Electronic Supplementary Material (ESI) for ChemComm.


# Synthesis of Pyrroles and Oxazoles based on Gold α-Imino Carbene Complexes

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CONTENTS

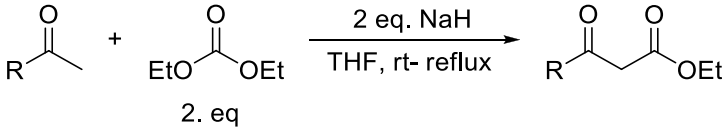
**General information**

All chemical reagents were purchased and used without further purification. All solvents were distilled under nitrogen from the following drying agents immediately before use: acetonitrile and dichloroethane were distilled from $P_2O_5$. Anhydrous pyridine and DBU were purchased from commercial suppliers and used without further purification. Systematic nomenclature for the compounds follows the numbering system as defined by IUPAC with assistance from CS Chemdraw software. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). After elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

$^{1}H$ and $^{13}C$ NMR spectra were measured at 298 K on a Bruker Avance III 400 Fourier Transform NMR spectrometer. Chemical shifts were reported in $\delta$ (ppm), relative to the internal standard of TMS. The signals observed are described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets). Coupling constants are reported as *J* value in Hz, 13C NMR are reported as $\delta$ (ppm) in downfield from TMS and relative to the signal of chloroform-*d* ($\delta$ 77.00, triplet).

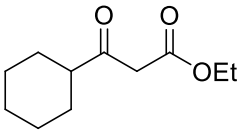
Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. The oil samples were examined under neat conditions. High Resolution Mass (HRMS) pectra were obtained using Q-Tof Premier LC HR mass spectrometer. Melting points are uncorrected and were recorded on a Buchi B-54 melting point apparatus.

**General procedure for synthesis of $\beta$-keto esters (A):**



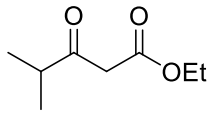

To an oven-dried 2 neck round bottomed flask under nitrogen, 2 eq. of NaH was added and stirred in THF 20 mL. Diethyl carbonate (2.eq) was added to the mixture at rt, and subsequently the ketone (5 mmol) was added dropwise. The mixture was allowed to stir at rt until hydrogen gas evolution has ceased, the mixture was then heated to reflux. Upon completion as indicated by TLC, the reaction mixture was cooled to 0℃ and quenched with aqueous $NH_4Cl$. The layers were separated, and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by column chromatography to afford the desired $\beta$-keto esters.

**Ethyl 3-cyclohexyl-3-oxopropanoate:[1]**



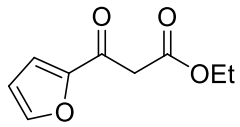

The title compound was prepared according to the general procedure (A). The product was obtained as a colourless oil in 1:10 mixture of enol and keto form. Yield 70%; $^1$H NMR of both enol and keto (400 MHz, $CDCl_3$) δ 12.1 (s, 1H), 5.00 (s, 1H), 4.18 (m, 2H), 3.47 (s, 2H), 2.45 (m, 1H), 1.88 (m, 2H), 1.78 (m, 2H), 1.67 (m, 2H), 1.27 (m, 10H); $^{13}$C NMR of both isomers (100 MHz, $CDCl_3$) δ 205.8, 182.7, 173.0, 167.4, 86.9, 61.2, 59.8, 50.8, 47.3, 43.4, 29.9, 28.1, 25.8, 25.6, 25.4, 14.2, 14.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_{11}H_{19}O_3$: 199.1334. Found: 199.1334.

**Ethyl 4-methyl-3-oxopentanoate :**



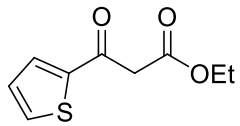

The title compound was prepared according to the general procedure (A). The product was obtained as a colourless oil in 1:1 mixture of enol and keto form. Yield 84%; $^{1}$H NMR of both enol and keto (400 MHz, $CDCl_3$) δ 12.1 (s, 1H), 4.94 (m, 1H), 4.15 (m, 2H), 3.45 (s, 2H), 2.69 (m, 1H), 2.38 (m, 1H), 1.26 (m, 6H), 1.10 (m, 6H); $^{13}$C NMR of both isomers (100 MHz, $CDCl_3$) δ 206.4, 183.5, 173.0, 167.3, 86.6, 63.6, 61.2, 59.8, 47.0, 41.1, 33.7, 29.6, 19.6, 17.8, 14.2, 14.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_8H_{15}O_3$: 159.1021. Found: 159.1031.

**Ethyl 3-(furan-2-yl)-3-oxopropanoate:[2]**




The title compound was prepared according to the general procedure (A). The product was obtained as a colourless oil in keto form. Yield 85%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 1H), 7.27 (d, *J* = 4.0 Hz, 1H), 6.57 (dd, *J* = 1.6, 3.6 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 181.0, 166.9, 151.9, 146.9, 118.2, 112.6, 61.4, 45.4, 14.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_9H_{11}O_4$: 183.0657. Found: 183.0643.

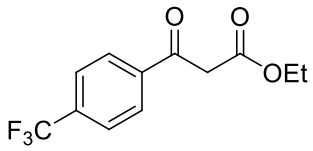
**Ethyl 3-oxo-3-(thiophen-2-yl)propanoate:[3]**




The title compound was prepared according to the general procedure (A). The product was obtained as a colourless oil in keto form. Yield 80%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 0.8, 3.6 Hz, 1H), 7.70 (dd, *J* = 0.8, 4.8 Hz, 1H), 7.15 (dd, *J* = 4.0, 5.2

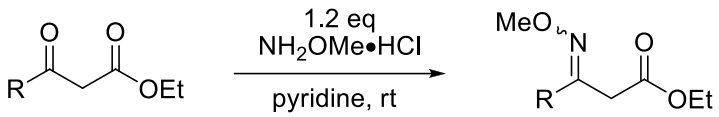
Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 184.9, 166.8, 143.1, 134.8, 133.2, 128.2, 61.4, 46.3, 13.9; HRMS (ESI) m/z [M+H]+: Calcd for $C_9H_{11}O_3S$: 199.0429. Found: 199.0431.

**Ethyl 3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate:[4]**



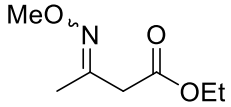

The title compound was prepared according to the general procedure (A). The product was obtained as a colourless oil in 1:2 mixture of enol and keto form. Yield 75%; $^1$H NMR of both isomers (400 MHz, $CDCl_3$) *δ* 12.6 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 4.23 (m, 2H), 4.01 (s, 2H), 1.30 (m, 3H); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{12}O_3F_3$: 261.0739. Found: 261.0738.

**General procedure for synthesis of oxime esters (B):**




To a solution of β-keto ester (5 mmol, 1 eq.) in pyridine (10 mL) was added $NH_2OMe$●HCl (1.2 eq.) and stirred at room temperature. Upon completion, the reaction was diluted with water and extracted with diethyl ether. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by column chromatography to afford the desired oxime ester.

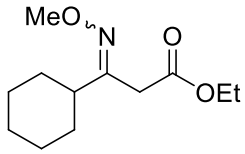
**Ethyl 3-(methoxyimino)butanoate:[5]**




The title compound was prepared according to the general procedure (B). The product was obtained as a colourless oil in 1:1 mixture of cis and trans. Yield: 95%; $^1$H NMR

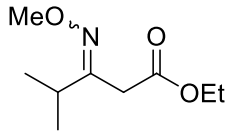
(400 MHz, $CDCl_3$) δ 4.17 (m, 4H), 3.86 (d, *J* = 1.2 Hz, 3H), 3.82 (d, *J* = 1.2 Hz, 3H), 3.32 (d, *J* = 0.8 Hz, 2H), 3.20 (d, *J* = 0.8 Hz, 2H), 1.96 (d, *J* = 0.8 Hz, 3H), 1.91 (d, *J* = 0.8 Hz, 3H), 1.27 (m, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 169.6, 168.8, 151.3, 150.3, 61.4, 61.3, 61.0, 60.9, 41.3, 35.2, 20.4, 14.3, 14.1, 14.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_7H_{14}NO_3$: 160.0974. Found: 160.0980.

**Ethyl 3-cyclohexyl-3-(methoxyimino)propanoate:[5]**



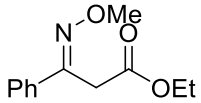

The title compound was prepared according to the general procedure (B). The product was obtained as a colourless oil in 1:6 mixture of cis and trans. $^1H$ NMR of both isomers (400 MHz, $CDCl_3$) *δ* 4.15 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.22 (s, 2H), 3.15 (s, 2H), 2.23 (m, 1H), 1.76 (m, 7H), 1.31 (m, 10H); $^{13}C$ NMR of trans isomer (100 MHz, $CDCl_3$) *δ* 169.1, 157.3, 151.3, 61.2, 60.7, 43.7, 32.9, 29.9, 26.0, 14.0. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{22}NO_3$: 228.1600. Found: 228.1597.

**Ethyl 3-(methoxyimino)-4-methylpentanoate:**



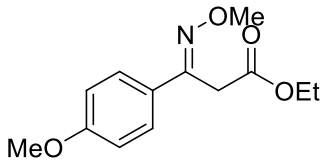

The title compound was prepared according to the general procedure (B). The product was obtained as a colourless oil in 1:4 mixture of cis and trans. $^1H$ NMR of trans isomers (400 MHz, $CDCl_3$) *δ* 4.14 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.21 (s, 2H), 2.58 (quint, *J* = 6.8 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 6H); $^{13}C$ NMR of trans isomer (100 MHz, $CDCl_3$) *δ* 169.0, 157.6, 61.1, 60.6, 33.6, 32.3, 19.5, 14.0. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{18}NO_3$: 188.1287. Found: 188.1291.

**(*E*)-Ethyl 3-(methoxyimino)-3-phenylpropanoate:[5]**



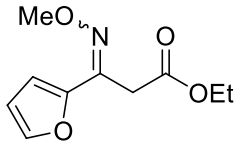

The title compound was prepared according to the general procedure (B). The product was obtained as a colourless oil. Yield: 88%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.63 (m, 2H), 7.37 (m, 3H), 4.14 (q, $J$ = 7.2 Hz, 2H), 4.00 (s, 3H), 3.75 (s, 2H), 1.20 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.8, 151.3, 135.3, 129.2, 128.4, 126.1, 62.1, 61.0, 33.2, 14.0. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{16}NO_3$: 222.1130. Found: 222.1128.

**(*E*)-Ethyl 3-(methoxyimino)-3-(4-methoxyphenyl)propanoate:[5]**




The title compound was prepared according to the general procedure (B). The product was obtained as a colourless oil. Yield: 87%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.58 (dd, $J$ = 2.0, 6.8 Hz, 2H), 6.88 (d, $J$ = 8.8 Hz, 2H), 4.14 (q, $J$ = 7.2 Hz, 2H), 4.00 (s, 3H), 3.80 (s, 2H), 3.72 (s, 2H), 1.21 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.9, 160.5, 150.8, 127.8, 127.5, 113.9, 62.0, 61.0, 55.2, 33.1, 14.0. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{18}NO_4$: 252.1236. Found: 252.1224.

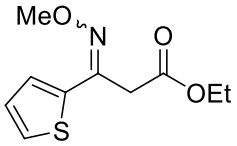
**Ethyl 3-(furan-2-yl)-3-(methoxyimino)propanoate:[5]**




The title compound was prepared according to the general procedure (B). The product was obtained as a colourless oil in 1:10 mixture of cis and trans. Yield: 85%; $^{1}$H NMR of trans isomer (400 MHz, $CDCl_3$) $\delta$ 7.46 (s, 1H), 6.66 (d, $J$ = 3.2 Hz, 1H), 6.44 (m, 1H), 4.15 (q, $J$ = 7.2 Hz, 2H), 3.99 (s, 3H), 3.65 (s, 2H), 1.23 (t, $J$ = 7.2 Hz, 3H); $^{13}$C

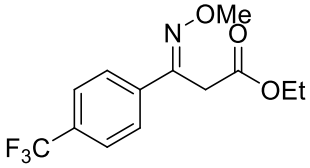
NMR (100 MHz, $CDCl_3$) $\delta$ 168.2, 149.0, 143.7, 143.6, 111.4, 110.2, 62.4, 61.0, 32.2, 14.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{14}NO_4$: 212.0932. Found: 212.0932.

**Ethyl 3-(methoxyimino)-3-(thiophen-2-yl)propanoate:**



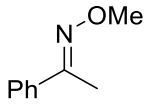

The title compound was prepared according to the general procedure (B). The product was obtained as a colourless oil in 1:2 mixture of cis and trans. Yield: 82%; $^1$H NMR of cis and trans isomers (400 MHz, $CDCl_3$) $\delta$ 7.50 (d, $J$ = 4.8 Hz, 1H), 7.39 (d, $J$ = 4.0 Hz, 1H), 7.27 (d, $J$ = 5.2 Hz, 1H), 7.19 (d, $J$ = 3.6 Hz, 1H), 7.05 (m, 1H), 6.99 (m, 1H), 4.14 (m, 2H), 4.07 (s, 3H), 3.96 (s, 3H), 3.73 (s, 2H), 3.67 (s, 2H), 1.21 (m, 3H); $^{13}$C NMR of both isomers (100 MHz, $CDCl_3$) $\delta$ 169.6, 168.2, 147.0, 143.8, 138.9, 131.5, 130.7, 129.1, 127.1, 127.0, 126.4, 125.5, 62.2, 62.1, 61.1, 61.1, 39.8, 33.2, 14.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{14}NO_3S$: 228.0694. Found: 228.0694.

**(*E*)-Ethyl 3-(methoxyimino)-3-(4-(trifluoromethyl)phenyl)propanoate:**



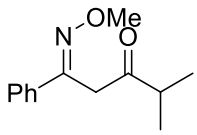

The title compound was prepared according to the general procedure (B). The product was obtained as a colourless oil. Yield: 80%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.66 (m, 4H), 4.15 (q, $J$ = 7.2 Hz, 2H), 4.10 (s, 3H), 1.13 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.4, 150.0, 138.7, 131.0 (q, $J$ = 33.3 Hz, C-$CF_3$), 128.5, 126.4, 125.4 (q, $J$ = 3.0 Hz, CH), 123.8 (q, $J$ = 253.5 Hz, $CF_3$), 62.5, 61.2, 32.8, 14.0; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = –-62.8 ppm. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{15}NO_3F_3$: 290.1004. Found: 290.1004.

**(*E*)-Acetophenone O-methyl oxime:[6]**



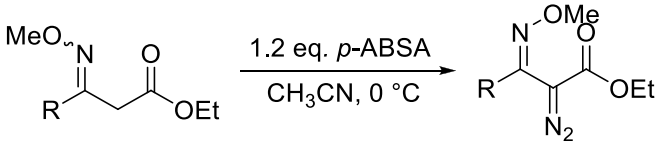

The title compound was prepared according to the literature.[7] The product was obtained as a colorless oil in 1:5 mixture of cis and trans. Yield: 96%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.35 (m, 3H), 4.00 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.6, 136.6, 129.0, 128.4, 126.0, 61.9, 12.6; HRMS (ESI) m/z [M+H]+: Calcd for $C_9H_{12}NO$: 150.0919. Found: 150.0923.

**(*E*)-1-(Methoxyimino)-4-methyl-1-phenylpentan-3-one:[7]**



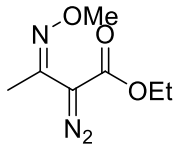

The title compound was prepared according to the literature.[7] The product was obtained as a colourless oil. Yield: 80%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 2H), 7.35 (m, 3H), 4.00 (s, 3H), 3.86 (s, 2H), 2.76 (quint, $J$ = 6.8 Hz, 1H), 1.12 (d, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 209.0, 152.5, 135.6, 129.2, 128.4, 126.1, 62.0, 40.6, 39.6, 18.3; HRMS (ESI) m/z [M+H]+: Calcd for $C_{13}H_{18}NO_2$: 220.1338. Found: 220.1340.

**General procedure for diazo compounds (C):**



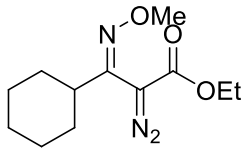

To a solution of α-diazo oxime ether (1 eq.) and 4-acetylbenzenesulfonyl azide, *p*-ABSA (1.2 eq.) in $CH_3CN$ at 0℃ was added dropwise DBU (1.2 eq.). The resulting orange solution was stirred for 30 min at 0℃ and allowed to warm to room temperature. The reaction mixture was concentrated and the crude material was purified by column chromatography to afford the desired diazo compound.

**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)butanoate (1a):[5]**



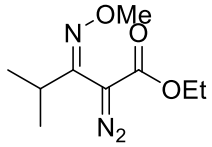

The title compound was prepared according to the general procedure (C). The product was obtained as a yellow oil. Yield: 56%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.24 (d, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.20 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.8, 141.5, 61.6, 61.1, 19.1, 14.3. HRMS (ESI) m/z [M+H]+: Calcd for $C_7H_{12}N_3O_3$: 186.0879. Found: 186.0874.

**(*Z*)-Ethyl 3-cyclohexyl-2-diazo-3-(methoxyimino)propanoate (1b):[5]**




The title compound was prepared according to the general procedure (C). The product was obtained as a yellow oil. Yield: 75%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 2.80 (m, 1H), 1.90 (d, *J* = 11.2 Hz, 2H), 1.77 (m, 2H), 1.67 (d, *J* = 11.6 Hz, 1H), 1.29 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.0, 148.1, 61.7, 60.9, 40.2, 31.4, 26.4, 26.1, 14.2; HRMS (ESI) m/z [M+H]+: Calcd for $C_{12}H_{20}N_3O_3$: 254.1505. Found: 254.1502.

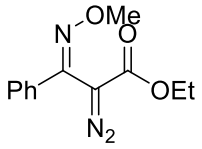
**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)-4-methylpentanoate (1c):**




The title compound was prepared according to the general procedure (C). The product was obtained as a yellow solid. Yield: 80%; $^{1}$H NMR (400 MHz, $CDCl_3$) *δ* 4.24 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.16 (quint, *J* = 7.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 164.0, 148.7, 61.8, 61.0, 30.6,

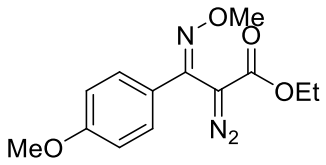
20.7, 14.3; HRMS (ESI) m/z [M+H]+: Calcd for $C_9H_{16}N_3O_3$: 214.1192. Found: 214.1197.

**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)-3-phenylpropanoate (1d):[5]**



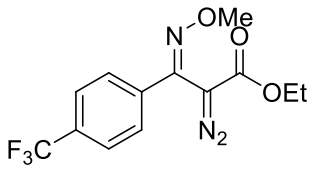

The title compound was prepared according to the general procedure (C). The product was obtained as a yellow solid. Yield: 85%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.37 (m, 3H), 4.10 (q, $J$ = 7.2 Hz, 2H), 4.04 (s, 3H), 1.08 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.8, 144.2, 133.7, 129.5, 128.2, 127.6, 62.6, 61.2, 14.0. HRMS(ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}N_3O_3$: 248.1035. Found: 248.1044.

**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)-3-(4-methoxyphenyl)propanoate (1e):[5]**



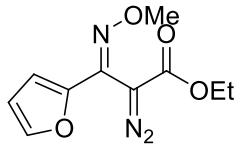

The title compound was prepared according to the general procedure (C). The product was obtained as a yellow solid. Yield: 87%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.47 (d, $J$ = 8.8 Hz, 2H), 6.88 (d, $J$ = 8.8 Hz, 2H), 4.13 (q, $J$ = 7.2 Hz, 2H), 4.02 (s, 3H), 3.81 (s, 3H), 1.13 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.8, 160.8, 143.7, 129.0, 126.0, 113.7, 62.4, 61.1, 55.2, 31.5, 22.6, 14.1, 14.0. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}N_3O_4$: 278.1141. Found: 278.1150.

**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)-3-(4-(trifluoromethyl)phenyl)propanoate (1f):**



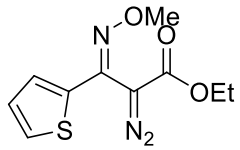
The title compound was prepared according to the general procedure (C). The product was obtained as a yellow solid. Yield: 90%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.66 (q, $J$ = 8.4 Hz, 4H), 4.15 (q, $J$ = 7.2 Hz, 2H), 4.10 (s, 3H), 1.13 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.4, 143.1, 137.3, 131.3 (q, $J$ = 32.2 Hz, C-$CF_3$), 128.0, 125.1 (q, $J$ = 3.7 Hz, CH), 123.9 (q, $J$ = 270.5 Hz, $CF_3$), 62.9, 61.3, 14.0; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = –62.8 ppm. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}N_3O_3F_3$: 316.0909. Found: 316.0912.

**(*E*)-Ethyl 2-diazo-3-(furan-2-yl)-3-(methoxyimino)propanoate (1g):[5]**




The title compound was prepared according to the general procedure (C). The product was obtained as a yellow solid. Yield: 77%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.47 (t, $J$ = 0.8 Hz, 1H), 6.66 (d, $J$ = 3.6 Hz, 1H), 6.45 (m, 1H), 4.19 (q, $J$ = 7.2 Hz, 2H), 4.04 (s, 3H), 1.19 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.4, 146.9, 143.7, 135.6, 111.5, 111.4, 62.8, 61.3, 14.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{12}N_3O_4$: 238.0828. Found: 238.0823.

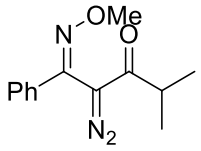
**(*E*)-Ethyl 2-diazo-3-(methoxyimino)-3-(thiophen-2-yl)propanoate (1h):**




The title compound was prepared according to the general procedure (C). The product was obtained as a yellow oil. Yield: 80%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.30 (dd, $J$ = 0.8, 4.8 Hz, 1H), 7.19 (dd, $J$ = 1.2, 3.6 Hz, 1H), 7.00 (dd, $J$ = 4.0, 5.2 Hz, 1H), 4.19 (q, $J$ = 7.2 Hz, 2H), 4.03 (s, 3H), 1.19 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz,

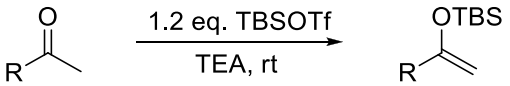
$CDCl_3$) $\delta$ 163.5, 138.6, 136.2, 128.3, 127.3, 127.0, 62.7, 61.2, 14.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{12}N_3O_3S$: 254.0599. Found: 254.0592.

**(*Z*)-2-Diazo-1-(methoxyimino)-4-methyl-1-phenylpentan-3-one (1i):[7]**



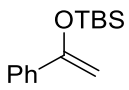

The title compound was prepared according to the general procedure (C). The product was obtained as a yellow oil. Yield: 85%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (m, 2H), 7.40 (m, 3H), 4.07 (s, 3H), 2.44 (quint, $J$ = 6.8 Hz, 1H), 0.99 (d, $J$ = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 197.3, 144.0, 133.8, 130.1, 128.8, 127.3, 62.7, 36.7, 18.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}N_3O_2$: 246.1243. Found: 246.1244.

**General procedure for synthesis of tert-Butyldimethylsilyl ether substrates (D):**




To a oven dried 2 neck round bottom flask under nitrogen was added the corresponding ketone (5 mmol, 1 eq.) in dry DCM (10 mL) and triethylamine (1.2 eq.). The reaction was stirred for 1h at room temperature and TBSOTf (1.1 eq.) was added dropwise. The reaction was allowed to stir for 2-3 h and quenched with cold aqueous $NH_4Cl$. The mixture was extracted with diethyl ether and dried with $MgSO_4$. After evaporation of solvents, the crude residue was purified by flash column chromatography on triethylamine deactivated silica (100% hexane).

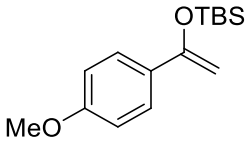
***tert*-Butyldimethyl(1-phenylvinyloxy)silane (2c):[8]**




The title compound was prepared according to the general procedure (D). The product was obtained as a colourless oil. Yield: 100%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 (m,

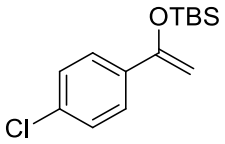
2H), 7.27 (m, 3H), 4.86 (d, *J* = 1.6 Hz, 1H), 4.39 (d, *J* = 1.6 Hz, 1H), 0.98 (s, 9H), 0.19 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.0, 137.8, 128.2, 128.1, 125.3, 90.9, 25.9, 18.4, -4.6; HRMS (ESI) m/z [M+H]+: Calcd for $C_{14}H_{23}OSi$: 235.1518. Found: 235.1524.

***tert*-Butyl(1-(4-methoxyphenyl)vinyloxy)dimethylsilane (2d):[9]**



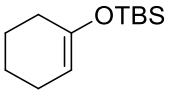

The title compound was prepared according to the general procedure (D). The product was obtained as a colourless oil. Yield: 96%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 9.2 Hz, 2H), 4.67 (d, *J* = 1.6 Hz, 1H), 4.23 (d, *J* = 1.6 Hz, 1H), 3.70 (s, 3H), 0.91 (s, 9H), 0.12 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.7, 155.8, 130.5, 126.6, 113.4, 89.3, 55.2, 25.9, 18.4, -4.6. HRMS (ESI) m/z [M+H]+: Calcd for $C_{15}H_{25}O_2Si$: 265.1624. Found: 265.1624.

***tert*-Butyl(1-(4-chlorophenyl)vinyloxy)dimethylsilane (2e):[9]**



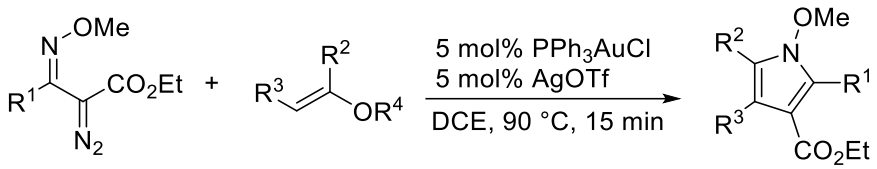

The title compound was prepared according to the general procedure (D). The product was obtained as a colourless oil. Yield: 95%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 2.0, 6.8 Hz, 2H), 7.26 (dd, *J* = 2.0, 6.8 Hz, 2H), 4.84 (d, *J* = 1.6 Hz, 1H), 4.41 (d, *J* = 1.6 Hz, 1H), 0.98 (s, 9H), 0.19 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.0, 136.3,133.9, 128.2, 126.6, 91.3, 25.8, 18.3, -4.7; HRMS (ESI) m/z [M+H]+: Calcd for $C_{14}H_{22}OClSi$: 269.1128. Found: 269.1122.

***tert*-Butyl(cyclohexenyloxy)dimethylsilane (2f):[9]**



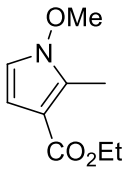
The title compound was prepared according to the general procedure (D). The product was obtained as a colourless oil. Yield: 95%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.86 (m, 1H), 1.99 (m, 4H), 1.65 (m, 2H), 1.50 (m, 2H), 0.92 (s, 9H), 0.12 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.5, 104.3, 29.9, 25.7, 23.8, 23.2, 22.4, 18.0, -4.4. HRMS (ESI) m/z [M+H]+: Calcd for $C_{12}H_{25}OSi$: 213.1675. Found: 213.1672.

**General procedure for synthesis of pyrrole (E):**




To a oven dried reaction tube was added 5 mol% of $PPh_3AuCl$ and 5 mol% of AgOTf in DCE (1 mL) and the mixture was allowed to stir for 5 mins at room temperature until a white precipitate forms. Vinyl ether (3eq.) or ethyl vinyl ether (10 eq.), followed by dropwise addition of α-diazo oxime ether (0.3 mmol, 1 eq.) in DCE (1.5 mL) was added to the mixture whilst stirring at room temperature. After the addition of the substrates, the reaction was heated at 90℃ for approximately 5- 15 mins and stopped upon seeing the mixture turn colourless with black precipitate forming. The crude was concentrated and purified by flash column chromatography to give pyrrole.

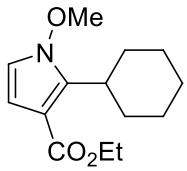
**Ethyl 1-methoxy-2-methyl-1*H*-pyrrole-3-carboxylate (3aa):**




The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 91%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.66 (d, $J$ = 3.2 Hz, 1H), 6.44 (d, $J$ = 3.2 Hz, 1H), 4.26 (q, $J$ = 7.2 Hz, 2H), 4.00 (s, 3H), 2.50 (s,

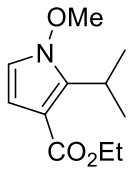
3H), 1.33 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.0, 130.9, 113.6, 107.9, 106.1, 66.6, 59.3, 14.4, 9.4. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{14}NO_3$: 184.0974. Found: 184.0977.

**Ethyl 2-cyclohexyl-1-methoxy-1*H*-pyrrole-3-carboxylate (3ba):**



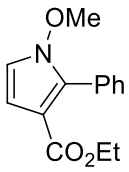

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 81%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.61 (d, $J$ = 3.6 Hz, 1H), 6.47 (d, $J$ = 3.2 Hz, 1H), 4.24 (q, $J$ = 7.2 Hz, 2H), 3.98 (s, 3H), 3.44 (m, 1H), 2.00 (m, 2H), 1.83 (m, 2H), 1.71 (m, 3H), 1.35 (m, 7H, triplet from –Et within the muliplet); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.8, 139.2, 113.4, 107.0, 106.8, 67.0, 59.4, 35.2, 30.2, 27.0, 25.8, 14.4. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{22}NO_3$: 252.1600. Found: 252.1602.

**Ethyl 2-isopropyl-1-methoxy-1*H*-pyrrole-3-carboxylate (3ca):**



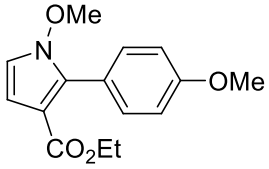

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 88%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.62 (d, $J$ = 3.2 Hz, 1H), 6.46 (d, $J$ = 3.2 Hz, 1H), 4.24 (q, $J$ = 6.8 Hz, 2H), 4.00 (s, 3H), 3.82 (quint, $J$ = 7.2 Hz, 1H), 1.37 (d, $J$ = 7.2 Hz, 6H), 1.33 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.7, 139.9, 113.4, 106.9, 106.5, 66.8, 59.4, 24.6, 20.4, 14.4. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{18}NO_3$: 212.1287. Found: 212.1291.

**Ethyl 1-methoxy-2-phenyl-1*H*-pyrrole-3-carboxylate (3da):**



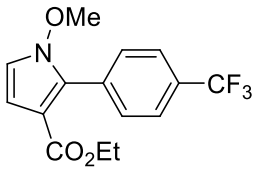

The title compound was prepared according to the general procedure (E). The product was obtained as a white solid. Yield: 91%; mp = 75.8-76.6℃; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.42 (m, 3H), 6.82 (d, $J$ = 3.6 Hz, 1H), 6.61 (d, $J$ = 3.2 Hz, 1H), 4.15 (q, $J$ = 7.2 Hz, 2H), 3.66 (s, 3H), 1.18 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.3, 132.8, 130.6, 128.8, 128.4, 127.7, 115.2, 109.4, 107.0, 66.7, 59.6, 14.2. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}NO_3$: 246.1130. Found: 246.1133.

**Ethyl 1-methoxy-2-(4-methoxyphenyl)-1*H*-pyrrole-3-carboxylate (3ea):**



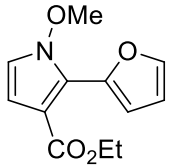

The title compound was prepared according to the general procedure (E). The product was obtained as a white solid. Yield: 80%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.49 (dd, $J$ = 2.0, 6.8 Hz, 2H), 6.95 (dd, $J$ = 2.0, 6.8 Hz, 2H), 6.79 (d, $J$ = 3.2 Hz, 1H), 6.58 (d, $J$ = 3.2 Hz, 1H), 4.17 (q, $J$ = 7.2 Hz, 2H), 3.85 (s, 3H), 3.66 (s, 3H), 1.21 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 159.7, 132.8, 131.9, 121.0, 115.0, 113.2, 109.0, 106.9, 66.5, 59.5, 55.2, 14.3. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{18}NO_4$: 276.1236. Found: 276.1240.

**Ethyl 1-methoxy-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-3-carboxylate (3fa):**



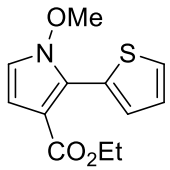
The title compound was prepared according to the general procedure (E). The product was obtained as a white solid. Yield: 90%; mp = 85.2-85.3℃; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69 (m, 4H), 6.87 (d, $J$ = 3.2 Hz, 1H), 6.63 (d, $J$ = 3.2 Hz, 1H), 4.17 (q, $J$ = 7.2 Hz, 2H), 3.68 (s, 3H), 3.66 (s, 3H), 1.21 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 132.4, 131.0, 130.2 (q, $J$ = 32.0 Hz, C-$CF_3$), 127.0, 124.6 (q, $J$ = 3.8 Hz, CH), 124.1 (q, $J$ = 270.5 Hz, $CF_3$), 116.0, 110.1, 107.5, 66.9, 59.8, 14.1; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = –62.7 ppm. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{15}NO_3F_3$: 314.1004. Found: 314.0994.

**Ethyl 2-(furan-2-yl)-1-methoxy-1H-pyrrole-3-carboxylate (3ga):**




The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 79%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.55 (dd, $J$ = 0.8, 1.6 Hz, 1H), 6.91 (dd, $J$ = 0.4, 3.2 Hz, 1H), 6.83 (d, $J$ = 3.2 Hz, 1H), 6.58 (d, $J$ = 3.2 Hz, 1H), 6.53 (dd, $J$ = 1.6, 3.2 Hz, 1H), 4.23 (q, $J$ = 7.2 Hz, 2H), 3.94 (s, 3H), 1.28 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.8, 142.7, 142.4, 122.6, 116.4, 112.7, 111.0, 110.6, 107.5, 67.3, 59.8, 14.3. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}NO_4$: 236.0923. Found: 236.0929.

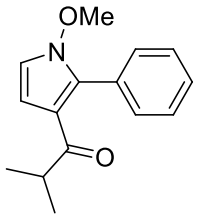
**Ethyl 1-methoxy-2-(thiophen-2-yl)-1*H*-pyrrole-3-carboxylate (3ha):**




The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 88%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.58 (dd,

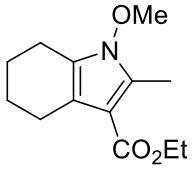
*J* = 1.2, 3.6 Hz, 1H), 7.44 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.11 (dd, *J* = 3.6, 4.8 Hz, 1H), 6.83 (d, *J* = 3.2 Hz, 1H), 6.60 (d, *J* = 3.2 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 130.1, 128.2, 127.2, 126.5, 125.8, 115.8, 110.2, 107.6, 66.8, 59.8, 14.2. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}NO_3S$: 252.0694. Found: 252.0702.

**1-(1-Methoxy-2-phenyl-1*H*-pyrrol-3-yl)-2-methylpropan-1-one (3ia):**



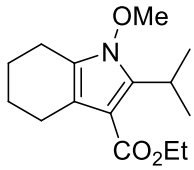

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 66%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51 (m, 2H), 7.43 (m, 3H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.56 (d, *J* = 3.2 Hz, 1H), 3.66 (s, 3H), 3.05 (quint, *J* = 6.8 Hz, 1H), 1.07 (d, *J* = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 200.6, 132.1, 130.5, 129.2, 128.6, 127.9, 117.4, 115.2, 106.5, 66.6, 36.8, 19.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{18}NO_2$: 244.1338. Found: 244.1346.

**Ethyl 1-methoxy-2-methyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3af):**



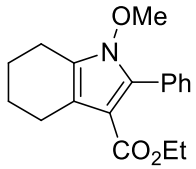

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 75%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.24 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 2.68 (t, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 6.0 Hz, 2H), 2.49 (s, 3H), 1.75 (m, 4H), 1.32 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.9, 129.9, 123.1, 115.0, 105.0, 65.7, 58.9, 23.5, 23.0, 22.5, 20.4, 14.5, 9.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{20}NO_3$: 238.1443. Found: 238.1444.

**Ethyl 2-isopropyl-1-methoxy-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3cf):**



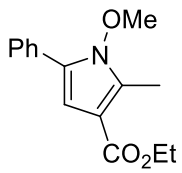

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 56%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.23 (q, $J$ = 7.2 Hz, 2H), 3.92 (s, 3H), 3.77 (quint, $J$ = 6.8 Hz, 1H), 2.67 (t, $J$ = 6.0 Hz, 2H), 2.56 (t, $J$ = 6.0 Hz, 2H), 1.37 (d, $J$ = 6.8 Hz, 6H), 1.33 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.7, 138.9, 123.3, 115.4, 104.1, 66.2, 59.1, 24.7, 23.5, 23.4, 22.5, 20.9, 20.6, 14.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{24}NO_3$: 266.1756. Found: 266.1753.

**Ethyl 1-methoxy-2-phenyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3df):**



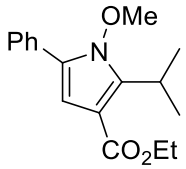

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 76%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.50 (m, 2H), 7.38 (m, 3H), 4.11 (q, $J$ = 7.2 Hz, 2H), 3.56 (s, 3H), 2.77 (t, $J$ = 6.4 Hz, 2H), 2.63 (t, $J$ = 6.4 Hz, 2H), 1.83 (m, 4H), 1.13 (t, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.2, 131.6, 130.6, 129.8, 127.9, 127.5, 124.7, 116.0, 106.6, 65.6, 59.1, 23.5, 23.1, 22.4, 20.6, 14.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{22}NO_3$: 300.1600. Found: 300.1596.

**Ethyl 1-methoxy-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (3ac):**



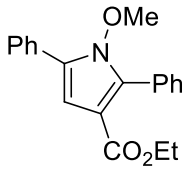
The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 82%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.67 (m, 2H), 7.39 (m, 2H), 7.28 (m, 1H), 4.29 (q, $J$ = 7.2 Hz, 2H), 3.71 (s, 3H), 2.60 (s, 3H), 1.36 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.0, 132.4, 130.4, 128.6, 127.1, 127.0, 126.5, 108.0, 105.3, 65.6, 59.5, 14.5, 9.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{18}NO_3$: 260.1287. Found: 260.1290.

**Ethyl 2-isopropyl-1-methoxy-5-phenyl-1*H*-pyrrole-3-carboxylate (3cc):**



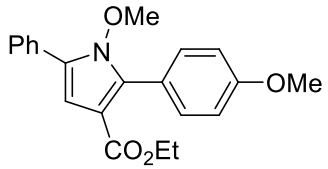

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 76%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (m, 2H), 7.53 (m, 2H), 7.41 (m, 1H), 4.32 (q, $J$ = 7.2 Hz, 2H), 4.00 (m, 1H), 3.82 (s, 3H), 1.59 (d, $J$ = 8.0 Hz, 6H), 1.50 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.6, 141.4, 130.4, 128.6, 127.1, 126.8, 126.7, 106.9, 106.5, 66.2, 59.5, 24.8, 20.7, 14.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{22}NO_3$: 288.1600. Found: 288.1595.

**Ethyl 1-methoxy-2,5-diphenyl-1*H*-pyrrole-3-carboxylate (3dc)**



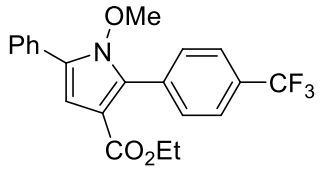

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 70%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 (m, 2H), 7.63 (m, 2H), 7.44 (m, 5H), 7.32 (m, 1H), 6.82 (s, 1H), 4.19 (q, $J$ = 7.2 Hz, 2H), 3.40 (s, 3H), 1.21 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.3, 134.3, 130.7, 130.2, 128.9, 128.7, 128.6, 128.4, 127.7, 127.4, 126.8, 109.5, 106.6, 65.5, 59.7, 14.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{20}NO_3$: 322.1443. Found: 322.1439.

**Ethyl 1-methoxy-2-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-3-carboxylate (3ec):**



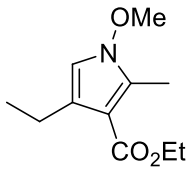

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 66%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.73 (m, 2H), 7.59 (m, 2H), 7.41 (t, $J$ = 7.2 Hz, 2H), 7.30 (t, $J$ = 7.2 Hz, 1H), 6.98 (dd, $J$ = 1.6, 6.8 Hz, 2H), 6.80 (s, 1H), 4.20 (q, $J$ = 7.2 Hz, 2H), 3.87 (s, 3H), 3.39 (s, 3H), 1.23 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 159.7, 134.4, 132.0, 130.3, 128.6, 128.4, 127.3, 126.8, 121.1, 113.2, 109.0, 106.5, 65.3, 59.7, 55.2, 14.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{22}NO_4$: 352.1549. Found: 352.1545.

**Ethyl 1-methoxy-5-phenyl-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-3-carboxylate (3fc):**



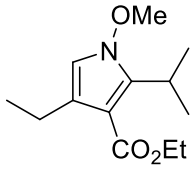

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 92%; mp = 114.1-115.1℃; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 (m, 6H), 7.44 (m, 2H), 7.34 (t, $J$ = 7.2 Hz, 1H), 6.83 (s, 1H), 4.21 (q, $J$ = 7.2 Hz, 2H), 3.39 (s, 3H), 1.23 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.0, 132.4, 131.1, 130.2 (q, $J$ = 32.3 Hz, C-$CF_3$), 129.8, 129.4, 128.8, 127.7, 127.0, 124.6 (q, $J$ = 3.8 Hz, CH), 124.1 (q, $J$ = 270.5 Hz, $CF_3$), 110.3, 106.9, 65.8, 60.0, 14.2; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = –-62.6 ppm. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{19}NO_3F_3$: 390.1317. Found: 390.1320.

**Ethyl 4-ethyl-1-methoxy-2-methyl-1*H*-pyrrole-3-carboxylate (3ab):**



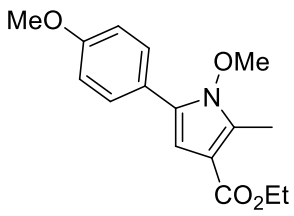

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 76%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.48 (s, 1H), 4.26 (q, $J$ = 7.2 Hz, 2H), 3.93 (s, 3H), 2.69 (q, $J$ = 7.6 Hz, 2H), 2.47 (s, 3H), 1.34 (t, $J$ = 7.2 Hz, 3H), 1.16 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.6, 131.5, 124.6, 111.2, 105.9, 66.3, 59.1, 20.0, 14.4, 14.4, 9.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{18}NO_3$: 212.1287. Found: 212.1283.

**Ethyl 4-ethyl-2-isopropyl-1-methoxy-1*H*-pyrrole-3-carboxylate (3cb):**




The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 77%; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.45 (s, 1H), 4.26 (q, $J$ = 7.2 Hz, 2H), 3.97 (s, 3H), 3.83 (m, 1H), 2.67 (q, $J$ = 10.8 Hz, 2H), 1.35 (d, $J$ = 7.2 Hz, 3H), 1.16 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.7, 140.1, 124.6, 111.3, 104.8, 66.4, 59.2, 24.9, 20.6, 20.4, 14.4, 14.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{22}NO_3$: 240.1600. Found: 240.1599.

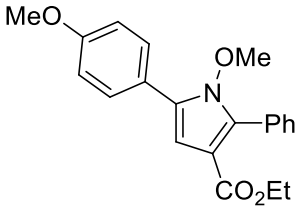
**Ethyl 1-methoxy-5-(4-methoxyphenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (3ad):**




The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 60%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd,

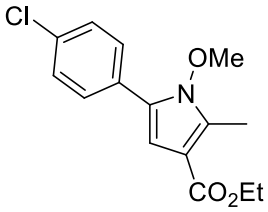
*J* = 2.0, 6.8 Hz, 2H), 6.93 (dd, *J* = 2.0, 6.8 Hz, 2H), 6.55 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 3.70 (s, 3H), 2.58 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.1, 158.8, 131.8, 128.0, 127.1, 123.1, 114.0, 107.7, 104.2, 65.4, 59.5, 55.2, 14.5, 9.9; HRMS (ESI) m/z [M+H]+: Calcd for $C_{16}H_{20}NO_4$: 290.1392. Found: 290.1389.

**Ethyl 1-methoxy-5-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (3dd):**




The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 70%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 4H), 6.96 (dd, *J* = 2.0, 8.8 Hz, 2H), 6.72 (d, *J* = 0.4 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 3.38 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.4, 159.0, 133.7, 130.7, 129.0, 128.6, 128.3, 127.6, 122.8, 114.1, 109.3, 105.5, 65.3, 59.7, 55.3, 14.2; HRMS (ESI) m/z [M+H]+: Calcd for $C_{21}H_{22}NO_4$: 352.1549. Found: 352.1551.

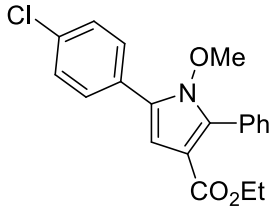
**Ethyl 5-(4-chlorophenyl)-1-methoxy-2-methyl-1*H*-pyrrole-3-carboxylate (3ae):**




The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 74%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 2.0, 6.8 Hz, 2H), 7.35 (dd, *J* = 2.0, 6.8 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 2.59 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.9,

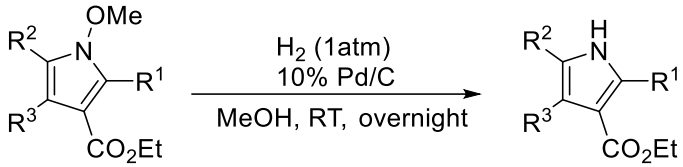
132.8, 132.7, 128.8, 127.6, 125.9, 108.2, 105.6, 65.7, 59.6, 14.5, 9.9; HRMS (ESI) m/z [M+H]+: Calcd for $C_{15}H_{17}NO_3Cl$: 294.0897. Found: 294.0905.

**Ethyl 5-(4-chlorophenyl)-1-methoxy-2-phenyl-1*H*-pyrrole-3-carboxylate (3de):**



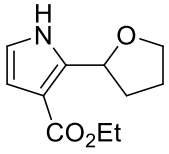

The title compound was prepared according to the general procedure (E). The product was obtained as a colourless oil. Yield: 70%; mp = 96.8-97.2°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 1.6, 6.4 Hz, 2H), 7.62 (dd, *J* = 1.6, 6.4 Hz, 2H), 7.42 (m, 5H), 6.81 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.39 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.1, 134.6, 133.2, 130.6, 128.9, 128.7, 128.6, 128.5, 127.9, 127.7, 127.4, 109.7, 106.8, 65.5, 59.8, 14.2; HRMS (ESI) m/z [M+H]+: Calcd for $C_{20}H_{19}NO_3Cl$: 356.1053. Found: 356.1049.

**General procedure for reduction of pyrrole (F):**



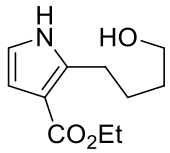

To a solution of the pyrrole (0.3 mmol) in MeOH (2 mL) was added 10% Pd/C under hydrogen gas (1 atm). The reaction mixture was stirred overnight at room temperature and filtered through a pad of celite and wash with 1:1 Hexane: Ethyl acetate. The crude was concentrated and purified by column chromatography to afford the pyrrole.

**Ethyl 2-(tetrahydrofuran-2-yl)-1*H*-pyrrole-3-carboxylate (4ga):**



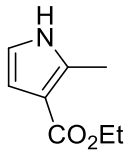
The title compound was prepared according to the general procedure (F). The product was obtained as a colourless oil. Yield: 35%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.80 (br, 1H), 6.60 (m, 2H), 5.41 (t, *J* = 7.0 Hz, 1H), 4.25 (m, 2H), 4.08 (m, 1H), 3.90 (m, 1H), 2.55 (m, 1H), 1.89 (m, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.9, 140.6, 115.5, 111.0, 110.0, 75.4, 68.9, 59.4, 33.4, 25.9, 14.5; HRMS (ESI) m/z [M+H]+: Calcd for $C_{11}H_{17}NO_3$: 210.1130. Found: 210.1131.

**Ethyl 2-(4-hydroxybutyl)-1*H*-pyrrole-3-carboxylate (4gb):**



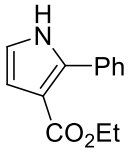

The title compound was prepared according to the general procedure (F). The product was obtained as a colourless oil. Yield: 45%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.48 (br, 1H), 6.57 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.72 (t, *J* = 2.4 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 1.76 (m, 2H), 1.62 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.6, 115.7, 111.4, 110.6, 62.5, 59.4, 31.5, 26.5, 25.8, 14.5; HRMS (ESI) m/z [M+H]+: Calcd for $C_{11}H_{19}NO_3$: 212.1287. Found: 212.1291.

**Ethyl 2-methyl-1*H*-pyrrole-3-carboxylate (4a):**



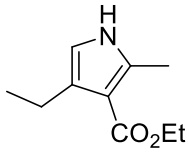

The title compound was prepared according to the general procedure (F). The product was obtained as a colourless oil. Yield: 86%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.17 (br, 1H), 6.57 (m, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7, 135.1, 115.7, 111.8, 110.5, 59.3, 14.5, 13.2; HRMS (ESI) m/z [M+H]+: Calcd for $C_8H_{13}NO_2$: 154.0868. Found: 154.0858.

**Ethyl 2-phenyl-1*H*-pyrrole-3-carboxylate (4b):**



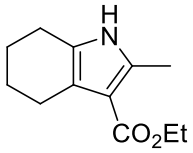
The title compound was prepared according to the general procedure (F). The product was obtained as a colourless oil. Yield: 91%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.49 (br, 1H), 7.57 (m, 2H), 7.37 (m, 3H), 6.74 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.0, 137.0, 132.1, 129.0, 128.2, 128.1, 117.6, 112.3, 112.2, 59.6, 14.3; HRMS (ESI) m/z [M+H]+: Calcd for $C_{13}H_{15}NO_2$: 216.1025. Found: 216.1025.

**Ethyl 4-ethyl-2-methyl-1*H*-pyrrole-3-carboxylate (4c):**



The title compound was prepared according to the general procedure (F). The product was obtained as a colourless oil. Yield: 93%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.00 (br, 1H), 6.36 (m, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.71 (m, 2H), 2.49 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 136.0, 128.7, 112.9, 110.2, 59.0, 20.2, 14.6, 14.5, 14.1; HRMS (ESI) m/z [M+H]+: Calcd for $C_{10}H_{17}NO_2$: 182.1181. Found: 182.1178.

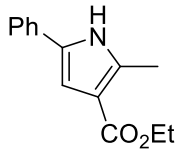
**Ethyl 2-methyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (4d):**



The title compound was prepared according to the general procedure (F). The product was obtained as a colourless oil. Yield: 87%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.88 (br, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.69 (m, 2H), 2.48 (m, 5H), 1.75 (m, 4H), 1.33 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.3, 134.0, 125.3, 118.6, 109.6, 58.9,

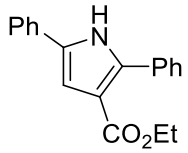
23.5, 23.3, 22.9, 22.4, 14.5, 13.6; HRMS (ESI) m/z [M+H]+: Calcd for $C_{12}H_{19}NO_2$: 208.1338. Found: 208.1336.

**Ethyl 2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (4e):**



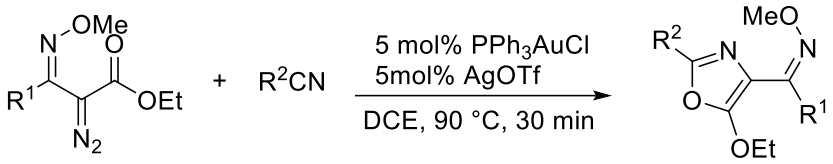

The title compound was prepared according to the general procedure (F). The product was obtained as a colourless oil. Yield: 79%; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (br, 1H), 7.45 (dd, *J* = 1.2, 8.4 Hz, 2H), 7.37 (m, 2H), 7.24 (m, 1H), 6.83 (d, *J* = 3.2 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.5, 136.1, 131.8, 129.9, 129.0, 126.6, 123.7, 113.5, 107.4, 59.5, 14.6, 13.4; HRMS (ESI) m/z [M+H]+: Calcd for $C_{14}H_{17}NO_2$: 230.1181. Found: 230.1176.

**Ethyl 2,5-diphenyl-1*H*-pyrrole-3-carboxylate (4f):**



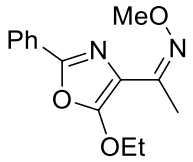

The title compound was prepared according to the general procedure (F). The product was obtained as a colourless oil. Yield: 90%; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.60 (br, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.40 (m, 5H), 7.27 (m, 1H), 7.01 (d, *J* = 3.2 Hz, 1H), 4.24 (q, *J* = 3.2 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.8, 137.7, 132.0, 131.7, 131.5, 129.1, 129.0, 128.4, 128.2, 127.1, 124.0, 113.9, 109.2, 59.8, 14.3; HRMS (ESI) m/z [M+H]+: Calcd for $C_{19}H_{19}NO_2$: 292.1338. Found: 292.1341.

**General procedure for synthesis of oxazoles (G):**



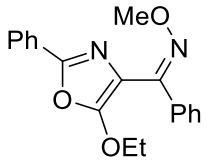

To a oven dried reaction tube was added 5 mol% of $PPh_3AuCl$ and 5 mol% of AgOTf in DCE (1 mL) and the mixture was allowed to stir for 5 mins at room temperature until a white precipitate forms. Benzonitrile (10 eq.), followed by dropwise addition of α-diazo oxime ether (0.3 mmol, 1 eq.) was added to the mixture whilst stirring at room temperature. After the addition of the substrates, the reaction was heated at 90℃ for approximately 30 mins. The crude was concentrated and purified by flash column chromatography to give the oxazole.

**(*Z*)-1-(5-Ethoxy-2-phenyloxazol-4-yl)ethanone *O*-methyl oxime (6aa):**




The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 81%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (m, 2H), 7.41 (m, 3H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 2.25 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 156.1, 151.9, 146.4, 129.8, 128.6, 127.2, 125.6, 110.6, 69.7, 61.6, 19.3, 15.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_{14}H_{17}N_2O_3$: 261.1239. Found: 261.1237.

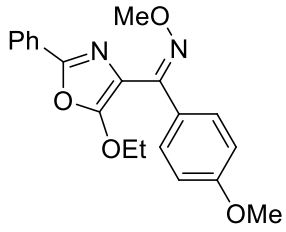
**(*Z*)-(5-Ethoxy-2-phenyloxazol-4-yl)(phenyl)methanone *O*-methyl oxime (6da):**




The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 89%; $^1$H NMR (400 MHz, $CDCl_3$) δ

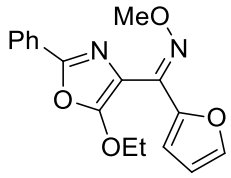
7.92 (m, 2H), 7.67 (m, 2H), 7.37 (m, 6H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.05 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 157.1, 152.3, 148.7, 134.7, 129.8, 129.3, 128.6, 128.2, 127.7, 127.2, 125.6, 108.1, 69.2, 62.4, 14.9; HRMS (ESI) m/z [M+H]+: Calcd for $C_{19}H_{19}N_2O_3$: 323.1396. Found: 323.1394.

**(*Z*)-(5-Ethoxy-2-phenyloxazol-4-yl)(4-methoxyphenyl)methanone *O*-methyl oxime (6ea):**




The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 87%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.40 (m, 3H), 6.89 (dd, *J* = 2.0, 7.2 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.04 (s, 3H), 3.82 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 160.7, 157.0, 152.2, 148.3, 129.7, 129.1, 128.6, 127.3, 127.3, 125.6, 113.7, 108.2, 69.1, 62.2, 55.2, 14.9; HRMS (ESI) m/z [M+H]+: Calcd for $C_{20}H_{21}N_2O_4$: 353.1501. Found: 353.1508.

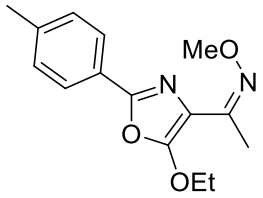
**(*E*)-(5-Ethoxy-2-phenyloxazol-4-yl)(furan-2-yl)methanone *O*-methyl oxime (6ga):**




The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 80%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 2H), 7.50 (d, *J* = 1.2 Hz, 1H), 7.41 (m, 3H), 6.72 (d, *J* = 3.2 Hz, 1H), 6.45 (dd, *J* = 1.6, 3.2 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.07 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 157.0, 152.1, 148.4, 143.7, 140.5, 129.8, 128.6,

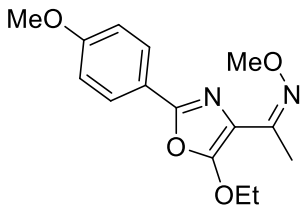
128.5, 127.1, 125.5, 113.6, 111.4, 69.3, 62.6, 14.9; HRMS (ESI) m/z [M+H]+: Calcd for $C_{17}H_{17}N_2O_4$: 313.1188. Found: 313.1191.

**(*Z*)-1-(5-Ethoxy-2-p-tolyloxazol-4-yl)ethanone *O*-methyl oxime (6ab):**



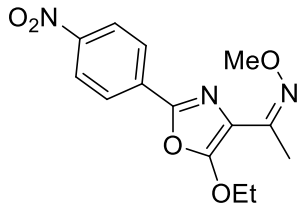

The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 83%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 2.38 (s, 3H), 2.24 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 155.9, 152.2, 146.4, 140.0, 129.3, 125.5, 124.5, 110.5, 69.7, 61.6, 21.4, 19.2, 15.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_{15}H_{19}N_2O_3$: 275.1396. Found: 275.1396.

**(*Z*)-1-(5-Ethoxy-2-(4-methoxyphenyl)oxazol-4-yl)ethanone *O*-methyl oxime (6ac):**



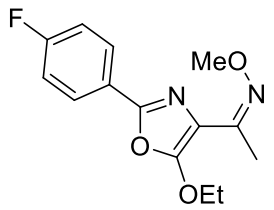

The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 86%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 3.84 (s, 3H), 2.24 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 161.0, 155.8, 152.1, 146.5, 127.2, 120.0, 114.0, 110.4, 69.7, 61.6, 55.3, 19.3, 15.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_{15}H_{19}N_2O_4$: 291.1345. Found: 291.1353.

**(*E*)-1-(5-Ethoxy-2-(4-nitrophenyl)oxazol-4-yl)ethanone *O*-methyl oxime (6ad):**



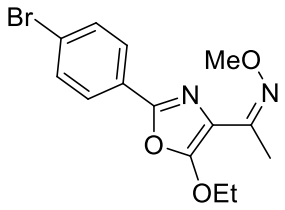

The titled compound was prepared according to the general procedure (G). The product was obtained as a yellow solid. Yield 76%; mp: 65.5-66.0℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 2.24 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 156.9, 149.5, 148.1, 145.9, 132.6, 126.0, 124.1, 111.6, 69.9, 61.7, 19.2, 15.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_{14}H_{16}N_3O_5$: 306.1090. Found: 306.1088.

**(*Z*)-1-(5-Ethoxy-2-(4-fluorophenyl)oxazol-4-yl)ethanone *O*-methyl oxime (6ae):**



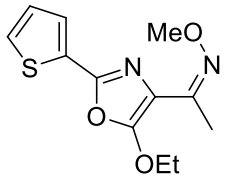

The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 78%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 2.24 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 165.0, 162.5, 156.1, 151.2, 146.3, 127.6 (d, *J* = 8.5 Hz, CH), 123.6 (d, *J* = 3.1 Hz, CH), 115.8 (d, *J* = 22.1 Hz, CH), 110.7, 69.8, 61.6, 19.2, 15.0; $^{19}$F NMR (376 MHz, $CDCl_3$): *δ* = –110.1 (m,1F); HRMS (ESI) m/z [M+H]+: Calcd for $C_{14}H_{16}N_2O_3F$: 279.1145. Found: 279.1140.

**(Z)-1-(2-(4-Bromophenyl)-5-ethoxyoxazol-4-yl)ethanone *O*-methyl oxime (6af):**



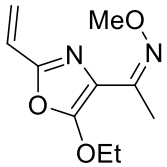

The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 70%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 1.6, 6.4 Hz, 2H), 7.55 (dd, *J* = 1.6, 6.4 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 2.24 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 156.2, 151.0, 146.2, 131.9, 127.0, 126.1, 124.2, 110.8, 69.8, 61.6, 19.2, 15.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_{14}H_{16}N_2O_3Br$: 339.0344. Found: 339.0348.

**(*Z*)-1-(5-Ethoxy-2-(thiophen-2-yl)oxazol-4-yl)ethanone *O*-methyl oxime (6ag):**




The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 80%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.79 (m, 1H), 7.53 (d, *J* = 4.8 Hz, 1H), 7.34 (m, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 2.23 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 155.5, 149.3, 146.2, 129.2, 126.5, 125.5, 124.3, 110.2, 69.8, 61.6, 19.2, 14.9; HRMS (ESI) m/z [M+H]+: Calcd for $C_{12}H_{15}N_2O_3S$: 267.0803. Found: 267.0800.

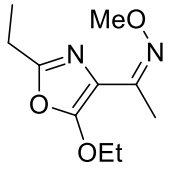
**(*Z*)-1-(5-Ethoxy-2-vinyloxazol-4-yl)ethanone O-methyl oxime (6ah):**




The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 75%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ

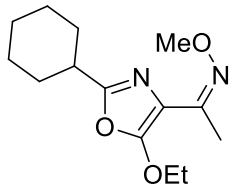
6.43 (dd, *J* = 11.2 Hz, 1H), 5.96 (d, *J* = 17.6 Hz, 1H), 5.52 (d, *J* = 11.6 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 2.18 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 155.8, 151.4, 145.8, 123.2, 120.0, 110.2, 69.5, 61.6, 19.1, 14.9; HRMS (ESI) m/z [M+H]+: Calcd for $C_{10}H_{15}N_2O_3$: 211.1083. Found: 211.1085.

**(*Z*)-1-(5-Ethoxy-2-ethyloxazol-4-yl)ethanone *O*-methyl oxime (6ai):**




The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 95%; $^1$H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.14 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.1, 155.9, 146.1, 108.9, 69.5, 61.6, 21.8, 19.2, 14.9, 11.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_{10}H_{17}N_2O_3$: 213.1239. Found: 213.1237.

**(*Z*)-1-(2-Cyclohexyl-5-ethoxyoxazol-4-yl)ethanone O-methyl oxime (6aj):**




The titled compound was prepared according to the general procedure (G). The product was obtained as a colourless oil. Yield 86%; $^1$H NMR (400 MHz, $CDCl_3$) δ 4.21 (m, 2H), 3.89 (s, 3H), 2.66 (dt, *J* = 2.8, 10.8 Hz, 1H), 2.16 (s, 3H), 1.99 (d, *J* = 12.8 Hz, 2H), 1.80 (d, *J* = 12.8 Hz, 2H), 1.69 (d, *J* = 11.2 Hz, 1H), 1.51 (q, *J* = 12.0 Hz, 2H), 1.30 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 158.4, 155.6, 146.5, 108.6, 69.3, 61.5, 37.7, 30.3, 25.7, 25.5, 19.2, 15.0; HRMS (ESI) m/z [M+H]+: Calcd for $C_{14}H_{23}N_2O_3$: 267.1709. Found: 267.1698.

**References**


**[1]** **T. Misaki, R. Nagase, K. Matsumoto, Y. Tanabe, *J. Am. Chem. Soc.* 2005, *127*, 2854-2855.**

**[2]** **J. S. Yadav, B. V. Subba Reddy, B. Eeshwaraiah, P. N. Reddy, *Tetrahedron* 2005, *61*, 875-878.**

**[3]** **M. G. Ferlin, G. Chiarelotto, V. Gasparotto, L. Dalla Via, V. Pezzi, L. Barzon, G. Palù, I. Castagliuolo, *J. Med. Chem.* 2005, *48*, 3417-3427.**

**[4]** **C. Pidathala, R. Amewu, B. Pacorel, G. L. Nixon, P. Gibbons, W. D. Hong, S. C. Leung, N. G. Berry, R. Sharma, P. A. Stocks, A. Srivastava, A. E. Shone, S. Charoensutthivarakul, L. Taylor, O. Berger, A. Mbekeani, A. Hill, N. E. Fisher, A. J. Warman, G. A. Biagini, S. A. Ward, P. M. O'Neill, *J. Med. Chem.* 2012, *55*, 1831-1843.**

**[5]** **E. Lourdusamy, L. Yao, C.-M. Park, *Angew. Chem. Int. Ed.* 2010, *49*, 7963-7967.**

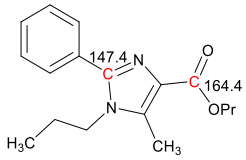
**[6]** **A. S. Tsai, M. l. Brasse, R. G. Bergman, J. A. Ellman, *Org. Lett.* 2010, *13*, 540-542.**

**[7]** **Y. Jiang, W. C. Chan, C.-M. Park, *J. Am. Chem. Soc.* 2012, *134*, 4104-4107.**

**[8]** **F. de Nanteuil, J. Waser, *Angew. Chem. Int. Ed.* 2011, *50*, 12075-12079.**

**[9]** **J. J. Song, Z. Tan, J. T. Reeves, D. R. Fandrick, N. K. Yee, C. H. Senanayake, *Org. Lett.* 2008, *10*, 877-880.**

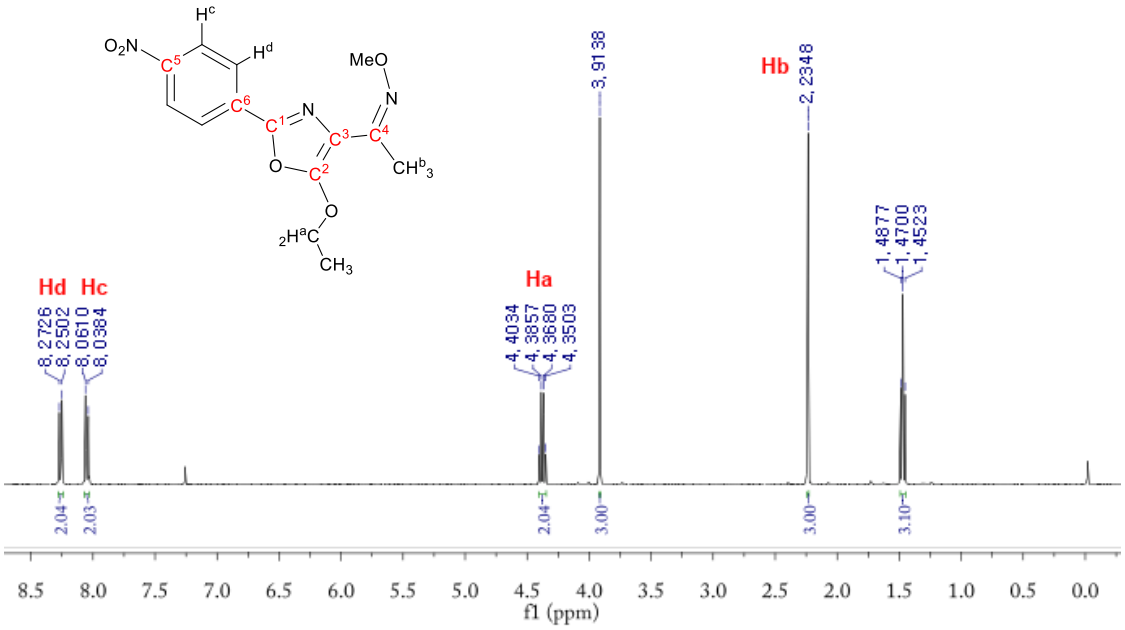
## NMR analysis of oxazole

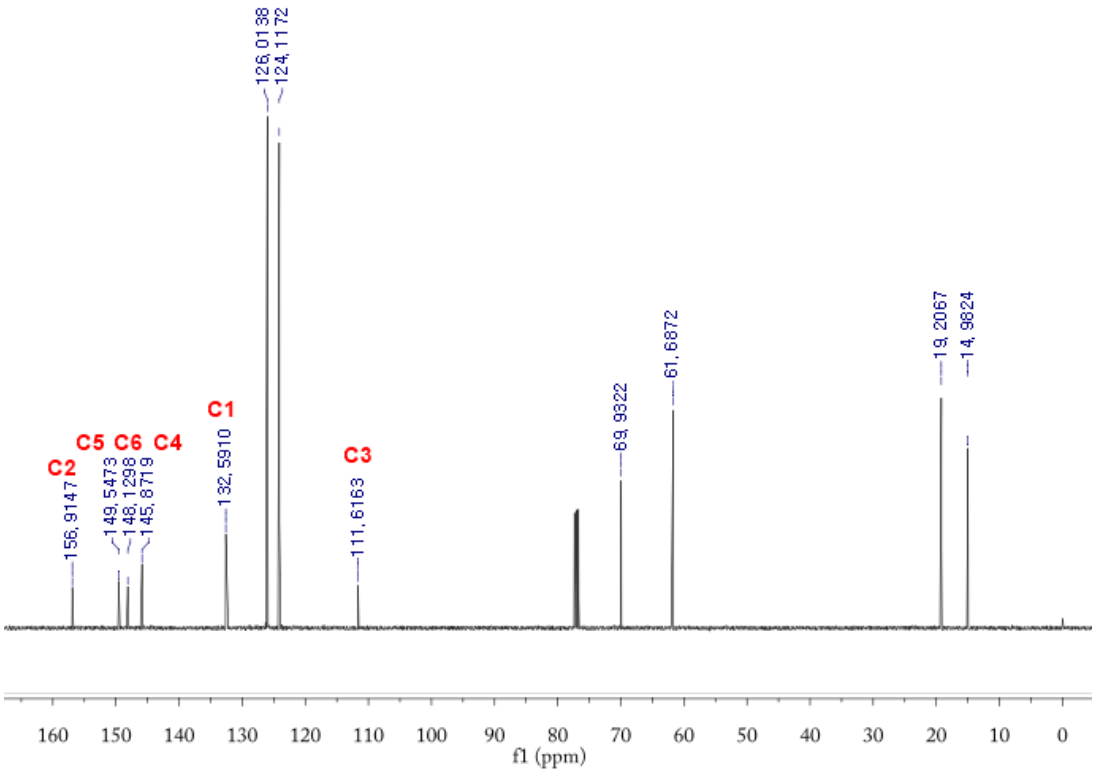


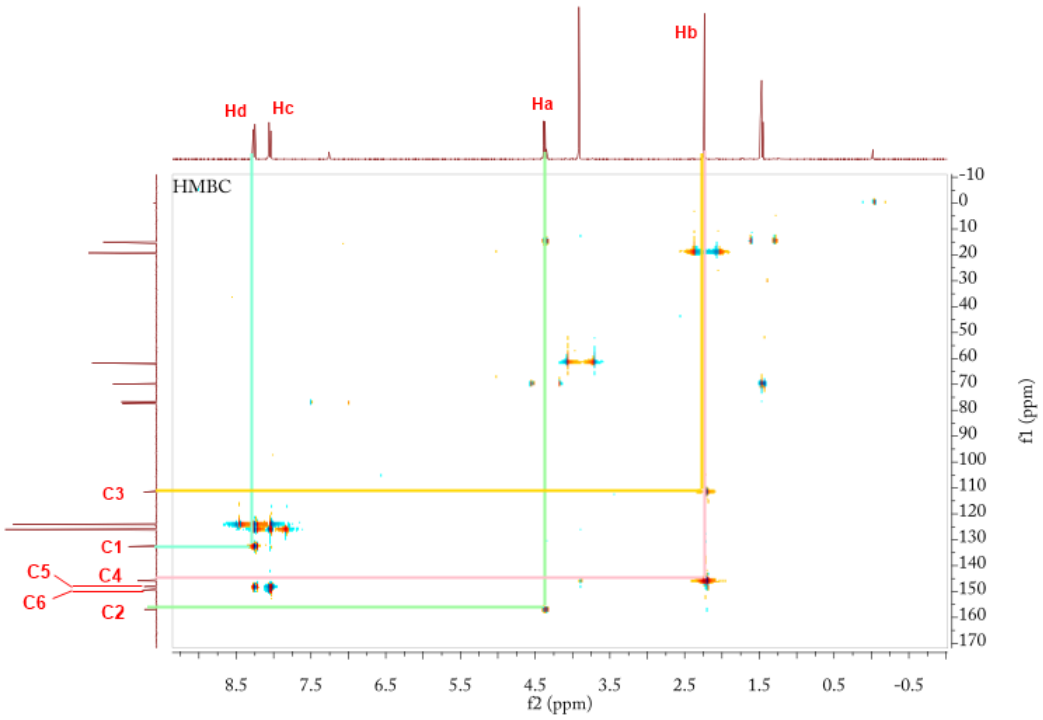

Imidazole nmr data

Ref. *J. Org. Chem.*, **2015**, *80* (9), pp 4729–4735

## (*E*)-1-(5-Ethoxy-2-(4-nitrophenyl)oxazol-4-yl)ethanone *O*-methyl oxime (6ad):



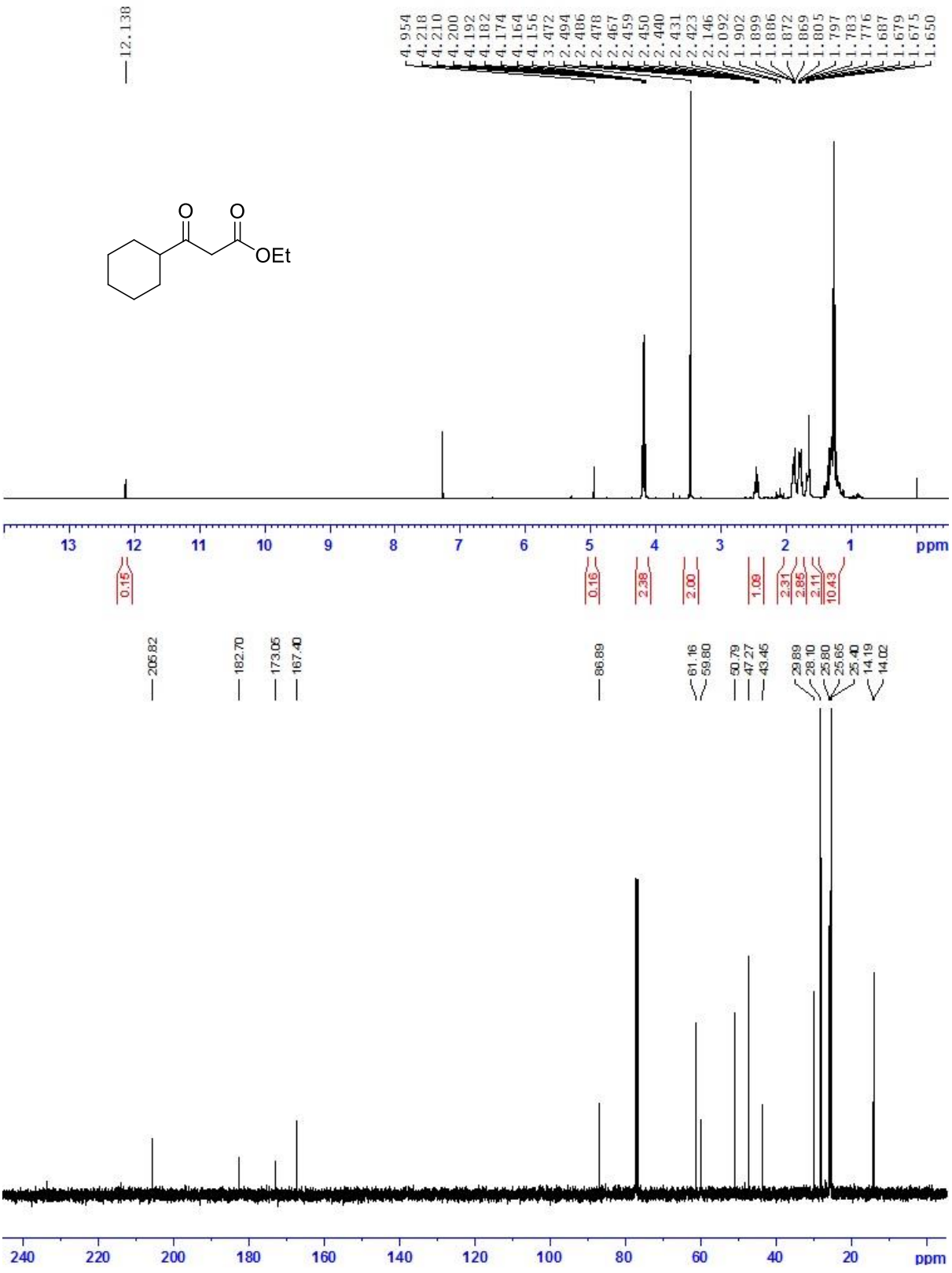


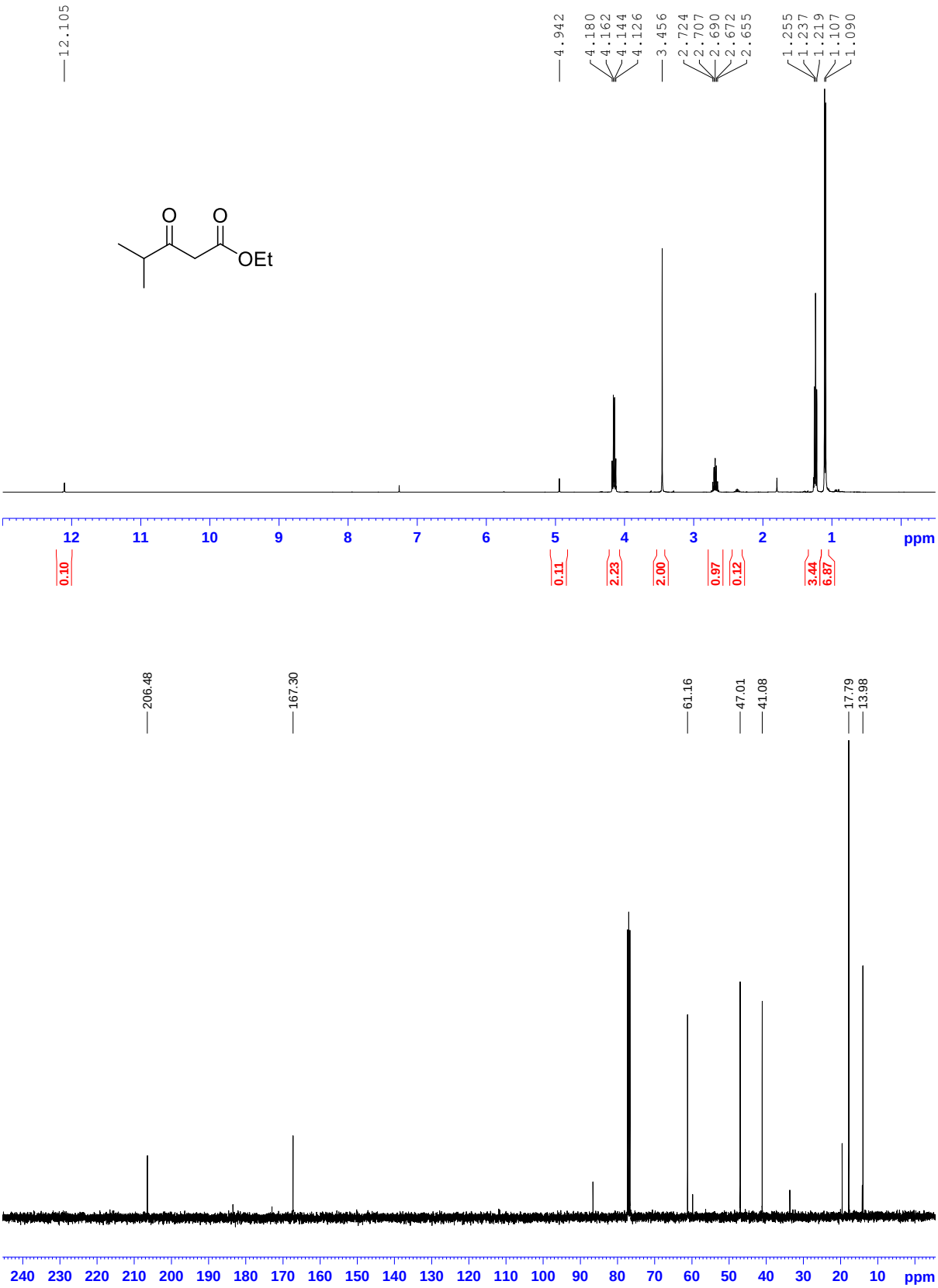

Correlation

$H^a$ - $C^2$ / $H^b$ - $C^3$, $C^4$ / $H^c$ – $C^5$, $C^6$ / $H^d$ - $C^1$, $C^5$

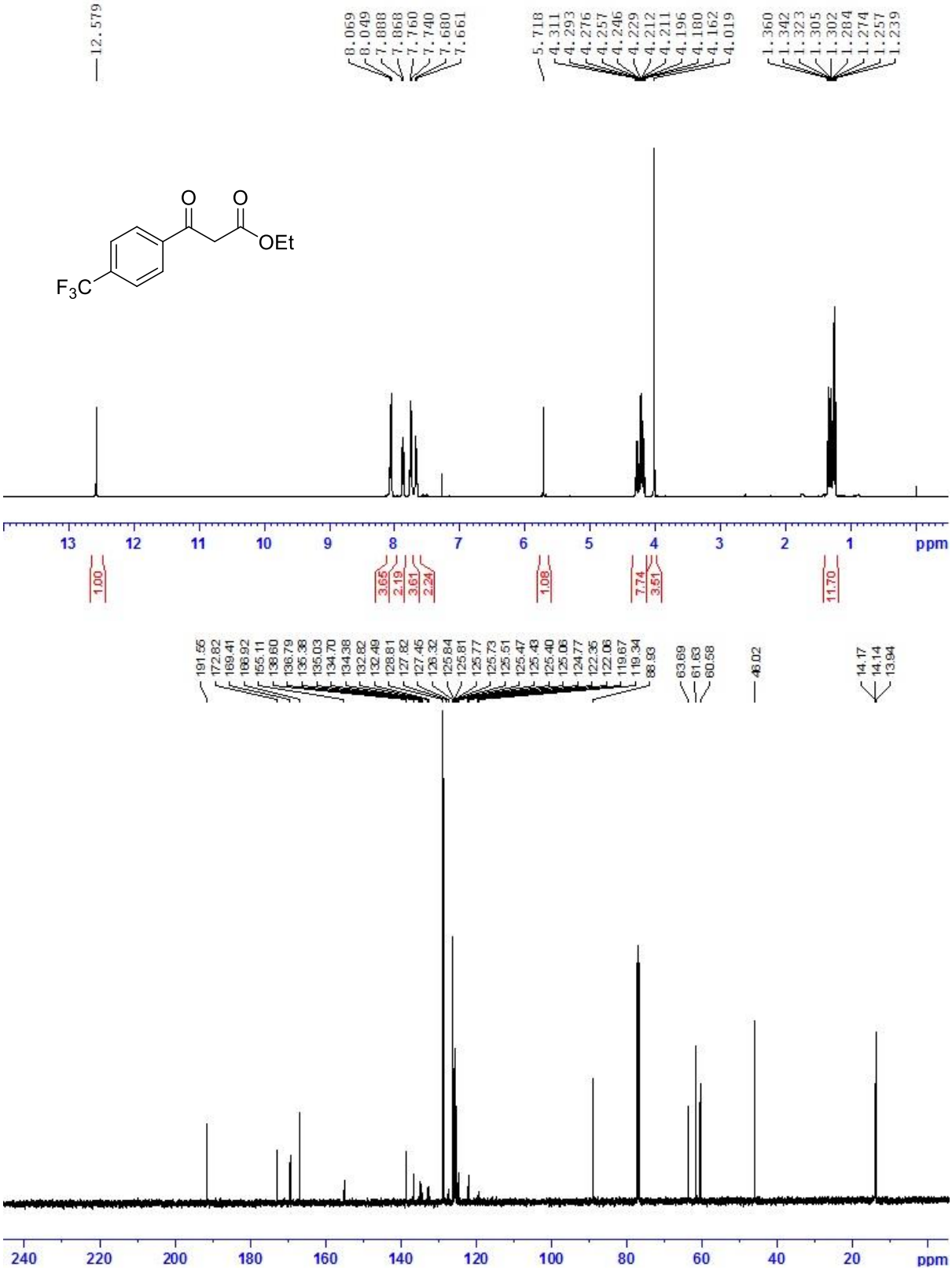
**Ethyl 3-cyclohexyl-3-oxopropanoate:**

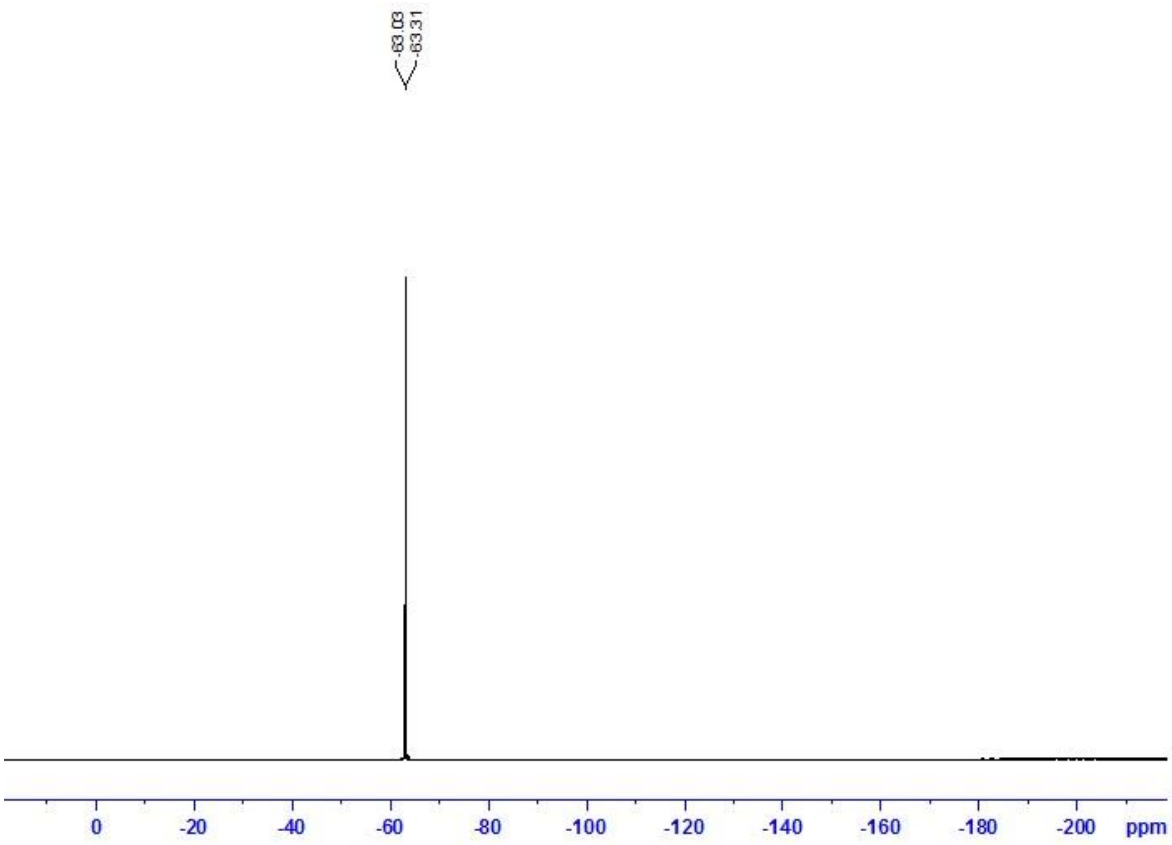


**Ethyl 4-methyl-3-oxopentanoate:**

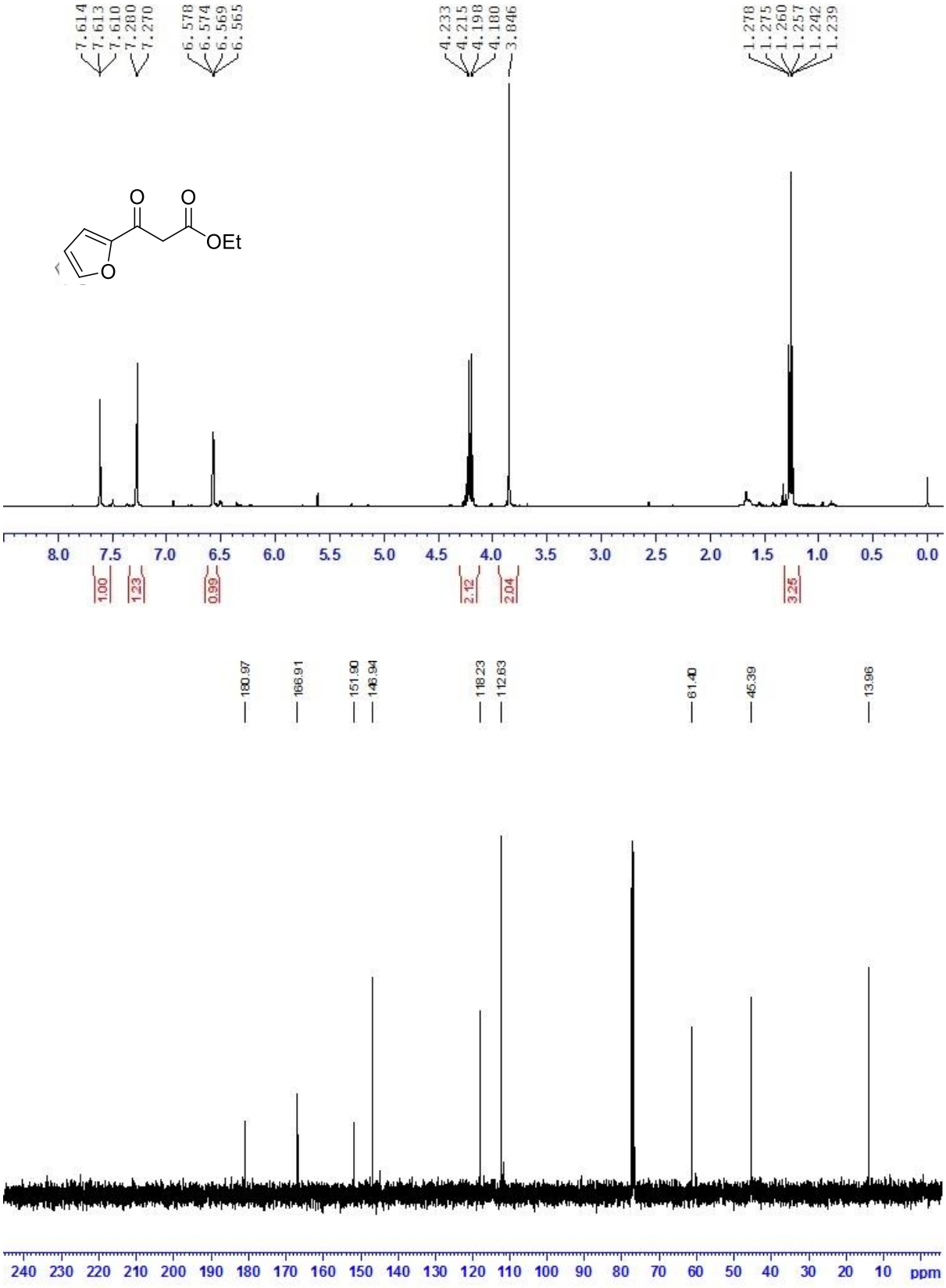


**Ethyl 3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate:**

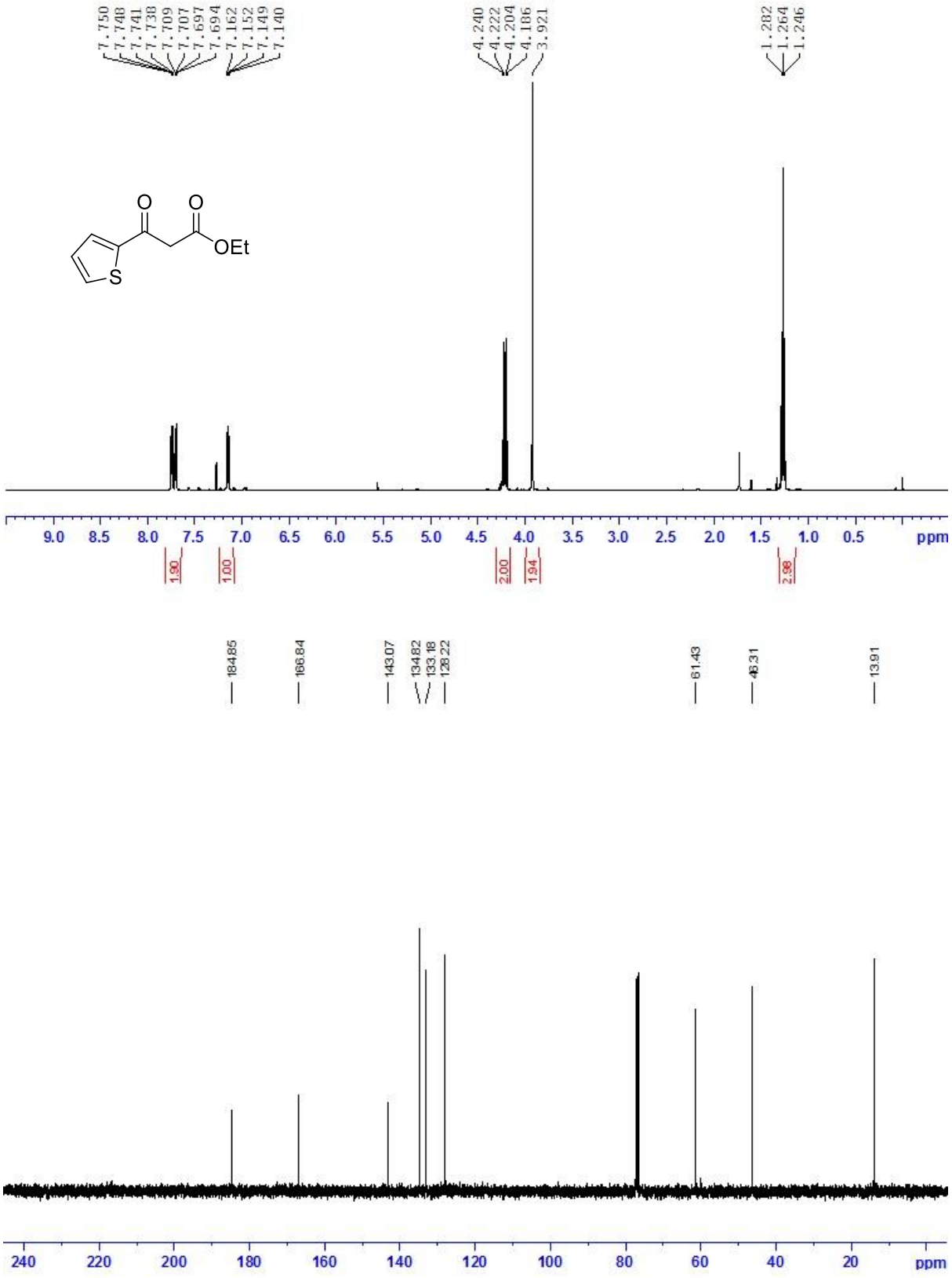



-63.03
-63.31
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

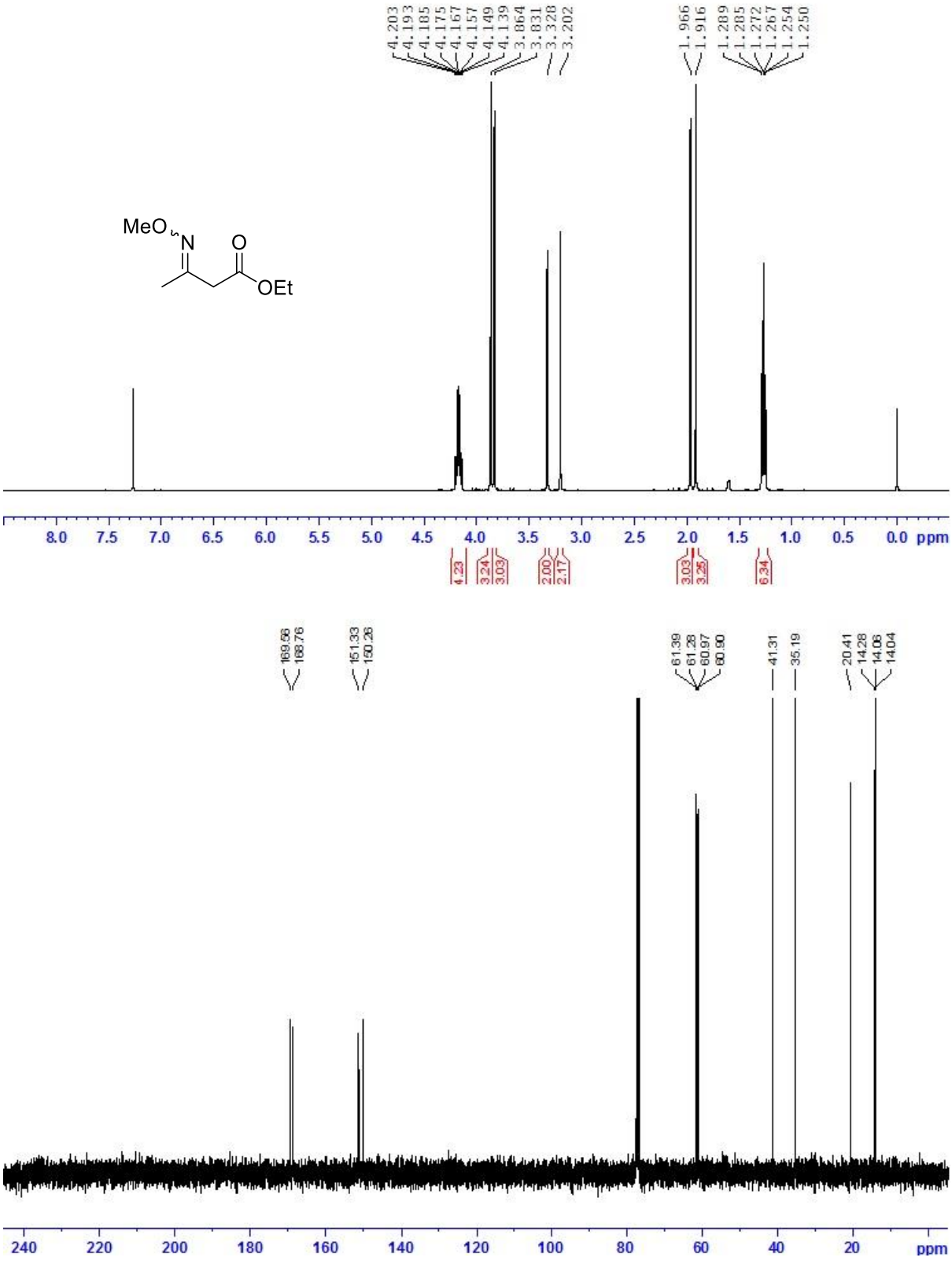
**Ethyl 3-(furan-2-yl)-3-oxopropanoate:**



**Ethyl 3-oxo-3-(thiophen-2-yl)propanoate:**



**Ethyl 3-(methoxyimino)butanoate:**



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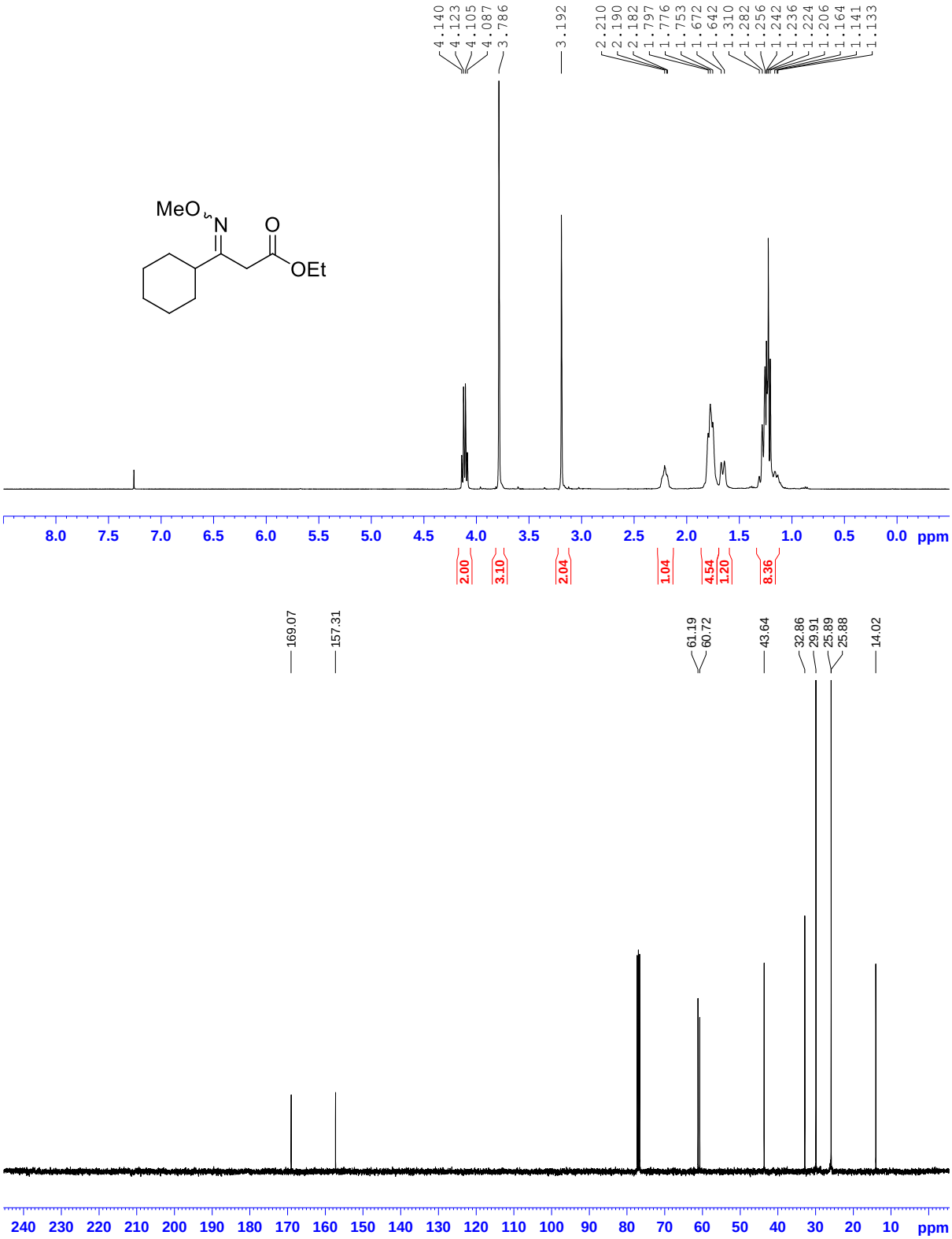

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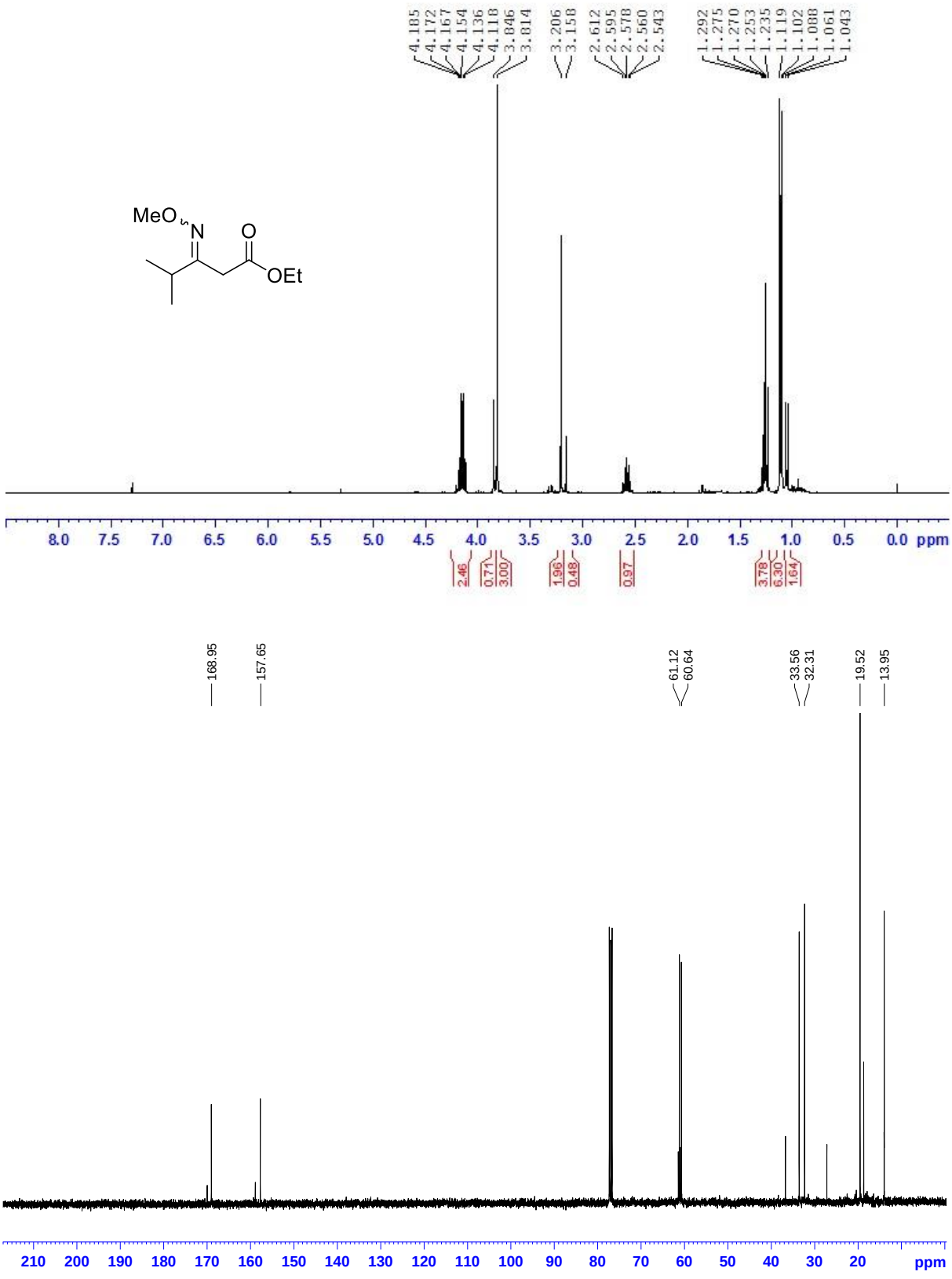
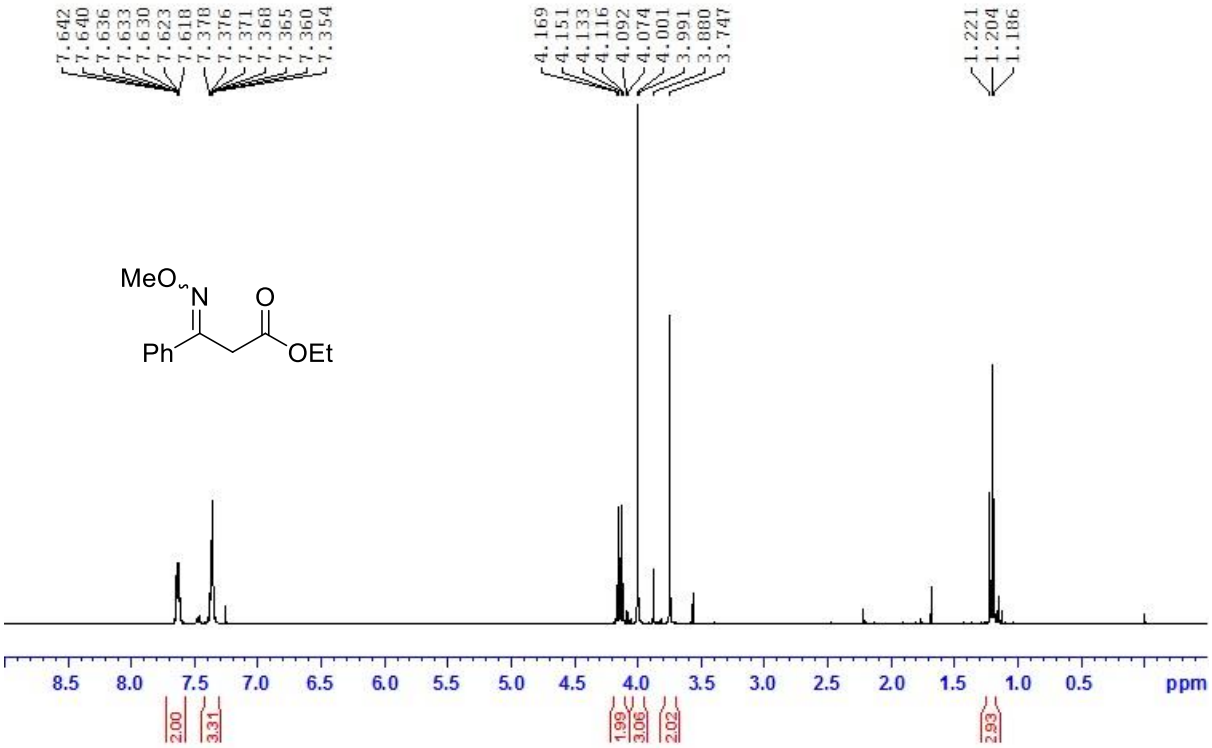
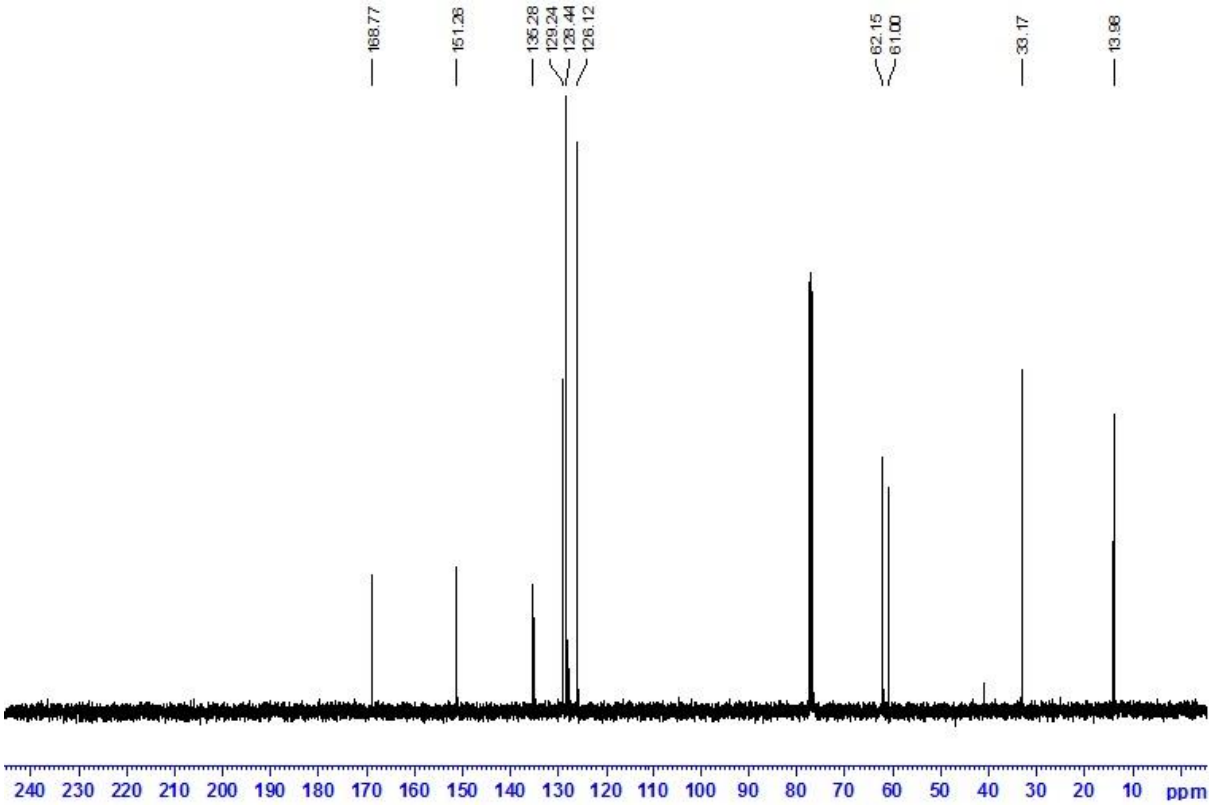
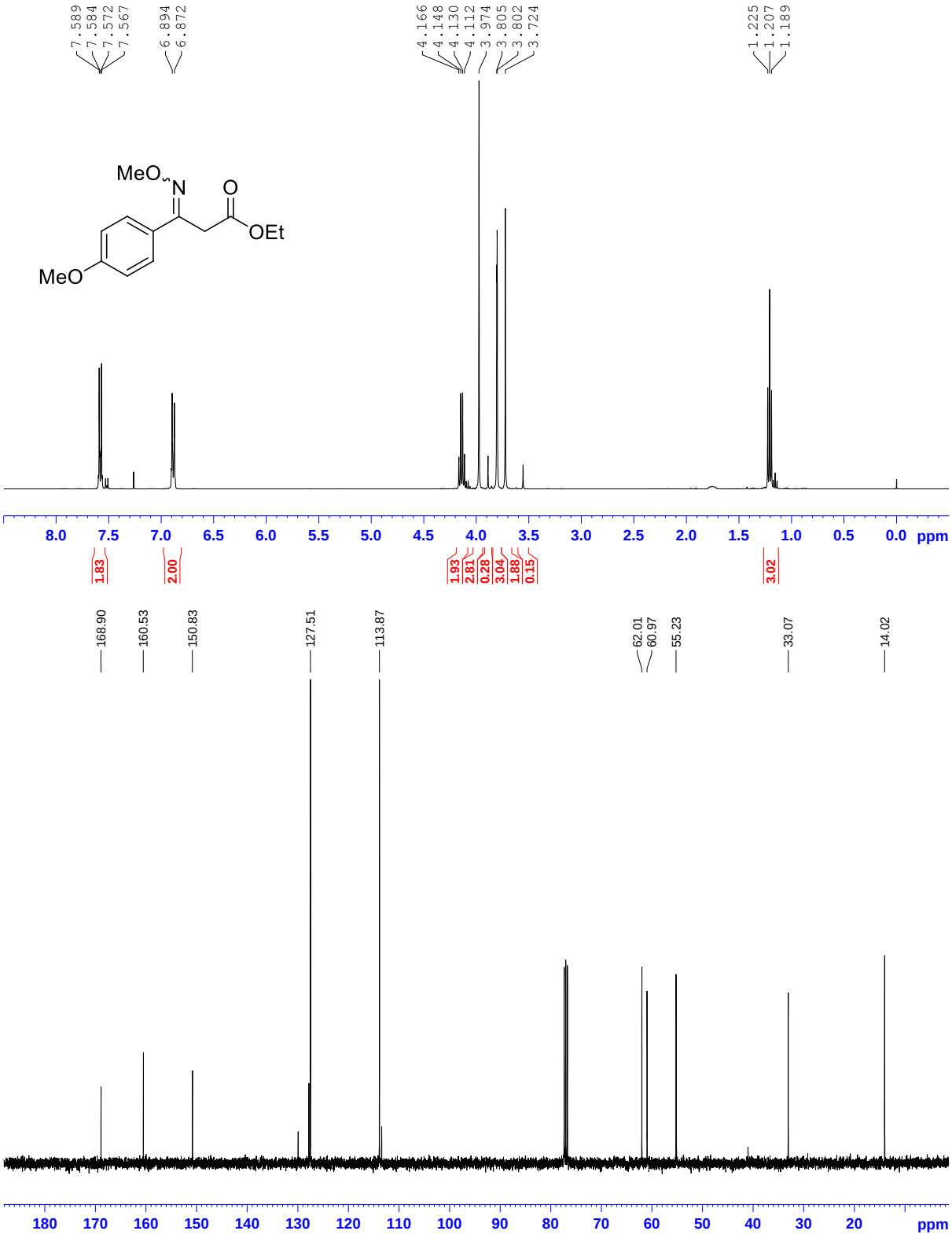


**(*E*)-Ethyl 3-(methoxyimino)-3-phenylpropanoate:**

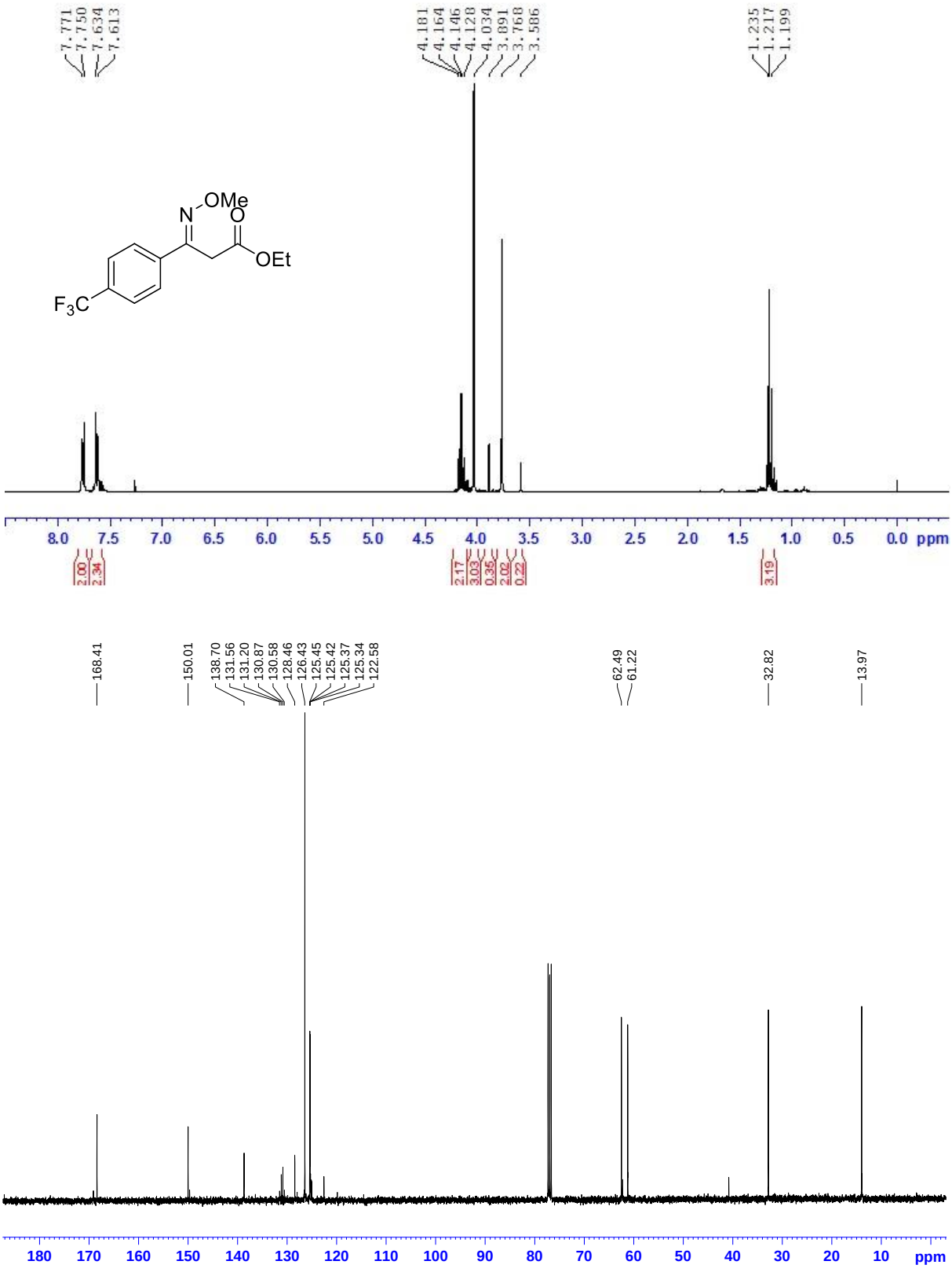


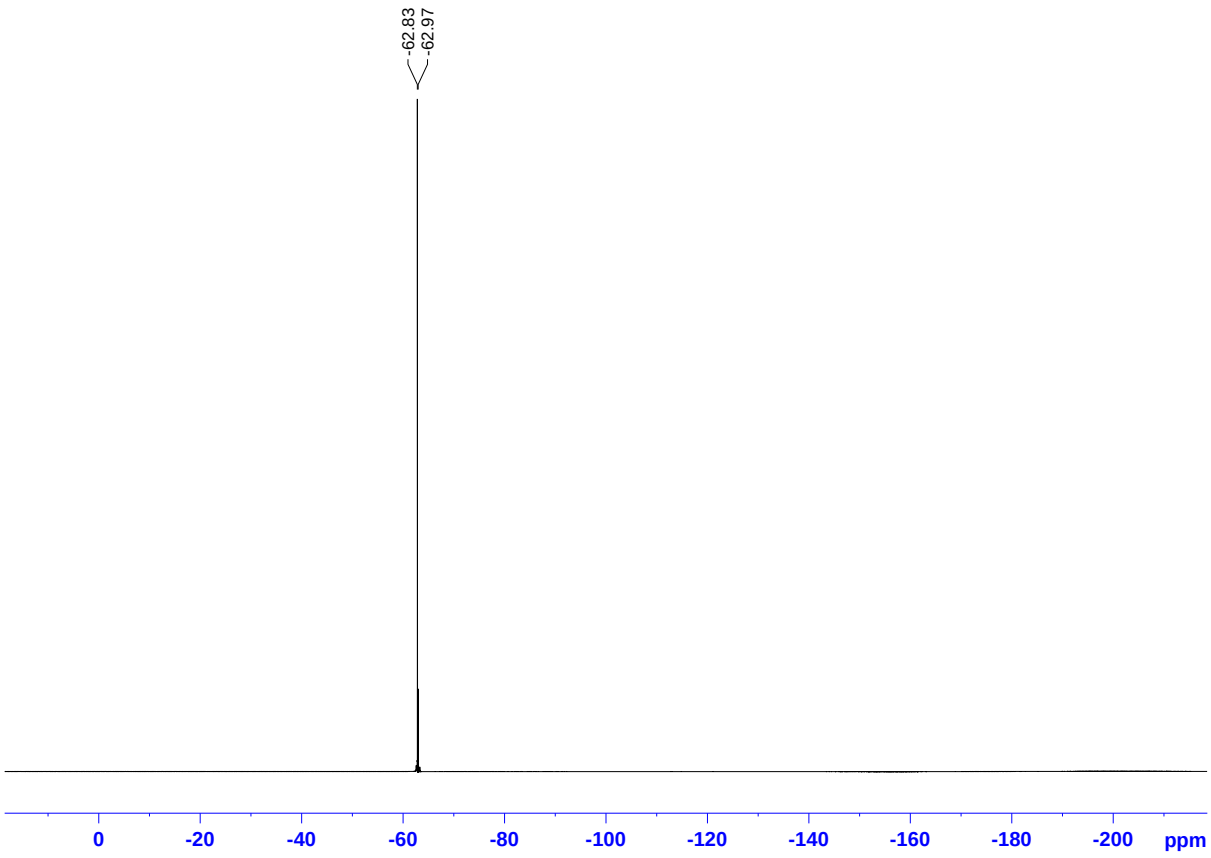



**(*E*)-Ethyl 3-(methoxyimino)-3-(4-methoxyphenyl)propanoate:**

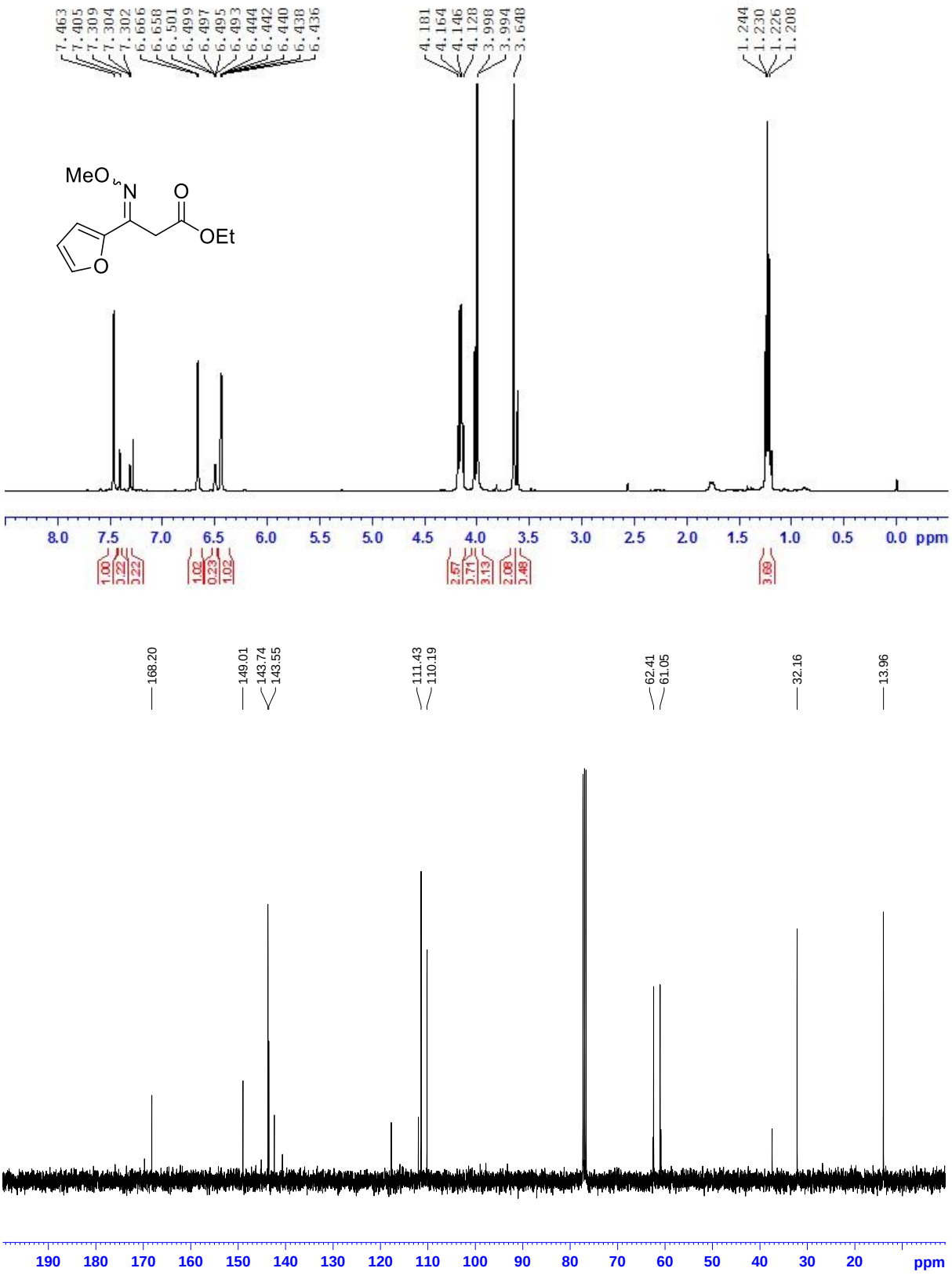


**(*E*)-ethyl 3-(methoxyimino)-3-(4-(trifluoromethyl)phenyl)propanoate:**

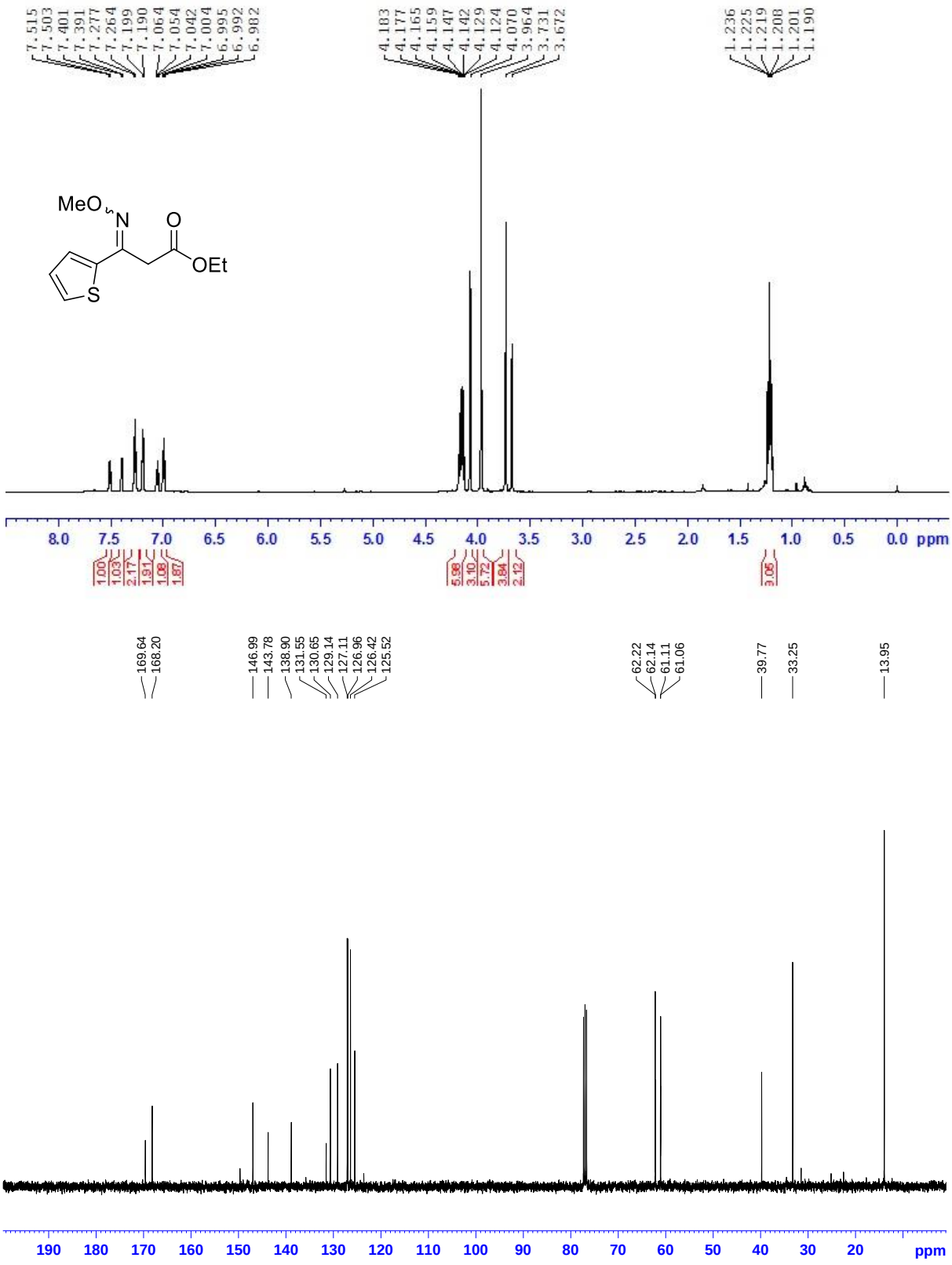



-62.83
-62.97
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

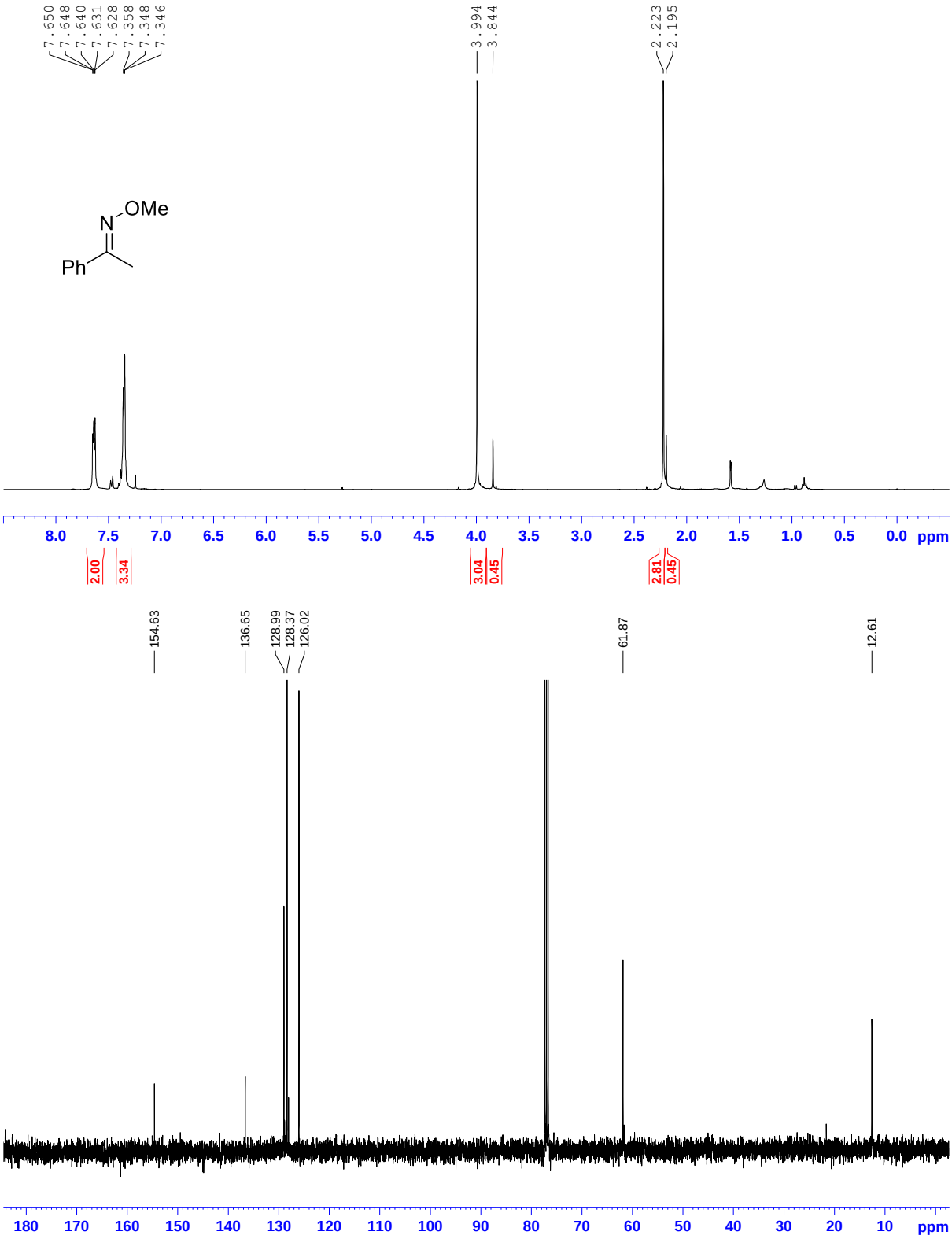
**Ethyl 3-(furan-2-yl)-3-(methoxyimino)propanoate:**



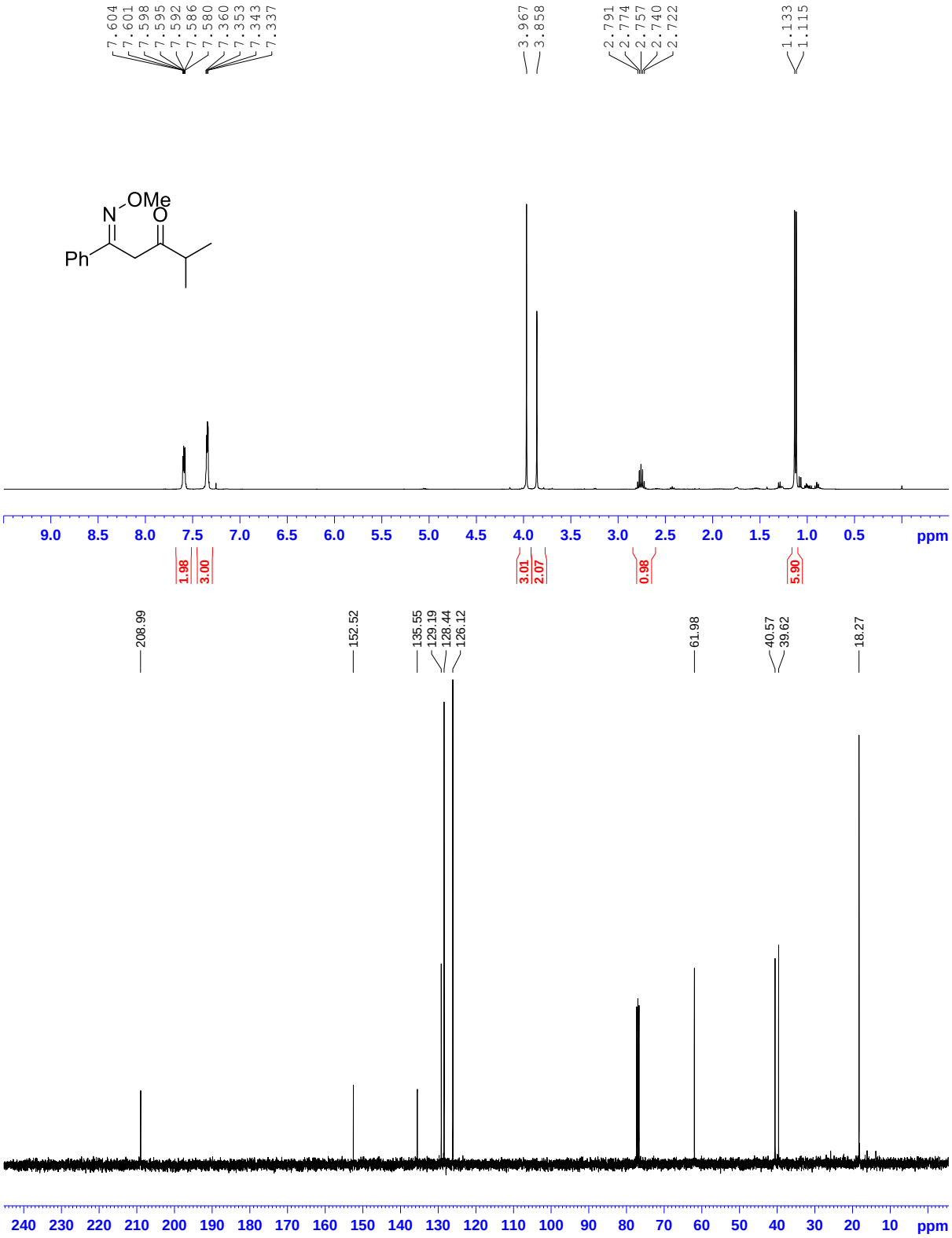
**Ethyl 3-(methoxyimino)-3-(thiophen-2-yl)propanoate:**



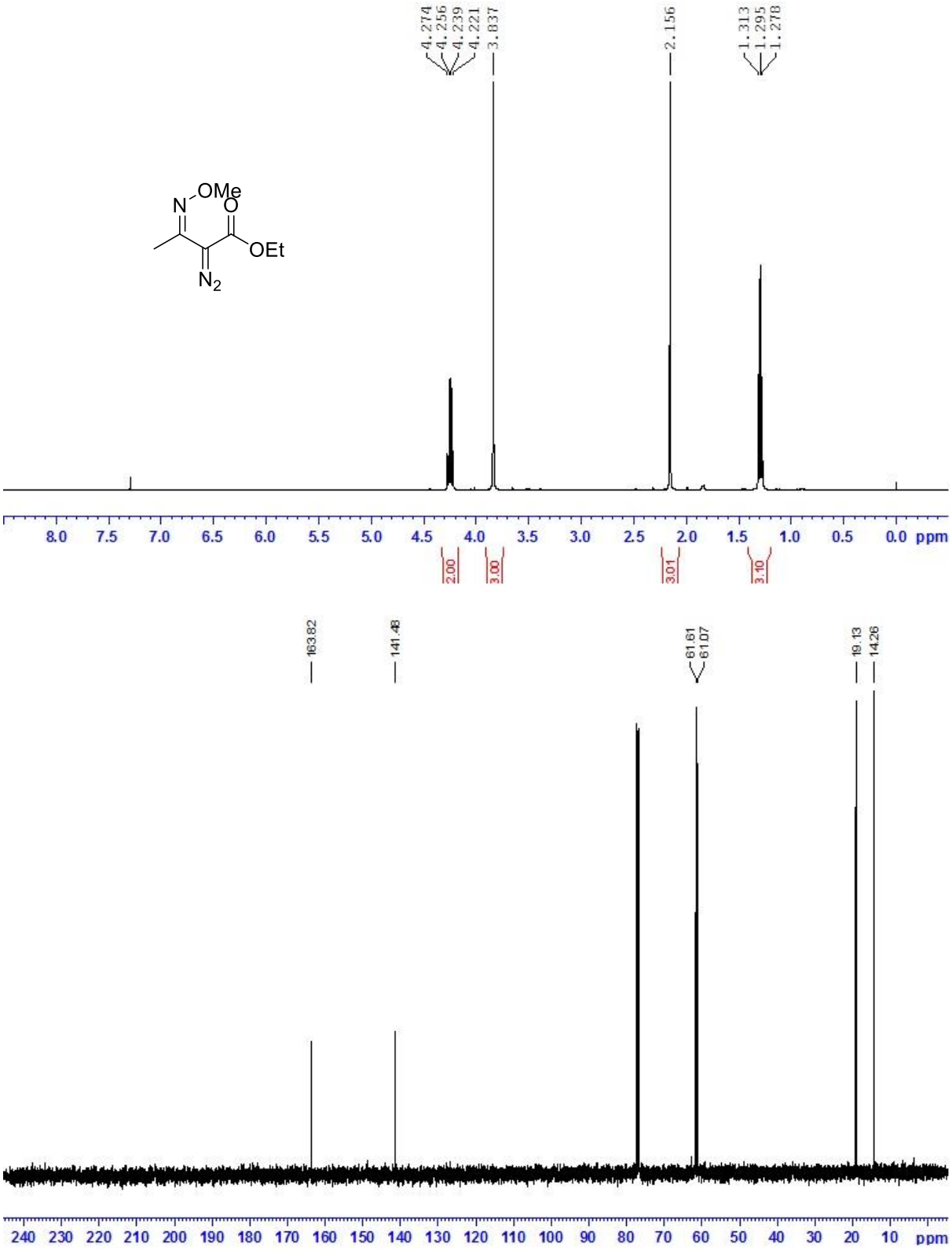
**(*E*)-acetophenone O-methyl oxime:**



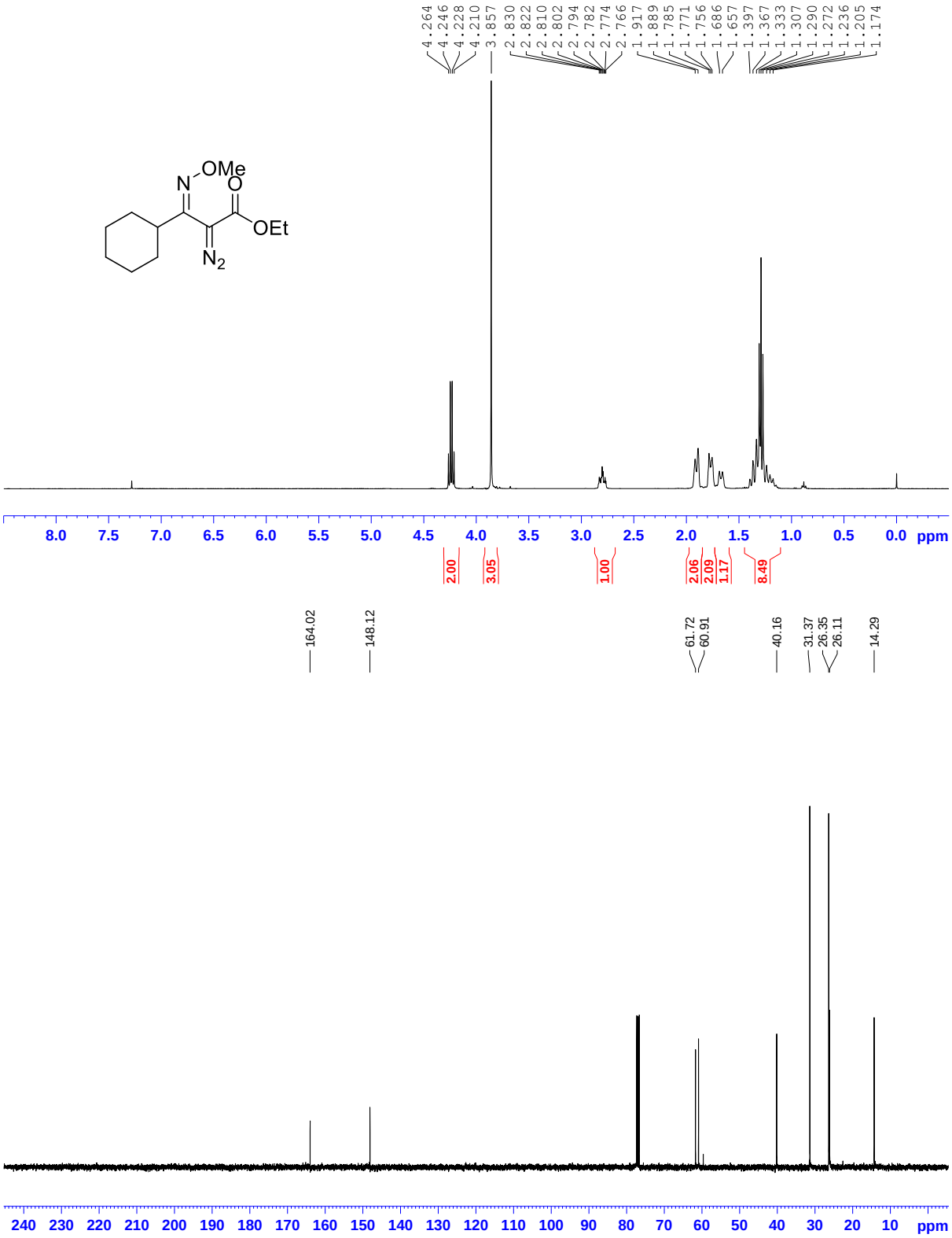
**(*E*)-1-(methoxyimino)-4-methyl-1-phenylpentan-3-one:**



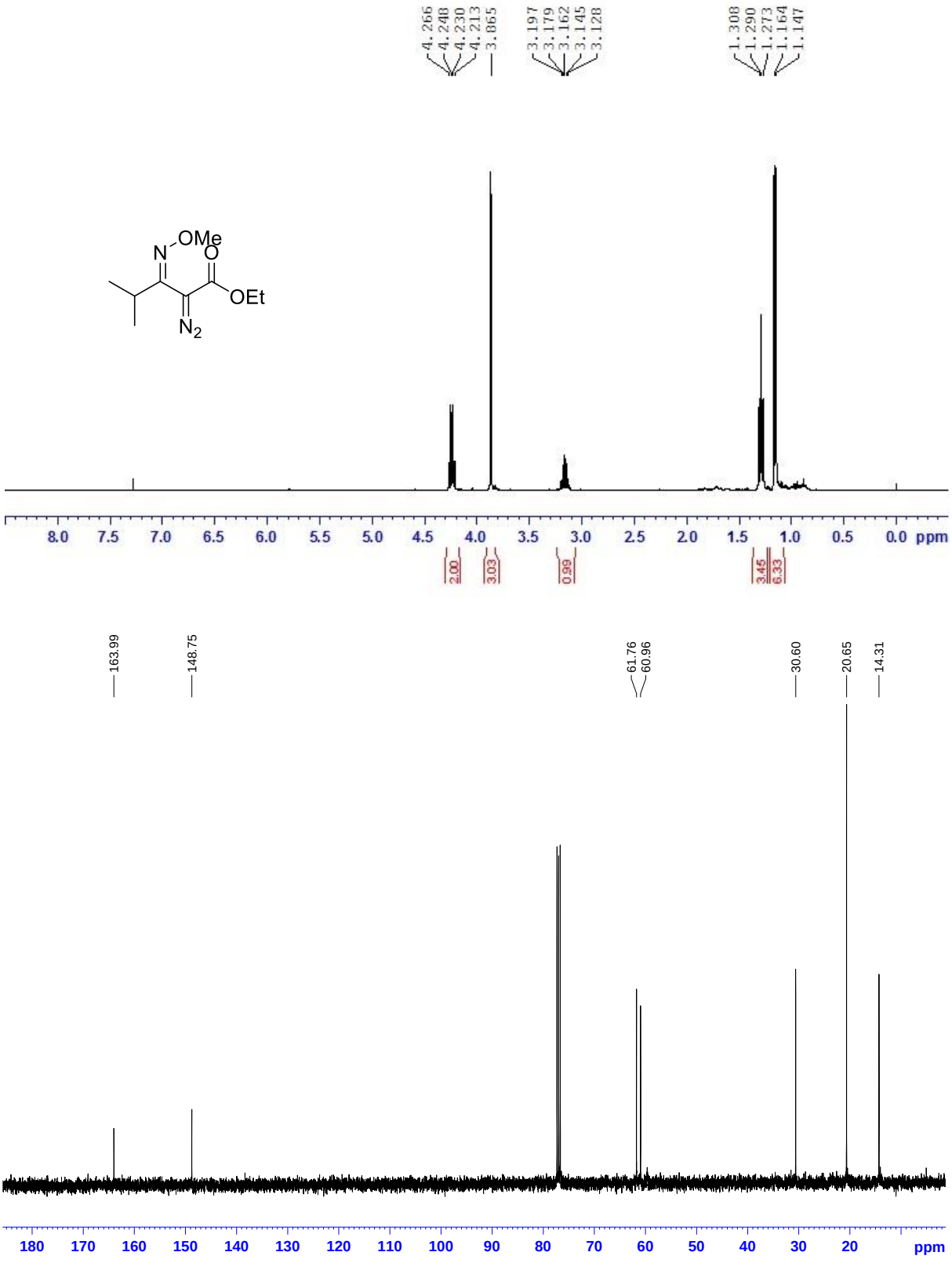
**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)butanoate (1a):**



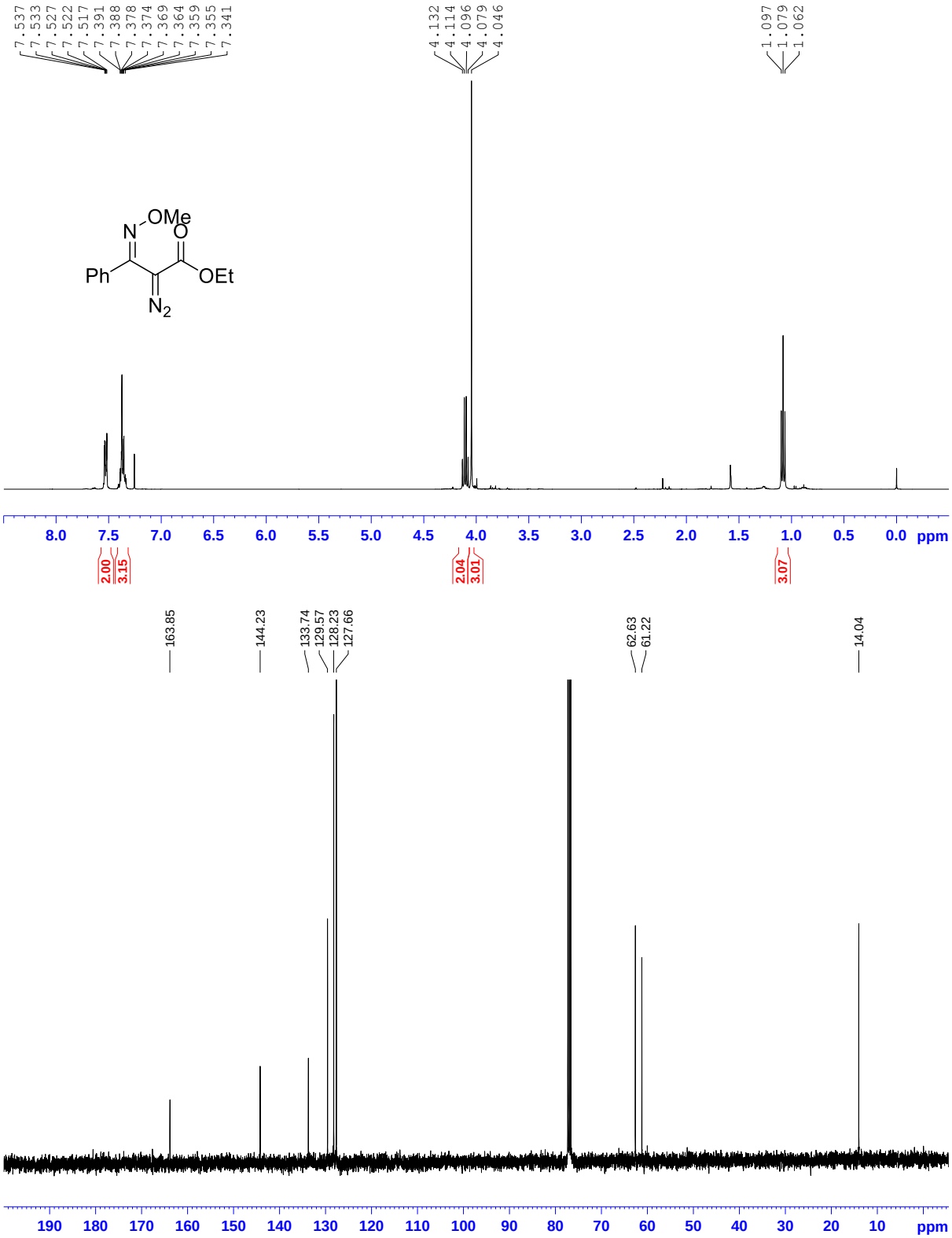
**(*Z*)-Ethyl 3-cyclohexyl-2-diazo-3-(methoxyimino)propanoate (1b):**



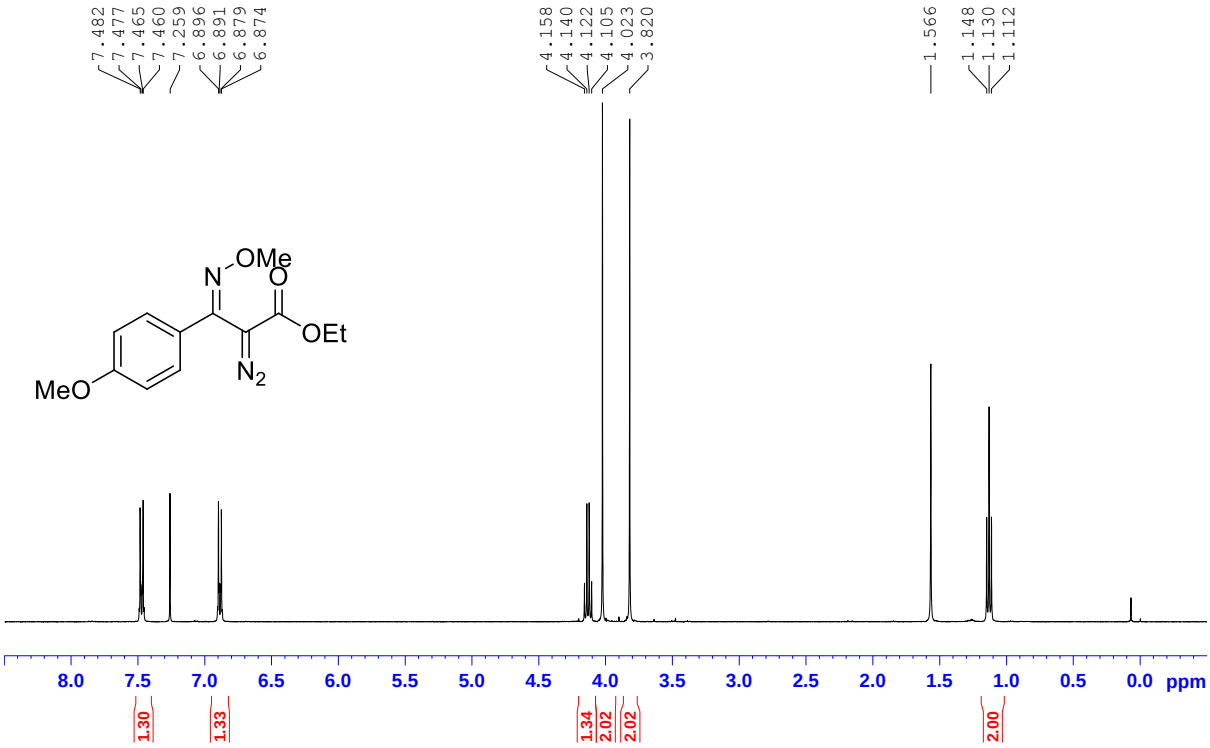
**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)-4-methylpentanoate (1c):**

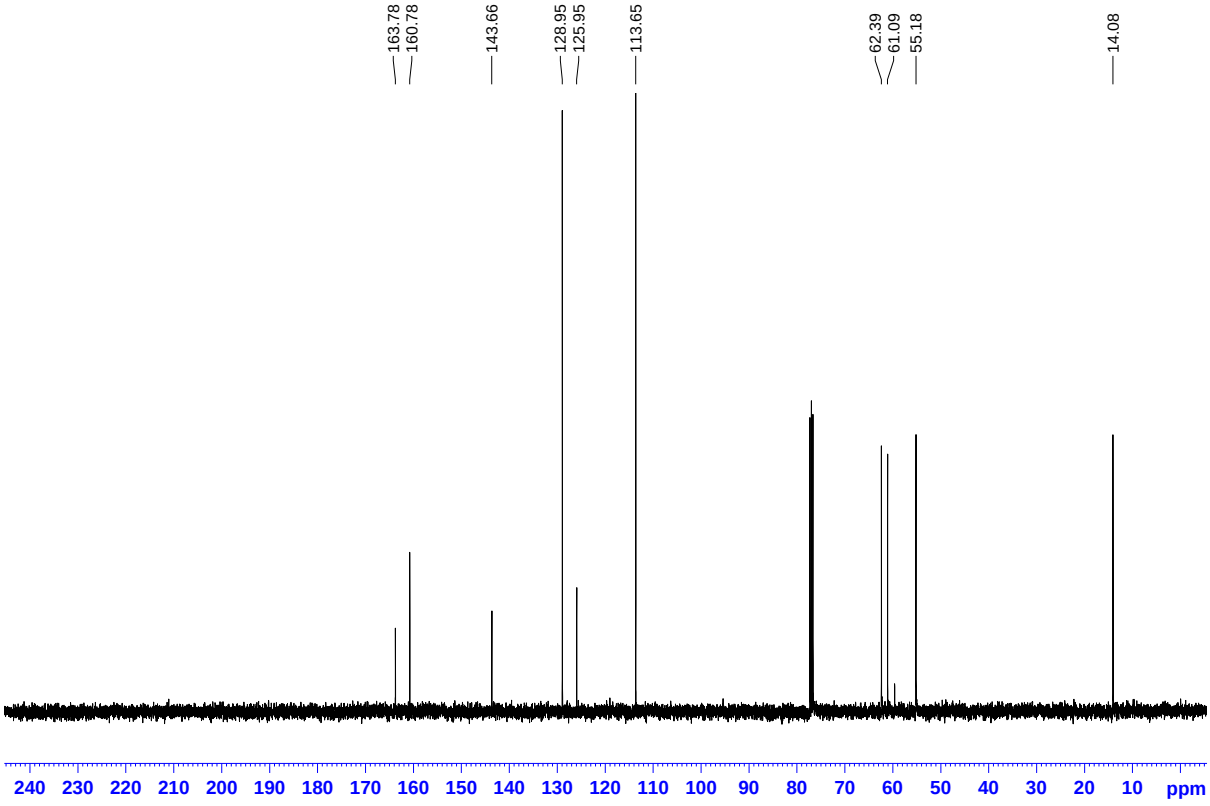


**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)-3-phenylpropanoate (1d):**

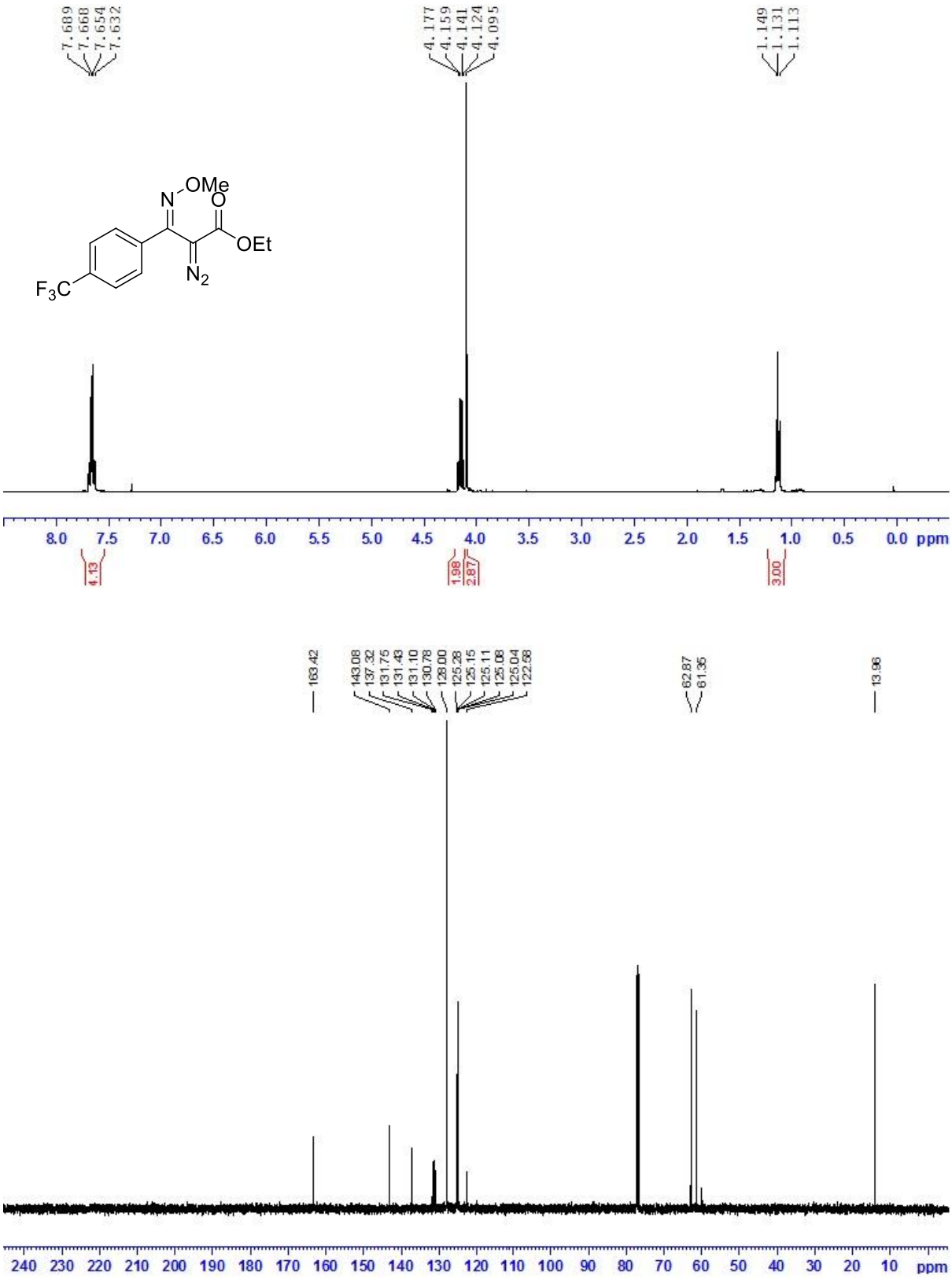


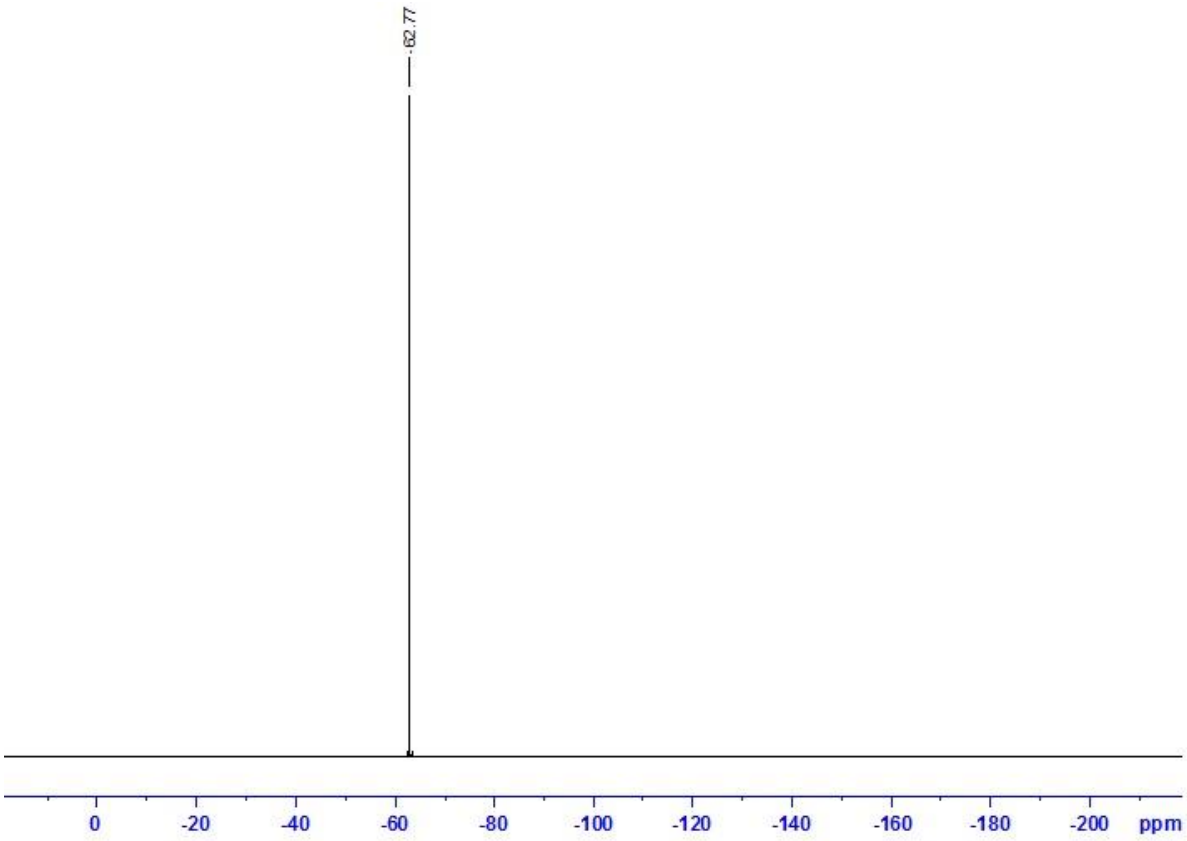
**(*Z*)-Ethyl 2-diazo-3-(methoxyimino)-3-(4-methoxyphenyl)propanoate (1e):**



**(*Z*)-ethyl 2-diazo-3-(methoxyimino)-3-(4-(trifluoromethyl)phenyl)propanoate (1f):**




-62.77
0
-20
-40
-60
-80
-100
-120
-140
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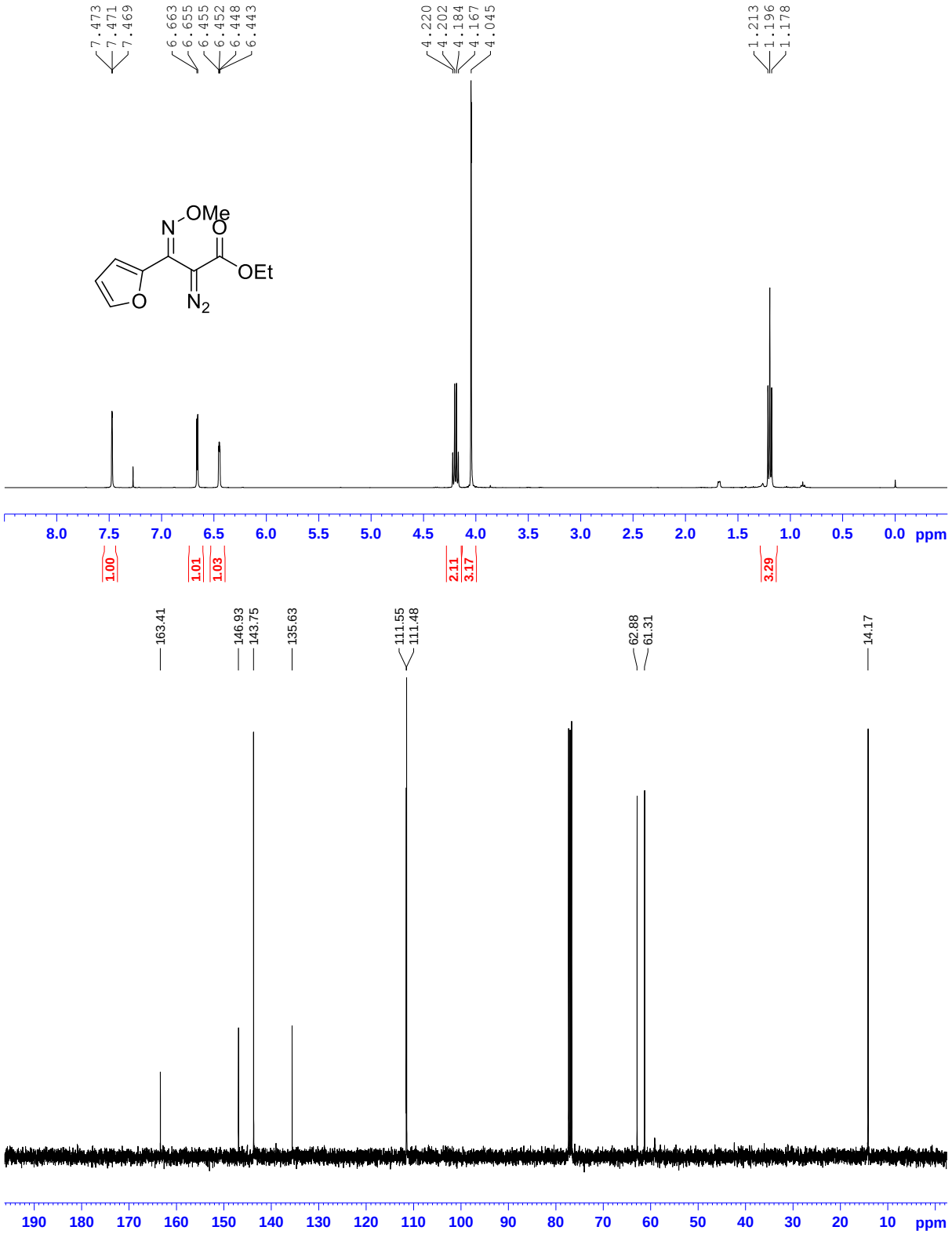
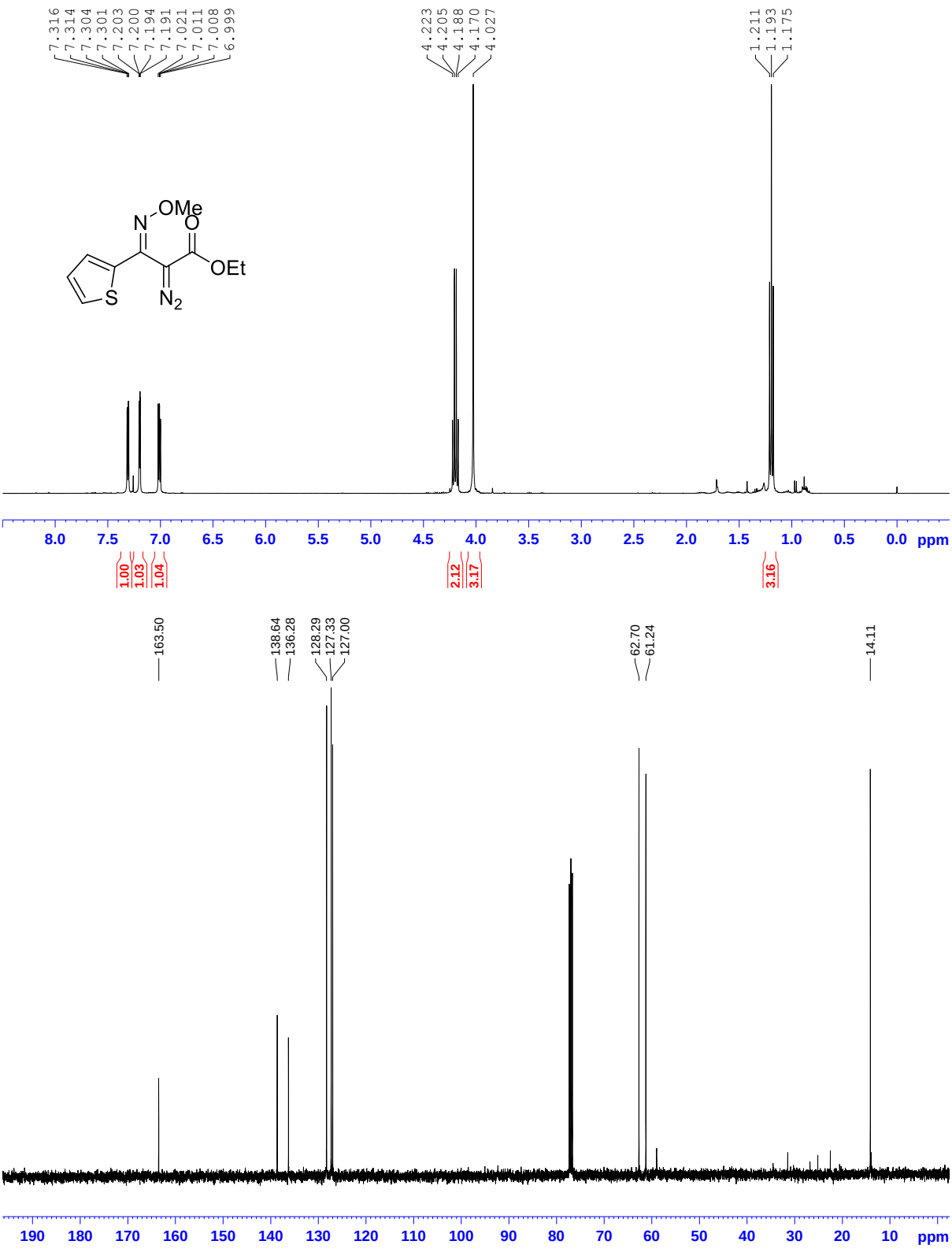
-180
-200
ppm

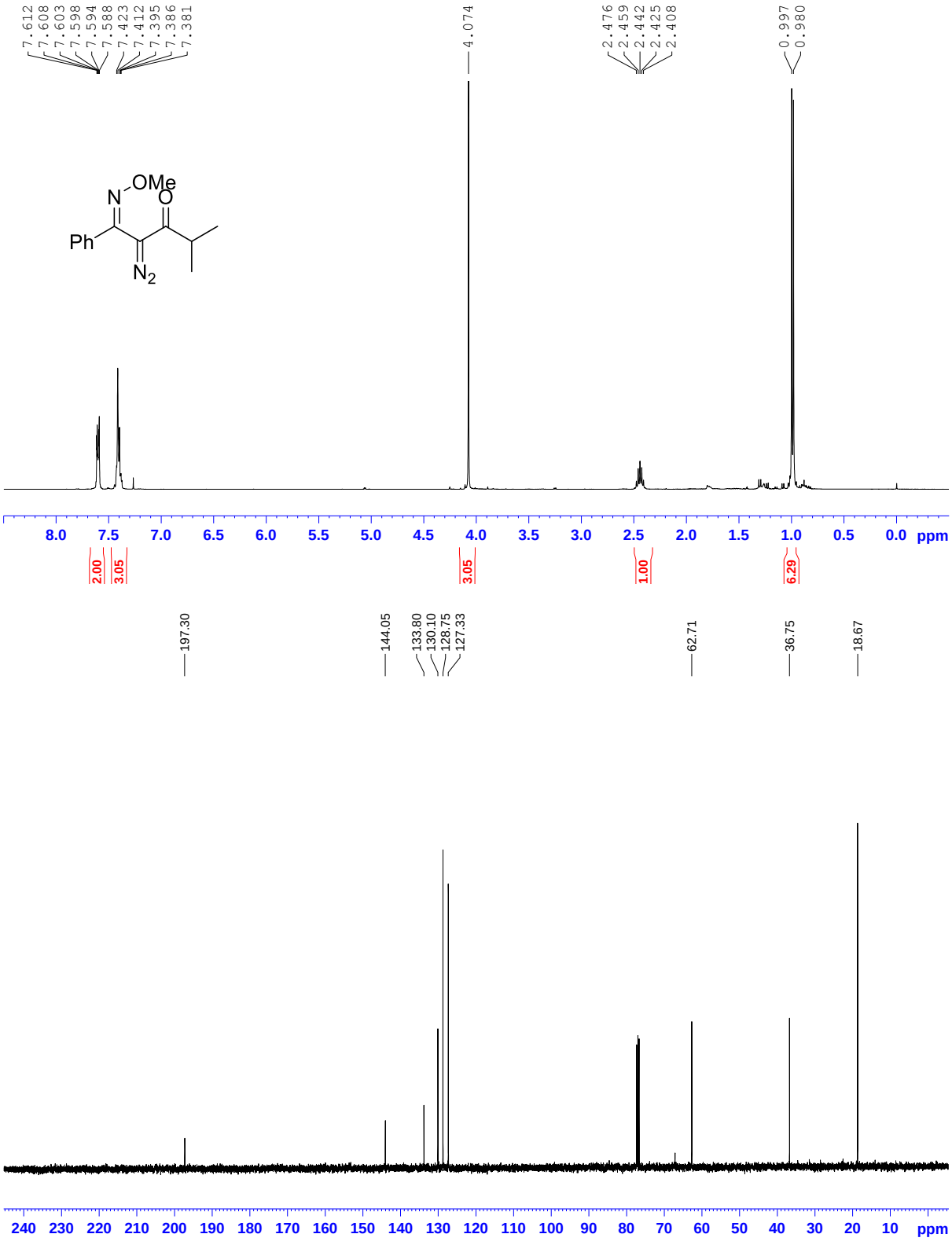
**(*E*)-Ethyl 2-diazo-3-(furan-2-yl)-3-(methoxyimino)propanoate (1g):**



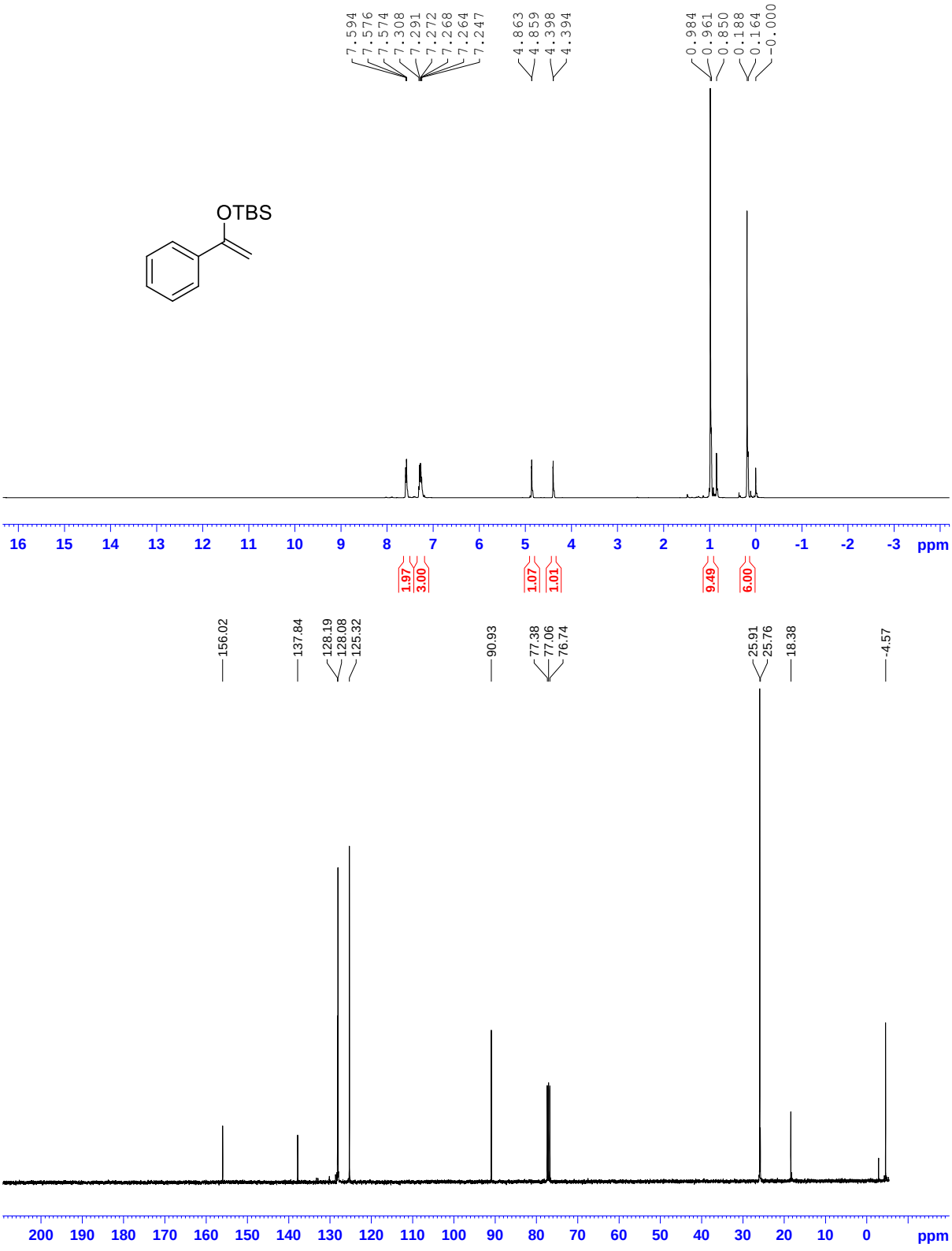
**(*E*)-Ethyl 2-diazo-3-(methoxyimino)-3-(thiophen-2-yl)propanoate (1h):**



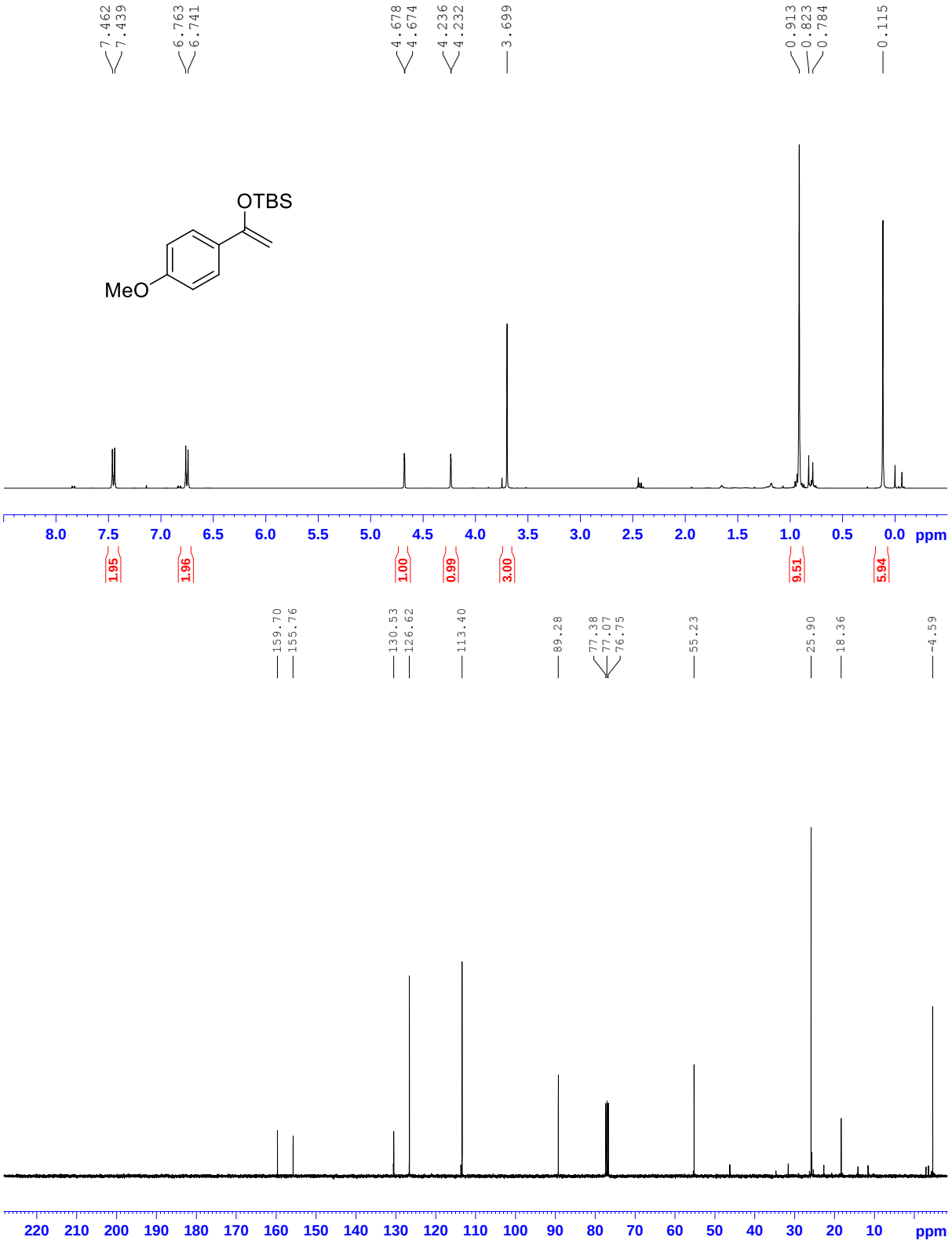
**(*Z*)-2-Diazo-1-(methoxyimino)-4-methyl-1-phenylpentan-3-one (1i):**



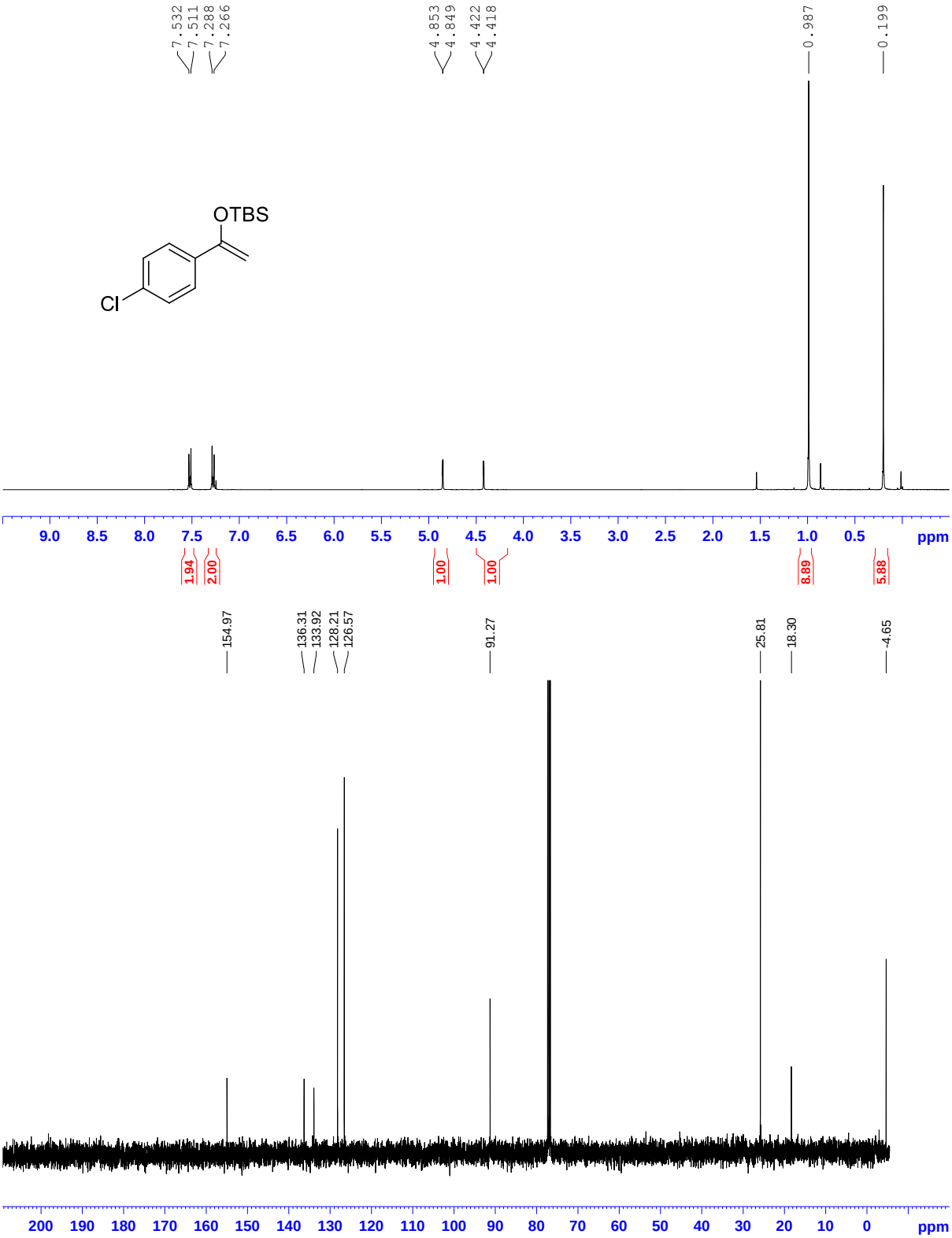
**tert-butyldimethyl(1-phenylvinyloxy)silane (2c):**



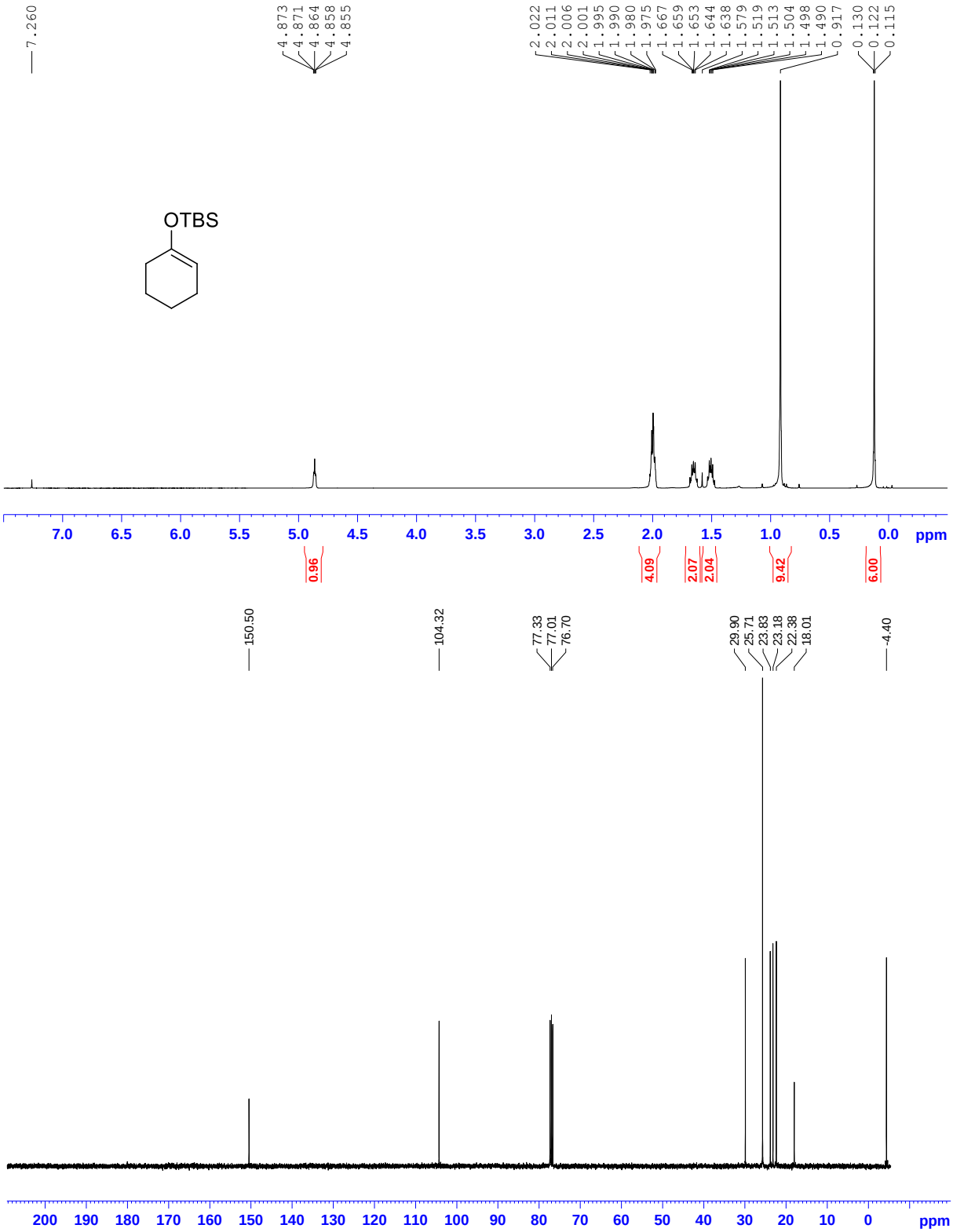
**tert-butyl(1-(4-methoxyphenyl)vinyloxy)dimethylsilane (2d):**



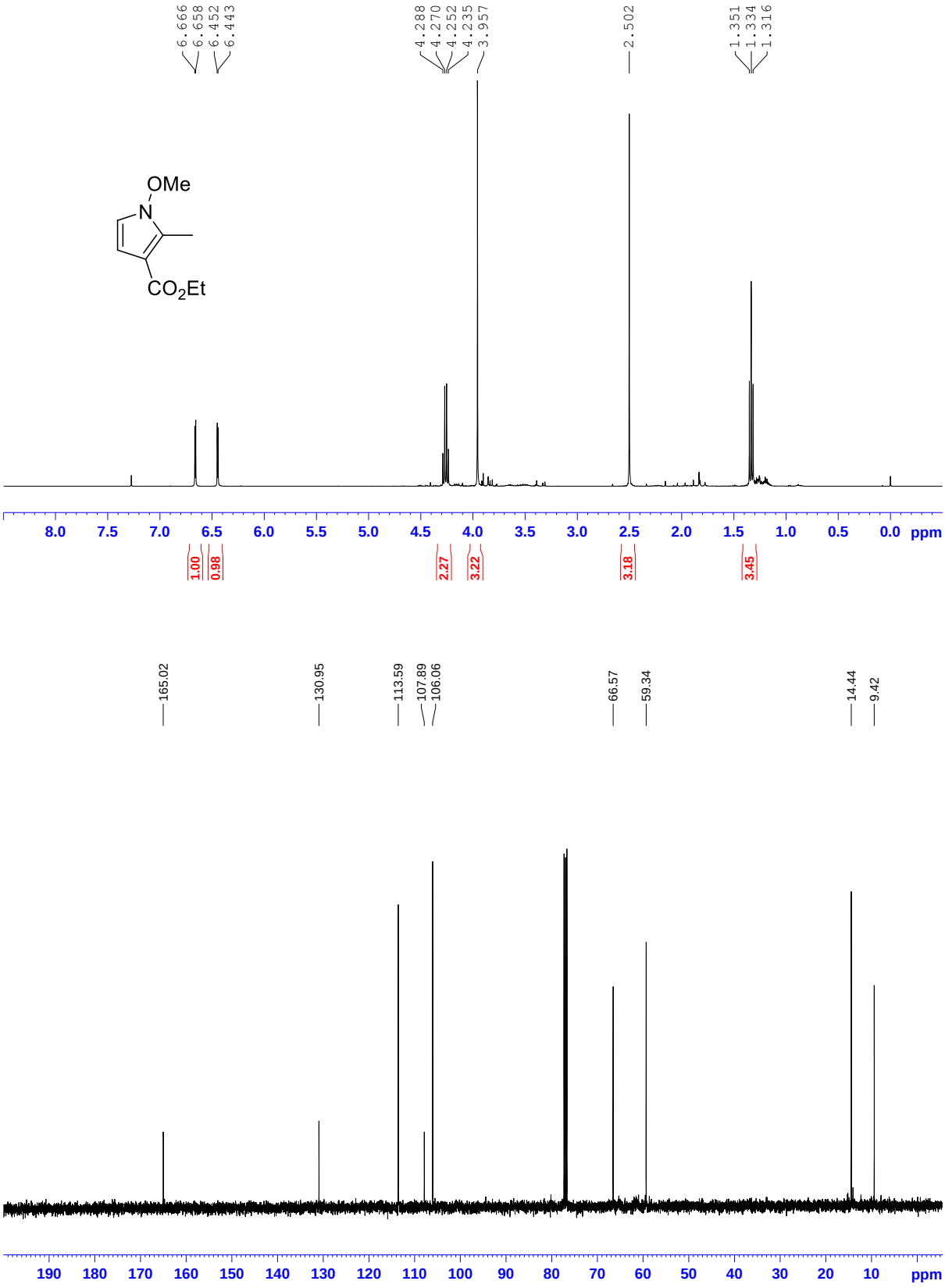
**tert-butyl(1-(4-chlorophenyl)vinyloxy)dimethylsilane (2e):**



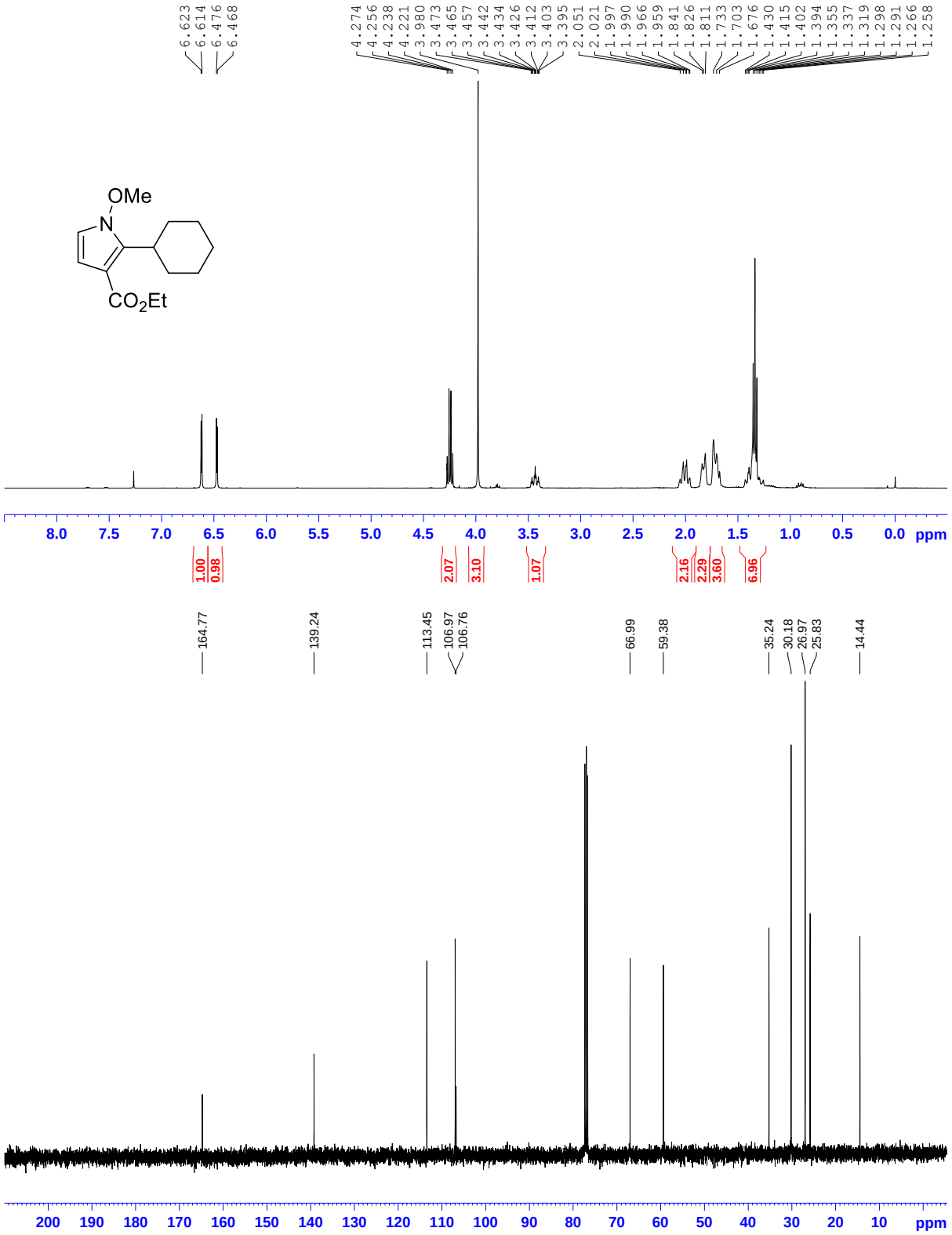
**tert-butyl(cyclohexenyloxy)dimethylsilane (2f):**



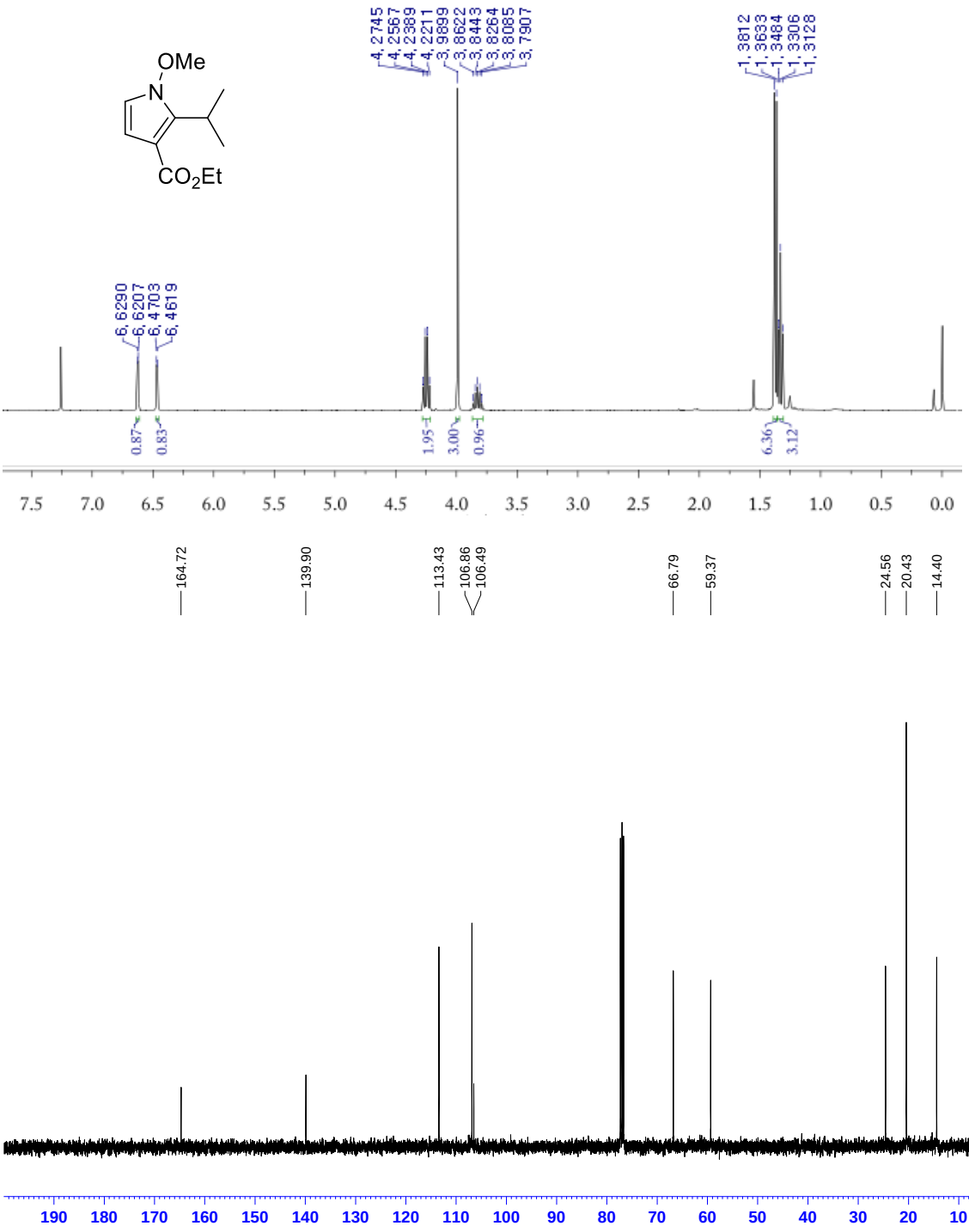
**Ethyl 1-methoxy-2-methyl-1*H*-pyrrole-3-carboxylate (3aa):**



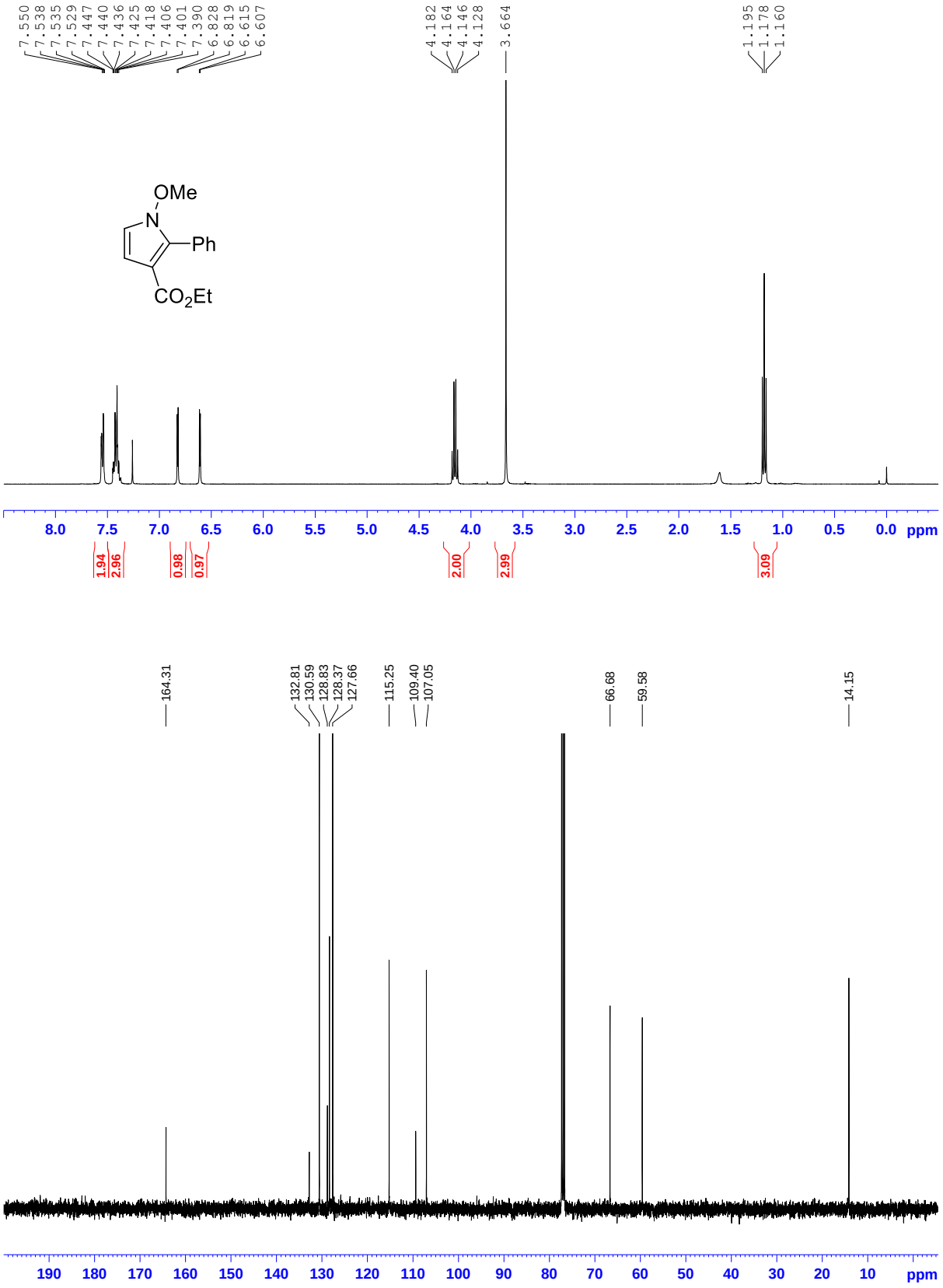
**Ethyl 2-cyclohexyl-1-methoxy-1*H*-pyrrole-3-carboxylate (3ba):**



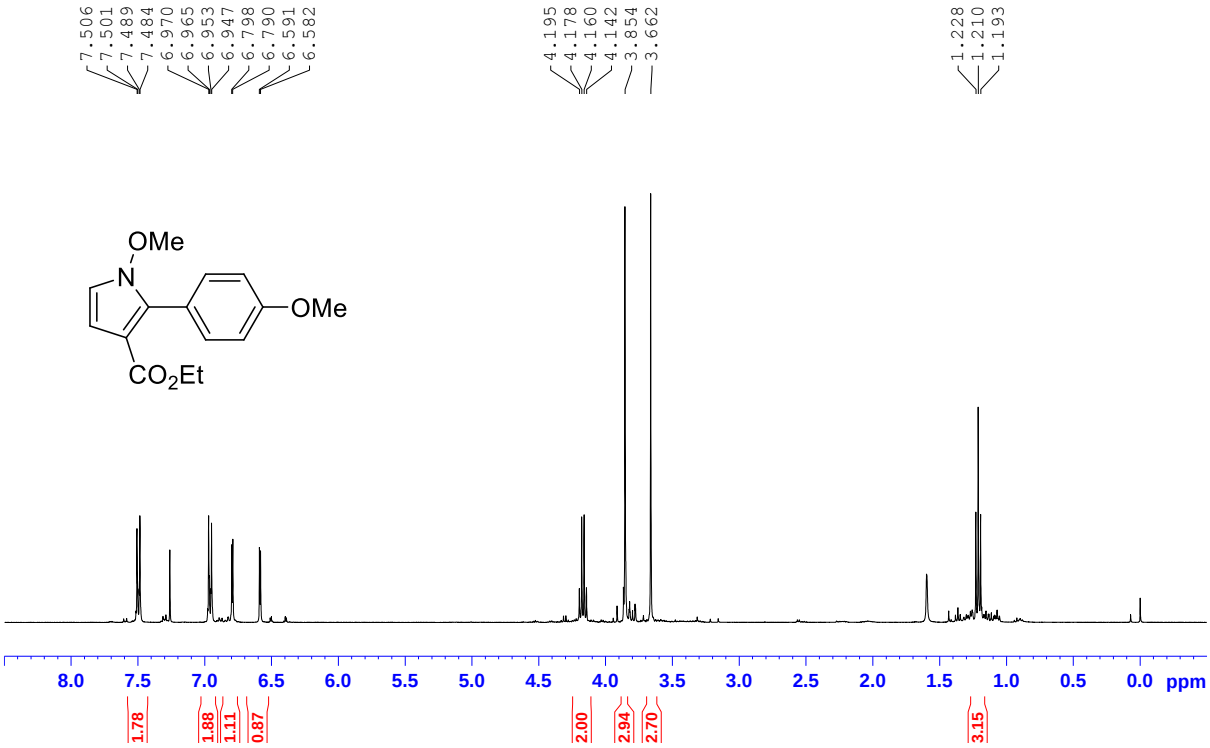
**Ethyl 2-isopropyl-1-methoxy-1*H*-pyrrole-3-carboxylate (3ca):**

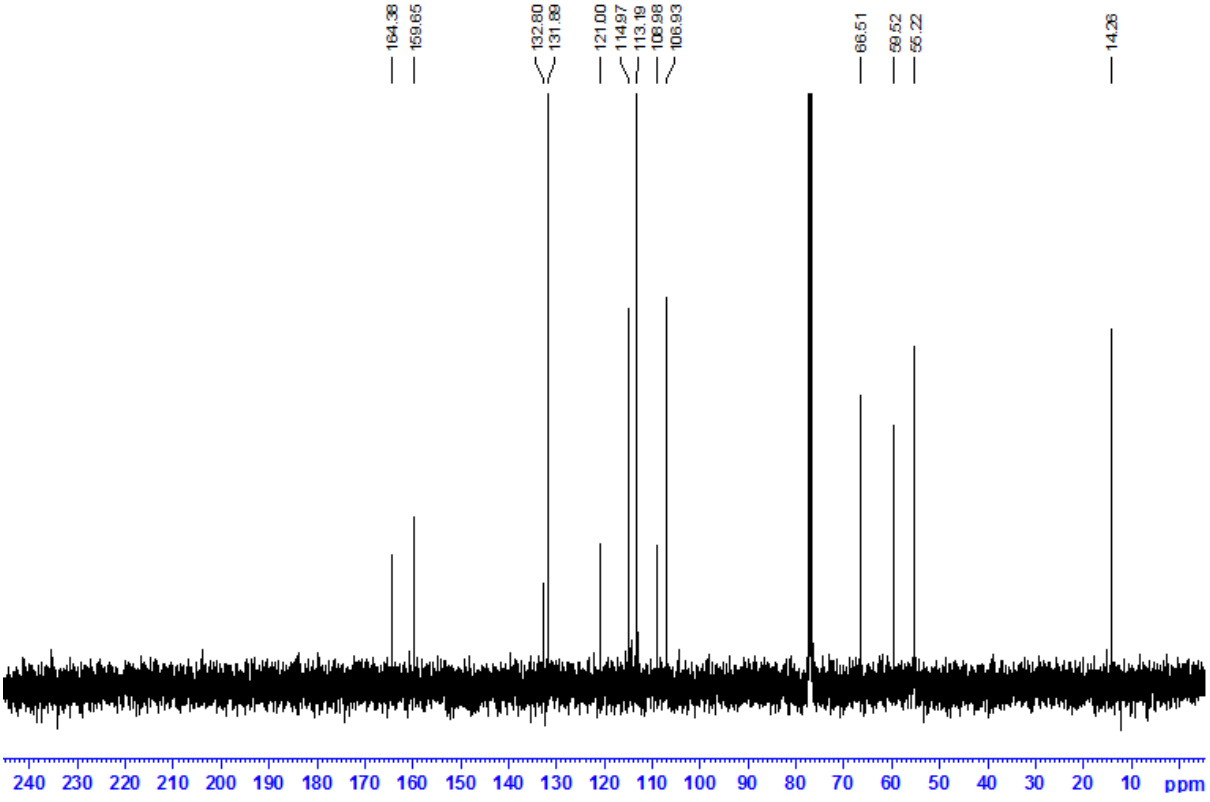


**Ethyl 1-methoxy-2-phenyl-1*H*-pyrrole-3-carboxylate (3da):**

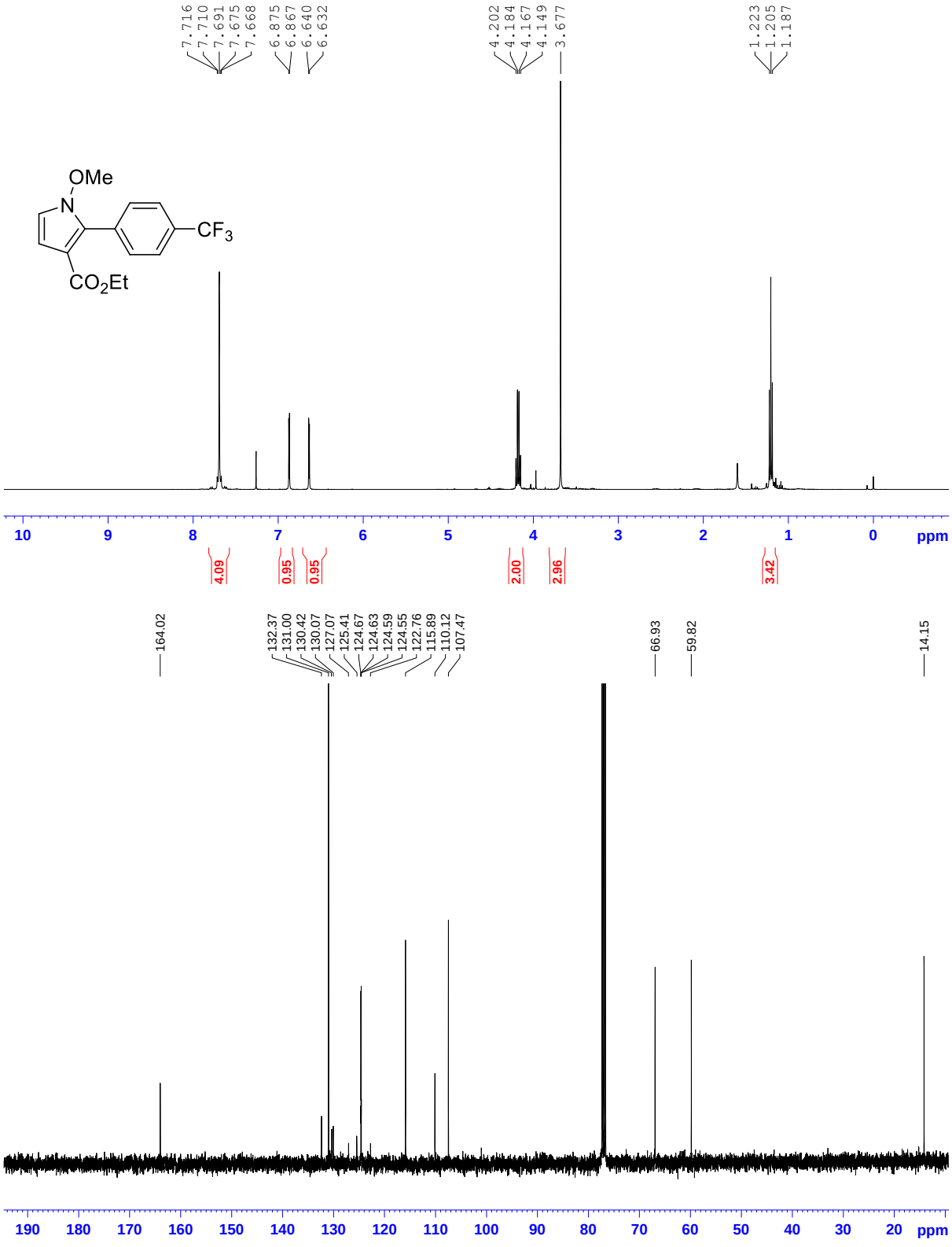


**Ethyl 1-methoxy-2-(4-methoxyphenyl)-1*H*-pyrrole-3-carboxylate (3ea):**

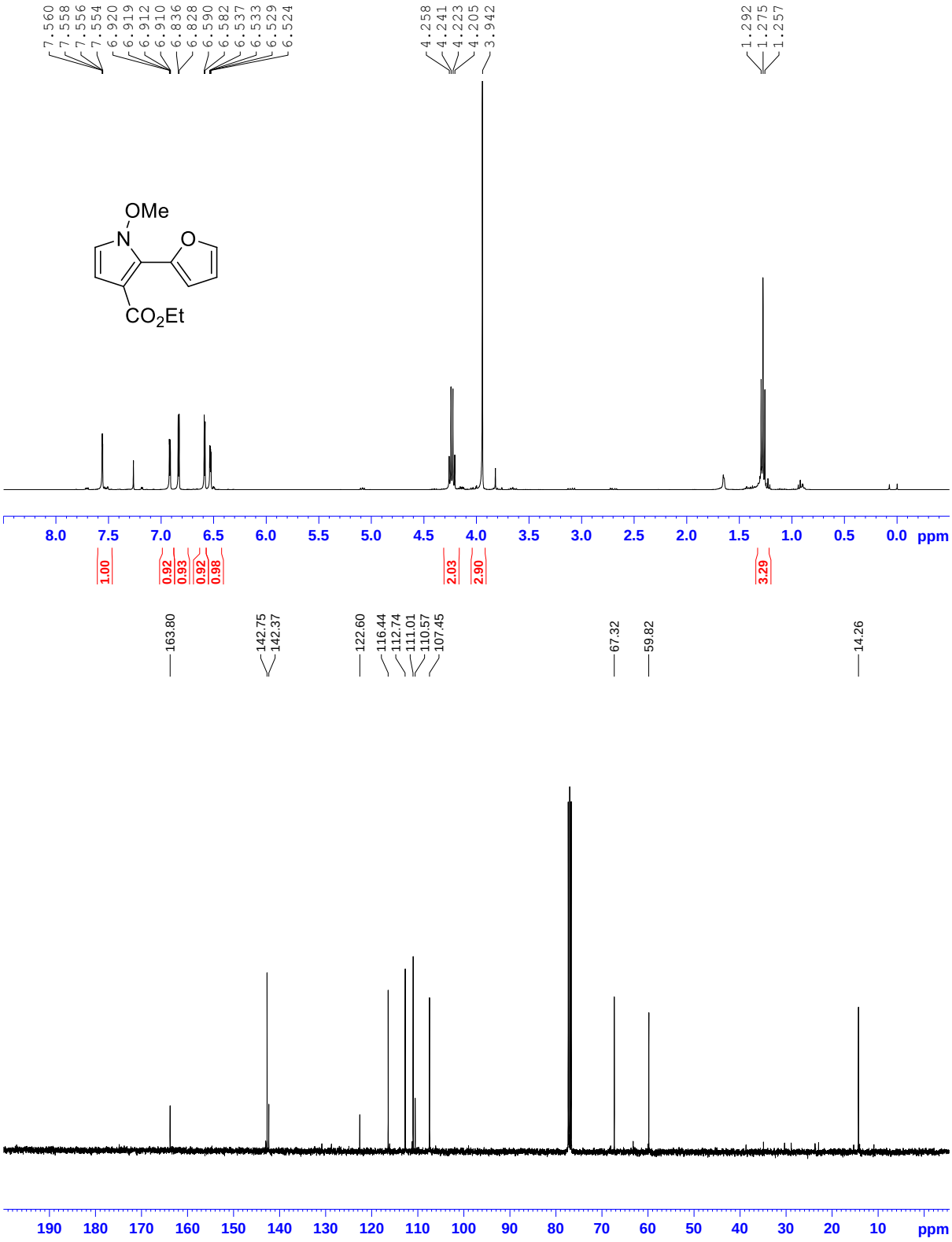


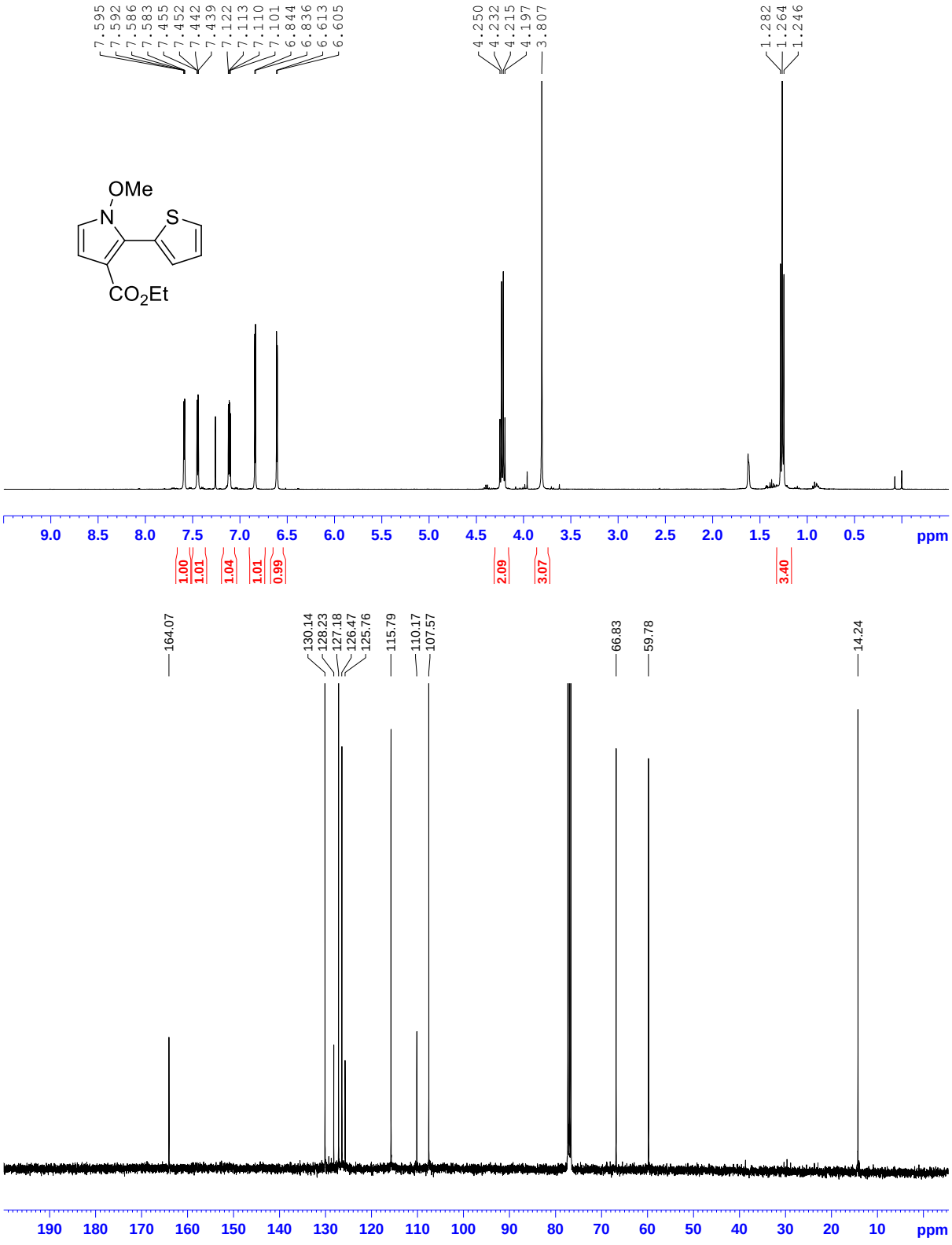
**Ethyl 1-methoxy-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-3-carboxylate (3fa):**



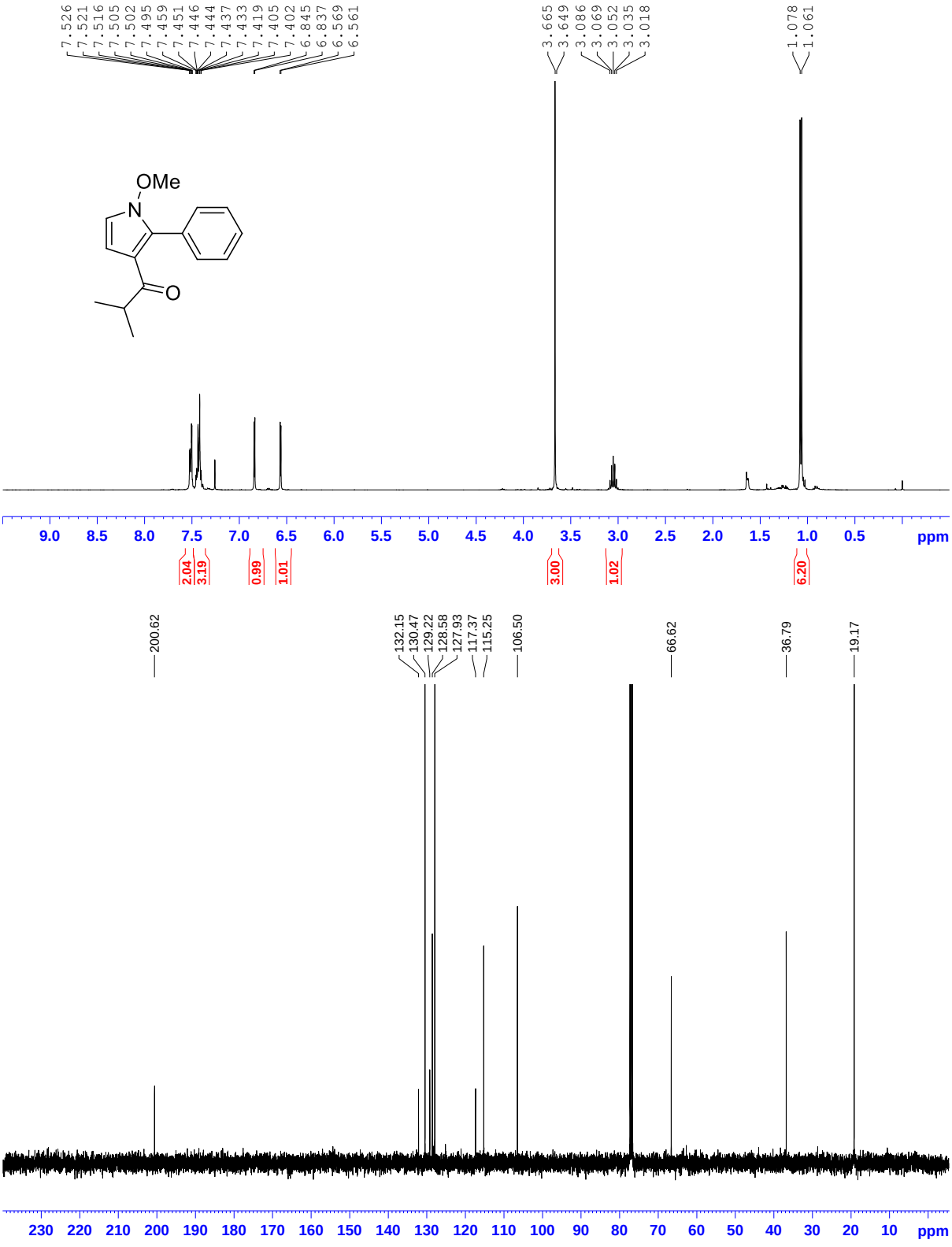
**Ethyl 2-(furan-2-yl)-1-methoxy-1H-pyrrole-3-carboxylate (3ga):**



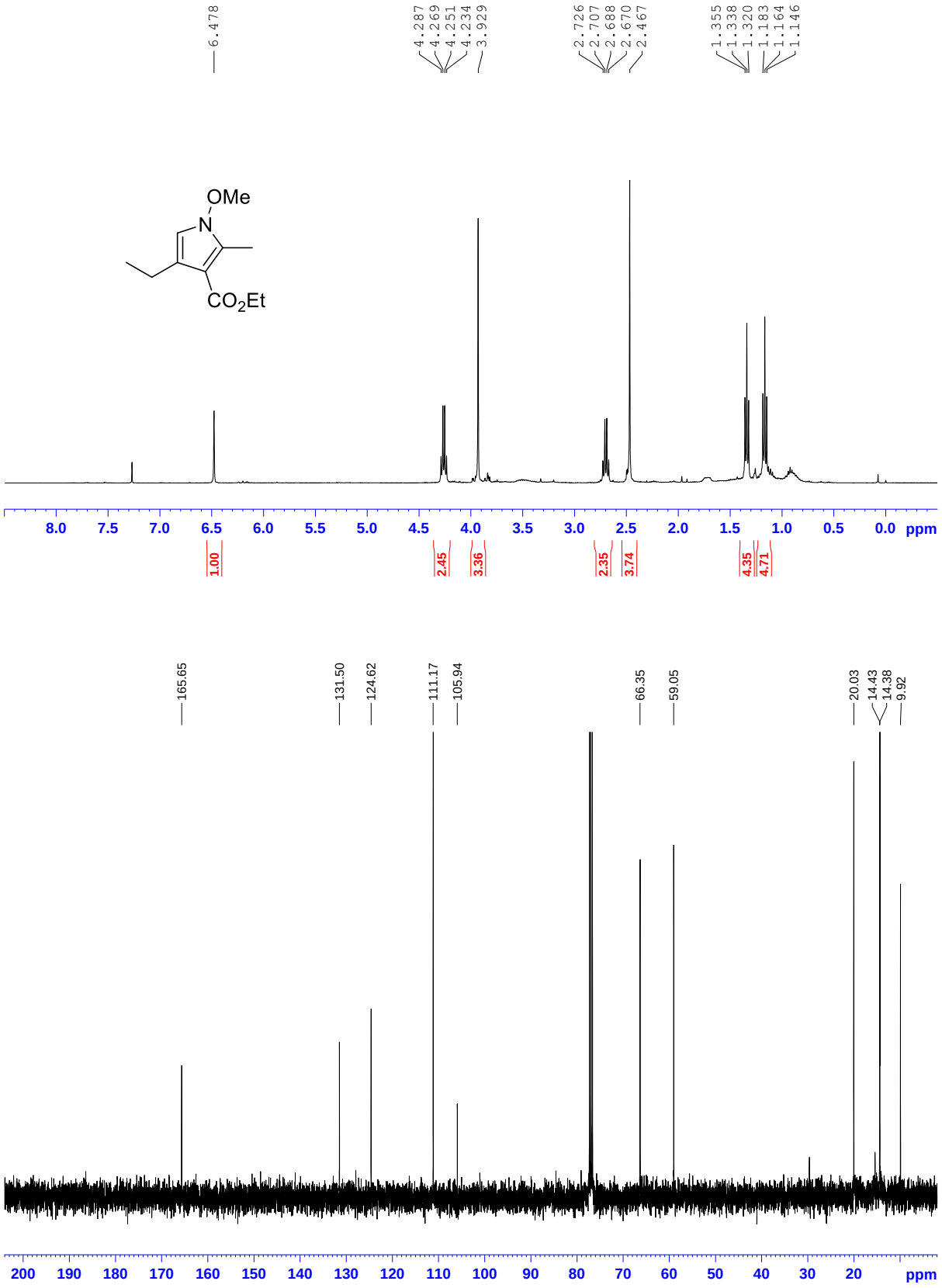
**Ethyl 1-methoxy-2-(thiophen-2-yl)-1*H*-pyrrole-3-carboxylate (3ha):**



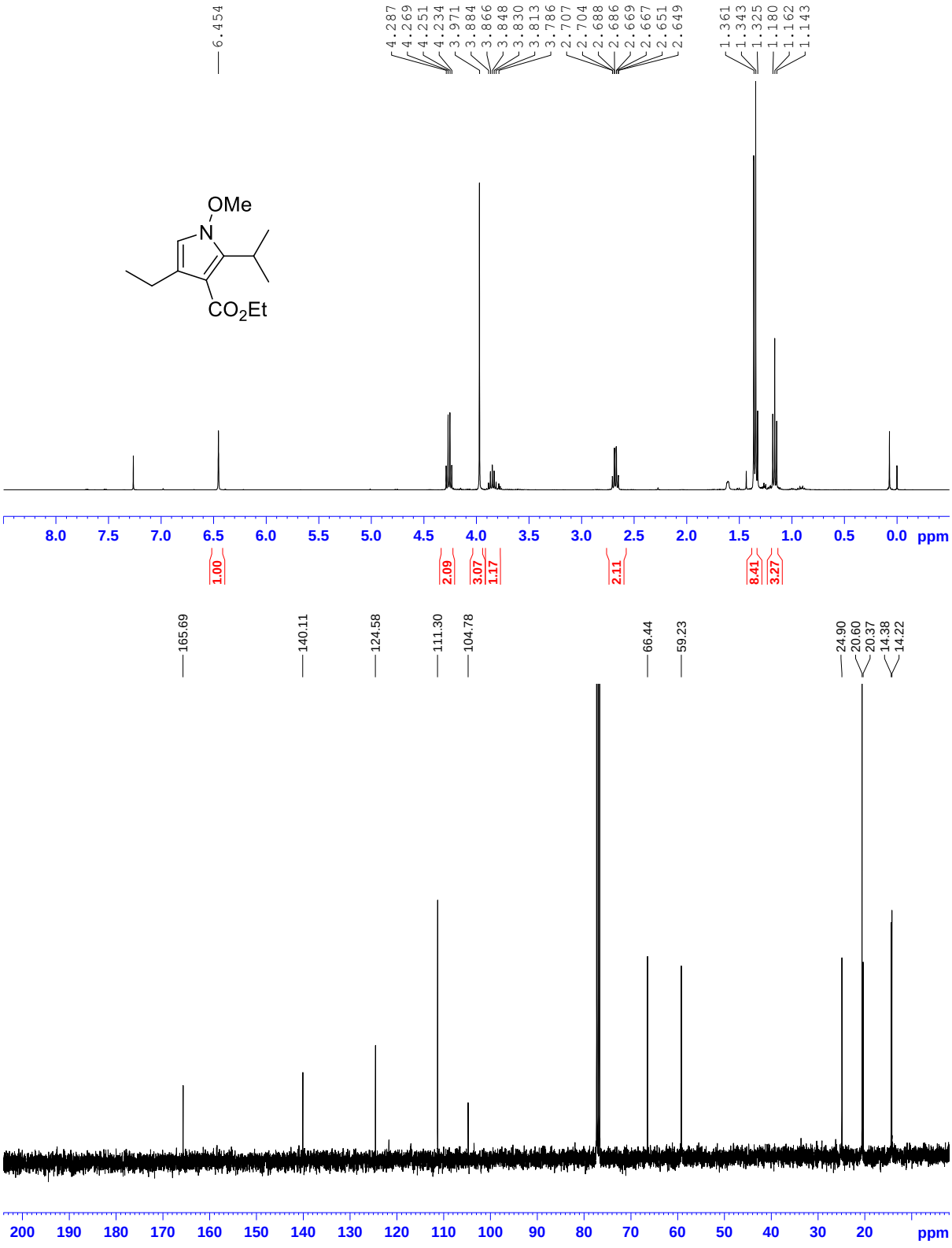
**1-(1-methoxy-2-phenyl-1*H*-pyrrol-3-yl)-2-methylpropan-1-one (3ia):**



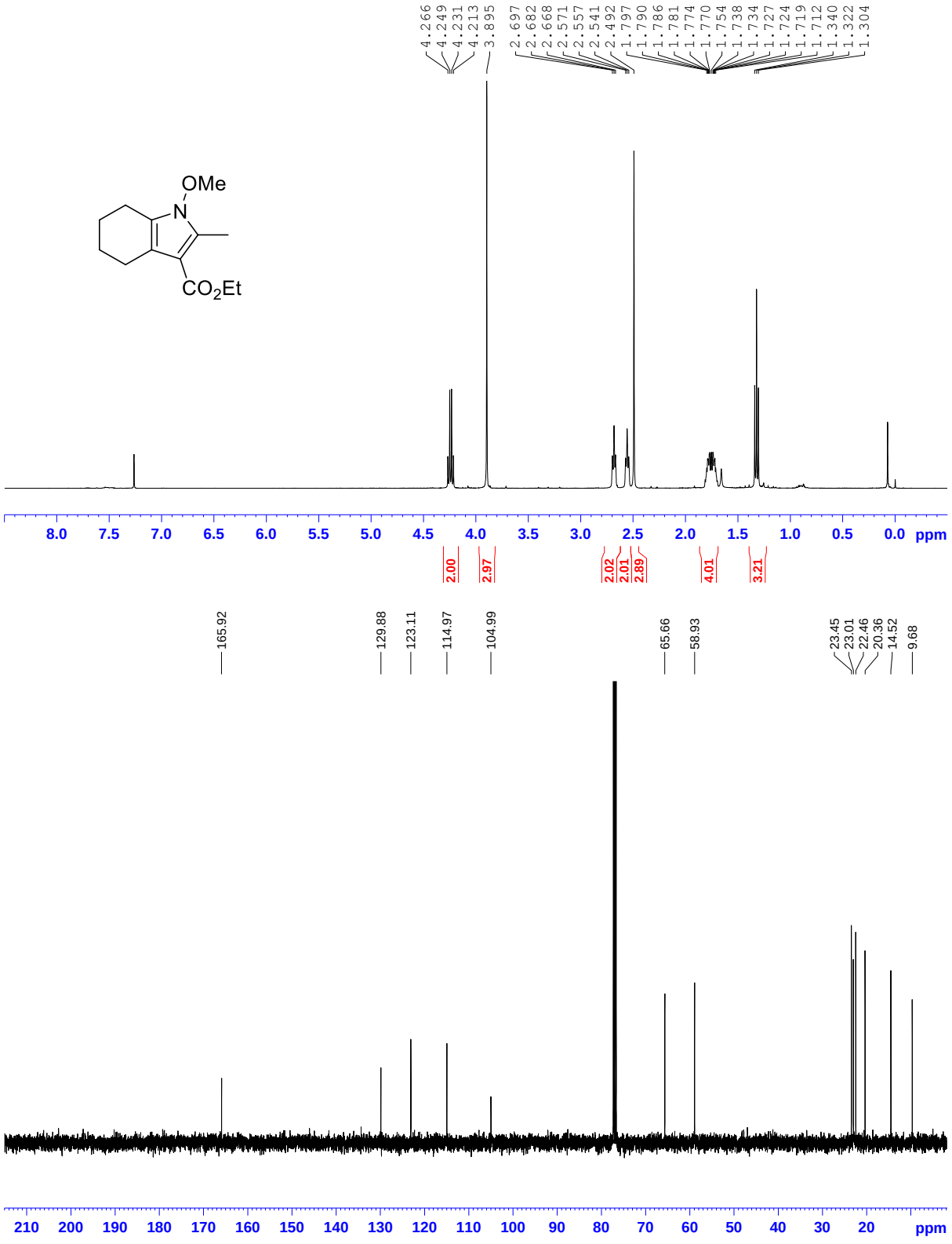
**Ethyl 4-ethyl-1-methoxy-2-methyl-1*H*-pyrrole-3-carboxylate (3ab):**



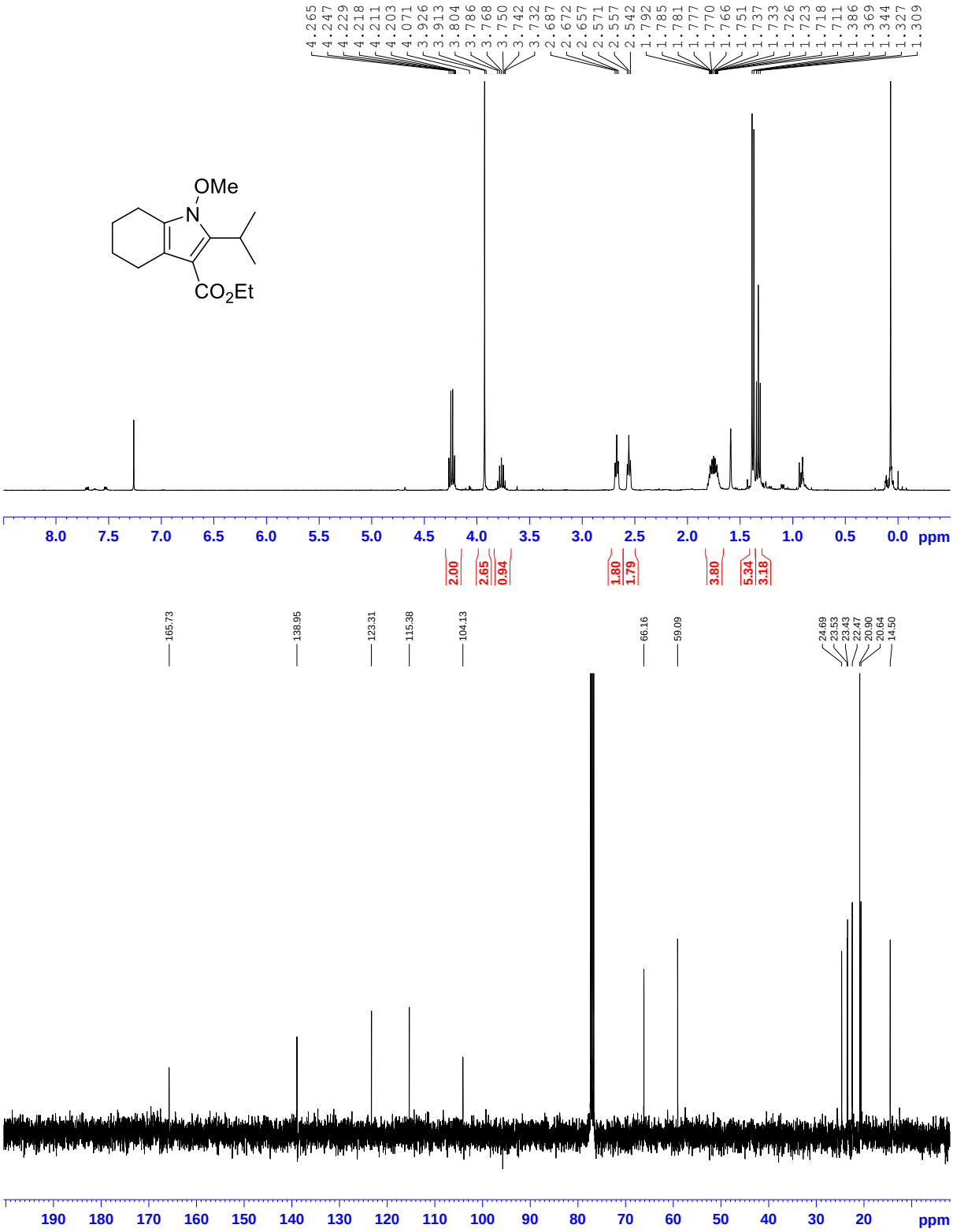
**Ethyl 4-ethyl-2-isopropyl-1-methoxy-1*H*-pyrrole-3-carboxylate (3cb):**



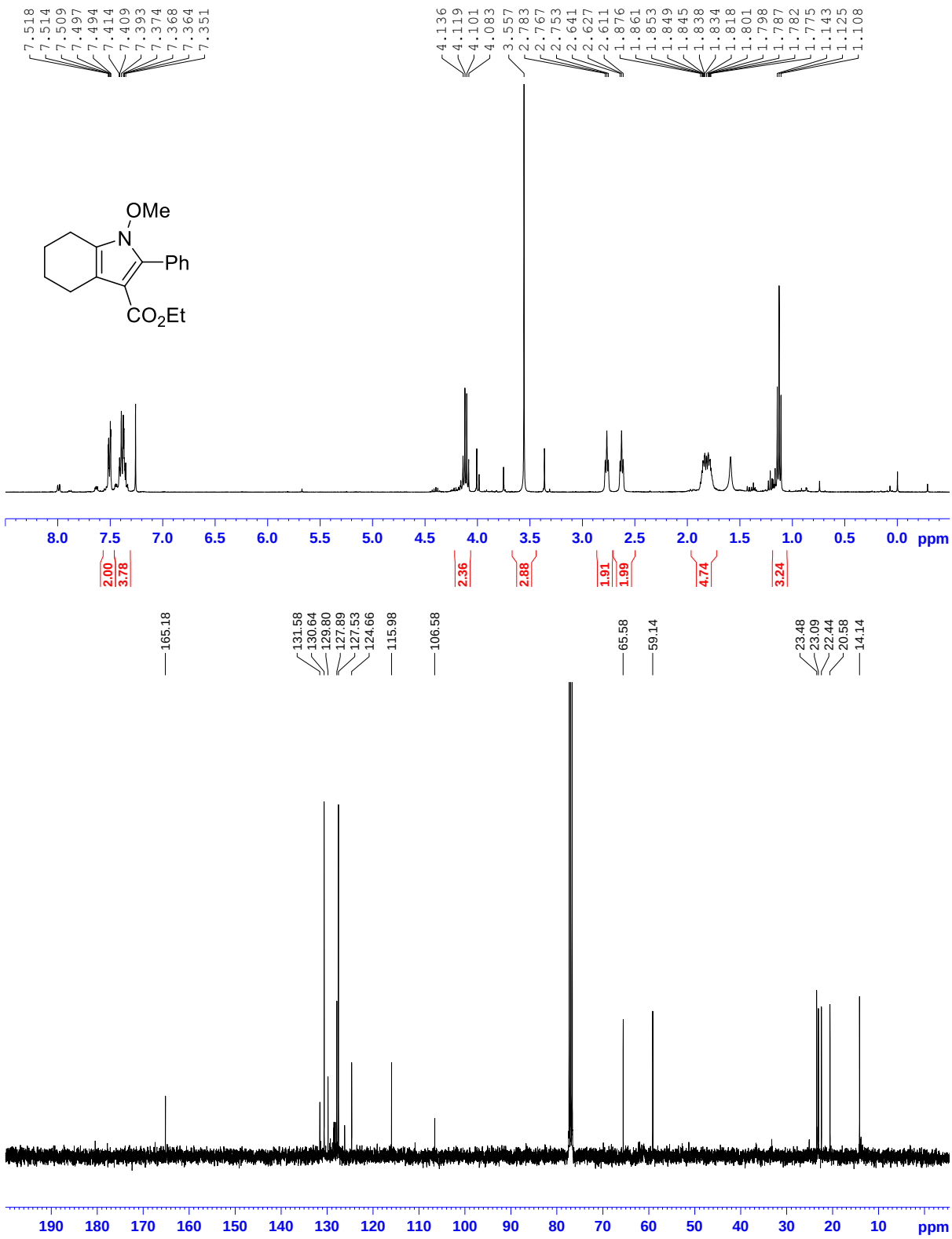
**Ethyl 1-methoxy-2-methyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3af):**



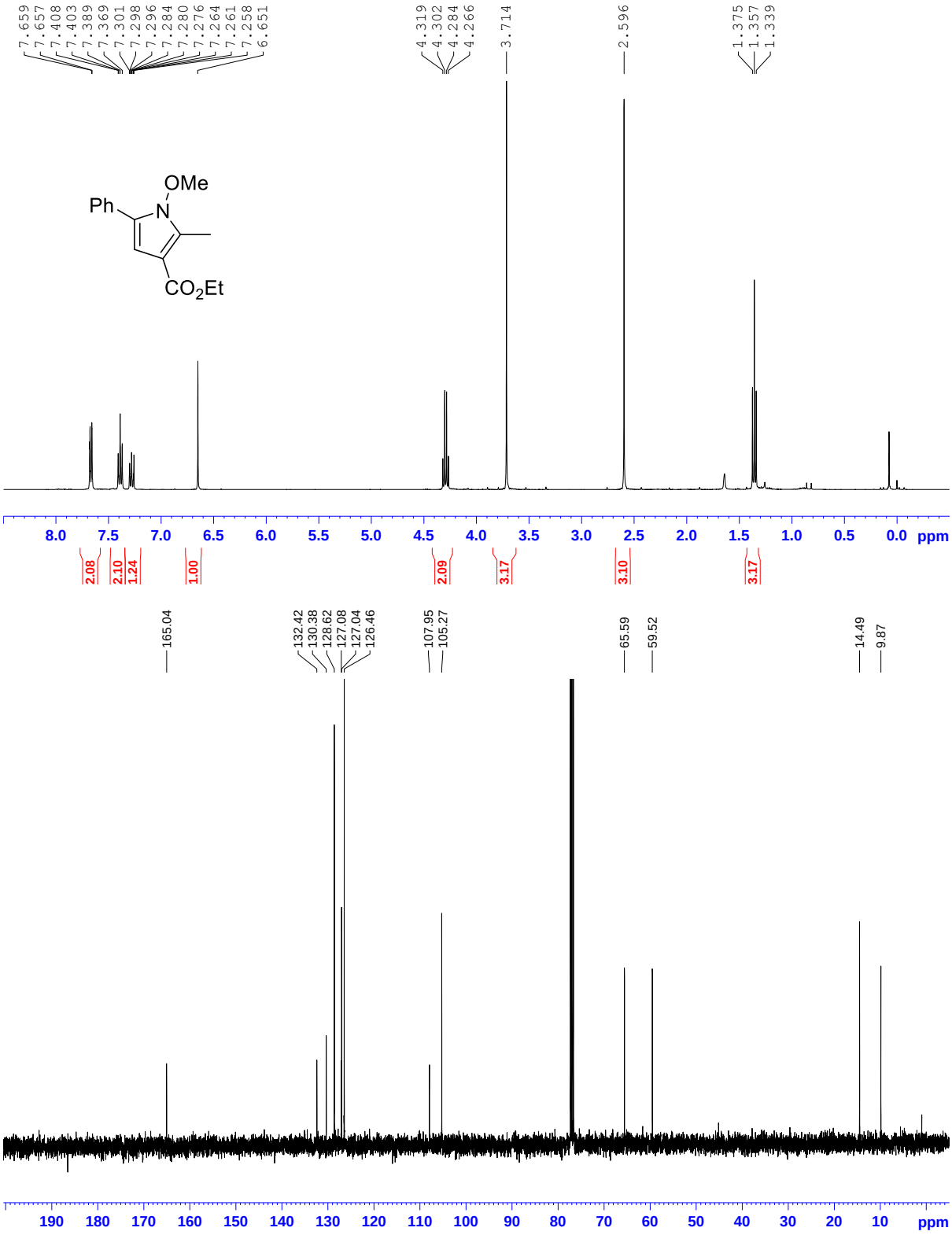
**Ethyl 2-isopropyl-1-methoxy-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3cf):**



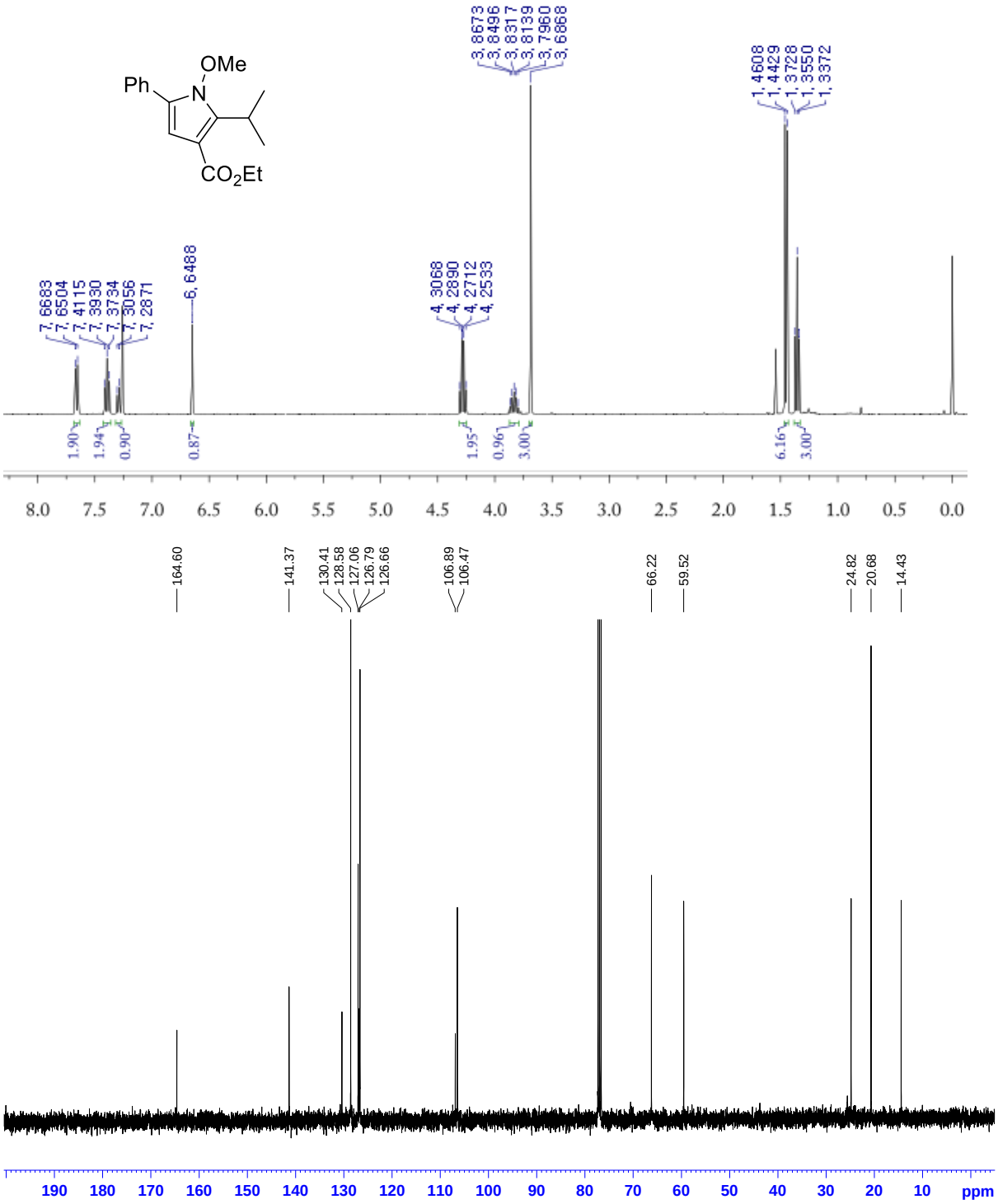
**Ethyl 1-methoxy-2-phenyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3df):**



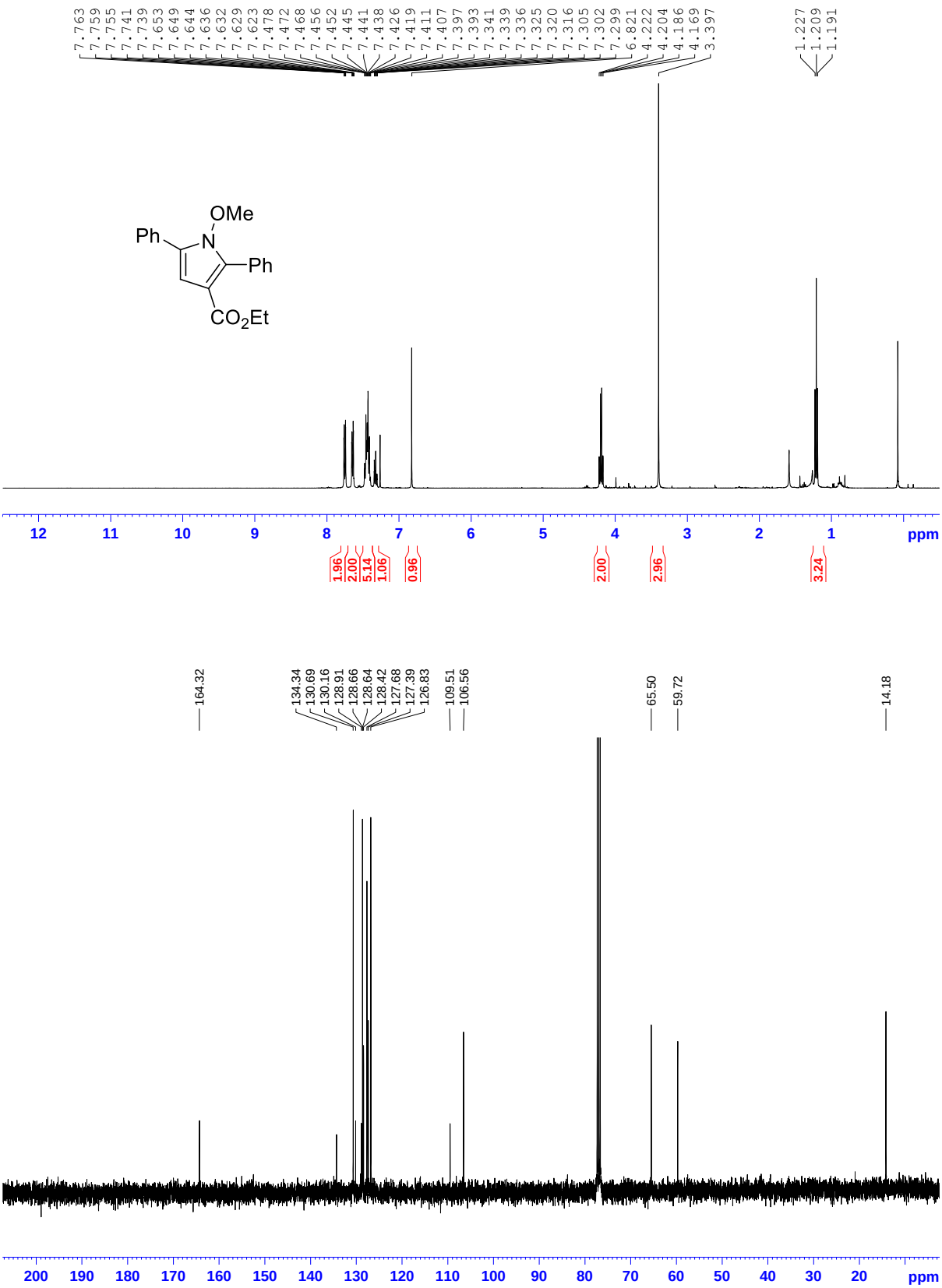
**Ethyl 1-methoxy-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (3ac):**



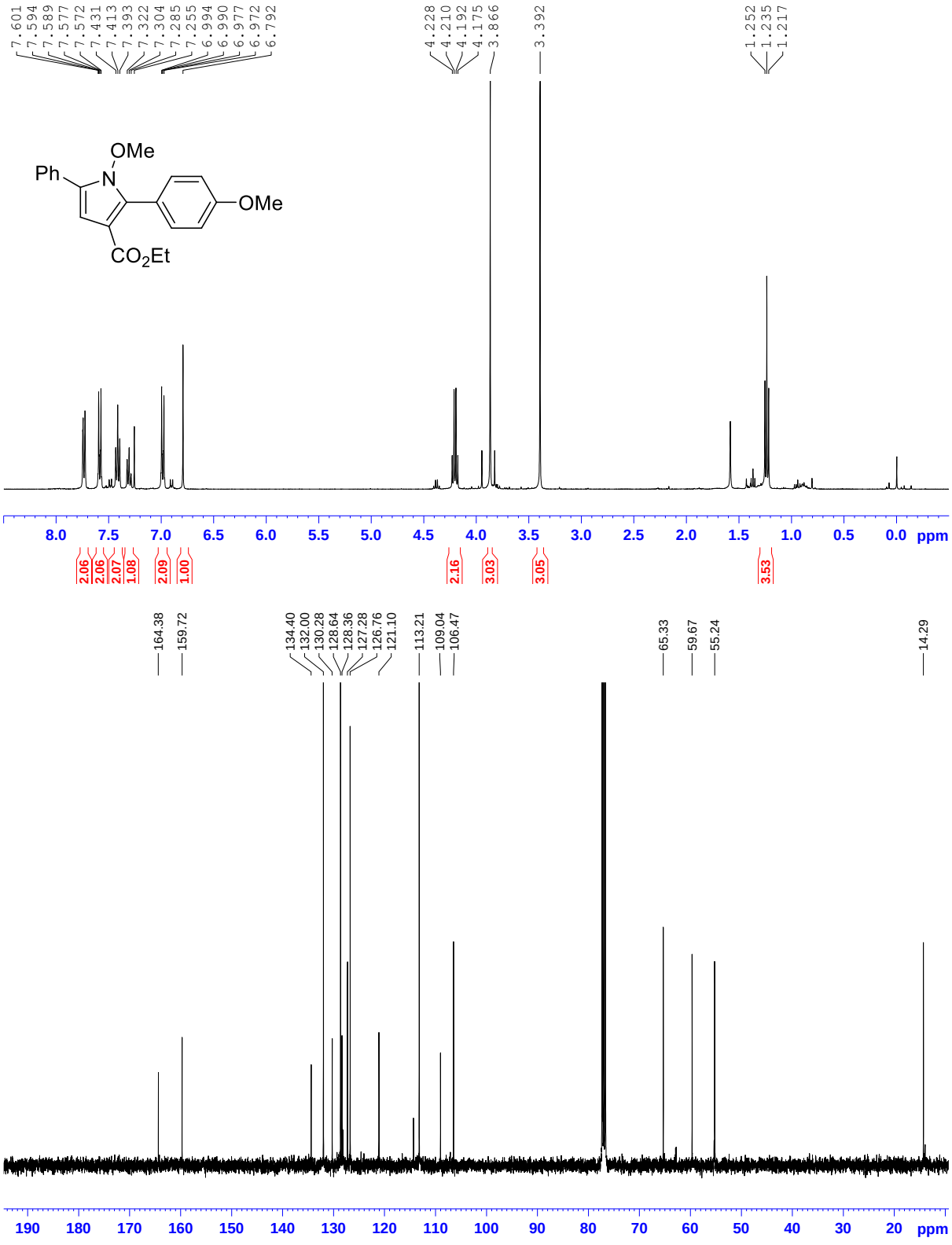
**Ethyl 2-isopropyl-1-methoxy-5-phenyl-1*H*-pyrrole-3-carboxylate (3cc):**



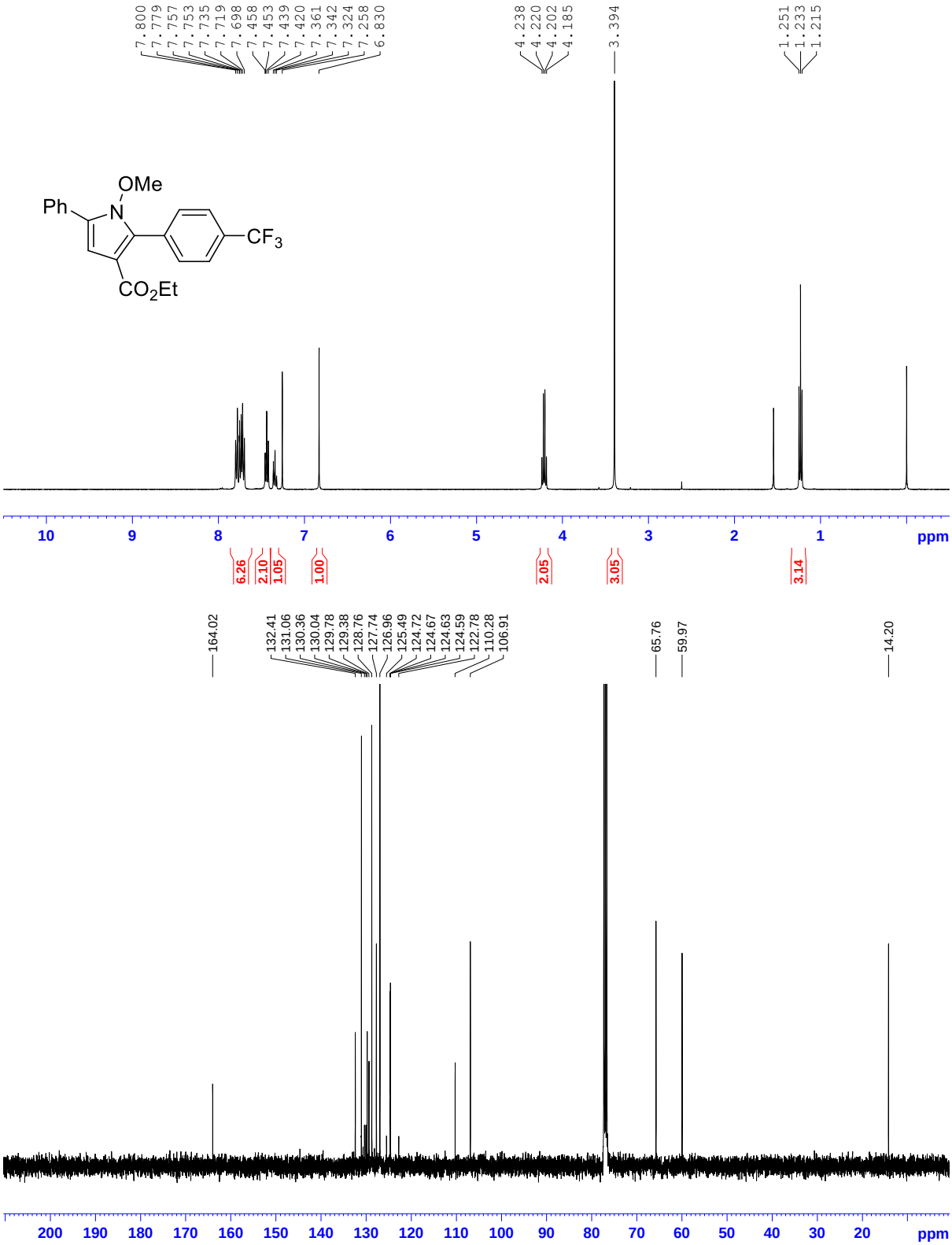
**Ethyl 1-methoxy-2,5-diphenyl-1*H*-pyrrole-3-carboxylate (3dc):**



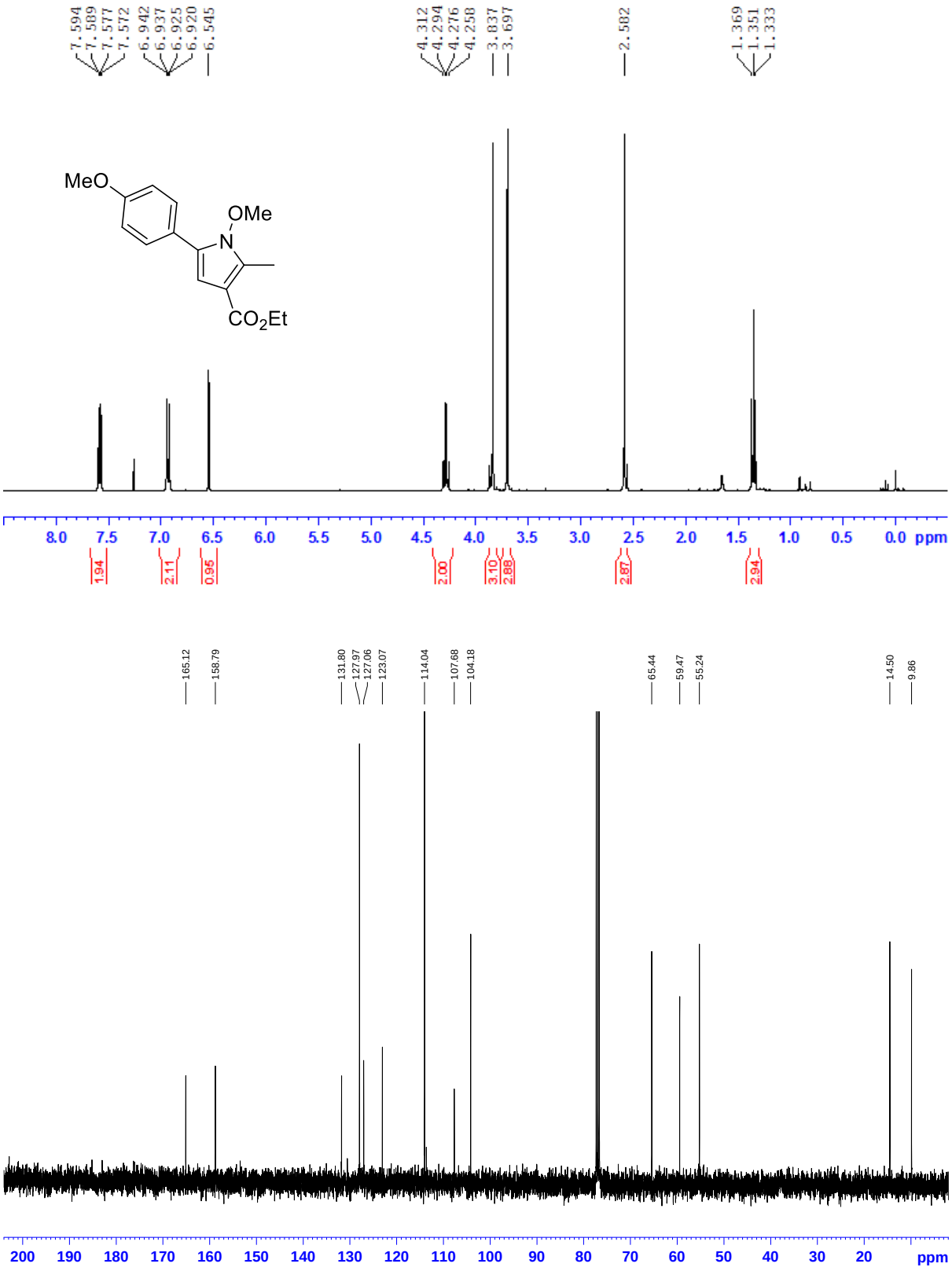
**Ethyl 1-methoxy-2-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-3-carboxylate (3ec):**



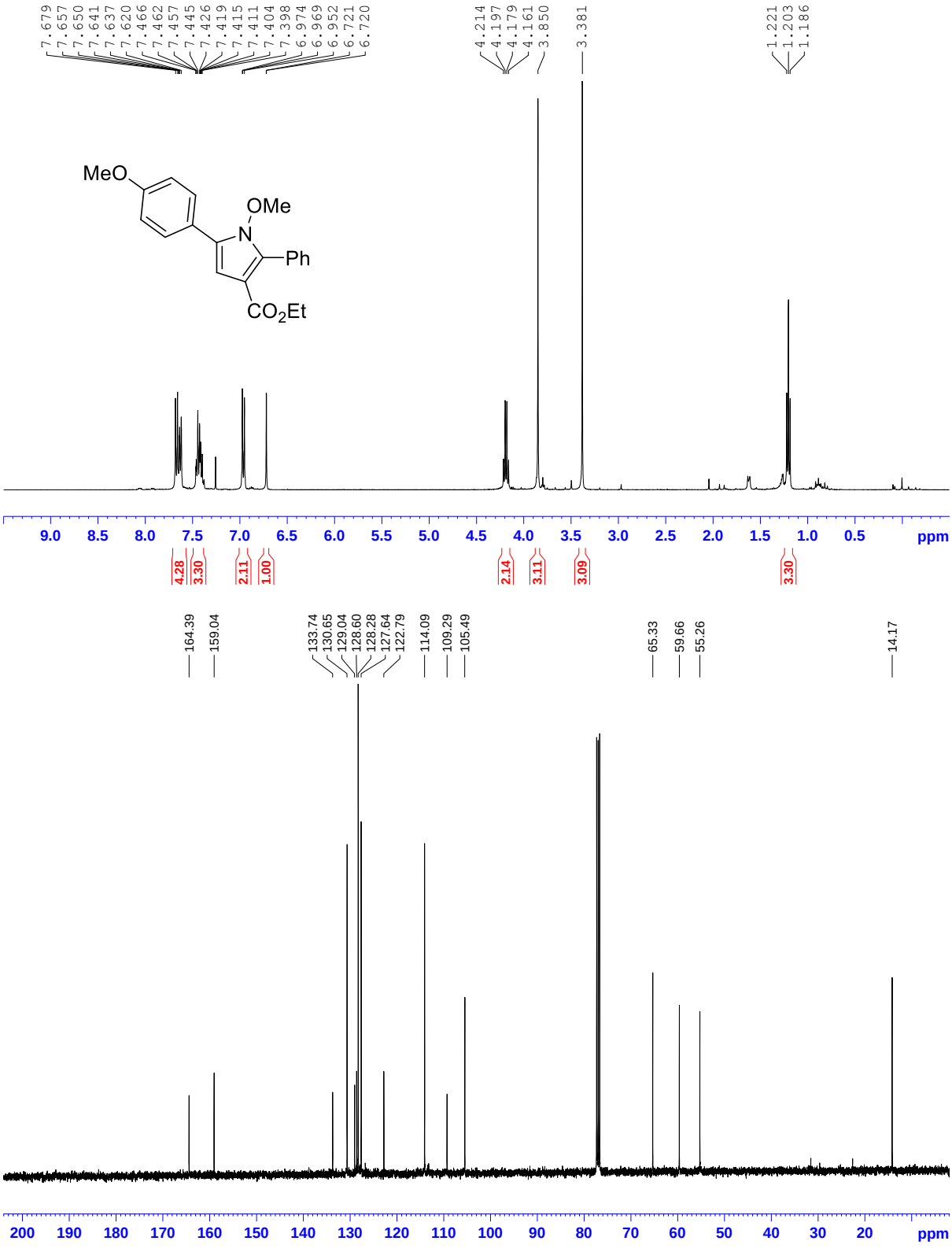
**Ethyl 1-methoxy-5-phenyl-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-3-carboxylate (3fc):**



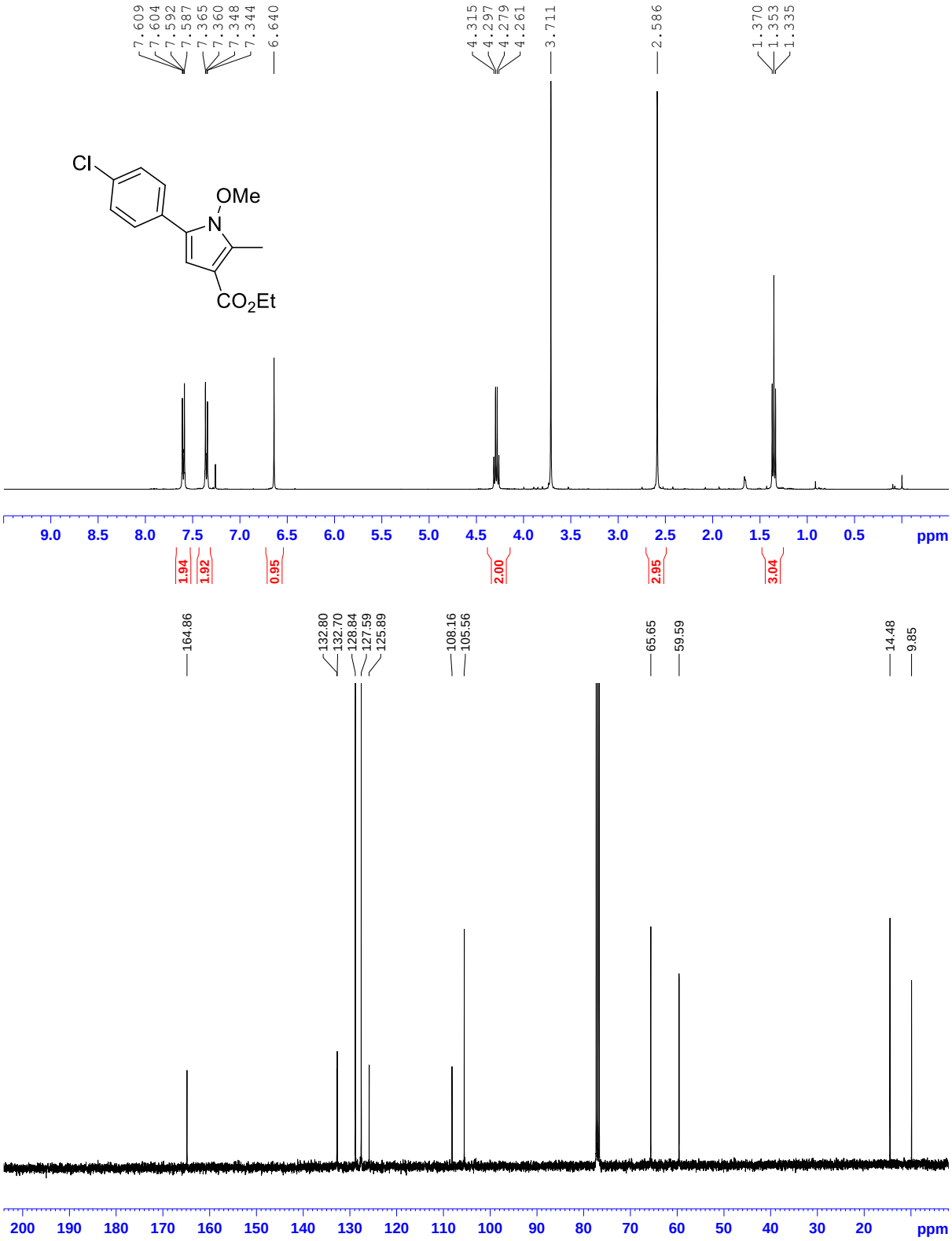
**Ethyl 1-methoxy-5-(4-methoxyphenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (3ad):**



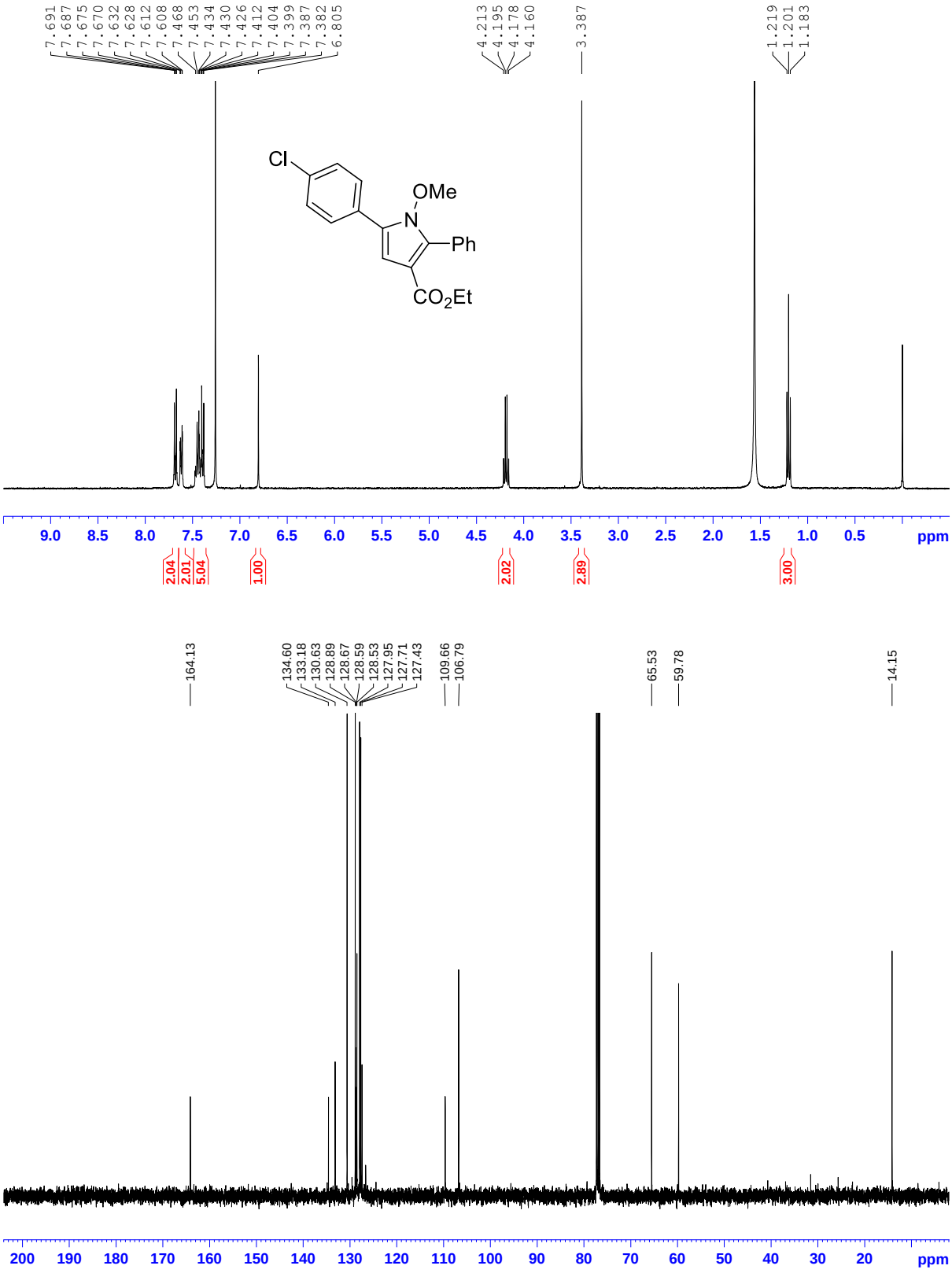
**Ethyl 1-methoxy-5-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (3dd):**



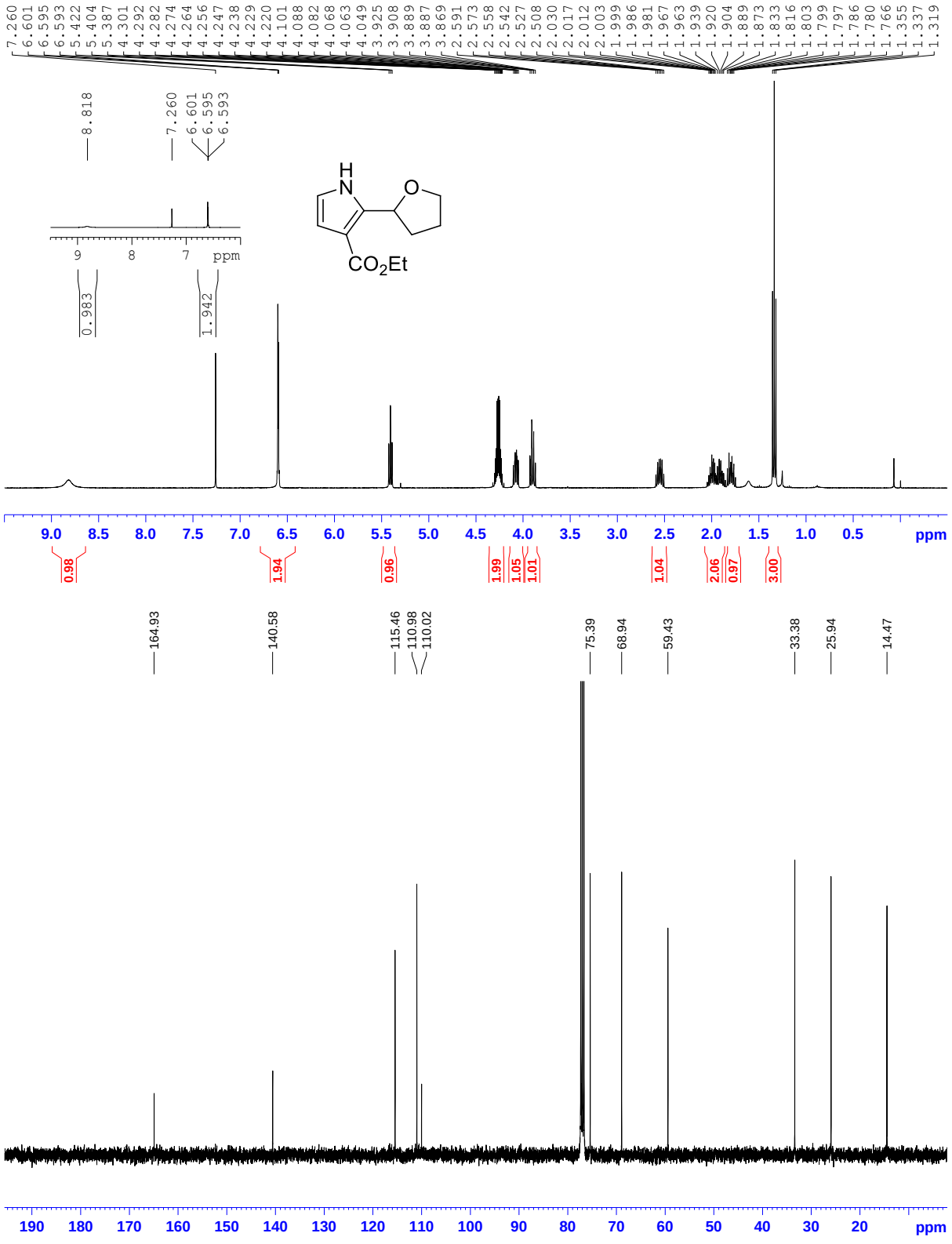
**Ethyl 5-(4-chlorophenyl)-1-methoxy-2-methyl-1*H*-pyrrole-3-carboxylate (3ae):**



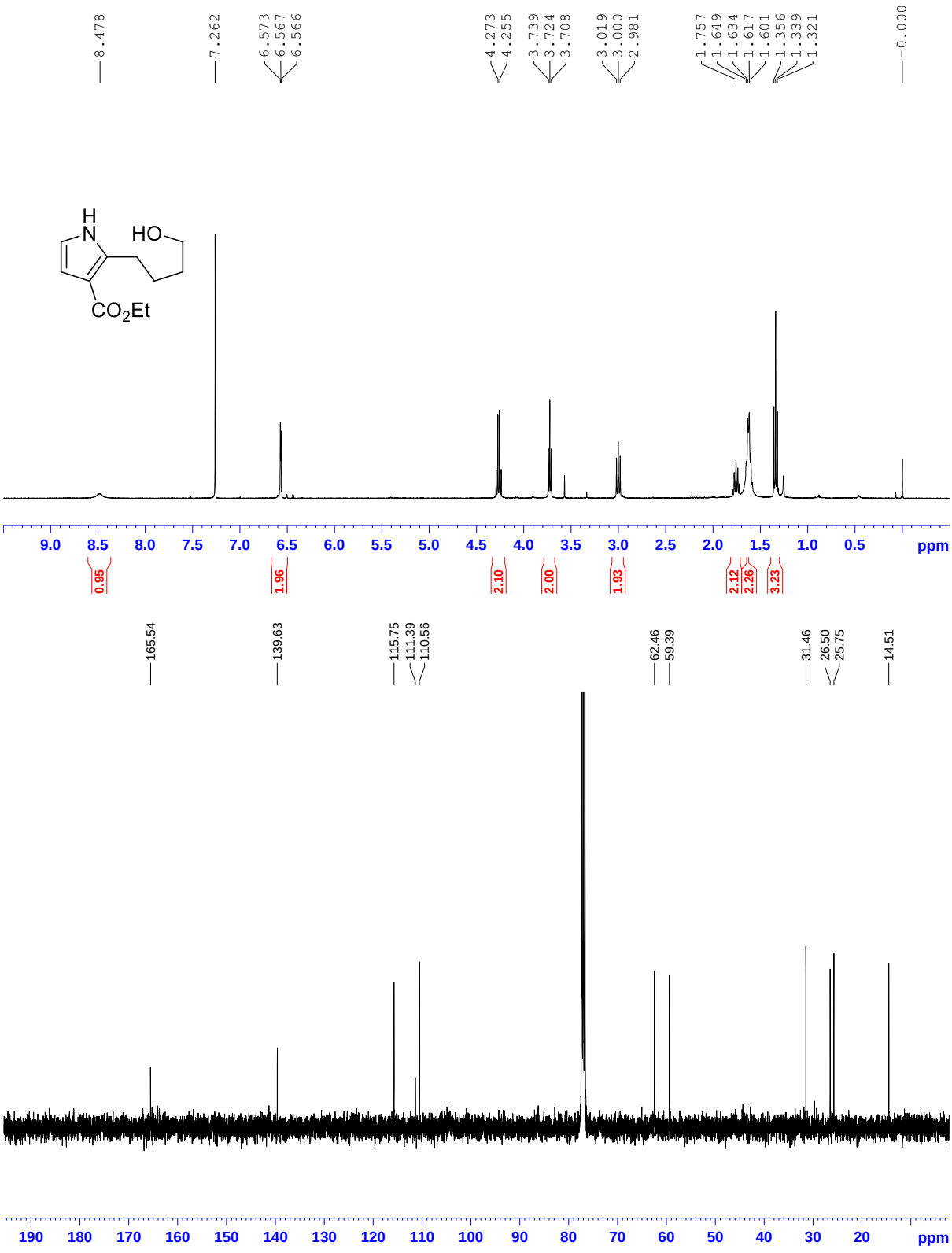
**Ethyl 5-(4-chlorophenyl)-1-methoxy-2-phenyl-1*H*-pyrrole-3-carboxylate (3de):**



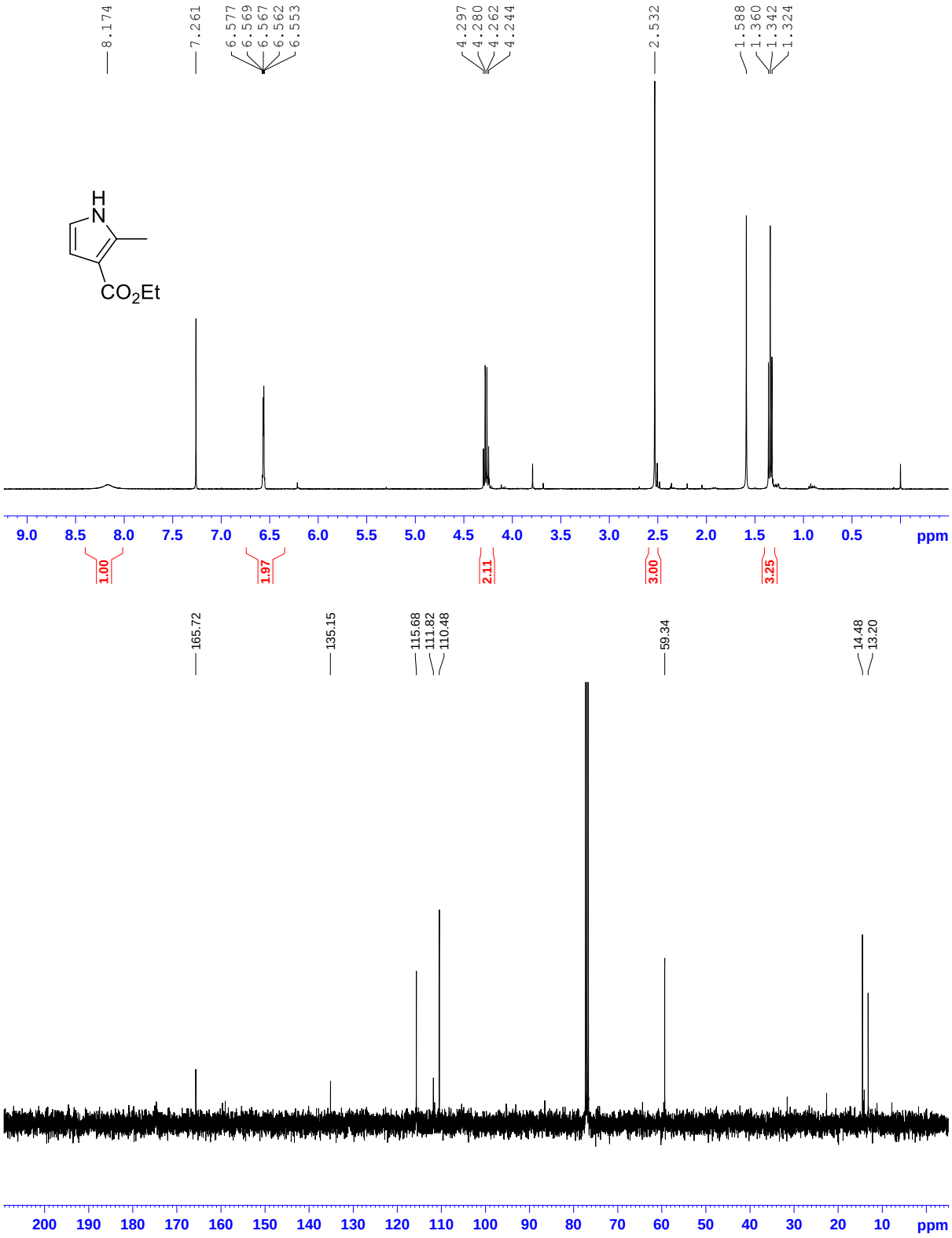
## Ethyl 2-(tetrahydrofuran-2-yl)-1*H*-pyrrole-3-carboxylate (4ga):



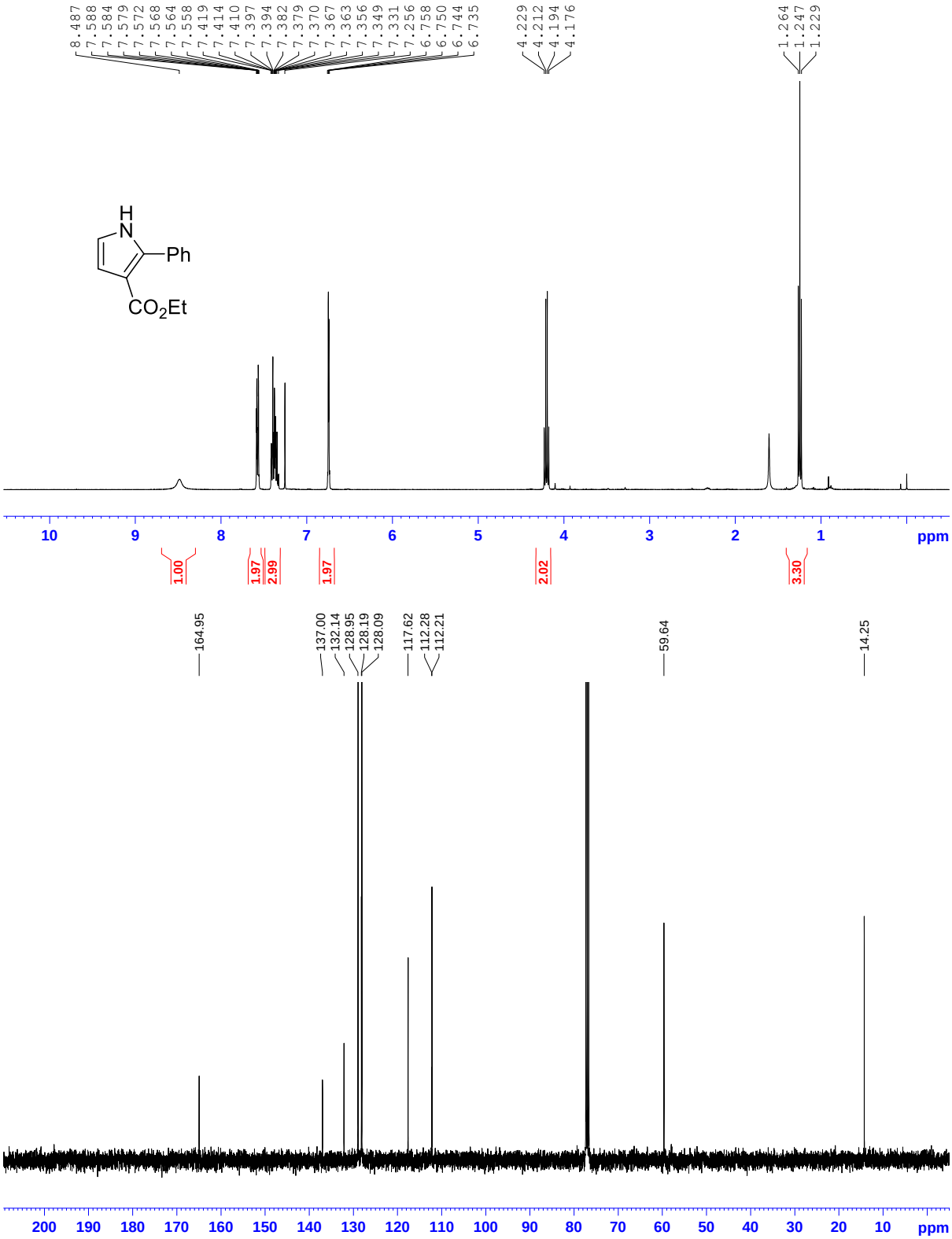
**Ethyl 2-(4-hydroxybutyl)-1*H*-pyrrole-3-carboxylate (4gb):**



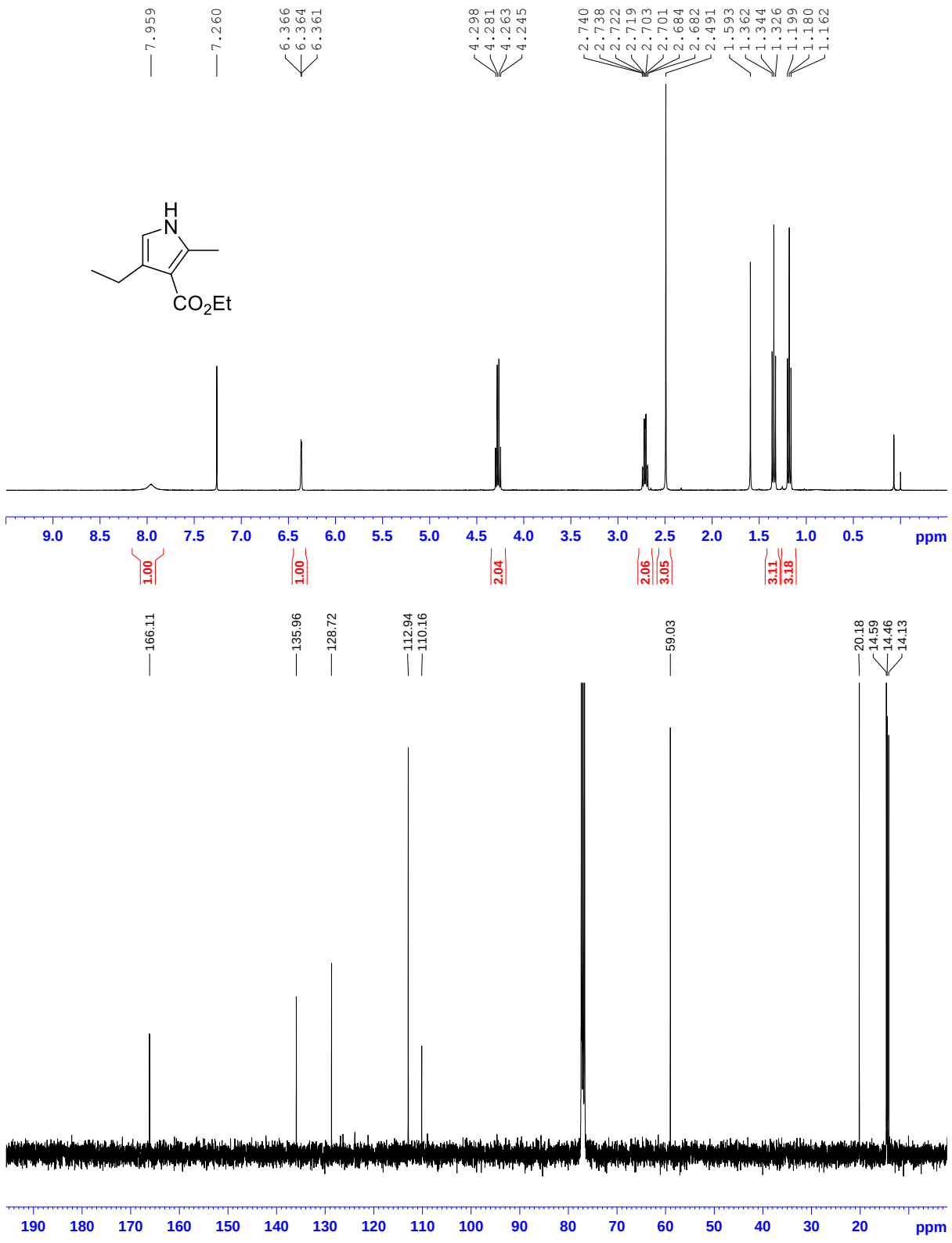
**Ethyl 2-methyl-1*H*-pyrrole-3-carboxylate (4a):**



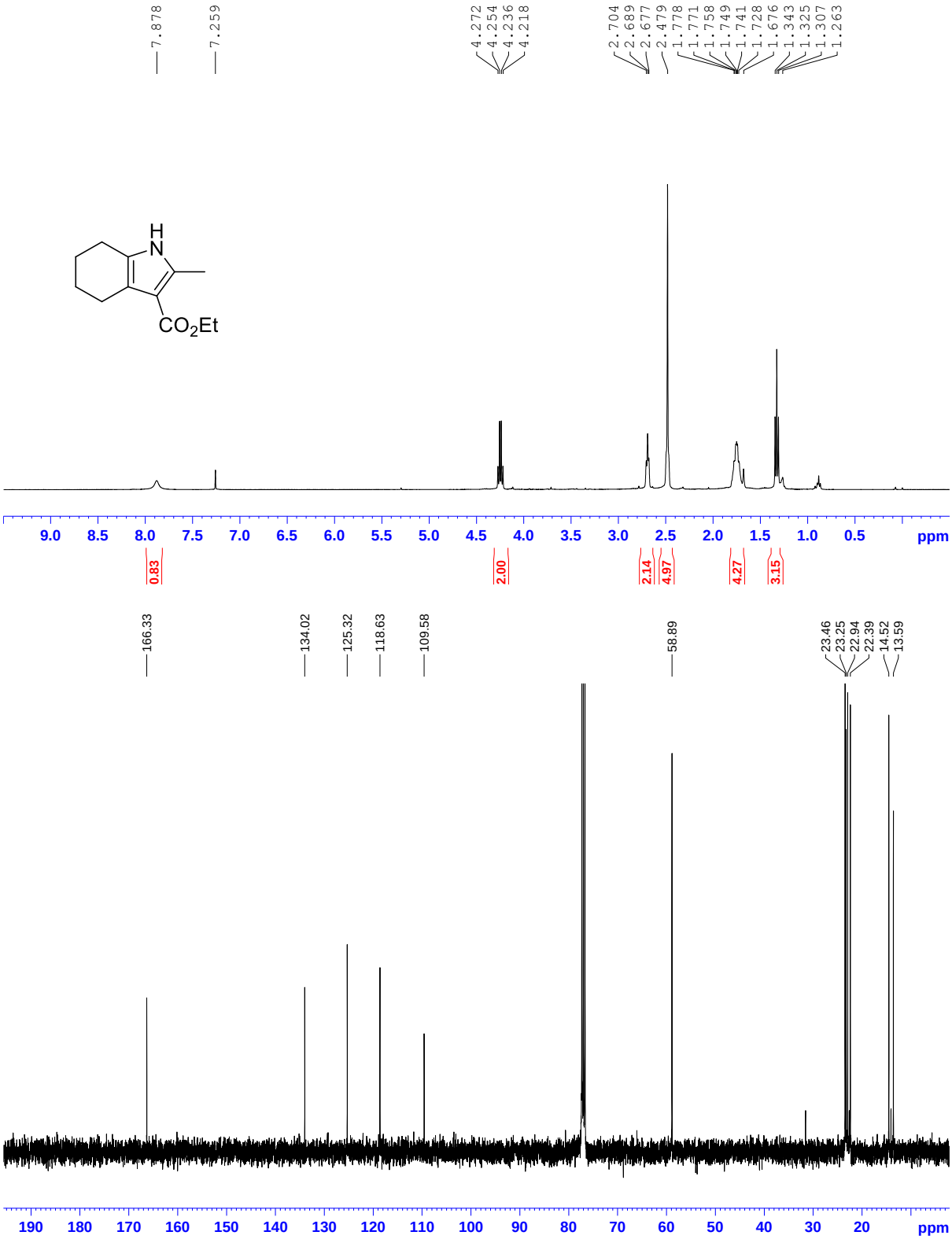
**Ethyl 2-phenyl-1*H*-pyrrole-3-carboxylate (4b):**



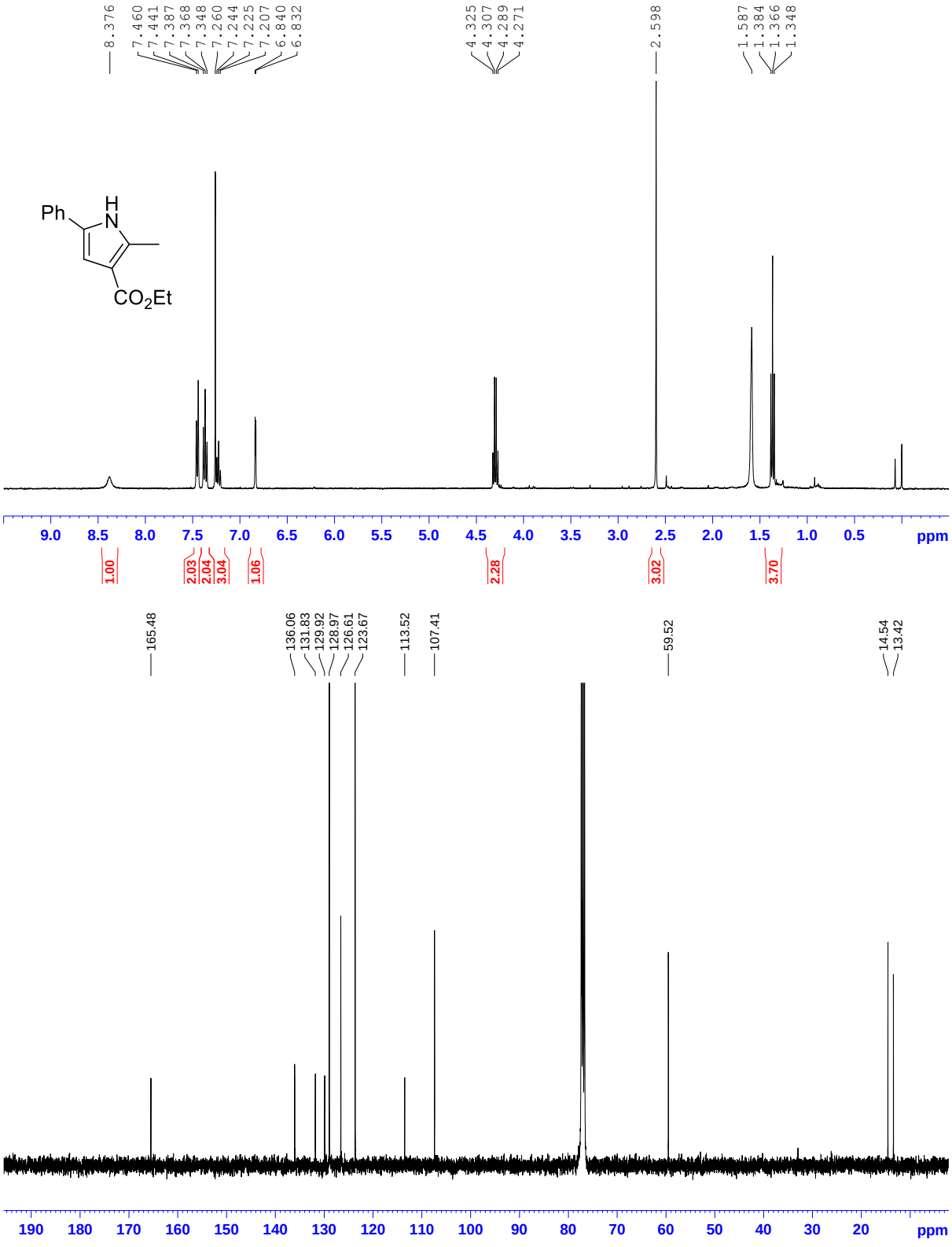
**Ethyl 4-ethyl-2-methyl-1*H*-pyrrole-3-carboxylate (4c):**



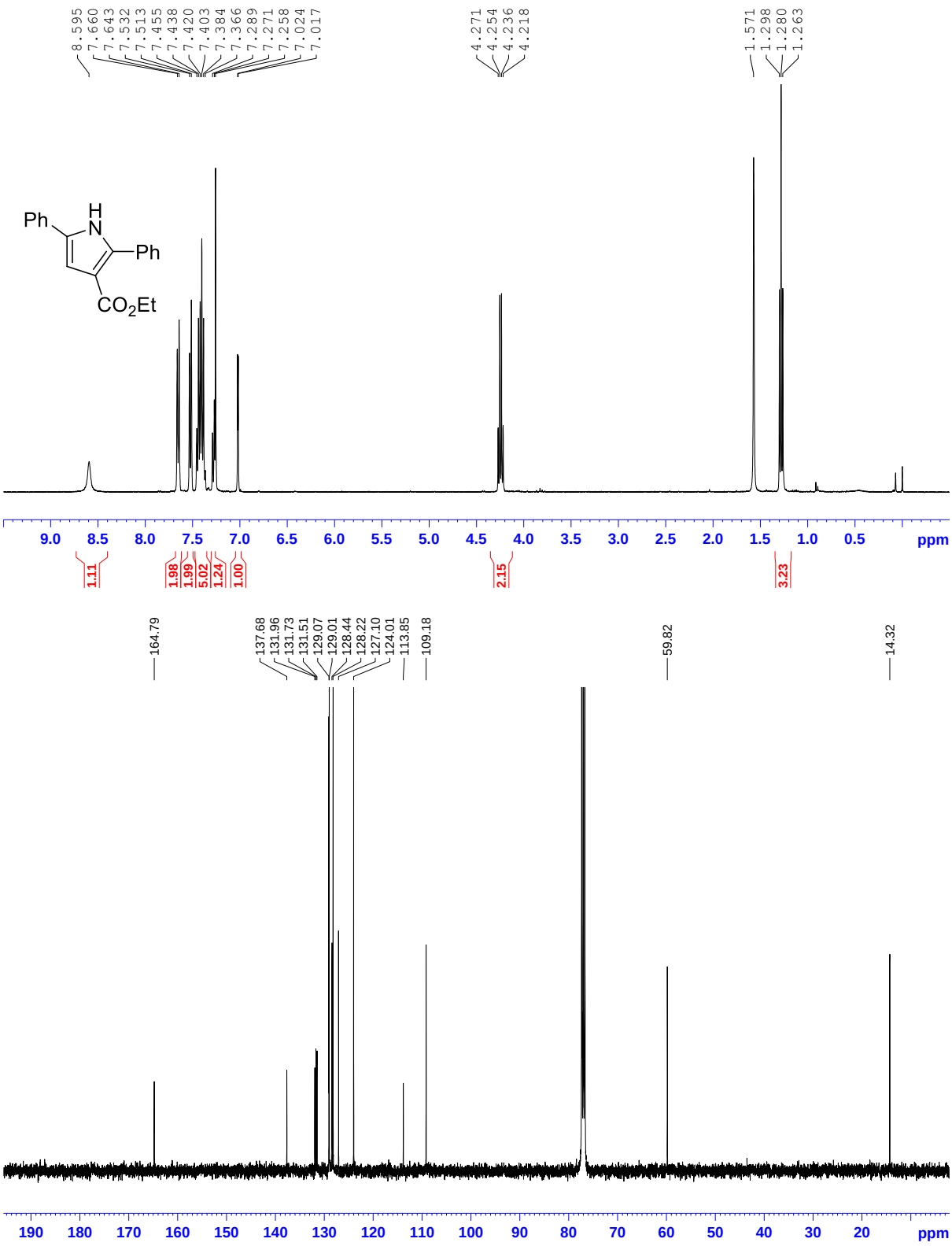
**Ethyl 2-methyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (4d):**



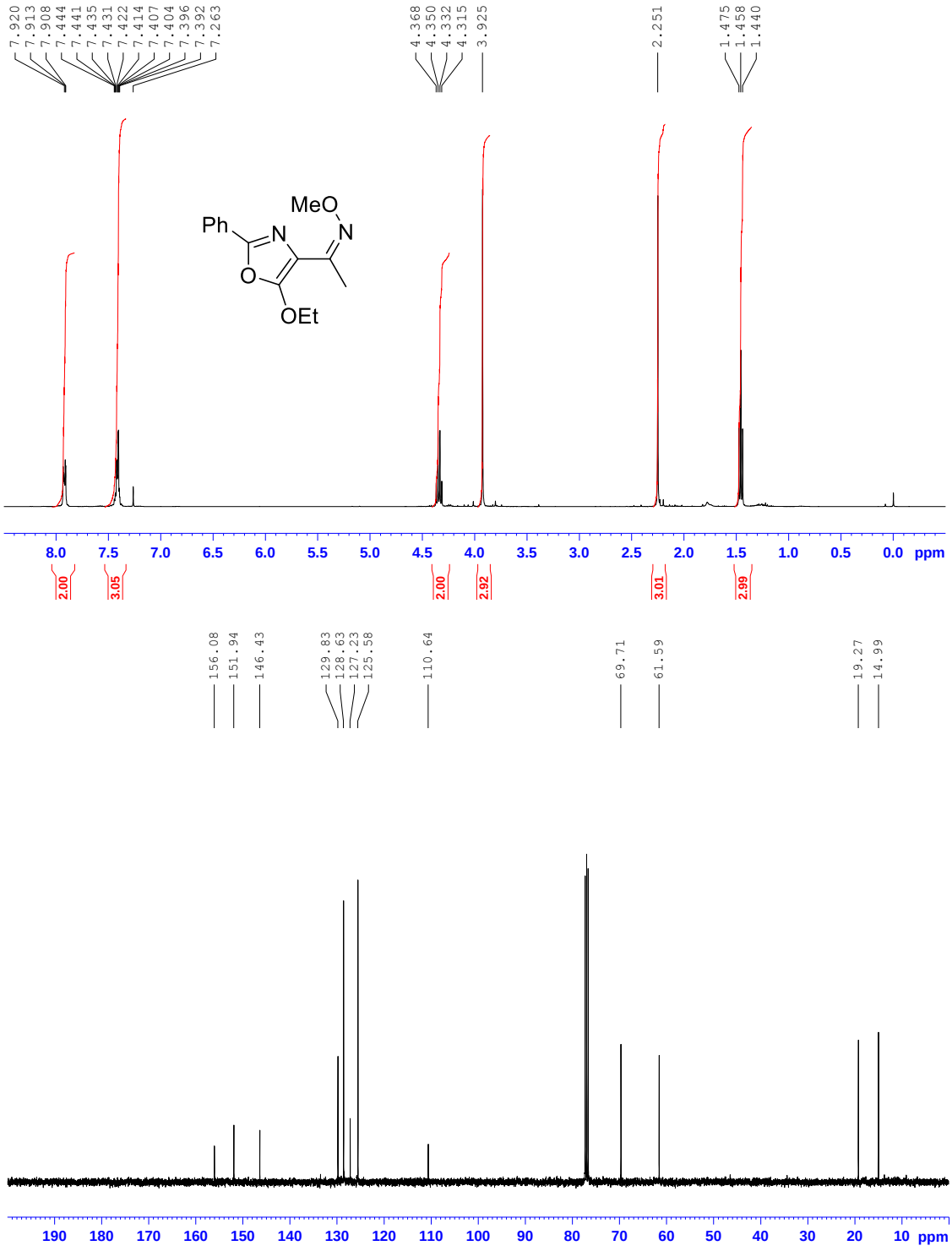
**Ethyl 2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (4e):**



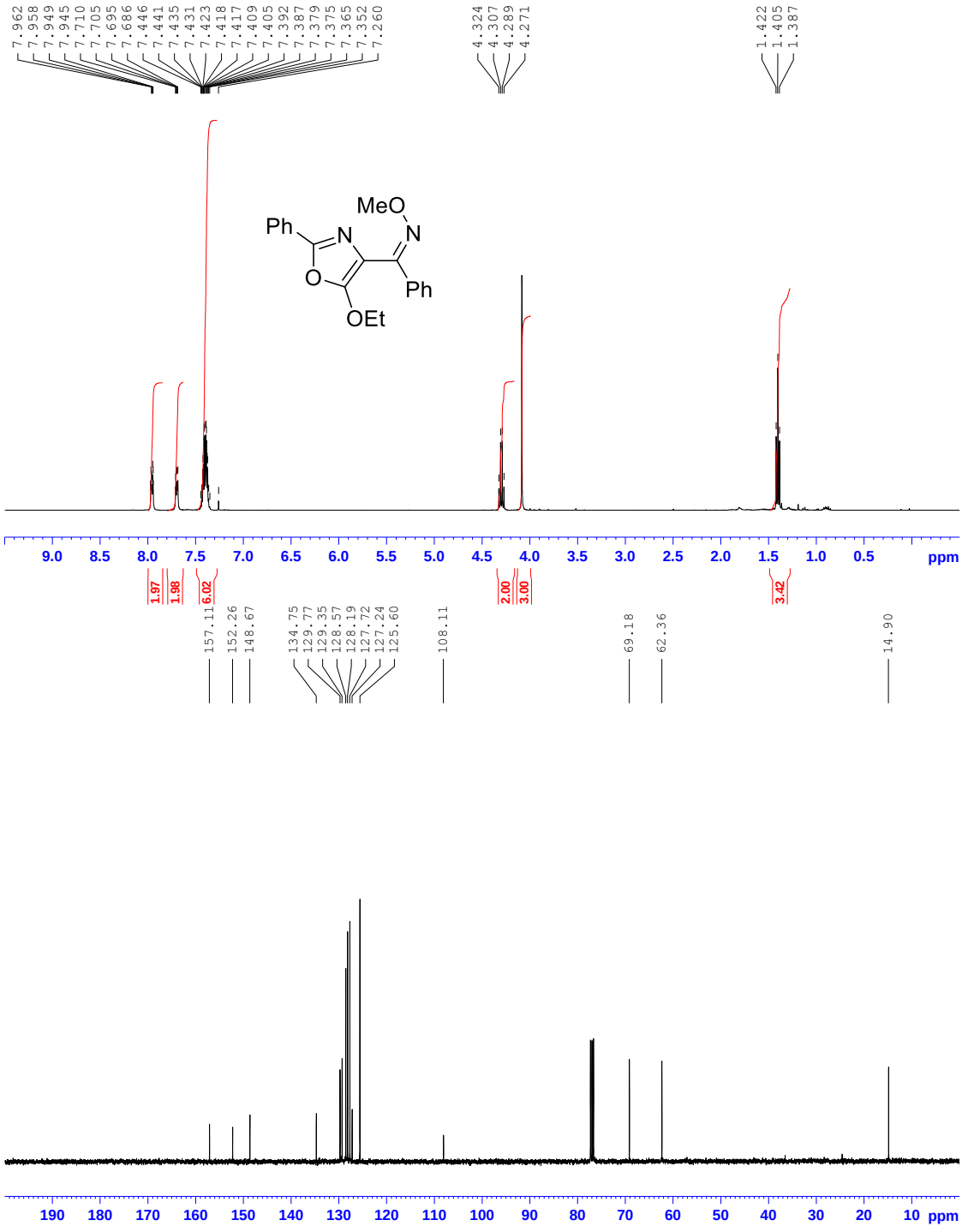
**Ethyl 2,5-diphenyl-1*H*-pyrrole-3-carboxylate (4f):**



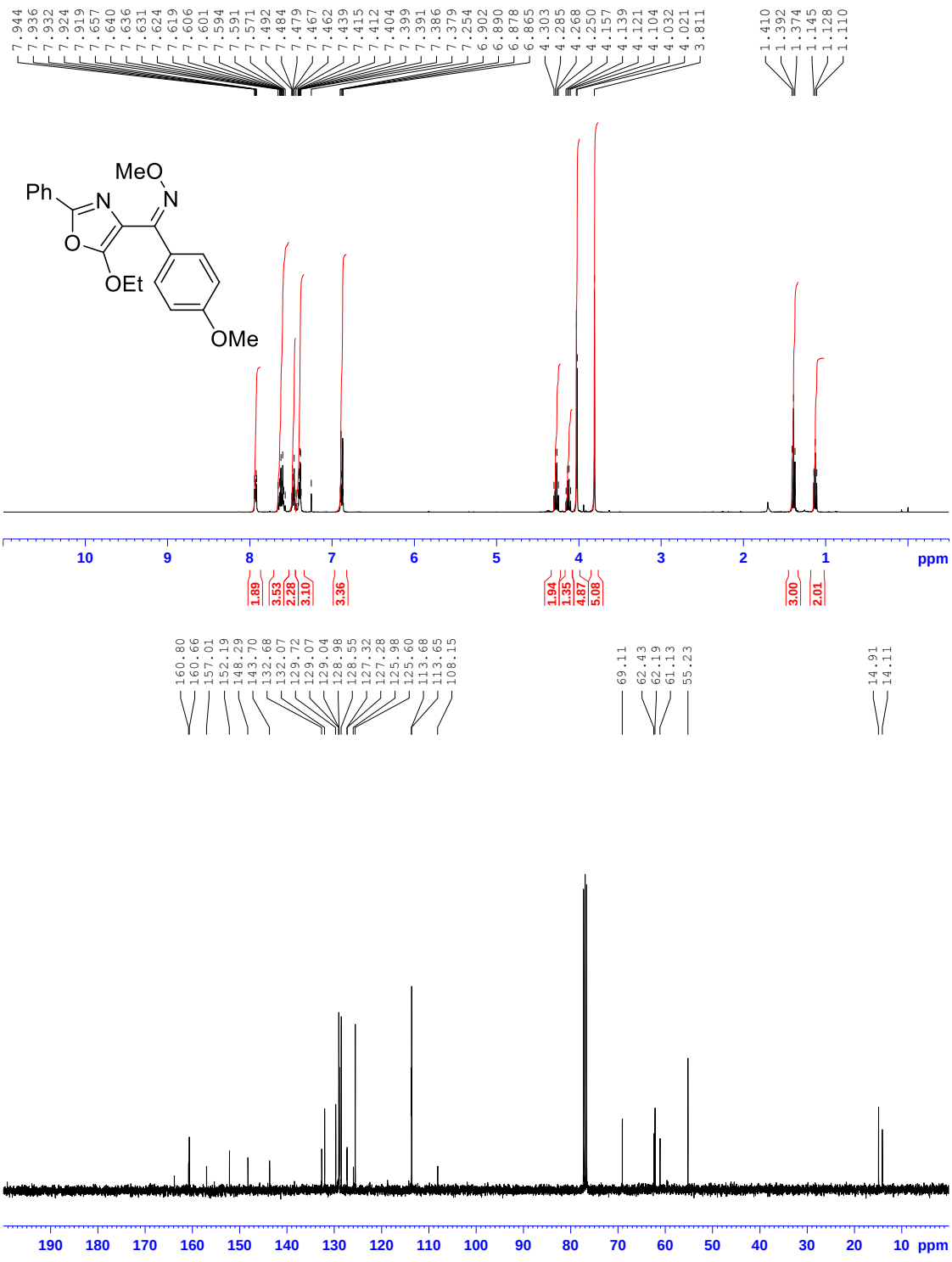
**(*Z*)-1-(5-Ethoxy-2-phenyloxazol-4-yl)ethanone *O*-methyl oxime (6aa):**



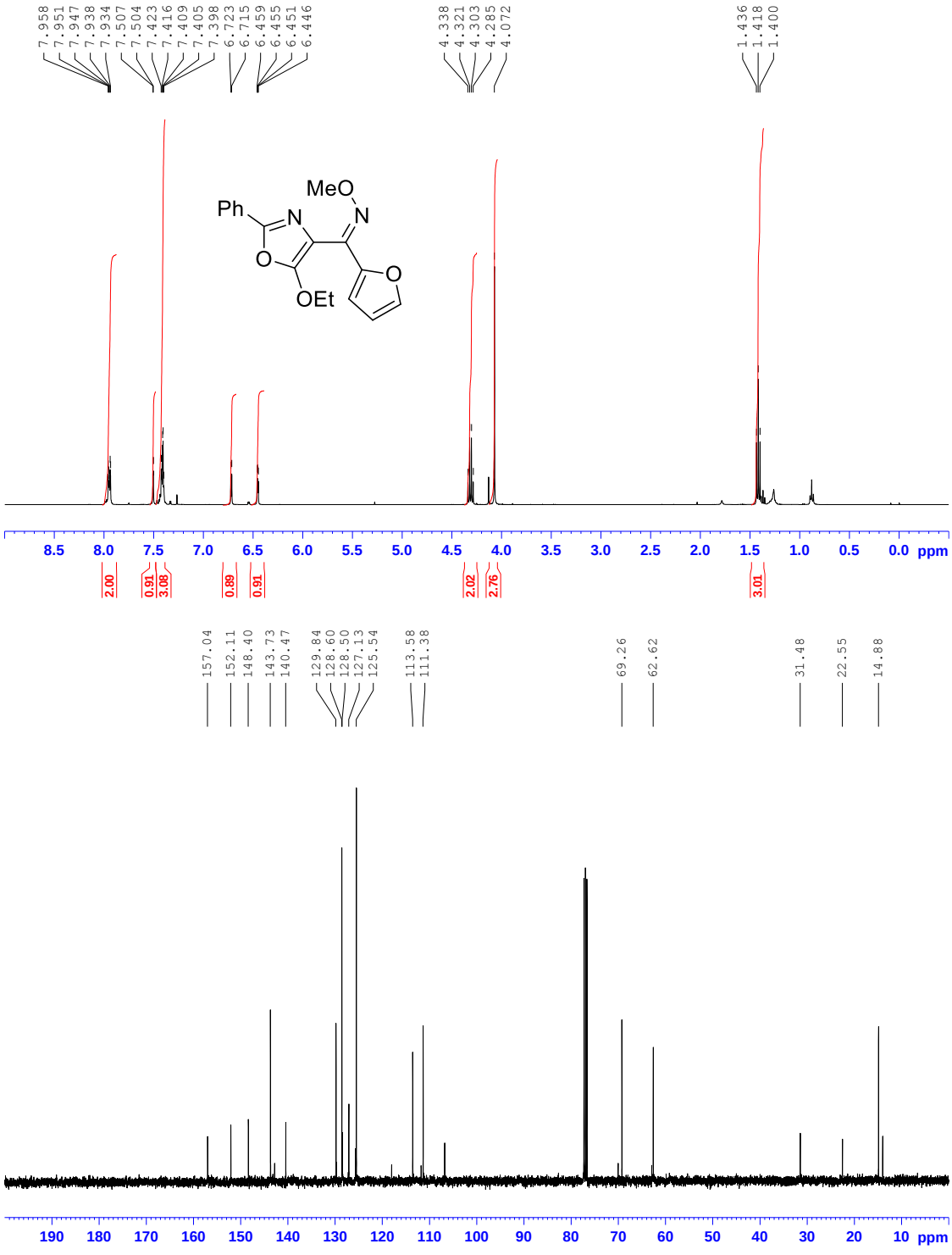
**(*Z*)-(5-Ethoxy-2-phenyloxazol-4-yl)(phenyl)methanone *O*-methyl oxime (6da):**



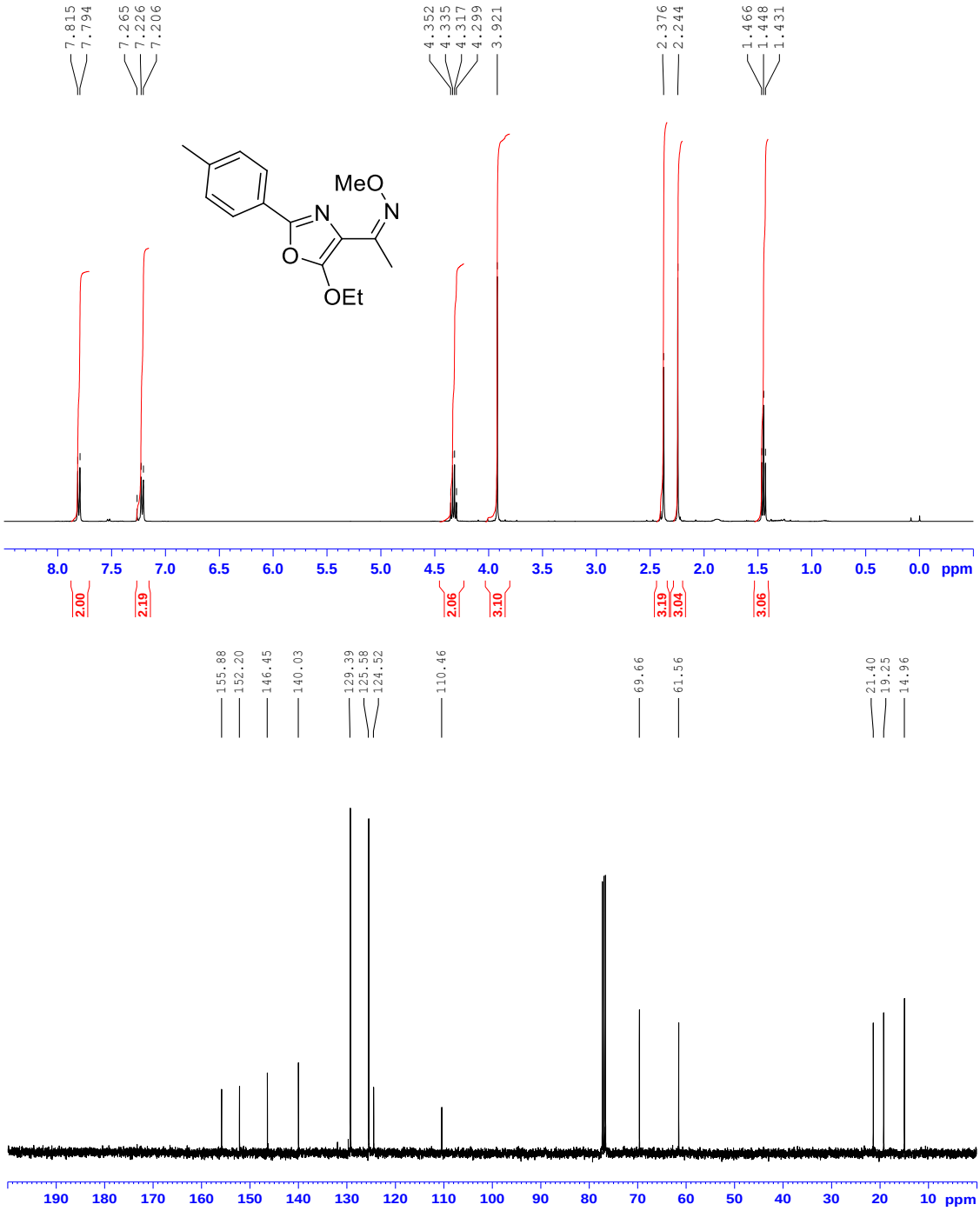
**(*Z*)-(5-Ethoxy-2-phenyloxazol-4-yl)(4-methoxyphenyl)methanone *O*-methyl oxime (6ea):**



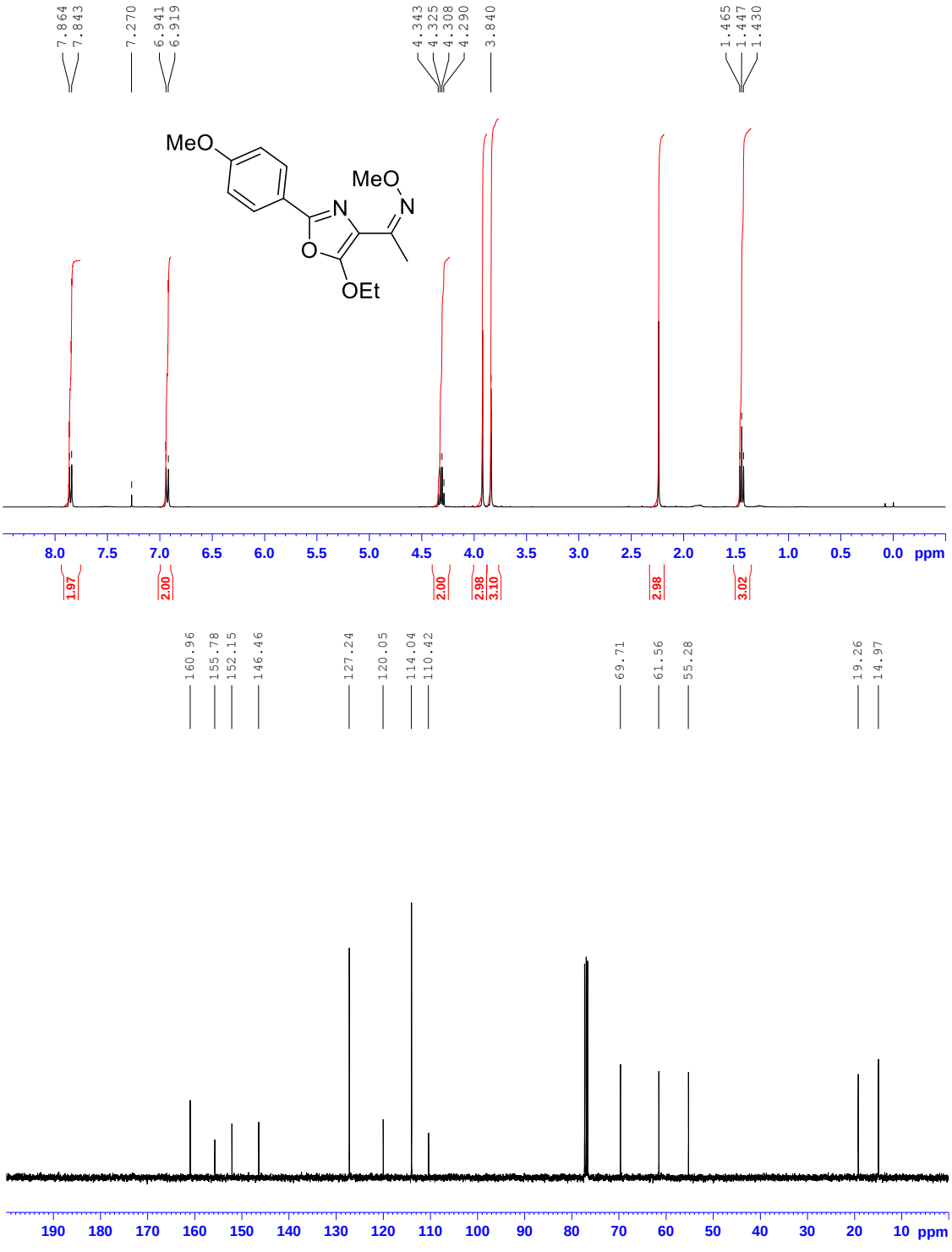
**(*E*)-(5-Ethoxy-2-phenyloxazol-4-yl)(furan-2-yl)methanone *O*-methyl oxime (6ga):**



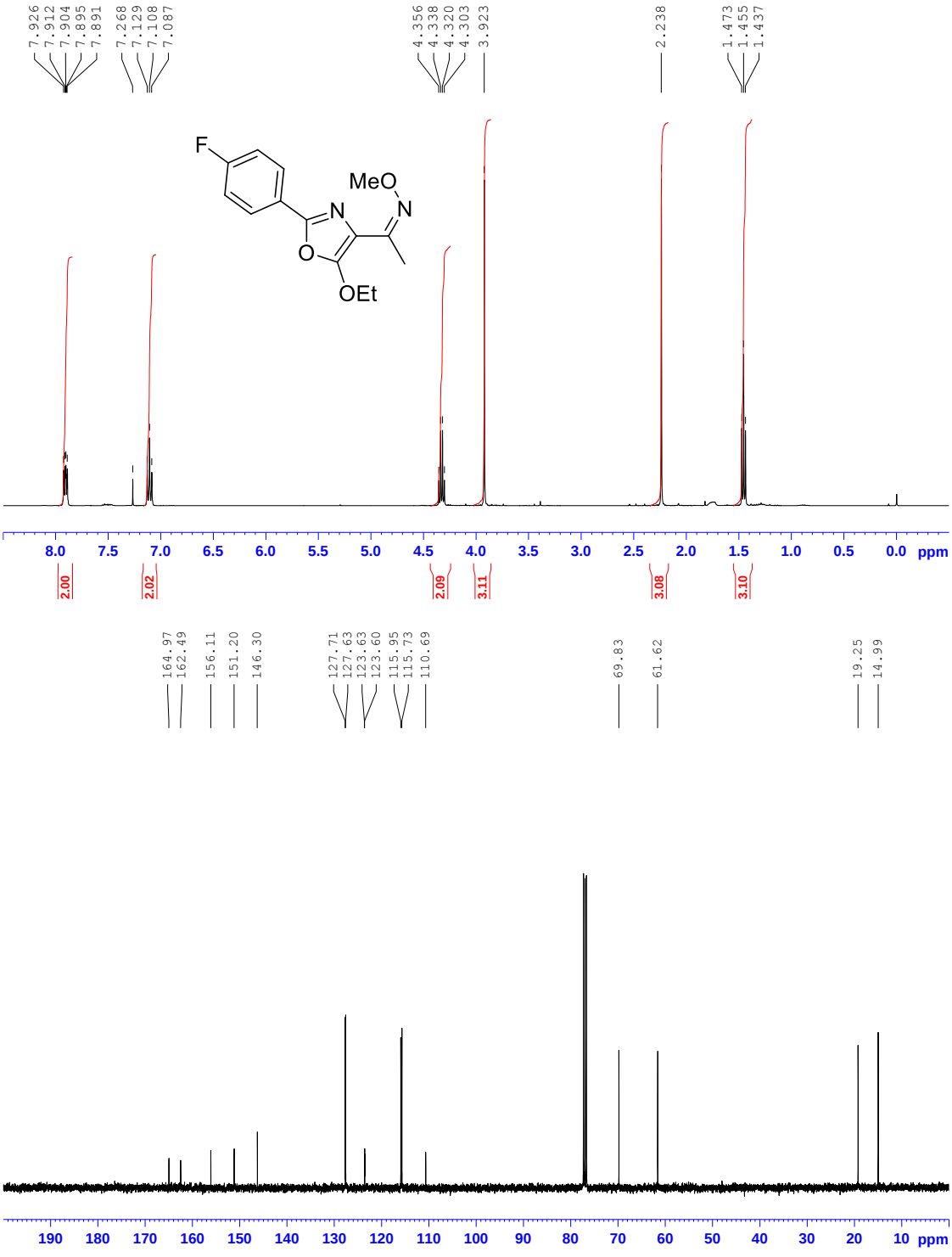
**(*Z*)-1-(5-Ethoxy-2-p-tolyloxazol-4-yl)ethanone *O*-methyl oxime (6ab):**



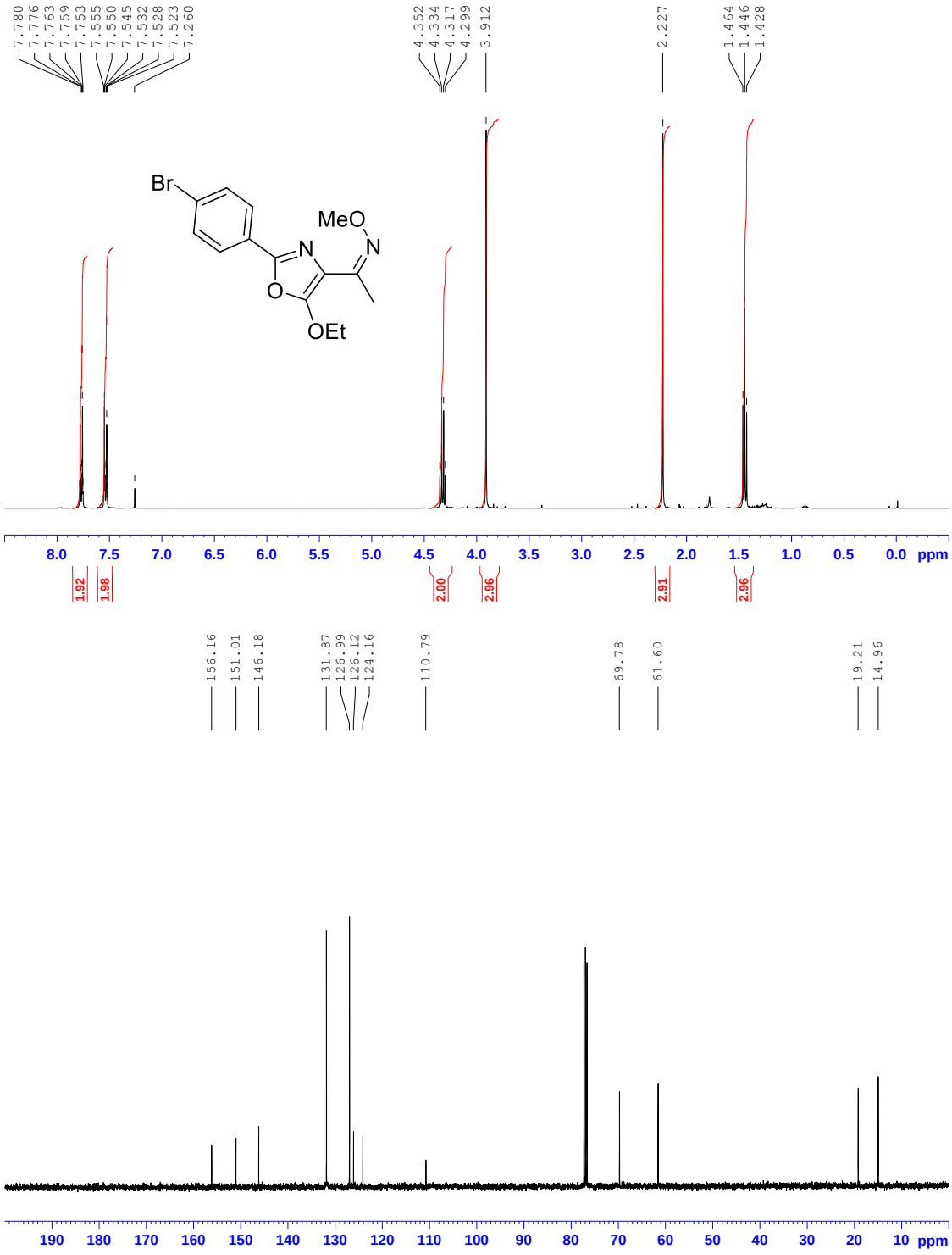
**(*Z*)-1-(5-Ethoxy-2-(4-methoxyphenyl)oxazol-4-yl)ethanone *O*-methyl oxime (6ac):**



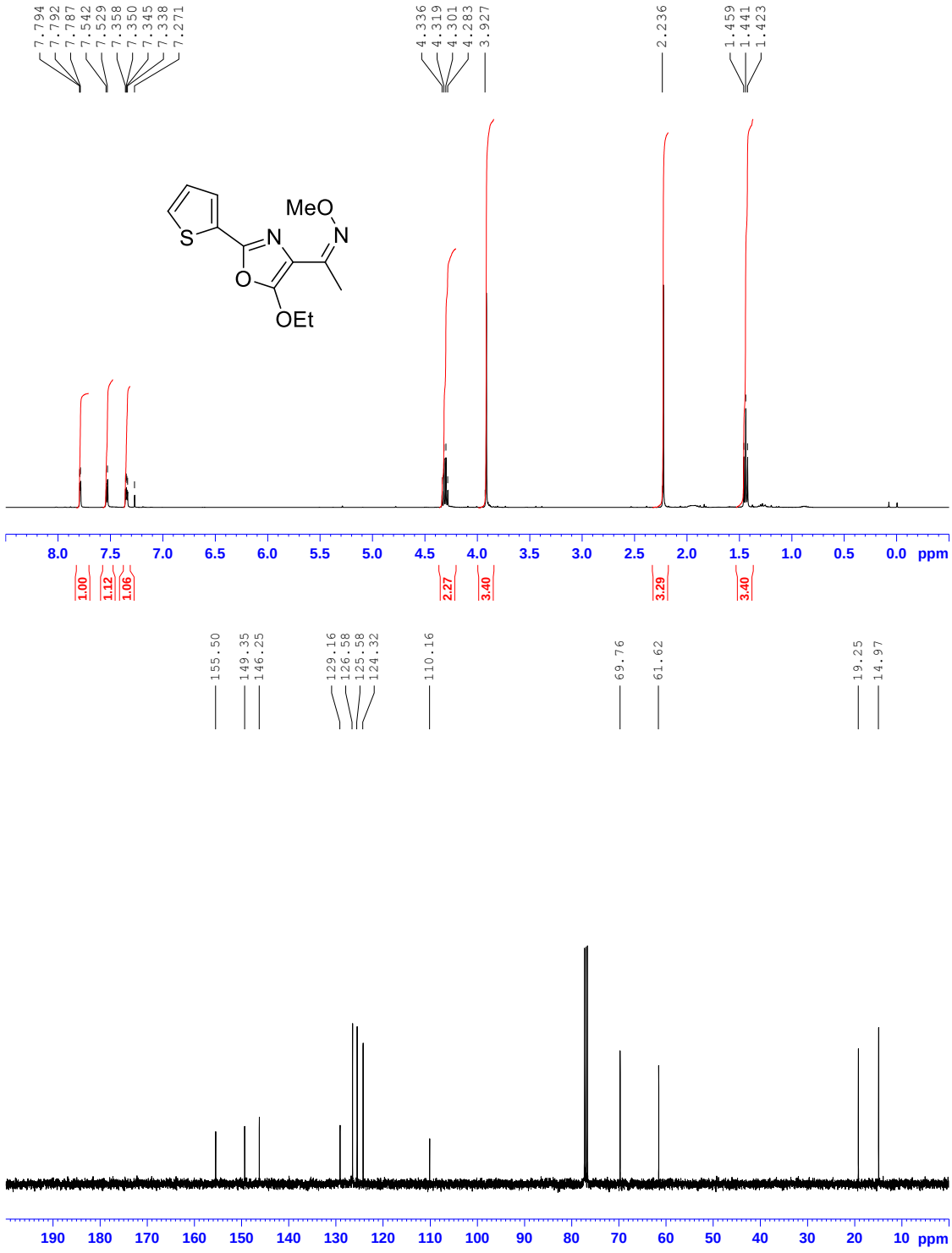
**(*Z*)-1-(5-Ethoxy-2-(4-fluorophenyl)oxazol-4-yl)ethanone *O*-methyl oxime (6ae):**



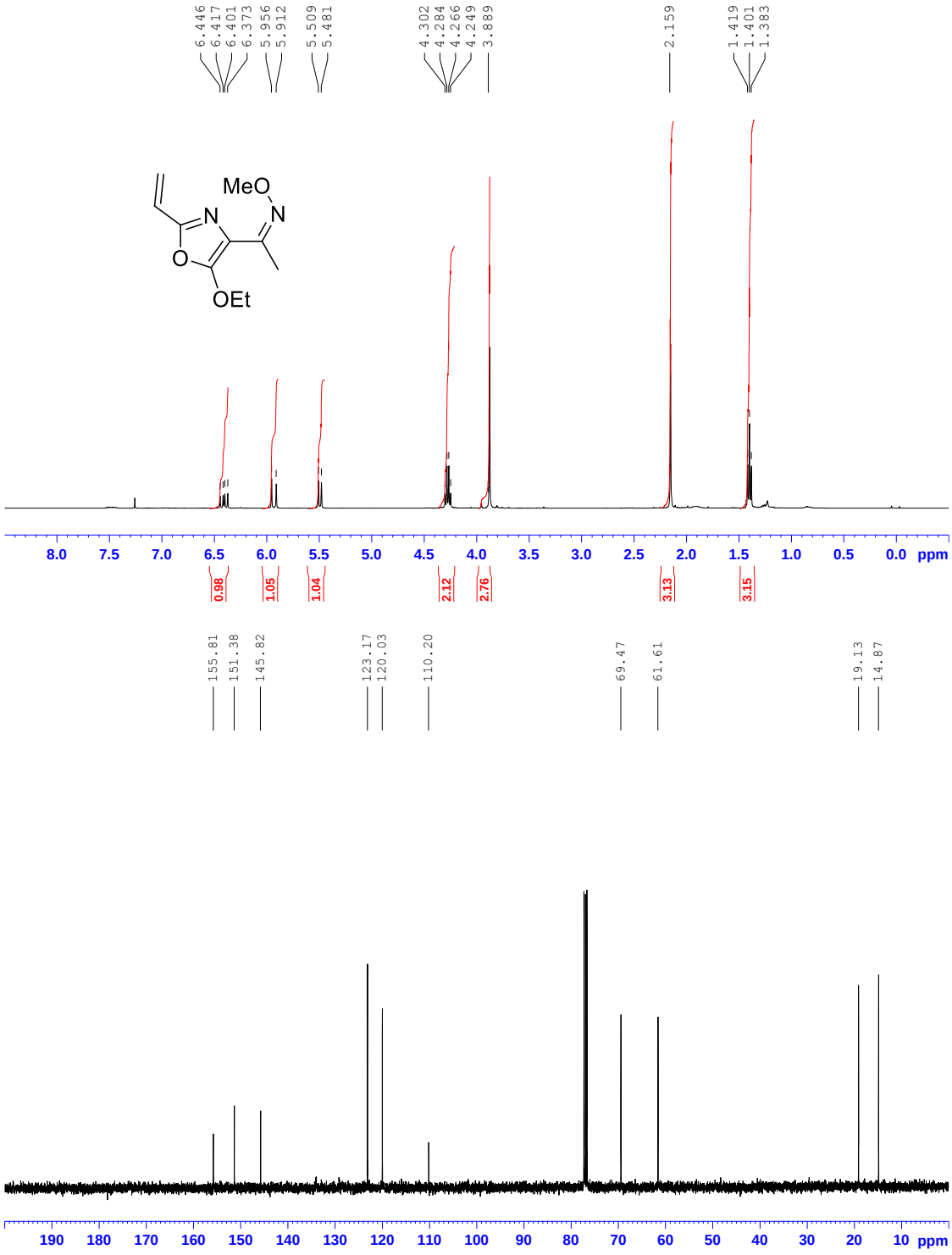
**(Z)-1-(2-(4-Bromophenyl)-5-ethoxyoxazol-4-yl)ethanone *O*-methyl oxime (6af):**



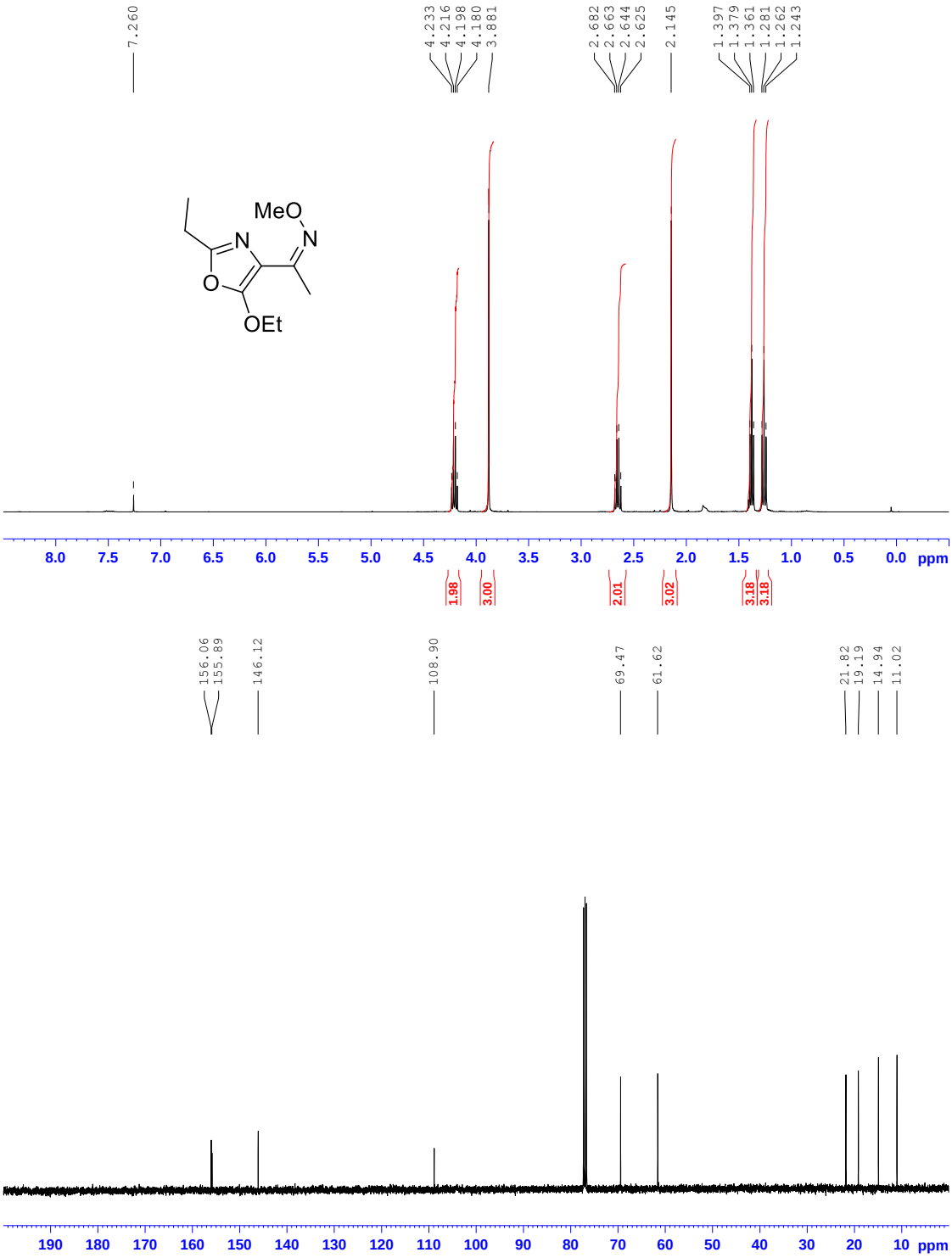
**(*Z*)-1-(5-Ethoxy-2-(thiophen-2-yl)oxazol-4-yl)ethanone *O*-methyl oxime (6ag):**



**(*Z*)-1-(5-Ethoxy-2-vinyloxazol-4-yl)ethanone O-methyl oxime (6ah):**



**(*Z*)-1-(5-Ethoxy-2-ethyloxazol-4-yl)ethanone *O*-methyl oxime (6ai):**



**(*Z*)-1-(2-Cyclohexyl-5-ethoxyoxazol-4-yl)ethanone O-methyl oxime (6aj):**