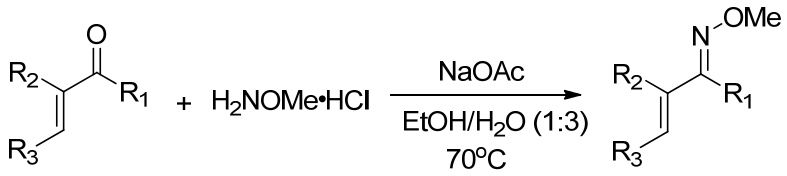
Supporting Information

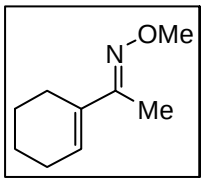
I. General Information

Unless noted, all catalytic reactions were set up inside an inert atmosphere (N_2) glovebox utilizing glassware that was oven-dried (150 ^oC) and evacuated while hot prior to use, whereas the work-up and isolation of the products from the catalytic reactions were conducted on the bench-top using standard techniques. Dichloroethane and other solvents were passed through a column of activated alumina under nitrogen and were stored in a glovebox over activated 4 Å molecular sieves prior to use. Chloroform-d1 (Cambridge Isotopes) was used as received. All aldehydes were freshly distilled or purified by flash column chromatography before use. Unless otherwise noted, all other reagents and materials were obtained from commercial suppliers and used without further purification. $[Cp^*RhCl_2]_2$[1] and *O*-methyl oximes[2] were synthesized according to published procedures. Chromatography was performed on Merck 60 230-240 mesh silica gel. ^1H and $^{13}C\{1H\}$ NMR characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1 and 125.8 MHz (respectively) with chemical shifts reported in parts per million relative to $CHCl_3$ (^1H NMR; 7.26 ppm, $^{13}C\{1H\}$ NMR; 77.00 ppm). IR spectra were recorded on a Nicolet 6700 FTIR spectrometer and only partial data are provided. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Mass spectra (HRMS) were obtained by the Keck Center of Yale University using a Bruker 9.4 TAPEXQe FT-ICR mass spectrometer.

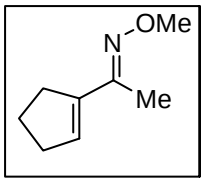
Preparation of Starting Materials



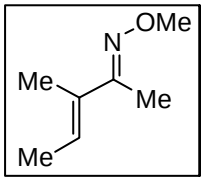
General Procedure for the Preparation of *O*-methyl oximes: To a round bottom flask equipped with a stir bar were added the indicated ketone (1.0 equiv), $MeONH_2$•HCl (2.7 equiv), and NaOAc (4.4 equiv) in EtOH/H_2O (1:3) as solvent. The flask was equipped with a reflux condenser, and the reaction mixture was heated at 70 °C for 2 h. After cooling to rt, the reaction mixture was diluted with ethyl acetate and was transferred to a separatory funnel. The organic layer was collected, and the aqueous layer was extracted with ethyl acetate (2 x 30 mL). The organic layers were combined, dried with Na_2SO_4, and concentrated. Purification by flash column chromatography with hexanes/ ethyl acetate (20:1) afforded the *O*-methyl oxime.



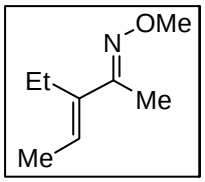
(*E*)-1-(Cyclohex-1-en-1-yl)ethanone *O*-methyl oxime (1a): Derived from 1-acetyl-1-cyclohexene (1.24 g, 10.0 mmol, 1.0 equiv), $MeONH_2$•HCl (2.26 g, 27.0 mmol, 2.7 equiv) and NaOAc (3.61 g, 44.0 mmol, 4.4 equiv) in 88 mL of H_2O and 30 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **1a** (0.842 g, 55% yield) as a colorless oil. IR (film): 2932, 1435, 1075, 1048 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.14–6.09 (m, 1H), 3.88 (s, 3H), 2.31–2.26 (m, 2H), 2.20–2.13 (m, 2H), 1.93 (s, 3H), 1.68–1.56 (m, 4H); ^{13}C {^1H} NMR ($CDCl_3$) δ 156.1, 135.0, 129.0, 61.6, 26.1, 24.6, 22.6, 22.3, 10.4; HRMS (ESI/$[M+H]^+$) calcd. for $C_9H_{16}NO$: 154.1226. found 154.1251.



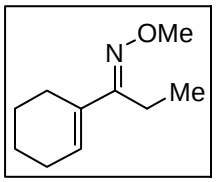
(*E*)-1-(Cyclopent-1-en-1-yl)ethanone *O*-methyl oxime (S1): Derived from 1-acetyl-1-cyclopentene (1.10 g, 10.0 mmol, 1.0 equiv), $MeONH_2$•HCl (2.26 g, 27.0 mmol, 2.7 equiv) and NaOAc (3.61 g, 44.0 mmol, 4.4 equiv) in 88 mL of H_2O and 30 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **S1** (1.06 g, 76% yield) as a colorless oil. IR (film): 2938, 2843, 1465, 1442, 1379, 1071, 1043 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.09–6.06 (m, 1H), 3.89 (s, 3H), 2.59–2.51 (m, 2H), 2.48–2.40 (m, 2H), 2.00 (s, 3H), 1.96–1.87 (m, 2H); ^{13}C {^1H} NMR ($CDCl_3$) δ 153.3, 141.6, 132.6, 61.7, 33.2, 31.6, 23.4, 11.8; HRMS (ESI/$[M+H]^+$) calcd. for $C_8H_{14}NO^+$ 140.1070. found 140.1061.



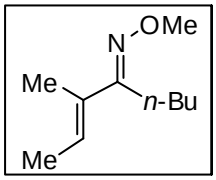
(*2E,3E*)-3-Methylpent-3-en-2-one *O*-methyl oxime (S2): Derived from *(E)*-3-methylpent-3-en-2-one (0.981 g, 10.0 mmol, 1.0 equiv), $MeONH_2$•HCl (2.26 g, 27.0 mmol, 2.7 equiv) and NaOAc (3.61 g, 44.0 mmol, 4.4 equiv) in 88 mL of H_2O and 30 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **S2** (0.550 g, 43% yield) as a colorless oil. IR (film): 2937, 2816, 1441, 1368, 1052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.97–5.89 (m, 1H), 3.89 (s, 3H), 1.95 (s, 3H), 1.84 (s, 3H), 1.79–1.74 (m, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 156.9, 133.9, 126.3, 61.7, 14.2, 12.4, 10.7; HRMS (ESI/$[M+H]^+$) calcd. for $C_7H_{14}NO^+$ 128.1070. found 128.1071.



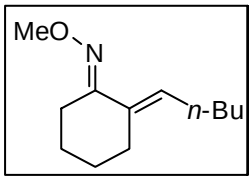
(*2E,3E*)-3-Ethylpent-3-en-2-one *O*-methyl oxime (S3): Derived from *(E)*-3-ethylpent-3-en-2-one (0.450 g, 4.01 mmol, 1.0 equiv),[3] $MeONH_2$•HCl (0.885 g, 10.8 mmol, 2.7 equiv) and NaOAc (1.46 g, 17.6 mmol, 4.4 equiv) in 30 mL of H_2O and 10 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **S3** (0.120 g, 21% yield) as a colorless oil. IR (film): 2965, 2936, 1465, 1145, 1051cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.86 (q, J = 7.1 Hz, 1H), 3.90 (s, 3H), 2.39 (q, J = 7.6 Hz, 2H), 1.93 (s, 3H), 1.77 (d, J = 7.1 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 155.7, 140.2, 125.6, 61.7, 19.8, 13.8, 13.6, 11.0.



(*E*)-1-(Cyclohex-1-en-1-yl)propan-1-one *O*-methyl oxime (S4): Derived from 1-(cyclohex-1-en-1-yl)propan-1-one (0.600 g, 4.34 mmol, 1.0 equiv),[5] $MeONH_2$•HCl (0.959 g, 11.7 mmol, 2.7 equiv) and NaOAc (1.59 g, 19.1 mmol, 4.4 equiv) in 35 mL of H_2O and 12 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **S4** (0.251 g, 35% yield) as a colorless oil. IR (film): 2934, 1465, 1435, 1069, 1046 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.21–6.02 (m, 1H), 3.87 (s, 3H), 2.45 (q, *J* = 7.6 Hz, 2H), 2.30–2.22 (m, 2H), 2.21-2.14 (m, 2H), 1.69–1.57 (m, 4H), 1.03 (t, *J* = 7.6 Hz, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 161.3, 133.6, 128.8, 61.6, 26.1, 24.8, 22.6, 22.3, 18.2, 11.9; HRMS (ESI/$[M+H]^+$) calcd. for $C_{10}H_{18}NO^+$ 168.1383. found 168.1393.

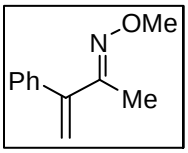


(*2E,4E*)-3-Methyloct-2-en-4-one *O*-methyl oxime (S5): Derived from (*E*)-3-methyl-2-octen-4-one (0.200 g, 1.43 mmol, 1.0 equiv),[7] $MeONH_2$•HCl (0.316 g, 3.85 mmol, 2.7 equiv) and NaOAc (0.526 g, 6.29 mmol, 4.4 equiv) in 12 mL of H_2O and 4 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **S5** (0.105 g, 43% yield) as a colorless oil. IR (film): 2957, 2932, 2862, 1462, 1052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.95–5.88 (m, 1H), 3.87 (s, 3H), 2.48–2.42 (m, 2H), 1.84–1.80 (s, 3H), 1.77 (d, *J* = 6.9 Hz, 3H), 1.44–1.28 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 161.2, 132.8, 126.1, 61.6, 29.5, 24.8, 23.2, 14.3, 14.0, 12.7; HRMS (ESI/$[M+H]^+$) calcd. for $C_{10}H_{20}NO^+$ 170.1545. found 170.1539.

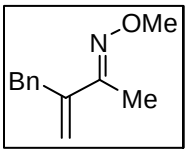


(*1E,2E*)-2-Pentylidenecyclohexanone *O*-methyl oxime (S6): Derived from (*E*)-2-pentylidenecyclohexanone (0.210 g, 1.26 mmol, 1.0 equiv),[6] $MeONH_2$•HCl (0.280 g, 3.40 mmol, 2.7 equiv) and NaOAc (0.460 g, 5.54 mmol, 4.4 equiv) in 10 mL of H_2O and 3 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **S6** (0.124 g, 50% yield) as a colorless oil. IR (film): 2932, 2859, 1465, 1049, 909, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.87 (tt, *J* = 7.4, 0.8 Hz, 1H), 3.88 (s, 3H), 2.49 (t, *J* = 6.5 Hz, 2H), 2.33 (t, *J* = 5.8 Hz, 2H), 2.05 (q, *J* = 7.3 Hz, 2H),

1.69–1.57 (m, 4H), 1.44–1.26 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 159.7, 132.8, 129.0, 61.4, 31.4, 27.49, 27.45, 25.6, 24.8, 23.8, 22.4, 14.0; HRMS (ESI/[M+H]$^+$) calcd. for $C_{12}H_{22}NO^+$ 196.1696. found 196.1613.



(*E*)-3-Phenylbut-3-en-2-one *O*-methyl oxime (1b): Derived from 3-phenyl-3-buten-2-one (1.01 g, 6.80 mmol, 1.0 equiv),[4] $MeONH_2$•HCl (1.51 g, 18.4 mmol, 2.7 equiv) and NaOAc (2.50 g, 29.9 mmol, 4.4 equiv) in 60 mL of H_2O and 20 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **1b** (0.65 g, 54% yield) as a colorless oil. IR (film): 2937, 1495, 1445, 1367, 1175, 1046 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35 – 7.29 (m, 5H), 5.52 (d, J = 1.2 Hz, 1H), 5.43 (d, J = 1.2 Hz, 1H), 3.92 (s, 3H), 1.99 (s, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 156.5, 146.7, 138.9, 128.2, 128.2, 127.9, 117.1, 62.0, 13.5; HRMS (ESI/[M+H]$^+$) calcd. for $C_{11}H_{14}NO^+$ 176.1070. found 176.1063.



(*E*)-3-Benzylbut-3-en-2-one *O*-methyl oxime (S7): Derived from 3-benzyl-3-buten-2-one (0.600 g, 3.75 mmol, 1.0 equiv),[4] $MeONH_2$•HCl (0.831 g, 10.1 mmol, 2.7 equiv) and NaOAc (1.38 g, 16.3 mmol, 4.4 equiv) in 30 mL of H_2O and 10 mL of EtOH. Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded the product **S7** (0.26 g, 38% yield) as a colorless oil. IR (film): 3027, 2936, 1495, 1453, 1126, 1048 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38–7.11 (m, 5H), 5.47–5.44 (s, 1H), 5.14–5.12 (s, 1H), 3.93 (s, 3H), 3.71 (s, 2H), 1.99 (s, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 158.3, 145.3, 140.4, 129.5, 128.2, 126.0, 117.4, 62.0, 38.4, 11.0; HRMS (ESI/[M+H]$^+$) calcd. for $C_{12}H_{16}NO^+$ 190.1226. found 190.1222.

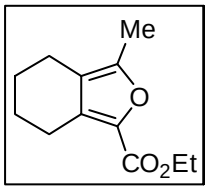
Purification of Ethyl Glyoxylate

Commercially available ethyl glyoxylate (50% solution in toluene, Aldrich) was purified by flash column chromatography on silica gel (ethyl acetate/ hexanes 20:1 to 1:1) and distilled (120 °C, 760 mm). The freshly distilled ethyl glyoxylate was transferred

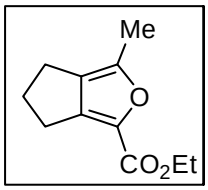
immediately to the glove box and stored at -25 °C under inert atmosphere (N_2). It was warmed to ambient temperature prior to its use.

III. Rh(III)-catalyzed Furan Synthesis by Addition to Ethyl Glyoxylate

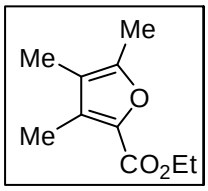
General procedure: In a N_2-filled glovebox, $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 0.025 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), the indicated *O*-methyl oxime (0.200 mmol, 1.0 equiv) and ethyl glyoxylate (40.8 mg, 0.400 mmol, 2.0 equiv) were added to a screw-capped conical vial with a stir bar followed by addition of DCE (0.66 mL, [*O*-methyl oxime] = 0.30 M). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath at 75 °C. After 16 h of stirring, the vial was removed from the oil bath and was cooled to ambient temperature. The mixture was filtered through a pad of celite and the solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.



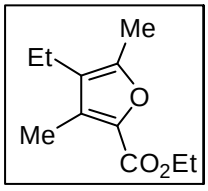
Ethyl 3-methyl-4,5,6,7-tetrahydroisobenzofuran-1-carboxylate (3a): Derived from (*E*)-1-(cyclohex-1-en-1-yl)ethanone *O*-methyl oxime (**1a**) (30.6 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3a** (35.0 mg, 84% yield) as a white powder (mp: 57 °C). IR (film): 2931, 1708, 1171 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.32 (q, *J* = 7.1 Hz, 2H), 2.82-2.70 (m, 2H), 2.45-2.32 (m, 2H), 2.24 (s, 3H), 1.73-1.62 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.8, 150.8, 136.9, 133.9, 119.4, 60.2, 22.9, 22.7, 22.6, 20.3, 14.7, 12.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{12}H_{17}O_3$: 209.1172. Found: 209.1166.



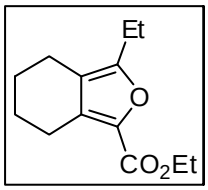
Ethyl 3-methyl-5,6-dihydro-4H-cyclopenta[c]furan-1-carboxylate (3b): Derived from (*E*)-1-(cyclopent-1-en-1-yl)ethanone *O*-methyl oxime (**S1**) (27.8 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3b** (29.2 mg, 70% yield) as a white powder (mp: 78 °C). IR (film): 2979, 2955, 1715, 1582, 1410, 1321, 1303, 1114 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.31 (q, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.57–2.50 (m, 2H), 2.40–2.31 (m, 2H), 2.27 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 159.4, 146.9, 144.5, 133.7, 130.8, 60.4, 31.8, 25.8, 23.3, 14.6, 13.3; HRMS (ESI/$[M+H]^+$) calcd. for $C_{11}H_{15}O_3$: 195.1016. Found: 195.1009.



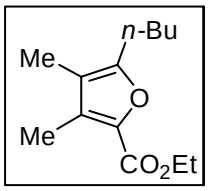
Ethyl 3,4,5-trimethylfuran-2-carboxylate (3c): Derived from (*2E*,*3E*)-3-methylpent-3-en-2-one *O*-methyl oxime (**S2**) (25.4 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3c** (32.4 mg, 89% yield) as a colorless oil. IR (film): 2980, 2924, 1697, 1562, 1311, 1187, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.35 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 2.24 (s, 3H), 1.89 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 160.0, 151.5, 138.0, 132.6, 118.1, 60.3, 14.6, 12.2, 10.1, 8.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{12}H_{17}O_3$: 209.1172. Found: 209.1166.



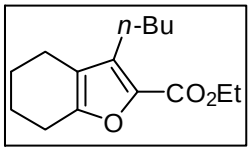
Ethyl 4-ethyl-3,5-dimethylfuran-2-carboxylate (3d): Derived from (*2E*,*3E*)-3-ethylpent-3-en-2-one *O*-methyl oxime (**S3**) (28.2 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3d** (26.7 mg, 68% yield) as a colorless oil. IR (film): 2967, 1699, 1559, 1423, 1304, 1160, 1076 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.33 (q, *J* = 7.1 Hz, 2H), 2.32 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 2.25 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 159.9, 151.3, 138.0, 132.0, 124.4, 60.3, 16.6, 14.7, 14.6, 12.1, 9.9; HRMS (ESI/$[M+H]^+$) calcd. for $C_{11}H_{17}O_3$: 197.1172. Found: 197.1170.



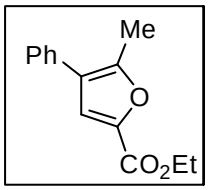
Ethyl 3-ethyl-4,5,6,7-tetrahydroisobenzofuran-1-carboxylate (3e): Derived from (*E*)-1-(cyclohex-1-en-1-yl)propan-1-one *O*-methyl oxime (**S4**) (33.4 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3e** (36.0 mg, 81% yield) as a colorless oil. IR (film): 2936, 2936, 1697, 1557, 1420, 1329, 1303, 1172, 1150, 1085 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.32 (q, *J* = 7.1 Hz, 2H), 2.81-2.75 (m, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.45–2.39 (m, 2H), 1.73–1.66 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.8, 155.8, 136.8, 133.8, 118.5, 60.2, 22.9, 22.7, 22.6, 20.3, 20.3, 14.7, 12.4; HRMS (ESI/$[M+H]^+$) calcd. for $C_{13}H_{19}O_3$: 223.1329. Found: 223.1230.



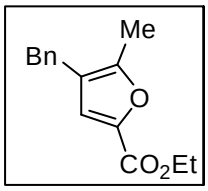
Ethyl 5-butyl-3,4-dimethylfuran-2-carboxylate (3f): Derived from (*2E,4E*)-3-methyloct-2-en-4-one *O*-methyl oxime (**S5**) (33.9 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3f** (37.4 mg, 83% yield) as a colorless oil. IR (film): 2957, 2930, 2872, 1699, 1559, 1420, 1313, 1209, 1163, 1070 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.37–4.29 (q, *J* = 7.4 Hz, 2H), 2.59 (apparent t, *J* = 7.6 Hz, 2H), 2.22 (s, 3H), 1.88 (s, 3H), 1.65–1.54 (m, 2H), 1.40–1.22 (m, 5H), 0.90 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.1, 155.6, 138.0, 132.3, 117.8, 60.3, 30.5, 26.3, 22.5, 14.6, 13.9, 10.1, 8.1; HRMS (ESI/$[M+H]^+$) calcd. for $C_{13}H_{21}O_3$: 225.1491. Found: 225.1465.



Ethyl 3-butyl-4,5,6,7-tetrahydrobenzofuran-2-carboxylate (3g): Derived from (*1E,2E*)-2-pentylidenecyclohexanone *O*-methyl oxime (**S6**) (39.1 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3g** (29.0 mg, 58% yield) as a colorless oil. IR (film): 2931, 1699, 1553, 1304, 1176, 1144, 1084 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.34 (q, *J* = 7.2 Hz, 2H), 2.70–2.66 (m, 2H), 2.64–2.59 (m, 2H), 2.38–2.33 (m, 2H), 1.86–1.79 (m, 2H), 1.76–1.70 (m, 2H), 1.53–1.45 (m, 2H), 1.39–1.31 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.0, 154.8, 138.1, 136.1, 120.5, 60.3, 31.9, 24.3, 23.6, 22.8, 22.8, 22.7, 20.7, 14.6, 14.1; HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{23}O_3$: 251.1642. Found: 251.1632.



Ethyl 5-methyl-4-phenylfuran-2-carboxylate (3h): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3h** (39.2 mg, 85% yield) as a white powder (mp: 56 °C). IR (film): 1616, 1319, 1160, 1110, 1065, 837 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.45–7.36 (m, 4H), 7.34–7.28 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.52 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.0, 152.7, 142.6, 132.8, 128.9, 127.7, 127.2, 123.8, 119.3, 61.0, 14.6, 13.6; HRMS (ESI/$[M+H]^+$) calcd. for $C_{14}H_{15}O_3$: 231.1016. Found: 231.1012.

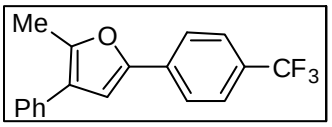


Ethyl 4-benzyl-5-methylfuran-2-carboxylate (3i): Derived from (*E*)-3-benzylbut-3-en-2-one *O*-methyl oxime (**S7**) (37.9 mg). Purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent afforded product **3i** (37.4 mg, 77% yield) as a colorless oil. IR (film): 2980, 1708, 1536, 1303, 1204, 1172, 1093 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.39–7.03 (m, 5H), 6.92 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 2H), 2.32 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.0, 153.2, 142.4, 139.9, 128.7, 128.4, 126.5, 121.1, 120.6, 60.8, 31.0, 14.5, 12.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{17}O_3$: 245.1172. Found: 245.1163.

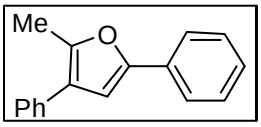
IV. Rh(III)-catalyzed Furan Synthesis by Addition to Aromatic and Aliphatic Aldehydes

General procedure: In a N_2-filled glovebox, $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.05 equiv), $AgSbF_6$ (13.7 mg, 0.0400 mmol, 0.20 equiv), the *O*-methyl oxime (0.200 mmol, 1.0 equiv) and the corresponding aldehyde (0.400 mmol, 2.0 equiv) were added to a screw-capped conical vial with a stir bar followed by addition of THF (0.66 mL, [*O*-methyl oxime] = 0.30 M). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-

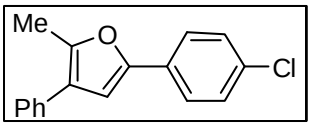
controlled oil bath at 90 °C. After 24 h of stirring, the vial was removed from the oil bath and was cooled to ambient temperature. The mixture was filtered through a pad of celite, and the solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.



2-Methyl-3-phenyl-5-(4-(trifluoromethyl)phenyl)furan (7a): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg) and 4-(trifluoromethyl)benzaldehyde (**5a**) (69.6 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product **7a** (45.9 mg, 76% yield) as a white powder (mp: 94-95 °C). IR (film): 2923, 1617, 1498, 1326, 1155, 1107, 1070, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.40–7.46 (m, 4H), 7.28-7.35 (m, 1H), 6.90 (s, 1H), 2.54 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 150.1, 148.8, 133.9, 133.6, 128.7, 128.5 (q, *J* = 30.2 Hz), 127.5, 126.7, 125.7 (q, *J* = 3.2 Hz), 124.2 (q, *J* = 272 Hz), 123.5, 123.3, 108.5, 13.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{18}H_{14}F_3O_3$: 303.0991. Found: 303.0964.

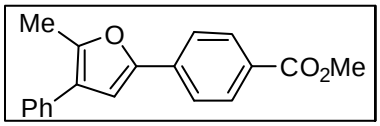


2-Methyl-3,5-diphenylfuran (7b): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg) and benzaldehyde (42.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product **7b** (24.4 mg, 52% yield) as a white powder (mp: 38-39 °C). IR (film): 1595, 1497, 1449, 1265, 1223, 1138, 1064, 989, 931 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.66-7.71 (m, 2H), 7.36-7.47 (m, 6H), 7.22-7.32 (m, 2H), 6.80 (s, 1H), 2.53 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 151.6, 147.6, 134.1, 130.8, 128.63, 128.59, 127.5, 127.0, 126.4, 123.4, 123.0, 106.4, 13.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{15}O$: 235.1117. Found: 235.1115.

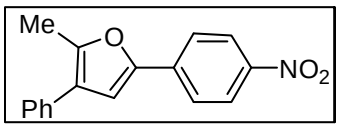


5-(4-Chlorophenyl)-2-methyl-3-phenylfuran (7c): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg) and 4-chlorobenzaldehyde (56.3 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent

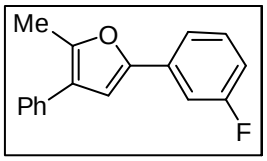
afforded product **7c** (34.9 mg, 65% yield) as a white powder (mp: 97-98 °C). IR (film): 1575, 1551, 1483, 1140, 1091, 1064, 930, 832 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.61 (d, J = 8.6 Hz, 2H), 7.40-7.49 (m, 4H), 7.36 (d, J = 8.6 Hz, 2H), 7.27-7.33 (m, 1H), 6.78 (s, 1H), 2.52 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.6, 147.9, 133.8, 132.6, 129.3, 128.8, 128.6, 127.5, 126.6, 124.6, 123.2, 106.9, 13.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{14}ClO$: 269.0728. Found: 269.0612.



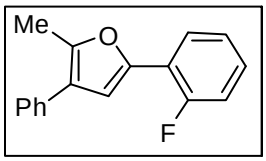
Methyl 4-(5-methyl-4-phenylfuran-2-yl)benzoate (7d): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg) and methyl 4-formylbenzoate (65.7 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (30:1) as eluent afforded product **7d** (44.4 mg, 76% yield) as a white powder (mp: 104-105 °C). IR (film): 2950, 2921, 1711, 1608, 1434, 1271, 1175, 1101, 963, 855 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.03-8.07 (m, 2H), 7.71-7.75 (m, 2H), 7.40-7.45 (m, 4H), 7.28-7.34 (m, 1H), 6.92 (s, 1H), 3.93 (s, 3H), 2.54 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.8, 150.6, 148.9, 134.7, 133.6, 130.1, 128.7, 128.1, 127.5, 126.7, 123.6, 122.9, 108.8, 52.0, 13.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{19}H_{17}O_3$: 293.1172. Found: 293.1175.



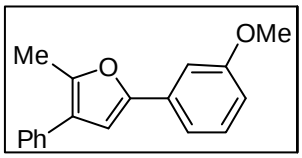
2-Methyl-5-(4-nitrophenyl)-3-phenylfuran (7e): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg) and 4-nitrobenzaldehyde (60.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (30:1) as eluent afforded product **7e** (45.8 mg, 82% yield) as a yellow powder (mp: 125-127 °C). IR (film): 2922, 1589, 1507, 1334, 1108, 850 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.22-8.26 (m, 2H), 7.76-7.79 (m, 2H), 7.42-7.47 (m, 4H), 7.31-7.36 (m, 1H), 7.00 (s, 1H), 2.55 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.2, 149.4, 146.0, 136.3, 133.1, 128.7, 127.5, 126.9, 124.3, 124.1, 123.3, 110.5, 13.3; HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{14}NO_3$: 2280.0968. Found: 280.0966.



5-(3-Fluorophenyl)-2-methyl-3-phenylfuran (7f): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg) and 3-fluorobenzaldehyde (49.7 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product **7f** (32.3 mg, 64% yield) as a white powder (mp: 46-47 °C). IR (film): 1612, 1587, 1558, 1497, 1446, 1267, 1183, 1136, 972, 867, 852 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.28-7.48 (m, 8H), 6.94 (tdd, *J* = 8.5, 2.6, 0.9 Hz, 1H), 6.82 (s, 1H), 2.53 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 163.18 (d, *J* = 244.9 Hz), 150.4 (d, *J* = 3.1 Hz), 148.1, 133.8, 132.9 (d, *J* = 8.5 Hz), 130.2 (d, *J* = 8.5 Hz), 128.6, 127.5, 126.6, 123.2, 119.0 (d, *J* = 2.8 Hz), 113.7 (d, *J* = 21.4 Hz), 110.2 (d, *J* = 23.5 Hz), 107.5, 13.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{14}FO$: 253.1023. Found: 253.1019.

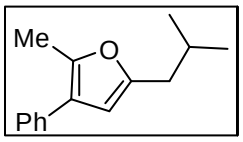


5-(2-Fluorophenyl)-2-methyl-3-phenylfuran (7g): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg) and 2-fluorobenzaldehyde (49.7 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product **7g** (33.8 mg, 67% yield) as a white powder (mp: 43-44 °C). IR (film): 1583, 1488, 1450, 1213, 1140, 1060, 964, 933, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.83-7.90 (m, 1H), 7.41-7.50 (m, 4H), 7.28-7.34 (m, 1H), 7.18-7.24 (m, 2H), 7.10-7.17 (m, 1H), 7.02 (d, *J* = 3.7 Hz, 1H), 2.56 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 158.4 (d, *J* = 250.2 Hz), 147.5, 145.7 (d, *J* = 2.9 Hz), 133.9, 128.6, 127.8 (d, *J* = 8.2 Hz), 127.5, 126.5, 125.6 (d, *J* = 3.3 Hz), 124.2 (d, *J* = 3.5 Hz), 123.3 (d, *J* = 1.4 Hz), 119.1 (d, *J* = 12.1 Hz), 115.8 (d, *J* = 21.5 Hz), 111.7 (d, *J* = 11.7 Hz), 13.1; HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{14}FO$: 253.1023. Found: 253.1012.

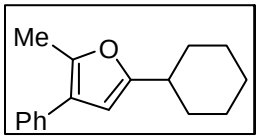


5-(3-Methoxyphenyl)-2-methyl-3-phenylfuran (7h): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg), $[Cp^*RhCl_2]_2$ (12.4 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (27.4 mg, 0.0800 mmol, 0.40 equiv) and 3-methoxybenzaldehyde (54.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (50:1) as eluent afforded product **7h** (36.5 mg, 69% yield) as a colorless oil. IR (film):

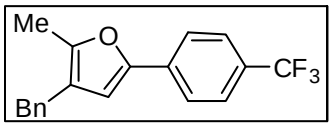
1596, 1556, 1489, 1432, 1285, 1242, 1207, 1136, 1043, 970, 907, 839 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.33-7.40 (m, 4H), 7.21-7.26 (m, 3H), 7.18 (s, 1H), 6.73-6.77 (m, 1H), 6.74 (s, 1H), 3.81 (s, 3H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.9, 151.4, 147.6, 134.0, 132.1, 129.7, 128.6, 127.5, 126.4, 123.0, 116.0, 112.8, 108.7, 106.8, 55.3, 13.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{18}H_{17}O_2$: 265.1223. Found: 265.1222.



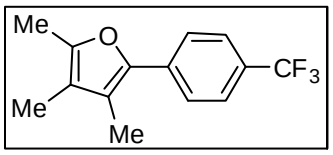
5-Isobutyl-2-methyl-3-phenylfuran (7i): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg), $[Cp^*RhCl_2]_2$ (12.4 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (27.4 mg, 0.0800 mmol, 0.40 equiv) and isobutyraldehyde (34.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product (**7i**) (22.3 mg, 52% yield) as a colorless oil. IR (film): 3031, 2955, 2925, 1603, 1577, 1496, 1466, 1222, 983, 950 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.25-7.32 (m, 4H), 7.12-7.18 (m, 1H), 6.04 (s, 1H), 2.39 (d, *J* = 7.0 Hz, 2H), 2.33 (s, 3H), 1.82-1.94 (m, 1H), 0.88 (d, *J* = 6.7 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.3, 145.7, 134.6, 128.5, 127.3, 126.0, 121.1, 107.1, 37.2, 27.9, 22.4, 13.1; HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{19}O$: 215.1430. Found: 215.1429.



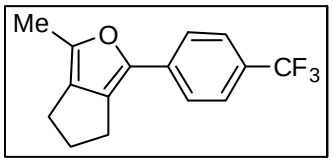
5-Cyclohexyl-2-methyl-3-phenylfuran (7j): Derived from (*E*)-3-phenylbut-3-en-2-one *O*-methyl oxime (**1b**) (35.0 mg), $[Cp^*RhCl_2]_2$ (12.4 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (27.4 mg, 0.0800 mmol, 0.40 equiv) and cyclohexanecarbaldehyde (48.9 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product **7j** (19.7 mg, 41% yield) as a colorless oil. IR (film): 2925, 2853, 1602, 1574, 1497, 1447, 1218, 1133, 949 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.35-7.40 (m, 4H), 7.21-7.26 (m, 1H), 6.09 (s, 1H), 2.55-2.65 (m, 1H), 2.42 (s, 3H), 2.01-2.09 (m, 2H), 1.78-1.84 (m, 2H), 1.69-1.75 (m, 1H), 1.33-1.44 (m, 4H), 1.22-1.30 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.8, 145.4, 134.7, 128.4, 127.3, 126.0, 121.0, 104.1, 37.2, 31.6, 26.0, 13.0; HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{21}O$: 241.1592. Found: 241.1542.



3-Benzyl-2-methyl-5-(4-(trifluoromethyl)phenyl)furan (7k): Derived from (*E*)-3-benzylbut-3-en-2-one *O*-methyl oxime (**S7**) (37.9 mg) and 4-(trifluoromethyl)benzaldehyde (**5a**) (69.6 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product **7k** (44.9 mg, 71% yield) as a white powder (mp: 39-40 °C). IR (film): 1613, 1320, 1162, 1108, 1067, 1014, 932, 908 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.30-7.35 (m, 2H), 7.21-7.26 (m, 3H), 6.54 (s, 1H), 3.76 (s, 2H), 2.37 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 149.9, 149.0, 140.4, 134.1, 128.5, 128.4, 128.2 (q, *J* = 30.5 Hz), 126.2, 125.6 (q, *J* = 3.9 Hz), 124.3 (q, *J* = 271.7 Hz), 123.1, 120.6, 109.6, 31.1, 11.8; HRMS (ESI/$[M+H]^+$) calcd. for $C_{19}H_{16}F_3O$: 317.1148. Found: 317.1149.



2,3,4-Trimethyl-5-(4-(trifluoromethyl)phenyl)furan (7l): Derived from (*2E,3E*)-3-methylpent-3-en-2-one *O*-methyl oxime (**S2**) (25.4 mg) and 4-(trifluoromethyl)benzaldehyde (**5a**) (69.6 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product **7l** (30.0 mg, 59% yield) as a colorless oil. IR (film): 2923, 1616, 1320, 1161, 1106, 1067, 1011, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 2.28 (s, 3H), 2.19 (s, 3H), 1.92 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 147.3, 144.7, 135.4, 127.4 (q, *J* = 32.6 Hz), 125.4 (q, *J* = 3.9 Hz), 124.6, 124.4 (q, *J* = 272.1 Hz), 119.8, 117.5, 11.7, 10.2, 8.3; HRMS (ESI/$[M+H]^+$) calcd. for $C_{14}H_{14}F_3O$: 255.0991. Found: 255.0990.

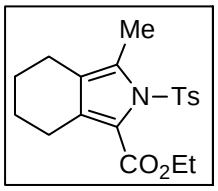


1-Methyl-3-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4H-cyclopenta[c]furan (7m): Derived from (*E*)-1-(cyclopent-1-en-1-yl)ethanone *O*-methyl oxime (**S1**) (27.8 mg) and 4-(trifluoromethyl)benzaldehyde (**5a**) (69.6 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using pure hexane as eluent afforded product **7m** (28.2 mg, 53% yield) as a white powder (mp: 44-46 °C). IR (film): 2926, 1611, 1329, 1162, 1117, 1062, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.54-7.62 (m, 4H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 7.1 Hz, 2H), 2.42 (p, *J* = 7.1 Hz, 2H), 2.29 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ

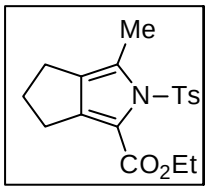
142.4, 140.4, 135.0, 132.6, 130.6, 127.0 (q, J = 32.2 Hz), 125.5 (q, J = 3.9 Hz), 124.4 (q, J = 272.1 Hz), 122.9, 32.1, 25.6, 22.9, 12.8; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{14}F_3O$: 267.0991. Found: 267.0990.

V. Rh(III)-catalyzed Pyrrole Synthesis

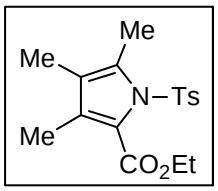
General procedure: In a N_2-filled glovebox, $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 0.025 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), the *O*-methyl oxime (0.20 mmol, 1.0 equiv) and (*E*)-ethyl 2-(tosylimino)acetate[8] (102.2 mg, 0.400 mmol, 2.0 equiv) were added to a screw-capped conical vial with a stir bar followed by addition of DCE (0.66 mL, [*O*-methyl oxime] = 0.30 M). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath at 90 °C. After 16 h of stirring, the vial was removed from the oil bath and was cooled to ambient temperature. The mixture was filtered through a pad of celite, and the solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.



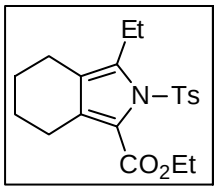
Ethyl 3-methyl-2-tosyl-4,5,6,7-tetrahydro-2H-isoindole-1-carboxylate (9a): Derived from (*E*)-1-(cyclohex-1-en-1-yl)ethanone *O*-methyl oxime (**1a**) (30.6 mg). Purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent afforded product **9a** (44.8 mg, 62% yield) as a white powder (mp: 75-77 °C). IR (film): 2926, 1717, 1364, 1332, 1168, 1127, 1084, 1004, 811 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.91 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 2.60-2.66 (m, 2H), 2.42 (s, 3H), 2.28-2.35 (m, 2H), 2.27 (s, 3H), 1.60-1.70 (m, 4H), 1.31 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.5, 144.3, 137.0, 133.0, 132.3, 129.5, 127.2, 122.4, 122.2, 60.8, 22.9, 22.8, 21.6, 21.4, 14.2, 12.4; HRMS (ESI/[M+H]+) calcd. for $C_{19}H_{24}NO_4S$: 362.1421. Found: 362.1418.



Ethyl 3-methyl-2-tosyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrole-1-carboxylate (9b): Derived from (*E*)-1-(cyclopent-1-en-1-yl)ethanone *O*-methyl oxime (**S1**) (27.8 mg). Purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent afforded product **9b** (41.7 mg, 60% yield) as a white powder (mp: 103-105 °C). IR (film): 1715, 1363, 1332, 1248, 1168, 1127, 1085, 1005, 906, 809 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.49 (td, *J* = 7.2, 0.9 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H), 2.20 -2.27 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.4, 145.0, 144.2, 137.3, 133.3, 130.4, 129.5, 127.4, 118.9, 60.5, 29.7, 27.0, 24.2, 21.6, 14.4, 14.3; HRMS (ESI/$[M+H]^+$) calcd. for $C_{18}H_{22}NO_4S$: 348.1264. Found: 348.1258.

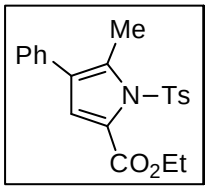


Ethyl 3,4,5-trimethyl-1-tosyl-1H-pyrrole-2-carboxylate (9c): Derived from (*2E*,*3E*)-3-methylpent-3-en-2-one *O*-methyl oxime (**S2**) (25.4 mg). Purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent afforded product **9c** (41.6 mg, 62% yield) as a colorless oil. IR (film): 2926, 1710, 1362, 1334, 1253, 1172, 1119, 1088, 1072, 813 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 2.23 (s, 3H), 2.05 (s, 3H), 1.79 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.5, 144.5, 136.4, 131.7, 130.3, 129.6, 127.0, 124.0, 121.7, 61.2, 21.6, 14.1, 12.2, 10.2, 9.1; HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{22}NO_4S$: 336.1264. Found: 336.1256.

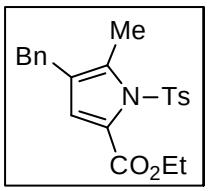


Ethyl 3-ethyl-2-tosyl-4,5,6,7-tetrahydro-2H-isoindole-1-carboxylate (9d): Derived from (*E*)-1-(cyclohex-1-en-1-yl)ethanone *O*-methyl oxime (**S4**) (30.6 mg). Purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent afforded product **9d** (49.6 mg, 66% yield) as a white powder (mp: 54-55 °C). IR (film): 2936, 1709, 1364, 1312, 1231, 1172, 1104, 1085, 1060, 909 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.72 (q, *J* = 7.4 Hz, 2H), 2.61-2.66 (m, 2H), 2.41 (s, 3H), 2.31-2.37 (m, 2H), 1.61-1.69 (m, 4H), 1.30 (t, *J* = 7.1 Hz,

3H), 1.05 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 161.7, 144.2, 138.3, 137.2, 133.2, 129.5, 127.0, 122.5, 122.3, 60.8, 22.81, 22.77, 22.7, 21.6, 21.3, 19.6, 14.2, 14.0; HRMS (ESI/$[M+H]^+$) calcd. $C_{20}H_{26}NO_4S$: 376.1577. Found: 376.1570.



Ethyl 5-methyl-4-phenyl-1-tosyl-1H-pyrrole-2-carboxylate (9e): Derived from (*E*)-3-benzylbut-3-en-2-one *O*-methyl oxime (**1b**) (37.9 mg). Purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent afforded product **9e** (59.9 mg, 78% yield) as a white powder (mp: 65-67 °C). IR (film): 1722, 1491, 1367, 1338, 1254, 1176, 1138, 1089, 1057, 813 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.05 (d, J = 8.2 Hz, 2H), 7.33–7.41 (m, 4H), 7.26-7.32 (m, 3H), 6.91 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.51 (s, 3H), 2.44 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 160.8, 145.0, 136.5, 134.1, 133.8, 129.7, 128.7, 128.5, 127.8, 127.2, 127.1, 126.2, 121.0, 61.3, 21.7, 14.1, 13.5; HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{22}NO_4S$: 384.1264. Found: 384.1257.



Ethyl 4-benzyl-5-methyl-1-tosyl-1H-pyrrole-2-carboxylate (9f): Derived from (*E*)-3-benzylbut-3-en-2-one *O*-methyl oxime (**S7**) (37.9 mg). Purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent afforded product **9f** (51.7 mg, 65% yield) as a colorless oil. IR (film): 1720, 1495, 1367, 1173, 1119, 1088, 1043, 906 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.97 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.23–7.28 (m, 2H), 7.17-7.21 (m, 1H), 7.04-7.08 (m, 2H), 6.62 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.68 (s, 2H), 2.44 (s, 3H), 2.40 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 160.8, 144.8, 139.6, 136.6, 134.5, 129.6, 128.5, 128.3, 127.5, 127.2, 126.2, 123.5, 122.2, 61.1, 31.8, 21.6, 14.1, 12.6; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{24}NO_4S$: 398.1421. Found: 398.1414.

VI. References:

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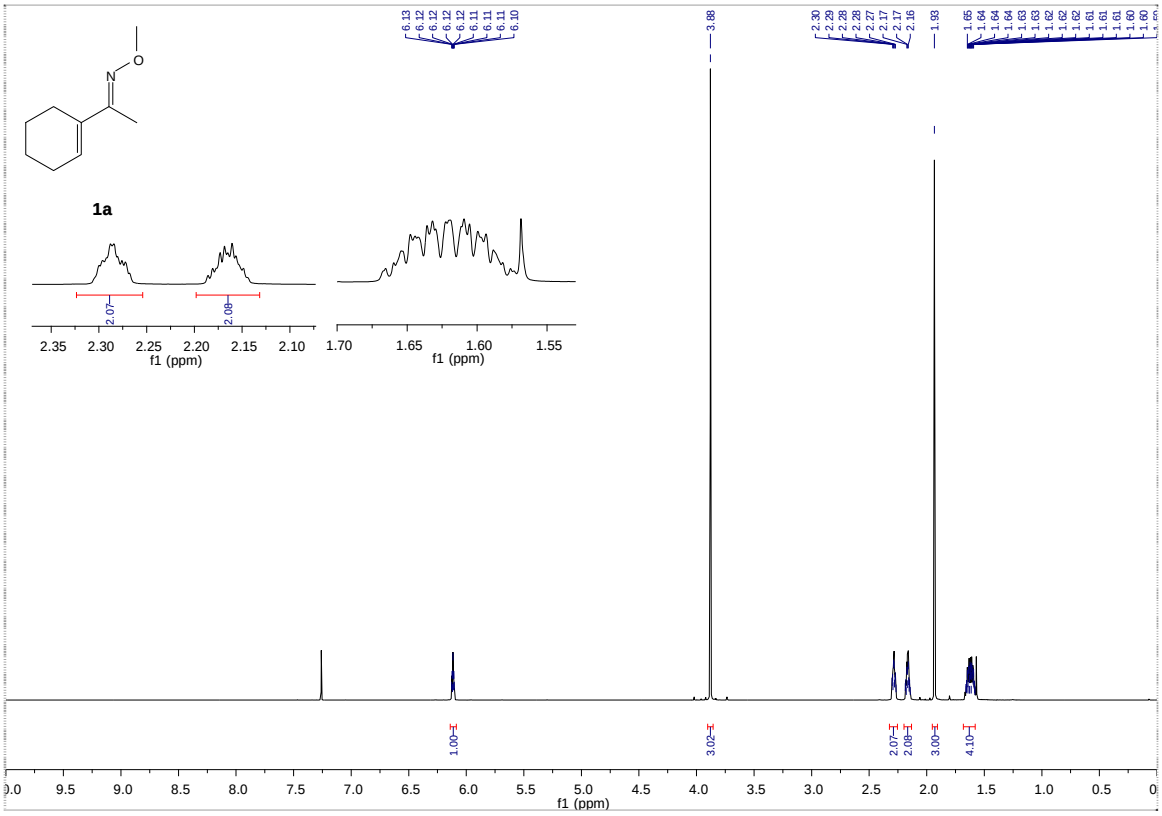
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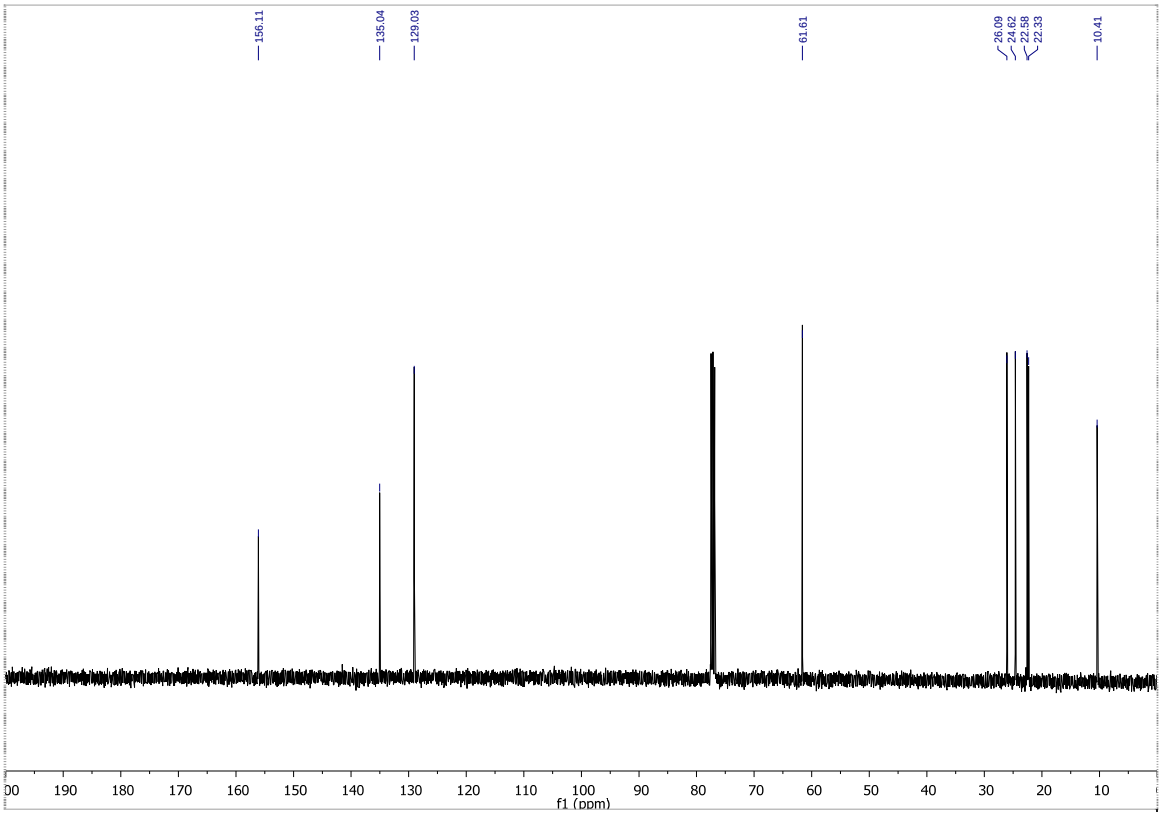
f1 (ppm)
f1 (ppm)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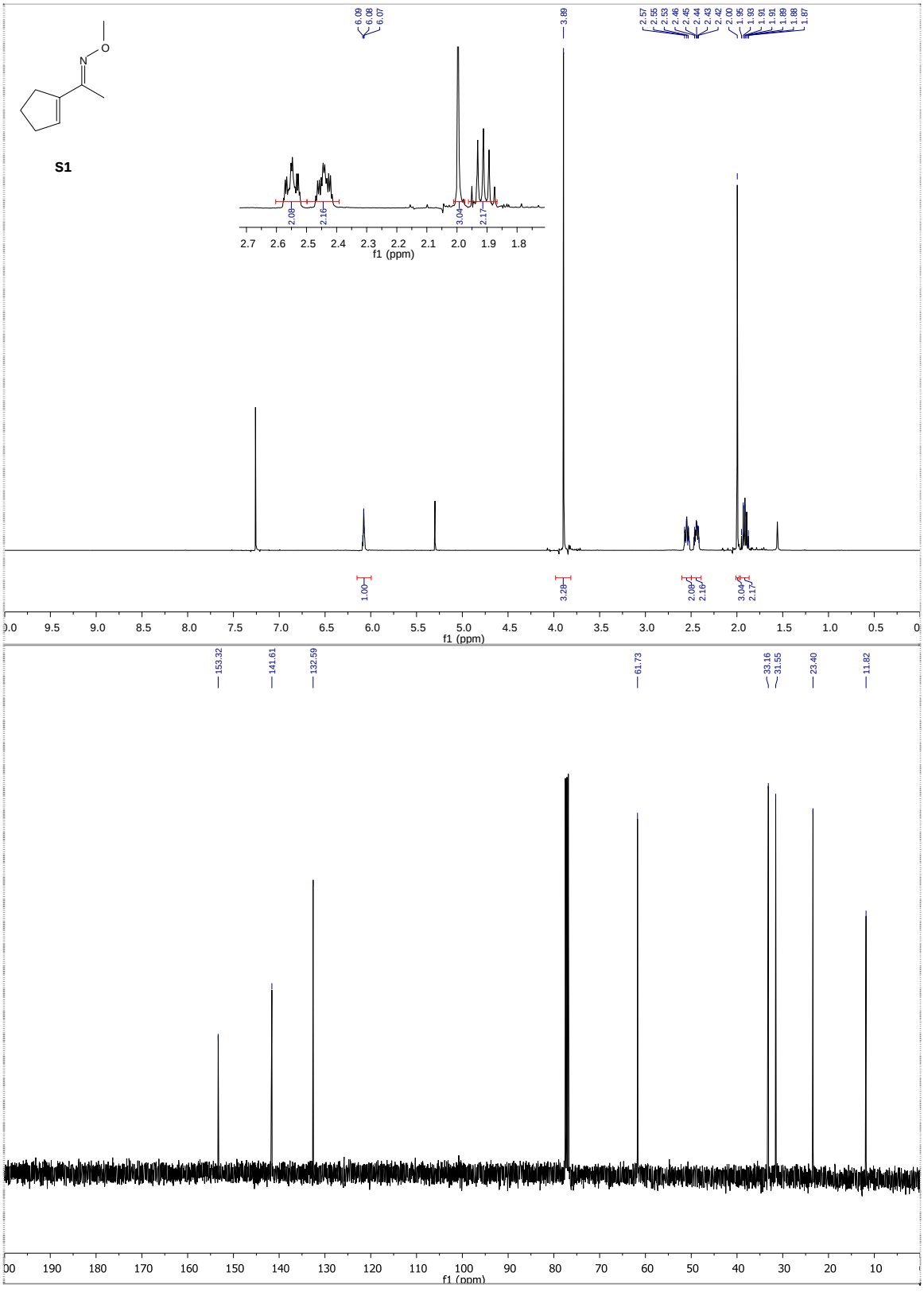
f1 (ppm)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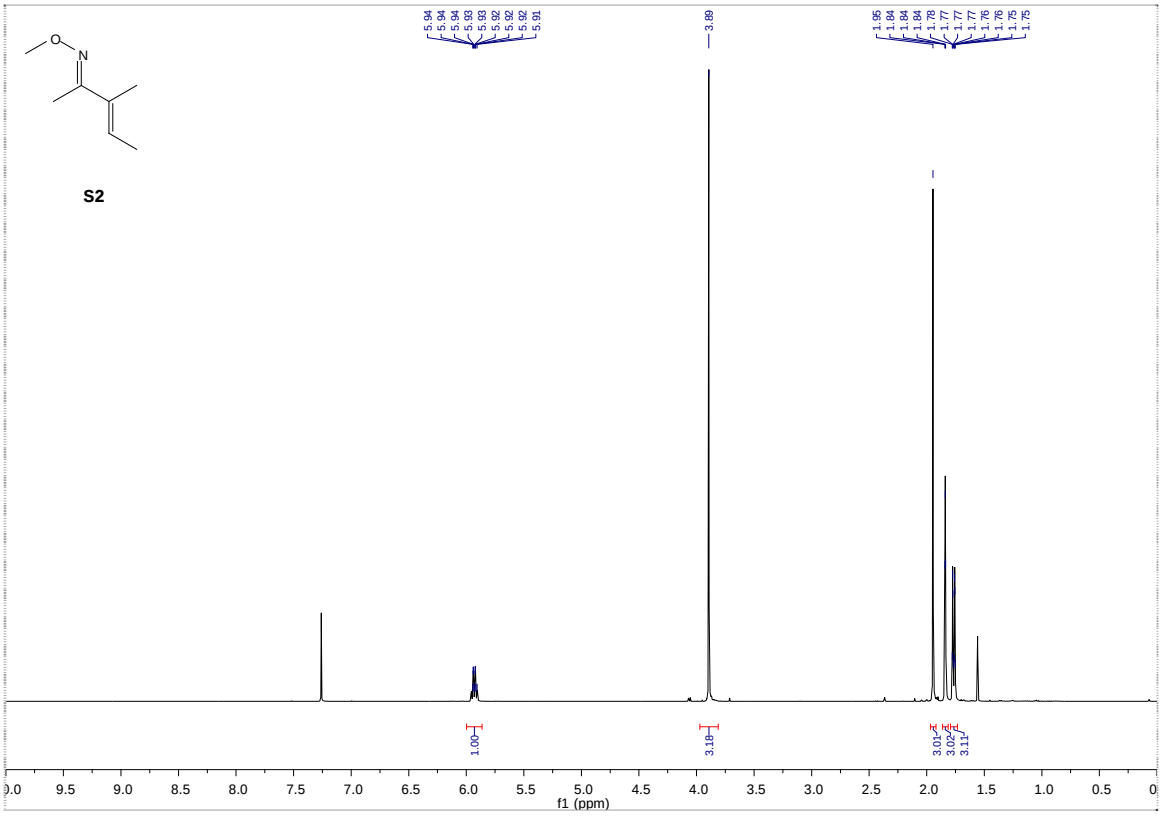
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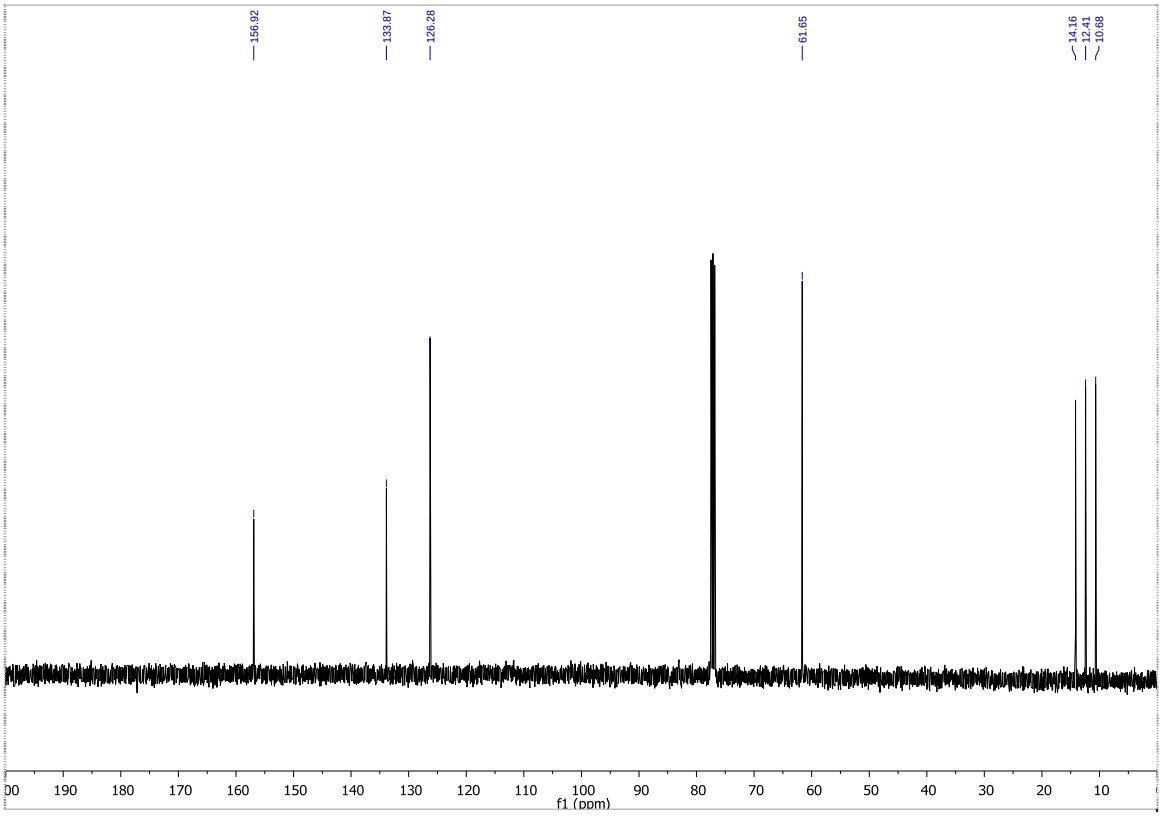
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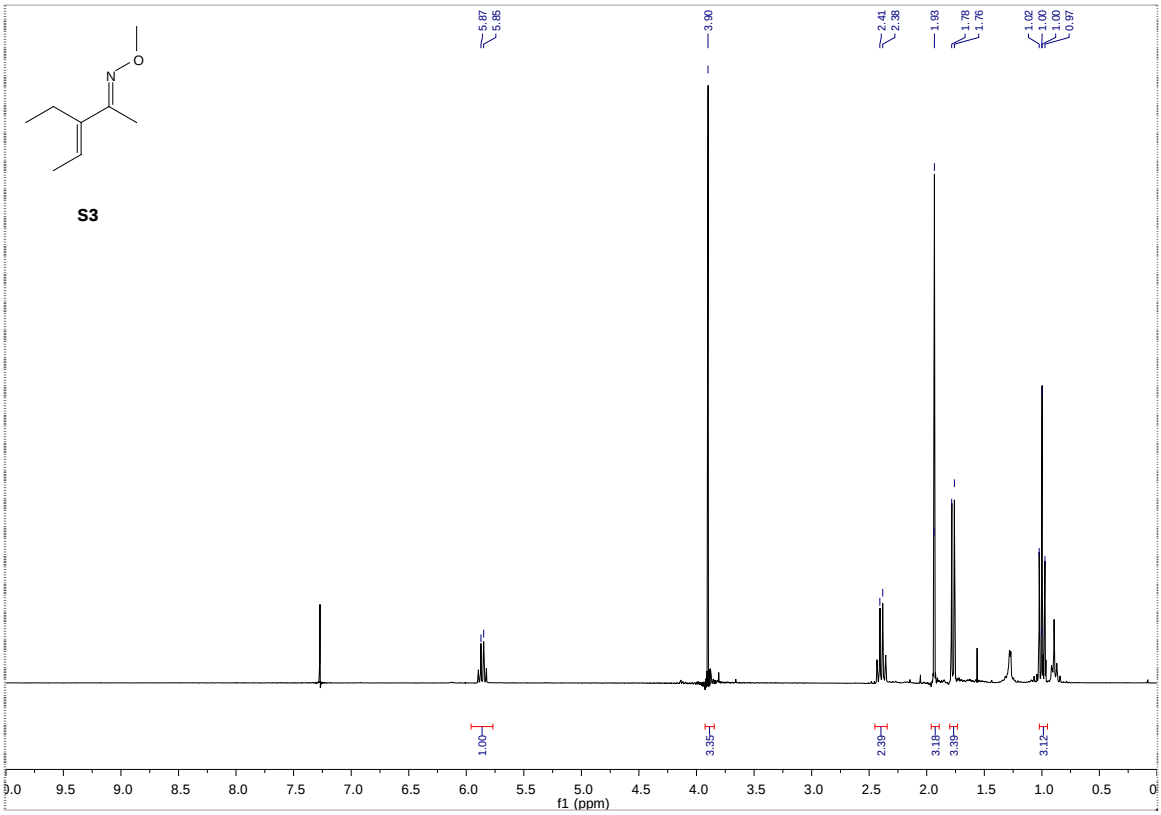
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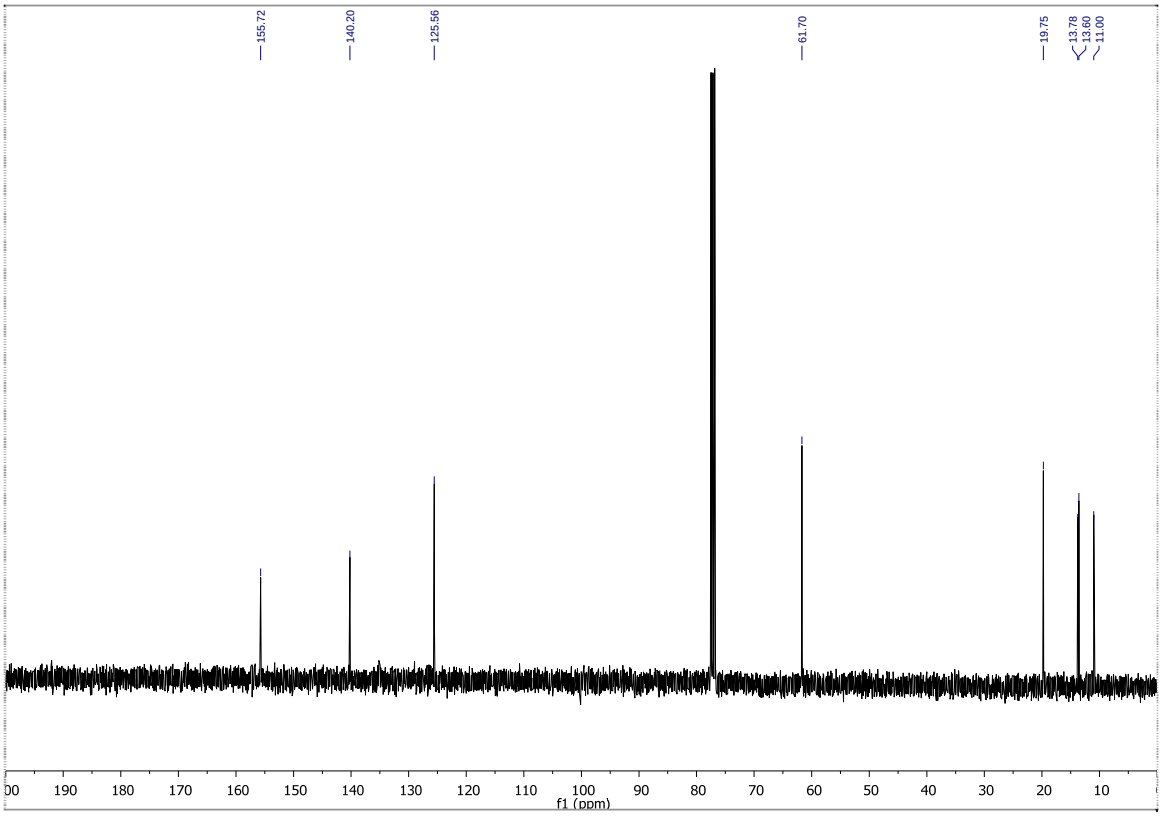
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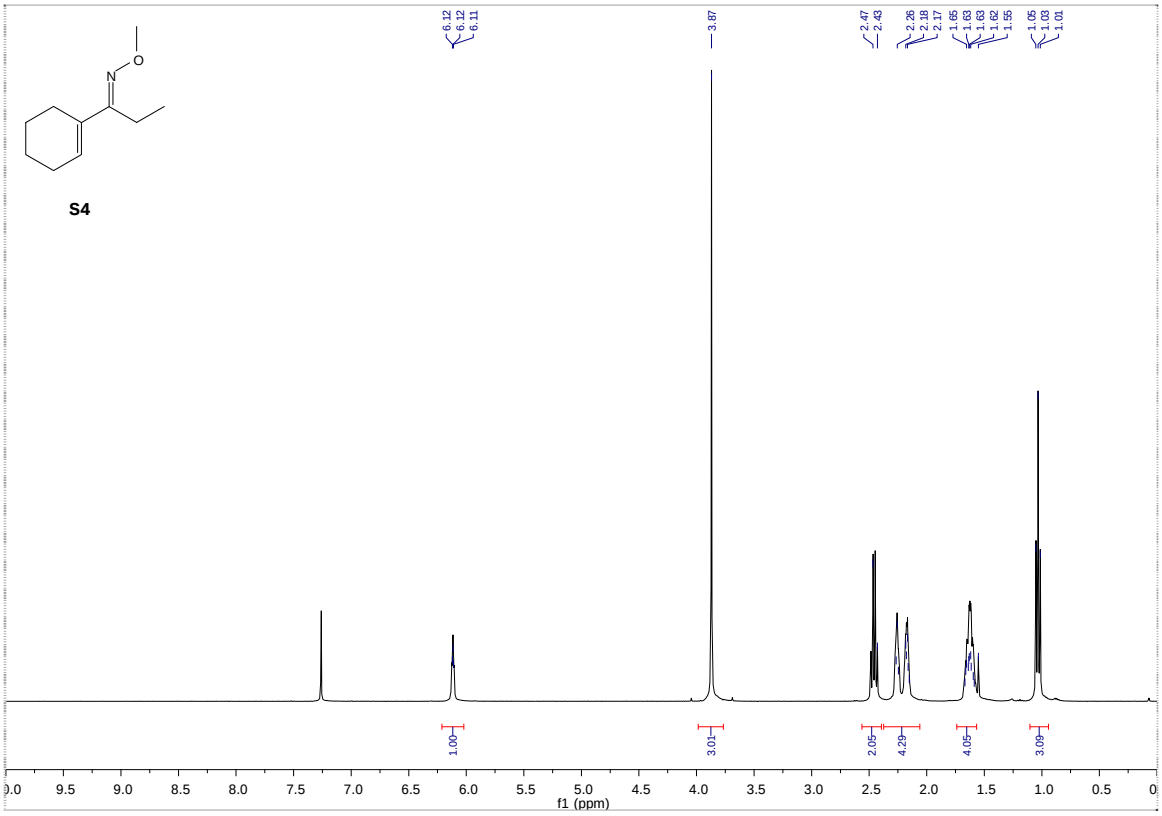
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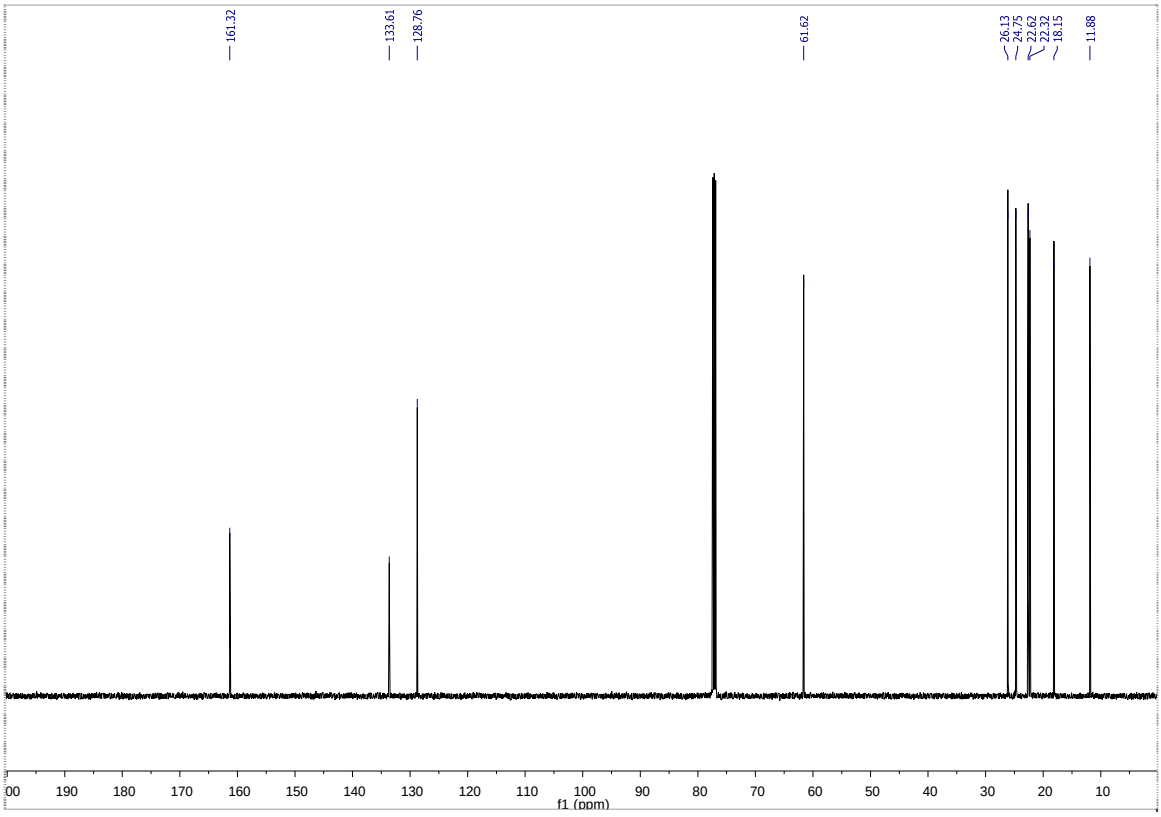
f1 (ppm)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22.32
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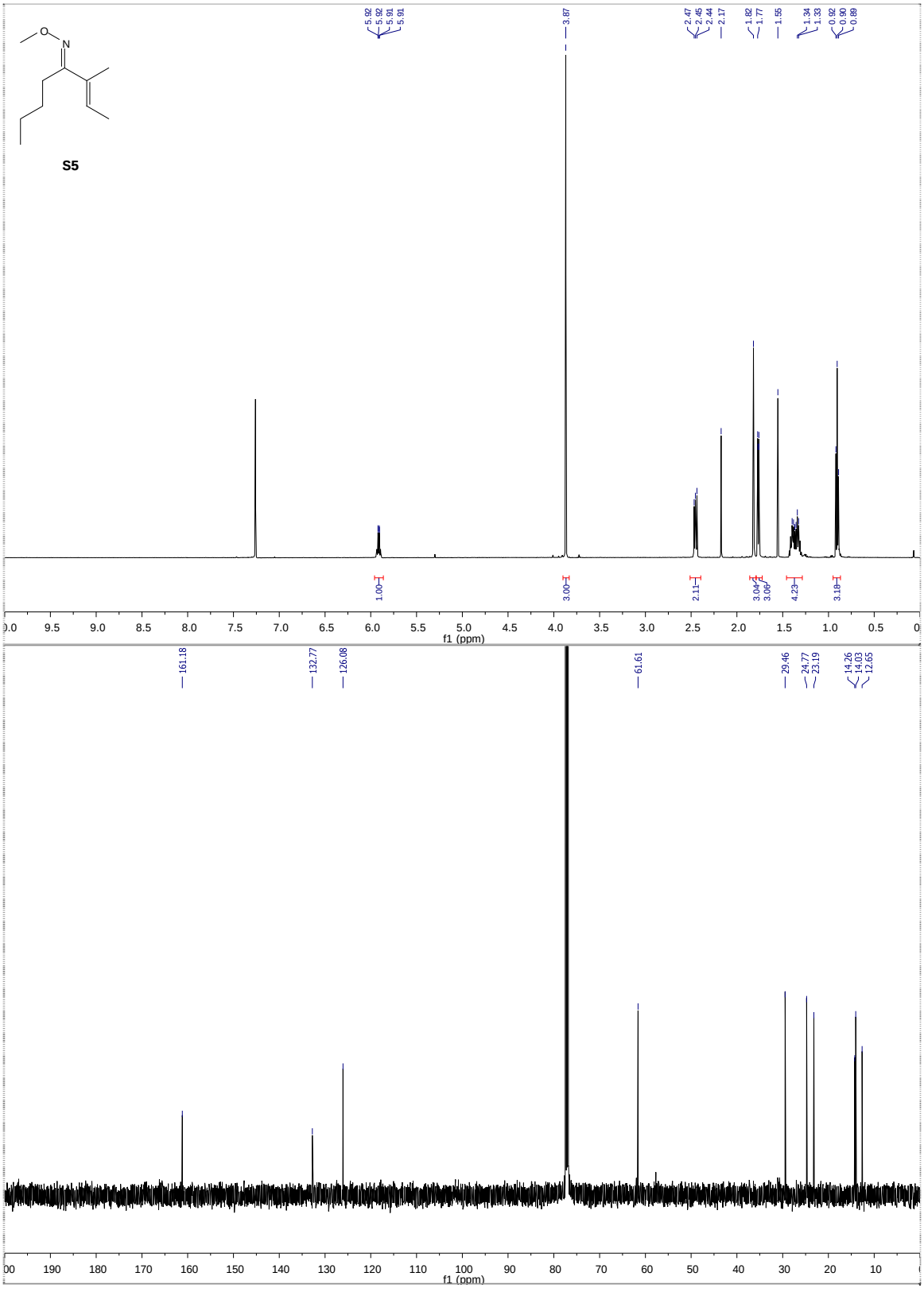
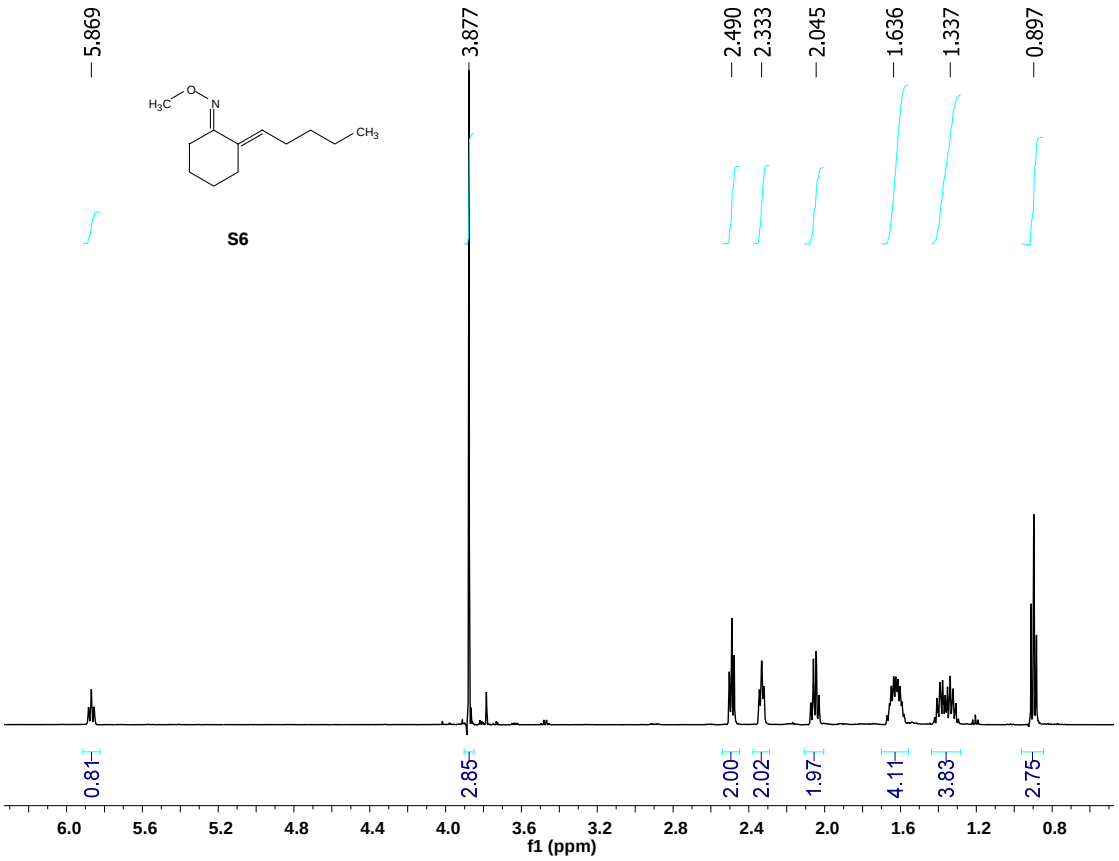
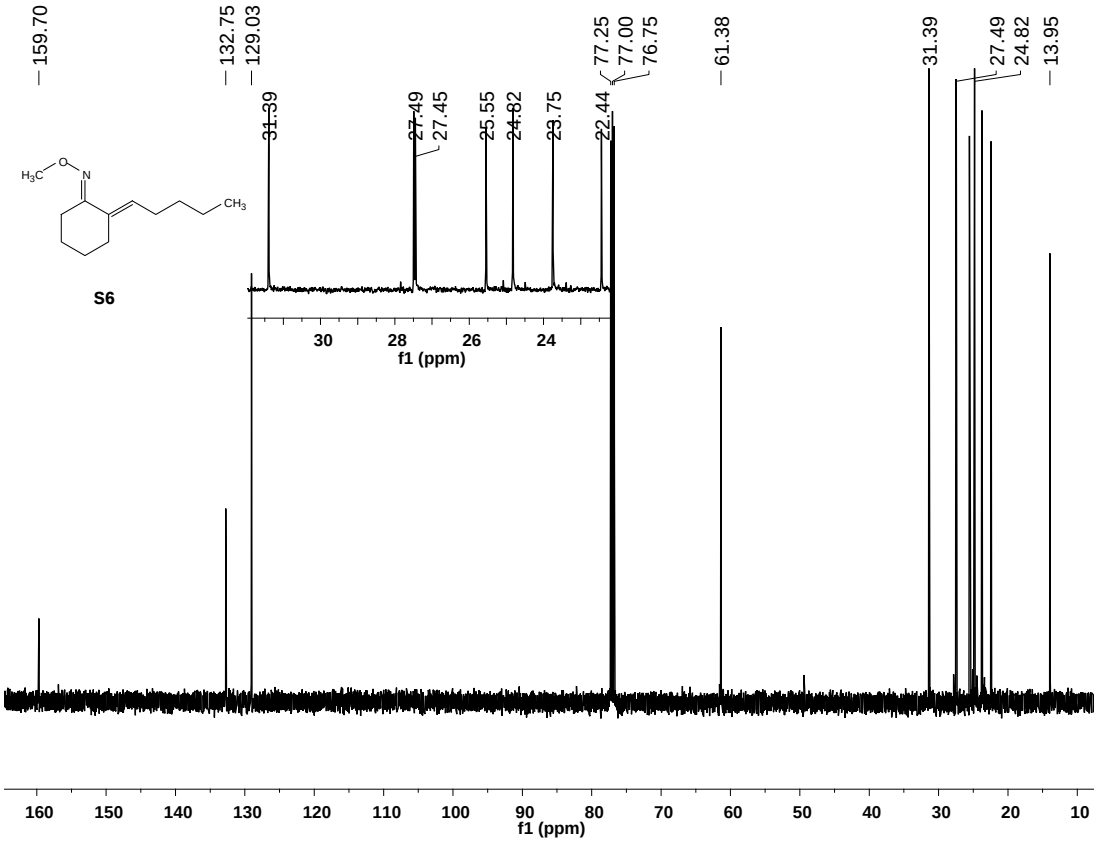
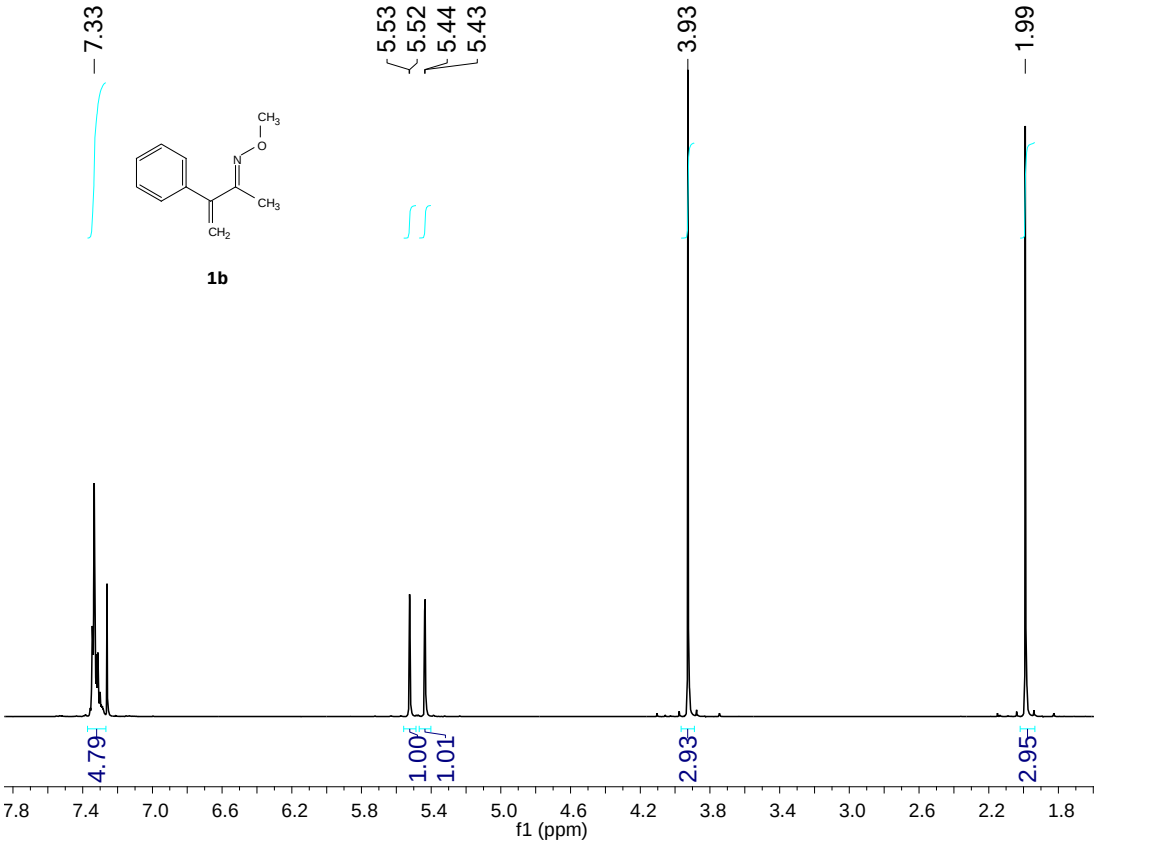
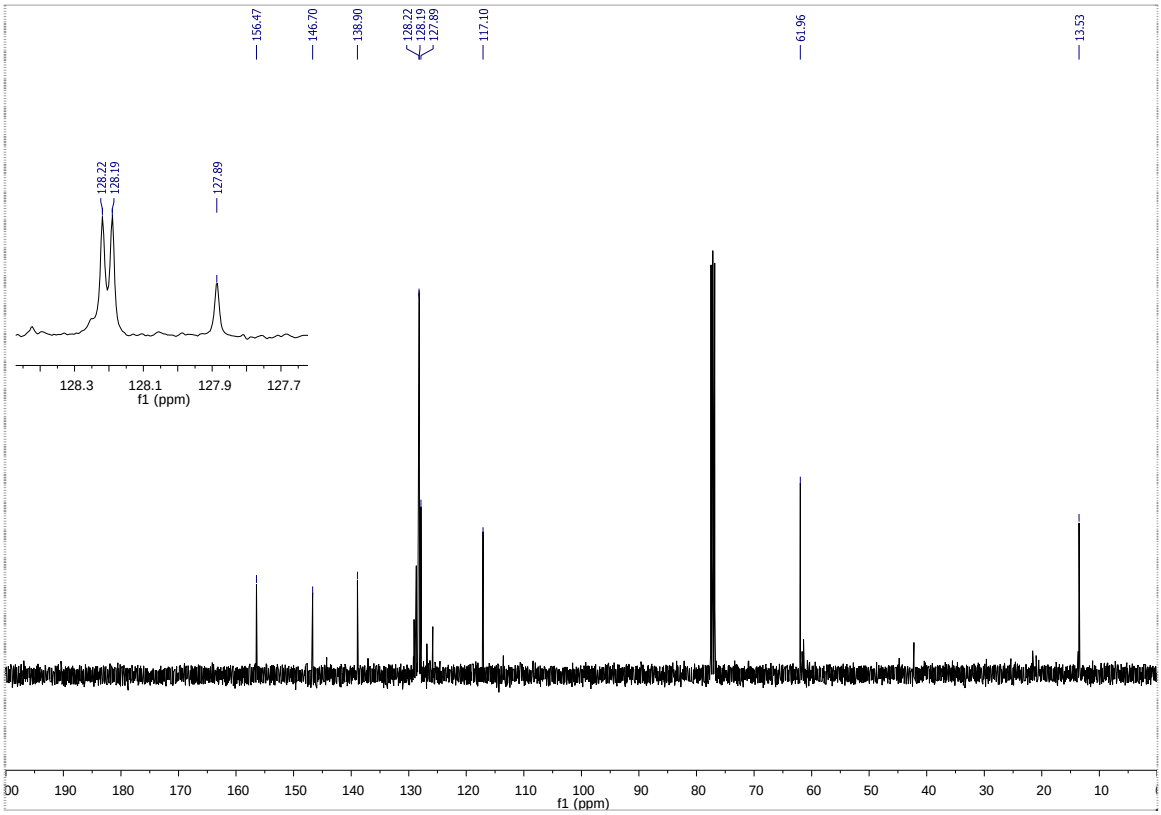
11.88
f1 (ppm)

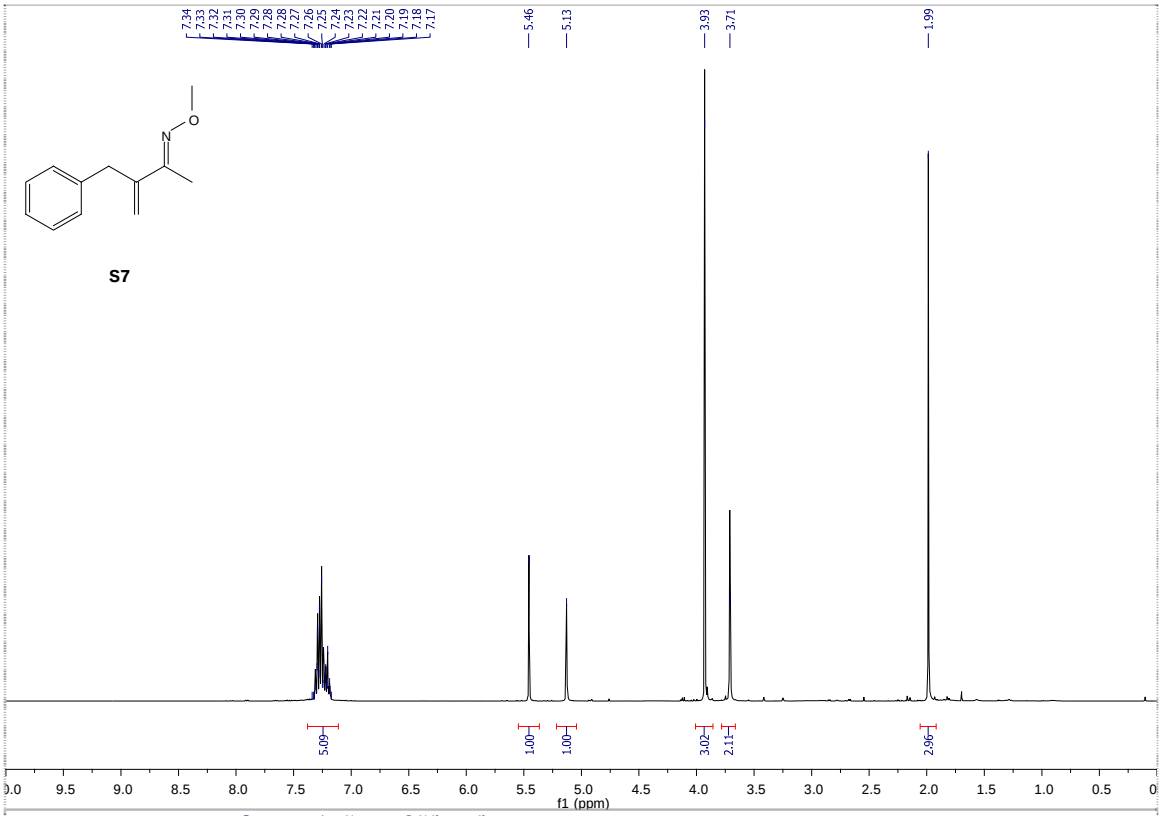

S5
5.92
5.92
5.91
5.91
3.87
2.47
2.45
2.44
2.17
1.82
1.77
1.55
1.34
1.33
0.92
0.90
0.89
1.00
3.00
2.11
3.04
3.06
4.23
3.18
f1 (ppm)
161.18
132.77
126.08
61.61
29.46
24.77
23.19
14.26
14.03
12.65
f1 (ppm)

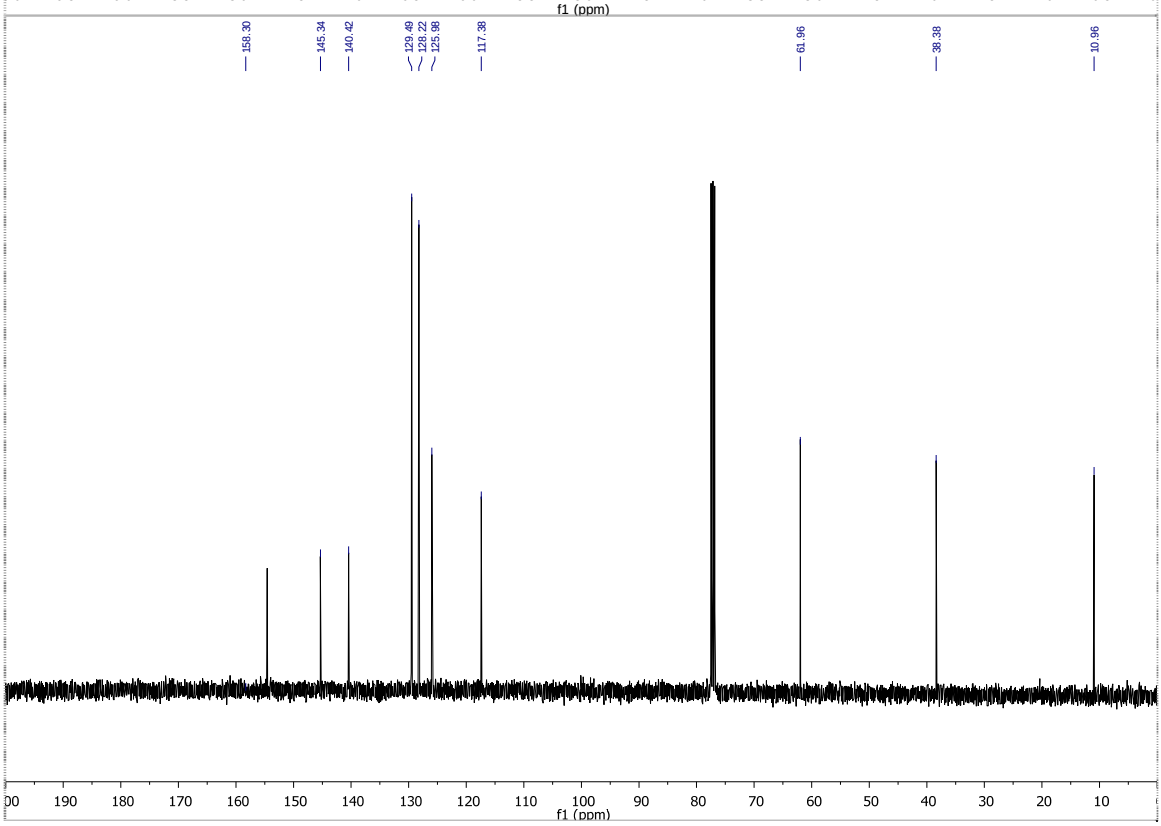

5.869
3.877
2.490
2.333
2.045
1.636
1.337
0.897
S6
0.81
2.85
2.00
2.02
1.97
4.11
3.83
2.75
6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8
f1 (ppm)

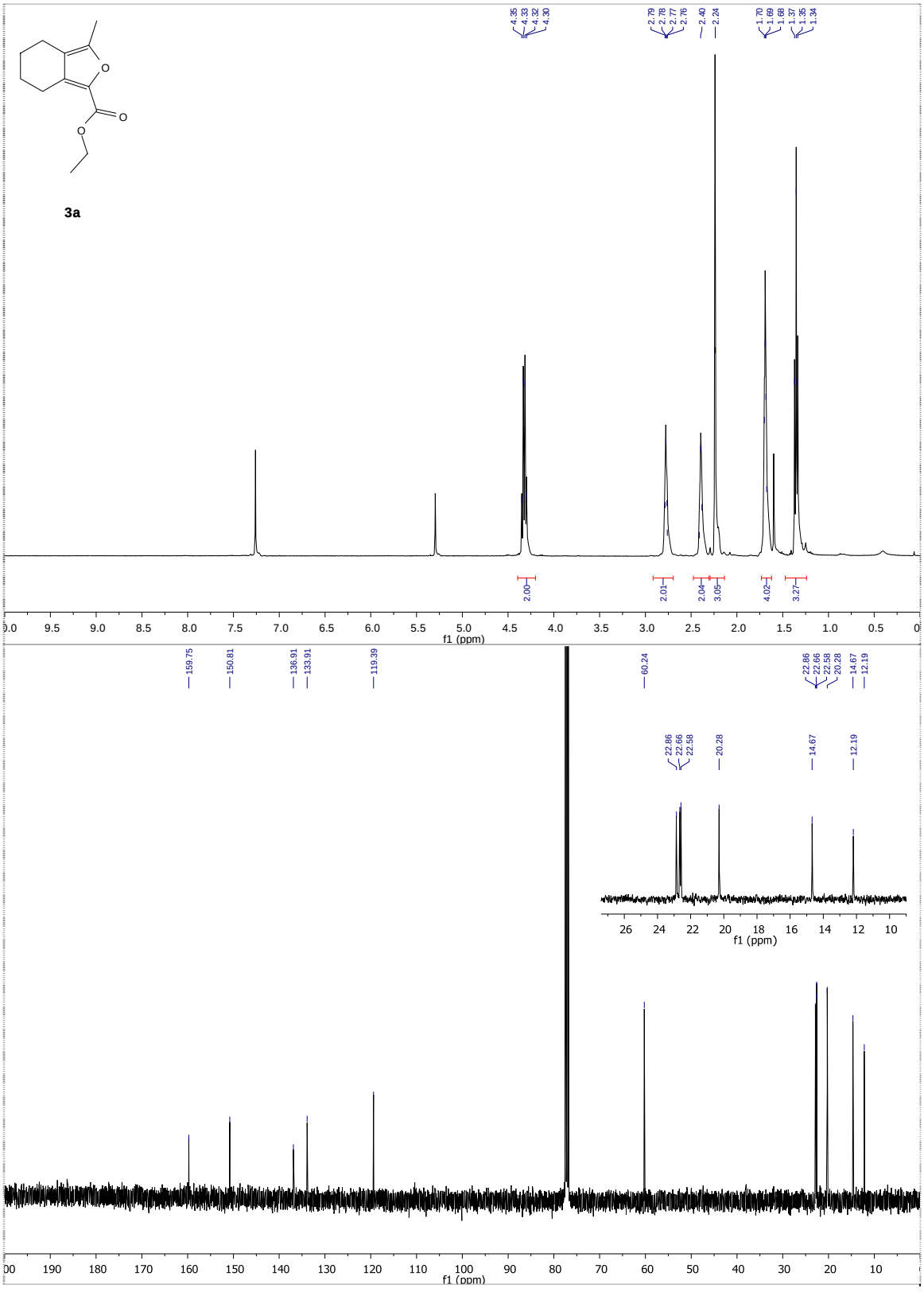

159.70
132.75
129.03
77.25
77.00
76.75
61.38
31.39
27.49
24.82
13.95
31.39
27.49
27.45
25.55
24.82
23.75
22.44
S6
30 28 26 24
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

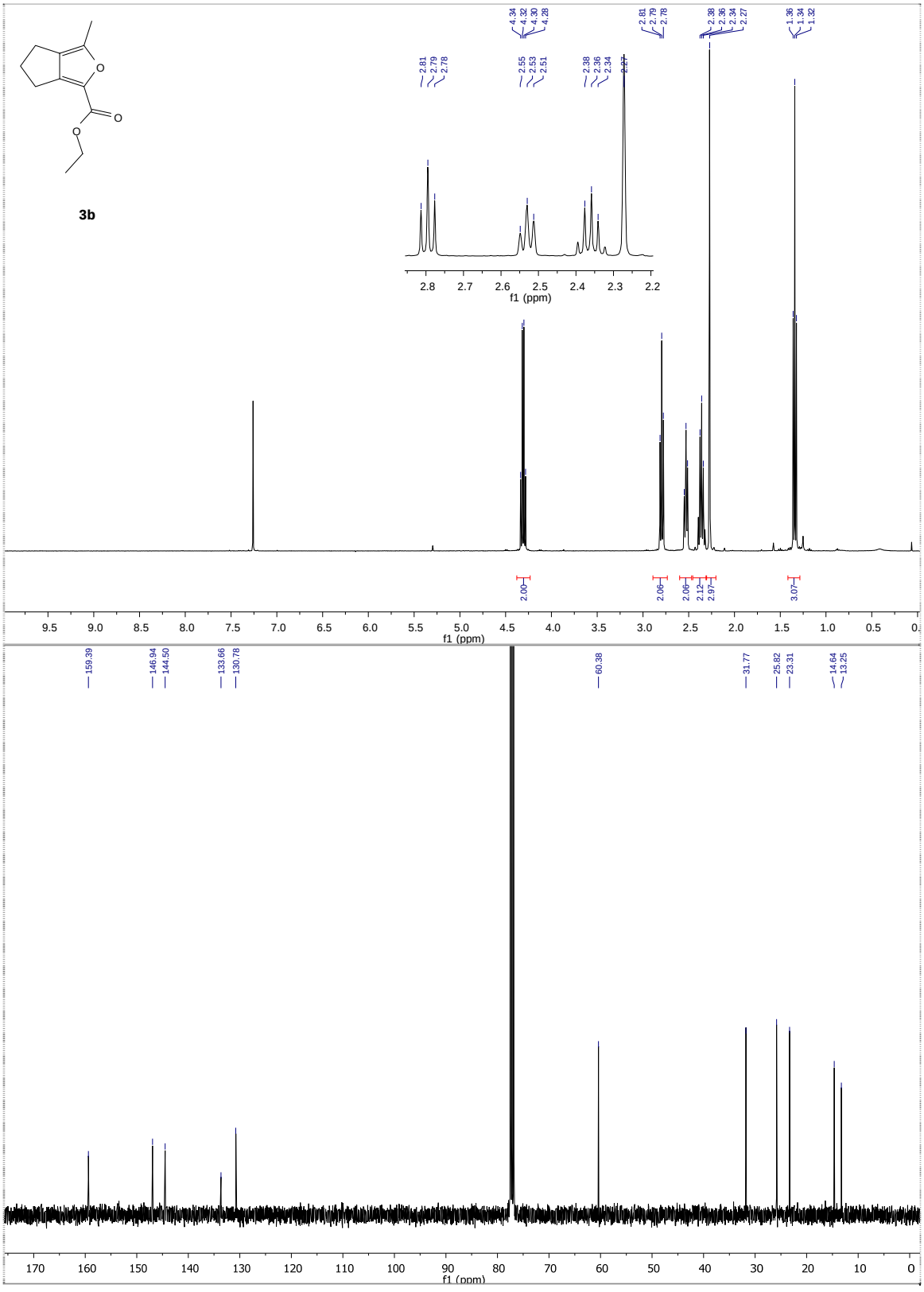

7.33
5.53
5.52
5.44
5.43
3.93
1.99
CH3
O
N
CH3
CH2
1b
4.79
1.00
1.01
2.93
2.95
7.8 7.4 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8
f1 (ppm)

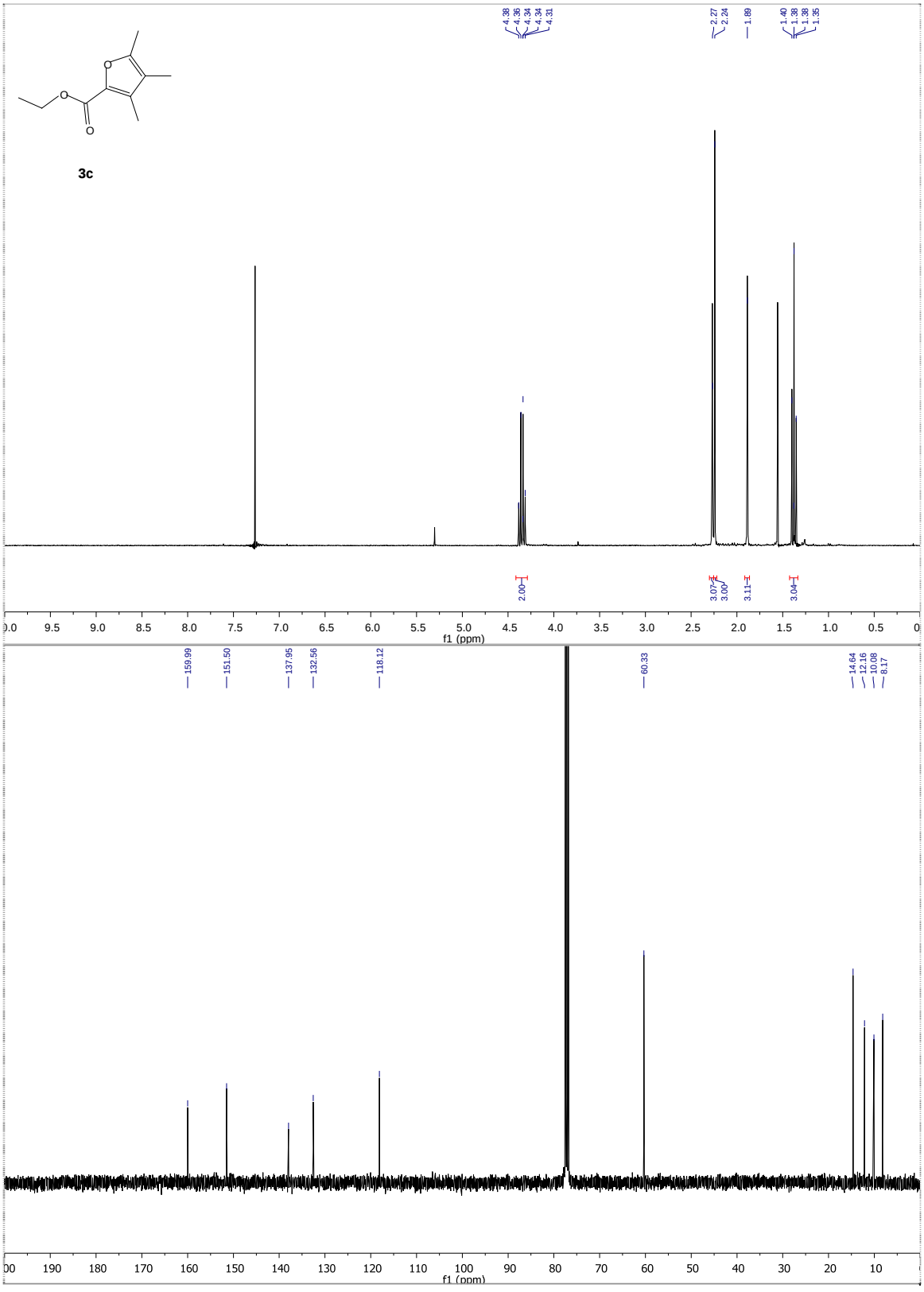

156.47
146.70
138.90
128.22
128.19
127.89
117.10
61.96
13.53
128.22
128.19
127.89
128.3 128.1 127.9 127.7
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

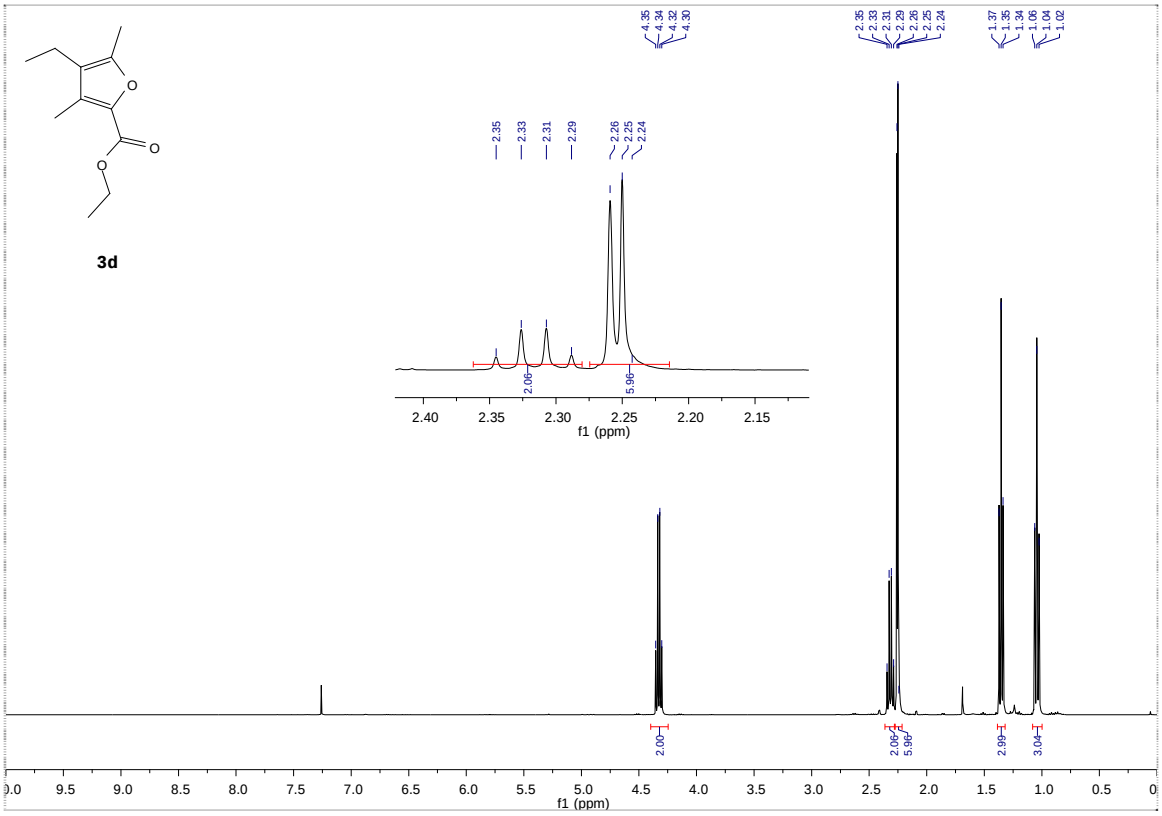

7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.17
5.46
5.13
3.93
3.71
1.99
N
O
S7
5.09
1.00
1.00
3.02
2.11
2.96
f1 (ppm)

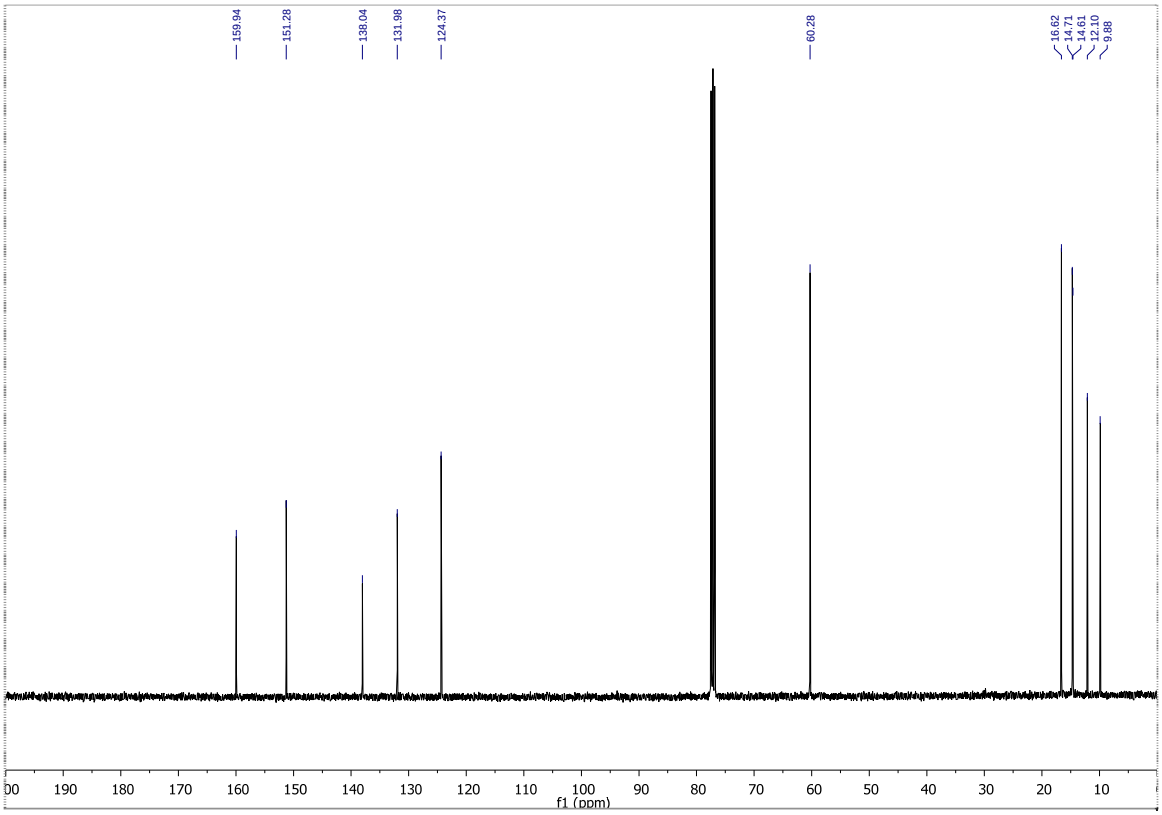

158.30
145.34
140.42
129.49
128.22
125.98
117.38
61.96
38.38
10.96
f1 (ppm)

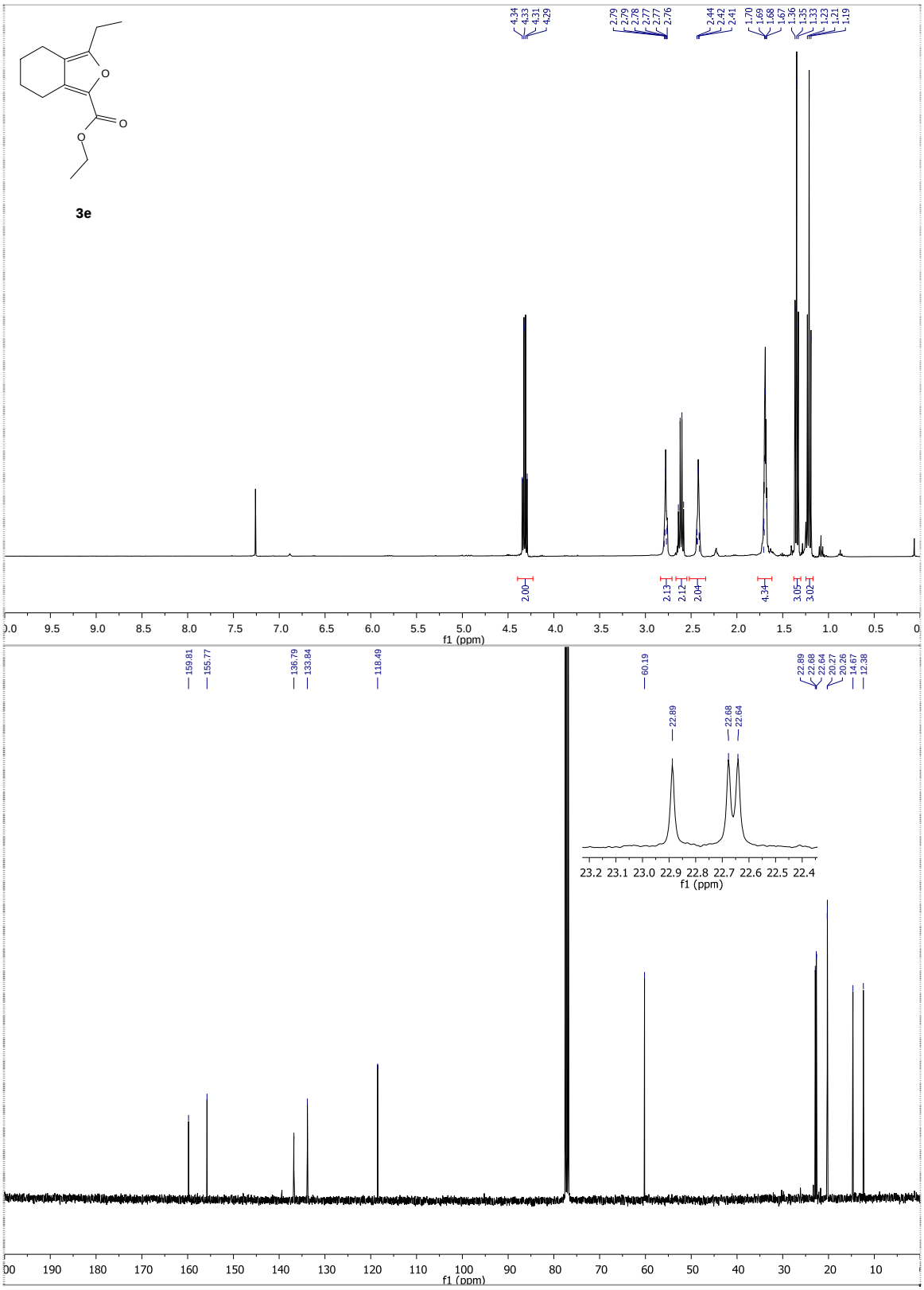

3a
4.35
4.33
4.32
4.30
2.79
2.78
2.77
2.76
2.40
2.24
1.70
1.69
1.68
1.37
1.35
1.34
2.00
2.01
2.04
3.05
4.02
3.27
f1 (ppm)
159.75
150.81
136.91
133.91
119.39
60.24
22.86
22.66
22.58
20.28
14.67
12.19
f1 (ppm)
f1 (ppm)

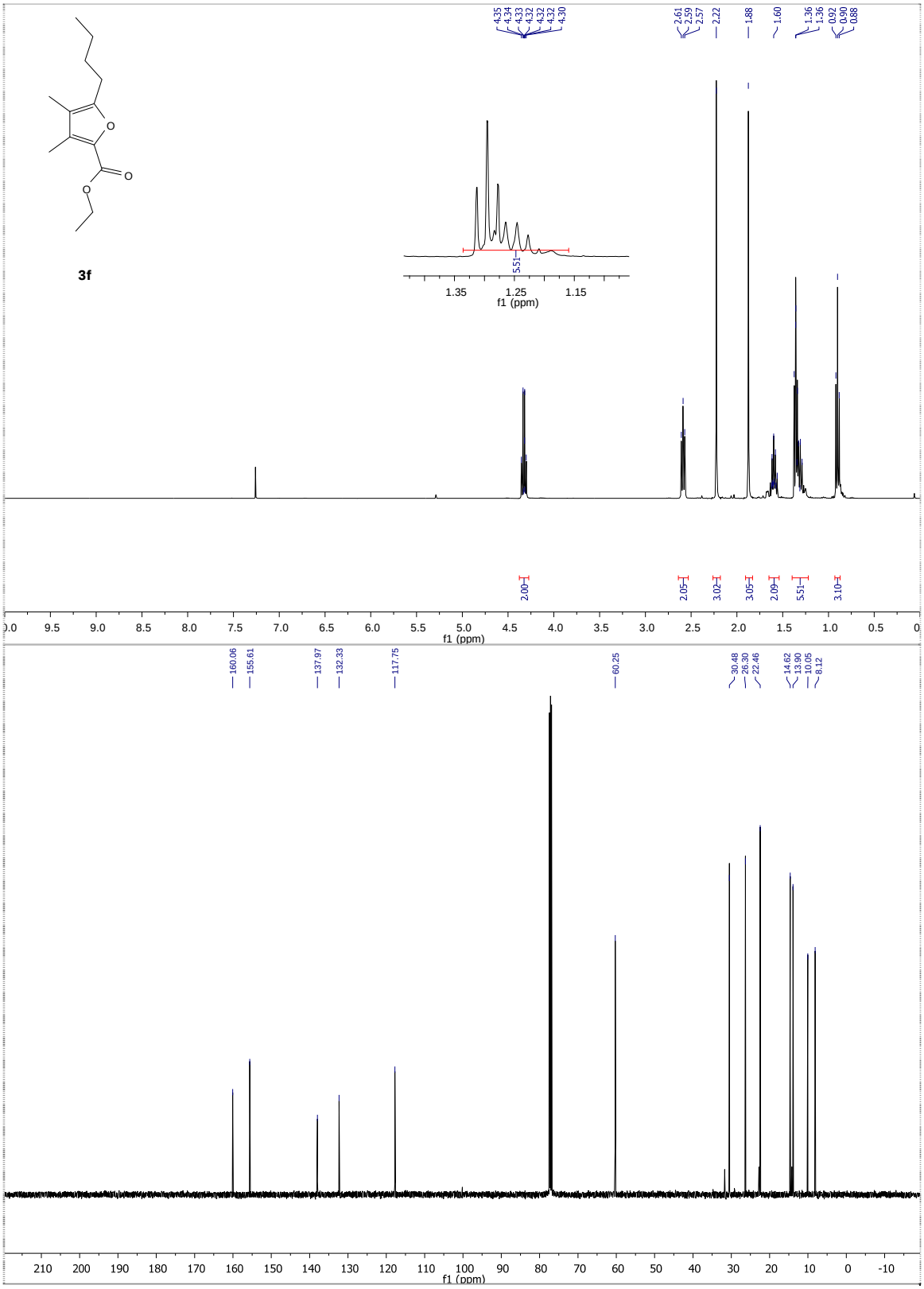

3b
f1 (ppm)
159.39
146.94
144.50
133.66
130.78
60.38
31.77
25.82
23.31
14.64
13.25

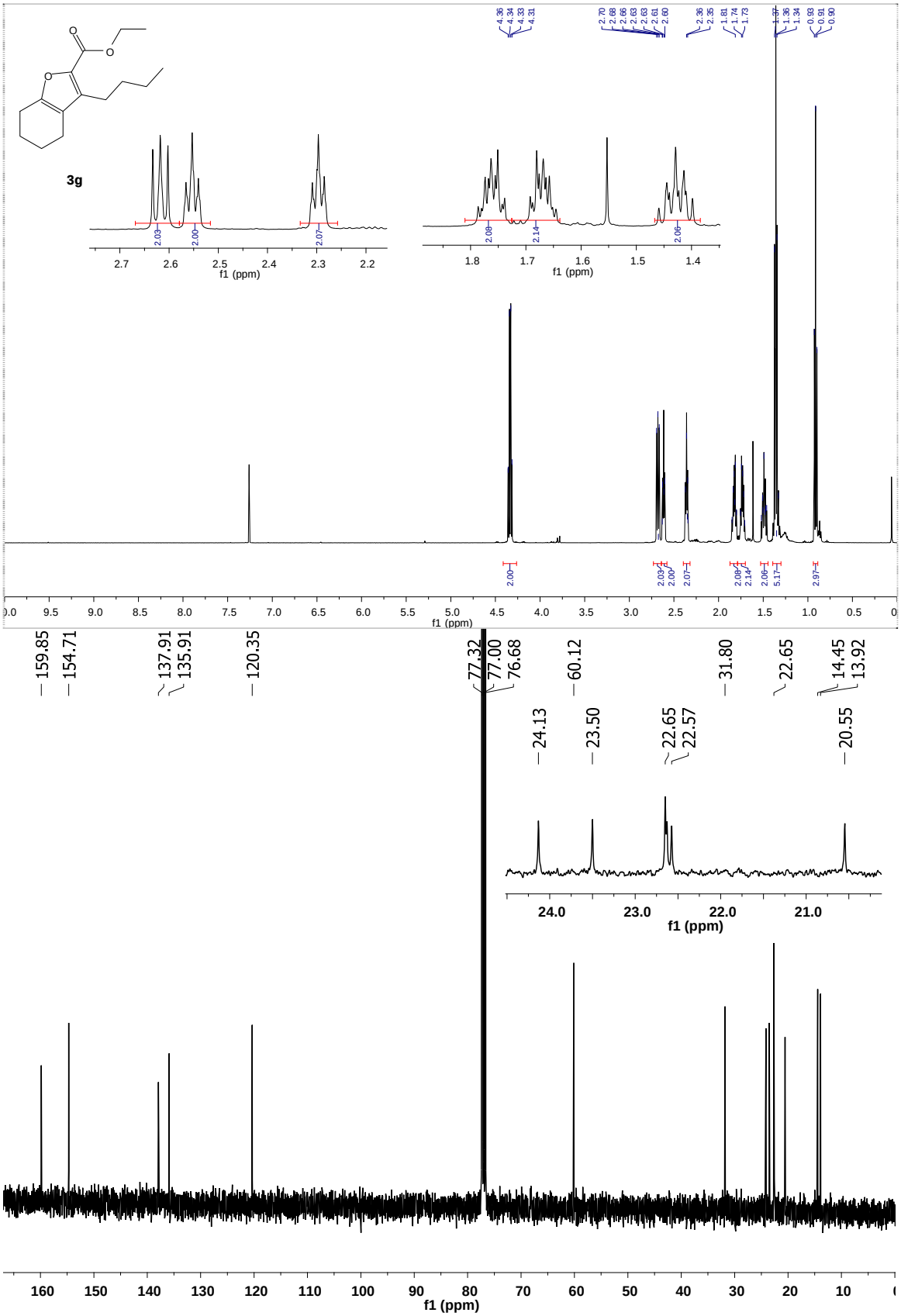

4.38
4.36
4.34
4.34
4.31
2.27
2.24
1.89
1.40
1.38
1.38
1.35
3c
2.00
3.07
3.00
3.11
3.04
f1 (ppm)
159.99
151.50
137.95
132.56
118.12
60.33
14.64
12.16
10.08
8.17
f1 (ppm)

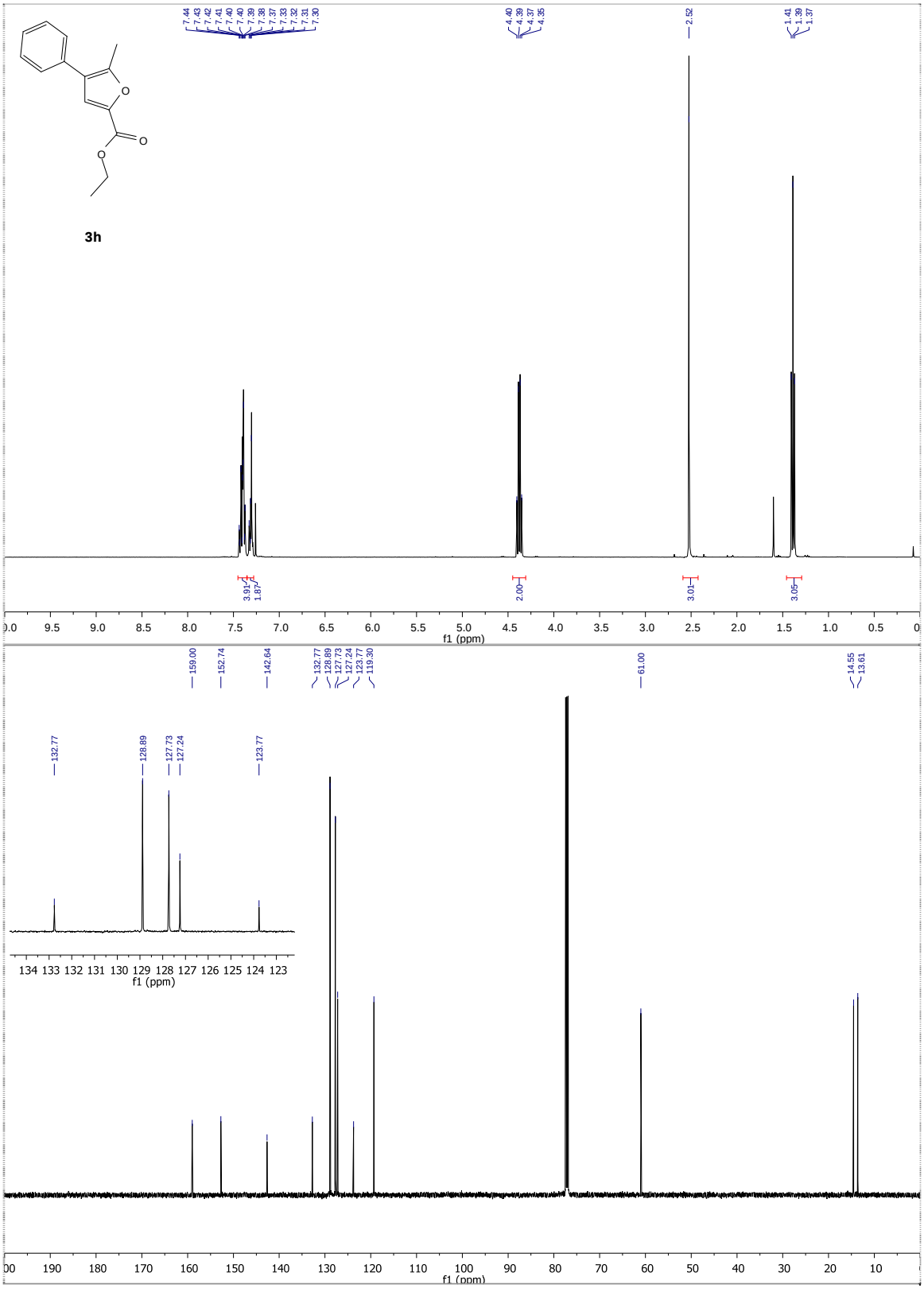

3d
4.35
4.34
4.32
4.30
2.35
2.33
2.31
2.29
2.26
2.25
2.24
1.37
1.35
1.34
1.06
1.04
1.02
2.06
5.96
f1 (ppm)
2.00
2.06
5.96
2.99
3.04

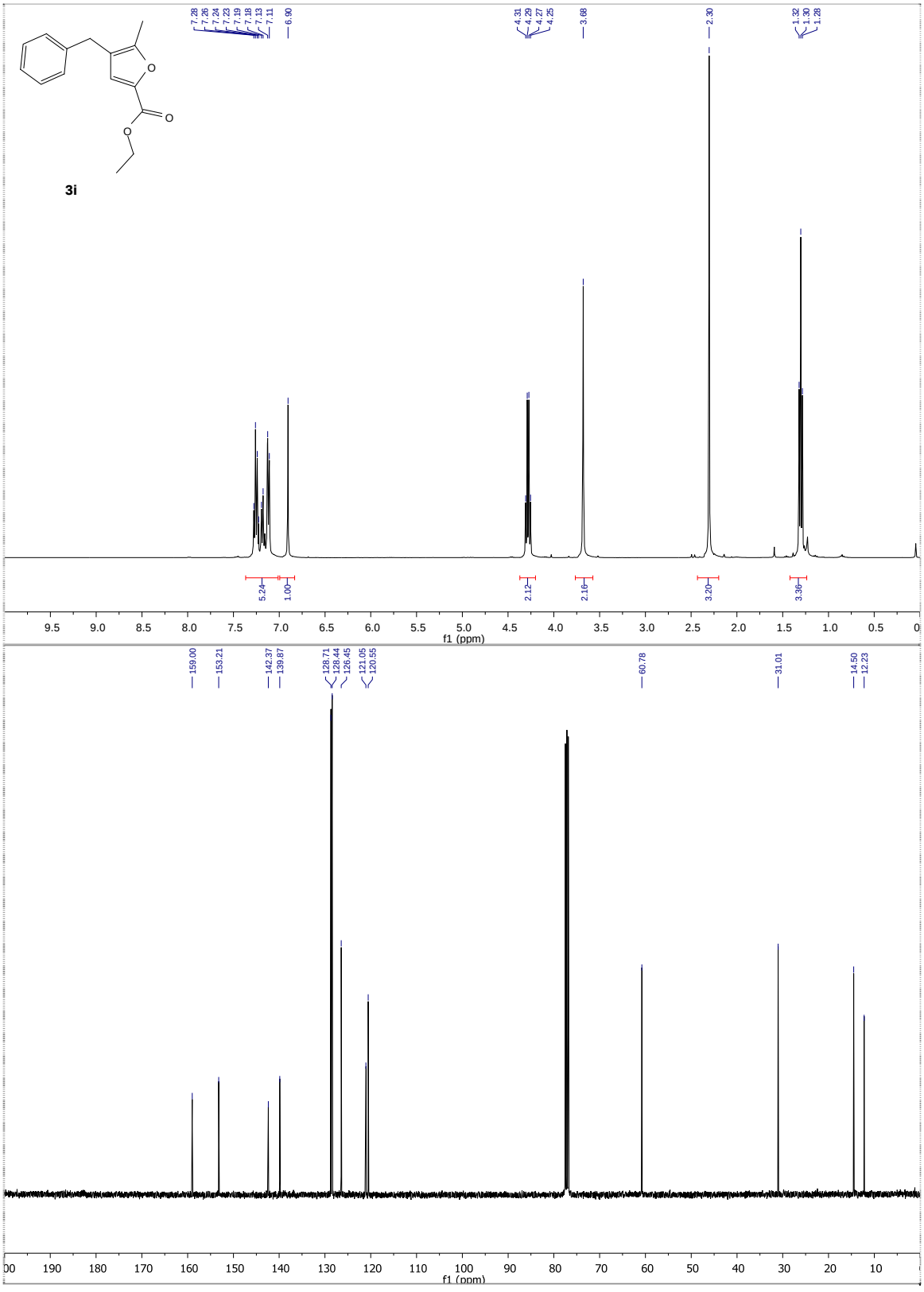

159.94
151.28
138.04
131.98
124.37
60.28
16.62
14.71
14.61
12.10
9.88
f1 (ppm)

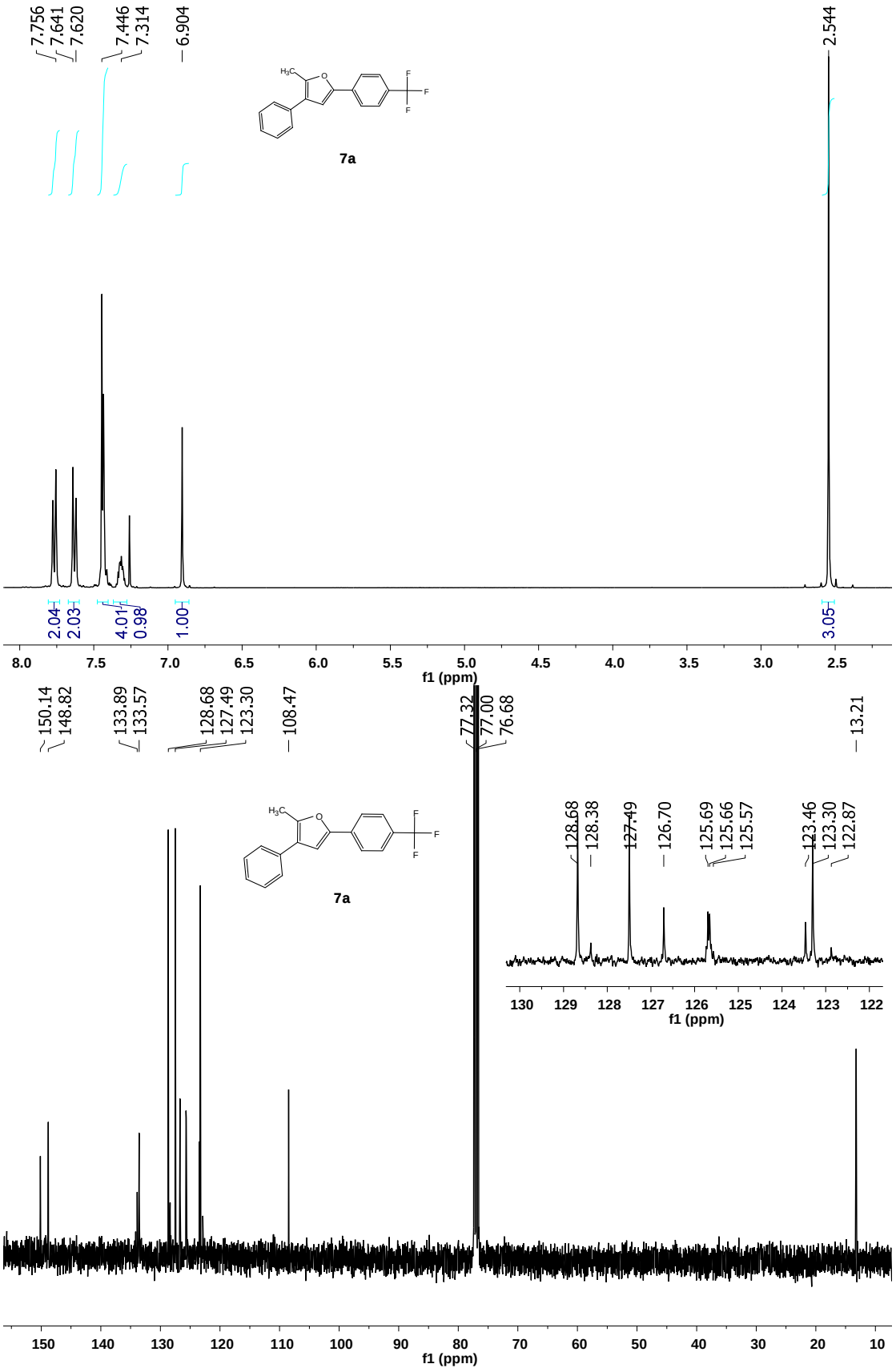

3e
4.34
4.33
4.31
4.29
2.79
2.79
2.78
2.77
2.77
2.76
2.44
2.42
2.41
1.70
1.69
1.68
1.67
1.36
1.35
1.33
1.23
1.21
1.19
2.00
2.13
2.12
2.04
4.34
3.05
3.02
f1 (ppm)
159.81
155.77
136.79
133.84
118.49
60.19
22.89
22.68
22.64
20.27
20.26
14.67
12.38
23.2 23.1 23.0 22.9 22.8 22.7 22.6 22.5 22.4
f1 (ppm)
f1 (ppm)

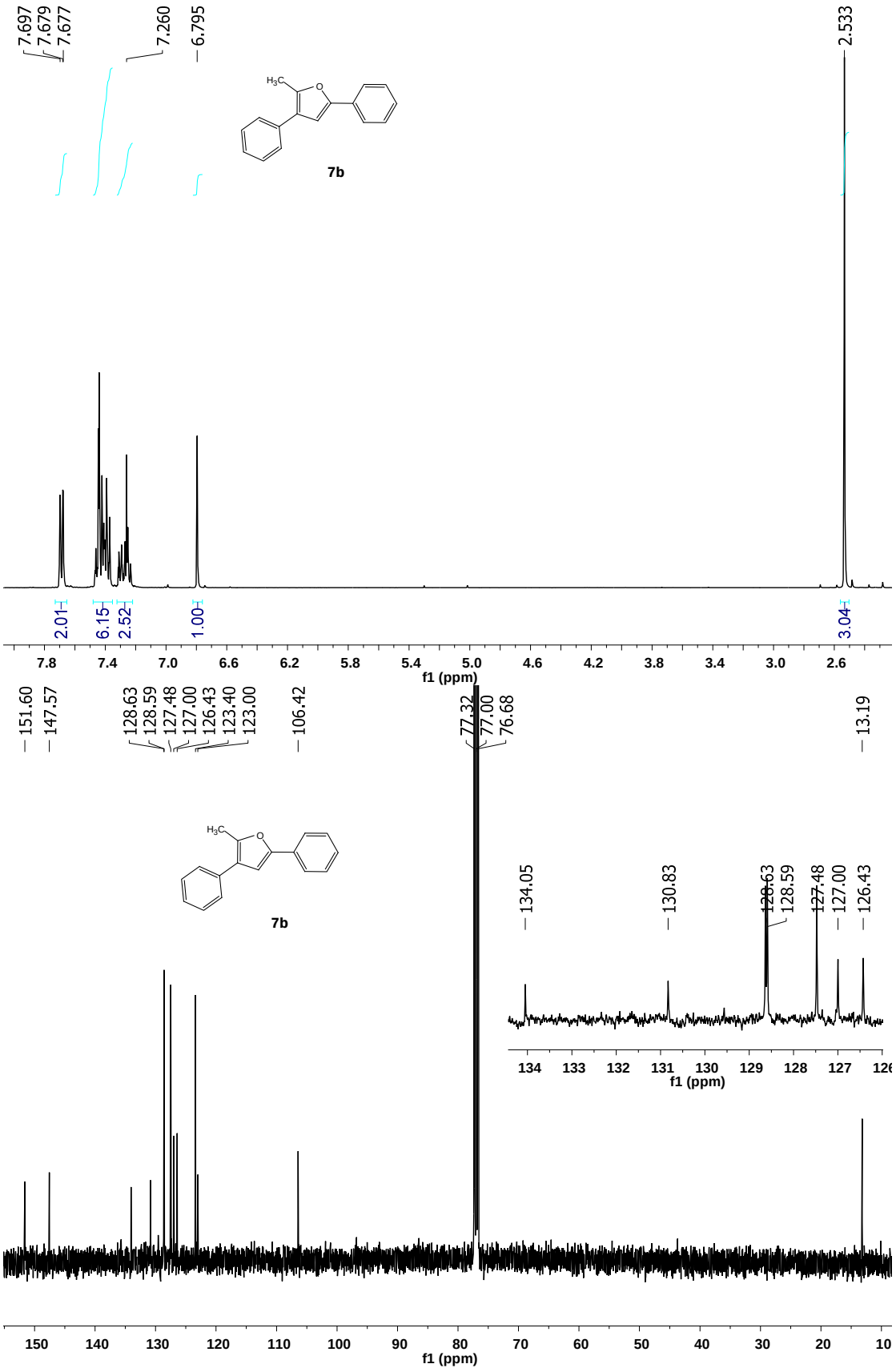

3f
4.35
4.34
4.33
4.32
4.32
4.32
4.30
2.61
2.59
2.57
2.22
1.88
1.60
1.36
1.36
0.92
0.90
0.88
5.51
1.35
1.25
1.15
f1 (ppm)
2.00
2.05
3.02
3.05
2.09
5.51
3.10
f1 (ppm)
160.06
155.61
137.97
132.33
117.75
60.25
30.48
26.30
22.46
14.62
13.90
10.05
8.12
f1 (ppm)

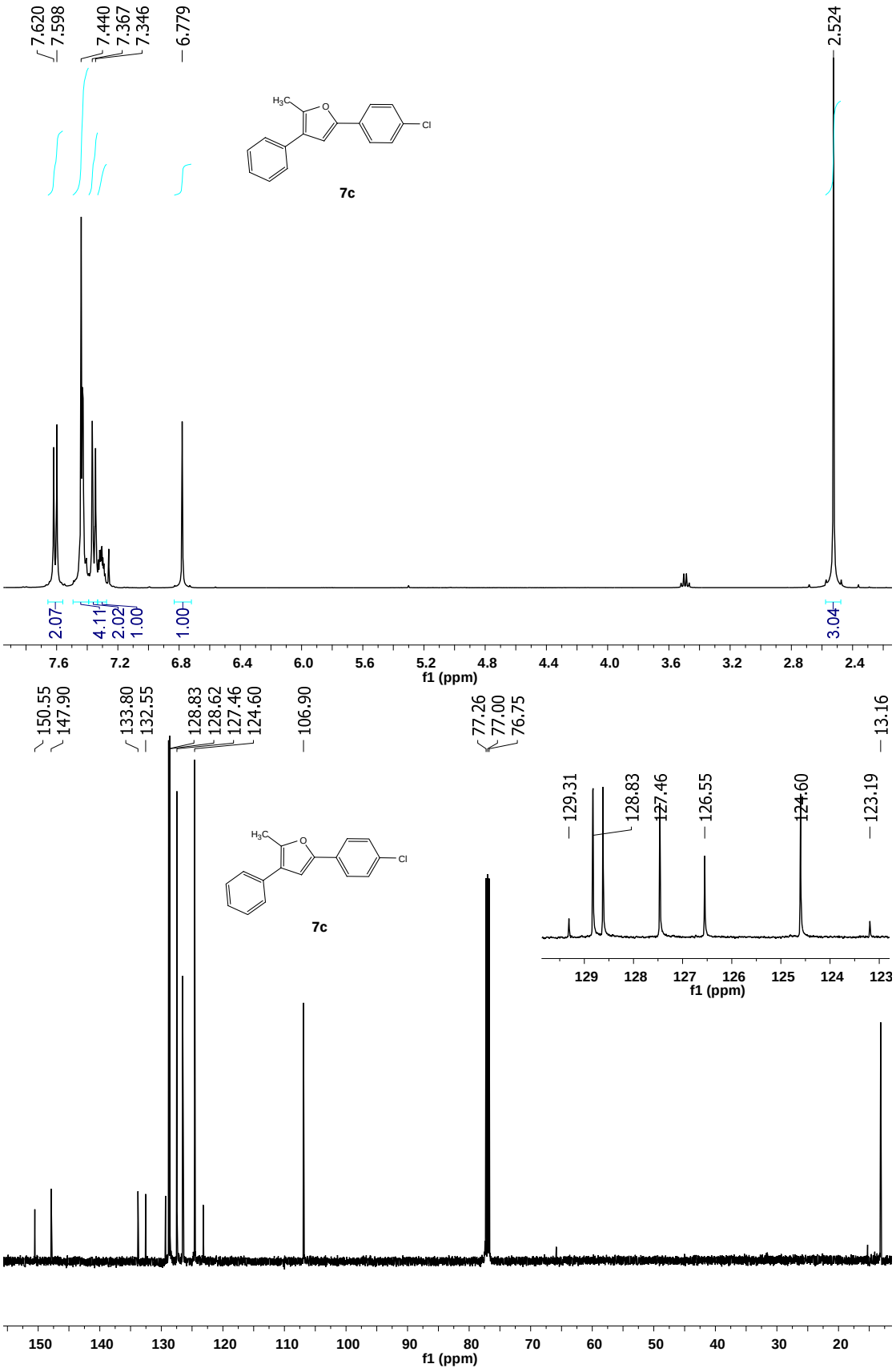

3g
f1 (ppm)
159.85
154.71
137.91
135.91
120.35
77.32
77.00
76.68
60.12
31.80
22.65
14.45
13.92
24.13
23.50
22.65
22.57
20.55

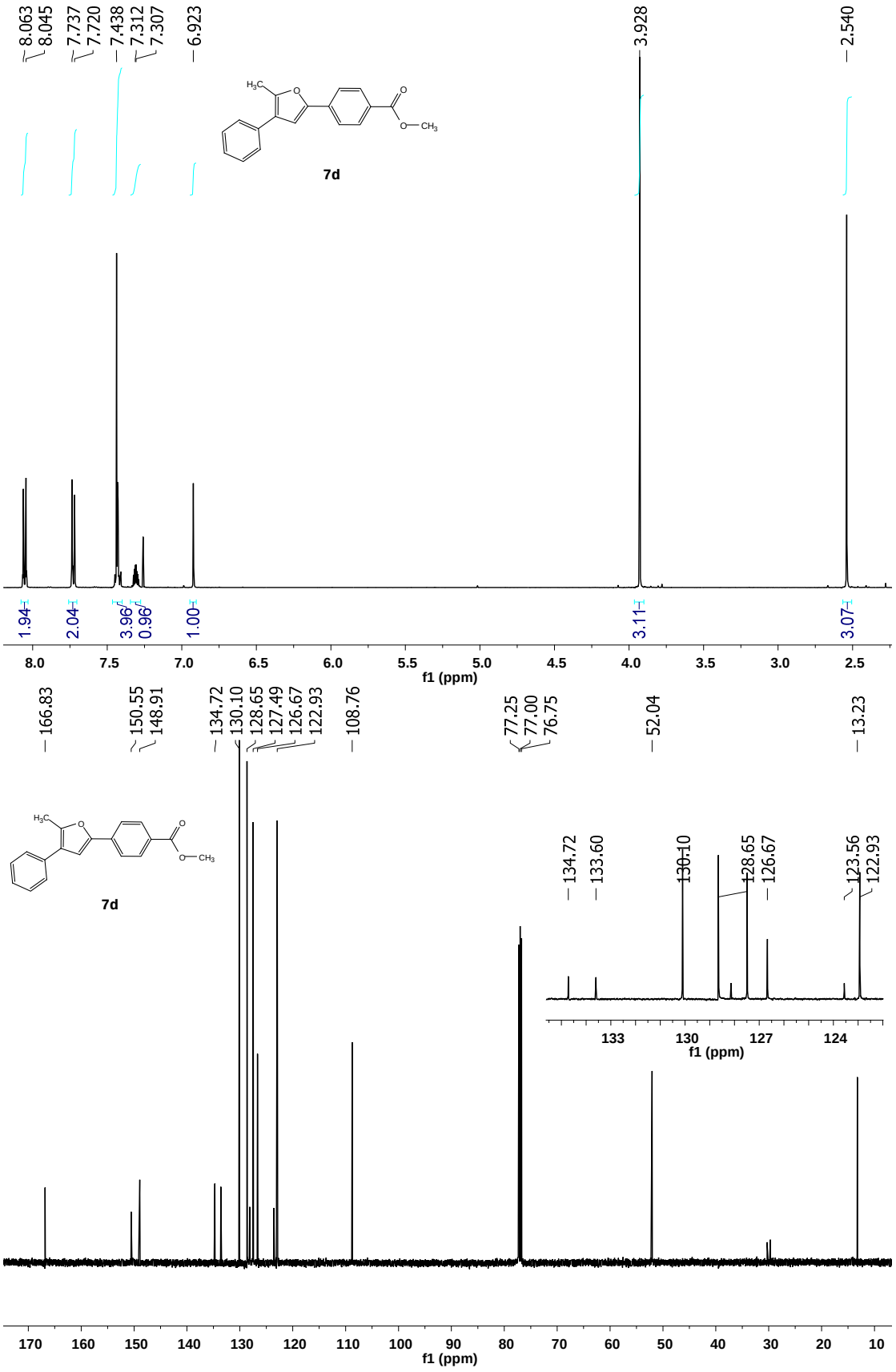

3h
7.44
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.33
7.32
7.31
7.30
4.40
4.39
4.37
4.35
2.52
1.41
1.39
1.37
3.91
1.87
2.00
3.01
3.05
f1 (ppm)
159.00
152.74
142.64
132.77
128.89
127.73
127.24
123.77
119.30
61.00
14.55
13.61
f1 (ppm)

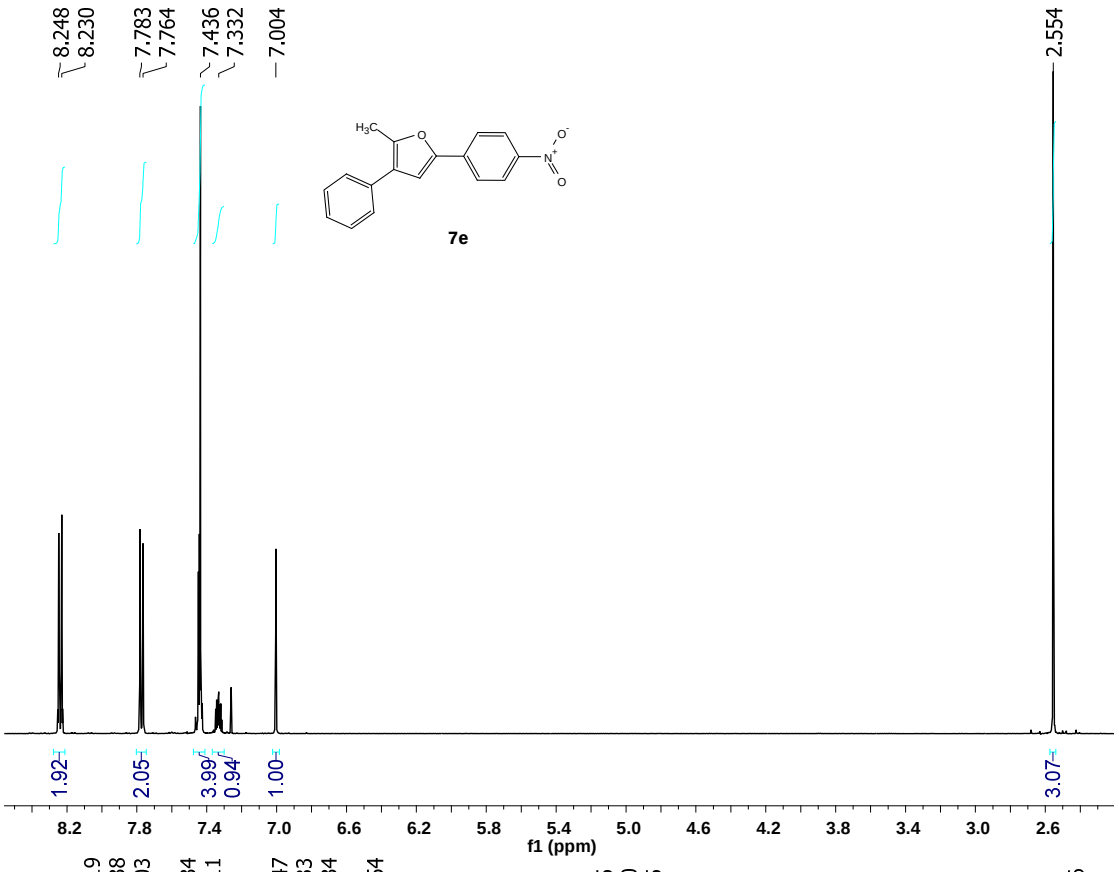

3i
7.28
7.26
7.24
7.23
7.19
7.18
7.13
7.11
6.90
4.31
4.29
4.27
4.25
3.68
2.30
1.32
1.30
1.28
5.24
1.00
2.12
2.16
3.20
3.36
f1 (ppm)
159.00
153.21
142.37
139.87
128.71
128.44
126.45
121.05
120.55
60.78
31.01
14.50
12.23
f1 (ppm)

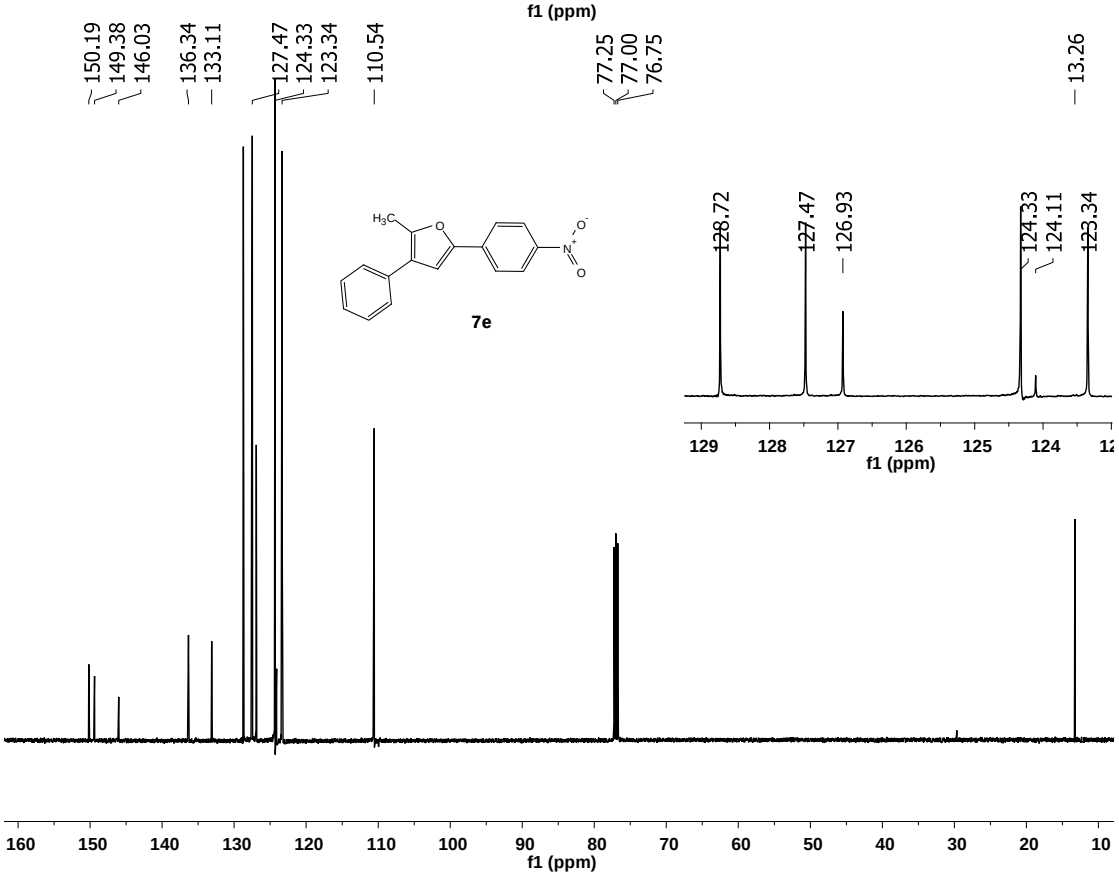

7.756
7.641
7.620
7.446
7.314
6.904
2.544
7a
2.04
2.03
4.01
0.98
1.00
3.05
f1 (ppm)
150.14
148.82
133.89
133.57
128.68
127.49
123.30
108.47
77.32
77.00
76.68
13.21
128.68
128.38
127.49
126.70
125.69
125.66
125.57
123.46
123.30
122.87
7a
f1 (ppm)

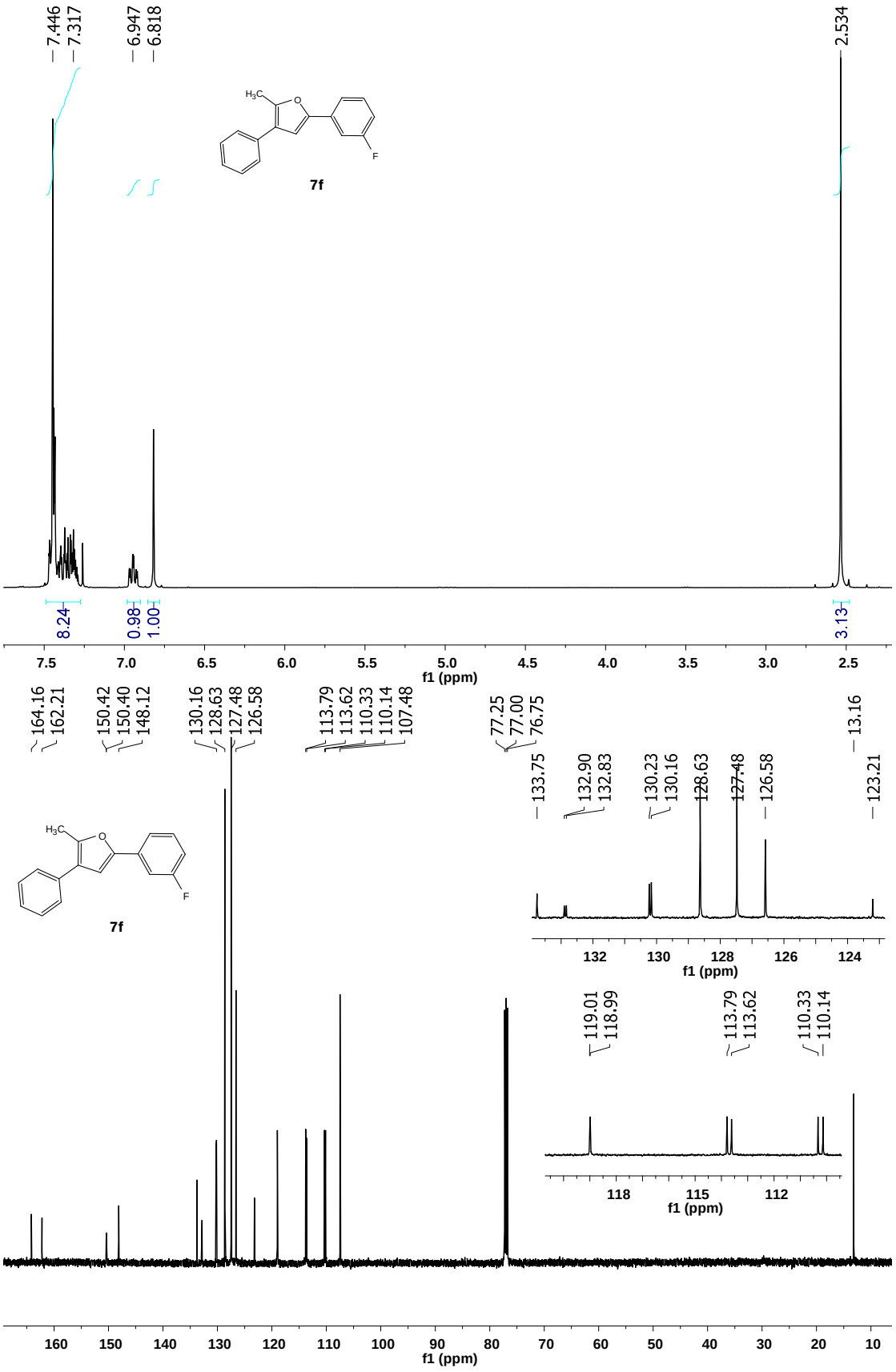

7.697
7.679
7.677
7.260
6.795
2.533
7b
2.01
6.15
2.52
1.00
3.04
f1 (ppm)
151.60
147.57
128.63
128.59
127.48
127.00
126.43
123.40
123.00
106.42
77.32
77.00
76.68
13.19
134.05
130.83
128.63
128.59
127.48
127.00
126.43
7b
f1 (ppm)

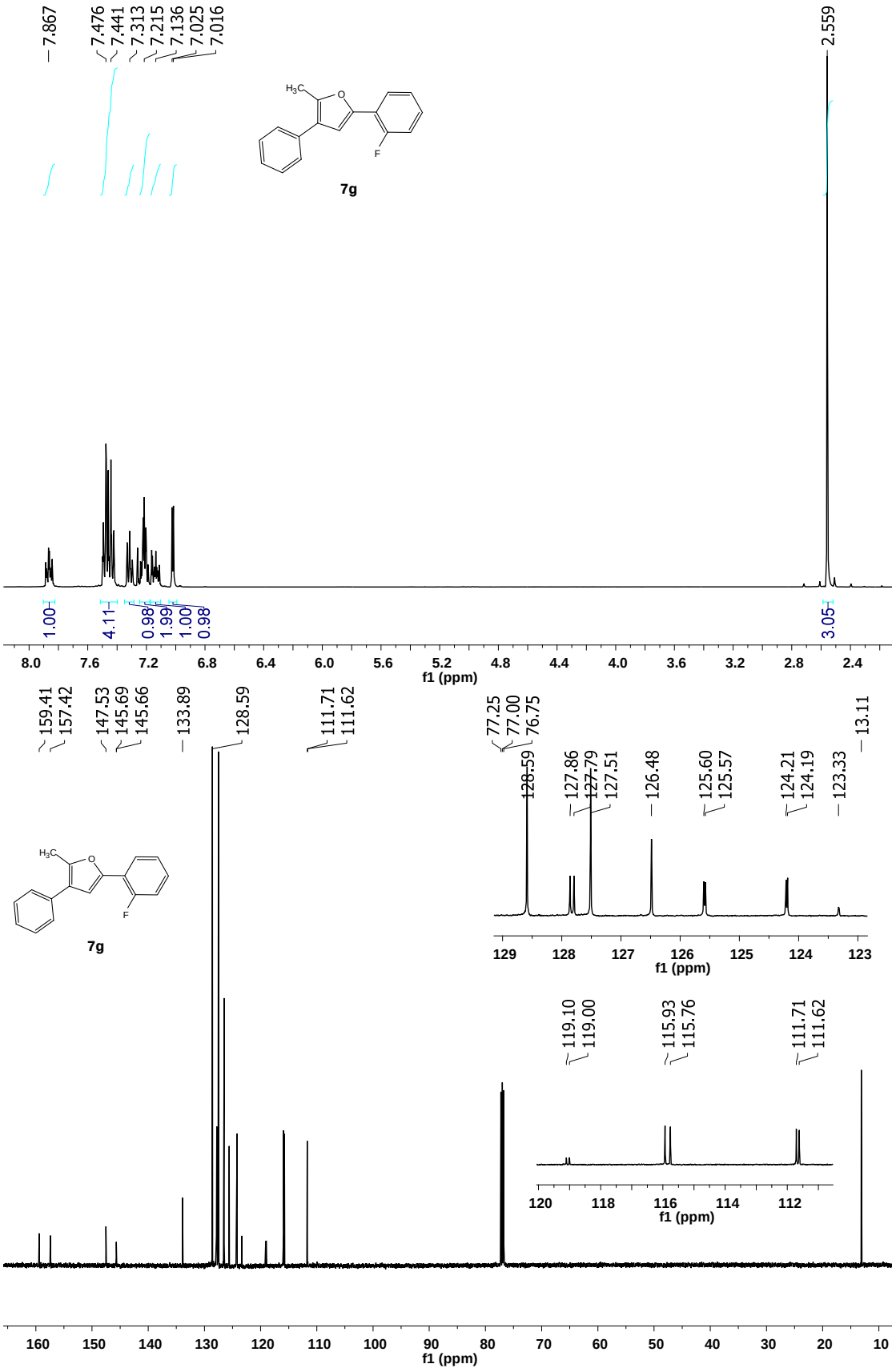

7.620
7.598
7.440
7.367
7.346
6.779
2.524
7c
2.07
4.11
2.02
1.00
1.00
3.04
f1 (ppm)
150.55
147.90
133.80
132.55
128.83
128.62
127.46
124.60
106.90
77.26
77.00
76.75
13.16
129.31
128.83
127.46
126.55
124.60
123.19
7c
f1 (ppm)
f1 (ppm)

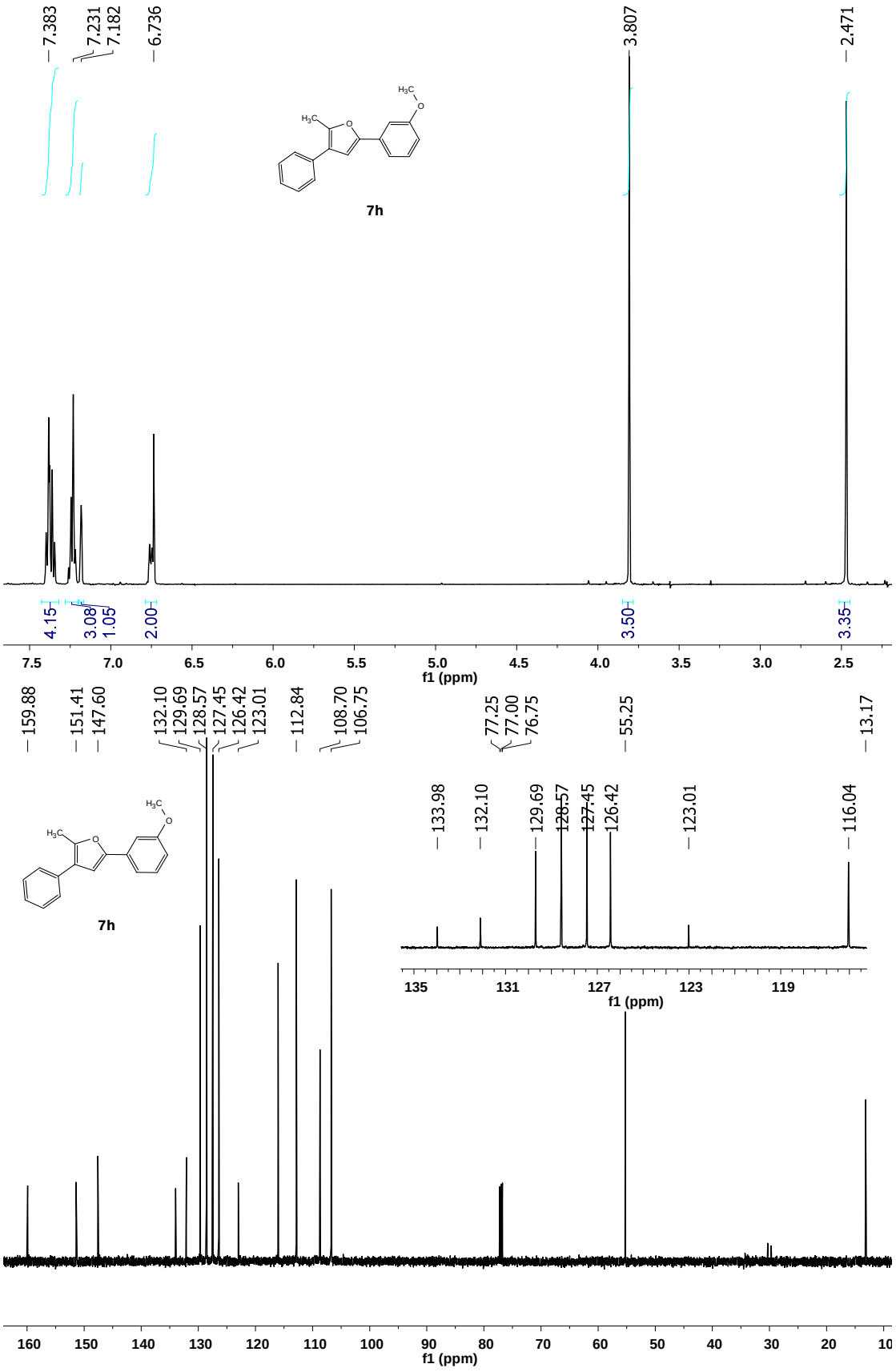

8.063
8.045
7.737
7.720
7.438
7.312
7.307
6.923
3.928
2.540
7d
1.94
2.04
3.96
0.96
1.00
3.11
3.07
f1 (ppm)
166.83
150.55
148.91
134.72
130.10
128.65
127.49
126.67
122.93
108.76
77.25
77.00
76.75
52.04
13.23
7d
133.60
123.56
f1 (ppm)

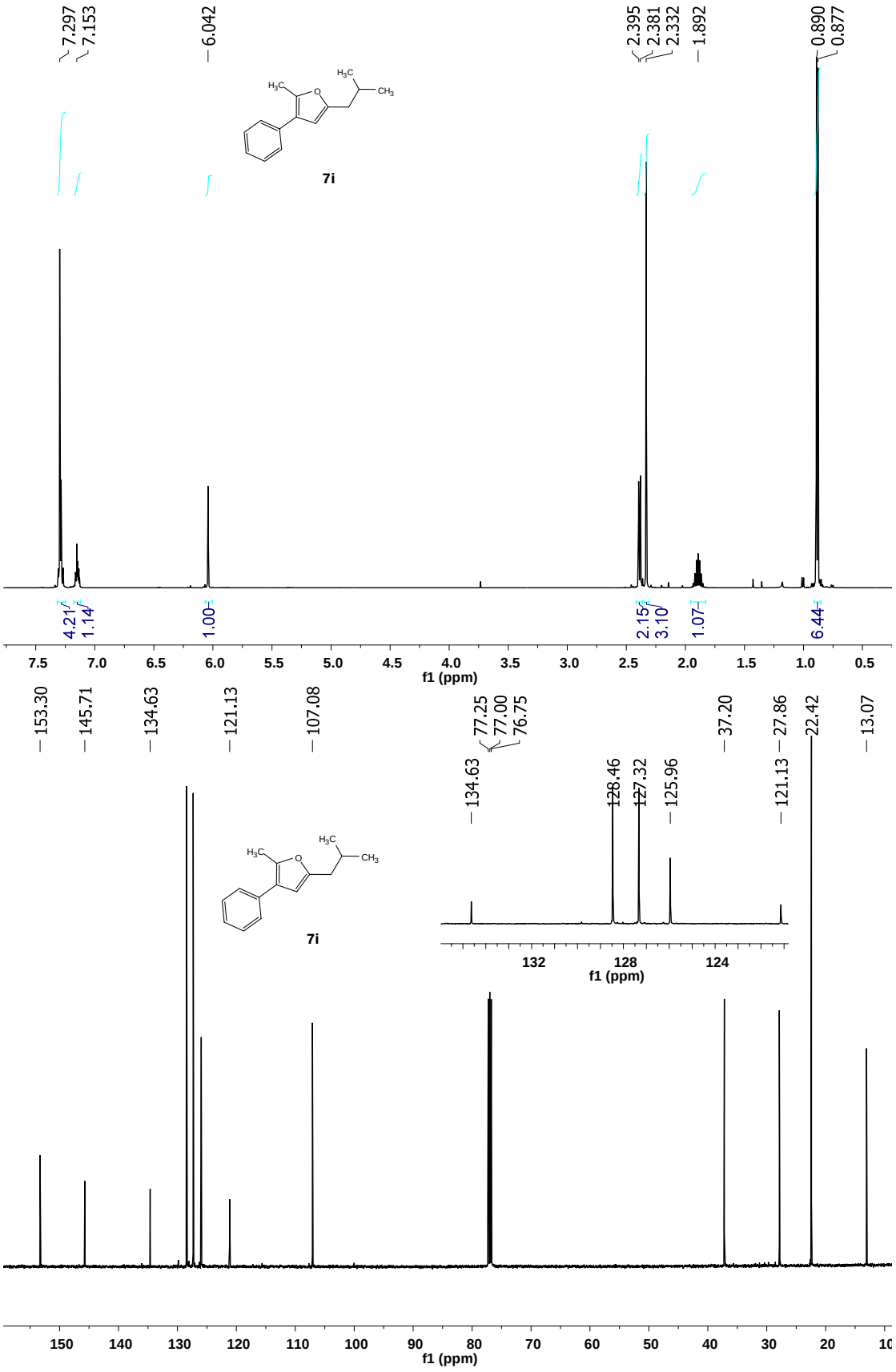

8.248
8.230
7.783
7.764
7.436
7.332
7.004
2.554
7e
1.92
2.05
3.99
0.94
1.00
3.07
f1 (ppm)

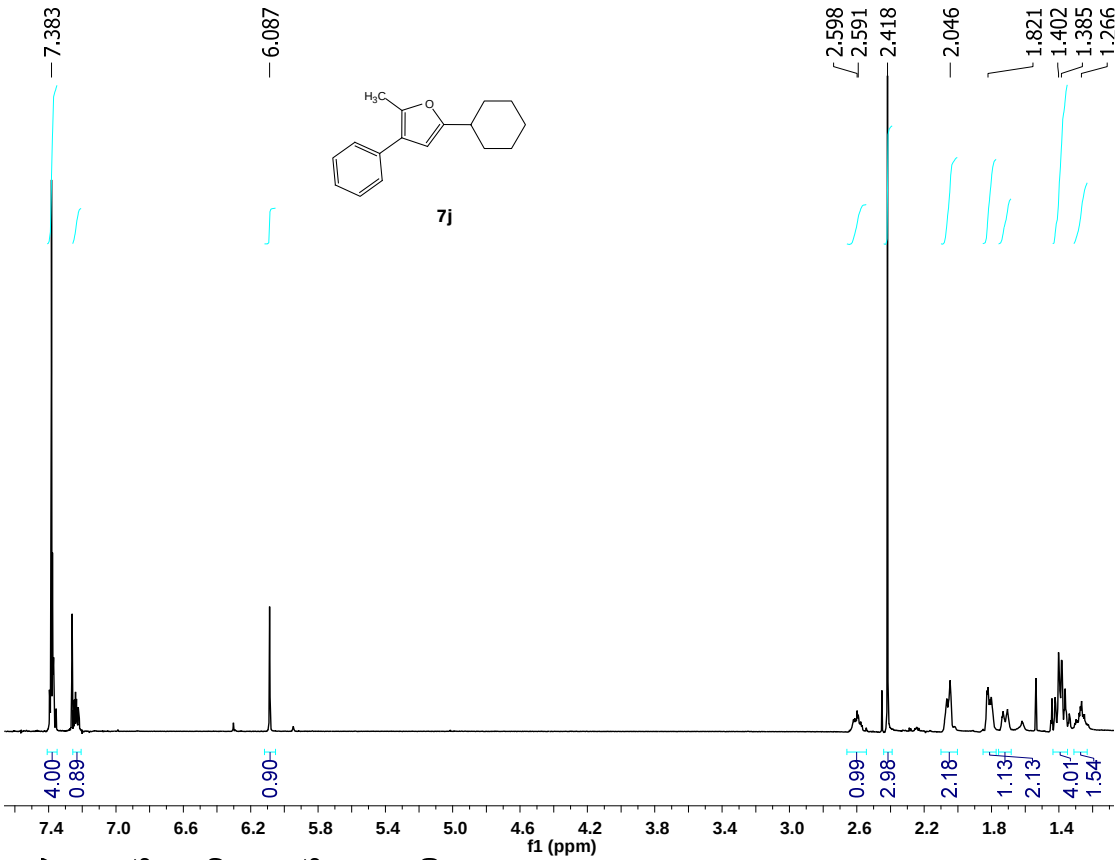

150.19
149.38
146.03
136.34
133.11
127.47
124.33
123.34
110.54
77.25
77.00
76.75
13.26
7e
128.72
127.47
126.93
124.33
124.11
123.34
f1 (ppm)

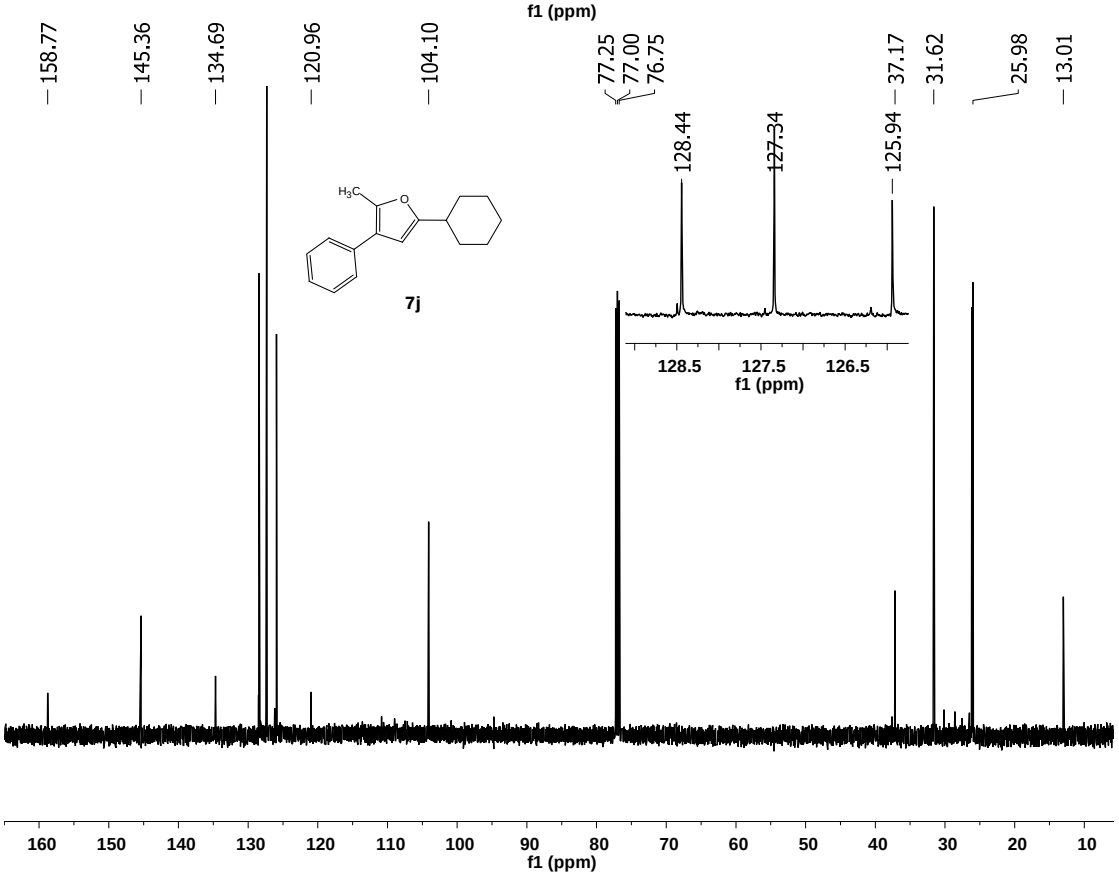

7.446
7.317
6.947
6.818
2.534
7f
8.24
0.98
1.00
3.13
f1 (ppm)
164.16
162.21
150.42
150.40
148.12
130.16
128.63
127.48
126.58
113.79
113.62
110.33
110.14
107.48
77.25
77.00
76.75
133.75
132.90
132.83
130.23
130.16
128.63
127.48
126.58
13.16
123.21
119.01
118.99
113.79
113.62
110.33
110.14
f1 (ppm)

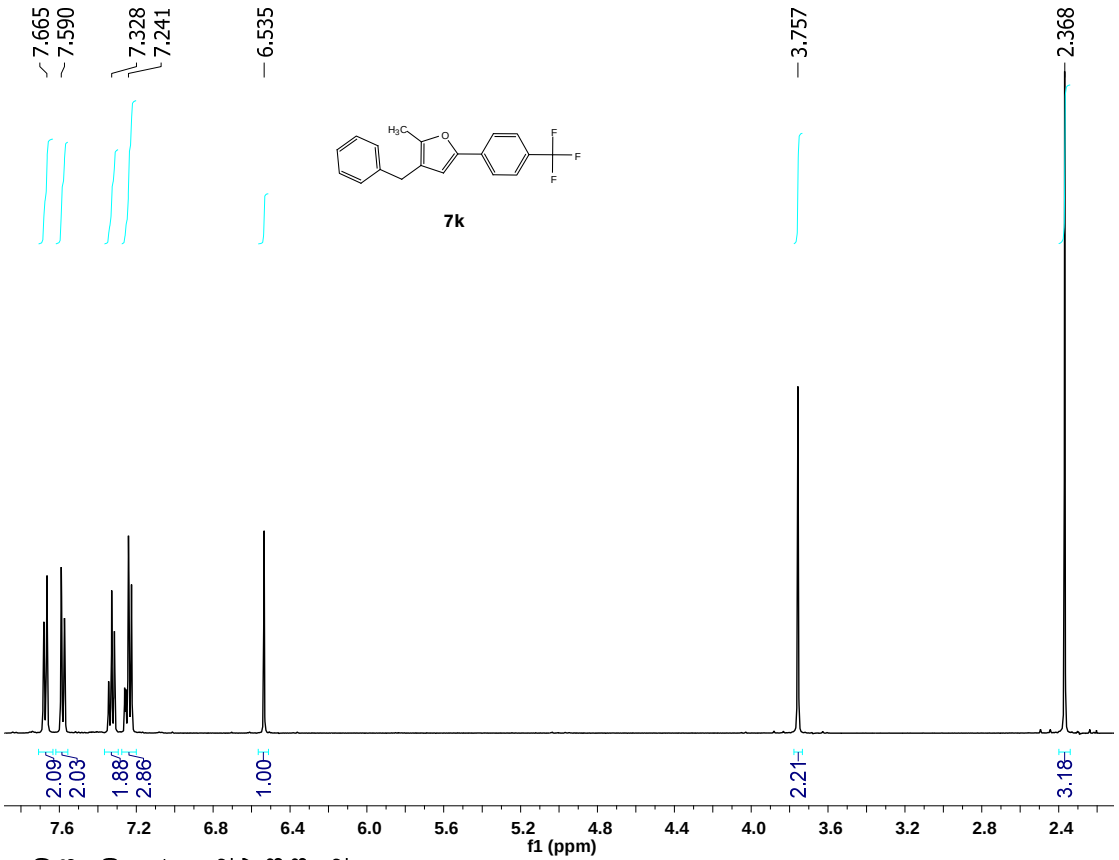

7.867
7.476
7.441
7.313
7.215
7.136
7.025
7.016
2.559
7g
1.00
4.11
0.98
1.99
1.00
0.98
3.05
f1 (ppm)
159.41
157.42
147.53
145.69
145.66
133.89
128.59
111.71
111.62
77.25
77.00
76.75
128.59
127.86
127.79
127.51
126.48
125.60
125.57
124.21
124.19
123.33
13.11
119.10
119.00
115.93
115.76
111.71
111.62

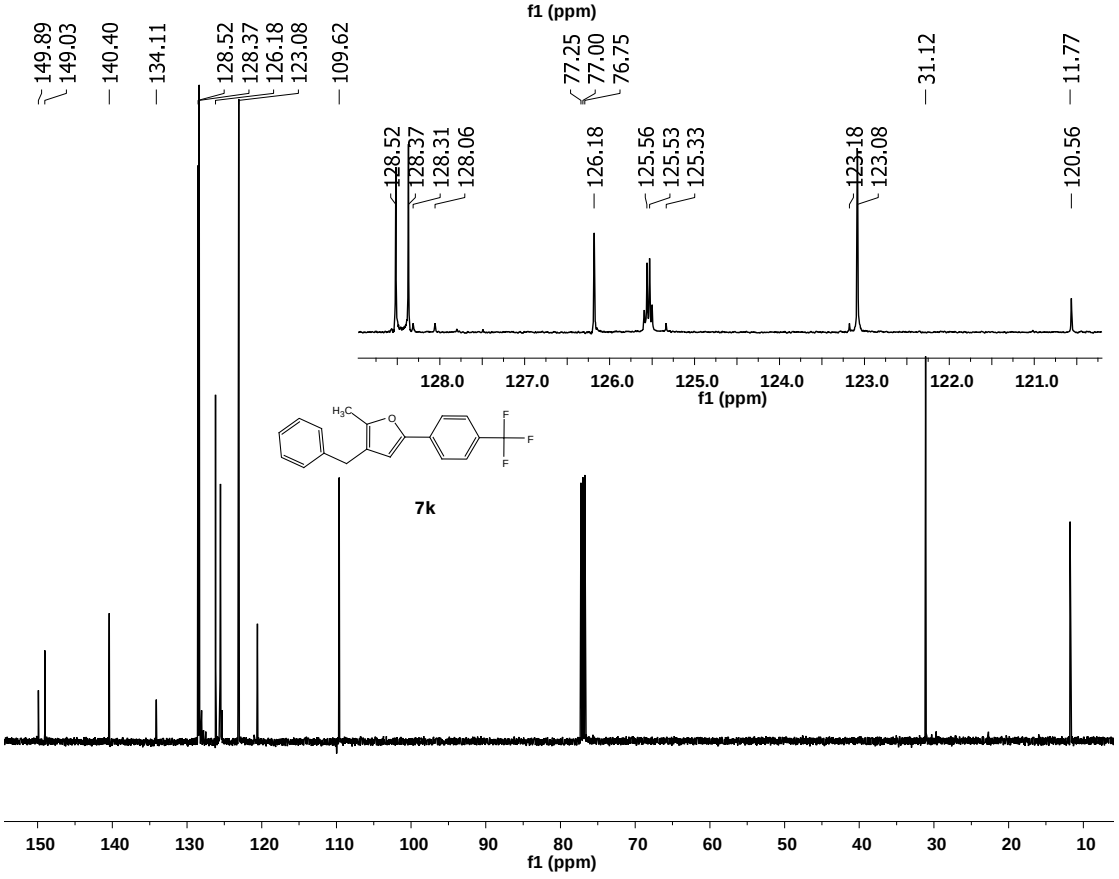

7.383
7.231
7.182
6.736
3.807
2.471
4.15
3.08
1.05
2.00
3.50
3.35
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)
7h
159.88
151.41
147.60
132.10
129.69
128.57
127.45
126.42
123.01
112.84
108.70
106.75
77.25
77.00
76.75
55.25
13.17
133.98
132.10
129.69
128.57
127.45
126.42
123.01
116.04
135
131
127
123
119
f1 (ppm)
7h
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

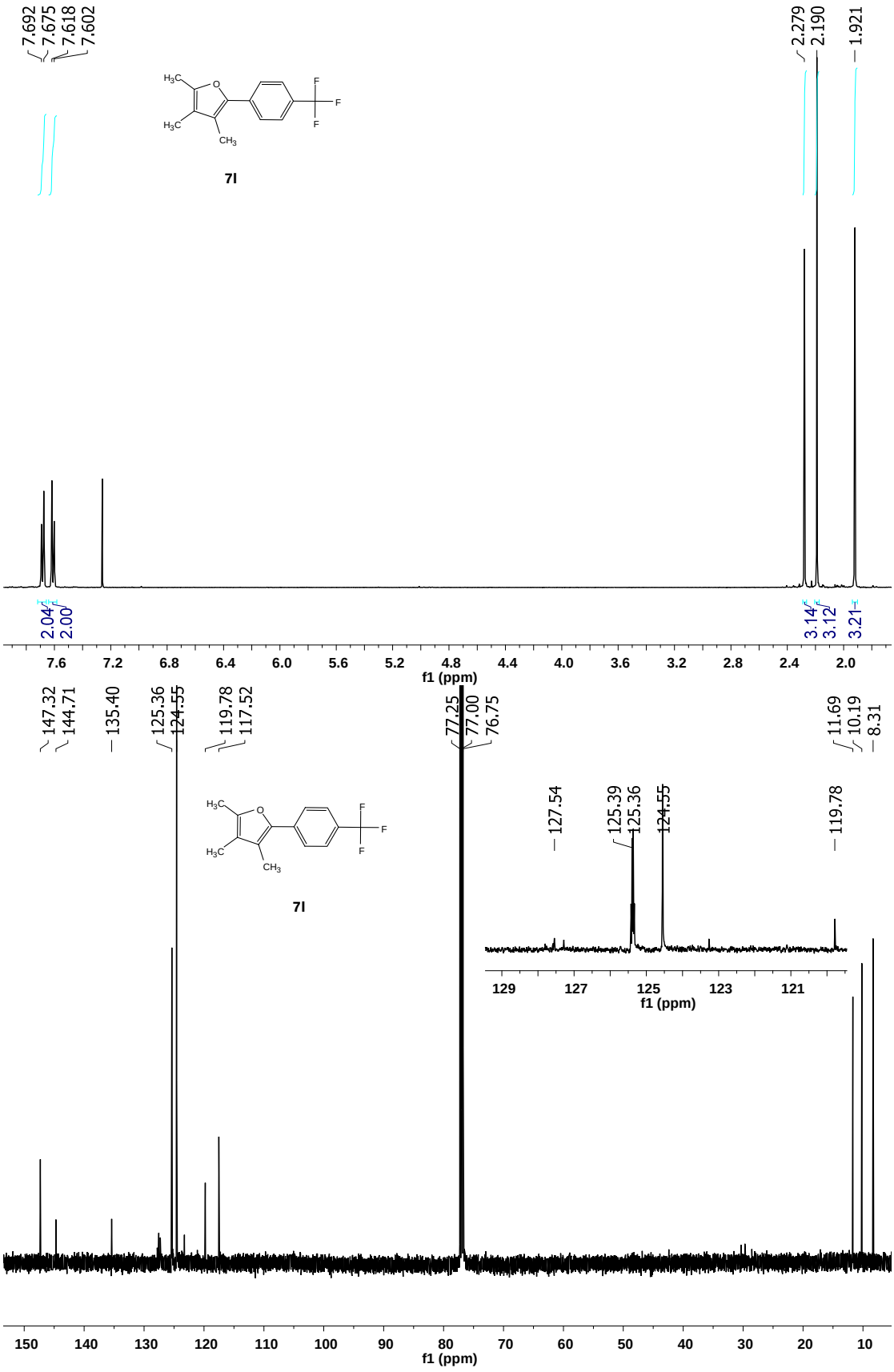

7.297
7.153
6.042
2.395
2.381
2.332
1.892
0.890
0.877
7i
4.21
1.14
1.00
2.15
3.10
1.07
6.44
f1 (ppm)
153.30
145.71
134.63
121.13
107.08
77.25
77.00
76.75
37.20
27.86
22.42
13.07
128.46
127.32
125.96
7i
f1 (ppm)

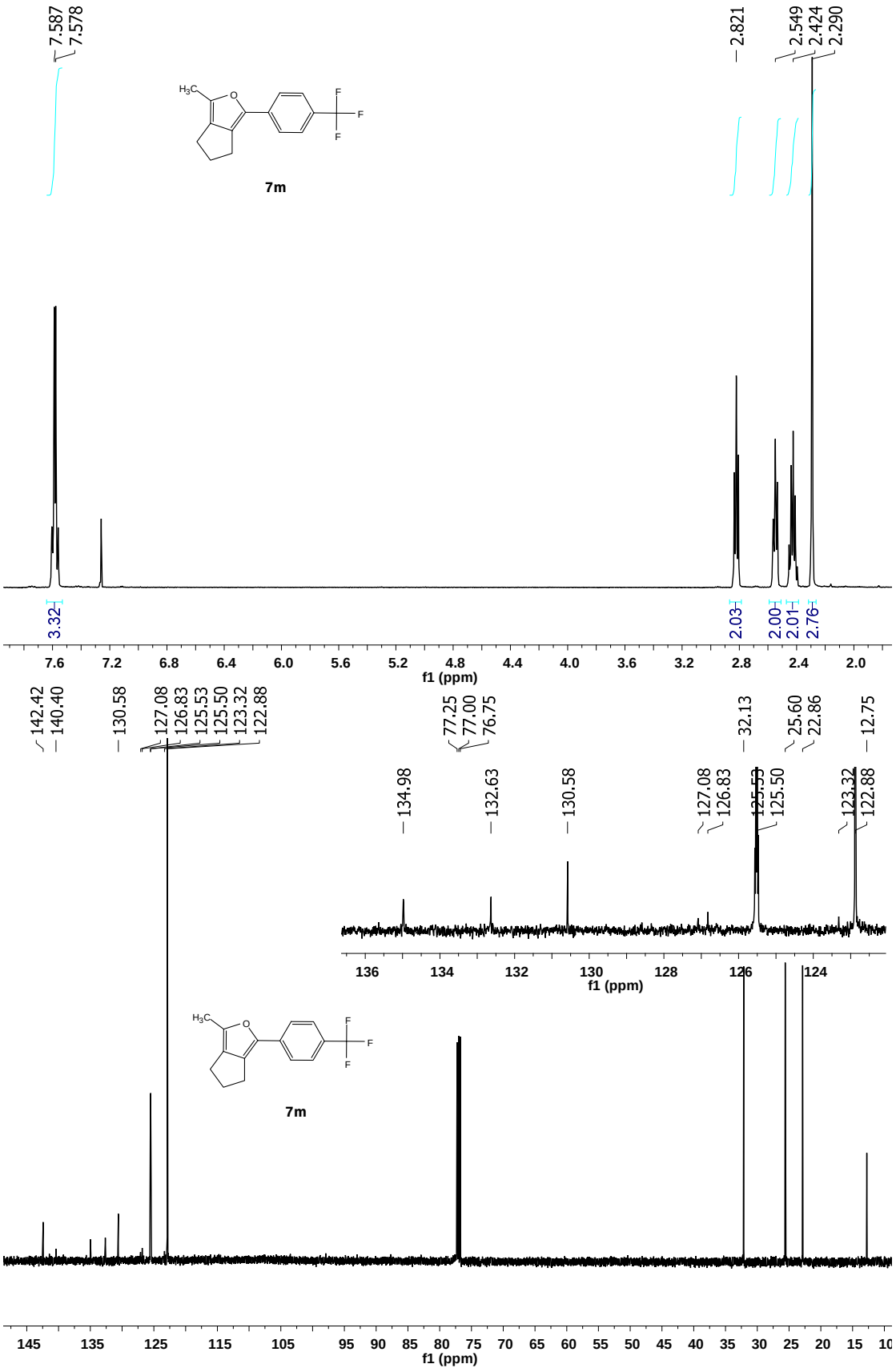

7.383
6.087
2.598
2.591
2.418
2.046
1.821
1.402
1.385
1.266
7j
4.00
0.89
0.90
0.99
2.98
2.18
1.13
2.13
4.01
1.54
f1 (ppm)

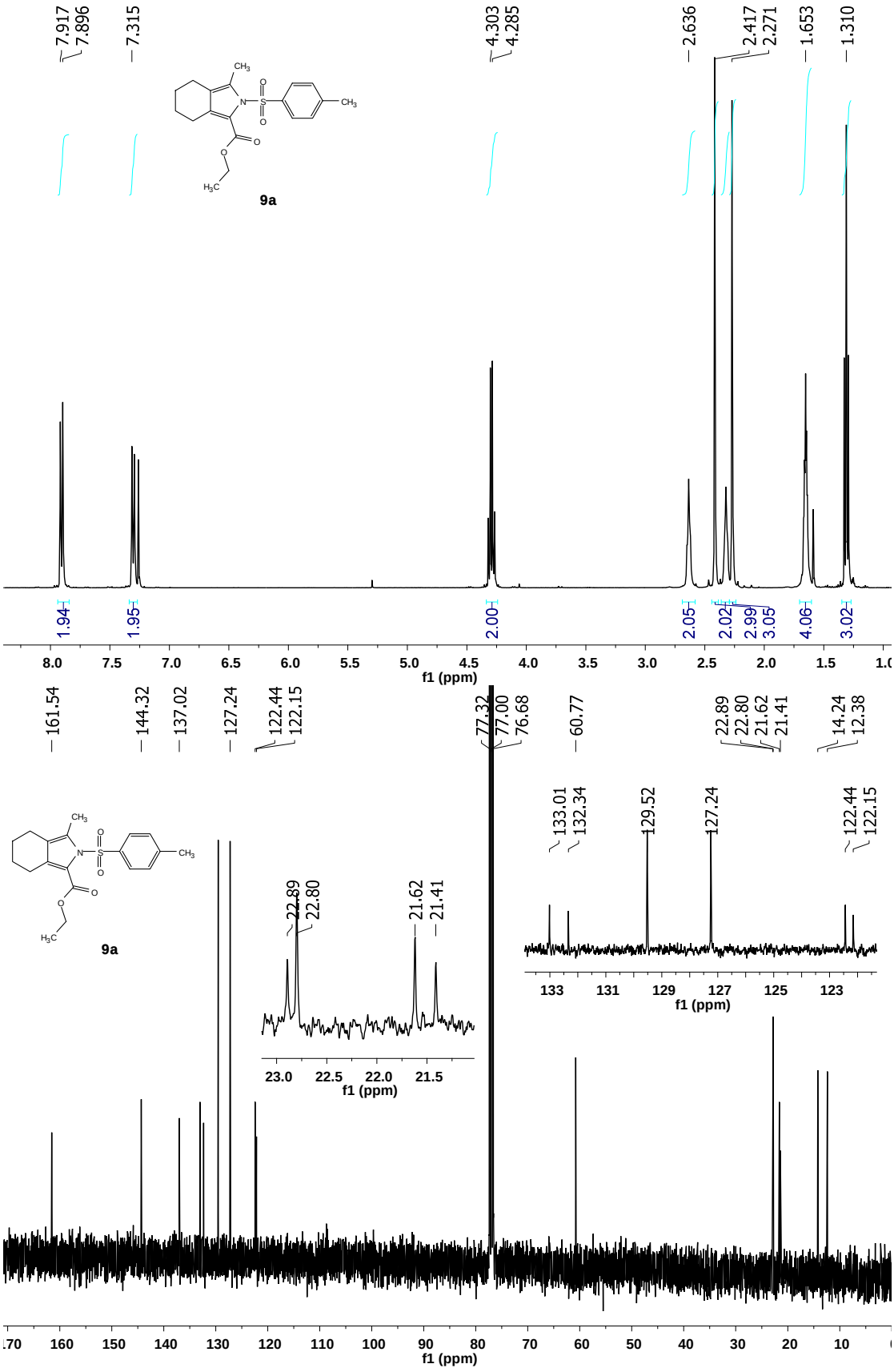

158.77
145.36
134.69
120.96
104.10
77.25
77.00
76.75
128.44
127.34
125.94
37.17
31.62
25.98
13.01
7j
128.5
127.5
126.5
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

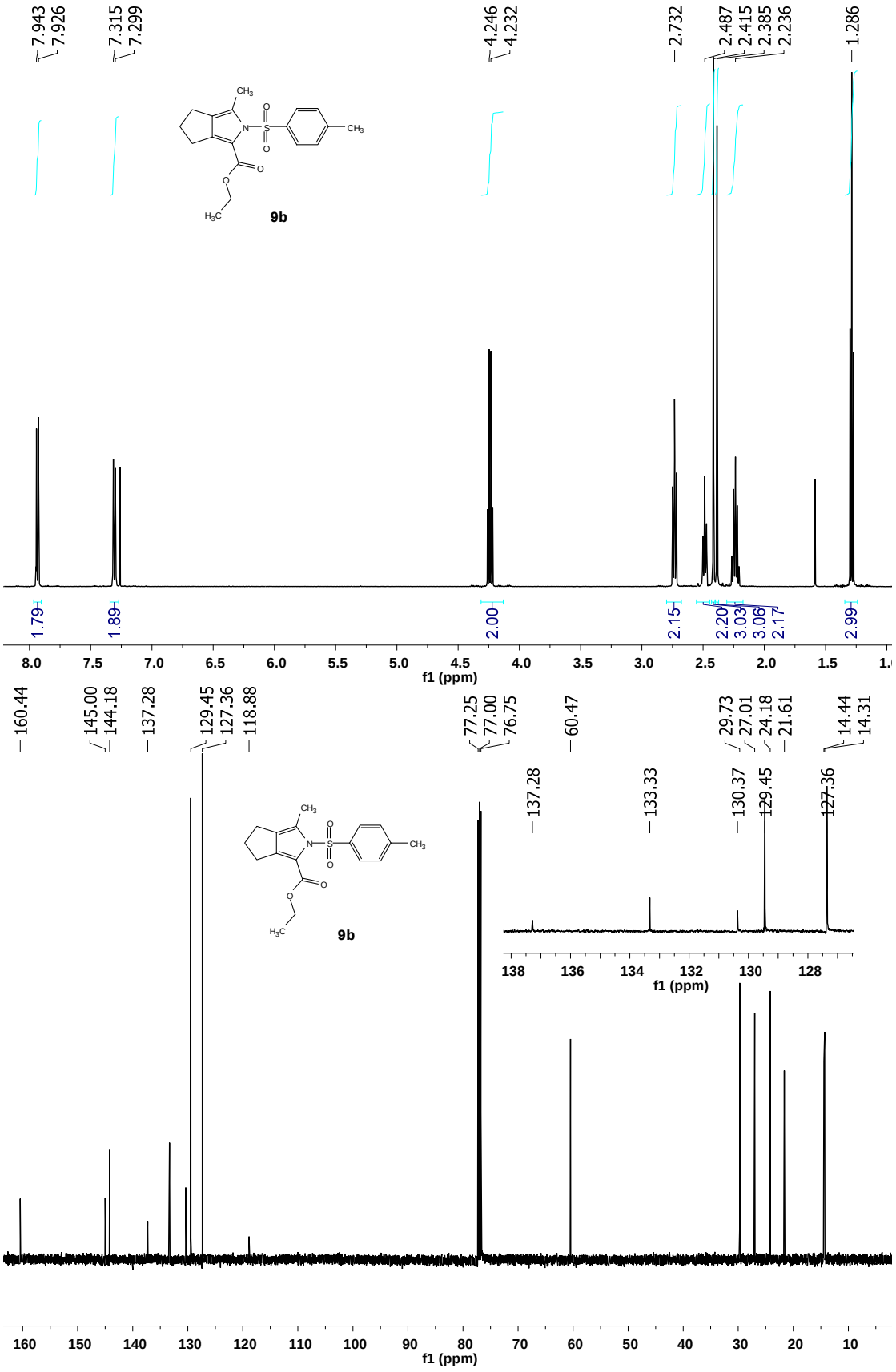

7.665
7.590
7.328
7.241
6.535
3.757
2.368
7k
2.09
2.03
1.88
2.86
1.00
2.21
3.18
f1 (ppm)

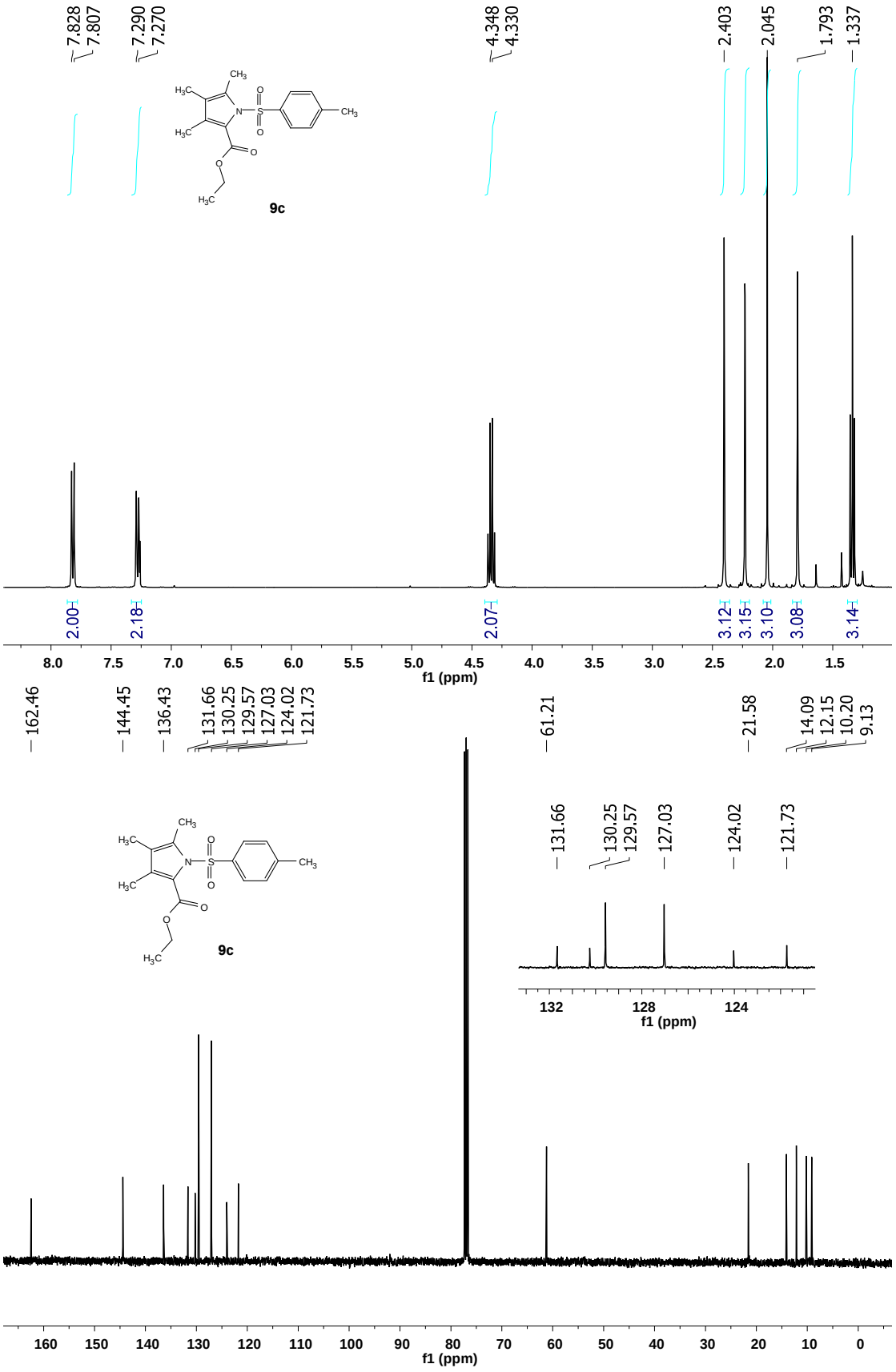

149.89
149.03
140.40
134.11
128.52
128.37
126.18
123.08
109.62
77.25
77.00
76.75
31.12
11.77
128.52
128.37
128.31
128.06
126.18
125.56
125.53
125.33
123.18
123.08
120.56
f1 (ppm)
7k
f1 (ppm)

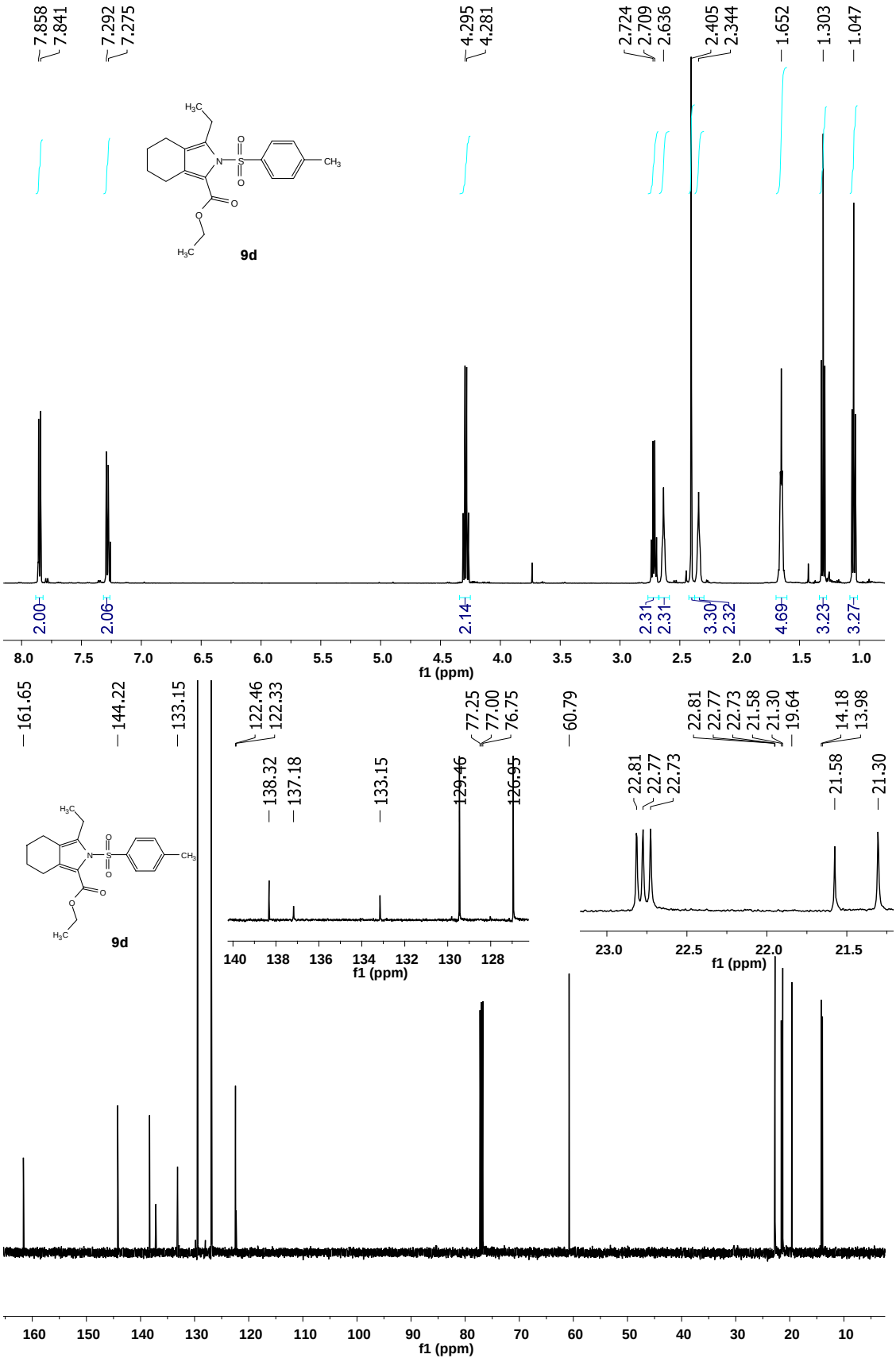

7.692
7.675
7.618
7.602
2.279
2.190
1.921
7l
2.04
2.00
3.14
3.12
3.21
f1 (ppm)
147.32
144.71
135.40
125.36
124.55
119.78
117.52
77.25
77.00
76.75
11.69
10.19
8.31
127.54
125.39
125.36
124.55
119.78
7l
f1 (ppm)

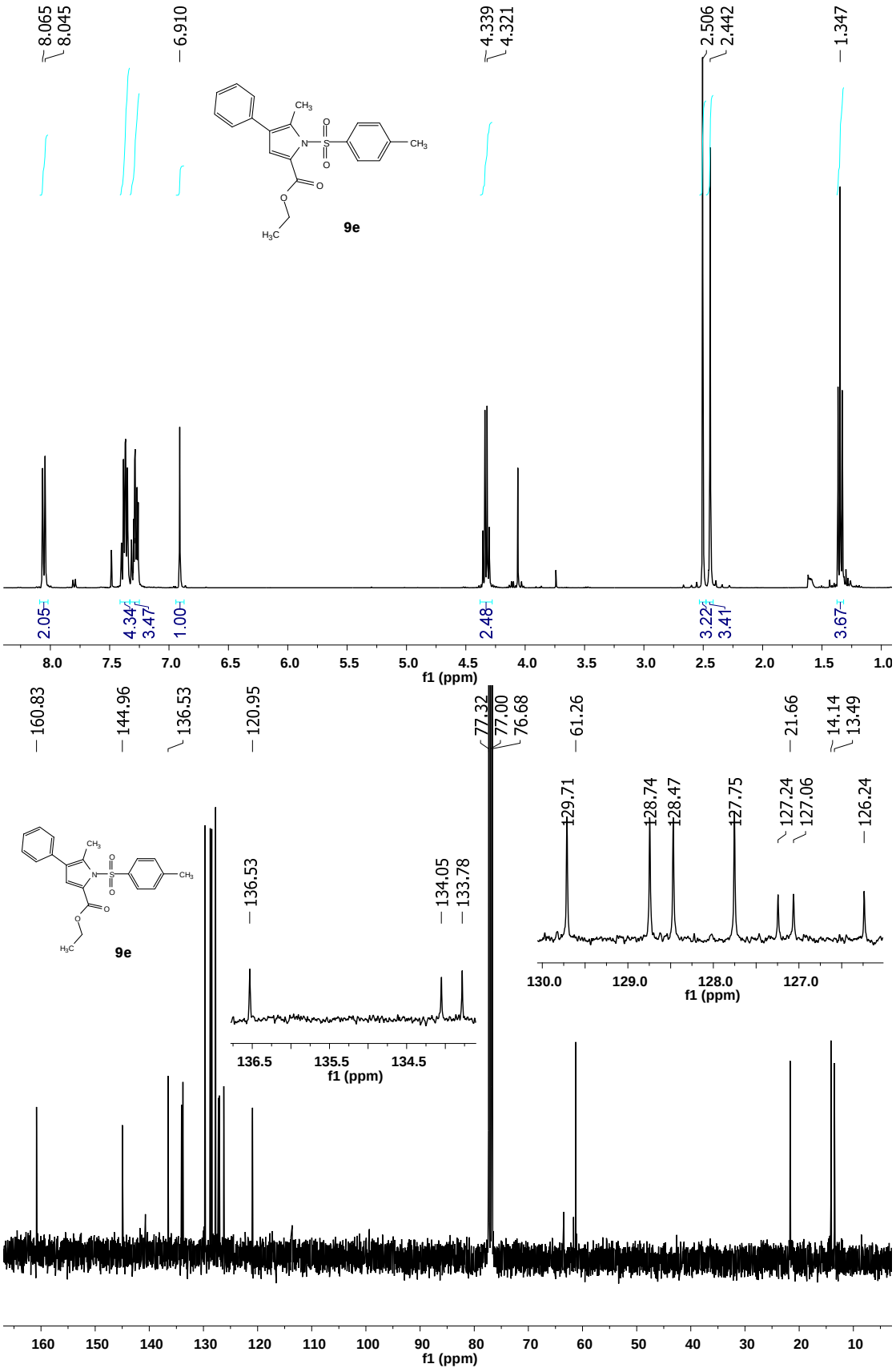

7.587
7.578
2.821
2.549
2.424
2.290
7m
3.32
2.03
2.00
2.01
2.76
f1 (ppm)
142.42
140.40
130.58
127.08
126.83
125.53
125.50
123.32
122.88
77.25
77.00
76.75
32.13
25.60
22.86
12.75
134.98
132.63
130.58
127.08
126.83
125.53
125.50
123.32
122.88
f1 (ppm)
7m
f1 (ppm)

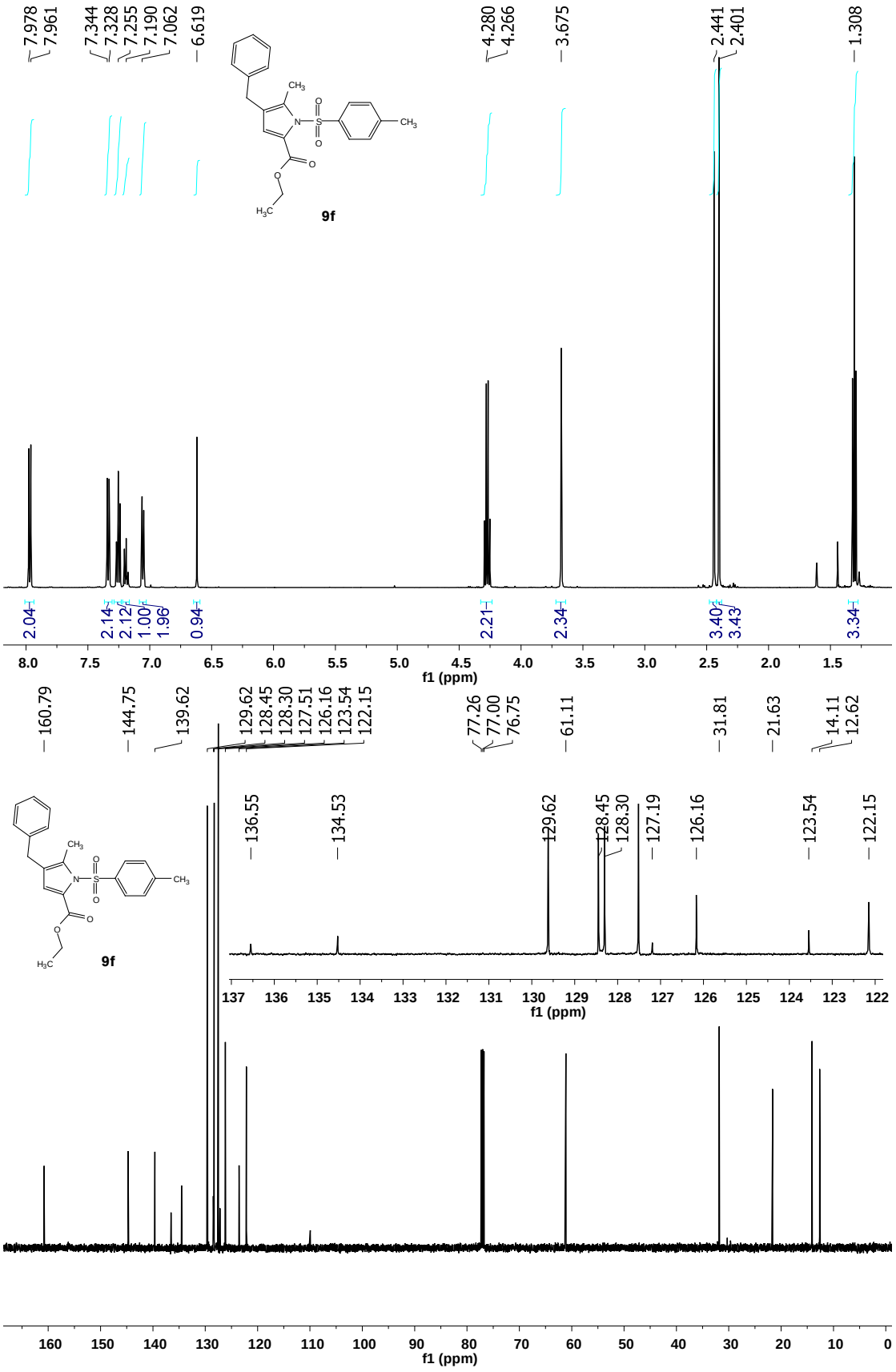

7.917
7.896
7.315
4.303
4.285
2.636
2.417
2.271
1.653
1.310
9a
1.94
1.95
2.00
2.05
2.02
2.99
3.05
4.06
3.02
f1 (ppm)
161.54
144.32
137.02
127.24
122.44
122.15
77.32
77.00
76.68
60.77
22.89
22.80
21.62
21.41
14.24
12.38
133.01
132.34
129.52
127.24
122.44
122.15
9a
f1 (ppm)


7.943
7.926
7.315
7.299
4.246
4.232
2.732
2.487
2.415
2.385
2.236
1.286
9b
1.79
1.89
2.00
2.15
2.20
3.03
3.06
2.17
2.99
f1 (ppm)
160.44
145.00
144.18
137.28
129.45
127.36
118.88
77.25
77.00
76.75
60.47
29.73
27.01
24.18
21.61
14.44
14.31
137.28
133.33
130.37
129.45
127.36
9b
f1 (ppm)


7.828
7.807
7.290
7.270
4.348
4.330
2.403
2.045
1.793
1.337
9c
2.00
2.18
2.07
3.12
3.15
3.10
3.08
3.14
f1 (ppm)
162.46
144.45
136.43
131.66
130.25
129.57
127.03
124.02
121.73
61.21
21.58
14.09
12.15
10.20
9.13
9c
f1 (ppm)


7.858
7.841
7.292
7.275
4.295
4.281
2.724
2.709
2.636
2.405
2.344
1.652
1.303
1.047
9d
2.00
2.06
2.14
2.31
2.31
3.30
2.32
4.69
3.23
3.27
f1 (ppm)
161.65
144.22
133.15
122.46
122.33
77.25
77.00
76.75
60.79
22.81
22.77
22.73
21.58
21.30
19.64
14.18
13.98
138.32
137.18
133.15
129.46
126.95
21.58
21.30
9d
f1 (ppm)
f1 (ppm)


8.065
8.045
6.910
4.339
4.321
2.506
2.442
1.347
9e
2.05
4.34
3.47
1.00
2.48
3.22
3.41
3.67
f1 (ppm)
160.83
144.96
136.53
120.95
77.32
77.00
76.68
61.26
21.66
14.14
13.49
129.71
128.74
128.47
127.75
127.24
127.06
126.24
134.05
133.78
f1 (ppm)
f1 (ppm)


7.978
7.961
7.344
7.328
7.255
7.190
7.062
6.619
4.280
4.266
3.675
2.441
2.401
1.308
9f
2.04
2.14
2.12
1.00
1.96
0.94
2.21
2.34
3.40
3.43
3.34
f1 (ppm)
160.79
144.75
139.62
129.62
128.45
128.30
127.51
126.16
123.54
122.15
77.26
77.00
76.75
61.11
31.81
21.63
14.11
12.62
136.55
134.53
129.62
128.45
128.30
127.19
126.16
123.54
122.15
9f
f1 (ppm)
f1 (ppm)