Supporting Information for

Synthesis of the Common Core Structure of the Stemofoline Alkaloids

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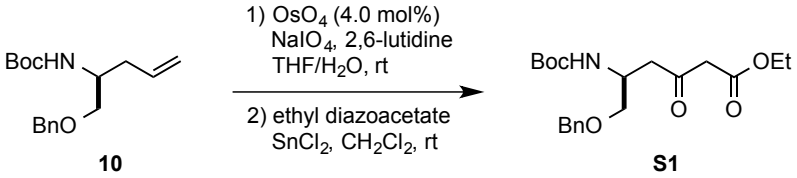
General. All non-aqueous reactions were carried out under an inert atmosphere of argon in oven-dried glassware unless otherwise noted. Dehydrated diethyl ether, tetrahydrofuran, methylene chloride and toluene were purchased from Kanto Chemicals Co., and were used after passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Dehydrated *N*,*N*-dimethylformamide were purchased from Kanto Chemicals Co., Inc. and stored over activated MS4A*. Dehydrated methanol, ethanol and acetonitrile were purchased from Wako Pure Chemical Industries, Ltd. and stored over activated MS3A. All other reagents were commercially available and used without further purification. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel $60F_{254}$. Preparative flash chromatography was performed using Silica Gel 60 (spherical, 40-100 μm) purchased from Kanto Chemical Co., Inc. ^{1}H and ^{13}C NMR were recorded on a JEOL ECS-400 spectrometer. Preparative thin layer chromatography (PTLC) separations were performed on Merck analytical plates (0.25 or 0.50 mm thick) precoated with silica gel 60 F_{254}. All ^{1}H NMR spectra are reported in units, parts per million (ppm) downfield from tetramethylsilane as the internal standard and coupling constants are indicated in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All ^{13}C NMR spectra are reported in ppm relative to the central line of the triplet for $CDCl_3$ at 77.0 ppm. Infrared spectra (IR) were recorded on a FT/IR-4100 Fourier Transform Infrared Spectrophotometer, and are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100LP AccuTOF LC-plus in positive electrospray ionization (ESI) method using PEG as the internal standard. Optical rotations were measured on a JASCO P-2200 Digital Polarimeter at room temperature, using the sodium D line. Melting points, determined on a Yanaco Micro Melting Point Apparatus, are uncorrected.

* Molecular sieves were "activated" in the following manner: A round-bottom flask containing molecular sieves was heated in a regular microwave for 1.5-2.0 minute and the flask was immediately evacuated. When cooled to room temperature, the flask was backfilled with argon. The above procedure was repeated three times.

Ethyl (*S*)-6-(benzyloxy)-5-((*tert*-butoxycarbonyl)amino)-3-oxohexanoate (S1)

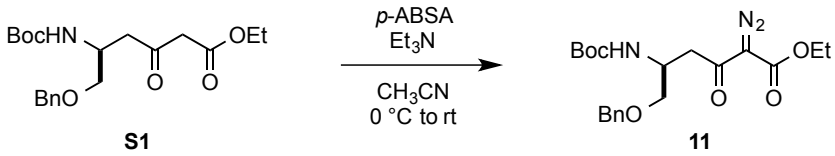


A 2-L, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **10** (47.9 g, 165 mmol) and 2,6-lutidine (19.2 mL, 165 mmol) in THF (274 mL) and H_2O (91 mL). The clear solution was stirred at 0 °C for 5 min, then $NaIO_4$ (106 g, 494 mmol) was added portionwise followed by OsO_4 solution (0.039 M in *t*-BuOH, 16.7 mL, 0.658 mmol). The solution was warmed to room temperature. White precipitate was observed during the reaction. After 12 h, the reaction mixture was filtered through Celite, and washed with EtOAc (200 mL) and partitioned between EtOAc (800 mL) and 5% $Na_2S_2O_3$ aq. (500 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (400 mL) twice. The combined organic phase was washed with brine (300 mL), dried over Na_2SO_4 (ca. 50 g), filtered and concentrated *in vacuo* to afford crude product (57.4 g), which was used in the next reaction without further purification. [EI10171]

A 2-L, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with the crude aldehyde and ethyl diazoacetate (28.0 g, 245 mmol) in CH_2Cl_2 (400 mL). The clear solution was stirred at 0 °C for 5 min, then $SnCl_2$ (12.4 g, 65.4 mmol) was added portionwise. The solution was warmed to room temperature and stirred overnight. After 12 h, the reaction mixture was filtered through Celite, and poured dropwise into the saturated NH_4Cl aq (100 mL). The resulting mixture was partitioned between CH_2Cl_2 (400 mL) and water (500 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (200 mL). The combined organic phase was washed with 1 M HCl aq. (200 mL), dried over Na_2SO_4 (ca. 50 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 9/1 to 4/1) to afford **S1** (42.5 g, 112 mmol, 68%) as colorless foam. [EI10173]

R*f* = 0.36 (*n*-hexane/EtOAc = 3/1, PMA);
$[\alpha]^{22}_{D}$ –4.1 (*c* = 1.00, $CHCl_3$);
IR (neat) 3370, 2979, 2933, 2869, 1736, 1714, 1650, 1505, 1455 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.41–7.24 (5H, m), 5.08 (1H, brs), 4.49 (2H, s), 4.18 (2H, q, *J* = 6.9 Hz), 4.20–4.15 (1H, m), 3.63–3.37 (4H, m), 2.86 (2H, brd, *J* = 6.0 Hz), 1.43 (9H, brs), 1.26 (3H, t, *J* = 6.9 Hz);
^{13}C-NMR ($CDCl_3$) δ 201.3 (C), 174.8 (C), 155.0 (C), 137.7 (C), 128.2 (CH), 127.5 (CH), 127.5 (CH), 79.2 (C), 72.9 (CH_2), 70.7 (CH_2), 61.1 (CH_2), 49.3 (CH_2), 46.6 (CH), 44.0 (CH_2), 28.1 (CH_3), 13.9 (CH_3); HRMS (ESI) calcd for $C_{20}H_{29}NNaO_6$ ($[M+Na]^+$) 402.1887, found 402.1876.

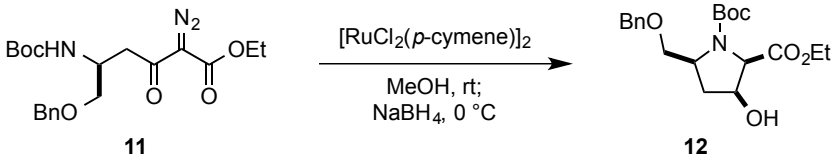
Ethyl (*S*)-6-(benzyloxy)-5-((*tert*-butoxycarbonyl)amino)-2-diazo-3-oxohexanoate (11)



A 1-L, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **S1** (40.0 g, 106 mmol) and *p*-ABSA (27.9 g, 116 mmol) in acetonitrile (353 mL). The clear solution was stirred at 0 °C for 5 min, then Et_3N (17.7 mL, 127 mmol) was added. The solution mixture was warmed to room temperature and stirred for 2 h, filtered through Celite and washed with EtOAc (300 mL). The resulting mixture was partitioned between EtOAc (200 mL) and 5% NH_4Cl aq. (400 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (200 mL) twice. The combined organic phase was washed with brine (300 mL), dried over Na_2SO_4 (ca. 50 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 8/1 to 5/1) to afford **11** (39.5 g, 97.4 mmol, 92%) as slightly yellow oil. [EI10176]

R*f* = 0.49 (*n*-hexane/EtOAc = 3/1, UV, PMA);
$[\alpha]^{22}_{D}$ +0.842 (*c* = 1.00, $CHCl_3$);
IR (neat) 3380, 2979, 2932, 2869, 2135, 1714, 1652, 1496, 1455 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.39–7.25 (5H, m), 5.16 (1H, brd, *J* = 7.3 Hz), 4.52 (1H, d, *J* = 12.4 Hz), 4.48 (1H, d, *J* = 12.4 Hz), 4.29 (2H, q, *J* = 7.1 Hz), 4.32–4.19 (1H, m), 3.62–3.52 (2H, m), 3.14 (2H, d, *J* = 6.0 Hz), 1.42 (9H, s), 1.32 (3H, t, *J* = 7.1 Hz);
^{13}C-NMR ($CDCl_3$) δ 196.7 (C), 161.1 (C), 155.1 (C), 137.8 (C), 128.1 (CH), 127.4 (CH), 127.4 (CH), 79.0 (C), 72.8 (CH_2), 71.4 (CH_2), 61.2 (CH_2), 47.3 (CH), 41.7 (CH_2), 28.1 (CH_3), 14.1 (CH_3);
HRMS (ESI) calcd for $C_{20}H_{27}N_3NaO_6$ ($[M+Na]^+$) 428.1792, found 428.1774.

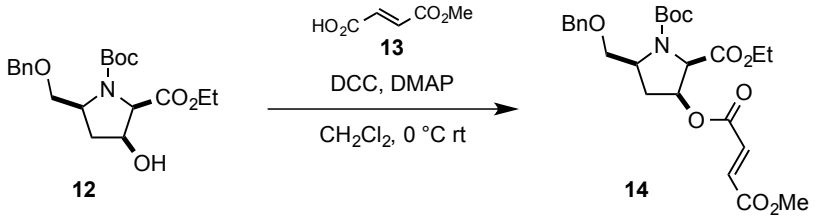
1-(*tert*-Butyl) 2-ethyl (2*R*,3*S*,5*S*)-5-((benzyloxy)methyl)-3-hydroxypyrrolidine-1,2-dicarboxylate (12)



A 1-L, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **11** (37.9 g, 93.5 mmol) in methanol (290 mL). The clear solution was stirred at room temperature and $[RuCl_2(p\text{-cymene})]_2$ (1.5 g, 2.45 mmol) was added. After 1.5 h and 3 h, additional portions of $[RuCl_2(p\text{-cymene})]_2$ (1.5 g, 2.45 mmol each) was added to the reaction mixture. The solution was stirred for 2.5 h and an aliquot of sample was checked with NMR to confirm the consumption of **11**. The reaction mixture was cooled to 0 °C and stirred for 10 min, then $NaBH_4$ (7.07 g, 187 mmol) was added portionwise. After stirring at 0 °C for 40 min, the reaction was quenched with saturated NH_4Cl aq. (100 mL) and partitioned between EtOAc (700 mL) and water (700 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (300 mL) twice. The combined organic extracts were washed with brine (300 mL), dried over Na_2SO_4 (ca. 50 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 8/1 to 3/1) to afford **12** (24.9 g, 65.6 mmol, 70%) as slightly yellow oil. [EI10178]

R*f* = 0.56 (*n*-hexane/EtOAc = 1/1, PMA);
$[\alpha]^{22}_{D}$ +8.97 (*c* = 1.01, $CHCl_3$);
IR (neat) 3400, 2977, 1757, 1736, 1700, 1456, 1389, 1367 cm^{-1};
^{1}H-NMR ($CDCl_3$) (5:3 mixture of two rotamers)
(***major***) δ 7.39–7.24 (5H, m), 4.99 (1H, d, *J* = 11.9 Hz), 4.75 (1H, d, *J* = 12.3 Hz), 4.58 (1H, d, *J* = 12.3), 4.57–4.41 (1H, m), 4.33 (1H, d, *J* = 5.5 Hz), 4.29–4.09 (3H, m), 4.05 (1H, dd, *J* = 10.1, 2.3 Hz), 3.49 (1H, dd, *J* = 18.4, 10.1 Hz), 2.45–2.31 (1H, m), 2.05–1.93 (1H, m), 1.47–1.36 (9H, m);
(***minor***) δ 7.39–7.24 (5H, m), 4.73 (1H, d, *J* = 11.0 Hz), 4.75 (1H, d, *J* = 12.3 Hz), 4.63 (1H, d, *J* = 12.3), 4.57–4.41 (1H, m), 4.40 (1H, d, *J* = 6.0 Hz), 4.29–4.09 (3H, m), 3.93–3.86 (1H, m), 3.49 (1H, dd, *J* = 18.4, 10.1 Hz), 2.45–2.31 (1H, m), 2.05–1.93 (1H, m), 1.47–1.36 (9H, m);
^{13}C-NMR ($CDCl_3$)
(***major*** and ***minor***) δ 168.8 (C), 168.3 (C), 154.1 (C), 136.9 (C), 128.2 (CH), 127.6 (CH), 127.4 (CH), 80.1 (C),73.6 (CH_2), 71.9 (CH), 70.7 (CH_2), 70.6 (CH_2), 67.2 (CH), 66.8 (CH), 60.4 (CH_2), 58.0 (CH), 57.8 (CH), 37.2 (CH_2), 36.4 (CH_2), 28.1 (CH_3), 28.0 (CH_3), 14.3 (CH_3) 14.1 (CH_3);
HRMS (ESI) calcd for $C_{20}H_{29}NNaO_6$ ($[M+Na]^+$) 402.1887, found 402.1886.

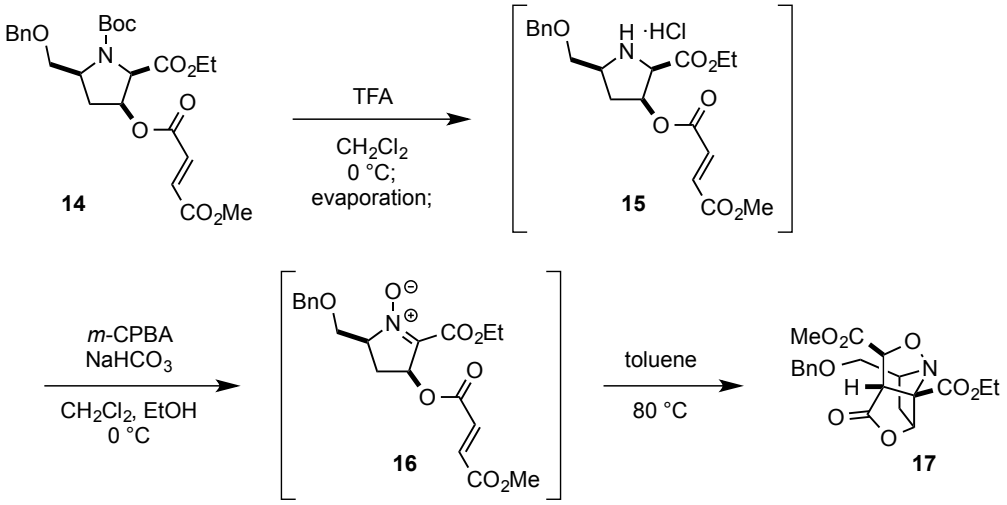
1-(*tert*-Butyl) 2-ethyl (2*R*,3*S*,5*S*)-5-((benzyloxy)methyl)-3-(((*E*)-4-methoxy-4-oxobut-2-enoyl) oxy)pyrrolidine-1,2-dicarboxylate (14)



A 1-L, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **12** (23.0 g, 60.8 mmol) and monomethyl fumarate **13** (11.5 g, 88.2 mmol) in CH_2Cl_2 (200 mL). The clear solution was stirred at 0 °C for 5 min, then dicyclohexyl carbodiimide (17.6 g, 85.0 mmol) and DMAP (371 mg, 3.04 mmol) were added. The solution was warmed to room temperature and stirred for 3.5 h. The reaction was quenched with saturated NH_4Cl aq. (50 mL), filtered through Celite and washed with CH_2Cl_2 (100 mL). The filtrate was partitioned between CH_2Cl_2 (100 mL) and water (500 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (300 mL) twice. The combined organic extracts were washed with $NaHCO_3$ aq. (200 mL) brine (200 mL), dried over Na_2SO_4 (ca. 50 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 8/1 to 4/1) to afford **14** (23.6 g, 48.0 mmol, 79%) as slightly yellow oil. [EI10182]

R*f* = 0.73 (*n*-hexane/EtOAc = 1/1, UV, PMA);
$[\alpha]^{22}_{D}$ –19.1 (*c* = 1.00, $CHCl_3$);
IR (neat) 3361,2935, 2859, 1732, 1706, 1665, 1645, 1497, 1454, 1392 cm^{-1};
^{1}H-NMR ($CDCl_3$) (3:2 mixture of two rotamers)
(***major***) δ 7.36-7.22 (5H, m), 6.78-6.62 (2H, m), 5.69-5.58 (1H, m), 4.72-4.40 (3H, m), 4.30-4.20 (1H, m), 4.20-4.03 (2H, m), 4.03-3.96 (1H, m), 3.82 (3H, s), 3.52 (1H, dd, *J* = 10.1, 9.2 Hz), 2.44-2.30 (1H, m), 2.29 (1H, dd, *J* = 3.2, 2.8 Hz), 1.48-1.37 (9H, m), 1.27-1.13 (2H, m);
(***minor***) δ 7.36-7.22 (5H, m), 6.78-6.62 (2H, m), 5.69-5.58 (1H, m), 4.72-4.40 (3H, m), 4.20-4.03 (3H, m), 3.90-3.84 (1H, m), 3.82 (3H, s), 3.52 (1H, dd, *J* = 10.1, 9.2 Hz), 2.44-2.30 (1H, m), 2.25 (1H, dd, *J* = 3.2, 2.8 Hz), 1.48-1.37 (9H, m), 1.27-1.13 (2H, m);
^{13}C-NMR ($CDCl_3$)
(***major*** and ***minor***) δ 168.4 (C), 168.0 (C), 165.0 (C), 163.3 (C), 153.9 (C), 153.4 (C), 138.3 (C), 138.1 (C), 134.0 (CH), 132.7 (CH), 128.4 (CH), 127.6 (CH×2), 80.8 (C), 74.1 (CH), 73.1 (CH), 73.1 (CH_2), 71.2 (CH_2), 70.7 (CH_2), 63.5 (CH), 63.0 (CH), 61.2 (CH_2), 56.4 (CH), 56.2 (CH), 52.4 (CH_3), 34.4 (CH_2), 33.6 (CH_2), 28.3 (CH_3), 28.2 (CH_3), 14.2 (CH_3), 14.1 (CH_3);
HRMS (ESI) calcd for $C_{25}H_{33}NNaO_9$ ($[M+Na]^+$) 514.2048, found 514.2051.

2a^1-Ethyl 1-methyl (1*S*,2a^1*S*,3*S*,4a*S*,6a*S*)-3-((benzyloxy)methyl)-6-oxotetrahydro-1*H*-2,5-dioxa-2a-azacyclopenta[*cd*]pentalene-1,2a^1(3*H*)-dicarboxylate (17)



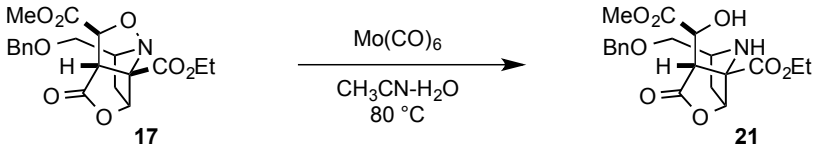
A 500-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **14** (13.0 g, 26.5 mmol) in CH_2Cl_2 (132 mL). The clear solution was stirred at 0 °C for 5 min, then TFA (26.5 mL) was added dropwise. After 3 h at 0 °C, the reaction mixture was diluted with toluene (100 mL) and concentrated *in vacuo* to afford the TFA salt **15**. The flask was charged with CH_2Cl_2 (132 mL) and EtOH (26.4 ml). The solution was stirred at –20 °C for 5 min, then $NaHCO_3$ (2.45 g, 29.2 mmol) was added. After stirring for 1 h at the same temperature, *m*-CPBA (16.2 g, 61.0 mmol) was added to the reaction mixture. The solution was warmed to 0 °C and stirred for 12 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. (50 mL). The resulting solution was partitioned between Et_2O (300 mL) and water (300 mL). The organic phase was collected and the aqueous phase was extracted with Et_2O (100 mL) twice. The combined organic phase was dried over Na_2SO_4 (ca. 50 g), filtered and concentrated *in vacuo* to afford crude product, which was used without further purification.

A 500-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with the crude product in toluene (260 mL). The clear solution was stirred at 80 °C for 3 h. The reaction mixture was partitioned between Et_2O (300 mL) and saturated $NaHCO_3$ aq. (300 mL). The organic phase was collected and the aqueous phase was extracted with Et_2O (150 mL) twice. The combined organic extracts were washed with brine (100 mL), dried over Na_2SO_4 (ca. 50 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 8/1 to 3/1) to afford **17** (6.7 g, 16.5 mmol, 62%, 3 steps) as slightly yellow oil. [EI10184, EI10185, EI10187, EI10007]

R*f* = 0.60 (*n*-hexane/EtOAc = 1/1, UV, PMA);
$[\alpha]^{24}_{D}$ +8.11 (*c* = 1.61, $CHCl_3$);

IR (neat) 2984, 2953, 2871, 1780, 1740, 1454, 1370 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.39–7.24 (5H, m), 5.28 (1H, dd, J = 8.0, 5.5 Hz), 4.88 (1H, s), 4.64 (1H, d, J = 12.1 Hz), 4.59 (1H, d, J = 12.1 Hz), 4.44 (1H, s), 4.32–4.21 (2H, m), 4.02 (1H, dd, J = 8.9, 5.3 Hz), 3.82 (3H, s), 3.77–3.65 (2H, m), 2.73 (1H, ddd, J = 13.8, 8.0, 6.4 Hz), 2.11 (1H, ddd, J = 13.8, 11.9, 5.5 Hz), 1.31 (3H, t, J = 7.1 Hz);
^{13}C-NMR ($CDCl_3$) δ 174.5 (C), 168.5 (C), 167.2 (C), 137.9 (C), 128.3 (CH), 127.6 (CH×2), 84.9 (CH), 83.9 (C), 79.7 (CH), 73.2 (CH_2), 68.5 (CH_2), 66.4 (CH), 62.9 (CH_2), 55.6 (CH_3), 53.0 (CH), 36.3 (CH_2), 13.9 (CH_3);
HRMS (ESI): calcd for $C_{20}H_{23}NNaO_8$ ([M+Na]$^+$) 428.1316, found 428.1306.

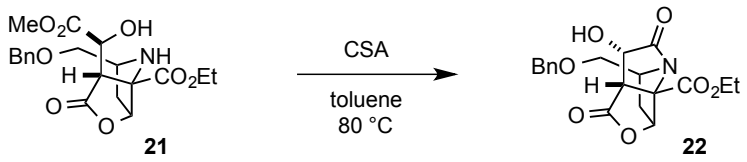
Ethyl (3*S*,3a*S*,5*S*,6a*S*)-5-((benzyloxy)methyl)-3-((*S*)-1-hydroxy-2-methoxy-2-oxoethyl)-2-oxohexahydro-3a*H*-furo[3,2-*b*]pyrrole-3a-carboxylate (21)



A 500-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **17** (4.84 g, 11.9 mmol) in CH_3CN (80 mL) and H_2O (643 μL). $Mo(CO)_6$ (4.08 g, 15.5 mmol) was added and the solution was stirred at 80 °C for 4.5 h. The reaction mixture was passed through silica gel pad, washed with EtOAc (50 mL) and concentrated *in vacuo*. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 4/1 to 1/1) to afford **21** (2.94 g, 7.22 mmol, 61%) as slightly yellow oil. [EI10194, EI10021]

R*f* = 0.47 (*n*-hexane/EtOAc = 1/1, UV, PMA);
$[\alpha]^{24}_D$ –33.4 (*c* = 1.00, $CHCl_3$);
IR (neat) 3337, 2953, 2861, 1782, 1736, 1496, 1454, 1367 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.39–7.24 (5H, m), 6.13 (1H, brd, J = 10.5 Hz), 4.98 (1H, dd, J = 6.6, 3.4 Hz), 4.80 (1H, dd, J = 10.5, 2.8 Hz), 4.57 (1H, d, J = 11.9 Hz), 4.50 (1H, d, J = 11.9 Hz), 4.49-4.22 (2H, m), 3.74 (3H, s), 3.71-3.64 (1H, m), 3.63 (1H, d, J = 2.8 Hz), 3.41 (1H, dd, J = 9.4, 4.8 Hz), 3.35 (1H, dd, J = 9.4, 7.2 Hz), 3.23 (1H, brs), 2.24 (1H, ddd, J = 15.6, 6.6, 6.6 Hz), 2.03 (1H, ddd, J = 9.9, 6.4, 3.4 Hz), 1.32 (3H, t, J = 6.9 Hz);
^{13}C-NMR ($CDCl_3$): δ 172.9 (C), 172.5 (C), 171.5 (C), 137.4 (C), 128.0 (CH), 127.4 (CH), 127.3 (CH), 85.2 (CH), 73.5 (C), 72.8 (CH_2), 71.9 (CH_2), 69.7 (CH), 62.7 (CH_2), 57.6 (CH), 52.0 (CH_3), 50.9 (CH), 33.3 (CH_2), 13.7 (CH_3);
HRMS (ESI) calcd for $C_{20}H_{25}NNaO_8$ ([M+Na]$^+$) 430.1472, found 430.1485.

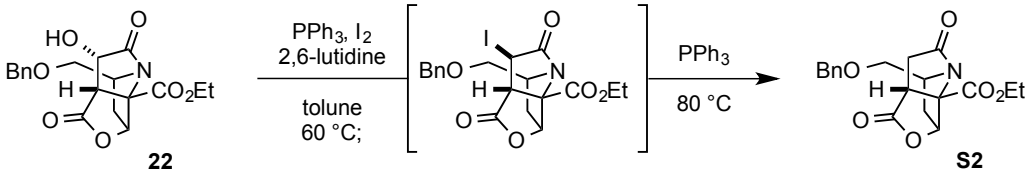
Ethyl (2a*S*,2a^1*S*,4*S*,7*S*,7a*S*)-4-((benzyloxy)methyl)-7-hydroxy-1,6-dioxohexahydrofuro[2,3,4-*gh*] pyrrolizine-2a^1(2a*H*)-carboxylate (22)



A 500-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **21** (3.45 g, 8.47 mmol) in toluene (170 mL) and EtOH (494 μL). CSA (2.46 g, 10.6 mmol) was added to the solution and stirred at 80 °C for 18 h. The reaction was cooled to 0 °C and quenched with saturated $NaHCO_3$ aq. (60 mL). The resulting mixture was partitioned between EtOAc (300 mL) and water (300 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (150 mL) twice. The combined organic phase was washed with brine (100 mL), dried over Na_2SO_4 (ca. 50 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 4/1 to 2/1) to afford **22** (2.53 g, 6.74 mmol, 80%) as slightly yellow solid. [EI10192, EI10028]

R*f* = 0.40 (*n*-hexane/EtOAc = 1/3, UV, PMA);
M.p. 116.9–120.0 °C;
$[\alpha]^{24}_{D}$ –62.0 (*c* = 1.15, $CHCl_3$);
IR (neat) 3446, 2981, 2926, 2861, 1786, 1721, 1455, 1369, 1297 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.39–7.24 (5H, m), 5.08 (1H, d, *J* = 6.0 Hz), 4.89 (1H, dd, *J* = 7.8, 7.8 Hz), 4.59 (1H, d, *J* = 11.7 Hz), 4.47 (1H, d, *J* = 11.7 Hz), 4.29 (2H, q, *J* = 7.12 Hz), 4.17 (1H, dd, *J* = 9.6, 5.1 Hz), 4.08–3.96 (1H, m), 3.92 (1H, dd, *J* = 9.6, 3.2 Hz), 3.79 (1H, d, *J* = 7.8 Hz), 3.23 (1H, d, *J* = 7.8 Hz), 2.64 (1H, ddd, *J* = 15.1, 9.4, 6.0 Hz), 2.52 (1H, dd, *J* = 15.1, 4.6 Hz), 1.33 (1H, t, *J* = 7.1 Hz);
^{13}C-NMR ($CDCl_3$) δ 171.8 (C), 170.9 (C), 167.1 (C), 137.7 (C), 128.1 (CH), 127.6 (CH), 127.4 (CH), 80.7 (CH), 75.8 (C), 72.8 (CH), 72.7 (CH_2), 66.4 (CH_2), 63.0 (CH_2), 58.1 (CH), 48.5 (CH), 35.9 (CH_2), 13.9 (CH_3);
HRMS (ESI) calcd for $C_{19}H_{21}NNaO_7$ ([M+Na]$^+$) 398.1210, found 398.1200.

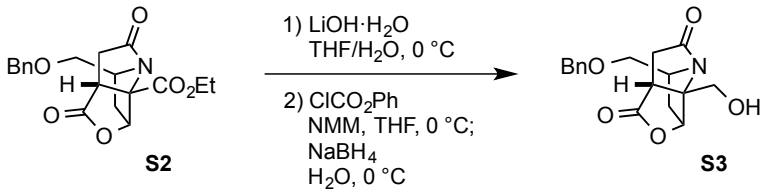
Ethyl (2a*S*,2a^1*S*,4*S*,7a*R*)-4-((benzyloxy)methyl)-1,6-dioxohexahydrofuro[2,3,4-*gh*]pyrrolizine-2a^1(2a*H*)-carboxylate (S2)



A 200-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **22** (1.77 g, 4.72 mmol) and 2,6-lutidine (1.65 mL, 14.2 mmol) in toluene (50 mL) and CH_2Cl_2 (10 mL). PPh_3 (1.61 g, 6.14 mmol) and I_2 (1.44 g, 5.66 mmol) were added to the solution at room temperature and stirred at the same temperature for 15 h. An additional 2,6-lutidine (550 μL, 4.72 mmol), PPh_3 (3.70 g, 14.2 mmol) and H_2O (0.212 ml, 11.8 mmol) were added to the solution and stirred at 80 °C for 35 h. After TLC analysis indicated the completion of the reaction, saturated $Na_2S_2O_3$ aq. (100 mL) was added to the mixture. The resulting mixture was partitioned between EtOAc (300 mL) and water (200 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (100 mL) twice. The combined organic phase was washed with brine (50 mL), dried over Na_2SO_4 (ca. 30 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 4/1 to 3/2) to afford **S2** (1.55 g, 4.31 mmol, 91%) as slightly yellow solid. [EI10060, EI10035]

R*f* = 0.63 (*n*-hexane/EtOAc = 1/3, UV, PMA);
M.p. 65.0–67.8 °C.
$[\alpha]^{24}_D$ –29.0 (*c* = 1.00, $CHCl_3$);
IR (neat) 3029, 2927, 2857, 1782, 1739, 1711, 1496, 1453, 1368, 1302 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.39–7.22 (5H, m), 5.18 (1H, d, *J* = 5.5 Hz), 4.57 (1H, d, *J* = 11.9 Hz), 4.44 (1H, d, *J* = 11.9 Hz), 4.29 (2H, q, *J* = 7.1 Hz), 4.12 (1H, dd, *J* = 9.4, 5.3 Hz), 4.01–3.93 (1H, m), 3.85 (1H, dd, *J* = 9.4, 2.5 Hz), 3.51 (1H, d, *J* = 8.2 Hz), 3.04 (1H, dd, *J* = 17.0, 8.2 Hz), 2.83 (1H, d, *J* = 17.0 Hz), 2.67 (1H, ddd, *J* = 15.1, 10.1, 5.5 Hz), 2.53 (1H, ddd, *J* = 15.1, 4.6 Hz), 1.33 (3H, t, *J* = 7.1 Hz);
^{13}C-NMR ($CDCl_3$): δ 174.6 (C), 172.1 (C), 168.0 (C), 137.8 (C), 128.0 (CH), 127.4 (CH), 127.3 (CH), 80.6 (CH), 79.9 (C), 72.6 (CH_2), 65.9 (CH_2), 62.6 (CH_2), 57.2 (CH), 44.1 (CH), 37.3 (CH_2), 36.9 (CH_2), 13.8 (CH_3);
HRMS (ESI) calcd for $C_{19}H_{21}NNaO_6$ ($[M+Na]^+$) 382.1261, found 382.1254.

(2a*S*,2a^1*R*,4*S*,7a*R*)-4-((Benzyloxy)methyl)-2a^1-(hydroxymethyl)hexahydrofuro[2,3,4-*gh*]pyrroliz ine-1,6-dione (S3)

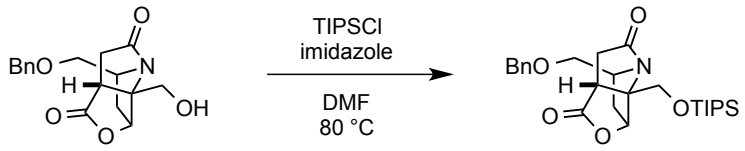


A 100-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **S2** (990 mg, 2.76 mmol) in THF (14 mL) and H_2O (7 mL). The clear solution was stirred at 0 °C for 5 min, then $LiOH·H_2O$ (151 mg, 3.59 mmol) was added. After 1 h, 1 M HCl aq. (5 mL) was added to the resulting solution. The resulting mixture was partitioned between EtOAc (50 mL) and water (50 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (50 mL) twice. The combined organic phase was washed with brine (50 mL), dried over Na_2SO_4 (ca. 20 g), filtered and concentrated *in vacuo* to afford crude product, which was used in the next reaction without further purification.

A 200-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with the crude carboxylic acid in THF (40 mL). The solution was stirred at 0 °C for 5 min, then $ClCO_2Ph$ (1.52 ml, 12.1 mmol) followed by *N*-methyl morpholine (1.59 mL, 14.5 mmol) was added. After 2.5 h at 0 °C, $NaBH_4$ (685 mg, 18.1 mmol) was added portionwise and water (10 mL) was added dropwise to the mixture over 10 min. After 10 min, the reaction mixture was quenched with saturated NH_4Cl aq. (20 mL). The resulting mixture was partitioned between EtOAc (200 mL) and water (150 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (100 mL) twice. The combined organic phase was washed with brine (50 mL), dried over Na_2SO_4 (ca. 20 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 4/1 to 1/1) to afford **S3** (747 mg, 2.36 mmol, 85%) as a colorless solid. [EI10209, EI10212, EI10094]

R*f* = 0.22 (EtOAc only, UV, PMA);
M.p. 129.1–134.2 °C;
$[\alpha]^{24}_D$ –24.7 (*c* = 1.07, $CHCl_3$);
IR (neat): 3420, 2925, 2864, 1772, 1684, 1454, 1397 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.38–7.25 (5H, m), 4.79 (1H, d, *J* = 6.0 Hz), 4.58 (1H, d, *J* = 11.9 Hz), 4.45 (1H, d, *J* = 11.9 Hz), 4.02 (1H, dd, *J* = 9.6, 5.0 Hz), 3.91 (1H, dd, *J* = 9.6, 3.2 Hz), 3.91–3.85 (1H, m), 3.81–3.78 (2H, m), 3.15 (1H, d, *J* = 8.2 Hz), 2.99 (1H, dd, *J* = 17.0, 8.2 Hz), 2.80 (1H, d, *J* = 17.0 Hz), 2.63 (1H, ddd, *J* = 15.1, 8.7, 6.0 Hz), 2.48 (1H, dd, *J* = 15.1, 5.7 Hz), 2.22 (1H, t, *J* = 5.0 Hz);
^{13}C-NMR ($CDCl_3$) δ 176.8 (C), 173.3 (C), 137.8 (C), 128.2 (CH), 127.5 (CH), 127.4 (CH), 80.6 (CH), 80.1 (C), 72.8 (CH_2), 66.4 (CH_2), 61.9 (CH_2), 56.6 (CH), 42.9 (CH), 37.9 (CH_2), 37.1 (CH_2);
HRMS (ESI) calcd for $C_{17}H_{19}NNaO_5$ ([M+Na]$^+$) 340.1155, found 340.1148.

(2a*S*,2a^1*R*,4*S*,7a*R*)-4-((Benzyloxy)methyl)-2a^1-(((triisopropylsilyl)oxy)methyl)hexahydrofuro[2,3,4-*gh*]pyrrolizine-1,6-dione (23)

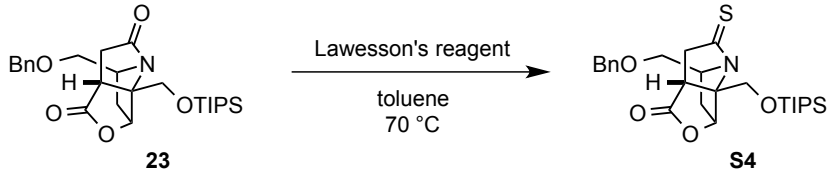


S3 **23**

A 100-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **S3** (742 mg, 2.34 mmol) in DMF (12 mL). The solution at room temperature was added imidazole (573 mg, 8.42 mmol) and TIPSCl (1.19 mL, 5.61 mmol) and the reaction mixture was stirred at 80 °C for 17 h. The reaction mixture was quenched with saturated NH_4Cl aq. (10 mL). The resulting mixture was partitioned between EtOAc (80 mL) and water (80 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (80 mL) twice. The combined organic phase was washed with brine (50 mL), dried over Na_2SO_4 (ca. 30 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 5/1 to 3/1) to afford **23** (1.05 g mg, 2.22 mmol, 95%) as colorless oil. [EI10214, EI10098]

R*f* = 0.53 (*n*-hexane/EtOAc = 2/1, UV, PMA);
$[\alpha]^{24}_{D}$ –11.0 (*c* = 1.07, $CHCl_3$);
IR (neat) 3454, 2943, 2866, 1777, 1699, 1641, 1463, 1366, 1121 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.37–7.26 (5H, m), 4.82 (1H, d, *J* = 5.5 Hz), 4.58 (1H, d, *J* = 12.2 Hz), 4.45 (1H, d, *J* = 12.2 Hz), 4.02 (1H, dd, *J* = 9.6, 5.5 Hz), 3.93 (1H, dd, *J* = 9.6, 2.7 Hz), 3.91–3.87 (1H, m), 3.83 (2H, s), 3.13 (1H, d, *J* = 7.5 Hz), 2.96 (1H, dd, *J* = 17.4, 7.5 Hz), 2.80 (1H, d, *J* = 17.4 Hz), 2.61 (1H, ddd, *J* = 15.1, 9.2, 5.5 Hz), 2.50 (1H, dd, *J* = 15.1, 5.0 Hz), 1.17–1.02 (21H, m);
^{13}C-NMR ($CDCl_3$) δ 176.3 (C), 172.6 (C), 138.0 (C), 128.1 (CH), 127.5 (CH), 127.3 (CH), 80.6 (CH), 79.8 (C), 72.9 (CH_2), 66.6 (CH_2), 63.7 (CH_2), 56.7 (CH), 42.6 (CH), 37.6 (CH_2), 37.3 (CH_2), 17.7 (CH_3), 11.6 (CH);
HRMS (ESI) calcd for $C_{26}H_{39}NNaO_5Si$ ($[M+Na]^+$) 496.2490, found 496.2487.

(2a*S*,2a^1*R*,4*S*,7a*R*)-4-((Benzyloxy)methyl)-6-thioxo-2a^1-(((triisopropylsilyl)oxy)methyl)hexahydrofuro[2,3,4-*gh*]pyrrolizin-1(2a*H*)-one (S4)

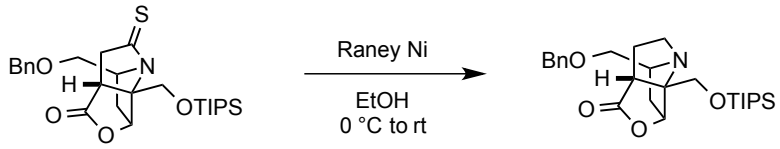


23 **S4**

A 50-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **23** (600 mg, 1.27 mmol) in toluene (13 mL). The solution at room temperature was added Lawesson's reagent (564 mg, 1.39 mmol) and the reaction mixture was stirred at 80 °C for 3.5 h. The reaction mixture was quenched with saturated $NaHCO_3$ aq. (5 mL). The resulting mixture was partitioned between Et_2O (100 mL) and water (100 mL). The organic phase was collected and the aqueous phase was extracted with Et_2O (50 mL) twice. The combined organic phase was washed with brine (50 mL), dried over Na_2SO_4 (ca. 20 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/benzene = 1/3 to 1/4 followed by *n*-hexane/EtOAc = 6/1) to afford **S4** (618 mg, 1.26 mmol, 99%) as white solid. [EI10101]

R*f* = 0.69 (*n*-hexane/EtOAc = 2/1, UV, PMA);
M.p. 74.9–77.8 °C;
$[\alpha]^{24}_D$ +45.8 (*c* = 1.03, $CHCl_3$);
IR (neat) 2942, 2865, 1789, 1770, 1446, 1413, 1323, 1126 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.38–7.22 (5H, m), 4.82 (1H, d, *J* = 4.1 Hz), 4.58 (1H, d, *J* = 11.9 Hz), 4.44 (1H, d, *J* = 11.9 Hz), 4.49–4.41 (1H, m), 4.20–4.10 (2H, m), 3.91 (2H, s), 3.51 (1H, d, *J* = 18.3 Hz), 3.43 (1H, dd, *J* = 18.3, 6.9 Hz), 3.13 (1H, d, *J* = 6.9 Hz), 2.78–2.65 (2H, m), 1.18–0.99 (21H, m);
^{13}C-NMR ($CDCl_3$) δ 199.5 (C), 175.5 (C), 137.9 (C), 128.1 (CH), 127.5 (CH), 127.4 (CH), 87.6 (CH), 79.1 (C), 72.6 (CH_2), 65.2 (CH_2), 62.8 (CH_2), 58.2 (CH), 51.8 (CH_2), 43.7 (CH), 37.3 (CH_2), 17.8 (CH_3), 11.6 (CH);
HRMS (ESI) calcd for $C_{26}H_{39}NNaO_4SSi$ ($[M+Na]^+$) 512.2261, found 512.2277.

(2a*S*,2a^1*R*,4*S*,7a*R*)-4-((Benzyloxy)methyl)-2a^1-(((triisopropylsilyl)oxy)methyl)hexahydrofuro[2,3,4-*gh*]pyrrolizin-1(2a*H*)-one (24)

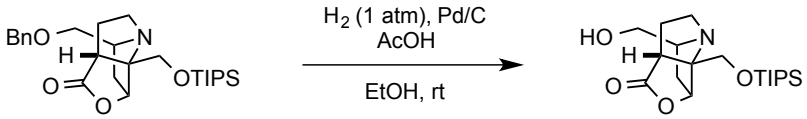


S4 **24**

A 100-mL, one-necked round-bottomed flask equipped with a three way cock and a magnetic stir bar was charged with **S4** (610 mg, 1.25 mmol) and Raney Ni (2.0 g) in EtOH (17 mL). After 4 h, the resulting slurry was filtered through Celite and washed with EtOH (30 mL) concentrated *in vacuo* to afford the crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 9/1 to 4/1) to afford **24** (530 mg, 1.15 mmol, 92%) as colorless oil. [EI10105]

R*f* = 0.50 (*n*-hexane/EtOAc = 2/1, UV, PMA);
$[\alpha]^{23}_{D}$ +0.457 (*c* = 1.06, $CHCl_3$);
IR (neat) 2943, 2865, 1773, 1463, 1361, 1196, 1119 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.42–7.26 (5H, m), 5.04 (1H, dd, *J* = 8.2, 4.6 Hz), 4.58 (1H, d, *J* = 12.4 Hz), 4.54 (1H, d, *J* = 12.4 Hz), 3.75 (1H, d, *J* = 10.1 Hz), 3.65 (1H, d, *J* = 10.1 Hz), 3.62 (1H, dd, *J* = 9.6, 7.8 Hz), 3.58–3.43 (2H, m), 3.08 (1H, d, *J* = 8.2 Hz), 2.96 (1H, dd, *J* = 9.2, 6.0 Hz), 2.61 (1H, ddd, *J* = 12.3, 9.2, 5.5 Hz), 2.39 (1H, ddd, *J* = 14.4, 8.2, 6.8 Hz), 2.28–2.11 (2H, m), 1.88 (1H, ddd, *J* = 14.4, 11.5, 4.6 Hz), 1.14–0.97 (21H, m);
^{13}C-NMR ($CDCl_3$) δ 179.2 (C), 137.6 (C), 128.3 (CH), 127.8 (CH), 127.7 (CH), 84.3 (CH), 81.7 (C), 73.3 (CH_2), 69.0 (CH_2), 64.4 (CH_2), 59.7 (CH), 47.3 (CH), 46.5 (CH_2), 34.9 (CH_2), 30.0 (CH_2), 17.8 (CH_3), 11.7 (CH);
HRMS (ESI) calcd for $C_{26}H_{41}NNaO_4Si$ ($[M+Na]^+$) 482.2697, found 482.2709.

(2a*S*,2a^1*R*,4*S*,7a*R*)-4-(Hydroxymethyl)-2a^1-(((triisopropylsilyl)oxy)methyl)hexahydrofuro[2,3,4-*gh*]pyrrolizin-1(2a*H*)-one (S5)

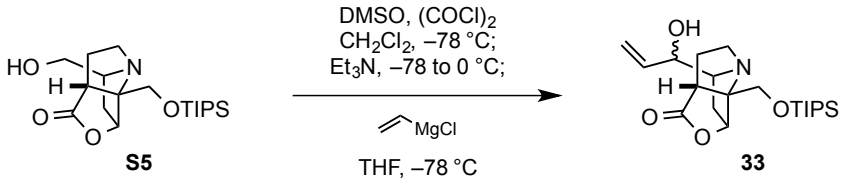


24 **S5**

A 50-mL, one-necked round-bottomed flask equipped with a three way cock and a magnetic stir bar was charged with **24** (586 mg, 1.27 mmol), AcOH (437 μL, 7.64 mmol) and Pd/C (542 mg, 0.510 mmol) in EtOH (8.5 mL). The suspension was stirred under H_2 atmosphere (balloon, 1 atm). After 5 h, the resulting solution was filtered through Celite and washed with EtOH (15 mL) concentrated *in vacuo* to afford the crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 2/1) to afford **S5** (392 mg, 1.06 mmol, 83%) as a slightly yellow solid. [EI10108]

R*f* = 0.21 (*n*-hexane/EtOAc = 1/3, UV, PMA);
M.p. 43.5–48.0 °C;
$[\alpha]^{24}_{D}$ +17.0 (*c* = 1.14, $CHCl_3$);
IR (neat) 2943, 2865, 1772, 1463, 1363, 1277, 1120 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 5.06 (1H, dd, *J* = 7.8, 4.6 Hz), 3.85 (1H, dd, *J* = 11.0, 8.7 Hz), 3.79 (1H, dd, *J* = 11.0, 4.8 Hz), 3.75 (1H, d, *J* = 10.1 Hz), 3.67 (1H, d, *J* = 10.1 Hz), 3.49–3.39 (1H, m), 3.09 (1H, d, *J* = 8.3 Hz), 3.03 (1H, dd, *J* = 9.2, 6.4 Hz), 2.66 (1H, ddd, *J* = 9.2, 5.8, 1.8 Hz), 2.40 (1H, ddd, *J* = 14.2, 7.8, 6.4 Hz), 2.28 (1H, dd, *J* = 12.8, 5.8 Hz), 2.23–2.13 (1H, m), 1.87 (1H, ddd, *J* = 14.2, 11.9, 4.6 Hz), 1.16–1.00 (21H, m);
^{13}C-NMR ($CDCl_3$) δ 179.2 (C), 84.5 (CH), 81.8 (C), 64.6 (CH_2), 62.3 (CH_2), 62.0 (CH), 47.4 (CH), 46.4 (CH_2), 34.4 (CH_2), 30.2 (CH_2), 17.9 (CH_3), 11.9 (CH);
HRMS (ESI) calcd for $C_{19}H_{35}NNaO_4Si$ ($[M+Na]^+$) 392.2228, found 392.2230.

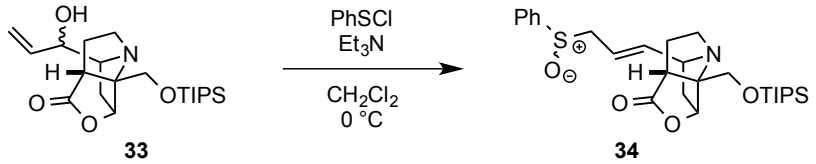
(2a*S*,2a^1*R*,4*S*,7a*R*)-4-(1-Hydroxyallyl)-2a^1-(((triisopropylsilyl)oxy)methyl)hexahydrofuro[2,3,4-*gh*]pyrrolizin-1(2a*H*)-one (33)



A 50-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with DMSO (273 μl, 3.85 mmol) in CH_2Cl_2 (7.7 mL). The clear solution was stirred at –78 °C for 5 min, then oxalyl chloride (234 μL) was added portionwise. After 30 min at the temperature, **S5** (569 mg, 1.54 mmol) in CH_2Cl_2 (7.7 mL) was added dropwise to the reaction mixture at –78 °C. After stirring for 40 min at –78 °C, Et_3N (1.07 mL, 7.69 mmol) was added. The solution was stirred at 0 °C for 30 min and –78 °C for 5 min, then vinyl magnesium chloride solution in THF (4.19 mL, 1.32 M, 5.54 mmol) was added at –78 °C. After stirring at –78 °C for 20 min, the reaction mixture was quenched with saturated NH_4Cl aq. (10 mL). The resulting mixture was partitioned between EtOAc (50 mL) and water (50 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (50 mL) twice. The combined organic phase was washed with brine (40 mL), dried over Na_2SO_4 (ca. 15 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 5/1 to 3/2) to afford **33** (540 mg, 1.36 mmol, 89%) as colorless oil. [EI10262]

R*f* = 0.33 (*n*-hexane/EtOAc = 1/3, UV, PMA);
$[\alpha]^{24}_{D}$ +4.13 (*c* = 0.975, $CHCl_3$);
IR (neat) 3445, 2943, 2866, 1772, 1685, 1462, 1363, 1278 cm^{-1};
^{1}H-NMR ($CDCl_3$) (5:1 mixture of two diastereomer) (***major***) δ 6.02 (1H, ddd, J = 16.5, 10.1, 6.4 Hz), 5.38 (1H, d, *J* = 16.5 Hz), 5.26 (1H, d, *J* = 10.1 Hz), 5.06–4.99 (1H, m), 4.31–4.20 (1H, m), 3.73 (1H, d, *J* = 10.1 Hz), 3.65 (1H, d, *J* = 10.1 Hz), 3.22–3.10 (1H, m), 3.05 (1H, d, *J* = 8.2 Hz), 3.01–2.90 (1H, m), 2.75–2.60 (1H, m), 2.55 (1H, dd, *J* = 13.8, 6.4 Hz), 2.24 (1H, dd, *J* = 12.8, 4.6 Hz), 2.18–2.04 (2H, m), 1.15–0.92 (21H, m); (***minor***) δ 5.80 (1H, ddd, *J* = 17.4, 10.0, 6.4 Hz), 5.38 (1H, d, *J* = 17.4 Hz), 5.22 (1H, d, *J* = 10.0 Hz), 5.07–4.98 (1H, m), 4.21 (1H, dd, *J* = 10.1, 6.4 Hz), 3.77 (1H, d, *J* = 10.1), 3.67 (1H, d, *J* = 10.1 Hz), 3.25–3.12 (2H, m), 3.08 (1H, d, *J* = 8.2 Hz), 2.75–2.63 (1H, m), 2.35–2.14 (3H, m), 1.87 (1H, ddd, *J* = 14.0, 11.9, 4.6 Hz), 1.15–0.92 (21H, m);
^{13}C-NMR ($CDCl_3$)
(***major*** and ***minor***) δ 179.3 (C), 179.1 (C), 139.4 (CH), 137.7 (CH), 117.1 (CH_2), 116.4 (CH_2), 84.6 (CH), 84.2 (CH), 81.8 (C), 81.5 (C), 73.5 (CH), 73.0 (CH), 65.1 (CH), 64.8 (CH), 64.9 (CH_2), 47.3 (CH), 47.1 (CH), 47.1 (CH_2), 46.5 (CH_2), 34.5 (CH_2), 34.2 (CH_2), 30.2 (CH_2), 29.9 (CH_2), 17.8 (CH_3), 11.7 (CH);
HRMS (ESI) calcd for $C_{21}H_{37}NNaO_4Si$ ([M+Na]$^+$) 418.2384, found 418.2384.

(2a*S*,2a^1*R*,4*S*,7a*R*)-4-((*E*)-3-(Phenylsulfinyl)prop-1-en-1-yl)-2a^1-(((triisopropylsilyl)oxy)methyl)hexahydrofuro[2,3,4-*gh*]pyrrolizin-1(2a*H*)-one (34)



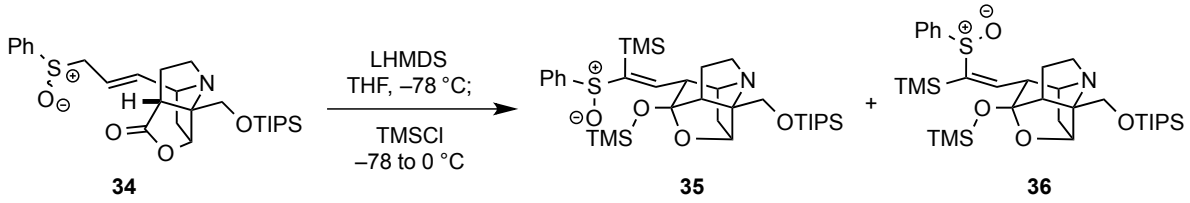
33 **34**

A 50-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **33** (175 mg, 0.442 mmol) in CH_2Cl_2 (8.9 mL). The solution was stirred at 0 °C for 5 min, then Et_3N (462 μL, 3.32 mmol) and phenylsulfenyl chloride (256 μL, 2.21 mmol)[1] was added. After stirring at 0 °C for 1 h, the reaction mixture was quenched with saturated NH_4Cl aq. (5 mL). The resulting mixture was partitioned between EtOAc (50 mL) and water (50 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (30 mL) twice. The combined organic phase was washed with brine (40 mL), dried over Na_2SO_4 (ca. 15 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 1/1 to 1/6 followed by EtOAc/MeOH = 9/1) to afford **34** (159 mg, 0.325 mmol, 74%) as pale yellow liquid. [EI10121, EI10235]

R*f* = 0.26 (*n*-hexane/EtOAc = 1/3, UV, PMA);
$[\alpha]^{21}_D$ –12.0 (*c* = 0.950, $CHCl_3$);
IR (neat) 2943, 2865, 1771, 1463, 1443, 1363, 1277, 1197, 1119 cm^{-1};
^{1}H-NMR ($CDCl_3$) (3:2 mixture of two diastereomer) (***major***) δ 7.61–7.46 (5H, m), 5.68 (1H, dd, *J* = 15.1, 6.9 Hz), 5.63–5.48 (1H, m), 4.98 (1H, ddd, *J* = 7.8, 4.5, 4.1 Hz), 3.79–3.70 (1H, m), 3.68 (1H, d, *J* = 10.1 Hz), 3.62 (1H, d, *J* = 10.1 Hz), 3.65–3.55 (1H, m), 3.48 (1H, dd, *J* = 12.8, 7.4 Hz), 3.06 (1H, d, *J* = 7.8 Hz), 2.81–2.69 (1H, m), 2.51–2.29 (2H, m), 2.20–2.05 (2H, m), 2.01 (1H, ddd, *J* = 14.2, 10.1, 4.1 Hz), 1.15–0.95 (21H, m); (***minor***) δ 7.61–7.46 (5H, m), 5.63–5.48 (2H, m), 4.98 (1H, ddd, *J* = 7.8, 4.5, 4.1 Hz), 3.79–3.70 (1H, m), 3.68 (1H, d, *J* = 10.1 Hz), 3.62 (1H, d, *J* = 10.1 Hz), 3.65–3.55 (1H, m), 3.39 (1H, dd, *J* = 12.8, 6.9 Hz), 3.06 (1H, d, *J* = 7.8 Hz), 2.81–2.69 (1H, m), 2.51–2.29 (2H, m), 2.20–2.05 (2H, m), 1.90 (1H, ddd, *J* = 14.2, 10.1, 4.1 Hz), 1.15–0.95 (21H, m);
^{13}C-NMR ($CDCl_3$) (***major*** and ***minor***) δ 179.1 (C), 142.8 (C), 142.5 (C), 137.0 (CH), 136.7 (CH), 131.1 (CH), 131.0 (CH), 129.1 (CH), 129.0 (CH), 124.2 (CH), 121.0 (CH), 120.8 (CH), 84.3 (CH), 81.7 (C), 81.6 (C), 64.9 (CH_2), 62.0 (CH), 61.9 (CH), 59.5 (C H_2), 58.9 (CH_2), 47.8 (CH_2), 47.7 (CH_2), 47.3 (CH), 37.0 (CH_2), 36.9 (CH_2), 30.4 (CH_2), 30.3 (CH_2), 17.9 (CH_3), 11.8 (CH);
HRMS (ESI) calcd for $C_{19}H_{28}N_2NaO_6Si$ ([M+Na]$^+$) 431.1609, found 431.1611.

(2*S*,2a*R*,2a^1*R*,6*S*,7a*S*,8*R*)-8-((*E*)-2-(Phenylsulfinyl)-2-(trimethylsilyl)vinyl)-2a^1-(((triisopropylsilyl)oxy)methyl)-2-((trimethylsilyl)oxy)octahydro-2,6-methanofuro[2,3,4-*gh*]pyrrolizine (35)

(2*S*,2a*R*,2a^1*R*,6*S*,7a*S*,8*R*)-8-((*Z*)-2-(Phenylsulfinyl)-2-(trimethylsilyl)vinyl)-2a^1-(((triisopropylsilyl)oxy)methyl)-2-((trimethylsilyl)oxy)octahydro-2,6-methanofuro[2,3,4-*gh*]pyrrolizine (36)



34 **35** **36**

A 25-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **34** (90.3 mg, 0.186 mmol) in THF (1.9 mL). The clear solution was stirred at –78 °C for 5 min, then LHMDS (715 μL, 1.3 M, 0.929 mmol) was added at the temperature. After stirring for 1 h, TMSCl (122 μL, 0.967 mmol) was added. The solution was slowly warmed to 0 °C over 1.5 h, and the reaction mixture was quenched with saturated NH_4Cl aq. (3 mL). The resulting mixture was partitioned between EtOAc (15 mL) and water (15 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (5 mL) twice. The combined organic phase was washed with brine (5 mL), dried over Na_2SO_4 (ca. 3 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 9/1 to 2/1) to afford **35** (71.9 mg, 0.111 mmol, 60%) as pale yellow solid and **36** (36.2 mg, 0.0559 mmol, 30%) as pale yellow foam. [EI10126, EI10236]

35:

R*f* = 0.62 (*n*-hexane/EtOAc = 1/2, UV, PMA);

M.p. 87 °C (decomp.);

$[\alpha]^{22}_{D}$ +55.5 (*c* = 0.945, $CHCl_3$);

IR (neat) 2947, 2894, 2866, 1584, 1464, 1336, 1250, 1223 cm^{-1};

^{1}H-NMR ($CDCl_3$) δ 7.69-7.62 (2H, m), 7.48-7.43 (3H, m), 7.39 (1H, d, *J* = 11.0 Hz), 4.55–4.50 (1H, m), 3.75 (1H, d, *J* = 10.1 Hz), 3.71 (1H, d, *J* = 10.1 Hz), 3.24–3.10 (2H, m), 3.10–2.96 (1H, m), 3.01 (1H, dd, *J* = 10.8, 3.4 Hz), 2.67 (1H, d, *J* = 6.4 Hz), 2.23 (1H, d, *J* = 11.9 Hz), 2.07–1.92 (1H, m), 1.92–1.82 (1H, m), 1.70–1.58 (1H, m), 1.18–1.01 (21H, m), 0.20 (9H, s), 0.05 (9H, s);

^{13}C-NMR ($CDCl_3$) δ 146.2 (C), 145.5 (C), 144.2 (CH), 131.2 (CH), 129.0 (CH), 127.7 (CH), 107.0 (C), 82.7 (C), 78.9 (CH), 65.8 (CH), 63.1 (CH_2), 53.4 (CH), 48.9 (CH_2), 44.4 (CH), 33.3 (CH_2), 26.9 (CH_2), 18.0 (CH_3), 11.9 (CH), 1.92 (CH_3), 0.11 (CH_3);

HRMS (ESI) calcd for $C_{33}H_{57}NNaO_4SSi_3$ ($[M+Na]^+$) 670.3208, found 670.3183.

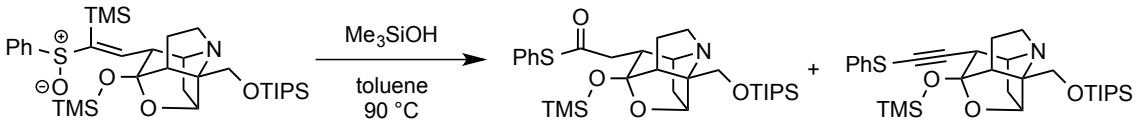
36:

R*f* = 0.72 (*n*-hexane/EtOAc = 1/2, UV, PMA);

$[\alpha]^{22}_{D}$ +48.4 (c = 0.745, $CHCl_3$);
IR (neat) 2946, 2894, 2864, 1469, 1456, 1250 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.60–7.52 (2H, m), 7.50–7.39 (3H, m), 6.88 (1H, d, J = 8.2 Hz), 4.54–4.47 (1H, m), 3.70 (1H, d, J = 10.3 Hz), 3.66 (1H, d, J = 10.3 Hz), 3.56 (1H, dd, J = 8.2, 3.6 Hz), 3.25–3.17 (1H, m), 3.13–3.00 (2H, m), 2.60 (1H, dd, J = 3.7, 3.2 Hz), 1.96–1.80 (2H, m), 1.69–1.61 (1H, m), 1.18–1.01 (21H, m), 0.18 (9H, s), 0.00 (9H, s);
^{13}C-NMR ($CDCl_3$) δ 151.0 (CH), 148.8 (C), 144.6 (C), 130.0 (CH), 129.1 (CH), 129.0 (CH), 106.9 (C), 82.8 (C), 78.6 (CH), 67.2 (CH), 62.8 (CH_2), 53.0 (CH), 48.7 (CH_2), 43.2 (CH), 33.6 (CH_2), 26.5 (CH_2), 18.0 (CH_3), 11.9 (CH), 1.80 (CH_3), 0.11 (CH_3);
HRMS (ESI) calcd for $C_{33}H_{57}NNaO_4SSi_3$ ([M+Na]$^+$) 670.3208, found 670.3195.

_S_-Phenyl 2-((2_S_,2a_R_,2a^1_R_,6_S_,7a_S_,8_R_)-2a^1-(((triisopropylsilyl)oxy)methyl)-2-((trimethylsilyl)oxy)octahydro-2,6-methanofuro[2,3,4-_gh_]pyrrolizin-8-yl)ethanethioate (38)

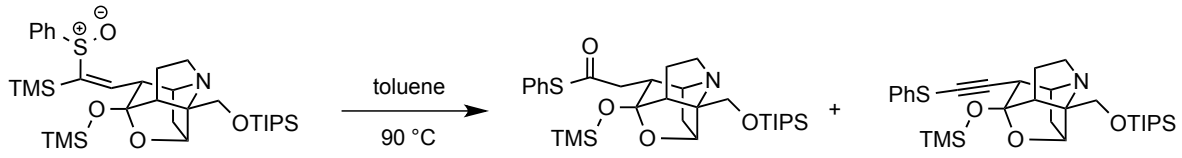
From 35:



35 **38** **39**

A 100-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **35** (169 mg, 0.261 mmol) and Me_3SiOH (1.16 mL, 10.4 mmol) in toluene (20 mL). The clear solution was stirred at 90 °C for 5 h. The reaction mixture was concentrated *in vacuo* to afford the crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 10/1 to 2/1) to afford **38** (108 mg, 0.188 mmol, 72%) as white solid and **39** (14.0 mg, 0.0251 mmol, 9.6%) as colorless foam. [EI10131, EI10233, EI10272]

From 36:



36 **38** **39**

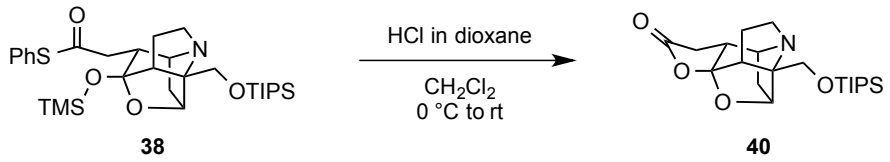
A 50-mL, one-necked round-bottomed flask equipped with a rubber septum and a magnetic stir bar was charged with **36** (88.5 mg, 0.137 mmol) in toluene (13 mL). The clear solution

was stirred at 90 °C for 5 h. The reaction mixture was concentrated *in vacuo* to afford the crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 10/1 to 2/1) to afford **38** (37.8 mg, 0.0656 mmol, 48%) as white solid and **39** (26.6 mg, 0.0478 mmol, 35%) as colorless foam. [EI10253, EI10273]

38 :
R*f* = 0.59 (*n*-hexane/EtOAc = 1/1, UV, PMA);
M.p. 67.3–71.3 °C;
$[\alpha]^{22}_{D}$ –3.59 (*c* = 1.00, $CHCl_3$);
IR (neat) 2945, 2890, 2866, 1710, 1464, 1250, 1225, 1100 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.47–7.38 (5H, m), 4.44–4.39 (1H, m), 3.68 (1H, d, *J* = 10.1 Hz), 3.65 (1H, d, *J* = 10.1 Hz), 3.25–3.19 (1H, m), 3.11 (1H, dd, *J* = 16.0, 5.0 Hz), 3.08–3.01 (2H, m), 2.62 (1H, dd, *J* = 3.7, 3.7 Hz), 2.53 (1H, dd, *J* = 16.0, 7.3 Hz), 2.49–2.43 (1H, m), 1.97–1.87 (3H, m), 1.63–1.54 (1H, m), 1.17–1.01 (21H, m), 0.17 (9H, s);
^{13}C-NMR ($CDCl_3$) δ 196.9 (C), 134.4 (CH), 129.3 (CH), 129.1 (CH), 128.0 (C), 106.7 (C), 82.6 (C), 78.5 (CH), 64.2 (CH), 62.7 (CH_2), 52.9 (CH), 48.7 (CH_2), 40.9 (CH_2), 38.1 (CH), 33.1 (CH_2), 26.8 (CH_2), 18.0 (CH_3), 11.9 (CH), 1.78 (CH_3);
HRMS (ESI) calcd for $C_{30}H_{49}NNaO_4SSi_2$ ($[M+Na]^+$) 598.2813, found 598.2822.

39 :
R*f* = 0.80 (*n*-hexane/EtOAc = 1/1, UV, Ce-PMA);
$[\alpha]^{21}_{D}$ –2.85 (*c* = 0.350, $CHCl_3$);
IR (neat) 2945, 2890, 2866, 1583, 1460, 1478, 1250, 1227 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 7.43 (2H, dd, *J* = 8.2, 7.4 Hz), 7.31 (2H, dd, *J* = 8.2, 7.3 Hz), 7.19 (1H, dd, *J* = 7.4, 7.3 Hz), 4.50–4.46 (1H, m), 3.71 (1H, d, *J* = 10.5 Hz), 3.67 (1H, d, *J* = 10.5 Hz), 3.45–3.40 (1H, m), 3.19–3.04 (1H, m), 3.04–2.93 (2H, m), 2.60 (1H, d, *J* = 6.0 Hz), 2.32 (1H, d, *J* = 11.9 Hz), 2.00–1.84 (2H, m), 1.71–1.60 (1H, m), 1.14–0.98 (21H, m), 0.18 (9H, s);
^{13}C-NMR ($CDCl_3$) δ 133.6 (C), 129.0 (CH), 126.0 (CH), 125.9 (CH), 106.2 (C), 98.1 (C), 82.6 (C), 78.9 (CH), 65.3 (CH), 63.0 (CH_2), 53.7 (CH), 48.8 (CH_2), 38.7 (CH), 34.6 (CH_2), 26.7 (CH_2), 18.0 (CH_3), 11.9 (CH), 1.77 (CH_3);
HRMS (ESI) calcd for $C_{30}H_{47}NNaO_3SSi_2$ ($M+Na^+$) 580.2707, found 580.2700.

(1*S*,5*R*,6*S*,8*S*,9*R*,13*R*)-9-(((Triisopropylsilyl)oxy)methyl)-2,14-dioxa-10-azapentacyclo[6.5.1.$0^{1,5}$.$0^{6,10}$.$0^{9,13}$]tetradecan-3-one (40)

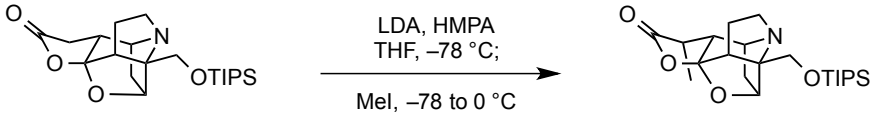


38 **40**

A 10-mL, screw cap glass test tube equipped with a magnetic stir bar was charged with **38** (12.1 mg, 0.0210 mmol) in CH_2Cl_2 (400 μL). The clear solution was stirred at 0 °C for 5 min, then HCl in dioxane (4 M, 105 μL, 0.420 mmol) was added at 0 °C. After stirring at room temperature overnight, the reaction mixture was quenched with saturated $NaHCO_3$ aq. (1 mL). The resulting mixture was partitioned between EtOAc (3 mL) and water (3 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (3 mL) twice. The combined organic phase was washed with brine (2 mL), dried over Na_2SO_4 (ca. 2 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 3/1) to afford **40** (6.0 mg, 0.0152 mmol, 73%) as colorless foam. [EI10240]

R*f* = 0.42 (EtOAc/MeOH = 8/1, UV, Ce-PMA);
$[\alpha]^{21}_{D}$ +32.6 (*c* = 0.235, $CHCl_3$);
IR (neat) 2943, 2890, 2865, 1806, 1463, 1146, 1103 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 4.46–4.42 (1H, brs), 3.78 (1H, d, *J* = 10.8 Hz), 3.75 (1H, d, *J* = 10.8 Hz), 3.50–3.44 (1H, m), 3.22 (1H, ddd, *J* = 13.8, 10.6, 5.0 Hz), 3.07 (1H, ddd, *J* = 13.8, 8.2, 4.6 Hz), 2.94 (1H, d, *J* = 6.4 Hz), 2.64 (1H, dd, *J* = 17.9, 14.2 Hz), 2.46–2.37 (2H, m), 2.07–1.95 (2H, m), 1.87 (1H, ddd, *J* = 13.8, 8.2, 5.0 Hz), 1.80–1.73 (1H, m), 1.17-0.98 (21H, m);
^{13}C-NMR ($CDCl_3$) δ 175.3 (C), 111.3 (C), 84.0 (C), 77.5 (CH), 63.3 (CH_2), 62.0 (CH), 48.9 (CH_2), 48.1 (CH), 38.3 (CH), 32.1 (CH_2), 30.0 (CH_2), 27.0 (CH_2), 18.0 (CH_3), 11.9 (CH);
HRMS (ESI) calcd for $C_{21}H_{35}NNaO_4Si$ ($[M+Na]^+$) 416.5816, found 416.5820.

(1*S*,4*R*,5*R*,6*S*,8*S*,9*R*,13*R*)-9-(((Triisopropylsilyl)oxy)methyl)-4-methyl-2,14-dioxa-10-azapentacyclo[6.5.1.$0^{1,5}$.$0^{6,10}$.$0^{9,13}$]tetradecan-3-one (41)

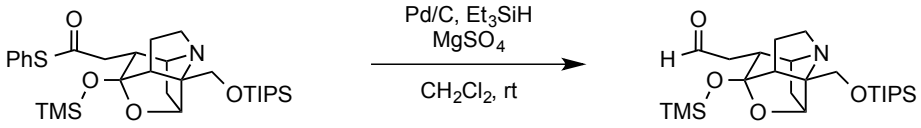


40 **41**

A 10-mL, screw cap glass test tube equipped with a rubber septum and a magnetic stir bar was charged with **40** (7.2 mg, 0.0183 mmol) and HMPA (3.2 μl, 0.0183 mmol) in THF (400 μL). The solution was stirred at –78 °C for 5 min, then freshly prepared LDA in THF (137 μL, 4.0 M, 0.458 mmol) was added. After the solution was stirred for 1 h at –78 °C, MeI (28.5 μL, 0.458 mmol) was added to the reaction mixture at –78 °C for 1 h. The solution was slowly warmed to 0 °C over 1 h. The reaction mixture was quenched with saturated NH_4Cl aq. (1 mL). The resulting mixture was partitioned between EtOAc (3 mL) and water (3 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (3 mL) twice. The combined organic phase was dried over Na_2SO_4 (ca. 3 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with preparative thin layer chromatography (*n*-hexane/EtOAc = 1/3) to afford **41** (4.9 mg, 0.0663 mmol, 66%) as slightly yellow oil. [EI10242]

R*f* = 0.13 (*n*-hexane/EtOAc = 1/3, UV, Ce-PMA);
$[\alpha]^{21}_{D}$ +24.5 (*c* = 0.245, $CHCl_3$);
IR (neat) 2943, 2891, 2865, 1800, 1734, 1464, 1337, 1269, 1221, 1111 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 4.52–4.48 (1H, m), 3.77 (1H, d, *J* = 10.6 Hz), 3.74 (1H, d, *J* = 10.6 Hz), 3.53–3.50 (1H, m), 3.19 (1H, ddd, *J* = 13.7, 10.1, 5.0 Hz), 3.01 (1H, ddd, *J* = 13.7, 8.7, 4.6 Hz), 2.90 (1H, d, *J* = 6.4 Hz), 2.84–2.72 (1H, m), 2.40 (1H, d, *J* = 9.2, 3.7 Hz), 2.15 (1H, d, *J* = 12.4 Hz), 2.06–1.93 (1H, m), 1.88–1.72 (2H, m), 1.48 (3H, d, *J* = 7.6 Hz), 1.18–0.99 (21H, m);
^{13}C-NMR ($CDCl_3$) δ 179.2 (C), 111.5 (C), 83.9 (C), 77.6 (CH), 63.2 (CH_2), 61.9 (CH), 48.7 (CH_2), 48.1 (CH), 39.2 (CH), 36.5 (CH), 33.9 (CH_2), 27.3 (CH_2), 18.0 (CH_3), 15.3 (CH_3), 11.9 (CH);
HRMS (ESI) calcd for $C_{22}H_{37}NNaO_4Si$ ($[M+Na]^+$) 430.2384, found 430.2379.

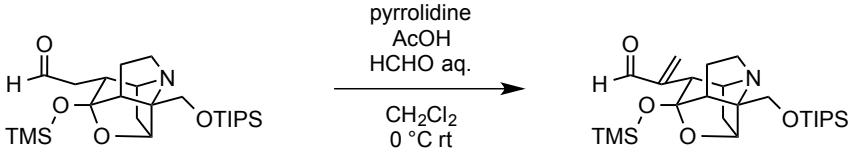
2-((2*S*,2a*R*,2a^1*R*,5*R*,6*S*,8*R*)-2a^1-(((Triisopropylsilyl)oxy)methyl)-2-((trimethylsilyl)oxy)octahydro-2,6-methanofuro[2,3,4-*gh*]pyrrolizin-8-yl)acetaldehyde (42)



A 10-mL, screw cap glass test tube equipped with a magnetic stir bar was charged with **38** (42.0 mg, 0.0729 mmol) and $MgSO_4$ (170 mg) in CH_2Cl_2 (1.5 mL). The suspension was stirred at room temperature for 5 min, then triethylsilane (70.6 μL, 0.437 mmol) and Pd/C (31.0 mg, 0.0292 mmol) was added. After stirring overnight, the reaction was filtered through Celite, washed with EtOAc (5 mL) and the solvent was evaporated *in vacuo* to give the crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 2/1 to 0/1) to afford **42** (31.0 mg, 0.0663 mmol, 91%) as colorless oil. [EI10256]

R*f* = 0.13 (*n*-hexane/EtOAc = 1/3, UV, Ce-PMA);
$[\alpha]^{24}_{D} = -11.1$ ($c = 0.270$, $CHCl_3$);
IR (neat) 2944, 2892, 2866, 1727, 1464, 1251, 1224, 1068 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 9.76 (1H, dd, J = 2.3, 1.4 Hz), 4.44–4.38 (1H, m), 3.69 (1H, d, J = 10.1 Hz), 3.66 (1H, d, J = 10.1 Hz), 3.22–3.14 (1H, m), 3.14–3.05 (2H, m), 2.83 (1H, ddd, J = 10.5, 7.9, 2.3 Hz), 2.62 (1H, dd, J = 5.0, 1.8 Hz), 2.45–2.39 (1H, m), 2.10 (1H, ddd, J = 5.5, 4.6, 1.4 Hz), 2.00–1.88 (2H, m), 1.85 (1H, d, J = 12.4 Hz), 1.62–1.52 (1H, m), 1.18–1.00 (21H, m), 0.12 (3H, s);
^{13}C-NMR ($CDCl_3$) δ 202.1 (C), 106.6 (C), 82.6 (C), 78.5 (CH), 64.8 (CH), 62.7 (CH_2), 52.6 (CH), 48.7 (CH_2), 41.1 (CH_2), 36.6 (CH), 33.1 (CH_2), 26.8 (CH_2), 18.0 (CH_3), 11.9 (CH), 1.61 (CH_3);
HRMS (ESI) calcd for $C_{24}H_{45}NNaO_4Si_2$ ($[M+Na]^+$) 490.2779, found 490.2777.

2-((2*S*,2a*R*,2a^1*R*,5*R*,6*S*,8*R*)-2a^1-(((Triisopropylsilyl)oxy)methyl)-2-((trimethylsilyl)oxy)octahydro-2,6-methanofuro[2,3,4-*gh*]pyrrolizin-8-yl)acrylaldehyde (S6)

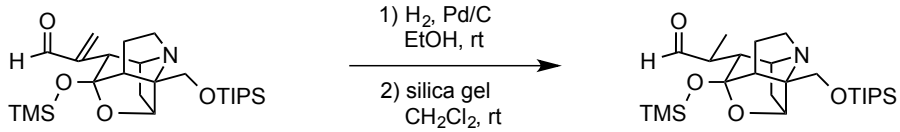


42 **S6**

A 10-mL, screw cap glass test tube equipped with a magnetic stir bar was charged with **42** (30.0 mg, 0.0641 mmol) in CH_2Cl_2 (3.0 mL). The solution was stirred at 0 °C for 5 min and HCHO aq. (26.0 μL, 0.321 mmol), pyrrolidine (10.5 μL, 0.128 mmol) and acetic acid (7.3 μL, 0.128 mmol) was added. After stirring at room temperature overnight, the reaction mixture was quenched with saturated NH_4Cl aq. (1 mL). The resulting mixture was partitioned between EtOAc (3 mL) and water (3 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (3 mL) twice. The combined organic phase was dried over Na_2SO_4 (ca. 1 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with preparative thin layer chromatography (*n*-hexane/EtOAc = 1/3) to afford **S6** (19.2 mg, 0.0400 mmol, 62%) as colorless oil. [EI10259]

R*f* = 0.74 (*n*-hexane/EtOAc = 1/3, UV, Ce-PMA);
$[\alpha]^{24}_{D}$ –39.8 (*c* = 0.950, $CHCl_3$);
IR (neat) 2944, 2892, 2866, 1718, 1691, 1464, 1360, 1251, 1176 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 9.43 (1H, s), 7.01 (1H, s), 6.29 (1H, s), 4.48–4.43 (1H, m), 3.71 (1H, d, *J* = 10.1 Hz), 3.67 (1H, d, *J* = 10.1 Hz), 3.26–3.01 (4H, m), 2.65 (1H, dd, *J* = 5.0, 1.8 Hz), 1.98–1.89 (2H, m), 1.87 (1H, d, *J* = 11.9 Hz), 1.54–1.47 (1H, m), 1.17–1.01 (21H, m), 0.13 (9H, s);
^{13}C-NMR ($CDCl_3$) δ 195.4 (C), 146.3 (C), 139.9 (CH_2), 106.8 (C), 82.9 (C), 78.6 (CH), 64.0 (CH), 62.9 (CH_2), 53.6 (CH), 48.8 (CH_2), 39.0 (CH), 32.7 (CH_2), 26.8 (CH_2), 18.0 (CH_3), 11.9 (CH), 1.80 (CH_3);
HRMS (ESI) calcd for $C_{25}H_{45}NNaO_4Si_2$ ([M+Na]$^+$) 502.2779, found 502.2772.

(2*S*)-2-((2*S*,2a*R*,2a^1*R*,5*R*,6*S*,8*R*)-2a^1-(((Triisopropylsilyl)oxy)methyl)-2-((trimethylsilyl)oxy)octahydro-2,6-methanofuro[2,3,4-*gh*]pyrrolizin-8-yl)propanal (43)



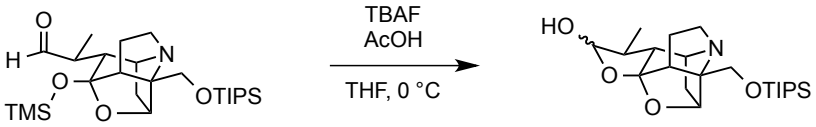
S6 **43**

A 10-mL, screw cap glass test tube equipped with a magnetic stir bar was charged with **S6** (18.3 mg, 0.0381 mmol) and Pd/C (8.1 mg, 7.63×10^{-3} mmol) in EtOH (400 μL). The suspension was stirred under H_2 atmosphere (balloon, 1 atm). After 4 h, the resulting solution was filtered through Celite and concentrated *in vacuo* to afford the crude product, which was used for the next reaction without further purification.

A 10-mL, screw test tube equipped with a magnetic stir bar was charged with the crude product (18.0 mg) in CH_2Cl_2 (500 μL). The solution was added silica gel (10.0 mg) at room temperature. After stirring overnight, the reaction was filtered through Celite and the solvent was evaporated *in vacuo* to give the crude product. The residue was purified with flash column chromatography on silica gel (*n*-hexane/EtOAc = 1/3) to afford **43** (13.1 mg, 0.0272 mmol, 71%) as colorless oil. [EI10263, EI10264, EI10277]

R*f* = 0.20 (*n*-hexane/EtOAc = 1/1, UV, Ce-PMA);
$[\alpha]^{23}_{D}$ –24.5 (*c* = 0.650, $CHCl_3$);
IR (neat) 2946, 2892, 2866, 1725, 1463, 1251, 1224, 1098 cm^{-1};
^{1}H-NMR ($CDCl_3$): δ 9.58 (1H, d, *J* = 3.6 Hz), 4.42–4.38 (1H, m), 3.70 (1H, d, *J* = 10.1 Hz), 3.67 (1H, d, *J* = 10.1 Hz), 3.24–3.19 (1H, m), 3.14–2.95 (2H, m), 2.71–2.62 (1H, m), 2.60 (1H, d, *J* = 6.0 Hz), 2.10 (1H, dd, *J* = 10.6, 3.7 Hz), 1.96–1.83 (2H, m), 1.83 (1H, d, *J* = 11.9 Hz), 1.64–1.56 (1H, m), 1.15–1.02 (21H, m), 0.97 (3H, d, *J* = 7.4 Hz), 0.12 (9H, s);
^{13}C-NMR ($CDCl_3$) δ 204.1 (CH), 107.0 (C), 82.6 (C), 78.4 (CH), 62.9 (CH_2), 62.6 (CH), 52.4 (CH), 48.7 (CH_2), 43.1 (CH), 42.0 (CH), 33.3 (CH_2), 26.8 (CH_2), 18.0 (CH_3), 11.9 (CH), 11.9 (CH_3), 1.56 (CH_3);
HRMS (ESI) calcd for $C_{25}H_{47}NNaO_4Si_2$ ($[M+Na]^+$) 504.2936, found 504.2944.

(1*S*,4*S*,5*R*,6*S*,8*S*,9*R*,13*R*)-9-(((Triisopropylsilyl)oxy)methyl)-4-methyl-2,14-dioxa-10-azapentacyclo[6.5.1.$0^{1,5}$.$0^{6,10}$.$0^{9,13}$]tetradecan-3-ol (44)

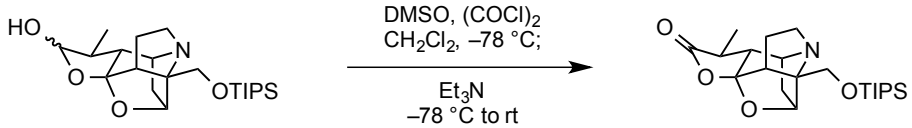


43 **44**

A 10-mL, screw cap glass test tube equipped with a magnetic stir bar was charged with **43** (6.9 mg) in THF (0.5 mL). The solution was stirred at 0 °C for 5 min and AcOH (2.1 μL, 0.0358 mmol) and TBAF (70% in THF, 13.4 μL, 0.0358 mmol) was added. After stirring for 1 h at 0 °C, the reaction mixture was quenched with saturated NH_4Cl aq. (1 mL). The resulting mixture was partitioned between EtOAc (3 mL) and water (3 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (3 mL) twice. The combined organic phase was dried over Na_2SO_4 (ca. 2 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with preparative thin layer chromatography (*n*-hexane/EtOAc = 1/3) to afford **44** (4.3 mg, 0.0105 mmol, 73%) as colorless oil. [EI10268, EI10278]

R*f* = 0.14 (EtOAc only, UV, Ce-PMA);
$[\alpha]^{21}_{D}$ –9.81 (*c* = 0.300, $CHCl_3$);
IR (neat) 2942, 2891, 2866, 1724, 1463, 1248, 1103 cm^{-1};
^{1}H-NMR ($CDCl_3$) (5:2 mixture of two diastereomer) (***major***) δ 5.03 (1H, d, *J* = 5.0 Hz), 4.39–4.35 (1H, m), 3.79 (2H, s), 3.45–3.40 (1H, m), 3.25–3.15 (1H, m), 3.09–2.97 (1H, m), 2.76 (1H, d, *J* = 6.0 Hz), 2.24–2.13 (1H, m), 2.06–1.61 (5H, m), 1.32–0.95 (24H, m); (***minor***) δ 5.50 (1H, d, *J* = 5.5 Hz), 4.30–4.28 (1H, m), 3.81 (2H, s), 3.51–3.47 (1H, m), 3.25–3.15 (1H, m), 3.09–2.97 (1H, m), 2.76 (1H, d, *J* = 6.0 Hz), 2.50–2.39 (1H, m), 2.06–1.61 (5H, m), 1.32–0.95 (24H, m);
^{13}C-NMR ($CDCl_3$) (***major*** and ***minor***) δ 112.4 (C), 108.3 (CH), 101.1 (CH), 83.1 (C), 77.7 (CH), 63.5 (CH_2), 61.4 (CH), 48.9 (CH_2), 48.8 (CH_2), 48.6 (CH), 48.4 (CH), 47.7 (CH), 43.0 (CH), 41.6 (CH), 36.0 (CH), 33.0 (CH_2), 32.7 (CH_2), 27.1 (CH_2), 18.0 (C H_3), 15.0 (CH_3), 11.9 (CH), 11.0 (CH_3);
HRMS (ESI) calcd for $C_{22}H_{39}NNaO_4Si$ ($[M+Na]^+$) 432.2541, found 432.2540.

(1*S*,4*S*,5*R*,6*S*,8*S*,9*R*,13*R*)-9-(((Triisopropylsilyl)oxy)methyl)-4-methyl-2,14-dioxa-10-azapentacyclo[6.5.1.$0^{1,5}$.$0^{6,10}$.$0^{9,13}$]tetradecan-3-one (45)



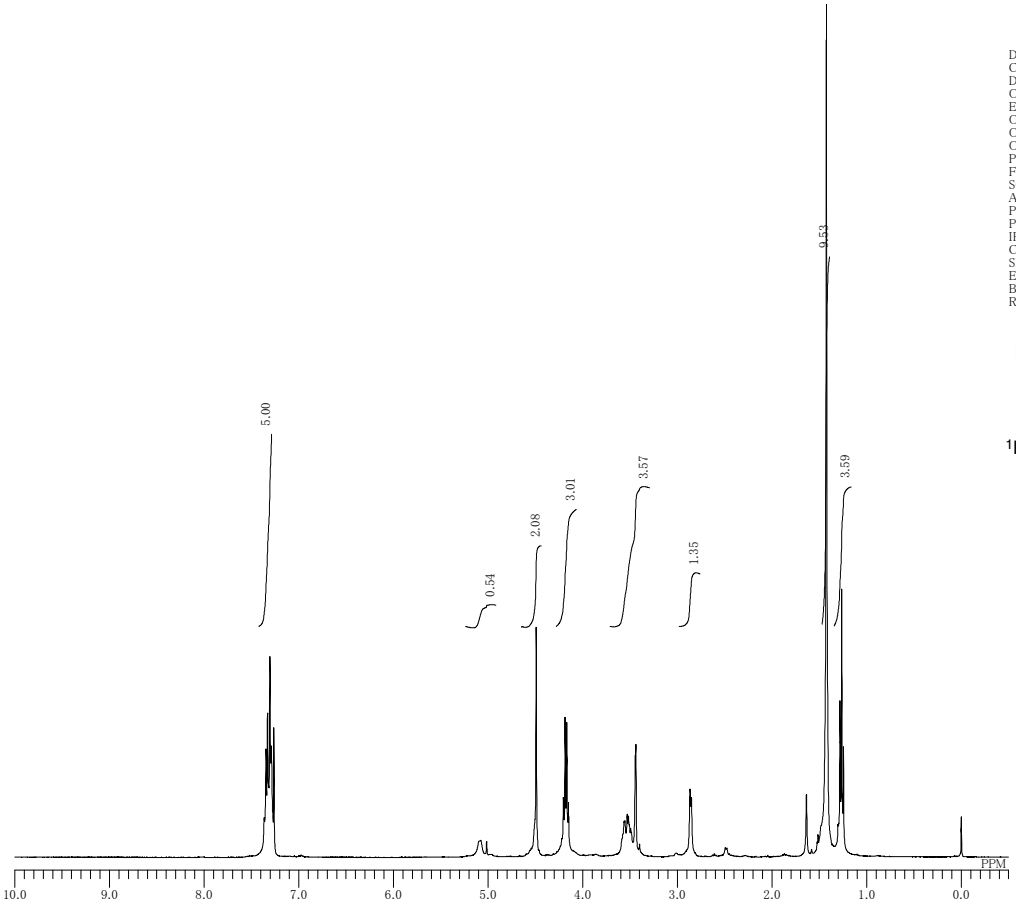
44 **45**

A 10-mL, screw cap glass test tube equipped with a magnetic stir bar was charged with DMSO (5.2 μL, 0.0732 mmol) in CH_2Cl_2 (300 μL). The clear solution was stirred at –78 °C for 5 min, then oxalyl chloride (3.7 μL) was added. After 30 min at the temperature, acetal **44** (4.3 mg, 0.0105 mmol) in CH_2Cl_2 (300 μL) was added dropwise to the reaction mixture at –78 °C. After stirring for 40 min at –78 °C, Et_3N (20.3 μL, 0.146 mmol) was added and reaction mixture was warmed to rt. After stirring at room temperature for 30 min, the reaction mixture was quenched with saturated NH_4Cl aq. (1 mL). The resulting mixture was partitioned between EtOAc (5 mL) and water (5 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (3 mL) twice. The combined organic phase was washed with brine (3 mL), dried over Na_2SO_4 (ca. 1 g), filtered and concentrated *in vacuo* to afford crude product. The residue was purified with preparative thin layer chromatography (*n*-hexane/EtOAc = 1/3) to afford **45** (3.7 mg, 0.00908 mmol, 86%) as colorless oil. [EI10270]

R*f* = 0.45 (EtOAc/MeOH = 8/1, UV, Ce-PMA);
$[\alpha]^{20}_{D}$ +8.65 (*c* = 0.175, $CHCl_3$);
IR (neat) 2943, 2891, 2866, 1801, 1463, 1273 cm^{-1};
^{1}H-NMR ($CDCl_3$) δ 4.47–4.43 (1H, m), 3.78 (1H, d, *J* = 10.4 Hz), 3.74 (1H, d, *J* = 10.4 Hz), 3.47–3.40 (1H, m), 3.22 (1H, ddd, *J* = 13.7, 10.6, 5.3 Hz), 3.05 (1H, ddd, *J* = 13.7, 8.7, 4.6 Hz), 2.93 (1H, d, *J* = 6.4 Hz), 2.06–1.93 (3H, m), 1.84 (1H, ddd, *J* = 14.2, 8.7, 5.3 Hz), 1.82–1.77 (1H, m), 1.27 (3H, d, *J* = 7.3 Hz), 1.17–1.01 (21H, m);
^{13}C-NMR ($CDCl_3$) δ 178.2 (C), 109.4 (C), 84.1 (C), 77.6 (CH), 63.3 (CH_2), 61.5 (CH), 48.9 (CH_2), 48.1 (CH), 45.7 (CH), 35.8 (CH), 32.3 (CH_2), 27.0 (CH_2), 18.0 (CH_3), 13.3 (CH_3), 11.9 (CH);
HRMS (ESI) calcd for $C_{22}H_{37}NNaO_4Si$ ($[M+Na]^+$) 430.2384, found 430.2390.

References

1. Barrett, A. G. M.; Dhanak, D.; Graboski, G. G.; Taylor, S. J. *Org. Synth.* **1993**, *68*, 8.



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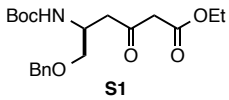
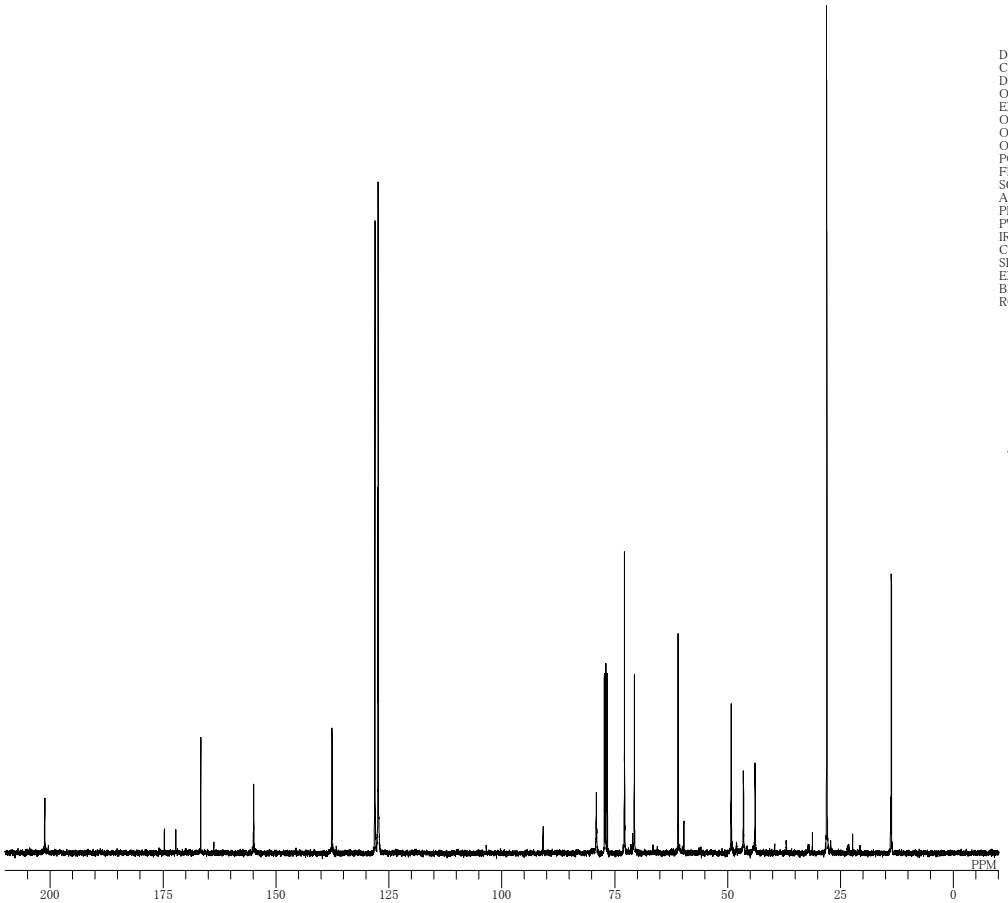


S1

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



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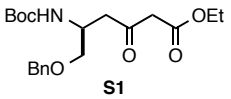
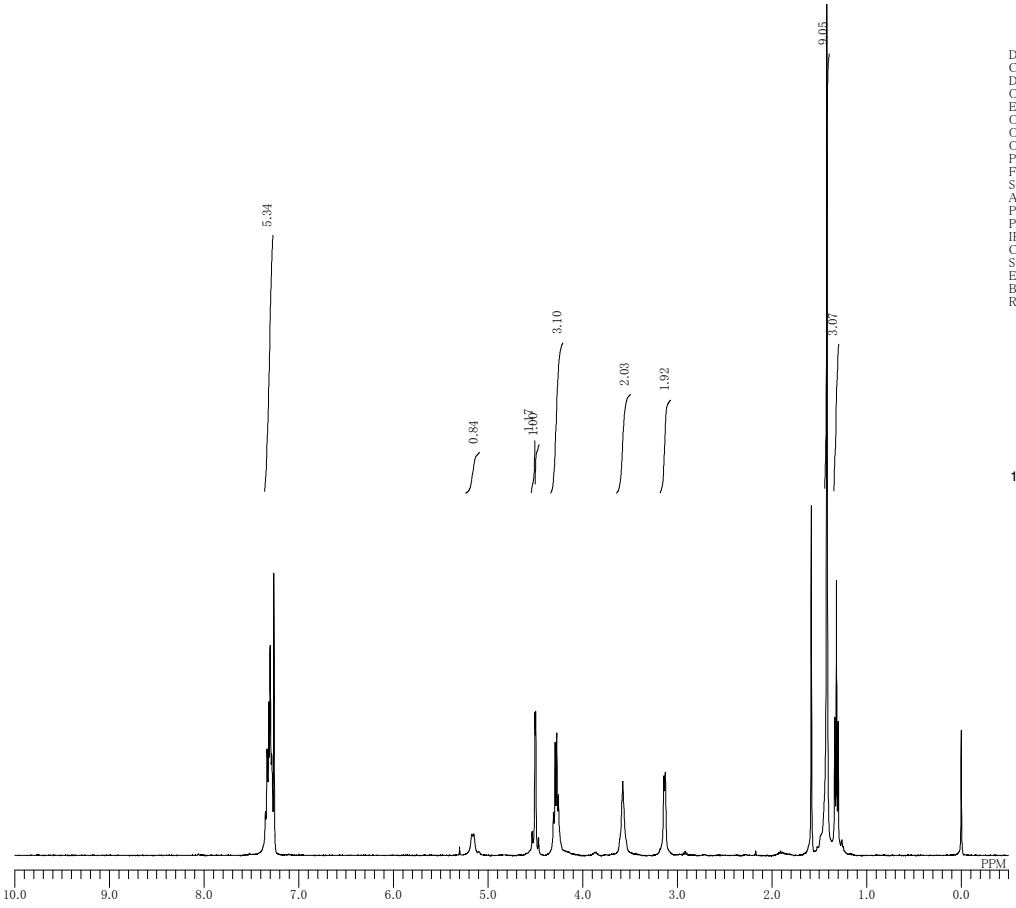


S1

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



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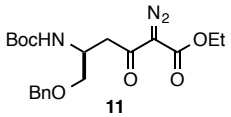
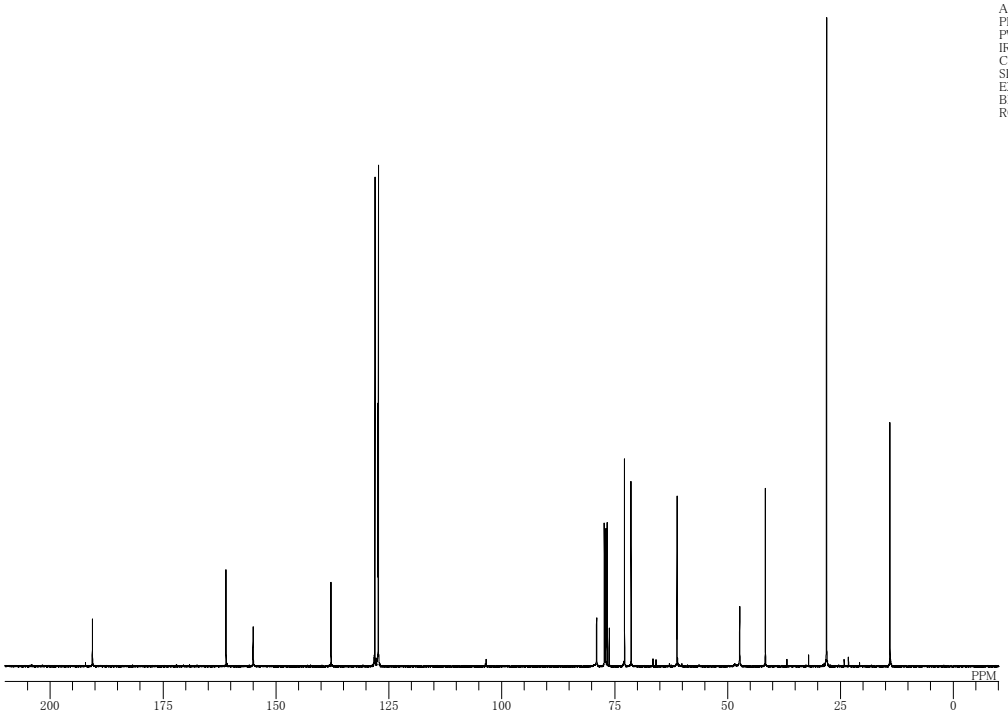


11

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



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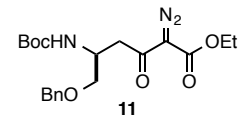
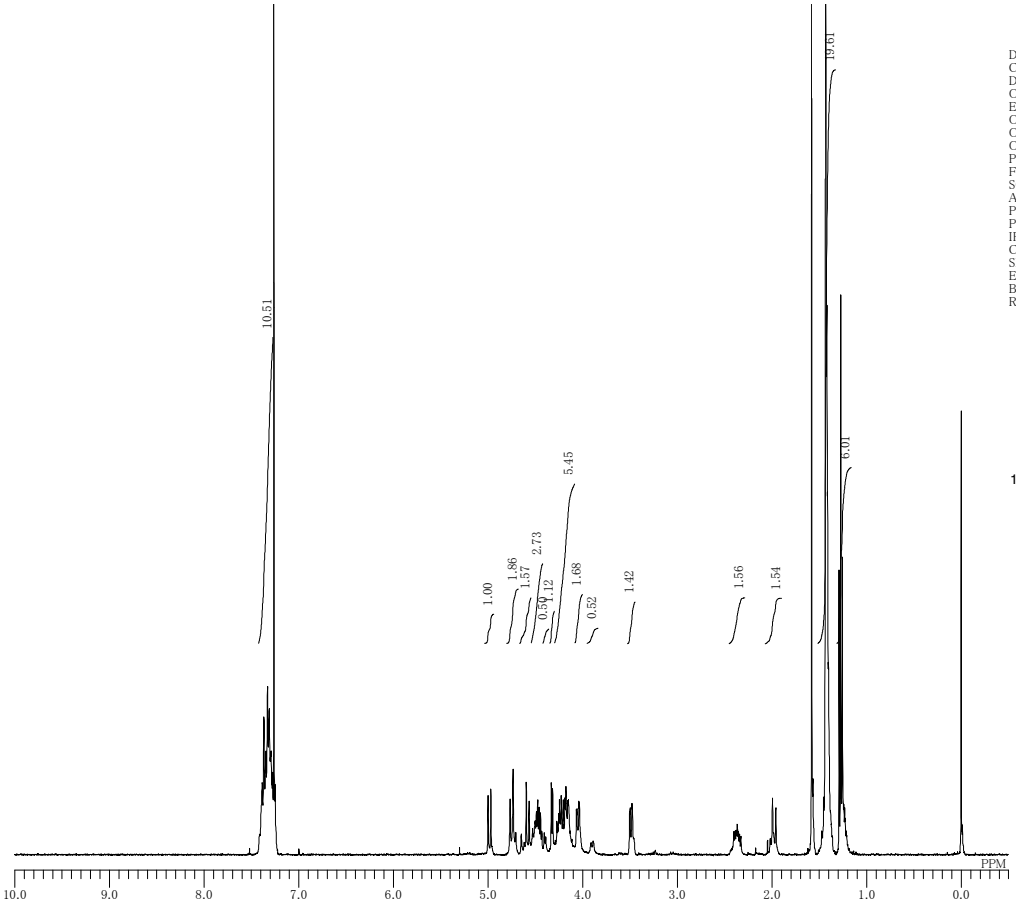
RGAIN 50



11

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



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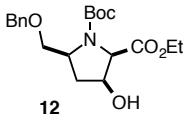
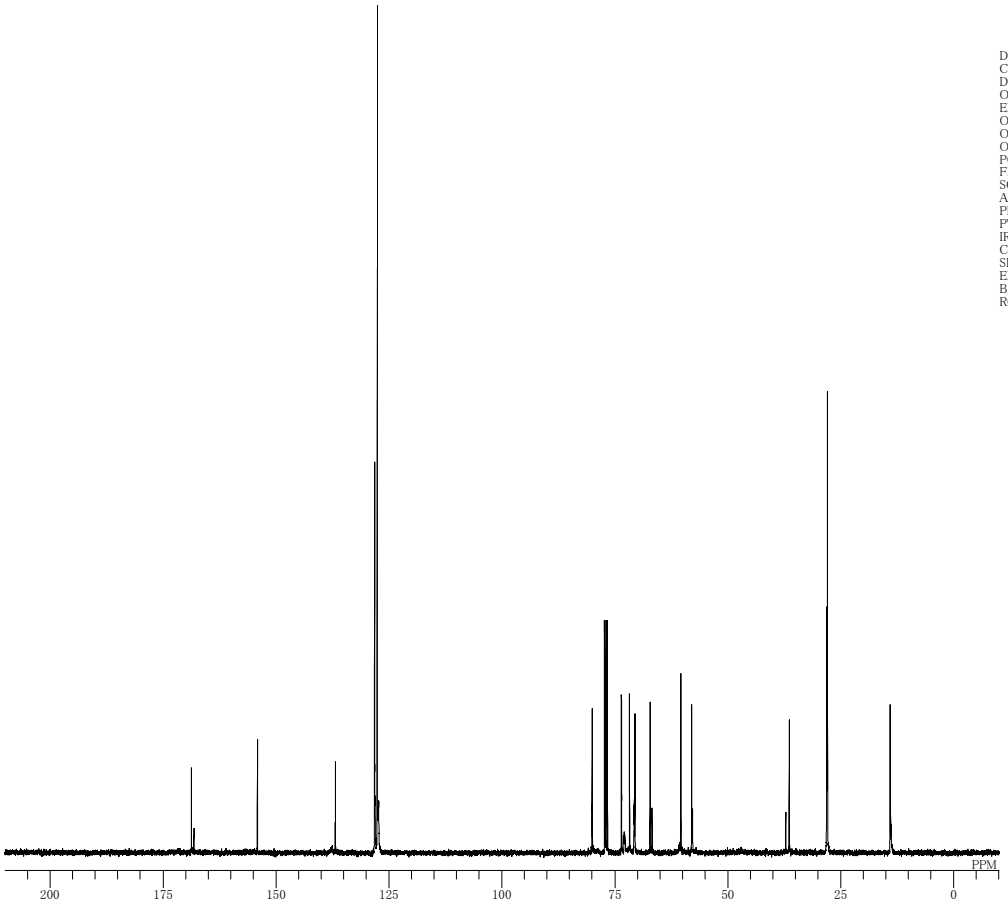
RGAIN 46



12

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



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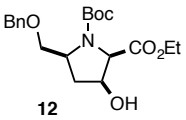
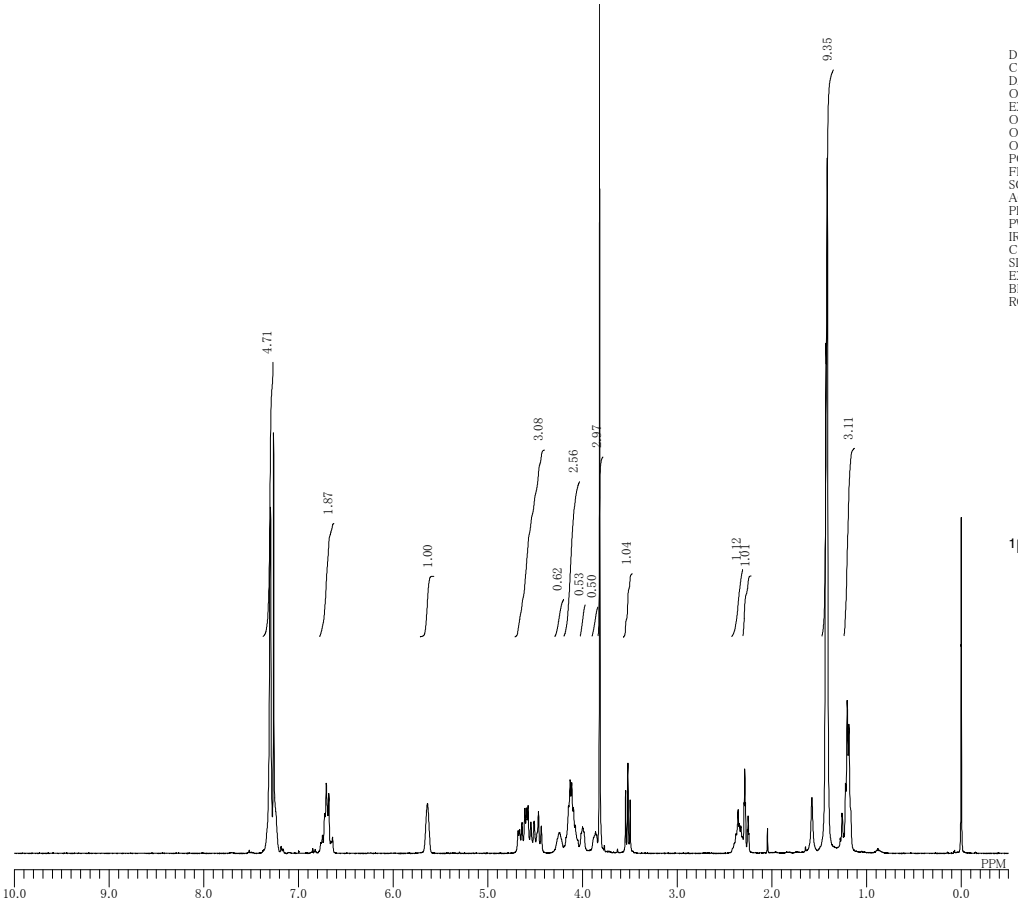


12

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



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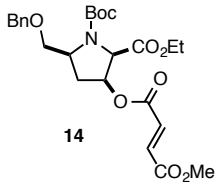
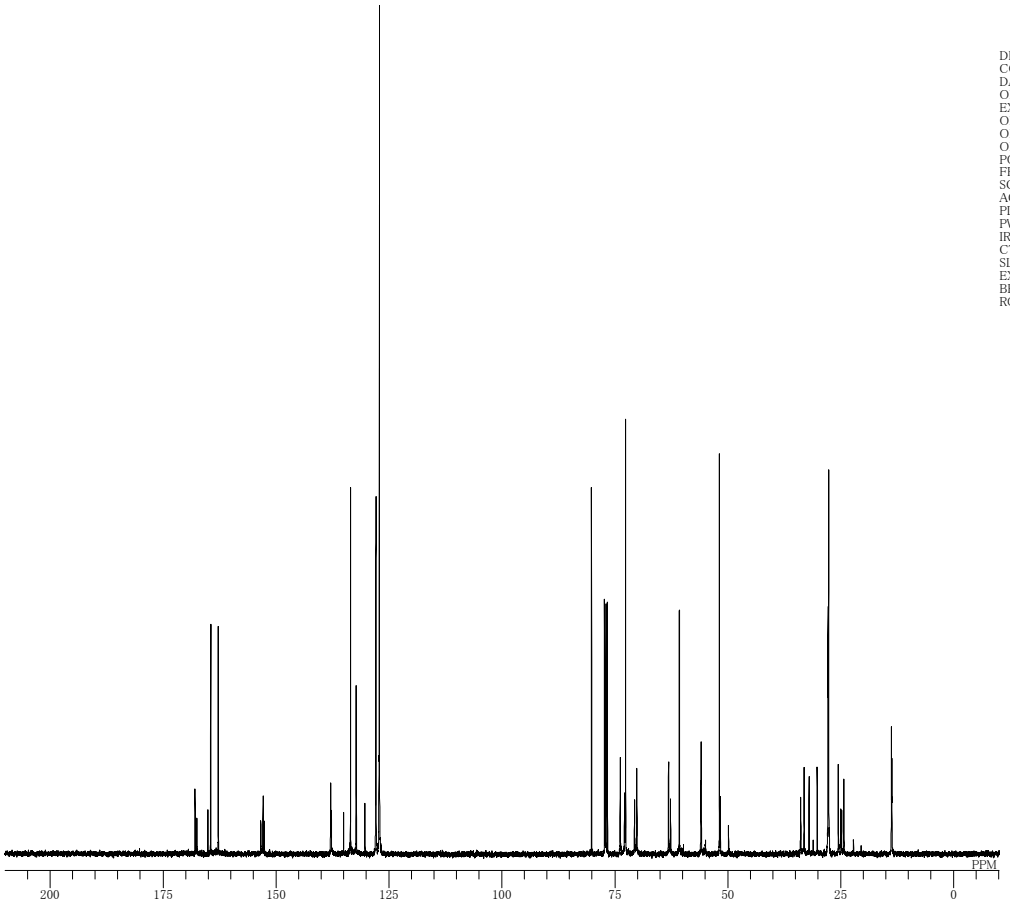
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

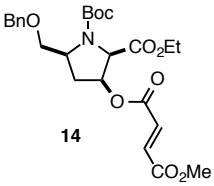


14

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

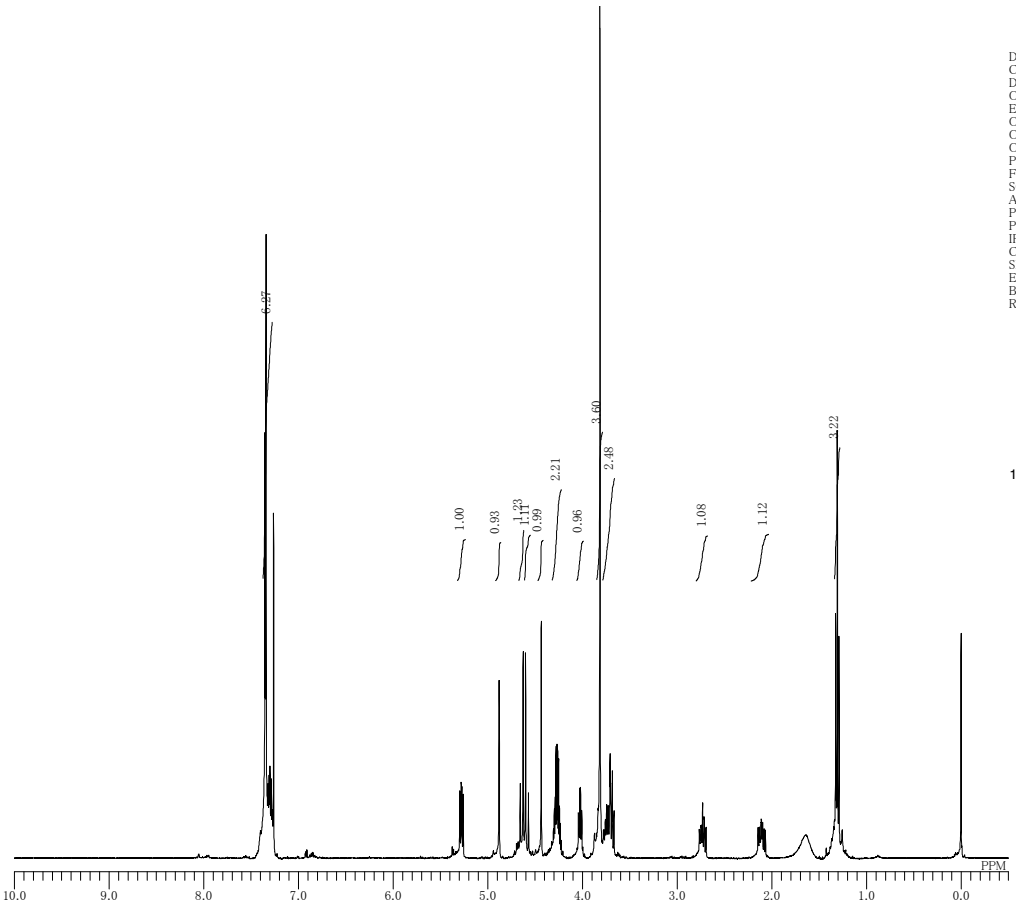


DFILE 14-carbon.als
COMNT
DATIM 17-12-2013 18:22:23
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 256
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 3.03 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

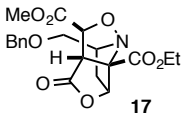


14

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

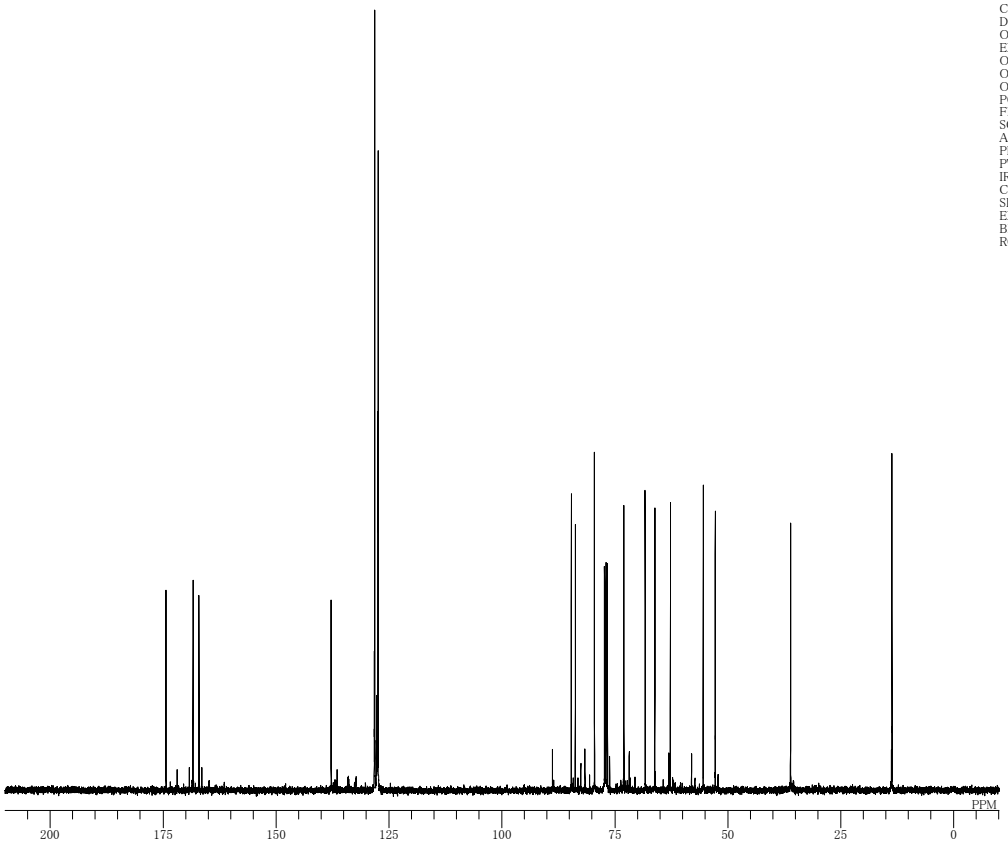


DFILE 17-proton.als
COMNT
DATIM 2013-09-03 18:21:01
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42

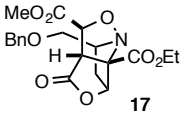


17

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



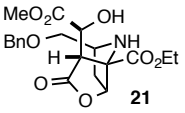
DFILE 17-carbon.als
COMNT
DATIM 24-12-2013 22:01:14
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 192
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 3.03 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50



17

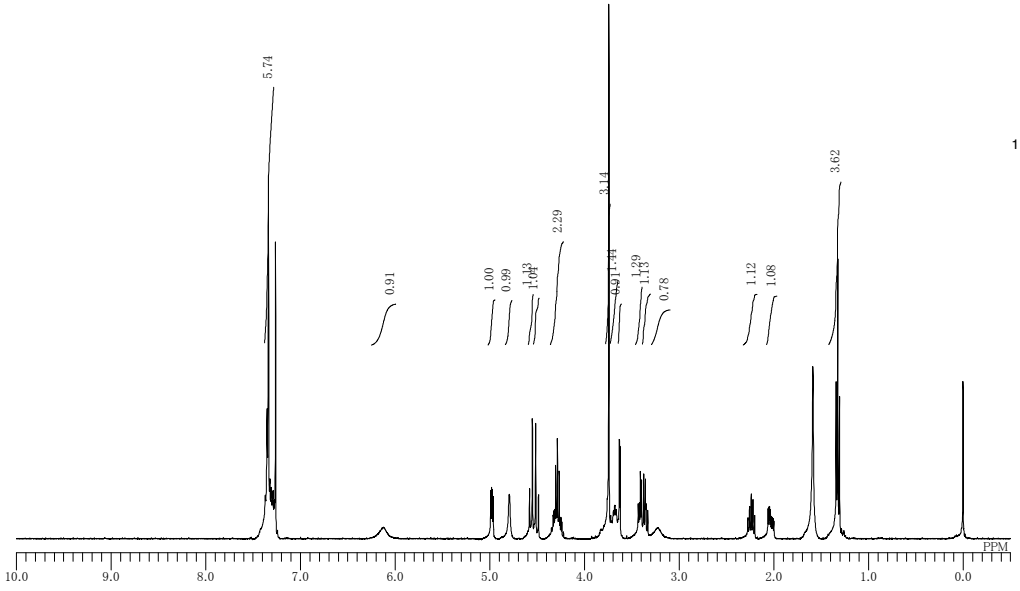
^{13}C NMR (100 MHz) in $CDCl_3$

DFILE	21-proton.als
COMNT	
DATIM	2013-09-24 15:42:44
OBNUC	1H
EXMOD	single_pulse.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	4.90 usec
IRNUC	1H
CTEMP	23.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	44

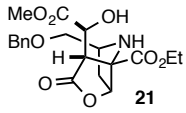


21

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

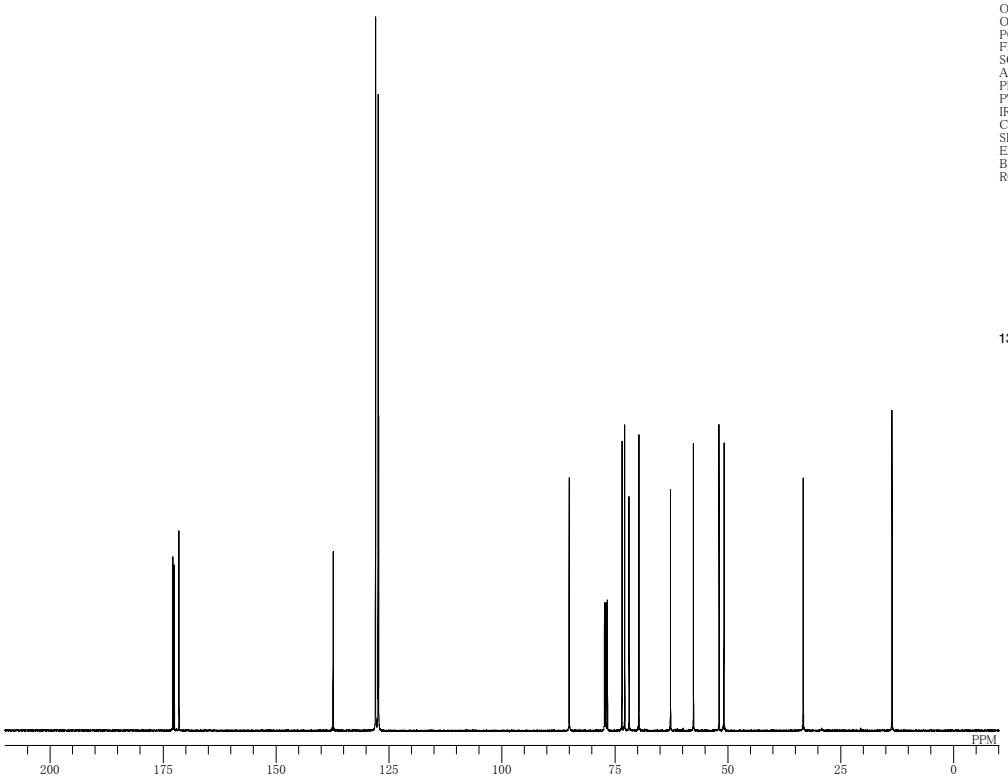


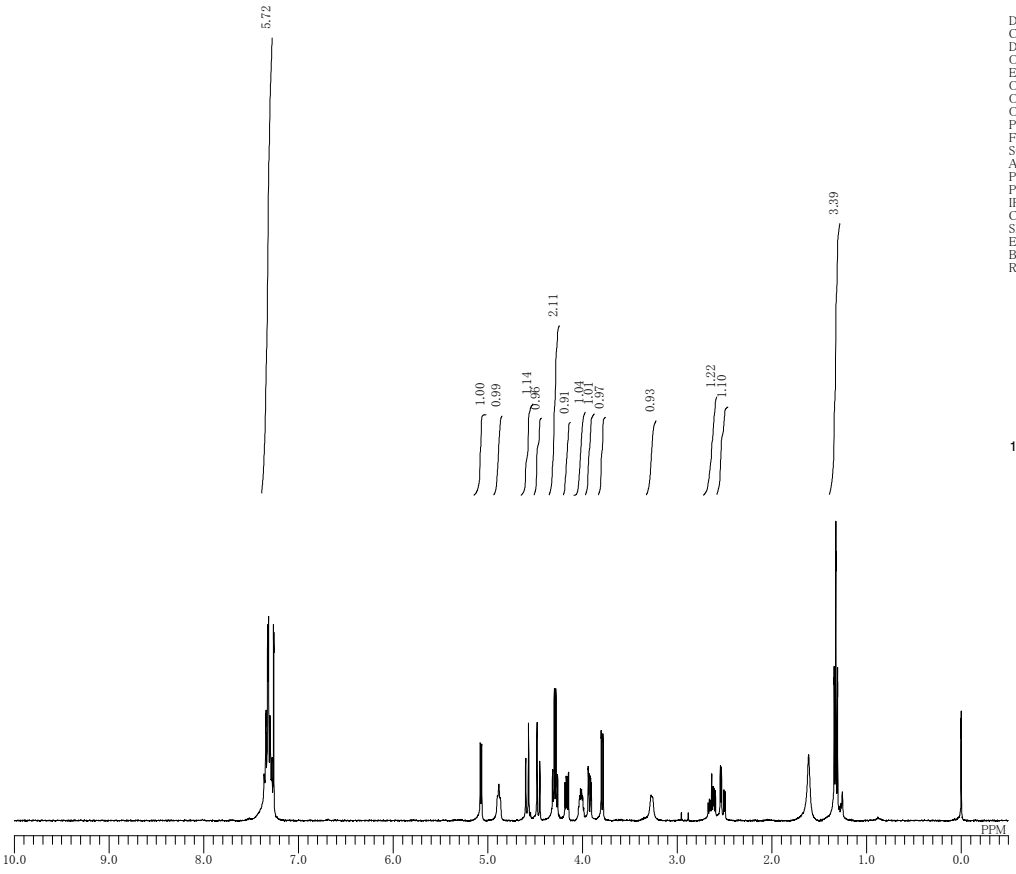
DFILE	21-carbon.als
COMNT	
DATIM	25-09-2013 01:02:31
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32767
FREQU	31407.04 Hz
SCANS	1500
ACQTM	1.0433 sec
PD	1.5000 sec
PW1	2.87 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	50



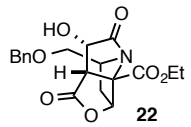
21

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



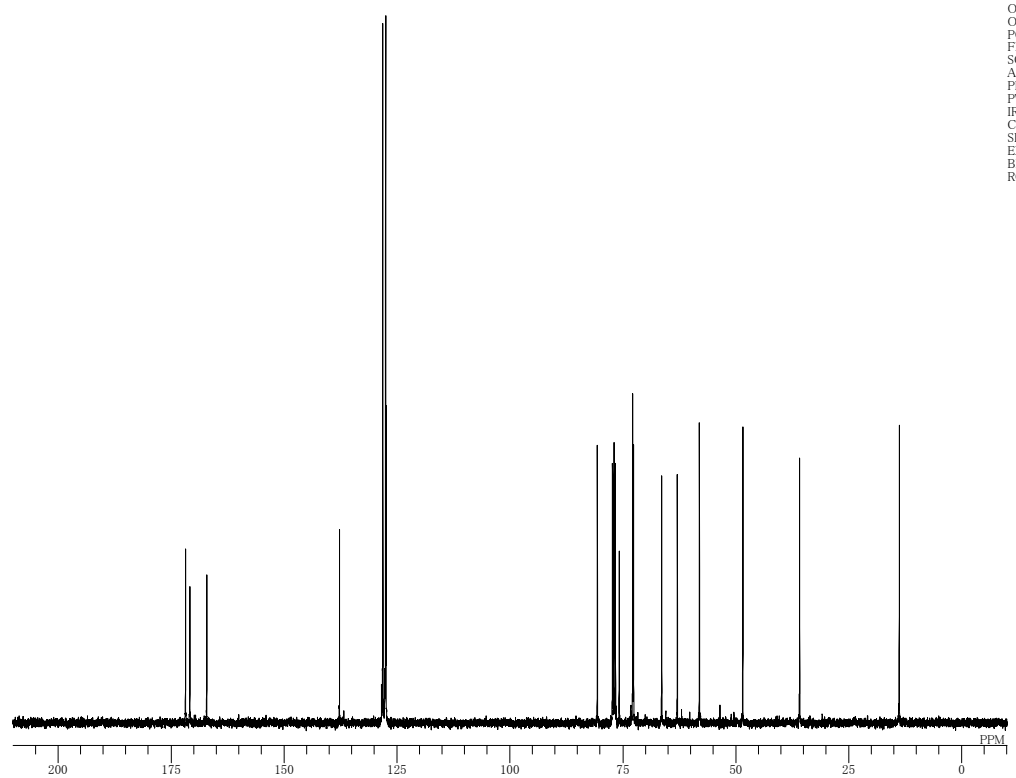


DFILE 22-proton.als
COMNT
DATIM 2013-09-27 17:35:18
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

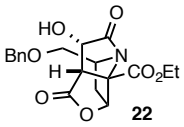


22

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

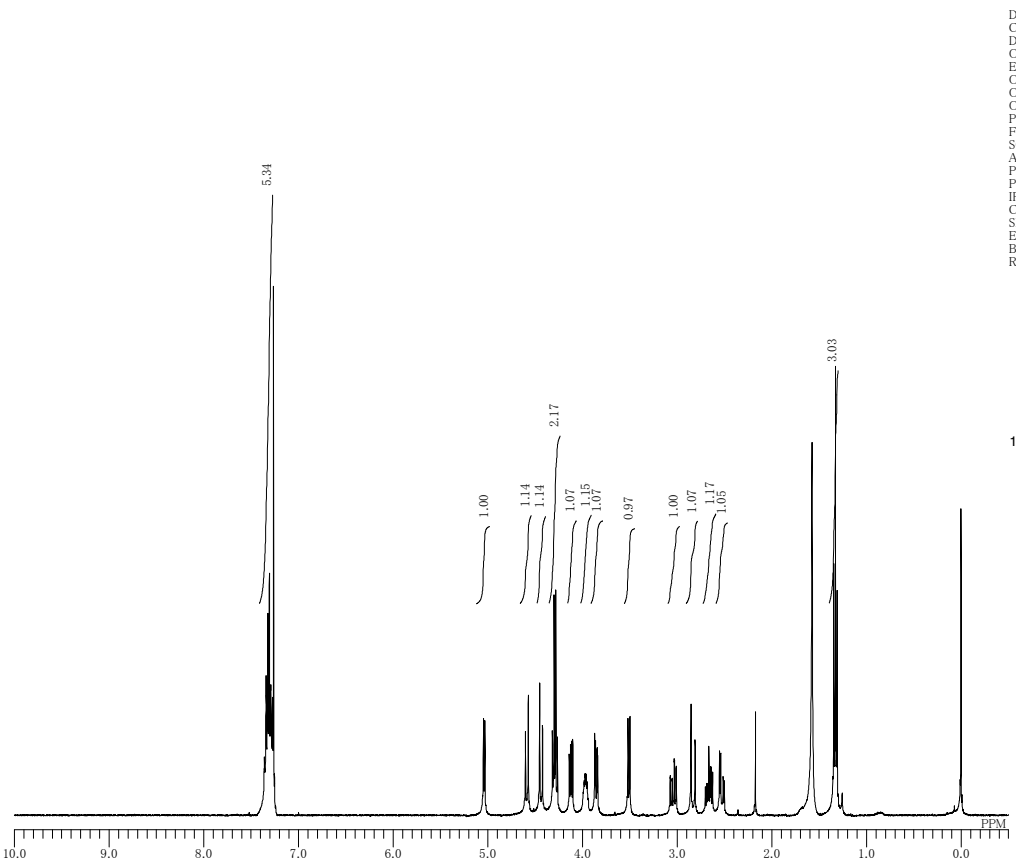


DFILE 22-carbon.als
COMNT
DATIM 27-09-2013 18:19:00
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 192
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

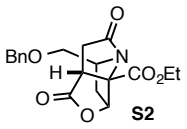


22

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

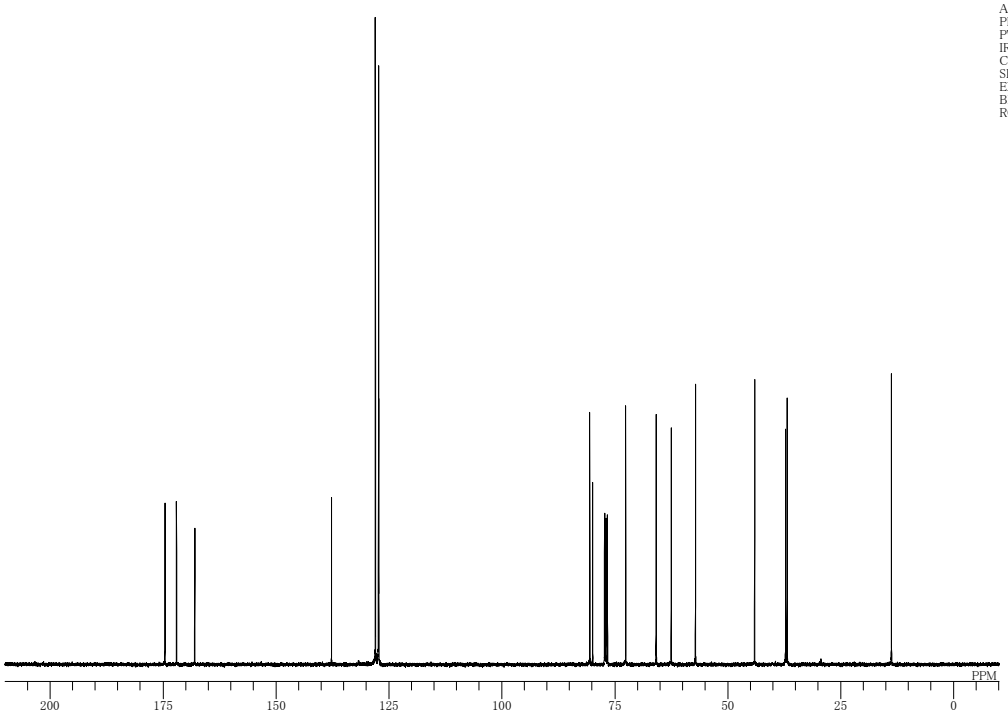


DFILE S2-proton.als
COMNT
DATIM 2013-10-02 19:03:30
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48

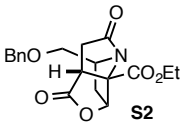


S2

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

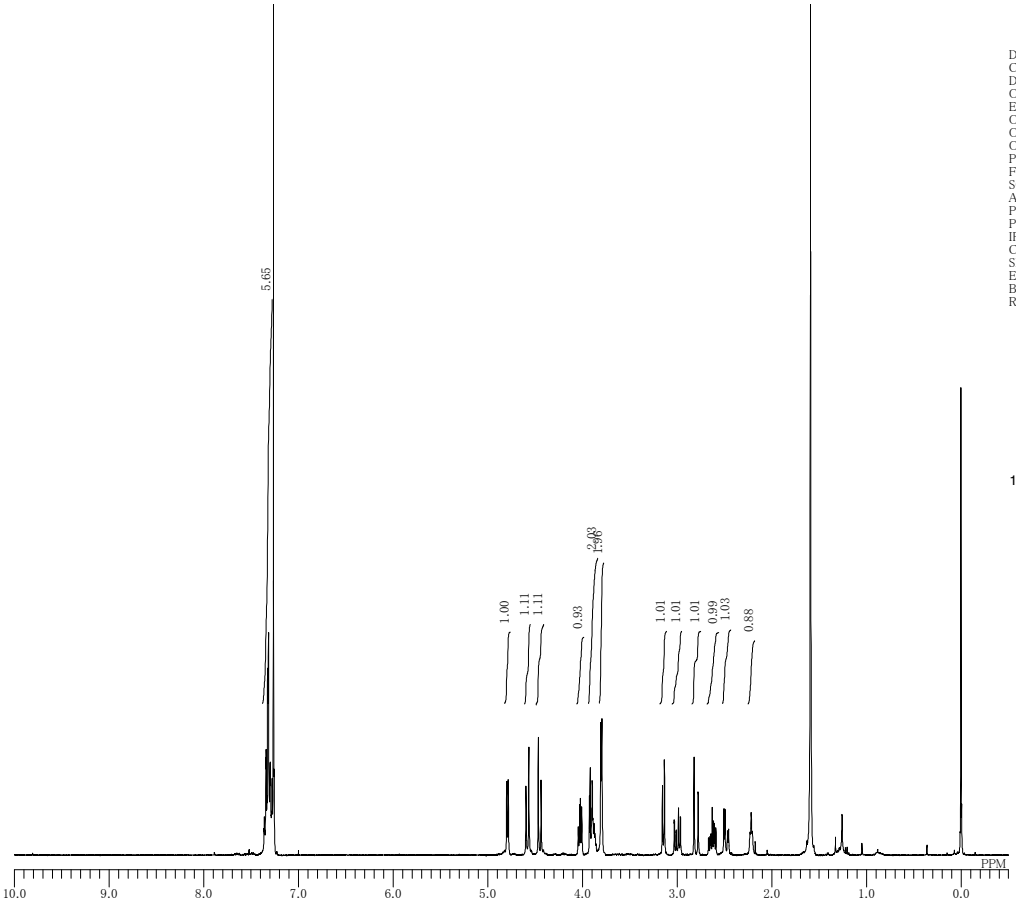


DFILE S2-carbon.als
COMNT
DATIM 30-09-2013 22:04:06
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 256
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

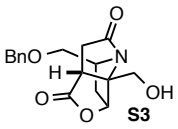


S2

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

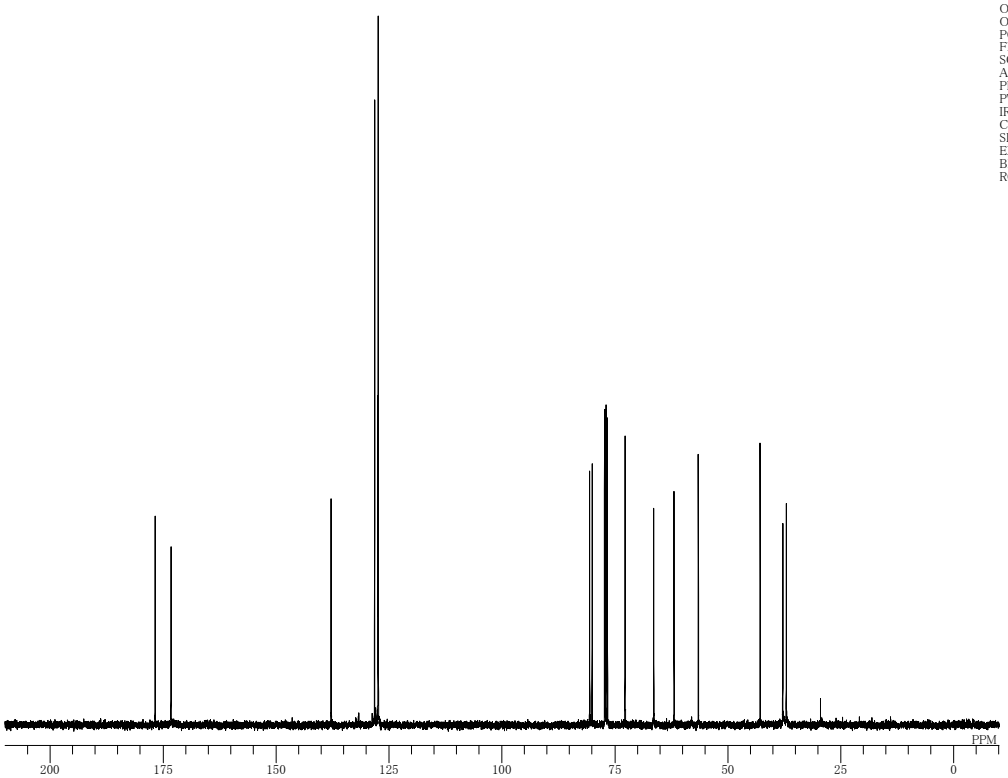


DFILE	S3-proton.als
COMNT	
DATIM	2013-10-24 20:29:46
OBNUC	1H
EXMOD	single_pulse.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	32
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	23.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	50

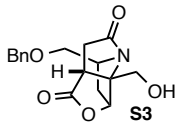


S3

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

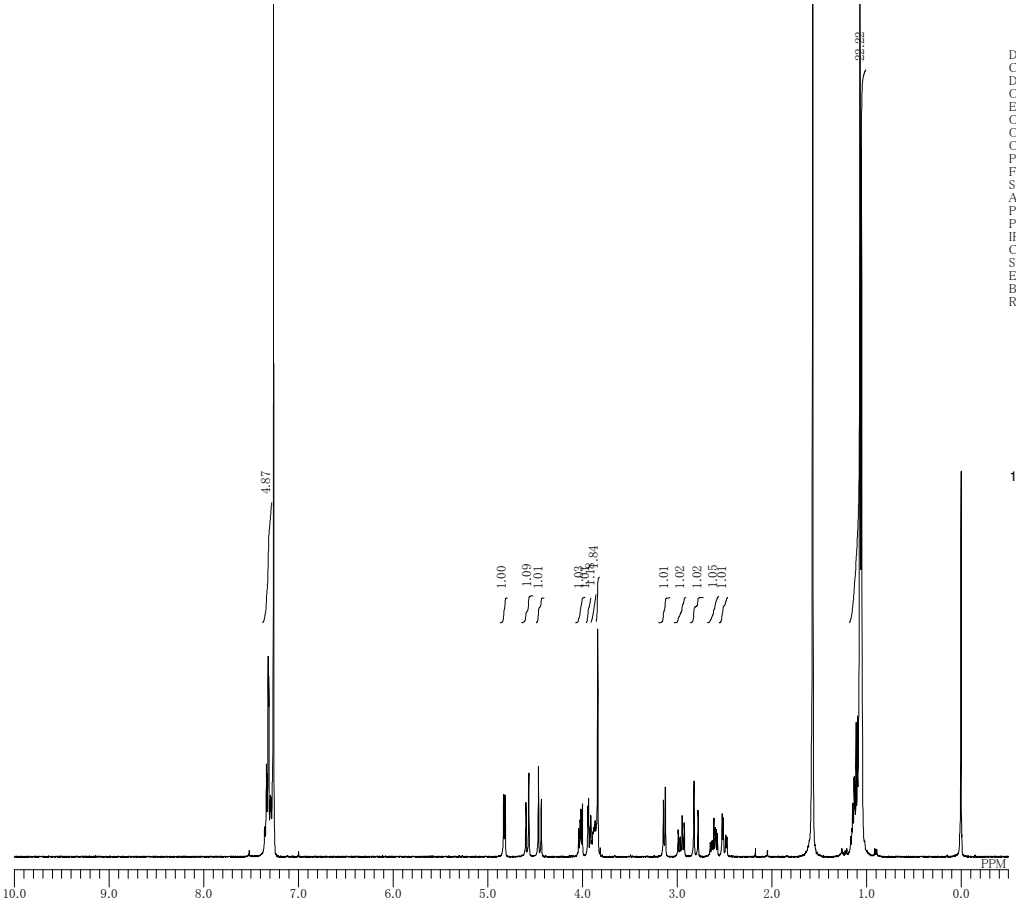


DFILE	S3-carbon.als
COMNT	
DATIM	24-10-2013 17:38:25
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32767
FREQU	31407.04 Hz
SCANS	256
ACQTM	1.0433 sec
PD	1.5000 sec
PW1	3.03 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	50

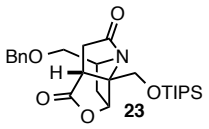


S3

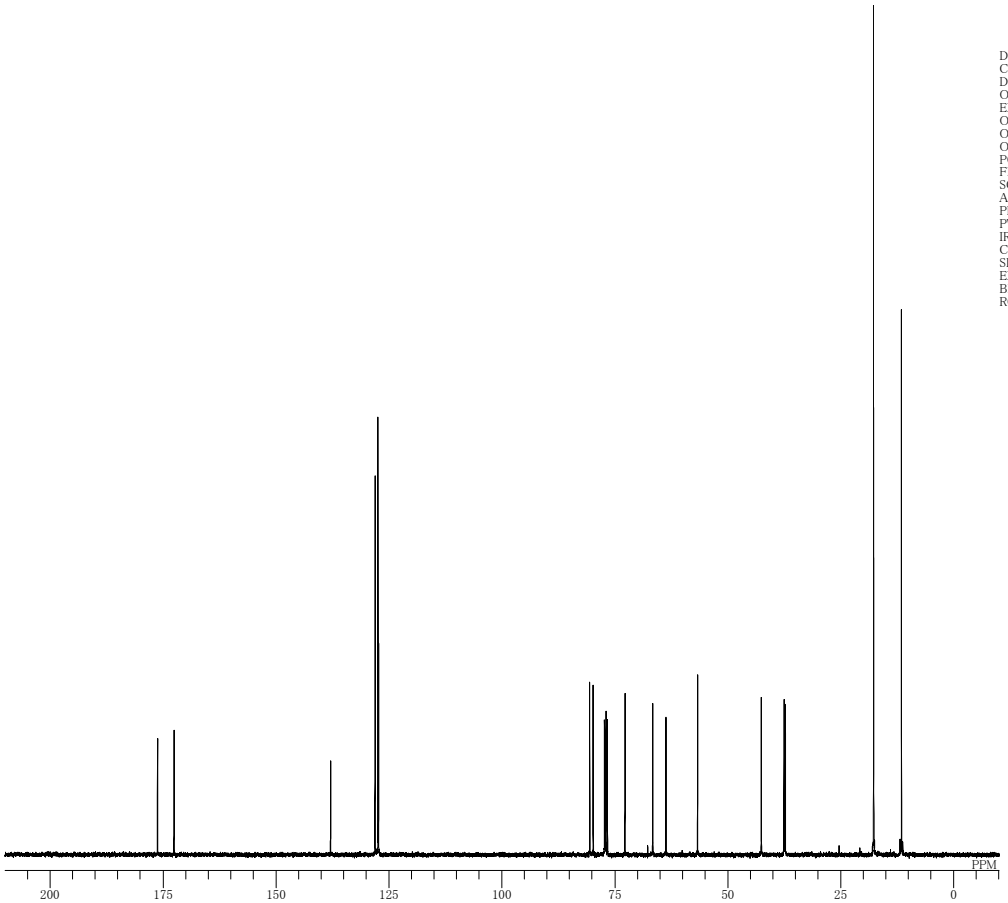
^{13}C NMR (100 MHz) in $CDCl_3$



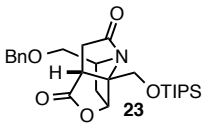
DFILE 23-proton.als
COMNT
DATIM 2013-10-25 23:26:27
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50



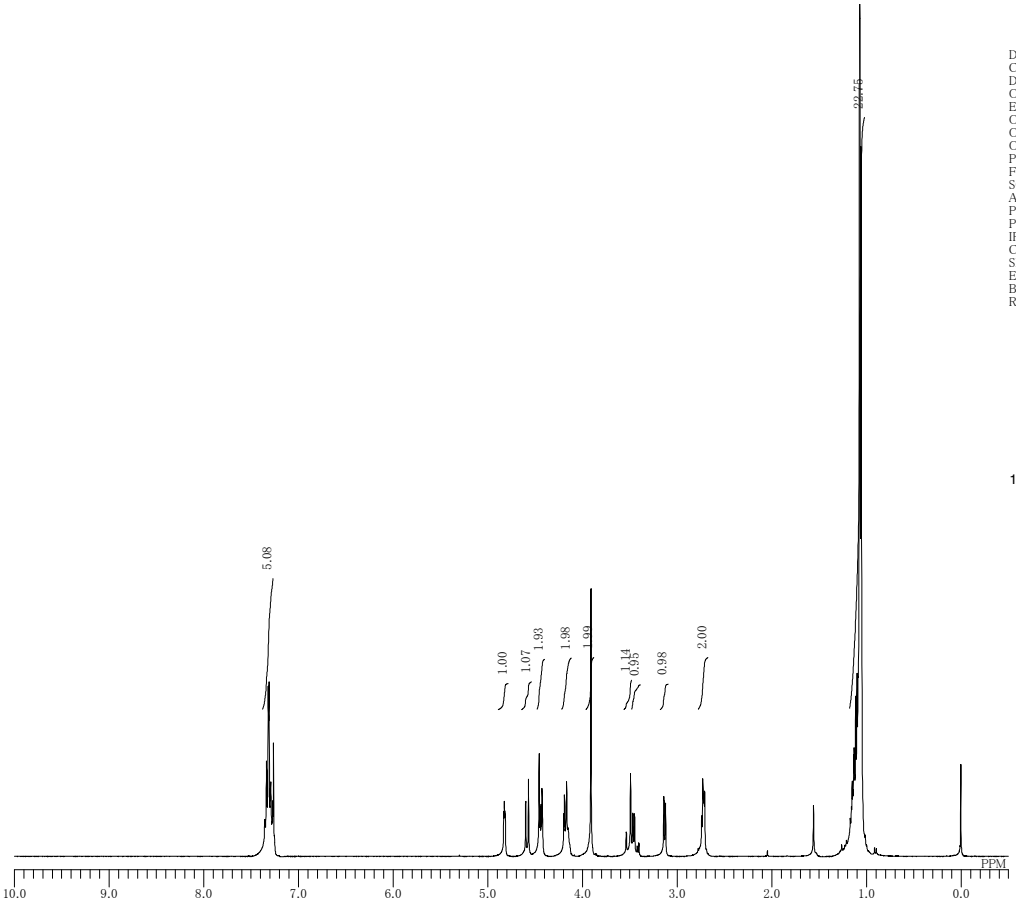
^{1}H NMR (400 MHz) in $CDCl_3$



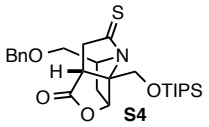
DFILE 23-carbon.als
COMNT
DATIM 25-10-2013 23:32:21
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 256
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 3.03 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50



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

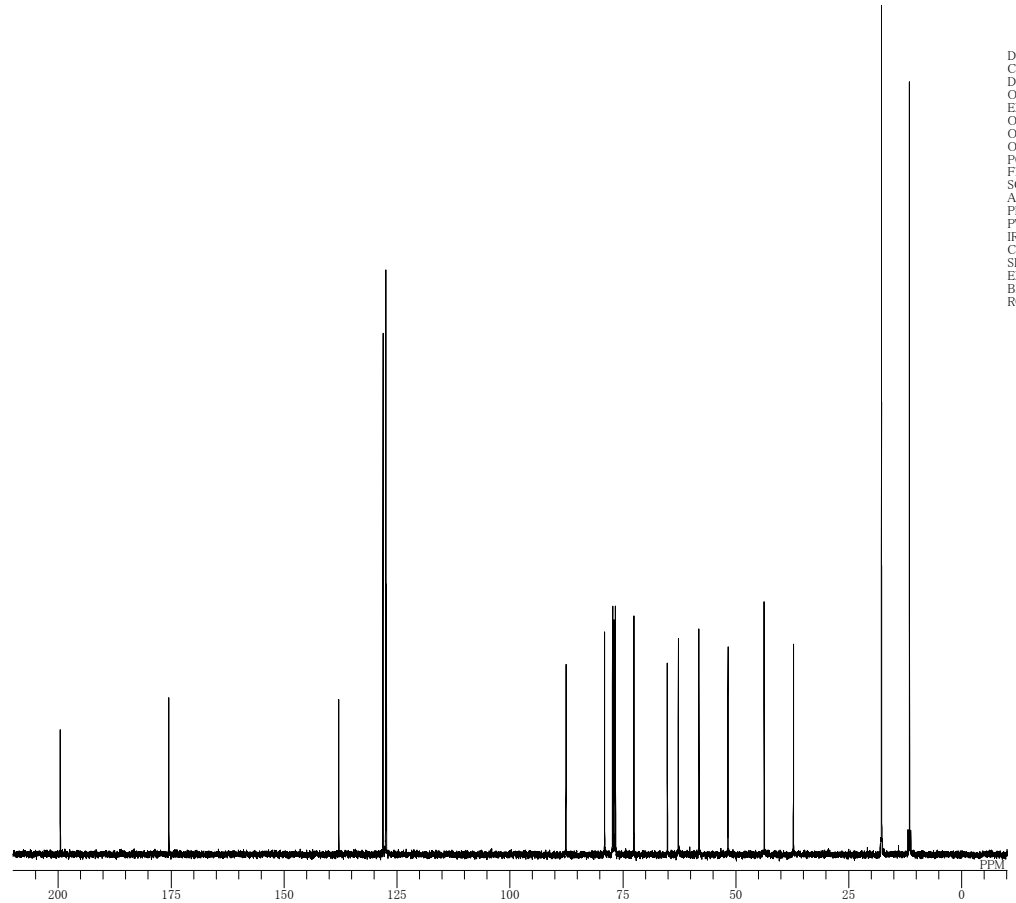


DFILE S4-proton.als
COMNT
DATIM 2014-03-20 22:09:44
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38

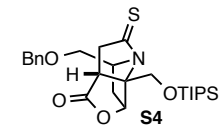


S4

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

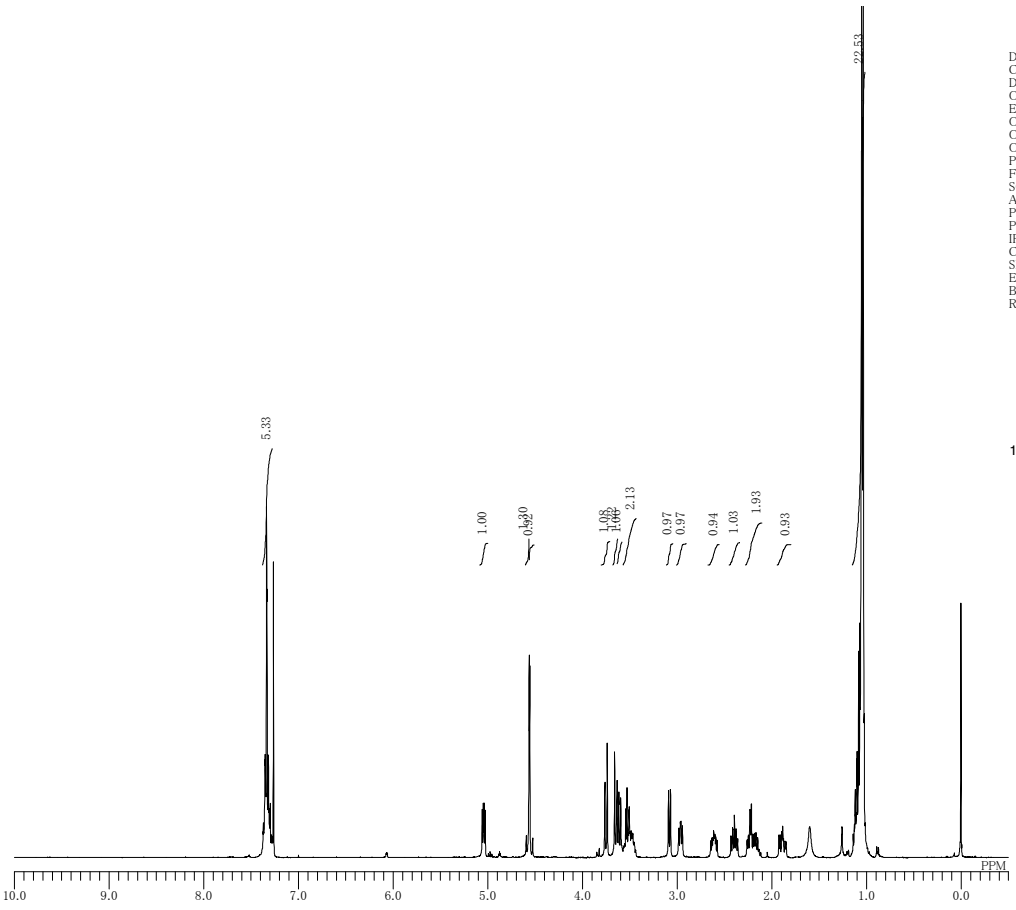


DFILE S4-carbon.als
COMNT
DATIM 28-10-2013 21:22:26
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 256
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 3.03 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

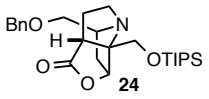


S4

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

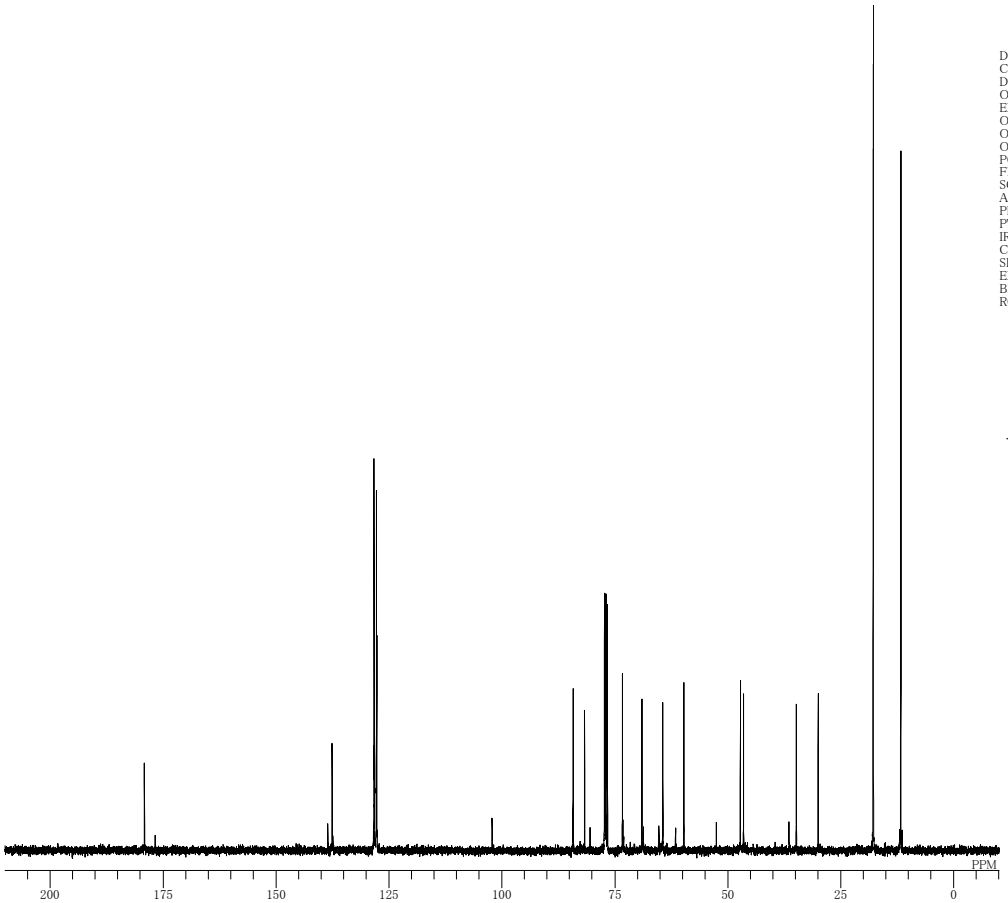


DFILE 24-proton.als
COMNT
DATIM 2013-10-30 10:23:16
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42

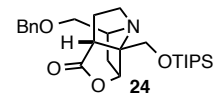


24

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

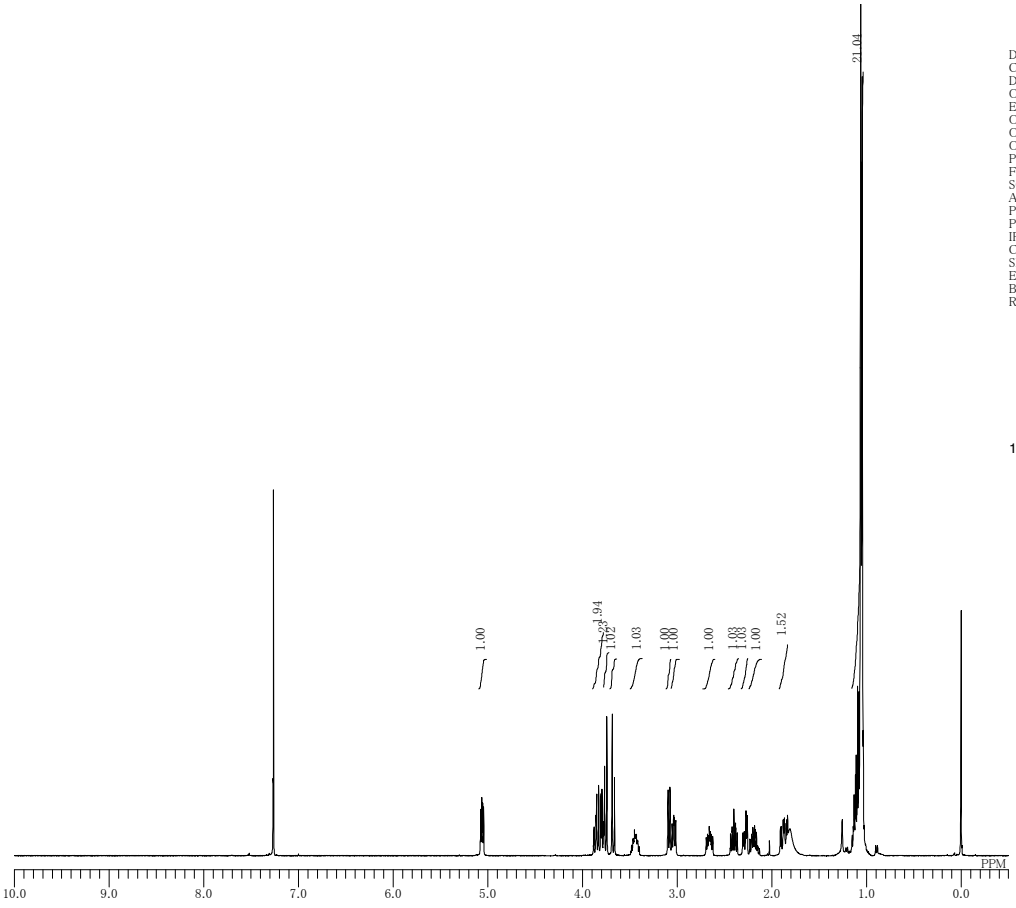


DFILE 24-carbon.als
COMNT
DATIM 29-10-2013 21:53:01
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 256
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 3.03 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

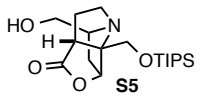


24

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

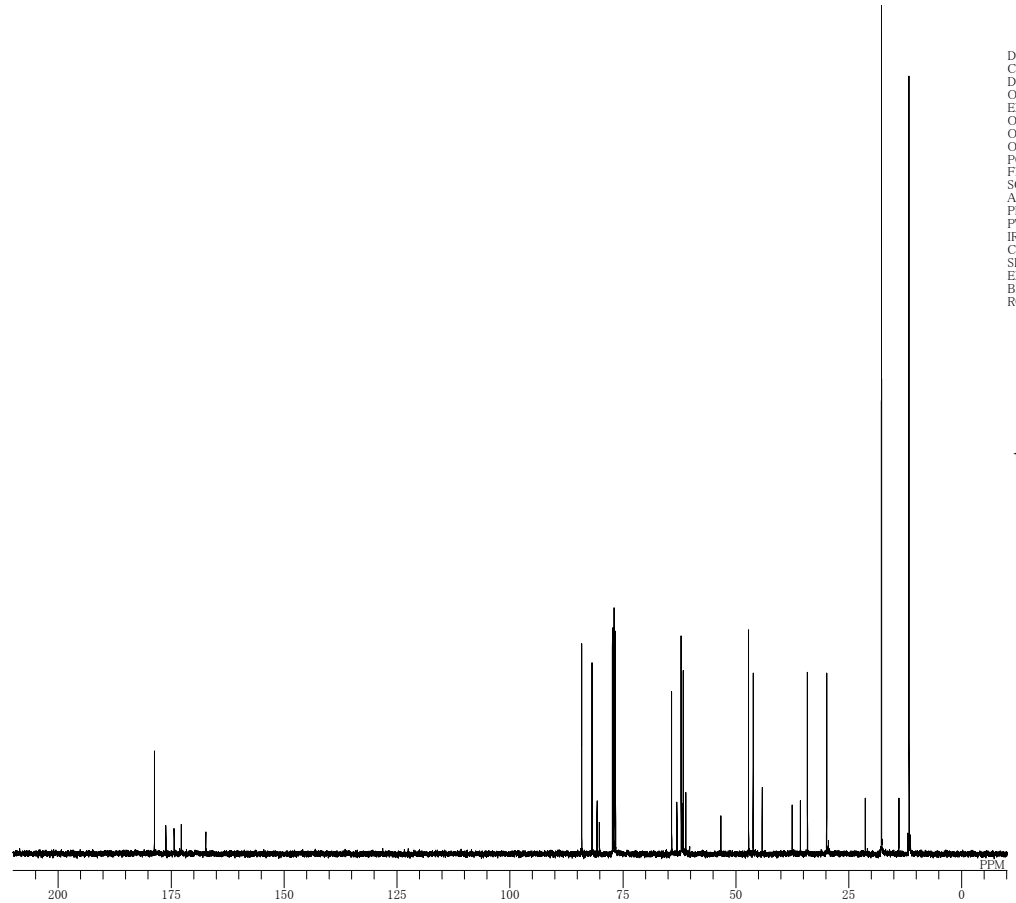


DFILE S5-proton.als
COMNT
DATIM 2013-11-01 14:38:26
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

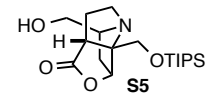


S5

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

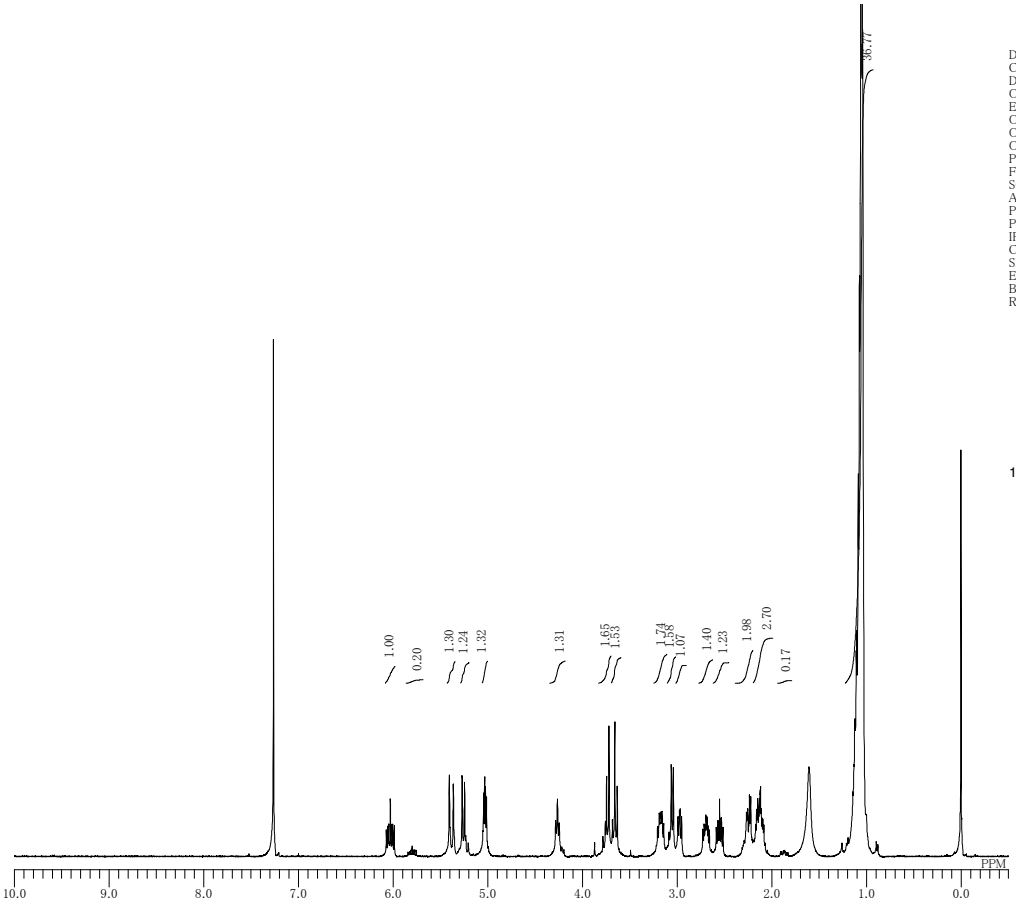


DFILE S5-carbon.als
COMNT
DATIM 31-10-2013 22:30:47
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 256
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 3.03 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

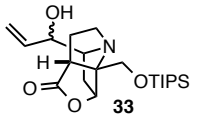


S5

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

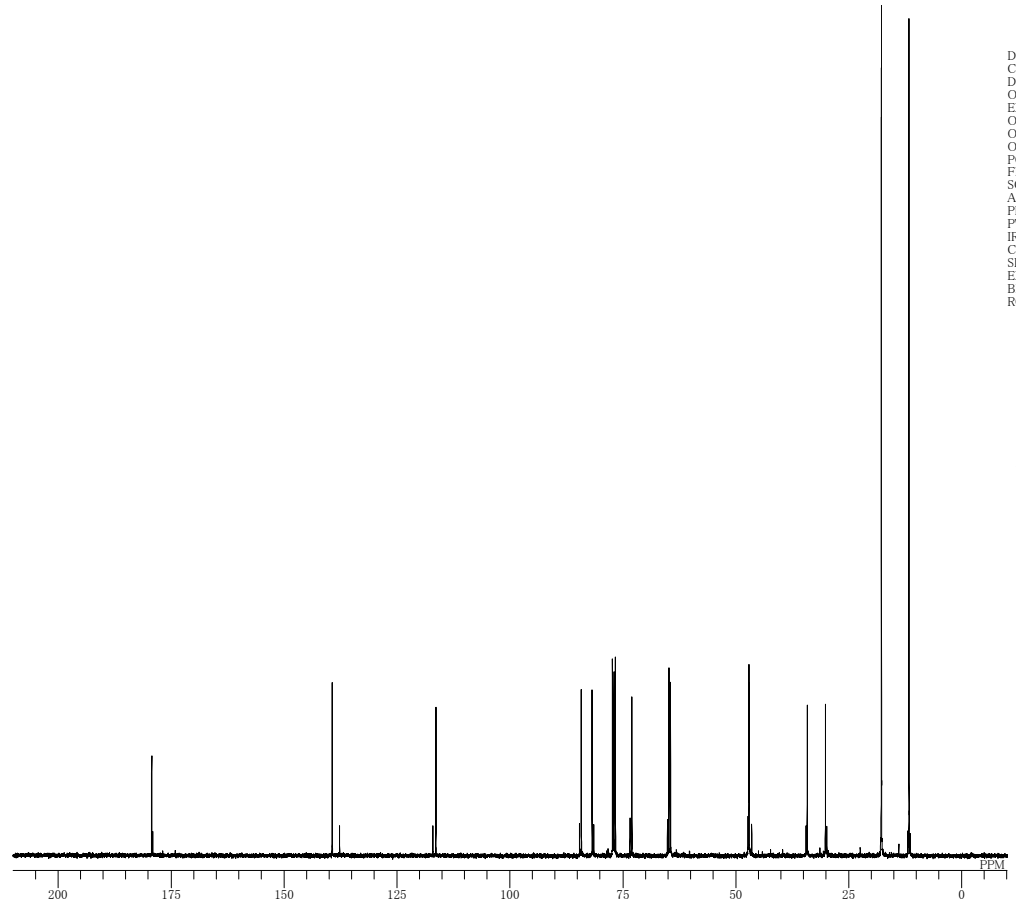


DFILE 33-proton.als
COMNT
DATIM 2014-03-01 19:21:48
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 25.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

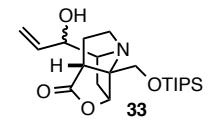


33

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

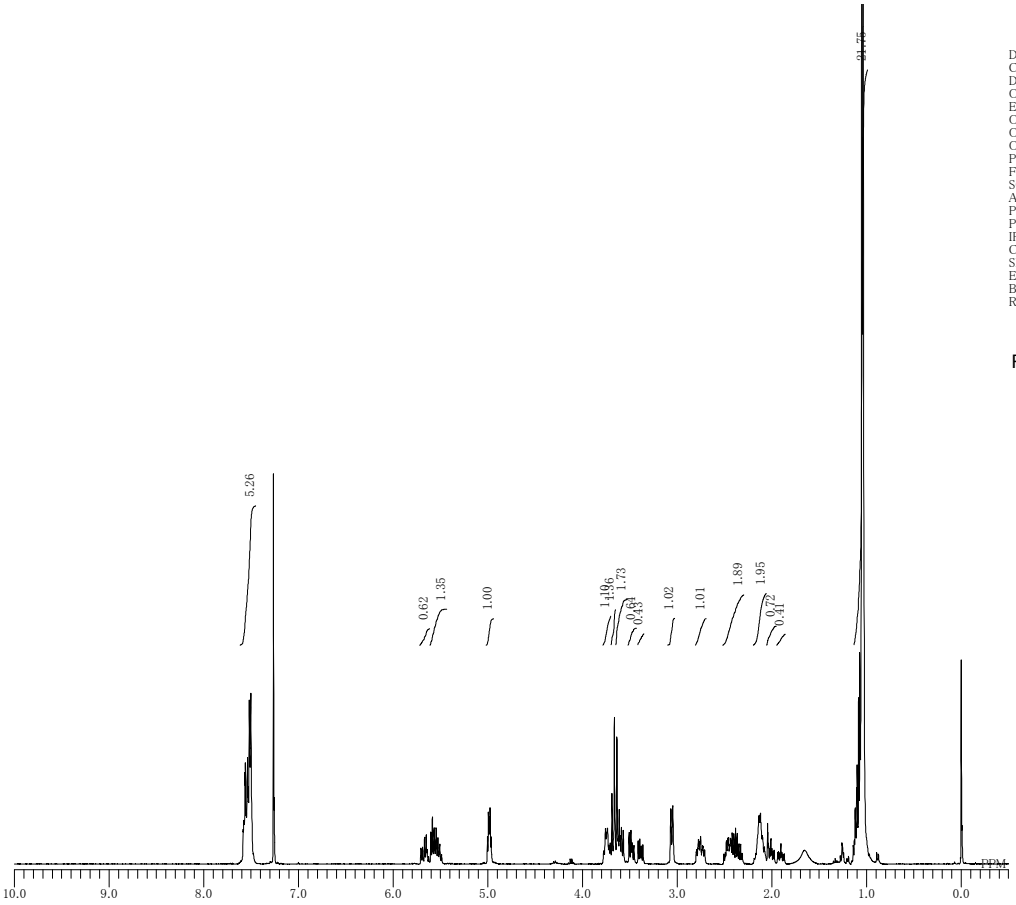


DFILE 33-carbon.als
COMNT
DATIM 01-03-2014 17:44:32
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 320
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

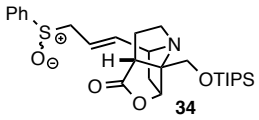


33

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

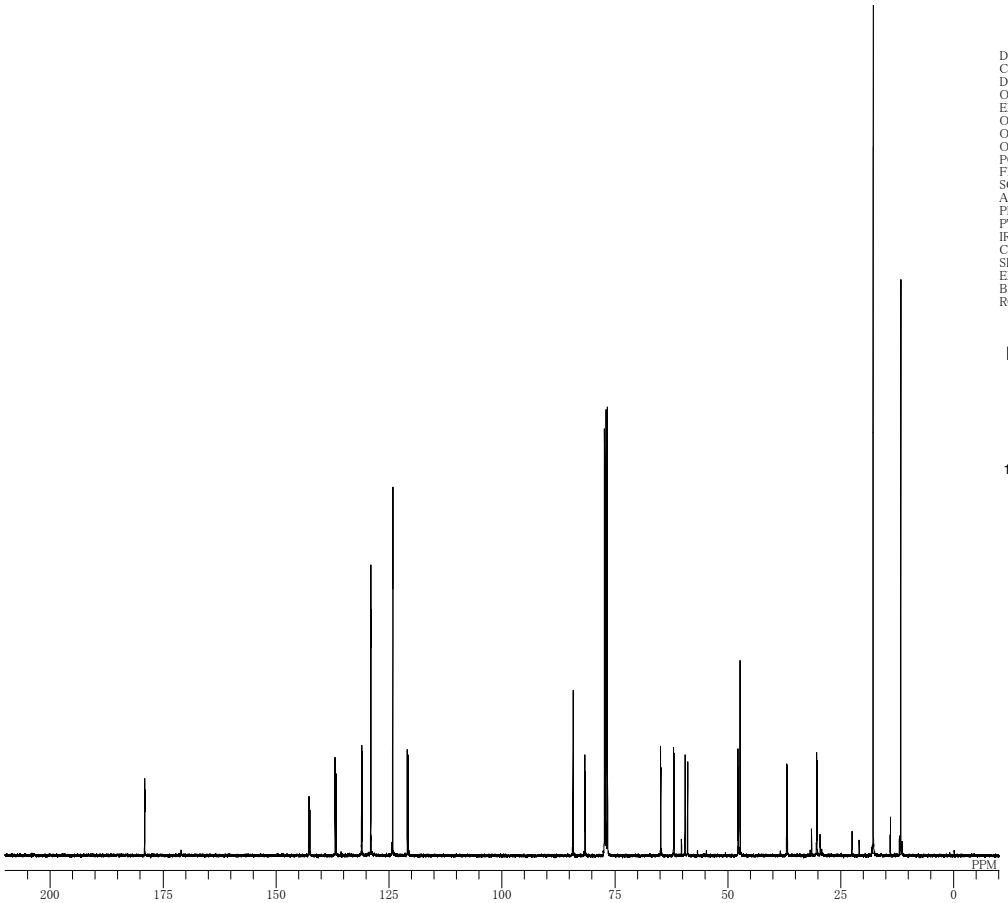


DFILE 34-proton.als
COMNT
DATIM 2013-11-06 20:32:49
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42

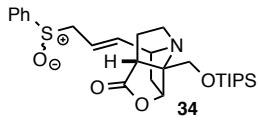


34

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

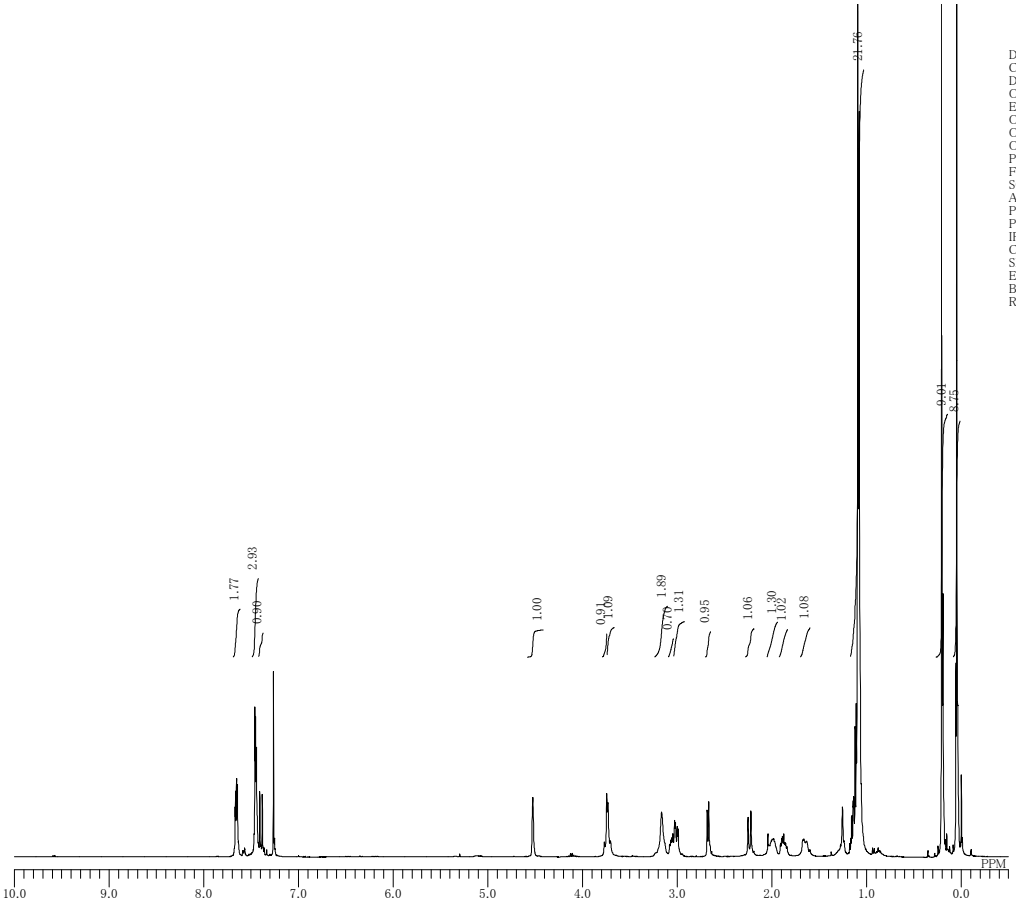


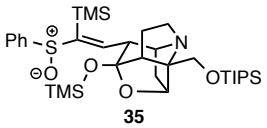
DFILE 34-carbon.als
COMNT
DATIM 07-11-2013 00:01:02
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 5000
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 3.03 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50



34

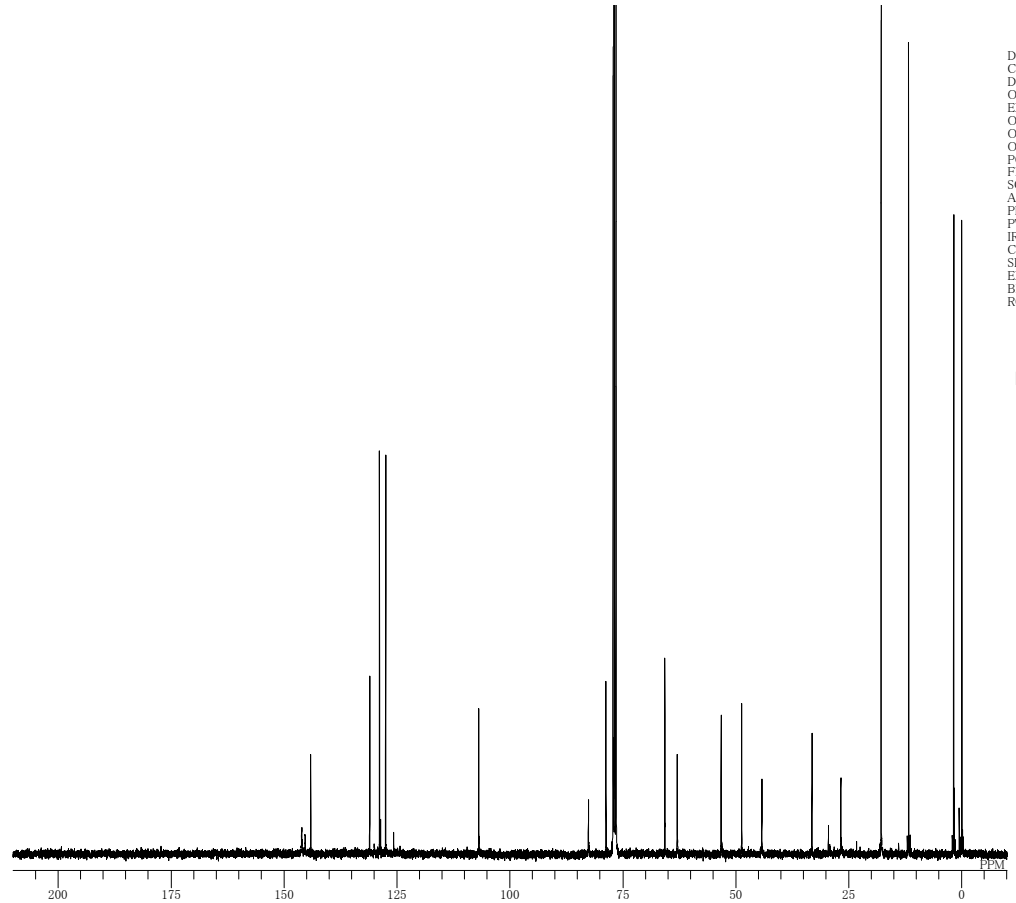
^{13}C NMR (100 MHz) in $CDCl_3$

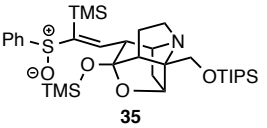




35

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

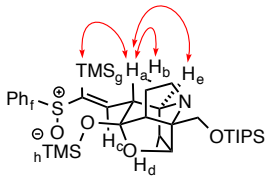




35

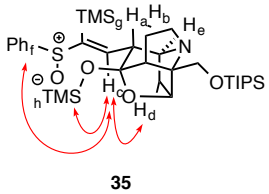
^{13}C NMR (100 MHz) in $CDCl_3$

nOe experiment of **35** (irradiation: Ha)

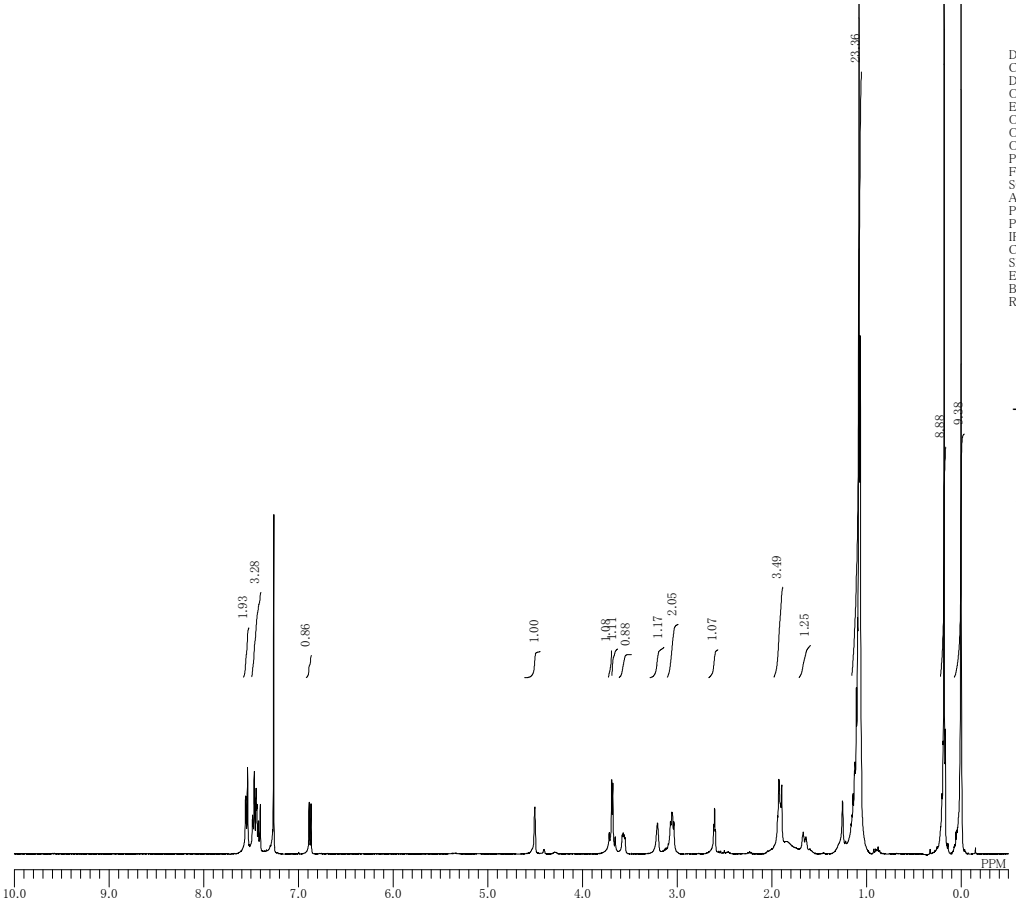


35

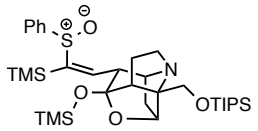
nOe experiment of **35** (irradiation: Hc)



35

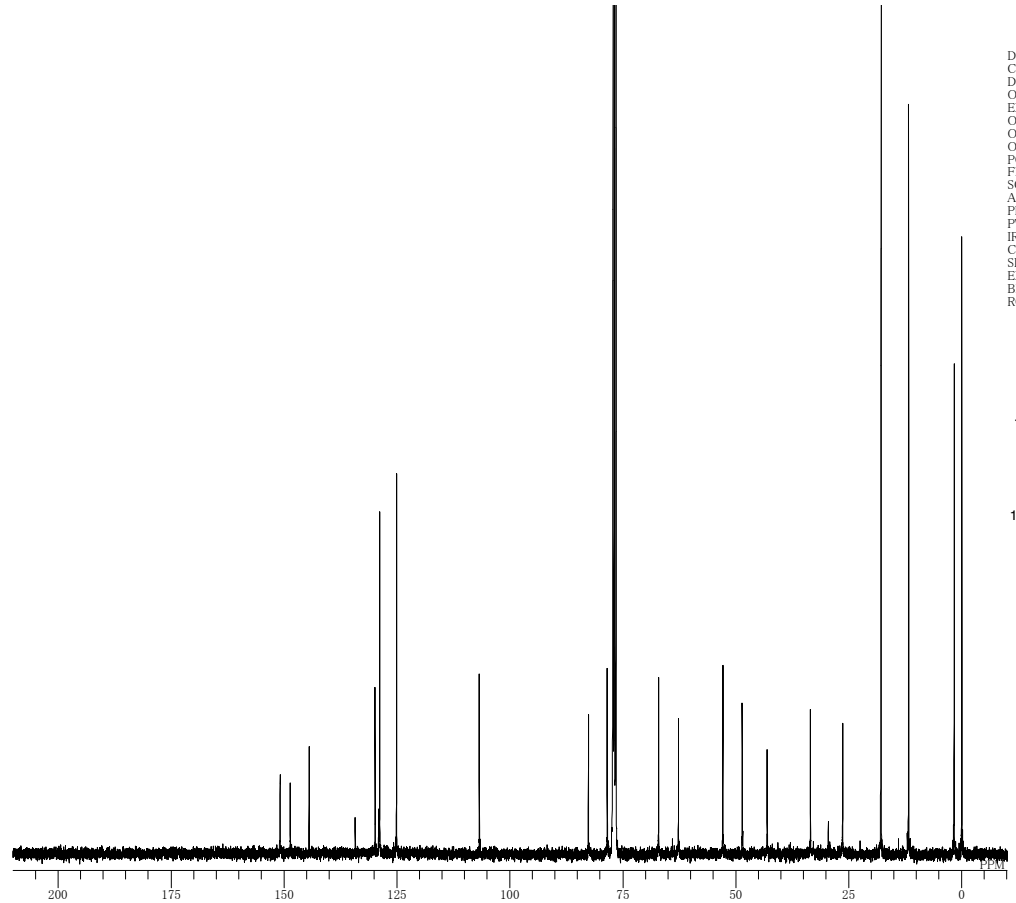


DFILE 36-proton.als
COMNT
DATIM 2013-11-10 19:06:00
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

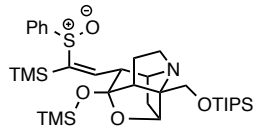


36

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



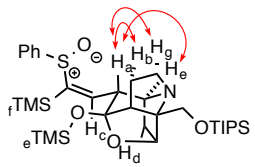
DFILE 36-carbon.als
COMNT
DATIM 09-11-2013 23:32:46
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 8000
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 3.03 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 50



36

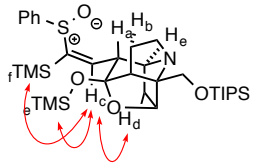
^{13}C NMR (100 MHz) in $CDCl_3$

nOe experiment of **36** (irradiation: Ha)

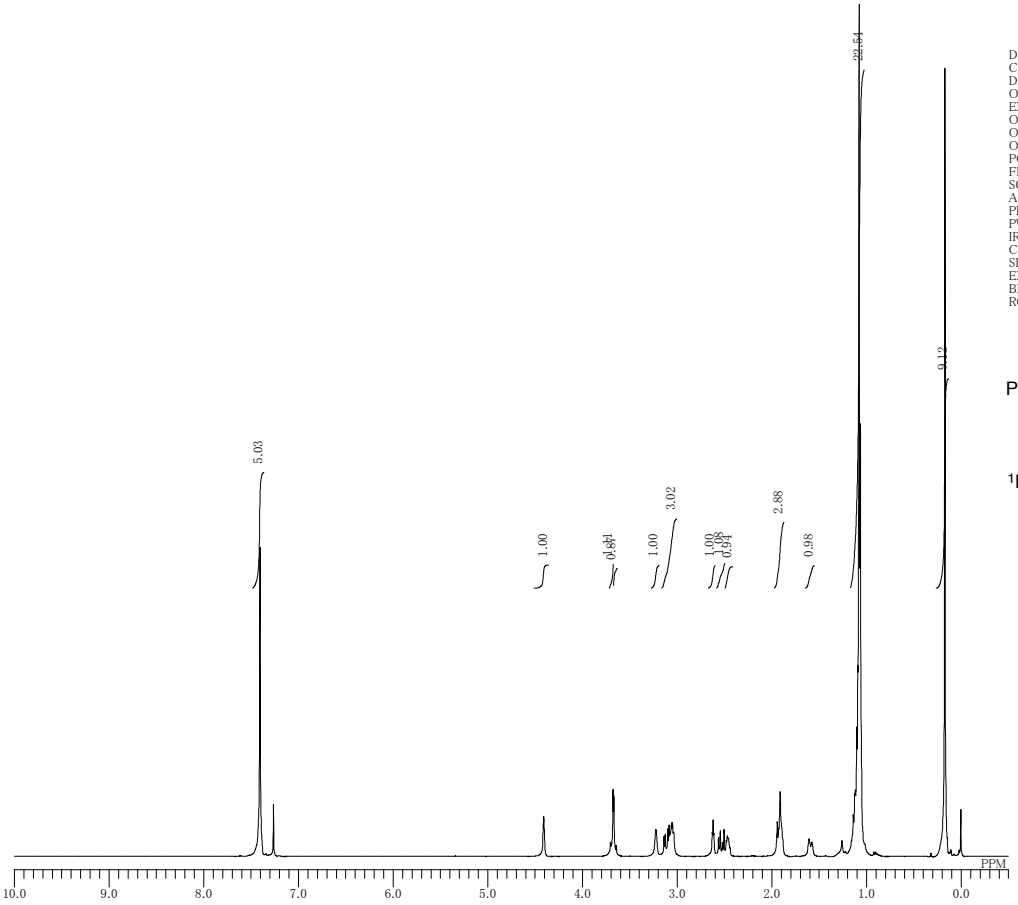


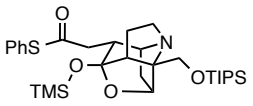
36

nOe experiment of **36** (irradiation: Hc)



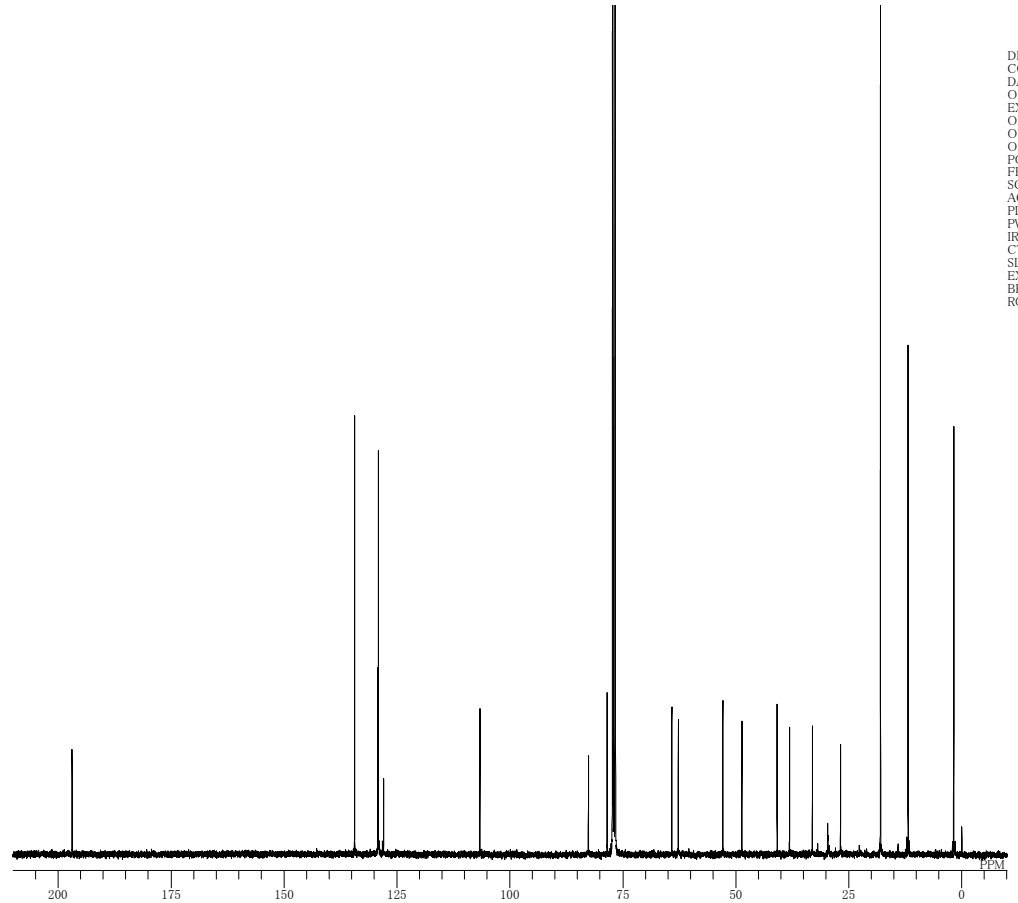
36

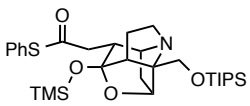




38

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

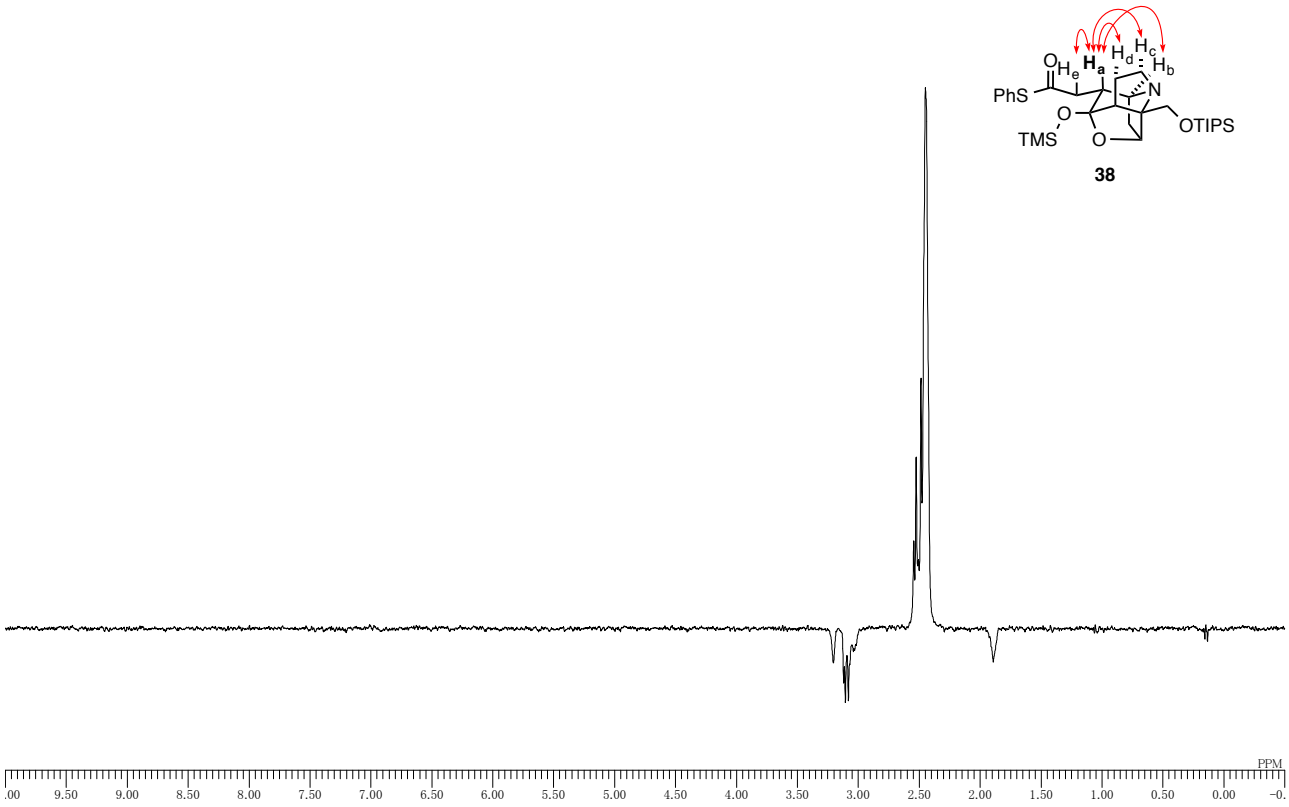


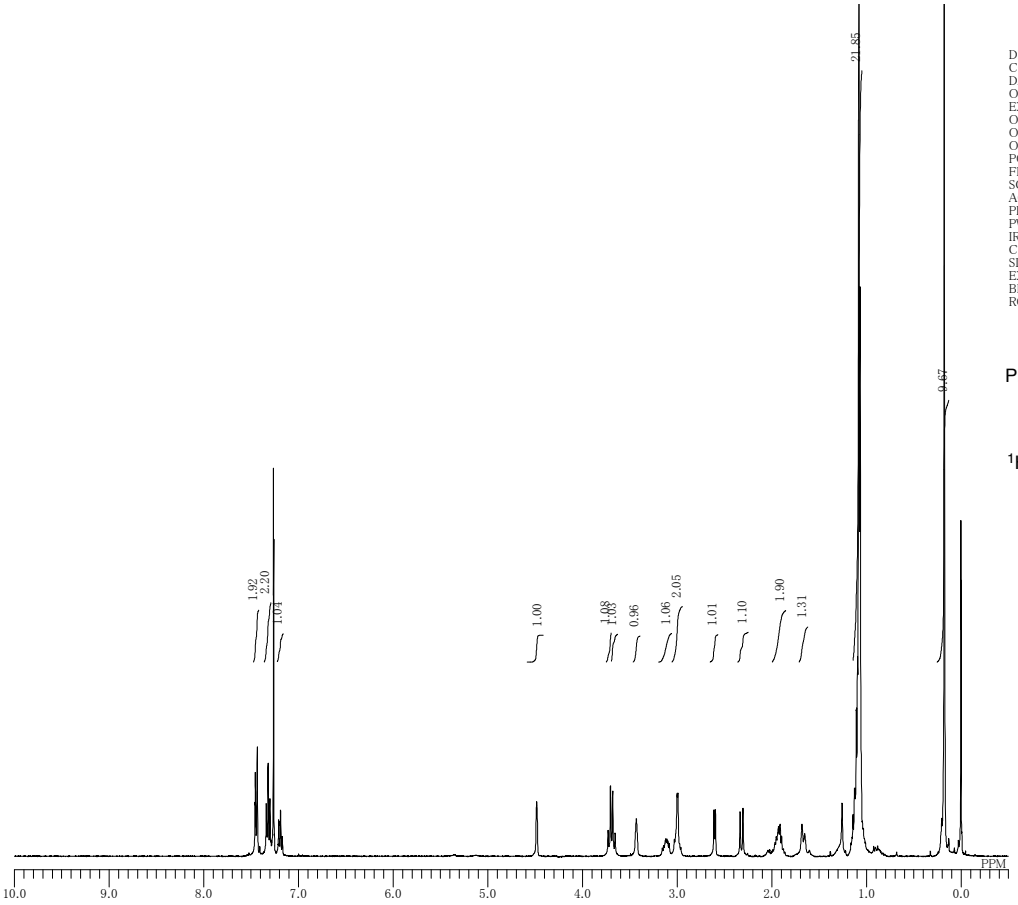


38

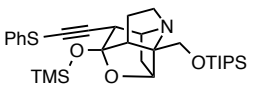
^{13}C NMR (100 MHz) in $CDCl_3$

nOe experiment of **38** (irradiation: Ha)



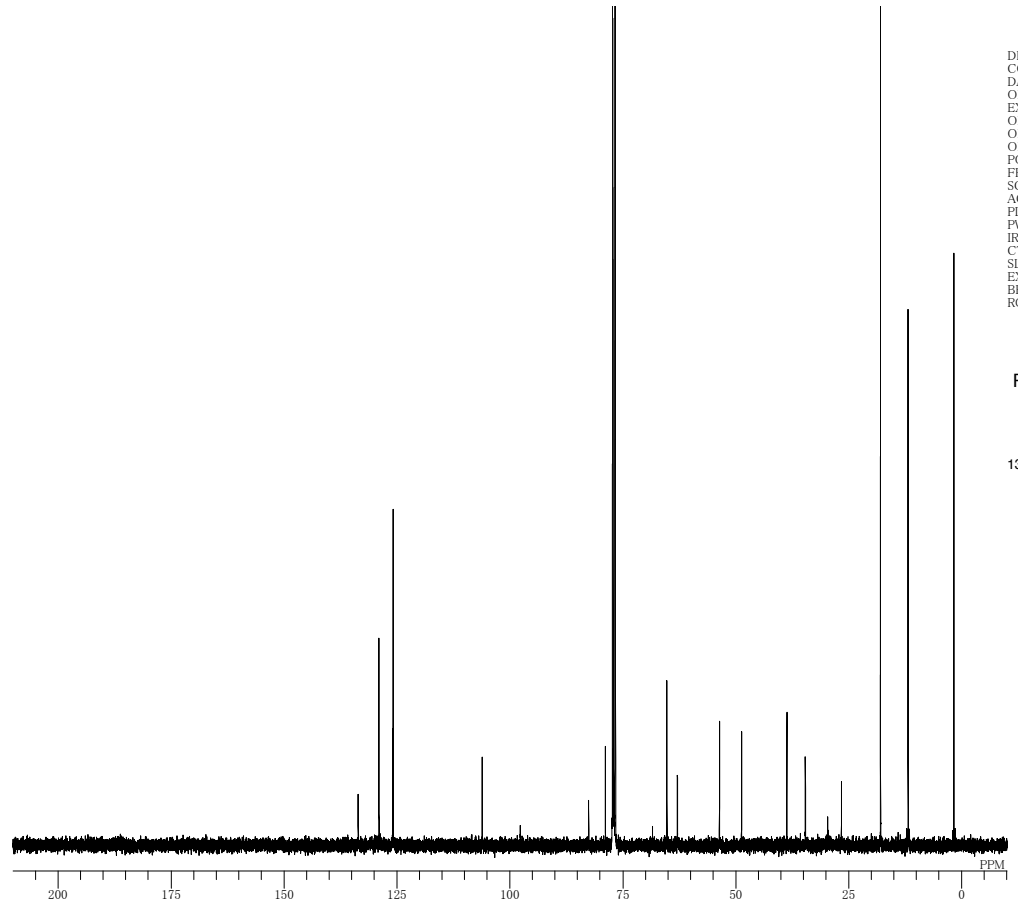


DFILE 39−proton.als
COMNT
DATIM 2014−02−18 22:09:22
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46

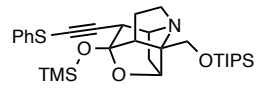


39

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

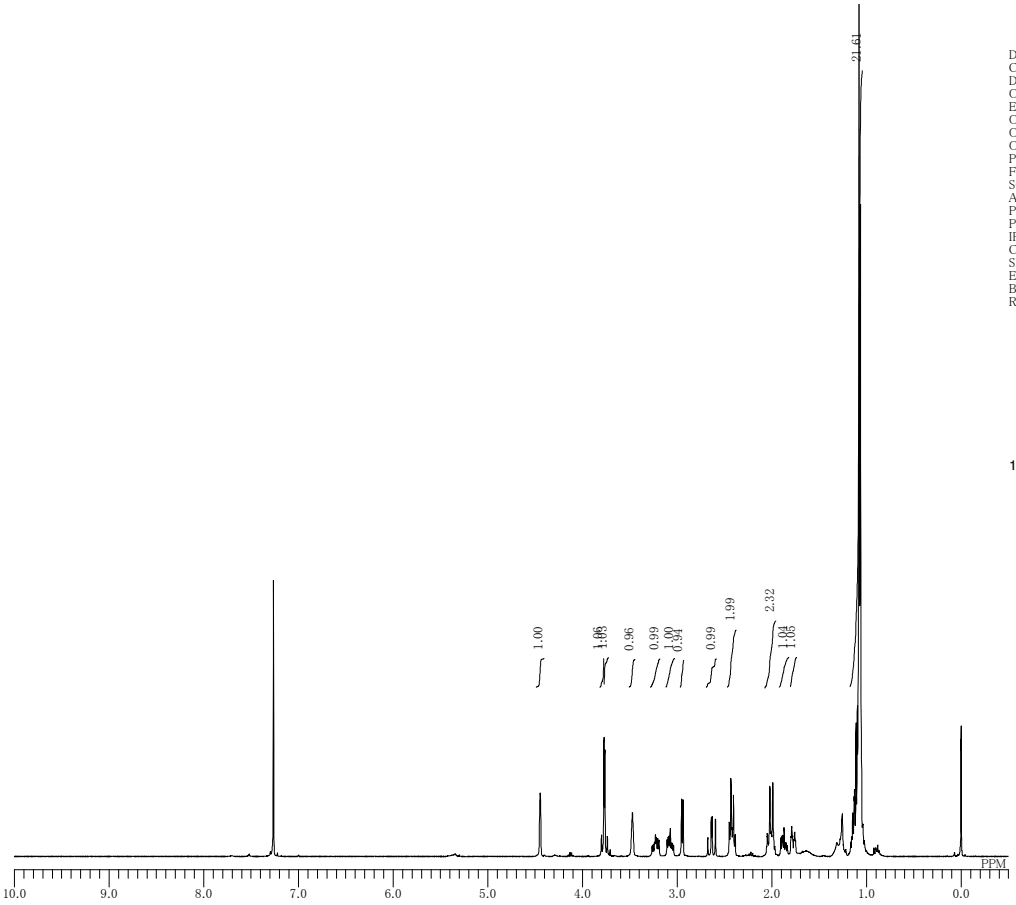


DFILE 39−carbon.als
COMNT
DATIM 09−02−2014 09:02:57
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 7000
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

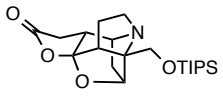


39

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

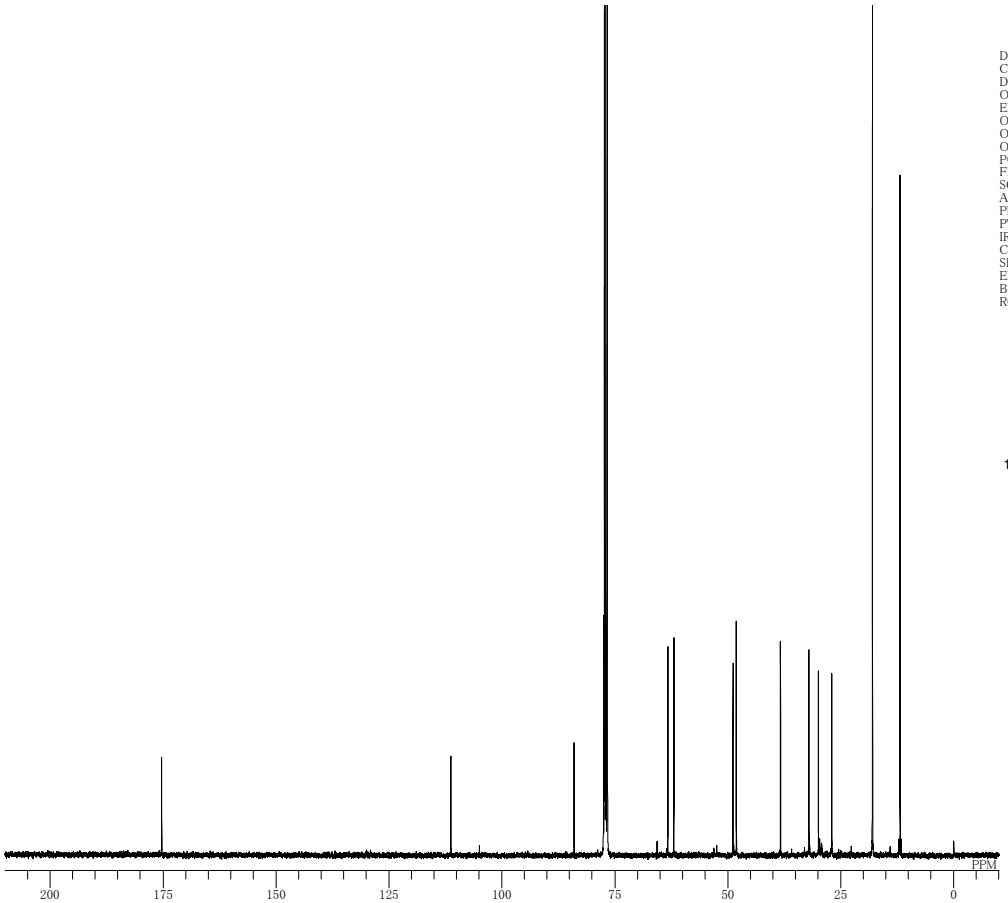


DFILE 40-proton.als
COMNT
DATIM 2014-02-06 14:20:59
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 21.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

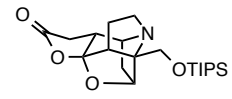


40

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

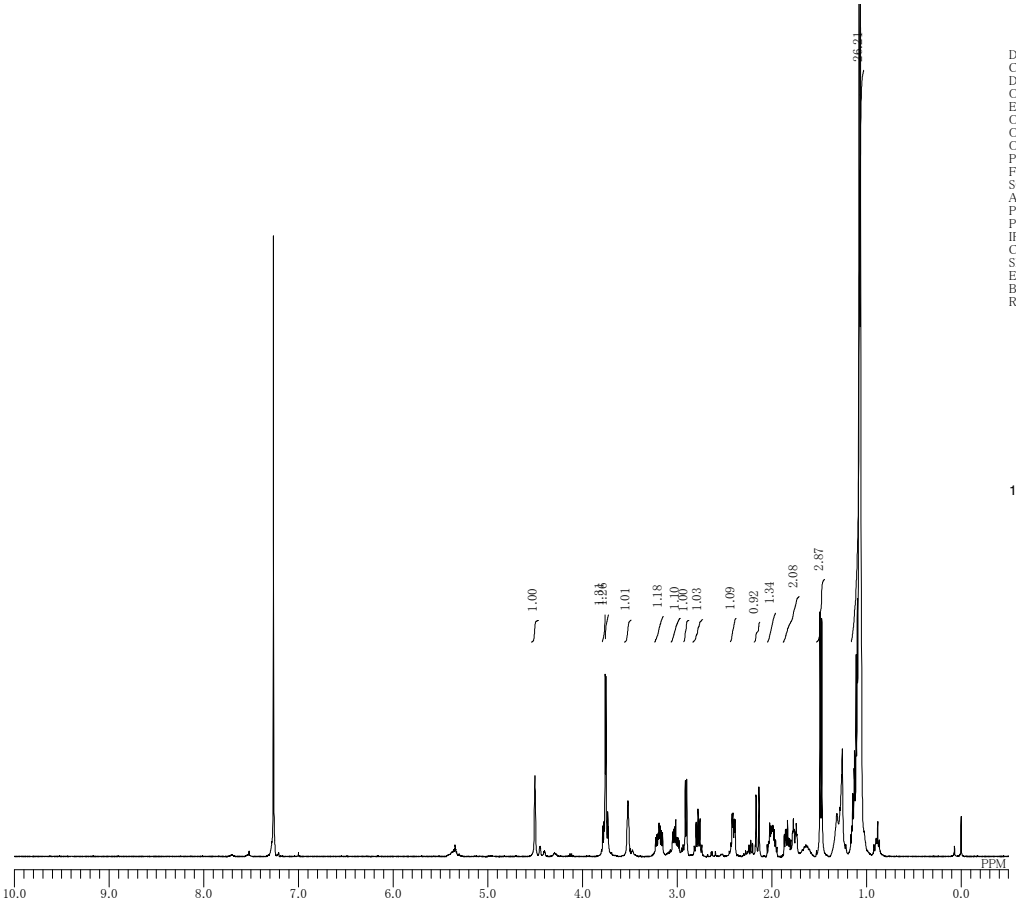


DFILE 40-carbon.als
COMNT
DATIM 07-02-2014 00:22:16
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 10500
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 50

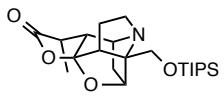


40

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

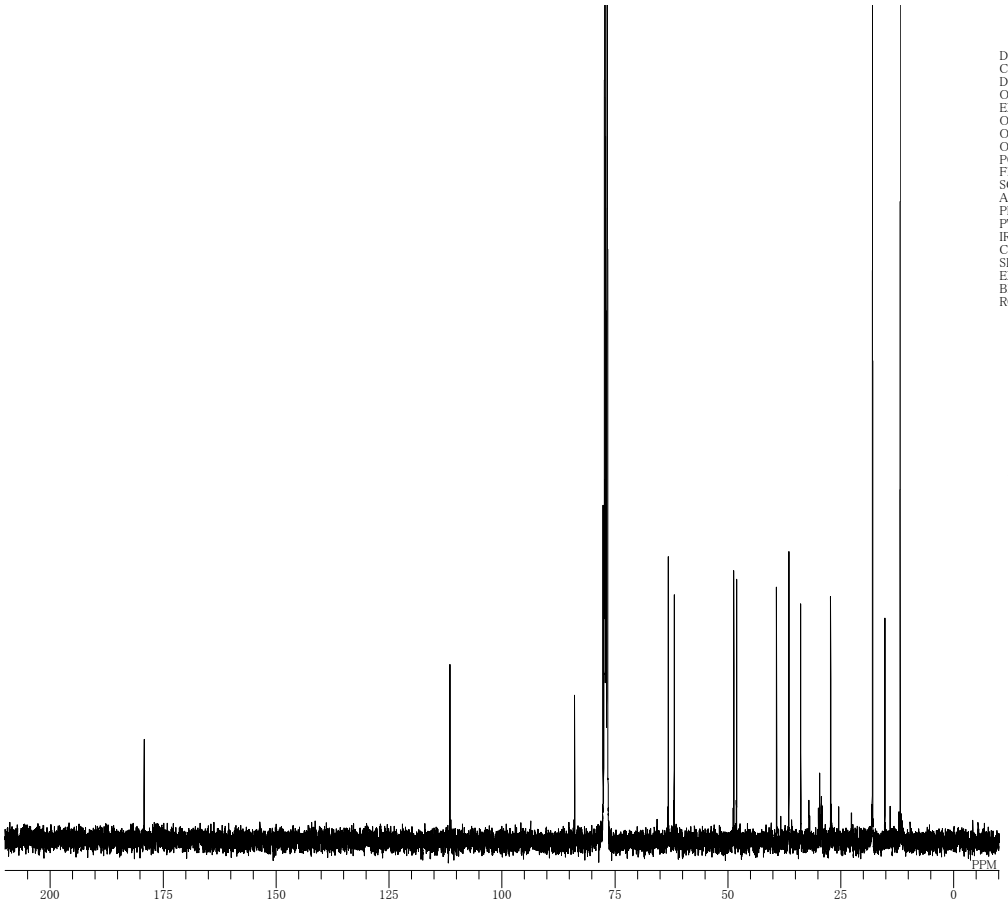


DFILE 41-proton.als
COMNT
DATIM 2014-02-11 18:15:00
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

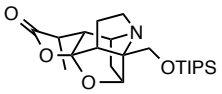


41

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



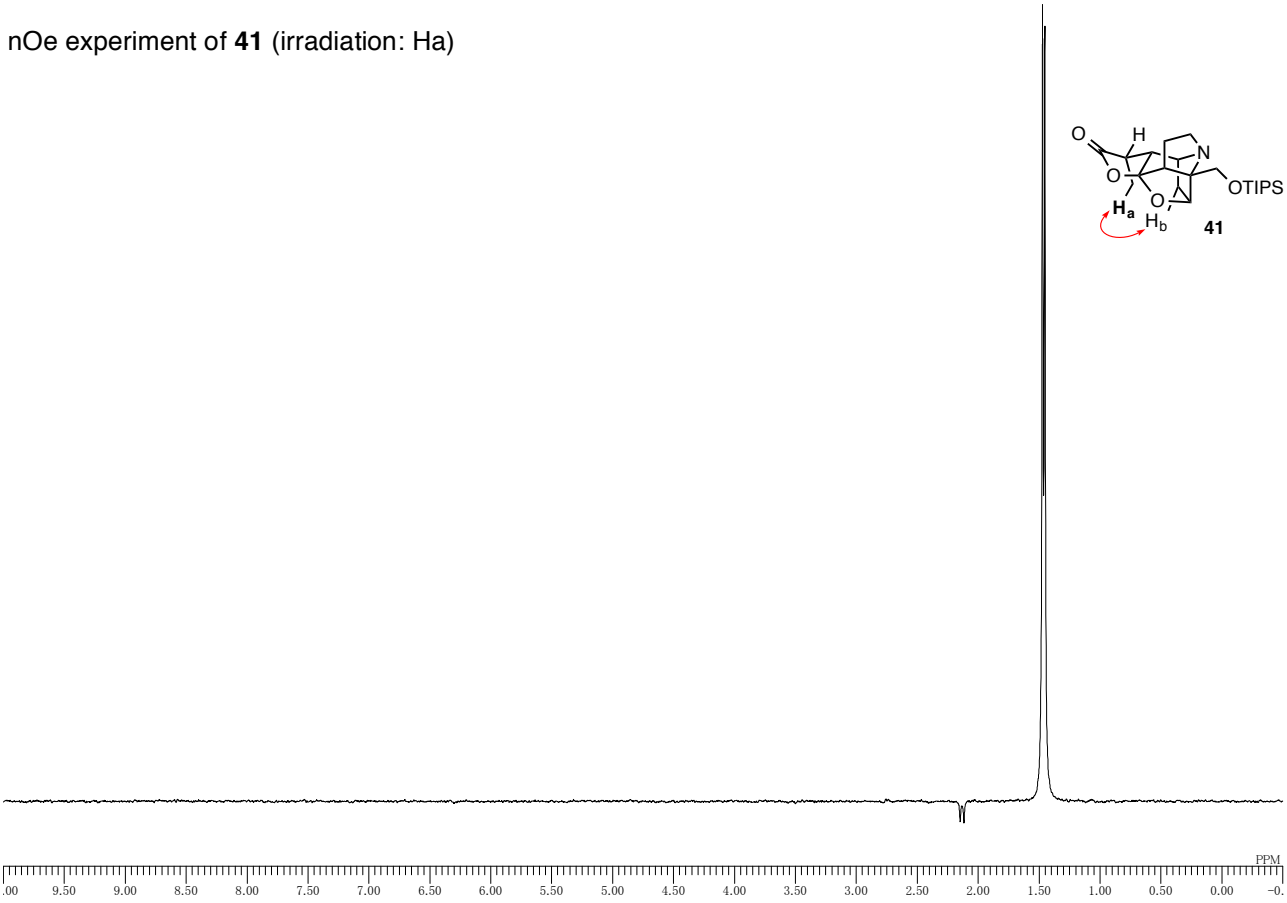
DFILE 41-carbon.als
COMNT
DATIM 11-02-2014 23:31:51
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 10000
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

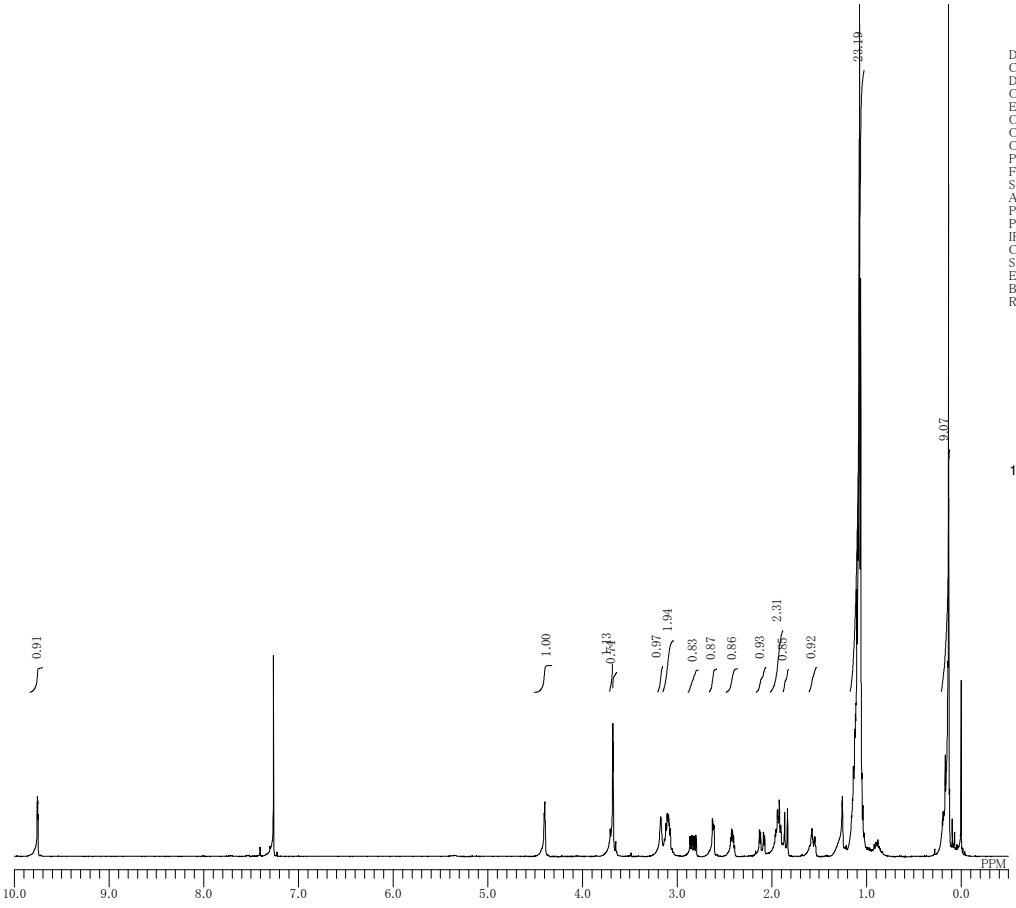


41

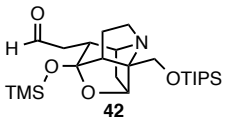
^{13}C NMR (100 MHz) in $CDCl_3$

nOe experiment of **41** (irradiation: Ha)



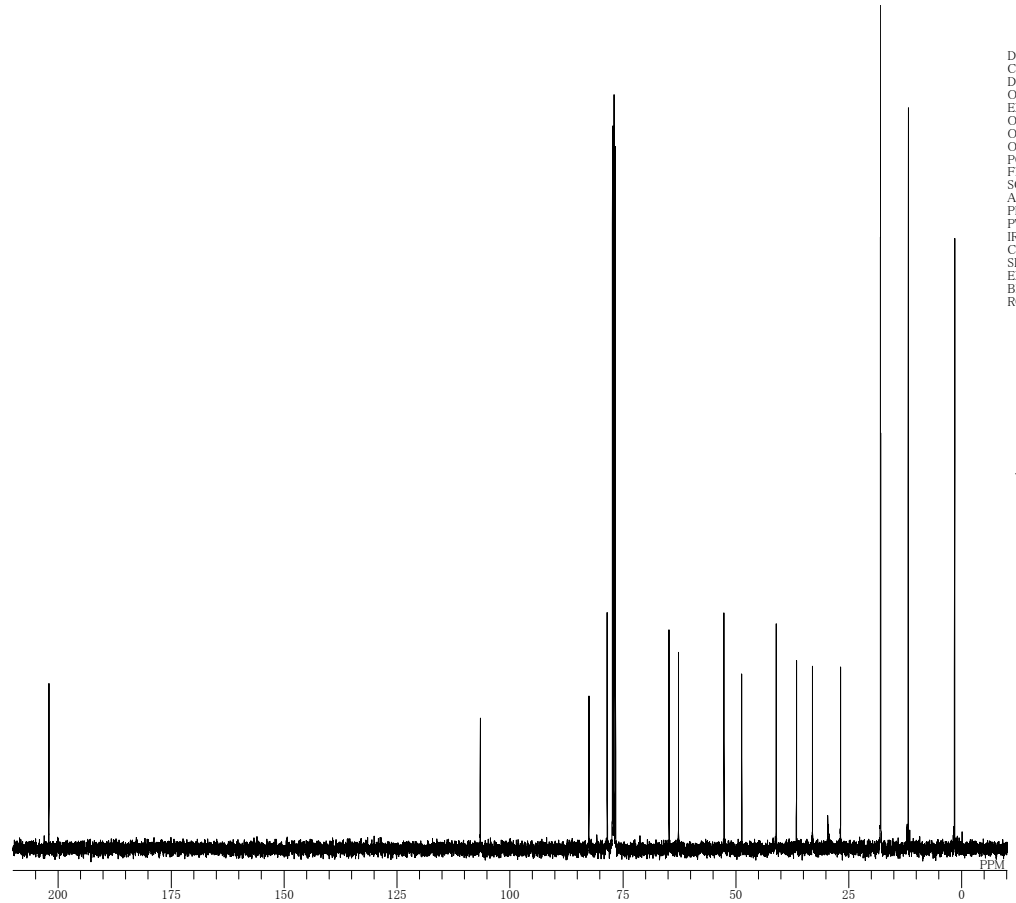


DFILE 42-proton.als
COMNT
DATIM 2014-02-23 17:24:28
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

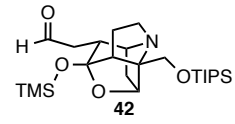


42

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

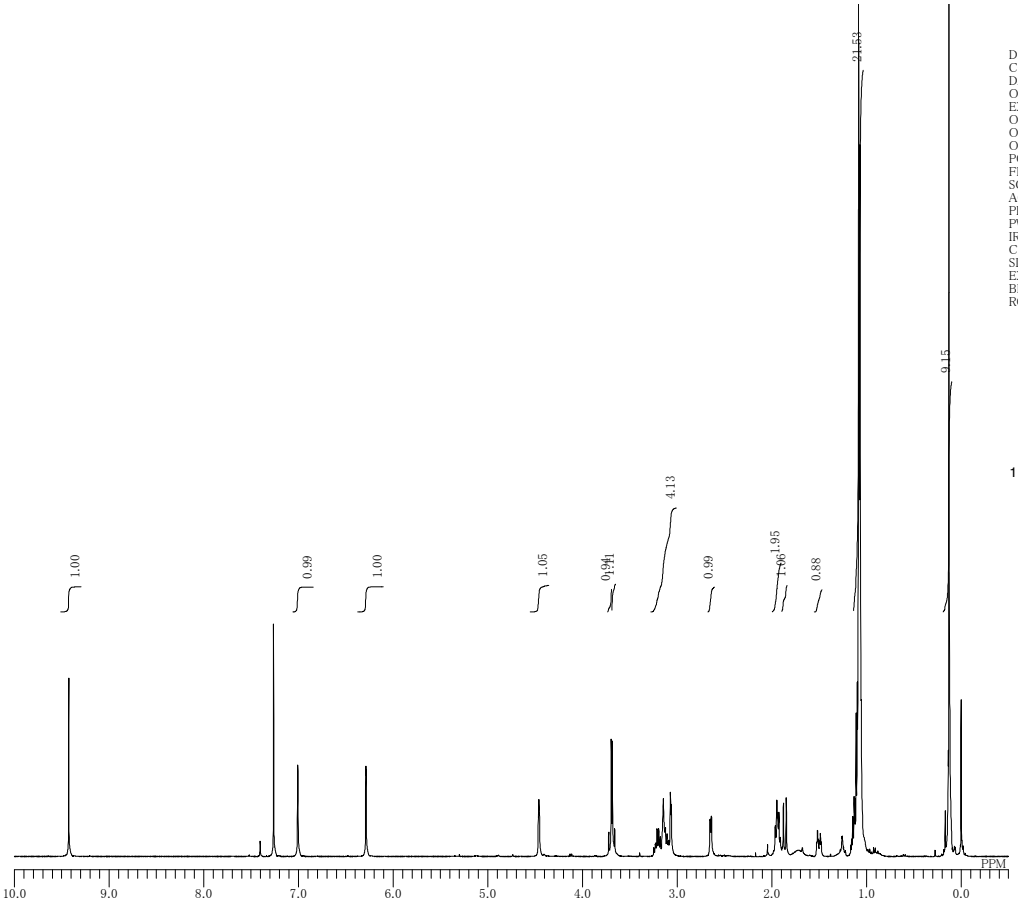


DFILE 42-carbon.als
COMNT
DATIM 21-02-2014 22:45:54
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 384
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

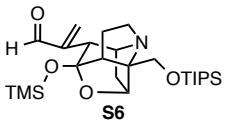


42

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

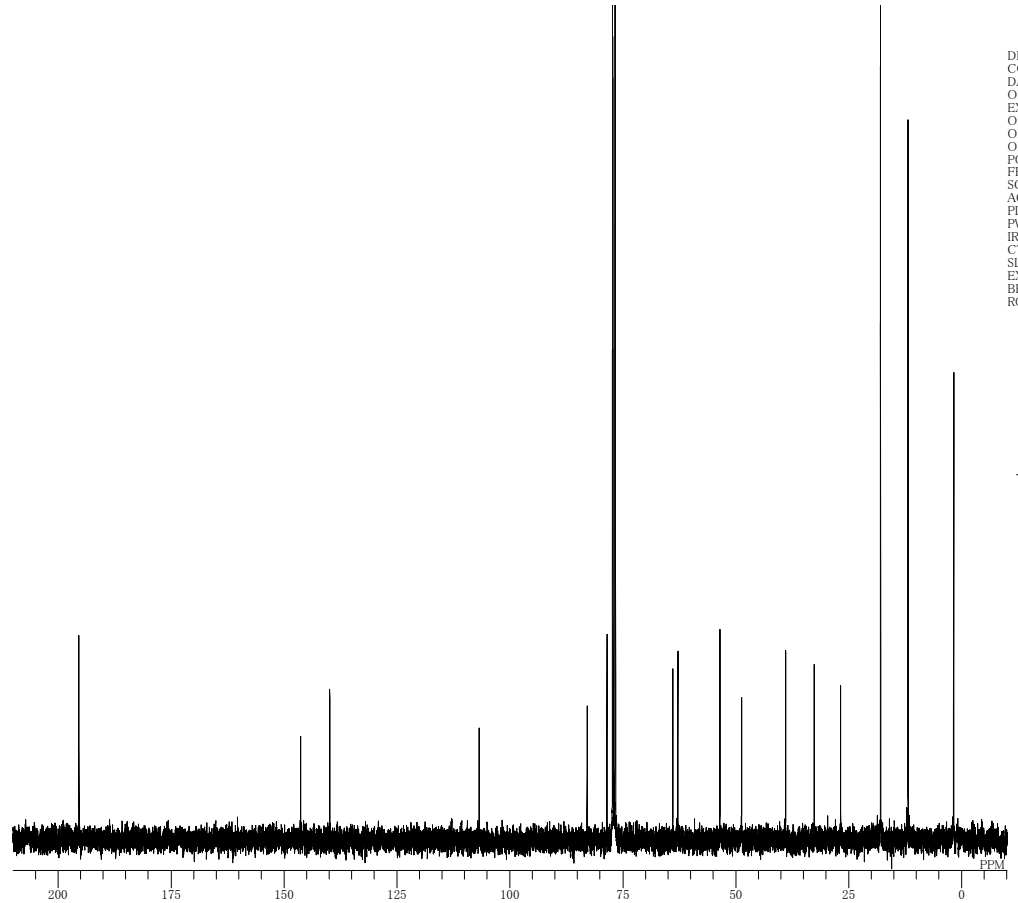


DFILE	S6-proton.als
COMNT	
DATIM	2014-02-27 18:49:23
OBNUC	1H
EXMOD	single_pulse.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	32
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	4.90 usec
IRNUC	1H
CTEMP	24.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

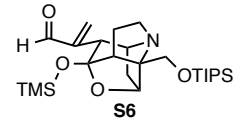


S6

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

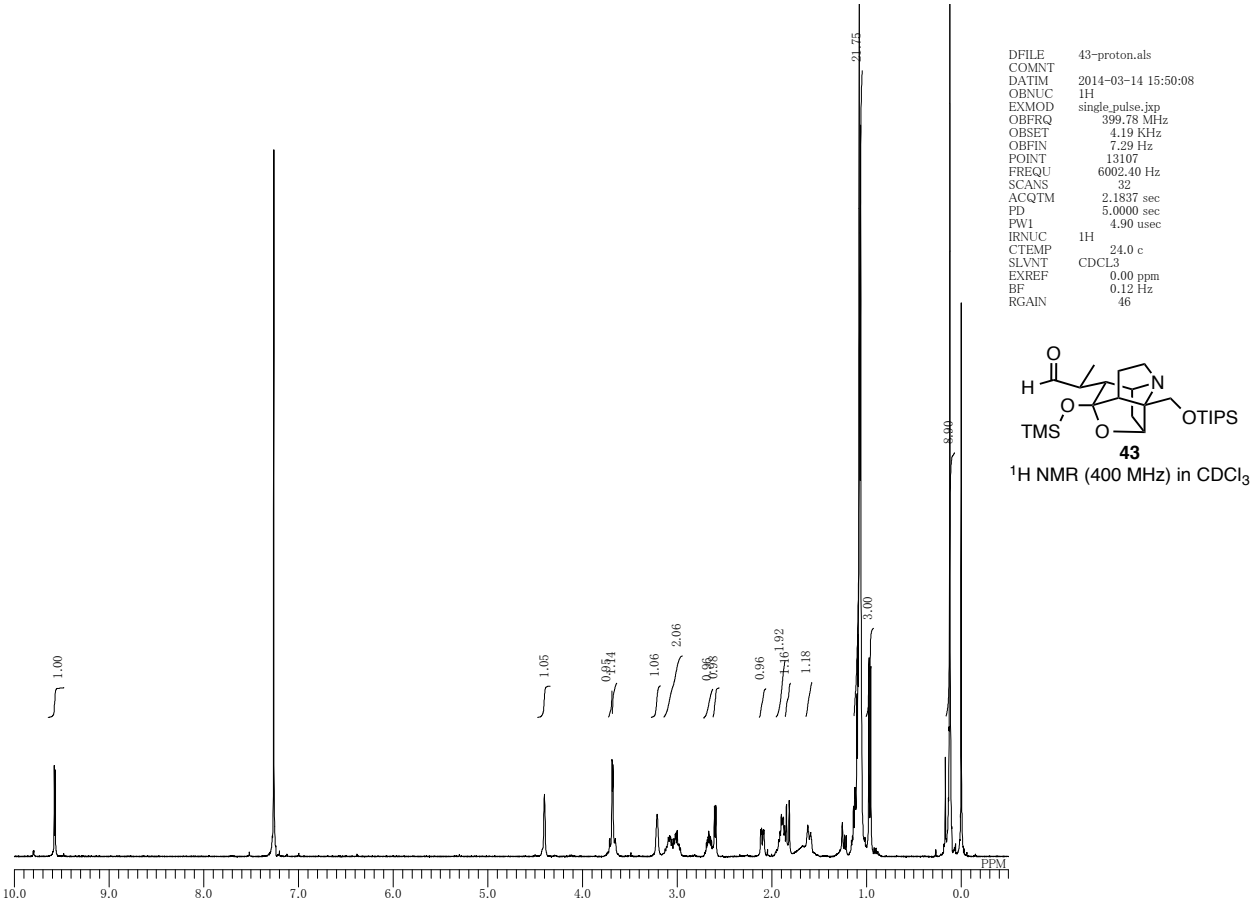


DFILE	S6-carbon.als
COMNT	
DATIM	27-02-2014 23:15:04
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32767
FREQU	31407.04 Hz
SCANS	256
ACQTM	1.0433 sec
PD	1.5000 sec
PW1	2.87 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	50



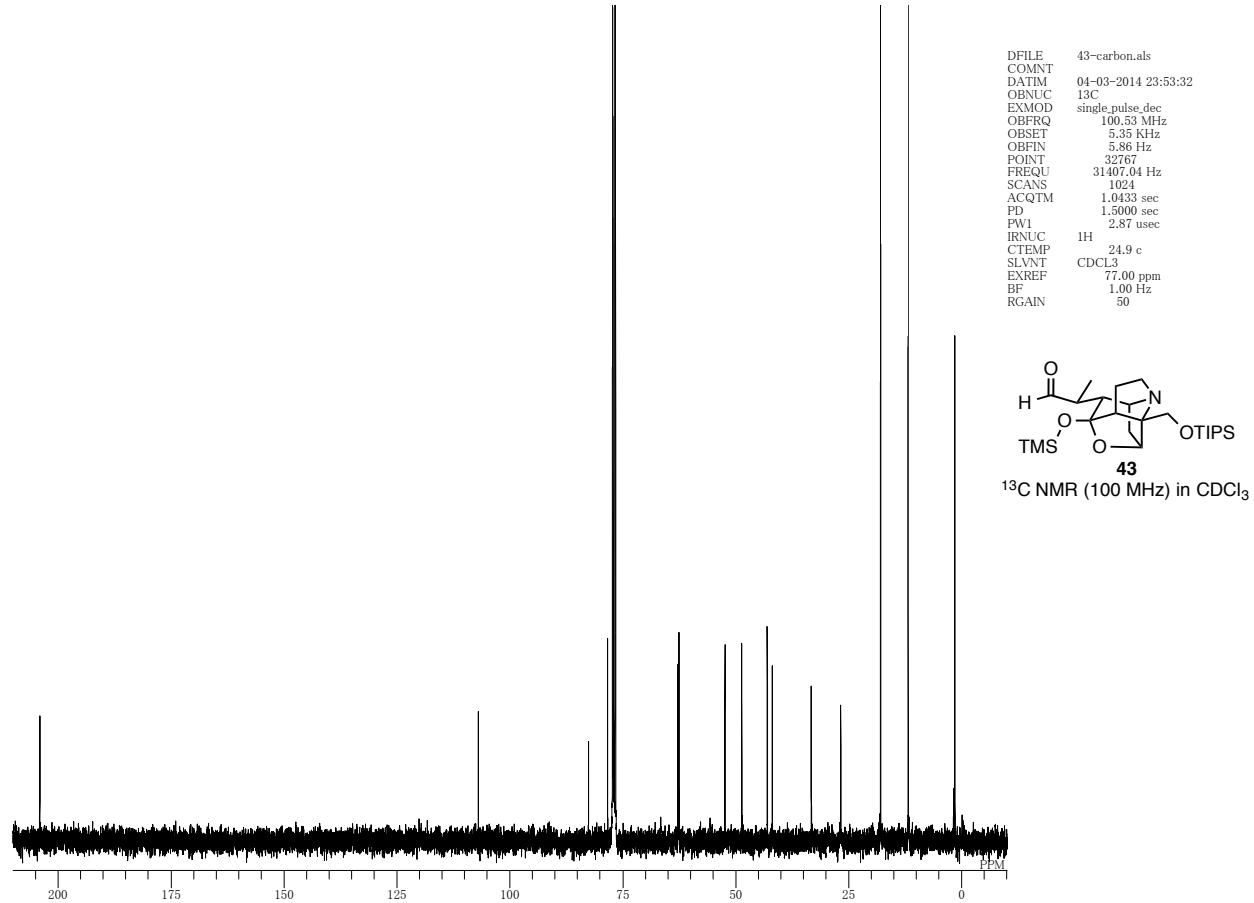
S6

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



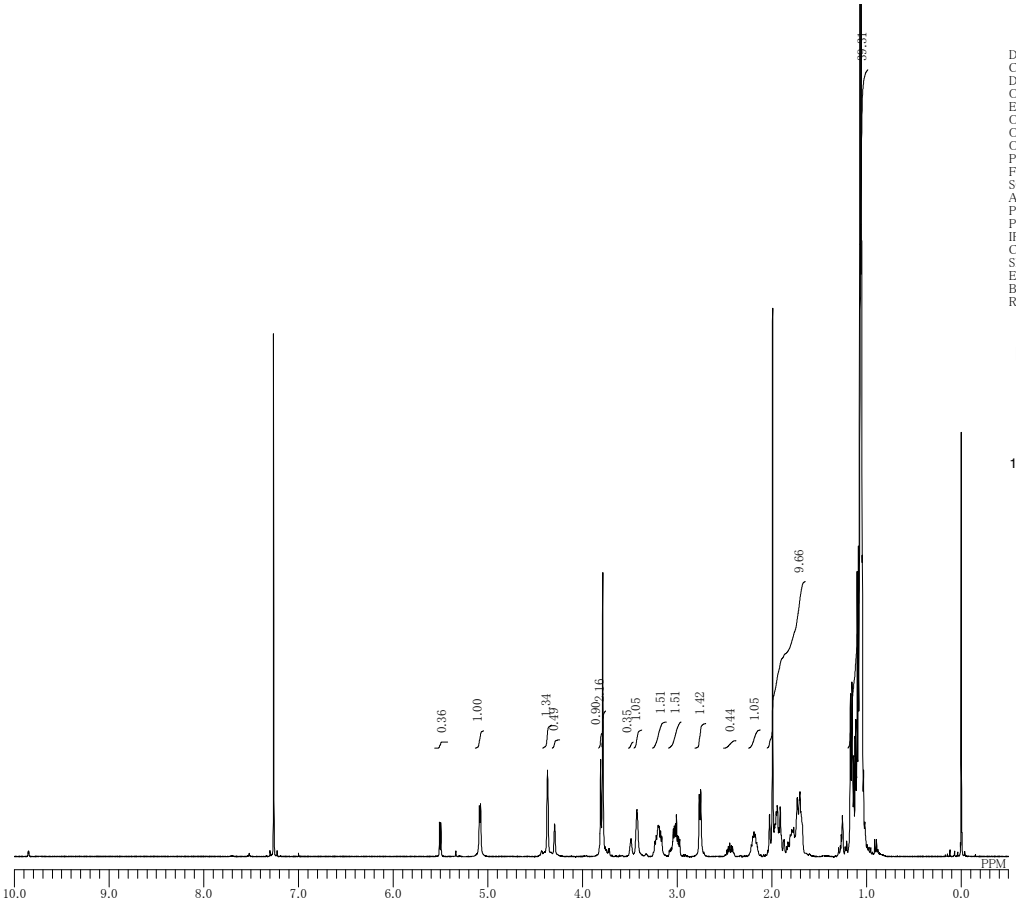
43

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

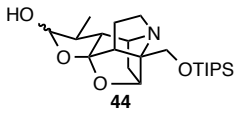


43

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

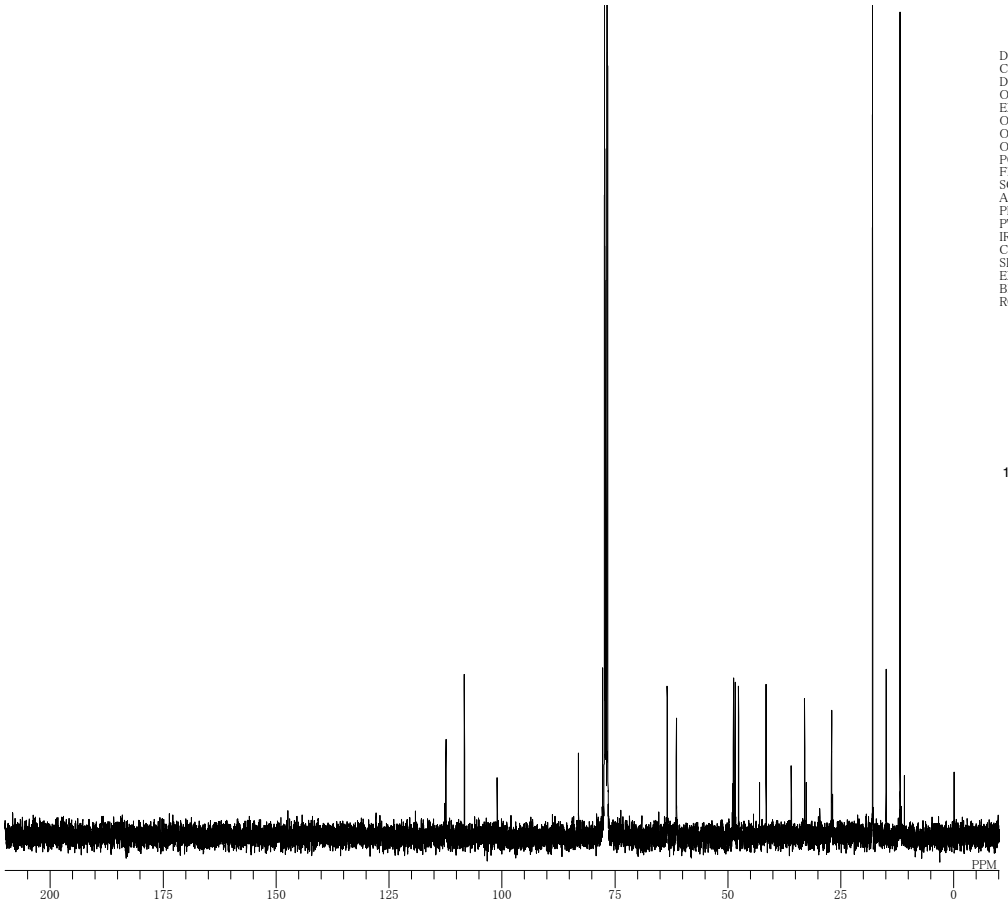


DFILE 44-proton.als
COMNT
DATIM 2014-03-14 18:01:16
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 32
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

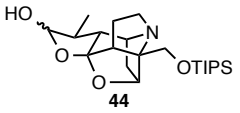


44

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

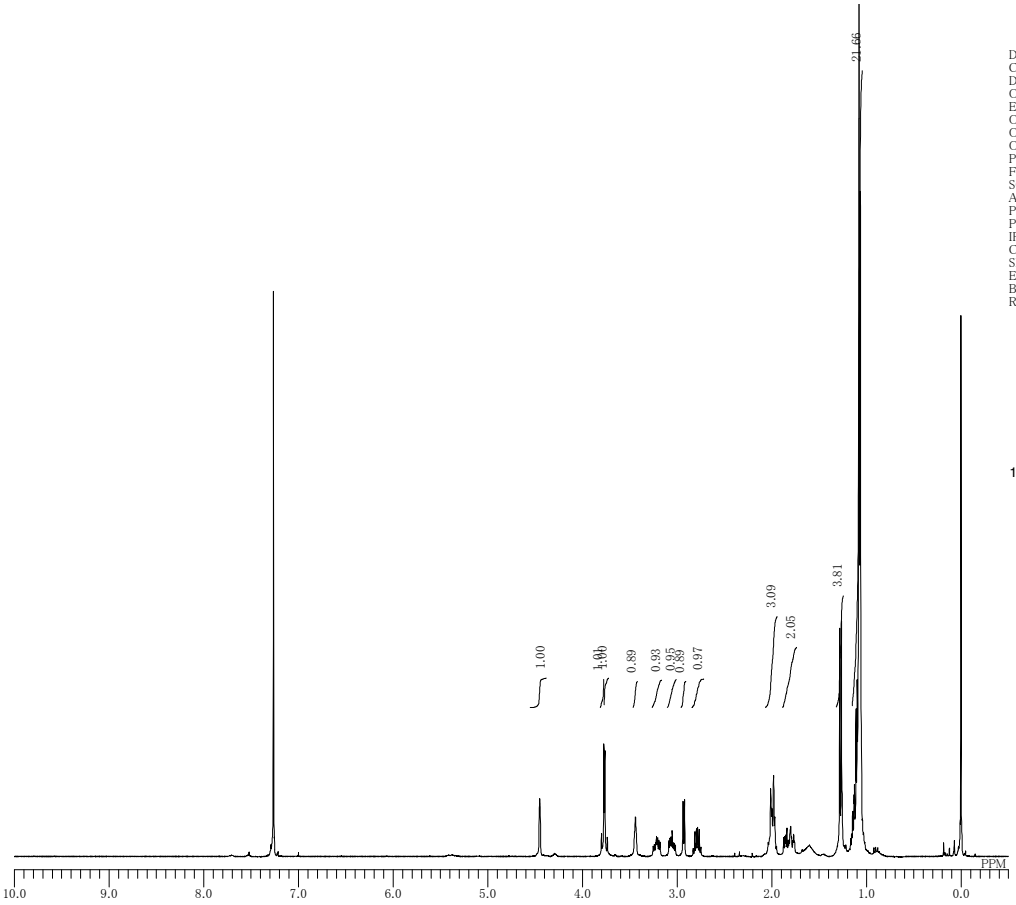


DFILE 44-carbon.als
COMNT
DATIM 17-03-2014 22:29:34
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 3000
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 25.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 50

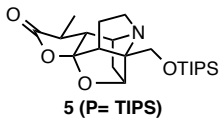


44

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

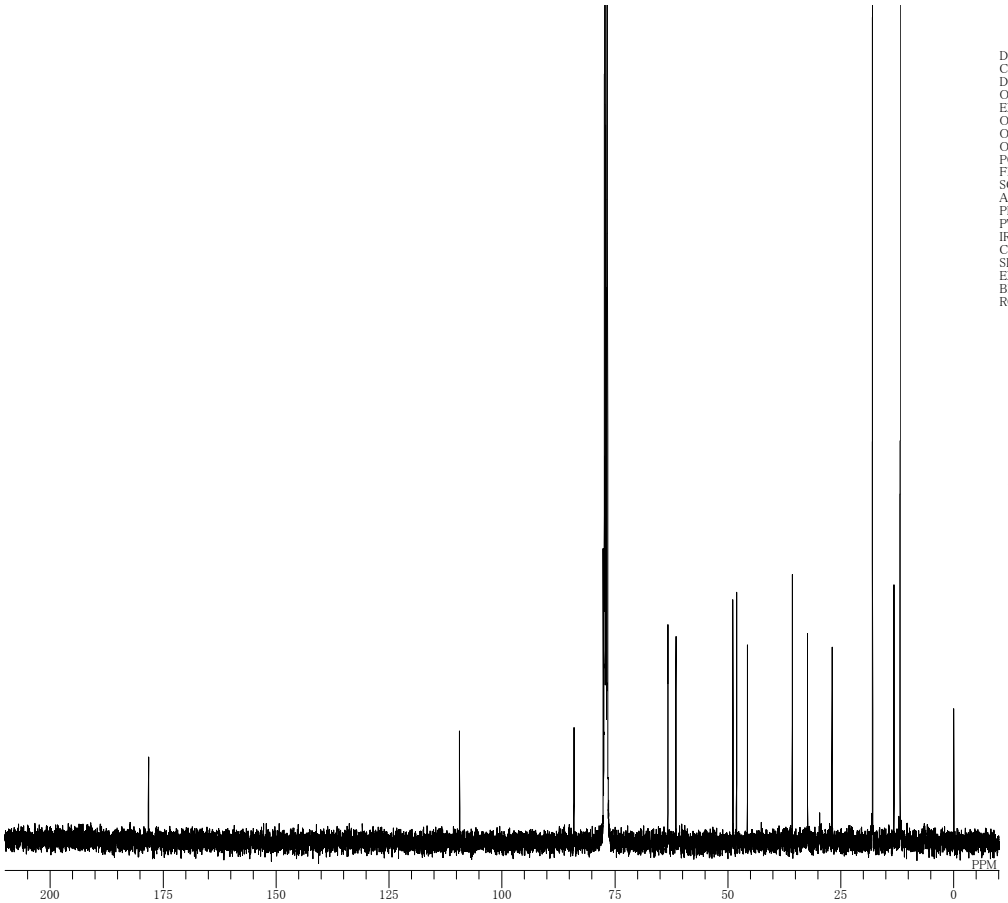


DFILE 5-proton.als
COMNT
DATIM 2014-03-08 16:28:13
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 64
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.90 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46

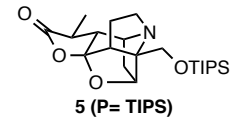


5 (P= TIPS)

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



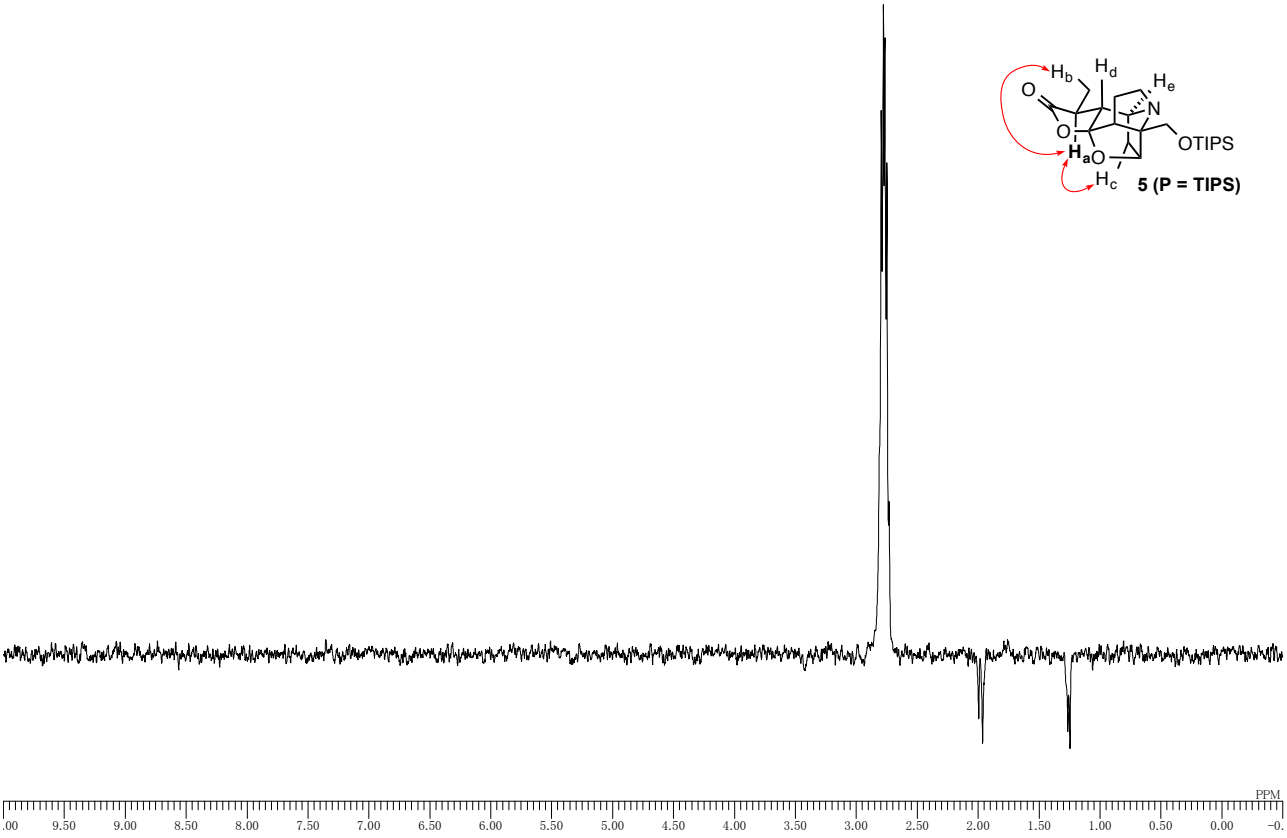
DFILE 5-carbon.als
COMNT
DATIM 11-03-2014 00:07:39
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32767
FREQU 31407.04 Hz
SCANS 12600
ACQTM 1.0433 sec
PD 1.5000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 50



5 (P= TIPS)

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

nOe experiment of **5 (P = TIPS)** (irradiation: Ha)



nOe experiment of **5 (P = TIPS)** (irradiation: Hb)