

Photo-Fries Rearrangement in Flow under Aqueous Micellar Conditions

Chia-Chen Chien, Shih-Chieh Kao, Chun-Jen Chen, and Yen-Ku Wu*

Department of Applied Chemistry, National Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan

E-mail: yenkuwu@nctu.edu.tw

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General Information

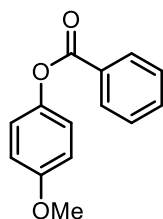
All air-sensitive reactions were conducted in flame-dried glassware under N₂ atmosphere by using Schenk techniques. Acetonitrile, 1,4-dioxane, tetrahydrofuran (THF), and dichloromethane (DCM) were purified by passage over activated alumina using a commercial solvent purification system. All other solvents (ACS grade) and commercially obtained reagents were used as received. Aluminum heating blocks were applied to all thermal reactions. Reactions were monitored by thin layer chromatography (TLC) on silica gel 60 Å F254 plates, visualized by UV (254 nm) and KMnO₄ (or phosphomolybdic acid) staining solution. Flash chromatography was performed on silica gel (230-400 mesh) with indicated eluents. Melting points were uncorrected. NMR spectra were measured at 400 or 600 MHz for ¹H spectra and 100 or 150 MHz for ¹³C spectra and calibrated from residual solvent signals (δ7.26 ppm for ¹H NMR and 77.16 ppm for ¹³C NMR in CDCl₃, δ2.5 ppm for ¹H NMR and 39.51 ppm for ¹³C NMR in DMSO). Chemical shifts were denoted in ppm (δ), and the following abbreviations were used to explain the multiplicities: s = singlet, br = broad, br s = broad singlet, br d = broad doublet, d = doublet, t = triplet, q = quartet, p = pentate, dd = doublet of doublets, td = triple of doublets, dt = double of triplets, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). FTIR spectra were recorded with ATR sampling technique and were reported in wave number (cm⁻¹). Mass spectra were recorded by using EI or ESI as specified in each case. For the flow reaction, syringe pump (NE-1000) was purchased from New Era Pump System, Inc.; UV light source (G8T5, 8W) was purchased from SANKYO DENKI Co.; FEP tubing (1 mm i.d.) was purchased from mK Company Ltd.

Synthesis and Characterization Data

General Procedure A for the Synthesis of Phenolic Esters

A round-bottom flask containing a phenol and an acid was vacuumed for 2 minutes. The whole system was backfilled with N₂, and then DCM (10 mL) was added to the flask. After the solution became clear, the flask was placed in an ice/water bath and then 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC; 1.0 equiv.) and 4-Dimethylaminopyridine (DMAP; 0.2 equiv.) was sequentially added to the flask. The resulting mixture was stirred overnight at room temperature. After the limiting reagent (either the phenol or the acid) was consumed as indicated by TLC analysis, the reaction mixture was diluted with DCM and extracted with water. The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude thus obtained was purified by flash column chromatography.

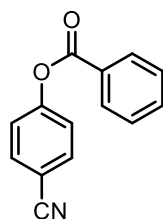
4-Methoxyphenyl benzoate (**1a**)¹



The reaction was conducted with 4-methoxyphenol (2.0 mmol) and benzoic acid (2.2 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 30/1) to afford **1a** (353 mg, 78 %) as white solid (m.p. 91-92 °C). R_f: 0.78 (hexanes/EtOAc = 2/1). IR (cast): 1728, 1503, 1453, 1265, 1245, 1193, 1181, 1172, 1102, 1081, 1061, 1032, 1022, 869, 828, 808, 754, 699, 683 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.15 (m, 2H), 6.96 (m, 2H), 3.83 (s, 3H); ¹³C NMR (400 MHz, CDCl₃): δ 165.50, 157.40, 144.51, 133.58, 130.20, 129.73, 128.62, 122.53, 114.60, 55.67; HRMS (EI, [M]⁺) for C₁₄H₁₂O₃ calcd. 228.0781, found: 228.0782.

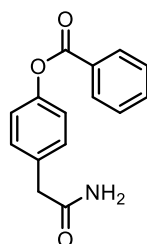
¹ W. Zu, C. Day, L. Wei, X. Jia and L. Xu, *Chem. Commun.*, 2020, **56**, 8273-8276.

4-Cyanophenyl benzoate (**1b**)¹



The reaction was conducted with 4-hydroxybenzotrile (4.0 mmol) and benzoic acid (2.0 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 10/1) to afford **1b** (366 mg, 82 %) as white solid (m.p. 95-97 °C). R_f : 0.78 (hexanes/EtOAc = 2/1). **IR** (cast): 2361, 2225, 1731, 1593, 1500, 1449, 1257, 1206, 1166, 1075, 1060, 1019, 879, 815, 698, 680, 665 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3): δ 8.16 (d, J = 7.1 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 7.4 Hz, 1H), 7.50 (t, J = 7.9 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H); **¹³C NMR** (400 MHz, CDCl_3): δ 164.16, 154.13, 134.07, 133.59, 130.16, 128.67, 128.53, 122.83, 118.17, 109.61; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{14}\text{H}_9\text{NO}_2$ calcd. 223.0627, found: 223.0625.

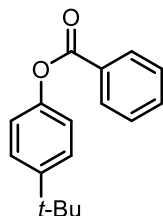
4-(2-Amino-2-oxoethyl)phenyl benzoate (**1c**)



A round-bottom flask containing 2-(4-hydroxyphenyl)acetamide (2 equiv.) and benzoic acid (2 mmol) was vacuumed for 2 minutes. The whole system was backfilled with N_2 , and then 10 mL of methanol was added to the flask. After the solution became clear, the flask was placed in an ice/water bath, and then EDC (1.0 equiv.) and DMAP (0.2 equiv.) was sequentially added to the flask. The resulting mixture was stirred overnight at room temperature. After the acid was consumed as indicated by TLC analysis, the reaction mixture was diluted with DCM and extracted with water. The combined organic layers were dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (DCM/methanol = 19/1) to afford **1c** (155 mg, 30 %) as white solid (m.p. 218-220 °C). R_f : 0.25 (DCM/methanol = 19/1). **IR** (cast): 3368, 3170, 1732, 1630, 1509, 1452, 1396, 1275, 1215, 1196, 1159, 1063, 1024, 789, 702 cm^{-1} ; **¹H NMR** (400 MHz, DMSO): δ 8.09 (d, J = 7.8 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 2H), 7.47 (s, 1H), 7.30 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 6.88 (s, 1H), 3.38 (s, 2H); **¹³C NMR** (400 MHz,

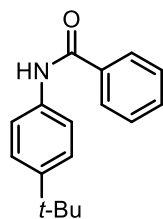
DMSO): δ 172.07, 164.65, 149.10, 134.26, 134.00, 130.11, 129.74, 128.96, 121.52, 41.50 [one sp^2 carbon is missing due to peak overlap]; HRMS (EI, $[M]^+$) for $C_{15}H_{13}NO_3$ calcd. 255.0889, found: 255.0888.

4-(*tert*-Butyl)phenyl benzoate (**1d**)²



The reaction was conducted with 4-(*tert*-butyl)phenol (2.0 mmol) and benzoic acid (1.0 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 50/1 to 30/1) to afford **1d** (199 mg, 79 %) as white solid (m.p. 97-99 °C). R_f : 0.71 (hexanes/EtOAc = 20/1). **IR** (cast): 2964, 1763, 1731, 1593, 1506, 1452, 1362, 1261, 1201, 1169, 1075, 1059, 1019, 871, 806, 703, 681 cm^{-1} ; **1H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.4 Hz, 2H), 7.65 (m, 1H), 7.52 (t, J = 8.4 Hz, 2H), 7.46 (m, 2H), 7.17 (dd, J = 8.8, 2.0 Hz, 2H), 1.37 (s, 9H); **^{13}C NMR** (400 MHz, $CDCl_3$): δ 165.42, 148.77, 148.70, 133.58, 130.25, 129.81, 128.63, 126.40, 121.10, 34.60, 31.55; **HRMS** (EI, $[M]^+$) for $C_{17}H_{18}O_2$ calcd. 254.1301, found: 254.1300.

N-(4-(*tert*-Butyl)phenyl)benzamide (**1d'**)³



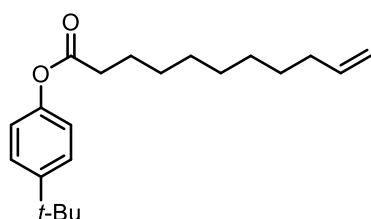
A round-bottom flask containing 4-(*tert*-butyl)aniline (4 mmol) and benzoyl chloride (4.4 mmol) was vacuumed for 2 minutes. The whole system was backfilled with N_2 , and then 20 mL of DCM was added to the flask. After the solution became clear, the flask was placed in an ice/water bath, and then *N,N*-diethylethanamine (1.1 equiv., 0.6 mL) was added to the flask. The resulting mixture was stirred for 2 hours at room temperature. After the aniline was consumed as indicated by TLC analysis, the reaction mixture was diluted with DCM and extracted with water. The organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue

² S. Chun and Y. K. Chung, *Org. Lett.*, 2017, **19**, 3787–3790.

³ S. De, J. Yin and D. Ma, *Org. Lett.*, 2017, **19**, 4864–4867.

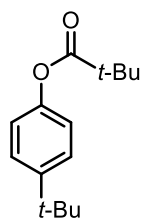
thus obtained was purified by flash column chromatography (hexanes/EtOAc = 60/1 to 30/1) to afford **1d'** (977 mg, 97 %) as white solid (m.p. 144-146 °C). R_f : 0.63 (hexanes/EtOAc = 20/1). **IR** (cast): 3289, 2959, 1645, 1514, 1486, 1267, 819, 707, 688, 647, 626, 611 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 8.17 (s, 1H), 7.84 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 1.33 (s, 9H); **^{13}C NMR** (400 MHz, CDCl_3): δ 166.05, 147.59, 135.45, 135.13, 131.72, 128.72, 127.18, 125.90, 120.34, 34.49, 31.46; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{17}\text{H}_{19}\text{NO}$ calcd. 253.1461, found: 253.1462.

4-(*tert*-Butyl)phenyl undec-10-enoate (**1e**)



The reaction was conducted with 4-(*tert*-butyl)phenol (10 mmol) and undec-10-enoic acid (5 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 30/1) to afford **1e** (1310 mg, 83 %) as colorless oil. R_f : 0.27 (hexanes/EtOAc = 30/1). **IR** (film): 2924, 2849, 1757, 1508, 1206, 1170, 1136, 1104, 1015, 992, 908, 851, 836, 722, 634 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 7.38 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 5.83 (m, 1H), 5.03-4.93 (m, 2H), 2.54 (m, 2H), 2.06 (m, 2H), 1.77 (m, 2H), 1.32 (m, 19H); **^{13}C NMR** (400 MHz, CDCl_3): δ 172.59, 148.57, 148.52, 139.26, 126.38, 120.97, 114.29, 34.54, 33.92, 31.54, 29.42, 29.33, 29.21, 29.18, 29.02, 25.10; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{21}\text{H}_{32}\text{O}_2$ calcd. 316.2396, found: 316.2393

4-(*tert*-Butyl)phenyl pivalate (**1f**)⁴

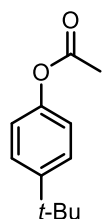


A round-bottom flask containing pivalic acid (1 mmol) was vacuumed for 2 minutes. The whole system was backfilled with N_2 . After the addition of DCM (12 mL), the flask was placed in an ice/water bath. Thionyl chloride (2 equiv., 0.15 mL) and DMF (1.3 equiv.,

⁴ H. Kitano, H. Ito and K. Itami, *Org. Lett.*, 2018, **20**, 2428–2432.

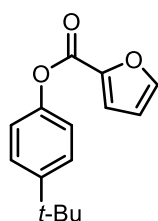
0.1 mL) was subsequently added to the flask at 0 °C. The resulting mixture was maintained at 0 °C and stirred for 1 hour. A solution of 4-(*tert*-butyl)phenol (1.05 mmol) in DCM (2 mL) was then introduced to the flask at 0 °C. The mixture was stirred for 4 hours at room temperature. The reaction mixture was diluted with DCM and extracted with water. The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 50/1 to 30/1) to afford **1f** (124 mg, 53 %) as white solid (m.p. 63-66 °C). *R_f*: 0.68 (hexanes/EtOAc = 20/1). **IR** (cast): 2964, 1746, 1507, 1260, 1205, 1169, 1123, 1102, 1077, 1056, 1022, 1015, 705 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ7.37 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 1.35 (s, 9H), 1.31 (s, 9H); **¹³C NMR** (400 MHz, CDCl₃): δ177.38, 148.88, 148.51, 126.36, 120.89, 39.19, 34.60, 31.57, 27.31; **HRMS** (EI, [M]⁺) for C₁₅H₂₂O₂ calcd. 234.1614, found: 234.1615.

1-(5-(*tert*-Butyl)-2-hydroxyphenyl)ethan-1-one (**1g**)⁵



The reaction was conducted with 4-(*tert*-butyl)phenol (6.0 mmol) and furan-2-carboxylic acid (4.0 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 30/1) to afford **1g** (793 mg, 82 %) as white solid (m.p. 117-120 °C). *R_f*: 0.37 (hexanes/EtOAc = 30/1). **IR** (cast): 2959, 1733, 1718, 1466, 1294, 1203, 1174, 1081, 1067, 1008, 926, 866, 775, 754, 595 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ7.26 (s, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 6.99 (s, 1H), 6.77 (d, *J* = 7.7 Hz, 2H), 6.18 (s, 1H), 0.96 (s, 9H); **¹³C NMR** (400 MHz, CDCl₃): δ157.02, 148.85, 147.89, 147.05, 144.03, 126.41, 120.94, 119.27, 112.18; **HRMS** (EI, [M]⁺) for C₁₅H₁₆O₃ calcd. 244.1094, found: 244.1093.

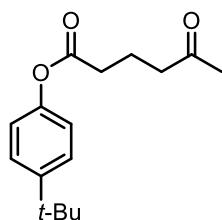
4-(*tert*-Butyl)phenyl furan-2-carboxylate (**1h**)



⁵ K. Gondo, J. Oyamada and T. Kitamura, *Org. Lett.*, 2015, **17**, 4778–4781.

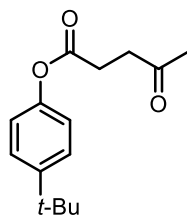
The reaction was conducted with 4-(*tert*-butyl)phenol (6.0 mmol) and furan-2-carboxylic acid (4.0 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 30/1) to afford **1h** (793 mg, 82 %) as white solid (m.p. 117-120 °C). R_f : 0.37 (hexanes/EtOAc = 30/1). **IR** (cast): 2959, 1733, 1718, 1466, 1294, 1203, 1174, 1081, 1067, 1008, 926, 866, 775, 754, 595 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 7.26 (s, 1H), 7.05 (d, $J = 7.7$ Hz, 2H), 6.99 (s, 1H), 6.77 (d, $J = 7.7$ Hz, 2H), 6.18 (s, 1H), 0.96 (s, 9H); **^{13}C NMR** (400 MHz, CDCl_3): δ 157.02, 148.85, 147.89, 147.05, 144.03, 126.41, 120.94, 119.27, 112.18, 34.51, 31.39; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{15}\text{H}_{16}\text{O}_3$ calcd. 244.1094, found: 244.1093.

4-(*tert*-Butyl)phenyl 5-oxohexanoate (**1i**)



The reaction was conducted with 4-(*tert*-butyl)phenol (3.6 mmol) and 5-oxohexanoic acid (4.0 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1 to 10/1) to afford **1i** (609 mg, 86 %) as colorless oil. R_f : 0.32 (hexanes/EtOAc = 10/1). **IR** (film): 2970, 1754, 1711, 1508, 1361, 1206, 1170, 1133, 1107, 1015 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 7.38 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 8.4$ Hz, 2H), 2.61-2.57 (m, 4H), 2.16 (s, 3H), 2.04-1.97 (m, 2H), 1.31 (s, 9H); **^{13}C NMR** (400 MHz, CDCl_3): δ 208.55, 172.51, 149.23, 148.88, 126.92, 121.45, 42.92, 35.09, 33.91, 32.05, 30.59, 19.47 [one sp^2 carbon is missing due to peak overlap]; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{16}\text{H}_{22}\text{O}_3$ calcd. 262.1563, found: 262.1558.

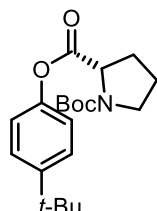
4-(*tert*-Butyl)phenyl 4-oxopentanoate (**1j**)



The reaction was conducted with 4-(*tert*-butyl)phenol (2.0 mmol) and 4-oxopentanoic acid (1.0 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 8/1) to afford **1j** (196 mg, 78 %) as colorless oil. R_f : 0.14 (hexanes/EtOAc = 8/1). **IR** (film): 2956, 2866, 1755, 1716, 1507, 1360, 1205, 1170, 1137, 1106, 1015, 914, 849 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 7.36

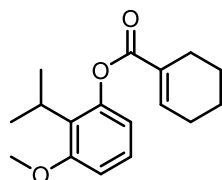
(d, $J = 8.7$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 2.80 (m, 4H), 2.18 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (400 MHz, CDCl_3): δ 206.42, 171.56, 148.53, 148.31, 126.22, 120.79, 37.86, 34.40, 31.37, 29.78, 28.15; HRMS (EI, $[\text{M}]^+$) for $\text{C}_{15}\text{H}_{20}\text{O}_3$ calcd. 248.1407, found: 248.1412.

1-(*tert*-Butyl) 2-(4-(*tert*-butyl)phenyl) pyrrolidine-1,2-dicarboxylate (**1k**)



A round-bottom flask containing 4-(*tert*-butyl)phenol (0.8 equiv.) and (*tert*-butoxycarbonyl)proline (2 mmol) was vacuumed for 2 minutes. The whole system was backfilled with N_2 , and then 10 mL of THF was added to the flask. After the solution became clear, EDC (1.0 equiv.) and DMAP (0.2 equiv.) was added at 0 °C. The resulting mixture was stirred overnight at room temperature. After the phenol was consumed as indicated by TLC analysis, the reaction mixture was diluted with DCM and extracted with water. The combined organic layers were dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 10/1) to afford **1k** (344 mg, 61 %) as white solid (m.p. 71-73 °C). R_f : 0.14 (hexanes/EtOAc = 10/1). The spectral data are reported as a mixture of *cis/trans* amide isomers. IR (cast): 2967, 2874, 1768, 1740, 1697, 1506, 1390, 1364, 1207, 1169, 1144, 1085, 917, 771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.35 (m, 2H), 7.00 (m, 2H), 4.50-4.40 (m, 1H), 3.62-3.39 (m, 2H), 2.38-1.86 (m, 4H), 1.45 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (400 MHz, CDCl_3): δ 171.67, 154.36, 153.68, 148.65, 148.42, 148.22, 126.31, 126.16, 120.74, 120.42, 80.04, 79.78, 59.14, 59.04, 46.57, 46.40, 31.38, 31.01, 29.98, 28.40, 24.41, 23.63; HRMS (EI, $[\text{M}+\text{H}]^+$) for $\text{C}_{20}\text{H}_{30}\text{NO}_4$ calcd. 348.2169, found: 348.2166.

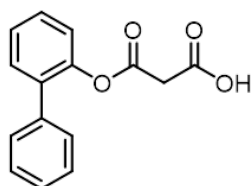
2-Isopropyl-3-methoxyphenyl cyclohex-1-ene-1-carboxylate (**1l**)



The reaction was conducted with 2-isopropyl-3-methoxyphenol (2.0 mmol) and cyclohex-1-ene-1-carboxylic acid (2.0 mmol) following the general procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 40/1 to

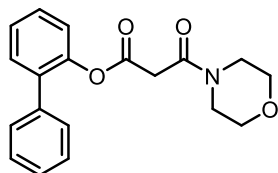
20/1) to afford **11** (364 mg, 65 %) as white solid (m.p. 77-78 °C). R_f : 0.46 (hexanes/EtOAc = 10/1). **IR** (cast): 2925, 2860, 1741, 1715, 1434, 1262, 1235, 1216, 1139, 1097, 1066, 1042, 1025, 771, 743, 732, 707, 683 cm^{-1} ; **^1H NMR** (600 MHz, CDCl_3): δ 7.25 (s, 1H), 7.15 (t, $J = 8.2$ Hz, 1H), 6.75 (dd, $J = 8.2, 1.9$ Hz, 1H), 6.63 (dd, $J = 8.2, 1.9$ Hz, 1H), 3.82 (s, 3H), 3.32 (m, 1H), 2.41 (m, 2H), 2.29 (m, 2H), 1.75 (m, 2H), 1.69 (m, 2H), 1.28 (d, $J = 7.1$ Hz, 6H); **^{13}C NMR** (600 MHz, CDCl_3): δ 166.21, 159.00, 149.78, 141.83, 130.04, 128.59, 126.55, 115.55, 108.61, 55.71, 26.10, 25.37, 24.40, 22.15, 21.49, 20.83; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{17}\text{H}_{22}\text{O}_3$ calcd. 174.1563, found: 174.1560.

3-([1,1'-Biphenyl]-2-yloxy)-3-oxopropanoic acid (**1m**)



A round-bottom flask containing 2,2-dimethyl-1,3-dioxane-4,6-dione (6.9 mmol) and [1,1'-biphenyl]-2-ol (8.3 mmol) was vacuumed for 2 minutes. The whole system was backfilled with N_2 . Then the mixture was stirred for 6 hours under refluxing conditions (oil bath temperature: 110-120 °C). After completion of the reaction indicated by TLC analysis, the reaction mixture was allowed to cool down and then diluted with DCM and extracted with water. The combined organic layers were dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (DCM/methanol = 19/1) to afford **1m** (1547 mg, 87 %) as colorless oil. R_f : 0.22 (DCM/methanol = 19/1). **IR** (film): 3419 (br), 3009, 1706, 1359, 1220, 1186, 1134, 754, 734, 700 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 9.50 (s, 1H), 7.46-7.36 (m, 8H), 7.24-7.22 (m, 1H), 3.47 (s, 2H); **^{13}C NMR** (400 MHz, CDCl_3): δ 171.44, 164.85, 147.36, 137.13, 134.85, 131.07, 128.94, 128.69, 128.43, 127.73, 126.92, 122.60, 40.96; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{15}\text{H}_{12}\text{O}_4$ calcd. 256.0730, found: 256.0727.

[1,1'-Biphenyl]-2-yl 3-morpholino-3-oxopropanoate (**1n**)



A round-bottom flask containing **1m** (1 mmol) and morpholine (1.5 mmol) was vacuumed for 2 minutes. The whole system was backfilled with N_2 , and then 10 mL of DCM was added to the flask. To the stirring mixture was added EDC (1.2 equiv.) at 0 °C.

The resulting mixture was stirred overnight at room temperature. After completion of the reaction indicated by TLC analysis, the reaction mixture was diluted with DCM and extracted with water. The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 2/1 to 2/7) to afford **1n** (179 mg, 58 %) as white solid (m.p. 95-97 °C). *R_f*: 0.17 (hexanes/EtOAc = 1/1). **IR** (cast): 2956, 2860, 1748, 1649, 1469, 1431, 1333, 1260, 1185, 1141, 1109, 1045, 971, 797, 772, 753, 737, 703, 595, 576 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.42-7.39 (m, 4H), 7.37-7.28 (m, 4H), 7.16 (d, *J* = 7.8 Hz, 1H), 3.54-3.53 (m, 4H), 3.46 (s, 2H), 3.38 (t, *J* = 4.6 Hz, 2H), 2.90 (t, *J* = 4.6 Hz, 2H); **¹³C NMR** (400 MHz, CDCl₃): δ 165.99, 163.58, 147.41, 137.51, 134.69, 130.88, 128.98, 128.78, 128.37, 127.52, 126.81, 122.60, 66.47, 66.25, 46.41, 42.14, 40.77; **HRMS** (EI, [M]⁺) for C₁₉H₁₉NO₄ calcd. 325.1308, found: 325.1306.

General Procedure B for the Photo-Fries rearrangement

The phenolic ester **1** (125 mg) was added into a 100 mL of 0.1 M aqueous solution of cetyltrimethylammonium bromide (CTAB). The mixture was stirred vigorously until compound **1** is fully dissolved. The mixture was pumped through an aluminum foil-covered FEP-tubing reactor (1.0 mm i.d.; 4.71 mL) at a rate determined by the indicated retention time (See **Figure S1**). The FEP tubing is coiled around a quartz cylinder (43 mm i.d.) and the UVC light (8W) is set up at the center (*NOTE: UVC light can cause eye and skin damage, so a precaution is essential for safety concerns*). The reaction mixture eluted from the outlet during the first 1 hour was discarded, and the subsequent portion was collected in a flask over 4 hours. The obtained mixture was diluted with DCM and extracted with brine. The combined organic layers were dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The mixture was then filtered through a pad of silica gel (hexanes/EtOAc = 5/1). The crude residue thus obtained was purified by flash column chromatography.

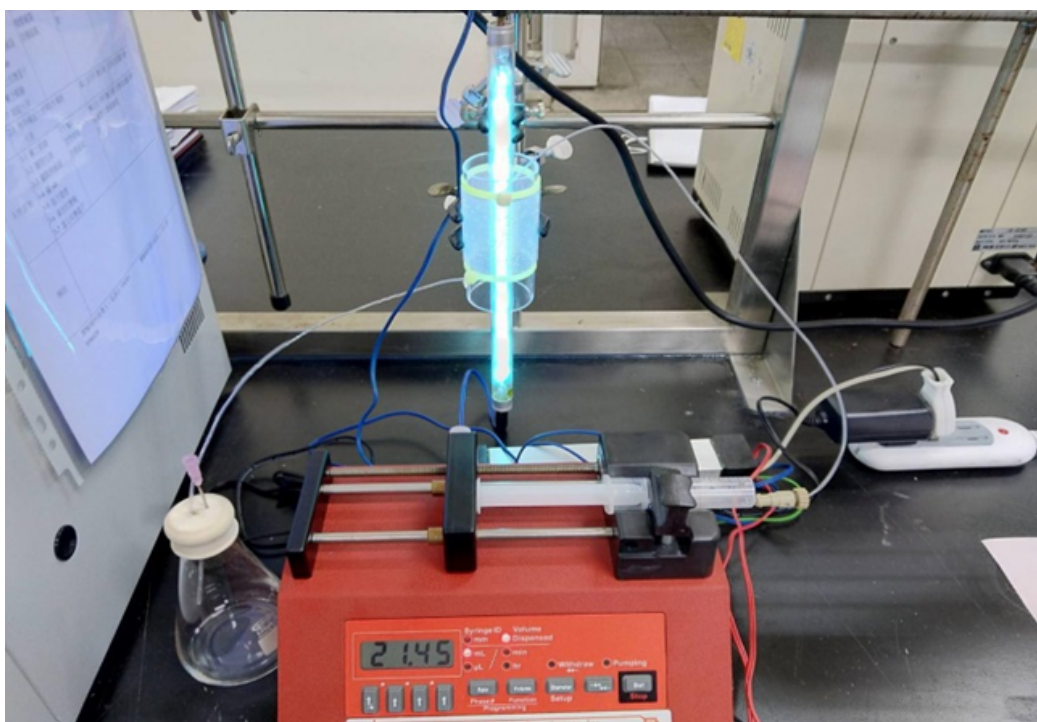
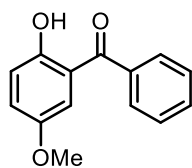


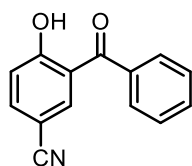
Figure S1. Experimental Setup (aluminum foil was removed for clarity) for the reaction.

(2-Hydroxy-5-methoxyphenyl)(phenyl)methanone (**2a**)⁶



The reaction was conducted with **1a** (19 mg) following the general procedure B. The retention time was 1.5 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1) to afford **2a** (10 mg, 51 %) as yellow oil. R_f : 0.29 (hexanes/EtOAc = 20/1). **IR** (film): 3441, 3001, 1708, 1418, 1358, 1220, 1091, 1037, 961, 906, 753, 705, 658 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3): δ 11.58 (s, 1H), 7.70 (d, J = 7.4 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.14 (dd, J = 9.0 Hz, 2.9 Hz, 1H), 7.06 (d, J = 2.9 Hz, 1H), 7.02 (d, J = 9.0 Hz, 1H), 3.70 (s, 3H); **¹³C NMR** (400 MHz, CDCl_3): δ 201.29, 157.65, 151.57, 138.03, 132.12, 129.22, 128.52, 124.20, 119.38, 118.83, 116.48, 56.07; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{14}\text{H}_{12}\text{O}_3$ calcd. 228.0781, found: 228.0774.

3-Benzoyl-4-hydroxybenzonitrile (**2b**)⁷

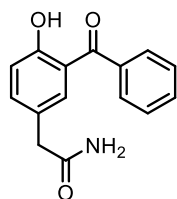


The reaction was conducted with **1b** (20 mg) following the general procedure B. The retention time was 1 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1 to 15/1) to afford **2b** (11 mg, 53 %) as white solid (m.p. 122-124 °C). R_f : 0.19 (hexanes/EtOAc = 20/1). **IR** (cast): 2229, 1621, 1592, 1477, 1443, 1342, 1299, 1255, 1225, 1179, 961, 846, 765, 696, 662, 572 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3): δ 12.47 (s, 1H), 7.96 (d, J = 2.0 Hz, 1H), 7.74 (dd, J = 2.0 Hz, 8.7 Hz, 1H), 7.68-7.66 (m, 3H), 7.56 (m, 2H), 7.16 (d, J = 8.7 Hz, 1H); **¹³C NMR** (400 MHz, CDCl_3): δ 200.54, 166.42, 138.73, 138.39, 136.62, 133.10, 129.31, 128.97, 120.22, 119.44, 118.32, 102.64; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{14}\text{H}_9\text{NO}_2$ calcd. 223.0627, found: 223.0621.

⁶ J. Hu, E. A. Adogla, Y. Ju, D. Fan and Q. Wang, *Chem. Commun.*, 2012, **48**, 11256-11258.

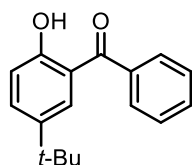
⁷ G. Slano, S. Crespi, M. Mella and S. M. Bonesi, *J. Org. Chem.*, 2019, **84**, 4338-4352.

2-(3-Benzoyl-4-hydroxyphenyl)acetamide (**2c**)



The reaction was conducted with **1c** (47 mg) following the general procedure B. The retention time was 1 hour. The crude product was purified by flash column chromatography (DCM/methanol = 19/1) to afford **2c** (24 mg, 51 %) as brown solid (m.p. 177-180 °C). R_f : 0.5 (DCM/methanol = 19/1). **IR** (cast): 3368, 3170, 1732, 1630, 1509, 1452, 1396, 1275, 1215, 1196, 1159, 1063, 1024, 789, 702 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 11.96 (s, 1H), 7.64 (m, 2H), 7.59-7.53 (m, 1H), 7.49-7.44 (m, 3H), 7.43 (dd, J = 8.5, 2.3 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 5.70 (s, 1H), 5.41 (s, 1H), 3.47 (s, 2H); **$^{13}\text{C NMR}$** (600 MHz, CDCl_3): δ 201.43, 173.37, 162.62, 137.75, 137.37, 134.22, 132.33, 129.31, 128.64, 124.96, 119.31, 119.26, 42.11; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{15}\text{H}_{13}\text{NO}_3$ calcd. 255.0889, found: 255.0890.

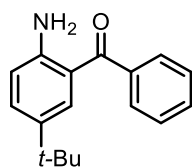
(5-(*tert*-Butyl)-2-hydroxyphenyl)(phenyl)methanone (**2d**)⁸



The reaction was conducted with **1d** (19 mg) following the general procedure B. The retention time was 1 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 50/1 to 30/1) to afford **2d** (13 mg, 67 %) as yellow oil. R_f : 0.66 (hexanes/EtOAc = 20/1). **IR** (film): 3069, 2964, 1629, 1597, 1482, 1445, 1337, 1298, 1262, 1245, 1226, 958, 695 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 11.84 (s, 1H), 7.68 (d, J = 7.7 Hz, 2H), 7.62-7.55 (m, 3H), 7.53-7.50 (m, 2H), 7.02 (d, J = 7.7 Hz, 1H), 1.25 (s, 9H); **$^{13}\text{C NMR}$** (400 MHz, CDCl_3): δ 201.77, 161.12, 141.44, 138.23, 134.05, 132.07, 129.93, 129.40, 128.44, 118.56, 118.04, 34.23, 31.39; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{17}\text{H}_{18}\text{O}_2$ calcd. 254.1301, found: 254.1299.

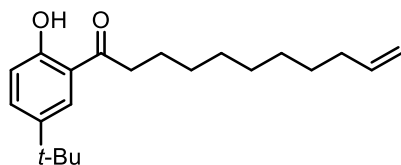
⁸ Z. Tong, Z. Tang, C.-T. Au and R. Qiu, *J. Org. Chem.*, 2020, **85**, 8533–8543.

(2-Amino-5-(*tert*-butyl)phenyl)(phenyl)methanone (2d'**)⁹**



The reaction was conducted with **1d'** (20 mg) following the general procedure B. The retention time was 3 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1 to 15/1) to afford **2d'** (8 mg, 40 %) as yellow solid (m.p. 80-82 °C). R_f : 0.19 (hexanes/EtOAc = 20/1). **IR** (cast): 3464, 3344, 2957, 1628, 1576, 1545, 1486, 1362, 1304, 1172, 955, 860, 822, 760, 711, 696, 653, 590 cm^{-1} ; **¹H NMR** (600 MHz, CDCl_3): δ 7.65 (d, J = 7.0 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.46-7.43 (m, 3H), 7.35 (dd, J = 2.3 Hz, 8.6 Hz, 1H), 6.70 (d, J = 8.6 Hz, 1H), 5.91 (s, 2H), 1.19 (s, 9H); **¹³C NMR** (600 MHz, CDCl_3): δ 199.20, 148.72, 140.29, 138.34, 131.93, 131.25, 130.76, 129.42, 128.15, 117.93, 116.98, 33.93, 31.36; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{17}\text{H}_{19}\text{NO}$ calcd. 253.1461, found: 253.1461.

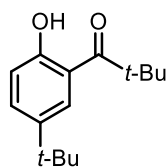
1-(5-(*tert*-Butyl)-2-hydroxyphenyl)undec-10-en-1-one (2e**)**



The reaction was conducted with **1e** (51 mg) following the general procedure B. The reaction time was 1.5 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1) to afford **2e** (31 mg, 62 %) as colorless oil. R_f : 0.3 (hexanes/EtOAc = 20/1). **IR** (film): 2923, 2854, 1763, 1639, 1486, 1462, 1363, 1262, 1206, 1170, 1138, 1105, 1015, 989, 907, 834, 785, 722, 620 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3): δ 12.24 (s, 1H), 7.70 (d, J = 2.4 Hz, 1H), 7.51 (dd, J = 8.8, 2.4 Hz, 1H), 6.91 (d, J = 8.8 Hz, 1H), 5.85-5.75 (m, 1H), 5.00-4.91 (m, 2H), 2.98 (t, J = 7.4 Hz, 2H), 2.02 (m, 2H), 1.74 (m, 2H), 1.39-1.31 (m, 19H); **¹³C NMR** (400 MHz, CDCl_3): δ 207.11, 160.48, 141.53, 139.28, 134.02, 125.91, 118.76, 118.21, 114.30, 38.41, 34.24, 33.92, 31.48, 29.85, 29.54, 29.45, 29.20, 29.04, 24.74; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{21}\text{H}_{32}\text{O}_2$ calcd. 316.2396, found: 316.2390.

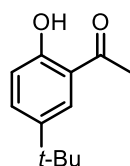
⁹ E.-Q. Ma, P. Wang, P.-H. Li and L.-P. Mo, *Res. Chem. Intermed.*, 2015, **41**, 6433–6441.

1-(5-(*tert*-Butyl)-2-hydroxyphenyl)-2,2-dimethylpropan-1-one (**2f**)¹⁰



The reaction was conducted with **1f** (19 mg) following the general procedure B. The retention time was 1.5 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 50/1 to 30/1) to afford **2f** (12 mg, 60 %) as colorless oil. R_f : 0.60 (hexanes/EtOAc = 20/1). **IR** (film): 2958, 2920, 2849, 2358, 1633, 1600, 1478, 1365, 1347, 1298, 1261, 1228, 1204, 1166, 976, 874, 824, 806, 772, 740 cm^{-1} ; **¹H NMR** (600 MHz, CDCl_3): δ 12.46 (s, 1H), 8.01 (d, J = 2.2 Hz, 1H), 7.46 (dd, J = 8.7, 2.2 Hz, 1H), 6.94 (d, J = 8.7 Hz, 1H), 1.45 (s, 9H), 1.31 (s, 9H); **¹³C NMR** (600 MHz, CDCl_3): δ 212.21, 161.43, 140.33, 133.10, 127.24, 118.81, 116.97, 44.60, 34.30, 31.56, 29.02; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{15}\text{H}_{22}\text{O}_2$ calcd. 234.1614, found: 234.1610.

1-(5-(*tert*-Butyl)-2-hydroxyphenyl)ethan-1-one (**2g**)¹¹

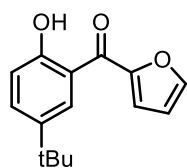


The reaction was conducted with **1g** (16 mg) following the general procedure B. The retention time was 1.5 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 40/1 to 30/1) to afford **2g** (12 mg, 60 %) as colorless oil. R_f : 0.46 (hexanes/EtOAc = 20/1). **IR** (film): 2964, 1644, 1487, 1365, 1322, 1263, 1244, 1223, 1198, 958, 634 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3): δ 12.12 (s, 1H), 7.68 (d, J = 2.4 Hz, 1H), 7.54 (dd, J = 2.4 Hz, 8.8 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 2.64 (s, 3H), 1.32 (s, 9H); **¹³C NMR** (400 MHz, CDCl_3): δ 204.72, 160.39, 141.71, 134.37, 126.61, 119.17, 118.15, 34.24, 31.47, 26.78; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{12}\text{H}_{16}\text{O}_2$ calcd. 192.1144, found: 192.1150.

¹⁰ T. Kitagawa, A. Miyabo, H. Fujii, T. Okazaki, T. Mori, M. Matsudou, T. Sugie and K. Takeuchi, *J. Org. Chem.*, 1997, **62**, 888–892.

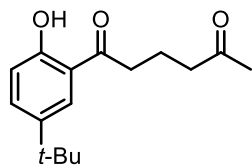
¹¹ T.-S. Jiang, B. Gan, X. Wang and X. Zhang, *Tetrahedron Lett.*, 2017, **58**, 4197–4199.

(5-(*tert*-Butyl)-2-hydroxyphenyl)(furan-2-yl)methanone (2h)



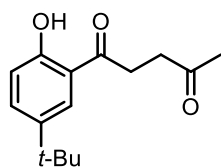
The reaction was conducted with **1h** (50 mg) following the general procedure B. The reaction time was 1 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1) to afford **2h** (28 mg, 56 %) as yellow oil. R_f : 0.35 (hexanes/EtOAc = 20/1). **IR** (film): 2962, 1626, 1584, 1558, 1485, 1461, 1363, 1335, 1300, 1253, 1235, 1176, 1015, 842, 815, 785, 758, 659, 592 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 11.83 (s, 1H), 8.23 (d, $J = 2.2$ Hz, 1H), 7.74 (s, 1H), 7.56 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.35 (d, $J = 3.6$ Hz, 1H), 6.98 (d, $J = 8.8$ Hz, 1H), 6.64 (m, 1H), 1.33 (s, 9H); **$^{13}\text{C NMR}$** (400 MHz, CDCl_3): δ 185.24, 161.17, 152.12, 147.24, 141.76, 133.89, 127.69, 120.87, 118.19, 118.03, 112.52, 34.35, 31.47; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{15}\text{H}_{16}\text{O}_3$ calcd. 244.1094, found: 244.1091.

1-(5-(*tert*-Butyl)-2-hydroxyphenyl)hexane-1,5-dione (2i)



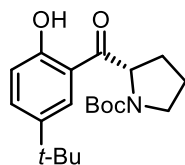
The reaction was conducted with **1i** (56 mg) following the general procedure B. The retention time was 1.5 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 30/1 to 10/1) to afford **2i** (31 mg, 56 %) as colorless oil. R_f : 0.45 (hexanes/EtOAc = 10/1). **IR** (film): 2962, 1712, 1638, 1486, 1363, 1295, 1261, 1206, 1171, 1137, 833, 779, 620 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 12.14 (s, 1H), 7.72 (s, 1H), 7.51 (d, $J = 8.8$ Hz, 1H), 6.91 (d, $J = 8.8$ Hz, 1H), 3.06-3.02 (m, 2H), 2.60-2.57 (m, 2H), 2.15 (s, 3H), 2.05-1.97 (m, 2H), 1.31 (s, 9H); **$^{13}\text{C NMR}$** (400 MHz, CDCl_3): δ 208.32, 206.26, 160.39, 141.75, 134.21, 125.91, 118.66, 118.16, 42.51, 37.23, 34.25, 31.44, 30.10, 18.41; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{16}\text{H}_{22}\text{O}_3$ calcd. 262.1563, found: 262.1560.

1-(5-(*tert*-Butyl)-2-hydroxyphenyl)pentane-1,4-dione (**2j**)



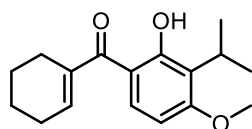
The reaction was conducted with **1j** (17 mg) following the general procedure B. The retention time was 1.5 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 15/1 to 10/1) to afford **2j** (8 mg, 49 %) as white solid (m.p. 63-65 °C). R_f : 0.14 (hexanes/EtOAc = 20/1). **IR** (cast): 2959, 2868, 1716, 1639, 1486, 1363, 1290, 1260, 1192, 1161, 998, 823, 779, 623 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 11.93 (s, 1H), 7.76 (d, J = 2.4 Hz, 1H), 7.53 (dd, J = 8.7, 2.4 Hz, 1H), 6.91 (d, J = 8.7 Hz, 1H), 3.35 (t, J = 6.2 Hz, 2H), 2.88 (t, J = 6.2 Hz, 2H), 2.27 (s, 3H), 1.31 (s, 9H); **$^{13}\text{C NMR}$** (400 MHz, CDCl_3): δ 207.16, 204.48, 160.23, 141.77, 134.29, 125.72, 118.67, 118.17, 36.77, 34.28, 32.19, 31.48, 30.24; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{15}\text{H}_{20}\text{O}_3$ calcd. 248.1407, found: 248.1400.

tert-Butyl 2-(5-(*tert*-butyl)-2-hydroxybenzoyl)pyrrolidine-1-carboxylate (**2k**)



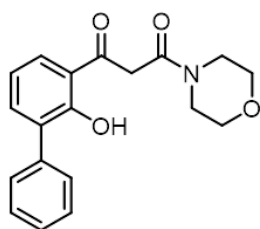
The reaction was conducted with **1k** (21 mg) following the general procedure B. The retention time was 30 minutes. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1 to 10/1) to afford **2k** (8 mg, 38 %) as white solid (m.p. 137-138 °C). $[\alpha]_D^{24}$ -10.22° (c 0.00587, chloroform) R_f : 0.1 (hexanes/EtOAc = 20/1). The spectral data are reported as a mixture of *cis/trans* amide isomers. **IR** (cast): 3373, 2967, 2871, 2372, 2330, 1700, 1684, 1636, 1399, 1388, 1363, 1260, 1157, 1119, 1111, 1081, 835, 788, 753 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 11.99-11.93 (m, 1H), 7.70 (s, 1H), 7.57-7.50 (m, 1H), 6.97-6.91 (m, 1H), 5.40-5.19 (m, 1H), 3.70-3.47 (m, 2H), 2.44-2.32 (m, 1H), 2.03-1.91 (m, 3H), 1.47 (s, 4H), 1.31-1.29 (m, 9H), 1.24 (s, 5H); **$^{13}\text{C NMR}$** (400 MHz, CDCl_3): δ 204.97, 203.89, 160.77, 160.64, 154.46, 153.63, 141.56, 141.41, 134.29, 125.18, 124.83, 118.23, 116.85, 116.75, 79.98, 60.82, 46.79, 46.64, 31.45, 31.31, 31.27, 30.43, 28.45, 28.12, 24.20, 23.73; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{20}\text{H}_{29}\text{NO}_4$ calcd. 347.2091, found: 347.2091.

Cyclohex-1-en-1-yl(2-hydroxy-3-isopropyl-4-methoxyphenyl)methanone (**2l**)



The reaction was conducted with **1l** (27 mg) following the general procedure B. The retention time was 1 hour. The crude product was purified by flash column chromatography (hexanes/EtOAc = 100/0 to 50/1) to afford **2l** (12 mg, 43 %) as colorless oil. R_f : 0.17 (hexanes). **IR** (film): 3393, 2919, 2866, 1712, 1591, 1492, 1359, 1270, 1257, 1218, 1115, 1096, 1076, 790, 683 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 12.70 (s, 1H), 7.55 (d, $J = 9.0$ Hz, 1H), 6.39 (d, $J = 9.0$ Hz, 1H), 6.19 (m, 1H), 3.86 (s, 3H), 3.61 (heptet, $J = 7.1$ Hz, 1H), 2.36 (m, 2H), 2.24 (m, 2H), 1.72 (m, 4H), 1.30 (d, $J = 7.1$ Hz, 6H); **^{13}C NMR** (400 MHz, CDCl_3): δ 202.73, 163.76, 163.05, 137.80, 136.69, 132.49, 123.09, 113.50, 101.88, 55.68, 25.55, 25.27, 23.93, 22.23, 21.82, 20.31; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{17}\text{H}_{22}\text{O}_3$ calcd. 274.1563, found: 274.1559.

1-(2-Hydroxy-[1,1'-biphenyl]-3-yl)-3-morpholinopropane-1,3-dione (**2m**)¹²



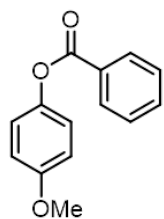
The reaction was conducted with **1n** (50 mg) following the general procedure B. The retention time was 40 minutes. The crude product was purified by flash column chromatography (hexanes/EtOAc = 2/1 to 1/2) to afford **2m** (16 mg, 33 %) as colorless oil. R_f : 0.27 (DCM/methanol = 19/1). **IR** (film): 3370, 2956, 2922, 2854, 1632, 1422, 1362, 1229, 1112 cm^{-1} ; **^1H NMR** (600 MHz, CDCl_3): δ 12.43 (s, 1H), 7.88 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.58 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.55 (m, 2H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.02 (t, $J = 7.8$ Hz, 1H), 4.18 (s, 2H), 3.70 (m, 6H), 3.54 (m, 2H); **^{13}C NMR** (600 MHz, CDCl_3): δ 200.09, 164.93, 160.35, 138.24, 136.82, 131.61, 130.34, 129.47, 128.37, 127.76, 119.38, 119.33, 66.88, 66.72, 47.19, 45.76, 42.62; **HRMS** (EI, $[\text{M}]^+$) for $\text{C}_{19}\text{H}_{19}\text{NO}_4$ calcd. 325.1308, found: 325.1308.

¹² R. J. Griffin, G. Fontana, B. T. Golding, S. Guiard, I. R. Hardcastle, J. J. J. Leahy, N. Martin, C. Richardson, L. Rigoreau, M. Stockley and G. C. M. Smith, *J. Med. Chem.*, 2005, **48**, 569–585.

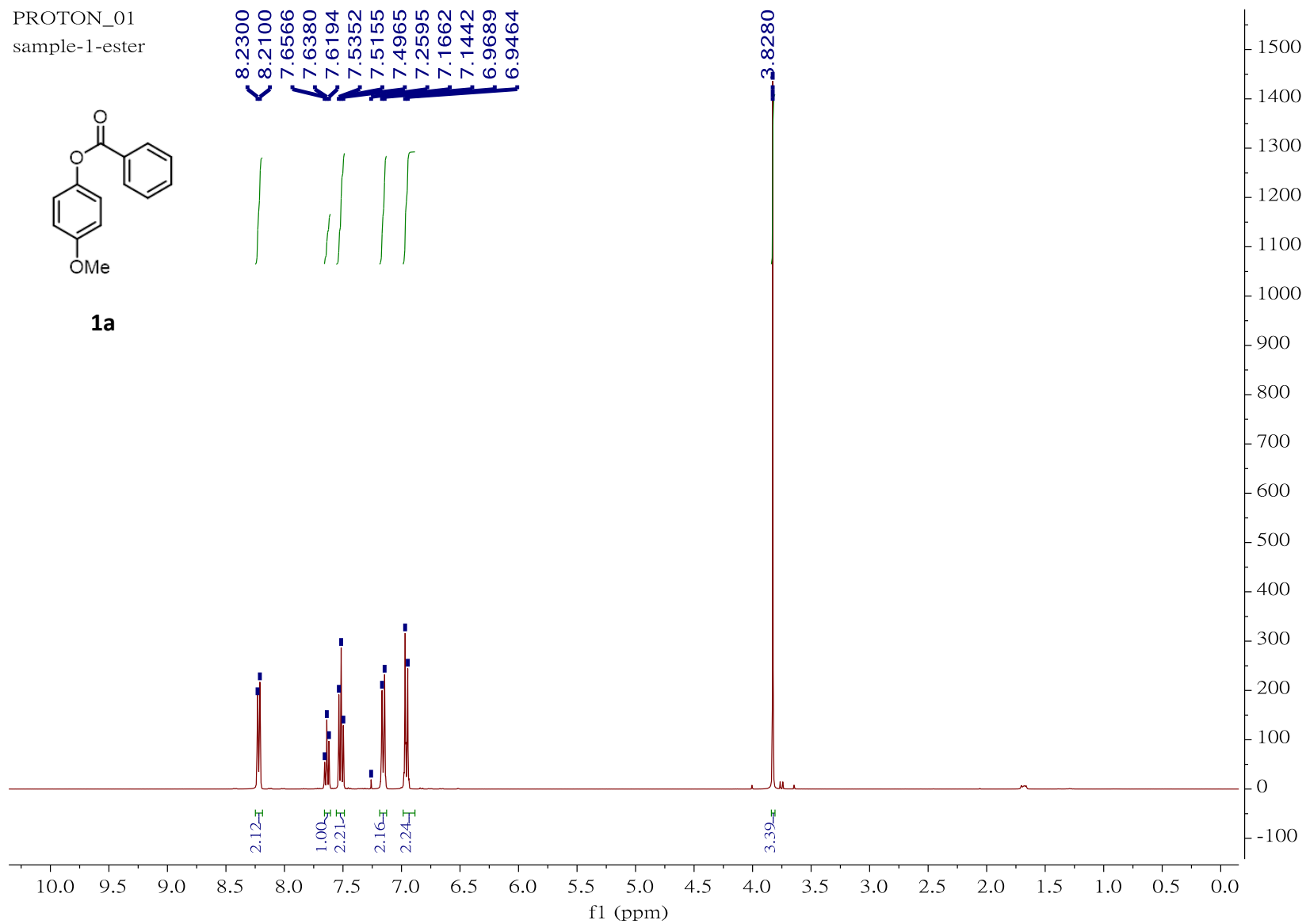
^1H and ^{13}C NMR Spectra

¹H NMR spectrum of compound 1a

PROTON_01
sample-1-ester

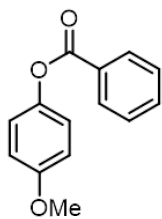


1a

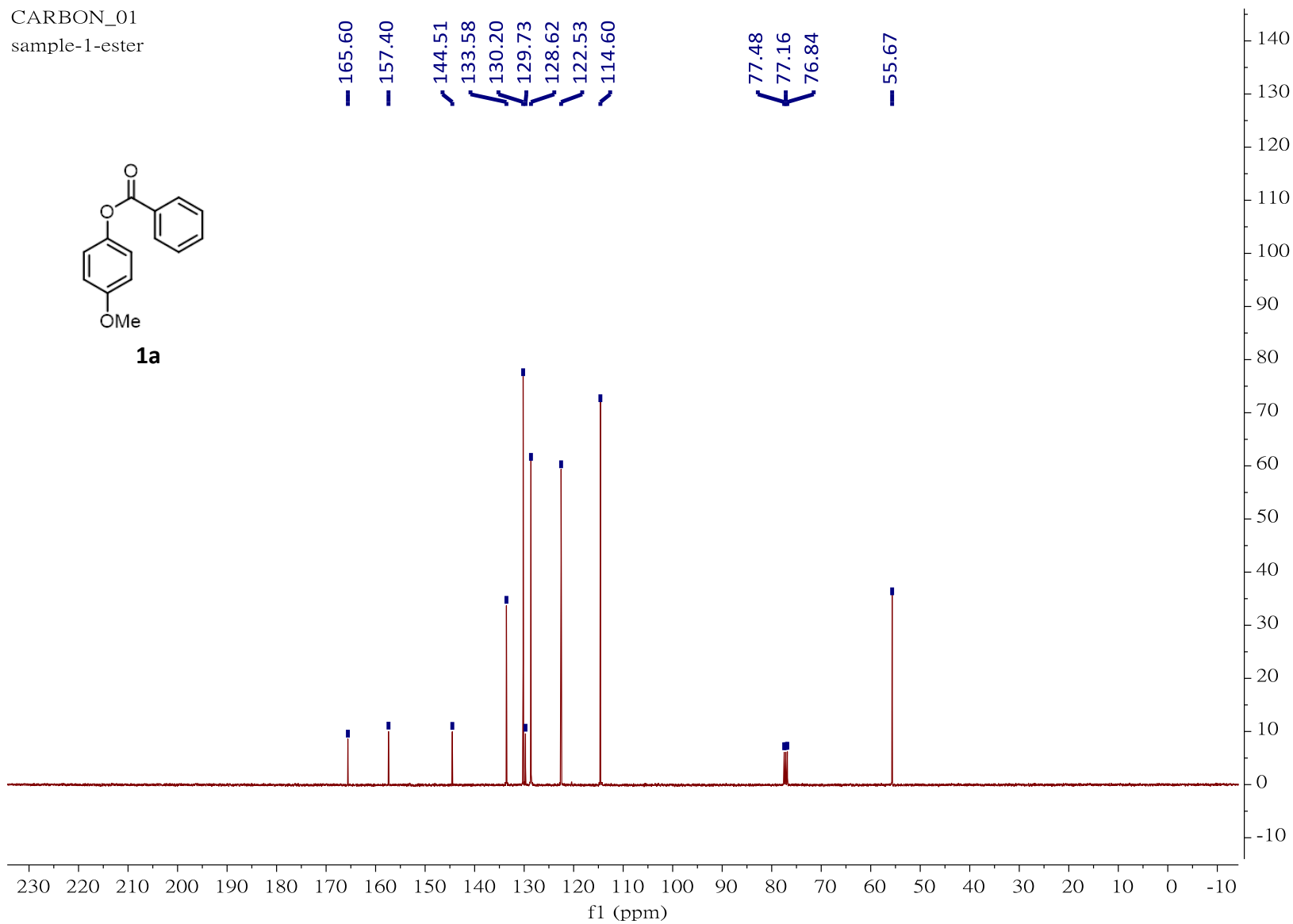


¹³C NMR spectrum of compound 1a

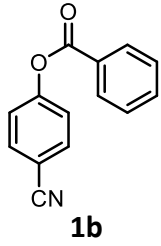
CARBON_01
sample-1-ester



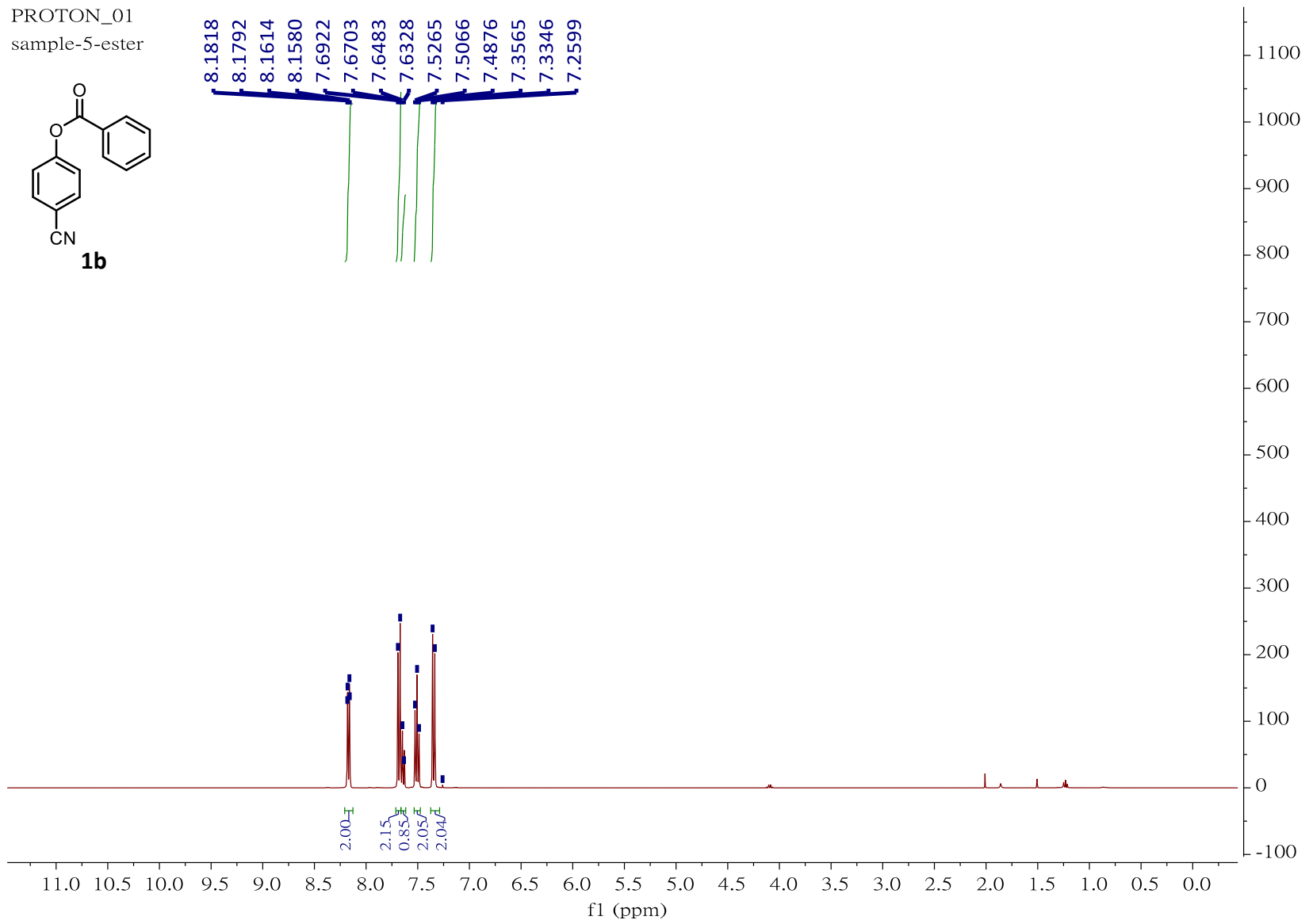
1a



PROTON_01
sample-5-ester

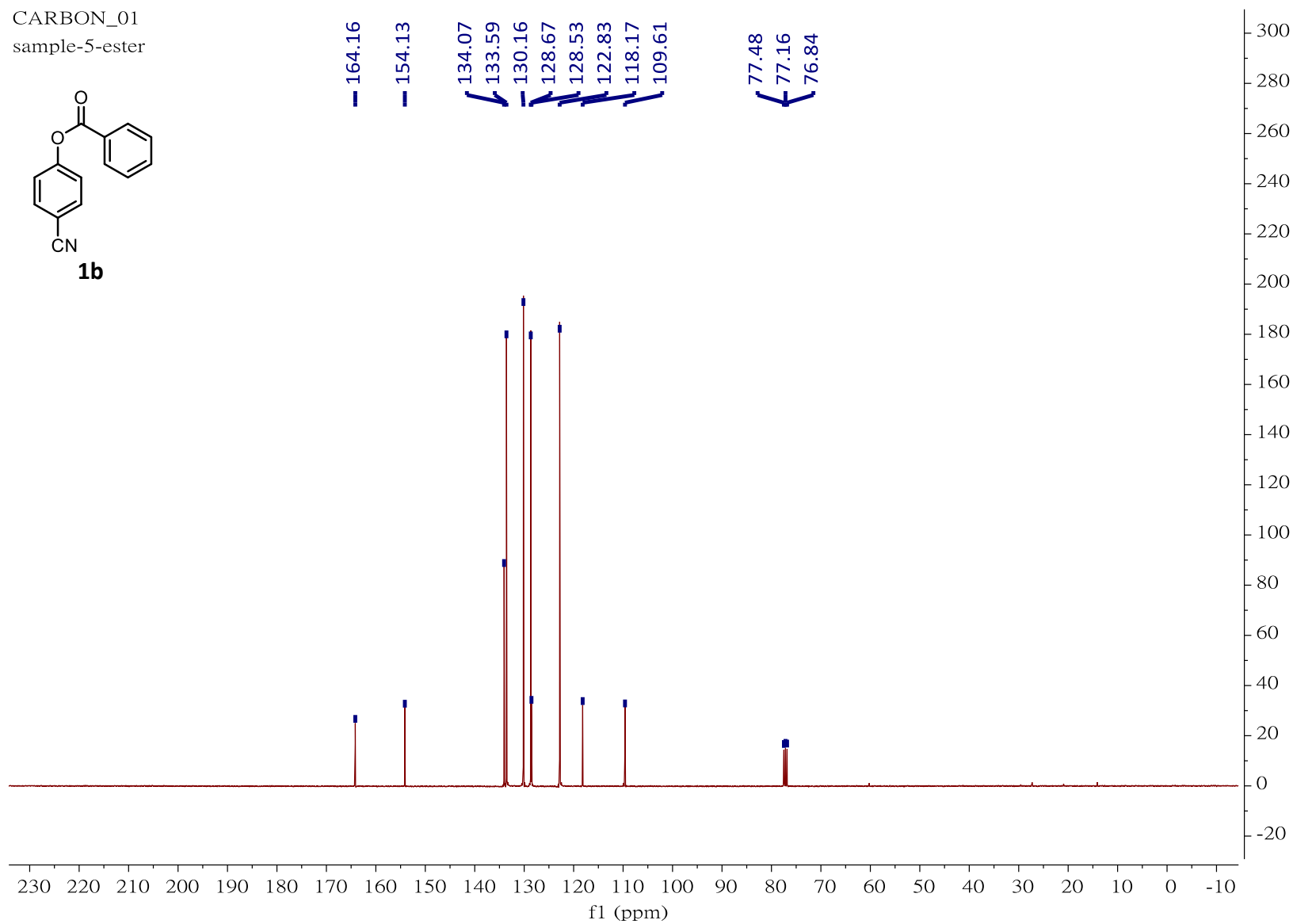
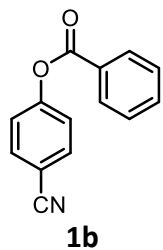


¹H NMR spectrum of compound 1b

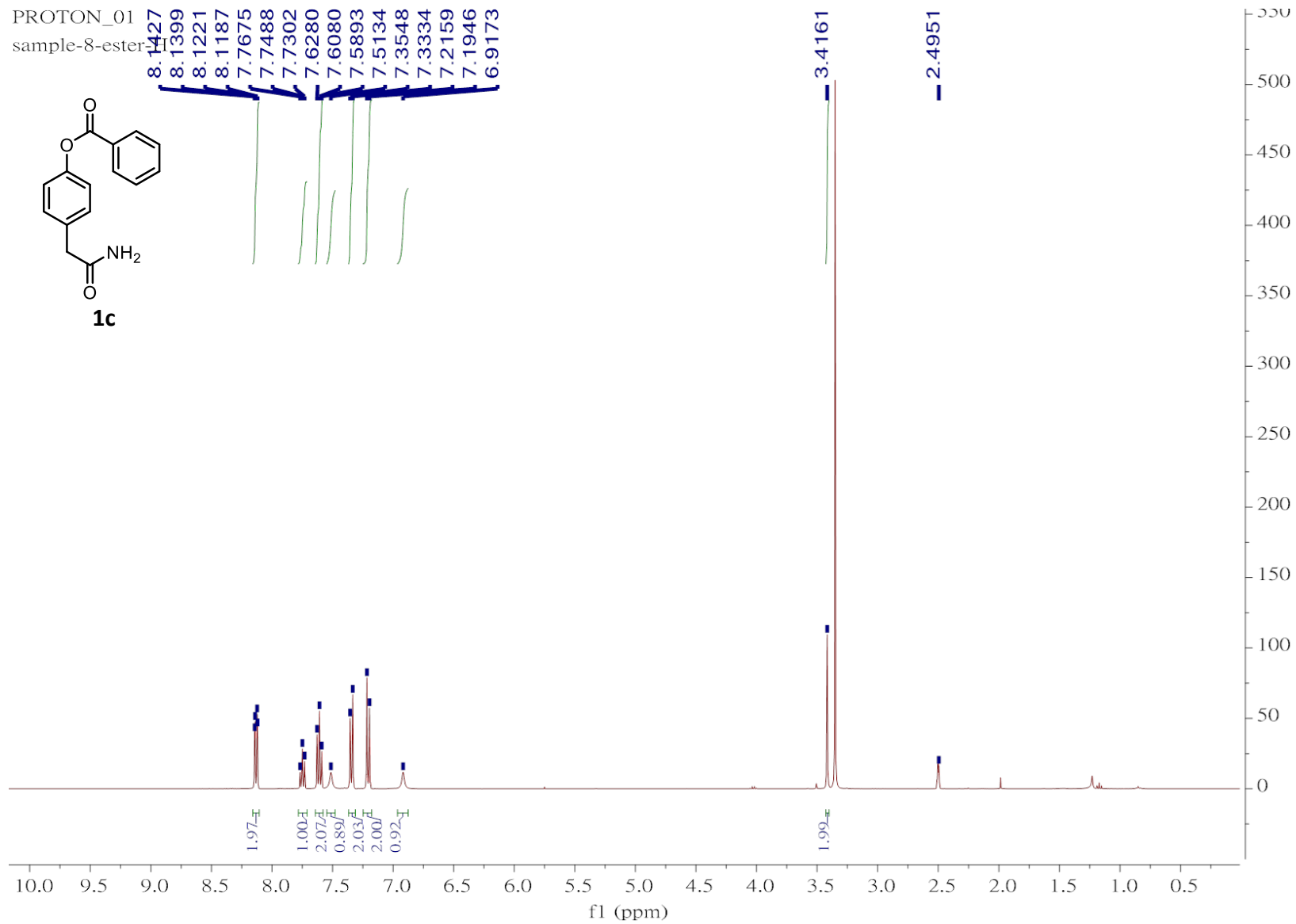


¹³C NMR spectrum of compound 1b

CARBON_01
sample-5-ester

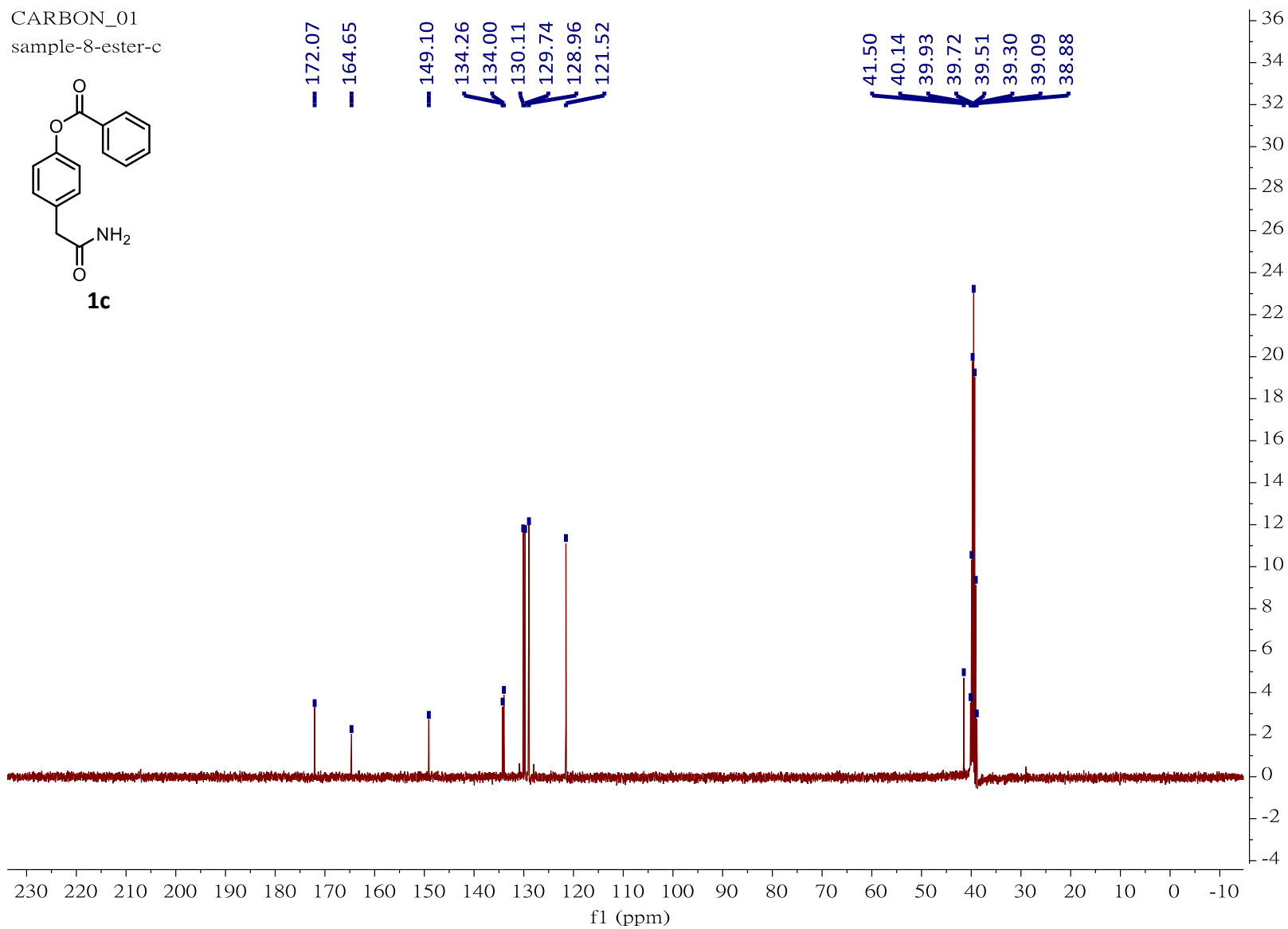
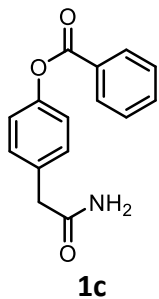


¹H NMR spectrum of compound 1c



¹³C NMR spectrum of compound 1c

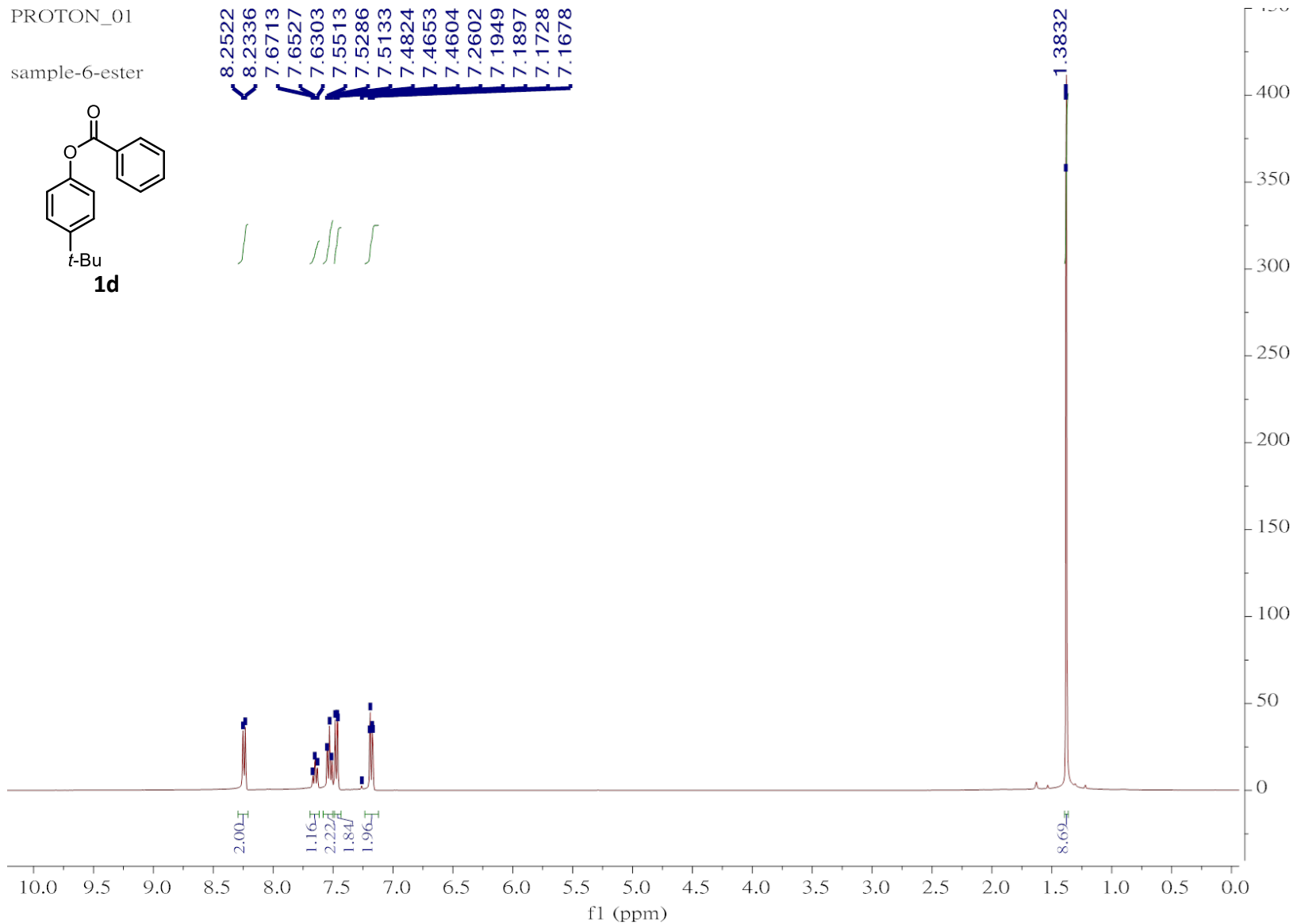
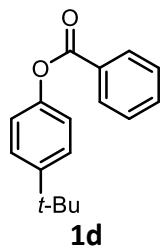
CARBON_01
sample-8-ester-c



¹H NMR spectrum of compound 1d

PROTON_01

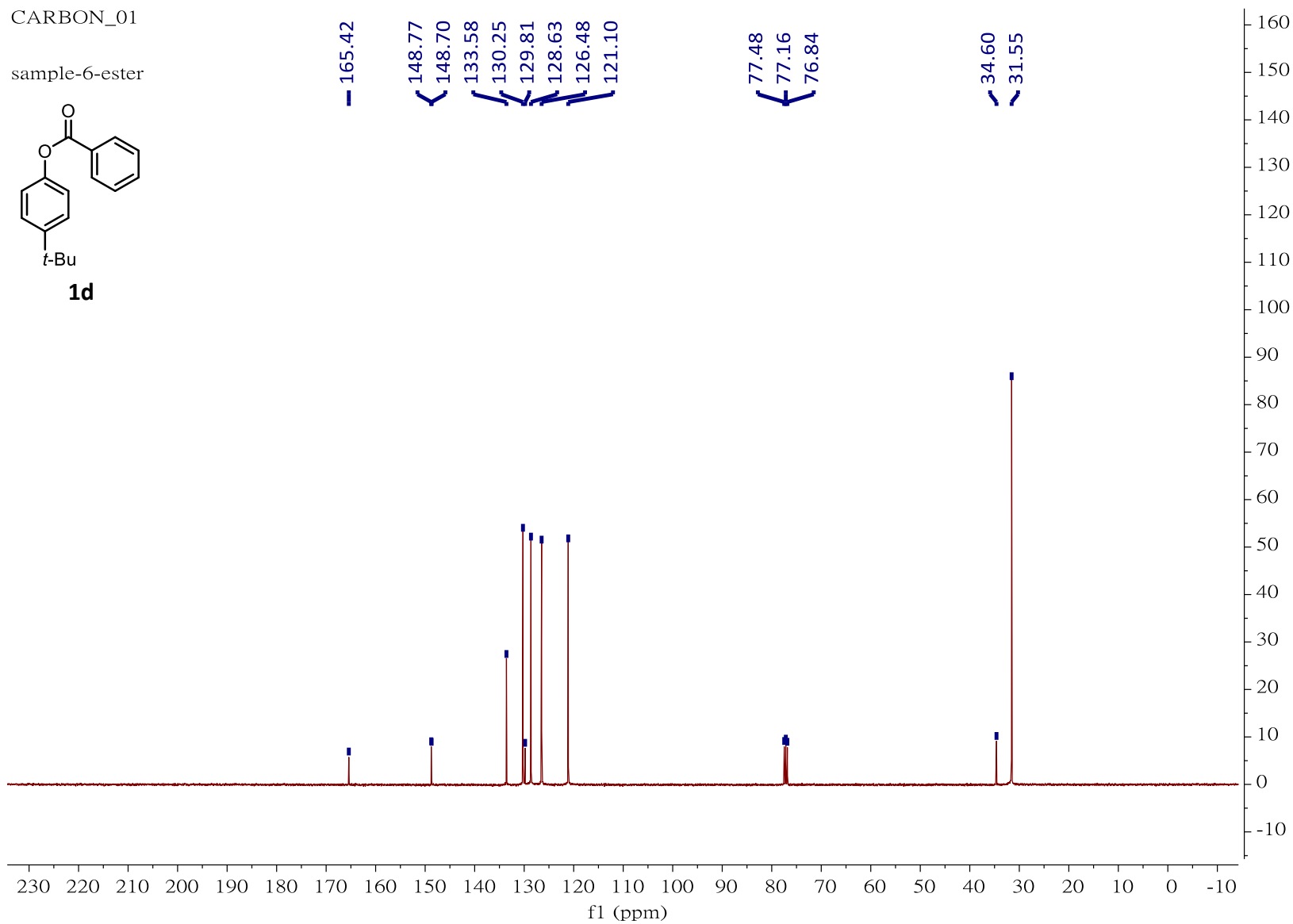
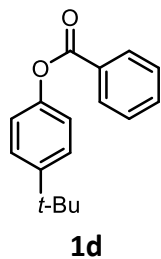
sample-6-ester



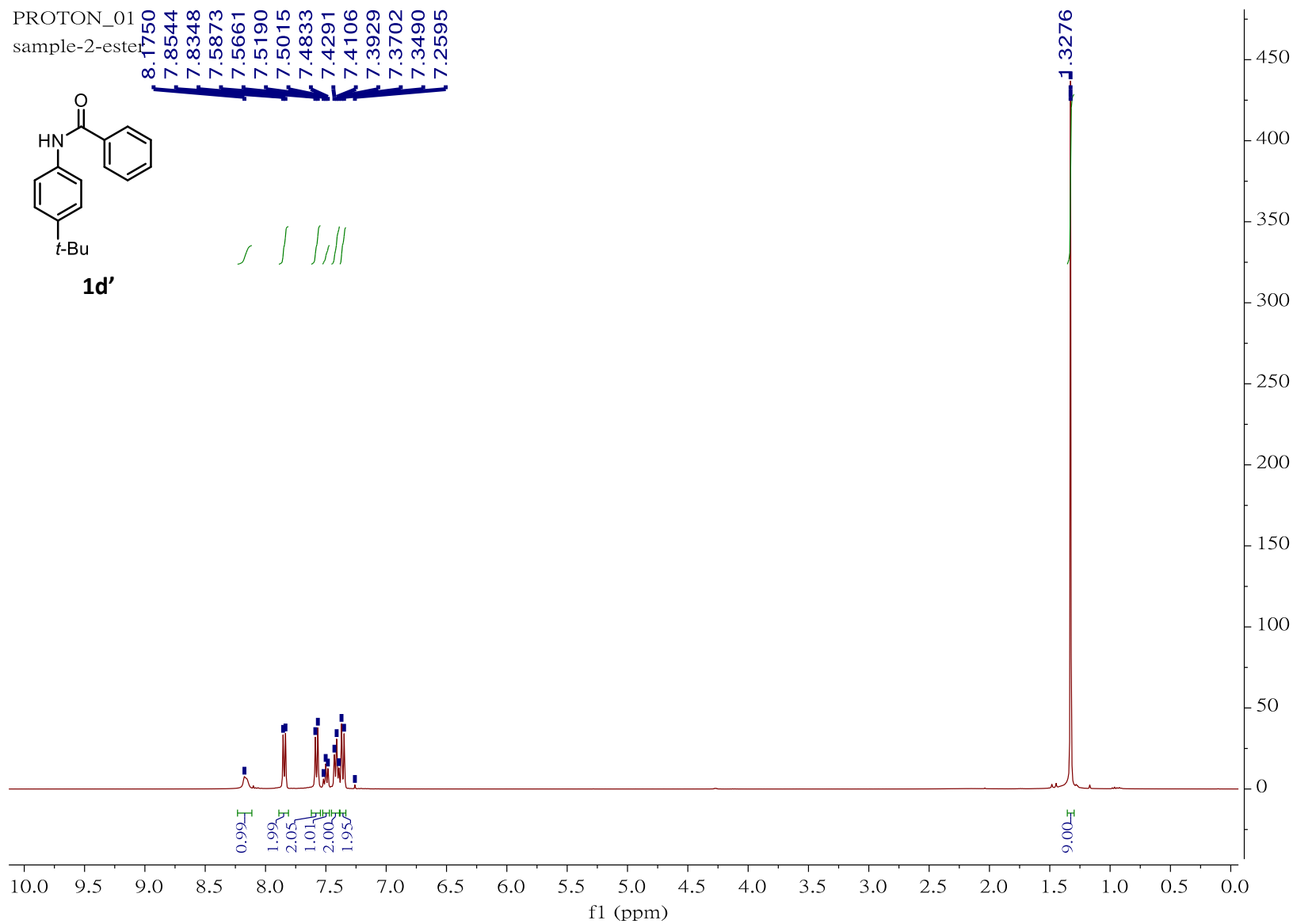
¹³C NMR spectrum of compound 1d

CARBON_01

sample-6-ester

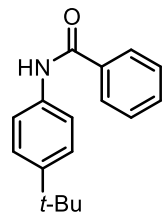


¹H NMR spectrum of compound 1d'

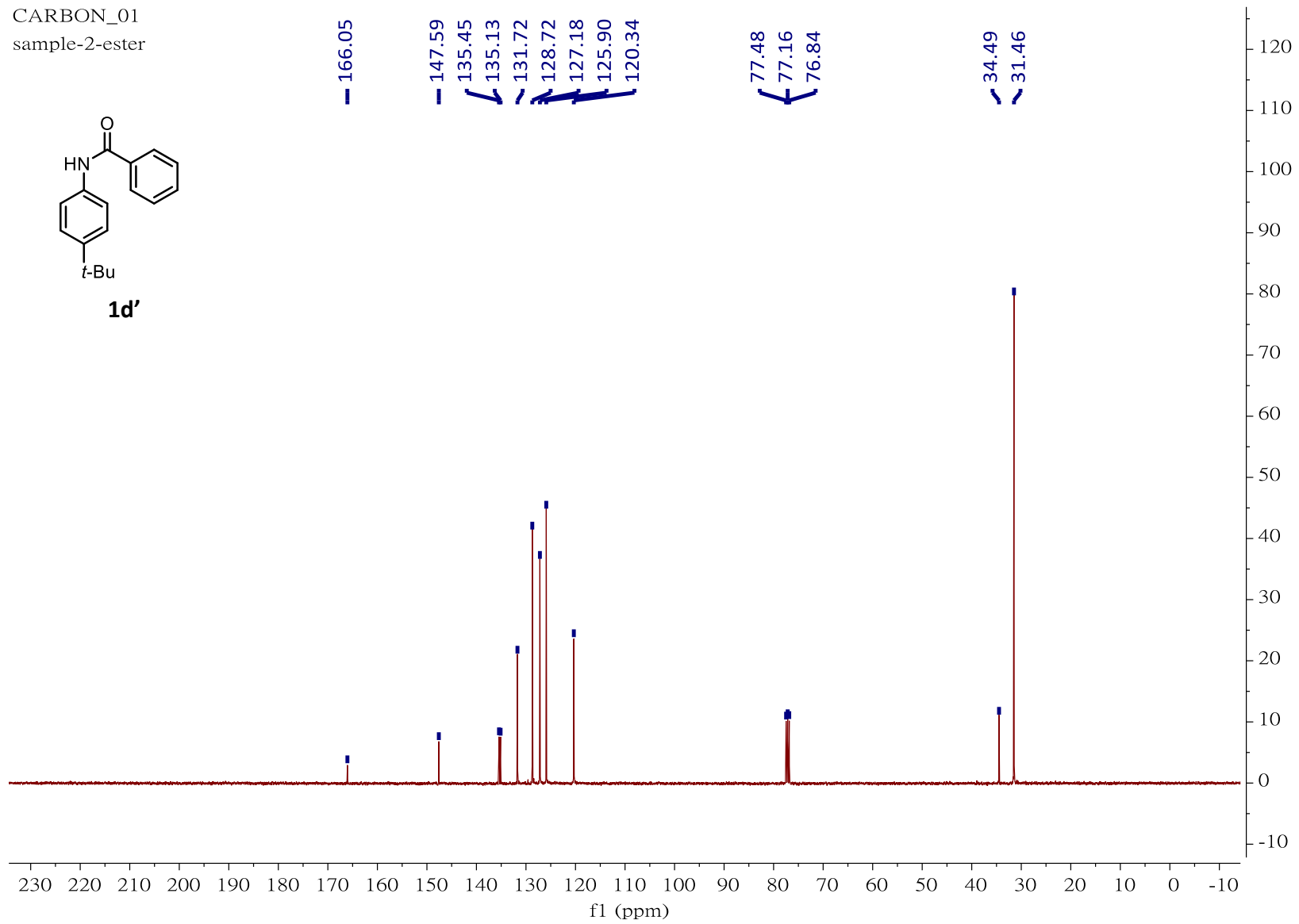


¹³C NMR spectrum of compound 1d'

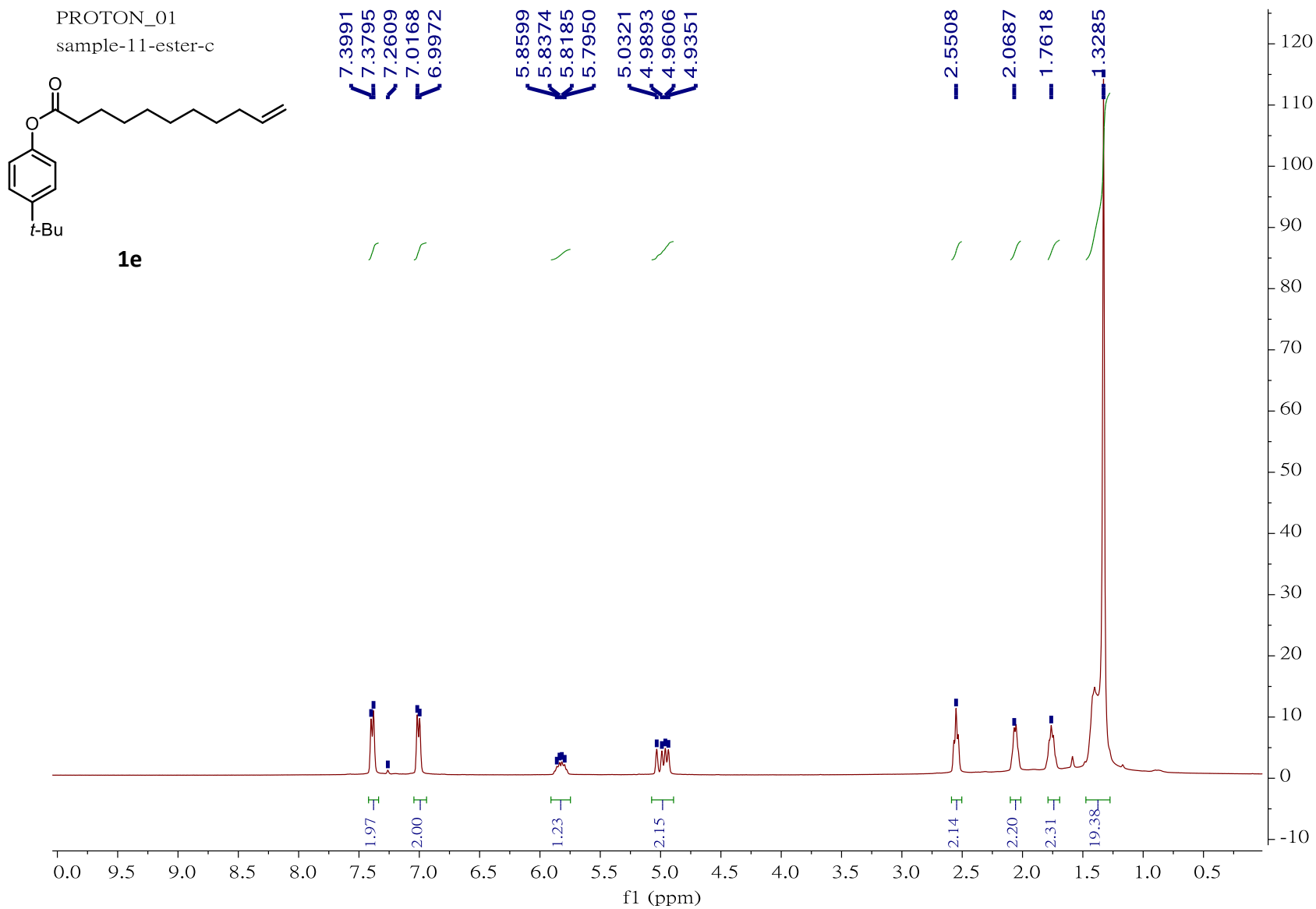
CARBON_01
sample-2-ester



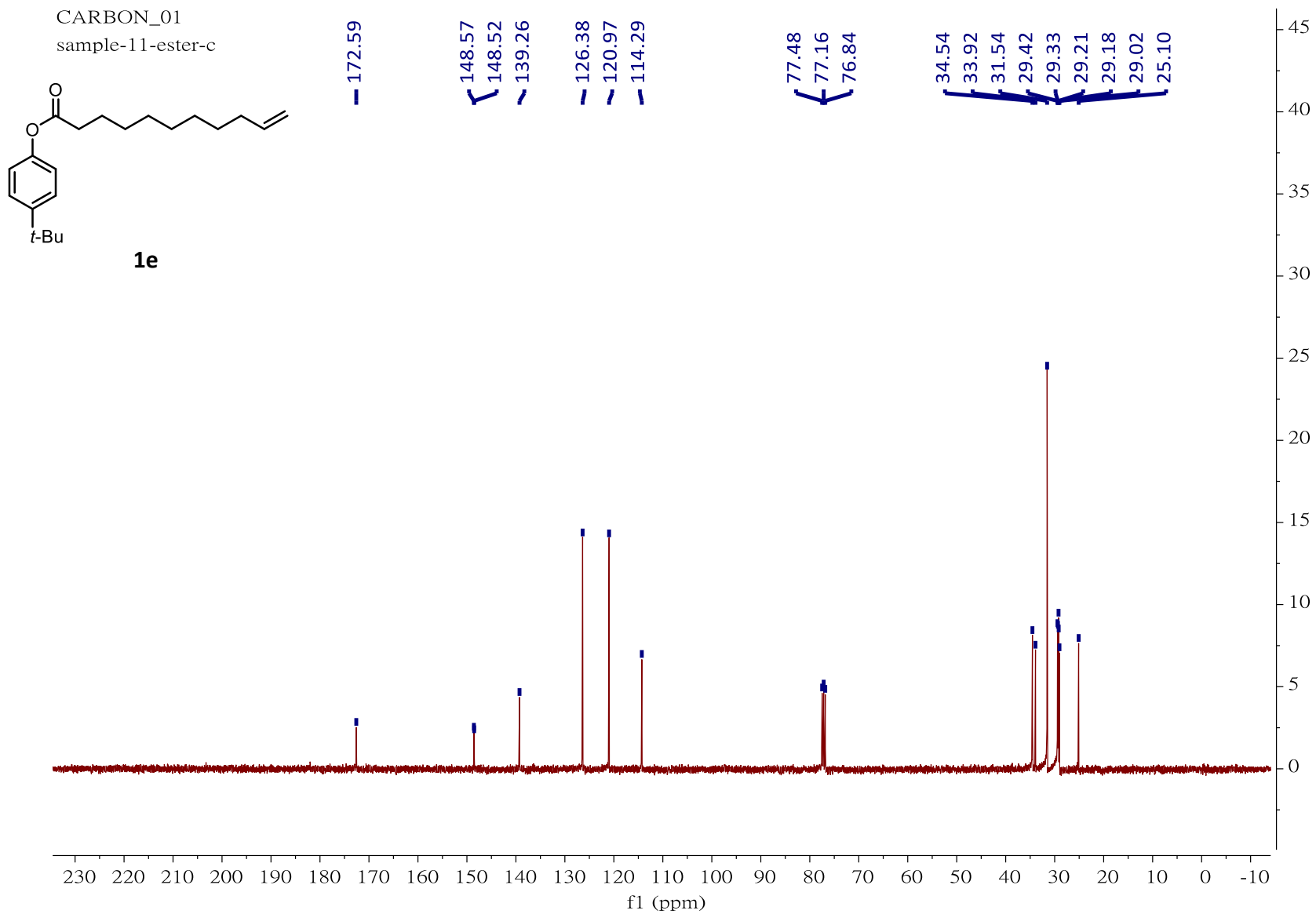
1d'



¹H NMR spectrum of compound 1e



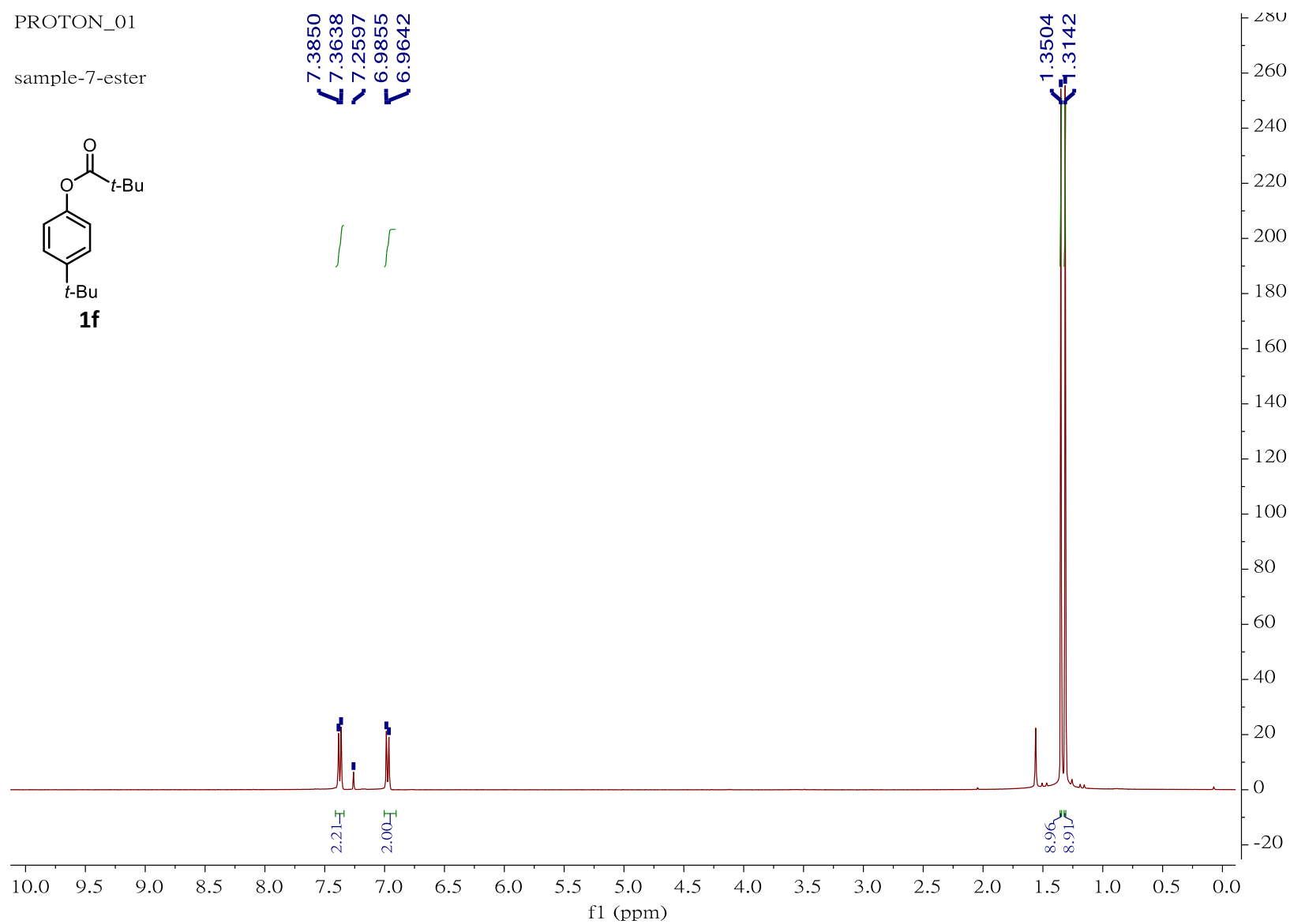
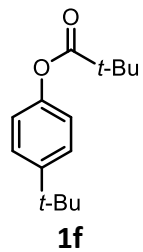
¹³C NMR spectrum of compound 1e



¹H NMR spectrum of compound 1f

PROTON_01

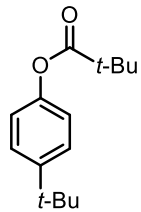
sample-7-ester



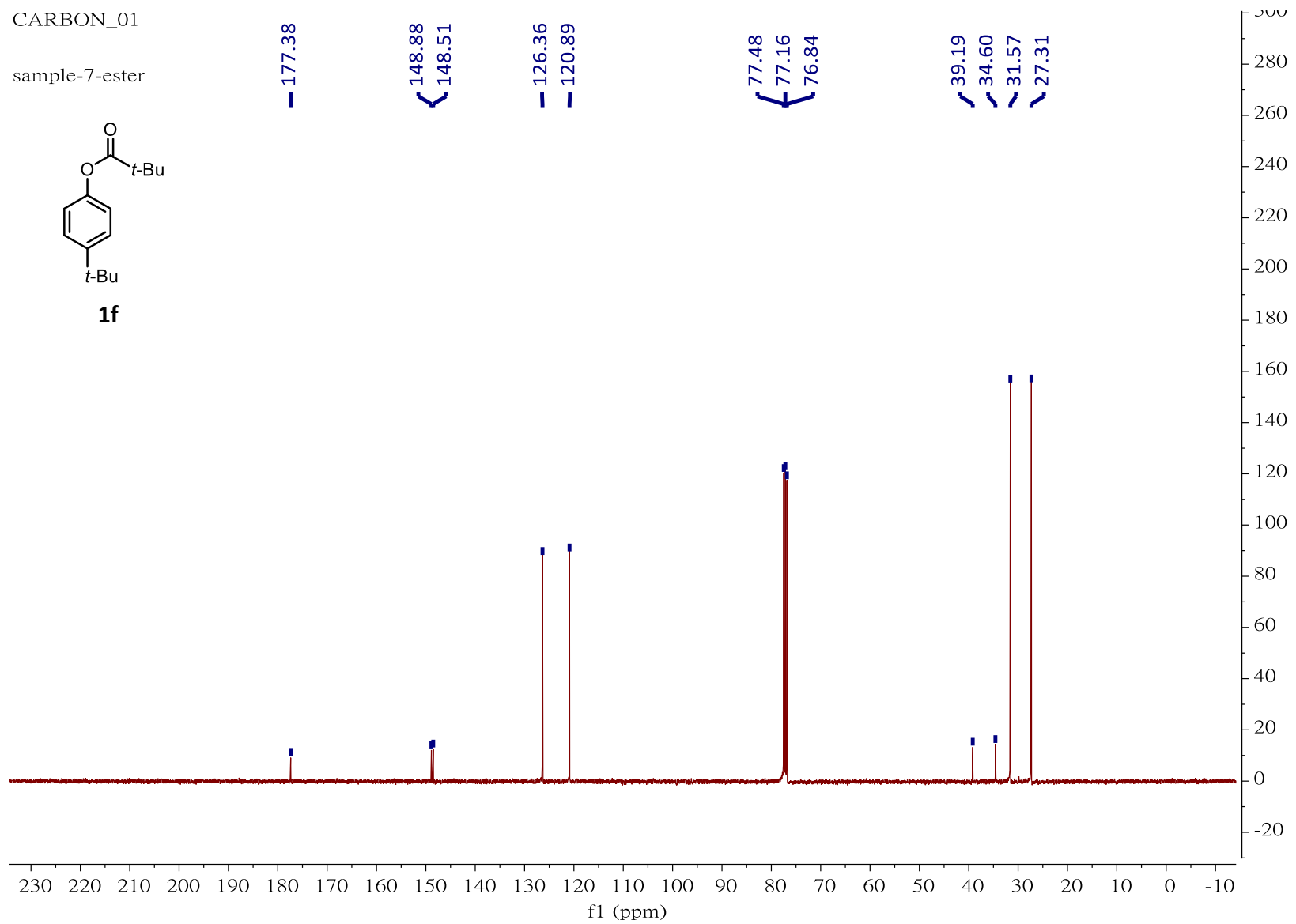
¹³C NMR spectrum of compound 1f

CARBON_01

sample-7-ester



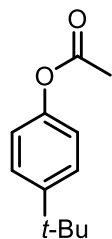
1f



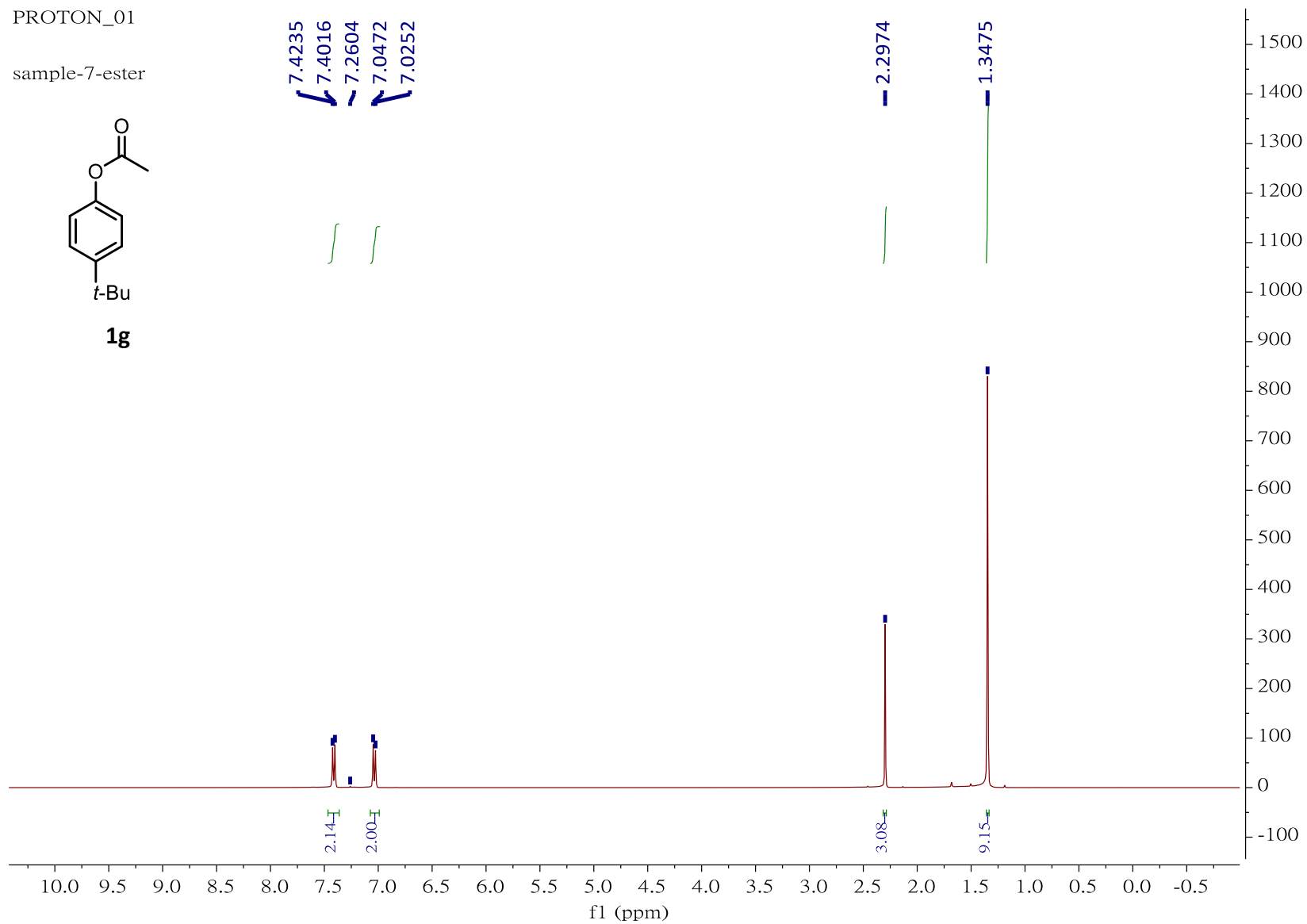
¹H NMR spectrum of compound 1g

PROTON_01

sample-7-ester



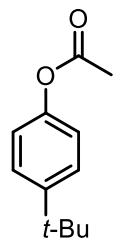
1g



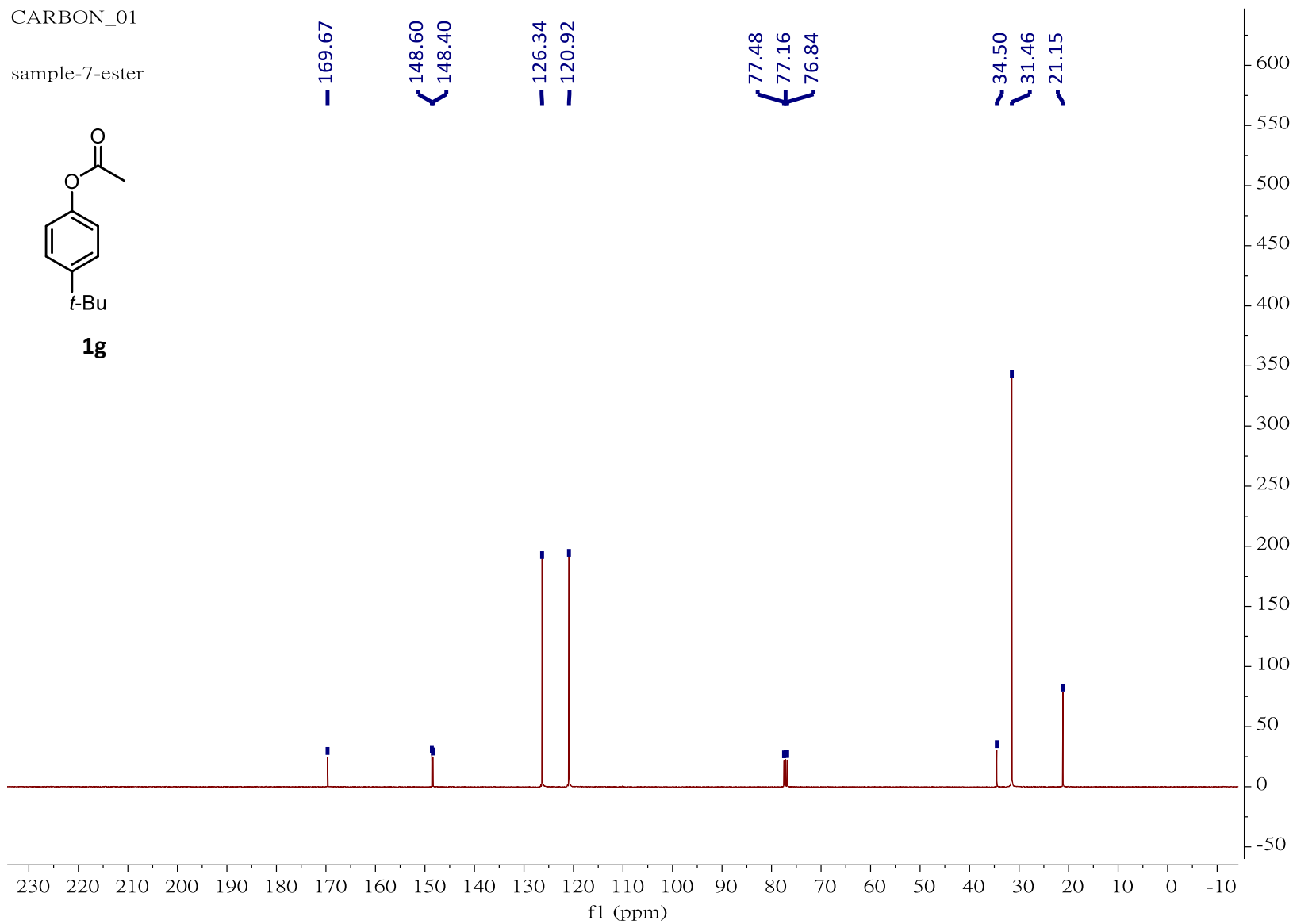
¹³C NMR spectrum of compound 1g

CARBON_01

sample-7-ester

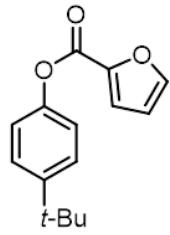


1g

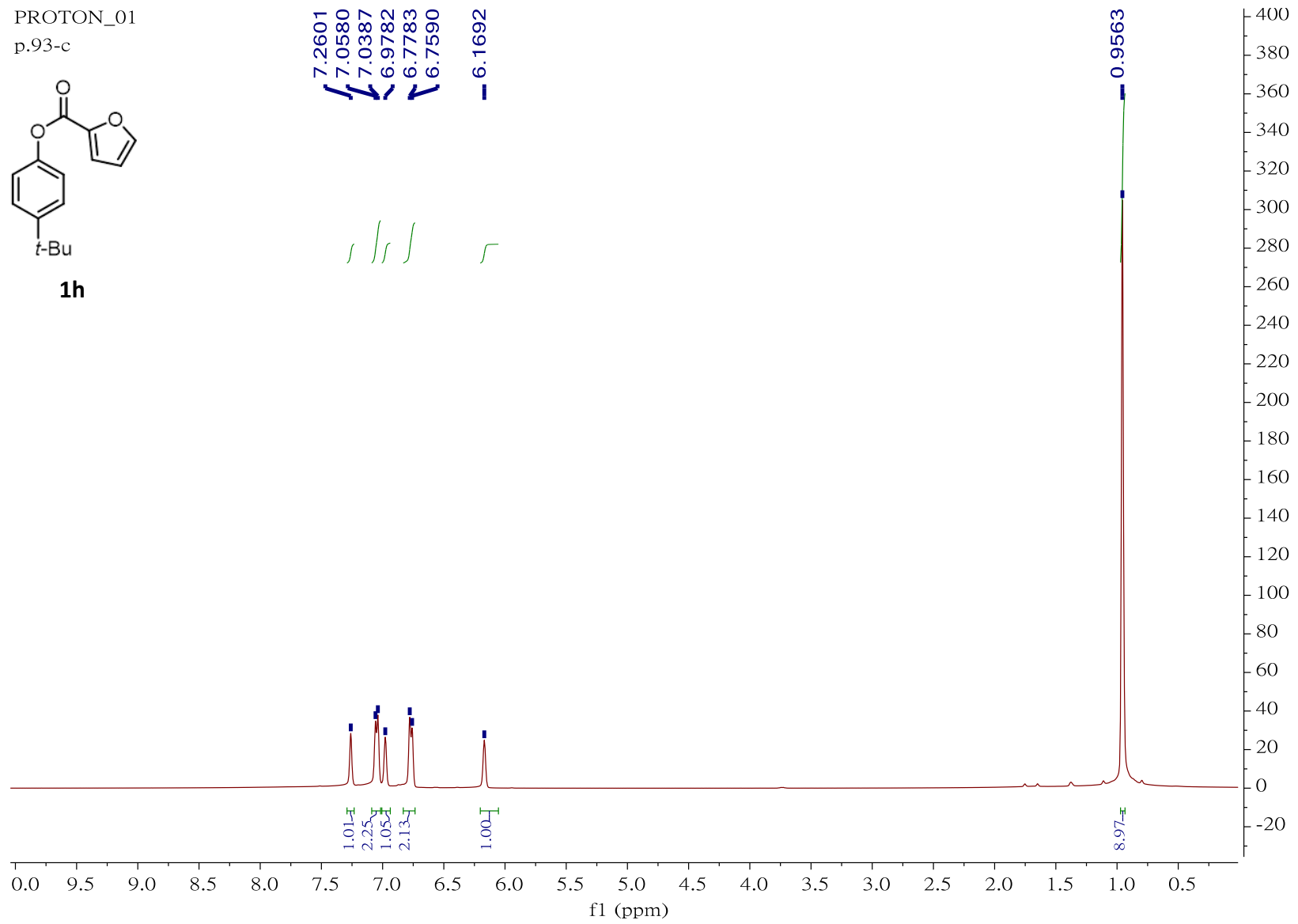


¹H NMR spectrum of compound 1h

PROTON_01
p.93-c

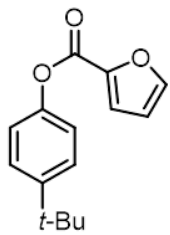


1h

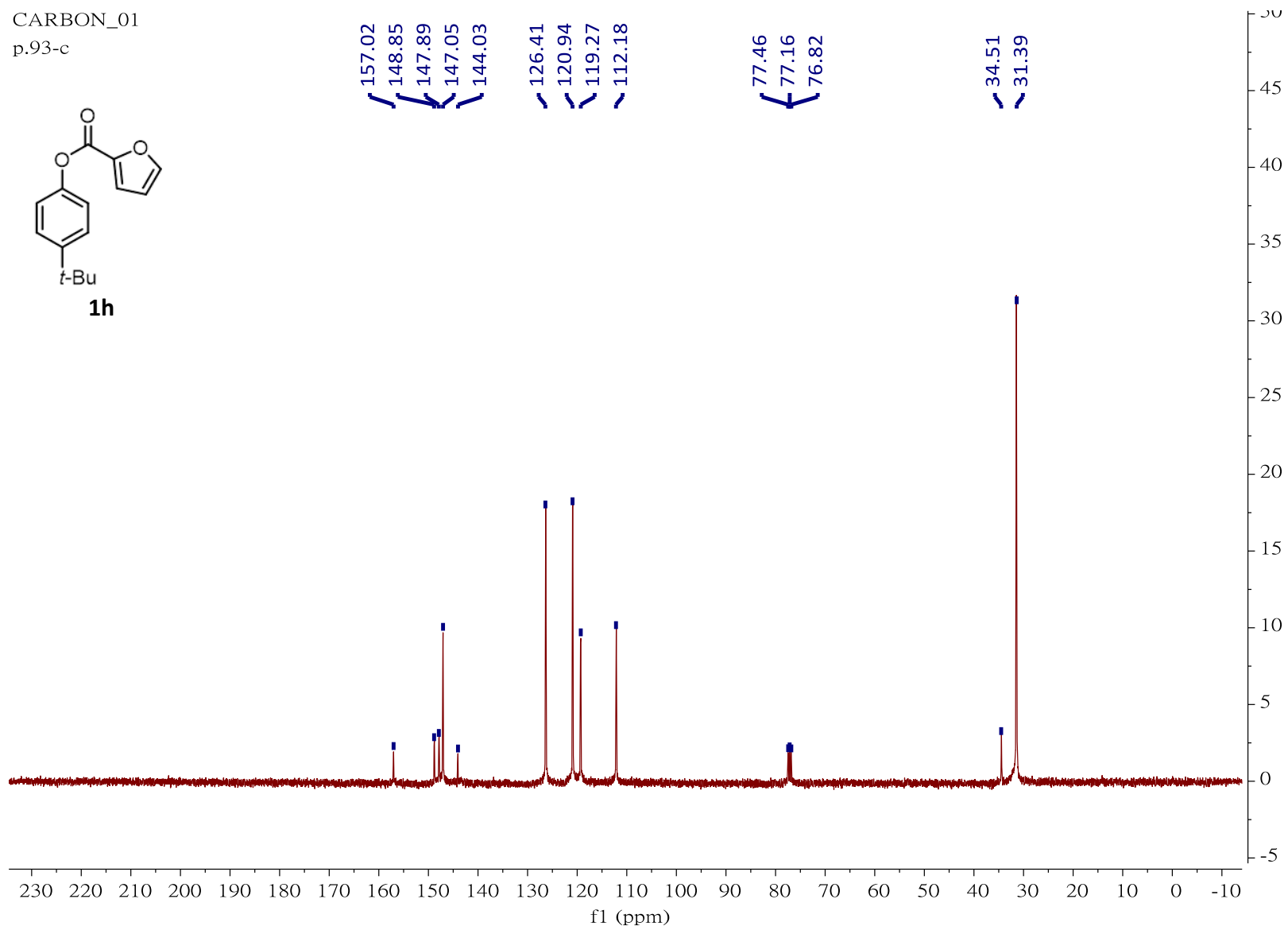


¹³C NMR spectrum of compound 1h

CARBON_01
p.93-c

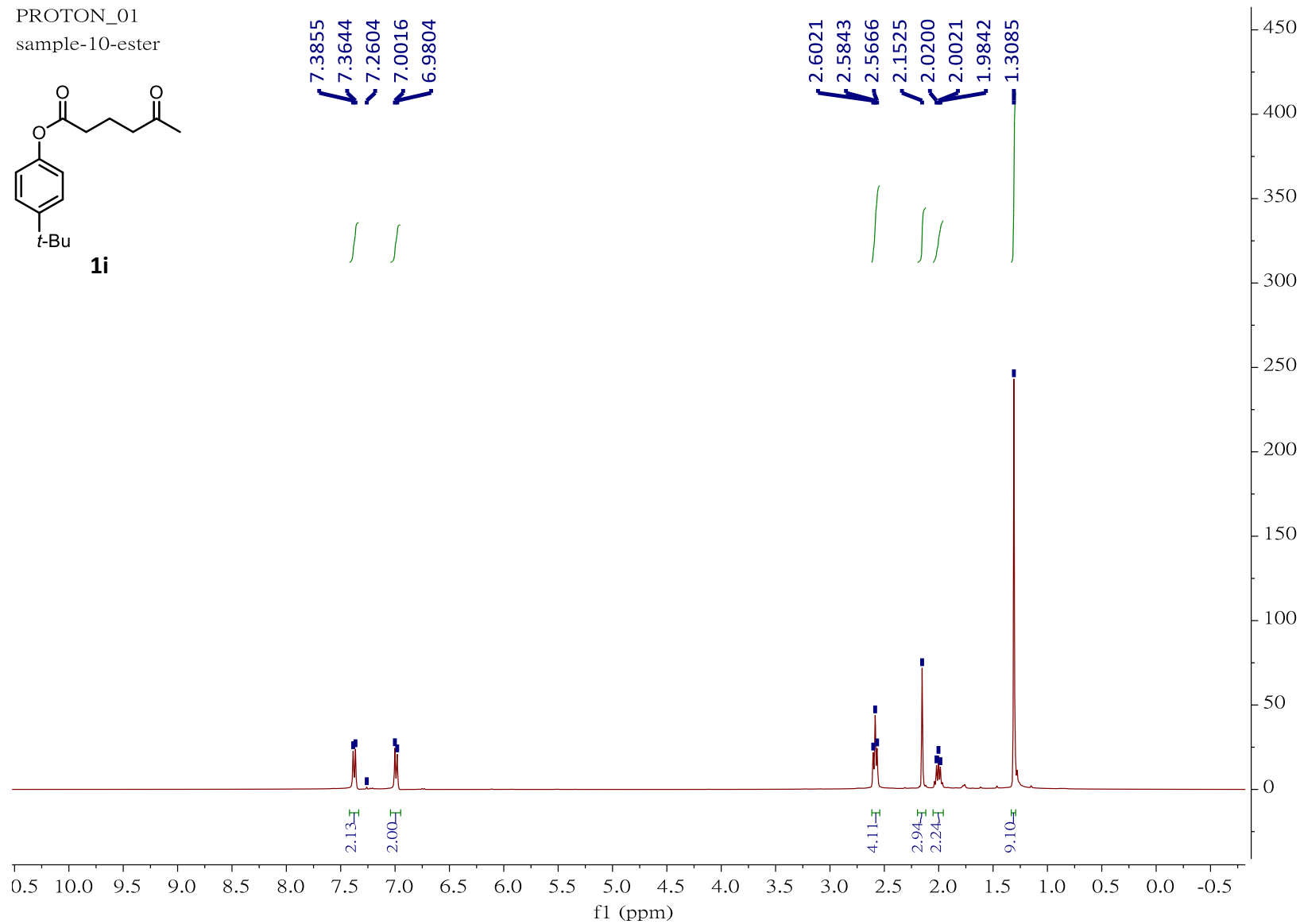
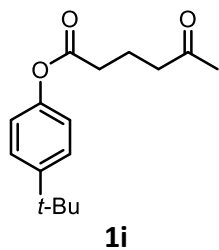


1h

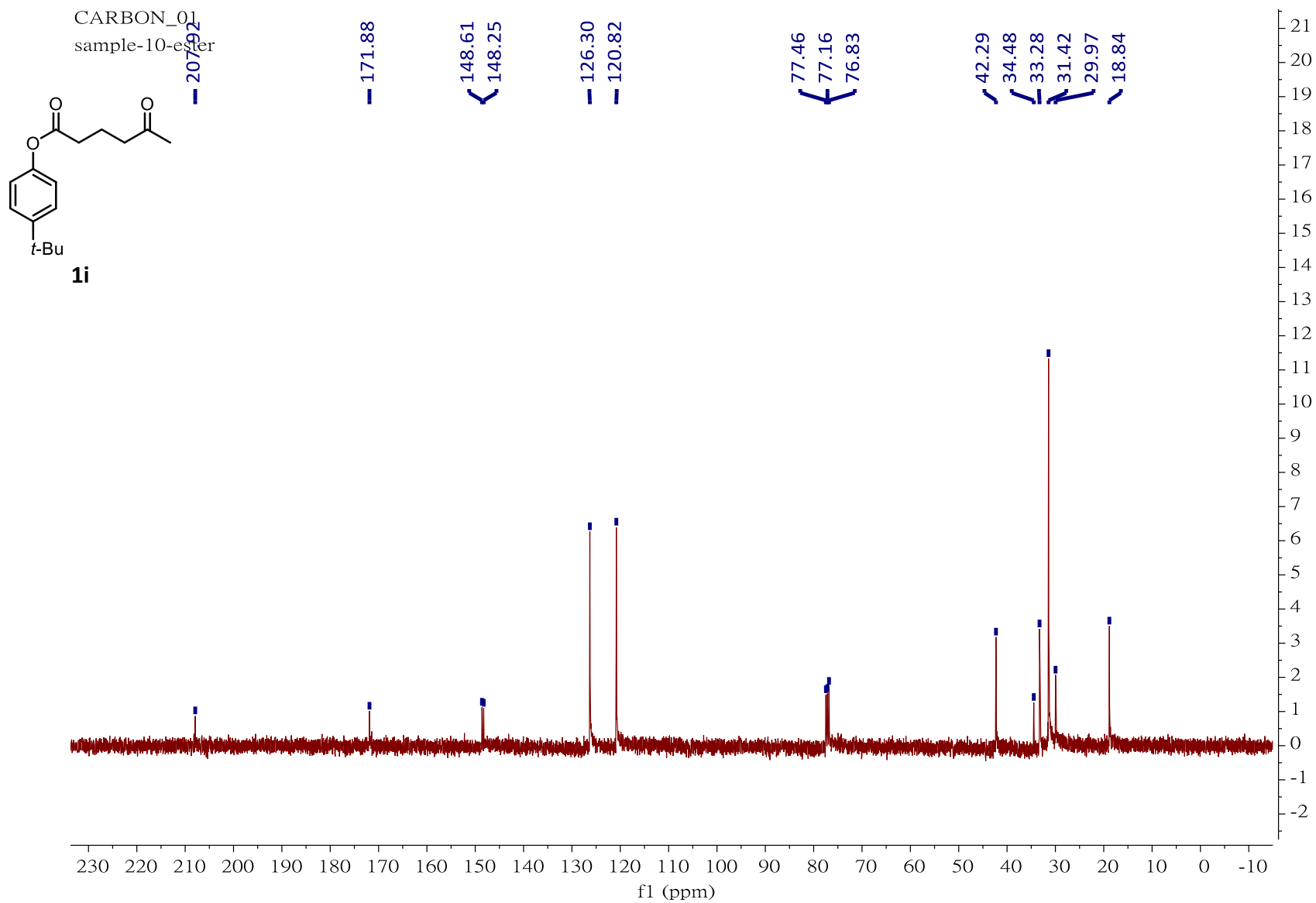


¹H NMR spectrum of compound 1i

PROTON_01
sample-10-ester



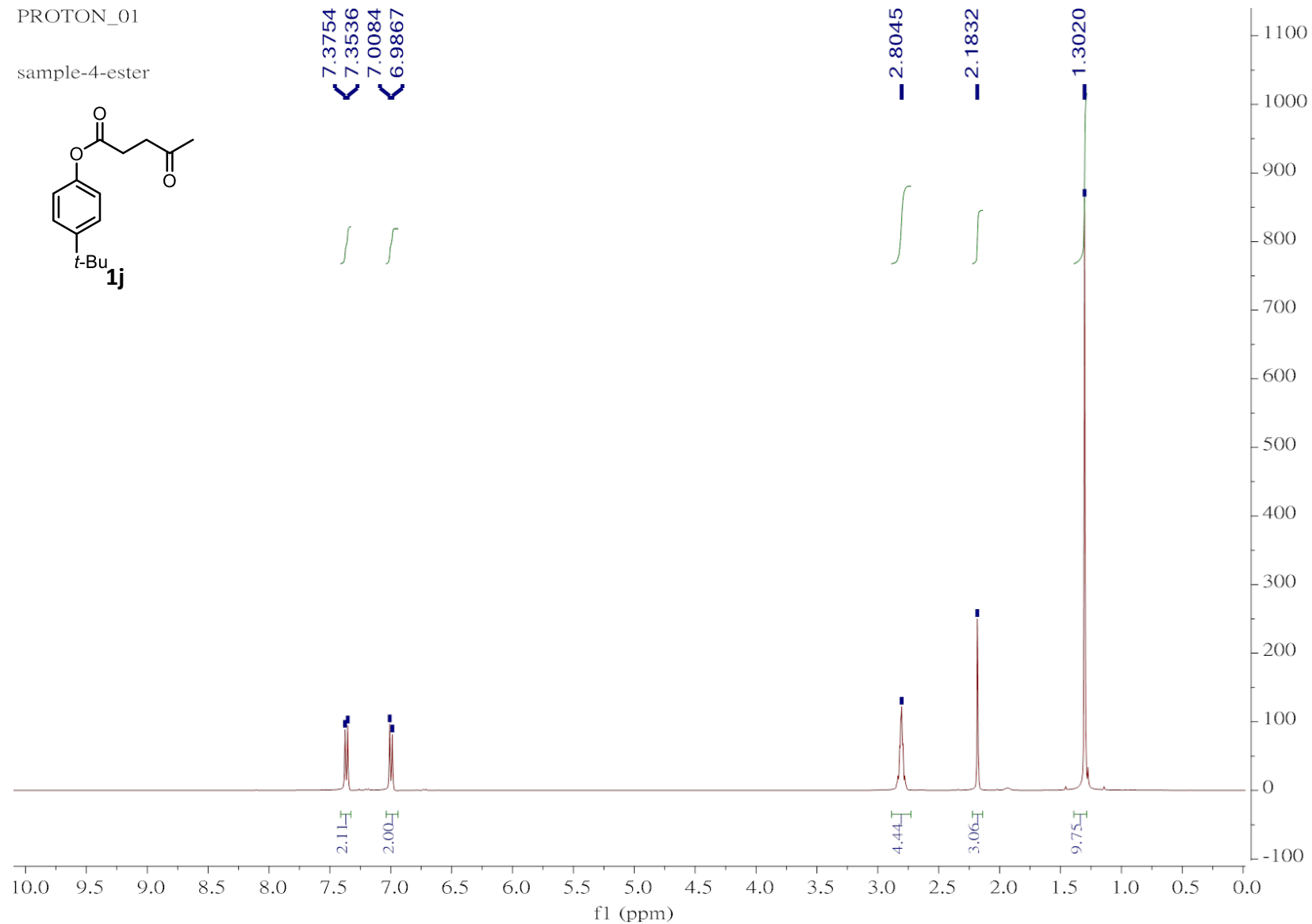
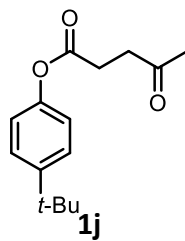
¹³C NMR spectrum of compound 1i



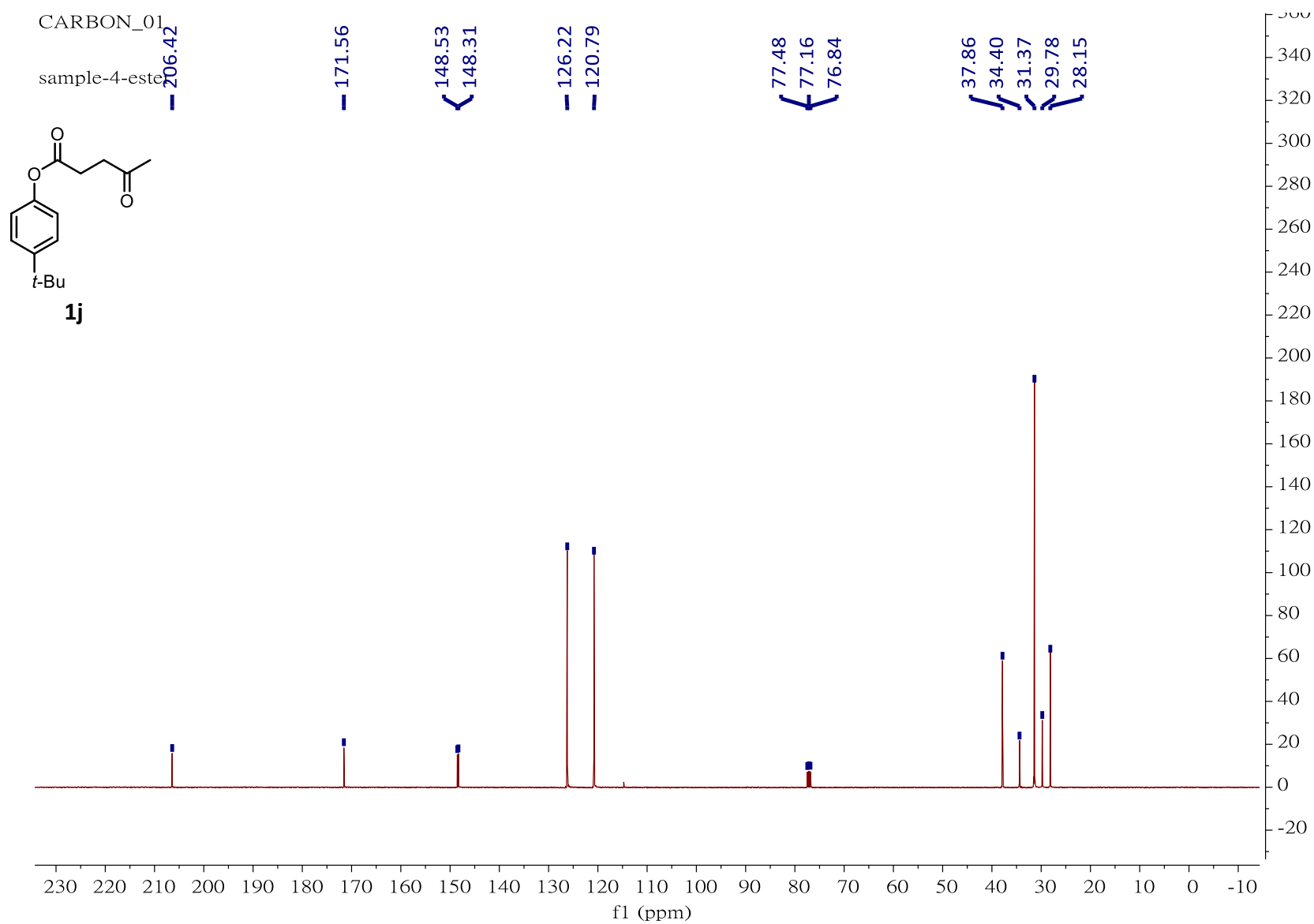
¹H NMR spectrum of compound 1j

PROTON_01

sample-4-ester

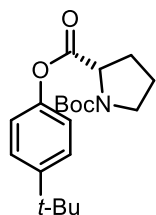


¹³C NMR spectrum of compound 1j

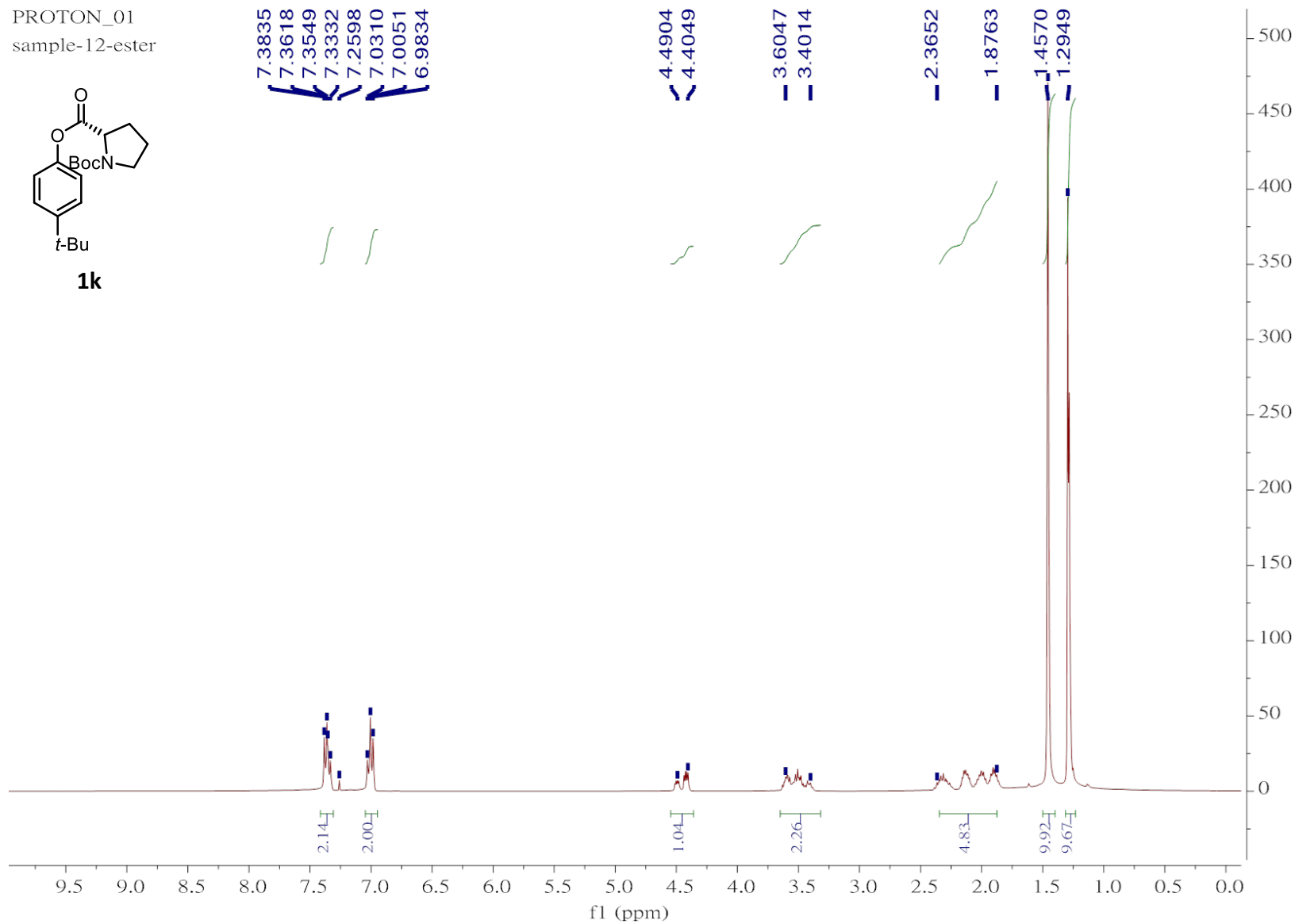


¹H NMR spectrum of compound 1k

PROTON_01
sample-12-ester

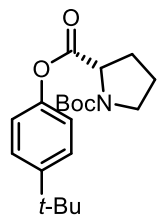


1k

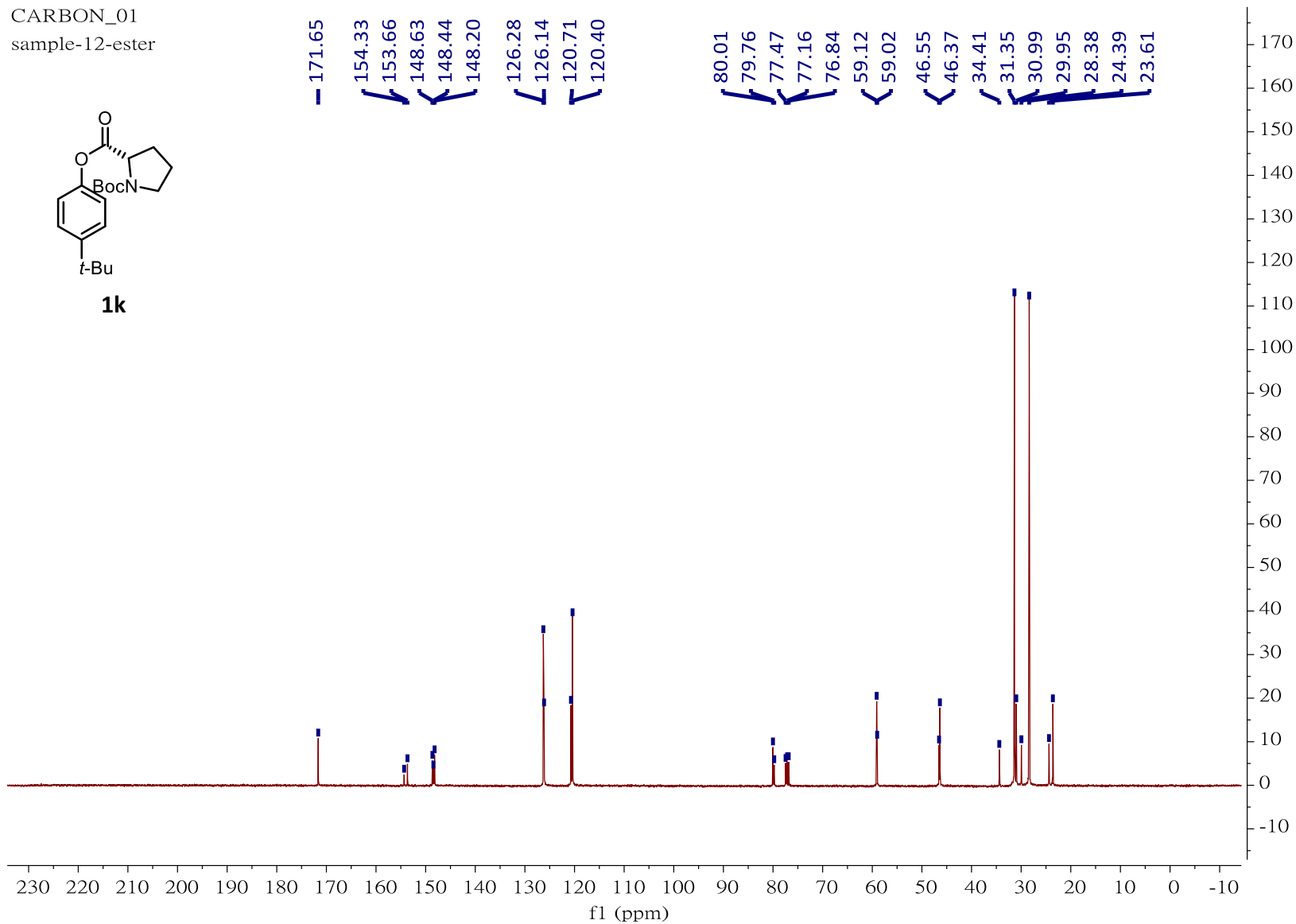


¹³C NMR spectrum of compound 1k

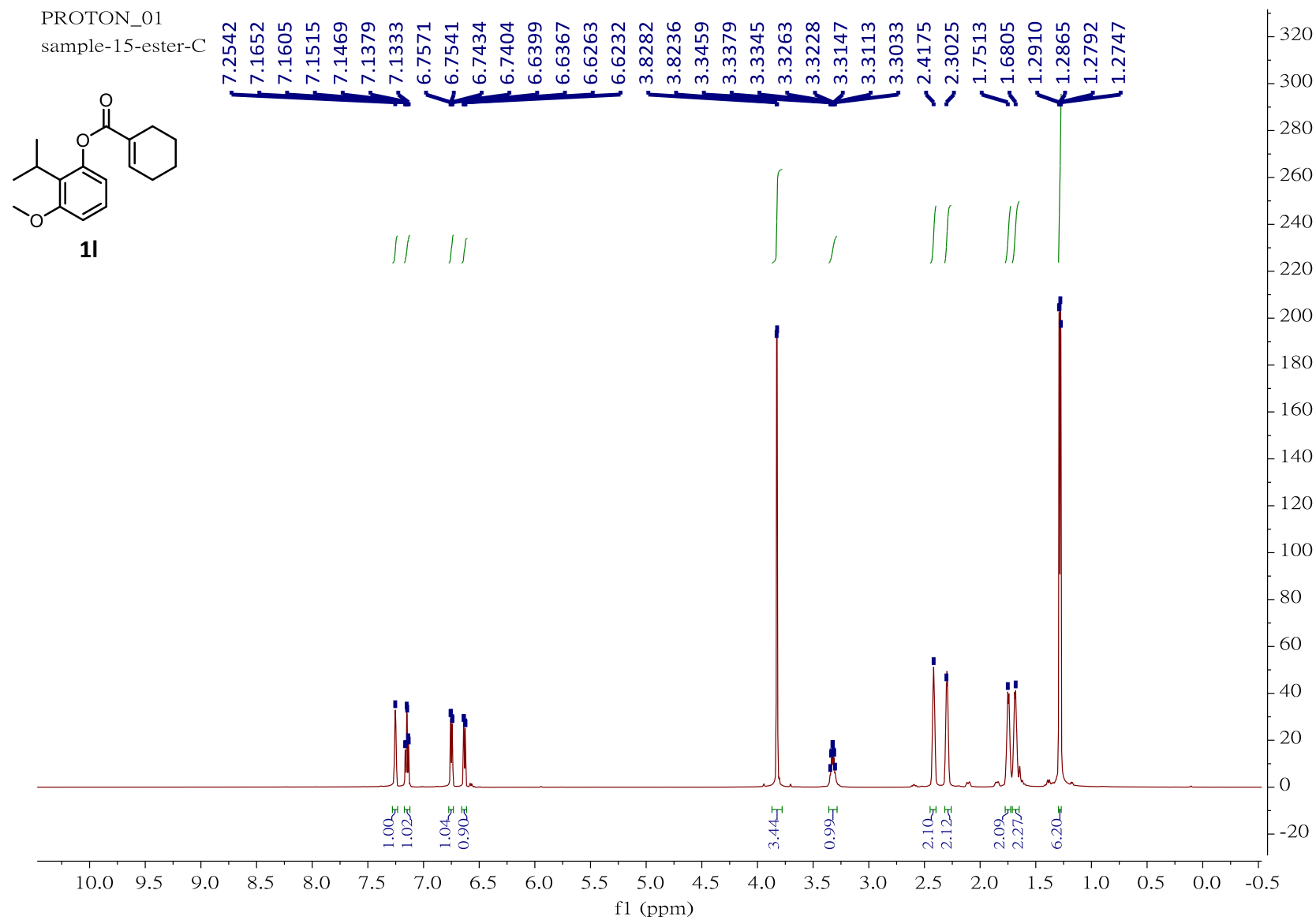
CARBON_01
sample-12-ester



1k

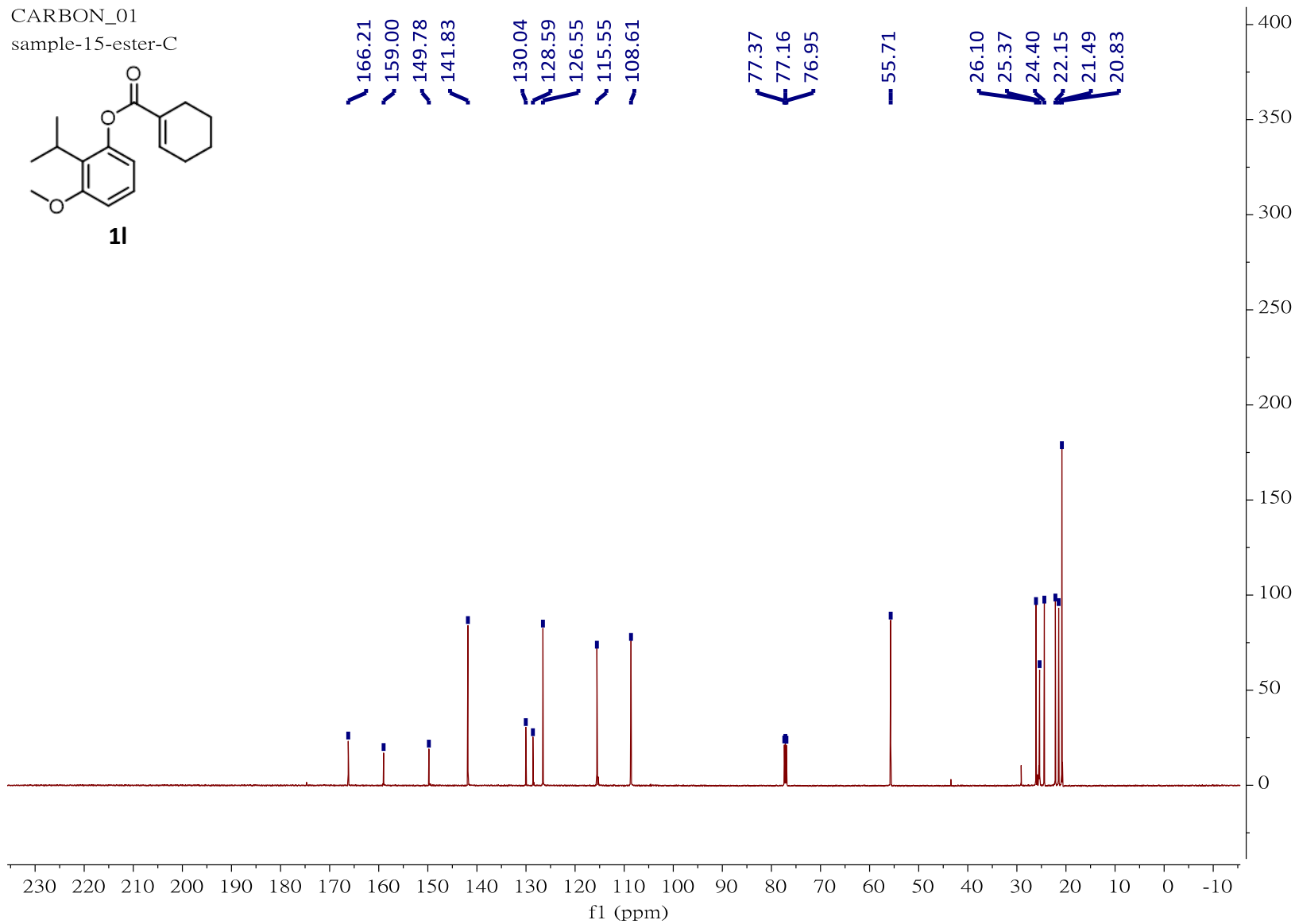
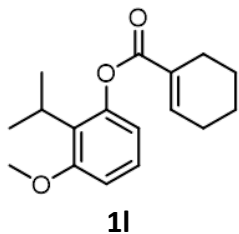


¹H NMR spectrum of compound 11

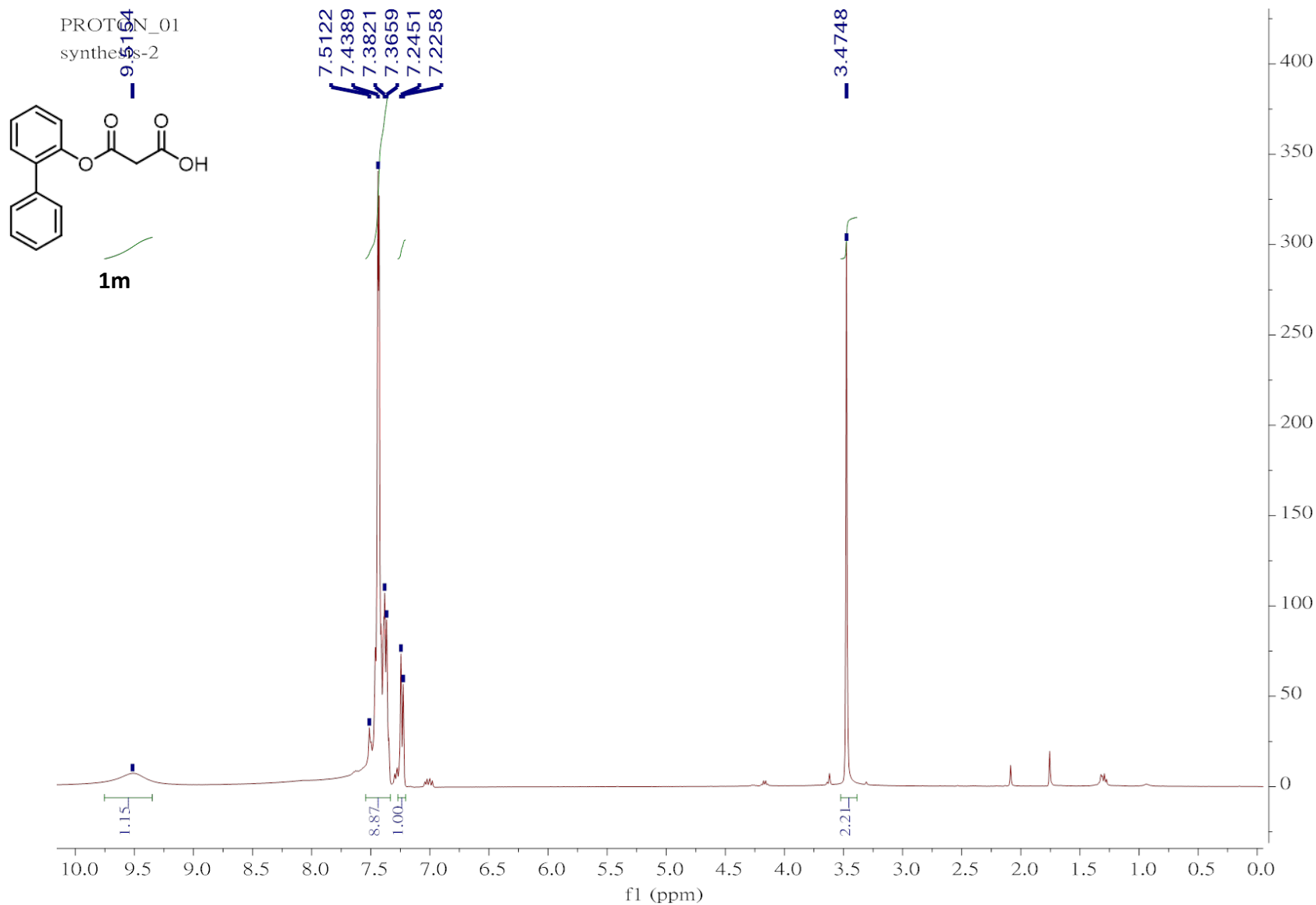


¹³C NMR spectrum of compound 1I

CARBON_01
sample-15-ester-C

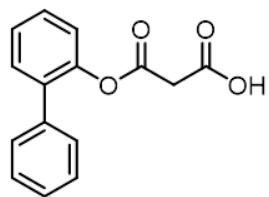


¹H NMR spectrum of compound 1m

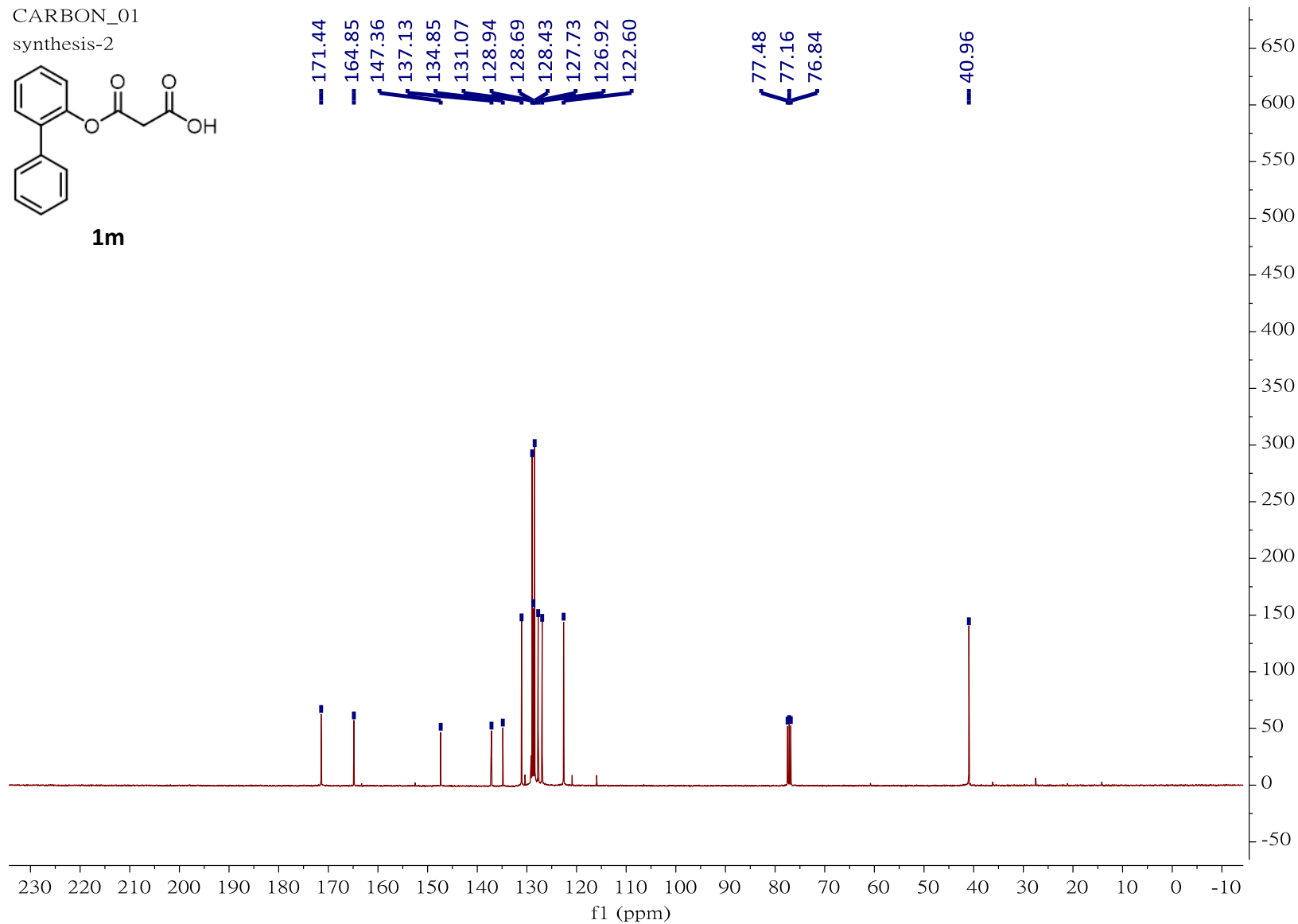


¹³C NMR spectrum of compound 1m

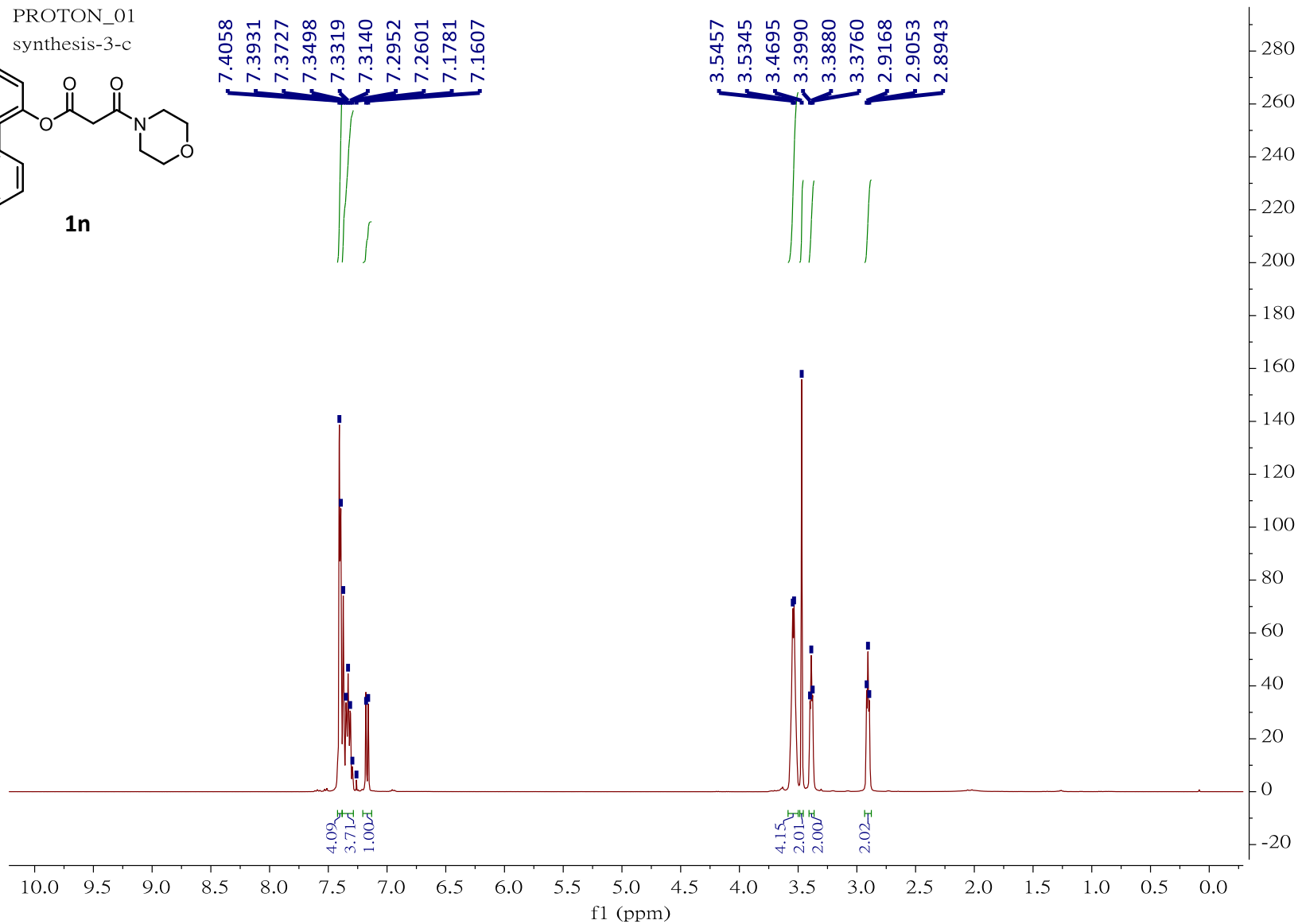
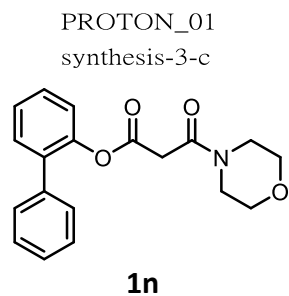
CARBON_01
synthesis-2



1m

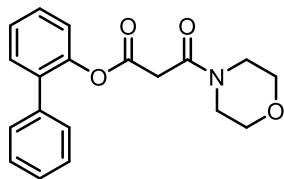


¹H NMR spectrum of compound 1n

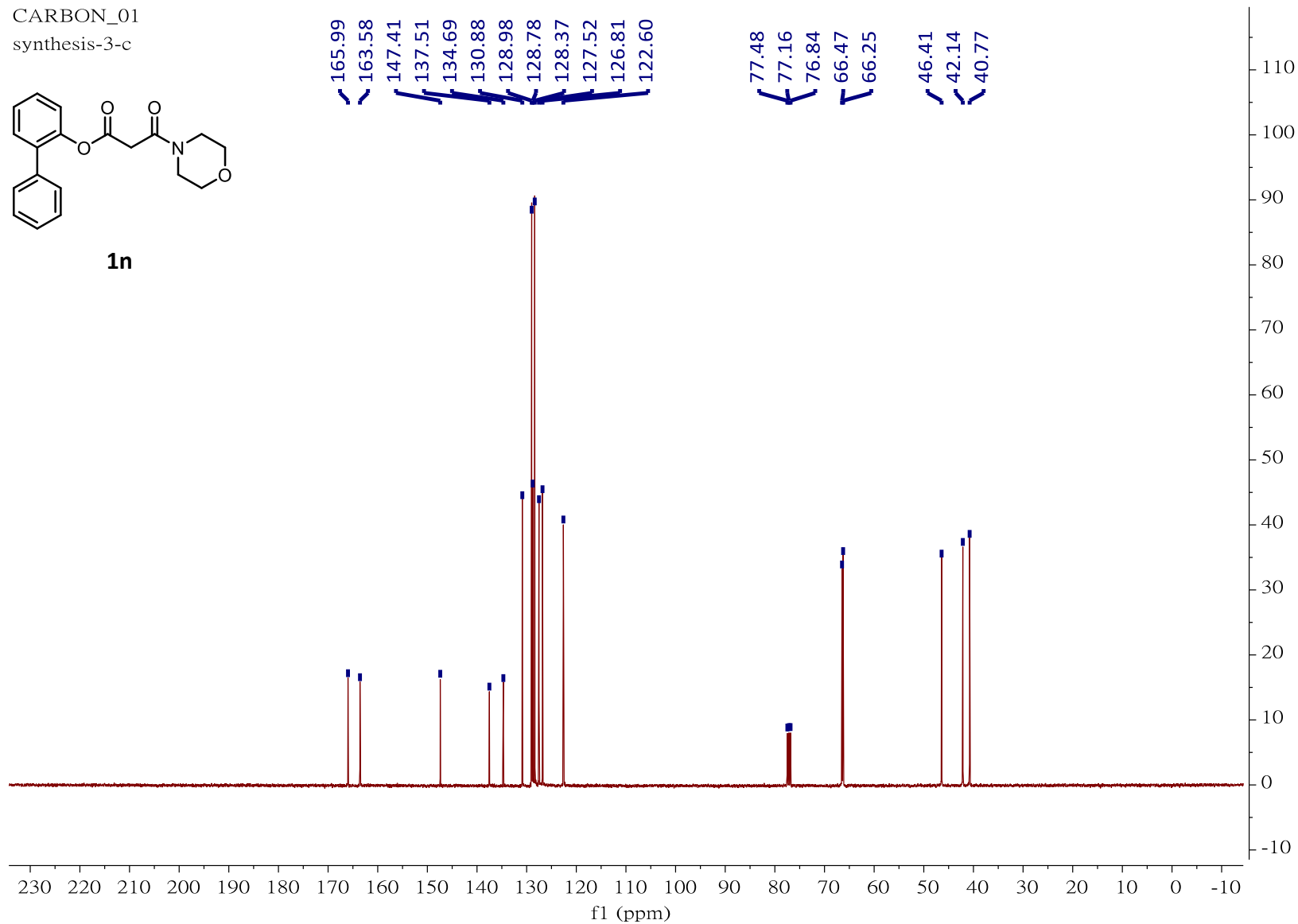


¹³C NMR spectrum of compound 1n

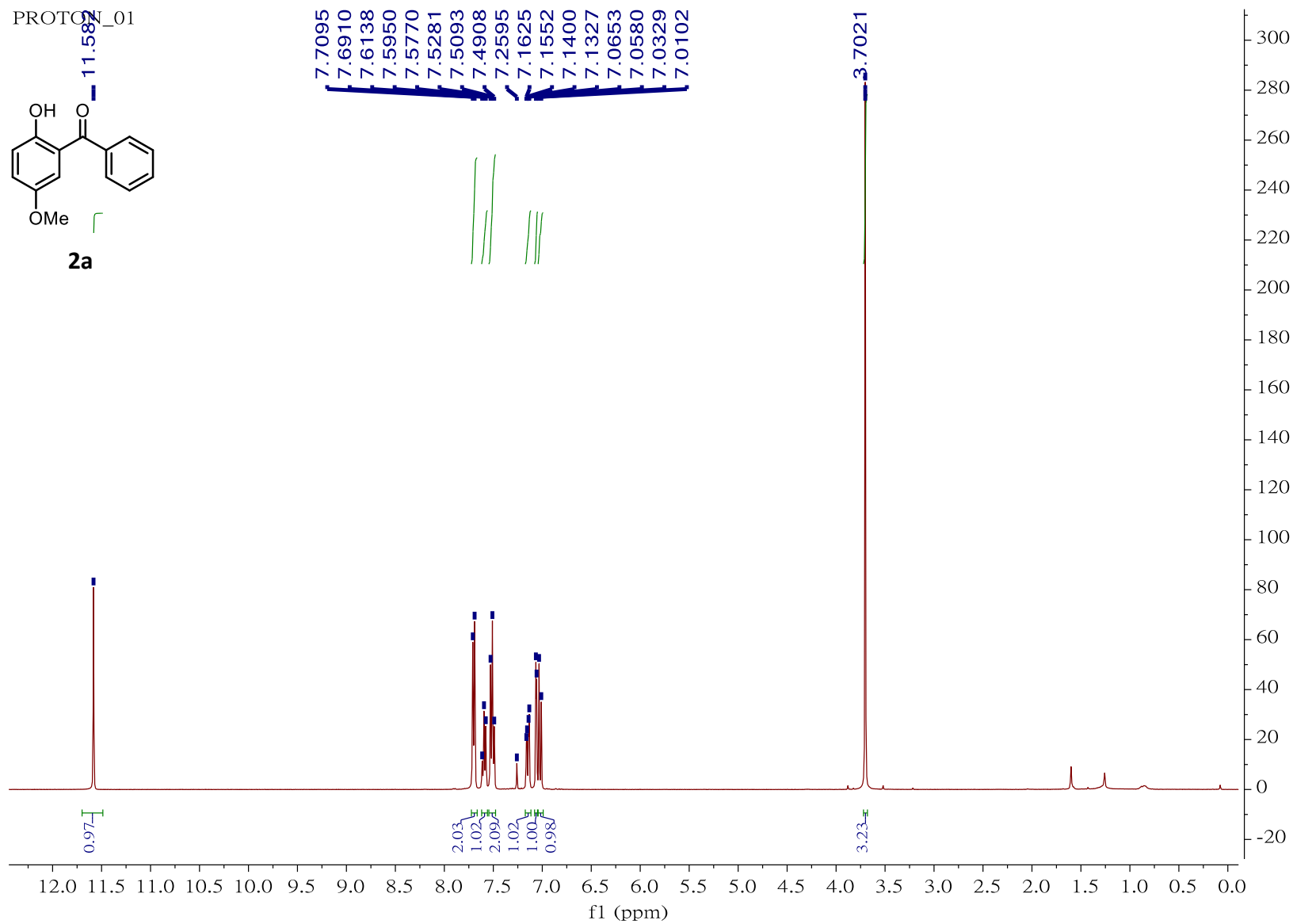
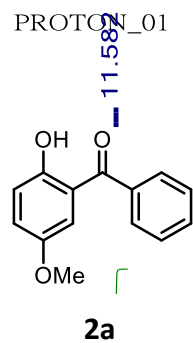
CARBON_01
synthesis-3-c



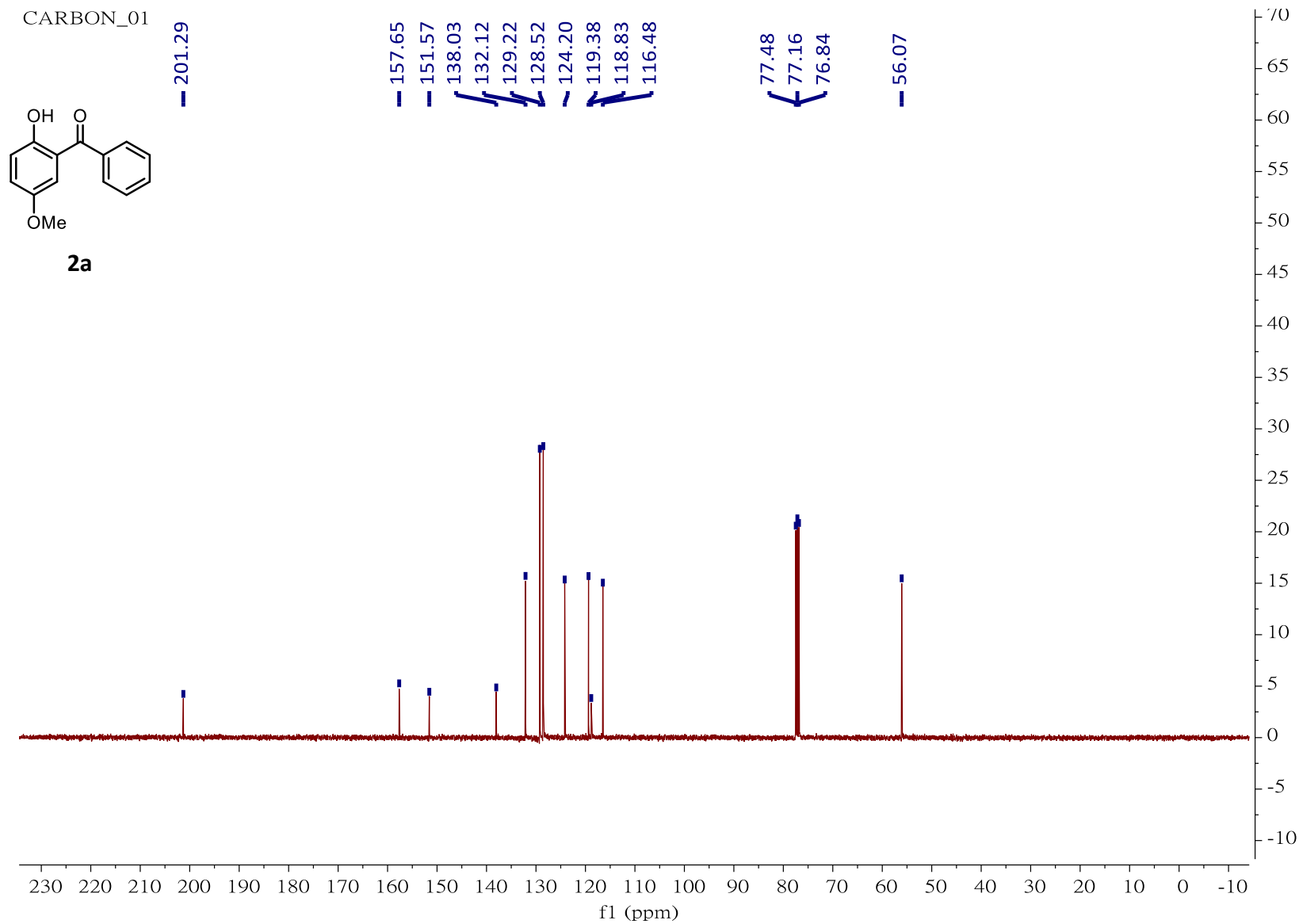
1n



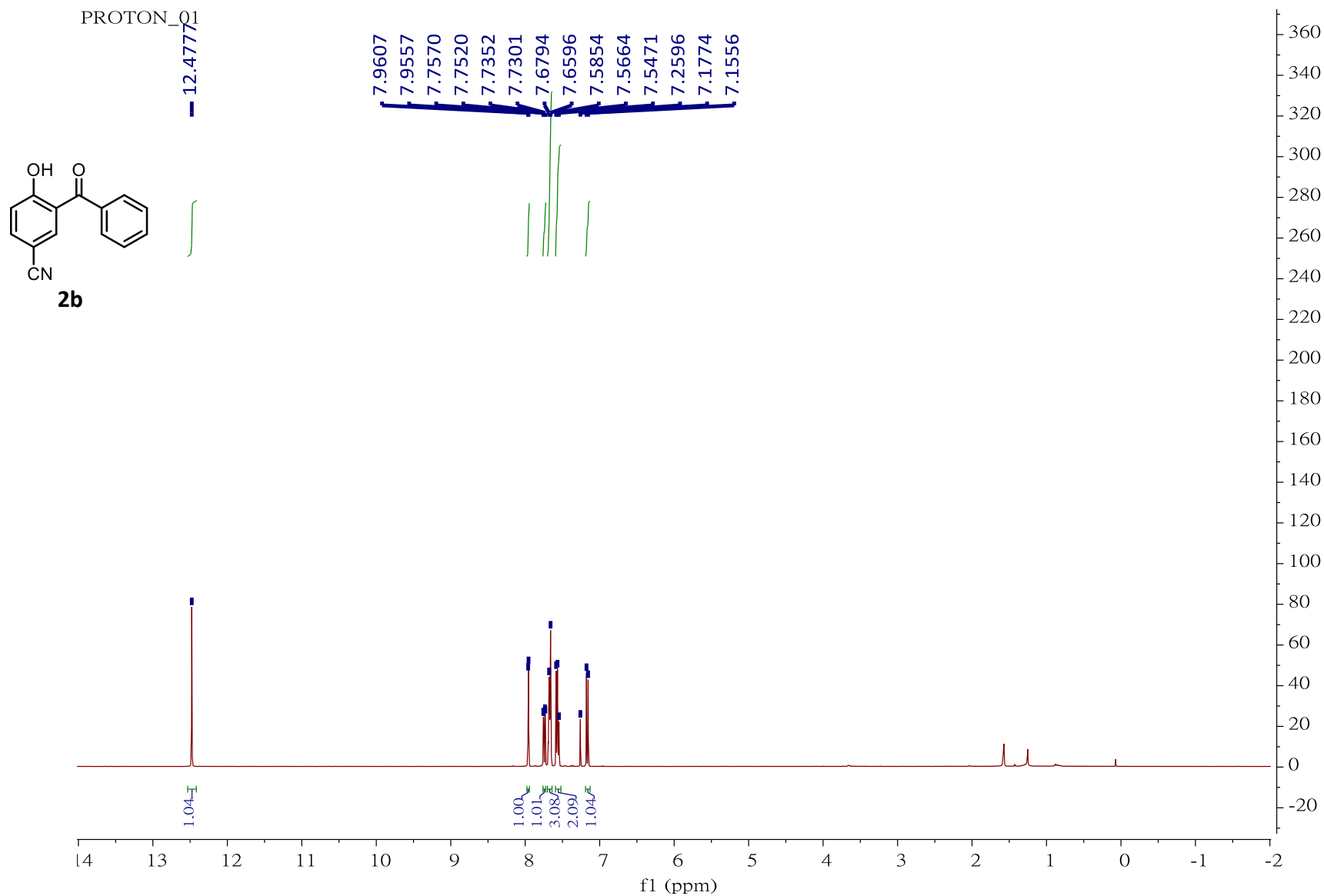
¹H NMR spectrum of compound 2a



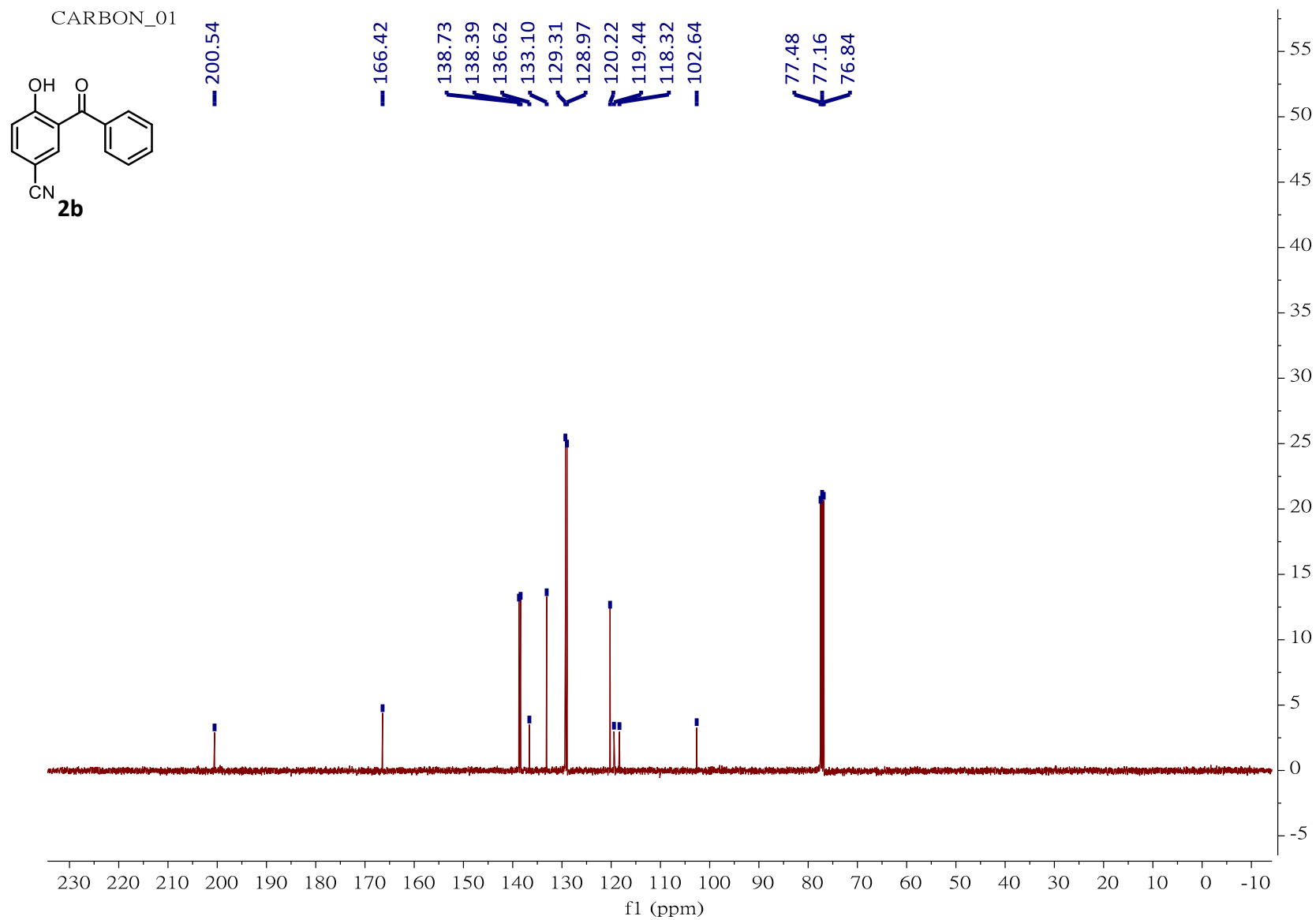
¹³C NMR spectrum of compound 2a

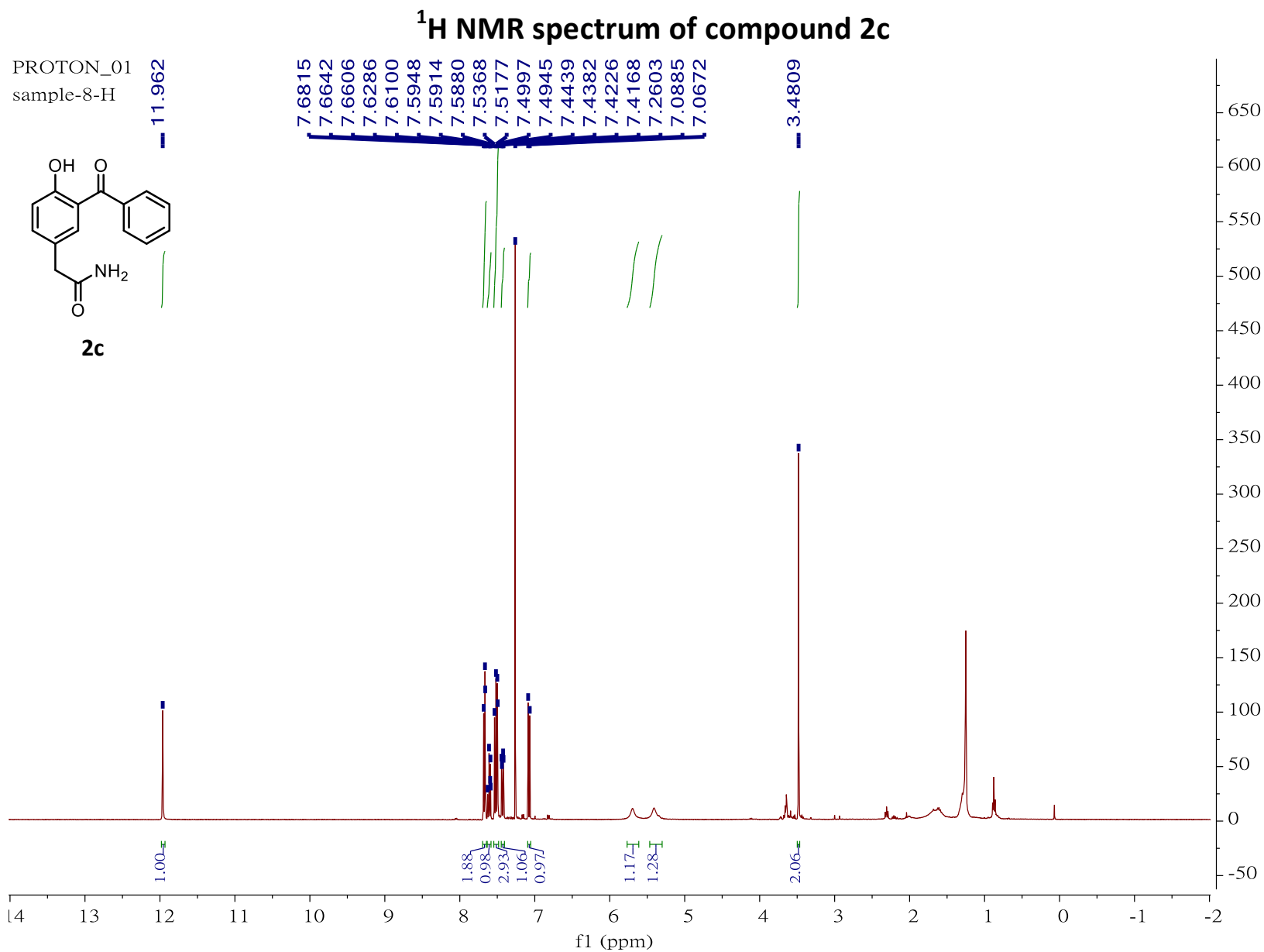


¹H NMR spectrum of compound 2b

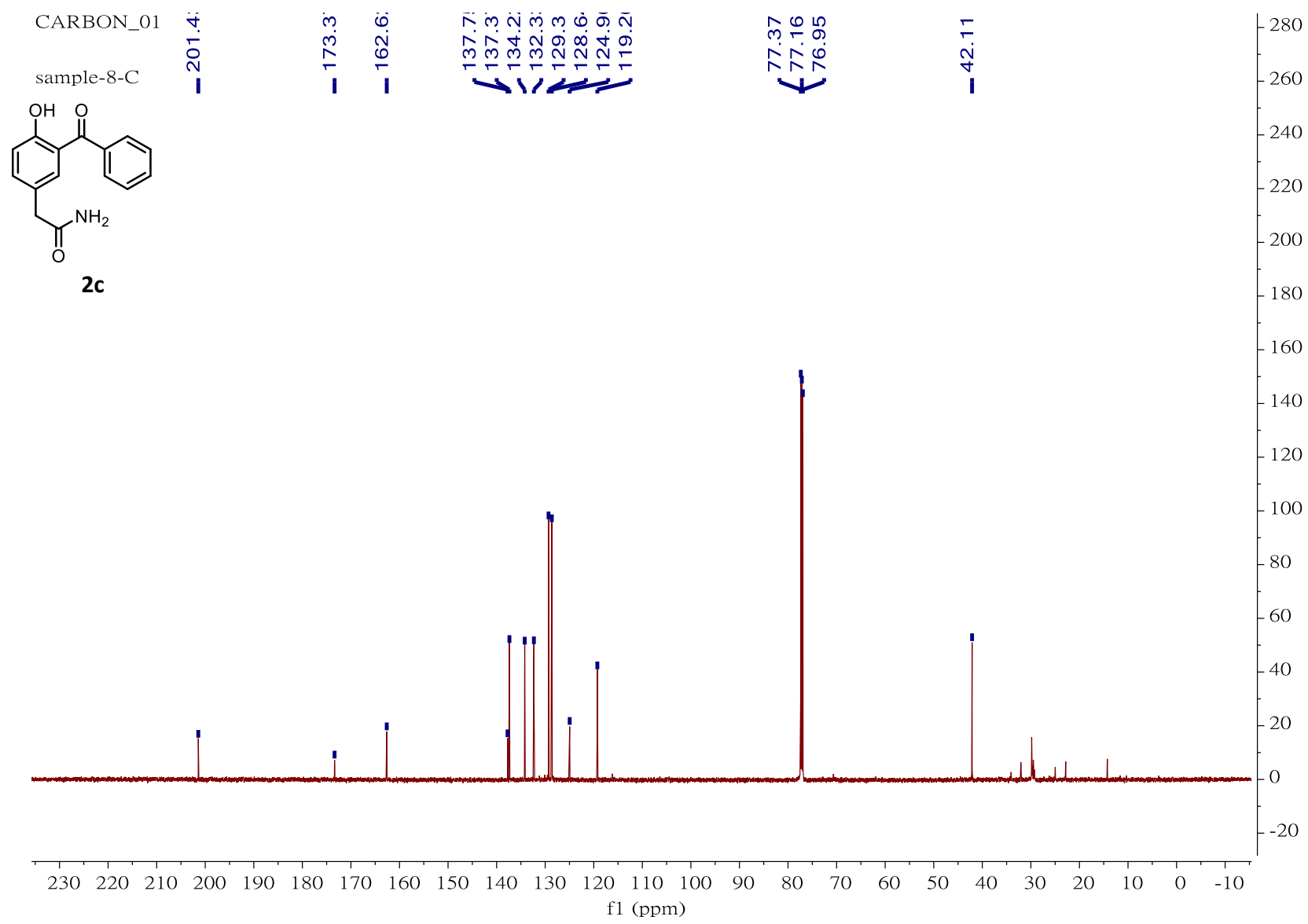


¹³C NMR spectrum of compound 2b



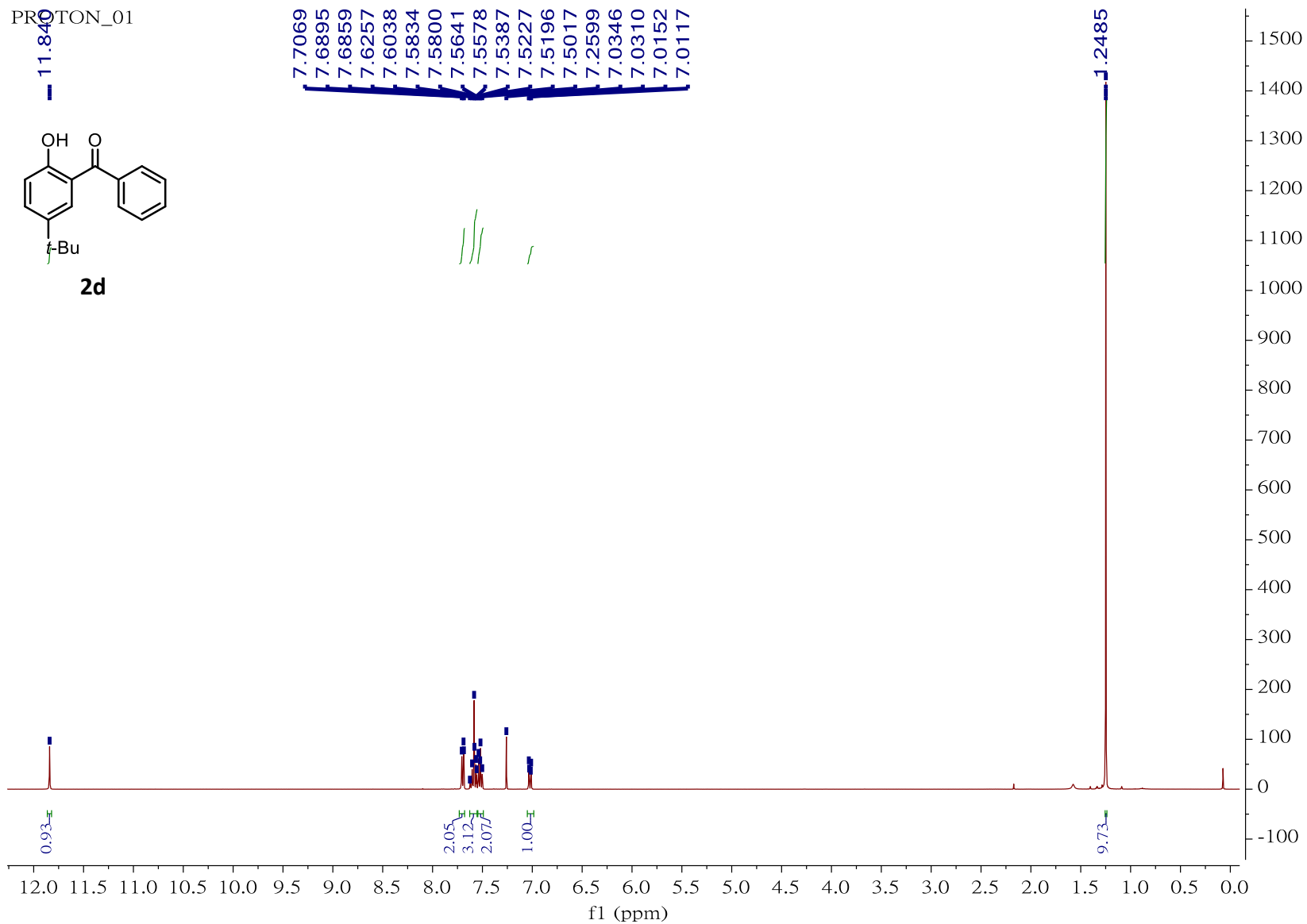
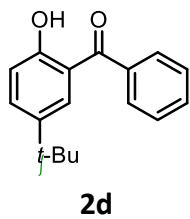


¹³C NMR spectrum of compound 2c

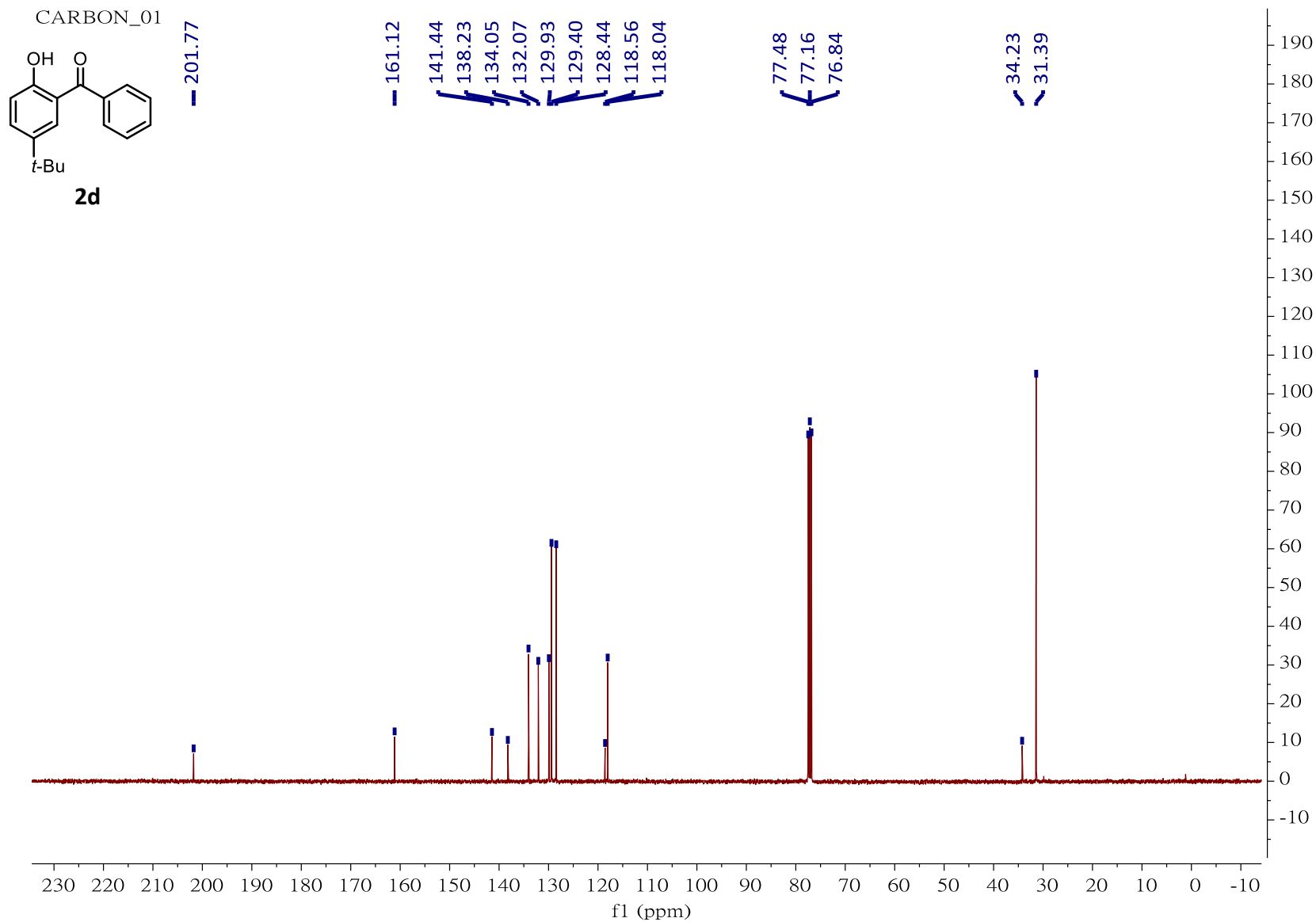


¹H NMR spectrum of compound 2d

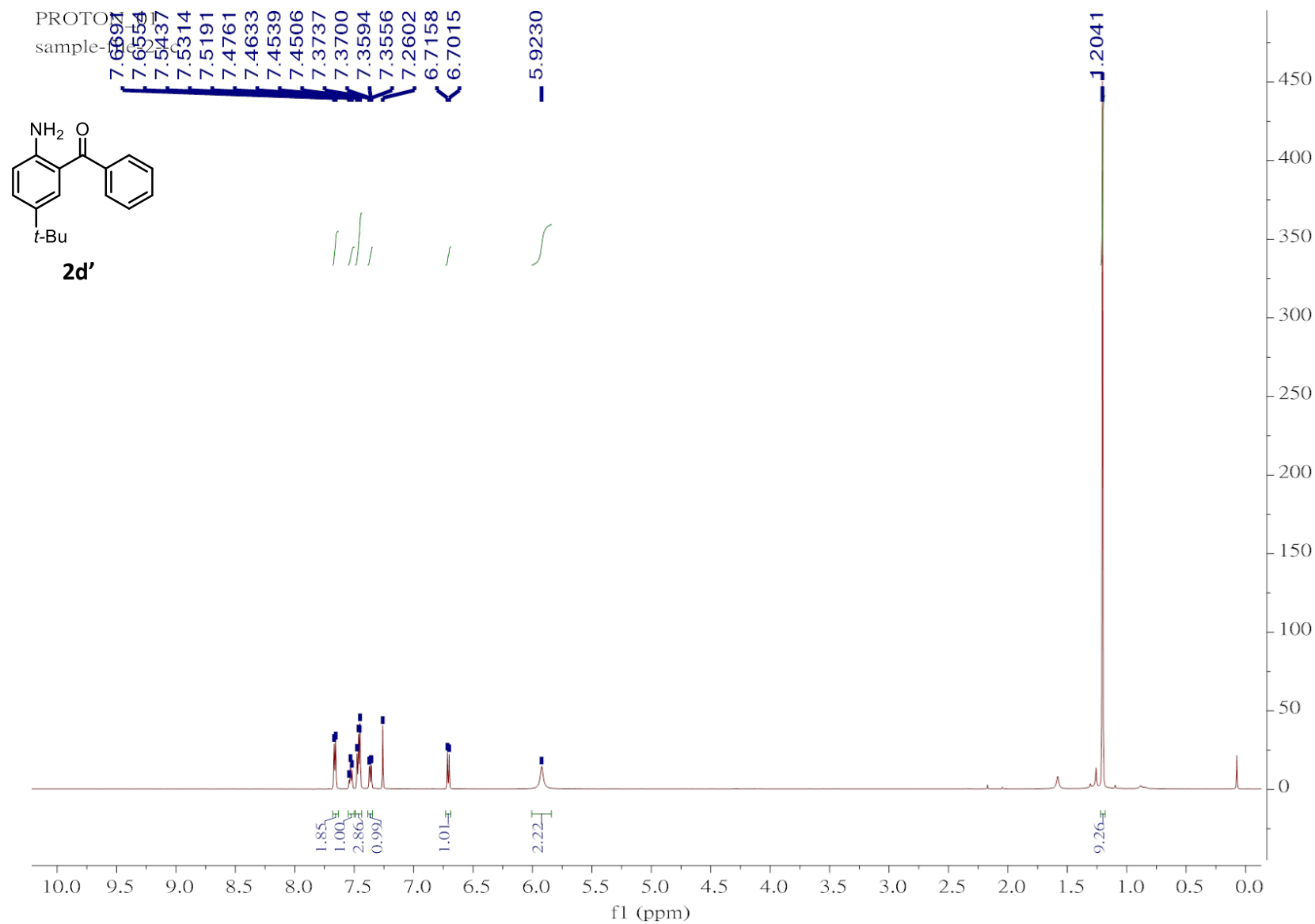
PR01 TON_01



¹³C NMR spectrum of compound 2d

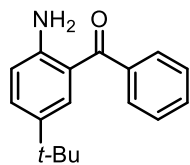


¹H NMR spectrum of compound 2d'

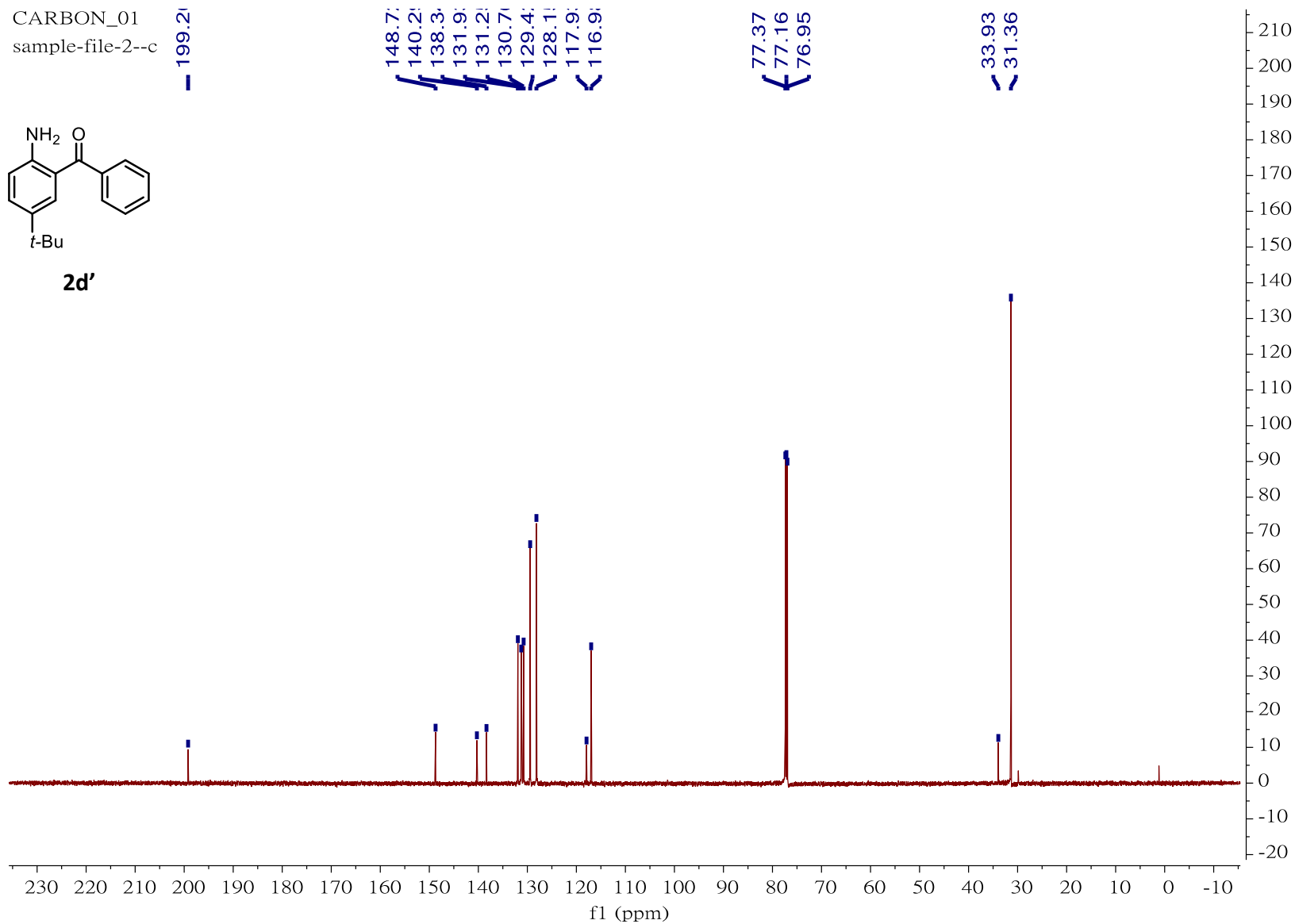


¹³C NMR spectrum of compound 2d'

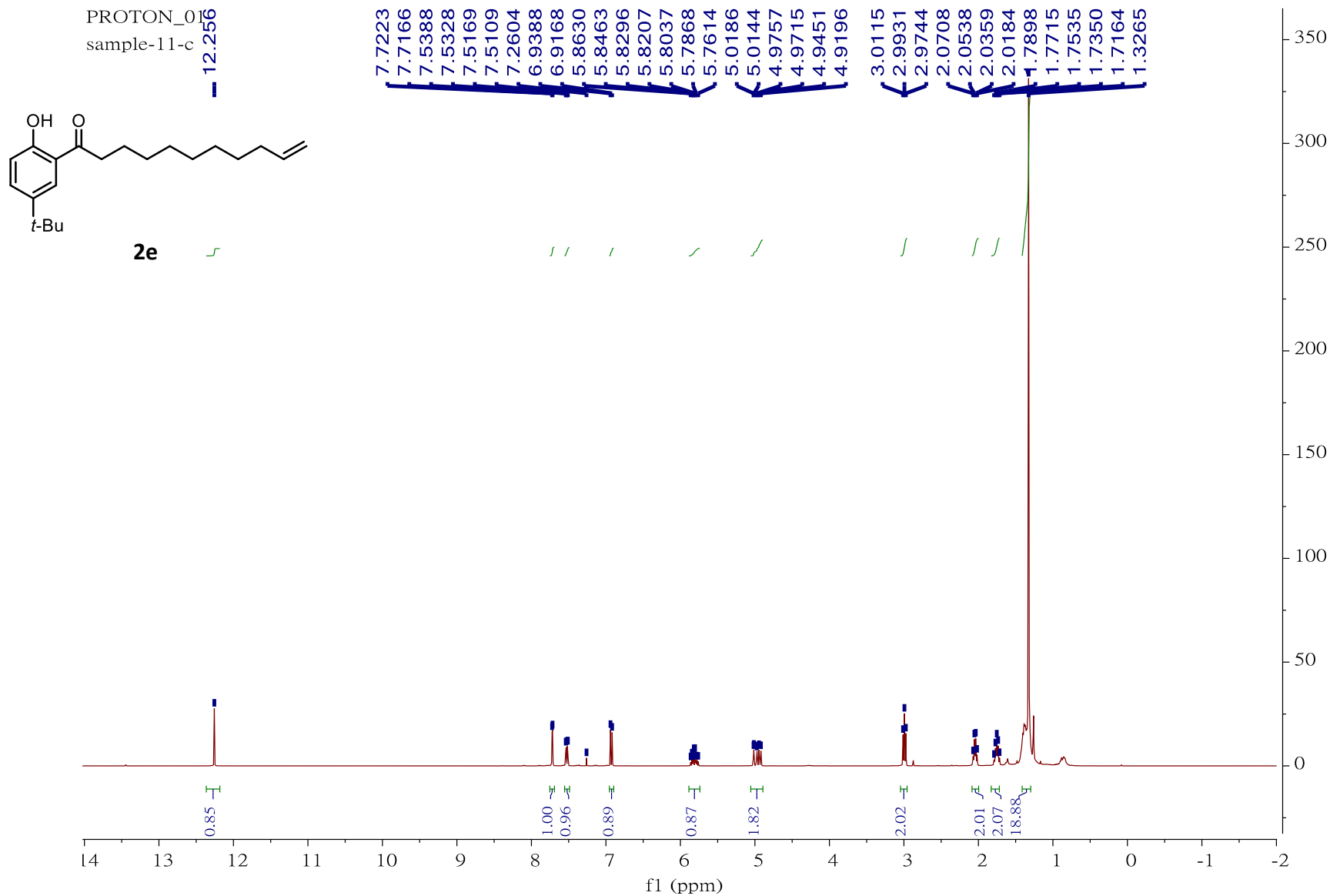
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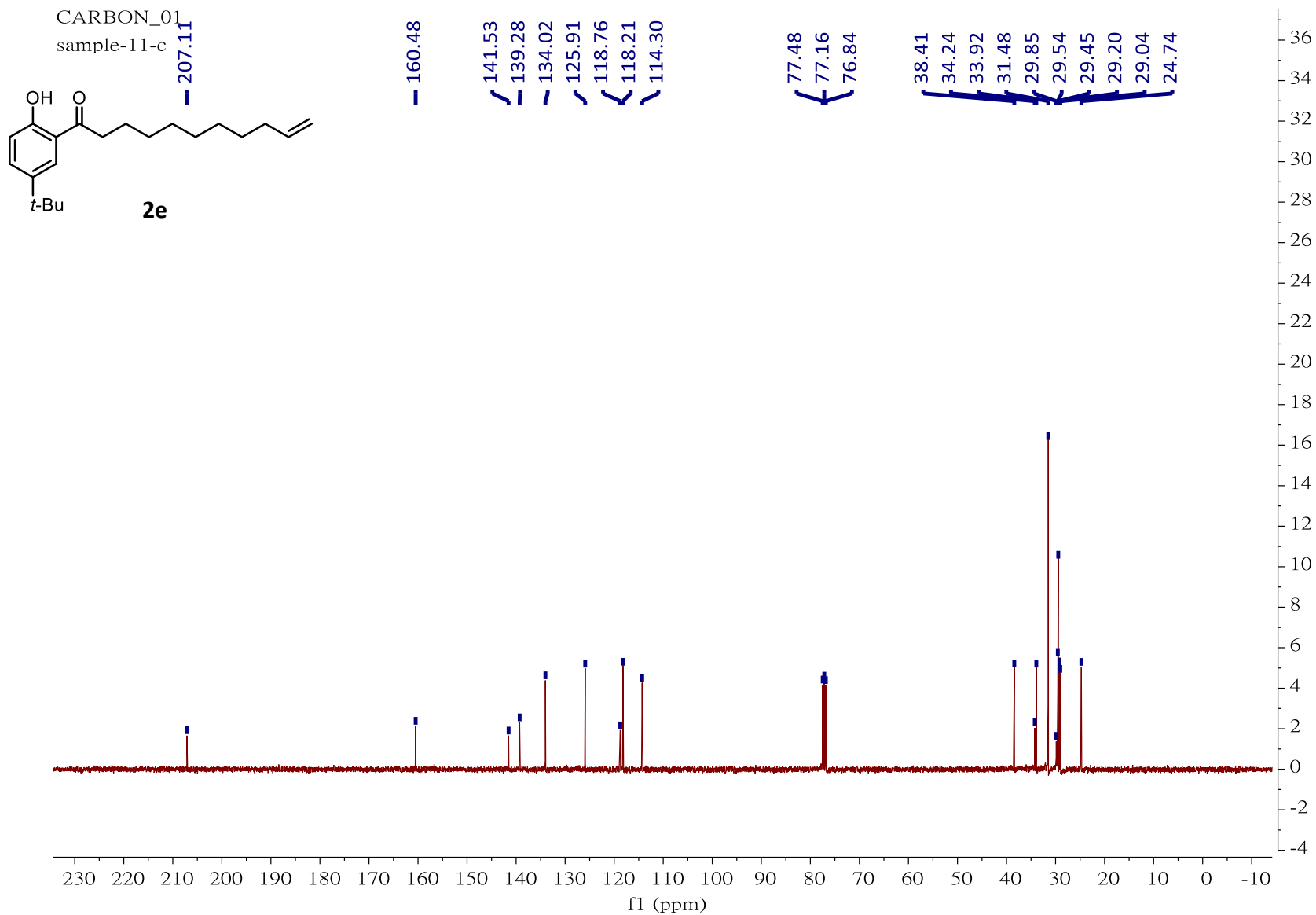
2d'



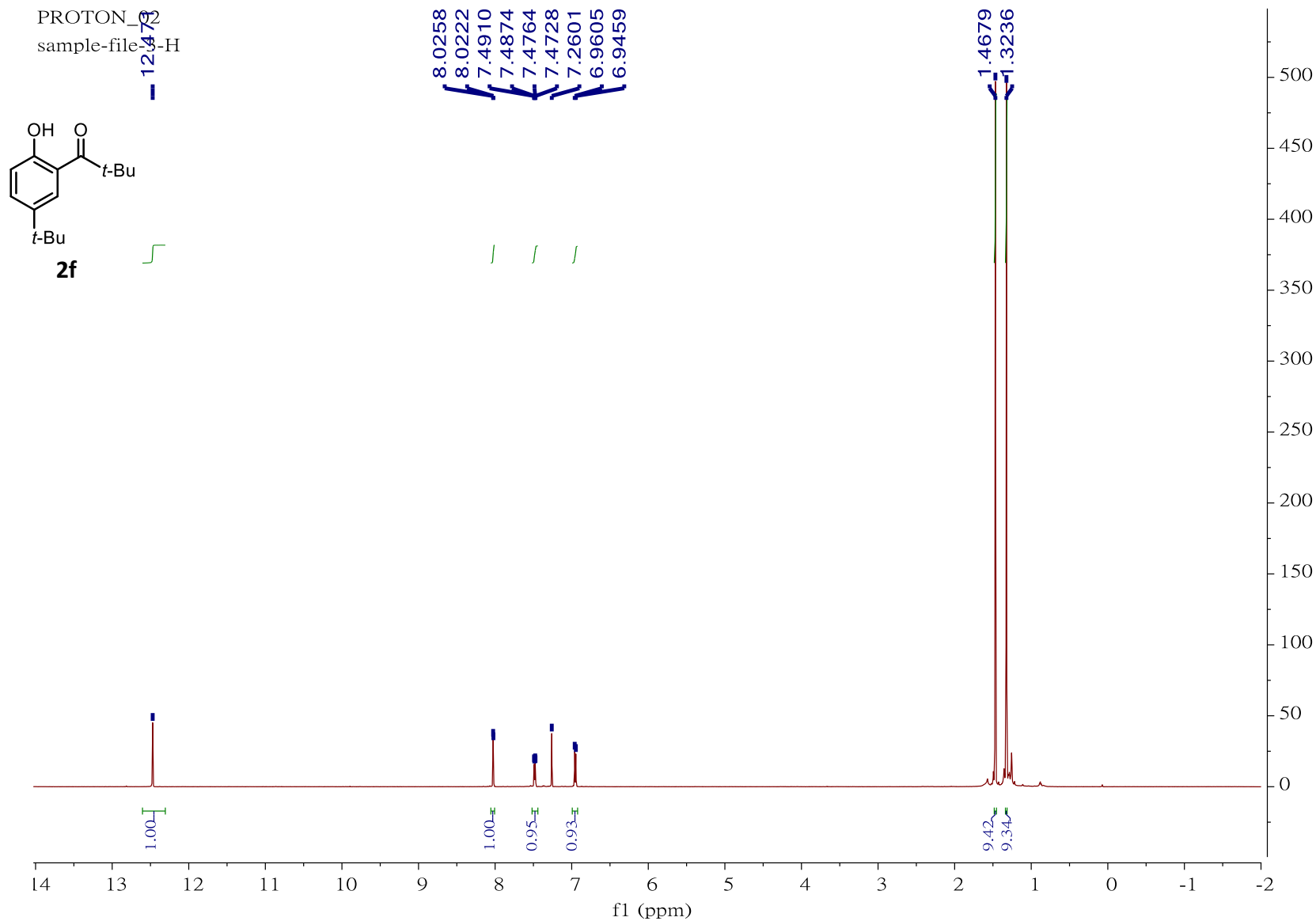
¹H NMR spectrum of compound 2e



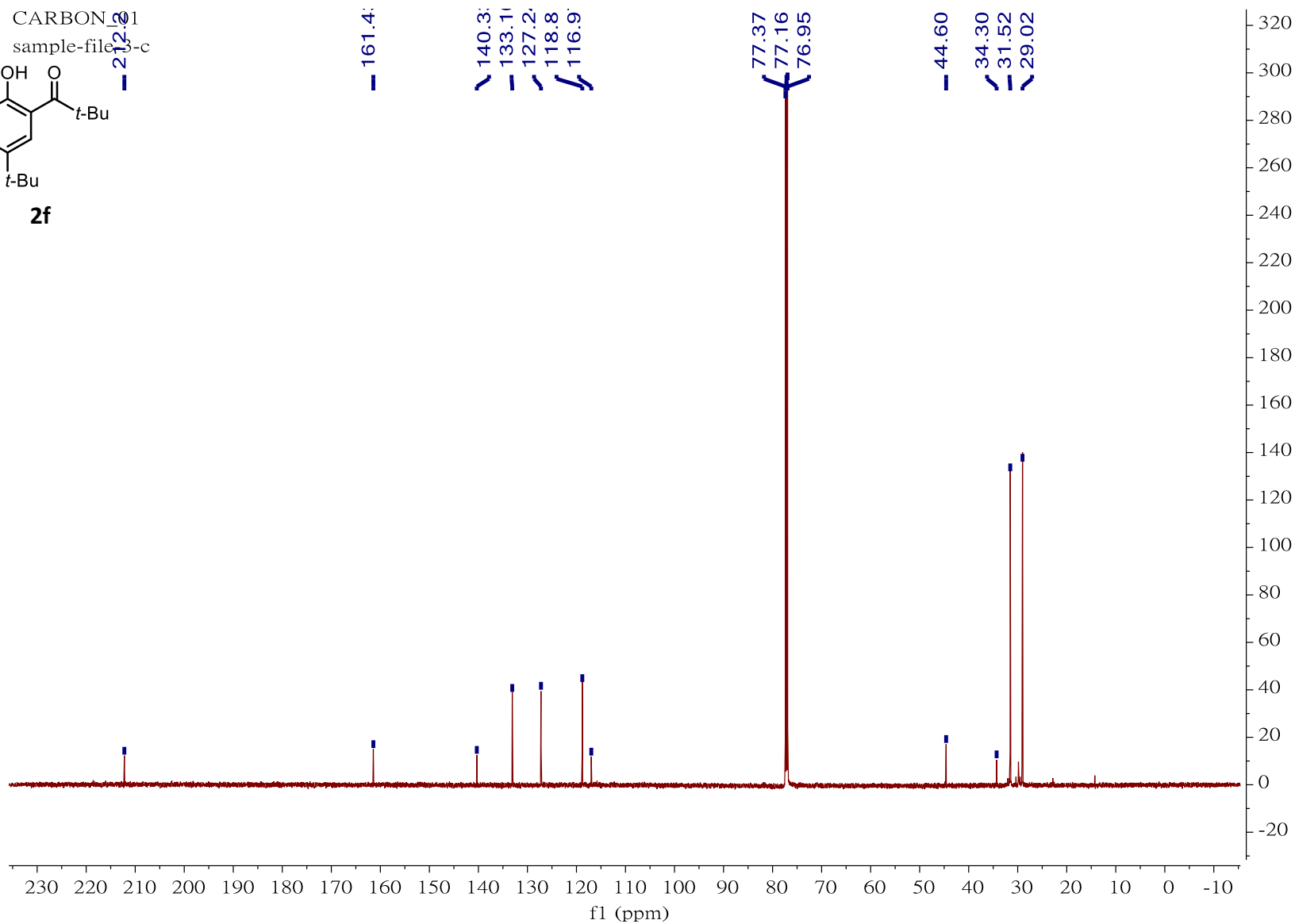
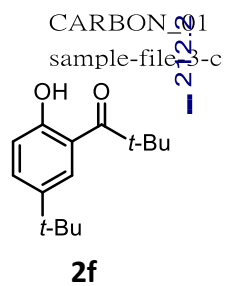
¹³C NMR spectrum of compound 2e



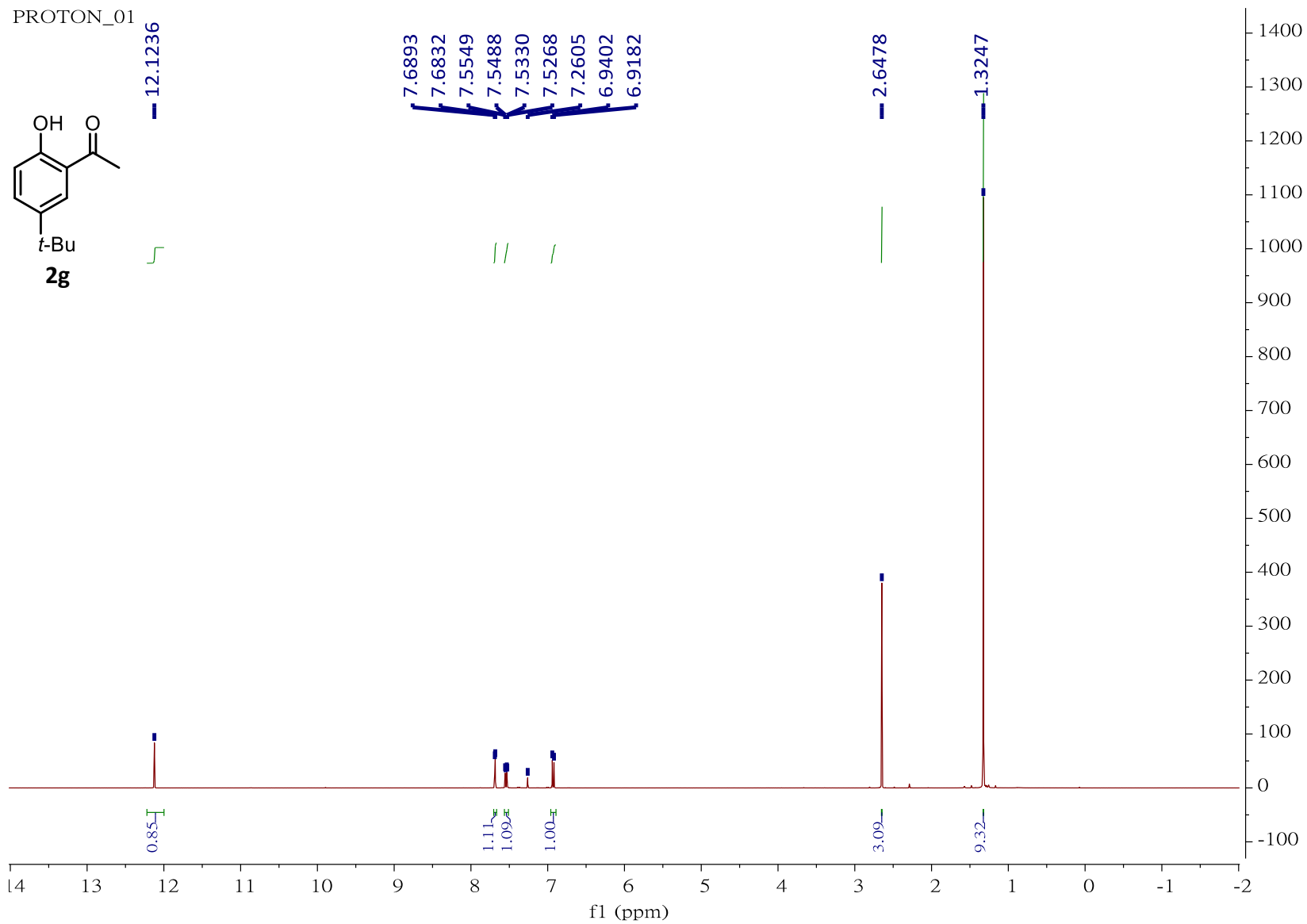
¹H NMR spectrum of compound 2f



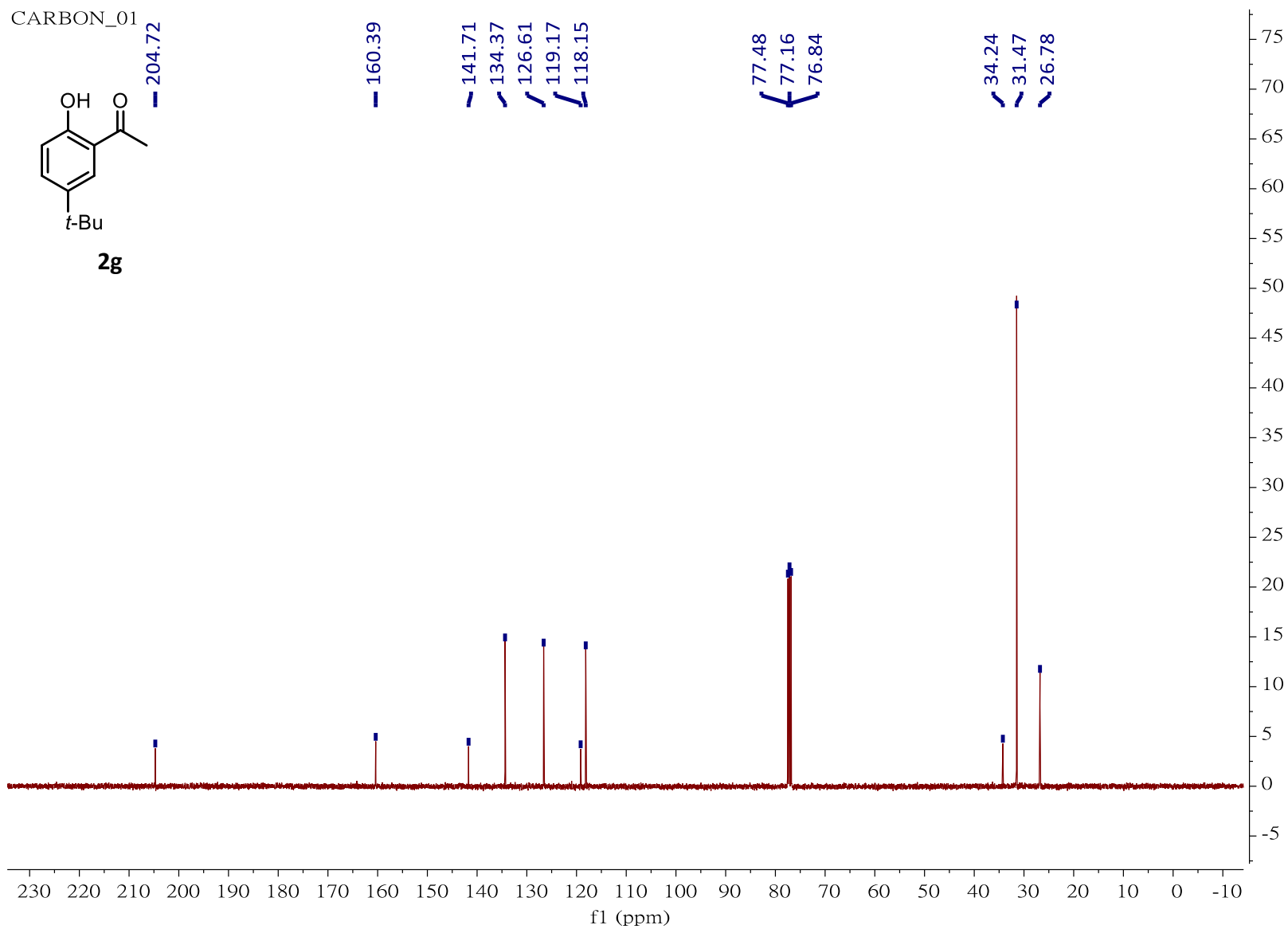
¹³C NMR spectrum of compound 2f



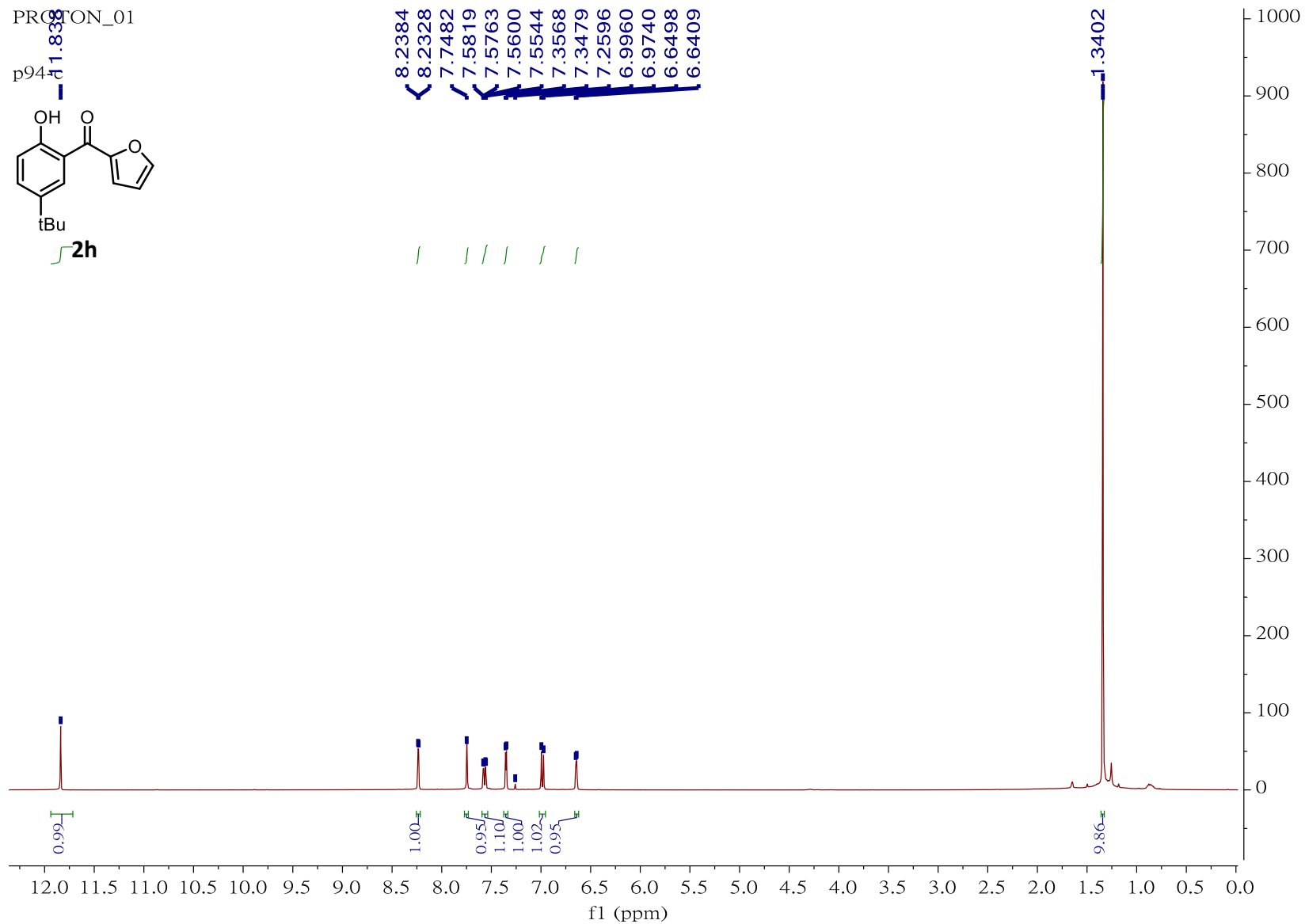
¹H NMR spectrum of compound 2g



¹³C NMR spectrum of compound 2g



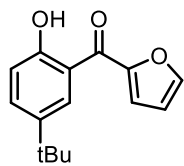
¹H NMR spectrum of compound 2h



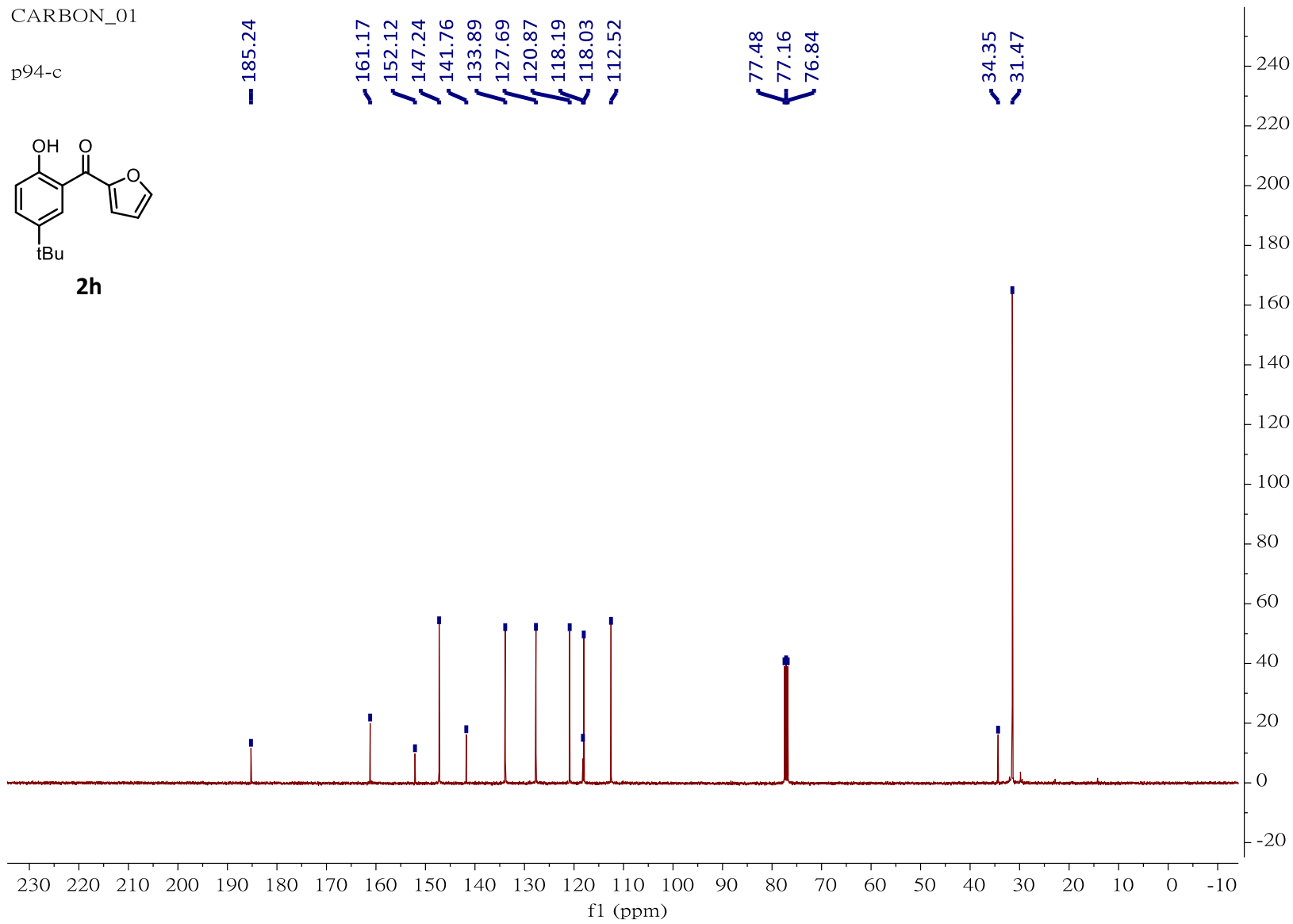
¹³C NMR spectrum of compound 2h

CARBON_01

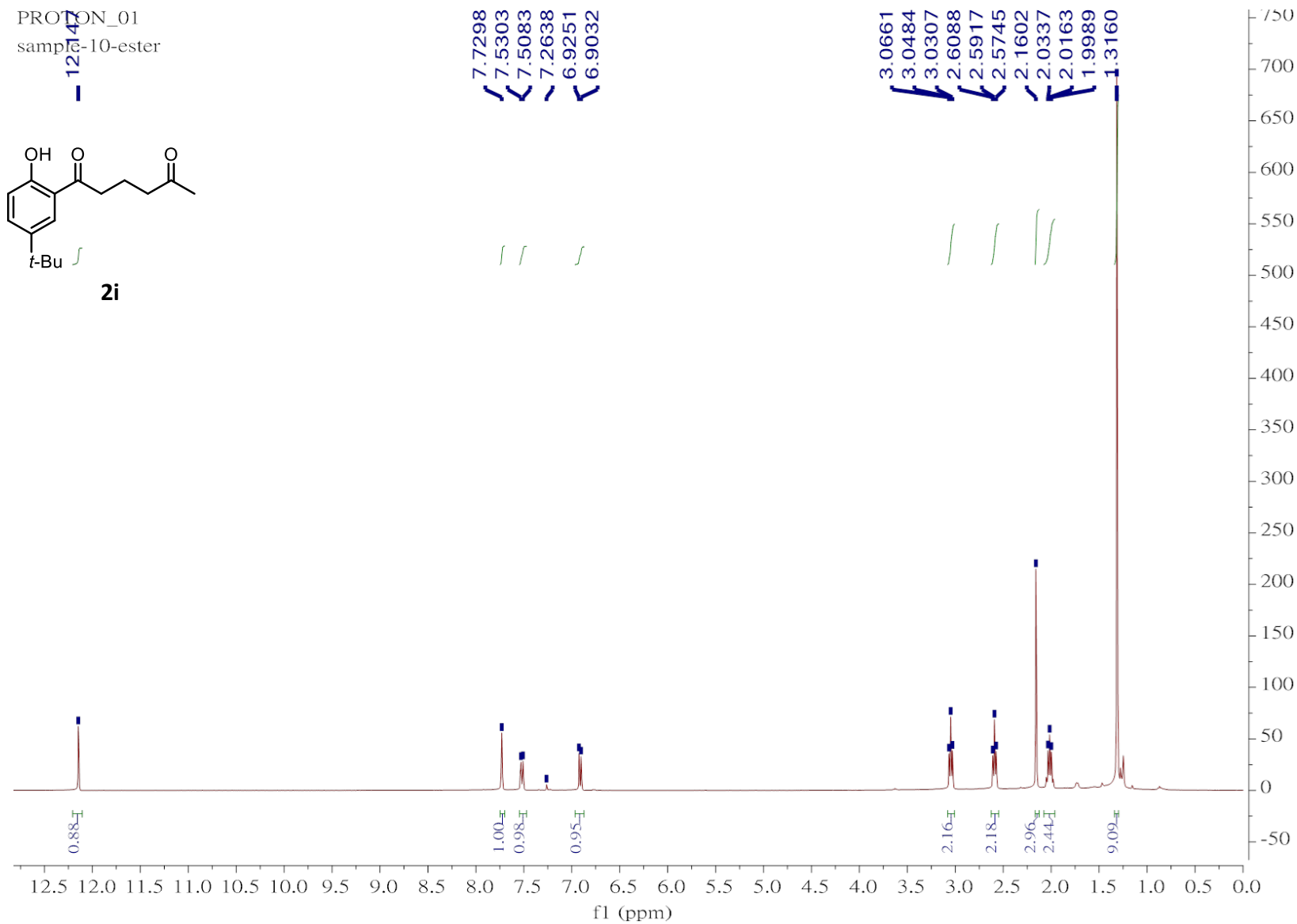
p94-c



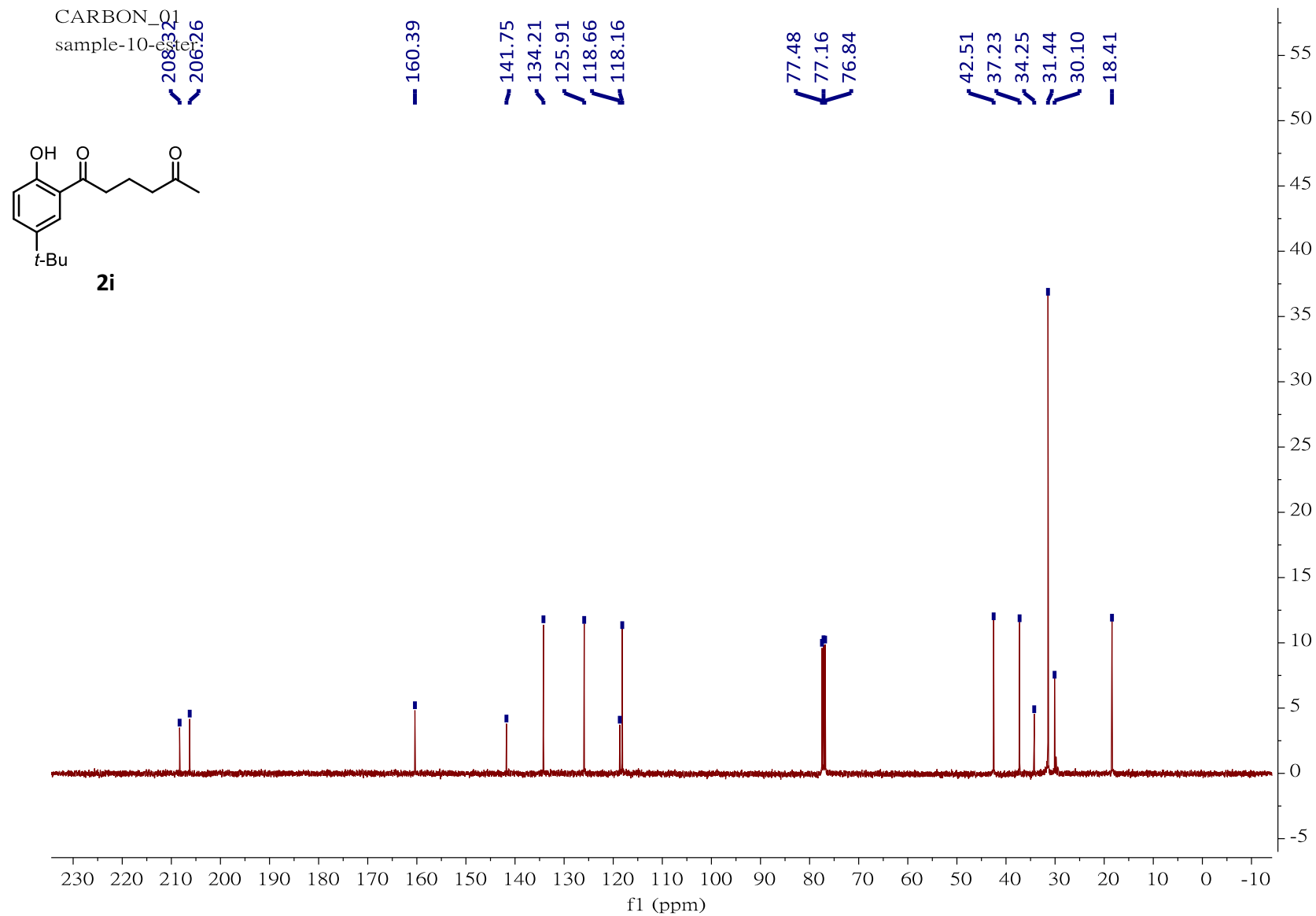
2h



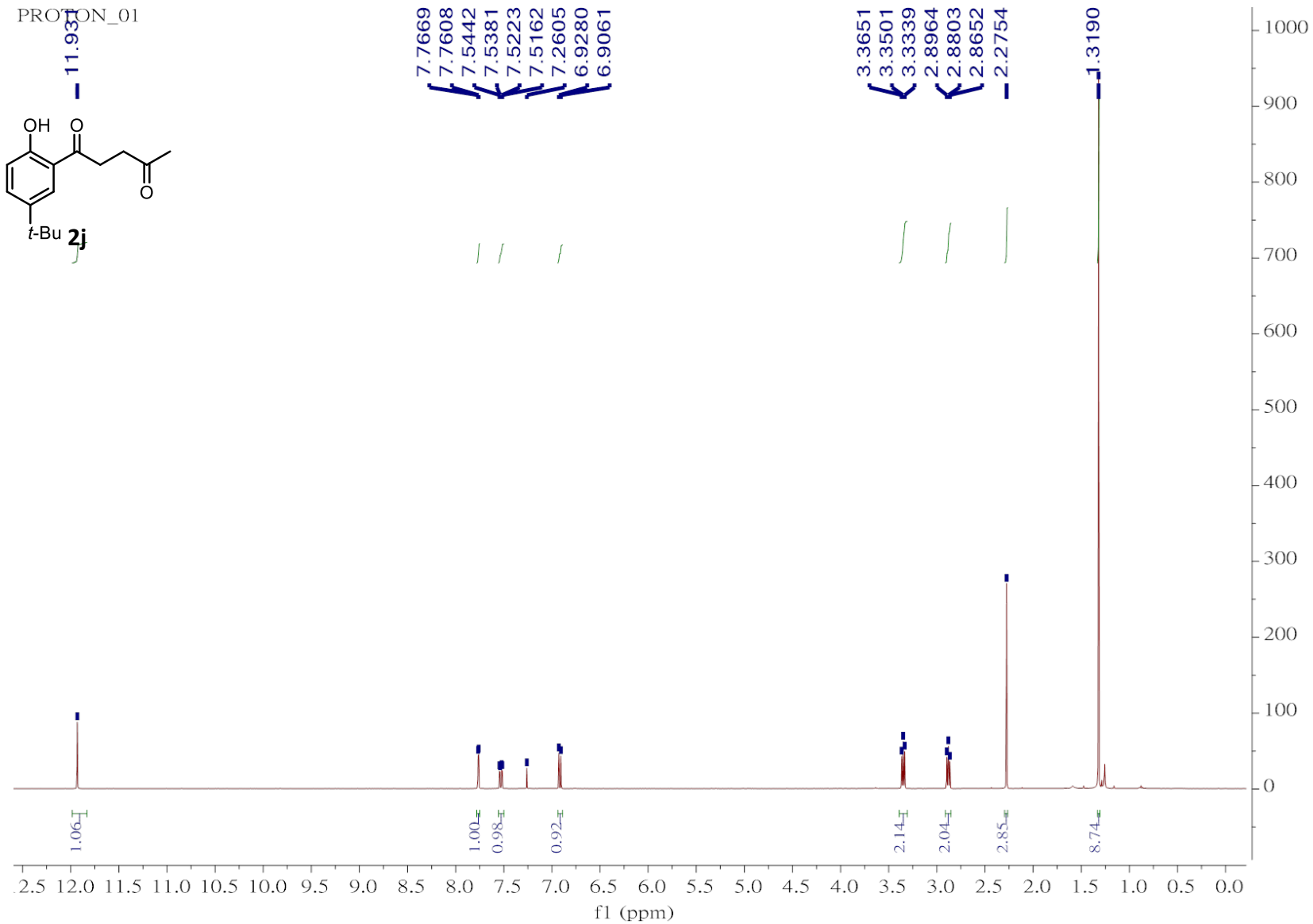
¹H NMR spectrum of compound 2i



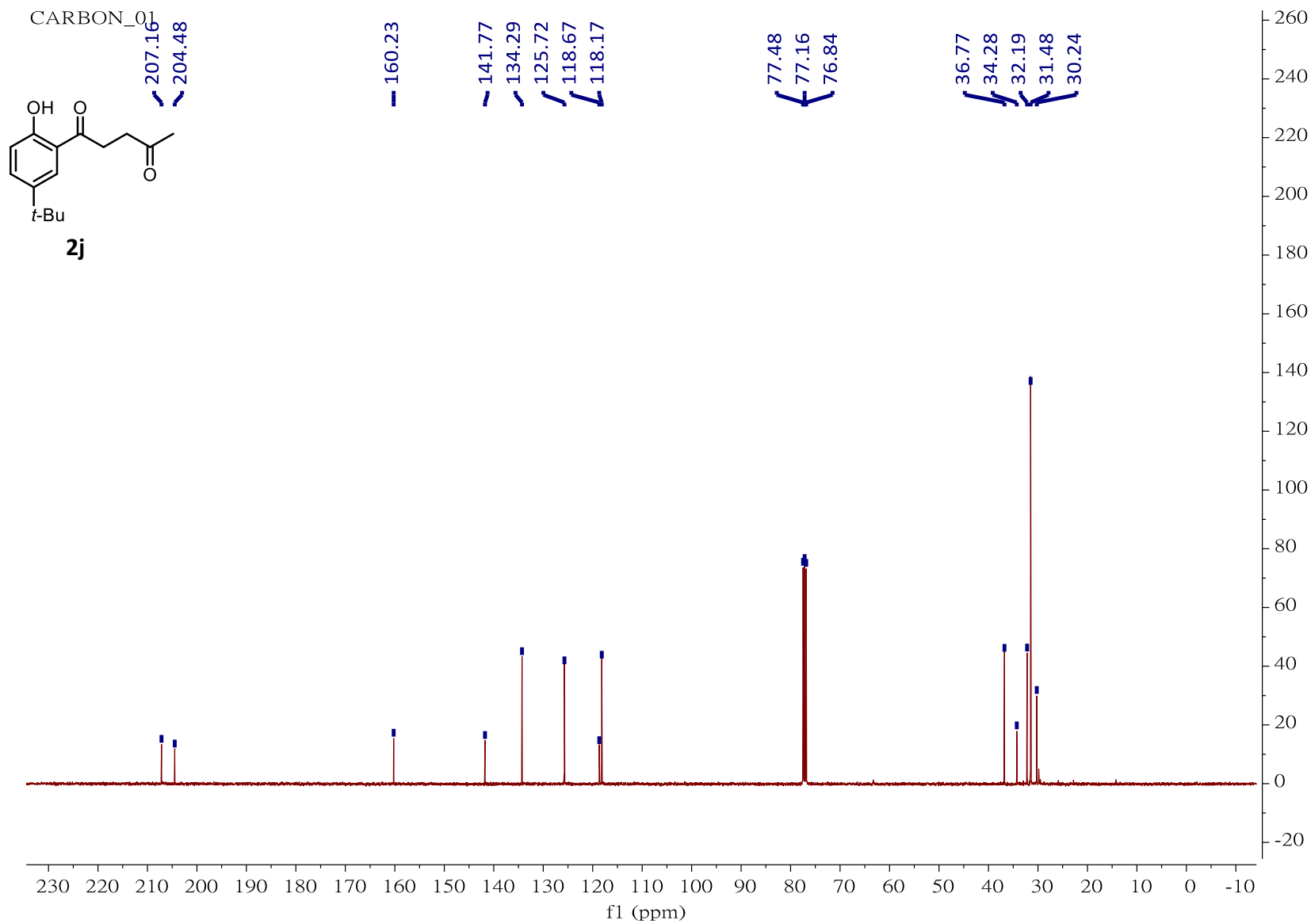
¹³C NMR spectrum of compound 2i



¹H NMR spectrum of compound 2j

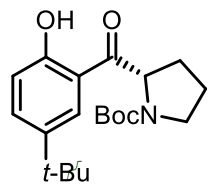


¹³C NMR spectrum of compound 2j

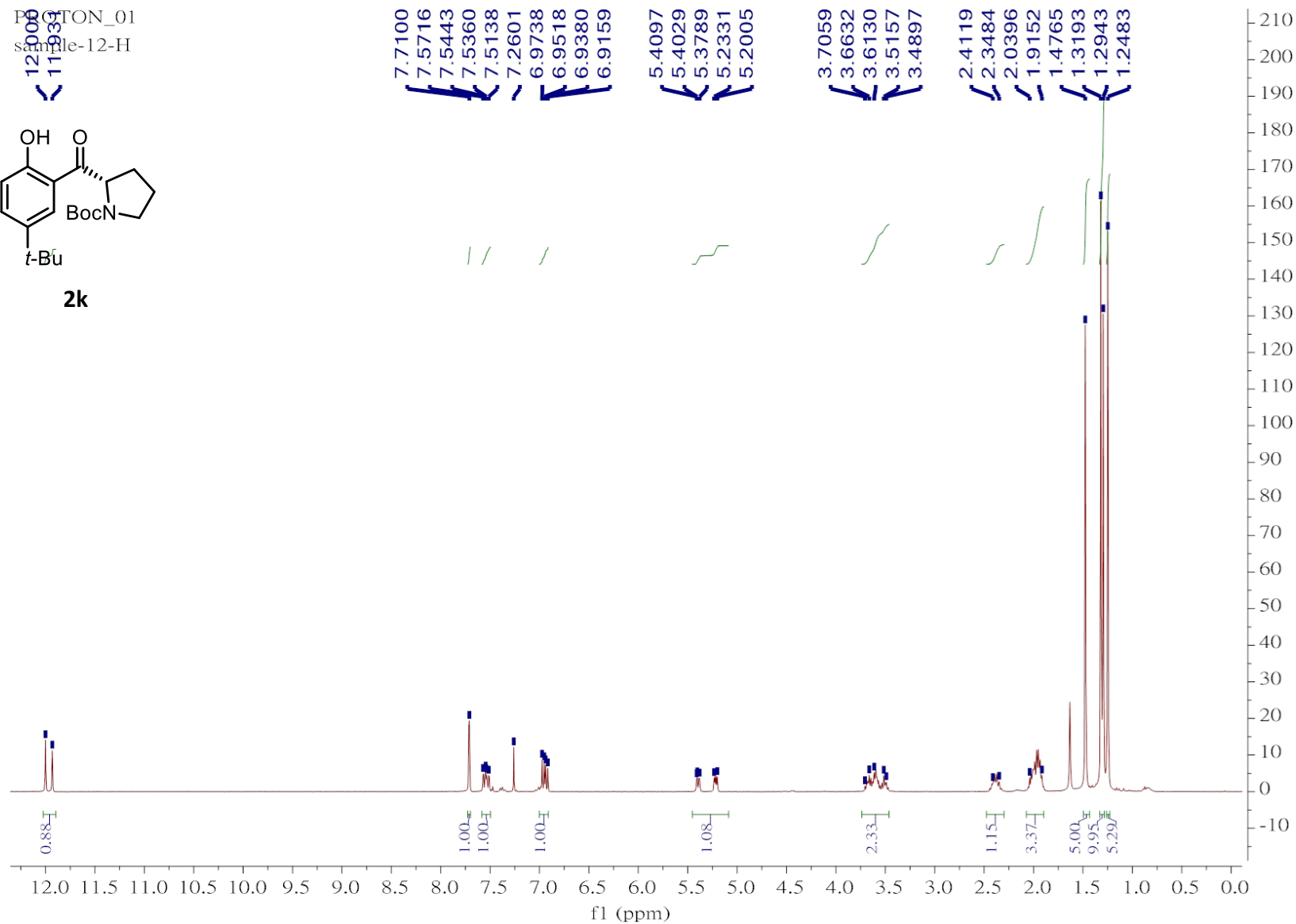


¹H NMR spectrum of compound 2k

PEPTON_01
sample-12-H

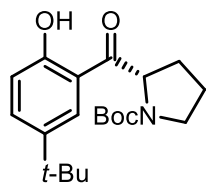


2k

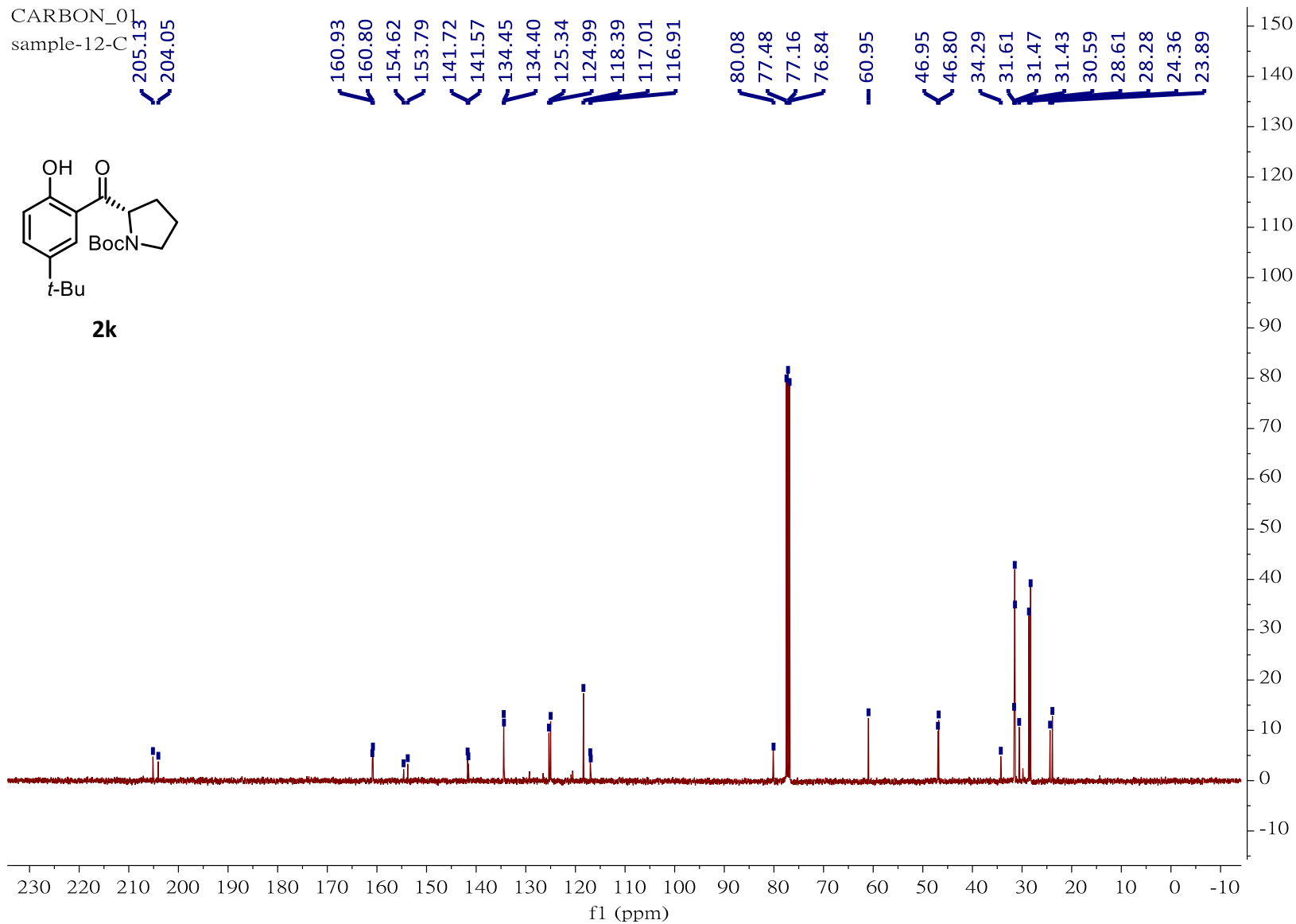


¹³C NMR spectrum of compound 2k

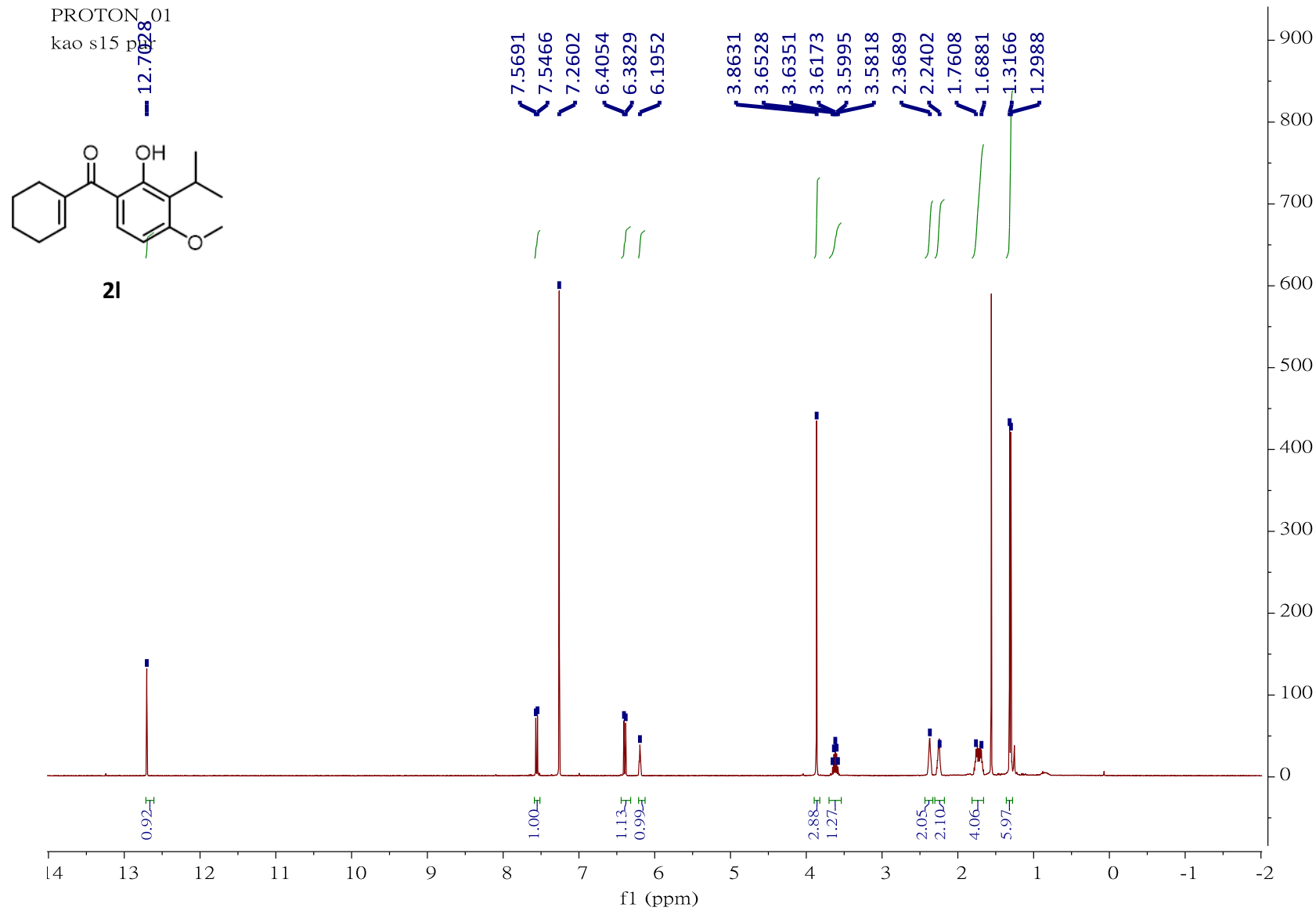
CARBON_01
sample-12-C
205.13
204.05



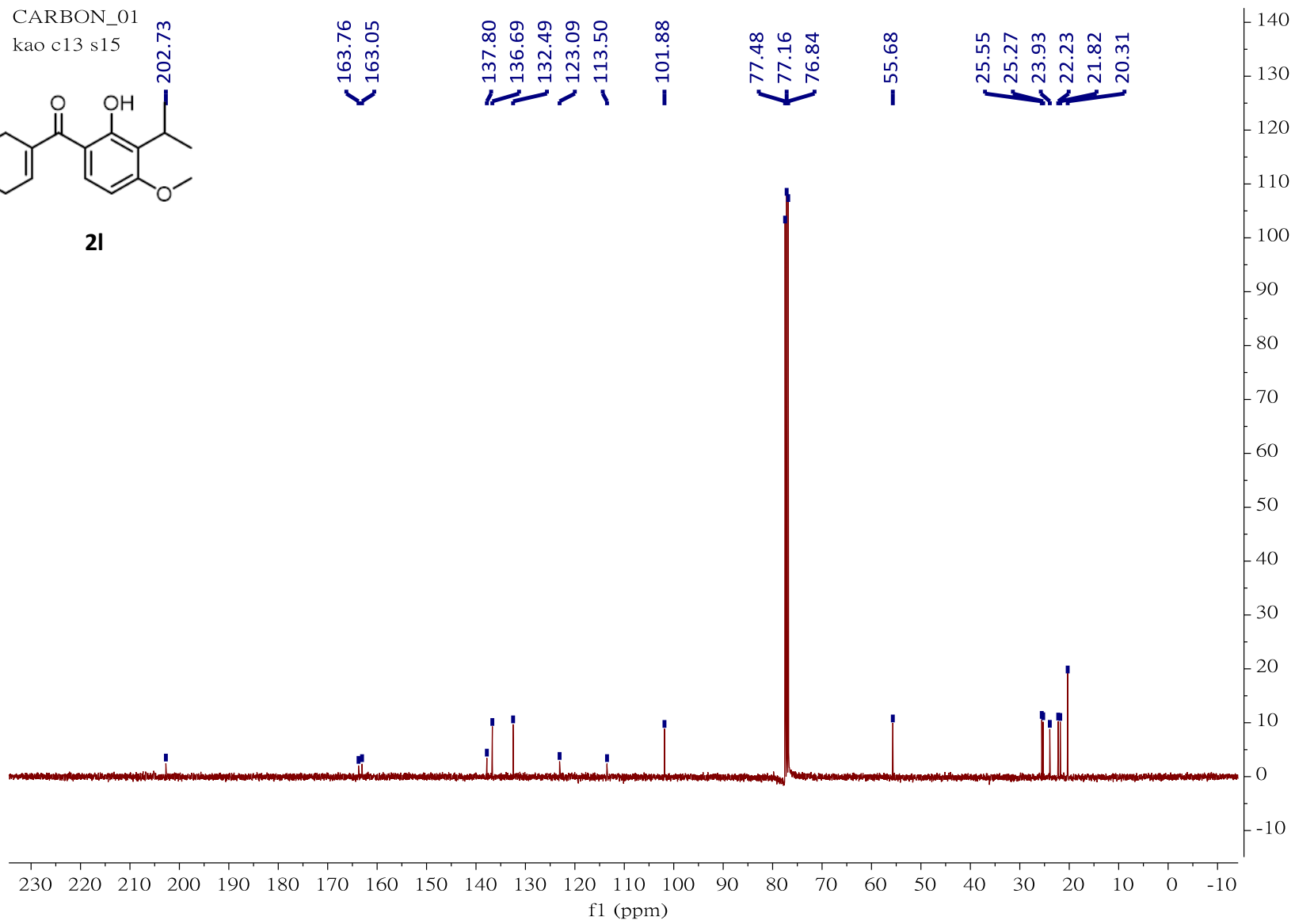
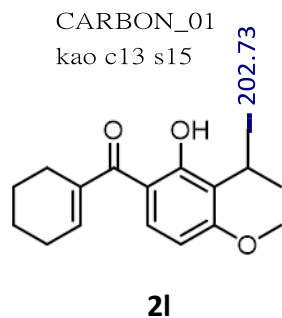
2k



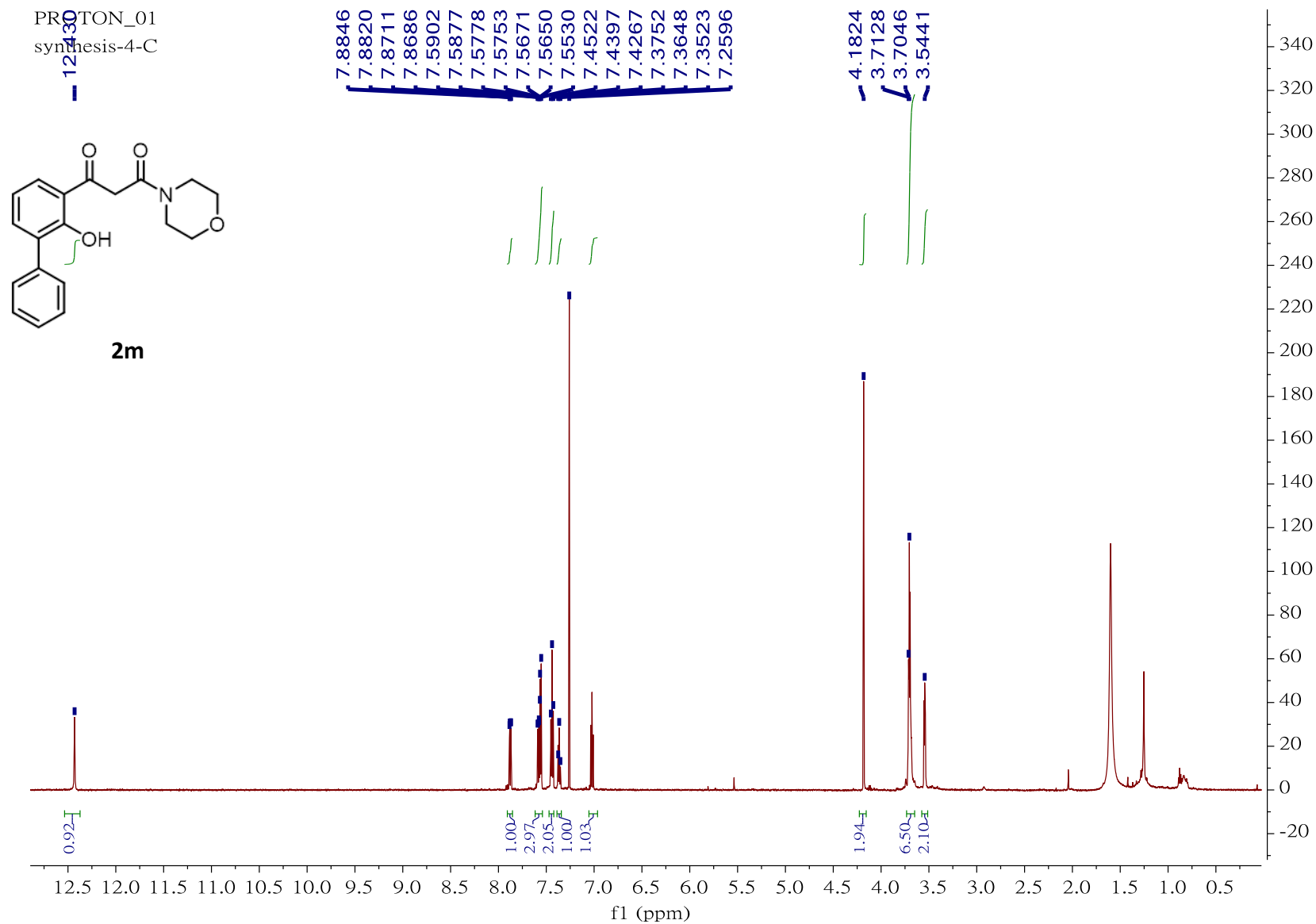
¹H NMR spectrum of compound 2I



¹³C NMR spectrum of compound 21



¹H NMR spectrum of compound 2m



¹³C NMR spectrum of compound 2m

