

Elucidation of the Structure of Pseudorubrifloridilactone B by Chemical Synthesis

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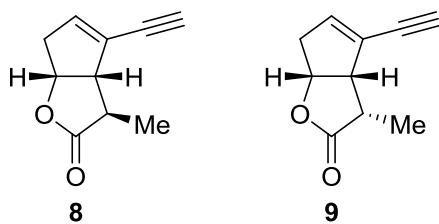
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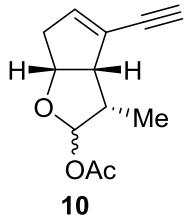
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I Experimental Procedures and Spectroscopic Data of Compounds

General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF) and toluene were distilled immediately before use from sodium-benzophenone ketyl. Methylene chloride (CH_2Cl_2), *N,N*-dimethylformamide (DMF), acetic anhydride (Ac_2O), triethylamine (Et_3N), *N,N*-diisopropylethylamine (*i*- Pr_2NEt), and 2,6-lutidine were distilled from calcium hydride and stored under an argon atmosphere. Methanol (MeOH) was distilled from magnesium and stored under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Adamas-beta®. Reactions were monitored by thin layer chromatography (TLC) carried out on MilliporeSigma glass TLC plates (silica gel 60 coated with F₂₅₄, 250 μm) using UV light for visualization and aqueous ammonium cerium nitrate/ammonium molybdate or basic aqueous potassium permanganate as a developing agent. SiliaFlash® P60 silica gel (particle size: 40–63 μm , pore size: 60 Å) was used for flash column chromatography. NMR spectra were recorded on a Bruker Avance III 400 MHz, an Agilent DD2 500 MHz, or a Bruker Avance III HD 600 MHz NMR spectrometer. The spectra were calibrated by using residual undeuterated solvents (for ^1H NMR) and deuterated solvents (for ^{13}C NMR) as internal references: undeuterated chloroform ($\delta_{\text{H}} = 7.26$ ppm) and CDCl_3 ($\delta_{\text{C}} = 77.16$ ppm); undeuterated pyridine ($\delta_{\text{H}} = 8.74$ ppm) and pyridine-d₅ ($\delta_{\text{C}} = 150.35$ ppm). The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrometer. Melting points (m.p.) are uncorrected and were recorded on an SGW X-4 apparatus. High-resolution mass spectra (HRMS) were recorded on a Bruker maXis 4G, a Bruker Apex III 7.0 Tesla, or a Waters Micromass GCT Premier mass spectrometer.

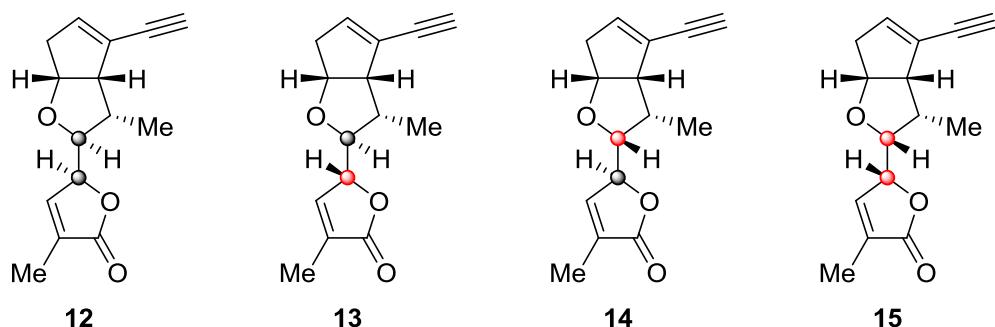


Bicyclic lactones 8 and 9: To a stirred solution of compound **7** [2.33 g, 6.12 mmol, prepared from α,β -unsaturated enone **6**¹ ($> 99\%$ ee) through a sequence reported by us previously²] in THF (25 mL) was added TBAF (15.0 mL, 1.0 M in THF, 15.0 mmol) at 0 °C. The mixture was allowed to warm to 22 °C and stir at that temperature for 2 h before aq. NaHCO₃ (20 mL) was added. The resultant mixture was extracted with EtOAc (3 × 30 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue was subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:8 → 1:6) as eluent to give bicyclic lactones **8** (684 mg, 69%) and **9** (222 mg, 22%) both as pale yellow foams. **8**: $[\alpha]_D^{24} = -49.5$ (*c* = 1.0 in CHCl₃); *R*_f = 0.25 (silica gel, EtOAc:petroleum ether 1:4); IR (film): ν_{max} = 3283, 2970, 2936, 2877, 1767, 1457, 1426, 1347, 1260, 1179, 1097, 1025, 957, 869, 827, 798, 650 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.10 (dd, *J* = 4.9, 2.3 Hz, 1 H), 5.16–5.11 (m, 1 H), 3.19–3.14 (m, 1 H), 3.01 (s, 1 H), 2.87–2.71 (m, 3 H), 1.39 (d, *J* = 7.7 Hz, 3 H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ = 179.10, 136.37, 124.06, 80.59, 80.40, 78.28, 56.01, 39.35, 38.54, 17.32 ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₁₀H₁₁O₂⁺ 163.0754, found 163.0754. **9**: $[\alpha]_D^{24} = -69.1$ (*c* = 0.40 in CHCl₃); *R*_f = 0.32 (silica gel, EtOAc:petroleum ether 1:3); IR (film): ν_{max} = 2956, 2936, 1769, 1701, 1605, 1456, 1388, 1286, 1259, 1177, 1031, 954, 814 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 6.21 (dd, *J* = 4.5, 2.1 Hz, 1 H), 5.08–5.03 (m, 1 H), 3.64–3.59 (m, 1 H), 3.03 (s, 1 H), 2.93 (dq, *J* = 9.2, 7.5 Hz, 1 H), 2.85–2.78 (m, 1 H), 2.78–2.72 (m, 1 H), 1.47 (d, *J* = 7.5 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 178.32, 139.58, 121.64, 80.67, 80.13, 79.84, 51.58, 39.31, 37.82, 12.08 ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₁₀H₁₁O₂⁺ 163.0754, found 163.0754. Similarly, *ent*-**8** and *ent*-**9** were prepared from *ent*-**6**¹ ($> 99\%$ ee). *ent*-**8**: $[\alpha]_D^{25} = +50.9$ (*c* = 1.1 in CHCl₃). *ent*-**9**: $[\alpha]_D^{25} = +69.8$ (*c* = 0.63 in CHCl₃).



Lactol acetate 10: To a stirred solution of bicyclic lactone **9** (2.48 g, 15.3 mmol) in CH₂Cl₂ (70 mL) was added DIBAL-H (18.0 mL, 1.0 M in cyclohexane, 18.0 mmol) at -78 °C. The mixture was allowed to stir at that temperature for 10 min before MeOH (15 mL) and saturated aq. potassium sodium tartrate (50 mL) were sequentially added. The resultant mixture was allowed to warm to 22 °C and stir at that temperature for 2 h. The mixture was extracted with EtOAc (3 × 50 mL), and the combined organic phases were washed with brine (50 mL), dried over anhydrous Na₂SO₄, and filtered. The volatiles were removed under vacuum, and the residue was dissolved in CH₂Cl₂ (50 mL). To this solution were sequentially added Et₃N (12.3 g, 17.0 mL, 122 mmol), 4-DMAP (187 mg, 1.53 mmol), and Ac₂O (7.78 g, 7.20 mL, 76.2 mmol) at 0 °C. The mixture was allowed to stir at that temperature for 5 min before aq. NaHCO₃ (100 mL) was added. The resultant mixture was extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography with EtOAc/petroleum ether (1:15) to give lactol acetate **10** [2.83 g, 90% for the two steps, 20:1 dr at the anomeric carbon] as a white foam. **10**: $[\alpha]_D^{27} = +52.9$ (*c* = 1.1 in CHCl₃); *R*_f = 0.24 (silica gel, EtOAc:petroleum ether 1:9); IR (film): $\nu_{\text{max}} = 3283, 2968, 2932, 1742, 1456, 1429, 1376, 1233, 1171, 1108, 1007, 977, 933, 911, 801 \text{ cm}^{-1}$; ¹H NMR (500 MHz, CDCl₃): $\delta = 6.15$ (d, *J* = 4.7 Hz, 0.05 H), 6.12 (dd, *J* = 5.0, 2.5 Hz, 0.05 H), 6.08 (dd, *J* = 4.4, 2.4 Hz, 1 H), 5.91 (s, 1 H), 4.96 (ddd, *J* = 7.6, 7.6, 2.5 Hz, 1 H), 4.90 (dd, *J* = 6.5, 6.5 Hz, 0.05 H), 3.57 (dd, *J* = 8.1, 8.1 Hz, 1 H), 3.34–3.28 (m, 0.05 H), 3.00 (s, 0.05 H), 2.97 (s, 1 H), 2.76–2.67 (m, 1.05 H), 2.61–2.47 (m, 2.10 H), 2.04 (s, 3 H), 1.98 (s, 0.15 H), 1.27 (d, *J* = 7.2 Hz, 0.15 H), 1.09 (d, *J* = 7.5 Hz, 3 H) ppm; ¹³C NMR (101 MHz, CDCl₃): $\delta = 170.42, 170.27, 139.19, 123.23, 121.92, 105.59, 99.63, 83.79, 83.63, 81.02, 80.66, 79.42, 79.30, 54.21, 53.71, 42.09, 41.73, 41.10, 39.51, 21.17, 21.02, 13.59, 10.12$ ppm; HRMS (*m/z*): [M + H]⁺ calcd for

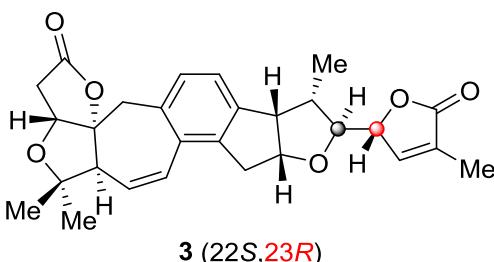
$C_{12}H_{15}O_3^+$ 207.1016, found 207.1015. Similarly, *ent*-**10** was prepared from *ent*-**9**. *ent*-**10**: $[\alpha]_D^{26} = -54.1$ ($c = 0.91$ in $CHCl_3$).



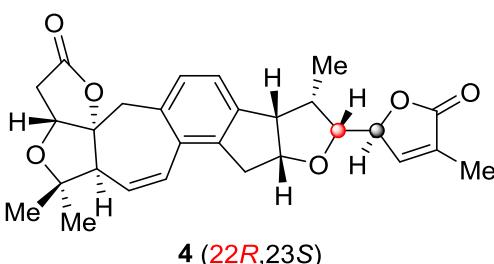
Tricyclic compounds 12, 13, 14, and 15: To a stirred solution of lactol acetate **10** (2.38 g, 11.5 mmol) and 2-siloxofuran **11**³ (3.91 g, 23.0 mmol) in toluene (60 mL) were sequentially added 2,6-lutidine (1.29 g, 1.40 mL, 12.0 mmol) and $BF_3 \cdot OEt_2$ (3.45 g, 3.00 mL, 24.3 mmol) at 22 °C. The mixture was allowed to stir at that temperature for 10 min before aq. $NaHCO_3$ (150 mL) was added. The resultant mixture was extracted with EtOAc (3 × 80 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4 , filtered, and concentrated under vacuum. The residue was subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:8 → 1:5) as eluent to give tricyclic compounds **12** (630 mg, 22%) as a white solid, **13** (962 mg, 34%) as a white foam, **14** (689 mg, 24%) as a white solid, and **15** (119 mg, 4%) as a white foam. **12**: $[\alpha]_D^{24} = -79.7$ ($c = 0.65$ in $CHCl_3$); $R_f = 0.13$ (silica gel, EtOAc:petroleum ether 1:4); IR (film): $\nu_{max} = 3250, 2954, 2926, 2857, 1732, 1657, 1457, 1183, 1075, 1046, 983, 927, 878, 771, 715\text{ cm}^{-1}$; 1H NMR (400 MHz, $CDCl_3$): $\delta = 7.02\text{--}6.99$ (m, 1 H), 6.22–6.17 (m, 1 H), 4.93–4.88 (m, 1 H), 4.70 (dd, $J = 6.3, 6.3$ Hz, 1 H), 3.64 (dd, $J = 9.2, 2.3$ Hz, 1 H), 3.37 (dd, $J = 7.0, 7.0$ Hz, 1 H), 2.99 (s, 1 H), 2.68–2.60 (m, 1 H), 2.60–2.51 (m, 1 H), 2.43 (d, $J = 19.4$ Hz, 1 H), 1.93 (s, 3 H), 1.28 (d, $J = 7.1$ Hz, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 174.32, 146.30, 141.51, 130.71, 122.12, 82.59, 82.29, 81.17, 79.88, 79.79, 56.31, 41.28, 39.16, 13.33, 10.94$ ppm; HRMS (m/z): $[M + H]^+$ calcd for $C_{15}H_{17}O_3^+$ 245.1172, found 245.1172. CCDC 1014568 contains the supplementary crystallographic data of **12** [m.p.: 183–184 °C (EtOAc:hexane 1:2)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. **13**: $[\alpha]_D^{24} = +46.7$ ($c = 1.1$ in $CHCl_3$); $R_f = 0.19$

(silica gel, EtOAc:petroleum ether 1:4); IR (film): $\nu_{\text{max}} = 3215, 2971, 2927, 1758, 1393, 1219, 1096, 1048, 957, 857, 772, 557 \text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.15\text{--}7.12$ (m, 1 H), 6.18 (dd, $J = 4.3, 1.9 \text{ Hz}$, 1 H), 4.83–4.78 (m, 2 H), 3.41 (dd, $J = 8.5, 5.9 \text{ Hz}$, 1 H), 3.44–3.37 (m, 1 H), 2.99 (s, 1 H), 2.74–2.68 (m, 1 H), 2.51–2.42 (m, 1 H), 2.39–2.28 (m, 1 H), 1.92 (dd, $J = 1.8, 1.8 \text{ Hz}$, 3 H), 1.27 (d, $J = 7.1 \text{ Hz}$, 3 H) ppm; ^{13}C NMR (101 MHz, CDCl_3): $\delta = 174.09, 147.10, 141.14, 130.54, 122.15, 84.39, 82.36, 82.19, 81.04, 79.76, 56.64, 41.07, 40.89, 13.88, 10.80 \text{ ppm}$; HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3^+$ 245.1172, found 245.1171. **14**: $[\alpha]_D^{23} = -122$ ($c = 1.0$ in CHCl_3); $R_f = 0.24$ (silica gel, EtOAc:petroleum ether 1:4); IR (film): $\nu_{\text{max}} = 3277, 2938, 2923, 2846, 1745, 1656, 1465, 1379, 1319, 1215, 1168, 1093, 1063, 1010, 959, 867, 674 \text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.24$ (dq, $J = 1.5, 1.5 \text{ Hz}$, 1 H), 6.10 (dd, $J = 4.5, 2.3 \text{ Hz}$, 1 H), 4.87–4.81 (m, 1 H), 4.64 (ddd, $J = 7.4, 7.4, 2.2 \text{ Hz}$, 1 H), 3.47 (dd, $J = 9.2, 5.6 \text{ Hz}$, 1 H), 3.47–3.41 (m, 1 H), 3.02 (s, 1 H), 2.76–2.64 (m, 2 H), 2.52–2.44 (m, 1 H), 1.91 (dd, $J = 1.7, 1.7 \text{ Hz}$, 3 H), 1.21 (d, $J = 7.4 \text{ Hz}$, 3 H) ppm; ^{13}C NMR (101 MHz, CDCl_3): $\delta = 174.11, 149.21, 139.42, 129.89, 122.90, 84.07, 82.44, 80.74, 79.73, 78.91, 56.78, 40.21, 38.05, 10.71, 10.57 \text{ ppm}$; HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3^+$ 245.1172, found 245.1172. CCDC 1060162 contains the supplementary crystallographic data of **14** [m.p.: 140–141 °C (EtOAc:hexane 1:2)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. **15**: $[\alpha]_D^{23} = +17.0$ ($c = 0.86$ in CHCl_3); $R_f = 0.11$ (silica gel, EtOAc:petroleum ether 1:4); IR (film): $\nu_{\text{max}} = 3265, 2968, 2923, 2852, 1754, 1456, 1385, 1337, 1260, 1093, 1061, 1028, 962, 858 \text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.00$ (dq, $J = 1.5, 1.5 \text{ Hz}$, 1 H), 6.11 (dd, $J = 4.4, 2.4 \text{ Hz}$, 1 H), 4.97–4.90 (m, 1 H), 4.67 (ddd, $J = 7.9, 7.9, 2.8 \text{ Hz}$, 1 H), 3.56 (dd, $J = 7.6, 5.0 \text{ Hz}$, 1 H), 3.47 (dd, $J = 8.2, 8.2 \text{ Hz}$, 1 H), 2.98 (s, 1 H), 2.78–2.66 (m, 1 H), 2.59–2.47 (m, 2 H), 1.93 (dd, $J = 1.8, 1.8 \text{ Hz}$, 3 H), 1.09 (d, $J = 7.2 \text{ Hz}$, 3 H) ppm; ^{13}C NMR (101 MHz, CDCl_3): $\delta = 173.46, 144.58, 139.53, 131.80, 121.82, 83.71, 81.93, 80.77, 80.73, 79.12, 57.00, 39.83, 37.08, 10.67, 10.58 \text{ ppm}$; HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3^+$ 245.1172, found 245.1172. Similarly, *ent*-**12**, *ent*-**13**, *ent*-**14**, and *ent*-**15** were prepared from *ent*-**10** and **11**. *ent*-**12**: $[\alpha]_D^{24} = +80.6$ ($c = 0.77$ in CHCl_3). *ent*-**13**: $[\alpha]_D^{24} =$

-46.5 ($c = 3.1$ in CHCl_3). **ent-14:** $[\alpha]_{\text{D}}^{23} = +121$ ($c = 1.2$ in CHCl_3). **ent-15:** $[\alpha]_{\text{D}}^{23} = -17.8$ ($c = 0.61$ in CHCl_3).

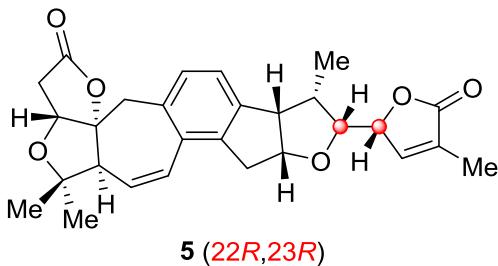


(23R)-Rubriflordilactone B (3): This compound was obtained as a white foam through a five-step sequence starting from compounds **13** and **16** [see preparation of pseudorubriflordilactone B (**26**) (*vide infra*) for details]. **3:** $[\alpha]_{\text{D}}^{27} = +86.0$ ($c = 0.20$ in CHCl_3); $R_f = 0.26$ (silica gel, $\text{EtOAc:petroleum ether } 1:1$); IR (film): $\nu_{\text{max}} = 2957, 2918, 1758, 1747, 1259, 1213, 1169, 1095, 1018, 862, 802, 777 \text{ cm}^{-1}$; ^1H NMR (500 MHz, pyridine- d_5): $\delta = 7.25$ (br s, 1 H), 7.21–7.12 (m, 2 H), 6.63 (d, $J = 12.1$ Hz, 1 H), 5.82 (br s, 1 H), 5.04–4.97 (m, 2 H), 4.43 (br s, 1 H), 3.77 (br s, 1 H), 3.21 (dd, $J = 18.3, 5.8$ Hz, 1 H), 3.44–2.80 (m, 6 H), 2.86 (d, $J = 18.3$ Hz, 1 H), 2.54–2.40 (m, 1 H), 1.87 (dd, $J = 1.5, 1.5$ Hz, 3 H), 1.34 (s, 3 H), 1.44–0.81 (m, 3 H), 1.08 (br s, 3 H) ppm; ^{13}C NMR (151 MHz, pyridine- d_5): $\delta = 175.44, 174.57, 147.92, 142.90, 140.24, 134.53, 133.11, 130.84, 129.97, 128.70, 126.41, 103.91, 85.43, 84.37, 83.75, 83.16, 80.53, 60.40, 54.92, 41.73, 41.31, 39.95, 36.34, 28.94, 22.55, 14.16, 11.15$ ppm; HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{31}\text{O}_6^+$ 463.2115, found 463.2111.

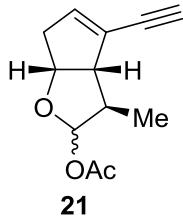


(22R)-Rubriflordilactone B (4): This compound was obtained as a white foam through a five-step sequence starting from compounds **14** and **16** [see preparation of pseudorubriflordilactone B (**26**) (*vide infra*) for details]. **4:** $[\alpha]_{\text{D}}^{27} = -38.1$ ($c = 0.89$ in CHCl_3); $R_f = 0.42$ (silica gel, $\text{EtOAc:petroleum ether } 1:1$); IR (film): $\nu_{\text{max}} = 3015, 2974, 2920, 2849, 1760, 1656, 1462, 1384, 1370, 1319, 1212, 1168, 1090, 1063, 1010, 936, 751 \text{ cm}^{-1}$; ^1H NMR (600 MHz, pyridine- d_5): $\delta = 7.19$ (d, $J = 7.3$ Hz, 1 H), 7.16 (br s, 1 H),

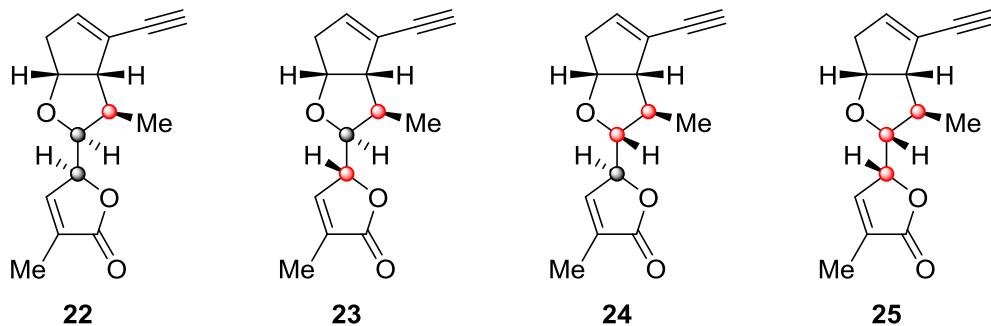
6.95 (br s, 1 H), 6.65 (d, J = 12.0 Hz, 1 H), 5.85 (br s, 1 H), 4.85 (br s, 1 H), 4.62 (dd, J = 7.9, 1.5 Hz, 1 H), 4.42 (br s, 1 H), 3.83 (dd, J = 7.5, 7.5 Hz, 1 H), 3.69 (dd, J = 6.6, 6.6 Hz, 1 H), 3.21 (dd, J = 18.3, 5.8 Hz, 1 H), 3.39–2.80 (m, 5 H), 2.85 (d, J = 18.3 Hz, 1 H), 2.78–2.70 (m, 1 H), 1.79 (s, 3 H), 1.35 (s, 3 H), 0.98 (s, 3 H), 1.33–0.62 (m, 3 H) ppm; ^{13}C NMR (151 MHz, pyridine-d₅): δ = 175.40, 174.33, 149.55, 142.38, 141.09, 133.61, 130.33, 130.20, 128.82, 126.22, 103.85, 85.55, 84.33, 84.08, 80.26, 60.60, 54.64, 41.60, 39.46, 39.38, 36.34, 29.04, 22.56, 12.25, 11.07 ppm; HRMS (*m/z*): [M + Na]⁺ calcd for C₂₈H₃₀O₆Na⁺ 485.1935, found 485.1931.



(22R,23R)-Rubriflordilactone B (5): This compound was obtained as a white foam through a five-step sequence starting from compounds **15** and **16** [see preparation of pseudorubriflordilactone B (**26**) (*vide infra*) for details]. **5**: $[\alpha]_D^{27} = -1.2$ (c = 0.34 in CHCl₃); R_f = 0.26 (silica gel, EtOAc:petroleum ether 1:1); IR (film): ν_{\max} = 3017, 2967, 2924, 2850, 1761, 1460, 1440, 1427, 1383, 1380, 1265, 1216, 1166, 1098, 1067, 1029, 859, 848, 802, 758 cm⁻¹; ^1H NMR (600 MHz, pyridine-d₅): δ = 7.19 (d, J = 7.5 Hz, 1 H), 7.10 (br s, 1 H), 7.05 (br s, 1 H), 6.62 (d, J = 12.1 Hz, 1 H), 5.83 (br s, 1 H), 4.99–4.93 (m, 1 H), 4.90–4.84 (m, 1 H), 4.41 (br s, 1 H), 3.92 (dd, J = 8.0, 8.0 Hz, 1 H), 3.62–3.57 (m, 1 H), 3.51–2.79 (m, 6 H), 2.86 (d, J = 18.2 Hz, 1 H), 2.50 (br s, 1 H), 1.90 (s, 3 H), 1.35 (s, 3 H), 1.53–0.51 (m, 3 H), 0.70 (br s, 3 H) ppm; ^{13}C NMR (151 MHz, pyridine-d₅): δ = 175.44, 174.55, 146.35, 142.40, 140.75, 131.99, 130.28, 128.81, 126.14, 104.01, 85.56, 85.17, 83.64, 82.10, 80.38, 60.48, 55.26, 41.51, 39.27, 38.78, 36.37, 29.05, 22.62, 12.25, 11.23 ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2109.



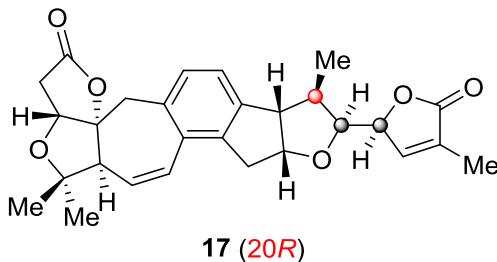
Lactol acetate 21: This compound (841 mg, 1.5:1 dr at the anomeric carbon) was obtained as a white foam from bicyclic lactone **8** (723 mg, 4.46 mmol) in 91% overall yield, by using a two-step protocol similar to that for preparation of lactol acetate **10** (*vide supra*). **21**: $[\alpha]_D^{23} = -22.8$ ($c = 0.44$ in CHCl_3); $R_f = 0.26$ (silica gel, $\text{EtOAc}:\text{petroleum ether}$ 1:9); IR (film): $\nu_{\text{max}} = 3283, 2971, 2935, 1742, 1459, 1429, 1373, 1239, 1174, 1114, 1010, 974, 894, 840 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 6.24$ (d, $J = 4.9$ Hz, 0.66 H), 6.02 (dd, $J = 4.9, 2.3$ Hz, 1 H), 5.95 (dd, $J = 4.4, 2.4$ Hz, 0.66 H), 5.87 (s, 1 H), 4.95 (dd, $J = 6.3, 6.3$ Hz, 1 H), 4.91 (ddd, $J = 7.1, 7.1, 1.4$ Hz, 0.66 H), 3.03–2.99 (m, 1 H), 2.98 (s, 0.66 H), 2.96 (s, 1 H), 2.97–2.93 (m, 0.66 H), 2.81–2.67 (m, 1.66 H), 2.67–2.51 (m, 2.66 H), 2.36–2.25 (m, 0.66 H), 2.08 (s, 1.98 H), 1.95 (s, 3 H), 1.17 (d, $J = 7.0$ Hz, 1.98 H), 1.12 (d, $J = 7.4$ Hz, 3 H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 170.53, 170.43, 136.30, 136.07, 125.32, 125.21, 104.60, 100.12, 83.50, 82.51, 79.85, 79.41, 79.21, 78.90, 59.07, 58.35, 44.10, 43.10, 41.52, 39.31, 21.28, 21.15, 17.95, 13.81$ ppm; HRMS (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{Na}^+$ 229.0835, found 229.0836. Similarly, *ent*-**21** was prepared from *ent*-**8**. *ent*-**21**: $[\alpha]_D^{26} = +23.4$ ($c = 1.1$ in CHCl_3).



Tricyclic compounds 22, 23, 24, and 25: To a stirred solution of lactol acetate **21** (822 mg, 3.98 mmol) and 2-siloxyfuran **11**³ (2.04 g, 12.0 mmol) in toluene (19 mL) were sequentially added 2,6-lutidine (423 mg, 460 μL , 3.95 mmol) and $\text{BF}_3 \text{ OEt}_2$ (1.15 g, 1.00 mL, 8.10 mmol) at 22 °C. The mixture was allowed to stir at that temperature for 10 min before aq. NaHCO_3 (50 mL) was added. The resultant

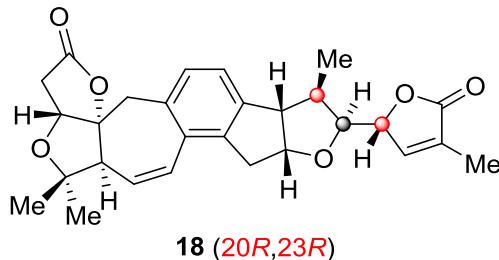
mixture was extracted with EtOAc (3×50 mL). The combined organic phases were washed with brine (80 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue was subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:8 → 1:4) as eluent to give tricyclic compounds **22** (80.9 mg, 8%) as a white foam, **23** (186 mg, 19%) as a white solid, **24** (315 mg, 32%) as a white foam, and **25** (259 mg, 27%) as a white foam. **22**: $[\alpha]_D^{24} = -138$ ($c = 0.58$ in CHCl₃); $R_f = 0.12$ (silica gel, EtOAc:p petroleum ether 1:4); IR (film): $\nu_{\text{max}} = 3268, 2962, 2926, 2878, 2096, 1757, 1659, 1456, 1382, 1325, 1260, 1203, 1162, 1099, 1072, 1052, 992, 956, 858, 754 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 6.98$ (dq, $J = 1.5, 1.5$ Hz, 1 H), 6.07 (dd, $J = 4.5, 2.3$ Hz, 1 H), 4.93–4.88 (m, 1 H), 4.80 (dd, $J = 6.4, 6.4$ Hz, 1 H), 3.76 (dd, $J = 5.6, 5.6$ Hz, 1 H), 3.13–3.08 (m, 1 H), 2.96 (s, 1 H), 2.74–2.63 (m, 1 H), 2.55–2.48 (m, 1 H), 2.47–2.40 (m, 1 H), 1.94 (dd, $J = 1.8, 1.8$ Hz, 3 H), 1.23 (d, $J = 7.1$ Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃): $\delta = 173.99, 145.25, 138.40, 131.93, 124.28, 81.81, 81.11, 79.77, 79.15, 61.25, 41.26, 40.17, 15.22, 10.95$ ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₁₅H₁₇O₃⁺ 245.1172, found 245.1172. **23**: $[\alpha]_D^{24} = +3.2$ ($c = 0.57$ in CHCl₃); m.p.: 128–129 °C; $R_f = 0.27$ (silica gel, EtOAc:p petroleum ether 1:4); IR (film): $\nu_{\text{max}} = 3256, 2980, 2947, 2911, 2869, 1751, 1659, 1459, 1325, 1290, 1263, 1206, 1168, 1090, 1058, 998, 965, 668 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.25$ –7.22 (m, 1 H), 6.08 (dd, $J = 4.7, 2.4$ Hz, 1 H), 4.78 (dd, $J = 5.6, 5.6$ Hz, 1 H), 4.75–4.70 (m, 1 H), 3.39 (dd, $J = 9.2, 4.6$ Hz, 1 H), 3.07 (d, $J = 4.5$ Hz, 1 H), 2.96 (s, 1 H), 2.73–2.61 (m, 2 H), 2.48 (d, $J = 19.3$ Hz, 1 H), 1.90 (dd, $J = 1.7, 1.7$ Hz, 3 H), 1.15 (d, $J = 7.2$ Hz, 3 H) ppm; ¹³C NMR (101 MHz, CDCl₃): $\delta = 174.19, 149.29, 138.50, 129.98, 124.17, 81.51, 80.61, 79.67, 79.39, 78.90, 61.47, 41.62, 38.62, 15.05, 10.82$ ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₁₅H₁₇O₃⁺ 245.1172, found 245.1172. CCDC 1400563 contains the supplementary crystallographic data of **23** [m.p.: 128–129 °C (EtOAc:hexane 1:3)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. **24**: $[\alpha]_D^{24} = -90.7$ ($c = 0.89$ in CHCl₃); $R_f = 0.23$ (silica gel, EtOAc:p petroleum ether 1:4); IR (film): $\nu_{\text{max}} = 3283, 2962, 2923, 2872, 2093, 1889, 1656, 1456, 1382, 1260, 1203, 1177, 1090, 1052, 950, 855, 799 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.16$ –7.13 (m, 1 H), 6.01–5.96 (m, 1 H), 4.70–4.63 (m, 2 H), 3.28 (dd, $J = 7.7, 5.6$ Hz, 1 H), 3.00 (s, 1 H), 2.96–2.91 (m,

1 H), 2.71–2.61 (m, 1 H), 2.53 (d, J = 19.0 Hz, 1 H), 2.48–2.39 (m, 1 H), 1.90 (dd, J = 1.7, 1.7 Hz, 3 H), 1.21 (d, J = 7.0 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, CDCl_3): δ = 174.13, 147.84, 136.43, 130.38, 125.81, 87.32, 82.53, 82.07, 79.70, 79.51, 61.60, 41.70, 40.18, 19.64, 10.75 ppm; HRMS (m/z): [M + H] $^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3^+$ 245.1172, found 245.1171. **25**: $[\alpha]_D^{24} = +22.7$ (c = 0.79 in CHCl_3); R_f = 0.16 (silica gel, EtOAc:petroleum ether 1:4); IR (film): ν_{max} = 3268, 2962, 2926, 2872, 2090, 1754, 1659, 1456, 1260, 1078, 1046, 962, 867, 796 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 6.96–6.94 (m, 1 H), 5.98 (dd, J = 4.7, 2.3 Hz, 1 H), 4.95–4.91 (m, 1 H), 4.64 (dd, J = 5.9, 5.9 Hz, 1 H), 3.67 (dd, J = 7.0, 5.0 Hz, 1 H), 2.96 (s, 1 H), 2.91–2.86 (m, 1 H), 2.68–2.59 (m, 1 H), 2.53 (dd, J = 19.1, 1.2 Hz, 1 H), 2.16–2.08 (m, 1 H), 1.94 (dd, J = 1.8, 1.8 Hz, 3 H), 1.18 (d, J = 6.9 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, CDCl_3): δ = 173.83, 145.75, 136.42, 131.58, 125.33, 85.83, 81.82, 80.72, 79.65, 79.21, 61.39, 39.77, 38.88, 19.30, 10.87 ppm; HRMS (m/z): [M + H] $^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3^+$ 245.1172, found 245.1172. Similarly, *ent*-**22**, *ent*-**23**, *ent*-**24**, and *ent*-**25** were prepared from *ent*-**21** and **11**. *ent*-**22**: $[\alpha]_D^{24} = +136$ (c = 0.99 in CHCl_3). *ent*-**23**: $[\alpha]_D^{23} = -3.6$ (c = 0.77 in CHCl_3). *ent*-**24**: $[\alpha]_D^{24} = +91.4$ (c = 0.94 in CHCl_3). *ent*-**25**: $[\alpha]_D^{24} = -24.2$ (c = 1.1 in CHCl_3).

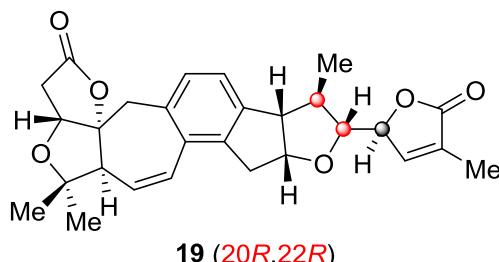


(20*R*)-Rubriflordilactone B (17): This compound was obtained as a white foam through a five-step sequence starting from compounds **22** and **16** [see preparation of pseudorubriflordilactone B (**26**) (*vide infra*) for details]. **17**: $[\alpha]_D^{27} = -132$ (c = 0.69 in CHCl_3); R_f = 0.21 (silica gel, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 3012, 2971, 2920, 2875, 1760, 1462, 1441, 1382, 1373, 1322, 1215, 1165, 1069, 1049, 1010, 933, 751 cm^{-1} ; ^1H NMR (600 MHz, pyridine-d₅): δ = 7.16 (br s, 1 H), 7.15 (d, J = 7.3 Hz, 1 H), 7.03 (br s, 1 H), 6.56 (d, J = 12.1 Hz, 1 H), 5.76 (br s, 1 H), 5.11–5.06 (m, 1 H), 5.03 (br s, 1 H), 4.41 (s, 1 H), 3.78 (br s, 1 H), 3.55 (dd, J = 6.3, 3.3 Hz, 1 H), 3.19 (dd, J = 18.3, 5.8 Hz, 1 H), 3.40–2.67 (m, 5 H), 2.85 (d, J = 18.3 Hz, 1 H), 2.46 (br s, 1 H), 1.83 (dd, J = 1.6, 1.6 Hz, 3 H), 1.35 (s, 3 H), 1.48–

0.92 (m, 3 H), 1.28 (d, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (151 MHz, pyridine-d₅): δ = 175.46, 174.70, 147.26, 143.65, 141.59, 134.67, 133.21, 131.39, 130.75, 128.78, 103.95, 85.46, 83.74, 82.47, 82.10, 80.56, 60.32, 58.95, 43.90, 41.79, 40.14, 36.33, 28.89, 22.55, 15.70, 11.18 ppm; HRMS (m/z): [M + Na]⁺ calcd for C₂₈H₃₀O₆Na⁺ 485.1935, found 485.1940.

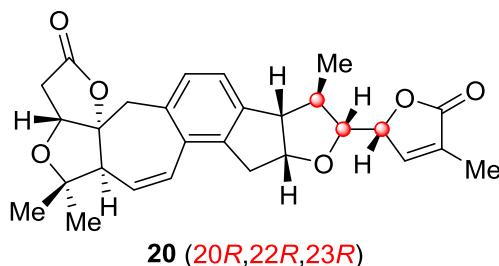


(20R,23R)-Rubriflordinilactone B (18): This compound was obtained as a white foam through a five-step sequence starting from compounds **23** and **16** [see preparation of pseudorubriflordinilactone B (**26**) (*vide infra*) for details]. **18:** $[\alpha]_D^{27} = +119$ ($c = 0.32$ in CHCl₃); $R_f = 0.29$ (silica gel, EtOAc:petroleum ether 1:1); IR (film): $\nu_{\text{max}} = 3011, 2962, 2926, 1761, 1386, 1369, 1320, 1262, 1210, 1169, 1087, 1059, 1010, 933, 802, 749, 670 \text{ cm}^{-1}$; ^1H NMR (400 MHz, pyridine-d₅): δ = 7.26 (br s, 1 H), 7.15 (d, J = 7.4 Hz, 1 H), 7.11 (br s, 1 H), 6.62 (d, J = 12.1 Hz, 1 H), 5.80 (br s, 1 H), 5.02 (dd, J = 5.4, 5.4 Hz, 1 H), 4.84 (d, J = 7.8 Hz, 1 H), 4.40 (br s, 1 H), 3.48 (d, J = 5.4 Hz, 1 H), 3.41–3.34 (m, 1 H), 3.30–2.72 (m, 6 H), 2.84 (dd, J = 18.3, 2.5 Hz, 1 H), 2.70–2.60 (m, 1 H), 1.75 (s, 3 H), 1.31 (s, 3 H), 1.38–0.54 (m, 3 H), 1.22 (d, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (151 MHz, pyridine-d₅): δ = 175.38, 174.25, 149.88, 143.07, 141.78, 134.59, 133.17, 130.91, 130.18, 128.89, 103.82, 85.44, 83.06, 82.66, 80.25, 79.79, 60.36, 59.04, 43.11, 41.68, 40.17, 36.31, 28.92, 22.55, 15.61, 11.12 ppm; HRMS (m/z): [M + Na]⁺ calcd for C₂₈H₃₀O₆Na⁺ 485.1935, found 485.1941.



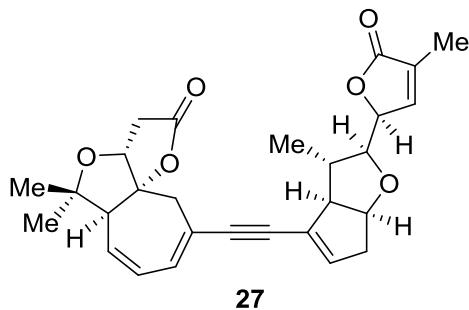
(20R,22R)-Rubriflordinilactone B (19): This compound was obtained as a white solid through a five-step sequence starting from compounds **24** and **16** [see preparation of pseudorubriflordinilactone B (**26**) (*vide infra*) for details].

(*vide infra*) for details]. **19**: $[\alpha]_D^{27} = -32.0$ ($c = 0.46$ in CHCl_3); m.p.: 238–239 °C (MeCN:water 1:3); $R_f = 0.42$ (silica gel, EtOAc:petroleum ether 1:1); IR (film): $\nu_{\text{max}} = 3017, 2970, 2924, 1758, 1462, 1443, 1386, 1372, 1320, 1216, 1166, 1092, 1068, 1051, 1007, 933, 755 \text{ cm}^{-1}$; ^1H NMR (400 MHz, pyridine-d₅): $\delta = 7.20\text{--}7.14$ (m, 2 H), 6.96 (br s, 1 H), 6.60 (dd, $J = 12.1, 2.0$ Hz, 1 H), 5.79 (br s, 1 H), 4.90–4.83 (m, 1 H), 4.67 (d, $J = 6.3$ Hz, 1 H), 4.42 (br s, 1 H), 3.53 (dd, $J = 6.6, 6.6$ Hz, 1 H), 3.32 (dd, $J = 6.0, 4.7$ Hz, 1 H), 3.22 (dd, $J = 18.4, 5.9$ Hz, 1 H), 3.31–2.75 (m, 5 H), 2.86 (d, $J = 18.4$ Hz, 1 H), 2.37 (br s, 1 H), 1.75 (dd, $J = 1.6, 1.6$ Hz, 3 H), 1.34 (s, 3 H), 1.38–0.73 (m, 3 H), 1.25 (d, $J = 6.9$ Hz, 3 H) ppm; ^{13}C NMR (151 MHz, pyridine-d₅): $\delta = 175.45, 174.40, 148.26, 144.71, 140.61, 134.52, 133.37, 130.93, 130.56, 128.81, 103.67, 87.81, 85.45, 84.04, 82.97, 80.46, 60.43, 59.06, 45.45, 41.86, 38.69, 36.34, 28.82, 22.53, 19.33, 11.02$ ppm; HRMS (*m/z*): [M + Na]⁺ calcd for $\text{C}_{28}\text{H}_{30}\text{O}_6\text{Na}^+$ 485.1935, found 485.1930. CCDC 1060734 contains the supplementary crystallographic data of **19** [m.p.: 238–239 °C (MeCN:water 1:3)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



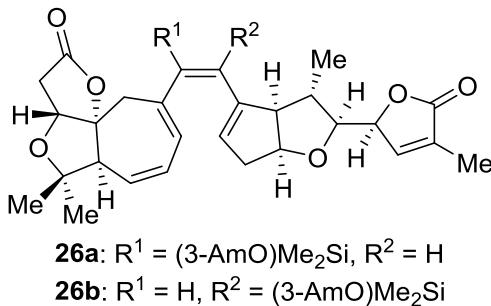
(20R,22R,23R)-Rubriflordilactone B (20): This compound was obtained as a white solid through a five-step sequence starting from compounds **25** and **16** [see preparation of pseudorubriflordilactone B (**26**) (*vide infra*) for details]. **20**: $[\alpha]_D^{26} = +113$ ($c = 0.33$ in CHCl_3); m.p.: 220–222 °C (MeCN:water 1:3); $R_f = 0.35$ (silica gel, EtOAc:petroleum ether 1:1); IR (film): $\nu_{\text{max}} = 2968, 2920, 1757, 1260, 1212, 1168, 1072, 1049, 1031, 802, 754 \text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.03\text{--}6.91$ (m, 2 H), 6.60 (d, $J = 12.1$ Hz, 1 H), 6.25 (br s, 1 H), 5.82 (br s, 1 H), 4.90 (ddd, $J = 6.3, 3.7, 3.7$ Hz, 1 H), 4.83–4.75 (m, 1 H), 4.33 (br s, 1 H), 3.87 (br s, 1 H), 3.34 (dd, $J = 5.5, 4.3$ Hz, 1 H), 3.20–2.53 (m, 6 H), 2.71 (d, $J = 18.5$ Hz, 1 H), 2.15–2.01 (m, 1 H), 1.81 (dd, $J = 1.7, 1.7$ Hz, 3 H), 1.39 (s, 3 H), 1.42–0.35 (m, 3 H), 1.26 (d, $J = 7.0$ Hz, 3 H) ppm; ^1H NMR (600 MHz, pyridine-d₅): $\delta = 7.14$ (d, $J = 7.5$ Hz, 1 H), 7.07 (br s, 1 H),

6.57 (d, $J = 12.1$ Hz, 1 H), 6.70–6.43 (m, 1 H), 5.77 (br s, 1 H), 4.92 (br s, 1 H), 4.88 (dd, $J = 6.0, 6.0$ Hz, 1 H), 4.41 (br s, 1 H), 3.83 (br s, 1 H), 3.36–2.78 (m, 7 H), 2.85 (d, $J = 18.3$ Hz, 1 H), 2.22 (br s, 1 H), 1.85 (s, 3 H), 1.36 (s, 3 H), 1.45–1.01 (m, 3 H), 1.19 (d, $J = 6.5$ Hz, 3 H) ppm; ^1H NMR (500 MHz, pyridine-d₅, 60 °C): $\delta = 7.16$ (d, $J = 7.5$ Hz, 1 H), 7.11 (d, $J = 7.3$ Hz, 1 H), 6.67–6.56 (m, 2 H), 5.83 (d, $J = 11.5$ Hz, 1 H), 4.50–4.36 (m, 3 H), 3.88 (br s, 1 H), 3.34 (br s, 1 H), 3.24 (d, $J = 17.0$ Hz, 1 H), 3.25–3.18 (m, 1 H), 3.15 (dd, $J = 18.3, 6.0$ Hz, 1 H), 3.12–3.06 (m, 1 H), 3.03 (d, $J = 13.4$ Hz, 1 H), 2.98 (br s, 1 H), 2.83 (d, $J = 18.3$ Hz, 1 H), 2.24 (br s, 1 H), 1.87 (s, 3 H), 1.39 (s, 3 H), 1.28–1.21 (m, 3 H), 1.06 (br s, 3 H) ppm; ^{13}C NMR (151 MHz, CDCl₃): $\delta = 174.65, 173.94, 146.03, 143.37, 139.97, 133.15, 132.48, 131.45, 129.75, 127.91, 123.58, 103.01, 86.52, 85.18, 83.61, 80.62, 79.81, 59.33, 58.23, 41.74, 41.03, 37.97, 35.77, 28.40, 22.24, 19.72, 10.85$ ppm; ^{13}C NMR (151 MHz, pyridine-d₅): $\delta = 175.41, 174.42, 147.19, 144.17, 140.61, 134.60, 133.30, 131.48, 130.66, 128.79, 128.27, 124.35, 103.70, 87.55, 85.37, 84.14, 81.69, 80.55, 60.31, 58.89, 42.10, 38.56, 36.34, 28.79, 22.50, 19.55, 11.24$ ppm; ^{13}C NMR (101 MHz, pyridine-d₅, 60 °C): $\delta = 175.05, 174.19, 146.97, 144.37, 140.67, 133.84, 131.60, 130.65, 129.09, 128.81, 124.33, 103.75, 87.70, 85.51, 84.19, 81.62, 79.74, 60.58, 59.10, 42.31, 41.57, 38.67, 36.42, 29.24, 22.67, 19.58, 11.12$ ppm; HRMS (m/z): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2110. CCDC 1060164 contains the supplementary crystallographic data of **20** [m.p.: 220–222 °C (MeCN:water 1:3)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



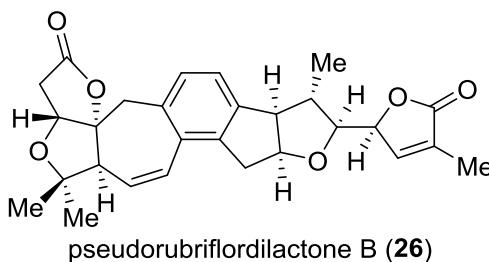
Conjugated trienylne 27: To a stirred solution of alkenyl triflate **16** (87.6 mg, 0.238 mmol) and terminal alkyne *ent*-**25** (63.9 mg, 0.262 mmol) in DMF (2.0 mL) were sequentially added LiCl (12.1 mg, 0.285 mmol), *i*-Pr₂NEt (77.9 mg, 105 μ L, 0.603 mmol), Pd(PPh₃)₄ (27.5 mg, 0.0238 mmol), and CuI

(13.6 mg, 0.0714 mmol) at 22 °C. The mixture was warmed to 70 °C and allowed to stir at that temperature for 1 h before EtOAc (10 mL) and saturated aq. NH₄Cl (10 mL) were sequentially added. The resultant mixture was extracted with EtOAc (3 × 15 mL), and the combined organic phases were washed with brine (10 mL), dried over anhydrous Na₂SO₄, and filtered. The volatiles were removed under vacuum, and the residue was purified by flash column chromatography with EtOAc/petroleum ether (1:3 → 3:2) to give conjugated trienye **27** (100 mg, 91%) as a pale yellow foam. **27**: [α]_D²⁴ = 27.6 (*c* = 0.53 in CHCl₃); *R*_f = 0.35 (silica gel, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 2959, 2917, 2867, 2850, 1780, 1755, 1454, 1378, 1215, 1174, 1077, 1044, 935, 751 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.98–6.95 (m, 1 H), 6.37 (d, *J* = 5.8 Hz, 1 H), 6.11 (ddd, *J* = 12.0, 5.8, 2.2 Hz, 1 H), 5.89–5.85 (m, 1 H), 5.79 (dd, *J* = 12.0, 4.7 Hz, 1 H), 4.95–4.91 (m, 1 H), 4.63 (dd, *J* = 6.0, 6.0 Hz, 1 H), 4.38 (d, *J* = 5.6 Hz, 1 H), 3.65 (dd, *J* = 7.2, 4.8 Hz, 1 H), 2.91–2.87 (m, 2 H), 2.83 (dd, *J* = 18.6, 5.9 Hz, 1 H), 2.75–2.60 (m, 3 H), 2.58–2.46 (m, 2 H), 2.14–2.03 (m, 1 H), 1.93 (dd, *J* = 1.6, 1.6 Hz, 3 H), 1.39 (s, 3 H), 1.17 (d, *J* = 6.9 Hz, 3 H), 1.14 (s, 3 H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ = 174.52, 174.05, 145.88, 135.02, 134.04, 131.58, 130.81, 127.75, 126.08, 120.47, 104.79, 93.53, 86.74, 85.76, 85.03, 81.93, 80.68, 78.79, 61.56, 60.37, 40.31, 40.02, 39.26, 35.83, 28.77, 22.53, 19.28, 10.97 ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2112.



Conjugated tetraenes 26a and 26b: To a stirred solution of conjugated trienye **27** (100 mg, 0.216 mmol) in toluene (3.0 mL) were sequentially added (3-AmO)SiMe₂H⁴ (**29**, 143 mg, 0.977 mmol) and Karsted catalyst (**28**, 25.0 μL, 2.0 wt% in xylene, 0.00218 mmol) at 22 °C. The resultant mixture was allowed to stir at that temperature for 10 min and then directed subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:4 → 1:1) as eluent to give a mixture of

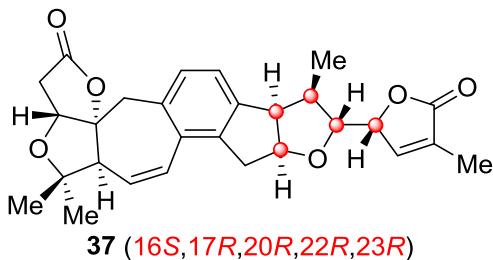
conjugated tetraenes **26a** and **26b** [113 mg, 86%, ca. 1:1 ratio] as a pale yellow foam. **26a** and **26b**: $[\alpha]_D^{24} = -257$ ($c = 1.0$ in CHCl_3); $R_f = 0.43$ (silica gel, EtOAc:petroleum ether 1:1); IR (film): $\nu_{\text{max}} = 3009, 2959, 2925, 2875, 1780, 1750, 1458, 1381, 1370, 1253, 1220, 1165, 1056, 1010, 935, 855, 789 \text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3): $\delta = 6.97$ (s, 1 H), 6.95 (s, 1 H), 6.36 (s, 1 H), 6.24–6.16 (m, 2 H), 6.12 (ddd, $J = 11.7, 5.7, 2.0 \text{ Hz}$, 1 H), 6.07 (ddd, $J = 11.8, 5.5, 2.9 \text{ Hz}$, 1 H), 5.88 (d, $J = 5.4 \text{ Hz}$, 1 H), 5.67 (dd, $J = 11.9, 3.7 \text{ Hz}$, 1 H), 5.58 (s, 1 H), 5.56 (dd, $J = 12.2, 2.9 \text{ Hz}$, 1 H), 5.33 (s, 1 H), 4.88 (s, 1 H), 4.84 (s, 1 H), 4.67–4.52 (m, 3 H), 4.31 (d, $J = 5.6 \text{ Hz}$, 1 H), 3.61–3.47 (m, 3 H), 3.50 (dd, $J = 9.0, 4.3 \text{ Hz}$, 1 H), 3.15 (dd, $J = 6.8, 6.8 \text{ Hz}$, 1 H), 2.91–2.40 (m, 15 H), 2.05 (dq, $J = 6.9, 6.9 \text{ Hz}$, 1 H), 1.95–1.87 (m, 1 H), 1.91 (s, 6 H), 1.52–1.39 (m, 8 H), 1.38 (s, 3 H), 1.37 (s, 3 H), 1.21 (s, 3 H), 1.15 (d, $J = 8.8 \text{ Hz}$, 3 H), 1.14 (s, 3 H), 1.02 (d, $J = 6.7 \text{ Hz}$, 3 H), 0.89–0.81 (m, 12 H), 0.31 (s, 3 H), 0.30 (s, 3 H), 0.22 (s, 3 H), 0.20 (s, 3 H) ppm; ^{13}C NMR (101 MHz, CDCl_3): $\delta = 175.45, 174.48, 174.01, 173.90, 149.47, 145.91, 145.70, 143.88, 141.50, 141.36, 141.16, 139.50, 137.00, 132.91, 131.25, 130.97, 129.25, 129.19, 129.10, 128.01, 127.66, 127.46, 124.92, 124.72, 106.48, 105.04, 85.99, 85.11, 84.94, 84.53, 82.42, 81.92, 80.53, 79.59, 79.41, 79.22, 75.63, 75.40, 61.23, 60.17, 59.76, 59.65, 41.16, 40.51, 40.40, 40.37, 39.69, 39.44, 35.79, 35.75, 29.32, 29.29, 29.24, 28.54, 28.41, 22.53, 22.41, 18.52, 17.56, 10.99, 10.95, 9.97, 9.92, –0.11, –0.34, –0.85, –1.04 ppm; HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{35}\text{H}_{49}\text{O}_7\text{Si}^+$ 609.3242, found 609.3242.$



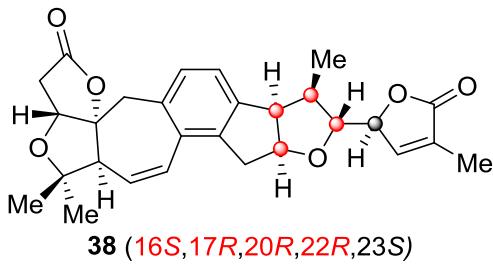
Pseudorubriflordilactone B (26): A mixture of conjugated tetraenes **26a** and **26b** (80.0 mg, 0.131 mmol, ca. 1:1 ratio) was dissolved in toluene (30 mL). The resultant solution was heated to 135 °C and allowed to stir at that temperature for 1 h before it was cooled to 22 °C. The solvent was evaporated under vacuum, and the residue (crude electrocyclization products) was dissolved in CH_2Cl_2 (5.0 mL). To the stirred solution was added DDQ (59.7 mg, 0.263 mmol) at 22 °C. The mixture was allowed to

stir at that temperature for 5 min before it was directly passed through a short plug of Al_2O_3 (neutral) with EtOAc (30 mL). The volatiles were removed under vacuum, and the residue (crude pentasubstituted arenes) was dissolved in MeOH/THF (3.6 mL, 1:5). To the stirred solution were sequentially added water (30.0 mg, 30.0 μL , 1.67 mmol) and AgF (83.3 mg, 0.657 mmol) at 22 °C. The mixture was allowed to stir in the dark at that temperature for 3 h before saturated aq. NH_4Cl (20 mL) was added. The resultant mixture was extracted with EtOAc (4×10 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4 , filtered, and concentrated under vacuum. The residue was purified by flash column chromatography with EtOAc/petroleum ether (1:3 → 3:2) to give pseudorubriflordilactone B (**26**; 45.2 mg, 74%) as a white foam. **26**: $[\alpha]_D^{26} = -131$ ($c = 0.43$ in CHCl_3); $[\alpha]_D^{27} = -58.9$ ($c = 0.036$ in MeOH); $R_f = 0.24$ (silica gel, EtOAc:petroleum ether 2:3); IR (film): $\nu_{\text{max}} = 3015, 2977, 2926, 2869, 1757, 1459, 1441, 1382, 1319, 1215, 1168, 1069, 1031, 796, 751$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.06\text{--}6.94$ (m, 2 H), 6.60 (dd, $J = 12.1, 1.5$ Hz, 1 H), 6.56 (s, 1 H), 5.75 (br s, 1 H), 4.93–4.86 (m, 1 H), 4.73 (br s, 1 H), 4.36 (br s, 1 H), 3.79 (dd, $J = 6.5, 5.0$ Hz, 1 H), 3.38–3.34 (m, 1 H), 3.19–2.63 (m, 6 H), 2.72 (d, $J = 18.5$ Hz, 1 H), 2.20–2.12 (m, 1 H), 1.82 (s, 3 H), 1.40 (s, 3 H), 1.29 (d, $J = 6.9$ Hz, 3 H), 1.37–1.15 (m, 3 H) ppm; ^1H NMR (500 MHz, pyridine-d₅): $\delta = 7.13$ (d, $J = 7.4$ Hz, 1 H), 7.10 (br s, 1 H), 6.90 (s, 1 H), 6.53 (d, $J = 12.2$ Hz, 1 H), 5.75 (br s, 1 H), 4.92–4.84 (m, 2 H), 4.45 (br s, 1 H), 3.76 (dd, $J = 6.6, 5.3$ Hz, 1 H), 3.41–2.81 (m, 7 H), 2.88 (d, $J = 18.3$ Hz, 1 H), 2.39–2.29 (m, 1 H), 1.78 (s, 3 H), 1.36 (s, 3 H), 1.45–1.01 (m, 3 H), 1.21 (d, $J = 6.8$ Hz, 3 H) ppm; ^1H NMR (600 MHz, pyridine-d₅, 60 °C): $\delta = 7.15$ (d, $J = 7.6$ Hz, 1 H), 7.12 (d, $J = 7.6$ Hz, 1 H), 6.86 (s, 1 H), 6.59 (dd, $J = 12.1, 1.7$ Hz, 1 H), 5.83 (d, $J = 9.5$ Hz, 1 H), 4.92 (dd, $J = 6.3, 6.3$ Hz, 1 H), 4.90–4.87 (m, 1 H), 4.47–4.43 (m, 1 H), 3.81 (dd, $J = 6.9, 5.0$ Hz, 1 H), 3.38–3.34 (m, 1 H), 3.24–3.15 (m, 3 H), 3.10–3.02 (m, 2 H), 2.99 (br s, 1 H), 2.85 (d, $J = 18.3$ Hz, 1 H), 2.38–2.32 (m, 1 H), 1.82 (s, 3 H), 1.40 (s, 3 H), 1.26 (d, $J = 6.9$ Hz, 3 H), 1.10 (br s, 3 H) ppm; ^{13}C NMR (151 MHz, CDCl_3): $\delta = 174.76, 173.83, 145.78, 143.54, 140.04, 133.19, 132.48, 131.30, 129.87, 128.02, 127.39, 123.38, 102.83, 86.45, 85.10, 83.53, 80.50, 79.91, 59.22, 58.15, 41.77, 41.65, 38.03, 35.78, 28.26, 22.13, 19.14, 10.93$ ppm; ^{13}C NMR (151 MHz, pyridine-d₅): $\delta = 175.63, 174.46, 147.28, 144.47, 140.80, 134.81, 133.29,$

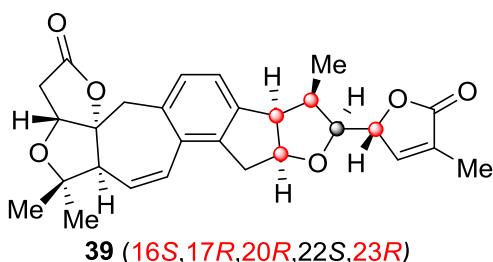
131.25, 130.70, 128.38, 123.61, 103.31, 87.34, 85.30, 83.93, 81.57, 80.72, 60.34, 58.79, 42.97, 41.97, 38.67, 36.33, 28.51, 22.35, 18.95, 11.17 ppm; ^{13}C NMR (101 MHz, pyridine-d₅, 60 °C): δ = 175.22, 174.21, 147.00, 144.62, 140.79, 133.95, 133.82, 131.38, 130.69, 129.13, 128.58, 124.08, 103.70, 87.51, 85.60, 84.03, 81.51, 79.85, 60.68, 59.04, 43.03, 41.65, 38.77, 36.42, 29.13, 22.56, 19.08, 11.03 ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2114. Similarly, *ent*-**26** was prepared from *ent*-**16** and **25**. *ent*-**26**: $[\alpha]_D^{26} = +128$ (*c* = 0.35 in CHCl₃); $[\alpha]_D^{26} = +60.3$ (*c* = 0.029 in MeOH).



(16S,17R,20R,22R,23R)-Rubriflordinolactone B (37): This compound was obtained as a white foam through a five-step sequence starting from compounds *ent*-**12** and **16** [see preparation of pseudorubriflordinolactone B (**26**) (*vide supra*) for details]. **37**: $[\alpha]_D^{27} = +83.7$ (*c* = 0.30 in CHCl₃); $R_f = 0.31$ (silica gel, EtOAc:petroleum ether 2:3); IR (film): $\nu_{\text{max}} = 3012, 2964, 2926, 2846, 1757, 1212, 1168, 1066, 1046, 1007, 933, 757 \text{ cm}^{-1}$; ^1H NMR (500 MHz, pyridine-d₅): δ = 7.17 (s, 1 H), 7.16–7.12 (m, 2 H), 6.61 (d, *J* = 12.2 Hz, 1 H), 5.77 (br s, 1 H), 5.07 (br s, 1 H), 4.91 (dd, *J* = 6.0, 6.0 Hz, 1 H), 4.46 (br s, 1 H), 3.79–3.69 (m, 1 H), 3.52 (dd, *J* = 9.4, 2.0 Hz, 1 H), 3.25 (dd, *J* = 18.4, 6.0 Hz, 1 H), 3.34–2.82 (m, 5 H), 2.89 (d, *J* = 18.4 Hz, 1 H), 2.80–2.67 (m, 1 H), 1.87 (s, 3 H), 1.37 (s, 3 H), 1.48–0.84 (m, 3 H), 1.12 (d, *J* = 7.0 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, pyridine-d₅): δ = 175.65, 175.00, 148.13, 143.22, 140.27, 130.58, 129.97, 128.55, 126.26, 103.57, 85.45, 83.84, 83.51, 80.81, 60.44, 54.46, 41.78, 39.99, 36.38, 28.68, 22.34, 13.84, 11.17 ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2115.

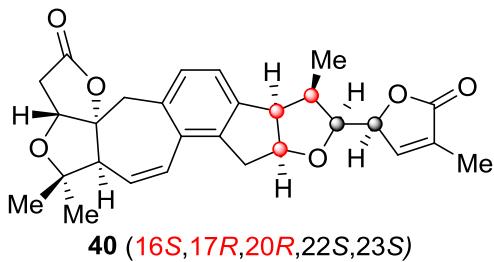


(16S,17R,20R,22R)-Rubriflordinilactone B (38): This compound was obtained as a white foam through a five-step sequence starting from compounds *ent*-**13** and **16** [see preparation of pseudorubriflordinilactone B (**26**) (*vide supra*) for details]. **38**: $[\alpha]_D^{27} = -149$ ($c = 0.44$ in CHCl_3); $R_f = 0.27$ (silica gel, $\text{EtOAc:petroleum ether } 2:3$); IR (film): $\nu_{\text{max}} = 3009, 2971, 2926, 2843, 1748, 1325, 1215, 1171, 1102, 1063, 1010, 757 \text{ cm}^{-1}$; ^1H NMR (400 MHz, pyridine- d_5): $\delta = 7.34\text{--}7.30$ (m, 1 H), 7.18–7.09 (m, 2 H), 6.64 (d, $J = 12.1$ Hz, 1 H), 5.78 (d, $J = 9.7$ Hz, 1 H), 5.02–4.96 (m, 2 H), 4.46 (br s, 1 H), 3.84–3.71 (m, 1 H), 3.46 (dd, $J = 8.7, 5.2$ Hz, 1 H), 3.26 (dd, $J = 18.4, 6.1$ Hz, 1 H), 3.32–2.83 (m, 5 H), 2.89 (d, $J = 18.4$ Hz, 1 H), 2.57–2.45 (m, 1 H), 1.87 (dd, $J = 1.7, 1.7$ Hz, 3 H), 1.37 (s, 3 H), 1.47–0.86 (m, 3 H), 1.12 (d, $J = 7.0$ Hz, 3 H) ppm; ^{13}C NMR (126 MHz, pyridine- d_5): $\delta = 175.64, 174.58, 147.97, 143.02, 140.21, 134.66, 133.18, 130.93, 129.98, 128.55, 126.24, 103.54, 85.40, 84.91, 83.93, 83.12, 80.61, 60.43, 54.70, 41.75, 41.30, 39.89, 36.37, 28.67, 22.30, 14.52, 11.16$ ppm; HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{31}\text{O}_6^+$ 463.2115, found 463.2113.

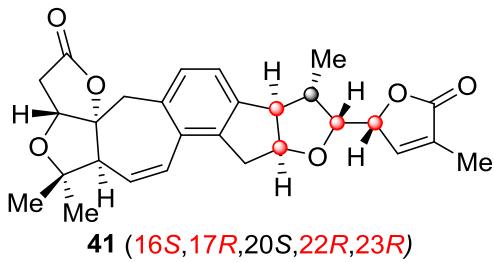


(16S,17R,20R,23R)-Rubriflordinilactone B (39): This compound was obtained as a white foam through a five-step sequence starting from compounds *ent*-**14** and **16** [see preparation of pseudorubriflordinilactone B (**26**) (*vide supra*) for details]. **39**: $[\alpha]_D^{27} = +62.9$ ($c = 0.55$ in CHCl_3); $R_f = 0.55$ (silica gel, $\text{EtOAc:petroleum ether } 2:3$); IR (film): $\nu_{\text{max}} = 3018, 2974, 2926, 2852, 1760, 1656, 1459, 1385, 1319, 1215, 1168, 1087, 1063, 1007, 796, 757 \text{ cm}^{-1}$; ^1H NMR (400 MHz, pyridine- d_5): $\delta = 7.23\text{--}7.18$ (m, 1 H), 7.16 (d, $J = 7.5$ Hz, 1 H), 7.12 (br s, 1 H), 6.65 (d, $J = 11.6$ Hz, 1 H), 5.84 (br s, 1

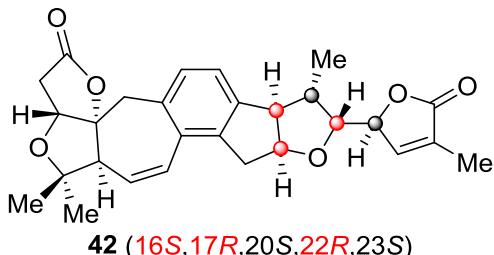
H), 4.92–4.84 (m, 1 H), 4.58 (d, J = 7.6 Hz, 1 H), 4.43 (br s, 1 H), 3.82 (dd, J = 7.6, 7.6 Hz, 1 H), 3.63 (dd, J = 8.5, 6.1 Hz, 1 H), 3.39–2.83 (m, 7 H), 2.79–2.68 (m, 1 H), 1.81 (s, 3 H), 1.37 (s, 3 H), 1.54–0.81 (m, 3 H), 1.07 (d, J = 7.3 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, pyridine-d₅): δ = 175.57, 174.35, 142.39, 141.11, 130.38, 130.17, 128.75, 126.03, 103.38, 85.47, 84.81, 84.15, 80.69, 80.16, 60.59, 54.61, 41.84, 39.85, 39.70, 36.37, 28.64, 22.35, 12.09, 11.09 ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2117.



(16S,17R,20R)-Rubriflordilactone B (40): This compound was obtained as a white foam through a five-step sequence starting from compounds *ent*-**15** and **16** [see preparation of pseudorubriflordilactone B (**26**) (*vide supra*) for details]. **40:** $[a]_D^{28} = +32.2$ (c = 0.53 in CHCl₃); R_f = 0.21 (silica gel, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 3015, 2971, 2926, 1763, 1218, 1165, 1090, 1063, 1025, 983, 757 cm⁻¹; ^1H NMR (500 MHz, pyridine-d₅): δ = 7.17–7.10 (m, 2 H), 7.05 (br s, 1 H), 6.57 (d, J = 12.1 Hz, 1 H), 5.78 (br s, 1 H), 5.05–5.00 (m, 1 H), 4.92–4.85 (m, 1 H), 4.43 (br s, 1 H), 3.89 (dd, J = 7.9, 7.9 Hz, 1 H), 3.65 (dd, J = 7.2, 5.0 Hz, 1 H), 3.42–2.77 (m, 6 H), 2.88 (d, J = 18.3 Hz, 1 H), 2.57–2.49 (m, 1 H), 1.90 (s, 3 H), 1.37 (s, 3 H), 1.58–0.98 (m, 3 H), 0.80 (d, J = 6.6 Hz, 3 H); ^{13}C NMR (126 MHz, pyridine-d₅): δ = 175.67, 174.67, 146.57, 142.63, 140.72, 131.98, 130.30, 128.57, 125.99, 103.53, 85.66, 85.24, 83.70, 82.13, 80.77, 60.52, 55.25, 42.01, 39.49, 38.86, 36.39, 28.69, 22.32, 12.40, 11.25 ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2117.

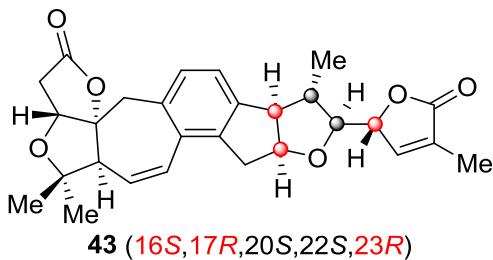


(16S,17R,22R,23R)-Rubriflordinolactone B (41): This compound was obtained as a white foam through a five-step sequence starting from compounds *ent*-**22** and **16** [see the preparation of pseudorubriflordinolactone B (**26**) (*vide supra*) for details]. **41:** $R_f = 0.15$ (silica, EtOAc:petroleum ether 1:1.5); $[\alpha]_D^{27} = +28.3$ ($c = 0.49$ in CHCl₃); IR (film): $\nu_{\max} = 3021, 2965, 2923, 2872, 1760, 1742, 1215, 1174, 1099, 1069, 1007, 930, 799, 754 \text{ cm}^{-1}$; ¹H NMR (400 MHz, pyridine-d₅): $\delta = 7.18\text{--}7.07$ (m, 3 H), 6.59 (d, $J = 10.8$ Hz, 1 H), 5.76 (d, $J = 11.3$ Hz, 1 H), 5.12–5.04 (m, 2 H), 4.43 (br s, 1 H), 3.67–3.61 (m, 1 H), 3.56 (dd, $J = 5.7, 1.5$ Hz, 1 H), 3.33–2.80 (m, 7 H), 2.60–2.47 (m, 1 H), 1.80 (s, 3 H), 1.35 (s, 3 H), 1.42–0.99 (m, 3 H), 1.24 (d, $J = 6.9$ Hz, 3 H) ppm; ¹³C NMR (126 MHz, pyridine-d₅): $\delta = 175.59, 174.62, 146.73, 143.42, 142.13, 133.19, 131.81, 130.74, 128.60, 103.59, 85.42, 83.32, 82.77, 82.69, 80.51, 60.38, 59.01, 43.74, 41.87, 40.21, 36.32, 28.73, 22.28, 15.44, 11.17$ ppm; HRMS (*m/z*): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2117.



(16S,17R,22R)-Rubriflordinolactone B (42): This compound was obtained as a white foam through a five-step sequence starting from compounds *ent*-**23** and **16** [see preparation of pseudorubriflordinolactone B (**26**) (*vide supra*) for details]. **42:** $[\alpha]_D^{27} = -175$ ($c = 0.43$ in CHCl₃); $R_f = 0.32$ (silica, EtOAc:petroleum ether 1:2); IR (film): $\nu_{\max} = 3015, 2968, 2923, 2875, 2852, 1760, 1655, 1465, 1438, 1215, 1171, 1087, 1060, 1007, 799, 757 \text{ cm}^{-1}$; ¹H NMR (400 MHz, pyridine-d₅): $\delta = 7.37\text{--}7.33$ (m, 1 H), 7.12 (d, $J = 7.7$ Hz, 1 H), 7.09 (d, $J = 7.7$ Hz, 1 H), 6.64 (d, $J = 12.2$ Hz, 1 H), 5.78 (d, $J = 10.4$ Hz, 1 H), 5.03–4.98 (m, 1 H), 4.92–4.86 (m, 1 H), 4.45 (br s, 1 H), 3.52 (d, $J = 5.5$ Hz, 1 H), 3.44–2.82 (m, 7 H), 2.89 (d, $J =$

18.5 Hz, 1 H), 2.73–2.63 (m, 1 H), 1.78 (dd, J = 1.6, 1.6 Hz, 3 H), 1.36 (s, 3 H), 1.43–1.00 (m, 3 H), 1.22 (d, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, pyridine-d₅): δ = 175.65, 174.30, 143.16, 142.07, 133.18, 130.89, 130.19, 128.66, 128.45, 103.55, 85.38, 82.95, 82.87, 80.62, 79.72, 60.40, 58.89, 43.30, 41.87, 40.23, 36.36, 28.70, 22.27, 15.46, 11.09 ppm; HRMS (m/z): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2112.



(16S,17R,23R)-Rubriflordilactone B (43): This compound was obtained as a white foam through a five-step sequence starting from compounds *ent*-**24** and **16** [see preparation of pseudorubriflordilactone B (**26**) (*vide supra*) for details]. **43:** $[\alpha]_D^{27} = +5.8$ ($c = 0.56$ in CHCl₃); $R_f = 0.37$ (silica gel, EtOAc:petroleum ether 2:3); IR (film): $\nu_{\text{max}} = 3015, 2965, 2923, 2852, 1763, 1263, 1215, 1168, 1090, 1063, 1007, 799, 754 \text{ cm}^{-1}$; ^1H NMR (400 MHz, pyridine-d₅): δ = 7.20–7.12 (m, 2 H), 7.07 (s, 1 H), 6.62 (d, J = 12.0 Hz, 1 H), 5.80 (br s, 1 H), 4.90 (dd, J = 5.3, 5.3 Hz, 1 H), 4.53 (br s, 1 H), 4.44 (br s, 1 H), 3.54 (dd, J = 5.9, 5.9 Hz, 1 H), 3.44–2.79 (m, 7 H), 2.88 (d, J = 18.4 Hz, 1 H), 2.52 (br s, 1 H), 1.76 (s, 3 H), 1.37 (s, 3 H), 1.49–0.97 (m, 3 H), 1.21 (d, J = 6.9 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, pyridine-d₅): δ = 175.60, 174.39, 148.44, 144.79, 140.92, 134.73, 133.33, 130.96, 130.56, 128.67, 103.43, 88.19, 85.44, 84.13, 82.82, 80.69, 60.50, 58.90, 44.74, 41.94, 38.92, 36.36, 28.74, 22.36, 19.90, 11.04 ppm; HRMS (m/z): [M + H]⁺ calcd for C₂₈H₃₁O₆⁺ 463.2115, found 463.2108.

II Anti-HIV Activity of Synthetic 26

The anti-HIV assay: The pseudotyped single-cycle infectious HIV-Luc/JRFL was produced by calcium phosphate-mediated co-transfection of HEK293T cells with pLAI-ΔEnv-Luc and an expression plasmid of JRFL envelope protein.^{5,6} The CD4⁺ T-lymphocyte cell line Hut/CCR5 (1.0×10^5) was infected by HIV-luc/JRFL (1.0 ng p24^{gag}) for 48 h, with the compound in the indicated concentration or without the compound. The anti-HIV drug azidothymidine (AZT; 50 ng/mL) served as a control. A commercially available kit from Promega was used to analyze the viral infection by measuring luciferase activity in the cell lysate, and the inhibition of viral infection was calculated. The Hut/CCR5 cells were maintained in RPMI medium 1640 supplemented with fetal bovine serum (10%), penicillin (100 U/mL), and streptomycin (100 µg/mL).

The cytotoxicity assay: Cytotoxicity of the compound against Hut/CCR5 cells was tested by MTT colorimetric assay.⁷ 100 µL of cells (1.0×10^5) were seeded onto a microtiter plate, and the compound in an certain concentration was added. The cells were incubated at 37 °C in a humidified atmosphere of 5% CO₂ for 48 h. Cytotoxicity of the compound was measured by using a standard protocol.⁷

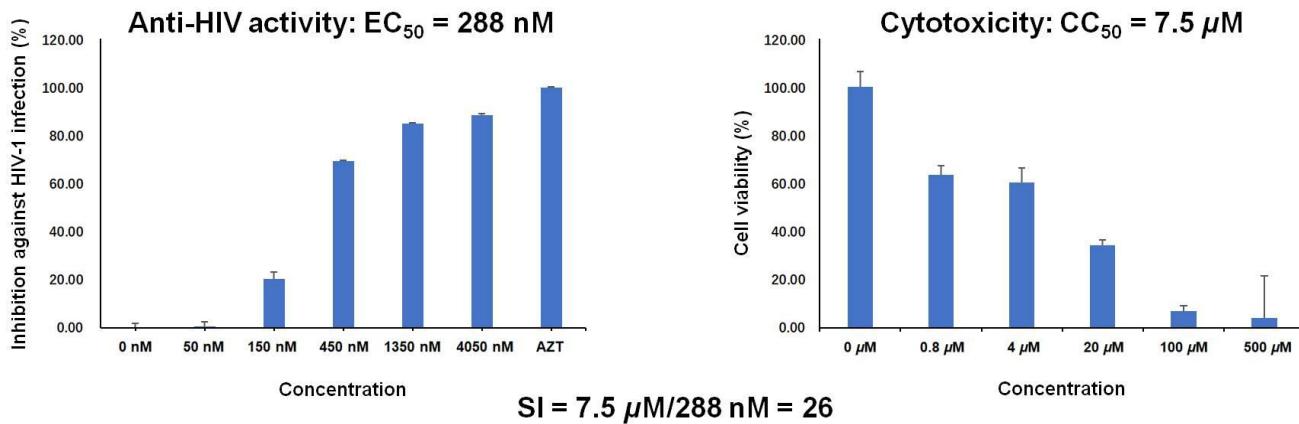
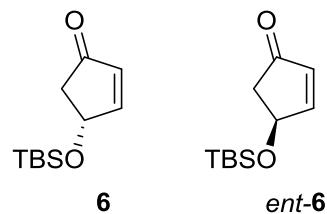
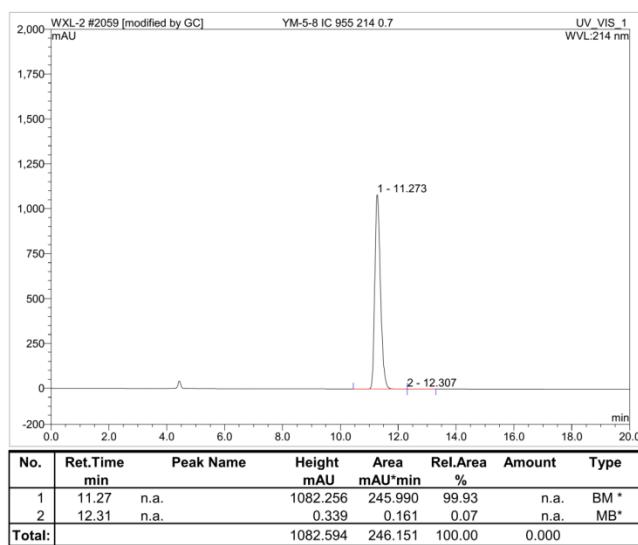
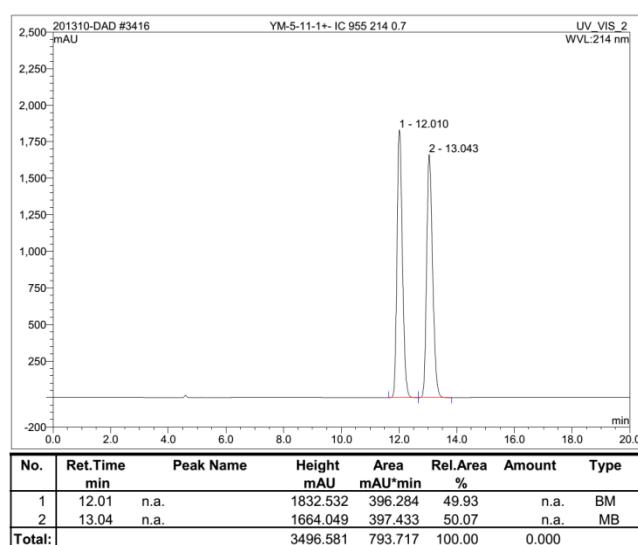


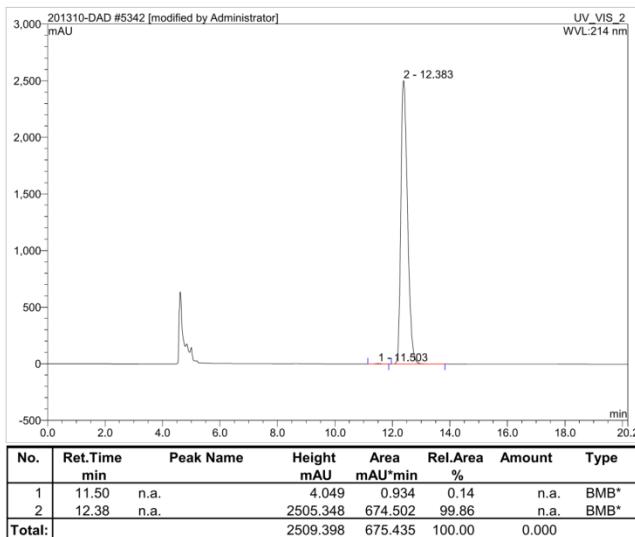
Figure S1. Anti-HIV activity and cytotoxicity of **26**. The selectivity index (SI) was 26.

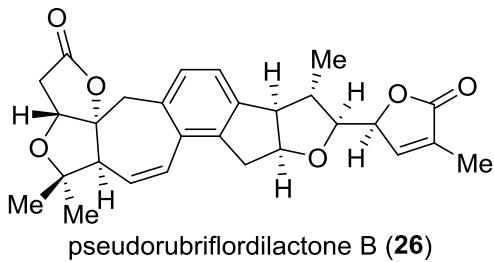
III HPLC Traces for Separating Enantiomers/Measuring Enantiomeric Excess



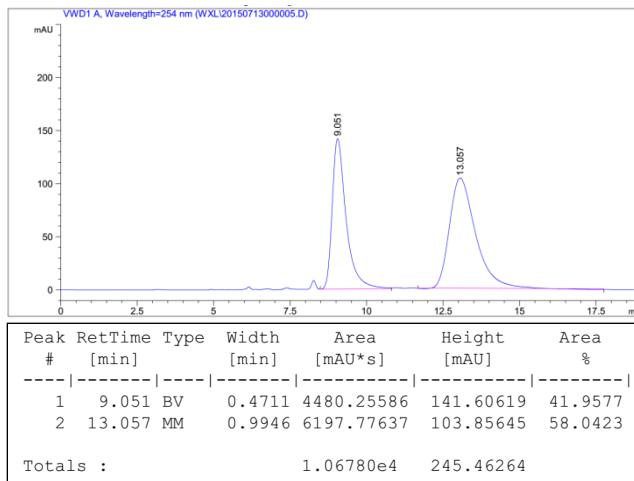
A sample of (\pm) -**6** was prepared through silylation of (\pm) -4-hydroxy-2-cyclopentenone.⁸ Enantioenriched **6**¹ and *ent*-**6**¹ were analyzed by HPLC (Lux Amylose-2 column, *i*-PrOH:hexane = 20:80, 0.70 mL/min) to determine the enantiomeric excesses. **6**: ee = 99.8%. *ent*-**6**: ee = 99.7%.

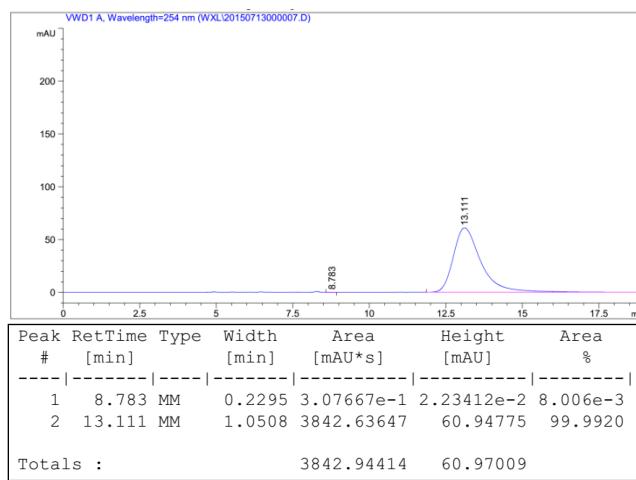
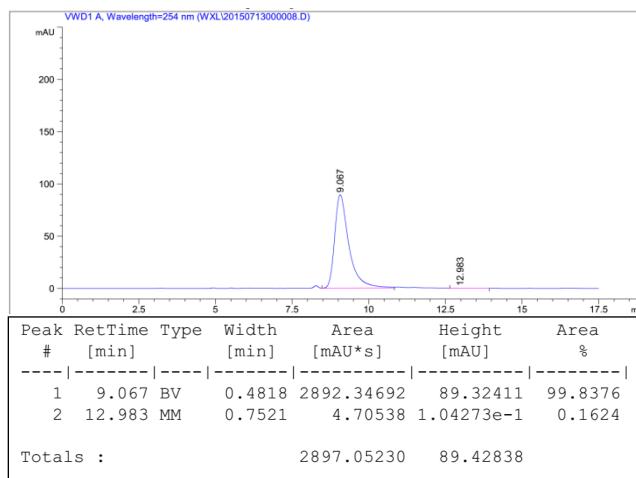






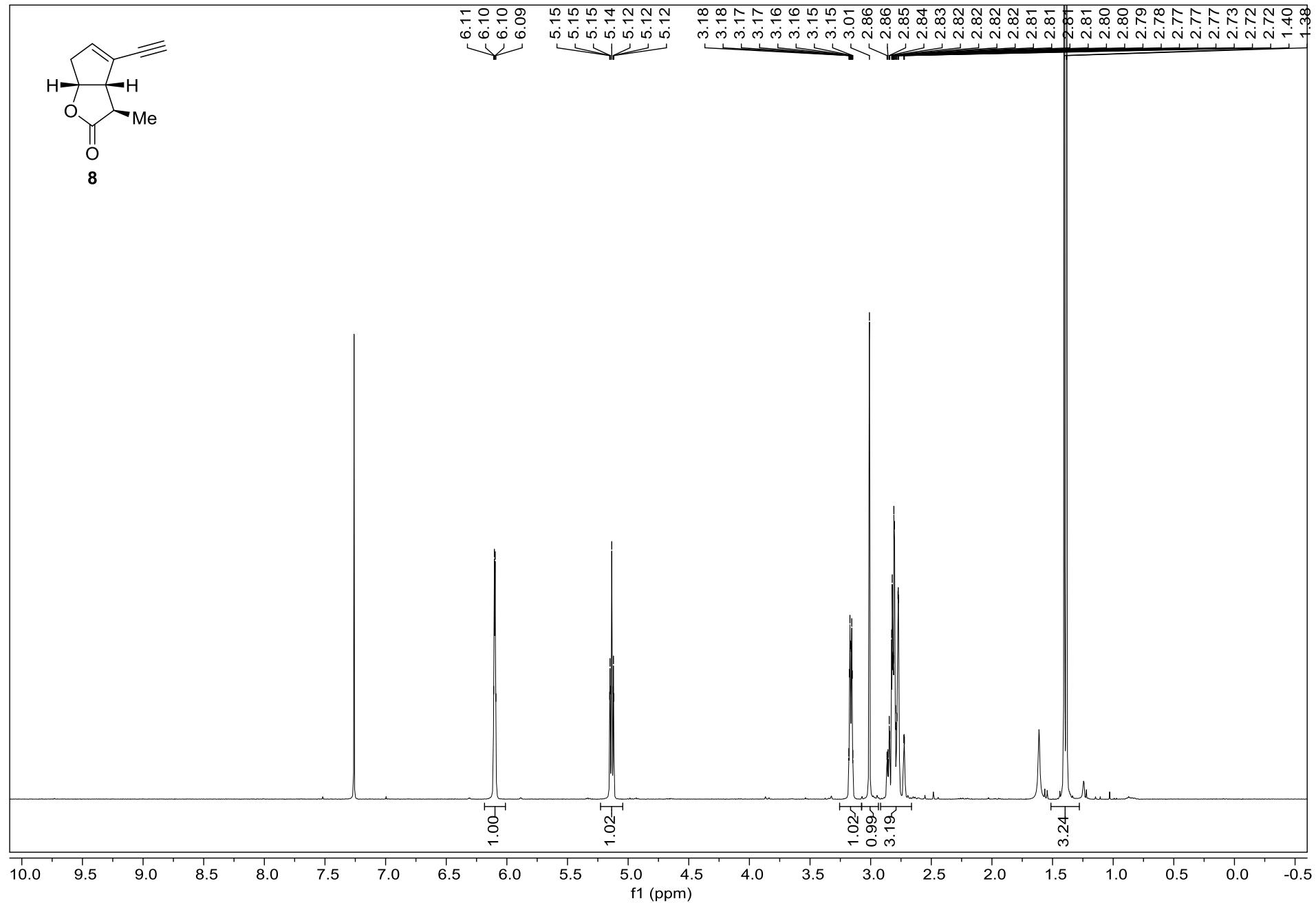
A sample of approximately racemic **26** was obtained by mixing **26** and *ent*-**26** in a ca. 1:1 ratio. This sample and the samples of enantioenriched **26** and *ent*-**26** were analyzed by HPLC (Lux 5u Cellulose-2 column, water:MeOH = 10:90, 0.70 mL/min) to determine the retention times. **26**: t_R = 9.067 min. *ent*-**26**: t_R = 13.111 min. The purpose of this experiment is not to measure the enantiomeric excess of **26** or that of *ent*-**26** but to determine the absolute configuration of naturally occurring pseudorubriflordilactone B, if it could be reisolated from nature in the future. Because both synthetic enantiomers are available as references, the HPLC retention time of the natural product could be used as a reliable descriptor of the absolute configuration, especially on a very small scale.



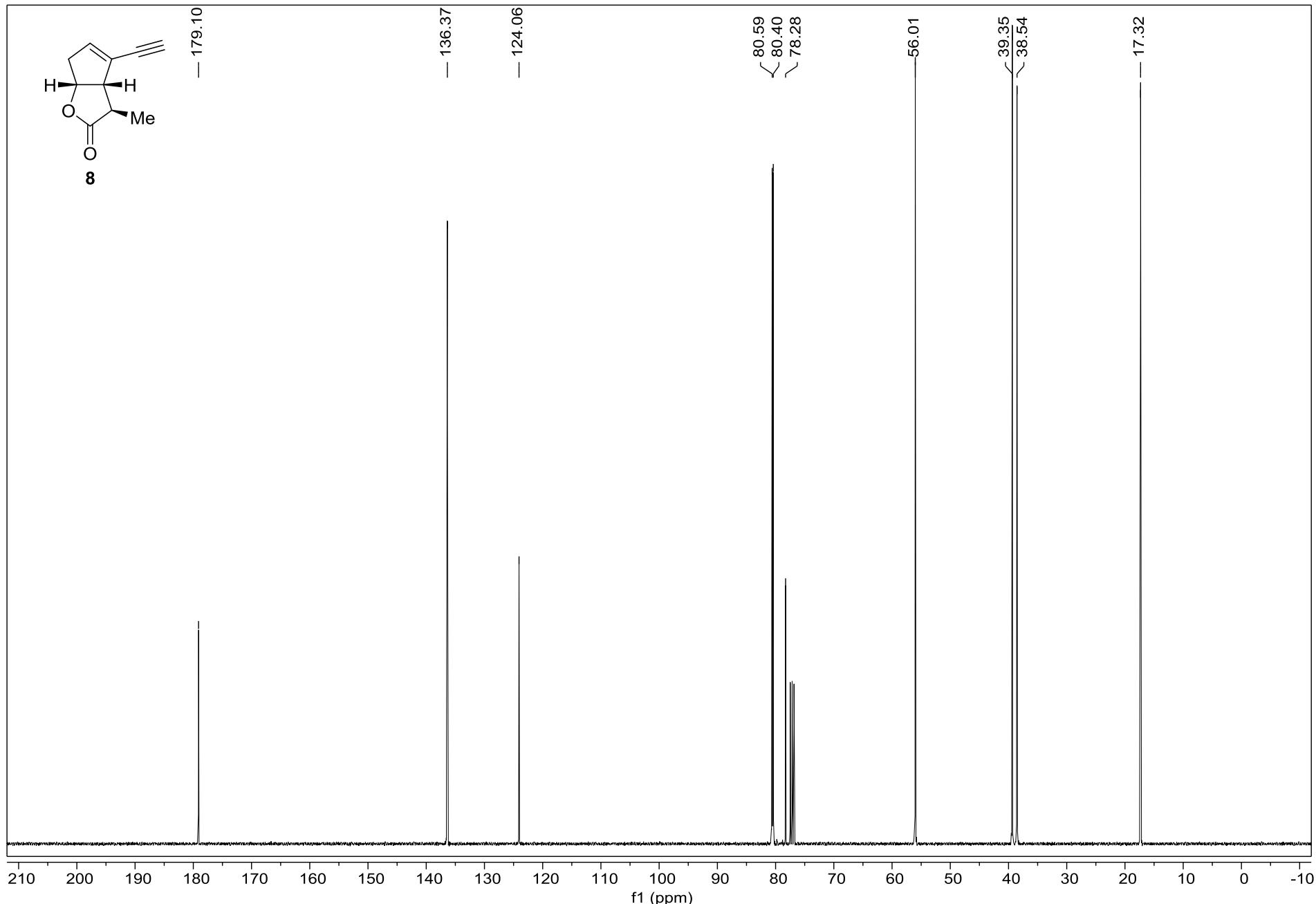


IV NMR Spectra of Compounds

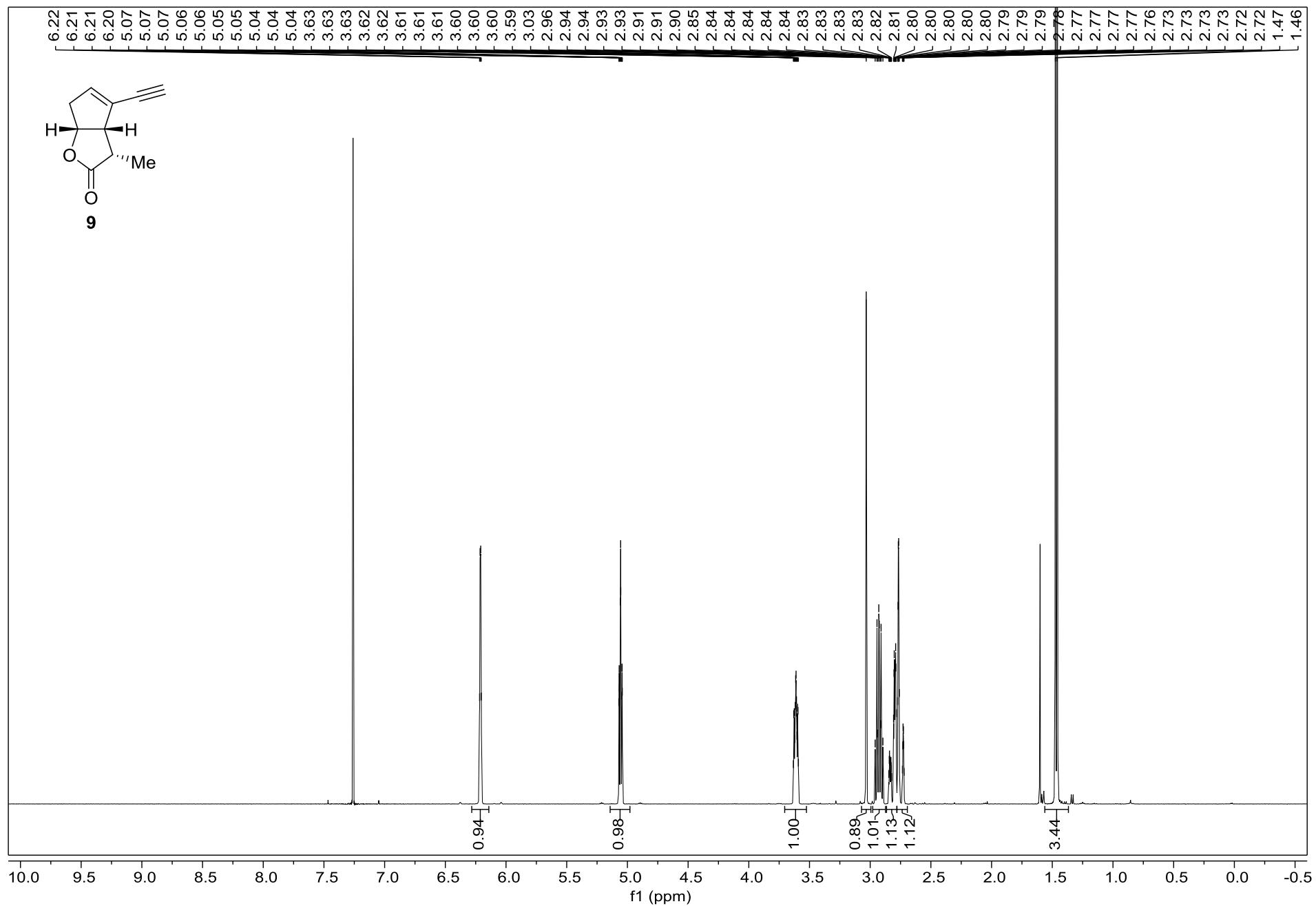
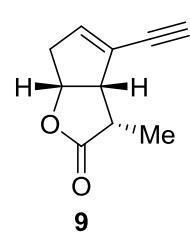
¹H NMR Spectrum of 8 (400 MHz, CDCl₃)



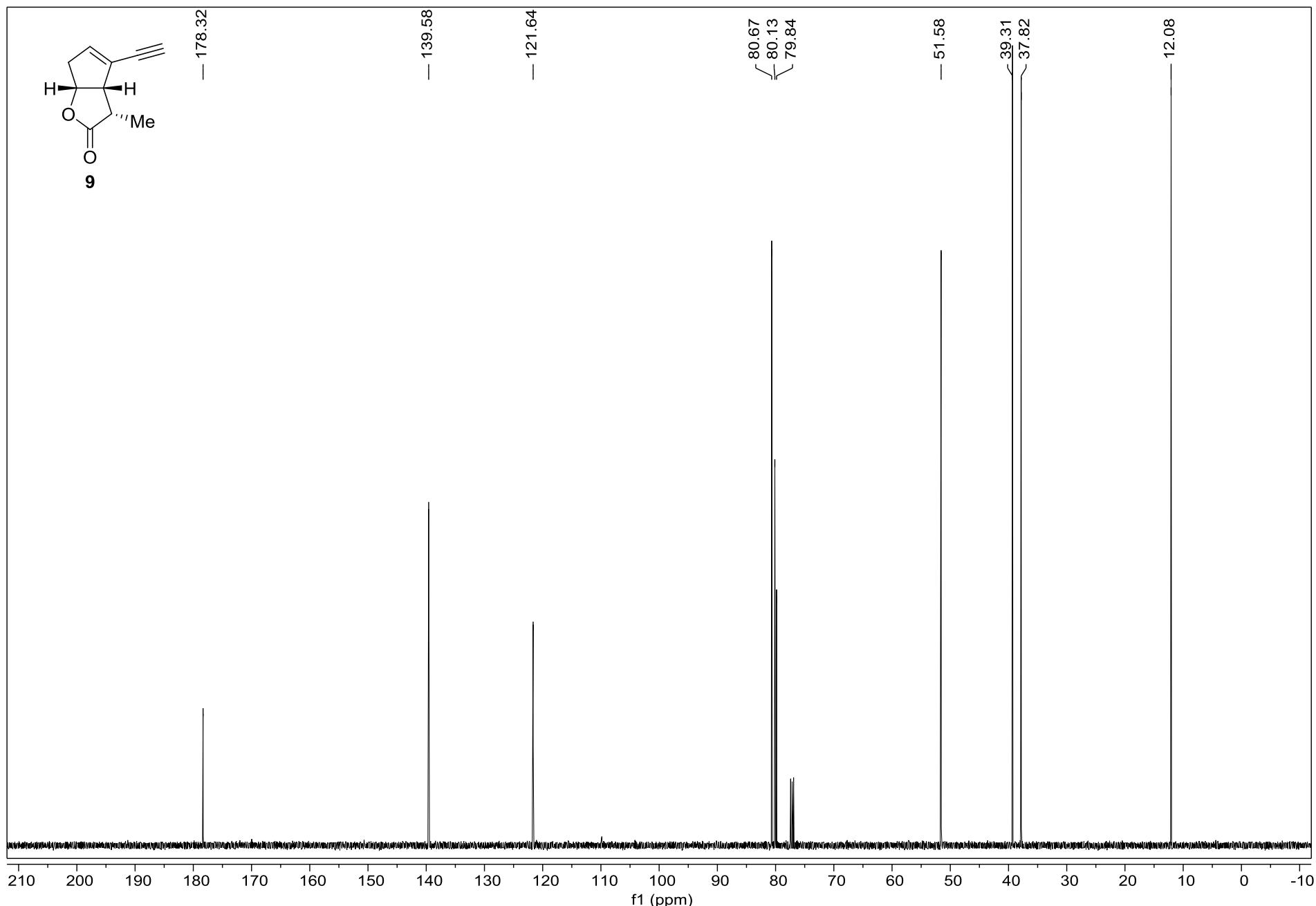
¹³C NMR Spectrum of 8 (101 MHz, CDCl₃)



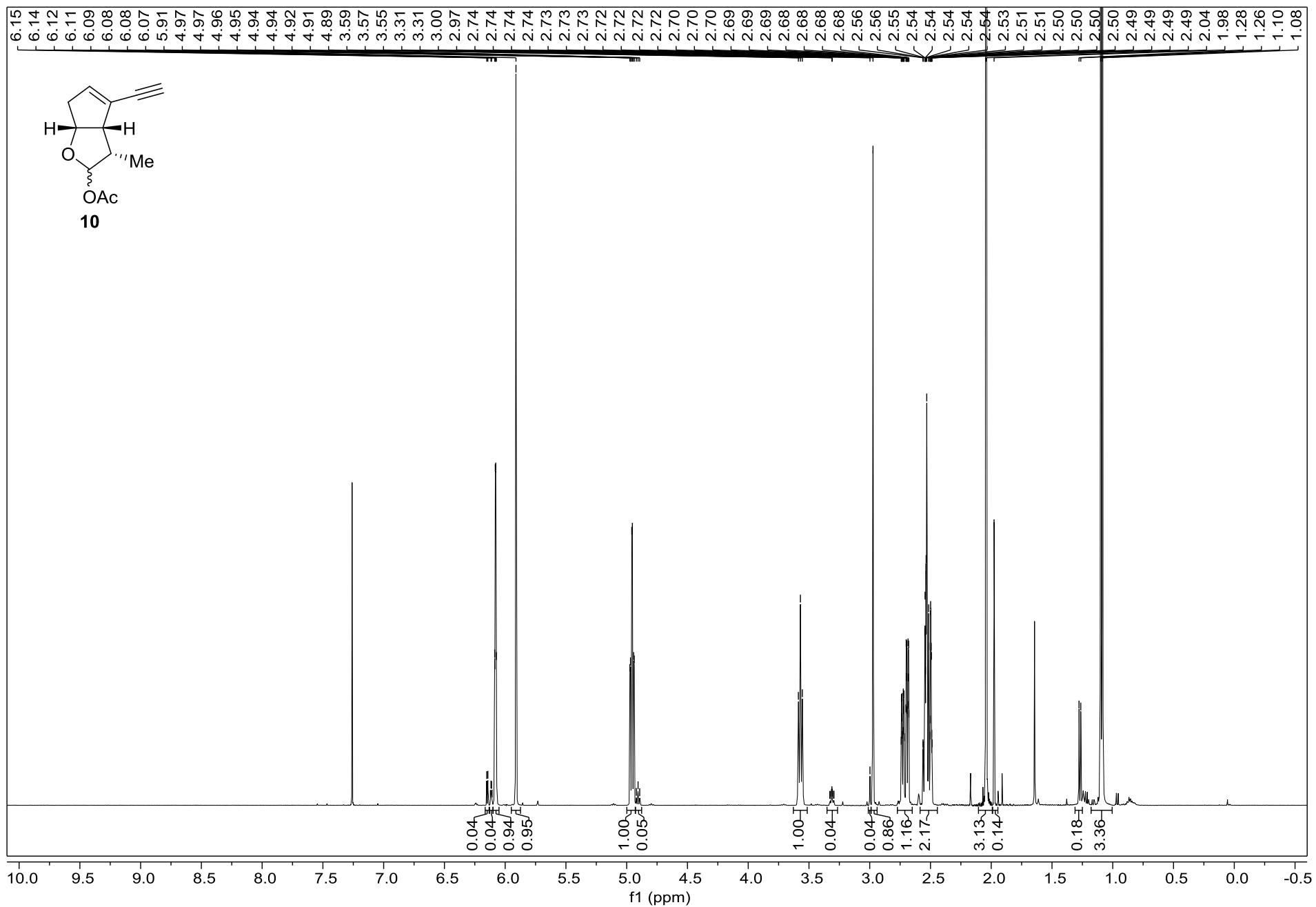
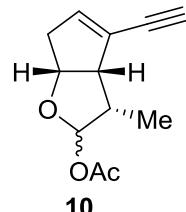
¹H NMR Spectrum of 9 (500 MHz, CDCl₃)



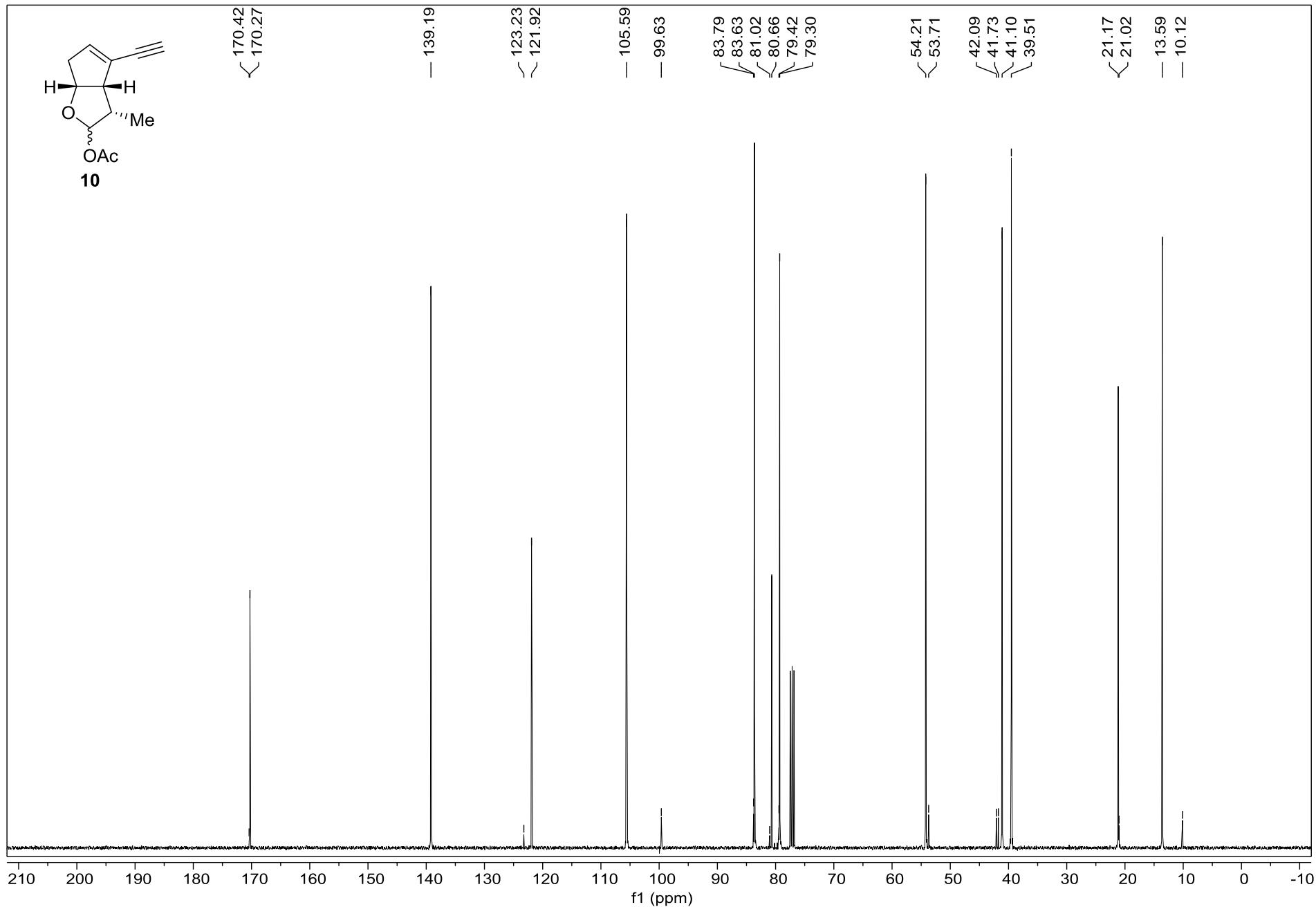
¹³C NMR Spectrum of **9** (126 MHz, CDCl₃)



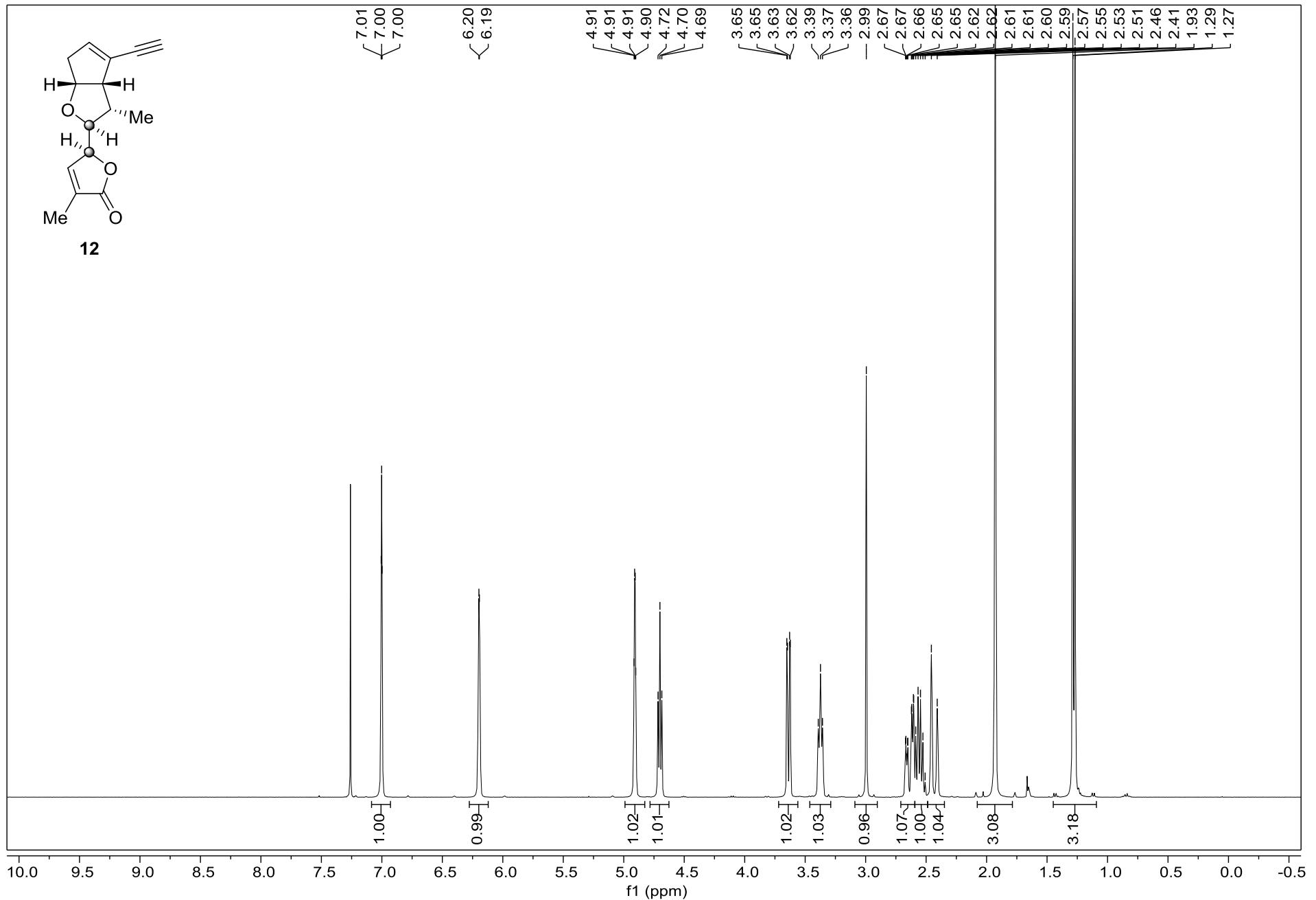
¹H NMR Spectrum of 10 (500 MHz, CDCl₃)



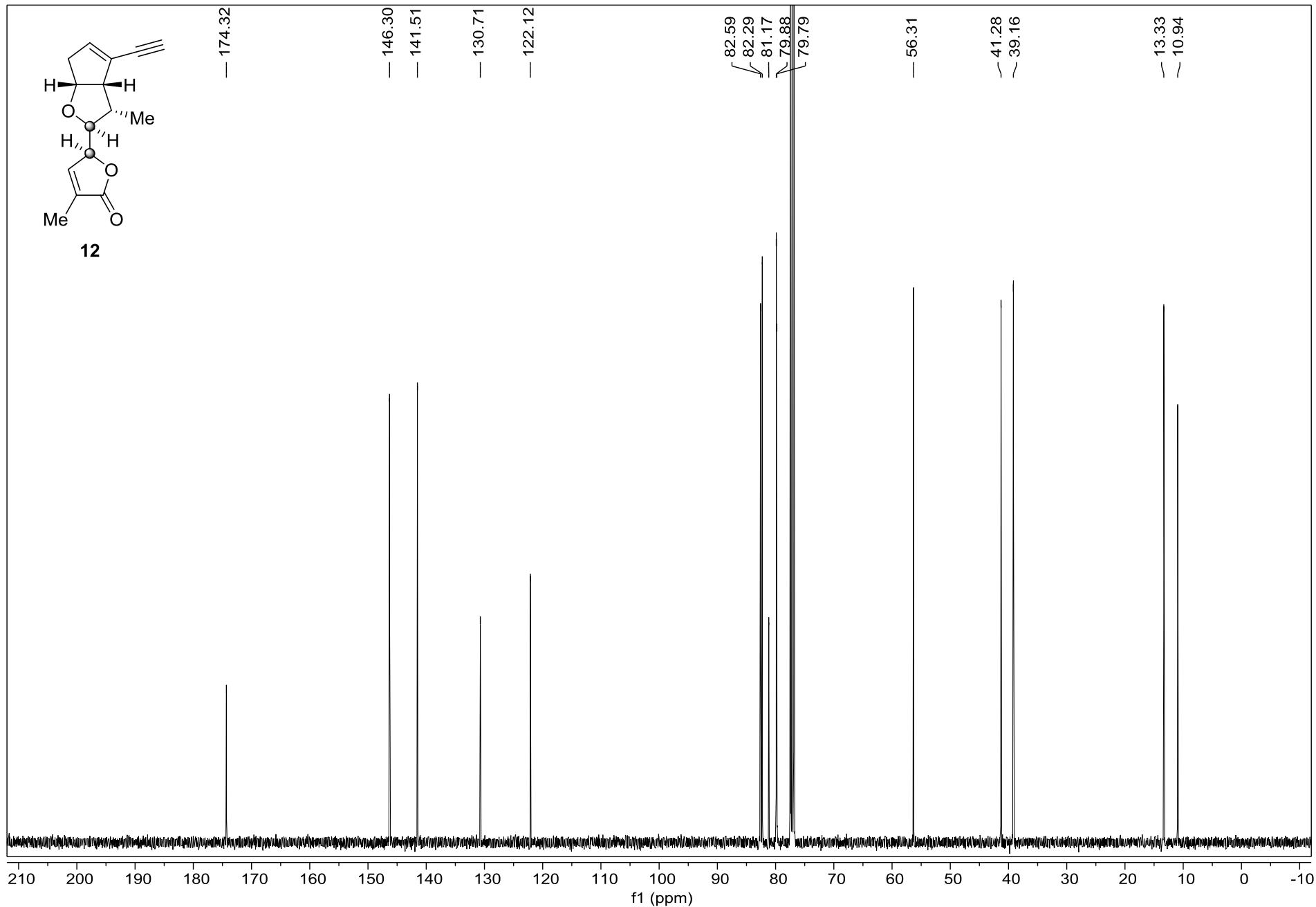
¹³C NMR Spectrum of **10** (101 MHz, CDCl₃)



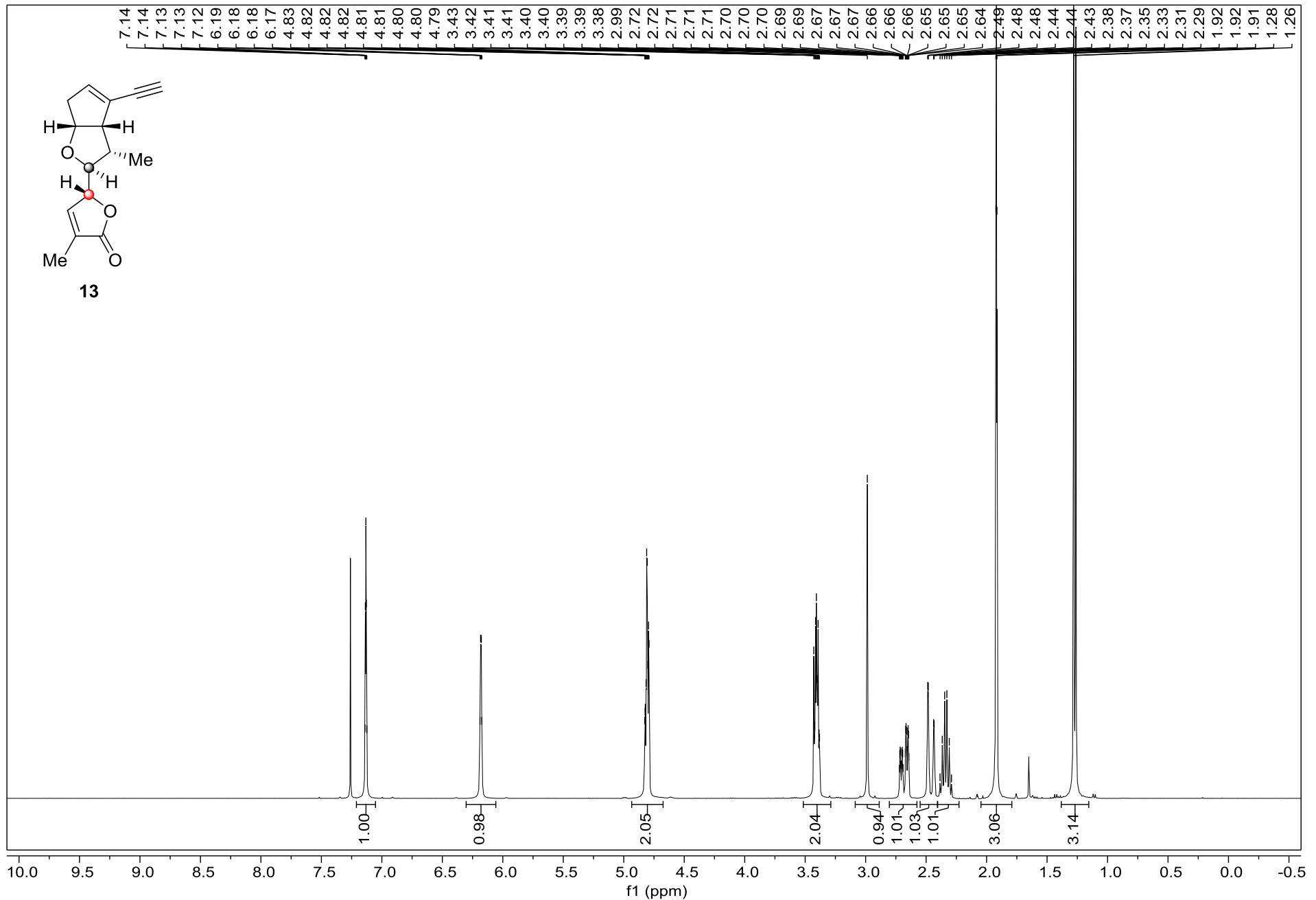
¹H NMR Spectrum of 12 (400 MHz, CDCl₃)



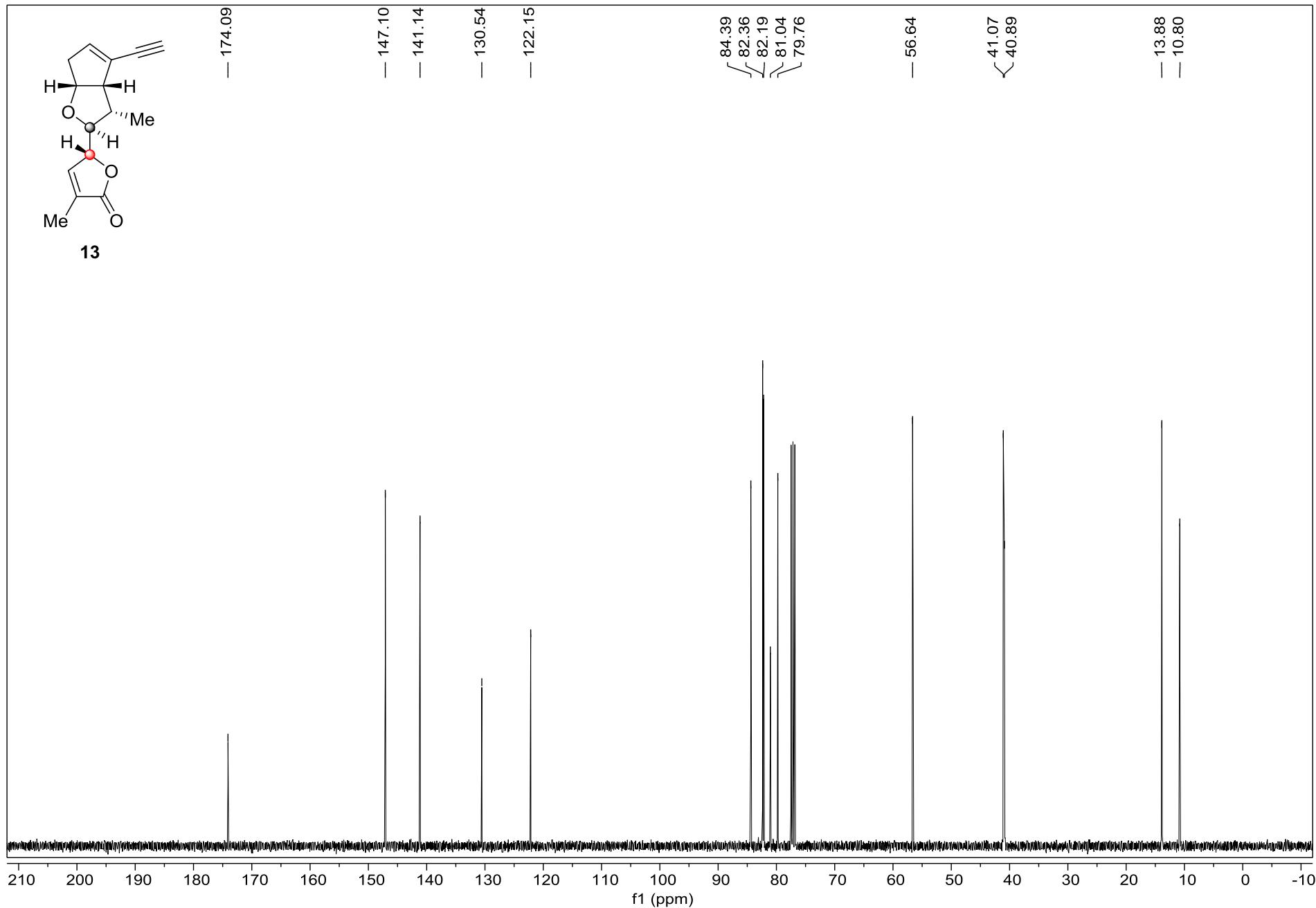
¹³C NMR Spectrum of 12 (101 MHz, CDCl₃)



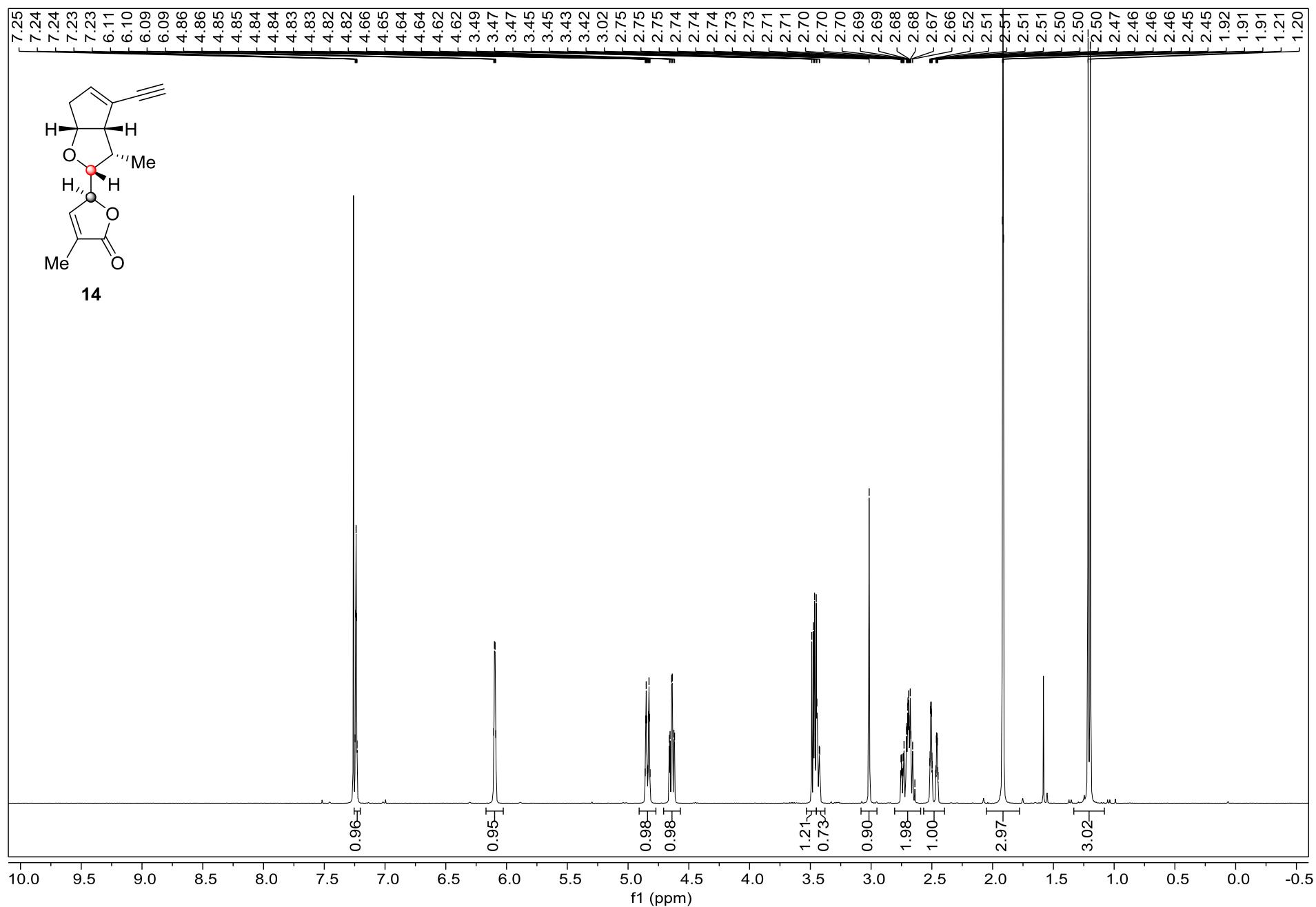
¹H NMR Spectrum of 13 (400 MHz, CDCl₃)



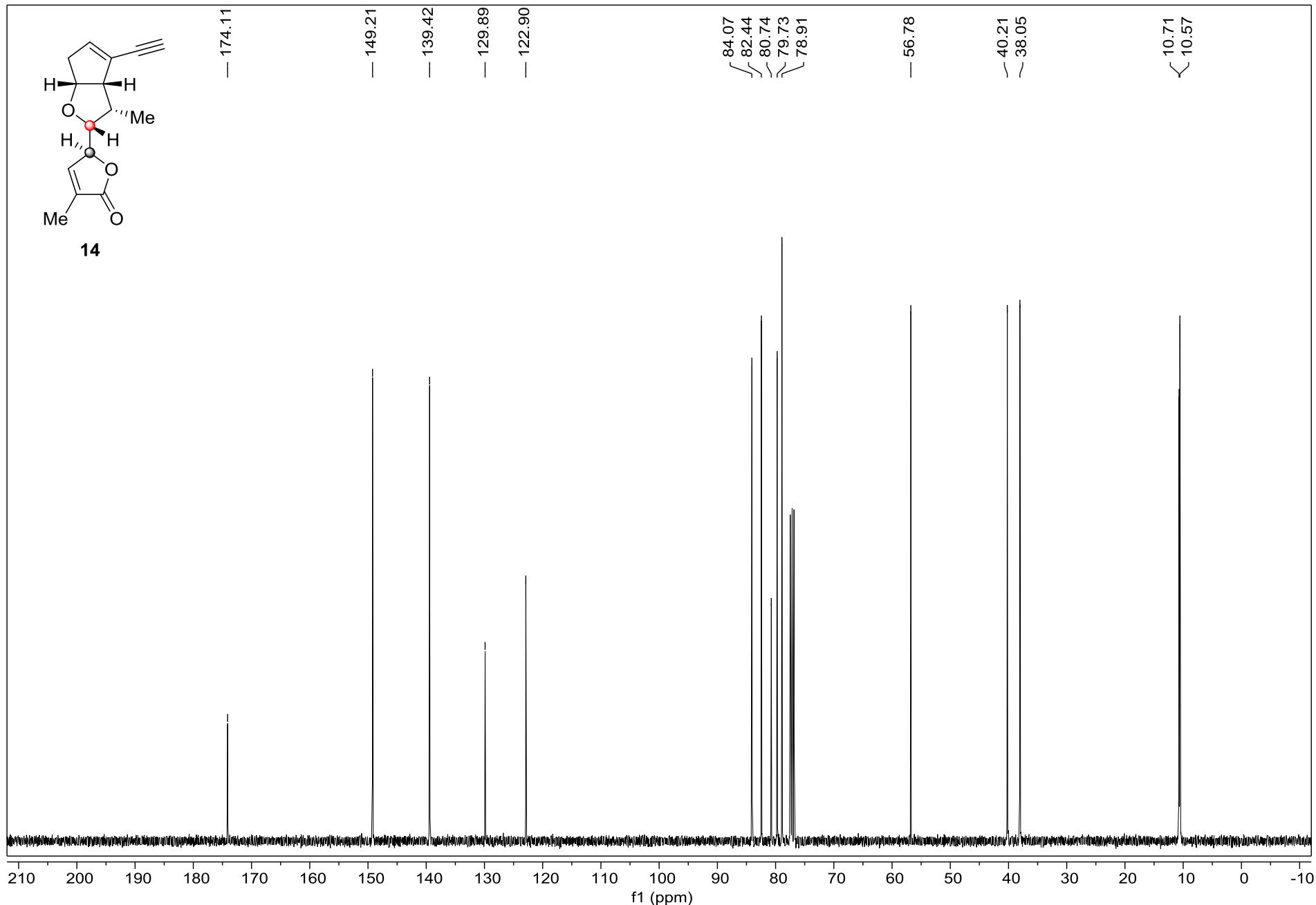
¹³C NMR Spectrum of 13 (101 MHz, CDCl₃)



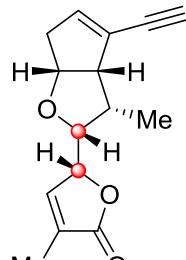
¹H NMR Spectrum of 14 (400 MHz, CDCl₃)



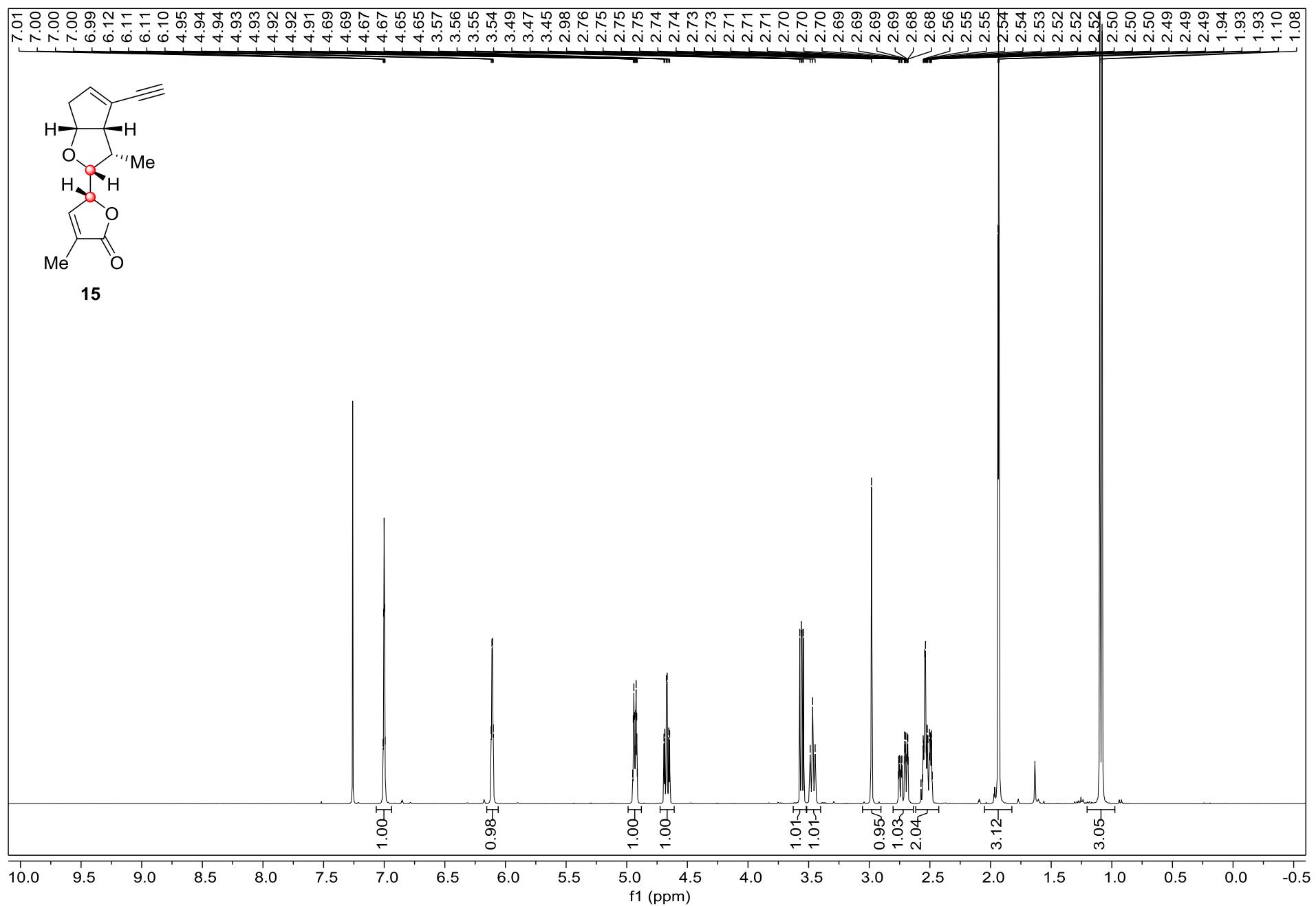
¹³C NMR Spectrum of 14 (101 MHz, CDCl₃)



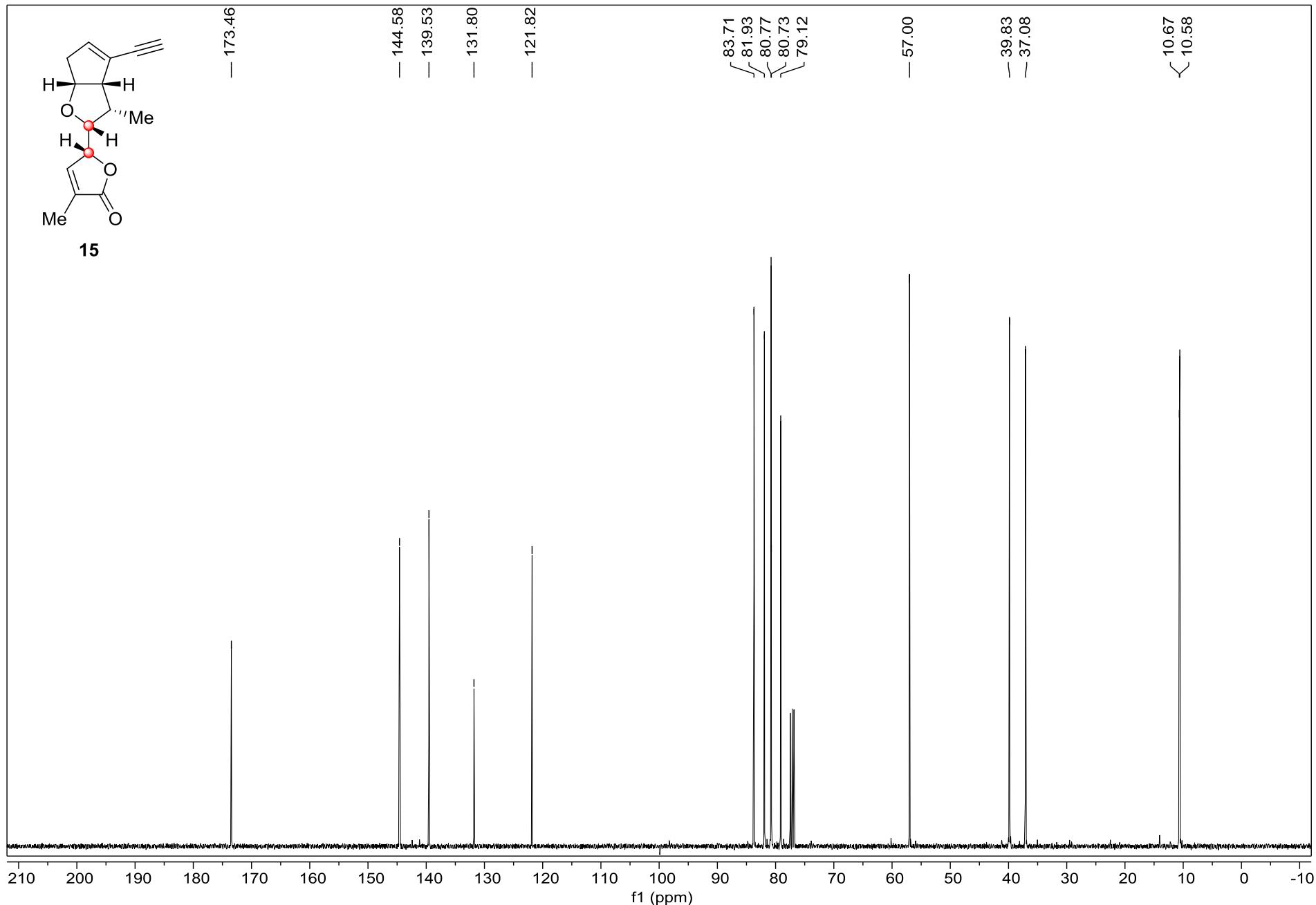
¹H NMR Spectrum of 15 (400 MHz, CDCl₃)



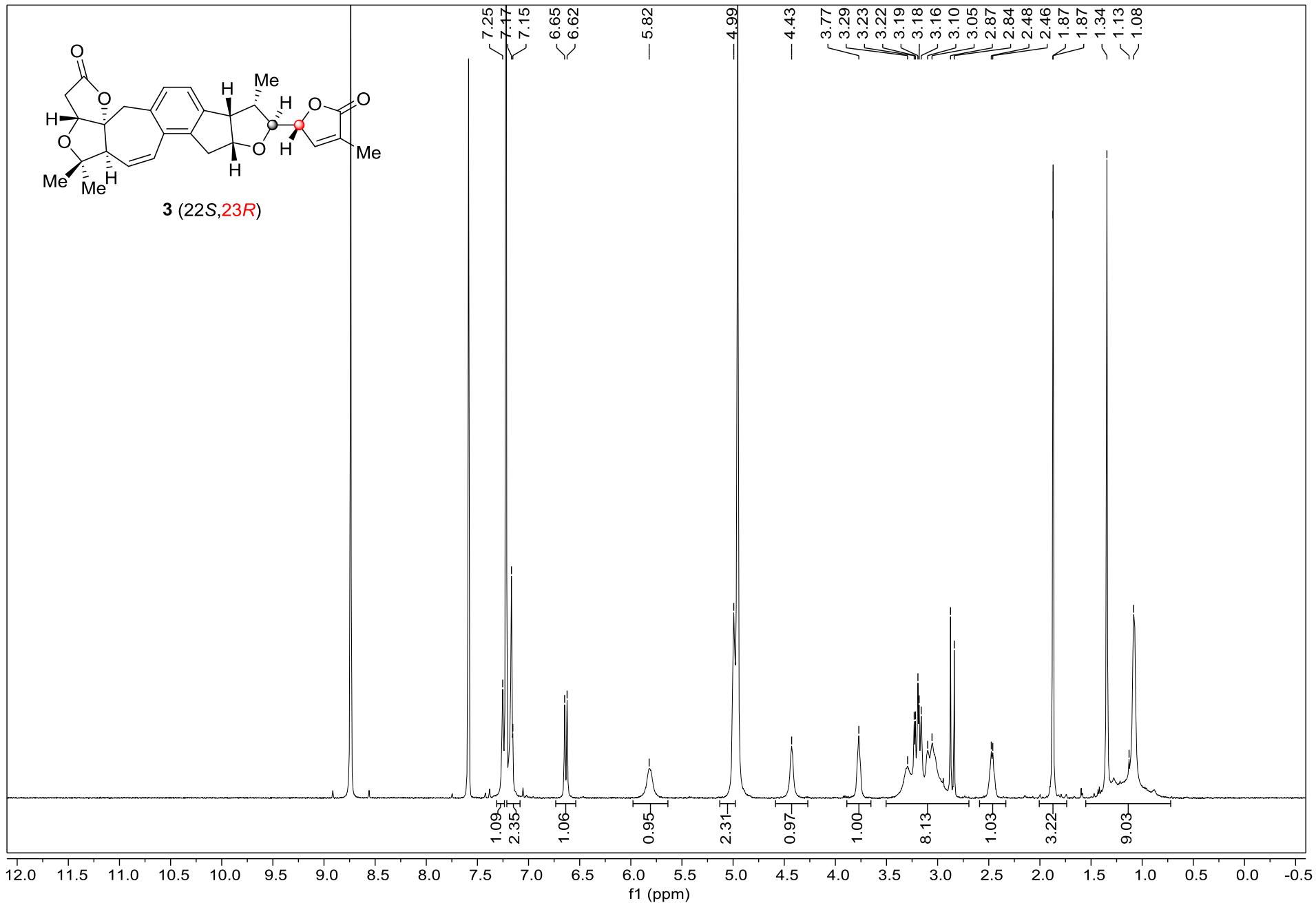
15



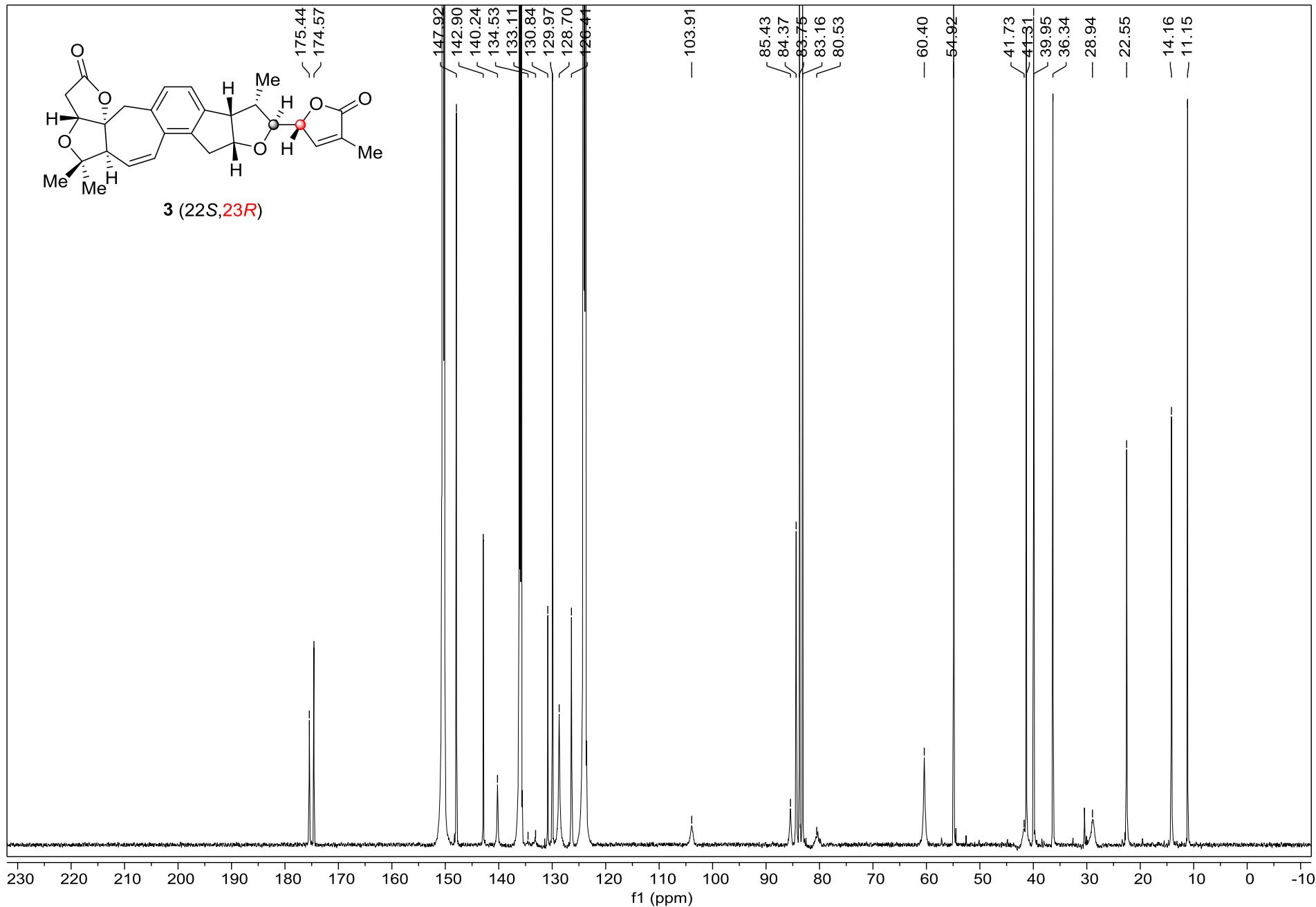
¹³C NMR Spectrum of 15 (101 MHz, CDCl₃)



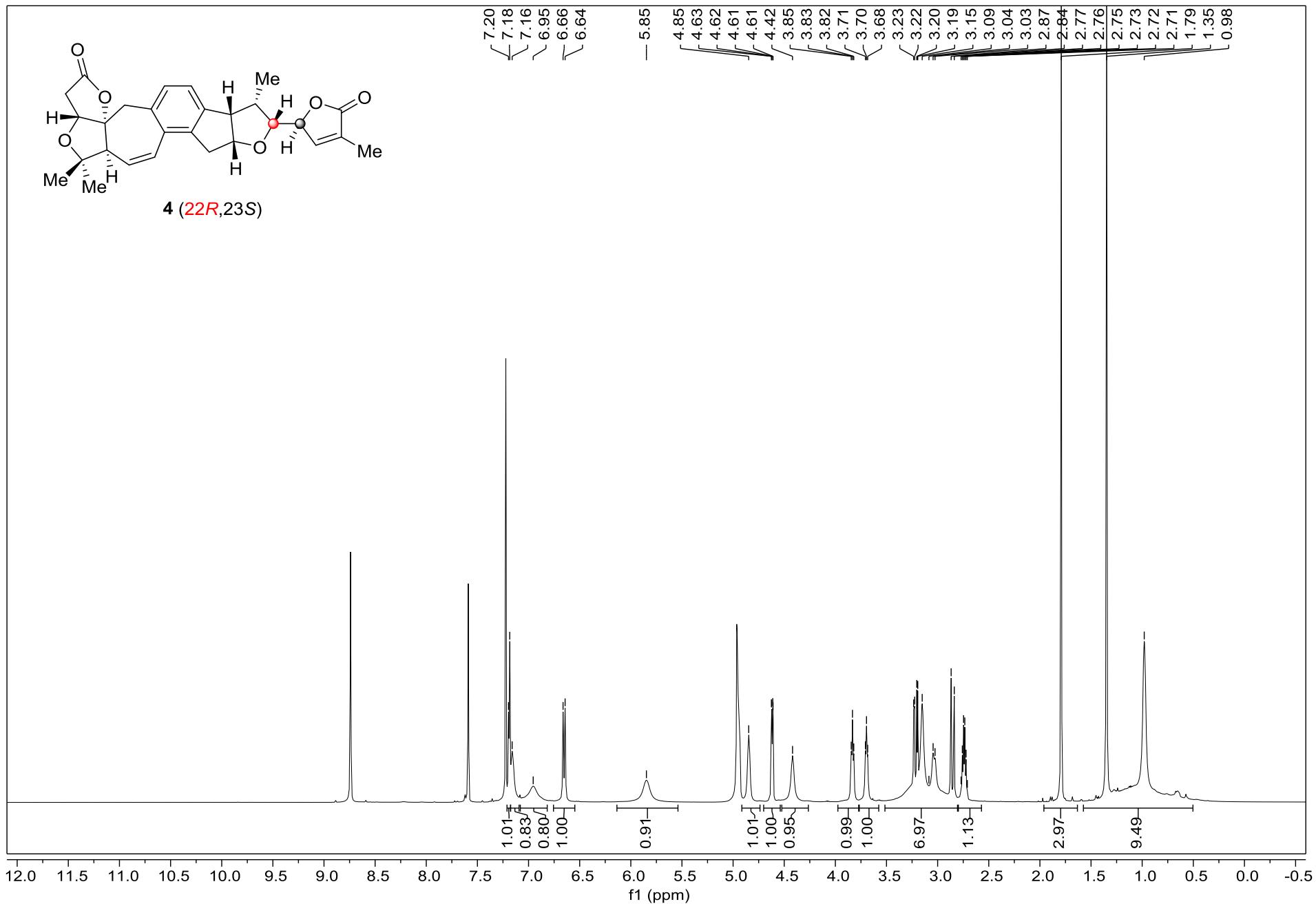
¹H NMR Spectrum of 3 (500 MHz, pyridine-d₅)



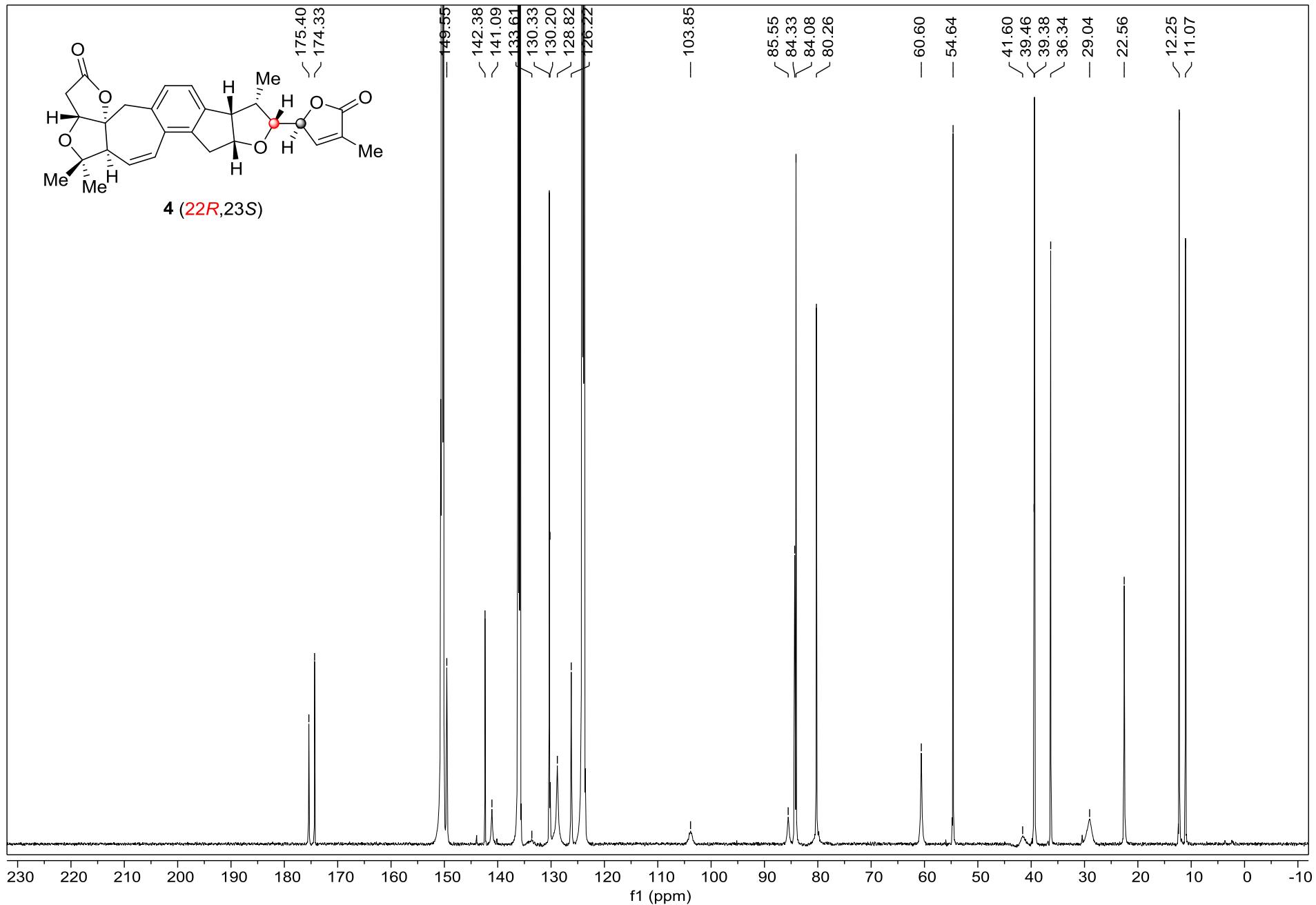
¹³C NMR Spectrum of 3 (151 MHz, pyridine-d₅)



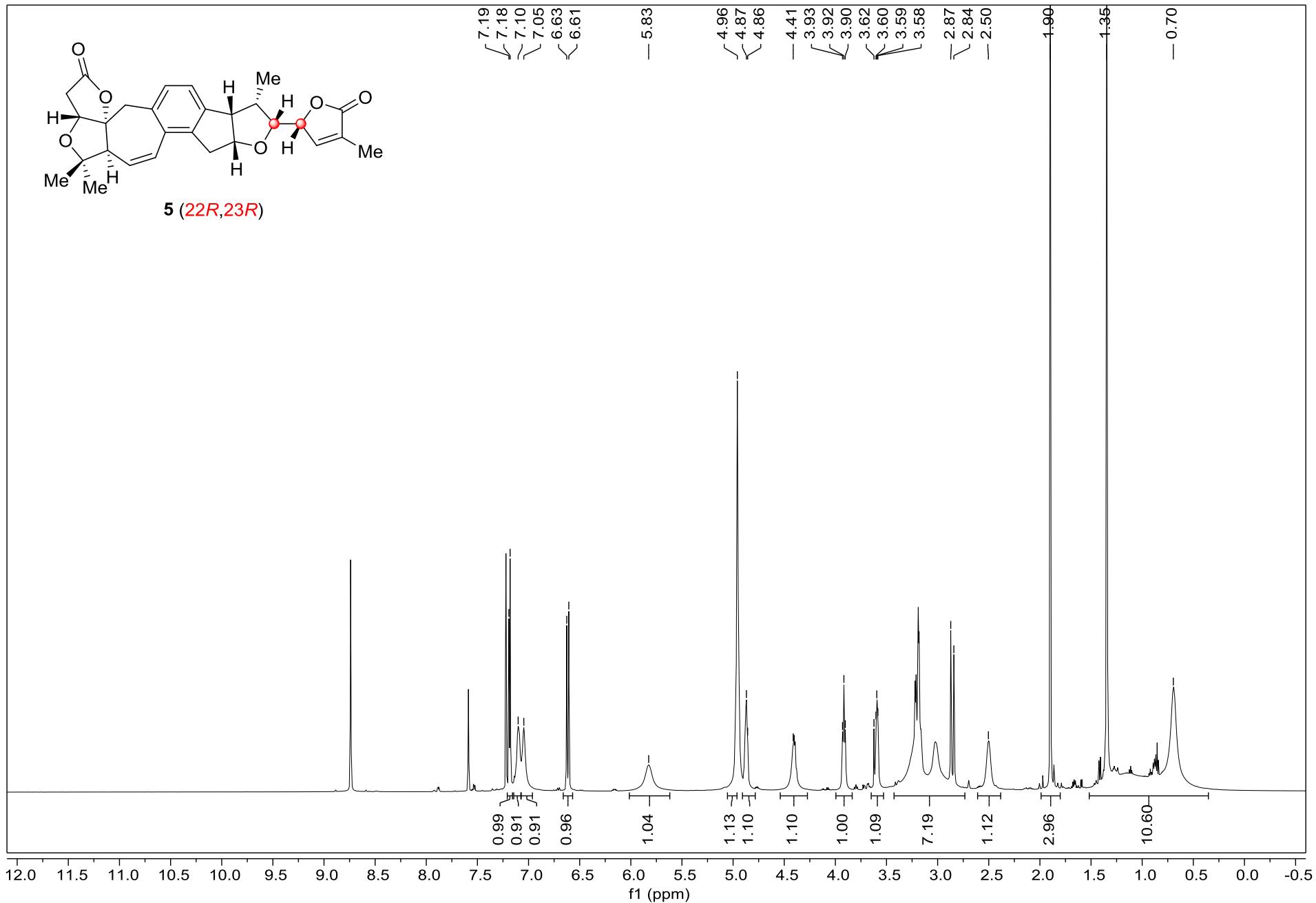
¹H NMR Spectrum of 4 (600 MHz, pyridine-d₅)



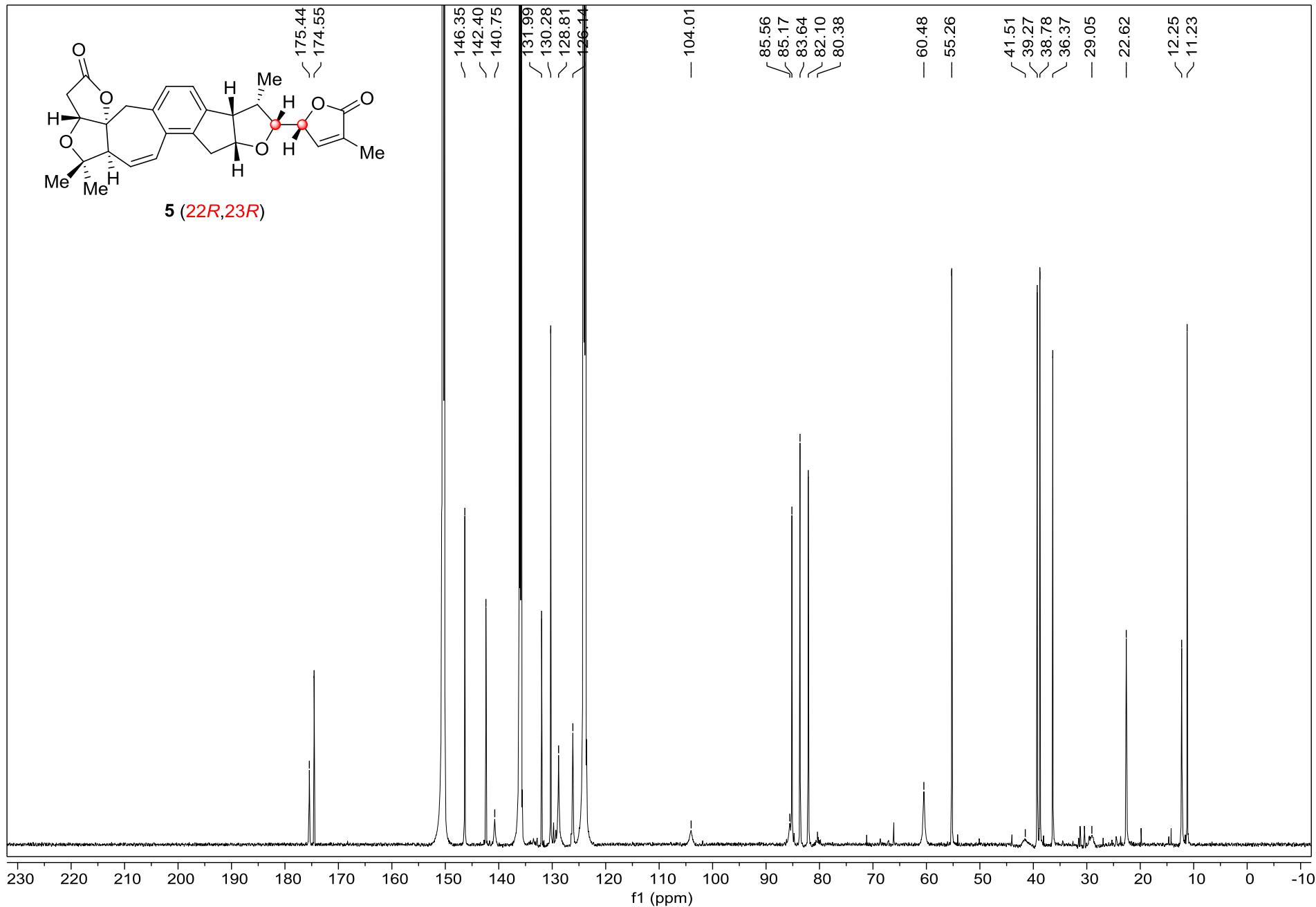
¹³C NMR Spectrum of 4 (151 MHz, pyridine-d₅)



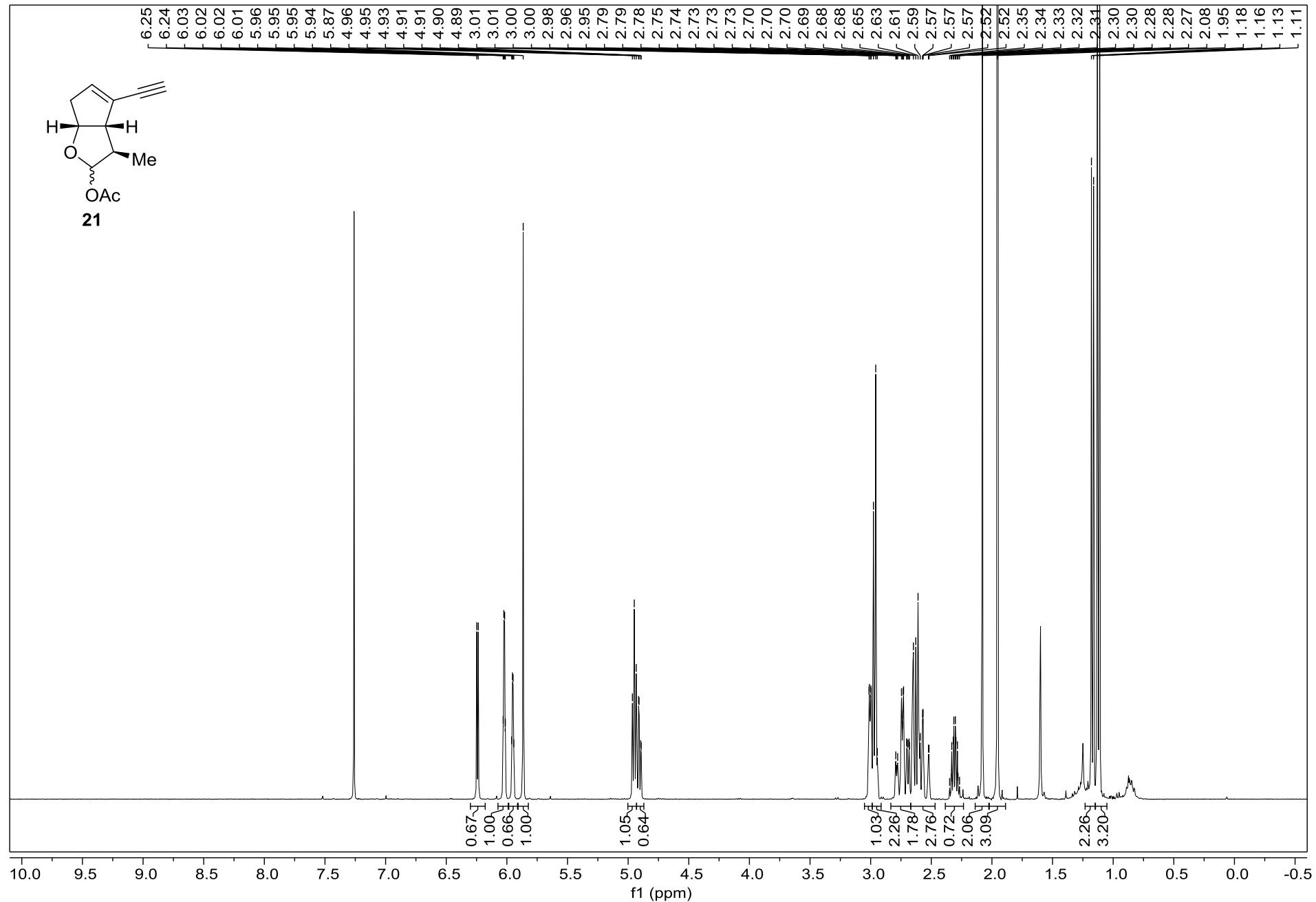
¹H NMR Spectrum of 5 (600 MHz, pyridine-d₅)



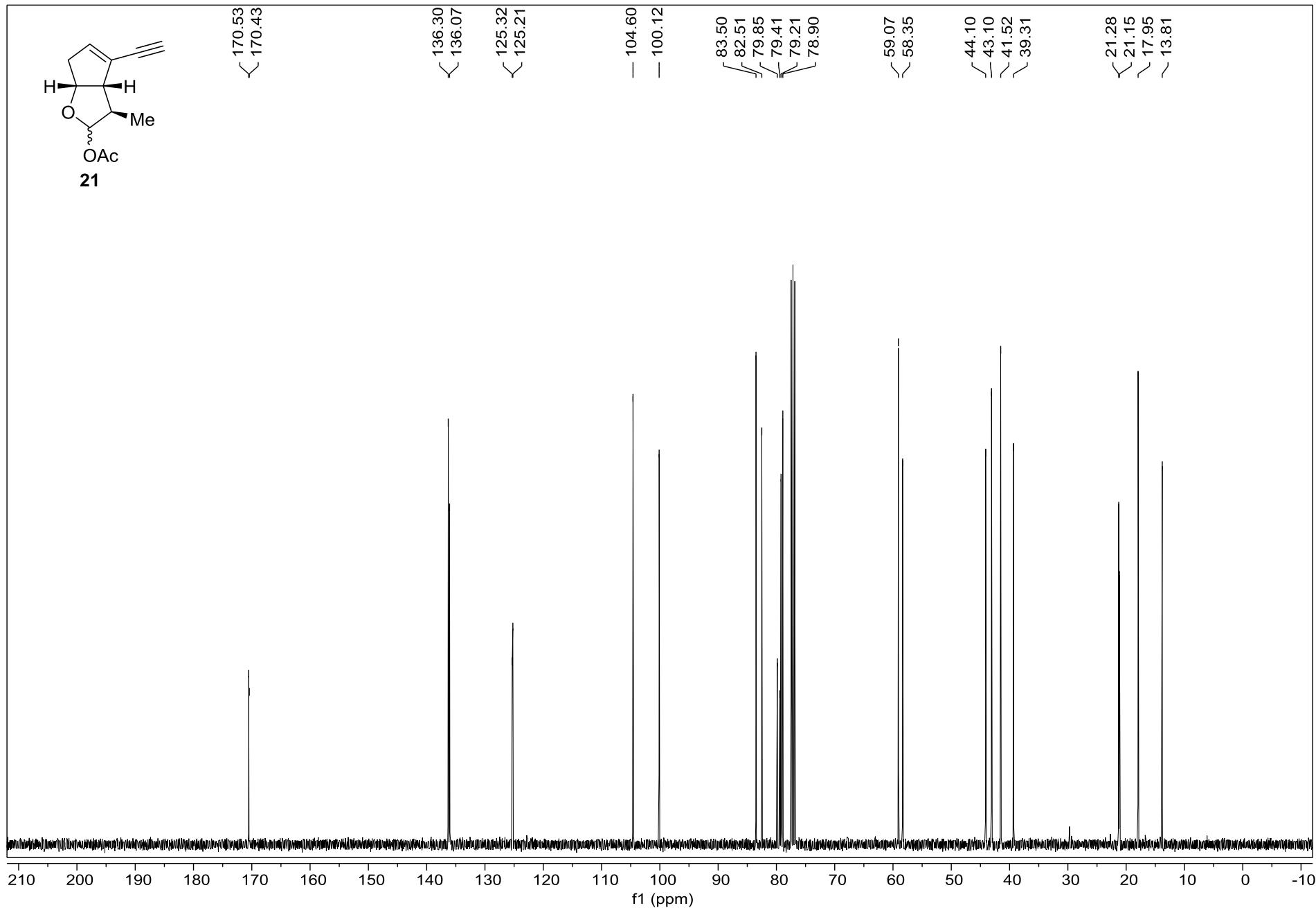
¹³C NMR Spectrum of 5 (151 MHz, pyridine-d₅)



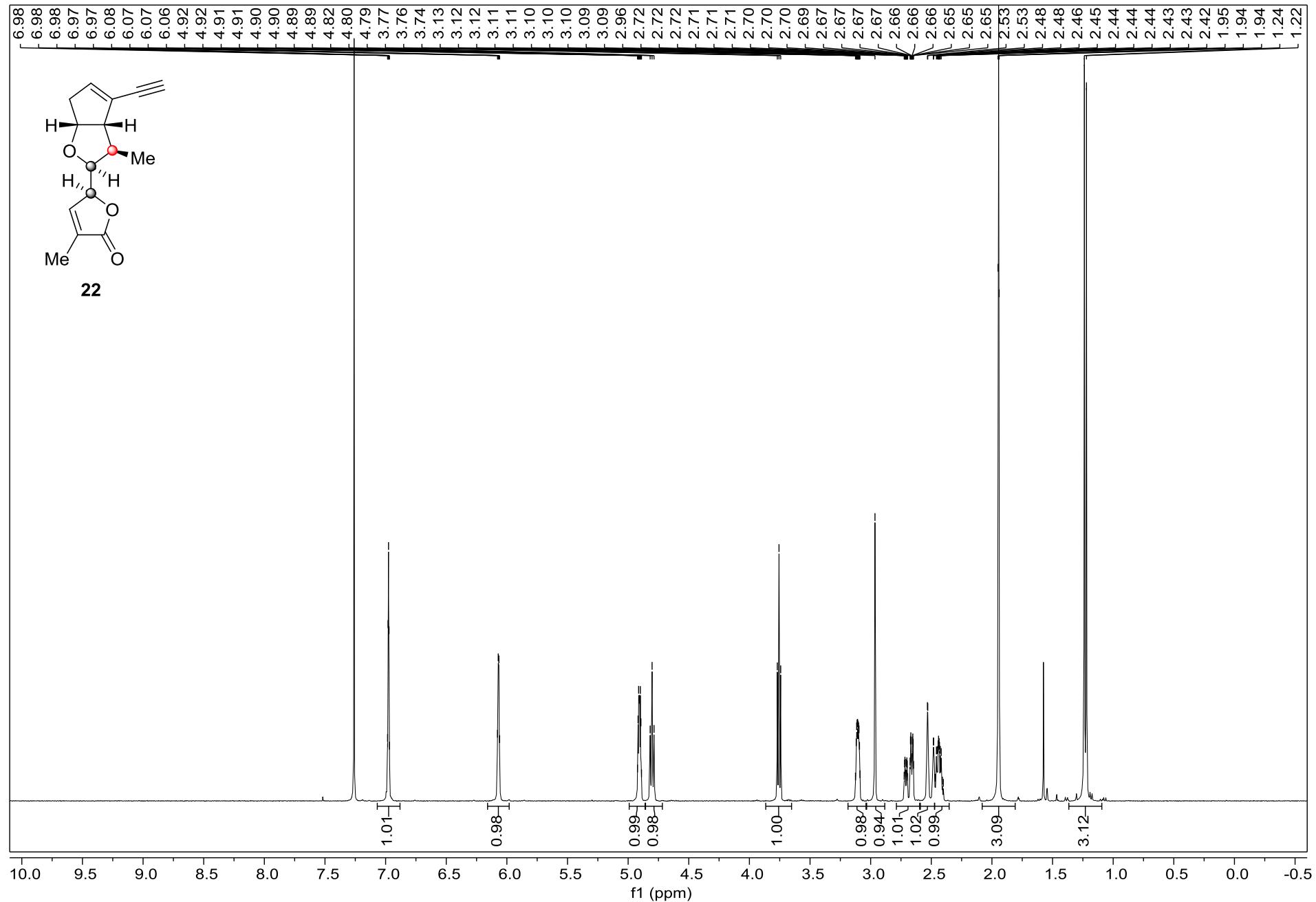
¹H NMR Spectrum of 21 (400 MHz, CDCl₃)



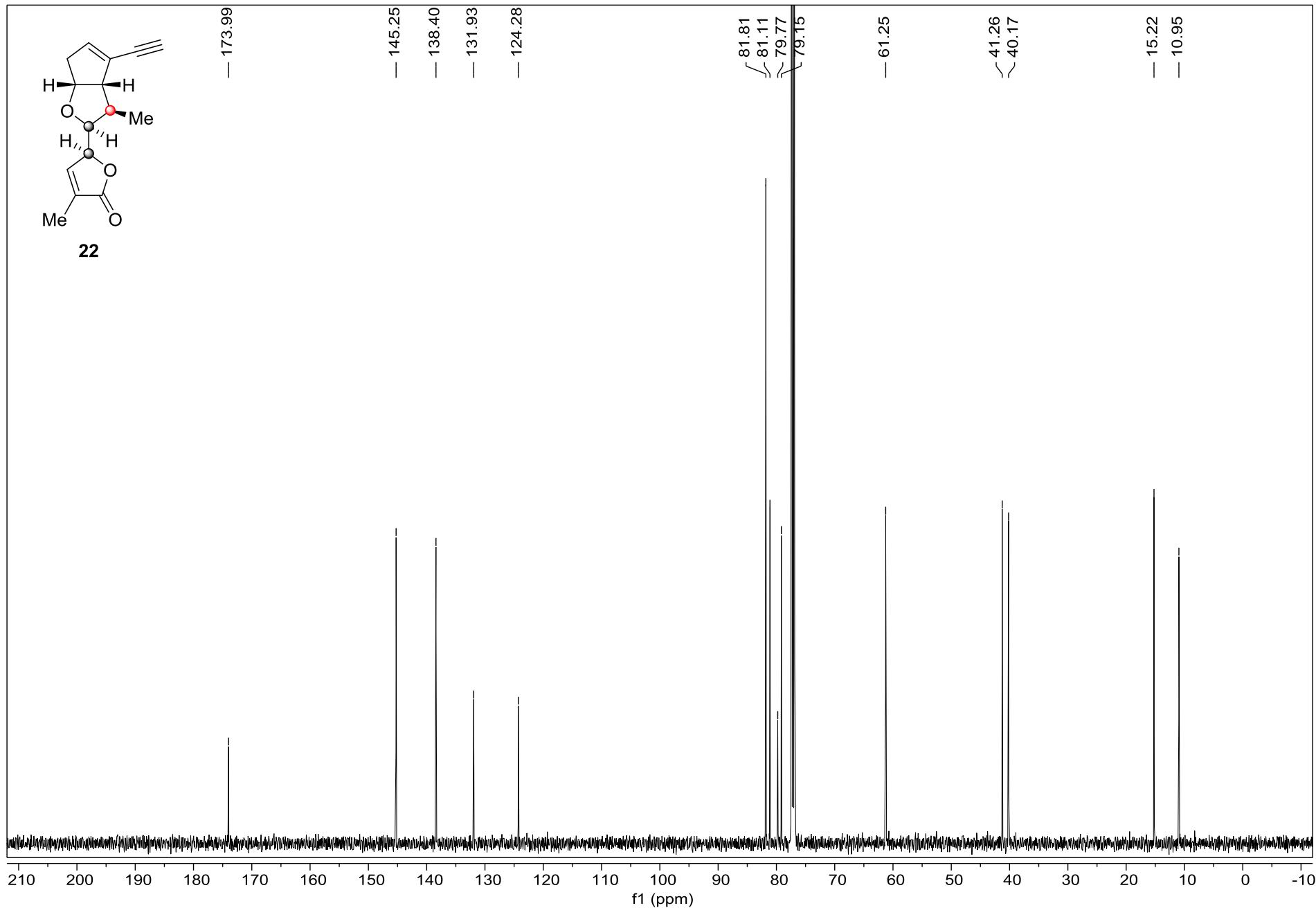
¹³C NMR Spectrum of 21 (101 MHz, CDCl₃)



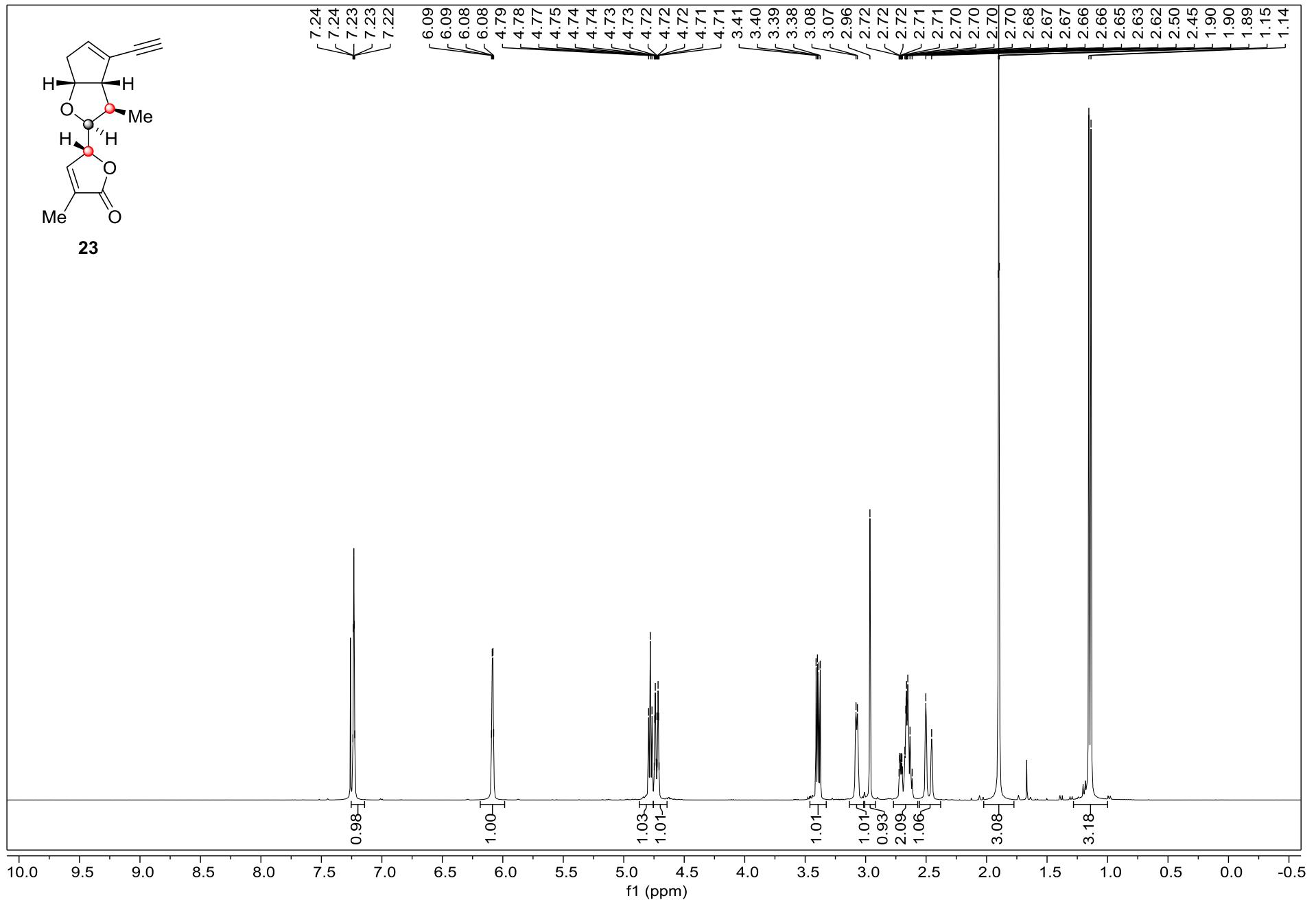
¹H NMR Spectrum of 22 (400 MHz, CDCl₃)



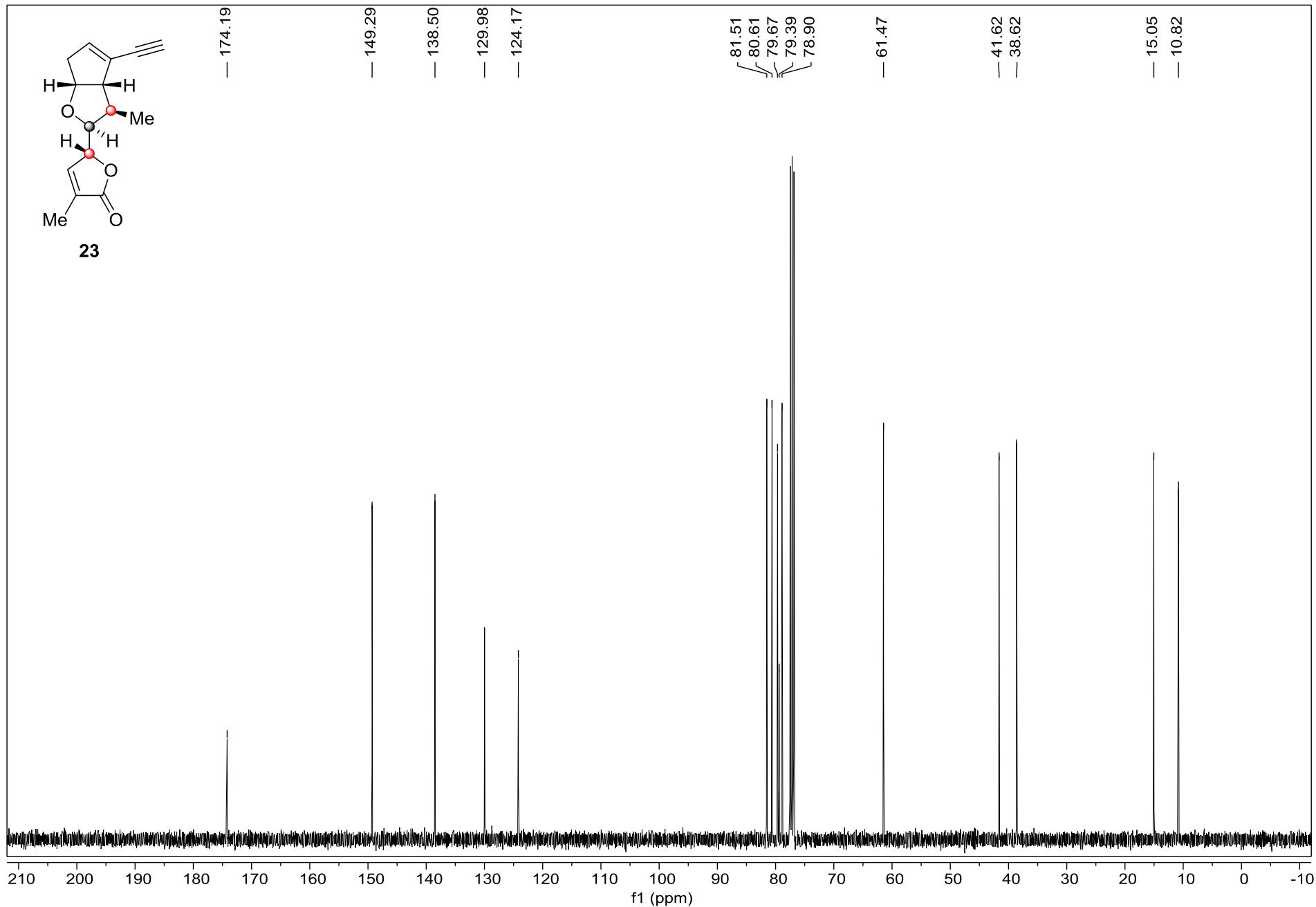
¹³C NMR Spectrum of 22 (126 MHz, CDCl₃)



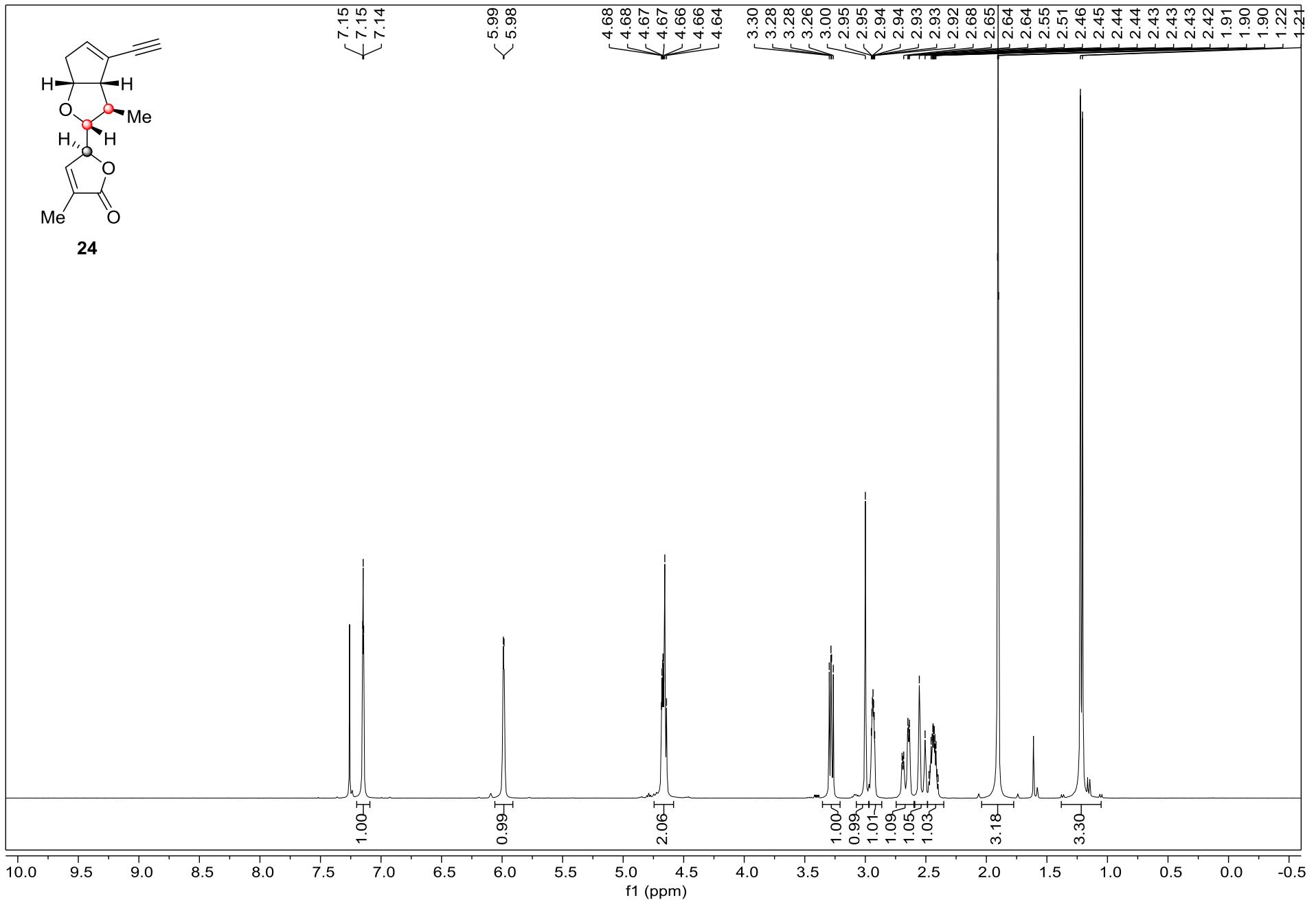
¹H NMR Spectrum of 23 (400 MHz, CDCl₃)



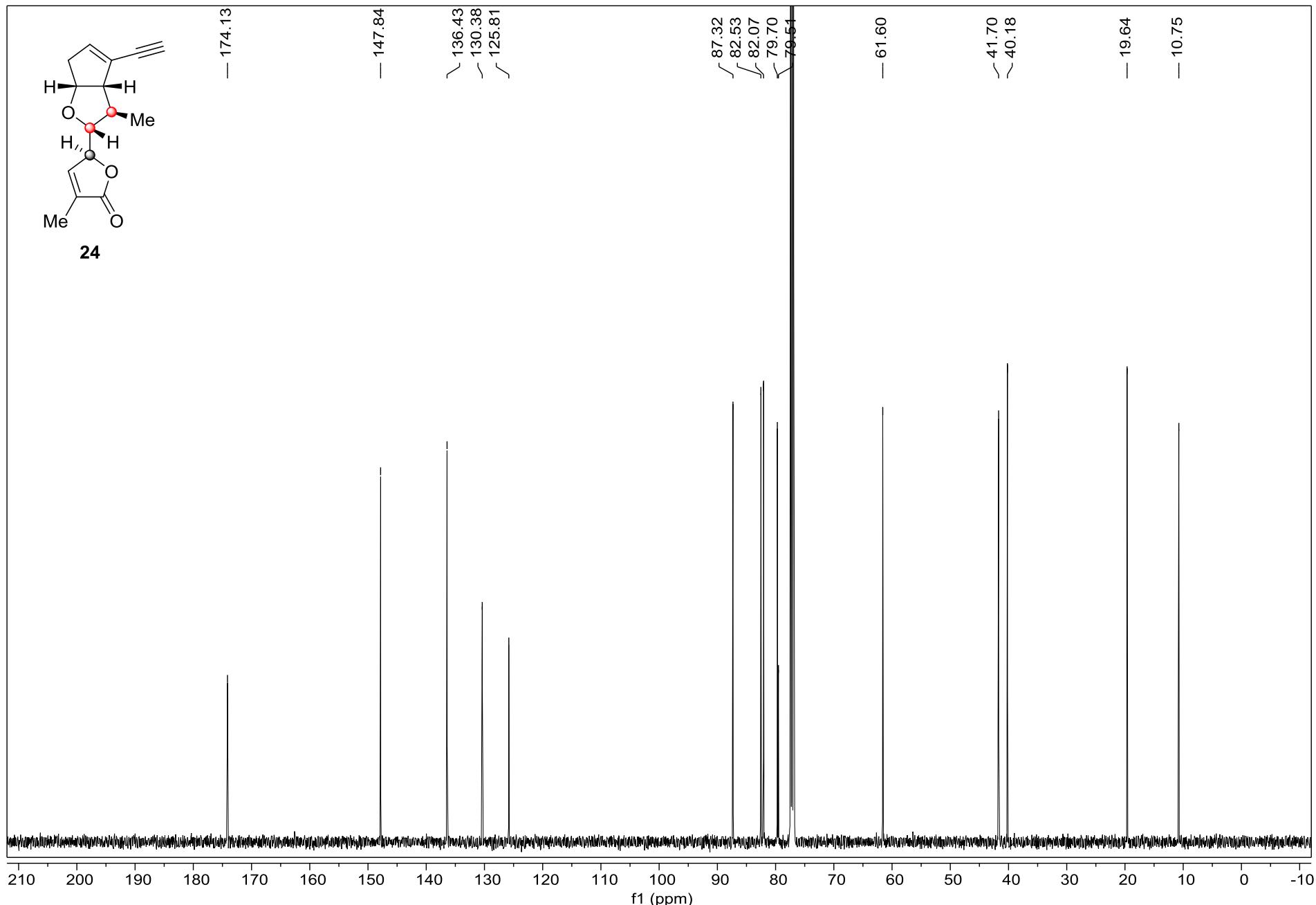
¹³C NMR Spectrum of 23 (101 MHz, CDCl₃)



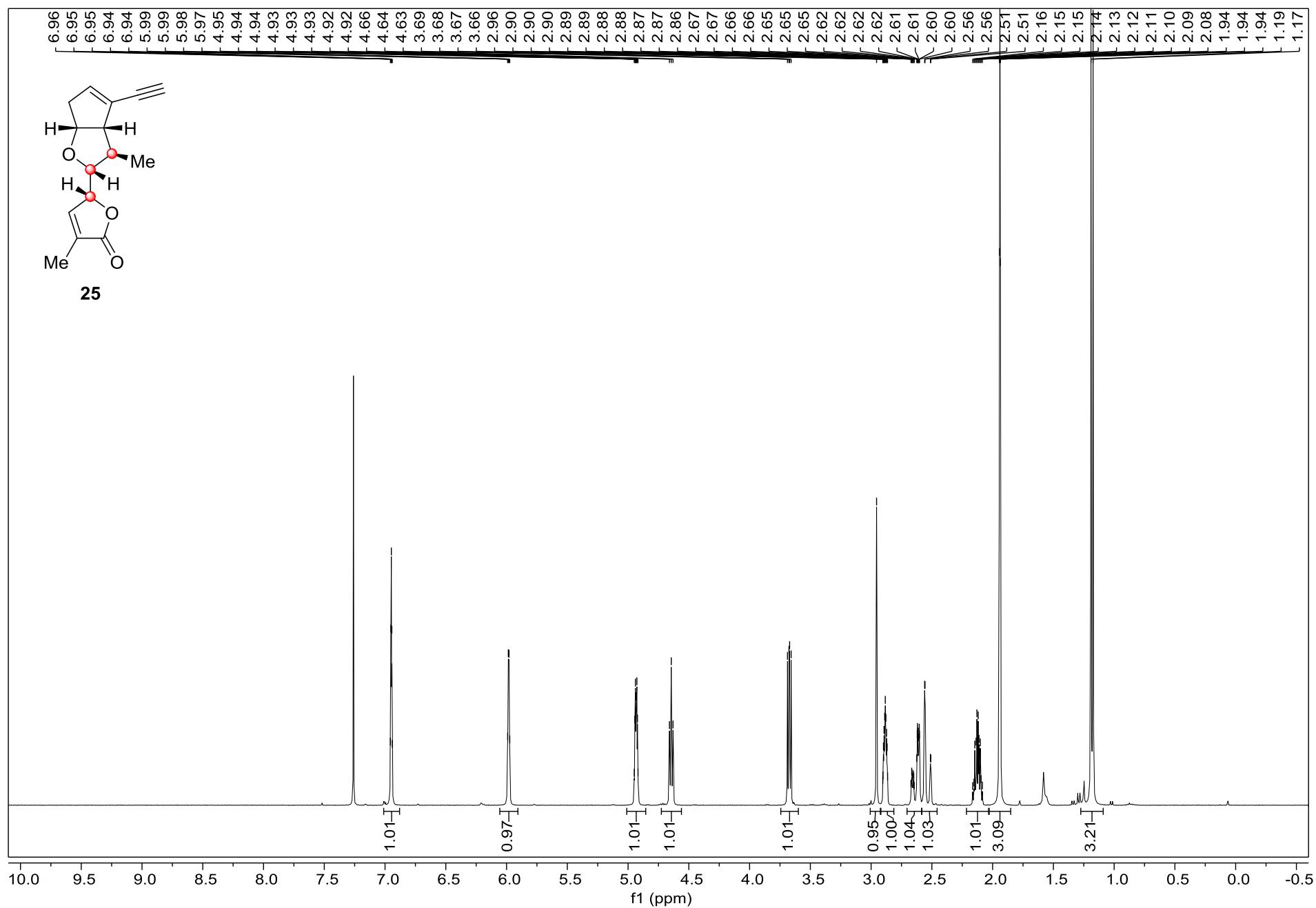
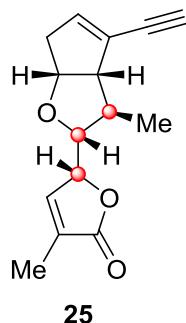
¹H NMR Spectrum of 24 (400 MHz, CDCl₃)



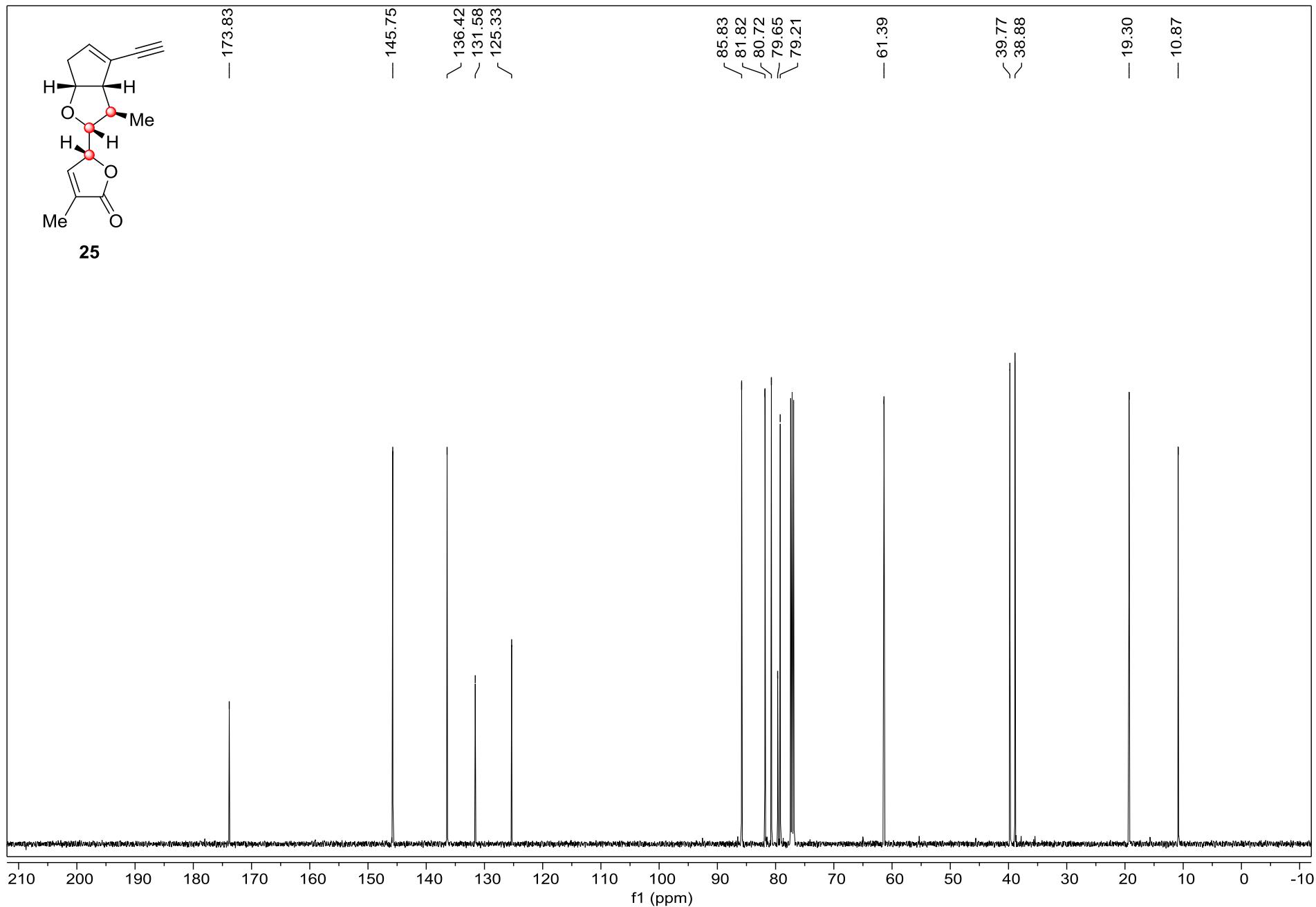
¹³C NMR Spectrum of 24 (126 MHz, CDCl₃)



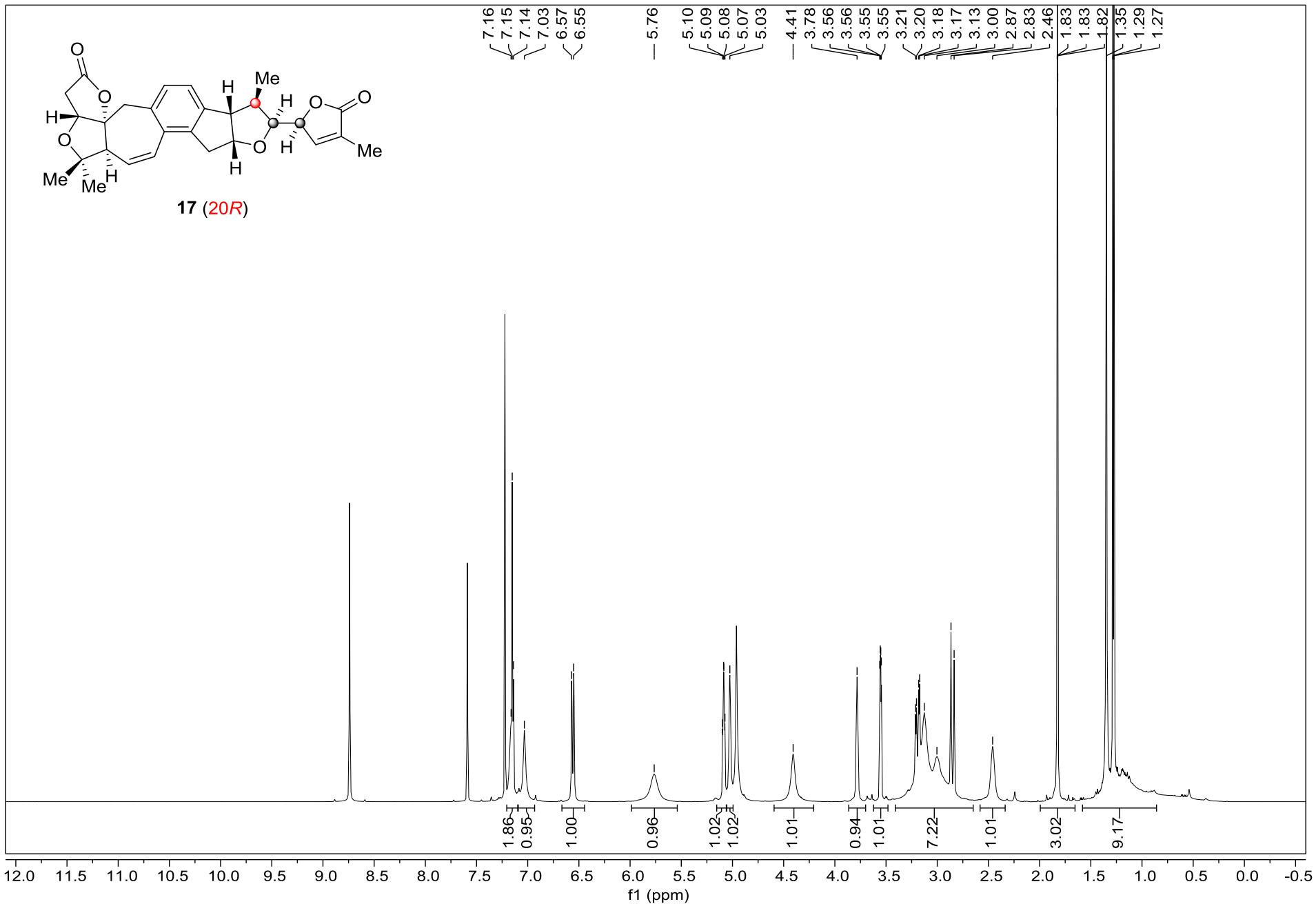
¹H NMR Spectrum of 25 (400 MHz, CDCl₃)



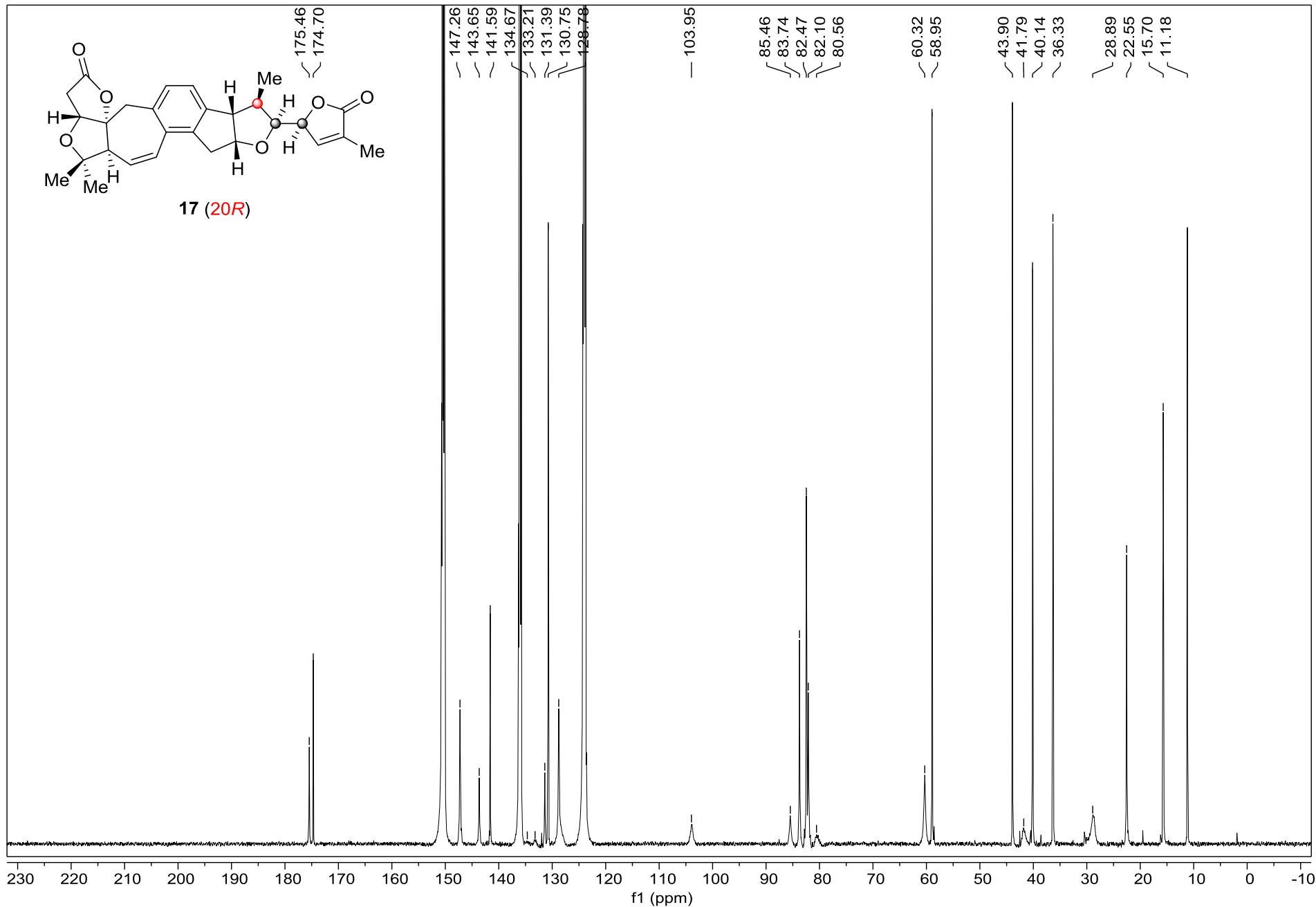
¹³C NMR Spectrum of 25 (126 MHz, CDCl₃)



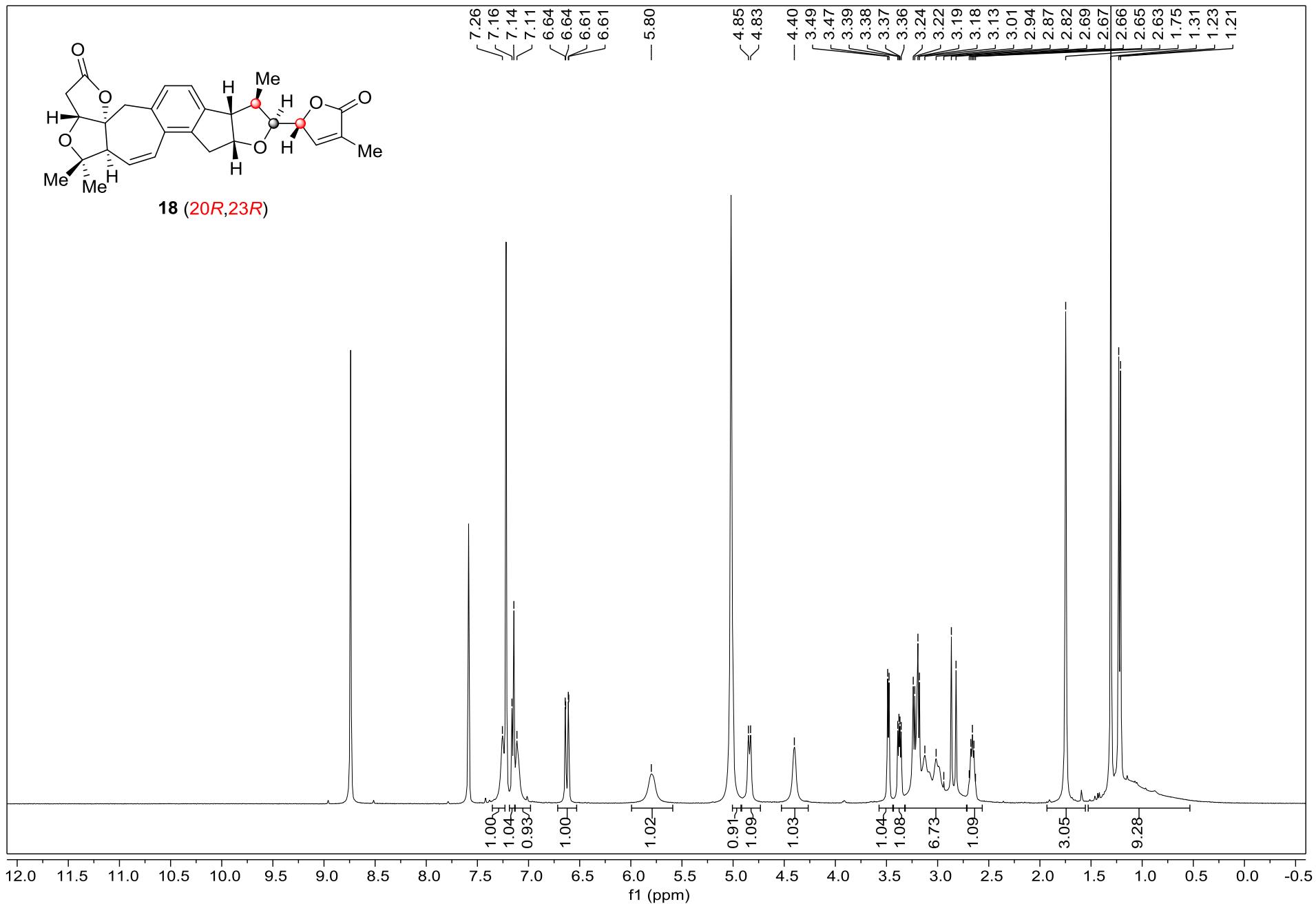
¹H NMR Spectrum of 17 (600 MHz, pyridine-d₅)



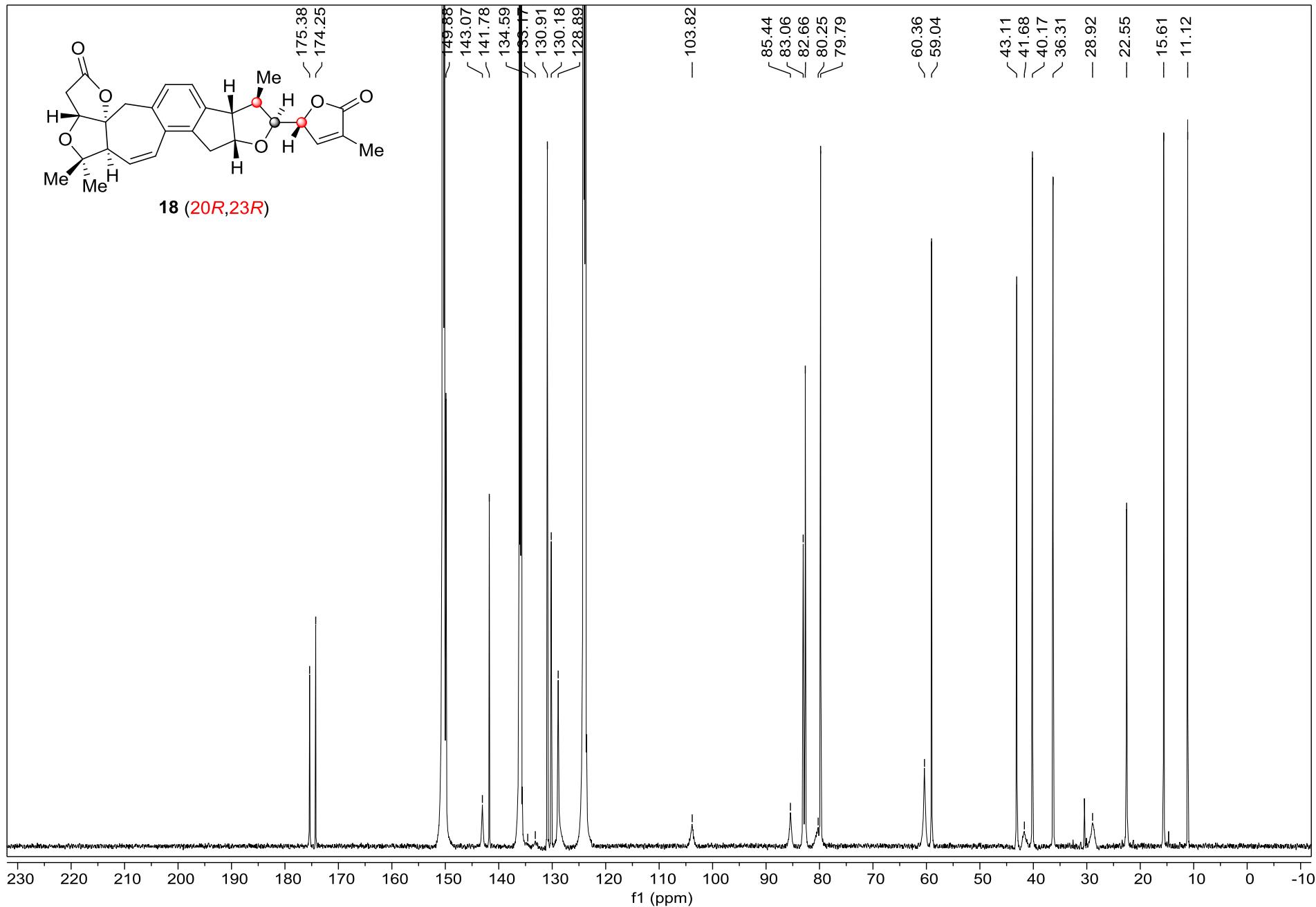
¹³C NMR Spectrum of 17 (151 MHz, pyridine-d₅)



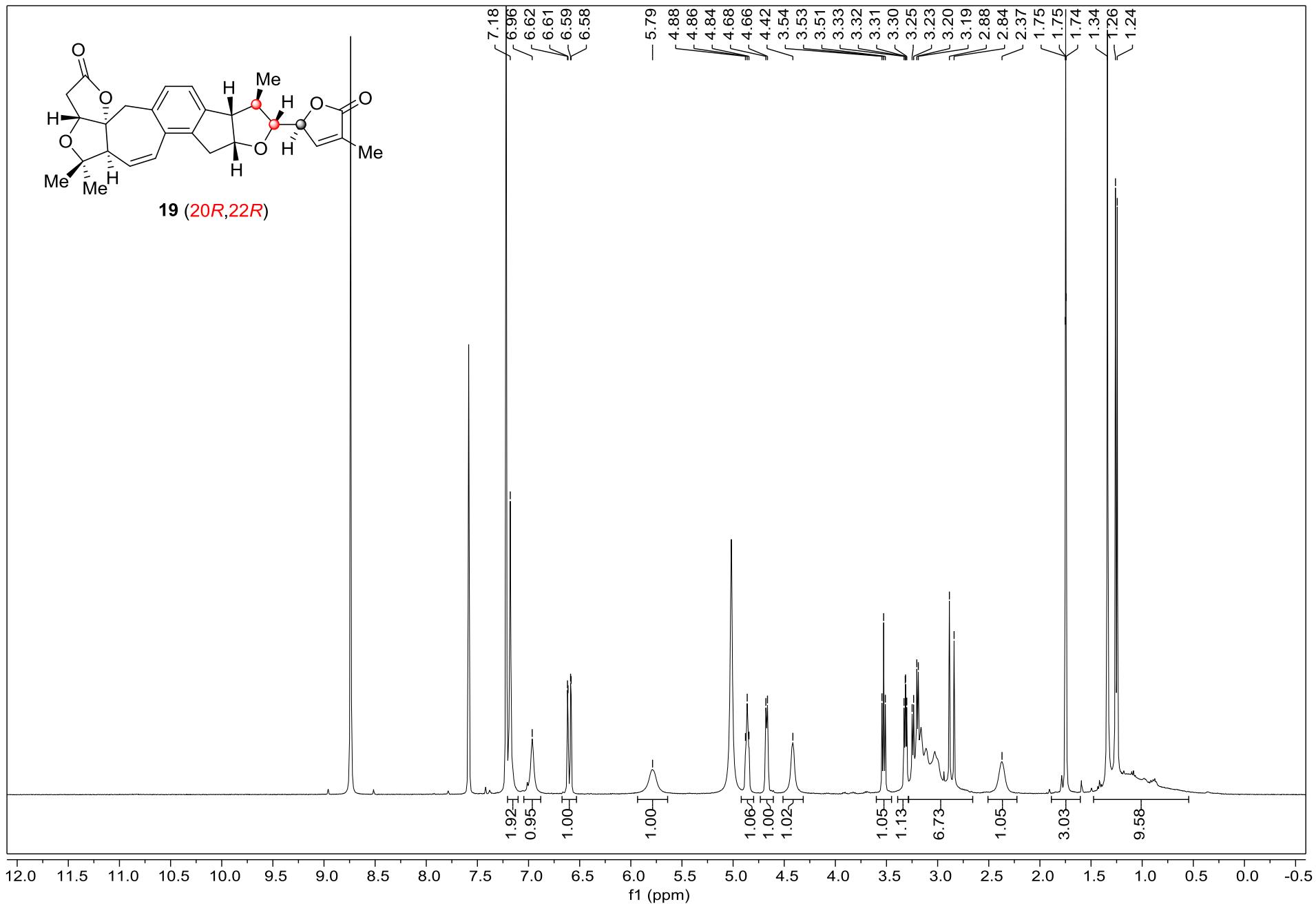
¹H NMR Spectrum of 18 (400 MHz, pyridine-d₅)



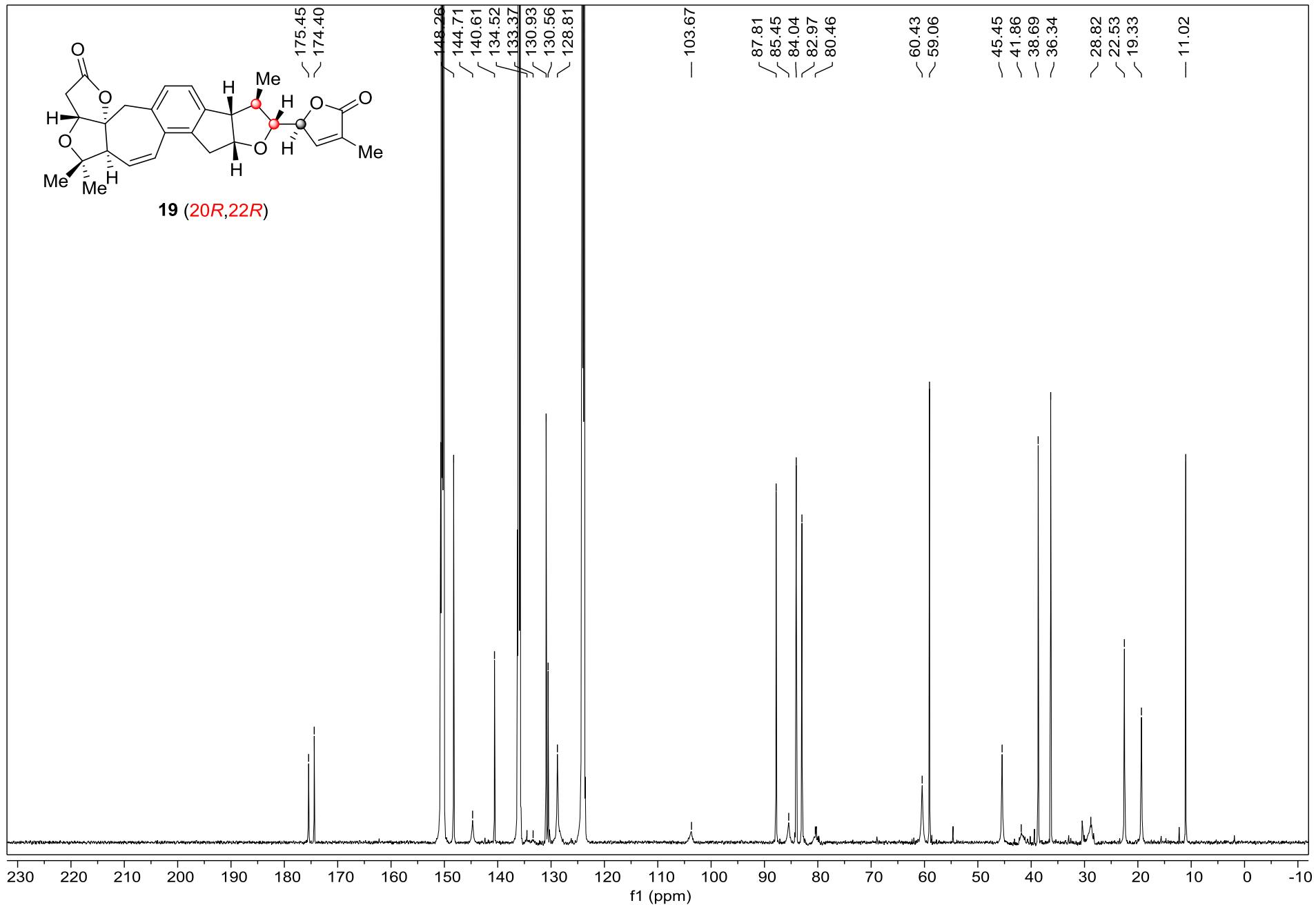
¹³C NMR Spectrum of 18 (151 MHz, pyridine-d₅)



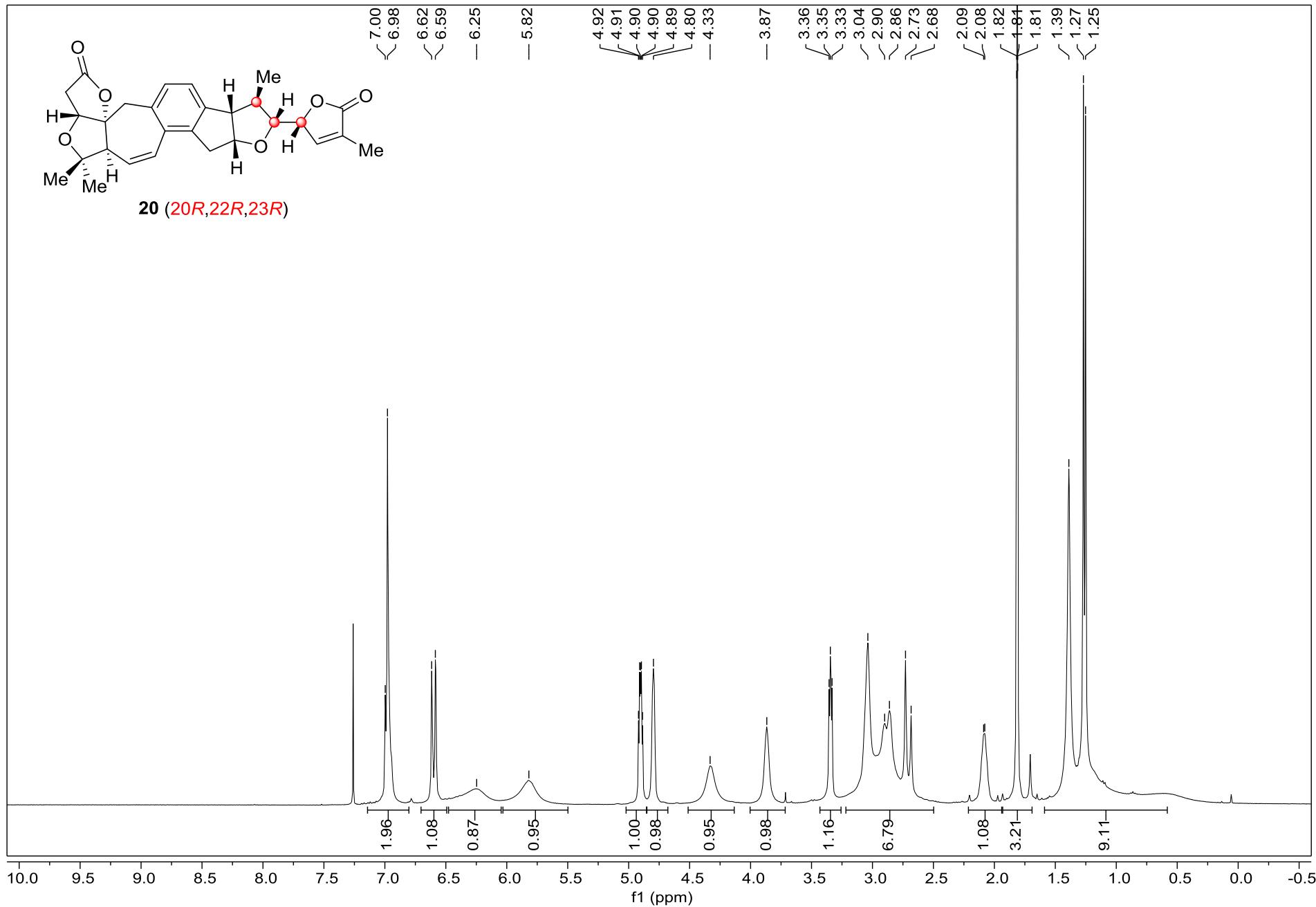
¹H NMR Spectrum of 19 (400 MHz, pyridine-d₅)



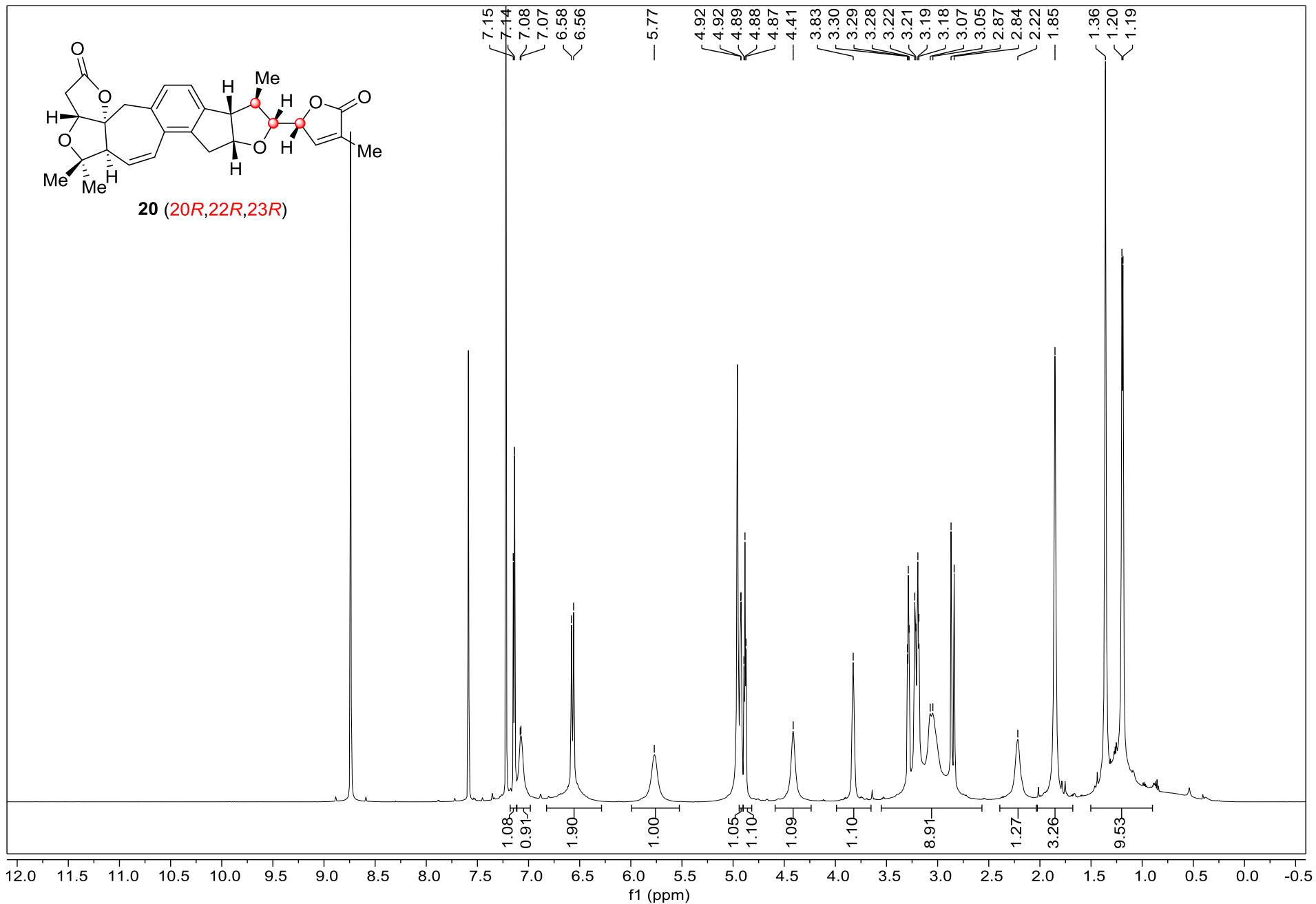
¹³C NMR Spectrum of 19 (151 MHz, pyridine-d₅)



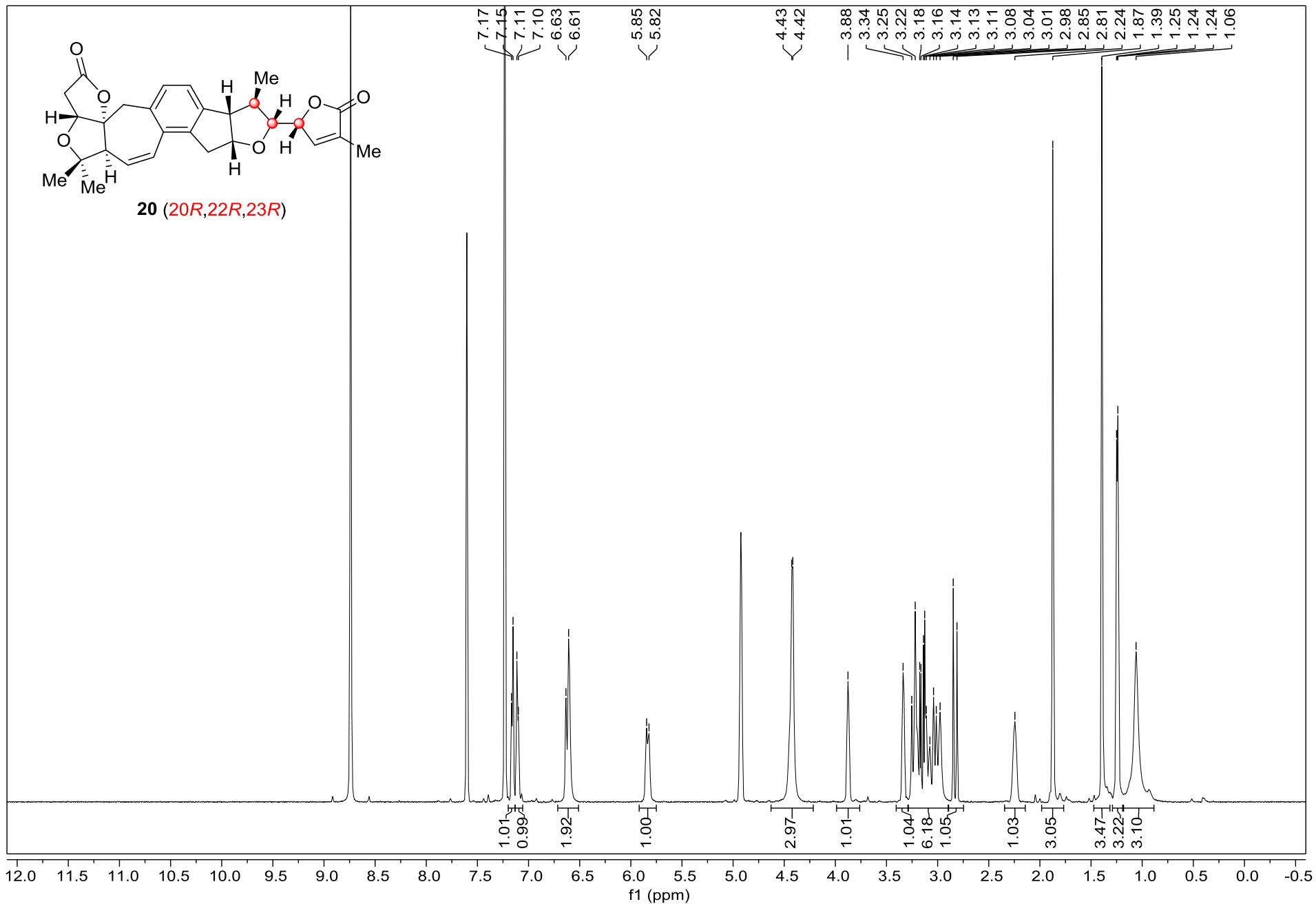
¹H NMR Spectrum of 20 (400 MHz, CDCl₃)



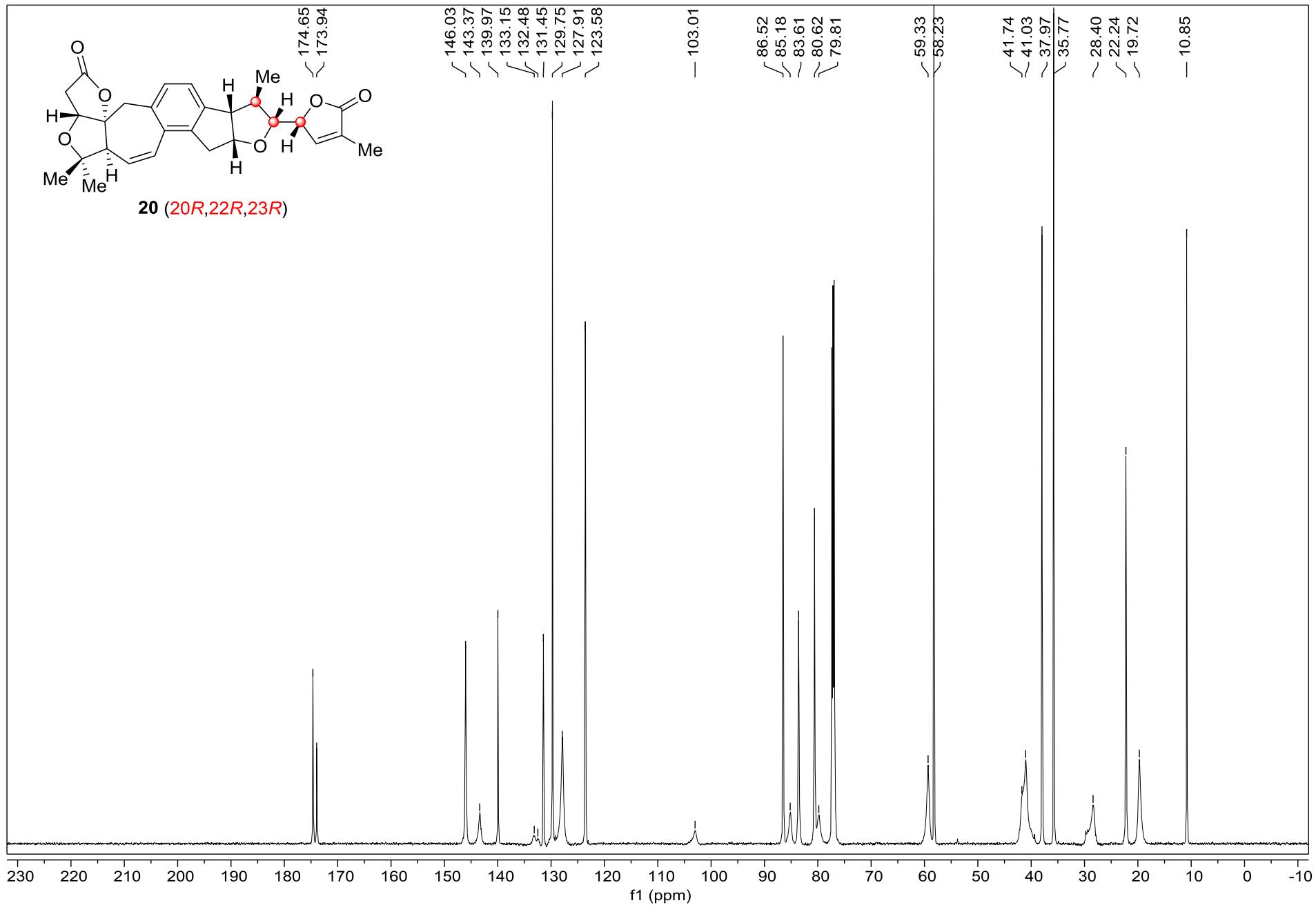
¹H NMR Spectrum of 20 (600 MHz, pyridine-d₅)



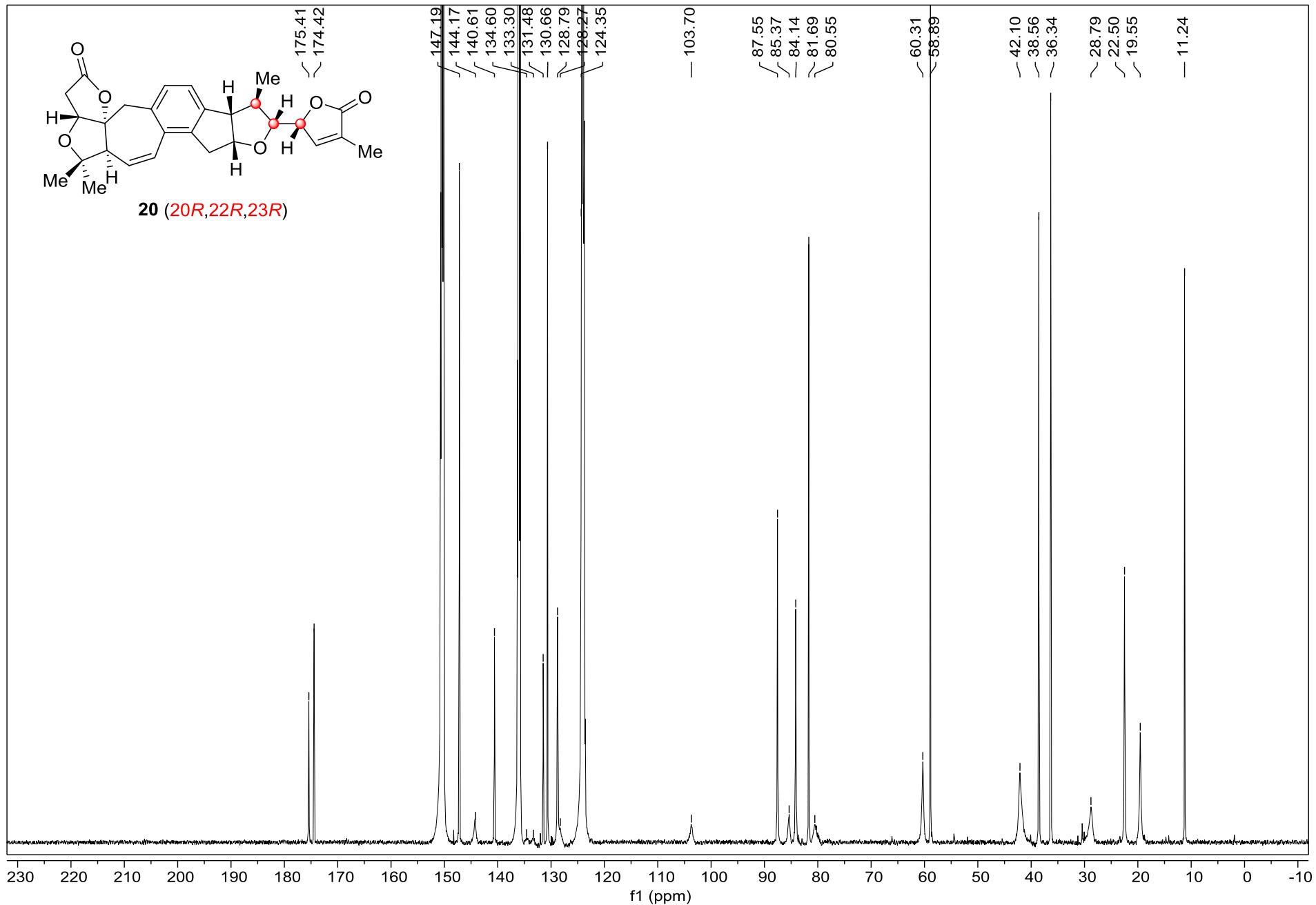
¹H NMR Spectrum of 20 (500 MHz, pyridine-d₅, 60 °C)



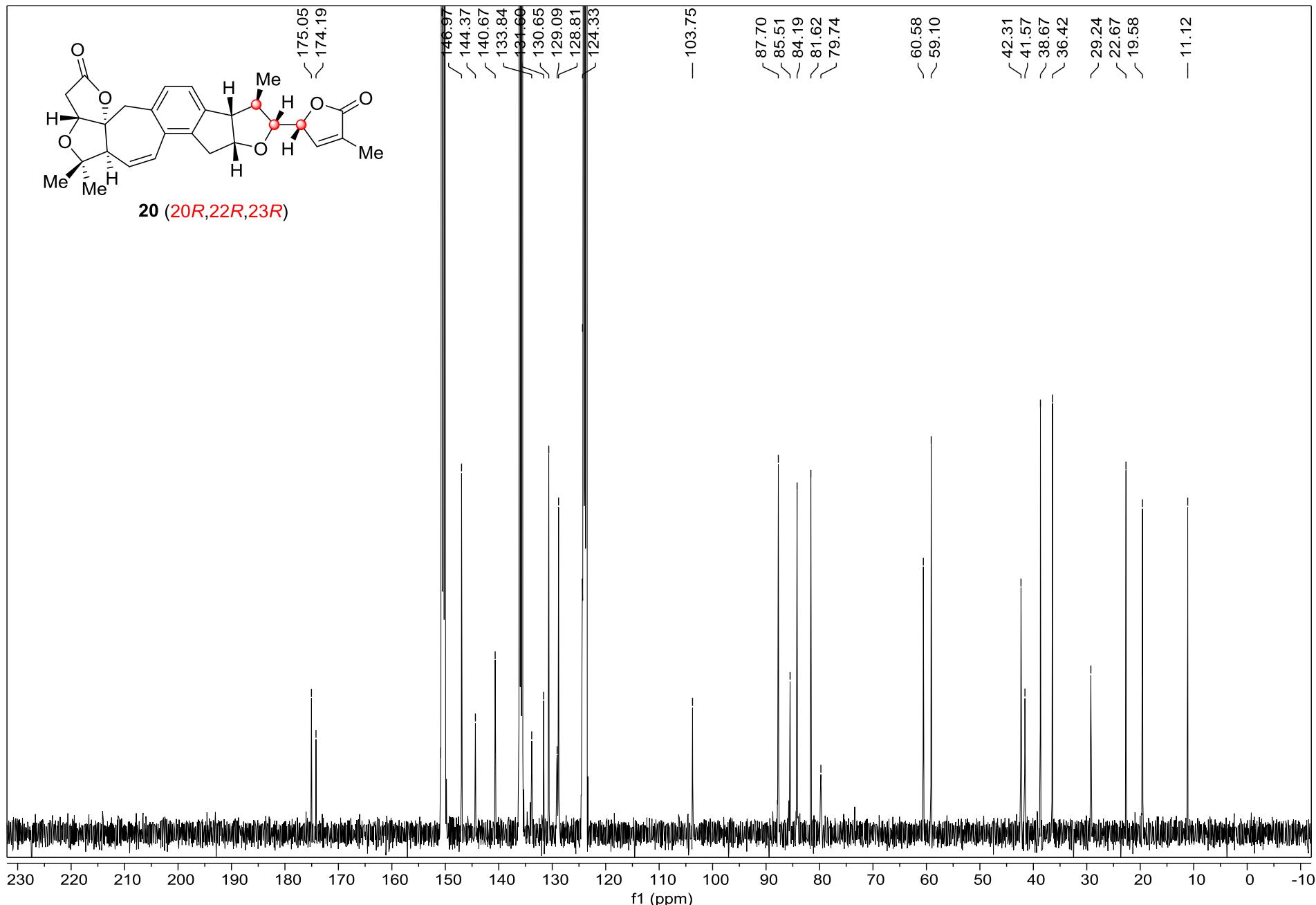
¹³C NMR Spectrum of 20 (151 MHz, CDCl₃)



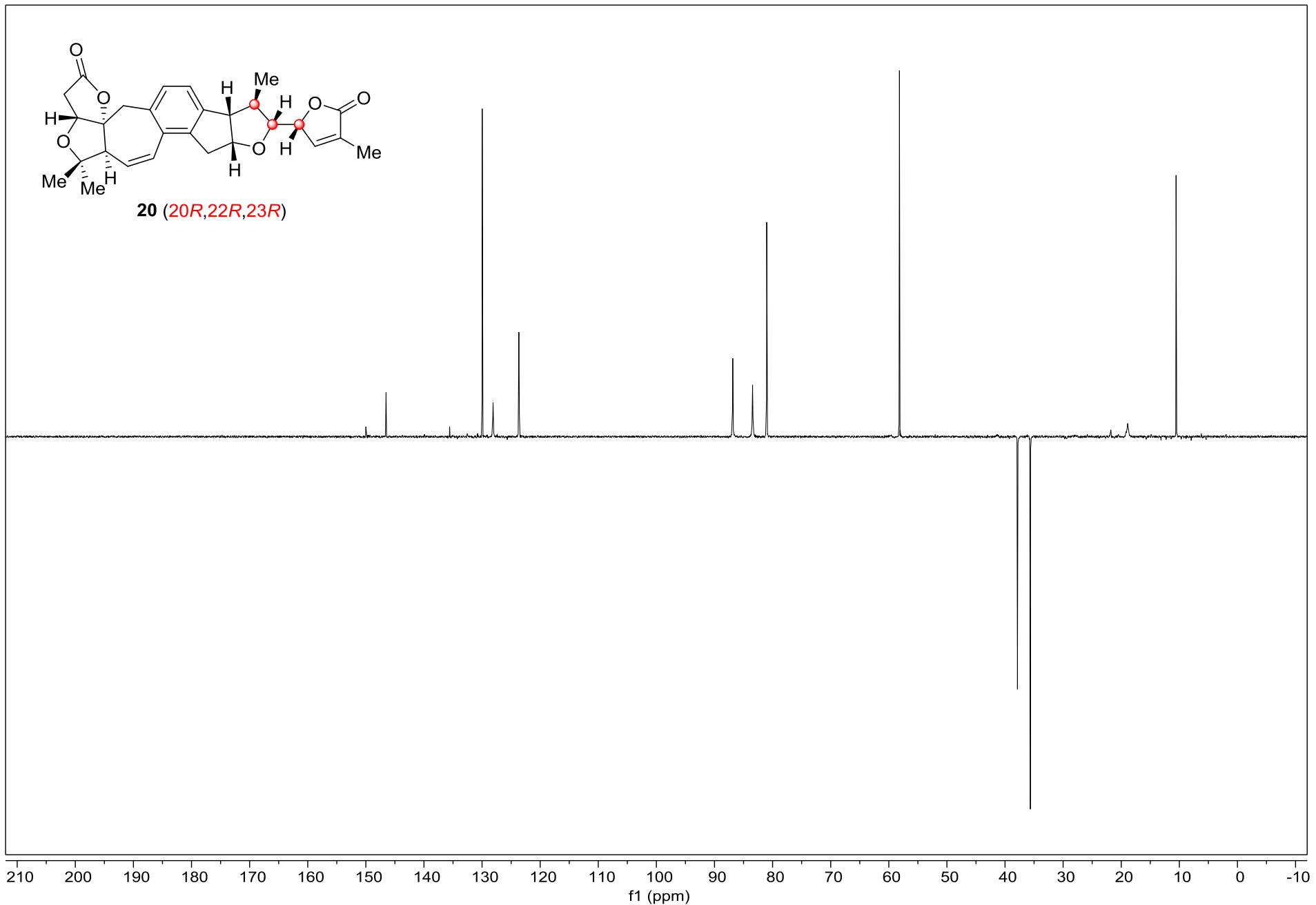
¹³C NMR Spectrum of 20 (151 MHz, pyridine-d₅)



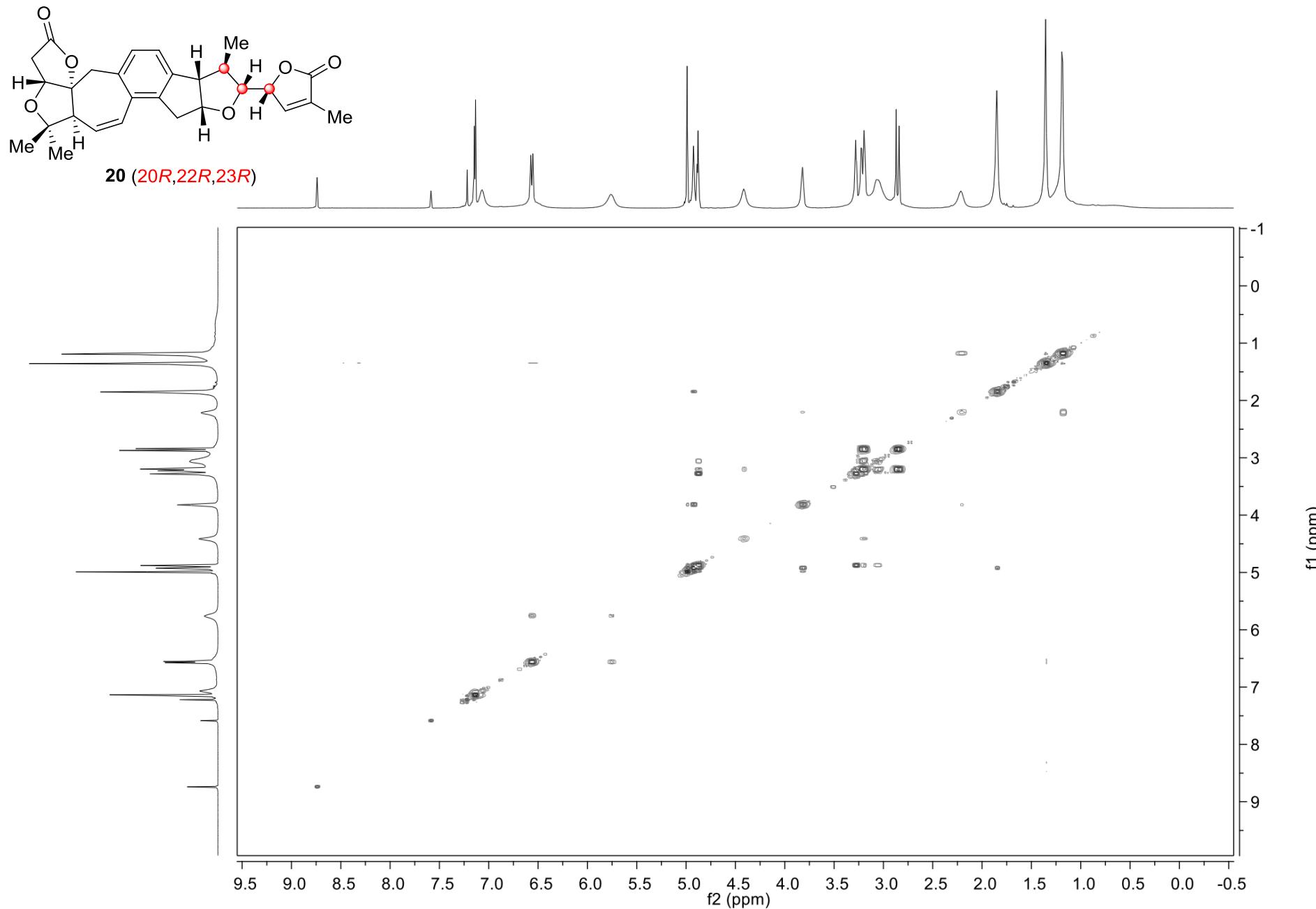
¹³C NMR Spectrum of 20 (101 MHz, pyridine-d₅, 60 °C)



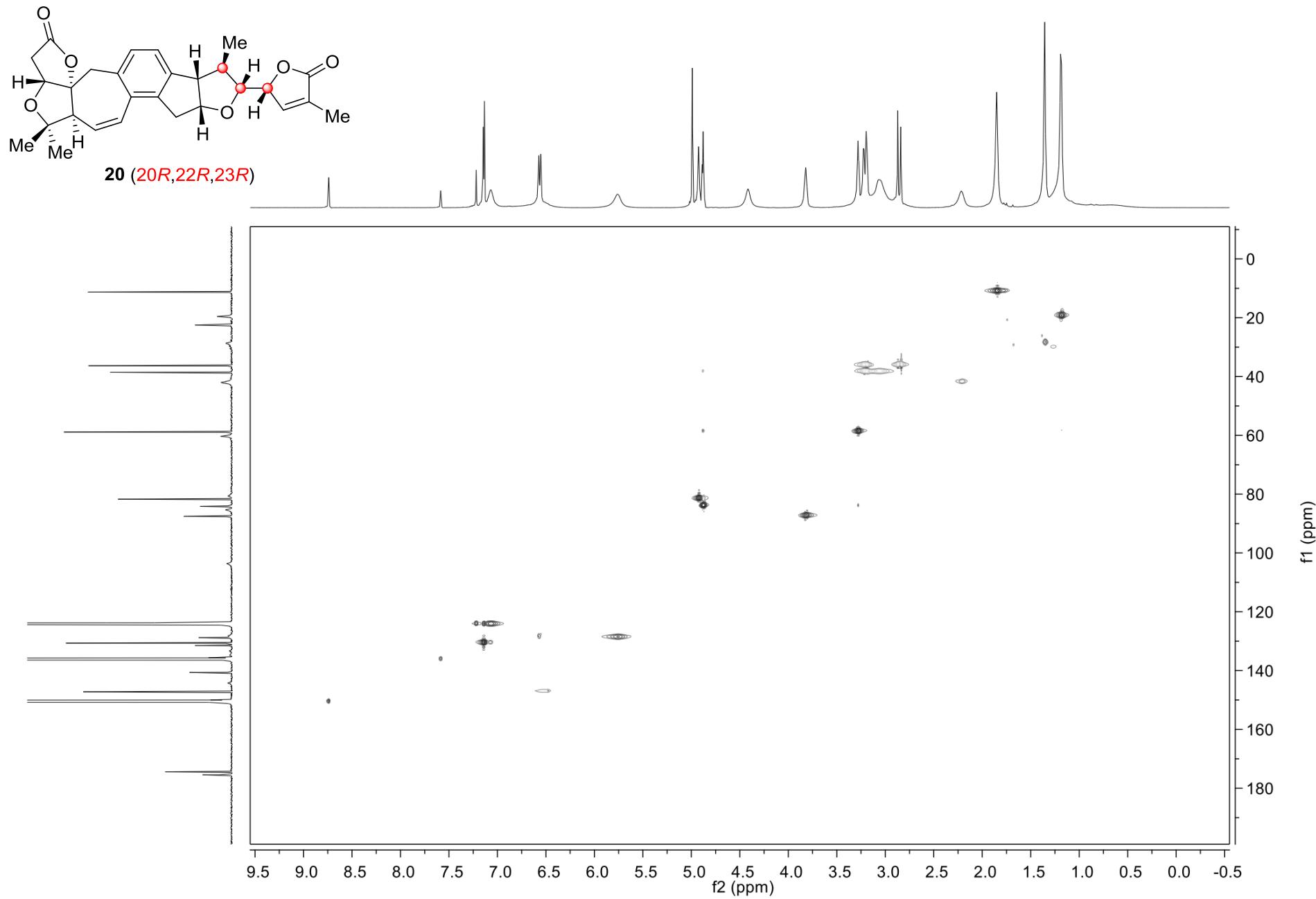
DEPT Spectrum of 20 (151 MHz, pyridine-d₅)



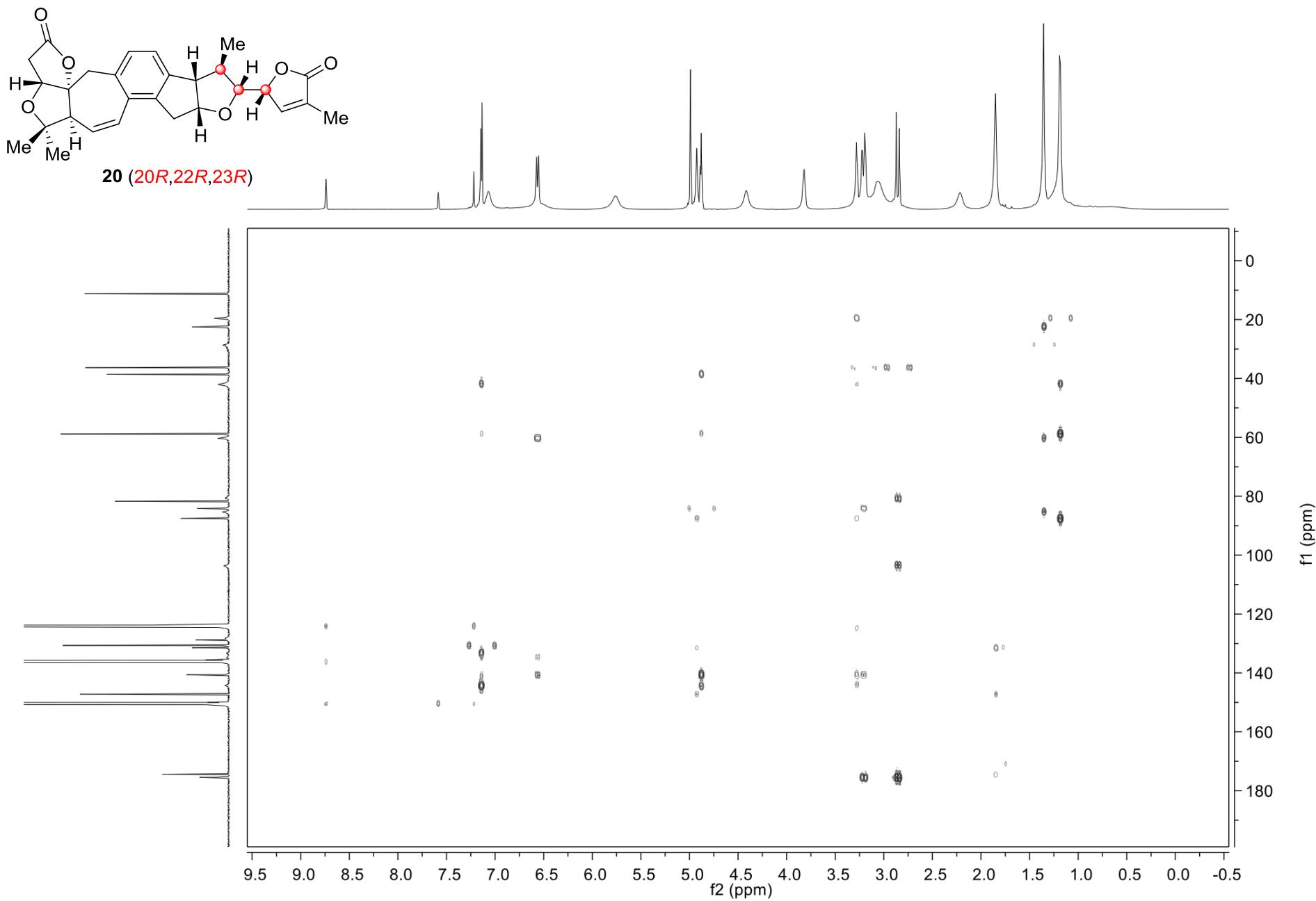
COSY Spectrum of 20 (pyridine-d₅)



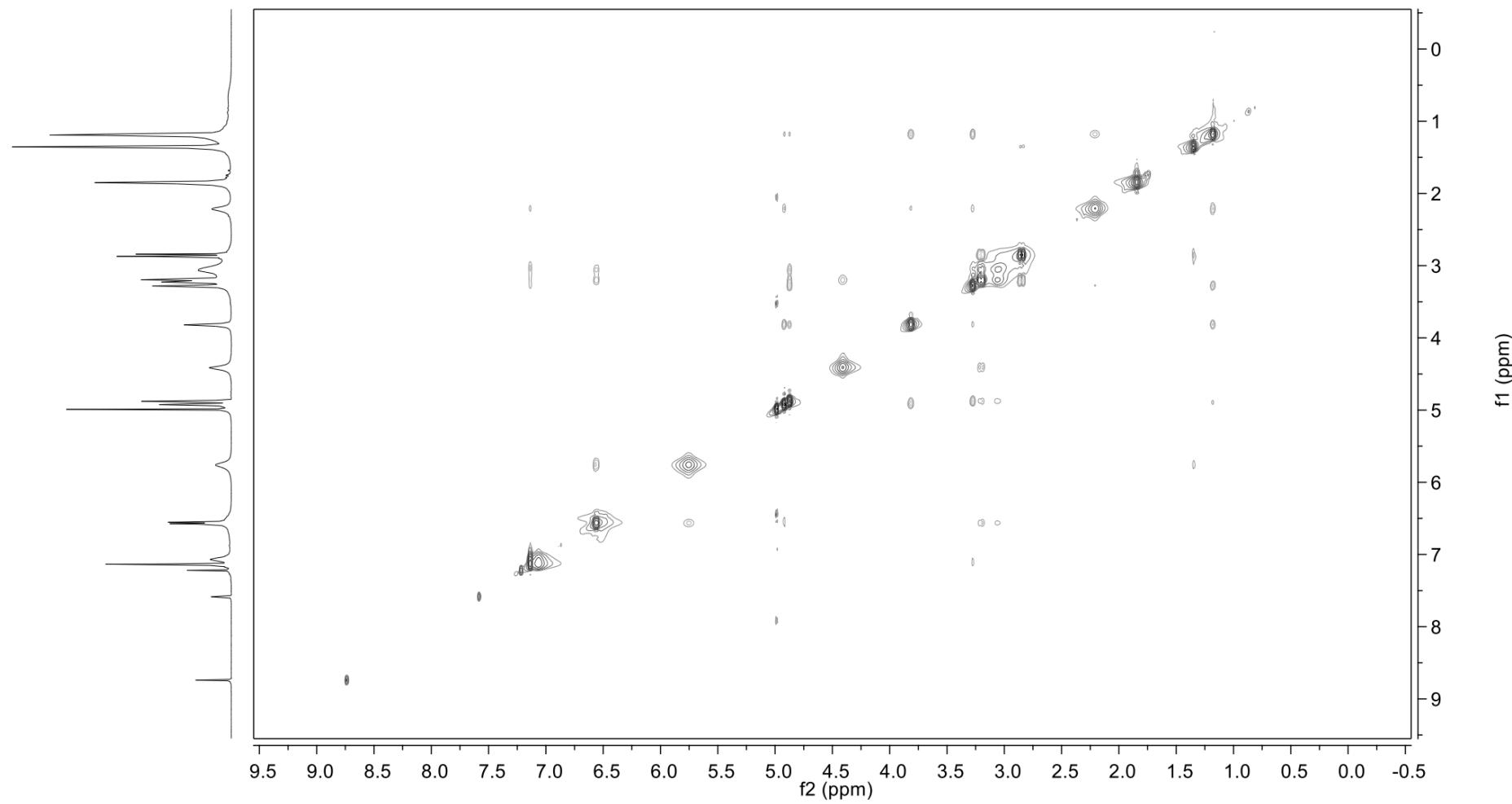
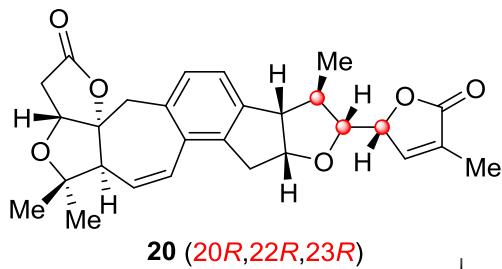
HMDS Spectrum of 20 (pyridine-d₅)



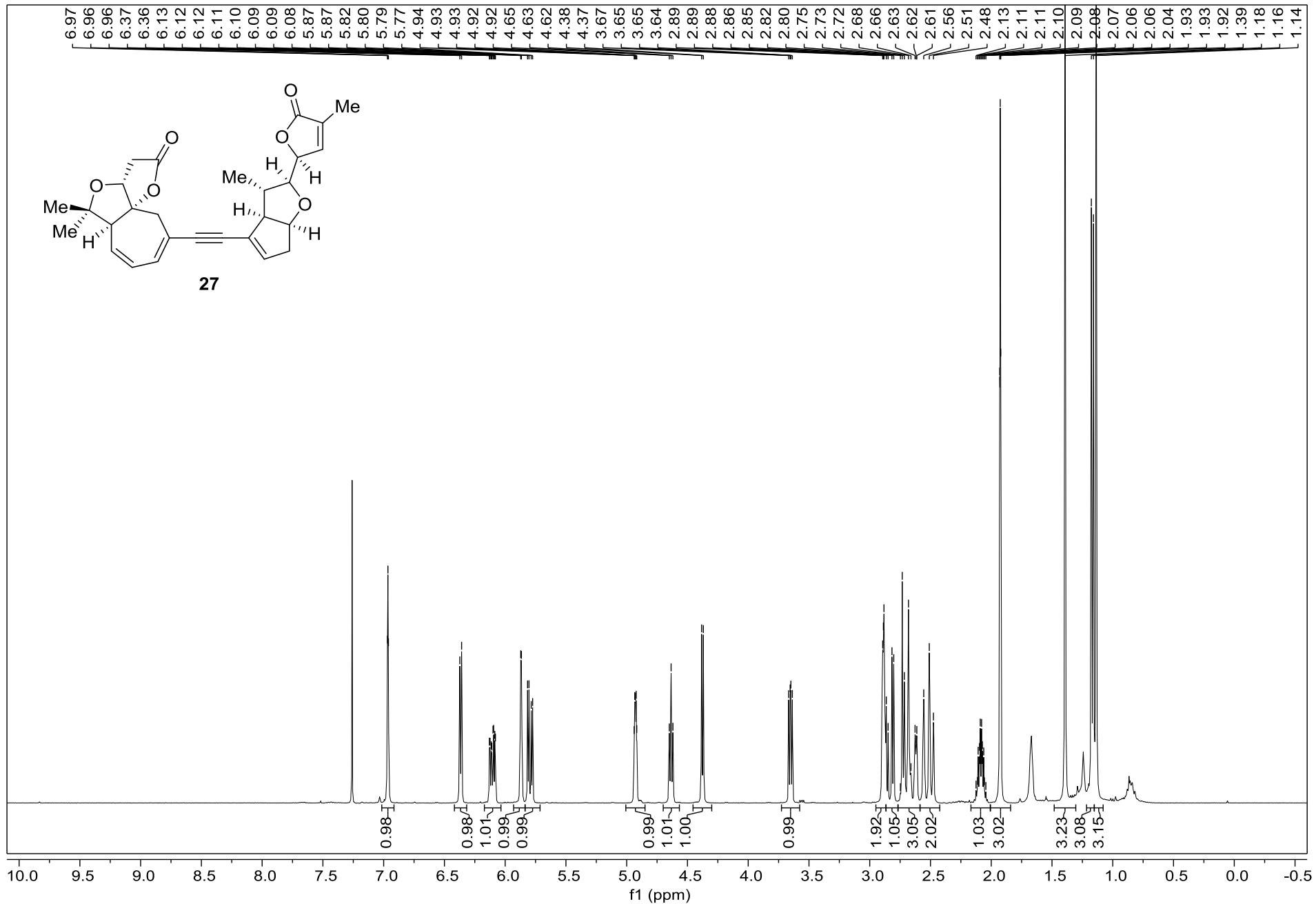
HMBC Spectrum of 20 (pyridine-d₅)



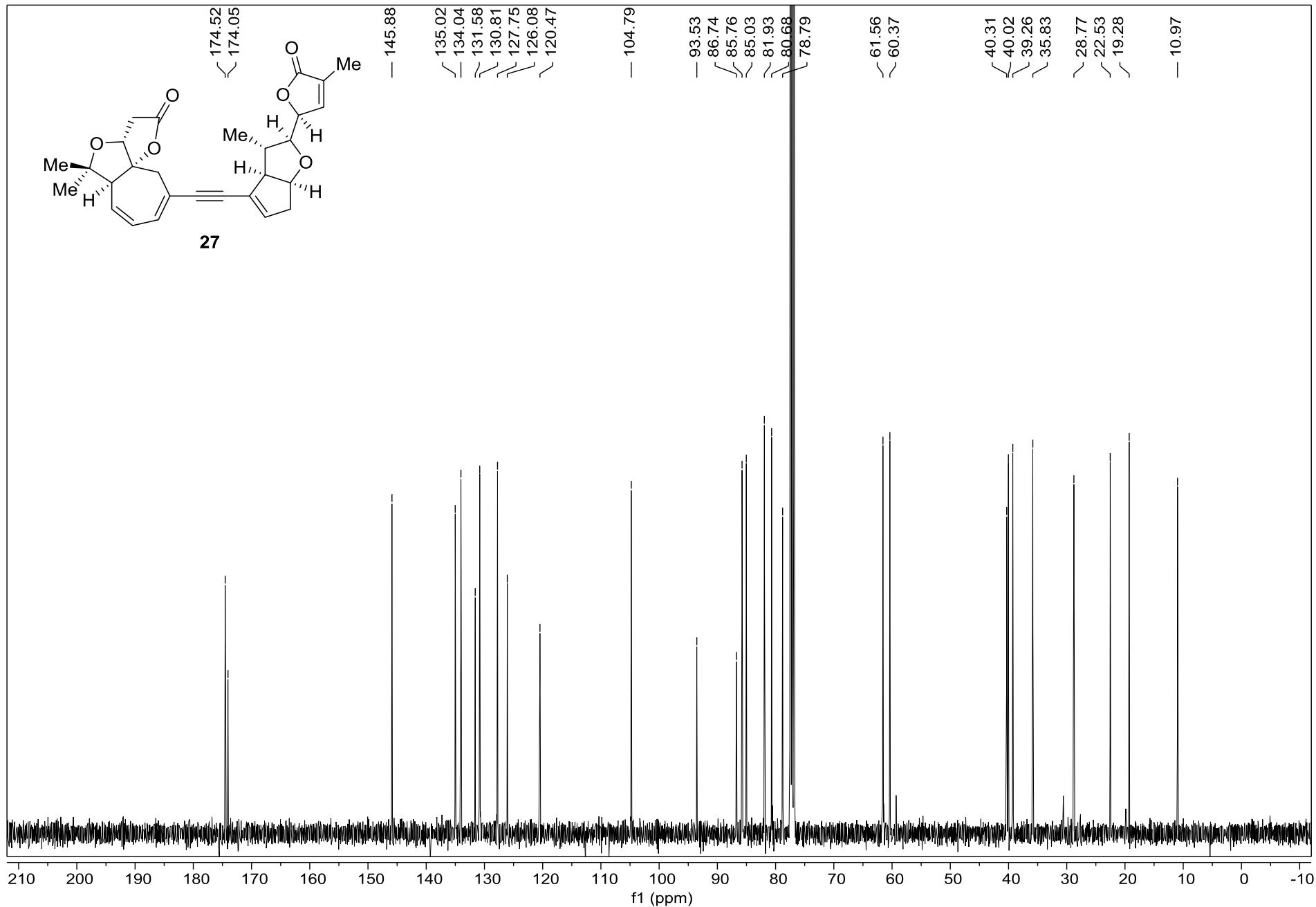
NOESY Spectrum of 20 (pyridine-d₅)



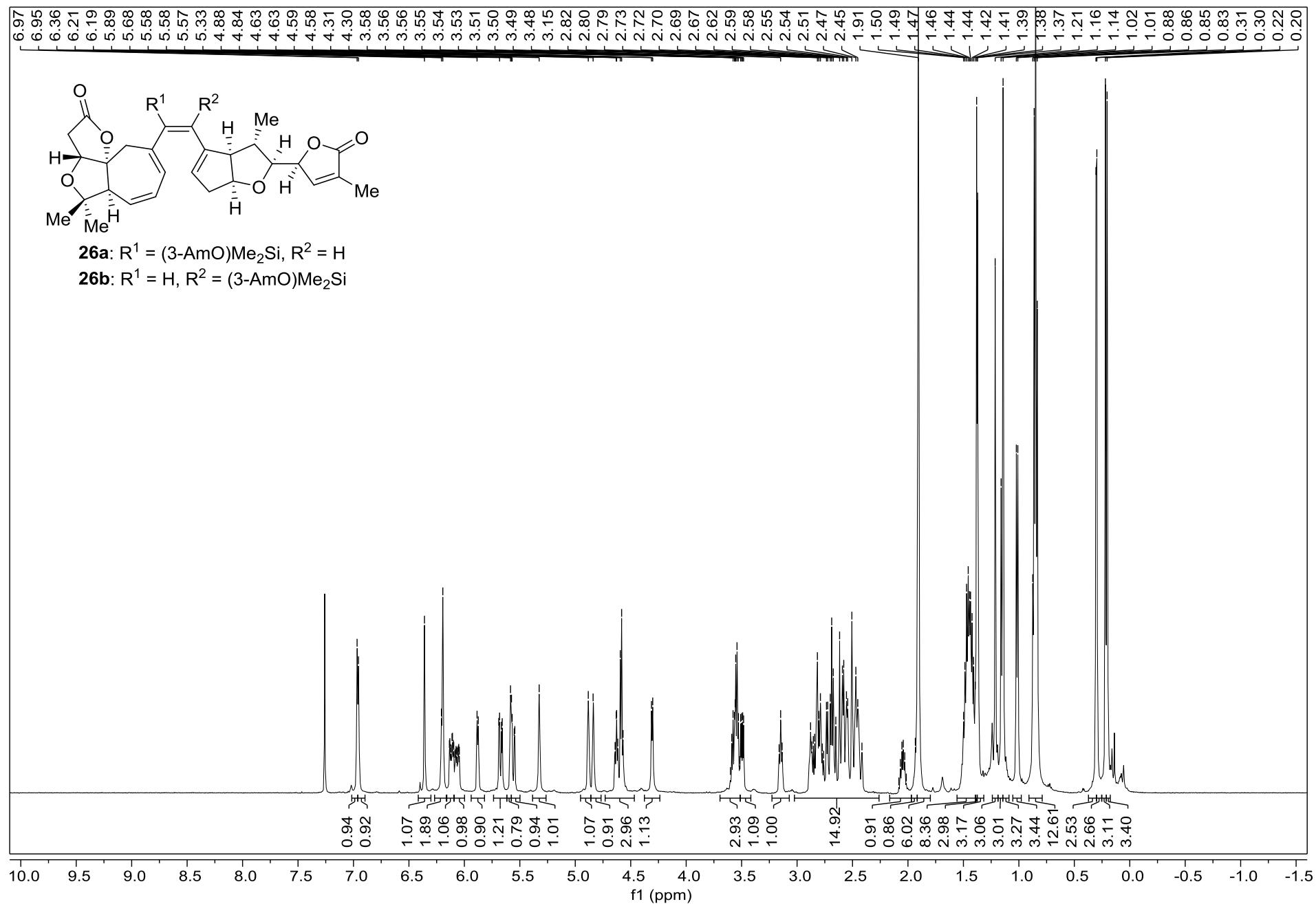
¹H NMR Spectrum of 27 (400 MHz, CDCl₃)



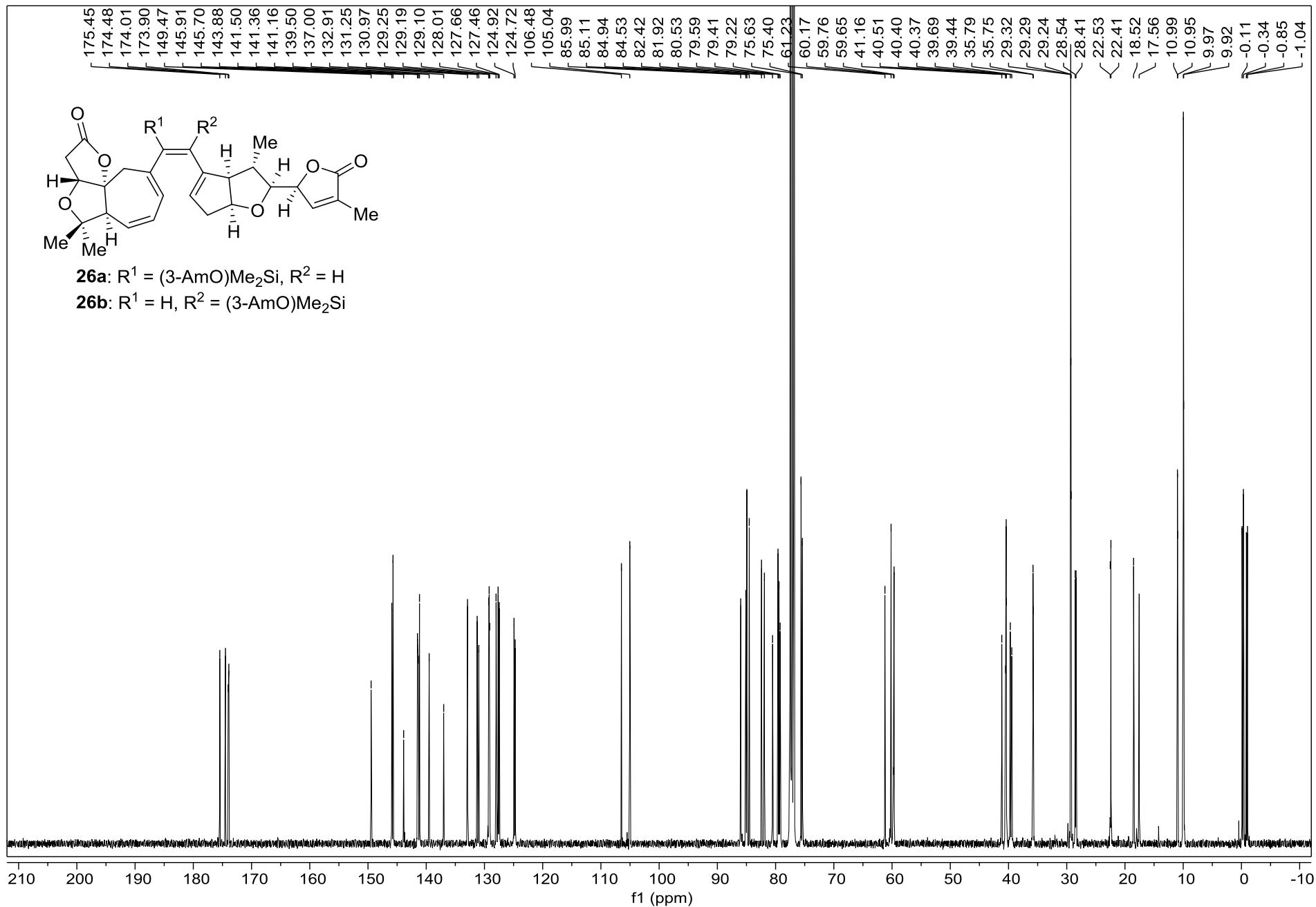
¹³C NMR Spectrum of 27 (101 MHz, CDCl₃)



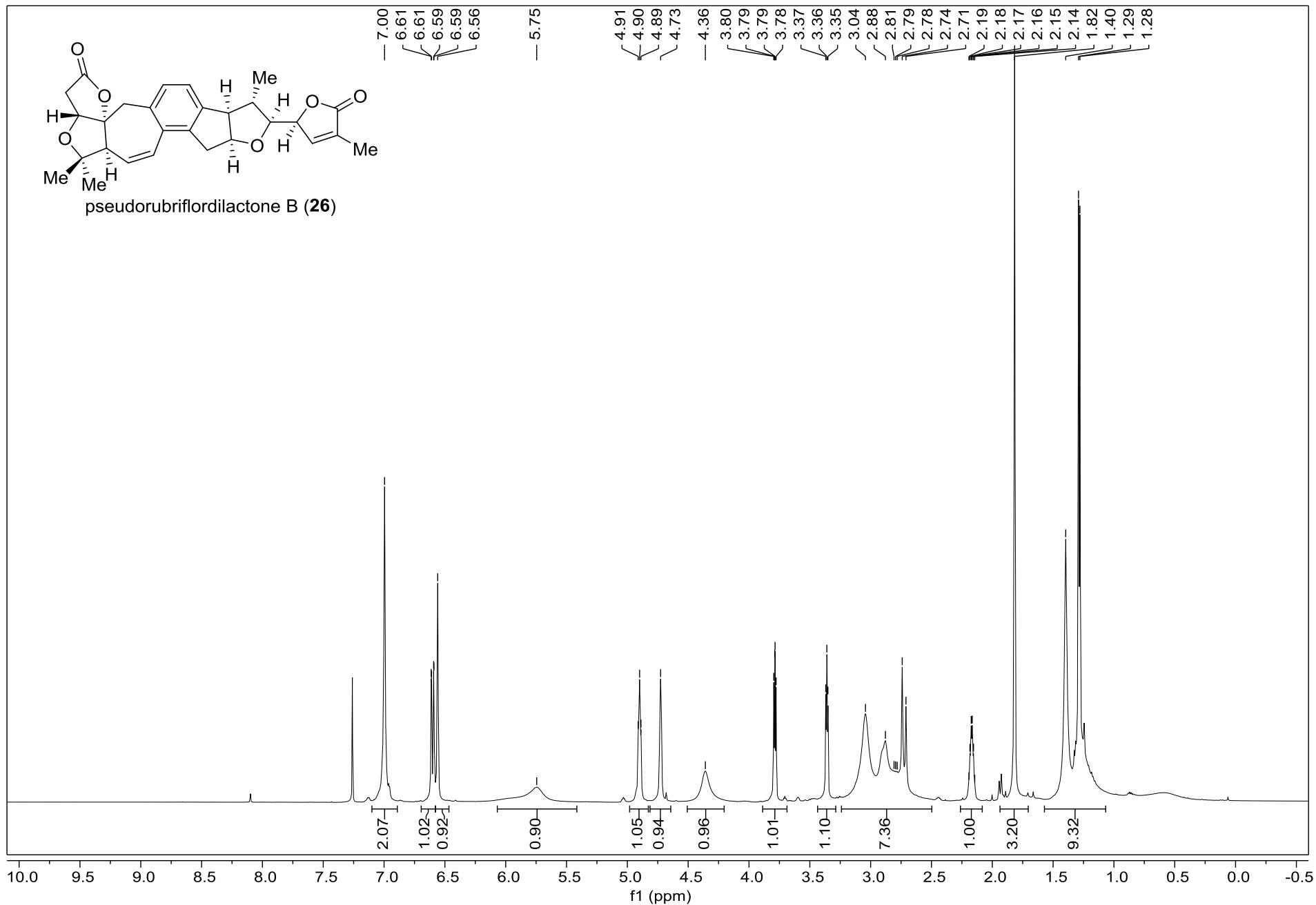
¹H NMR Spectrum of 26a and 26b (500 MHz, CDCl₃)



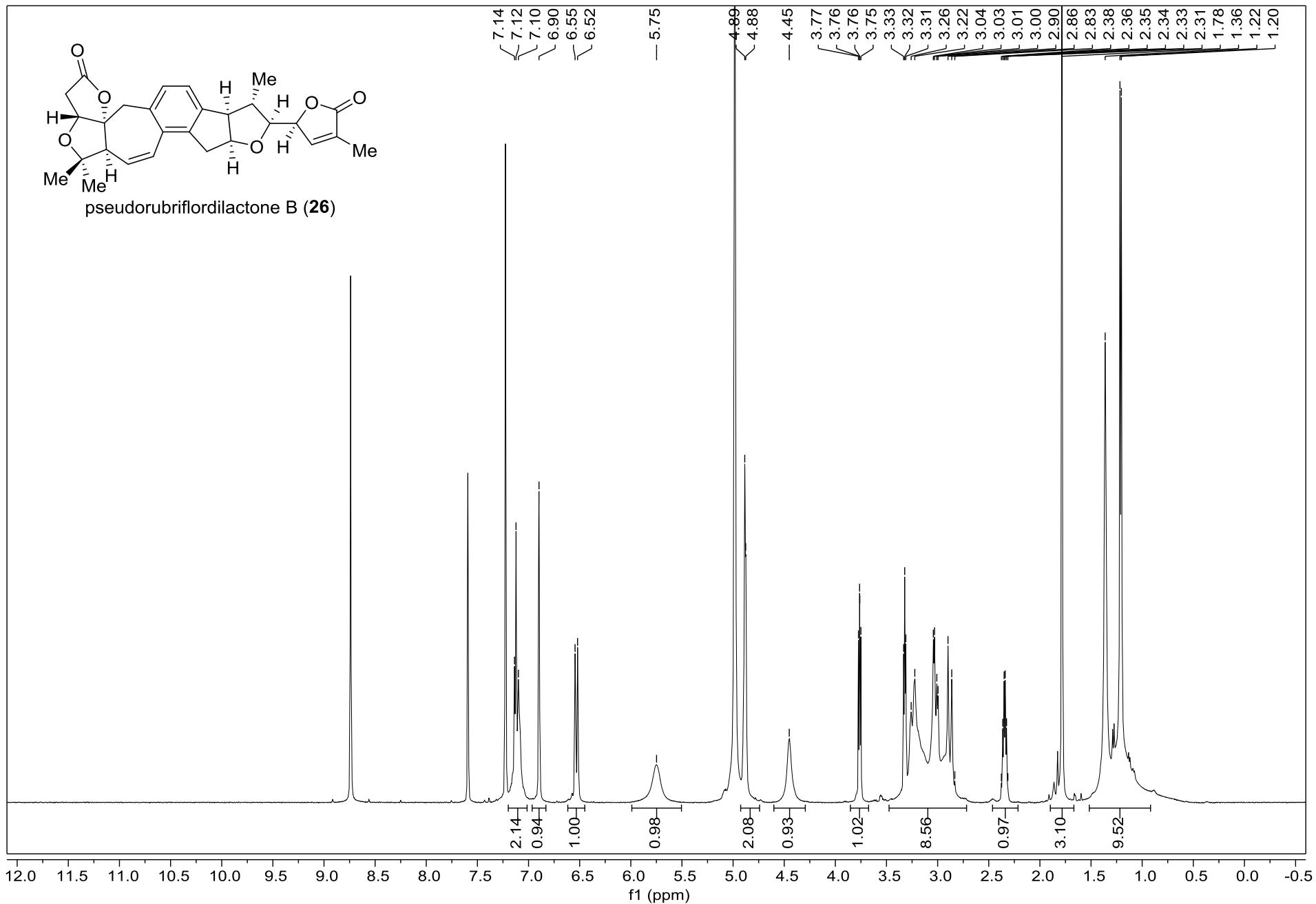
¹³C NMR Spectrum of 26a and 26b (101 MHz, CDCl₃)



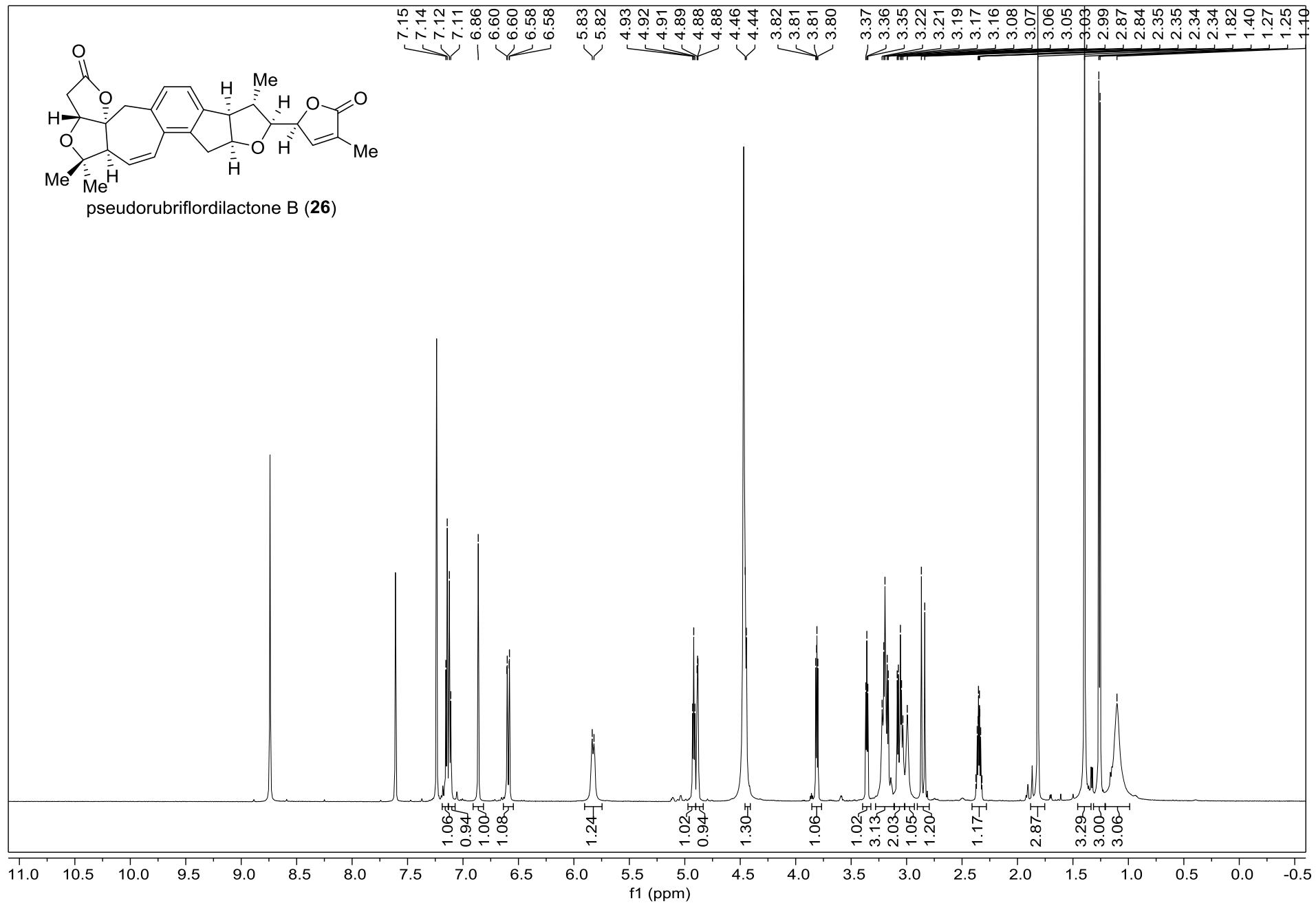
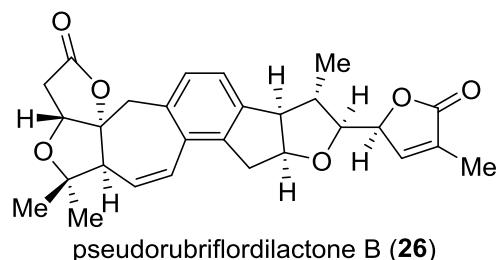
¹H NMR Spectrum of 26 (400 MHz, CDCl₃)



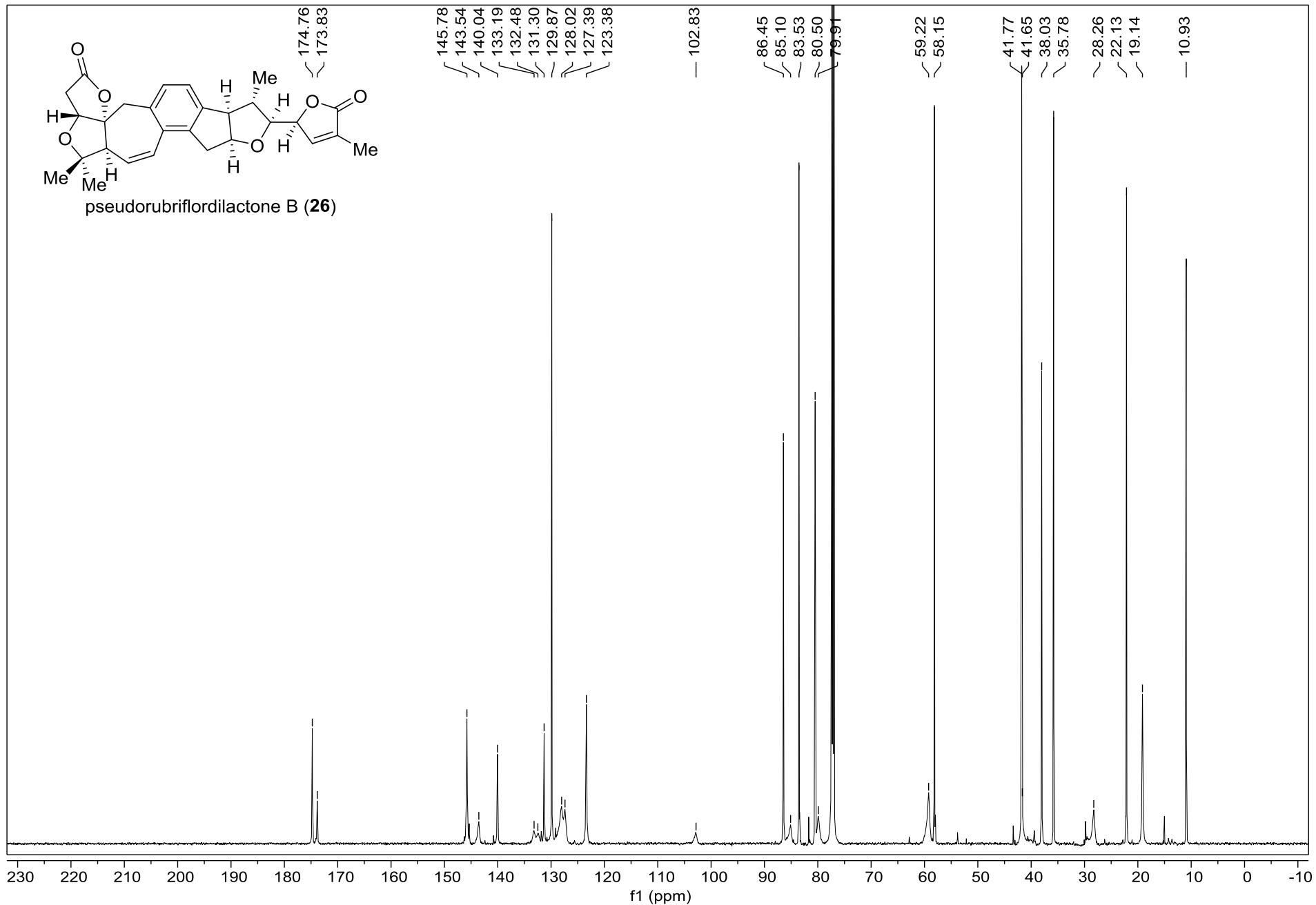
¹H NMR Spectrum of 26 (500 MHz, pyridine-d₅)



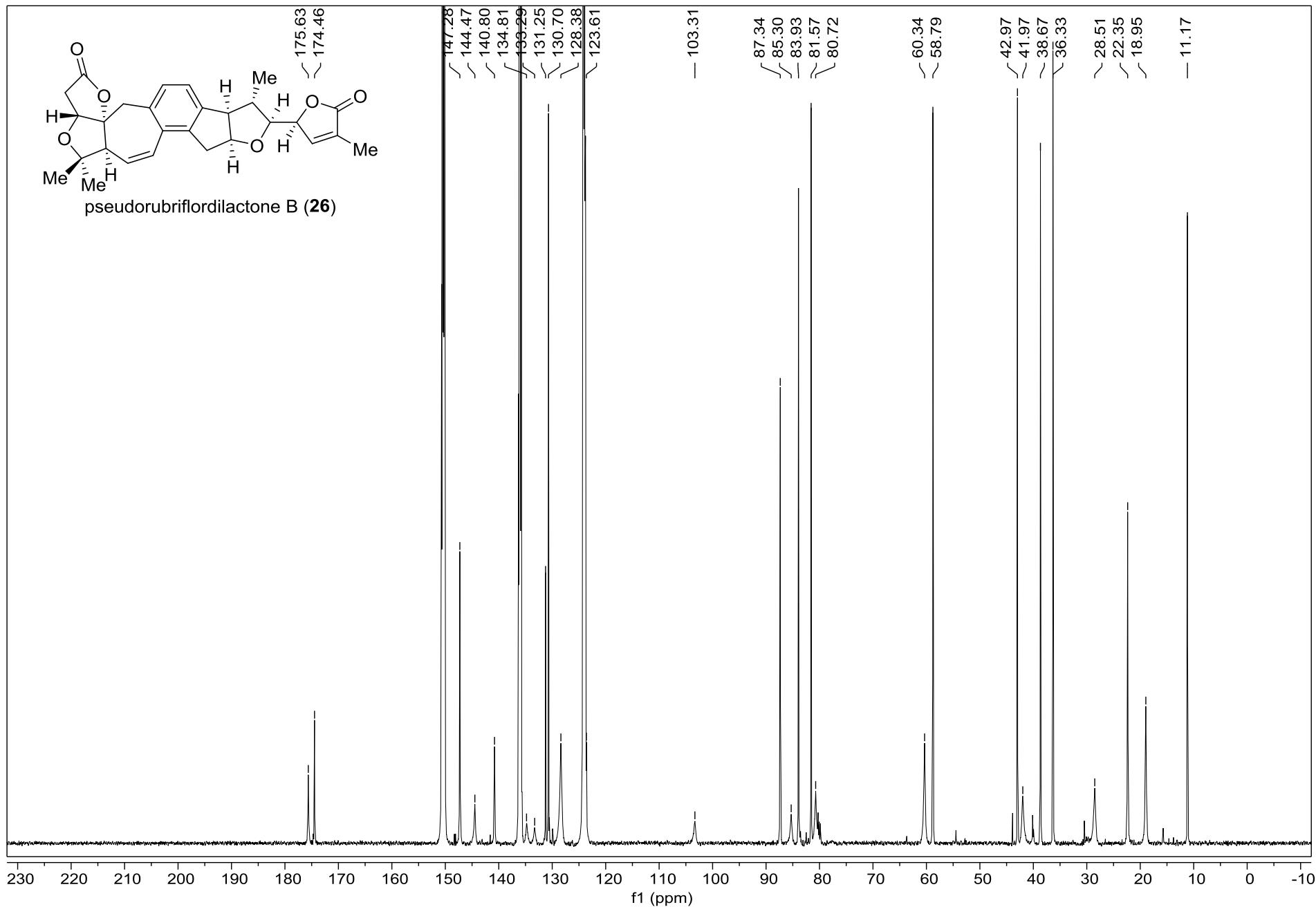
¹H NMR Spectrum of 26 (600 MHz, pyridine-d₅, 60 °C)



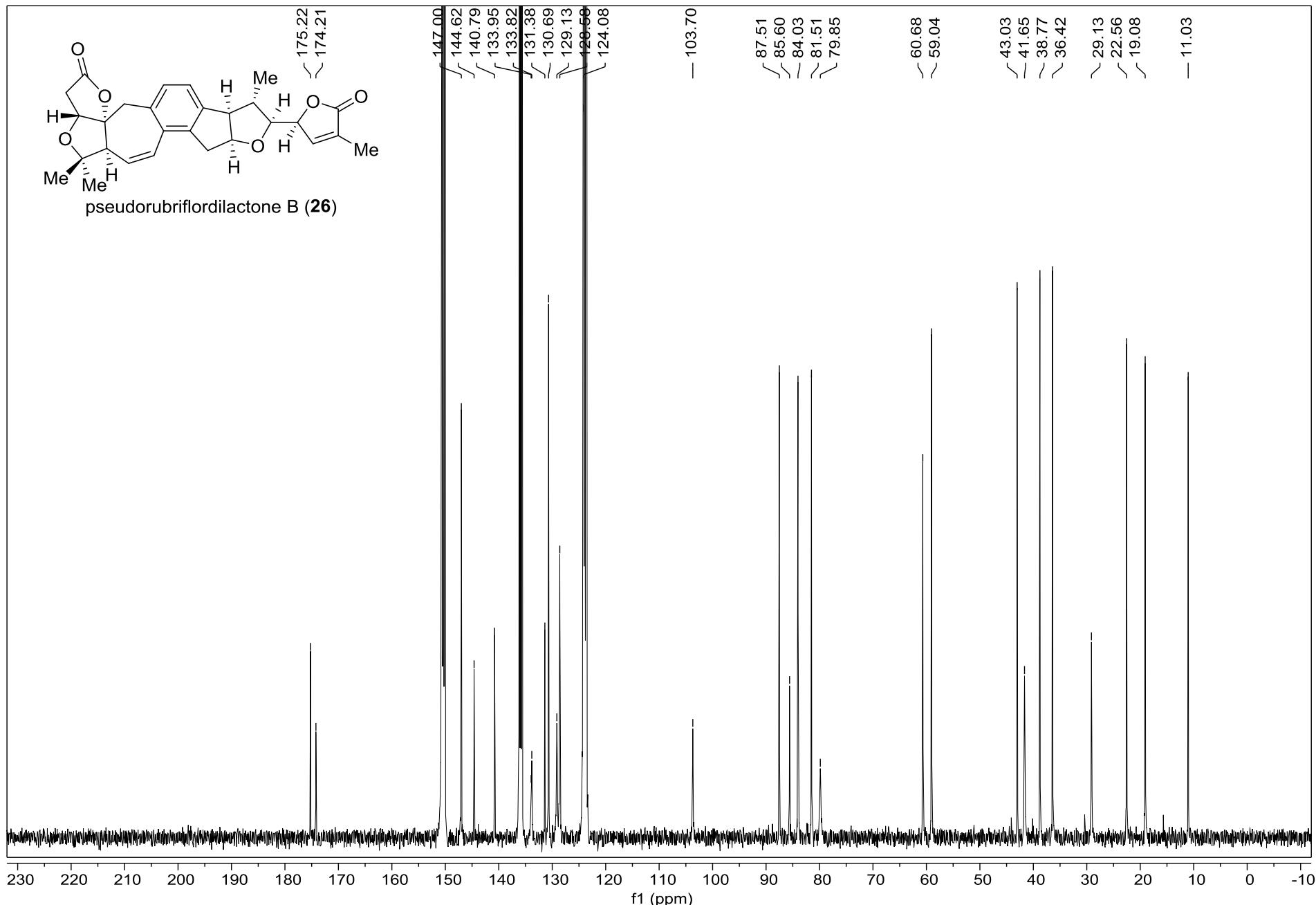
¹³C NMR Spectrum of 26 (151 MHz, CDCl₃)



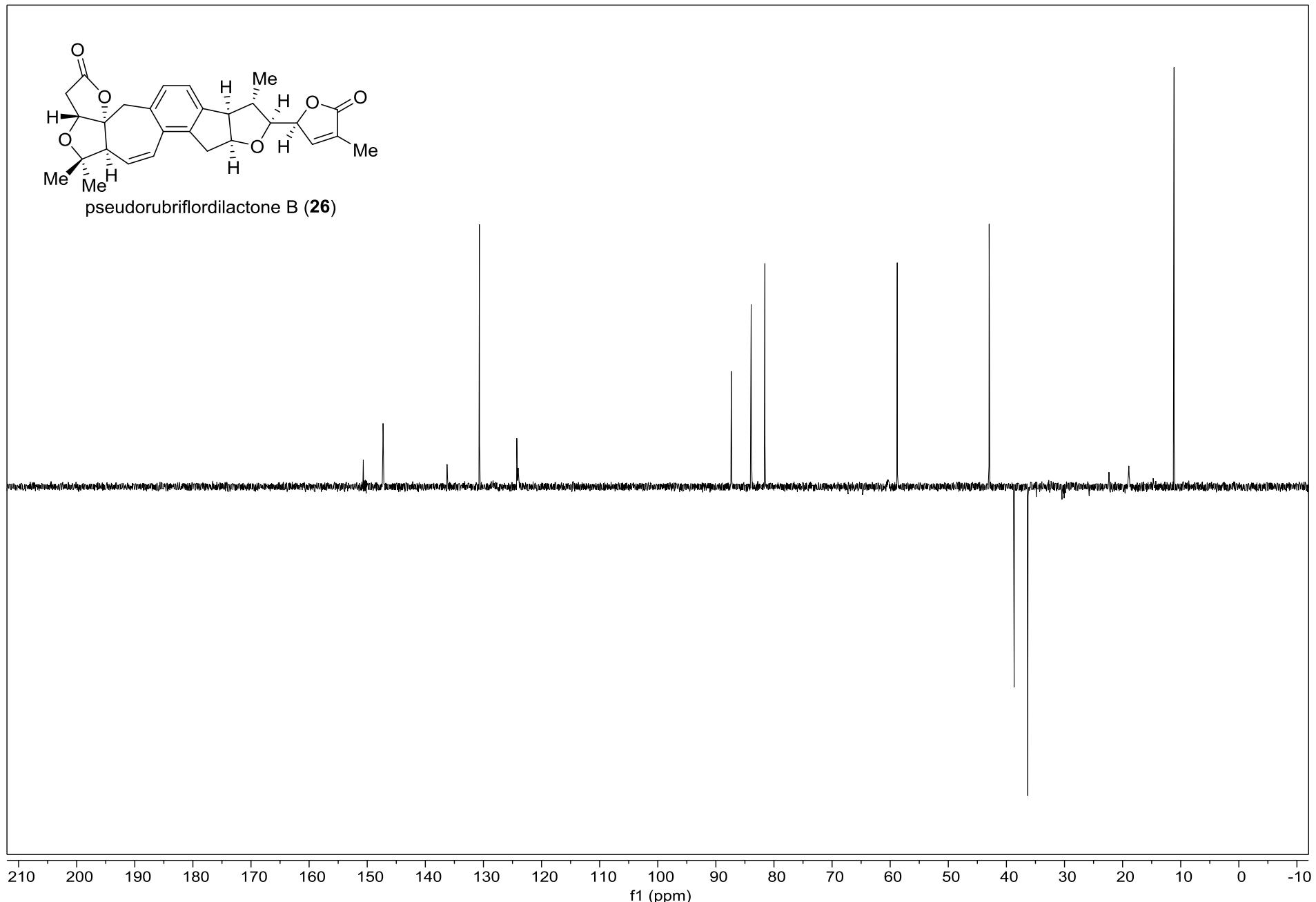
¹³C NMR Spectrum of 26 (151 MHz, pyridine-d₅)



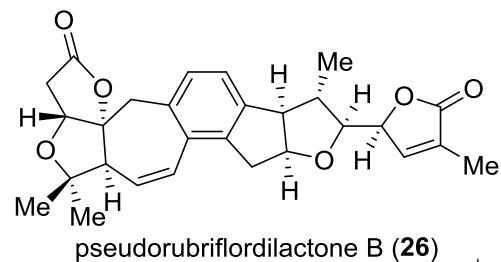
¹³C NMR Spectrum of 26 (101 MHz, pyridine-d₅, 60 °C)



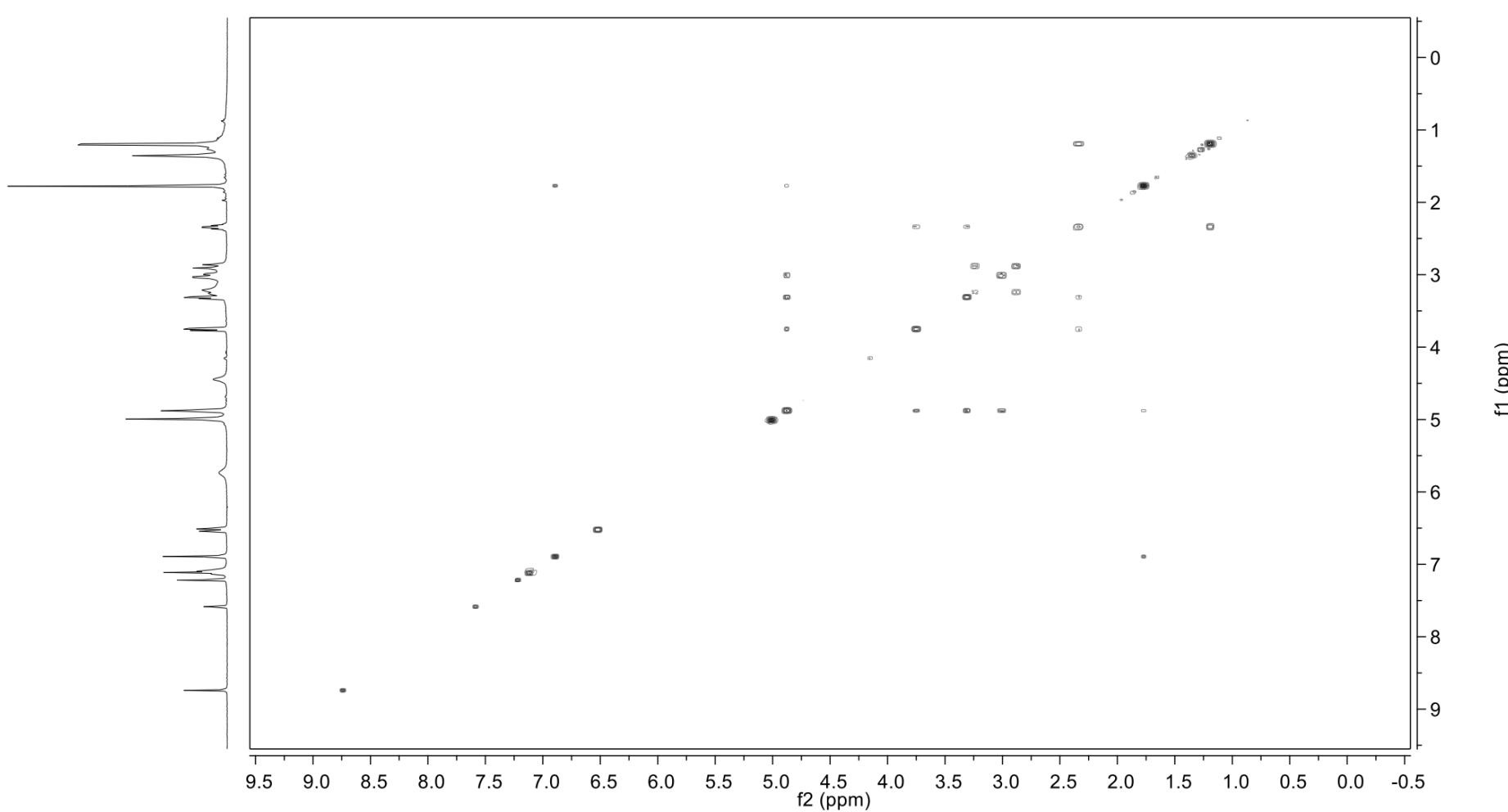
DEPT Spectrum of 26 (151 MHz, pyridine-d₅)



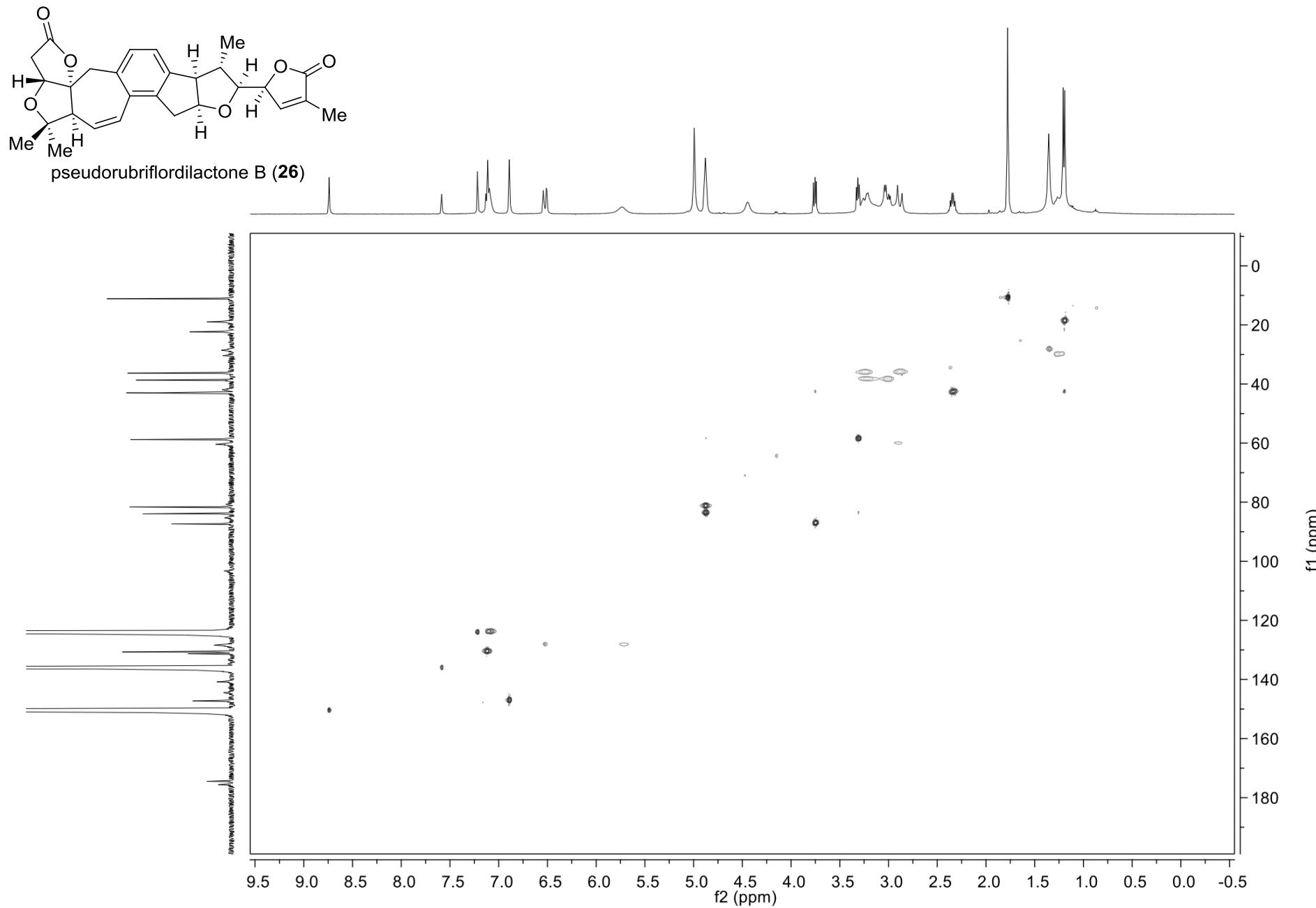
COSY Spectrum of 26 (pyridine-d₅)



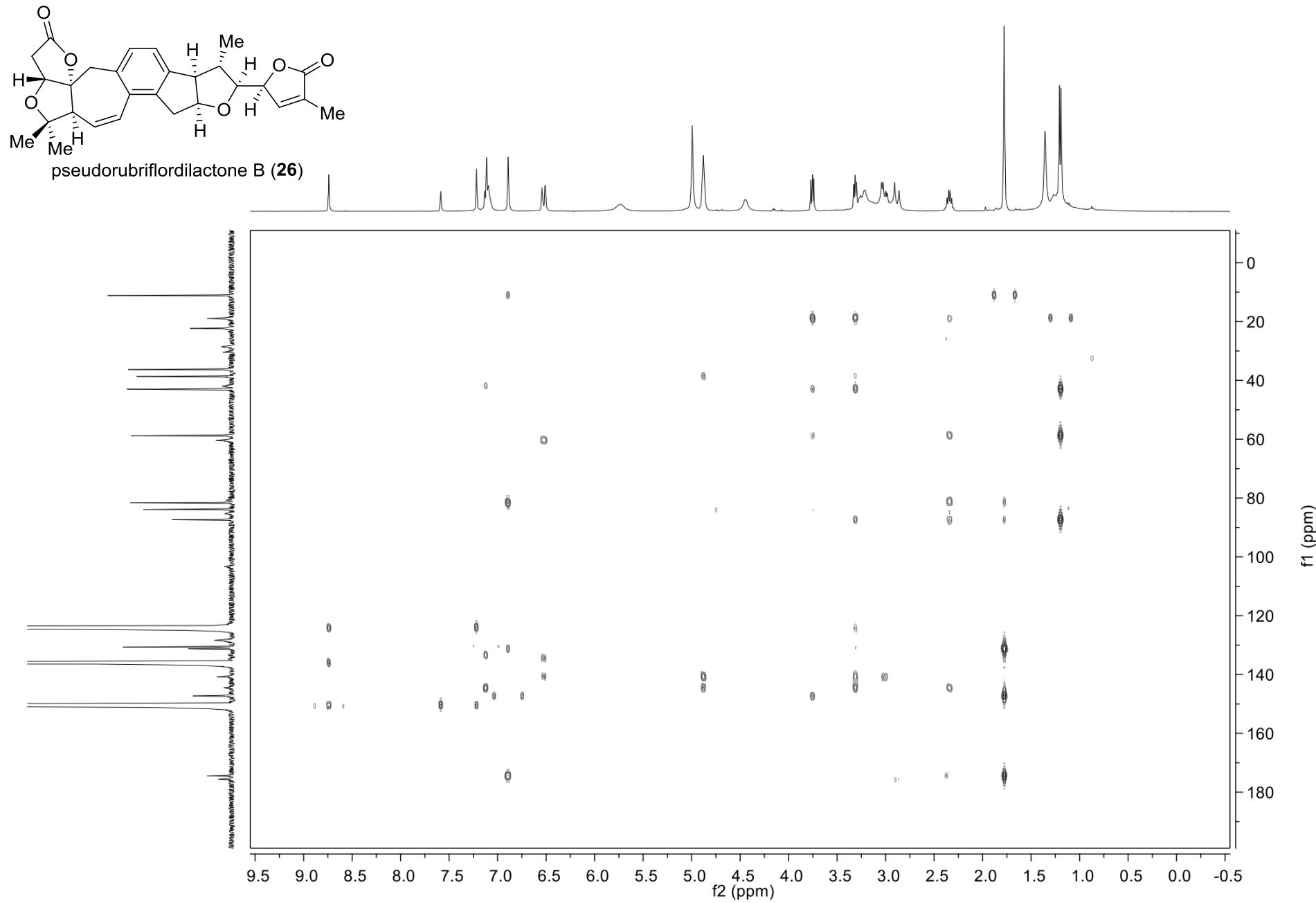
pseudorubrifloridilactone B (26)



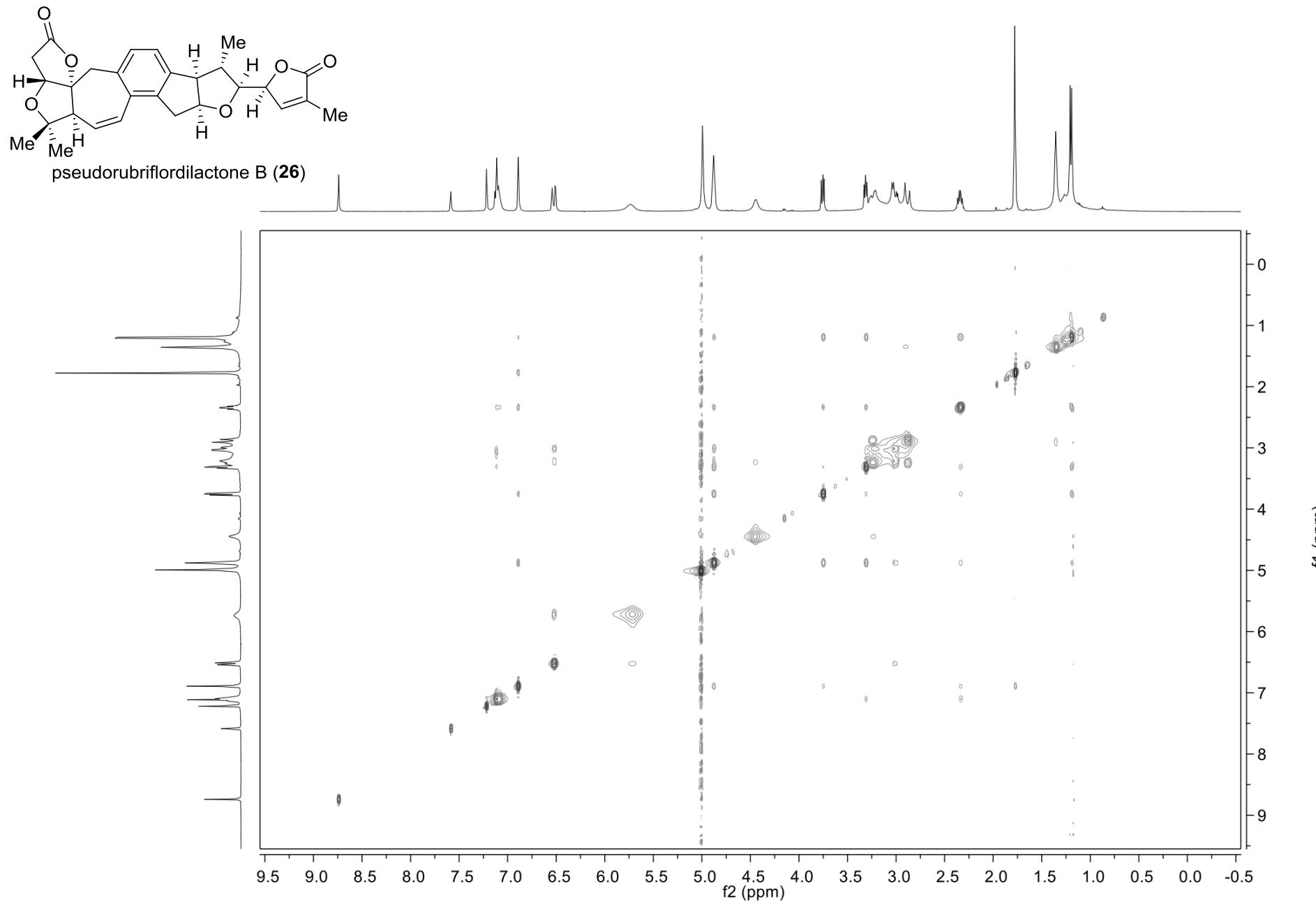
HMBC Spectrum of 26 (pyridine-d₅)



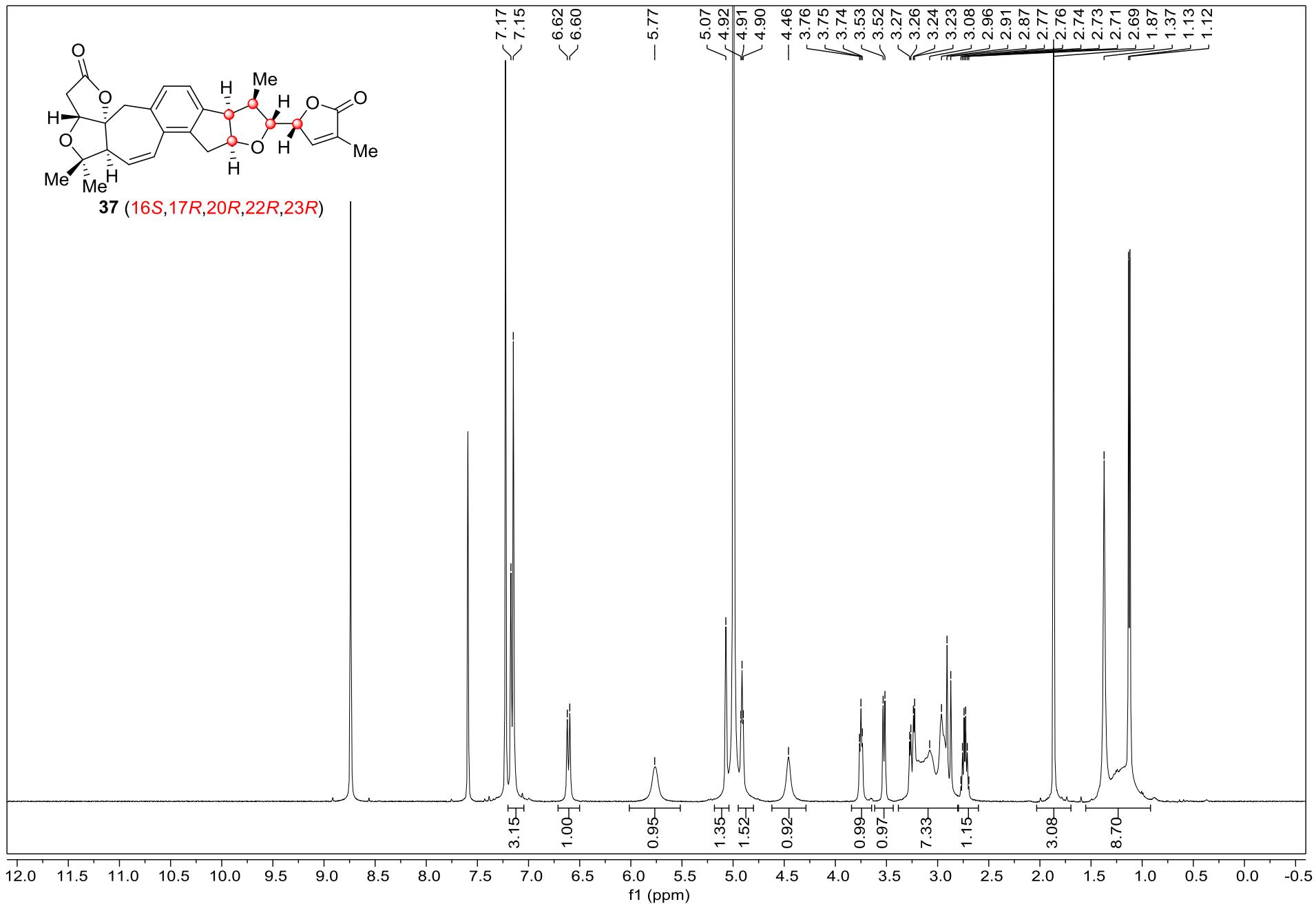
HMBC Spectrum of 26 (pyridine-d₅)



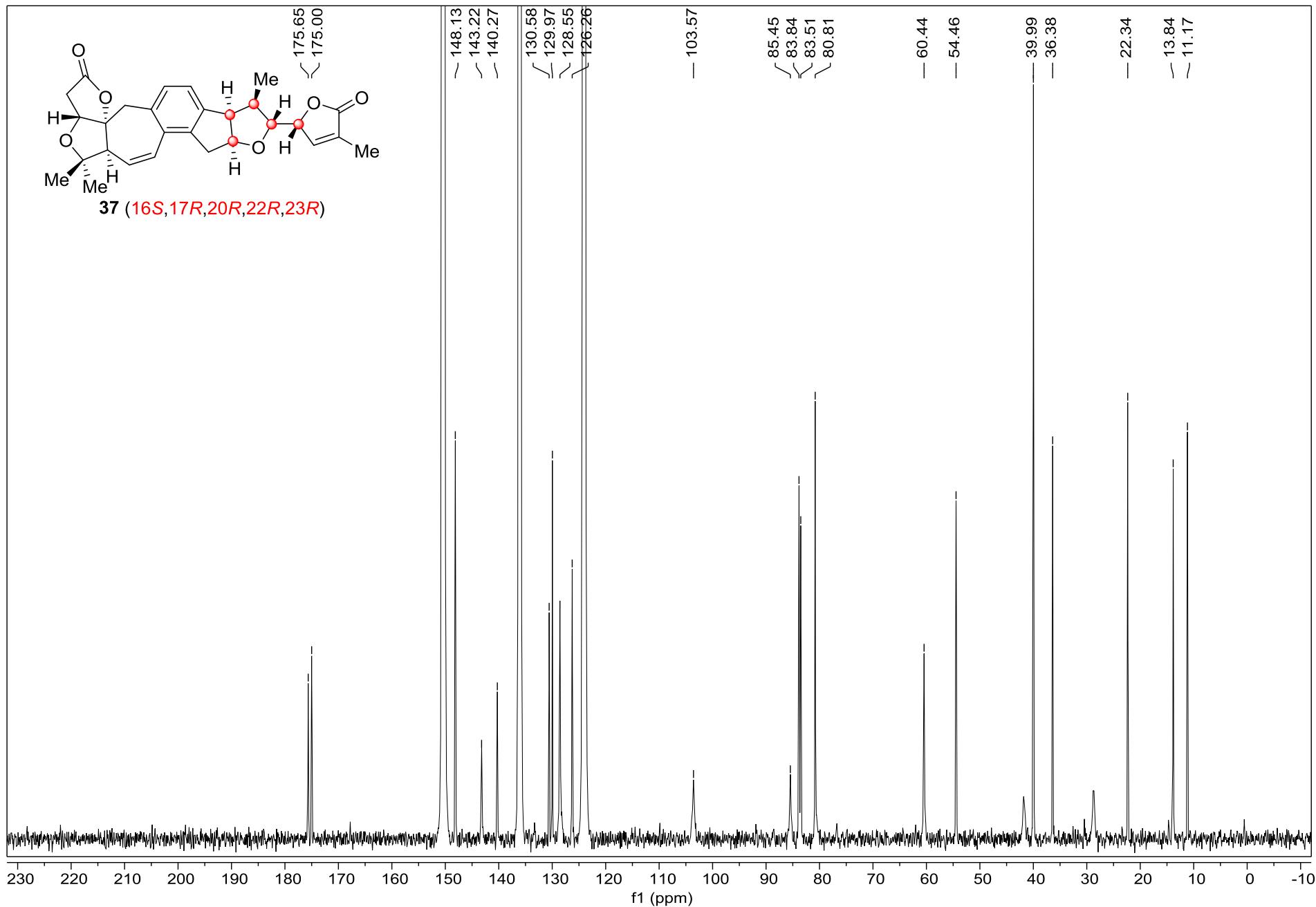
NOESY Spectrum of 26 (pyridine-d₅)



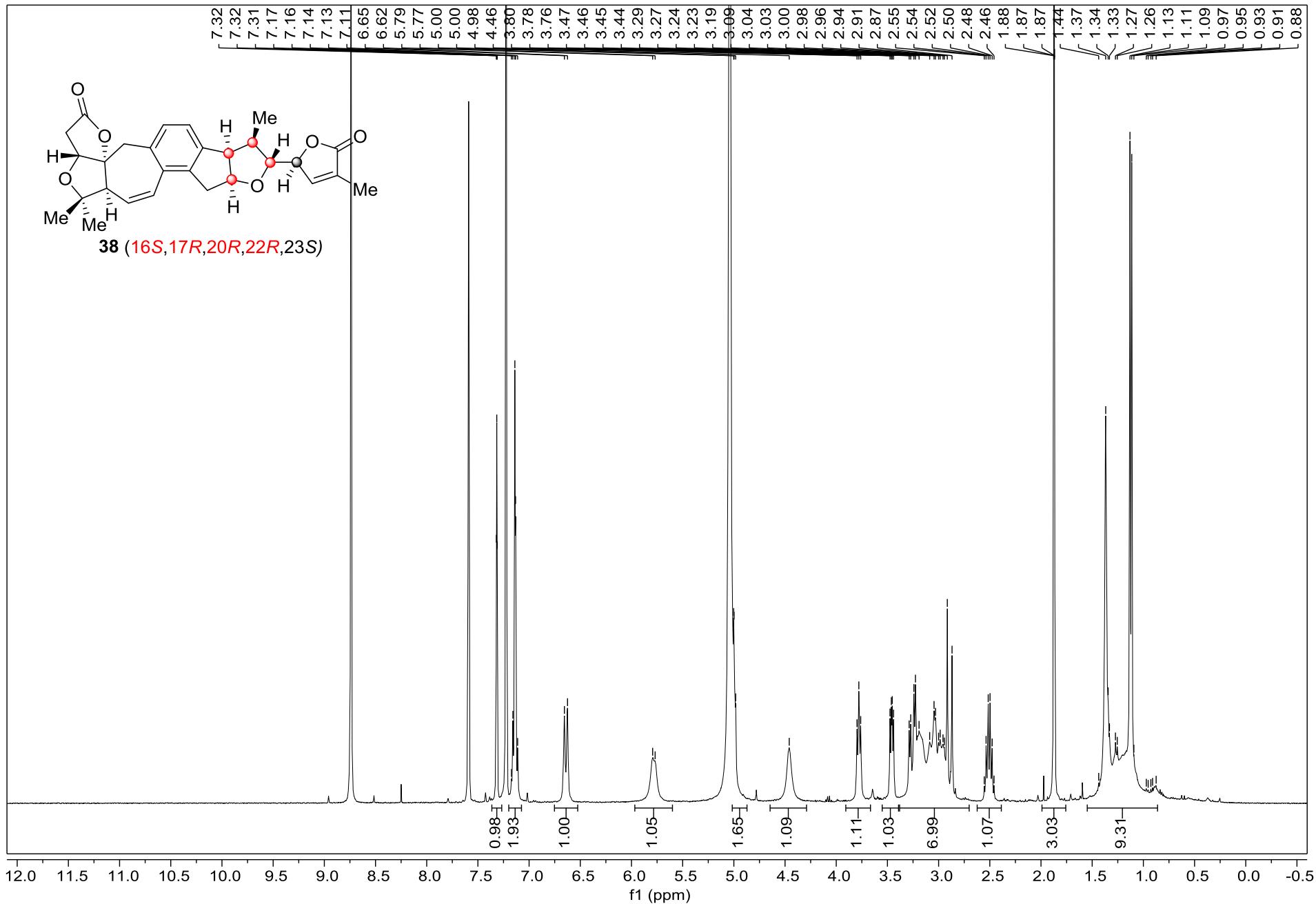
¹H NMR Spectrum of 37 (500 MHz, pyridine-d₅)



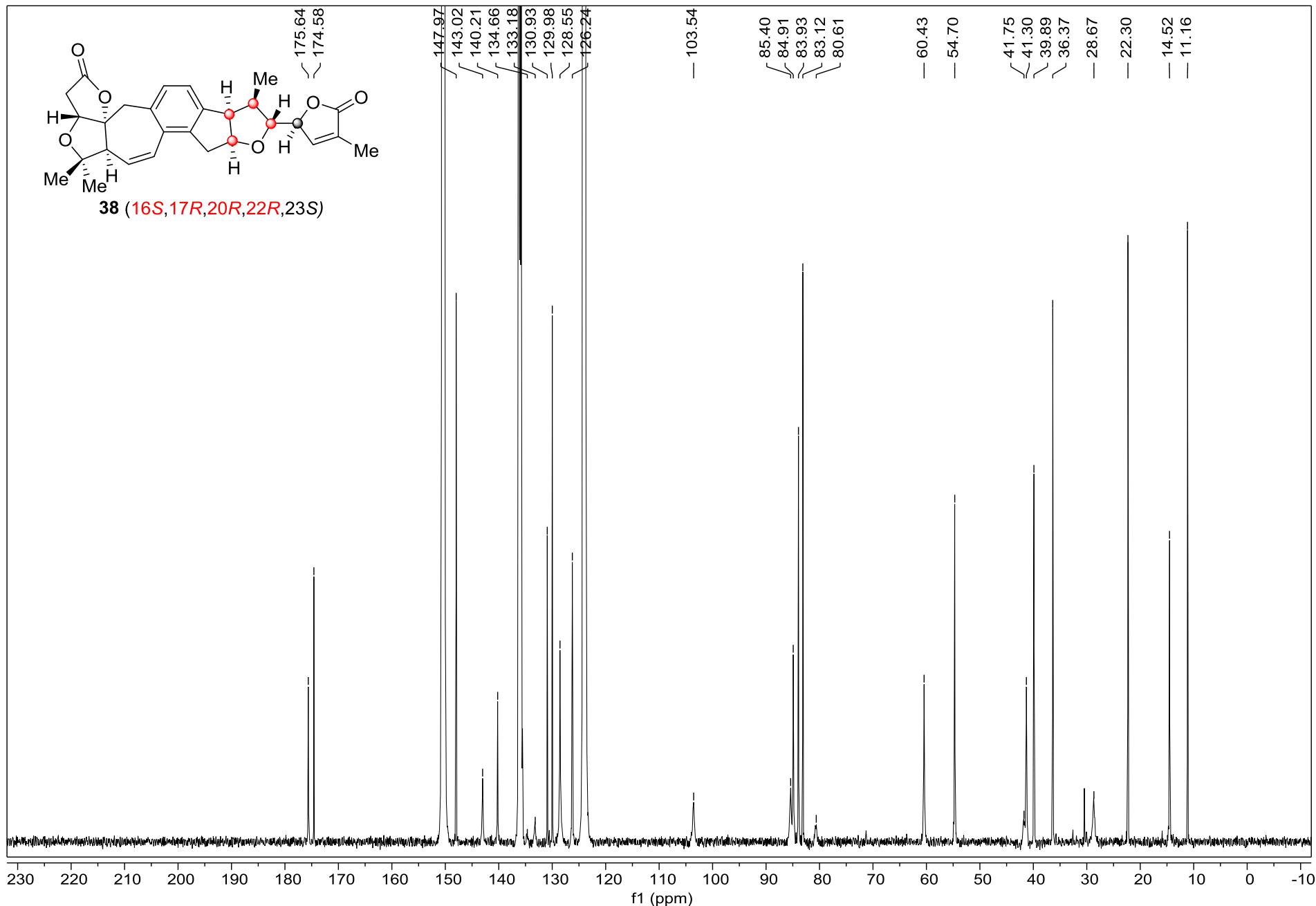
¹³C NMR Spectrum of 37 (126 MHz, pyridine-d₅)



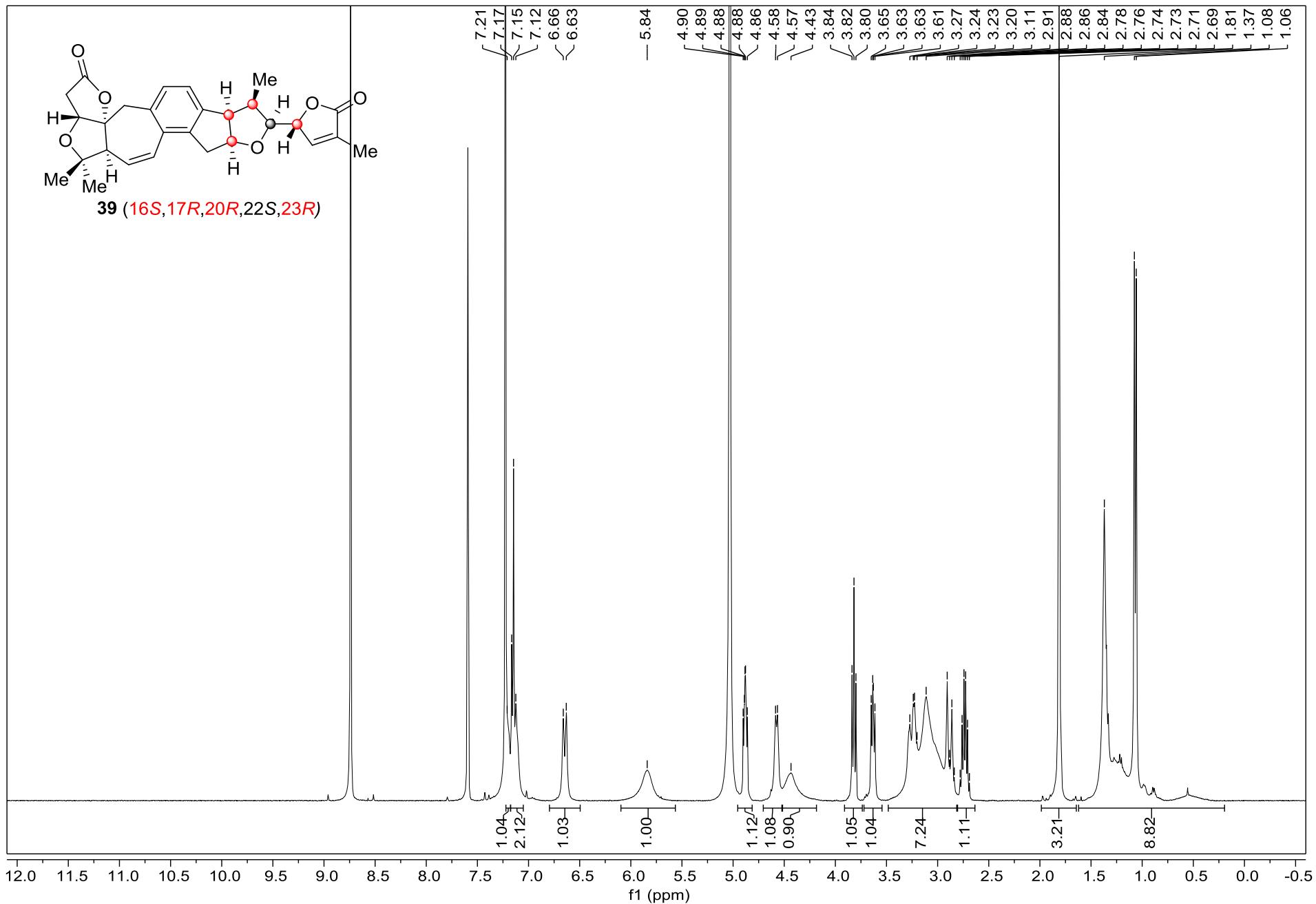
¹H NMR Spectrum of 38 (400 MHz, pyridine-d₅)



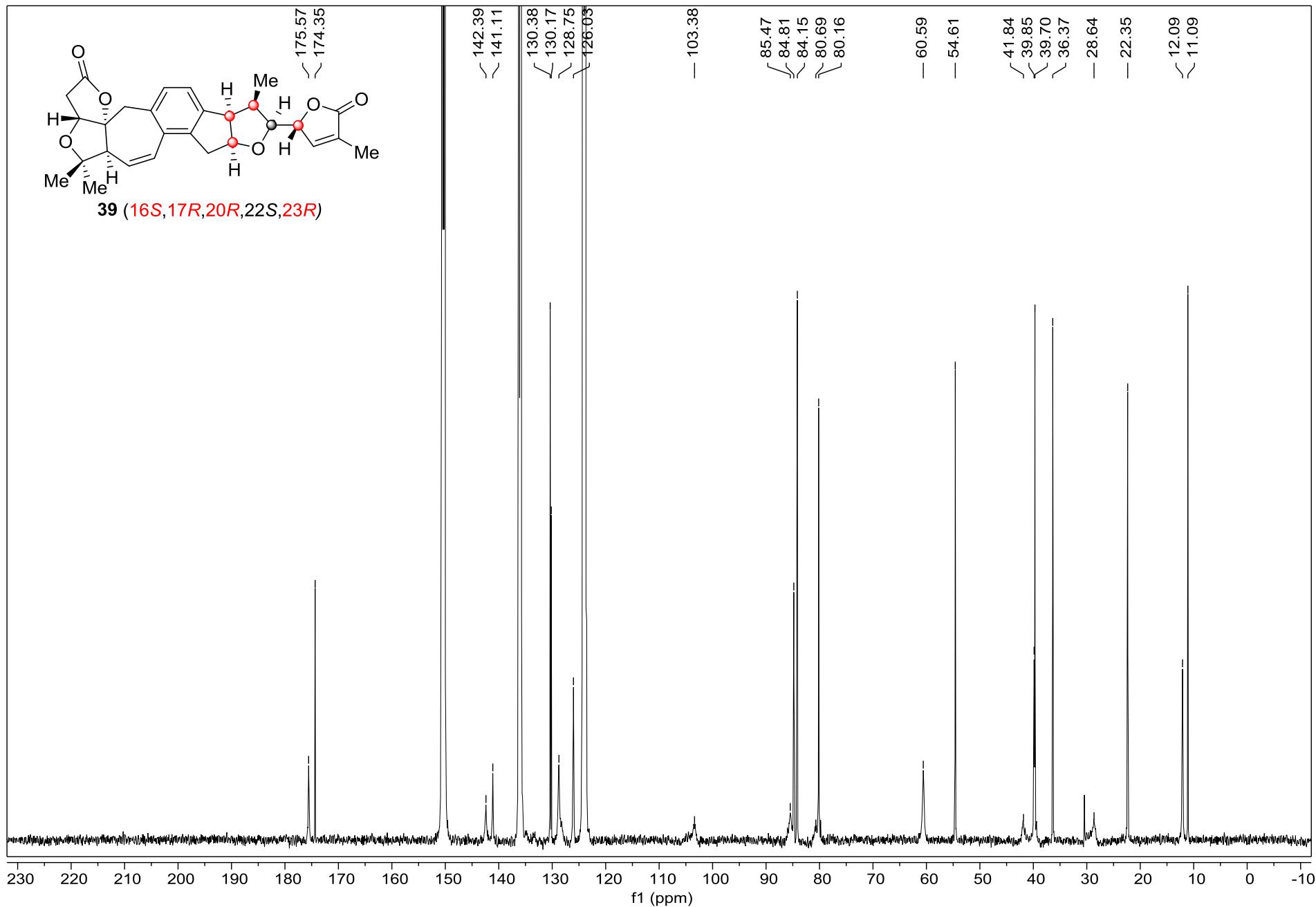
¹³C NMR Spectrum of 38 (126 MHz, pyridine-d₅)



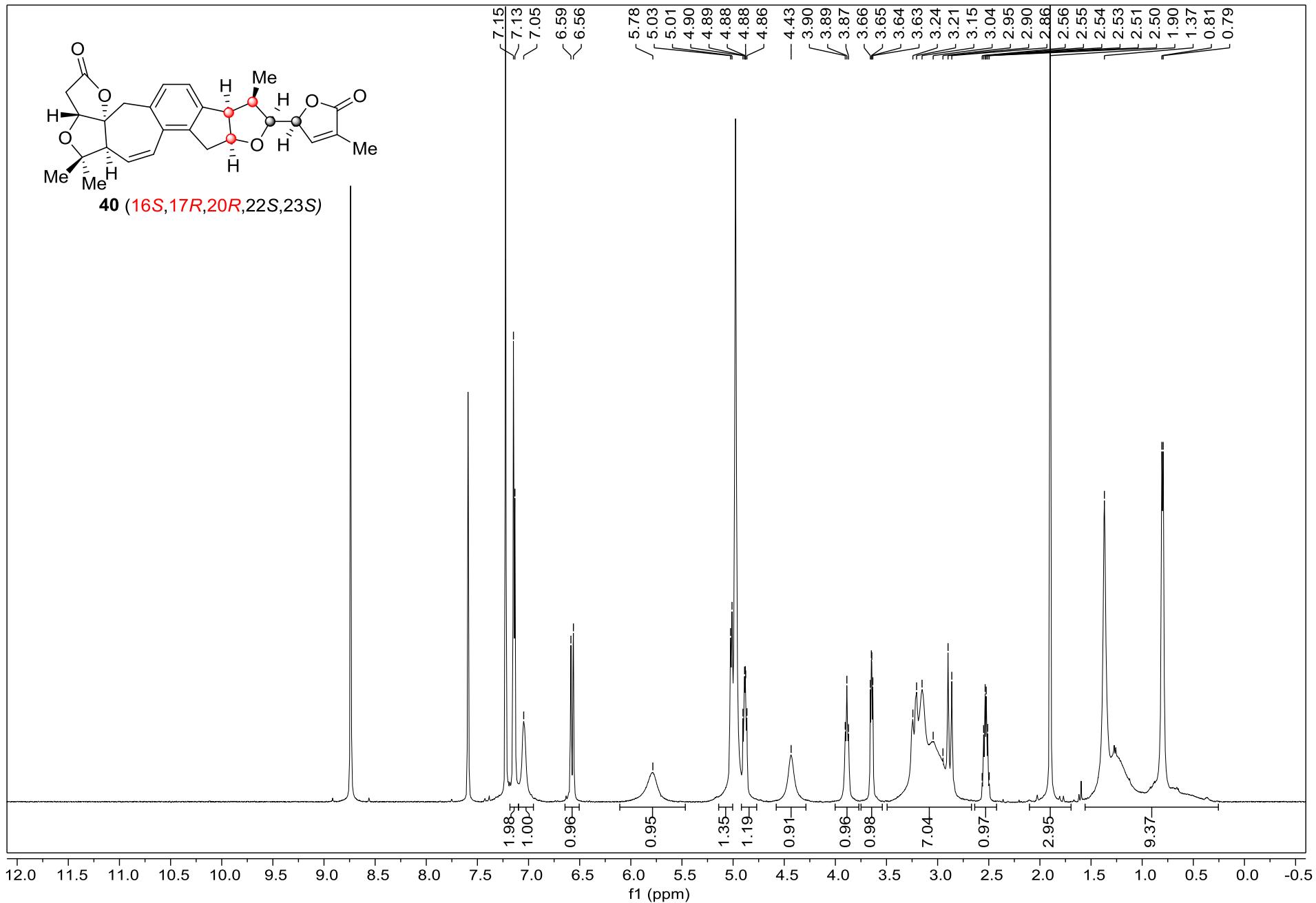
¹H NMR Spectrum of 39 (400 MHz, pyridine-d₅)



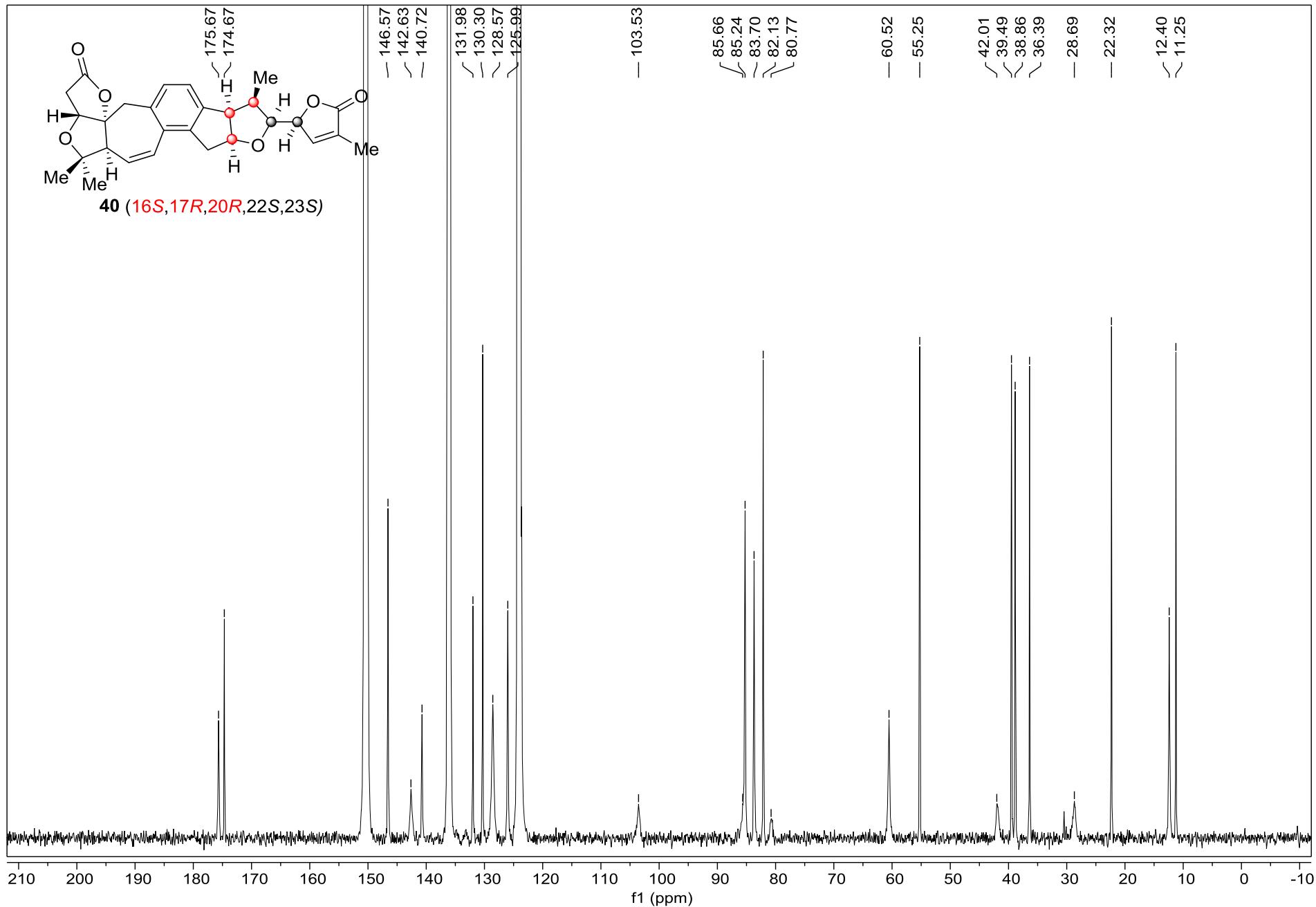
¹³C NMR Spectrum of 39 (126 MHz, pyridine-d₅)



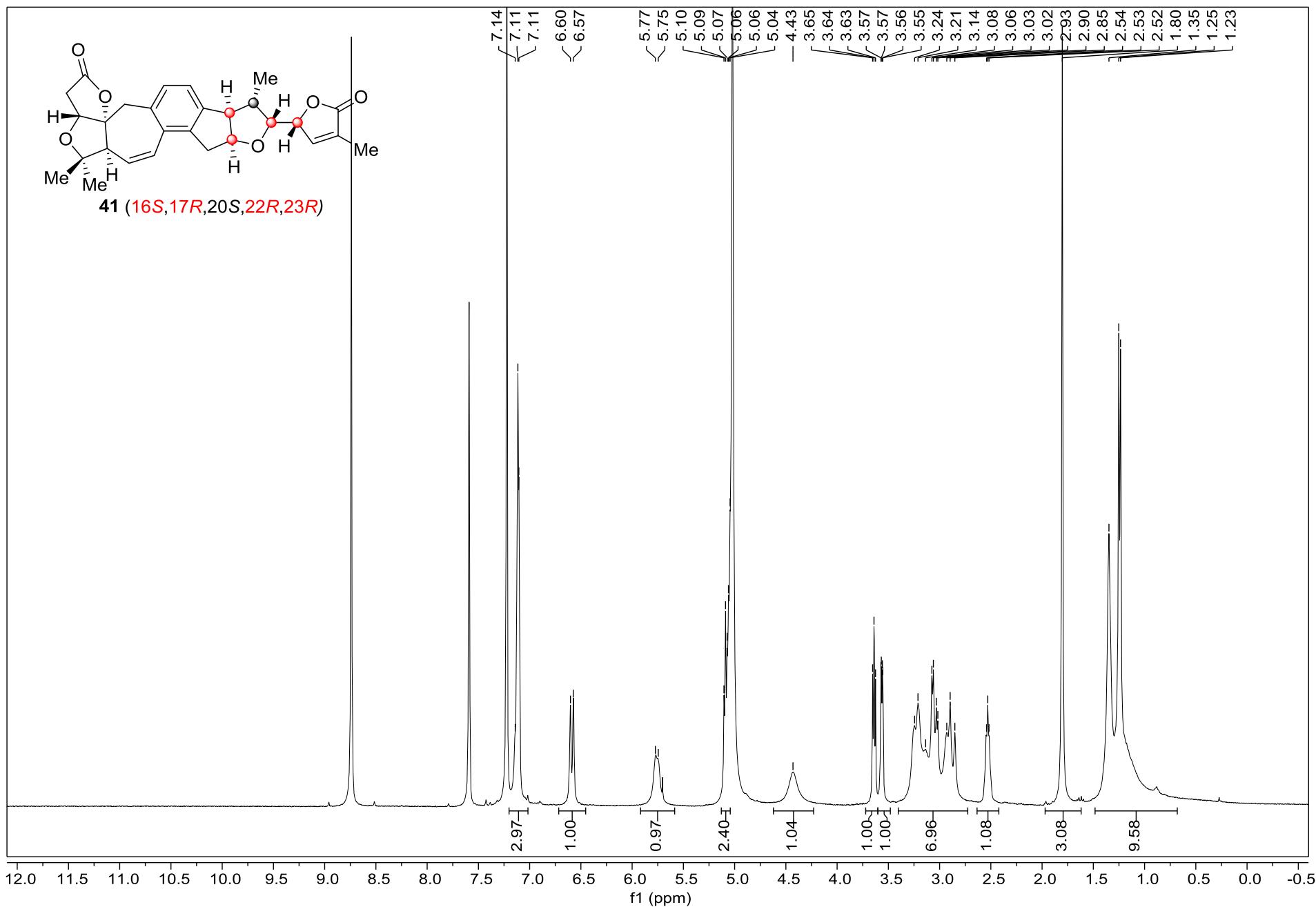
¹H NMR Spectrum of 40 (500 MHz, pyridine-d₅)



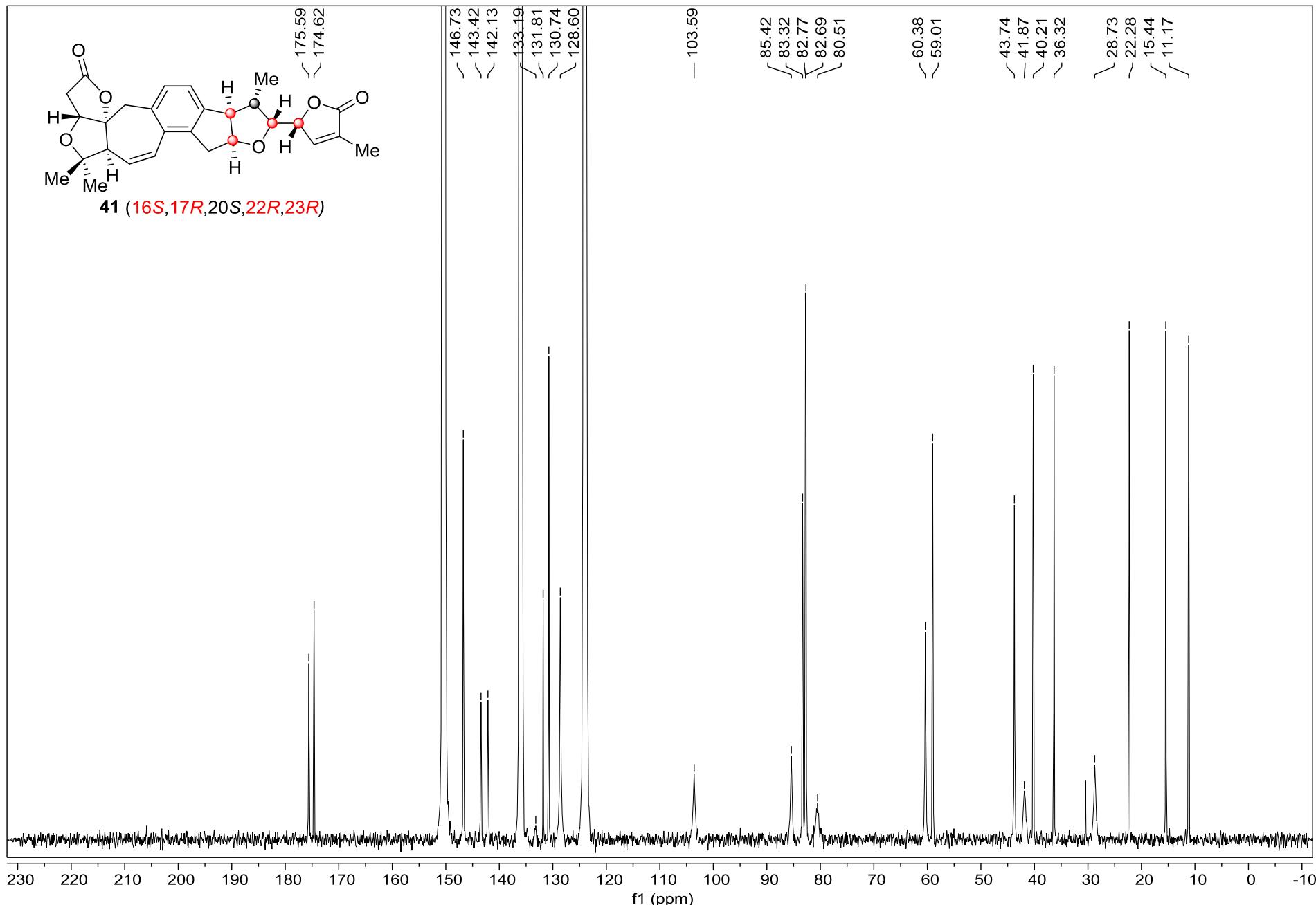
¹³C NMR Spectrum of 40 (126 MHz, pyridine-d₅)



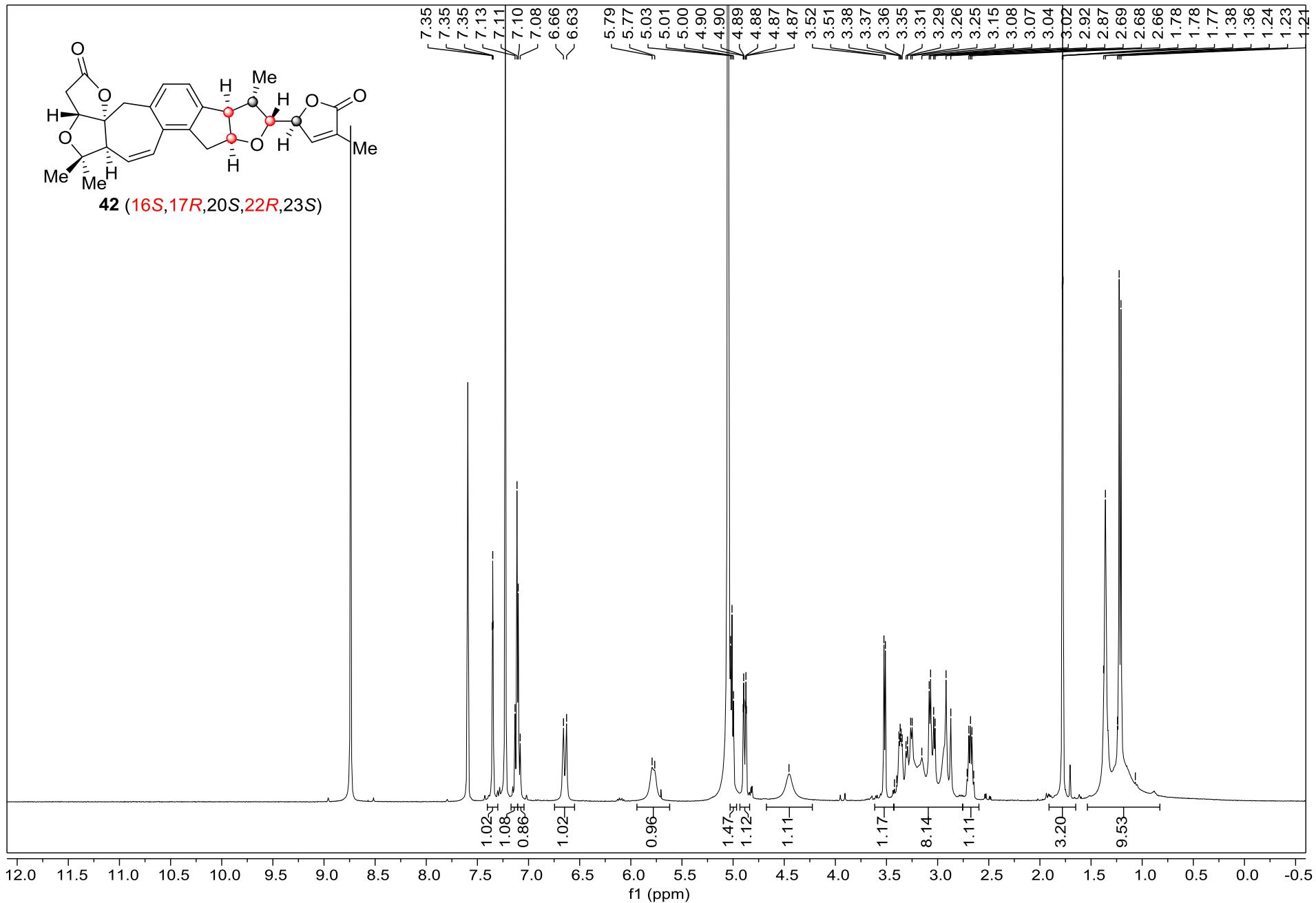
¹H NMR Spectrum of 41 (400 MHz, pyridine-d₅)



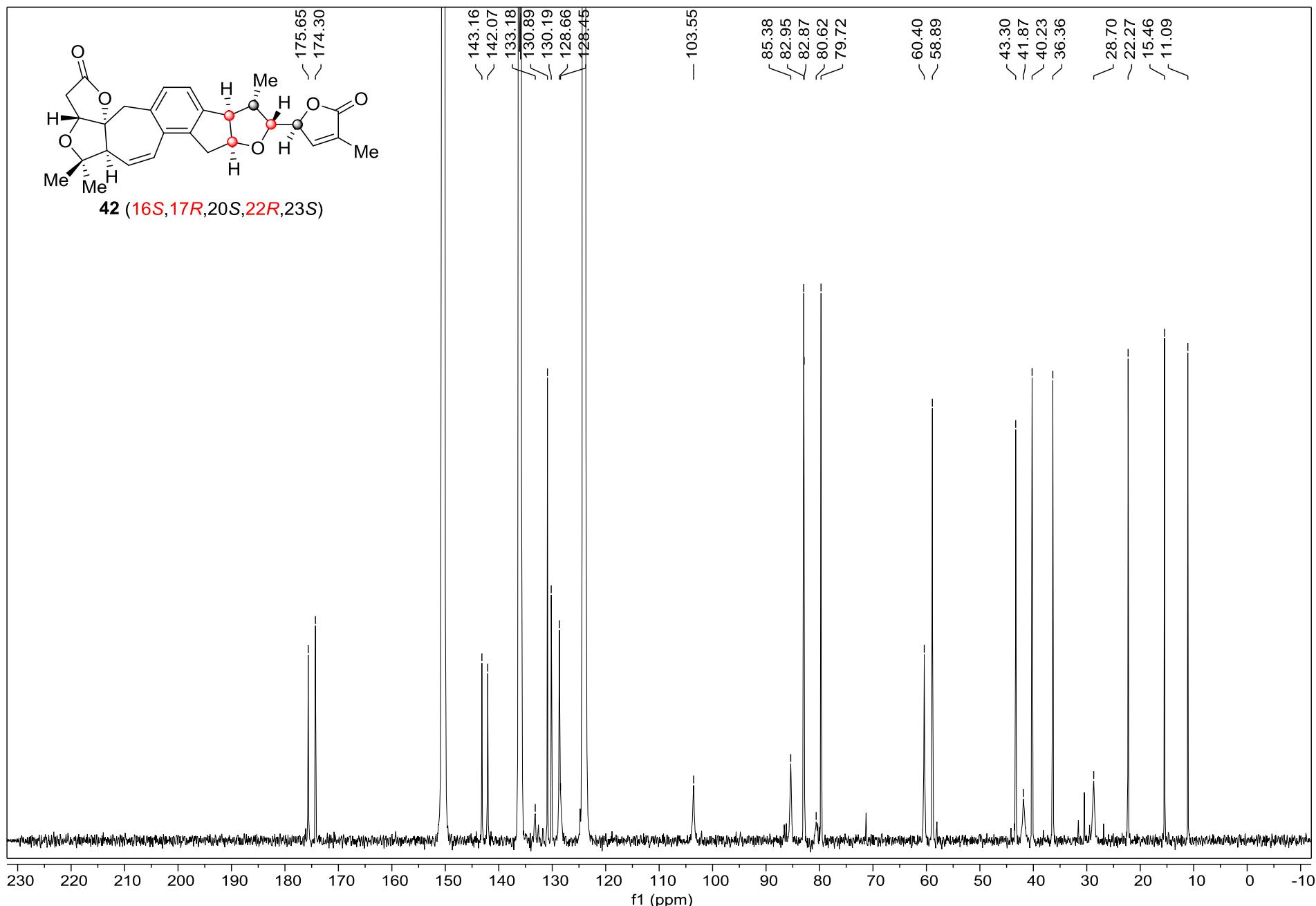
¹³C NMR Spectrum of 41 (126 MHz, pyridine-d₅)



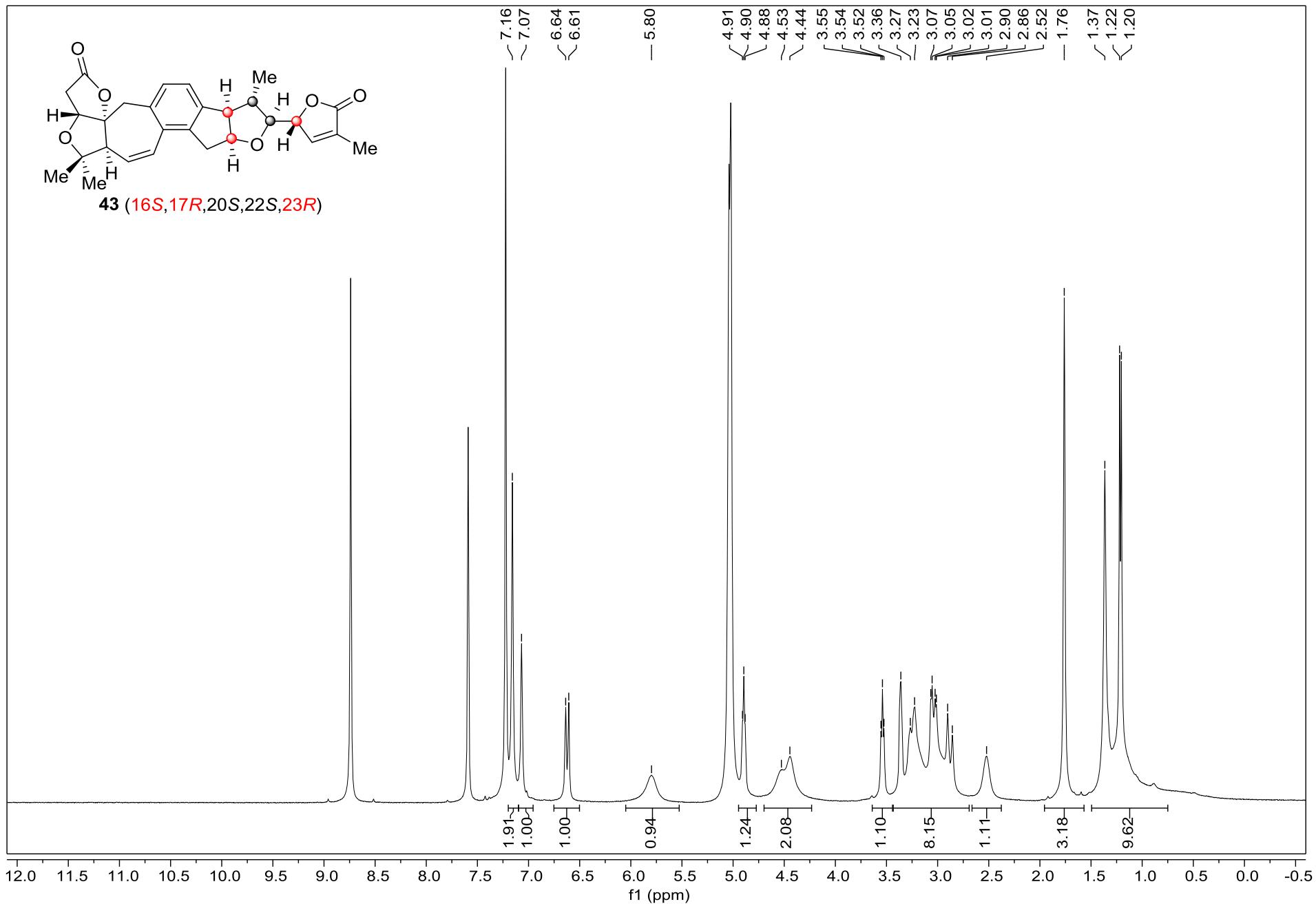
¹H NMR Spectrum of 42 (400 MHz, pyridine-d₅)



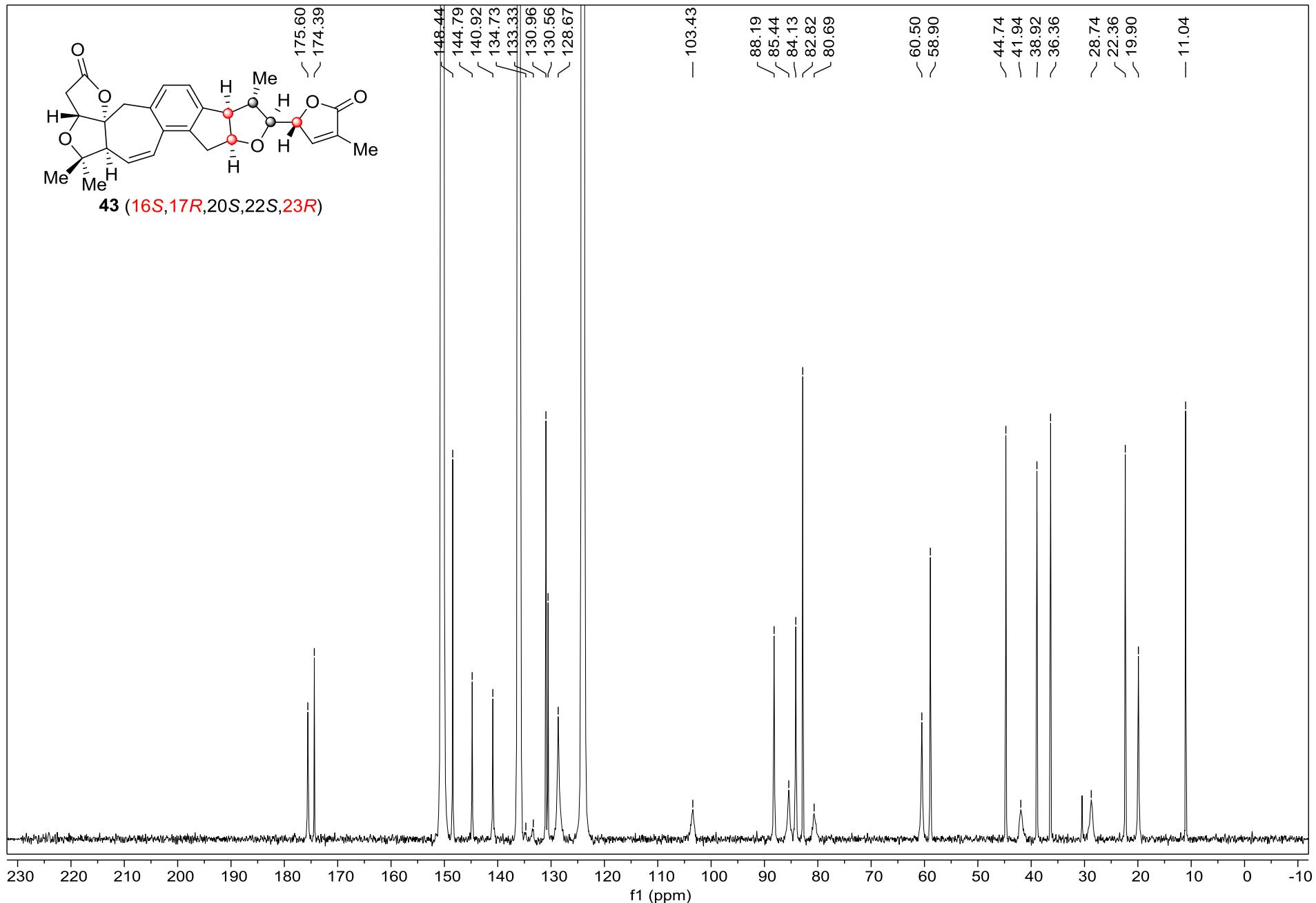
¹³C NMR Spectrum of 42 (126 MHz, pyridine-d₅)



¹H NMR Spectrum of 43 (400 MHz, pyridine-d₅)

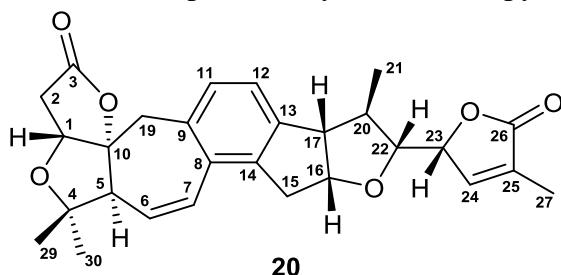


¹³C NMR Spectrum of 43 (126 MHz, pyridine-d₅)



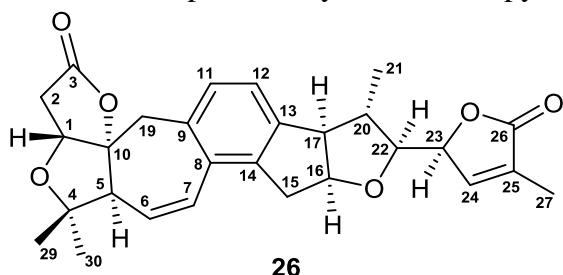
V Assignment of ^1H and ^{13}C NMR Spectra of Synthetic **20** and **26**

Table S1. Assignment of ^1H and ^{13}C NMR spectra of synthetic **20** in pyridine-d₅.



Carbon number	δ_{H} [ppm, mult, J (Hz)]	δ_{C} (ppm)
1	4.41 (br s)	80.55
2 α	3.36–2.78 (m, overlapped)	36.34
2 β	2.85 (d, 18.3)	—
3	—	175.41
4	—	85.37
5	3.36–2.78 (m, overlapped)	60.31
6	5.77 (br s)	128.79
7	6.57 (d, 12.1)	128.27
8	—	133.30
9	—	134.60
10	—	103.70
11	7.14 (d, 7.5)	130.66
12	7.07 (br s)	124.35
13	—	144.17
14	—	140.61
15 α	3.36–2.78 (m, overlapped)	38.56
15 β	3.36–2.78 (m, overlapped)	—
16	4.88 (dd, 6.0, 6.0)	84.14
17	3.36–2.78 (m, overlapped)	58.89
19 α	3.36–2.78 (m, overlapped)	42.10
19 β	3.36–2.78 (m, overlapped)	—
20	2.22 (br s)	42.10
21	1.19 (3 H, d, 6.5)	19.55
22	3.83 (br s)	87.55

23	4.92 (br s)	81.69
24	6.70–6.43 (m)	147.19
25	–	131.48
26	–	174.42
27	1.85 (3 H, s)	11.24
29	1.36 (3 H, s)	28.79
30	1.45–1.01 (3 H, m)	22.50

Table S2. Assignment of ^1H and ^{13}C NMR spectra of synthetic **26** in pyridine-d₅.

Carbon number	δ_{H} [ppm, mult, <i>J</i> (Hz)]	δ_{C} (ppm)
1	4.45 (br s)	80.72
2 α	3.41–2.81 (m, overlapped)	36.33
2 β	2.88 (d, 18.3)	—
3	—	175.63
4	—	85.30
5	3.41–2.81 (m, overlapped)	60.34
6	5.75 (br s)	128.38
7	6.53 (d, 12.2)	128.38
8	—	133.29
9	—	134.81
10	—	103.31
11	7.13 (d, 7.4)	130.70
12	7.10 (br s)	123.61
13	—	144.47
14	—	140.80
15 α	3.41–2.81 (m, overlapped)	38.67
15 β	3.41–2.81 (m, overlapped)	—
16	4.92–4.84 (m, overlapped)	83.93
17	3.41–2.81 (m, overlapped)	58.79
19 α	3.41–2.81 (m, overlapped)	41.97
19 β	3.41–2.81 (m, overlapped)	—
20	2.39–2.29 (m)	42.97
21	1.21 (3 H, d, 6.8)	18.95
22	3.76 (dd, 6.6, 5.3)	87.34
23	4.92–4.84 (m, overlapped)	81.57

24	6.90 (s)	147.28
25	—	131.25
26	—	174.46
27	1.78 (3 H, s)	11.17
29	1.36 (3 H, s)	28.51
30	1.45–1.01 (3 H, m)	22.35

VI Comparison of the ^{13}C NMR Spectra of Authentic Pseudorubrifordilactone B and Synthetic 26

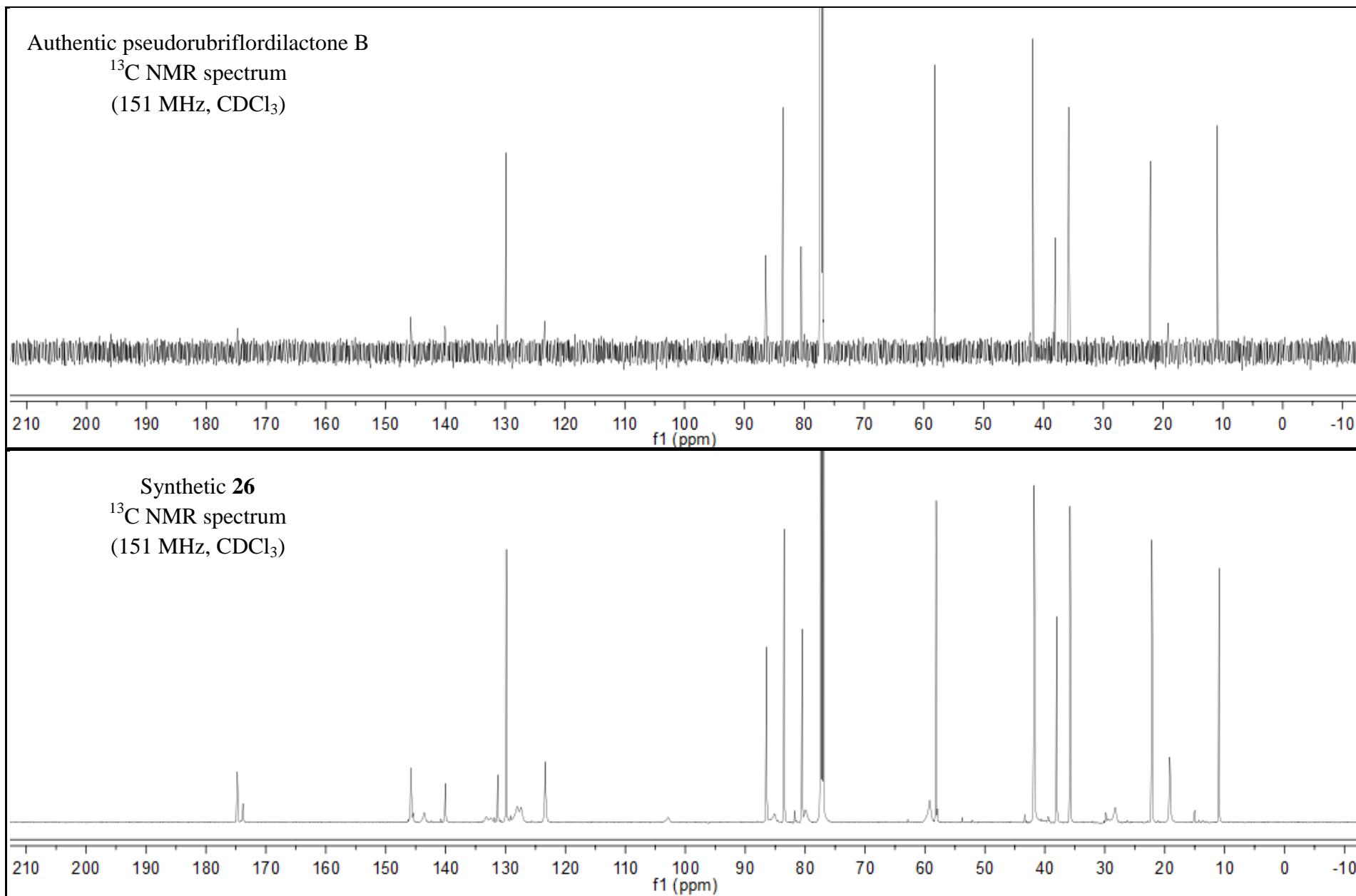
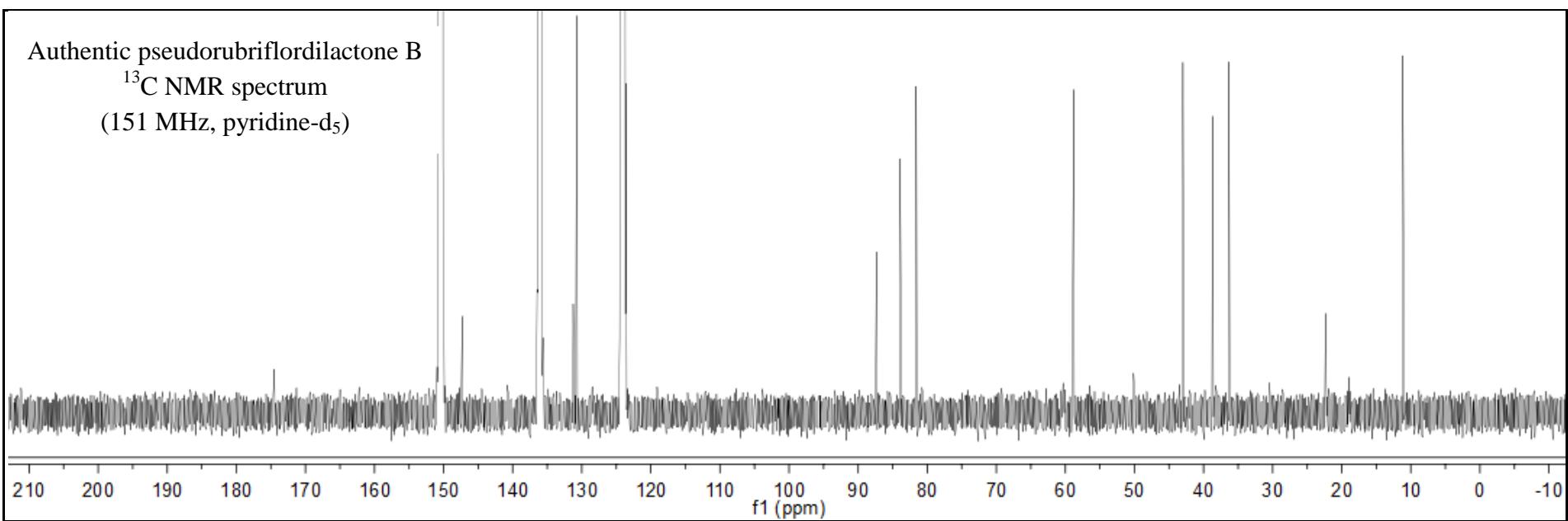


Figure S2. Comparison of the ^{13}C NMR spectra (CDCl_3) of authentic pseudorubrifordilactone B and synthetic 26.

Authentic pseudorubrifloridilactone B
 ^{13}C NMR spectrum
(151 MHz, pyridine-d₅)



Synthetic **26**
 ^{13}C NMR spectrum
(151 MHz, pyridine-d₅)

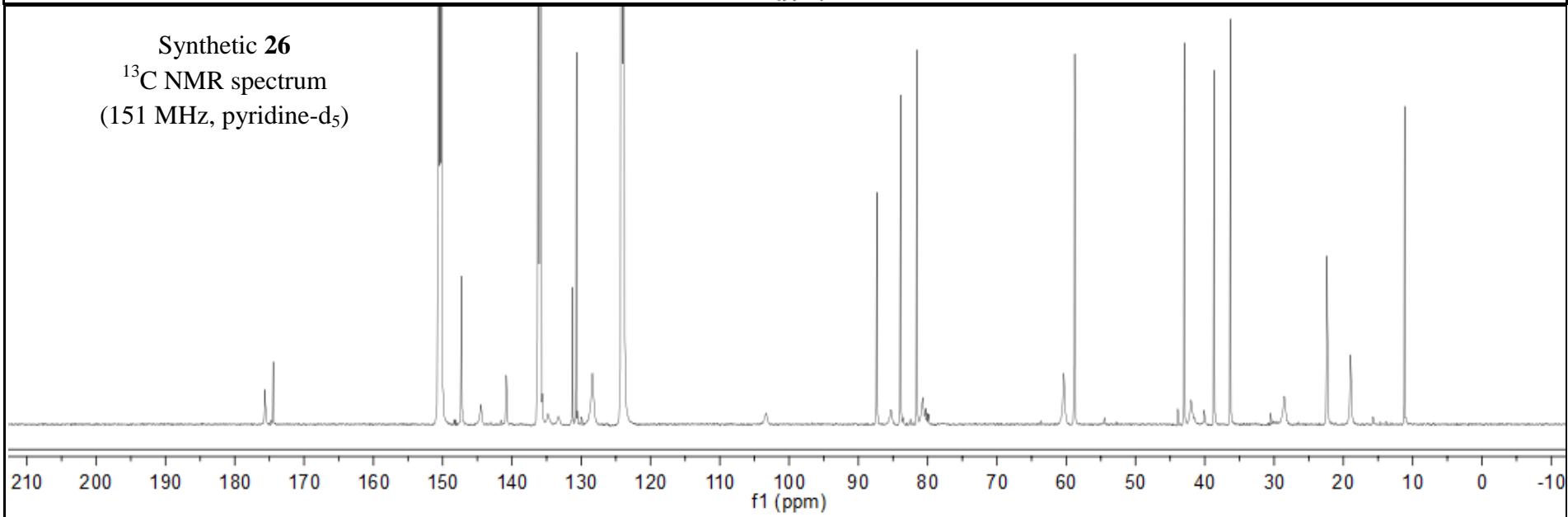
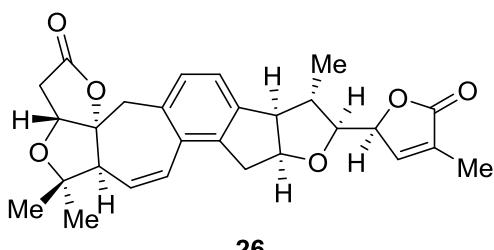


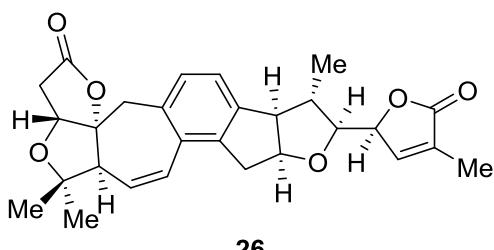
Figure S3. Comparison of the ^{13}C NMR spectra (pyridine-d₅) of authentic pseudorubrifloridilactone B and synthetic **26**.

Table S3. Comparison of the ^1H NMR data (CDCl_3) of authentic pseudorubriflordilactone B and synthetic **26**.



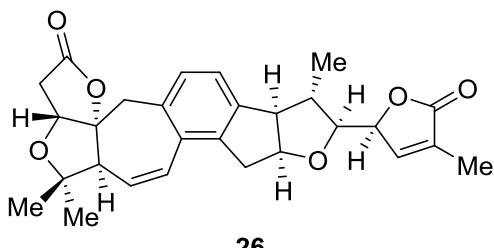
Authentic pseudorubriflordilactone B δ_{H} [ppm, mult, J (Hz)] 600 MHz	Synthetic 26 δ_{H} [ppm, mult, J (Hz)] 400 MHz	Err (Natural–Synthetic) $\Delta\delta_{\text{H}}$ (ppm)
7.00 2 H, overlapped	7.06–6.94 2 H, m	–
6.61 1 H, dd, 12.1, 2.2	6.60 1 H, dd, 12.1, 1.5	+0.01
6.56 1 H, m	6.56 1 H, s	–
5.74 1 H, br s	5.75 1 H, br s	–0.01
4.91 1 H, m	4.93–4.86 1 H, m	–
4.74 1 H, m	4.73 1 H, br s	–
4.37 1 H, br s	4.36 1 H, br s	+0.01
3.79 1 H, dd, 6.8, 4.8	3.79 1 H, dd, 6.5, 5.0	0
3.37 1 H, dd, 6.0, 4.6	3.38–3.34 1 H, m	–
3.05 3 H, overlapped	3.19–2.63 6 H, m	–
2.88 3 H, overlapped		
2.74 1 H, d, 18.6	2.72 1 H, d, 18.5	+0.02
2.18 1 H, m	2.20–2.12 1 H, m	–
1.82 3 H, t, 1.8	1.82 3 H, s	0
1.40 3 H, s	1.40 3 H, s	0
1.29 3 H, d, 6.9	1.29 3 H, d, 6.9	0
1.27 3 H, overlapped	1.37–1.15 3 H, m	–

Table S4. Comparison of the ^1H NMR data (pyridine-d₅) of authentic pseudorubrifloridilactone B and synthetic **26**.



Authentic pseudorubrifloridilactone B δ_{H} [ppm, mult, J (Hz)] 600 MHz	Synthetic 26 δ_{H} [ppm, mult, J (Hz)] 500 MHz	Err (Natural–Synthetic) $\Delta\delta_{\text{H}}$ (ppm)
7.12 1 H, d, 7.0	7.13 1 H, d, 7.4	-0.01
7.08 1 H, overlapped	7.10 1 H, br s	-
6.90 1 H, br s	6.90 1 H, s	-
6.52 1 H, d, 12.1	6.53 1 H, d, 12.2	-0.01
5.70 1 H, br s	5.75 1 H, br s	-0.05
4.88 2 H, m	4.92–4.84 2 H, m	-
4.46 1 H, br s	4.45 1 H, br s	+0.01
3.75 1 H, dd, 7.0, 5.0	3.76 1 H, dd, 6.6, 5.3	-0.01
3.31 1 H, overlapped	3.41–2.81 7 H, m	-
3.24 2 H, overlapped		
3.02 3 H, overlapped		
2.99 1 H, overlapped		
2.89 1 H, d, 17.2	2.88 1 H, d, 18.3	+0.01
2.34 1 H, m	2.39–2.29 1 H, m	-
1.78 3 H, br s	1.78 3 H, s	-
1.36 3 H, s	1.36 3 H, s	0
1.26 3 H, overlapped	1.45–1.01 3 H, m	-
1.19 3 H, d, 6.8	1.21 3 H, d, 6.8	-0.02

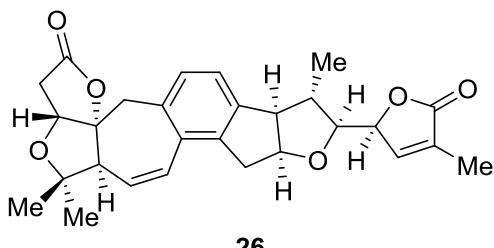
Table S5. Comparison of the ^{13}C NMR data (CDCl_3) of authentic pseudorubrifloridilactone B and synthetic **26**.



Authentic pseudorubrifloridilactone B δ_{C} (ppm) 151 MHz	Synthetic 26 δ_{C} (ppm) 151 MHz	Err (Natural–Synthetic) $\Delta\delta_{\text{C}}$ (ppm)
174.80	174.76	+0.04
—	173.83	—
145.81	145.78	+0.03
—	143.54	—
140.08	140.04	+0.04
—	133.19	—
—	132.48	—
131.37	131.30	+0.07
129.90	129.87	+0.03
—	128.02	—
—	127.39	—
123.40	123.38	+0.02
—	102.83	—
86.48	86.45	+0.03
—	85.10	—
83.57	83.53	+0.04
80.52	80.50	+0.02
—	79.91	—
—	59.22	—
58.19	58.15	+0.04
41.81	41.77	+0.04
—	41.65	—
38.06	38.03	+0.03

35.82	35.78	+0.04
—	28.26	—
22.16	22.13	+0.03
19.19	19.14	+0.05
10.97	10.93	+0.04

Table S6. Comparison of the ^{13}C NMR data (pyridine-d₅) of authentic pseudorubrifloridilactone B and synthetic **26**.



Authentic pseudorubrifloridilactone B δ_{C} (ppm) 151 MHz	Synthetic 26 δ_{C} (ppm) 151 MHz	Err (Natural–Synthetic) $\Delta\delta_{\text{C}}$ (ppm)
—	175.63	—
174.48	174.46	+0.02
147.30	147.28	+0.02
—	144.47	—
140.79	140.80	-0.01
—	134.81	—
—	133.29	—
131.24	131.25	-0.01
130.70	130.70	0
—	128.38	—
—	123.61	—
—	103.31	—
87.35	87.34	+0.01
—	85.30	—
83.93	83.93	0
81.59	81.57	+0.02
—	80.72	—
—	60.34	—
58.79	58.79	0
42.98	42.97	+0.01
—	41.97	—
38.67	38.67	0
36.33	36.33	0

–	28.51	–
22.34	22.35	-0.01
18.97	18.95	+0.02
11.17	11.17	0

VII References

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