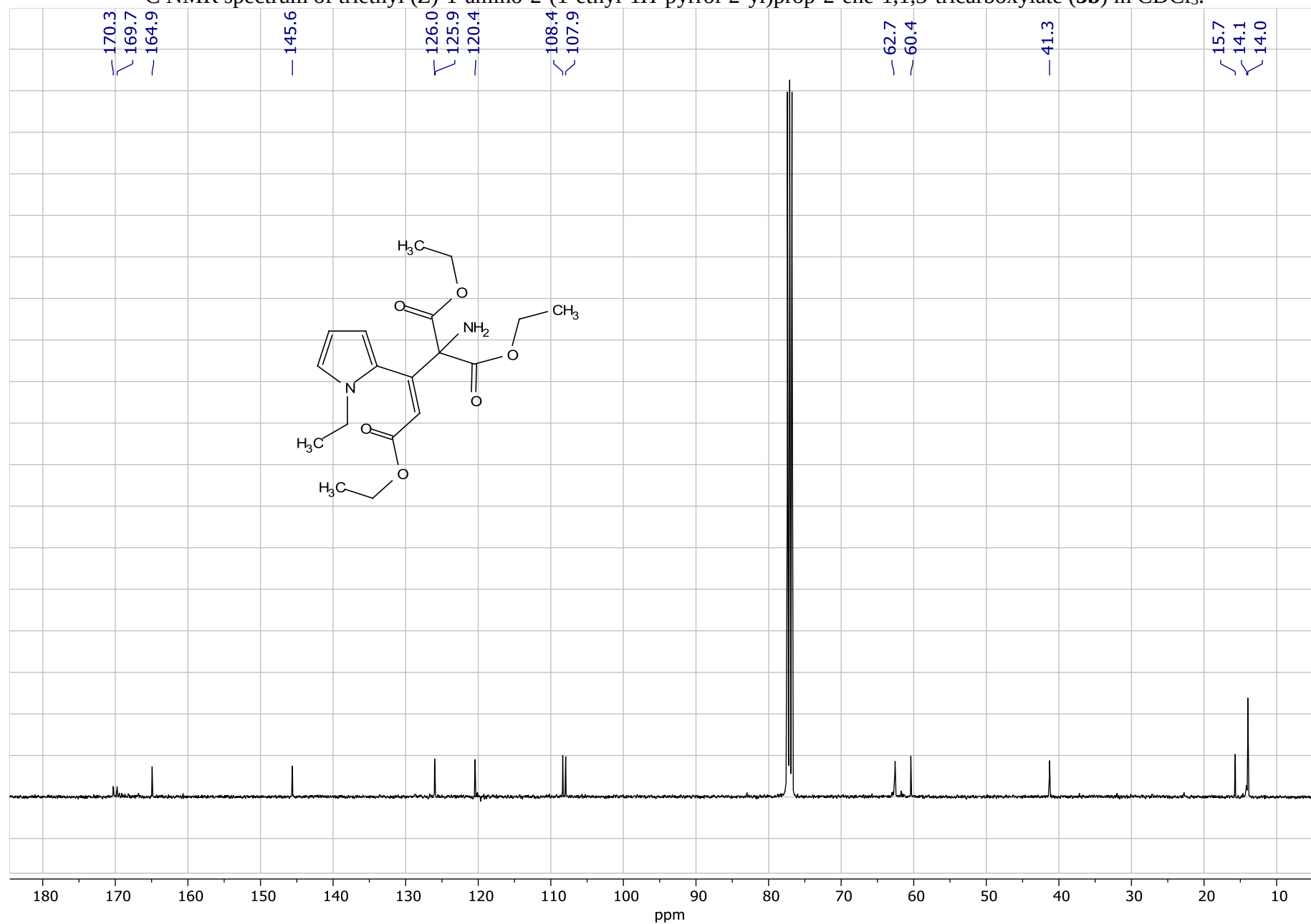
^{13}C NMR spectrum of triethyl (Z)-1-amino-2-(1-methyl-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3a**) in CDCl_3 .



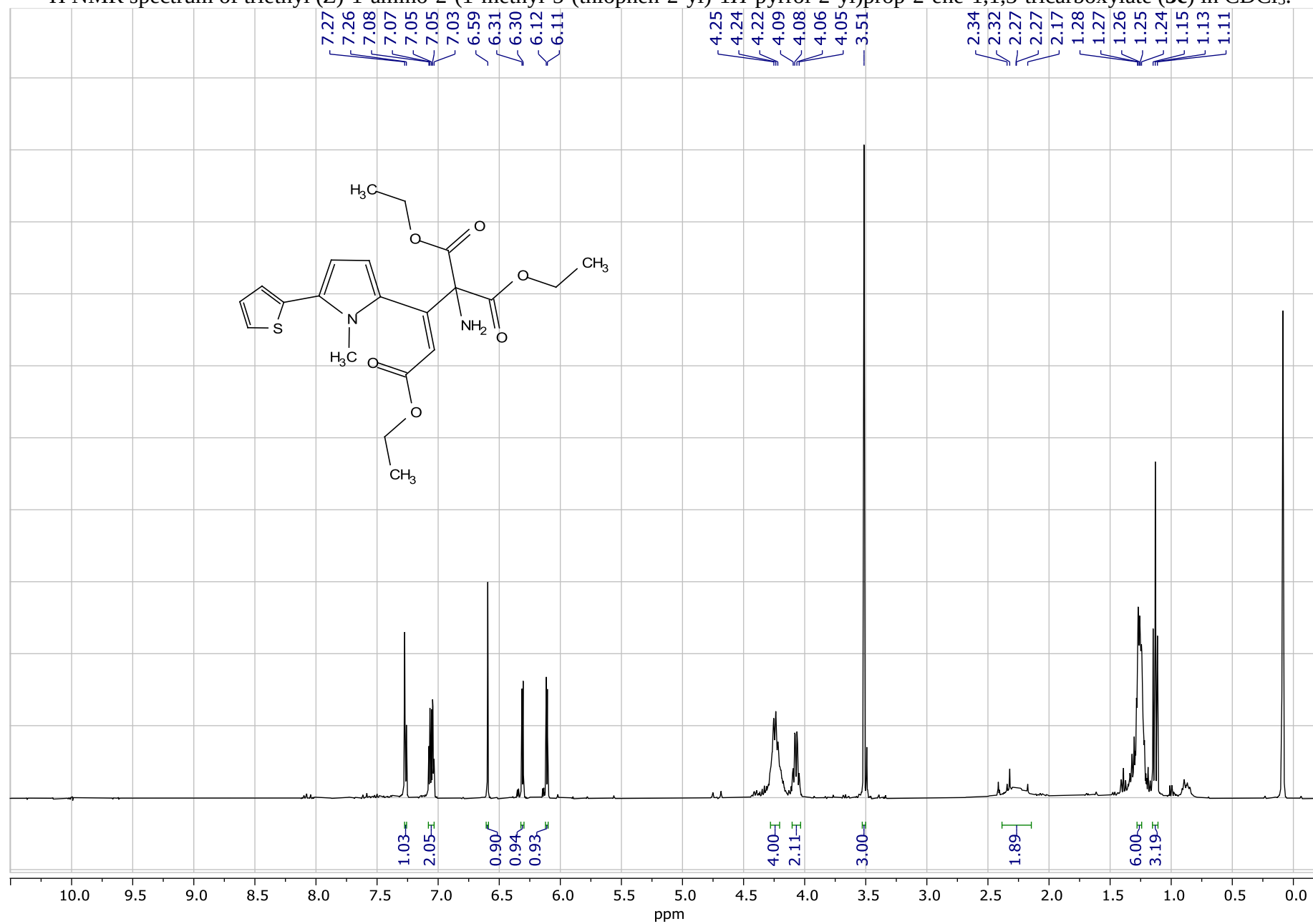
^1H NMR spectrum of triethyl (Z)-1-amino-2-(1-ethyl-1*H*-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3b**) in CDCl_3 .



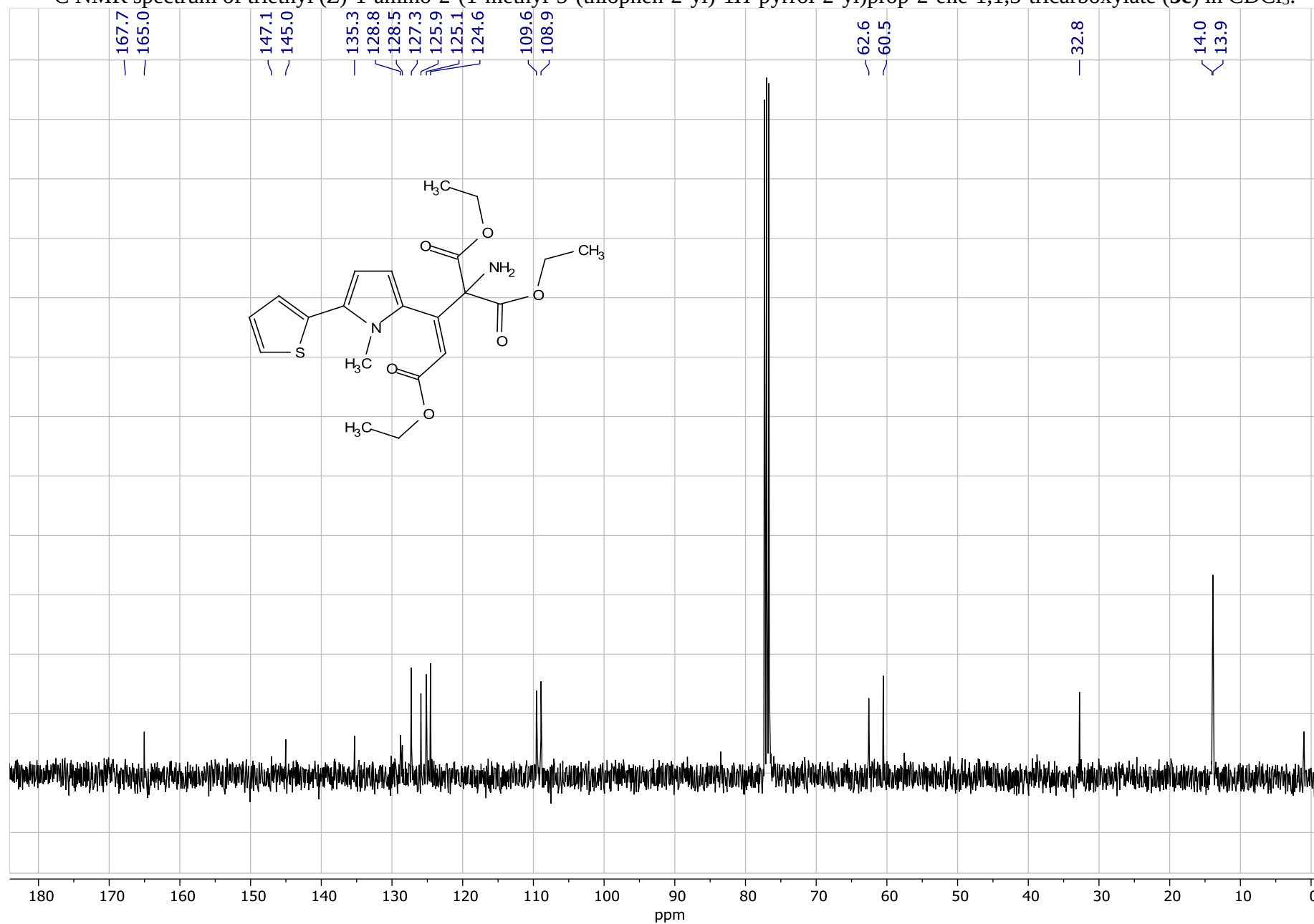
¹³C NMR spectrum of triethyl (Z)-1-amino-2-(1-ethyl-1*H*-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3b**) in CDCl₃.



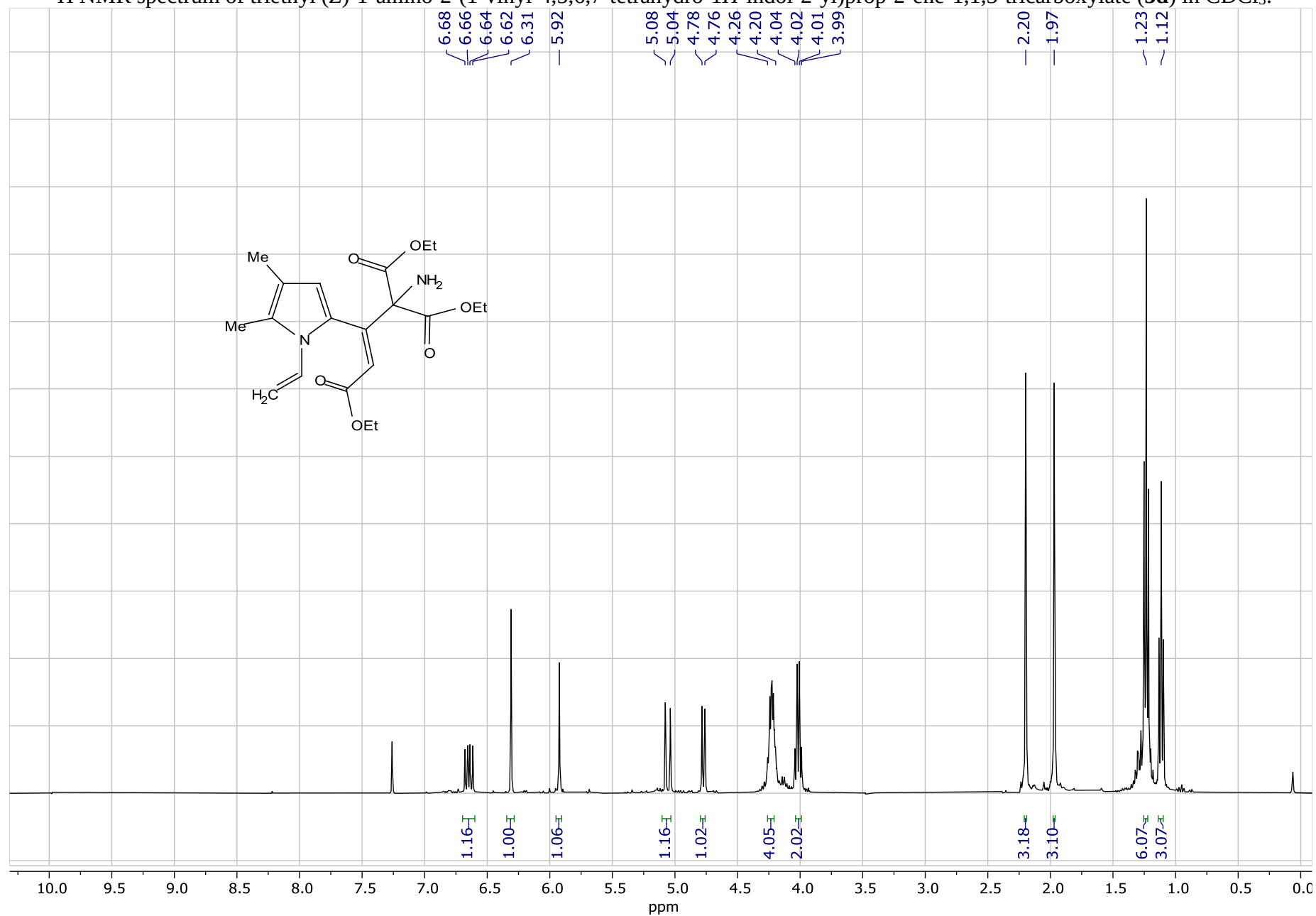
^1H NMR spectrum of triethyl (Z)-1-amino-2-(1-methyl-5-(thiophen-2-yl)-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3c**) in CDCl_3 .



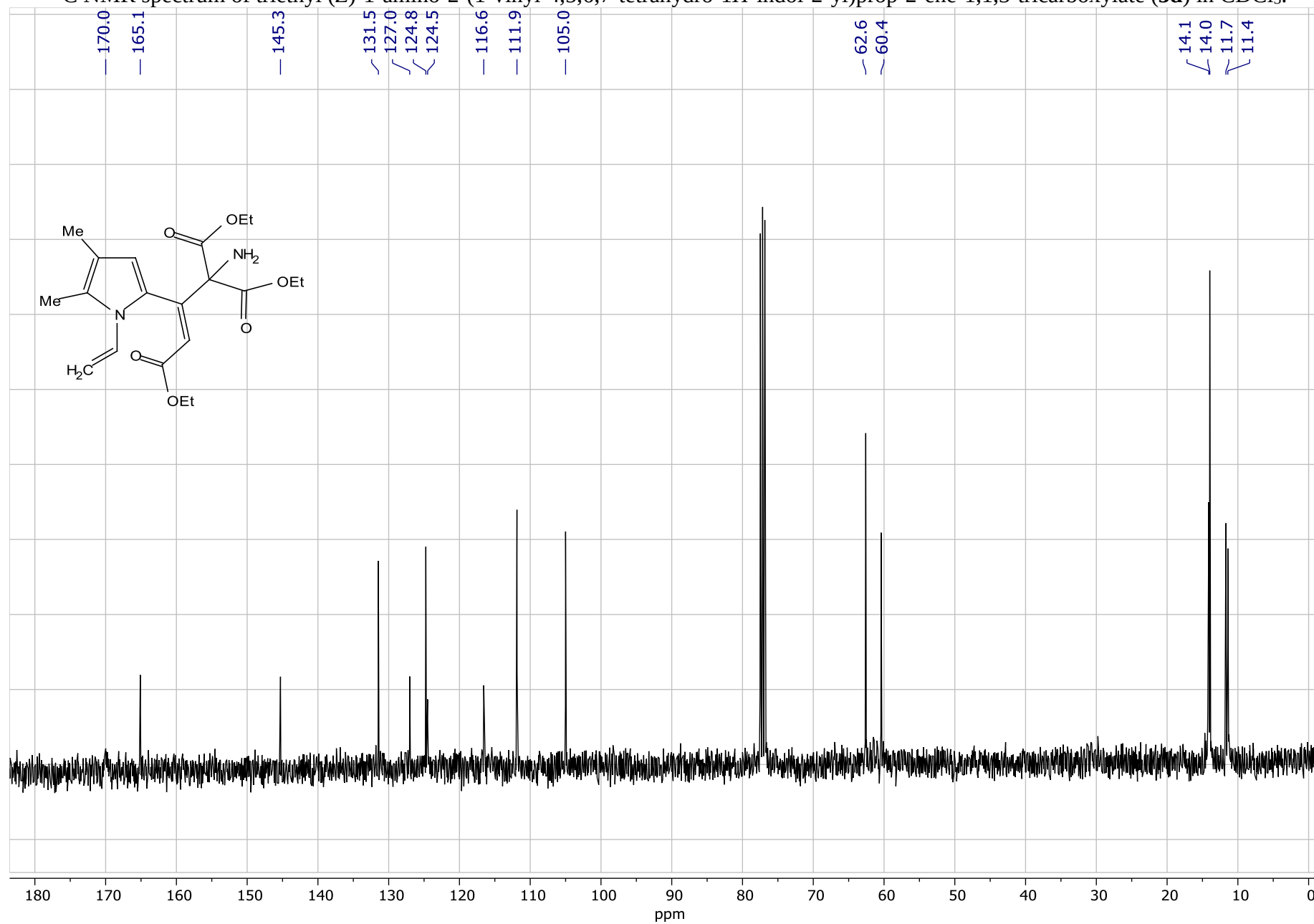
^{13}C NMR spectrum of triethyl (*Z*)-1-amino-2-(1-methyl-5-(thiophen-2-yl)-1*H*-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3c**) in CDCl_3 .



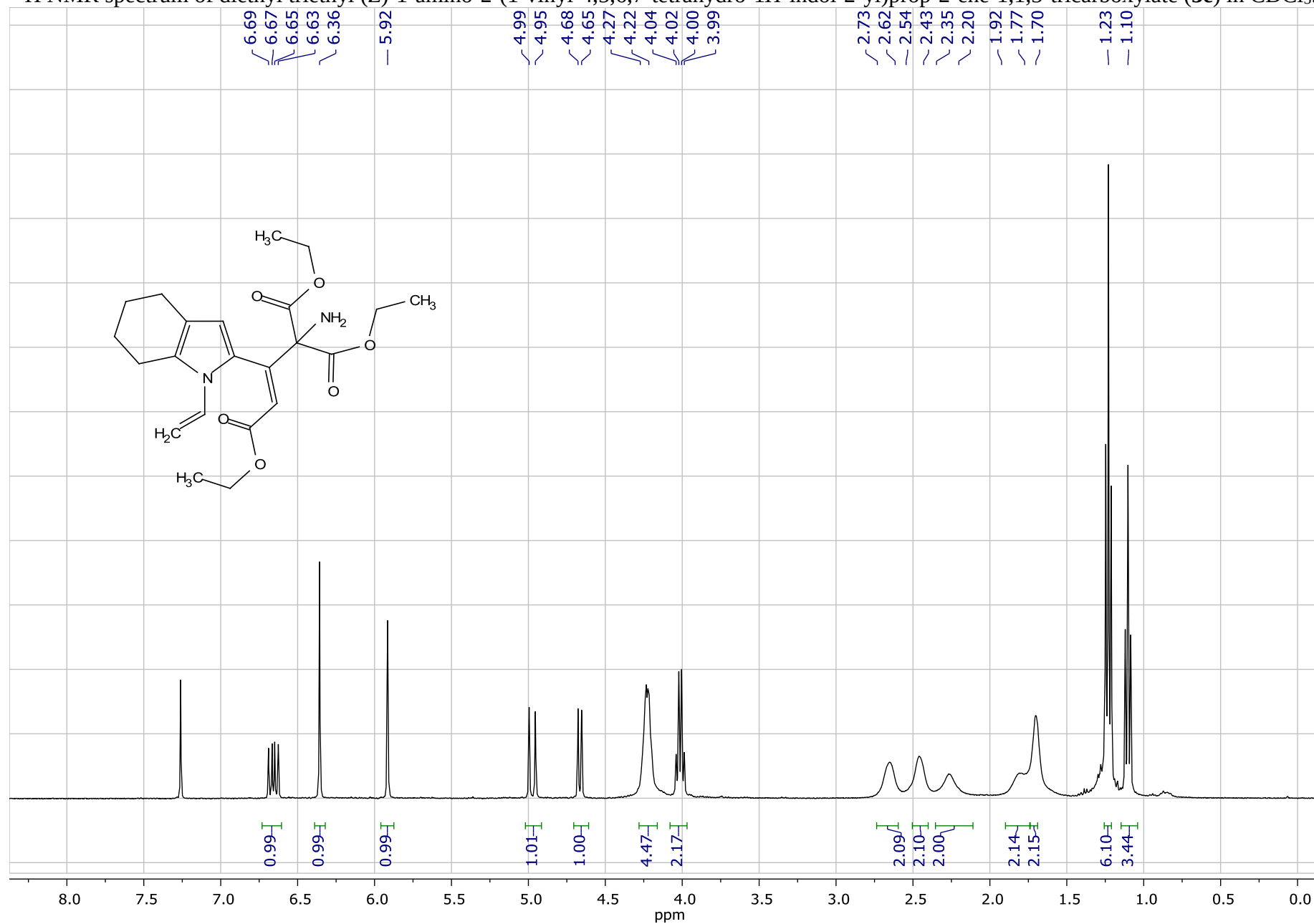
¹H NMR spectrum of triethyl (*Z*)-1-amino-2-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3d**) in CDCl₃.



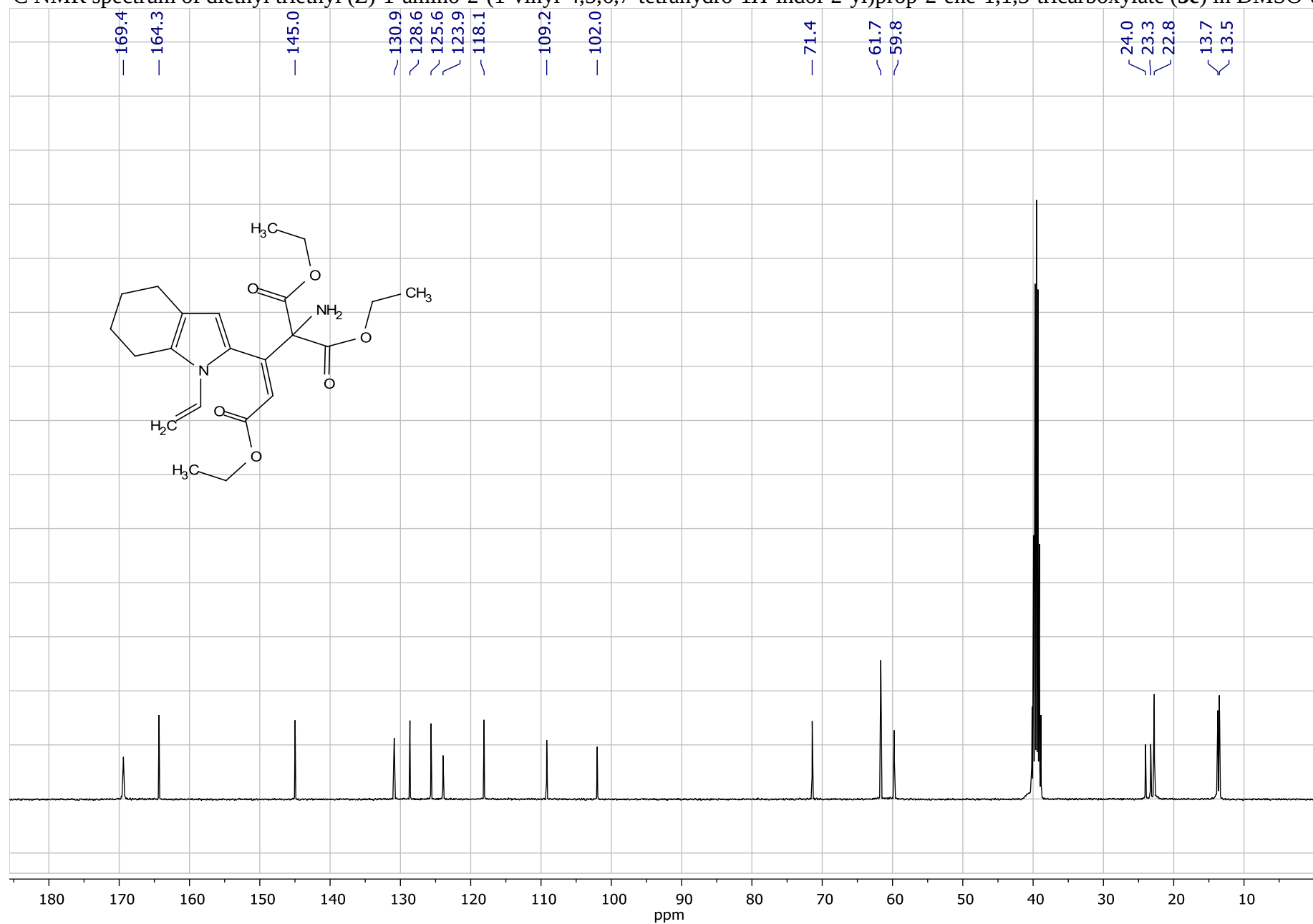
^{13}C NMR spectrum of triethyl (Z)-1-amino-2-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3d**) in CDCl_3 .



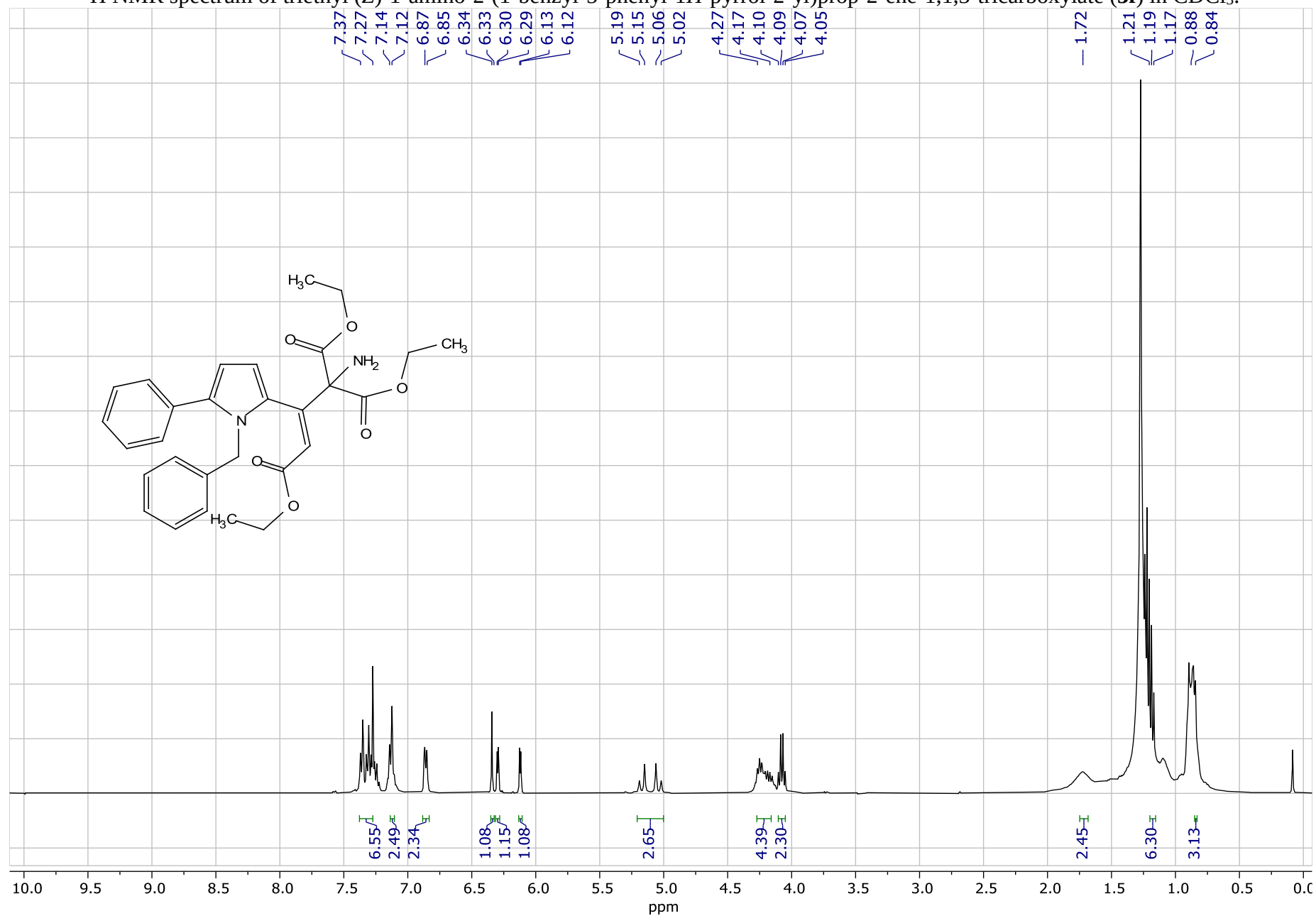
^1H NMR spectrum of diethyl triethyl (Z)-1-amino-2-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3e**) in CDCl_3 .



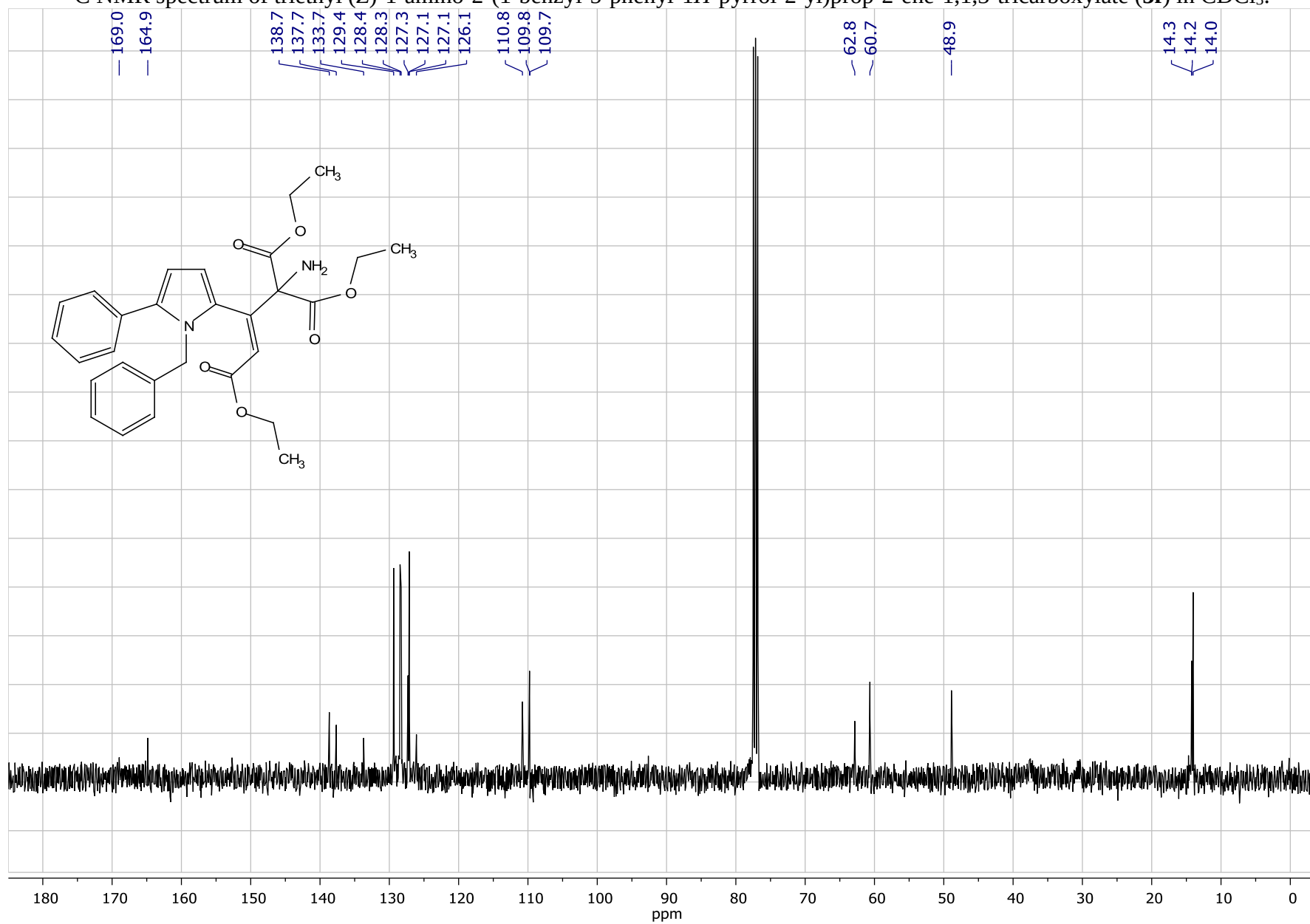
¹³C NMR spectrum of diethyl triethyl (Z)-1-amino-2-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3e**) in DMSO-d₆.



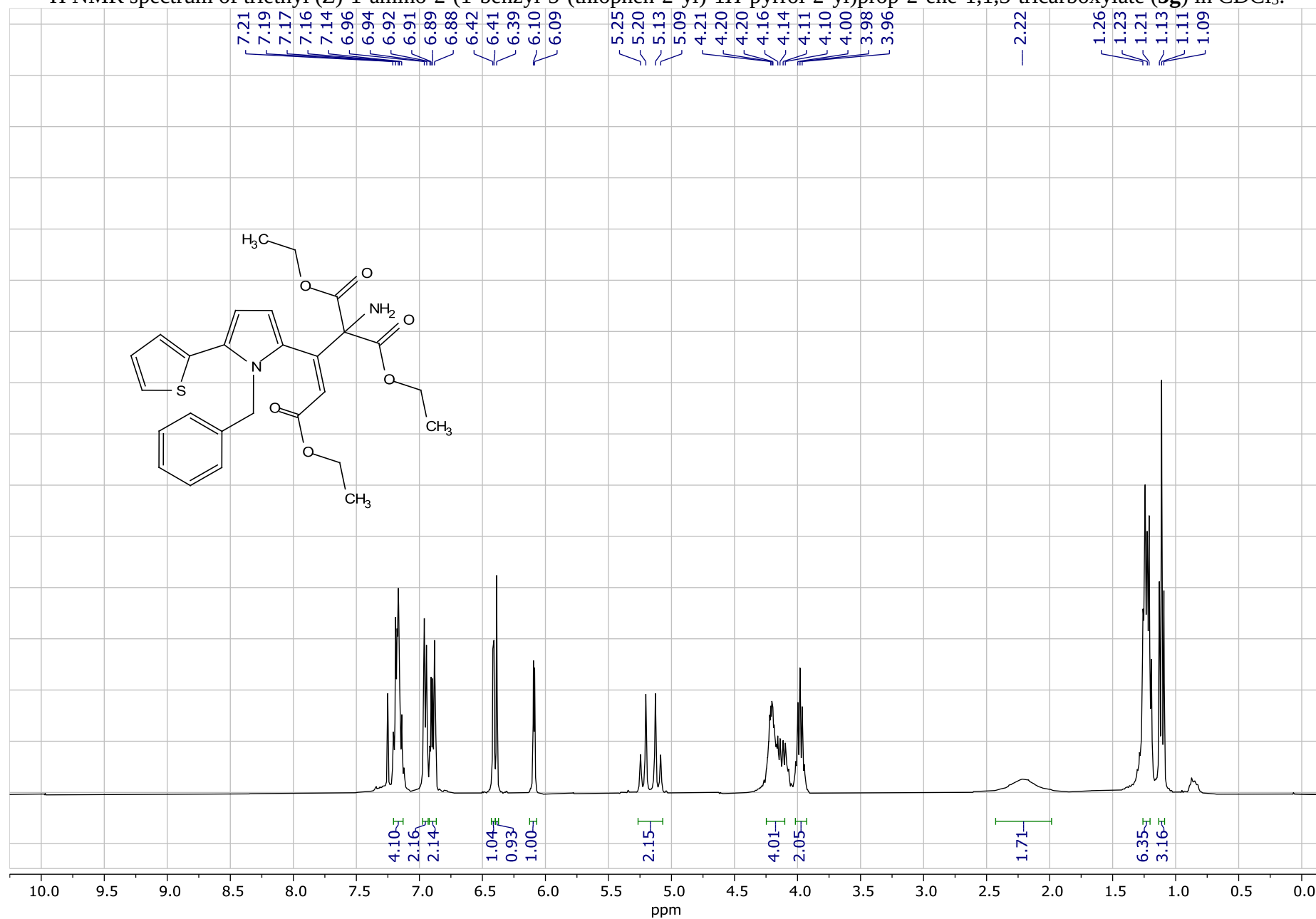
¹H NMR spectrum of triethyl (Z)-1-amino-2-(1-benzyl-5-phenyl-1*H*-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3f**) in CDCl₃.



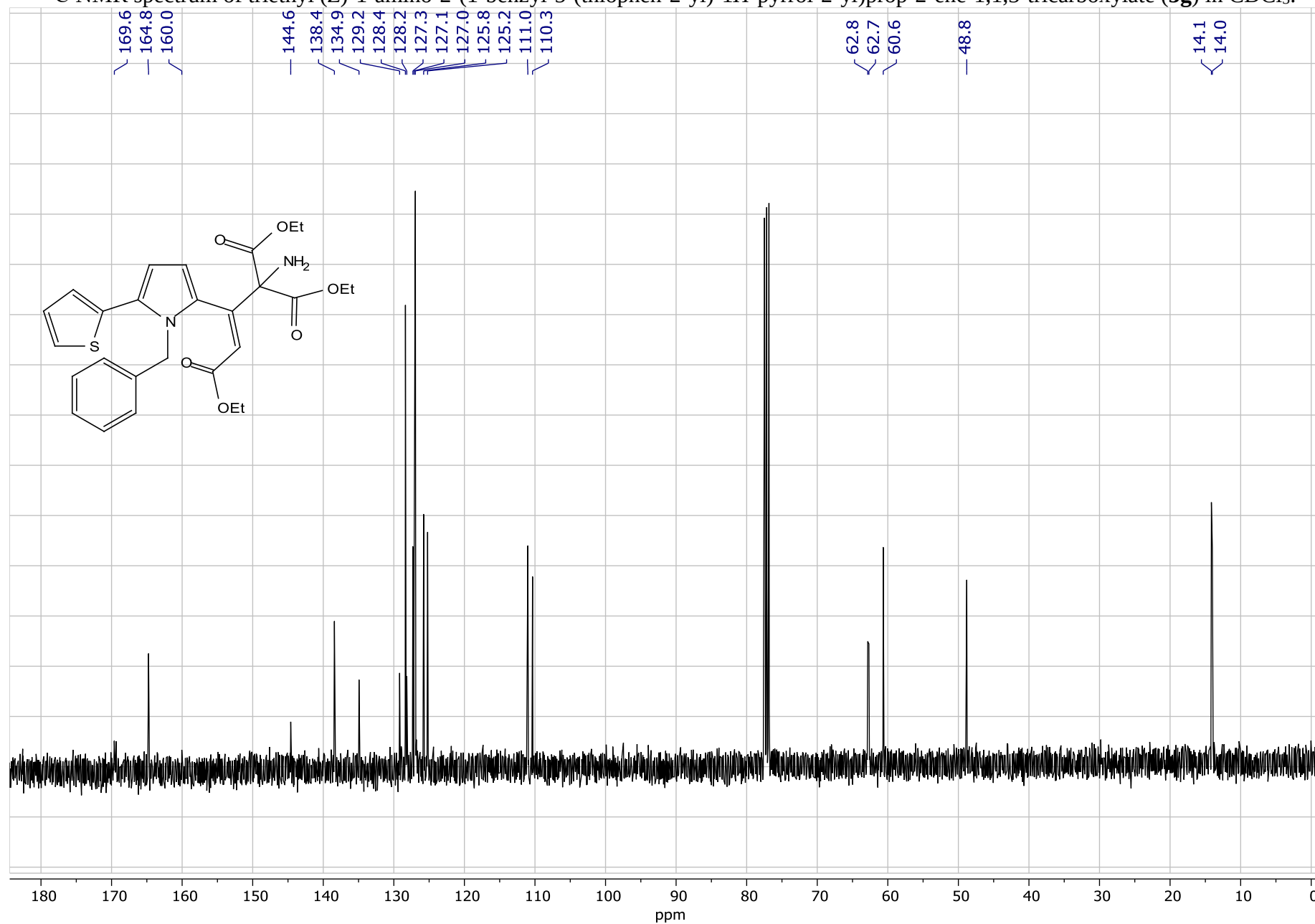
^{13}C NMR spectrum of triethyl (Z)-1-amino-2-(1-benzyl-5-phenyl-1*H*-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3f**) in CDCl_3 .



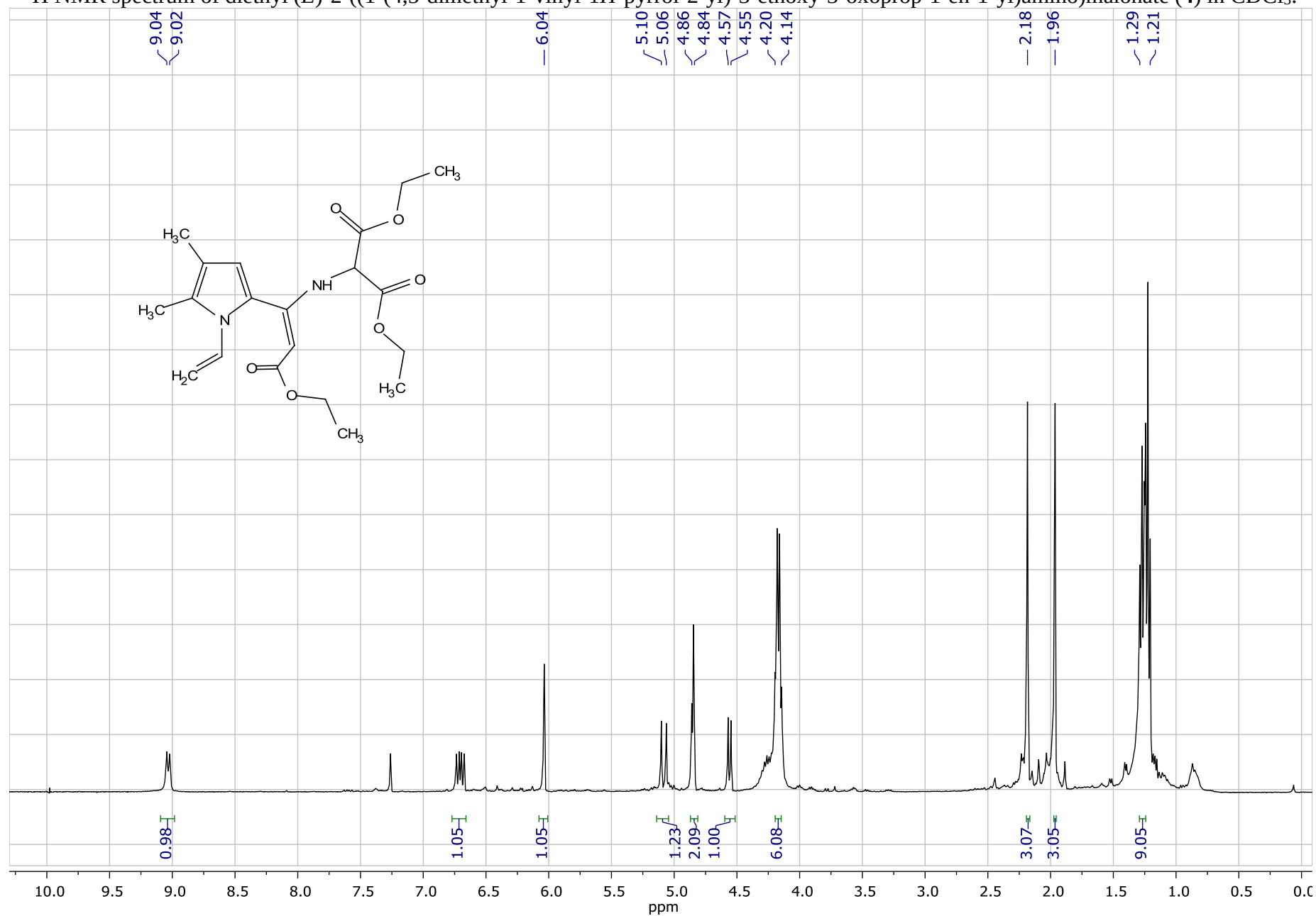
^1H NMR spectrum of triethyl (Z)-1-amino-2-(1-benzyl-5-(thiophen-2-yl)-1*H*-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3g**) in CDCl_3 .



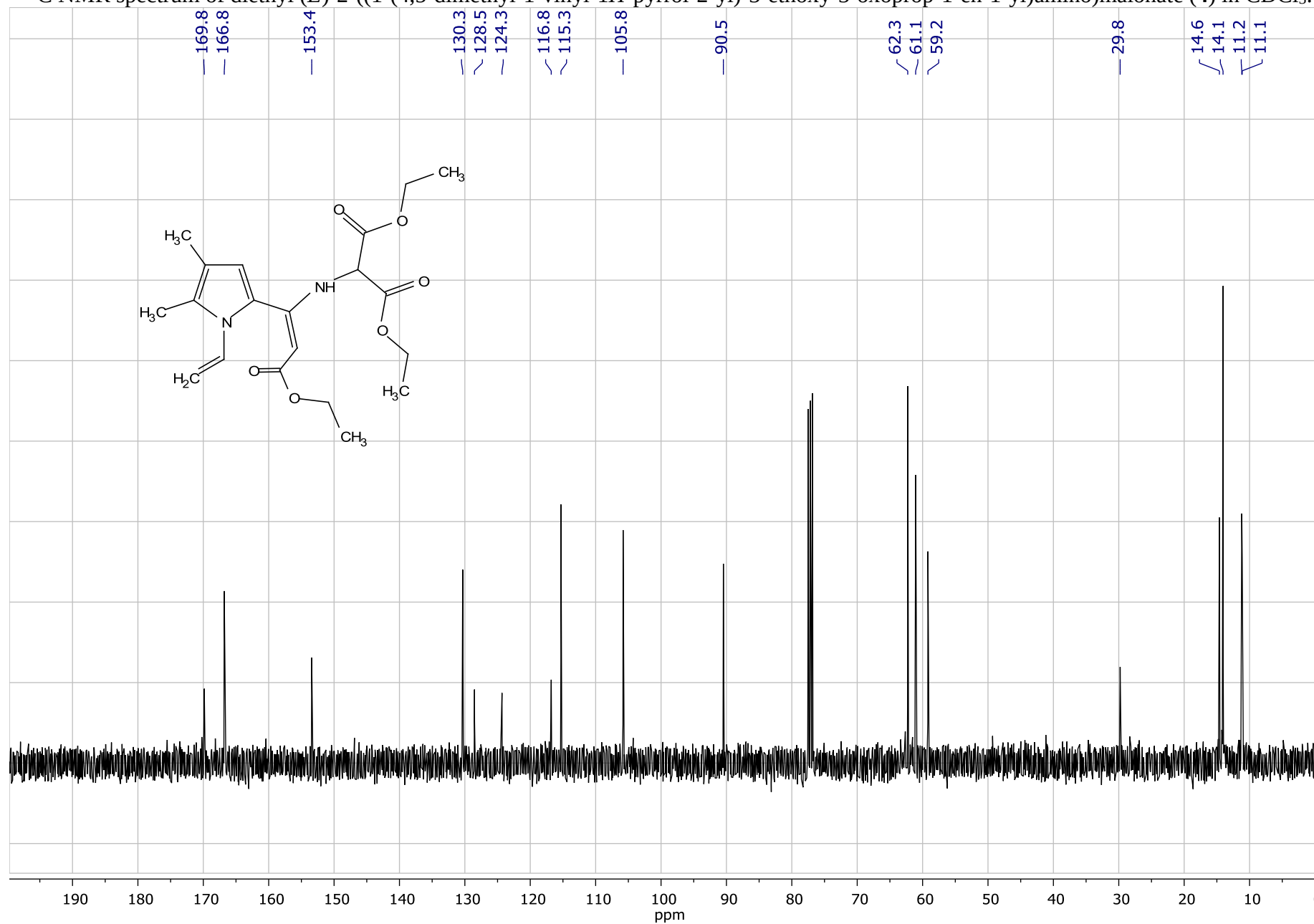
^{13}C NMR spectrum of triethyl (Z)-1-amino-2-(1-benzyl-5-(thiophen-2-yl)-1H-pyrrol-2-yl)prop-2-ene-1,1,3-tricarboxylate (**3g**) in CDCl_3 .



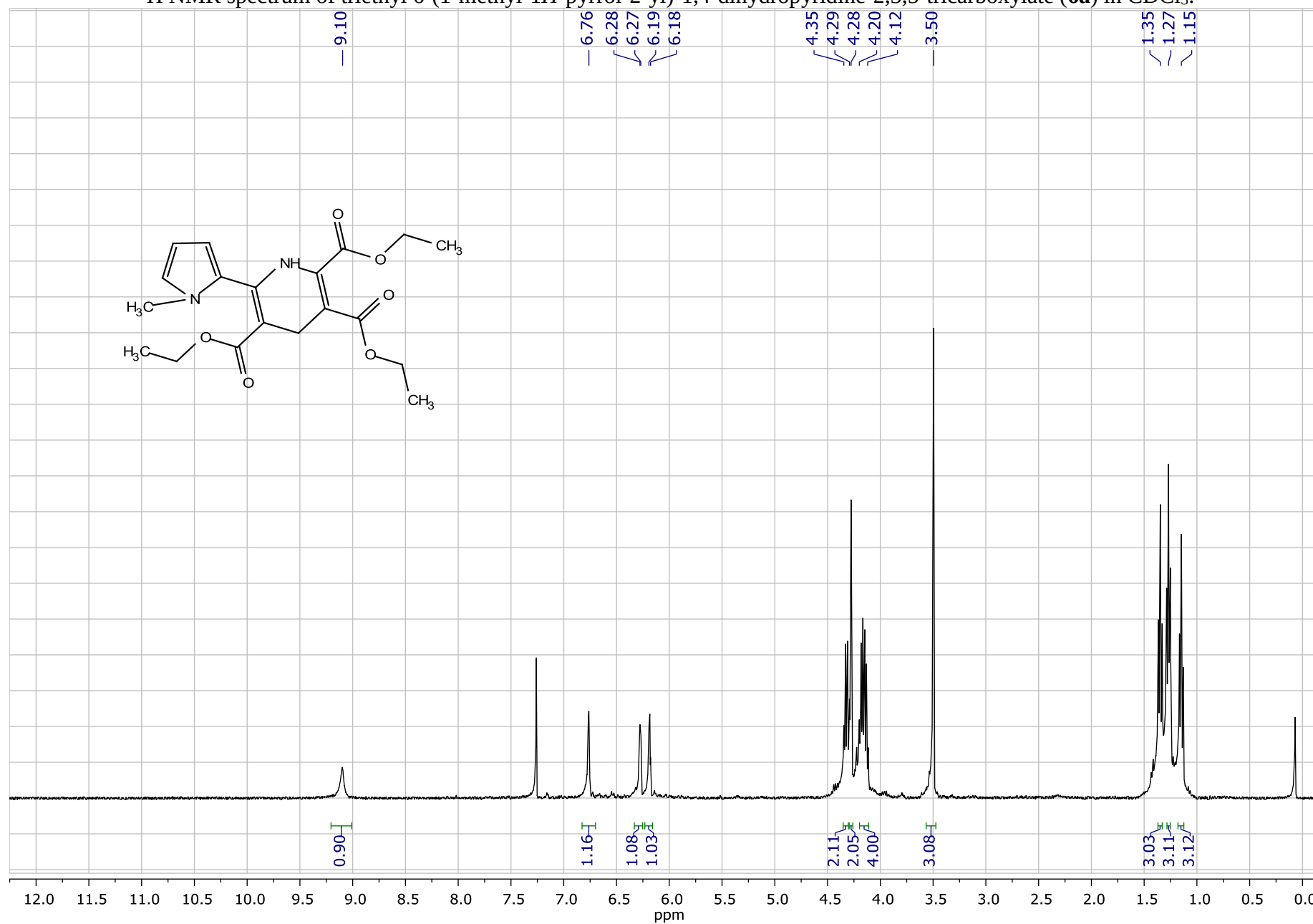
^1H NMR spectrum of diethyl (*E*)-2-((1-(4,5-dimethyl-1-vinyl-1*H*-pyrrol-2-yl)-3-ethoxy-3-oxoprop-1-en-1-yl)amino)malonate (**4**) in CDCl_3 .



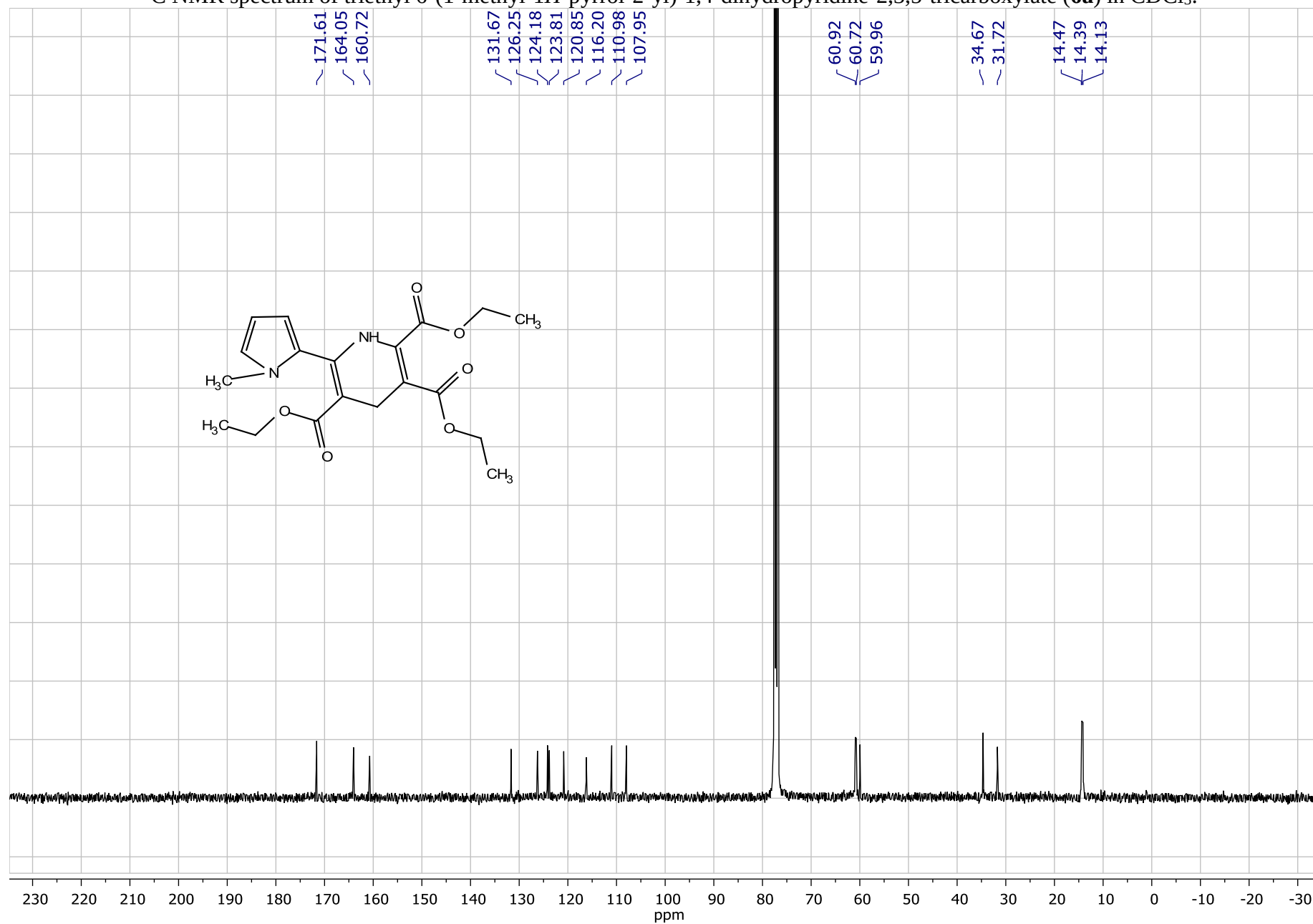
^{13}C NMR spectrum of diethyl (*E*)-2-((1-(4,5-dimethyl-1-vinyl-1*H*-pyrrol-2-yl)-3-ethoxy-3-oxoprop-1-en-1-yl)amino)malonate (**4**) in CDCl_3 .



¹H NMR spectrum of triethyl 6-(1-methyl-1*H*-pyrrol-2-yl)-1,4-dihydropyridine-2,3,5-tricarboxylate (**6a**) in CDCl₃.



¹³C NMR spectrum of triethyl 6-(1-methyl-1*H*-pyrrol-2-yl)-1,4-dihydropyridine-2,3,5-tricarboxylate (**6a**) in CDCl₃.



¹H NMR spectrum of triethyl 6-(1-ethyl-1*H*-pyrrol-2-yl)-1,4-dihydropyridine-2,3,5-tricarboxylate (**6b**) in CDCl₃

