Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Directed Studies Towards The Total Synthesis of (+)-13-Deoxytedanolide: Simple and Convenient Synthesis of C8-C16 fragment

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Usual procedures

All reagents were obtained from commercial sources and used as supplied unless otherwise stated. Anhydrous THF, Et_2O, Toluene and CH_2Cl_2 were obtained from a MBraun® SPS-800 solvent purification system. Light petroleum refers to the fraction of petrol ether that was distilled between 40 °C and 65 °C.

The reactions were magnetically stirred and monitored by TLC, which were performed on Merck® 60F254 plates and achieved under a 254 nm UV ligh, visualized with an aqueous solution of potassium permanganate or an ethanolic solution of molybdophosphoric acid, followed by treatment with a heat gun.

Flash chromatography was performed with Merck® Kieselgel 60 (230-400) mesh silica gel.

Physical data and spectroscopic measurements

NMR data were recorded on a Bruker Avance 300 and 400 spectrometer in C_6D_6 or $CDCl_3$ and chemical shifts (δ) were given in ppm relative to the residual non-deutered solvent signal for ^1H NMR (C_6D_6: 7.16 ppm), ($CDCl_3$: 7.26 ppm) and relative to the deutered solvent signal for ^{13}C NMR (C_6D_6: 128.06 ppm), ($CDCl_3$: 77.16 ppm); coupling constants (*J*) are in Hertz, and the classical abbreviations are used to describe the signal multiplicity (s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, dd = doublet of doublets, dt = doublets of triplets, br = broad, etc..). NMR Spectra were assigned using information ascertained from DEPT, HMQC and NOE experiments.

High resolution mass spectra (HRMS) have been performed using a mass spectrometer equipped with pneumatically assisted atmospheric pressure ionization. The sample was ionized in positive mode electrospray in the following conditions: electrospray voltage (ISV): 5500 V; orifice voltage (OR): 70 V; nebulising gas flow pressure (air): 0.6 psi. The mass spectrum was obtained using a time of flight analyzer (TOF). The measure was realized in triplicate. The sample was dissolved in methanol (500 µL) then diluted (dilution factor 4/10000) in a methanolic solution of ammonium acetate (3 mM). The sample solution was infused in the ionization source at a 5 µL/min flow rate.

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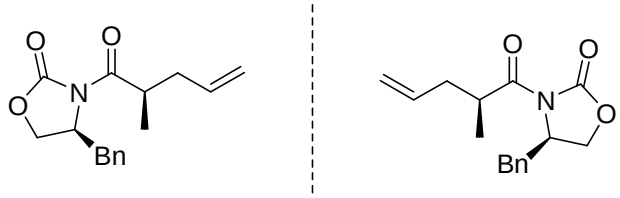
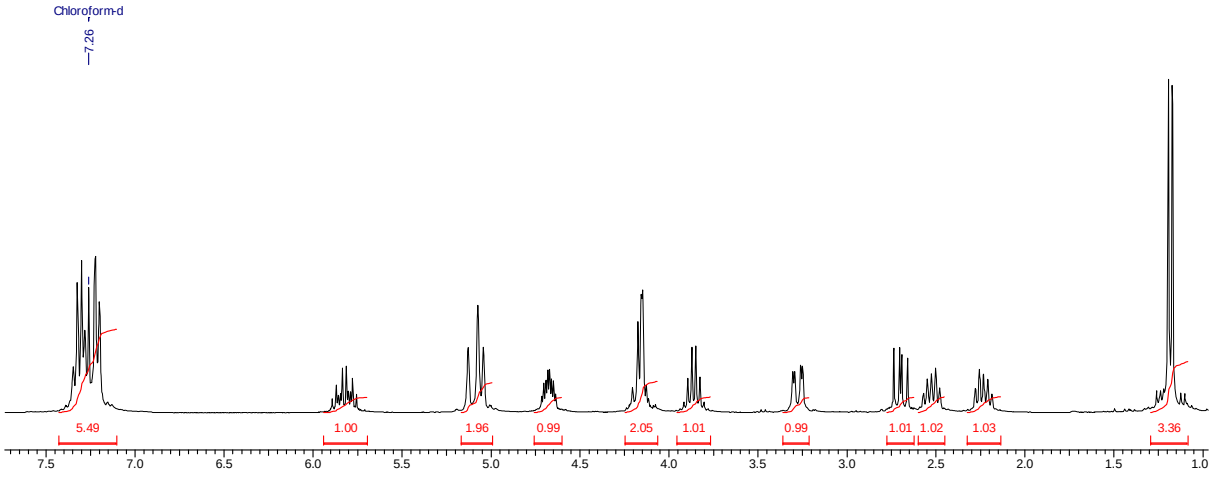


(*S*)-**14** (*R*)-**14**

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 2.19-2.28 (1H, m, C*H*$_2$),), 2.48-2.57 (1H, m, C*H*$_2$), 2.69 (1H, dd, *J* = 13.4 and 9.8 Hz, C*H*$_2$), 3.27 (1H, dd, *J* = 13.4 and 3.2 Hz, C*H*$_2$), 3.36 (1H, m, *J* = 6.8 Hz, C*H*), 4.11-4.21 (2H, m, C*H*$_2$), 4.64-4.71 (1H, m, C*H*), 5.04-5.13 (2H, m, C*H*$_2$), 5.76-5.89 (m, 1H, C*H*), 7.20-7.35 (5H, m, C*H*$_{Ar}$); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 16.5 (CH_3), 37.2 (CH), 38.0 (CH_2), 38.1 (CH_2), 55.4 (CH), 66.1 (CH_2), 117.3 (CH_2), 127.4 (CH_{Ar}), 129.0 (2 x CH_{Ar}), 129.5 (2 x CH_{Ar}), 135.4 (CH), 135.5 (C_{Ar}), 153.2 (C), 176.6 (C); (*S*)-**14** $[\alpha]^{19}_{D}$ = +38.0 (*c* 1, $CHCl_3$); (*R*)-**14** $[\alpha]^{19}_{D}$ = -39.0 (*c* 1, $CHCl_3$)



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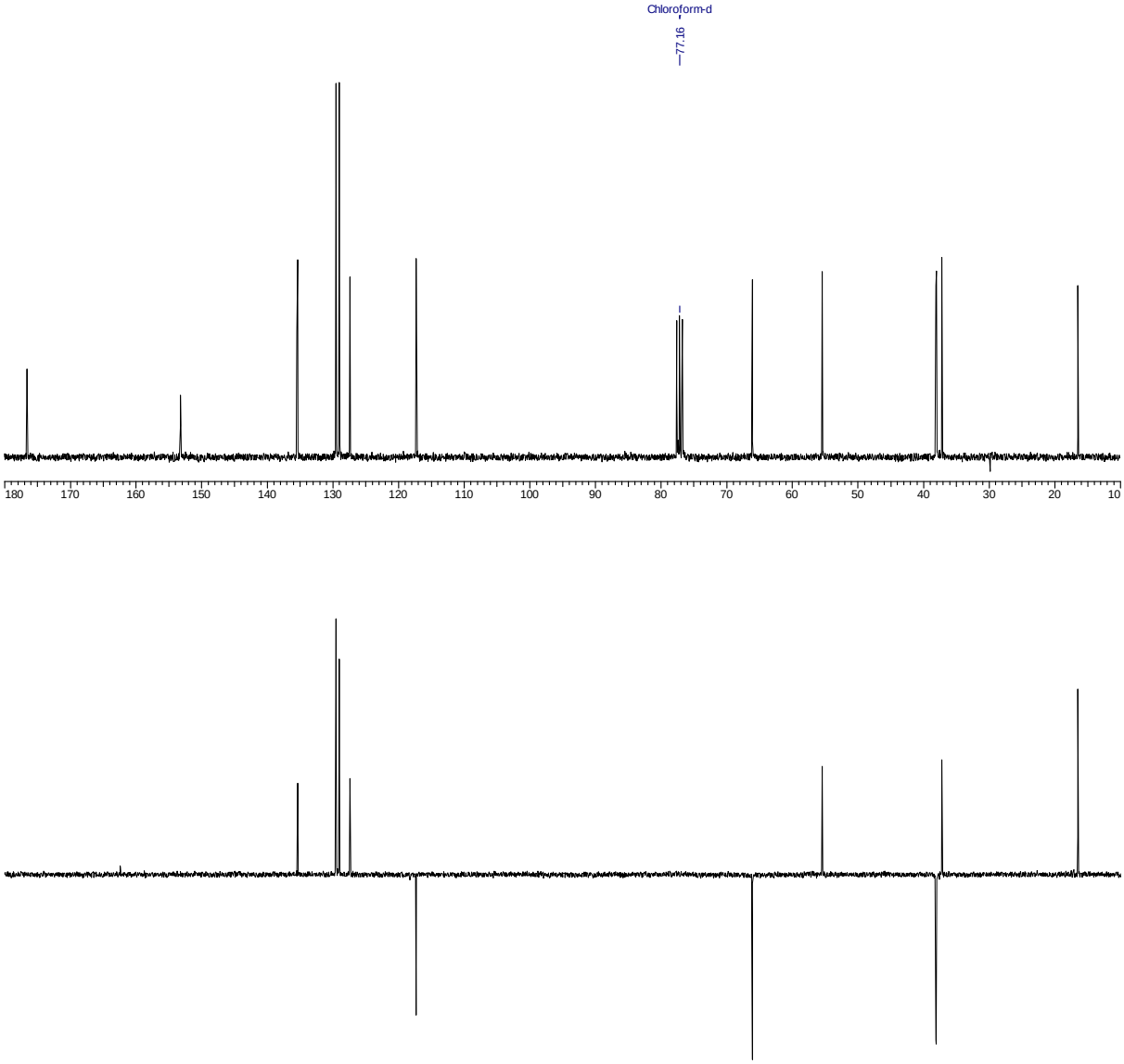

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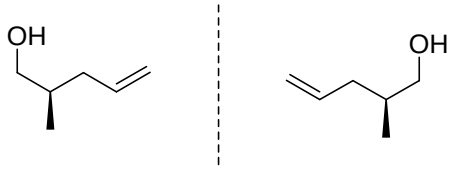
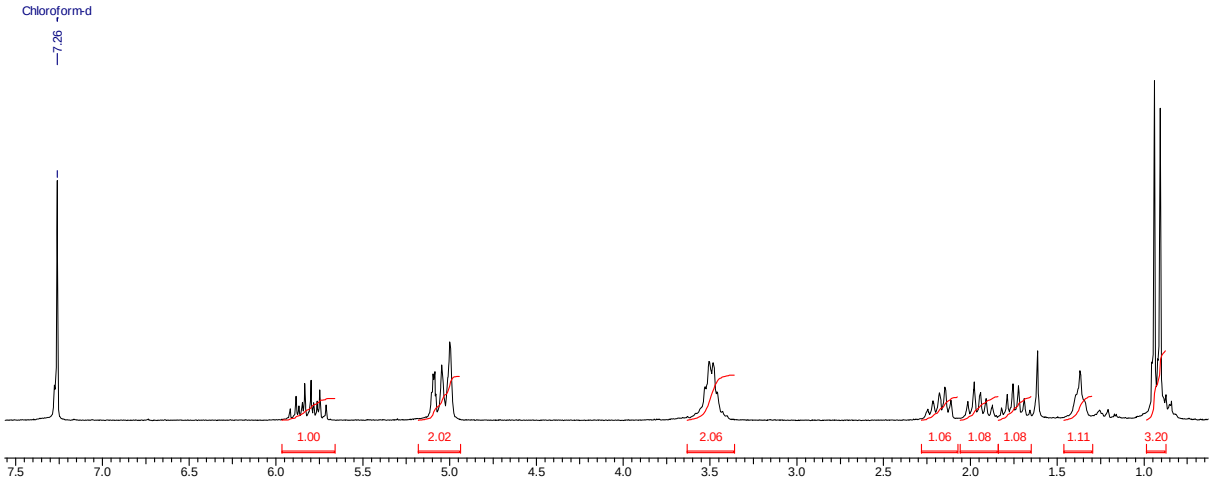
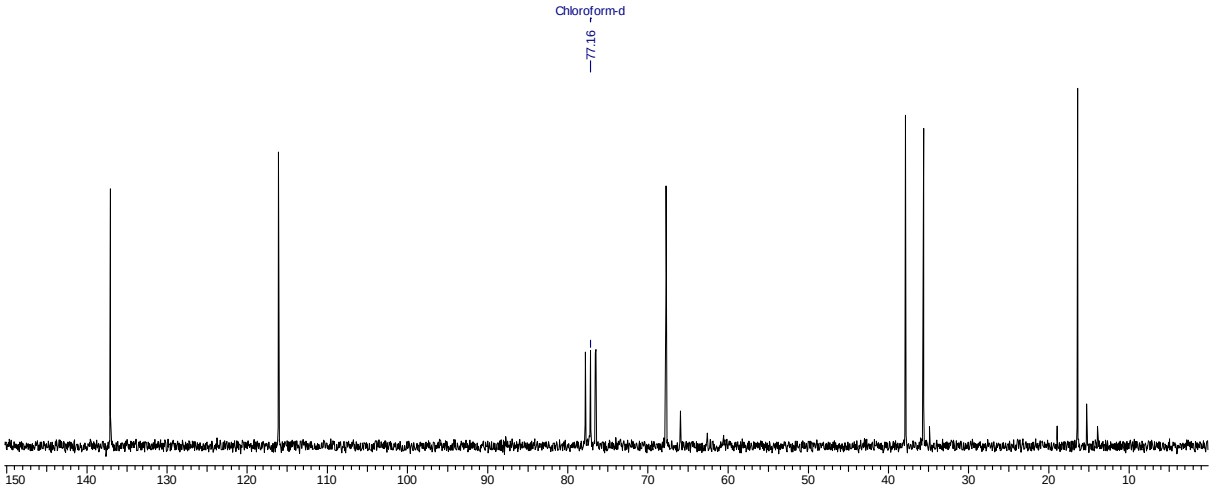


(*S*)-**15** (*R*)-**15**

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (3H, d, *J* = 6.7 Hz, C*H*$_3$), 1.37 (1H, br s, O*H*), 1.65-1.82 (1H, m, C*H*), 1.87-2.01 (1H, m, C*H*$_2$), 2.11-2.25 (1H, m, C*H*$_2$), 3.40-3.55 (2H, m, C*H*$_2$), 4.99-5.09 (2H, m, C*H*$_2$), 5.71-5.92 (m, 1H, C*H*), **^{13}C NMR** (50 MHz, $CDCl_3$) δ 16.4 (CH_3), 35.6 (CH), 37.9 (CH_2), 67.7 (CH_2), 116.1 (CH_2), 137.1 (CH); (*R*)-**15** $[\alpha]^{19}_{D}$ = +4.3 (*c* 1, $CHCl_3$); (*S*)-**15** $[\alpha]^{24}_{D}$ = -2.6 (*c* 1, $CHCl_3$)





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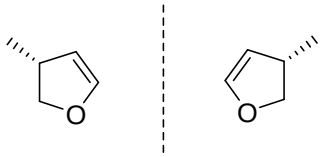
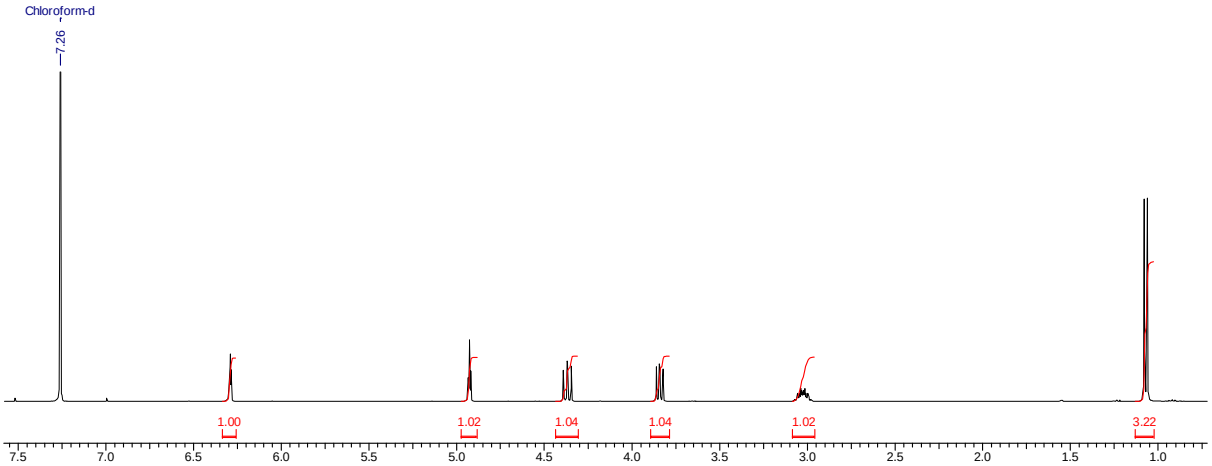
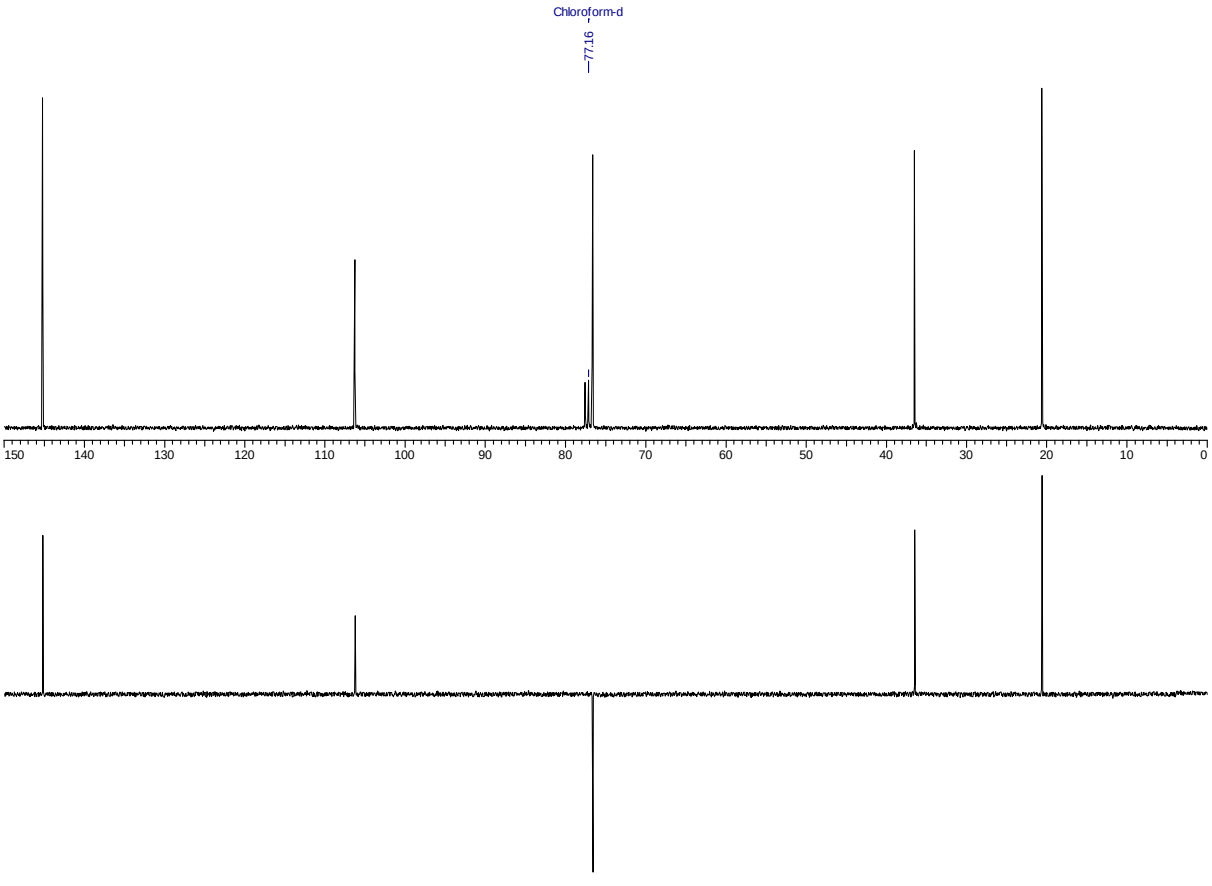


(*S*)-**12** (*R*)-**12**

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (3H, d, J = 6.8 Hz, CH_3), 2.98-3.07 (1H, m, CH), 3.85 (1H, dd, J = 8.8 and 6.8 Hz, CH_2), 4.37 (1H, dd, J = 9.8 and 8.8 Hz, CH_2), 4.93 (1H, t, J = 2.5 Hz, CH), 6.29 (1H, t, J = 2.5 Hz, CH); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 20.6 (CH_3), 36.5 (CH), 76.7 (CH_2), 106.3 (CH), 145.2 (CH).





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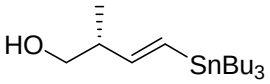

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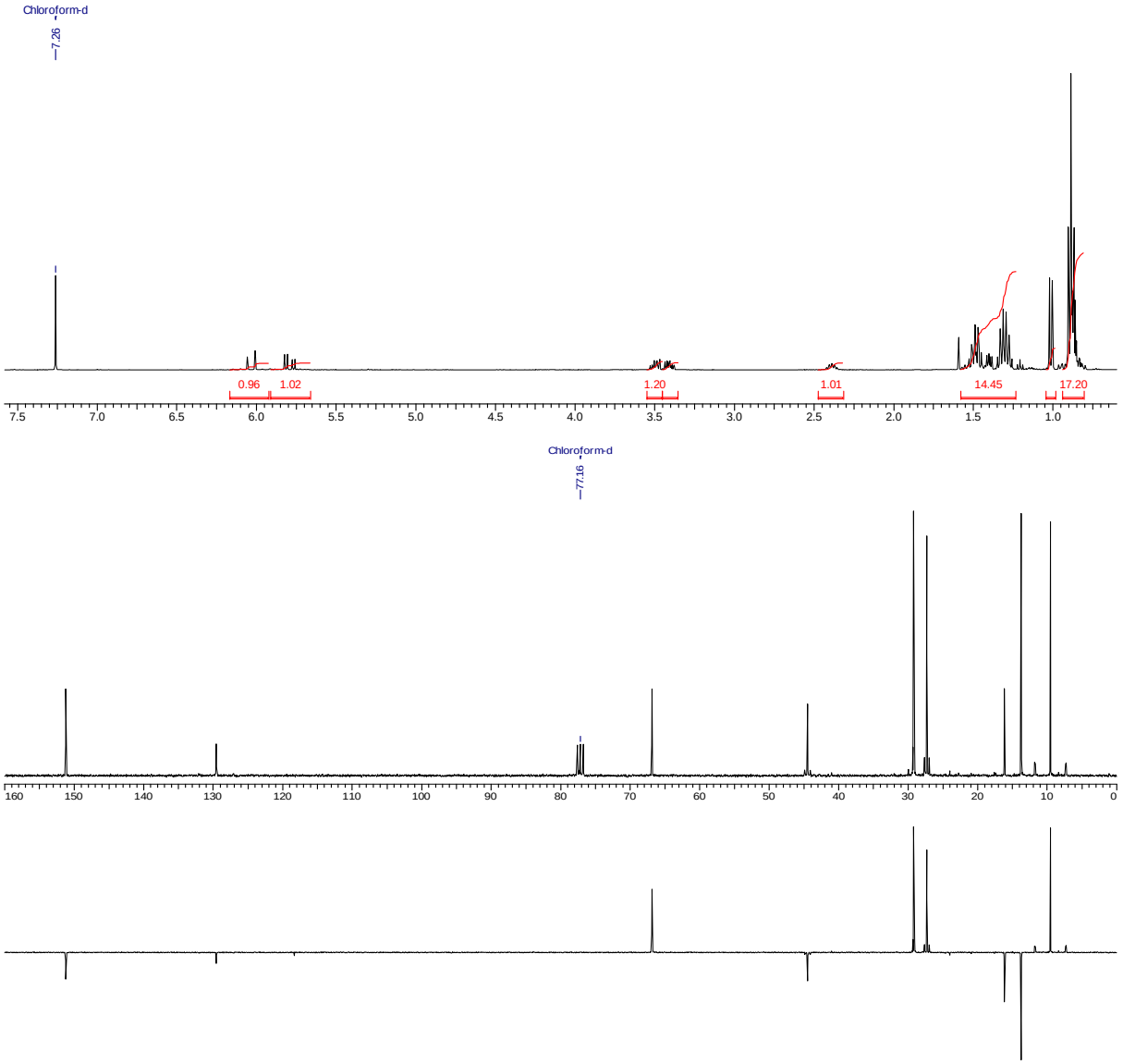
[α]$^{24}_{D}$ +21.4, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.84-0.90 (15H, m, 3 x C*H*$_3$ and 3 x C*H*$_2$), 1.02 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 1.24-1.53 (12H, m, 6 x C*H*$_2$), 2.34-2.44 (1H, m, C*H*), 3.38-3.44 (1H, m, C*H*$_2$), 3.47-3.53 (1H, m, C*H*$_2$), 5.79 (1H, dd, *J* = 19.0 and 7.0 Hz, $^{3}J_{Sn\text{-}H}$ = 70 Hz, C*H*), 5.99 (1H, br d, *J* = 19.0 Hz, $^{2}J_{Sn\text{-}H}$ = 18 Hz, C*H*); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 9.5 (3 x CH_2, $^{1}J_{Sn\text{-}C}$ = 334 Hz), 13.4 (3 x CH_3), 16.1 (CH_3), 27.3 (3 x CH_2, $^{3}J_{Sn\text{-}C}$ = 54 Hz), 29.2 (3 x CH_2, $^{2}J_{Sn\text{-}C}$ = 21 Hz), 44.5 (CH, $^{3}J_{Sn\text{-}C}$ = 57 Hz), 66.9 (CH_2), 129.5 (C3, CH, $^{2}J_{Sn\text{-}C}$ = 23 Hz), 151.2 (CH); **IR** (thin film) ν_{max} = 3325, 2956, 2923, 2871, 2852, 1597, 1455, 1376, 1072, 1031, 990 cm^{-1}; **LRMS** *m/z* (ESI) 399.$(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{17}H_{37}OSn$ $[M+H]^+$: 377.1860, found 377.1861.



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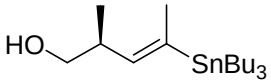

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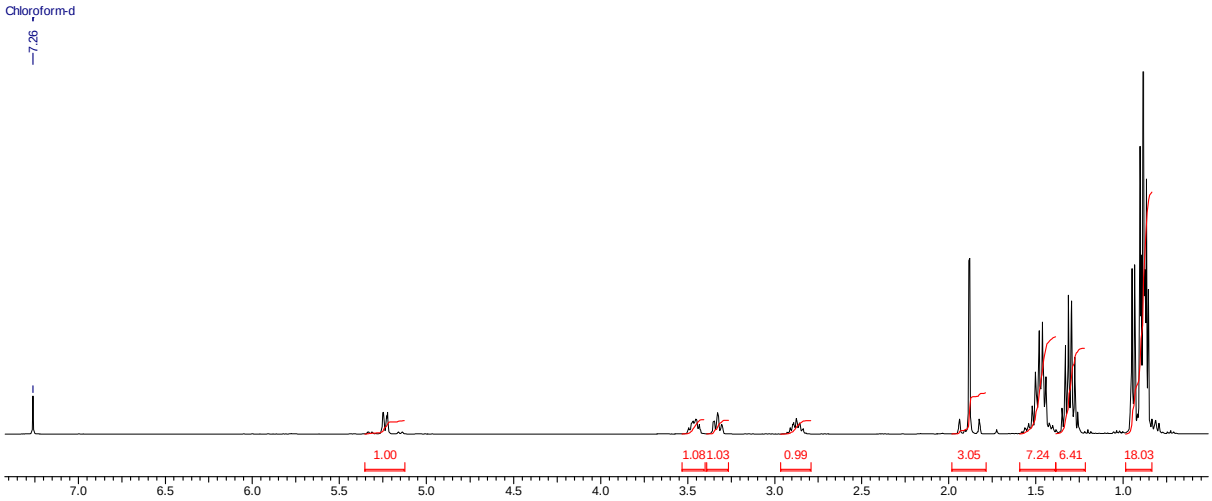
[α]$^{21}_{D}$ -31.8 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.84-0.98 (18H, 4 x CH_3 and 3 x CH_2), 1.16-1.56 (12H, m, 6 x CH_2), 1.88 (3H, d, *J* = 1.9 Hz, $^{3}J_{Sn\text{-}H}$ = 44Hz, CH_3), 2.77-2.99 (1H, m, C*H*), 3.30-3.36 (1H, m, CH_2), 3.43-3.50 (1H, m, CH_2), 5.23 (1H, dq, *J* = 9.0 and 1.9 Hz, $^{3}J_{Sn\text{-}H}$ = 70 Hz, C*H*); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 9.3 (3 x CH_2, $^{1}J_{Sn\text{-}C}$ = 322 Hz), 13.8 (3 x CH_3), 16.9 (CH_3), 19.7 (CH_3), 27.5 (C9, 3 x CH_2, $^{3}J_{Sn\text{-}C}$ = 54 Hz), 29.3 (3 x CH_2, $^{2}J_{Sn\text{-}C}$ = 20 Hz), 35.3 (CH_3, $^{3}J_{Sn\text{-}C}$ = 53 Hz), 67.7 (CH_2), 141.2 (C), 143.1 (CH, $^{2}J_{Sn\text{-}C}$ = 24 Hz); **IR** (thin film) ν_{max} = 3330, 2955, 2924, 2871, 2850, 1456, 1377, 1071, 1030, 970 cm^{-1}; **HRMS** (ESI) *m/z* calcd for $C_{18}H_{39}OSn$ $[M+H]^+$: 391.2017, found 391.2017.



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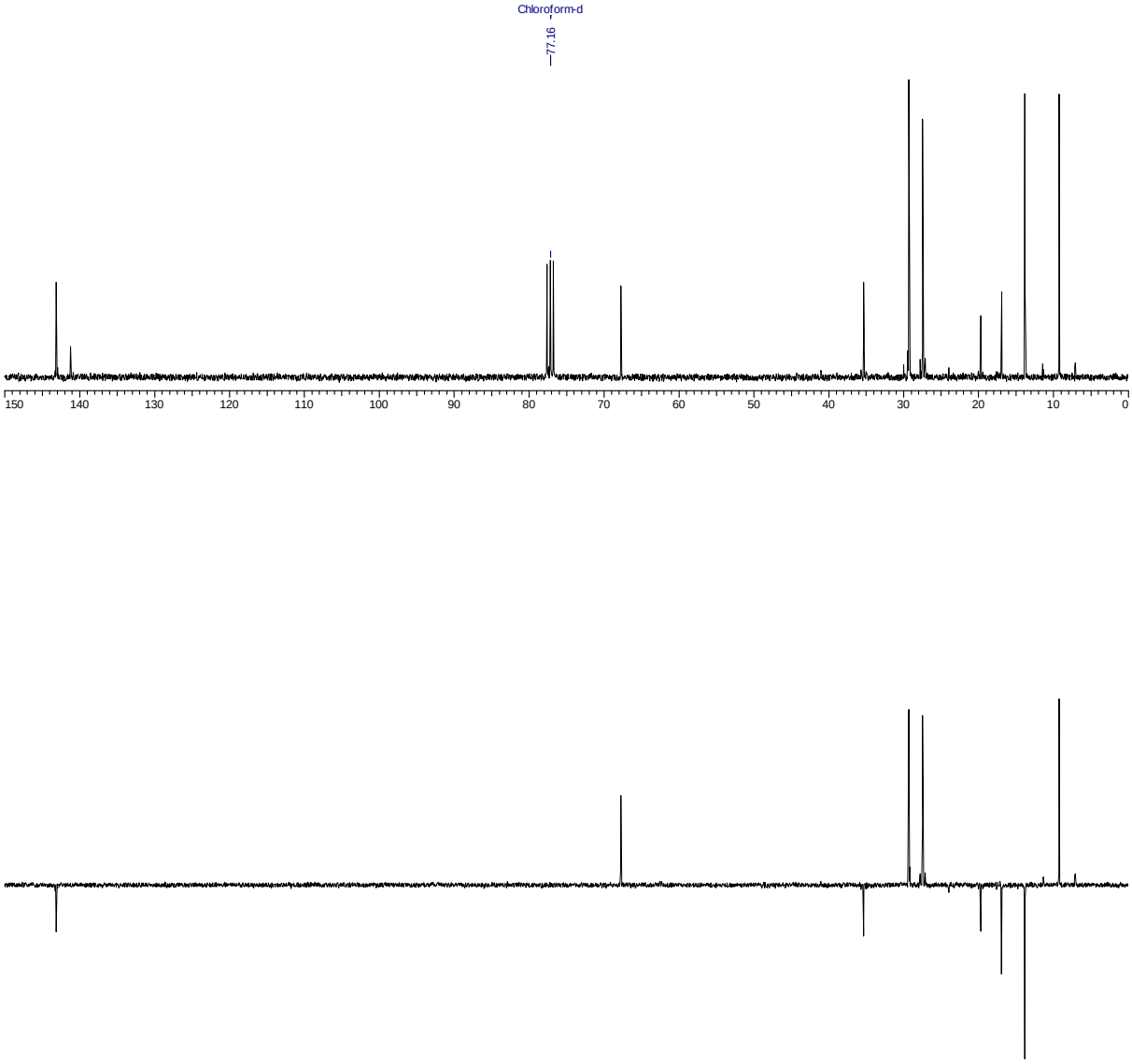

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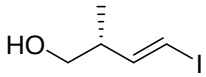

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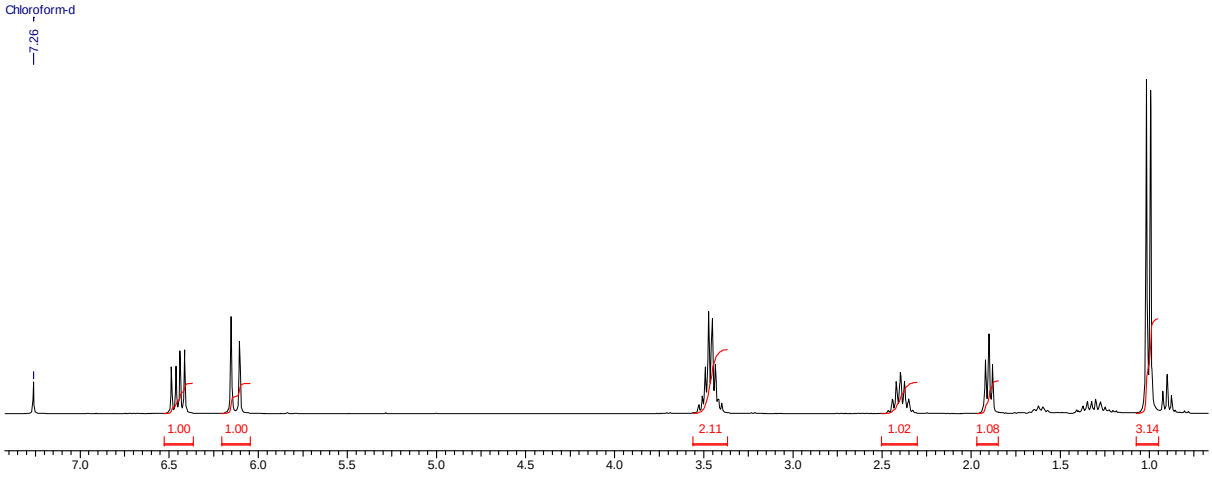
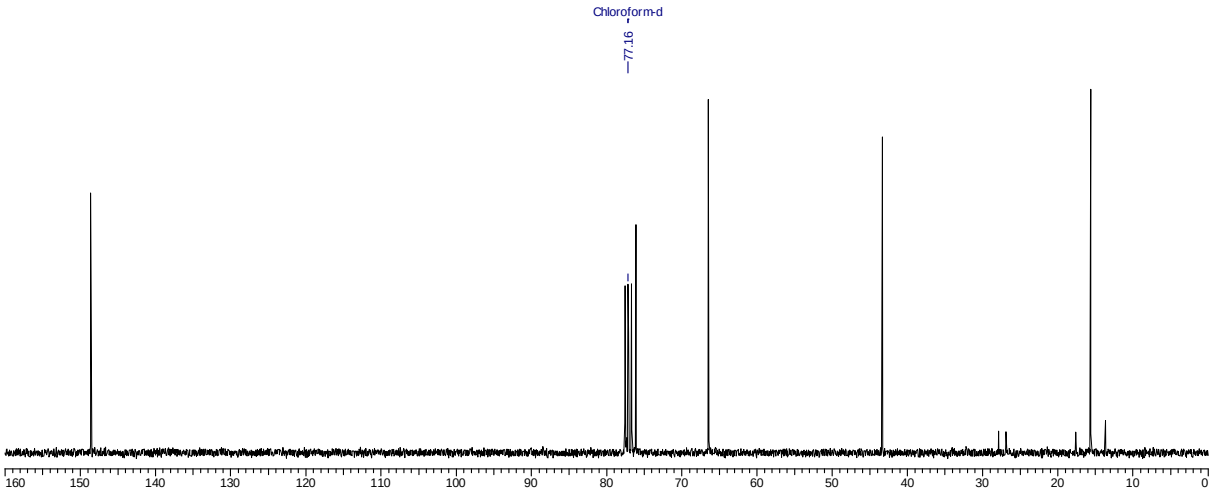
[α]$^{25}_{D}$ +23.1, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.00 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 1.88-1.92 (1H, m, OH), 2.33-2.46 (1H, m, C*H*), 3.40-3.53 (2H, m, C*H*$_2$), 6.12 (1H, d, *J* = 14.5 Hz, C*H*), 6.45 (1H, dd, *J* = 14.5 and 7.9 Hz, C*H*); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 15.6 (CH_3), 43.4 (CH), 66.5 (CH_2), 76.2 (CH), 148.6 (CH).





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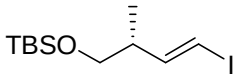

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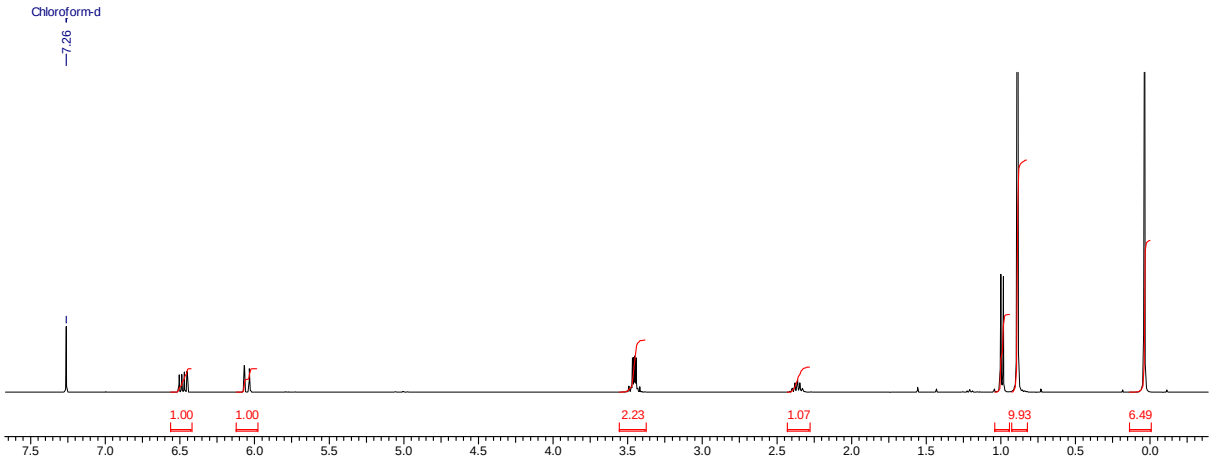
[α]$^{25}_{D}$ +20.8, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.05 (6H, s, 2 x C*H*$_3$), 0.90 (9H, s, 3 x C*H*$_3$), 1.01 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 2.33-2.40 (1H, m, C*H*), 3.45 (1H, dd, *J* = 9.8 and 6.4 Hz, C*H*$_2$), 3.48 (1H, dd, *J* = 9.8 and 6.4 Hz, C*H*$_2$), 6.06 (1H, br dd, *J* = 14.6 Hz, C*H*), 6.49 (1H, dd, *J* = 14.6 and 6.5 Hz, C*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ -5.2 (2 x CH_3), 15.7 (CH_3), 18.4 (C), 26.0 (3 x CH_3), 43.3 (CH), 67.0 (CH_2), 75.2 (CH), 149.2 (CH); **IR** (thin film) ν_{max} = 2955, 2928, 2856, 1605, 1471, 1386, 1361, 1252, 1187, 1088, 1024, 1006, 947 cm^{-1}; **LRMS** *m/z* (ESI) 349 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{11}H_{24}OSiI$ $[M+H]^+$: 327.0636, found 327.0640



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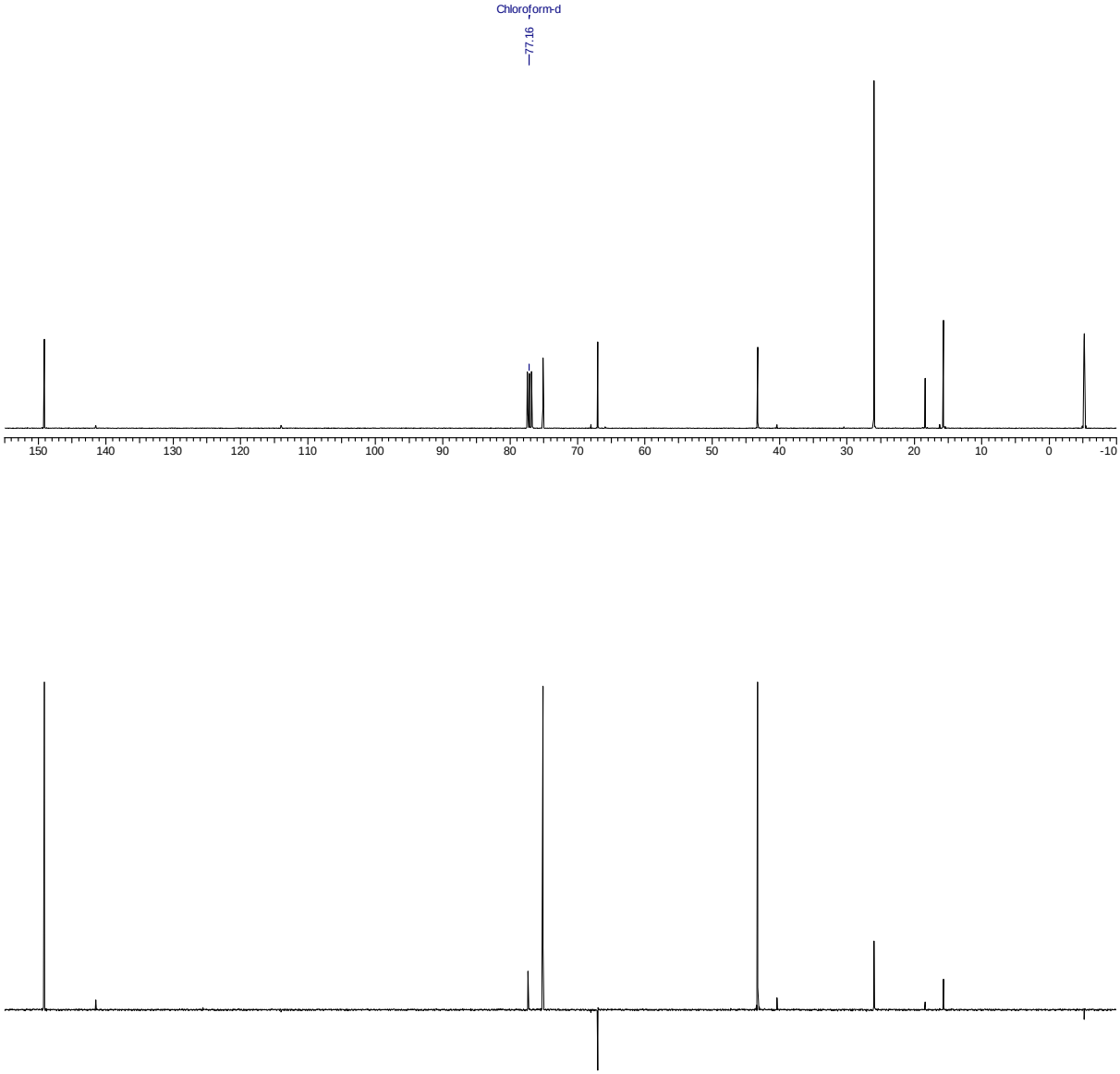

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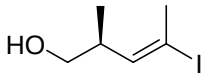

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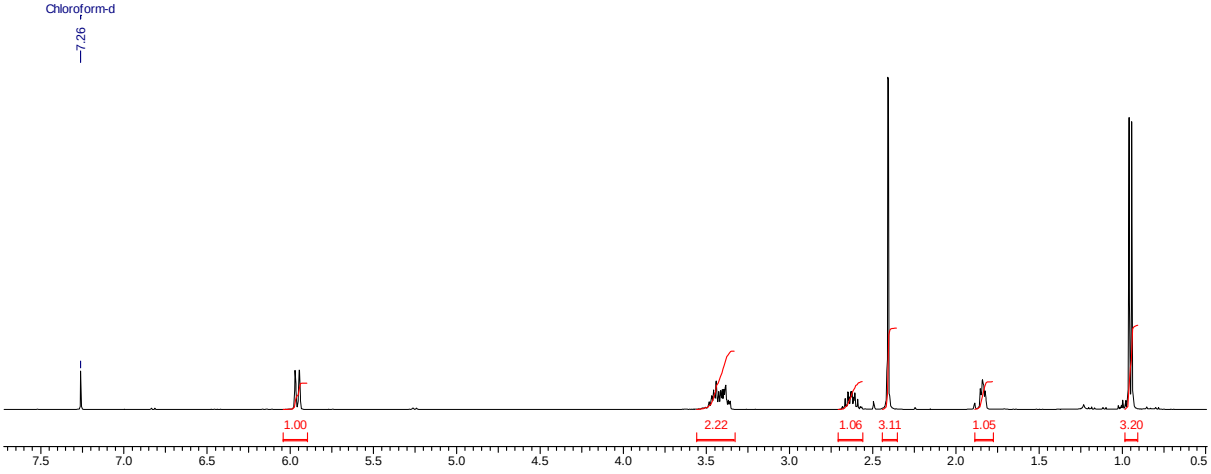
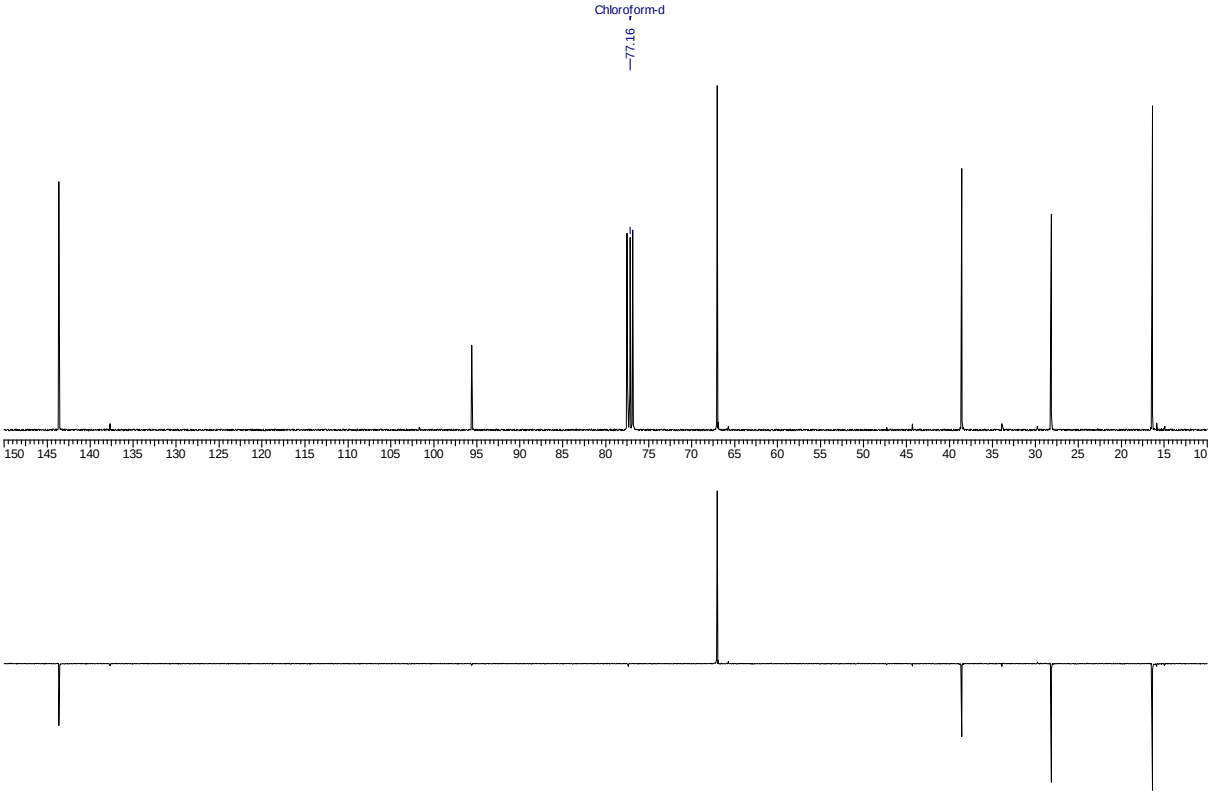
[α]$^{25}_{D}$ -31.3, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.95 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 1.82-1.85 (1H, m, O*H*), 2.41 (3H, d, *J* = 1.5 Hz, C*H*$_3$), 2.57-2.68 (1H, m, C*H*), 3.36-3.51 (2H, m, C*H*$_2$), 5.96 (1H, br dq, *J* = 9.8, 1.5 Hz, C*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 16.4 (CH_3), 28.2 (CH_3), 38.6 (CH), 67.0 (CH_2), 95.6 (CH), 143.6 (CH); **IR** (thin film) ν_{max} = 3332, 2958, 2926, 2870, 1635, 1429, 1377, 1217, 1119, 1076, 1030, 996, cm^{-1}; **LRMS** *m/z* (ESI) 249 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_6H_{15}NOI$ $[M+NH_4]^+$: 244.0193, found 244.0185.





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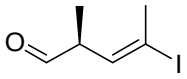

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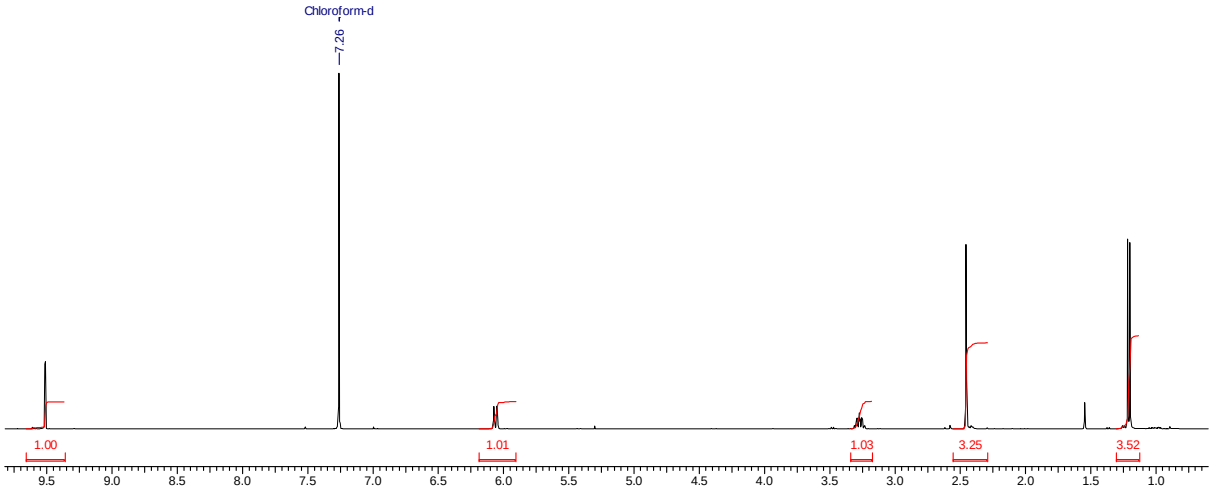
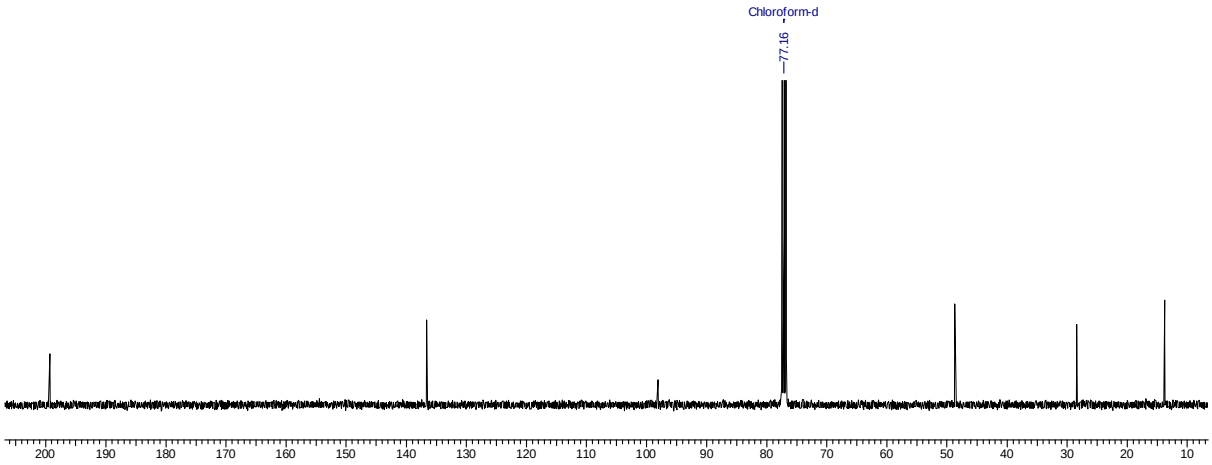
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (3H, d, *J* = 7.0 Hz, C*H*$_3$), 2.46 (3H, d, *J* = 1.5 Hz, C*H*$_3$), 3.23-3.31 (1H, m, C*H*), 6.06 (1H, br dq, *J* = 9.3, 1.5 Hz, C*H*), 9.51 (1H, d, *J* = 1.7 Hz, C*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.8 (CH_3), 28.4 (CH_3), 48.8 (CH), 67.0 (CH_2), 98.1 (CH), 136.6 (CH), 199.3 (CHO).





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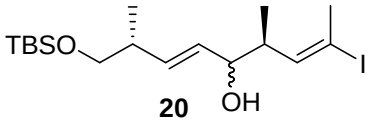

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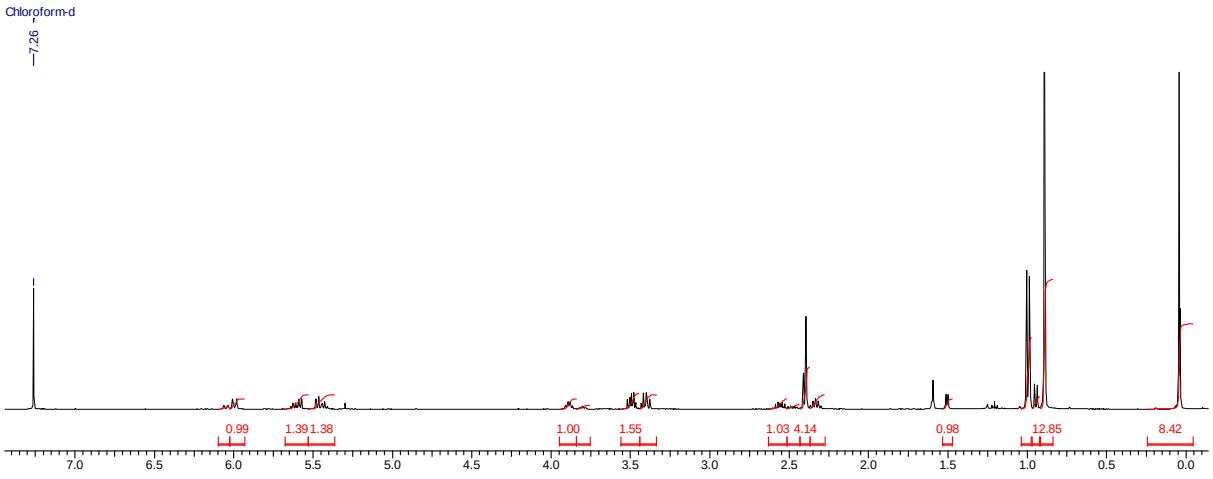
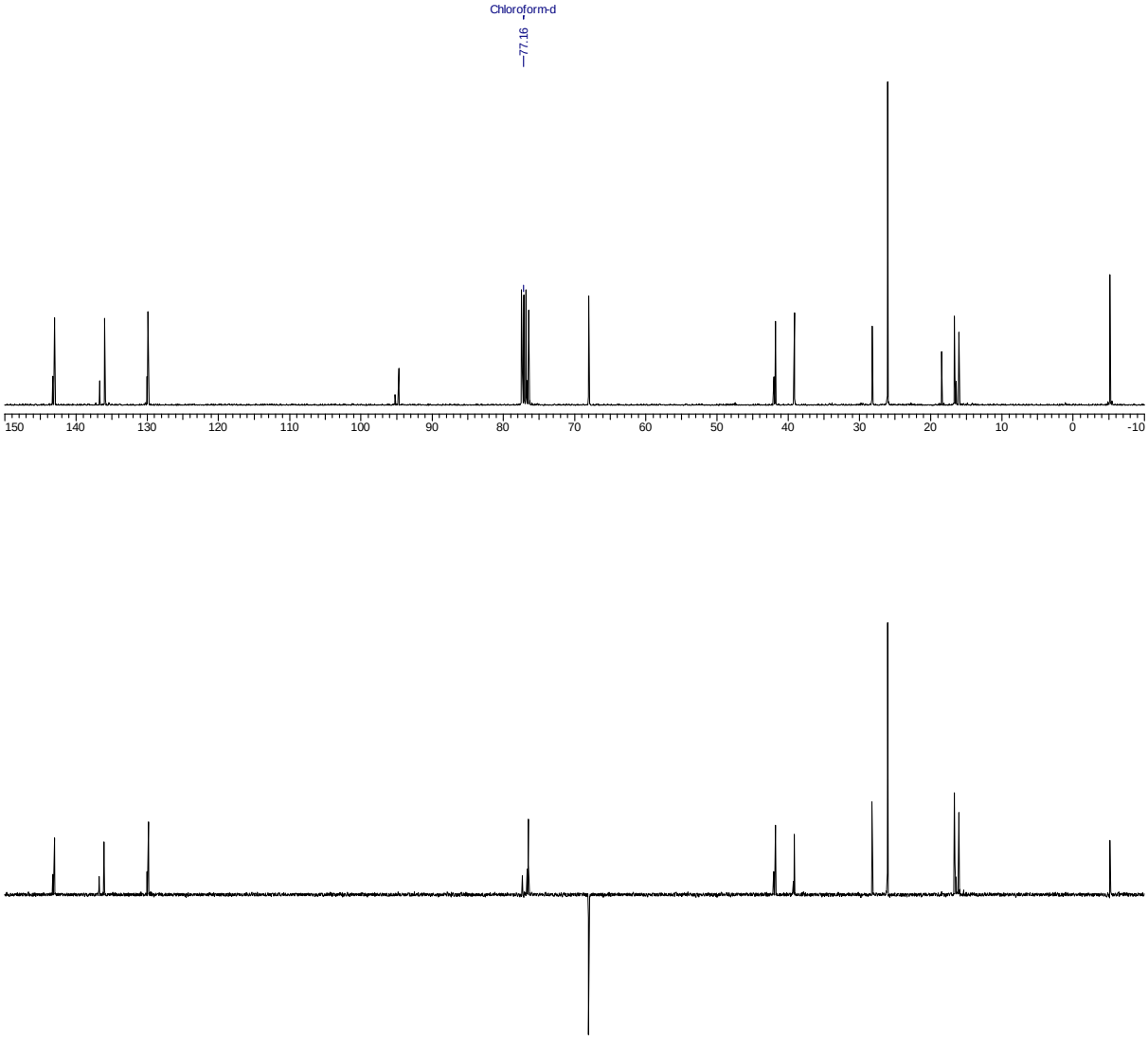
Major diastereoisomer only: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.05 (6H, s, 2 x C*H*$_3$), 0.89 (1H, s, 3 x C*H*$_3$), 1.00 (6H, d, *J* = 6.8 Hz, 2 x C*H*$_3$), 1.66 (1H, br s, O*H*), 2.29-2.36 (1H, m, C*H*), 2.39 (3H, d, *J* = 1.5 Hz, C*H*$_3$), 2.50-2.59 (1H, m, C*H*), 3.40 (1H, dd, *J* = 9.8 and 6.8 Hz, C*H*$_2$), 3.49 (1H, dd, *J* = 9.8 and 6.3 Hz, C*H*$_2$), 3.88 (1H, app br t, *J* = 6.5 Hz, C*H*), 5.45 (1H, br dd, *J* = 15.6 and 6.8 Hz, C*H*), 5.60 (1H, br dd, *J* = 15.6 and 6.3 Hz, C*H*), 5.99 (1H, br dq, *J* = 9.8 and 1.5 Hz, C*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ -5.3 (2 x CH_3), 15.9 (CH_3), 16.5 (CH_3), 18.3 (C), 25.9 (3 x CH_3), 28.1 (CH_3), 39.0 (CH), 41.7 (CH), 67.9 (CH_2), 76.3 (CH), 94.6 (CI), 129.8 (CH), 135.8 (CH), 142.9 (CH); **IR** (thin film) ν_{max} = 3419, 2958, 2930, 2858, 1638, 1473, 1388, 1257, 1089, 1009, 974 cm^{-1}; **LRMS** *m/z* (ESI) 447 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{17}H_{37}NO_2SiI$ $[M+NH_4]^+$: 442.1633, found 442.1633.



Supporting Information



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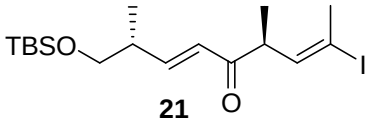
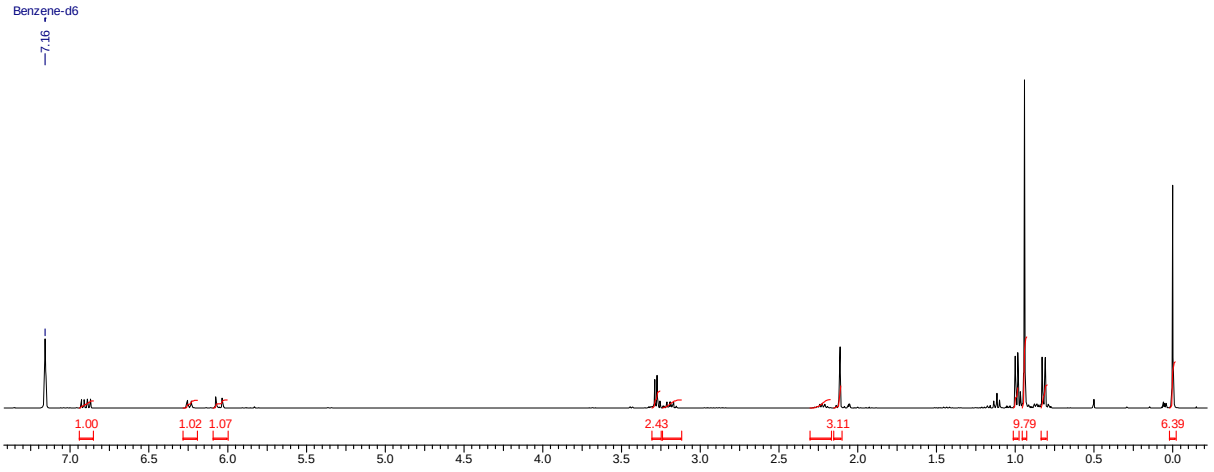
Supporting Information

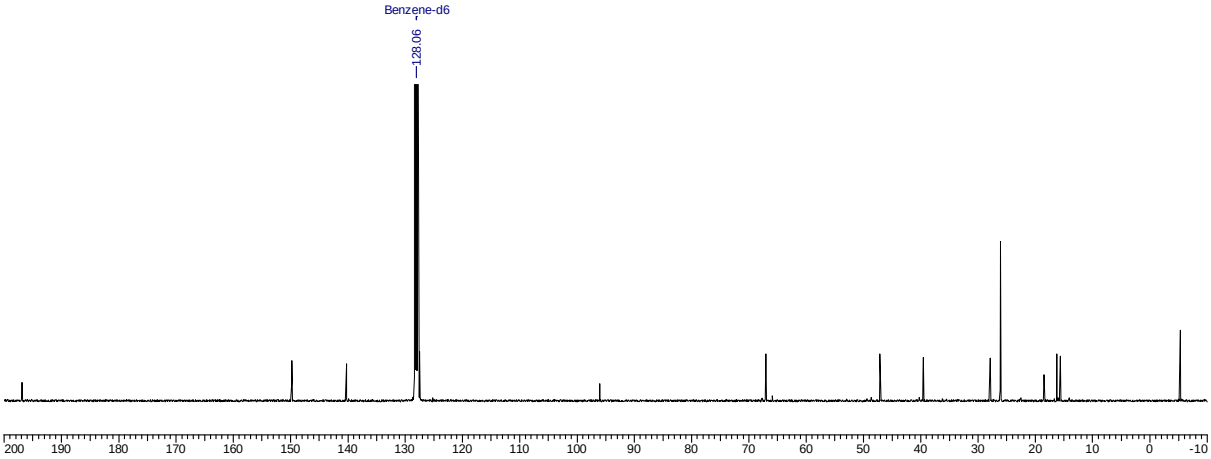


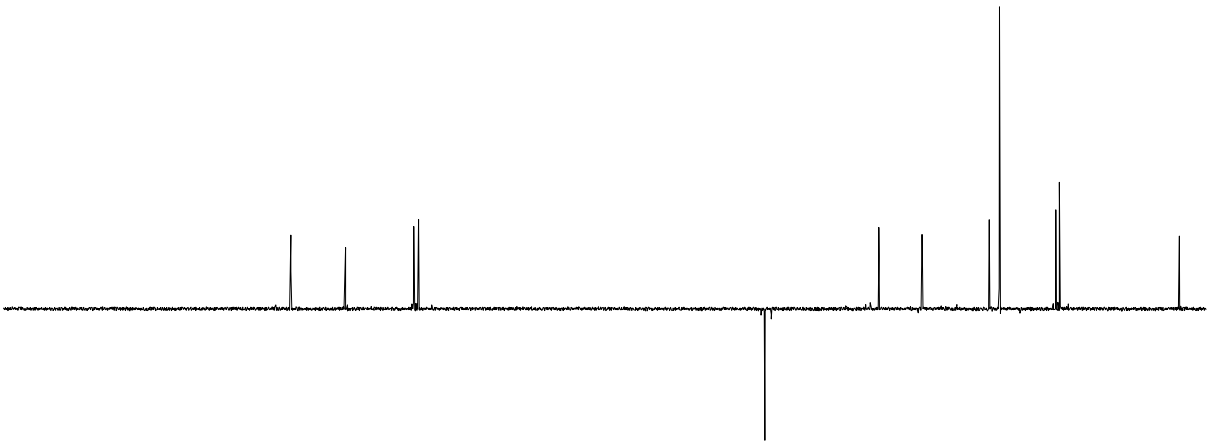
21

[α]$^{21}_{D}$ +52.5 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, C_6D_6) δ 0.00 (6H, s, 2 x C*H*$_3$), 0.82 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 0.94 (9H, s, 3 x C*H*$_3$), 0.99 (3H, d, *J* = 7.0 Hz, C*H*$_3$), 2.12 (3H, br d, *J* = 1.5 Hz, C*H*$_3$), 2.22 (1H, app sept, *J* = 6.3 Hz, C*H*), 3.19 (1H, dq, *J* = 9.8 and 7.0 Hz, C*H*), 3.28 (2H, d, *J* = 6.0 Hz, C*H*$_2$), 6.06 (1H, br dd, *J* = 15.8 and 1.3 Hz, C*H*), 6.25 (1H, br dq, *J* = 9.8 and 1.5 Hz, C*H*), 6.90 (1H, dd, *J* = 15.8 and 7.3 Hz, C*H*); **^{13}C NMR** (100 MHz, C_6D_6) δ -5.3 (2 x CH_3), 15.7 (CH_3), 16.3 (CH_3), 18.5 (C), 26.1 (3 x CH_3), 27.9 (CH_3), 39.6 (CH), 47.2 (CH), 67.1 (CH_2), 96.1 (C), 127.5 (CH), 140.3 (CH), 149.8 (CH), 196.9 (C); **IR** (thin film) ν_{max} = 2955, 2927, 2854, 1697, 1673, 1626, 1471, 1459, 1253, 1189, 1129, 1097, 1084, 1029, 980 cm^{-1}; **LRMS** *m/z* (ESI) 445 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{17}H_{32}O_2SiI$ $[M+H]^+$: 423.1211, found 423.1211.

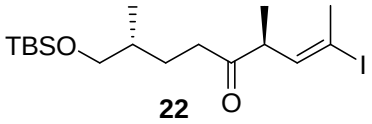


Supporting Information



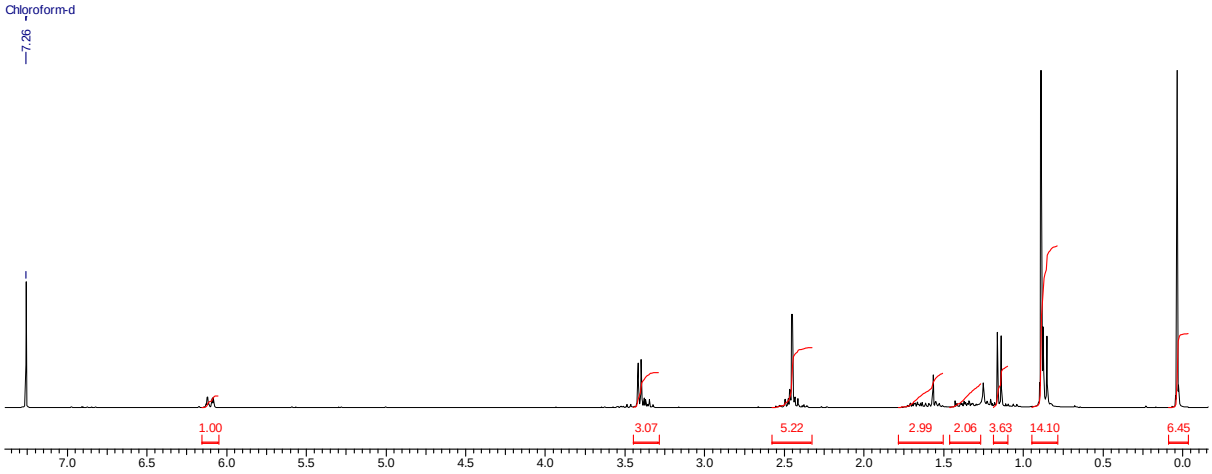


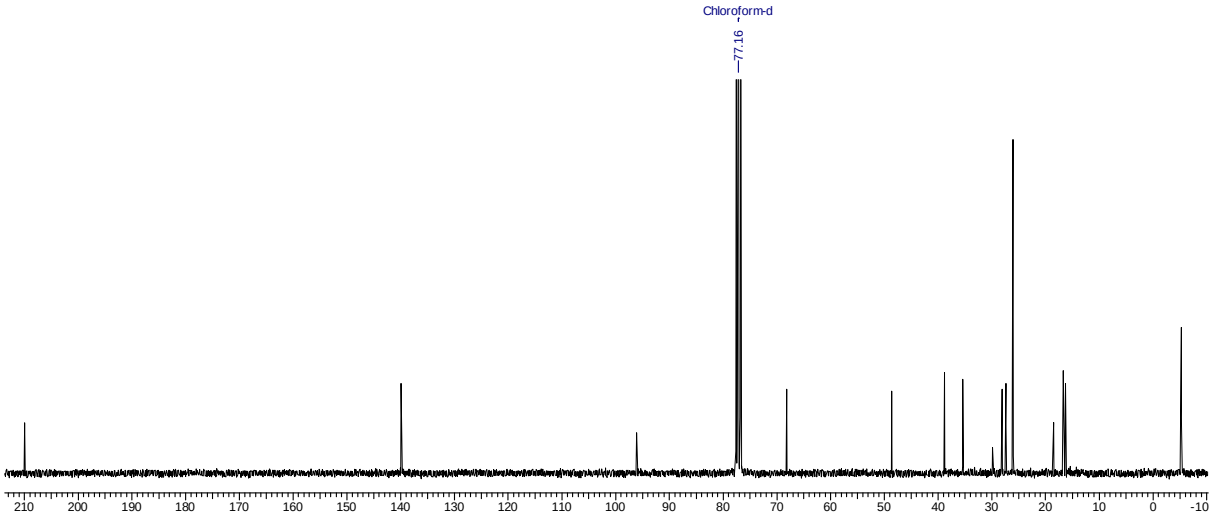
Supporting Information



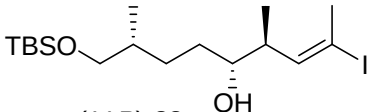
22

[α]$^{22}_{D}$ +65.6, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.05 (6H, s, 2 x C*H*$_3$), 0.87 (3H, d, *J* = 6.6 Hz, C*H*$_3$), 0.90 (9H, s, 3 x C*H*$_3$), 1.16 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 1.30-1.43 (1H, m, C*H*$_2$), 1.51-1.62 (1H, m, C*H*), 1.62-1.73 (1H, m, C*H*$_2$), 2.36-2.55 (2H, m, C*H*$_2$), 2.46 (3H, d, *J* = 1.5 Hz, C*H*$_3$), 3.33-3.40 (1H, m, C*H*), 3.42 (2H, d, *J* = 5.9 Hz, C*H*$_2$), 6.12 (1H, dq, *J* = 10.0 and 1.5 Hz, C*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ -5.2 (2 x CH_3), 16.3 (CH_3), 16.8 (CH_3), 18.5 (C), 26.1 (3 x CH_3), 27.4 (CH_2), 28.1 (CH_3), 35.4 (CH), 38.8 (CH_2), 48.7 (CH), 68.2 (CH_2), 96.1 (C), 139.9 (CH), 209.9 (C); **IR** (thin film) ν_{max} = 2955, 2929, 2883, 2856, 1716, 1472, 1462, 1434, 1252, 1117, 1091, 1037, 1028, 1005 cm^{-1}; **LRMS** *m/z* (ESI) 447 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{17}H_{34}O_2SiI$ $[M+H]^+$: 425.1367, found 425.1367.



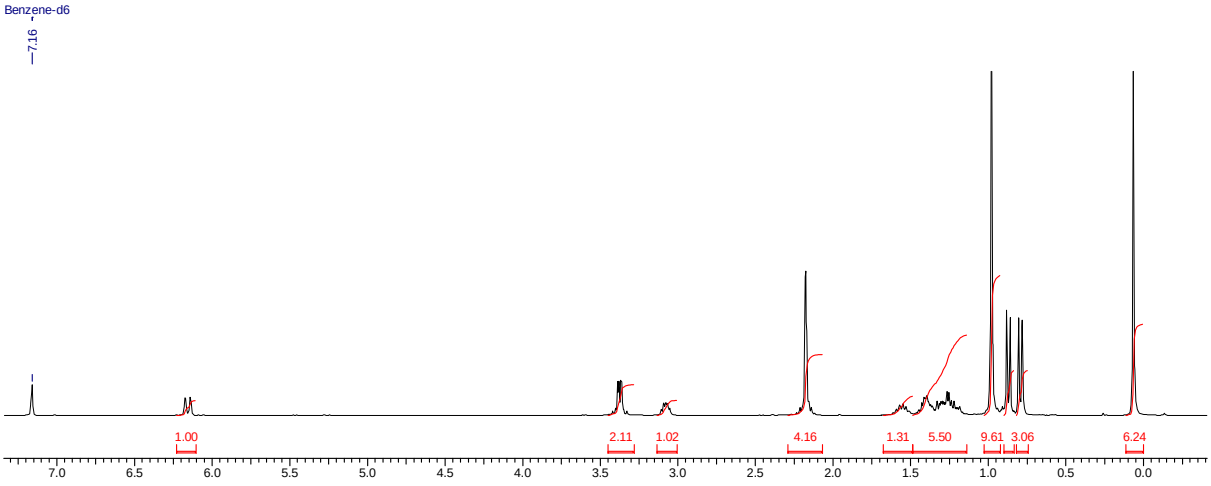


Supporting Information

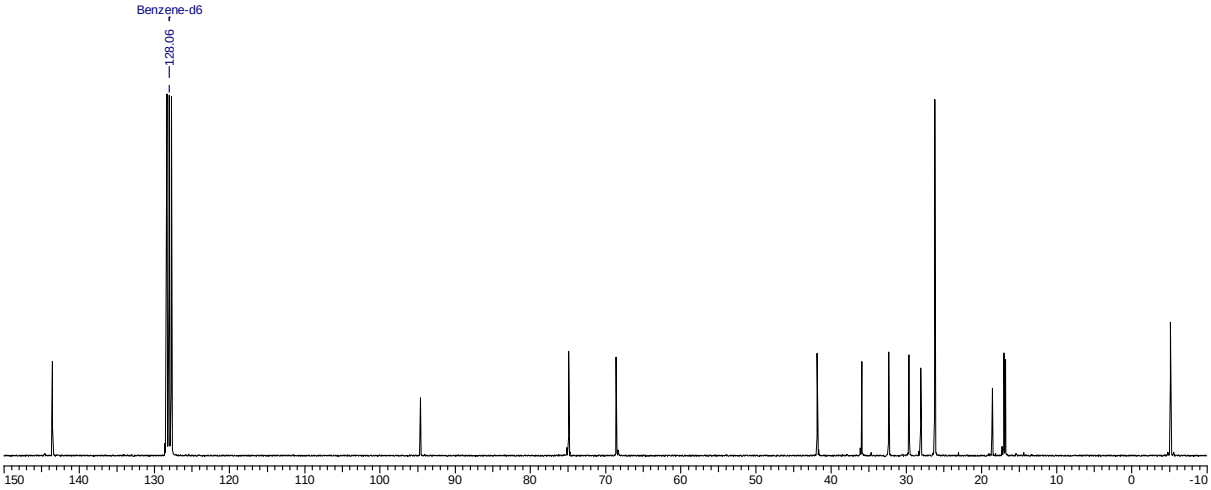


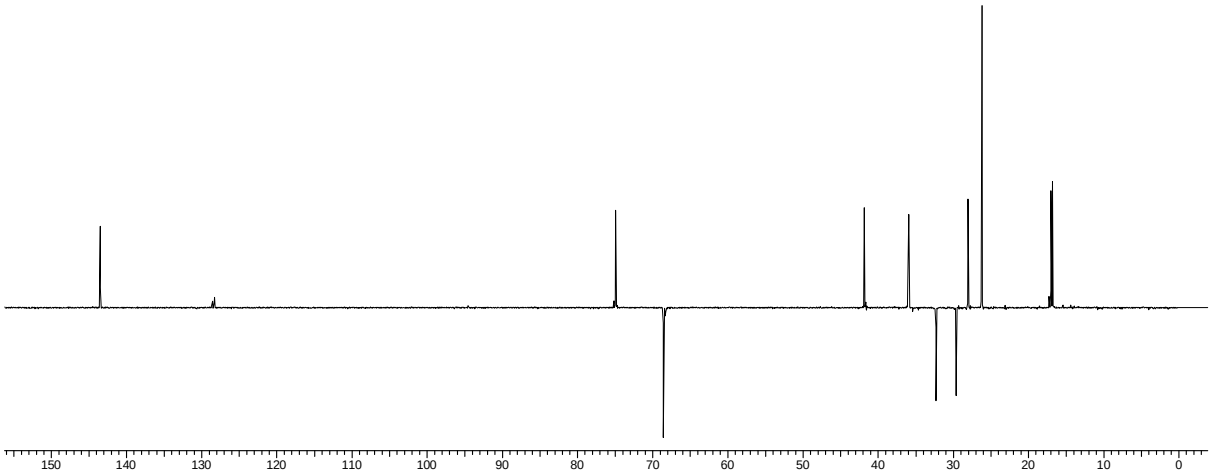
(11*R*)-**23**

[α]$^{36}_{D}$ -23.0, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (300 MHz, C_6D_6) δ 0.07 (6H, s, 2 x CH_3), 0.79 (3H, d, *J* = 6.9 Hz, CH_3), 0.87 (3H, d, *J* = 6.7 Hz, CH_3), 0.98 (9H, s, 3 x CH_3), 1.19-1.45 (5H, m, 2 x CH_2 and O*H*), 1.51-1.61 (1H, m, C*H*), 2.12-2.24 (1H, m, C*H*), 2.17 (3H, d, *J* = 1.3 Hz, CH_3), 3.05-3.11 (1H, m, C*H*), 3.33-3.42 (1H, m, CH_2), 6.16 (1H, br dq, *J* = 10.0 and 1.3 Hz, C*H*); **^{13}C NMR** (75 MHz, C_6D_6) δ -5.1 (2 x CH_3), 16.8 (CH_3), 17.1 (CH_3), 18.6 (C), 26.3 (3 x CH_3), 28.1 (CH_3), 29.7 (CH_2), 32.4 (CH_2), 36.0 (CH), 41.9 (CH), 68.6 (CH_2), 74.9 (CH), 94.6 (C), 143.5 (CH); **IR (thin film)** ν_{max} = 3397, 2954, 2928, 2856, 1462, 1377, 1361, 1251, 1090 cm^{-1}; LRMS *m/z* (ESI) 449 $(M+Na)^+$; **HRMS *m/z*** (ESI) calcd for $C_{17}H_{36}O_2SiI$ $[M+H]^+$: 427.1524, found 427.1523.



Supporting Information





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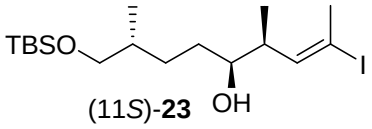
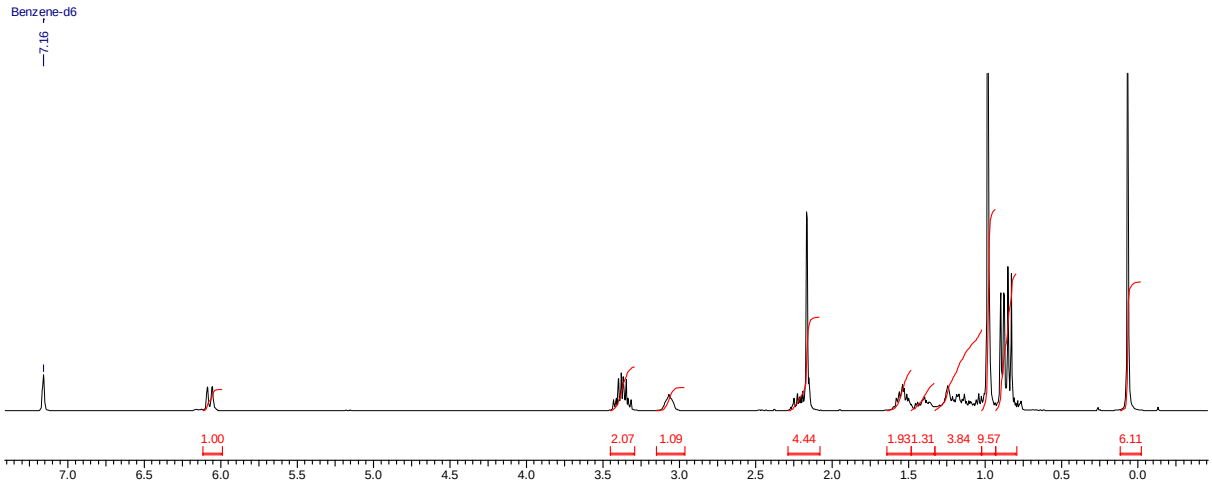


(11*S*)-**23**

[α]$^{36}_{D}$ -31.8, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (300 MHz, C_6D_6) δ 0.07 (6H, s, 2 x C*H*$_3$), 0.84 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 0.89 (3H, d, *J* = 6.4 Hz, C*H*$_3$), 0.98 (9H, s, 3 x C*H*$_3$), 0.99-1.06 (1H, m, C*H*$_2$), 1.11-1.21 (1H, m, C*H*$_2$), 1.25 (1H, br s, O*H*), 1.35-1.46 (1H, m, C*H*$_2$), 1.48-1.60 (2H, m, C*H* and C*H*$_2$), 2.17 (3H, d, *J* = 1.5 Hz, C*H*$_3$), 2.19-2.27 (1H, m, C*H*), 3.03-3.11 (1H, m, C*H*), 3.34 (1H, dd, *J* = 9.8 and 5.6 Hz, C*H*$_2$), 3.41 (1H, dd, *J* = 9.8 and 5.6 Hz, C*H*$_2$), 6.08 (1H, dq, *J* = 10.0 and 1.5 Hz, C*H*); **^{13}C NMR** (75 MHz, C_6D_6) δ -5.1 (2 x CH_3), 15.5 (CH_3), 17.3 (CH_3), 18.6 (C), 26.3 (3 x CH_3), 28.0 (CH_3), 29.8 (CH_2), 32.4 (CH_2), 36.1 (CH_3), 42.0 (CH), 68.3 (CH_2), 75.2 (CH), 94.1 (C), 144.5 (CH); **IR** (thin film) ν_{max} = 3358, 2954, 2928, 2856, 1633, 1462, 1378, 1361, 1252, 1092 cm^{-1}; **LRMS** *m/z* (ESI) 449 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{17}H_{36}O_2SiI$ $[M+H]^+$: 427.1524, found 427.1521.



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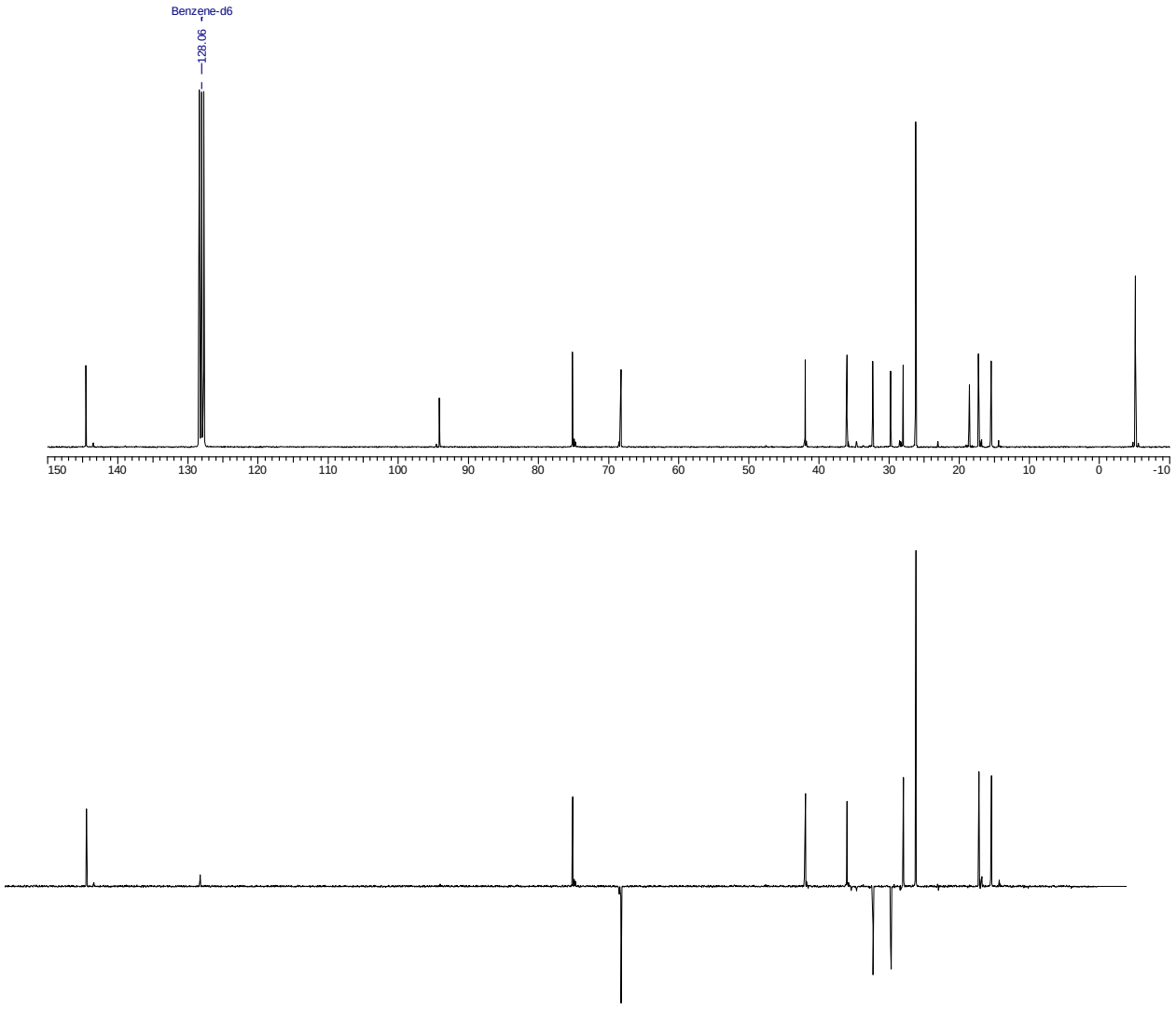

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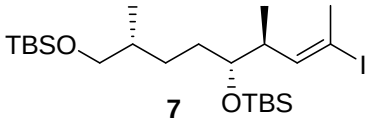
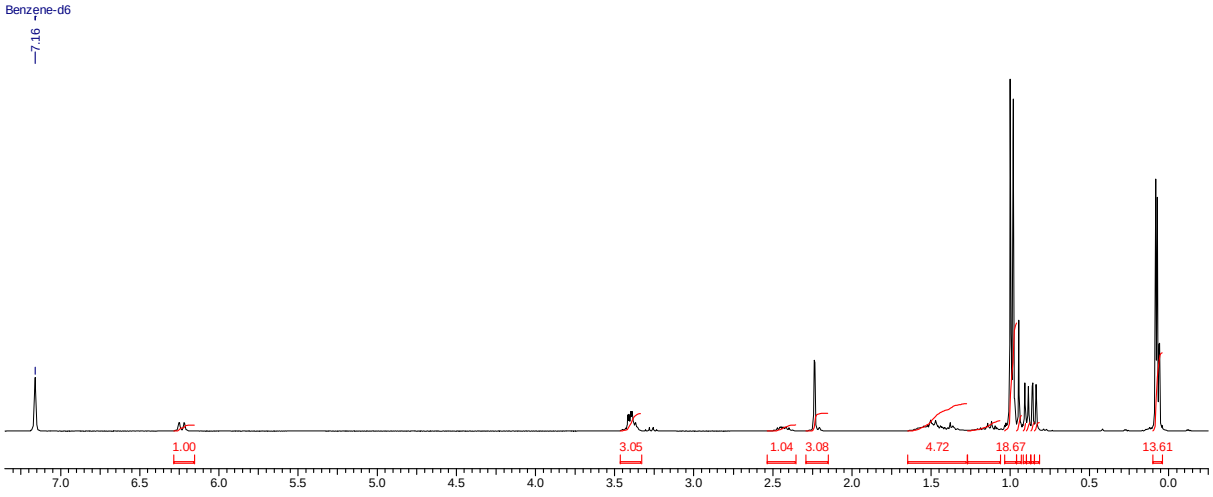
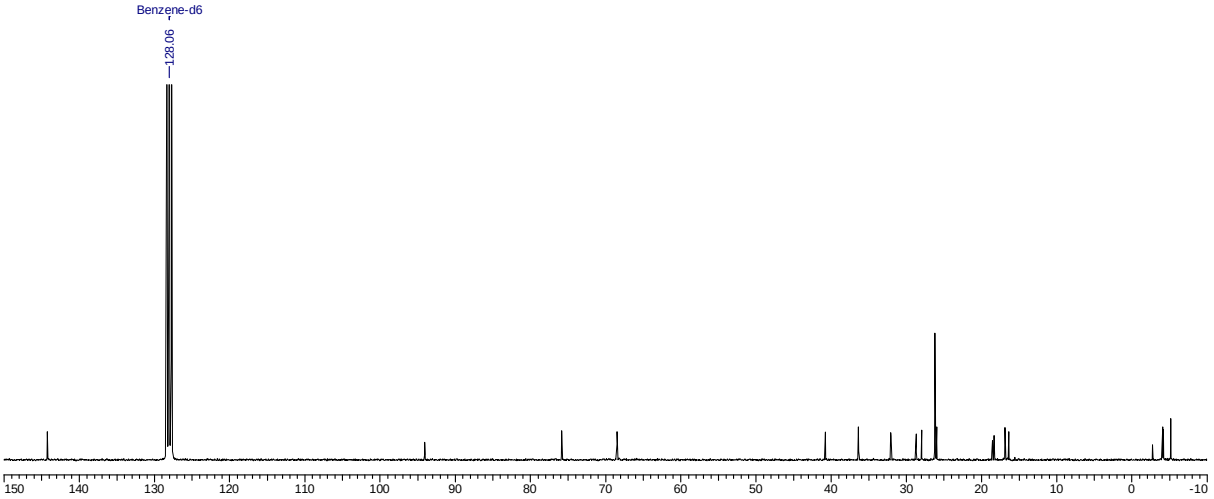


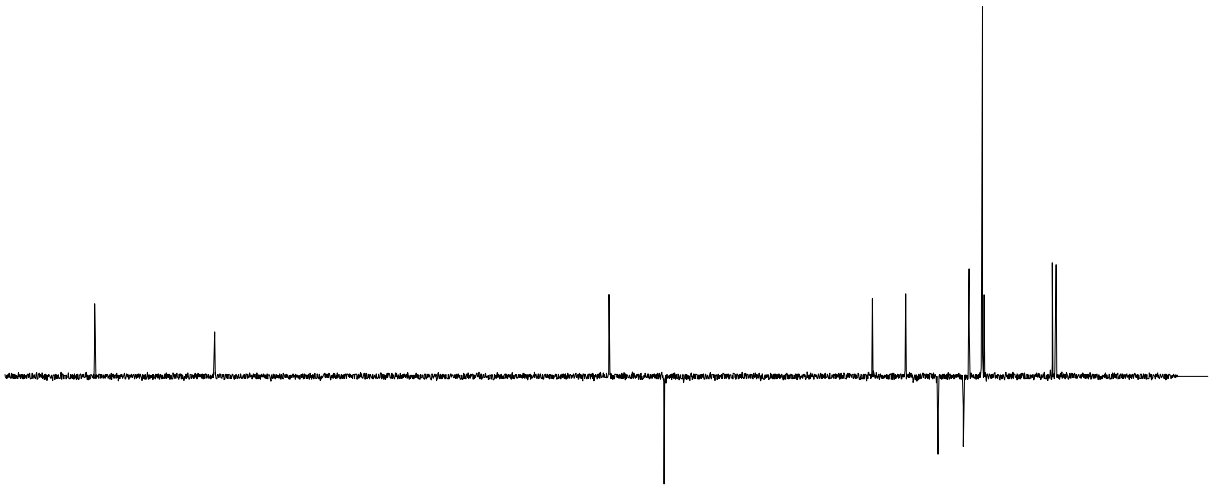
7

[α]$^{25}_{D}$ -33.3, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (300 MHz, C_6D_6) δ 0.07 (6H, s, 2 x CH_3), 0.08 (6H, s, 2 x CH_3), 0.85 (3H, d, *J* = 6.8 Hz, CH_3), 0.90 (3H, d, *J* = 6.5 Hz, CH_3), 0.98 (9H, s, 3 x CH_3), 1.00 (9H, s, 3 x CH_3), 1.10-1.20 (1H, m, C*H*$_2$), 1.33-1.61 (4H, m, CH_2 and C*H*$_2$ and CH), 2.24 (3H, d, *J* = 1.5 Hz, CH_3), 2.37-2.49 (1H, m, CH), 3.35-3.45 (3H, m, CH and CH_2), 6.24 (1H, dq, *J* = 10.0 and 1.4 Hz, CH); **^{13}C NMR** (100 MHz, C_6D_6) δ -5.2 (2 x CH_3), -4.1 (CH_3), -4.0 (CH_3), 16.4 (CH_3), 16.9 (CH_3), 18.3 (C), 18.6 (CH_3), 26.2 (3 x CH_3), 26.2 (3 x CH_3), 28.0 (CH_3), 28.7 (CH_2), 32.1 (CH_2), 36.4 (CH), 40.8 (CH), 68.5 (CH_2), 75.9 (CH), 94.1 (C), 144.3 (CH); **LRMS** *m/z* (ESI) 563 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{23}H_{53}NO_2Si_2I$ $[M+NH_4]^+$: 558.2654, found 558.2651.

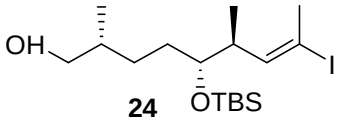


Supporting Information



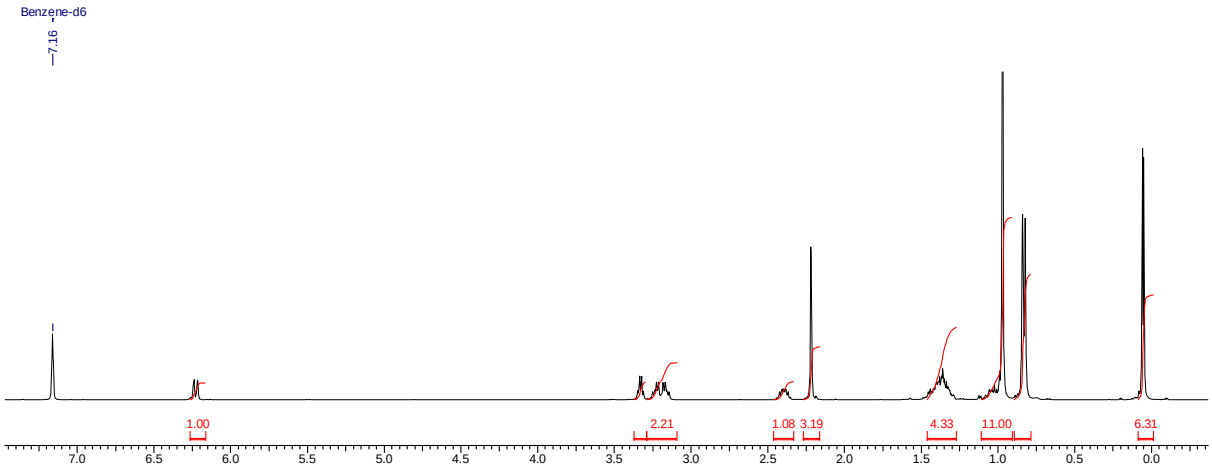


Supporting Information

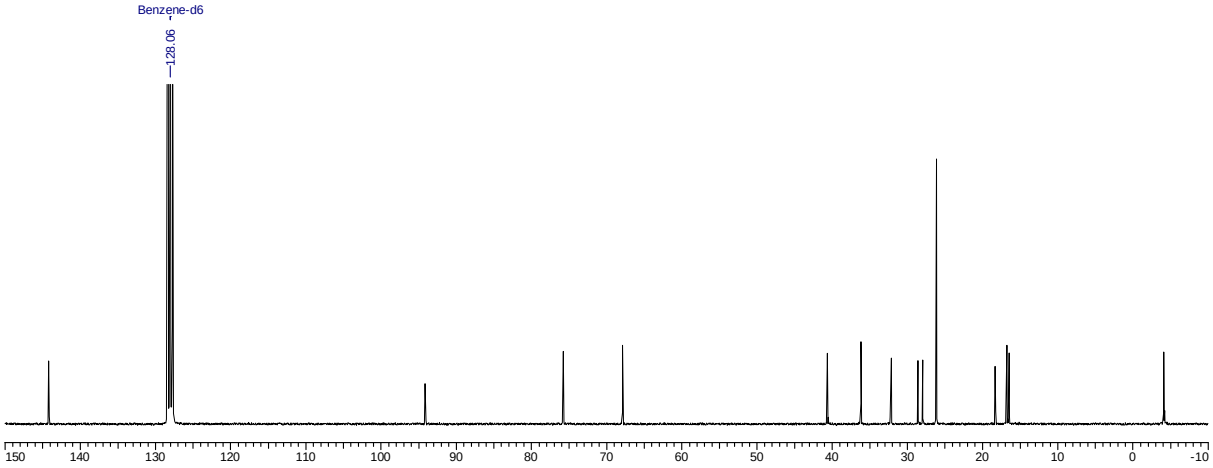


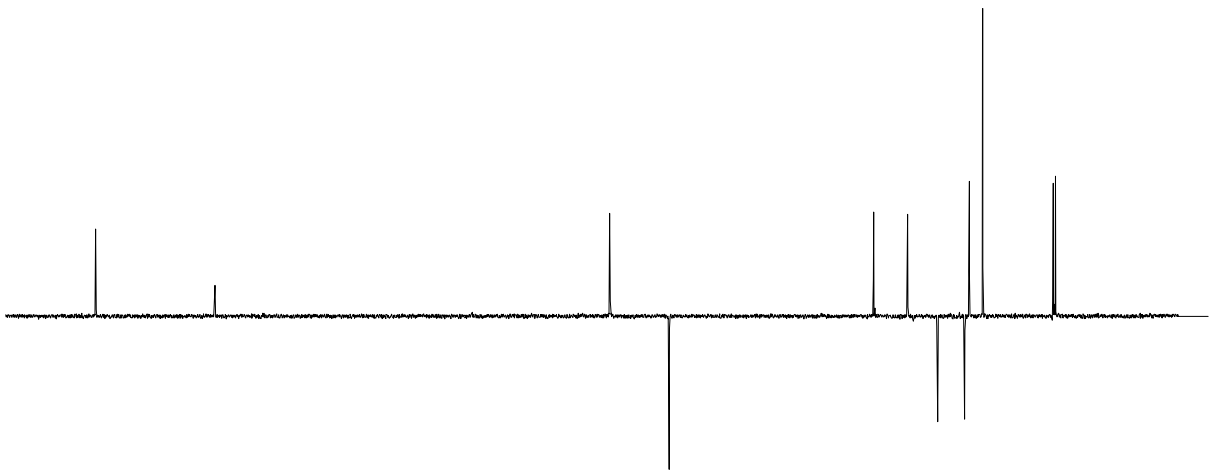
24

[α]$^{25}_{D}$ -32.8, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, C_6D_6) δ 0.05 (3H, s, CH_3), 0.06 (3H, s, CH_3), 0.83 (2 x 3H, 2 x d overlapped, *J* = 6.7 Hz, 2 x C*H*$_3$), 0.97 (9H, s, 3 x C*H*$_3$), 1.01-1.06 (1H, m, C*H*$_2$), 1.29-1.49 (4H, m, C*H*$_2$ and C*H*$_2$ and C*H*), 2.22 (3H, d, *J* = 1.5 Hz, C*H*$_3$), 2.35-2.44 (1H, m, C*H*), 3.17 (1H, dd, *J* = 10.0 and 6.0 Hz, C*H*$_2$), 3.23 (1H, dd, *J* = 10.3 and 5.5 Hz, C*H*$_2$), 3.33 (1H, q, *J* = 5.0 Hz, C*H*), 6.23 (1H, br dq, *J* = 10.0 and 1.5 Hz, C*H*); **^{13}C NMR** (75 MHz, C_6D_6) δ -4.2 (CH_3), -4.1 (CH_3), 16.5 (CH_3), 16.8 (CH_3), 18.3 (C), 26.2 (3 x CH_3), 28.0 (CH_3), 28.6 (CH_2), 32.2 (CH_2), 36.2 (CH), 40.7 (CH), 67.9 (CH_2), 75.8 (CH), 94.1 (C), 144.2 (CH); **LRMS** *m/z* (ESI) 449 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{17}H_{36}O_2SiI$ $[M+H]^+$: 427.1524, found 427.1517.

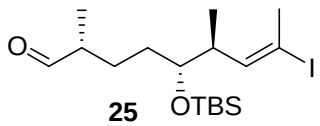


Supporting Information



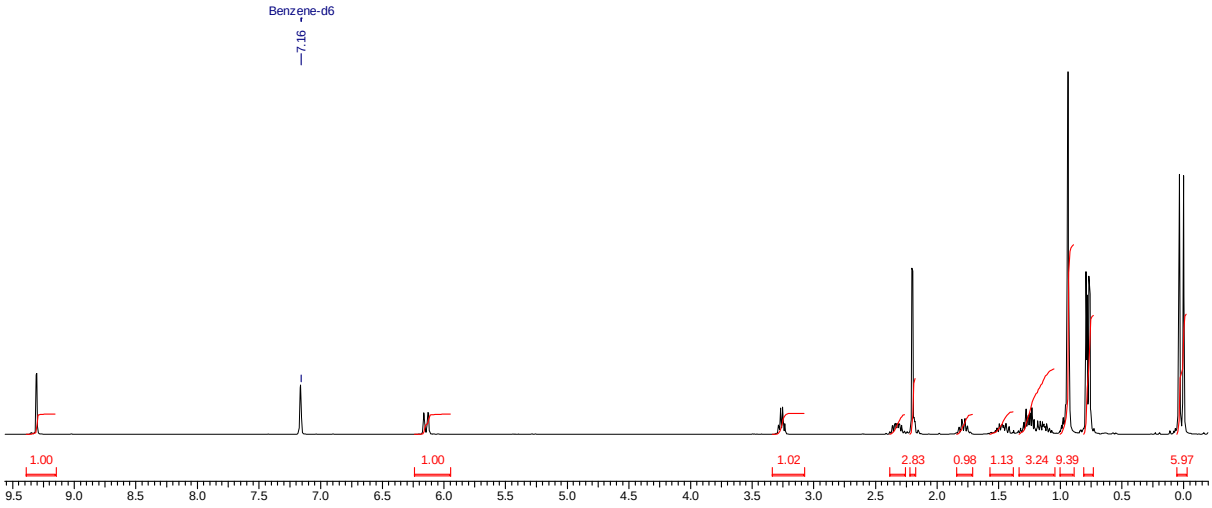


Supporting Information

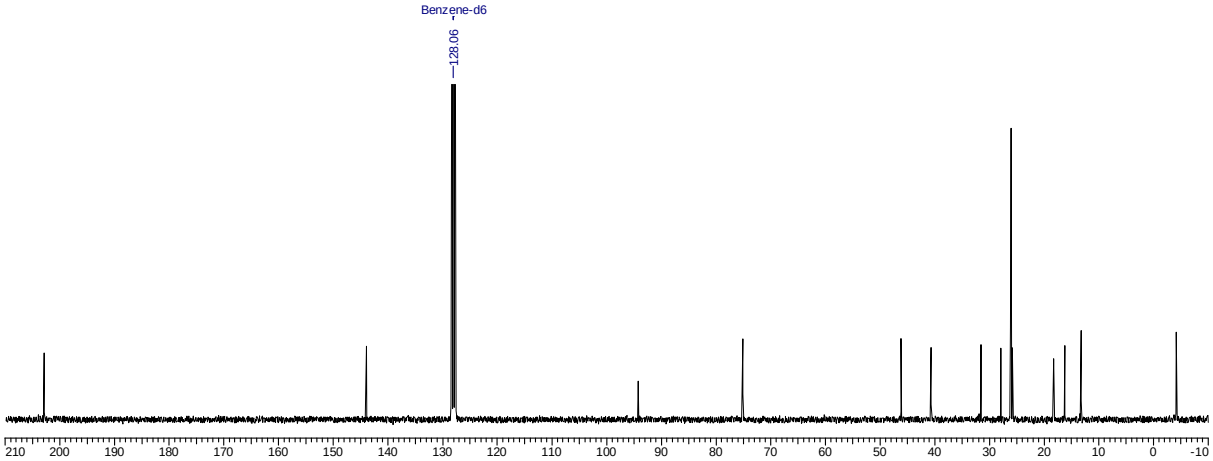


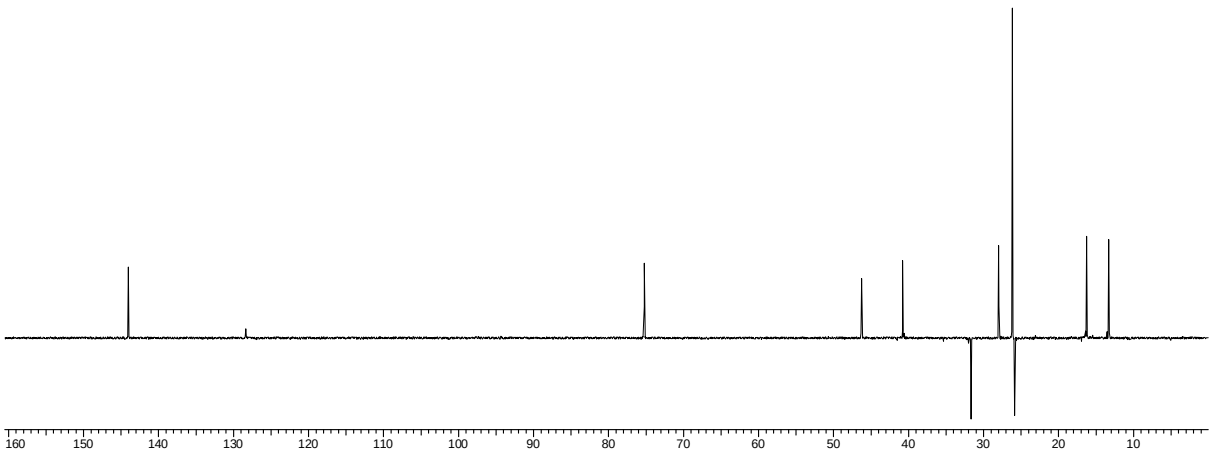
25

[α]$^{28}_{D}$ -46.0, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (300 MHz, C_6D_6) δ 0.00 (3H, s, C*H*$_3$), 0.03 (3H, s, C*H*$_3$), 0.77 (3H, d, *J* = 6.9 Hz, C*H*$_3$), 0.78 (3H, d, *J* = 7.1 Hz, C*H*$_3$), 0.94 (9H, s, 3 x C*H*$_3$), 1.07-1.16 (1H, m, C*H*$_2$), 1.18-1.32 (2H, m, C*H*$_2$), 1.41-1.56 (1H, m, C*H*$_2$), 1.73-1.84 (1H, m, C*H*), 2.20 (3H, d, *J* = 1.5 Hz, C*H*$_3$), 2.24-2.41 (1H, m, C*H*), 3.26 (1H, q, *J* = 5.5 Hz, C*H*), 6.14 (1H, br dq, *J* = 10.0 and 1.5 Hz, C*H*), 9.30 (1H, d, *J* = 1.3 Hz, C*H*); **^{13}C NMR** (75 MHz, C_6D_6) δ -4.2 (CH_3), -4.1(CH_3), 13.3 (CH_3), 16.2 (CH_3), 18.3 (CH_3), 25.8 (CH_2), 26.1 (3 x CH_3), 27.9 (CH_3), 31.6 (CH_2), 40.8 (CH), 46.2 (CH), 75.2 (CH), 94.3 (C), 144.0 (CH), 202.9 (CH); **IR** (thin film) ν_{max} = 2256, 2931, 2858, 1709, 1472, 1464, 1379, 1361, 1254, 1067, 1045, 1027, 1006 cm^{-1}; **LRMS** *m/z* (ESI) 447 $(M+Na)^+$

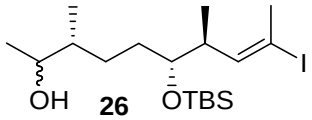


Supporting Information





Supporting Information



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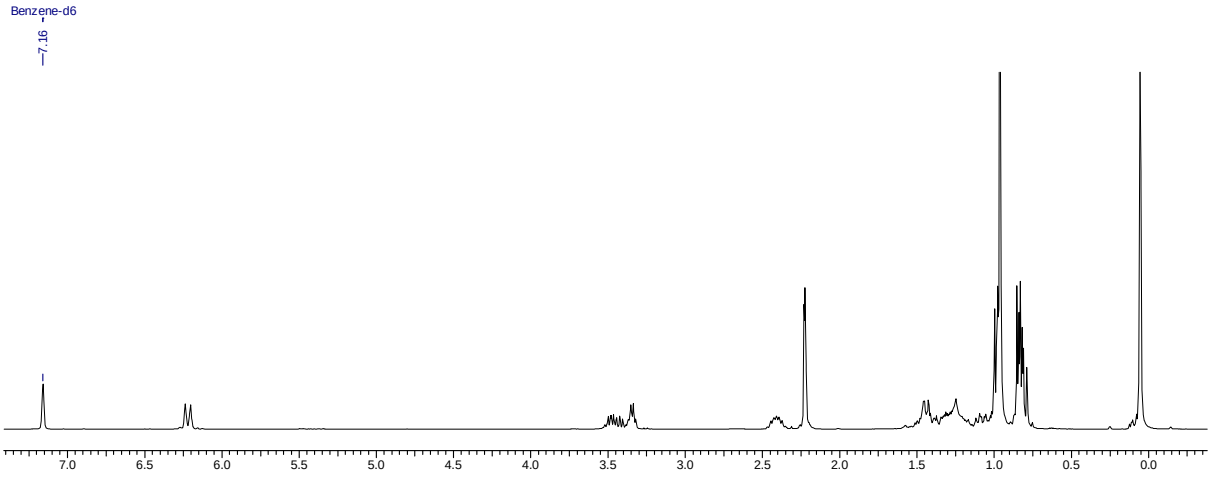
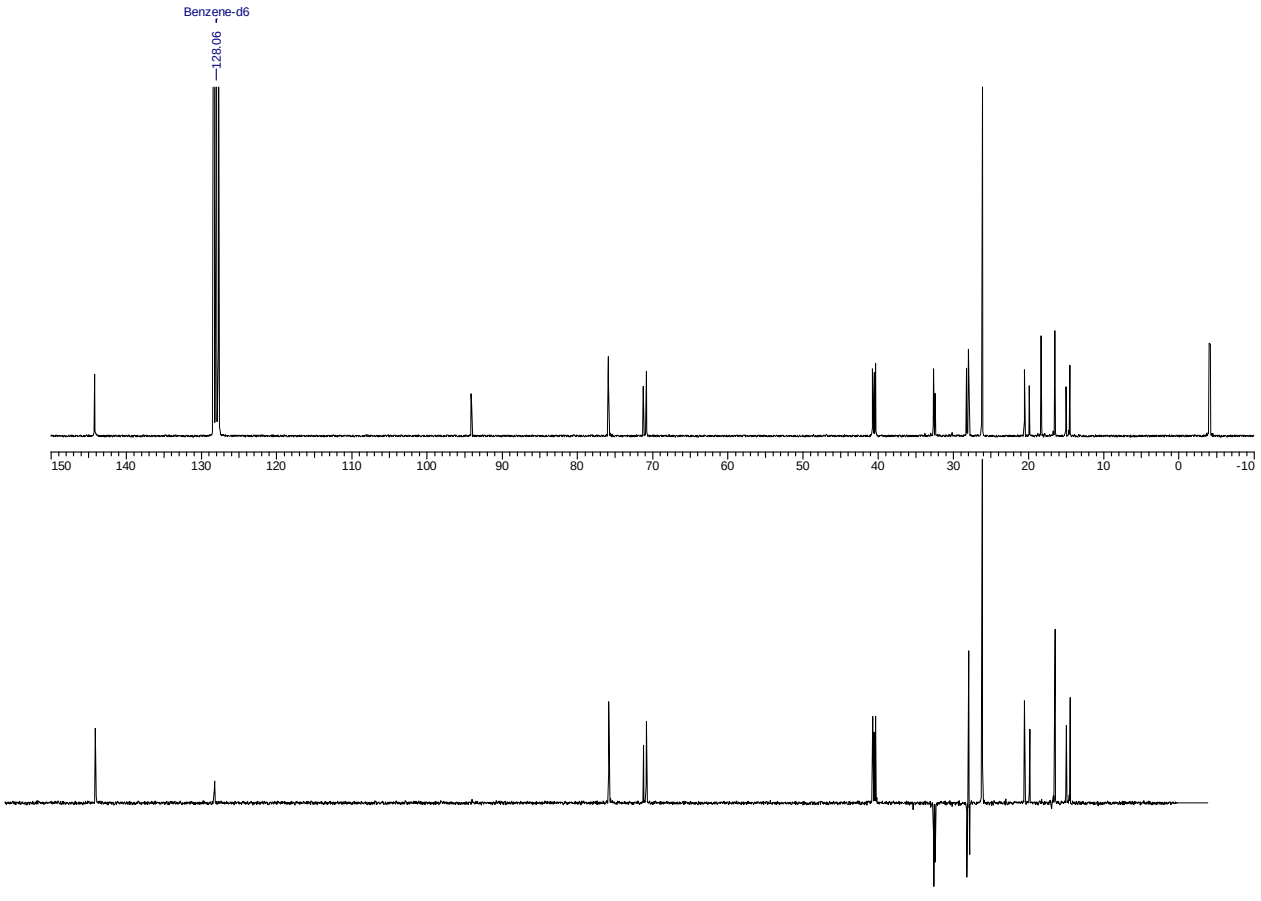
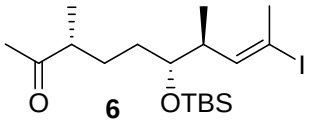
The alcool is not described because the mixture of diastereomers.

IR (thin film) ν_{max} = 3364, 2957, 2928, 2883, 2857, 1471, 1461, 1406, 1378, 1361, 1253, 1065, 1027, 1004, 942 cm^{-1}; **LRMS** *m/z* (ESI) 463 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{18}H_{38}O_2SiI$ $[M+H]^+$: 441.1680, found 441.1667.



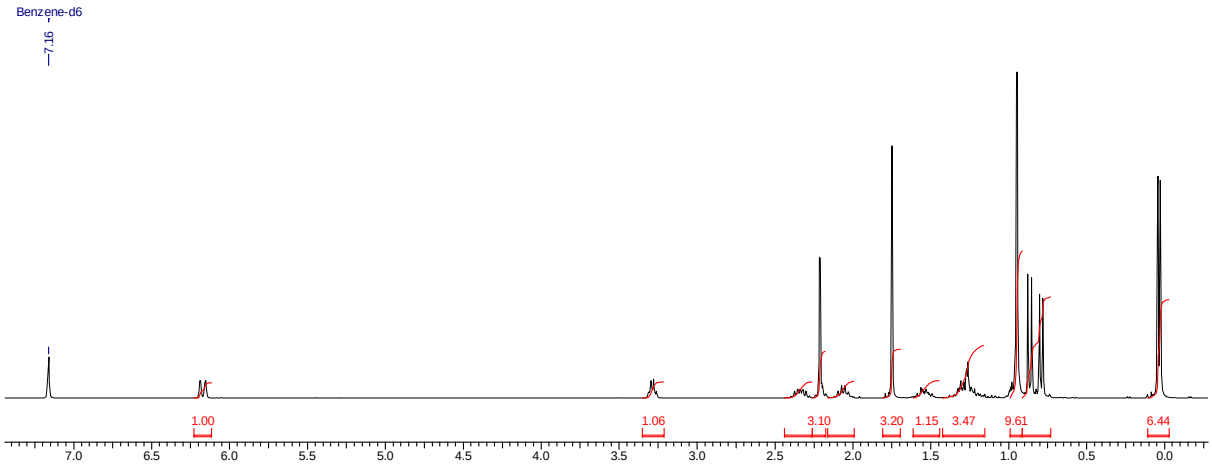


Supporting Information



6

[α]$^{36}_{D}$ -28.6, (*c* 1.0, $CHCl_3$); **^{1}H NMR** (300 MHz, C_6D_6) δ 0.03 (3H, s, C*H*$_3$), 0.04 (3H, s, C*H*$_3$), 0.79 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 0.87 (3H, d, *J* = 7.0 Hz, C*H*$_3$), 0.95 (9H, s, 3 x C*H*$_3$), 1.15-1.38 (3H, m, C*H*$_2$ and C*H*$_2$), 1.49-1.59 (1H, m, C*H*$_2$), 1.75 (3H, s, C*H*$_3$), 2.01-2.10 (1H, m, C*H*), 2.21 (3H, d, *J* = 1.5 Hz, C*H*$_3$), 2.28-2.40 (1H, m, C*H*), 3.26-3.31 (1H, m, C*H*), 6.17 (1H, br dq, *J* = 10.0 and 1.5 Hz, C*H*); **^{13}C NMR** (75 MHz, C_6D_6) δ -4.2 (CH_3), -4.1 (CH_3), 16.3 (CH_3), 16.5 (CH_3), 18.3 (C), 26.2 (3 x CH_3), 27.8 (CH_3), 28.0 (CH_3), 28.3 (CH_2), 32.3 (CH_2), 40.7 (CH), 47.0 (CH), 75.4 (CH), 94.3 (CH), 144.0 (CH), 209.6 (CH); **IR** (thin film) ν_{max} = 2955, 2929, 2856, 1713, 1471, 1461, 1378, 1359, 1253, 1170, 1067, 1043, 1026, 1006, 940 cm^{-1}; **LRMS** *m/z* (ESI) 461 $(M+Na)^+$; **HRMS** *m/z* (ESI) calcd for $C_{18}H_{36}O_2SiI$ $[M+H]^+$: 439.1524, found 439.1517.



Supporting Information