Electronic Supplementary Information

The Baylis-Hillman acetates in organic synthesis: Development of a facile strategy for synthesis of functionalized unsaturated benzo-fused macrocyclic ethers and [n] metacyclophanes

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Contents **Page**

(1) General & experimental procedures with all spectral data 2-53

a) Crystal data & ORTEP diagram of compound **6a** 22-23

b) Crystal data & ORTEP diagram of compound **6c-*E*** 25

c) Crystal data & ORTEP diagram of compound **6c-*Z*** 26-27

d) Crystal data & ORTEP diagram of compound **6k** 36-37

e) Crystal data & ORTEP diagram of compound **6m** 38-39

f) Crystal data & ORTEP diagram of compound **6n** 40

g) Crystal data & ORTEP diagram of compound **6o** 41

h) Crystal data & ORTEP diagram of compound **7a-*E*** 42

i) Crystal data & ORTEP diagram of compound **7a-*Z*** 43-44

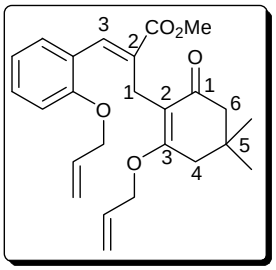
j) Crystal data & ORTEP diagram of compound **7g** 51-52

(2) NMR Spectra 54-121

EXPERIMENTAL SECTION

General Remarks: Melting Points were recorded on a Superfit (India) capillary melting point apparatus and were uncorrected. Infrared spectra were recorded on a JASCO FT / IR 5300 spectrophotometer. All the spectra were calibrated against polystyrene absorption at 1601 cm^{-1}. Solid samples were recorded as KBr wafers and liquid samples as thin film between NaCl plates. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker-AVANCE-400 spectrometer in deuterochloroform ($CDCl_3$) with tetramethylsilane (TMS, δ = 0) as an internal standard for ^{1}H NMR and chloroform-*d* middle peak of the triplet (δ = 77.10 ppm) as an internal standard for ^{13}C NMR. Elemental analyses were recorded on a Thermo-Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on Shimadzu-LCMS-2010A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K and 100 K on a Bruker SMART APEX CCD area detector system or Oxford Diffraction Xcalibur Eos Gemini diffractometer equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å).

General procedure: Synthesis of 3-allyloxy-2-[(2*E*)-3-(2-allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-5,5-dimethylcyclohex-2-enone (5a): A mixture of methyl 3-acetoxy-3-(2-allyloxyphenyl)-2-methylenepropanoate (**1a**, 0.58g, 2 mmol), 5,5-dimethyl-1,3-cyclohexanedione (**2a**, 0.28g, 2 mmol) and K_2CO_3 (0.276g, 2 mmol) in DMF (3 mL) was stirred at room temperature for 6 h. Then allyl bromide (**4a**, 1.21 g, 0.87 mL, 10 mmol) and K_2CO_3 (0.276g, 2 mmol) were added and stirring continued for 4 h. Then the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 x 25 mL). Combined organic layer was washed with saturated NaCl solution (3 x 10 mL) and was dried over anhydrous Na_2SO_4. Solvent was evaporated and the crude product, thus obtained, was purified by silica gel column chromatography (30% ethyl acetate in hexanes) to furnish the title compound (**5a**) as a colorless viscous liquid in 68% (0.558 g) yield.

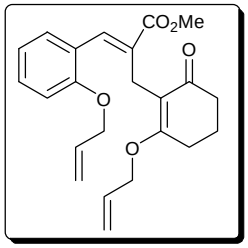


IR (neat) : υ 1712, 1641, 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 0.96 (s, 6H), 2.11 (s, 2H), 2.25 (s, 2H), 3.55 (s, 2H), 3.74 (s, 3H), 4.37 (d, J = 4.8 Hz, 2H), 4.55 (d, J = 4.8 Hz, 2H), 5.12-5.31 (m, 3H), 5.35-5.46 (m, 1H), 5.73-5.89 (m, 1H), 5.98-6.13 (m, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.86-6.93 (m, 1H), 7.18-7.24 (m, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.45, 28.39, 31.91, 39.30, 50.24, 51.77, 68.21, 69.00, 111.71, 116.88, 117.28, 117.57, 120.28, 125.61, 129.25, 130.35, 132.22, 133.15, 133.31, 133.97, 156.39, 169.19, 169.48, 197.29; LCMS (m/z) : 411 $(M+H)^+$.

In addition, peaks at δ 1.09 (s), 3.60 (s), 3.75 (s) and 6.73 (s) with low intensity also appeared indicating that they arise from minor (*Z*)-isomer(≈5%)

E:Z (95:5) Ratio is determined by the integration of isomeric olefinic protons at δ 7.74 & 6.73.

3-Allyloxy-2-[(2*E*)-3-(2-allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]cyclohex-2-enone (5b):

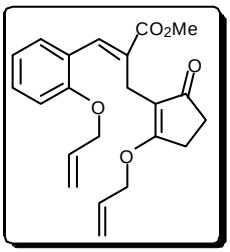


Yield: 67%; reaction time: (6h + 4h); colorless liquid; IR (neat) : υ 1711, 1645, 1612 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 1.71-1.82 (m, 2H), 2.19 (t, J = 6.4 Hz, 2H), 2.37 (t, J = 6.0 Hz, 2H), 3.54 (s, 2H), 3.75 (s, 3H), 4.37 (d, J = 4.8 Hz, 2H), 4.55 (d, J = 4.4 Hz, 2H), 5.12-5.31 (m, 3H), 5.40 (d, J = 17.2 Hz, 1H), 5.72-5.88 (m, 1H), 5.97-6.12 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.87-6.92 (m, 1H), 7.17-7.24 (m, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.74, 21.50, 25.43, 36.34, 51.74, 68.31, 68.96, 111.62, 117.24, 117.61, 118.06, 120.22, 125.72, 129.15, 130.23, 132.46, 132.97, 133.30, 134.00, 156.20, 169.12, 171.10, 197.42; LCMS (m/z) : 383 $(M+H)^+$.

In addition, peaks at δ 1.95-2.06 (m), 2.59 (t), 3.45 (s), 3.59 (s), 4.49 (d, J = 4.8 Hz), 6.72 (s) and 7.16 (d, J = 8.0 Hz) with low intensity also appeared indicating that they arise from minor (*Z*)-isomer(≈5%).

E:Z (95:5) Ratio is determined by the integration of isomeric olefinic protons at δ 7.71 & 6.72.

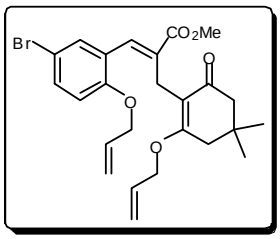
3-Allyloxy-2-[(2*E*)-3-(2-allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]cyclopent-2-enone (5c):



Yield: 58%; reaction time: (6h + 4h); pale yellow solid; mp: 84-86 ^{0}C; IR (KBr) : υ 1712, 1682, 1626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37-2.43 (m, 2H), 2.57-2.64 (m, 2H), 3.35 (s, 2H), 3.77 (s, 3H), 4.55-4.65 (m, 4H), 5.20-5.35 (m, 3H), 5.40 (d, J = 17.2 Hz, 1H), 5.80-5.94 (m, 1H), 5.98-6.13 (m, 1H), 6.82-6.97 (m, 2H), 7.20-7.26 (m, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.65, 24.73, 33.36, 51.85, 69.07, 69.67, 111.89, 117.30, 117.98, 118.45, 120.41, 125.24, 129.61, 129.84, 130.26, 132.29, 133.24, 135.33, 156.56, 168.80, 183.51, 203.88; LCMS (m/z) : 369 $(M+H)^+$.

^{1}H & ^{13}C NMR spectra did not indicate the presence of any significant amounts of minor (*Z*)-isomer.

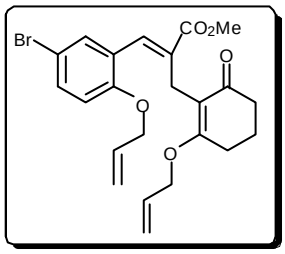
3-Allyloxy-2-[(2*E*)-3-(2-allyloxy-5-bromophenyl)-2-methoxycarbonylprop-2-en-1-yl]-5,5-dimethylcyclohex-2-enone (5d):



Yield: 56%; reaction time: (6h + 4h); pale yellow solid; mp: 78-80^{0}C; IR (KBr) : υ 1711, 1626, 1599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (s, 6H), 2.14 (s, 2H), 2.31 (s, 2H), 3.51 (s, 2H), 3.76 (s, 3H), 4.45 (d, J = 4.8 Hz, 2H), 4.53 (d, J = 4.8 Hz, 2H), 5.16-5.32 (m, 3H), 5.38 (d, J = 17.6 Hz, 1H), 5.76-5.91 (m, 1H), 5.95-6.10 (m, 1H), 6.72 (d, J = 8.8 Hz, 1H), 7.30 (dd, J = 8.8 & 2.0 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.65, 28.43, 31.89, 39.24, 50.19, 51.87, 68.27, 69.29, 112.45, 113.52, 116.43, 117.61, 117.66, 127.62, 131.63, 132.01, 132.70, 132.80, 133.00, 133.59, 155.46, 168.96, 169.46, 197.02; LCMS (m/z) : 489 $(M+H)^+$, 491 $[(M+H)^+ +2)]$.

^{1}H & ^{13}C NMR spectra did not indicate the presence of minor (*Z*)-isomer.

3-Allyloxy-2-[(2*E*)-3-(2-allyloxy-5-bromophenyl)-2-methoxycarbonylprop-2-en-1-yl]cyclo-hex-2-enone (5e):



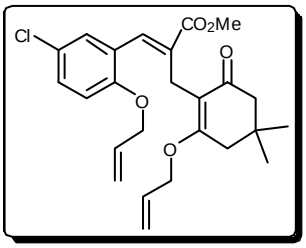
Yield: 62%; reaction time: (6h + 4h); pale yellow solid; mp: 80-82 ^{0}C; IR (KBr) : υ 1718, 1626, 1601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78-1.89 & 1.99-2.03 (2m, 2H), 2.24 & 2.39 (2t, J = 6.4 Hz, 2H), 2.44 & 2.59 (2t, J = 6.0 Hz, 2H), 3.46 & 3.50 (2s, 2H), 3.62 & 3.77 (2s, 3H), [4.45 (d, J = 5.2 Hz), 4.53 (d, J = 4.8 Hz) & 4.55-4.60 (m), (4H)], 5.16-5.32 (m, 3H), 5.38 (d, J = 17.2 Hz, 1H), 5.77-5.92 (m, 1H), 5.95-6.10 (m, 1H), 6.60 & 7.57 (2s, 1H)$^{\Delta}$, 6.70 & 6.71 (2d, J = 8.8 Hz, 1H), 7.30 (dd, J = 8.8 & 2.0 Hz, 1H), 7.38 (s, 1H)*; ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.82, 21.76, 25.46, 36.34, 51.93, 68.46, 69.31, 112.35, 113.46, 117.66, 117.82, 127.75, 131.57, 132.23, 132.78, 132.86, 133.80, 155.36, 168.98, 171.17, 197.22; LCMS (m/z) : 461 $(M+H)^+$, 463 $[(M+H)^+ +2]$.

* Unresolved doublet.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈6%).

$^{\Delta}$*E:Z* Ratio (94:6) is determined by the integration of isomeric olefinic protons at δ 7.57 & 6.60.

3-Allyloxy-2-[(2*E*)-3-(2-allyloxy-5-chlorophenyl)-2-methoxycarbonylprop-2-en-1-yl]-5,5-dimethylcyclohex-2-enone (5f):



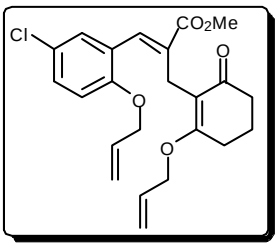
Yield: 66%; reaction time: (6h + 4h); pale yellow solid; mp: 70-72 ^{0}C; IR (KBr) : υ 1712, 1626, 1599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 & 1.09 (2s, 6H), 2.14 & 2.25 (2s, 2H), 2.31 & 2.45 (2s, 2H), 3.41 & 3.51 (2s, 2H), 3.62 & 3.76 (2s, 3H), 4.44 (d, *J* = 4.8 Hz, 2H), 4.53 (d, *J* = 4.8 Hz, 2H), 5.15-5.33 (m, 3H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.77-5.91 (m, 1H), 5.95-6.09 (m, 1H), 6.62 & 7.61 (2s, 1H)$^{\Delta}$, 6.70 & 6.76 (2d, *J* = 8.8 Hz, 1H), [7.11(d)* & 7.16 (dd), (*J* = 8.8 & 2.0 Hz), (1H)], 7.32 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.69, 28.45, 31.93, 39.30, 50.24, 51.90, 68.29, 69.42, 113.08, 116.51, 117.63, 117.72, 125.16, 127.20, 128.70, 129.98, 132.17, 132.90, 133.04, 133.58, 155.03, 169.01, 169.45, 197.07; LCMS (m/z) : 445 $(M+H)^{+}$, 447 $[(M+H)^{+}+2)]$.

* Unresolved doublet of doublet.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈3%).

$^{\Delta}$*E:Z* (97:3) Ratio is determined by the integration of isomeric olefinic protons at δ 7.61 & 6.62.

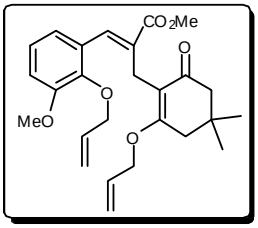
3-Allyloxy-2-[(2*E*)-3-(2-allyloxy-5-chlorophenyl)-2-methoxycarbonylprop-2-en-1-yl]cyclo-hex-2-enone (5g):



Yield: 62%; reaction time: (6h + 4h); colorless solid; mp: 86-88 ^{0}C; IR (KBr) : υ 1716, 1624, 1599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78-1.87 (m, 2H), 2.23 (t, J = 6.4 Hz, 2H), 2.43 (t, J = 6.0 Hz, 2H), 3.50 (s, 2H), 3.77 (s, 3H), 4.44 (d, J = 4.8 Hz, 2H), 4.53 (d, J = 4.4 Hz, 2H), 5.15-5.32 (m, 3H), 5.38 (d, J = 17.6 Hz, 1H), 5.77-5.92 (m, 1H), 5.95-6.09 (m, 1H), 6.76 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 8.8 Hz, 1H), 7.27 (s, 1H)*, 7.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.82, 21.74, 25.45, 36.35, 51.89, 68.43, 69.40, 113.01, 117.61, 117.81, 125.04, 127.30, 128.61, 129.99, 132.32, 132.91, 133.79, 154.89, 168.96, 171.10, 197.18; LCMS (m/z) : 417 $(M+H)^+$, 419 $[(M+H)^+ +2)]$. * It merges with $CHCl_3$ peak.

^{1}H and ^{13}C NMR spectra did not indicate the presence of minor (*Z*)-isomer.

3-Allyloxy-2-[(2*E*)-3-(2-allyloxy-3-methoxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-5,5-dimethylcyclohex-2-enone (5h):



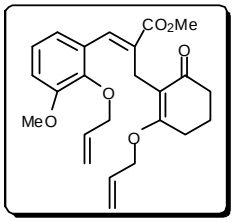
Yield: 57%; reaction time: (6h + 4h); colorless liquid; IR (neat) : υ 1712, 1645, 1614 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 & 1.09 (2s, 6H), 2.05 & 2.12 (2s, 2H), 2.28 & 2.45 (2s, 2H), 3.46 & 3.54 (2s, 2H), 3.58 & 3.74 (2s, 3H), 3.81 & 3.84 (2s, 3H), 4.39 & 4.41 (2d, J = 4.8 Hz, 2H), 4.46 & 4.55 (2d, J = 6.0 Hz, 2H), 5.14-5.27 (m, 3H), 5.33 (d, J = 17.2 Hz, 1H), 5.76-5.90

(m, 1H), 6.00-6.14 (m, 1H), 6.67 & 7.71 (2s, 1H)$^{\Delta}$, [6.70-6.82 (m), 6.85 (d, J = 8.0 Hz) & 6.90-7.11 (m), (3H)]; ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.60, 28.39, 31.92, 39.31, 50.25, 51.79, 55.85, 68.24, 74.34, 112.22, 116.58, 117.61, 117.72, 122.11, 123.51, 130.86, 133.00, 133.13, 133.77, 134.27, 146.25, 152.62, 169.06, 169.52, 197.27; LCMS (m/z) : 441 $(M+H)^+$.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈5%).

$^{\Delta}$*E:Z* (95:5) Ratio is determined by the integration of isomeric olefinic protons at δ 7.71 & 6.67 .

3-Allyloxy-2-[(2*E*)-3-(2-allyloxy-3-methoxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-cyclohex-2-enone (5i):

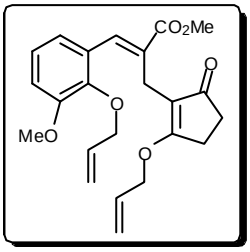


Yield: 62%; reaction time: (6h + 4h); colorless liquid; IR (neat) : υ 1712, 1647, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74-1.85 & 1.99-2.06 (2m, 2H), [2.21 (t, J = 6.8 Hz), 2.30-2.40 (m), (2H)], 2.41 & 2.61 (2t, J = 6.0 Hz, 2H), 3.41 & 3.53 (2s, 2H), 3.59 & 3.75 (2s, 3H), 3.82 & 3.84 (2s, 3H), 4.39 & 4.41 (2d, J = 5.2 Hz, 2H), 4.45 & 4.56 (2d, J = 5.6 Hz, 2H), 4.90-5.02 & 5.13-5.28 (2m, 3H), 5.33 (d, J = 17.2 Hz, 1H), 5.76-5.90 (m, 1H), 6.00-6.13 (m, 1H), 6.63 & 7.68 (2s, 1H)$^{\Delta}$, [6.71-6.81 (m) & 6.84 (dd, J = 6.8 & 2.0 Hz), (1H)], 6.90-7.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.75, 21.60, 25.46, 36.36, 51.77, 55.83, 68.37, 74.26, 112.12, 117.68, 117.80, 122.06, 123.44, 130.92, 132.95, 133.20, 133.80, 134.26, 146.05, 152.52, 169.02, 171.20, 197.44; LCMS (m/z) : 413 $(M+H)^+$.

The underlined chemical shift values with low intensity are attributed to the presence of minor (*Z*)-isomer (≈7%).

$^{\Delta}$*E*:*Z* Ratio (93:7) is determined by the integration of isomeric olefinic protons at δ 7.68 and 6.63.

3-Allyloxy-2-[(2*E*)-3-(2-allyloxy-3-methoxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-cyclopent-2-enone (5j):



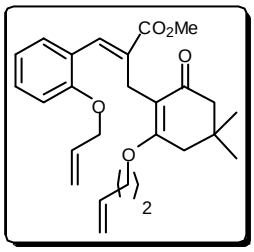
Yield: 65%; reaction time: (6h + 4h); colorless liquid; IR (neat) : υ 1712, 1689, 1631 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37-2.45 & 2.46-2.52 (2m, 2H), 2.59-2.66 & 2.69-2.74 (2m, 2H), 3.30 & 3.33 (2s, 2H), 3.59 & 3.77 (2s, 3H), 3.82 & 3.85 (2s, 3H), 4.39 & 4.46 (2d, *J* = 6.0 Hz, 2H), 4.59 & 4.68 (2d, *J* = 4.8 Hz, 2H), 5.14-5.41 (m, 4H), 5.82-5.98 (m, 1H), 6.00-6.13 (m, 1H), 6.71 & 7.85 (2s, 1H)$^{\Delta}$, 6.73 & 6.87 (2d, *J* = 8.4 Hz, 1H), 6.81 & 6.92 (2d, *J* = 7.6 Hz, 1H), 6.96-7.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.53, 24.61, 33.24, 51.78, 55.73, 69.64, 74.29, 112.44, 117.68, 117.93, 118.11, 121.81, 123.61, 130.38, 130.53, 132.17, 134.04, 135.33, 146.23, 152.56, 168.51, 183.58, 203.82; LCMS (m/z) : 399 $(M+H)^{+}$.

The underlined chemical shift values with low intensity are due to the presence of minor (*Z*)-isomer (≈5%).

$^{\Delta}$*E:Z* (95:5) Ratio is determined by the integration of isomeric olefinic protons at δ 7.85 & 6.71.

2-[(2*E*)-3-(2-Allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-3-(but-3-enyloxy)-5,5-dimethylcyclohex-2-enone (5k): A mixture of methyl 3-acetoxy-3-(2-allyloxyphenyl)-2-methylenepropanoate (**1a**, 0.58g, 2 mmol), 5,5-dimethyl-1,3-cyclohexanedione (**2a**, 0.28g, 2 mmol) and K_2CO_3 (0.276g, 2 mmol) in DMF (3 mL) was stirred at room temperature for 6 h. Then 4-bromo-1-butene (**4b**, 0.54 g, 0.4 mL, 4 mmol) and K_2CO_3 (0.276g, 2 mmol) were added and heated to 80 ^{0}C for 2 h. Then the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 x 25 mL). Combined organic layer was washed with saturated

NaCl solution (3 x 10 mL) and was dried over anhydrous Na_2SO_4. Solvent was evaporated and the crude product thus obtained was purified by silica gel column chromatography (30% ethyl acetate in hexanes) to afford compound **5k**, in 56% (0.471 g) as a colorless liquid.



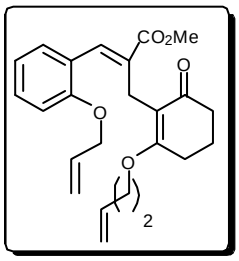
IR (neat) : υ 1714, 1651, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 0.97 & 1.10 (2s, 6H), [(2.09 (s), 2.23-2.31 (m) & 2.41-2.49 (m), (6H))], 3.42 & 3.55 (2s, 2H), 3.58 & 3.74 (2s, 3H), 3.85 & 4.01 (2t, J = 6.8 Hz, 2H), 4.48-4.52 & 4.53-4.59 (2m, 2H), 4.98-5.07 & 5.07-5.16 (2m, 2H), 5.21-5.24 & 5.24-5.30 (2m, 1H), 5.35-5.38 & 5.39-5.46 (2m, 1H), 5.61-5.73 & 5.75-5.86 (2m, 1H), 5.98-6.12 (m, 1H), 6.70 & 7.75 (2s, 1H)$^{\Delta}$, [6.81 & 6.84 (2d, J = 8.4 Hz) & 6.87-6.93 (m), 2H], [7.15-7.25 (m) & 7.38 (d, J = 7.6 Hz) *, 2H]; ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.37, 27.04, 28.40, 28.64, 31.76, 32.06, 33.72, 34.03, 39.40, 50.13, 51.35, 51.69, 67.08, 67.23, 68.92, 69.03, 111.63, 111.93, 115.30, 116.36, 117.08, 117.22, 117.39, 117.67, 120.21, 120.34, 125.48, 128.20, 128.68, 129.23, 130.35, 132.19, 132.51, 133.25, 133.43, 133.64, 133.69, 155.69, 156.36, 169.10, 169.48, 170.26, 170.85, 197.18, 197.20; LCMS (m/z): 425 $(M+H)^+$.

* It looks like unresolved doublet of doublet.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈ 20%).

$^{\Delta}$*E:Z* (80:20) Ratio is determined by the integration of isomeric olefinic protons at δ 7.75 & 6.70.

2-[(2*E*)-3-(2-Allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-3-(but-3-enyloxy)cyclohex-2-enone (5l):

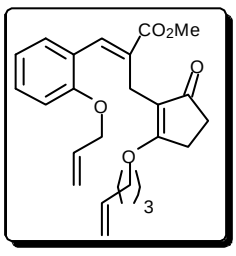


Yield: 60%; reaction time: (6h + 2h); colorless liquid; IR (neat) : υ 1712, 1643, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.68-1.79 & 1.98-2.06 (2m, 2H), [(2.17 (t, J = 6.4 Hz), 2.22-2.33 (m), 2.36 (t, J = 6.0 Hz), 2.42-2.49 (m) & 2.59 (t, J = 6.4 Hz), (6H))], 3.42 & 3.54 (2s, 2H), 3.59 & 3.76 (2s, 3H), 3.85 & 4.03 (2t, J = 6.8 Hz, 2H), 4.49 & 4.55 (2d, J = 4.8 Hz, 2H), 4.98-5.14 (m, 2H), 5.20-5.31 (m, 1H), 5.35-5.47 (m, 1H), 5.61-5.74 & 5.76-5.84 (2m, 1H), 5.97-6.12 (m, 1H), 6.69 & 7.72 (2s, 1H)$^{\Delta}$, 6.79-6.93 (m, 2H), 7.15-7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.58, 20.83, 21.32, 25.33, 25.45, 26.88, 33.60, 33.90, 36.17, 51.31, 51.63, 67.06, 67.23, 68.81, 111.43, 111.85, 116.38, 116.86, 117.14, 117.31, 117.40, 117.61, 120.08, 120.30, 125.54, 125.99, 128.09, 128.64, 129.10, 130.16, 132.33, 133.18, 133.34, 133.62, 133.74, 155.61, 156.07, 168.98, 170.23, 171.19, 172.73, 197.31; LCMS (m/z): 397 $(M+H)^{+}$.

The underlined chemical shift values with low intensity are attributed to the presence of minor (*Z*)-isomer (≈15%).

$^{\Delta}$*E:Z* (85:15) Ratio is determined by the integration of isomeric olefinic protons at δ 7.72 & 6.69.

2-[(2*E*)-3-(2-Allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-3-(pent-4-enyloxy)cyclopent-2-enone (5m):

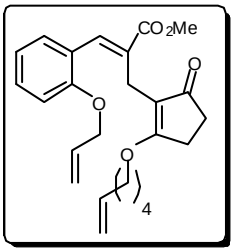


Yield: 64%; reaction time: (6h + 2h); colorless liquid; IR (neat) : υ 1714, 1633 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66-1.85 (m, 2H), 2.05-2.15 & 2.16-2.20 (2m, 2H), 2.34-2.42 & 2.48-2.52 (2m, 2H), 2.55-2.62 & 2.65-2.70 (2m, 2H), 3.30 & 3.33 (2s, 2H), 3.58 & 3.77 (2s, 3H), 4.04 & 4.17 (2t, J = 6.0 Hz, 2H), 4.51 & 4.57 (2d, J = 5.2 Hz, 2H), 4.93-5.04 (m, 2H), 5.27 (dd, J = 10.4 & 1.2 Hz, 1H), 5.40 (dd, J = 17.2 & 1.2 Hz, 1H), 5.68-5.80 (m, 1H), 5.98-6.12 (m, 1H), 6.79 & 7.90 (2s, 1H)$^{\Delta}$, 6.82 & 6.86 (2d, J = 8.4 Hz, 1H), 6.89-6.94 (m, 1H), 7.14-7.20 & 7.24-7.32 (2m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.67, 24.84, 28.41, 29.56, 33.24, 51.80, 68.46, 69.00, 111.82, 115.64, 117.27, 117.88, 120.35, 125.11, 129.62, 129.83, 130.16, 133.18, 135.09, 137.18, 156.53, 168.70, 183.91, 203.88; LCMS (m/z): 397 $(M+H)^{+}$.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈5%).

$^{\Delta}$*E:Z* (95:5) Ratio is determined by the integration of isomeric olefinic protons at δ 7.90 & 6.79.

2-[(2*E*)-3-(2-Allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-3-(hex-5-enyloxy)cyclo-pent-2-enone (5n):

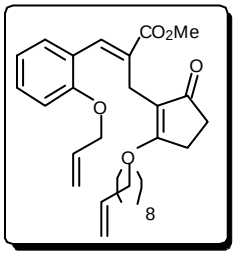


Yield: 65%; reaction time: (6h + 2h); colorless liquid; IR (neat) : υ 1712, 1689, 1633 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38-1.48 (m, 2H), 1.59-1.69 (m, 2H), 1.98-2.08 (m, 2H), 2.36-2.43 (m, 2H), 2.54-2.63 (m, 2H), 3.33 (s, 2H), 3.77 (s, 3H), 4.03 (t, J = 6.4 Hz, 2H), 4.54-4.62 (m, 2H), 4.90-5.03 (m, 2H), 5.27(dd, J = 10.4 & 1.2 Hz, 1H), 5.40 (dd, J = 17.6 & 1.2 Hz, 1H), 5.67-5.81 (m,1H), 5.98-6.12 (m, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.88-6.92 (m, 1H), 7.21-7.33 (m, 2H), 7.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.67, 24.78, 24.82, 28.82, 33.20, 33.23, 51.78,

68.99, 69.19, 111.81, 114.91, 117.23, 117.83, 120.33, 125.13, 129.58, 129.80, 130.16, 133.17, 135.04, 138.12, 156.51, 168.69, 183.94, 203.86; LCMS (m/z): 411 $(M+H)^+$.

^1H & ^{13}C NMR spectra did not indicate the presence of minor (*Z*)-isomer.

2-[(2*E*)-3-(2-Allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-3-(dec-9-enyloxy)cyclo-pent-2-enone (5o):

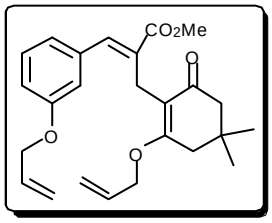


Yield: 67%; reaction time: (6h + 2h); colorless liquid; IR (neat) : υ 1714, 1697, 1631 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.20-1.42 (m, 10H), 1.57-1.66 & 1.68-1.73 (2m, 2H), 1.97-2.07 (m, 2H), 2.37-2.44 & 2.45-2.50 (2m, 2H), 2.56-2.63 & 2.65-2.70 (2m, 2H), 3.29 & 3.32 (2s, 2H), 3.58 & 3.77 (2s, 3H), 4.02 & 4.15 (2t, J = 6.4 Hz, 2H), 4.47-4.52 & 4.56-4.62 (2m, 2H), 4.89-5.03 (m, 2H), [5.22-5.25 (m) & 5.27 (dd, J = 10.4 & 1.6 Hz), (1H)], [(5.36-5.38 (m), 5.40 (dd, J = 17.2 & 1.6 Hz), 5.42-5.46 (m), (1H)], 5.72-5.88 (m, 1H), 5.98-6.12 (m, 1H), 6.77 & 7.89 (2s, 1H)$^{\Delta}$, 6.82 & 6.85 (2d, J = 8.4 Hz, 1H), 6.86-6.92 & 6.93-7.02 (2m, 1H), 7.13-7.20 & 7.21-7.32 (2m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.72, 24.87, 25.61, 28.87, 29.01, 29.19, 29.31, 29.44, 33.26, 33.75, 51.80, 69.01, 69.44, 111.82, 114.20, 117.26, 117.82, 120.35, 125.18, 129.60, 129.84, 130.21, 133.20, 135.07, 139.11, 156.55, 168.74, 184.08, 203.93; LCMS (m/z): 468 $(M+H)^+$.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈7%).

$^{\Delta}$*E:Z* (93:7) Ratio is determined by the integration of isomeric olefinic protons at δ 7.89 & 6.77.

3-Allyloxy-2-[(2*E*)-3-(3-allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-5,5-dimethyl-cyclohex-2-enone (5p):

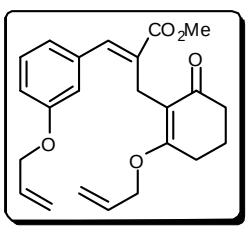


Yield: 63%; reaction time: (6h + 4h); colorless liquid; IR (neat) : υ 1712, 1649, 1614 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 0.97 & 1.01 (2s, 6H), 2.14 & 2.16 (2s, 2H), 2.26 & 2.28 (2s, 2H), 3.41 & 3.61 (2s, 2H), 3.62 & 3.74 (2s, 3H), [4.40 (d, J = 4.4 Hz) & 4.46-4.51 (m), 2H], [4.52 (d, J = 4.4 Hz) & 4.53-4.58 (m), 2H], 5.15-5.32 (m, 3H), 5.40 (d, J = 17.2 Hz, 1H), 5.73-5.88 (m, 1H), 5.98-6.12 (m, 1H), 6.50 & 7.52 (2s, 1H)$^{\Delta}$, 6.82 (d, J = 8.4 Hz, 1H), 6.93 (s, 1H), 6.97 (d, J = 7.6 Hz, 1H), 7.20-7.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.39, 28.34, 31.86, 39.26, 50.20, 51.86, 68.20, 68.79, 114.43, 115.50, 116.35, 117.64, 122.04, 129.08, 132.55, 132.98, 133.27, 137.45, 137.49, 158.34, 169.24, 169.61, 197.21; LCMS (m/z): 411 $(M+H)^{+}$.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈5%).

$^{\Delta}$ *E:Z* (95:5) Ratio is determined by the integration of isomeric olefinic protons at δ 7.52 & 6.50.

3-Allyloxy-2-[(2*E*)-3-(3-allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]cyclohex-2-enone (5q):



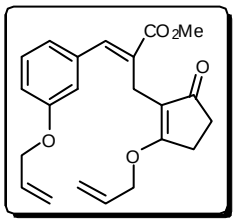
Yield: 69%; reaction time: (6h + 4h); colorless liquid; IR (neat) : υ 1712, 1651, 1606 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 1.77-1.87 (m, 2H), 2.24 (t, J = 6.4 Hz, 2H), 2.41 (t, J = 6.4 Hz, 2H), 3.59 (s, 2H), 3.76 (s, 3H), 4.40 (d, J = 4.4 Hz, 2H), 4.51 (d, J = 4.8 Hz, 2H), 5.16-5.33 (m, 3H), 5.40 (d, J = 17.2 Hz, 1H), 5.76-5.89 (m, 1H), 5.99-6.12 (m, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.89 (s, 1H), 6.92 (d, J = 7.6 Hz, 1H), 7.18-7.24 (m, 1H), 7.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.76, 21.61, 25.47, 36.36, 51.86, 68.35, 68.78, 114.44, 115.25, 117.54, 117.68, 117.72, 121.92, 129.03, 132.69, 132.84, 133.27, 137.39, 137.60, 158.29, 169.25, 171.32, 197.50; LCMS (m/z): 383 $(M+H)^+$.

In addition, peaks at δ 3.42 (s), 3.63 (s), 4.48 (d)*, 4.57 (d)* and 6.50 (s) with low intensity also appeared indicating that they arise from minor (*Z*)-isomer (≈3%).

E :Z (97:3*)* Ratio is determined by the integration of isomeric olefinic protons at δ 7.52 & 6.50.

* Unresolved doublet.

3-Allyloxy-2-[(2*E*)-3-(3-allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]cyclopent-2-enone (5r):



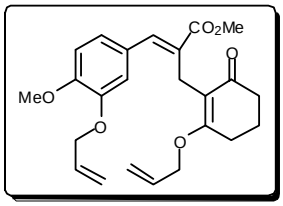
Yield: 52%; reaction time: (6h + 4h); colorless liquid; IR (neat) : υ 1712, 1689, 1628 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 2.39-2.46 & 2.47-2.52 (2m, 2H), 2.58-2.66 & 2.69-2.74 (2m, 2H), 3.28 & 3.40 (2s, 2H), 3.63 & 3.77 (2s, 3H), 4.49 & 4.52 (2d, J = 5.2 Hz, 2H), 4.59 & 4.71 (2d, J = 4.8 Hz, 2H), 5.22-5.35 (m, 3H), 5.40 (d, J = 17.2 Hz, 1H), 5.80-5.96 (m, 1H), 5.99-6.12 (m, 1H), 6.59 & 7.66 (2s, 1H) $^{\Delta}$, 6.79 & 6.85 (2d, J = 8.4 Hz, 1H), 6.91-6.99 (m, 2H), 7.18 & 7.23 (2d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.15, 24.47, 33.10, 51.70, 68.47, 69.51,

114.71, 115.12, 117.33, 117.56, 117.77, 121.86, 129.05, 129.88, 131.95, 132.95, 136.76, 138.75, 158.17, 168.47, 183.72, 203.59; LCMS (m/z) : 369$(M+H)^+$.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈4%).

$^{\Delta}$ *E :Z* (96:4) Ratio is determined by the integration of isomeric olefinic protons at δ 7.66 & 6.59.

3-Allyloxy-2-[(2*E*)-3-(3-allyloxy-4-methoxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-cyclohex-2-enone (5s):



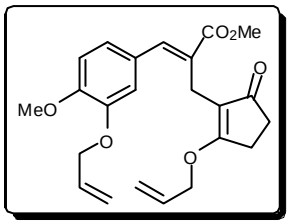
Yield: 63%; reaction time: (6h + 4h); colorless liquid; IR (neat) : υ 1703, 1639, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : *δ* 1.79-1.91 & 1.98-2.04 (2m, 2H), 2.29 & 2.37 (2t, *J* = 6.4 Hz, 2H), 2.44 & 2.61 (2t, *J* = 6.0 Hz, 2H), 3.41 & 3.63 (2s, 2H), 3.66 & 3.75 (2s, 3H), 3.84 & 3.87 (2s, 3H), 4.42 & 4.55* (2d, *J* = 4.8 Hz, 2H), 4.58 & 4.68* (2d, *J* = 5.2 Hz, 2H), 5.15-5.33 (m, 3H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.74-5.89 (m, 1H), 6.01-6.15 (m, 1H), 6.47 & 7.48 (2s, 1H) $^{\Delta}$, 6.81 & 6.83 (2d, *J* = 8.4 Hz, 1H), 6.94 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : *δ* 20.81, 21.71, 25.61, 36.47, 51.77, 55.97, 68.40, 69.89, 111.14, 114.80, 117.73, 118.08, 123.17, 128.90, 130.64, 132.86, 133.26, 137.39, 147.45, 149.46, 169.52, 171.42, 197.61; LCMS (m/z) : 413 $(M+H)^+$.

The underlined chemical shift values with low intensity arise due to the presence of minor (*Z*)-isomer (≈3%).

$^{\Delta}$ *E:Z* (97:3) Ratio is determined by the integration of isomeric olefinic protons at δ 7.48 & 6.47.

* Unresolved doublet.

3-Allyloxy-2-[(2*E*)-3-(3-allyloxy-4-methoxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-cyclopent-2-enone (5t):

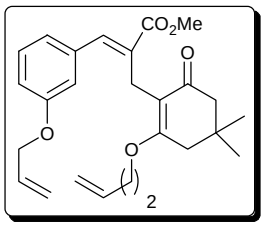


Yield: 67%; reaction time: (6h + 4h); colorless solid; mp: 64-66 ^{0}C; IR (KBr) : υ 1697, 1626, 1593 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.41-2.49 (m, 2H), 2.61-2.68 (m, 2H), 3.44 (s, 2H), 3.77 (s, 3H), 3.88 (s, 3H), 4.58 (s, 4H), 5.21-5.36 (m, 3H), 5.39 (d, J = 17.2 Hz, 1H), 5.80-5.95 (m, 1H), 6.01-6.15 (m, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.94-7.05 (m, 2H), 7.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.47, 24.77, 33.38, 51.91, 55.94, 69.77, 111.27, 114.86, 118.00, 118.07, 123.50, 127.80, 128.36, 132.17, 133.17, 139.09, 147.57, 149.78, 169.12, 183.91, 203.96; LCMS (m/z) : 399 $(M+H)^{+}$.

In addition, peaks at δ 2.49-2.52 (m), 2.69-2.74 (m), 3.28 (s), 3.65 (s), 3.87 (s), 4.69-4.71 (m), 6.55 (s) and 6.80 (d, J = 8.4 Hz) with low intensity also appeared indicating that they arise from minor (*Z*)-isomer (≈3%).

E :*Z* (97:3) Ratio is determined by the integration of isomeric olefinic protons at δ 7.62 & 6.55.

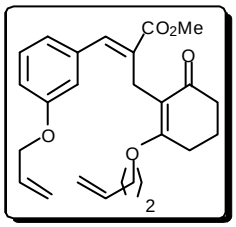
2-[(2*E*)-3-(3-Allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-3-(but-3-enyloxy)-5,5-dimethylcyclohex-2-enone (5u):



Yield: 58%; reaction time: (6h + 2h); colorless liquid; IR (neat) : υ 1712, 1645, 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.99 (s, 6H), 2.13 (s, 2H), 2.20-2.32 (m, 4H), 3.60 (s, 2H), 3.75 (s, 3H), 3.89 (t, J = 6.8 Hz, 2H), 4.50-4.56 (m, 2H), 5.00-5.10 (m, 2H), 5.23-5.31 (m, 1H), 5.37-5.45 (m, 1H), 5.63-5.76 (m, 1H), 5.99-6.10 (m, 1H), 6.82 (dd, J = 8.4 & 2.4 Hz, 1H), 6.92-6.96 (m, 1H), 6.97 (d, J = 8.0 Hz, 1H), 7.20-7.24 (m, 1H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.41, 28.41, 31.78, 33.87, 39.47, 50.16, 51.85, 67.16, 68.79, 114.40, 115.62, 116.02, 117.56, 117.66, 122.13, 129.07, 132.72, 133.27, 133.55, 137.22, 137.46, 158.36, 169.22, 169.64, 197.21; LCMS (m/z): 425 $(M+H)^+$.

^1H & ^{13}C NMR spectra did not indicate the presence of any significant amounts of minor (*Z*)-isomer.

2-[(2*E*)-3-(3-Allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-3-(but-3-enyloxy)cyclohex-2-enone (5v):

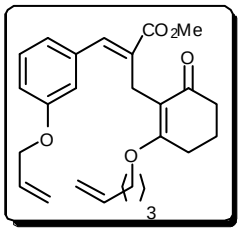


Yield: 62%; reaction time: (6h + 2h); colorless liquid; IR (neat) : υ 1712, 1645, 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 1.73-1.85 (m, 2H), 2.23 (t, J = 6.4 Hz, 2H), 2.26-2.33 (m, 2H), 2.40 (t, J = 6.0 Hz, 2H), 3.58 (s, 2H), 3.77 (s, 3H), 3.90 (t, J = 6.8 Hz, 2H), 4.52 (d, J = 5.2 Hz, 2H), 4.99-5.10 (m, 2H), 5.27 (dd, J = 10.4 & 1.2 Hz, 1H), 5.40 (dd, J = 17.2 & 1.2 Hz, 1H), 5.63-5.78 (m, 1H), 5.98-6.12 (m, 1H), 6.82 (dd, J = 8.0 & 1.6 Hz, 1H), 6.89 (s, 1H), 6.93 (d, J = 7.6 Hz,1H), 7.17-7.24 (m, 1H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.71, 21.60, 25.51, 33.80, 36.32, 51.82, 67.21, 68.77, 114.37, 115.32, 117.18, 117.55, 117.66, 121.94, 129.00,

132.83, 133.27, 133.58, 137.18, 137.59, 158.28, 169.19, 171.32, 197.41; LCMS (m/z): 397 $(M+H)^+$.

^1H & ^{13}C NMR spectra did not indicate the presence of minor (*Z*)-isomer.

2-[(2*E*)-3-(3-Allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-3-(pent-4-enyloxy)-cyclohex-2-enone (5w):

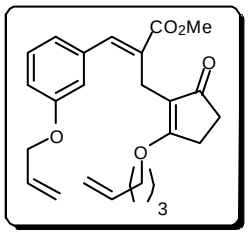


Yield: 61%; reaction time: (6h + 2h); colorless liquid; IR (neat) : υ 1712, 1645, 1608 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 1.60-1.72 (m, 2H), 1.75-1.85 (m, 2H), 2.01-2.10 (m, 2H), 2.23 (t, *J* = 6.4 Hz, 2H), 2.40 (t, *J* = 6.0 Hz, 2H), 3.59 (s, 2H), 3.76 (s, 3H), 3.85 (t, *J* = 6.4 Hz, 2H), 4.51 (d, *J* = 5.2 Hz, 2H), 4.93-5.04 (m, 2H), 5.27 (dd, *J* = 10.4 & 1.2 Hz, 1H), 5.40 (dd, *J* = 17.2 & 1.6 Hz, 1H), 5.67-5.81 (m, 1H), 5.98-6.11 (m, 1H), 6.82 (dd, *J* = 8.0 & 1.6 Hz, 1H), 6.89 (s, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 7.17-7.25 (m, 1H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.69, 21.60, 25.52, 28.41, 29.69, 36.27, 51.80, 67.13, 68.73, 114.38, 115.30, 115.44, 116.87, 117.61, 121.92, 128.99, 132.86, 133.24, 137.12, 137.34, 137.54, 158.26, 169.14, 171.68, 197.44; LCMS (m/z) : 411 $(M+H)^+$.

In addition, peaks at δ 2.59 (t), 3.38 (s), 3.64 (s), 4.03 (t) and 6.47 (s) with low intensity also appeared indicating that they are due to the presence of minor (*Z*)-isomer (≈3%).

E :Z (97:3) Ratio is determined by the integration of isomeric olefinic protons at δ 7.51 & 6.47.

2-[(2*E*)-3-(3-Allyloxyphenyl)-2-methoxycarbonyl-prop-2-ene-1-yl]-3-(pent-4-enyloxy)-cyclopent-2-enone (5x):

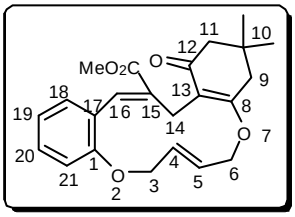


Yield: 69%; reaction time: (6h + 2h); colorless liquid; IR (neat) : υ 1714, 1689, 1624 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.66-1.79 & 1.80-1.89 (2m, 2H), 2.07-2.15 & 2.16-2.22 (2m, 2H), 2.37-2.45 & 2.46-2.50 (2m, 2H), 2.56-2.64 & 2.66-2.71 (2m, 2H), 3.25 & 3.39 (2bs, 2H), 3.64 & 3.78 (2s, 3H), 4.05 & 4.18 (2t, J = 6.4 Hz, 2H), 4.51 (d, J = 5.2 Hz, 2H), 4.93-5.04 (m, 2H), 5.27 (dd, J = 10.4 & 1.2 Hz, 1H), 5.40 (dd, J = 17.2 & 1.2 Hz, 1H), 5.67-5.82 (m, 1H), 5.97-6.11 (m, 1H), 6.55 & 7.66 (2s, 1H)$^{\Delta}$, 6.77-6.99 (m, 3H), 7.15-7.19 & 7.20-7.29 (2m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.46, 24.91, 28.46, 29.59, 33.28, 51.98, 68.58, 68.81, 115.02, 115.51, 115.74, 117.54, 117.68, 122.18, 129.32, 130.22, 133.22, 137.05, 137.13, 139.04, 158.47, 168.76, 184.20, 203.89; LCMS (m/z) : 397 $(M+H)^{+}$.

The underlined chemical shift values with low intensity are attributed to the presence of minor (*Z*)-isomer (≈4%).

$^{\Delta}$*E:Z* (96:4) Ratio is determined by the integration of isomeric olefinic protons at δ 7.66 & 6.55.

General procedure: Synthesis of (4*E*,15*E*)-10,10-dimethyl-2,7-dioxa-15-methoxycarbonyl-tricyclo[15.4.0.0^{8,13}]henicosane-1(17),4,8(13),15,18,20-hexaen-12-one (6a): To a stirred solution of 3-allyloxy-2-[(2*E*)-3-(2-allyloxyphenyl)-2-methoxycarbonylprop-2-en-1-yl]-5,5-dimethylcyclohex-2-enone (**5a**, 0.205g, 0.5 mmol) in dichloromethane (50 mL) at reflux temperature was added 1M Ti(O-^{i}Pr)$_4$ (0.1 mL, 20 mol%) in dichloromethane. After stirring for 1 h Grubbs' 1st generation catalyst (12.3 mg, 3 mol%) in dichloromethane (10 mL) was added drop wise and stirring continued for another 4 h at reflux temperature. Reaction mixture was allowed to cool to room temperature and quenched with saturated $NaHCO_3$ solution. Organic layer was separated and the aqueous layer was washed with dichloromethane (3 x 25 mL). Combined Organic layer was dried over anhydrous Na_2SO_4. Solvent was evaporated and the crude product was purified by silica gel column chromatography (40% ethyl acetate / hexanes) followed by re-crystallization (35% ethyl acetate in hexanes) to provide the title compound (**6a**) as a colorless solid in 70% (0.133 g) yield.



Mp: 146-148 ^{0}C; IR (KBr) : υ 1714, 1645, 1606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 0.96 (s, 6H), 2.19 (s, 2H), 2.24 (s, 2H), 3.64 (s, 2H), 3.72 (s, 3H), 4.18 (s, 2H), 4.32-4.92 (b, 2H), 5.50-5.64 (m, 1H), 5.98-6.12 (m, 1H), 7.04-7.15 (m, 2H), 7.24-7.32 (m, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.45, 28.44, 32.01, 39.38, 50.38, 51.82, 66.28, 75.24, 117.30, 122.36, 123.71, 128.59, 130.00, 130.28, 131.26, 131.83, 132.94, 134.78, 156.57, 169.22, 169.48, 197.09; LCMS (m/z) : 383 $(M+H)^+$; Analysis calc'd. for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85; Found: C, 72.36; H, 6.79.

To understand more about broad peak at δ 4.32-4.92, we recorded ^{1}H NMR spectra at -40^{0}C

^{1}H NMR at -40 ^{0}C (400 MHz, $CDCl_3$**)** : δ 0.95 (s, 3H), 1.06 (s, 3H), 2.18-2.46 (m, 4H), 3.53 & 3.72 (ABq, J = 14.8 Hz, 2H)*, 3.74 (s, 3H), 4.09-4.17 (m, 1H), 4.23-4.34 (m, 2H), 4.98 (dd, J =

11.6 & 4.4 Hz, 1H), 5.50-5.63 (m, 1H), 5.98-6.14 (m, 1H), 7.08-7.20 (m, 2H), 7.32-7.43 (m, 2H), 7.84 (s, 1H).

* One peak of the AB quartet merges with singlet at δ 3.74.

The following differences were observed between ^{1}H NMR spectra at room temperature and at -40 ^{0}C.

1. Singlet at δ 0.96 (6H) at room temperature appeared as two singlets, one at δ 0.95 (3H) and the second one at δ 1.06 (3H) at -40 ^{0}C.

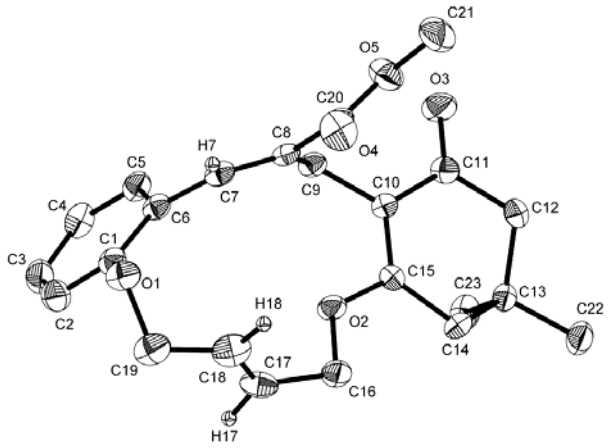
2. Singlets at δ 2.19 (2H) & 2.24 (2H) at room temperature appeared as a multiplet at δ 2.18-2.46 (4H) at -40 ^{0}C.

3. Singlet at δ 3.64 (2H) at room temperature appeared as a AB quartet at δ 3.53 & 3.72 (2H) at -40 ^{0}C.

4. Singlet at δ 4.18 (2H) and broad peak at δ 4.32-4.92 (2H) at room temperature appeared as (two) multiplets at δ 4.09-4.17 (1H) & 4.23-4.34 (2H) and a doublet of doublet (dd) at δ 4.98 (1H) at -40 ^{0}C.

These differences may be attributed to the conformational changes at low temperature (rigid conformation) and room temperature (flexible conformation).

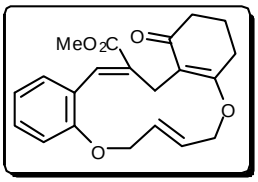
Crystal data for 6a: Empirical formula, $C_{23}H_{26}O_5$; Formula weight, 382.44; crystal color, colorless; habit, block; crystal dimensions, 0.20 x 0.18 x 0.10 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 12.6354(9) Å, b = 10.1017(7) Å, c = 15.6517(11) Å, α = 90.00, β = 95.2200(10), γ = 90.00; V = 1989.5(2) Å^3; space group, p2(1)/c; Z = 4; D_{cald} = 1.277 g / cm^3; F_{000} = 816; λ (Mo-Kα) = 0.71073 Å; $R(I \geq 2\sigma_1)$ = 0.0975, wR^2 = 0.1945. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **6a** CCDC # 914817).



ORTEP diagram of compound **6a**

We have obtained single crystals of the compounds 6a, 6c-E, 6c-Z, 6k, 6m, 6n, 6o, 7a-E, 7a-Z, and 7g from 35-40% ethyl acetates in hexanes).

(4*E*,15*E*)-2,7-Dioxa-15-methoxycarbonyltricyclo[15.4.0.0^{8,13}]henicosane-1(17),4,8(13),15,18-20-hexaen-12-one (6b):



Yield: 63%; reaction time: (1h + 4h); colorless solid; mp: 156-158 ^{0}C; IR (KBr) : υ 1714, 1645, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.80 (b, 2H), 2.25-2.45 (m, 4H), 3.63 (s, 2H), 3.73 (s, 3H), 4.21 (d, J = 5.6 Hz, 2H), 4.35-4.88 (m, 2H), 5.52-5.65 (m, 1H), 5.96-6.08 (m, 1H), 7.01-7.14 (m, 2H), 7.28-7.38 (m, 2H), 7.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.63, 25.34, 36.49, 51.74, 66.28, 75.01, 118.52, 122.14, 123.50, 128.73, 129.95, 130.41, 131.23, 131.97, 132.98, 134.75, 156.46, 169.23, 171.17, 197.49; LCMS (m/z) : 355 $(M+H)^+$; Analysis calc'd. for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26; Found: C, 71.25; H, 6.21.

To understand more about broad peak at δ 4.35-4.88, we recorded ^{1}H NMR spectra at -40 ^{0}C.

^{1}H NMR at -40 ^{0}C (400 MHz, $CDCl_3$**)** : δ 1.80-2.02 (m, 2H), 2.28-2.65 (m, 4H), 3.51 & 3.73 (ABq, J = 15.2 Hz, 2H)*, 3.74 (s, 3H), 4.15-4.40 (m, 3H), 4.95-5.07 (m, 1H), 5.52-5.67 (m, 1H), 5.98-6.14 (m, 1H), 7.08-7.23 (m, 2H), 7.28-7.44 (m, 2H), 7.83 (s, 1H).

* One peak of the AB quartet merges with singlet at δ 3.74.

The following differences were observed between ^{1}H NMR spectra at room temperature and at -40 ^{0}C.

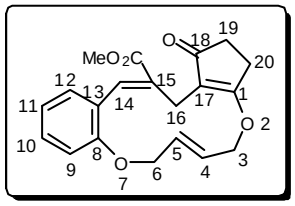
1. Singlet at δ 3.63 (2H) at room temperature appeared as a AB quartet at δ 3.51 & 3.73 (2H) at -40 ^{0}C.

2. Doublet at δ 4.21 (2H) and multiplet at δ 4.35-4.88 (2H) at room temperature appeared as (two) multiplets at δ 4.15-4.40 (3H) & 4.95-5.07 (1H) at -40 ^{0}C.

These differences may be attributed to the conformational changes at low temperature (rigid-conformation) and room temperature (flexible conformation).

(E) and (Z)-Isomers of the compounds ***6c***, ***6j***, ***7a-e*** *were separated by silica gel column chromatography [solvent system: 50% ethyl acetate in hexanes (for compounds* ***6c***, ***6j***, ***7c***, ***7e****) and 40% ethyl acetate in hexanes ((for compounds* ***7a***,***7b***, ***7d****). In all these cases (E)-isomers eluted first (less polar) while (Z)-isomers eluted later (more polar).* ***[(E) and (Z)-stereochemistry refers to the newly formed double bond after RCM reaction] .***

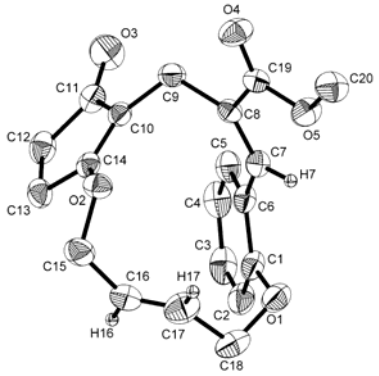
(4*E*,14*E*)-2,7-Dioxa-15-methoxycarbonyltricyclo[15.3.0.0^{8,13}]icosane-1(17),4,8(13),9,11,14-hexaen-18-one (6c-*E*):



Yield: 53%; reaction time: (1h + 4h); colorless solid; mp: 142-144 ^{0}C; IR (KBr) : υ 1699, 1633, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.21 (bs, 4H), 3.56 (s, 2H), 3.85 (s, 3H), 4.39 (d, J =

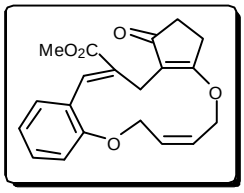
6.4 Hz, 2H), 4.59 (b, 2H), 5.60-5.72 (m, 1H), 5.97-6.10 (m, 1H), 6.96-7.06 (m, 2H), 7.20-7.33 (m, 2H), 7.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 19.58, 24.71, 33.61, 52.34, 66.52, 74.43, 120.32, 121.33, 123.42, 129.23, 129.47, 129.95, 130.13, 130.32, 134.20, 135.38, 156.06, 169.20, 183.35, 204.30; LCMS (m/z) : 341 $(M+H)^+$; Analysis calc'd. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92; Found: C, 70.45; H, 5.87.

Crystal data for 6c-*E*: Empirical formula, $C_{20}H_{20}O_5$; Formula weight, 340.36; crystal color, colorless; habit, block; crystal dimensions, 0.28 x 0.20 x 0.14 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 9.5864(7) Å, b = 12.2835(9) Å, c = 14.5863(10) Å, α = 90.00, β = 97.9790(10), γ = 90.00; V = 1701.0(2) Å^3; space group, p2(1)/n; Z = 4; D_{cald} = 1.329 g / cm^3; F_{000} = 720; λ (Mo-Kα) = 0.71073 Å; R(I≥2σ$_1$) = 0.0567, wR^2 = 0.1340. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **6c-*E*** CCDC # 914818).



ORTEP diagram of compound **6c-*E***

(4*Z*,14*E*)-2,7-Dioxa-15-methoxycarbonyltricyclo[15.3.0.0^{8,13}]icosane-1(17),4,8(13),9,11,14-hexaen-18-one (6c-*Z*):



Yield: 35%; reaction time: (1h + 4h); colorless solid; mp: 144-146 ^{0}C; IR (KBr) : υ 1695, 1631, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.32-2.37 (m, 2H), 2.39-2.45 (m, 2H), 3.37 (d, J = 0.8 Hz, 2H), 3.76 (s, 3H), 4.61 (dd, J = 5.6 & 0.8 Hz, 2H), 4.82 (dd, J = 5.6 & 0.8 Hz, 2H),

5.64-5.75 (m, 1H), 5.91-6.00 (m, 1H), 6.91 (dd, *J* = 8.4 & 0.8 Hz, 1H), 6.99-7.05 (m, 1H), 7.11 (dd, *J* = 7.6 & 0.8 Hz, 1H), 7.21-7.25 (m, 1H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.18, 25.45, 33.20, 51.97, 65.70, 66.41, 117.34, 117.66, 122.37, 126.59, 127.72, 129.25, 130.46, 131.48, 131.76, 137.29, 155.17, 167.97, 183.34, 203.81; LCMS (m/z) : 341 $(M+H)^+$; Analysis calc'd. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92; Found: C, 70.45; H, 5.98.

Following differences were observed between ^{1}H and ^{13}C NMR spectra of (E)- & (Z)- isomers ***(this stereochemistry refers to the newly formed double bond after RCM reaction) .***

In ^{1}H NMR spectra:

1. Broad singlet at δ 2.21 (4H) of (E)-isomer appeared as two multiplets at δ 2.32-2.37 (2H) & 2.39-2.45 (2H) in (Z) -isomer.

2. Doublet at δ 4.39 (2H) and broad singlet at δ 4.59 (2H) of (E)-isomer appeared as doublet of doublets (dd) at δ 4.61 (2H) & 4.82 (2H) in (Z)-isomer.

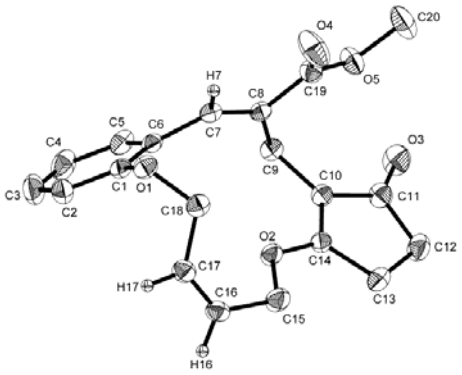
3. Multiplets at δ 6.96-7.06 (2H) & 7.20-7.33 (2H) of (E)-isomer appeared as (two) doublet of doublets (dd) at δ 6.91(1H) & 7.11 (1H) and (two) multiplets at δ 6.99-7.05 (1H), 7.21-7.25 (1H) in (Z)-isomer.

In ^{13}C NMR spectra:

4. Allyloxy carbons (C_3 & C_6) of (E)-isomer appeared at δ 66.52 & 74.43 while the same carbons in (Z)-isomer appeared at δ 65.70 & 66.41.

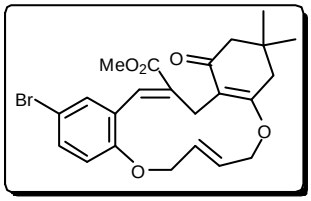
Crystal data for 6c-*Z*: Empirical formula, $C_{20}H_{20}O_5$; Formula weight, 340.36; crystal color, colorless; habit, plate; crystal dimensions, 0.20 x 0.18 x 0.10 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 20.440(6) Å, b = 10.579(3) Å, c = 7.873(2) Å, α = 90.00, β = 92.119(5), γ = 90.00; V = 1701.1(8) Å^3; space group, p2(1)/c; Z = 4; D_{cald} = 1.329 g / cm^3; F_{000} = 720; λ (Mo-Kα) = 0.71073 Å; R($I \geq 2\sigma_1$) = 0.0503, wR^2 = 0.1175. Detailed X-ray

crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **6c-*Z*** CCDC # 914819).



ORTEP diagram of compound **6c-*Z***

(4*E*,15*E*)-19-Bromo-10,10-dimethyl-2,7-dioxa-15- methoxycarbonyltricyclo-[15.4.0.0^{8,13}] henicosane-1(17),4,8(13),15,18,20-hexaen-12-one (6d):



Yield: 61%; reaction time: (1h + 4h); colorless solid; mp: 136-138 ^{0}C; IR (KBr) : υ 1714, 1657, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 0.98 (s, 6H), 2.22 (s, 2H), 2.25 (s, 2H), 3.62 (b, 2H), 3.72 (s, 3H), 4.18 (b, 2H), 4.29-4.92 (m, 2H), 5.52-5.63 (m, 1H), 5.96-6.08 (m, 1H), 6.96 (d, J = 8.4 Hz, 1H), 7.39 (dd, J = 8.4 & 2.0 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.44, 28.40, 31.99, 39.30, 50.28, 51.90, 66.11, 75.42, 116.55, 116.79, 124.13, 128.97, 132.64, 132.74, 133.10, 133.18, 155.58, 168.84, 169.52, 196.78; LCMS (m/z) : 461 $(M+H)^+$, 463 $[(M+H)^+ +2]$; Analysis calc'd. for $C_{23}H_{25}BrO_5$: C, 59.88; H, 5.46; Found: C, 59.95; H, 5.40.

In addition, two singlets, one at δ 0.99 and the other one at δ 3.71 with low intensity also appeared. These may be attributed to the presence of minor (*Z*)-isomer (≈2%) at C4-C5 double bond.

To understand more about broad peak at δ 4.29-4.92, we recorded ^{1}H NMR spectra at -40 ^{0}C.

^{1}H NMR at -40 ^{0}C (400 MHz, $CDCl_3$**)** : δ 0.98 (s, 3H), 1.07 (s, 3H), 2.20-2.48 (m, 4H), 3.48 & 3.72 (ABq, J = 15.2 Hz, 2H)*, 3.74 (s, 3H), 4.09-4.34 (m, 3H), 4.98 (dd, J = 11.6 & 4.0 Hz, 1H), 5.50-5.64 (m, 1H), 5.97-6.10 (m, 1H), 7.03 (d, J = 9.2 Hz, 1H), 7.40-7.52 (m, 2H), 7.73 (s, 1H).

* One peak of the AB quartet merges with singlet at δ 3.74.

The following differences were observed between ^{1}H NMR spectra at room temperature and at -40 ^{0}C.

1. Singlet at δ 0.98 (6H) at room temperature appeared as two singlets, one at δ 0.98 (3H) and the second one at δ 1.07 (3H) at -40 ^{0}C.

2. Singlets at δ 2.22 (2H) & 2.25 (2H) at room temperature appeared as a multiplet at δ 2.20-2.48 (4H) at -40 ^{0}C.

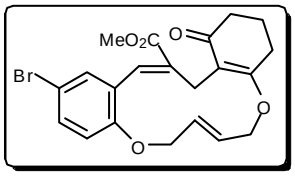
3. Broad singlet at δ 3.62 (2H) at room temperature appeared as a AB quartet at δ 3.48 & 3.72 (2H) at -40 ^{0}C.

4. Broad singlet at δ 4.18 (2H) and multiplet at δ 4.29-4.92 (2H) at room temperature appeared as a multiplet at δ 4.09-4.34 (3H) and a doublet of doublet at δ 4.98 (1H) at -40 ^{0}C.

5. Doublet of doublet at δ 7.39 (1H) and doublet at δ 7.45 (1H) at room temperature appeared as a multiplet at δ 7.40-7.52 (2H) at -40 ^{0}C.

These differences may be attributed to the conformational changes at low temperature (rigid conformation) and room temperature (flexible conformation).

(4*E*,15*E*)-19-Bromo-2,7-dioxa-15-methoxycarbonyltricyclo[15.4.0.0^{8,13}]henicosane-1(17),4-8(13),15,18,20-hexaen-12-one (6e):



Yield: 58%; reaction time: (1h + 4h); colorless solid; mp: 168-170 ^{0}C; IR (KBr) : υ 1707, 1643, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.83 (b, 2H), 2.28-2.50 (m, 4H), 3.62 (b, 2H), 3.73 (s, 3H), 4.22 (b, 2H), 4.33-5.06 (m, 2H), 5.54-5.65 (m, 1H), 5.94-6.09 (m, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.36-7.45 (m, 2H), 7.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.59, 20.64, 25.26, 36.39, 51.84, 66.06, 75.17, 116.29, 117.95, 123.89, 129.14, 132.69, 132.85, 133.06, 133.13, 133.19, 155.43, 168.85, 171.16, 197.18; LCMS (m/z) : 433 $(M+H)^+$, 435 $[(M+H)^+ +2]$; Analysis calc'd. for $C_{21}H_{21}BrO_5$: C, 58.21; H, 4.89; Found: C, 58.31; H, 4.82.

In addition, peaks at δ 3.51 (s), 5.66-5.75 (m), 6.80 (d), 7.19-7.21 (m), and 7.31 (d) with low intensity [probably due to presence of the minor (*Z*)-isomer (≈3%) (C4-C5 double bond)] also appeared.

To understand more about broad peak at δ 4.33-5.06, we recorded ^{1}H NMR spectrum at -40 ^{0}C.

^{1}H NMR at -40 ^{0}C (400 MHz, $CDCl_3$**)** : δ 1.82-2.00 (m, 2H), 2.30-2.64 (m, 4H), 3.48 & 3.73 (ABq, J = 15.2 Hz, 2H)*, 3.75 (s, 3H), 4.18-4.36 (m, 3H), 4.98 (dd, J = 11.6 & 3.6 Hz, 1H), 5.53-5.65 (m, 1H), 5.96-6.09 (m, 1H), 7.03 (d, J = 8.4 Hz, 1H), 7.35-7.47 (m, 2H), 7.71 (s, 1H).

* One peak of the AB quartet merges with singlet at δ 3.75.

In addition, peaks at δ 5.70-5.80 (m), 6.85 (d), 7.18-7.21 (m), 7.36 (d) and 7.72 (s) with low intensity also appeared. These may arise due to the presence of the minor (*Z*)-isomer (≈3%) (C4-C5 double bond).

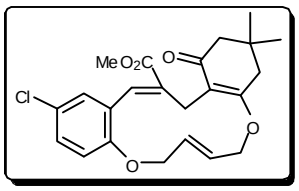
The following differences were observed between ^1H NMR spectra at room temperature and at -40 ^0C.

1. Broad singlet at δ 3.62 (2H) at room temperature appeared as a AB quartet at δ 3.48 & 3.73 (2H) at -40 ^0C.

2. Broad singlet at δ 4.22 (2H) and multiplet at δ 4.33-5.06 (2H) at room temperature appeared as a multiplet at δ 4.18-4.36 (3H) and a doublet of doublet at δ 4.98 (1H) at -40 ^0C.

These differences may be attributed to the conformational changes at low temperature (rigid-conformation) and room temperature (flexible conformation).

(4*E*,15*E*)-19-Chloro-10,10-dimethyl-2,7-dioxa-15-methoxycarbonyltricyclo[15.4.0.0^{8,13}]-henicosane-1(17),4,8(13),15,18,20-hexaen-12-one (6f):



Yield: 68%; reaction time: (1h + 4h); colorless solid; mp: 114-116 ^0C; IR (KBr) : υ 1705, 1649, 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : *δ* 0.98 (s, 6H), 2.22 (s, 2H), 2.25 (s, 2H), 3.62 (b, 2H), 3.72 (s, 3H), 4.18 (b, 2H), 4.30-4.86 (m, 2H), 5.50-5.63 (m, 1H), 5.94-6.08 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 7.21-7.29 (m, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : *δ* 20.47, 28.41, 32.02, 39.31, 50.28, 51.93, 66.13, 75.50, 116.79, 123.74, 128.95, 129.80, 129.90, 132.71, 133.07, 133.27, 155.06, 168.89, 169.55, 196.85; LCMS (m/z) : 417 $(M+H)^+$, 419 $[(M+H)^+ +2]$; Analysis calc'd. for $C_{23}H_{25}ClO_5$: C, 66.26; H, 6.04; Found: C, 66.38; H, 6.10.

In addition, singlets at δ 1.02, 3.50, 3.70, multiplets at δ 5.61-5.72, 5.92-5.98, 7.08-7.11, 7.18-7.21 and a doublet at δ 6.87 with low intensity also appeared. These may be due to presence of the minor (*Z*)-isomer (≈2%) (C4-C5 double bond).

To understand more about broad peak at δ 4.30-4.86, we recorded ^{1}H NMR spectra at -40 ^{0}C.

^{1}H NMR at -40 ^{0}C (400 MHz, $CDCl_3$**)** : δ 0.98 (s, 3H), 1.07 (s, 3H), 2.18-2.48 (m, 4H), 3.49 & 3.72 (ABq, J = 15.2 Hz, 2H)*, 3.74 (s, 3H), 4.10-4.34 (m, 3H), 4.98 (dd, J = 11.6 & 4.4 Hz, 1H), 5.51-5.65 (m, 1H), 5.98-6.11 (m, 1H), 7.09 (d, J = 9.2 Hz, 1H), 7.26-7.38 (m, 2H), 7.73 (s, 1H).

* One peak of AB quartet merges with singlet at δ 3.74.

In addition, singlets at δ 1.04, 7.74, multiplets at δ 5.70-5.80, 7.20-7.25 and a doublet at δ 6.92 with low intensity also appeared (probably due to the presence of the minor (*Z*)-isomer (≈2%) at C4-C5 double bond).

The following differences were observed between ^{1}H NMR spectra at room temperature and at -40 ^{0}C.

1. Singlet at δ 0.98 (6H) at room temperature appeared as (two) singlets at δ 0.98 (3H) & 1.07 (3H) at -40 ^{0}C.

2. Singlets at δ 2.22 (2H) & 2.25 (2H) at room temperature appeared as a multiplet at δ 2.18-2.48 (4H) at -40 ^{0}C.

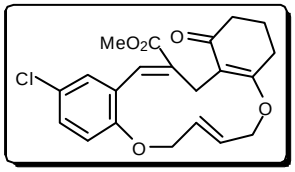
3. Broad singlet at δ 3.62 (2H) at room temperature appeared as a AB quartet at δ 3.49 & 3.72 (2H) at -40 ^{0}C.

4. Broad singlet at δ 4.18 (2H) and multiplet at δ 4.30-4.86 (2H) at room temperature appeared as a multiplet δ 4.10-4.34 (3H) and a doublet of doublet at δ 4.98(1H) at -40 ^{0}C.

5. Multiplet at δ 7.21-7.29 (1H) and doublet at δ 7.31 (1H) at room temperature appeared as a multiplet at δ 7.26-7.38 (2H) at -40 ^{0}C.

These differences may be attributed to the conformational changes at low temperature (rigid conformation) and room temperature (flexible conformation).

(4*E*,15*E*)-19-Chloro-2,7-dioxa-15-methoxycarbonyltricyclo[15.4.0.0^{8,13}]henicosane-1(17),4,-8(13),15,18,20-hexaen-12-one (6g):



Yield: 61%; reaction time: (1h + 4h); colorless solid; mp: 158-160 ^{0}C; IR (KBr) : υ 1707, 1645, 1608 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.83 (b, 2H), 2.30-2.52 (m, 4H), 3.62 (b, 2H), 3.73 (s, 3H), 4.22 (b, 2H), 4.32-4.90 (m, 2H), 5.52-5.65 (m, 1H), 5.95-6.08 (m, 1H), 7.02 (d, J = 8.4 Hz, 1H), 7.21-7.32 (m, 2H), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.63, 20.67, 25.29, 36.39, 51.86, 66.10, 75.26, 118.00, 123.50, 128.67, 129.11, 129.73, 130.02, 132.68, 132.76, 133.21, 154.94, 168.90, 171.18, 197.22; LCMS (m/z) : 389 $(M+H)^+$, 391 $[(M+H)^+ +2]$; Analysis calc'd. for $C_{21}H_{21}ClO_5$: C, 64.87; H, 5.44; Found: C, 64.75; H, 5.49.

In addition, doublets at δ 6.88 & 7.08 and a multiplet at δ 7.15-7.20 with low intensity also appeared. These may be attributed to the minor (*Z*)-isomer (≈2%) (C4-C5 double bond).

To understand more about broad peak at δ 4.32-4.90, we recorded ^{1}H NMR spectra at -40 ^{0}C.

^{1}H NMR at -40 ^{0}C (400 MHz, $CDCl_3$**)** : δ 1.82-1.98 (m, 2H), 2.30-2.65 (m, 4H), 3.48 & 3.73 (ABq, J = 14.8 Hz, 2H)*, 3.75 (s, 3H), 4.17-4.35 (m, 3H), 4.98 (dd, J = 11.6 & 4.4 Hz, 1H), 5.56-5.65 (m, 1H), 5.96-6.09 (m, 1H), 7.08 (d, J = 8.4 Hz, 1H), 7.23-7.35 (m, 2H), 7.72 (s, 1H).

* One peak of the AB quartet merges with singlet at δ 3.75.

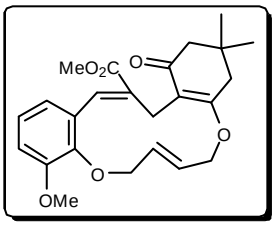
The following differences were observed between ^{1}H NMR spectra at room temperature and at -40 ^{0}C.

1. Broad singlet at δ 3.62 (2H) at room temperature appeared as a AB quartet at δ 3.48 & 3.73 (2H) at -40 ^{0}C.

2. Broad singlet at δ 4.22 (2H) and multiplet at δ 4.32-4.90 (2H) at room temperature appeared as a multiplet at δ 4.17-4.35 (3H) and a doublet of doublet at δ 4.98 (1H) at -40 ^{0}C.

These differences may be attributed to the conformational changes at low temperature (rigid-conformation) and room temperature (flexible conformation).

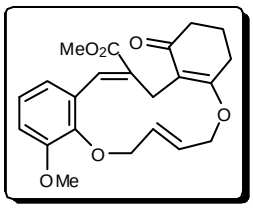
(4*E*,15*E*)-10,10-Dimethyl-2,7-dioxa-21-methoxy-15-methoxycarbonyltricyclo[15.4.0.0^{8,13}]-henicosane-1(17),4,8(13),15,18,20-hexaen-12-one (6h):



Yield: 56%; reaction time: (1h + 4h); colorless solid; mp: 134-136 ^{0}C; IR (KBr) : υ 1703, 1645, 1626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : *δ* 0.91 (s, 3H), 1.04 (s, 3H), 2.12-2.38 (m, 4H), 3.57 & 3.70 (ABq, *J* = 15.6 Hz, 2H)*, 3.72 (s, 3H), 3.87 (s, 3H), 4.03-4.13 (m, 1H), 4.24-4.31 (m, 1H), 4.33-4.42 (m, 1H), 4.77 (dd, *J* = 12.0 & 4.8 Hz, 1H), 5.47-5.58 (m, 1H), 6.05-6.18 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.01-7.09 (m, 1H), 7.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : *δ* 20.63, 28.36, 28.50, 32.00, 39.33, 50.37, 51.82, 55.85, 66.28, 72.60, 112.39, 117.29, 122.16, 124.02, 128.50, 132.01, 132.45, 133.89, 134.80, 144.33, 153.08, 169.29, 169.54, 197.12; LCMS (m/z) : 413 (M+H)$^+$; Analysis calc'd. for $C_{24}H_{28}O_6$: C, 69.88; H, 6.84; Found: C, 69.76; H, 6.90.

* One peak of the AB quartet merges with singlet at *δ* 3.72.

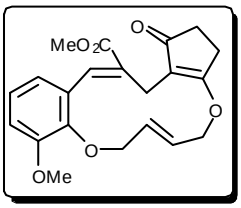
(4*E*,15*E*)-2,7-Dioxa-21-methoxy-15-methoxycarbonyltricyclo[15.4.0.0^{8,13}]henicosane-1(17)-4,8(13),15,18,20-hexaen-12-one (6i):



Yield: 59%; reaction time: (1h + 4h); colorless solid; mp: 150-152 ^{0}C; IR (KBr) : υ 1712, 1645, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.73-1.96 (m, 2H), 2.21-2.54 (m, 4H), 3.55 & 3.71 (ABq, J = 15.6 Hz, 2H)*, 3.72 (s, 3H), 3.88 (s, 3H), 4.09-4.17 (m, 1H), 4.24-4.32 (m, 1H), 4.36-4.44 (m, 1H), 4.77 (dd, J = 12.0 & 4.8 Hz, 1H), 5.48-5.61 (m, 1H), 6.05-6.18 (m, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.98-7.09 (m, 1H), 7.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.67, 20.80, 25.31, 36.46, 51.67, 55.82, 66.21, 72.48, 112.33, 118.40, 122.23, 123.80, 128.57, 132.12, 132.43, 133.96, 134.72, 144.20, 153.01, 169.26, 171.18, 197.44; LCMS (m/z) : 385 $(M+H)^{+}$; Analysis calc'd. for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29; Found: C, 68.83; H, 6.22.

* One peak of the AB quartet merges with singlet at δ 3.72.

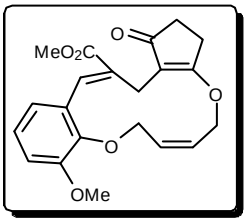
(4*E*,14*E*)-2,7-Dioxa-9-methoxy-15-methoxycarbonyltricyclo[15.3.0.0^{8,13}]icosane-1(17),4-8(13),9,11,14-hexaen-18-one (6j-*E*):



Yield: 48%; reaction time: (1h + 4h); colorless solid; mp: 110-112 ^{0}C; IR (KBr) : υ 1707, 1685, 1631 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.07-2.25 (m, 2H), 2.32-2.44 (m, 2H), 3.51 & 3.61 (ABq J = 17.6 Hz, 2H), 3.84 & 3.85 (2s, 6H), 4.31-4.50 (m, 3H), 4.77 (dd, J = 12.0 & 4.0 Hz, 1H), 5.56-5.66 (m, 1H), 6.06-6.18 (m, 1H), 6.83 (dd, J = 8.0 & 1.6 Hz, 1H), 6.92 (dd, J = 8.0 &

1.6 Hz, 1H), 6.95-7.02 (m, 1H), 7.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 19.75, 24.68, 33.60, 52.32, 55.79, 66.21, 72.33, 112.55, 120.37, 121.60, 123.80, 129.10, 129.32, 131.61, 135.28, 135.49, 144.05, 152.66, 169.25, 183.27, 204.33; LCMS (m/z) : 371 $(M+H)^+$; Analysis calc'd. for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99; Found: C, 68.21; H, 6.05.

(4*Z*,14*E*)-2,7-Dioxa-9-methoxy-15-methoxycarbonyltricyclo[15.3.0.0^{8,13}]icosane-1(17),4-8(13),9,11,14-hexaen-18-one (6j-*Z*):



Yield: 30%; reaction time: (1h + 4h); colorless solid; mp: 150-152 ^{0}C; IR (KBr) : υ 1705, 1693, 1631 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.32-2.38 (m, 2H), 2.42-2.49 (m, 2H), 3.44 (s, 2H), 3.77 (s, 3H), 3.86 (s, 3H), 4.48 (bs, 2H), 4.81 (b, 2H), 5.63-5.72 (m, 1H), 6.08-6.18 (m, 1H), 6.78 (d, J = 7.6 Hz, 1H)*, 6.86 (dd, J = 8.4 & 1.2 Hz, 1H), 6.98-7.06 (m, 1H), 7.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 19.95, 24.55, 33.45, 51.98, 55.90, 64.42, 69.84, 112.04, 118.44, 122.28, 123.82, 125.11, 130.53, 130.65, 133.89, 136.19, 145.12, 153.00, 168.21, 183.48, 203.10; LCMS (m/z) : 371 $(M+H)^+$; Analysis calc'd. for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99; Found: C, 68.17; H, 5.94.

* Unresolved doublet of doublet (dd).

Following differences were observed between ^{1}H & ^{13}C NMR spectra of (E) & (Z) isomers ***(this stereochemistry refers to the newly formed double bond after RCM reaction)***.

In ^{1}H NMR spectra:

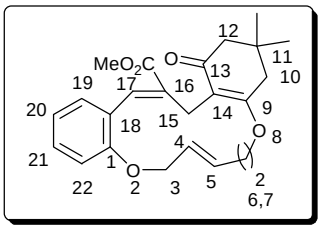
1. AB quartet at δ 3.51 & 3.61 (2H) of (E)-isomer appeared as a singlet at δ 3.44 (2H) in (Z)-isomer.

2. Multiplet at δ 4.31-4.50 (3H) and doublet of doublet at δ 4.77 (1H) of (E)-isomer appeared as a (two) broad singlets at δ 4.48 (2H) & 4.81(2H) in (Z)-isomer.

In ^{13}C NMR spectra:

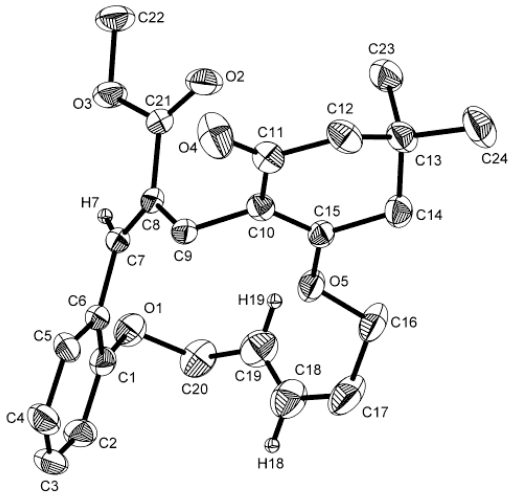
3. Allyloxy carbons (C_3 & C_6) of (E)-isomer appeared at δ 66.21 & 72.33 where as these carbons appeared at δ 64.42 & 69.84 in (Z)-isomer.

(4*E*,16*E*)-11,11-Dimethyl-2,8-dioxa-16-methoxycarbonyltricyclo[16.4.0.0^{9,14}]docosane-1(18)-4,9(14),16,19,21-hexaen-13-one (6k):



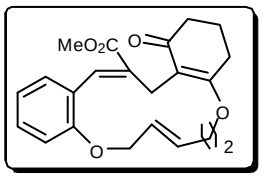
Yield: 70%; reaction time: (1h + 2h); colorless solid; mp: 120-122 ^{0}C; IR (KBr) : υ 1716, 1641, 1606 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) : *δ* 1.03 (s, 6H), 2.23 (s, 4H), 2.28 (s, 2H), 3.62 (s, 2H), 3.69 (s, 3H), 3.95 (t, *J* = 5.2 Hz, 2H), 4.64 (s, 2H), 5.57-5.70 (m, 2H), 6.96-7.04 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.22-7.30 (m, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : *δ* 21.14, 28.61, 31.75, 32.02, 39.77, 49.97, 51.69, 65.56, 73.06, 116.11, 119.42, 122.50, 126.68, 129.58, 129.65, 130.68, 131.10, 132.03, 133.99, 156.93, 168.98, 169.04, 197.19; LCMS (m/z): 397 $(M+H)^+$; Analysis calc'd for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12; Found: C, 72.59; H, 7.18.

Crystal data for 6k: Empirical formula, $C_{24}H_{28}O_5$; Formula weight, 396.48; crystal color, colorless; habit, block; crystal dimensions, 0.48 x 0.44 x 0.40 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a = 8.4362(9) Å, b = 10.6638(12) Å, c = 12.5335(14) Å, α = 76.146(2), β = 79.366(2), γ = 84.811(2); V = 1074.7(2) Å^3; space group, p-1; Z = 2; D_{cald} = 1.225 g / cm^3; F_{000} = 480; λ (Mo-Kα) = 0.71073 Å; R(I≥2σ$_1$) = 0.0850, wR^2 = 0.2211. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **6k** CCDC # 917199).



ORTEP diagram of compound **6k**

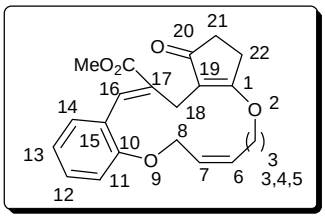
(4*E*,16*E*)-2,8-Dioxa-16-methoxycarbonyltricyclo[16.4.0.0^{9,14}]docosane-1(18),4,9(14),16,19-21-hexaen-13-one (6l):



Yield: 78%; reaction time: (1h + 2h); colorless solid; mp: 144-146 ^{0}C; IR (KBr) : υ 1712, 1637, 1606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.84-1.94 (m, 2H), 2.19-2.27 (m, 2H), 2.35 (t, J = 6.8 Hz, 2H), 2.43 (t, J = 6.0 Hz, 2H), 3.60 (s, 2H), 3.70 (s, 3H), 3.96 (t, J = 5.2 Hz, 2H), 4.59-4.72 (m, 2H), 5.57-5-71 (m, 2H), 6.96-7.04 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.22-7.29 (m,1H), 7.31 (d, J = 7.6 Hz, 1H), 7.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.76, 21.17, 25.77, 31.90, 36.16, 51.46, 65.55, 73.03, 117.25, 119.36, 122.36, 126.66, 129.50, 129.63, 130.60, 131.15, 132.12, 134.00, 156.75, 168.90, 170.71, 197.41; LCMS (m/z): 369 $(M+H)^{+}$; Analysis calc'd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57; Found: C, 71.85; H, 6.51.

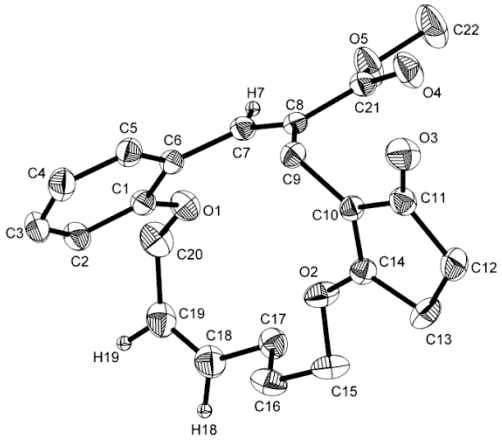
In addition, (three) doublets at δ 6.92, 7.12, 7.20 and a singlet at δ 7.65 with low intensity also appeared. These may be attributed to the minor (*Z*)-isomer (≈2%) (at C4-C5 double bond).

(6*Z*,16*E*)-2,9-Dioxa-17-methoxycarbonyltricyclo[17.3.0.0^{10,15}]docosane-1(19),6,10(15),11,13-16-hexaen-20-one (6m):



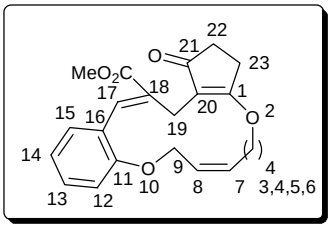
Yield: 82%; reaction time: (1h + 2h); colorless solid; mp: 124-126 ^{0}C; IR (KBr) : υ 1699, 1633 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.60-1.72 (m, 2H), 2.24-2.30 (m, 2H), 2.38-2.50 (m, 4H), 3.39 (s, 2H), 3.75 (s, 3H), 3.97 (t, *J* = 5.2 Hz, 2H), 4.56 (d, *J* = 4.0 Hz, 2H), 5.62-5.78 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.91-7.00 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.20-7.28 (m, 1H), 7.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : *δ* 20.51, 24.64, 24.78, 28.92, 33.14, 51.77, 65.88, 68.14, 112.39, 117.56, 120.85, 124.14, 125.74, 129.35, 130.15, 130.49, 134.42, 136.62, 156.20, 168.29, 183.87, 203.64; LCMS (m/z): 369 $(M+H)^+$; Analysis calc'd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57; Found: C, 71.58; H, 6.65.

Crystal data for 6m: Empirical formula, $C_{22}H_{24}O_5$; Formula weight, 368.41; crystal color, colorless; habit, block; crystal dimensions, 0.48 x 0.44 x 0.40 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a = 8.6741(9) Å, b = 9.1126(9) Å, c = 12.8419(11) Å, α = 96.627(7), β = 102.887(8), γ = 106.395(9); V = 931.84(15) Å^3; space group, p-1; Z = 2; D_{cald} = 1.313 g / cm^3; F_{000} = 392; λ (Mo-Kα) = 0.71073 Å; R(I≥2σ$_1$) = 0.0471, wR^2 = 0.1214. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **6m** CCDC # 915410).



ORTEP diagram of compound **6m**

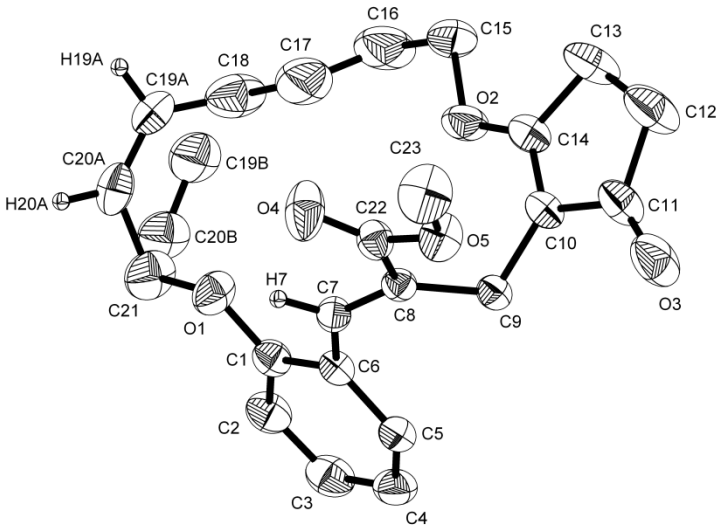
(7*Z*,17*E*)-2,10-Dioxa-18-methoxycarbonyltricyclo[18.3.0.0^{11,16}]tricosane-1(20),7,11(16),12-14,17-hexaen-21-one (6n):



Yield: 91%; reaction time: (1h + 2h); colorless solid; mp: 152-154 ^{0}C; IR (KBr) : υ 1714, 1689, 1626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.44-1.52 (m, 2H), 1.60-1.68 (m, 2H), 2.08-2.16 (m, 2H), 2.23-2.30 (m, 2H), 2.35-2.42 (m, 2H), 3.46 (s, 2H), 3.74 (s, 3H), 3.91 (t, J = 6.0 Hz, 2H), 4.44 (d, J = 6.4 Hz, 2H), 5.86-5.98 (m, 2H), 6.84 (d, J = 8.8 Hz, 1H), 6.85-6.96 (m, 1H), 7.20-7.30 (m, 2H), 7.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 20.23, 24.43, 24.86, 27.45, 28.85, 33.27, 51.80, 62.21, 68.44, 110.60, 117.77, 120.09, 124.04, 124.71, 129.12, 129.60, 130.46, 135.53, 138.03, 156.50, 168.74, 183.80, 203.64; LCMS (m/z): 383 $(M+H)^+$; Analysis calcd for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85; Found: C, 72.38; H, 6.79.

In addition, (three) singlets at δ 3.41, 3.76, 7.90, a doublet at δ 4.60 and a multiplet at δ 5.60-5.81 with low intensity also appeared. These may arise due to the presence of minor (*Z*)-isomer (≈2%) (C7-C8 double bond).

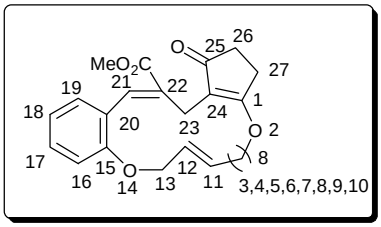
Crystal data for 6n: Empirical formula, $C_{23}H_{26}O_5$; Formula weight, 382.44; crystal color, colorless; habit, block; crystal dimensions, 0.36 x 0.28 x 0.24 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 12.4423(16) Å, b = 12.3999(16) Å, c = 13.5967(18) Å, α = 90.00, β = 97.190(2), γ = 90.00; V = 2081.2(5) $Å^3$; space group, p2(1)/n; Z = 4; D_{cald} = 1.221 g / cm^3; F_{000} = 816; λ (Mo-Kα) = 0.71073 Å; R($I \geq 2\sigma_1$) = 0.0662, wR^2 = 0.2083. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **6n** CCDC # 917200).



ORTEP diagram of compound **6n**

*Each of carbons, C19 and C20, exhibit disorder, they are modeled using two positions of 0.6 and 0.4 occupancy each***.**

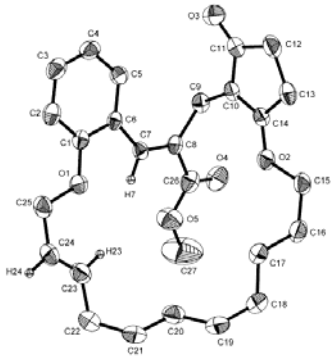
(11*E*,21*E*)-2,14-Dioxa-22-methoxycarbonyltricyclo[22.3.0.0^{15,20}]heptacosane-1(24),11-15(20),16,18,21-hexaen-25-one (6o):



Yield: 85%; reaction time: (1h + 2h); colorless solid; mp: 107-108 ^{0}C; IR (KBr) : υ 1711, 1680, 1624 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.09-1.35 (m, 8H), 1.34-1.42 (m, 2H), 1.50-1.62 (m, 2H), 2.09-2.15 (m, 2H), 2.35-2.43 (m, 2H), 2.54-2.62 (m, 2H), 3.39 (s, 2H), 3.78 (s, 3H), 4.02 (t,

J = 5.2 Hz, 2H), 4.56 (d, *J* = 5.6 Hz, 2H), 5.62-5.80 (m, 2H), 6.87-6.98 (m, 2H), 7.20-7.30 (m, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.59, 24.89, 25.55, 26.78, 27.79, 28.59, 29.38, 29.85, 31.44, 33.24, 51.88, 69.41, 69.67, 113.67, 117.90, 120.71, 125.30, 125.88, 129.47, 129.62, 130.17, 134.57, 135.71, 156.66, 168.85, 183.99, 204.02; LCMS (m/z): 439 $(M+H)^+$; Analysis calc'd for $C_{27}H_{34}O_5$: C, 73.94; H, 7.81; Found: C, 73.85; H, 7.78.

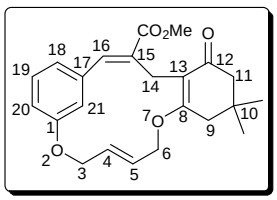
Crystal data for 6o: Empirical formula, $C_{27}H_{34}O_5$; Formula weight, 438.54; crystal color, colorless; habit, block; crystal dimensions, 0.48 x 0.40 x 0.20 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 12.518(2) Å, b = 8.3814(13) Å, c = 23.699(4) Å, α = 90.00, β = 103.330(3), γ = 90.00; V = 2419.5(7) $Å^3$; space group, p2(1)/c; Z = 4; D_{cald} = 1.204 g / cm^3; F_{000} = 944; λ (Mo-Kα) = 0.71073 Å; R(I≥2σ_1) = 0.0828, wR^2 = 0.2250. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **6o** CCDC # 915411).



ORTEP diagram of compound **6o**

In the compounds 7a-E-7e-E/7a-Z-7e-Z, stereochemistry refers to the newly formed double bond after RCM reaction.

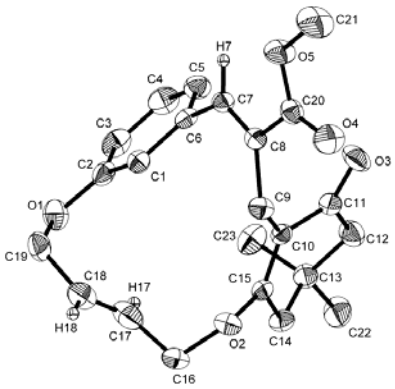
(4*E*,15*E*)-10,10-Dimethyl-2,7-dioxa-15-methoxycarbonyltricyclo[15.3.1.0^{8,13}]henicosane-1(21),4,8(13),15,17,19-hexaen-12-one (7a-*E*):



Yield: 56%; reaction time: (1h + 4h); colorless solid; mp: 170-172 ^{0}C; IR (KBr): υ 1705, 1651, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 6H), 2.08 (s, 2H), 2.27 (s, 2H), 3.43 (s, 2H), 3.79 (s, 3H), 4.43 (d, J = 7.2 Hz, 2H), 4.60-4.68 (m, 2H), 5.68-5.78 (m, 1H), 5.80-5.90 (m, 1H), 6.67 (s, 1H)*, 6.79 (d, J = 7.6 Hz, 1H), 6.88 (dd, J = 8.0 & 2.4 Hz, 1H), 7.19-7.25 (m, 1H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.79, 28.36, 32.03, 39.95, 50.63, 51.94, 66.97, 69.03, 117.05, 118.35, 118.99, 122.93, 129.15, 129.54, 132.31, 132.65, 137.07, 137.13, 157.06, 168.48, 169.25, 197.22; LCMS (m/z): 383 $(M+H)^+$; Analysis calc'd. for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85; Found : C, 72.15; H, 6.91.

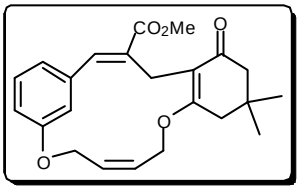
* Unresolved doublet.

Crystal data for 7a-*E*: Empirical formula, $C_{23}H_{26}O_5$; Formula weight, 382.44; crystal color, colorless; habit, block; crystal dimensions, 0.28 x 0.18 x 0.10 mm^3; crystal system, orthorhombic; lattice type, primitive; lattice parameters, a = 12.1101(10) Å, b = 12.3001(10) Å, c = 13.4920(11) Å, α = 90.00, β = 90.00, γ = 90.00; V = 2009.7(3) Å^3; space group, p2(1)p2(1)p2(1); Z = 4; D_{cald} = 1.264 g / cm^3; F_{000} = 816; λ (Mo-Kα) = 0.71073 Å; R(I≥2σ$_1$) = 0.0631, wR^2 = 0.1395. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **7a-*E*** CCDC # 915412).



ORTEP diagram of compound **7a-*E***

(4*Z*,15*E*)-10,10-Dimethyl-2,7-dioxa-15-methoxycarbonyltricyclo[15.3.1.$0^{8,13}$]henicosane-1(21),4,8(13),15,17,19-hexaen-12-one (7a-*Z*):



Yield: 27%; reaction time: (1h + 4h); colorless solid; mp: 162-164 ^{0}C; IR (KBr): υ 1709, 1649, 1622 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 6H), 2.18 (s, 2H), 2.33 (s, 2H), 3.53 (s, 2H), 3.76 (s, 3H), 4.59-4.68 (m, 2H), 4.82-4.92 (m, 2H), 5.82-5.94 (m, 2H), 6.79 (d, J = 7.6 Hz, 1H), 6.85 (dd, J = 8.0 & 1.6 Hz, 1H), 7.18-7.25 (m, 1H), 7.39 (s, 1H), 7.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.14, 28.43, 31.99, 39.89, 50.24, 51.99, 61.83, 65.14, 113.60, 117.55, 117.83, 122.70, 125.63, 129.38, 132.84, 134.07, 137.66, 158.00, 168.51, 169.12, 197.35; LCMS (m/z): 383 $(M+H)^+$; Analysis calc'd. for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85; Found : C, 72.36; H, 6.79.

Following differences were observed between ^{1}H & ^{13}C NMR spectra of (E)- &(Z)- isomers.

In ^{1}H NMR spectra:

1. Multiplets at δ 5.68-5.78 (1H) and 5.80-5.90 (1H) of (E)-isomer appeared as one multiplet at δ 5.82-5.94 (2H) in (Z)-isomer.

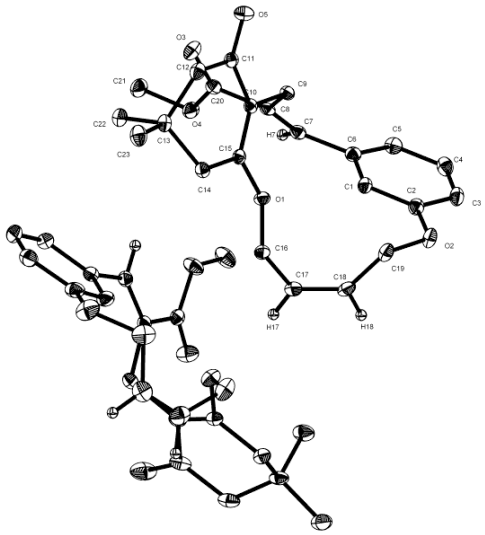
2. Singlet at δ 6.67 (1H) of (E)-isomer appeared as a singlet at δ 7.39 (1H) in (Z)-isomer.

In ^{13}C NMR spectra:

3. Allyloxy carbons (C_3 & C_6) of (E)-isomer appeared at δ 66.97 & 69.03 where as these carbons appeared at δ 61.83 & 65.14 in (Z)-isomer.

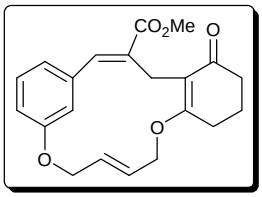
Crystal data for 7a-*Z*: Empirical formula, $C_{23}H_{26}O_5$; Formula weight, 382.44; crystal color, colorless; habit, block; crystal dimensions, 0.40 x 0.36 x 0.30 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 25.1535(18) Å, b = 8.7953(6) Å, c = 36.307(3) Å, α = 90.00, β = 96.4190(10), γ = 90.00; V = 7982.0(10) Å^3; space group, c2/c; Z = 16; D_{cald} = 1.273 g / cm^3; F_{000} = 3264; λ (Mo-Kα) = 0.71073 Å; R($I \geq 2\sigma_1$) = 0.0595, wR^2 = 0.1482. Detailed X-ray

crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **7a-*Z*** CCDC # 917201).



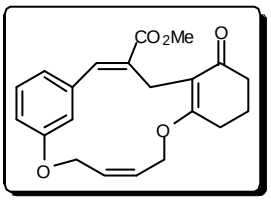
ORTEP diagram of compound **7a-*Z***

(4*E*,15*E*)-2,7-Dioxa-15-methoxycarbonyltricyclo[15.3.1.0^{8,13}]henicosane-1(21),4,8(13),15,17-19-hexaen-12-one (7b-*E*):



Yield: 58%; reaction time: (1h + 4h); colorless solid; mp: 126-128 ^{0}C; IR (KBr): υ 1707, 1647, 1608 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.82 (m, 2H), 2.19 (t, J = 6.4 Hz, 2H), 2.40 (t, J = 6.0 Hz, 2H), 3.43 (s, 2H), 3.80 (s, 3H), 4.45 (d, J = 7.2 Hz, 2H), 4.64 (d, J = 4.4 Hz, 2H), 5.68-5.79 (m, 1H), 5.80-5.89 (m, 1H), 6.62 (s, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.88 (dd, J = 8.0 & 2.0 Hz, 1H), 7.18-7.25 (m, 1H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.59, 22.17, 25.87, 36.80, 51.98, 66.88, 68.75, 116.89, 118.16, 120.52, 122.64, 129.15, 129.55, 132.28, 132.66, 137.07, 137.29, 156.94, 169.29, 170.34, 197.47; LCMS (m/z): 355 $(M+H)^{+}$; Analysis calc'd. for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26; Found : C, 71.08; H, 6.31.

(4*Z*,15*E*)-2,7-Dioxa-15-methoxycarbonyltricyclo[15.3.1.0^{8,13}]henicosane-1(21),4,8(13),15,17-19-hexaen-12-one (7b-*Z*):



Yield: 32%; reaction time: (1h + 4h); colorless solid; mp: 130-132 ^{0}C; IR (KBr): υ 1718, 1655, 1602 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82-1.92 (m, 2H), 2.28 (t, J = 6.4 Hz, 2H), 2.45 (t, J = 6.0 Hz, 2H), 3.53 (s, 2H), 3.78 (s, 3H), 4.58-4.68 (m, 2H), 4.82-4.92 (m, 2H), 5.82-5.94 (m, 2H), 6.78 (d, J = 7.6 Hz, 1H), 6.85 (dd, J = 8.0 & 2.0 Hz, 1H), 7.18-7.25 (m, 1H), 7.32 (s, 1H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.90, 21.34, 25.93, 36.45, 51.97, 62.03, 65.50, 113.83, 117.49, 118.60, 122.66, 125.49, 129.31, 132.99, 134.10, 137.46, 137.77, 157.99, 169.19, 170.35, 197.63; LCMS (m/z): 355 $(M+H)^{+}$; Analysis calc'd. for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26; Found : C, 71.36; H, 6.19.

Following differences were observed between ^{1}H & ^{13}C NMR spectra of (E)- & (Z)- isomers.

In ^{1}H NMR spectra:

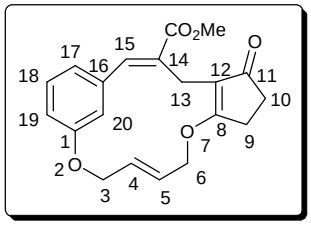
1. Multiplets at δ 5.68-5.79 (1H) and 5.80-5.89 (1H) of (E)-isomer appeared as one multiplet at δ 5.82-5.94 (2H) in (Z)-isomer.

2. Singlet at δ 6.62 (1H) of (E)-isomer appeared as a singlet at δ 7.32 (1H) in (Z)-isomer.

In ^{13}C NMR spectra

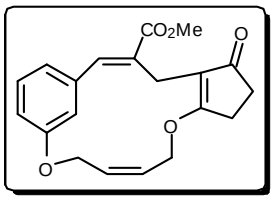
3. Allyloxy carbons (C_3 & C_6) of (E)-isomer appeared at δ 66.88 & 68.75 where as these carbons appeared at δ 62.03 & 65.50 in (Z)-isomer.

(4*E*,14*E*)-2,7-Dioxa-14-methoxycarbonyltricyclo[14.3.1.0^{8,12}]icosane-1(20),4,8(12),14,16,18-hexaen-11-one (7c-*E*):



Yield: 48%; reaction time: (1h + 4h); colorless solid; mp: 116-118 ^{0}C; IR (KBr): υ 1716, 1687, 1624 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36-2.42 (m, 2H), 2.52-2.60 (m, 2H), 3.29 (s, 2H), 3.84 (s, 3H), 4.56-4.67 (m, 4H), 5.74-5.94 (m, 2H), 6.57 (s, 1H), 6.85 (d, J = 7.2 Hz, 1H), 6.92 (dd, J = 8.0 & 2.4 Hz, 1H), 7.21-7.28 (m, 1H), 7.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.52, 25.25, 33.85, 52.07, 68.28, 69.51, 117.33, 118.95, 121.82, 123.05, 127.95, 129.30, 130.92, 132.15, 136.99, 138.45, 157.34, 168.96, 183.03, 204.10; LCMS (m/z): 341 $(M+H)^{+}$; Analysis calc'd. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92; Found : C, 70.68; H, 5.88.

(4*Z*,14*E*)-2,7-Dioxa-14-methoxycarbonyltricyclo[14.3.1.0^{8,12}]icosane-1(20),4,8(12),14,16,18-hexaen-11-one (7c-*Z*):



Yield: 31%; reaction time: (1h + 4h); colorless solid; mp: 146-148 ^{0}C; IR (KBr): υ 1716, 1685, 1630 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45-2.52 (m, 2H), 2.67-2.73 (m, 2H), 3.40 (s, 2H), 3.78 (s, 3H), 4.73 (d, J = 6.4 Hz, 2H), 4.96 (d, J = 4.8 Hz, 2H), 5.86-6.00 (m, 2H), 6.84-6.92 (m, 2H), 7.23-7.32 (m, 1H), 7.63(s, 1H), 7.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.65, 24.78, 33.59, 52.06, 63.47, 64.74, 113.36, 117.62, 119.29, 123.21, 123.61, 129.59, 130.56, 136.93,

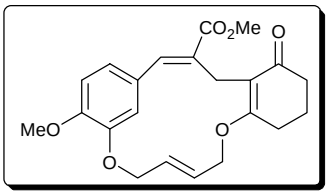
137.12, 139.29, 158.01, 168.87, 182.86, 203.40; LCMS (m/z): 341 $(M+H)^+$; Analysis calc'd. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92; Found : C, 70.45; H, 5.88.

Following differences were observed between ^1H & ^{13}C NMR spectra of (E)- & (Z)- isomers.

1. Singlet at δ 6.57 (1H) of (E)-isomer appeared as a singlet at δ 7.63 (1H) in (Z)-isomer in ^1H NMR spectra .

2. Allyloxy carbons (C_3 & C_6) of (E)-isomer appeared at δ 68.28 & 69.51 where as these carbons appeared at δ 63.47 & 64.74 in (Z)-isomer in ^{13}C NMR spectra.

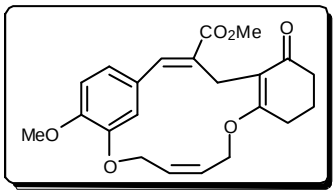
(4*E*,15*E*)-2,7-Dioxa-20-methoxy-15-methoxycarbonyltricyclo[15.3.1.0^{8,13}]henicosane-1(21)-4,8(13),15,17,19-hexaen-12-one (7d-*E*):



Yield: 53%; reaction time: (1h + 4h); colorless solid; mp: 112-114 ^{0}C; IR (KBr): υ 1701, 1651, 1606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.79-1.89 (m, 2H), 2.24 (t, *J* = 6.8 Hz, 2H), 2.45 (t, *J* = 6.0 Hz, 2H), 3.44 (s, 2H), 3.79 (s, 3H), 3.89 (s, 3H), 4.47 (d, *J* = 7.2 Hz, 2H), 4.63 (d, *J* = 4.8 Hz, 2H), 5.65-5.78 (m, 1H), 5.84-5.96 (m, 1H), 6.72 (d, *J* = 1.6 Hz, 1H), 6.80-6.90 (m, 2H), 7.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 20.72, 22.12, 25.98, 36.90, 51.89, 55.89, 66.86, 69.42, 111.29, 119.92, 120.60, 124.40, 128.71, 129.84, 131.56, 132.31, 136.86, 145.54, 150.15, 169.52, 170.44, 197.43; LCMS (m/z): 385 $(M+H)^+$; Analysis calc'd. for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29; Found : C, 68.61; H, 6.22.

In addition, peaks at *δ* 1.90-1.95 (m), 2.32 (t), 2.51 (t), 3.59 (s), 3.76 (s), 4.96 (d), 7.47 (s) and 7.56 (d) also appeared with low intensity. These may arise due to the presence minor (*Z*)-isomeric (≈ 5 %).

(4*Z*,15*E*)-2,7-Dioxa-20-methoxy-15-methoxycarbonyltricyclo[15.3.1.0^{8,13}]henicosane-1(21)-4,8(13),15,17,19-hexaen-12-one (7d-*Z*):



Yield: 33%; reaction time: (1h + 4h); colorless solid; mp: 124-126 ^{0}C; IR (KBr): υ 1701, 1649, 1618 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89-1.98 (m, 2H), 2.32 (t, J = 6.0 Hz, 2H), 2.52 (t, J = 6.0 Hz, 2H), 3.59 (s, 2H), 3.76 (s, 3H), 3.89 (s, 3H), 4.61-4.66 (m, 2H), 4.89-5.01 (m, 2H), 5.85-6.00 (m, 2H), 6.78-6.90 (m, 2H), 7.47 (s, 1H),7.52 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.93, 21.29, 26.06, 36.58, 51.89, 55.96, 61.97, 65.82, 111.26, 114.43, 118.91, 124.16, 125.37, 128.98, 131.06, 134.68, 137.41, 146.95, 149.36, 169.45, 170.06, 197.73; LCMS (m/z): 385 $(M+H)^+$; Analysis calc'd. for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29; Found : C, 68.88; H, 6.21. In addition, peaks with low intensity appeared at δ 1.80-1.89 (m), 2.22 (t), 2.49 (t), 3.44 (s), 3.80 (s), 4.48 (d) and 7.51 (s) probably due to the presence of minor (*E*)-isomer (≈ 4 %).

Following differences were observed between ^{1}H & ^{13}C NMR spectra of (E)- & (Z)- isomers.

In ^{1}H NMR spectra:

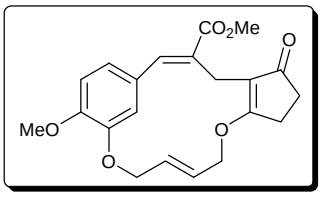
1. Multiplets at δ 5.65-5.78 (1H) and 5.84-5.96 (1H) of (E)-isomer appeared as a single multiplet at δ 5.85-6.00 (2H) in (Z)-isomer.

2. Doublet at δ 6.72 (1H) of (E)-isomer appeared as a doublet at δ 7.52 (1H) in (Z)-isomer.

In ^{13}C NMR spectra

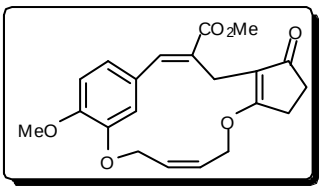
3. Allyloxy carbons (C_3 & C_6) of (E)-isomer appeared at δ 66.86 & 69.42 where as these carbons appeared at δ 61.97 & 65.82 in (Z)-isomer.

(4*E*,14*E*)-2,7-Dioxa-19-methoxy-14-methoxycarbonyltricyclo[14.3.1.0^{8,12}]icosane-1(20),4-8(12),14,16,18-hexaen-11-one (7e-*E*):



Yield: 48%; reaction time: (1h + 4h); colorless solid; mp: 150-152 ^{0}C; IR (KBr): υ 1718, 1682, 1616 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39-2.44 (m, 2H), 2.55-2.61 (m, 2H), 3.32 (s, 2H), 3.83 (s, 3H), 3.89 (s, 3H), 4.58-4.68 (m, 4H), 5.74-5.86 (m, 1H), 5.92-6.04 (m, 1H), 6.67 (d, J = 1.6 Hz, 1H), 6.85-6.94 (m, 2H), 7.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.61, 25.22, 33.86, 51.99, 55.83, 68.09, 70.15, 111.48, 120.62, 121.35, 124.82, 128.35, 128.42, 129.53, 131.75, 138.24, 145.71, 150.79, 169.12, 182.98, 203.94; LCMS (m/z): 371 $(M+H)^+$; Analysis calc'd. for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99; Found : C, 68.25; H, 6.05.

(4*Z*,14*E*)-2,7-Dioxa-19-methoxy-14-methoxycarbonyltricyclo[14.3.1.0^{8,12}]icosane-1(20),4-8(12),14,16,18-hexaen-11-one (7e-*Z*):



Yield: 28%; reaction time: (1h + 4h); colorless solid; mp: 184-186 ^{0}C; IR (KBr): υ 1701, 1680, 1624 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45-2.52 (m, 2H), 2.67-2.74 (m, 2H), 3.44 (s, 2H), 3.77 (s, 3H), 3.91 (s, 3H), 4.73 (d, J = 6.4 Hz, 2H), 5.07 (d, J = 5.2 Hz, 2H), 5.86-6.04 (m, 2H), 6.88 (s, 2H), 7.59 (s, 1H), 7.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.54, 24.72, 33.59, 51.94, 55.92, 63.41, 65.22, 111.21, 113.57, 119.31, 123.53, 124.43, 128.29, 128.53, 137.23,

139.11, 146.92, 149.27, 169.08, 182.69, 203.39; LCMS (m/z): 371 $(M+H)^+$; Analysis calc'd. for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99; Found : C, 68.21; H, 5.91.

Following differences were observed between ^1H & ^{13}C NMR spectra of (E)- & (Z)- isomers.

In ^1H NMR spectra:

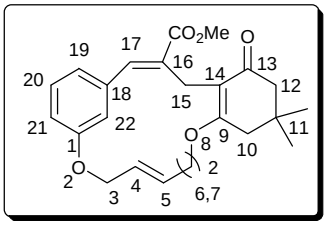
1. Multiplets at δ 5.74-5.86 (1H) and 5.92-6.04 (1H) of (E)-isomer appeared as one multiplet at δ 5.86-6.04 (2H) in (Z)-isomer.

2. Doublet at δ 6.67 (1H) of (E)-isomer appeared as a singlet at δ 7.59 (1H) in (Z)-isomer.

In ^{13}C NMR spectra:

3. Allyloxy carbons (C_3 & C_6) of (E)-isomer appeared at δ 68.09 & 70.15 where as these carbons appeared at δ 63.41 & 65.22 in (Z)-isomer.

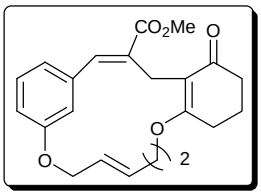
(4*E*,16*E*)-11,11-Dimethyl-2,8-dioxa-16-methoxycarbonyltricyclo[16.3.1.0^{9,14}]docosane-1(22)-4,9(14),16,18,20-hexaen-13-one (7f):



Yield: 70%; reaction time: (1h + 2h); colorless solid; mp: 102-104 ^{0}C; IR (KBr): υ 1709, 1641, 1616 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 0.96 (s, 6H), 2.11 (s, 2H), 2.23 (s, 2H), 2.35-2.46 (m, 2H), 3.57 (s, 2H), 3.83 (s, 3H), 3.91 (t, *J* = 5.2 Hz, 2H), 4.64 (d, *J* = 1.2 Hz, 2H), 5.55-5.64 (m, 1H), 5.65-5.74 (m, 1H), 6.72 (d, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H)*, 6.95 (s, 1H), 7.14-7.22 (m, 1H), 7.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 20.47, 28.45, 31.90, 32.59, 39.22, 50.32, 52.06, 66.60, 67.44, 114.15, 115.89, 117.45, 122.36, 127.60, 129.12, 130.18, 133.51, 136.28, 137.55, 157.46, 168.87, 169.73, 197.36; LCMS (m/z): 397 $(M+H)^+$; Analysis calc'd. for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12; Found: C, 72.81; H, 7.08.

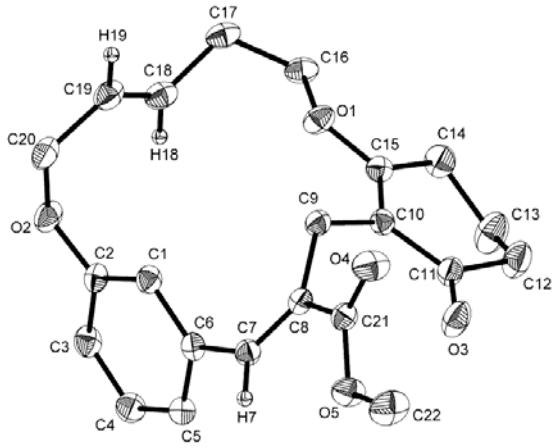
* Unresolved doublet of doublet (dd).

(4*E*,16*E*)-2,8-Dioxa-16-methoxycarbonyltricyclo[16.3.1.0^{9,14}]docosane-1(22),4,9(14),16,18-20-hexaen-13-one (7g):



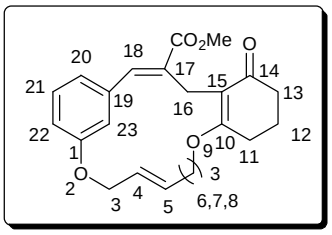
Yield: 79%; reaction time: (1h + 2h); colorless solid; mp: 120-122 ^{0}C; IR (KBr): υ 1699, 1641, 1606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78-1.88 (m, 2H), 2.23 (t, J = 6.0 Hz, 2H), 2.34-2.43 (m, 4H), 3.55 (s, 2H), 3.84 (s, 3H), 3.92 (t, J = 5.2 Hz, 2H), 4.64 (d, J = 2.8 Hz, 2H), 5.55-5.64 (m, 1H), 5.65-5.73 (m, 1H), 6.72 (d, J = 7.2 Hz, 1H), 6.84 (dd, J = 8.0 & 2.4 Hz, 1H), 6.90 (s, 1H), 7.15-7.21 (m, 1H), 7.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.72, 20.77, 25.31, 32.47, 36.49, 51.97, 66.57, 67.50, 114.21, 116.98, 117.40, 122.24, 127.64, 129.04, 130.10, 133.59, 136.17, 137.60, 157.44, 169.73, 170.70, 197.58; LCMS (m/z): 369 $(M+H)^{+}$; Analysis calc'd. for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57; Found: C, 71.63; H, 6.61.

Crystal data for 7g: Empirical formula, $C_{22}H_{24}O_5$; Formula weight, 368.41; crystal color, colorless; habit, block; crystal dimensions, 0.20 x 0.18 x 0.10 mm^3 ; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 15.8167(12) Å, b = 8.2210(6) Å, c = 15.9694(12) Å, α = 90.00, β = 116.3120(10), γ = 90.00; V = 1861.3(2) Å^3; space group, p2(1)/n; Z = 4; D_{cald} = 1.315 g / cm^3; F_{000} = 784; λ (Mo-Kα) = 0.71073 Å; R(I≥2σ$_1$) = 0.0519, wR^2 = 0.1368. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **7g** CCDC # 915413).



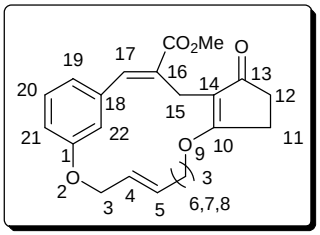
ORTEP diagram of compound **7g**

(4*E*,17*E*)-2,9-Dioxa-17-methoxycarbonyltricyclo[17.3.1.0^{10,15}]tricosane-1(23),4,10(15),17,19-21-hexaen-14-one (7h):

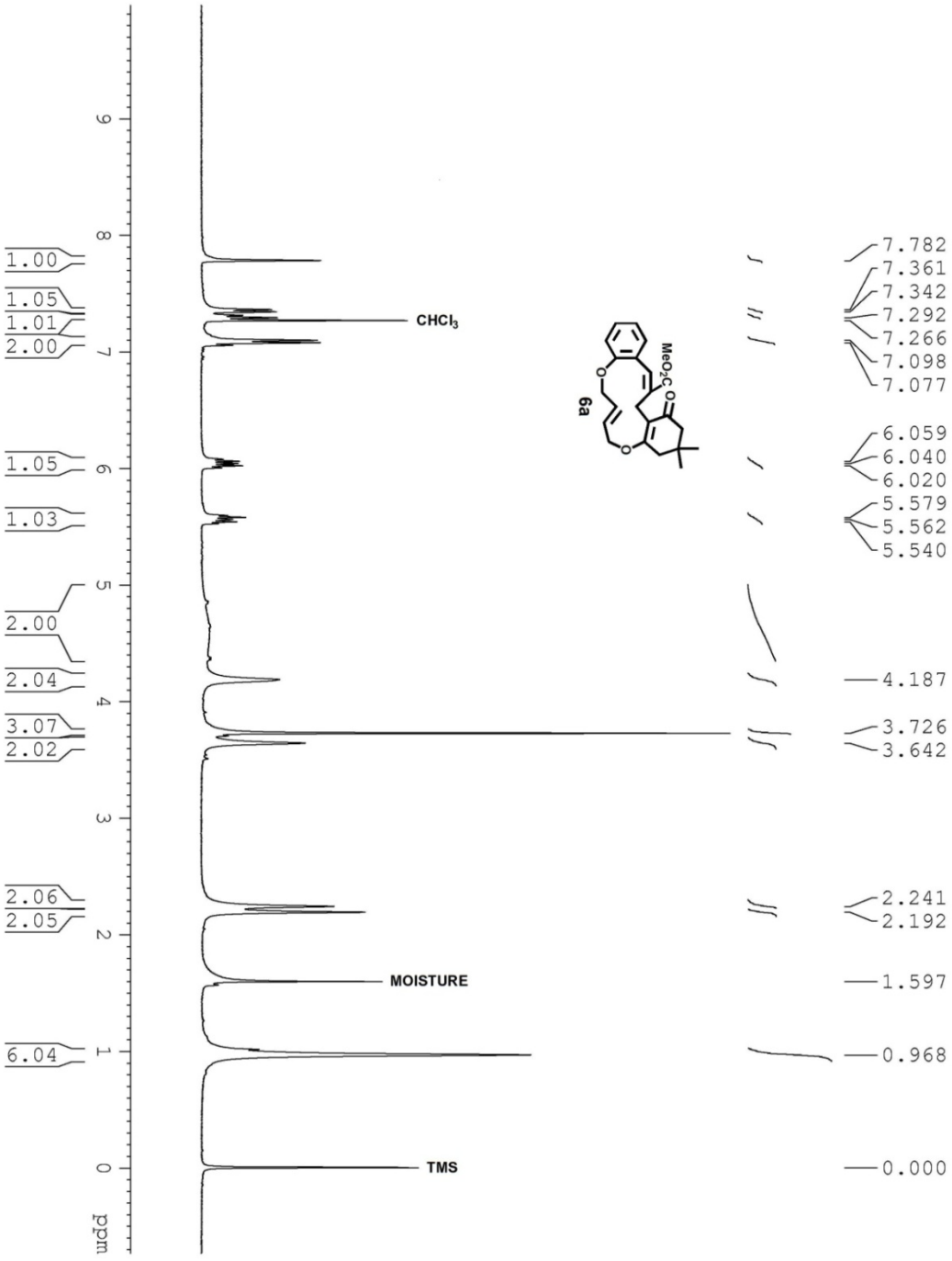


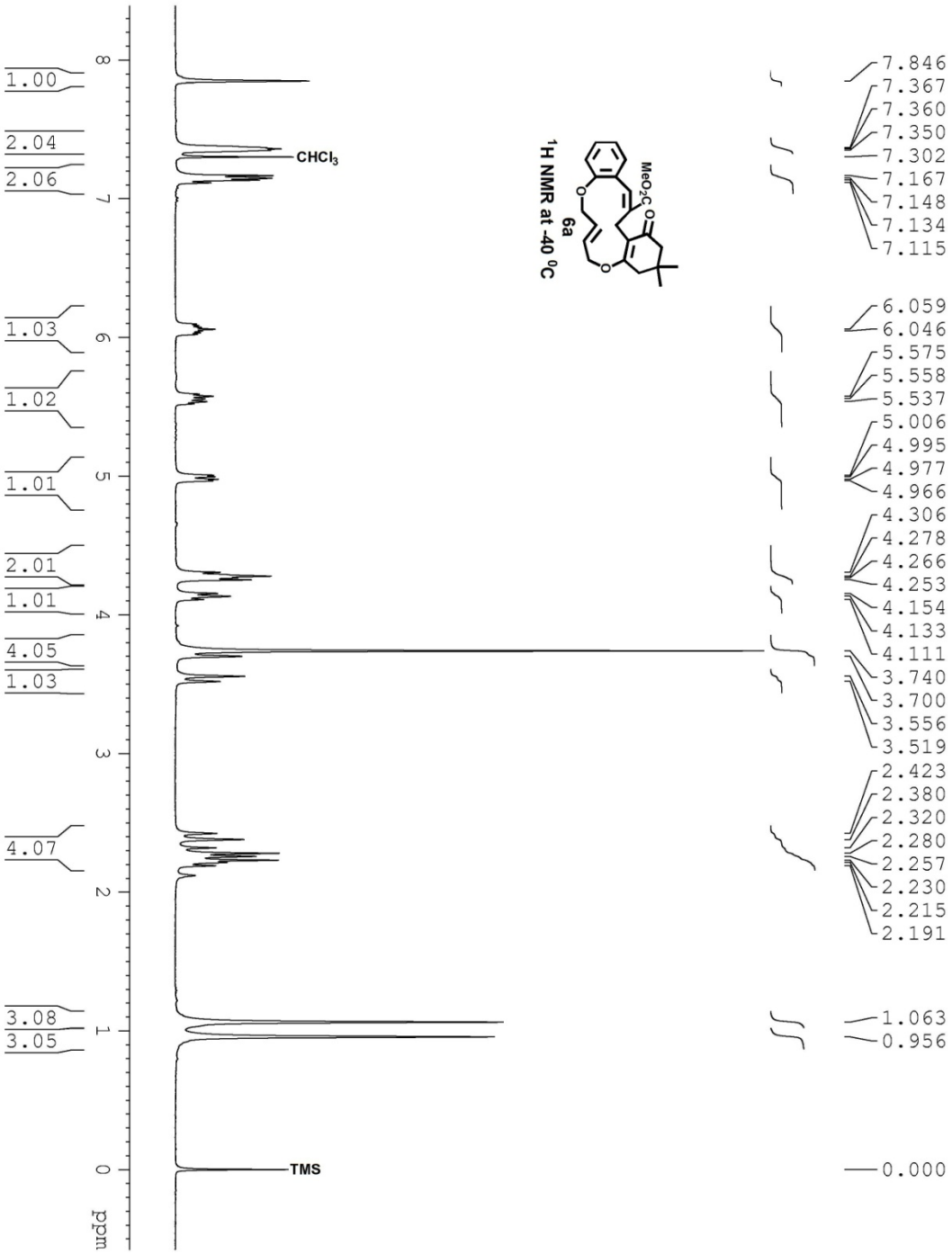
Yield: 81%; reaction time: (1h + 2h); colorless solid; mp: 80-82 ^{0}C; IR (KBr): υ 1712, 1655, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.64-1.72 (m, 2H), 1.78-1.88 (m, 2H), 2.03-2.14 (m, 2H), 2.26 (t, J = 6.8 Hz, 2H), 2.35 (t, J = 6.0 Hz, 2H), 3.52 (s, 2H), 3.74 (s, 3H), 3.79 (t, J = 6.4 Hz, 2H), 4.64 (d, J = 4.8 Hz, 2H), 5.46-5.58 (m, 1H), 5.66-5.80 (m, 1H), 6.78-6.92 (m, 3H), 7.17-7.24 (m, 1H), 7.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.78, 21.33, 25.75, 28.59, 29.21, 36.44, 51.82, 66.80, 68.79, 114.94, 117.39, 117.79, 122.09, 126.76, 129.12, 132.54, 134.85, 137.50, 137.61, 157.63, 169.21, 171.71, 197.10; LCMS (m/z): 383 $(M+H)^{+}$; Analysis calcd. for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85; Found: C, 72.35; H, 6.79.

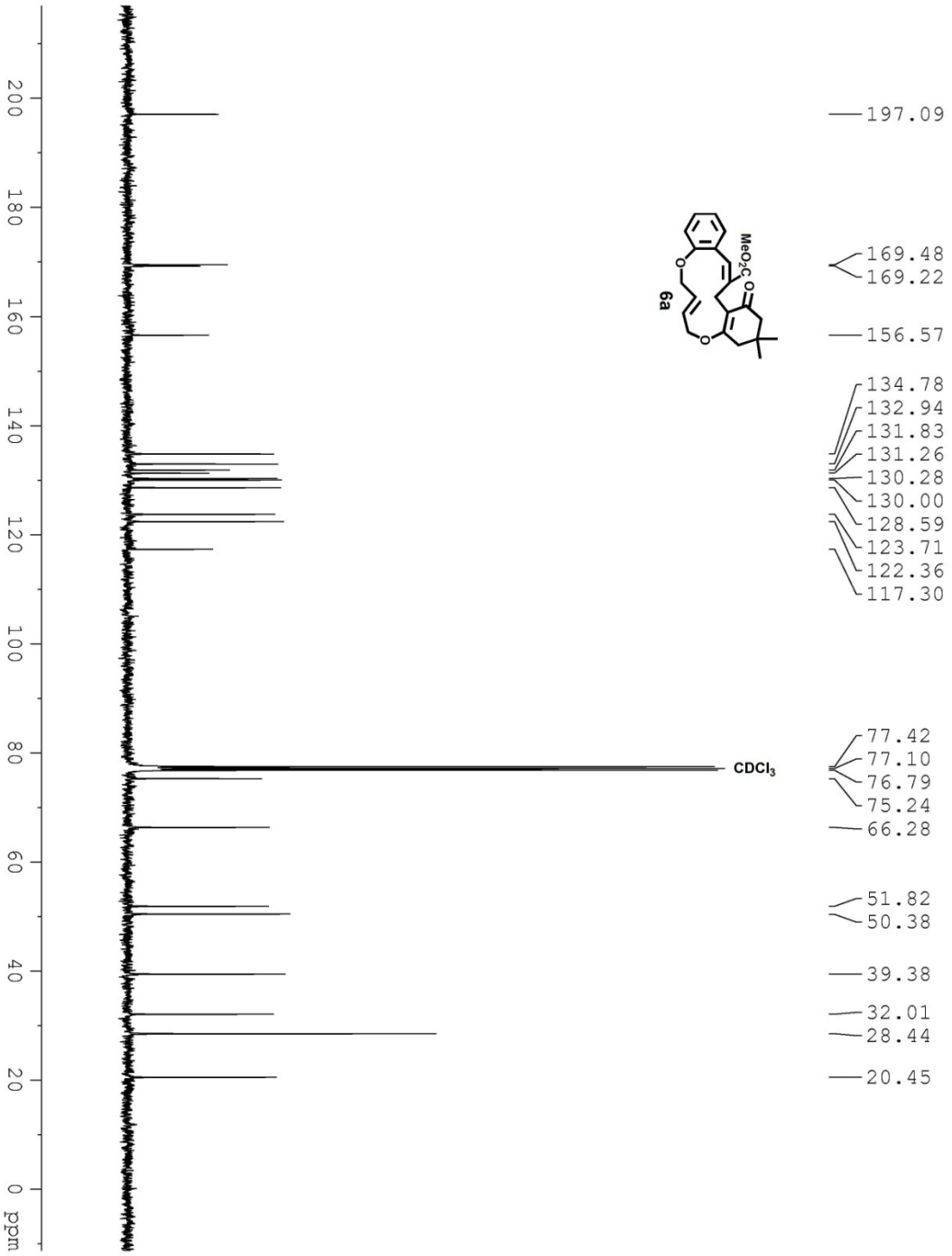
(4*E*,16*E*)-2,9-Dioxa-16-methoxycarbonyltricyclo[16.3.1.0^{10,14}]docosane-1(22),4,10(14),16,18-20-hexaen-13-one (7i):

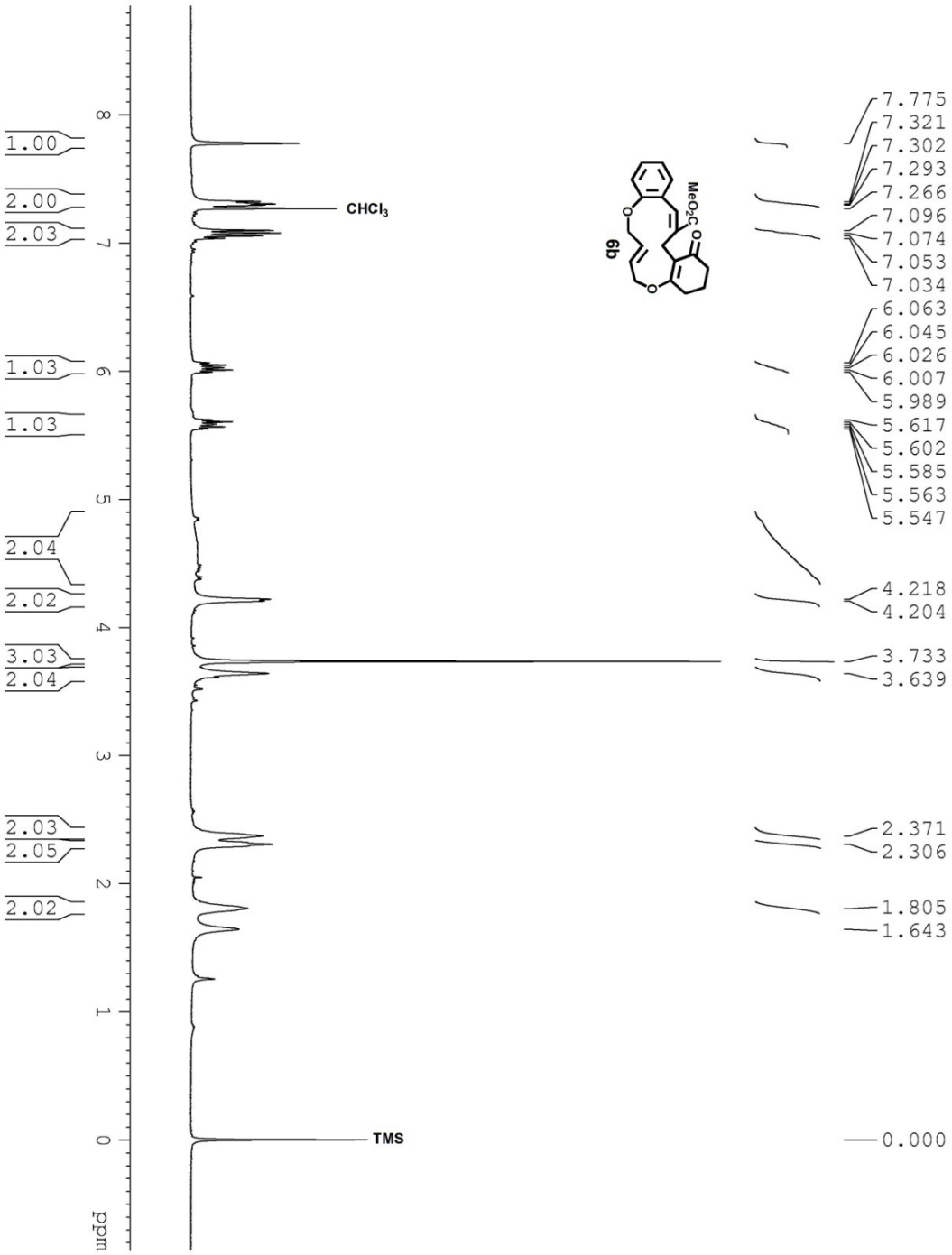


Yield: 85%; reaction time: (1h + 2h); colorless solid; mp: 80-82 ^{0}C; IR (KBr): υ 1711, 1678, 1616 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82-1.92 (m, 2H), 2.26-2.38 (m, 2H), 2.39-2.50 (m, 2H), 2.58-2.68 (m, 2H), 3.49 (s, 2H), 3.86 (s, 3H), 4.15 (t, J = 4.8 Hz, 2H), 4.55 (d, J = 6.4 Hz, 2H), 5.64- 5.76 (m, 1H), 5.86-5.98 (m, 1H), 6.82-6.94 (m, 2H), 6.98 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.61, 23.69, 25.06, 28.35, 33.31, 52.16, 63.98, 67.28, 114.26, 115.91, 117.59, 123.42, 126.25, 129.30, 130.63, 133.98, 137.07, 137.70, 158.36, 169.33, 183.44, 203.36; LCMS (m/z): 369 $(M+H)^{+}$; Analysis calcd. for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57; Found: C, 71.63; H, 6.51.





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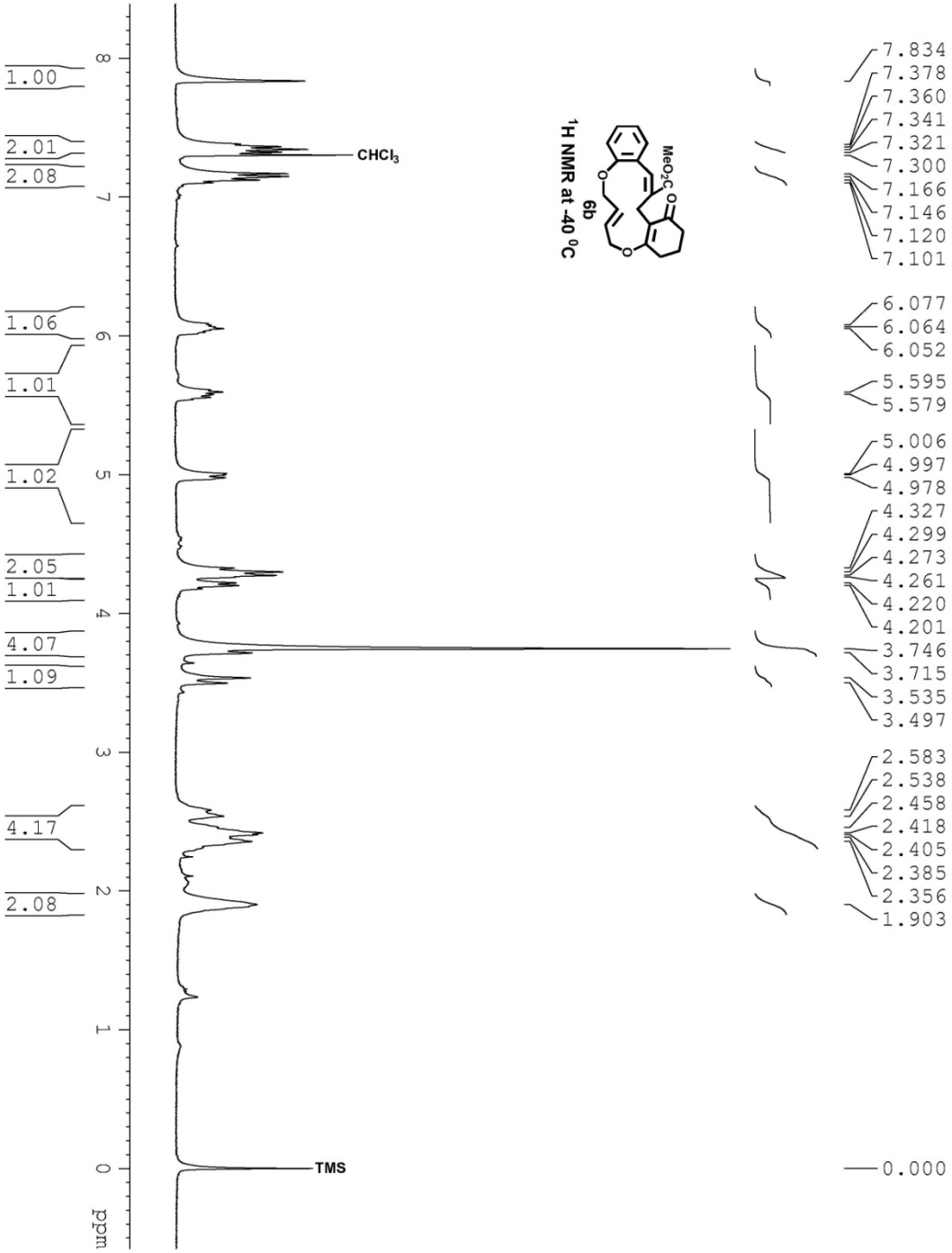
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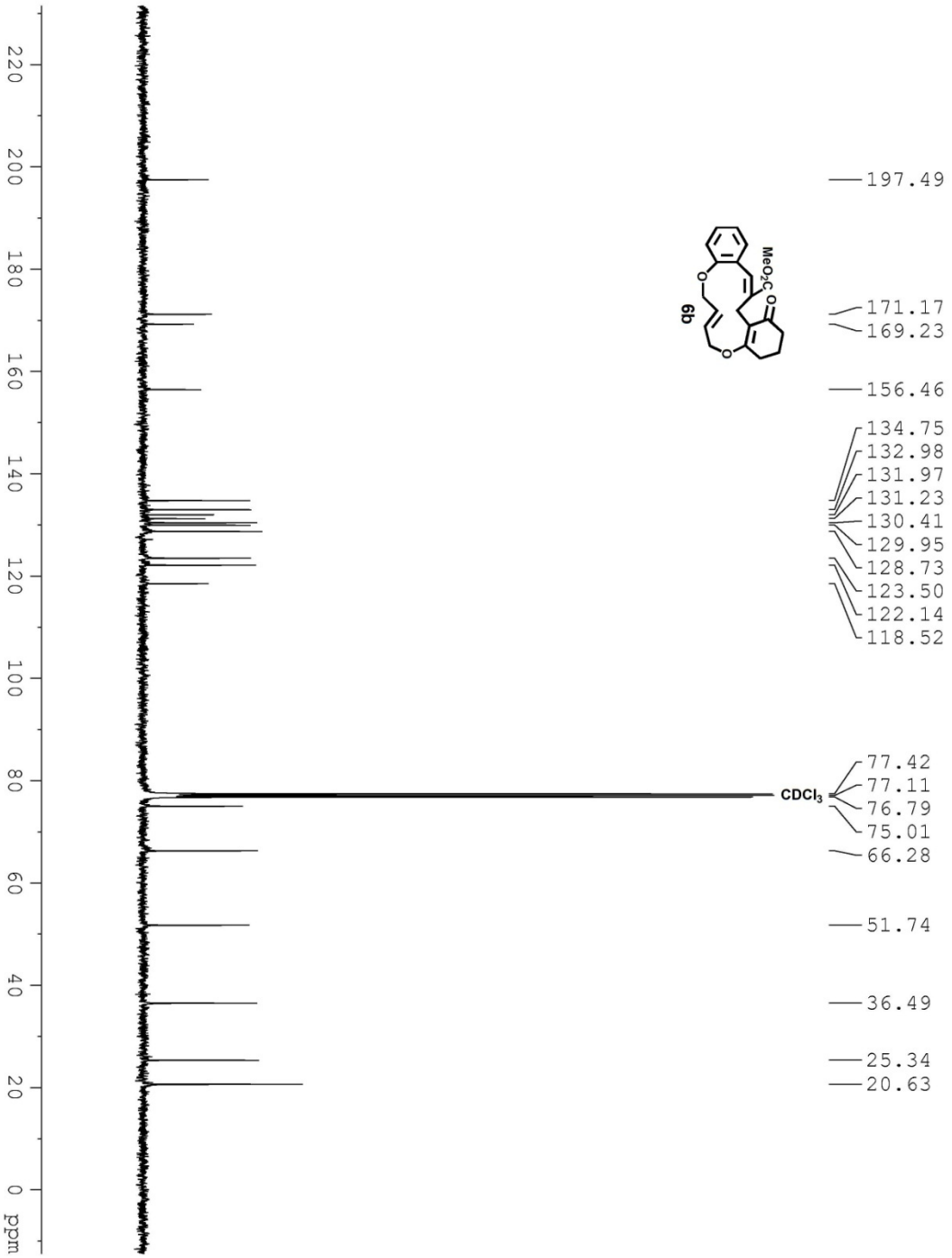
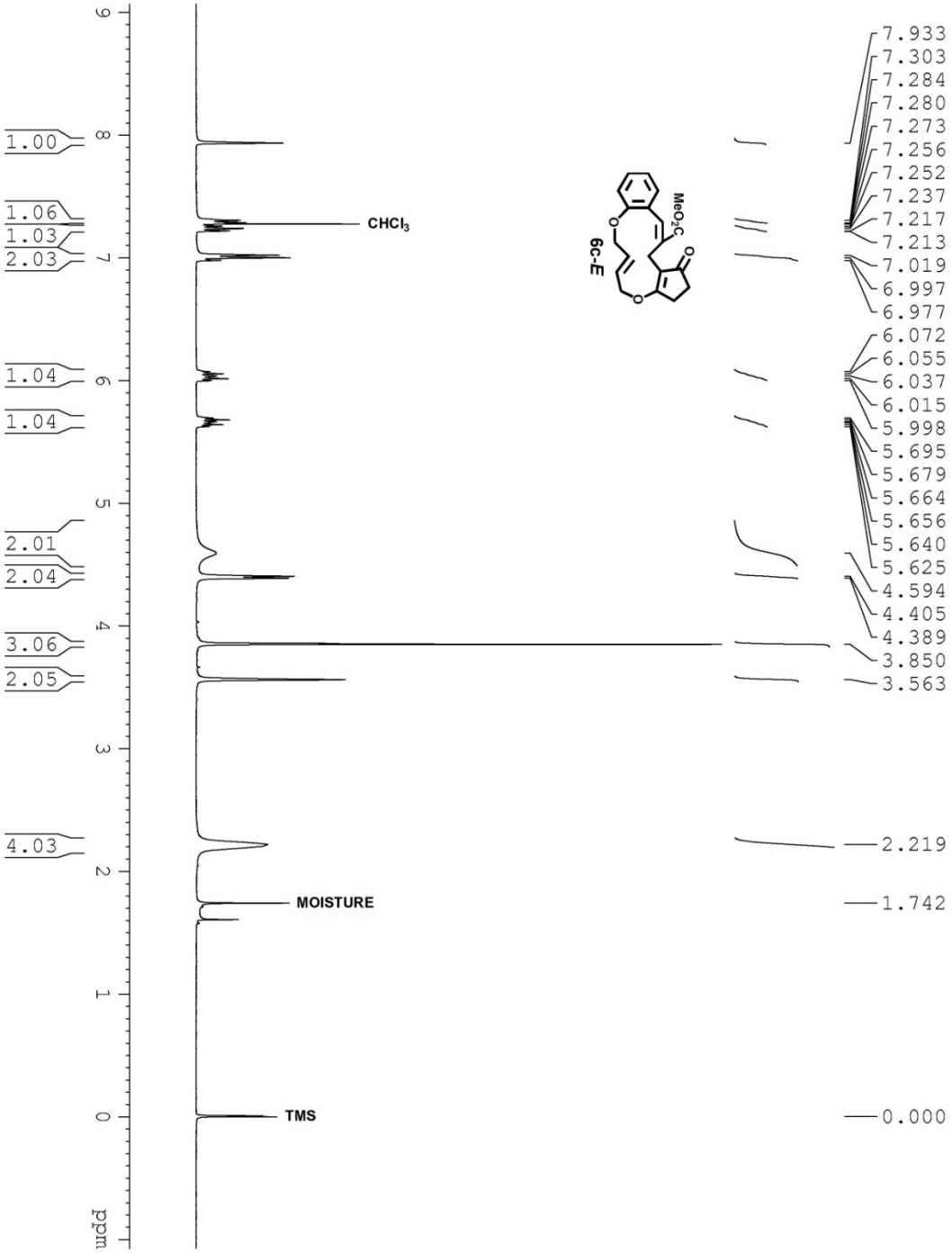
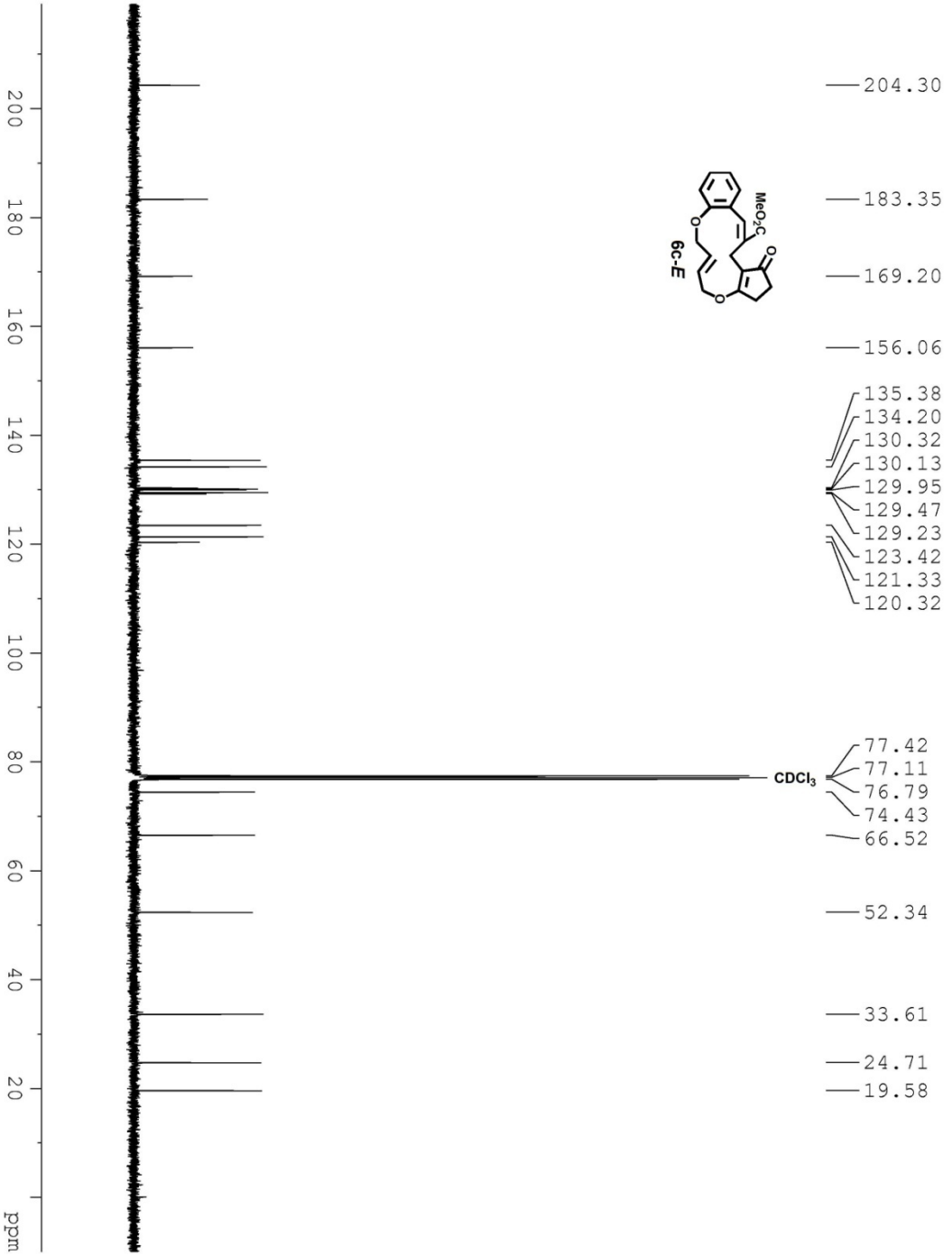
4.327
4.299
4.273
4.261
4.220
4.201
3.746
3.715
3.535
3.497
2.583
2.538
2.458
2.418
2.405
2.385
2.356
1.903
0.000



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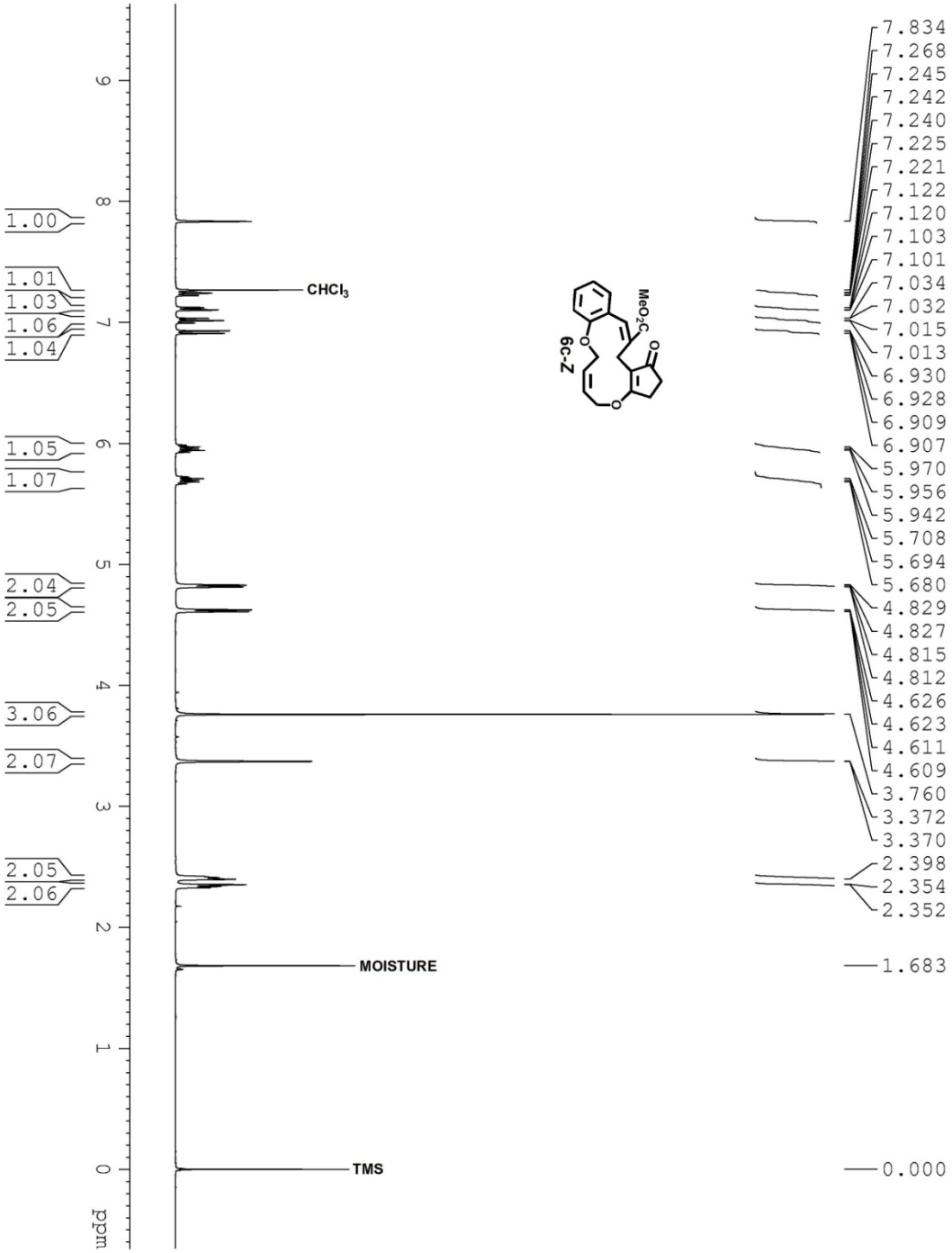
183.35
169.20
156.06
135.38
134.20
130.32
130.13
129.95
129.47
129.23
123.42
121.33
120.32
77.42
77.11
76.79
74.43
66.52
52.34
33.61
24.71
19.58
CDCl3
MeO2C
6c-E
200
180
160
140
120
100
80
60
40
20
ppm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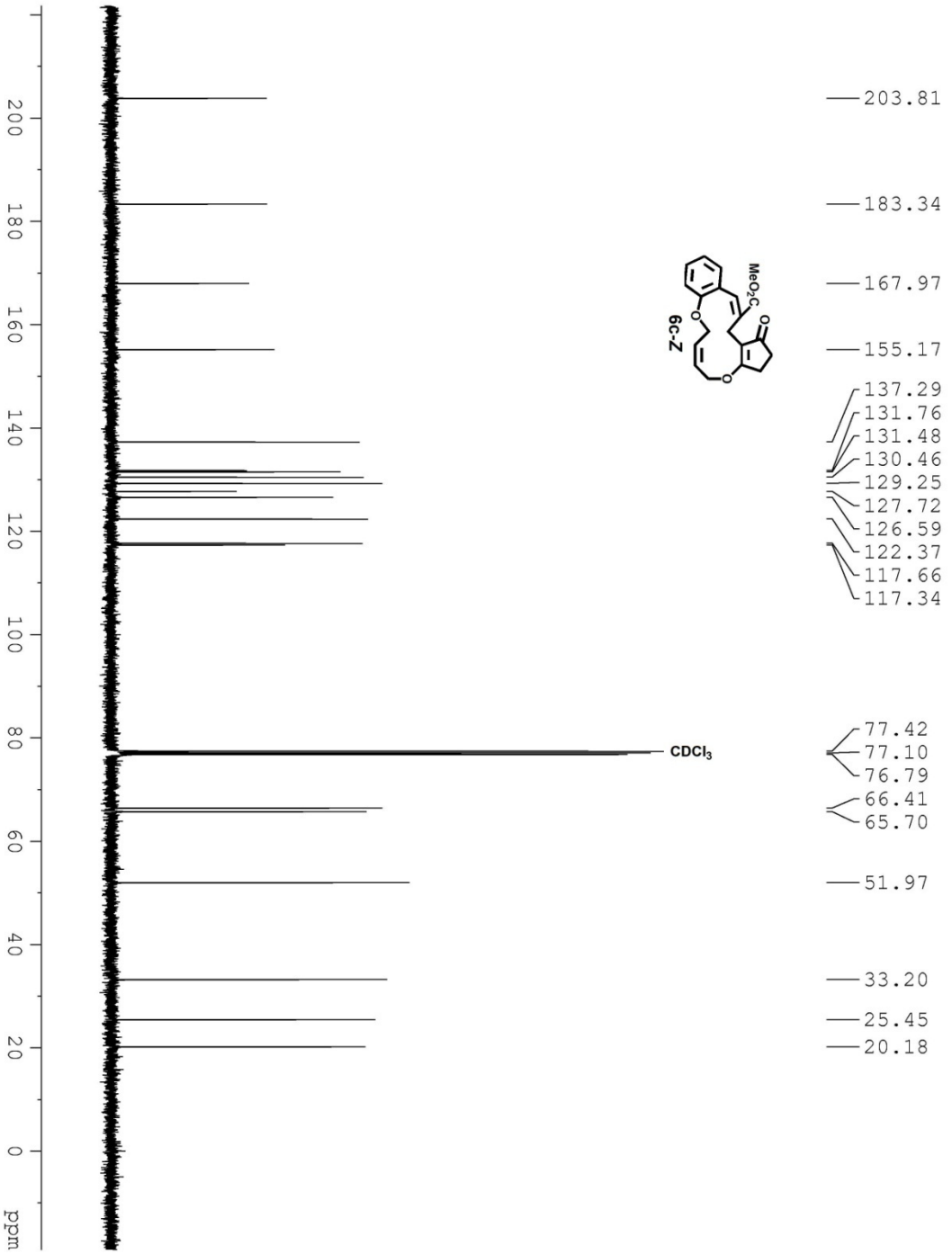
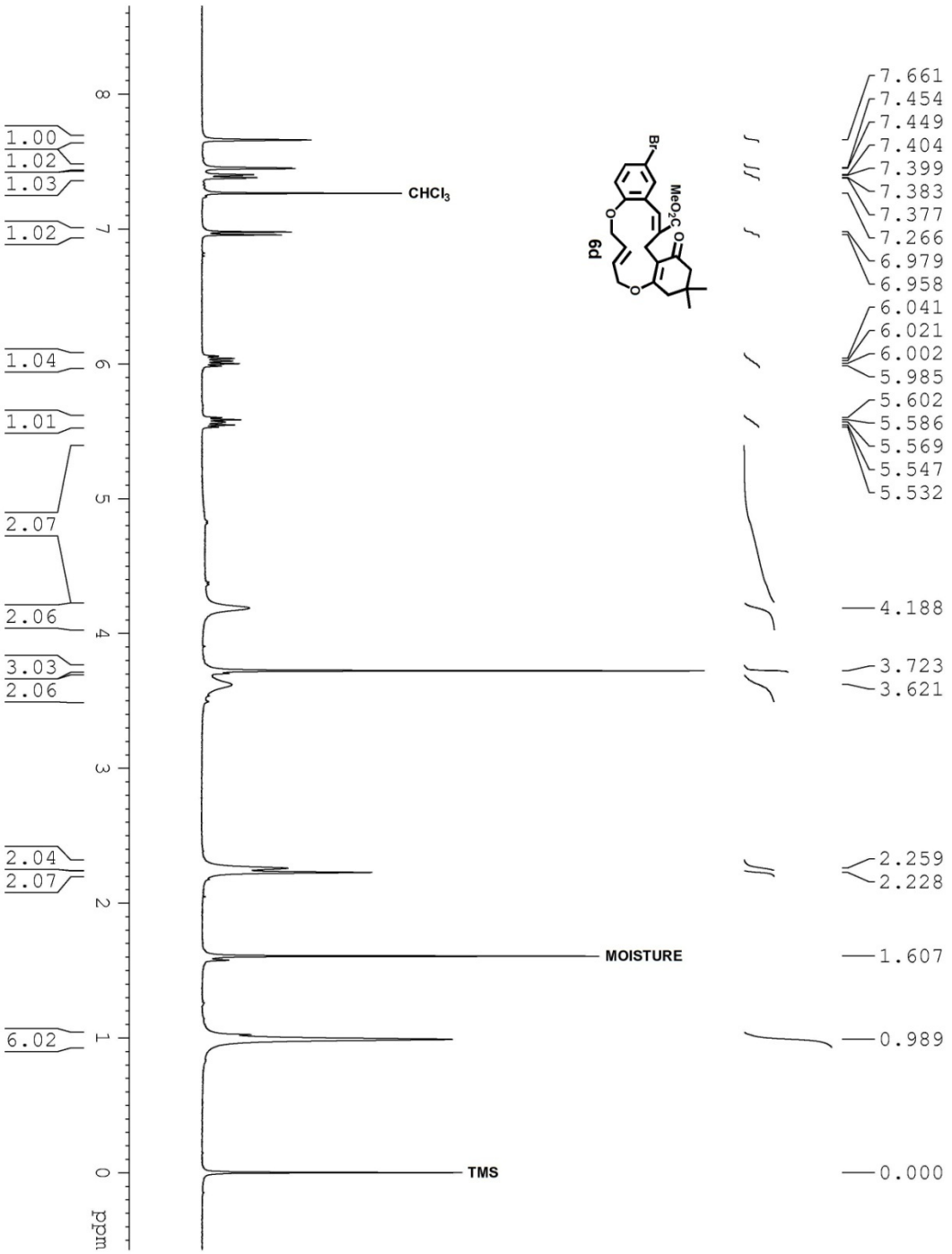
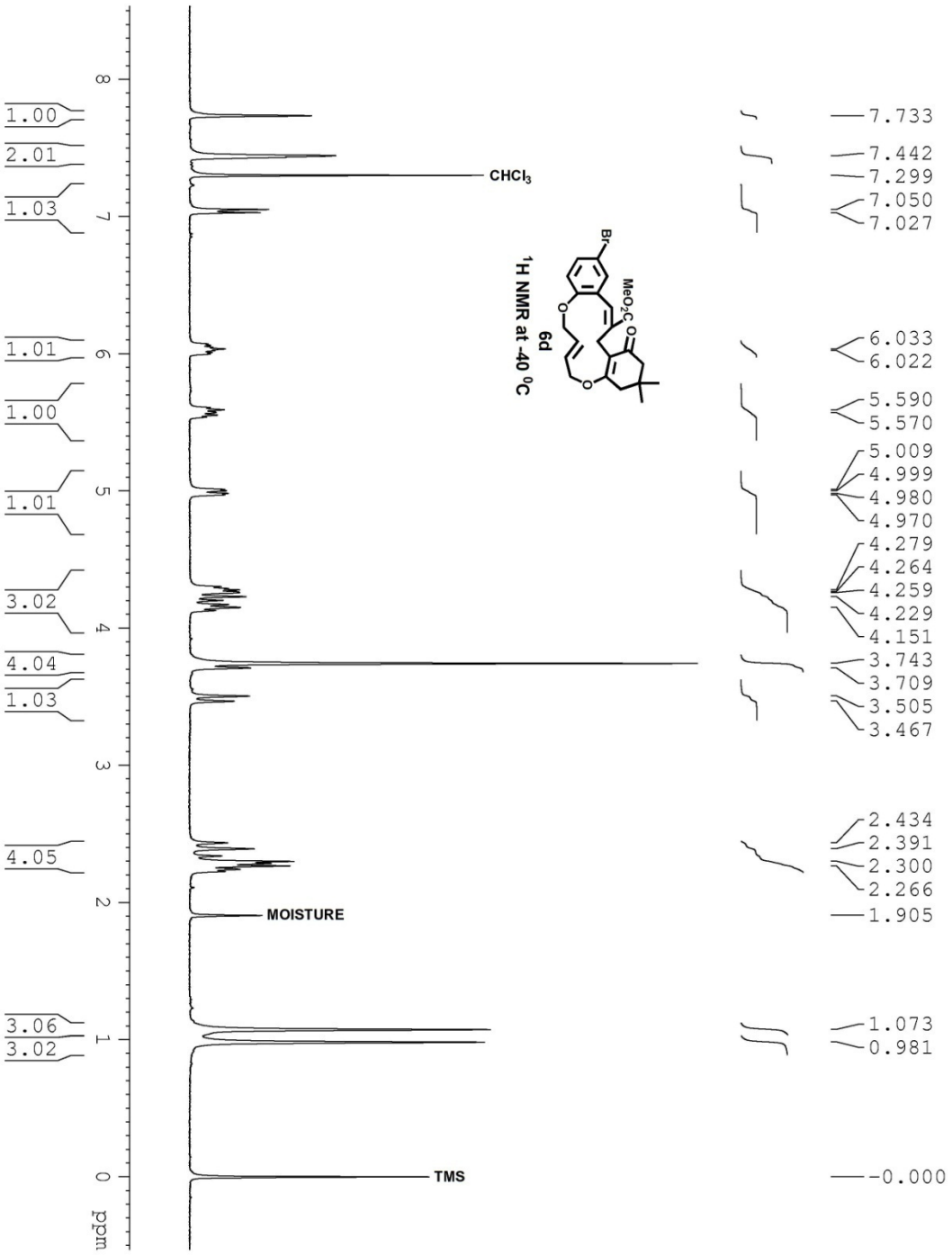
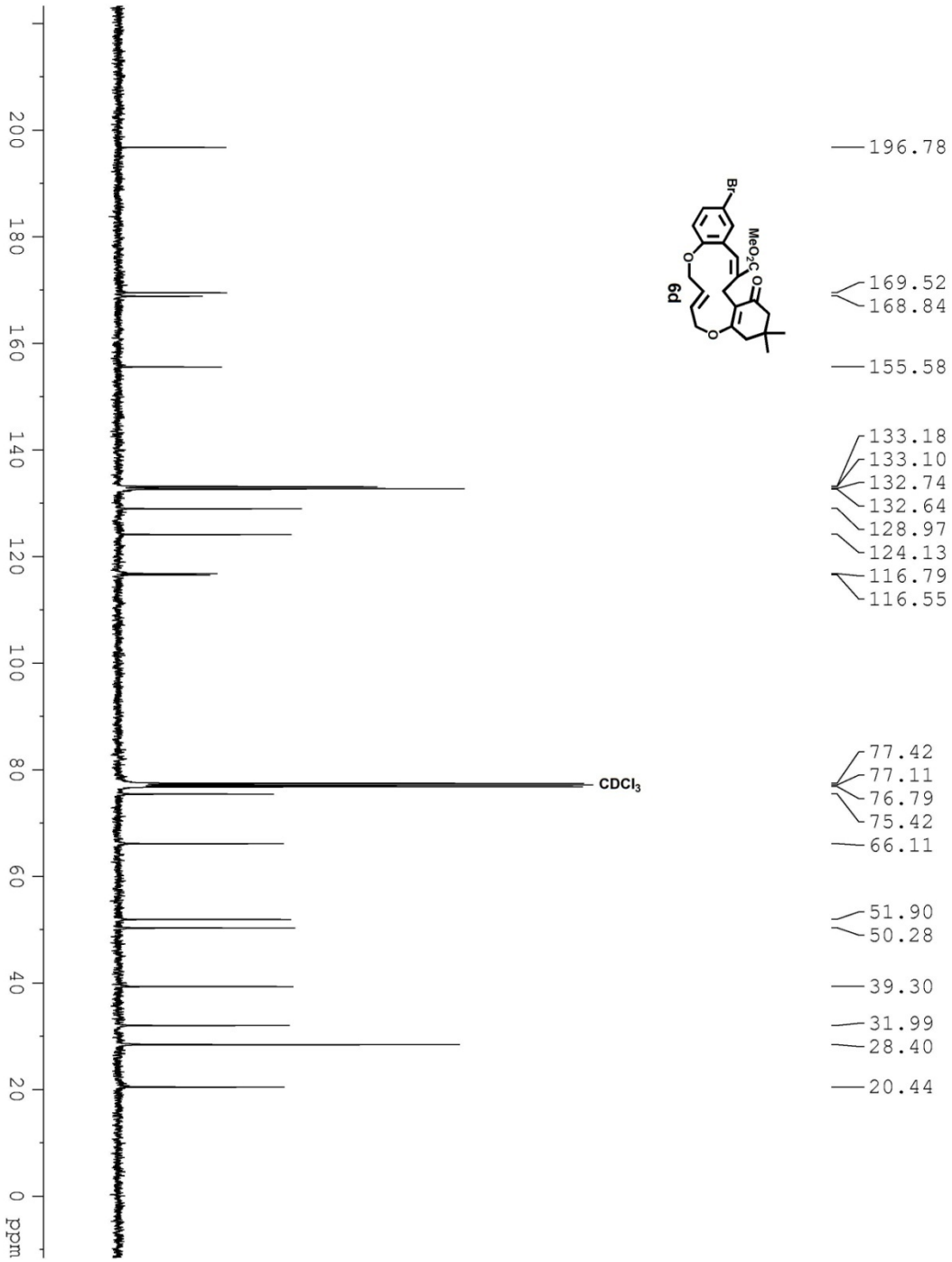
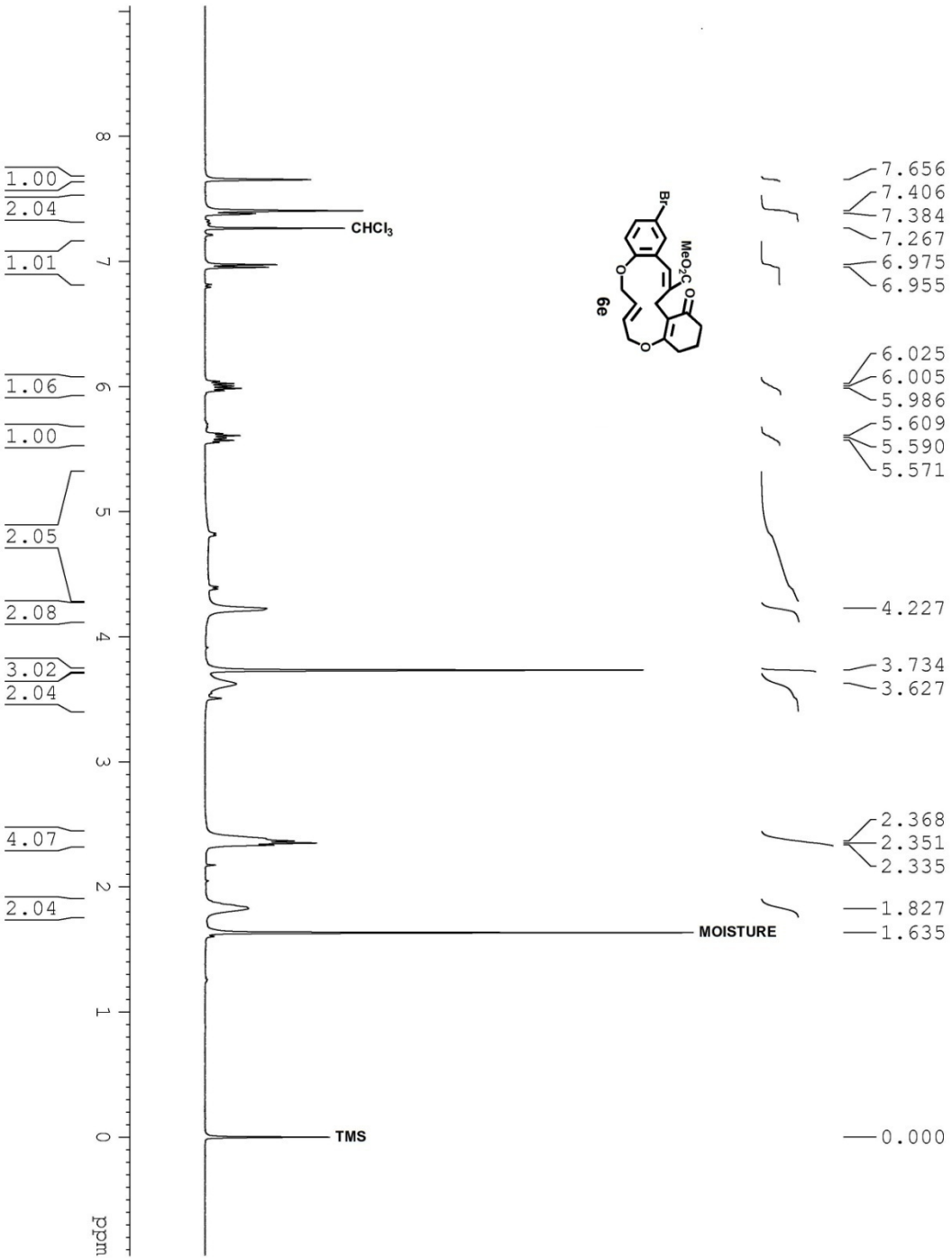
7.245
7.242
7.240
7.225
7.221
7.122
7.120
7.103
7.101
7.034
7.032
7.015
7.013
6.930
6.928
6.909
6.907
5.970
5.956
5.942
5.708
5.694
5.680
4.829
4.827
4.815
4.812
4.626
4.623
4.611
4.609
3.760
3.372
3.370
2.398
2.354
2.352
1.683
0.000
1.00
1.01
1.03
1.06
1.04
1.05
1.07
2.04
2.05
3.06
2.07
2.05
2.06
CHCl3
MOISTURE
TMS
MeO2C
6c-Z
ppm

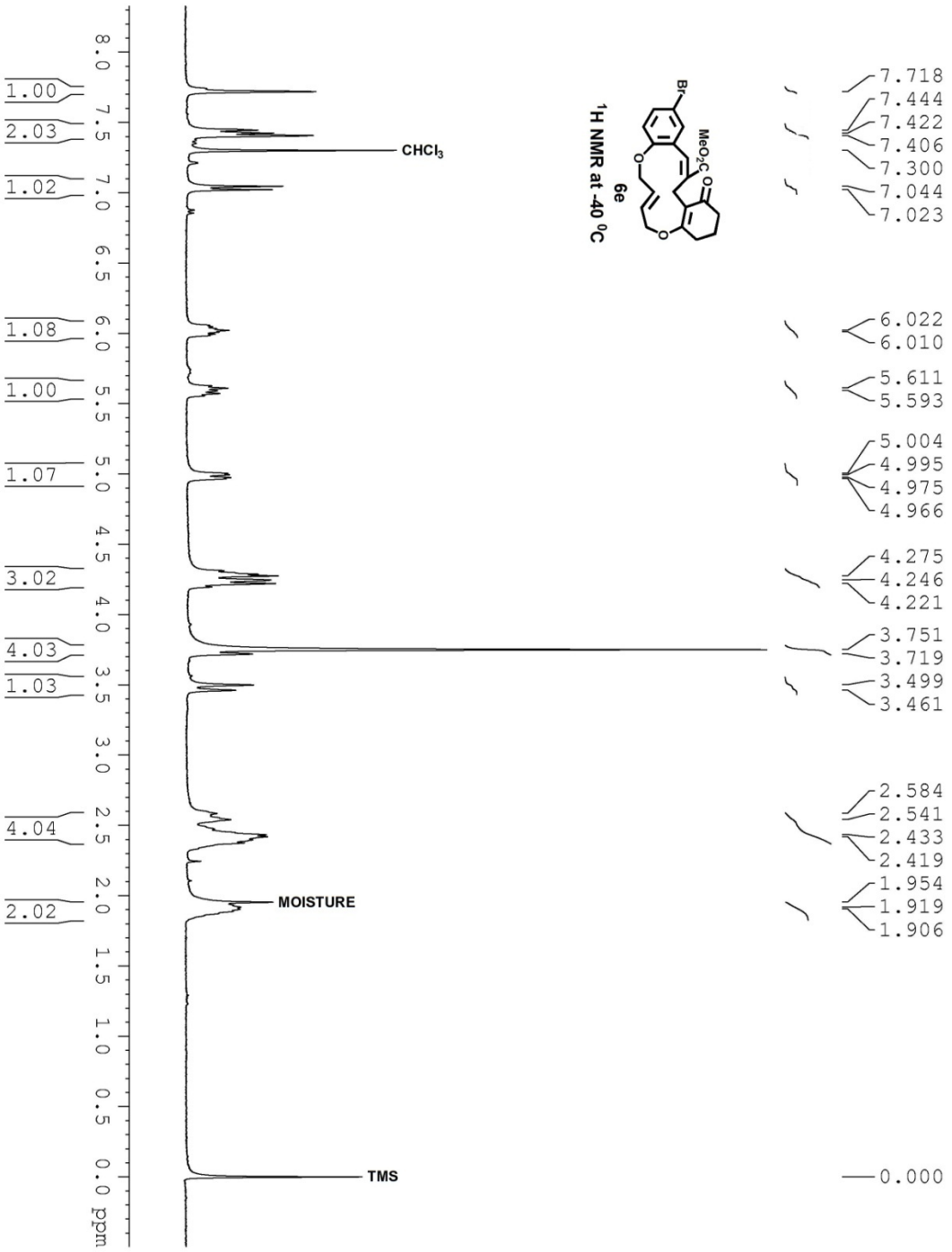


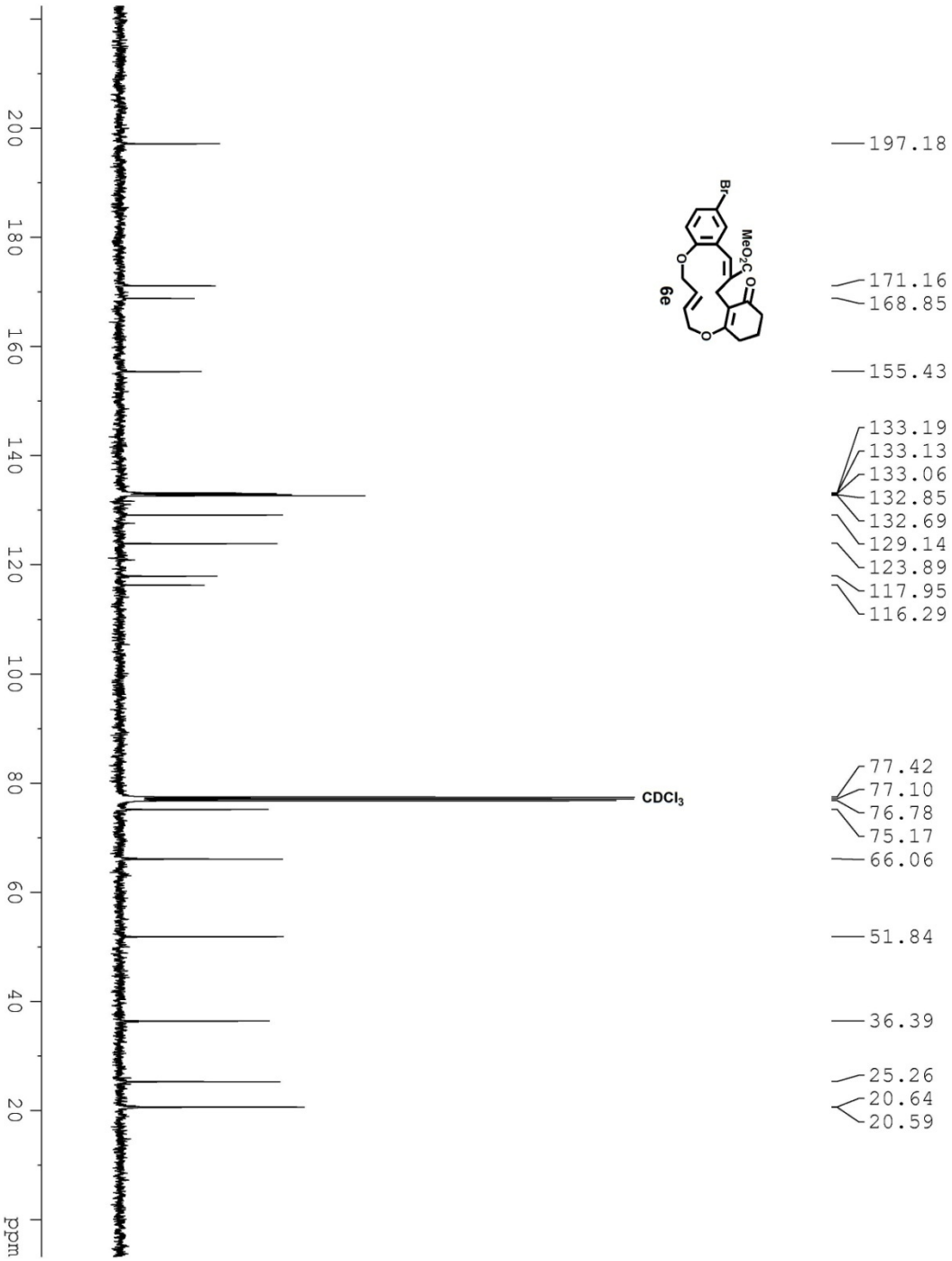


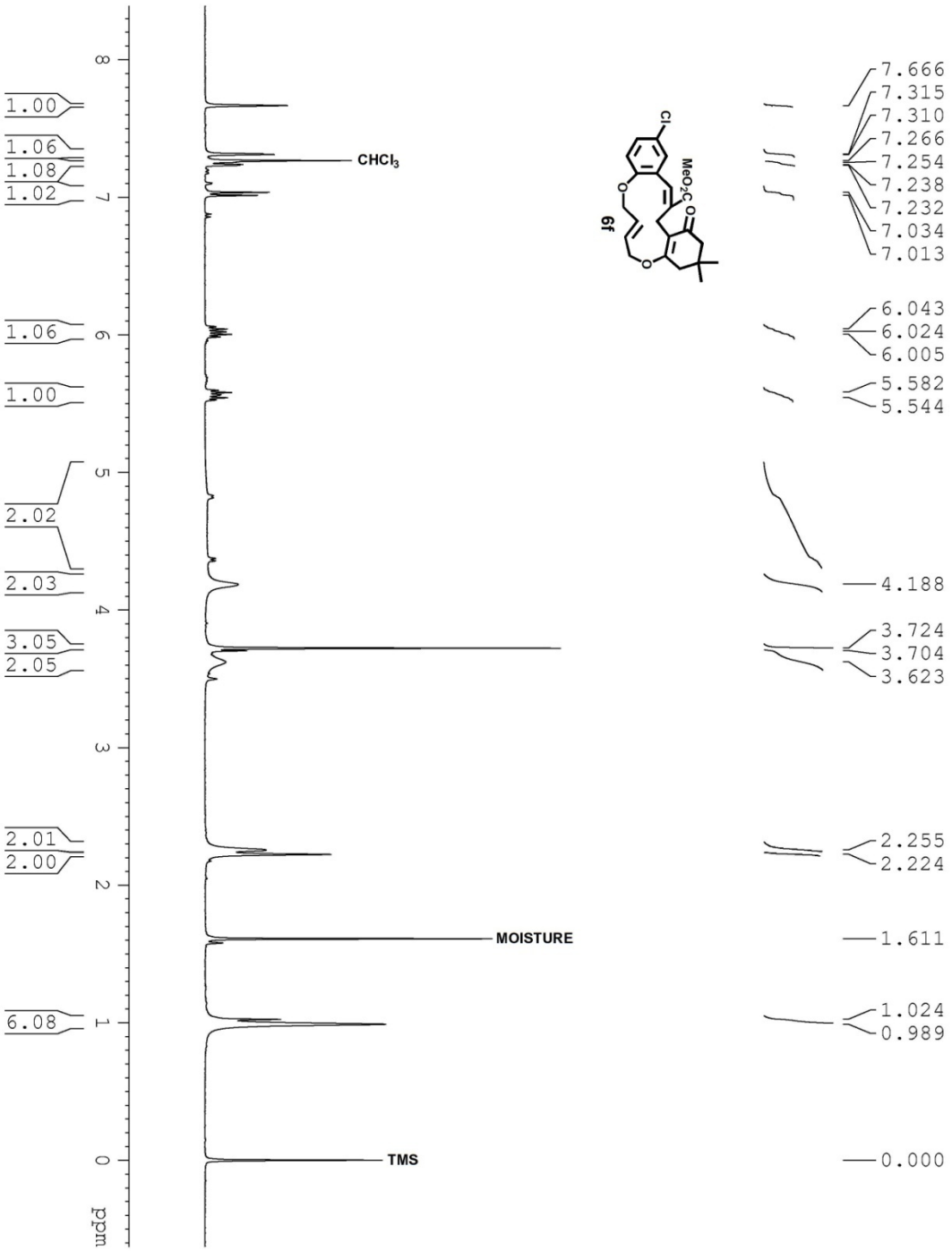


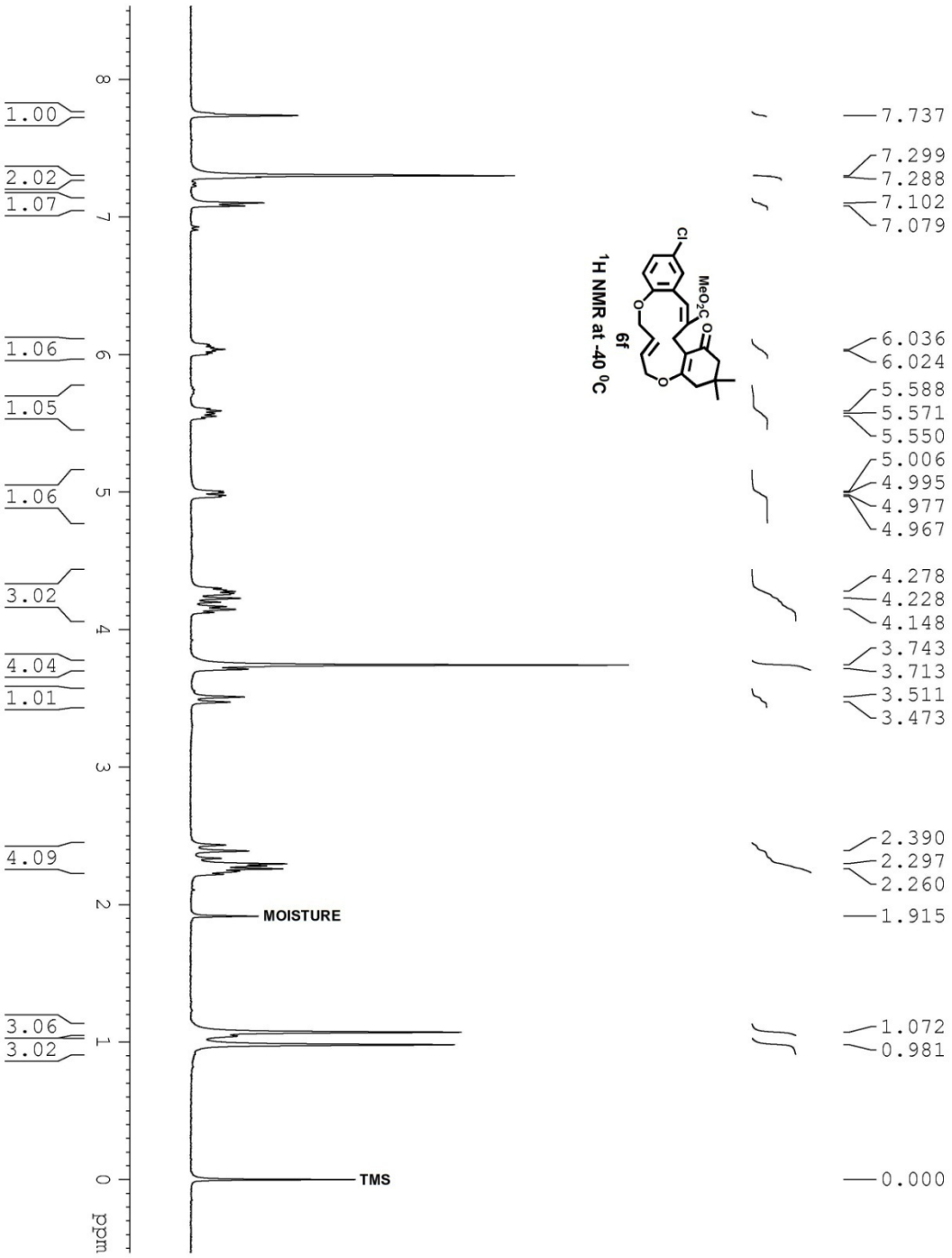


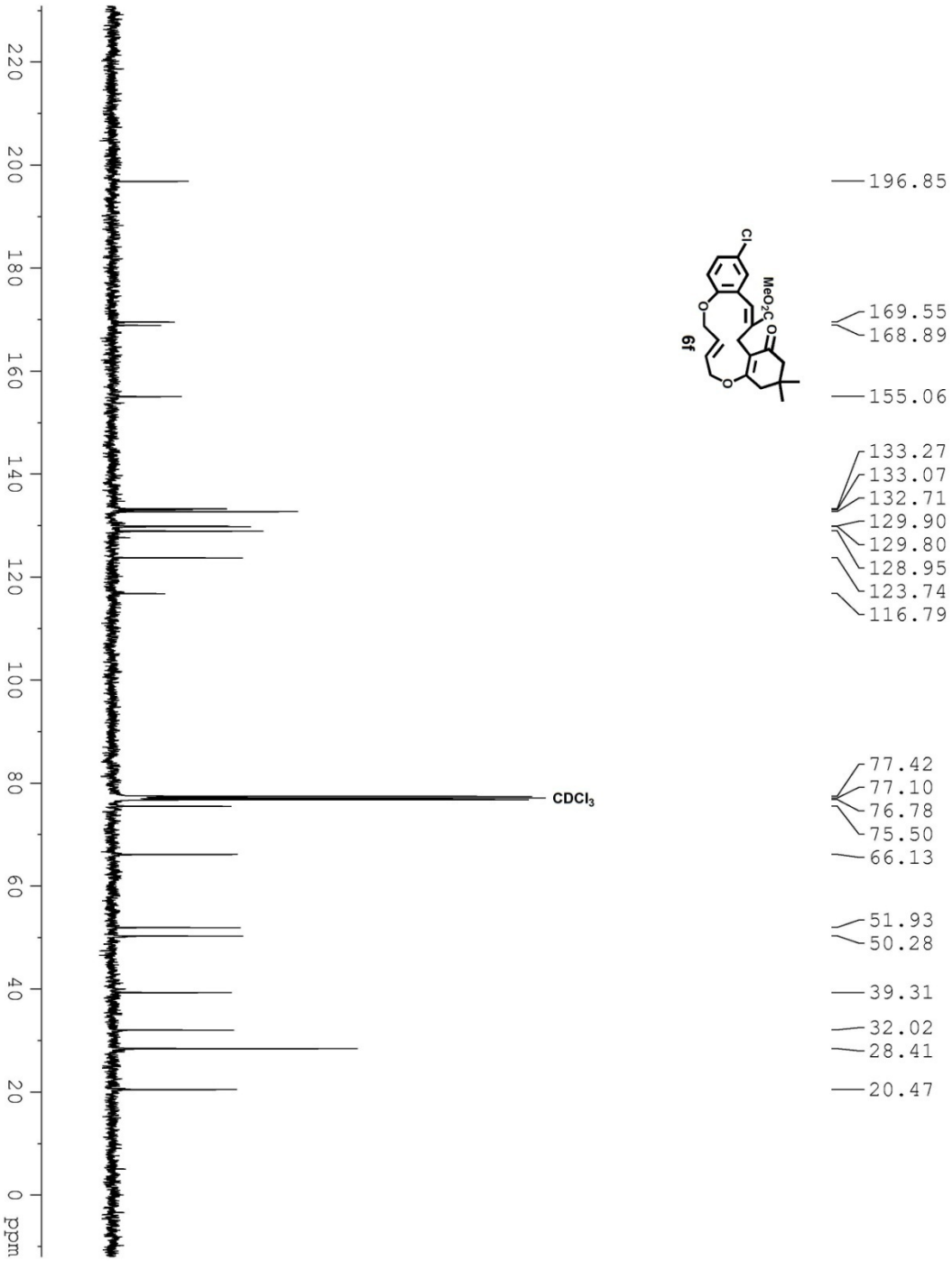

1.00
2.04
1.01
1.06
1.00
2.05
2.08
3.02
2.04
4.07
2.04
CHCl3
TMS
MOISTURE
6e
Br
MeO2C
7.656
7.406
7.384
7.267
6.975
6.955
6.025
6.005
5.986
5.609
5.590
5.571
4.227
3.734
3.627
2.368
2.351
2.335
1.827
1.635
0.000
ppm

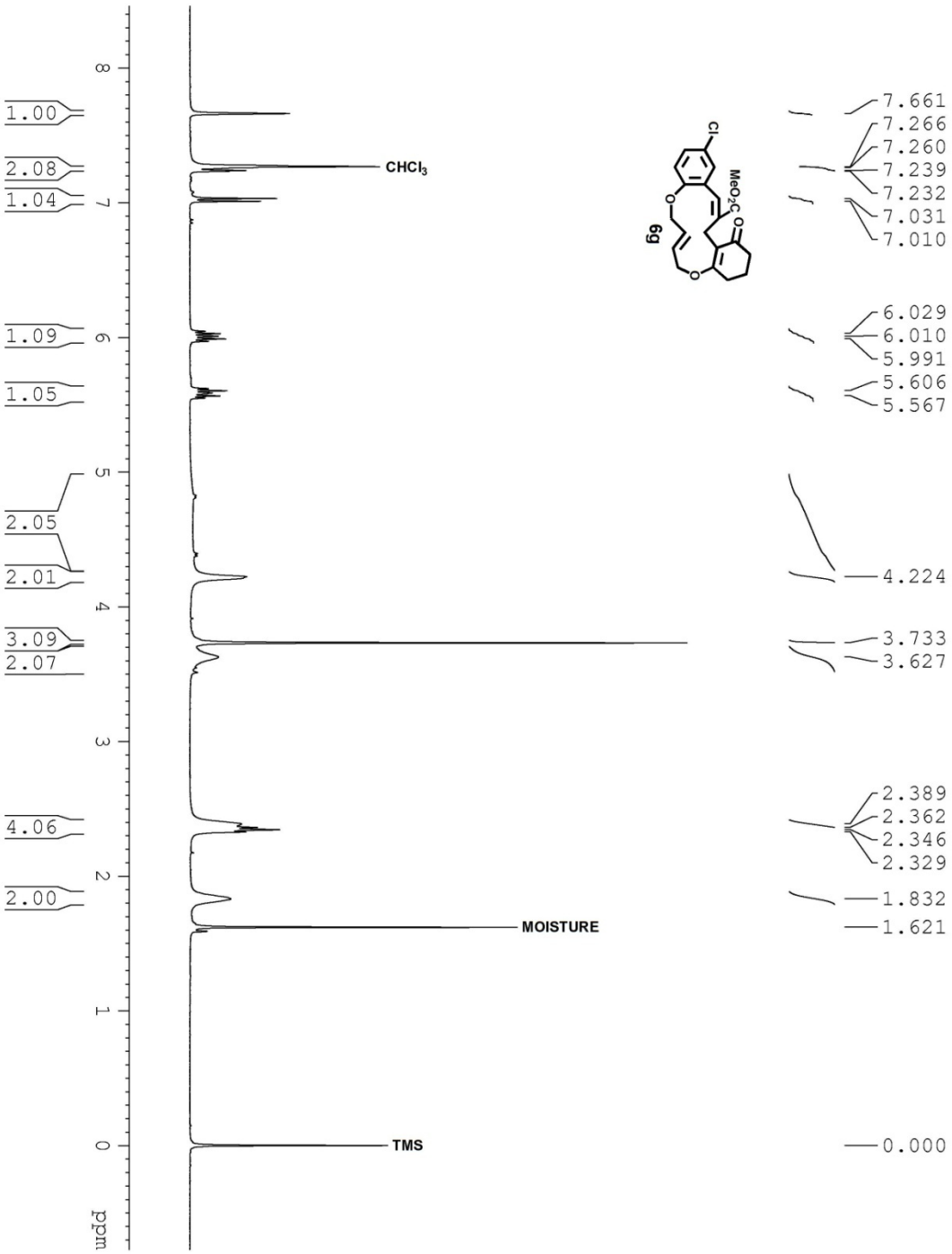


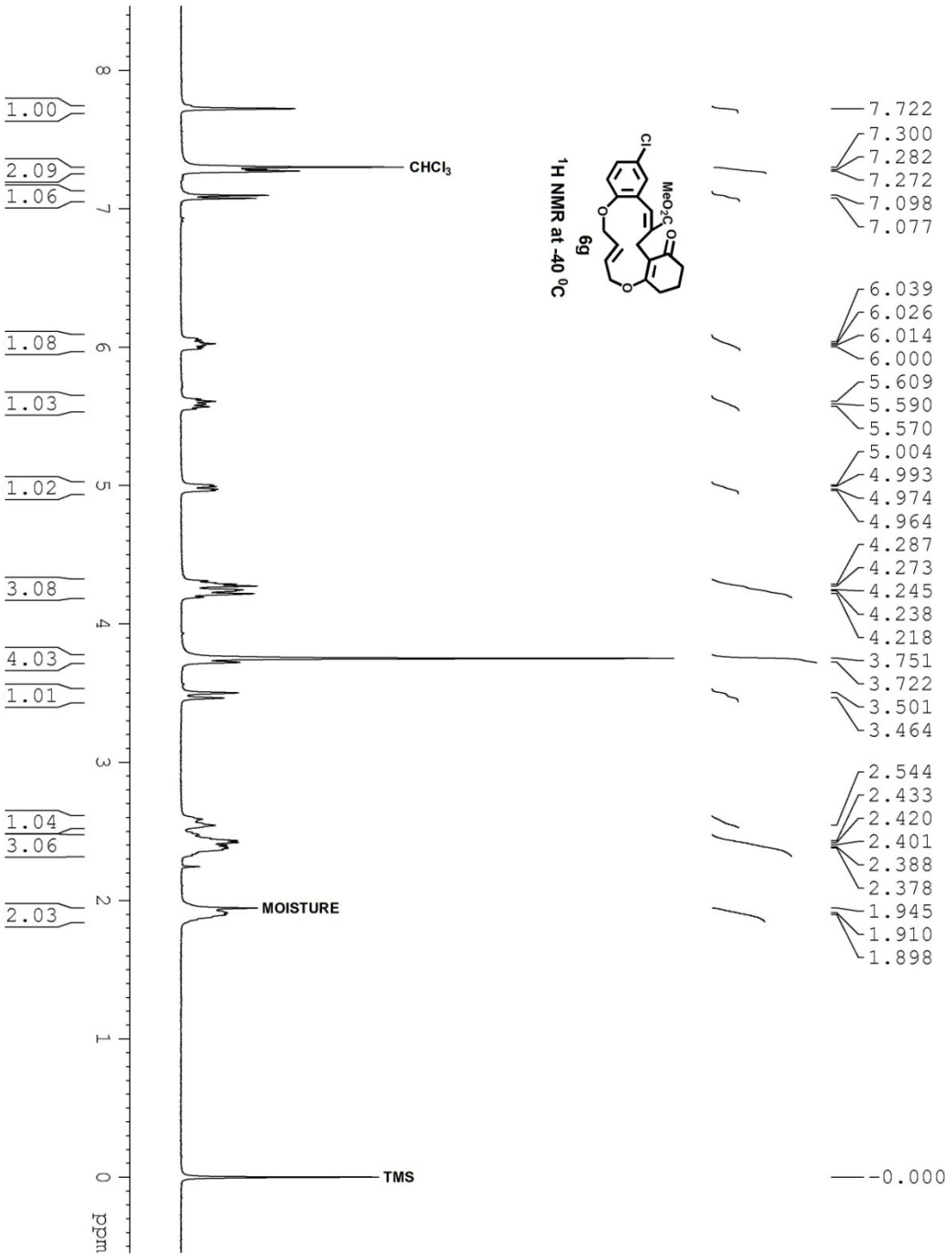









1.00
2.08
1.04
1.09
1.05
2.05
2.01
3.09
2.07
4.06
2.00
CHCl3
MOISTURE
TMS
ppm
8
7
6
5
4
3
2
1
0
6g
7.661
7.266
7.260
7.239
7.232
7.031
7.010
6.029
6.010
5.991
5.606
5.567
4.224
3.733
3.627
2.389
2.362
2.346
2.329
1.832
1.621
0.000


1H NMR at -40 °C
6g
Cl
MeO2C
O
CHCl3
MOISTURE
TMS
ppm
0
1
2
3
4
5
6
7
8
1.00
2.09
1.06
1.08
1.03
1.02
3.08
4.03
1.01
1.04
3.06
2.03
7.722
7.300
7.282
7.272
7.098
7.077
6.039
6.026
6.014
6.000
5.609
5.590
5.570
5.004
4.993
4.974
4.964
4.287
4.273
4.245
4.238
4.218
3.751
3.722
3.501
3.464
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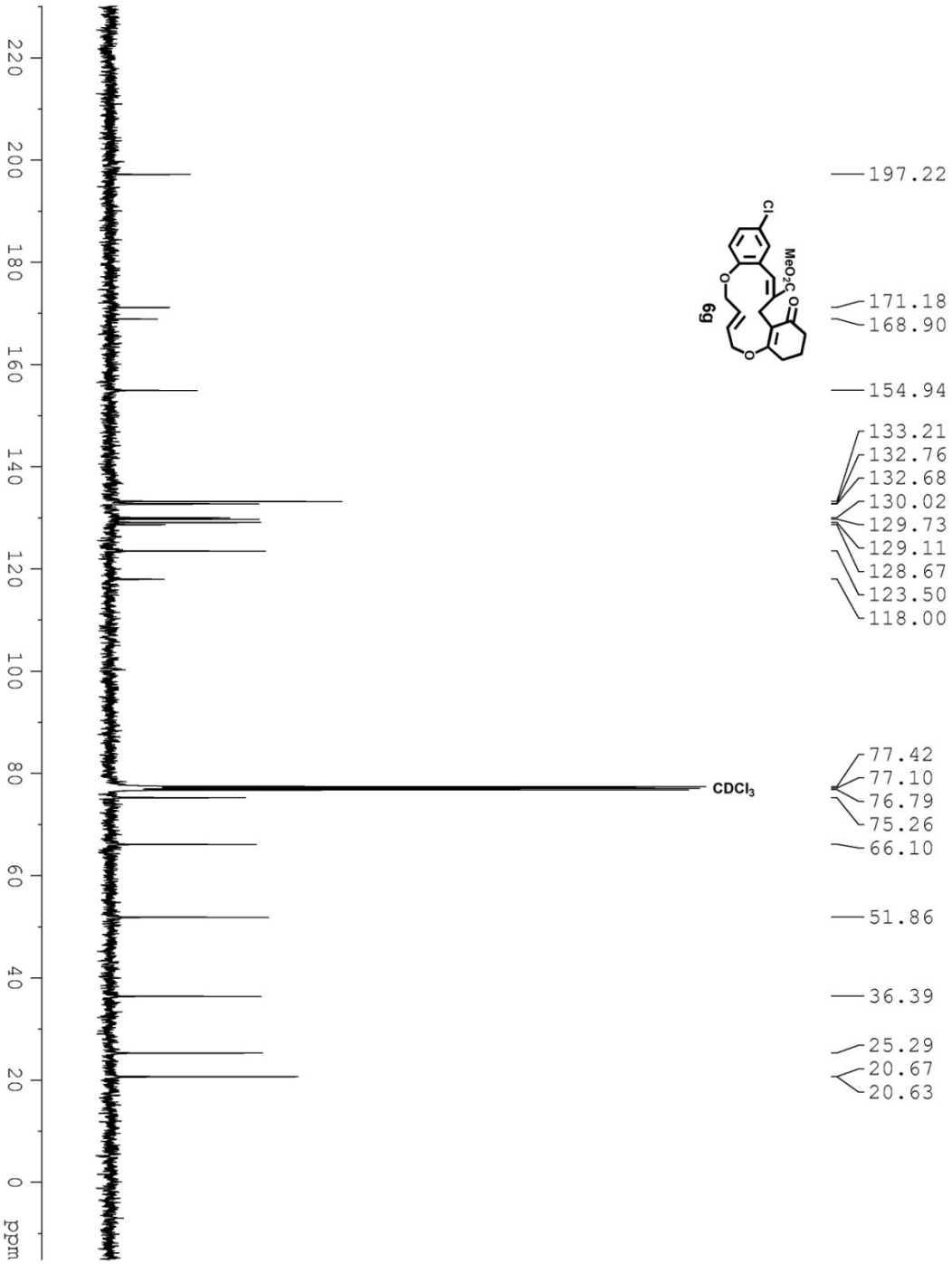
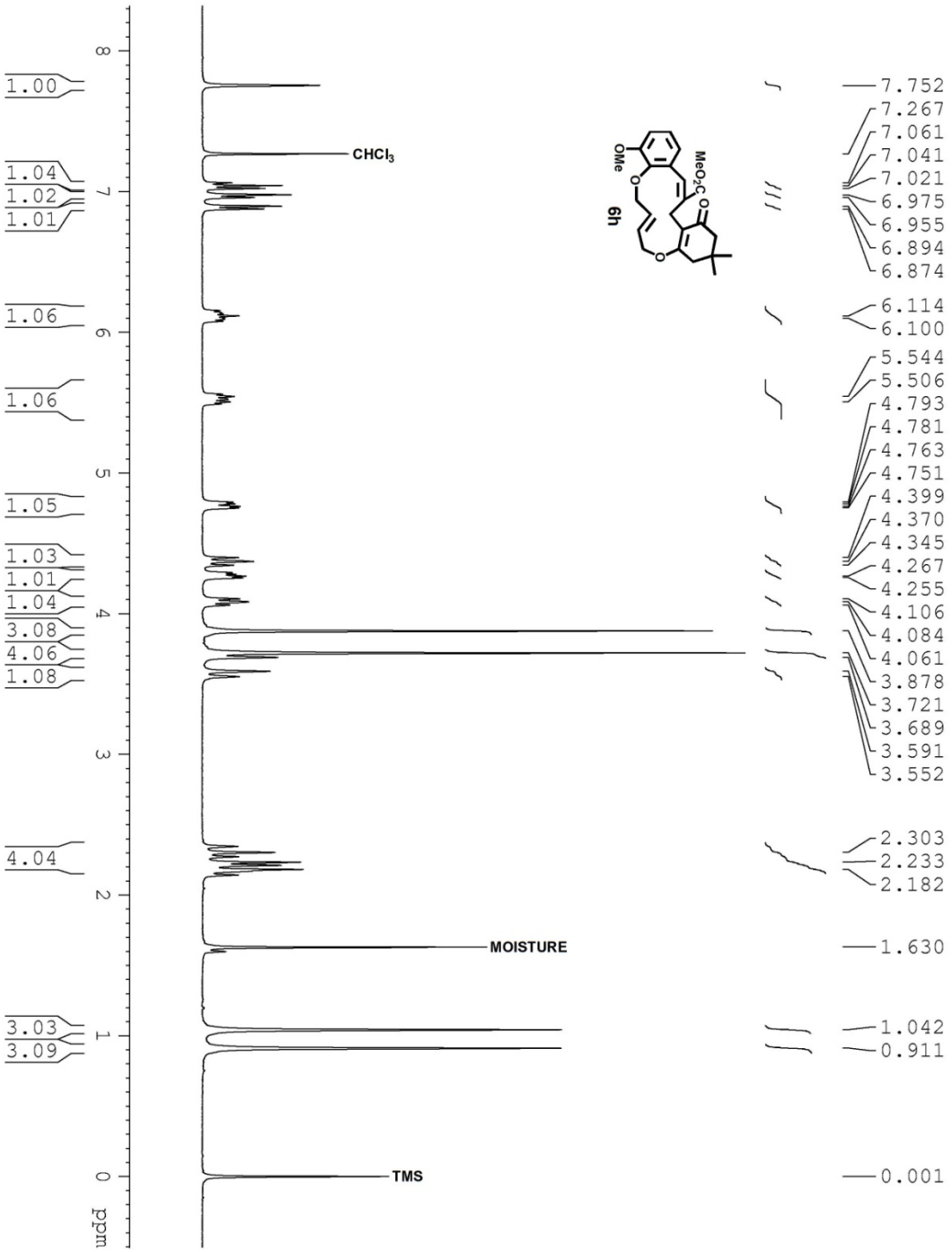
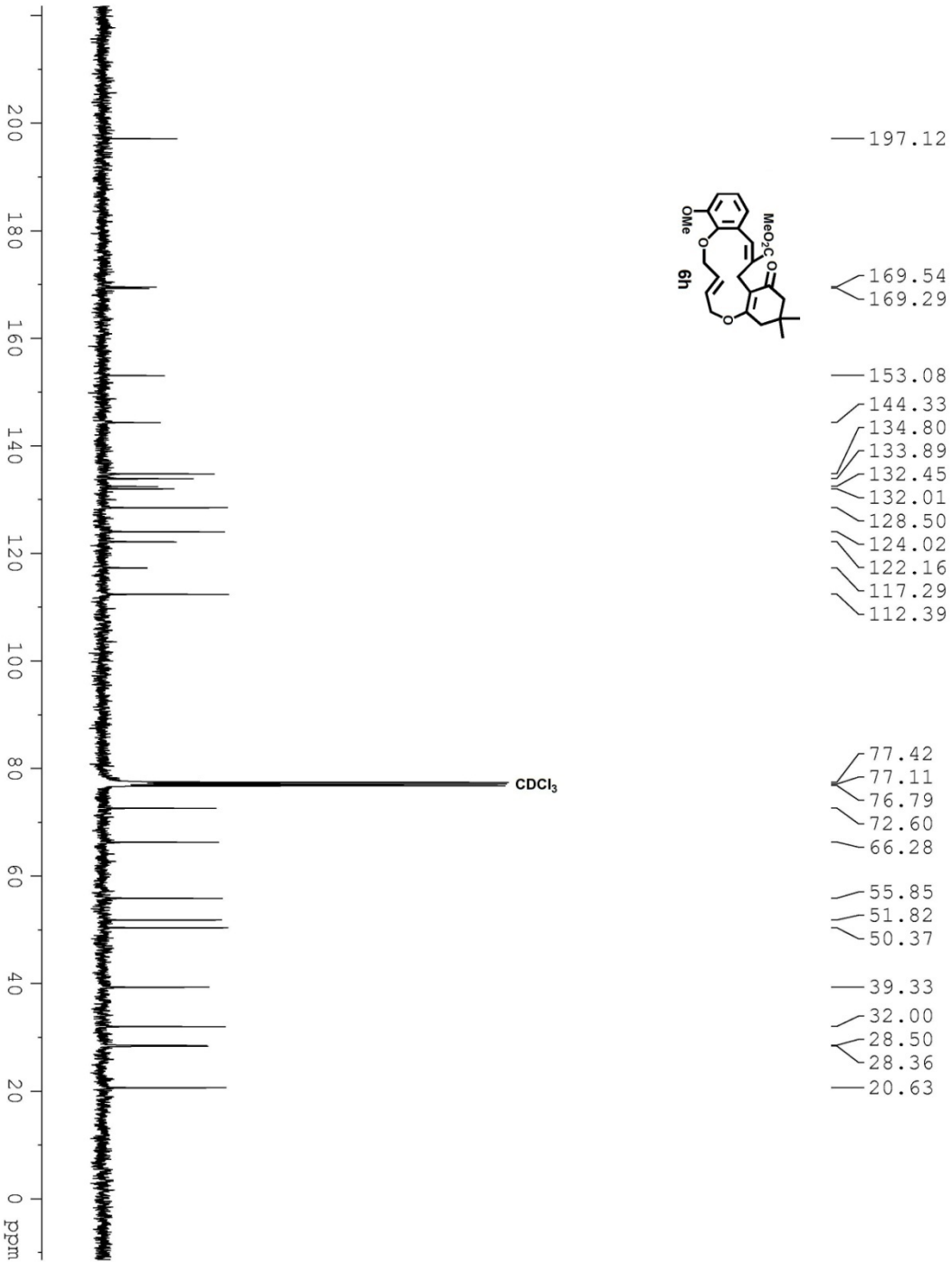
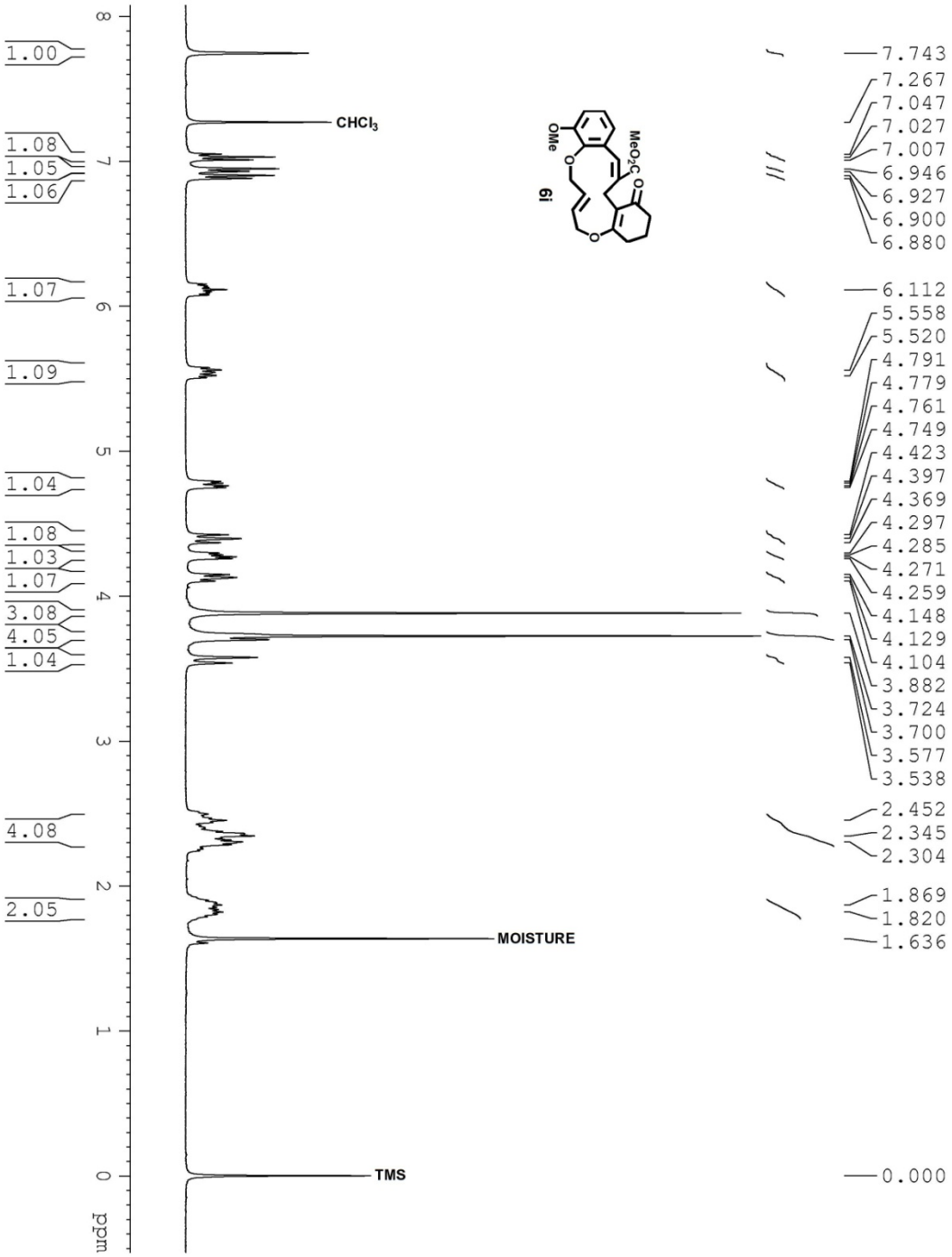
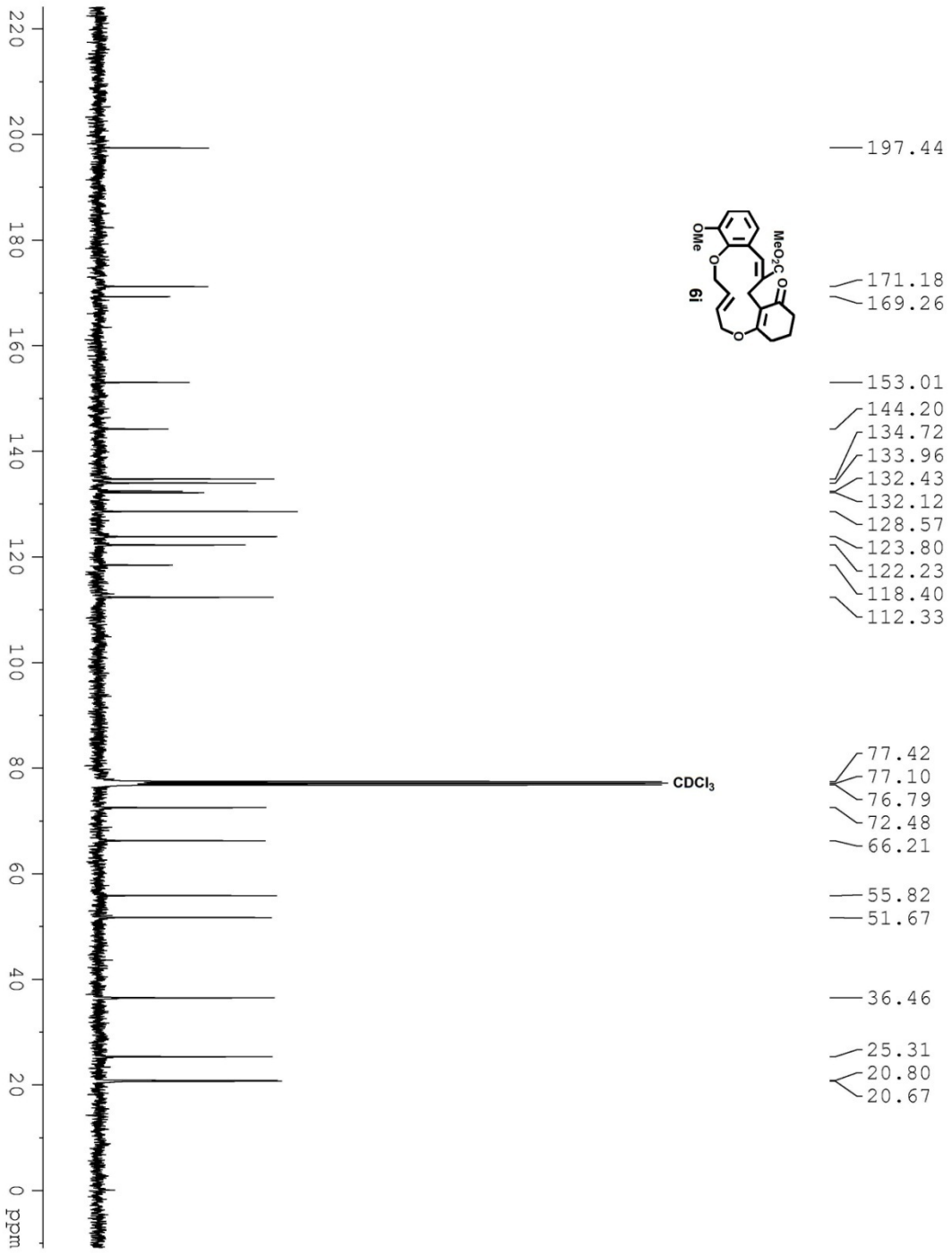
2.433
2.420
2.401
2.388
2.378
1.945
1.910
1.898
-0.000

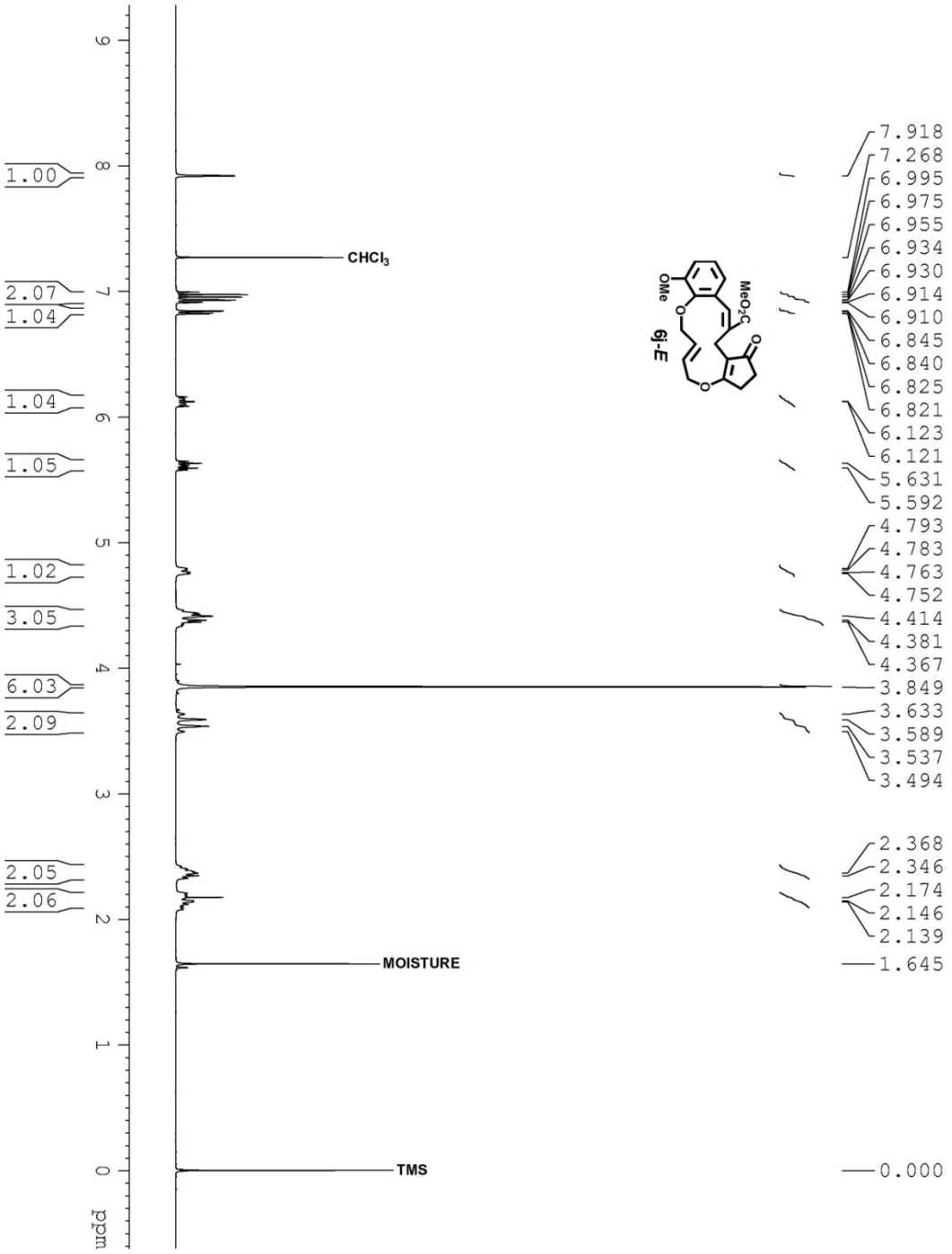











1.00
2.07
1.04
1.04
1.05
1.02
3.05
6.03
2.09
2.05
2.06
CHCl3
MOISTURE
TMS
ppm
OMe
MeO2C
6j-E
7.918
7.268
6.995
6.975
6.955
6.934
6.930
6.914
6.910
6.845
6.840
6.825
6.821
6.123
6.121
5.631
5.592
4.793
4.783
4.763
4.752
4.414
4.381
4.367
3.849
3.633
3.589
3.537
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2.346
2.174
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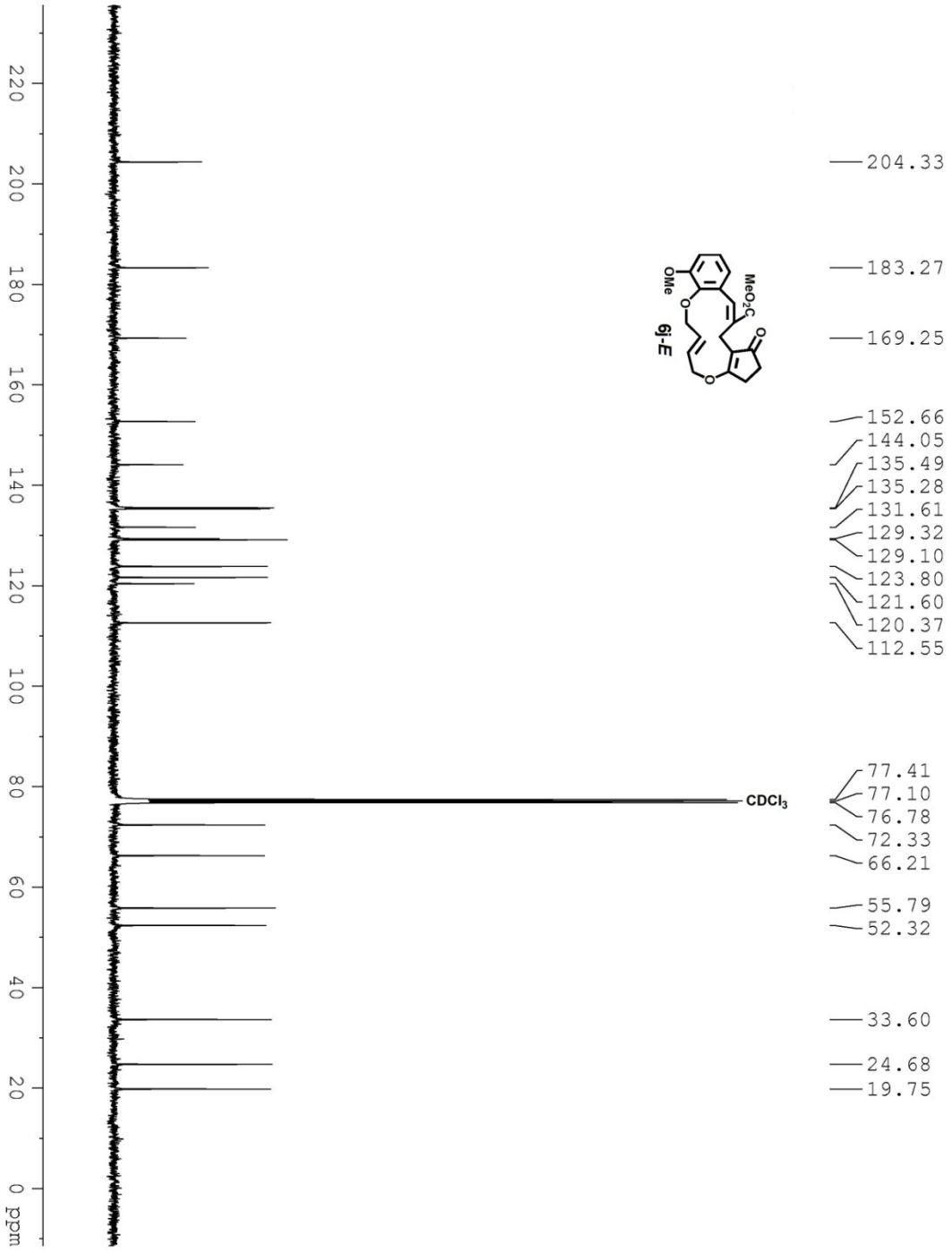
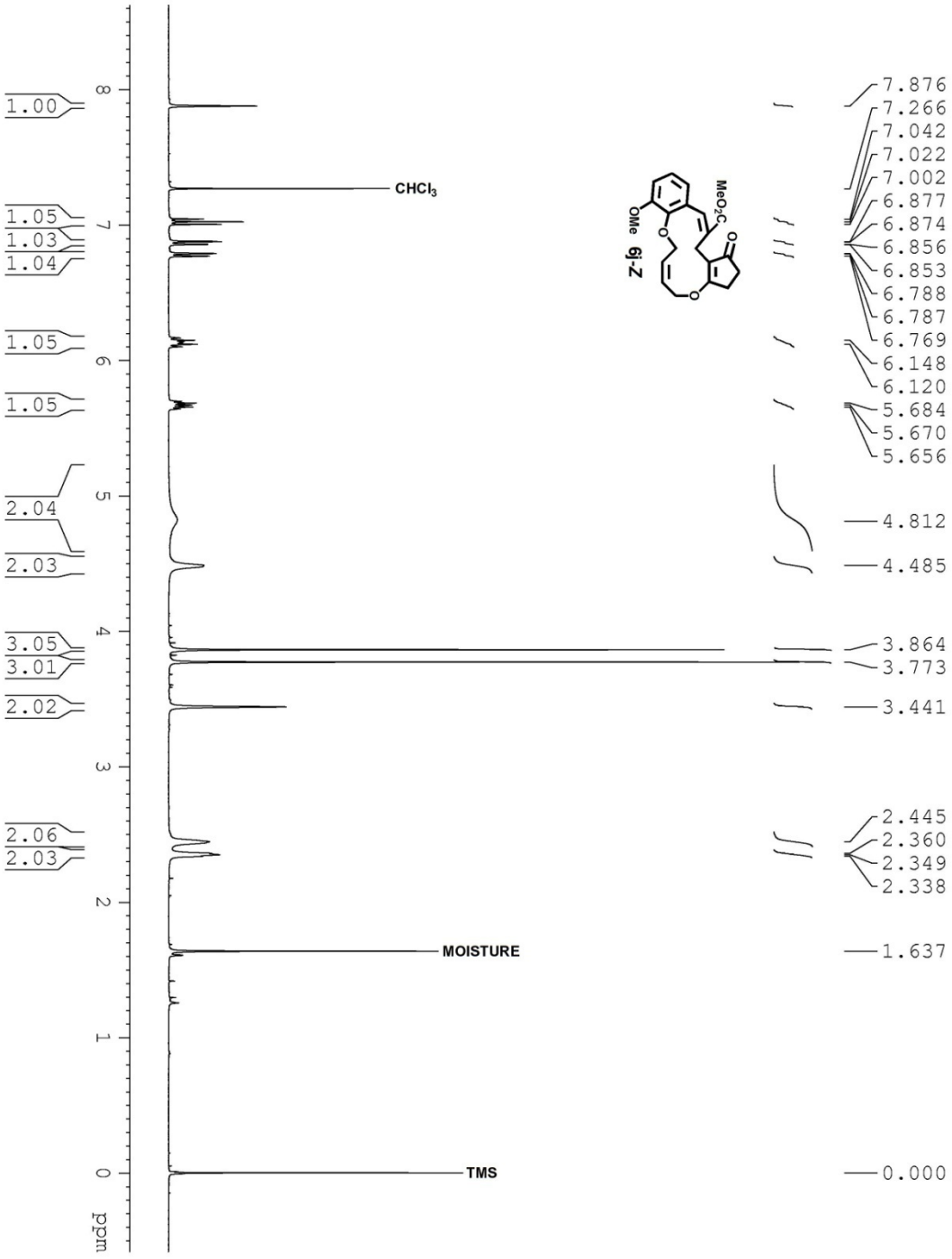
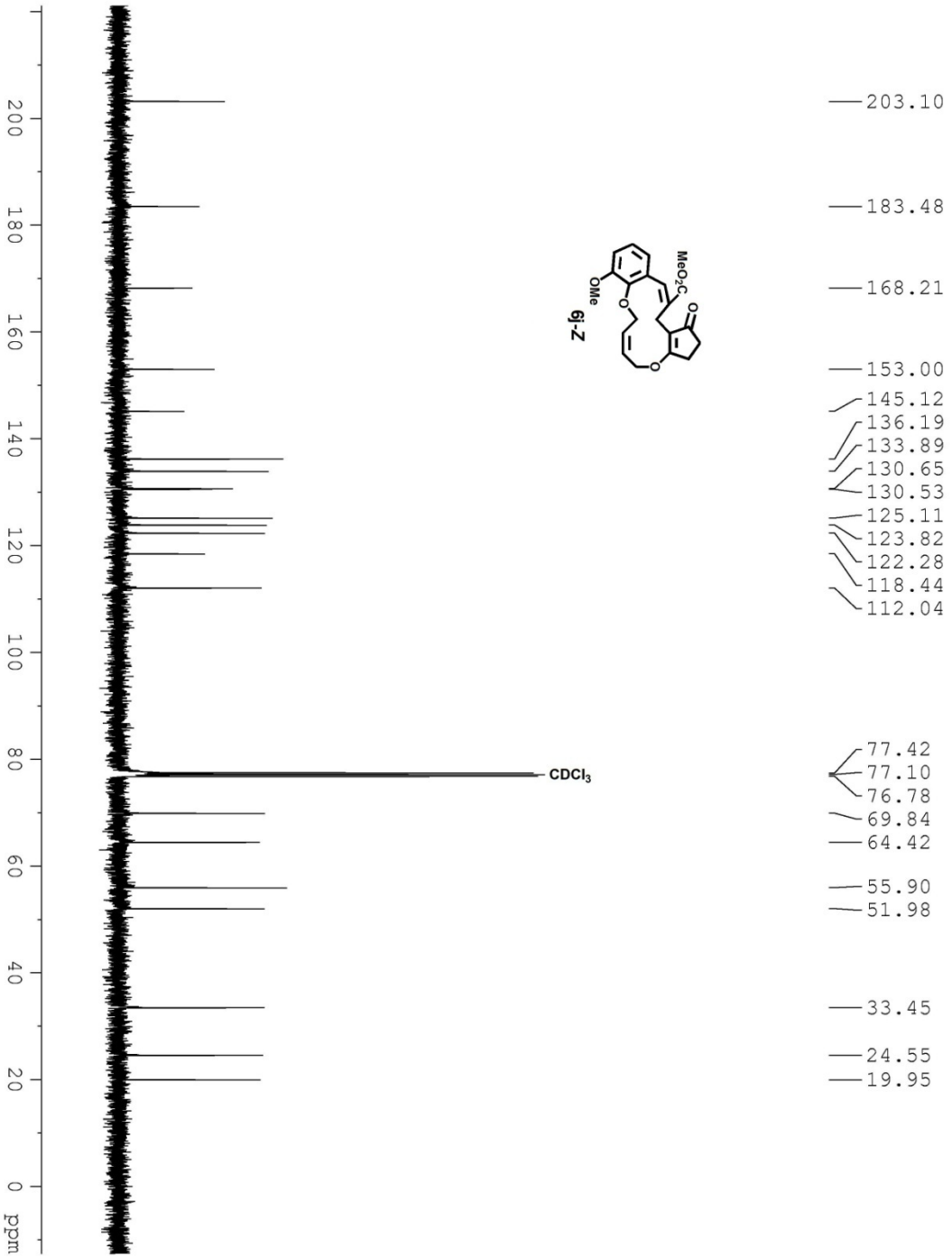
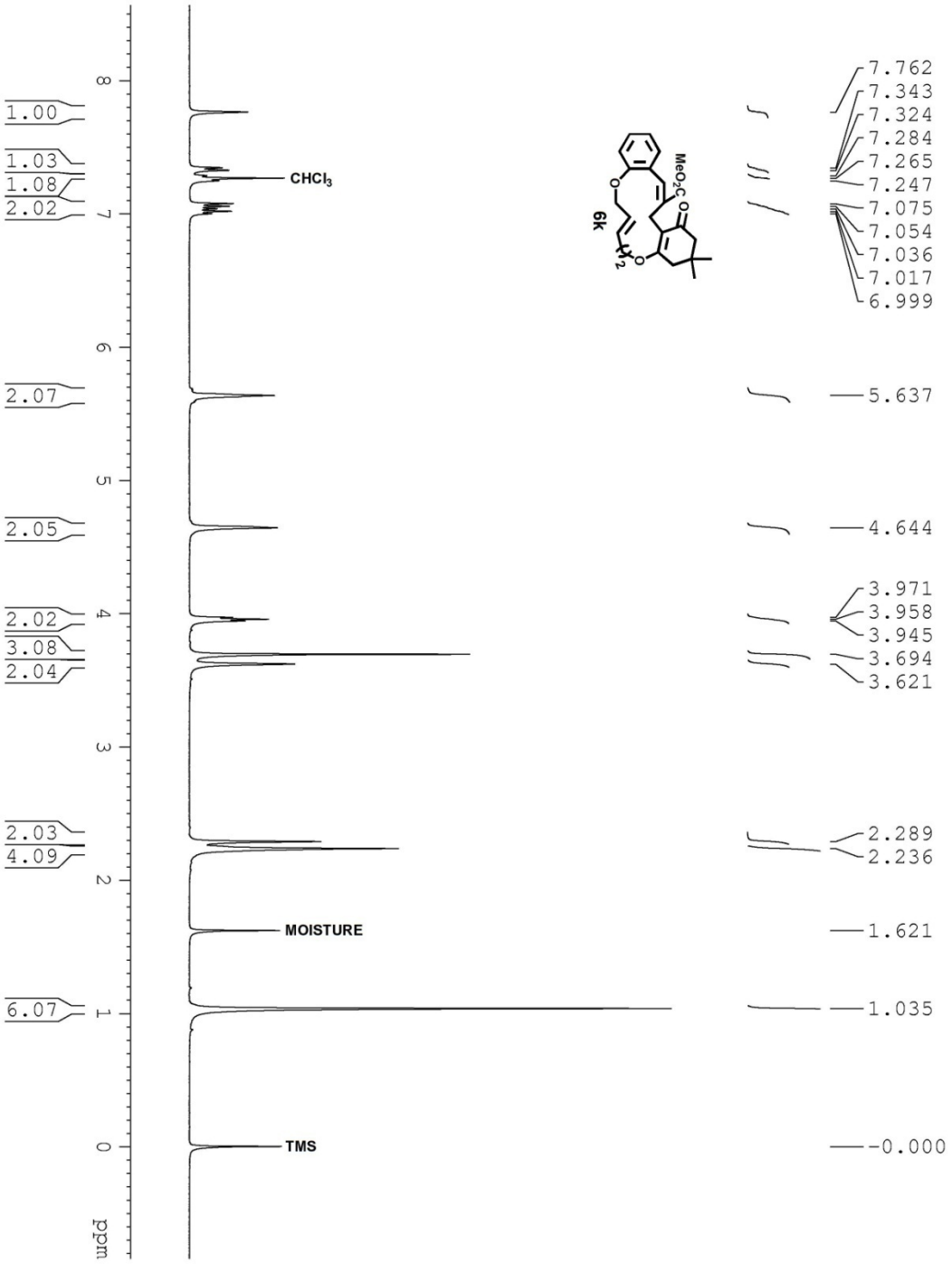
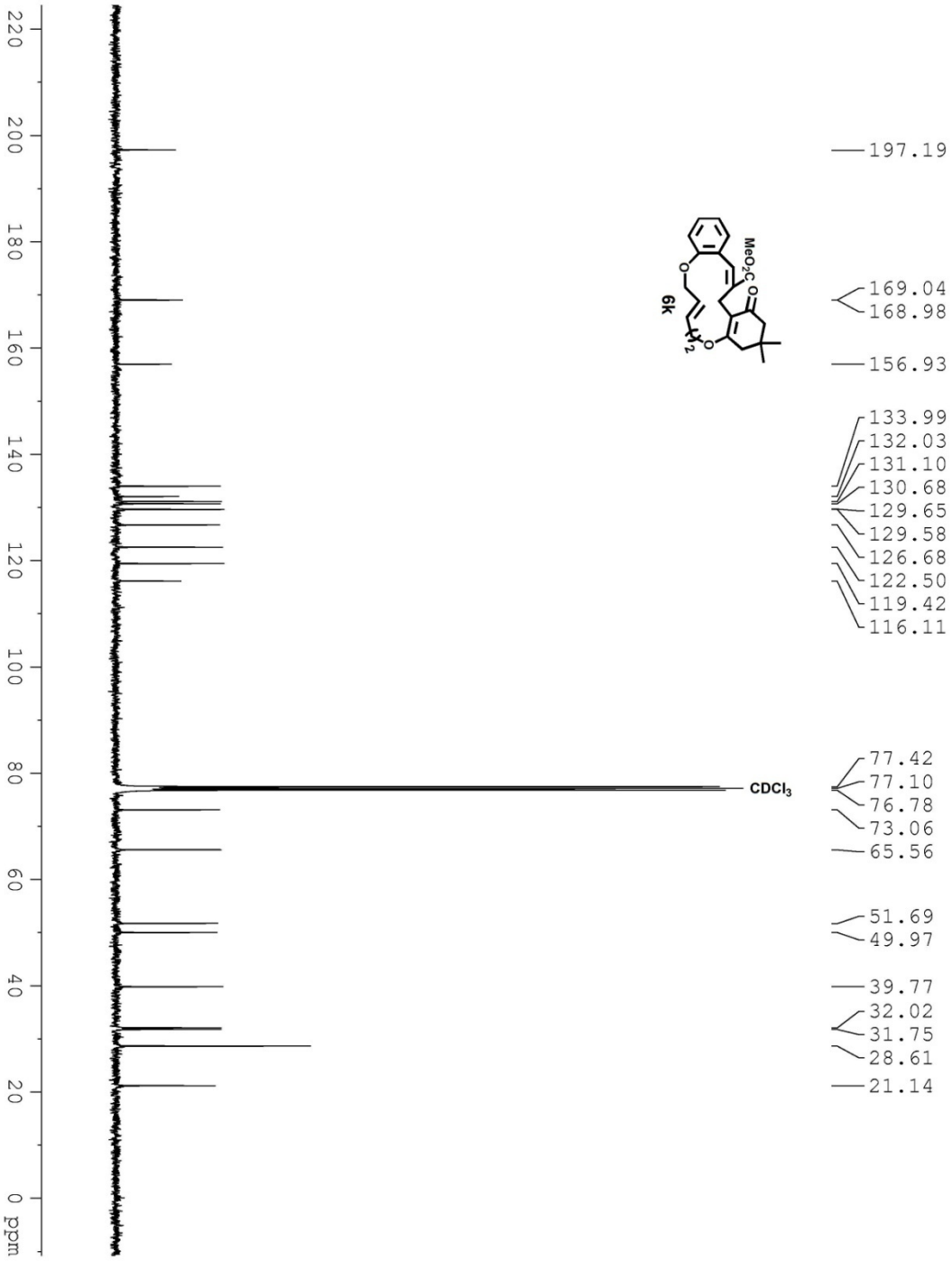
2.139
1.645
0.000

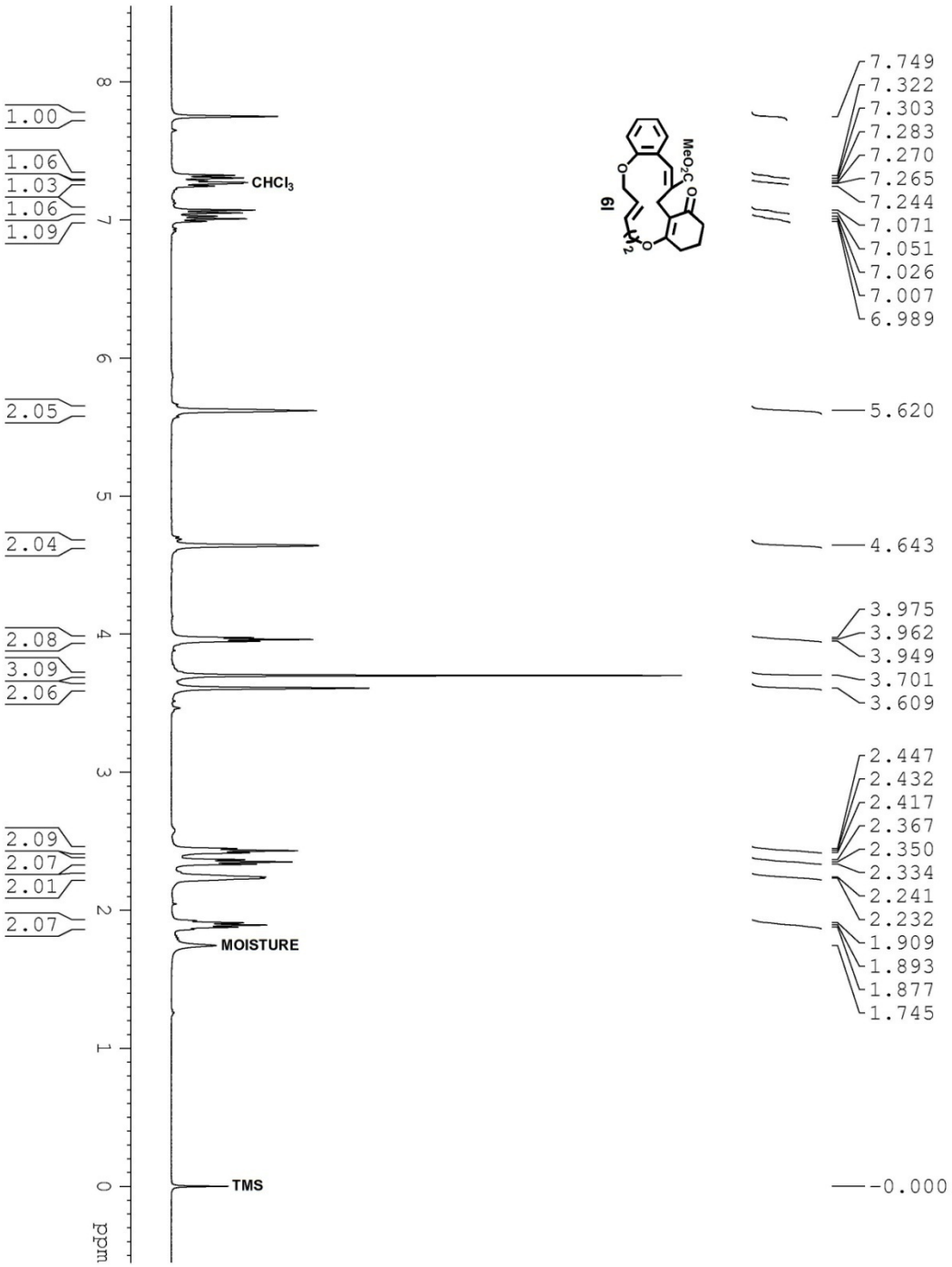







1.00
1.03
1.08
2.02
2.07
2.05
2.02
3.08
2.04
2.03
4.09
6.07
CHCl3
MOISTURE
TMS
ppm
6k
MeO2C
7.762
7.343
7.324
7.284
7.265
7.247
7.075
7.054
7.036
7.017
6.999
5.637
4.644
3.971
3.958
3.945
3.694
3.621
2.289
2.236
1.621
1.035
-0.000




1.00
1.06
1.03
1.06
1.09
2.05
2.04
2.08
3.09
2.06
2.09
2.07
2.01
2.07
CHCl3
MOISTURE
TMS
ppm
8
7
6
5
4
3
2
1
0
MeO2C
O
O
O
O
6l
7.749
7.322
7.303
7.283
7.270
7.265
7.244
7.071
7.051
7.026
7.007
6.989
5.620
4.643
3.975
3.962
3.949
3.701
3.609
2.447
2.432
2.417
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2.350
2.334
2.241
2.232
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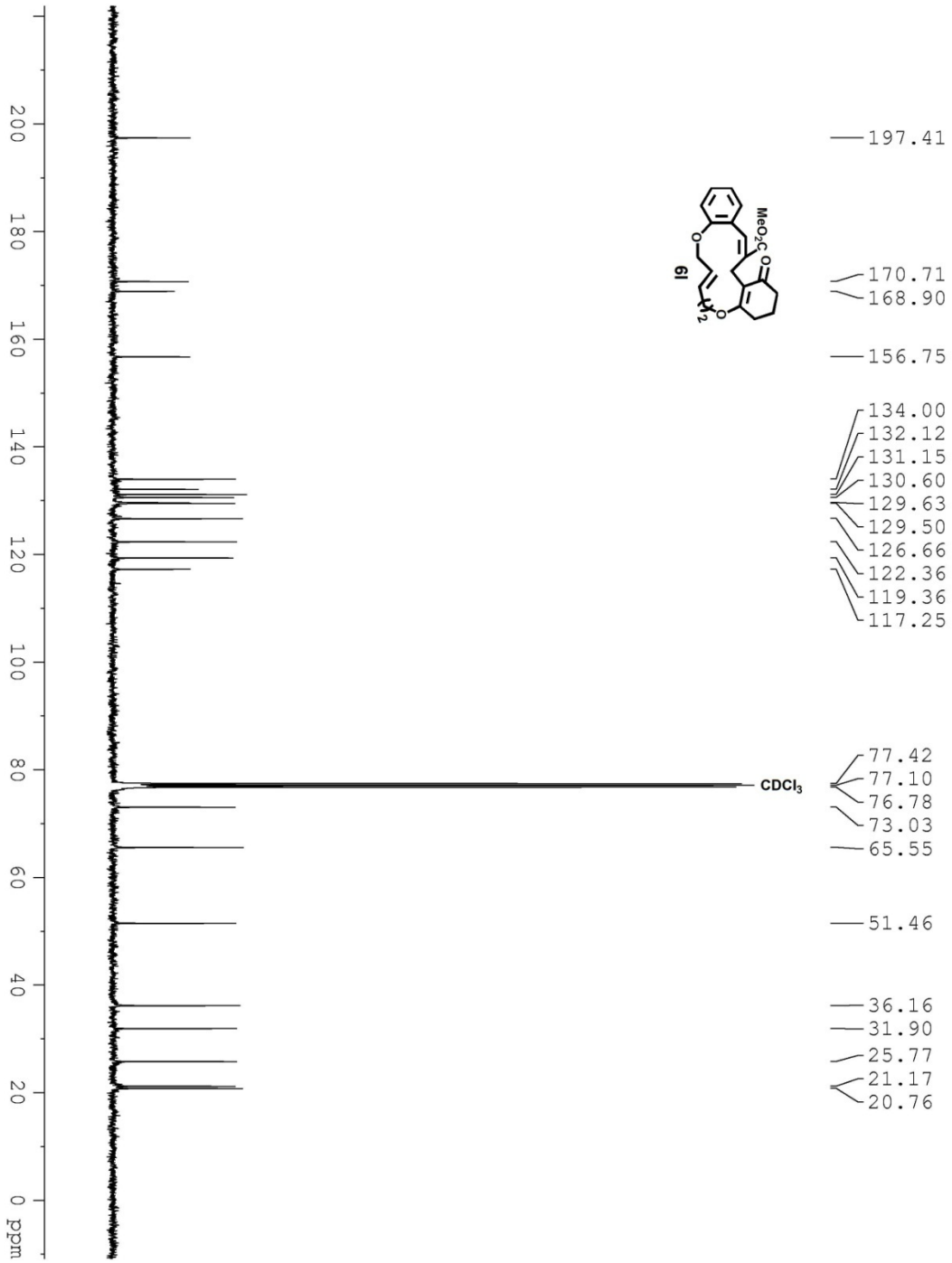
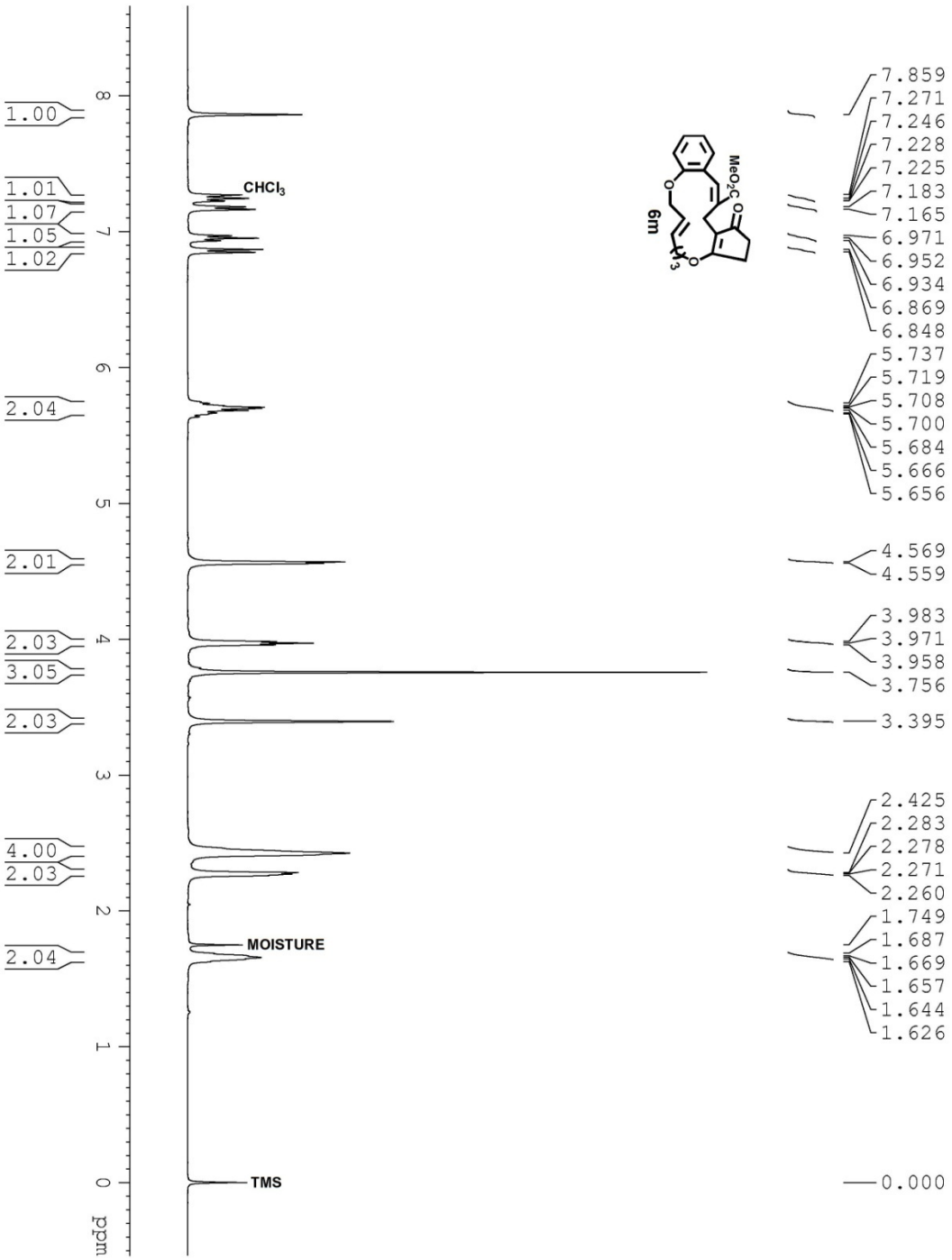
1.893
1.877
1.745
-0.000




1.00
1.01
1.07
1.05
1.02
2.04
2.01
2.03
3.05
2.03
4.00
2.03
2.04
CHCl3
MOISTURE
TMS
ppm
6m
MeO2C
7.859
7.271
7.246
7.228
7.225
7.183
7.165
6.971
6.952
6.934
6.869
6.848
5.737
5.719
5.708
5.700
5.684
5.666
5.656
4.569
4.559
3.983
3.971
3.958
3.756
3.395
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2.271
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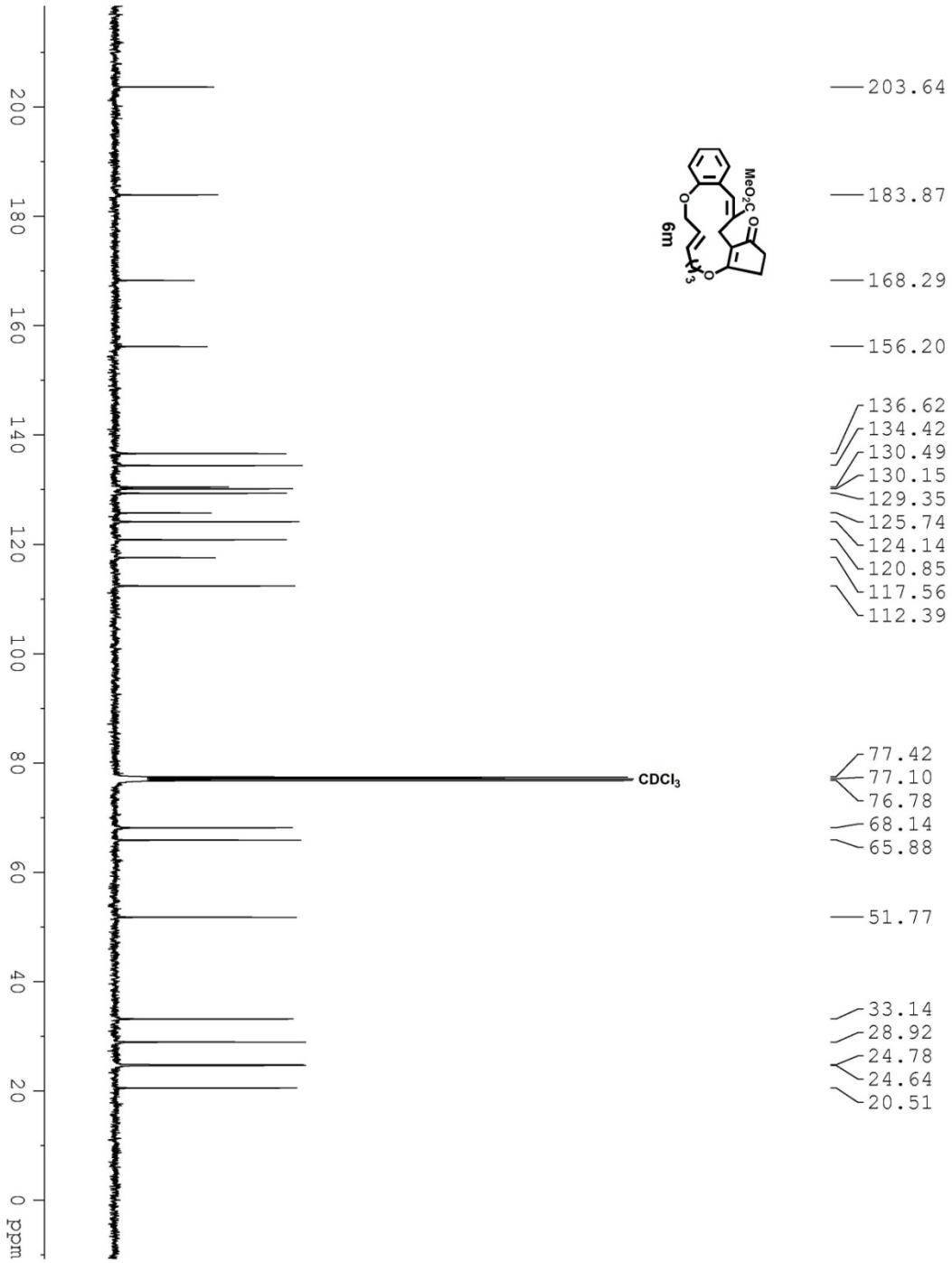
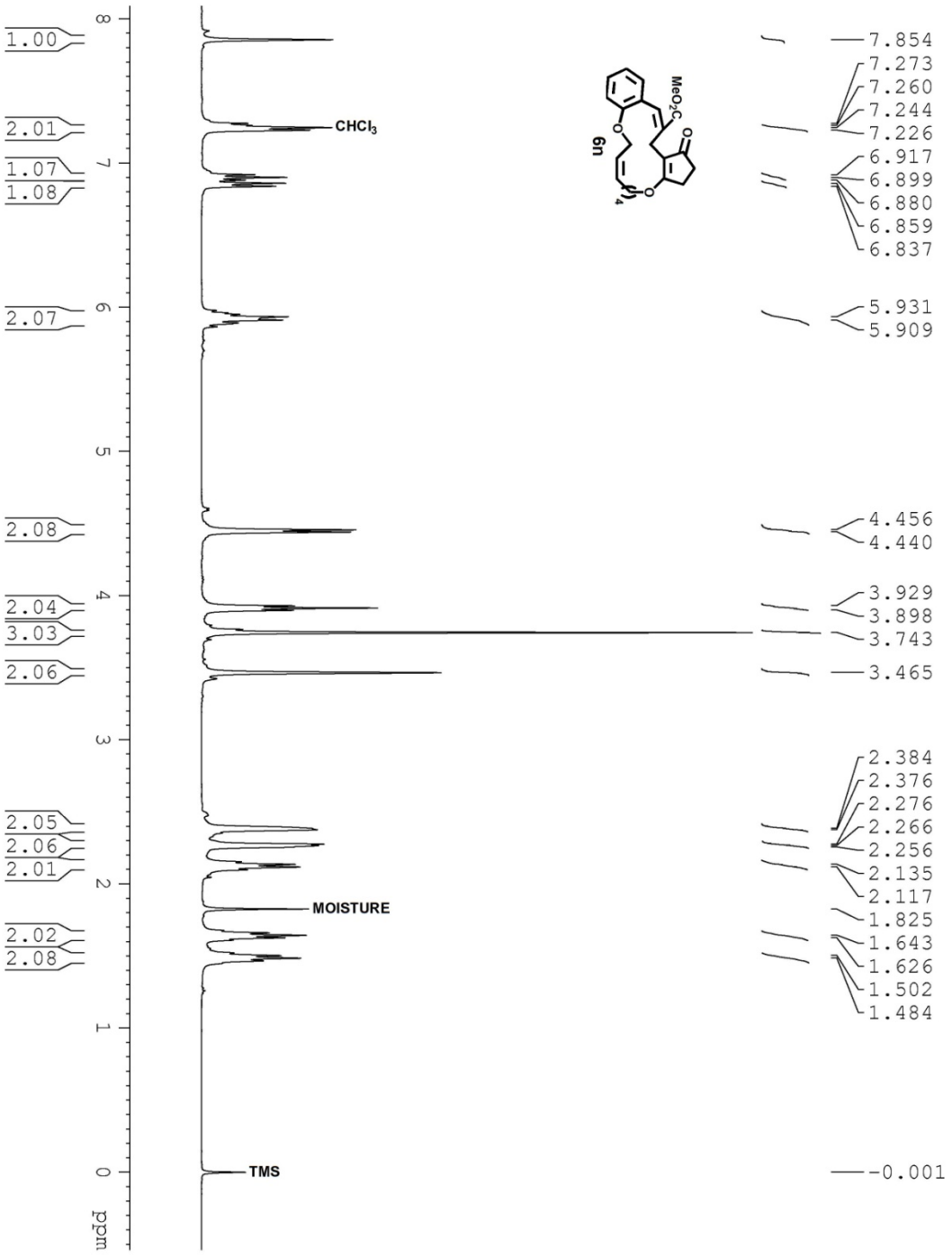
1.626
0.000




1.00
2.01
1.07
1.08
2.07
2.08
2.04
3.03
2.06
2.05
2.06
2.01
2.02
2.08
CHCl3
MOISTURE
TMS
ppm
6n
MeO2C
7.854
7.273
7.260
7.244
7.226
6.917
6.899
6.880
6.859
6.837
5.931
5.909
4.456
4.440
3.929
3.898
3.743
3.465
2.384
2.376
2.276
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2.256
2.135
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1.626
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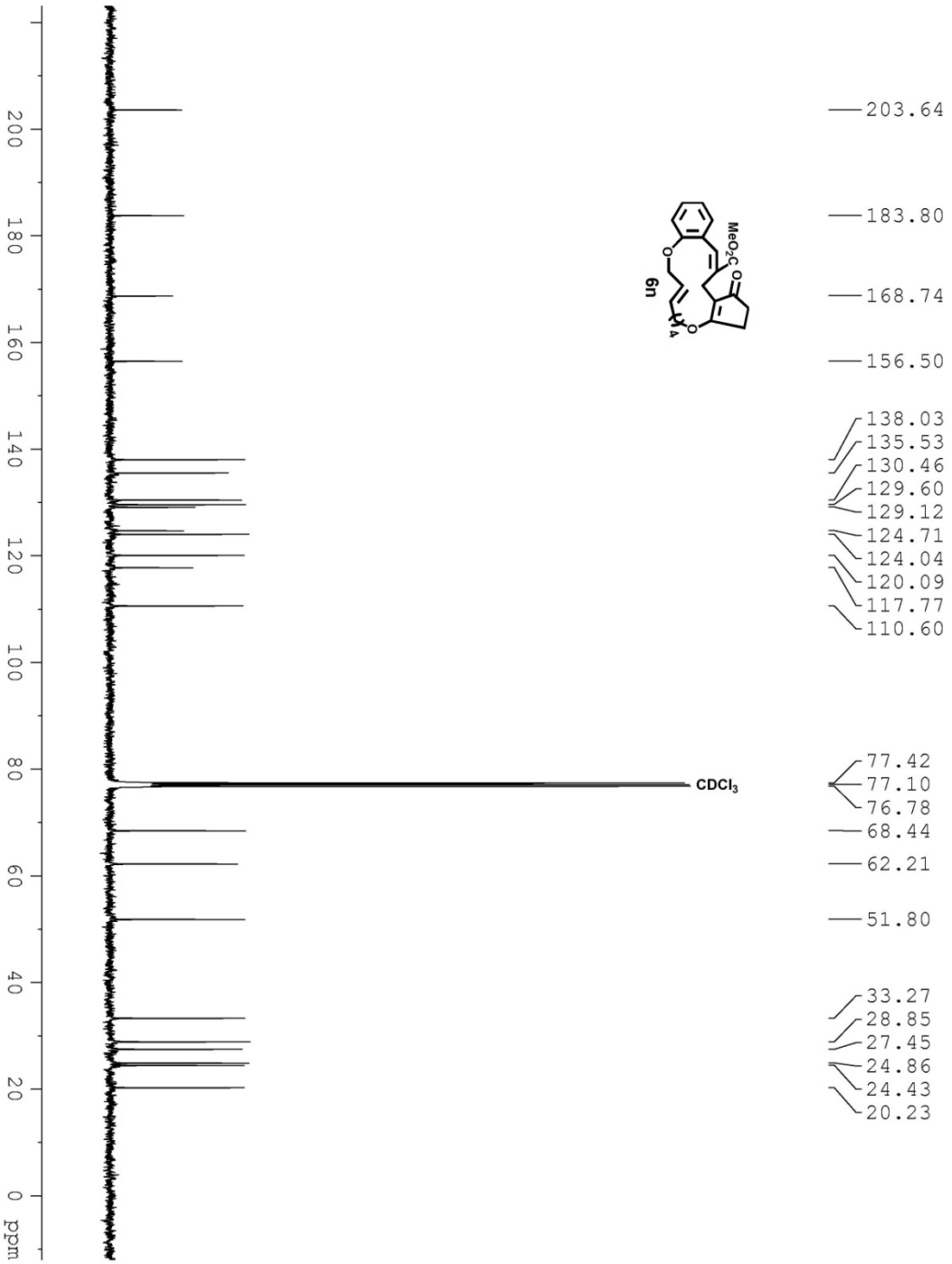
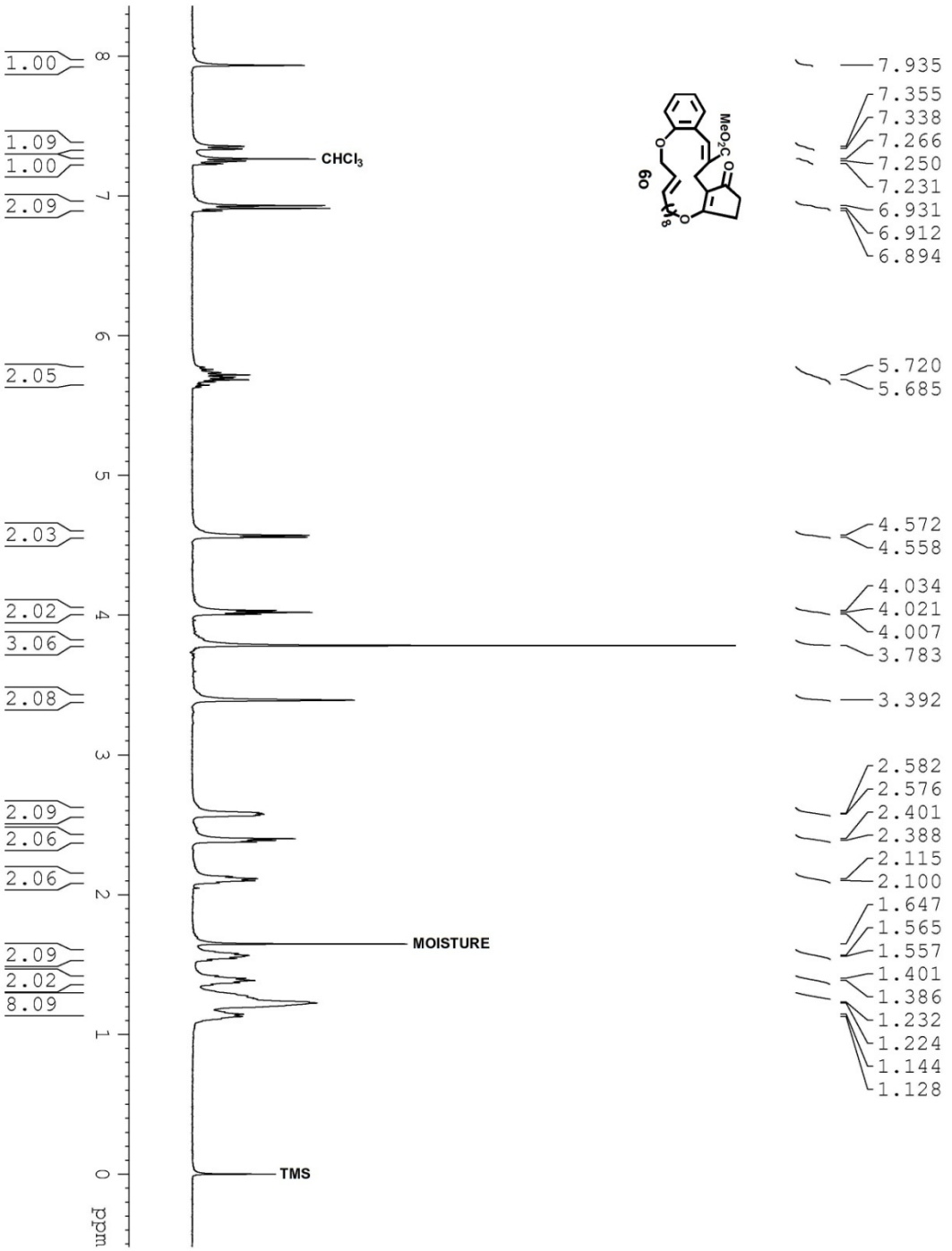
1.484
-0.001




1.00
1.09
1.00
2.09
2.05
2.03
2.02
3.06
2.08
2.09
2.06
2.06
2.09
2.02
8.09
CHCl3
MOISTURE
TMS
ppm
6o
MeO2C
7.935
7.355
7.338
7.266
7.250
7.231
6.931
6.912
6.894
5.720
5.685
4.572
4.558
4.034
4.021
4.007
3.783
3.392
2.582
2.576
2.401
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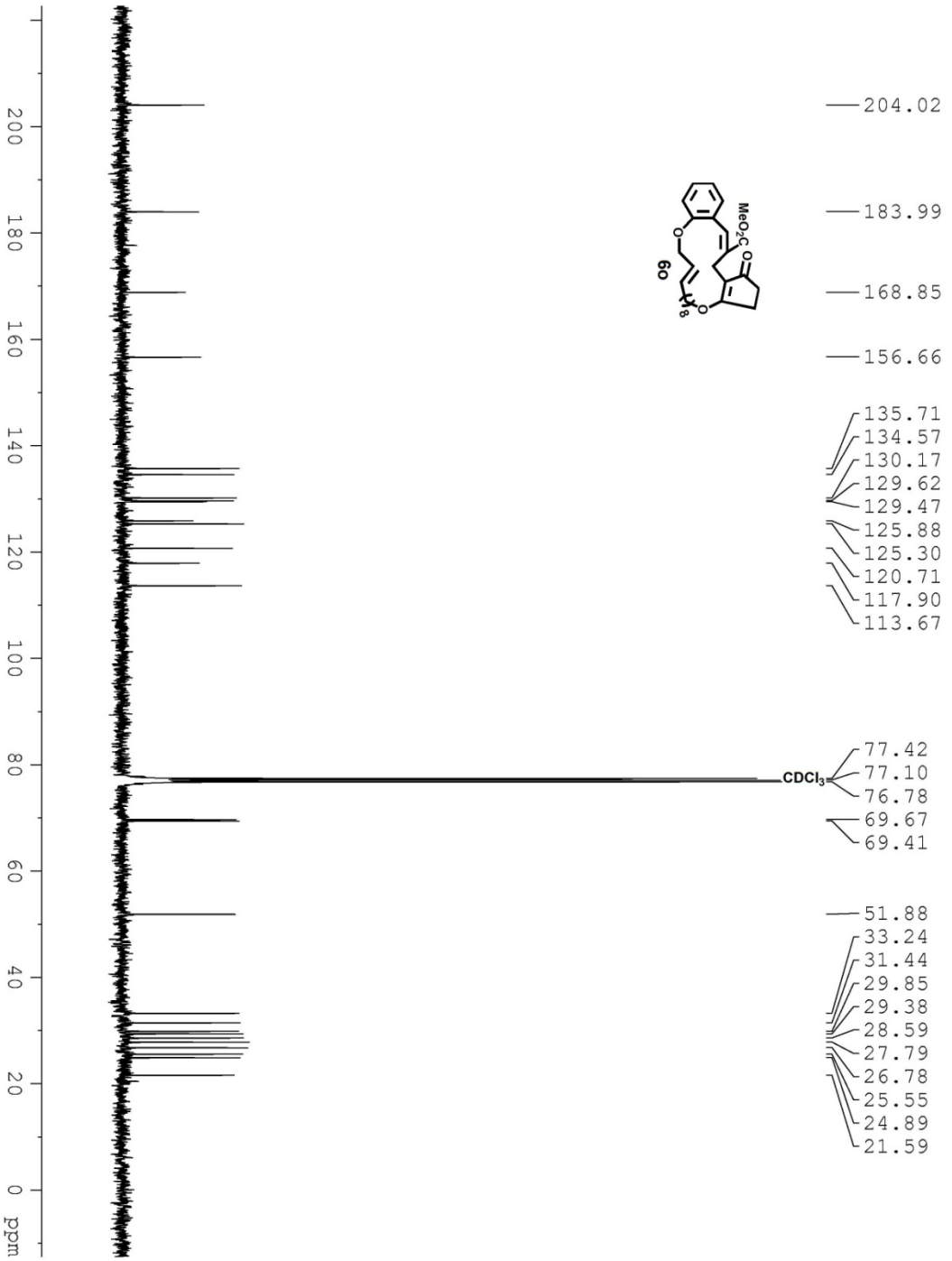
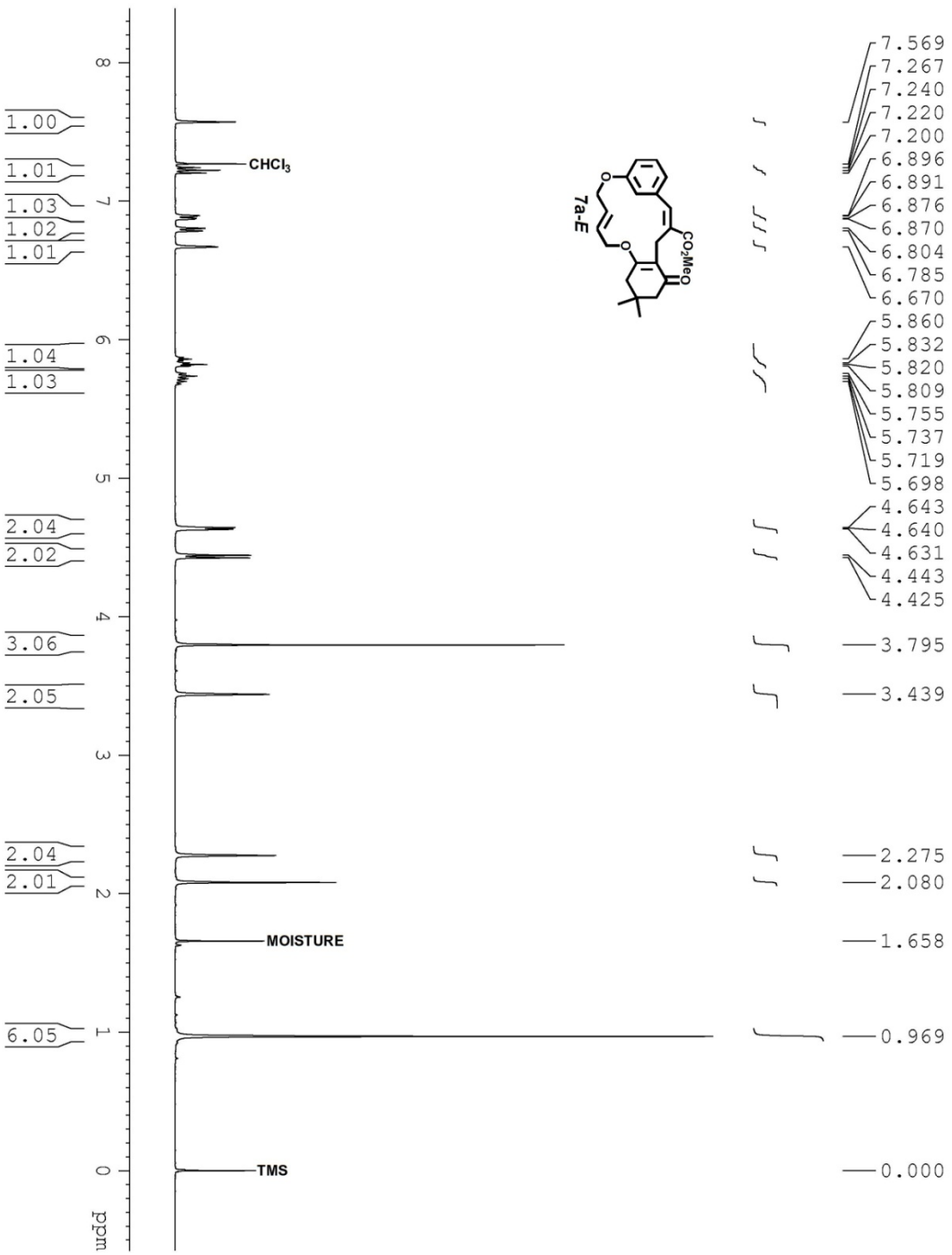
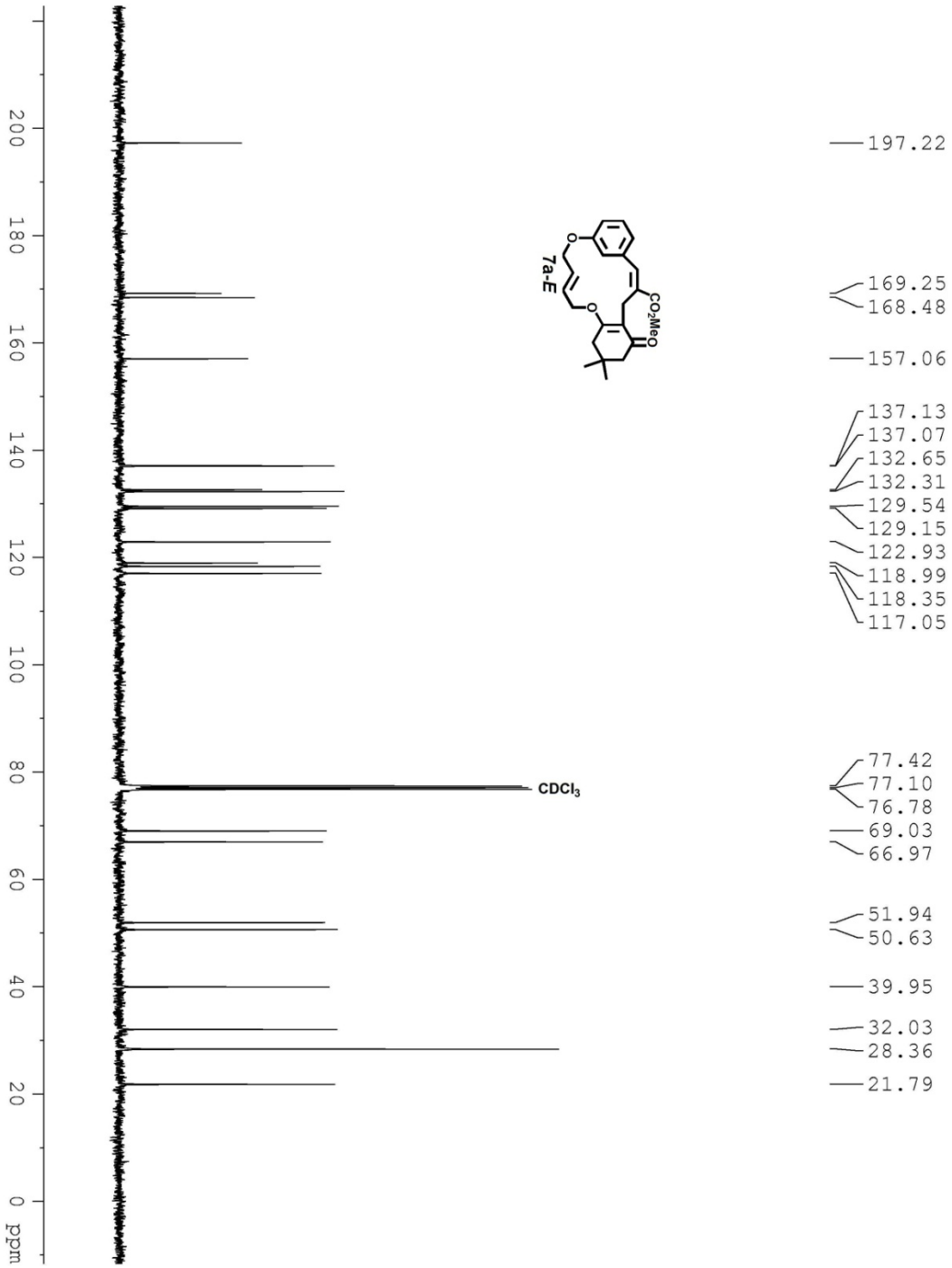
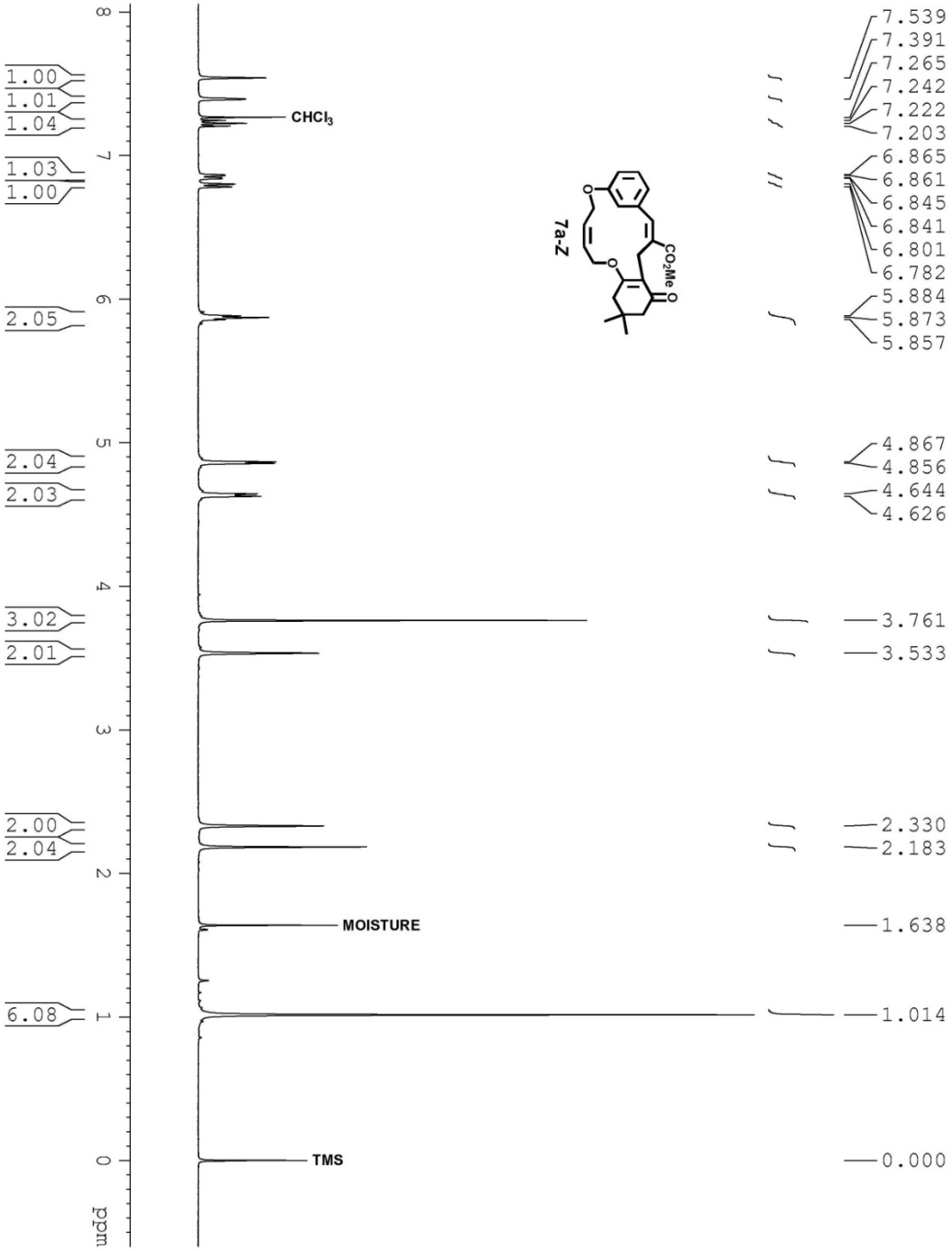
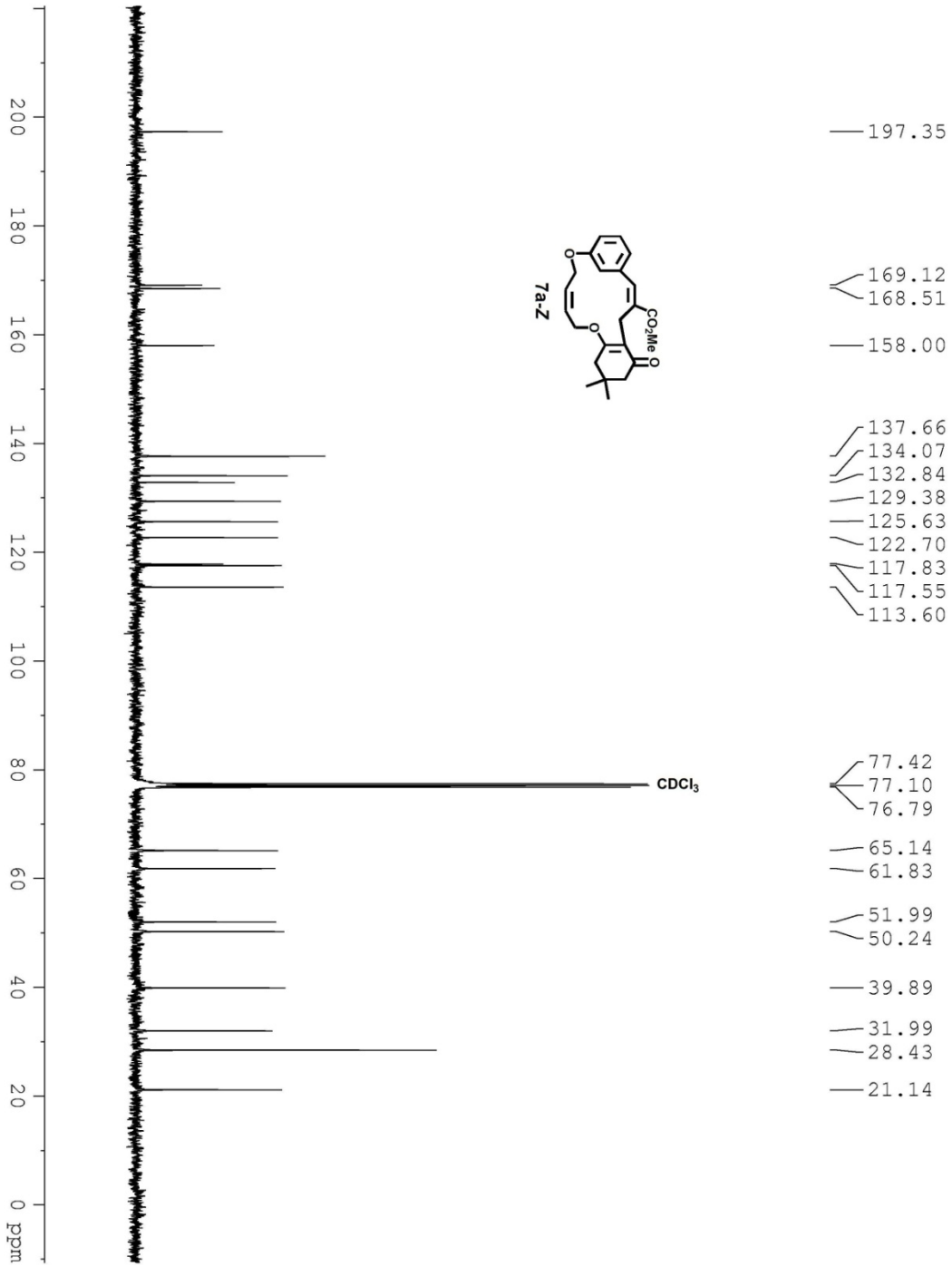
1.401
1.386
1.232
1.224
1.144
1.128

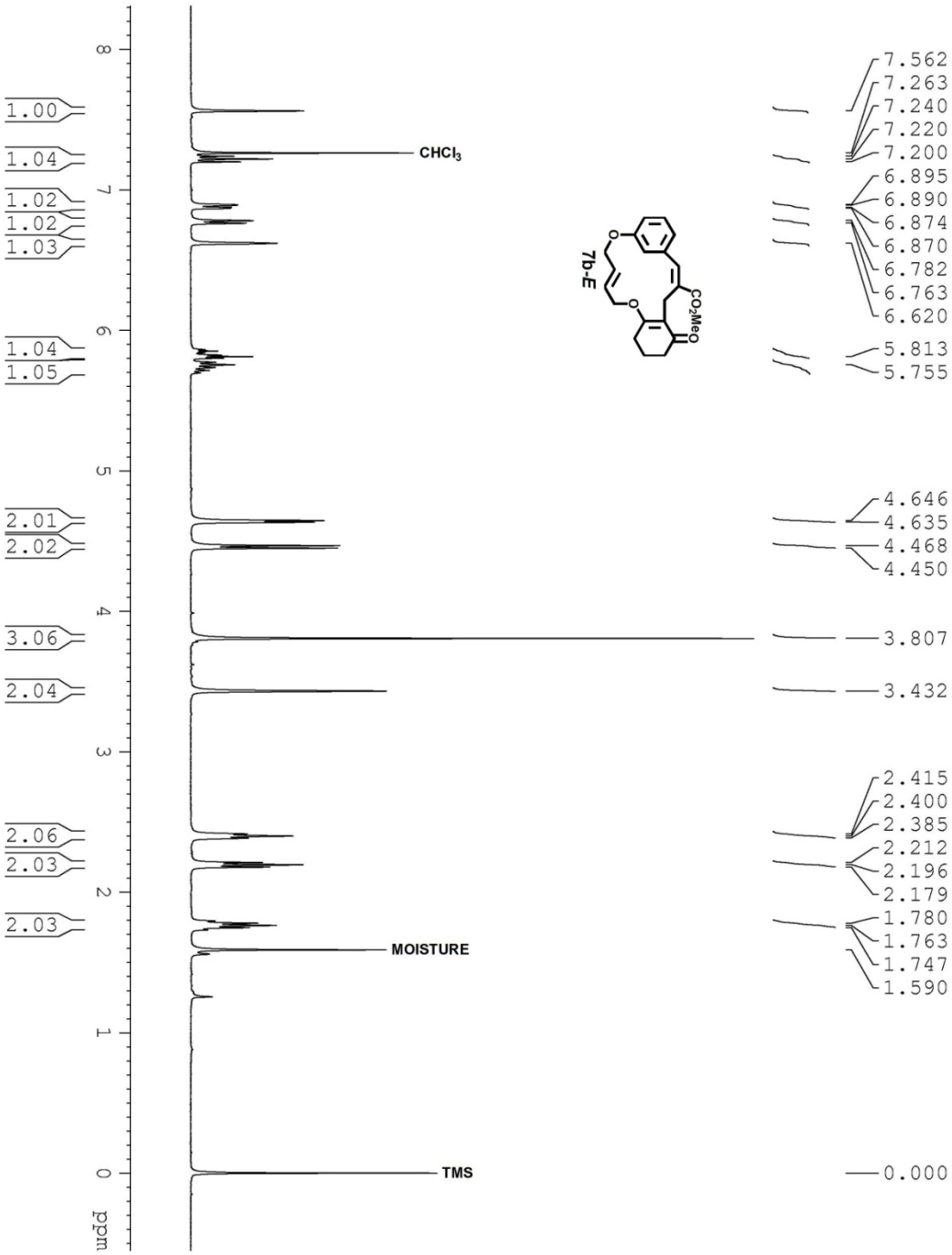


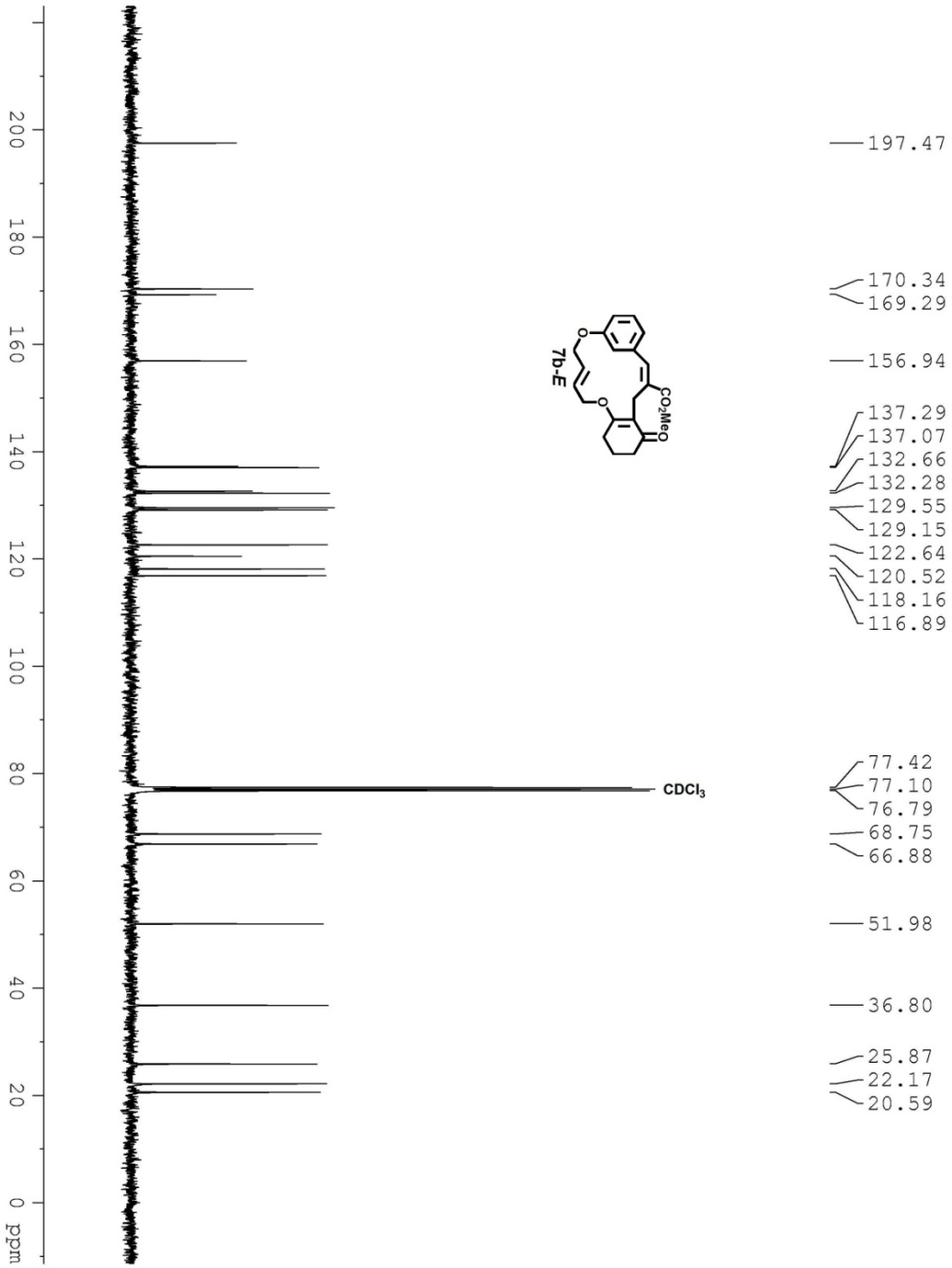


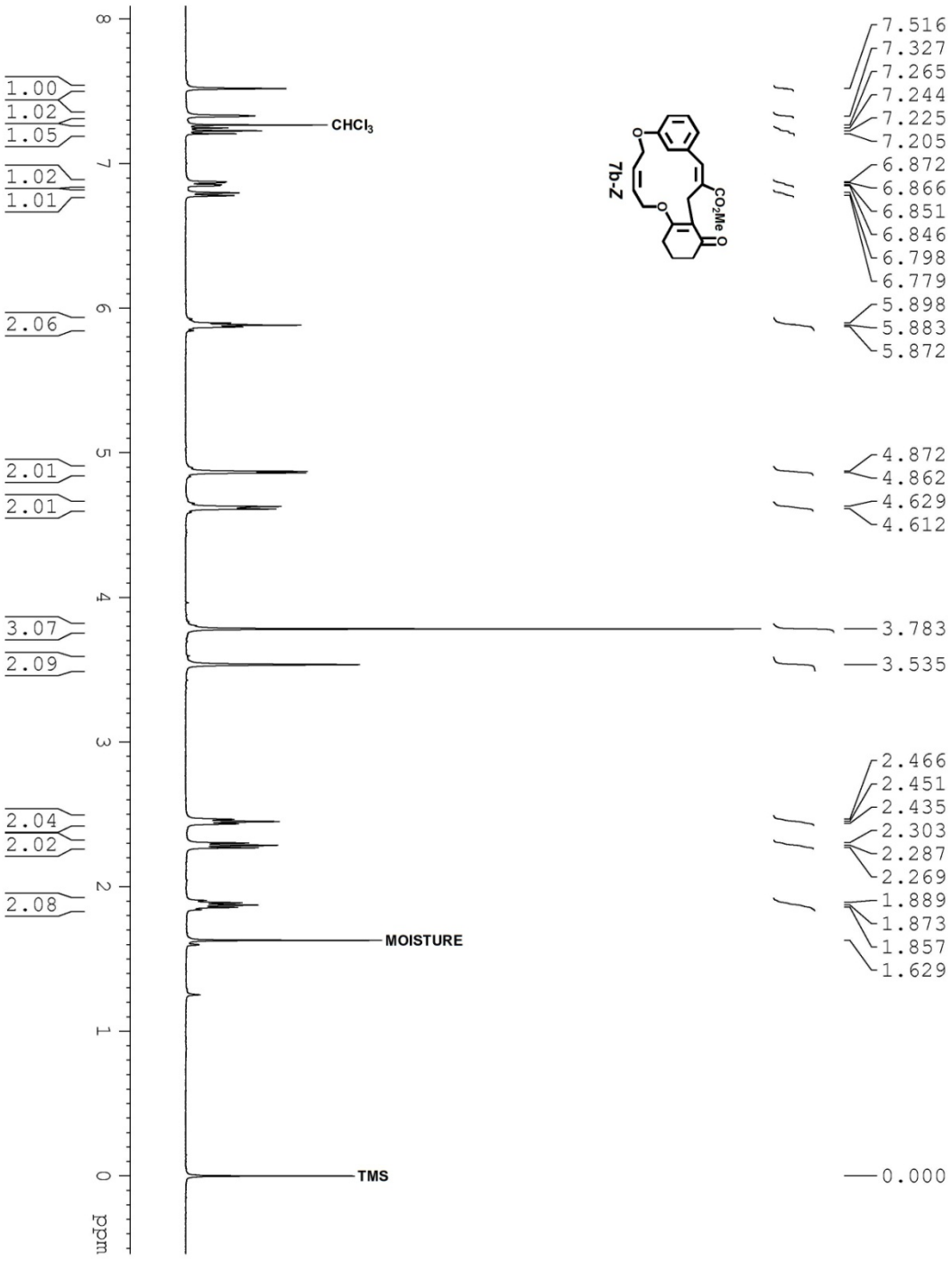


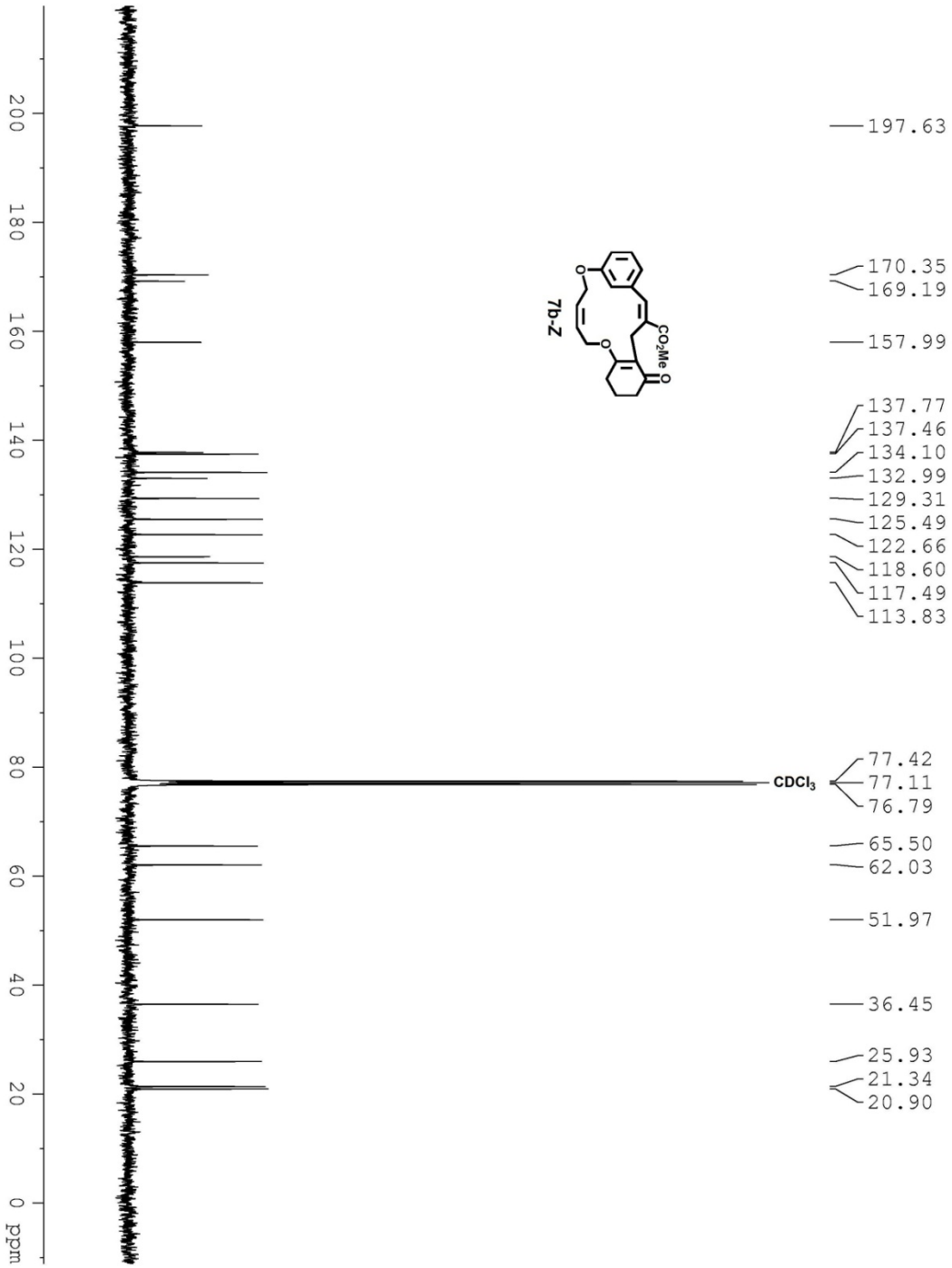


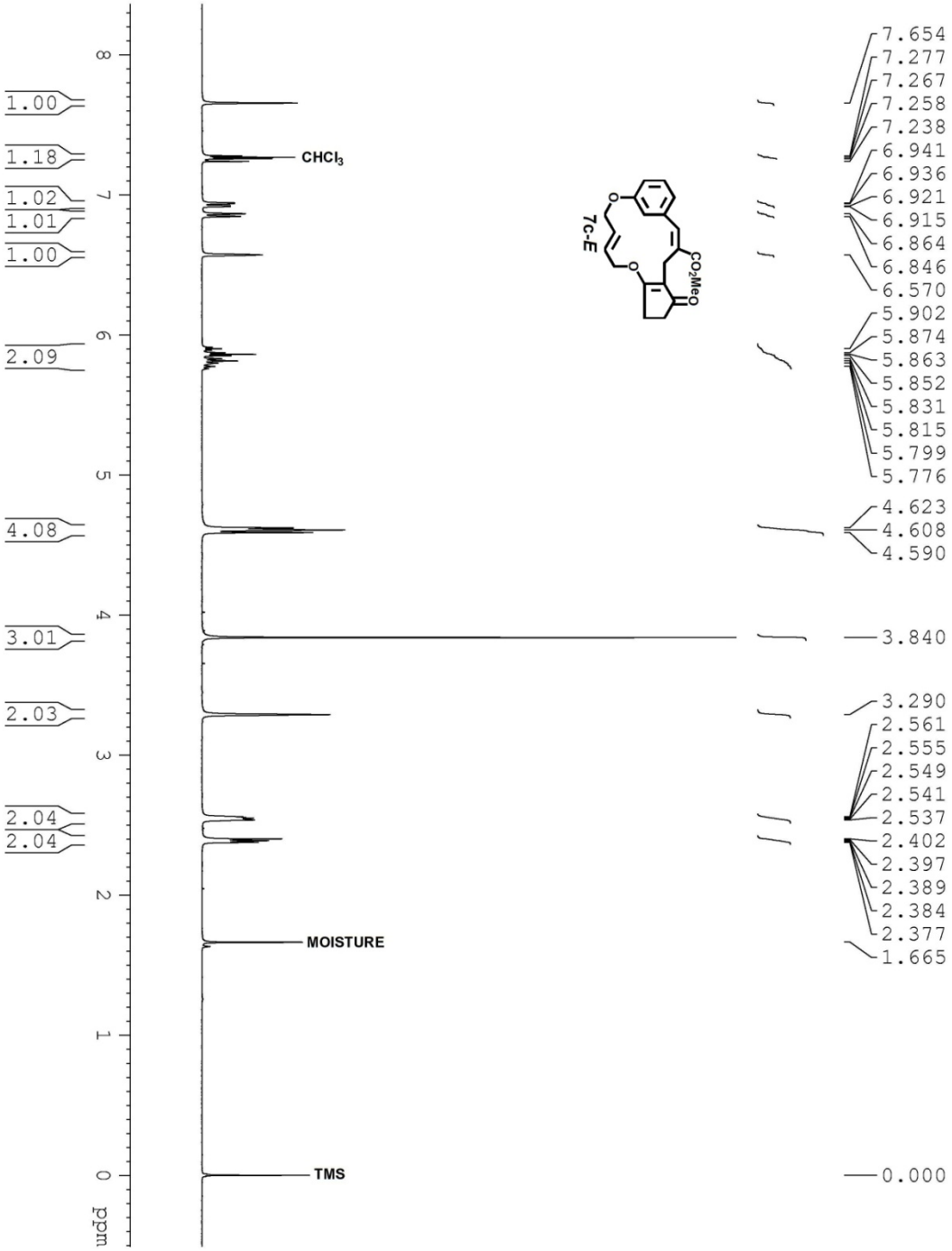


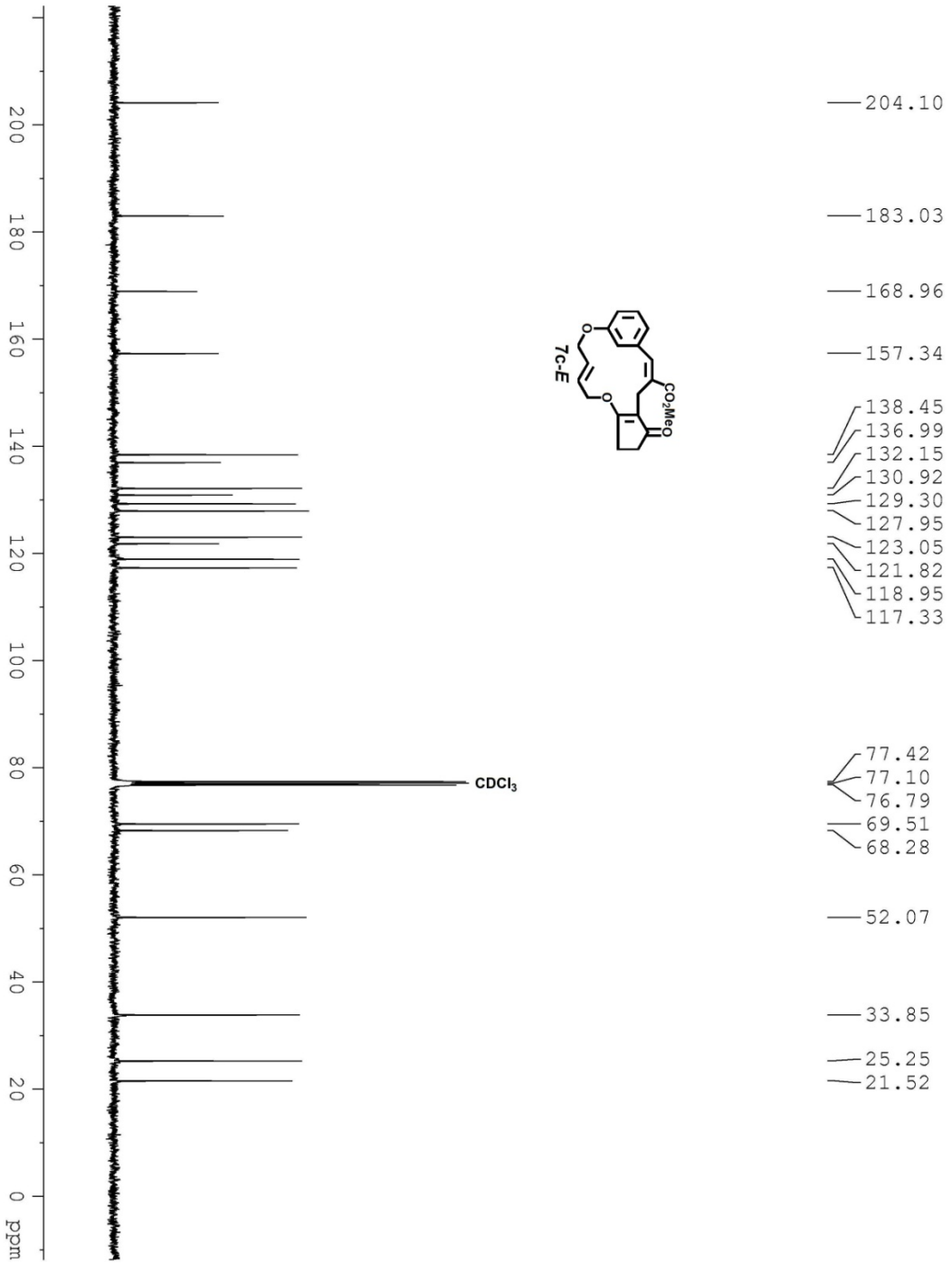


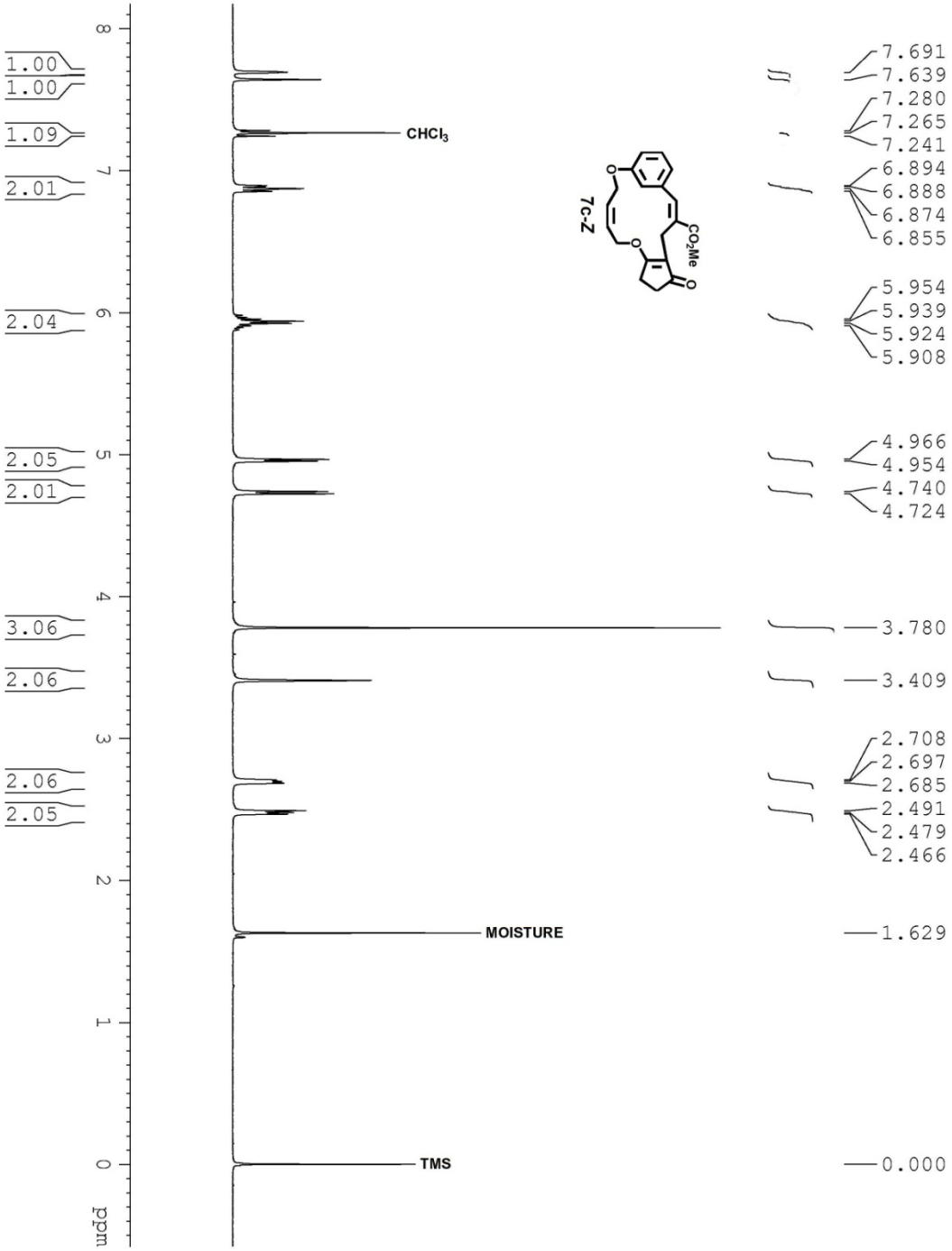


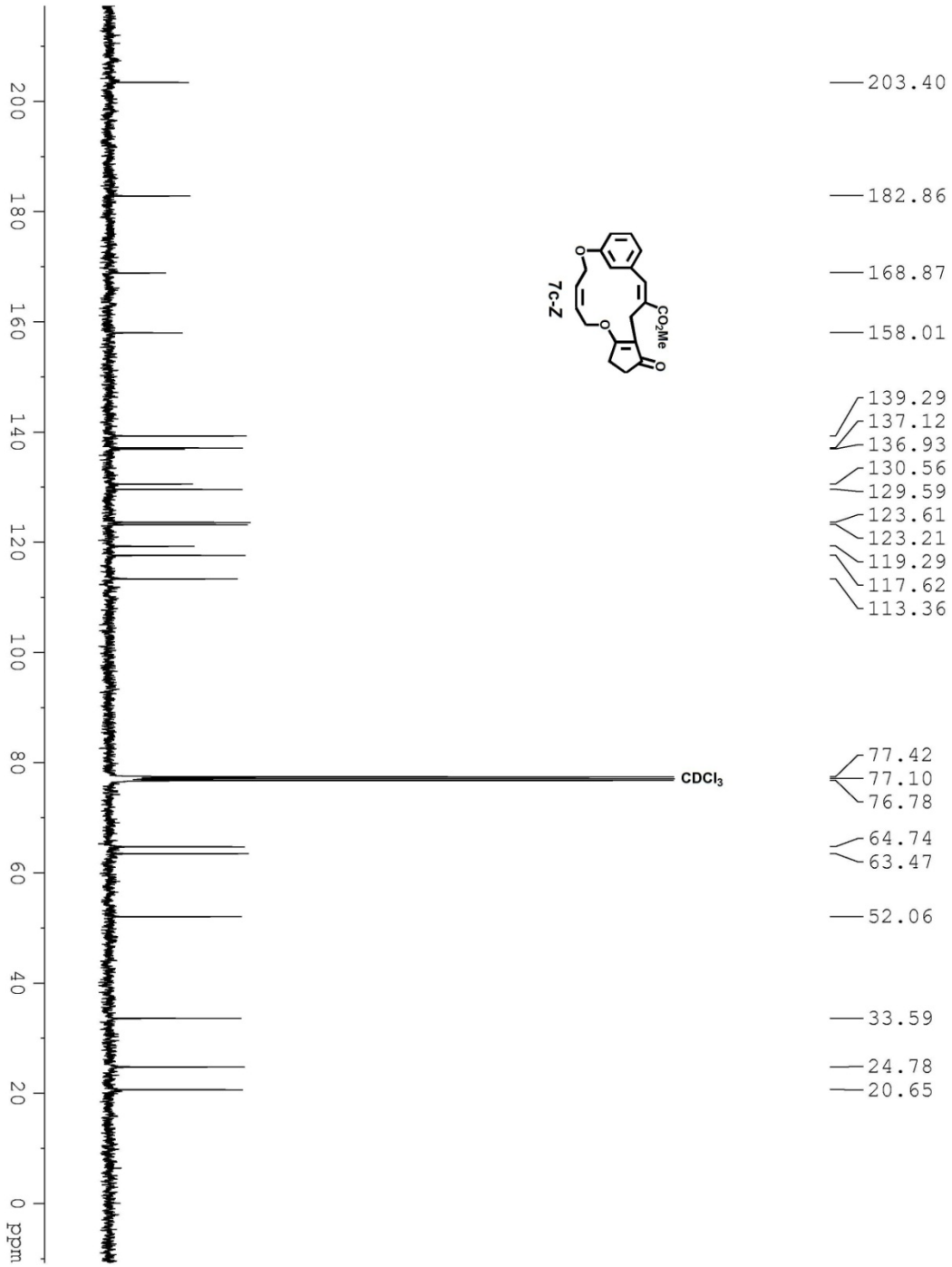








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CO2Me
O
O
O
CDCl3
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130.56
129.59
123.61
123.21
119.29
117.62
113.36
77.42
77.10
76.78
64.74
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24.78
20.65
200
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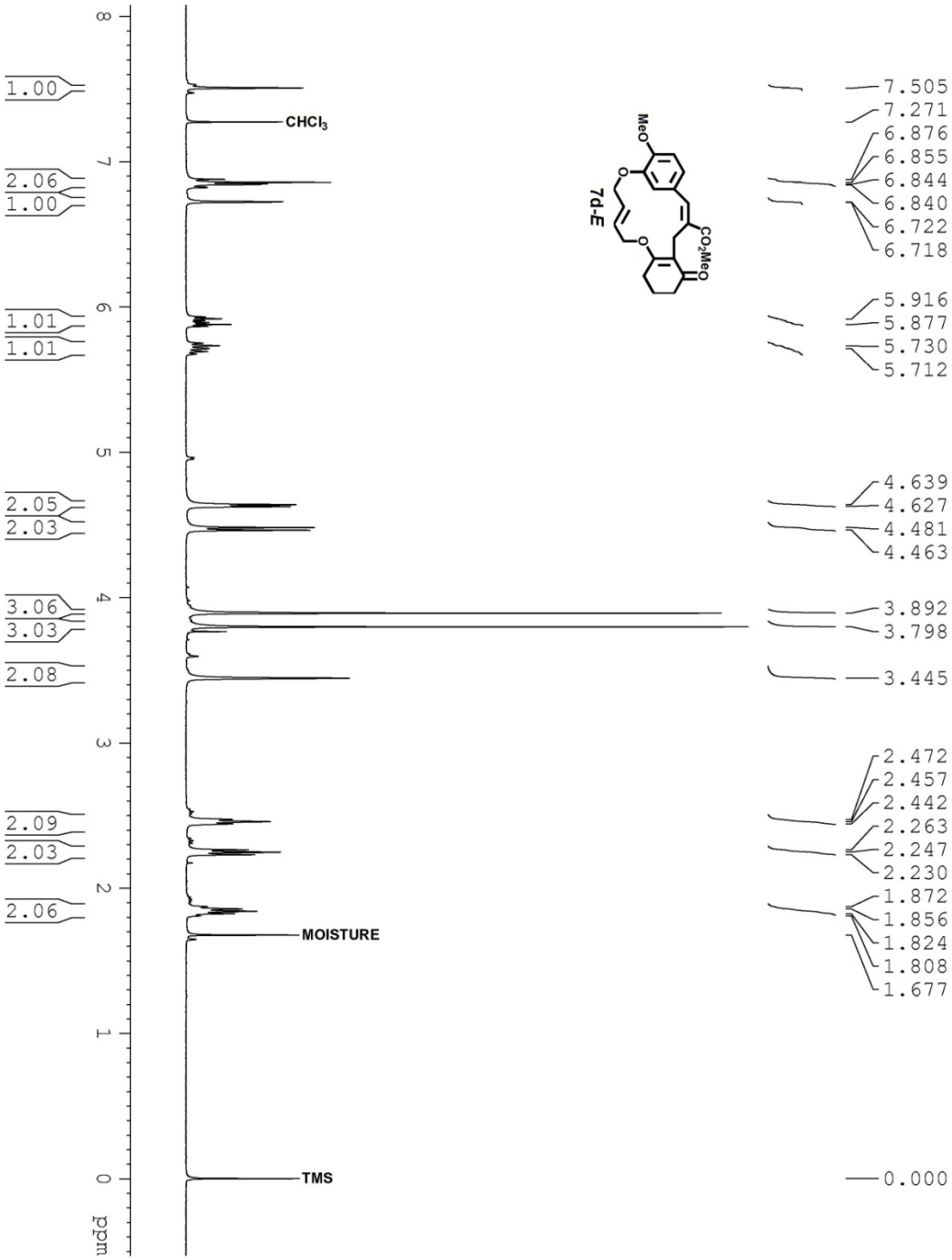
140
120
100
80
60
40
20
0
ppm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3.06
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2.03
2.06
CHCl3
MOISTURE
TMS
ppm
MeO
CO2MeO
7d-E
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7.271
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6.855
6.844
6.840
6.722
6.718
5.916
5.877
5.730
5.712
4.639
4.627
4.481
4.463
3.892
3.798
3.445
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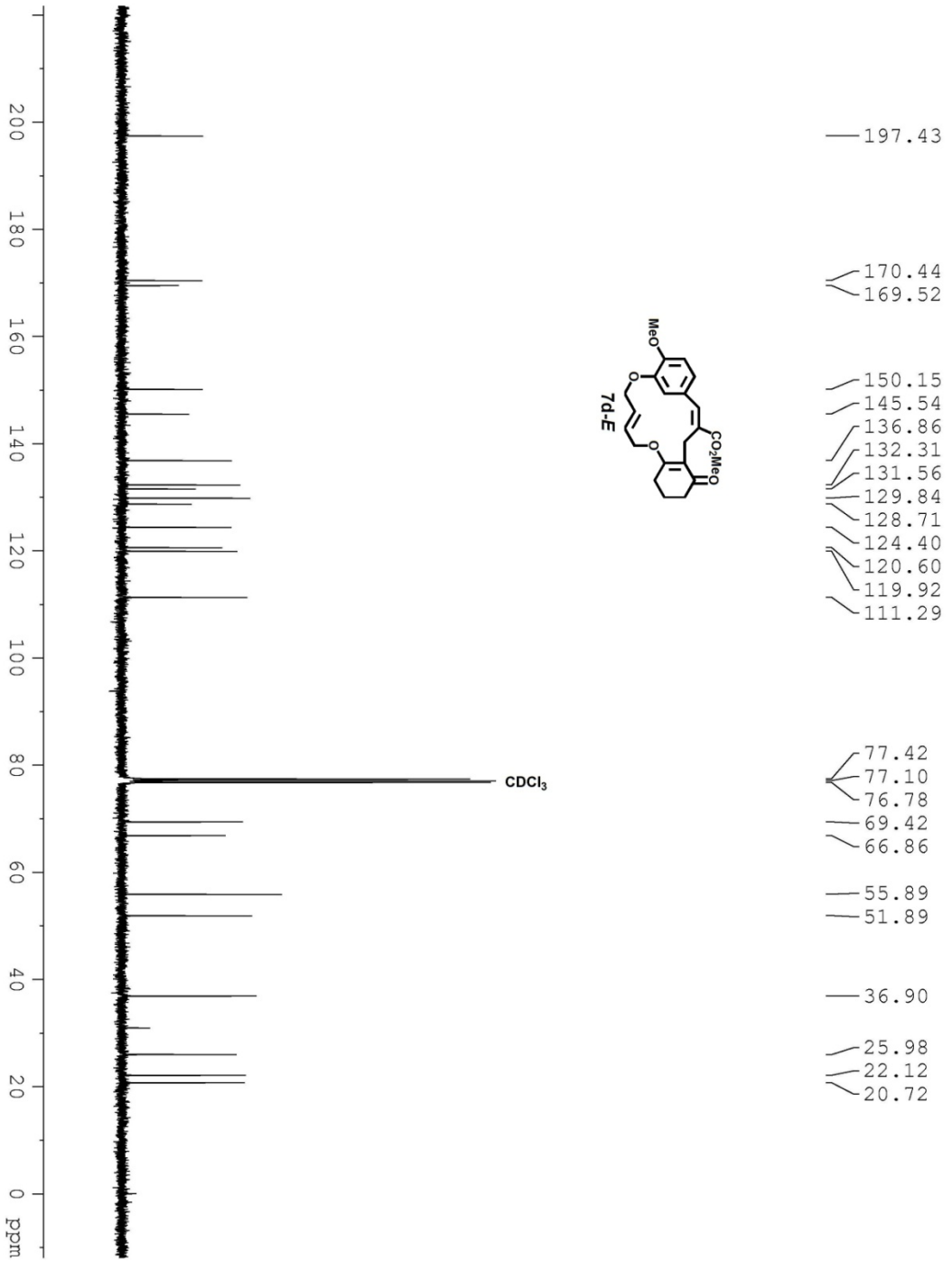

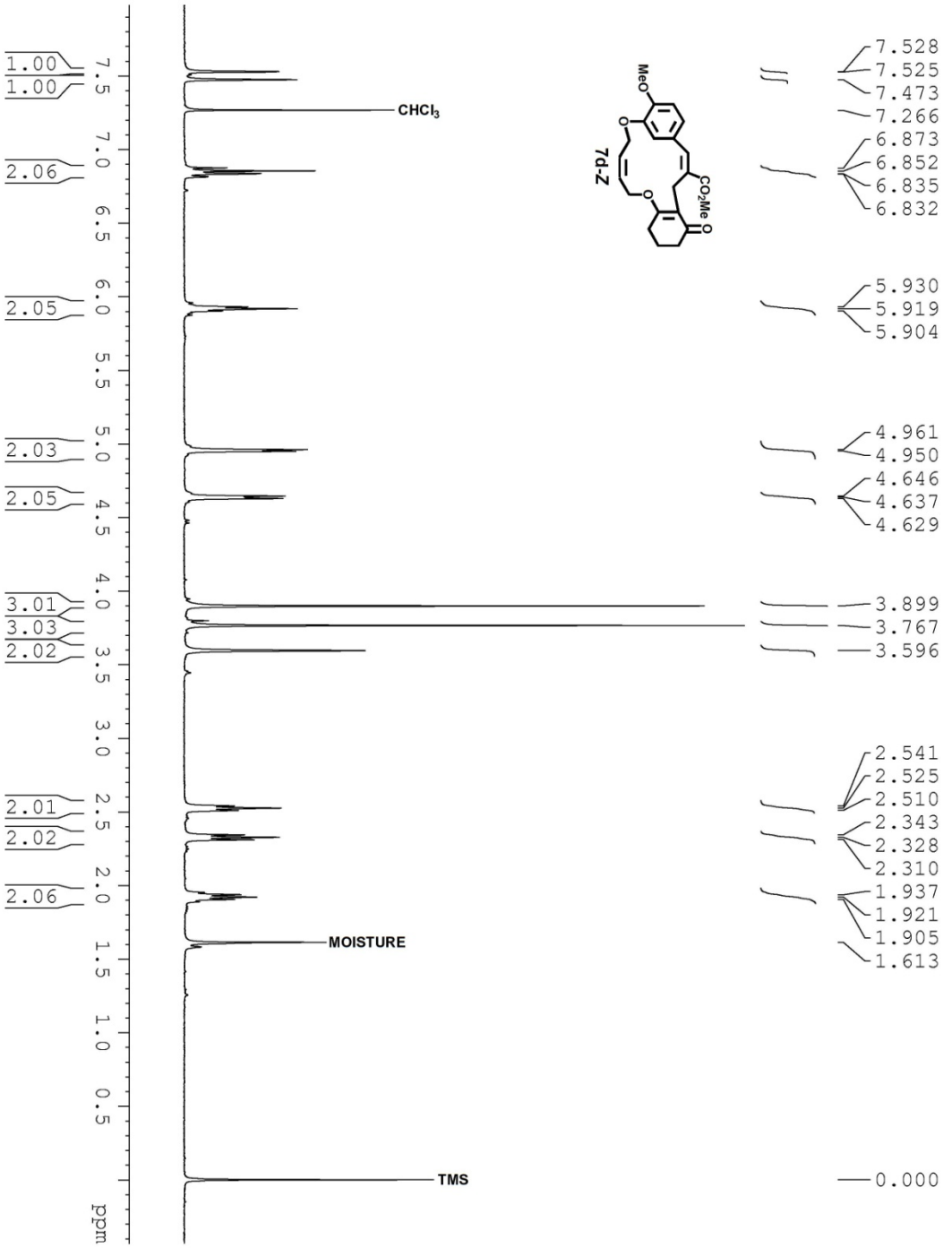
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2.02
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
CHCl3
MOISTURE
TMS
MeO
7d-Z
CO2Me
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7.525
7.473
7.266
6.873
6.852
6.835
6.832
5.930
5.919
5.904
4.961
4.950
4.646
4.637
4.629
3.899
3.767
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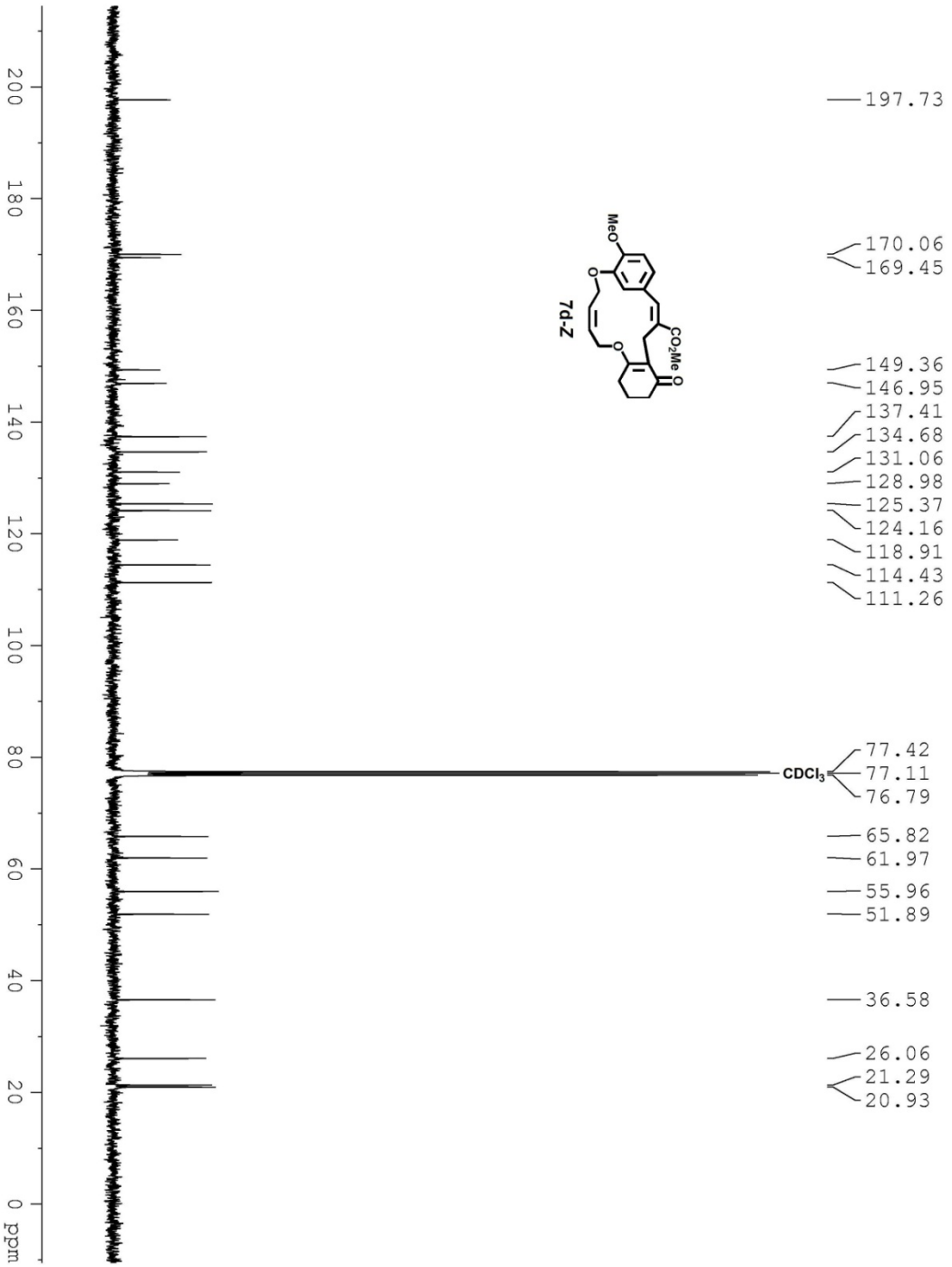

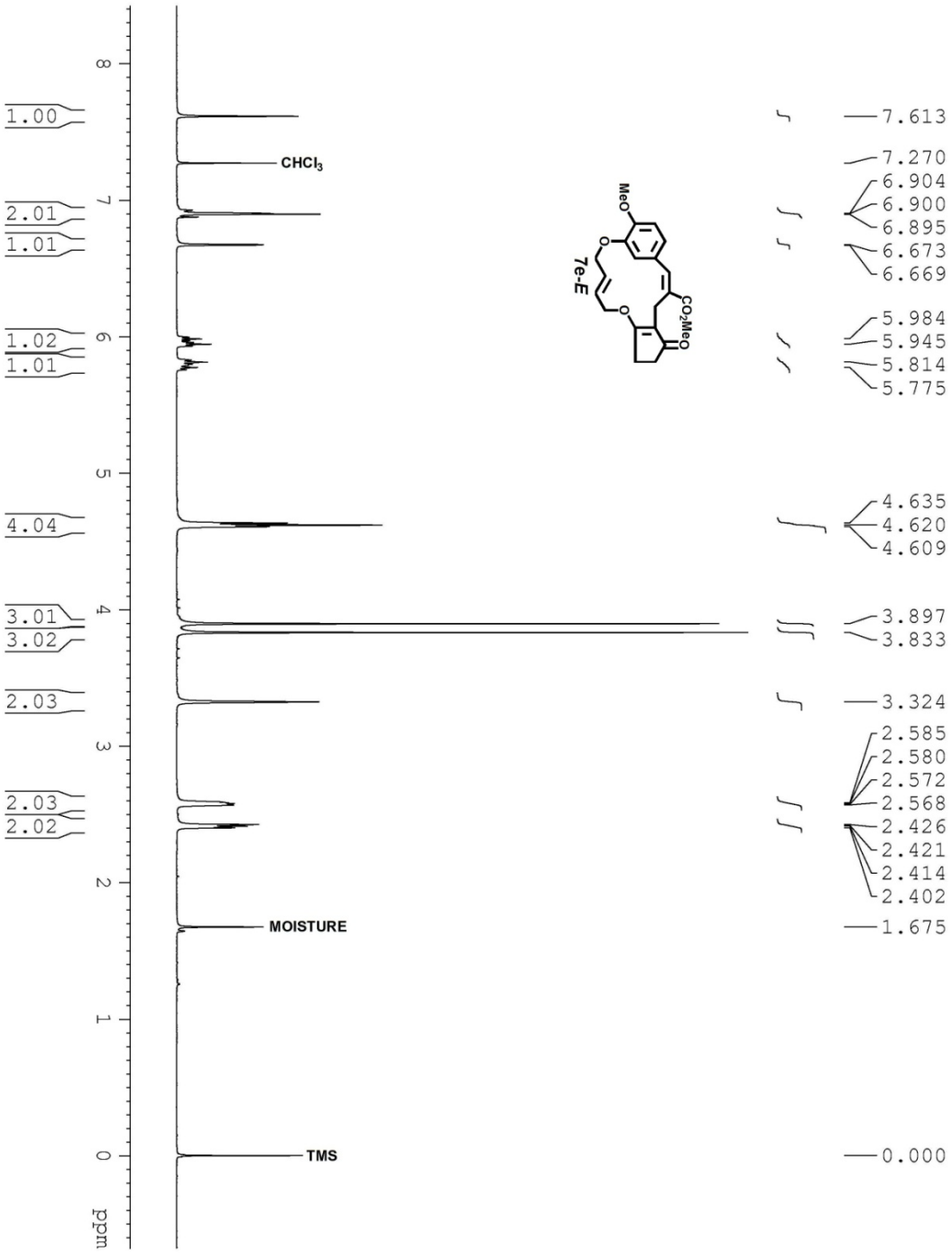

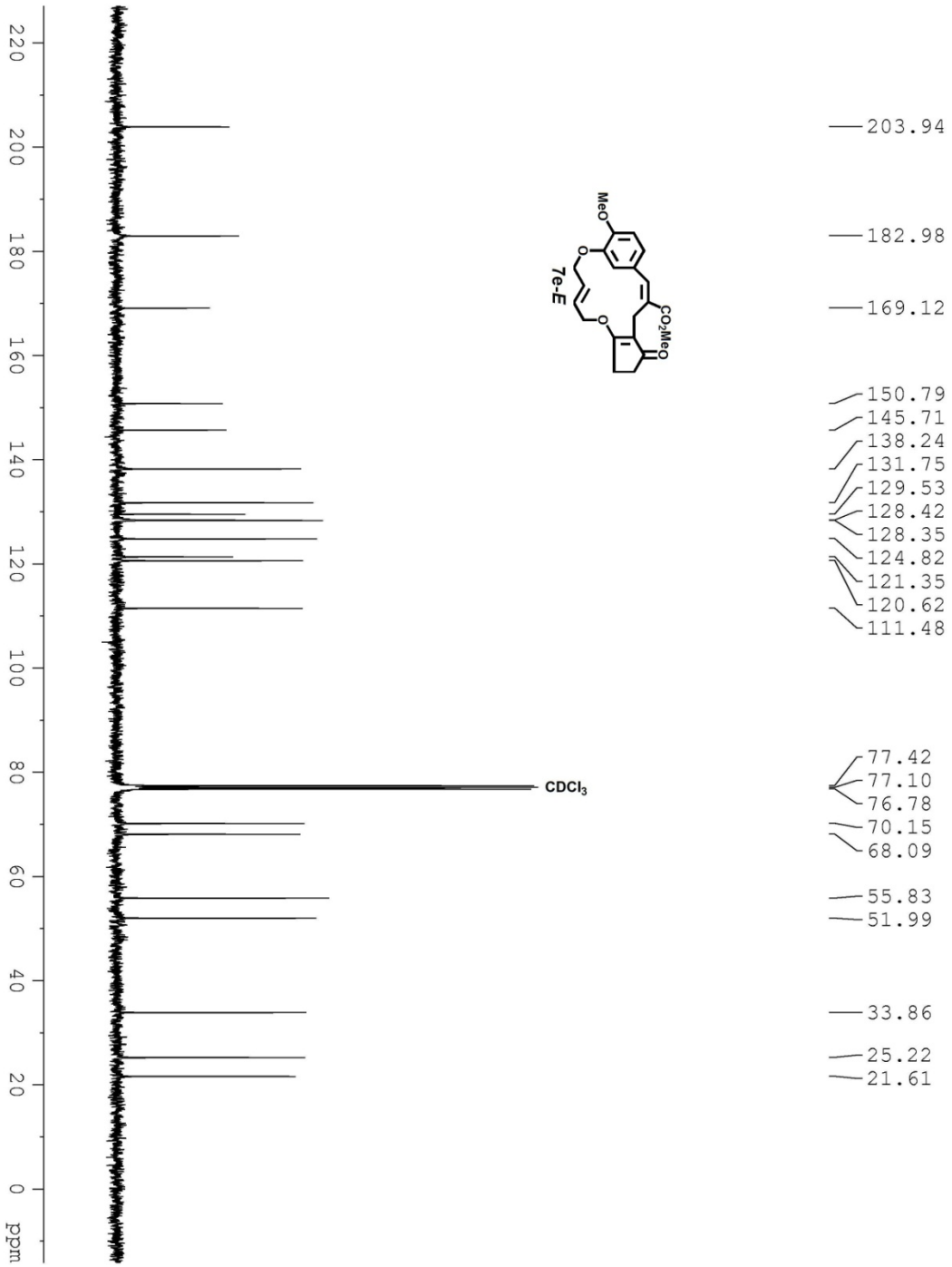

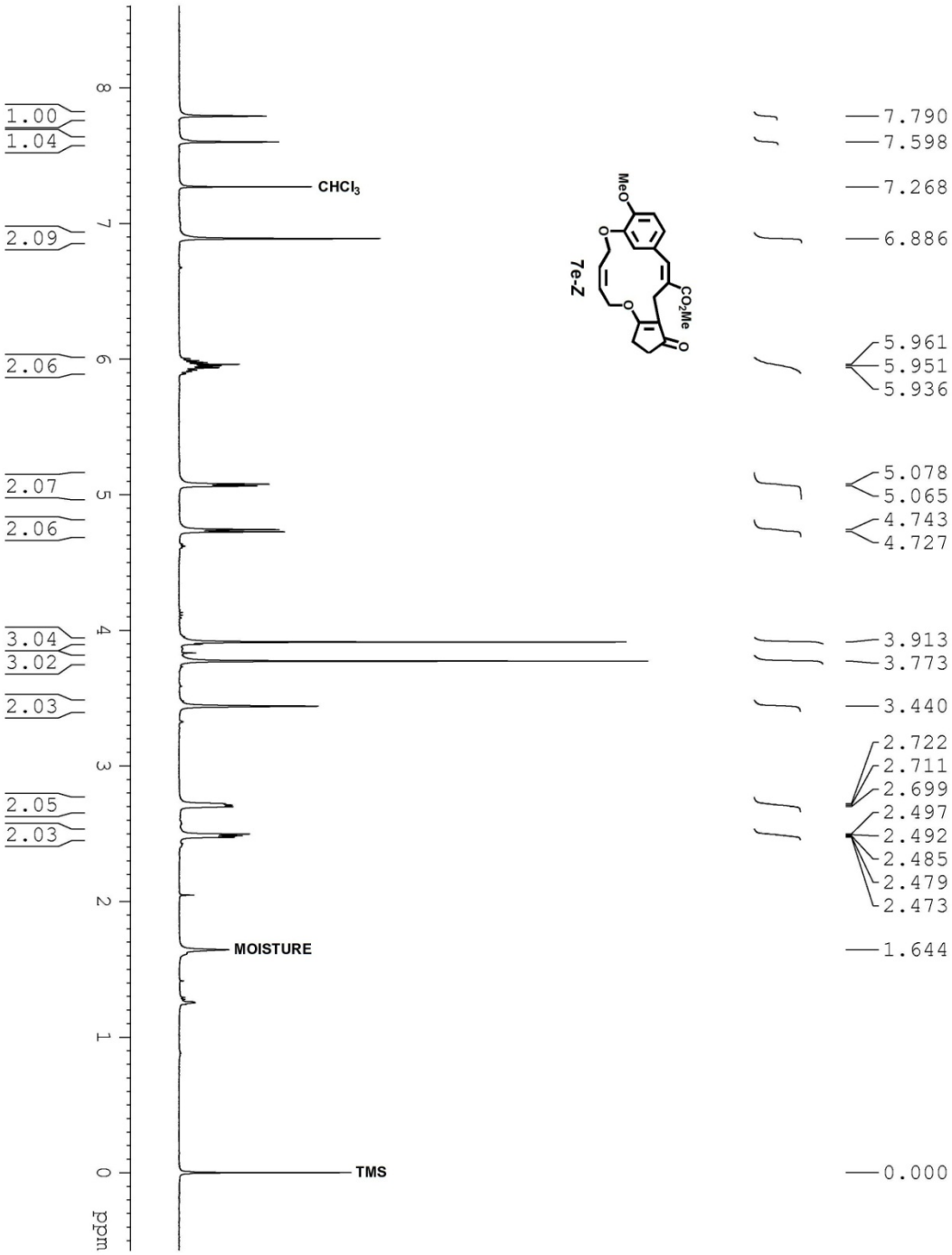

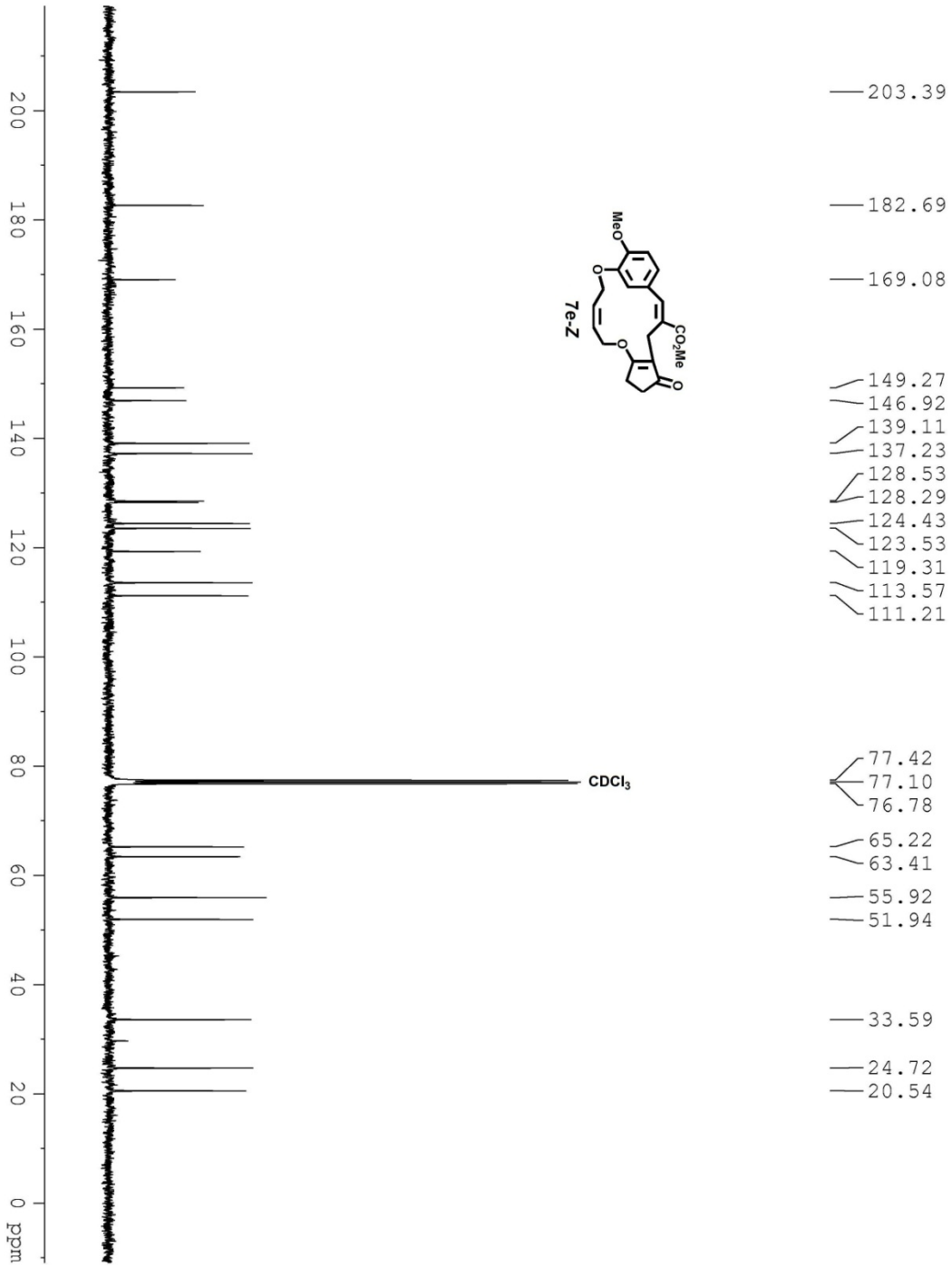

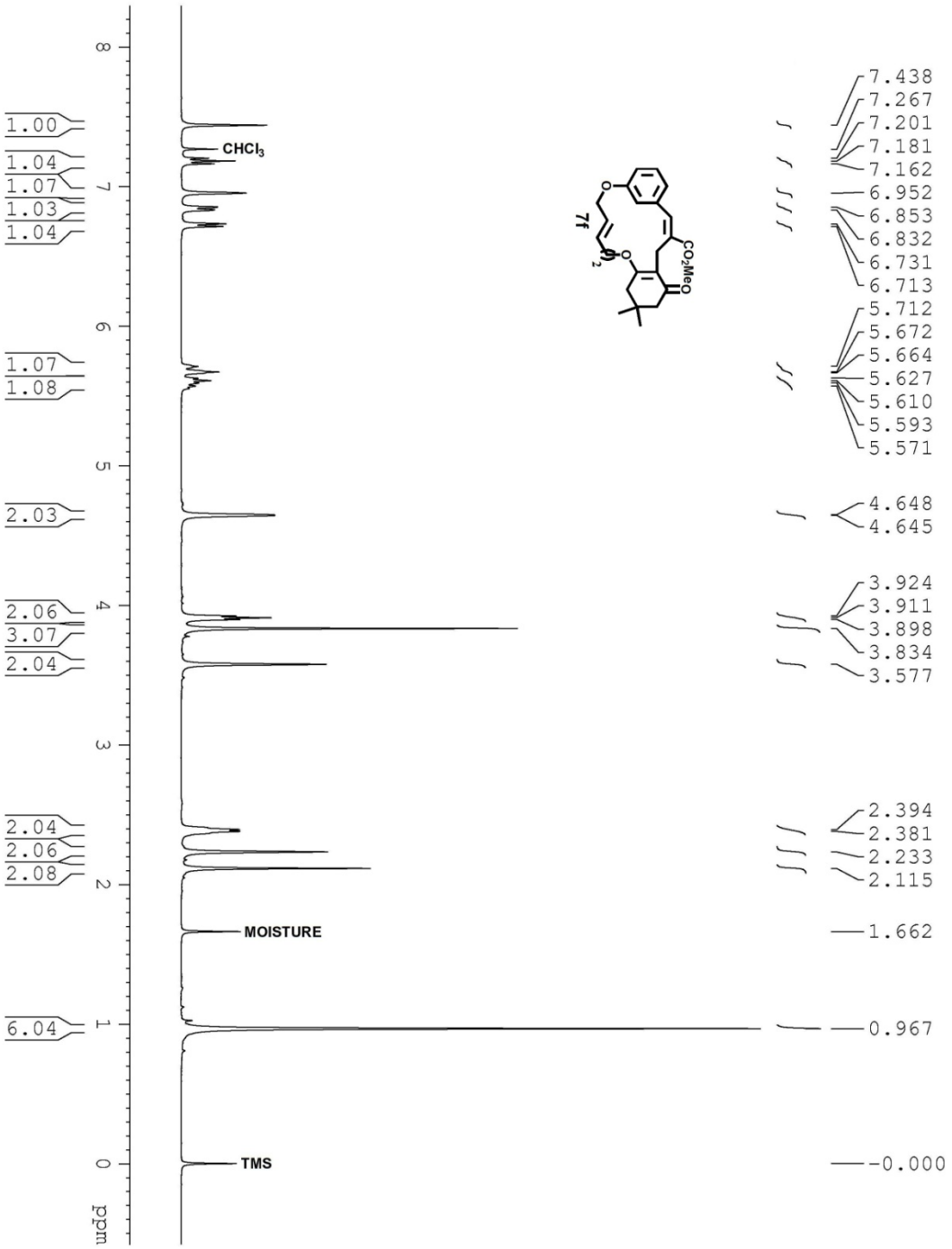

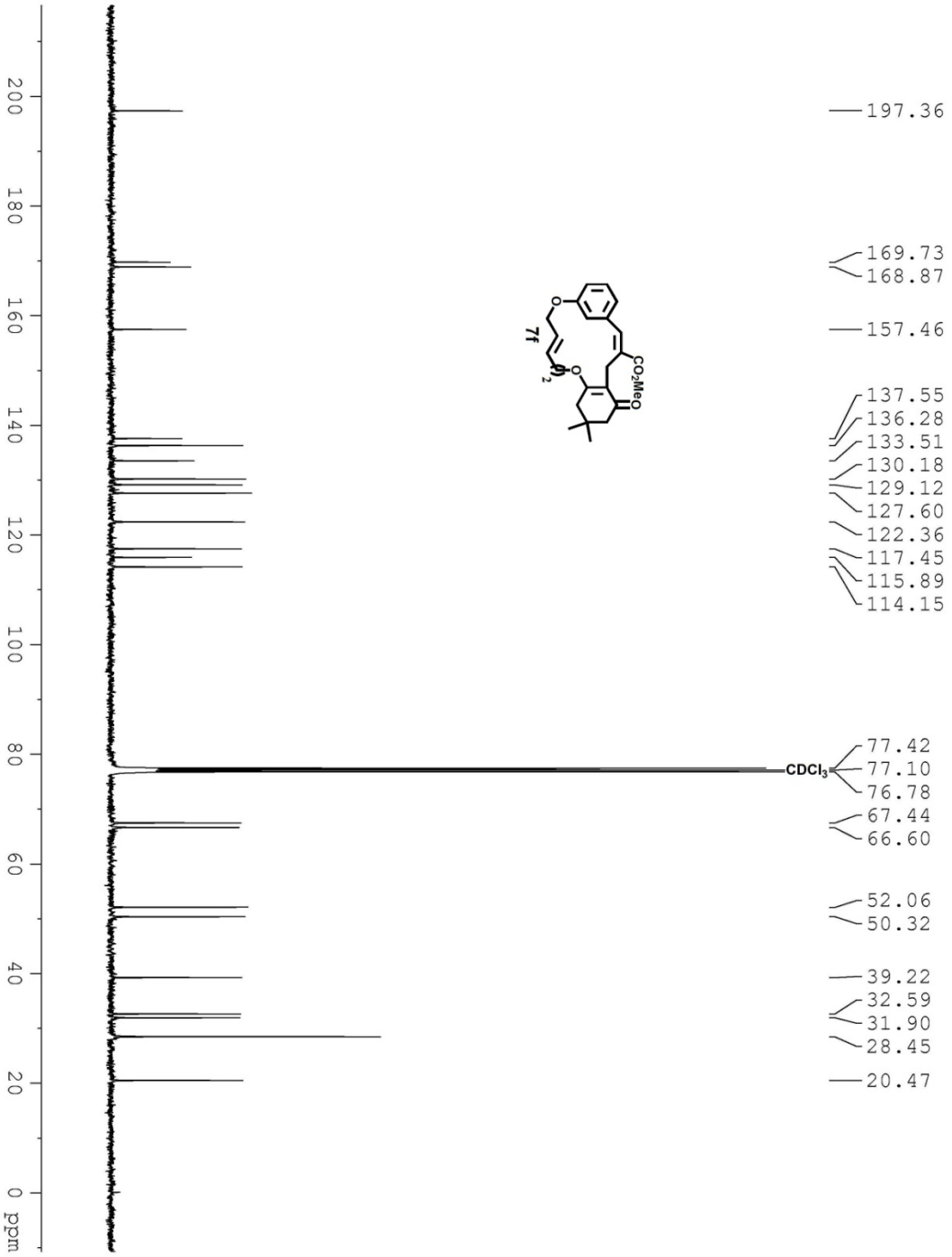

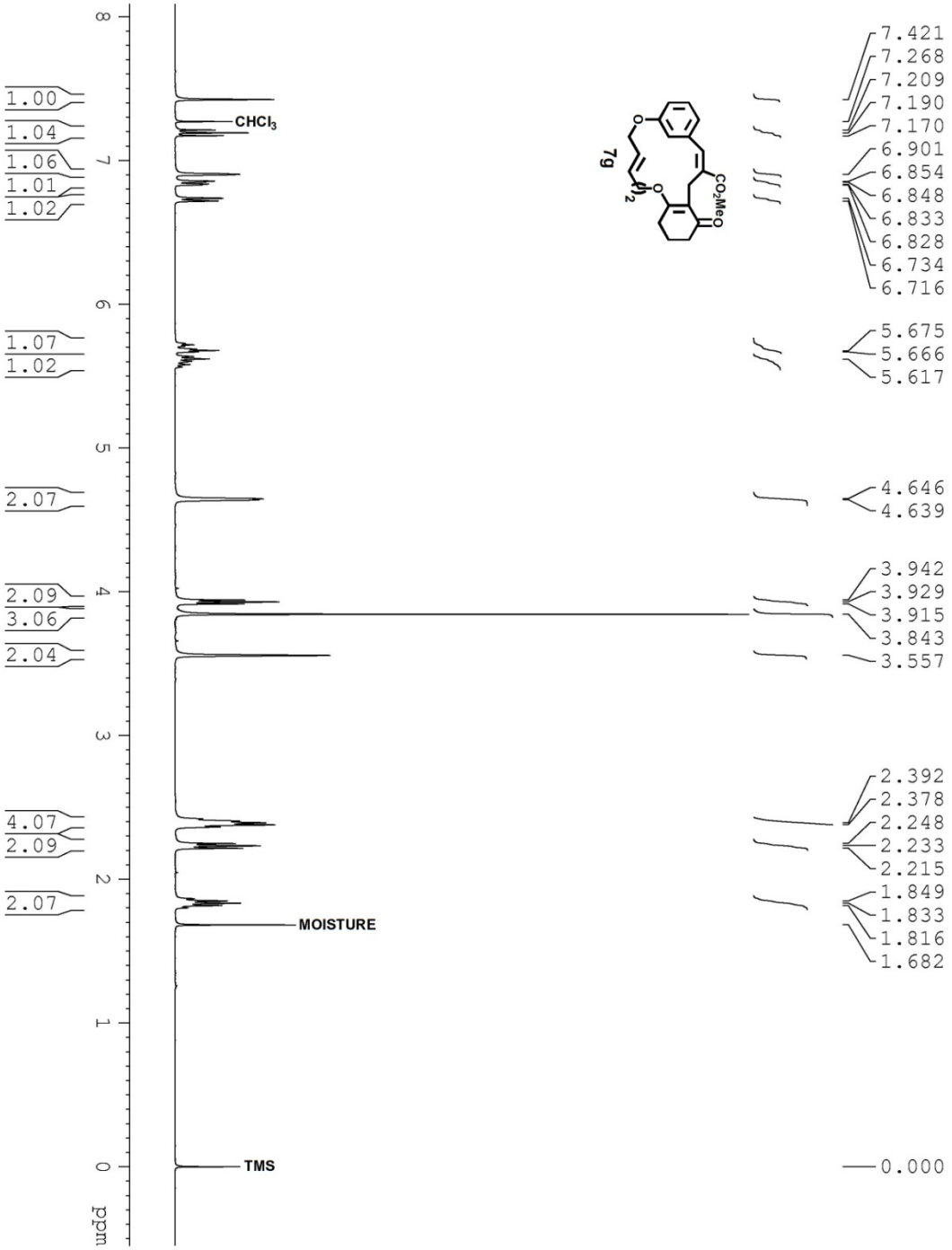

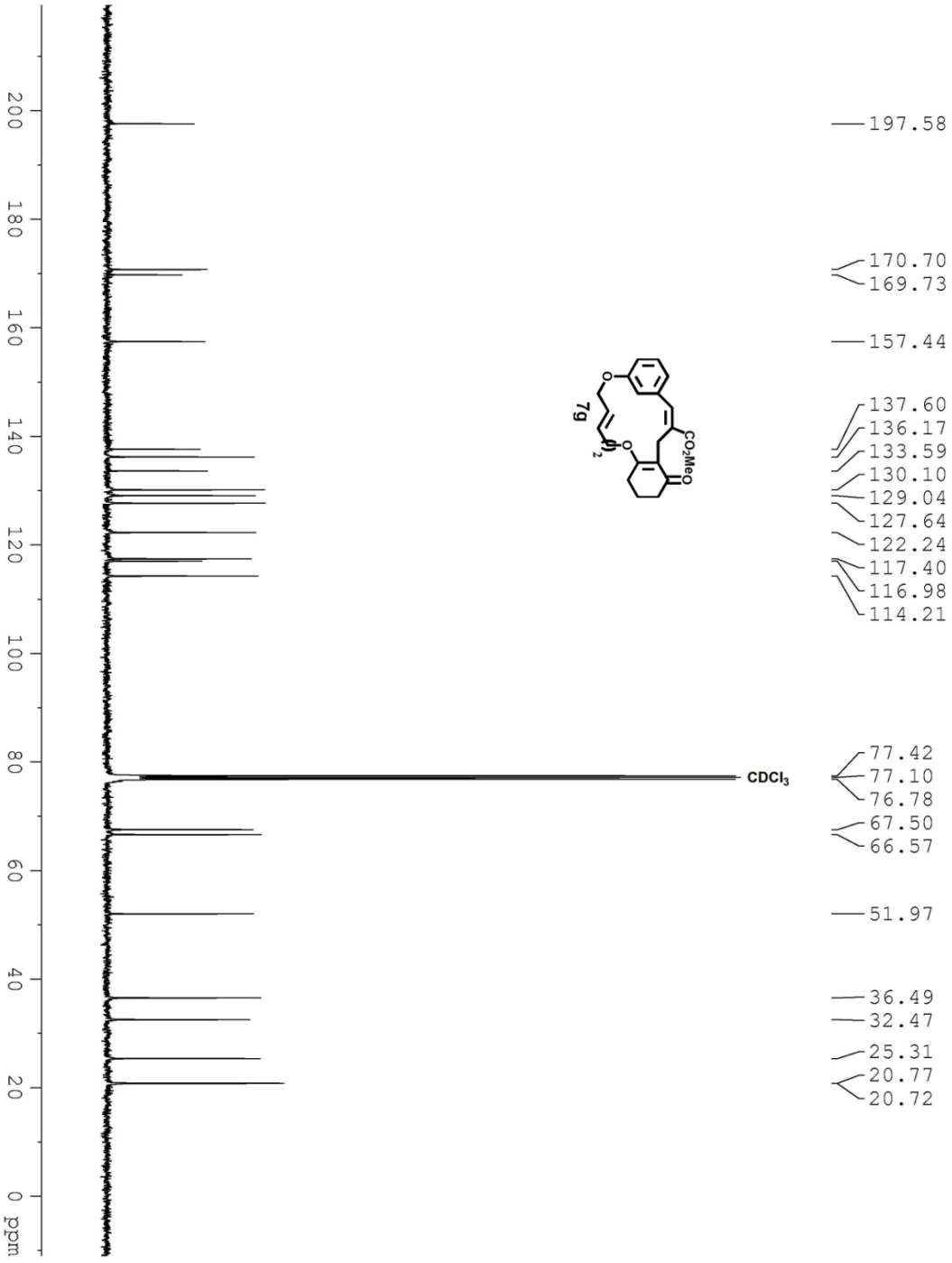

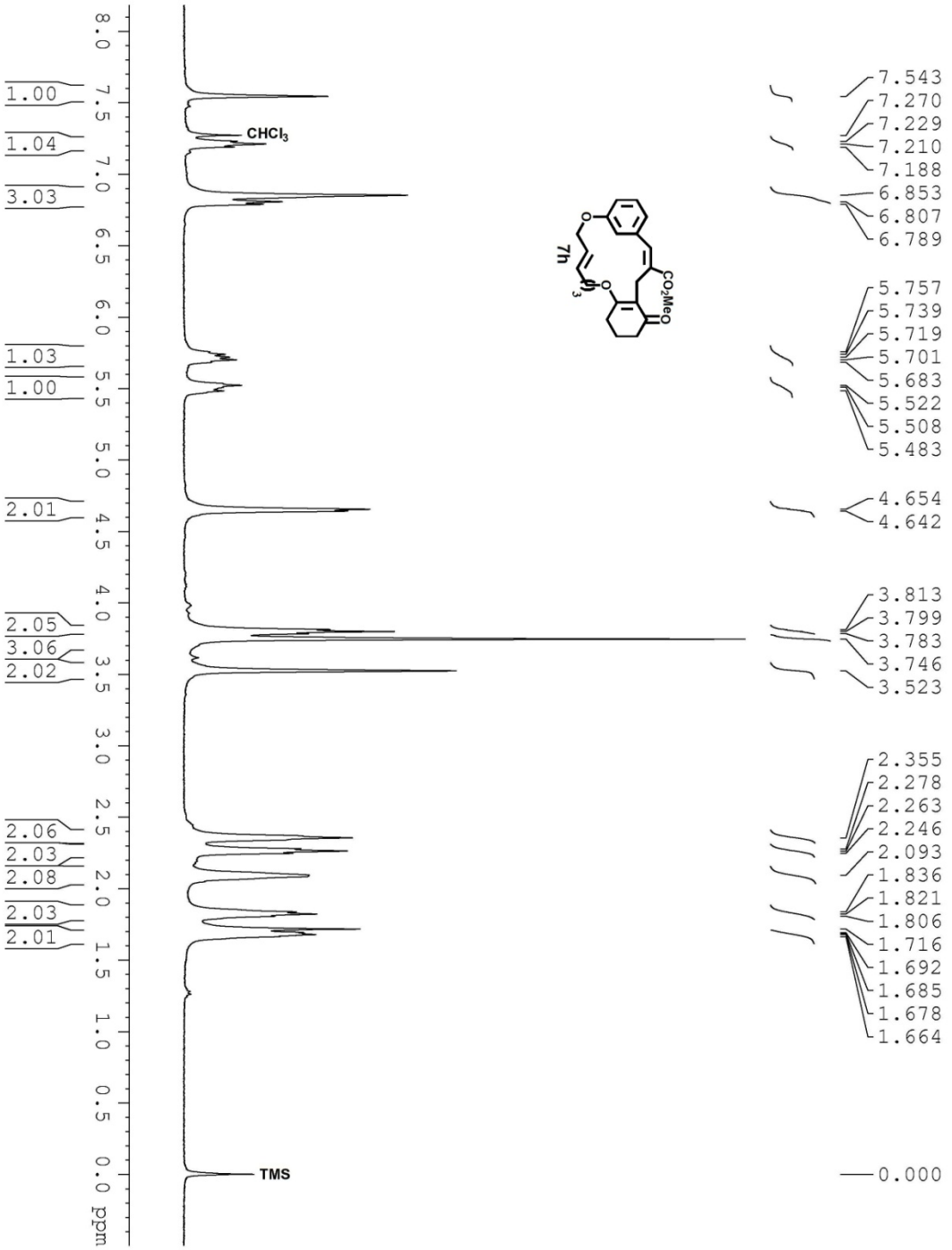

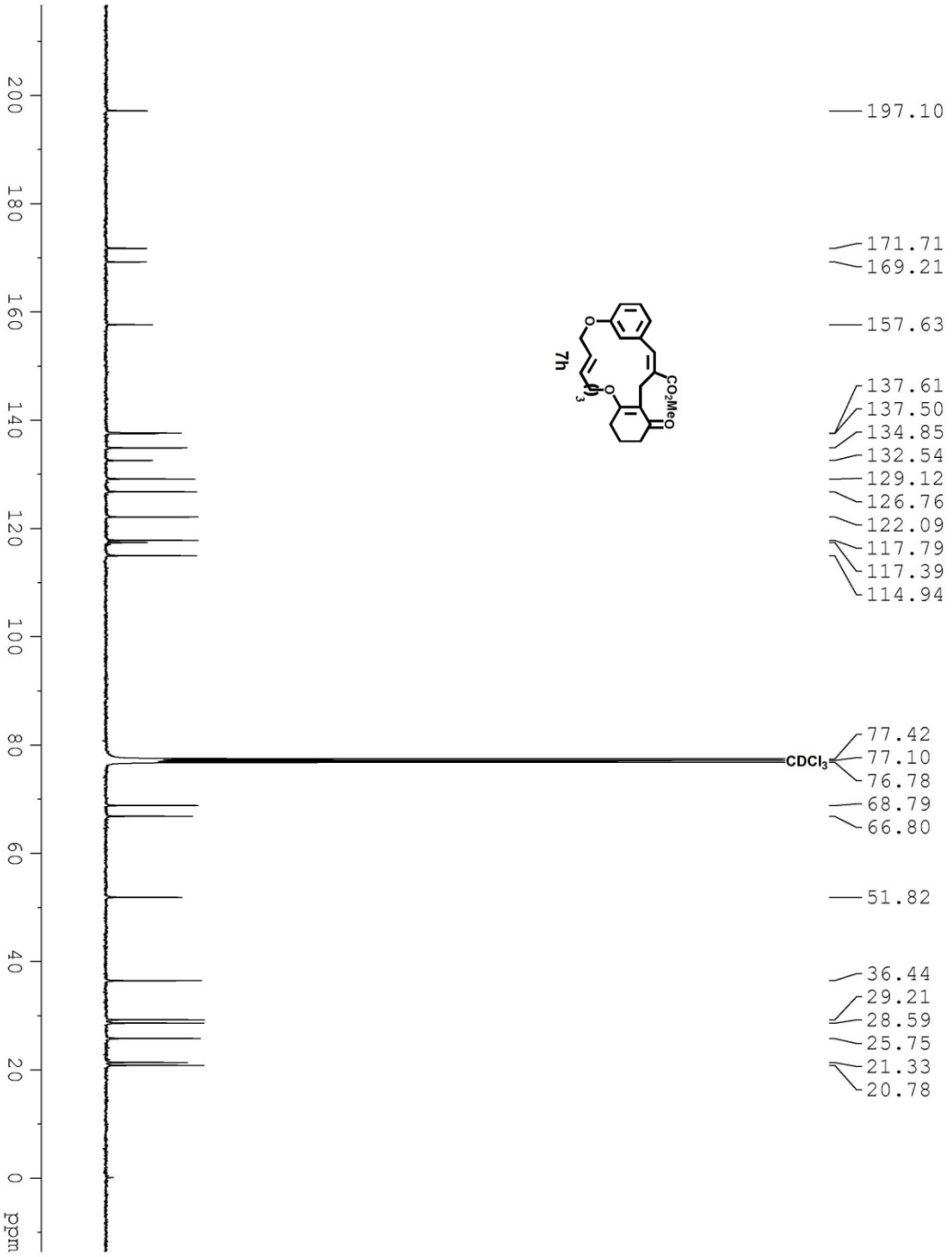

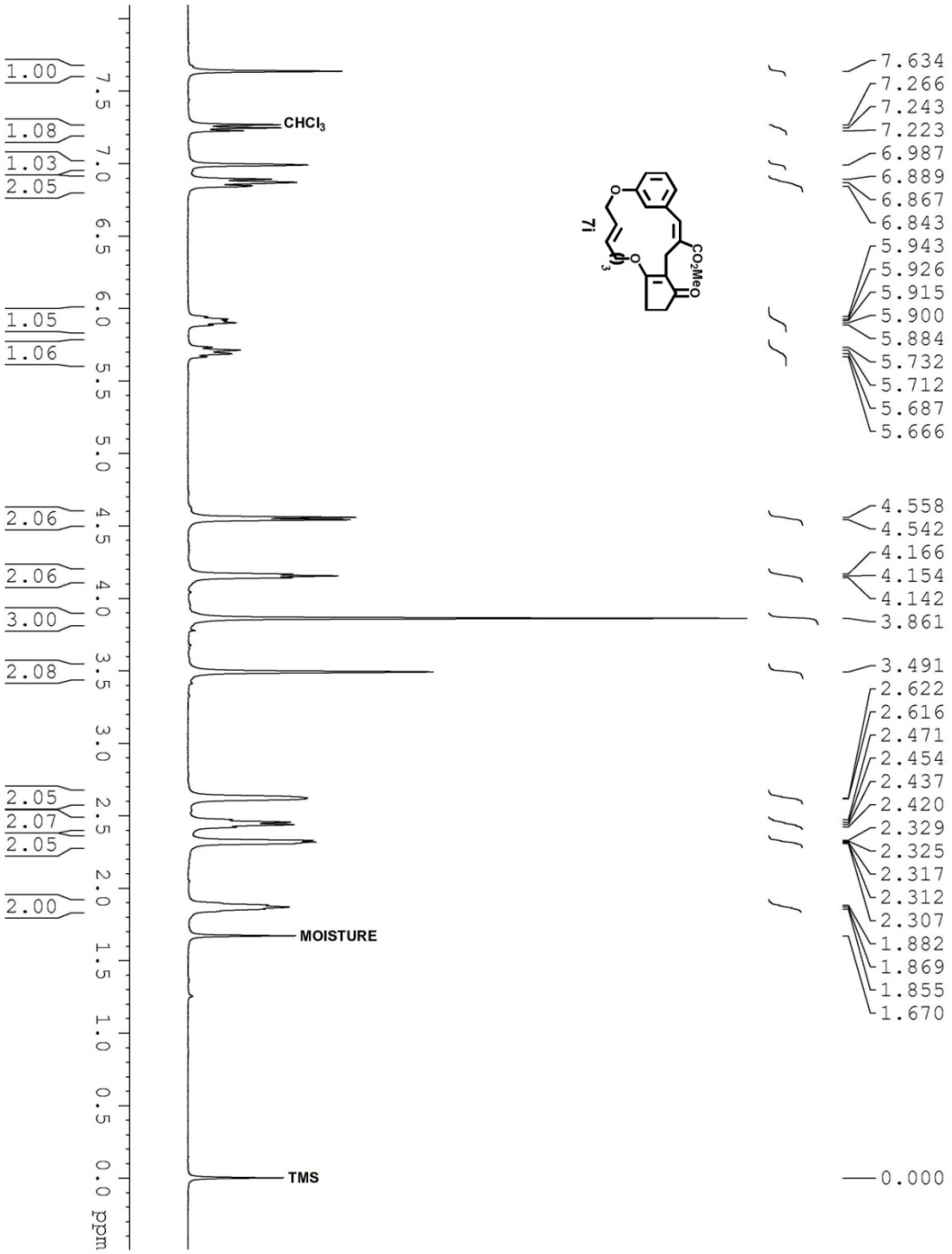
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6.0
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1.0
0.5
0.0
ppm
CHCl3
MOISTURE
TMS
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