Photooxygenation of Azidoalkyl Furans:Catalyst Free Triazole and New Endoperoxide Rearrangement

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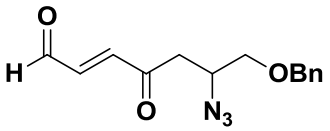
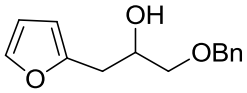
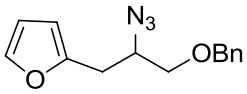
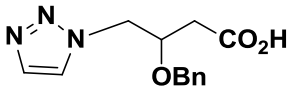
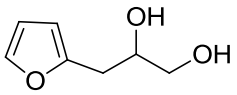
Table of Contents











1. General Information

All reactions were performed under nitrogen atmosphere. All commercial reagents and chromatography solvents were used as obtained unless otherwise stated. Anhydrous solvents were distilled over appropriate drying agents prior to use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254}. Fluka Silica gel 60 (0.063-0.2 mm) was used for column chromatography. Radial chromatography plates were prepared with Merck silica gel 60 PF_{254}-gypsium. TLC visualization was accomplished with UV light (254 nm) and by staining with ethanolic PMA (phosphomolybdic acid) solution. Elemental analyses were performed on a Leco CHNS-932. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer. High resolution mass spectra were measured on a Bruker Daltonics micrOTOF-Q. NMR spectra were recorded using a Varian 200 MHz NMR instrument (^{1}H NMR at 200 MHz, ^{13}C NMR at 50 MHz) or a Varian 400 MHz instrument (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz). ^{1}H NMR data are reported as follows: chemical shift (δ ppm), multiplicity (s=singlet, d=dublet, dd=doublet of doublets, ddd=doublet of doublets of doublets, brs=broad singlet, t=triplet, q=quartet, quint=quintet, m=multiplet or otherwise stated), integration, coupling constant (*J*, Hz). ^{13}C NMR data are given in terms of chemical shift (δ ppm).

2. General Procedures for Starting Materials

2a. General procedure for the benzyl protection of alcohols

To a suspension of NaH (2 equiv) in dry THF was added alcohol at 0 ^{o}C under argon atmosphere and stirred for 30 min. BnBr (1.2 equiv) was then added to the reaction mixture and allowed to warm to rt. The reaction was monitored with TLC. Upon completion, the reaction was quenched with water and concentrated in vacuo. Residue was extracted with ethyl acetate, dried over with Na_2SO_4, filtered, and then the solvent was removed under reduced pressure. The residue was purified by radial chromatography or column chromatography (EtOAc/hexanes) to afford the benzyl protected alcohol.

2b. General procedure for the preparation of alkylfurans

To a solution of furan in anhydrous THF was added *n*-BuLi at -78 ^{o}C under nitrogen atmosphere. The resulting mixture was stirred for 2 h while warming to -5 ^{o}C. After 2 h at -5 ^{o}C, it was treated with glycidol, aldehydes and alkyl halides. Upon completion judged by TLC, the reaction was

quenched with saturated aqueous NH_4Cl. The reaction mixture was extracted with EtOAc. The organic layers were dried over with Na_2SO_4, filtered and concentrated in vacuo. The residues were purified by radial chromatography or column chromatography (EtOAc/hexanes) to afford the corresponding alkylfurans.

2c. General Procedure for azidoalkylfurans from alcohols

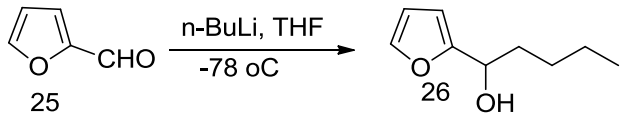
To a solution of alcohol (1 equiv) in dry DCM was added NEt_3 (1.2 equiv) at 0 ^oC under argon atmosphere and stirred for 5 min. MsCl (1.1 equiv) was then added and allowed to warm to rt. Upon the completion of the reaction judged by TLC, it was quenched with H_2O. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over with Na_2SO_4 and concentrated in vacuo. The residue was used directly without further purification.

A mixture of NaN_3 (4 equiv) and crude material in DMF was heated at 70 ^oC under argon atmosphere. Upon completion judged by TLC, the reaction was quenched with H_2O and extracted with hexane or ethyl acetate. The organic layer was dried over with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by radial chromatography or column chromatography (EtOAc/hexanes) to afford azidoalkylfuran.

2d. General Procedure for azidoalkylfuran from furanalkylhalide

A mixture of furan or methyl furanalkylhalide (1 equiv) and NaN_3 (4 equiv) in DMF was heated at 70 ^oC under nitrogen atmosphere. Upon completion judged by TLC, the reaction was quenched with H_2O. The aqueous mixture was extracted with hexane or ethyl acetate. The combined layer was dried over with Na_2SO_4 and concentrated in vacuo. The residue was purified by radial or column chromatography (silica gel, hexane) to afford the pure furan or methyl furanalkylhalide derivative.

1-(Furan-2-yl)pentan-1-ol (26)



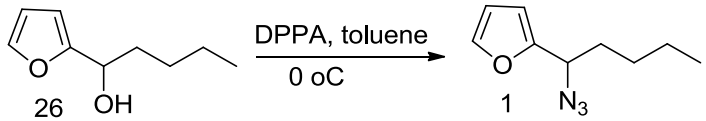
To a solution of furfural (4.5 g, 46.83 mmol) in dry THF (100 mL) at -78 ºC under N_2 was added *n*-BuLi (29 mL, 46.83 mmol, 1.6 M solution in hexanes). The reaction mixture was stirred a further 1.5 h at -78 ºC. After 1.5 h, the reaction mixture was quenched with NH_4Cl (50 mL) and extracted with EtOAc (2x50 mL). The combined organic layers were dried over with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by silica gel column chromotography (1:4, EtOAc/hexanes) to afford **26** (4.6 g, 64%, R_f=0.36, 1:4) as a light yellow liquid.

IR (neat, cm^{-1}) 3348, 2957, 2933, 2862, 1504, 1466, 1378, 1148.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J*=0.9 Hz, 1H), 6.31 (m, 1H), 6.21 (d, *J*=3.2 Hz, 1H), 4.64 (t, *J*=6.8 Hz, 1H), 2.11 (s, 1H), 1.90-1.79 (m, 2H), 1.45-1.22 (m, 4H), 0.90 (t, *J*=7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 142.0, 110.3, 106.0, 68.0, 35.5, 27.9, 22.7, 14.2.

2-(1-Azidopentyl)furan (1)



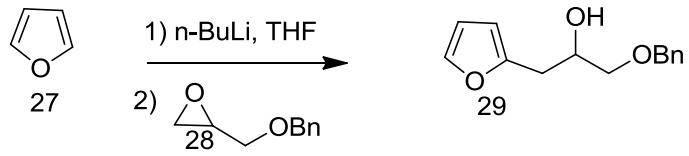
To a solution of **27** (4.6 g, 29.85 mmol) in dry toluene (100 mL) at 0 ^{o}C under N_2 was added DPPA (7.72 mL, 35.82 mmol) followed by DBU (5.35 mL, 35.82 mmol). The reaction mixture was allowed to warm to rt and stirred for 13 h. It was washed with water (50 mL) and NH_4Cl (50 mL). The mixture was extracted with EtOAc (3x75 mL). The combined organic layers were dried over with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by silica gel column chromotography to afford **1** (3.71 g, 69%, R_f=0.7, EtOAc/hexanes, 1:4) as a light yellow liquid.

IR (neat, cm^{-1}) 3053, 2959, 2863, 2101, 1265, 1012.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J*=0.9 Hz, 1H), 6.36 (m, 1H), 6.30 (d, *J*=3.2 Hz, 1H), 4.37 (t, *J*=7.4 Hz, 1H), 1.94-1.82 (m, 2H), 1.45-1.26 (m, 4H), 0.91 (t, *J*=6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 142.9, 110.4, 107.8, 59.1, 32.5, 28.5, 22.5, 14.2.

1-(Benzyloxy)-3-(furan-2-yl)propan-2-ol (29)



The general procedure for the preparation of alkylfurans was employed with dry THF (80 mL), **28** 14.00 g (85.26 mmol), furan (12.4 mL, 170.65 mmol), *n*-BuLi (72.00 mL, 179.17 mmol, 2.5 M in hexanes). Purification by silica gel column chromatography afforded **29** (7.00 g, 35%, R_f=0.16, EtOAc/hexanes, 1:5) as a yellow liquid.

IR (neat, cm^{-1}) 3432, 3116, 3064, 3031, 2914, 2863, 1599, 1497, 1507, 1453, 1098, 1028, 1008.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 6H), 6.30 (dd, *J*=3.1 Hz, *J*=1.9 Hz, 1H), 6.11-6.08 (m,1H), 4.59-4.53 (m, 2H), 4.12 (m,1H), 3.54 (dd, *J*=9.5 Hz, *J*=3.66 Hz, 1H), 3.42 (dd, *J*=9.5 Hz, *J*=6.8 Hz, 1H), 2.91-2.80 (m, 2H), 2.43 (d, *J*=4.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 141.7, 138.1, 128.7, 128.0, 128.0, 110.5, 107.2, 73.7, 73.6, 69.5, 32.6.

2-(2-Azido-3-(benzyloxy)propyl)furan (4)

The general procedure for the azidoalkylfurans from alcohols was employed with DCM (80 mL), **29** (3.06 g, 13.17 mmol), MsCl (1.03 mL, 13.19 mmol) and NEt_3 (2.75 mL, 19.78 mmol) to afford the crude (4.06 g).

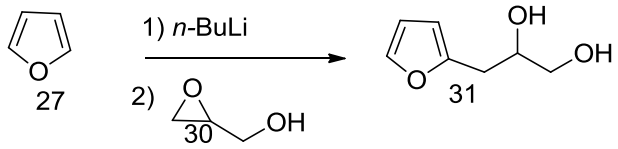
DMF (15 mL), NaN_3 (4.30 g, 65.95 mmol) and the crude (3.50 g). Purification by silica gel column chromatography afforded **4** (2.95 g, 87%, R_f=0.75, EtOAc/hexanes, 1:9) as a yellow liquid.

IR (neat, cm^{-1}) 3707, 3031, 2863, 2110, 1504, 1454, 1362, 1266.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 6H), 6.32 (dd, *J*=3.2 Hz, *J*=1.9 Hz, 1H), 6.12 (dd, *J*=3.2 Hz, *J*=0.7 Hz, 1H), 4.58 (s, 2H), 3.87 (m, 1H), 3.61 (dd, *J*=9.9 Hz, *J*=4.0 Hz, 1H), 3.52 (dd, *J*=9.9 Hz, *J*=6.6 Hz, 1H), 2.92 (dd, *J*=15.2 Hz, *J*=6.1 Hz, 1H), 2.86 (dd, *J*=15.2 Hz, *J*=7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 141.9, 138.0, 128.7, 128.0, 127.8, 110.6, 107.7, 73.7, 72.1, 60.6, 30.1.

3-(Furan-2-yl)propane-1,2-diol (31)



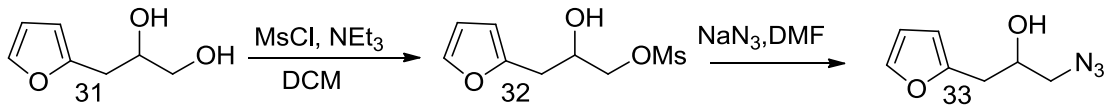
The general procedure for the preparation of alkylfurans was employed with THF (60 mL), glycidol (2.00 g, 27.00 mmol), furan (4.00 mL, 54.00 mmol) and *n*-BuLi (35.40 mL, 56.70 mmol, 1.6 M in hexanes). Purification by silica gel column chromatography afforded **31** (2.98 g, 78%, R_f=0.3, EtOAc/hexanes, 3:2) as a yellow liquid.

IR (neat, cm^{-1}) 3432, 3116, 3064, 3031, 2914, 2863, 1599, 1497, 1507, 1453, 1098, 1028, 1008.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 1H), 6.28 (dd, *J*=3.1 Hz, *J*=1.9 Hz, 1H), 6.08 (m, 1H), 3.95 (m, 1H), 3.63-3.41 (m, 4H), 2.82-2.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 141.8, 110.6, 107.3, 71.1, 66.1, 32.3.

1-Azido-3-(furan-2-yl)propan-2-ol (33)



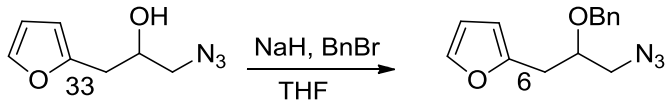
The general procedure for azidoalkylfurans from alcohols was employed with DCM (70 mL), **31** (3.46 g, 24.35 mmol), MsCl (1.9 mL, 24.35 mmol) and NEt_3 (6.77 mL, 48.53 mmol) to afford crude **32** (5.36 g, 24.35 mmol). It was used in the next step without purification.

DMF (20 mL), NaN_3 (6.33 g, 97.40 mmol) and the crude **32** (5.36 g). Purification by silica gel column chromatography afforded **33** (1.33 g, 33%, R_f=0.7, EtOAc/hexanes, 2:3) as a yellow liquid.

IR (neat, cm^{-1}) 3399, 2923, 2104, 1599, 1507, 1441, 1347, 1290, 1146, 1081, 1009.

^{1}H NMR (400MHz, $CDCl_3$) δ 7.35 (m, 1H), 6.31 (dd, *J*=2.9 Hz, *J*=2.1 Hz, 1H), 6.14 (m, 1H), 4.06 (m, 1H), 3.38 (dd, *J*=12.5 Hz, *J*=3.8 Hz, 1H), 3.29 (dd, *J*=12.5 Hz, *J*=6.7 Hz, 1H), 2.86 (d, *J*=6.3 Hz, 2H), 2.38 (d, *J*=4.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 142.2, 110.6, 107.8, 69.8, 56.1, 33.4.**2-(3-Azido-2-(benzyloxy)propyl)furan (6)**



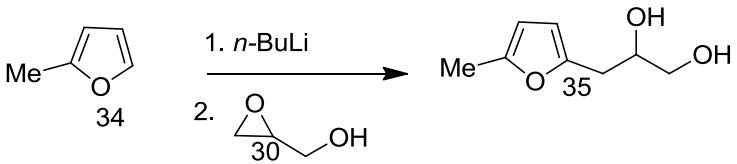
The general procedure for the benzyl protection of alcohols was employed with dry THF (30 mL), **33** (1.38 g, 8.25 mmol), NaH (396.20 mg, 16.50 mmol) and BnBr (1.30 mL, 10.73 mmol). Purification by silica gel column chromatography afforded **6** (1.86 g, 88%, R_f=0.8, EtOAc/hexanes, 1:4) as a light yellow liquid.

IR (neat, cm^{-1}) 3448, 3065, 3031, 2924, 2868, 2101, 1599, 1506, 1454, 1350, 129.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.33 (m, 6H), 6.37 (dd, *J*=3.2 Hz, *J*=1.9 Hz, 1H), 6.17 (m, 1H), 4.65 (d, *J*=11.5 Hz, 1H), 4.61 (d, *J*=11.5 Hz, 1H), 3.92 (m, 1H), 3.38 (dd, *J*=12.9 Hz, *J*=3.8 Hz, 1H), 3.33 (dd, *J*=12.9 Hz, *J*=6.1 Hz, 1H), 3.03 (dd, *J*=15.1 Hz, *J*=6.0 Hz, 1H), 2.94 (dd, *J*=15.1 Hz, *J*=6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 141.8, 138.2, 128.7, 2x128.1, 110.8, 107.7, 77.3, 72.3, 54.0, 31.2.

3-(5-Methylfuran-2-yl)propane-1,2-diol (35)



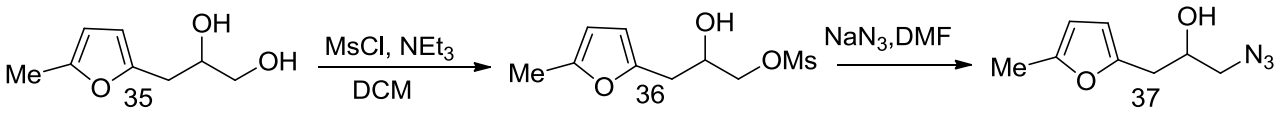
The general procedure for the preparation of alkylfurans was employed with THF (60 mL), glycidol (2.26 g, 30.5 mmol), 2-methylfuran (5.50 mL, 61.00 mmol), and *n*-BuLi (41.80 mL, 67.10 mmol, 1.6 M in hexanes). Purification on silica gel chromatography afforded **35** (3.20 g, 74%) as a yellow liquid.

IR (neat, cm^{-1}) 3395, 2924, 1713, 1646, 1570, 1429, 1356.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (d, *J*=2.8 Hz, 1H), 5.83 (m, 1H), 3.93 (m, 1H), 3.80 (s, 2H), 3.60 (d, *J*=9.8 Hz, 1H), 3.43 (dd, *J*=11.4 Hz, *J*=7.1 Hz, 1H), 2.75-2.64 (m, 2H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 150.4, 107.9, 106.3, 71.2, 66.1, 32.4, 13.7.

1-Azido-3-(5-methylfuran-2-yl)propan-2-ol (37)



The general procedure for azidoalkylfurans from alcohols was employed with DCM (80 mL), **35** (2.93 g, 18.76 mmol), MsCl (1.46 mL, 18.76 mmol) and NEt_3 (3.90 mL, 28.13 mmol) to afford crude **36** (4.13 g). It was used in next step without purification.

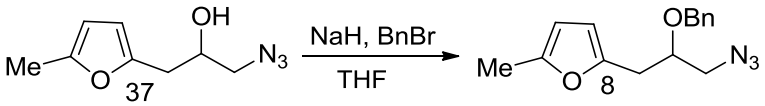
DMF (18 mL), NaN_3 (4.88 g, 75.04 mmol) and the crude **36** (4.13 g). Purification by silica gel column chromatography afforded **37** (1.61 g, 47%, R_f=0.6, EtOAc/hexanes, 1:4) as a yellow liquid.

IR (neat, cm^{-1}) 3365, 2924, 2103, 1614, 1570.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (d, *J*=3.0 Hz, 1H), 5.87 (m, 1H), 4.04 (m, 1H), 3.38 (dd, *J*=12.5 Hz, *J*=3.9 Hz, 1H), 3.30 (dd, *J*=12.5 Hz, *J*=6.7 Hz, 1H), 2.80 (d, *J*=6.3 Hz, 2H), 2.30 (brs, 1H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 149.4, 108.6, 106.4, 69.8, 56.1, 33.6, 13.7.

2-(3-Azido-2-(benzyloxy)propyl)-5-methylfuran (8)



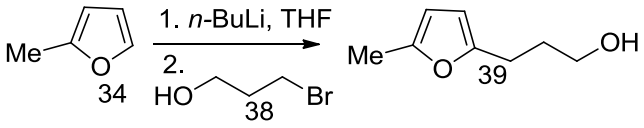
The general procedure for the benzyl protection of alcohols was employed with dry THF (35 mL), **37** (1.61 g, 8.88 mmol), NaH (426.00 mg, 17.76 mmol) and BnBr (1.97 mL, 11.52 mmol). Purification by silica gel column chromatography afforded **8** (1.90 g, 79%, R_f=0.8, EtOAc/hexanes, 1:4) as a colorless liquid.

IR (neat, cm^{-1}) 3031, 2922, 2101, 1618, 1569, 1496, 1453.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 5.99 (d, *J*=3.0 Hz, 1H), 5.90 (m, 1H), 4.63 (d, *J*=11.5 Hz, 1H), 4.60 (d, *J*=11.5 Hz, 1H), 3.87 (m, 1H), 3.37 (dd, *J*=13.0 Hz, *J*=3.9 Hz, 1H), 3.32 (dd, *J*=13.0 Hz, *J*=6.2 Hz, 1H), 2.96 (dd, *J*=15.1 Hz, *J*=5.8 Hz, 1H), 2.84 (dd, *J*=15.1 Hz, *J*=7.0 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 149.8, 138.2, 128.6, 128.1, 128.0, 108.3, 106.4, 77.4, 72.2, 54.0, 31.2, 13.7.

3-(5-Methylfuran-2-yl)propan-1-ol (39)

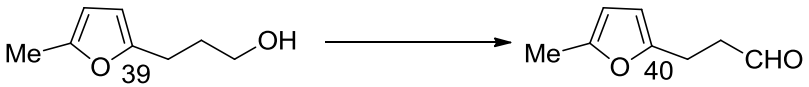


The general procedure for the preparation of alkylfurans was employed with dry THF (60 mL), 3-bromo-1-propanol (4.50 g, 32.37 mmol), 2-methlyfuran (5.58 g, 6.13 mL, 67.98 mmol) and *n*-BuLi (44.51 mL, 71.22 mmol, 1.6 M in hexanes). Purification by silica gel column chromatography afforded **39** (3.52 g, 78%, *Rf*=0.3, EtOAc/hexane, 1:4) as a yellow liquid.

IR (neat, cm^{-1}) 3337, 2950, 2924, 2878, 1618, 1571, 1447.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (d, *J*=2.9 Hz, 1H), 5.84 (m, 1H), 3.69 (t, *J*=6.4 Hz, 2H), 2.67 (t, *J*=7.4 Hz, 2H), 2.25 (s, 3H), 1.92-1.85 (m, 2H), 1.48 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 150.6, 106.0, 105.8, 62.4, 31.4, 24.6, 13.7.**3-(5-Methylfuran-2-yl)propanal (46)**[1]



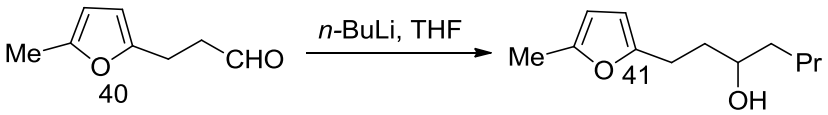
To a solution of DMSO (0.50 g, 0.46 mL, 6.43 mmol) in dry DCM (25 mL) was added $COCl_2$ (1.90 mL, 3.79 mmol) at -78 ^oC under nitrogen atmosphere and stirred for 15 min. After 15 min NEt_3 was added and stirred for 30 min at -78 ^oC. **39** (0.41g, 2.92 mmol) in dry DCM (5 mL) was then added and then allowed to warm to -25 ^oC over 1.5 h. The reaction mixture was then quenched with H_2O and concentrated in vacuo. The residue was extracted with EtOAc, dried over with Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by radial chromatography (1:4 EtOAc/hexanes) to afford **40** (0.28 g, 70%, *Rf*=0.66, EtOAc/hexane, 1:4) as a yellow liquid.

IR (neat, cm^{-1}) 2960, 2923, 2832, 2722, 1726, 1570, 1436, 1388, 1287.

^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (m, 1H), 5.87 (d, *J*=2.8 Hz, 1H), 5.83 (m, 1H), 2.92 (t, *J*=7.2 Hz, 2H), 2.75 (t, *J*=7.3 Hz, 2H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 152.1, 151.0, 106.3, 106.2, 42.2, 21.0, 13.7.

1-(5-Methylfuran-2-yl)heptan-3-ol (41)



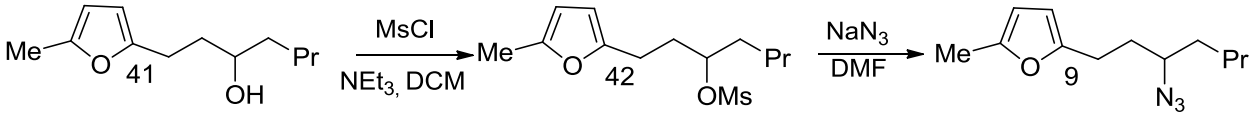
To a solution of **40** (0.61 g, 4.42 mmol) in dry THF (15 mL) was added *n*-BuLi (5.52 mL, 8.83 mmol, 1.6 M in hexanes) at -78 ^oC under nitrogen atmosphere. The resulting mixture was stirred overnight while warming to rt. It was then quenched with saturated aqueous NH_4Cl solution and concentrated in vacuo. The residue was extracted with EtOAc, dried over with Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by radial chromatography (1:4 EtOAc/hexanes) to afford **41** (0.50 g, 58%, R_f=0.5, EtOAc/hexanes, 1:4) as a light yellow liquid.

IR (neat, cm^{-1}) 3360, 2931, 2859, 1617, 1571, 1454, 1375.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (d, *J*=2.9 Hz, 1H), 5.83 (m, 1H), 3.63 (m, 1H), 2.80-2.60 (m, 2H), 2.24 (s, 3H), 1.86-1.76 (m, 1H), 1.75-1.64 (m, 1H), 1.59-1.22 (m, 6H), 0.90 (t, *J*=7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 150.6, 106.0, 105.7, 71.5, 37.4, 36.0, 28.0, 24.6, 23.0, 14.3, 13.7.

2-(3-Azidoheptyl)-5-methylfuran (9)



The general procedure for azidoalkylfurans from alcohols was employed with DCM (15 mL), **41** (0.23 g, 1.18 mmol)**,** MsCl (0.11 mL, 1.42 mmol) and NEt_3 (0.25 mL, 1.77 mmol) to afford crude **42** (0.32 g). It was used in the next step without purification.

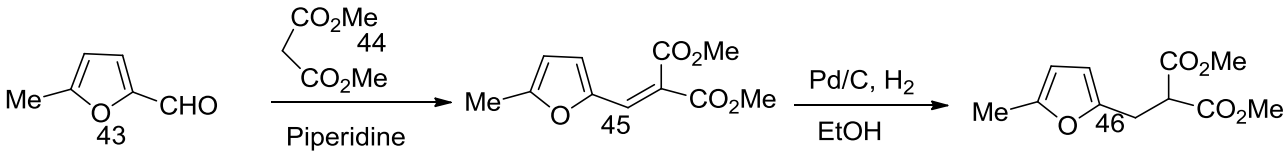
DMF (10 mL), NaN_3 (0.3 g, 4.72 mmol) and the crude **42** (0.32 g). Purification by silica gel column chromatography afforded **9** (0.18 g, 70%, R_f=0.86, EtOAc/hexanes, 1:4) as a yellow liquid.

IR (neat, cm^{-1}) 2951, 2932, 2860, 2100, 1571, 1453, 1245.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (d, *J*=2.9 Hz, 1H), 5.85 (m, 1H), 3.23 (m, 1H), 2.80-2.60 (m, 2H), 2.26 (s, 3H), 1.85 (m, 1H), 1.78 (m, 1H), 1.60-1.53 (m, 2H), 1.48-1.26 (m, 4H), 0.92 (t, *J*=7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 150.8, 106.1x2, 62.5, 34.4, 33.2, 28.4, 25.0, 22.8, 14.2, 13.7.

Dimethyl 2-((5-methylfuran-2-yl)methyl)malonate (46)



A solution of dimethyl malonate (1.98 g, 1.72 mL, 15.00 mmol) and piperidine (2.55 g, 2.97 mL, 29.97 mmol) in toluene (40 mL) was heated at 100 ^{o}C under nitrogen atmosphere and stirred for 1 h. After 1h, 5-methylfurfural (1.50 g, 1.35 mL, 13.62 mmol) was added and stirred for 15 h at the same temperature. The reaction mixture was then quenched with H_2O and extracted with EtOAc, dried over with Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by column chromatography (1:4 EtOAc/Hexanes) to afford **45** (2.57 g, 84%, R_f=0.33, EtOAc/hexanes, 1:4) as a yellow liquid.

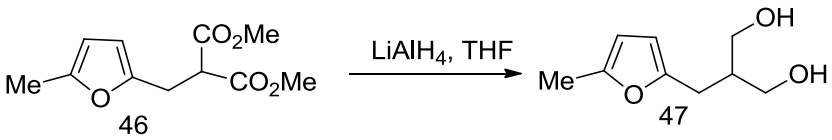
A mixture of **45** (2.48 g, 11.06 mmol) and 124 mg of Pd/C (5%) in EtOH (150 mL) with stirring was washed three times with hydrogen gas filled in a balloon. Then the reaction was maintained under hydrogen for 4.5 h. Pd/C was filtered off and the solvent was removed in vacuo. The residue was purified by column chromatography (1:4 EtOAc/Hexanes) to afford **46 (**1.95 g, 78%, R_f=0.80, EtOAc/hexanes, 1:4) as a colorless liquid.

IR (neat, cm^{-1}) 3011, 2957, 2841, 1735, 1619, 1437, 1347, 1281, 1243, 1204, 1160.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (d, *J*=3.0 Hz, 1H), 5.81 (m, 1H), 3.75-3.70 (m, 7H), 3.19 (d, *J*=7.7 Hz, 2H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 151.4, 149.8, 107.6, 106.3, 52.8, 51.2, 27.7, 13.7.

2-((5-Methylfuran-2-yl)methyl)propane-1,3-diol (47)



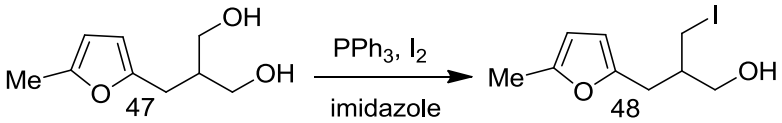
To a suspension of LAH (1.67 g, 44.00 mmol) in dry THF (80 mL) was added **46** (1.98 g, 8.75 mmol) in dry THF (10 mL) under argon atmosphere and heated to 70 ^{o}C for 10 h. The reaction mixture was then quenched with acetone and H_2O. The solid material was filtered. The filtrate was extracted with EtOAc (2x30 mL) and washed with (2x20 mL). The combined organic layers were dried over with Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by column chromatography (3:2 EtOAc/hexanes) to afford **47** (1.24 g, 83%, R_f=0.45, EtOAc/hexanes, 3:2) as a yellow oil.

IR (neat, cm^{-1}) 3340, 2922, 1569, 1433, 1260, 1213.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, *J*=2.8 Hz, 1H), 5.85 (m, 1H), 3.81 (dd, *J*=10.8 Hz, *J*=4.1 Hz, 2H), 3.69 (dd, *J*=10.8 Hz, *J*=6.6 Hz, 2H), 2.62 (d, *J*=7.2 Hz, 2H), 2.24 (s, 5H), 2.11 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 151.0, 107.2, 106.2, 65.7, 41.9, 26.8, 13.8.

3-Iodo-2-((5-methylfuran-2-yl)methyl)propan-1-ol (48)

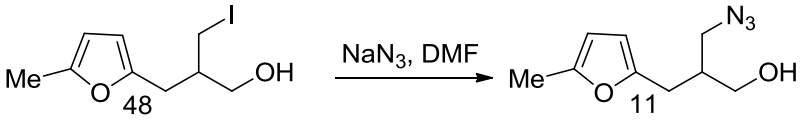


To a solution of **47** (300 mg, 1.70 mmol) in dry THF (15 mL) was added imidazole (130.92 mg, 1.92 mmol) and PPh_3 (503.62 mg, 1.92 mmol) sequentially at 0 ^{o}C under nitrogen atmosphere and stirred for 1 min. The resulting mixture was treated immediately with iodine (633.51 mg, 2.49 mmol) and stirred for 18 h while warming to rt. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (10 mL) and extracted with EtOAc (2x20 mL). The combined organic layers were dried over with Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by column chromatography (1:4 EtOAc/Hexanes) to afford the pure yellow liquid **48** (318 mg, 65%, R_f=0.49, EtOAc/hexanes, 1:4).

IR (neat, cm^{-1}) 3328, 2943, 2920, 2876, 1568, 1428, 1342.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (d, *J*=2.8 Hz, 1H), 5.85 (m, 1H), 3.68 (dd, *J*=11.0 Hz, *J*=5.1 Hz, 1H), 3.57 (dd, *J*=11.0 Hz, *J*=6.5 Hz, 1H), 3.36 (dd, *J*=9.9 Hz, *J*=4.9 Hz, 1H), 3.25 (dd, *J*=9.9 Hz, *J*=5.5 Hz, 1H), 2.68 (dd, *J*=15.1 Hz, *J*=6.6 Hz, 1H), 2.62 (dd, *J*=15.1 Hz, *J*=7.3 Hz, 1H), 2.24 (s, 3H), 1.86 (m, 1H), 1.67 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 151.0, 107.9, 106.2, 65.1, 41.4, 30.1, 13.8, 11.1.**3-Azido-2-((5-methylfuran-2-yl)methyl)propan-1-ol (11)**



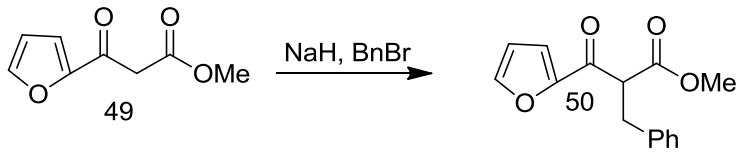
The general procedure for the preparation of azidoalkylfuran from alkylhalide was employed with DMF (5 mL), NaN_3 (70 mg, 1.08 mmol) and **48** (72.00 mg, 0.26 mmol). Purification by silica gel column chromatography afforded **11** (50 mg, 98%, R_f=0.7, EtOAc/hexanes, 1:1) as a light yellow liquid.

IR (neat, cm^{-1}) 3367, 2924, 2876, 2100, 1568, 1450, 1290.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (d, *J*=2.9 Hz, 1H), 5.86 (m, 1H), 3.73-3.60 (m, 2H), 3.44 (dd, *J*=12.2 Hz, *J*=5.5 Hz, 1H), 3.39 (dd, *J*=12.2 Hz, *J*=6.4 Hz, 1H), 2.66 (d, *J*=7.0 Hz, 2H), 2.25 (s, 3H), 2.12 (m, 1H), 1.60 (brs, H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 151.2, 107.7, 106.2, 63.4, 52.5, 40.6, 27.6, 13.7.

Methyl 2-benzyl-3-(furan-2-yl)-3-oxopropanoate (50)



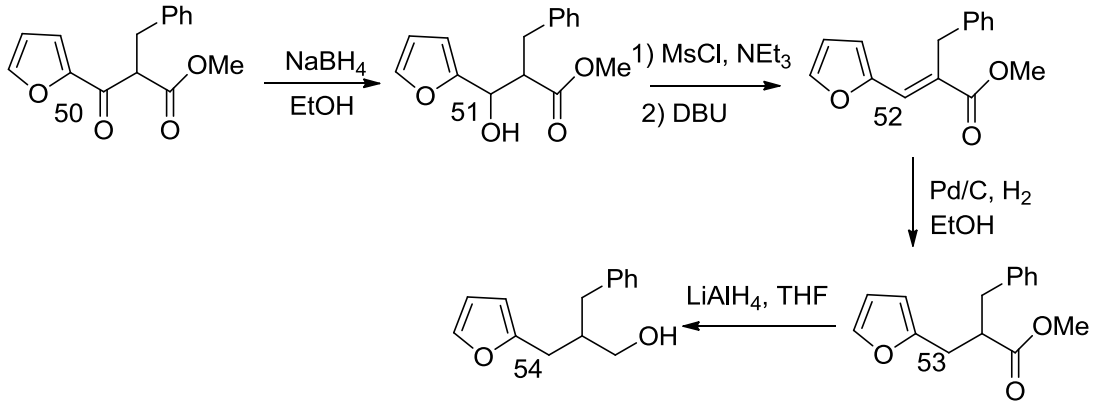
A suspension of **49**[2] (800 mg, 4.76 mmol) and NaH (171 mg, 7.14 mmol) in dry THF (20 mL) was stirred for 5 min at 0 ^oC under argon atmosphere. Then BnBr (896 mg, 0.62 mL, 5.24 mmol) was added and the reaction mixture was heated at 60 ^oC for 15 h. The reaction was then quenched with H_2O (10 mL). It was extracted with EtOAc, dried over with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (1:4 EtOAc/Hexanes) to afford **50** (824 mg, 67%, R_f=0.33, EtOAc/hexanes, 1:4) as a light yellow liquid.

IR (neat, cm^{-1}) 3136, 3028, 2953, 2847, 1742, 1674, 1566, 1496, 1465, 1393.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J*=1.6 Hz, *J*=0.7 Hz, 1H), 7.28-7.15 (m, 6H), 6.52 (dd, *J*=3.6 Hz, *J*=1.7 Hz, 1H), 4.44 (t, *J*=7.5 Hz, 1H), 3.66 (s, 3H), 3.31 (d, *J*=7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 183.3, 169.6, 152.1, 147.4, 138.4, 129.2, 128.7, 126.9, 119.1, 112.9, 56.2, 52.8, 34.6.

Methyl 2-benzyl-3-(furan-2-yl)propanoate (54)



To a solution of **50** (550 mg, 2.13 mmol) in EtOH (15 mL) was added $NaBH_4$ (80.6 mg, 2.13 mmol) at -78 ^{o}C and stirred for 5 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl solution. The solid material was filtrated. The filtrate was concentrated in vacuo. The residue was diluted with DCM (2x15 mL) and washed with H_2O (8 mL). The organic layer was separated, dried over with Na_2SO_4, filtered, and then concentrated in vacuo to afford the crude **51** (330 mg). It was used in the next step without further purification.

To a solution of the crude **51** (330 mg) in dry DCM (20 mL) was added MsCl (174.6 mg, 0.12 mL, 1.52 mmol) and NEt_3 (1.30 g 1.77 mL, 12.7 mmol) at 0 ^{o}C under nitrogen atmosphere. The reaction was stirred for 15 h while warming to rt. DBU was then added and stirred for 15 h. The reaction mixture was quenched with H_2O (10 mL) and extracted with DCM (2x20 mL). The organic layer was dried over with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (1:4 EtOAc/Hexanes) to afford **52** (228 mg, 74%, R_f=0.66, EtOAc/hexanes, 1:4) as a yellow liquid.

A mixture of **52** (300 mg, 1.24 mmol) and 30 mg of Pd/C (10%) in EtOH (40 mL) with stirring was washed three times with hydrogen gas filled in a balloon. Then the reaction was maintained under hydrogen for 5 h. Pd/C was filtered off and the solvent was removed in vacuo. The residue was purified by column chromatography to yield **53 (**250 mg, 83%, R_f=0.7, EtOAc/hexanes, 1:4) as a colorless liquid.

IR (neat, cm^{-1}) 3024, 2955, 2913, 1737, 1604, 1506, 1429, 1366, 1261.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.10 (m, 6H), 6.27 (dd, *J*=3.0 Hz, *J*=1.9 Hz, 1H), 6.03 (d, *J*=2.7 Hz, 1H), 3.58 (s, 3H), 3.10-2.94 (m, 3H), 2.87-2.77 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 153.1, 141.6, 139.0, 129.1, 128.6, 126.7, 110.4, 106.7, 51.8, 46.8, 38.0, 30.3.

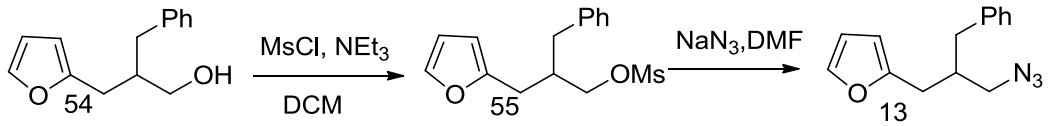
To a suspension of LAH (172.30 mg) in dry THF (20 mL) was added **53** (177 mg, 1.13 mmol) in 3 mL of THF under argon atmosphere at 0 ^{o}C and stirred for 10 h while warming to rt. The reaction mixture was then quenched with acetone (15 mL) and H_2O (8 mL). The residue was filtered and concentrated under vacuo. The filtrate was extracted with EtOAc (2x20 mL) and washed with H_2O (2x10 mL). The combined layers were dried over with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (1:4 EtOAc/Hexanes) to afford **54** (142 mg, 58%, R_f=0.3, EtOAc/hexanes, 1:4) as a colorless liquid.

IR (neat, cm^{-1}) 3359, 3085, 3062, 3027, 2925, 1599, 1507, 1496, 1454, 1383, 1358, 1148, 1060, 1028, 1007.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 3H), 7.19-7.16 (m, 3H), 6.28 (dd, *J*=3.1 Hz, *J*=1.9 Hz, 1H), 6.03 (dd, *J*=3.1 Hz, *J*=0.6 Hz, 1H), 3.48 (dd, *J*=10.9 Hz, *J*=5.2 Hz, 2H), 2.74-2.59 (m, 4H), 2.20 (m, 1H), 1.83 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 141.2, 140.3, 129.2, 128.4, 126.1, 110.3, 106.6, 64.2, 42.2, 37.2, 29.3.

2-(3-Azido-2-benzylpropyl)furan (13)



The general procedure for the mesylation of alcohols was employed with DCM (20 mL), **54** (142 mg, 0.66 mmol)**,** MsCl (1.06 mL, 0.74 mmol) and NEt_3 (0.14 mL, 1.01 mmol) to afford crude **55** (197 mg). It was used in the next step without purification.

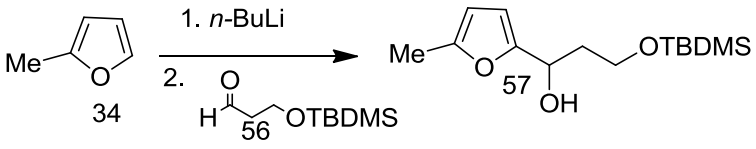
The general procedure for the preparation of azidoalkylfuran from alcohols was employed with DMF (10 mL), NaN_3 (174 mg, 2.68 mmol) and the crude **55** (197 mg). Purification by silica gel column chromatography afforded **13** (116 mg, 73%, R_f=0.83, EtOAc/hexanes, 1:4) as a light yellow liquid.

IR (neat, cm^{-1}) 3028, 2925, 2857, 2099, 1600, 1506, 1452, 1351, 1289.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (m, 6H), 6.30 (dd, *J*=3.2 Hz, *J*=1.9 Hz, 1H), 6.07 (dd, *J*=3.2 Hz, *J*=0.6 Hz, 1H), 3.22 (d, *J*=5.3 Hz, 2H), 2.70 (d, *J*=6.8 Hz, 2H), 2.66 (d, *J*=7.3 Hz, 2H), 2.25 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 141.4, 139.4, 129.2, 128.5, 126.3, 110.2, 107.0, 53.5, 40.0, 37.8, 30.0.

3-(tert-Butyldimethylsilyloxy)-1-(5-methylfuran-2-yl)propan-1-ol (57)



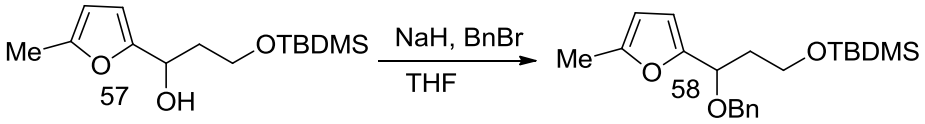
The general procedure for the preparation of alkylfurans with dry THF (60 mL), 3-(*tert*-butyldimethylsilyloxy)propanal **(56)**[3]**,** (2.39 g, 12.69 mmol) 2-methlyfuran (1.38 mL, 15.27 mmol) and *n*-BuLi (11.27 mL, 18.04 mmol, 1.6 M in hexanes). Purification by silica gel column chromatography afforded **57** (2.5 g, 73%, R_f=0.59, EtOAc/hexanes, 1:4) as a yellow liquid.

IR (neat, cm^{-1}) 3428, 3071, 2931, 2858, 1582, 1472, 1427, 1390.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (d, *J*= 3.0 Hz, 1 H), 5.89 (m,1H), 4.88 (dd, *J*= 8.2 Hz, *J*= 3.7 Hz, 1 H), 3.89 (m, 1H), 3.82 (m, 1H), 3.44 (brs, 1H), 2.27 (s, 3H), 2.12-1.96 (m, 2H), 0.90 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 151.6, 106.6, 106.1, 67.6, 61.9, 37.4, 26.1, 18.4, 13.7, 2x-5.3.

(3-(Benzyloxy)-3-(5-methylfuran-2-yl)propoxy)(tert-butyl)dimethylsilane (58)



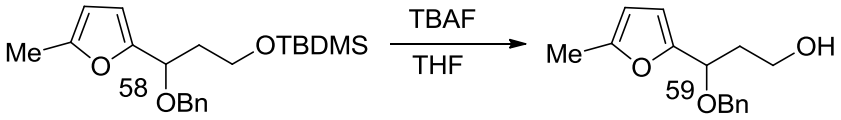
The general procedure for the benzyl protection of alcohols was employed with dry THF (60 mL), **57** (7.00 g, 25.88 mmol), NaH (1.24 g, 51.82 mmol) and BnBr (3.70 mL, 31.09 mmol). Purification by silica gel column chromatography afforded **58** (8.40 g, 90%, R_f=0.73, EtOAc/hexanes, 1:9) as a colorless liquid.

IR (neat, cm^{-1}) 3457, 3089, 3065, 3031, 2954, 2928, 2857, 1562, 1496, 1455.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.26 (m, 5H), 6.19 (d, *J*= 3.01 Hz, 1 H), 5.95 (d, *J*= 2.8 Hz, 1 H), 4.60-4.50 (m, 2H), 4.40 (d, *J*= 11.8 Hz, 1H), 3.79 (m, 1H), 3.65 (m, 1H), 2.32 (s, 3H), 2.22 (m, 1H), 2.05 (m, 1H), 0.91 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 152.2, 138.9, 138.0, 129.2, 129.0, 128.6, 128.5, 128.0, 127.6, 109.3, 106.1, 71.2, 70.5, 59.7, 37.6, 26.2, 18.5, 13.8, -5.1.

3-(Benzyloxy)-3-(5-methylfuran-2-yl)propan-1-ol (59)



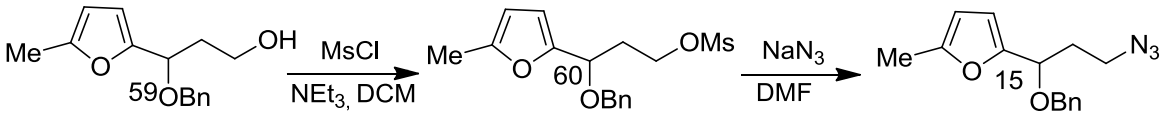
To a solution of **58** (8.10 g, 22.46 mmol) in dry THF (80 mL) was added TBAF (33.73 mL, 33.73 mmol, 1 M in THF) at 0 ^{o}C under nitrogen atmosphere and allowed to warm to rt overnight. The reaction was quenched with H_2O (20 mL) and concentrated in vacuo and extracted with EtOAc (2x30 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (1:4 EtOAc/Hexanes) to afford **59** (5.42 g, 98%, R_f=0.3, EtOAc/hexanes, 1:4) as a yellow liquid.

IR (neat, cm^{-1}) 3410, 3064, 3031, 2924, 2875, 1562, 1497, 1454, 1389.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 5H), 6.20 (d, *J*= 3.0 Hz, 1 H), 5.94 (m, 1H), 4.57-4.53 (m, 2H), 4.36 (d, *J*=11.8 Hz, 1 H), 3.80 (m, 1H), 3.72 (m, 1H), 2.43 (brs, 1H), 2.31 (s, 3 H), 2.25 (m, 1H), 1.99 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 152.1, 138.3, 128.6, 128.1, 127.9, 109.4, 106.2, 73.1, 70.6, 60.7, 37.0, 13.8.

2-(3-Azido-1-(benzyloxy)propyl)-5-methylfuran (15)



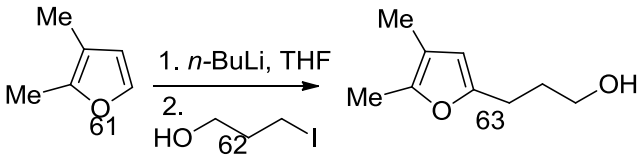
The general procedure for azidoalkylfurans from alcohols was employed with DCM (20 mL), **59** (1.12 g, 4.55 mmol)**,** MsCl (0.39 mL, 5.00 mmol) and NEt_3 (0.76 mL, 5.46 mmol) to afford crude **60** (1.74 g). It was used in the next step without further purification.

DMF (20 mL), NaN_3 (1.18 g, 18.20 mmol) and the crude **60** (1.74 g). Purification by silica gel column chromatography afforded **15** (1.10 g, 89%, R_f=0.65, EtOAc/hexanes, 1:9) as a light yellow liquid.

IR (neat, cm^{-1}) 3031, 2926, 2865, 2097, 1740, 1562, 1496, 1453, 1353.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 5H), 6.20 (d, *J*= 3.0 Hz, 1 H), 5.94 (m, 1H), 4.54 (d, *J*= 11.8 Hz, 1 H), 4.42 (dd, *J*= 8.5 Hz, *J*= 5.4 Hz, 1 H), 4.34 (d, *J*= 11.8 Hz, 1 H), 3.45 (dt, *J*=12.4 Hz, *J*= 6.7 Hz, 1 H), 3.36 (dt, *J*= 12.4 Hz, *J*= 6.5 Hz, 1H), 2.31 (s, 3H), 2.24 (m, 1H), 2.02 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 151.6, 138.4, 128.6, 128.1, 127.8, 109.8, 106.2, 71.3, 70.5, 48.3, 33.9, 13.8.**3-(4,5-Dimethylfuran-2-yl)propan-1-ol (69)**



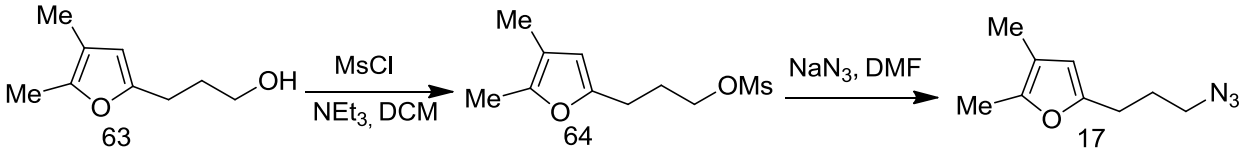
The general procedure for the preparation of alkylfurans with dry THF (30 mL), 3-iodo-1-propanol (845 mg, 4.54 mmol), 2-3-dimethylfuran (916 mg, 1.00 mL, 9.53 mmol) and n-BuLi (4.00 mL, 9.98 mmol, 2.5 M in hexanes). Purification by silica gel column chromatography afforded **63** (327 mg, 47%, R_f=0.2, EtOAc/hexanes, 1:4) as a yellow liquid.

IR (neat, cm^{-1}) 3390, 2924, 2872, 1712, 1576, 1451, 1260.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (s, 1H), 3.68 (t, *J*=6.3 Hz, 2H), 2.63 (t, *J*=7.4 Hz, 2H), 2.15 (s, 3H), 1.89 (s, 3H), 1.85 (dd, *J*=13.9 Hz, *J*=6.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 145.5, 114.2, 108.3, 62.2, 31.2, 24.3, 11.2, 9.9.

5-(3-Azidopropyl)-2,3-dimethylfuran (17)



The general procedure for azidoalkylfurans from alcohols was employed with DCM (15 mL), **63** (256 mg, 1.66 mmol)**,** MsCl (0.15 mL, 2.00 mmol) and NEt_3 (0.35 mL, 2.5 mmol). Purification by silica gel column chromatography afforded crude **64** (385 mg, 1.66 mmol). It was used in the next step without further purification.

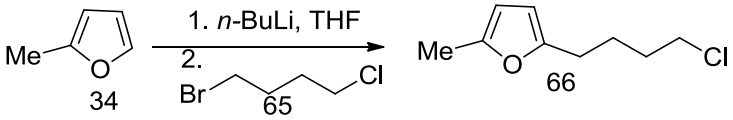
DMF (5 mL), NaN_3 (432 mg, 6.64 mmol) and the crude **64** (385 mg, 1.66 mmol). Purification by silica gel column chromatography afforded **17** (196 mg, 66%, R_f=0.83, EtOAc/hexanes, 1:9) as a light yellow liquid.

IR (neat, cm^{-1}) 2945, 2925, 2859, 2098, 1642, 1579, 1450, 1261.

^1H NMR (400 MHz, $CDCl_3$) δ 5.79 (s, 1H), 3.31 (t, *J*=6.8 Hz, 2H), 2.63 (t, *J*=6.8 Hz, 2H), 2.16 (s, 3H), 1.95-1.83 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 146.0, 114.5, 109.0, 50.9, 27.8, 25.2, 11.5, 10.1.

2-(4-Chlorobutyl)-5-methylfuran (66)



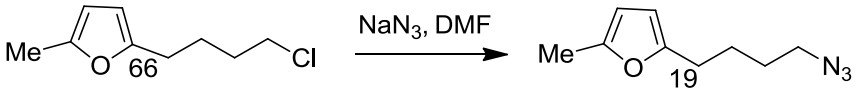
The general procedure for the preparation of alkylfurans with dry THF (40 mL), 1-chloro-4-iodopentane (3.04 g, 17.73 mmol), 2-dimethylfuran (1.76 mL, 19.50 mmol) and *n*-BuLi (14.40 mL, 23.04 mmol, 1.6 M in hexanes). Purification by silica gel column chromatography afforded **66** (2.5 g, 82%, R_f=0.33, in hexanes) as a yellow liquid.

IR (neat, cm^{-1}) 3473, 2947, 2921, 2866, 1773, 1685, 1618, 1569, 1449.

^1H NMR (400 MHz, $CDCl_3$) δ 5.88-5.84 (m, 2H), 3.55 (t, *J*=6.4 Hz, 2H), 2.61 (t, *J*=7.0 Hz, 2H), 2.26 (s, 3H), 1.88-1.74 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.6, 106.0, 105.9, 45.0, 32.2, 27.5, 25.7, 13.7.

2-(4-Azidobutyl)-5-methylfuran (19)



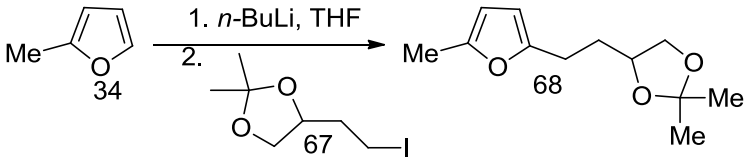
The general procedure for the preparation of azidoalkylfuran from alkylhalide was employed with DMF (20 mL), NaN_3 (3.62 g, 55.80 mmol) and **66** (2.40 g, 13.90 mmol). Purification by silica gel column chromatography afforded **19** (2.3 g, 92%, R_f=0.82, EtOAc/hexanes, 1:9) as a light yellow liquid.

IR (neat, cm^{-1}) 3105, 2944, 2867, 2100, 1617, 1570, 1454, 1352.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88-5.85 (m, 2H), 3.29 (t, *J*=6.6 Hz, 2H), 2.62 (t, *J*=7.1 Hz, 2H), 2.27 (s, 3H), 1.80-1.62 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.5, 106.0, 105.9, 51.4, 28.5, 27.7, 25.6, 13.6.

2,2-Dimethyl-4-(2-(5-methylfuran-2-yl)ethyl)-1,3-dioxolane (68)



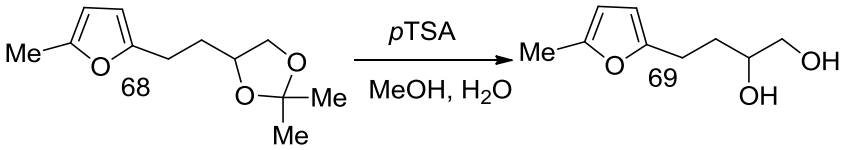
The general procedure for the preparation of alkylfurans with dry THF (40 mL), 4-(2-iodoethyl)-2,2-dimethyl-1,3-dioxolane **(67)**[4] (2.60 g, 10.15 mmol), 2-methylfuran (1.67 g, 12.7 mL, 20.31 mmol) and *n*-BuLi (12.69 mL, 20.31 mmol, 1.6 M in hexanes). Purification by silica gel column chromatography afforded **68** (1.76 g, 82%, R_f=0.6, EtOAc/hexanes, 1:9) as a yellow liquid.

IR (neat, cm^{-1}) 2985, 2937, 2873, 1571, 1455, 1378, 1370, 1218, 1155, 1109, 1068, 1021.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (d, *J*=2.8 Hz, 1H), 5.84 (m, 1H), 4.11 (m, 1H), 4.01 (dd, *J*=7.9 Hz, *J*=6.0 Hz, 1H), 3.52 (t, *J*=7.3 Hz, 1H), 2.75-2.58 (m, 2H), 2.24 (s, 3H), 1.99-1.79 (m, 2H), 1.40 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 150.7, 109.0, 106.0, 105.9, 75.5, 69.4, 32.4, 27.2, 25.9, 24.6, 13.7.

4-(5-Methylfuran-2-yl)butane-1,2-diol (69)



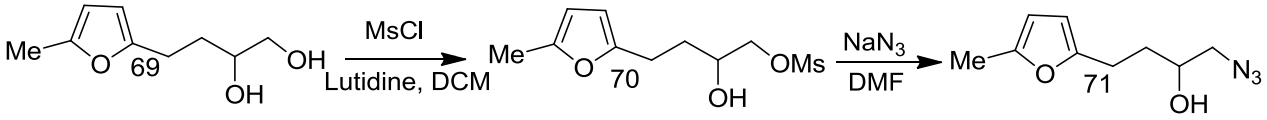
To a solution of **68** (1.76 g, 8.37 mmol) in MeOH:H_2O (60 mL:10 mL) was added *p*TSA (176 mg) and stirred for 20 h at rt. It was concentrated in vacuo and extracted with EtOAc (2x30 mL) and washed with H_2O (15 mL). The combined layer was dried over with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography to afford **69** (1.30 g, 91%, R_f=0.2, EtOAc/hexanes 3:2) as a yellow liquid.

IR (neat, cm^{-1}) 3369, 2923, 1571, 1451, 1219, 1092, 1045, 1021.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (d, *J*=2.9 Hz, 1H), 5.84 (m, 1H), 3.75 (m, 1H), 3.65 (dd, *J*=11.1 Hz, *J*=3.1 Hz, 1H), 3.47 (dd, *J*=11.1 , *J*=7.6 Hz, 1H), 2.80-2.63 (m, 2H), 2.24 (s, 3H), 1.80-1.70 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 150.8, 106.1, 106.0, 71.7, 66.9, 31.8, 24.4, 13.7.

1-Azido-4-(5-methylfuran-2-yl)butan-2-ol (71)



The general procedure for azidoalkylfurans from alcohols was employed with DCM (60 mL), **69** (1.2 g, 7.05 mmol)**,** MsCl (0.89 g, 0.60 mL, 7.76 mmol) and lutidine (7.56 g, 8.20 mL, 70.55 mmol). Purification by silica gel column chromatography afforded crude **70** (1.75 g). It was used in the next step without further purification.

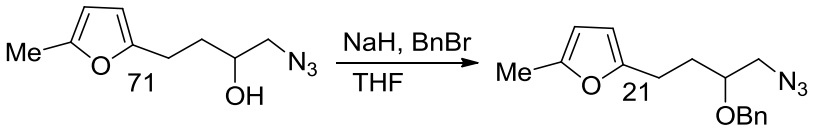
DMF (20 mL), NaN_3 (2.30 g, 35.2 mmol) and the crude **70** (1.75 g). Purification by column chromatography afforded **71** (1.10 g, 80%, R_f=0.46, EtOAc/hexanes, 1:4) as a light yellow liquid.

IR (neat, cm^{-1}) 3670, 2918, 2852, 2102, 1445, 1284, 1213, 1073, 1021.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (d, *J*=2.9, 1H), 5.84 (m, 1H), 3.80 (m, 1H), 3.37 (dd, *J*=12.4, *J*=3.4, 1H), 3.27 (dd, *J*=12.4, *J*=7.3, 1H), 2.79-2.65 (m, 2H), 2.25 (s, 3H), 1.85-1.75 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 150.9, 106.2, 106.1, 70.3, 57.2, 32.9, 24.3, 13.7.

2-(4-Azido-3-(benzyloxy)butyl)-5-methylfuran (21)

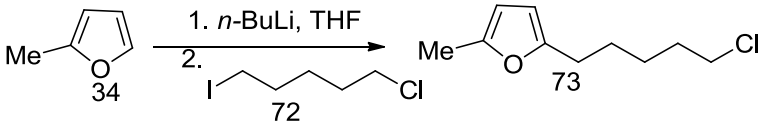


The general procedure for the benzyl protection of alcohols was employed with dry THF (35 mL), **71** (768 mg, 3.94 mmol), NaH (189.05 mg, 7.88 mmol) and BnBr (0.61 mL, 5.12 mmol). Purification by silica gel column chromatography afforded **21** (1.02 g, 91%, R_f=0.66, EtOAc/hexanes, 1:9) as a yellow liquid.

IR (neat, cm^{-1}) 3027, 2928, 2863, 2100, 1566, 1492, 1454, 1344, 1281, 1218, 1089, 1021.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 5H), 5.85-5.82 (m, 2H), 4.66 (d, *J*=11.4 Hz, 1H), 4.57 (d, *J*=11.4 Hz, 1H), 3.60 (m, 1H), 3.77 (dd, *J*=12.9 Hz, *J*=4.1 Hz, 1H), 3.30 (dd, *J*=12.9 Hz, *J*=5.9 Hz, 1H), 2.74-2.61 (m, 2H), 2.25 (s, 3H), 2.00-1.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 150.7, 138.2, 128.7, 128.2, 128.0, 106.1, 106.0, 77.5, 72.3, 54.2, 31.0, 24.0, 13.7.**2-(5-Chloropropyl)-5-methylfuran (73)**



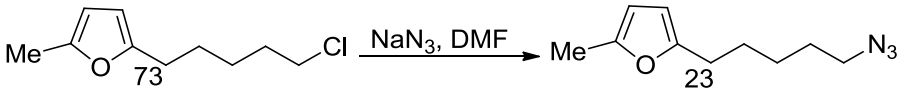
The general procedure for the preparation of alkylfurans with dry THF (40 mL), 1-chloro-5-iodopentane **(72)** (2.50 g, 1.50 mL, 10.75 mmol), 2-methylfuran (0.97 g, 1.07 mL, 11.81 mmol) and *n*-BuLi (8.73 mL, 14.0 mmol, 1.6 M in hexanes). Purification by silica gel column chromatography afforded **73** (1.67 g, 83%, R_f=0.89, EtOAc/hexanes, 1:9) as a yellow liquid.

IR (neat, cm^{-1}) 3101, 2939, 2862, 1681, 1618, 1570, 1453.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86-5.84 (m, 2H), 3.54 (t, *J*=6.7 Hz, 2H), 2.59 (t, *J*=7.5 Hz, 2H), 2.26 (s, 3H), 1.84-1.77 (m, 2H), 1.70-1.60 (m, 2H), 1.54-1.45 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 150.4, 106.0, 105.6, 45.2, 32.6, 28.1, 27.7, 26.6, 13.7.

2-(5-Azidopropyl)-5-methylfuran (23)



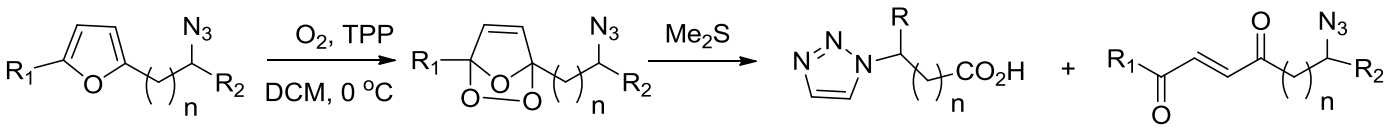
The general procedure for the preparation of azidoalkylfuran from alkylhalide was employed with DMF (25 mL), NaN_3 (2.18 g, 33.5 mmol) and **73** (1.56 g, 8.36 mmol). Purification by silica gel column chromatography afforded **23** (1.60 g, 99%, R_f=0.77, EtOAc/hexanes, 5:95) as a light yellow liquid.

IR (neat, cm^{-1}) 3327, 3104, 2937, 2862, 2516, 2098, 1618, 1570, 1454, 1351.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86-5.83 (m, 2H), 3.27 (t, *J*=6.9 Hz, 2H), 2.58 (t, *J*=7.5 Hz, 2H), 2.25 (s, 3H), 1.70-1.59 (m, 4H), 1.47-1.38 (m, 2H).

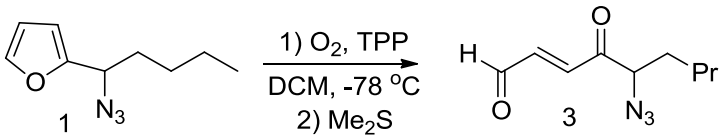
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 150.4, 106.0, 105.6, 51.6, 28.8, 28.1, 27.9, 26.5, 13.7.

2e. General procedures for photooxygenation



A solution of 3-azidoalkylfuran (**9**) (1 equiv) in DCM (10 mL) was illuminated at 0 °C with a halogen lamp (500 Watt) in the presence of TPP (ca.) while oxygen was bubbled through the solution. The reaction was kept at the same temperature during the reaction. The reaction was monitored by TLC. Upon the consumption of the starting material, the reaction was treated with Me_2S (10 equiv) at 0 °C or –78 ºC and allowed to warm to rt overnight. After removal of the solvent, the residue was triturated with DCM/hexanes to obtain the corresponding triazole.

Photooxygenation of 1

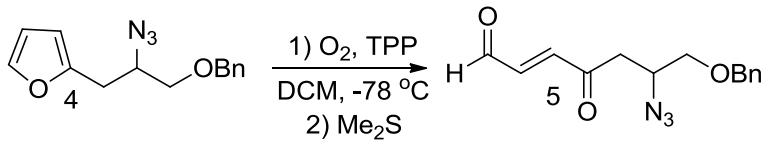


The general procedure was employed with **1** (100 mg, 0.56 mmol), TPP (ca.), DCM, O_2 at -78 ºC. The solvent was evaporated. The crude product was 176 mg as a light brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (d, *J*=7.30 Hz, 1H), 7.14 (d, *J*=16.0 Hz, 1H), 6.91 (dd, *J*=16.0, 7.30 Hz, 1H), 4.08 (dd, *J*=8.35, 5.30 Hz, 1H), 1.85-1.74 (m, 2H), 1.39-1.23 (m, 4H), 0.92 (t, *J*=7.1, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 192.5, 140.4, 139.3, 67.7, 30.6, 28,0, 22.5, 14.0.

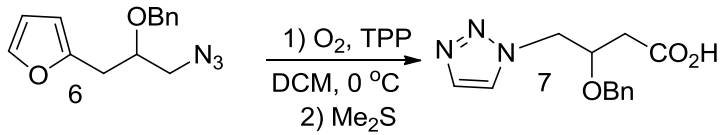
Photooxygenation of 4



The general procedure was employed with DCM, **4** (154 mg, 0.60 mmol), TPP (ca.) and Me_2S (0.85 mL, 11.57 mmol). ^{1}H NMR from the crude material showed same characteristic signals belonged to **5**. It was very unstable at rt and on usual chromatography adsorbents for full characterization.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, *J*=7.1 Hz, 1H), 7.35-7.25 (m, 5H), 7.35-7.20 (m, 5H), 6.85 (d, *J*=16.1 Hz, 1H), 6.77 (dd, *J*=16.1, *J*=7.1 Hz, 1H), 4.58-4.51 (m, 2 H), 4.14 (m, 1H), 3.58-3.56 (d, *J*=5.5 Hz, 2H), 2.89 (m, 1H).

Photooxygenation of 6



The general procedure was employed with DCM, **6** (232 mg, 0.90 mmol), TPP (ca.) and Me_2S (0.66 mL, 9.02 mmol). Trituration provided **7** (207 mg, 88%) as a white solid. Mp 90.5- 91.5 °C.

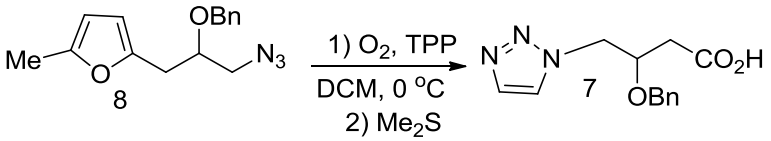
IR (neat, cm^{-1}) 3137, 3031, 2919, 2560, 1720, 1496, 1452, 1401, 1351, 1251, 1284, 1205, 1075;

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (brs, 1H), 7.72 (s, 1H), 7.65 (s, 1H), 7.35-7.20 (m, 5H), 4.66 (dd, *J*=14.2 Hz, *J*=3.8 Hz, 1H), 4.60 (d, *J*=11.3 Hz, 1H), 4.57 (dd, *J*=14.2 Hz, *J*=6.4 Hz, 1H), 4.38 (d, *J*=11.3 Hz, 1H), 4.29 (m, 1H), 2.63 (dd, *J*=15.0 Hz, *J*=4.6 Hz, 1H), 2.58 (dd, *J*=15.0 Hz, *J*=4.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 137.3, 133.6, 128.8, 128.3, 128.1, 125.5, 74.5, 72.6, 53.4, 37.0.

HRMS (ESI) ($M+H^+$): calcd for 262.1192 ($C_{13}H_{16}N_3O_3$), found 262.1185.

Photooxygenation of 8



The general procedure was employed with DCM, **8** (108 mg, 0.39 mmol), TPP (ca.) and Me_2S (0.30 mL, 9.02 mmol). Trituration provided **7** (75.00 mg, 74%) as a white solid. Mp 90.5- 91.5 °C.

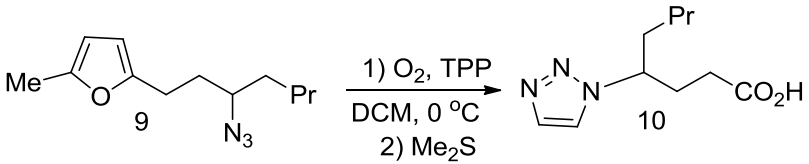
IR (neat, cm^{-1}) 3137, 3031, 2919, 2560, 1720, 1496, 1452, 1401, 1351, 1251, 1284, 1205, 1075;

^1H NMR (400 MHz, $CDCl_3$) δ 11.09 (brs, 1H), 7.71 (d, *J*=0.9 Hz, 1H), 7.64 (d, *J*=3.0 Hz, 1H), 7.35-7.20 (m, 5H), 4.66 (dd, *J*=14.2 Hz, *J*=3.8 Hz, 1H), 4.60 (d, *J*=11.3 Hz, 1H), 4.57 (dd, *J*=14.2 Hz, *J*=6.4 Hz, 1H), 4.38 (d, *J*=11.3 Hz, 1H), 4.33-4.27 (m, 1H), 2.63 (dd, *J*=15.0 Hz, *J*=4.6 Hz, 1H), 2.58 (dd, *J*=15.0 Hz, *J*=4.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 137.3, 133.6, 128.8, 128.3, 128.1, 125.5, 74.5, 72.6, 53.4, 37.0.

HRMS (ESI) ($M+H^+$): calcd for 262.1192 ($C_{13}H_{16}N_3O_3$), found 262.1185.

Photooxygenation of 9



The general procedure was employed with DCM, **9** (119 mg, 0.54 mmol), TPP (ca.) and Me_2S (0.40 mL, 5.38 mmol). Trituration provided **10** (99 mg, 87%) as a white solid. Mp 67.5-68.8 °C.

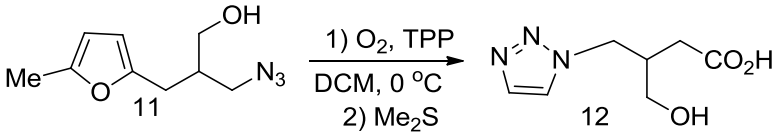
IR (neat, cm^{-1}) 3425, 3160, 3137, 2952, 2860, 2508, 1712, 1574, 1487, 1467, 1459.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (brs, 1H), 7.72 (s, 1H), 7.57 (s, 1H), 4.60 (m, 1H), 2.30-2.08 (m, 4H), 1.98-1.79 (m, 2H), 1.35-1.10 (m, 3H), 1.01 (m, 1H), 0.81 (t, *J*=7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 133.7, 122.7, 61.6, 35.5, 31.0, 30.8, 28.2, 22.4, 14.0.

HRMS (ESI) ($M-H^+$): calcd for 210.1242 ($C_{10}H_{16}N_3O_2$), found 210.1248.

Photooxygenation of 11



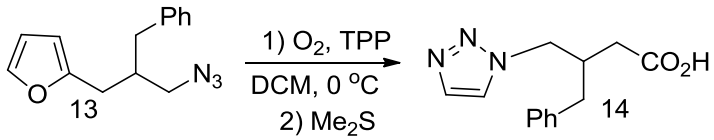
The general procedure was employed with DCM, **11** (90 mg, 0.46 mmol), TPP (ca.) and Me_2S (0.34 mL, 4.61mmol). Trituration provided **10** (65 mg, 76%) as a white solid. Mp 56.7-57.8 °C.

IR (neat, cm^{-1}) 3512, 3145, 3083, 2925, 2103, 1775, 1467, 1439, 1420.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.59 (s, 1H), 4.49 (d, *J*=7.4 Hz, 2H), 4.43 (dd, *J*=9.6 Hz, *J*=7.3 Hz, 1H), 4.18 (dd, *J*=9.6 Hz, *J*=5.6 Hz, 1H), 3.27 (m, 1H), 2.73 (dd, *J*=17.8 Hz, *J*=8.7 Hz, 1H), 2.38 (dd, *J*=17.8 Hz, *J*=6.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 134.4, 124.2, 70.5, 51.7, 36.4, 32.2.

HRMS (ESI) ($M-H^+$): calcd for 184.0722 ($C_7H_{10}N_3O_3$), found 184.0734.**Photooxygenation of 13**



The general procedure was employed with DCM, **13** (116 mg, 0.48 mmol), TPP (ca.) and Me_2S (0.35 mL, 4.81 mmol). Trituration provided **14** (105 mg, 90%) as a white solid. Mp 143.7-144.8 °C.

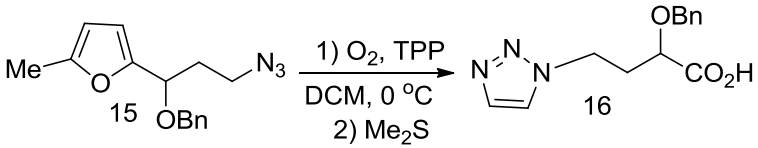
IR (neat, cm^{-1}) 3446, 3164, 3125, 3024, 3004, 2950, 2931, 2905, 2543, 1878, 1732, 1494, 1407.

^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.56 (s, 1H), 7.35-7.17 (m, 5H), 4.45 (d, *J*=6.3 Hz, 2H), 2.82-2.62 (m, 3H), 2.42-2.27 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 138.3, 134.0, 129.4, 129.0, 127.0, 124.6, 52.5, 38.3, 38.0, 35.2.

HRMS (ESI) ($M-H^+$): calcd for 244.1086 ($C_{13}H_{14}N_3O_2$), found 244.1096.

Photooxygenation of 15



The general procedure was employed with DCM, **15** (233.00 mg, 0.86 mmol), TPP (ca.) and Me_2S (0.63 mL, 8.60 mmol). Trituration provided **16** (180 mg, 80%) as a white solid. Mp 110-111 °C.

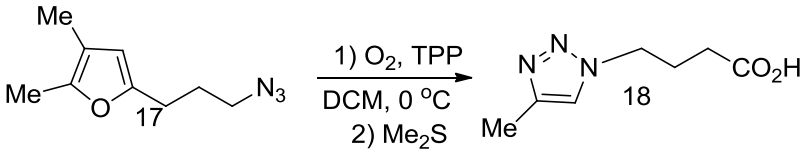
IR (neat, cm^{-1}) 3444, 3129, 3030, 2932, 2862, 1605, 1497, 1454, 1432, 1315.

^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (brs, 1H), 7.65 (s, 1H), 7.39 (s, 1H), 7.33 (s, 5H), 4.77 (d, *J*=11.4 Hz, 1H), 4.51 (t, *J*=6.5 Hz, 2H), 4.41 (d, *J*=11.4 Hz, 1H), 3.92 (dd, *J*= 4.5 Hz, *J*=7.3 Hz, 1H), 2.50-2.34 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 137.2, 133.5, 128.5, 2x128.4, 124.4, 74.6, 72.8, 46.5, 33.2.

HRMS (ESI) ($M+H^+$): calcd for 262.1192 ($C_{13}H_{16}N_3O_3$), found 262.1185.

Photooxygenation of 17



The general procedure was employed with DCM, **17** (260 mg, 1.45 mmol), TPP (ca.) and Me_2S (1.07 mL, 14.50 mmol). Trituration provided **18** (219 mg, 89%) as a white solid. Mp 85.7-86.7 °C.

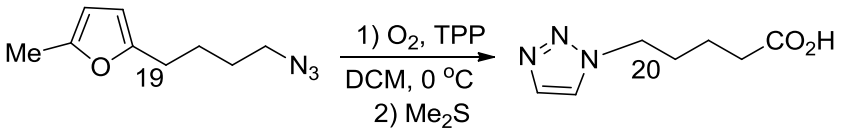
IR (neat, cm^{-1}) 3740, 3322, 3141, 3091, 2956, 2863, 2098, 1804, 1740, 1555, 1415, 1345.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 4.40 (t, *J*=6.7 Hz, 2H), 2.47 (t, *J*=7.0 Hz, 2H), 2.34 (s, 3H), 2.23 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 143.9, 121.6, 48.6, 31.9, 24.9, 11.0.

HRMS (ESI) ($M+H^+$): calcd for 170.0930 ($C_7H_{12}N_3O_2$), found 170.0929.

Photooxygenation of 19



The general procedure was employed with DCM, **19** (203.00 mg, 1.13 mmol), TPP (ca.) and Me_2S (0.83 mL, 11.3 mmol). Trituration provided **20** (140 mg, 73%) as a white solid. Mp 103-104 ^oC.

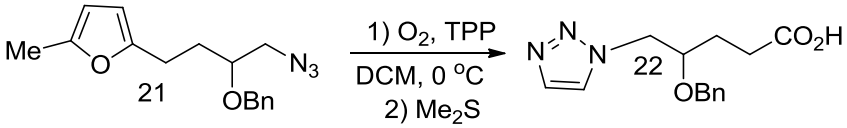
IR (neat, cm^{-1}) 3611, 3158, 2951, 2511, 1922, 1717, 1483, 1441, 1414.

^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.56 (s,1H), 4.42 (t, *J*=7.0 Hz, 2H), 2.41 (t, *J*=7.2 Hz, 2H), 2.0 (m, 2H), 1.67 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 134.0, 123.5, 50.0, 33.2, 29.7, 21.8.

HRMS (ESI) ($M+H^+$): calcd for 170.0930 ($C_7H_{12}N_3O_2$), found 170.0930.

Photooxygenation of 21



The general procedure was employed with DCM, **21** (102 mg, 0.36 mmol), TPP (ca.) and Me_2S (0.26 mL, 3.58 mmol). The solvent was removed and residue was filtered through a pad of silica gel with DCM/methanol to give **22** (60 mg, 60%, R_f=0.5, DCM/methanol, 1:9) as a yellow liquid.

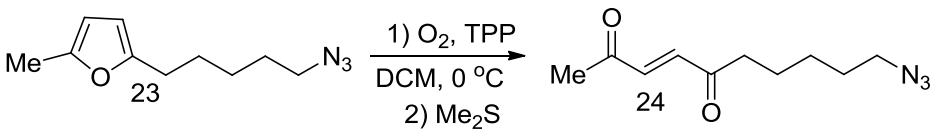
IR (neat, cm^{-1}) 3637, 3121, 3022, 2931, 2879, 2599, 1722, 1451, 1347, 1256, 1220, 1078, 1021.

^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.63 (s,1H), 7.35-7.20 (m, 5H), 4.56 (dd, *J*=14.1, *J*=3.6, 1H), 4.41 (dd, *J*=14.1, *J*=6.77, 1H), 4.30 (d, *J*=11.3, 1H), 3.93 (m, 1H), 2.48 (t, *J*=7.2, 2H), 1.93-1.77 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 177.4, 137.5, 2x133.8, 128.8, 128.7, 3x128.3, 2x128.1, 2x125.1, 76.8, 72.6, 53.4, 2x29.5, 27.1.

HRMS (ESI) ($M+H^+$): calcd for 276.1348 ($C_{14}H_{18}N_3O_3$), found 276.1355.

Photooxygenation of 23



The general procedure was employed with DCM, **23** (153 mg, 0.79 mmol), TPP (ca.) and Me_2S (0.58 mL, 7.92 mmol). The solvent was removed and residue was filtered through a pad of silica gel with EtOAc/hexanes to give **24** (129 mg, 78%, R_f=0.5, EtOAc/hexanes, 2:3) as a yellow liquid.

IR (neat, cm^{-1}) 2935, 2092, 1693, 1609, 1391, 1257, 1182.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (s, 2H), 3.23 (t, *J*=6.9 Hz, 2H), 2.52 (t, *J*=7.3 Hz, 2H), 2.25 (s, 3H), 1.67-1.52 (m, 4H), 1.42-1.32 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 200.6, 2x135.9, 51.4, 42.3, 30.0, 28.9, 26.3, 23.0.

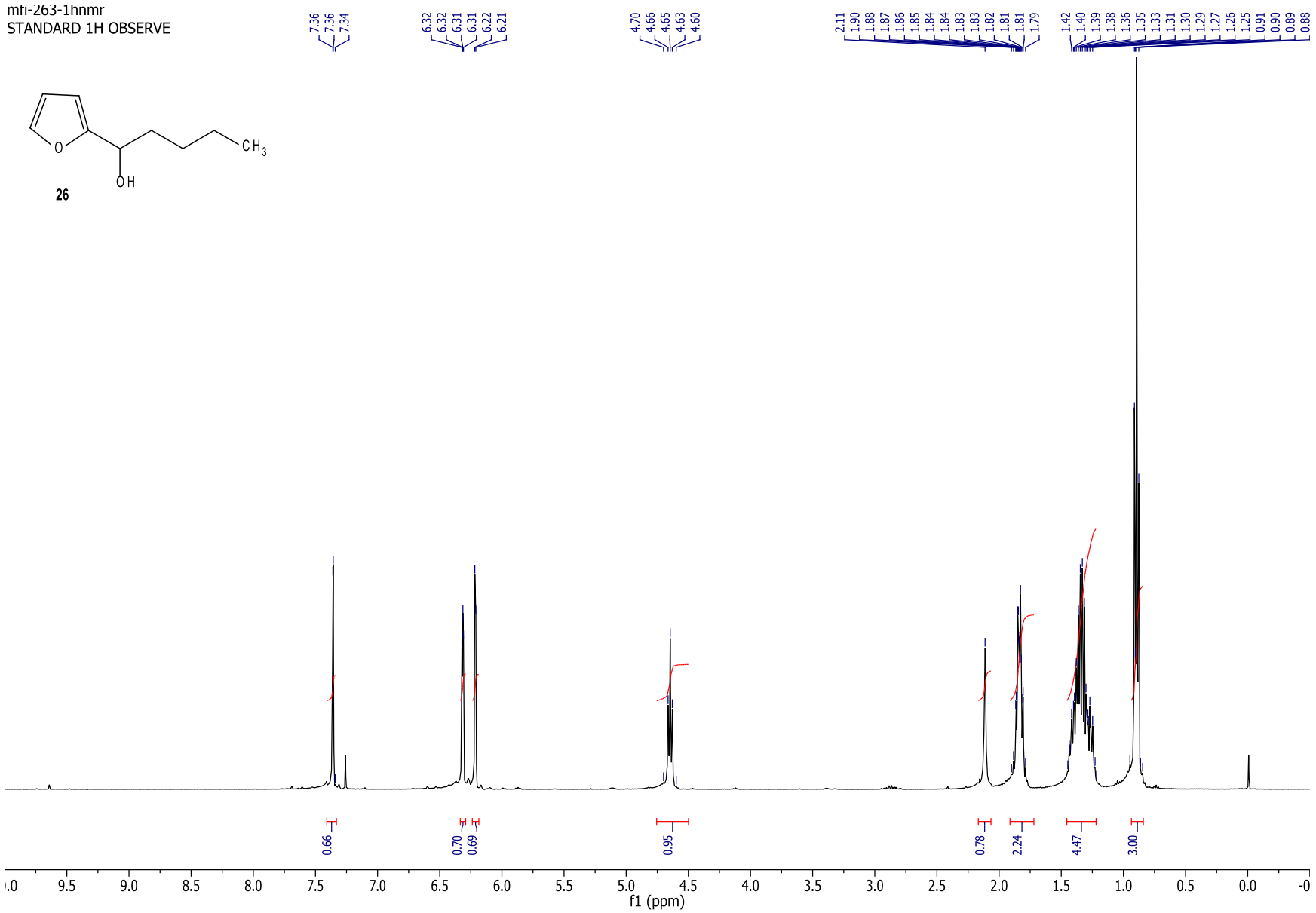
3. References

(1) Williams, P. D.; LeGoff, E. *Tetrahedron Lett.* **1985**, *26*, 1367.

(2) Gademann, K.; Bethuel, Y. *Angew. Chem.; Int. Ed.* **2004**, *43*, 3327.

(3) Liang, Q.; De Brabander, J. K. *Tetrahedron* **2011**, *67*, 5046.

(4) (a) Adiyaman, M.; Li, H.; Lawson, J. A; Hwang, S-W.; Khanapure, S. P.; FitzGerald, G. A.; Rokach, J. *Tetrahedron Lett.* **1997**, *38*, 3339. (b) Kumar, C. R.; Tsai, C-H.; Chao, Y-S.; Lee, J-C. *Chem.--Eur. J.* **2011,** *17*, 8696.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4.66
4.65
4.63
4.60
2.11
1.90
1.88
1.87
1.86
1.85
1.84
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1.39
1.38
1.36
1.35
1.33
1.31
1.30
1.29
1.27
1.26
1.25
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0.88
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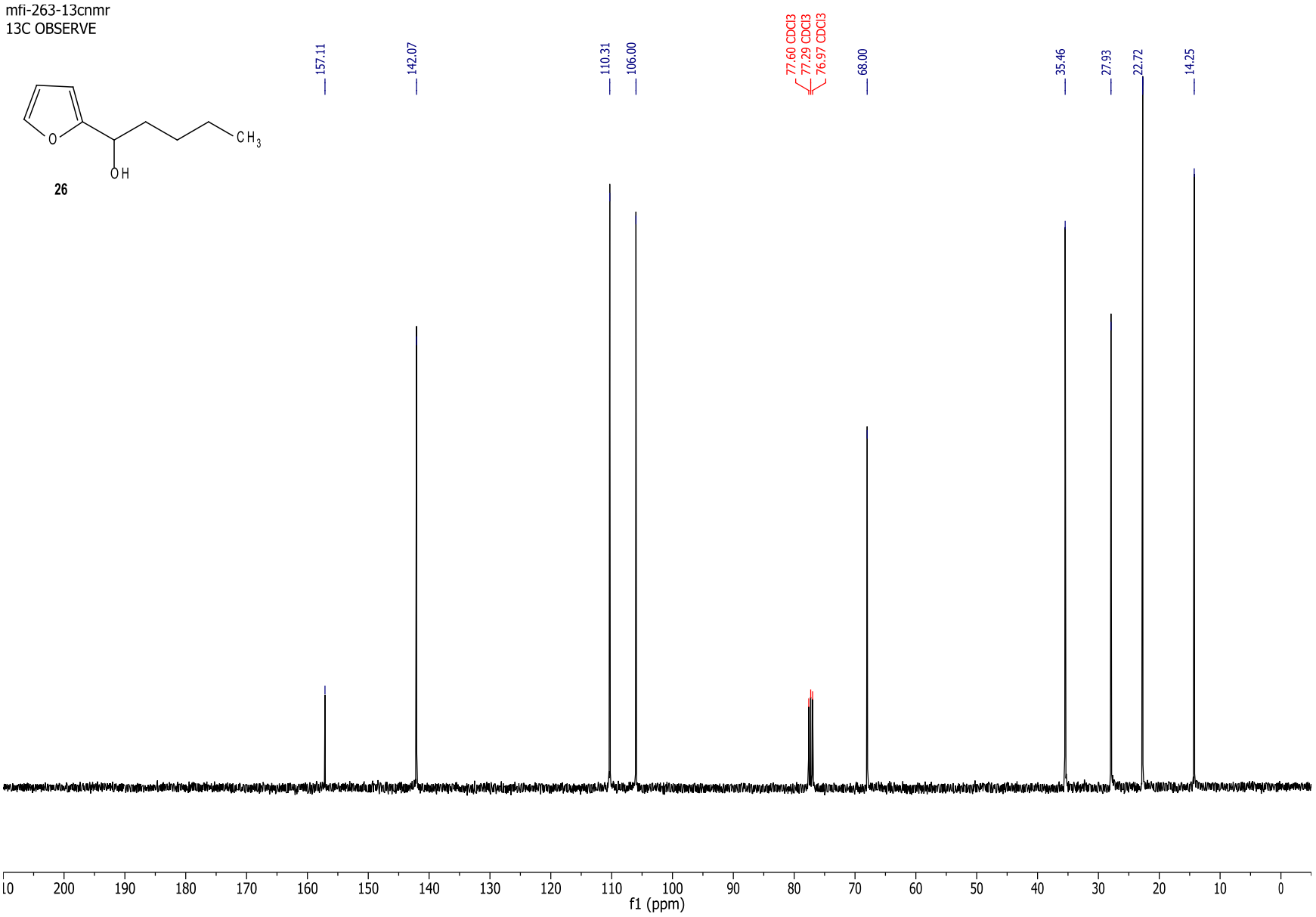
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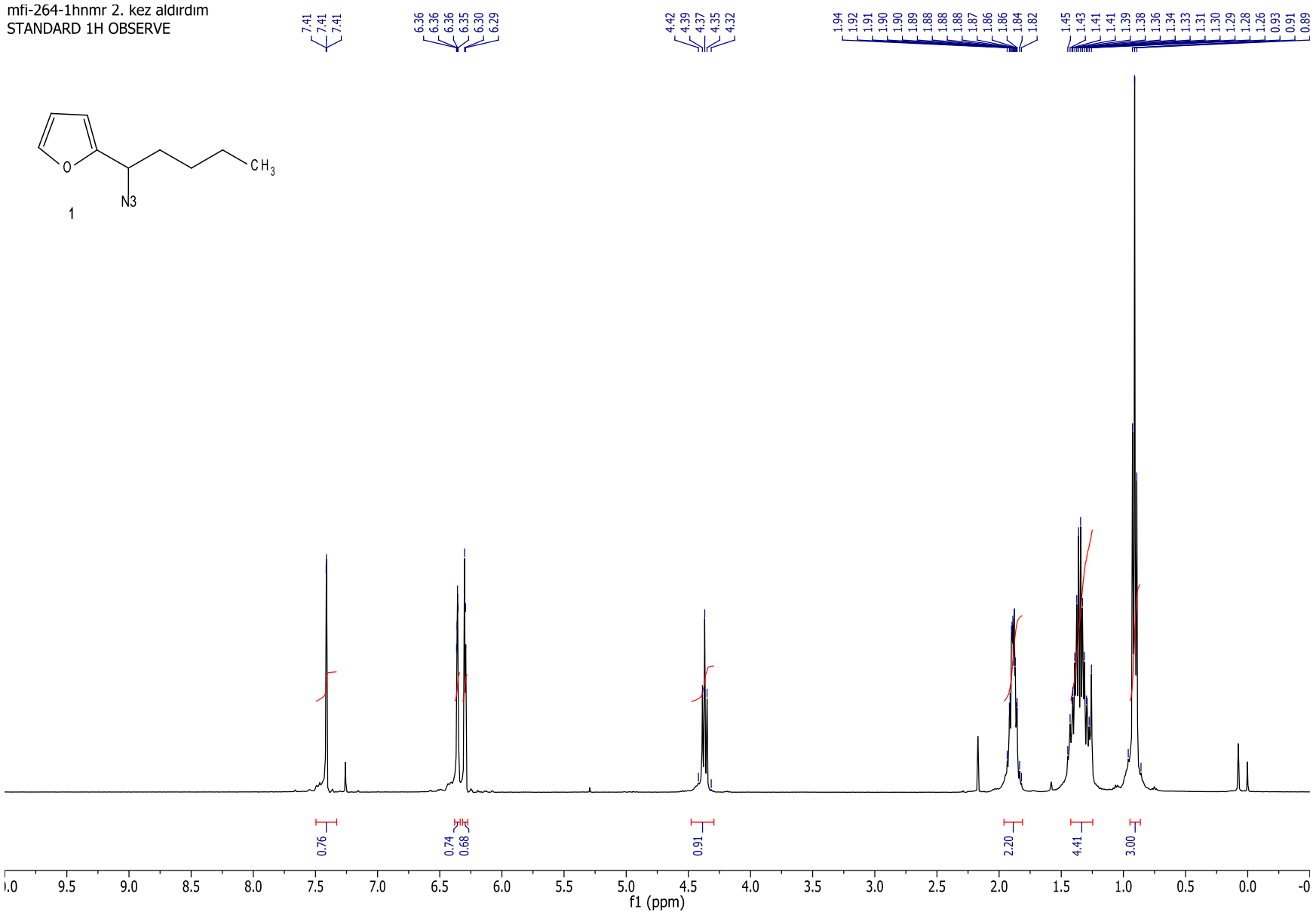
22.72
14.25
O
OH
CH3
26
f1 (ppm)


mfi-264-1hnmr 2. kez aldırdım
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4.42 4.39 4.37 4.35 4.32
1.94 1.92 1.91 1.90 1.90 1.89 1.88 1.88 1.88 1.87 1.86 1.86 1.84 1.82
1.45 1.43 1.41 1.41 1.39 1.38 1.36 1.34 1.33 1.31 1.30 1.29 1.28 1.26 0.93 0.91 0.89
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3.00
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mfi-264-13cnmr
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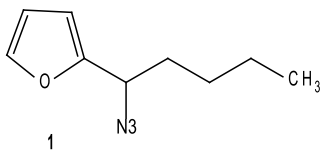

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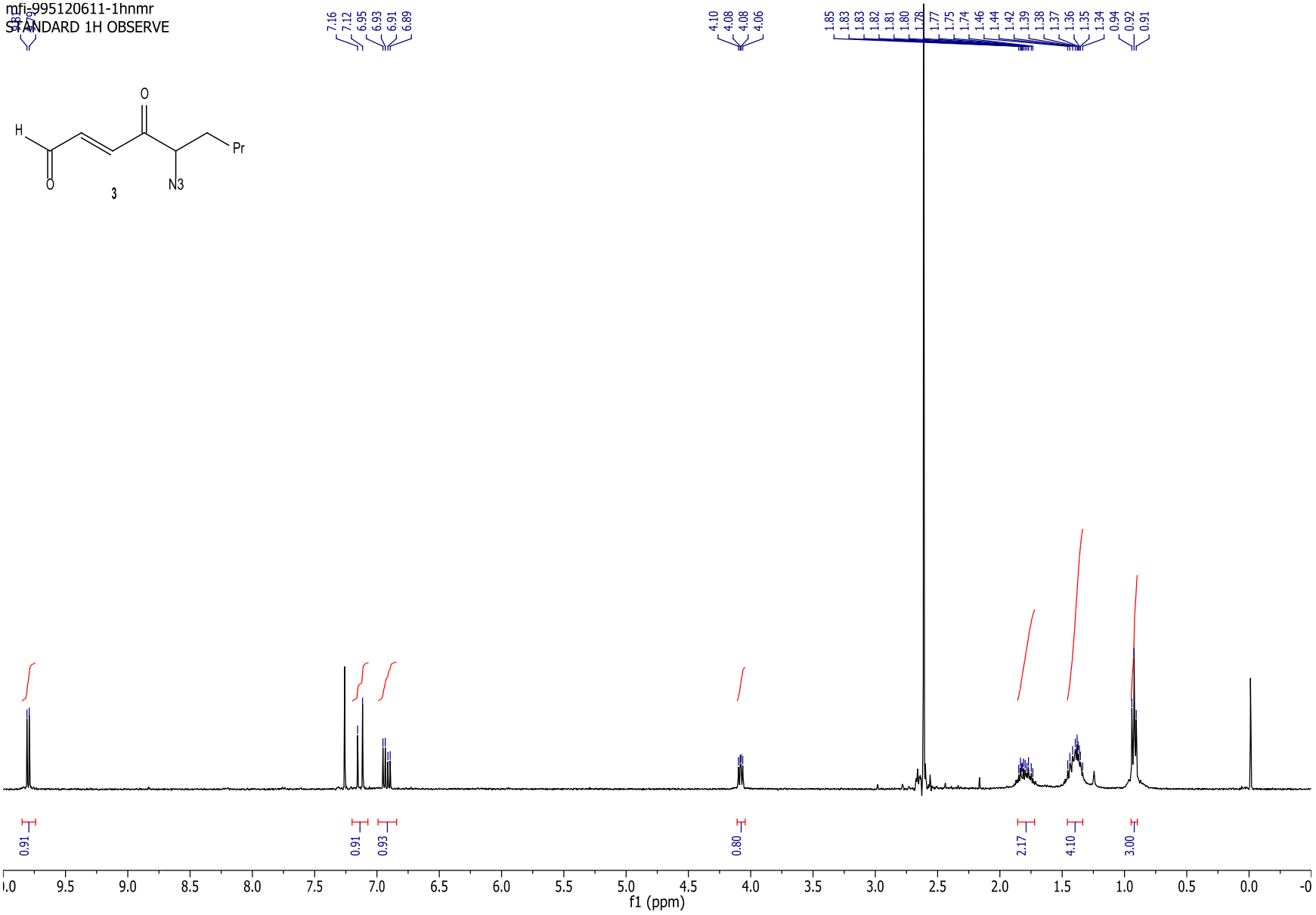
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1.35
1.34
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0.91
0.93
0.80
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9.5
9.0
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7.0
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4.0
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f1 (ppm)

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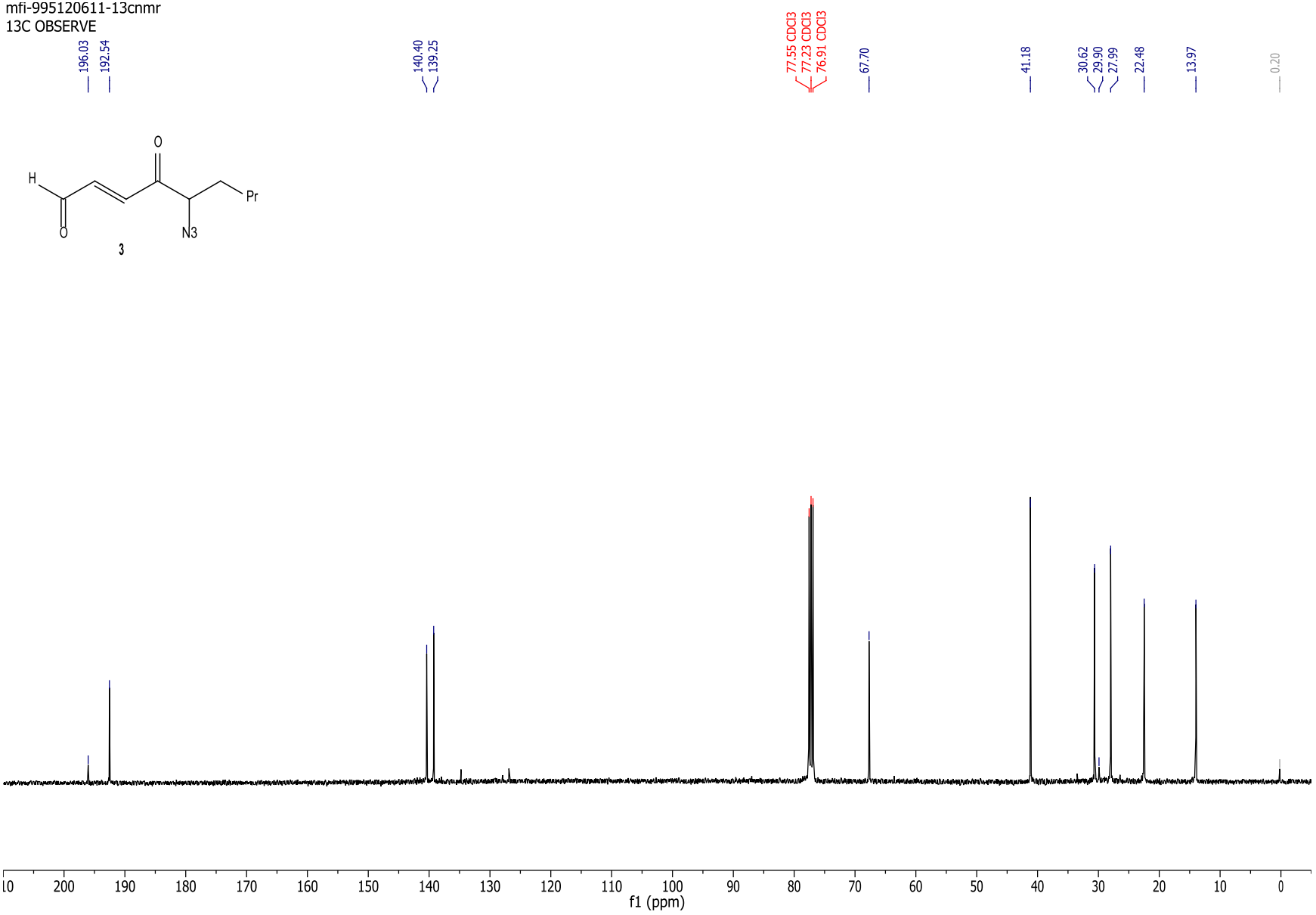

61-h (1)
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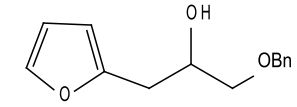

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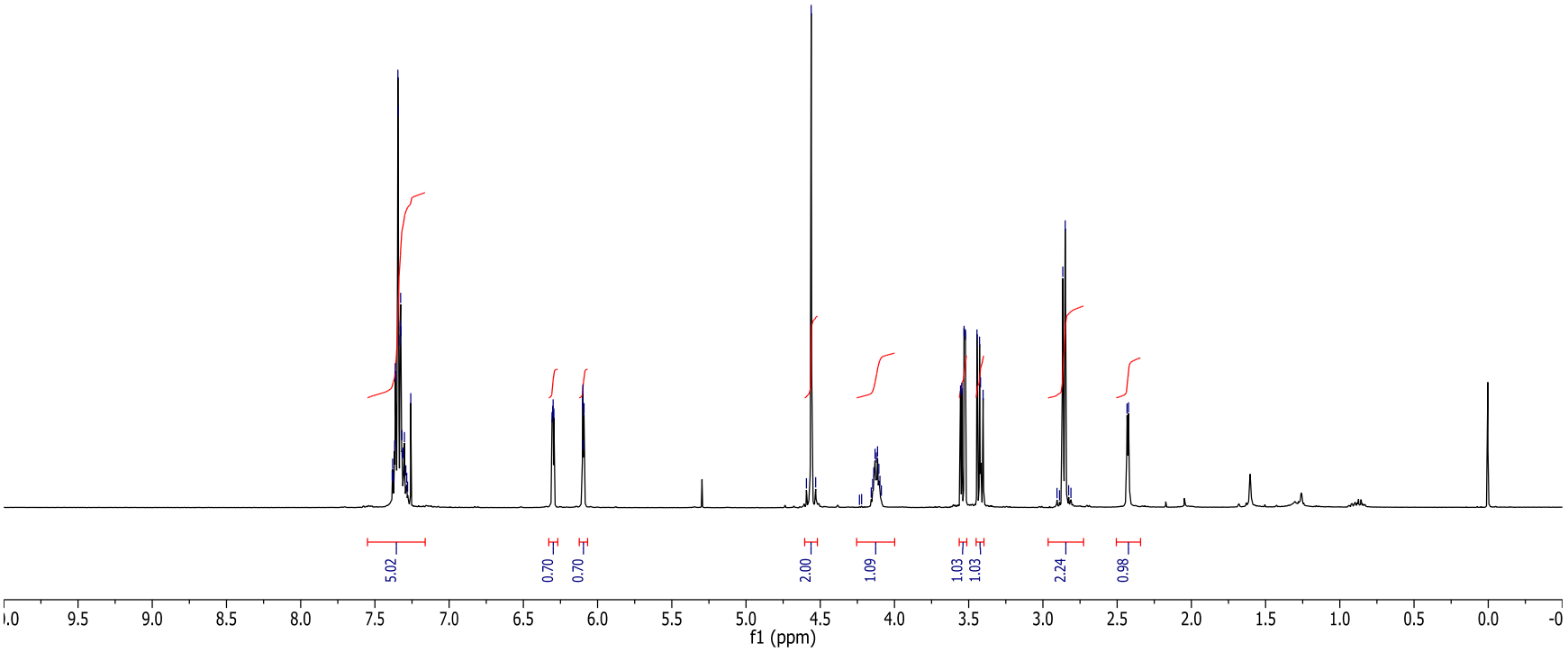

61-c
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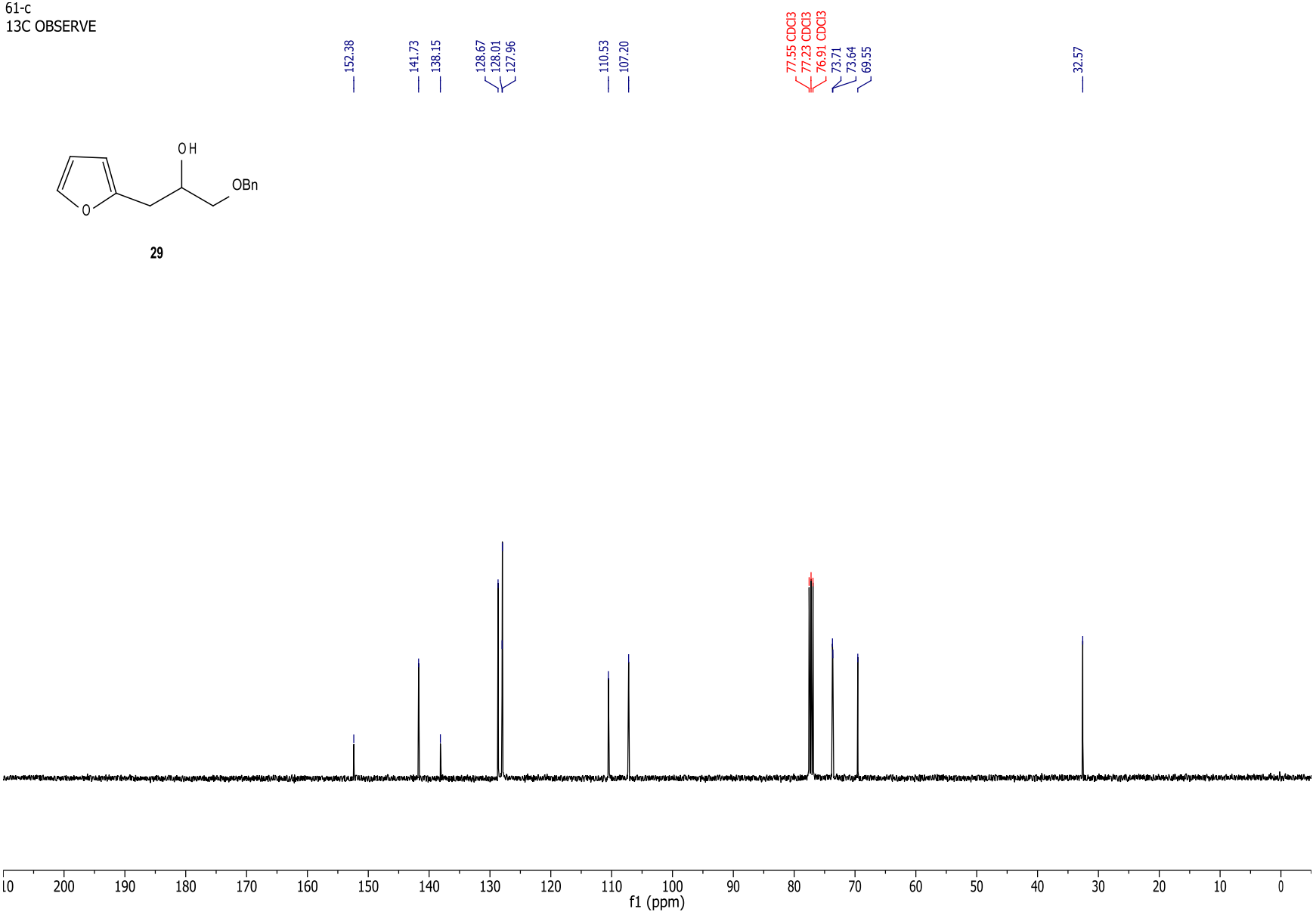

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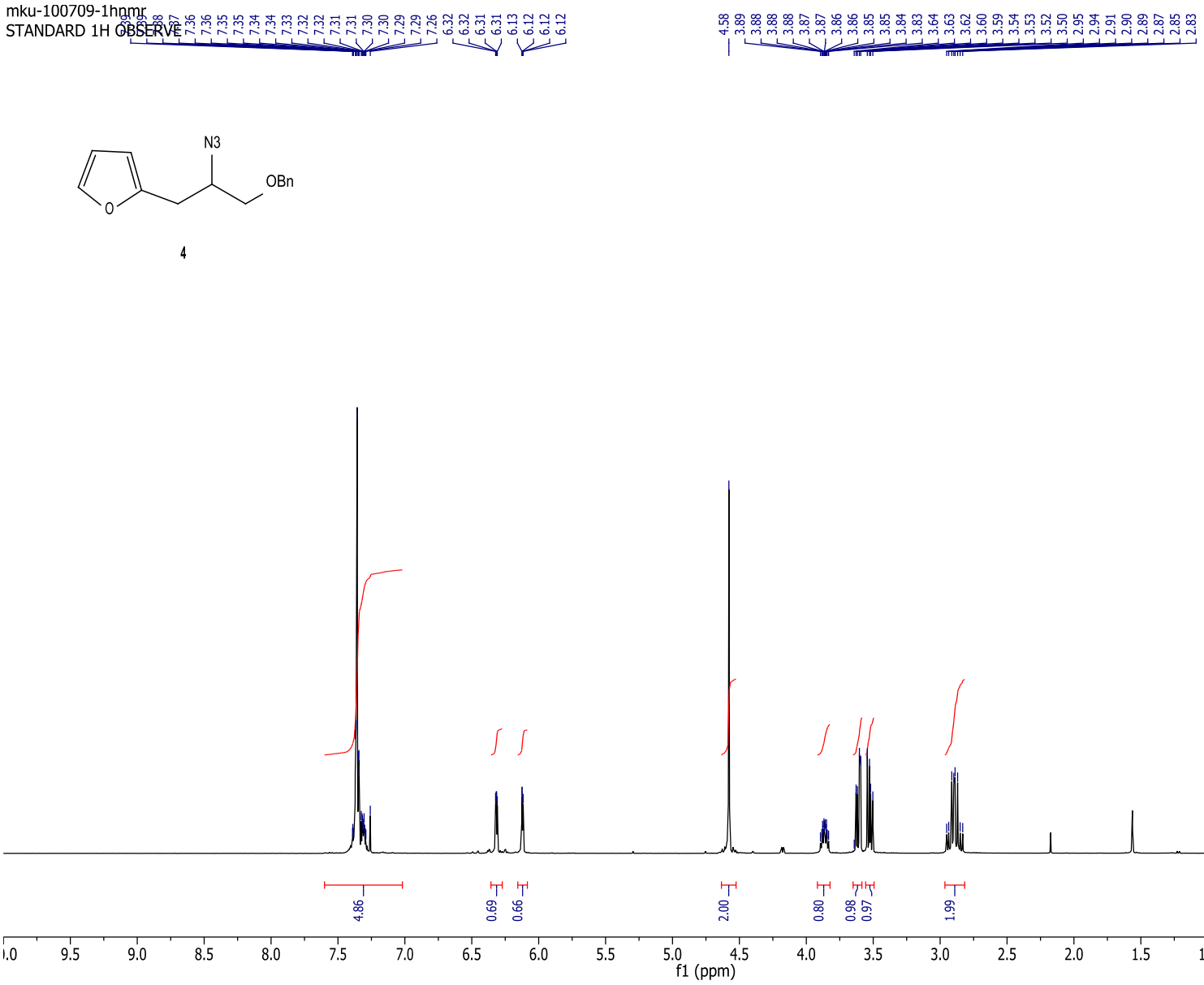

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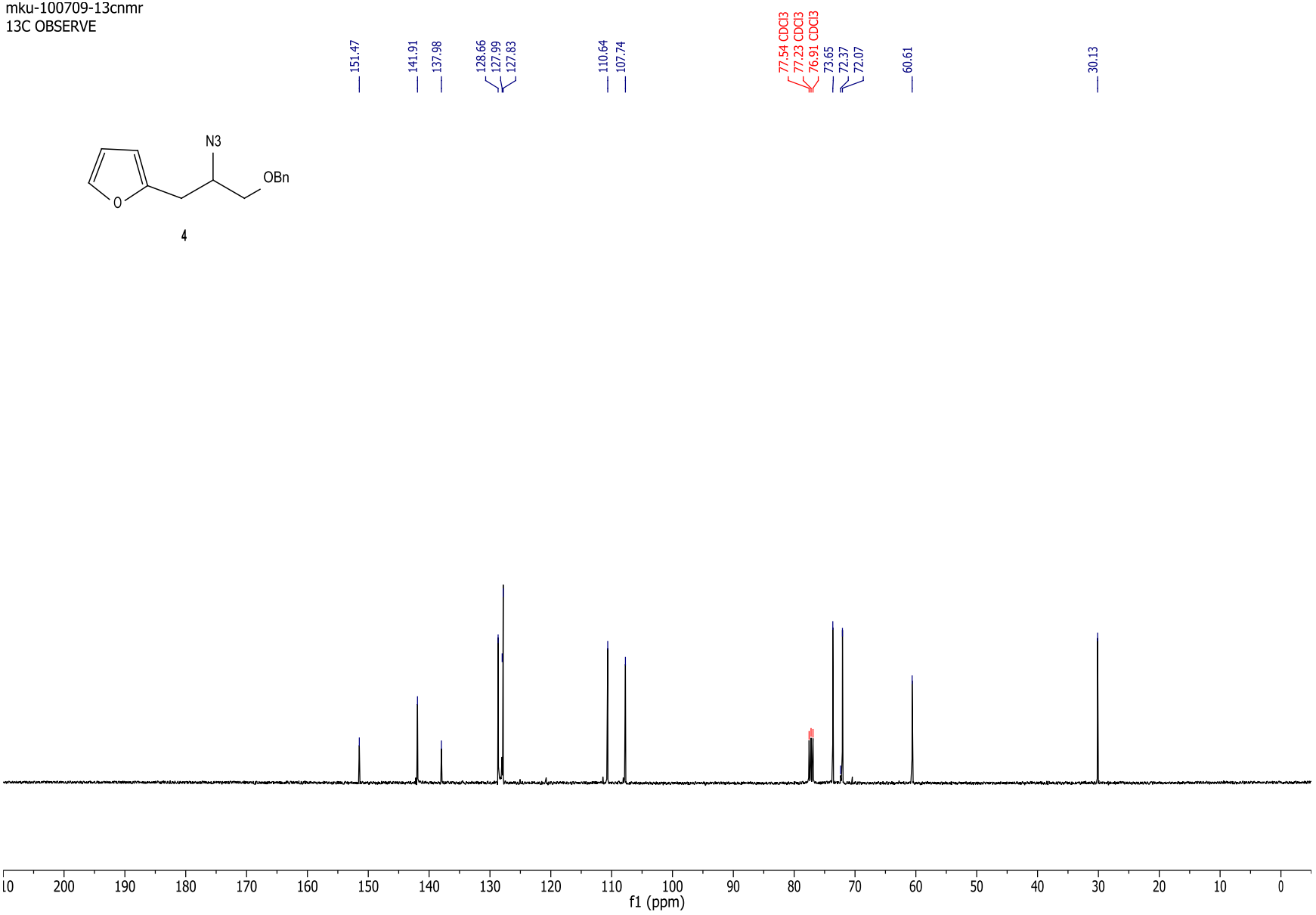

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21	1802.983	4.510	8.4				
22	1726.869	4.320	6.5				
23	1658.806	4.149	5.5				
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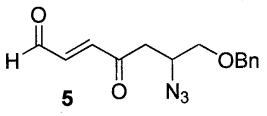

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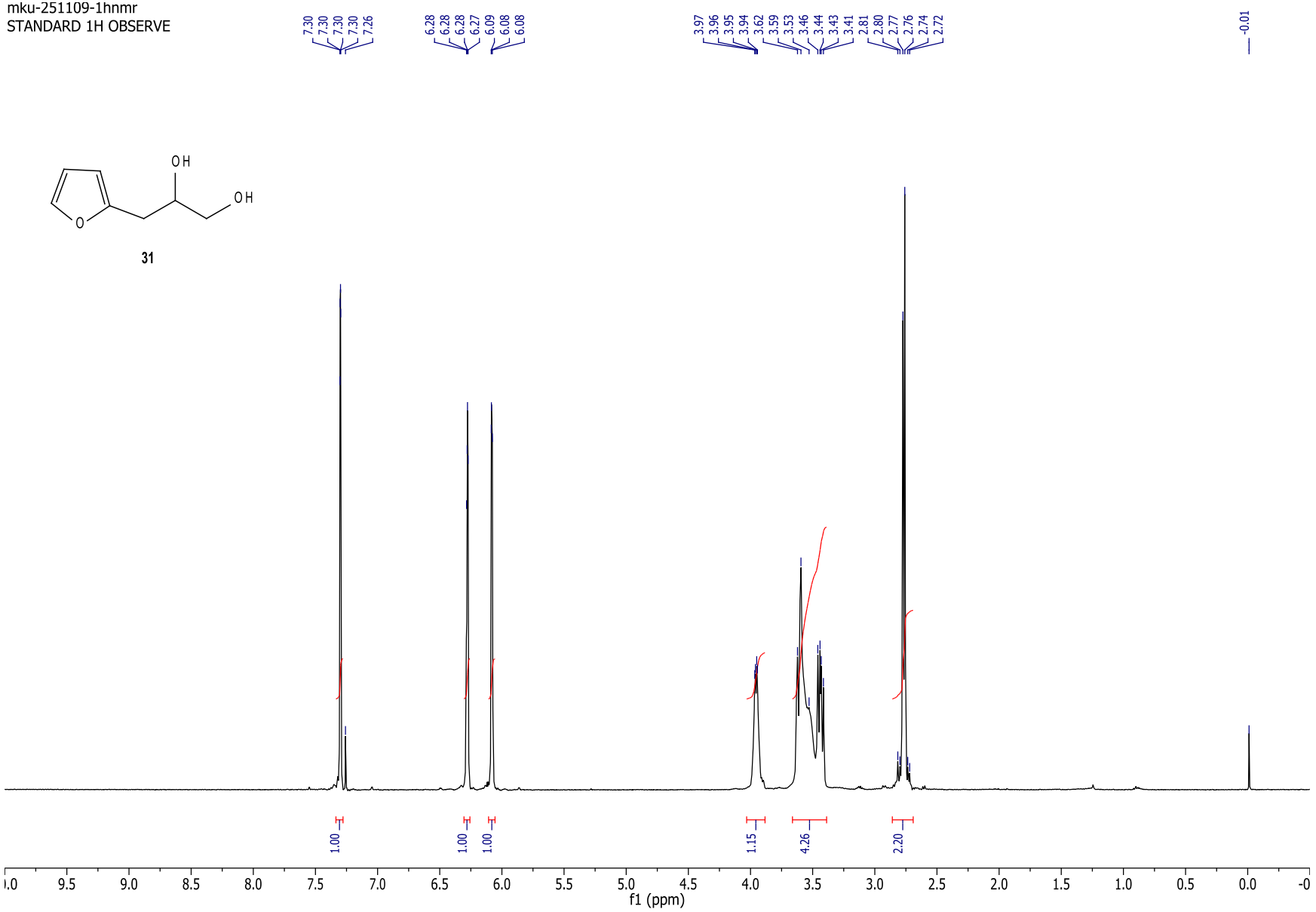

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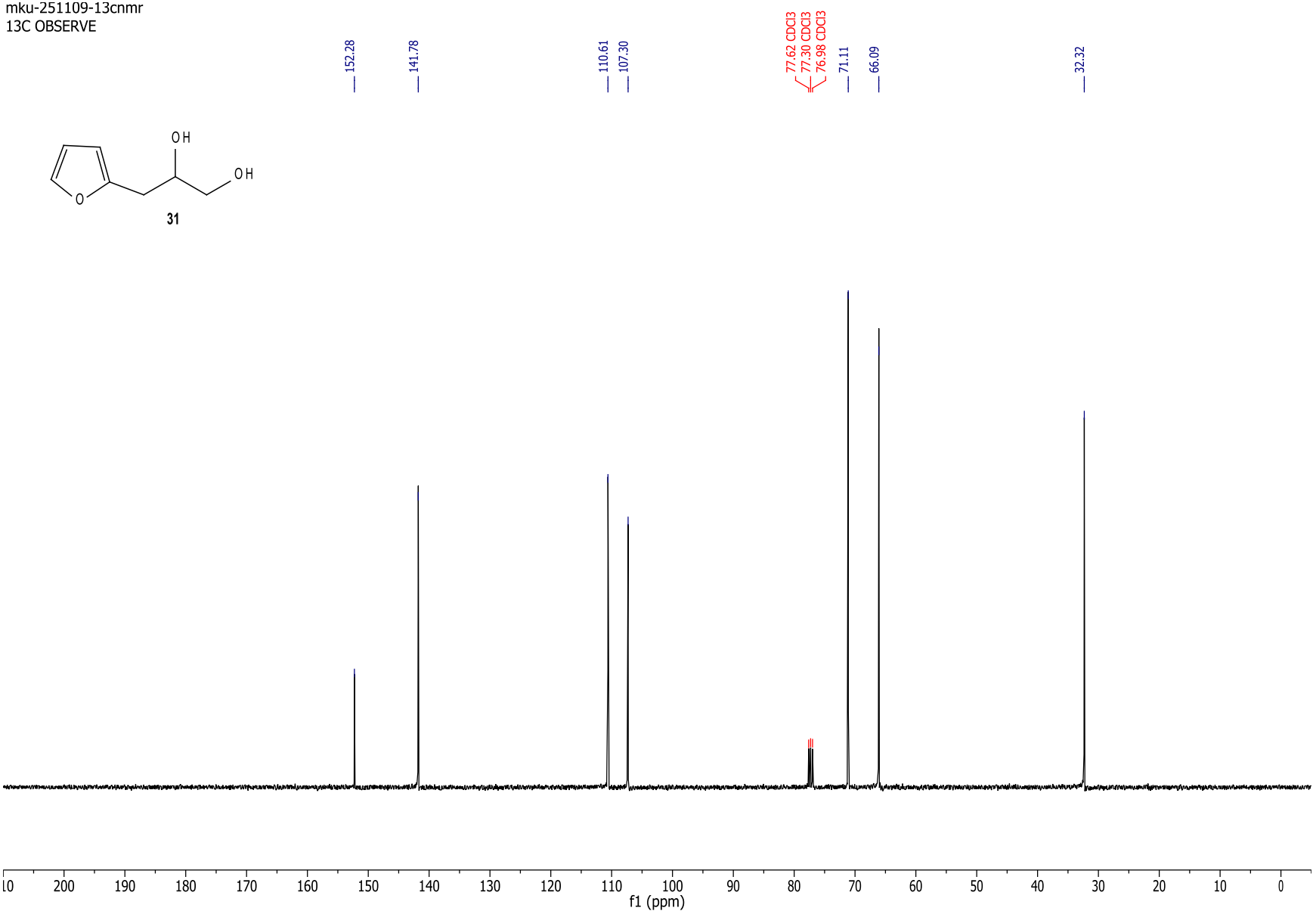

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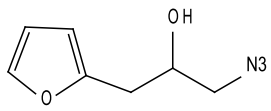

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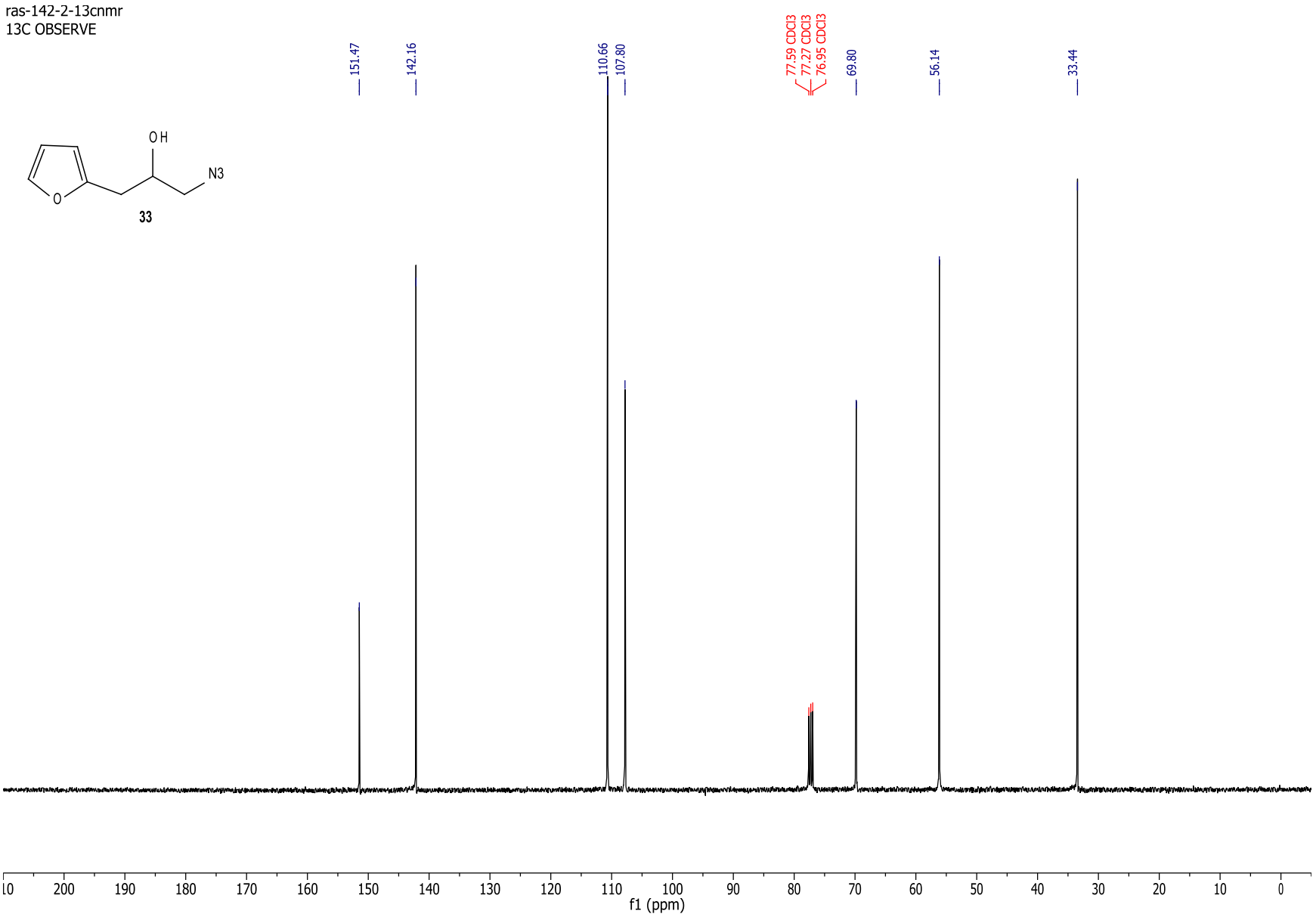
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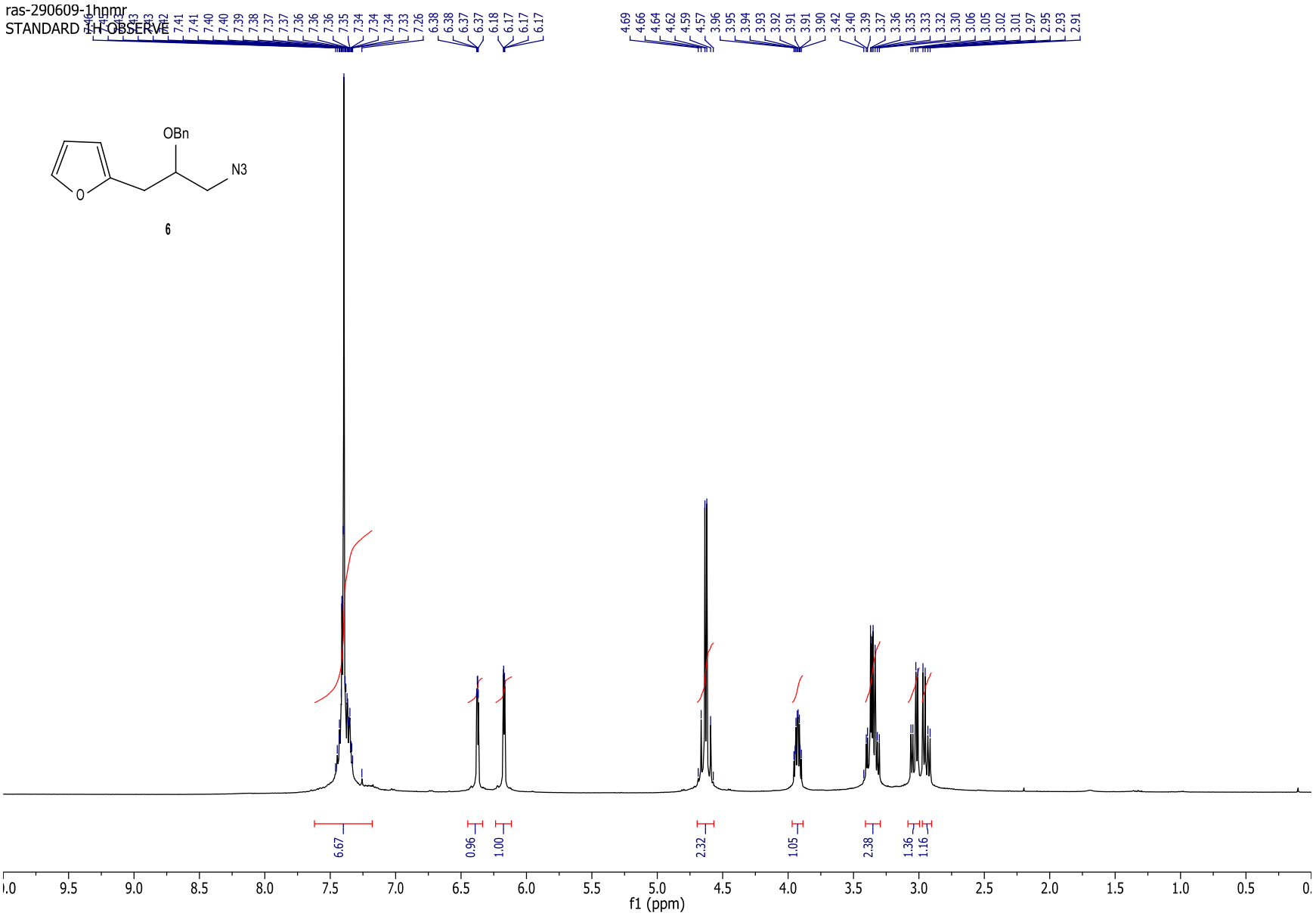
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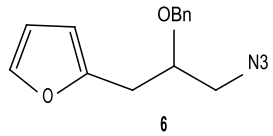

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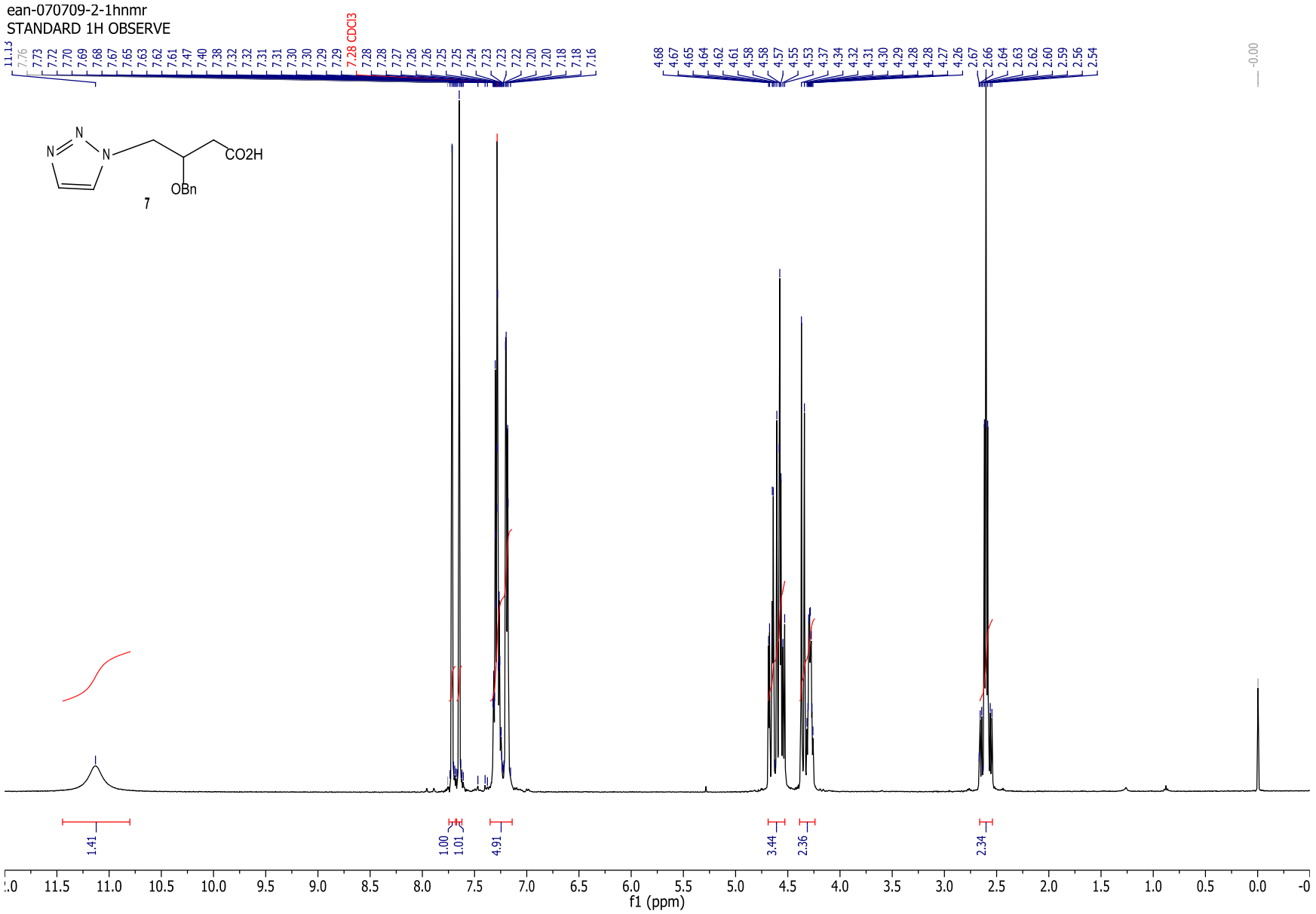
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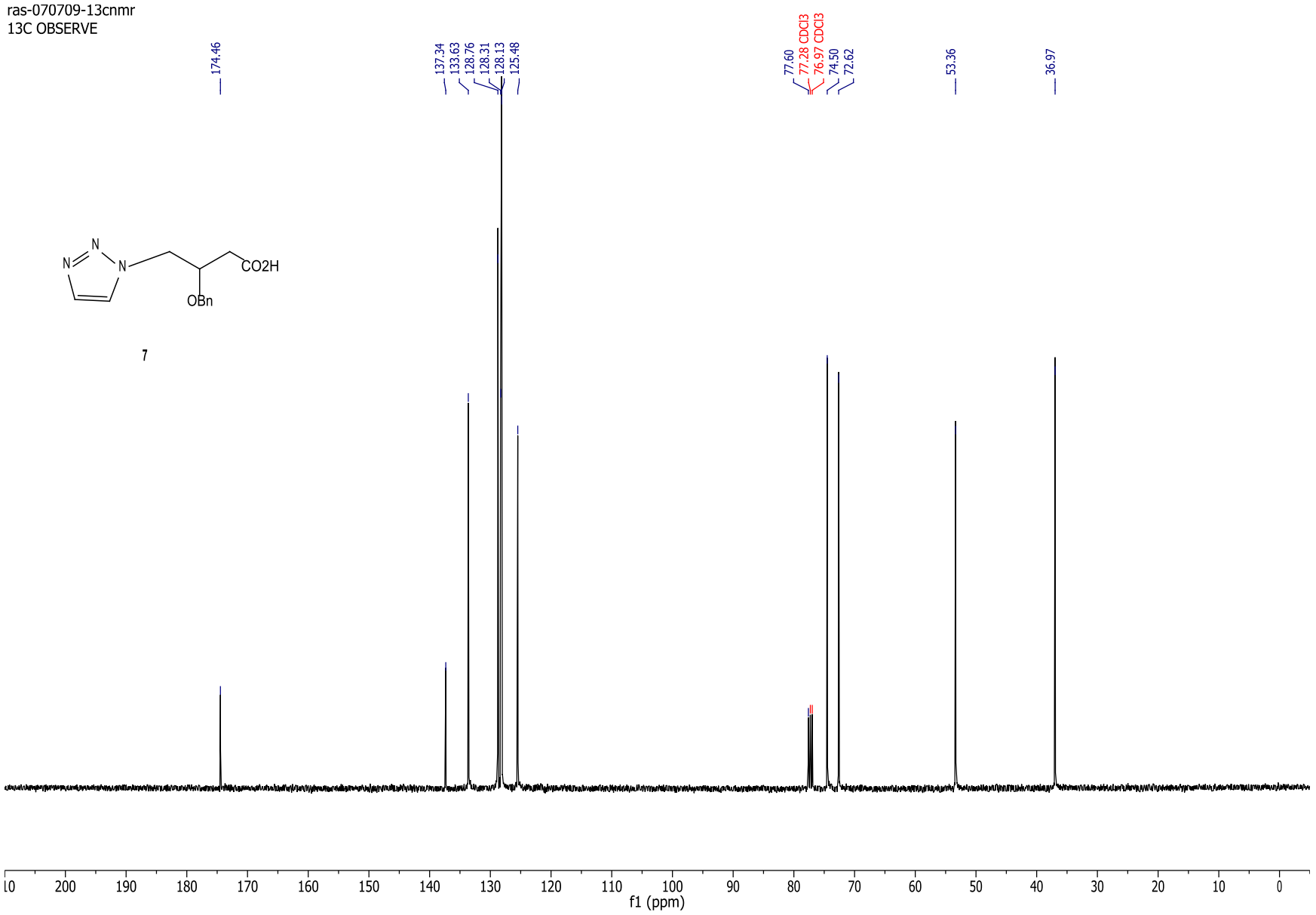
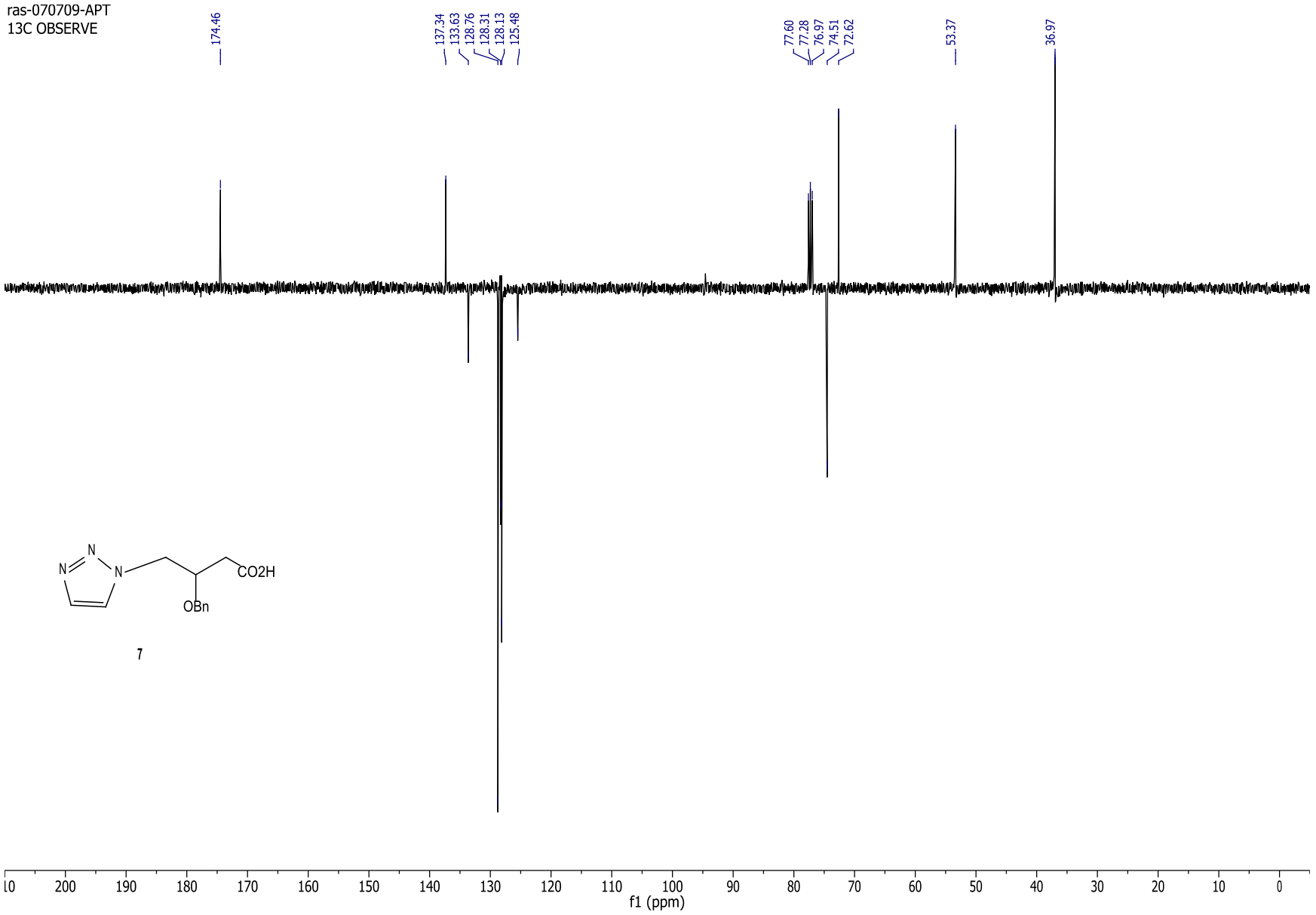
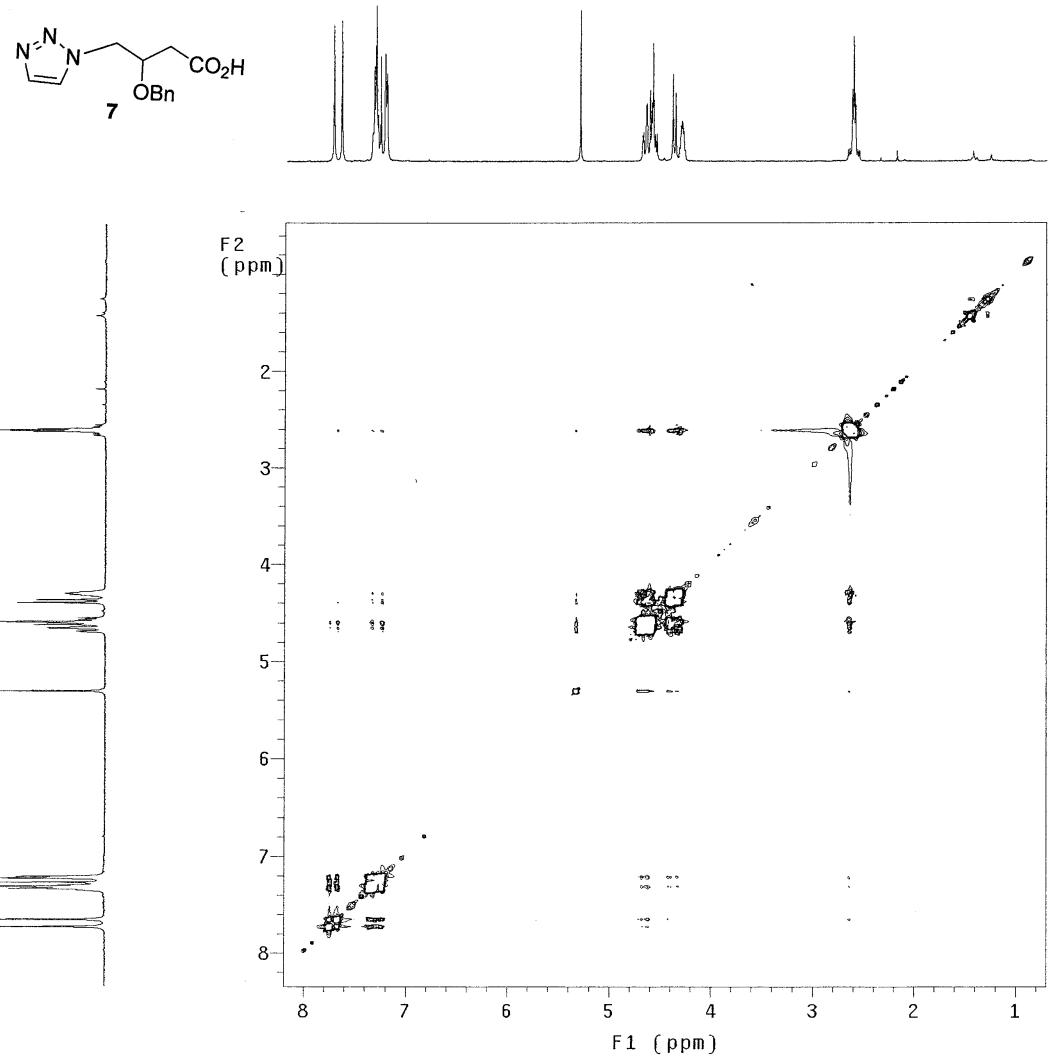
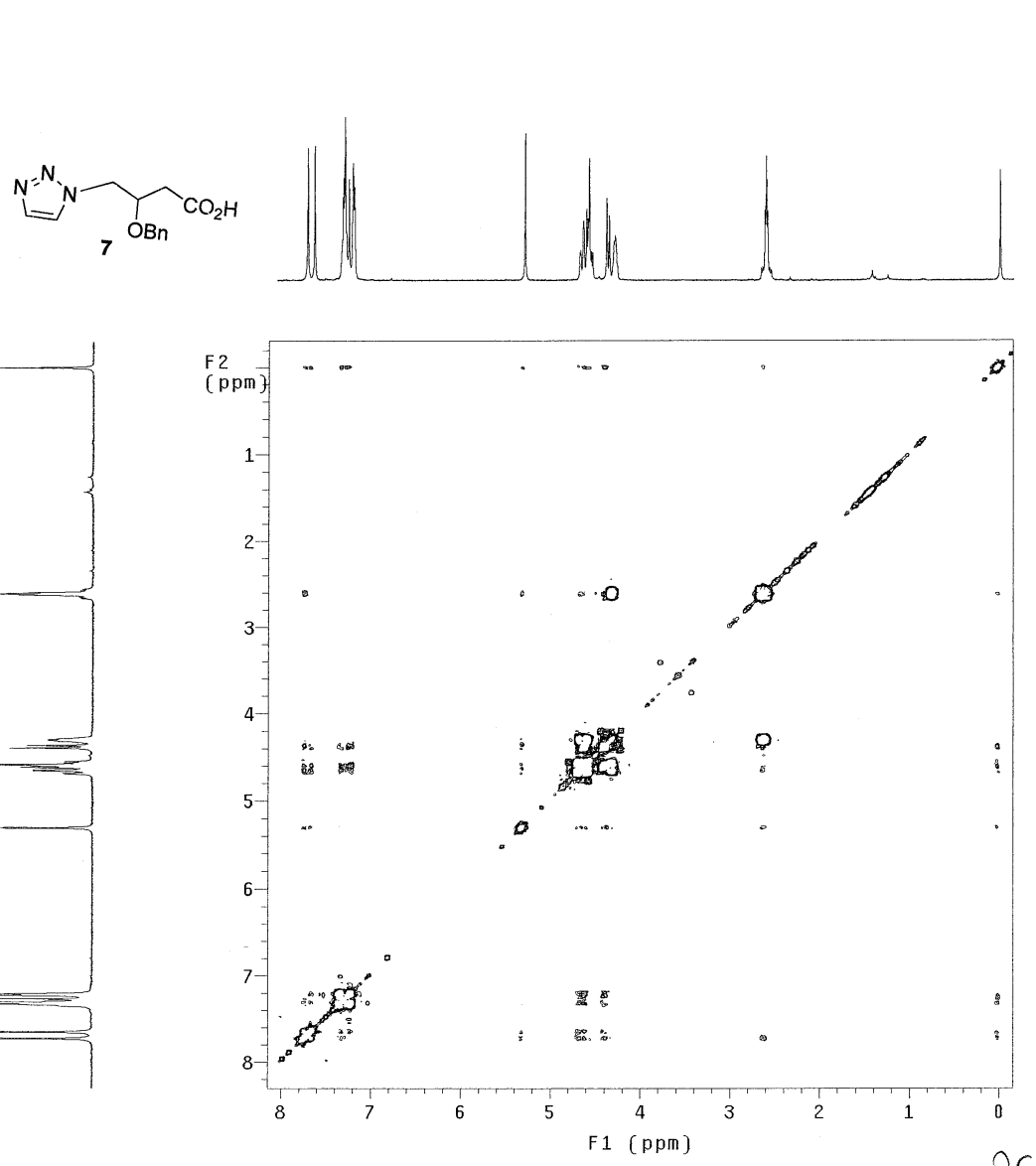
2.34
f1 (ppm)

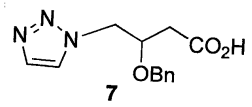

ras-070709-13cnmr
13C OBSERVE
174.46
137.34
133.63
128.76
128.31
128.13
125.48
77.60
77.28 CDCl3
76.97 CDCl3
74.50
72.62
53.36
36.97
N
N
N
CO2H
OBn
7
f1 (ppm)


ras-070709-APT
13C OBSERVE
174.46
137.34
133.63
128.76
128.31
128.13
125.48
77.60
77.28
76.97
74.51
72.62
53.37
36.97
N
N
N
CO2H
OBn
7
f1 (ppm)

EA(215) NOESY

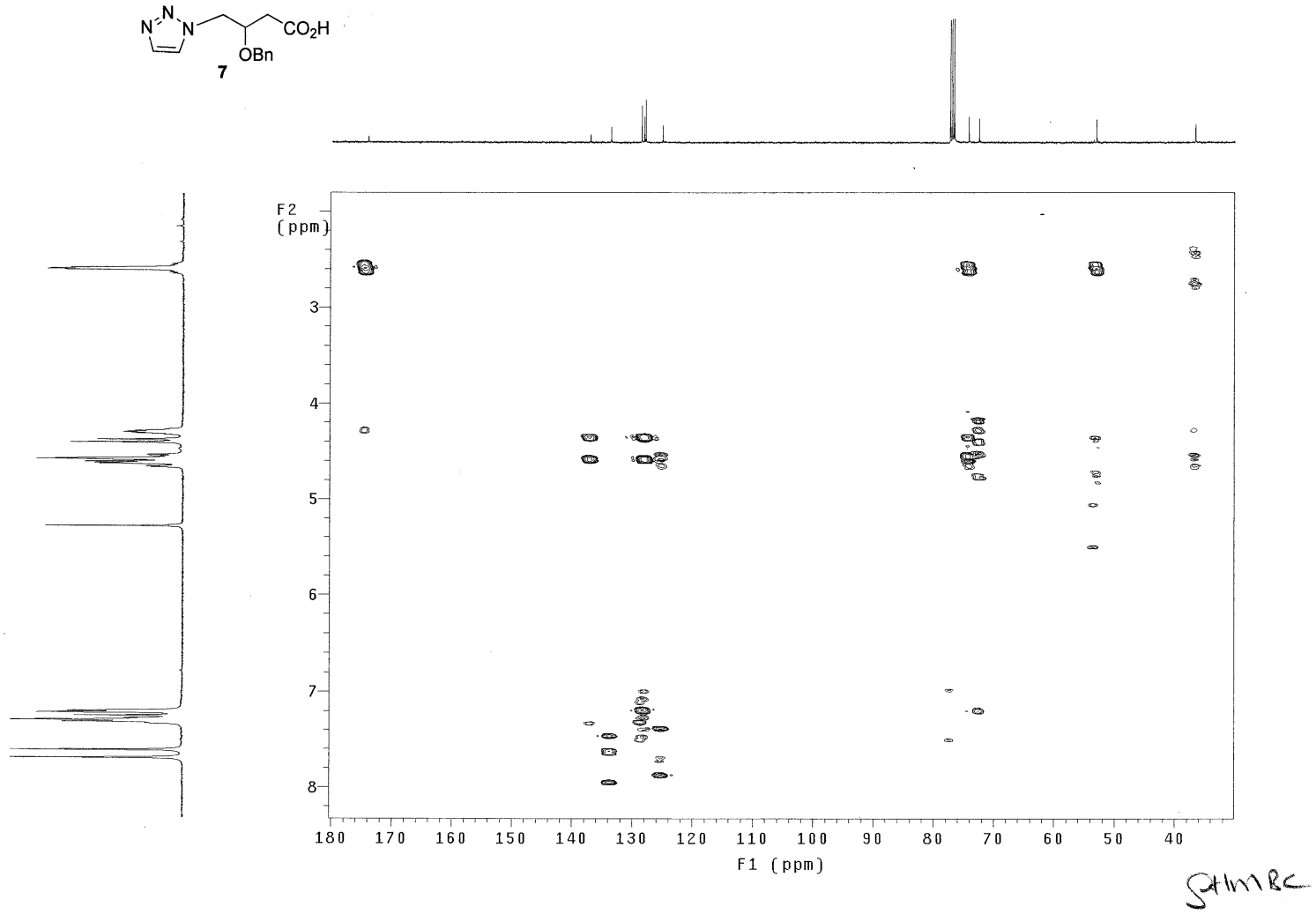



N
N
N
CO2H
OBn
7
F2
(ppm)
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
0
F1 (ppm)

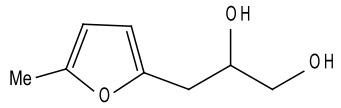

N
N
N
CO2H
OBn

7

F2
(ppm)
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
130
120
110
100
90
80
70
60
50
40
F1 (ppm)


7
OBn
CO2H
F2 (ppm)
F1 (ppm)

mku-120509-1hnmr
STANDARD 1H OBSERVE



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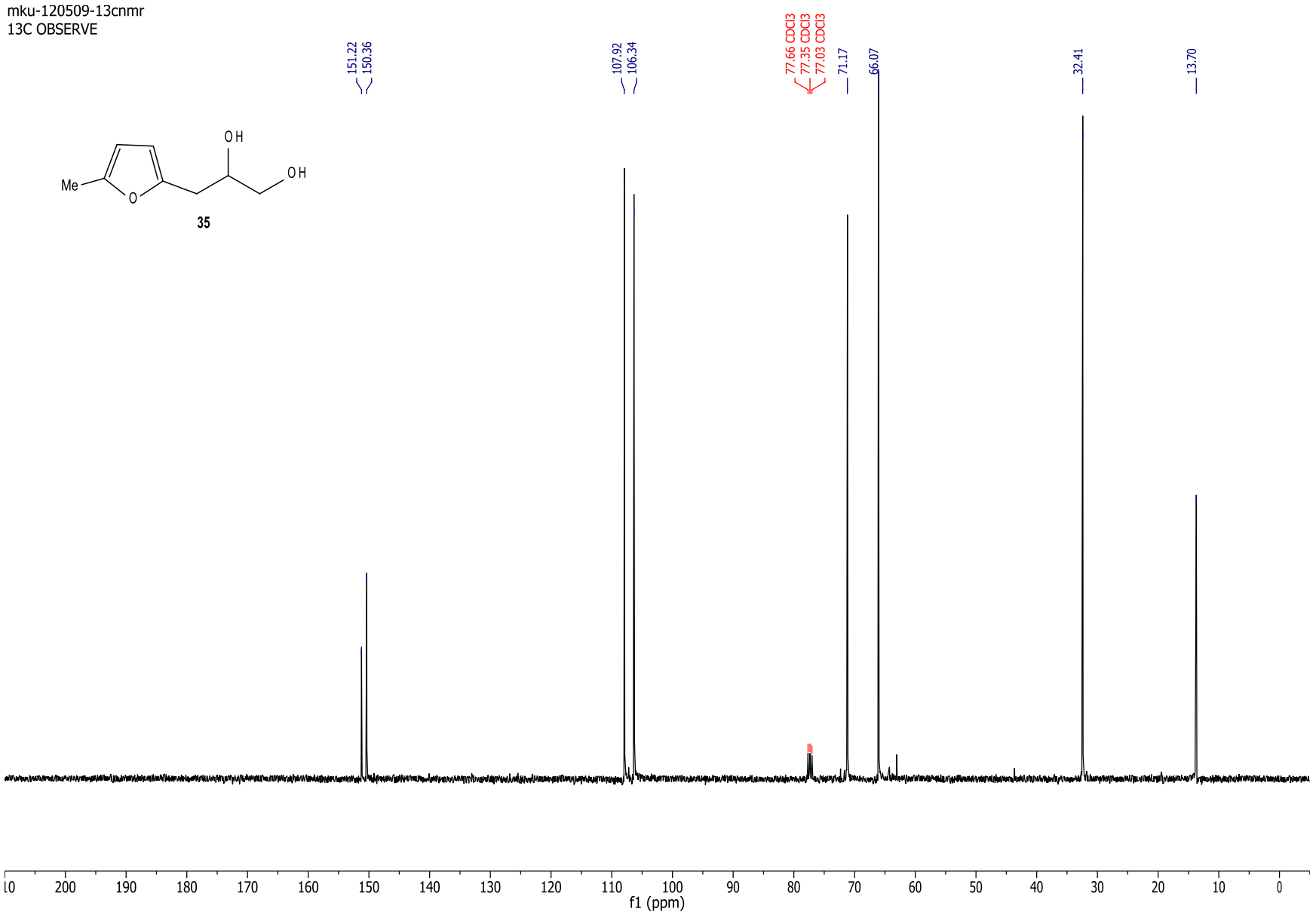
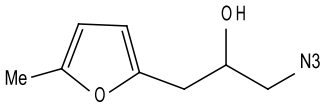

mku-120509-13cnmr
13C OBSERVE
151.22
150.36
107.92
106.34
77.66 CDCl3
77.35 CDCl3
77.03 CDCl3
71.17
66.07
32.41
13.70
OH
OH
Me
O
35
f1 (ppm)

mku-140709-2-1hnmr
STANDARD 1H OBSERVE



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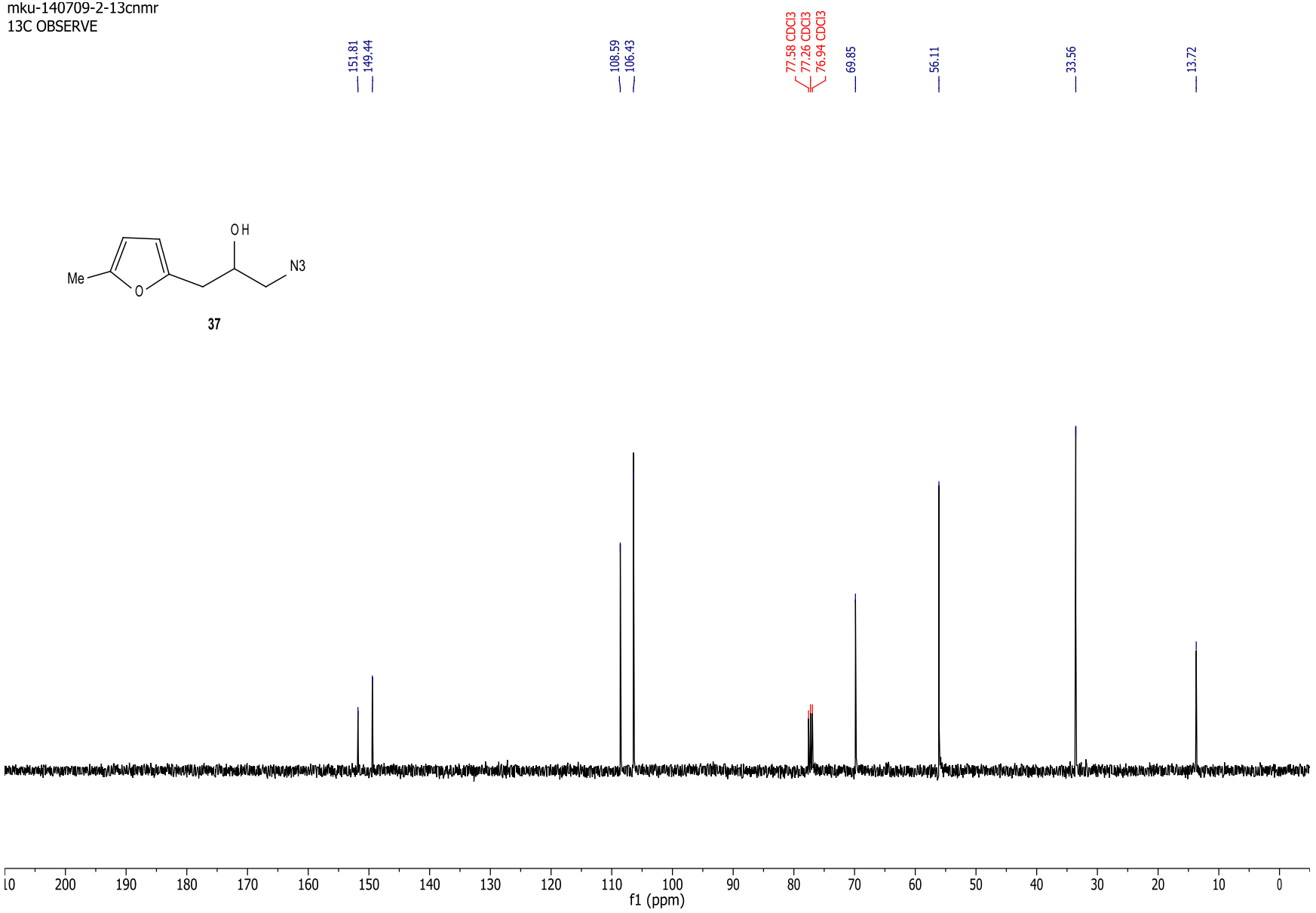
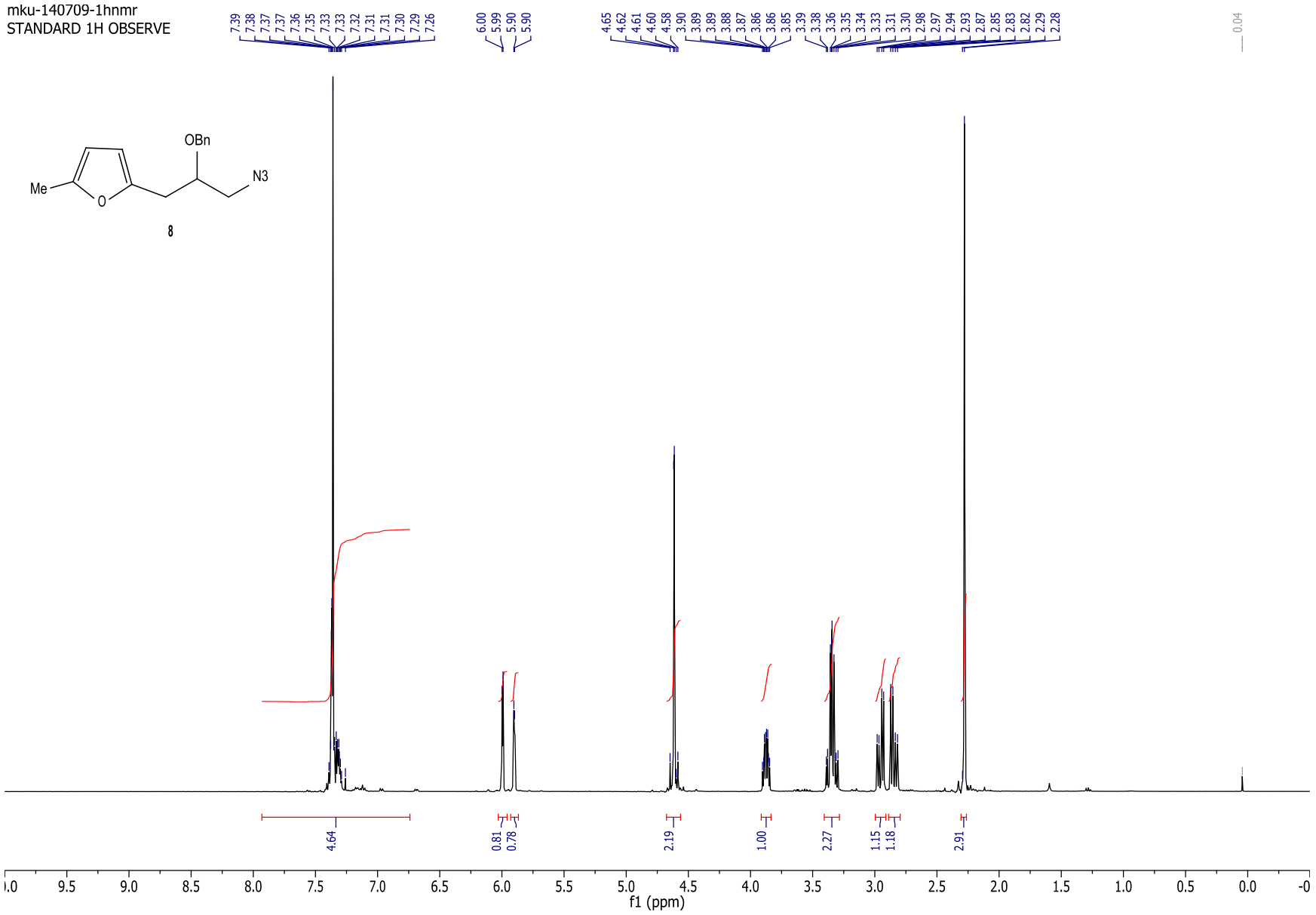
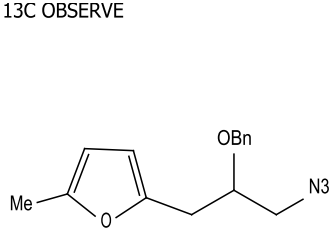
mku-140709-2-13cnmr
13C OBSERVE




mku-140709-1hnmr
STANDARD 1H OBSERVE
OBn
Me
O
N3
8
f1 (ppm)

13C OBSERVE



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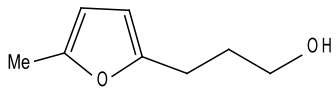
mku-410-1hnmr
STANDARD 1H OBSERVE



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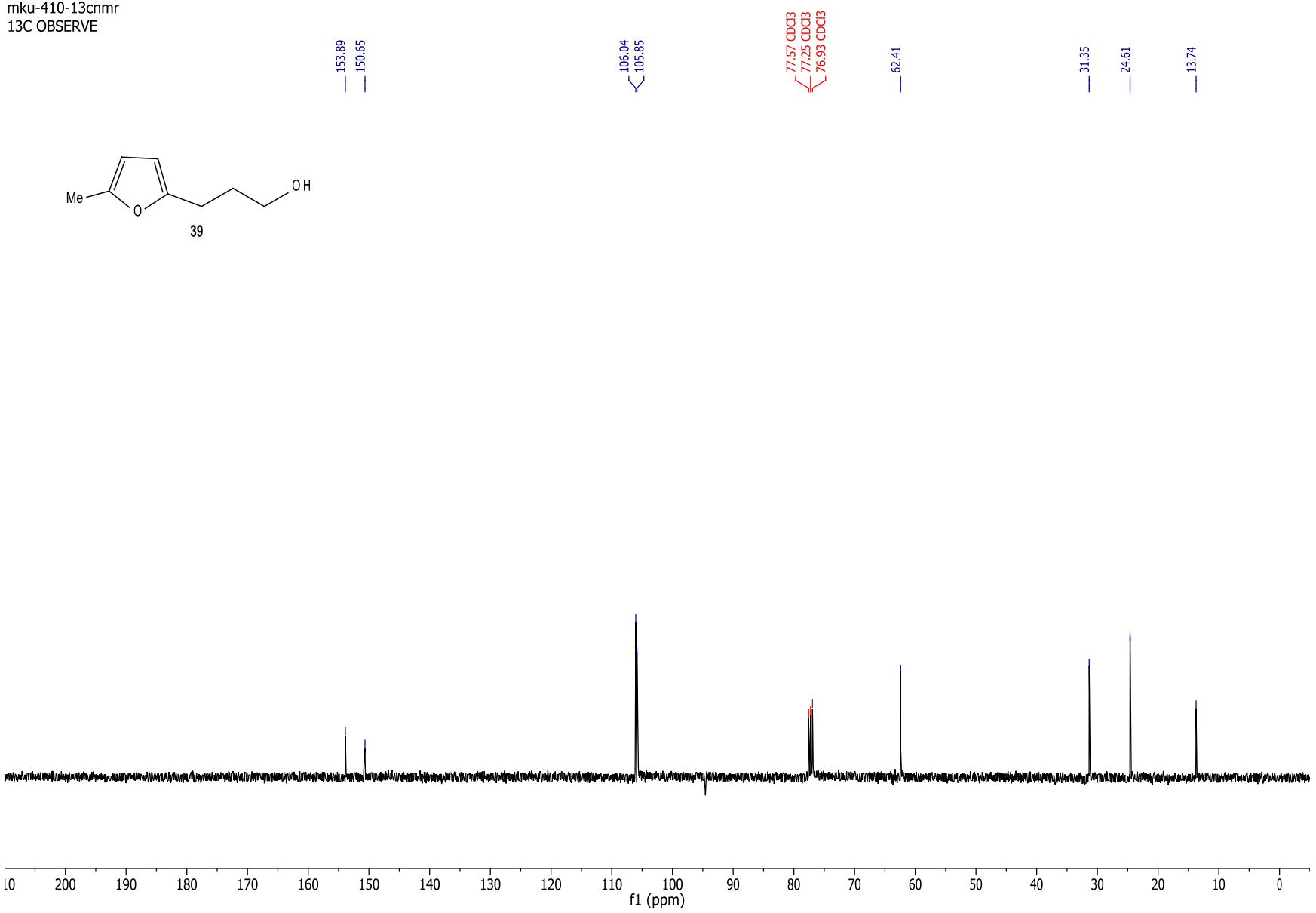
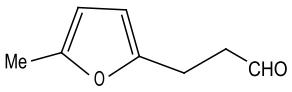
mku-410-13cnmr
13C OBSERVE



mku-161210-1hnmr
STANDARD 1H OBSERVE



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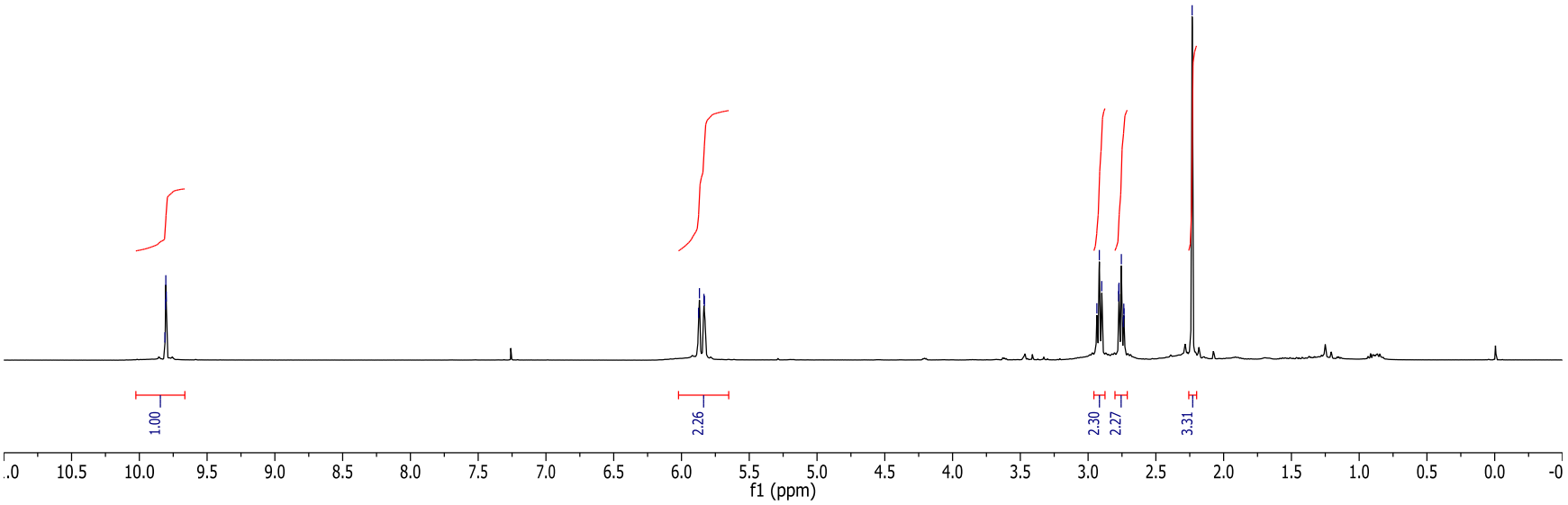

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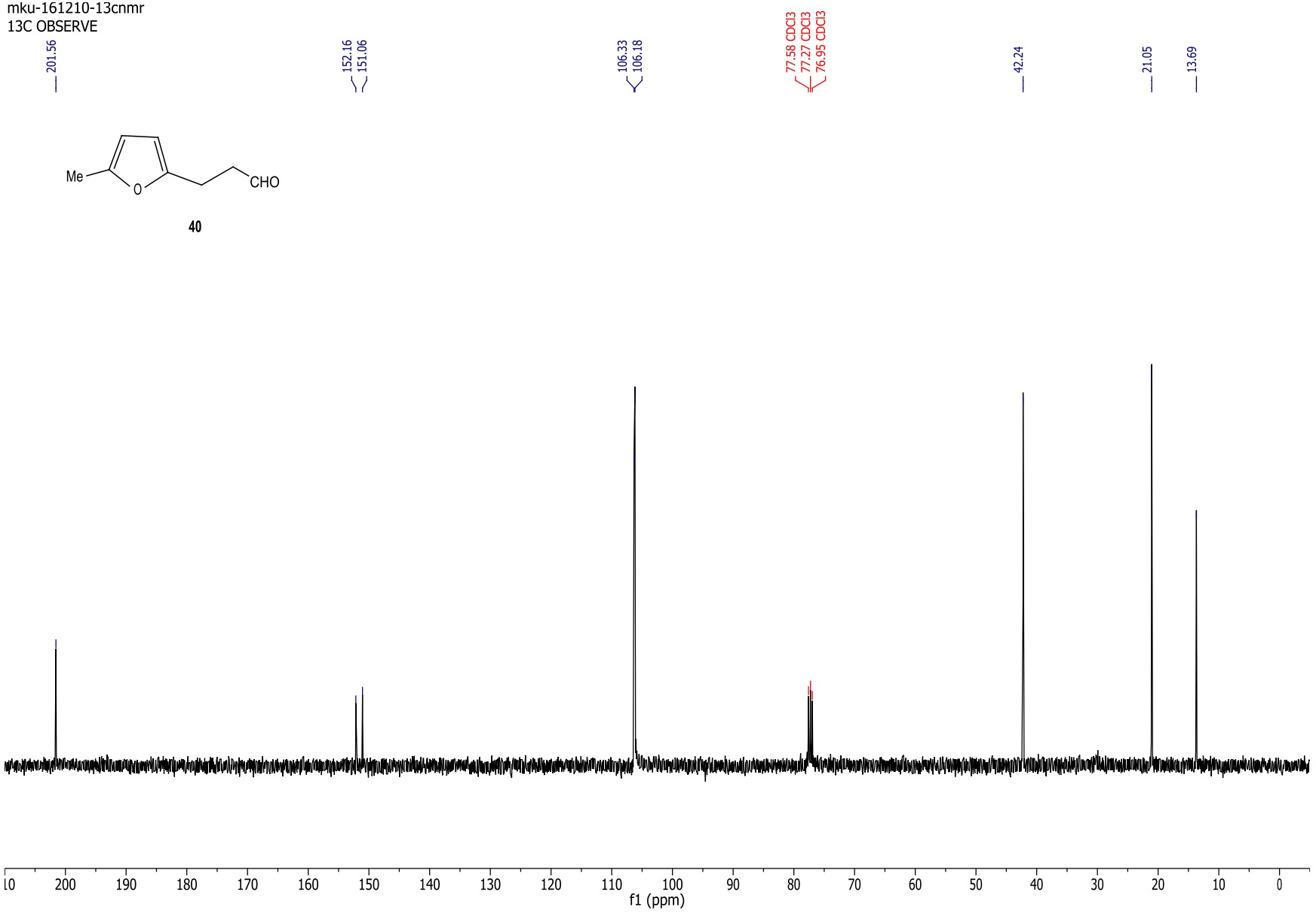
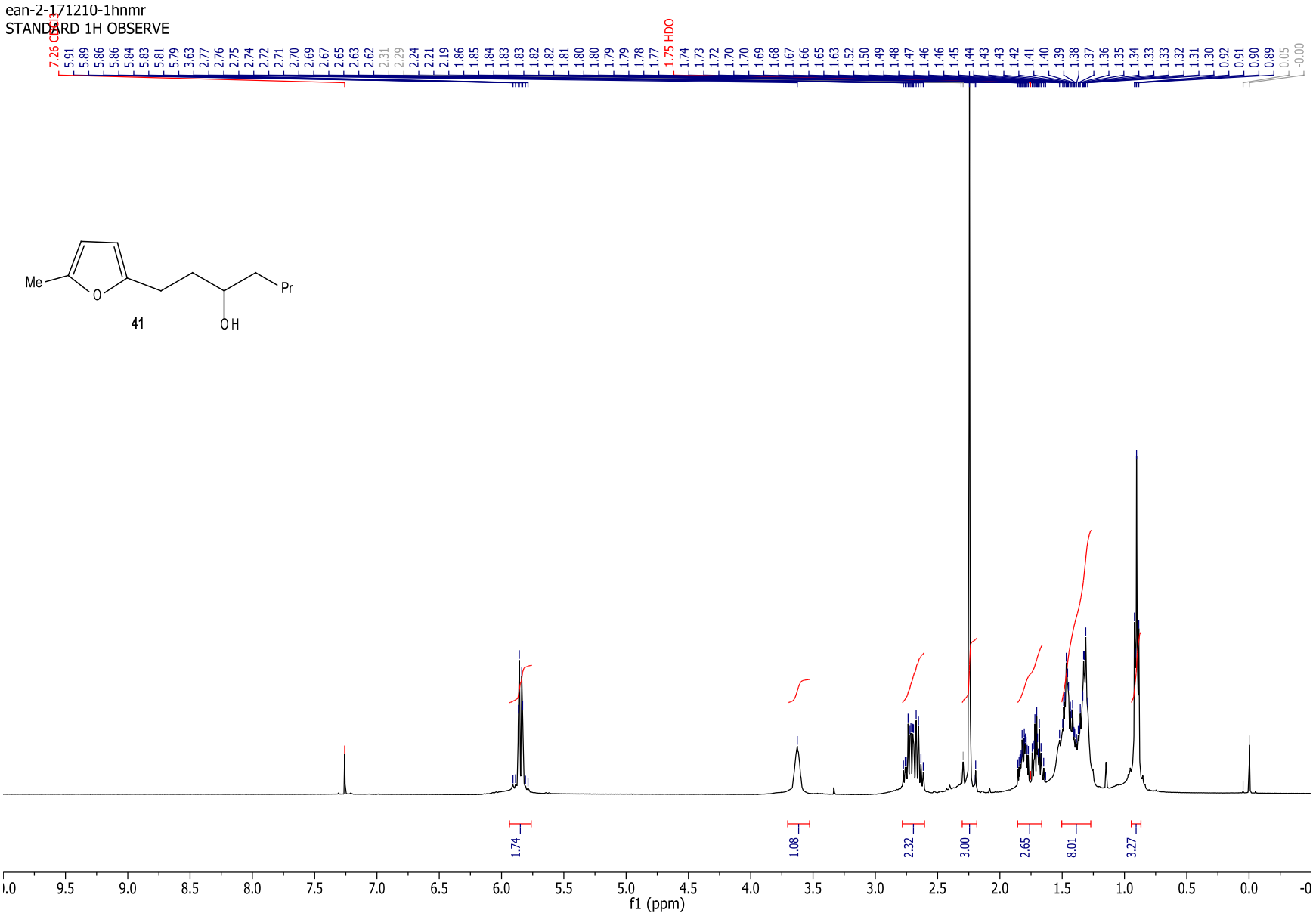
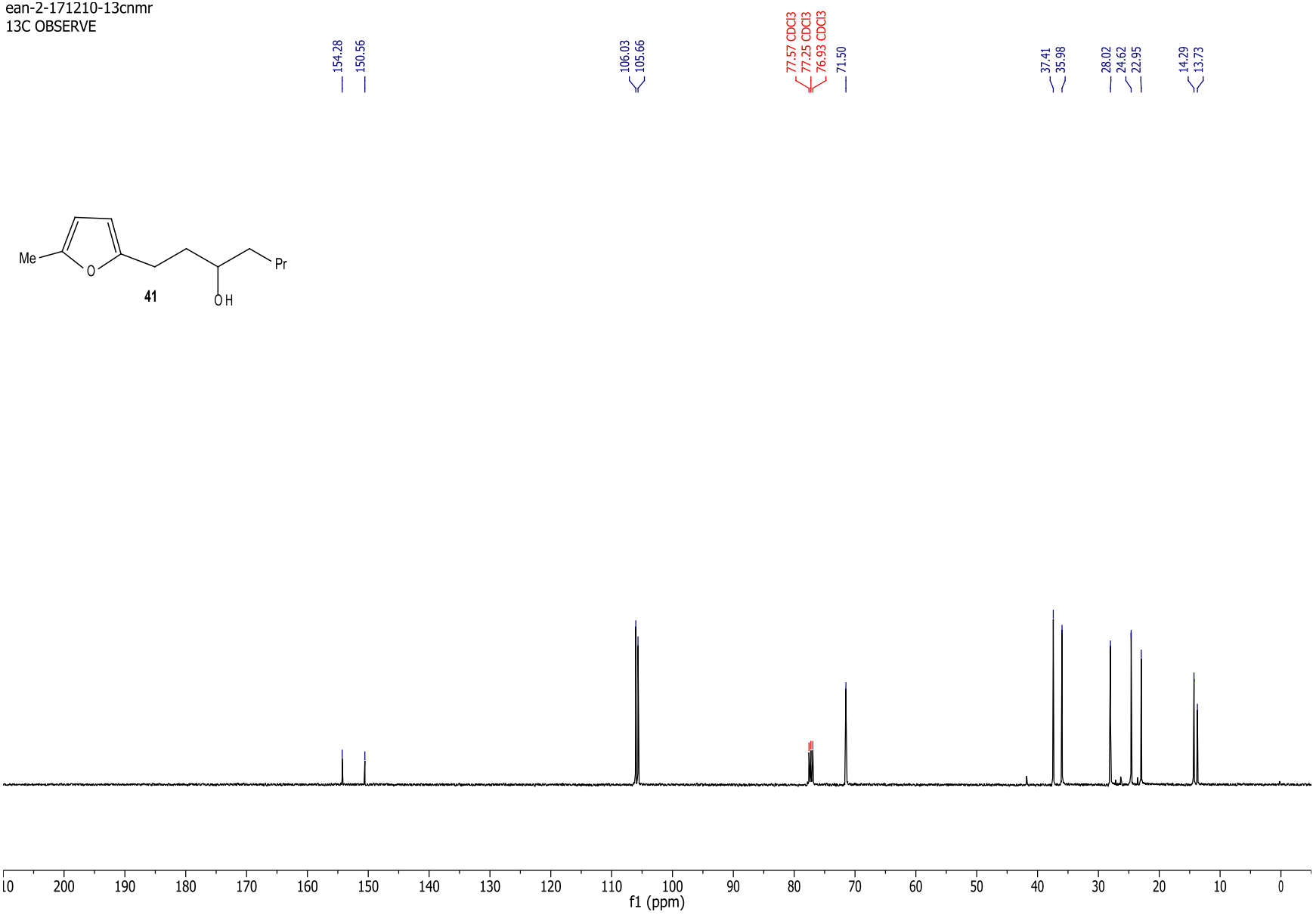
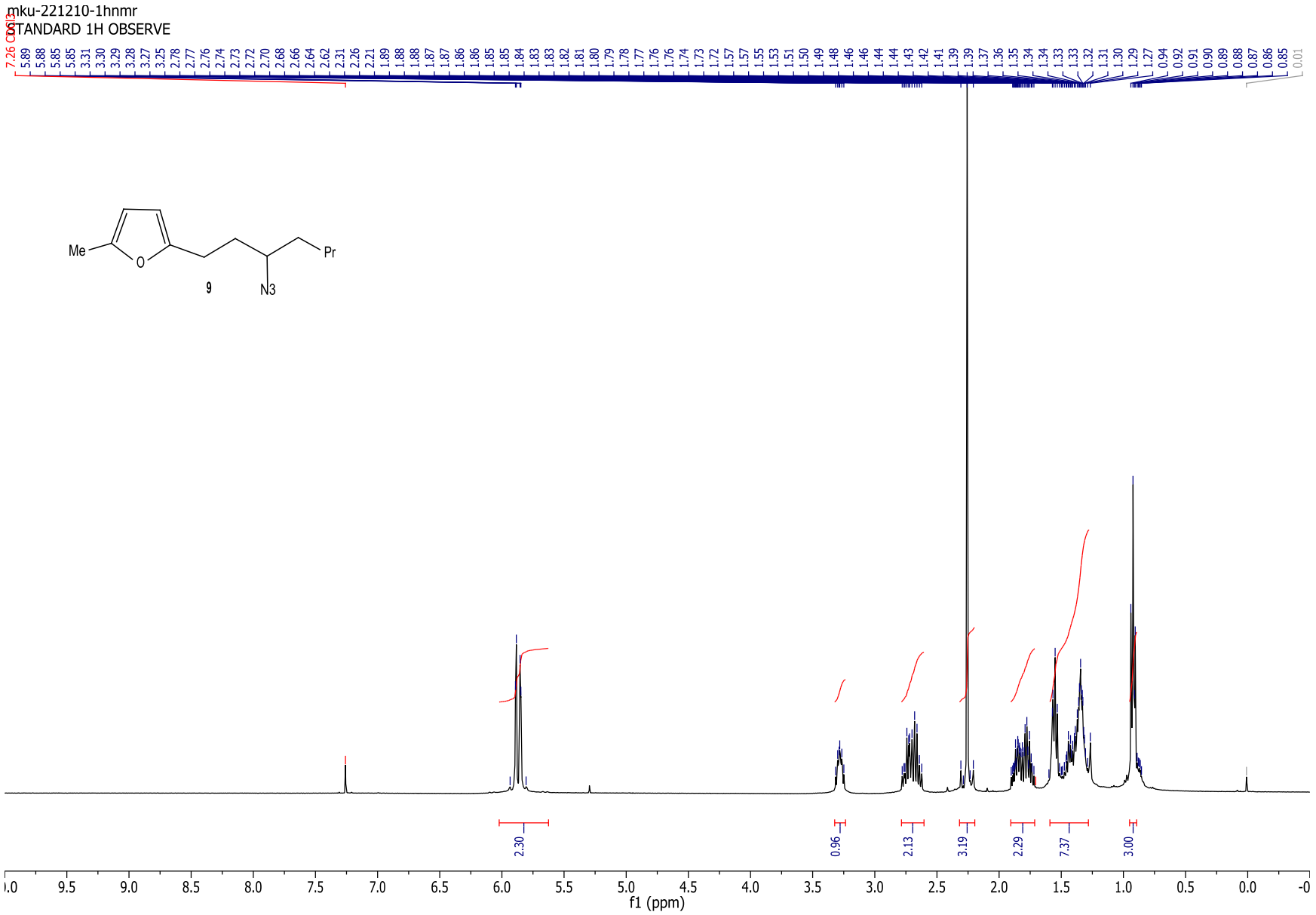


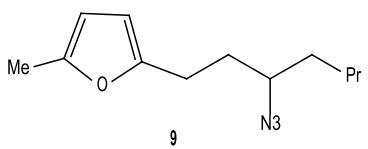

ean-2-171210-1hnmr
STANDARD 1H OBSERVE
Me
O
Pr
OH
41
f1 (ppm)

ean-2-171210-13cnmr
13C OBSERVE



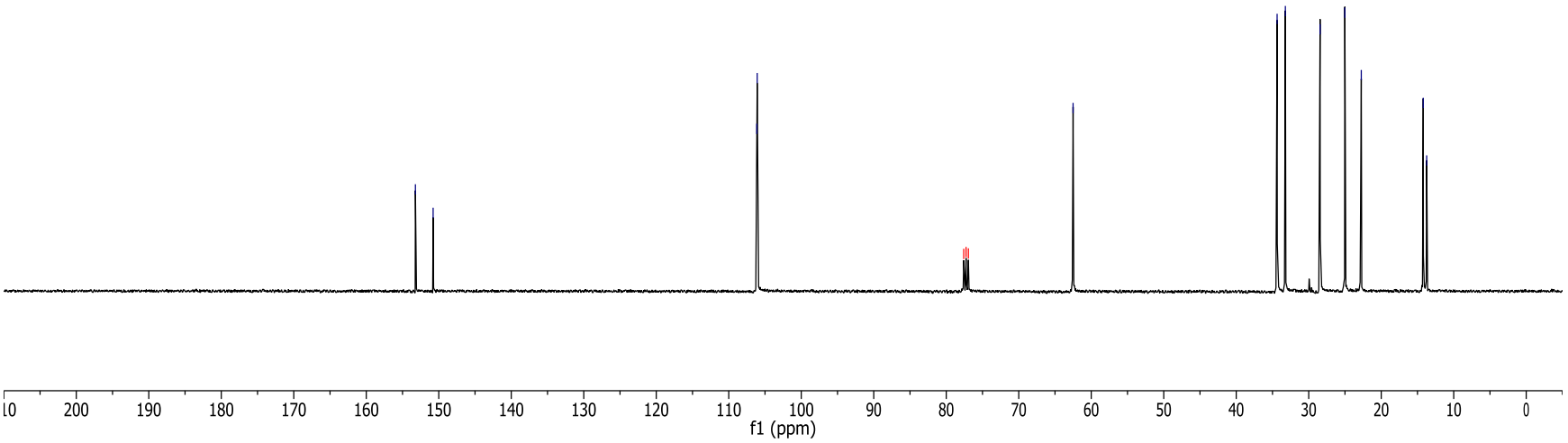

mku-221210-1hnmr
STANDARD 1H OBSERVE
Me
O
Pr
N3
2.30
0.96
2.13
3.19
2.29
7.37
3.00
f1 (ppm)

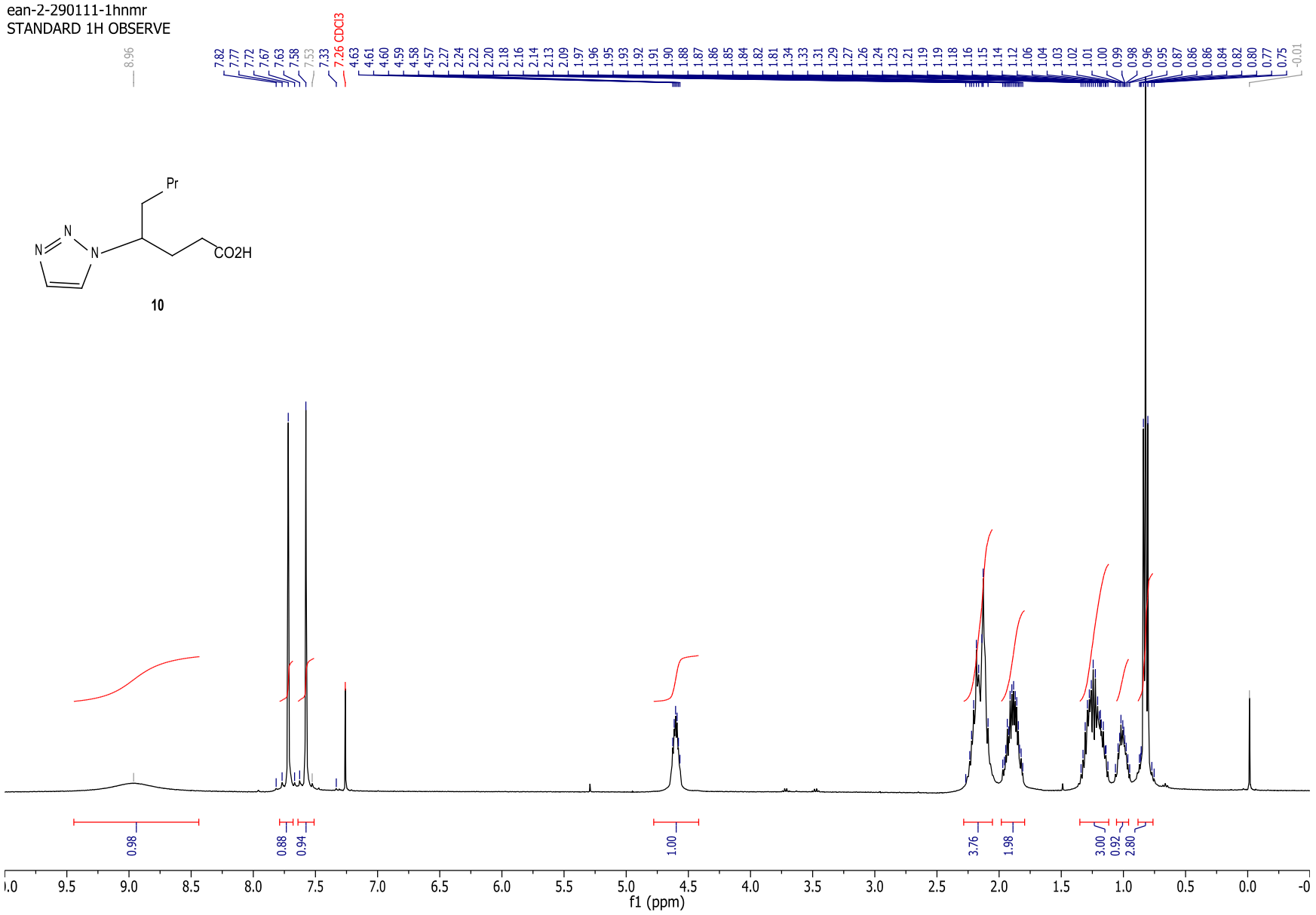
mku-221210-13cnmr
13C OBSERVE



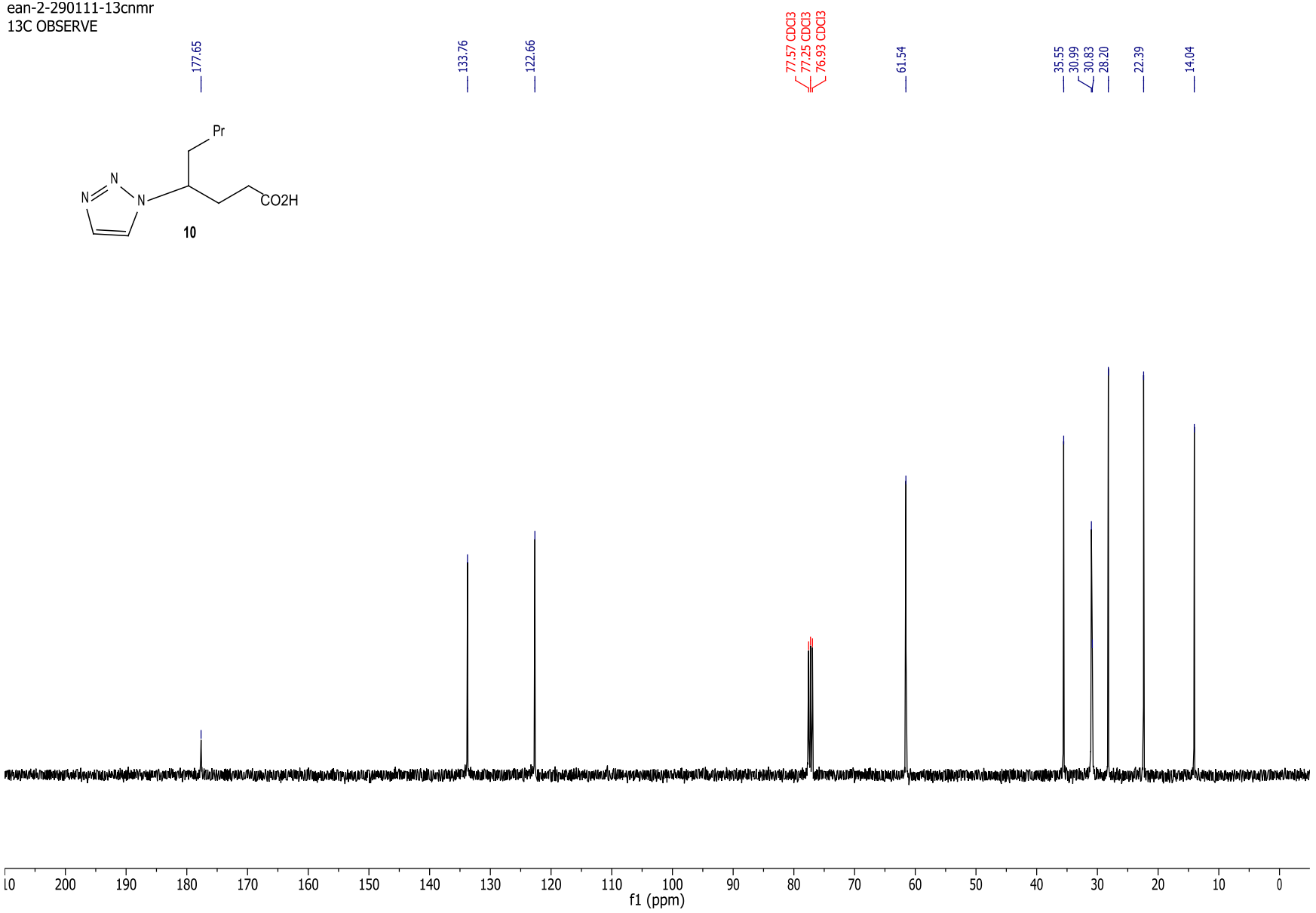
9

153.22
150.78
106.14
106.08
77.58 CDCl3
77.27 CDCl3
76.95 CDCl3
62.51
34.36
33.23
28.43
25.02
22.75
14.20
13.73

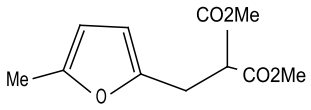



ean-2-290111-1hnmr
STANDARD 1H OBSERVE
CDCl3
Pr
CO2H
10
f1 (ppm)

ean-2-290111-13cnmr
13C OBSERVE

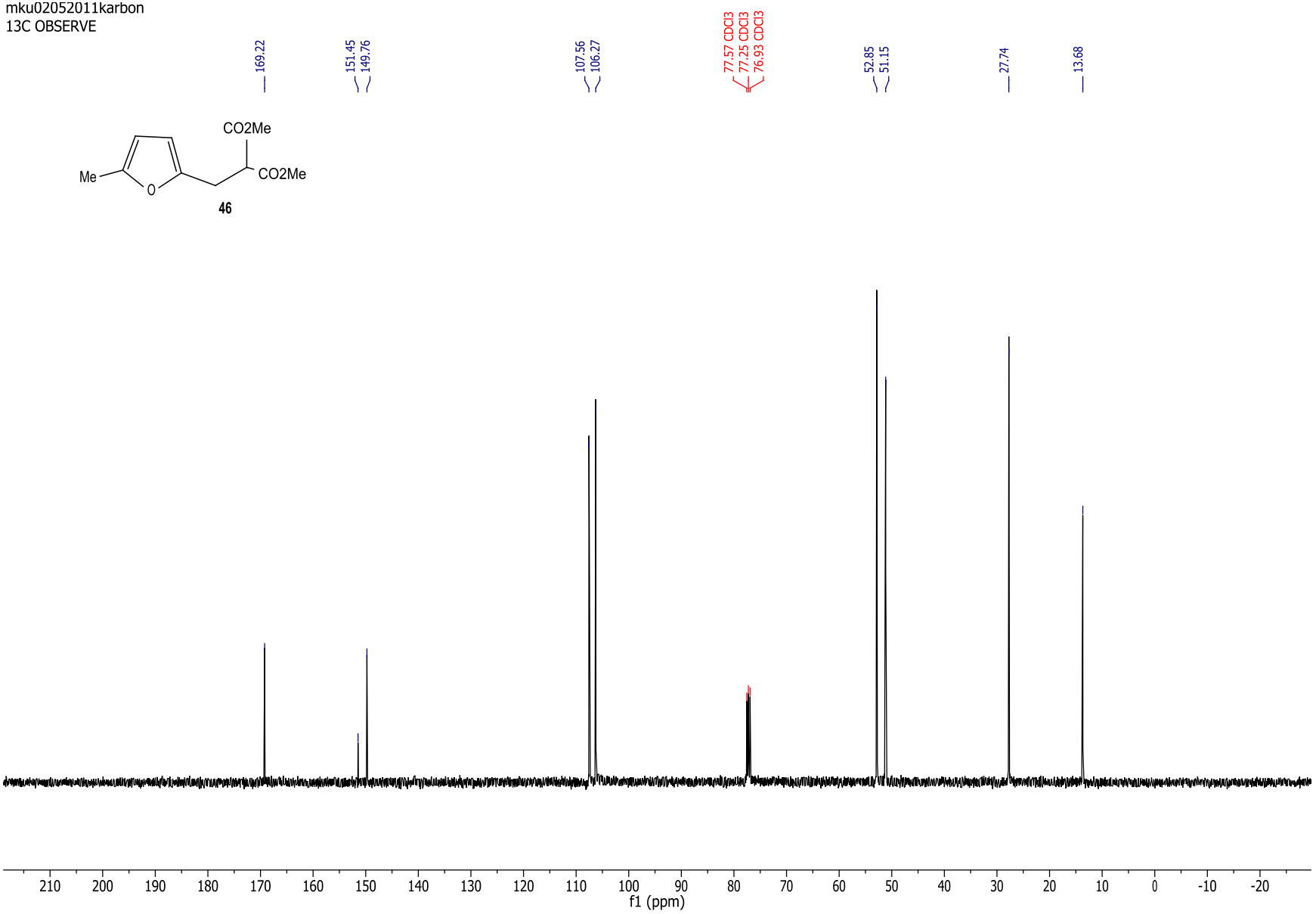


mku02052011proton
STANDARD 1H OBSERVE

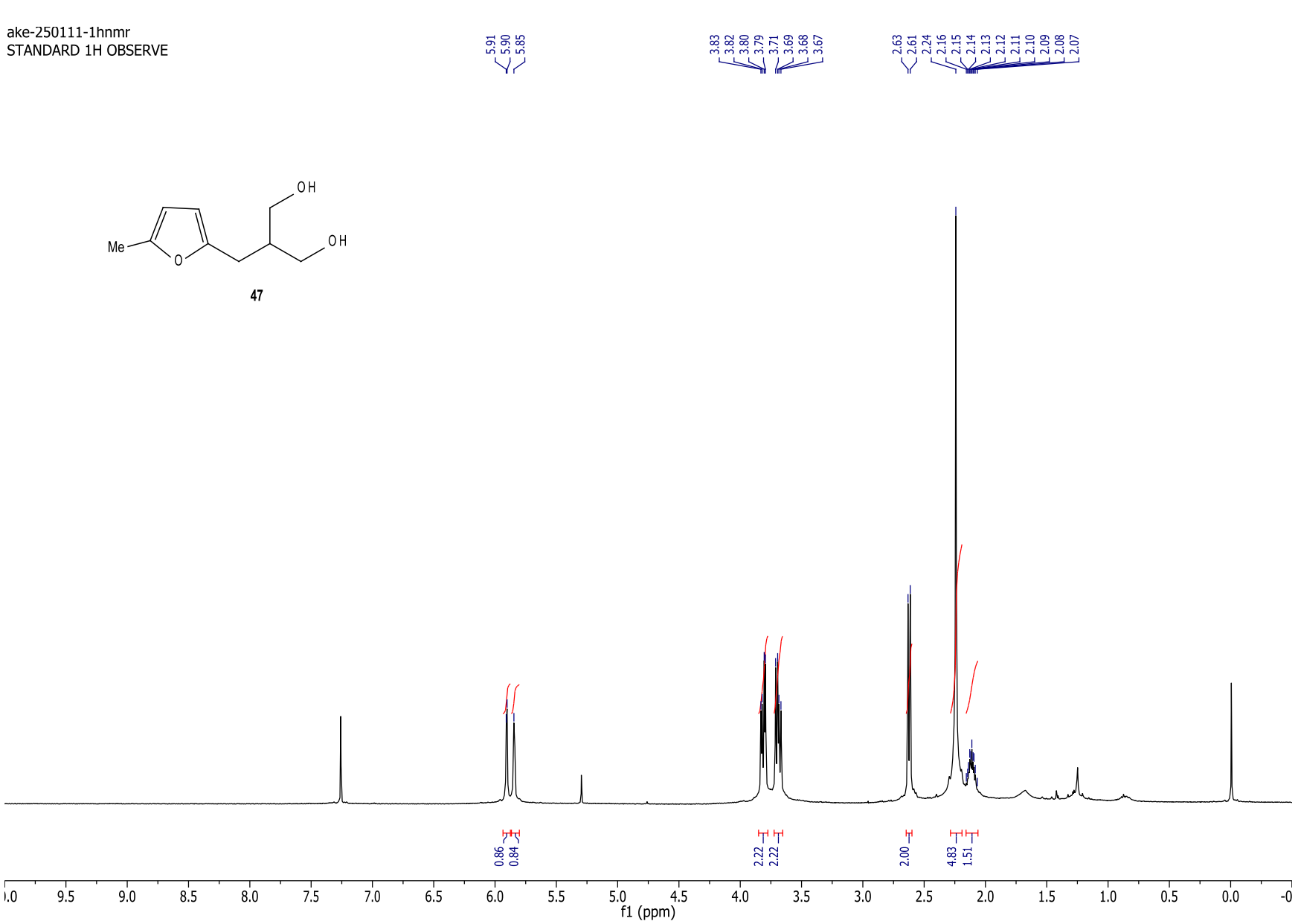


46

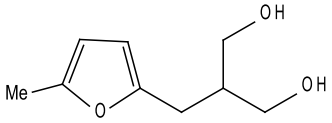
mku02052011karbon
13C OBSERVE



ake-250111-1hnmr
STANDARD 1H OBSERVE



ake-250111-13cnmr
13C OBSERVE



47

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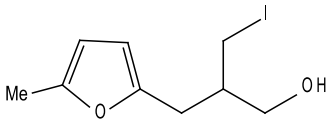
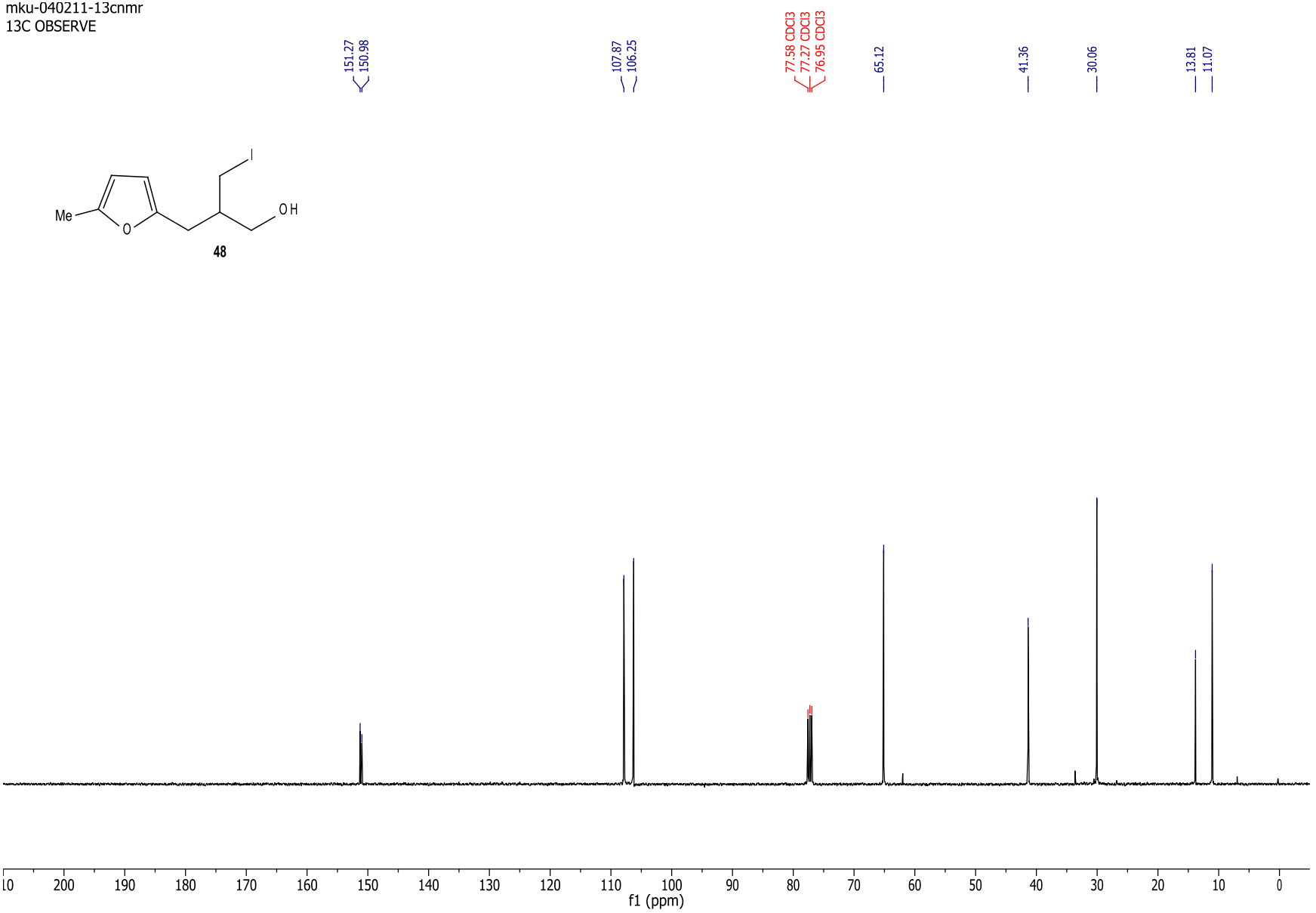
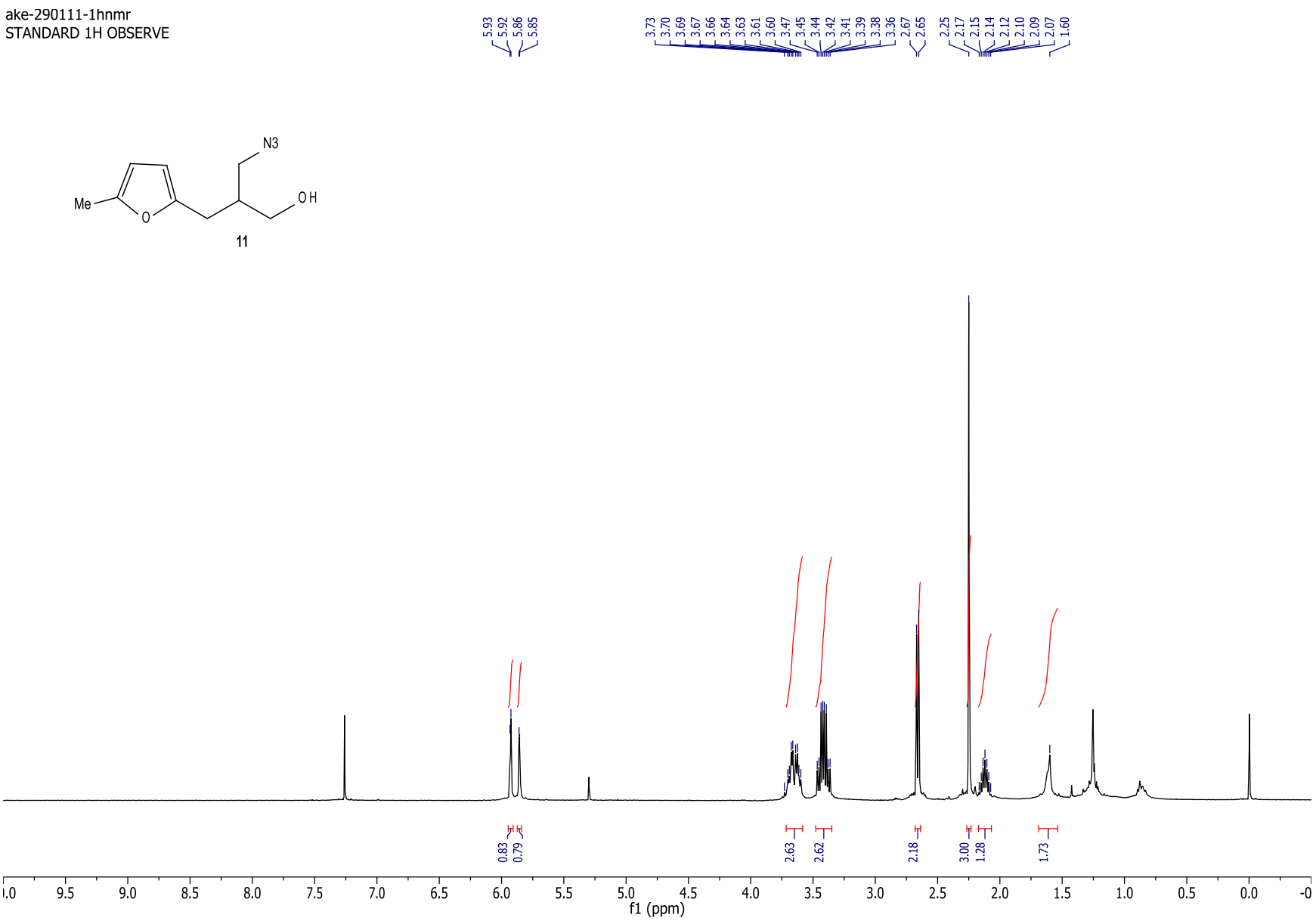


48

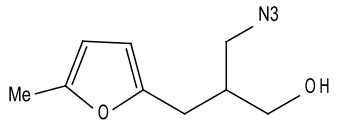
mku-040211-13cnmr
13C OBSERVE



ake-290111-1hnmr
STANDARD 1H OBSERVE

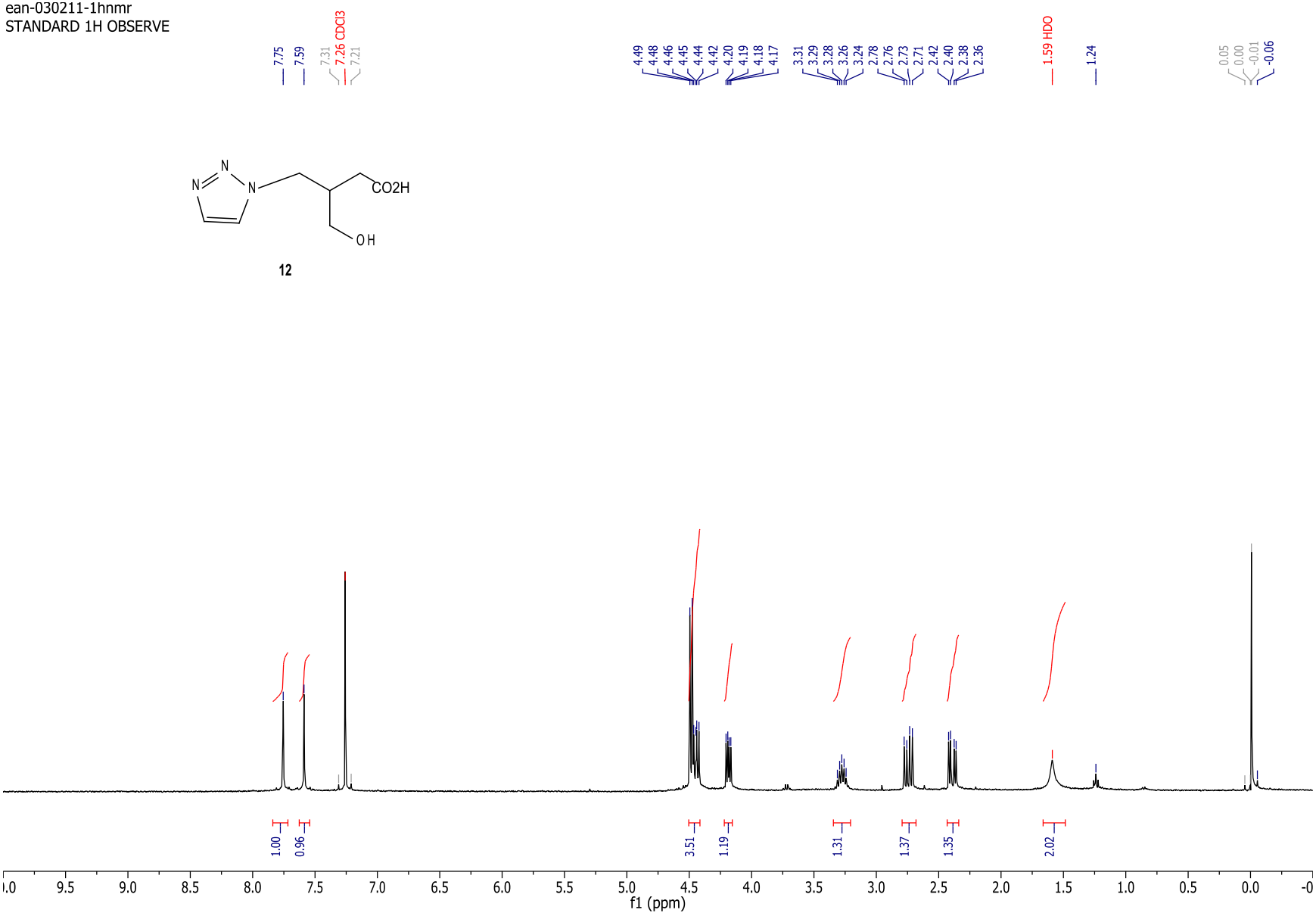


ake-290111-13cnmr
13C OBSERVE



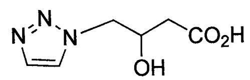
11

ean-030211-1hnmr
STANDARD 1H OBSERVE



12

INDEX	FREQUENCY	PPM	HEIGHT
1	17625.220	175.340	3.5
2	13509.822	134.399	20.6
3	12489.983	124.254	14.3
4	7820.191	77.797	3.4
5	7797.953	77.576	28.6
6	7787.218	77.469	5.0
7	7765.748	77.256	30.7
8	7755.780	77.156	4.8
9	7733.543	76.935	29.8
10	7086.366	70.497	27.0
11	5193.145	51.663	22.9
12	3658.785	36.399	22.9
13	3238.580	32.218	27.3



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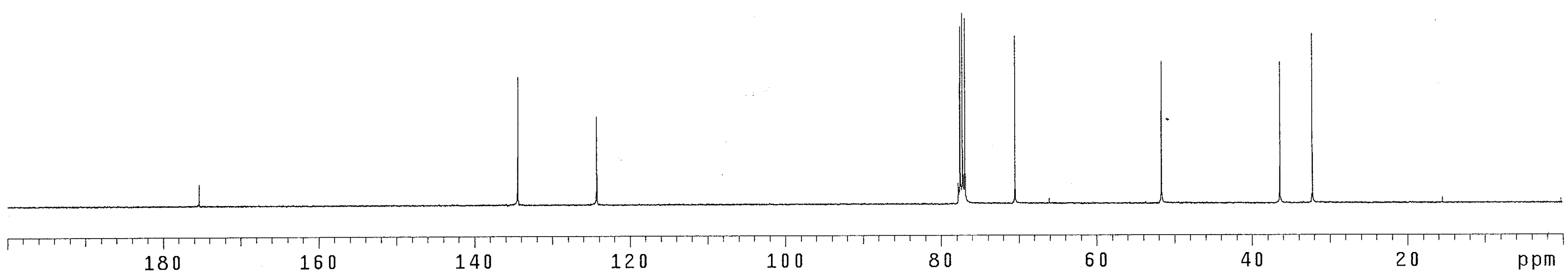

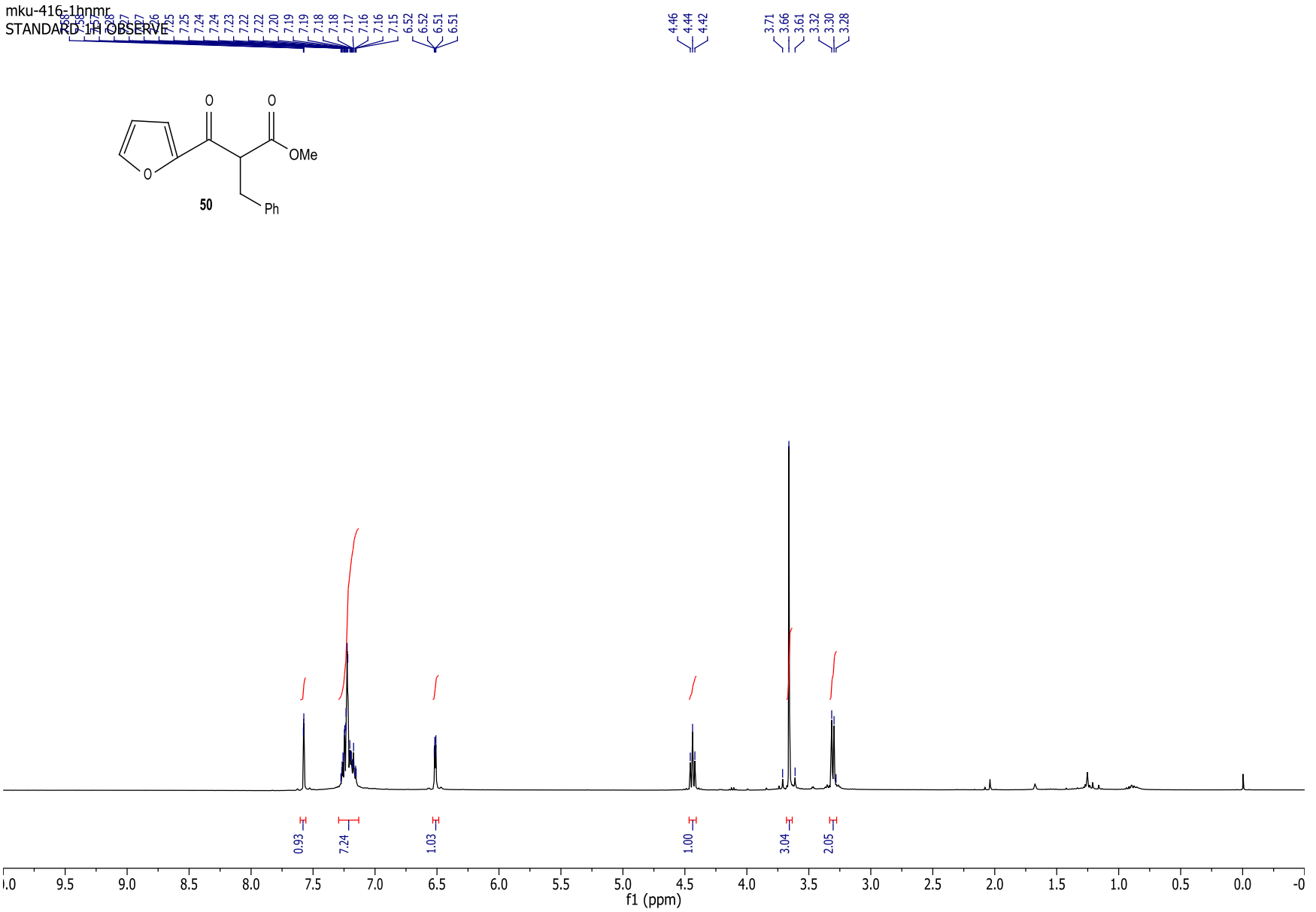
mku-416-1hnmr
STANDARD 1H OBSERVE
7.25
7.24
7.24
7.23
7.22
7.22
7.20
7.19
7.19
7.18
7.18
7.17
7.16
7.16
7.15
6.52
6.52
6.51
6.51
4.46
4.44
4.42
3.71
3.66
3.61
3.32
3.30
3.28
O
O
OMe
O
Ph
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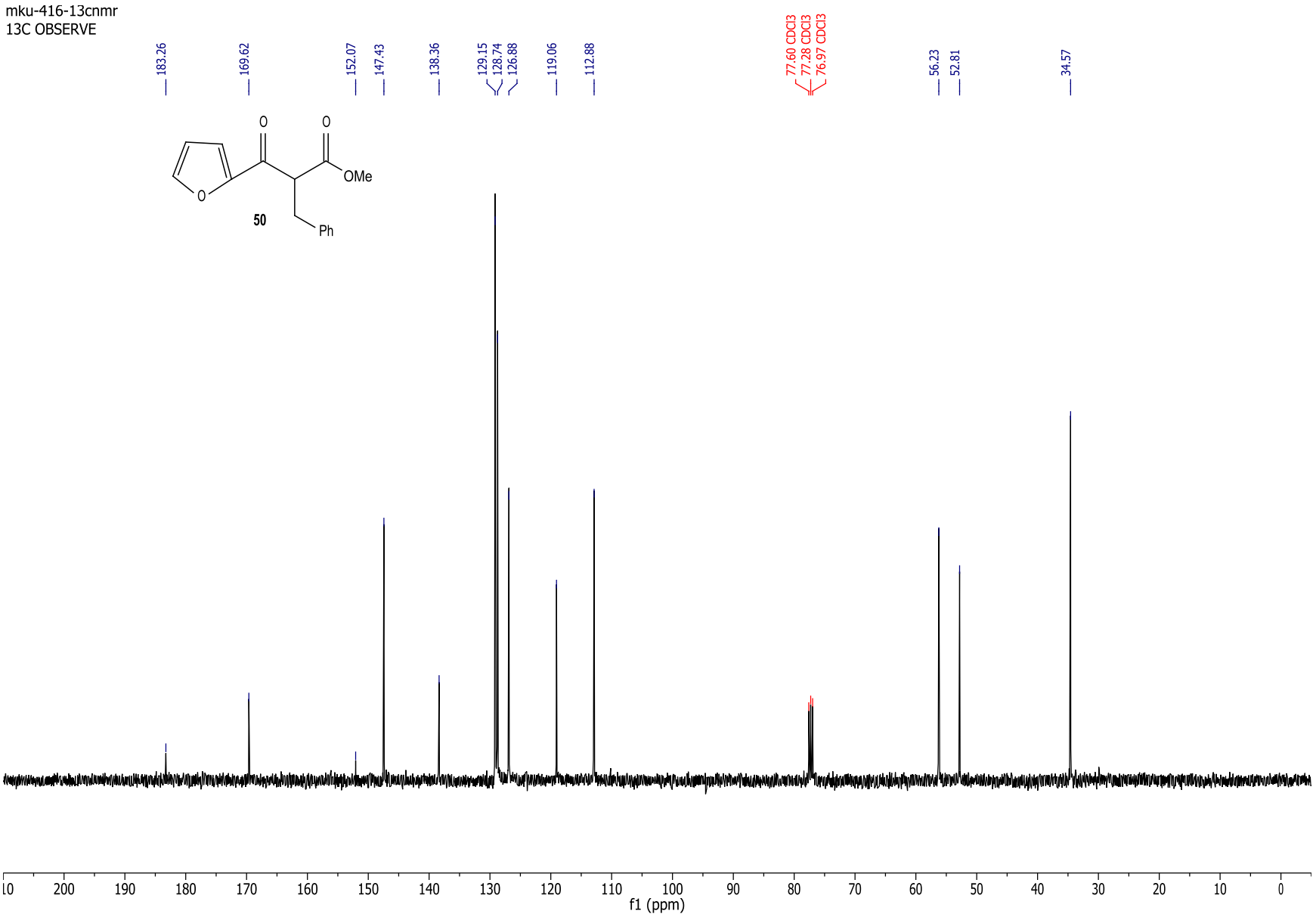
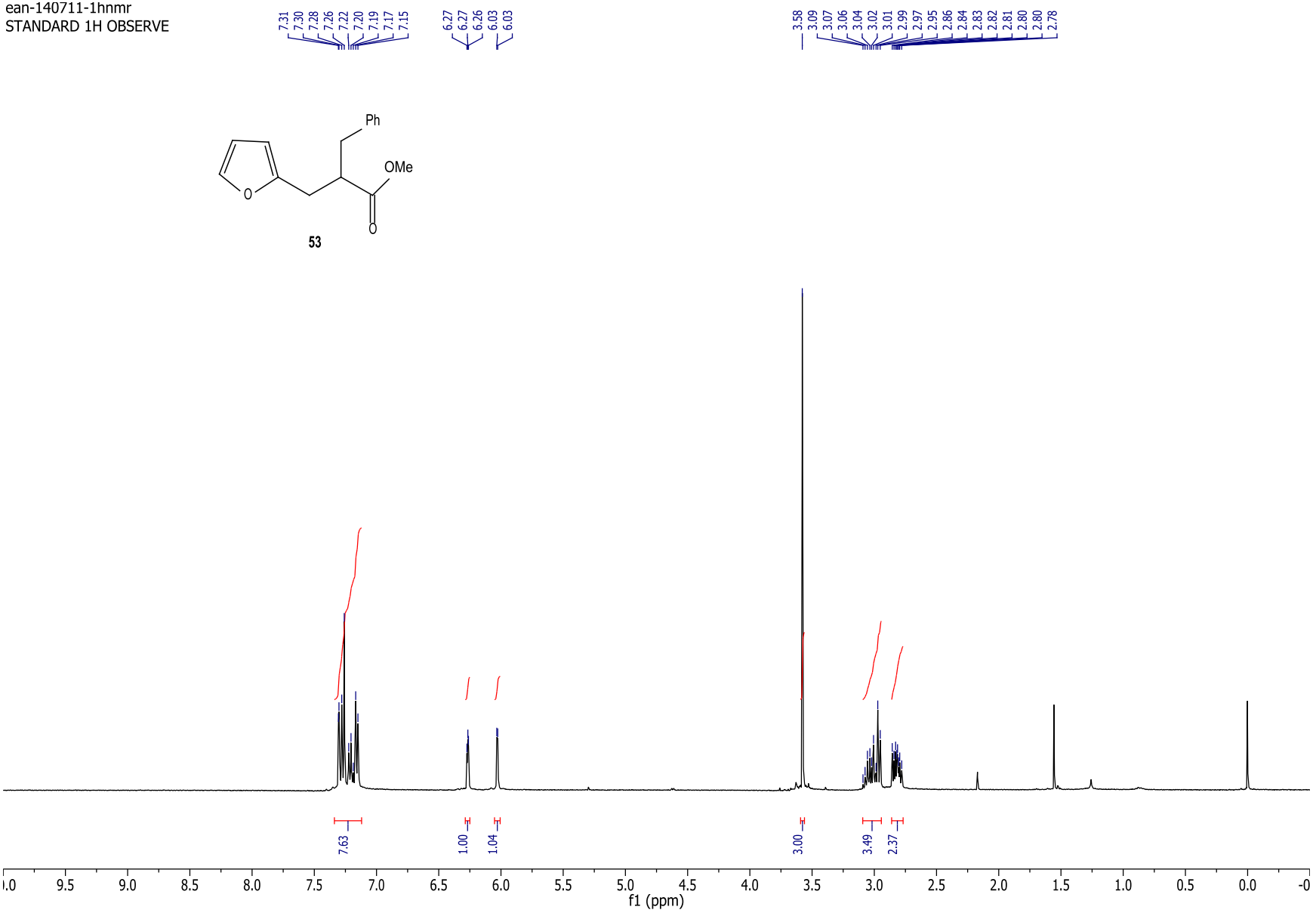
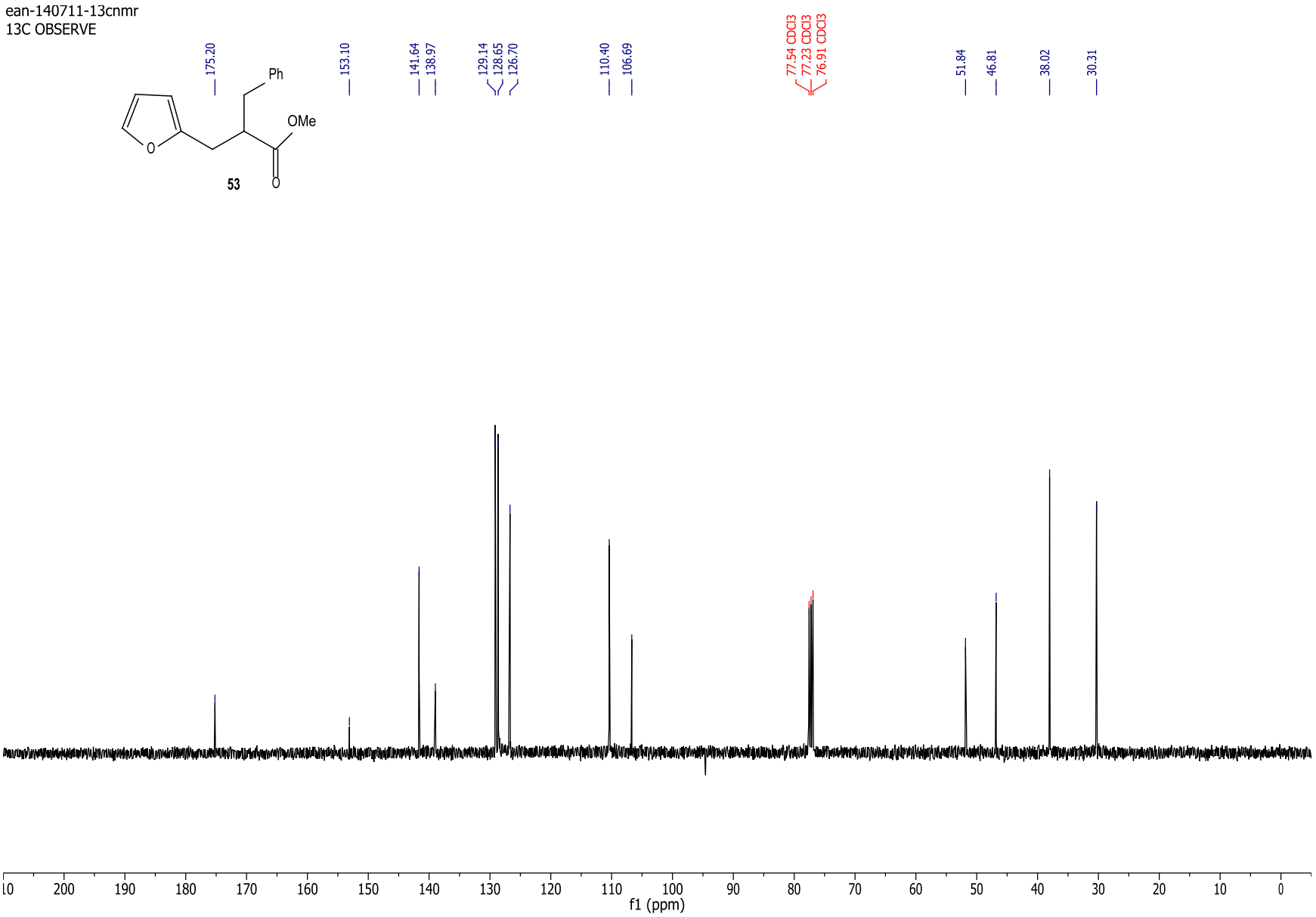
7.24
1.03
1.00
3.04
2.05
f1 (ppm)

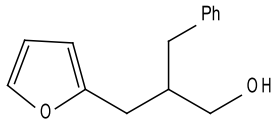

mku-416-13cnmr
13C OBSERVE
183.26
169.62
152.07
147.43
138.36
129.15
128.74
126.88
119.06
112.88
77.60 CDCl3
77.28 CDCl3
76.97 CDCl3
56.23
52.81
34.57
O
O
O
OMe
Ph
50
f1 (ppm)

ean-140711-1hnmr
STANDARD 1H OBSERVE




ean-140711-13cnmr
13C OBSERVE
175.20
153.10
141.64
138.97
129.14
128.65
126.70
110.40
106.69
77.54 CDCl3
77.23 CDCl3
76.91 CDCl3
51.84
46.81
38.02
30.31
Ph
OMe
O
O
53
f1 (ppm)

Mustafa
Lialh4



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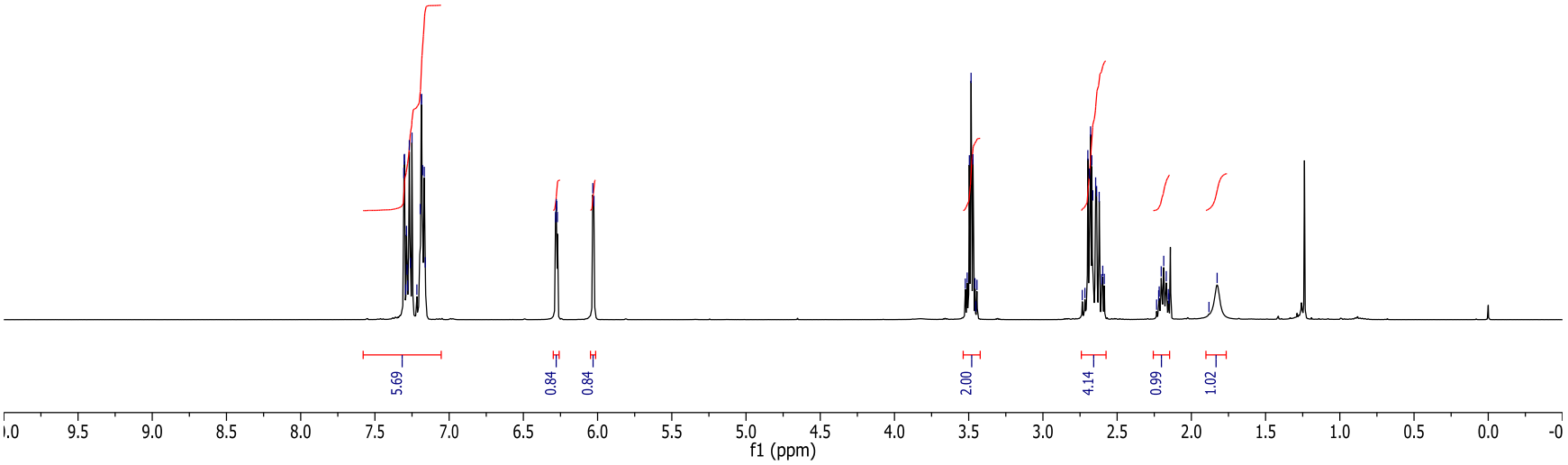
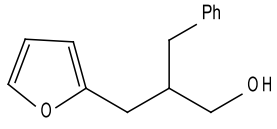
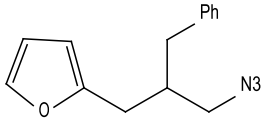


Mustafa
Lialh4



54

Mustafa
N3



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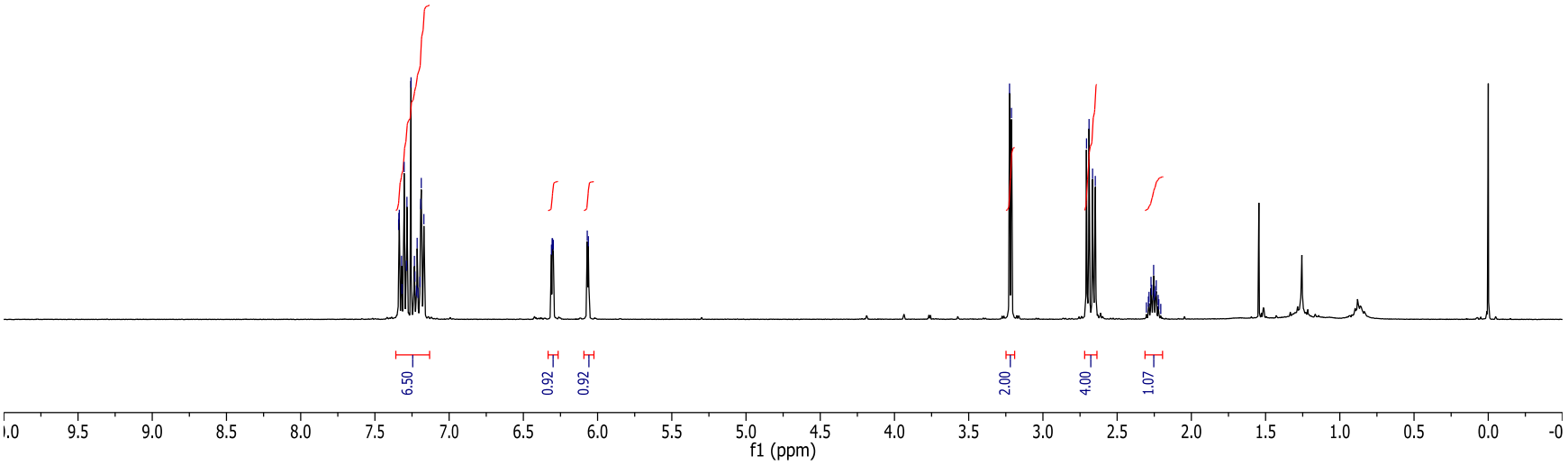
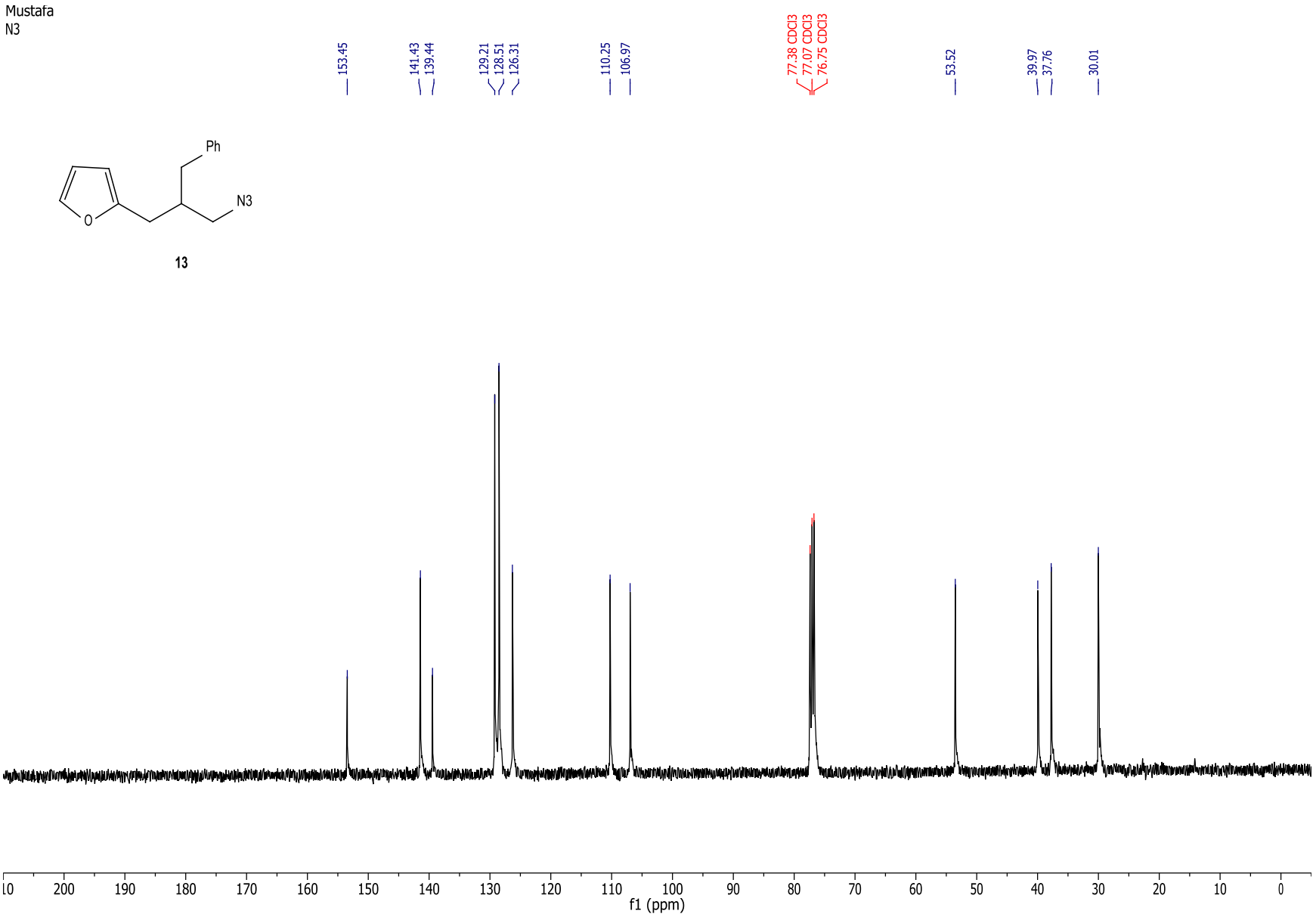
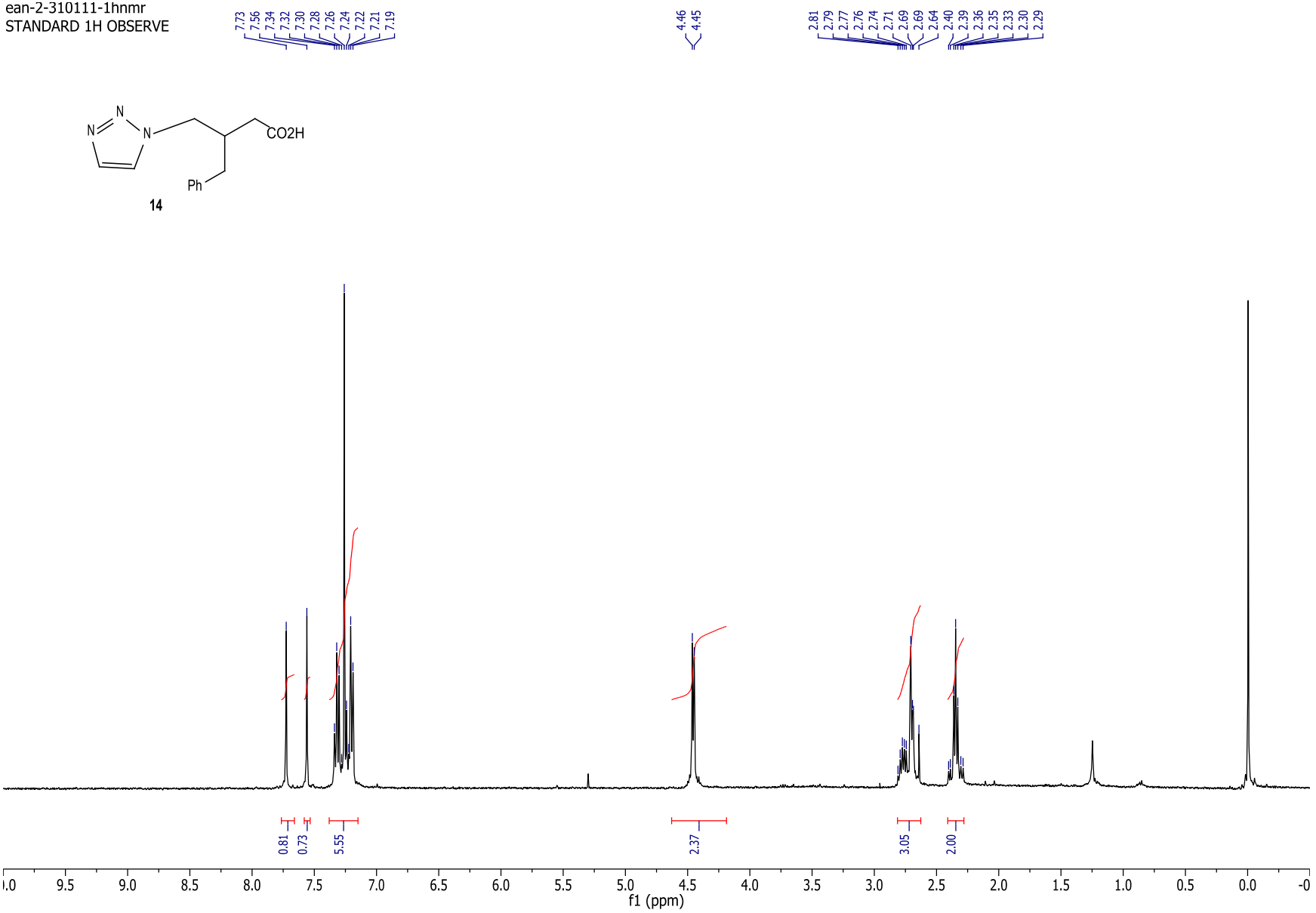


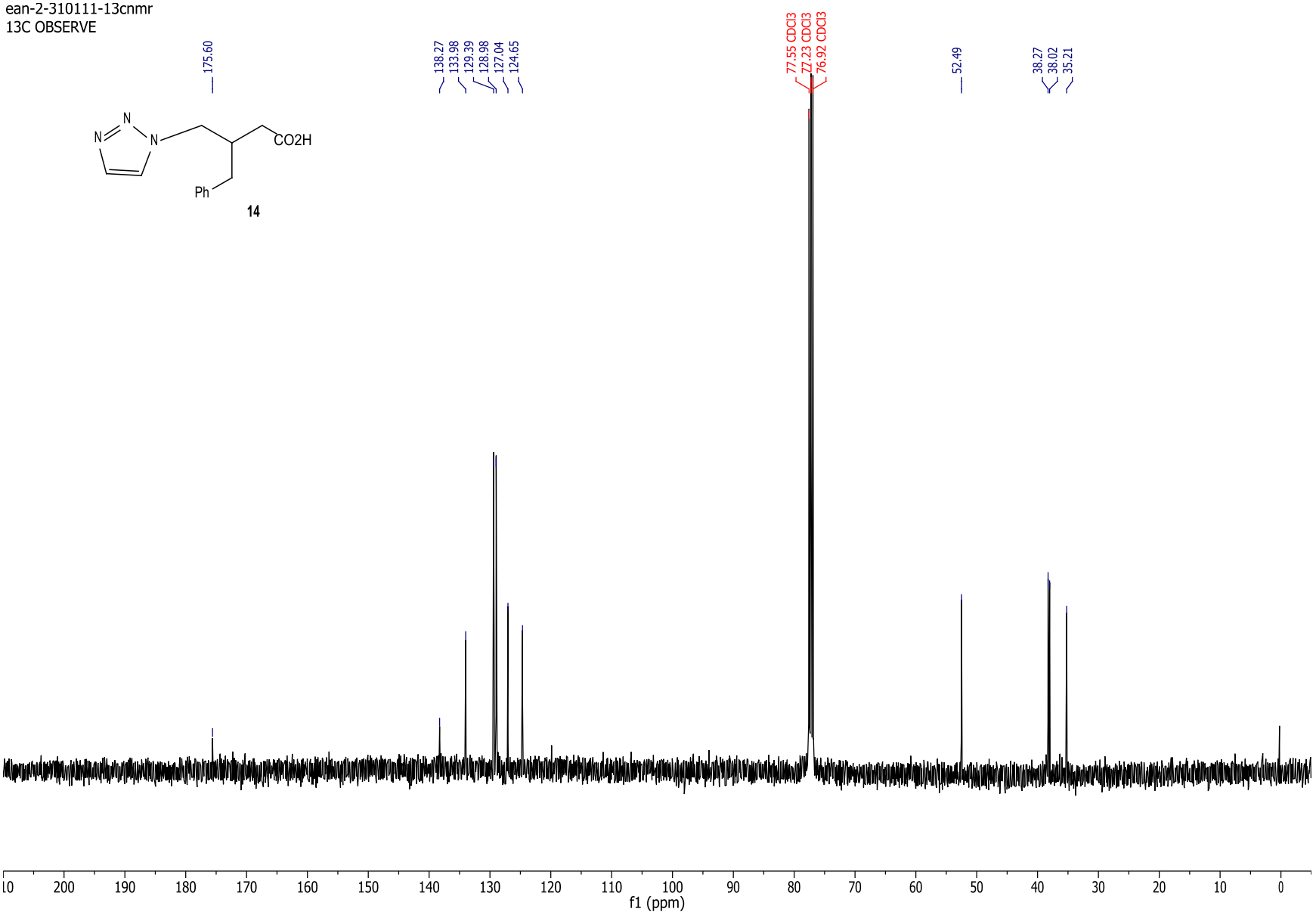
Mustafa
N3



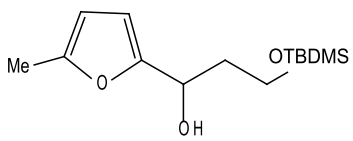
13

ean-2-310111-1hnmr
STANDARD 1H OBSERVE

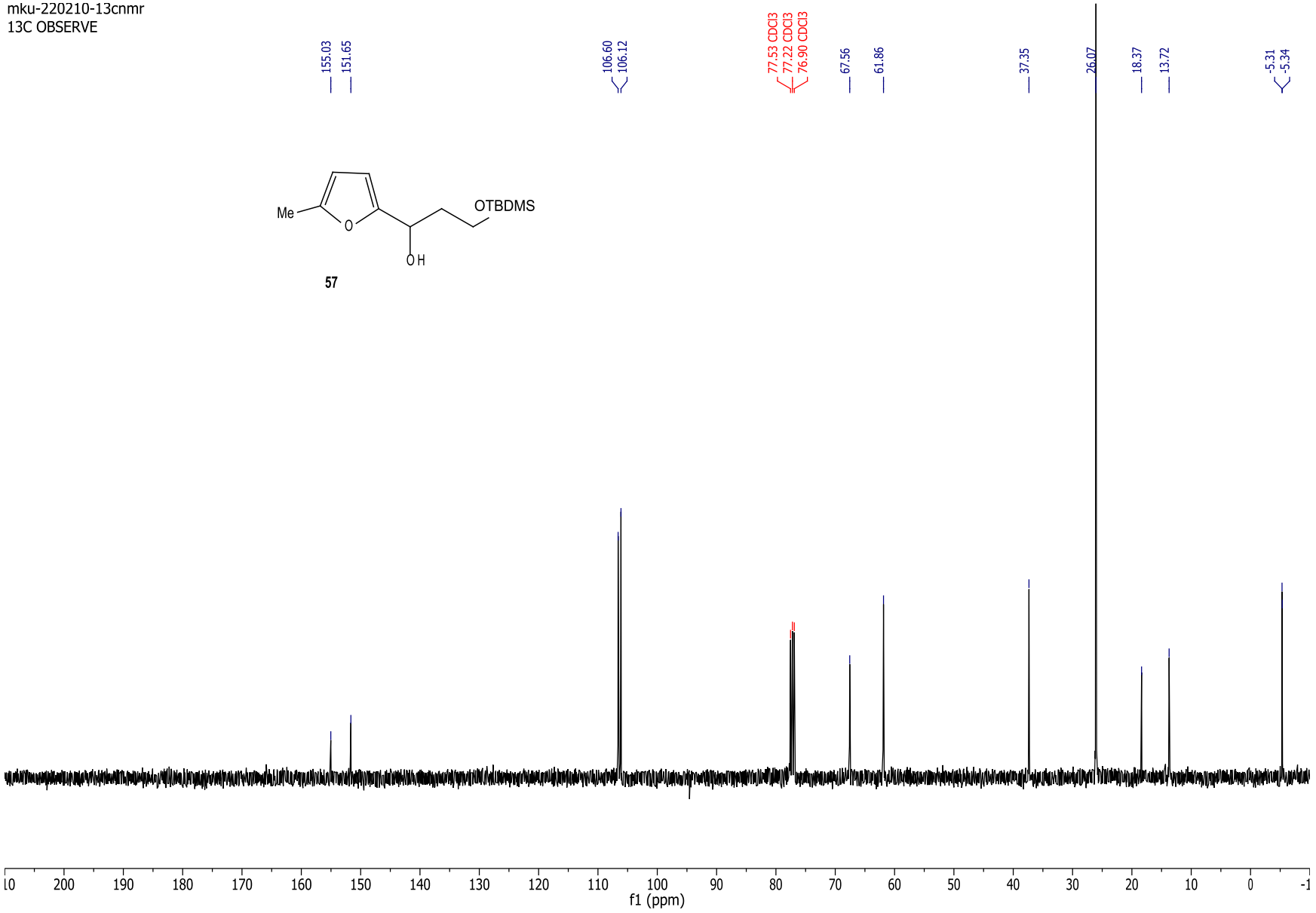



ean-2-310111-13cnmr
13C OBSERVE
175.60
138.27
133.98
129.39
128.98
127.04
124.65
77.55 CDCl3
77.23 CDCl3
76.92 CDCl3
52.49
38.27
38.02
35.21
CO2H
Ph
14
f1 (ppm)

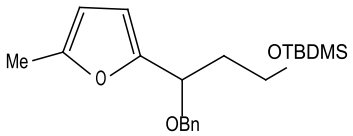
mku-220210-1hnmr
STANDARD 1H OBSERVE



57

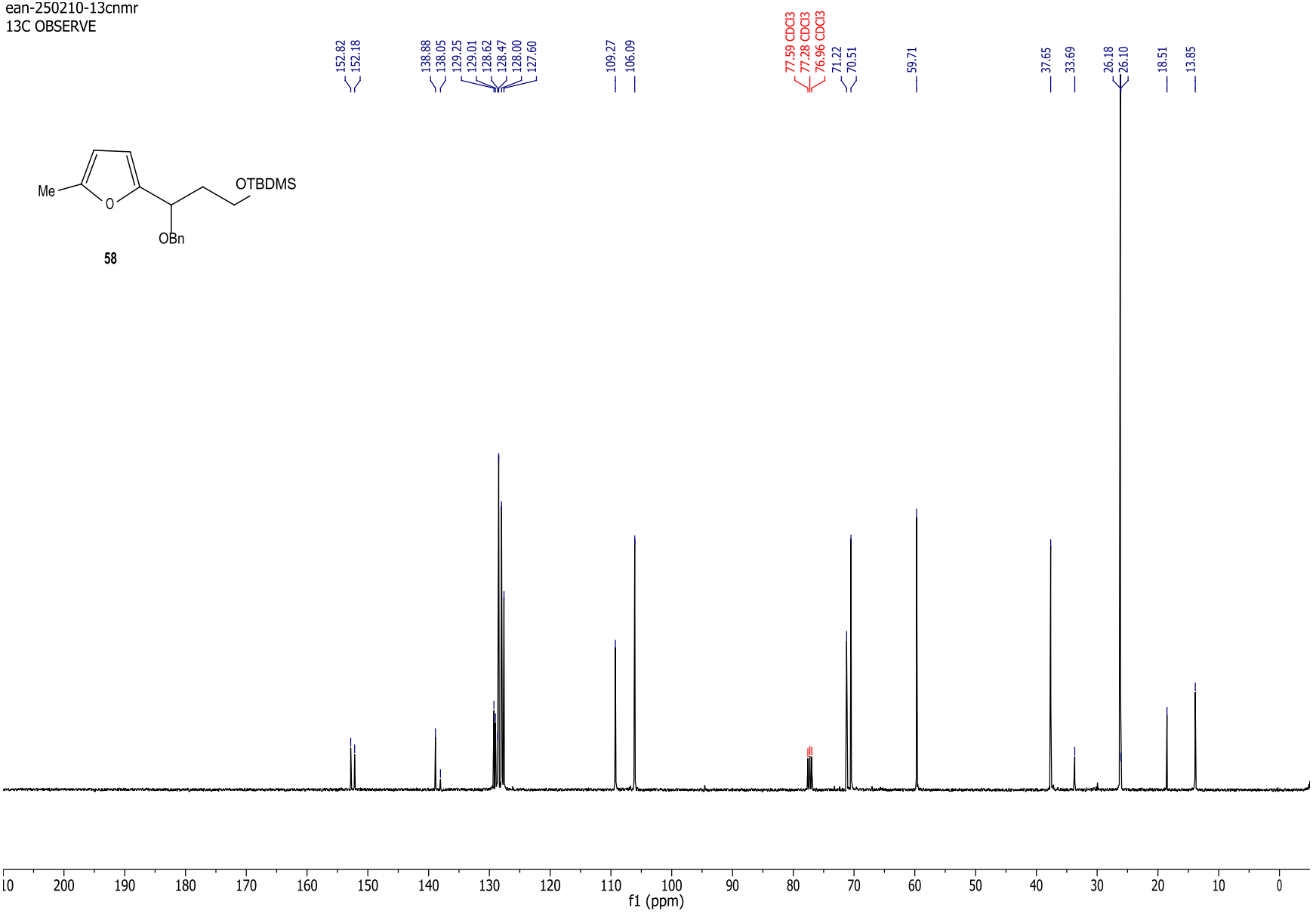

mku-220210-13cnmr
13C OBSERVE
155.03
151.65
106.60
106.12
77.53 CDCl3
77.22 CDCl3
76.90 CDCl3
67.56
61.86
37.35
26.07
18.37
13.72
-5.31
-5.34
Me
O
OH
OTBDMS
57
f1 (ppm)

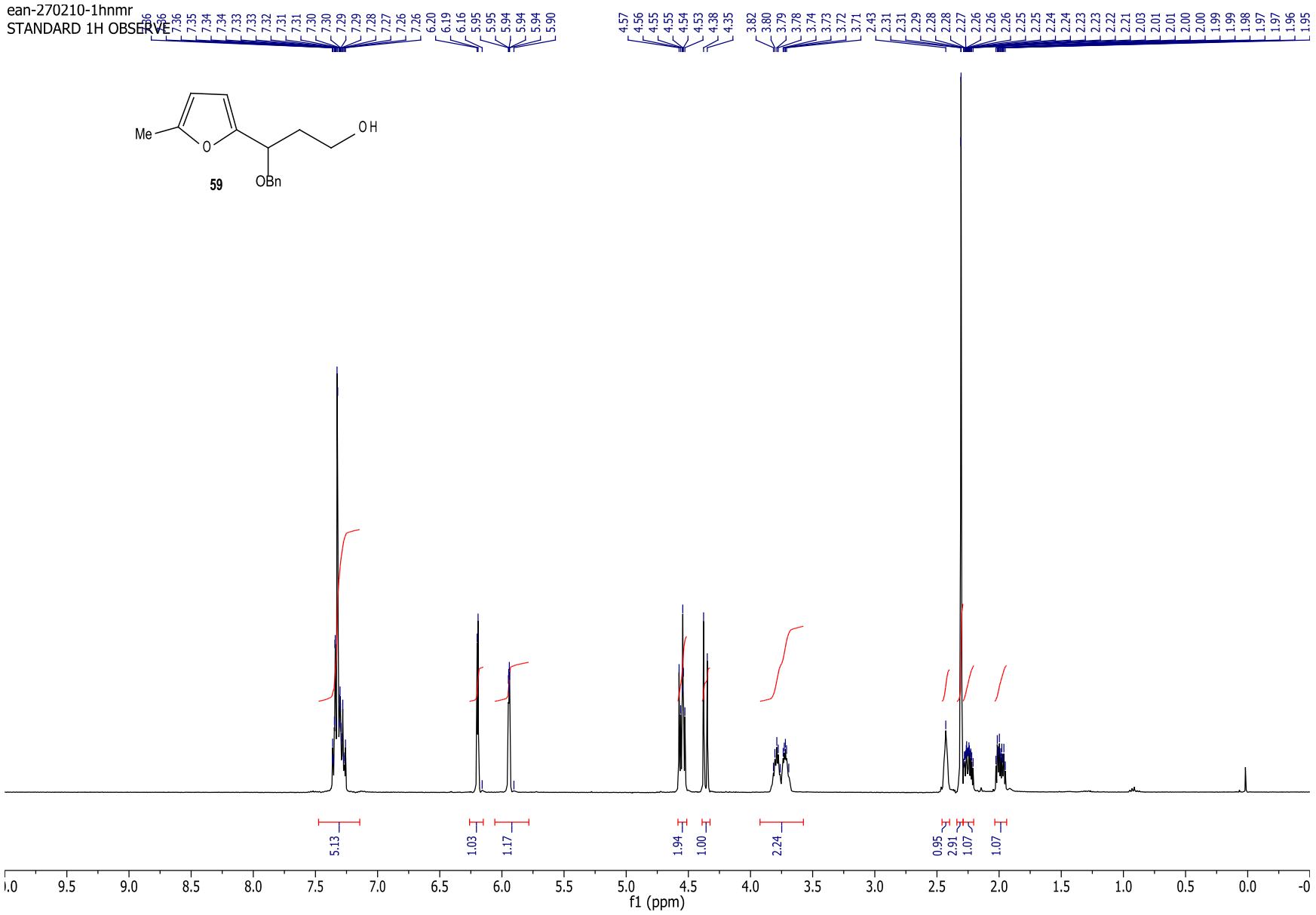
ean-250210-1hnmr
STANDARD 1H OBSERVE

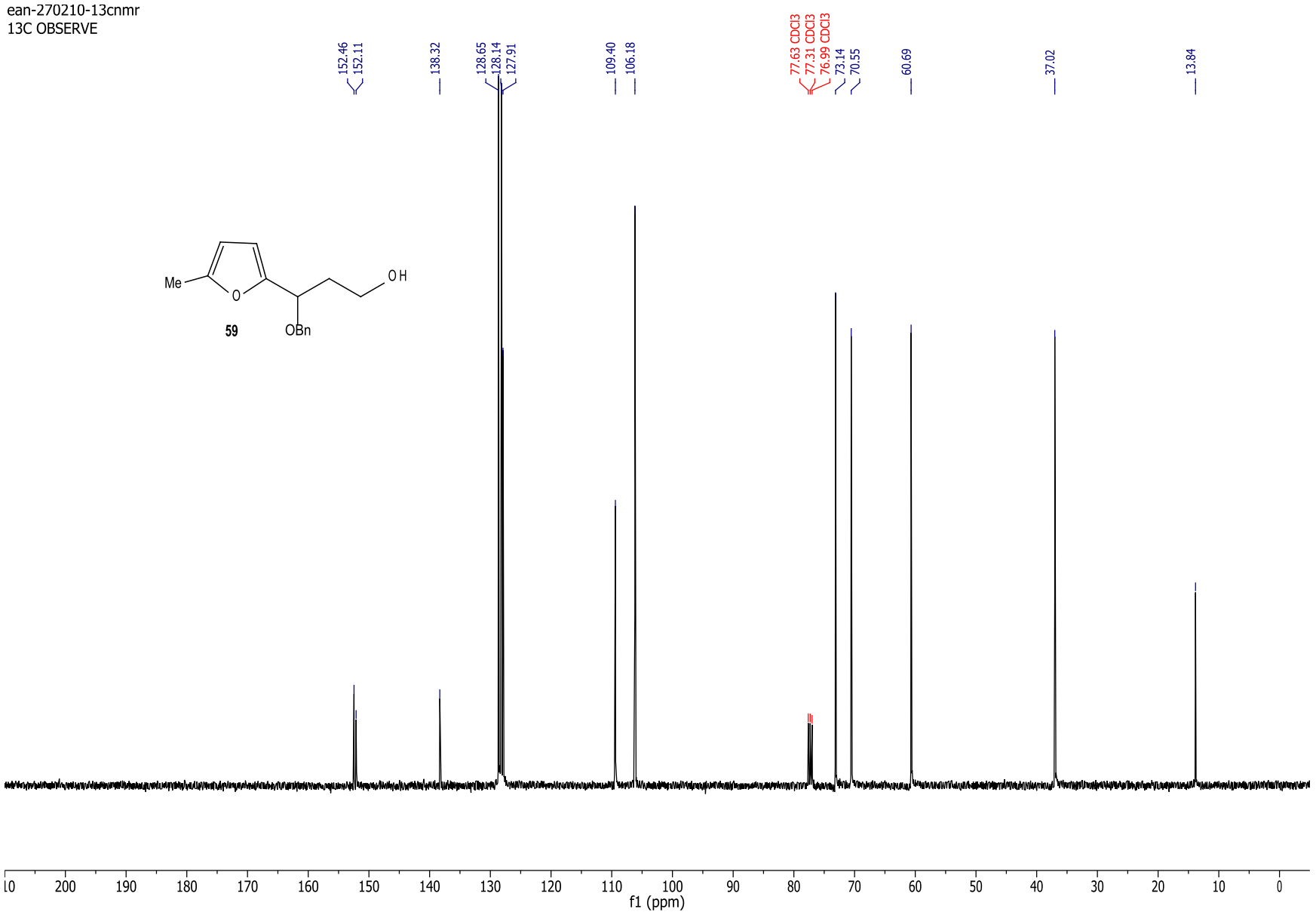


58

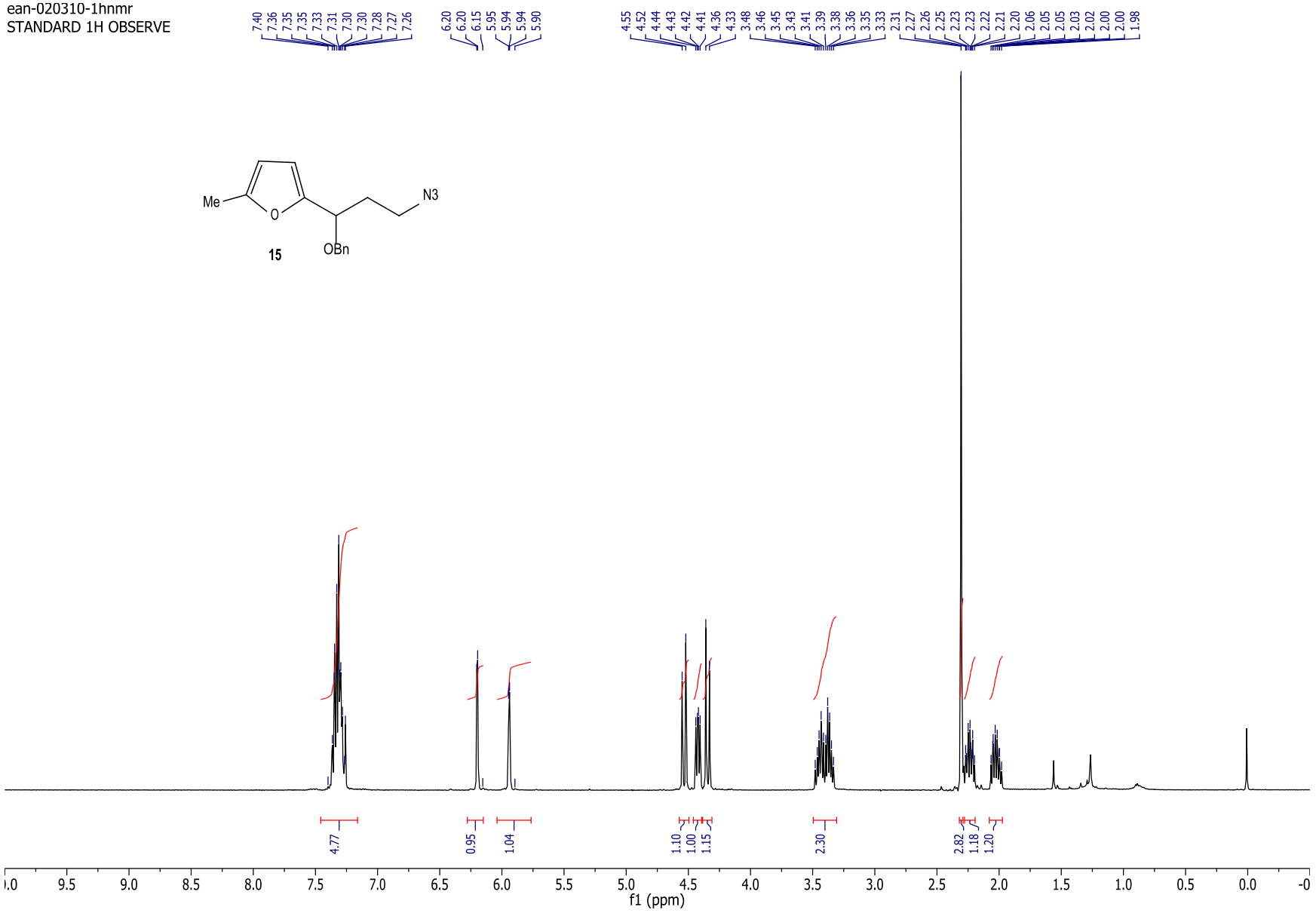
ean-250210-13cnmr
13C OBSERVE



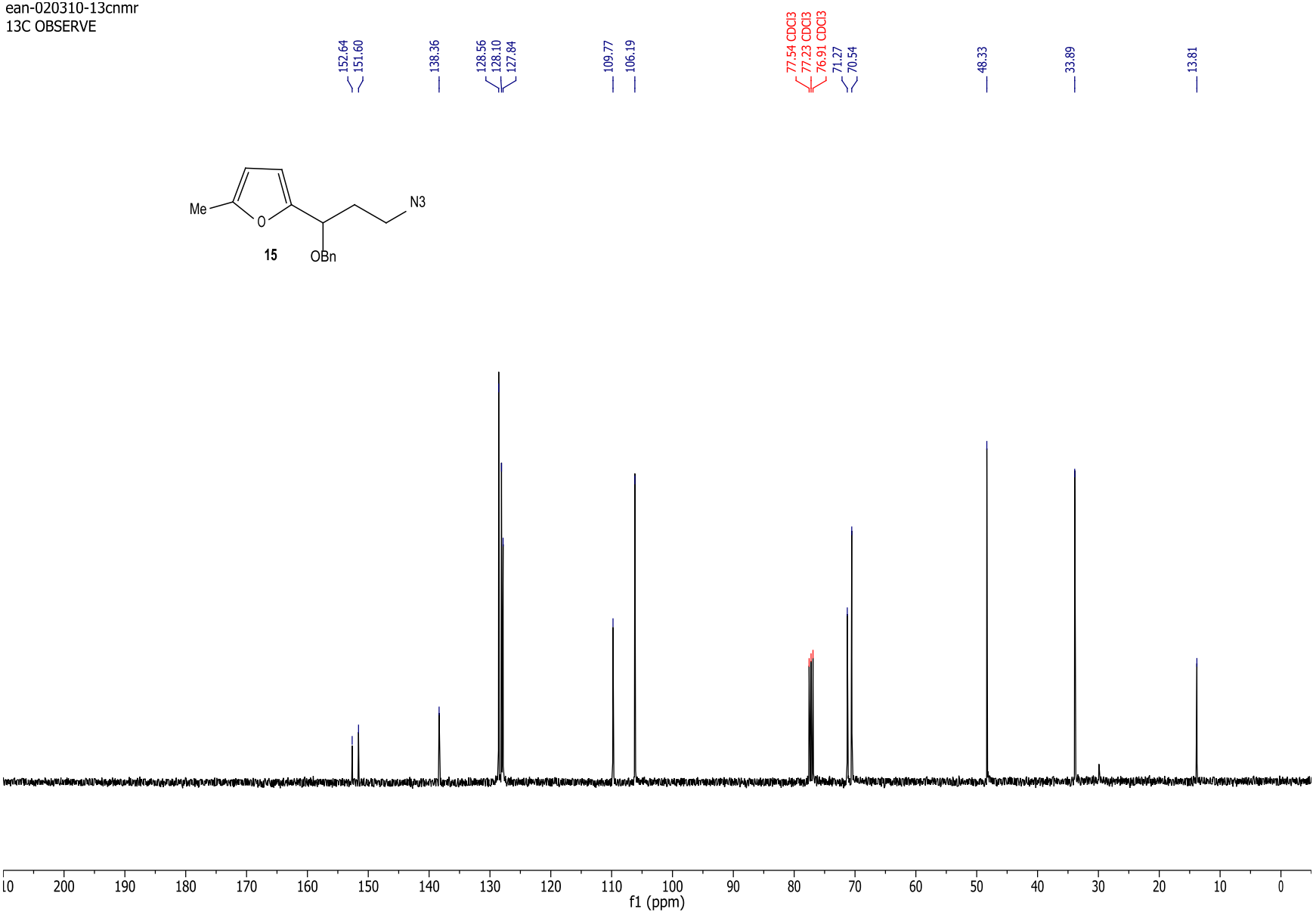

ean-270210-1hnmr
STANDARD 1H OBSERVE
Me
O
OH
OBn
59
5.13
1.03
1.17
1.94
1.00
2.24
0.95
2.91
1.07
1.07
f1 (ppm)

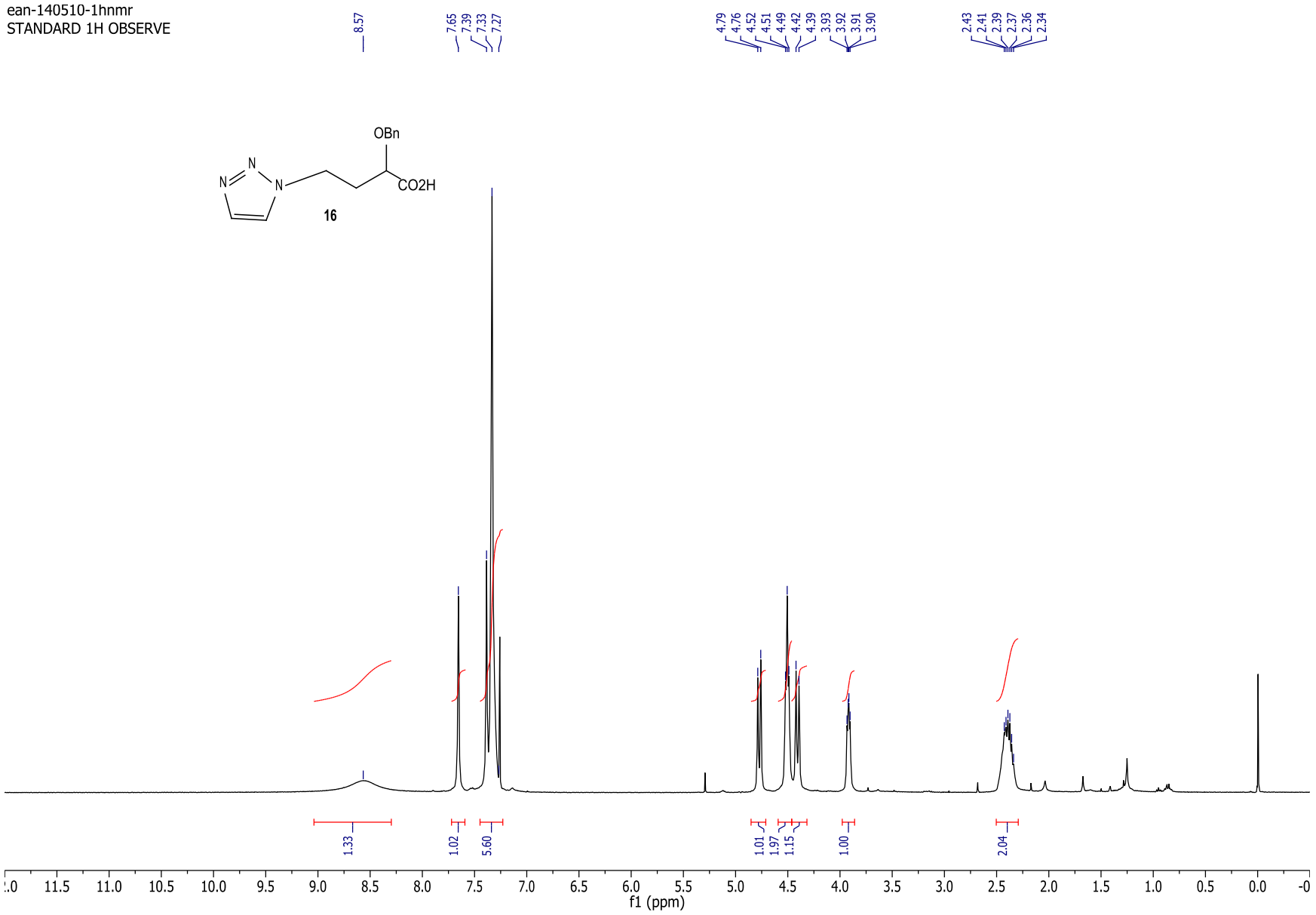

ean-270210-13cnmr
13C OBSERVE
152.46
152.11
138.32
128.65
128.14
127.91
109.40
106.18
77.63 CDCl3
77.31 CDCl3
76.99 CDCl3
73.14
70.55
60.69
37.02
13.84
Me
O
OH
OBn
59
f1 (ppm)

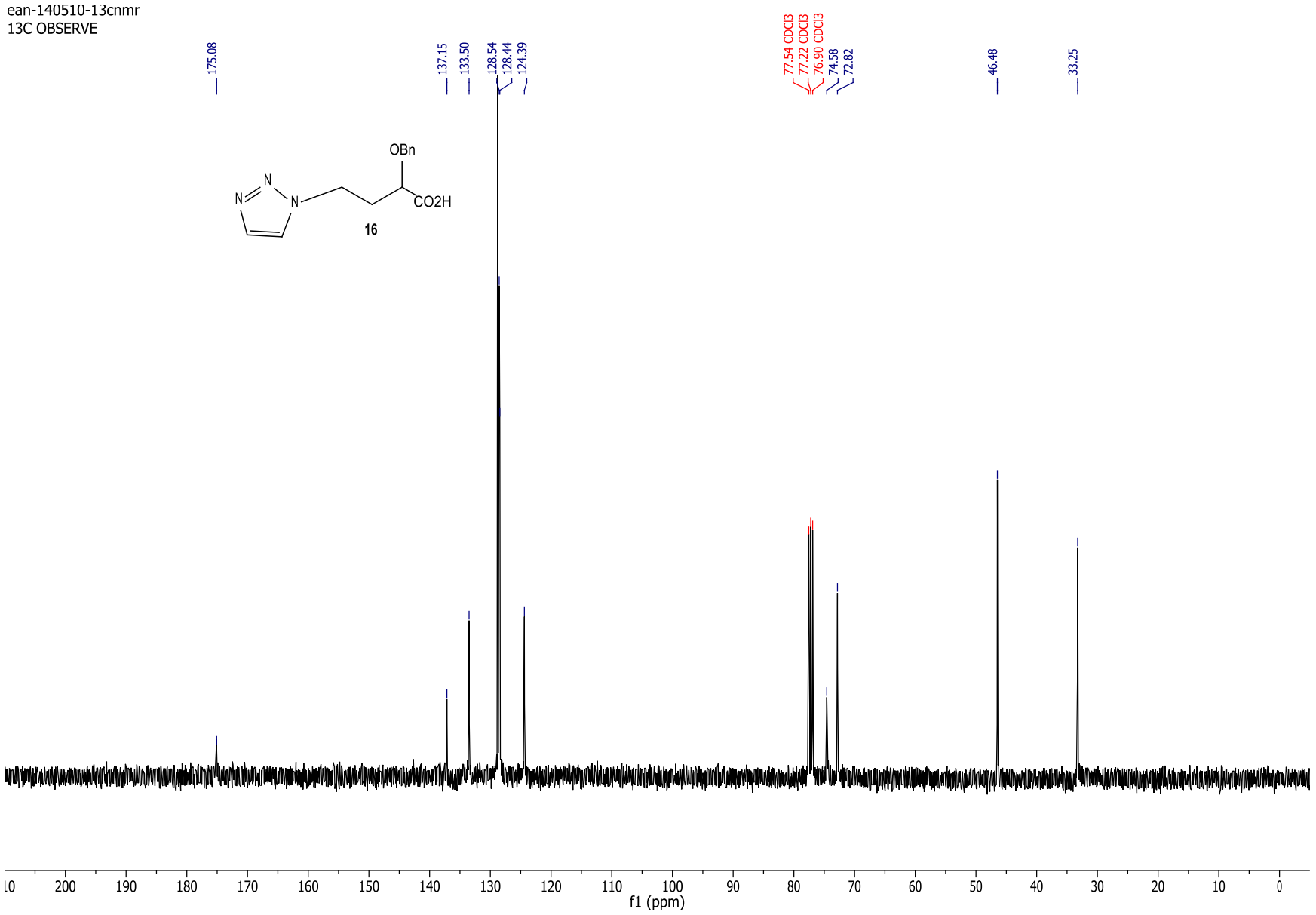
ean-020310-1hnmr
STANDARD 1H OBSERVE



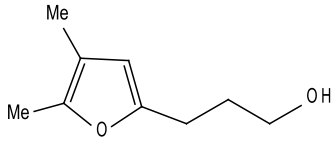
ean-020310-13cnmr
13C OBSERVE




ean-140510-1hnmr
STANDARD 1H OBSERVE
8.57
7.65
7.39
7.33
7.27
4.79
4.76
4.52
4.51
4.49
4.42
4.39
3.93
3.92
3.91
3.90
2.43
2.41
2.39
2.37
2.36
2.34
OBn
CO2H
16
1.33
1.02
5.60
1.01
1.97
1.15
1.00
2.04
f1 (ppm)

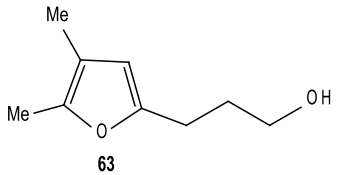

ean-140510-13cnmr
13C OBSERVE
175.08
137.15
133.50
128.54
128.44
124.39
77.54 CDCl3
77.22 CDCl3
76.90 CDCl3
74.58
72.82
46.48
33.25
OBn
CO2H
16
f1 (ppm)

Mustafa
mku-426-3



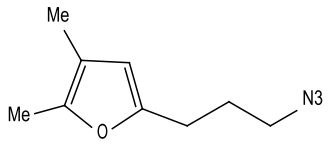
63

Mustafa
mku-426-3



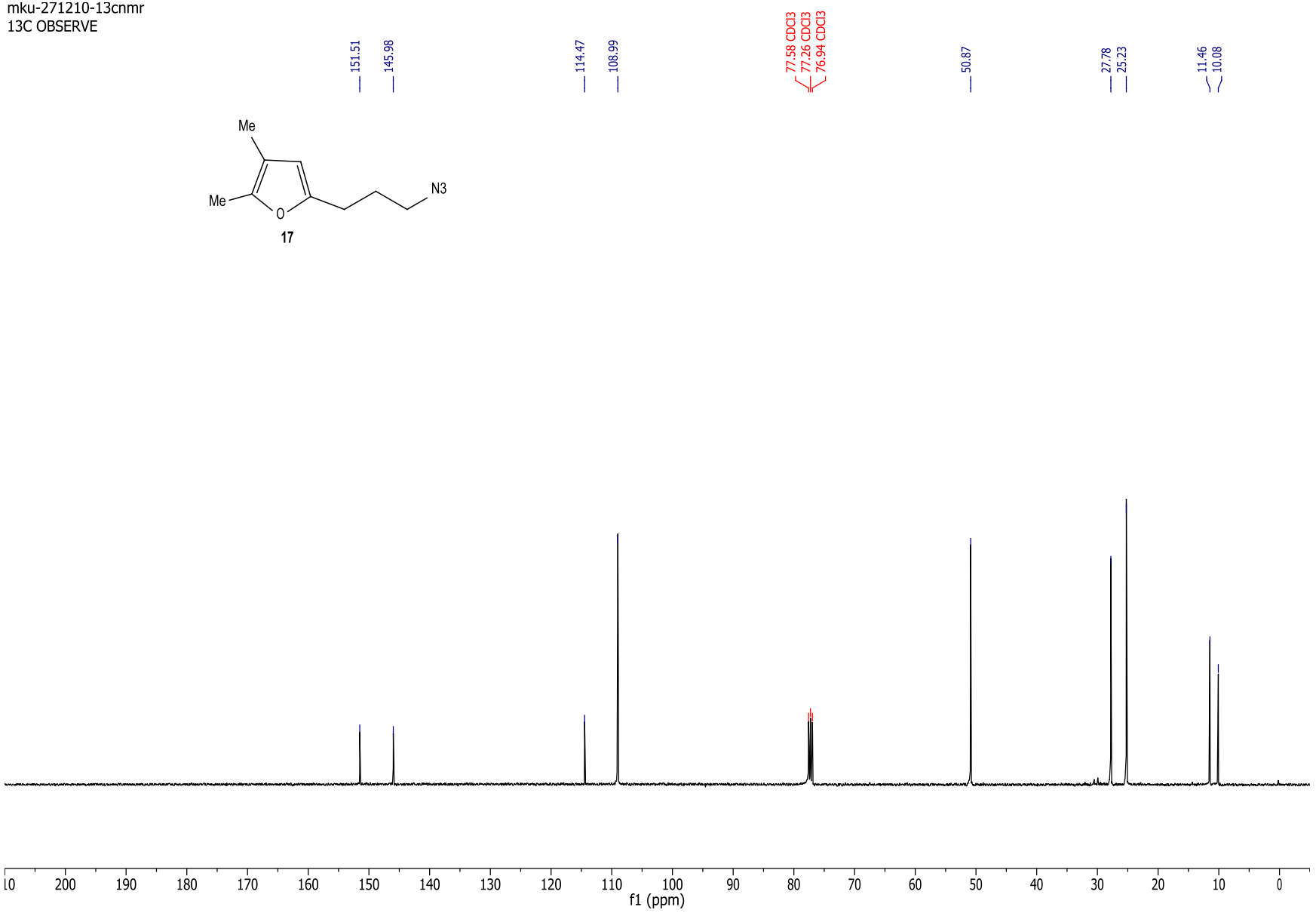
63

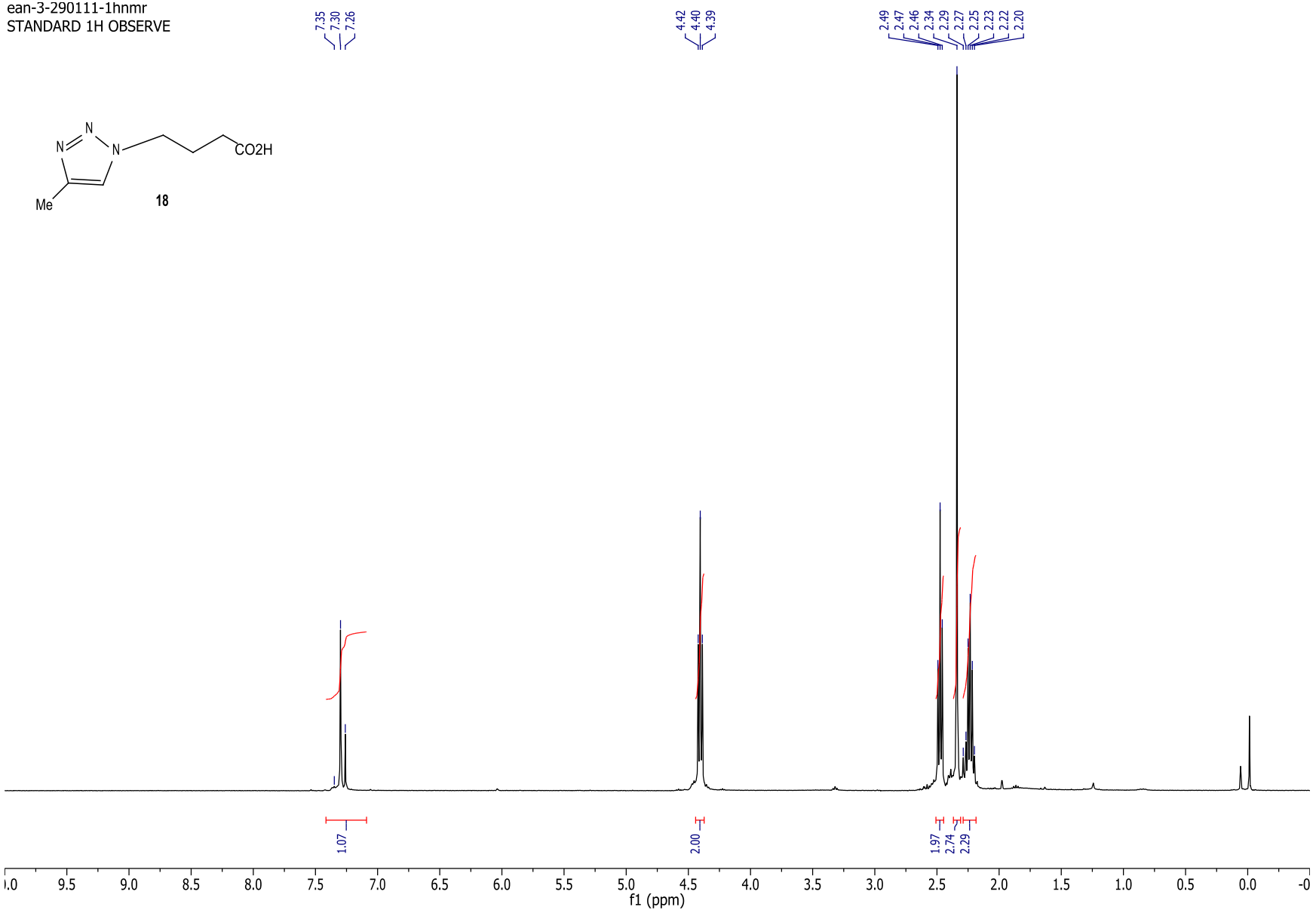
mku-271210-1hnmr
STANDARD 1H OBSERVE

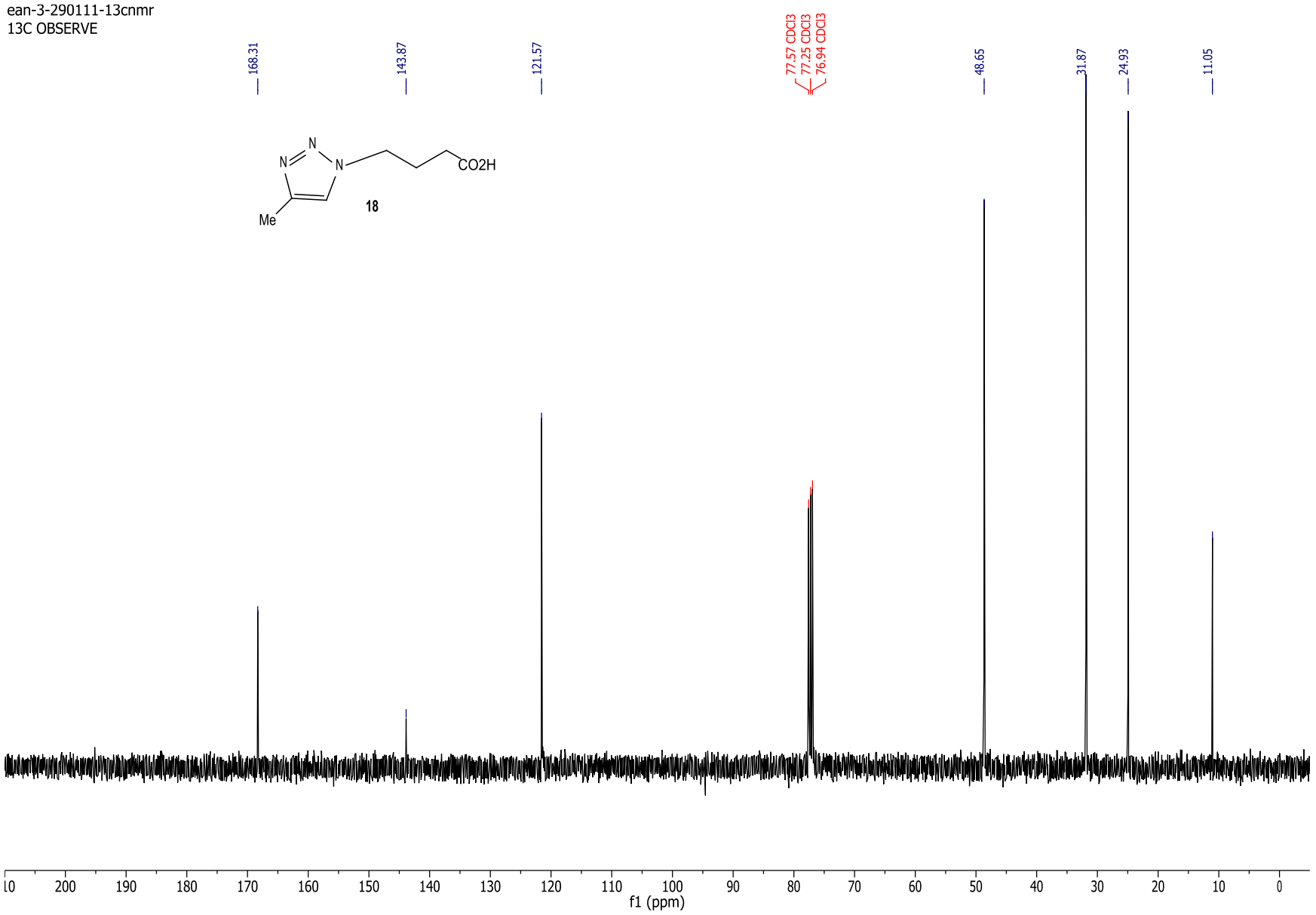


17

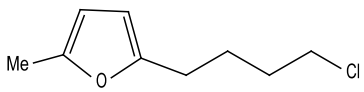
mku-271210-13cnmr
13C OBSERVE




ean-3-290111-1hnmr
STANDARD 1H OBSERVE
7.35
7.30
7.26
4.42
4.40
4.39
2.49
2.47
2.46
2.34
2.29
2.27
2.25
2.23
2.22
2.20
N
N
N
CO2H
Me
18
1.07
2.00
1.97
2.74
2.29
f1 (ppm)

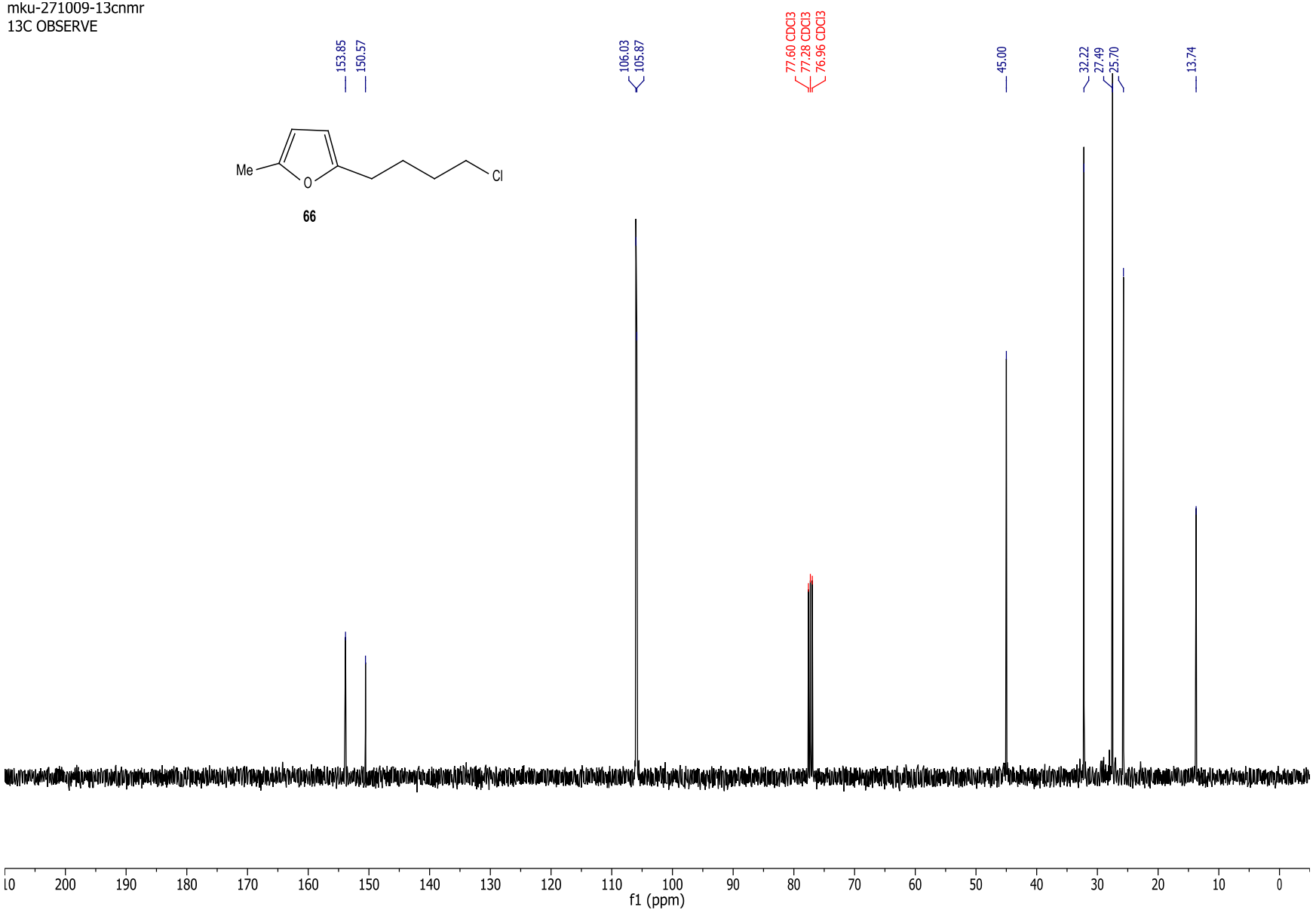

ean-3-290111-13cnmr
13C OBSERVE
168.31
143.87
121.57
77.57 CDCl3
77.25 CDCl3
76.94 CDCl3
48.65
31.87
24.93
11.05
N
N
N
CO2H
Me
18
f1 (ppm)

mku-271009-1hnmr
STANDARD 1H OBSERVE

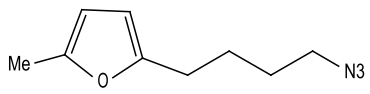


66

mku-271009-13cnmr
13C OBSERVE

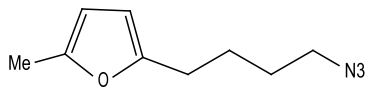


ras-271009-1hnmr
STANDARD 1H OBSERVE



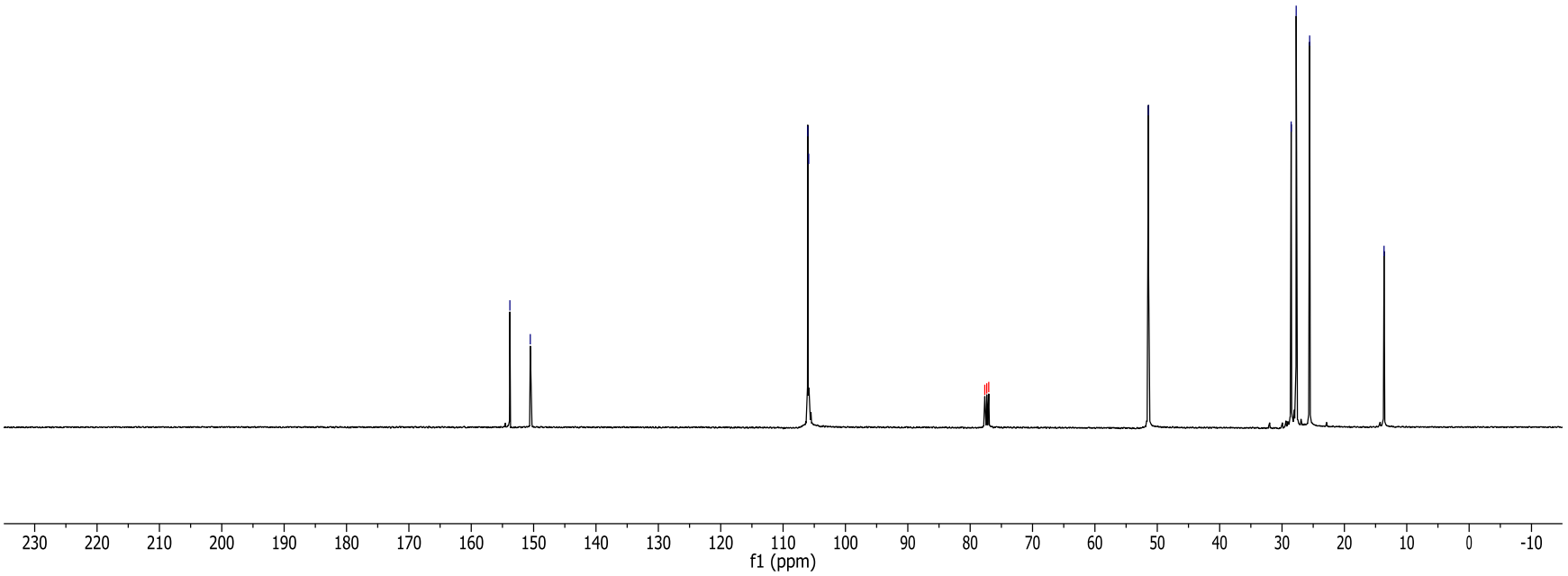
19

ras-271009-13cnmr
13C OBSERVE

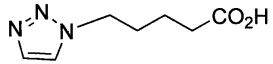


19

153.81
150.53
106.05
105.89
77.66 CDCl3
77.34 CDCl3
77.02 CDCl3
51.42
28.53
27.73
25.57
13.64



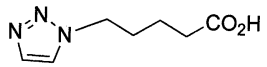
INDEX	FREQUENCY	PPM	HEIGHT
1	3087.593	7.724	26.0
2	3086.860	7.722	29.9
3	3026.371	7.570	26.8
4	3025.271	7.568	31.5
5	2901.727	7.259	31.1
6	1774.066	4.438	19.2
7	1767.100	4.420	35.8
8	1759.768	4.402	19.1
9	969.379	2.425	19.3
10	962.413	2.407	39.1
11	955.081	2.389	20.7
12	813.941	2.036	4.9
13	806.609	2.018	12.1
14	803.676	2.010	6.4
15	801.476	2.005	9.5
16	799.277	1.999	14.7
17	796.344	1.992	9.7
18	794.144	1.987	6.7
19	791.211	1.979	12.1
20	784.246	1.962	5.6
21	679.032	1.699	5.8
22	672.066	1.681	13.3
23	666.934	1.668	9.2
24	664.001	1.661	15.0
25	662.168	1.656	10.8
26	656.303	1.642	12.2
27	512.962	1.283	5.3
28	509.663	1.275	6.2
29	497.565	1.245	21.3



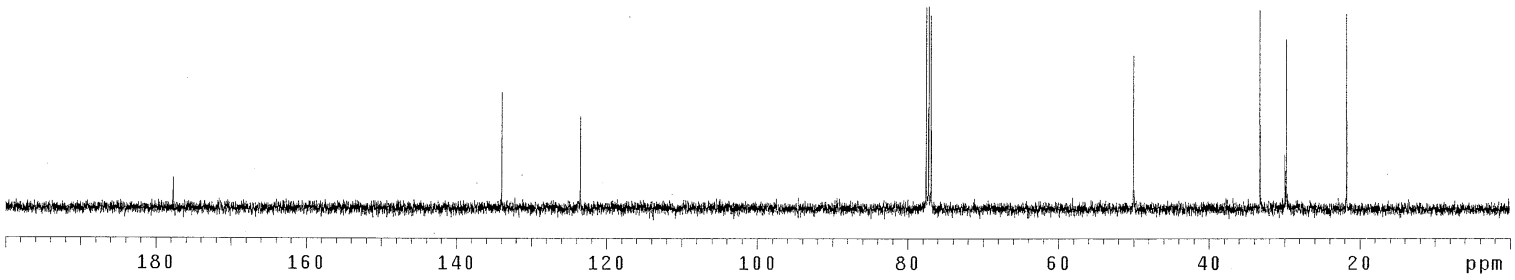
20

MK-210 mk-210 S_8

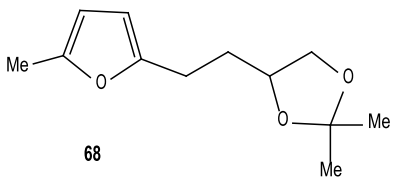
INDEX	FREQUENCY	PPM	HEIGHT
1	17865.581	177.731	5.1
2	13466.338	133.967	19.3
3	12416.501	123.522	15.3
4	7794.473	77.541	33.3
5	7762.428	77.223	33.4
6	7730.384	76.904	31.9
7	5027.207	50.012	25.4
8	3339.533	33.223	32.8
9	3005.356	29.898	9.0
10	2988.570	29.731	28.0
11	2187.460	21.761	32.1



20



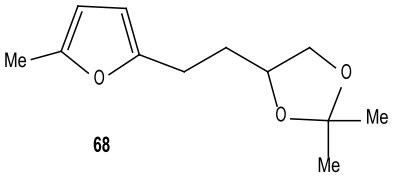
mku-270511-1hnmr
STANDARD 1H OBSERVE



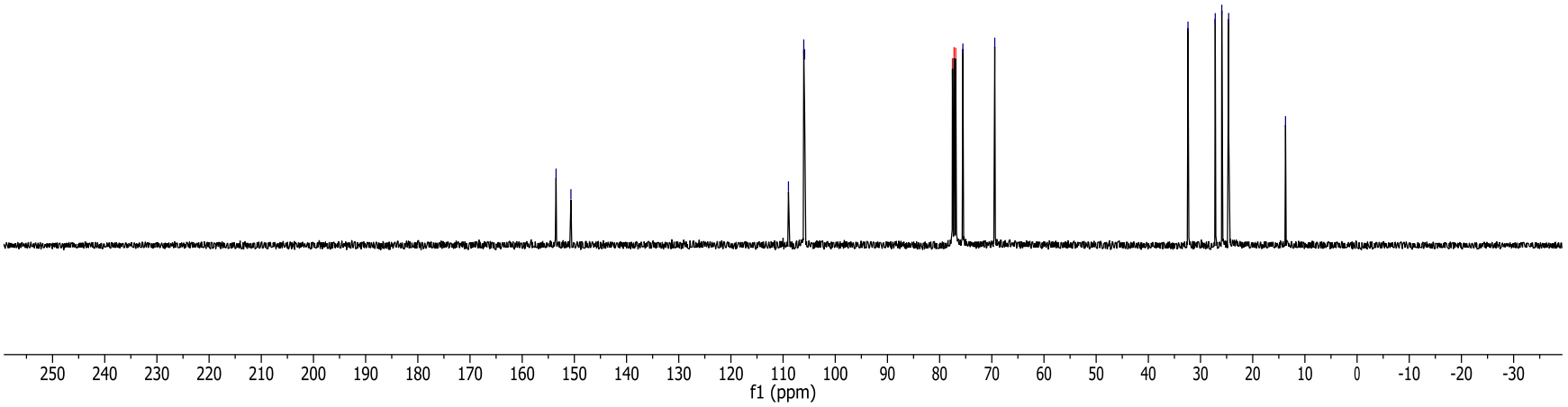
68

mku-270511-13cnmr
13C OBSERVE

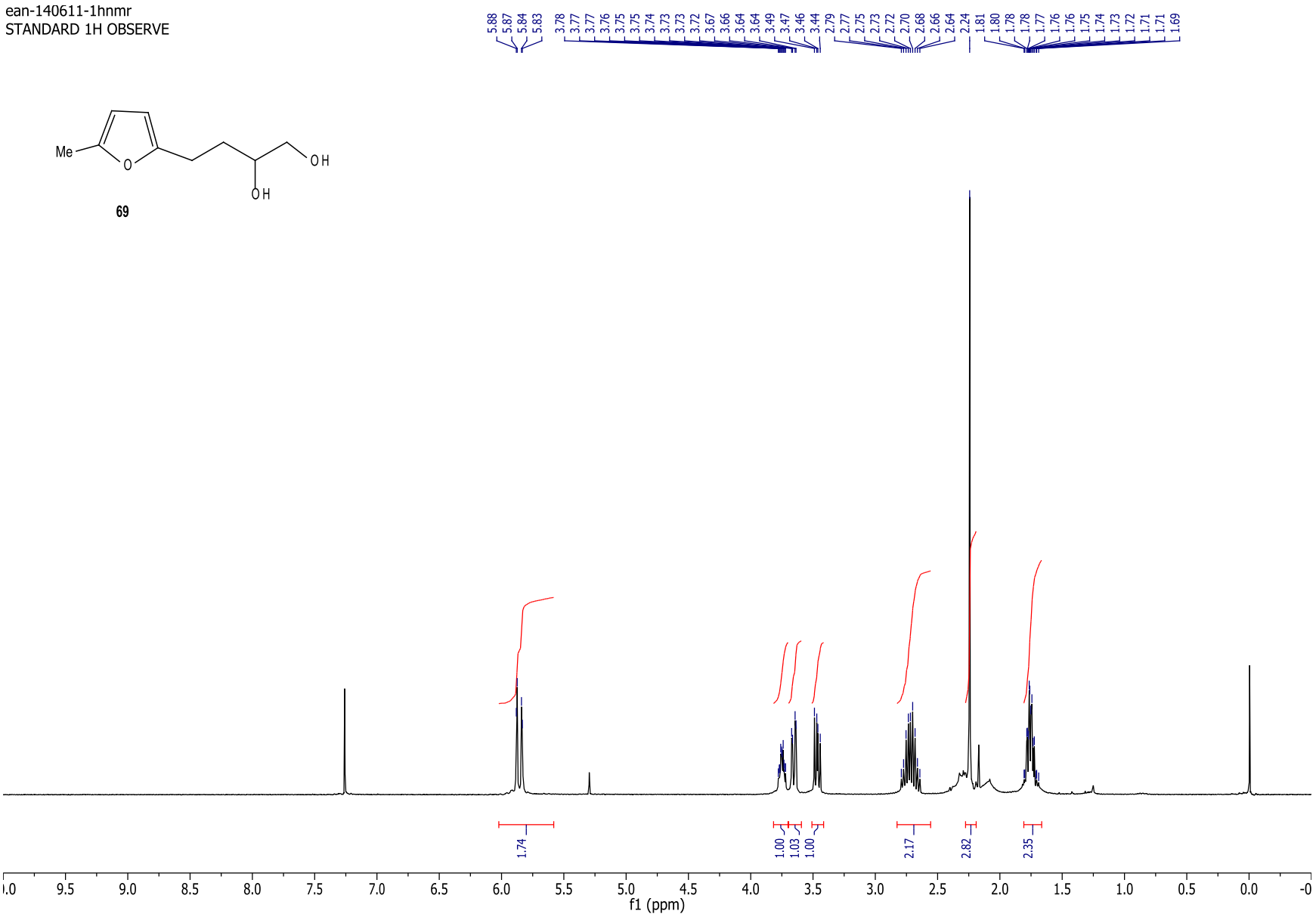
153.51
150.66
108.97
106.04
105.87
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
75.54
69.43
32.41
27.18
25.93
24.61
13.71



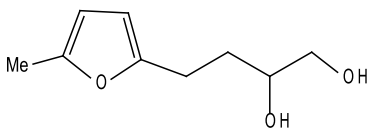
68



ean-140611-1hnmr
STANDARD 1H OBSERVE

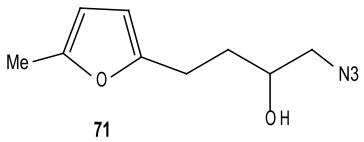


ean-140611-13cnmr
13C OBSERVE

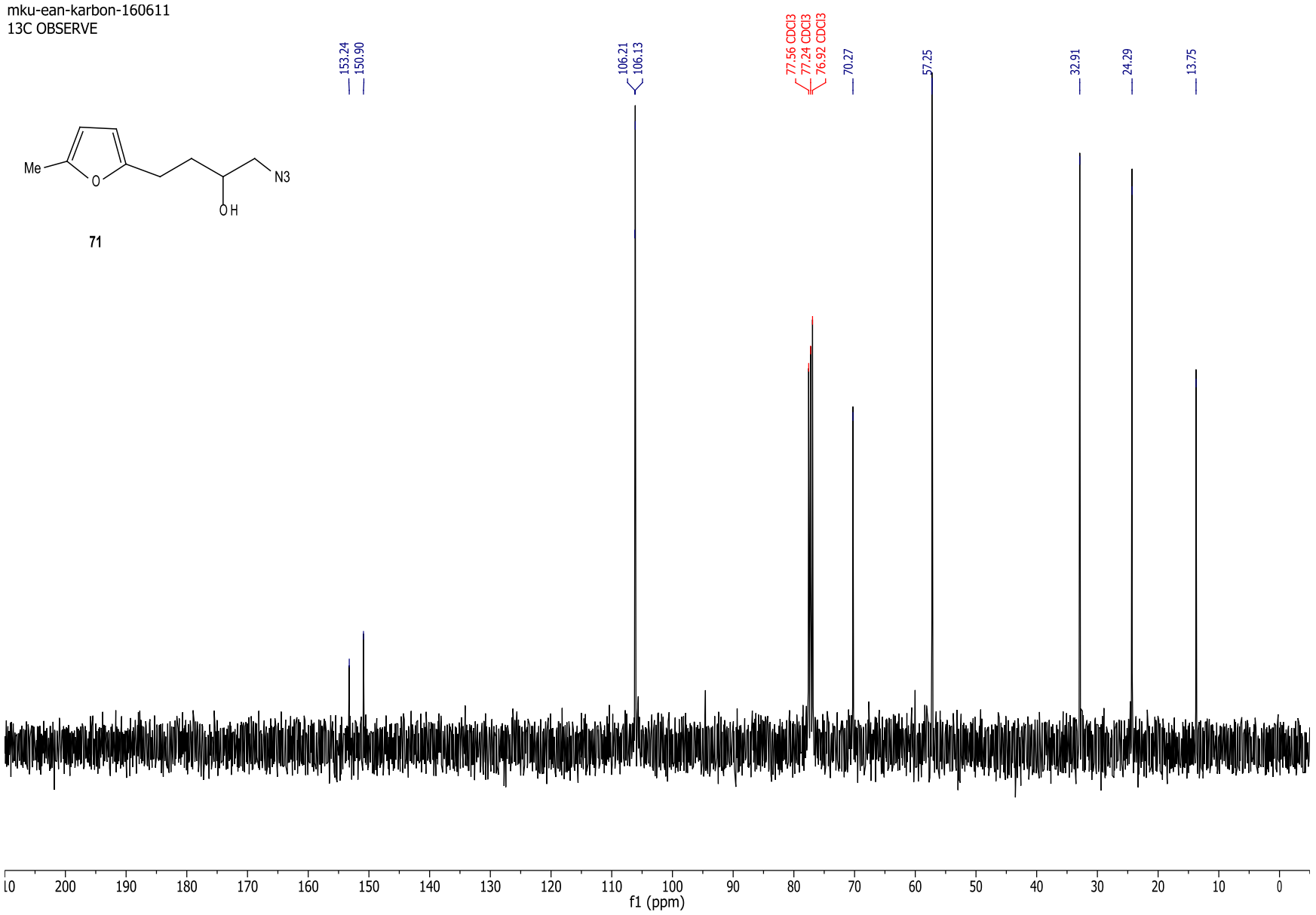


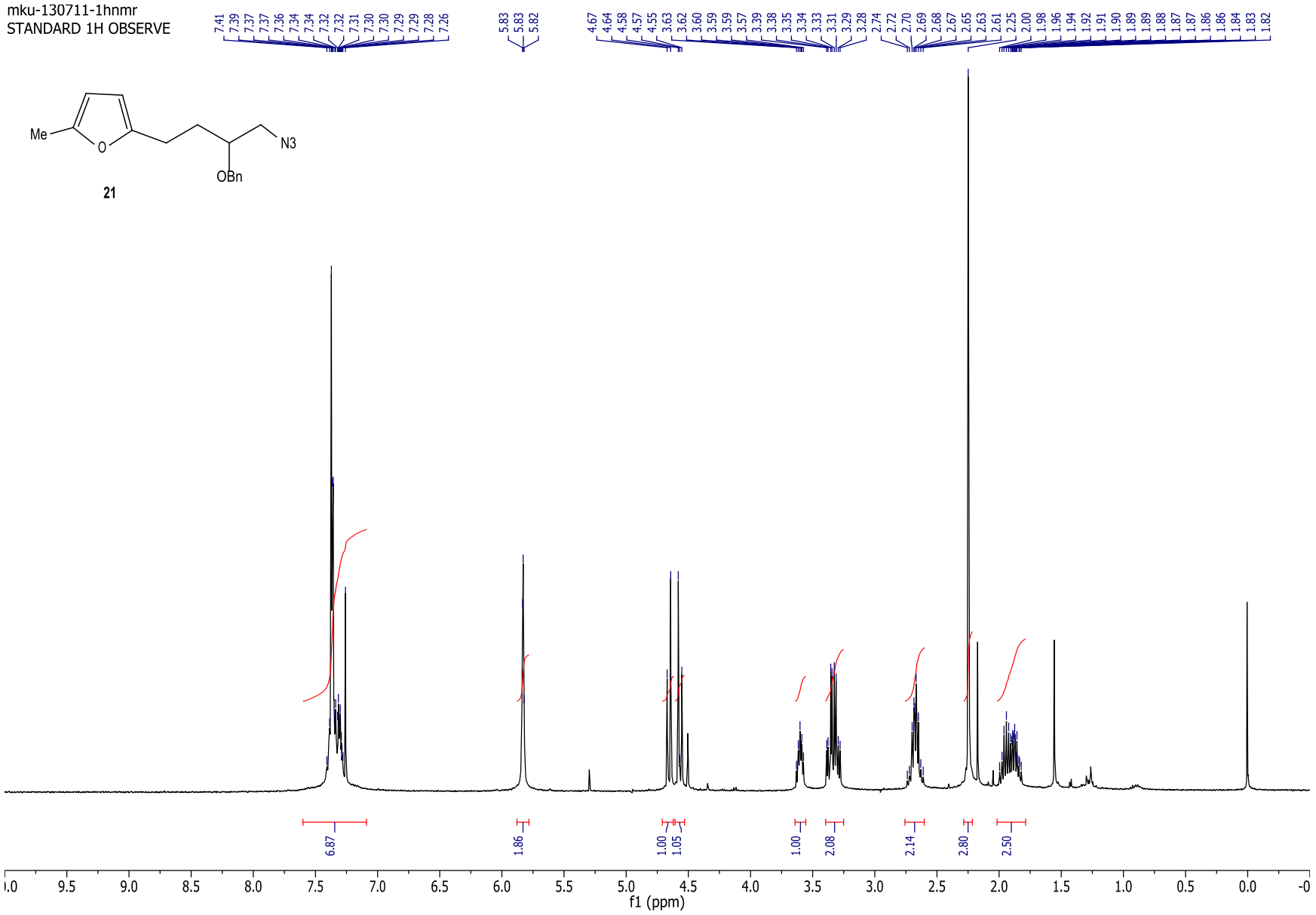
69

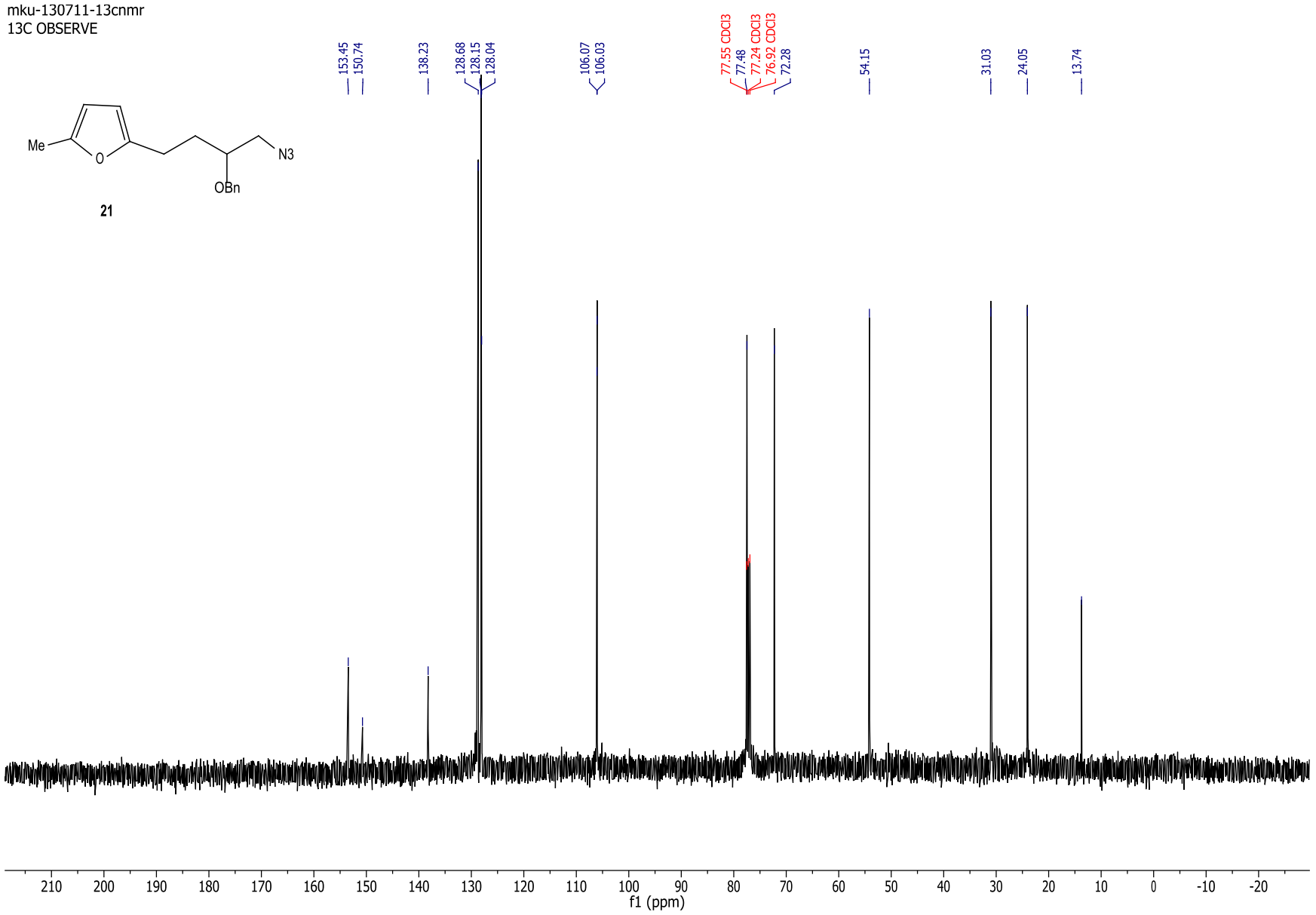
ean-2-170611-1hnmr
STANDARD 1H OBSERVE



71


mku-ean-karbon-160611
13C OBSERVE
153.24
150.90
106.21
106.13
77.56 CDCl3
77.24 CDCl3
76.92 CDCl3
70.27
57.25
32.91
24.29
13.75
Me
O
N3
OH
71
f1 (ppm)


mku-130711-1hnmr
STANDARD 1H OBSERVE
Me
O
N3
OBn
21
f1 (ppm)

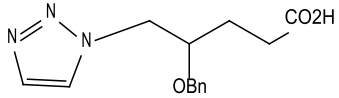

mku-130711-13cnmr
13C OBSERVE
153.45
150.74
138.23
128.68
128.15
128.04
106.07
106.03
77.55 CDCl3
77.48
77.24 CDCl3
76.92 CDCl3
72.28
54.15
31.03
24.05
13.74
Me
O
N3
OBn
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

ean-110811-1hnmr
STANDARD 1H OBSERVE

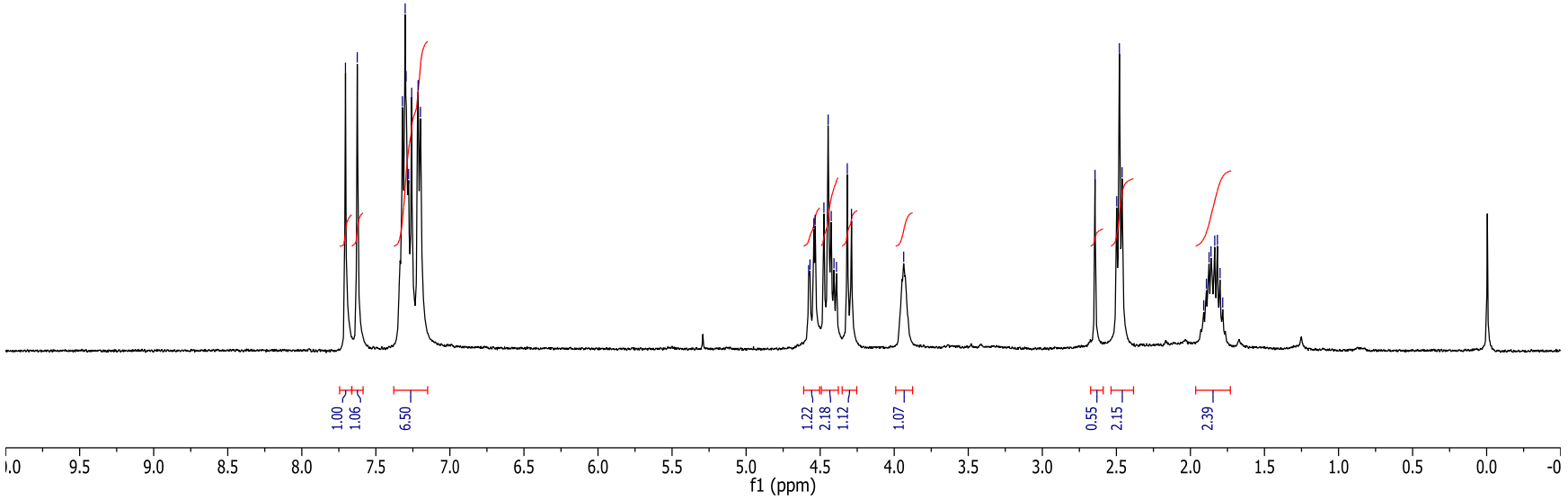
7.71 7.63 7.32 7.30 7.30 7.28 7.26 7.21 7.20

4.58 4.57 4.54 4.53 4.47 4.45 4.43 4.41 4.39 4.32 4.29 3.94

2.64 2.50 2.48 2.46 1.91 1.89 1.87 1.86 1.84 1.82 1.80 1.78

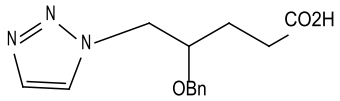


22

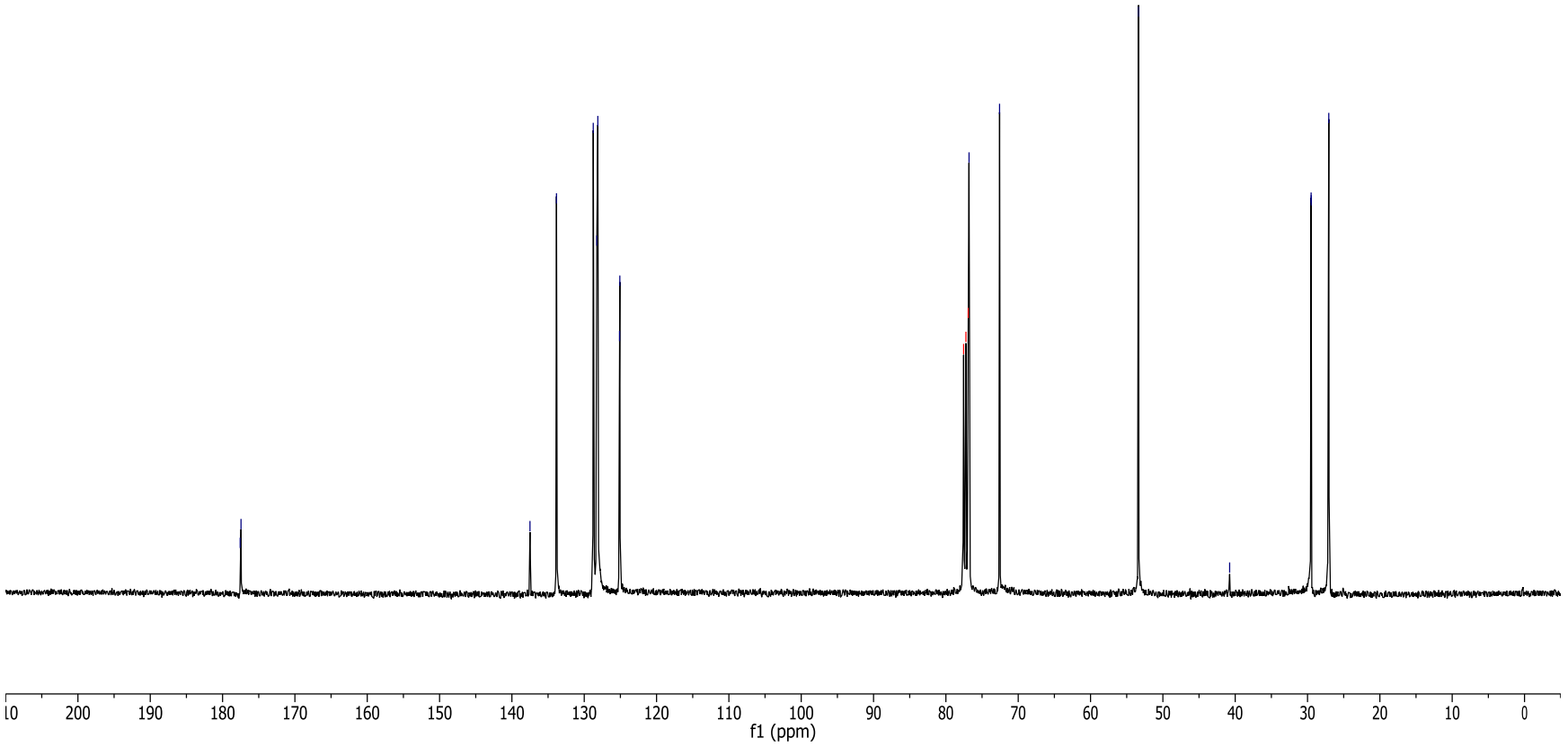


ean-110811-13cnmr
13C OBSERVE

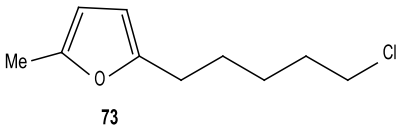
177.57
177.45
137.50
133.84
128.75
128.26
128.12
125.12
125.08
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
76.80
72.58
53.37
40.77
29.50
29.49
27.06



22

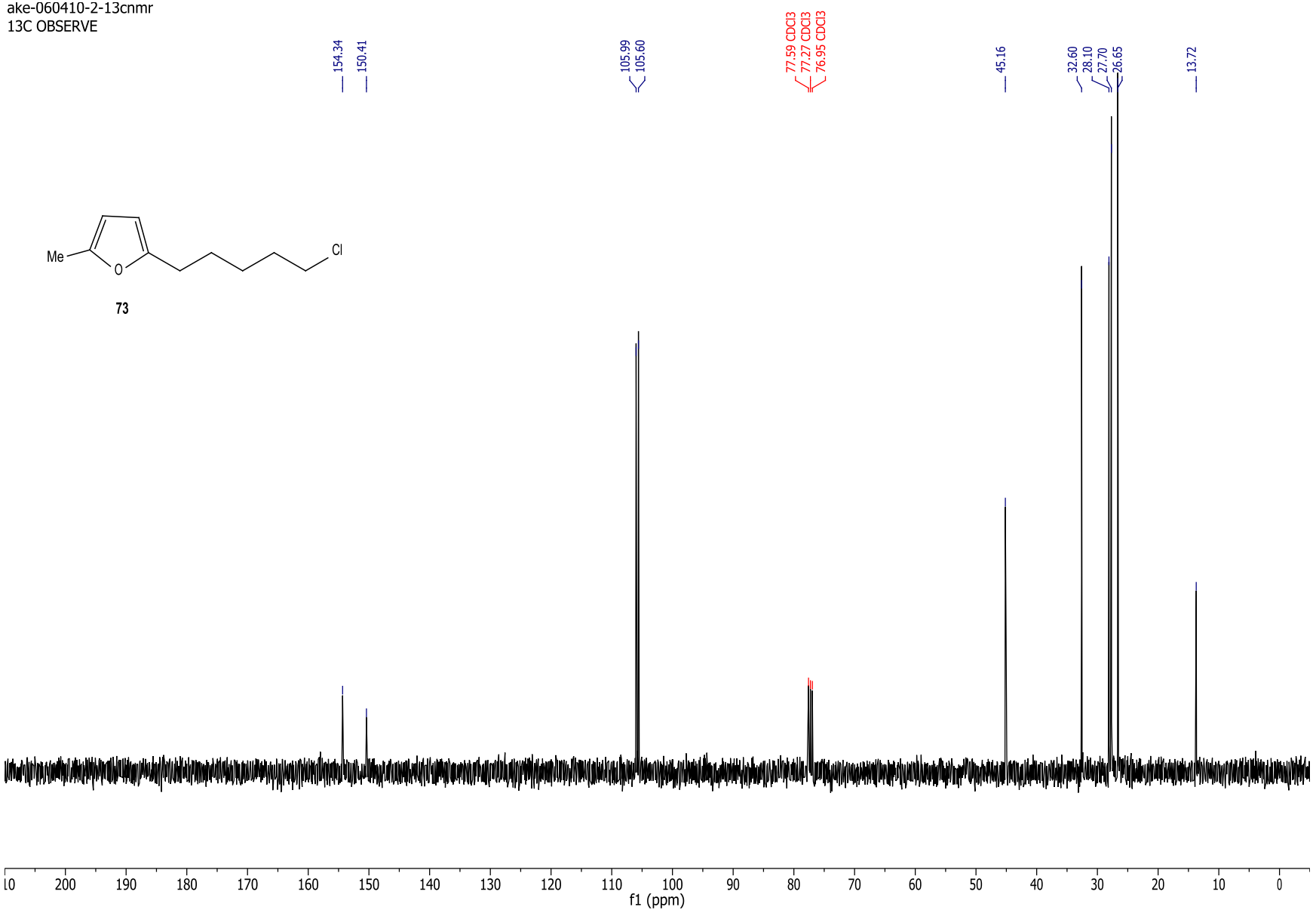


ake-060410-2-1hnmr
STANDARD 1H OBSERVE

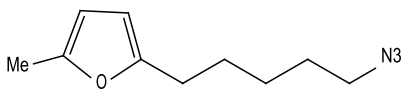


73

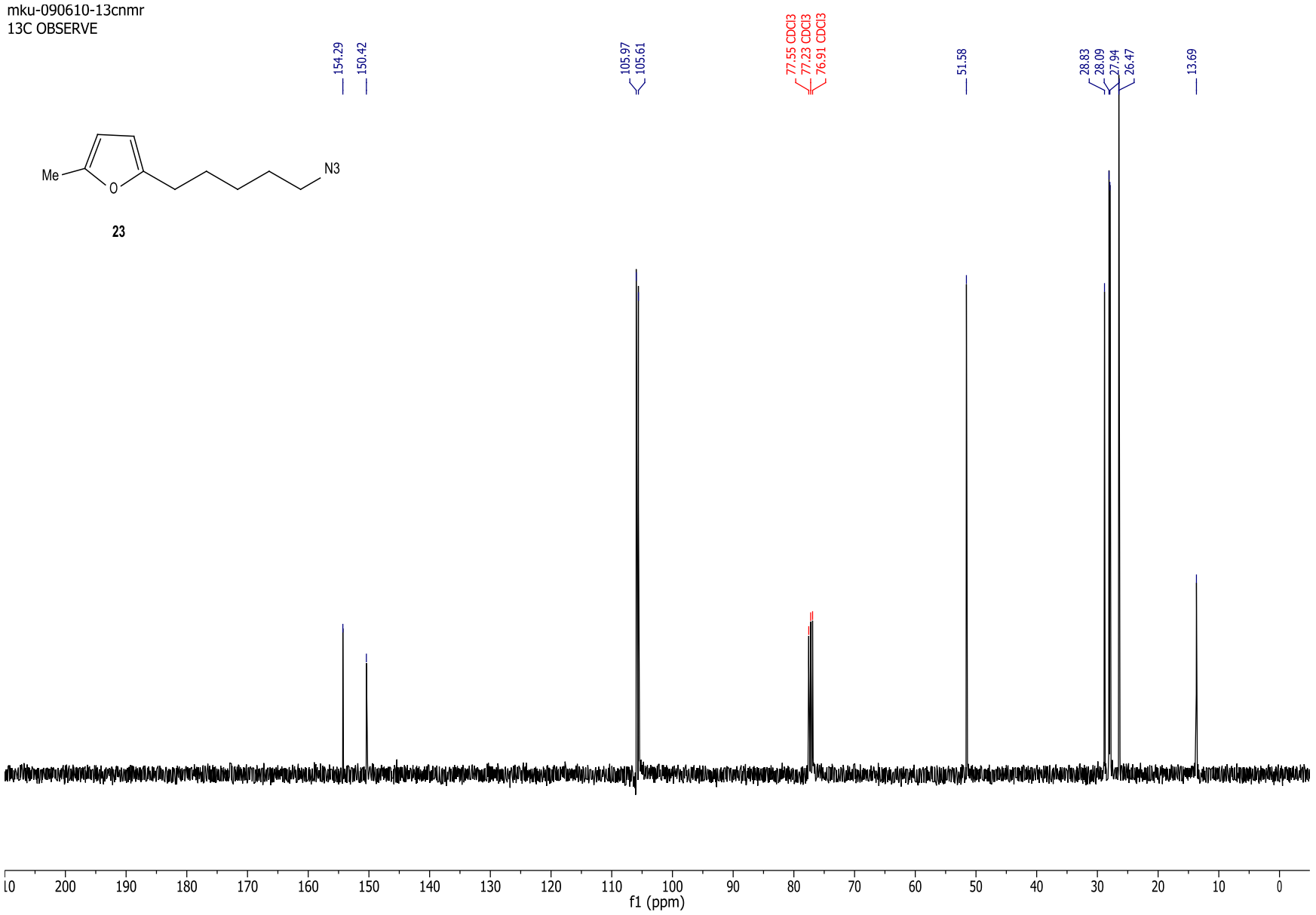
ake-060410-2-13cnmr
13C OBSERVE



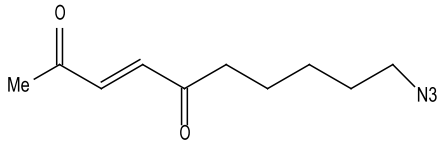
mku-090610-1hnmr
STANDARD 1H OBSERVE



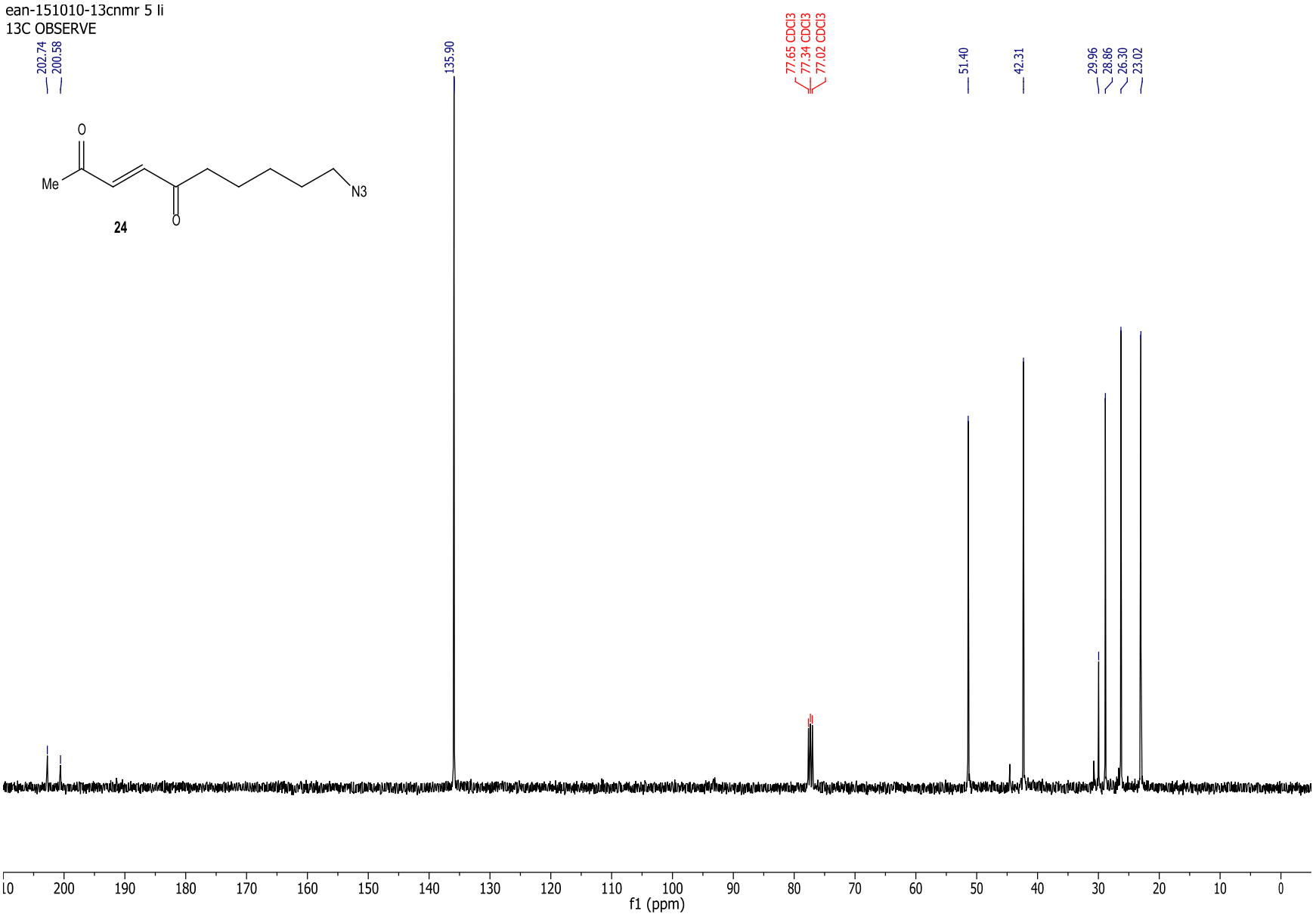
23


mku-090610-13cnmr
13C OBSERVE
154.29
150.42
105.97
105.61
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
51.58
28.83
28.09
27.94
26.47
13.69
Me
O
N3
23
f1 (ppm)

ean-151010-1hnmr
STANDARD 1H OBSERVE



24


ean-151010-13cnmr 5 li
13C OBSERVE
202.74
200.58
135.90
77.65 CDCl3
77.34 CDCl3
77.02 CDCl3
51.40
42.31
29.96
28.86
26.30
23.02
O
Me
N3
O
24
f1 (ppm)