Synthesis of spiro ketals, orthoesters and orthocarbonates by CpRu-catalyzed decomposition of α-diazo-β-ketoesters

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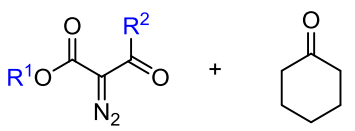
1. GENERAL REMARKS

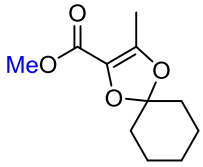
Dry CH_2Cl_2 was used without any purification. Carbonyl containing moieties, unless otherwise specified, are acquired from commercial sources and used without further purification. $[CpRu(CH_3CN)_3][PF_6]$,[1] benzylated estrone **8m**[2] and 5-methoxy-3-methylfuran-2(5H)-one **9e**[3] were prepared according to the literature procedures. Analytical thin-layer chromatography (TLC) was performed with Merk Silica gel 60 F_{254} plates. Column chromatography (Fluka silica gel 60, 40 μm) was performed in air. NMR spectra were recorded on Brucker AMX-400 or ARX-500 at room temperature. ^{1}H NMR: chemical shifts are given in ppm relative to Me_4Si with solvent resonances used as internal standards (7.26 ppm for $CDCl_3$ and 2.05 ppm for acetone-d_6). Data were reported as follows: chemical shift (δ) in ppm on the δ scale, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplet and m = multiplet), coupling constant (Hz) and integration. ^{13}C NMR: chemicals shifts were given in ppm relative to Me_4Si with solvent resonances used as internal standards (77.16 ppm for $CDCl_3$ and 29.84 ppm for acetone-d_6). IR spectra were recorded with a Perkin-Elmer 1650 FT-IR spectrometer using a diamond ATR Golden Gate sampling. Melting points (mp) were measured in open capillary tubes with a Buchi B-550 melting points apparatus and are uncorrected. Electrospray mass spectra were obtained on a Finnigan SSQ 7000 spectrometer by the Department of Mass Spectroscopy of the University of Geneva.

2. REACTIVITY COMPARISON OF [CpRu(CH$_3$CN)$_3$][BAr$_F$] AND [CpRu(CH$_3$CN)$_3$][PF$_6$]

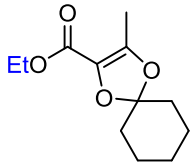
In a 2 mL screw-cap vial equipped with a magnetic stirring bar, 1,10-phenanthroline (1.5 mg, 8 µmol, 2.5 mol%) and [CpRu(CH$_3$CN)$_3$][BAr$_F$] (9 mg, 8 µmol, 2.5 mol%) or [CpRu(CH$_3$CN)$_3$][PF$_6$] (3.5 mg, 8 µmol, 2.5 mol%) are dissolved in 0.60 mL of dry dichloromethane. The vial is flushed with argon and capped. The resulting deep red solution is stirred for 10 minutes at 25 °C before the addition of cyclohexanone **8a** (33 µL, 0.32 mmol) and the desired diazo (0.32 mmol). The solution is stirred at 60 °C for the time indicated in the table. The conversion and the yield were measured by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal reference.

Table S1. Comparison [CpRu(CH$_3$CN)$_3$][PF$_6$] *vs* [CpRu(CH$_3$CN)$_3$][BAr$_F$]

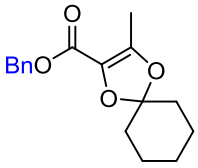




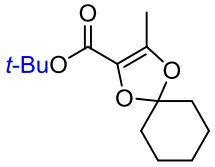
4a t: 1.5 h
[BAr$_F$] conv: 73%, y: 62%
[PF$_6$] conv: 64%, y: 51%



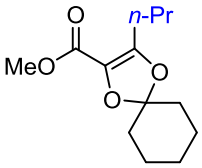
4b t: 1.5 h
[BAr$_F$] conv: 78%, y: 63%
[PF$_6$] conv: 63%, y: 58%



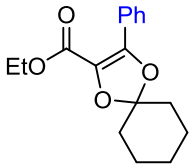
4c t: 1.5 h
[BAr$_F$] conv: 60%, y: 50%
[PF$_6$] conv: 44%, y: 38%



4d t: 1.5 h
[BAr$_F$] conv: 48%, y: 46%
[PF$_6$] conv: 16%, y: 14%



4e t: 1.5 h
[BAr$_F$] conv: 68%, y: 64%
[PF$_6$] conv: 51%, y: 48%



4f t: 12 h
[BAr$_F$] conv: 23%, y: 18%
[PF$_6$] conv: 18%, y: 13%

3. GENERAL PROCEDURE FOR THE SYNTHESIS OF COMPOUNDS 4

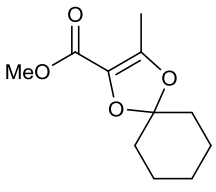
In a 2 mL screw-cap vial equipped with a magnetic stirring bar, 1,10-phenanthroline (1.5 mg, 8 μmol, 2.5 mol%) and [CpRu(CH_3CN)$_3$][BAr_F] (9 mg, 8 μmol, 2.5 mol%) are dissolved in 0.60 mL of dry dichloromethane. The vial is flushed with argon and capped. The resulting deep red solution is stirred for 10 minutes at 25 °C before the addition of cycloketone **8** (0.32 mmol) and the desired diazo keto-ester **3** (0.32 mmol). The solution is stirred at 60 °C until full conversion (^{1}H NMR monitoring). The crude mixture is purified by column chromatography (pentane/Et_2O, SiO_2) to afford insertion products of type **4**. Spectroscopic data for compound **4b** are consistent with those reported in the literature.[4]

4. PROCEDURE FOR THE REACTION ON LARGER SCALE

In a 25 mL flask equipped with a magnetic stirring bar and a refrigerator, 1,10-phenanthroline (39.7 mg, 0.2 mmol, 2.5 mol%) and [CpRu(CH_3CN)$_3$][BAr_F] (225 mg, 0.2 mmol, 2.5 mol%) are dissolved in 15 mL of dry 1,2-dichloroethane, under argon. The resulting deep red solution is stirred for 10 minutes at 25 °C before the addition of cyclohexanone **8a** (785 mg, 8 mmol) and diazo ketoester **3a** (1.136 g, 8 mmol). The solution is stirred at 60 °C until full conversion (^{1}H NMR monitoring, 3 hours). The crude mixture is purified by column chromatography (SiO_2, pentane:Et_2O, 9:1) to afford insertion product **4a** as a colourless oil 1.23 g, in 73% yield.

5. ANALYSIS DATA OF COMPOUNDS 4

Methyl 3-methyl-1,4-dioxaspiro[4.5]dec-2-ene-2-carboxylate (4a).

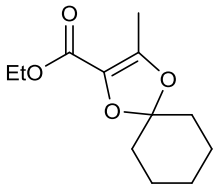


Starting from the corresponding α-diazo-β-ketoester **3a** (46 μL, 0.32 mmol) and cyclohexanone **8a** (33 μL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (68 mg, 75% yield). Analysis data correspond to the data reported in the literature.[5]

Rf = 0.55 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, acetone-*d*$_6$):** δ 3.71 (s, 3H), 2.14 (s, 3H), 1.78 (t, *J* = 6 Hz, 4H), 1.63 (m, 4H) and 1.46 (q, *J* = 6 Hz, 2H) ppm; **^{13}C NMR (100 MHz, acetone-*d*$_6$):** δ 161.8 (C), 148.3

(C), 127.0 (C), 115.9 (C), 51.3 (CH_3), 35.3 (2 x CH_2), 25.1 (CH_2), 23.7 (2 x CH_2) and 11.6 (CH_3) ppm; **IR (neat):** 1712, 1670, 1346, 1139 and 1107 cm^{-1}.

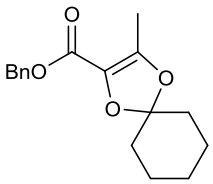
Methyl 3-methyl-1,4-dioxaspiro[4.5]dec-2-ene-2-carboxylate (4b).



Starting from the corresponding α-diazo-β-ketoester **3a** (50 µL, 0.32 mmol) and cyclohexanone **8a** (33 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (57 mg, 79% yield). Analysis data correspond to the data reported in the literature.[4]

Rf = 0.55 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.27 (q, *J* = 7 Hz, 2H), 2.18 (s, 3H), 1.90-1.48 (m, 4H) and 1.32 (t, *J* = 7 Hz, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.6 (C), 148.0 (C), 126.5 (C), 115.7 (C), 60.6 (CH_2), 35.0 (2 x CH_2), 24.7 (CH_2), 23.0 (2 x CH_2), 14.6 (CH_3) and 11.6 (CH_3) ppm; **IR (neat):** 1712, 1670, 1346, 1139 and 1107 cm^{-1}; **IR (neat):** 2938, 1707, 1671, 1330 and 1102 cm^{-1}; **HR-MS (ESI)** *m/z* calculated for $C_{12}H_{19}O_4^+$ 227.1277 observed 227.1284.

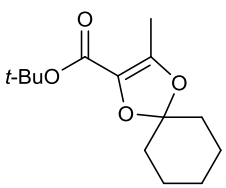
Benzyl 3-methyl-1,4-dioxaspiro[4.5]dec-2-ene-2-carboxylate (4c).



Starting from the corresponding α-diazo-β-ketoester **3c** (70 mg, 0.32 mmol) and cyclohexanone **8a** (33 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 9:1) as a colourless oil (51 mg, 55% yield).

Rf = 0.79 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.42-7.30 (m, 5H), 5.25 (s, 2H), 2.16 (s, 3H) and 1.91-1.32 (m, 10H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$):** δ 161.3 (C), 148.4 (C), 136.2 (C), 128.6 (2 x CH), 128.4 (2 x CH), 128.3 (CH), 126.4 (C), 115.8 (C), 66.1 (CH_2), 34.8 (2 x CH_2), 24.7(CH_2), 23.0 (2 x CH_2) and 12.0 (CH_3) ppm; **IR (neat):** 1709, 1670, 1332, 1136 and 1099 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{17}H_{21}O_4^+$ 289.1434 observed 289.1434.

***tert*-butyl 3-methyl-1,4-dioxaspiro[4.5]dec-2-ene-2-carboxylate (4d).**

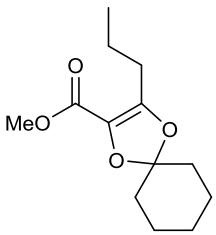


Starting from the corresponding α-diazo-β-ketoester **3d** (59 µL, 0.32 mmol) and cyclohexanone **8a** (33 µL, 0.32 mmol) and following the general procedure, the desired

compound was obtained after purification by column of silica gel (pentane:Et_2O 9:1) as a colourless oil (62 mg, 75% yield).

Rf = 0.85 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.12 (s, 3H), 1.85-1.55 (m, 8H), 1.51 (s, 9H) and 1.47-1.33 (m, 2H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.9 (C), 146.3 (C), 127.4 (C), 115.0 (C), 81.3 (C), 34.9 (2 x CH_2), 28.5 (3 x CH_3), 24.8 (CH_2), 23.1 (2 x CH_2) and 12.0 (CH_3) ppm; **IR (neat):** 1710, 1671, 1359, 1108 and 1052 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{14}H_{23}O_4^+$ 255.1591 observed 255.1590.

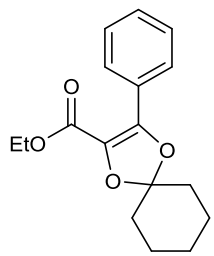
Methyl 3-propyl-1,4-dioxaspiro[4.5]dec-2-ene-2-carboxylate (4e).



Starting from the corresponding α-diazo-β-ketoester **3e** (54 µL, 0.32 mmol) and cyclohexanone **8a** (33 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 9:1) as a colourless oil (65 mg, 85% yield).

Rf = 0.67 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.78 (s, 3H), 2.56 (t, *J* = 7 Hz, 2H), 1.92-1.44 (m, 11H), 1.44-1.29 (m, 1H) and 0.95 (t, *J* = 7 Hz, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.9 (C), 151.9 (C), 126.2 (C), 115.6 (C), 51.5 (CH_3), 34.8 (2 x CH_2), 27.3 (CH_2), 24.7 (CH_2), 23.1 (2 x CH_2), 20.3 (CH_2) and 13.6 (CH_3) ppm; **IR (neat):** 1711, 1665, 1350, 1140 and 1110 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{13}H_{21}O_4^+$ 241.1434 observed 241.1434.

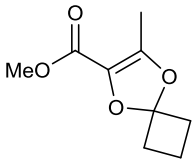
Methyl 3-phenyl-1,4-dioxaspiro[4.5]dec-2-ene-2-carboxylate (4f).



Starting from the corresponding α-diazo-β-ketoester **3f** (65 mg, 0.32 mmol) and cyclohexanone **8a** (33 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 9:1) as a colourless oil (14 mg, 15% yield).

Rf = 0.74 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12-7.80 (m, 2H), 7.40-7.38 (m, 3H), 4.38-4.33 (m, 2H), 2.24-1.94 (m, 2H), 1.90-1.87 (m, 2H), 1.80-1.67 (m, 3H) and 1.67-1.07 (m, 6H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.13 (C), 147.08 (C), 129.98 (CH), 128.54 (2xCH), 128.01 (2xCH), 127.73 (C), 126.50 (C), 114.96 (C), 60.98 (CH_2), 34.78 (CH_2), 24.77 (CH_2), 23.17 (CH_2) and 14.43 (CH_3) ppm; **IR (neat):** 1744, 1695, 1448, 1234, 1106 and 1019 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{17}H_{21}O_4^+$ 289.1434 observed 289.1435.

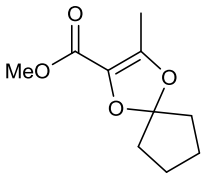
Methyl 7-methyl-5,8-dioxaspiro[3.4]oct-6-ene-6-carboxylate (4g).



Starting from the corresponding α-diazo-β-ketoester **3a** (46 µL, 0.32 mmol) and cyclobutanone **8g** (24 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (37 mg, 63% yield).

Rf = 0.54 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.81 (s, 3H), 2.65-2.42 (m, 4H), 2.19 (s, 3H) and 1.84-1.69 (m, 2H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.3 (C), 148.2 (C), 126.3 (C), 115.2 (C), 51.7 (CH_3), 37.2 (2 x CH_2), 11.6 (CH_2) and 10.8 (CH_3) ppm; **IR (neat):** 1712, 1677, 1350, 1290, 1125, 908 and 731 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_9H_{13}O_4^+$ 185.0808 observed 185.0809.

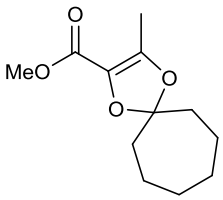
Methyl 3-methyl-1,4-dioxaspiro[4.4]non-2-ene-2-carboxylate (4h).



Starting from the corresponding α-diazo-β-ketoester **3a** (46 µL, 0.38 mmol) and cyclopentanone **8h** (28 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (52 mg, 82% yield).

Rf = 0.54 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.80 (s, 3H), 2.18 (s, 3H), 2.12-1.88 (m, 4H) and 1.86-1.66 (m, 4H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.6 (C), 148.5 (C), 126.5 (C), 124.8(C), 51.7 (CH_3), 37.2 (2 x CH_2), 23.4 (2 x CH_2) and 11.7 (CH_3) ppm; **IR (neat):** 1711, 1674, 1345, 1193, 1134 and 1095 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{10}H_{15}O_4^+$ 199.0965 observed 199.0965.

Methyl 3-methyl-1,4-dioxaspiro[4.6]undec-2-ene-2-carboxylate (4i).

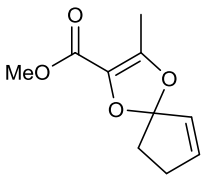


Starting from the corresponding α-diazo-β-ketoester **3a** (46 µL, 0.32 mmol) and cycloheptanone **8i** (38 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (60 mg, 83% yield).

Rf = 0.71 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.79 (s, 3H), 2.17 (s, 3H), 2.06-2.02 (m, 4H) and 1.68-1.57 (m, 8H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.9 (C), 148.2 (C), 126.0 (C), 119.8 (C),

51.6 (CH_3), 38.5 (2 x CH_2), 29.3 (2 x CH_2), 21.6 (2 x CH_2) and 11.8 (CH_3) ppm; **IR (neat):** 1711, 1672, 1345, 1137 and 1100 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{12}H_{19}O_4^+$ 227.1278 observed 227.1279.

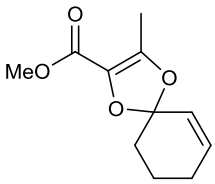
Methyl 3-methyl-1,4-dioxaspiro[4.4]nona-2,6-diene-2-carboxylate (4j).



Starting from the corresponding α-diazo-β-ketoester **3a** (46 µL, 0.32 mmol) and cyclopent-2-en-1-one **8j** (27 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 9:1) as a colourless oil (40 mg, 65% yield).

Rf = 0.40 (SiO_2, pentane:Et_2O, 9:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.21 (dt, *J* = 6 and 2 Hz, 1H), 5.85 (dt, *J* = 6 and 2 Hz, 1H), 3.80 (s, 3H), 2.52-2.43 (m, 2H), 2.43-2.22 (m, 2H) and 2.20 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.4 (C), 148.4 (C), 140.1 (CH), 134.8 (C), 128.2 (CH), 126.5 (C), 51.7 (CH_3), 35.2 (CH_2), 29.8 (CH_2) and 11.6 (CH_3) ppm; **IR (neat):** 1718, 1674, 1352, 1138 and 1107 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{10}H_{13}O_4^+$ 197.0808 observed 197.0809.

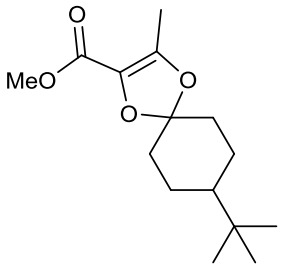
Methyl 3-methyl-1,4-dioxaspiro[4.5]deca-2,6-diene-2-carboxylate (4k).



Starting from the corresponding α-diazo-β-ketoester **3a** (46 µL, 0.32 mmol) and cyclohex-2-en-1-one **8k** (31 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 9:1) as a colourless oil (45 mg, 67% yield).

Rf = 0.39 (SiO_2, pentane:Et_2O, 9:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.09 (dt, *J* = 10 and 4 Hz, 1H), 5.85-5.76 (m, 1H), 3.79 (s, 3H), 2.19 (s, 3H), 2.12-2.00 (m, 4H) and 1.92-1.73 (m, 2H) ppm; **^{13}C NMR (100 MHz, Acetone):** δ 161.6 (C), 148.4 (C), 136.0 (CH), 126.8 (C), 125.7 (CH), 112.2 (C), 51.3 (CH_3), 33.8 (CH_2), 25.1 (CH_2), 20.4 (CH_2) and 11.4 (CH_3) ppm; **IR (neat):** 1714, 1674, 1350, 1148 and 1107 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{11}H_{15}O_4^+$ 211.0965 observed 211.0963.

Methyl 8-(tert-butyl)-3-methyl-1,4-dioxaspiro[4.5]dec-2-ene-2-carboxylate (4l).

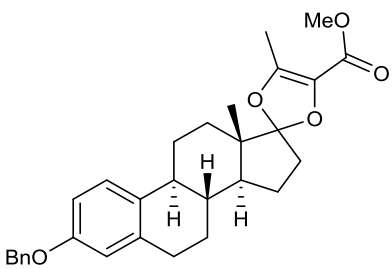


Starting from the corresponding α-diazo-β-ketoester **3a** (46 µL, 0.32 mmol) and 4-tert-butylcyclohexanone **8l** (49 mg, 0.32 mmol) and following the general procedure, the two diastereoisomers (1:1 mixture) were obtained after purification by column of silica gel (pentane:Et_2O 9:1) as a colourless oil (first eluted: 35 mg, 40% yield and second eluted: 36 mg 41% yield).

First eluted: Rf = 0.57 (SiO_2, pentane:Et_2O, 9:1); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 3.79 (s, 3H), 2.17 (s, 3H), 2.16-2.12 (m, 2H), 1.80-1.71 (m, 2H), 1.56-1.48 (m, 2H), 1.47-1.35 (m, 2H), 1.05 (tt, *J* = 12 and 3, 1H) and 0.88 (s, 9H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$):** δ 162.0 (C), 148.5 (C), 126.3 (C), 115.4 (C), 51.5 (CH_3), 47.0 (CH), 35.0 (2 x CH_2), 32.5 (C), 27.9 (3 x CH_3), 24.1 (2 x CH_2) and 11.8 (CH_3) ppm; **IR (neat):** 1713, 1675, 1442, 1346, and 1111 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{15}H_{25}O_4^+$ 269.1747 observed 269.1753.

Second eluted: Rf = 0.43 (SiO_2, pentane:Et_2O, 9:1); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 3.80 (s, 3H), 2.19 (s, 3H), 2.16-2.09 (m, 2H), 1.80-1.74 (m, 2H), 1.62 (td, *J* = 14 and 4, 2H), 1.38-1.27 (m, 2H), 1.06 (ddt, *J* = 12, 9 and 3, 1H) and 0.88 (s, 9H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$):** δ 161.9 (C), 148.4 (C), 126.4 (C), 116.0 (C), 51.6 (CH_3), 46.7 (CH), 35.0 (2 x CH_2), 32.5 (C), 27.8 (3 x CH_3), 23.94 (2 x CH_2) and 11.83 (CH_3) ppm; **IR (neat):** 1712, 1674, 1443, 1346, and 1121cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{15}H_{25}O_4^+$ 269.1747 observed 269.1753.

Methyl (8R,9S,13S,14S)-3-(benzyloxy)-5',13-dimethyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolane]-4'-carboxylate (4m).



Starting from the corresponding α-diazo-β-ketoester **3a** (46 µL, 0.32 mmol) and benzylated estrone **8m** (115 mg, 0.32 mmol) and following the general procedure, the two diastereoisomers (1:1 mixture) were obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (137 mg, 90% yield).

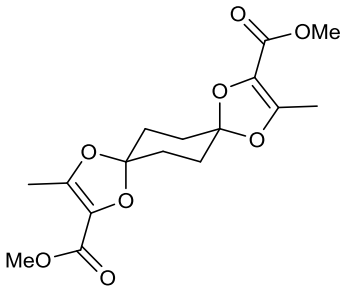
Mp: 61 °C; **Rf** = 0.44 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45-7.41 (m, 4H), 7.38 (t, *J* = 7.5 Hz, 4H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.19 (ddd, *J* = 8.8, 4.8 and 1.0 Hz, 2H), 6.79 (t, *J* = 2.9 Hz, 1H), 6.77 (t, *J* = 2.9 Hz, 1H), 6.73-6.71 (m, 2H), 5.03 (s, 4H), 3.81 (s, 3H), 3.80 (s, 3H), 2.89-2.79 (m, 4H), 2.36-2.23 (m, 4H), 2.20 (s, 3H), 2.20 (s, 3H), 2.19- 2.06 (m, 2H), 1.94-1.32 (m, 20H), 0.94 (s, 3H) and 0.87 (s, 3H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$):** δ 161.5 (C), 161.4 (C), 156.9 (C), 156.9 (C), 149.1 (C), 148.3 (C), 138.13 (C), 138.09 (C), 137.5 (2 x C), 132.9 (C), 132.8 (C), 128.7 (4 x CH), 128.0 (2 x CH), 127.6 (4 x CH), 127.4 (C), 126.6 (C), 126.5

(2 x CH), 125.4 (C), 125.0 (C), 115.0 (2 x CH), 112.5 (2 x CH), 70.1 (2 x CH_2), 51.7 (CH_3), 51.6 (CH_3), 48.4 (CH), 48.2 (CH), 47.3 (C), 46.9 (C), 43.7 (CH), 43.4 (CH), 39.1 (2 x CH), 34.9 (2 x CH_2), 30.0 (CH_2), 29.90 (2 x CH_2), 29.85 (CH_2), 27.1 (CH_2), 26.9 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 22.3 (CH_2), 22.2 (CH_2), 13.8 (CH_3), 13. 7 (CH_3), 11.6 (CH_3) and 11.4 (CH_3) ppm; **IR (CDCl₃):** 1712, 1676, 1609, 1499, 1440, 1349, 1137 and 1110 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{30}H_{35}O_5^+$ 475.2479 observed 475.2480.

Dimethyl 3,11-dimethyl-1,4,9,12-tetraoxadispiro[4.2.4^8.2^5]tetradeca-2,10-diene-2,10-dicarboxylate (4n and 4n').

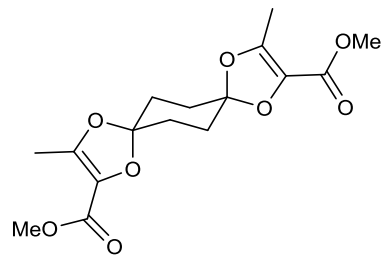
Starting from the corresponding α-diazo-β-ketoester **3a** (2 equiv, 92 µL, 0.64 mmol) and cyclohexane-1,4-dione **8n** (72 mg, 0.64 mmol) and following the general procedure, the two diastereoisomers (1:1 mixture) were obtained after purification by column of silica gel (pentane:Et_2O 7:3) as a white solid (first eluted: 40 mg, 37% yield and second eluted: 37 mg 34% yield).

First eluted – *trans* diastereomer (4n):



The *trans* configuration was established by X-Ray diffraction studies on X-ray quality crystals obtained by slow evaporation of solvent (CH_2Cl_2). **Mp:** 181.0 °C; **Rf** = 0.25 (SiO_2, pentane:Et_2O, 7:3); **^{1}H NMR (500 MHz, CDCl₃):** δ 3.80 (s, 6H), 2.18 (s, 6H) and 2.15-2.02 (m, 8H) ppm; **^{13}C NMR (125 MHz, CDCl₃):** δ 161.6 (2 x C), 148.3 (2 x C), 126.5 (2 x C), 113.9 (2 x C), 51.7 (2 x CH_3), 31.0 (4 x CH_2) and 11.7 (2 x CH_3) ppm; **IR (neat):** 1711, 1678, 1344, 1118 and 1078 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{16}H_{21}O_8^+$ 341.1231 observed 341.1231.

Second eluted – *cis* diastereomer (4n'):



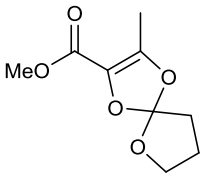
The *cis* configuration was established by X-Ray diffraction studies on X-ray quality crystals obtained by slow evaporation of solvent (pentane/Et_2O). **Mp:** 161 °C; **Rf** = 0.21 (SiO_2, pentane:Et_2O, 7:3); **^{1}H NMR (500 MHz, CDCl₃):** δ 3.79 (s, 6H), 2.19 (s, 6H) and 2.18-1.99 (m, 8H). ppm; **^{13}C NMR (125 MHz, CDCl₃):** δ 161.6 (2 x C), 148.2 (2 x C), 126.5 (2 x C), 113.8 (2 x C), 51.6 (2 x CH_3), 31.0 (4 x CH_2), and 11.7 (2 x CH_3) ppm; **IR (neat):** 1714, 1676, 1349, 1118 and 1122 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{16}H_{21}O_8^+$ 341.1231 observed 341.1232.

6. GENERAL PROCEDURE FOR THE SYNTHESIS OF COMPOUNDS 5

In a 2 mL screw-cap vial equipped with a magnetic stirring bar, 1,10-phenanthroline (1.5 mg, 8 µmol, 2.5 mol%) and [CpRu(CH_3CN)$_3$][BAr_F] (9 mg, 8 µmol, 2.5 mol%) were dissolved in 0.60 mL of dry CH_2Cl_2. The vial was flushed with argon and capped. The resulting deep red solution was stirred for 20 minutes at 25 °C before the addition of desired lactone **9** (1 equiv, 0.32 mmol) and diazo **3a** (3 equiv, 0.96 mmol). The solution was stirred at 60 °C until full conversion (^{1}H NMR monitoring). The crude mixture was purified by column chromatography (Pentane/Et_2O, SiO_2) to afford insertion products of type **5**.

7. ANALYSIS DATA OF COMPOUNDS 5

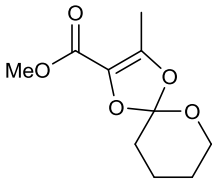
Methyl 3-methyl-1,4,6-trioxaspiro[4.4]non-2-ene-2-carboxylate (5a).



Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and γ-butyrolactone **9a** (26 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (14 mg, 78% yield).

Rf = 0.26 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.10 (td, *J* = 7 and 3 Hz, 2H), 3.81 (s, 3H), 2.43-2.29 (m, 2H), 2.24 (s, 3H) and 2.18-2.09 (m, 2H) ppm; **^{13}C NMR (100 MHz, acetone-*d*$_6$):** δ 160.9 (C), 147.0 (C), 132.7 (C), 126.6 (C), 69.3 (CH_2), 51.5 (CH_3), 34.9 (CH_2), 24.8 (CH_2) and 11.2 (CH_3) ppm; **IR (neat):** 1720, 1681, 1353, 1126 and 1062 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_9H_{13}O_5^+$ 201.0758 observed 201.0759.

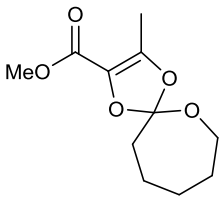
Methyl 3-methyl-1,4,6-trioxaspiro[4.5]dec-2-ene-2-carboxylate (5b).



Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and δ-valerolactone **9b** (30 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (46 mg, 67% yield).

Rf = 0.30 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, acetone-*d*$_6$):** δ 3.91-3.83 (m, 2H), 3.75 (s, 3H), 2.19 (s, 3H), 1.96-1.82 (m, 4H) and 1.63-1.57 (m, 2H) ppm; **^{13}C NMR (100 MHz, acetone-*d*$_6$):** δ 161.2 (C), 147.6 (C), 127.0 (C), 122.9 (C), 65.3 (CH_2), 51.5 (CH_3), 32.9 (CH_2), 24.6 (CH_2), 21.5 (CH_2) and 11.3 (CH_3) ppm; **IR (neat):** 1715, 1679, 1348, 1104 and 1035 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{10}H_{15}O_5^+$ 215.0914 observed 215.0906.

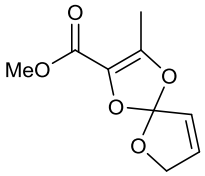
Methyl 3-methyl-1,4,6-trioxaspiro[4.6]undec-2-ene-2-carboxylate (5c).



Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and ε-caprolactone **9c** (36 µL, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (60 mg, 82% yield).

^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 3.82-3.75 (m, 2H), 3.73 (s, 3H), 2.28-2.23 (m, 2H), 2.16 (s, 3H) and 1.75-1.62 (m, 6H) ppm; **^{13}C NMR (100 MHz, acetone-*d*$_6$):** δ 161.2 (C), 147.3 (C), 128.0 (C), 126.6 (C), 65.5 (CH_2), 51.4 (CH_3), 37.4 (CH_2), 31.4 (CH_2), 29.6 (CH_2, signal overlapped with solvent), 22.9 (CH_2) and 11.3 (CH_3) ppm; **IR (neat):** 1713, 1678, 1349, 1099 and 1064 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{11}H_{17}O_5^+$ 229.1071 observed 229.1065.

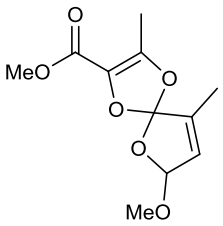
Methyl 3-methyl-1,4,6-trioxaspiro[4.4]nona-2,8-diene-2-carboxylate (5d).



Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and furan-2(5H)one γ-crotonolactone **9d** (27 µl, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 6:4) as a colourless oil (36 mg, 57% yield).

Rf = 0.40 (SiO_2, pentane:Et_2O, 6:4); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.53 (dt, *J* = 6 and 2 Hz, 1H), 5.81 (dt, *J* = 6 and 2 Hz, 1H), 4.75-4.72 (m, 2H), 3.82 (s, 3H) and 2.27 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.7 (C), 146.9 (C), 136.1 (CH), 133.8 (C), 126.2 (C), 122.2 (CH), 73.9 (CH_2), 51.8 (CH_3) and 11.3 (CH_3) ppm; **IR (MeOH):** 1718, 1684, 1655, 134.8 and 1259 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_9H_{11}O_5^+$ 197.0444 observed 197.0445.

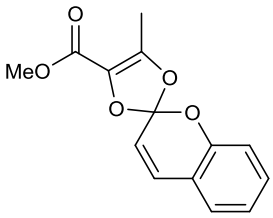
Methyl 3-methyl-1,4,6-trioxaspiro[4.4]nona-2,8-diene-2-carboxylate (5e).



Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and 5-methoxifuran-2(5H)-one[3] **9e** (37 mg, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (54 mg, 70% yield). The product is obtained as a 1:1 mixture of two diastereoisomers.

Rf = 0.19 (SiO_2, pentane:Et_2O, 8:2);); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.88 (dt, *J* = 3 and 2 Hz, 2H), 5.70 (t, *J* = 1 Hz, 1H), 5.66 (t, *J* = 1 Hz, 1H), 3.82 (s, 3H), 3.82 (s, 3H), 3.43 (s, 3H), 3.39 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H) and 1.81 (s, 6H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.6 (C), 160.5 (C), 147.7 (C), 147.1 (C), 142.8 (C), 137.4 (C), 137.3 (C), 130.6 (C), 128.5 (2 x CH), 127.1 (C), 126.6 (C), 105.7 (CH), 105.3 (CH), 55.3 (CH_3), 54.4 (CH_3), 51.9 (CH_3), 51.8 (CH_3), 11.4 (CH_3), 11.3 (CH_3), 10.54 (CH_3) and 10.53 (CH_3) ppm; **IR (neat):** 1716, 1208, 1094 and 1009 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{11}H_{15}O_6^+$ 243.0863 observed 243.0863.

Methyl 5'-methylspiro[chromene-2,2'-[1,3]dioxole]-4'-carboxylate (5f).



Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and coumarin **9f** (47 mg, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:Et_2O 8:2) as a colourless oil (53 mg, 64% yield).

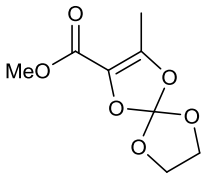
Rf = 0.56 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, acetone-*d_6*):** δ 7.44-7.32 (m, 2H), 7.17 (dd, *J* = 10 and 1 Hz, 1H), 7.10 (td, *J* = 8 and 1 Hz, 1H), 7.01 (ddt, *J* = 8, 1 and 0.5 Hz, 1H), 5.95 (d, *J* = 10 Hz, 1H), 3.78 (s, 3H) and 2.27 (s, 3H) ppm; **^{13}C NMR (100 MHz, acetone-*d_6*):** δ 160.7 (C), 151.0 (C), 146.6 (C), 131.5 (CH), 131.4 (CH), 128.4 (CH), 126.5 (C), 123.4 (CH), 121.2 (C), 119.1 (C), 116.7 (2 x CH), 51.8 (CH_3) and 11.1 (CH_3) ppm; **IR (neat):** 1721, 1684, 1350, 1257, 1156, 1113 and 1039 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_{14}H_{13}O_5^+$ 261.0758 observed 261.0757.

8. GENERAL PROCEDURE FOR THE SYNTHESIS AND ANALYSIS DATA OF COMPOUND 6

In a 2 mL screw-cap vial equipped with a magnetic stirring bar, 1,10-phenanthroline (1.5 mg, 8 µmol, 2.5 mol%) and $[CpRu(CH_3CN)_3][BAr_F]$ (9 mg, 8 µmol, 2.5 mol%) were dissolved in 0.60 mL of dry CH_2Cl_2. The vial was flushed with argon and capped. The resulting deep red solution was stirred for 20 minutes at 25 °C before the addition of carbonate **10** (1 equiv, 0.64 mmol) and diazo **3a** (3 equiv, 0.96 mmol). The solution was stirred at 60 °C until full conversion (^{1}H NMR monitoring). The crude mixture was purified by column chromatography (Pentane/Et_2O/Et_3N, SiO_2) to afford insertion products of type **6.**

9. ANALYSIS DATA OF COMPOUNDS 6

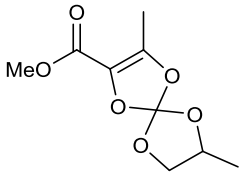
Methyl 3-methyl-1,4,6,9-tetraoxaspiro[4.4]non-2-ene-2-carboxylate (6a).



Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and carbonate **10a** (28 mg, 0.32 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (Pentane/Et_2O/Et_3N, 8:2:1) as a colourless oil (46 mg, 36% yield).

Rf = 0.32 (SiO_2, Pentane/Et_2O/Et_3N, 6:3:1); **^{1}H NMR (400 MHz, acetone-*d*$_6$):** δ 4.26 (m, 4H), 3.76 (s, 3H) and 2.21 (s, 3H) ppm; **^{13}C NMR (100 MHz, acetone-*d*$_6$):** δ 160.3 (C), 146.8 (C), 137.0 (C), 126.9 (C), 66.8 (2 x CH_2), 51.7 (CH_3) and 11.0 (CH_3); **IR (neat):** 1713, 1684, 1354, 1167, 1115, 1081 and 1044 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_8H_{11}O_6^+$ 203.0550 observed 203.0543.

Methyl 3,7-dimethyl-1,4,6,9-tetraoxaspiro[4.4]non-2-ene-2- (6b).

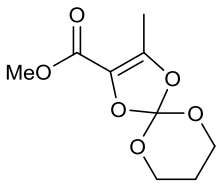


Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and carbonate **10b** (33 mg, 0.32 mmol) and following the general procedure, the desired compound was obtained as a 1:1 mixture of two diastereoisomers. After purification by column of silica gel (Pentane/Et_2O/Et_3N, 8:1:1) only one diastereoisomer was recovered as a colourless oil (18 mg, 27% yield).

Rf = 0.25 (SiO_2, pentane:Et_2O, 8:2); **^{1}H NMR (400 MHz, acetone-*d*$_6$)**: δ 4.70-4.52 (m, 1H), 4.33 (dd, *J* = 8 and 6, 1H), 3.80 (t, *J* = 8, 1H), 3.76 (s, 3H), 2.20 (s, 3H) and 1.35 (d, *J* = 6, 3H); **^{13}C NMR (100 MHz, acetone-*d*$_6$):** δ 160.4 (C), 146.8 (C), 136.5 (C), 126.8 (C), 75.4 (CH), 72.36 (CH_2), 51.70(CH_3), 18.26(CH_3) and 11.01(CH_3);

IR (neat): 1715, 1685, 1656, 1354, 1160, 1116, 1076 and 779 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_9H_{12}O_6^+$ 217.0707 observed 217.0707.

Methyl 3-methyl-1,4,6,10-tetraoxaspiro[4.5]dec-2-ene-2-carboxylate (6c).



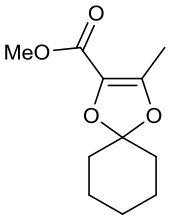
Starting from the corresponding α-diazo-β-ketoester **3a** (138 µL, 0.96 mmol) and carbonate **10c** (33 mg, 0.64 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (Pentane/Et_2O/Et_3N, 7:2:1) as a colourless oil (50 mg, 72% yield).

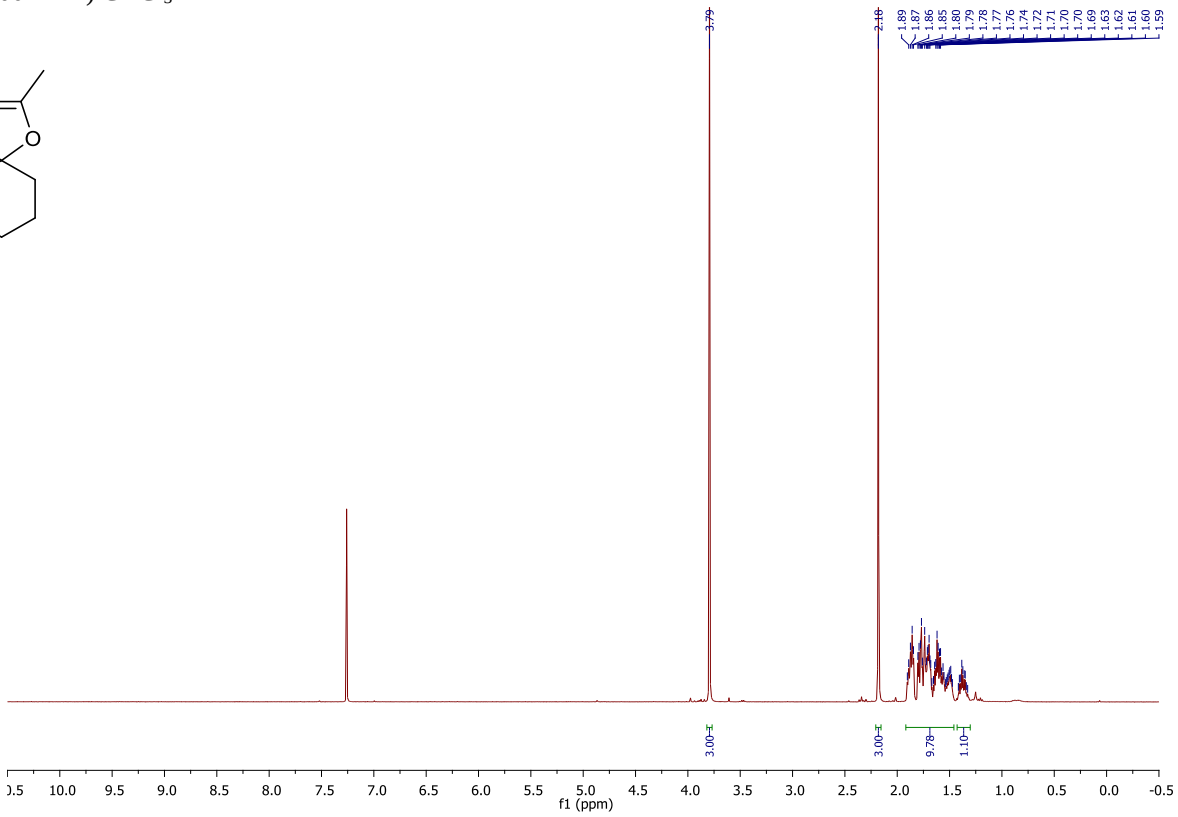
Rf = 0.22 (SiO_2, pentane:Et_2O, 7:3); **^{1}H NMR (400 MHz, acetone-*d*$_6$):** δ 4.37-4.03 (m, 4H), 3.76 (s, 3H), 2.21 (s, 3H) and 1.97-1.81 (m, 2H) ppm; **^{13}C NMR (100 MHz, acetone-*d*$_6$):** δ 160.5 (C), 147.2 (C), 127.5 (C), 127.2 (C), 64.4 (2 x CH_2), 51.7 (CH_3), 23.76 (CH_2) and 11.2 (CH_3); **IR (neat):** 1721, 1688, 1355, 1150, 1111 and 1083 cm^{-1}; **HR-MS (EI)** *m/z* calculated for $C_9H_{13}O_6^+$ 217.0707 observed 217.0708.

10. ^{1}H NMR AND ^{13}C-NMR SPECTRA OF NEW COMPOUNDS

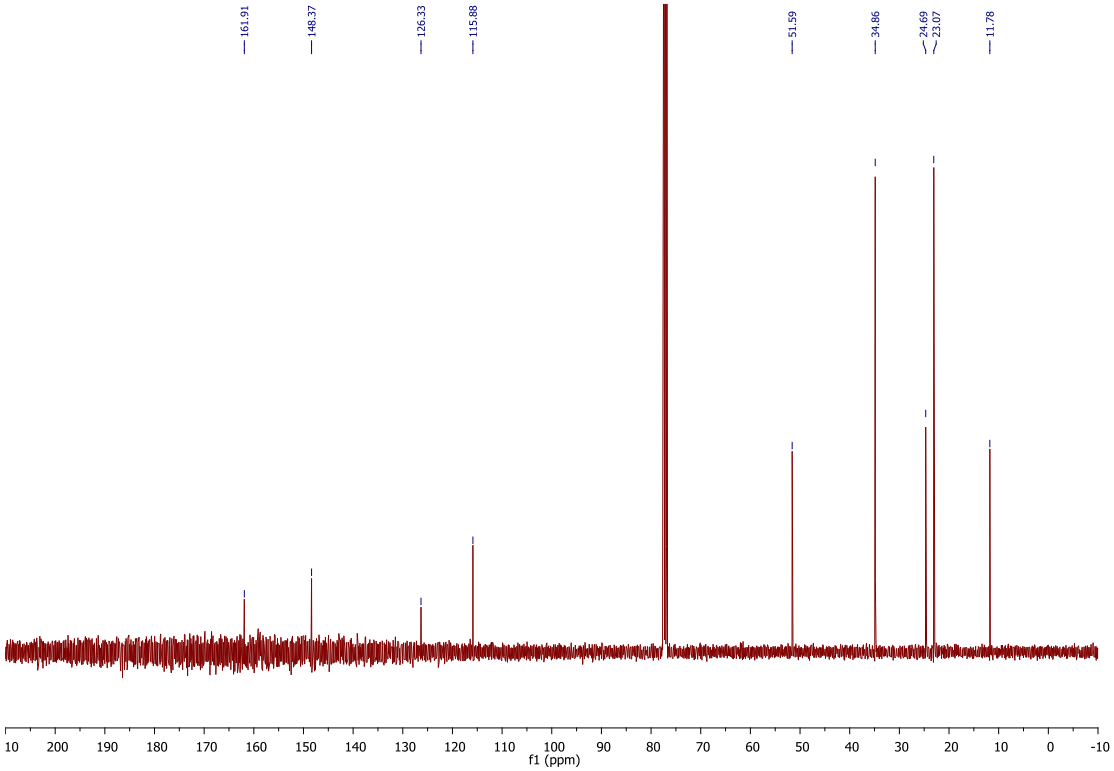
Adduct 4a was reported by Alonso, M. E.; Garcia, M. D.; Chitty, A. W., *J. Org. Chem.* **1985**, *50*, 3445-3449. New spectra are now provided.

^{1}H NMR (400 MHz) $CDCl_3$



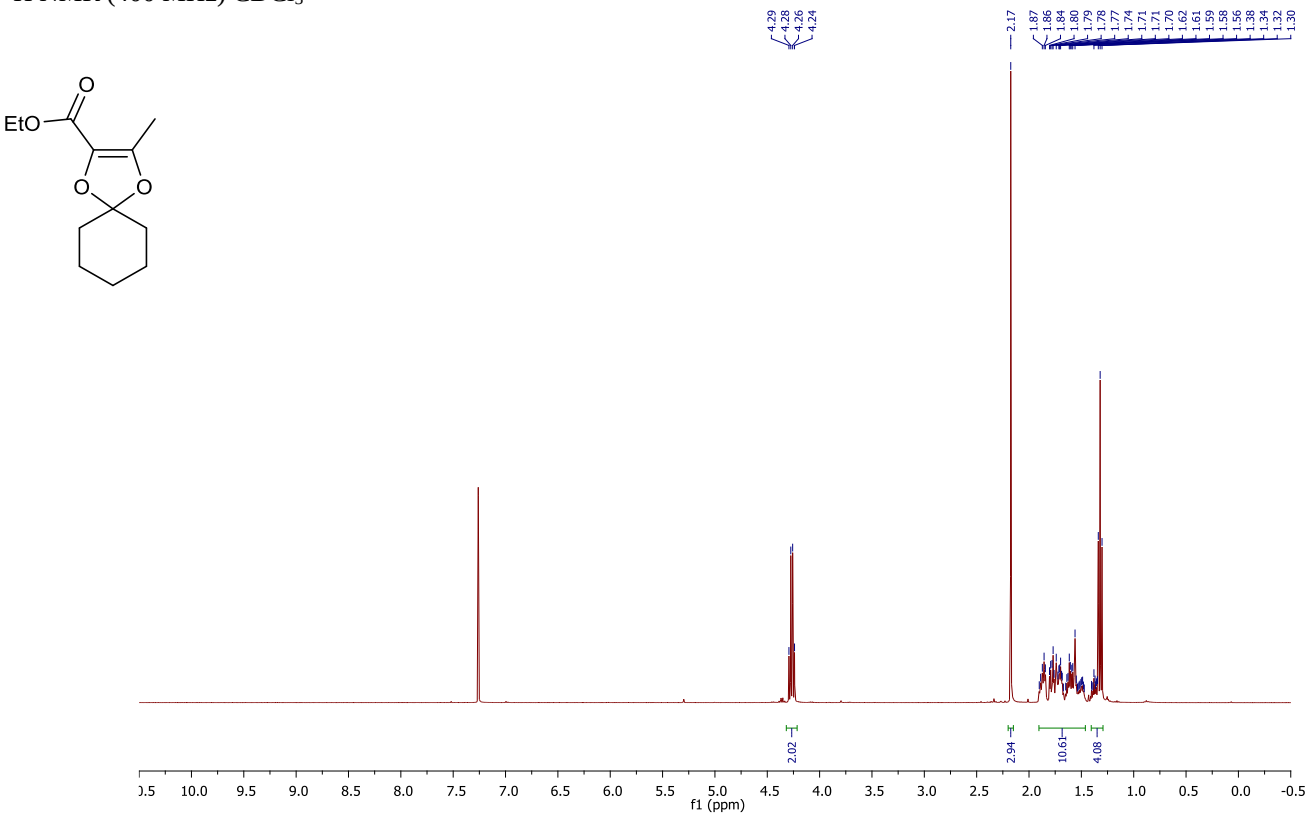


^{13}C NMR (100 MHz) $CDCl_3$



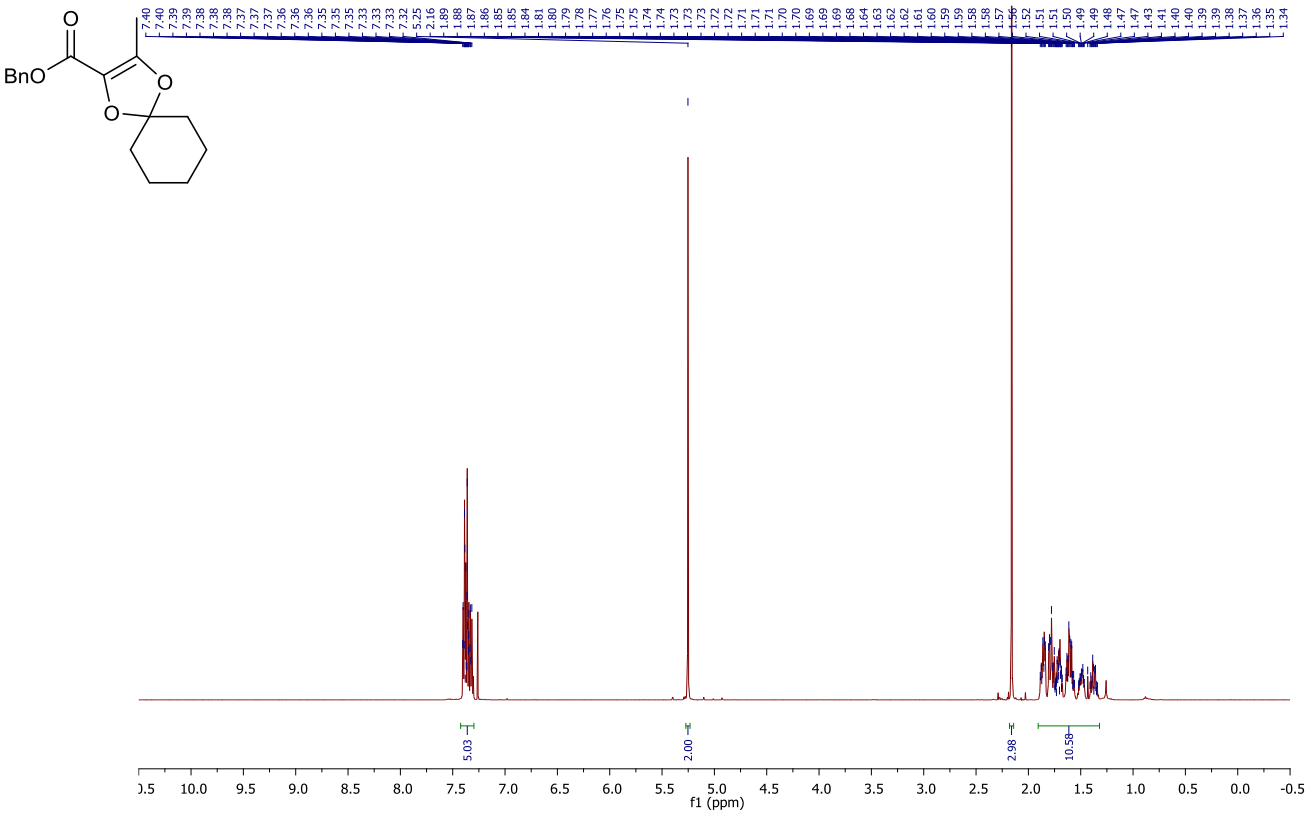
Adduct 4b was reported previously by Austeri, M.; Rix, D.; Zeghida, W.; Lacour, J., *Org. Lett.* **2011**, *13*, 1394-1397.

^{1}H NMR (400 MHz) $CDCl_3$

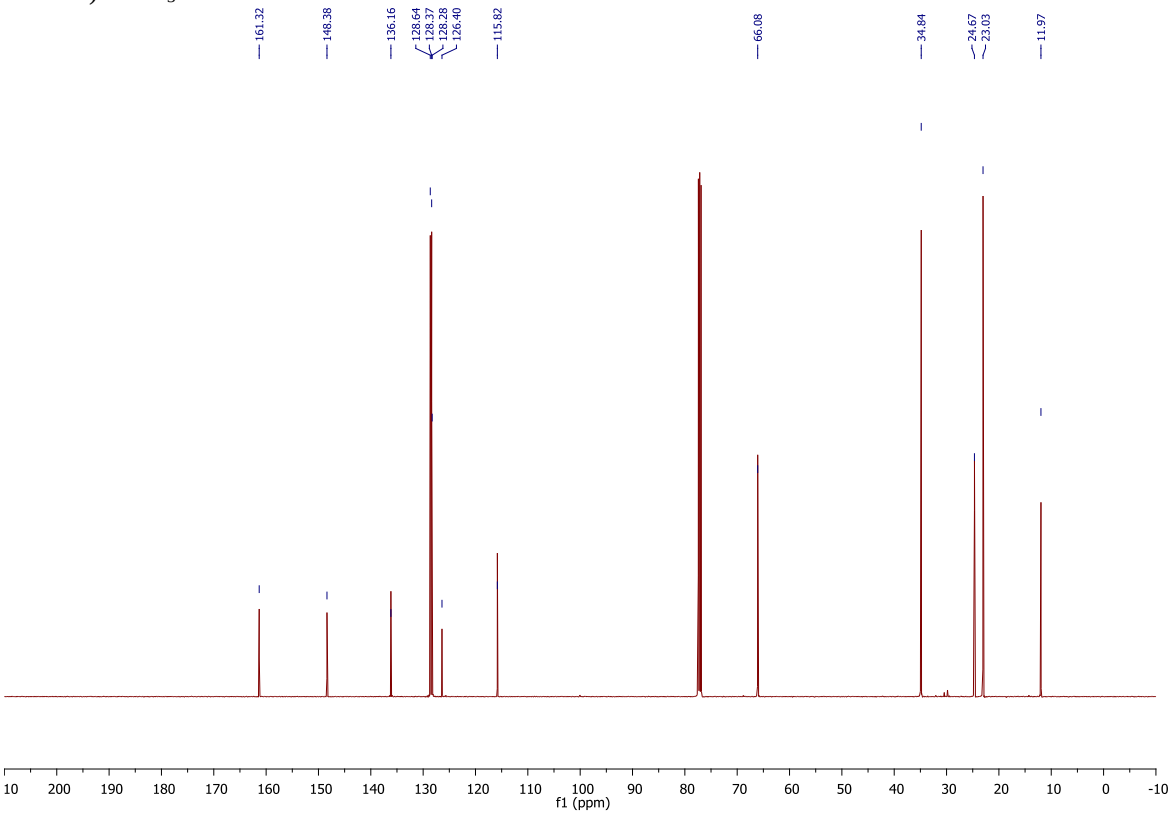


Adduct 4c

^{1}H NMR (500 MHz) $CDCl_3$

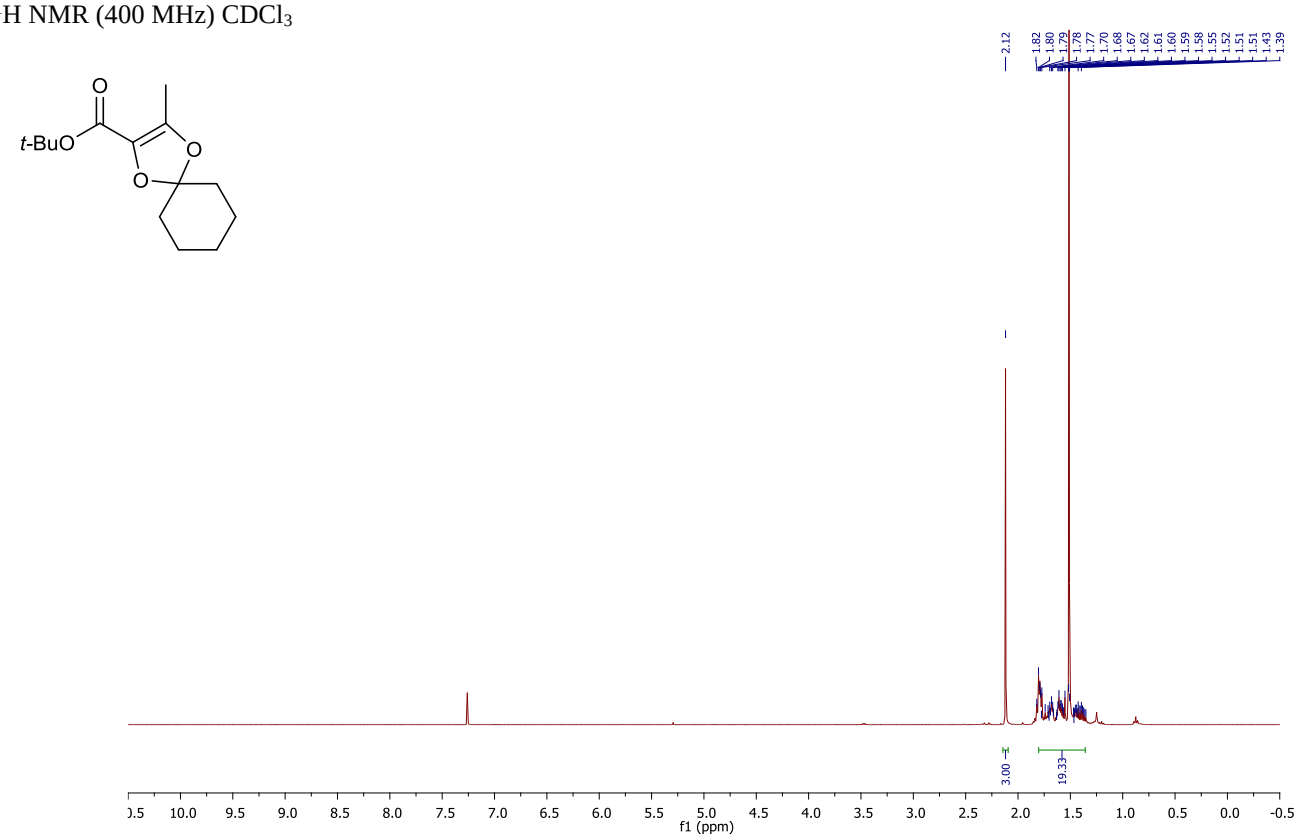


^{13}C NMR (126 MHz) $CDCl_3$

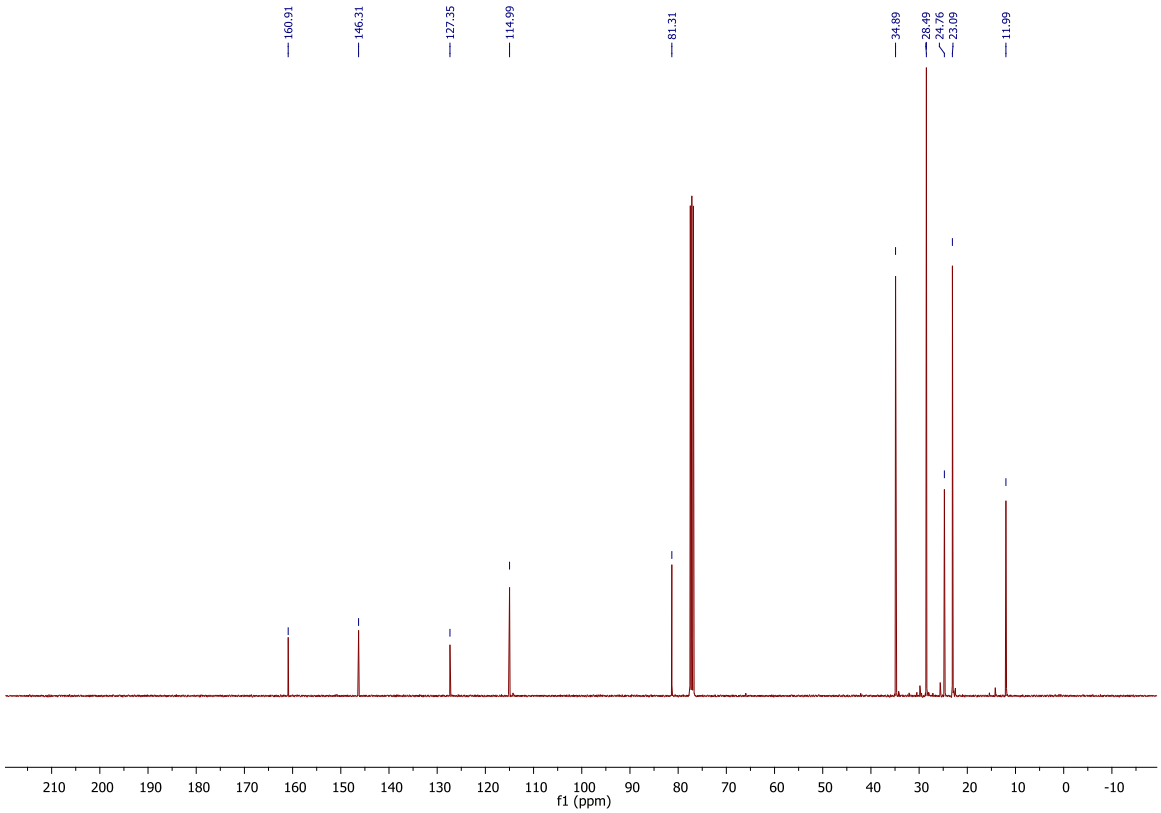


Adduct 4d

^{1}H NMR (400 MHz) $CDCl_3$

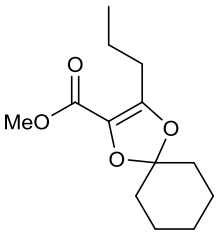


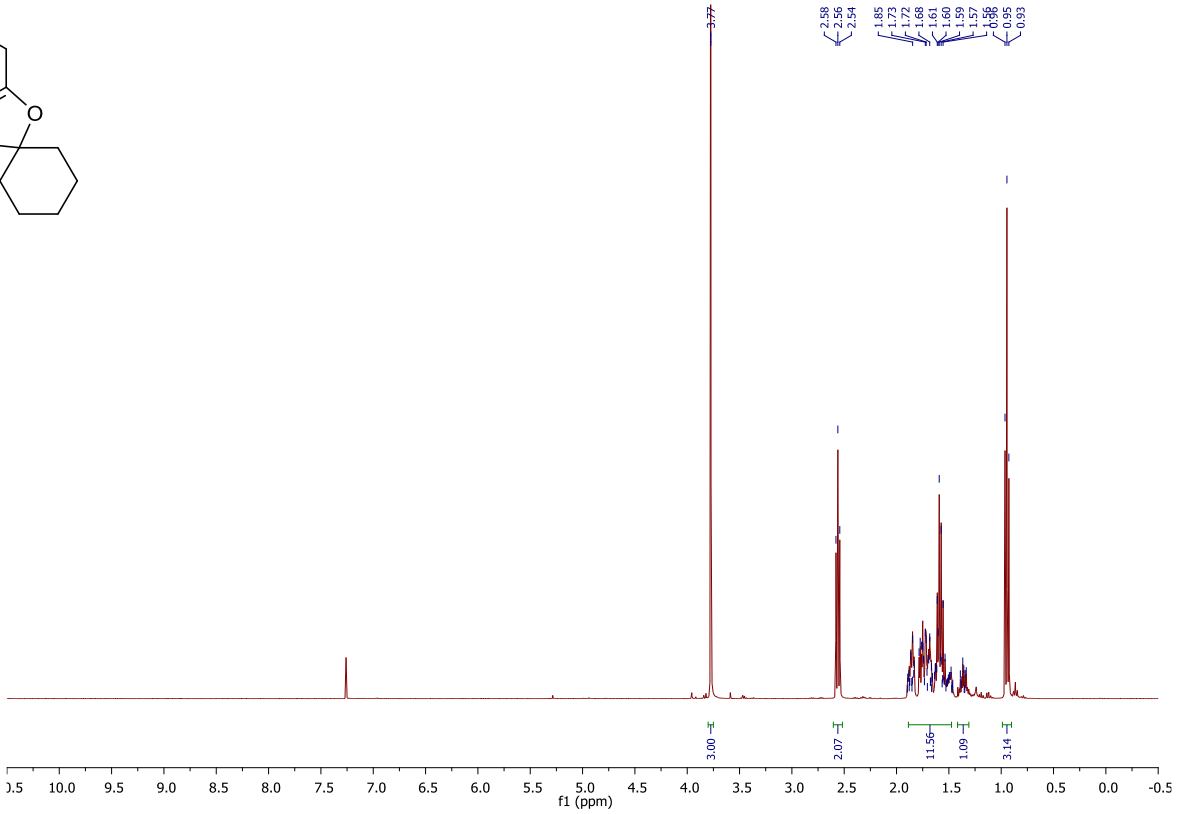
^{13}C NMR (100 MHz) $CDCl_3$



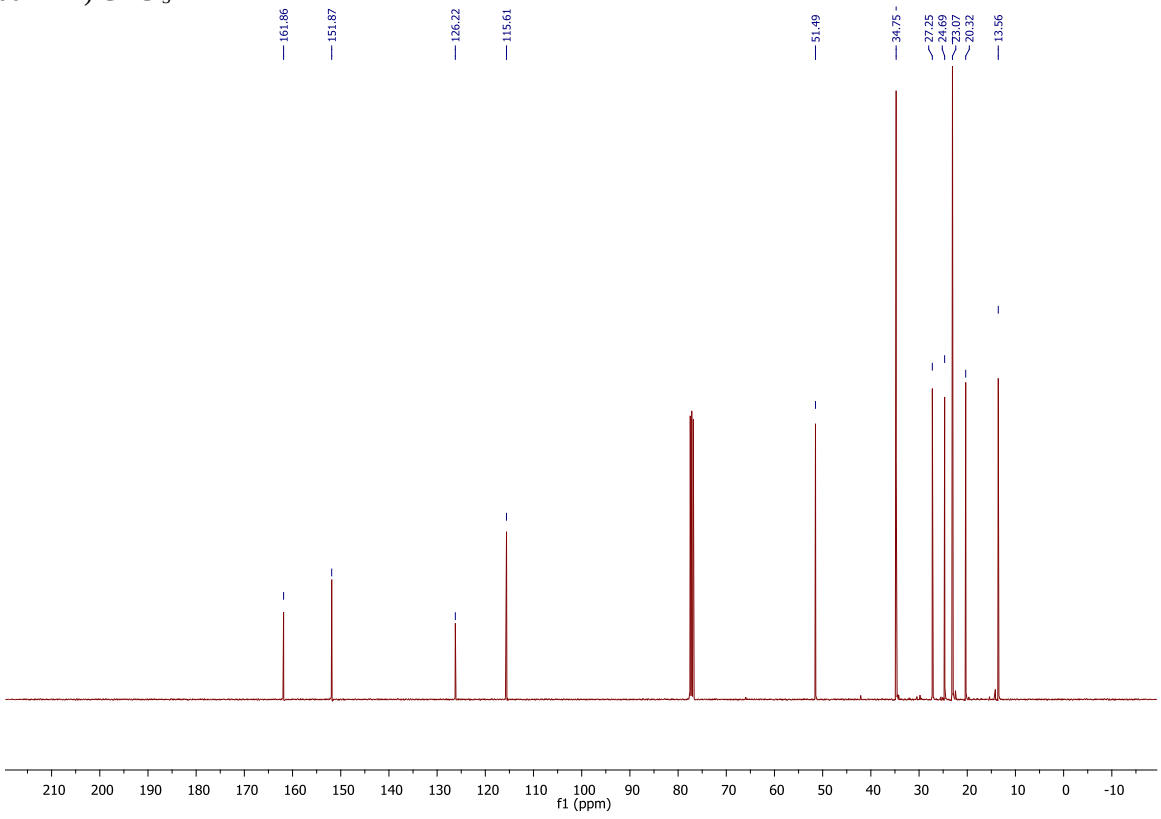
Adduct 4e

^{1}H NMR (400 MHz) $CDCl_3$



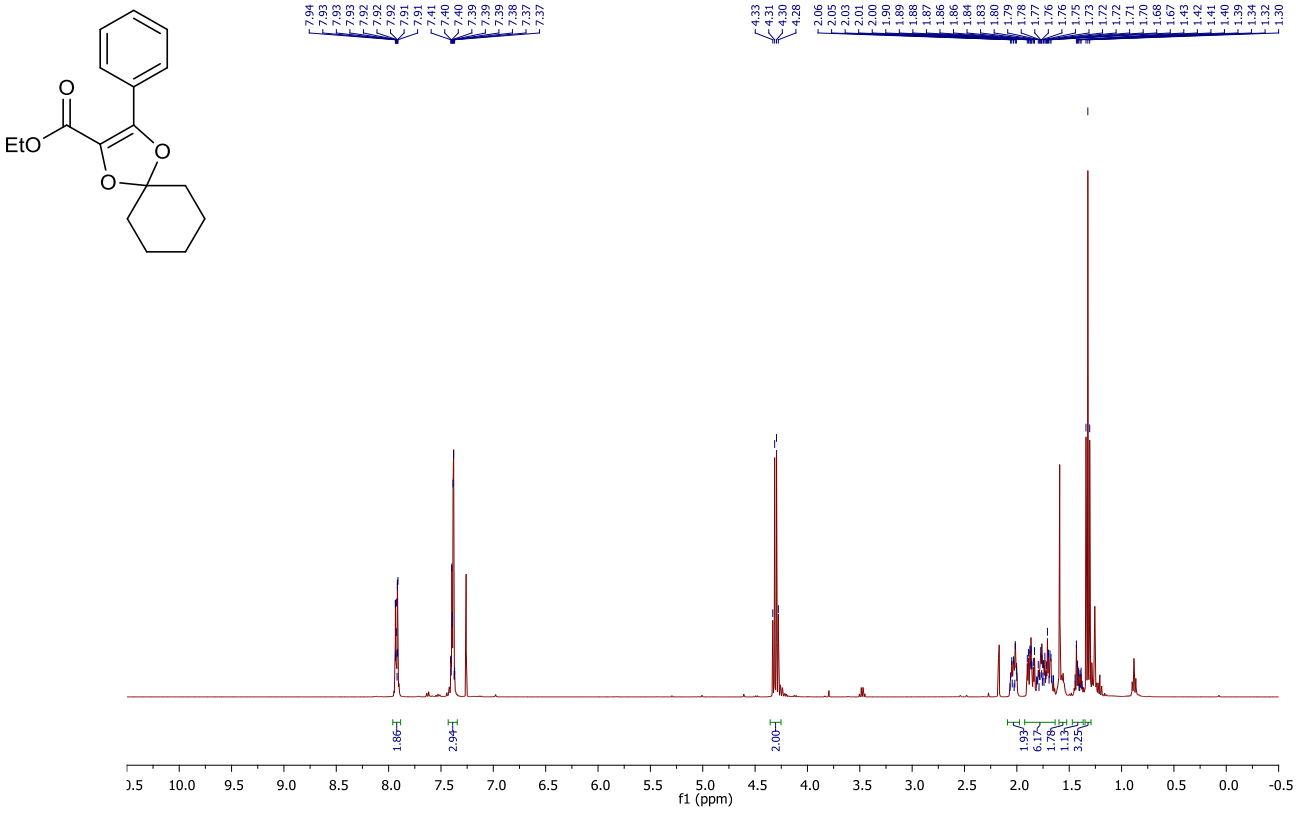


^{13}C NMR (100 MHz) $CDCl_3$

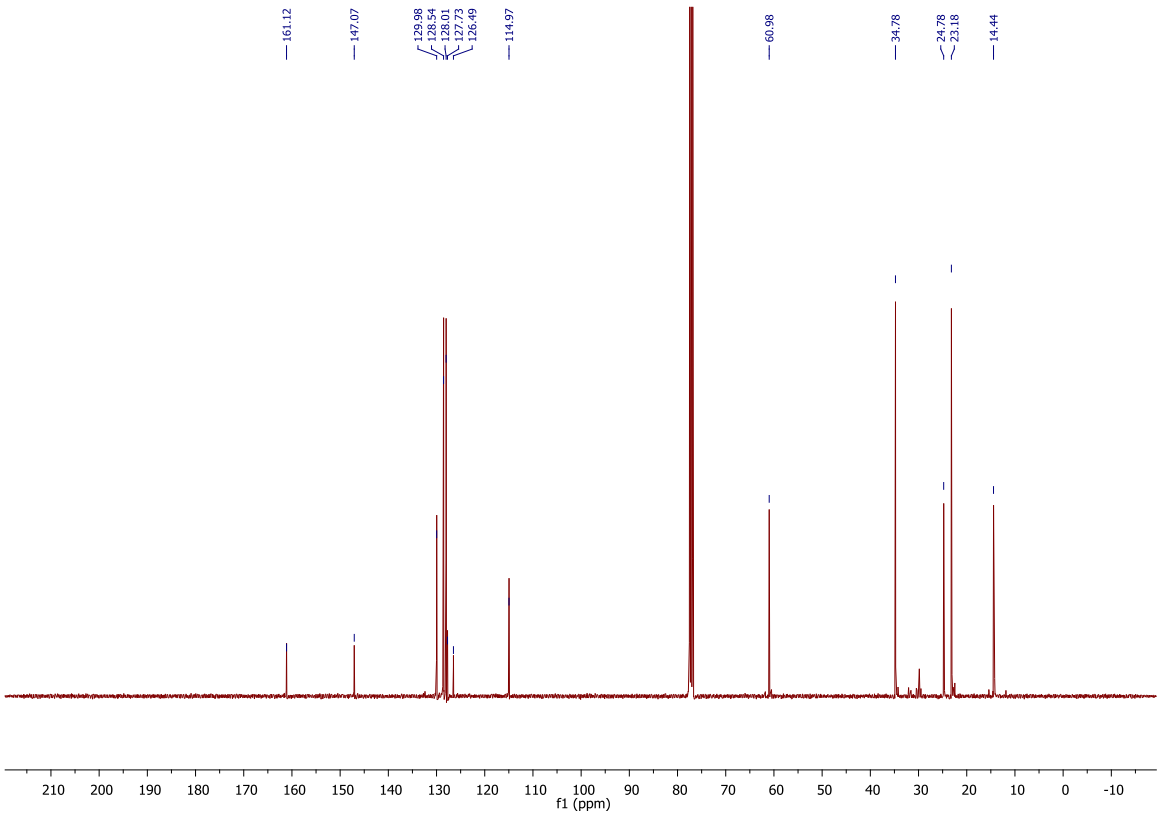


Adduct 4f

^{1}H NMR (400 MHz) $CDCl_3$

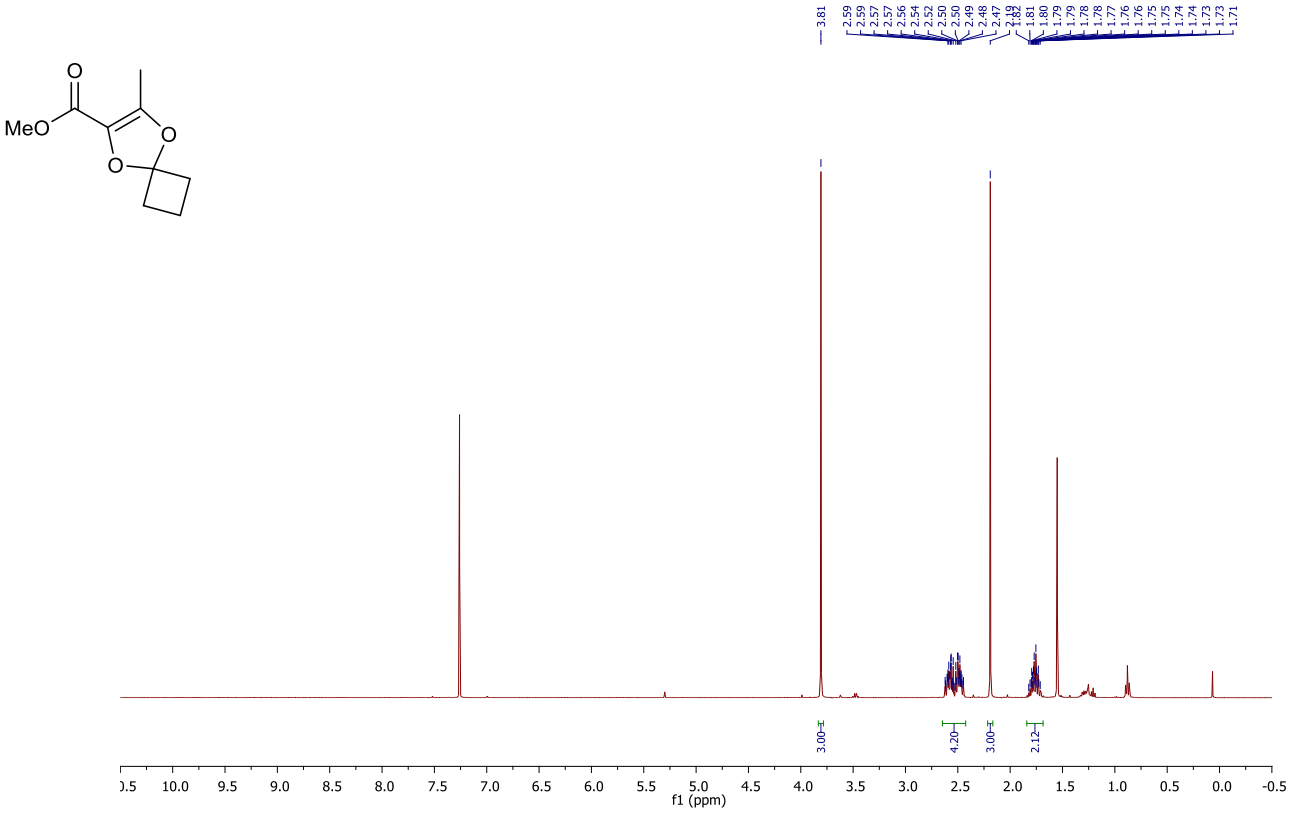


^{13}C NMR (100 MHz) $CDCl_3$

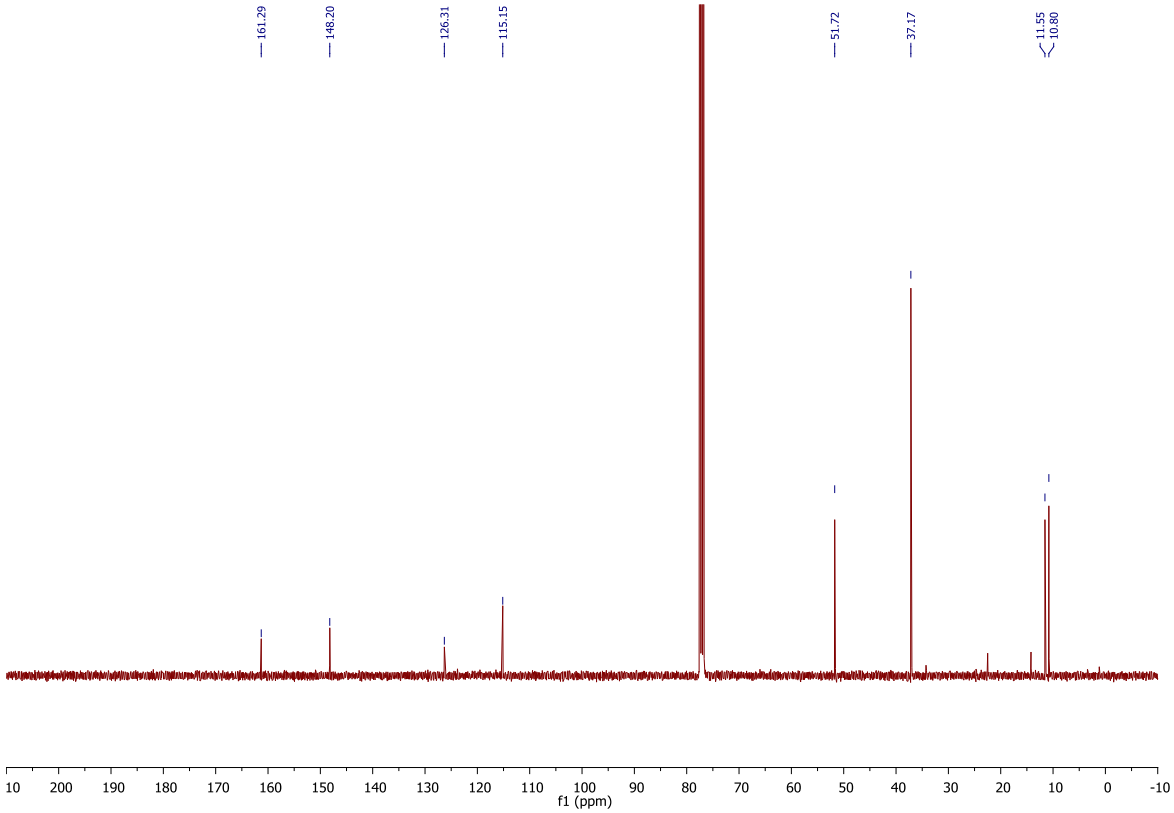


Adduct 4g

^{1}H NMR (400 MHz) $CDCl_3$

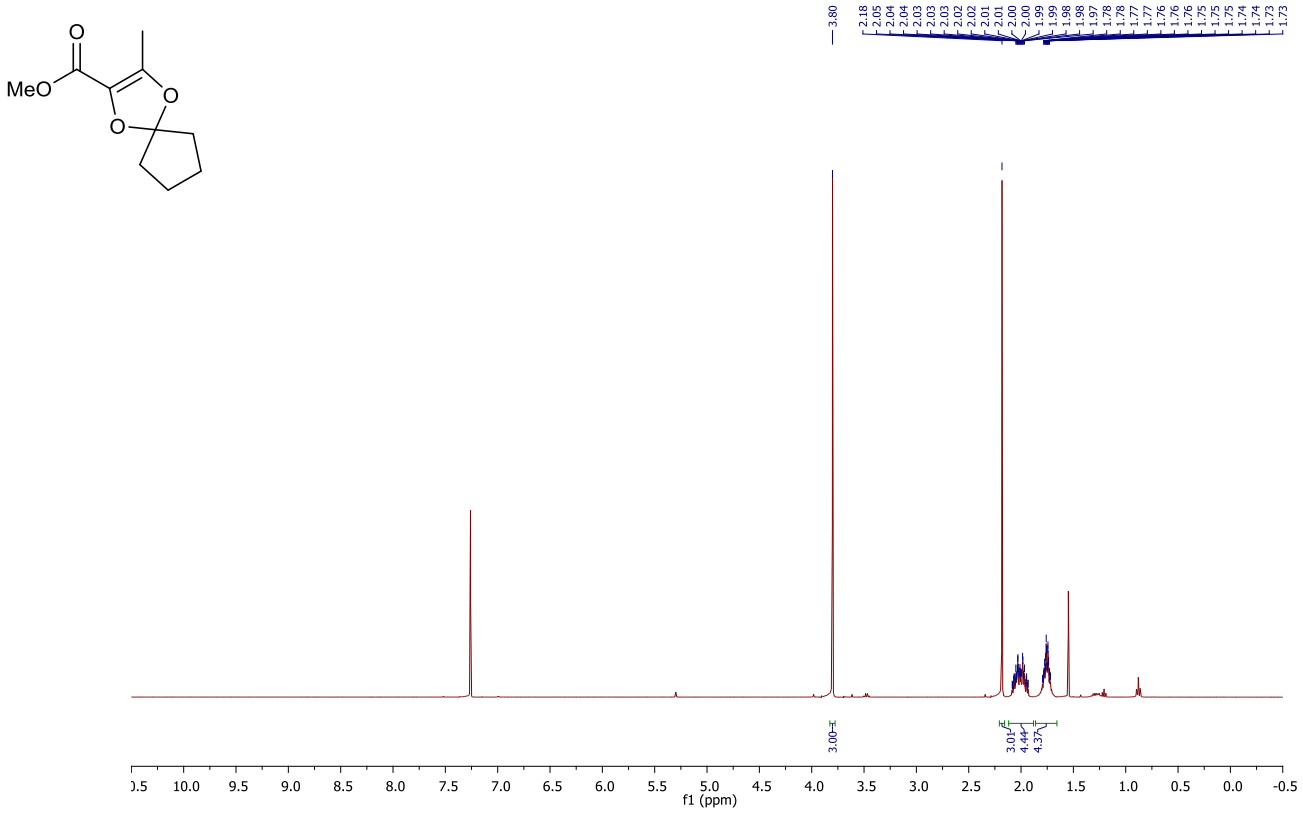


^{13}C NMR (100 MHz) $CDCl_3$

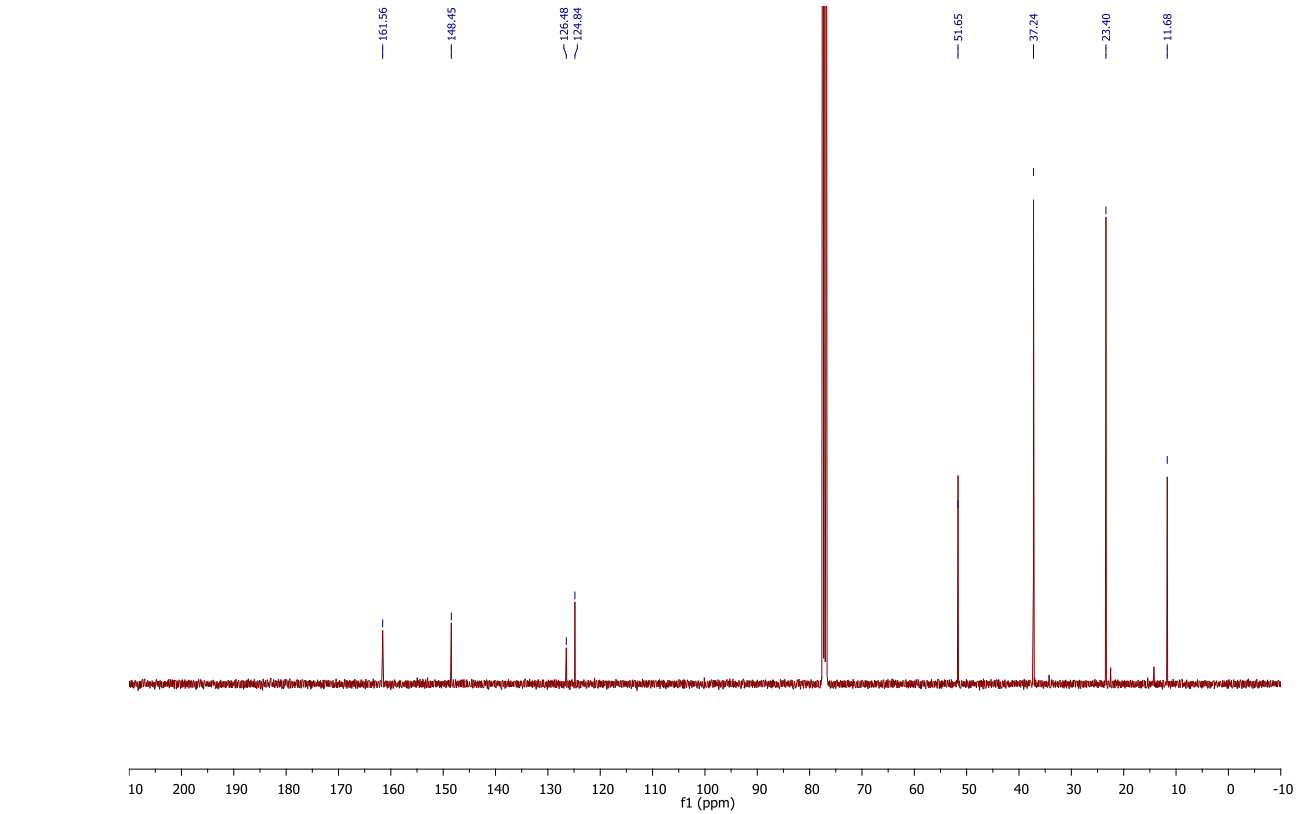


Adduct 4h

^{1}H NMR (400 MHz) $CDCl_3$

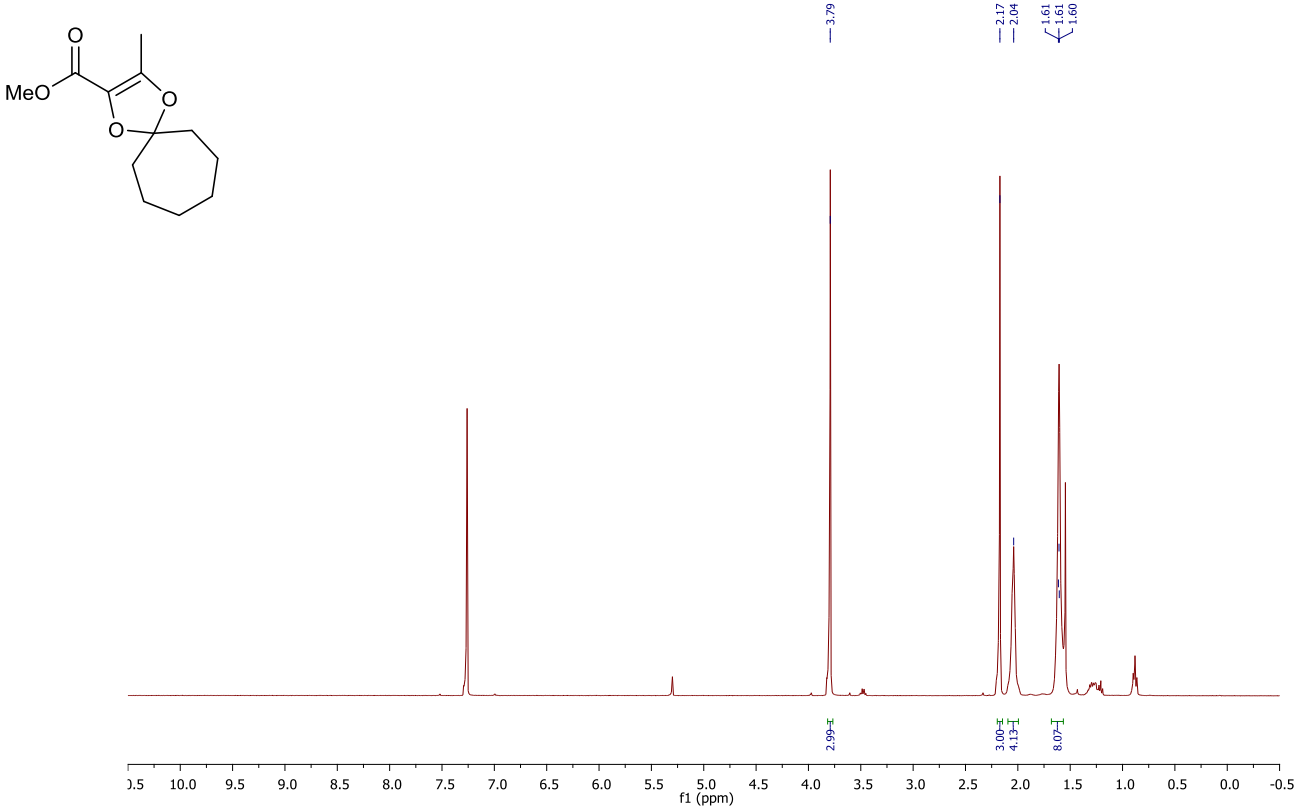


^{13}C NMR (100 MHz) $CDCl_3$

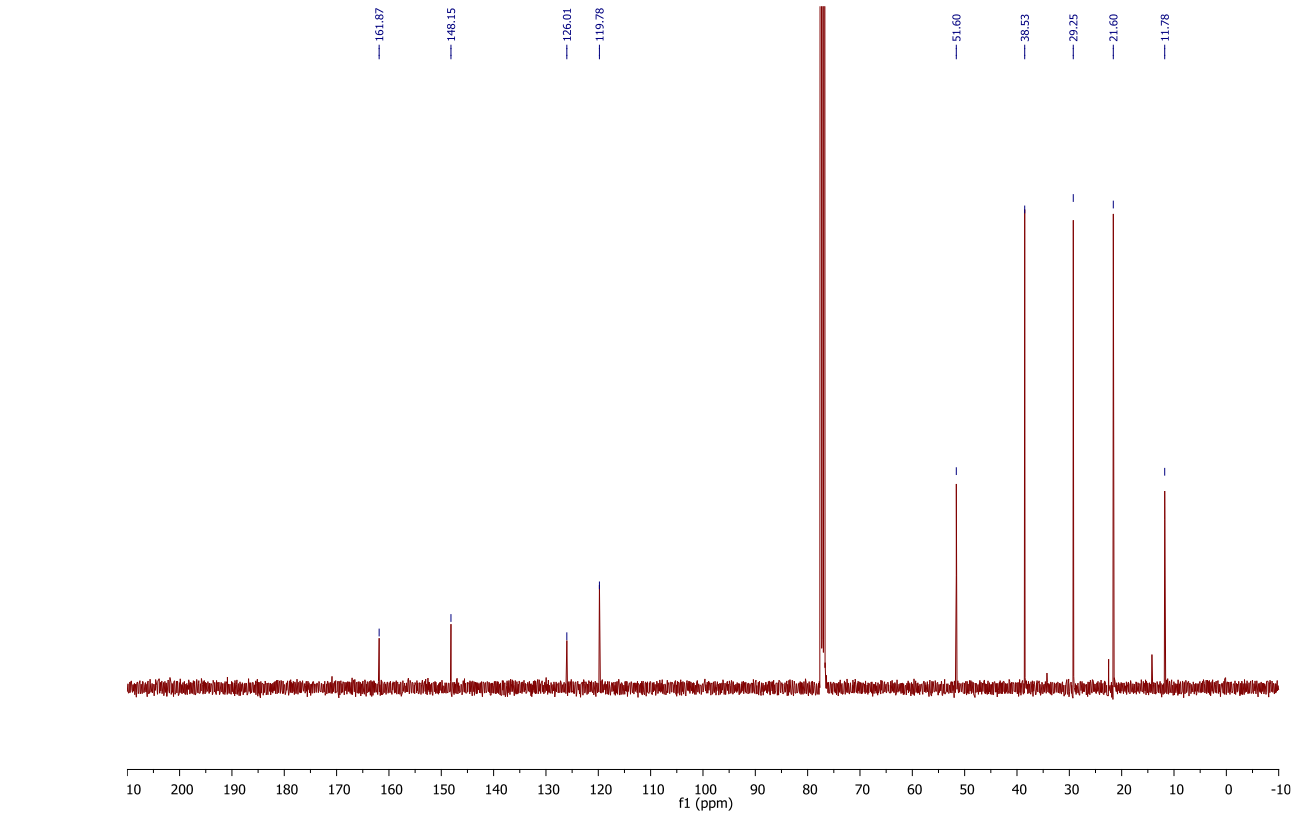


Adduct 4i

^{1}H NMR (400 MHz) $CDCl_3$

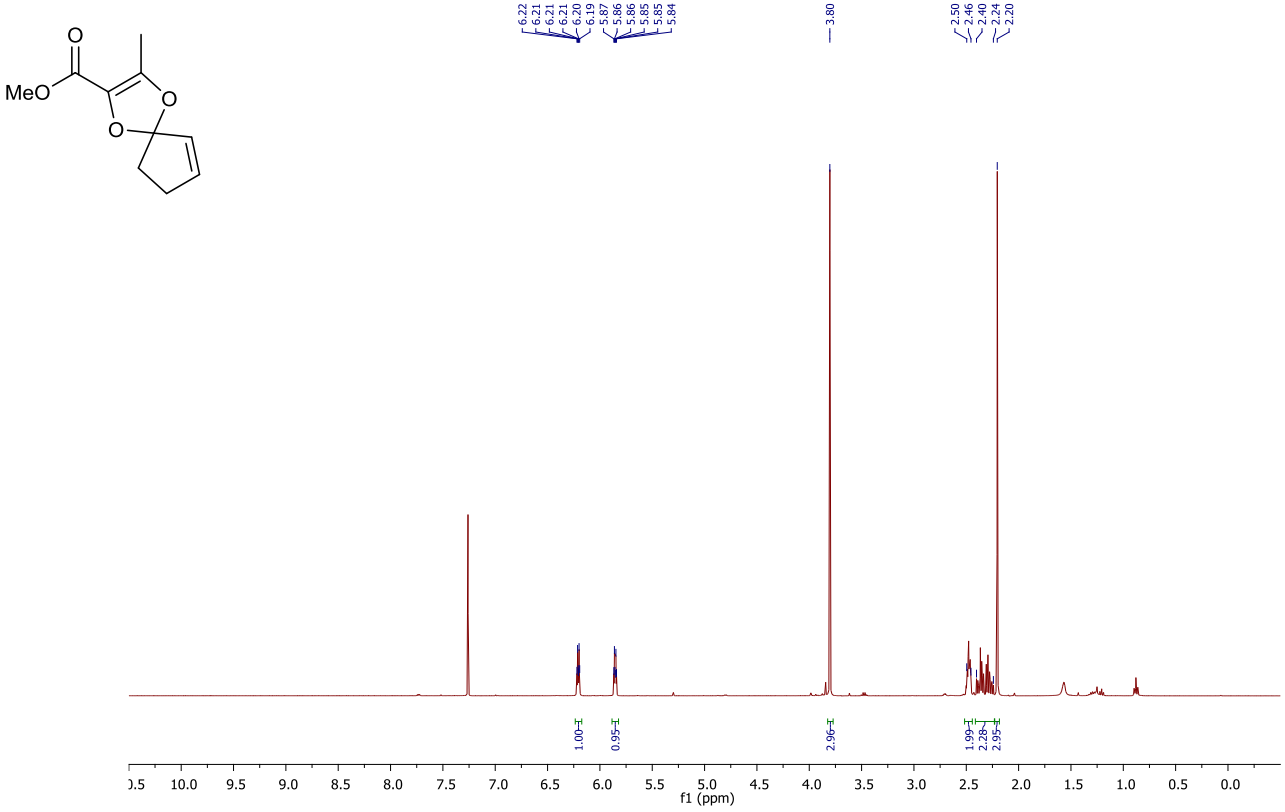


^{13}C NMR (100 MHz) $CDCl_3$

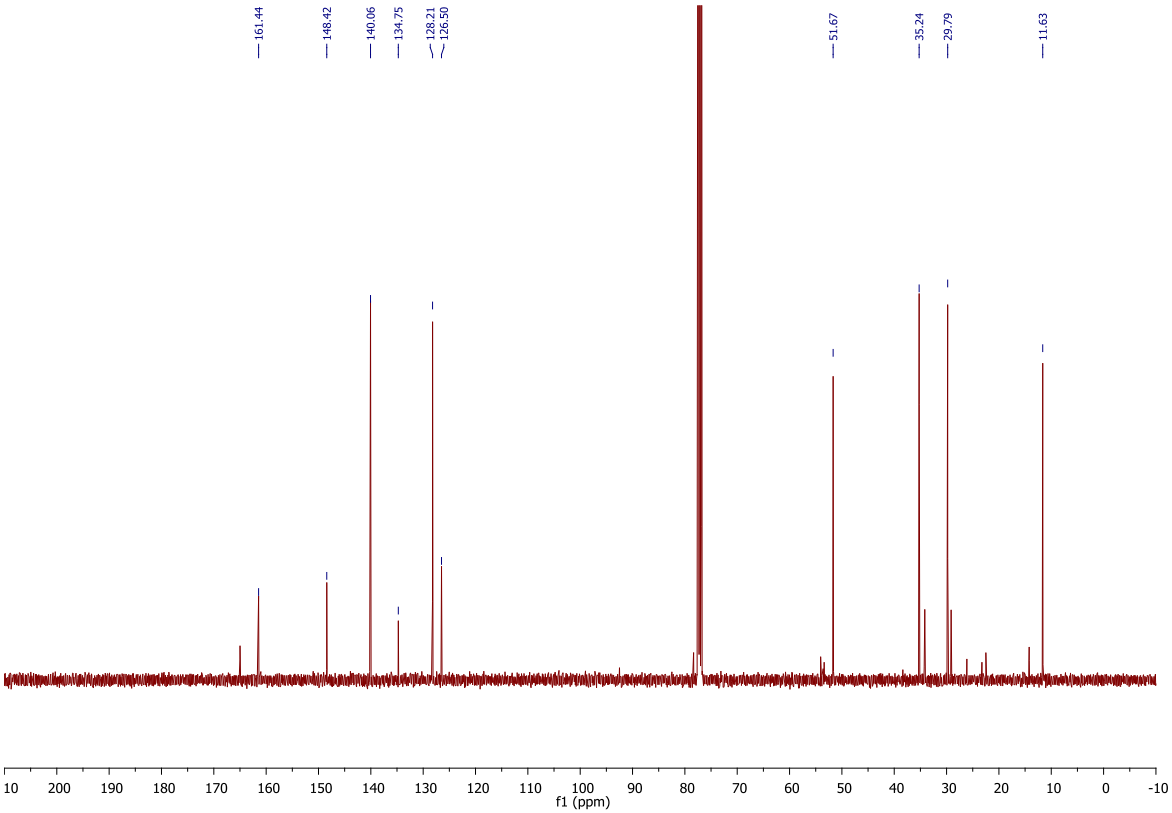


Adduct 4j

^{1}H NMR (400 MHz) $CDCl_3$

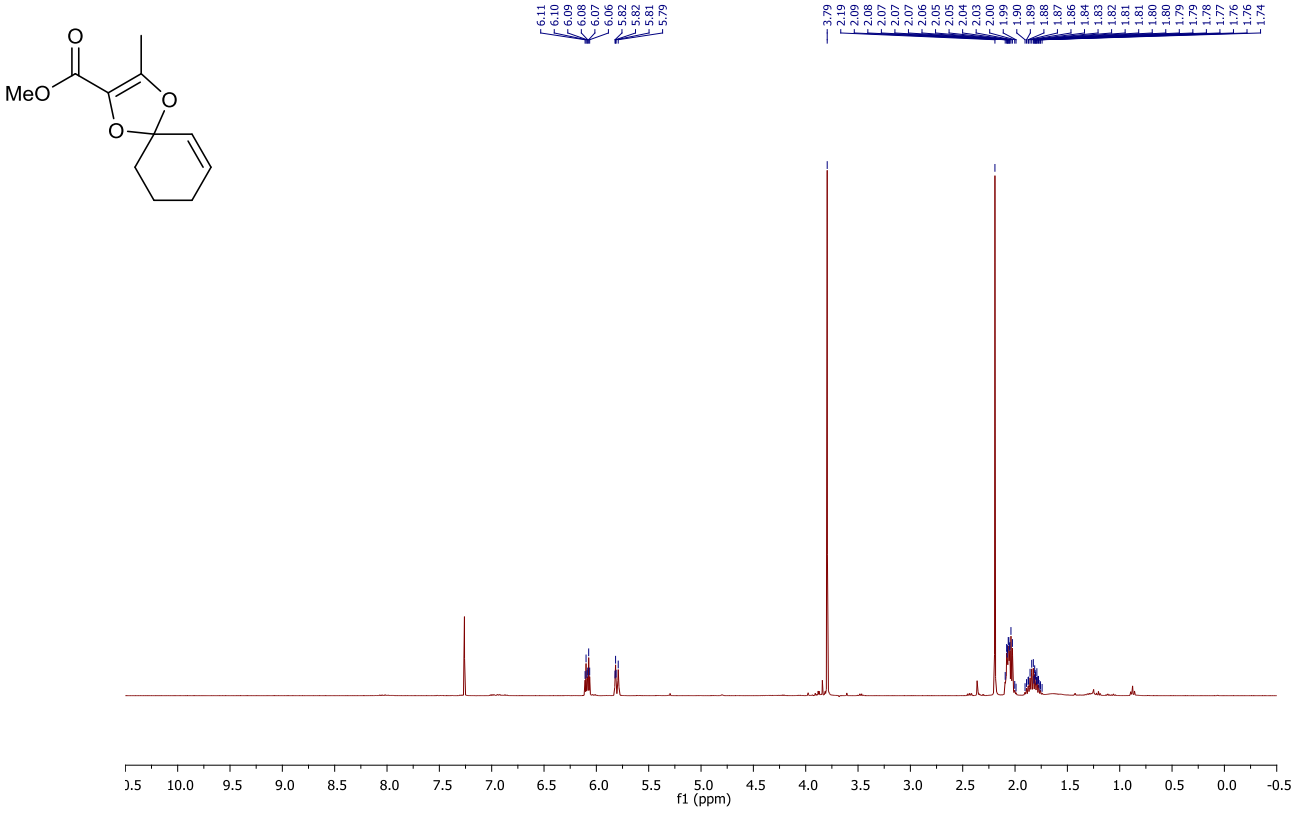


^{13}C NMR (100 MHz) $CDCl_3$

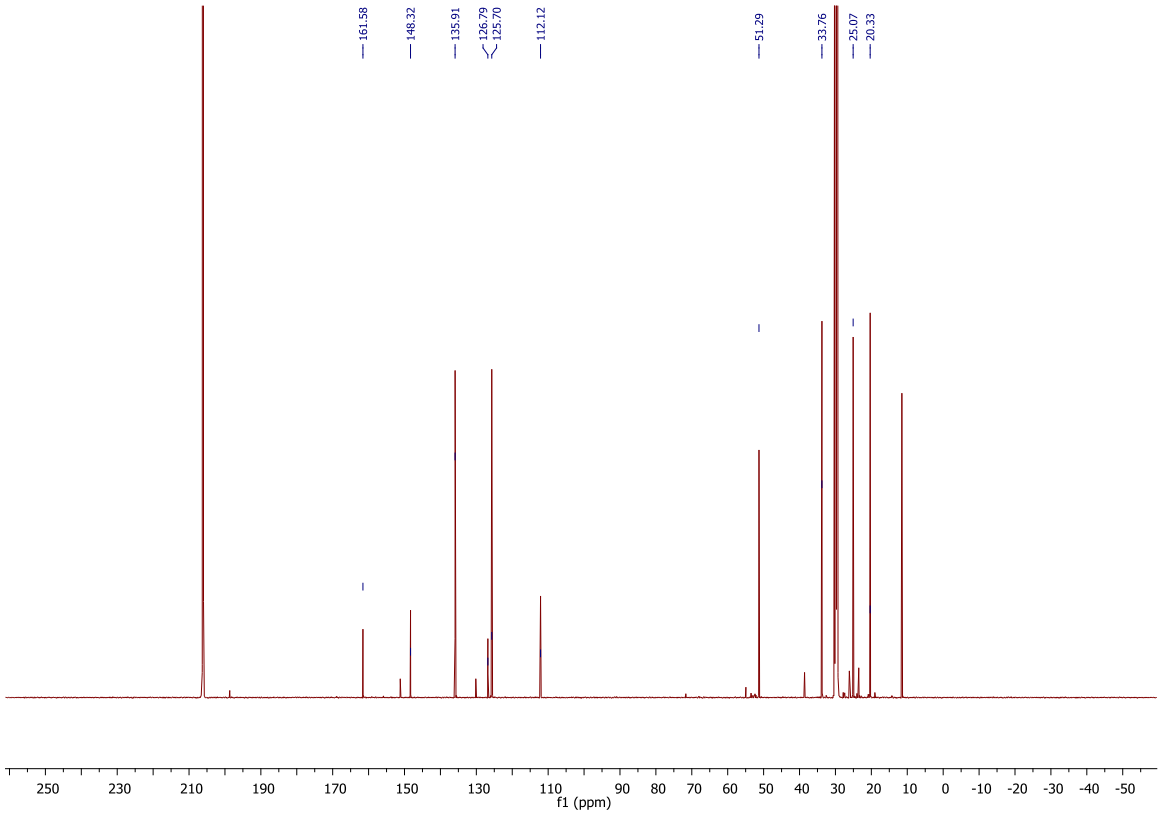


Adduct 4k

^{1}H NMR (400 MHz) $CDCl_3$

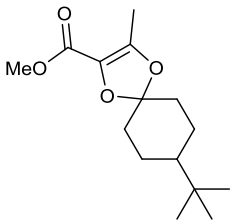


^{13}C NMR (100 MHz) acetone-d_6

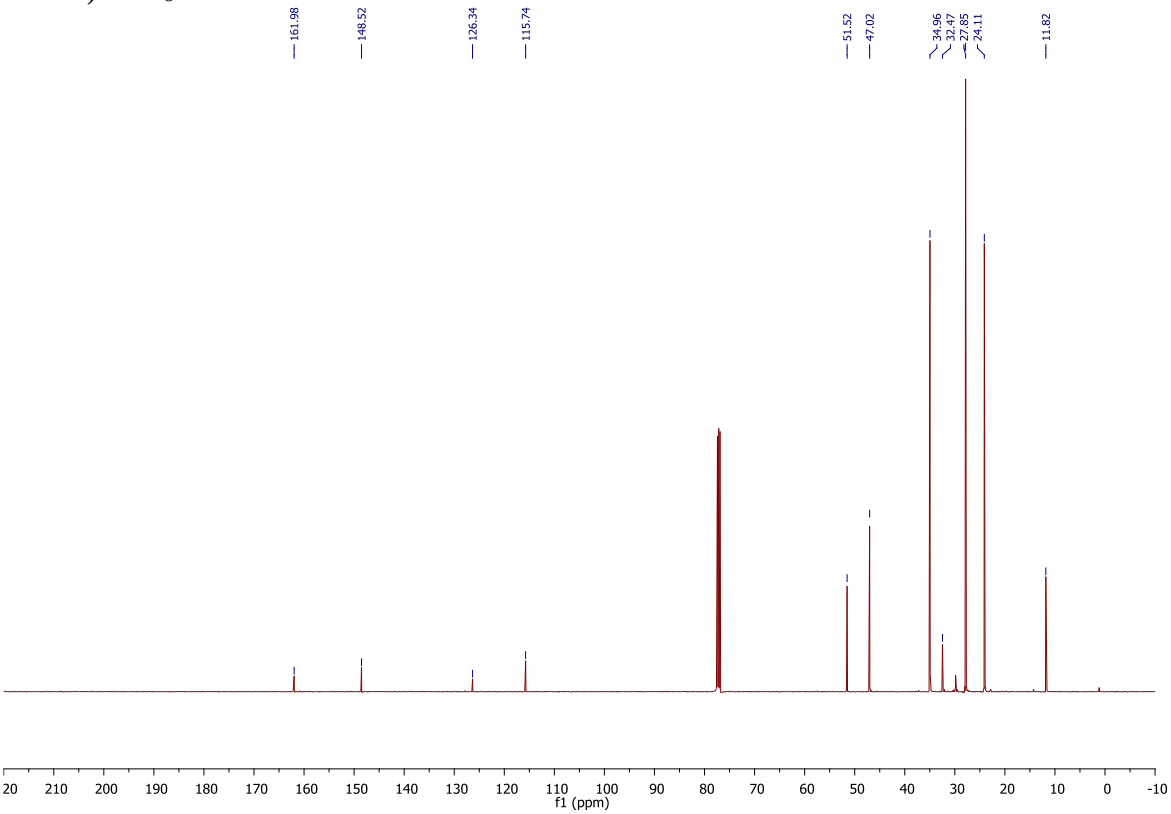


Adduct 4l first eluted

^{1}H NMR (500 MHz) $CDCl_3$

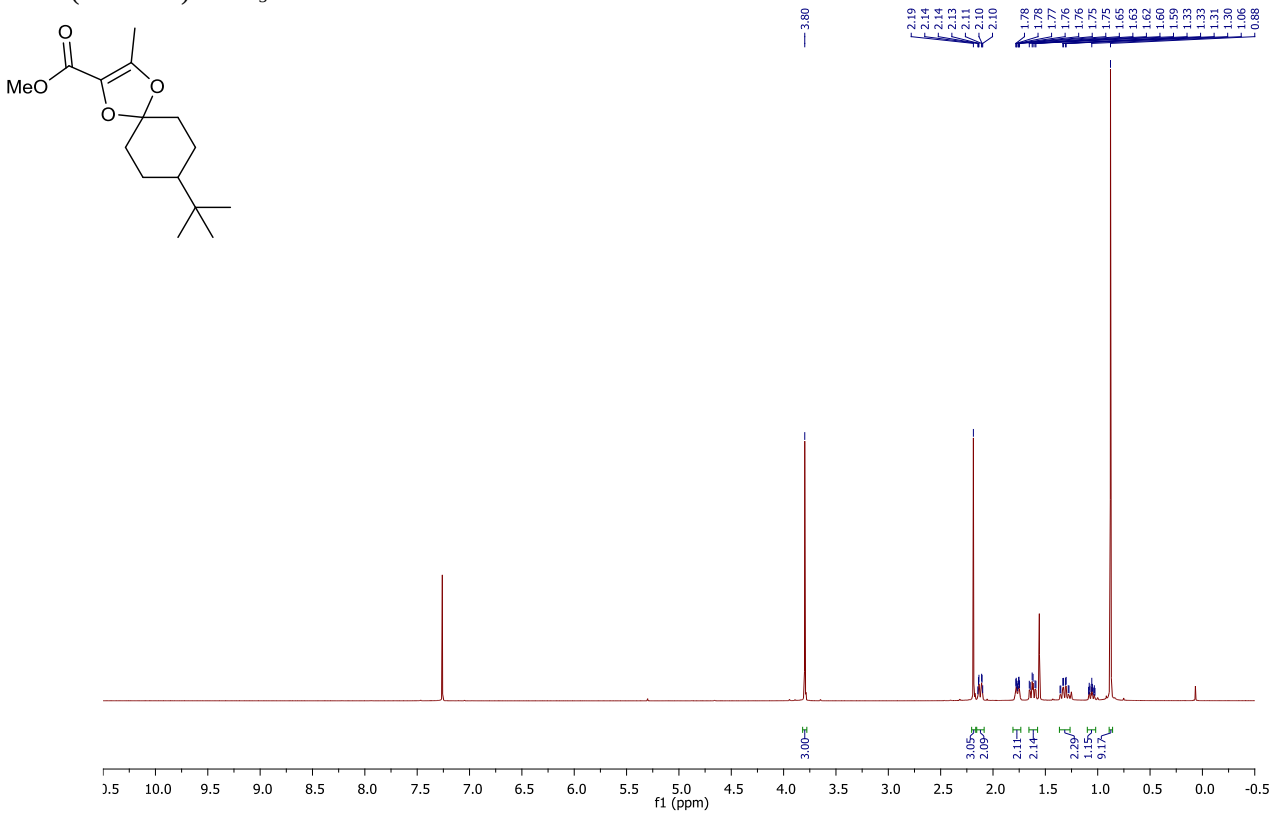


^{13}C NMR (126 MHz) $CDCl_3$

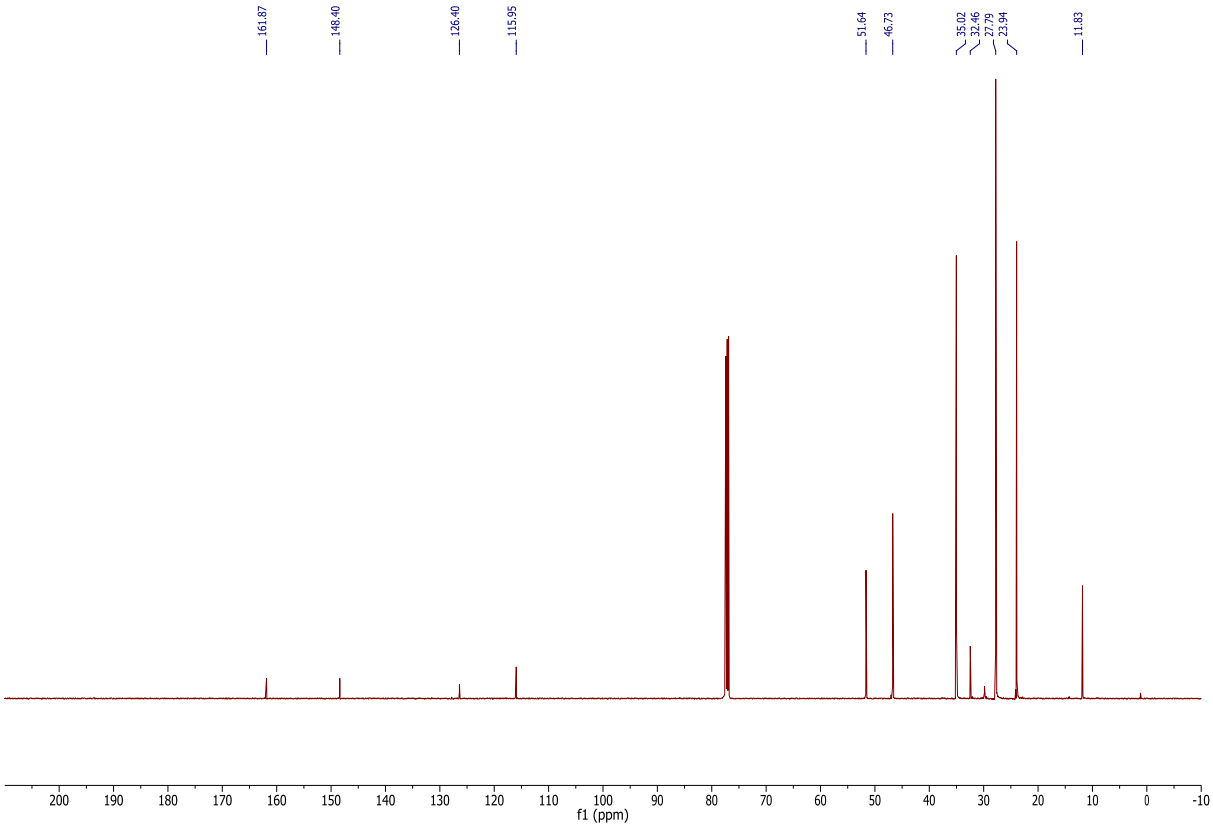


Adduct 4l second eluted

^{1}H NMR (500 MHz) $CDCl_3$

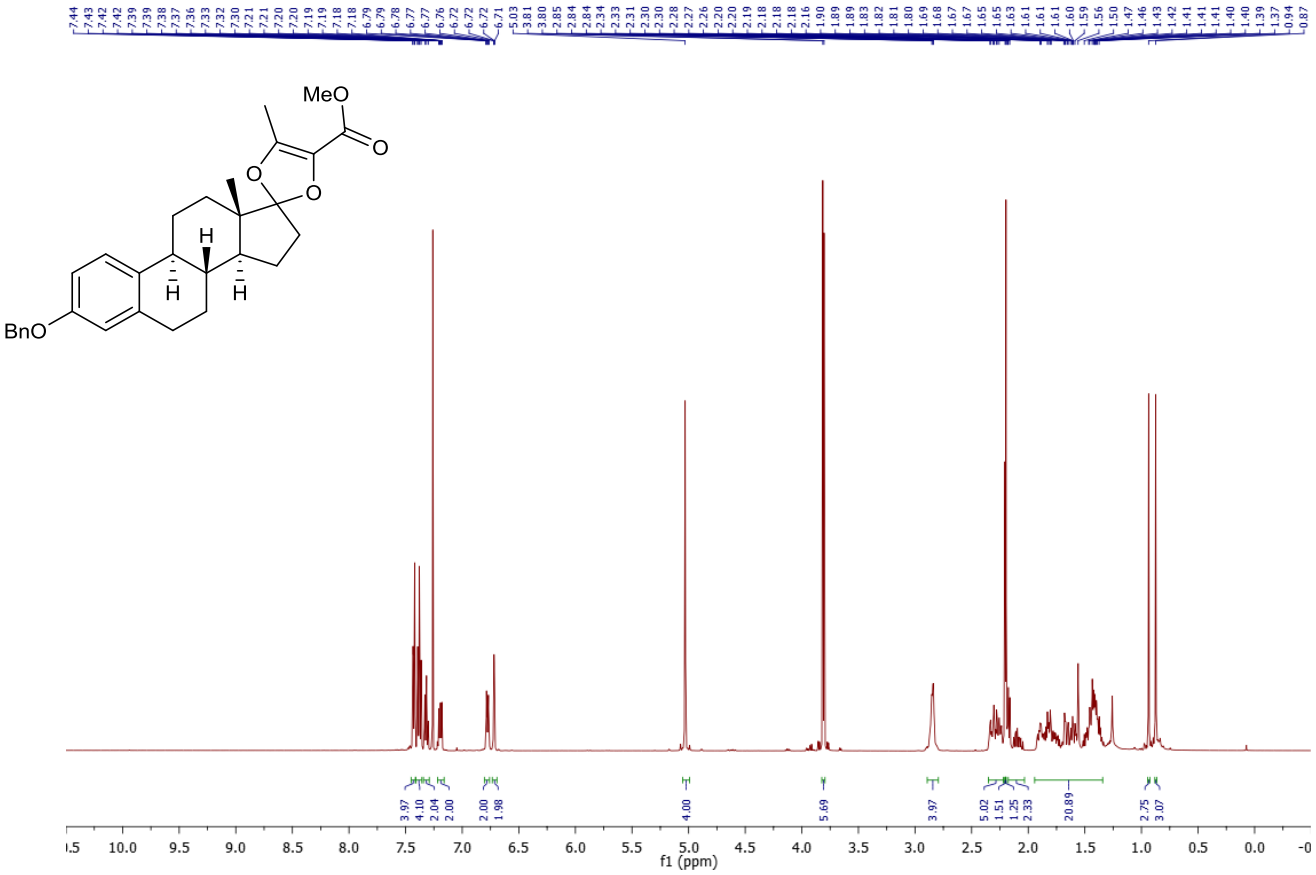


^{13}C NMR (126 MHz) $CDCl_3$

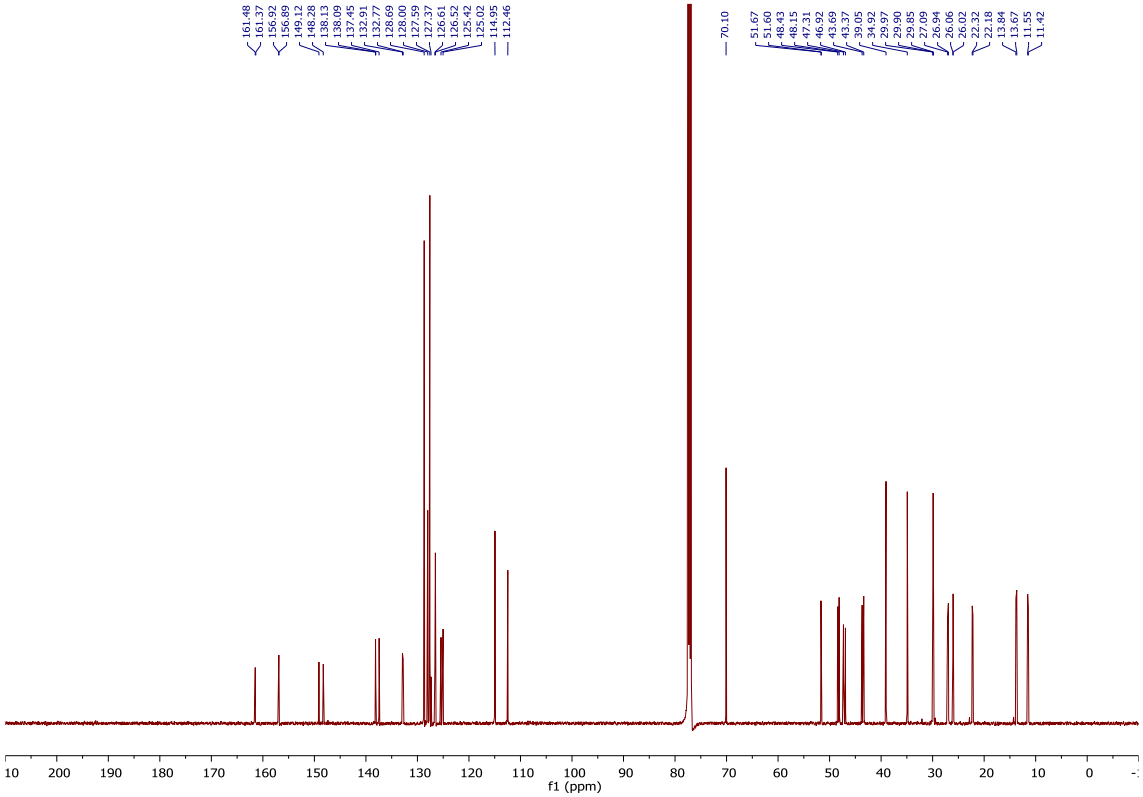


Adduct 4m

^{1}H NMR (400 MHz) $CDCl_3$

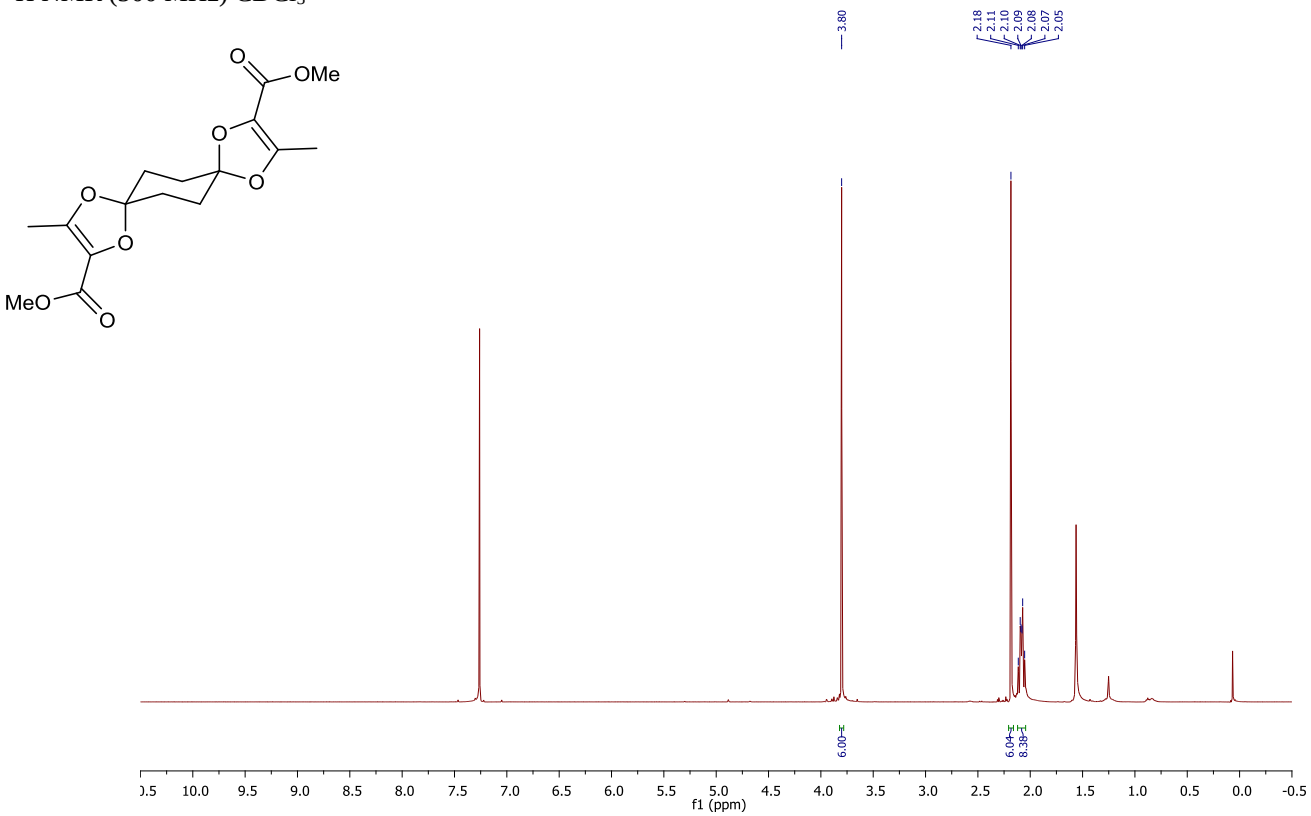


^{13}C NMR (100 MHz) $CDCl_3$

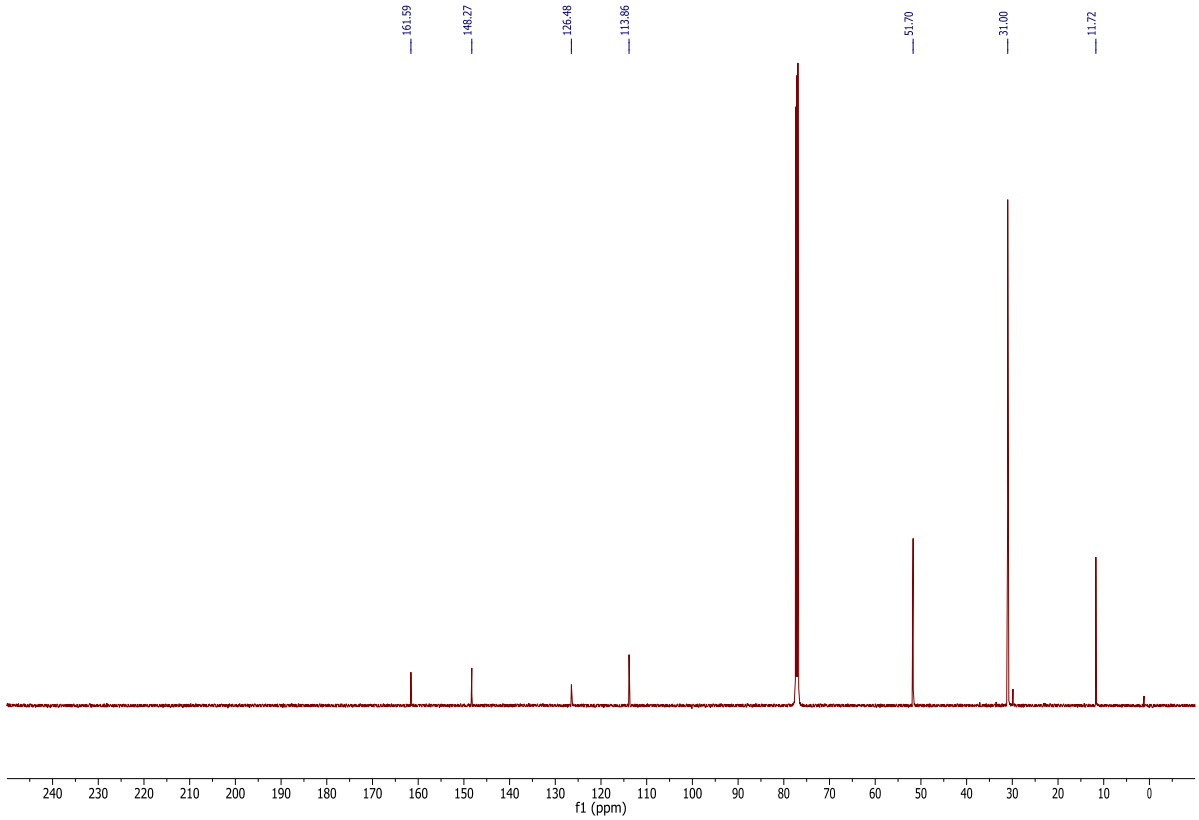


Adduct 4n *trans* diastereomer

^{1}H NMR (500 MHz) $CDCl_3$

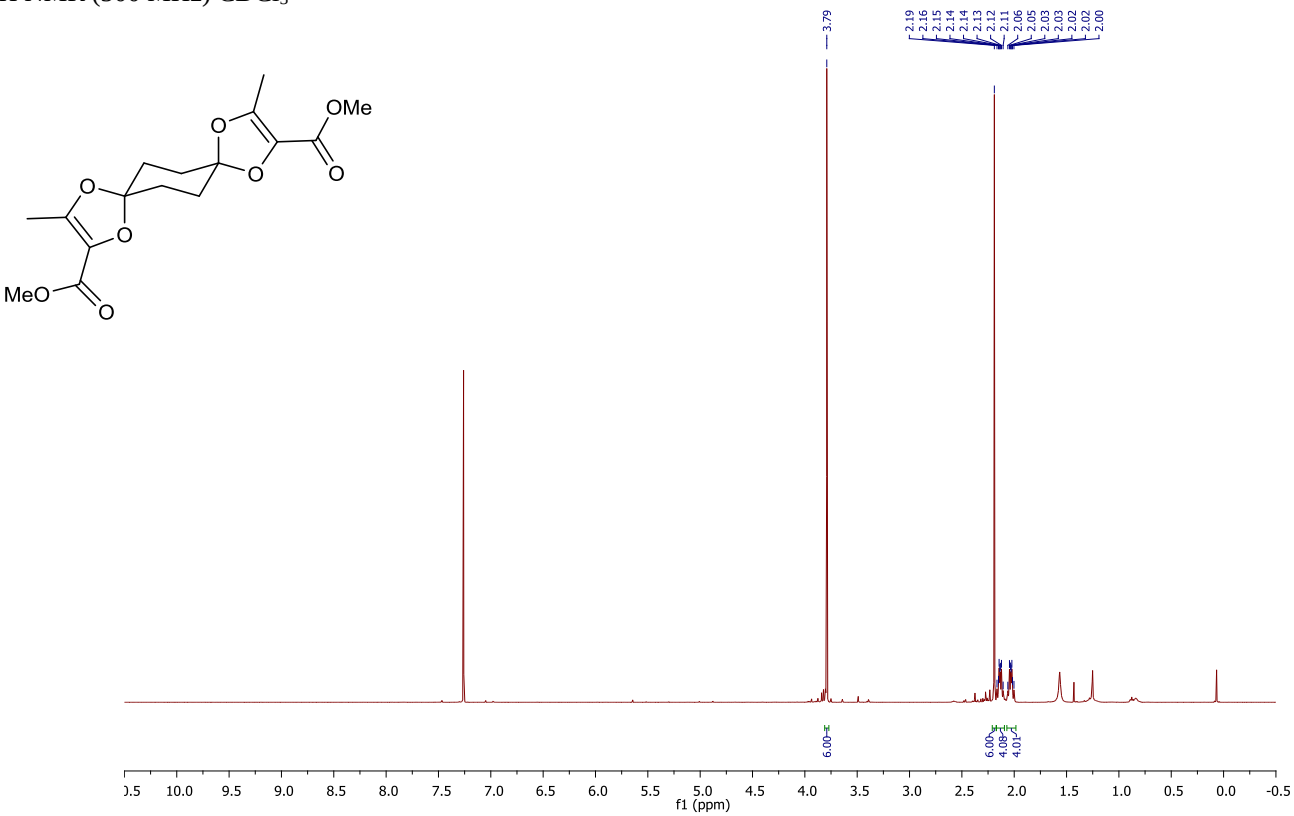


^{13}C NMR (126 MHz) $CDCl_3$

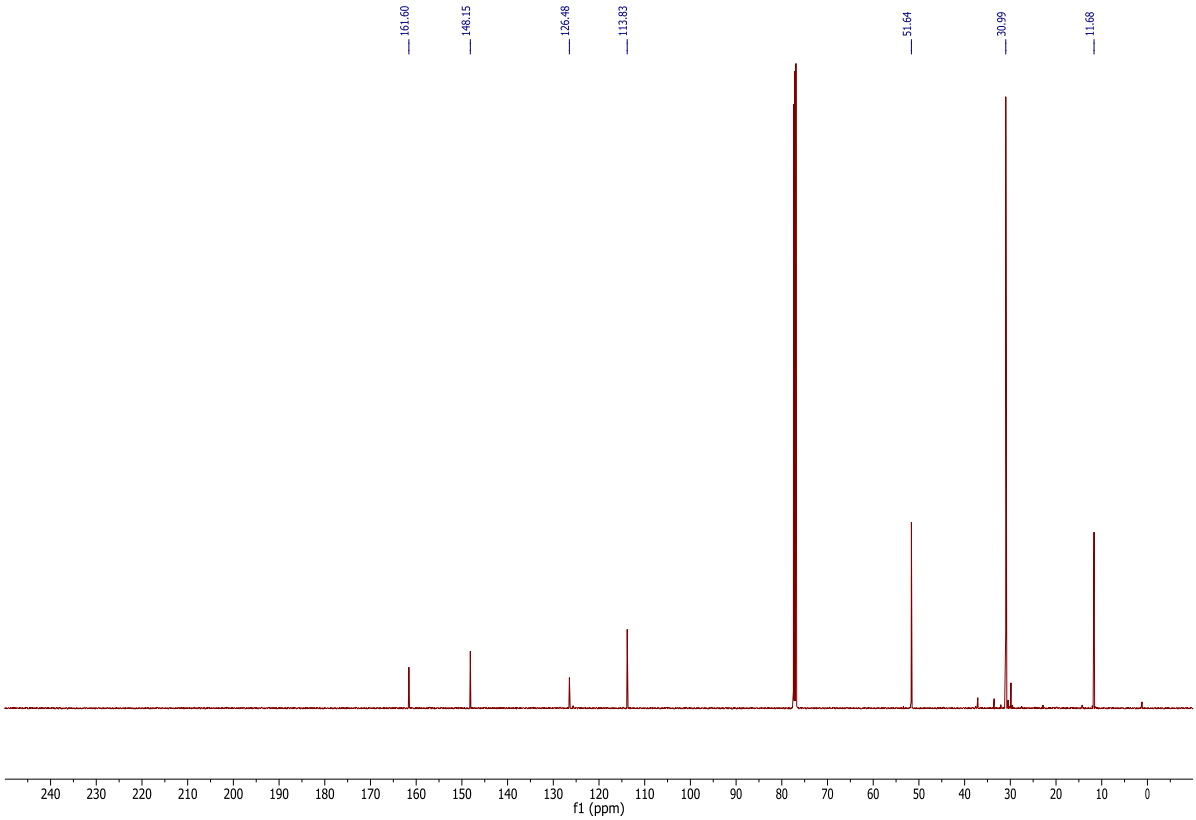


Adduct 4n' *cis* diastereomer

^{1}H NMR (500 MHz) $CDCl_3$

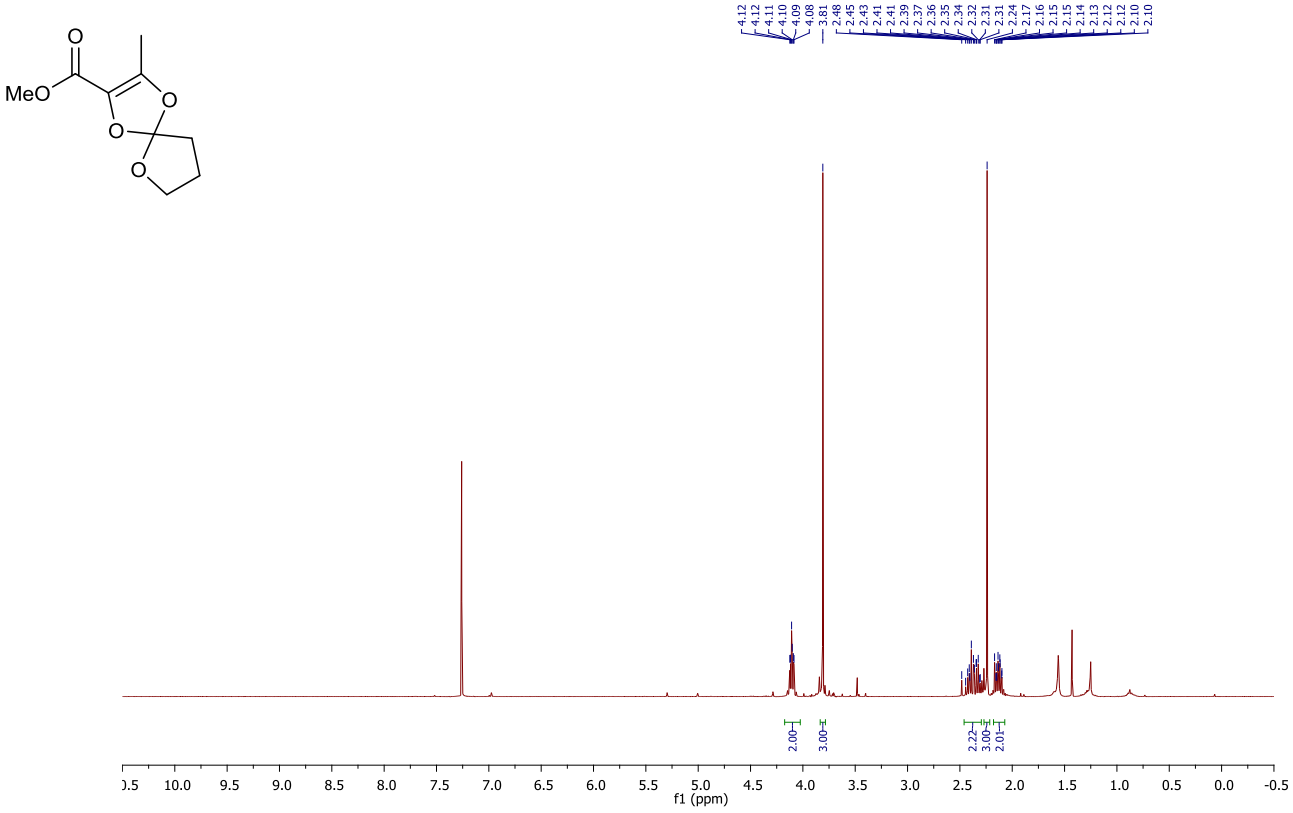


^{13}C NMR (126 MHz) $CDCl_3$

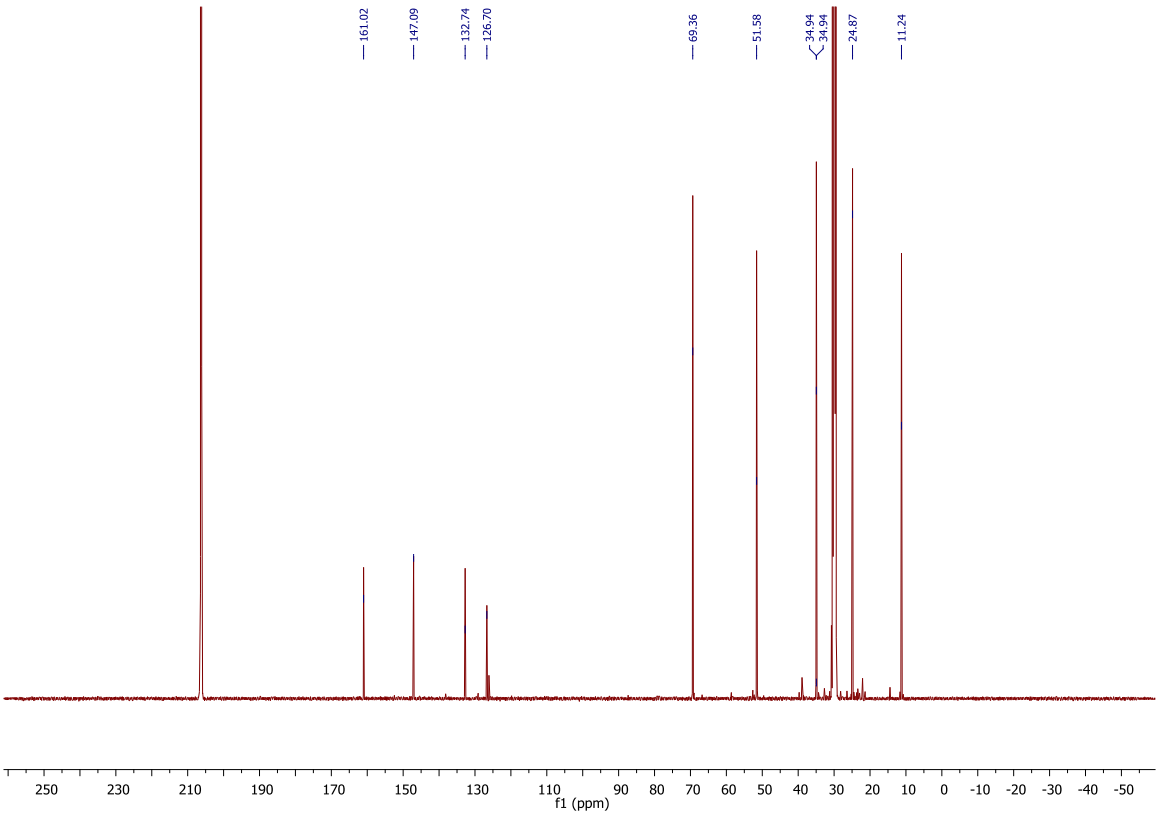


Adduct 5a

^{1}H NMR (400 MHz) $CDCl_3$

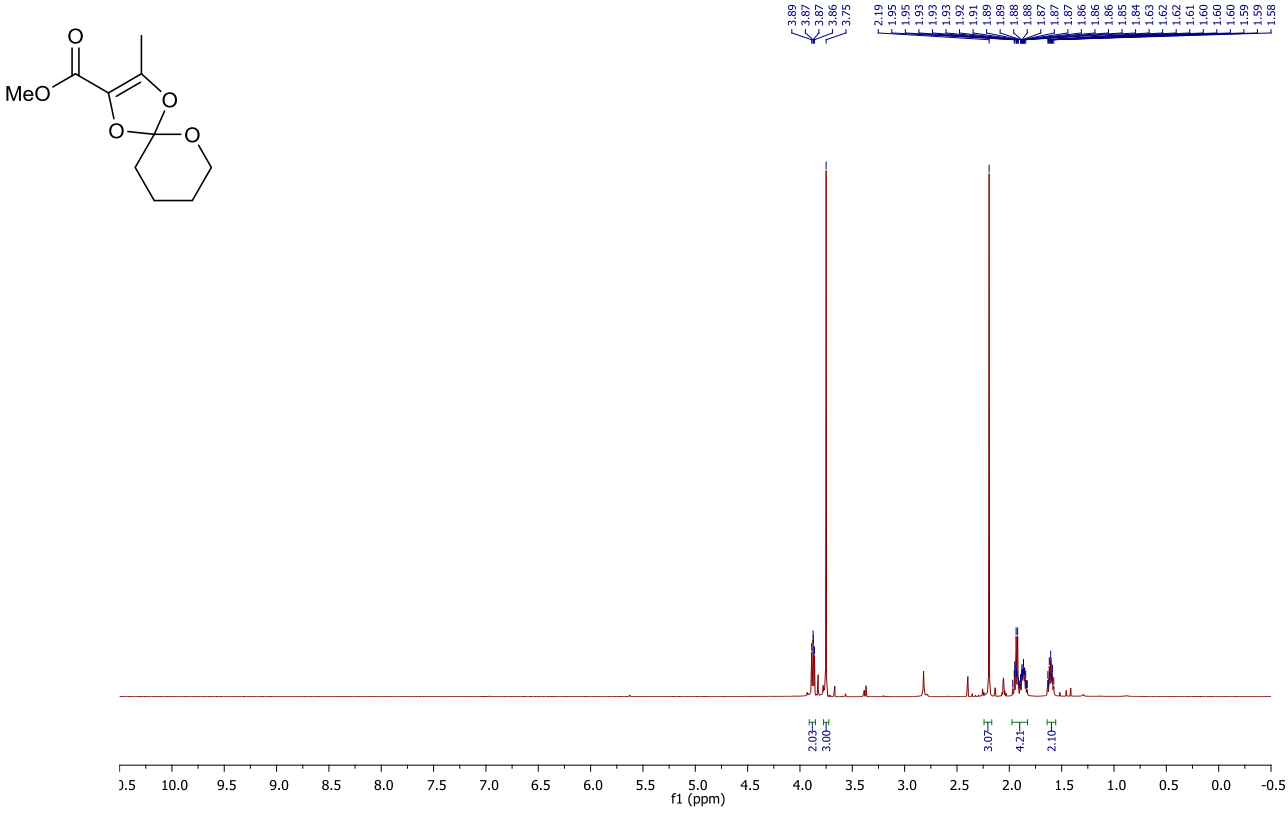


^{13}C NMR (100 MHz) $CDCl_3$

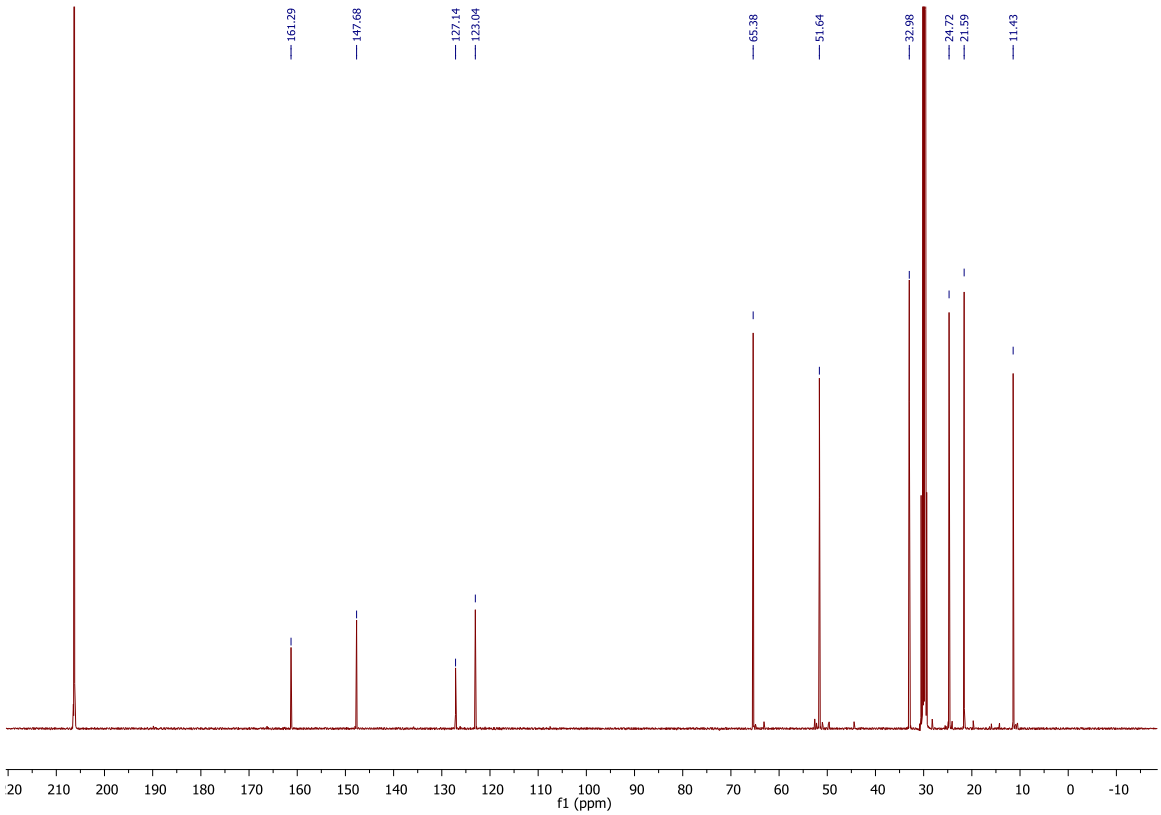


Adduct 5b

^{1}H NMR (400 MHz) acetone-d_6

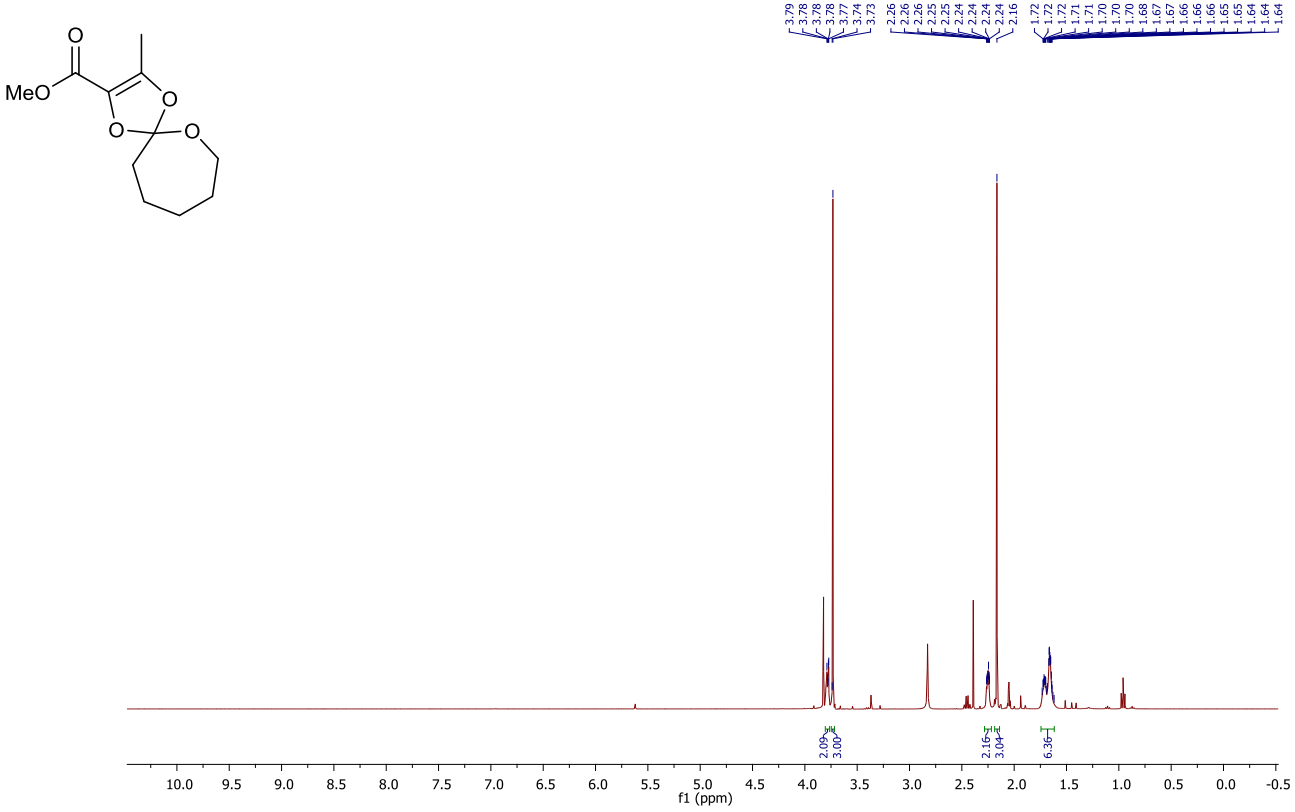


^{13}C NMR (100 MHz) acetone-d_6

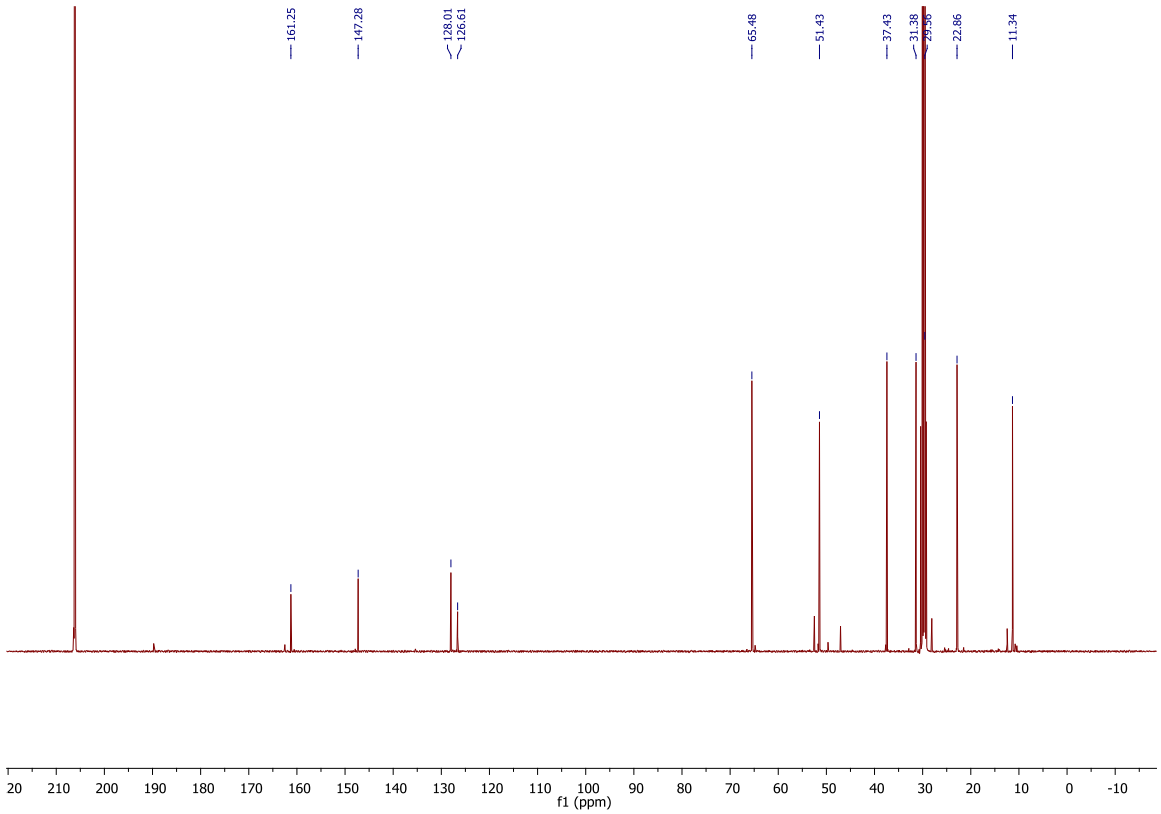


Adduct 5c

^{1}H NMR (400 MHz) acetone-d_6

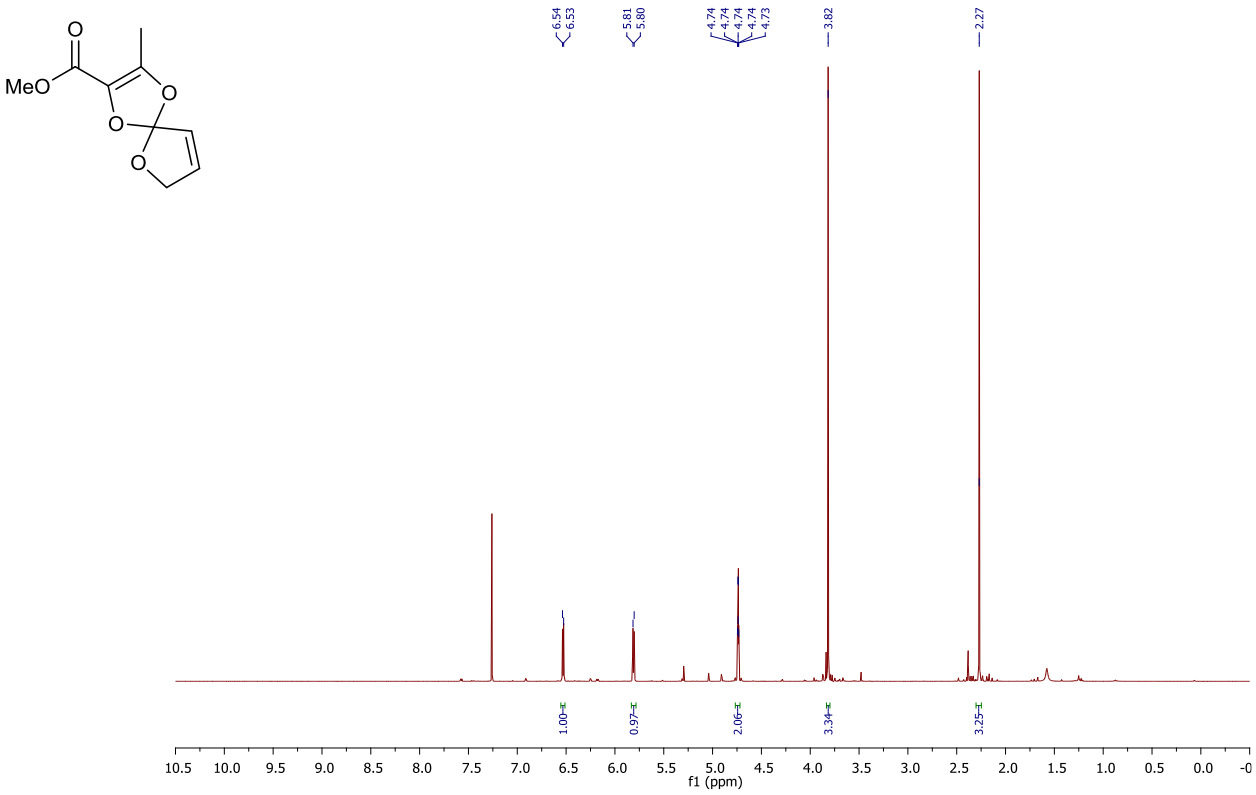


^{13}C NMR (100 MHz) acetone-d_6

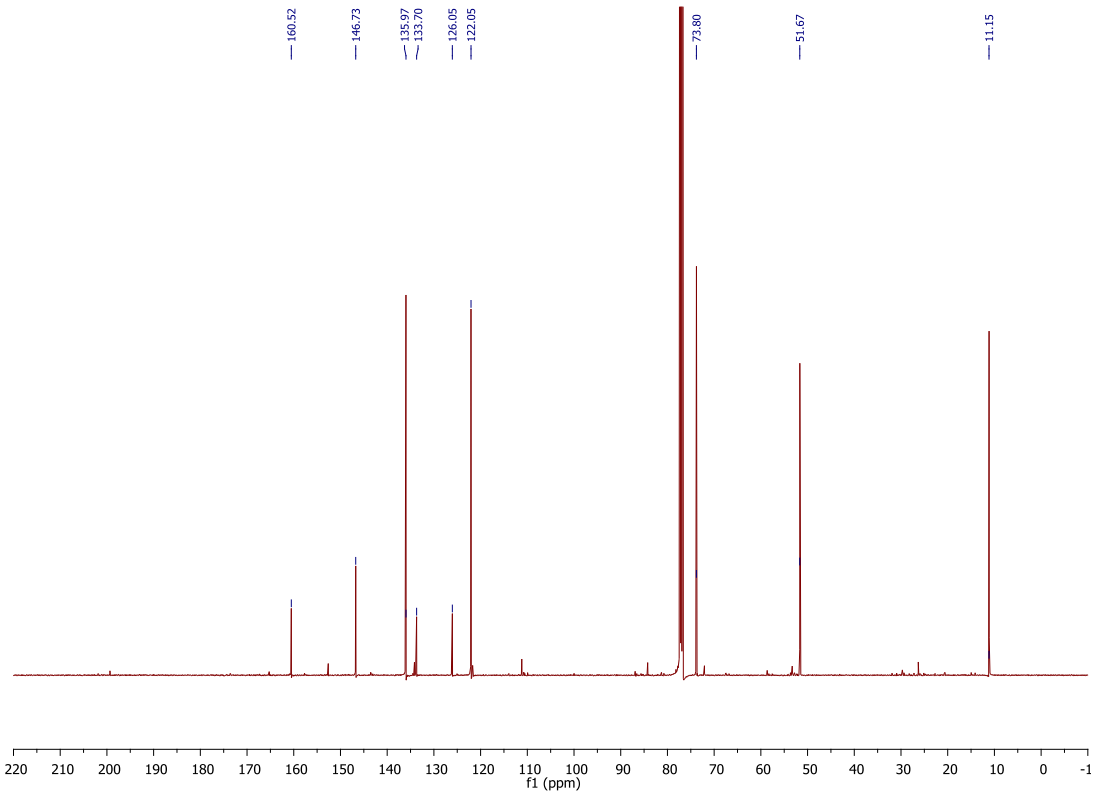


Adduct 5d

^{1}H NMR (400 MHz) $CDCl_3$

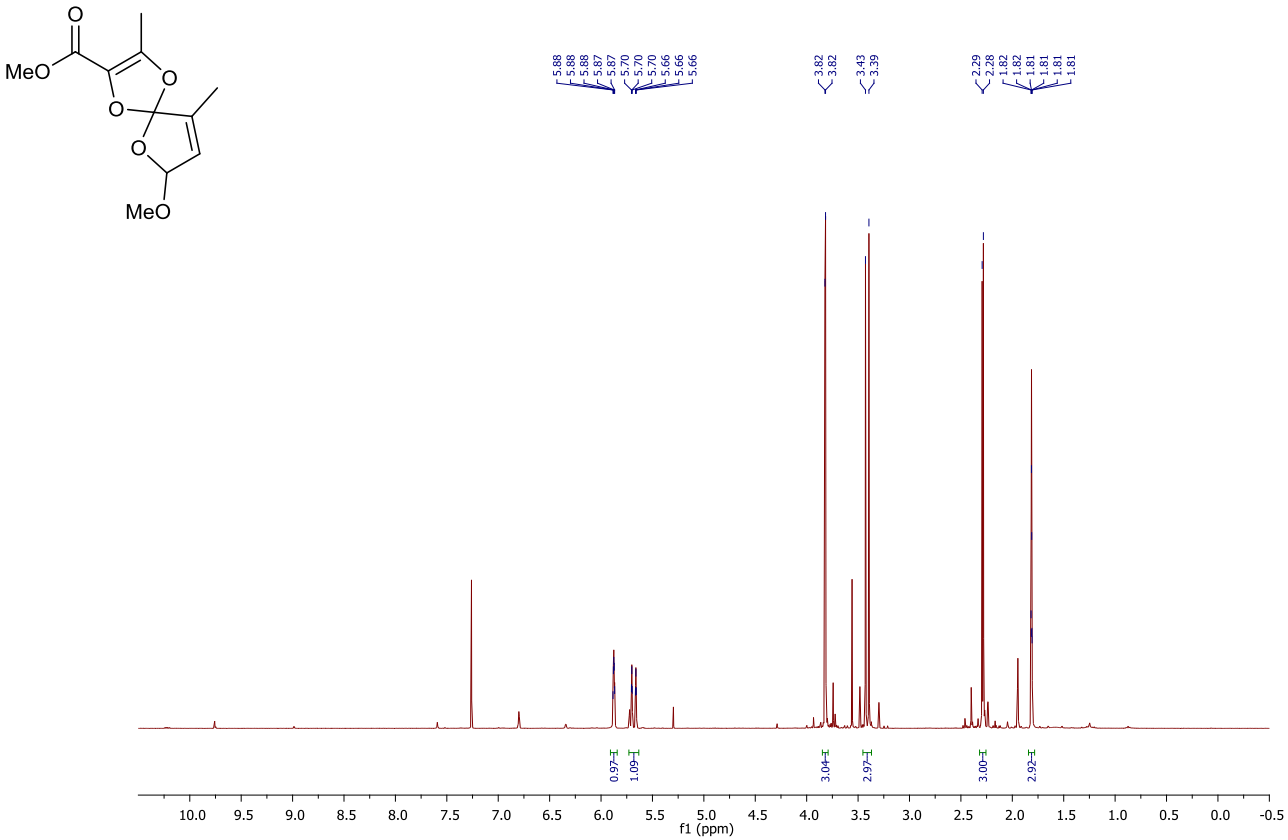


^{13}C NMR (100 MHz) $CDCl_3$

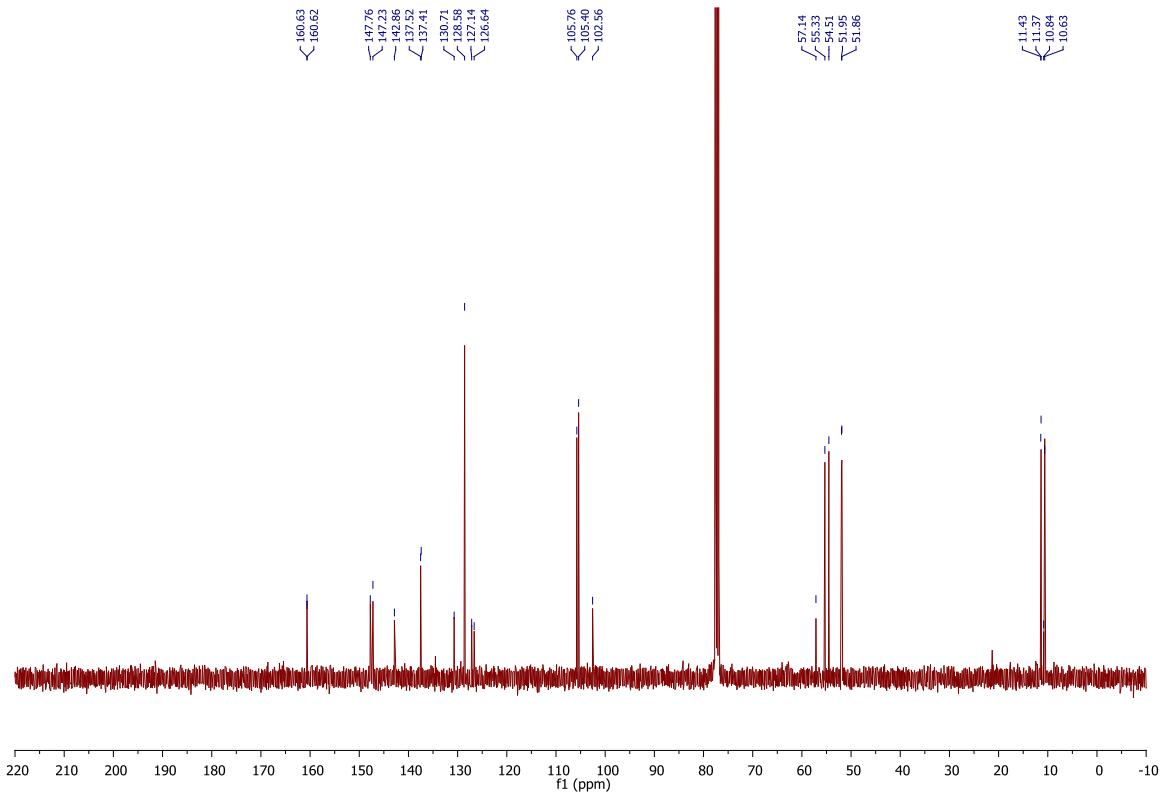


Adduct 5e

^{1}H NMR (400 MHz) $CDCl_3$

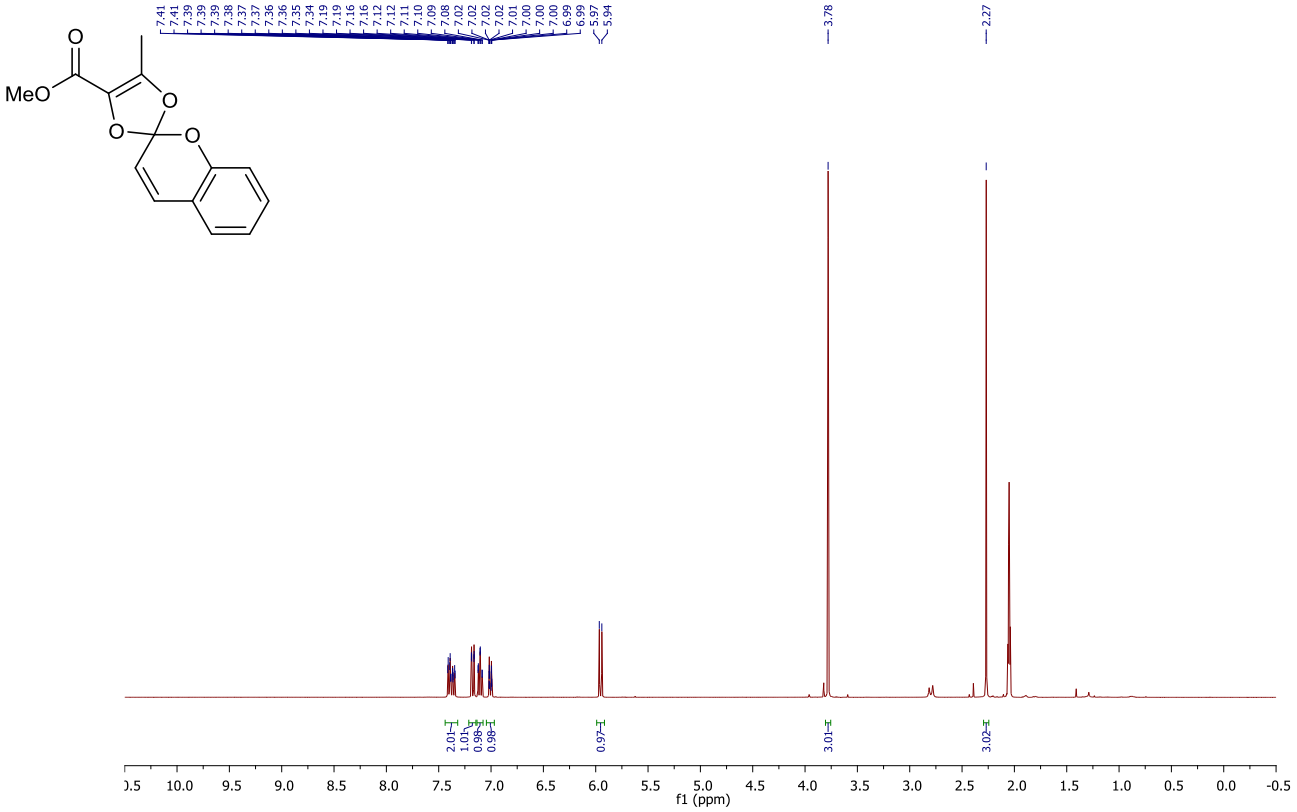


^{13}C NMR (100 MHz) $CDCl_3$

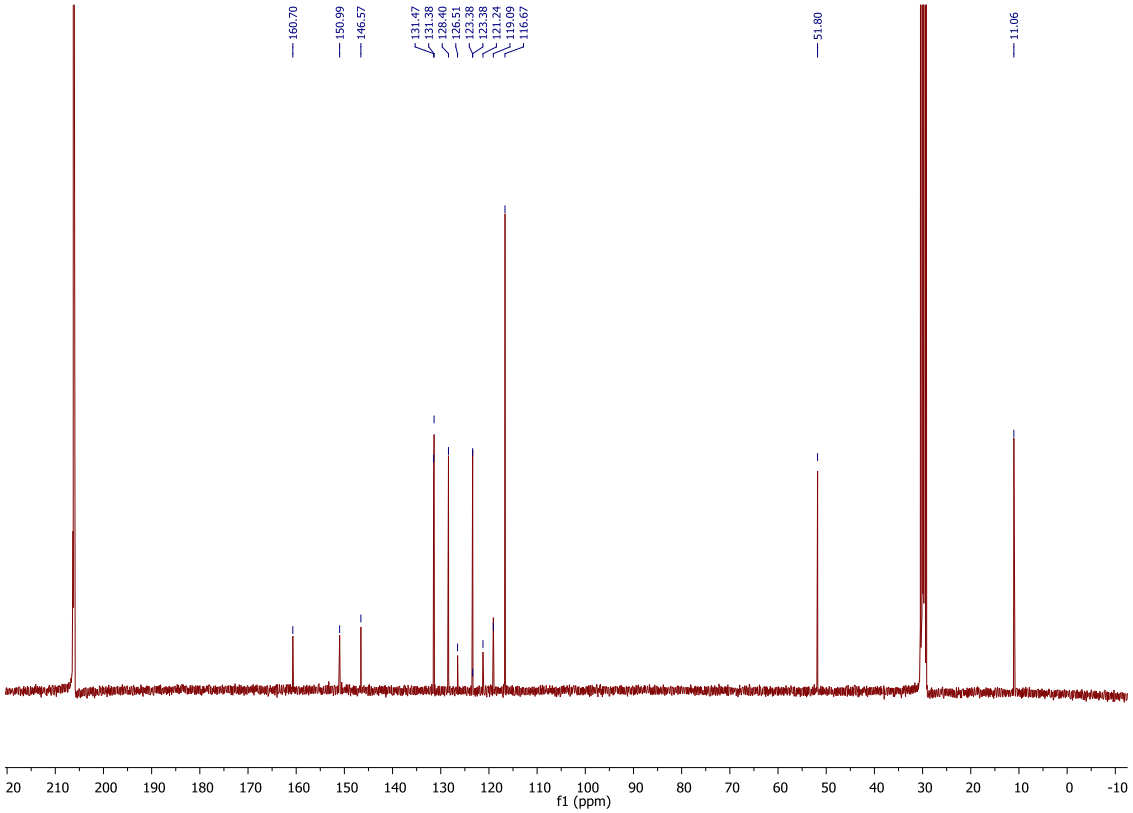


Adduct 5f

^{1}H NMR (400 MHz) acetone-d_6

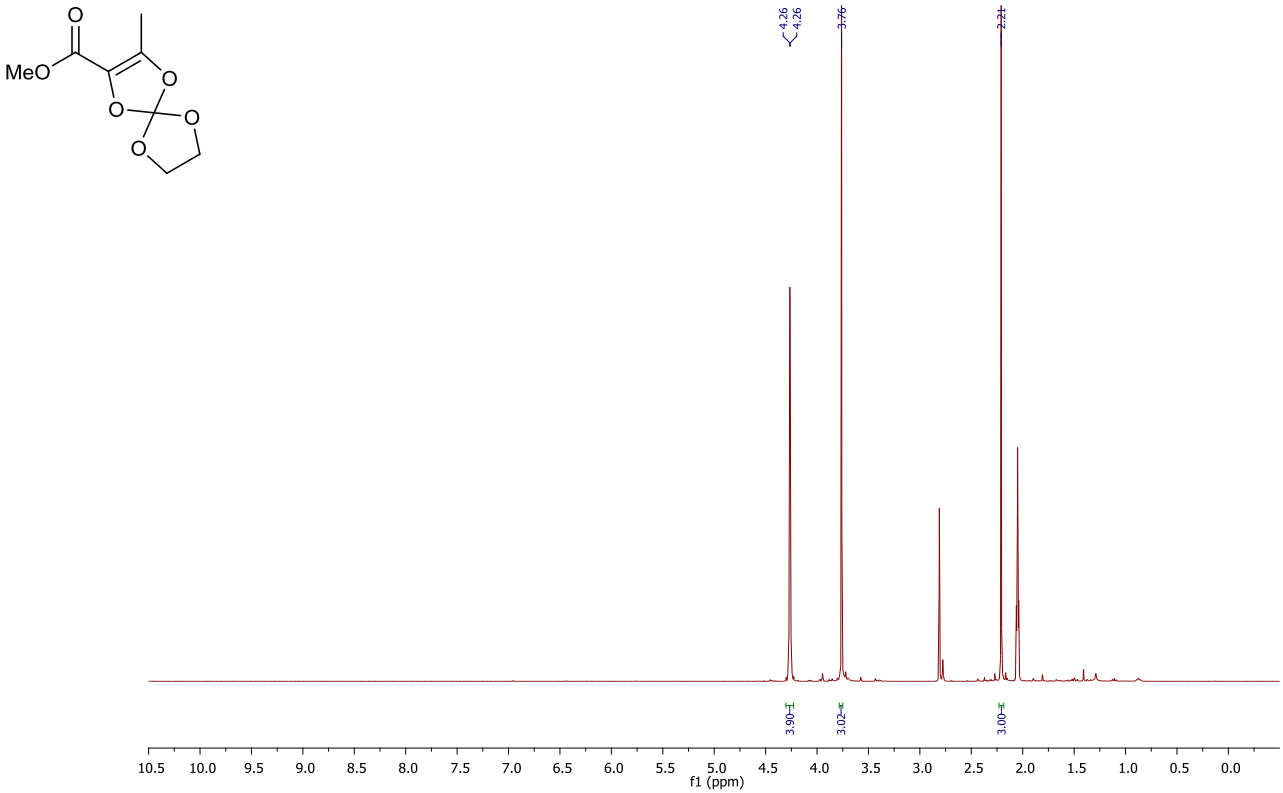


^{13}C NMR (100 MHz) acetone-d_6

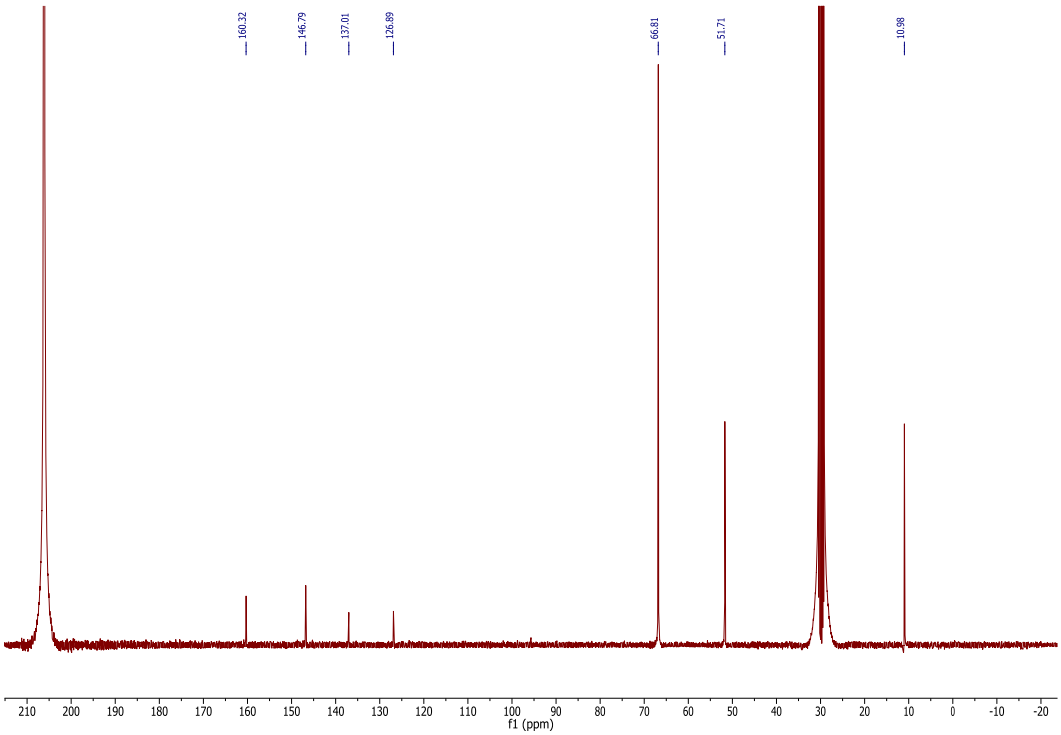


Adduct 6a

^{1}H NMR (400 MHz) $CDCl_3$ acetone-d_6

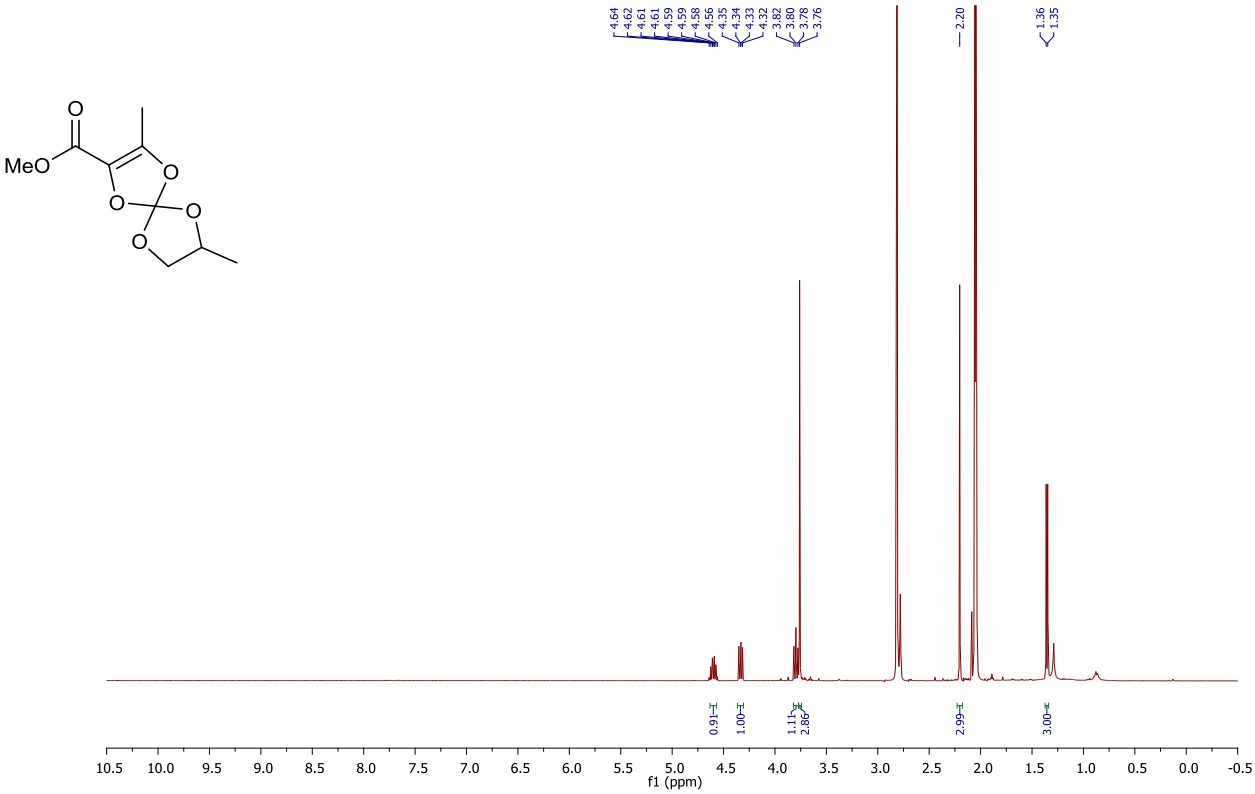


^{13}C NMR (100 MHz) acetone-d_6

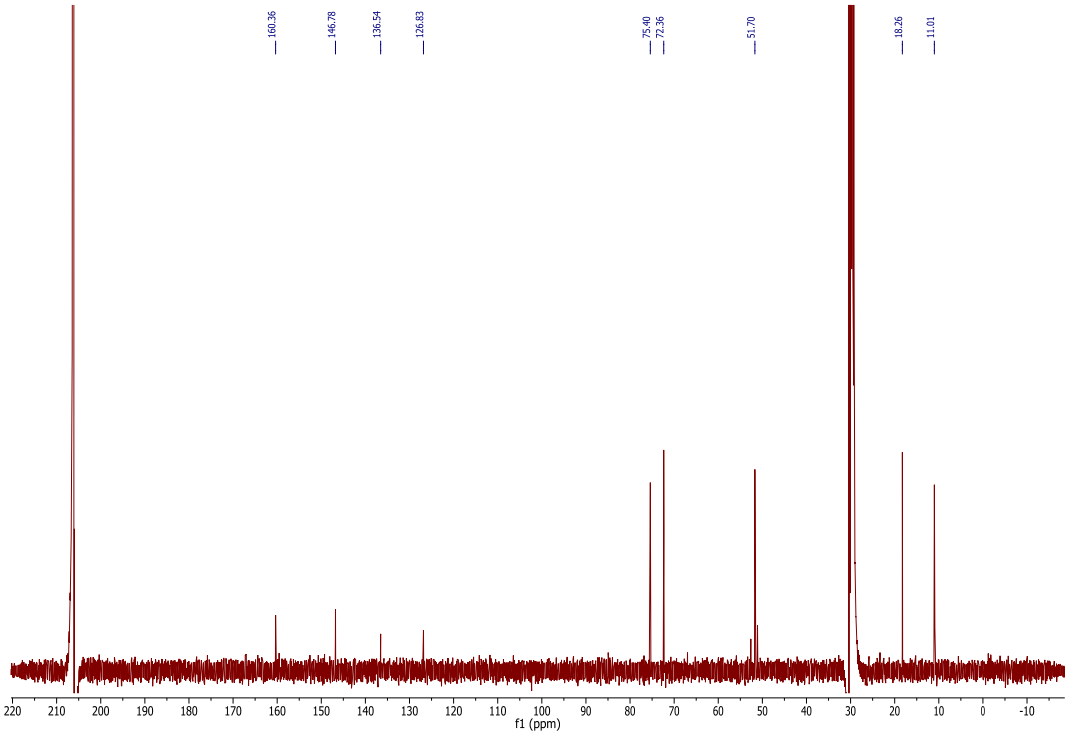


Adduct 6b

^{1}H NMR (400 MHz) $CDCl_3$ acetone-d_6

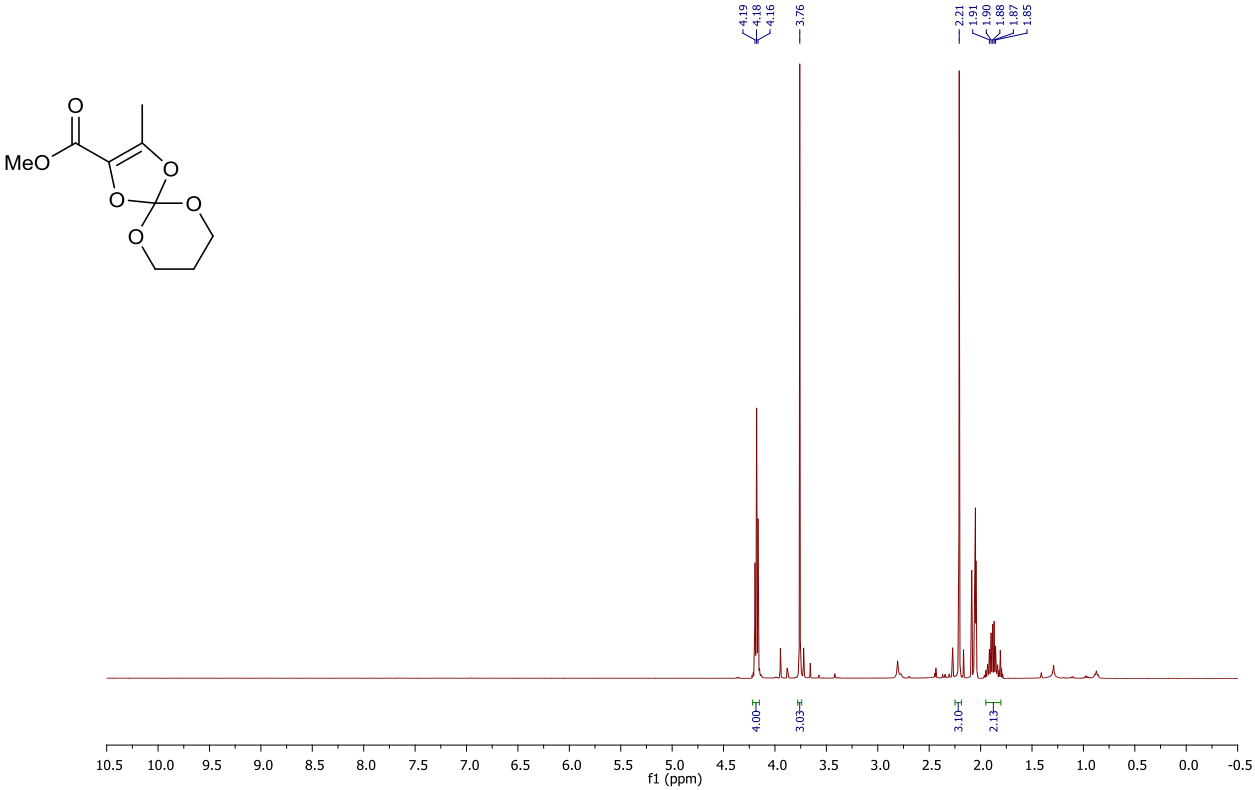


^{13}C NMR (100 MHz) acetone-d_6

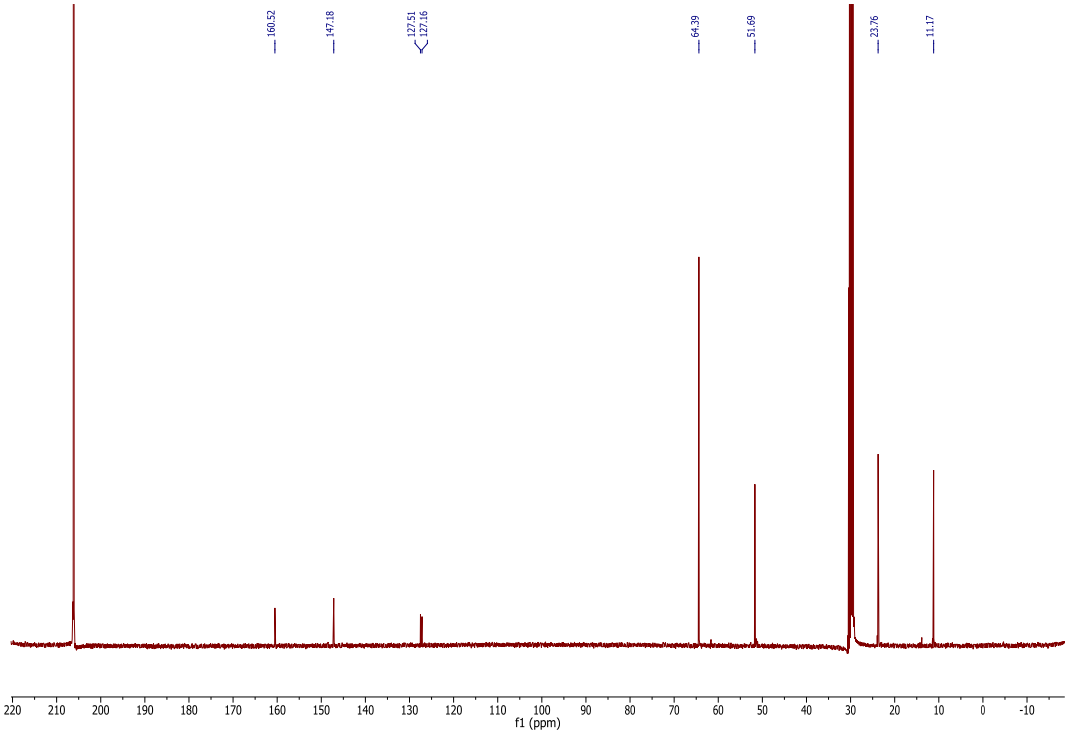


Adduct 6c

^{1}H NMR (400 MHz) $CDCl_3$ acetone-d_6



^{13}C NMR (100 MHz) acetone-d_6



11.X-RAY DATA AND TABLES OF ADDUCTS 4n AND 4n'

Adduct 4n

Table 1 Crystal data and structure refinement for **4n**.

Identification code	shelxl	
Empirical formula	C_{16} H_{20} O_8	
Formula weight	340.32	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 18.5685(5) Å	α= 90°.
	b = 6.67667(14) Å	β= 108.928(3)°.
	c = 13.8200(4) Å	γ = 90°.
Volume	1620.70(7) $Å^3$	
Z	4	
Density (calculated)	1.395 Mg/m^3	
Absorption coefficient	0.958 mm^{-1}	
F(000)	720	
Crystal size	0.1957 x 0.1758 x 0.0581 mm^3	
Theta range for data collection	5.04 to 73.15°.	
Index ranges	-22<=h<=21, -8<=k<=8, -15<=l<=16	
Reflections collected	4694	
Independent reflections	1585 [R(int) = 0.0164]	
Completeness to theta = 66.97°	99.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.949 and 0.865	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1585 / 0 / 111	
Goodness-of-fit on F^2	1.670	
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1554	
R indices (all data)	R1 = 0.0458, wR2 = 0.1629	
Largest diff. peak and hole	0.246 and -0.162 $e.Å^{-3}$	

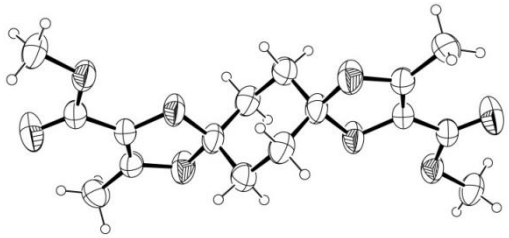


Figure 1 ORTEP view of the crystal structure of **4n**.
Thermal ellipsoids are drawn at 50 % probability level.

Adduct 4n'

Table 1. Crystal data and structure refinement for **4n'**.

Identification code	shelxl	
Empirical formula	C16 H20 O8	
Formula weight	340.32	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.60173(18) Å	α= 90°.
	b = 12.9474(2) Å	β= 97.478(2)°.
	c = 13.2032(3) Å	γ = 90°.
Volume	1627.43(6) $Å^3$	
Z	4	
Density (calculated)	1.389 Mg/m^3	
Absorption coefficient	0.955 mm^{-1}	
F(000)	720	
Crystal size	0.3015 x 0.2292 x 0.0623 mm^3	
Theta range for data collection	4.80 to 73.32°.	
Index ranges	-11<=h<=11, -15<=k<=15, -16<=l<=15	
Reflections collected	12682	
Independent reflections	3223 [R(int) = 0.0197]	
Completeness to theta = 67.50°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.944 and 0.823	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3223 / 0 / 221	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0977	
R indices (all data)	R1 = 0.0402, wR2 = 0.1023	
Largest diff. peak and hole	0.247 and -0.197 $e.Å^{-3}$	

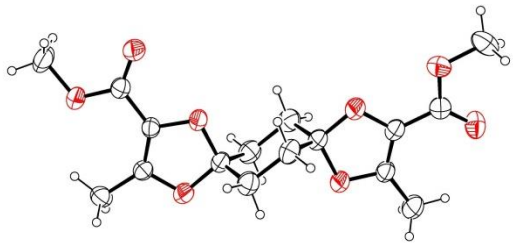


Figure 1. Ortep view of **4n'**. Thermal ellipsoids are drawn at 50% probability level.

Table 2. Bond lengths [Å] and angles [°] for le472_abs.

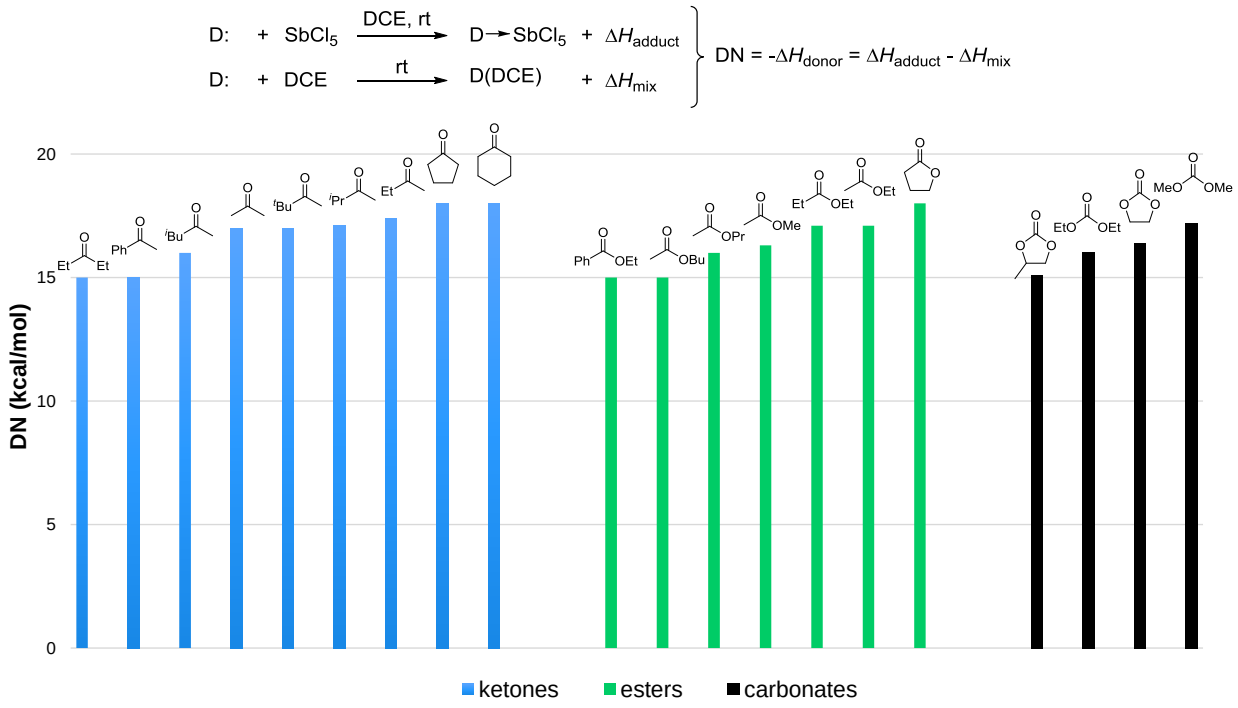
O(1)-C(2)	1.3396(15)	O(7)-C(15)	1.2105(16)
O(1)-C(1)	1.4424(16)	O(8)-C(15)	1.3353(16)
O(2)-C(2)	1.2068(15)	O(8)-C(16)	1.4534(18)
O(3)-C(4)	1.3666(15)	C(1)-H(1A)	0.9800
O(3)-C(6)	1.4508(15)	C(1)-H(1B)	0.9800
O(4)-C(3)	1.3867(14)	C(1)-H(1C)	0.9800
O(4)-C(6)	1.4428(15)	C(2)-C(3)	1.4554(16)
O(5)-C(12)	1.3647(15)	C(3)-C(4)	1.3374(17)
O(5)-C(9)	1.4611(15)	C(4)-C(5)	1.4776(17)
O(6)-C(14)	1.3841(15)	C(5)-H(5A)	0.9800
O(6)-C(9)	1.4376(16)	C(5)-H(5B)	0.9800
		C(5)-H(5C)	0.9800
		C(6)-C(7)	1.5088(18)
		C(6)-C(11)	1.511(2)

C(7)-C(8)	1.524(2)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.5054(19)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.5136(19)
C(10)-C(11)	1.528(2)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(14)	1.3314(19)
C(12)-C(13)	1.4757(18)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.4548(18)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800

C(2)-O(1)-C(1)	115.70(11)
C(4)-O(3)-C(6)	107.21(9)
C(3)-O(4)-C(6)	105.91(9)
C(12)-O(5)-C(9)	106.40(10)
C(14)-O(6)-C(9)	105.74(10)
C(15)-O(8)-C(16)	114.73(12)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(2)-C(2)-O(1)	124.69(11)
O(2)-C(2)-C(3)	123.74(11)
O(1)-C(2)-C(3)	111.57(10)
C(4)-C(3)-O(4)	111.10(11)
C(4)-C(3)-C(2)	133.02(11)
O(4)-C(3)-C(2)	115.82(10)
C(3)-C(4)-O(3)	110.08(11)
C(3)-C(4)-C(5)	134.32(12)
O(3)-C(4)-C(5)	115.57(11)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
O(4)-C(6)-O(3)	105.67(9)
O(4)-C(6)-C(7)	109.52(11)
O(3)-C(6)-C(7)	108.96(11)
O(4)-C(6)-C(11)	109.58(11)
O(3)-C(6)-C(11)	110.31(11)
C(7)-C(6)-C(11)	112.58(11)
C(6)-C(7)-C(8)	110.65(11)
C(6)-C(7)-H(7A)	109.5
C(8)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
C(8)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	108.1
C(9)-C(8)-C(7)	111.70(11)
C(9)-C(8)-H(8A)	109.3
C(7)-C(8)-H(8A)	109.3
C(9)-C(8)-H(8B)	109.3
C(7)-C(8)-H(8B)	109.3
H(8A)-C(8)-H(8B)	107.9
O(6)-C(9)-O(5)	105.41(9)
O(6)-C(9)-C(8)	109.33(11)
O(5)-C(9)-C(8)	108.75(11)
O(6)-C(9)-C(10)	111.45(12)
O(5)-C(9)-C(10)	108.16(11)
C(8)-C(9)-C(10)	113.39(11)
C(9)-C(10)-C(11)	110.63(11)
C(9)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
C(11)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
C(6)-C(11)-C(10)	110.60(11)
C(6)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11A)	109.5
C(6)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	108.1
C(14)-C(12)-O(5)	110.29(11)
C(14)-C(12)-C(13)	133.98(12)
O(5)-C(12)-C(13)	115.72(12)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-O(6)	111.23(11)
C(12)-C(14)-C(15)	127.60(12)
O(6)-C(14)-C(15)	120.97(11)
O(7)-C(15)-O(8)	123.91(12)
O(7)-C(15)-C(14)	123.47(12)
O(8)-C(15)-C(14)	112.62(11)
O(8)-C(16)-H(16A)	109.5
O(8)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
O(8)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

12. DONOR NUMBERS OF KETONES, ESTERS AND CARBONATES (GUTMANN'S SCALE OF SOLVENT LEWIS BASICITY)



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