Synthesis and shift-reagent-assisted full NMR assignment of the bacterial (Z_8,E_2,ω)-undecaprenol

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Electronic Supplementary Information

Contents

Experimental Section

Synthesis. Synthesis of compound **3** from *E*,*E*-farnesol was published previously by our laboratory.[1] Undecaprenol **2** was purchased from American Radiolabeled Chemicals, Inc.

Compound 7. Phosphorus tribromide (34 μL, 0.36 mmol) in dry ether (0.8 mL) was added dropwise to a mixture of heptaprenol **3**[2] (0.4 g, 0.8 mmol) and pyridine (6 μL) in dry ether (2 mL) at ice-water temperature. The resulting solution was stirred for 2 h at the same temperature. The brown mixture was poured into a mixture of ice and water and then washed with hexanes. The separated organic layer was washed with a series of aqueous solutions (water, saturated $NaHCO_3$, and brine), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue, the resultant bromide intermediate, was purified by column chromatography on silica gel. This intermediate (0.3 g, 0.5 mmol) was dissolved in acetonitrile:DMF:ether (1:1:1, 3 mL) and the solution was added dropwise to a suspension of sodium *p*-toluenesulfinate (0.18 g, 1.0 mmol) in DMF (5 mL) in an ice-water bath. The mixture was brought to room temperature over a few minutes and was allowed to stir for 6 h. The mixture was diluted with ethyl acetate and was washed sequentially with water and brine, dried over anhydrous $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. Compound **7** was purified by column chromatography on silica gel (0.3 g, 59% calculated from **3**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60, 1.61, 1.65, 1.68, 1.73 (8 × s, 24H), 1.75 - 2.14 (m, 24H), 2.44 (s, 3H, $CH_3C_6H_4$-), 3.78 (d, J = 8.0 Hz, 2H, -SO_2CH_2-), 4.95 (t, J = 6.7 Hz, 1H), 5.06-5.16 (m, 5H), 5.20 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 16.19 (q), 16.20 (q), 17.9 (q), 21.8 (q, $CH_3C_6H_4$-), 23.5 (q), 23.64 (q), 23.67 (q), 23.75 (q), 25.9 (q), 26.0 (t), 26.5 (t), 26.6 (t), 26.8 (t), 26.9 (t), 32.18 (t), 32.26 (t), 32.32 (t), 32.41 (t), 39.92 (t), 39.94 (t), 56.2 (t, -SO_2CH_2-), 111.2 (d, -SO_2CH_2CH=), 124.2 (d, -CH_2CH=), 124.3 (d, -CH_2*C*H=), 124.4 (d, -CH_2*C*H=), 124.6 (d, -CH_2*C*H=), 125.0 (d, -CH_2*C*H=), 125.1 (d, -CH_2*C*H=), 128.6 (d), 129.8 (d), 131.5 (s), 135.1 (s), 135.4 (s), 135.57 (s), 135.61 (s), 136.1 (s), 136.2 (s), 144.6 (s), 146.0 (s); HRMS (ESI/Q-TOF) *m/z* $[M+Na]^+$ Calcd 655.4519 for $C_{42}H_{64}O_2SNa$; found 655.4528.

Compound 8. The sulfone **7** (300 mg, 470 μmol) was dissolved in a mixture of anhydrous THF and hexamethylphosphoramide (HMPA) (4:1, 5 mL) and the resulting solution was cooled to –78 ºC. *n*-Butyllithium (0.4 mL, 640 μmol, 1.6 M in hexane) was added dropwise to this solution, which was stirring for 1 h at the same temperature. A solution of bromide **5**[2] (430 mg, 700 μmol) in anhydrous THF-HMPA (4:1, 2 mL) was added dropwise to the sulfone solution and the mixture was allowed to stir for an additional 3 h at –78 ºC. After warming the mixture to iced-water temperature, it was poured into a mixture of ice and water and the mixture was washed with hexanes-ether (1:1). The separated organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford compound **8** (470 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57 - 1.78 (m, 38H), 1.91 - 2.10 (m, 30H), 2.35 - 2.70 (m, 4H), 2.41, 2.44 (2 × s, 6H, -$SO_2C_6H_4CH_3$), 3.79 - 3.87 (m, 2H, -$CHSO_2C_6H_4CH_3$), 3.98 (d, *J* = 6.6 Hz, 2H, -CH_2OBn), 4.49 (s, 2H, -OCH_2Ph), 4.83 - 5.02 (m, 4H), 5.05 - 5.19 (m, 6H), 5.41 (t, *J* = 6.8 Hz, 1H, -C*H*CH_2OBn), 7.26 - 7.36 (m, 9H), 7.67 - 7.74 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 16.2 (q), 17.9 (q), 21.80, 21.84 (2 × q, $CH_3C_6H_4$), 23.48 (q), 23.50 (q), 23.52 (q), 23.61 (q), 23.65 (q), 23.68 (q), 23.77 (q), 23.79 (q), 25.8 (t), 25.9 (q), 26.0 (t), 26.4 (t), 26.5 (t), 26.75 (t), 26.78 (t), 26.81 (t), 26.9 (t), 30.2 (t), 30.5 (t), 32.12 (t), 32.17 (t), 32.27 (t), 32.33 (t), 32.4 (t), 39.91 (t), 39.93 (t), 63.3, 63.4 (2 × d, *C*HTs), 66.5 (t, *C*H_2OBn), 72.3 (t, O*C*H_2Ph), 117.9 (d, -CH_2*C*H=), 118.0 (d, -CH_2*C*H=), 122.4 (d, BnOCH_2*C*H=), 124.25 (d, -

CH_2*C*H=), 124.27 (d, -CH_2*C*H=), 124.4 (d, -CH_2*C*H=), 124.5 (d, -CH_2*C*H=), 124.96 (d, -CH_2*C*H=), 125.01 (d, -CH_2*C*H=), 127.7 (d), 127.9 (d, -CH_2*C*H=), 128.0 (d), 128.3 (d, -CH_2*C*H=), 128.5 (d), 129.3 (d), 129.4 (d), 129.53 (d), 129.61 (d, ArH), 130.63 (s), 130.9 (s), 131.4 (s), 135.05 (s), 135.14 (s), 135.4 (s), 135.57 (s), 135.64 (s), 135.9 (s), 138.7 (s), 140.2 (s), 144.5 (s), 144.55 (s), 144.62 (s), 144.8 (s), 145.1 (s); HRMS (ESI/Q-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{76}H_{108}O_5S_2Na$ 1187.7530; found 1187.7547.

Compound 1. Ethylamine (50 mL) was added to a flask containing lithium (100 mg, 8.6 mmol) at –78 ºC and ether (10 mL) was added. After stirring for 10 min at –78 ºC, an ethereal solution of compound **8** (470 mg, 400 μmol in 10 mL) was added dropwise to the blue solution over 20 min. After stirring for 40 min at –78 ºC, the reaction was quenched by the addition of isoprene (5 mL) and MeOH (10 mL). After addition of saturated NH_4Cl, the reaction mixture was washed with ethyl acetate. The combined ethyl acetate layer was washed with brine, dried over anhydrous $MgSO_4$, filtered through a layer of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **1** (190 mg, 61%). The complete assignment of ^1H and ^{13}C NMR is given in Table S1. HRMS (ESI/Q-TOF) *m/z* $[M+Na]^+$ Calcd 789.6884 for $C_{55}H_{90}ONa$; found 789.6842.

NMR Spectroscopy. The structures of undecaprenol **1** and **2** [10 mg of each was dissolved in 600 μL C_6D_6 (100%, 99.96 atom % D) containing 10 mg Eu(hfc)$_3$] were determined by interpretation of the 2D homonuclear DQF-COSY, TOCSY, ROESY and heteronuclear ^1H-^{13}C HSQC, HSQC-TOCSY, HMBC NMR spectra. All NMR spectra were recorded at 25 °C on a four-channel Bruker AVANCE II spectrometer at field strength of 18.79 T using a 5-mm inverse triple-resonance (TCI) $^1H/^{13}C/^{15}N$, z-axis PFG cryoprobe, and running the TopSpin 3.2, pl6 software. The above spectra were measured by employing ordinary pulse sequences in the Bruker pulse sequence library. To enhance spectral resolution, linear prediction and zero filling were applied to the time domain data. Also, the squared shifted sine weighting window functions were used before 2D Fourier transformation. The homonuclear spectra and the ^{1}H dimension in heteronuclear spectra were referenced to the residual solvent signal (C_6D_6, δ_H 7.15 ppm). The ^{13}C dimension in the heteronuclear spectra was referenced indirectly.[2] Resonance signals in the measured spectra exhibited slight downfield shifts as the samples stayed in the magnet longer. Consequently, Table S1 contains values of the proton and carbon chemical shifts for carbons with directly attached protons corresponding to the positions of the crosspeaks in the HSQC spectra. The chemical-shift values for the quaternary carbons then correspond to the positions of the crosspeaks in the HMBC spectra.

References

(1) Hesek, D.; Lee, M.; Zajíček, J.; Fisher, J. F.; Mobashery, S. *J. Am. Chem. Soc.* **2012**, *134*, 13881-13888.

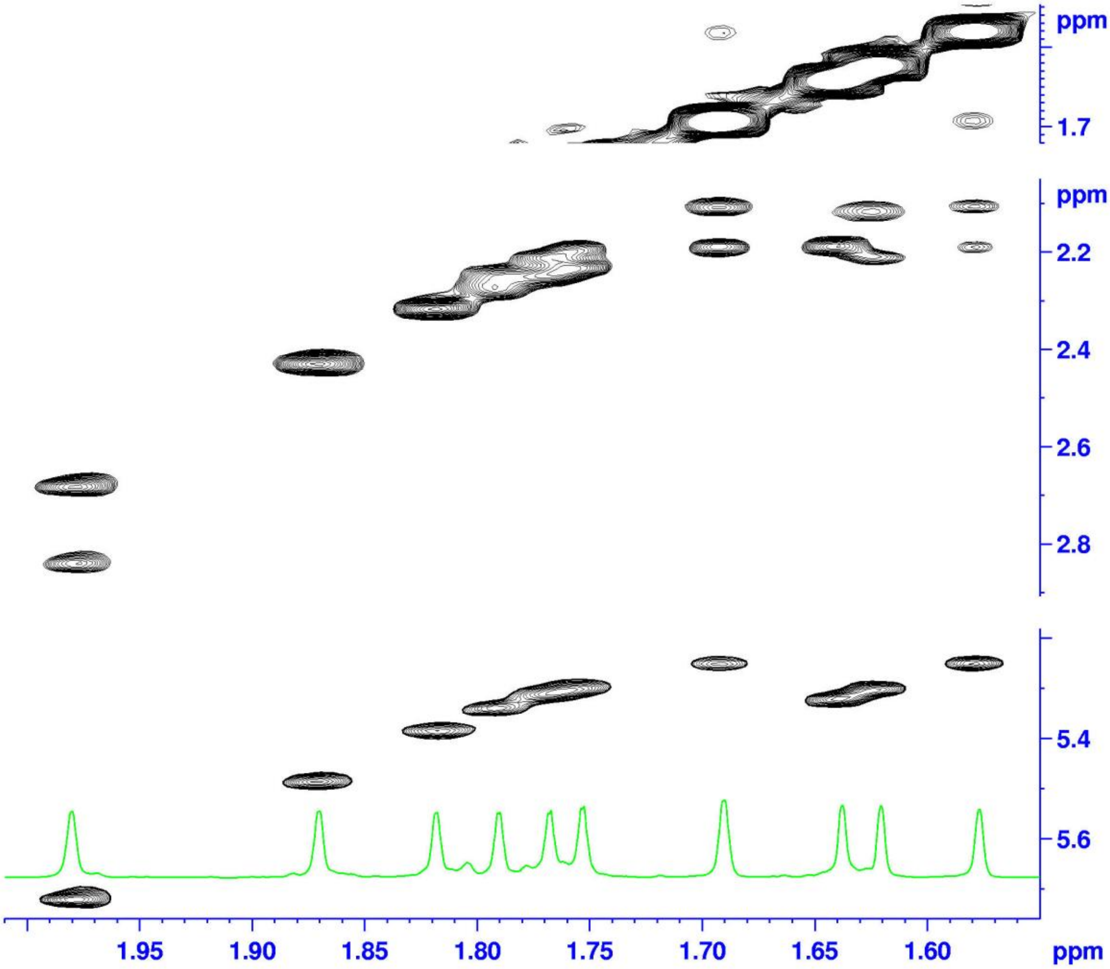
(2) Wishart, D. S.; Bigam, C. G.; Yao, J.; Abildgaard, F.; Dyson, H. J.; Oldfield, E.; Markley, J. L.; Sykes, B. D. *J. Biomol. NMR* **1995**, *6*, 135-140.

Table S1. NMR spectroscopic data for **1** (synthetic sample) and **2** (from *Magnolin kobus*) in C_6D_6 at 298 K (800.13 MHz).^{a,b}

1 + Eu(hfc)$_3$					**2 + Eu(hfc)$_3$**				
unit		^{13}C δ [ppm]^{c,d}	^{1}H δ [ppm]^{c}	HMBC connectivities	unit		^{13}C δ [ppm]^{c,d}	^{1}H δ [ppm]^{c}	HMBC connectivities
CH$_2$-1			14.37		CH$_2$-1			18.02	
CH-2	*Z*	129.09	11.50		CH-2	*Z*	129.51	10.35	
C-3		143.62			C-3		142.98		
CH$_2$-4		35.42	4.83	2, 3, 5, 6, 55	CH$_2$-4		34.90	4.01	2, 3, 5, 6, 55
CH$_2$-5		28.33	3.77	3, 4, 6, 7	CH$_2$-5		28.21	3.48	3, 4, 6, 7
CH-6	*Z*	126.54	6.70	4, 5, 7, 8, 54	CH-6	*Z*	126.33	6.41	4, 5, 8, 54
C-7		137.08			C-7		137.14		
CH$_2$-8		33.35	2.88	6, 7, 9, 10, 54	CH$_2$-8		33.27	2.74	6, 7, 9, 10, 54
CH$_2$-9		27.41	2.70	7, 8, 10, 11	CH$_2$-9		27.34	2.61	7, 8, 10, 11
CH-10	*Z*	126.02	5.71	8, 9, 11, 12, 53	CH-10	*Z*	125.93	5.65	8, 9, 11, 12, 53
C-11		135.83			C-11		136.02		
CH$_2$-12		32.97	2.45	10, 11, 13, 14, 53	CH$_2$-12		32.90	2.40	10, 11, 13, 53
CH$_2$-13		27.19	2.41	11, 12, 14, 15	CH$_2$-13		27.14	2.40	11, 12, 14, 15
CH-14	*Z*	125.83	5.47	12, 13, 15, 16, 52	CH-14	*Z*	125.82	5.45	12, 13, 52
C-15		135.58			C-15		135.83		
CH$_2$-16		32.85	2.33	14, 15, 17, 18, 52	CH$_2$-16		32.83	2.29	14, 17, 18, 52
CH$_2$-17		27.09	2.32		CH$_2$-17		27.10	2.30	15, 16, 18, 19
CH-18	*Z*	125.79	5.39	16, 17, 19, 20, 51	CH-18	*Z*	125.75	5.37	16, 17, 19, 20, 51
C-19		135.46			C-19		135.73		
CH$_2$-20		32.77	2.25	21, 51	CH$_2$-20		32.76	2.23	^{e}
CH$_2$-21		27.07	2.26	19, 20, 22, 23	CH$_2$-21		27.07	2.25	^{e}
CH-22	*Z*	125.73	5.34	20, 21, 23, 24, 50	CH-22	*Z*	125.72	5.33	20, 21, 24, 50
C-23		135.45			C-23		135.69		
CH$_2$-24		32.72	2.23	25, 50	CH$_2$-24		32.75	2.23	^{e}
CH$_2$-25		27.03	2.23	24	CH$_2$-25		27.04	2.24	^{e}
CH-26	*Z*	125.72	5.32	24, 25, 27, 28, 49	CH-26	*Z*	125.65	5.31	24, 25, 28, 49
C-27		135.43			C-27		135.76		
CH$_2$-28		32.74	2.30	^{e}	**CH$_2$-28**		**32.45**	**2.19**	^{e}
CH$_2$-29		27.03	2.21	^{e}	CH$_2$-29		27.14	2.20	^{e}
CH-30	*Z*	125.60	5.29	28, 29, 31, 32, 48	**CH-30**	*E*	**124.76**	5.33	28, 29, 32, 48
C-31		135.49			C-31		135.69		
CH$_2$-32		32.46	2.18	^{e}	**CH$_2$-32**		**40.30**	**2.12**	^{e}
CH$_2$-33		27.14	2.19	^{e}	CH$_2$-33		27.21	2.20	^{e}
CH-34	*E*	124.78	5.32	32, 33, 35, 36, 47	CH-34	*E*	124.85	5.31	32, 33, 36, 47
C-35		135.38			C-35		135.38		
CH$_2$-36		40.30	2.12	34, 35, 37, 47	CH$_2$-36		40.30	2.12	^{e}
CH$_2$-37		27.19	2.21		CH$_2$-37		27.21	2.21	^{e}
CH-38	*E*	124.87	5.29	36, 37, 39, 40, 46	CH-38	*E*	124.90	5.30	36, 37, 40, 46
C-39		135.12			C-39		135.25		
CH$_2$-40		40.30	2.10	38, 39, 41, 42, 46	CH$_2$-40		40.30	2.11	^{e}
CH$_2$-41		27.32	2.19		CH$_2$-41		27.30	2.19	^{e}
CH-42	*ω*	125.02	5.25	40, 41, 43, 44, 45	CH-42	*ω*	125.03	5.25	40, 41, 44, 45
C-43		131.21			C-43		131.46		
CH$_3$-44	*ω*	17.82	1.58	42, 43, 45	CH$_3$-44	*ω*	25.91	1.69	42, 43, 45
CH$_3$-45	*ω*	25.92	1.69	42, 43, 44	CH$_3$-45	*ω*	17.82	1.58	42, 43, 44
CH$_3$-46	*E*	16.20	1.62	38, 39, 40	CH$_3$-46	*E*	16.20	1.62	38, 39, 40
CH$_3$-47	*E*	16.19	1.64	34, 35, 36	CH$_3$-47	*E*	16.20	1.63	34, 35, 36
CH$_3$-48	*Z*	23.73	1.75	30, 31, 32	**CH$_3$-48**	*E*	**16.20**	**1.65**	30, 31, 32
CH$_3$-49	*Z*	23.76	1.77	26, 27, 28	CH$_3$-49	*Z*	23.76	1.76	26, 27, 28
CH$_3$-50	*Z*	23.80	1.79	22, 23, 24	CH$_3$-50	*Z*	23.78	1.78	22, 23, 24
CH$_3$-51	*Z*	23.82	1.82	18, 19, 20	CH$_3$-51	*Z*	23.81	1.81	18, 19, 20
CH$_3$-52	*Z*	23.87	1.86	14, 15, 16	CH$_3$-52	*Z*	23.85	1.86	14, 15, 16
CH$_3$-53	*Z*	23.98	1.98	10, 11, 12	CH$_3$-53	*Z*	23.92	1.95	10, 11, 12
CH$_3$-54	*Z*	24.19	2.19	6, 7, 8	CH$_3$-54	*Z*	24.12	2.11	6, 7, 8
CH$_3$-55	*Z*	25.73	3.11	2, 3, 4	CH$_3$-55	*Z*	25.35	2.82	2, 3, 4

^{a}C, CH-, CH_2-, and CH_3- are colored in white, blue, pink, and gray. ^{b}The numbers for **2** that are significantly different from those for **1** are in bold. ^{c}The proton and carbon chemical shift values for carbons with directly attached protons represent positions of the corresponding crosspeaks in the HSQC spectra. ^{d}The chemical shift values of quaternary carbons represent positions of the corresponding crosspeaks in the HMBC spectra. ^{e}The connectivities could not be unambiguously established due to strong signal overlaps.

TOCSY spectra of compound **1** + Eu(hfc)$_3$



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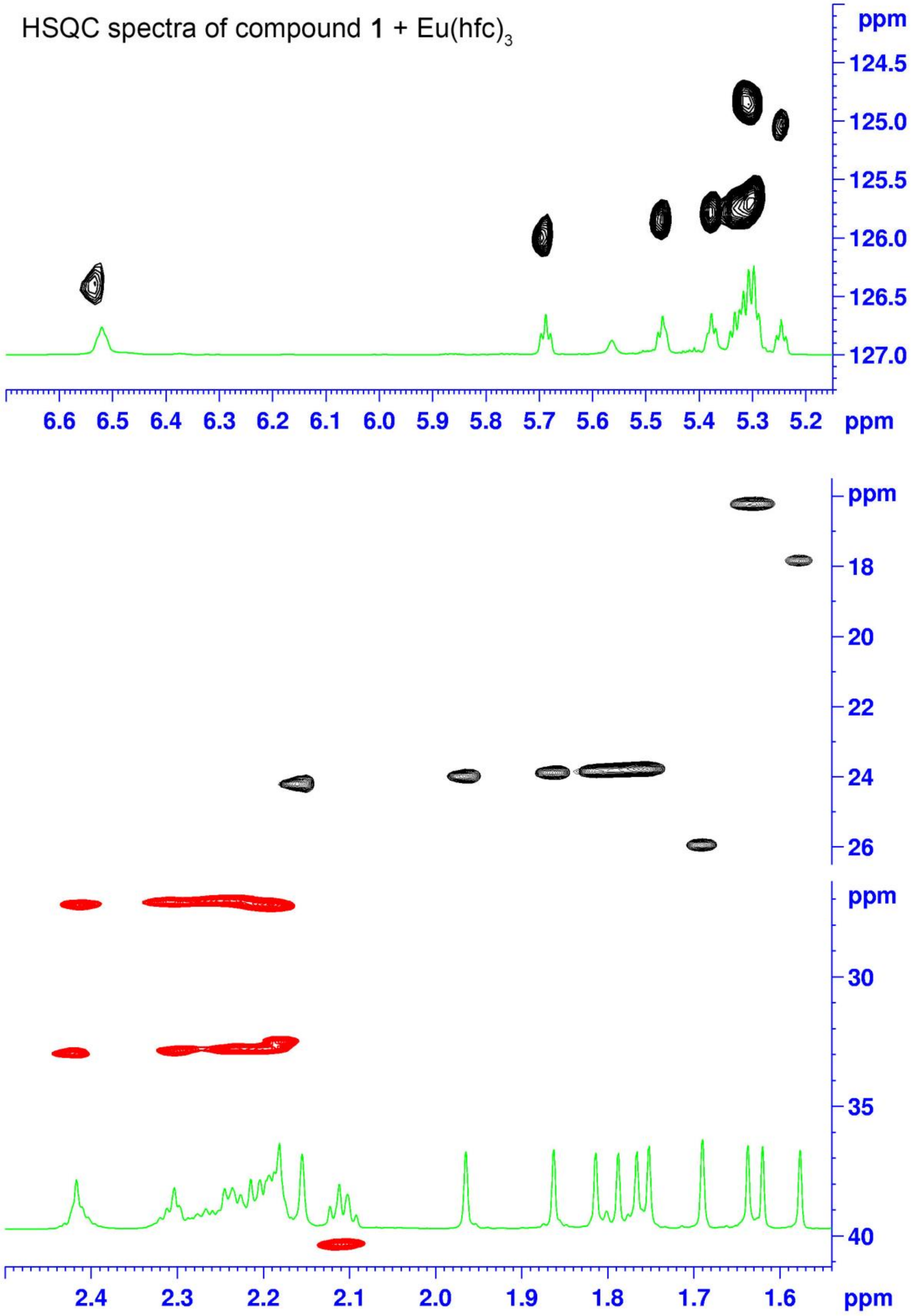

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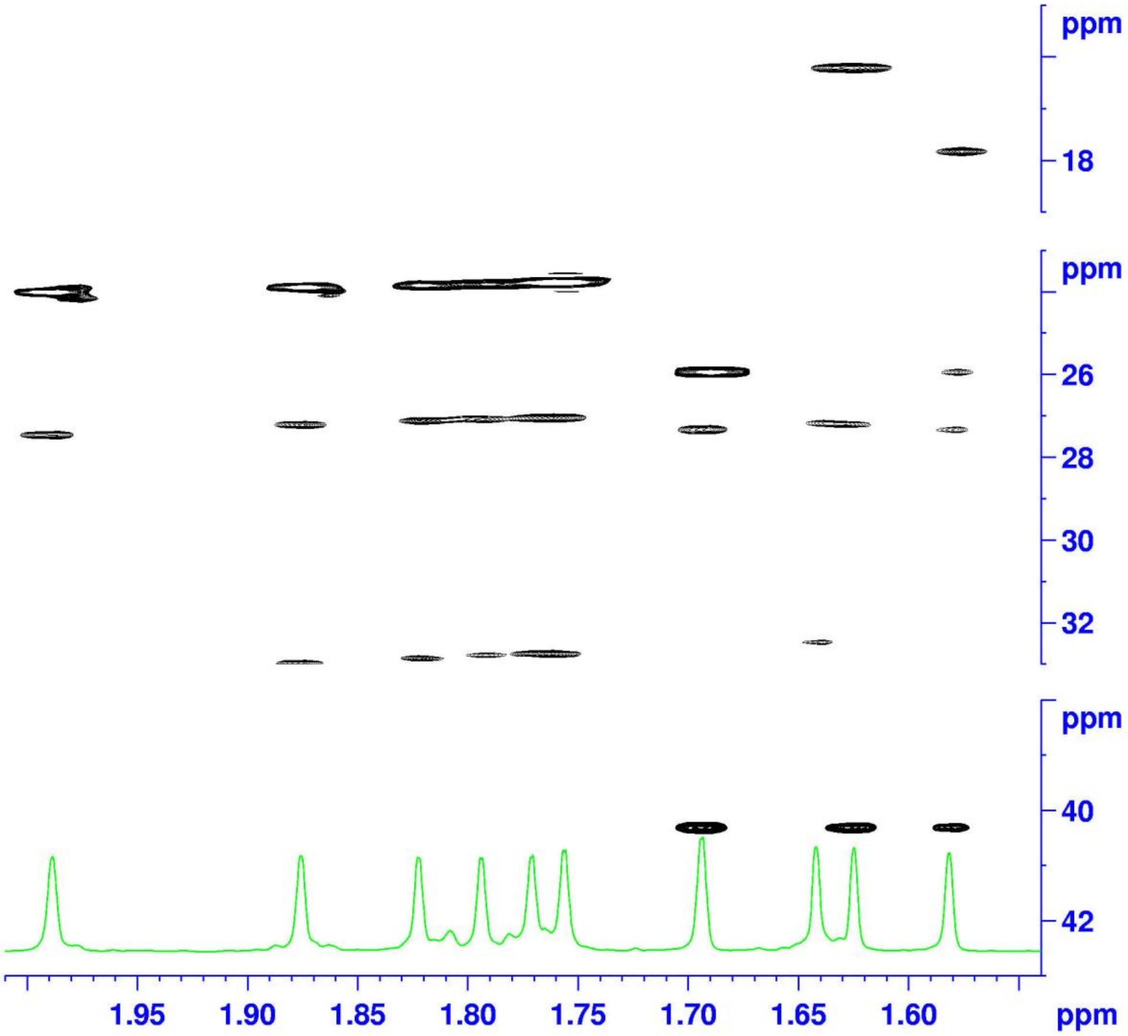
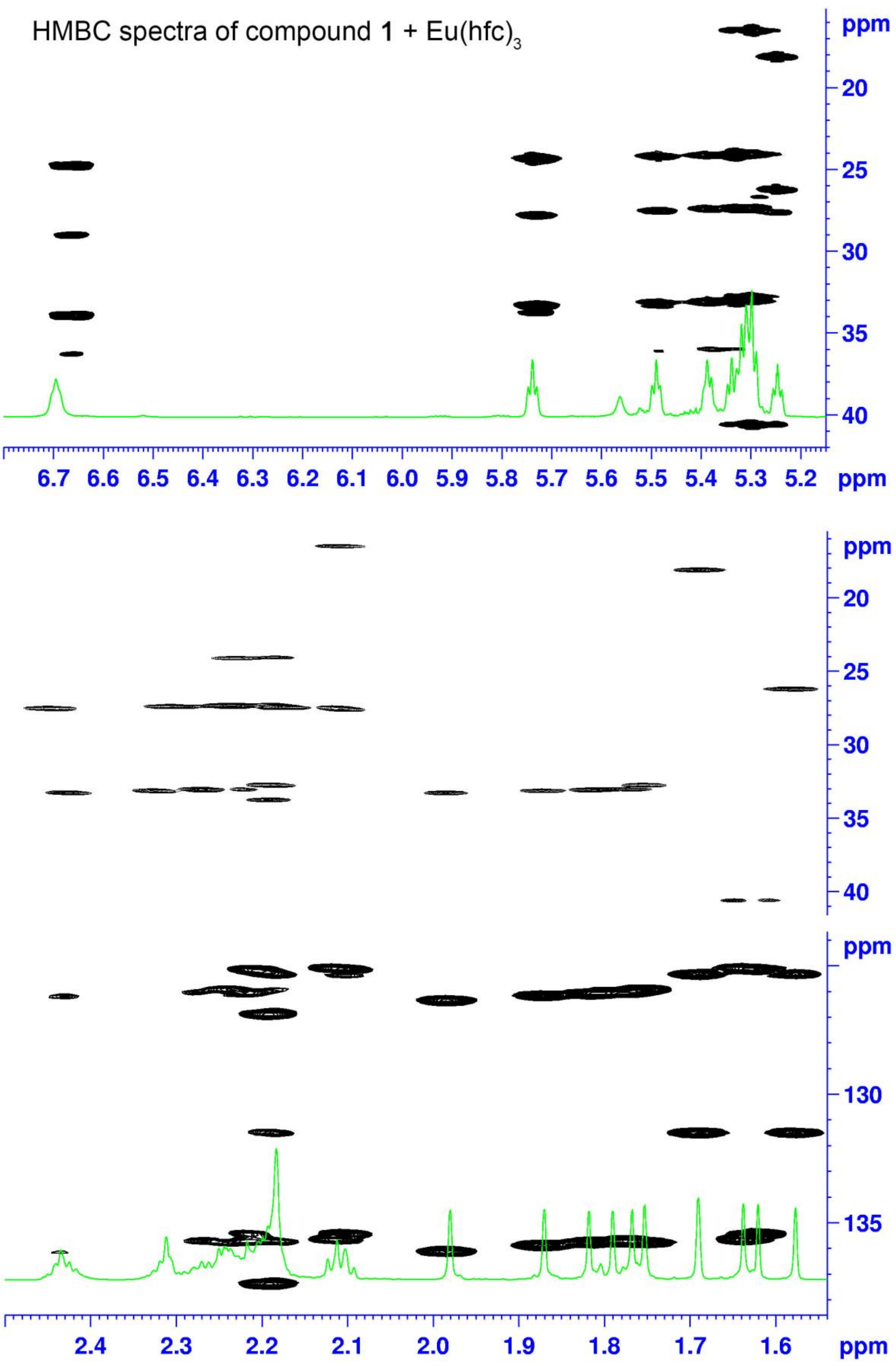


HMBC spectra of compound **1** + Eu(hfc)$_3$



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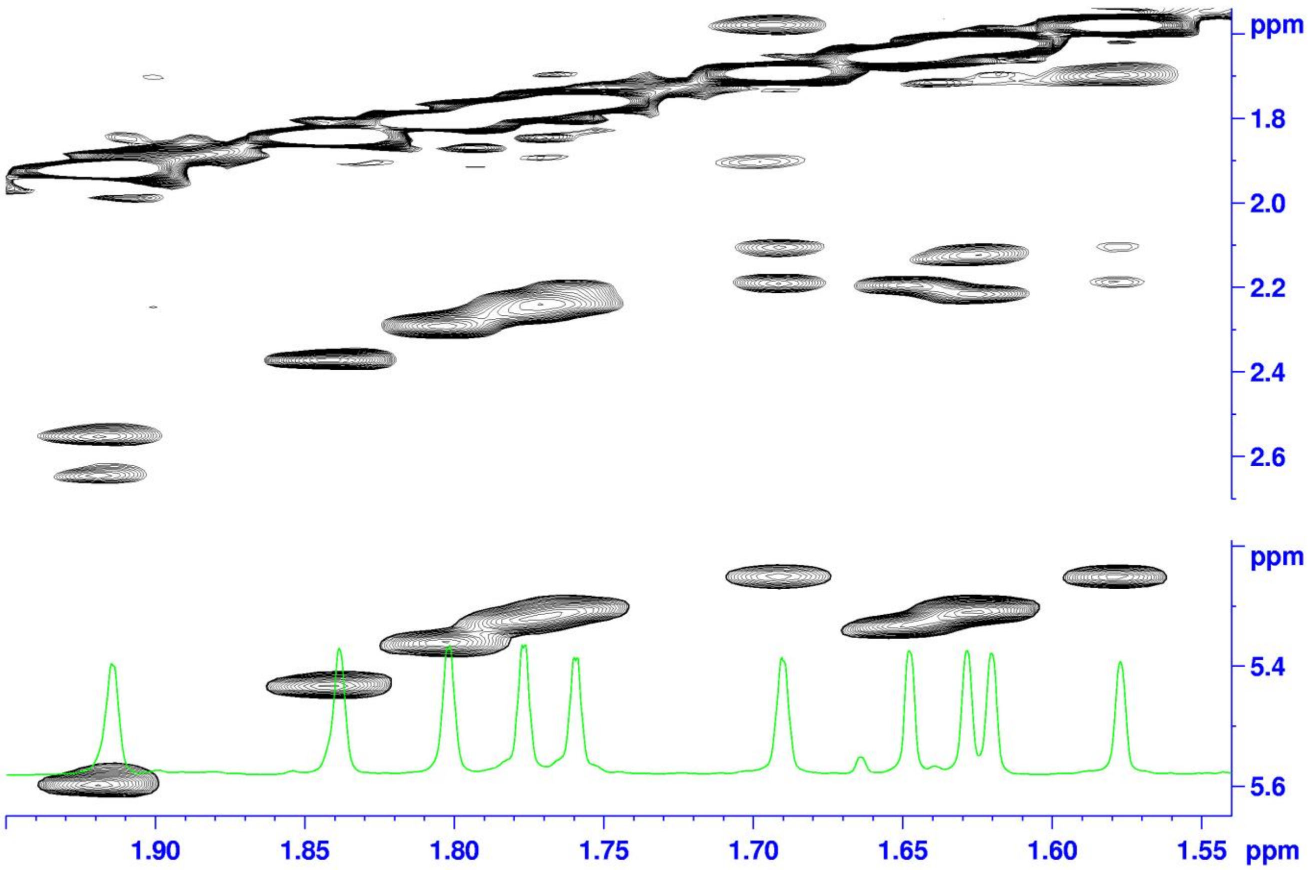

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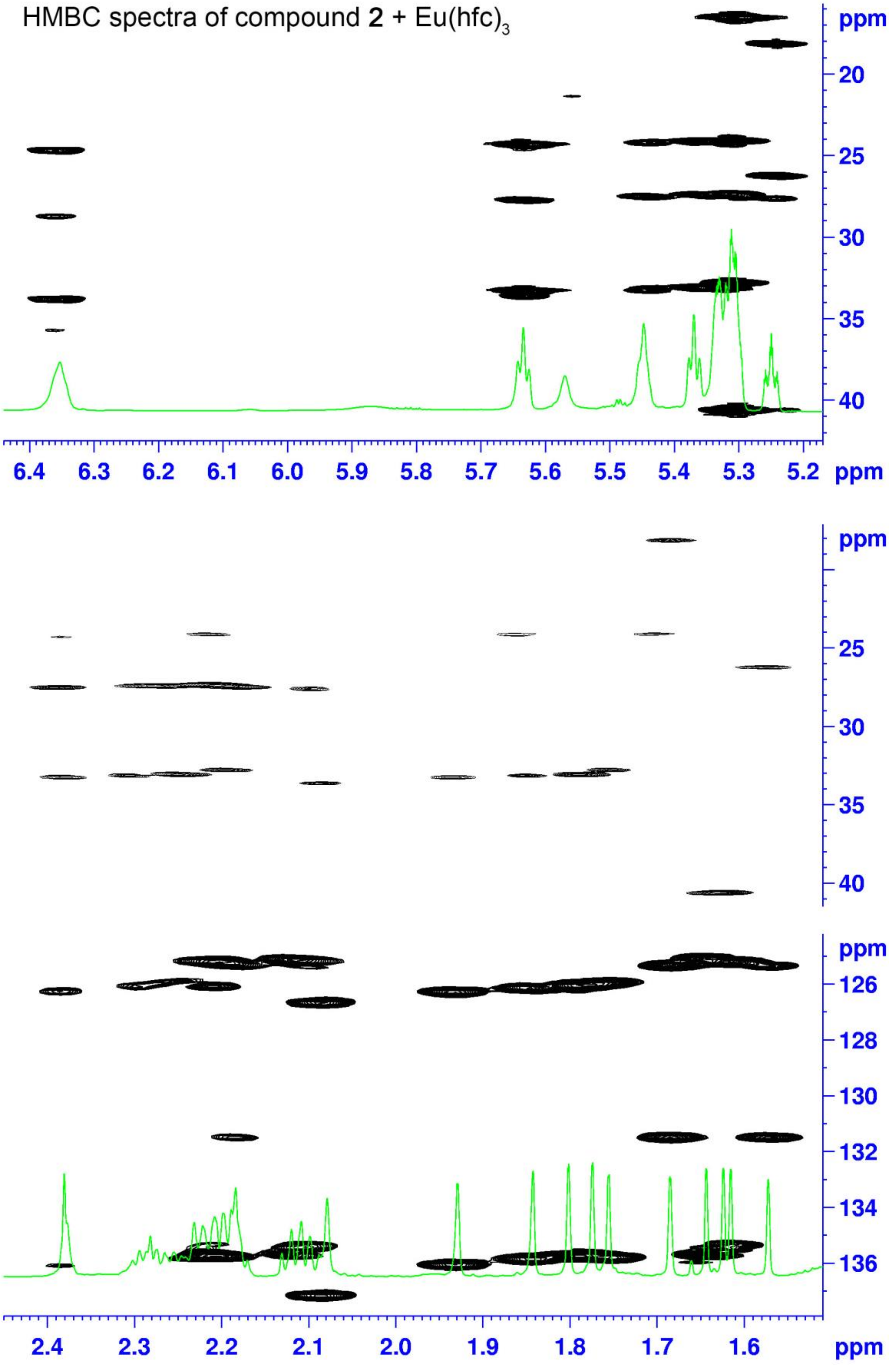

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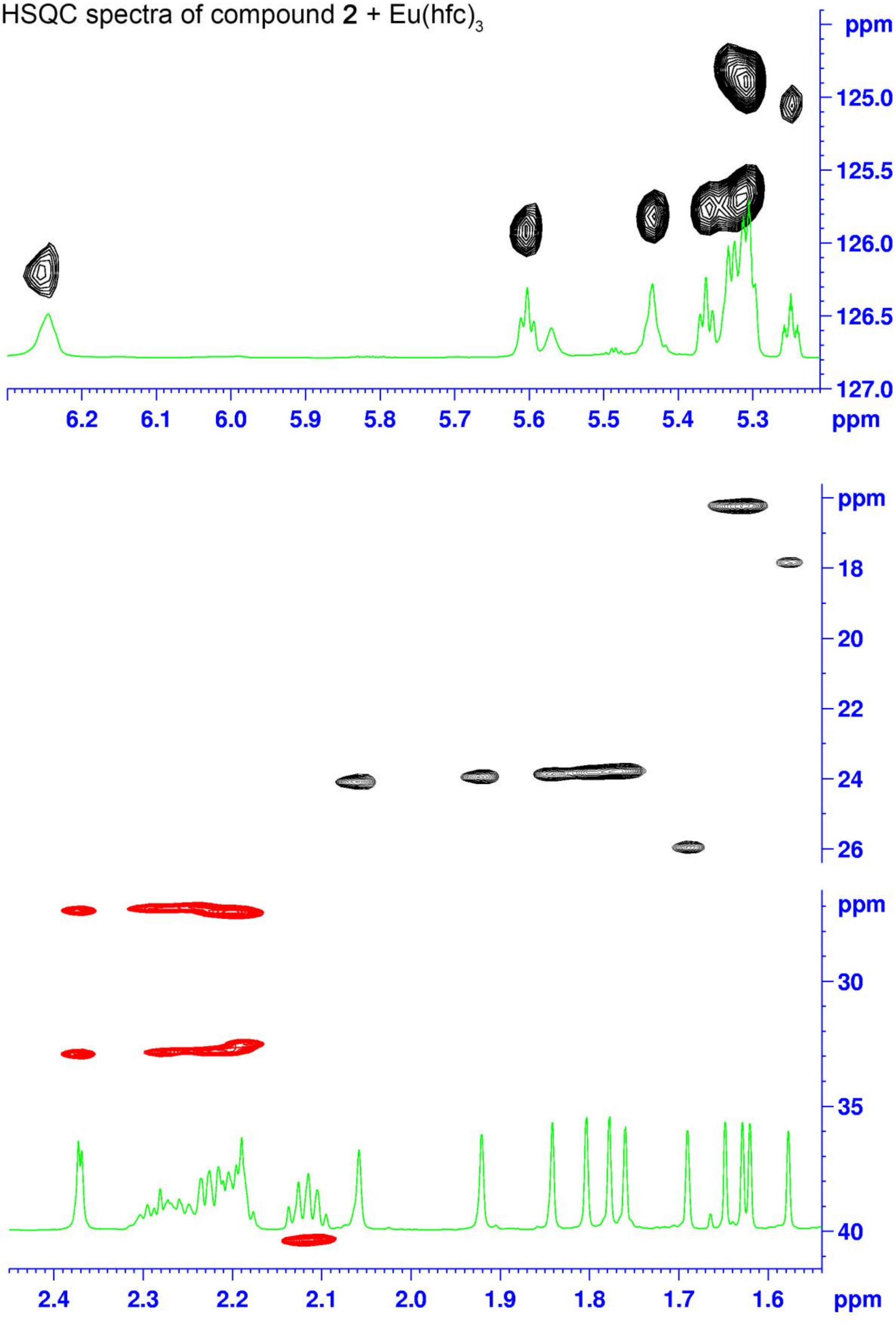

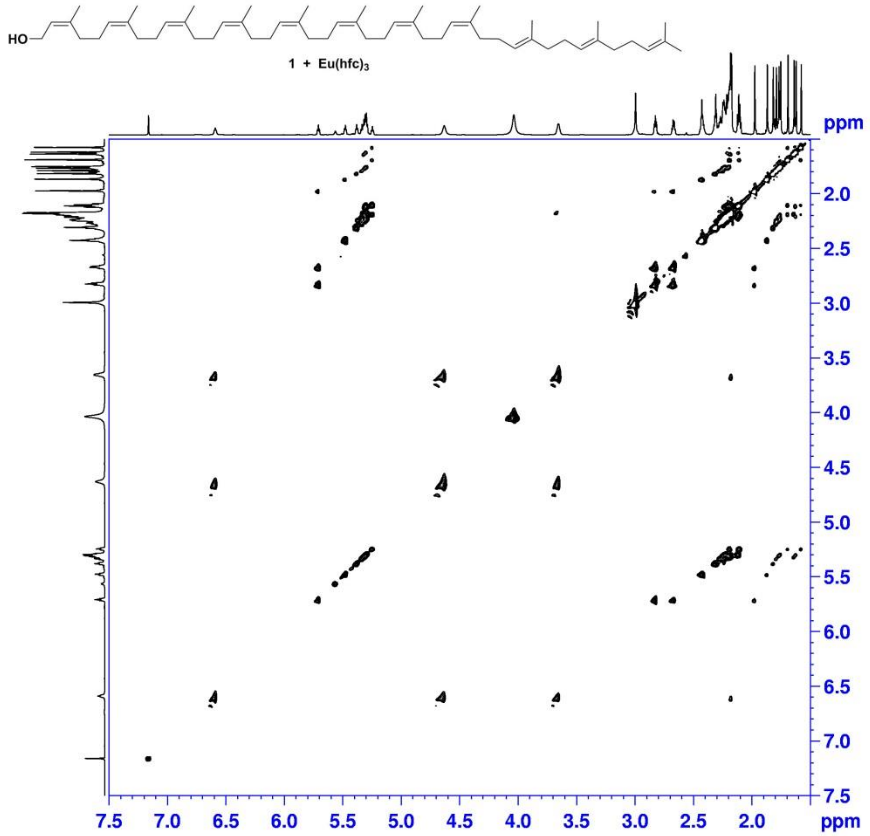

TOCSY

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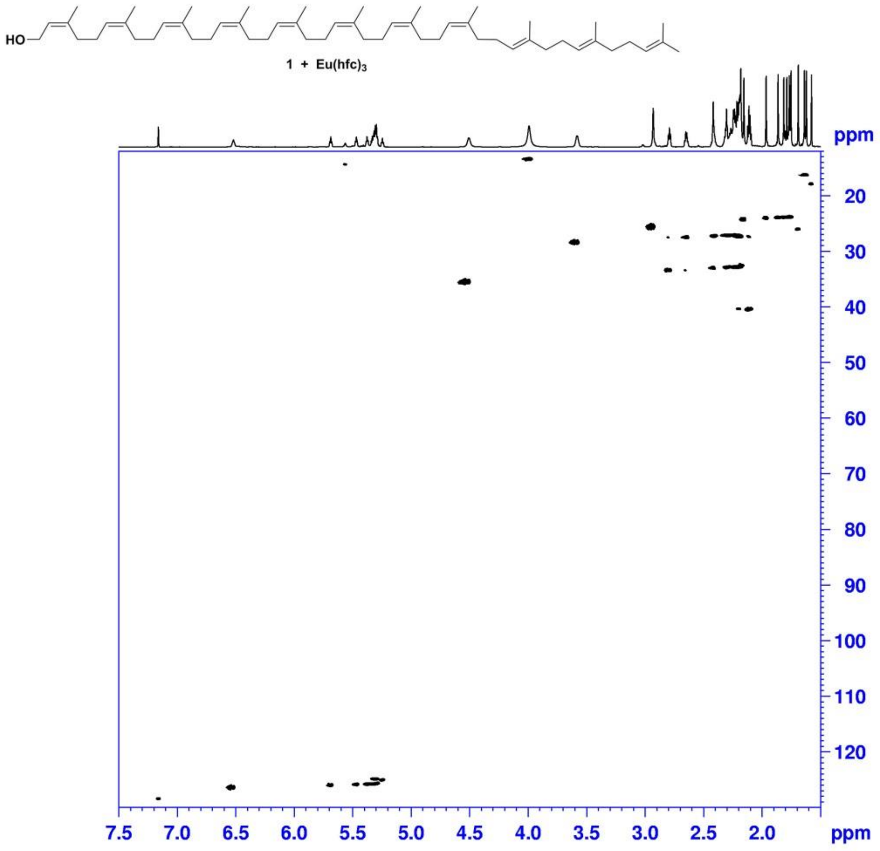

HSQC

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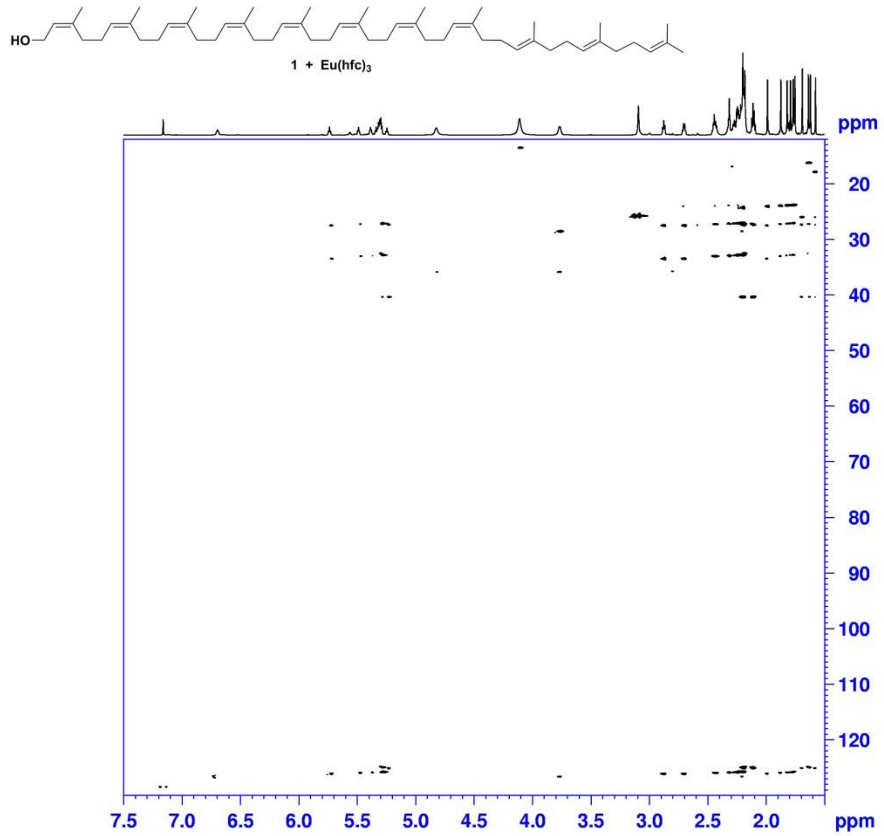

HSQC-TOCSY

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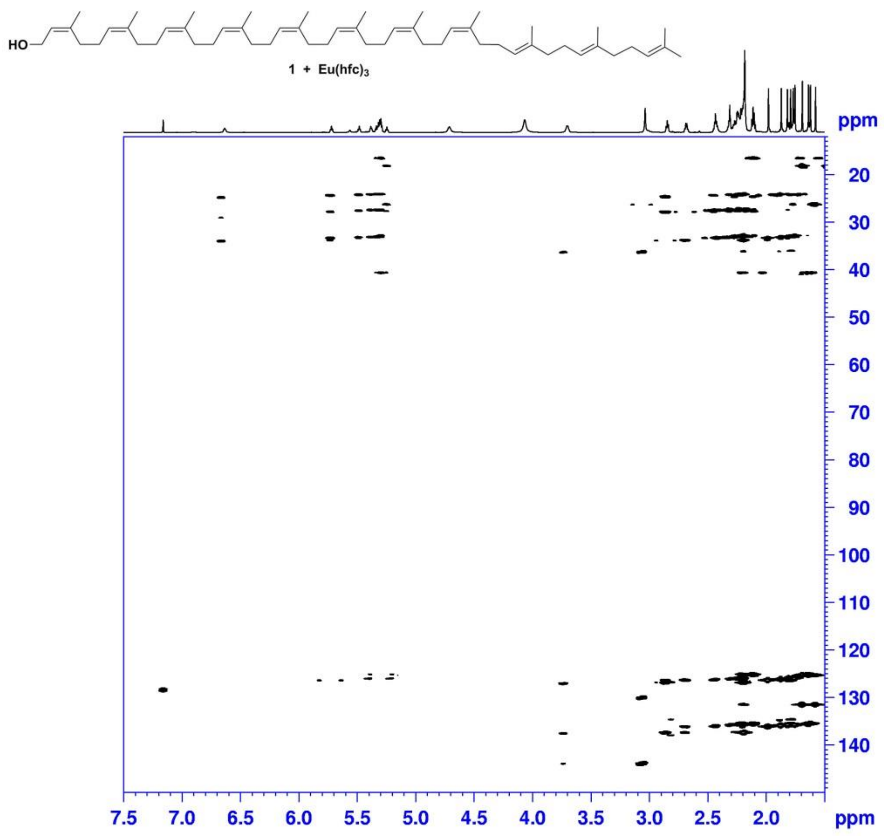
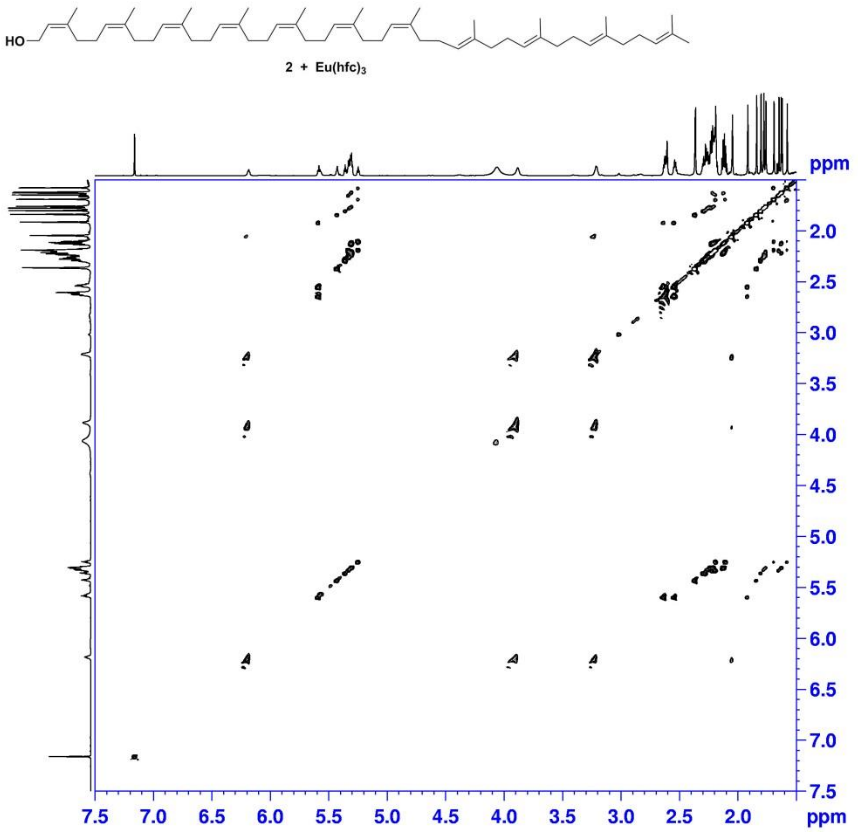
GB                      0
```



HMBC

```
NAME         UPH-B1-15-15
EXPNO                   6
PROCNO                  1
Date_            20130719
Time                18.04
INSTRUM             spect
PROBHD   5 mm CPTCI 1H-
PULPROG     hmbcgpl2ndqf
TD                   2048
SOLVENT              C6D6
NS                     48
DS                     32
SWH            16741.072 Hz
FIDRES          8.174352 Hz
AQ             0.0612169 sec
RG                   5790
DW                 29.867 usec
DE                  30.00 usec
TE                  301.9 K
CNST6        125.0000000
CNST7        160.0000000
CNST13         8.0000000
D0            0.00000300 sec
D1            1.20000005 sec
D6            0.06250000 sec
D16           0.00020000 sec
IN0           0.00001770 sec

======== CHANNEL f1 ========
SFO1         800.1835866 MHz
NUC1                   1H
P1                   8.60 usec
P2                  17.20 usec
ND0                     2
TD                   1024
SFO1            201.2215 MHz
FIDRES         27.586512 Hz
SW                140.386 ppm
FnMODE                 QF
SI                   2048
SF           800.1799913 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
SI                   2048
MC2                    QF
SF           201.2052726 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
```

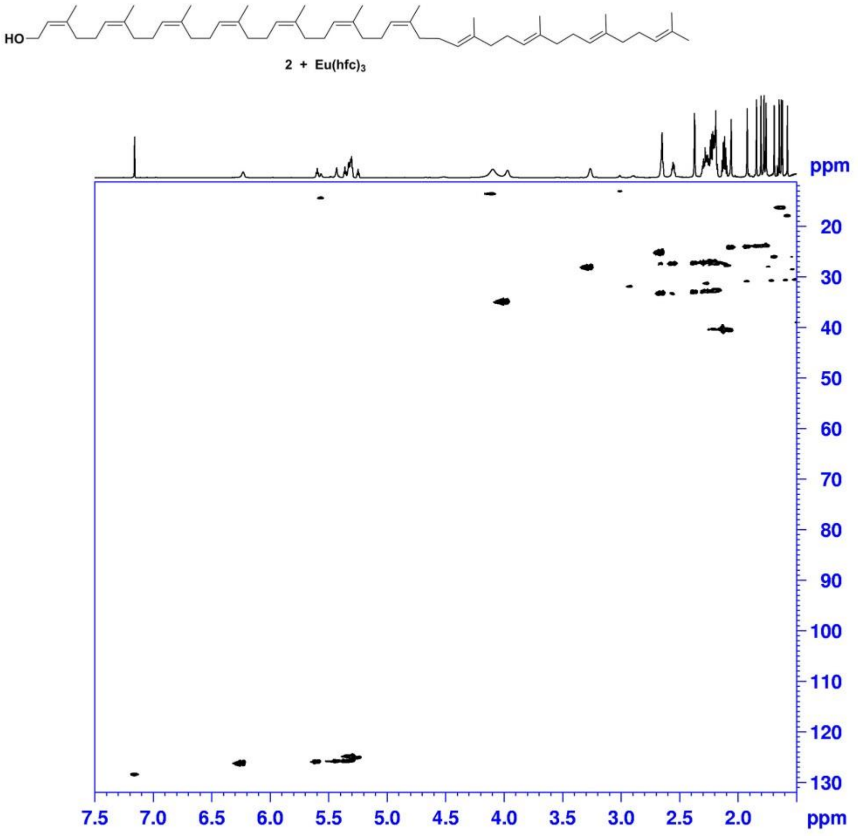


2 + Eu(hfc)$_3$

TOCSY

```
NAME              UPH-16
EXPNO                  2
PROCNO                 1
Date_           20160422
Time               17.59
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG         dipsi2ph
TD                  2048
SOLVENT             C6D6
NS                    40
DS                    64
SWH            20161.291 Hz
FIDRES          9.844380 Hz
AQ             0.0508404 sec
RG                 17.08
DW                24.800 usec
DE                 30.00 usec
TE                 301.9 K
D0            0.00001423 sec
D1            1.10000002 sec
D9            0.06100000 sec
D12           0.00002000 sec
D20           0.00200000 sec
D21           0.00300000 sec
IN0           0.00004960 sec
L1                    22

======== CHANNEL f1 ========
SFO1         800.1846758 MHz
NUC1                  1H
P1                  8.30 usec
P6                 24.00 usec
ND0                    1
TD                  1024
SFO1            800.1847 MHz
FIDRES         19.688761 Hz
SW                25.196 ppm
FnMODE       States-TPPI
SI                  4096
SF           800.1799925 MHz
WDW                QSINE
SSB                    3
LB                  0.00 Hz
GB                     0
PC                  1.00
SI                  4096
MC2          States-TPPI
SF           800.1799915 MHz
WDW                QSINE
SSB                    3
LB                  0.00 Hz
GB                     0
```

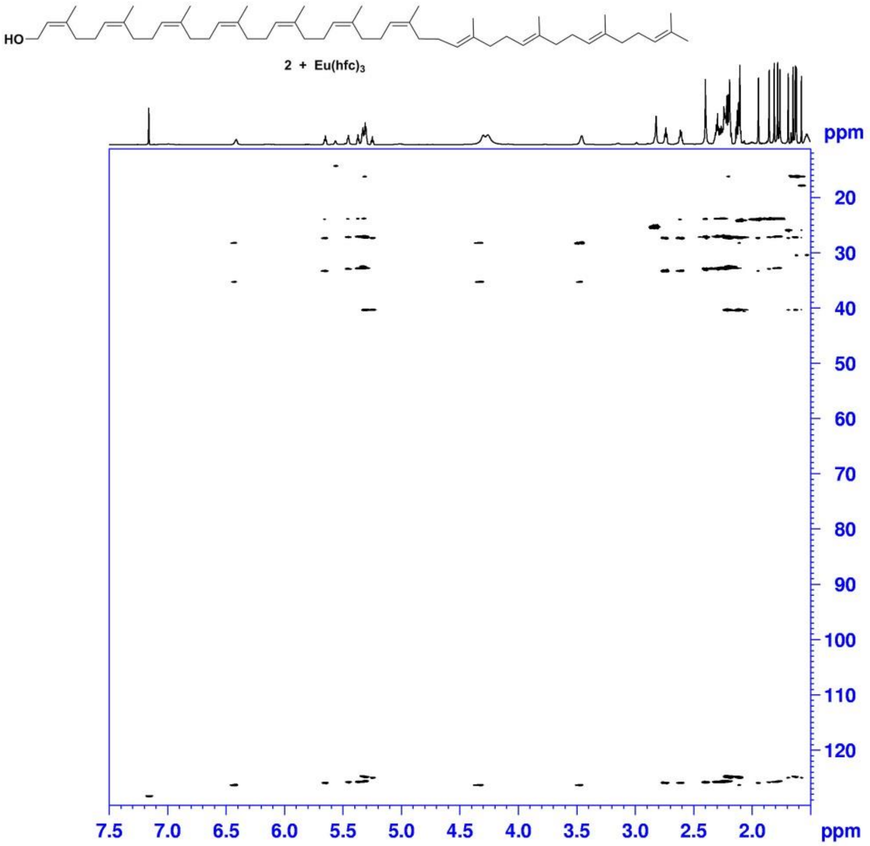


2 + Eu(hfc)$_3$

HSQC

```
NAME              UPH-16
EXPNO                  4
PROCNO                 1
Date_           20160423
Time               10.20
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG hsqcedetgpsisp2.2
TD                  2048
SOLVENT             C6D6
NS                    48
DS                    64
SWH            20161.291 Hz
FIDRES          9.844380 Hz
AQ             0.0508404 sec
RG                  2580
DW                24.800 usec
DE                 30.00 usec
TE                 301.9 K
CNST2        145.0000000
CNST17        -0.5000000
D0            0.00000300 sec
D1            1.10000002 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
D21           0.00344828 sec
D24           0.00086207 sec
IN0           0.00001770 sec

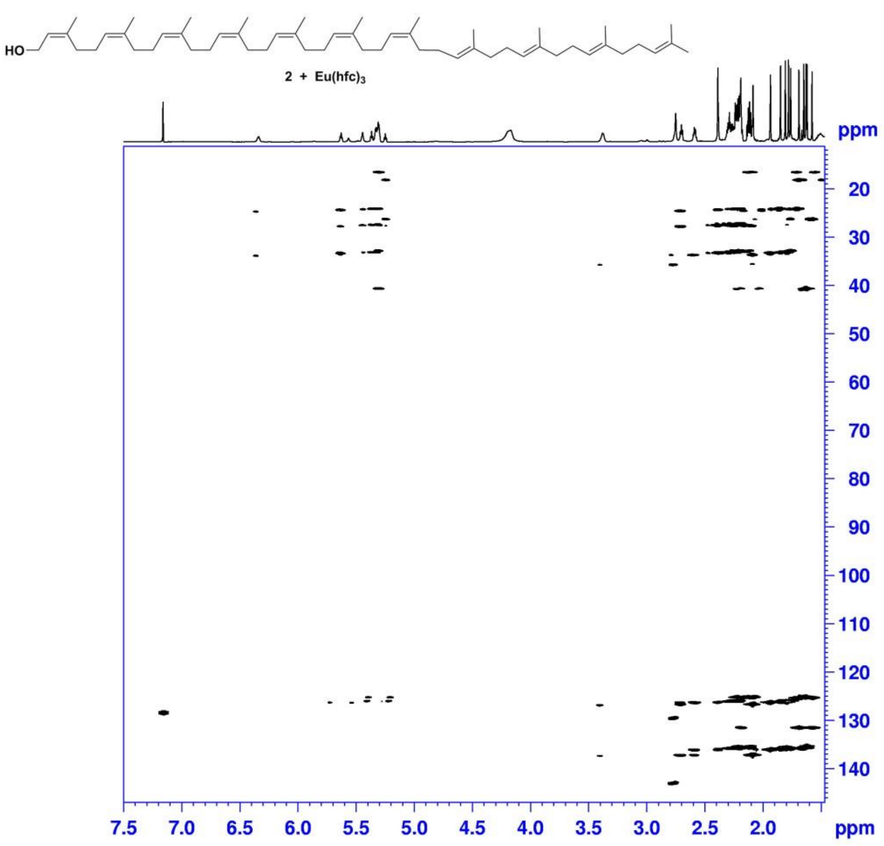
======== CHANNEL f1 ========
SFO1         800.1846758 MHz
NUC1                  1H
P1                  8.30 usec
P2                 16.60 usec
P28              1000.00 usec
ND0                    2
TD                  1024
SFO1         201.2205 MHz
FIDRES         27.586512 Hz
SW               140.386 ppm
FnMODE    Echo-Antiecho
SI                  2048
SF           800.1799903 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.00
SI                  2048
MC2        echo-antiecho
SF           201.2053279 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
```



HSQC-TOCSY

```
NAME              UPH-16
EXPNO                 10
PROCNO                 1
Date_           20160425
Time               18.02
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG hsqcdietgpsisp.2
TD                  2048
SOLVENT             C6D6
NS                    48
DS                    64
SWH           20161.291 Hz
FIDRES         9.844380 Hz
AQ            0.0508404 sec
RG                  3250
DW               24.800 usec
DE                30.00 usec
TE                301.9 K
CNST2       145.0000000
CNST17       -0.5000000
D0           0.00000300 sec
D1           1.10000002 sec
D4           0.00172414 sec
D9           0.06100000 sec
D11          0.03000000 sec
D16          0.00020000 sec
D24          0.00086207 sec
IN0          0.00001770 sec
L1                    22

======== CHANNEL f1 ========
SFO1        800.1846758 MHz
NUC1                  1H
P1                  8.45 usec
P2                 16.90 usec
P6                 24.00 usec
P28              1000.00 usec
ND0                    2
TD                  1024
SFO1           201.2205 MHz
FIDRES        27.586512 Hz
SW              140.386 ppm
FnMODE      Echo-Antiecho
SI                  2048
SF          800.1799947 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.00
SI                  2048
MC2         echo-antiecho
SF          201.2053398 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
```



HMBC

```
NAME              UPH-16
EXPNO                  8
PROCNO                 1
Date_           20160424
Time               16.22
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG      hmbcgpl2ndqf
TD                  2048
SOLVENT             C6D6
NS                    56
DS                    64
SWH           20161.291 Hz
FIDRES         9.844380 Hz
AQ            0.0508404 sec
RG                  5160
DW               24.800 usec
DE                30.00 usec
TE                301.9 K
CNST6       125.0000000
CNST7       165.0000000
CNST13        8.0000000
D0           0.00000300 sec
D1           1.10000002 sec
D6           0.06250000 sec
D16          0.00020000 sec
IN0          0.00001770 sec

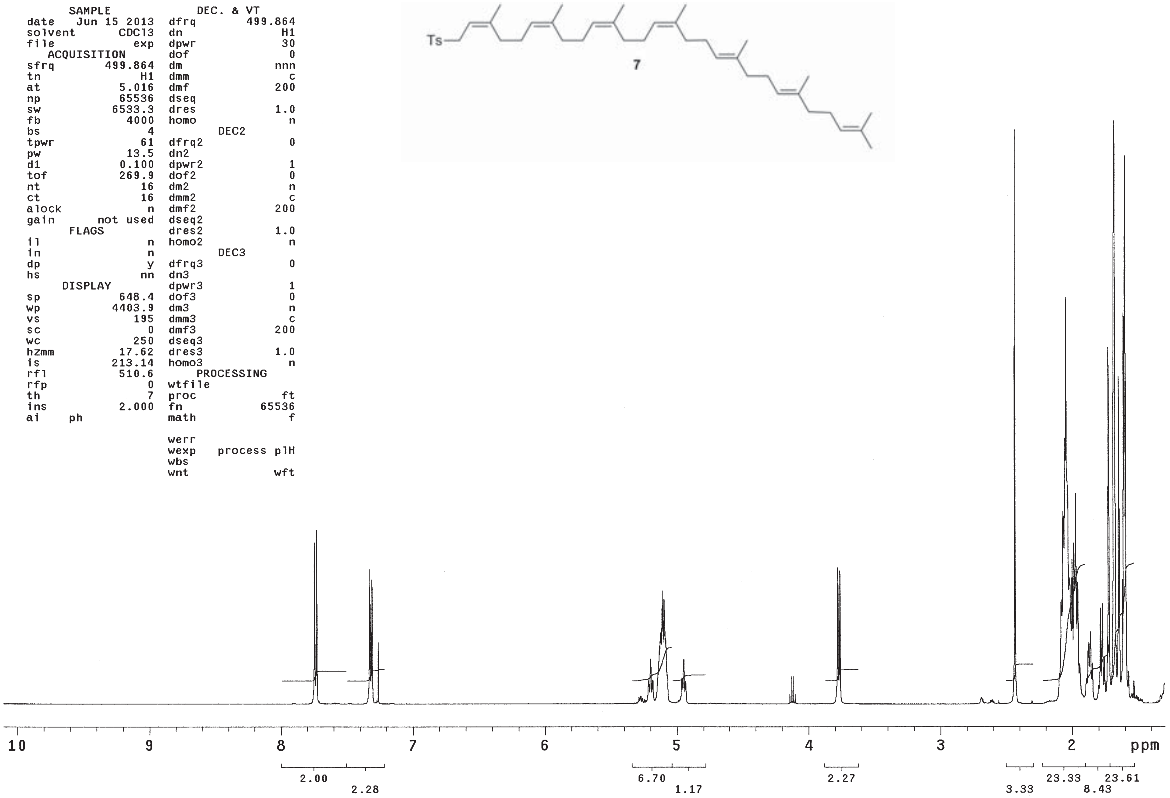
======== CHANNEL f1 ========
SFO1        800.1846758 MHz
NUC1                  1H
P1                  8.30 usec
P2                 16.60 usec
ND0                    2
TD                  1024
SFO1           201.2215 MHz
FIDRES        27.586512 Hz
SW              140.386 ppm
FnMODE                QF
SI                  2048
SF          800.1799956 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
SI                  2048
MC2                   QF
SF          201.2052726 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
```

```
UPH-13

exp1  s2pul

      SAMPLE              DEC. & VT
date   Jun 15 2013  dfrq        499.864
solvent      CDC13  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       499.864  dm              nnn
tn              H1  dmm               c
at           5.016  dmf             200
np           65536  dseq
sw          6533.3  dres            1.0
fb            4000  homo              n
bs               4         DEC2
tpwr            61  dfrq2             0
pw            13.5  dn2
d1           0.100  dpwr2             1
tof          269.9  dof2              0
nt              16  dm2               n
ct              16  dmm2              c
alock            n  dmf2            200
gain      not used  dseq2
      FLAGS         dres2           1.0
il               n  homo2             n
in               n         DEC3
dp               y  dfrq3             0
hs              nn  dn3
     DISPLAY        dpwr3             1
sp           648.4  dof3              0
wp          4403.9  dm3               n
vs             195  dmm3              c
sc               0  dmf3            200
wc             250  dseq3
hzmm         17.62  dres3           1.0
is          213.14  homo3             n
rfl          510.6      PROCESSING
rfp              0  wtfile
th               7  proc             ft
ins          2.000  fn            65536
ai    ph            math              f

                    werr
                    wexp   process p1H
                    wbs
                    wnt             wft
```

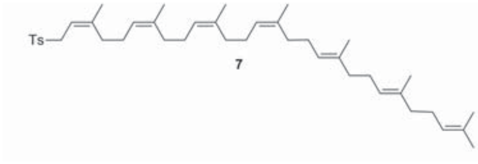


```
UPH-13

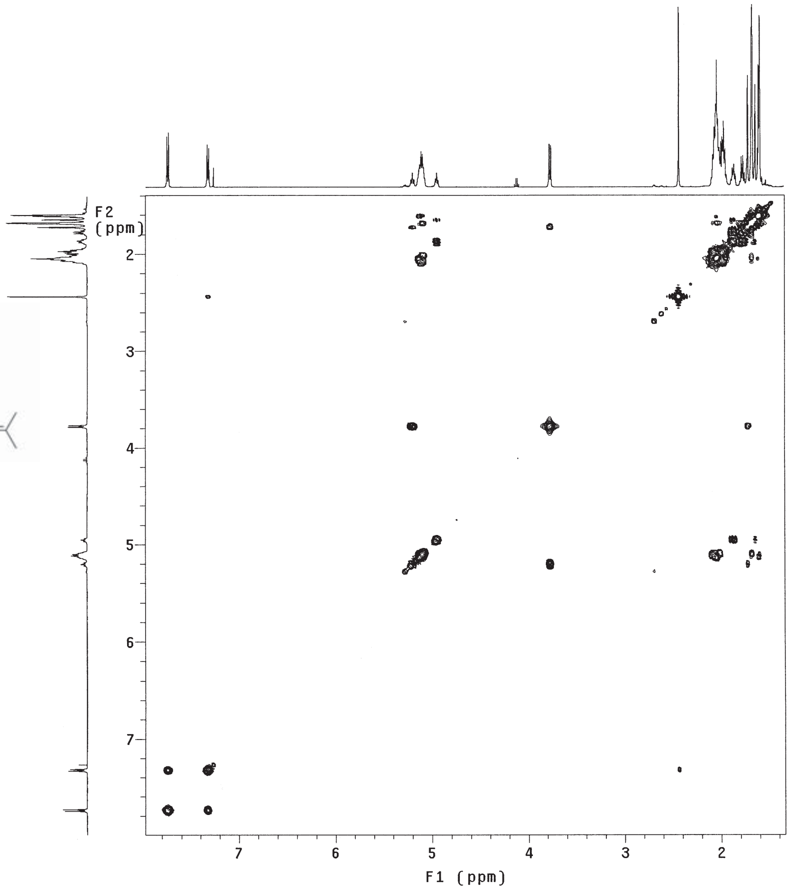
Pulse Sequence: relayh

 Solvent: CDC13
 Ambient temperature
INOVA-500  "nmr2a.chem.nd.edu"

 Relax. delay 1.300 sec
 COSY 90-90
 Acq. time 0.135 sec
 Width    3785.9 Hz
 2D Width 3785.9 Hz
 32 repetitions
 256 increments
OBSERVE   H1, 499.8611751 MHz
DATA PROCESSING
 Sine bell 0.068 sec
F1 DATA PROCESSING
 Sine bell 0.034 sec
FT size 1024 x 1024
Total time 3 hr, 22 min, 9 sec
```



7

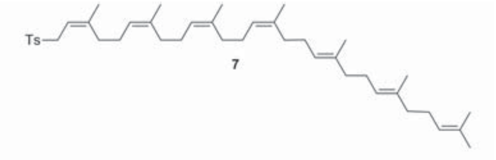


```
UPH-13

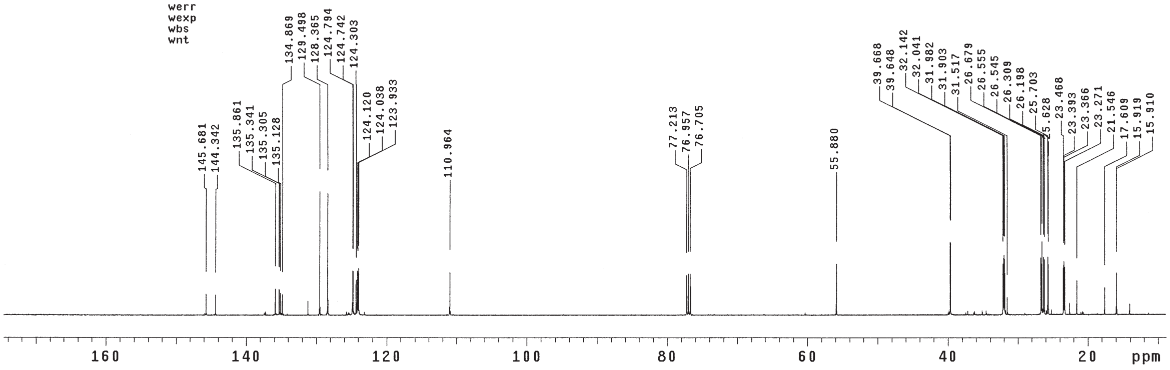
exp7  s2pul

      SAMPLE               DEC. & VT
date   Jun 15 2013  dfrq        499.864
solvent      CDCl3  dn               H1
file           exp  dpwr             40
   ACQUISITION      dof               0
sfrq       125.702  dm              yyy
tn             C13  dmm               w
at           1.215  dmf         8787.35
np           65536  dseq
sw         26963.3  dres            1.0
fb           15000  homo              n
bs               4          DEC2
tpwr            52  dfrq2             0
pw            15.0  dn2
d1           1.800  dpwr2             1
tof          144.5  dof2              0
nt          120000  dm2               n
ct            7724  dmm2              c
alock            n  dmf2          10000
gain      not used  dseq2
      FLAGS         dres2           1.0
il               n  homo2             n
in               n          DEC3
dp               y  dfrq3             0
hs              nn  dn3
     DISPLAY        dpwr3             1
sp          1113.5  dof3              0
wp         20833.0  dm3               n
vs             122  dmm3              c
sc               0  dmf3          10000
wc             250  dseq3
hzmm         83.33  dres3           1.0
is          500.00  homo3             n
rfl         1437.4      PROCESSING
rfp              0  lb             1.00
th               3  wtfile
ins        100.000  proc             ft
ai   cdc   ph       fn           131072
                    math              f

                    werr
                    wexp
                    wbs
                    wnt
```

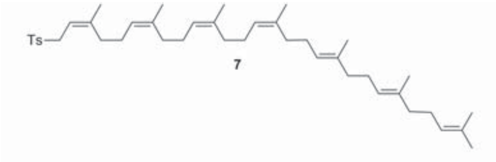


7

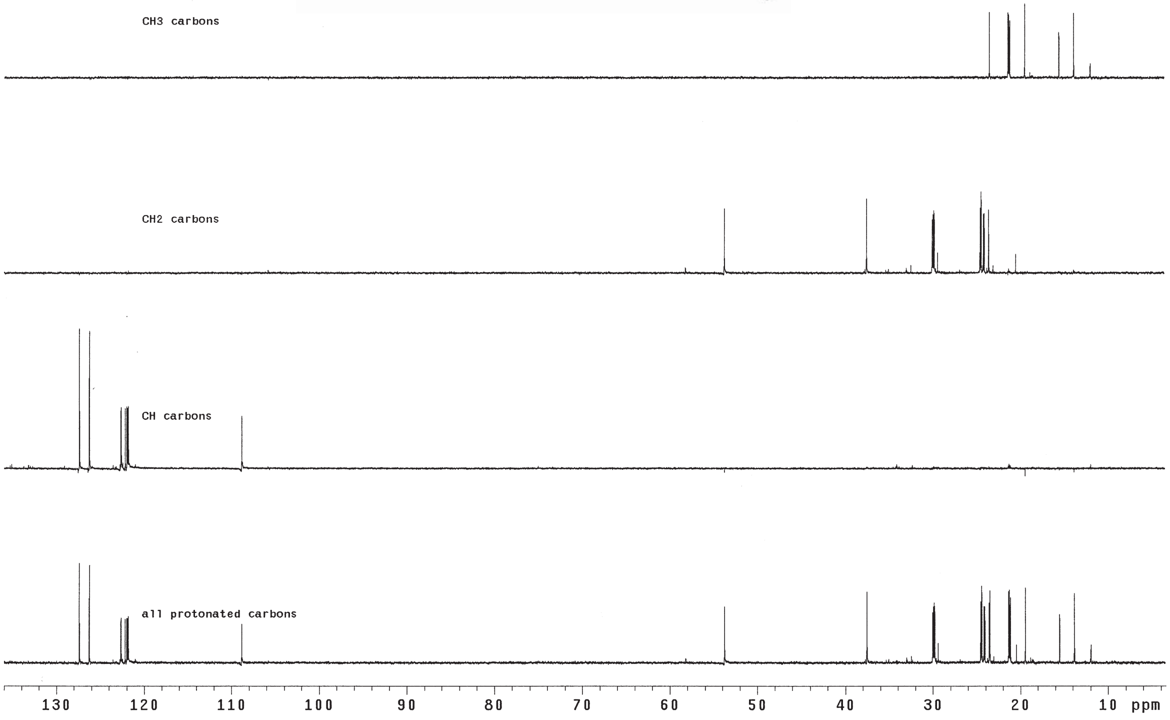


UPH-13

Pulse Sequence: dept



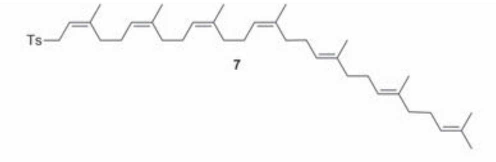
7



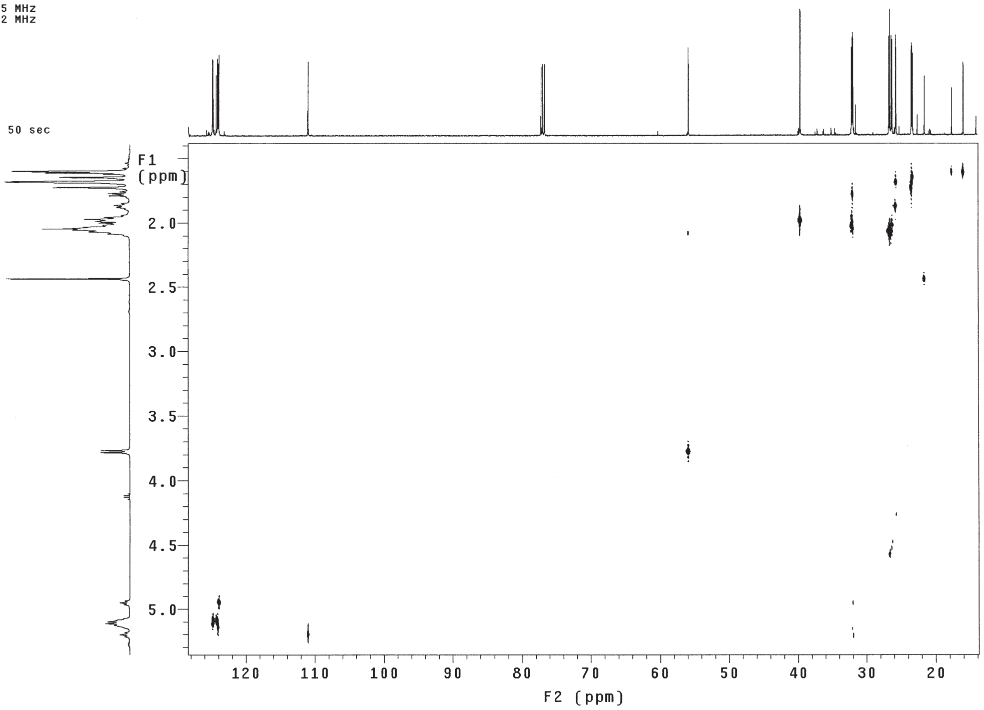
```
UPH-13

Pulse Sequence: hetcor
 Solvent: CDCl3
 Ambient temperature
User:  1-14-87
INOVA-500  "nmr2a.chem.nd.edu"

 Relax. delay 1.500 sec
 Acq. time 0.111 sec
 Width    18403.5 Hz
 2D Width 3940.3 Hz
 32 repetitions
 256 increments
OBSERVE  C13, 125.6902015 MHz
DECOUPLE  H1, 499.8634762 MHz
 Power 40 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
F1 DATA PROCESSING
 Line broadening 0.3 Hz
FT size 4096 x 1024
Total time 3 hr, 47 min, 50 sec
```



7

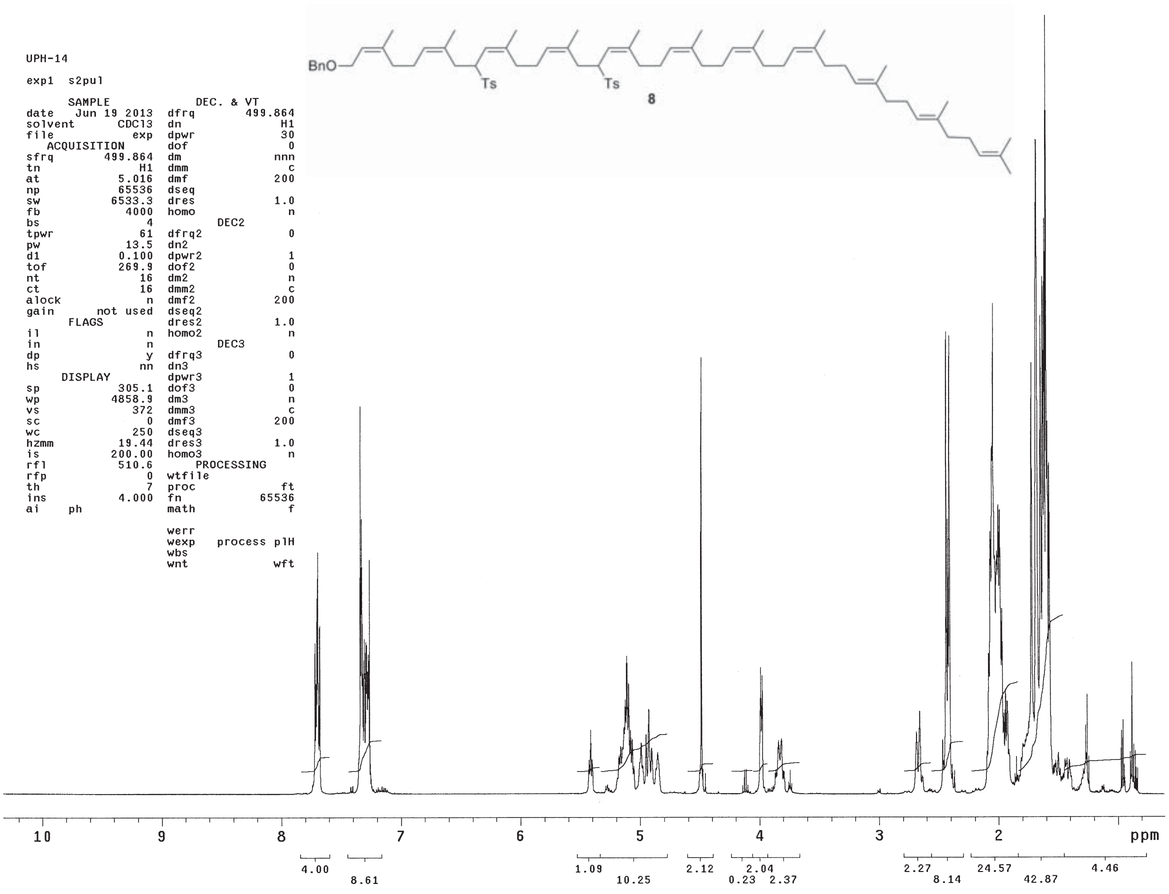


```
UPH-14

exp1  s2pul

      SAMPLE             DEC. & VT
date   Jun 19 2013  dfrq       499.864
solvent      CDCl3  dn              H1
file           exp  dpwr            30
   ACQUISITION      dof              0
sfrq       499.864  dm             nnn
tn              H1  dmm              c
at           5.016  dmf            200
np           65536  dseq
sw          6533.3  dres           1.0
fb            4000  homo             n
bs               4          DEC2
tpwr            61  dfrq2            0
pw            13.5  dn2
d1           0.100  dpwr2            1
tof          269.9  dof2             0
nt              16  dm2              n
ct              16  dmm2             c
alock            n  dmf2           200
gain      not used  dseq2
      FLAGS         dres2          1.0
il               n  homo2            n
in               n          DEC3
dp               y  dfrq3            0
hs              nn  dn3
     DISPLAY        dpwr3            1
sp           305.1  dof3             0
wp          4858.9  dm3              n
vs             372  dmm3             c
sc               0  dmf3           200
wc             250  dseq3
hzmm         19.44  dres3          1.0
is          200.00  homo3            n
rfl          510.6     PROCESSING
rfp              0  wtfile
th               7  proc            ft
ins          4.000  fn           65536
ai    ph            math             f

                    werr
                    wexp   process p1H
                    wbs
                    wnt            wft
```



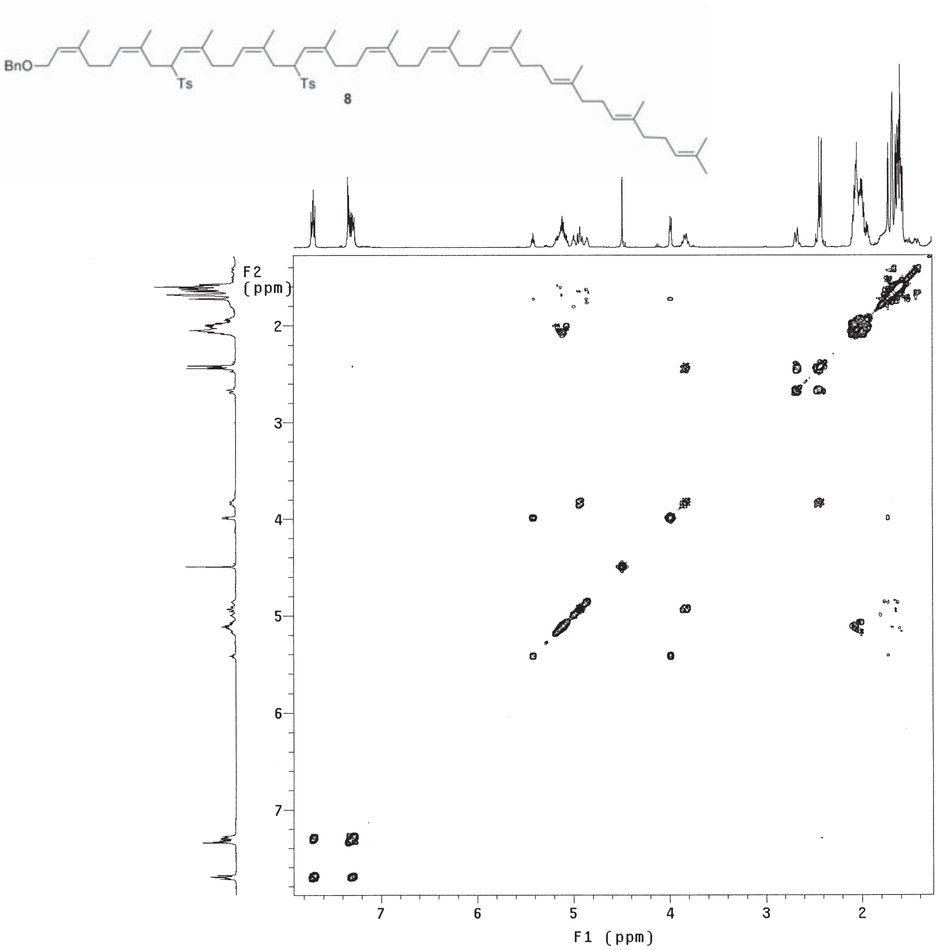
8

```
UPH-14

Pulse Sequence: relayh

 Solvent: CDCl3
 Ambient temperature
INOVA-500  "nmr2a.chem.nd.edu"

 Relax. delay 1.300 sec
 COSY 90-90
 Acq. time 0.137 sec
 Width    3734.3 Hz
 2D Width 3734.3 Hz
 8 repetitions
 256 increments
OBSERVE   H1, 499.8611751 MHz
DATA PROCESSING
 Sine bell 0.069 sec
F1 DATA PROCESSING
 Sine bell 0.034 sec
FT size 1024 x 1024
Total time 50 min, 45 sec
```

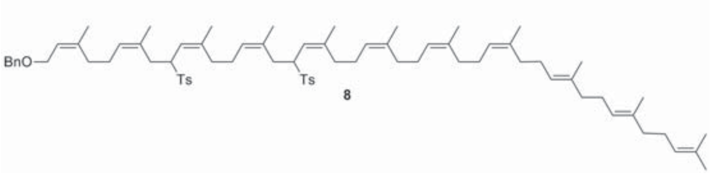


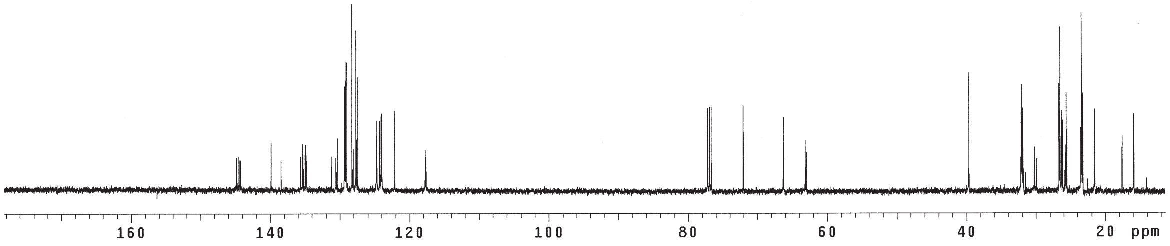
```
UPH-14

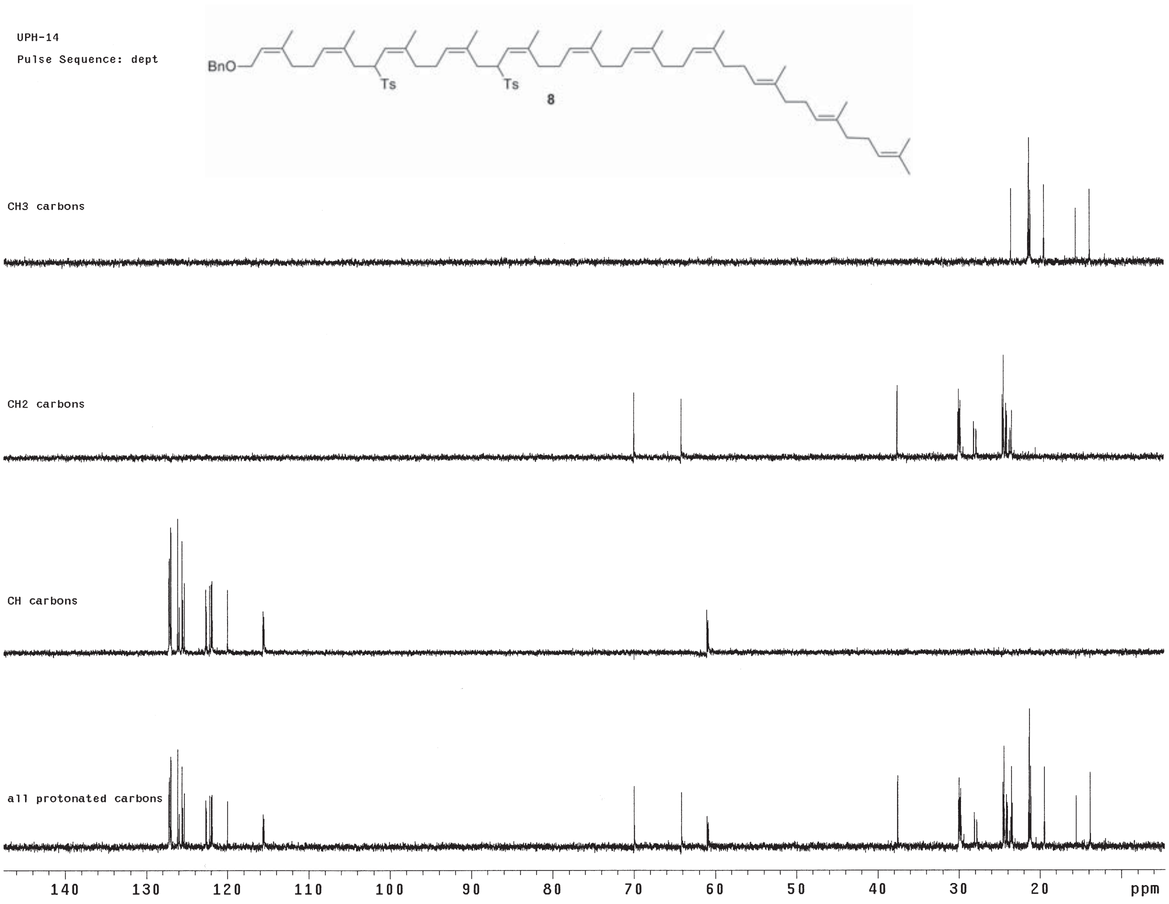
exp7  s2pul

      SAMPLE              DEC. & VT
date   Jun 20 2013  dfrq        499.864
solvent      CDCl3  dn               H1
file           exp  dpwr             40
   ACQUISITION      dof               0
sfrq       125.702  dm              yyy
tn             C13  dmm               w
at           1.215  dmf         8787.35
np           65536  dseq
sw         26963.3  dres            1.0
fb           15000  homo              n
bs               4           DEC2
tpwr            52  dfrq2             0
pw            15.0  dn2
d1           1.800  dpwr2             1
tof          144.5  dof2              0
nt           12000  dm2               n
ct             360  dmm2              c
alock            n  dmf2          10000
gain      not used  dseq2
      FLAGS         dres2           1.0
il               n  homo2             n
in               n           DEC3
dp               y  dfrq3             0
hs              nn  dn3
     DISPLAY        dpwr3             1
sp          1432.7  dof3              0
wp         20974.9  dm3               n
vs             365  dmm3              c
sc               0  dmf3          10000
wc             250  dseq3
hzmm         83.90  dres3           1.0
is          500.00  homo3             n
rfl         1437.4       PROCESSING
rfp              0  lb             1.00
th               6  wtfile
ins        100.000  proc             ft
ai   cdc   ph       fn           131072
                    math              f

                    werr
                    wexp
                    wbs
                    wnt
```







```
UPH-14

Pulse Sequence: hetcor
 Solvent: CDCl3
 Ambient temperature
User:  1-14-87
INOVA-500  "nmr2a.chem.nd.edu"

 Relax. delay 1.500 sec
 Acq. time 0.111 sec
 Width    18403.5 Hz
 2D Width 3682.9 Hz
 16 repetitions
 256 increments
OBSERVE  C13, 125.6902015 MHz
DECOUPLE  H1, 499.8634332 MHz
 Power 40 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
F1 DATA PROCESSING
 Line broadening 0.3 Hz
FT size 4096 x 1024
Total time 1 hr, 54 min, 7 sec
```