Electronic Supplementary Material (ESI) for ChemComm.

Electronic supplementary information for: Tailoring flavins for visible light photocatalysis: Organocatalytic [2+2] cycloaddition mediated by flavin derivative and visible light

Viktor Mojr, Eva Svobodová, Karolína Straková, Tomáš Neveselý, Josef Chudoba, Hana Dvořáková and Radek Cibulka*

University of Chemistry and Technology, Technická 5, 166 28 Prague 6, Czech Republic;

*corresponding author: cibulkar@vscht.cz.

Contents

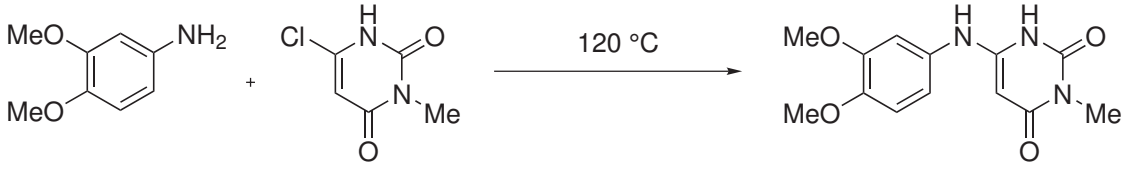
1 Synthetic procedures and characterizations

1.1 General procedures

NMR spectra were recorded with an Agilent 400-MR DDR2 (399.94 MHz for ^{1}H and 100.58 MHz for ^{13}C), a Varian Mercury Plus 300 (299.97 MHz for ^{1}H, 75.44 MHz for ^{13}C and 282.23 MHz for ^{19}F), a Bruker Avance III 600 MHz (600.13 MHz for ^{1}H and 150.92 MHz for ^{13}C) and a Bruker Avance III 500 MHz (500.13 MHz for ^{1}H, 470.39 MHz for ^{19}F and 125.77 MHz for ^{13}C) at 298 K. Chemical shifts δ are given in ppm using residual solvent or tetramethylsilane as an internal standard for ^{1}H and ^{13}C NMR and CFC-11 for ^{19}F NMR. High-resolution mass spectra were obtained on an LTQ Orbitrap Velos (Thermo Fisher Scientific), equipped with an orbitrap mass analyzer. The mass spectrometer was operated in ESI mode (ESI source temperature 250 °C, potential 3000 V) and in APCI mode (APCI source temperature 250 °C, spray current 4.0 μA) with a mass range from 200 to 2000 a.m.u. UV-VIS spectra were measured in quartz cuvettes (d = 1 cm) on a Varian Cary 50 spectrophotometer against a pure solvent. TLC analyses were carried out on a DC Alufolien Kieselgel 60 F254 (Merck). Preparative column chromatography separations were performed on a silica gel Kieselgel 60 (0.040–0.063 mm) (Merck). Melting points were measured on a Boetius melting point apparatus and are uncorrected. Starting materials, reagents and substrates were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using standard procedures. 6-Chloro-3-methyluracil **13** was prepared according to the known procedure.[1]

1.2 Synthesis of catalyst 2

6-(3,4-Dimethoxyphenylamino)-3-methyluracil (14)[2]

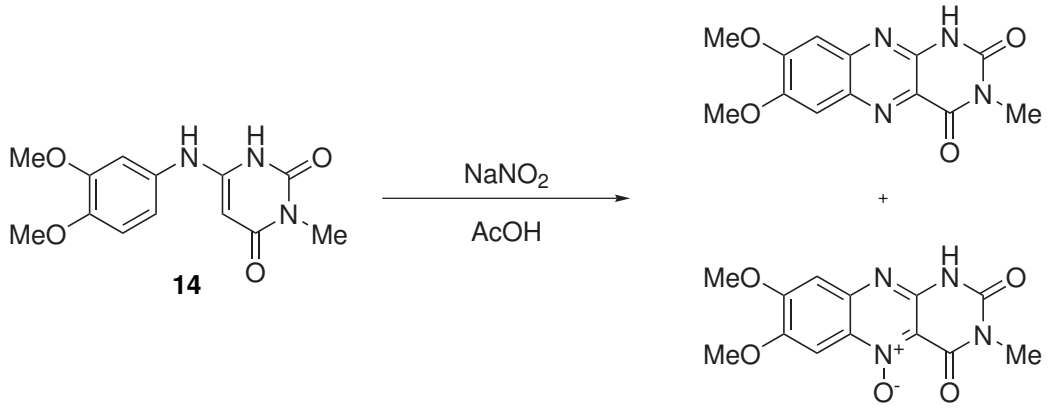


13 **14**

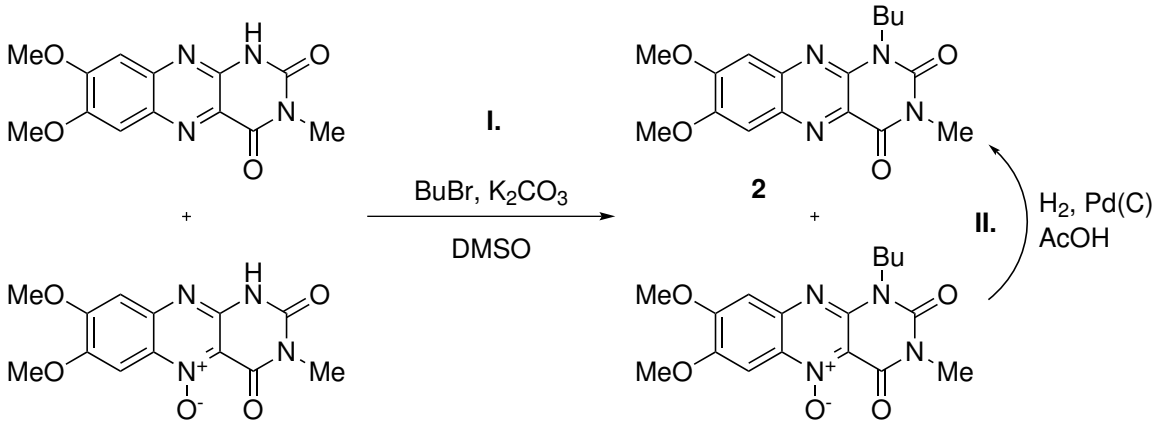
A mixture of 6-chloro-3-methyluracil **13** (0.35 g, 2.18 mmol) and 3,4-dimethoxyaniline (1.0 g, 6.54 mmol) was stirred and heated at 120 °C for 3 h. After cooling, the mixture was treated with ether. Crude product was filtered and washed with methanol and acetone to obtain white powder (0.50 g, 83 %, m.p. 304–306 °C). ^{1}H NMR (300 MHz, DMSO-d^6) δ 10.47 (*br*s, 1H), 7.98 (s, 1H), 6.95 (d, J = 8.5 Hz, 1H), 6.81 (d, J = 2.3 Hz, 1H), 6.75 (dd, J = 8.5, 2.4 Hz, 1H), 4.65 (d, J = 1.9 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.05 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d^6) δ 163.9,

152.3, 151.7, 149.8, 147.2, 131.1, 116.8, 112.8, 109.3, 75.6, 56.4, 56.3, 26.7. HR-MS (ESI^+): For $C_{13}H_{16}N_3O_4^+$ $[M+H]^+$ calculated 278.11353, found 278.11362, for $C_{13}H_{15}N_3O_4Na^+$ $[M+Na]^+$ calculated 300.09548, found 300.09583.

1-Butyl-7,8-dimethoxy-3-methylalloxazin (2)[3]



Into the vigorously stirred suspension of uracil **14** (0.45 g, 1.6 mmol) in 4 mL of acetic acid, sodium nitrite (0.55 g, 8.0 mmol) was added by small portions. After 10 min, mixture was diluted by water (30 mL). Crude product was isolated by filtration and washed with water, acetone, and ether. Yellow–green very fine powder (0.42 g, m. p. > 300 °C decomp.), containing 7,8-dimethoxy-3-methylalloxazin and 7,8-dimethoxy-3-methylalloxazin-5-oxide (*cca* 7 : 4), as unseparable products was used for further synthesis without purification. ^{1}H NMR (300 MHz, DMSO-d^6) *alloxazine set of signals:* δ 12.05 (s, 1H), 7.51 (s, 1H), 7.21 (s, 1H), 4.00 (s, 3H), 3.96 (s, 3H), 3.30 (s, 3H); *alloxazine-5-oxide set of signals:* δ 12.01 (s, 1H), 7.61 (s, 1H), 7.14 (s, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 3.21 (s, 3H). MS (ESI^-, DMSO): *m/z* (%): 287.1 (65) $[M_A - H]^-$, 303.1 (100) $[M_B - H]^-$.

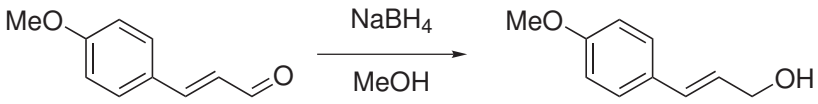


The mixture of alloxazine and alloxazine-5-oxide (0.30 g) was suspended in dry DMSO (15 mL). After addition of finely powdered dry potassium carbonate (0.86 g, 6.2 mmol), flavin compounds dissolved into dark yellow solution. Then butyl bromide (450 μL, 4.2 mmol) was added

and the reaction mixture was stirred under argon for 3 days. Reaction was monitored by TLC. The mixture was acidified with acetic acid (5 mL), diluted with water (100 mL) and extracted with ethyl acetate (2×125 mL). Collected organic layers were dried over $MgSO_4$ and evaporated. Light yellow solid was diluted in acetic acid (100 mL), palladium on charcoal (10%, 15 mg, 14 μmol) was added and the reaction mixture was stirred in autoclave under hydrogen (10 BAR) overnight. Hydrogenation catalyst was removed from the mixture by filtration through funnel with celite. Acetic acid was evaporated, light yellow solid was dried in vacuo. Product was purified by flash column chromatography (hexane/ethyl acetate ~ 1 : 1) and recrystalized from acetic acid/water. Obtained very fine light yellow needles still contained acetic acid. Short treatment in boiling ether resulted pure product (0.32 g, 0.93 mmol, 80 % over 3 steps), m. p. 257–261 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.24 (s, 1H), 4.46–4.38 (m, 2H), 4.12 (s, 3H), 4.04 (s, 3H), 3.58 (s, 3H), 1.84–1.71 (m, 2H), 1.57–1.37 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 156.5, 152.5, 150.5, 144.4, 141.9, 137.4, 126.4, 107.4, 105.0, 56.7, 56.5, 42.4, 29.8, 29.0, 20.1, 13.9. HR-MS (ESI$^+$): For $C_{17}H_{21}N_4O_4^+$ $[M+H]^+$ calculated 345.15573, found 345.15586, for $C_{17}H_{20}N_4O_4Na^+$ $[M+Na]^+$ calculated 367.13768, found 367.13795, for $C_{17}H_{20}N_4O_4K^+$ $[M+K]^+$ calculated 383.11161, found 383.11163.

1.3 Syntheses of substrates

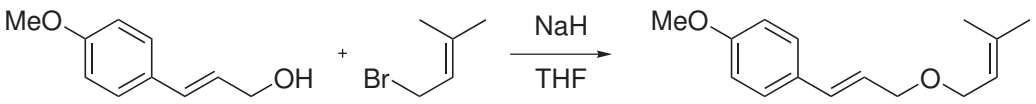
(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ol (15)[4]



15

(*E*)-3-(4-Methoxyphenyl)prop-2-enal (23 g, 0.14 mol) was dissolved in dry methanol (230 mL) under argon. The solution was cooled to 0 °C, then sodium borohydride was added (3.9 g, 0.10 mol). The reaction mixture was stirred at room temperature for 1 h, then water was added dropwise for quenching. The mixture was extracted with ether (3×200 mL). Collected organic phases were washed with brine, dried over $MgSO_4$ and evaporated. By recrystalization from toluene/hexane, white flakes (20.4 g, 87 %) were obtained, m. p. 76–78 °C (lit.[5] 72–75 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 6.89–6.83 (m, 2H), 6.56 (d, J = 15.9 Hz, 1H), 6.24 (dt, J = 15.8, 5.9 Hz, 1H), 4.30 (d, J = 4.8 Hz, 2H), 3.81 (s, J = 2.5 Hz, 3H), 1.40 (s, 1H).

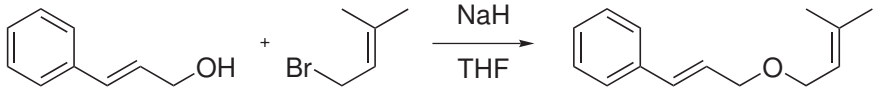
(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-yl 3-methylbut-2-en-1-yl ether (3a)[6]



15 **3a**

Into the suspension of sodium hydride (60% *w*/*w* in mineral oil, 0.59 g, 14.6 mmol) in dry THF (20 mL), a solution of alcohol **15** (2.00 g, 12.2 mmol) in dry THF (25 mL) was added dropwise under argon. The reaction mixture was cooled to 0 °C and a solution of 1-bromo-3-methylbut--2-ene (90%, 2.47 g, 14.9 mmol) in dry THF (22 mL) was added slowly by a syringe. Mixture was stirred at r. t. for 3 days and the reaction was quenched by adding aqueous solution of ammonium chloride. Phases were separated and the water phase was extracted with ether. Combined organic phases were washed with brine, dried over $MgSO_4$ and evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Clear oil (1.83 g, 65 %) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.28 (m, 2H), 6.92–6.79 (m, 2H), 6.55 (dt, J = 15.9, 1.4 Hz, 1H), 6.18 (dtd, J = 15.9, 6.2, 0.5 Hz, 1H), 5.39 (dddt, J = 7.6, 7.0, 2.8, 1.4 Hz, 1H), 4.11 (dd, J = 6.2, 1.4 Hz, 2H), 4.01 (dddd, J = 7.7, 1.9, 1.2, 0.7 Hz, 2H), 3.81 (s, 3H), 1.76 (d, J = 1.2 Hz, 3H), 1.69 (dd, J = 1.2, 0.6 Hz, 3H).

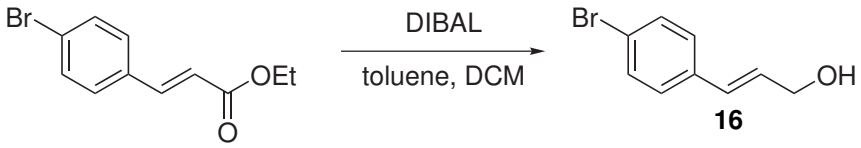
(*E*)-3-Phenylprop-2-en-1-yl 3-methylbut-2-en-1-yl ether (3b)[6]



3b

(*E*)-3-Phenylprop-2-en-1-ol (1.68 g, 12.5 mmol) was dissolved in dry THF (10 mL). Sodium hydride (60% *w*/*w* in mineral oil, 0.64 g, 16.0 mmol) was added and the reaction mixture was stirred under argon for 10 min. Then a solution of 1-bromo-3-methylbut-2-ene (90%, 2.25 g, 13.6 mmol) in dry THF (10 mL) was added dropwise. Reaction was quenched after 2 days by addition of water (20 mL). Phases were separated, water phase was extracted with ether (3×30 mL), collected organic phases were washed with brine, dried over $MgSO_4$ and evaporated. Crude product was purified by vacuum distillation resulting colorless oil (1.72 g, 68 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.20 (m, 5H), 6.61 (d, J = 16.0 Hz, 1H), 6.31 (dt, J = 15.9, 6.0 Hz, 1H), 5.44–5.36 (m, 1H), 4.14 (dd, J = 6.1, 1.4 Hz, 2H), 4.02 (d, J = 7.0 Hz, 2H), 1.77 (s, 3H), 1.69 (s, 3H).

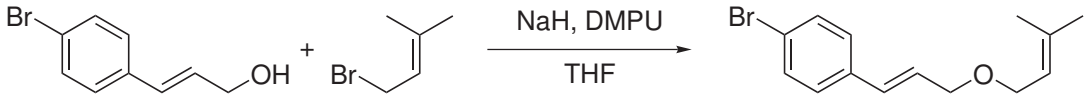
(*E*)-3-(4-Bromophenyl)prop-2-en-1-ol (16)[7]



16

The solution of ethyl (*E*)-3-(4-bromophenyl)prop-2-enoate (2.0 g, 98%, 7.7 mmol) in dry dichloromethane (23 mL) was cooled to -78 °C under argon. In *cca* 40 min, 1M solution of diisobutylaluminium hydride (16.5 mL, 16.5 mmol) in toluene was added dropwise into the solution. Reaction was monitored by TLC. The reaction was quenched after 30 min by adding 10% solution of sodium hydroxide in water (30 mL) and the reaction mixture was stirred until room temperature was achieved. Phases were separated, water phase was extracted with dichloromethane (3×30 mL), collected organic phases were dried over $MgSO_4$ and evaporated. White crystals (1.63 g, 99 %) were pure enough for further synthesis, m. p. 64–67 °C (lit.[8] 63–65 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.28–7.22 (m, 2H), 6.57 (d, J = 15.9 Hz, 1H), 6.36 (dt, J = 15.9, 5.5 Hz, 1H), 4.32 (dd, J = 5.5, 1.5 Hz, 2H).

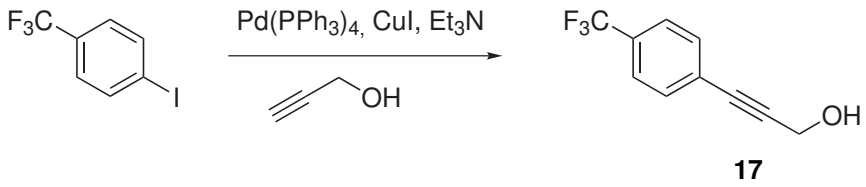
(*E*)-3-(4-Bromophenyl)prop-2-en-1-yl 3-methylbut-2-en-1-yl ether (3c)



16 **3c**

Into the cooled (-78 °C) mixture of alcohol **16** (1.48 g, 6.9 mmol), 1-bromo-3-methylbut-2-ene (90%, 2.29 g, 13.9 mmol) and DMPU (4.2 mL, 34.7 mmol) in dry THF (30 mL), sodium hydride (60% *w*/*w* in mineral oil, 0.39 g, 8.3 mmol) was added under argon. The cooling bath was removed and the reaction mixture was stirred at r. t. for 2.5 h. Reaction was quenched by adding saturated aqueous solution of ammonium chloride. Phases were separated and the water phase was extracted with ether. Combined organic phases were washed with brine, dried over $MgSO_4$ and evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Clear oil (1.66 g, 85 %) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.28–7.20 (m, 2H), 6.55 (dt, J = 15.9, 1.4 Hz, 1H), 6.30 (dt, J = 15.9, 5.9 Hz, 1H), 5.39 (tdt, J = 7.0, 2.8, 1.4 Hz, 1H), 4.11 (dd, J = 5.9, 1.5 Hz, 2H), 4.02 (dt, J = 7.0, 0.9 Hz, 2H), 1.76 (d, J = 1.2 Hz, 3H), 1.69 (d, J = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.44, 135.90, 131.76, 131.03, 128.09, 127.40, 121.46, 121.06, 70.50, 66.90, 25.96, 18.20. HR-MS (APCI$^+$): For $C_{14}H_{18}BrO^+$ $[M+H]^+$ calculated 281.05355, found 281.05341.

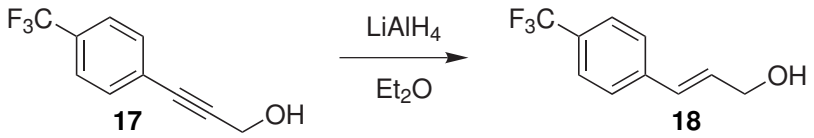
3-(4-Trifluoromethylphenyl)prop-2-yn-1-ol (17)[9, 10]



17

To the mixture of tetrakis(triphenylphosphine) palladium(0) (0.30 g, 0.3 mmol), copper(I) iodide (0.31 g, 1.6 mmol), 4-(trifluoromethyl)iodobenzene (2.28 g, 8.4 mmol) and dry triethylamine (45 mL), propargyl alcohol (0.58 g, 10.3 mmol) was added under nitrogen. After stirring overnight, the reaction was quenched by adding of ammonium chloride (aqueous solution) and extracted with dichloromethane (3×30 mL). Combined organic layers were dried over Na_2SO_4 and solvents were evaporated. Column chromatography (dichloromethane/MeOH from 100 : 1 to 10 : 1) gave alkyne **17** (1.57 g, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 4.52 (d, J = 6.2 Hz, 2H), 1.93–1.84 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.04, 130.41 (q, J = 32.7 Hz), 126.50, 125.40 (q, J = 3.8 Hz), 123.98 (q, J = 272.4 Hz), 89.76, 84.51, 51.67. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.41. HR-MS (ESI$^-$): For $C_{10}H_6F_3O^-$ [M-H]$^-$ calculated 199.03762, found 199.03740.

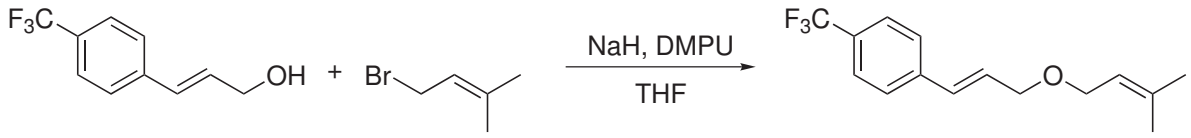
(*E*)-3-(4-Trifluoromethylphenyl)prop-2-en-1-ol (18)[11]



17 **18**

Into the cooled (0 °C) mixture of $LiAlH_4$ (125 mg, 3.3 mmol) and dry diethyl ether (5 mL), the solution of alkyne **17** (505 mg, 2.5 mmol) in dry diethyl ether (10 mL) was added dropwise under nitrogen. Reaction mixture was stirred for 3 hours at 0 °C and after reaching room temperature overnight. Reaction was quenched by adding water and aqueous solution of HCl. Mixture was extracted with ether (3×30 mL), organic phase was dried over $MgSO_4$ and evaporated. Column chromatography (dichloromethane/MeOH 100 : 3) gave alkene **18** (320 mg, 63 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 16.0 Hz, 1H), 6.46 (dt, J = 16.0, 5.3 Hz, 1H), 4.37 (d, J = 4.3 Hz, 2H), 2.17 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.17, 131.23, 129.58, 129.29, 126.55, 125.53 (q, J = 3.8 Hz), 123.64 (q, J = 271.0 Hz), 63.31. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.01. HR-MS (APCI$^-$): For $C_{10}H_8F_3O^-$ [M-H]$^-$ calculated 201.05272, found 201.05274.

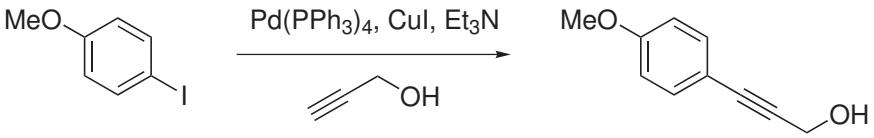
(*E*)-3-(4-Trifluoromethylphenyl)prop-2-en-1-yl 3-methylbut-2-en-1-yl ether (3d)



18 **3d**

Into the cooled (-78 °C) solution of alcohol **18** (265 mg, 1.3 mmol) and 1-bromo-3-methylbut-2-ene (90%, 400 mg, 2.9 mmol) in dry THF (12 mL), sodium hydride (60% *w*/*w* in mineral oil, 70 mg, 1.75 mmol) and DMPU (800 mg, 6.2 mmol) were carefully added under nitrogen. The reaction mixture was stirred for 3 hours and after reaching the room temperature overnight. The reaction was quenched by adding ammonium chloride (aqueous solution), the product was isolated by extraction with dichloromethane (3×25 mL), organic phase was dried over $MgSO_4$ and evaporated. Column chromatography (hexane/ethyl acetate 25 : 1) gave 270 mg (77 %) of ether **3d**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 6.65 (dt, J = 15.9, 1.5 Hz, 1H), 6.40 (dt, J = 16.0, 5.7 Hz, 1H), 5.40 (ddq, J = 8.4, 5.6, 1.4 Hz, 1H), 4.16 (dd, J = 5.8, 1.5 Hz, 2H), 4.07–3.99 (m, 2H), 1.77 (q, J = 1.1 Hz, 3H), 1.70 (d, J = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.47 (q, J = 1.6 Hz), 137.59, 130.60, 129.49 (q, J = 32.0), 129.40, 126.70, 125.64 (q, J = 3.8), 124.33 (q, J = 271.8 Hz), 121.00, 70.32, 67.06, 25.98, 18.22. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.96. HR-MS (APCI$^+$): For $C_{15}H_{18}F_3O^+$ calculated 271.13043, found 271.13031.

3-(4-Methoxyphenyl)prop-2-yn-1-ol (19)[8]

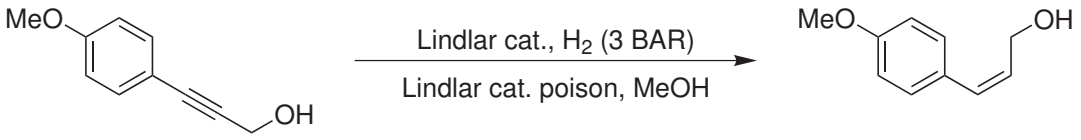


19

To the mixture of tetrakis(triphenylphosphine) palladium(0) (1.48 g, 1.3 mmol), copper(I) iodide (0.40 g, 2.1 mmol), 4-iodoanisole (6.24 g, 25.7 mmol) and dry triethylamine (50 mL), propargyl alcohol (1.75 g, 31.2 mmol) was added under nitrogen. After stirring overnight, the reaction was quenched by adding ammonium chloride (aqueous solution) and the mixture was extracted with dichloromethane (5×50 mL). Combined organic layers were dried over $MgSO_4$ and solvents were evaporated. Column chromatography (dichloromethane) and crystalization (toluene/hexane) gave alkyne **19** (2.56 g, 61 %) as a white solid, m.p. 62–65 °C (lit.[12] 62.5–64.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.34 (m, 2H), 6.84 (d, J = 8.9 Hz, 2H), 4.48 (d, J = 6.1 Hz, 2H), 3.81 (s, 3H), 1.68 (t, J = 6.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

159.92, 133.33, 114.76, 114.10, 85.98, 85.84, 55.43, 51.90. HR-MS (APCI$^-$): For $C_{11}H_{13}O_2^+$ $[M+MeOH]^+$ calculated 177.09101, found 177.09105.

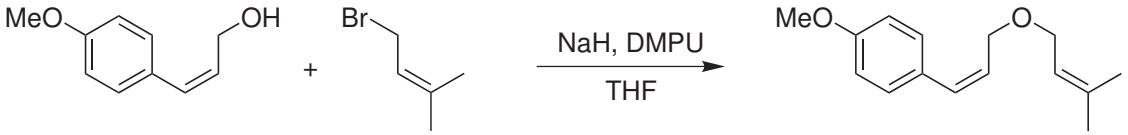
(*Z*)-3-(4-Methoxyphenyl)prop-2-en-1-ol (20)[13]



19 **20**

Into the solution of alkyne **19** (500 mg, 3 mmol) in dry methanol (20 mL), Lindlar catalyst (110 mg) and Lindlar catalyst poison (3,6-dithiaoctane-1,8-diol, 30 mg, 0.16 mmol) were added. The reaction mixture was stirred in autoclave under hydrogen (3 BAR) for 3 days. After filtration through celite and evaporation of solvent, 480 mg (97 %) of alkene **20** was obtained, m.p. 37–40 °C (lit.[14] 45–50 °C). Product contained *cca* 10 % of (*E*)-isomer and was without any purification used for preparation of ether (*Z*)-**3a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 9.1$ Hz, 2H), 6.51 (d, $J = 11.7$ Hz, 1H), 5.78 (dt, $J = 11.7$, 6.5 Hz, 1H), 4.43 (dd, $J = 6.3$, 1.4 Hz, 2H), 3.81 (s, 3H), 1.56 (t, $J = 5.3$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.94, 130.78, 130.23, 129.53, 129.32, 113.83, 59.91, 55.42. HR-MS (APCI$^+$): For $C_{10}H_{13}O$ $[M+H]^+$ calculated 165.09101, found 165.09073.

(*Z*)-3-(4-Methoxyphenyl)prop-2-en-1-yl 3-methylbut-2-en-1-yl ether ((*Z*)-3a)

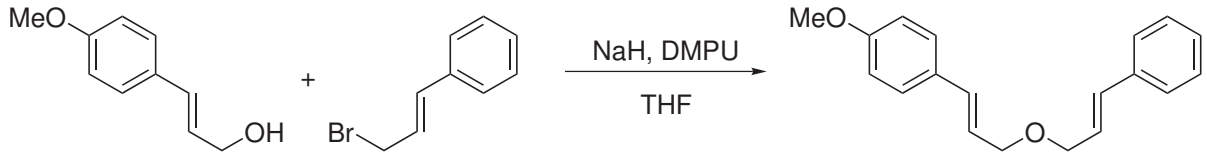


20 (*Z*)-**3a**

The solution of alcohol **20** (150 mg, 0.90 mmol) and 1-bromo-3-methylbut-2-ene (90%, 300 mg, 2.00 mmol) in dry THF (10 mL) was cooled to -78 °C under nitrogen. Sodium hydride (60% *w*/*w* in mineral oil, 45 mg, 1.13 mmol) and DMPU (480 mg, 3.75 mmol) were carefully added and the reaction mixture was stirred for 2 hours at -78 °C and after reaching the room temperature overnight. The reaction was quenched by adding of ammonium chloride (aqueous solution). The mixture was extracted with dichloromethane (3×10 mL). Organic phase was dried over Na_2SO_4 and evaporated. Column chromatography (hexane/ethyl acetate from 20 : 1 to 10 : 1) gave 160 mg (74 %) of ether (*Z*)-**3a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–7.10 (m, 2H), 6.94–6.80 (m, 2H), 6.53 (dt, $J = 11.8$, 1.8 Hz, 1H), 5.78 (dt, $J = 11.8$, 6.4 Hz, 1H), 5.38 (ddq, $J = 8.4$, 5.6, 1.4 Hz, 1H), 4.24 (dd, $J = 6.4$, 1.7 Hz, 2H), 3.99 (dt, $J = 7.2$, 0.8 Hz, 2H), 3.82 (s, 3H), 1.74 (q, $J = 0.9$ Hz, 3H), 1.70–1.59 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.82,

137.38, 131.19, 130.23, 129.59, 127.69, 121.13, 113.72, 66.93, 66.87, 55.37, 25.93, 18.12. HR-MS (APCI$^+$): For $C_{15}H_{20}O_2Na^+$ $[M+Na]^+$ calculated 255.13555, found 255.13547.

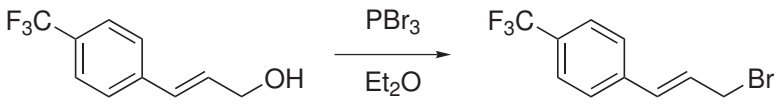
Cinnamyl (*E*)-3-(4-methoxyphenyl)prop-2-en-1-yl ether (5a)[15, 16]



15 **5a**

The solution of (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol **15** (1.05 g, 6.4 mmol) and cinnamyl bromide (1.25 g, 6.3 mmol) in dry THF (50 mL) was cooled to -78 °C under nitrogen. Sodium hydride (60% *w*/*w* in mineral oil, 0.27 g, 6.7 mmol) and DMPU (1.26 g, 9.8 mmol) were carefully added and the reaction mixture was stirred for 3 hours at -78 °C and after reaching the room temperature overnight. The reaction was quenched by adding of ammonium chloride (aqueous solution). The mixture was extracted with dichloromethane (4×30 mL). Organic phase was dried over Na_2SO_4 and evaporated. Column chromatography (hexane/ethyl acetate 10 : 1) gave 1.43 g (80 %) of slightly yellow solid ether **5a**, m.p. 33–34 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dt, J = 7.8, 1.5 Hz, 2H), 7.40–7.30 (m, 4H), 7.27 (dd, J = 7.2, 1.6 Hz, 1H), 6.92–6.85 (m, 2H), 6.70–6.64 (m, 1H), 6.64–6.58 (m, 1H), 6.36 (dtd, J = 15.9, 6.0, 1.7 Hz, 1H), 6.28–6.17 (m, 1H), 4.25–4.19 (m, 4H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.41, 136.85, 132.57, 132.43, 129.58, 128.65, 127.80, 127.75, 126.59, 126.22, 123.81, 114.08, 71.06, 70.72, 55.35. HR-MS (ESI$^+$): For $C_{19}H_{20}O_2Na^+$ $[M+Na]^+$ calculated 303.13555, found 303.13574.

(*E*)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-yl bromide (21)[17]

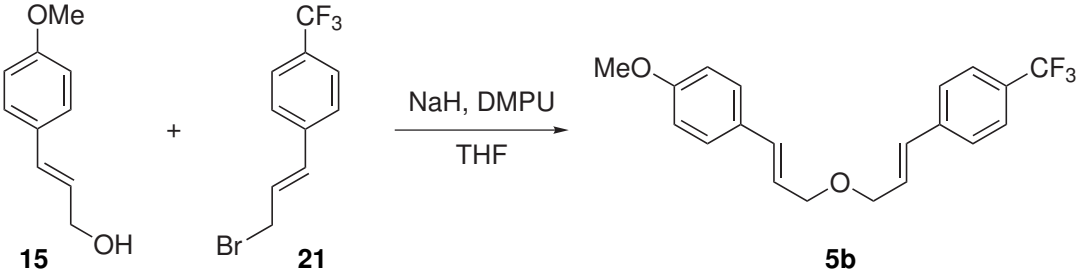


18 **21**

The solution of alcohol **18** (115 mg, 0.55 mmol) in dry diethyl ether (3 mL) was cooled to 0 °C under nitrogen. At this temperature, phosphorus tribromide (170 mg, 0.60 mmol) in diethyl ether (1 mL) was added dropwise and the reaction mixture was stirred for 1 h. Then the reaction mixture was diluted with diethyl ether (10 mL) and sodium hydrogen carbonate (saturated aqueous solution) was added. Phases were separated and the product was isolated by extraction with diethyl ether (3×10 mL), combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. Bromide **21** (120 mg, 80 %) was used for preparation of ether

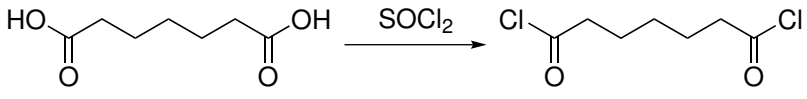
5b without any purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.53 (m, 2H), 7.53–7.43 (m, 2H), 6.67 (d, J = 15.7 Hz, 1H), 6.48 (dt, J = 15.5, 7.6 Hz, 1H), 4.15 (d, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.39, 133.06, 130.21 (q, J = 32.7 Hz), 127.98, 127.03, 125.76 (q, J = 3.8 Hz), 124.18 (q, J = 272.1 Hz), 32.57. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.09.

(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-yl (*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-yl ether (5b)



The solution of alcohol **15** (80 mg, 0.45 mmol) and bromide **21** (120 mg, 0.45 mmol) in dry THF (10 mL) was cooled to -78 °C under nitrogen. At this temperature, sodium hydride (60% *w*/*w* in mineral oil, 20 mg, 0.50 mmol) and DMPU (260 mg, 2.00 mmol) were carefully added and the reaction mixture was stirred for 3 hours and after reaching the room temperature overnight. The reaction was quenched by adding of ammonium chloride (aqueous solution). Mixture was extracted with dichloromethane (3×15 mL). Organic phase was dried over $MgSO_4$ and evaporated. Column chromatography (hexane/ethyl acetate 10:1) gave 95 mg (60 %) of ether **5b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.54 (m, 2H), 7.53–7.45 (m, 2H), 7.39–7.31 (m, 2H), 6.91–6.82 (m, 2H), 6.68 (d, J = 16.0 Hz, 1H), 6.59 (d, J = 15.9 Hz, 1H), 6.42 (dt, J = 16.0, 5.7 Hz, 1H), 6.20 (dt, J = 15.9, 6.3 Hz, 1H), 4.25–4.17 (m, 4H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.49, 140.38, 132.73, 130.77, 129.52 (q, J = 32.5), 129.47, 129.07, 127.86, 126.73, 125.66 (q, J = 3.9), 123.55, 114.12, 71.44, 70.34, 55.43. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.96. HR-MS (APCI$^-$): For $C_{20}H_{18}F_3O_2^-$ [M-H]$^-$ calculated 347.12644, found 347.12622.

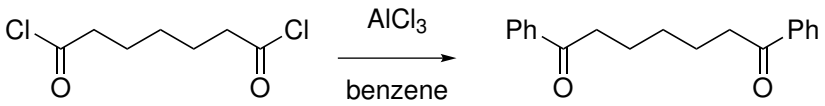
Pimelic dichloride (22)[18]



22

To the suspension of pimelic acid (2.40 g, 0.015 mol) in thionyl chloride (5.95 g, 0.05 mol), droplet of dimethyl formamide was added. Mixture was refluxed for 3 h. Colorless liquid (2.37 g, 80 %) was obtained by fractional distillation (86–88 °C, 0.25 Torr). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.91 (t, J = 7.2 Hz, 4H), 1.81–1.67 (m, 4H), 1.50–1.36 (m, 2H).

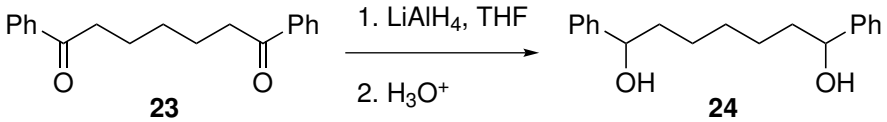
1,7-Diphenylheptane-1,7-dione (23)[19, 20]



22 **23**

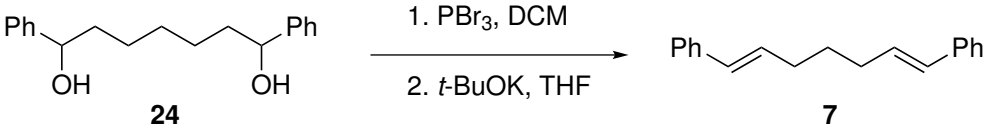
To the suspension of dry aluminium chloride (5.00 g, 37.5 mmol) in benzene (25 mL), pimelic dichloride **22** (2.37 g, 12.0 mmol) was aded dropwise. Reaction mixture was refluxed for 3 h, then cooled and poured over slush of ice (100 g) with concentrated sulphuric acid (10 mL). Phases were separated, water phase was extracted with dichloromethane (3×50 mL). Combined organic phases were dried over $MgSO_4$ and evaporated. Raw product was dissolved in acetone (50 mL) and refluxed with activated carbon, then filtered and evaporated. After recrystalization from isopropyl alcohol, dione **23** (2.34 g, 69 %) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00–7.93 (m, 4H), 7.60–7.52 (m, 2H), 7.50–7.42 (m, 4H), 3.13–2.85 (m, 4H), 1.95–1.67 (m, 4H), 1.56–1.43 (m, 2H).

(1*E*,6*E*)-1,7-Diphenylhepta-1,6-diene (7)[21]



23 **24**

To the suspension of lithium aluminium hydride (0.76 g, 0.02 mol) in dry THF (20 mL), solution of dione **23** (1.41 g, 0.05 mol) in dry THF (10 mL) was added. The mixture was refluxed for 1 h, then cooled and quenched with ethanol, poured over slush of crushed ice (100 g) with sulfuric acid (10 mL). Phases were separated, water phase was extracted with dichloromethane (3×50 mL). Combined organic phases were dried over $MgSO_4$ and evaporated. Raw product **24** (1.37 g, 96 %) was used for further synthesis without purification.

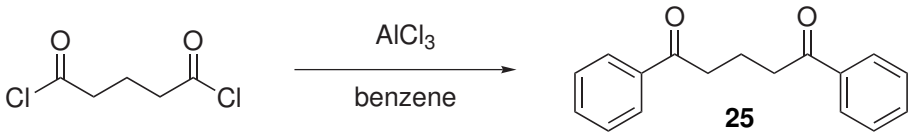


24 **7**

To the solution of diol **24** (0.28 g, 1 mmol) in dichloromethane (10 mL), phosphorus tribromide (0.32 g, 1.2 mmol) was added while cooling in crushed ice and salt bath (approx. -17 °C). After 30 min, water (40 mL) was added and organic layer was separated. Water phase was extracted with dichloromethane (20 mL). Organic phases were combined, dried over $MgSO_4$, and evaporated. Resulting dibromide was dissolved in dry THF (20 mL) under nitrogen and potassium *tert*-butoxide (0.50 g, 4.45 mmol) was aded. The reaction mixture was stirred for 2 h at room

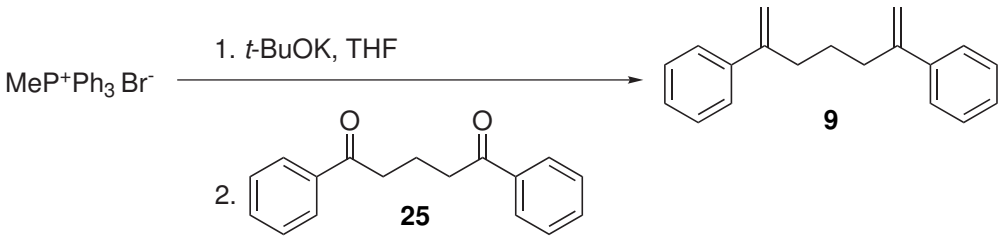
temperature, then quenched with water (100 mL). Phases were separated, water phase was extracted with dichloromethane (3×50 mL). Organic phases were combined, dried over $MgSO_4$ and evaporated. Crude product was purified by column chromatography (hexane/ethyl acetate ~ 50 : 1). Clear oil (60 mg, 24 %) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.14 (m, 10H), 6.41 (d, J = 15.8 Hz, 2H), 6.25 (dt, J = 15.8, 6.9 Hz, 2H), 2.28 (qd, J = 7.0, 1.4 Hz, 4H), 1.67 (p, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.94, 130.74, 130.30, 128.62, 126.99, 126.06, 32.65, 29.13.

1,5-Diphenylpentane-1,5-dione (25)[22]



The glutaryl dichloride (3.38 g, 0.02 mol) was added dropwise to the solution of aluminium chloride (6.67 g, 0.05 mol) in benzene (25 mL). Resulting mixture was refluxed for 3 hours. Than the mixture was cooled and poured over slush of ice (100 g) with concentrated sulphuric acid (10 mL). Water phase was extracted with dichloromethane (3×50 mL). Collected organic layers were dried over $MgSO_4$ and evaporated. Crude product was disolved in acetone (50 mL) and refluxed with activated carbon, then filtered and evaporated. Column chromatography (hexane/ethyl acetate 5 : 1) gave diketone **25** (2.81 g, 56 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00–7.96 (m, 4H), 7.59–7.52 (m, 2H), 7.46 (ddt, J = 8.3, 6.7, 1.2 Hz, 4H), 3.13 (t, J = 6.9 Hz, 4H), 2.21 (p, J = 6.9 Hz, 2H).

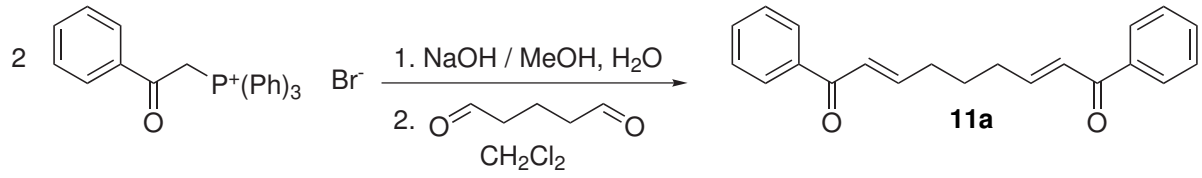
2,6-Diphenylhepta-1,6-diene (9)[23]



The potassium *tert*-butoxide (1.40 g, 12.5 mmol) was added to the suspension of methyltriphenylphosphonium bromide (4.46 g, 12.5 mmol) in dry THF (15 mL). The mixture was stirred under nitrogen for 2 hours. A solution of dione **25** (1.75 g, 5 mmol) in dry THF (10 mL) was added, and the reaction mixture was stirred vigorously for 5 days. After that, the mixture was poured into water (100 mL) and extracted with dichloromethane (3×50 mL). Organic layer was dried over $MgSO_4$ and evaporated. The column chromatography (hexane/ethylacetate 50 : 1) gave 2,6-diphenylhepta-1,6-diene **9** (344 mg, 20 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.24

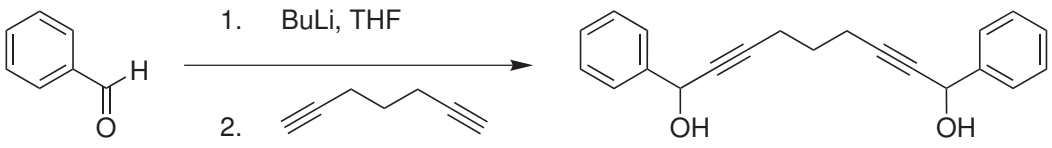
(m, 10H), 5.27 (d, J = 1.5 Hz, 2H), 5.05 (q, J = 1.4 Hz, 2H), 2.54 (ddd, J = 8.5, 7.4, 1.3 Hz, 4H), 1.69–1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.20, 141.15, 128.23, 127.27, 126.10, 112.45, 34.79, 26.61.

(2*E*,7*E*)-1,9-Diphenylnona-2,7-diene-1,9-dione (11a)[24, 25]



Into the solution of (2-oxo-2-phenylethyl)triphenylphosphonium bromide (2.06 g, 4.5 mmol) in methanol (50 mL) and water (50 mL) sodium hydroxide (in the form of 1.5M aqueous solution) was added until the pH value of the reaction mixture reached 8. The mixture was stirred vigorously overnight. After evaporation of methanol, dichloromethane (80 mL) and water (20 mL) were added to the residue and water phase was extracted with dichloromethane (3×40 mL). Combined organic layers were dried over $MgSO_4$ and evaporated to obtain crude ylide **26** (1.70 g, 99 %). The solution of ylide **26** (1.00 g, 2.6 mmol) and glutaraldehyde (50% solution in water, 1.20 g, 1.0 mmol) in dichloromethane (3 mL) was vigorously stirred at r.t. for 5 days. The column chromatography (dichloromethane/ethyl acetate from 100 : 1 to 100 : 4) gave the product **11a** (0.10 g, 33 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 4H), 7.60–7.51 (m, 2H), 7.51–7.42 (m, 4H), 7.06 (dt, J = 15.3, 6.8 Hz, 2H), 6.92 (d, J = 15.4 Hz, 2H), 2.40 (q, J = 7.1 Hz, 4H), 1.79 (p, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.59, 148.48, 137.82, 132.70, 128.53, 128.50, 126.47, 32.15, 26.68. HR-MS (APCI$^+$): For $C_{21}H_{21}O_2^+$ $[M+H]^+$ calculated 305.15361, found 305.15385.

1,9-Diphenylnona-2,7-diyne-1,9-diol (27)

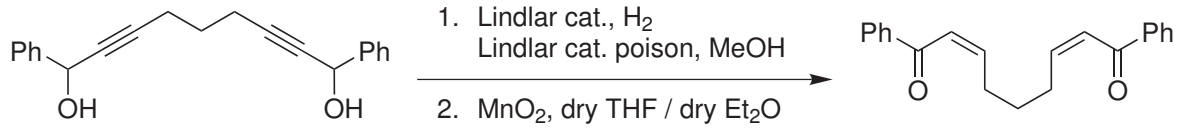


27

To a solution of hepta-1,6-diyne (350 mg, 3.8 mmol) in anhydrous THF (10 mL) at -78 °C under nitrogen atmosphere, *n*-BuLi (2.5M solution in hexanes, 3 mL, 7.5 mmol) was added. The reaction mixture was stirred at this temperature for 1 h and then at r.t. for 1.5 h. After cooling to -78 °C, the benzaldehyde (800 mg, 7.5 mmol) in anhydrous THF (5 mL) was added to the reaction mixture and was left at -78 °C for 1h and after reaching the room temperature for

3h. Reaction was quenched by adding of aqueous NH_4Cl and extracted with Et_2O (3×30 mL). Combined organic layers were dried over $MgSO_4$ and evaporated. The column chromatography (dichloromethane/ethyl acetate ~ 100 : 5) gave the product **27** (810 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 4H), 7.41–7.30 (m, 6H), 5.45 (s, 2H), 2.42 (td, J = 7.0, 1.9 Hz, 4H), 2.28 (s, 2H), 1.79 (p, J = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.21, 128.71, 128.41, 126.72, 86.48, 80.89, 64.93, 27.49, 18.25 (d, J = 0.8 Hz). HR-MS (ESI$^+$): For $C_{21}H_{18}O_2Na^+$ $[M+Na]^+$ calculated 325.11990, found 325.12009.

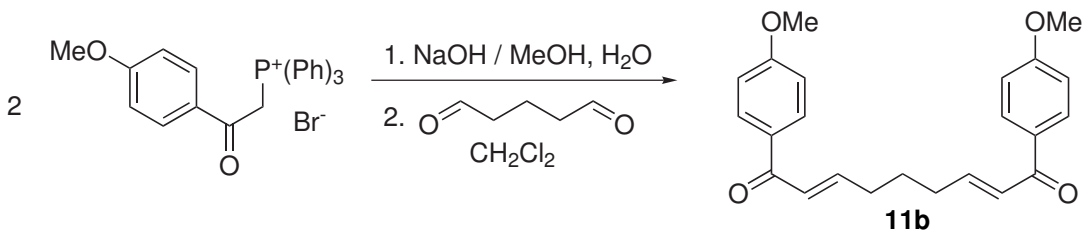
(2*Z*,7*Z*)-1,9-Diphenylnona-2,7-diene-1,9-dione ((*Z*,*Z*)-11a)



27 (*Z*,*Z*)-**11a**

To a solution of diyne **27** (800 mg, 2.6 mmol) in anhydrous methanol (60 mL), Lindlar catalyst (250 mg) and Lindlar catalyst poison (3,6-dithiaoctane-1,8-diol, 40 mg, 0.2 mmol) were added. Hydrogen was bubbled through the reaction mixture for 5 hours. After filtration through celite and evaporation of solvent, 800 mg (99 %) of alkene was obtained as a (2*Z*,7*Z*) isomer, which was used without any purification for preparation of diketone (*Z*,*Z*)-**11a**. ^{1}H NMR (300 MHz, $CDCl_3$) of 1,9-diphenylnona-2,7-diene-1,9-diol: δ 7.41–7.22 (m, 10H), 5.66 (dd, J = 11.1, 8.1 Hz, 2H), 5.57 (t, J = 7.1 Hz, 2H), 2.82–2.70 (m, 4H), 2.03 (d, J = 3.5 Hz, 2H), 1.62–1.41 (m, 2H). To a solution of alcohol (620 mg, 2 mmol) in anhydrous THF (50 mL) and Et_2O (25 mL) MnO_2 (10 g, 115 mmol) was added and the reaction mixture was stirred for 4 days vigorously. Excess of MnO_2 was removed by filtration through celite, washed with Et_2O and solvents were evaporated. The column chromatography (dichloromethane) gave (*Z*,*Z*)-**11a** (210 mg, 35 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.89 (m, 4H), 7.57–7.49 (m, 2H), 7.44 (td, J = 6.8, 1.5 Hz, 4H), 6.82 (dt, J = 11.6, 1.7 Hz, 2H), 6.35 (dt, J = 11.6, 7.4 Hz, 2H), 2.69 (qd, J = 7.5, 1.7 Hz, 2H), 1.70 (p, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.12, 148.87, 138.64, 132.80, 128.66, 128.47, 124.92, 29.52, 28.80. HR-MS (ESI$^+$): For $C_{21}H_{22}NaO_2^+$ $[M+Na]^+$ calculated 329.15120, found 329.15155.

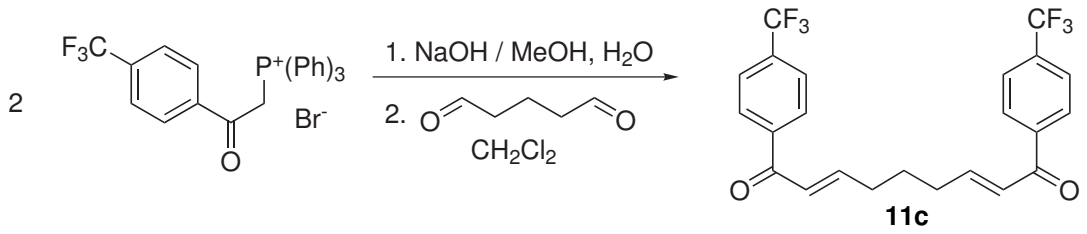
(2*E*,7*E*)-1,9-Bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione (11b)[26]



11b

Into the solution of (2-(4-methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide (1.47 g, 3.0 mmol) in methanol (50 mL) and water (50 mL) sodium hydroxide (in the form of 1.5M aqueous solution) was added until the pH value of the reaction mixture reached 10. The mixture was stirred vigorously overnight. After evaporation of methanol, dichloromethane (80 mL) and water (20 mL) were added to the residue and water phase was extracted with dichloromethane (3×30 mL). Combined organic layers were dried over $MgSO_4$ and evaporated to obtain the ylide **28** (1.14 g, 98 %). The solution of ylide **28** (1.13 g, 2.7 mmol) and glutaraldehyde (50% solution in water, 275 mg, 1.4 mmol) in dichloromethane (5 mL) was vigorously stirred at r.t. for 10 days. The column chromatography (dichloromethane/ethyl acetate from 100 : 1 to 100 : 5) gave the product **11b** (340 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.7 Hz, 4H), 7.04 (dt, J = 15.2, 6.8 Hz, 2H), 6.98–6.88 (m, 6H), 3.87 (s, 6H), 2.38 (q, J = 7.0 Hz, 4H), 1.77 (p, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.83, 163.34, 147.49, 130.80, 130.70, 126.11, 113.76, 55.45, 32.11, 26.79. HR-MS (APCI$^+$): For $C_{23}H_{25}O_4^+$ $[M+H]^+$ calculated 365.17474, found 365.17459.

(2*E*,7*E*)-1,9-Bis(4-(trifluoromethyl)phenyl)nona-2,7-diene-1,9-dione (11c)



11c

Into the solution of (2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)triphenylphosphonium bromide (1.27 g, 2.4 mmol) in methanol (50 mL) and water (50 mL) sodium hydroxide (in the form of 1.5M aqueous solution) was added until the pH value of the reaction mixture reached 8. The mixture was stirred vigorously overnight. After evaporation of methanol, dichloromethane (100 mL) was added to the residue and water phase was extracted with dichloromethane (3×30 mL). Organic layers were dried over Na_2SO_4 and evaporated to obtain the ylide **29** (1.00 g, 93 %). The solution of ylide **29** (975 mg, 2.2 mmol) and glutaraldehyde (50% solution in water, 200 mg, 1.0 mmol) in dichloromethane (3 mL) was vigorously stirred at r.t. for 3 days. The column chromatography (dichloromethane) gave the product **11c** (108 mg, 25 %), m.p. 66–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.7 Hz, 4H), 7.74 (d, J = 8.5 Hz, 2H), 7.10 (dt, J = 15.4, 6.9 Hz, 2H), 6.89 (dt, J = 15.4, 1.4 Hz, 2H), 2.53–2.32 (m, 4H), 1.80 (p, J = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.77, 149.98, 140.79, 134.22 (q, J = 32.8 Hz), 129.01, 126.38, 125.77 (q, J = 3.7 Hz), 123.77 (q, J = 272.7 Hz), 32.41, 26.74. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.08 . HR-MS (ESI$^+$): For $C_{23}H_{18}F_6O_2Na^+$ $[M+Na]^+$ calculated 463.11032, found 463.11057.

2 [2+2] Photocycloadditions

2.1 General procedures

For all photocatalytic experiments, Schlenck technique was used. Oxygen was removed from the solutions by three freeze-pump-thaw cycles using argon as an inert gas.

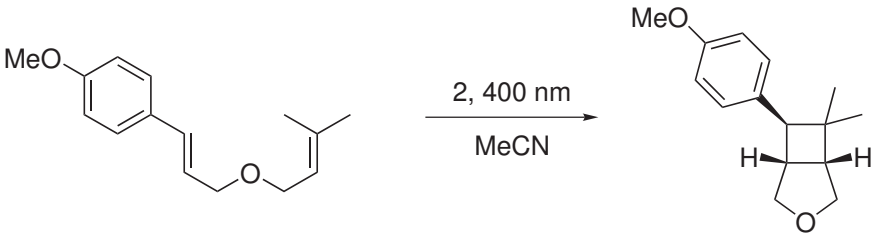
2.2 Experiments on analytical scale

Reactions were performed in Schlenck tube with inner diameter at 5 mm mounted on an optical bench with high power LED emitor LED Engin LZC-70UA00 as a light source. A solution of flavin catalyst **2** in $CDCl_3$ (0.02M, 25 µL, 5×10^{-7} mol) was added to the Schlenck tube and the solvent was evaporated by blowing a moderate stream of air into the tube for 5 min. Then the solution of corresponding substrate (0.1M, 200 µL, 2×10^{-5} mol) in deuterated solvent and 800 µL of the same deuterated solvent was added. Reaction tube was sealed with magnetic stirring bar inside and the oxygen was removed. Schlenck tube was irradiated for an appropriate time and then the reaction mixture was transferred to the NMR cuvette.

2.3 Experiments on preparative scale

Reactions were performed in Schlenck tube with inner diameter at 22 mm. A solution of flavin catalyst **2** in $CDCl_3$ (0.02M, 250 µL, 5×10^{-6} mol) was added to the Schlenck tube and the solvent was evaporated by blowing a moderate stream of air into the tube for 10 min. Substrate (2×10^{-4} mol) and acetonitrile (20 mL) were added. Reaction tube was sealed with magnetic stirring bar inside and the oxygen was removed. Schlenck tube was irradiated on laboratory apparatus with six high power LED emitors LED Engin LZ4-00UA00 directly shining on the tube from three directions at distance of 5 mm from the tube wall. The apparatus including the reaction tube is actively air-cooled by 120mm fan from the bottom (see A.10 for apparatus picture). After evaporation of solvents, the crude product was purified by chromatography or sublimation (see below for details). NMR spectra of known products corresponded to those already published (references given at the name of the cycloadduct).

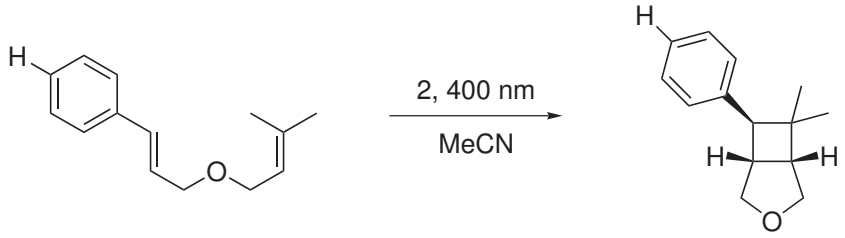
(1*R,5*R**,7*R**)-7-(4-Methoxyphenyl)-6,6-dimethyl-3-oxabicyclo[3.2.0]heptane (4a)[6]**



4a

After 10 min of irradiation, water (30 mL) was added and the product was extracted with ether (2×30 mL), organic layers were combined, washed twice with water, dried over $MgSO_4$ and evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Clear oil was isolated (38 mg, 82 %, *dr* > 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.03 (m, 2H), 6.88–6.83 (m, 2H), 4.22–4.10 (m, 1H), 3.80 (s, 3H), 3.78 (d, J = 8.7 Hz, 1H), 3.56–3.47 (m, 1H), 3.47–3.37 (m, 1H), 3.21 (td, J = 7.7, 4.5 Hz, 1H), 2.92 (d, J = 7.4 Hz, 1H), 2.43–2.35 (m, 1H), 1.08 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.87, 132.75, 128.58, 113.41, 72.04, 69.10, 55.21, 51.24, 46.53, 38.44, 37.18, 26.17, 24.15. HR-MS (APCI$^+$): For $C_{15}H_{21}O_2^+$ $[M+H]^+$ calculated 233.15361, found 233.15348.

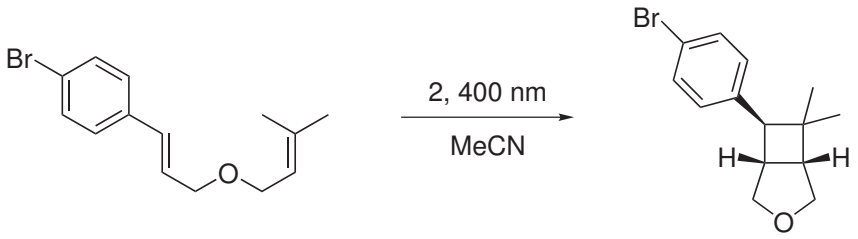
(1*R,5*R**,7*R**)-6,6-Dimethyl-7-phenyl-3-oxabicyclo[3.2.0]heptane (4b)[6]**



4b

After 10 min of irradiation, water (30 mL) was added and the product was extracted with ether (2×30 mL), organic layers were combined, washed twice with water, dried over $MgSO_4$ and evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Clear oil was isolated (35 mg, 87 %, *dr* > 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.11 (m, 5H), 4.18 (ddd, J = 10.0, 0.6 Hz, 1H), 3.80 (dd, J = 9.1, 0.8 Hz, 1H), 3.52 (dd, J = 10.1, 6.7 Hz, 1H), 3.45 (ddt, J = 9.0, 4.5, 0.5 Hz, 1H), 3.28 (td, J = 7.7, 4.5 Hz, 1H), 3.00 (d, J = 7.3 Hz, 1H), 2.41 (ddt, J = 8.1, 6.7, 0.7 Hz, 1H), 1.12 (s, 3H), 0.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.73, 128.11, 127.77, 126.04, 72.20, 69.25, 52.03, 46.72, 38.10, 26.35, 24.36. HR-MS (APCI$^+$): For $C_{14}H_{19}O^+$ $[M+H]^+$ calculated 203.14304, found 203.14301.

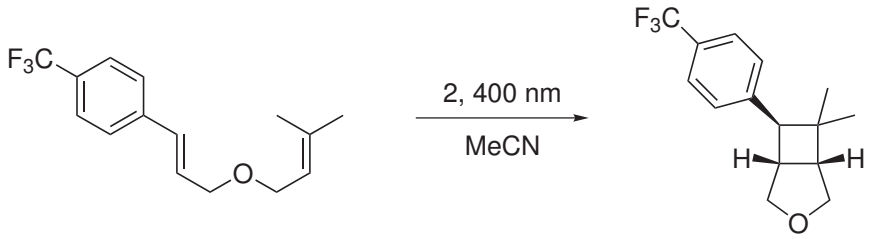
(1*R,5*R**,7*R**)-7-(4-Bromophenyl)-6,6-dimethyl-3-oxabicyclo[3.2.0]heptane (4c)**



4c

After 45 min of irradiation, acetonitrile was evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Slightly yellow oil was isolated (42 mg, 76 %, $dr > 10:1$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.36 (m, 2H), 7.08–6.90 (m, 2H), 4.16 (dd, $J = 10.1$, 1.1 Hz, 1H), 3.77 (d, $J = 9.0$ Hz, 1H), 3.50 (dd, $J = 10.1$, 6.7 Hz, 1H), 3.43 (dd, $J = 9.0$, 4.5 Hz, 1H), 3.21 (td, $J = 7.7$, 4.5 Hz, 1H), 2.93 (d, $J = 7.3$ Hz, 1H), 2.44–2.36 (m, 1H), 1.09 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.59, 131.06, 129.30, 119.69, 71.93, 69.05, 51.37, 46.55, 38.06, 37.23, 26.17, 24.16. HR-MS (ESI$^+$): For $C_{14}H_{18}BrO^+$ $[M+H]^+$ calculated 281.05355, found 281.05347. For structure assignement by NMR see Section A.4.

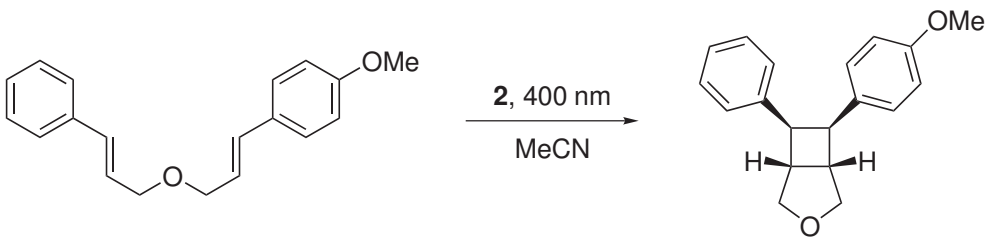
(1*R,5*R**,7*R**)-6,6-Dimethyl-7-[4-(trifluoromethyl)phenyl]-3-oxabicyclo[3.2.0]heptane (4d)**



4d

After 30 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (dichloromethane). Clear oil was isolated (44 mg, 81 %, $dr > 10:1$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.51 (m, 2H), 7.27–7.22 (m, 2H), 4.18 (dt, $J = 10.3$, 0.7 Hz, 1H), 3.79 (d, $J = 9.1$ Hz, 1H), 3.52 (dd, $J = 10.1$, 6.7 Hz, 1H), 3.45 (dd, $J = 9.1$, 4.4 Hz, 1H), 3.29 (td, $J = 7.7$, 4.4 Hz, 1H), 3.04 (d, $J = 7.3$ Hz, 1H), 2.43 (ddt, $J = 7.5$, 5.6, 1.2 Hz, 1H), 1.13 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.76, 128.20 (q, $J = 32.3$ Hz), 127.82, 124.92 (q, $J = 3.8$ Hz), 124.33 (q, $J = 271.7$ Hz), 71.90, 69.04, 51.69, 46.58, 37.90, 37.51, 26.19, 24.18. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.79. HR-MS (APCI$^+$): For $C_{15}H_{18}F_3O^+$ $[M+H]^+$ calculated 271.13043, found 271.13045.

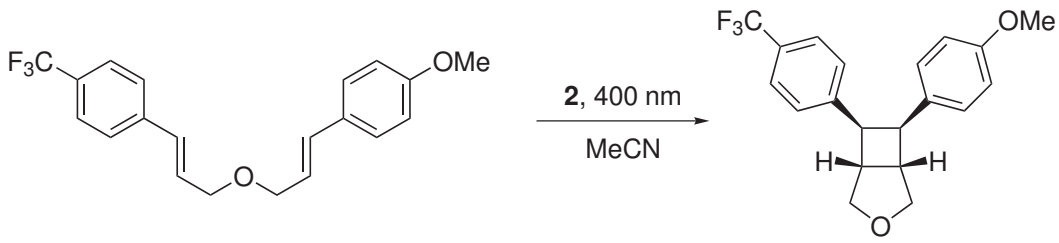
(1*R,5*S**,6*R**,7*S**)-6-(4-Methoxyphenyl)-7-phenyl-3-oxabicyclo[3.2.0]heptane (6a)[17]**



6a

After 10 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (hexane/ethyl acetate ~ 10 : 1). White solid was isolated (34 mg, 61 %, *dr* ~ 7 : 3). For ^{1}H NMR and ^{13}C NMR, see Section A.4. HR-MS (APCI^{+}): For $C_{19}H_{21}O_2^+$ $[M+H]^+$ calculated 281.15361, found 281.15353.

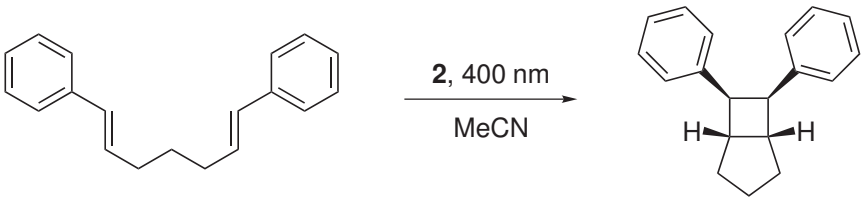
(1*R,5*S**,6*R**,7*S**)-6-(4-Methoxyphenyl)-7-[4-(trifluoromethyl)phenyl]-3-oxabicyclo-[3.2.0]heptane (6b)**



6b

After 10 min of irradiation, acetonitrile was evaporated. Crude product was purified by sublimation. Slightly yellow grease was obtained (68 mg, 97 %, *dr* ~ 5 : 1). For ^{1}H NMR and ^{13}C NMR, see Section A.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.74. HR-MS (APCI^{-}): For $C_{20}H_{18}F_3O_2^-$ $[M-H]^-$ calculated 347.12644, found 347.12620.

(1*R*,5*S*,6*R*,7*S*)-6,7-Diphenylbicyclo[3.2.0]heptane (8)[27]

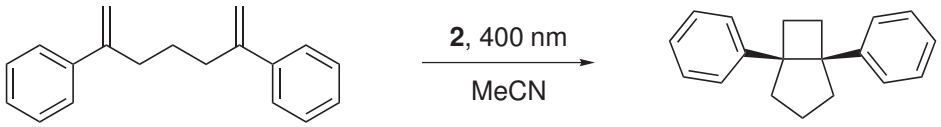


8

After 90 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (hexane/ethyl acetate ~ 10 : 1). Clear oil was isolated (18 mg, 42 %, *dr* ~ 7 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.02 (m, 4H), 7.00–6.92 (m, 6H), 3.50 (d, $J = 4.1$ Hz, 2H), 3.16–3.06 (m, 2H), 2.20–2.03 (m, 1H), 2.02–1.92 (m, 1H), 1.85–1.70 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.05, 128.24, 127.48, 125.14, 47.63, 41.57, 32.94, 25.73. HR-MS (APCI$^+$): For $C_{19}H_{21}^+$ $[M+H]^+$ calculated 249.16378, found 249.16328.

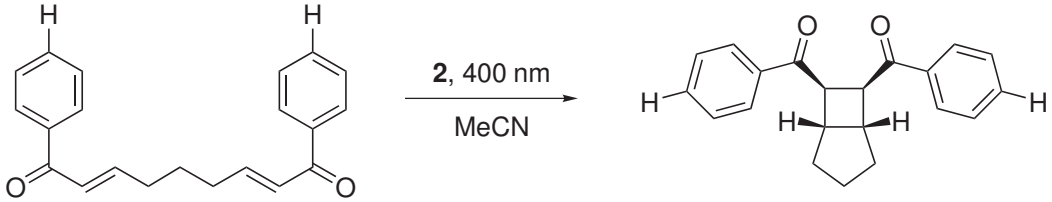
cis-1,5-Diphenylbicyclo[3.2.0]heptane (10)[28]



10

After 25 min of irradiation, acetonitrile was evaporated. Crude product was purified by sublimation. White solid was isolated (40 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.07 (m, 4H), 7.08–6.99 (m, 2H), 6.98–6.90 (m, 4H), 2.63–2.48 (m, 2H), 2.37–2.19 (m, 1H), 2.19–2.03 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.18, 127.49, 127.23, 125.05, 56.95, 42.67, 29.91, 25.04. HR-MS (APCI$^+$): For $C_{19}H_{21}^+$ $[M+H]^+$ calculated 249.16378, found 249.15380.

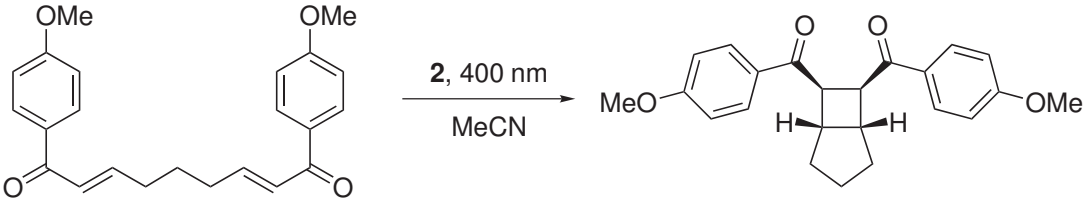
(1*R*,5*S*,6*R*,7*S*)-6,7-Dibenzoylbicyclo[3.2.0]heptane (12a)[29]



12a

After 40 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (dichloromethane). Slightly yellow solid was isolated (40 mg, 70 %, $dr \sim 5:1$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.73 (m, 4H), 7.48–7.41 (m, 2H), 7.39–7.31 (m, 4H), 3.89–3.83 (m, 2H), 3.25–3.15 (m, 2H), 2.09–1.96 (m, 2H), 1.90–1.80 (m, 2H), 1.76–1.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.61, 136.35, 132.50, 128.45, 127.77, 48.30, 39.10, 32.47, 25.23. HR-MS (APCI$^+$): For $C_{21}H_{21}O_2^+$ $[M+H]^+$ calculated 305.15361, found 305.15396.

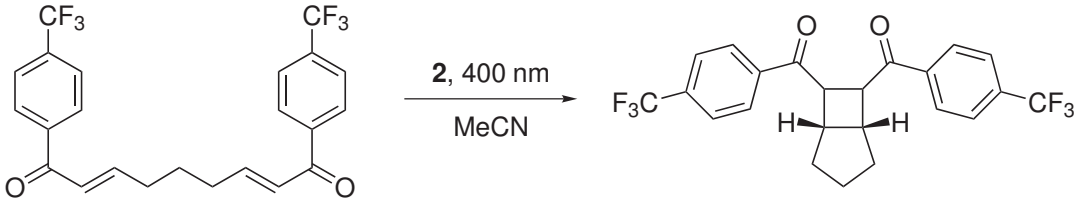
(1*R*,5*S*,6*R*,7*S*)-6,7-Bis-(4-methoxybenzoyl)bicyclo[3.2.0]heptane (12b)[30]



12b

After 45 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (hexane/ethyl acetate ~ 10 : 1). Isolated in two fractions as a white solid (49 mg, 67 %, *dr* ~ 4 : 1). Analysis for major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.67 (m, 4H), 6.92–6.72 (m, 4H), 3.91–3.83 (m, 2H), 3.80 (s, 6H), 3.22–3.16 (m, 2H), 2.05–1.97 (m, 2H), 1.86–1.78 (m, 2H), 1.73–1.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.41, 163.04, 130.08, 129.67, 113.73, 55.49, 48.19, 39.21, 32.62, 25.42. HR-MS (APCI$^+$): For $C_{23}H_{25}O_4^+$ $[M+H]^+$ calculated 365.17474, found 365.17535.

6,7-Bis-[4-(trifluoromethyl)benzoyl]bicyclo[3.2.0]heptane (12c)



12c

After 40 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (dichloromethane). (1*R**,5*S**,6*R**,7*R**)-**12c** (26 mg) and (1*R*,5*S*,6*R*,7*S*)-**12c** (25 mg) isolated as white solids (overall yield 58 %, *dr* ~ 1 : 1). (1*R**,5*S**,6*R**,7*R**)-**12c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.02 (m, 4H), 7.79–7.70 (m, 4H), 4.57 (dd, J = 10.3, 7.8 Hz, 1H), 4.27 (dd, J = 7.6, 6.3 Hz, 1H), 3.34–3.22 (m, 1H), 3.12–3.01 (m, 1H), 1.93–1.75 (m, 3H), 1.62–1.50 (m, 1H), 1.49–1.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.15, 197.19, 138.52 (d, J = 32.2 Hz), 134.71 (d, J = 32.6 Hz), 129.09, 128.81, 126.05 (q, J = 3.6 Hz), 125.90 (q, J = 3.5 Hz), 125.05 (q, J = 3.9 Hz), 122.34 (q, J = 4.0 Hz), 43.39, 43.11, 40.71, 40.45, 32.19, 28.55, 25.59. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.57, -63.58. (1*R*,5*S*,6*R*,7*S*)-**12c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 4H), 7.66–7.61 (m, 4H), 3.96–3.83 (m, 2H), 3.21 (dq, J = 4.1, 2.4 Hz, 2H), 2.13–1.99 (m, 2H), 1.93–1.82 (m, 2H), 1.80–1.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.73, 138.98, 134.20 (q, J = 32.8 Hz), 128.23, 125.80 (q, J = 3.7 Hz), 123.66 (q, J = 272.5 Hz), 48.55, 39.26, 32.55, 25.31. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.62. HR-MS (ESI$^-$): For $C_{23}H_{17}F_6O_2^-$ $[M]^-$ calculated 439.11382, found 439.11282.

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A Appendix

A.1 NMR Spectra of catalyst 2

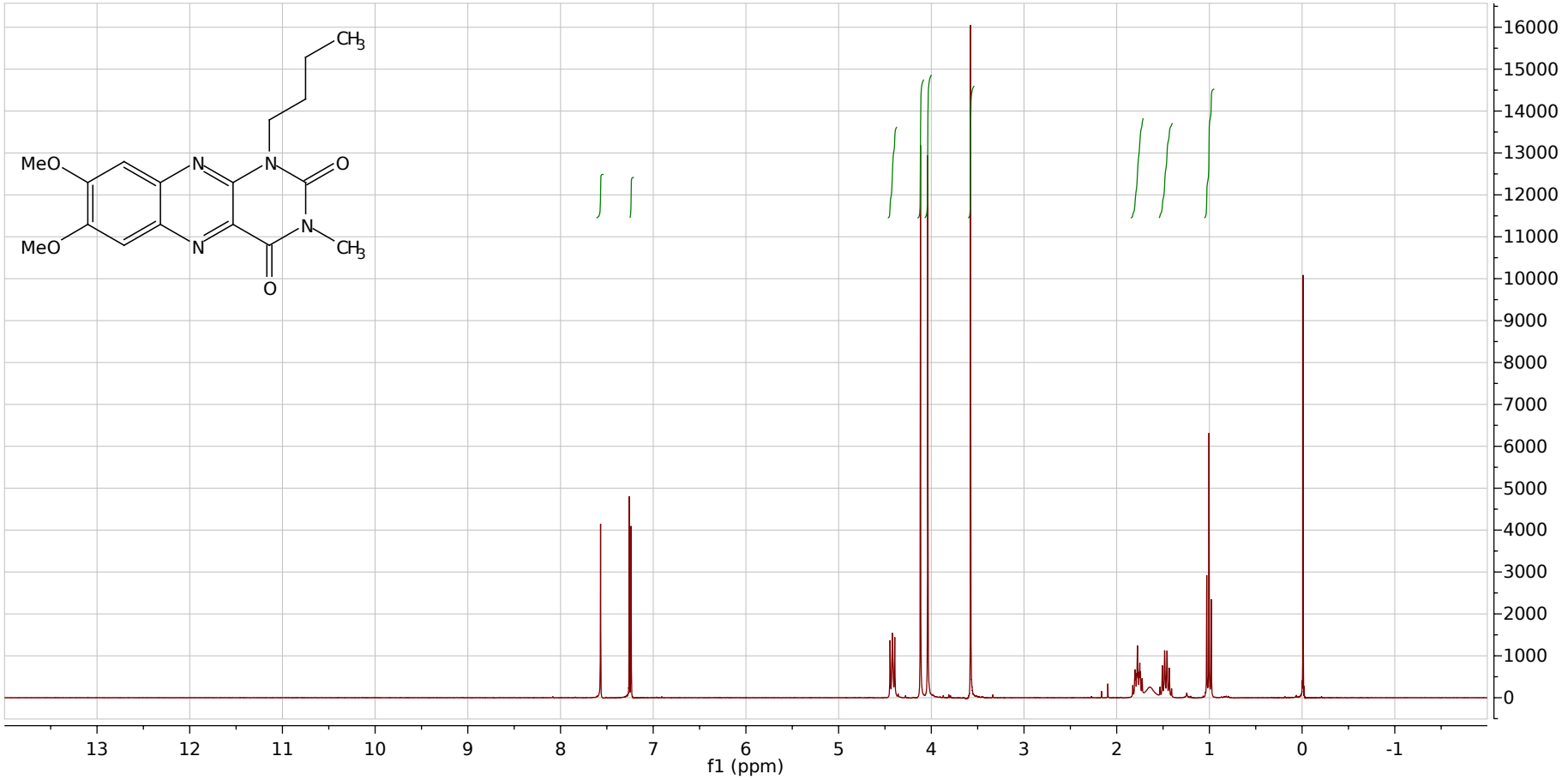


Figure S1: ^{1}H NMR Spectrum of catalyst **2**

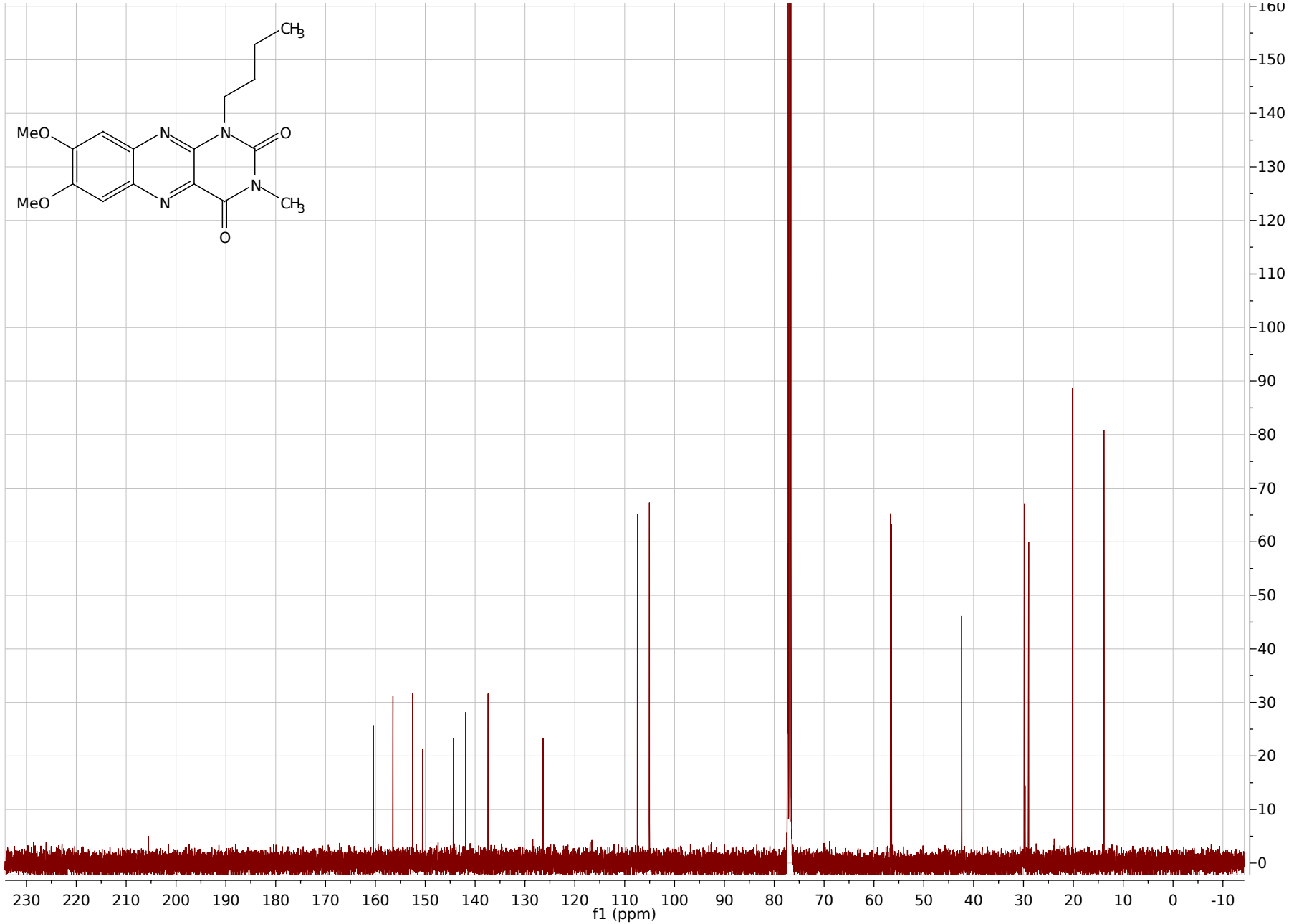


Figure S2: ^{13}C NMR Spectrum of catalyst **2**

A.2 NMR Spectra of substrates

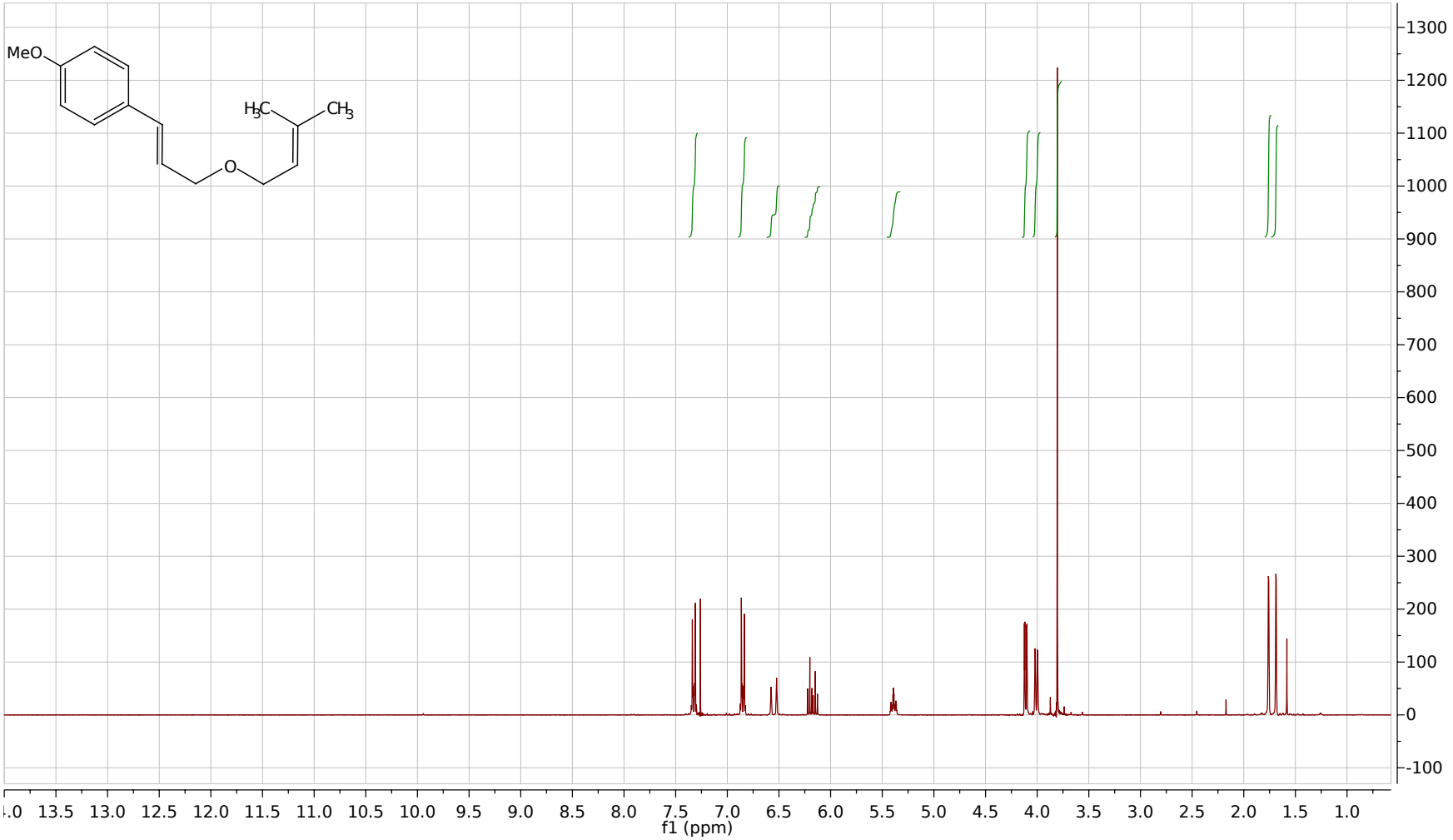


Figure S3: ^{1}H NMR Spectrum of substrate **3a**.

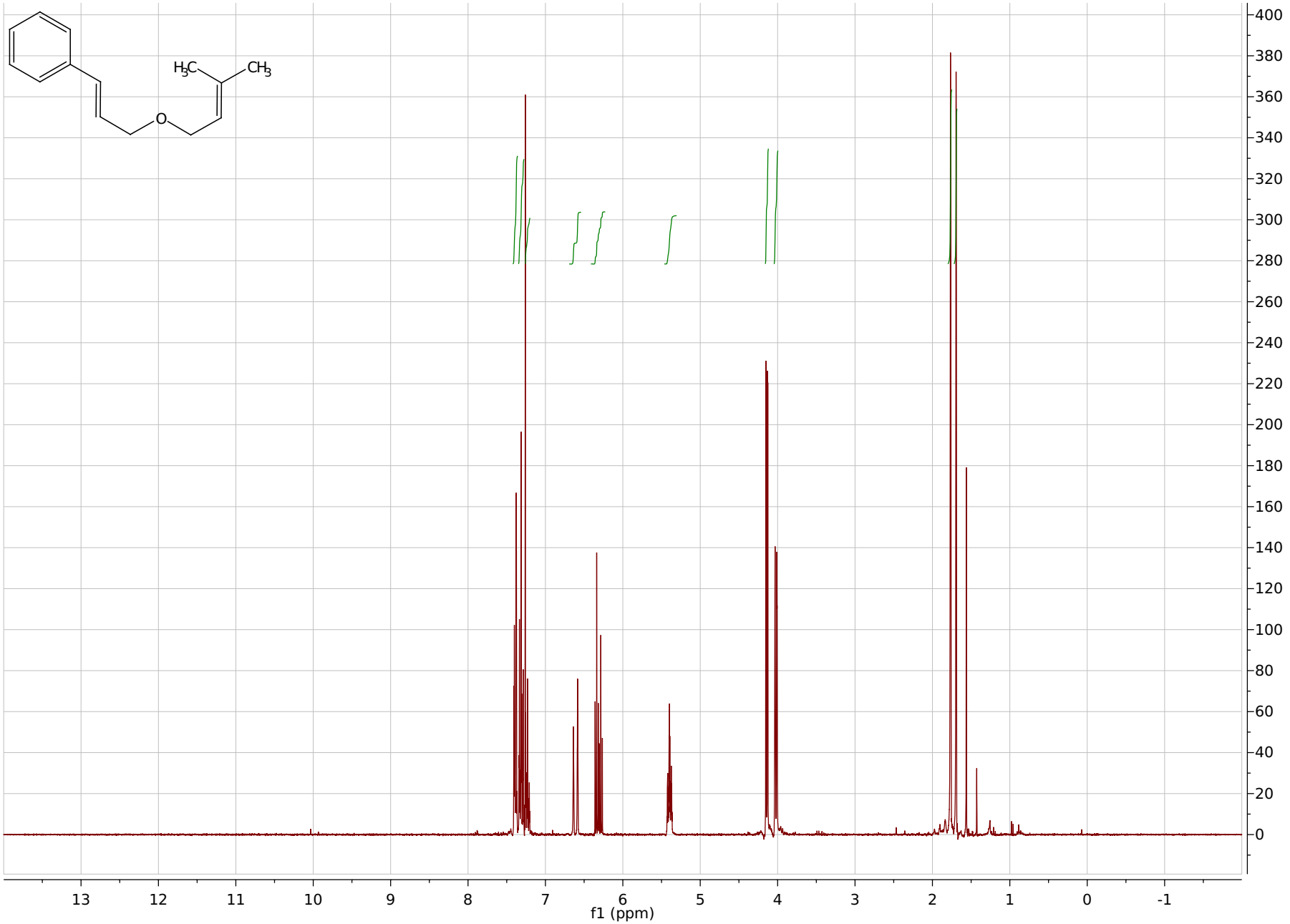


Figure S4: ^{1}H NMR Spectrum of substrate **3b**.

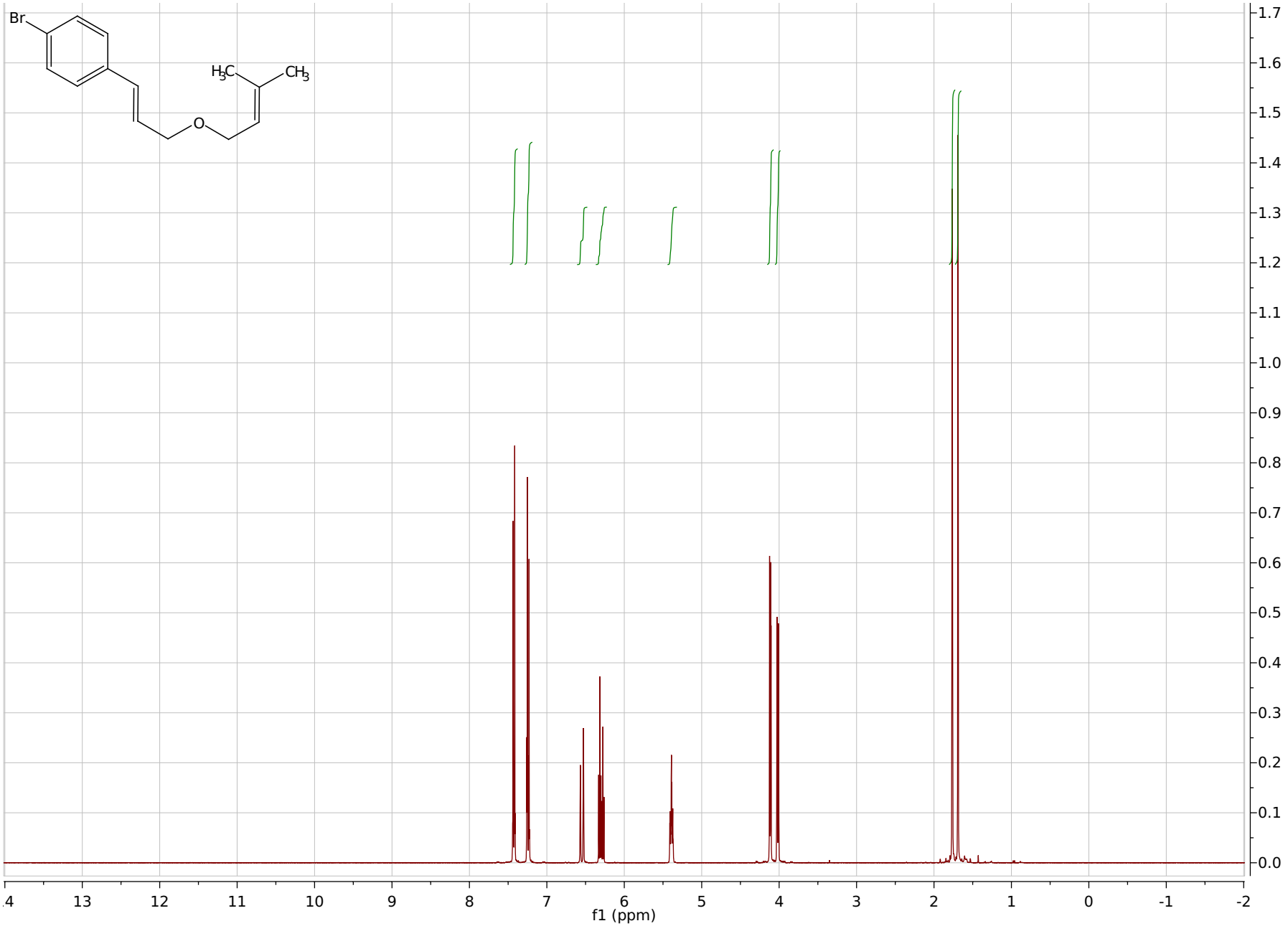


Figure S5: ^{1}H NMR Spectrum of substrate **3c**.

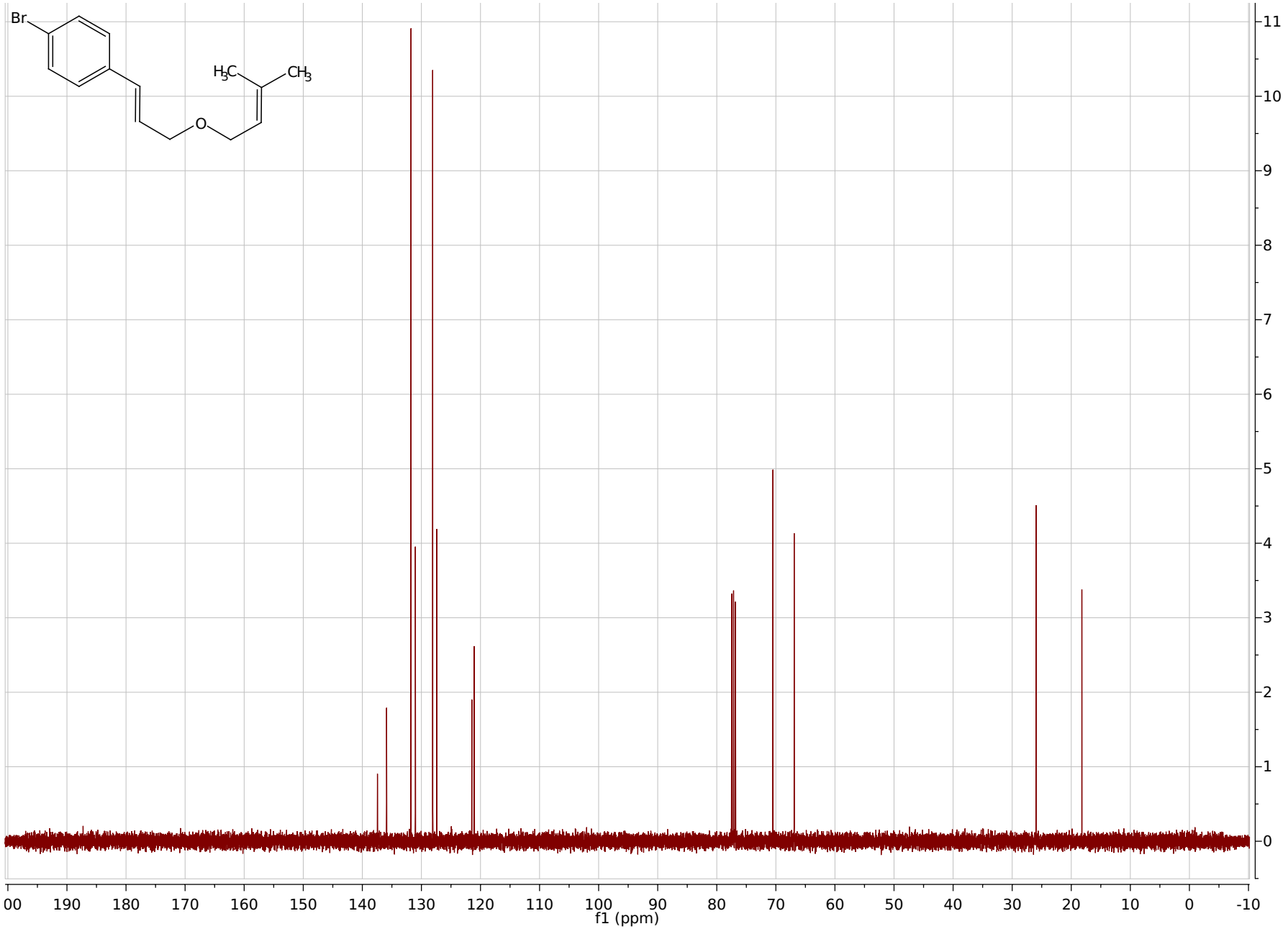


Figure S6: ^{13}C NMR Spectrum of substrate **3c**.

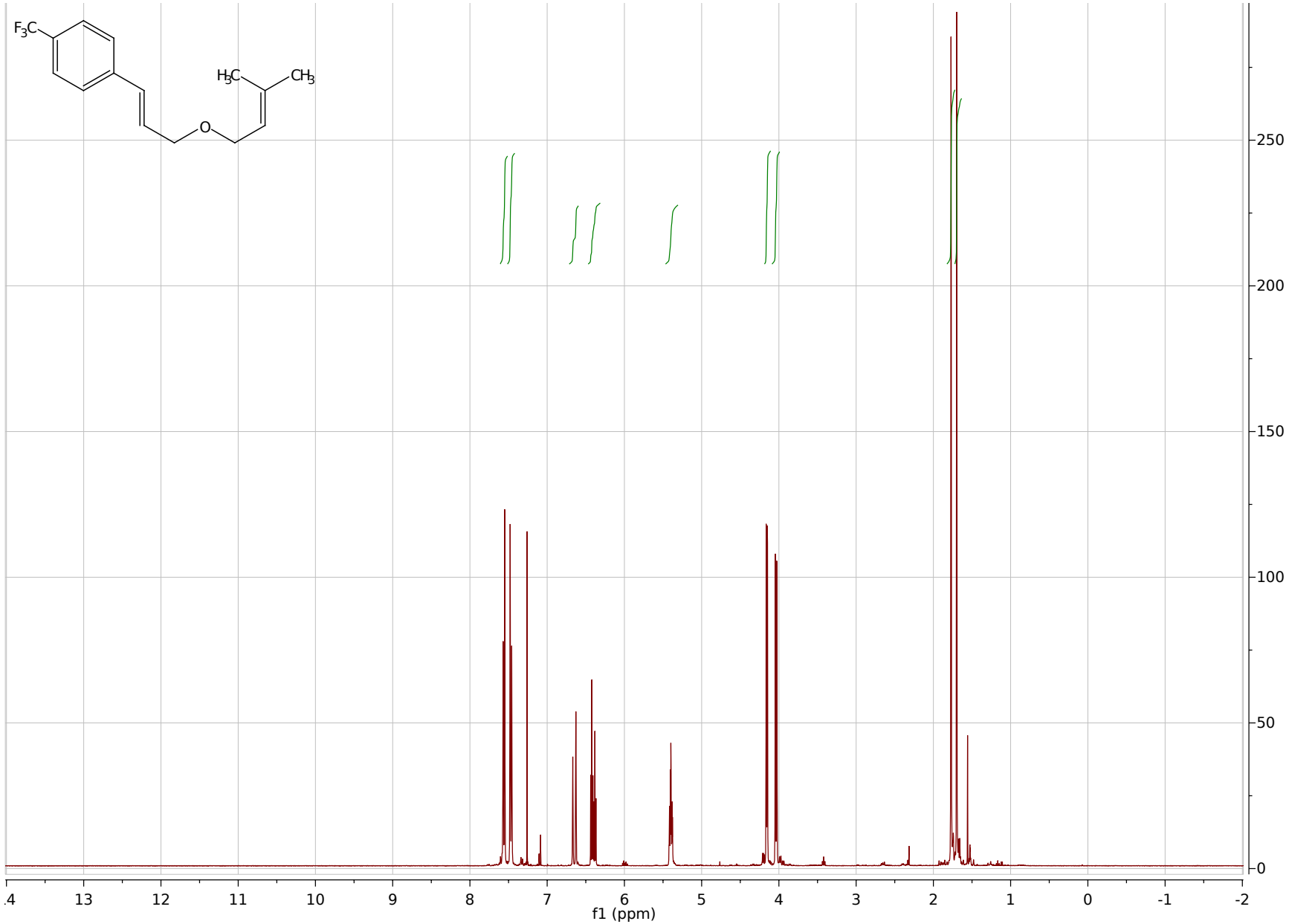


Figure S7: ^{1}H NMR Spectrum of substrate **3d**.

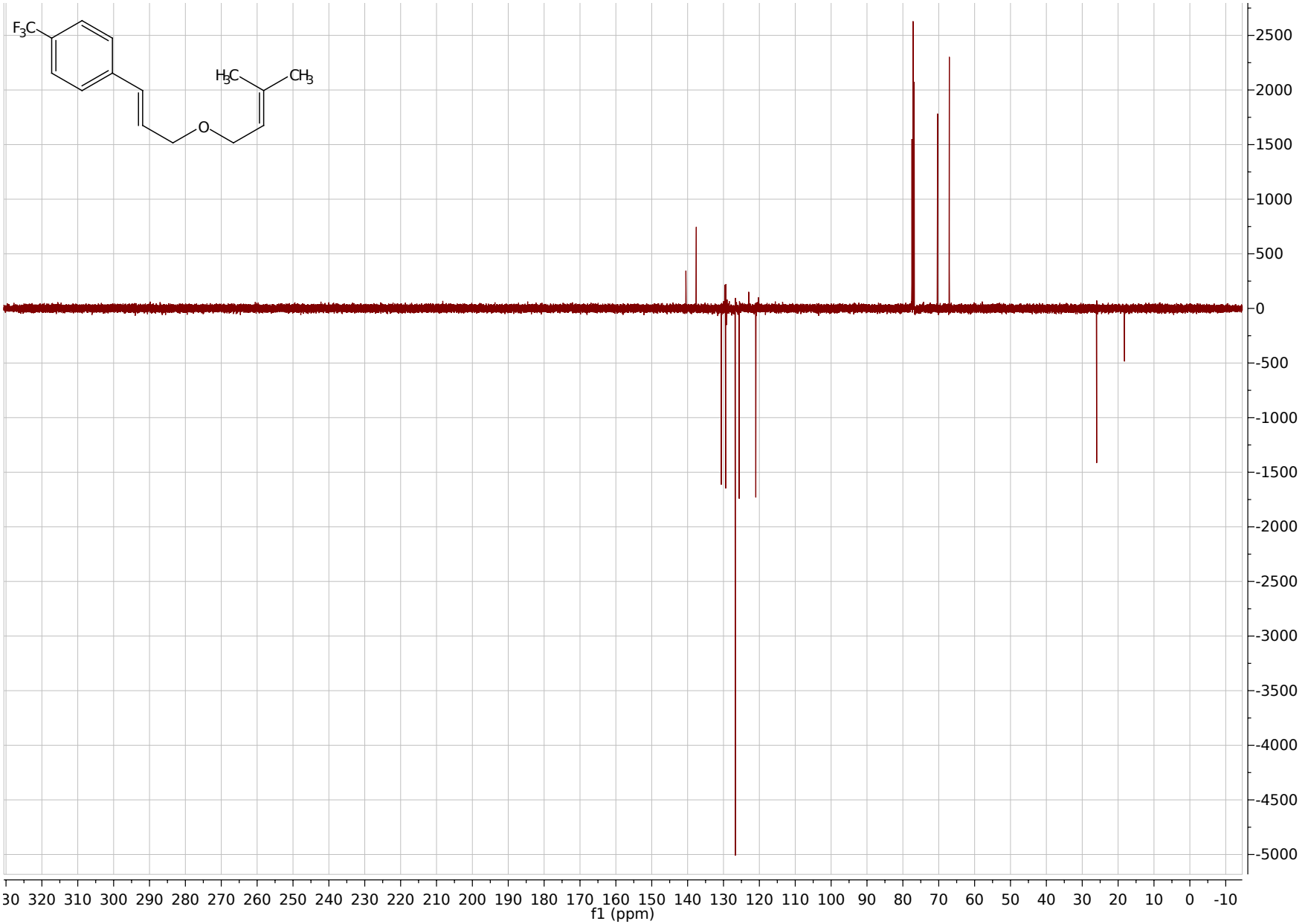


Figure S8: ^{13}C NMR Spectrum of substrate **3d**.

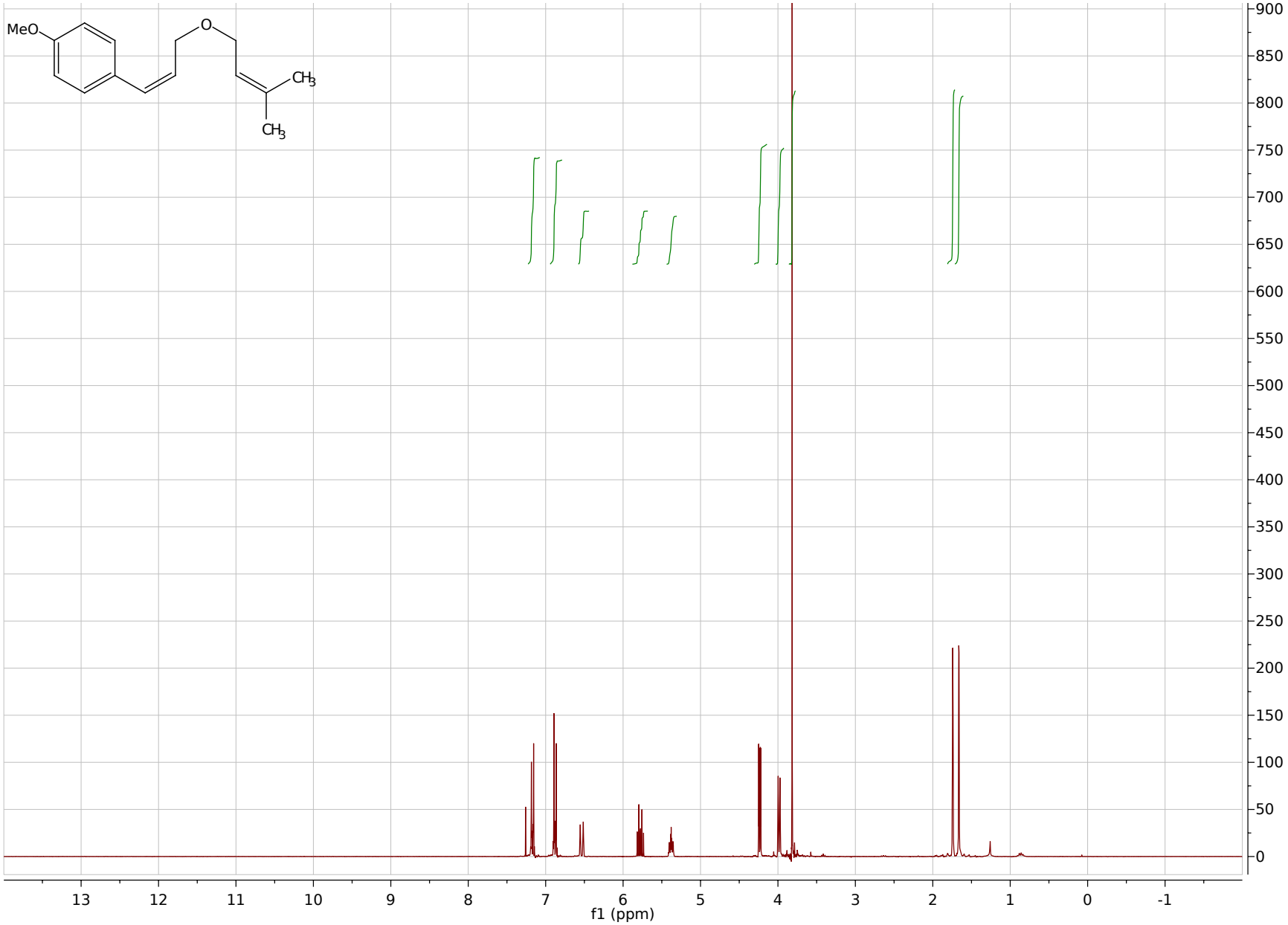


Figure S9: ^{1}H NMR Spectrum of substrate (*Z*)-**3a**.

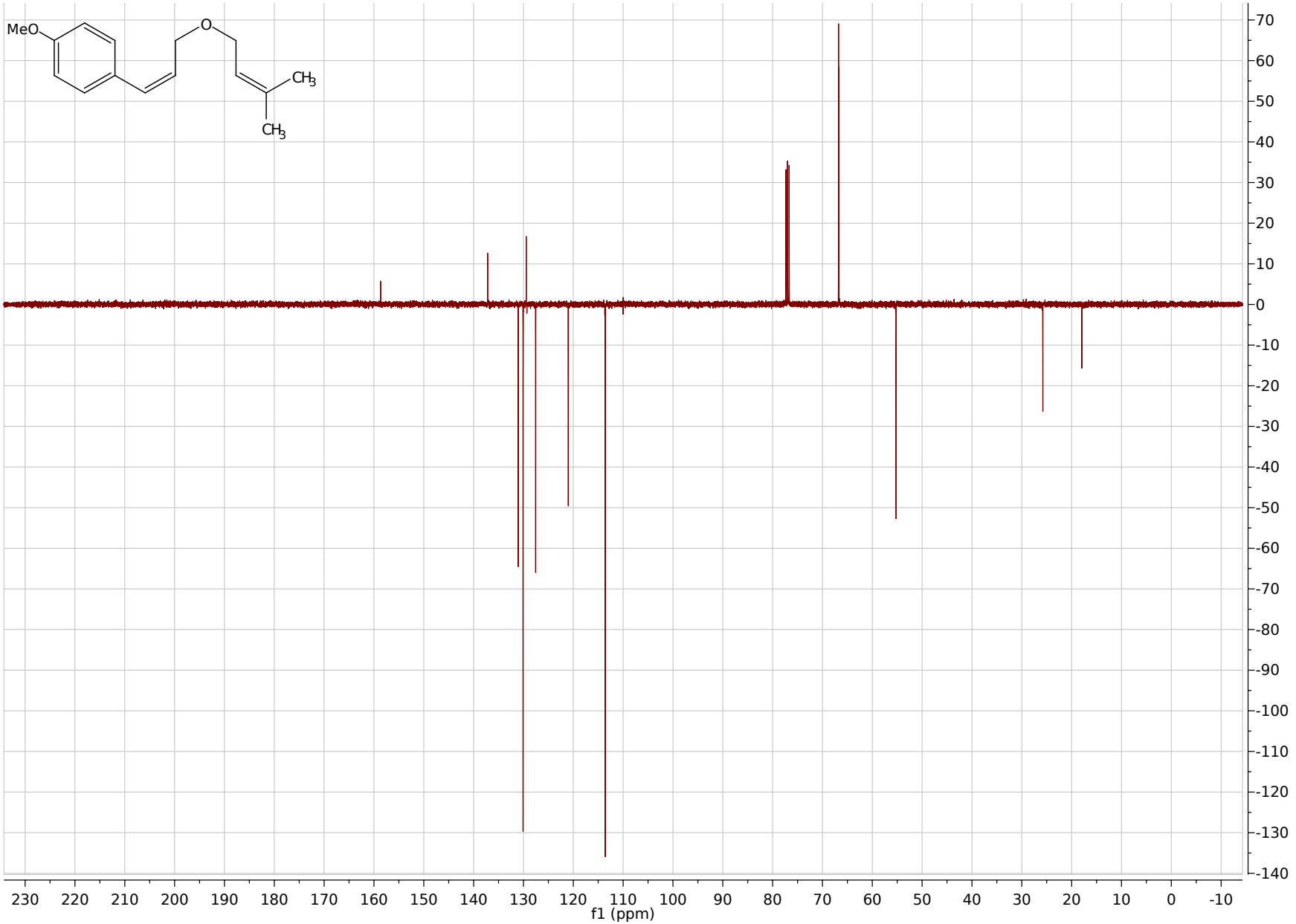


Figure S10: ^{13}C NMR Spectrum of substrate (*Z*)-**3a**.

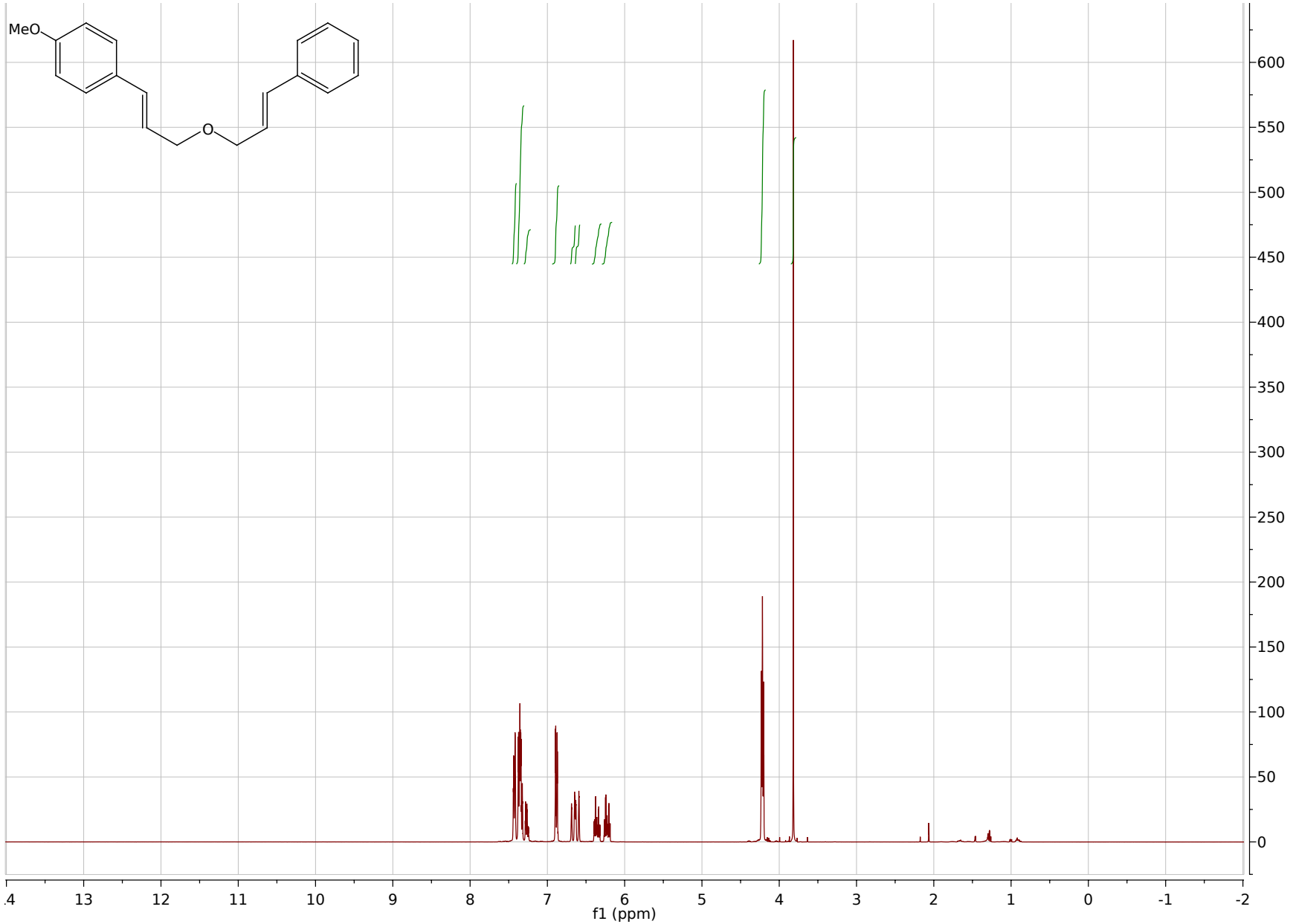


Figure S11: ^{1}H NMR Spectrum of substrate **5a**.

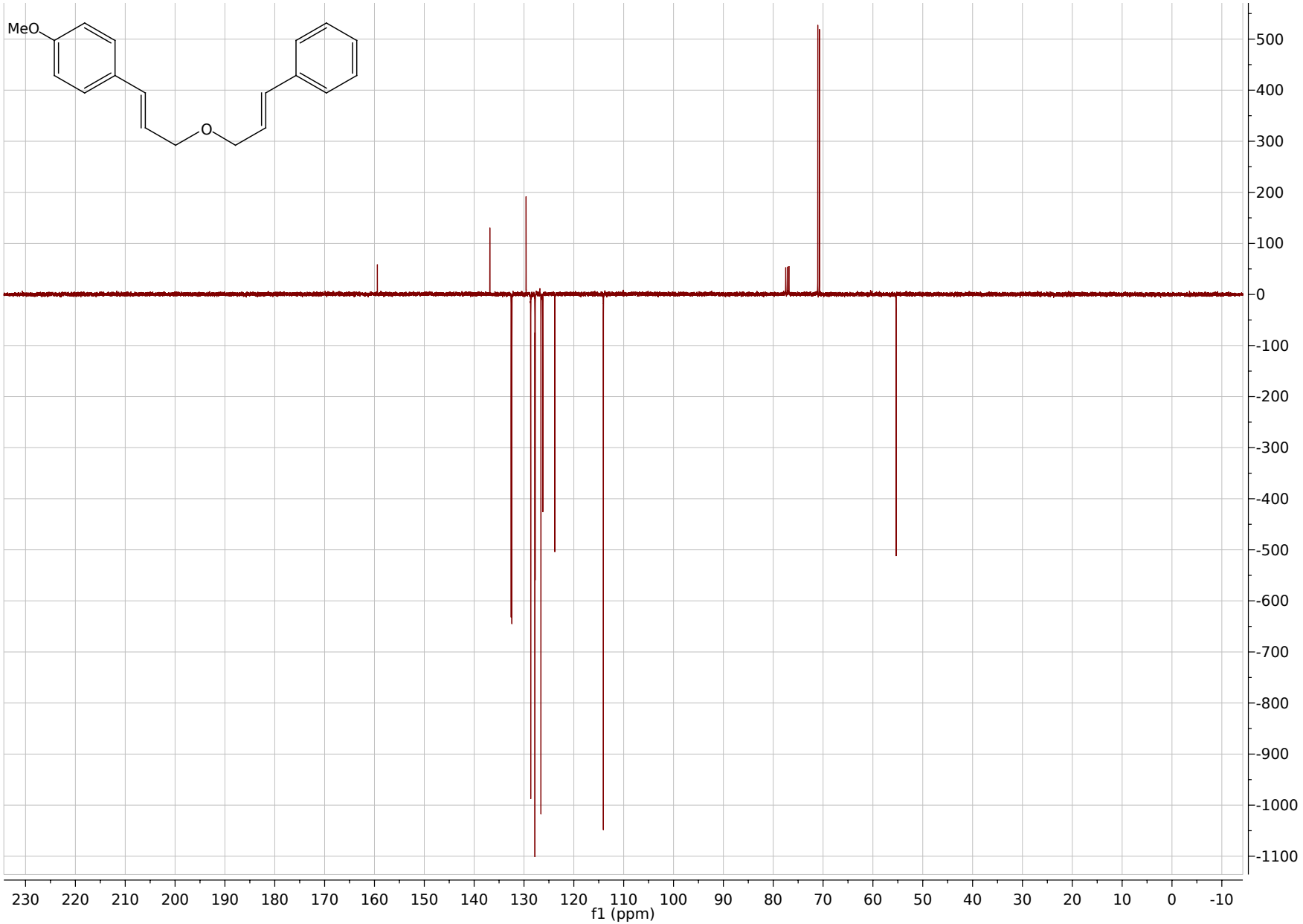


Figure S12: ^{13}C NMR Spectrum of substrate **5a**.

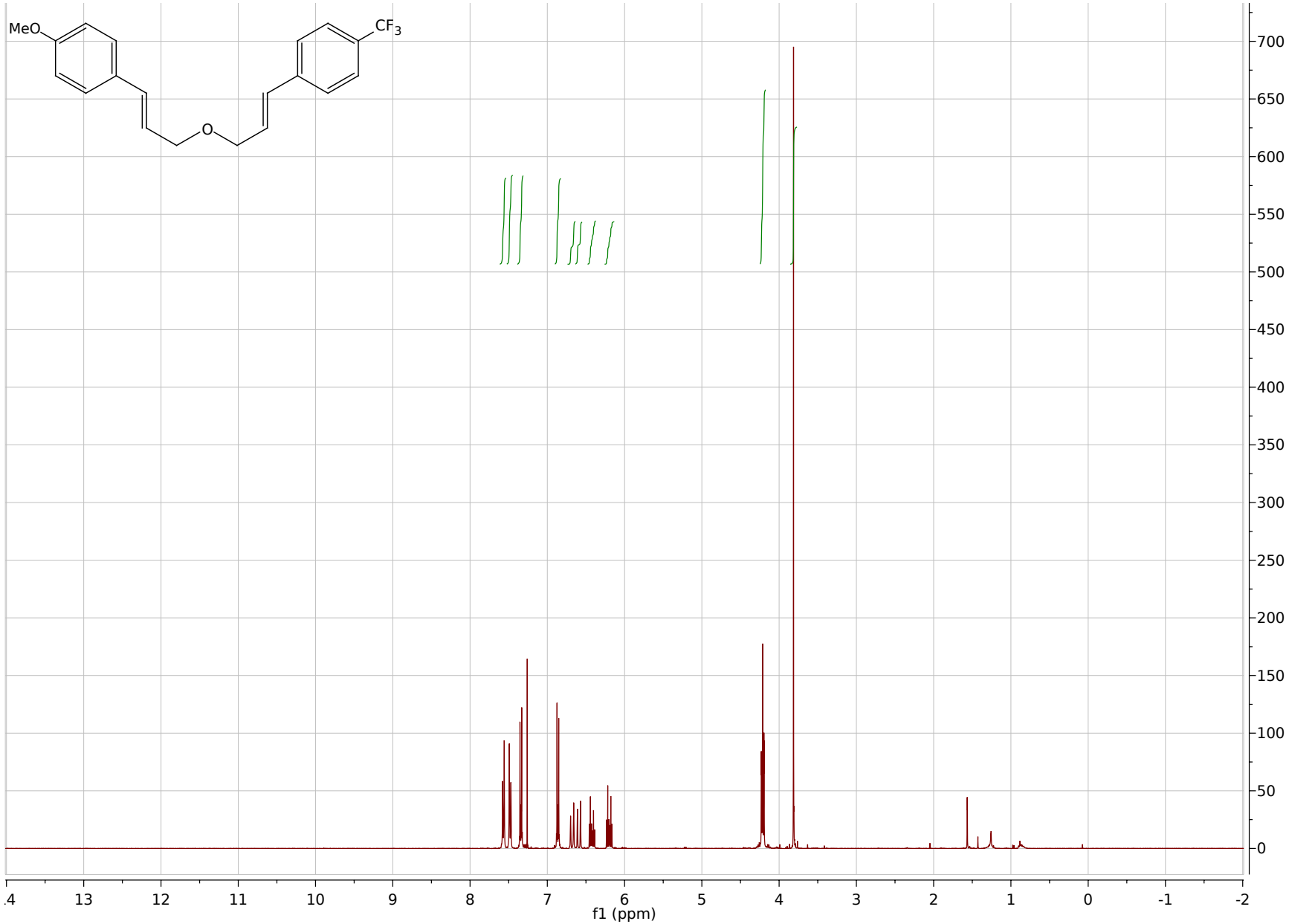


Figure S13: ^{1}H NMR Spectrum of substrate **5b**.

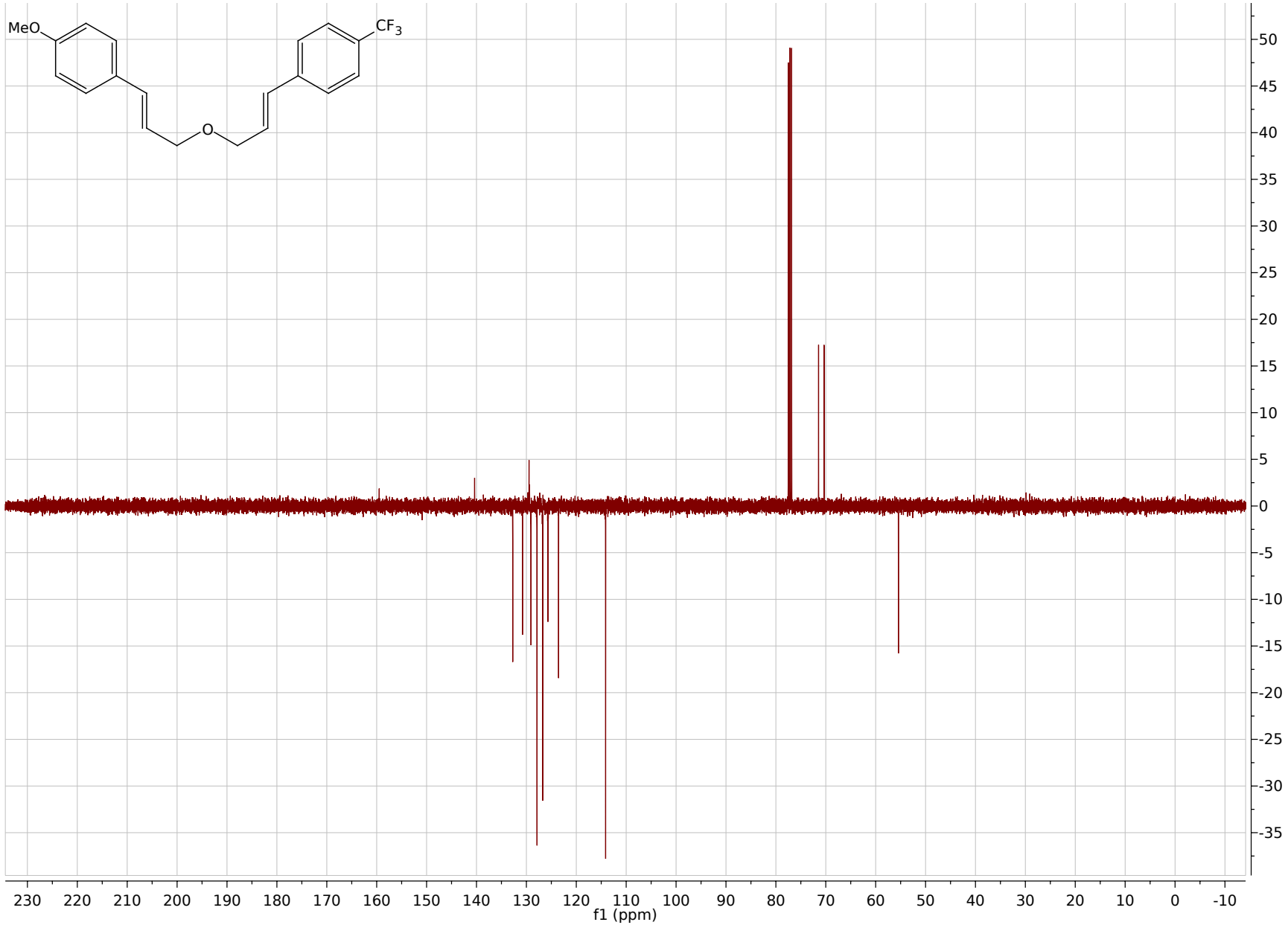


Figure S14: ^{13}C NMR Spectrum of substrate **5b**.

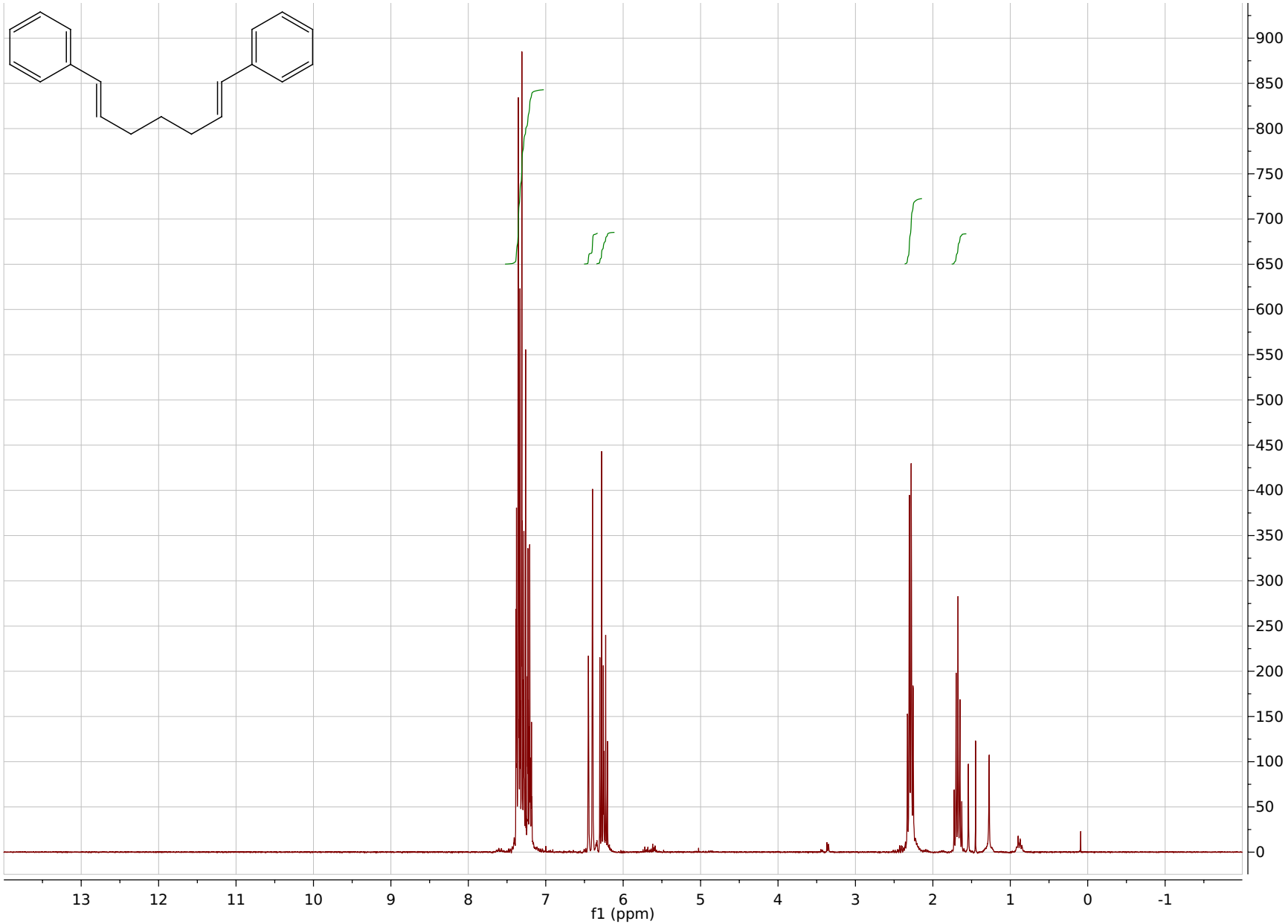


Figure S15: ^{1}H NMR Spectrum of substrate **7**.

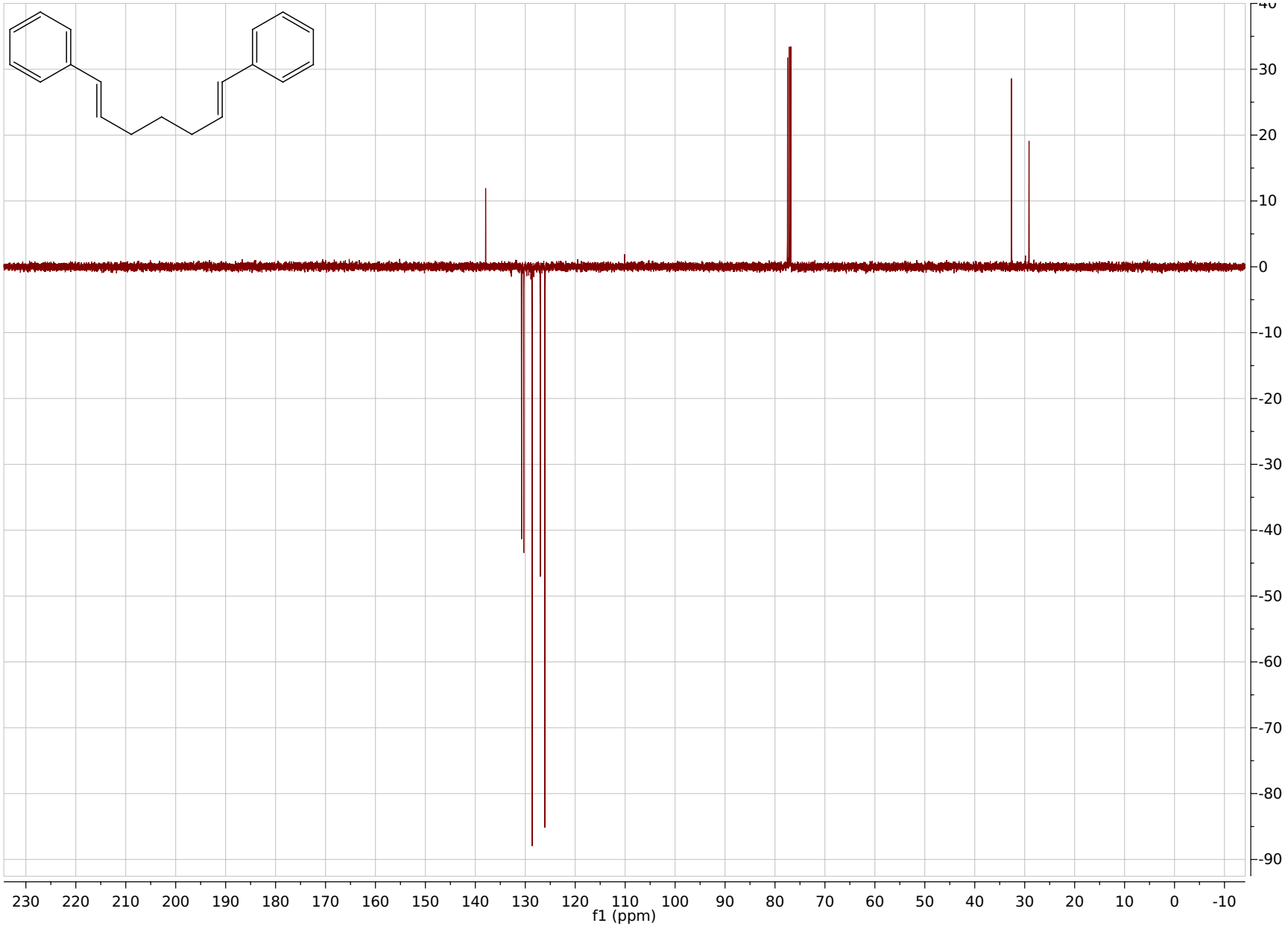


Figure S16: ^{13}C NMR Spectrum of substrate **7**.

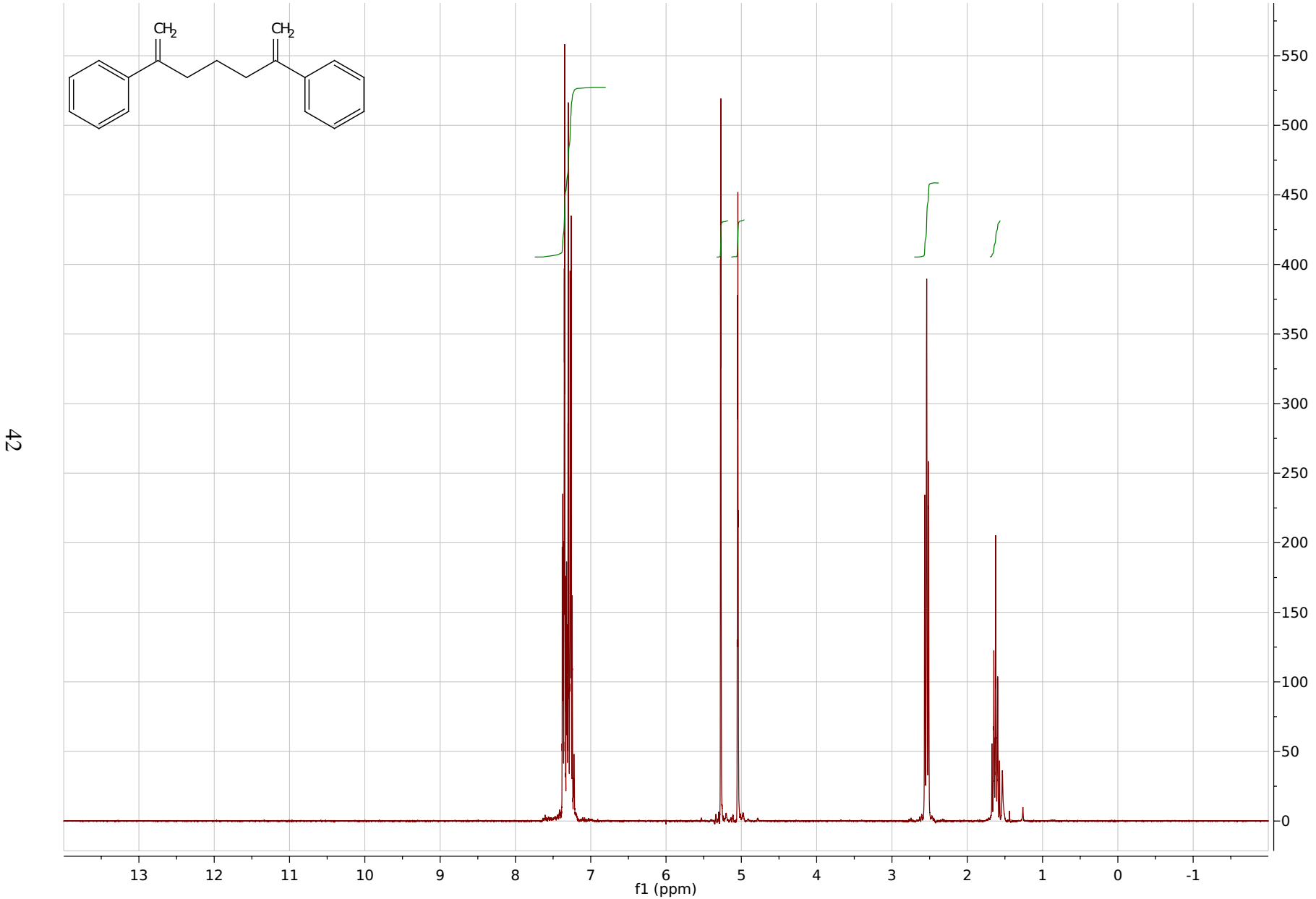


Figure S17: ^{1}H NMR Spectrum of substrate **9**.

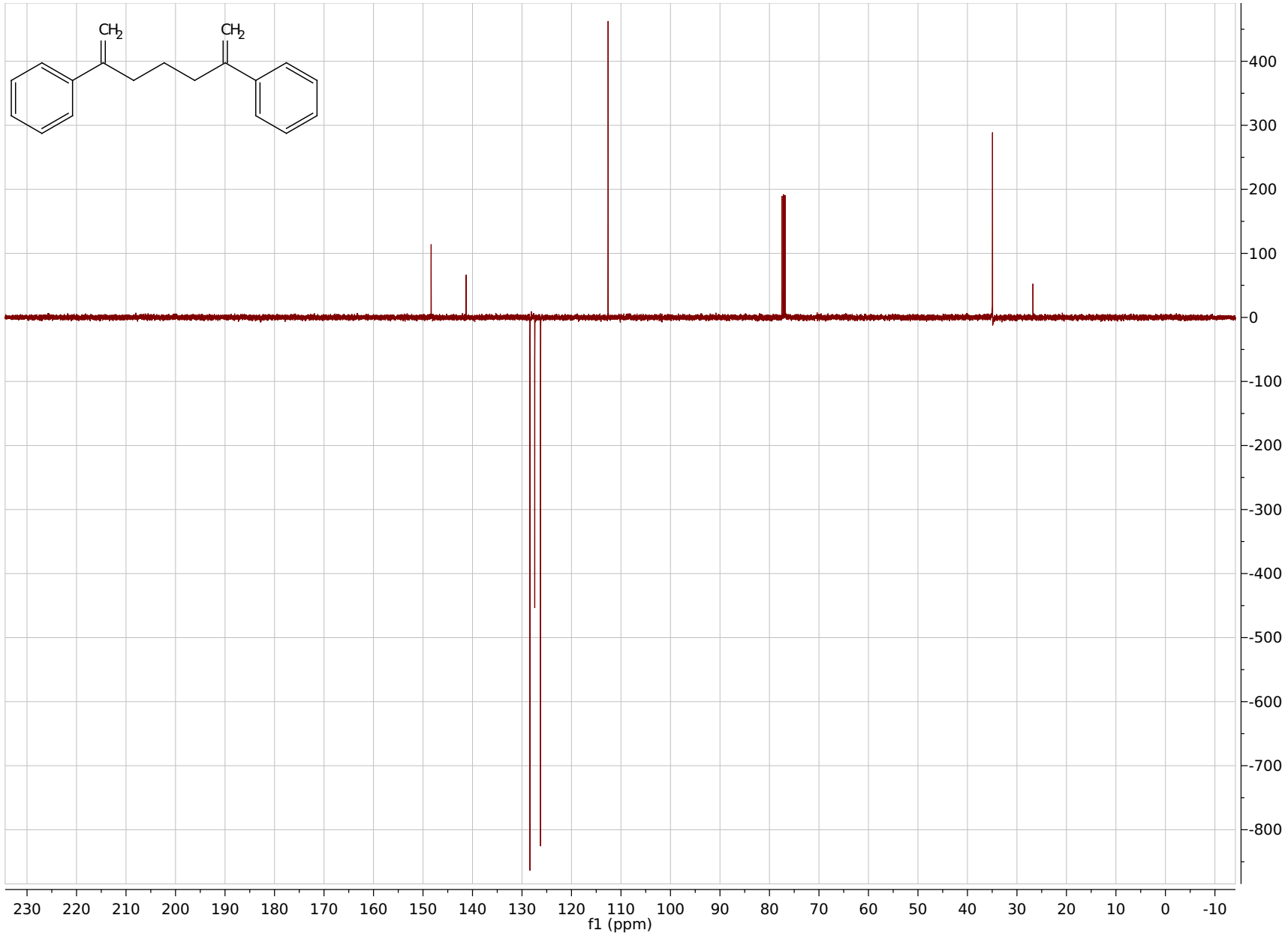


Figure S18: ^{13}C NMR Spectrum of substrate **9**.

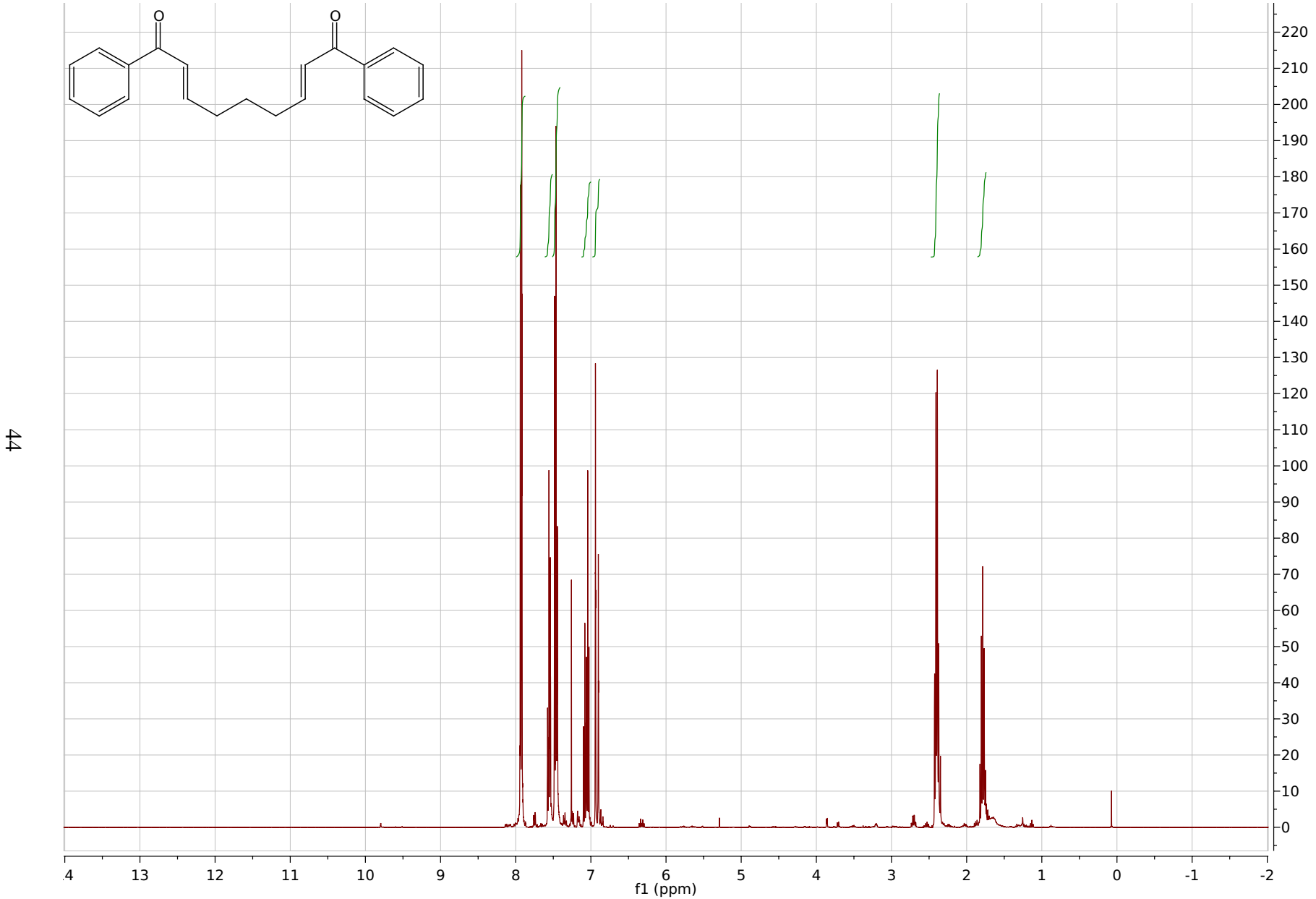


Figure S19: ^{1}H NMR Spectrum of substrate **11a**.

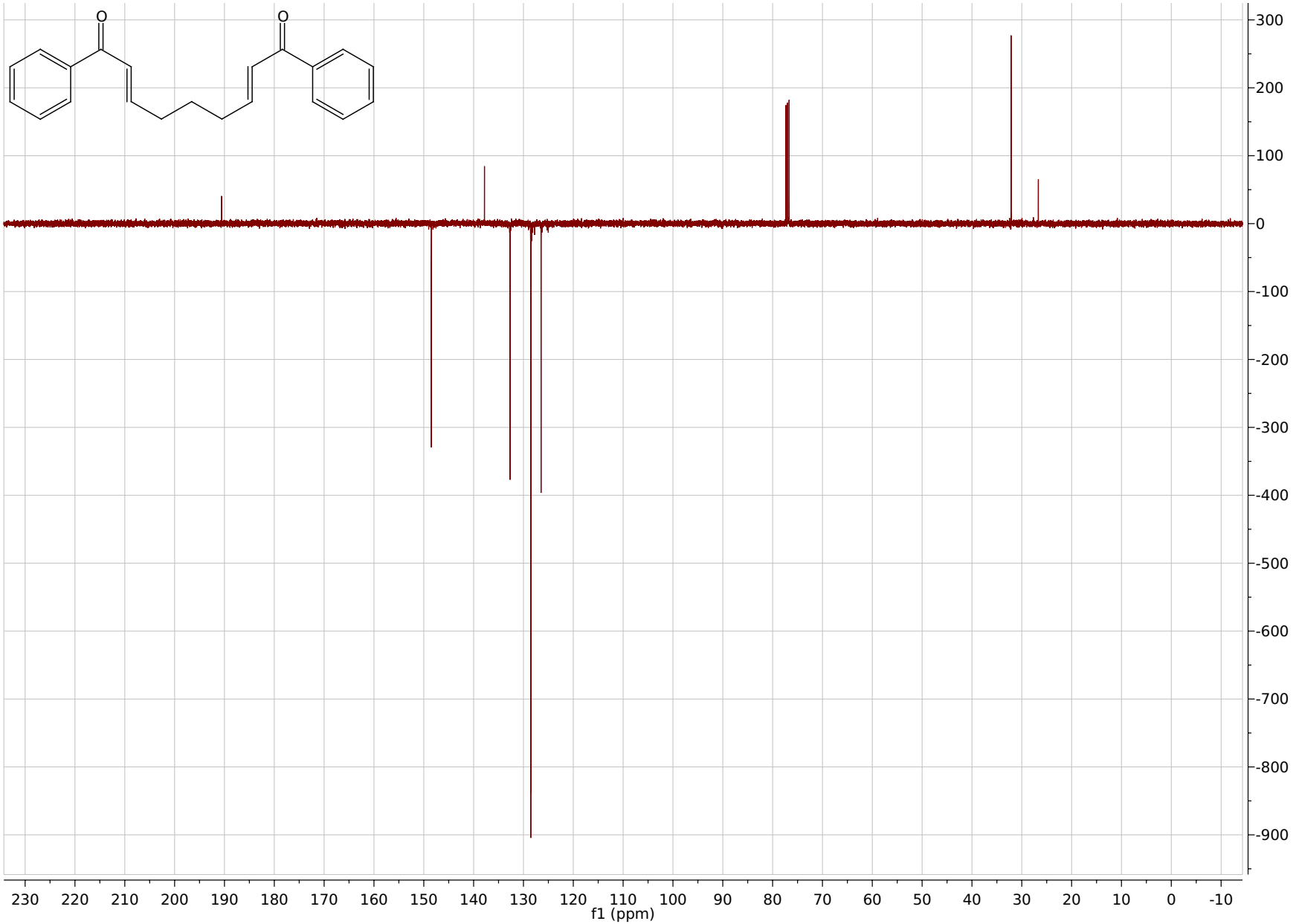


Figure S20: ^{13}C NMR Spectrum of substrate **11a**.

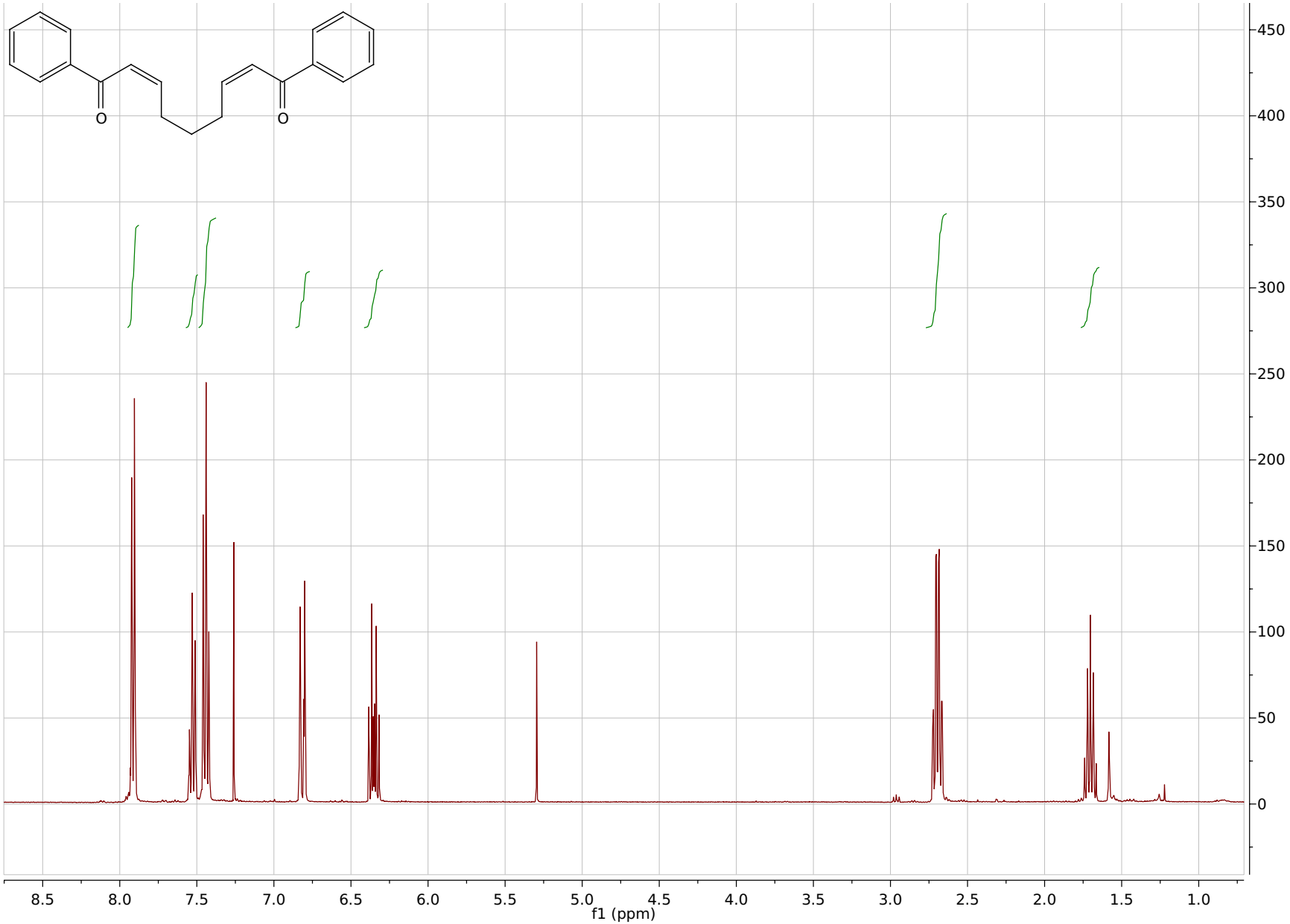


Figure S21: ^{1}H NMR Spectrum of substrate (*Z*,*Z*)-**11a**.

Figure S22: ^{13}C NMR Spectrum of substrate (*Z*,*Z*)-**11a**.

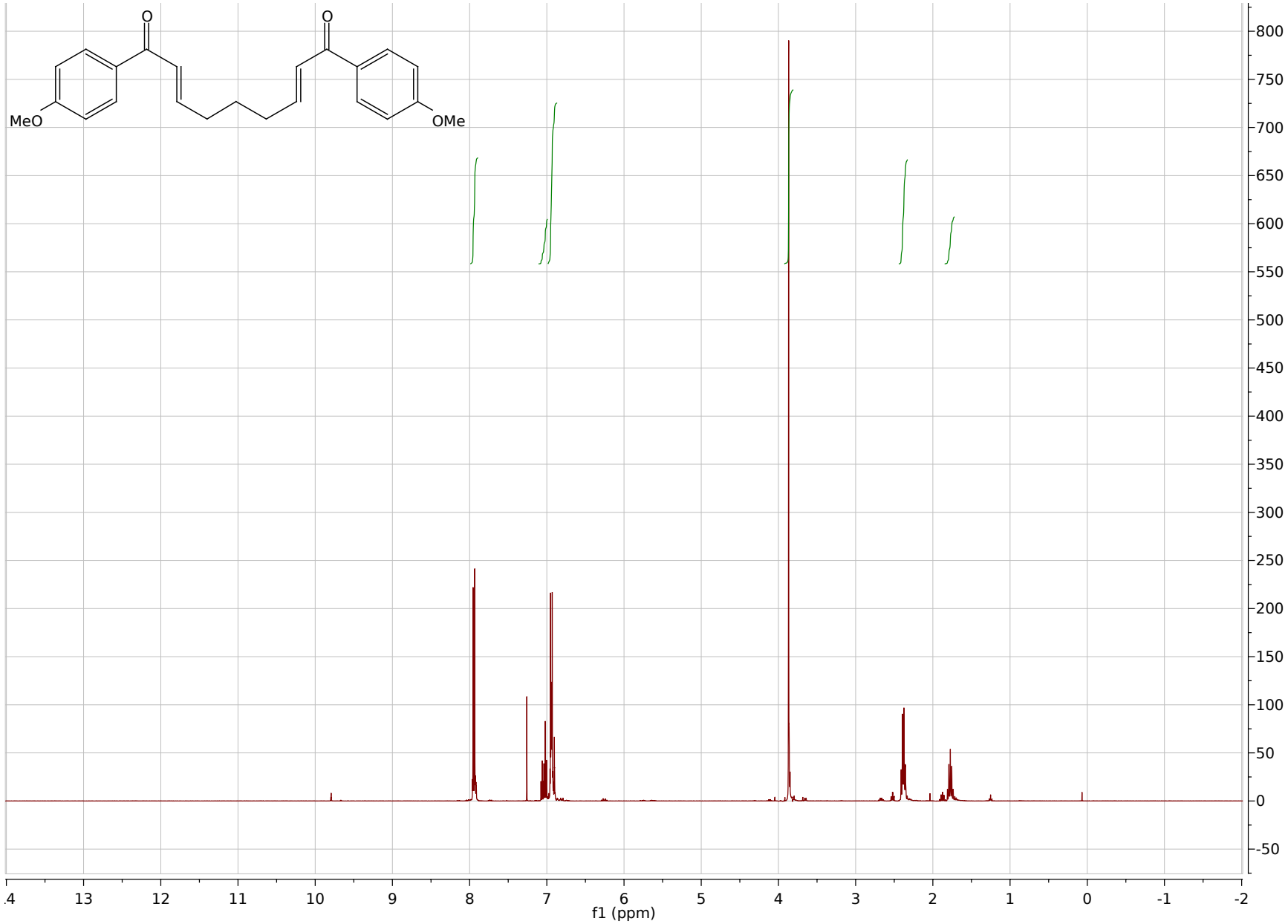


Figure S23: ^{1}H NMR Spectrum of substrate **11b**.

Figure S24: ^{13}C NMR Spectrum of substrate **11b**.

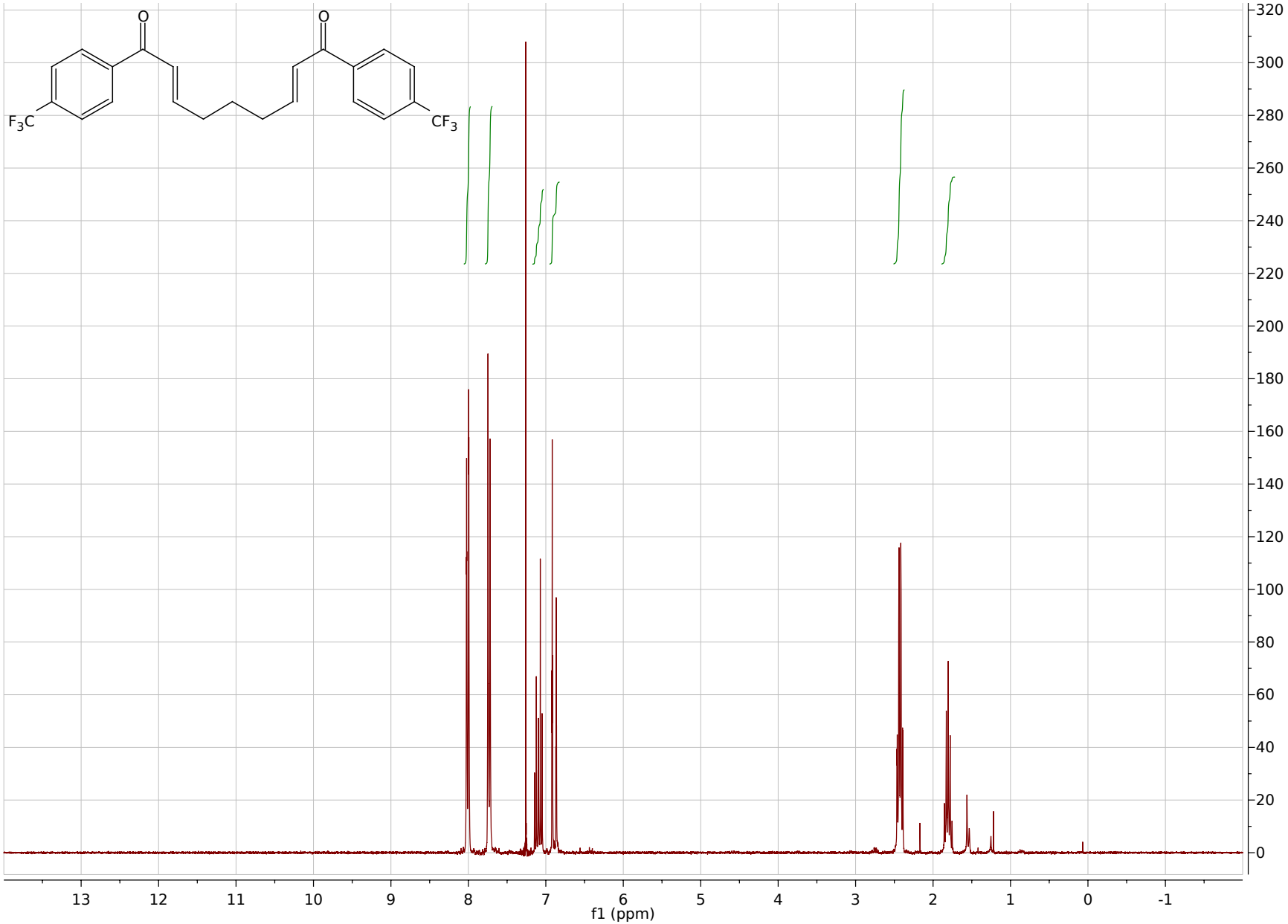


Figure S25: ^{1}H NMR Spectrum of substrate **11c**.

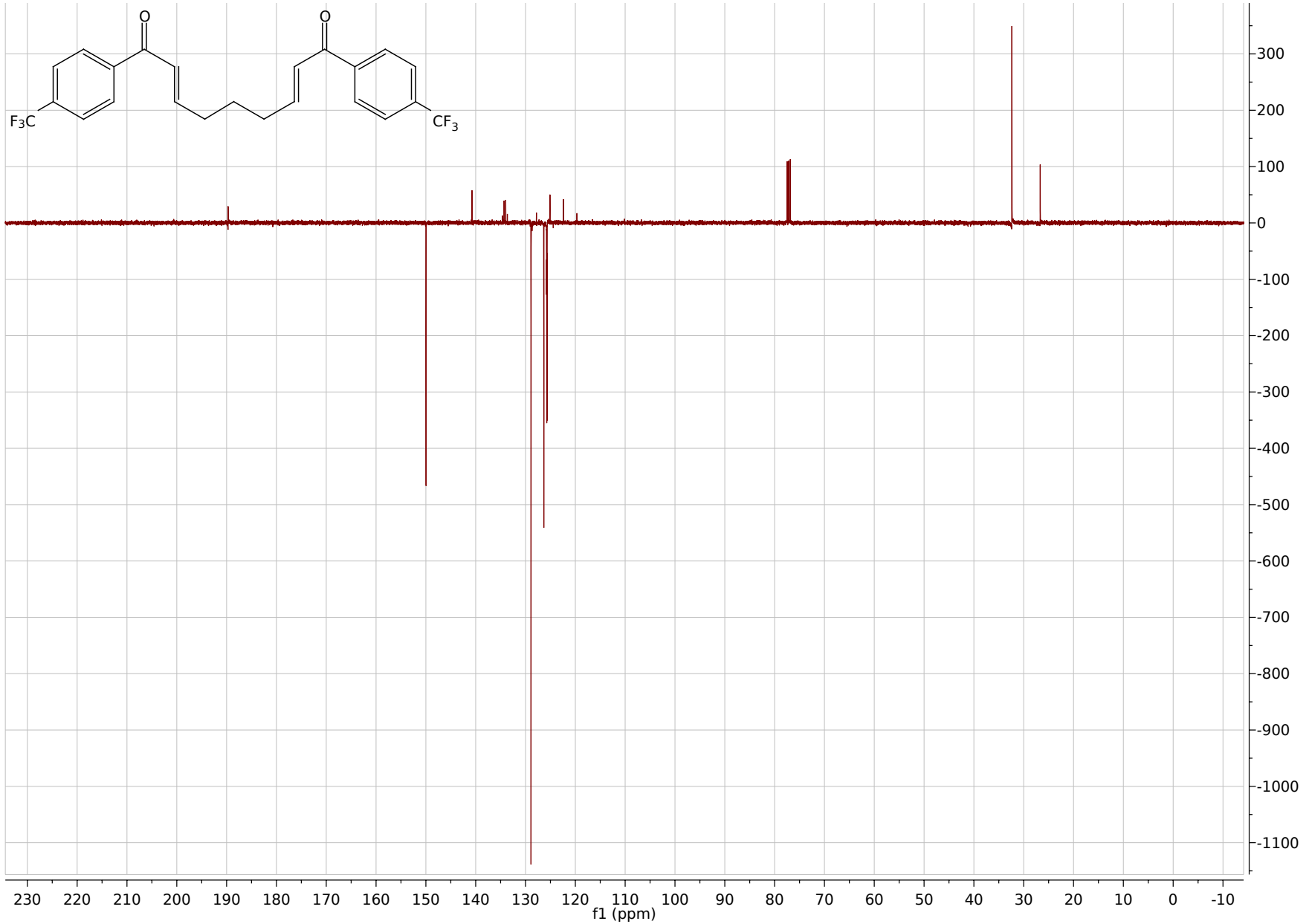


Figure S26: ^{13}C NMR Spectrum of substrate **11c**.

A.3 NMR Spectra of cycloadducts

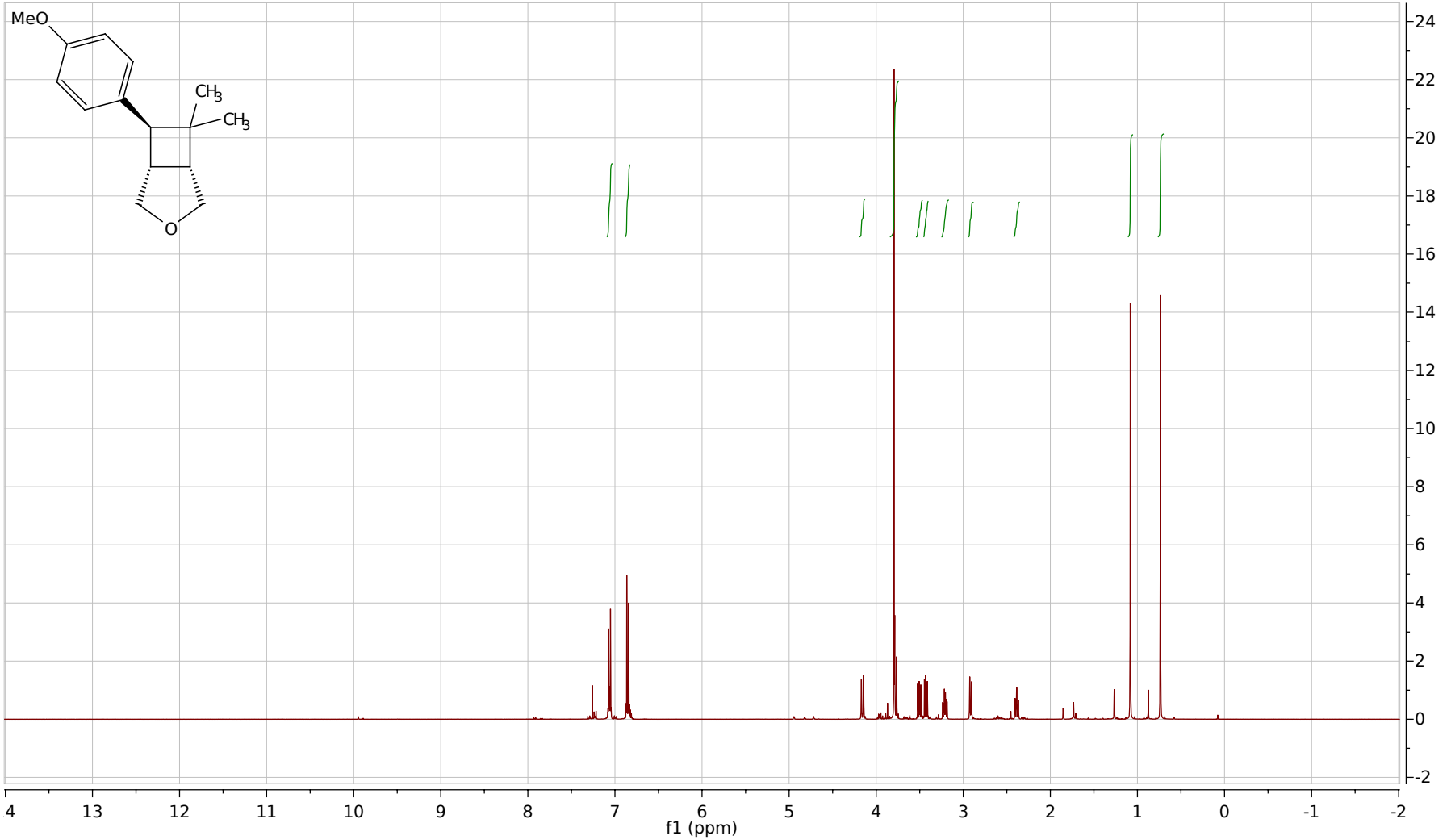


Figure S27: ^{1}H NMR Spectrum of cycloadduct **4a**.

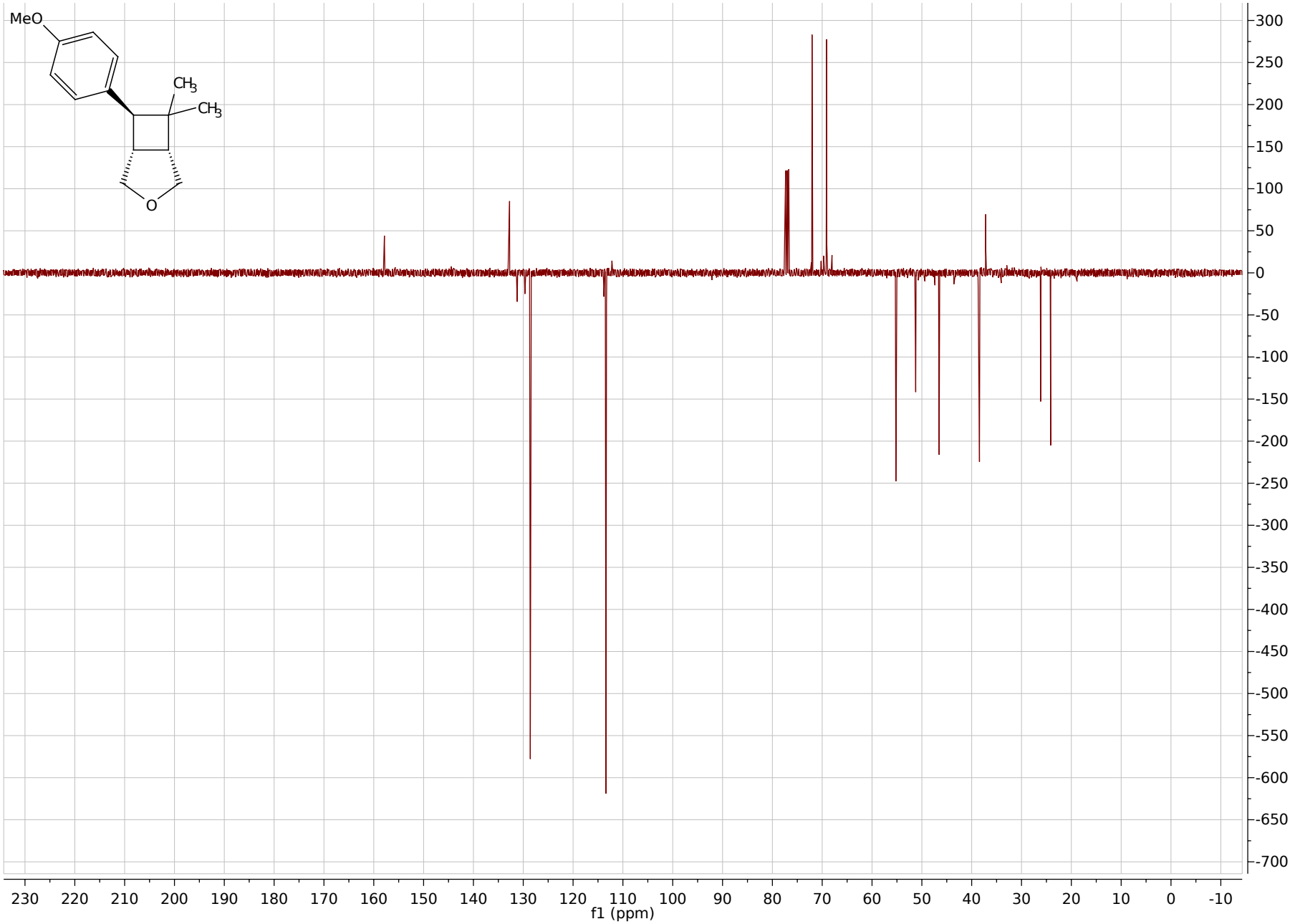


Figure S28: ^{13}C NMR Spectrum of cycloadduct **4a**.

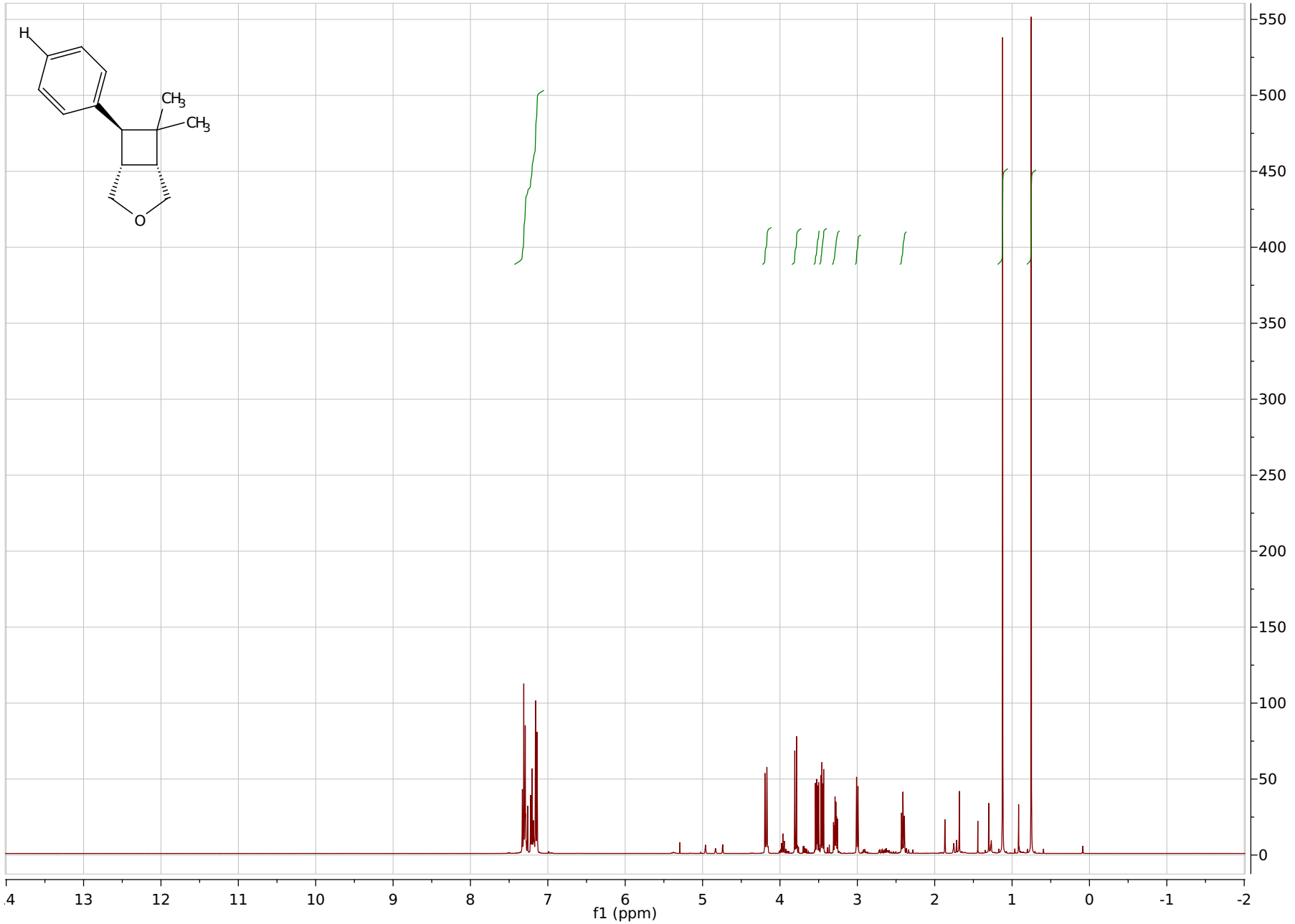


Figure S29: ^{1}H NMR Spectrum of cycloadduct **4b**.

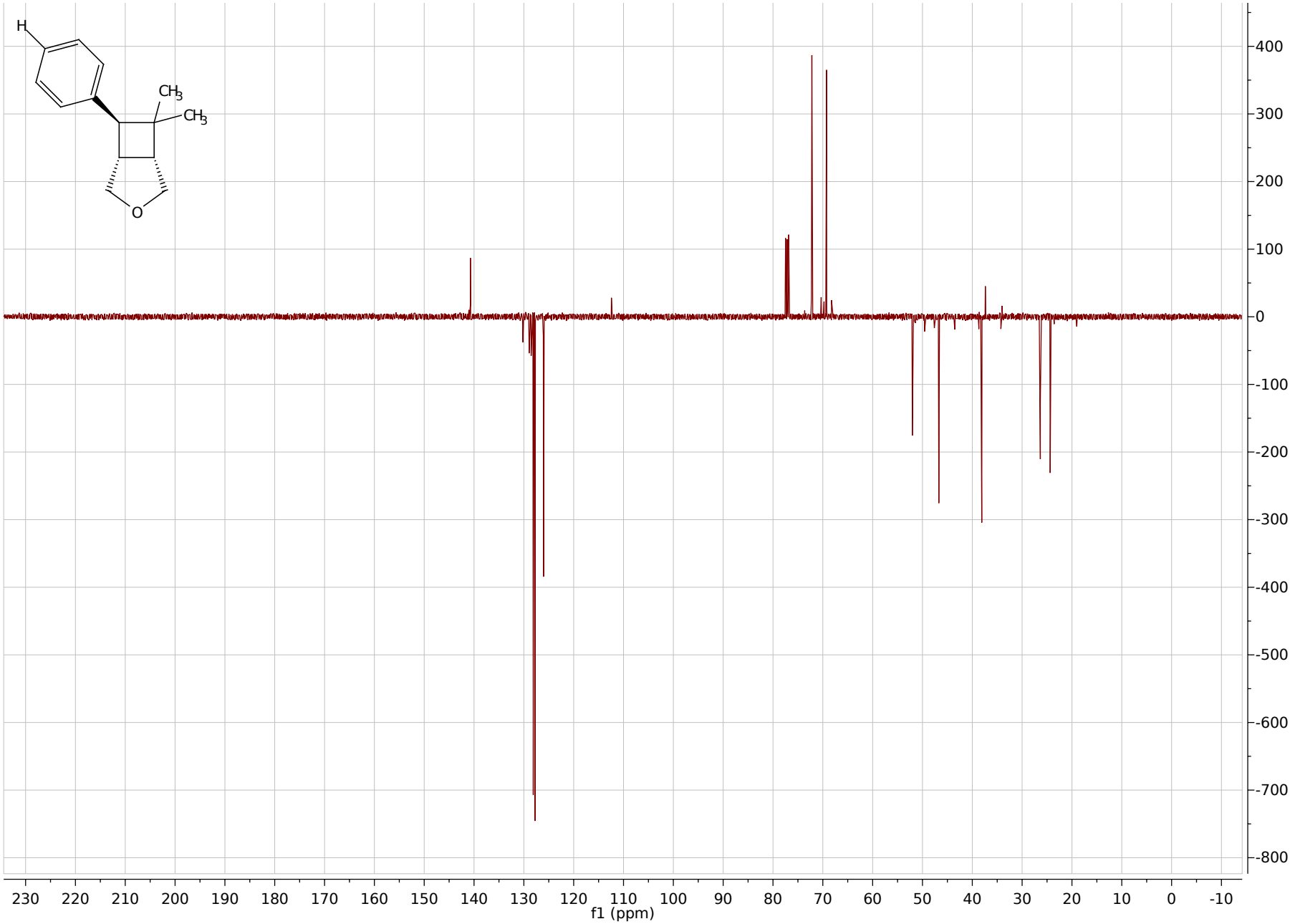


Figure S30: ^{13}C NMR Spectrum of cycloadduct **4b**.

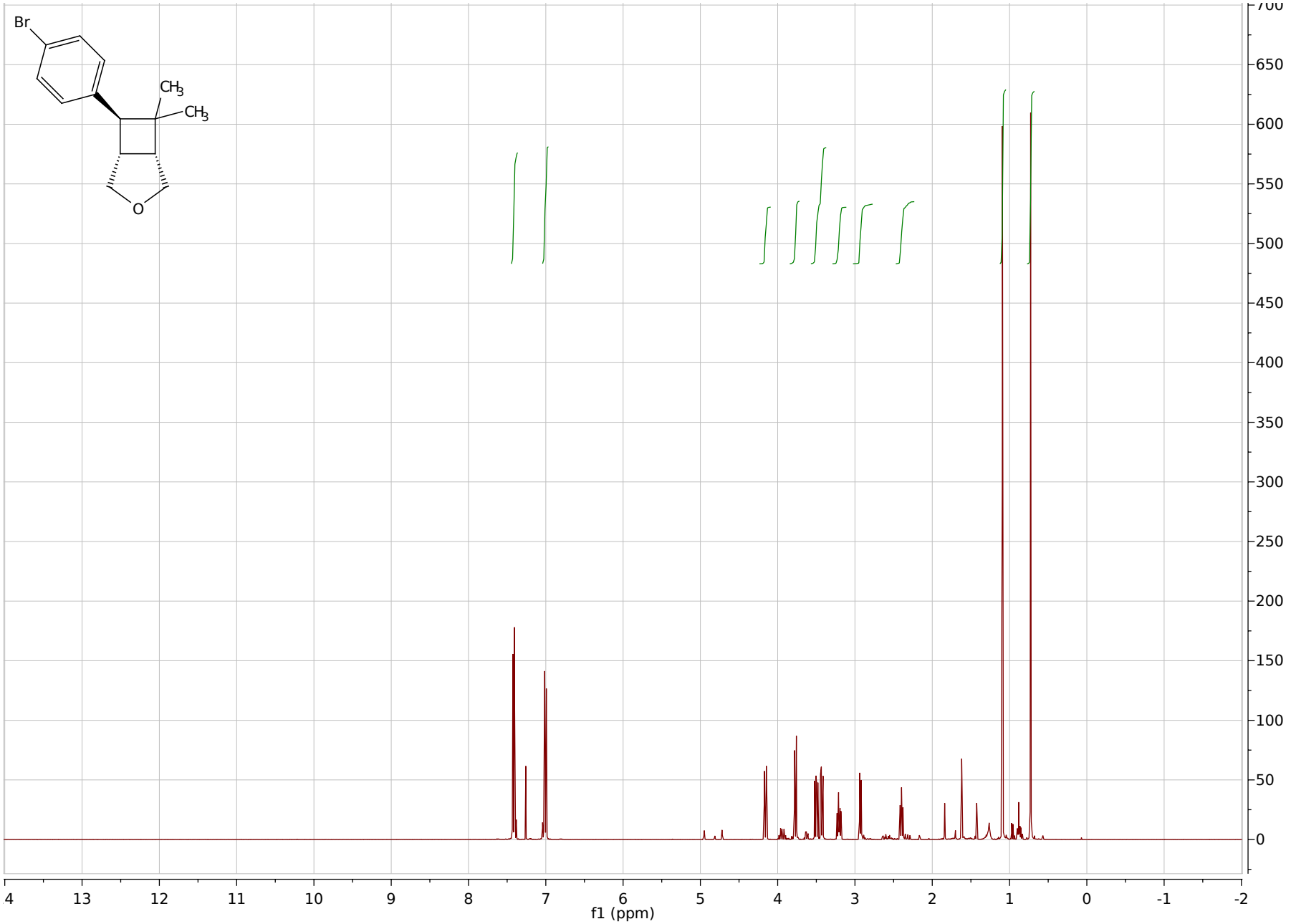


Figure S31: ^{1}H NMR Spectrum of cycloadduct **4c**.

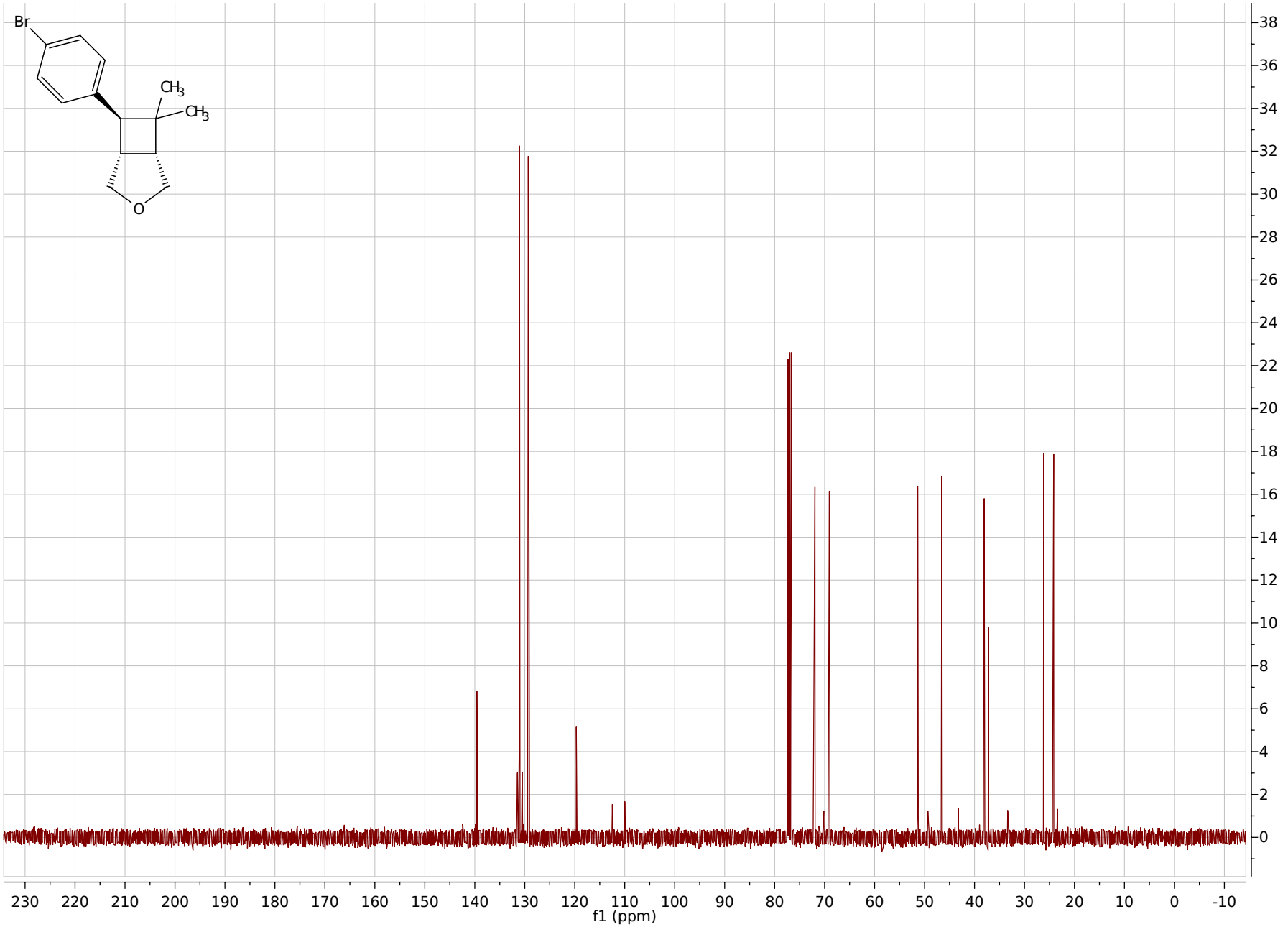


Figure S32: ^{13}C NMR Spectrum of cycloadduct **4c**.

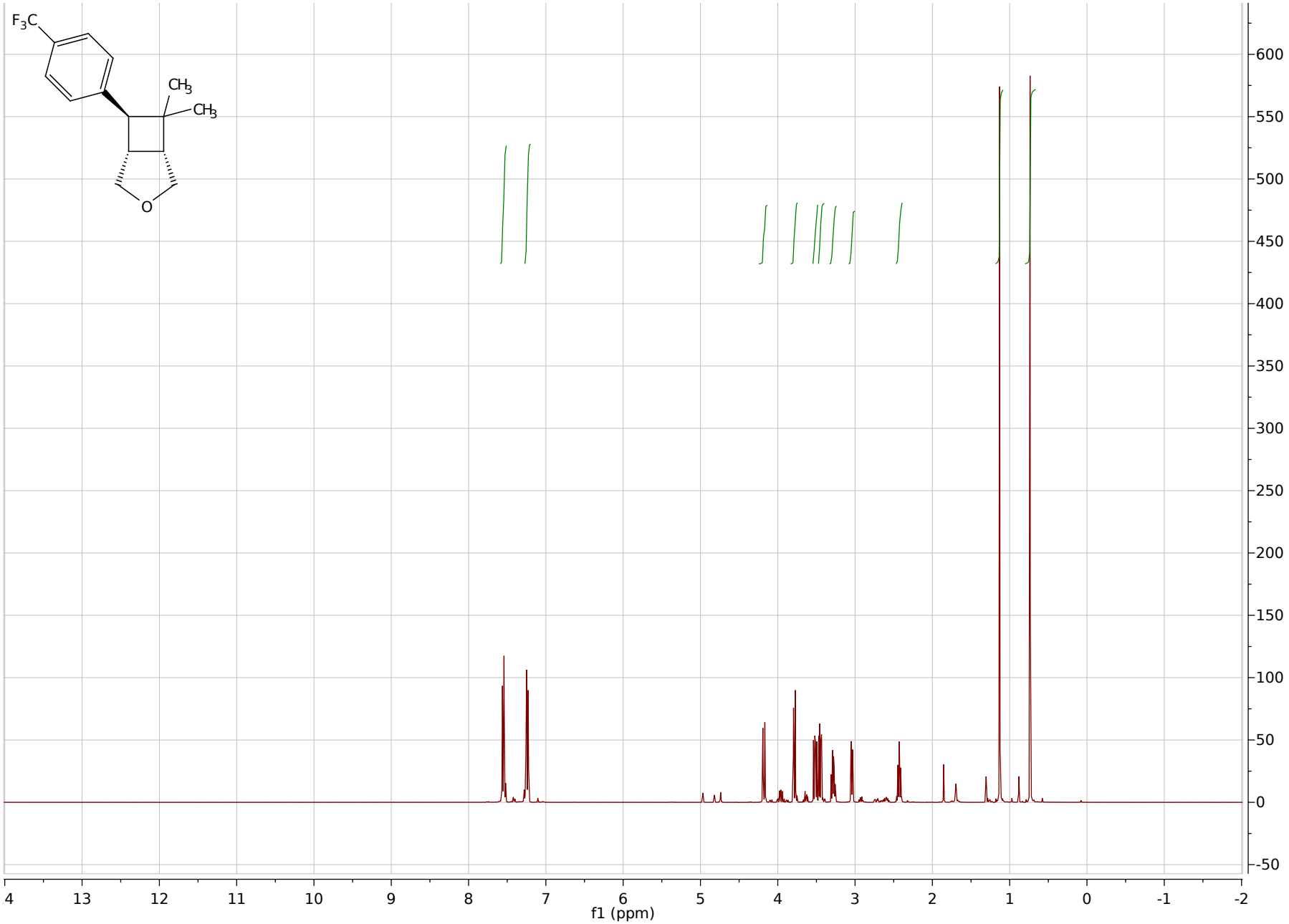


Figure S33: ^{1}H NMR Spectrum of cycloadduct **4d**.

Figure S34: ^{13}C NMR Spectrum of cycloadduct **4d**.

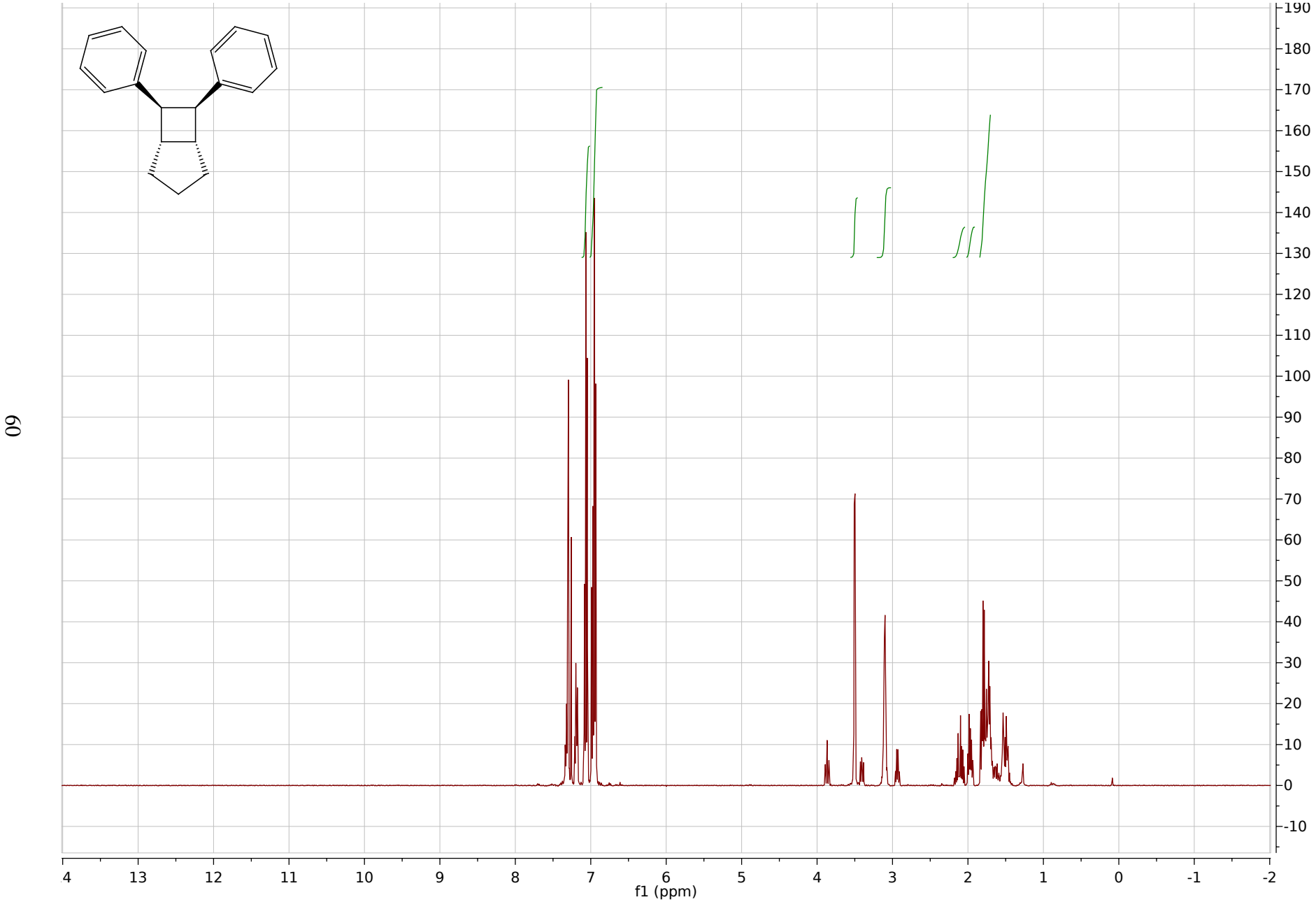


Figure S35: ^{1}H NMR Spectrum of cycloadduct **8**.

Figure S36: ^{13}C NMR Spectrum of cycloadduct **8**.

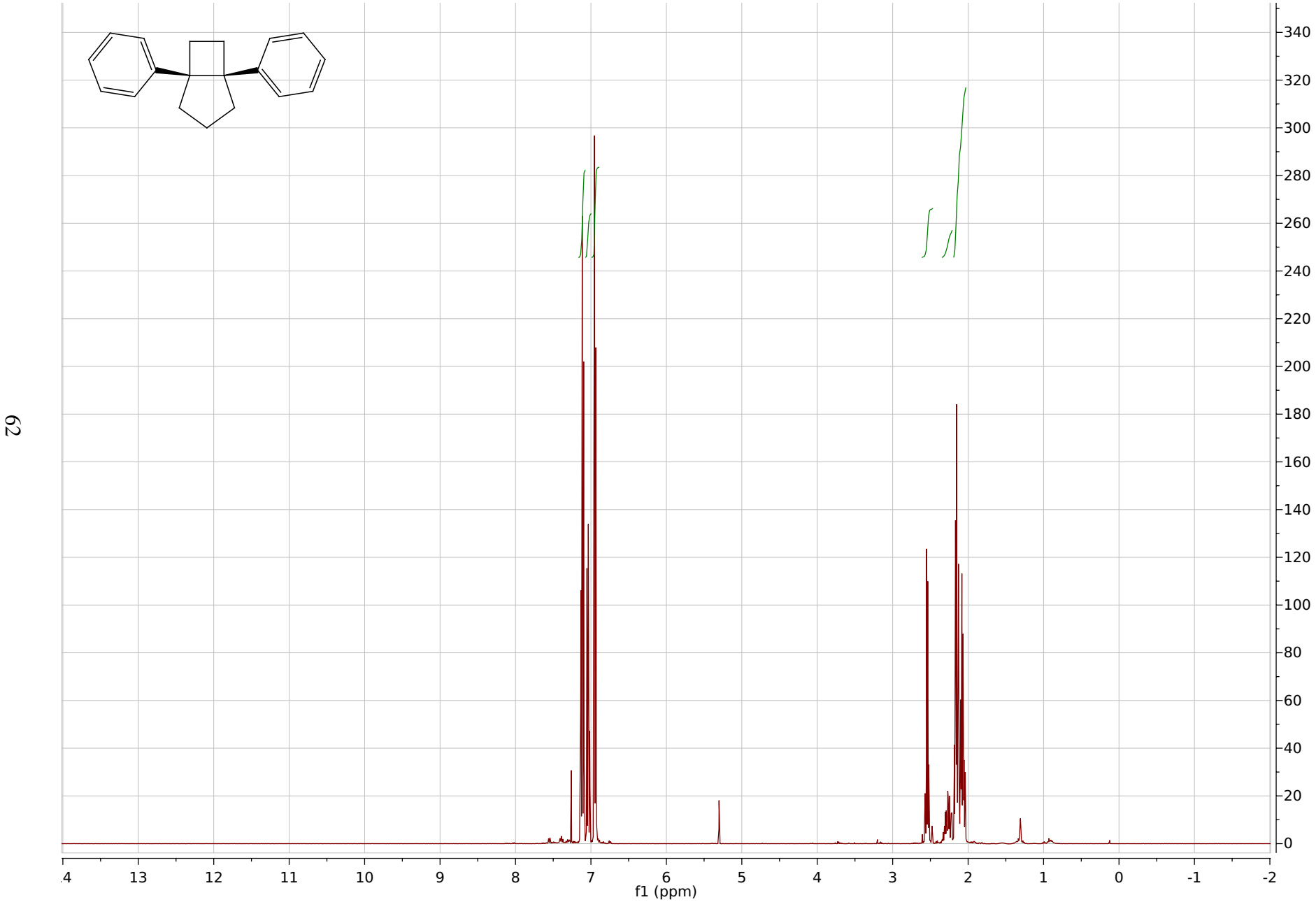


Figure S37: ^{1}H NMR Spectrum of cycloadduct **10**.

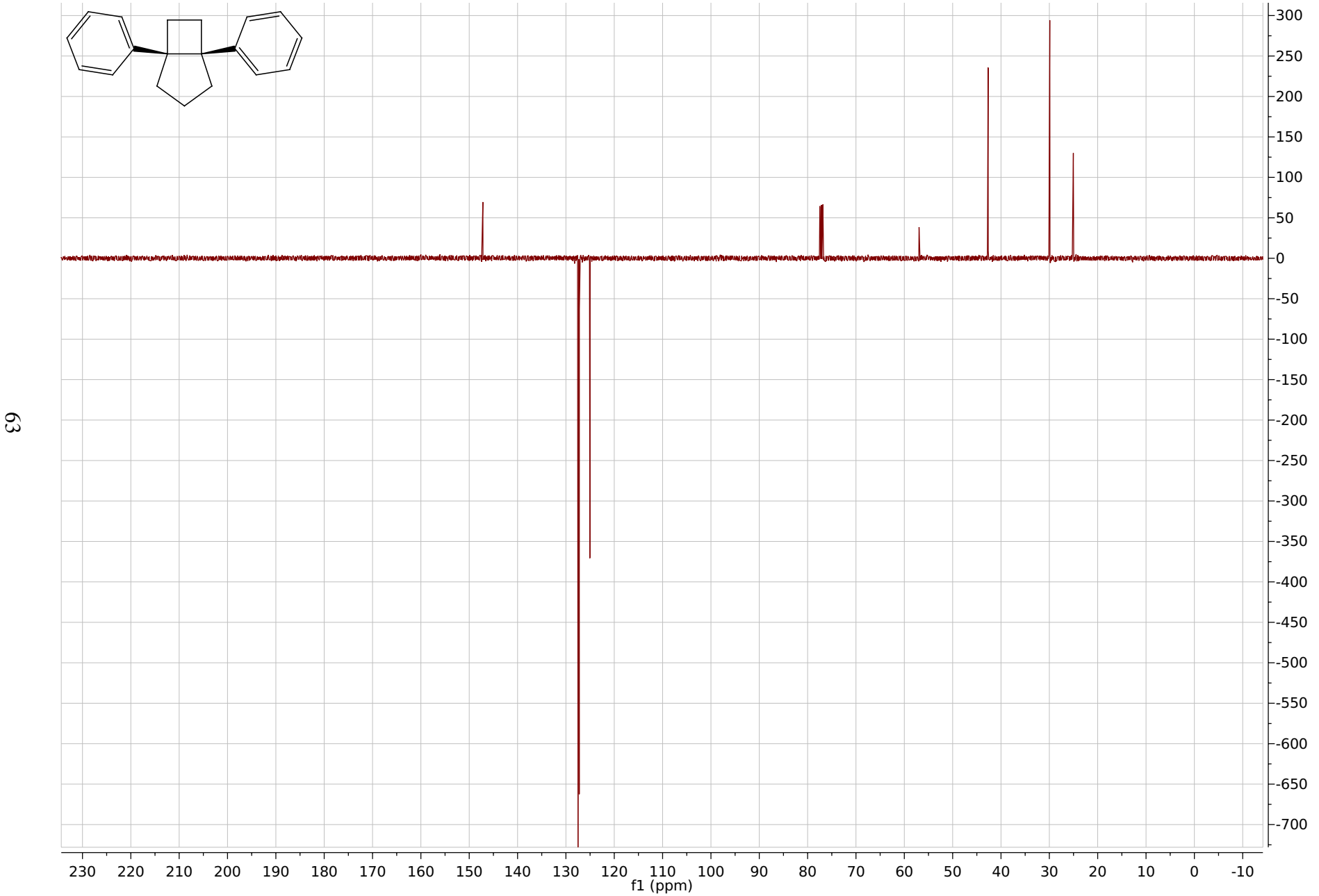


Figure S38: ^{13}C NMR Spectrum of cycloadduct **10**.

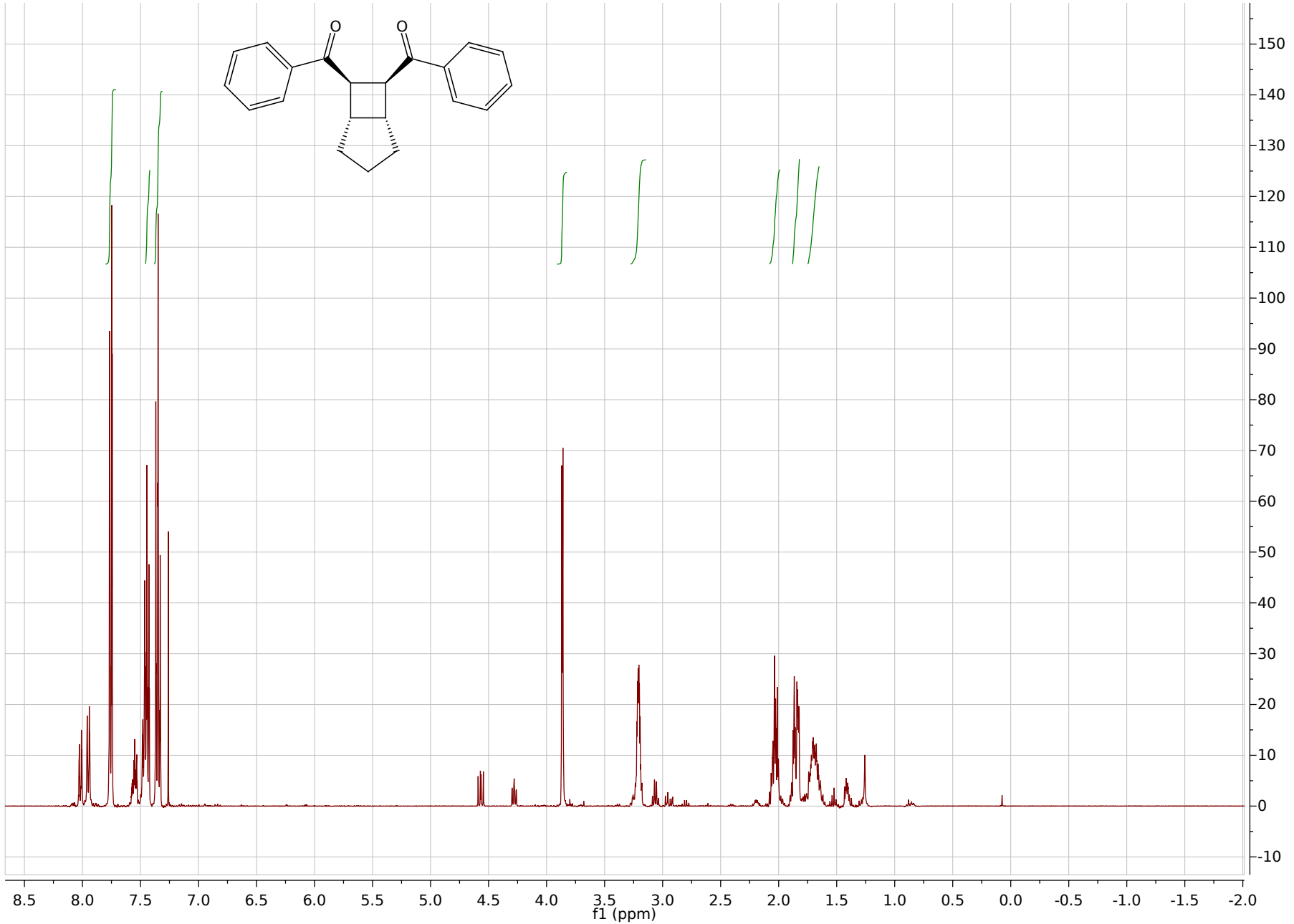


Figure S39: ^{1}H NMR Spectrum of cycloadduct **12a** (with minor *trans*-isomer).

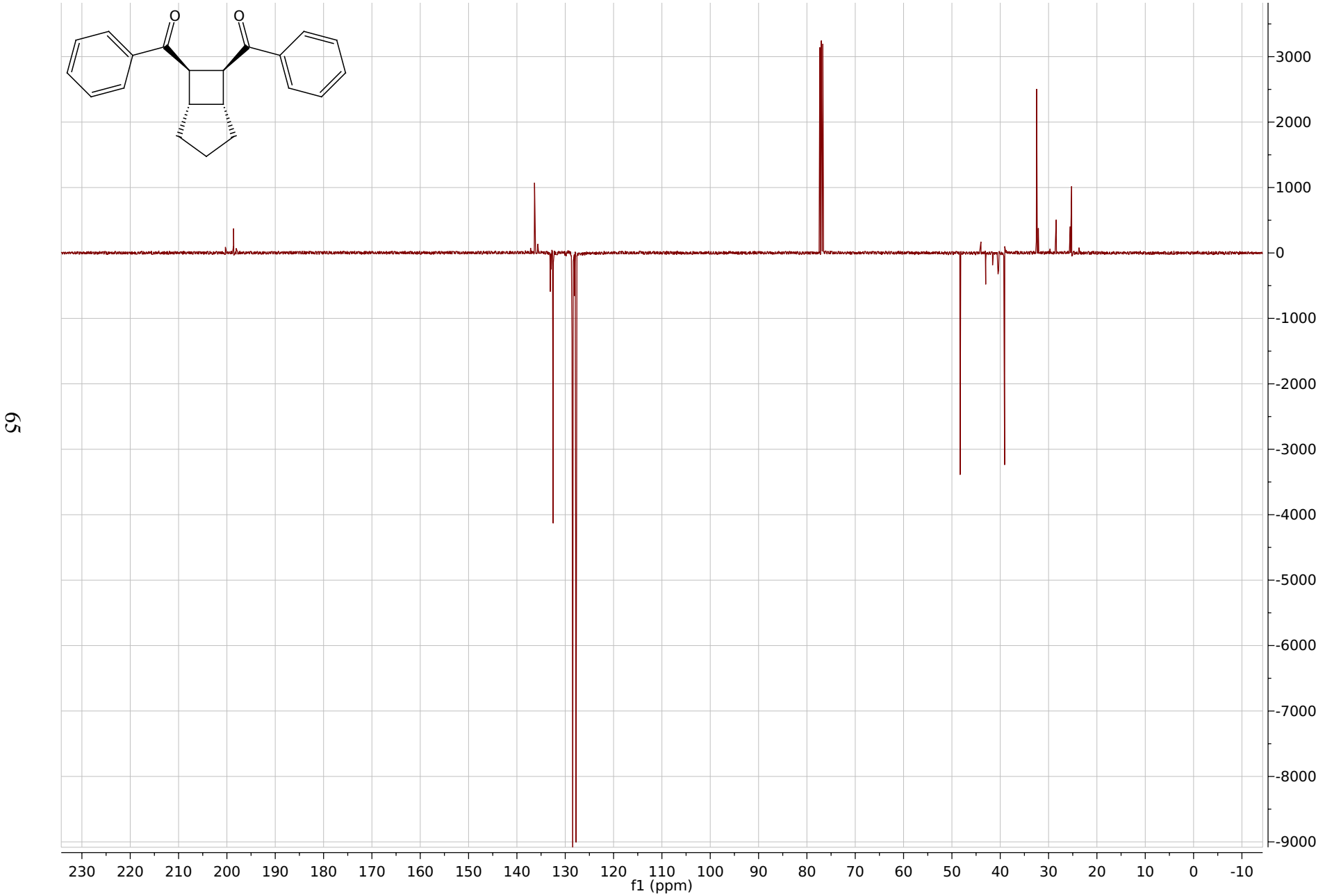


Figure S40: ^{13}C NMR Spectrum of cycloadduct **12a**.

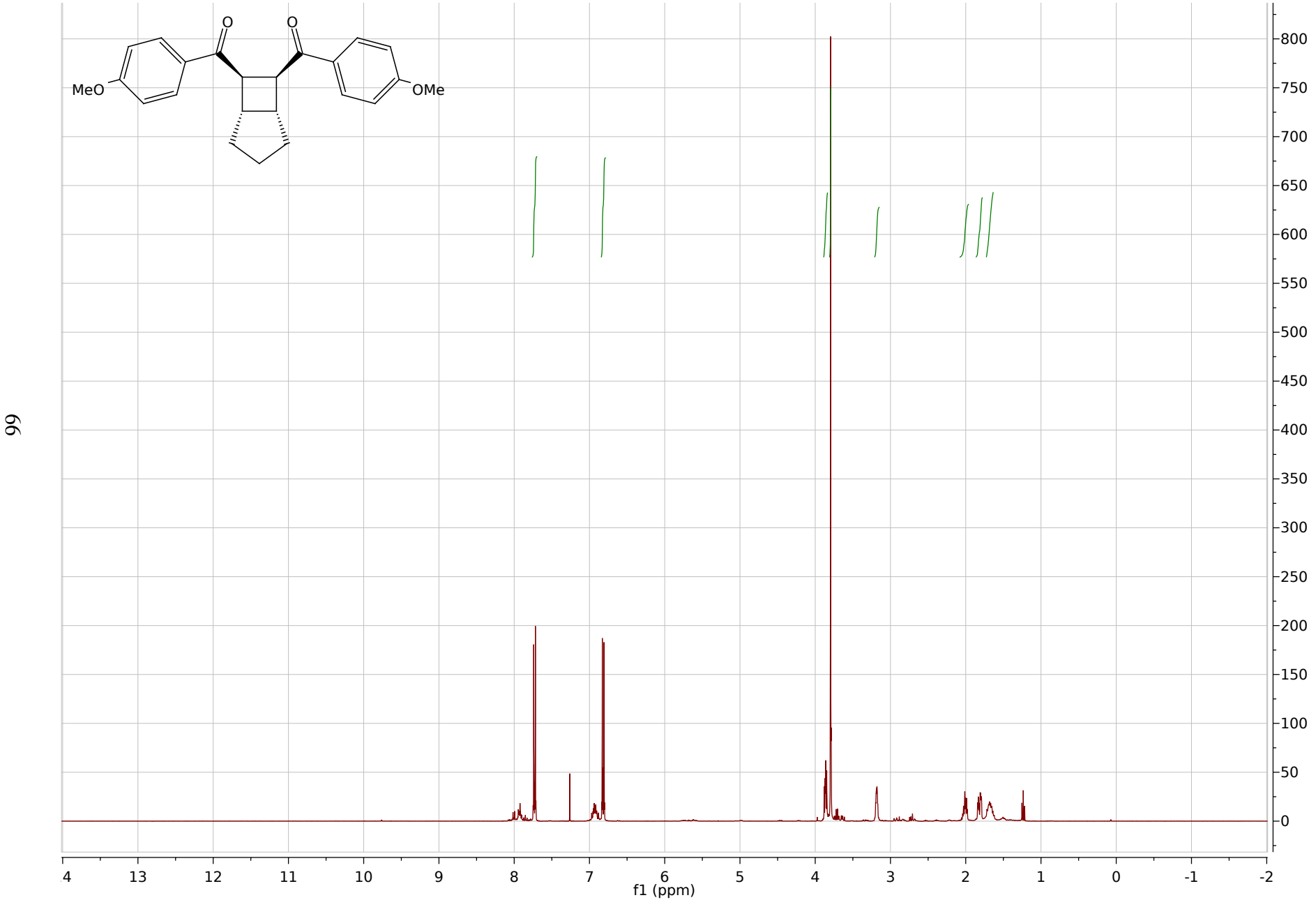


Figure S41: ^{1}H NMR Spectrum of cycloadduct **12b**.

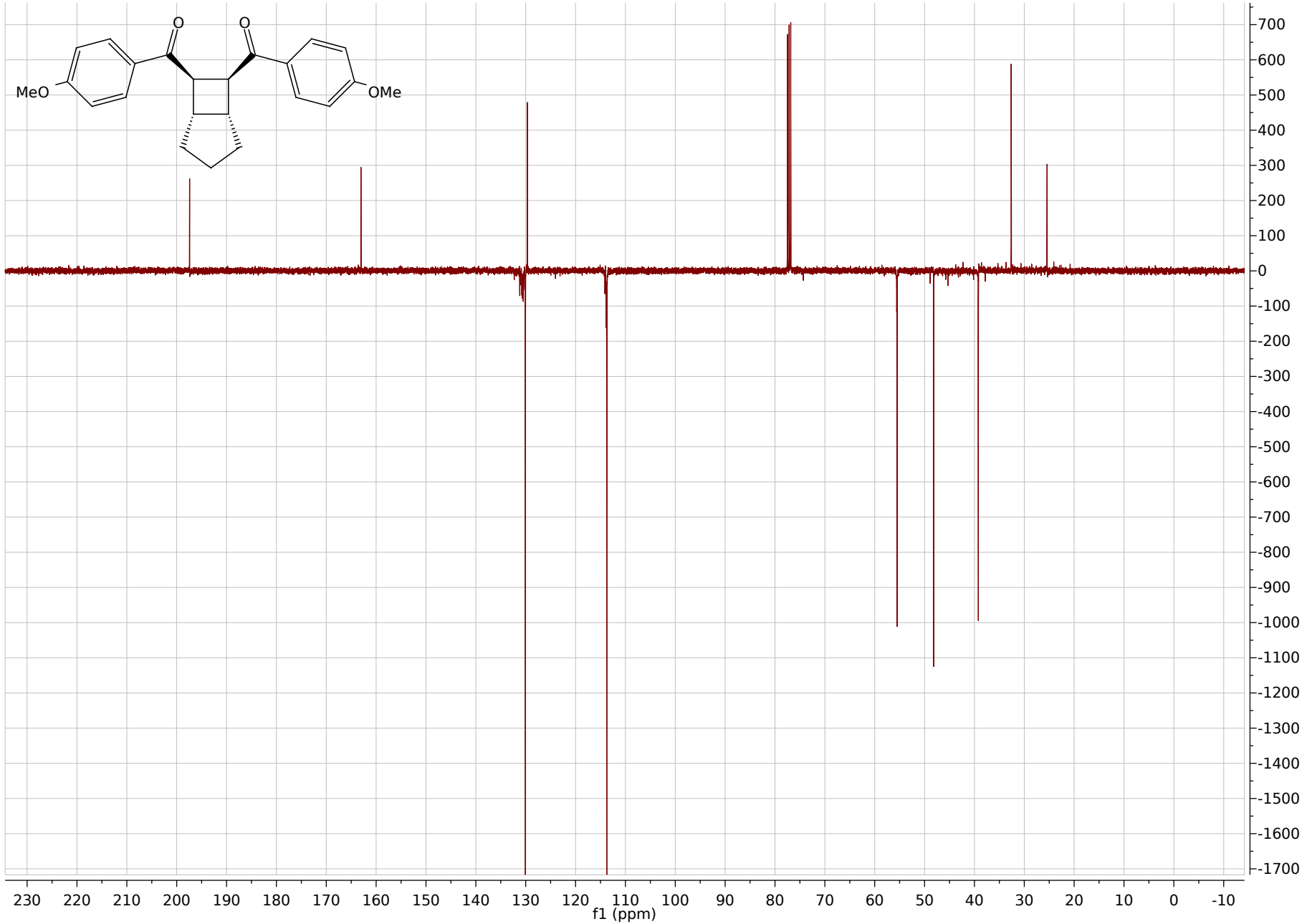


Figure S42: ^{13}C NMR Spectrum of cycloadduct **12b**.

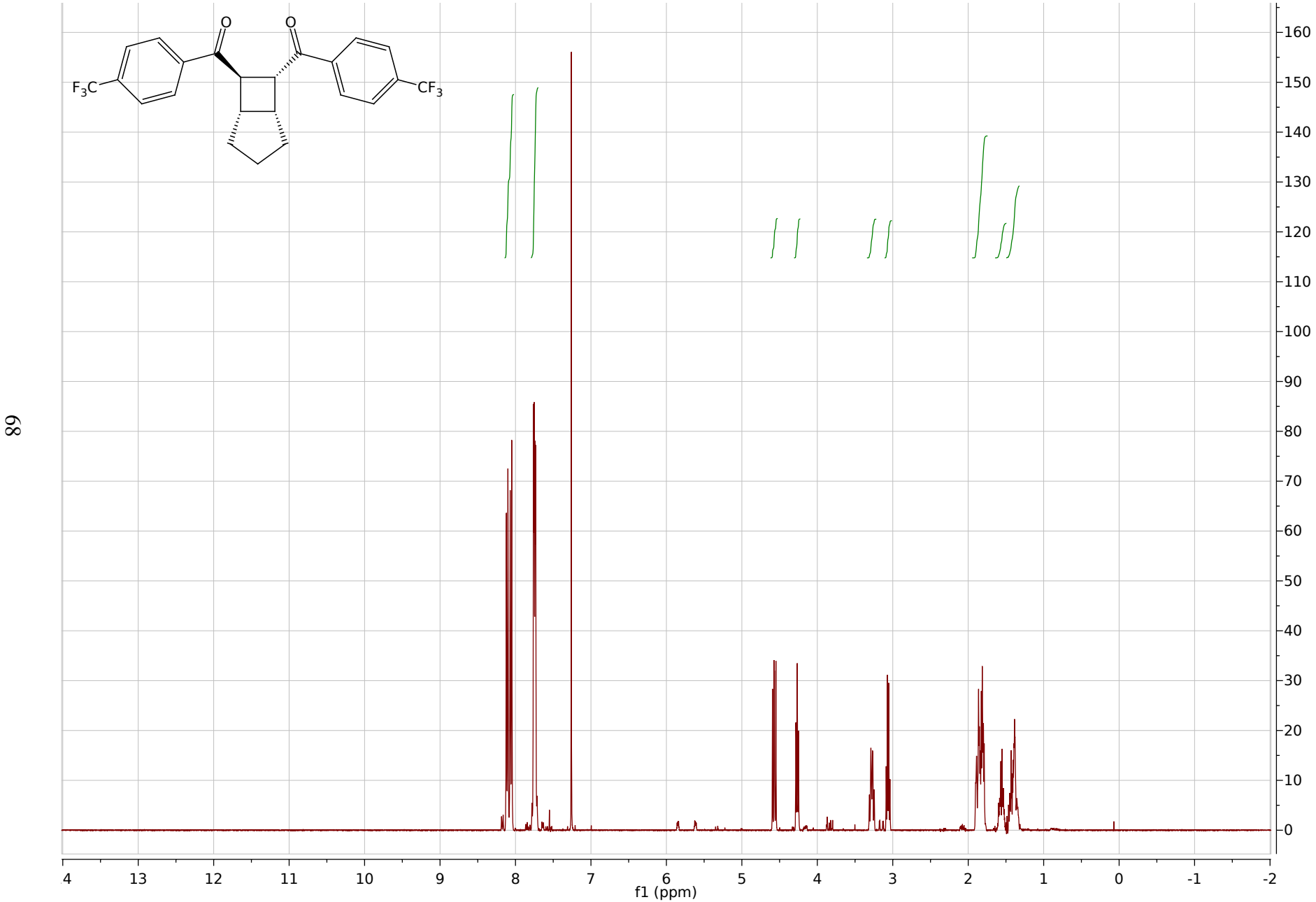


Figure S43: ^{1}H NMR Spectrum of cycloadduct (1*R**,5*S**,6*R**,7*R**)-**12c**.

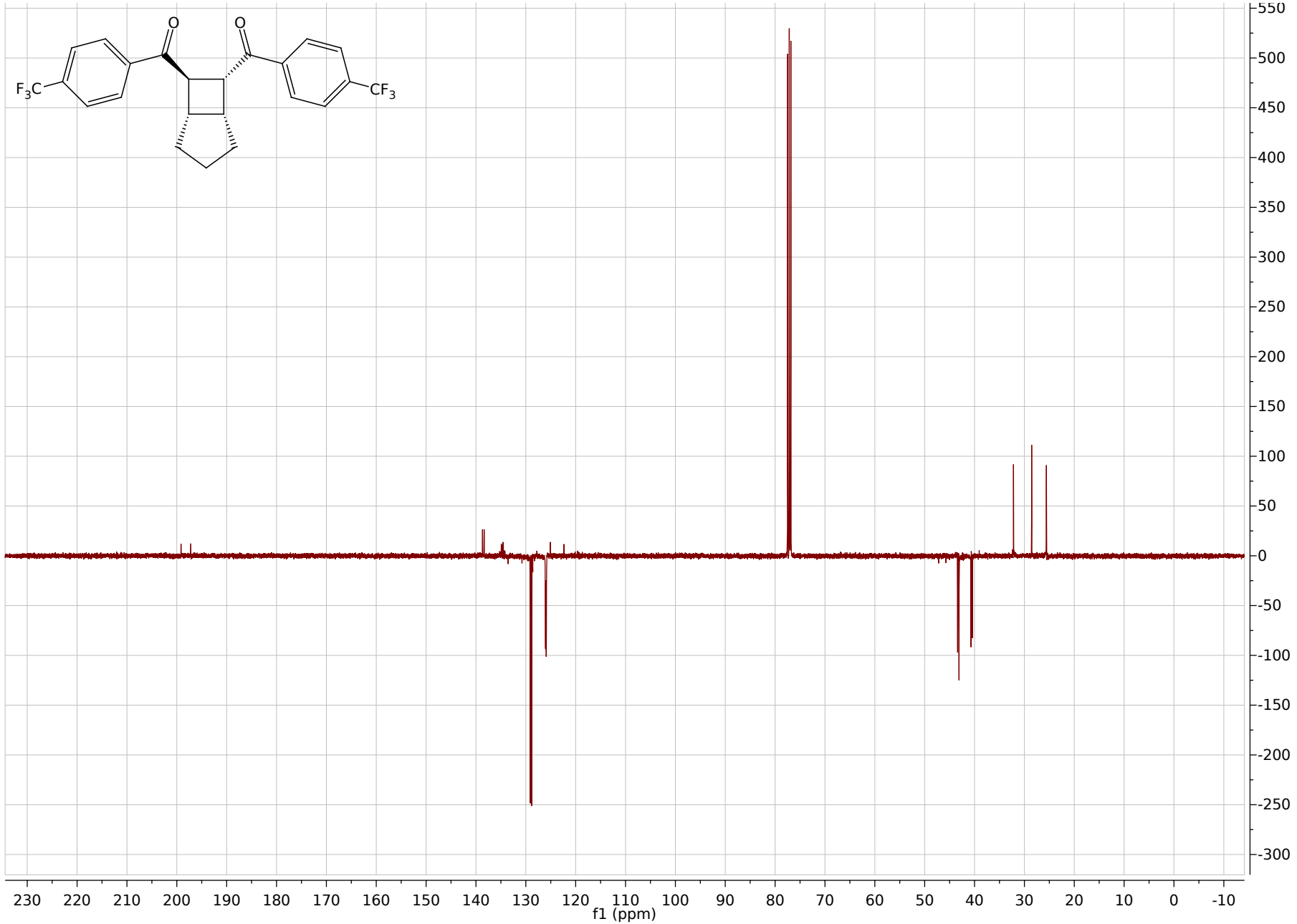


Figure S44: ^{13}C NMR Spectrum of cycloadduct (1*R**,5*S**,6*R**,7*R**)-**12c**.

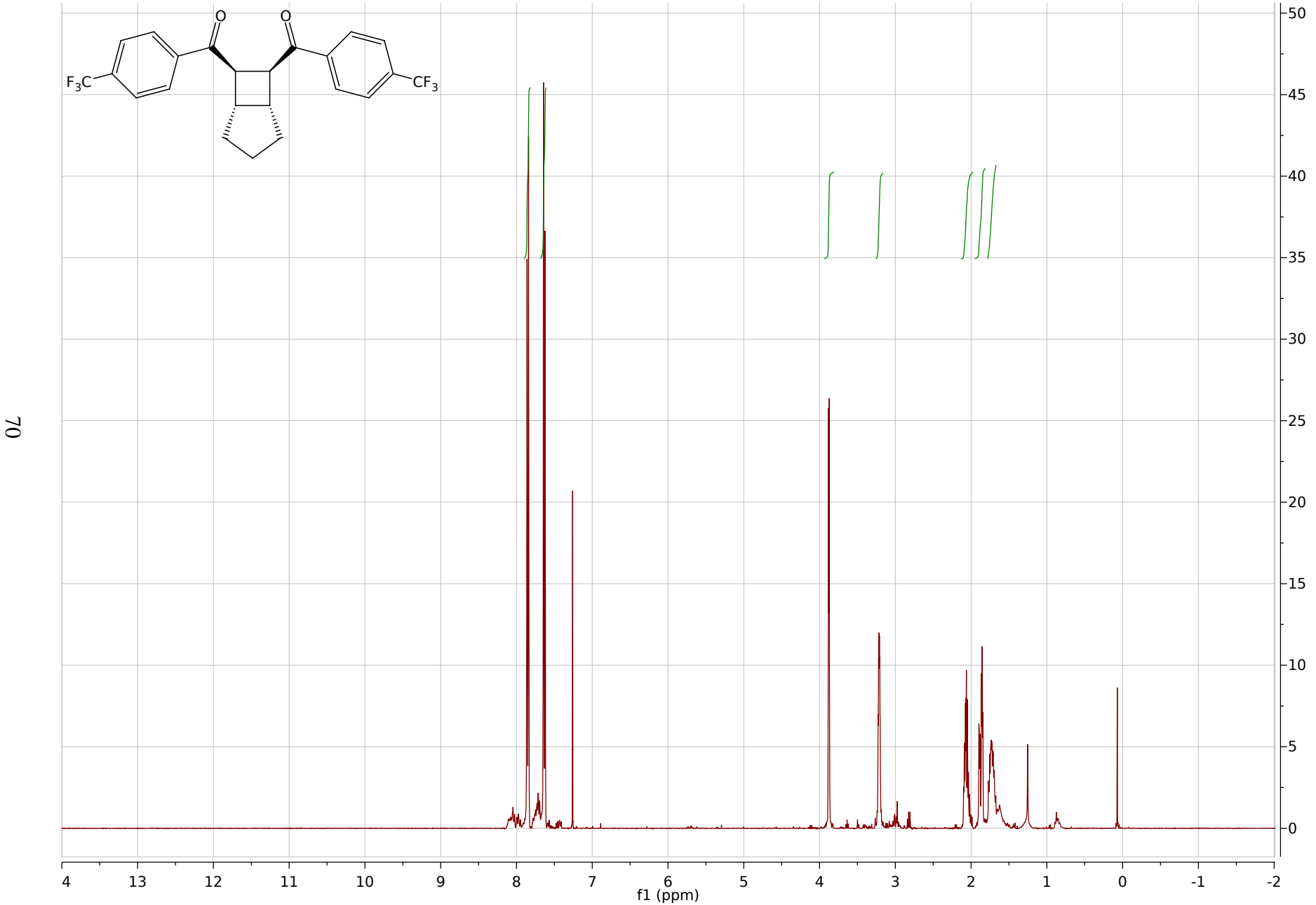


Figure S45: ^{1}H NMR Spectrum of cycloadduct (1*R*,5*S*,6*R*,7*S*)-**12c**.

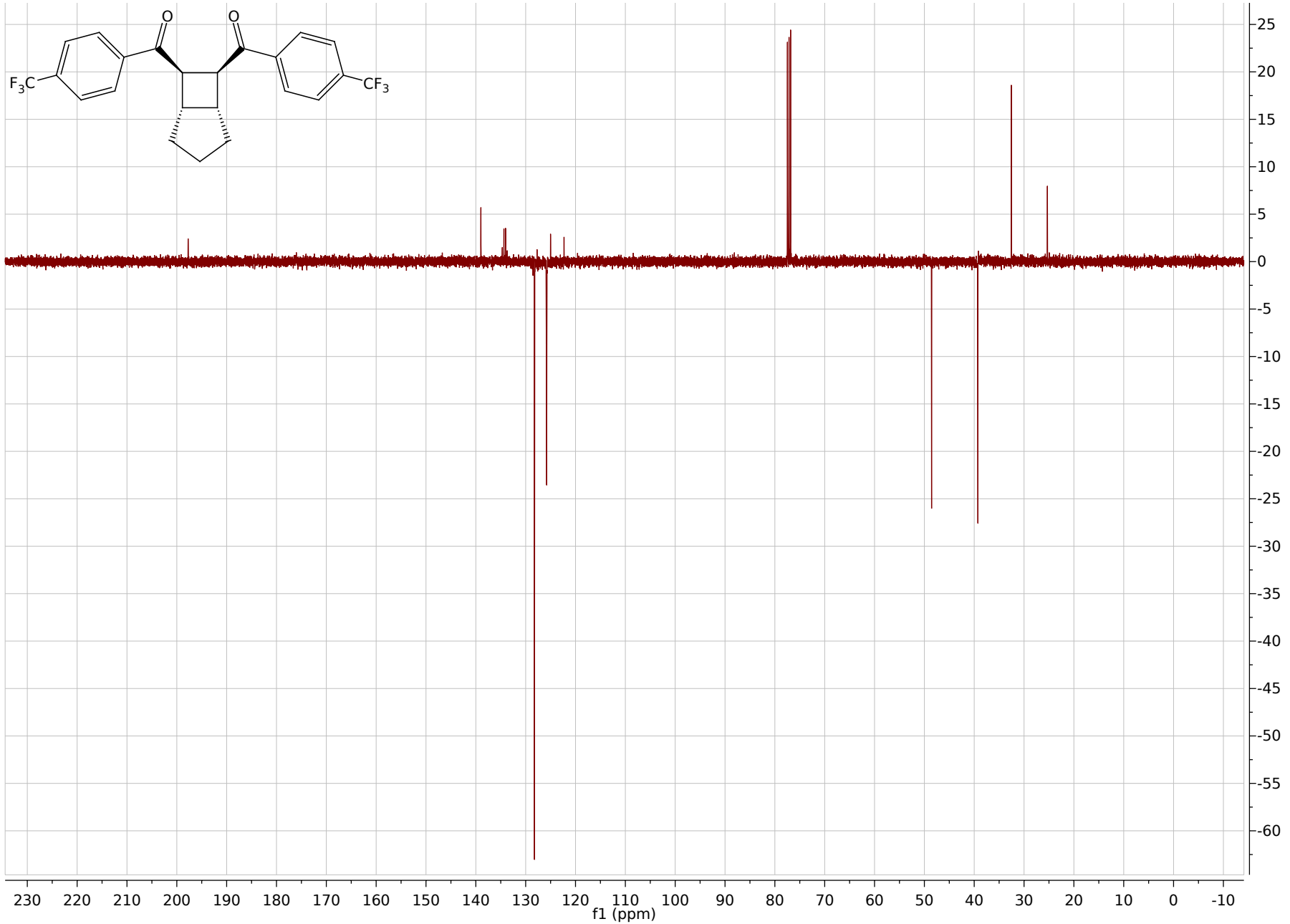


Figure S46: ^{13}C NMR Spectrum of cycloadduct (1*R*,5*S*,6*R*,7*S*)-**12c**.

A.4 Examples of signals assignement of cycloadducts

(1*R,5*R**,7*R**)-7-(4-Bromophenyl)-6,6-dimethyl-3-oxabicyclo[3.2.0]heptane (4c)**

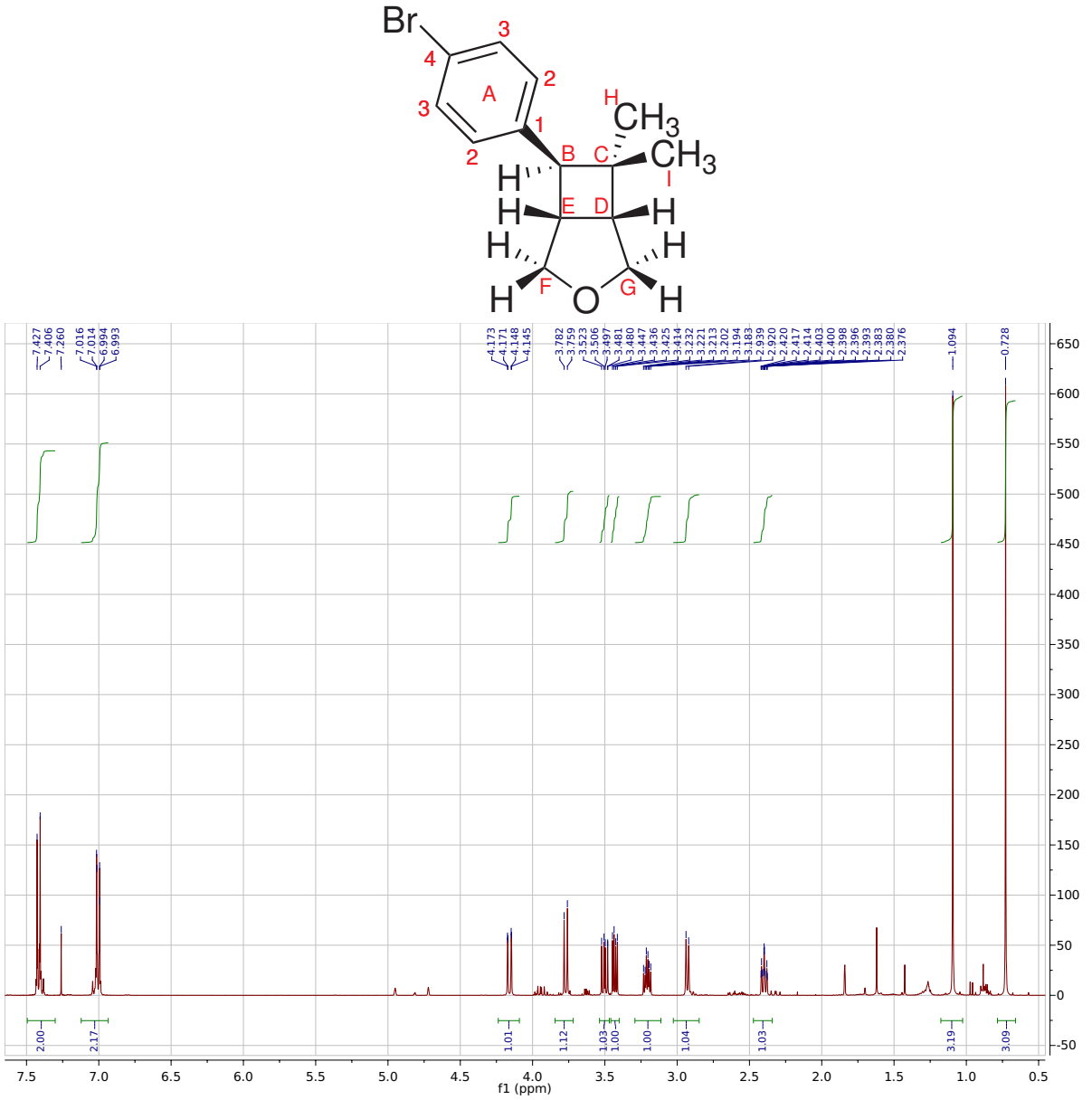


Figure S47: **4c**:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.36 (m, 2H, H–*A3*), 7.08–6.90 (m, 2H, H–*A2*), 4.16 (dd, $J = 10.1$, 1.1 Hz, 1H, H–*G*-down), 3.77 (d, $J = 9.0$ Hz, 1H, H–*F*-down), 3.50 (dd, $J = 10.1$, 6.7 Hz, 1H, H–*G*-up), 3.43 (dd, $J = 9.0$, 4.5 Hz, 1H, H–*F*-up), 3.21 (td, $J = 7.7$, 4.5 Hz, 1H, H–*E*), 2.93 (d, $J = 7.3$ Hz, 1H, H–*B*), 2.44–2.36 (m, 1H, H–*D*), 1.09 (s, 3H, CH_3–*H*), 0.73 (s, 3H, CH_3–*I*).

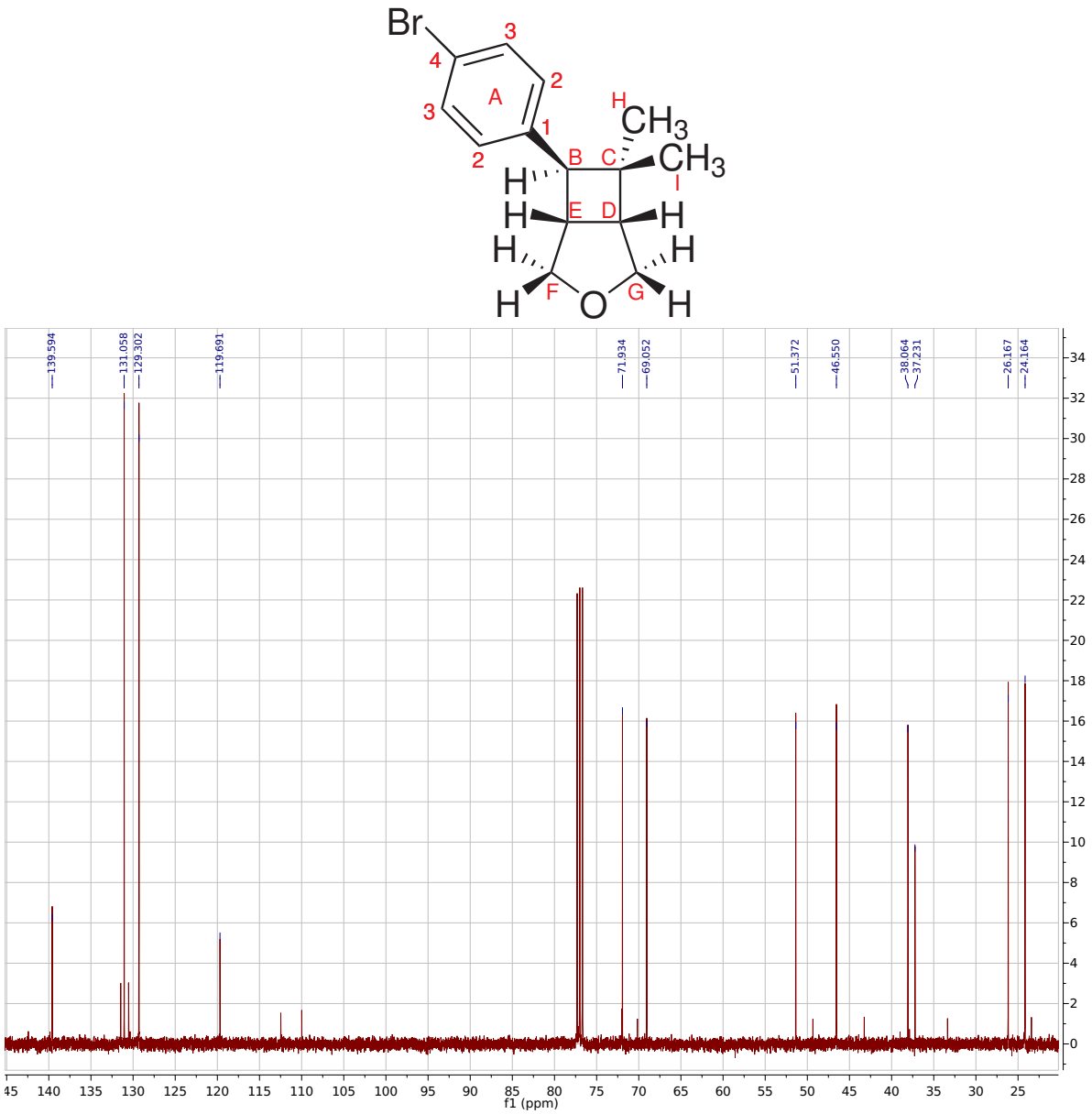


Figure S48: **4c**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.59 (4° C–*A4*), 131.06 (CH–*A3*), 129.30 (CH–*A2*), 119.69 (4° C–*A1*), 71.93 (CH_2–*F*), 69.05 (CH_2–*G*), 51.37 (CH–*B*), 46.55 (CH–*D*), 38.06 (CH–*E*), 37.23 (4° C–*C*), 26.17 (CH_3–*I*), 24.16 (CH_3–*H*).

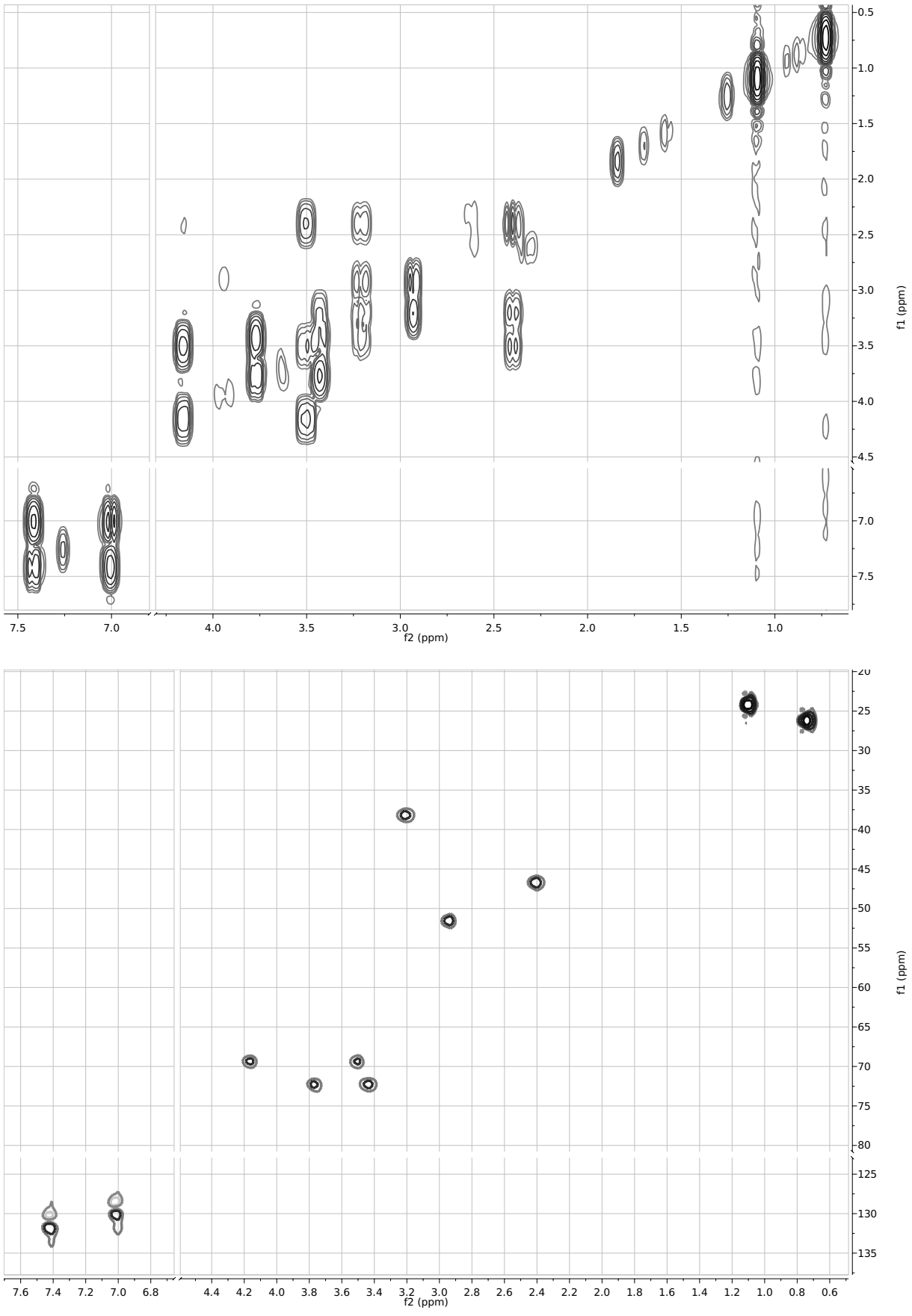


Figure S49: **4c**: COSY and HMQC spectra for assignement explanation.

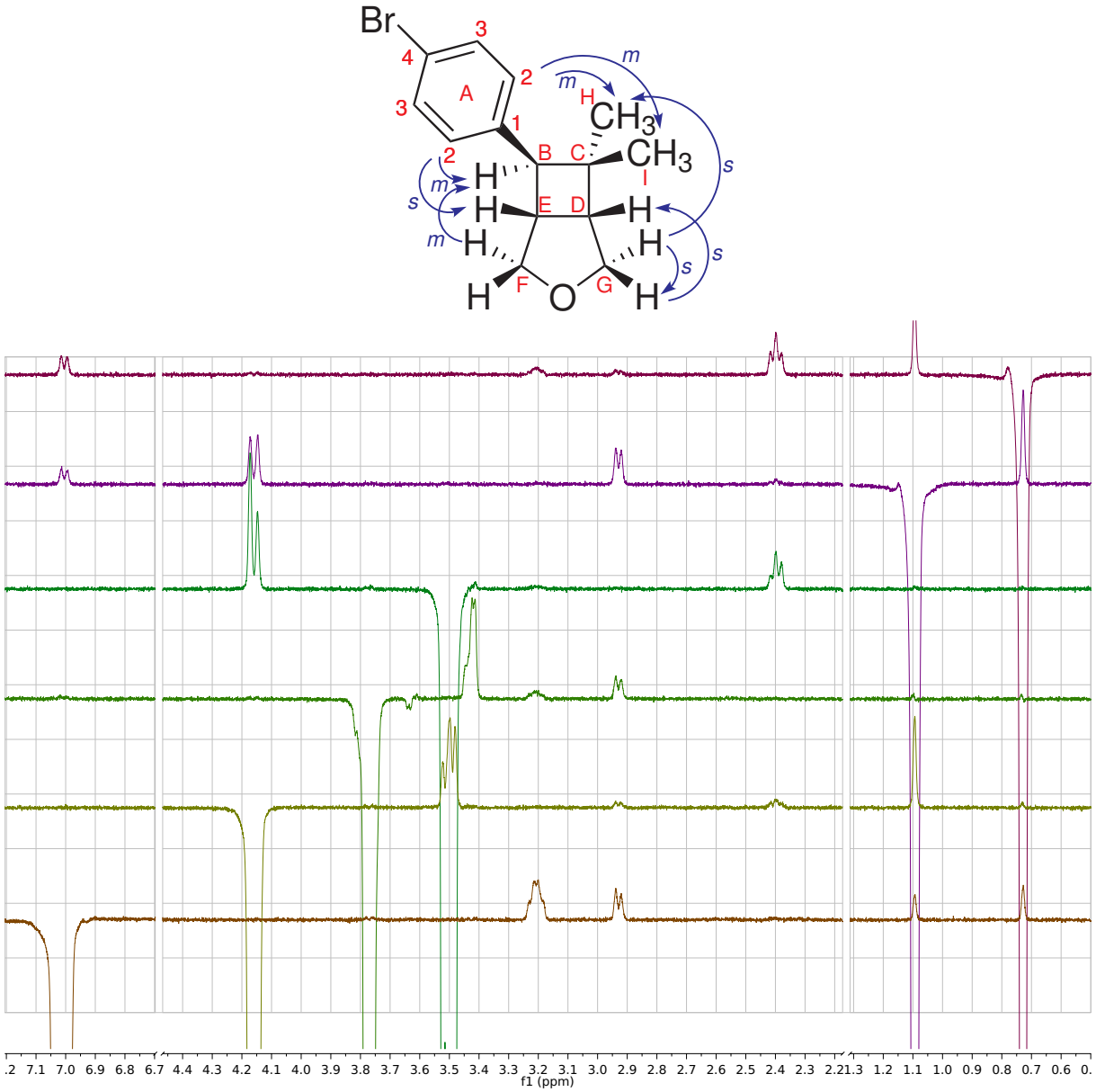


Figure S50: **4c**: NOE spectra for assignement explanation.

(1*R,5*S**,6*R**,7*S**)-6-(4-Methoxyphenyl)-7-phenyl-3-oxabicyclo[3.2.0]heptane (6a)**

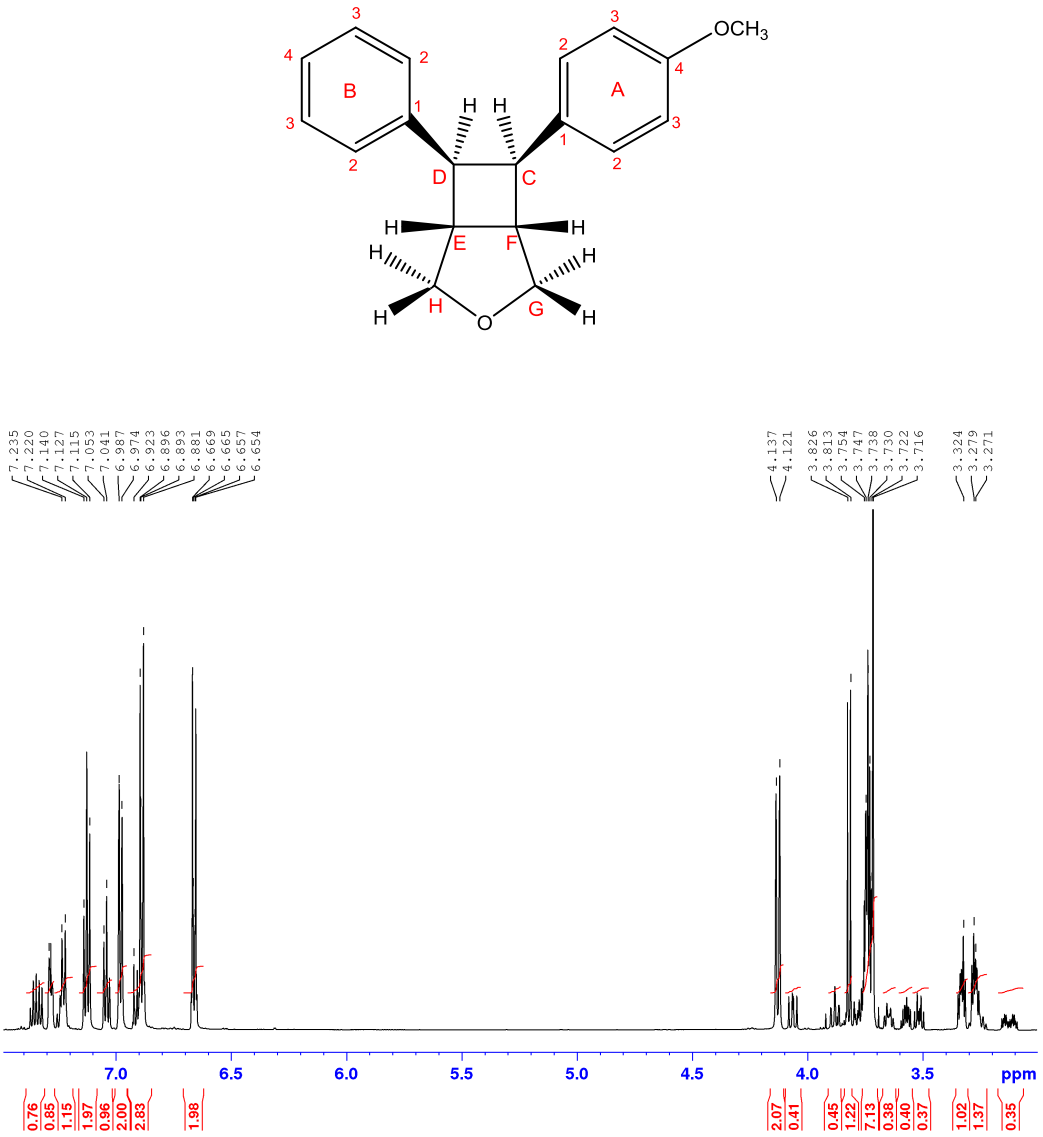


Figure S51: **6a**: ^{1}H NMR (600.13 MHz, $CDCl_3$) δ 7.13 (dd, 2H, J = 7.3, 7.3 Hz, H–*B3*), 7.04 (dd, 1H, J = 7.3, 7.3 Hz, H–*B4*), 6.98 (d, 2H, J = 7.3 Hz, H–*B2*), 6.89 (d, 2H, J = 6.9 Hz, H–*A2*), 6.66 (d, 2H, J = 6.9 Hz, H–*A3*), 4.13 (d, 2H, J = 9.5 Hz, H–*G*,*H*-down), 3.77–3.70 (overlapped m, 4H, H–*C*, H–*D*, H–*G*,*H*-up), 3.72 (s, 3H, OCH_3), 3.36–3.30 (m, 1H, H–*E*), 3.30–3.25 (m, 1H, H–*F*).

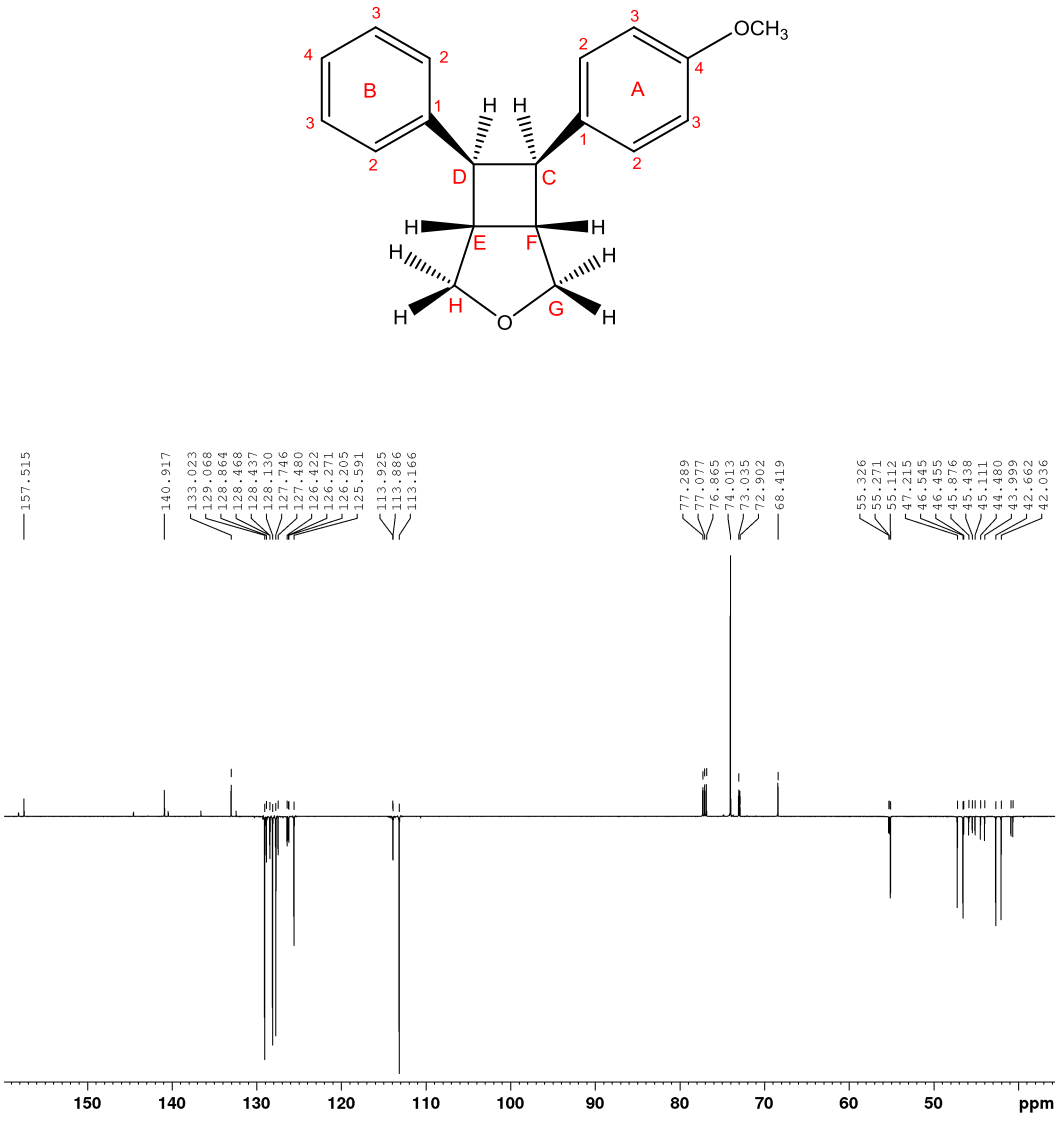


Figure S52: **6a**: ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 157.5 (4° C–*A4*), 140.9 (4° C–*B1*), 133.0 (4° C–*A1*), 129.1 (CH–*A2*), 128.1 (CH–*B2*), 127.8 (CH–*B3*), 125.6 (CH–*B4*), 113.2 (CH–*A3*), 74.0 (CH_2–*G* and CH_2–*H*), 55.1 (OCH_3), 47.2 and 46.5 (CH_2–*D* and CH_2–*C*), 42.7 and 42.0 (CH_2–*E* and CH_2–*F*).

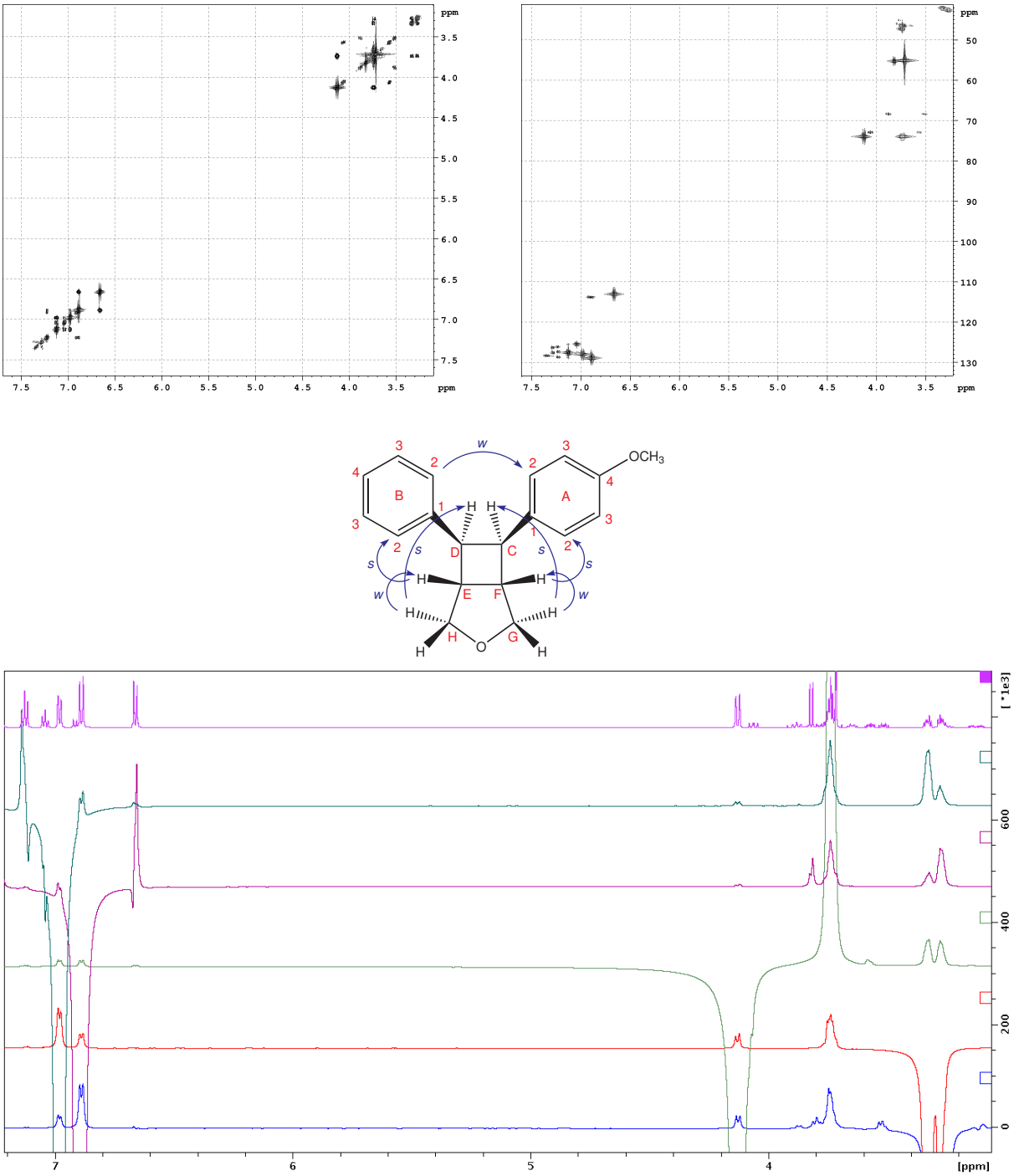


Figure S53: **6a**: COSY, HMQC and NOE spectra for assignement explanation.

(1*R,5*S**,6*R**,7*S**)-6-(4-Methoxyphenyl)-7-[4-(trifluoromethyl)phenyl]-3-oxabicyclo[3.2.0]-heptane (6b)**

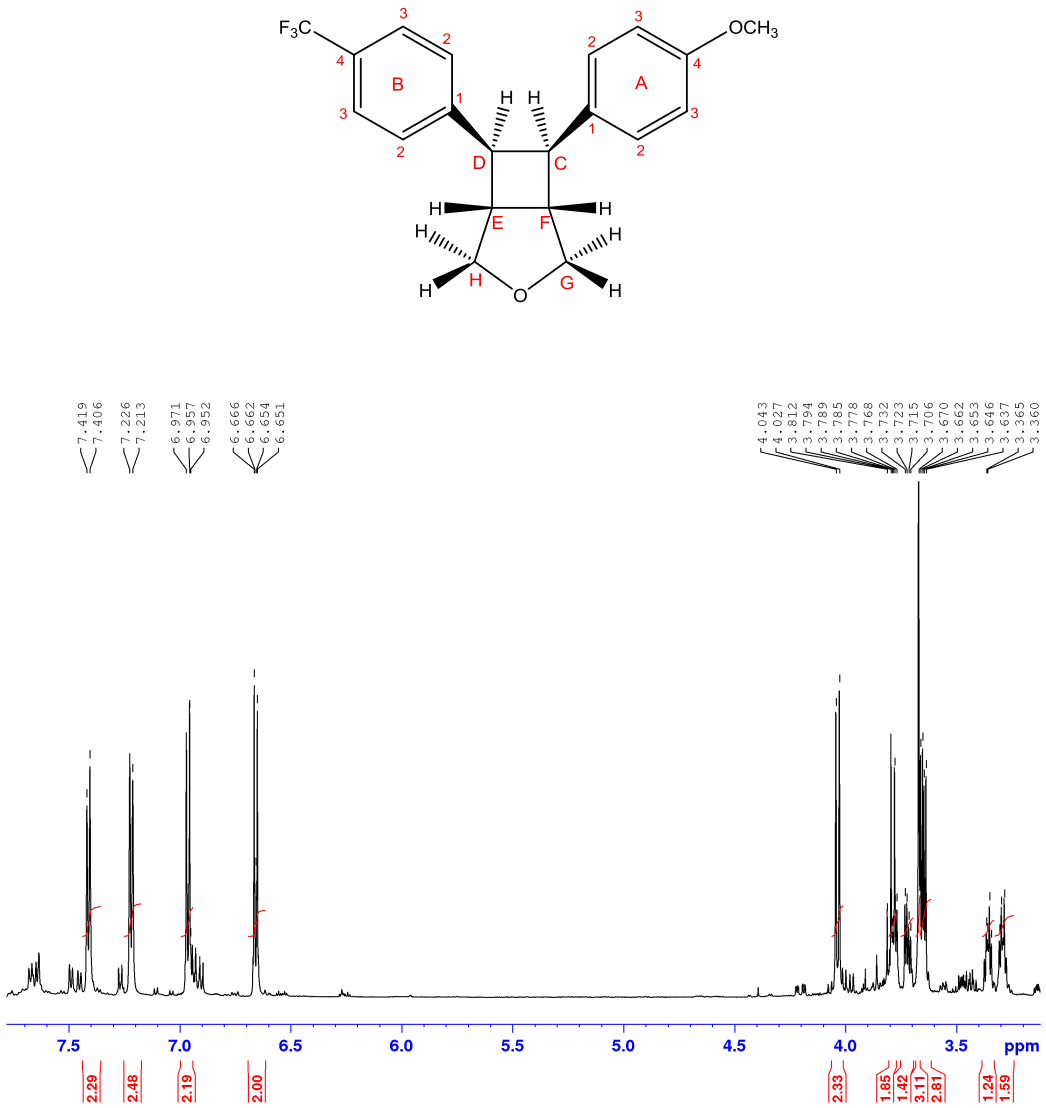


Figure S54: **6b**: ^{1}H NMR (600.13 MHz,CD_3CN) δ 7.41 (d, 2H, J = 8.1 Hz, H–*B3*), 7.22 (d, 2H, J = 8.1 Hz, H–*B2*), 6.96 (d, 2H, J = 8.7 Hz, H–*A2*), 6.66 (d, 2H, J = 8.7 Hz, H–*A3*), 4.04 (d, 2H, J = 9.4 Hz, H–*G*,*H*-down), 3.79 (overlapped 1H, H–*D*), 3.72 (dd, 1H, J = 5.1, 10.1 Hz, H–*C*), 3.67 (s, 3H, OCH_3), 3.65 (dd, 2H, J = 5.4, 9.4 Hz, H–*G*,*H*-up), 3.38–3.32 (m, 1H, H–*E*), 3.32–3.25 (m, 1H, H–*F*).

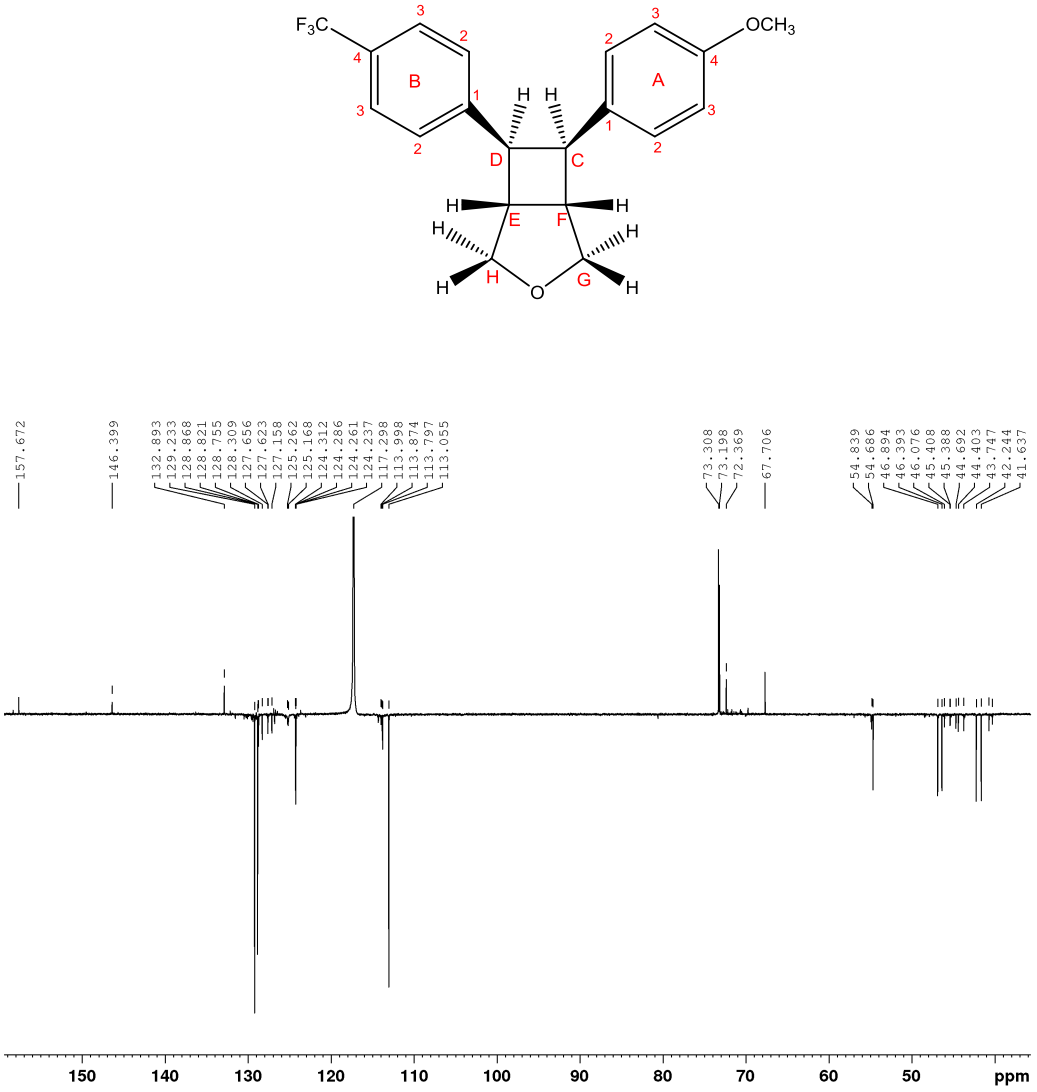


Figure S55: **6b**: ^{13}C NMR (150.92 MHz, CD_3CN) δ 157.7 (4° C–*A4*), 146.4 (4° C–*B1*), 132.9 (4° C–*A1*), 129.2 (CH–*A2*), 128.9 (CH–*B2*), 126.8 (q, $J = 31.5$ Hz, kv. C–*B4*), 124.6 (q, $J = 273$ Hz, CF_3), 124.3 (q, $J = 3.7$ Hz, CH–*B3*), 113.1 (CH–*A3*), 73.3 and 73.2 (CH_2–*G* and CH_2–*H*), 54.7 (OCH_3), 46.9 (CH_2–*D*), 46.4 (CH_2–*C*), 42.2 (CH_2–*F*), 41.6 (CH_2–*E*).

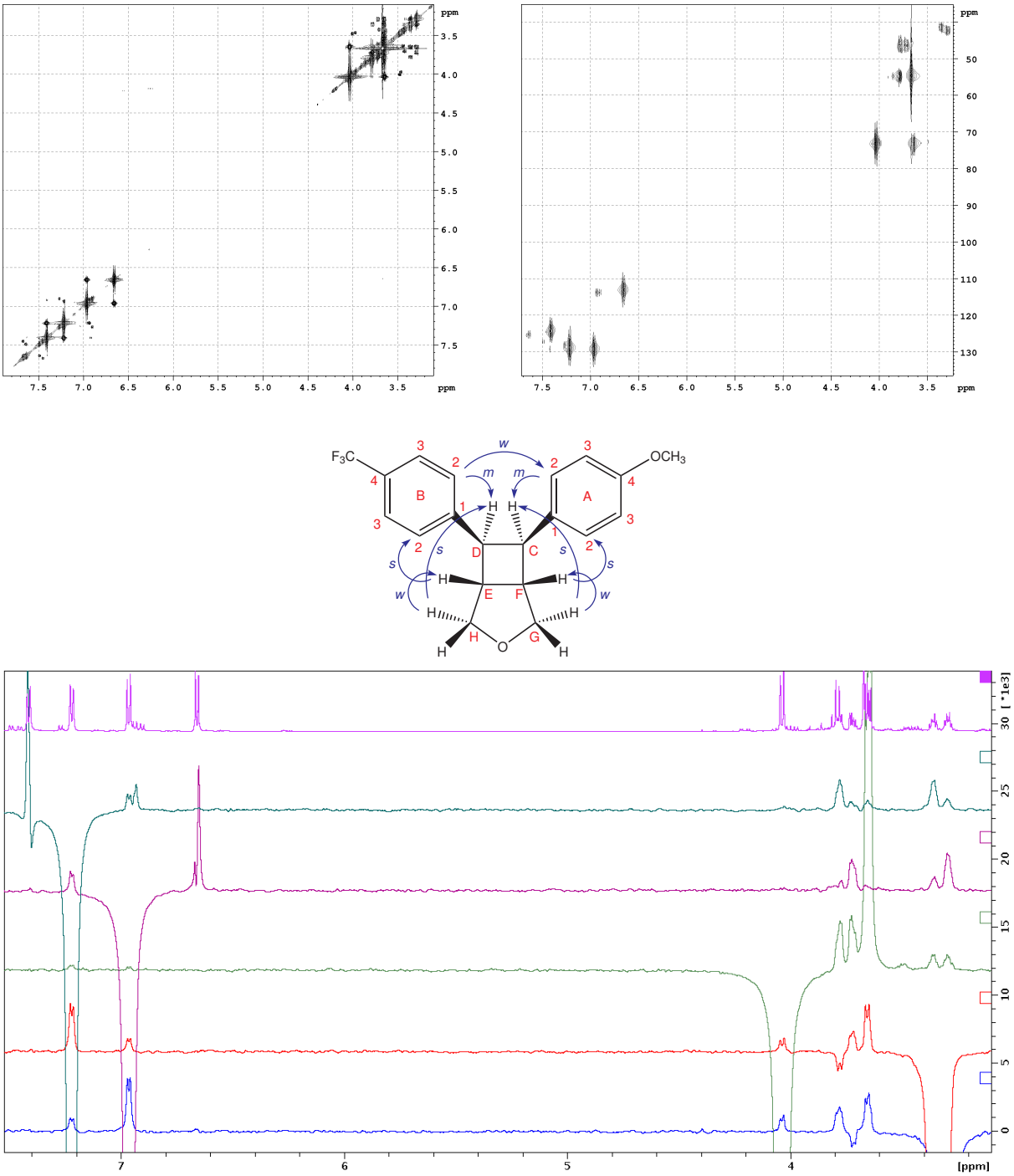


Figure S56: **6b**: COSY, HMQC and NOE spectra for assignement explanation.

A.5 UV-VIS spectra of substrates 3

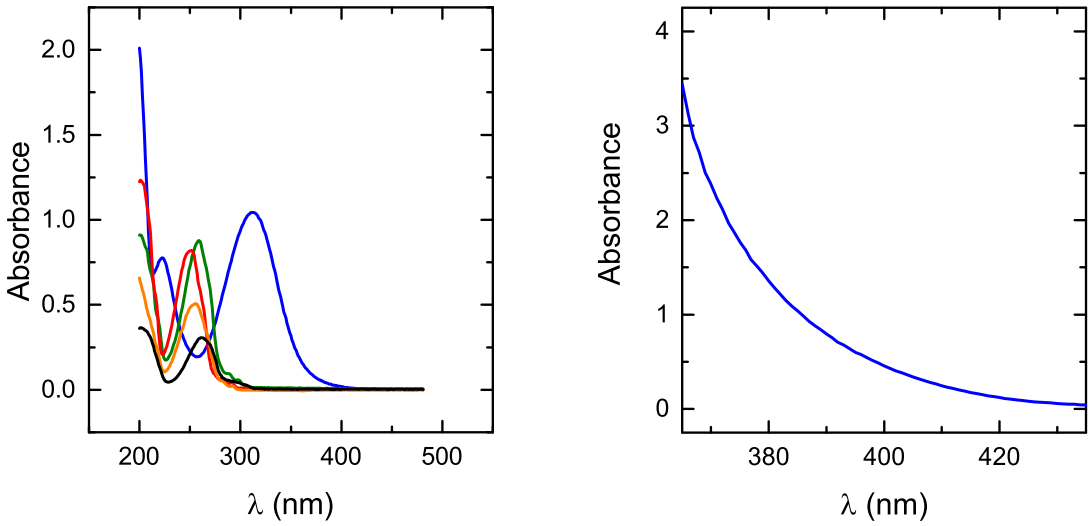
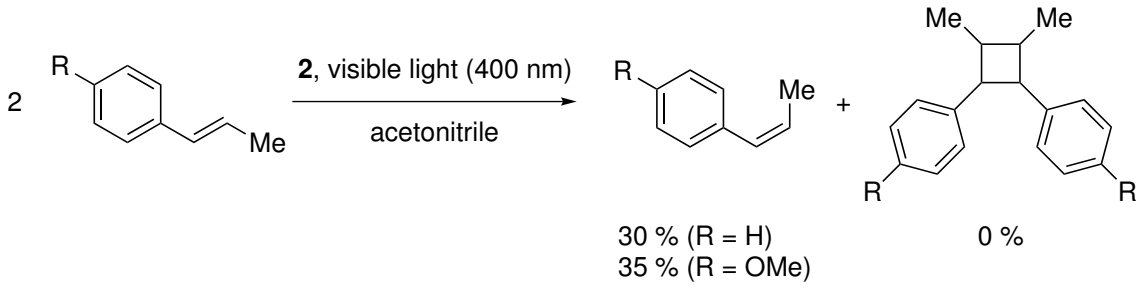


Figure S57: Left: UV-VIS spectra of substrates **3a-d**, including spectrum of **3e** (R = NO_2). – **3a** $c = 2.5\times10^{-5}$ mol L^{-1}, – **3b** $c = 5.0\times10^{-5}$ mol L^{-1}, – **3c** $c = 5.0\times10^{-5}$ mol L^{-1}, – **3d** $c = 2.7\times10^{-5}$ mol L^{-1}, – **3e** $c = 5.5\times10^{-5}$ mol L^{-1}. Right: Narrow band of higher concentrated spectrum of **3e** $c = 2.0\times10^{-3}$ mol L^{-1}.

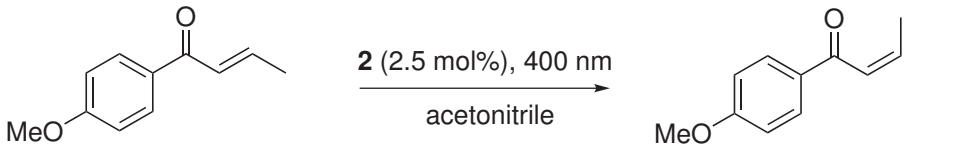
A.6 Intermolecular [2+2] cycloadditions



Scheme S1: Intermolecular [2+2] cycloaddition of *trans*-anethole or phenylpropene was not observed, only *E*/*Z*-isomerization occured (see main text).

A.7 *E*/*Z* Photoisomerization sensitized with flavin 2

Triplet *E*/*Z* photoisomerization sensitized with flavin **2** was observed in the case of *trans*-anethole (see A.6) and (*E*)-1-(4-methoxyphenyl)-but-2-en-1-one (Scheme S2) as examples of substituted styrenes and arylenones, respectively.

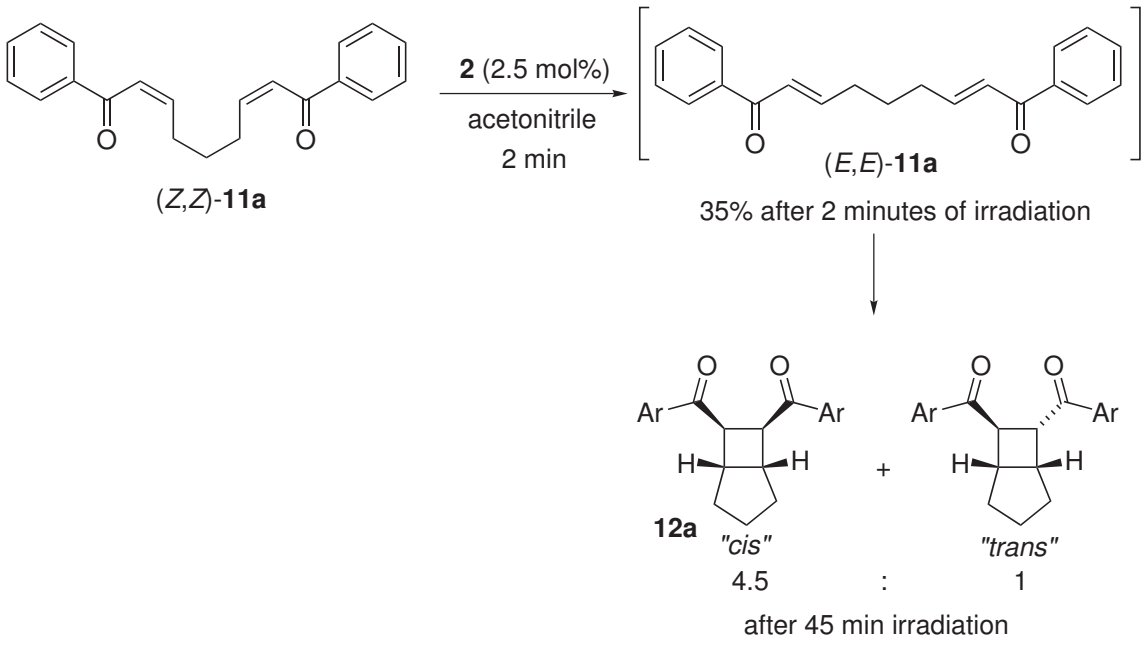


25% after 20 min irradiation

Scheme S2: *E*/*Z* Photoisomerization of (*E*)-1-(4-methoxyphenyl)-but-2-en-1-one sensitized with flavin **2**.

A.8 *E*/*Z* Photoisomerization of (*Z*,*Z*)-11a followed by [2+2] cycloaddition sensitized with flavin 2

Triplet *E*/*Z* photoisomerization producing mixture (*Z*,*Z*)-**11a** : (*E*,*E*)-**11a** 2 : 1 was observed after short (2 min) irradiation of (*Z*,*Z*)-**11a** in the presence of 2.5 mol% of **2**. Only traces of cyclobutane **12a** were detected after this short irradiation. On the other hand, after 45 minutes, conversion of (*Z*,*Z*)-**11a** to **12a** was completed. The product was the mixture of stereoisomers of similar composition (*cis* : *trans* = 4.5 : 1) as we observed starting from (*E*,*E*)-**11a** (*cis* : *trans* = 5 : 1).



Scheme S3: *E*/*Z* Photoisomerization and [2+2] cycloaddition of **11a** sensitized with flavin **2**.

A.9 Kinetic profile of 3a [2+2] cycloaddition to 4a on analytical scale

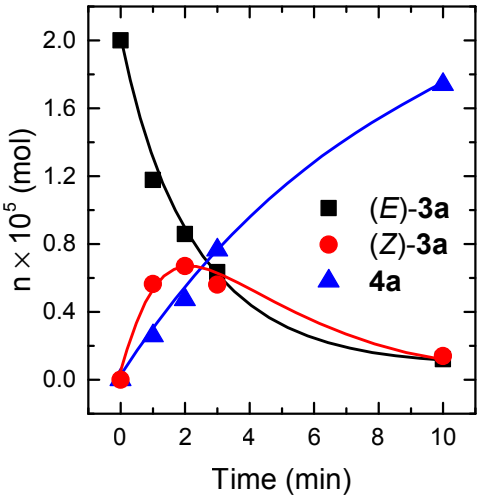


Figure S58: Time progress of reaction mixture composition during the cycloaddition of **3a** on analytical scale.

A.10 Laboratory apparatus (illuminator) for preparative experiments

Figure S59: Front view of the switched on apparatus on magnetic stirrer with reaction mixture in Schlenk tube (cyan fluorescence of **2** occurs).

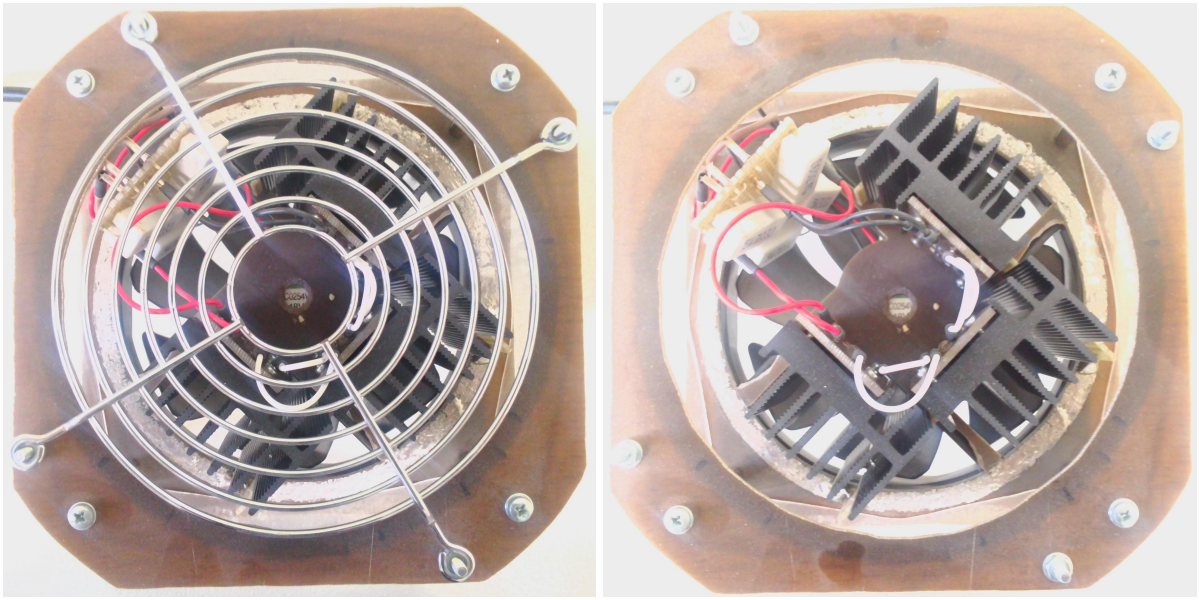


Figure S60: Top view of the apparatus with and without grating.

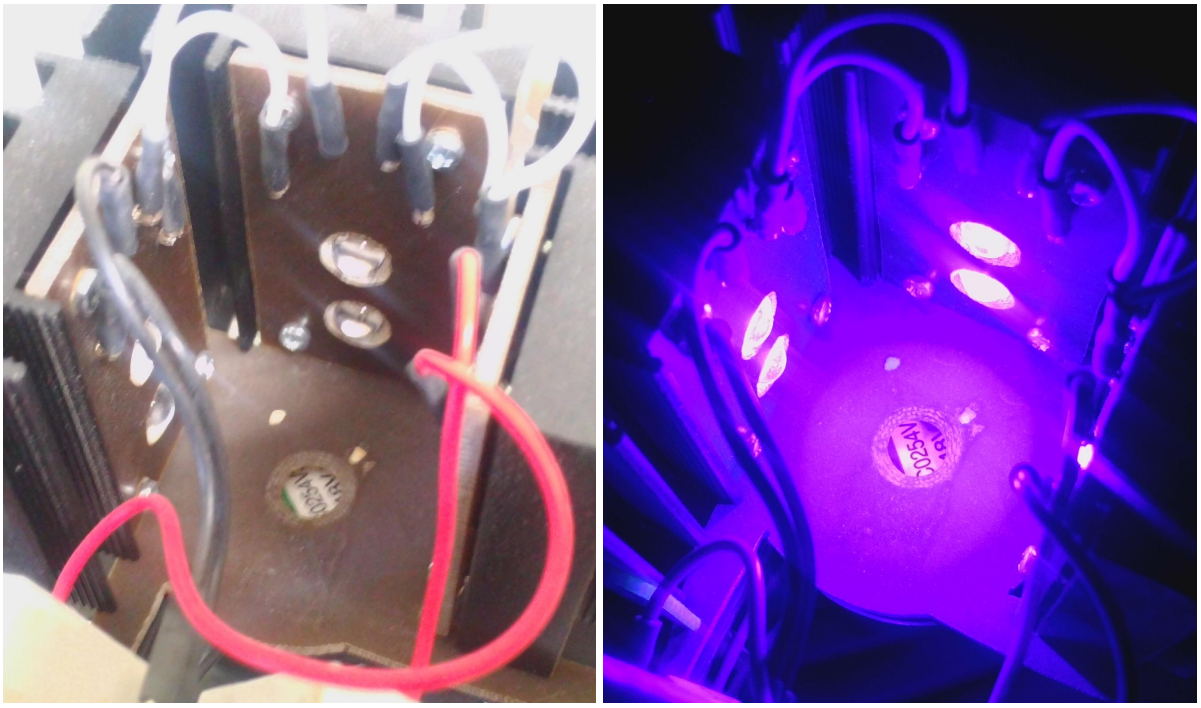


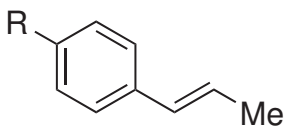
Figure S61: Detailed view of LEDs.

A.11 Estimated free-energy changes for electron transfer from dienes to alloxazine

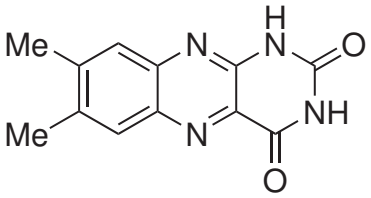
The change in free Gibbs energy ΔG_{eT} of the electron transfer from the substituted methylstyrene (see formula below) to the excited alloxazines (lumichrome was used as model compound with all characteristics known) in singlet state were calculated from the observed reduction potentials using the Rehm-Weller equation (1),[31, 32]

$$\Delta G_{eT} = 96.4(E^{ox}_{1/2} - E^{red}_{1/2} - \frac{e^2}{\varepsilon a} - E^{0\text{–}0}) \quad (1)$$

in which $E^{ox}_{1/2}$ and $E^{red}_{1/2}$ are the oxidation potential of the substrate and the reduction potential of alloxazine (-1.3 V, value for lumichrome),[33] $\frac{e^2}{\varepsilon a}$ is the Coulomb term (-0.06 eV)[33] and $E^{0\text{–}0}$ is the lumichrome excitation energy (2.92 eV).[33]



substituted styrene



lumichrome

R	$E^{ox}_{1/2}$ [V][a]	ΔG [kJ mol^{-1}][b]
MeO	1.17	-38
Me	1.47	-9
H	1.68	12
Cl	1.70	13
CF_3	2.30	70
α-methylstyrene	1.85	22

[a] Values from the reference[34–36] obtained in acetonitrile vs SCE. [b] Free energy changes calculated from equation (1) using $E^{red}_{1/2}$(lumichrome) = -1.3 V vs SCE.[33]