Supporting information

Fe–Catalyzed Domino Intramolecular Nucleophilic Substitution of 4–hydroxy Chromen–2–one and Pyran–2–one/ Ring–opening of Activated Arene: An Easy Access to 2,3–Disubstituted Furo[3,2,–*c*]coumarins and Furo[3,2,–*c*]pyran–4–ones via Non–symmetric Triarylmethanes

Wayland E. Noland*, Honnaiah Vijay Kumar, Arjun Sharma, Binyuan Wei and Selamawit Girmachew

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455. Email– nolan001@umn.edu

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I. General experimental information

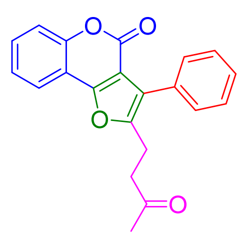
Solvents like anhydrous toluene, anhydrous THF, 200 proof ethanol, DCM, ethyl acetate, hexanes and reagents like alkyl–, aryl–aldehydes, 4–hydroxycoumarin, coumarin, 2–methylfuran, 4–hydroxy–6–methyl–2–pyrone, anhydrous $MgSO_4$, 1,3,5 trimethoxybenzene, $Fe_2(SO_4)_3 \cdot xH_2O$ were purchased and used without further purification. Melting points were recorded on a Mel-Temp and are uncorrected (Sigma Aldrich Co., St. Louis, MO). Flash chromatography was performed using 150-Å silica gel. Thin-layer chromatography analyses were performed on plastic-backed plates pre-coated with 0.2-mm of silica with F254 indicator. Thin-layer chromatography developing solvents were mixtures of ethyl acetate and hexane. Chemical shifts (δ, ppm) for NMR spectra were referenced to the solvent ($CDCl_3$ at 7.26, CD_2Cl_2 at 5.32, for ^1H; $CDCl_3$ at 77.16, CD_2Cl_2 at 53.84 for ^{13}C). ^{13}C NMR spectra were proton decoupled. Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 7200 FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Bruker BioTOF II ESITOF instrument with poly (ethylene oxide) as an internal calibrant, or a Finnegan Mat 95 EI spectrophotometer or an Agilent 7200 GC/QTOF spectrophotometer with perfluorokerosene as an internal calibrant.

II. General procedure for the synthesis of furo[3,2,–*c*]coumarins

A 50 mL round bottom flask was charged with aldehydes (1 mmol, 1 equiv), 2–methyl furan (1 mmol, 1 equiv) and 4– hydroxycoumarin (1 mmol, 1 equiv) in anhydrous toluene (10 mL). To this reaction mixture, $Fe_2(SO_4)_3 \bullet xH_2O$ (15 mol%, 60 mg) was added and the solution was stirred at reflux temperature for 6 h in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by rotovap. The residue was dissolved in DCM (15 mL), washed with distilled water (3 × 15 mL) and dried over anhydrous $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate).

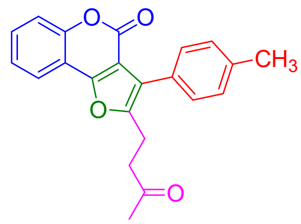
The general method from above was used for the preparation of following furo[3,2,–c]coumarins:

2-(3-oxobutyl)-3-phenyl-4H-furo[3,2-c]chromen-4-one **13a**



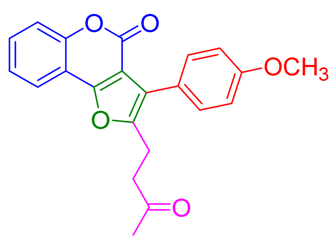
White solid, 288.3 mg, 87% yield, m.p. 124-126 °C; R_f = 0.34 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 1739, 1632, 1502, 737, 703; ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.90 (dd, J = 7.8, 1.7 Hz, 1H), 7.57 – 7.35 (m, 8H), 3.13 – 3.07 (m, 2H), 2.92 (dd, J = 8.2, 6.7 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 206.5, 157.9, 156.8, 154.5, 152.8, 130.8, 130.4, 128.6, 128.3, 124.8, 121.0, 120.9, 117.4, 113.2, 110.1, 41.5, 30.0, 21.1; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{21}H_{16}O_4$ 332.1043; Found: 332.1037.

2-(3-oxobutyl)-3-(p-tolyl)-4H-furo[3,2-c]chromen-4-one **13b**



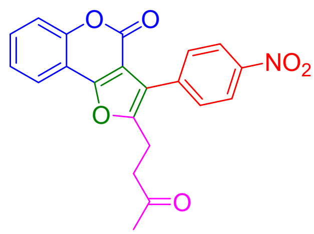
Brown solid, 270.1 mg, 78% yield, m.p. 123-125 °C; R_f = 0.38 (EtOAc:Hexanes = 1:3, SiO_2); flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 2920, 1744, 1630, 1515, 826, 754; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.27 (m, 7H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.5, 157.8, 156.5, 153.6, 152.6, 138.0, 130.5, 129.8, 129.2, 126.7, 124.4, 121.0, 120.7, 117.3, 112.9, 110.0, 41.6, 30.0, 21.5, 20.9; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{22}H_{18}O_4$ 346.1200; Found: 346.1208.

3-(4-methoxyphenyl)-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13c**



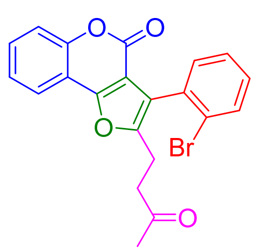
Brown solid, 304.2 mg, 84% yield, m.p. 110-112 °C; R_f = 0.41 (EtOAc:Hexanes = 1:3, SiO_2; Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:12, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 1737, 1632, 1515, 742, 704; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.43 (dd, *J* = 8.9, 2.3 Hz, 3H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 3.13 (dd, *J* = 8.3, 6.8 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.5, 159.5, 157.9, 156.5, 153.4, 152.5, 131.2, 130.5, 124.4, 121.9, 120.7, 117.3, 114.0, 112.9, 110.0, 55.4, 41.5, 30.0, 20.9; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{22}H_{18}O_5$ 362.1149; Found: 362.1149.

3-(4-nitrophenyl)-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13d**



Yellow solid, 300.4 mg, 80% yield, m.p. 121-122 °C; R_f = 0.33 (EtOAc:Hexanes = 1:3, SiO_2); flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 1716, 1630, 1600, 736, 703; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 – 8.27 (m, 2H), 7.86 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.54 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.45 – 7.34 (m, 2H), 3.13 (t, *J* = 7.4 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.1, 157.6, 157.1, 154.8, 152.6, 147.4, 136.8, 131.1, 131.0, 124.7, 123.6, 120.8, 119.2, 117.3, 112.4, 109.3, 40.9, 30.0, 20.8.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{21}H_{15}NO_6$ 377.0849; Found: 377.0849.

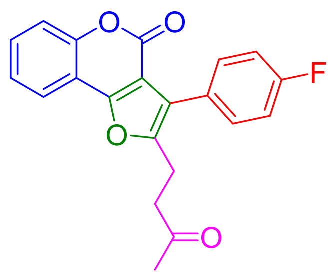
3-(2-bromophenyl)-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13e**



Brown oil, 311.8 mg, 76% yield; R_f = 0.32 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 1741, 1634, 1502, 738, 704; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.44 – 7.27 (m, 5H), 2.97 (td, *J* =

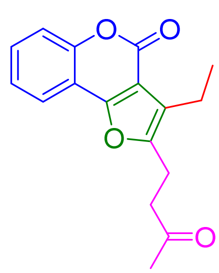
7.4, 1.6 Hz, 2H), 2.90 – 2.82 (m, 2H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.4, 157.3, 156.3, 154.5, 152.6, 133.0, 132.1, 131.3, 130.6, 130.2, 127.5, 124.9, 124.5, 120.8, 119.8, 117.4, 112.9, 110.9, 41.0, 29.9, 21.0; HRMS (EI-TOF) *m/z*: [M]$^+$Calcd for $C_{21}H_{15}BrO_4$ 410.0154; Found: 410.0148.

3-(4-fluorophenyl)-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13f**



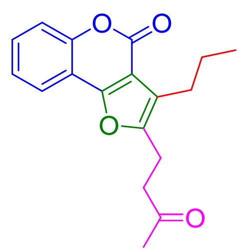
Brown solid, 269.4 mg, 77% yield, m.p. 128-129°C; R_f = 0.45 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:15, SiO_2); IR (film) ν_{max}/cm^{-1} 3056, 2986, 1736, 1633, 739, 704; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55 – 7.42 (m, 4H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 7.15 (t, *J* = 8.7 Hz, 2H), 3.11 (dd, *J* = 8.2, 6.7 Hz, 2H), 2.92 (dd, *J* = 8.1, 6.7 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 164.0, 161.5, 157.8, 156.6, 153.8, 152.6, 131.8, 131.8, 130.7, 125.7, 124.5, 120.8, 120.1, 117.4, 115.7, 115.5, 112.8, 109.8, 41.4, 30.0, 20.8; HRMS (EI-TOF) *m/z*: [M]$^+$Calcd for $C_{21}H_{15}FO_4$ 350.0949; Found: 350.0940.

3-ethyl-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13g**



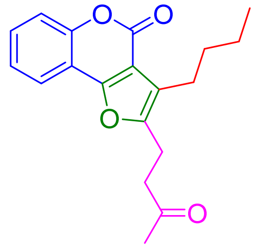
White solid, 235.8 mg, 83% yield, m.p. 98-100°C; R_f = 0.36 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3408, 3057, 2967, 2875, 1733, 704; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 3.02 (dd, *J* = 7.8, 6.6 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.71 (q, *J* = 7.5 Hz, 2H), 2.21 (s, 3H), 1.24 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 158.5, 156.3, 152.6, 152.5, 130.2, 124.4, 121.4, 120.6, 117.3, 113.1, 110.9, 41.8, 30.1, 20.2, 17.0, 15.3; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{17}H_{16}O_4$ 284.1043; Found: 284.1044.

2-(3-oxobutyl)-3-propyl-4H-furo[3,2-c]chromen-4-one **13h**



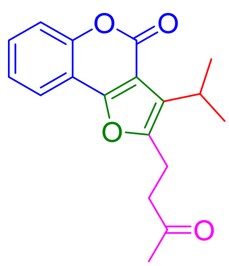
Yellow solid, 244.4 mg, 82% yield, m.p. 78-79°C; R_f = 0.35 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3420, 3058, 2962, 2932, 1740, 737; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.40 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.30 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 3.06 – 2.99 (m, 2H), 2.92 – 2.85 (m, 2H), 2.71 – 2.63 (m, 2H), 2.22 (s, 3H), 1.72 – 1.64 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.7, 158.5, 156.3, 153.2, 152.5, 130.2, 124.4, 120.6, 119.6, 117.3, 113.1, 111.0, 41.8, 30.1, 25.4, 23.5, 20.3, 13.9.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{18}H_{18}O_4$ 298.1200; Found: 298.1200.

3-butyl-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13i**



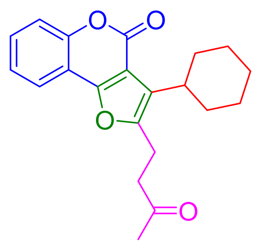
White solid, 271.5 mg, 87% yield, m.p. 99-100°C; R_f = 0.41 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:15, SiO_2); IR (film) ν_{max}/cm^{-1} 3057, 2958, 2861, 1740, 1266, 704; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.44 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.38 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.31 – 7.27 (m, 1H), 3.00 (td, *J* = 7.1, 6.5, 0.9 Hz, 2H), 2.91 – 2.85 (m, 2H), 2.71 – 2.65 (m, 2H), 2.21 (s, 3H), 1.60 (tt, *J* = 9.0, 6.8 Hz, 2H), 1.36 (dq, *J* = 14.7, 7.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.7, 158.4, 156.2, 153.0, 152.5, 130.1, 124.3, 120.5, 119.8, 117.2, 113.1, 111.0, 41.8, 32.5, 30.1, 23.2, 22.5, 20.2, 14.0; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{19}H_{20}O_4$ 312.1356; Found: 312.1349.

3-isopropyl-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13j**



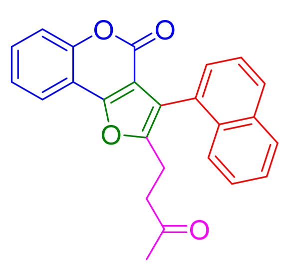
White solid, 250.4 mg, 84% yield, m.p. 123-126°C; R_f = 0.37 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3424, 3019, 2929, 2853, 1738, 748; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.39 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.29 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 3.18 (hept, J = 7.0 Hz, 1H), 3.09 – 3.03 (m, 2H), 2.87 (dd, J = 8.1, 6.7 Hz, 2H), 2.21 (s, 3H), 1.38 (d, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 206.6, 158.2, 156.8, 152.6, 151.7, 130.2, 125.7, 124.3, 120.6, 117.1, 112.9, 110.5, 42.1, 30.1, 24.9, 22.1, 20.8; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{18}H_{18}O_4$ 298.1200; Found: 298.1210.

3-cyclohexyl-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13k**



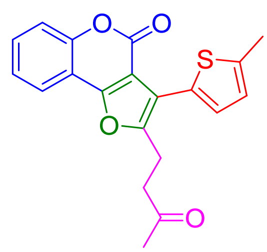
Yellow solid, 229.2 mg, 68% yield, m.p. 127-128°C; R_f = 0.40 (EtOAc:Hexanes = 1:3, SiO_2); Flash Column Chromatography Eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3681, 3018, 2924, 1730, 1216, 745; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (dd, J = 7.9, 1.5 Hz, 1H), 7.46 (td, J = 7.8, 7.2, 1.6 Hz, 1H), 7.40 (d, J = 8.3 Hz, 1H), 7.31 – 7.27 (m, 1H), 3.07 (dd, J = 8.2, 6.8 Hz, 2H), 2.88 (t, J = 7.5 Hz, 2H), 2.80 (tt, J = 12.3, 3.6 Hz, 1H), 2.22 (s, 3H), 1.96 (td, J = 12.2, 3.7 Hz, 2H), 1.84 (q, J = 5.1, 4.3 Hz, 2H), 1.77 – 1.63 (m, 3H), 1.39 (td, J = 9.1, 2.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 206.8, 158.2, 156.7, 152.5, 152.0, 130.2, 124.9, 124.3, 120.6, 117.1, 113.0, 110.6, 42.2, 35.1, 31.9, 30.1, 26.9, 25.8, 21.0.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{21}H_{22}O_4$ 338.1513; Found: 338.1518.

3-(naphthalen-1-yl)-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13l**



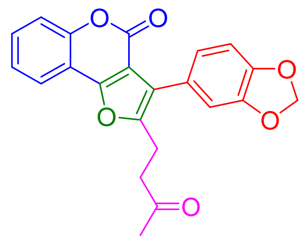
Brown oil, 301.8 mg, 79% yield; R_f = 0.38 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 2985, 1741, 1508, 1266, 702; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (t, *J* = 7.4 Hz, 3H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.47 (m, 4H), 7.45 – 7.36 (m, 3H), 2.94 (tt, *J* = 15.6, 7.4 Hz, 2H), 2.77 (qdd, *J* = 17.9, 8.4, 6.4 Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.4, 157.4, 156.6, 154.9, 152.7, 133.8, 132.5, 130.6, 129.2, 128.7, 128.5, 127.5, 126.5, 126.1, 125.4, 124.5, 120.8, 118.7, 117.4, 113.0, 111.6, 41.3, 29.8, 21.0.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{25}H_{18}O_4$ 382.1200; Found: 382.1198.

3-(5-methylthiophen-2-yl)-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13m**



Brown solid, 249.7 mg, 71% yield. m.p. 119-120°C; R_f = 0.24 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:8, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 2985, 2923, 1735, 1265, 703; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.43 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 6.79 (dt, *J* = 3.6, 1.2 Hz, 1H), 3.26 (dd, *J* = 8.4, 6.8 Hz, 2H), 2.93 (dd, *J* = 8.5, 6.8 Hz, 2H), 2.53 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.4, 157.6, 156.6, 153.9, 152.6, 141.0, 130.8, 129.5, 127.4, 125.9, 124.5, 120.8, 117.3, 115.0, 112.7, 109.7, 41.6, 30.0, 21.5, 15.4.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{20}H_{16}O_4S$ 352.0764; Found: 352.0761.

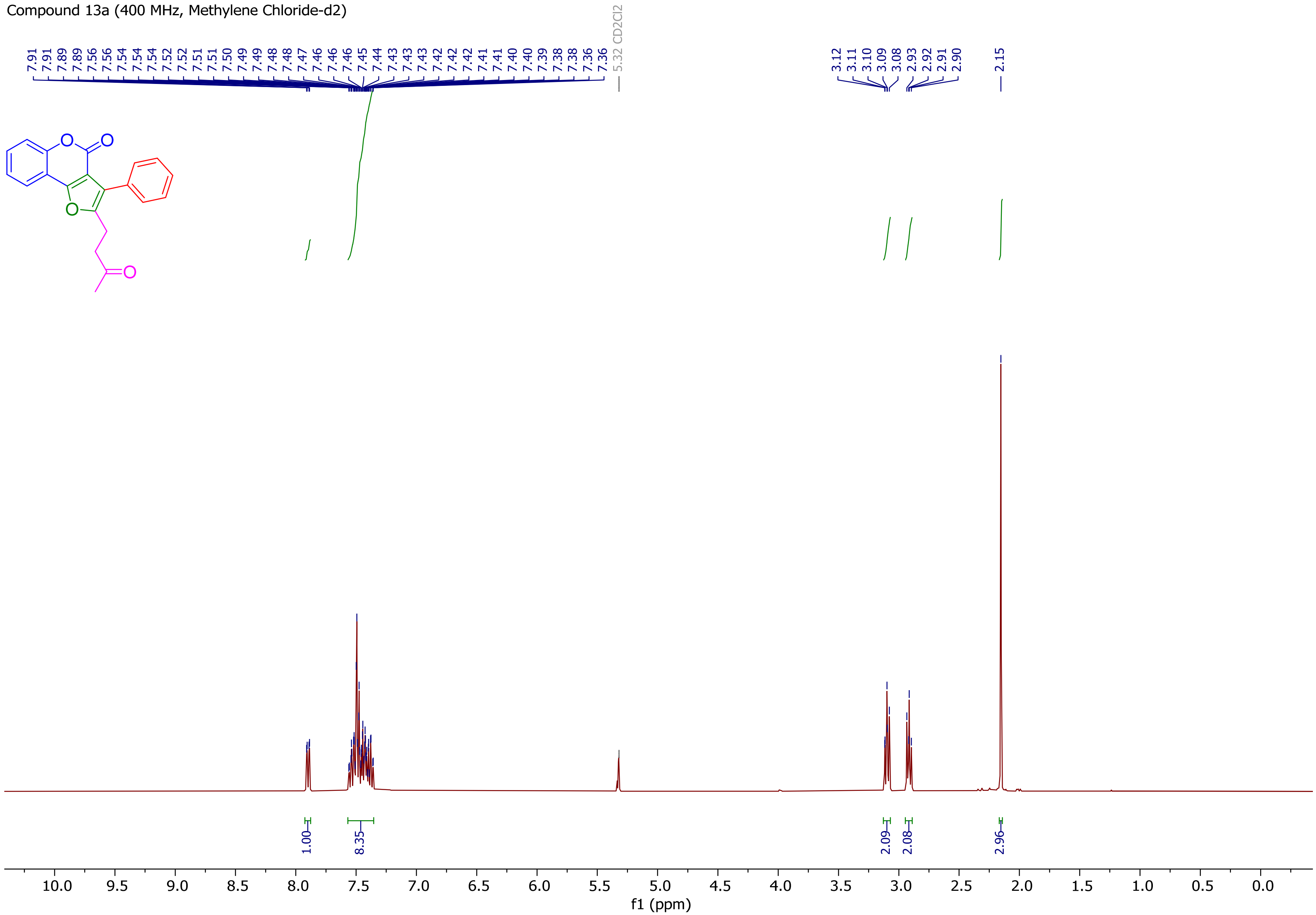
3-(benzo[d][1,3]dioxol-5-yl)-2-(3-oxobutyl)-4H-furo[3,2-c]chromen-4-one **13n**



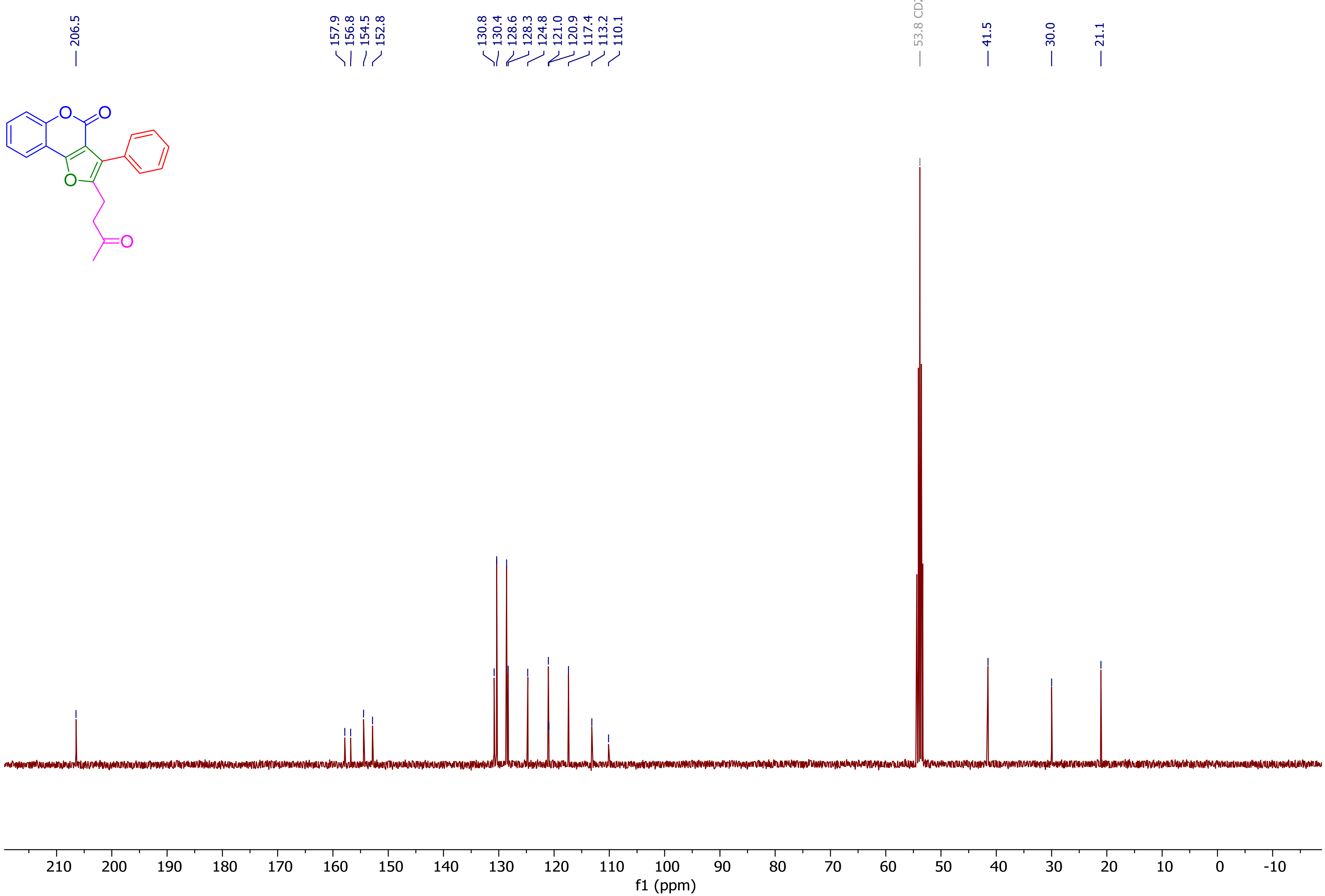
Brown solid, 308.4 mg, 82% yield. m.p. 93-95°C; R_f = 0.18 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:8, SiO_2); IR (film) ν_{max}/cm^{-1} 3413, 3058, 2987, 2901, 1732, 613; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.50 (td, *J* = 7.8, 7.2, 1.6 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.32 (m, 1H), 6.98 (d, *J* = 1.7 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.01 (s, 2H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.4, 157.8, 156.5, 153.7, 152.6, 147.7, 147.7, 130.6, 124.5, 123.6, 123.3, 120.8, 120.7, 117.3, 112.9, 110.6, 109.9, 108.4, 101.4, 41.5, 30.0, 20.8.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{22}H_{16}O_6$ 376.0941; Found: 376.0930.

III. ^{1}H and ^{13}C NMR Spectra for Furo[3,2,–*c*]coumarins 13 a-n

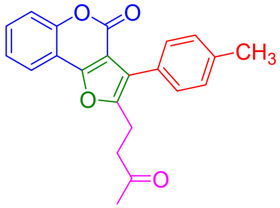
Compound 13a (400 MHz, Methylene Chloride-d2)

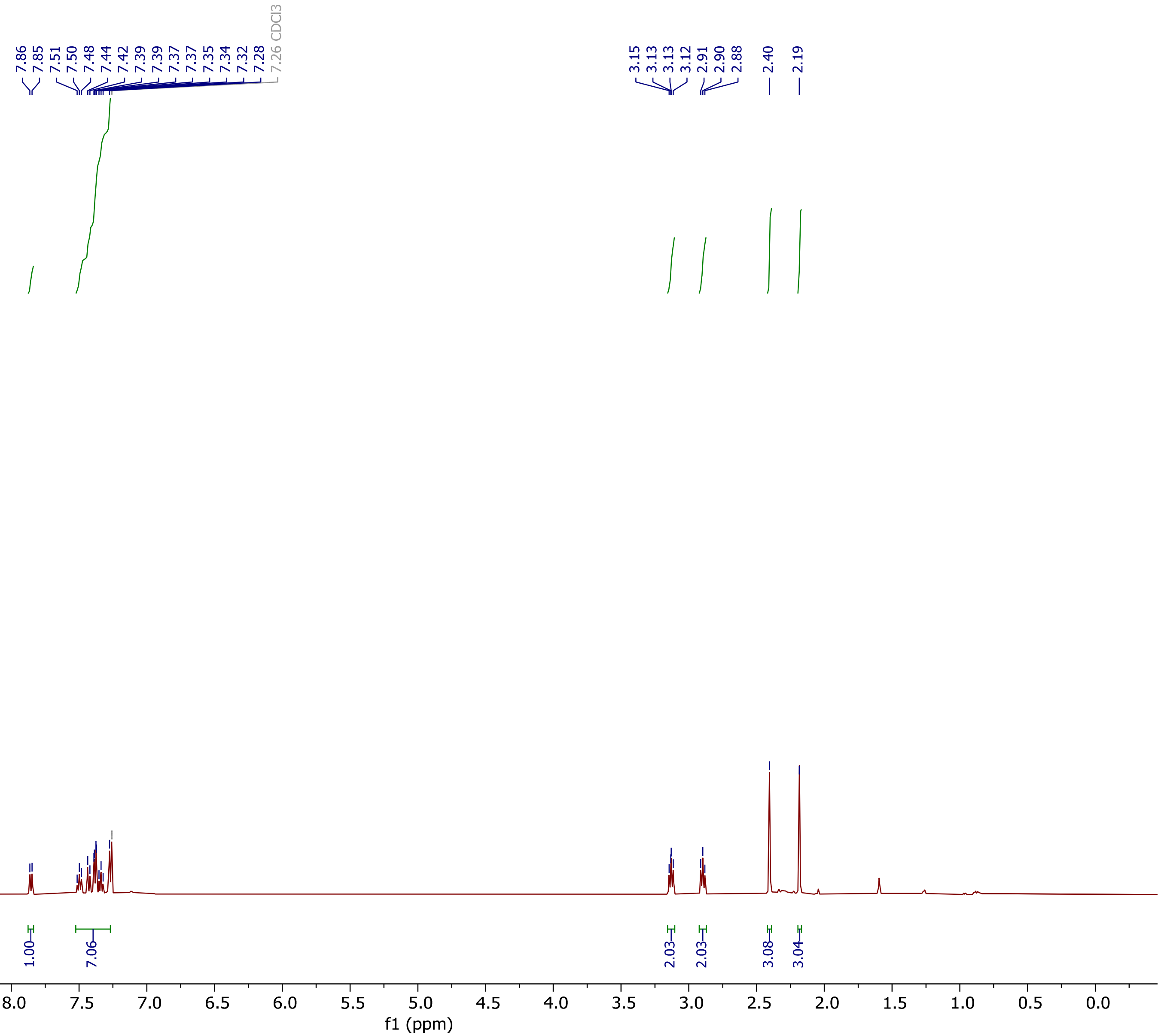


Compound 13a (101 MHz, Methylene Chloride-d2)

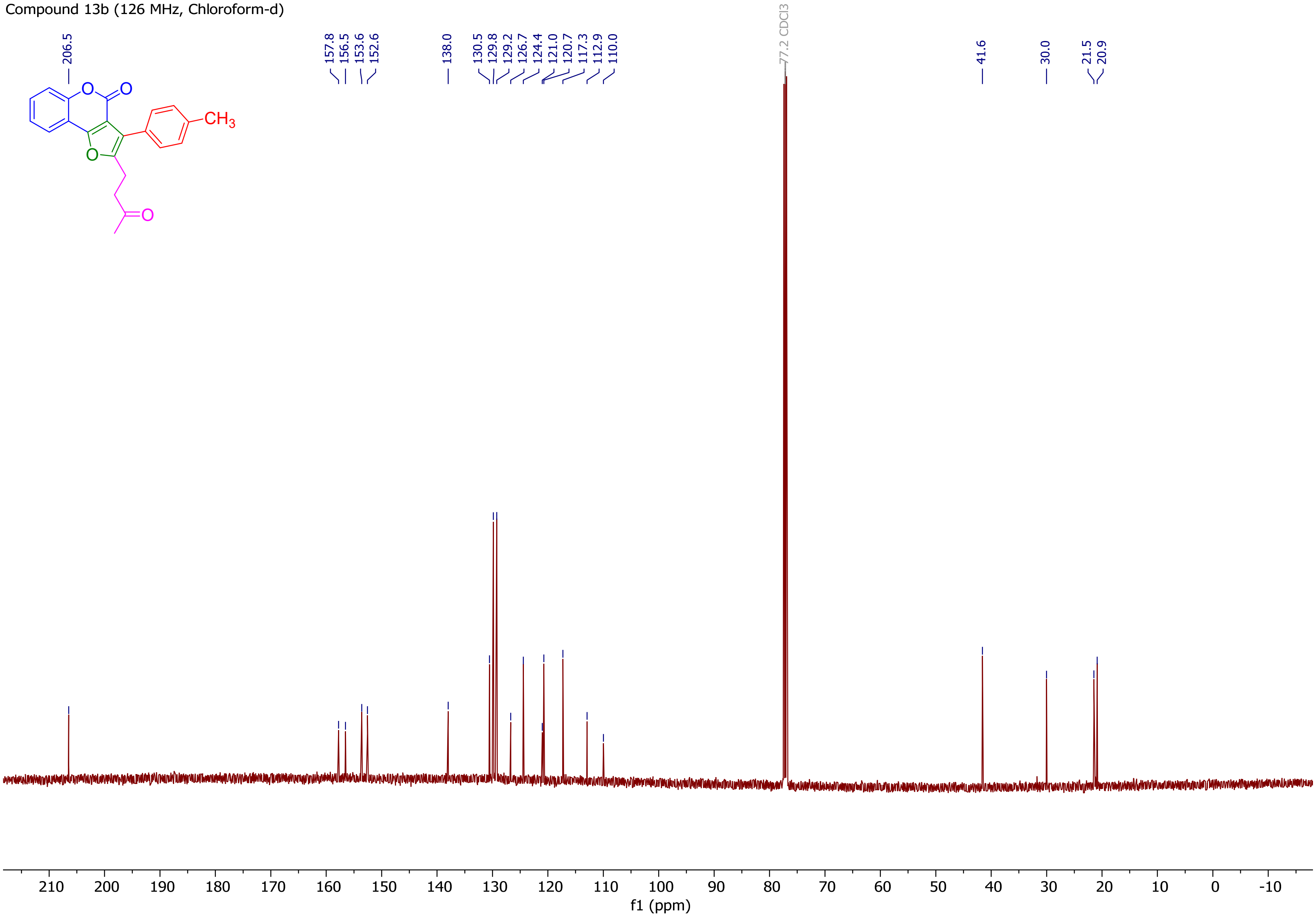


Compound 13b (500 MHz, Chloroform-d)

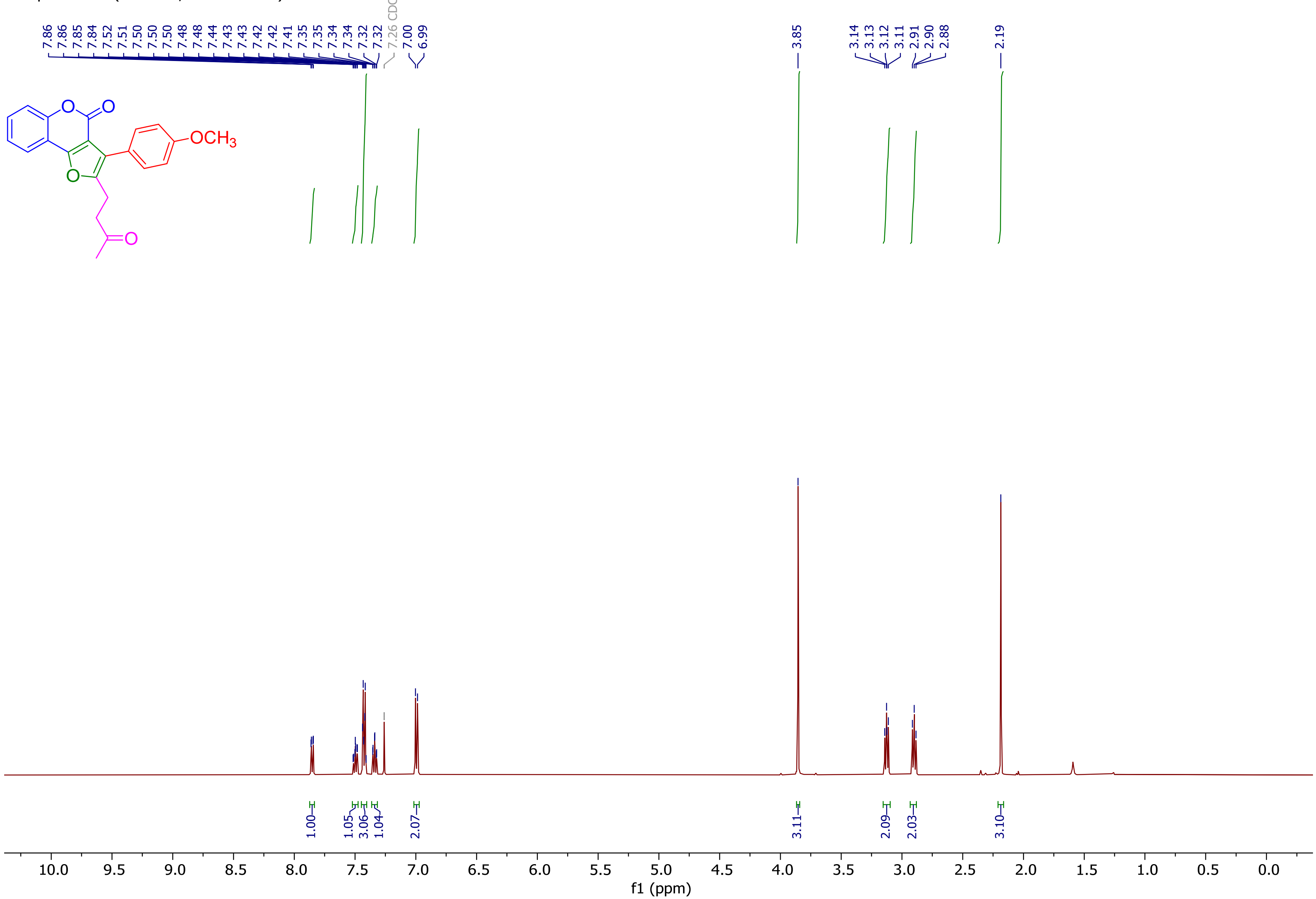




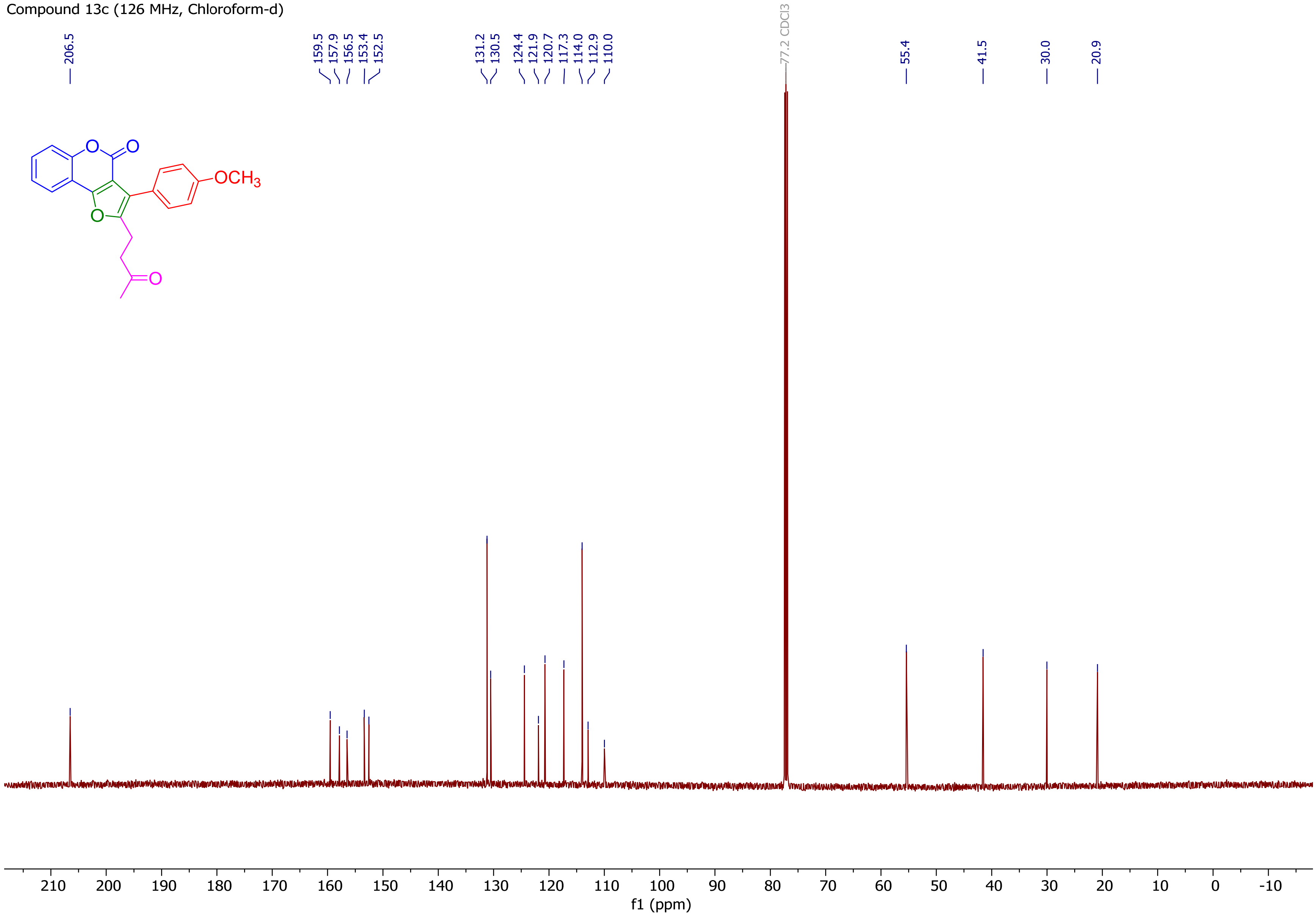
Compound 13b (126 MHz, Chloroform-d)



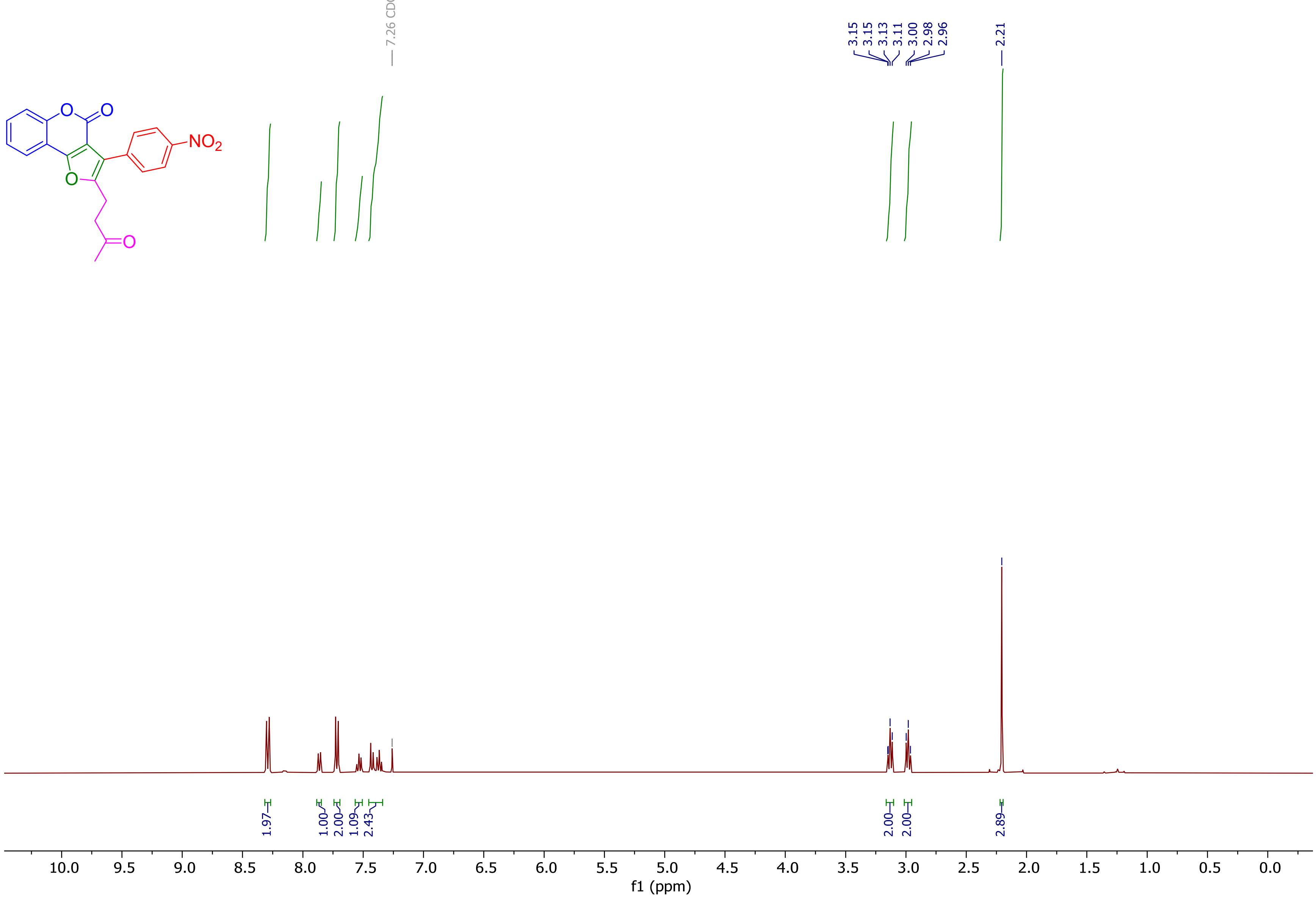
Compound 13c (500 MHz, Chloroform-d)



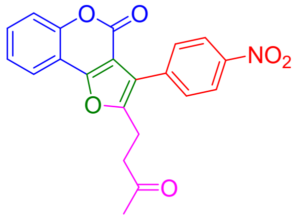
Compound 13c (126 MHz, Chloroform-d)

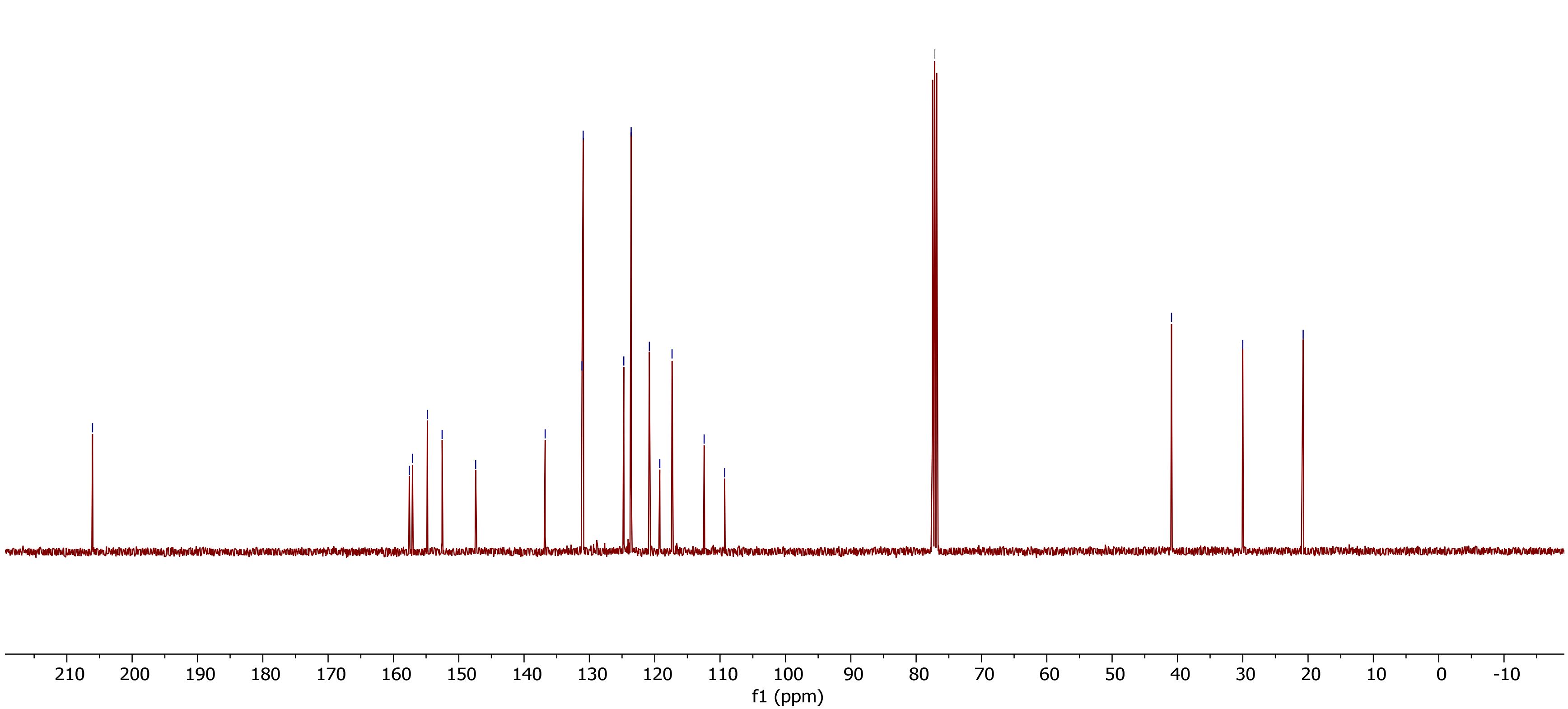


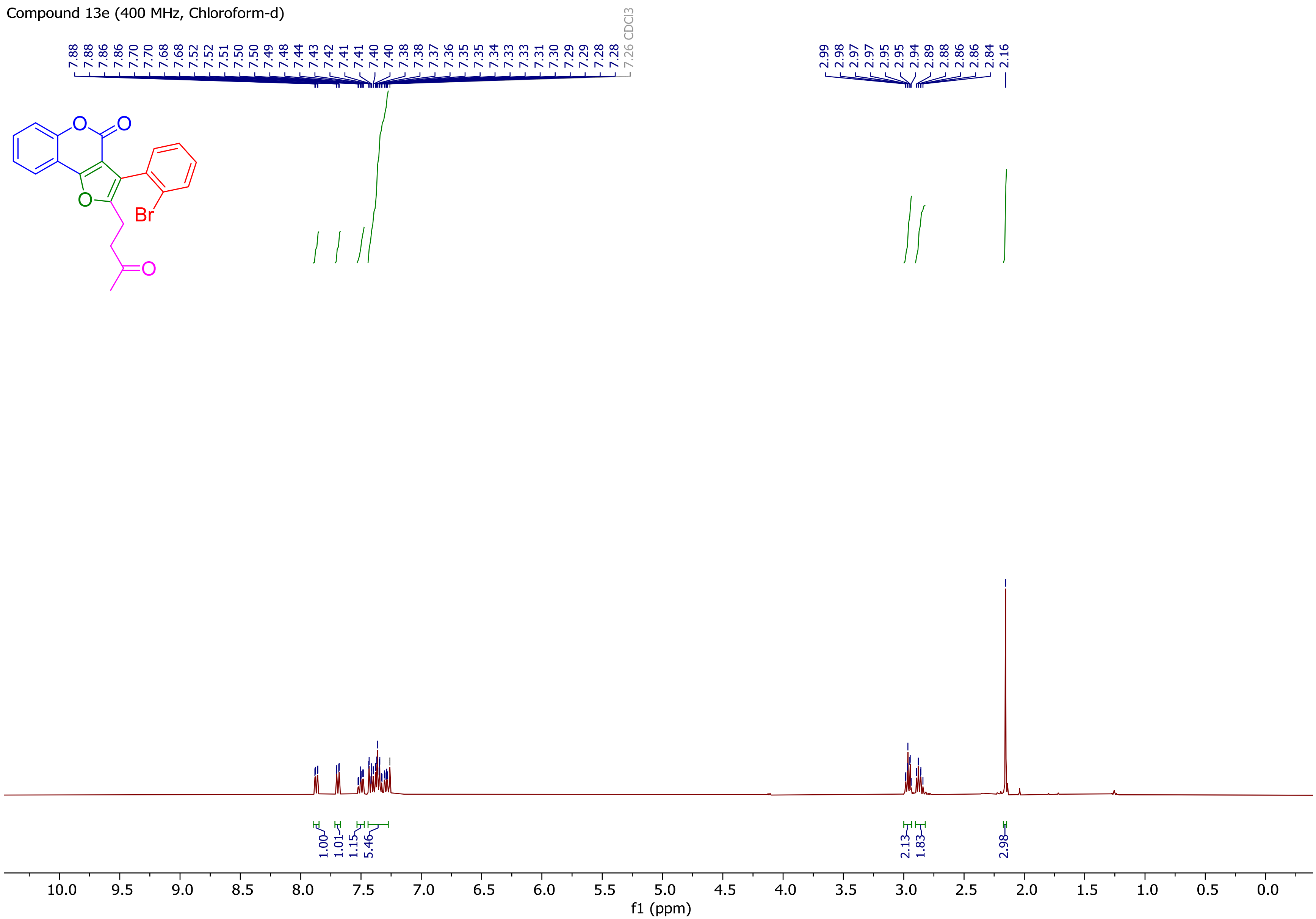
Compound 13d (400 MHz, Chloroform-d)



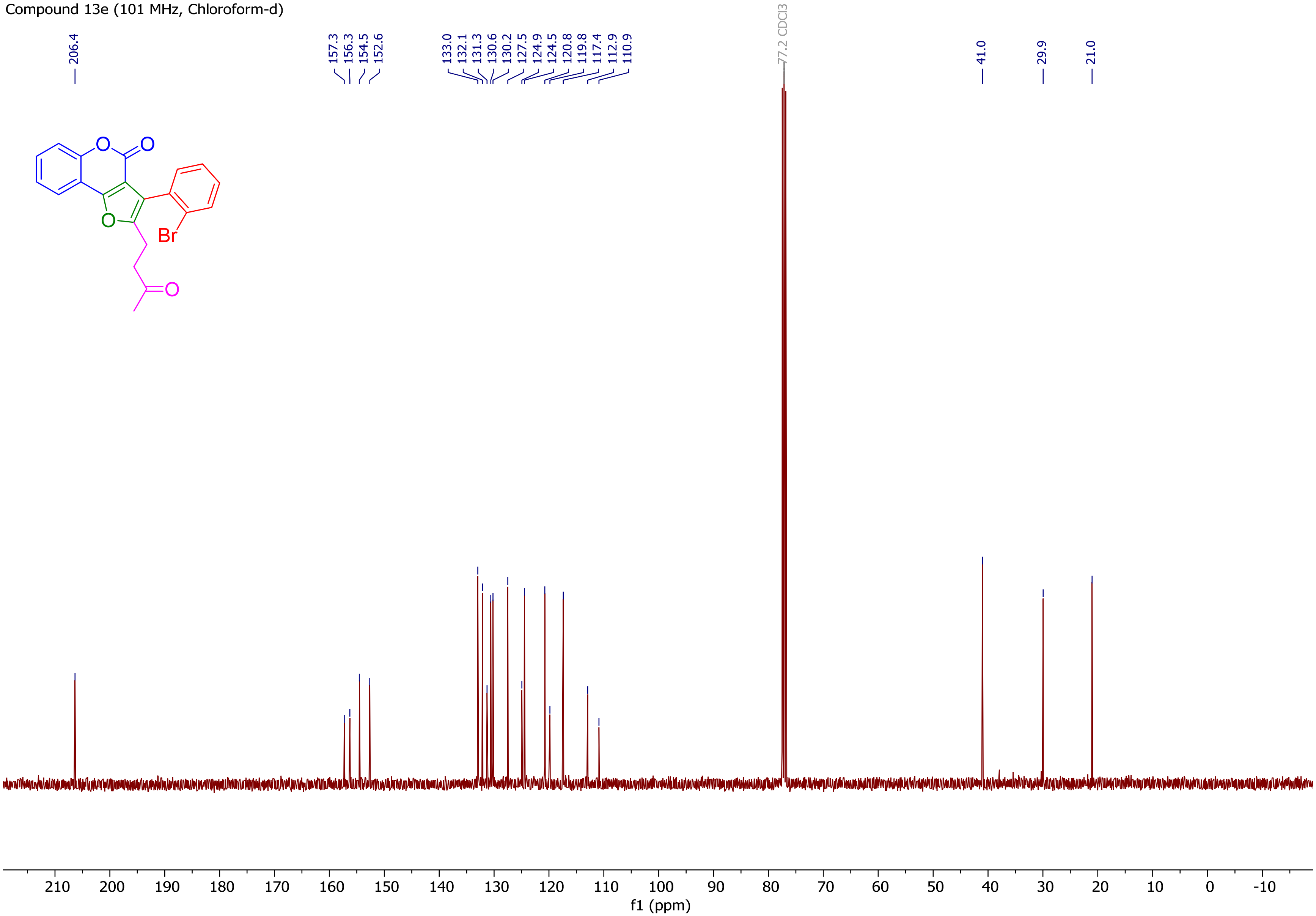
Compound 13d (101 MHz, Chloroform-d)



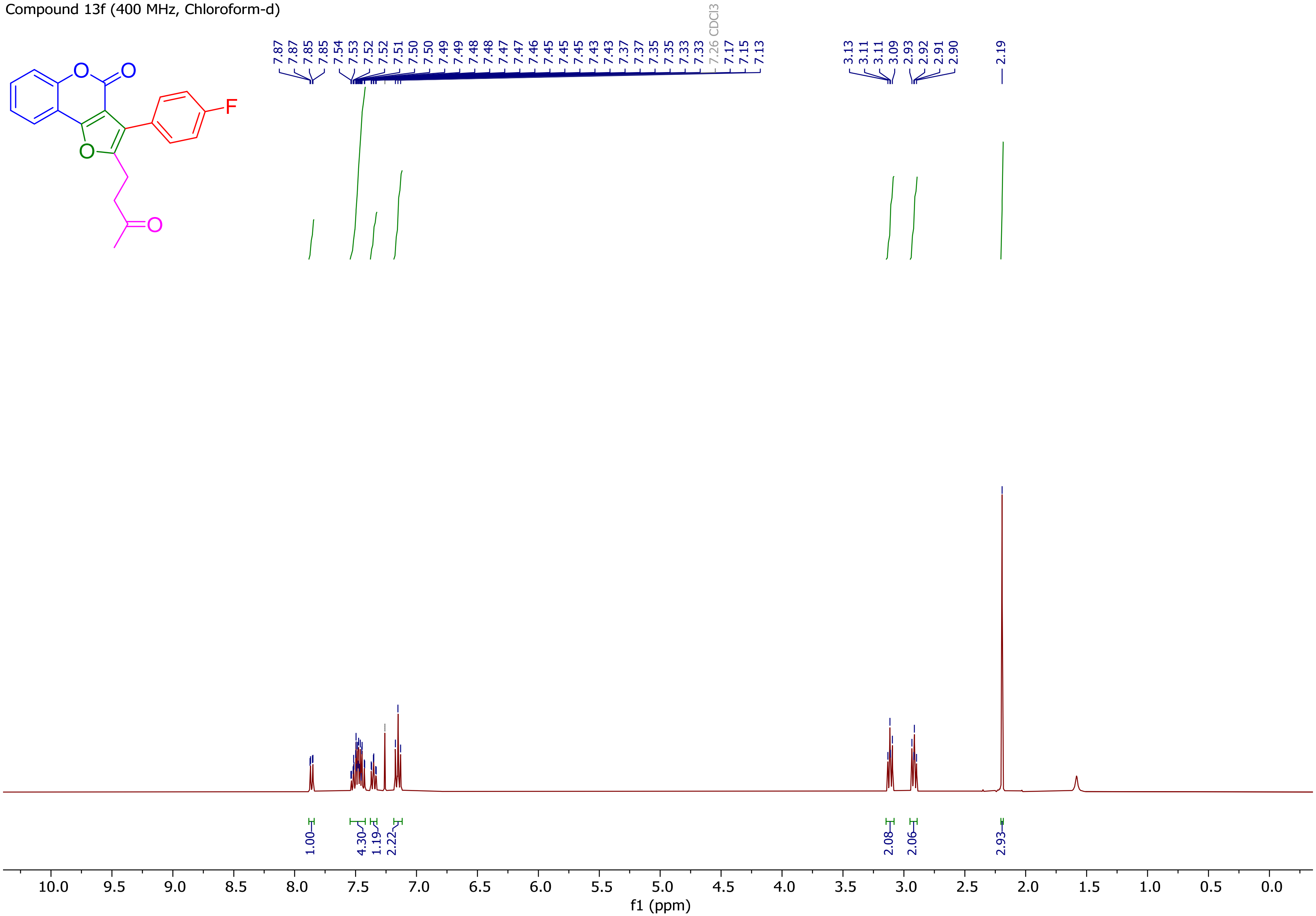



Compound 13e (400 MHz, Chloroform-d)
7.88
7.88
7.86
7.70
7.70
7.68
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.38
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.31
7.30
7.29
7.29
7.28
7.26 CDCl3
2.99
2.98
2.97
2.97
2.95
2.95
2.94
2.89
2.88
2.86
2.86
2.84
2.16
O
O
O
Br
O
1.00
1.01
1.15
5.46
2.13
1.83
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

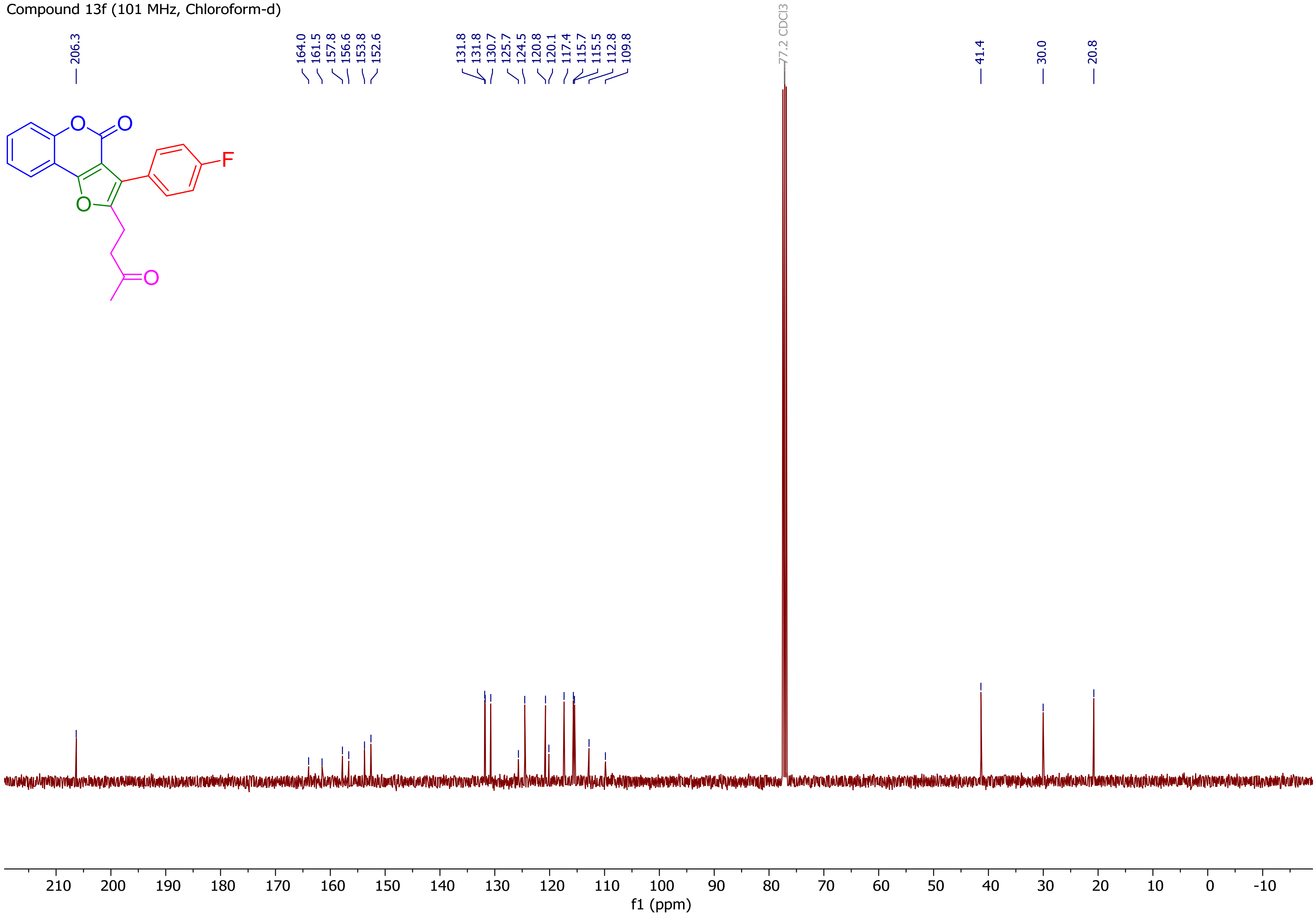
Compound 13e (101 MHz, Chloroform-d)



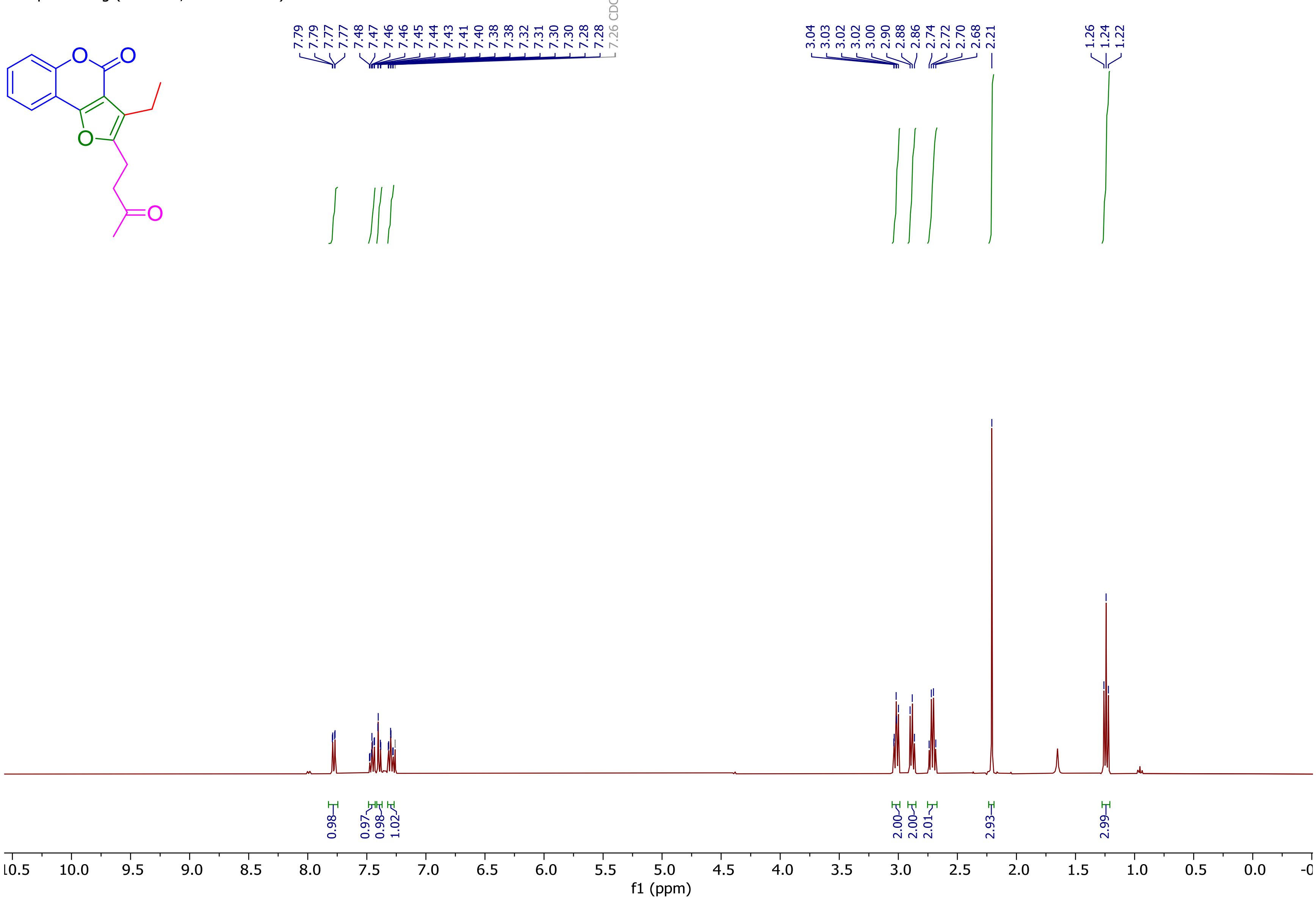
Compound 13f (400 MHz, Chloroform-d)



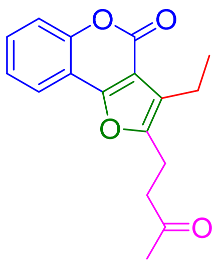
Compound 13f (101 MHz, Chloroform-d)

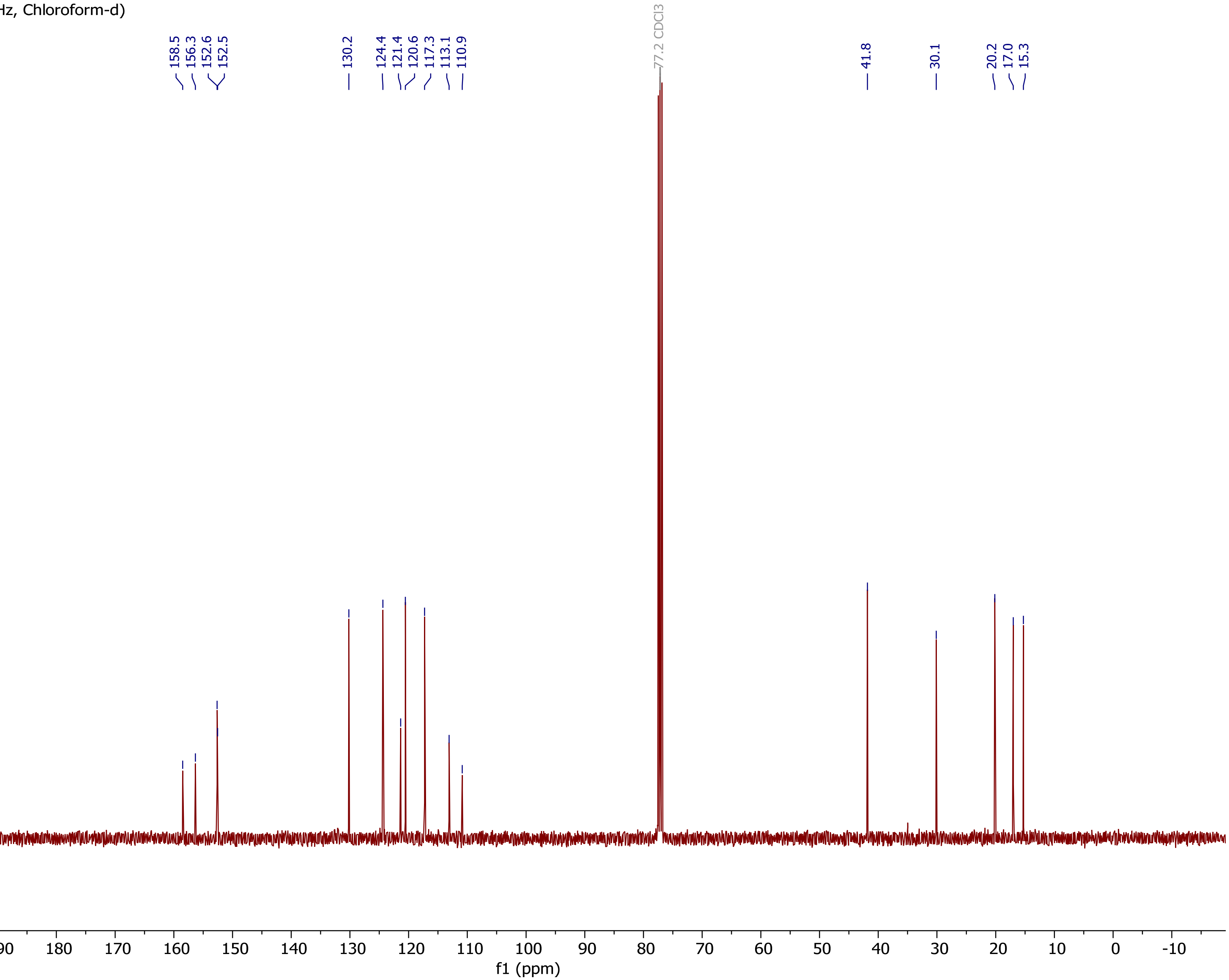


Compound 13g (400 MHz, Chloroform-d)

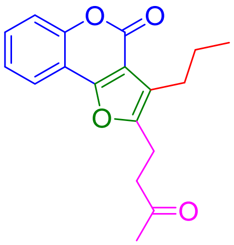


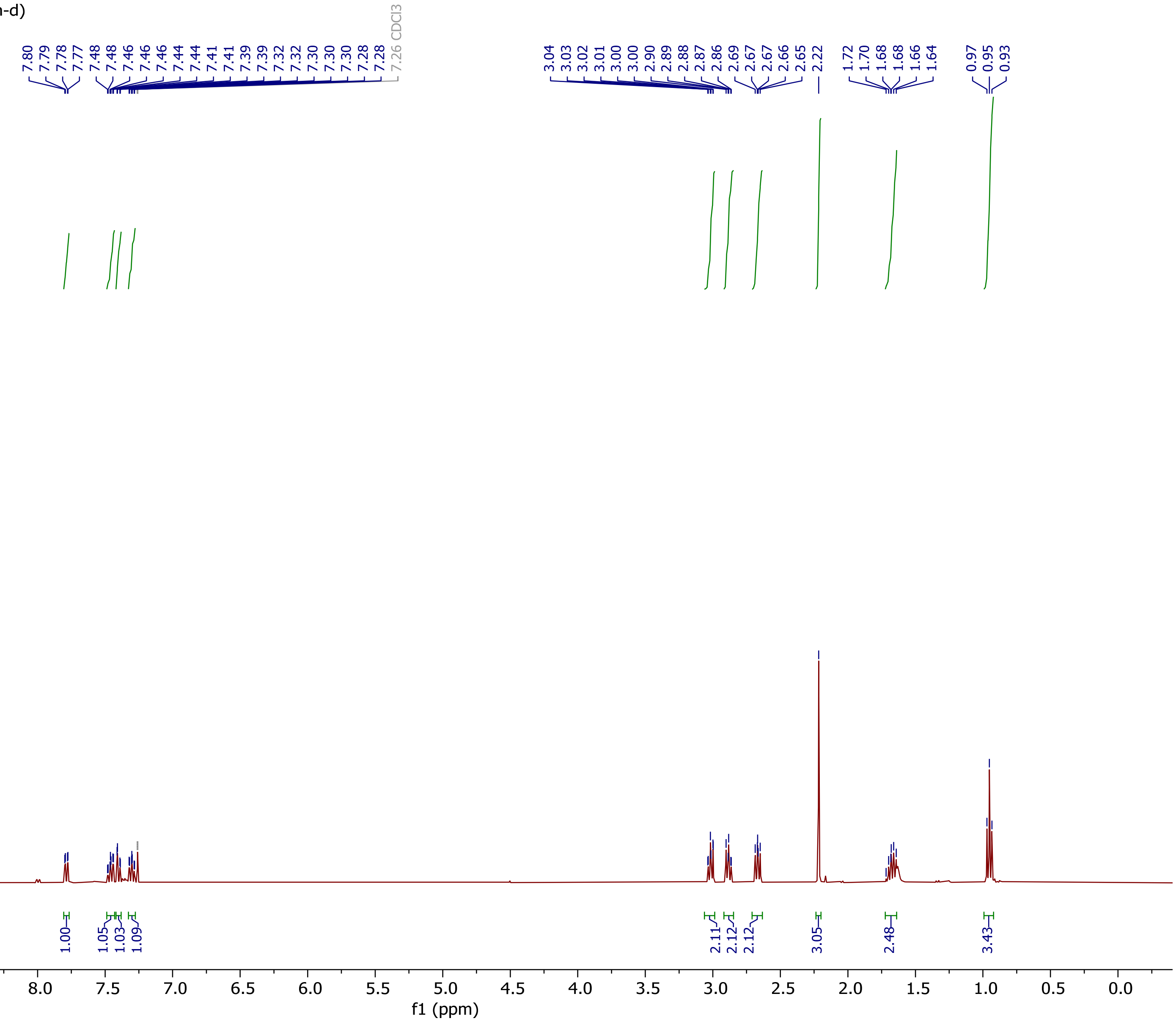
Compound 13g (101 MHz, Chloroform-d)



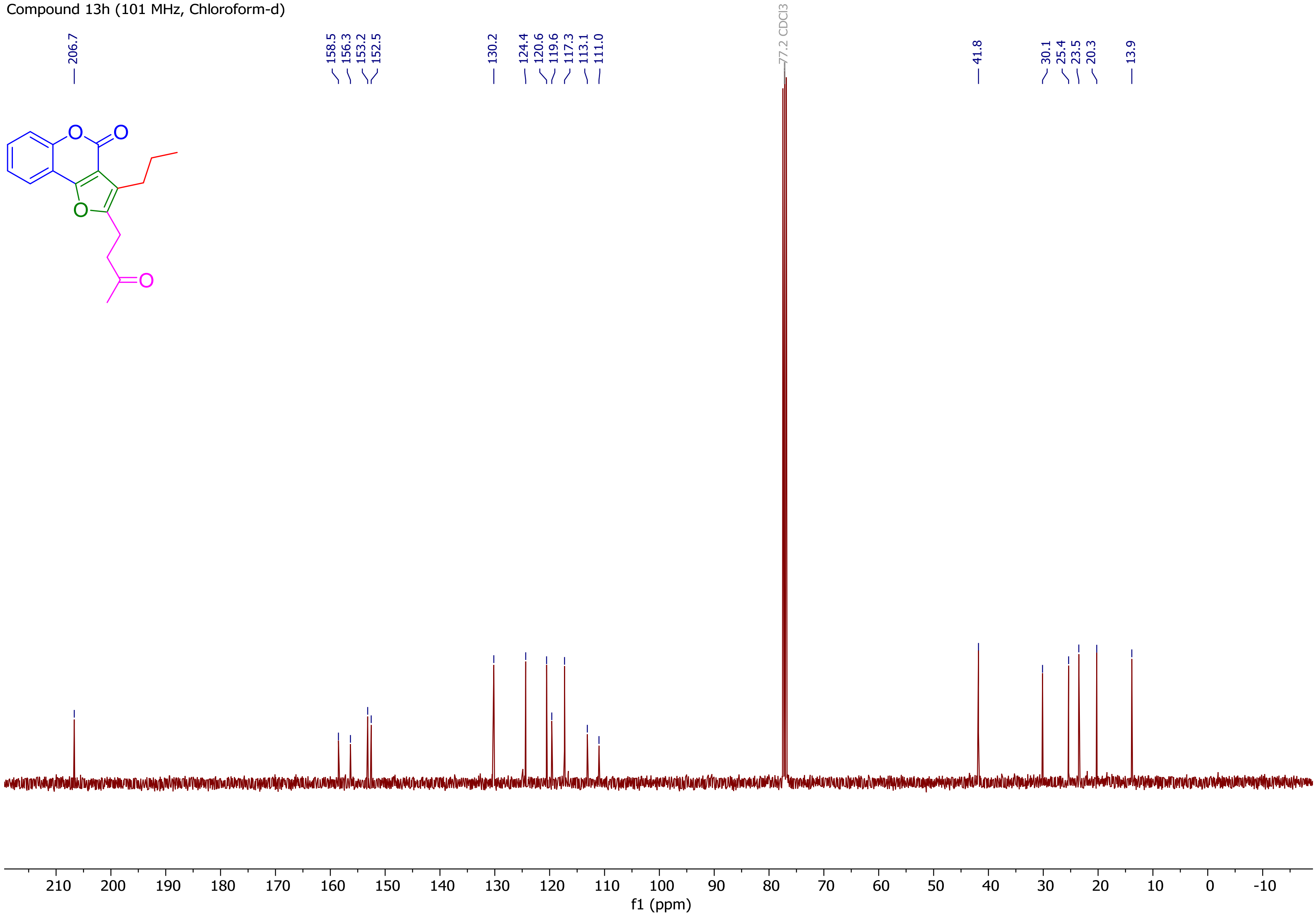


Compound 13h (400 MHz, Chloroform-d)

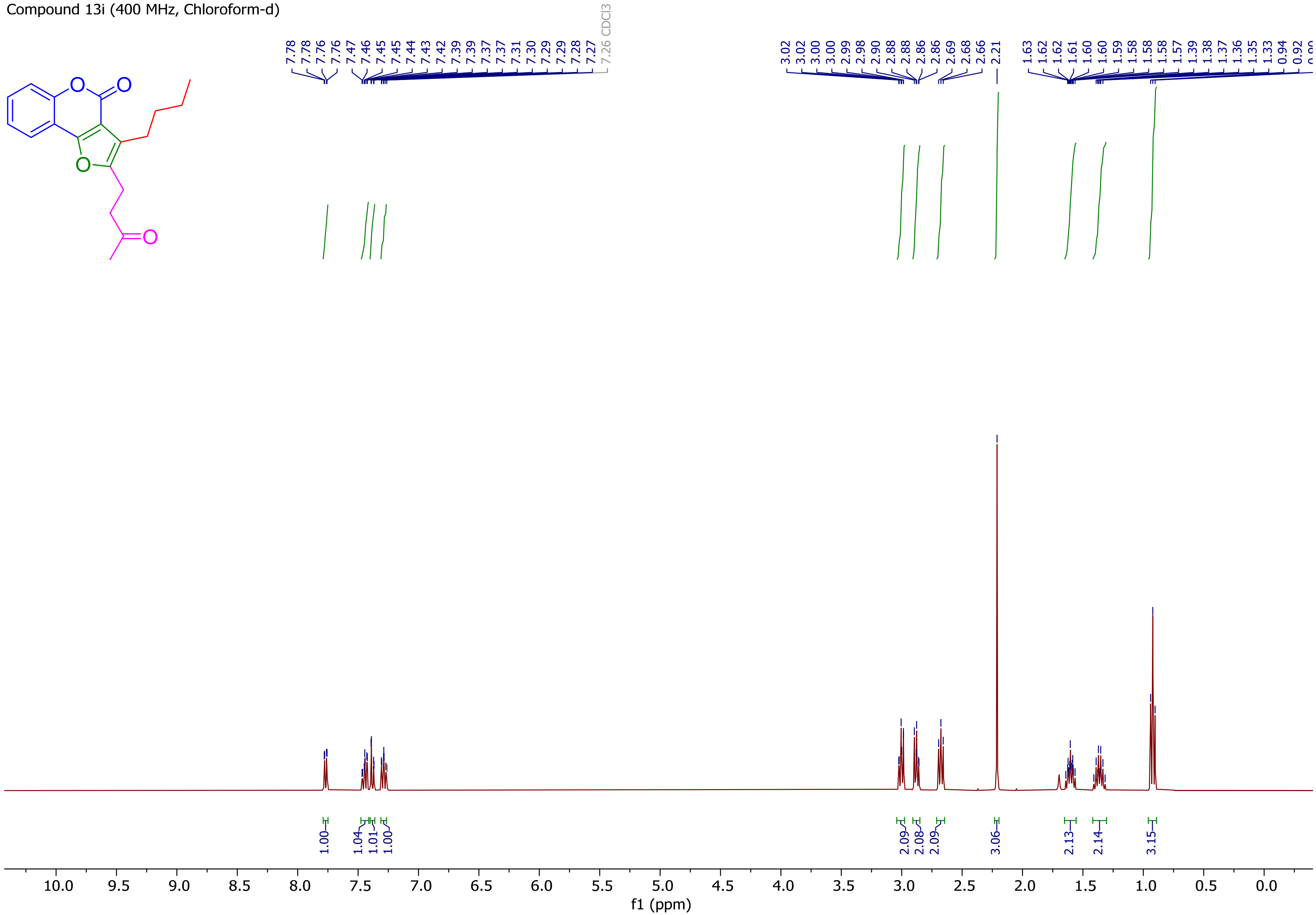




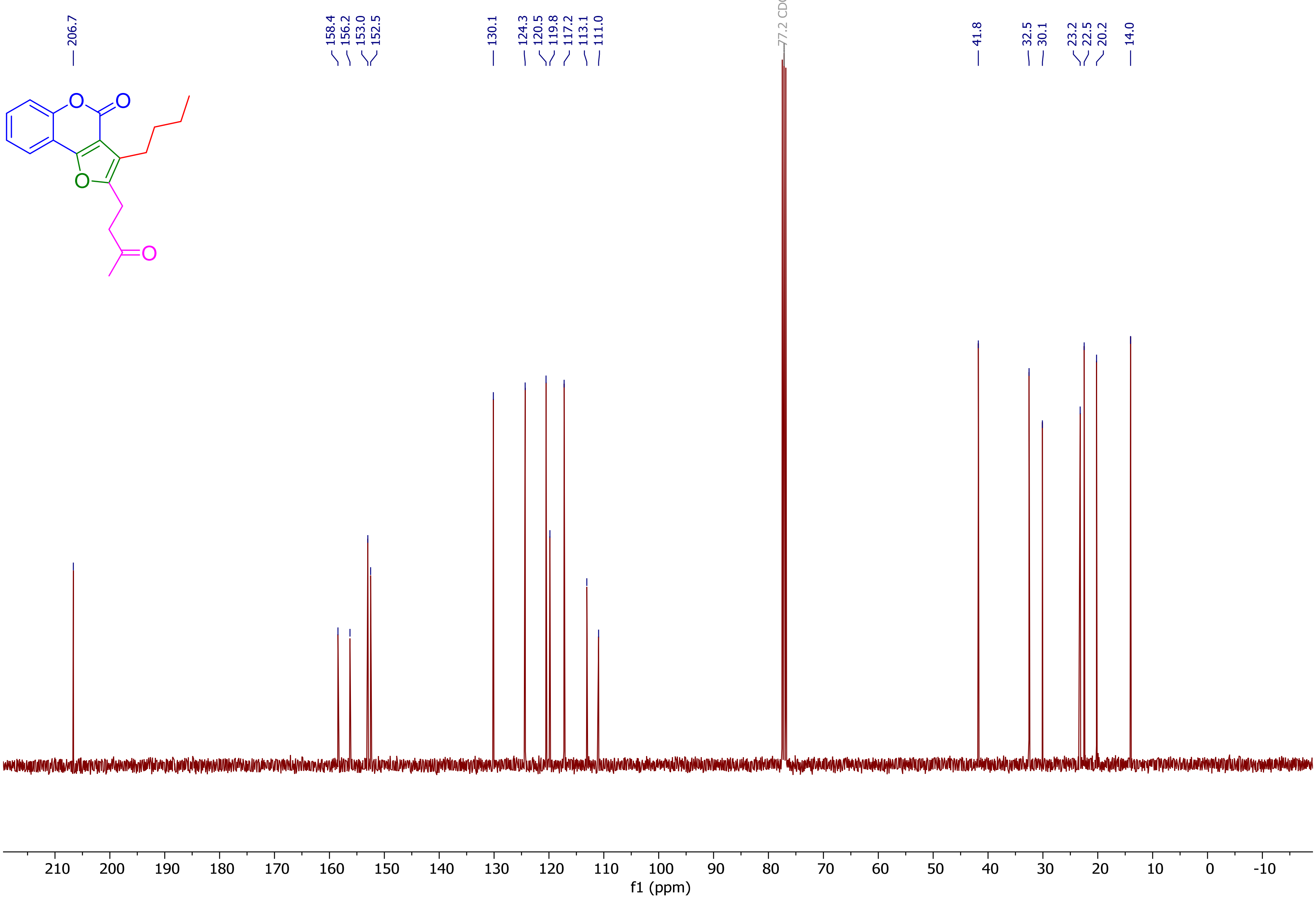
Compound 13h (101 MHz, Chloroform-d)



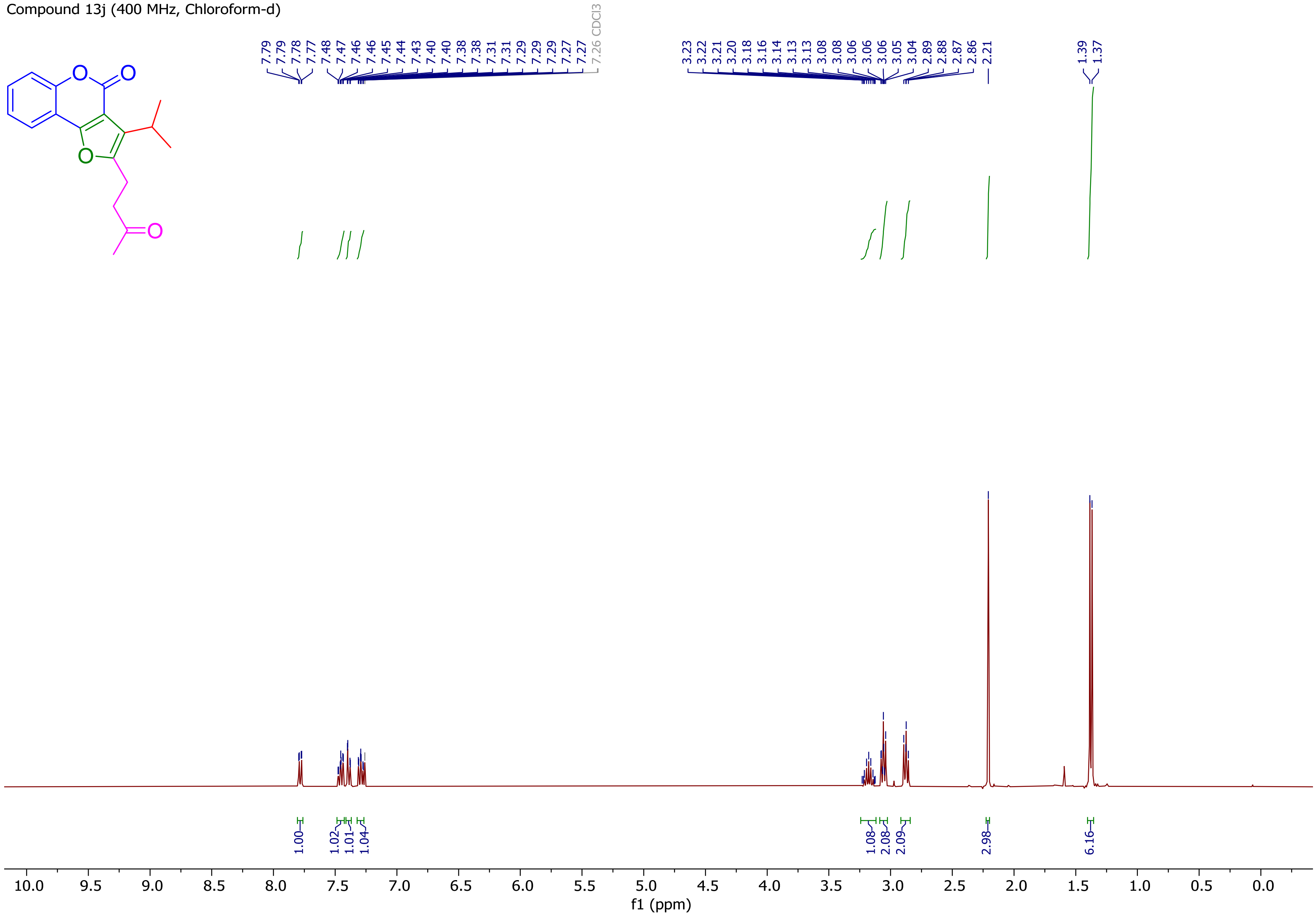
Compound 13i (400 MHz, Chloroform-d)



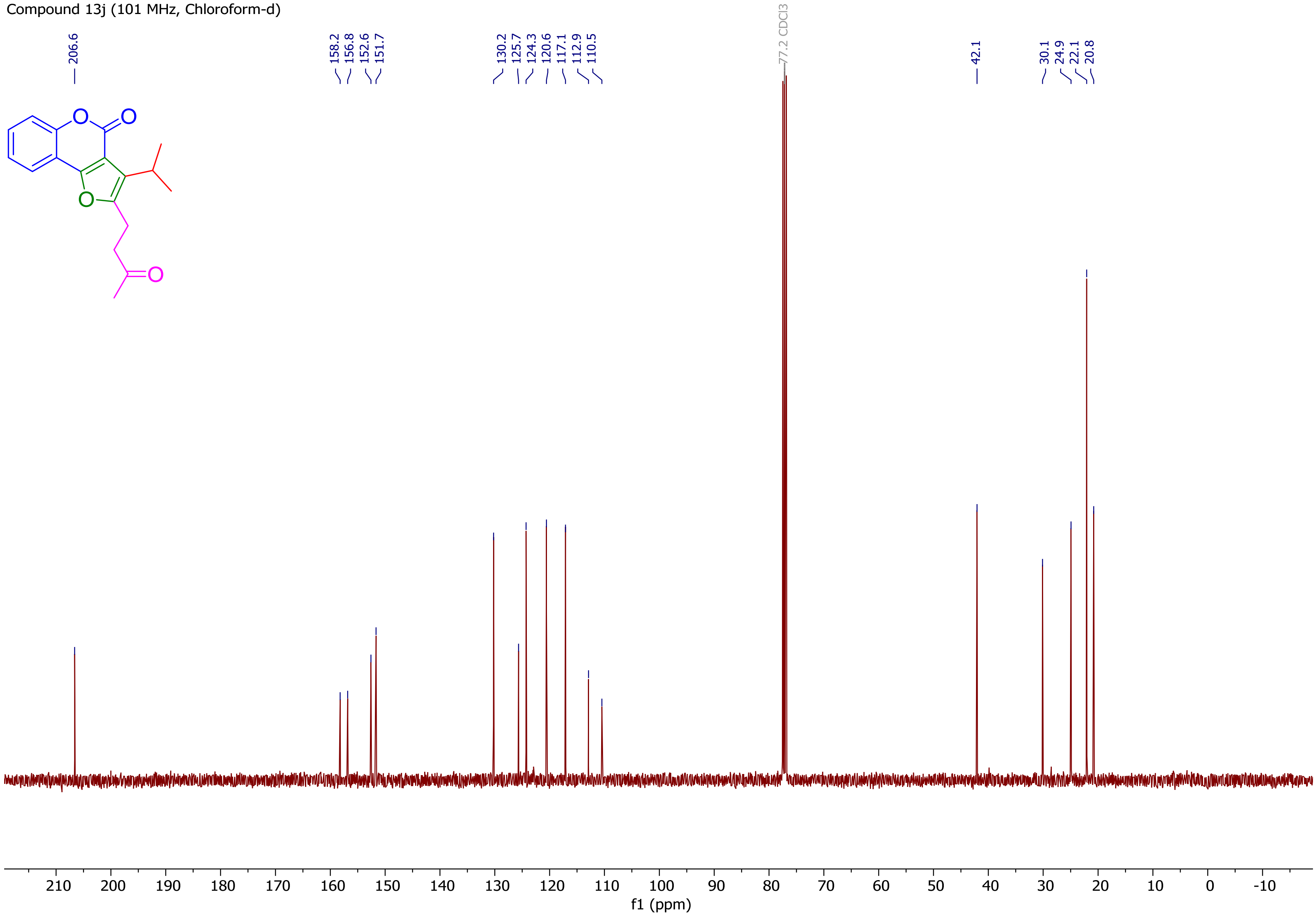
Compound 13i (101 MHz, Chloroform-d)



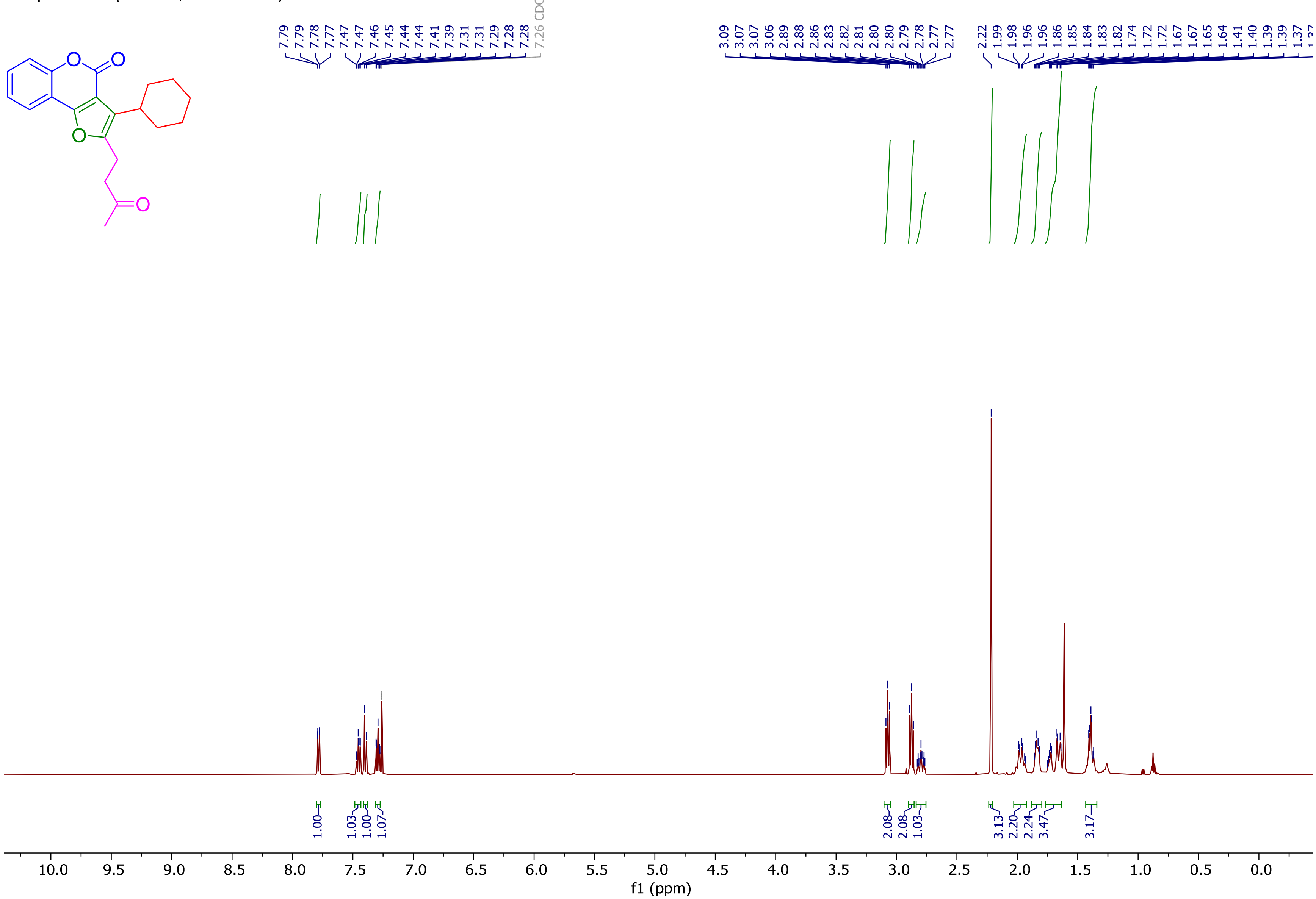
Compound 13j (400 MHz, Chloroform-d)



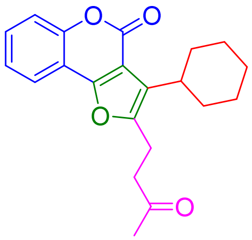
Compound 13j (101 MHz, Chloroform-d)

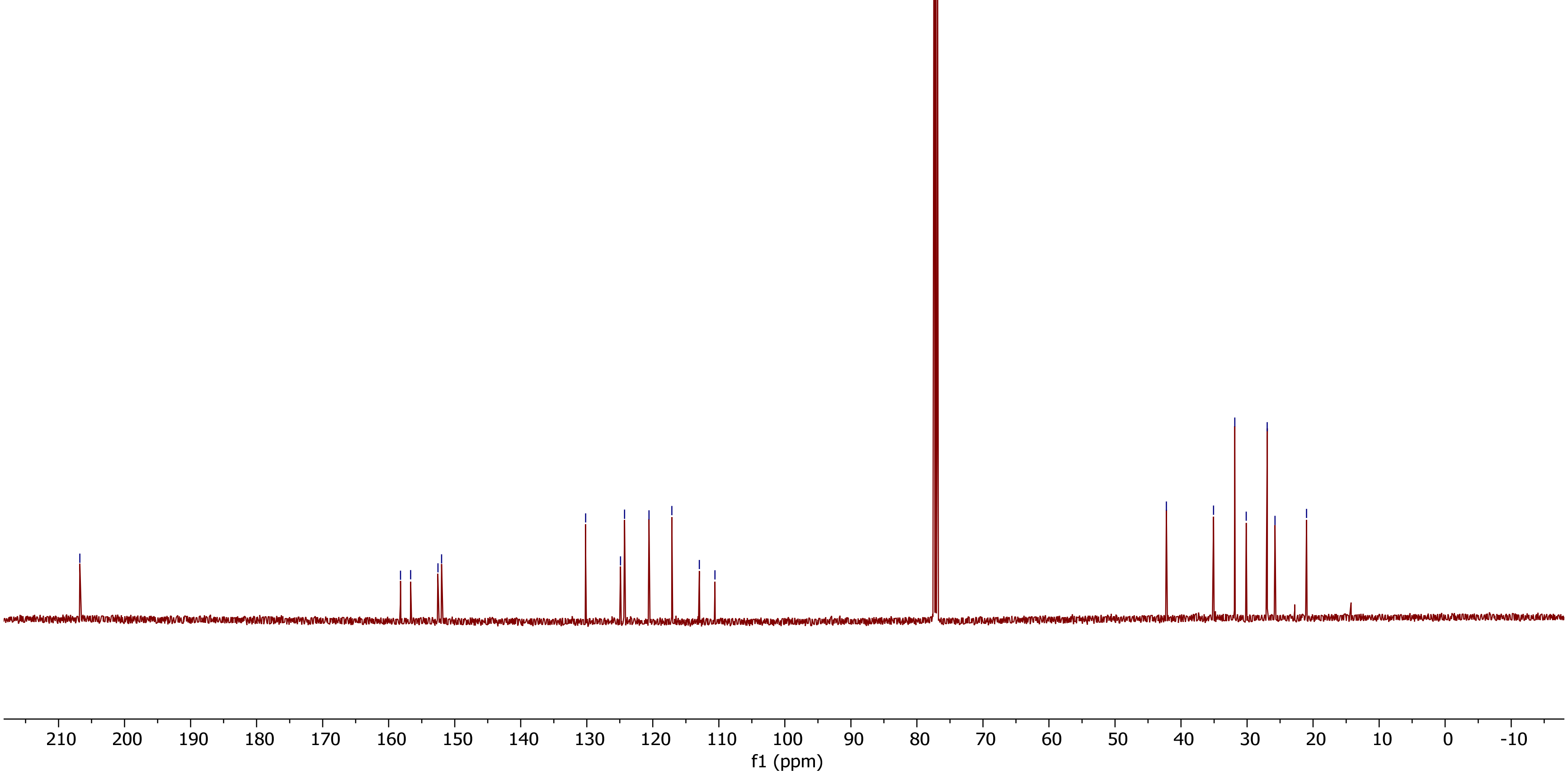


Compound 13k (500 MHz, Chloroform-d)

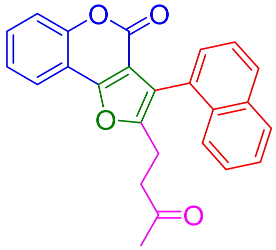


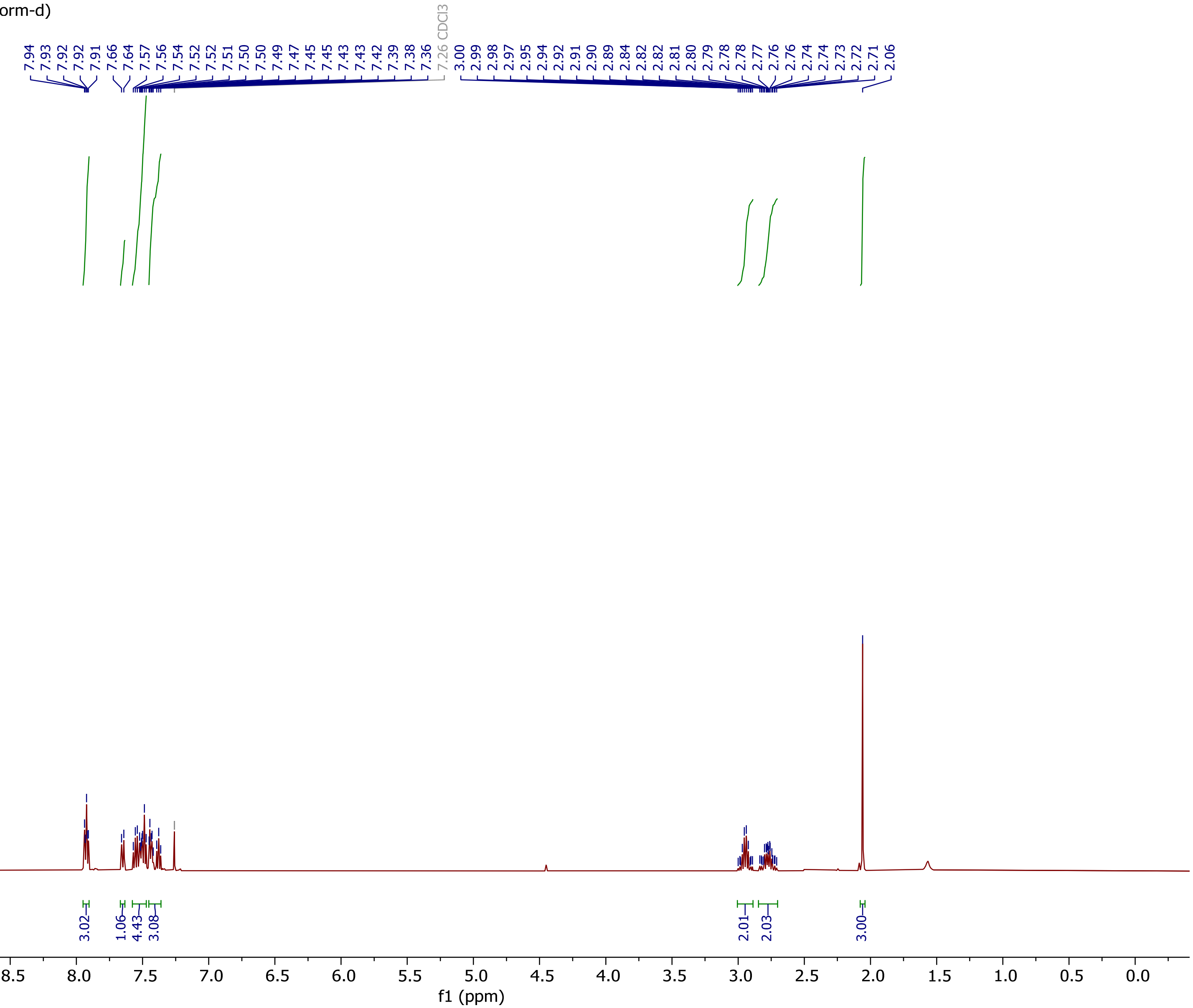
Compound 13k (126 MHz, Chloroform-d)



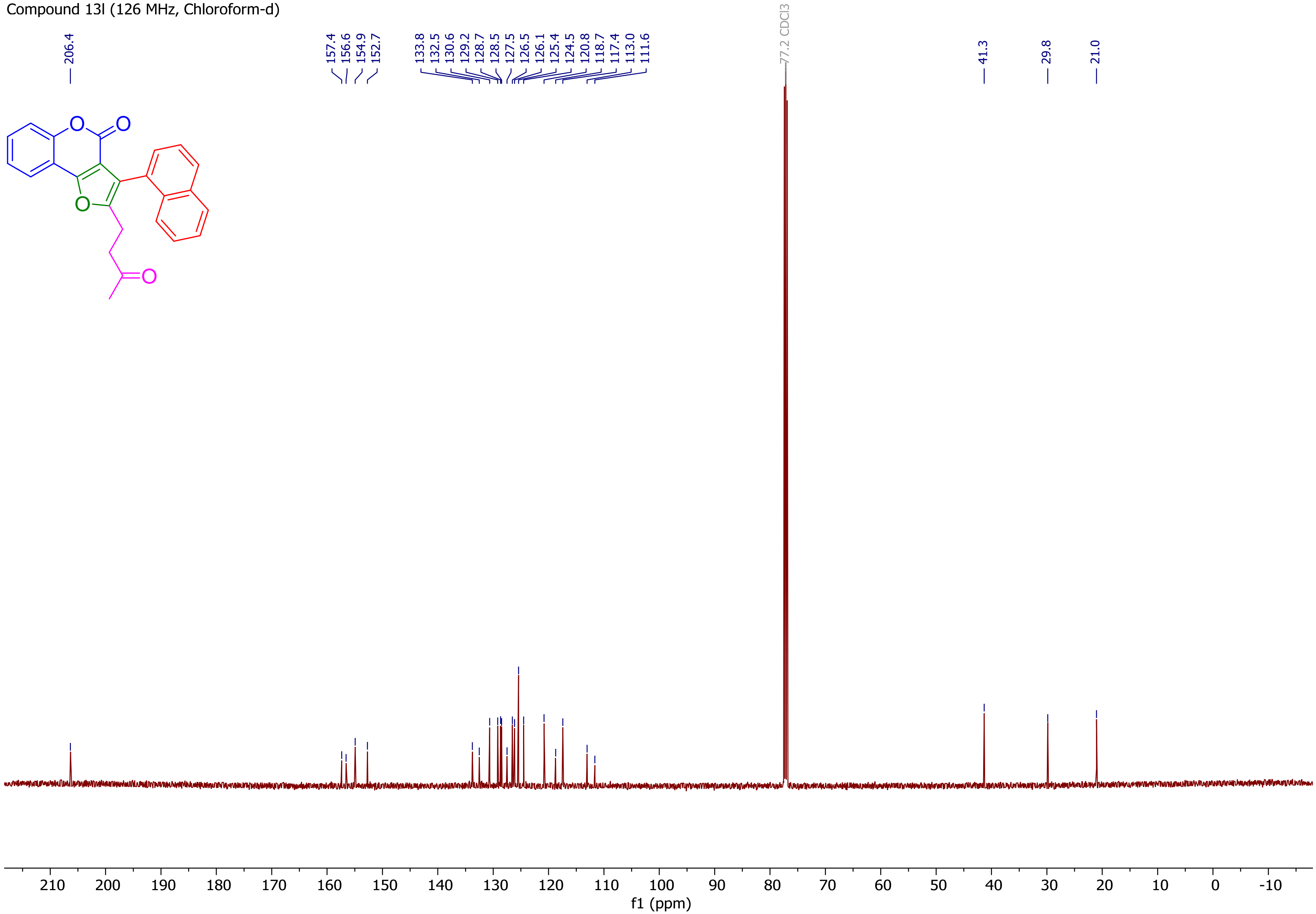


Compound 13l (500 MHz, Chloroform-d)

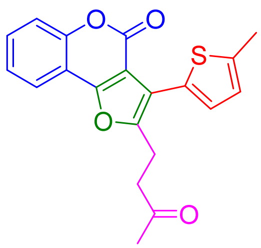


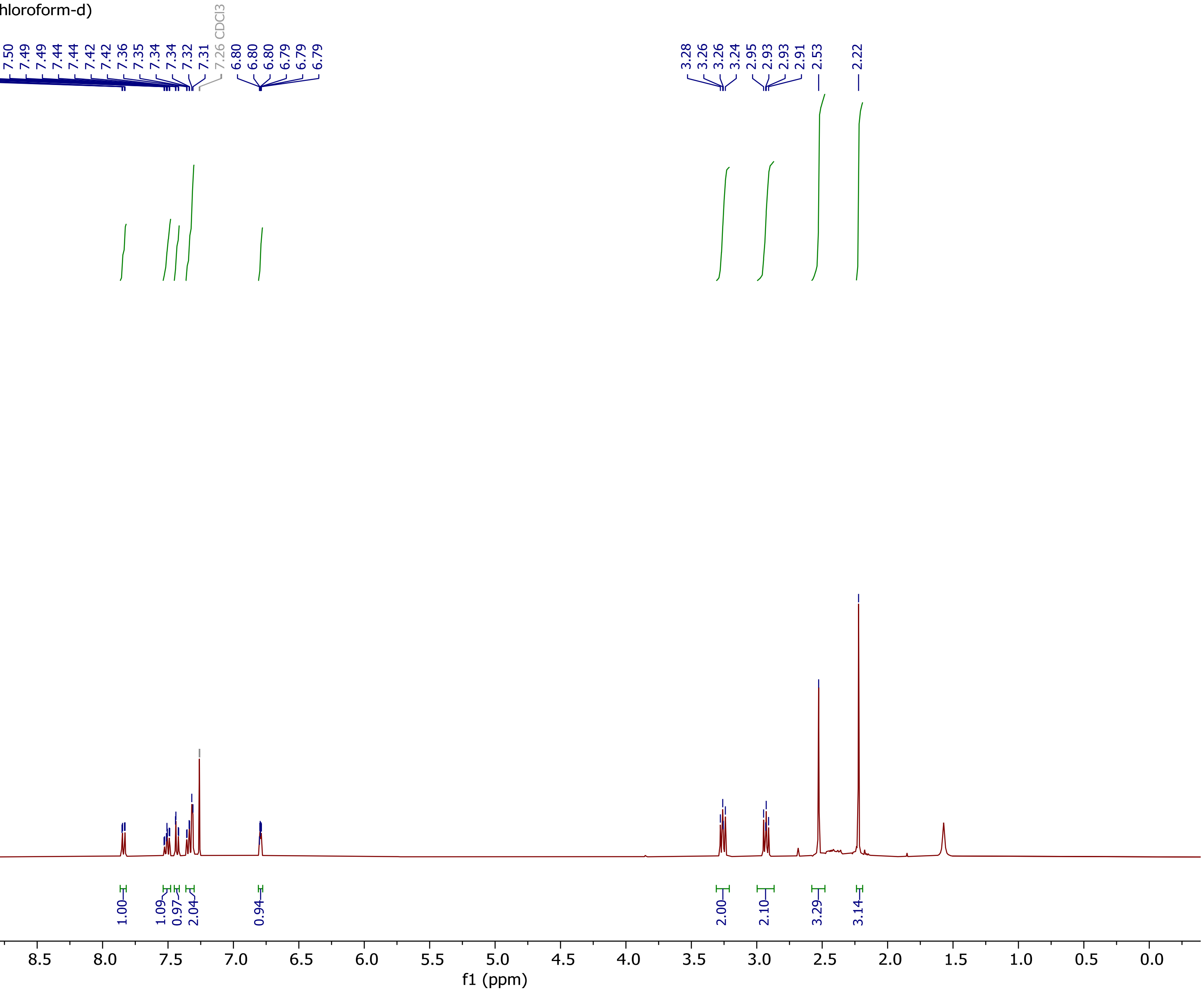


Compound 13l (126 MHz, Chloroform-d)

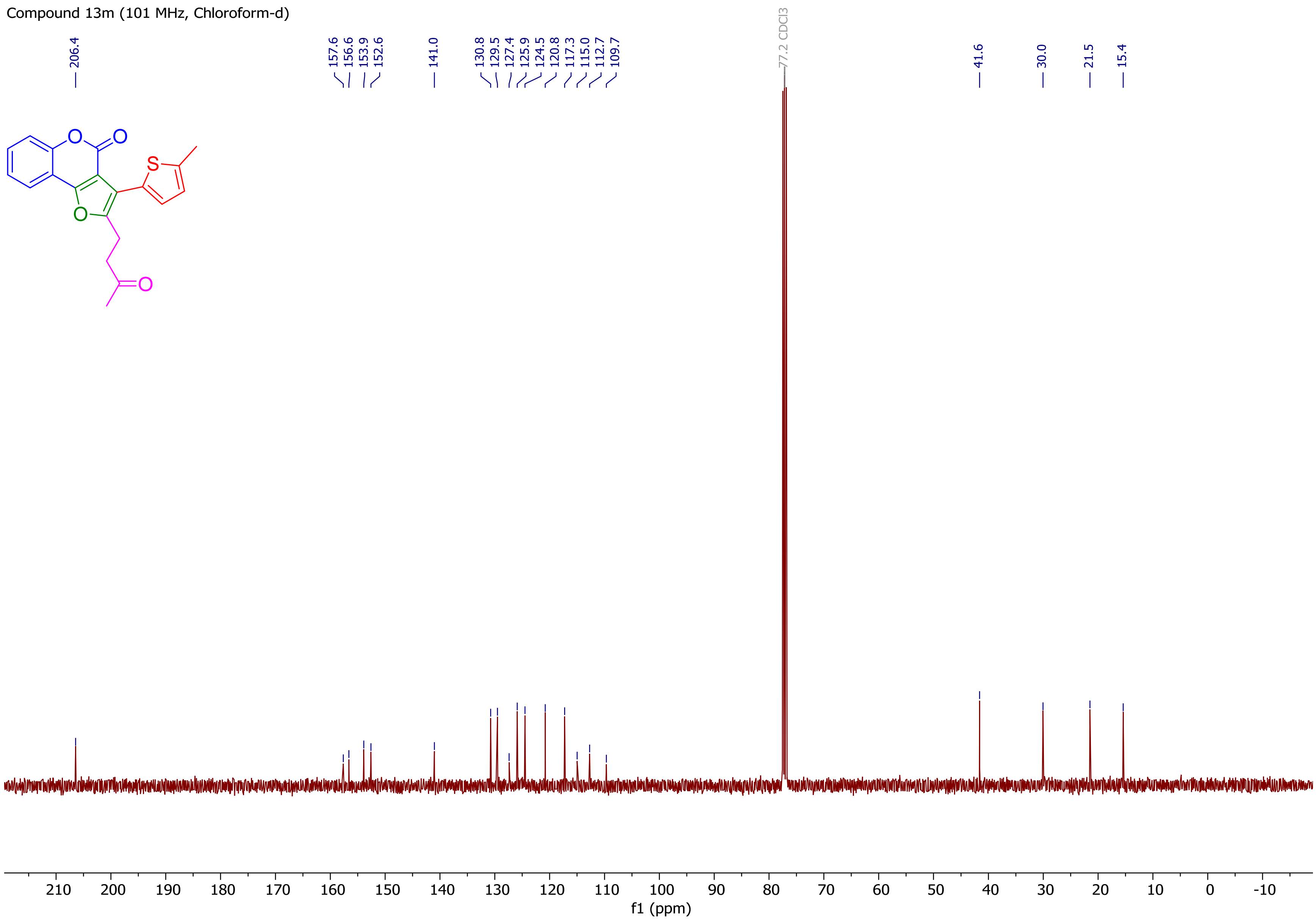


Compound 13m (400 MHz, Chloroform-d)

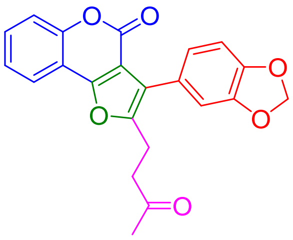


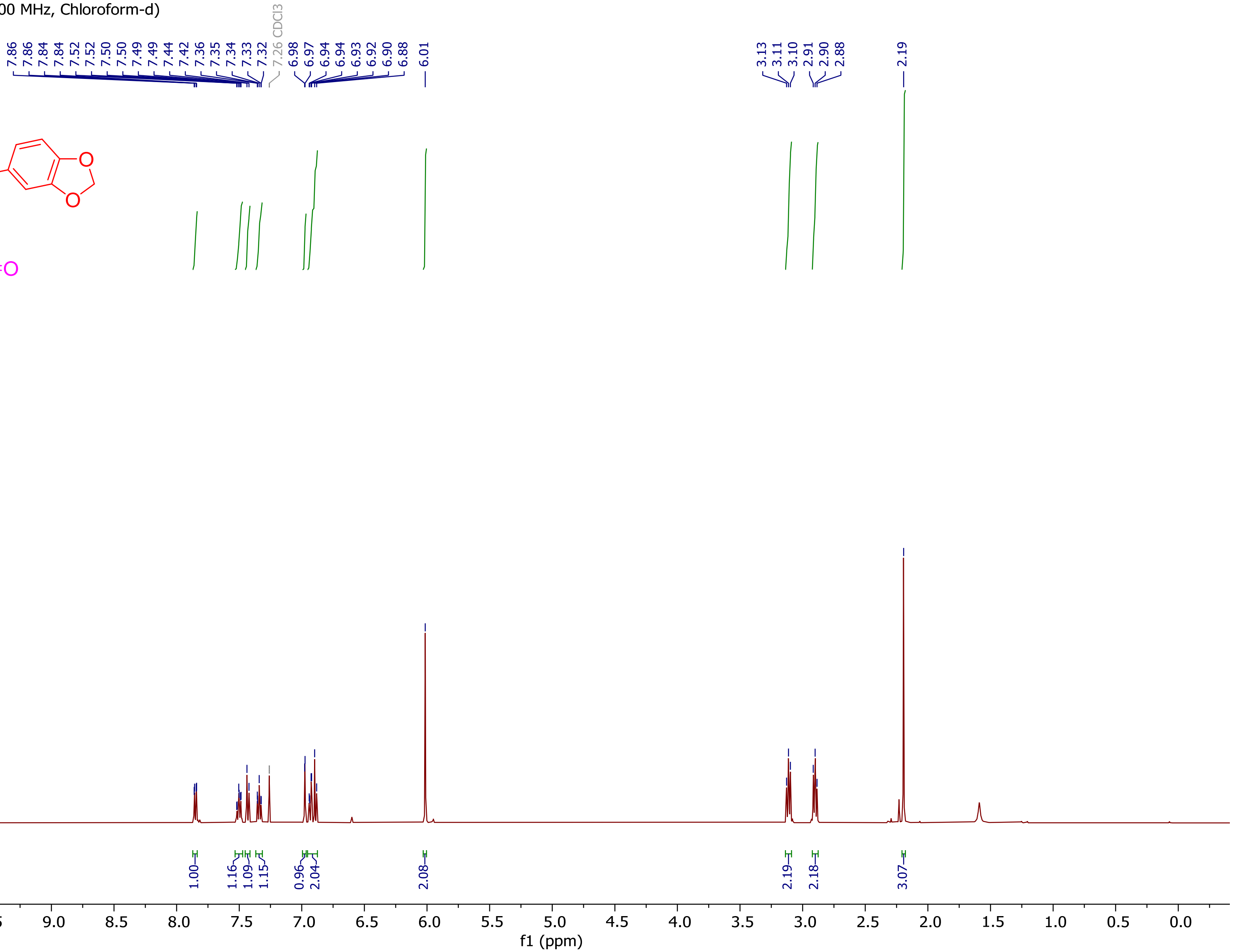


Compound 13m (101 MHz, Chloroform-d)

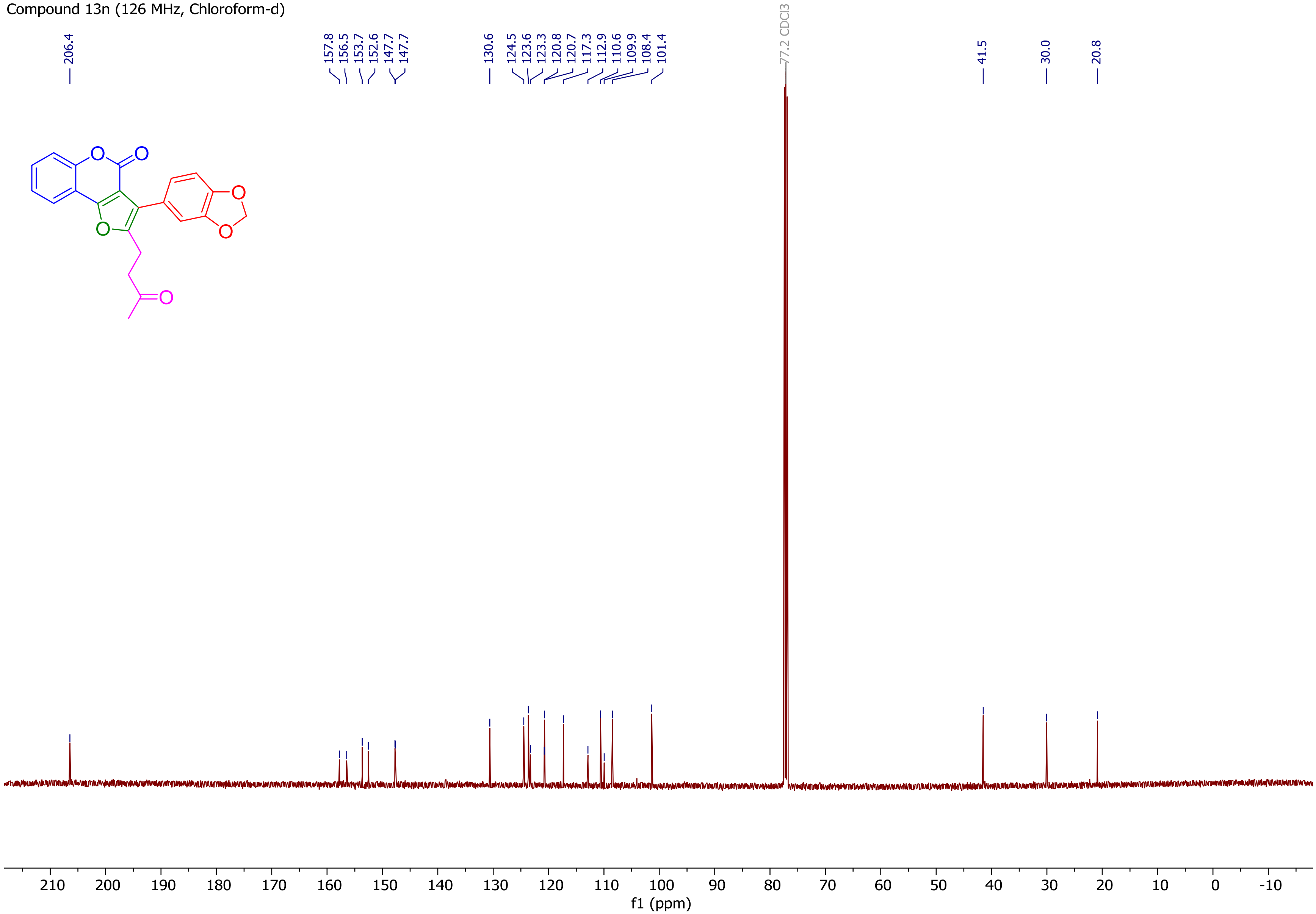


Compound 13n (500 MHz, Chloroform-d)



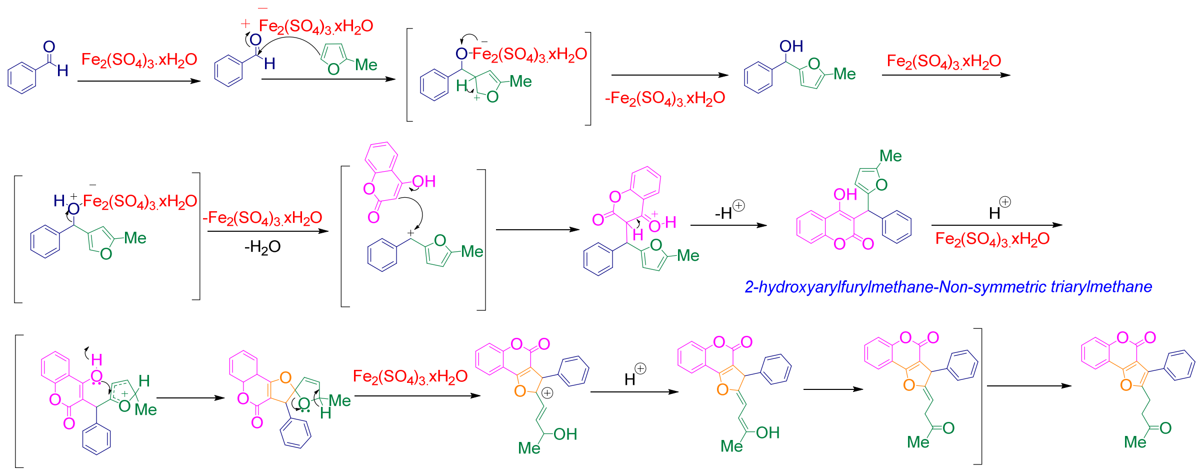


Compound 13n (126 MHz, Chloroform-d)



IV. Plausible mechanism for Fe–catalyzed domino reaction

Scheme S1. Plausible mechanism for Fe–catalyzed domino intramolecular nucleophilic substitution of 4–hydroxy chromen–2–one/ ring–opening of activated arene



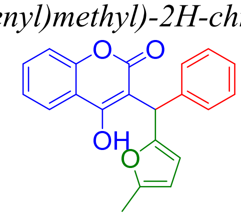
During the course of these reactions we observed that the initial yellow color of the suspension changed to dark red, providing a clue to the mechanistic pathway of this reaction. A plausible reaction mechanism for the Fe–catalyzed domino process is shown (Scheme S1). In the first step, coordination of the carbonyl *O*−atom with a Fe–atom results in a color change. Concurrently, a nucleophilic attack by the activated arene, 2–methylfuran–3–*C* atom at the carbonyl–*C* atom takes place. In the second step, elimination of ferric sulfate hydroxide occurs with subsequent nucleophilic attack by the enol–part of 4–hydroxycoumarin–3–*C* atom at the carbonyl–*C* atom. This is immediately followed by a proton transfer and elimination of water to afford 2–hydroxyarylfurylmethane, a non–symmetric triarylmethane. The 2−hydroxyarylfurylmethane undergoes a domino–reaction, commencing with protonation of the furan ring at the 5^{th} position with subsequent intramolecular nucleophilic attack of the oxygen atom by the hydroxyl group of 4–hydroxycoumarin at the α–position of the furanium ion. Finally, the reaction proceeds further with opening of the furan ring and recyclization to afford furo[3,2,–*c*]coumarin. Despite the favorable orientation of the –OH group, a mechanism with the participation of a molecule of water and the formation of an intermediate 1,4–dicarbonyl compound is also not excluded, since selective protonation of the furan ring is not required in this case.

V. General procedure for the synthesis of non-symmetric triarylmethanes 14 a-n

A 50 mL round bottom flask was charged with aldehydes (1 mmol, 1.0 equiv), 2-methyl furan (1 mmol, 1 equiv) and 4- hydroxycoumarin (1 mmol, 1 equiv) in anhydrous THF (10 mL). To this reaction mixture, $Fe_2(SO_4)_3$•$x$$H_2O$ (15 mol%, 60 mg) was added and the solution was stirred at reflux temperature for 5 h in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by rotovap. The residue was dissolved in DCM (15 mL), washed using distilled water (3 × 15 mL) and dried over $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate).

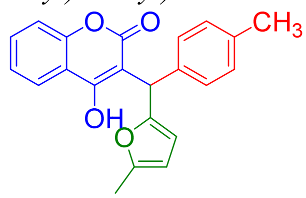
The general method from above was used for the preparation of following non-symmetrical triarylmethanes:

4-hydroxy-3-((5-methylfuran-2-yl)(phenyl)methyl)-2H-chromen-2-one **14a**



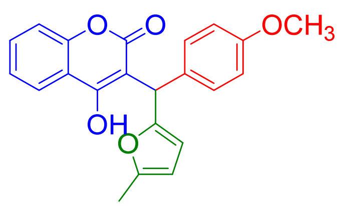
Brown solid, 278.7 mg, 87% yield. m.p. 64-66°C; R_f = 0.54 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:25, SiO_2);IR (film) ν_{max}/cm^{-1} 3347, 3060, 2923, 1713, 1610, 756; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.37 – 7.26 (m, 6H), 6.11 (d, *J* = 3.1 Hz, 1H), 5.97 (dd, *J* = 3.2, 1.3 Hz, 1H), 5.94 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 161.4, 153.3, 152.8, 152.1, 138.4, 132.3, 129.2, 127.9, 127.7, 124.1, 123.5, 116.6, 116.2, 110.4, 106.7, 105.5, 40.9, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{21}H_{16}O_4$ 355.0941; Found 355.0949.

4-hydroxy-3-((5-methylfuran-2-yl)(p-tolyl)methyl)-2H-chromen-2-one **14b**



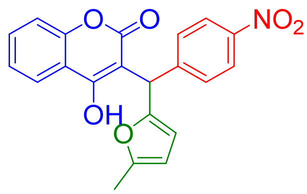
Brown oil, 283.4 mg, 82% yield.; R_f = 0.51 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3358, 3053, 2986, 2923, 1702, 820; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.47 (s, 1H), 7.35 – 7.26 (m, 2H), 7.16 (s, 4H), 6.12 (d, *J* = 3.1 Hz, 1H), 5.97 (dd, *J* = 3.2, 1.3 Hz, 1H), 5.91 (s, 1H), 2.34 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 161.3, 153.1, 152.8, 152.2, 137.5, 135.3, 132.3, 129.9, 127.8, 124.0, 123.5, 116.5, 116.2, 110.2, 106.7, 105.7, 40.6, 21.2, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{22}H_{18}O_4$ 369.1097; Found 369.1112.

4-hydroxy-3-((4-methoxyphenyl)(5-methylfuran-2-yl)methyl)-2H-chromen-2-one **14c**



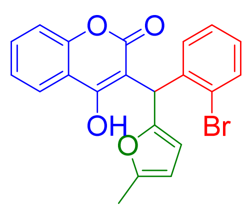
Brown oil, 304.2 mg, 84% yield.; R_f = 0.48 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3360, 3054, 2986, 1706, 1627, 738; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.44 (s, 1H), 7.30 (ddd, *J* = 15.9, 8.2, 1.1 Hz, 2H), 7.21 – 7.16 (m, 2H), 6.90 – 6.84 (m, 2H), 6.10 (d, *J* = 3.1 Hz, 1H), 5.96 (dd, *J* = 3.1, 1.2 Hz, 1H), 5.86 (s, 1H), 3.79 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4, 161.3, 159.2, 153.2, 152.8, 152.4, 132.3, 130.2, 129.1, 124.1, 123.5, 116.6, 116.3, 114.6, 110.2, 106.7, 105.7, 55.4, 40.2, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{22}H_{18}O_5$ 385.1046; Found 385.1051.

4-hydroxy-3-((5-methylfuran-2-yl)(4-nitrophenyl)methyl)-2H-chromen-2-one **14d**



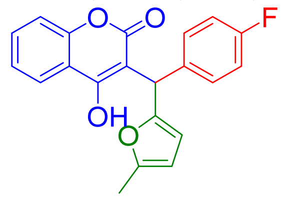
Yellow solid, 308.6 mg, 80% yield. m.p. 195-197°C; R_f = 0.43 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3684, 3366, 3029, 1702, 1627, 669; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.14 (m, 2H), 7.85 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.59 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.37 – 7.28 (m, 2H), 6.17 (d, *J* = 3.1 Hz, 1H), 6.02 (d, *J* = 1.3 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2, 161.8, 153.9, 152.8, 150.6, 147.4, 145.9, 132.9, 128.9, 124.4, 124.2, 123.7, 116.7, 116.0, 111.1, 107.1, 104.4, 40.9, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{21}H_{15}NO_6$ 400.0792; Found 400.0778.

3-((2-bromophenyl)(5-methylfuran-2-yl)methyl)-4-hydroxy-2H-chromen-2-one **14e**



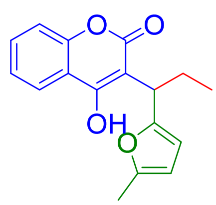
White solid, 332.4 mg, 84% yield. m.p. 186-187°C; R_f = 0.49 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3354, 3054, 2986, 1708, 1629, 738; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.55 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.31 (ddd, *J* = 14.2, 8.3, 1.2 Hz, 3H), 7.26 – 7.15 (m, 2H), 6.09 (s, 1H), 5.95 (qd, *J* = 3.1, 1.1 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.6, 161.7, 154.1, 152.9, 151.0, 137.9, 134.2, 132.4, 129.5, 128.5, 128.1, 125.5, 124.1, 123.4, 116.7, 116.0, 110.8, 106.8, 104.5, 42.4, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{21}H_{15}BrO_4$ 433.0046; Found 433.0049.

3-((4-fluorophenyl)(5-methylfuran-2-yl)methyl)-4-hydroxy-2H-chromen-2-one **14f**



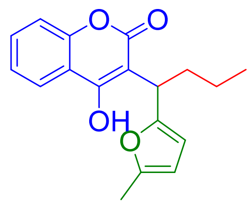
Brown solid, 259.3 mg, 74% yield. m.p. 142-144°C; R_f = 0.44 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3350, 3056, 2987, 1714, 1627, 704; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.35 – 7.26 (m, 2H), 7.26 – 7.20 (m, 2H), 7.05 – 6.98 (m, 2H), 6.10 (d, *J* = 3.1 Hz, 1H), 5.97 (dd, *J* = 3.1, 1.2 Hz, 1H), 5.90 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5, 163.3, 161.4, 161.0, 153.5, 152.8, 152.0, 134.0, 133.9, 132.5, 129.6, 129.5, 124.1, 123.5, 116.6, 116.1, 116.1, 115.9, 110.5, 106.8, 105.3, 40.3, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{21}H_{15}FO_4$ 373.0914; Found 373.0908.

4-hydroxy-3-(1-(5-methylfuran-2-yl)propyl)-2H-chromen-2-one **14g**



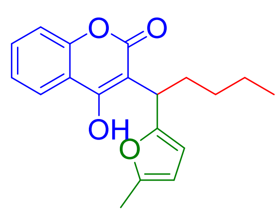
Yellow solid, 216.7 mg, 76% yield. m.p. 79-81°C; R_f = 0.52 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3360, 3019, 2970, 2877, 1702, 756; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.80 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.22 (m, 1H), 6.22 (d, *J* = 3.1 Hz, 1H), 5.96 (dd, *J* = 3.1, 1.2 Hz, 1H), 4.48 (t, *J* = 7.9 Hz, 1H), 2.30 (d, *J* = 1.0 Hz, 3H), 2.13 – 2.02 (m, 1H), 1.92 (dt, *J* = 13.5, 7.3 Hz, 1H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 160.6, 153.2, 152.5, 152.4, 132.0, 123.9, 123.3, 116.5, 116.4, 108.6, 106.7, 106.3, 36.8, 24.8, 13.7, 12.3.; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$Calcd for $C_{17}H_{16}O_4$ 307.0941; Found 307.0951.

4-hydroxy-3-(1-(5-methylfuran-2-yl)butyl)-2H-chromen-2-one **14h**



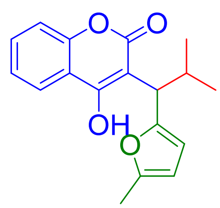
Yellow solid, 232.6 mg, 78% yield. m.p. 101-103°C; R_f = 0.54 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3366, 3054, 2962, 1702, 1627, 705; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.80 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.29 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.21 (d, *J* = 3.1 Hz, 1H), 5.96 (dd, *J* = 3.1, 1.3 Hz, 1H), 4.58 (t, *J* = 7.9 Hz, 1H), 2.31 (d, *J* = 1.0 Hz, 3H), 2.08 – 1.97 (m, 1H), 1.85 (dddd, *J* = 13.5, 9.4, 7.4, 6.2 Hz, 1H), 1.46 – 1.30 (m, 2H), 0.93 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 160.6, 153.4, 152.5, 152.3, 132.0, 123.9, 123.3, 116.5, 116.4, 108.4, 106.7, 106.6, 35.1, 33.8, 20.9, 14.0, 13.7.; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$Calcd for $C_{18}H_{18}O_4$ 321.1097; Found 321.1085.

4-hydroxy-3-(1-(5-methylfuran-2-yl)pentyl)-2H-chromen-2-one **14i**



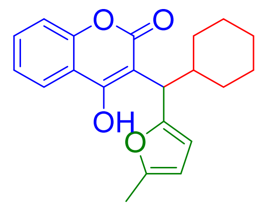
Yellow solid, 269.7 mg, 85% yield. m.p. 100-103°C; R_f = 0.47 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3054, 1702, 1627, 1423, 1265, 705; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.80 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.26 – 7.21 (m, 1H), 6.21 (d, *J* = 3.1 Hz, 1H), 5.96 (dd, *J* = 3.1, 1.2 Hz, 1H), 4.55 (t, *J* = 7.9 Hz, 1H), 2.31 (s, 3H), 2.10 – 1.99 (m, 1H), 1.88 (ddt, *J* = 12.6, 6.6, 4.2 Hz, 1H), 1.41 – 1.28 (m, 4H), 0.91 – 0.84 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 160.6, 153.4, 152.5, 152.4, 132.0, 123.9, 123.3, 116.5, 116.4, 108.4, 106.7, 106.6, 35.2, 31.4, 29.8, 22.7, 14.0, 13.7.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{19}H_{20}O_4$ 335.1254; Found 335.1251.

4-hydroxy-3-(2-methyl-1-(5-methylfuran-2-yl)propyl)-2H-chromen-2-one **14j**



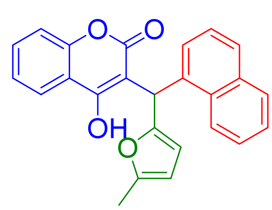
Brown solid, 241.6 mg, 81% yield. m.p. 142-144°C; R_f = 0.49 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3374, 3018, 2965, 2925, 1686, 755; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 7.28 (dd, *J* = 8.1, 4.9 Hz, 2H), 6.15 (d, *J* = 3.1 Hz, 1H), 5.94 (dd, *J* = 3.1, 1.3 Hz, 1H), 4.29 (d, *J* = 10.8 Hz, 1H), 2.46 (dp, *J* = 10.7, 6.6 Hz, 1H), 2.33 (d, *J* = 1.0 Hz, 3H), 0.95 (dd, *J* = 17.9, 6.5 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.1, 160.4, 153.2, 152.5, 151.3, 132.0, 124.0, 123.5, 116.6, 116.4, 109.1, 107.0, 106.0, 42.4, 30.1, 21.5, 20.8, 13.7.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{18}H_{18}O_4$ 321.1097; Found 321.1088.

3-(cyclohexyl(5-methylfuran-2-yl)methyl)-4-hydroxy-2H-chromen-2-one **14k**



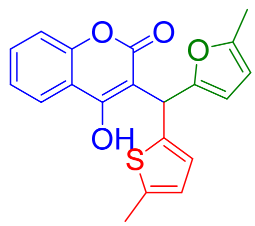
Yellow oil, 219.2 g, 64% yield.; R_f = 0.57 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3682, 3378, 3019, 2932, 2856, 2400, 1715, 755; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.30 – 7.26 (m, 2H), 6.13 (d, *J* = 3.1 Hz, 1H), 5.93 (dd, *J* = 3.1, 1.3 Hz, 1H), 4.37 (d, *J* = 10.9 Hz, 1H), 2.33 (s, 3H), 2.10 (tdd, *J* = 11.0, 7.7, 3.4 Hz, 1H), 1.63 (ddd, *J* = 39.9, 16.3, 8.9 Hz, 5H), 1.24 – 1.00 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.1, 160.4, 152.8, 152.5, 151.3, 132.0, 123.9, 123.5, 116.6, 116.4, 109.2, 107.0, 105.6, 41.3, 39.2, 31.9, 31.0, 26.3, 26.3, 26.2, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{21}H_{22}O_4$ 361.1410; Found 361.1414.

4-hydroxy-3-((5-methylfuran-2-yl)(naphthalen-1-yl)methyl)-2H-chromen-2-one **14l**



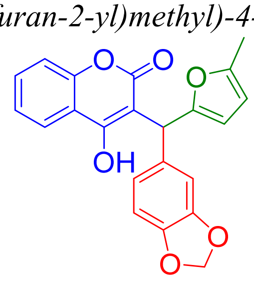
Red solid, 298.3 mg, 78% yield. m.p. 184-185°C; R_f = 0.41 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3397, 3054, 2987, 1702, 1629, 705; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 6.4, 3.5 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.71 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.44 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.21 (m, 2H), 6.57 (s, 1H), 6.02 (d, *J* = 3.1 Hz, 1H), 5.96 – 5.93 (m, 1H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.0, 162.4, 153.5, 152.9, 151.2, 135.5, 134.5, 132.3, 131.7, 129.3, 129.0, 127.2, 126.6, 125.5, 124.5, 124.0, 124.0, 123.4, 116.6, 116.0, 110.5, 106.7, 105.2, 38.8, 13.9; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{25}H_{18}O_4$ 405.1097; Found 405.1088.

4-hydroxy-3-((5-methylfuran-2-yl)(5-methylthiophen-2-yl)methyl)-2H-chromen-2-one **14m**



Brown solid, 289.8 mg, 77% yield. m.p. 78-80°C; R_f = 0.49 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3373, 3054, 2986, 1706, 1628, 704; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.69 (s, 1H), 7.55 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 6.68 (dd, *J* = 3.5, 1.4 Hz, 1H), 6.59 (dd, *J* = 3.5, 1.2 Hz, 1H), 6.25 (d, *J* = 3.1 Hz, 1H), 6.04 (s, 1H), 5.96 (dd, *J* = 3.0, 1.3 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.1, 161.7, 153.0, 152.8, 151.2, 140.7, 139.4, 132.5, 126.1, 125.0, 124.1, 123.6, 116.6, 116.2, 109.6, 106.7, 105.5, 36.7, 15.5, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{20}H_{16}O_4S$ 375.0662; Found 375.0672.

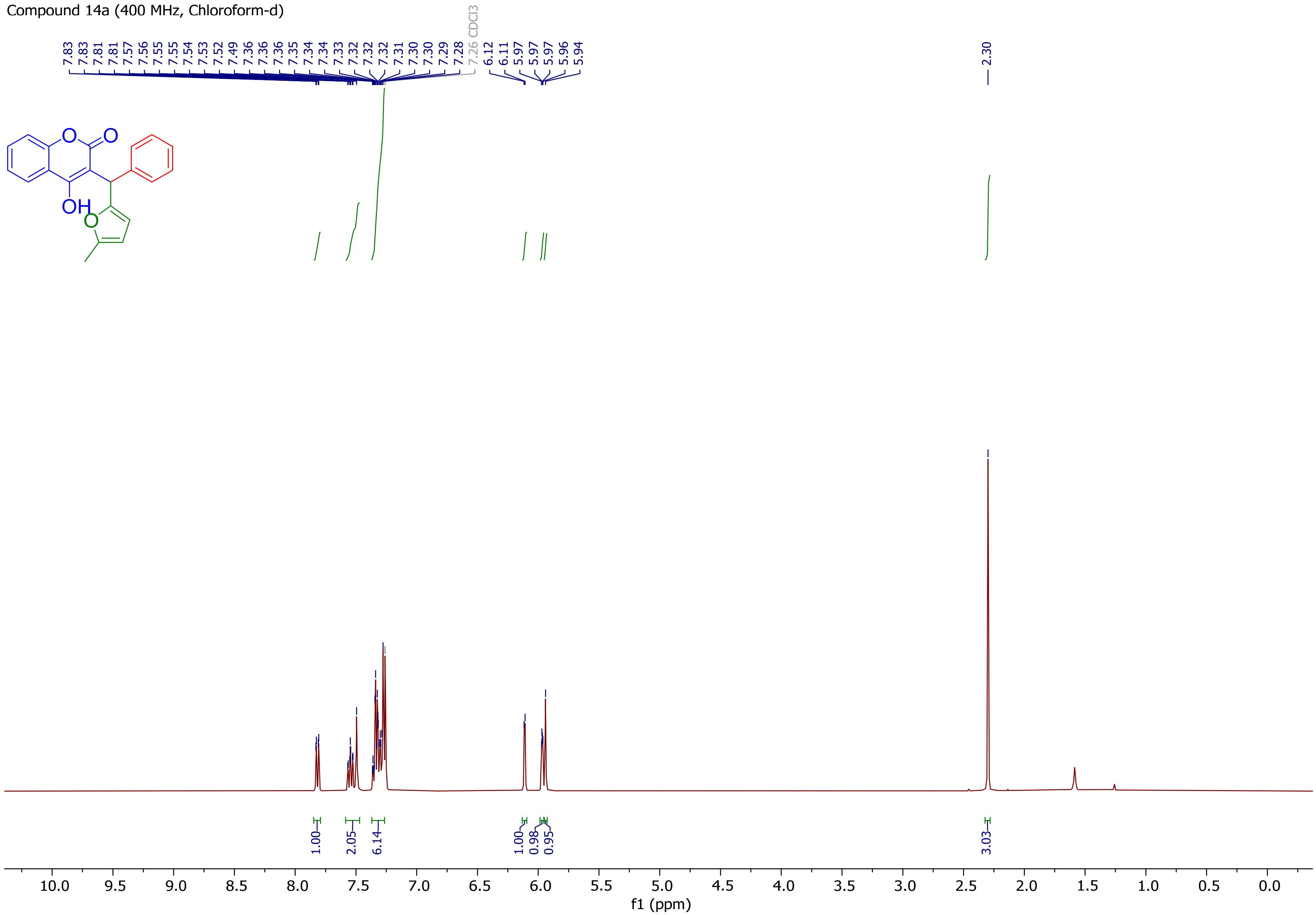
3-(benzo[d][1,3]dioxol-5-yl(5-methylfuran-2-yl)methyl)-4-hydroxy-2H-chromen-2-one **14n**



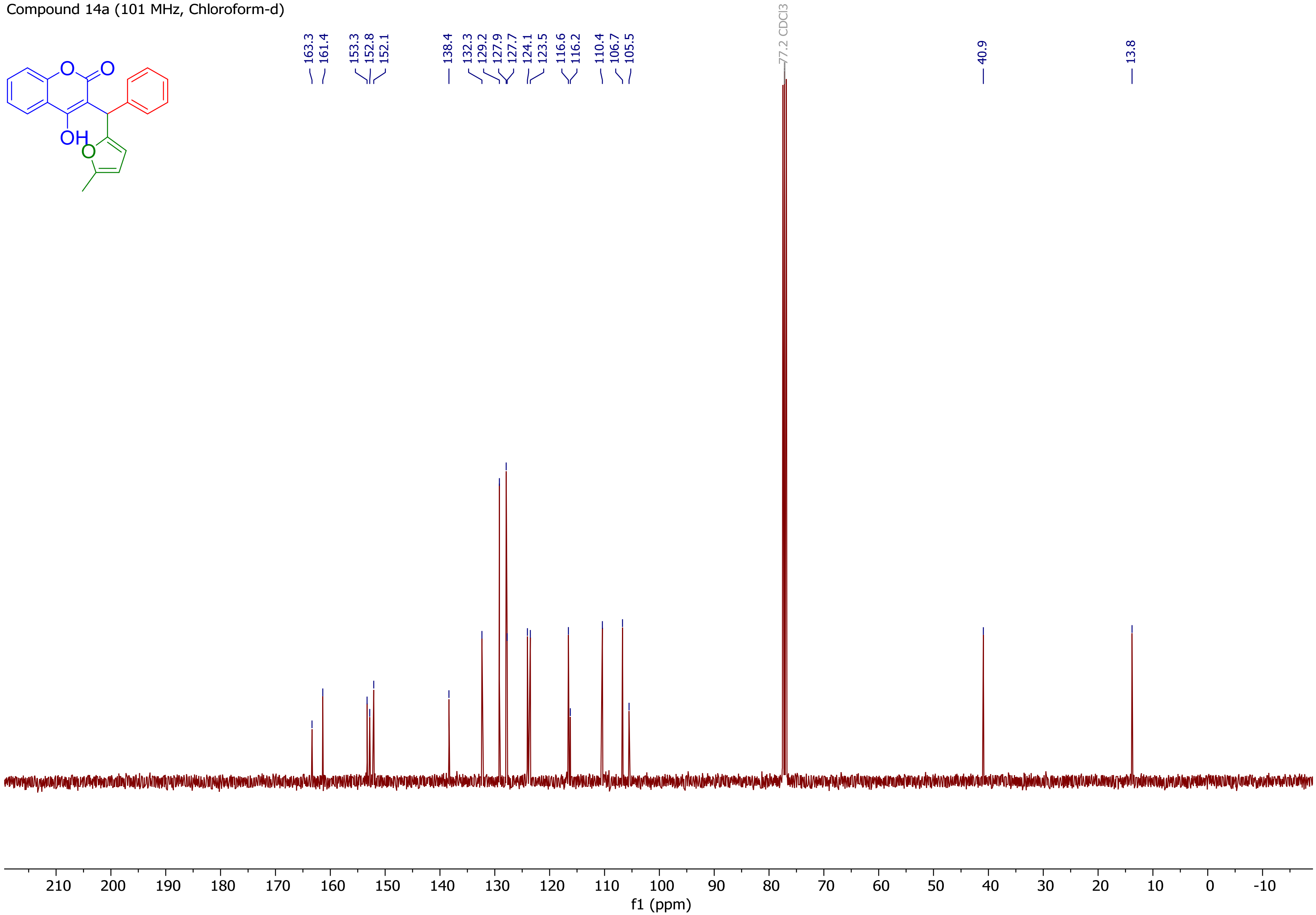
Red solid, 257.1 mg, 73% yield. m.p. 72-74°C; R_f = 0.44 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:80 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3054, 2987, 1703, 1628, 1575, 705; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54 (ddd, *J* = 8.5, 7.4, 1.6 Hz, 1H), 7.48 (s, 1H), 7.31 (dd, *J* = 18.6, 8.0 Hz, 2H), 6.79 – 6.73 (m, 2H), 6.73 – 6.68 (m, 1H), 6.13 (d, *J* = 3.1 Hz, 1H), 5.96 (d, *J* = 6.4 Hz, 3H), 5.83 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.3, 161.4, 153.3, 152.8, 152.0, 148.5, 147.3, 132.4, 132.1, 124.1, 123.5, 120.9, 116.6, 116.2, 110.3, 108.7, 108.6, 106.7, 105.6, 101.4, 40.6, 13.8.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{22}H_{16}O_6$ 399.0839; Found 399.0824.

VI. ^{1}H and ^{13}C NMR Spectra for non-symmetric triarylmethanes 14 a-n

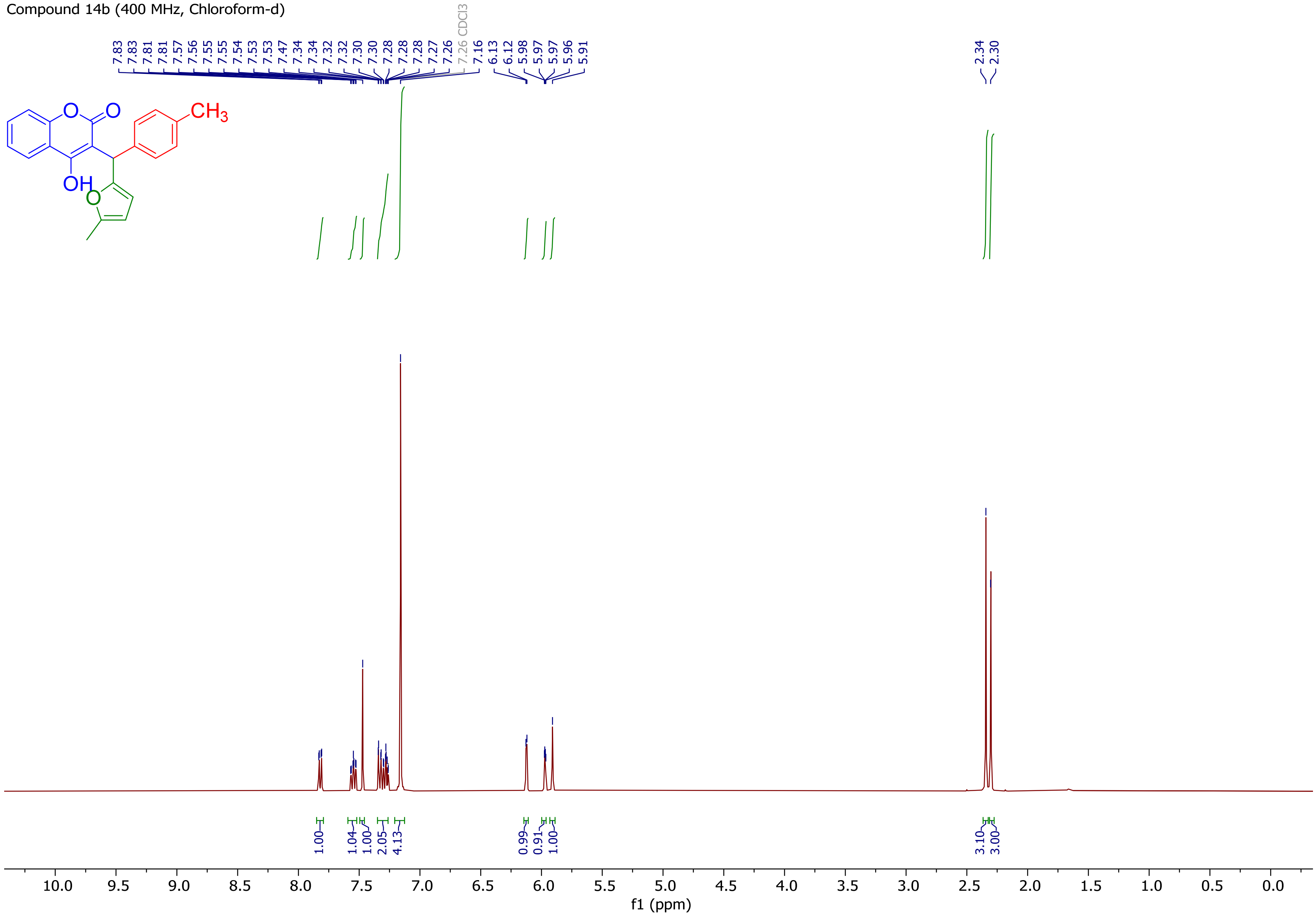
Compound 14a (400 MHz, Chloroform-d)



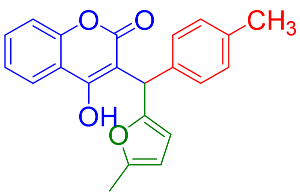
Compound 14a (101 MHz, Chloroform-d)

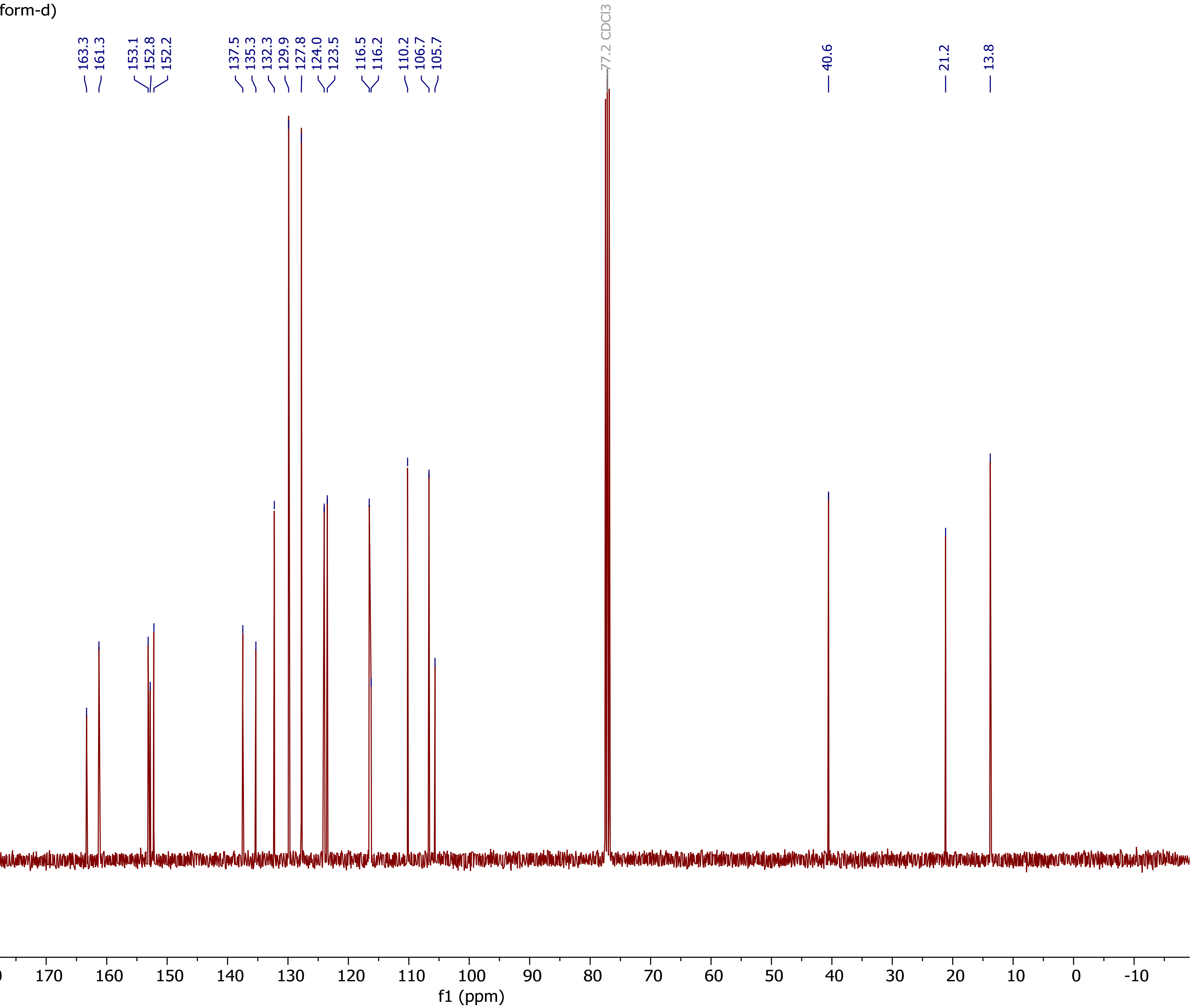


Compound 14b (400 MHz, Chloroform-d)

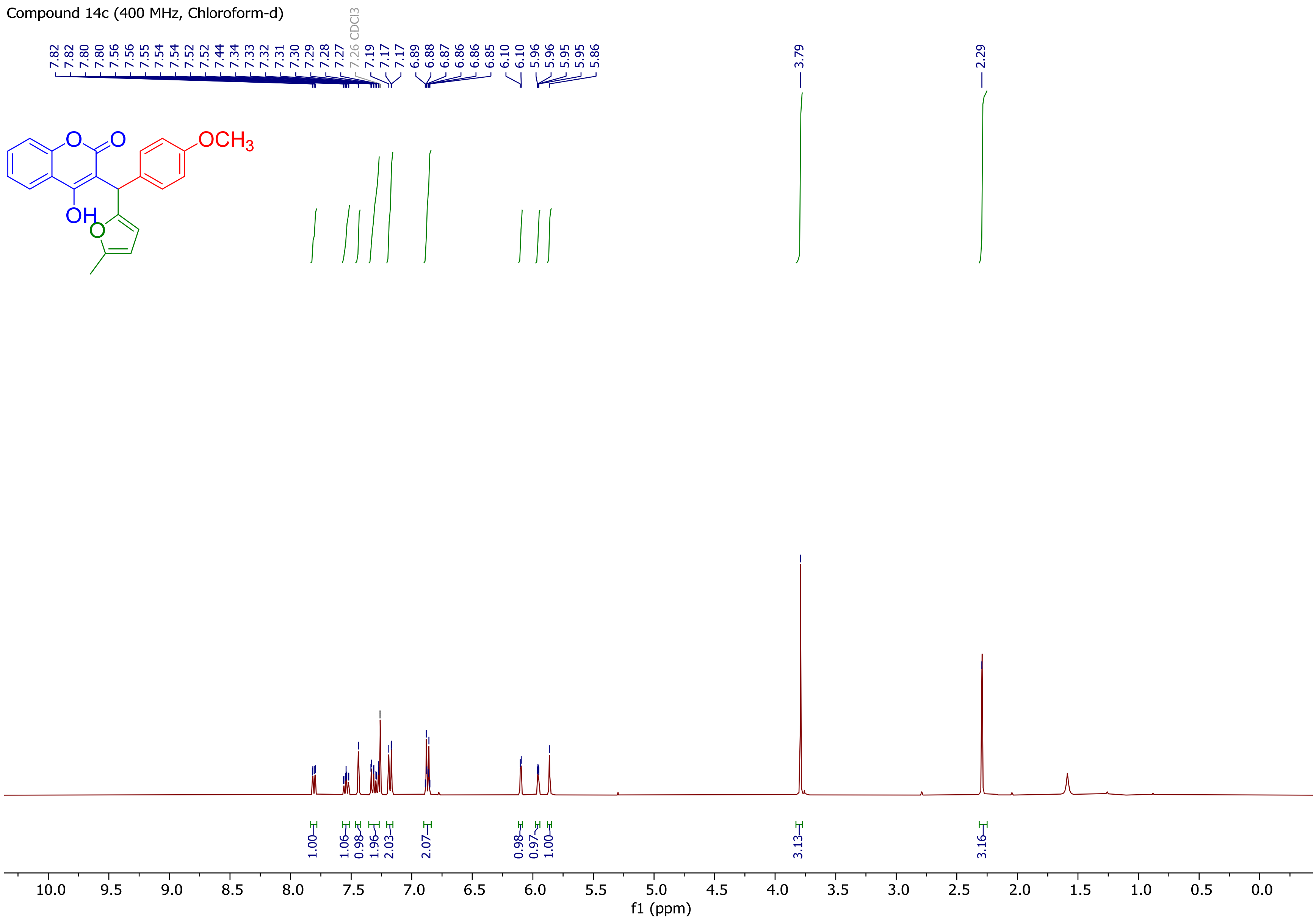


Compound 14b (101 MHz, Chloroform-d)

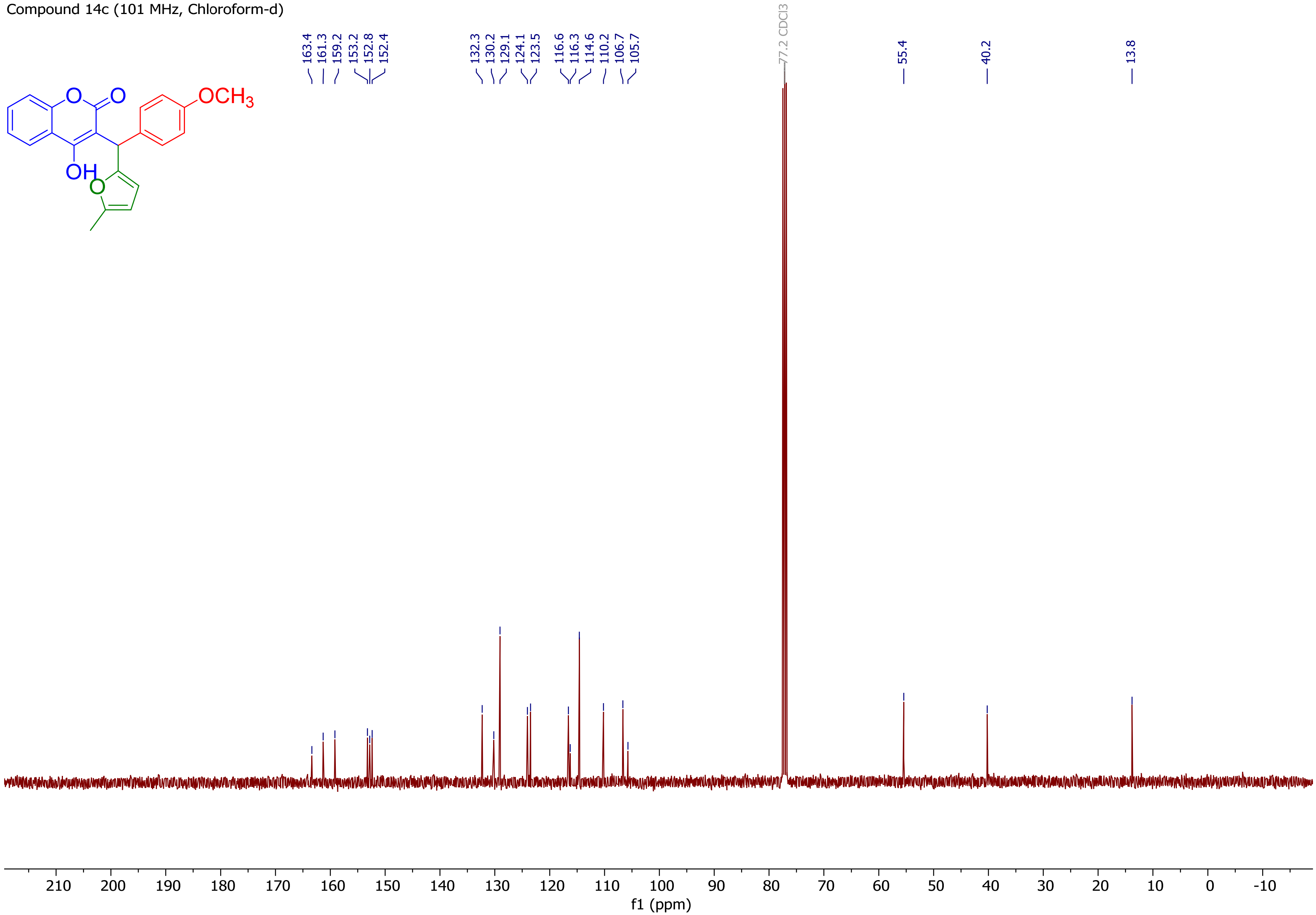




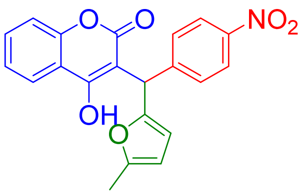
Compound 14c (400 MHz, Chloroform-d)

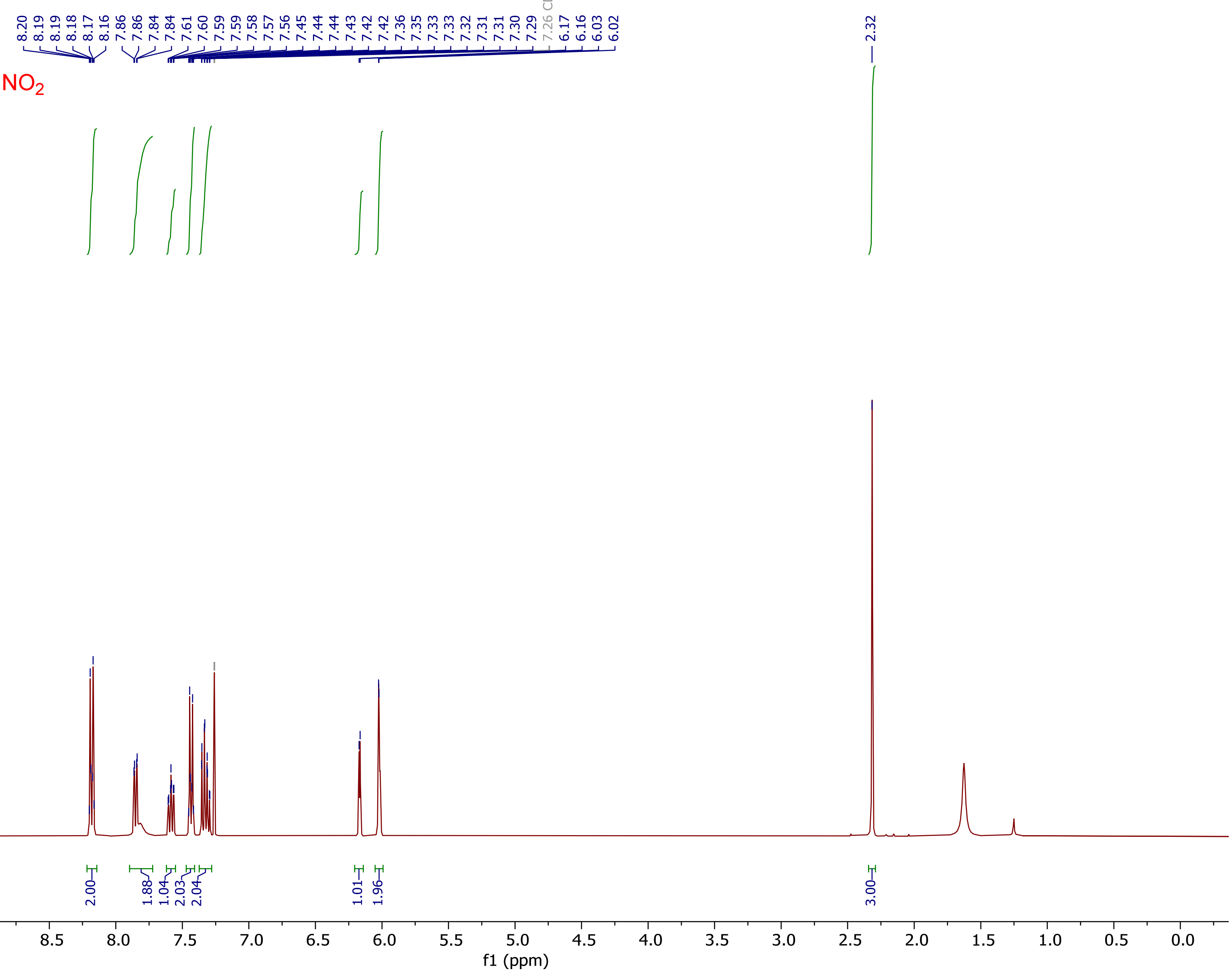


Compound 14c (101 MHz, Chloroform-d)

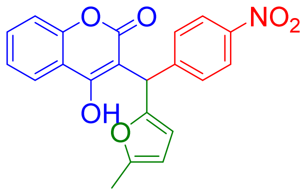


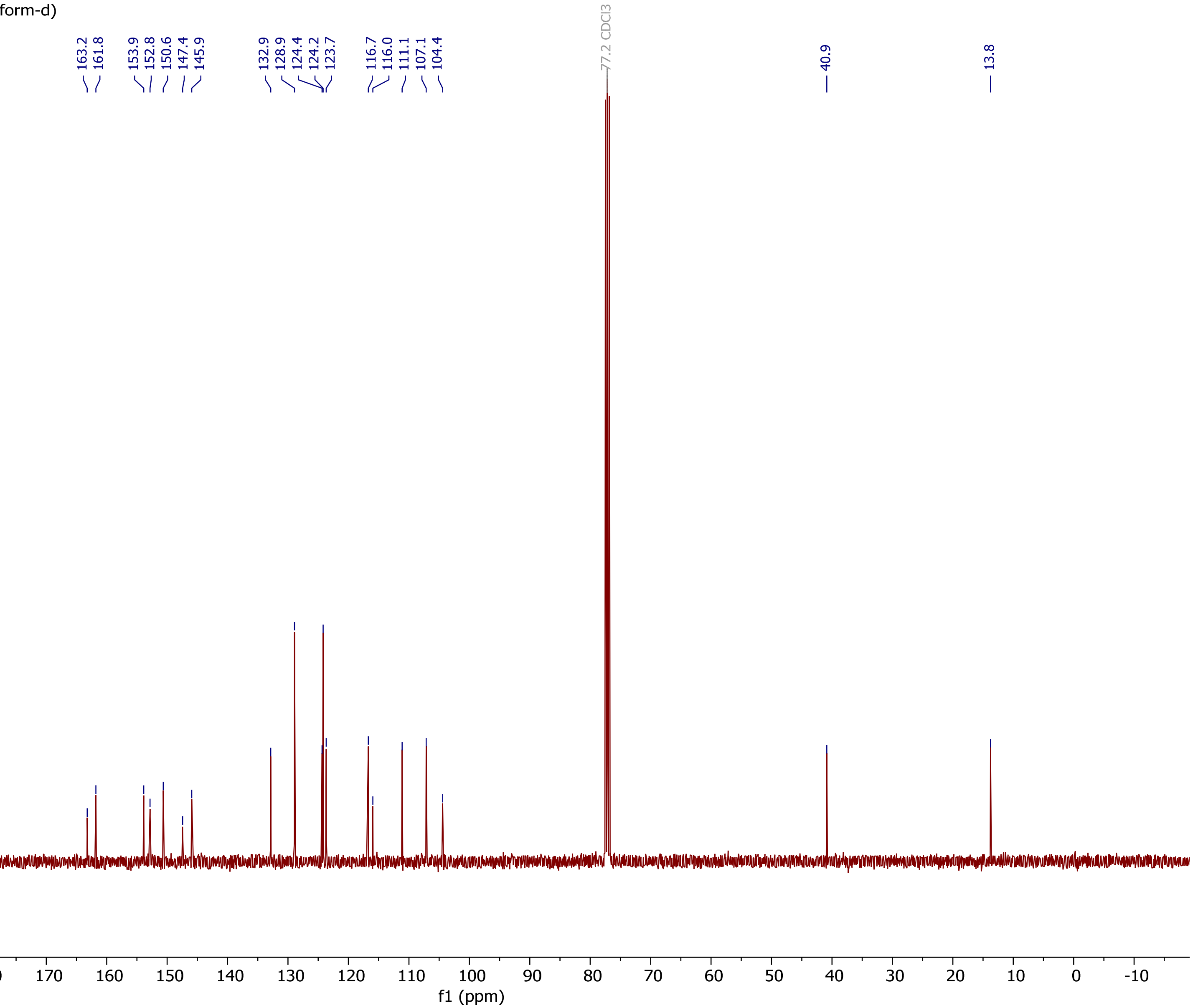
Compound 14d (400 MHz, Chloroform-d)



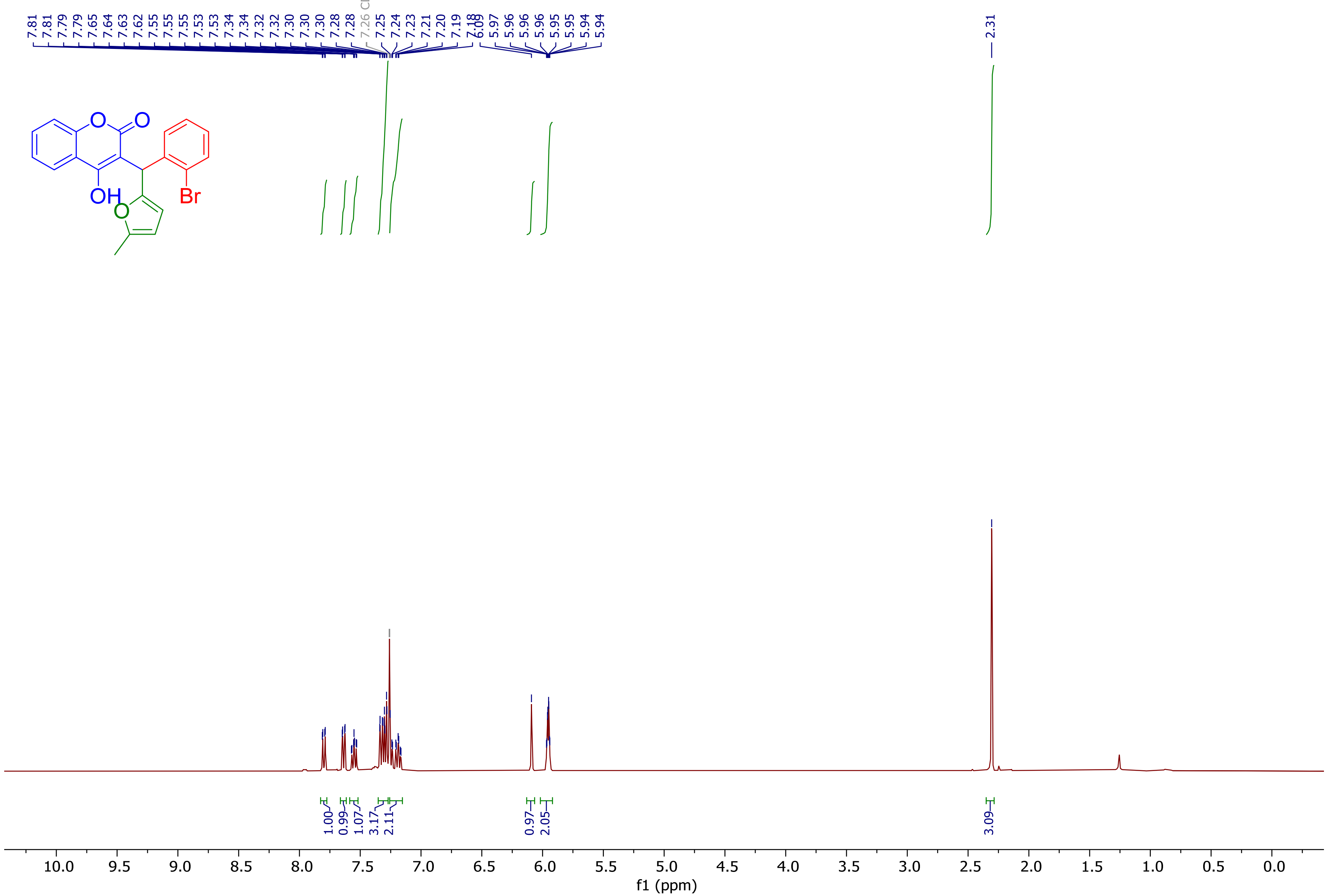


Compound 14d (101 MHz, Chloroform-d)

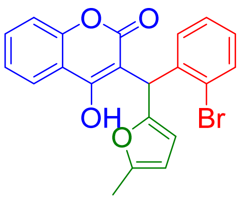


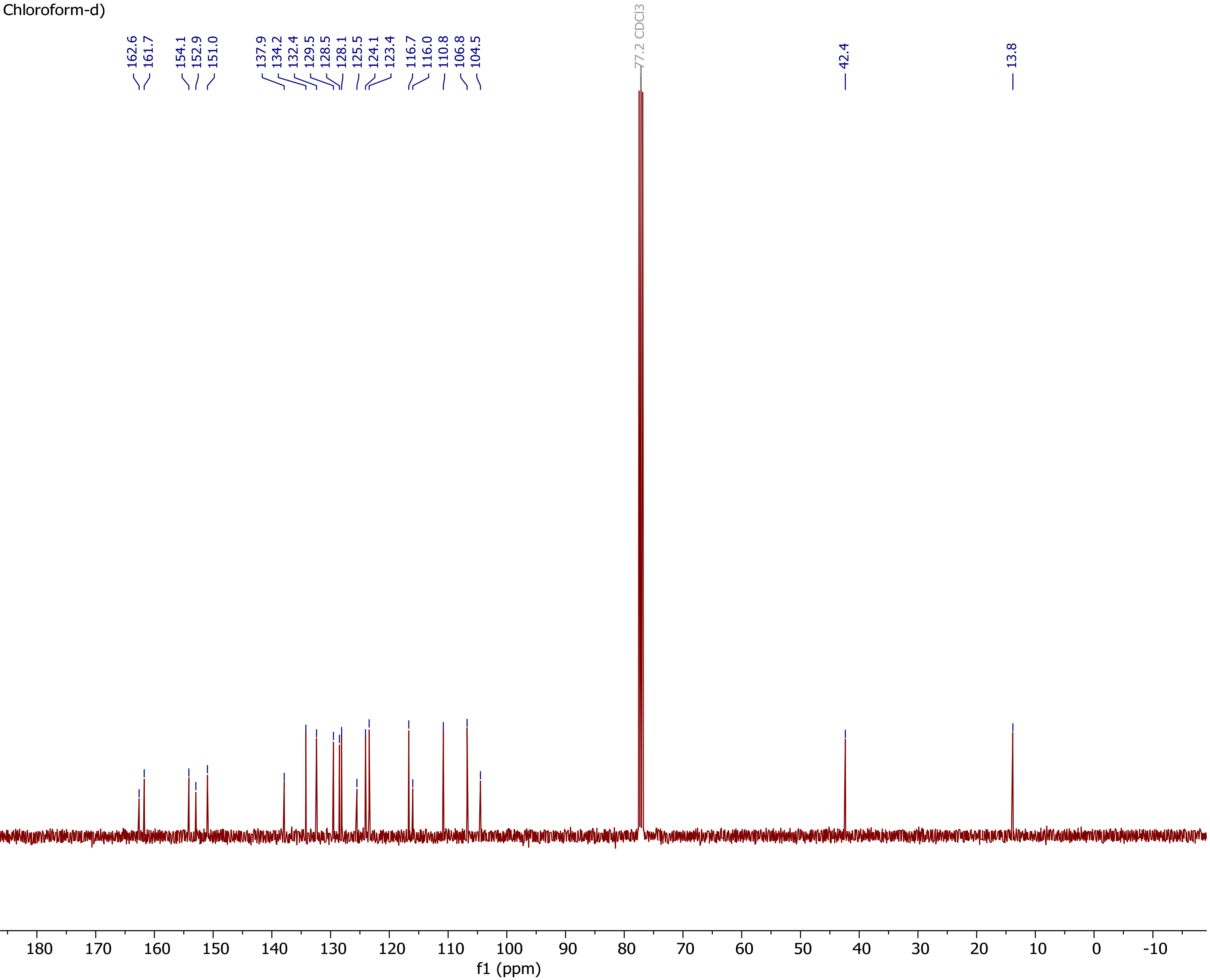


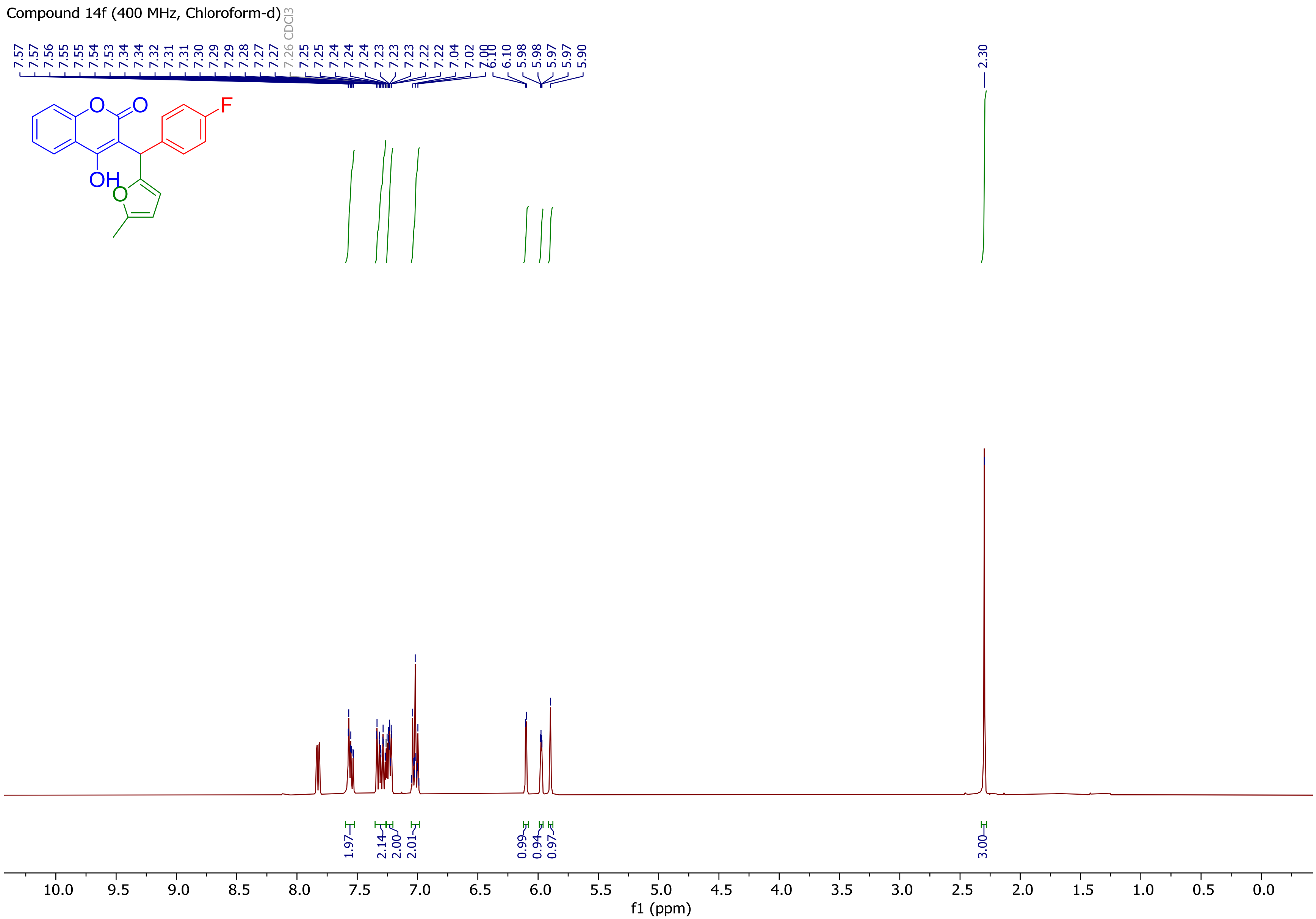
Compound 14e (400 MHz, Chloroform-d)



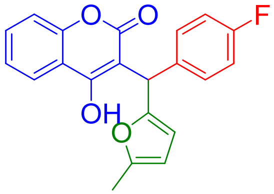
Compound 14e (101 MHz, Chloroform-d)

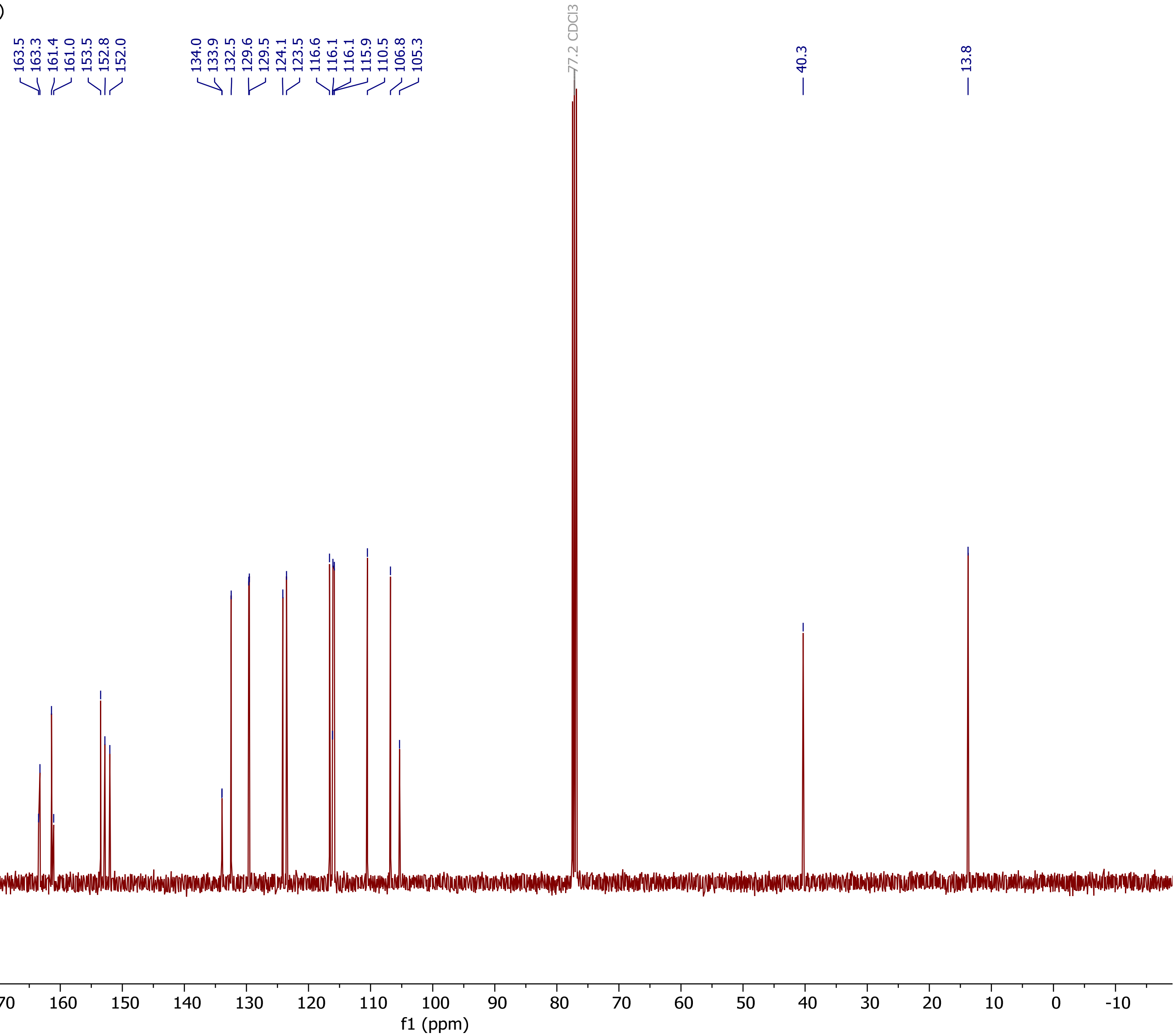




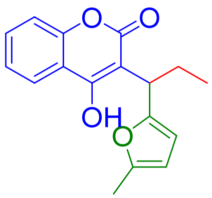

Compound 14f (400 MHz, Chloroform-d)
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.34
7.34
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26 CDCl3
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.04
7.02
7.00
6.10
6.10
5.98
5.98
5.97
5.97
5.90
2.30
O
O
F
OH
O
1.97
2.14
2.00
2.01
0.99
0.94
0.97
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

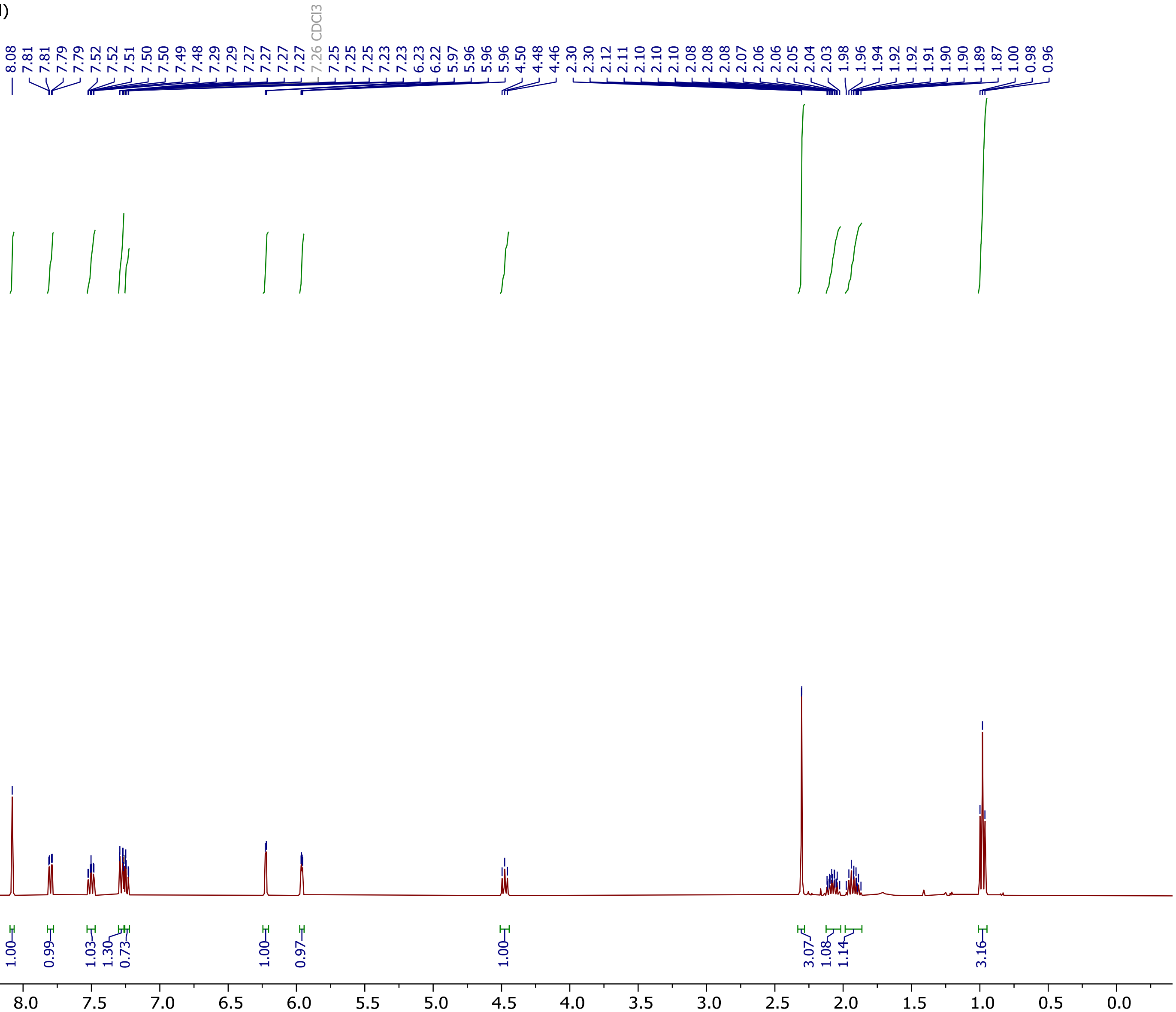
Compound 14f (101 MHz, Chloroform-d)



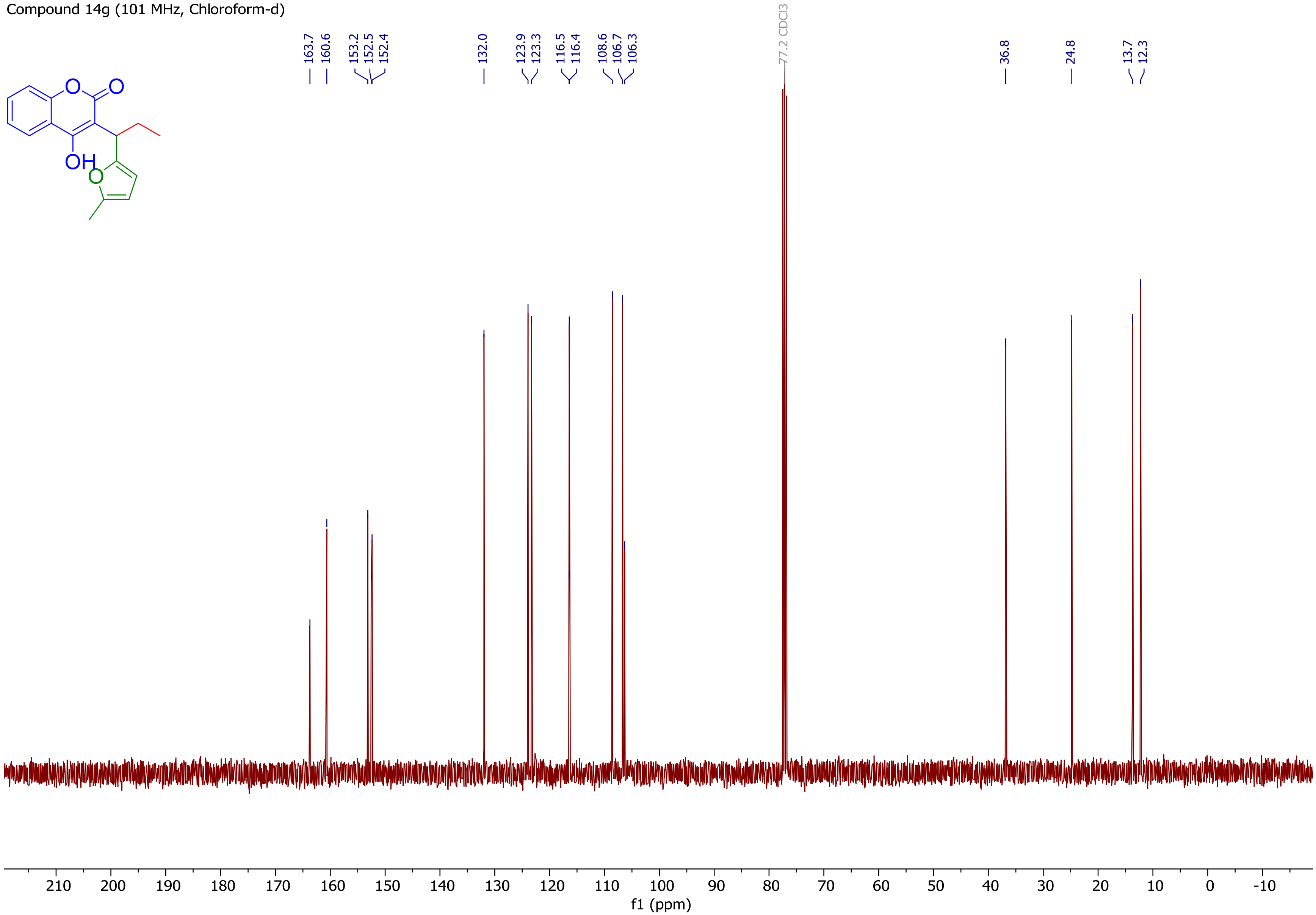


Compound 14g (400 MHz, Chloroform-d)

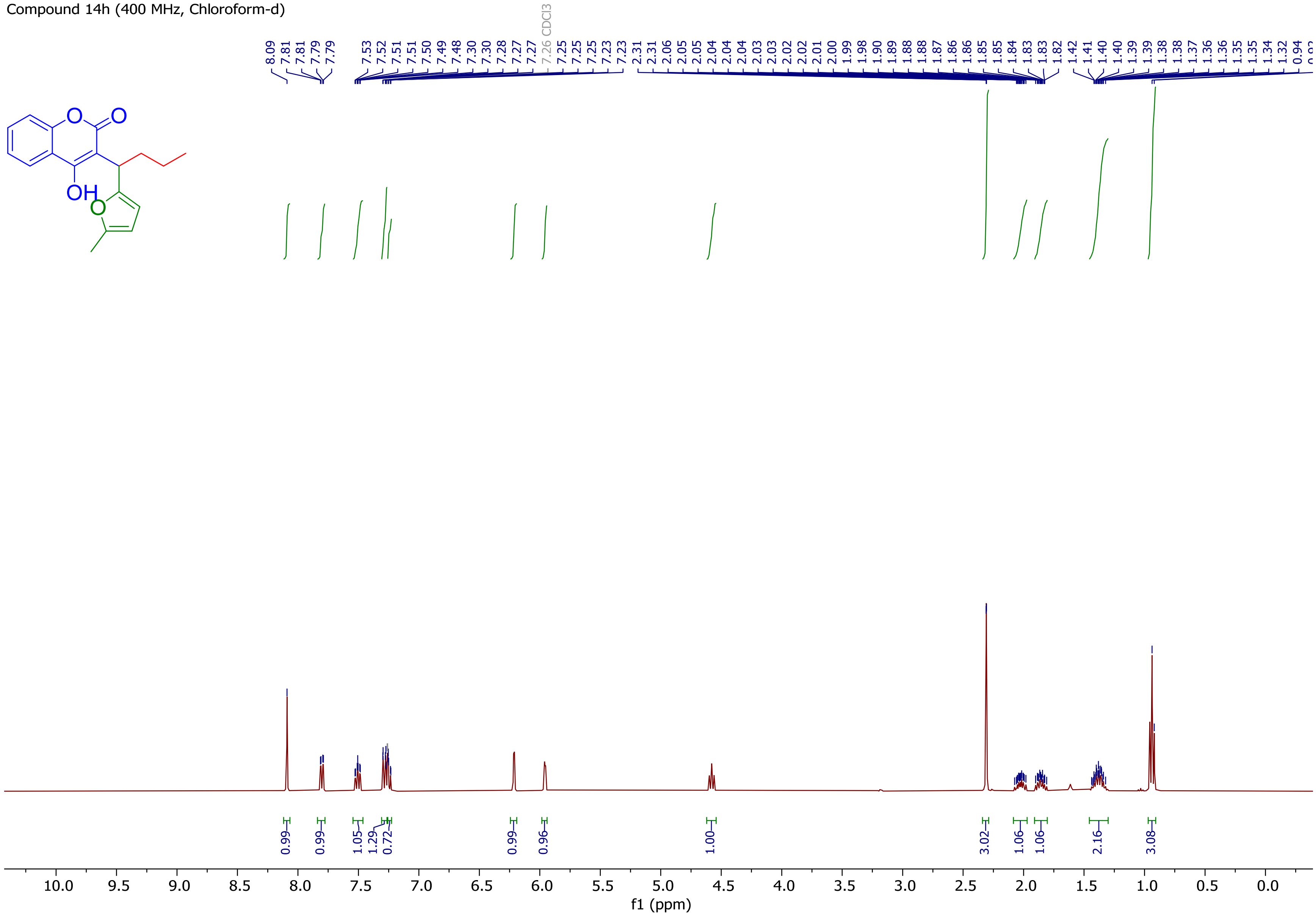




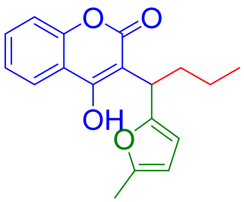
Compound 14g (101 MHz, Chloroform-d)

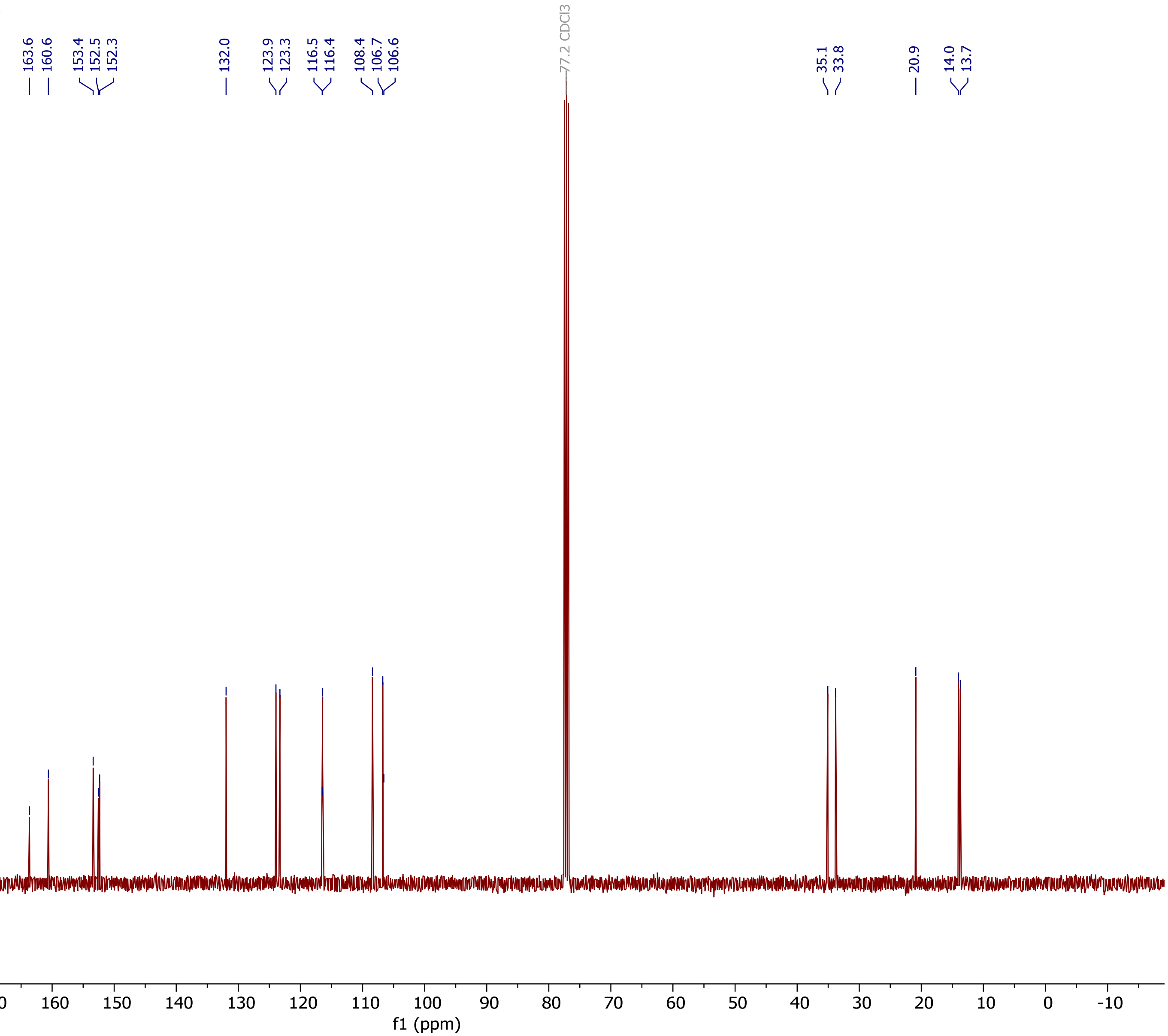


Compound 14h (400 MHz, Chloroform-d)

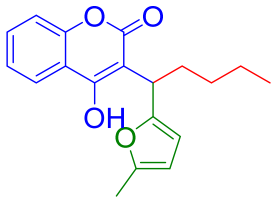


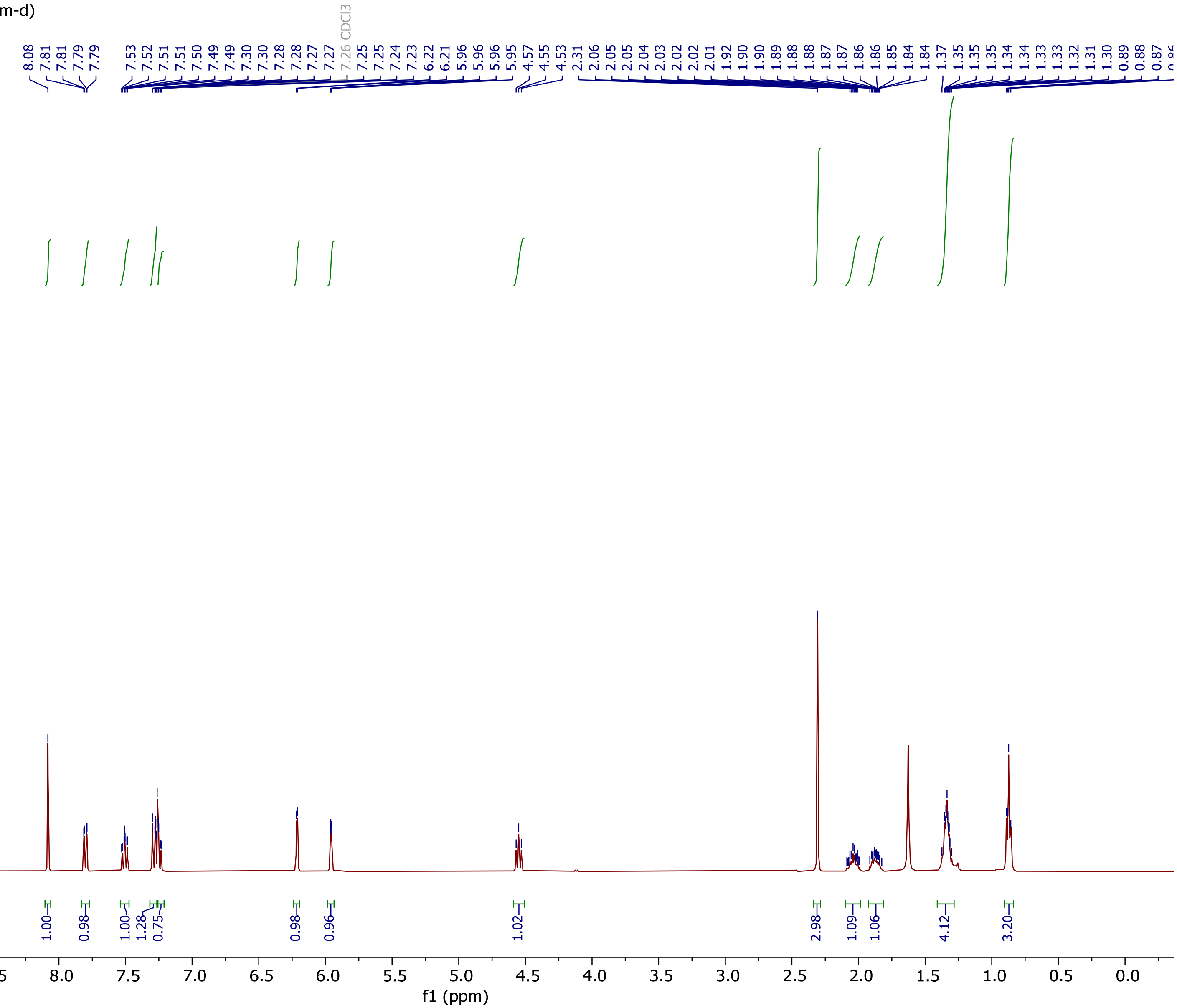
Compound 14h (101 MHz, Chloroform-d)



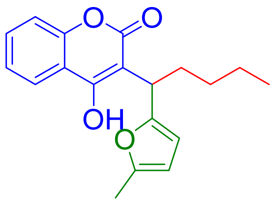


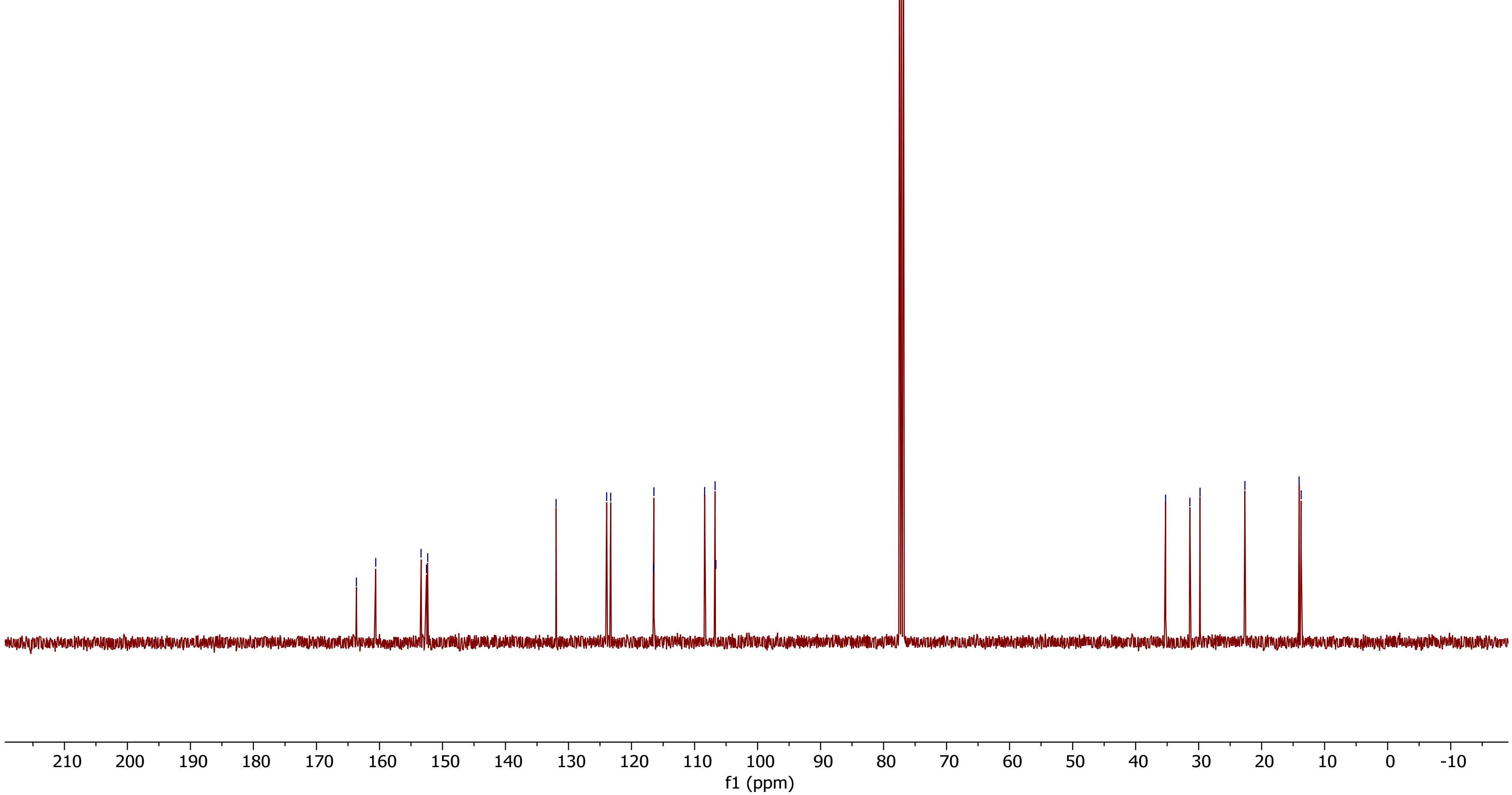
Compound 14i (400 MHz, Chloroform-d)



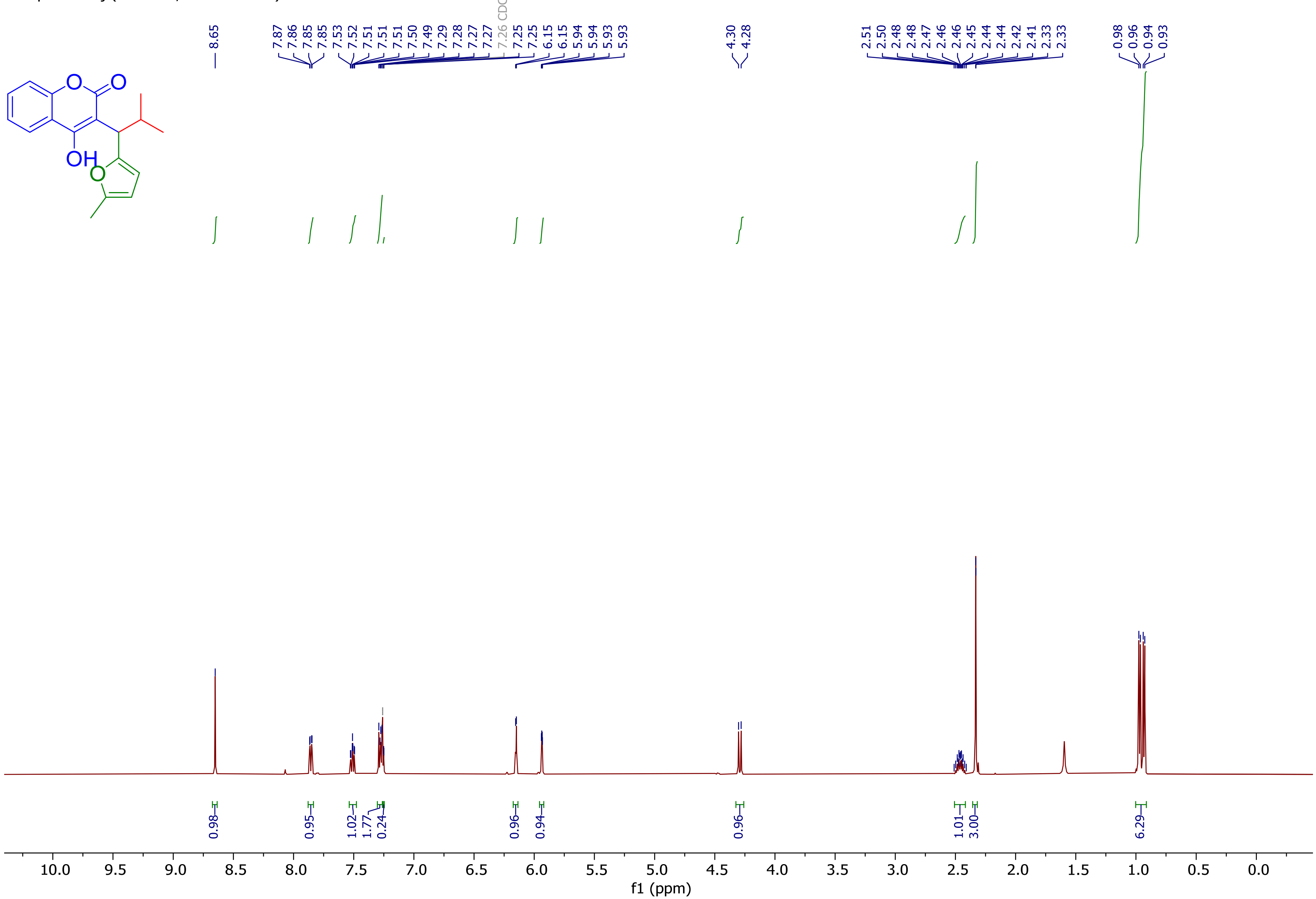


Compound 14i (101 MHz, Chloroform-d)

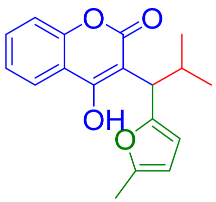


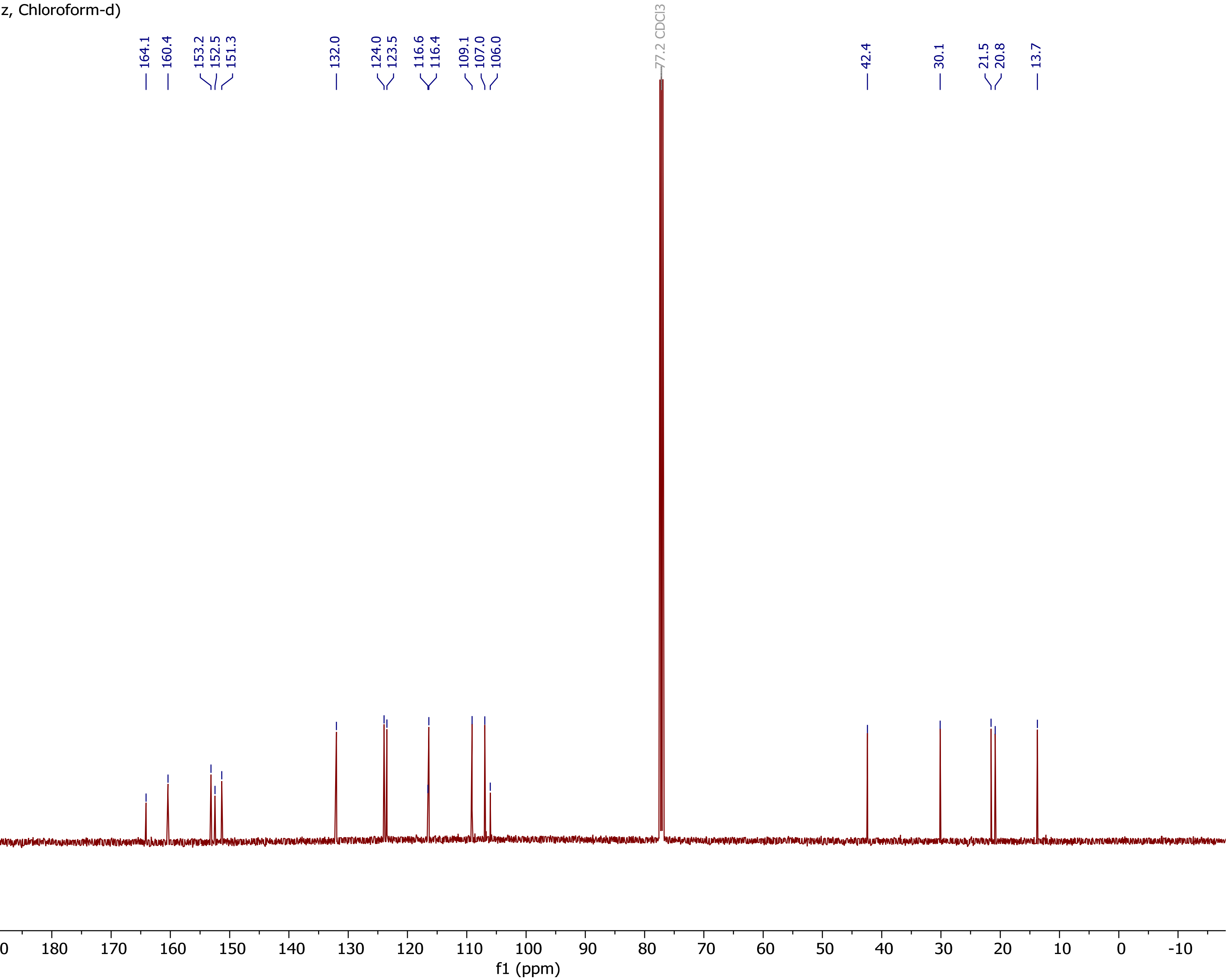


Compound 14j (500 MHz, Chloroform-d)

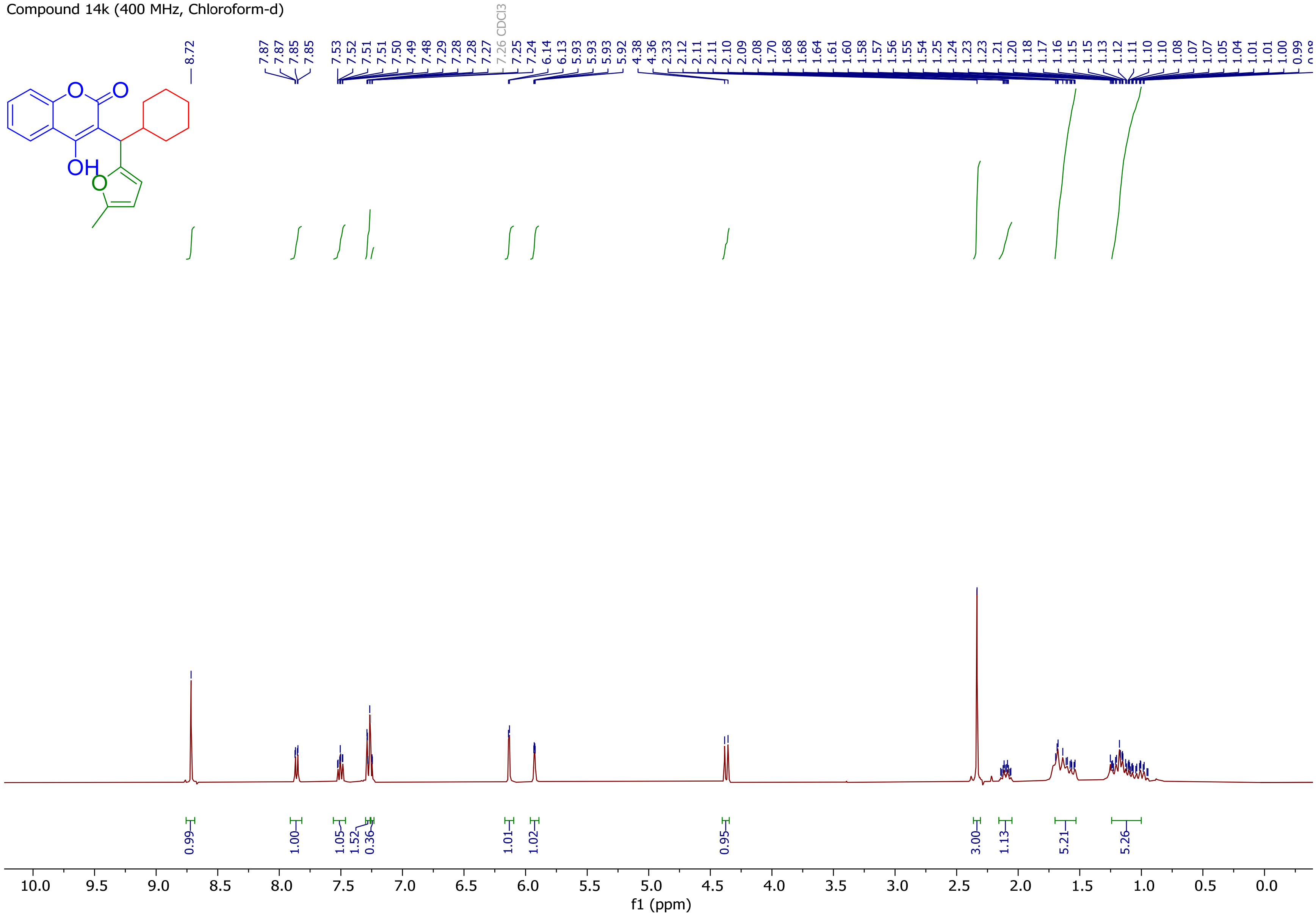


Compound 14j (126 MHz, Chloroform-d)

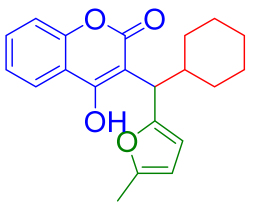


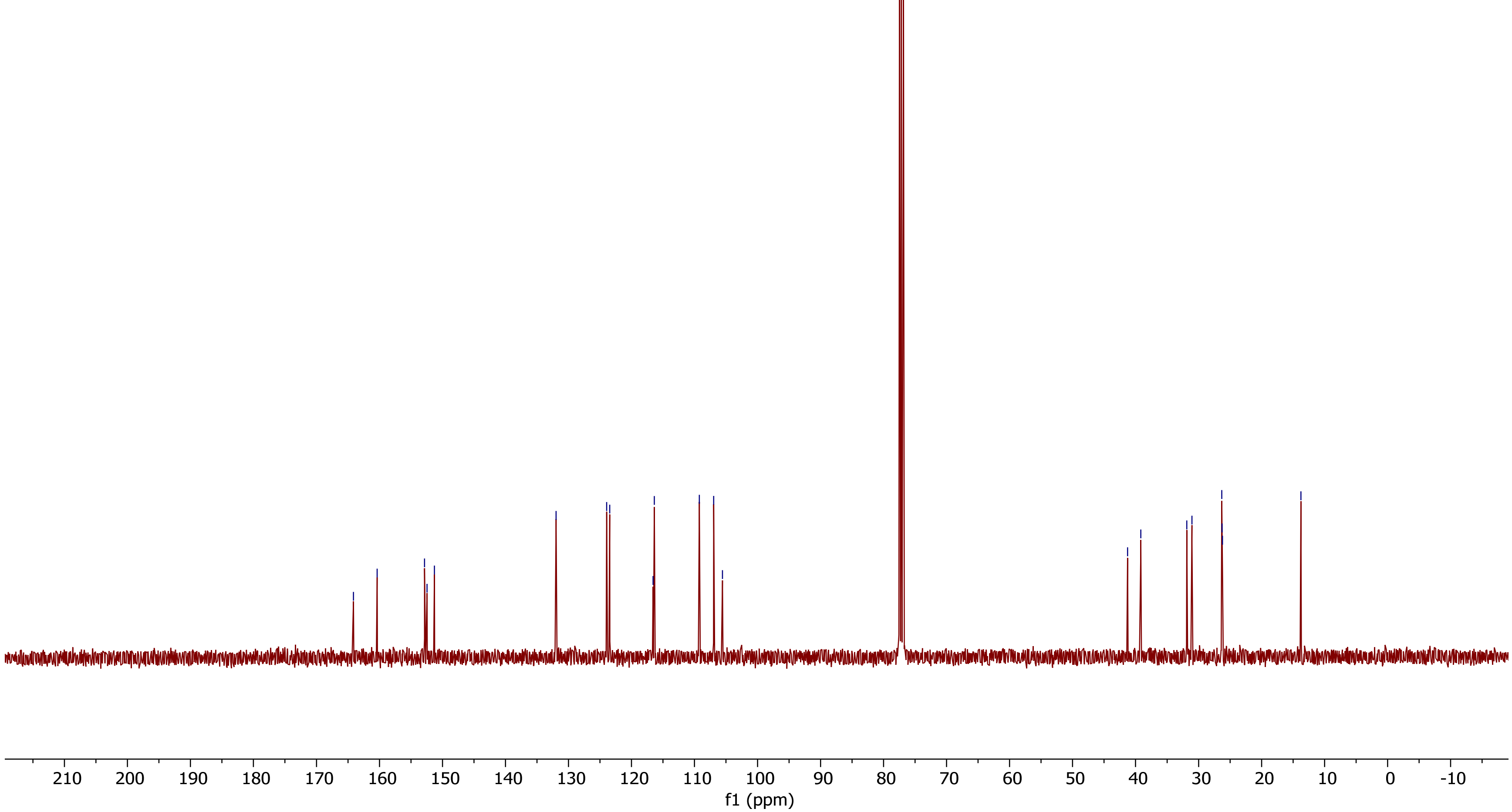


Compound 14k (400 MHz, Chloroform-d)

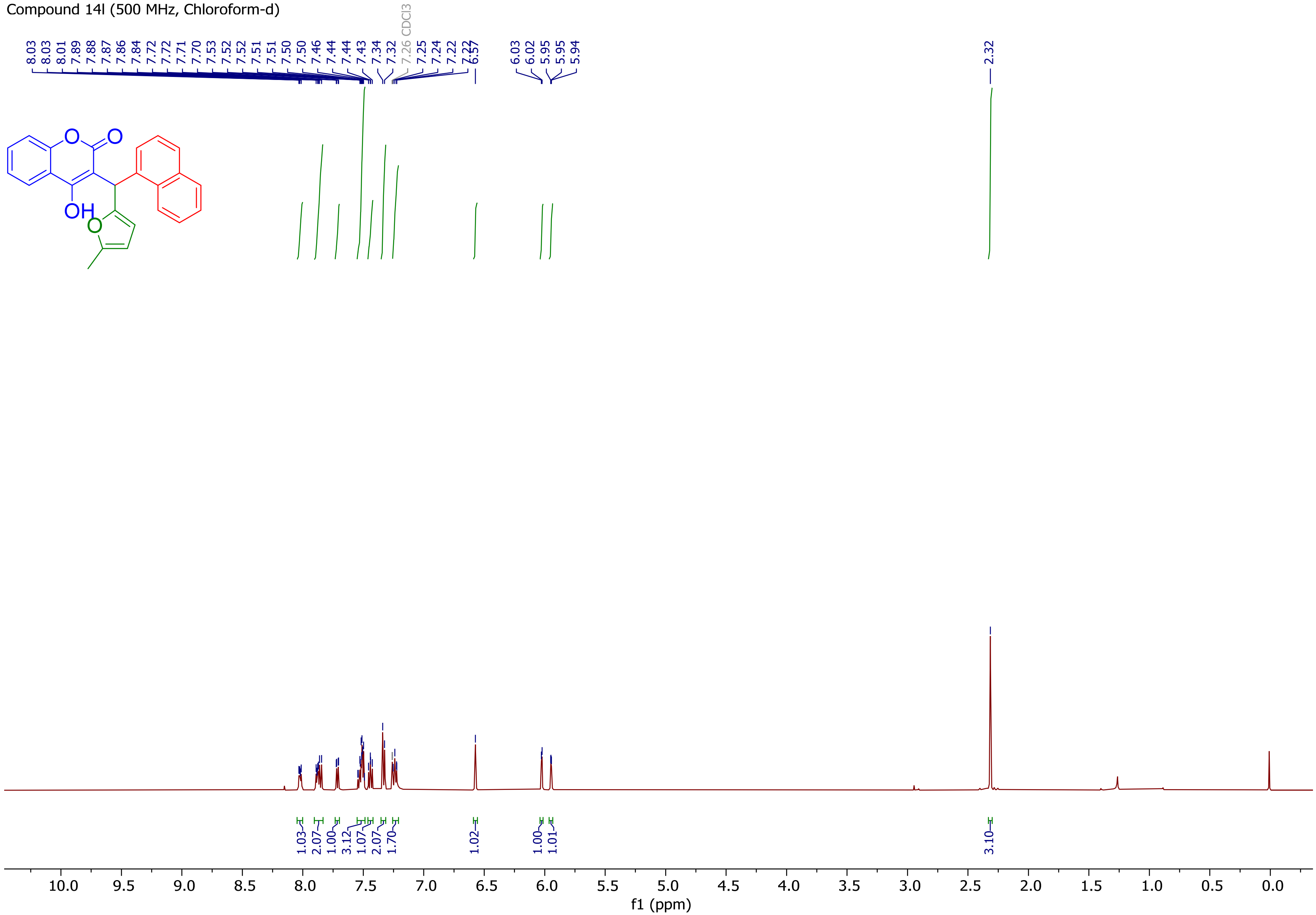


Compound 14k (101 MHz, Chloroform-d)

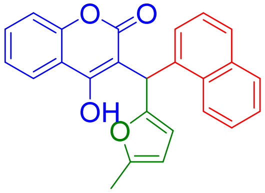


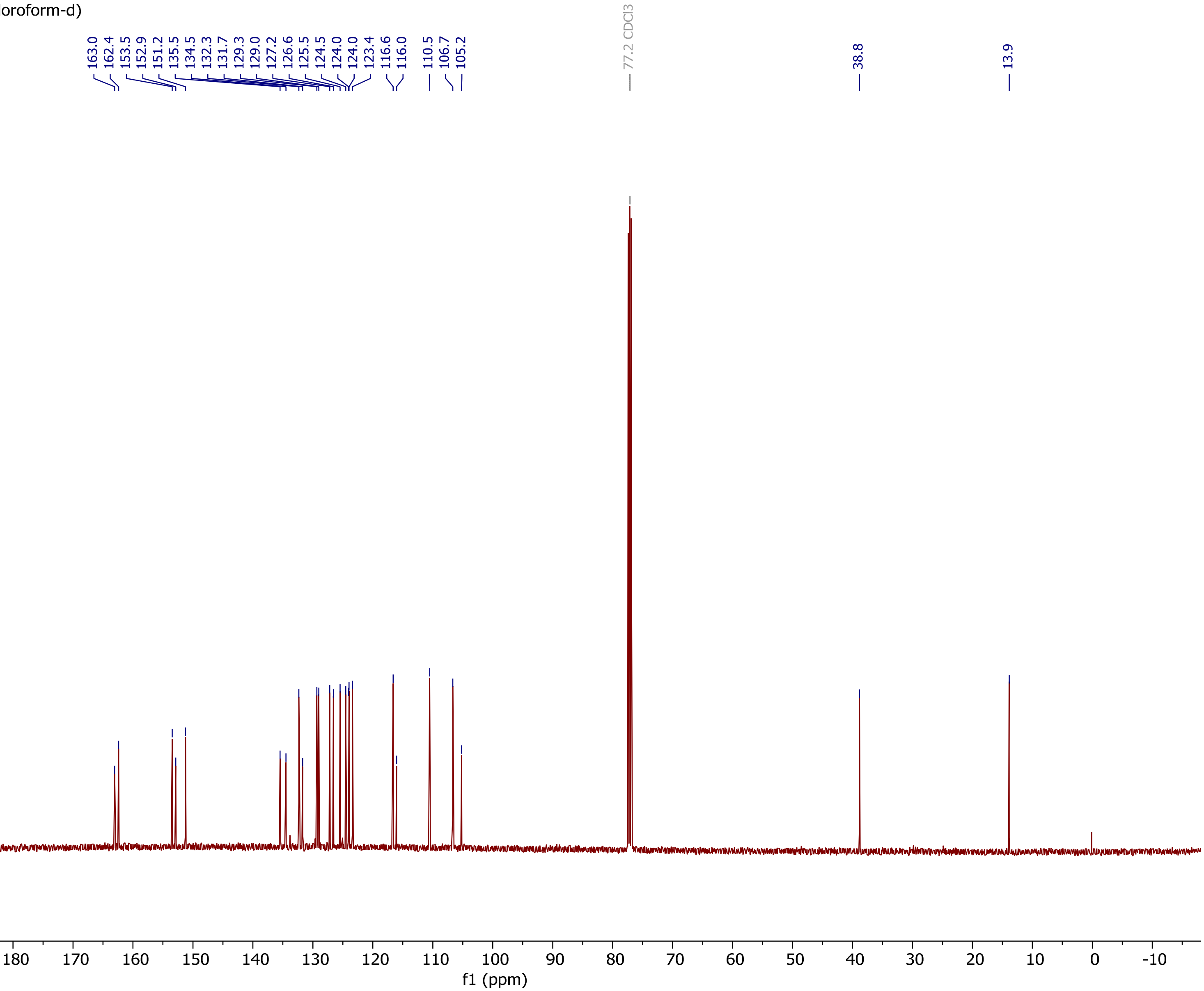


Compound 14l (500 MHz, Chloroform-d)

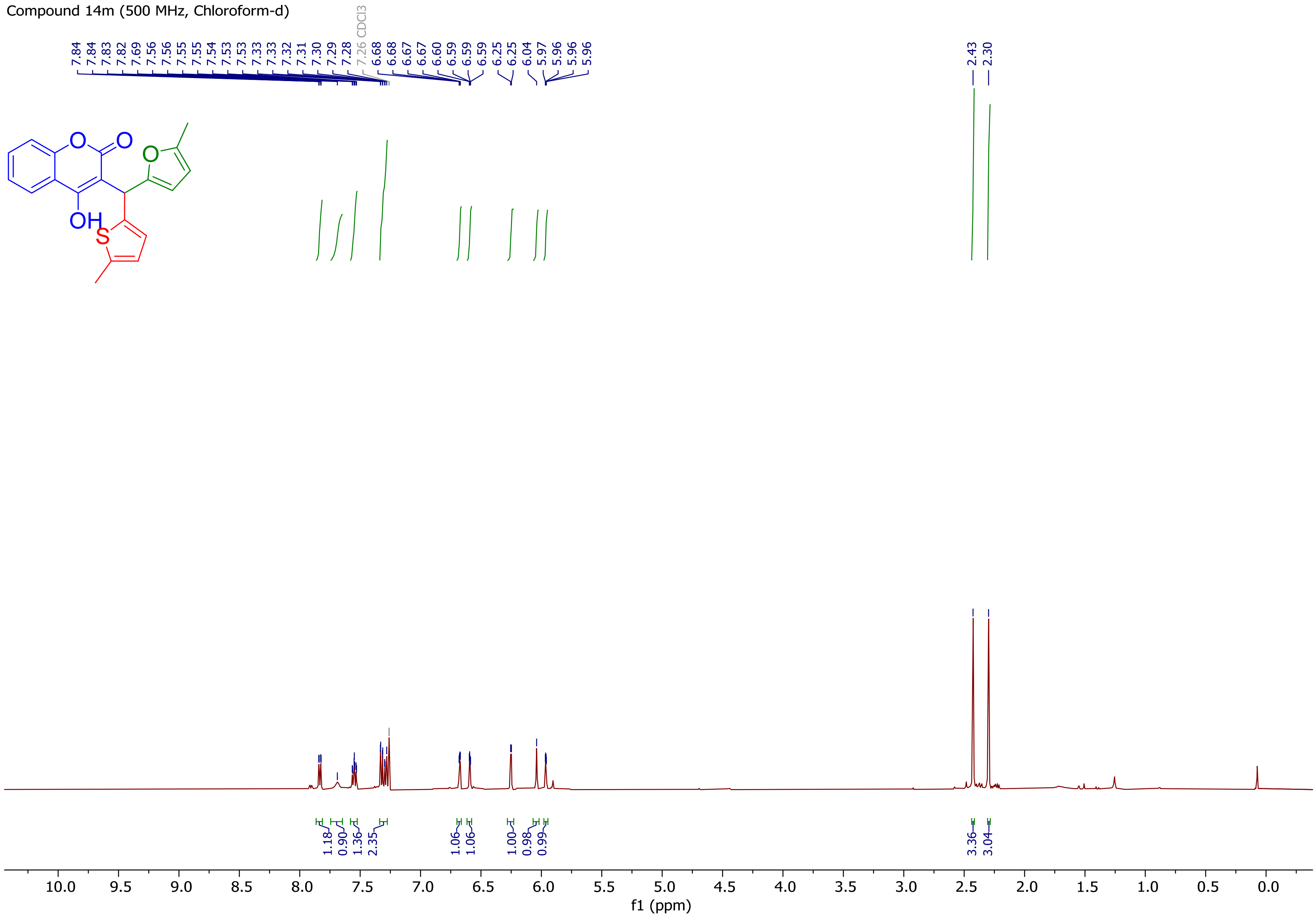


Compound 14l (126 MHz, Chloroform-d)

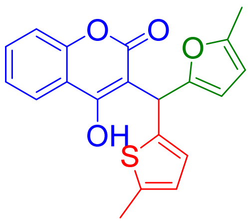


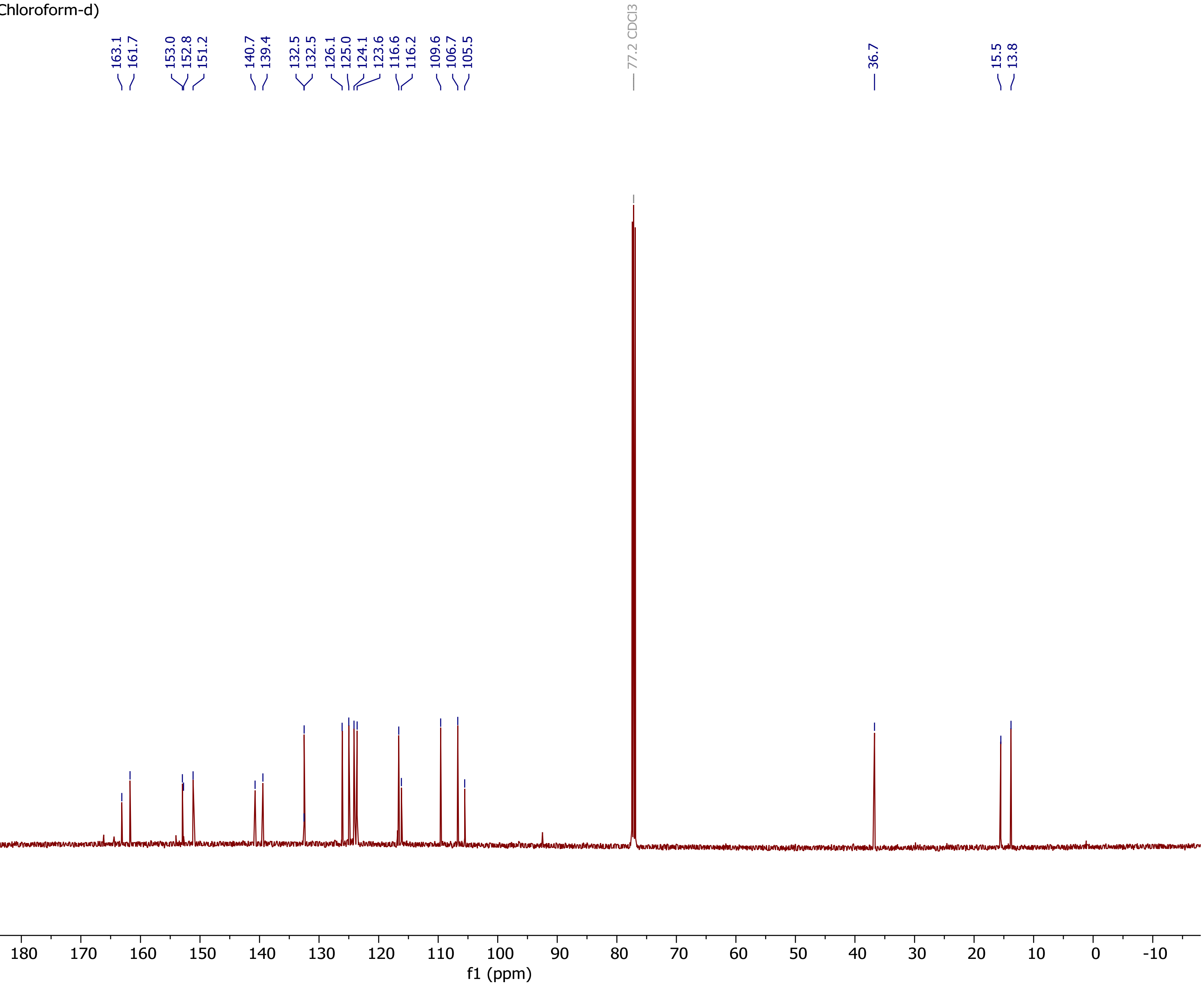


Compound 14m (500 MHz, Chloroform-d)

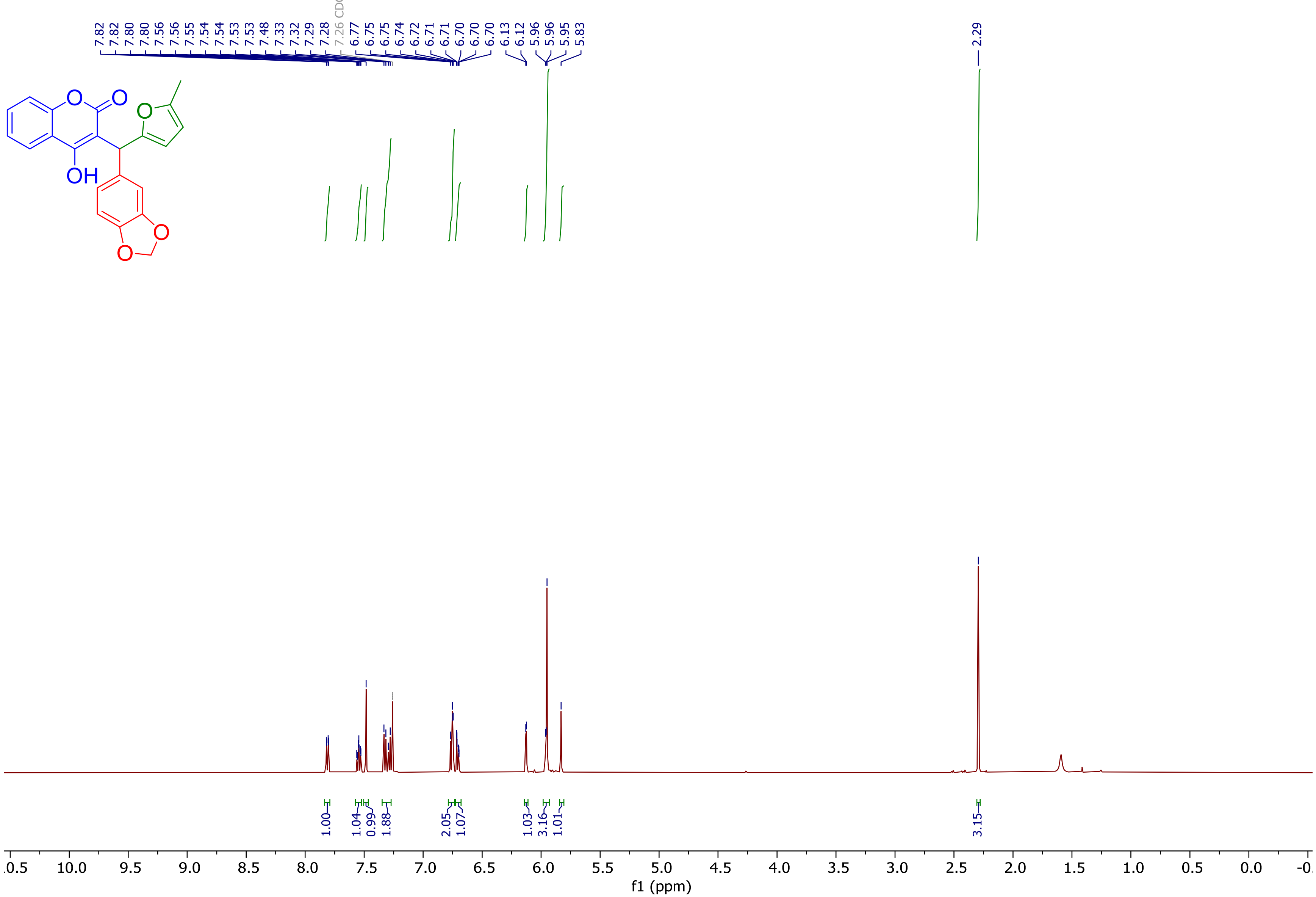


Compound 14m (126 MHz, Chloroform-d)

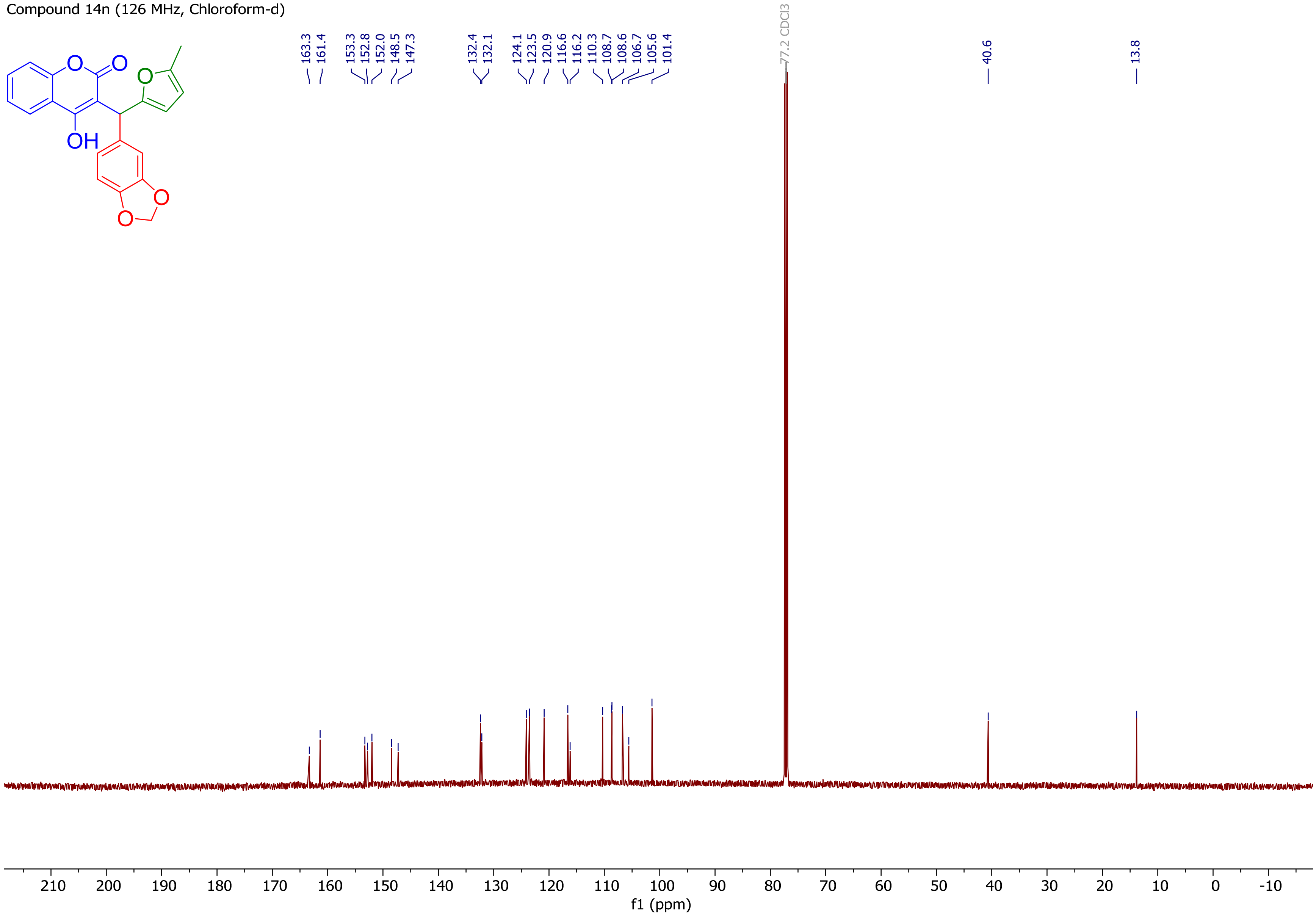




Compound 14n (500 MHz, Chloroform-d)

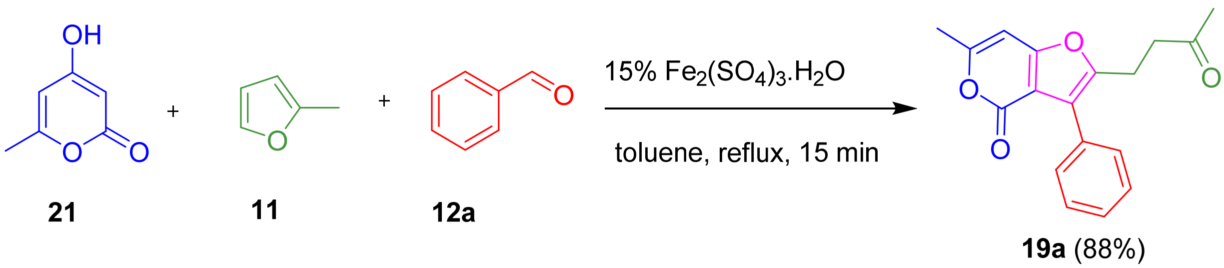


Compound 14n (126 MHz, Chloroform-d)



VII. Optimization of reaction conditions for the synthesis of Furo[3,2-*c*]pyran-4-ones 19 a-j

Table S1. Optimized reaction conditions for the synthesis of Furo[3,2-*c*]pyran-4-ones



entry	catalyst	cat. load[a] (mol%)	solvent	temp (ºC)	time (h)	yield[b] (%)
1	none	0	toluene	reflux	24	0[c]
2	$Fe_2(SO_4)_3 \cdot xH_2O$	5	toluene	rt	24	49
3	$Fe_2(SO_4)_3 \cdot xH_2O$	10	toluene	reflux	0.25	73
4	$Fe_2(SO_4)_3 \cdot xH_2O$	15	toluene	reflux	0.25	88
5	$Fe_2(SO_4)_3 \cdot xH_2O$	20	toluene	reflux	0.25	71
6	$Fe_2(SO_4)_3 \cdot xH_2O$	25	toluene	reflux	0.25	44
7	Fe_2O_3	15	toluene	reflux	24	8
8	$FeCl_3$	15	toluene	reflux	24	33
9	$FeBr_3$	15	toluene	reflux	24	9
10	$Sc(OTf)_3$	15	toluene	reflux	24	72
11	CH_3COOH	15	toluene	reflux	24	21

12	CF_3COOH	15	toluene	reflux	24	27
13	HCl	15	toluene	reflux	24	11
14	$Fe_2(SO_4)_3•xH_2O$	15	EtOH	reflux	24	0[c]
15	$Fe_2(SO_4)_3•xH_2O$	15	DCM	reflux	24	0[c]
16	$Fe_2(SO_4)_3•xH_2O$	15	EtOAc	reflux	24	35
17	$Fe_2(SO_4)_3•xH_2O$	15	THF	reflux	24	0[c]
18	$Fe_2(SO_4)_3•xH_2O$	15	$CHCl_3$	reflux	24	45

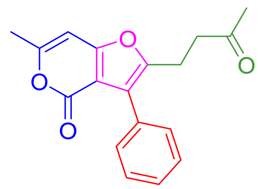
Reaction condition: 4–hydroxy–6–methyl–2–pyrone (1 mmol), 2–methylfuran (1 mmol) and benzaldehyde (1 mmol). [a]Based on electrophile. [b]Isolated yields of 2–alkyl–3–arylfuro Furo[3,2-*c*]pyran-4-ones **19a**. [c]No desired product was observed.

VIII. General procedure for the synthesis of furo[3,2,–*c*]pyran-4-ones 19 a-j

A 50 mL round bottom flask was charged with aldehydes (1 mmol, 1 equiv), 2-methyl furan (1 mmol, 1 equiv) and 4–hydroxy–6–methyl–2–pyrone (1 mmol, 1 equiv) in anhydrous toluene (10 mL). To this reaction mixture, $Fe_2(SO_4)_3•xH_2O$ (15 mol%, 60 mg) was added and the solution was stirred at reflux temperature for 15 min in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by rotovap. The residue was dissolved in DCM (15 mL), washed using distilled water (3 × 15 mL) and dried over $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate).

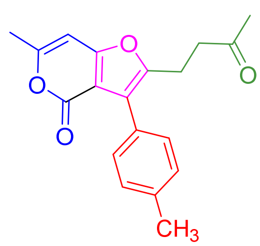
The general method from above was used for the preparation of following furo[3,2,–c]pyran-4-ones:

6-methyl-2-(3-oxobutyl)-3-phenyl-4H-furo[3,2-c]pyran-4-one **19a**



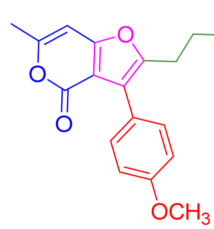
Brown solid, 245.7 mg, 88% yield. m.p. 75-77°C; R_f = 0.18 (EtOAc:Hexanes = 1:2, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:2, SiO_2); IR (film) ν_{max}/cm^{-1} 3056, 2987, 2925, 1733, 1320, 737; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.94 (d, *J* = 1.6 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.35 (s, 1H), 5.99 (s, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.6, 160.9, 159.7, 159.4, 151.8, 147.7, 147.5, 123.6, 123.5, 119.4, 110.5, 108.4, 107.7, 101.3, 95.6, 41.4, 30.0, 20.7, 20.3.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{18}H_{16}O_4$ 296.1043; Found: 296.1047.

6-methyl-2-(3-oxobutyl)-3-(p-tolyl)-4H-furo[3,2-c]pyran-4-one **19b**



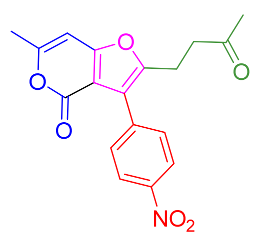
Brown oil, 263.6 mg, 85% yield.; R_f = 0.14 (EtOAc:Hexanes = 1:2, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:2, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 2987, 2924, 1735, 1266, 738; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.36 (s, 1H), 3.03 (t, *J* = 7.6 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.6, 161.0, 159.6, 159.4, 151.8, 137.7, 129.7, 129.2, 127.0, 119.6, 107.7, 95.6, 41.5, 30.0, 21.4, 20.7, 20.3.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{19}H_{18}O_4$ 310.1200; Found: 310.1189.

3-(4-methoxyphenyl)-6-methyl-2-(3-oxobutyl)-4H-furo[3,2-c]pyran-4-one **19c**



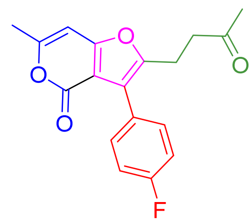
Brown oil, 280.4 mg, 83% yield.; R$_f$ = 0.25 (EtOAc:Hexanes = 1:2, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:1, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 3018, 2925, 2837, 1735, 736; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 8.3, 7.6 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.90 (ddd, *J* = 8.4, 2.7, 1.0 Hz, 1H), 6.37 (d, *J* = 1.0 Hz, 1H), 3.84 (s, 3H), 3.06 (dd, *J* = 8.2, 6.7 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.33 (d, *J* = 1.0 Hz, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 161.1, 159.7, 159.5, 159.3, 152.1, 131.3, 129.4, 122.2, 119.6, 115.6, 113.9, 107.6, 95.6, 55.4, 41.4, 30.0, 20.8, 20.3.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{19}H_{18}O_4$ 326.1149; Found: 326.1139.

6-methyl-3-(4-nitrophenyl)-2-(3-oxobutyl)-4H-furo[3,2-c]pyran-4-one **19d**



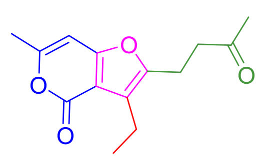
Orange solid, 264.2 mg, 82% yield. m.p. 150-152°C; R$_f$ = 0.38 (EtOAc:Hexanes = 1:1, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:1.5, SiO_2); IR (film) ν_{max}/cm^{-1} 3058, 2988, 2924, 1736, 1346, 737; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 6.41 (s, 1H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.2, 161.4, 160.4, 159.1, 153.2, 147.2, 137.1, 130.8, 123.6, 118.0, 107.1, 95.5, 40.8, 29.9, 20.6, 20.3.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{18}H_{15}NO_6$ 341.0894; Found: 341.0891.

3-(4-fluorophenyl)-6-methyl-2-(3-oxobutyl)-4H-furo[3,2-c]pyran-4-one **19e**



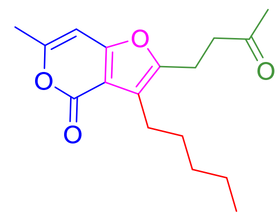
Brown oil, 266.8 mg, 85% yield.; R_f = 0.18 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:2, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 2987, 2926, 2305, 1732, 748; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.38 (m, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 6.37 (d, *J* = 1.1 Hz, 1H), 3.00 (dd, *J* = 8.2, 6.8 Hz, 2H), 2.82 (dd, *J* = 8.1, 6.7 Hz, 2H), 2.32 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.5, 163.5, 161.6, 161.1, 159.8, 159.4, 152.0, 131.7, 131.6, 126.0, 125.9, 118.8, 115.6, 115.4, 107.6, 95.6, 41.2, 30.0, 20.6, 20.3.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{18}H_{15}FO_4$ 314.0949; Found: 314.0939.

3-ethyl-6-methyl-2-(3-oxobutyl)-4H-furo[3,2-c]pyran-4-one **19f**



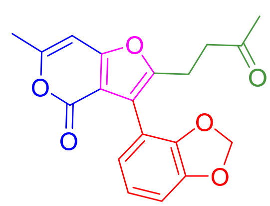
Yellow solid, 200.7 mg, 81% yield. m.p. 119-120°C; R_f = 0.22 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:3, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 2986, 2935, 1732, 1265, 705; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.28 (d, *J* = 1.0 Hz, 1H), 2.90 (d, *J* = 7.6 Hz, 2H), 2.82 – 2.75 (m, 2H), 2.62 (q, *J* = 7.5 Hz, 2H), 2.29 (d, *J* = 0.9 Hz, 3H), 2.17 (s, 3H), 1.20 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.8, 160.8, 160.1, 159.1, 150.8, 119.9, 108.8, 95.7, 41.8, 30.1, 20.3, 20.0, 17.0, 15.3.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{14}H_{16}O_4$ 248.1043; Found: 248.1033.

6-methyl-2-(3-oxobutyl)-3-pentyl-4H-furo[3,2-c]pyran-4-one **19g**



Brown solid, 249.4 mg, 86 % yield. m.p. 60-62°C; R_f = 0.22 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:3, SiO_2); IR (film) ν_{max}/cm^{-1} 3057, 2957, 2859, 1736, 1266, 738, 688; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.28 (s, 1H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 2.17 (s, 3H), 1.59 (p, *J* = 7.5 Hz, 2H), 1.33 – 1.27 (m, 4H), 0.88 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.8, 160.8, 160.1, 159.0, 151.2, 118.5, 108.8, 95.7, 41.7, 31.5, 30.1, 30.1, 23.5, 22.6, 20.3, 20.1, 14.2.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{17}H_{22}O_4$ 290.1513; Found: 290.1501.

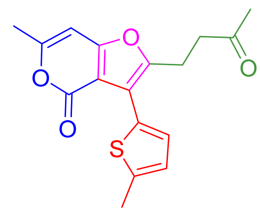
3-(benzo[d][1,3]dioxol-4-yl)-6-methyl-2-(3-oxobutyl)-4H-furo[3,2-c]pyran-4-one **19h**



Brown oil, 251.6 mg, 74% yield.; R_f = 0.11 (EtOAc:Hexanes = 1:2, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:1, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 2987, 2926, 1733, 1653, 734; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.94 (d, *J* = 1.6 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.36 (d, *J* = 1.0 Hz, 1H), 5.99 (s, 2H), 3.02 (dd, *J* = 8.3, 6.7 Hz, 2H), 2.81 (dd, *J* = 8.3, 6.7

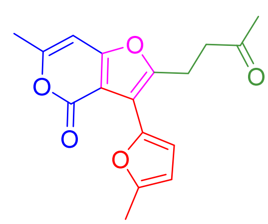
Hz, 2H), 2.33 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 160.9, 159.7, 159.4, 151.9, 147.7, 147.5, 123.6, 123.5, 119.5, 110.5, 108.4, 101.3, 95.6, 41.4, 30.0, 20.7, 20.3.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{19}H_{16}O_6$ 340.0941; Found: 340.0943.

6-methyl-3-(5-methylthiophen-2-yl)-2-(3-oxobutyl)-4H-furo[3,2-c]pyran-4-one **19i**



Brown oil, 195.6 mg, 62% yield.; R_f = 0.31 (EtOAc:Hexanes = 1:2, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:3, SiO_2); IR (film) ν_{max}/cm^{-1} 3054, 2987, 1718, 1591, 1422, 737; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 3.5 Hz, 1H), 6.75 (dd, *J* = 3.5, 1.2 Hz, 1H), 6.33 (d, *J* = 1.0 Hz, 1H), 3.16 (dd, *J* = 8.4, 6.8 Hz, 2H), 2.84 (dd, *J* = 8.4, 6.8 Hz, 2H), 2.50 (d, *J* = 1.1 Hz, 3H), 2.32 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.5, 161.0, 159.9, 159.3, 151.9, 140.6, 129.3, 127.9, 125.9, 113.7, 107.4, 95.5, 41.5, 30.0, 21.3, 20.3, 15.4.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{17}H_{16}O_4S$ 316.0764; Found: 316.0759.

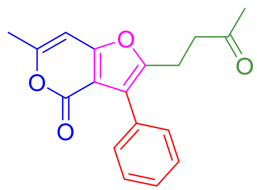
6-methyl-3-(5-methylfuran-2-yl)-2-(3-oxobutyl)-4H-furo[3,2-c]pyran-4-one **19j**

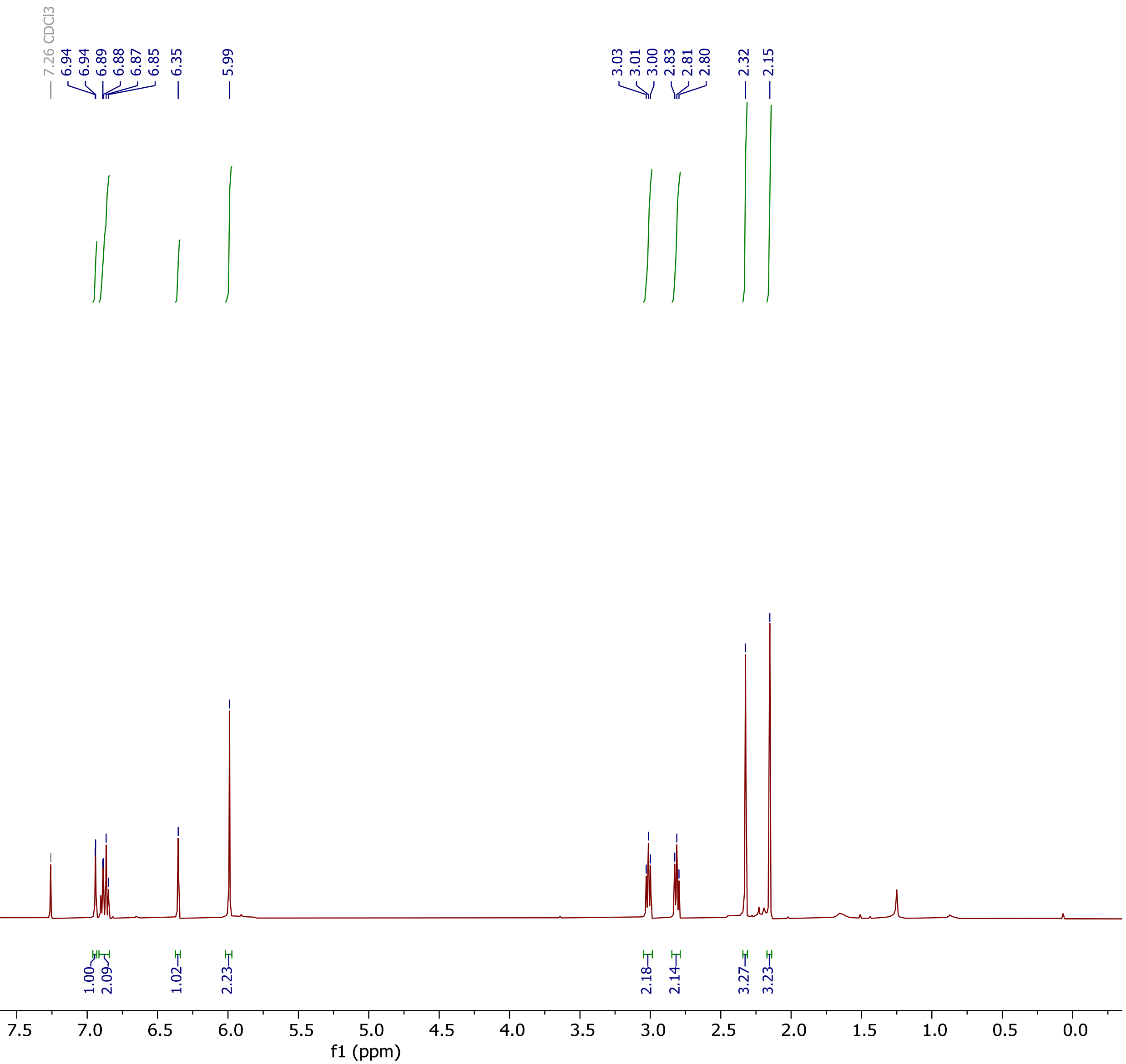


Brown oil, 201.1 mg, 67% yield.; R_f = 0.40 (EtOAc:Hexanes = 1:2, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:10 to 1:2, SiO_2); IR (film) ν_{max}/cm^{-1} 3054, 2924, 1716, 1652, 1622, 738, 704; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 3.3 Hz, 1H), 6.34 (d, *J* = 1.2 Hz, 1H), 6.09 (dd, *J* = 3.1, 1.2 Hz, 1H), 3.34 (dd, *J* = 8.4, 6.8 Hz, 2H), 2.92 – 2.86 (m, 2H), 2.35 (s, 3H), 2.34 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.1, 161.2, 159.9, 159.4, 151.8, 151.2, 143.6, 112.7, 110.5, 107.8, 106.0, 95.5, 41.8, 29.9, 22.3, 20.2, 13.8.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{17}H_{16}O_5$ 300.0992; Found: 300.0992.

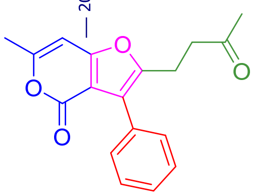
IX. ^{1}H and ^{13}C NMR Spectra for Furo[3,2,–*c*]pyran-4-ones 19 a-j

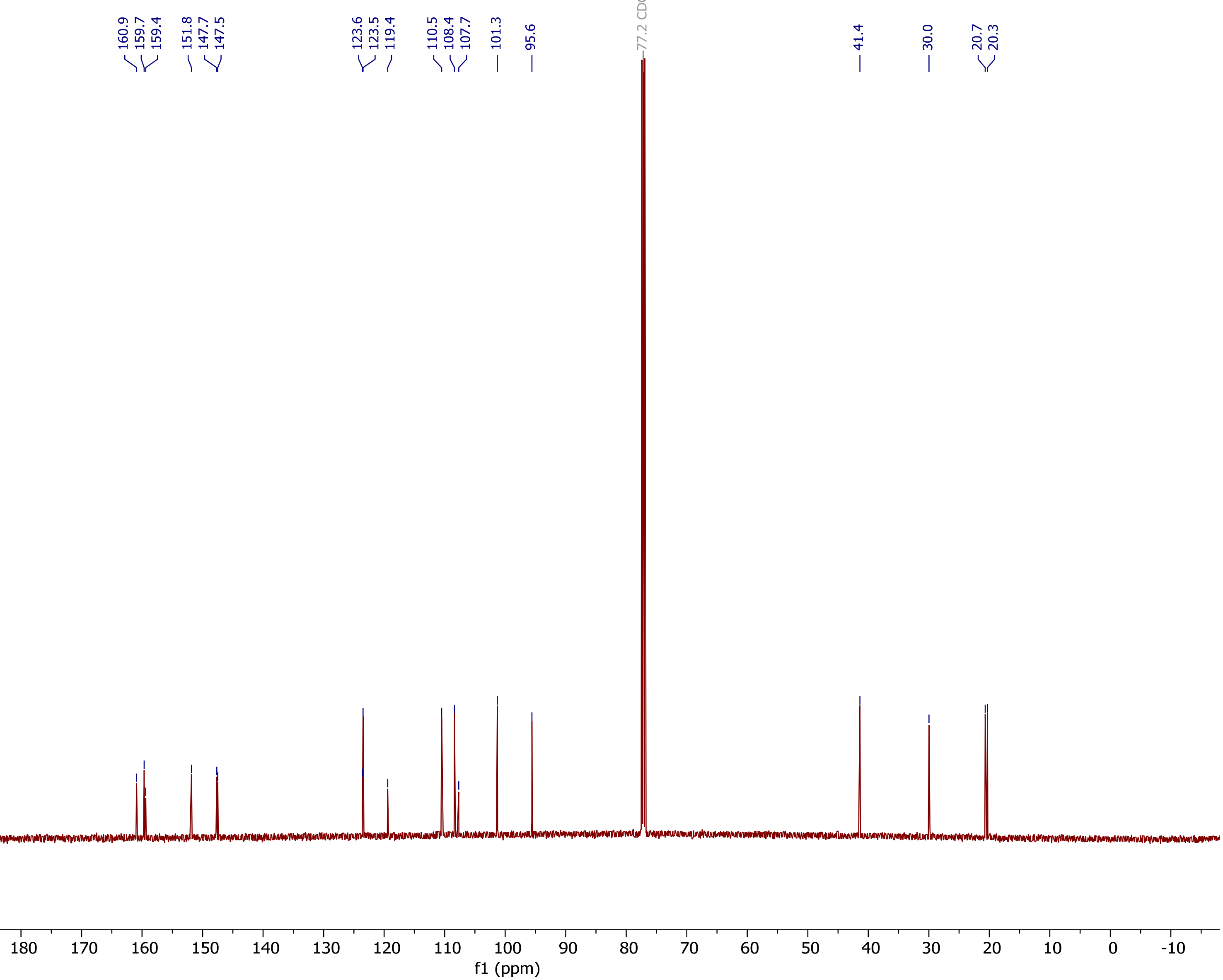
Compound 19a (500 MHz, Chloroform-d)



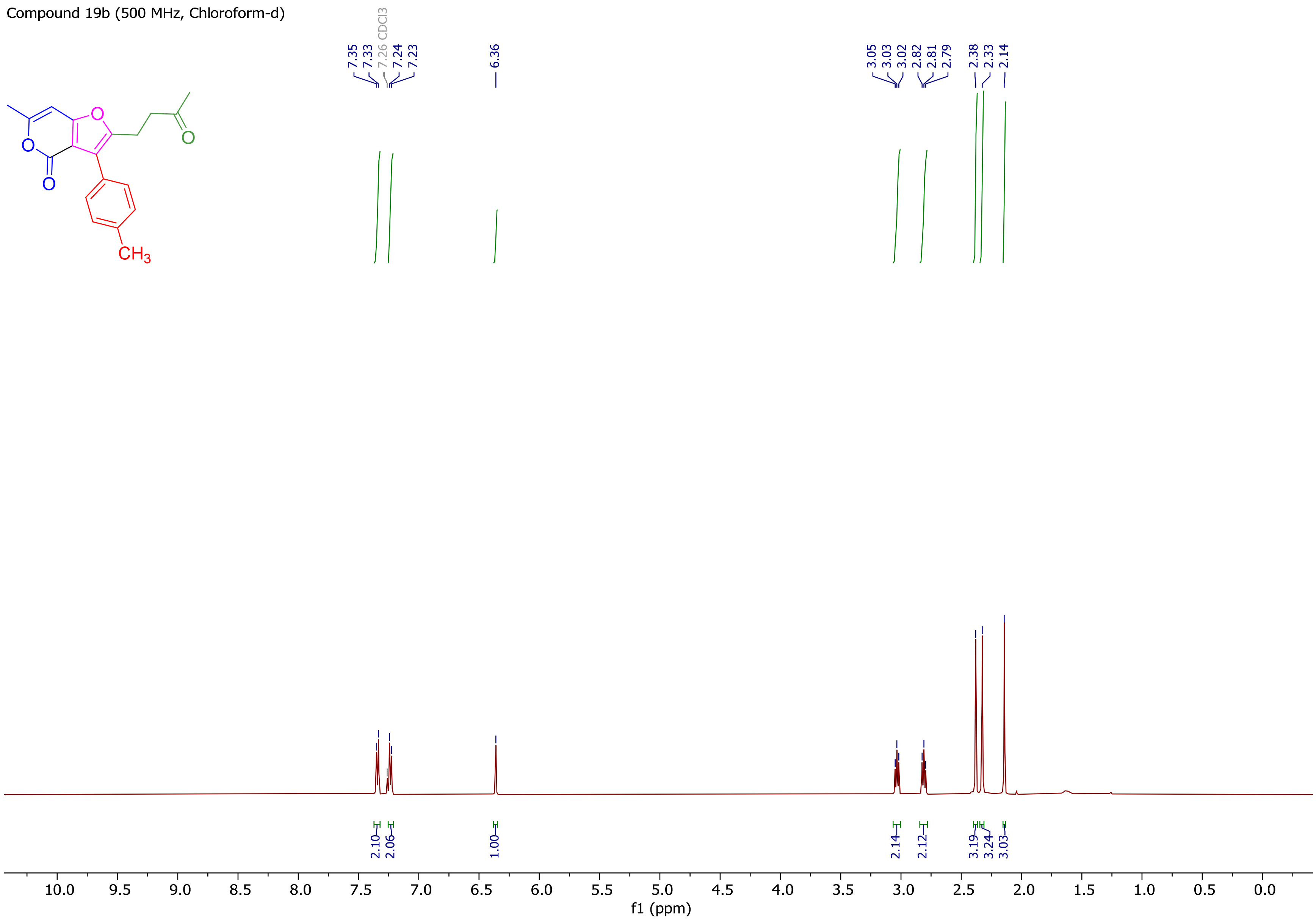


Compound 19a (126 MHz, Chloroform-d)

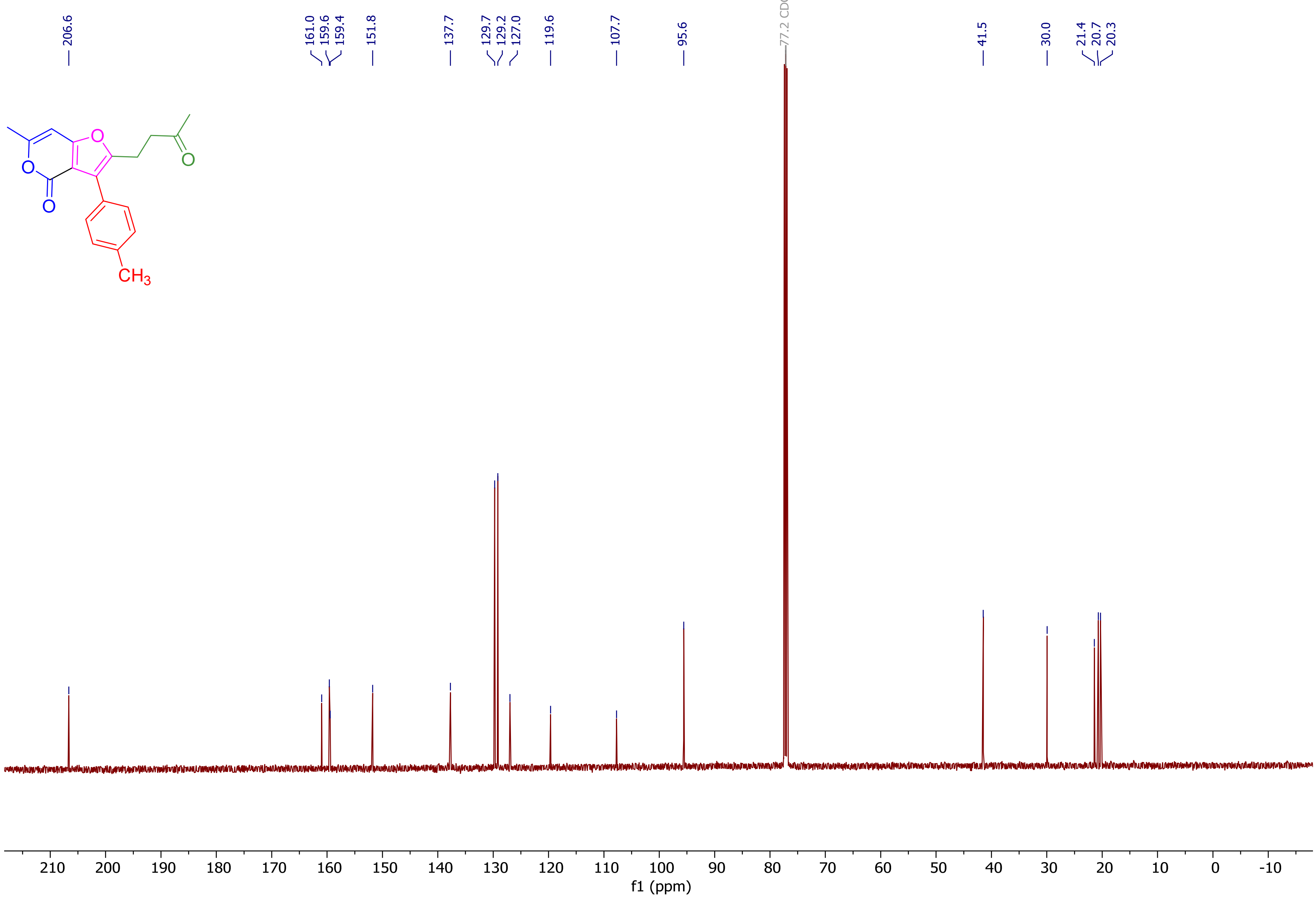




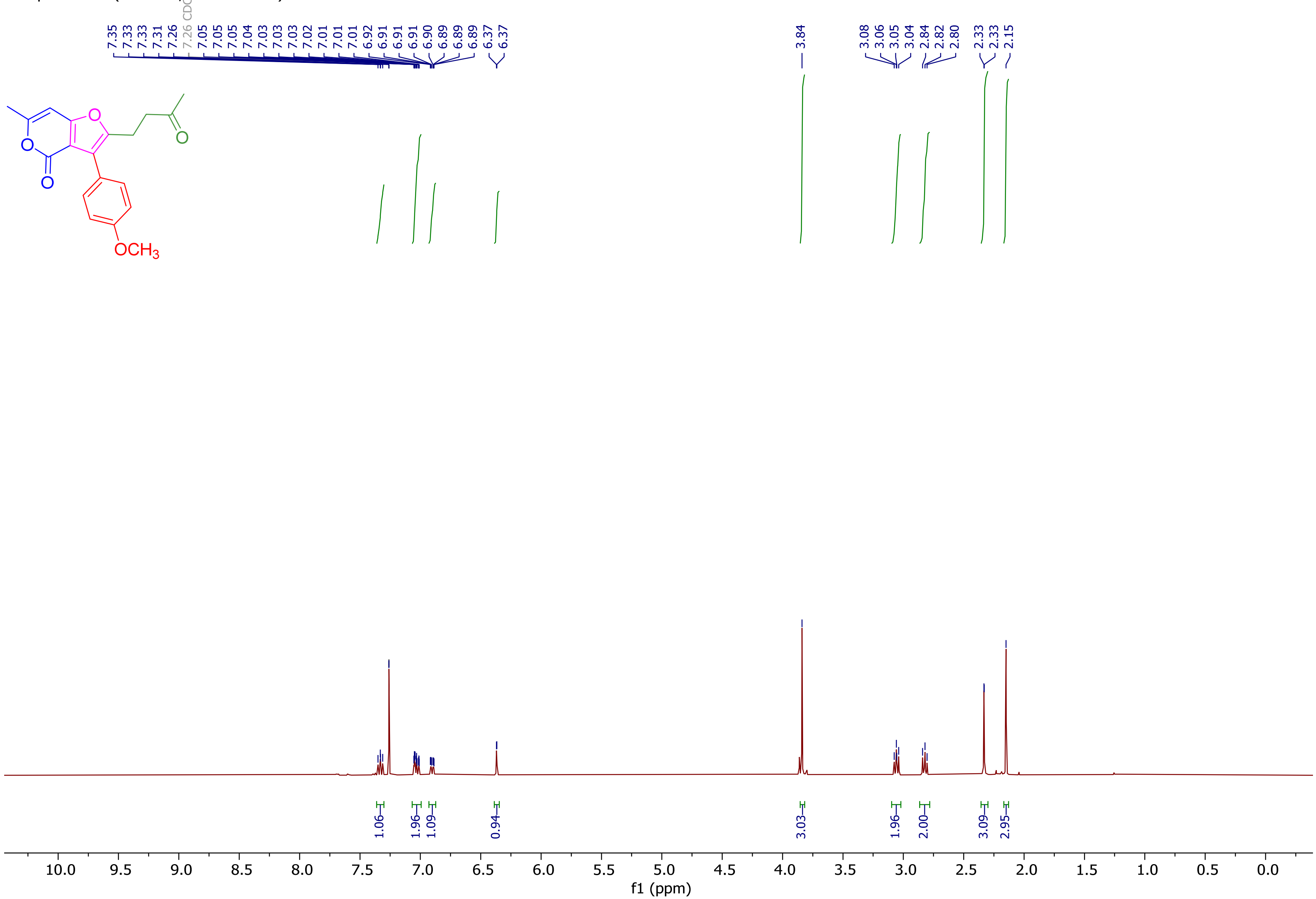
Compound 19b (500 MHz, Chloroform-d)



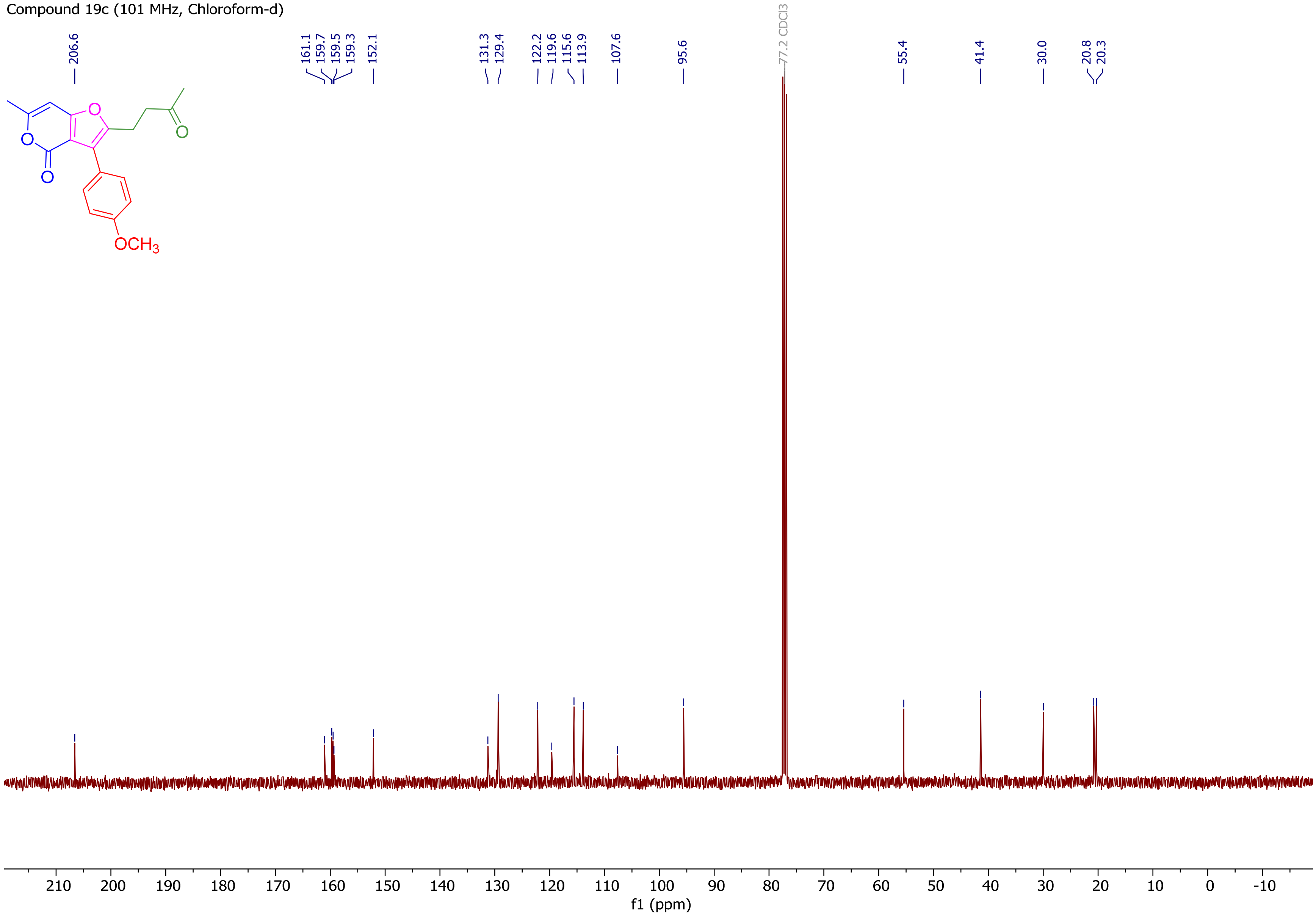
Compound 19b (126 MHz, Chloroform-d)



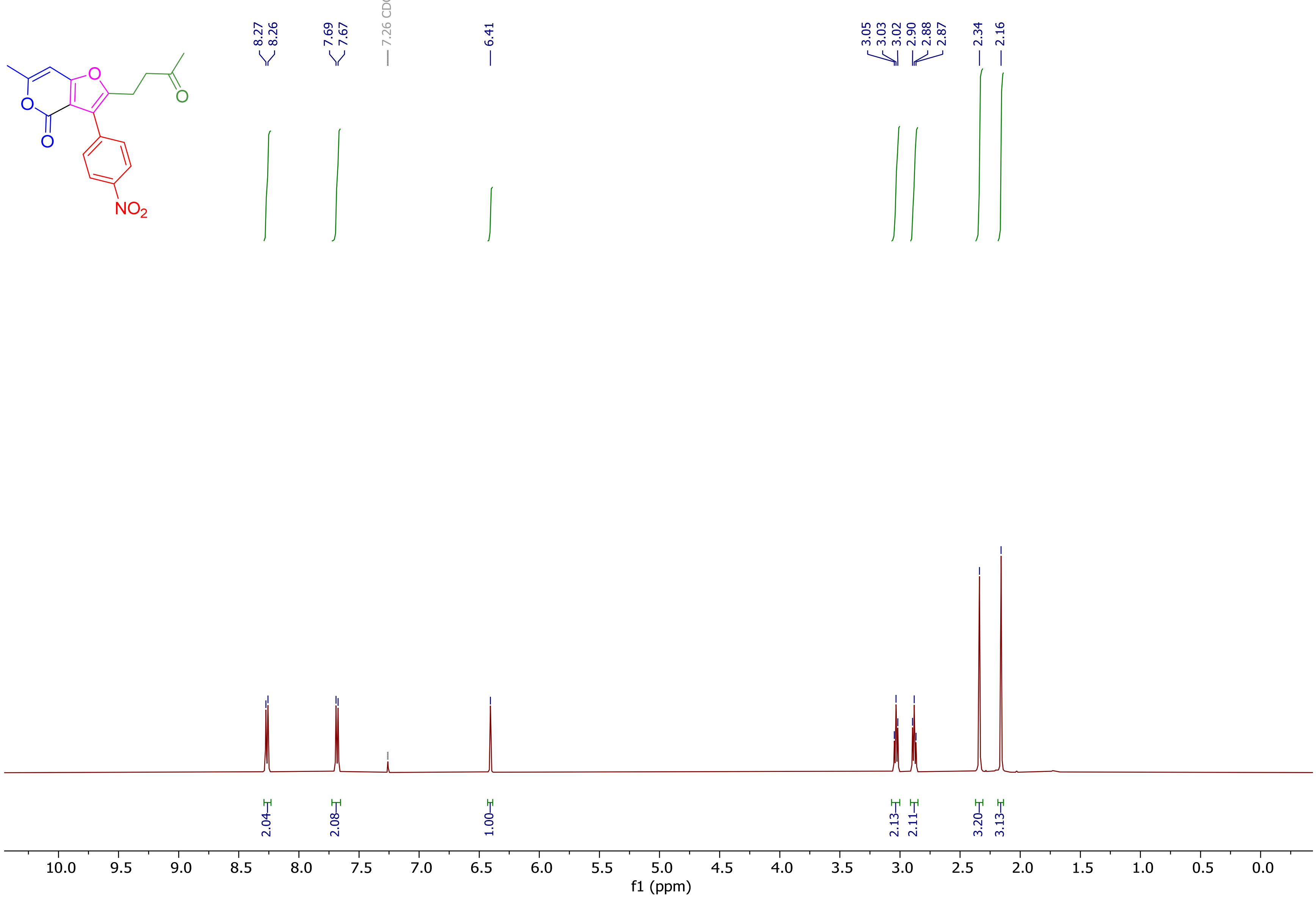
Compound 19c (400 MHz, Chloroform-d)



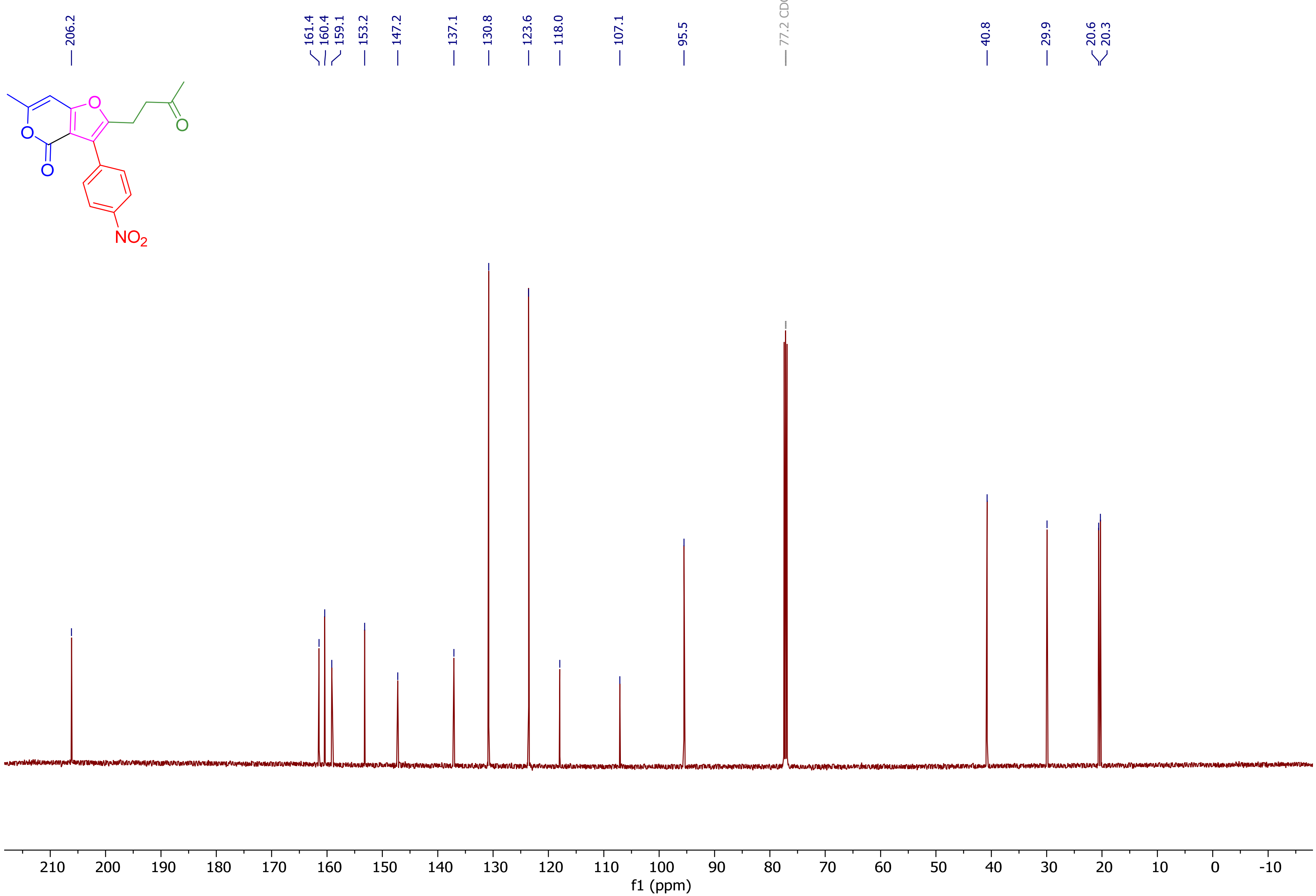
Compound 19c (101 MHz, Chloroform-d)



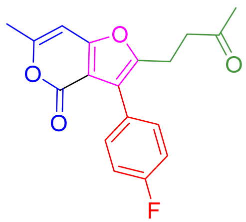
Compound 19d (500 MHz, Chloroform-d)

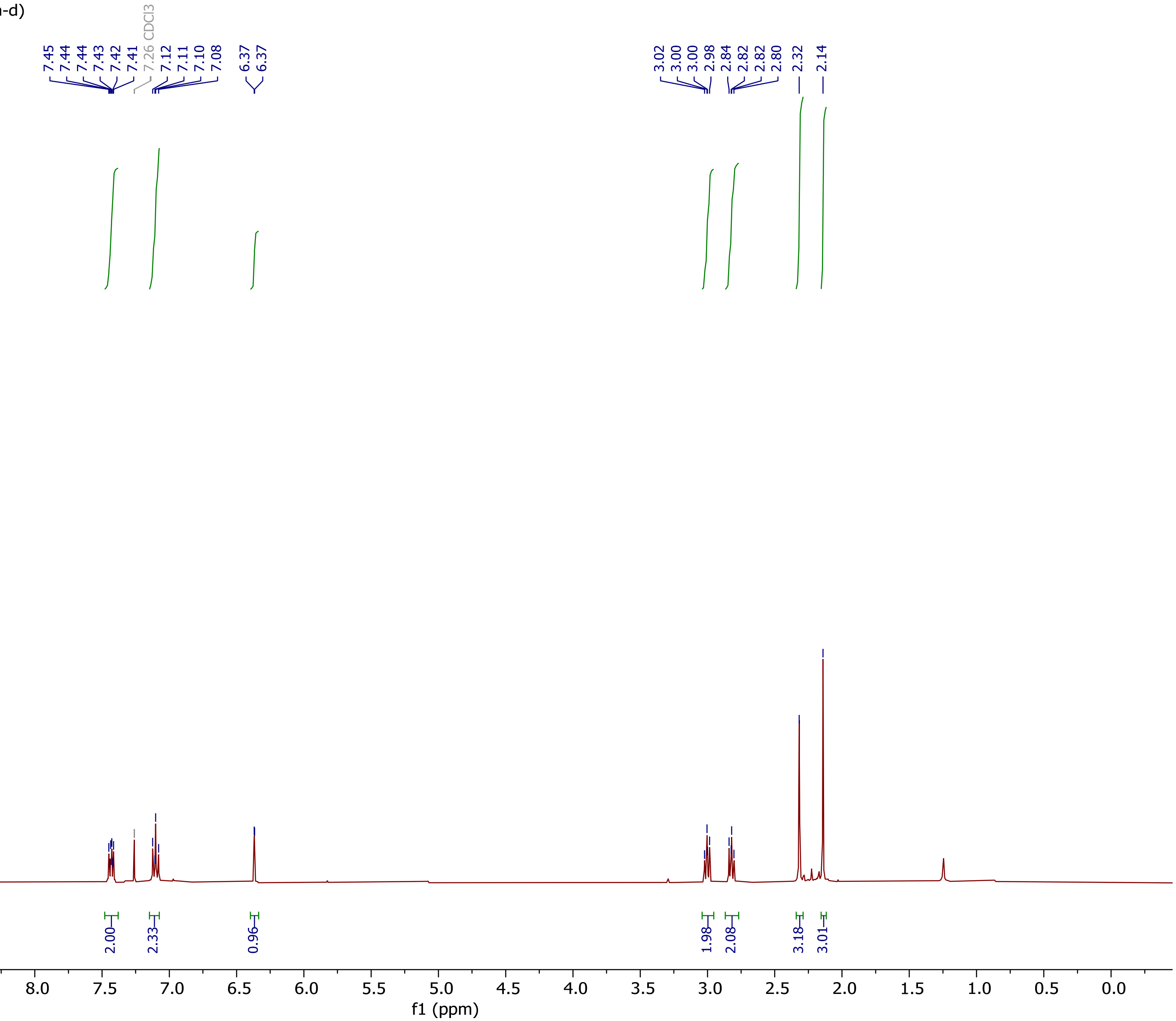


Compound 19d (126 MHz, Chloroform-d)

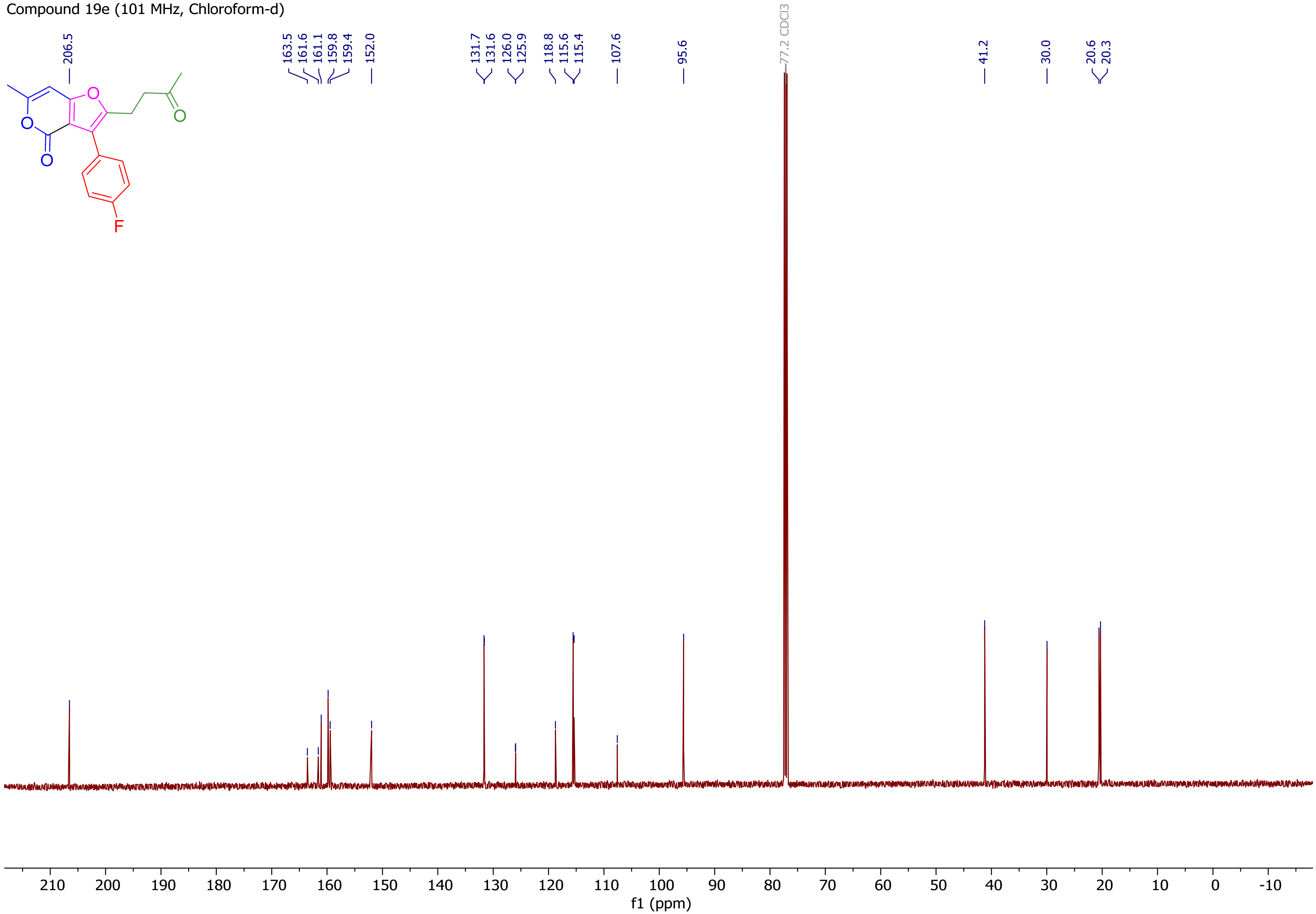


Compound 19e (400 MHz, Chloroform-d)

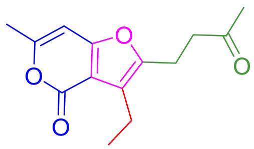


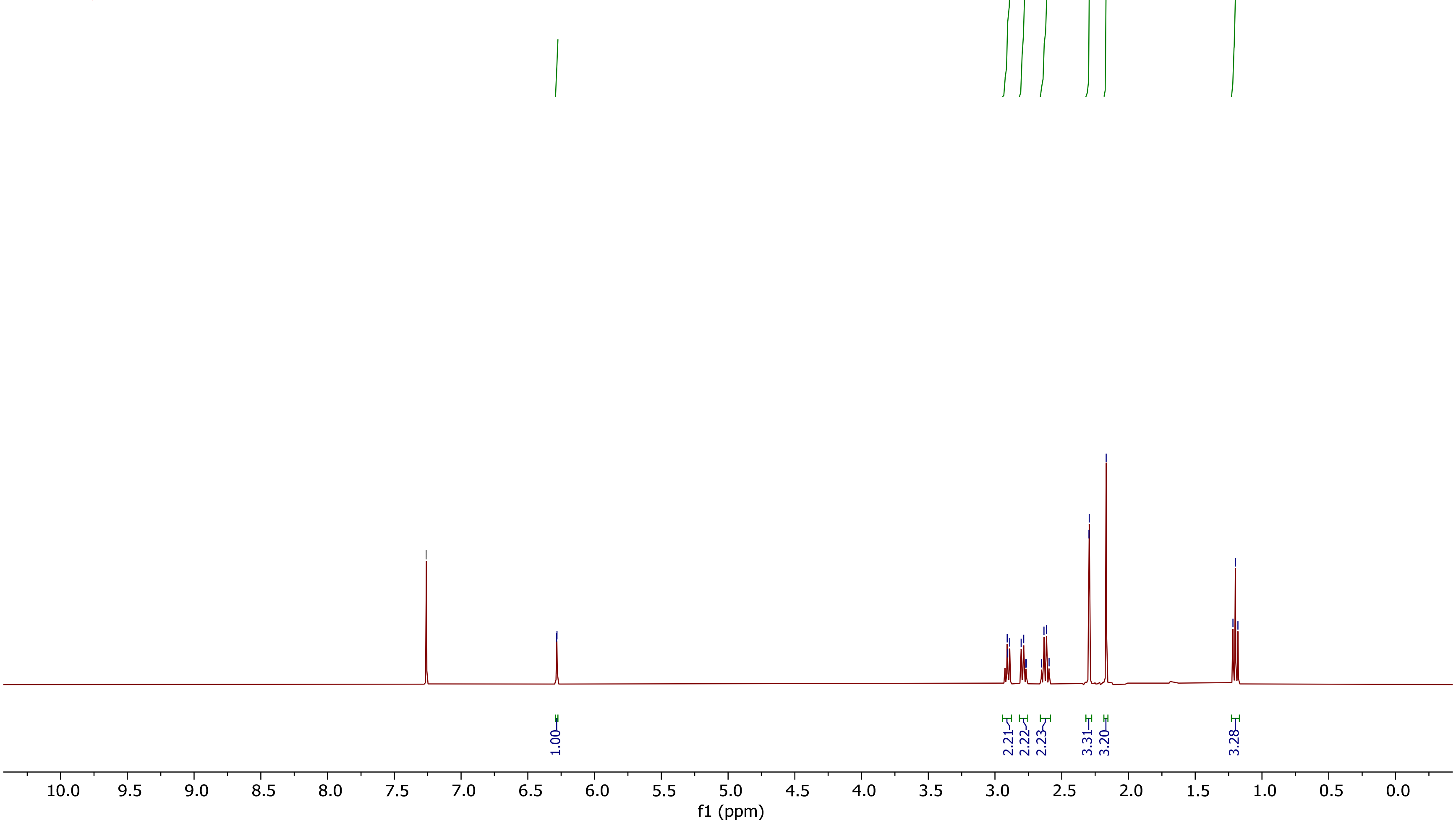


Compound 19e (101 MHz, Chloroform-d)

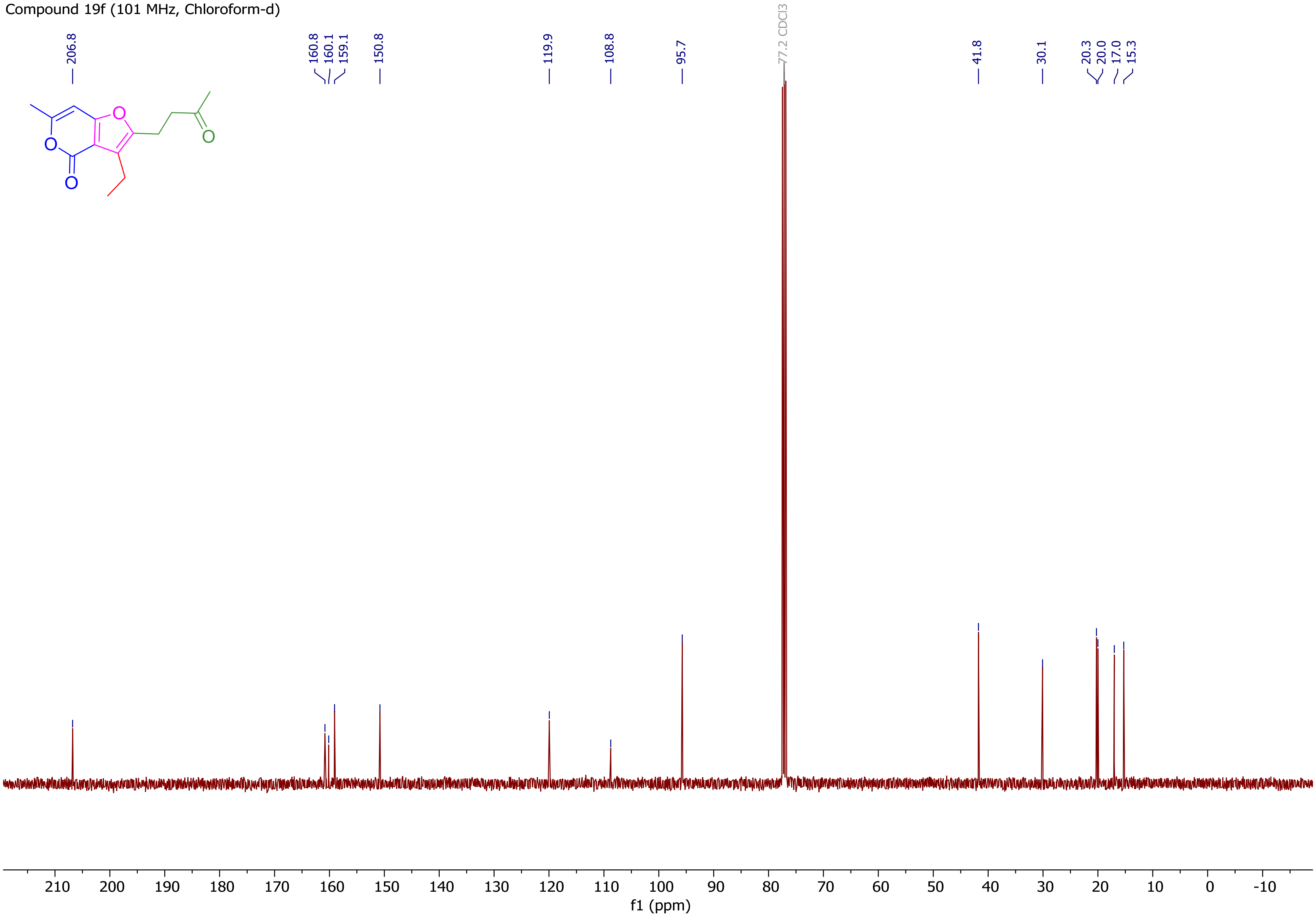


Compound 19f (400 MHz, Chloroform-d)

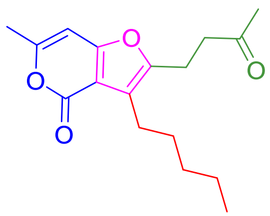


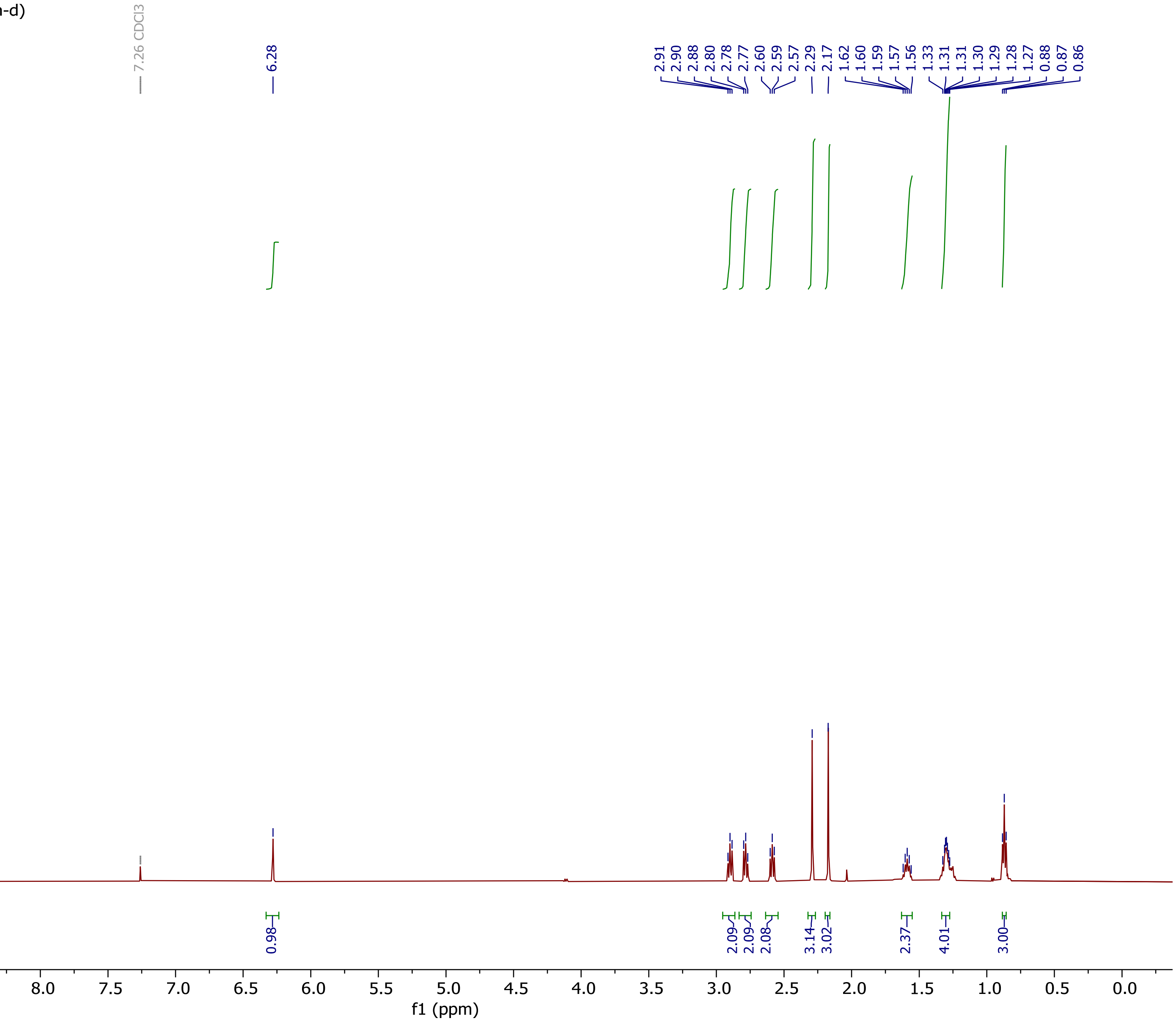


Compound 19f (101 MHz, Chloroform-d)

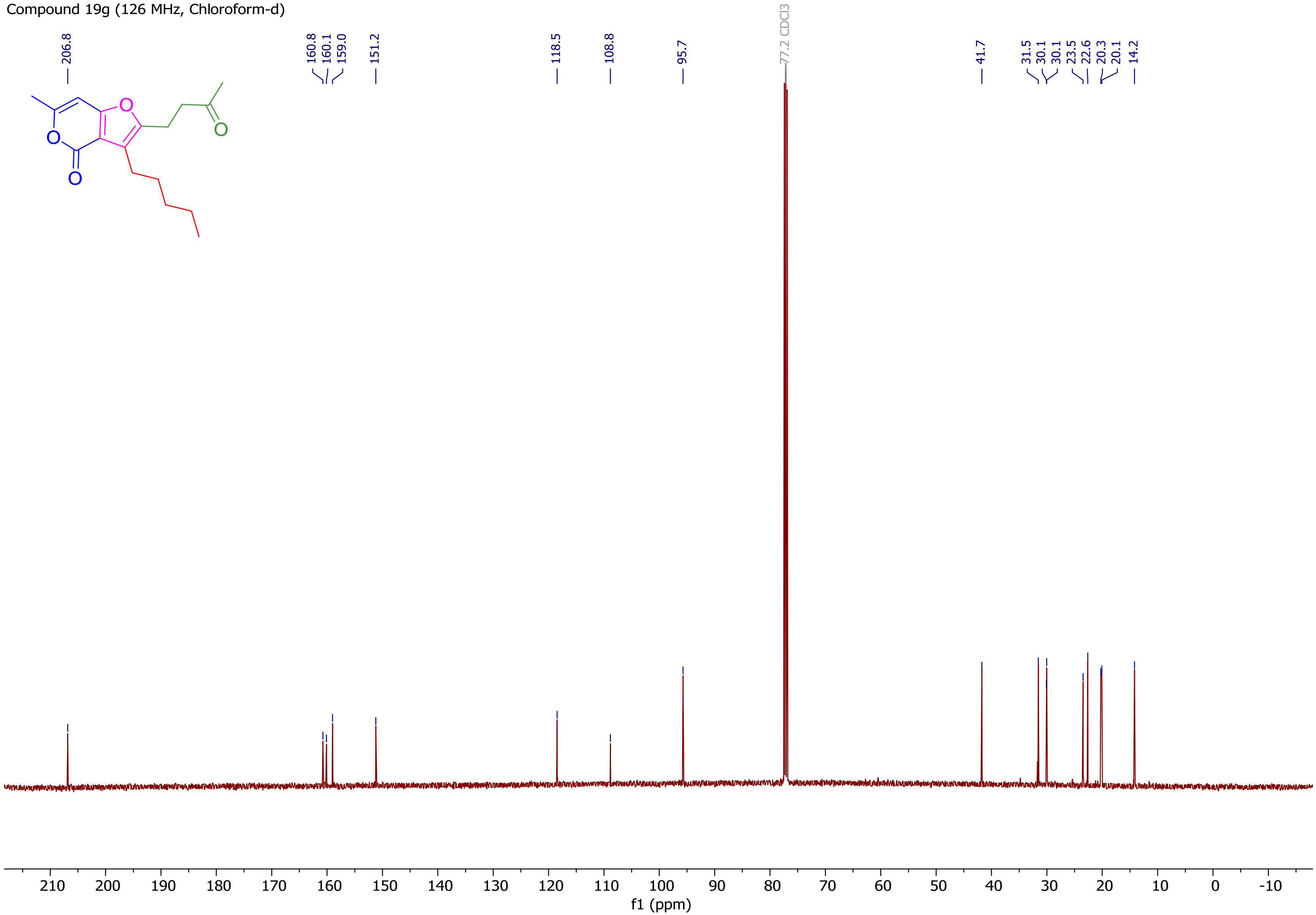


Compound 19g (500 MHz, Chloroform-d)

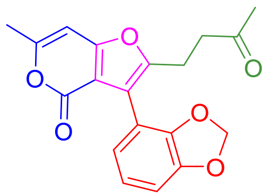


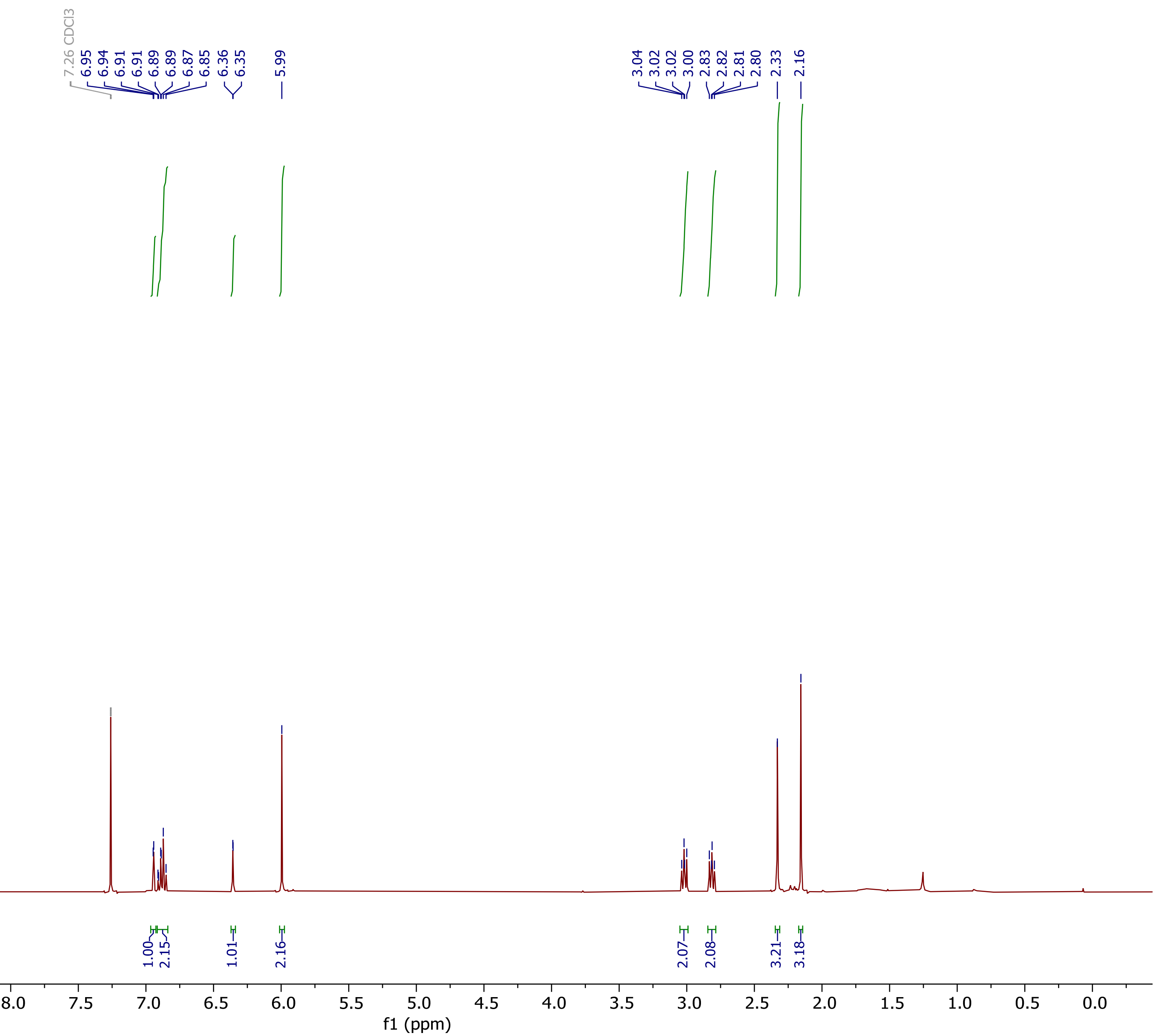


Compound 19g (126 MHz, Chloroform-d)

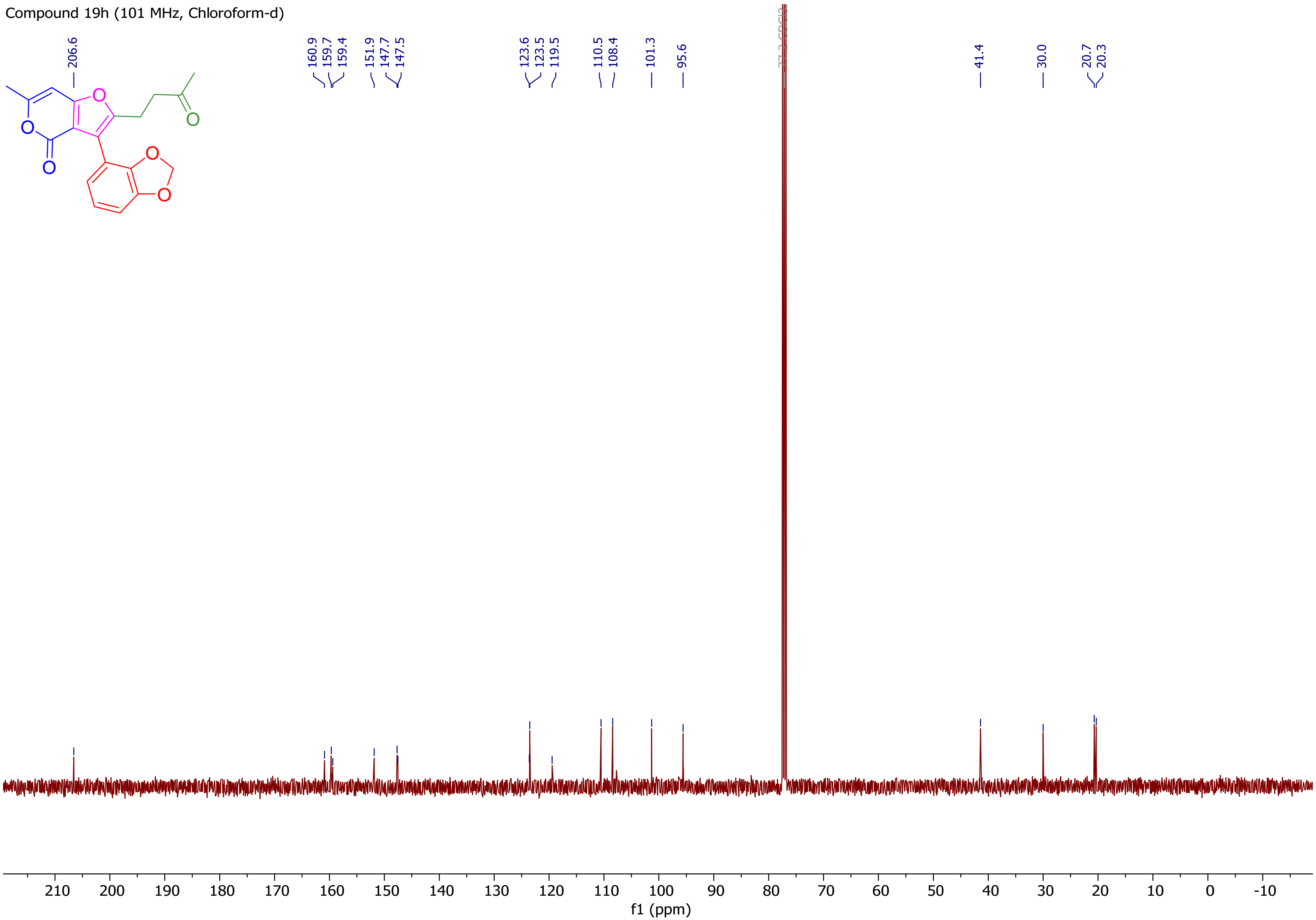


Compound 19h (400 MHz, Chloroform-d)

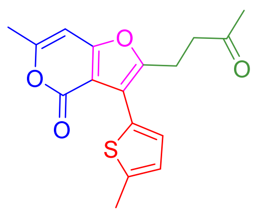


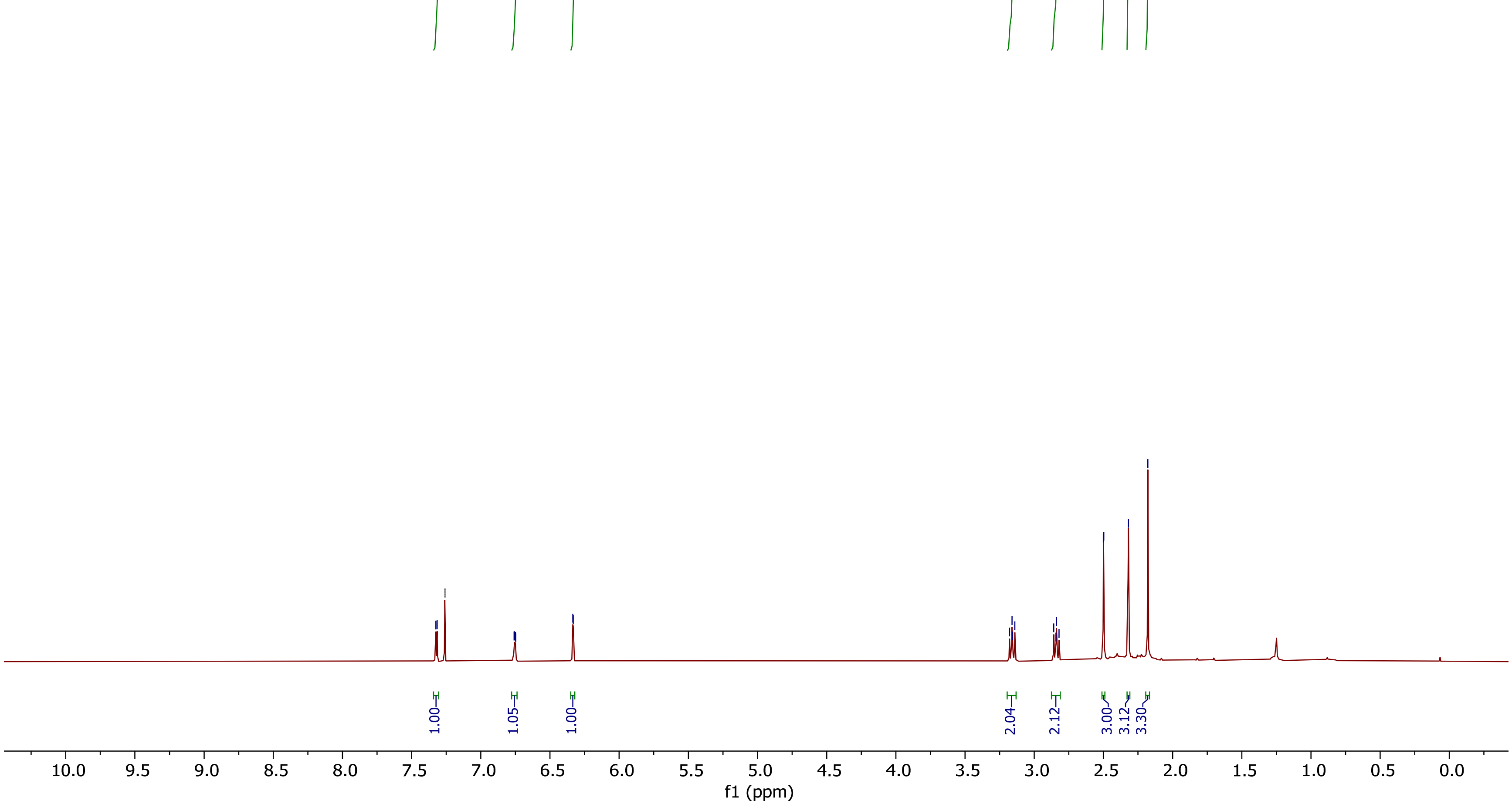


Compound 19h (101 MHz, Chloroform-d)

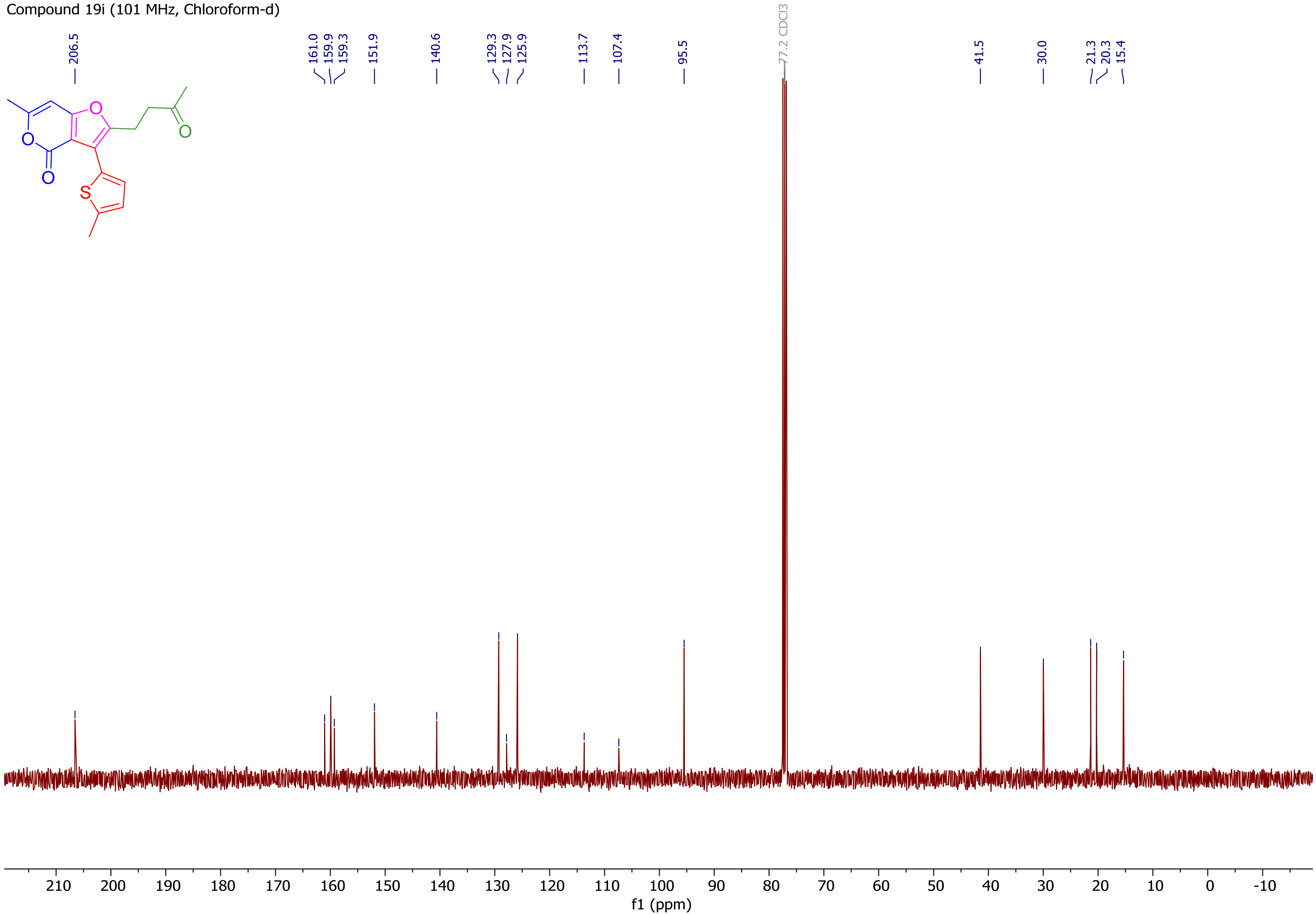


Compound 19i (400 MHz, Chloroform-d)

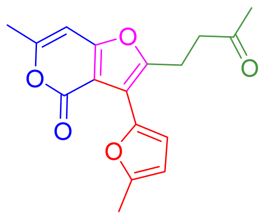


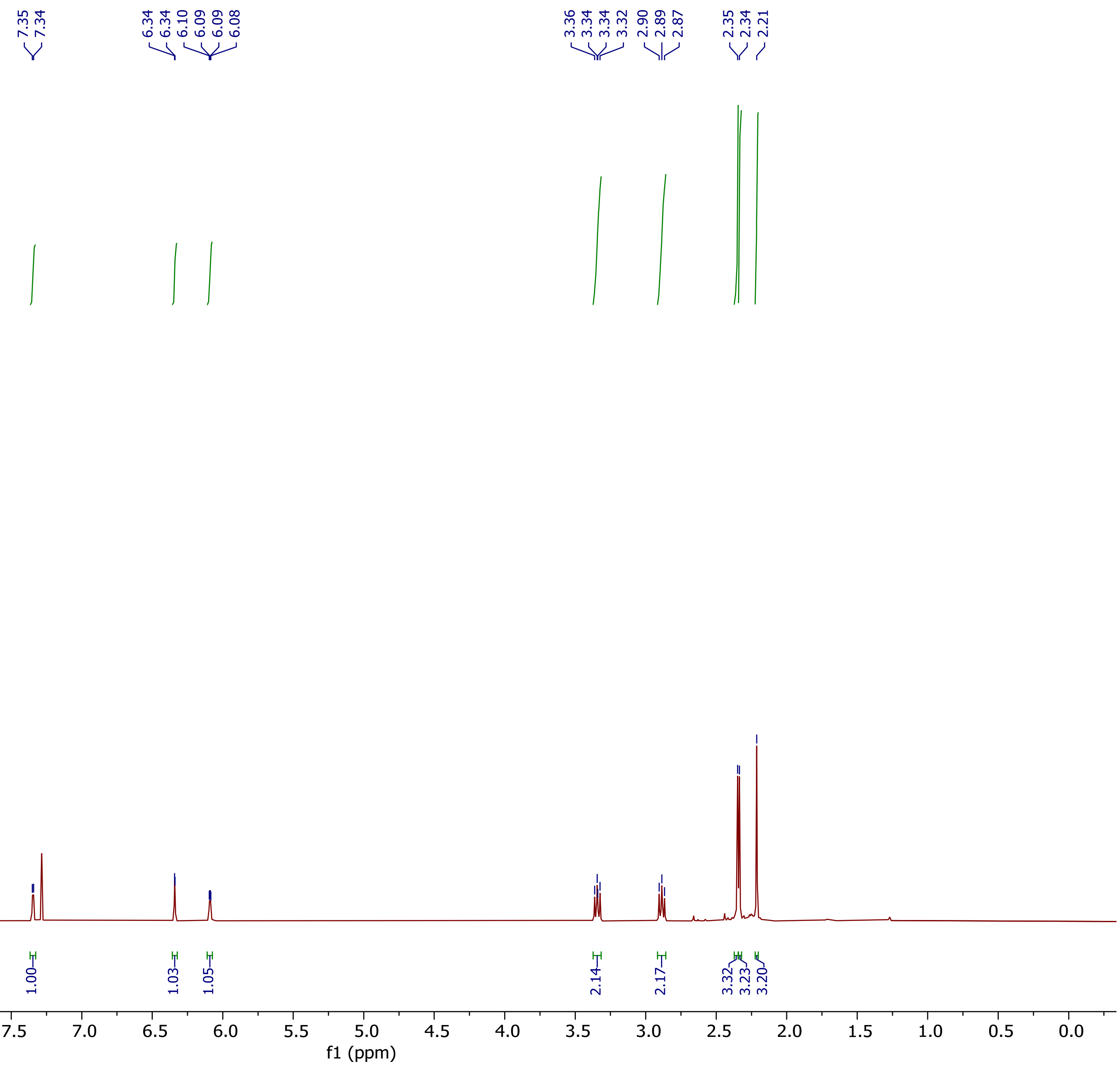


Compound 19i (101 MHz, Chloroform-d)

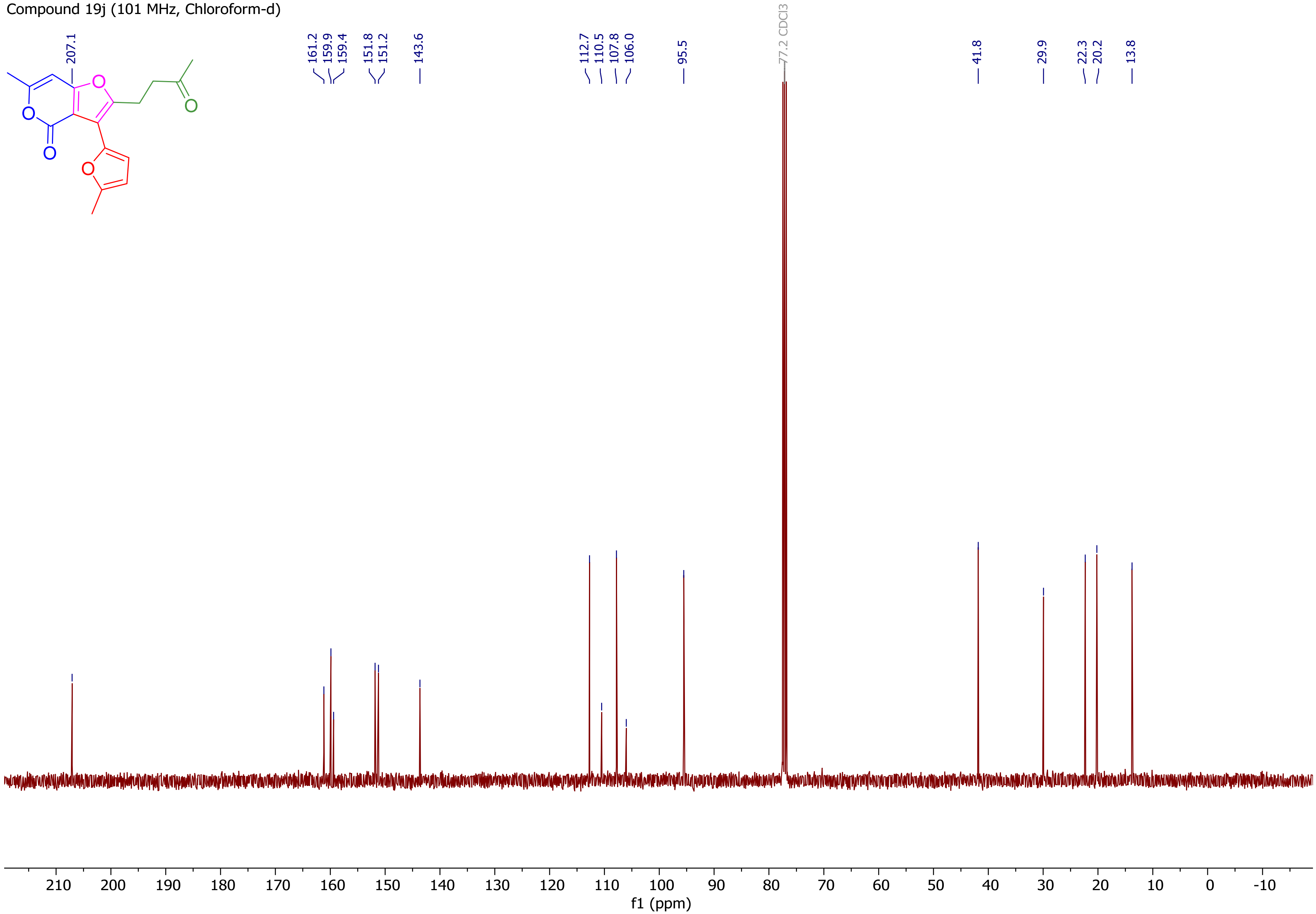


Compound 19j (400 MHz, Chloroform-d)





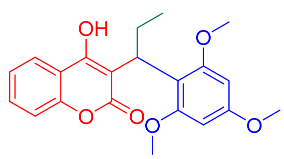
Compound 19j (101 MHz, Chloroform-d)



X. Procedure for the synthesis of Phenprocoumon analogue 23

A 50 mL round bottom flask was charged with benzaldehyde (1 mmol, 1 equiv), 1,3,5-trimethoxybenze (1 mmol, 1 equiv) and 4- hydroxycoumarin (1 mmol, 1 equiv) in anhydrous tetrahydrofuran (25 mL). To this reaction mixture, $Fe_2(SO_4)_3 \cdot xH_2O$ (60 mg, 15 mol%) was added and the solution was stirred at reflux temperatures for 5 hours in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by rotovap. The residue was dissolved in DCM (15 mL), washed using distilled water (3 × 15 mL) and dried over $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate).

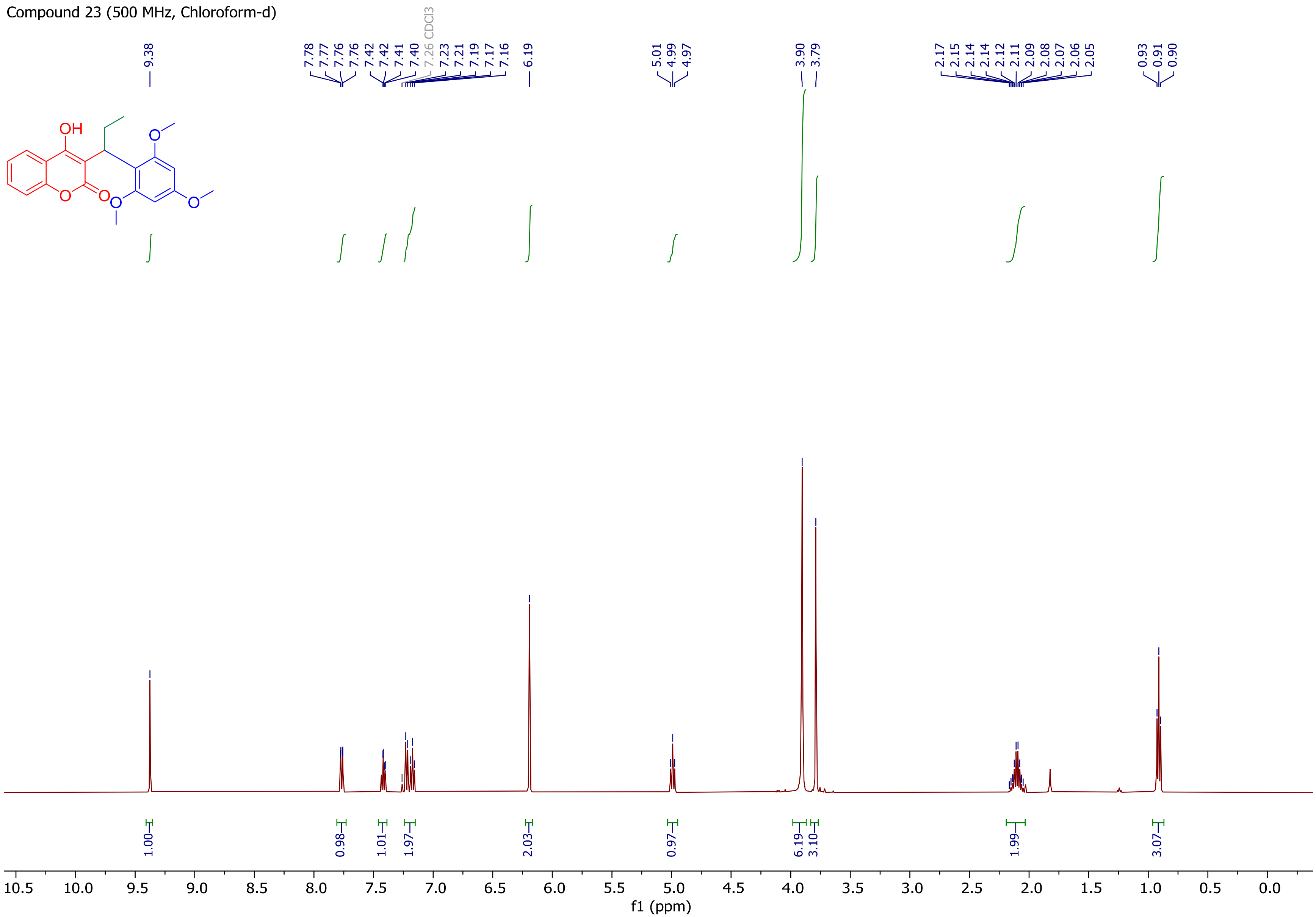
4-hydroxy-3-(1-(2,4,6-trimethoxyphenyl)propyl)-2H-chromen-2-one **23.**



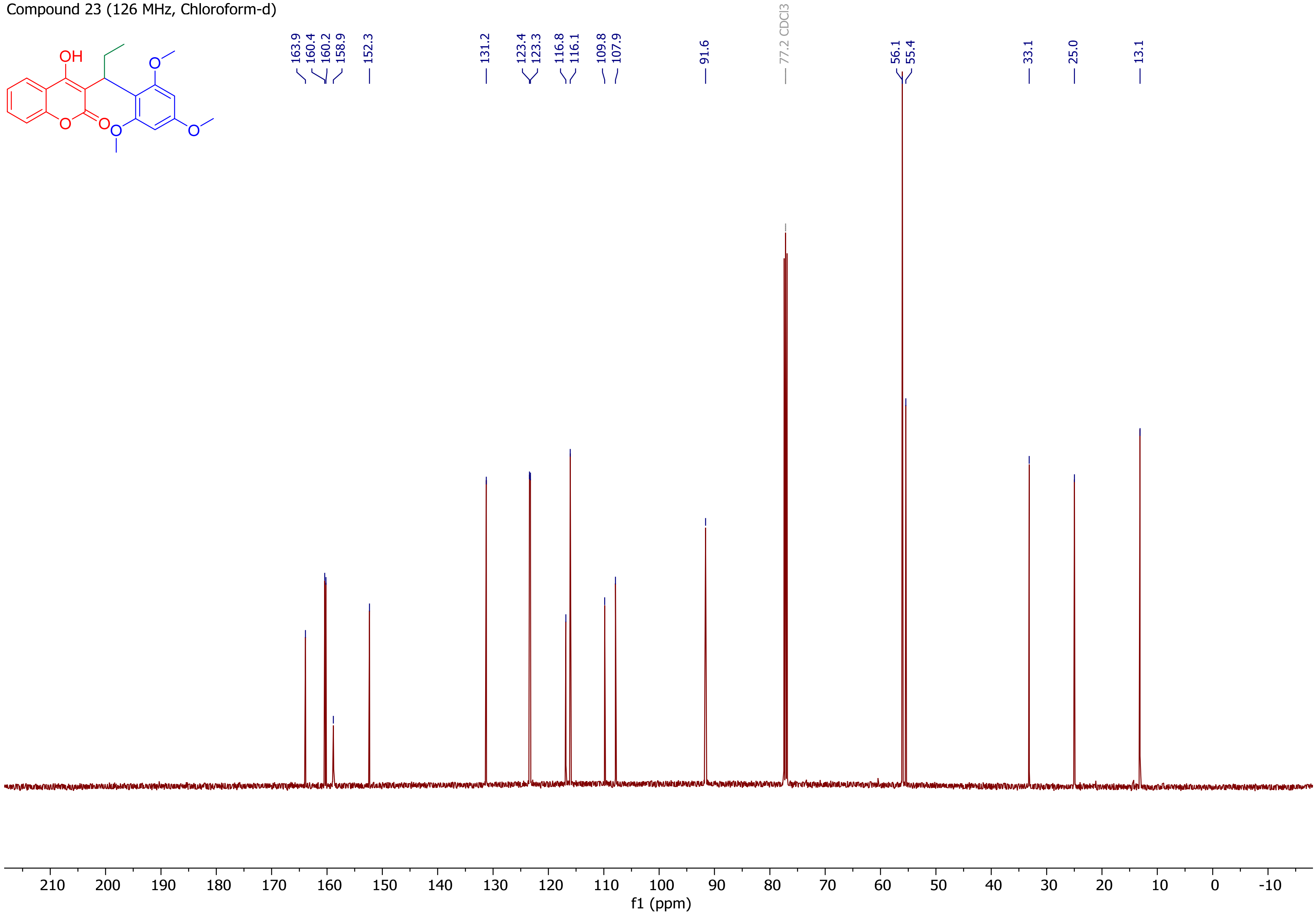
White solid, 313.6 mg, 84% yield. m.p. 136-138°C; $R_f = 0.56$ (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:70 to 1:20, SiO_2); IR (film) ν_{max}/cm^{-1} 3174, 3056, 2959, 2840, 1697, 704; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.38 (s, 1H), 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.24 – 7.15 (m, 2H), 6.19 (s, 2H), 4.99 (t, *J* = 8.4 Hz, 1H), 3.90 (s, 6H), 3.79 (s, 3H), 2.10 (h, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.9, 160.4, 160.2, 158.9, 152.3, 131.2, 123.4, 123.3, 116.8, 116.1, 109.8, 107.9, 91.6, 56.1, 55.4, 33.1, 25.0, 13.1.; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calcd for $C_{21}H_{22}O_6$ 393.3902; Found 393.3918.

XI. ^{1}H and ^{13}C NMR Spectra for Phenprocoumon analogue 23

Compound 23 (500 MHz, Chloroform-d)

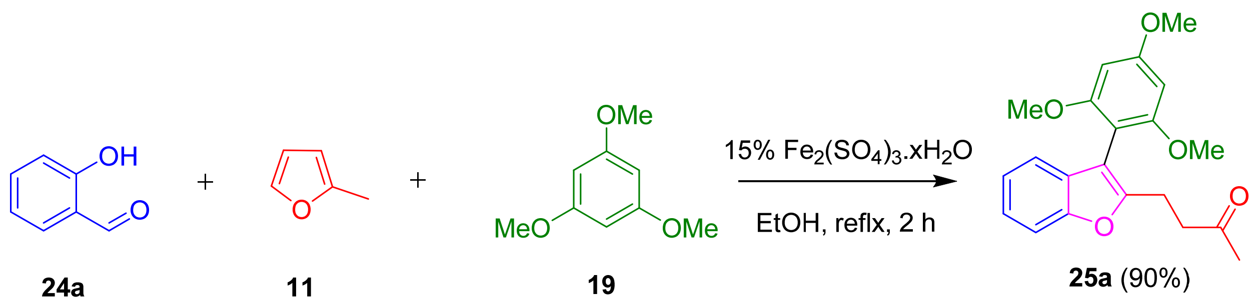


Compound 23 (126 MHz, Chloroform-d)



XII. Optimization of reaction conditions for the synthesis of benzofurans 25 a-f

Table S2. Optimized reaction conditions for the synthesis of benzofurans **25 a-f**



entry	catalyst	cat. load[a] (mol%)	solvent	temp (ºC)	time (h)	yield[b] (%)
1	none	0	EtOH	reflux	24	0[c]
2	$Fe_2(SO_4)_3{\bullet}xH_2O$	5	EtOH	rt	24	59
3	$Fe_2(SO_4)_3{\bullet}xH_2O$	10	EtOH	reflux	2	74
4	$Fe_2(SO_4)_3{\bullet}xH_2O$	15	EtOH	reflux	2	90
5	$Fe_2(SO_4)_3{\bullet}xH_2O$	20	EtOH	reflux	2	77
6	$Fe_2(SO_4)_3{\bullet}xH_2O$	25	EtOH	reflux	2	52
7	Fe_2O_3	15	EtOH	reflux	24	10
8	$FeCl_3$	15	EtOH	reflux	24	32
9	$FeBr_3$	15	EtOH	reflux	24	12
10	$Sc(OTf)_3$	15	EtOH	reflux	24	52
11	CH_3COOH	15	EtOH	reflux	24	19

12	CF_3COOH	15	EtOH	reflux	24	22
13	HCl	15	EtOH	reflux	24	6
14	$Fe_2(SO_4)_3{\bullet}xH_2O$	15	toluene	reflux	24	71
15	$Fe_2(SO_4)_3{\bullet}xH_2O$	15	DCM	reflux	24	0[c]
16	$Fe_2(SO_4)_3{\bullet}xH_2O$	15	EtOAc	reflux	24	29
17	$Fe_2(SO_4)_3{\bullet}xH_2O$	15	THF	reflux	24	0[c]
18	$Fe_2(SO_4)_3{\bullet}xH_2O$	15	$CHCl_3$	reflux	24	43

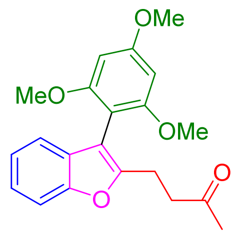
Reaction condition: salicylaldehyde (1 mmol), 2–methylfuran (1 mmol) and 1,3,5-trimethoxybenze (1 mmol). [a]Based on electrophile. [b]Isolated yields of benzofurans 25a. [c]No desired product was observed.

XIII. General procedure for the synthesis of benzofurans 25 a-f

A 50 mL round bottom flask was charged with a substituted salicylaldehyde (1 mmol, 1 equiv), 2-methyl furan (1 mmol, 1 equiv) and 1,3,5-trimethoxybenze (1 mmol, 1 equiv) in ethanol (10 mL). To this reaction mixture, $Fe_2(SO_4)_3{\bullet}xH_2O$ (15 mol%, 60 mg) was added and the solution was stirred at reflux temperatures for 2 hours in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by vacuo. The residue was dissolved in DCM (15 mL), washed using distilled water (3 × 15 mL) and dried over $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate).

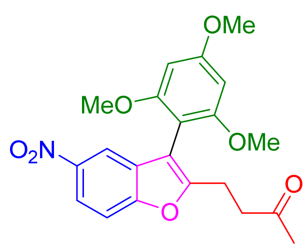
The general method from above was used for the preparation of following benzofurans:

4-(3-(2,4,6-trimethoxyphenyl)benzofuran-2-yl)butan-2-one **25a**



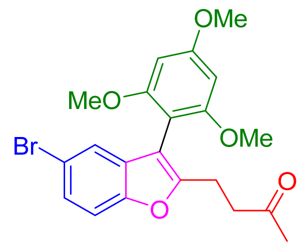
Yellow oil, 293.3 mg, 90% yield.; R_f = 0.38 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:60 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3054, 2986, 2941, 1716, 1456, 738, 705; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.39 (m, 1H), 7.22 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 6.26 (s, 2H), 3.89 (s, 3H), 3.72 (s, 6H), 2.94 – 2.84 (m, 4H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.9, 161.4, 159.3, 154.7, 154.2, 130.0, 123.0, 122.1, 120.7, 110.8, 109.0, 101.8, 91.0, 55.8, 55.5, 41.4, 30.0, 22.1.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{21}H_{22}O_5$ 354.1462; Found: 354.1456.

4-(5-nitro-3-(2,4,6-trimethoxyphenyl)benzofuran-2-yl)butan-2-one **25b**



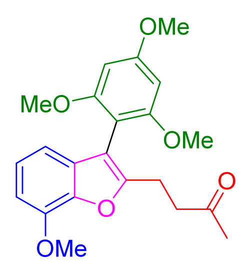
Yellow oil, 266.2 mg, 81% yield.; R_f = 0.31 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:60 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3682, 3020, 2964, 2941, 2841, 1717; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 8.9, 2.4 Hz, 1H), 8.09 (d, *J* = 2.4 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 6.26 (s, 2H), 3.90 (s, 3H), 3.74 (s, 6H), 2.93 (ddd, *J* = 8.5, 6.3, 1.7 Hz, 2H), 2.91 – 2.84 (m, 2H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.2, 162.0, 159.2, 158.3, 157.3, 144.0, 130.7, 119.1, 117.4, 111.0, 110.2, 99.8, 91.0, 55.8, 55.6, 40.9, 30.0, 22.0.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{21}H_{21}NO_7$ 399.1313; Found: 399.1308.

4-(5-bromo-3-(2,4,6-trimethoxyphenyl)benzofuran-2-yl)butan-2-one **25c**



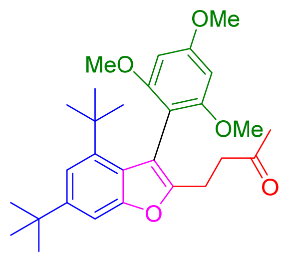
Brown oil, 312.2 mg, 78% yield.; R_f = 0.37 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:60 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3054, 3003, 2962, 2940, 2840, 1718, 704; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.26 (m, 3H), 6.24 (s, 2H), 3.88 (s, 3H), 3.73 (s, 6H), 2.92 – 2.81 (m, 4H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.4, 161.6, 159.2, 156.2, 153.0, 132.0, 125.7, 123.3, 115.3, 112.2, 108.7, 100.8, 90.9, 55.7, 55.5, 41.1, 29.9, 22.0.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{21}H_{21}BrO_5$ 432.0567; Found: 432.0579.

4-(7-methoxy-3-(2,4,6-trimethoxyphenyl)benzofuran-2-yl)butan-2-one **25d**



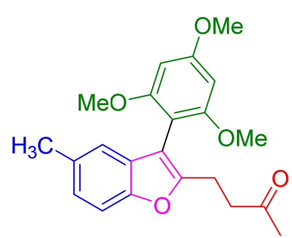
Brown solid, 326.7 mg, 85% yield. m.p. 103-105°C; R_f = 0.32 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:60 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3055, 2962, 2940, 2839, 1716, 784, 703; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.05 (t, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.24 (s, 2H), 4.01 (s, 3H), 3.88 (s, 3H), 3.71 (s, 6H), 2.90 (s, 4H), 2.13 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.8, 161.4, 159.3, 154.9, 145.1, 143.4, 131.7, 122.7, 113.3, 109.4, 105.5, 101.7, 91.0, 56.2, 55.8, 55.5, 41.5, 29.9, 22.0.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{22}H_{24}O_6$ 384.1567; Found: 384.1574.

4-(4,6-di-tert-butyl-3-(2,4,6-trimethoxyphenyl)benzofuran-2-yl)butan-2-one **25e**



Brown solid, 349.7 mg, 75% yield. m.p. 140-143°C; R_f = 0.39 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:60 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 2956, 2869, 2838, 1717, 1603, 974, 735; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 1.9 Hz, 1H), 6.27 (s, 2H), 3.90 (s, 3H), 3.75 (s, 6H), 2.94 – 2.82 (m, 4H), 2.17 (s, 3H), 1.52 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.0, 161.2, 159.3, 153.8, 150.7, 144.6, 132.9, 129.5, 117.7, 115.0, 108.5, 102.4, 91.0, 55.8, 55.5, 41.7, 34.9, 34.6, 32.1, 30.3, 30.0, 22.4.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{29}H_{38}O_5$ 466.2714; Found: 466.2694.

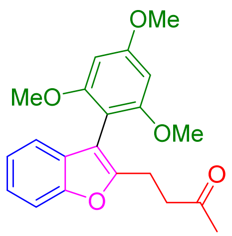
4-(5-methyl-3-(2,4,6-trimethoxyphenyl)benzofuran-2-yl)butan-2-one **25f**

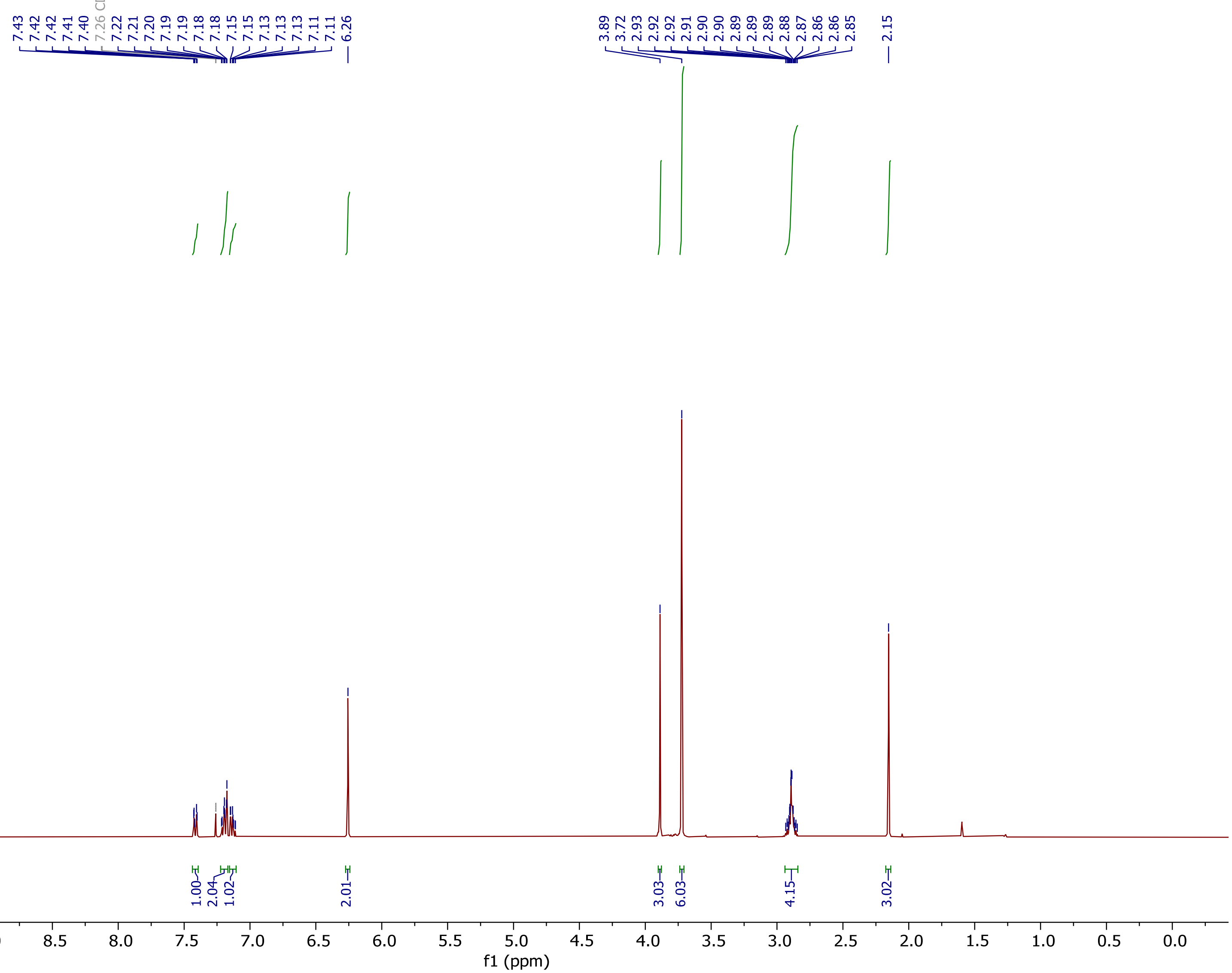


Yellow oil, 320.3 mg, 83% yield.; R_f = 0.35 (EtOAc:Hexanes = 1:3, SiO_2); Flash column chromatography eluent: EtOAc:Hexanes (1:60 to 1:10, SiO_2); IR (film) ν_{max}/cm^{-1} 3053, 2939, 2839, 1716, 1600, 737, 703; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.3 Hz, 1H), 7.00 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.95 (dt, *J* = 1.8, 0.8 Hz, 1H), 6.25 (s, 2H), 3.89 (s, 3H), 3.72 (s, 6H), 2.86 (q, J = 2.4 Hz, 4H), 2.37 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.0, 161.4, 159.4, 154.8, 152.7, 131.5, 130.1, 124.2, 120.4, 110.3, 108.7, 101.9, 91.0, 55.8, 55.5, 41.5, 30.0, 22.1, 21.5.; HRMS (EI-TOF) *m/z*: $[M]^+$Calcd for $C_{22}H_{24}O_5$ 368.1618; Found: 368.1616.

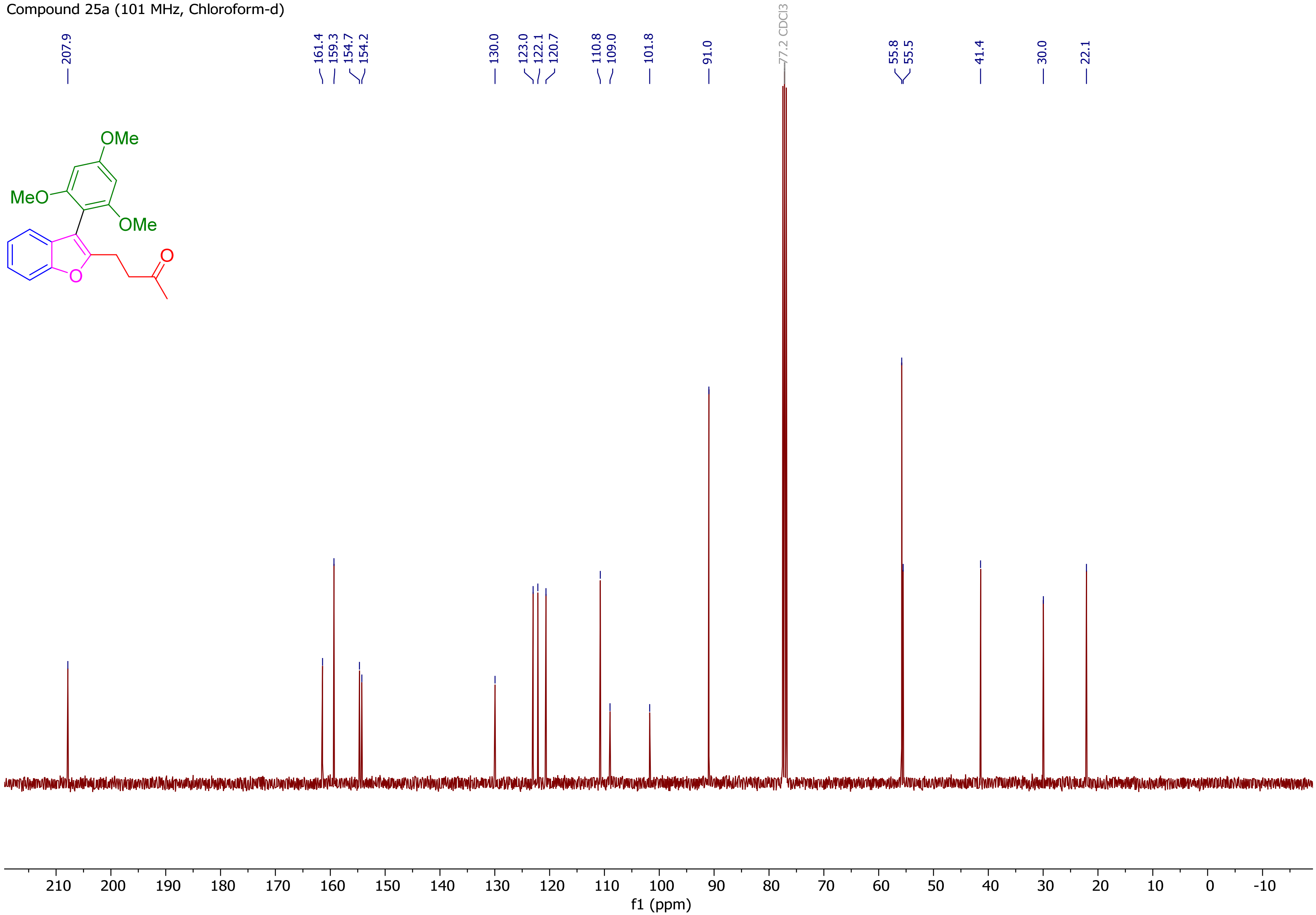
XIV. [1]H and [13]C NMR Spectra for benzofurans 25 a-f

Compound 25a (400 MHz, Chloroform-d)

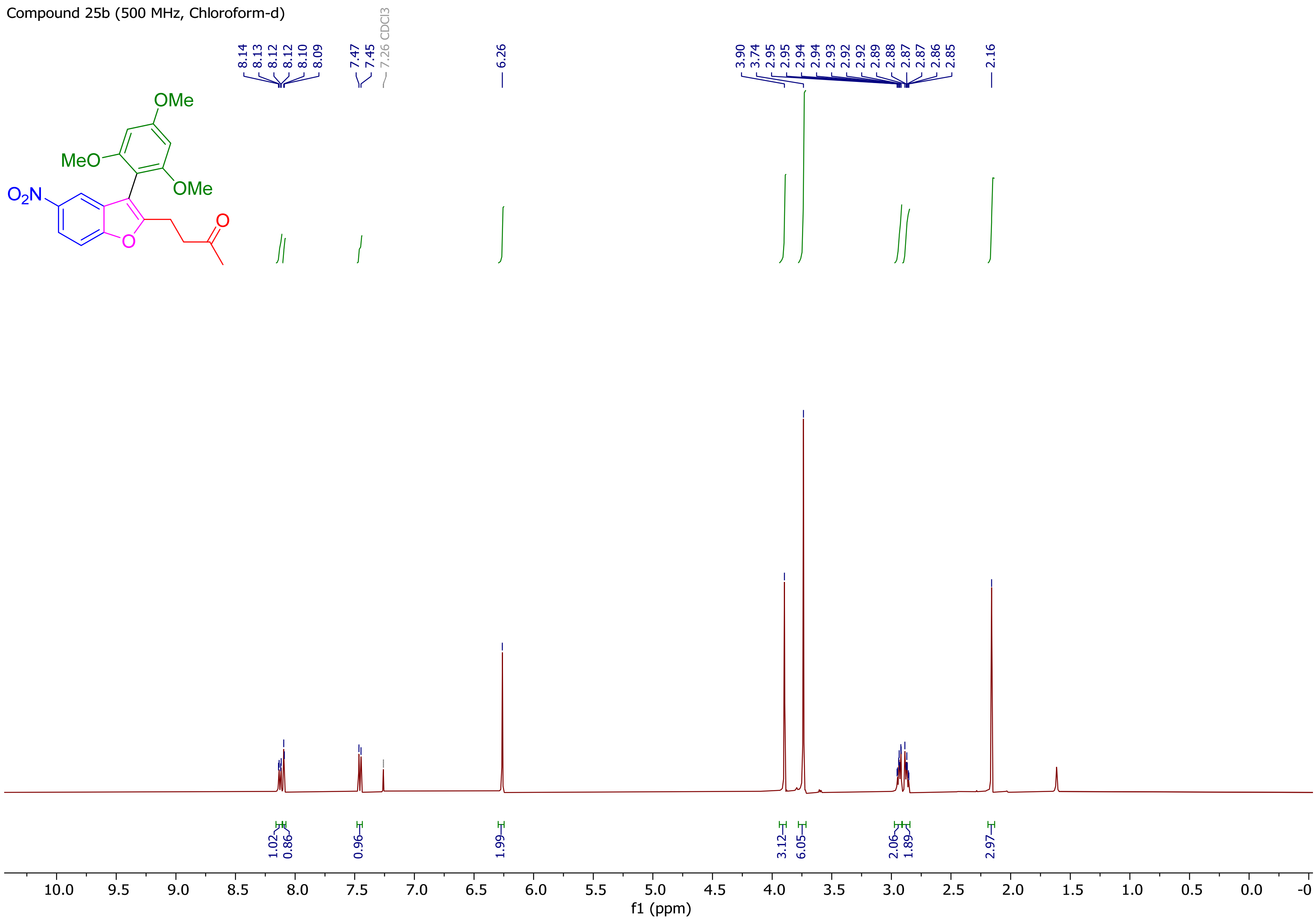




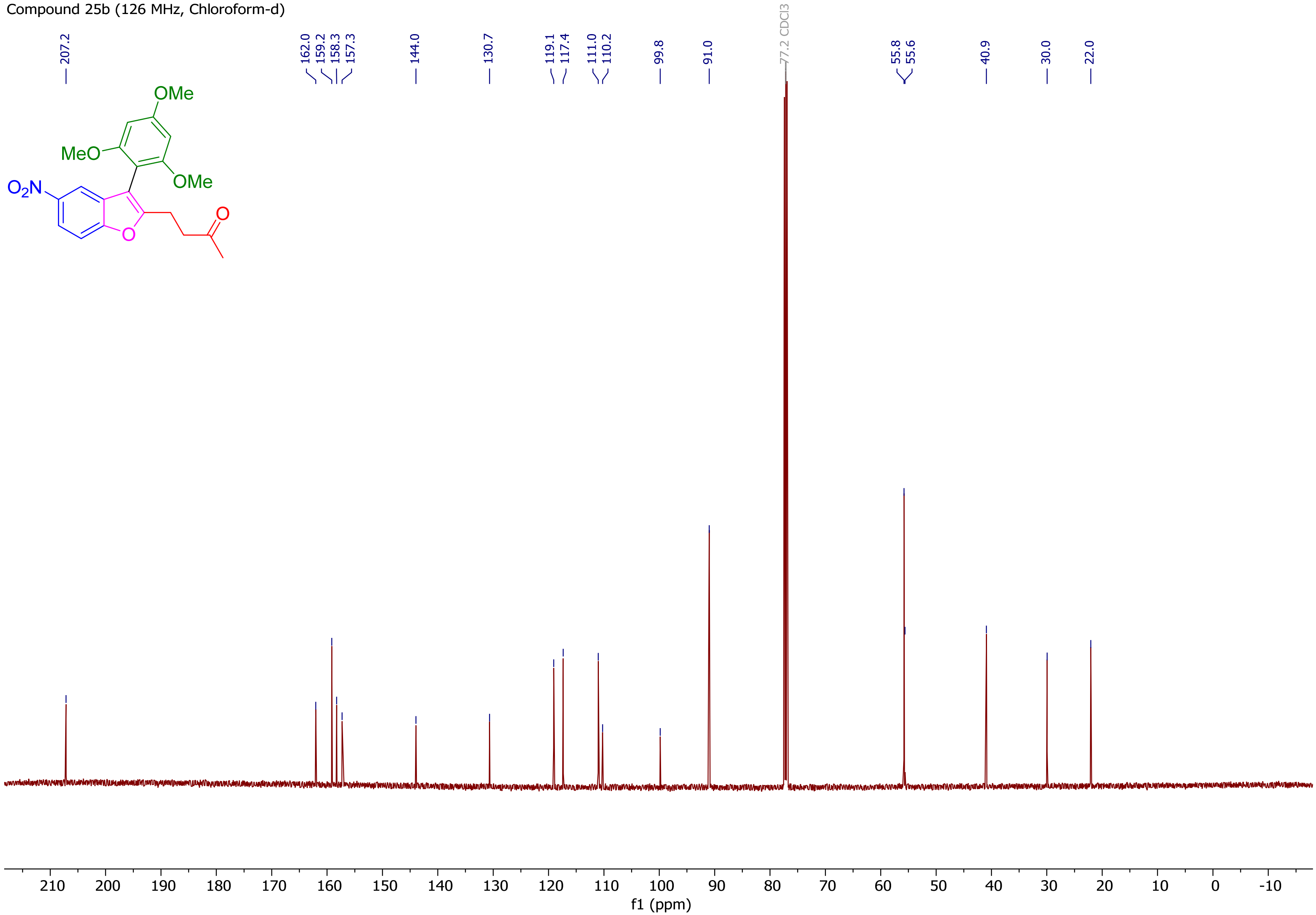
Compound 25a (101 MHz, Chloroform-d)



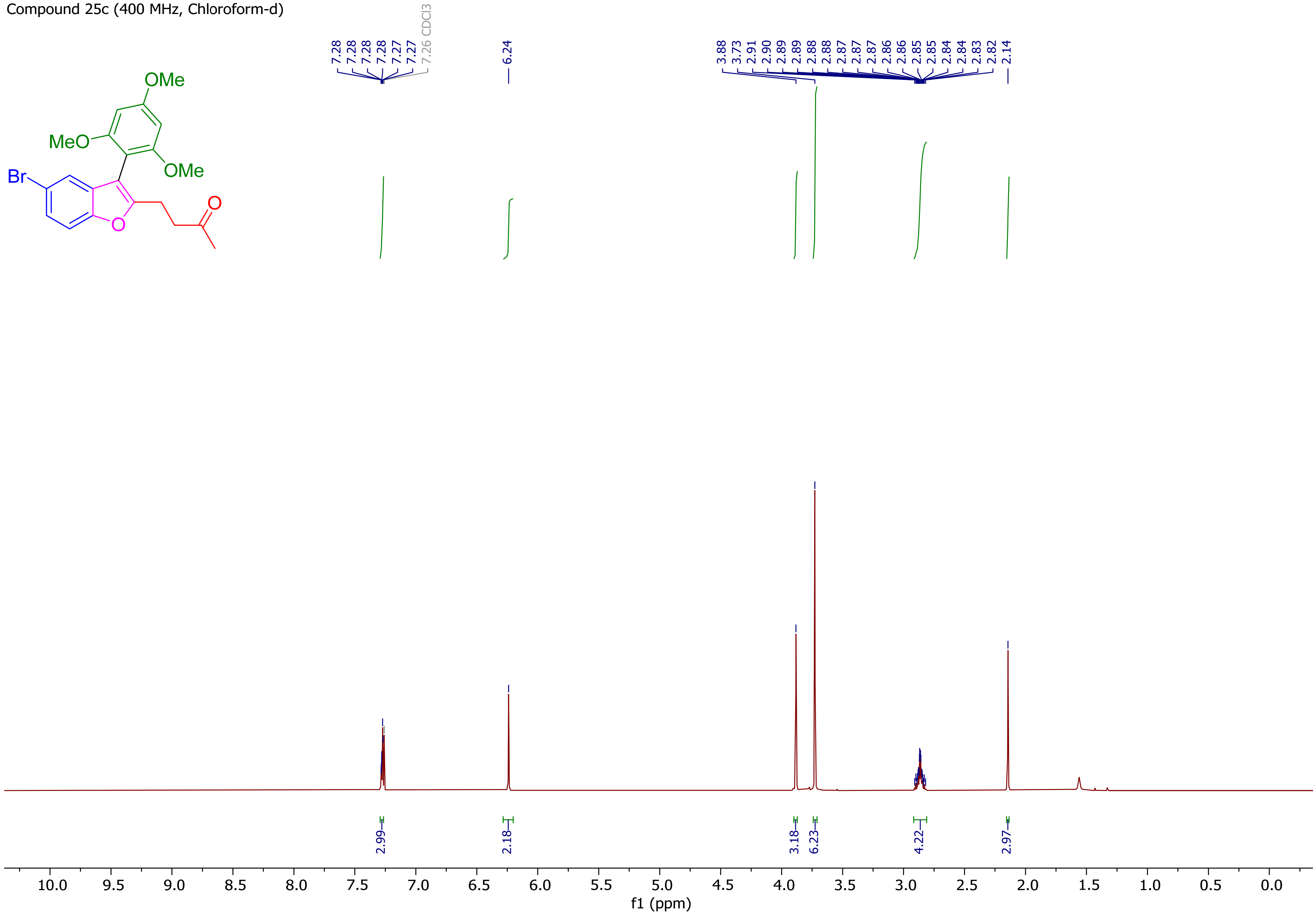
Compound 25b (500 MHz, Chloroform-d)



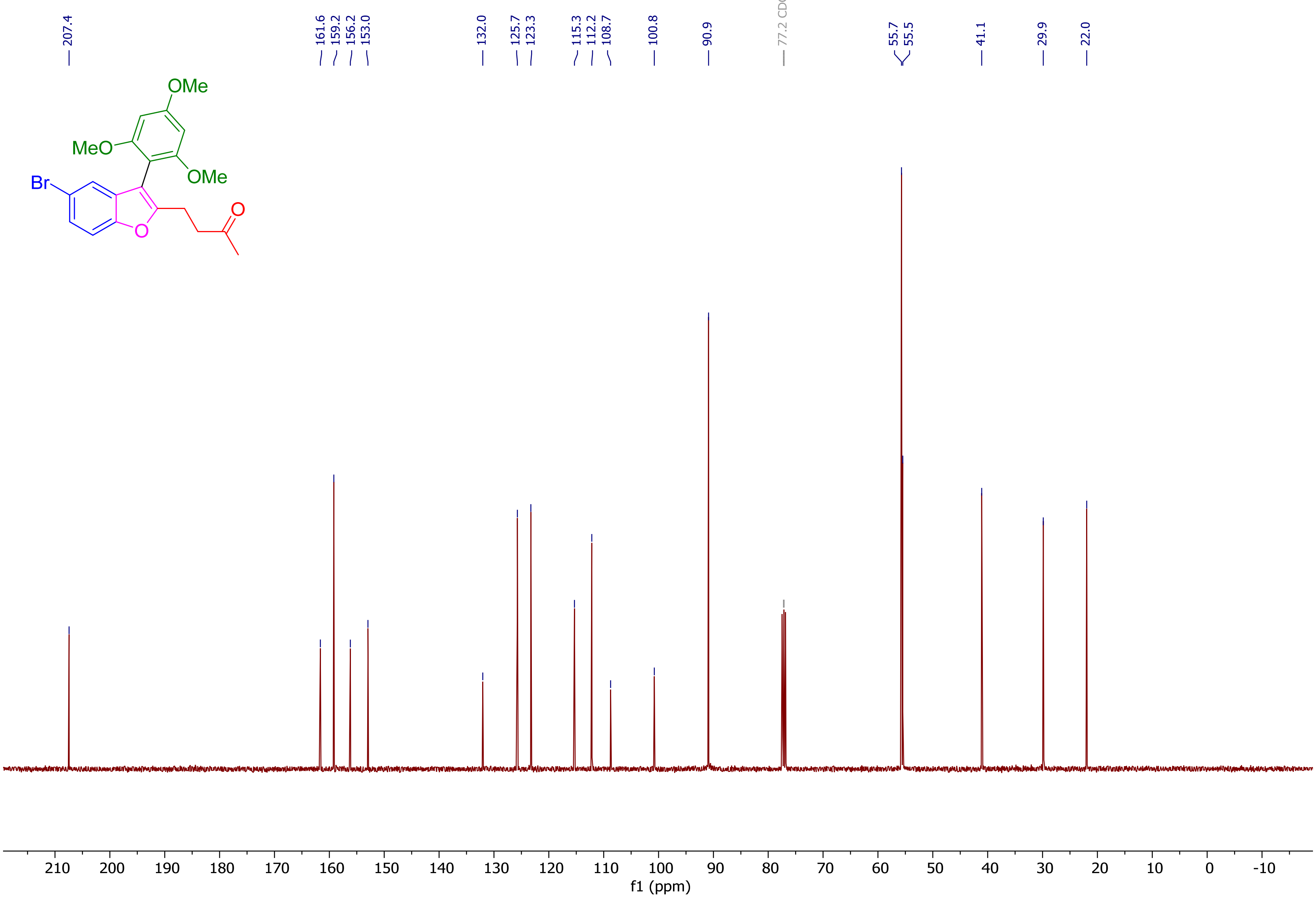
Compound 25b (126 MHz, Chloroform-d)



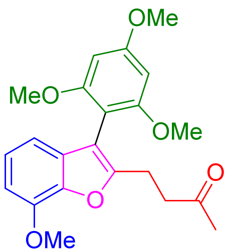
Compound 25c (400 MHz, Chloroform-d)

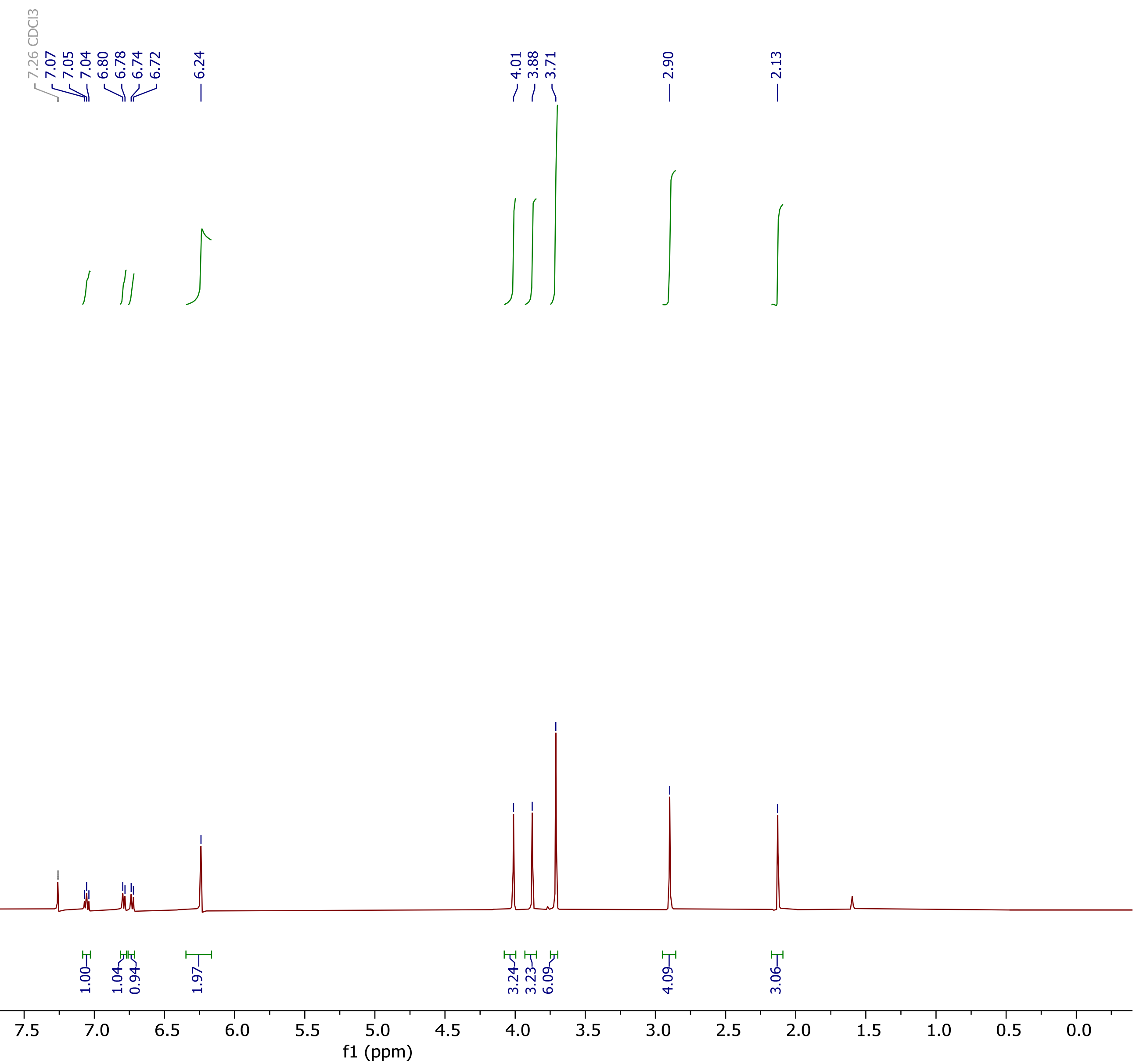


Compound 25c (101 MHz, Chloroform-d)

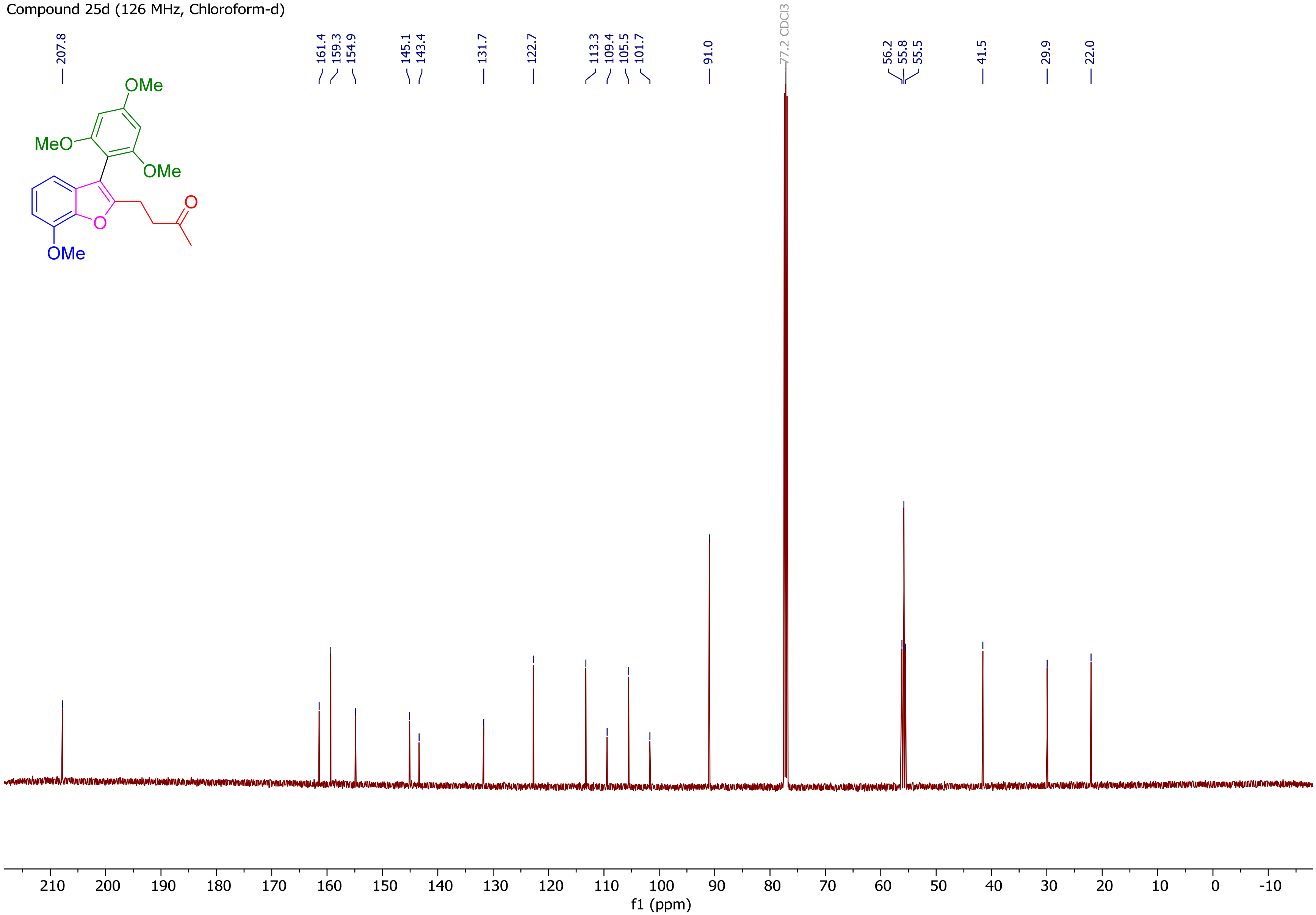


Compound 25d (500 MHz, Chloroform-d)

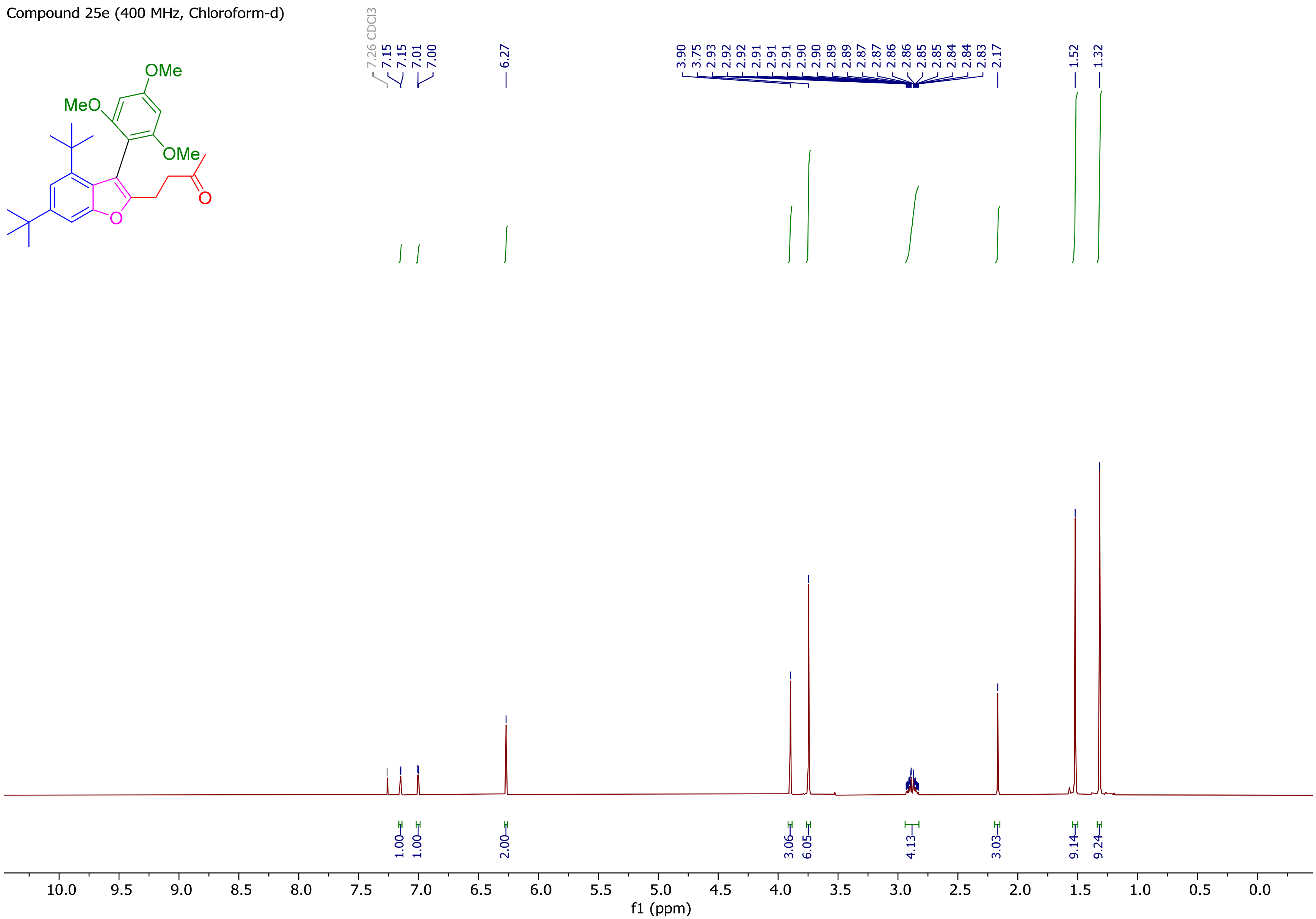




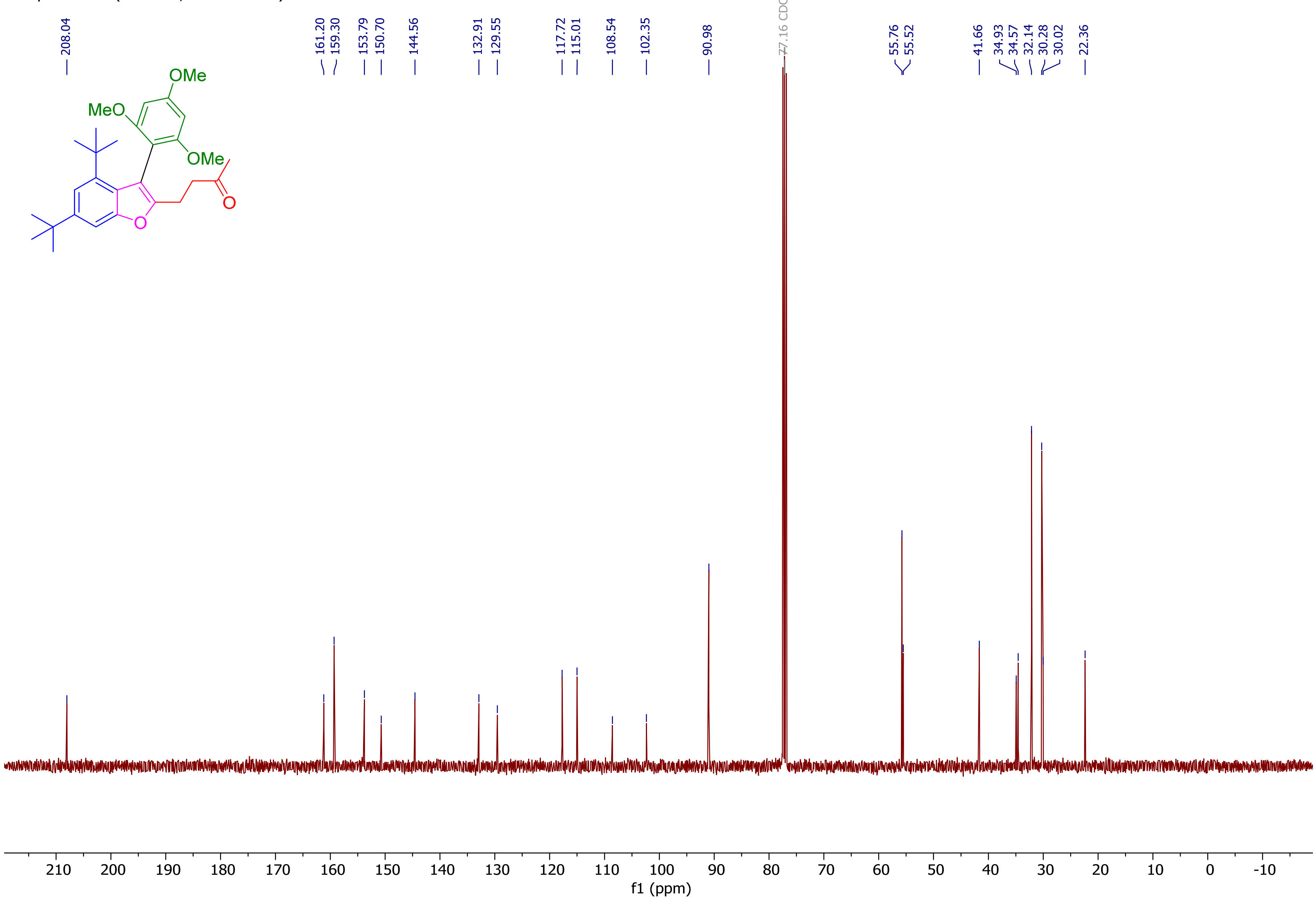
Compound 25d (126 MHz, Chloroform-d)



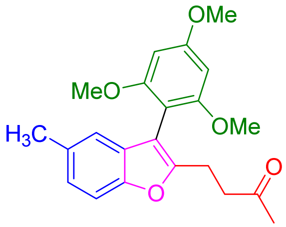
Compound 25e (400 MHz, Chloroform-d)

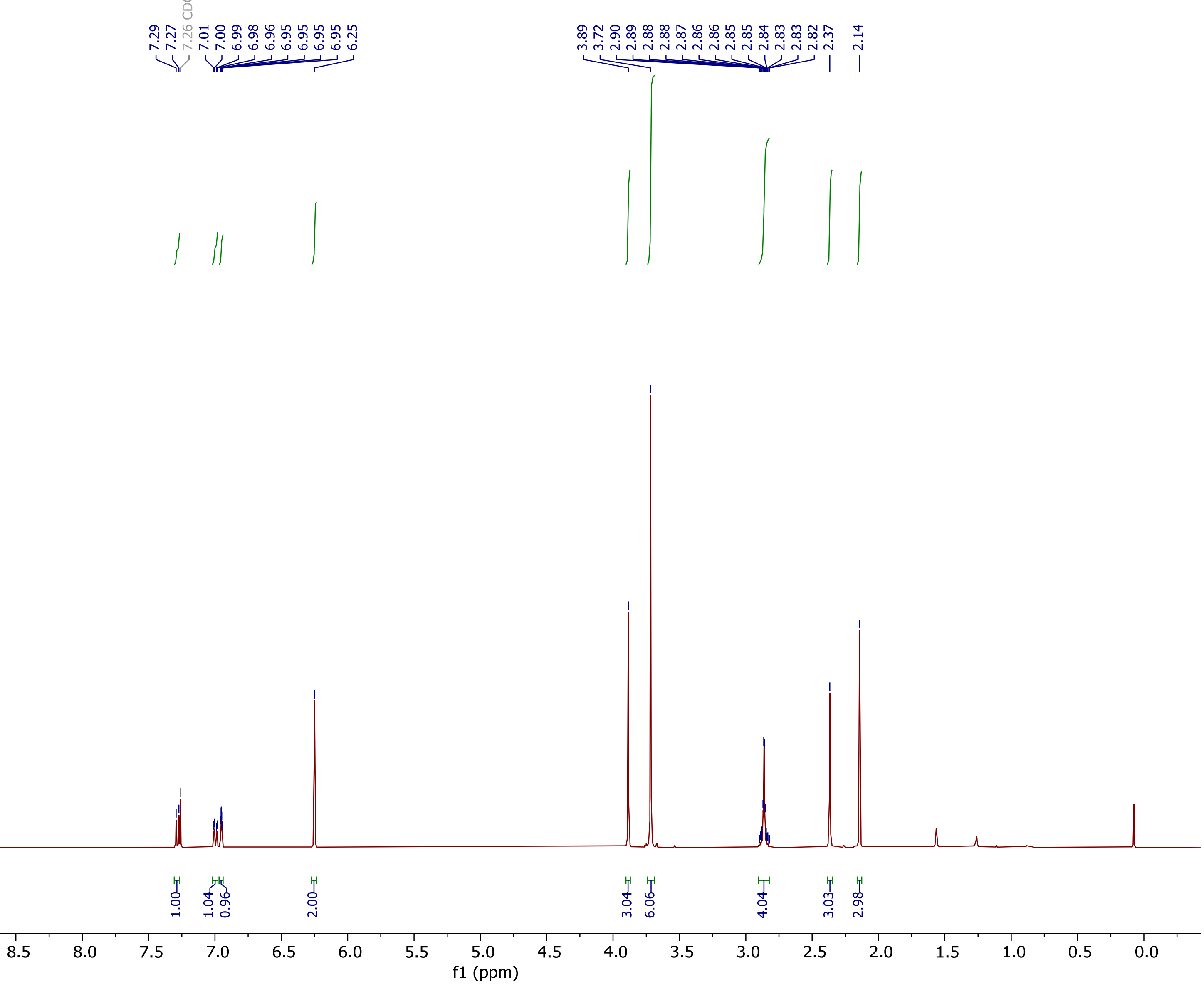


Compound 25e (101 MHz, Chloroform-d)

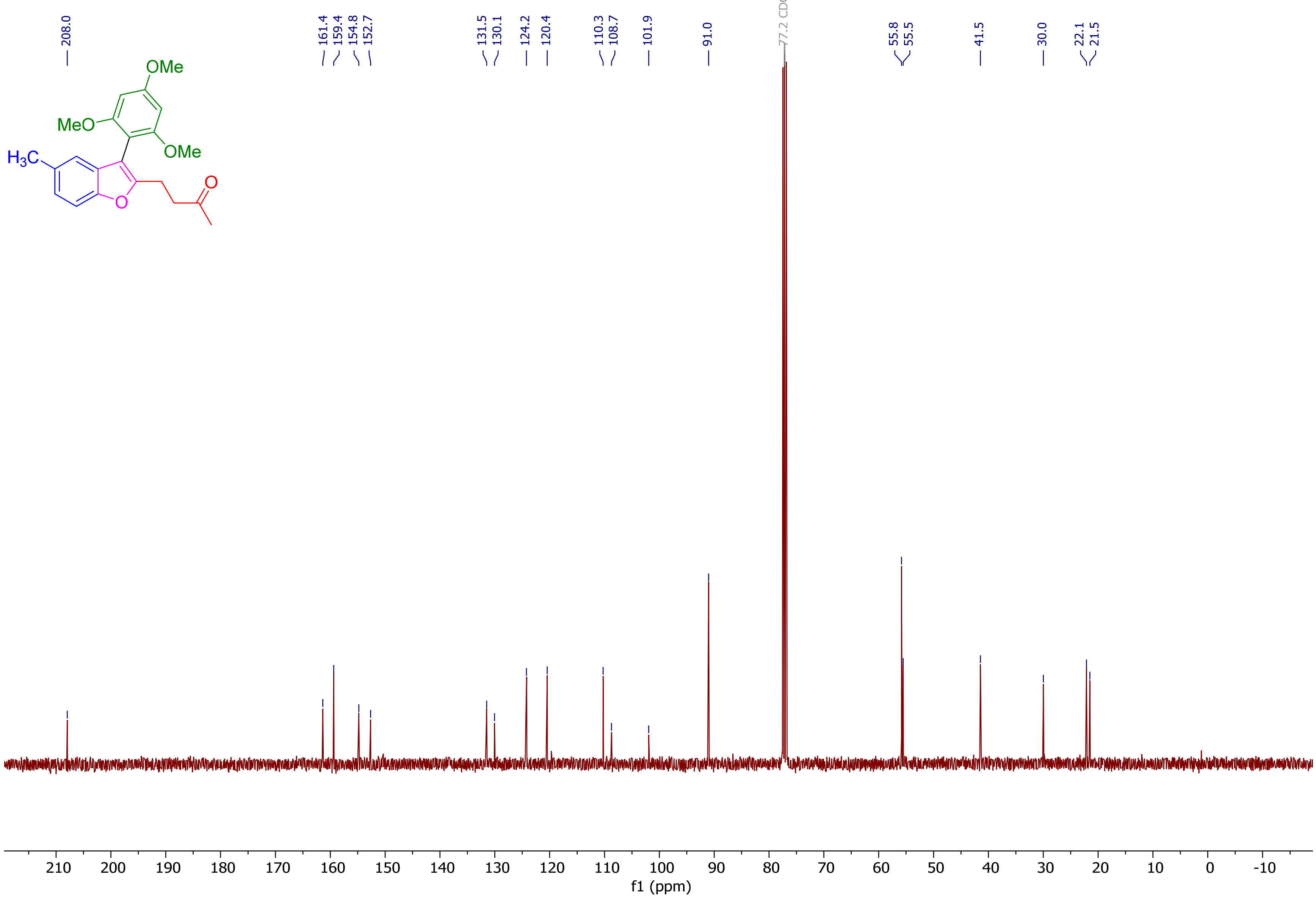


Compound 25f (400 MHz, Chloroform-d)



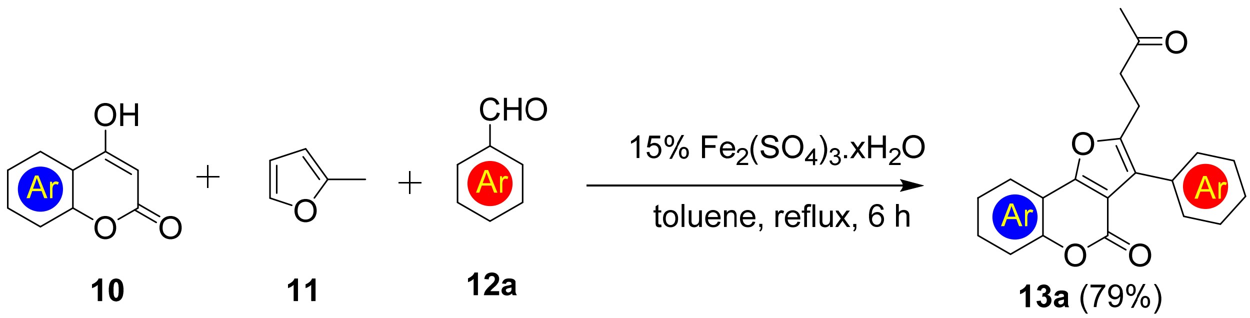


Compound 25f (101 MHz, Chloroform-d)



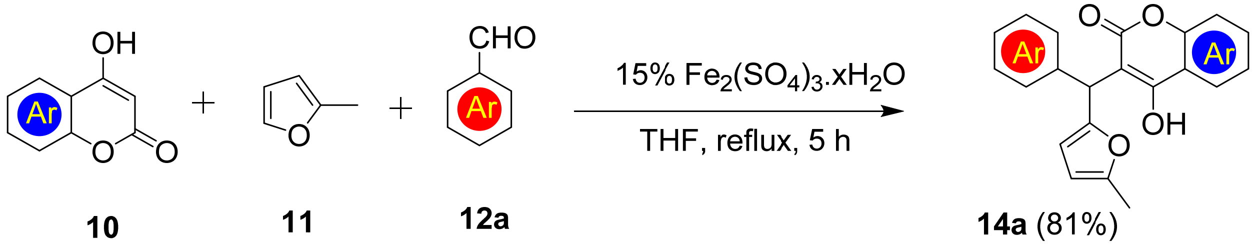
XV. Procedure for gram scale reactions

Scheme S2. Reaction conditions for gram-scale synthesis of **13a.**



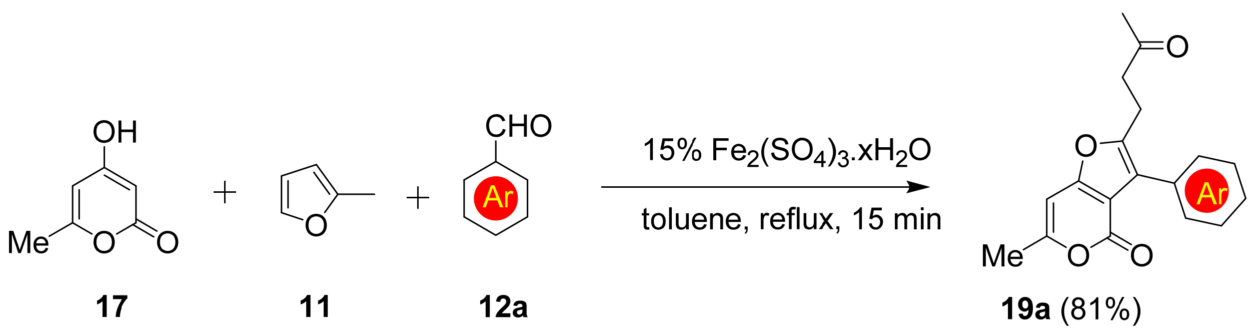
A 250 mL round bottom flask was charged with benzaldehyde (10 mmol, 1 equiv), 2-methyl furan (10 mmol, 1 equiv) and 4- hydroxycoumarin (10 mmol, 1 equiv) in anhydrous toluene (25 mL). To this reaction mixture, $Fe_2(SO_4)_3$•$x$$H_2O$ (15 mol%, 60 mg) was added and the solution was stirred at reflux temperature for 6 h in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by rotovap. The residue was dissolved in DCM (30 mL), washed using distilled water (3 × 30 mL) and dried over $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate) to yield **13a** as a grey solid (251.8 g, 79% yield).

Scheme S3. Reaction conditions for gram-scale synthesis of **14a.**



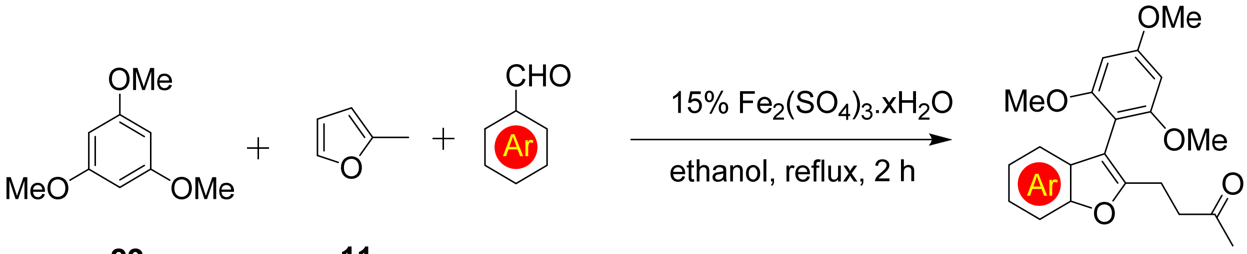
A 250 mL round bottom flask was charged with benzaldehyde (10 mmol, 1 equiv), 2-methyl furan (10 mmol, 1 equiv) and 4- hydroxycoumarin (10 mmol, 1 equiv) in anhydrous THF (25 mL). To this reaction mixture, $Fe_2(SO_4)_3$•$x$$H_2O$ (15 mol%, 60 mg) was added and the solution was stirred at reflux temperature for 5 h in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by rotovap. The residue was dissolved in DCM (30 mL), washed using distilled water (3 × 30 mL) and dried over $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate) to yield **14a** as a brown solid (268.7 g, 81% yield).

Scheme S4. Reaction conditions for gram-scale synthesis of **19a.**



A 250 mL round bottom flask was charged with benzaaldehyde (10 mmol, 1 equiv), 2-methyl furan (10 mmol, 1 equiv) and 4–hydroxy–6–methyl–2–pyrone (10 mmol, 1 equiv) in anhydrous toluene (25 mL). To this reaction mixture, $Fe_2(SO_4)_3{\bullet}xH_2O$ (15 mol%, 60 mg) was added and the solution was stirred at reflux temperature for 15 min in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by rotovap. The residue was dissolved in DCM (30 mL), washed using distilled water (3 × 30 mL) and dried over $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate) to yield **19a** as a dark brown solid (236.7 g, 81% yield).

Scheme S5. Reaction conditions for gram-scale synthesis of **25a.**



A 250 mL round bottom flask was charged with a substituted salicylaldehyde (9 mmol, 1 equiv), 2-methyl furan (9 mmol, 1 equiv) and 1,3,5-trimethoxybenze (9 mmol, 1 equiv) in ethanol (20 mL). To this reaction mixture, $Fe_2(SO_4)_3 \cdot xH_2O$ (15 mol%, 60 mg) was added and the solution was stirred at reflux temperatures for 2 hours in an oil bath. The reaction mixture was cooled to room temperature and the organic solvent was removed by vacuo. The residue was dissolved in DCM (25 mL), washed using distilled water (3 × 25 mL) and dried over $MgSO_4$. The product was then purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate) to yield **25a** as a light yellow oil (284.8 mg, 79% yield).

XVI. Single crystal X-ray diffraction of compound 13d

Data collection

A crystal (approximate dimensions 0.190 x 0.180 x 0.140 mm^3) was placed onto the tip of a 0.1 mm Mitegen loop and mounted on a Bruker VENTURE PHOTON-III diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 410 reflections. The data collection was carried out using CuK□ radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 8.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in □ or □ at different detector positions in 2□. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2936 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

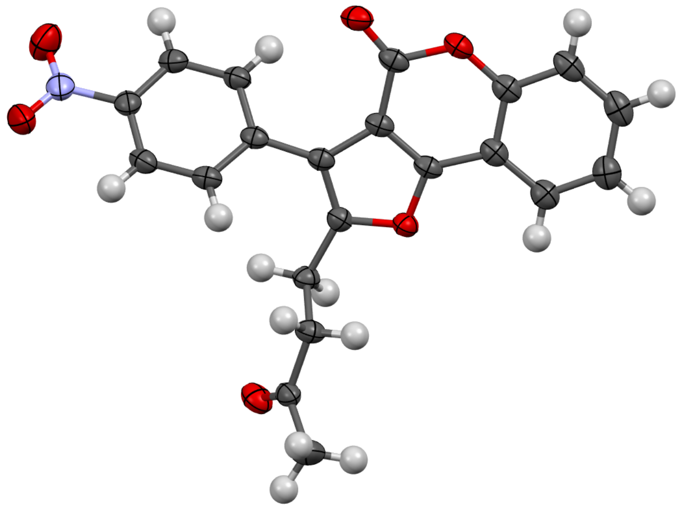
Structure solution and refinement

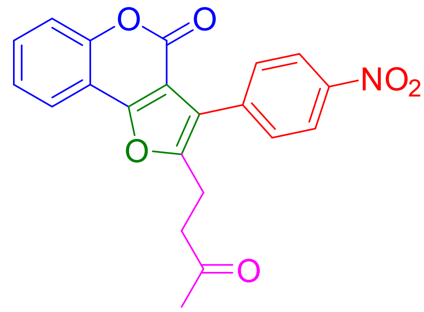
The structure was solved using SHELXT-2014/5 (Sheldrick, 2015)[4] and refined using SHELXL-2018/3 (Sheldrick, 2015).[4] The space group C2/c was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0406 and $wR2$ = 0.1031 (F^2, obs. data).

Structure description

The structure is a structural isomer of the one originally suggested. The positions of C13 and C19 were predicted to be in opposite positions.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.





13d

Figure S1. ORTEP diagram (80% probability ellipsoids) of **13d**

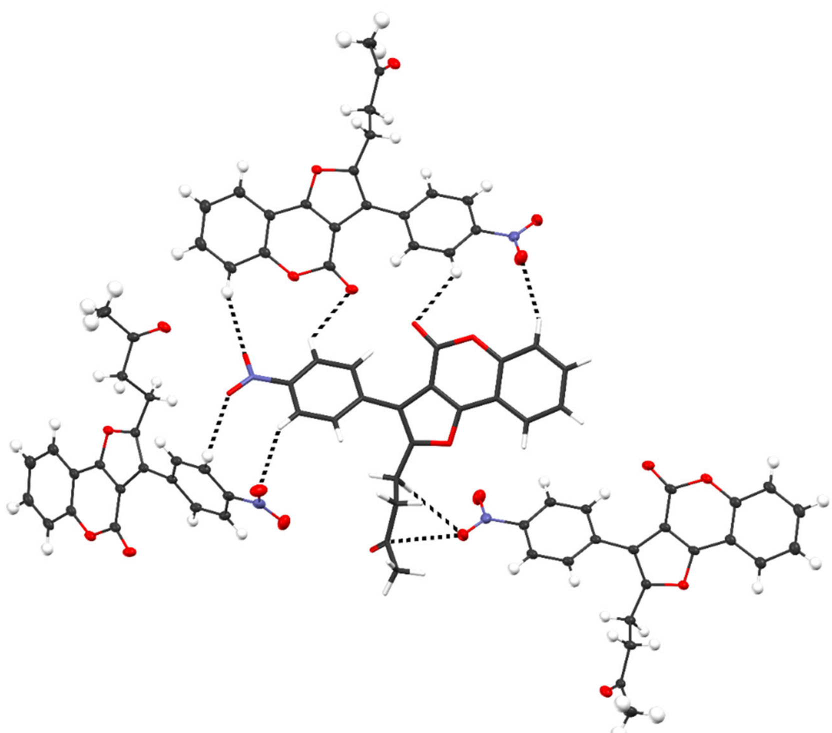


Figure S2: Intermolecular interactions in crystal structure of **13d**

Table S3. Crystal data and structure refinement of **13d**, CCDC:1961601.

Identification code	19070z	
Empirical formula	$C_{21}H_{15}NO_6$	
Formula weight	377.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 18.9040(8) Å	α = 90°
	b = 7.2383(3) Å	β = 96.279(2)°
	c = 25.7728(11) Å	γ = 90°
Volume	3505.4(3) $Å^3$	
Z	8	
Density (calculated)	1.430 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	
F(000)	1568	
Crystal color, morphology	Colourless, Block	
Crystal size	0.190 x 0.180 x 0.140 mm^3	
Theta range for data collection	2.168 to 30.561°	
Index ranges	$-26 \leq h \leq 26$, $-9 \leq k \leq 10$, $-36 \leq l \leq 36$	
Reflections collected	26887	
Independent reflections	5379 [*R*(int) = 0.0297]	
Observed reflections	4597	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7461 and 0.6986	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5379 / 0 / 254	
Goodness-of-fit on F^2	1.039	
Final *R* indices [*I*>2sigma(*I*)]	$R1$ = 0.0406, $wR2$ = 0.1031	
R indices (all data)	$R1$ = 0.0499, $wR2$ = 0.1094	
Largest diff. peak and hole	0.413 and -0.234 e.$Å^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 19070z. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	6877(1)	5159(1)	4514(1)	18(1)
C2	7580(1)	4605(1)	4583(1)	17(1)
C3	7872(1)	3923(2)	4149(1)	20(1)
C4	8582(1)	3397(2)	4204(1)	21(1)
C5	9002(1)	3538(2)	4684(1)	21(1)
C6	8707(1)	4191(2)	5116(1)	19(1)
C7	7989(1)	4717(1)	5070(1)	16(1)
C8	7602(1)	5344(1)	5481(1)	15(1)
C9	6899(1)	5832(1)	5426(1)	15(1)
C10	6500(1)	5805(1)	4913(1)	17(1)
O11	5892(1)	6268(1)	4794(1)	21(1)
O12	7883(1)	5467(1)	5986(1)	16(1)
C13	7337(1)	6050(1)	6266(1)	15(1)
C14	7539(1)	6163(2)	6839(1)	16(1)
C15	8057(1)	7749(2)	6988(1)	17(1)
C16	8376(1)	7643(2)	7550(1)	17(1)
O17	8119(1)	6703(1)	7870(1)	23(1)
C18	9036(1)	8781(2)	7690(1)	28(1)
C19	6723(1)	6310(1)	5942(1)	15(1)
C20	6041(1)	6857(1)	6121(1)	15(1)
C21	5399(1)	6010(2)	5927(1)	17(1)
C22	4771(1)	6418(2)	6137(1)	18(1)
C23	4792(1)	7725(2)	6533(1)	17(1)
C24	5412(1)	8648(2)	6720(1)	18(1)
C25	6034(1)	8196(2)	6514(1)	16(1)
O26	3627(1)	7126(1)	6676(1)	31(1)
N26	4140(1)	8153(2)	6767(1)	22(1)
O27	4141(1)	9523(2)	7051(1)	32(1)

Table S5. Bond lengths [Å] and angles [°] for 19070z.

O1-C2	1.3813(13)	C14-H14B	0.9900
O1-C10	1.3953(13)	C15-C16	1.5093(14)
C2-C3	1.3914(15)	C15-H15A	0.9900
C2-C7	1.4010(14)	C15-H15B	0.9900
C3-C4	1.3868(17)	C16-O17	1.2110(14)
C3-H3	0.9500	C16-C18	1.5050(16)
C4-C5	1.3993(16)	C18-H18A	0.9800
C4-H4	0.9500	C18-H18B	0.9800
C5-C6	1.3831(16)	C18-H18C	0.9800
C5-H5	0.9500	C19-C20	1.4696(14)
C6-C7	1.4029(15)	C20-C25	1.4030(14)
C6-H6	0.9500	C20-C21	1.4032(14)
C7-C8	1.4245(15)	C21-C22	1.3890(15)
C8-O12	1.3533(12)	C21-H21	0.9500
C8-C9	1.3668(14)	C22-C23	1.3882(15)
C9-C10	1.4478(14)	C22-H22	0.9500
C9-C19	1.4487(14)	C23-C24	1.3877(15)
C10-O11	1.2050(13)	C23-N26	1.4645(14)
O12-C13	1.3889(13)	C24-C25	1.3831(15)
C13-C19	1.3672(14)	C24-H24	0.9500
C13-C14	1.4871(14)	C25-H25	0.9500
C14-C15	1.5310(15)	O26-N26	1.2244(14)
C14-H14A	0.9900	N26-O27	1.2328(14)

C2-O1-C10	124.30(8)	C6-C5-C4	119.82(11)
O1-C2-C3	117.33(9)	C6-C5-H5	120.1
O1-C2-C7	121.81(9)	C4-C5-H5	120.1
C3-C2-C7	120.86(10)	C5-C6-C7	119.76(10)
C4-C3-C2	118.65(10)	C5-C6-H6	120.1
C4-C3-H3	120.7	C7-C6-H6	120.1
C2-C3-H3	120.7	C2-C7-C6	119.58(10)
C3-C4-C5	121.31(11)	C2-C7-C8	114.01(10)
C3-C4-H4	119.3	C6-C7-C8	126.40(10)
C5-C4-H4	119.3	O12-C8-C9	110.96(9)

O12-C8-C7	123.77(9)	H18A-C18-H18B	109.5
C9-C8-C7	125.23(9)	C16-C18-H18C	109.5
C8-C9-C10	119.65(10)	H18A-C18-H18C	109.5
C8-C9-C19	106.59(9)	H18B-C18-H18C	109.5
C10-C9-C19	133.76(10)	C13-C19-C9	105.20(9)
O11-C10-O1	116.99(9)	C13-C19-C20	124.16(9)
O11-C10-C9	128.15(10)	C9-C19-C20	130.56(9)
O1-C10-C9	114.86(9)	C25-C20-C21	118.92(10)
C8-O12-C13	106.50(8)	C25-C20-C19	119.33(9)
C19-C13-O12	110.75(9)	C21-C20-C19	121.68(9)
C19-C13-C14	135.01(10)	C22-C21-C20	120.69(10)
O12-C13-C14	114.17(8)	C22-C21-H21	119.7
C13-C14-C15	112.20(9)	C20-C21-H21	119.7
C13-C14-H14A	109.2	C23-C22-C21	118.34(10)
C15-C14-H14A	109.2	C23-C22-H22	120.8
C13-C14-H14B	109.2	C21-C22-H22	120.8
C15-C14-H14B	109.2	C24-C23-C22	122.63(10)
H14A-C14-H14B	107.9	C24-C23-N26	118.12(10)
C16-C15-C14	112.34(9)	C22-C23-N26	119.25(10)
C16-C15-H15A	109.1	C25-C24-C23	118.25(10)
C14-C15-H15A	109.1	C25-C24-H24	120.9
C16-C15-H15B	109.1	C23-C24-H24	120.9
C14-C15-H15B	109.1	C24-C25-C20	121.09(10)
H15A-C15-H15B	107.9	C24-C25-H25	119.5
O17-C16-C18	121.93(10)	C20-C25-H25	119.5
O17-C16-C15	122.29(10)	O26-N26-O27	123.57(10)
C18-C16-C15	115.78(10)	O26-N26-C23	118.54(10)
C16-C18-H18A	109.5	O27-N26-C23	117.88(10)
C16-C18-H18B	109.5		

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters (Å^{2}x 10^3) for 19070z. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	23(1)	18(1)	13(1)	-1(1)	0(1)	-1(1)
C2	22(1)	12(1)	15(1)	2(1)	2(1)	-2(1)
C3	30(1)	14(1)	14(1)	1(1)	4(1)	-3(1)
C4	31(1)	14(1)	19(1)	0(1)	9(1)	-2(1)
C5	24(1)	17(1)	23(1)	1(1)	7(1)	0(1)
C6	22(1)	17(1)	17(1)	1(1)	3(1)	-1(1)
C7	21(1)	13(1)	14(1)	1(1)	3(1)	-2(1)
C8	20(1)	14(1)	12(1)	1(1)	-1(1)	-2(1)
C9	19(1)	13(1)	13(1)	1(1)	-1(1)	-2(1)
C10	23(1)	13(1)	14(1)	0(1)	-1(1)	-3(1)
O11	22(1)	22(1)	18(1)	-2(1)	-4(1)	1(1)
O12	16(1)	20(1)	12(1)	0(1)	1(1)	-1(1)
C13	16(1)	15(1)	14(1)	-1(1)	1(1)	-2(1)
C14	16(1)	19(1)	13(1)	1(1)	0(1)	-1(1)
C15	19(1)	19(1)	13(1)	1(1)	-1(1)	-3(1)
C16	18(1)	19(1)	15(1)	-3(1)	-1(1)	5(1)
O17	30(1)	24(1)	14(1)	1(1)	1(1)	3(1)
C18	22(1)	38(1)	24(1)	-8(1)	-3(1)	-4(1)
C19	17(1)	12(1)	14(1)	0(1)	0(1)	-2(1)
C20	18(1)	14(1)	13(1)	1(1)	-1(1)	0(1)
C21	18(1)	16(1)	15(1)	-2(1)	-2(1)	0(1)
C22	16(1)	20(1)	17(1)	0(1)	-2(1)	0(1)
C23	17(1)	20(1)	15(1)	1(1)	0(1)	3(1)
C24	22(1)	17(1)	14(1)	-2(1)	-1(1)	1(1)
C25	18(1)	15(1)	15(1)	0(1)	-2(1)	-2(1)
O26	21(1)	35(1)	38(1)	0(1)	7(1)	-1(1)
N26	19(1)	28(1)	16(1)	1(1)	0(1)	6(1)
O27	26(1)	44(1)	26(1)	-14(1)	-1(1)	10(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 19070z.

	x	y	z	U(eq)
H3	7591	3819	3822	24
H4	8787	2932	3910	25
H5	9489	3187	4713	25
H6	8989	4282	5444	22
H14A	7761	4983	6964	19
H14B	7104	6340	7016	19
H15A	8445	7717	6759	21
H15B	7803	8939	6929	21
H18A	9141	8836	8070	42
H18B	8959	10034	7551	42
H18C	9437	8213	7539	42
H21	5393	5148	5648	20
H22	4339	5817	6014	21
H24	5408	9566	6983	22
H25	6465	8802	6640	20

Table S8. Torsion angles [°] for 19070z.

C10-O1-C2-C3	177.41(9)	C14-C15-C16-O17	-17.12(15)
C10-O1-C2-C7	-2.52(15)	C14-C15-C16-C18	162.88(10)
O1-C2-C3-C4	178.47(9)	O12-C13-C19-C9	0.74(12)
C7-C2-C3-C4	-1.60(16)	C14-C13-C19-C9	-175.87(11)
C2-C3-C4-C5	0.15(16)	O12-C13-C19-C20	177.58(9)
C3-C4-C5-C6	0.84(17)	C14-C13-C19-C20	0.98(19)
C4-C5-C6-C7	-0.39(17)	C8-C9-C19-C13	-0.54(11)
O1-C2-C7-C6	-178.03(9)	C10-C9-C19-C13	-179.86(11)
C3-C2-C7-C6	2.05(16)	C8-C9-C19-C20	-177.10(10)
O1-C2-C7-C8	3.38(14)	C10-C9-C19-C20	3.57(19)
C3-C2-C7-C8	-176.55(10)	C13-C19-C20-C25	40.75(15)
C5-C6-C7-C2	-1.03(16)	C9-C19-C20-C25	-143.25(11)
C5-C6-C7-C8	177.38(11)	C13-C19-C20-C21	-136.08(11)
C2-C7-C8-O12	176.63(9)	C9-C19-C20-C21	39.91(17)
C6-C7-C8-O12	-1.85(17)	C25-C20-C21-C22	-3.25(16)
C2-C7-C8-C9	-0.83(15)	C19-C20-C21-C22	173.60(10)
C6-C7-C8-C9	-179.32(11)	C20-C21-C22-C23	2.00(16)
O12-C8-C9-C10	179.59(9)	C21-C22-C23-C24	0.73(16)
C7-C8-C9-C10	-2.67(16)	C21-C22-C23-N26	-178.95(10)
O12-C8-C9-C19	0.15(12)	C22-C23-C24-C25	-2.12(16)
C7-C8-C9-C19	177.89(10)	N26-C23-C24-C25	177.57(10)
C2-O1-C10-O11	178.85(10)	C23-C24-C25-C20	0.80(16)
C2-O1-C10-C9	-1.07(14)	C21-C20-C25-C24	1.82(15)
C8-C9-C10-O11	-176.40(11)	C19-C20-C25-C24	-175.10(10)
C19-C9-C10-O11	2.9(2)	C24-C23-N26-O26	-166.81(10)
C8-C9-C10-O1	3.51(14)	C22-C23-N26-O26	12.89(15)
C19-C9-C10-O1	-177.23(10)	C24-C23-N26-O27	12.36(15)
C9-C8-O12-C13	0.29(11)	C22-C23-N26-O27	-167.94(10)
C7-C8-O12-C13	-177.49(10)		
C8-O12-C13-C19	-0.66(11)		
C8-O12-C13-C14	176.71(9)		
C19-C13-C14-C15	-113.42(13)		
O12-C13-C14-C15	70.05(12)		
C13-C14-C15-C16	-168.59(9)		

Table S9. Hydrogen bonds for 19070z [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C3-H3...O26#1	0.95	2.60	3.4357(15)	146.9
C14-H14A...O27#2	0.99	2.61	3.2433(14)	121.5
C22-H22...O1#1	0.95	2.64	3.5620(13)	165.0
C22-H22...O11#1	0.95	2.57	3.2324(13)	127.1
C24-H24...O27#3	0.95	2.54	3.2496(14)	131.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x+1/2,y-1/2,z #3 -x+1,y,-z+3/2

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