(Supporting Information)

Synthesis of DEDEE via the Palladium Catalyzed Reaction of Conjugated Diynes. A New Building Block for Molecular Scaffolding

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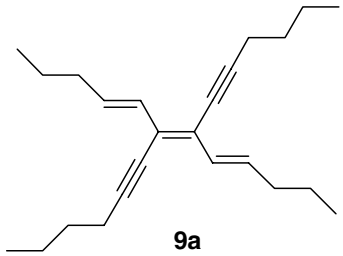
General: Spectroscopic measurements were carried out with the following instruments: JEOL LA-300 (^{1}H and ^{13}C NMR), and SHIMADZU FTIR-8200 (FT-IR).

Materials: The acetic acid, diynes **8a** and **8b** were commercially available from Kanto, Aldrich, and Farchan and were used without further purification. The diynes **8c**-**8d** were prepared according to published procedure.[S1]

[S1] Alami, M.; Ferri, F. , *Tetrahedron Lett.* **1996**, *37*, 2763.

General procedure for the dimerization of diyne 8 to give 9. To an argon flushed mixture of dry THF and $Pd(PPh_3)_4$ (0.025 mmol, 28.9 mg), was added the diynes **8** (0.5 mmol) and acetic acid (1.5 eq) in a Wheaton microreactor and the mixture was stirred at 40°C for 3-4 days. The reaction is not sensitive to air and opening the reaction vessel to allow air actually increases the reaction rate. The start of the reaction is indicated by a darkening of the reaction mixture from a previously clear yellow solution. After the completion of the reaction, which was monitored by GC, the mixture was then filtered through a short silica column using ethyl acetate as eluent. Separation by silica column chromatography (hexane as an eluent), and further purification by gpc, afforded the dimerized product **9**.

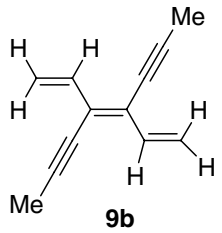
(E)-7,8-Di-pent-1-enyl-tetradec-7-ene-5,9-diyne (9a):



9a

Yellowish oil. Rf: 0.25 (Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.73 (d, J=15.2 Hz, 2H), 6.23 (m, 2H), 2.47 (t, J=6.8 Hz, 4H), 2.14 (q, J=7.1, 6.6 Hz, 4H), 1.62-1.41 (m, 12H), 0.92 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) 135.7, 129.1, 125.4, 101.6, 76.7, 35.0, 30.9, 22.4, 22.0, 19.5, 13.8, 13.6 ppm; IR (CCl_4) 3028, 2958, 2931, 2871, 2223 (C≡C), 1718 (w), 1685 (w), 1635, 1596, 1465, 1492, 1379, 1326, 1299, 1251, 1128, 1105, 1080, 1055, 964, 900 cm^{-1}; HRMS calcd for $C_{24}H_{36}$: 324.2817, found: 324.2853.

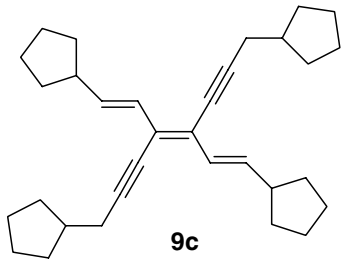
(E)-4,5-Divinyl-oct-4-ene-2,6-diyne (9b):



9b

Yellowish oil. Rf: 0.33 (Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.06 (dd, J=10.1, 16.8 Hz, 2H), 5.77 (dd, J=1.8, 16.8 Hz, 2H), 5.30 (dd, J=1.8, 10.1 Hz, 2H), 2.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) 135.1, 127.9, 118.8, 98.2, 74.7, 4.7 ppm; IR (CCl_4) 3090, 2980, 2916, 2848, 2233 (C≡C), 1843, 1647, 1438, 1409, 1400, 1372, 1301, 1259, 1157, 1076, 989, 918 cm^{-1}; HRMS calcd for $C_{12}H_{12}$: 156.0939, found: 156.0953.

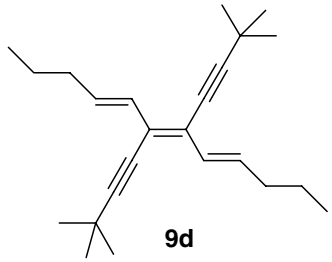
(E)-4,5-Bis-(2-cyclopentyl-vinyl)-1,8-dicyclopentanyl-oct-4-ene-2,6-diyne (9c):



9c

Yellowish oil. Rf: 0.33 (Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.74 (d, J=15.2 Hz, 2H), 6.20 (m, 2H), 2.55 (m, 2H), 2.47 (d, J=6.8 Hz, 4H), 2.13 (m, 2H), 1.86-1.75 (m, 8H), 1.70-1.52 (m, 16H), 1.40-1.28 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) 140.3, 127.3, 125.5, 101.1, 76.9, 43.7, 39.2, 33.3, 32.0, 25.7, 25.4, 25.2 ppm; IR (CCl_4) 3010, 2950, 2868, 2219 (C≡C), 1726 (w), 1685, 1629, 1450, 1425, 1357, 1326, 1311, 1166, 1105, 1066, 1022, 964 cm^{-1}; HRMS calcd for $C_{32}H_{44}$: 428.3443, found: 428.3423.

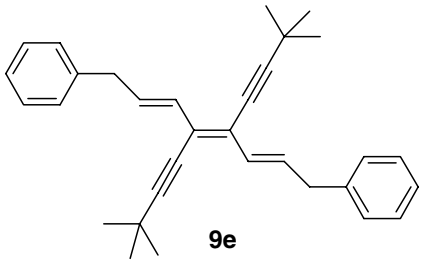
(E)-6,7-Bis-(3,3-dimethyl-but-1-ynyl-dodeca-4,6,8-triene (9d):



9d

Yellowish solid. Rf: 0.48 (Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.70 (d, J=15.2 Hz, 2H), 6.20 (m, 2H), 2.14 (q, J=6.8, 6.6 Hz, 4H), 1.50-1.40 (m, 4H), 1.30 (s, 18H), 0.92 (t, J=7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) 135.4, 128.9, 125.1, 109.8, 75.2, 34.9, 31.9, 28.5, 22.2, 13.8 ppm; IR (CCl_4) 3005, 2966, 2931, 2871, 2216 (C≡C), 1774 (w), 1712 (w), 1693, 1596, 1456, 1361, 1344, 1288, 1251, 1203, 1128, 1083, 1055, 991, 964 cm^{-1}; Anal calcd for $C_{24}H_{36}$ (%): calcd: C 88.81, H 11.19; found: C 88.59, H 11.09; HRMS calcd for $C_{24}H_{36}$: 324.2817, found: 324.2834.

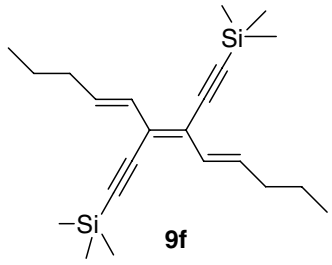
(E)-4,5-Bis-(3,3-dimethyl-but-1-ynyl)-1,8-diphenyl-oct-2,4,6-triene (9e):



9e

Colorless crystal ($CHCl_3$/hexane/ether). Rf: 0.22 (Hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.29 (m, 4H), 7.22 (m, 6H), 6.68 (d, J=15.2 Hz, 2H), 6.39 (m, 2H), 3.53 (d, J=6.4 Hz, 4H), 1.23 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) 139.9, 133.9, 130.2, 128.8, 128.4, 126.1, 125.5, 110.1, 74.8, 39.0, 31.0, 28.4 ppm; IR (KBr) 3082, 3060, 3030, 3003, 2970, 2929, 2885, 2866, 2821, 2204 (C≡C), 1633 (w) 1607, 1492, 1452, 1419, 1359, 1338, 1321, 1286, 1251, 1203, 1072, 1028, 970, 920 cm^{-1}; Anal calcd for $C_{32}H_{36}$ (%): calcd: C 91.37, H 8.63; found: C 91.11, H 8.59; HHRMS calcd for $C_{32}H_{36}$: 420.2817, found: 420.2849.

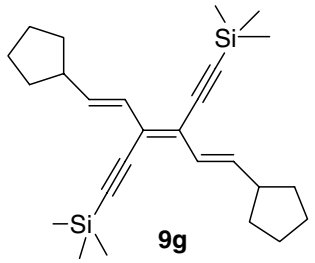
(E) 6,7-Bis-trimethyl silanylethynyl-dodeca-4,6,8,triene (9f):



9f

Yellowish oil. Rf: 0.55 (Hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.45 (d, J=15.4 Hz, 2H), 6.05 (m, 2H), 1.93 (q, J=7.2, 6.0 Hz, 4H), 1.25 (m, 4H), 0.69 (t, J=7.3 Hz, 6H), 0.0 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) 137.1, 128.2, 126.2, 100.8, 77.2, 35.0, 22.2, 13.8, 0.0 ppm; IR (CCl_4) 3030, 2960, 2931, 2873, 2150 (C≡C), 1892, 1637, 1458, 1407, 1379, 1338, 1249, 1018, 964 cm^{-1}; HRMS calcd for $C_{22}H_{36}Si_2$: 356.2356, found: 356.2367.

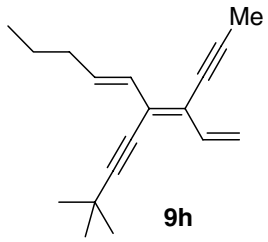
(E)-3,4-Bis-trimethylsilanylethynyl-1,6-dicyclopentanyl-hexa-2,4,6-triene (9g):



9g

Yellowish oil. Rf: 0.5 (Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.68 (d, J=15.4 Hz, 2H), 6.24 (m, 2H), 2.56 (m, 2H), 1.80 (m, 4H), 1.68-1.53 (m, 8H), 1.37 (m, 4H), 0.23 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) 141.6, 126.4, 126.3, 106.9, 100.9, 43.7, 33.1, 25.1, 0.03 ppm; IR (CCl_4) 3030, 2956, 2869, 2148 (C≡C), 1631, 1450, 1407, 1355, 1334, 1309, 1249, 1215, 1164, 1101, 1022, 983, 964 cm^{-1}; HRMS calcd for $C_{22}H_{40}Si_2$: 408.2669, found: 408.2648.

(E)-5-(3,3-Dimethyl-but-1-ynyl)-4-vinyl-deca-4,6-dien-2-yne (9h):



9h

One mmol each for **8b** and **8d** were mixed according to the general procedure. Separation via preparative gpc was carried out to give 16 % of **9b**, 16 % of **9d** and 33 % of **9h**. Yellowish oil. Rf: 0.46 (Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02 (m, J=17.0, 10.3 Hz, 1H), 6.73 (dt, J=1.5, 15.2 Hz, 1H), 6.28 (m, J=15.2, 7.1 Hz, 1H), 5.71 (dd, J=1.8, 17.0 Hz, 1H), 5.24 (dd, J=1.8, 10.3 Hz, 1H), 2.18 (q, J=7.3, 7.1 Hz, 2H), 2.12 (s, 3H), 1.46 (m, J=7.3 Hz, 2H), 1.31 (s, 9H), 0.93 (t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) 137.1, 135.3, 128.8, 127.7, 125.2, 117.4, 110.5, 97.3, 75.0, 74.8, 34.9, 31.0, 28.4, 22.5, 13.8, 4.8 ppm; IR (neat) 3090, 3030, 2966, 2929, 2871, 2223 (C≡C), 1720, 1678, 1625, 1600, 1560, 1456, 1370, 1361, 1338, 1301, 1276, 1203, 1055, 1028, 985, 966, 910 cm^{-1}; HRMS calcd for $C_{18}H_{24}$: 240.1878, found: 240.1891.

The stereochemistry of **9h** was determined by NOE experiment as shown in Figure S1.

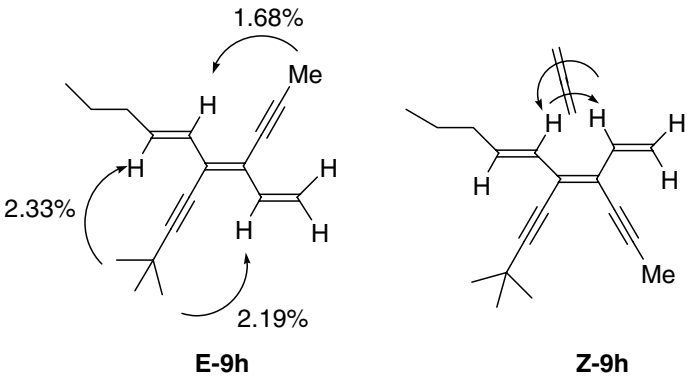
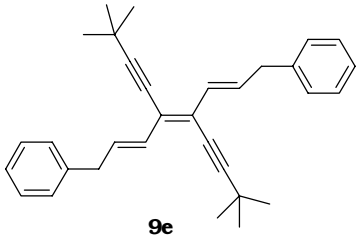
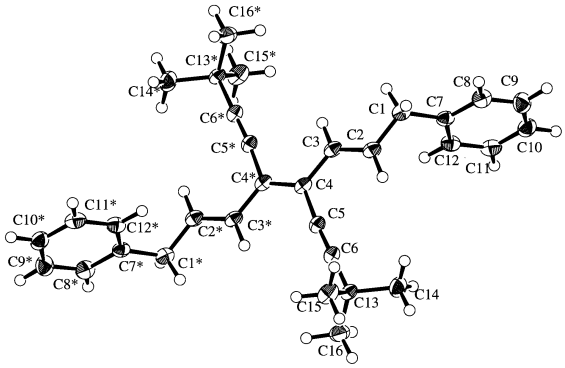


Figure S1: NOE Correlations of **9h.**

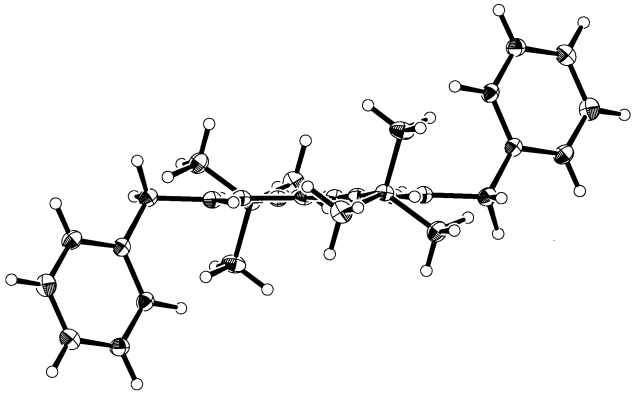
ORTEP of **9e**:



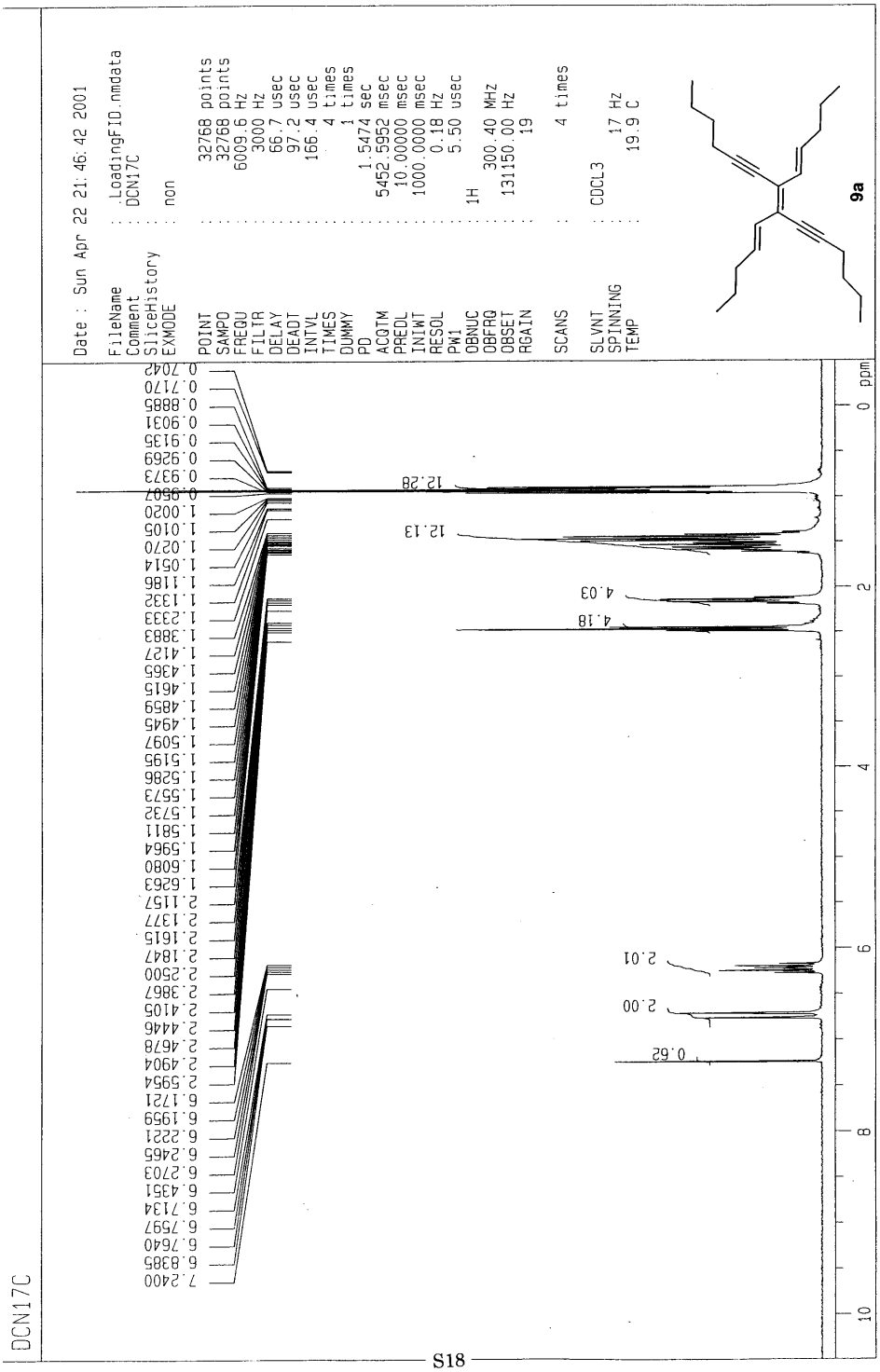
9e



ORTEP Drawing of **9e** (Top view)



(Side view)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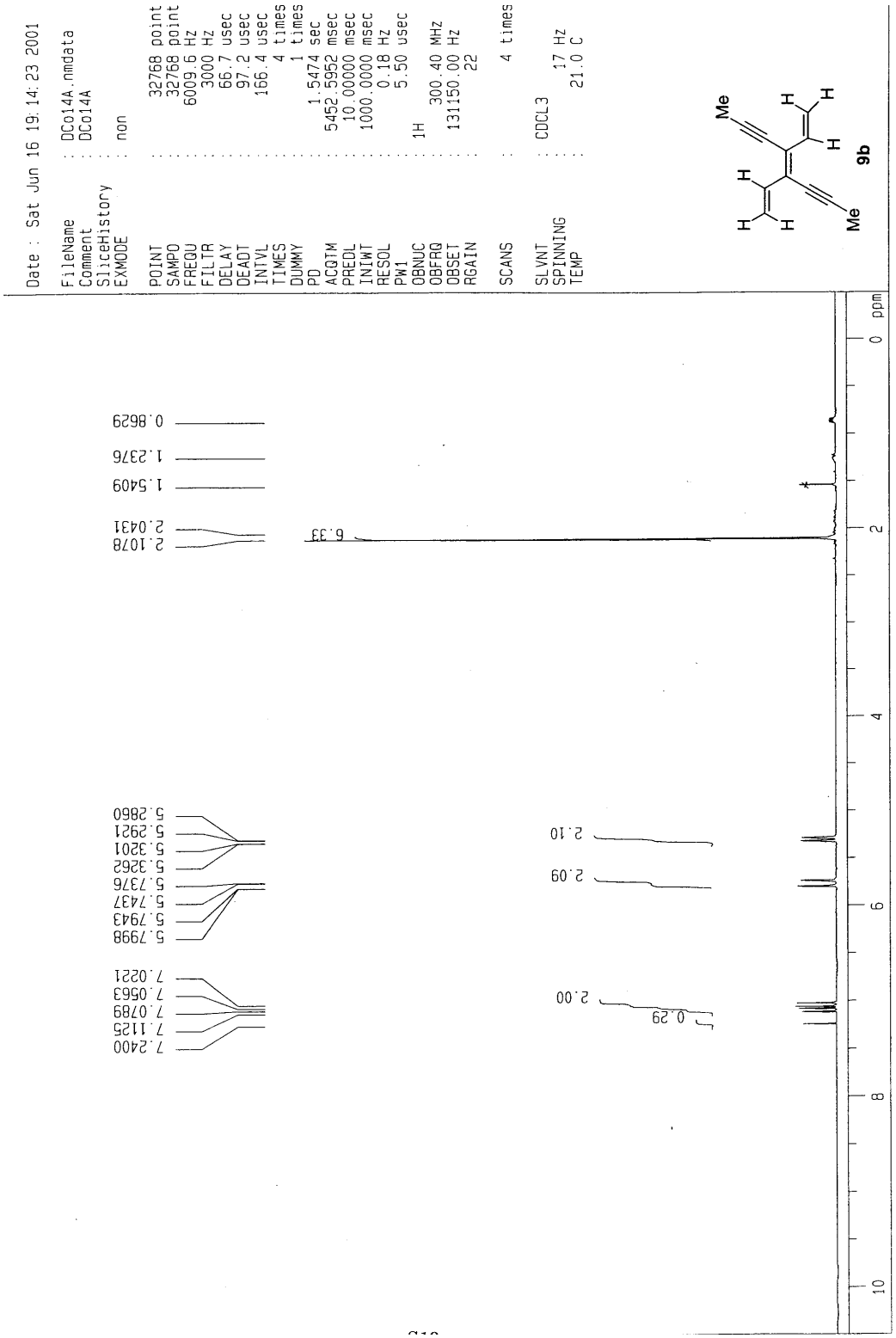
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H
H
H
H
Me
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2.1078
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5.2860
5.2921
5.3201
5.3262
5.7376
5.7437
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6
8
10
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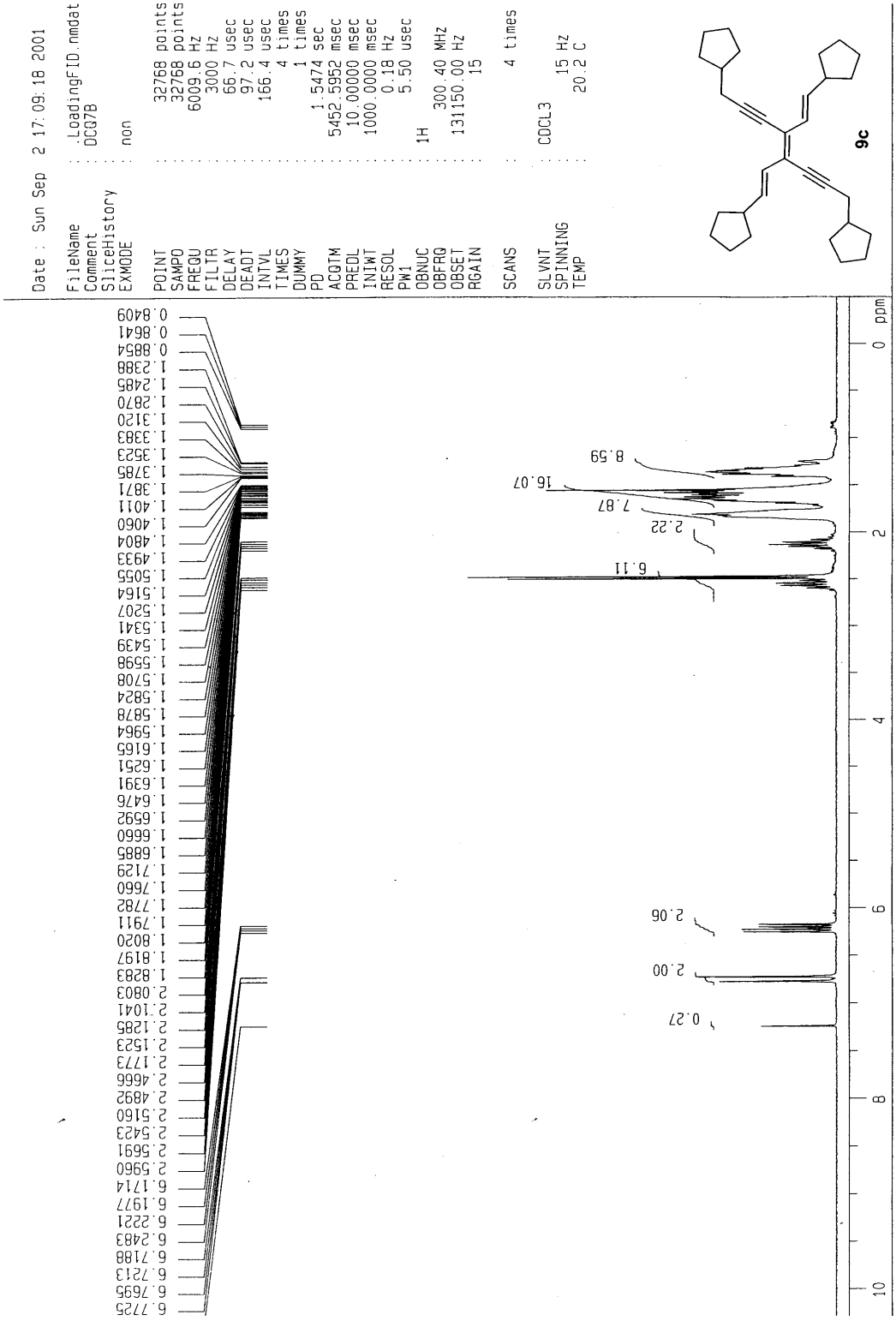
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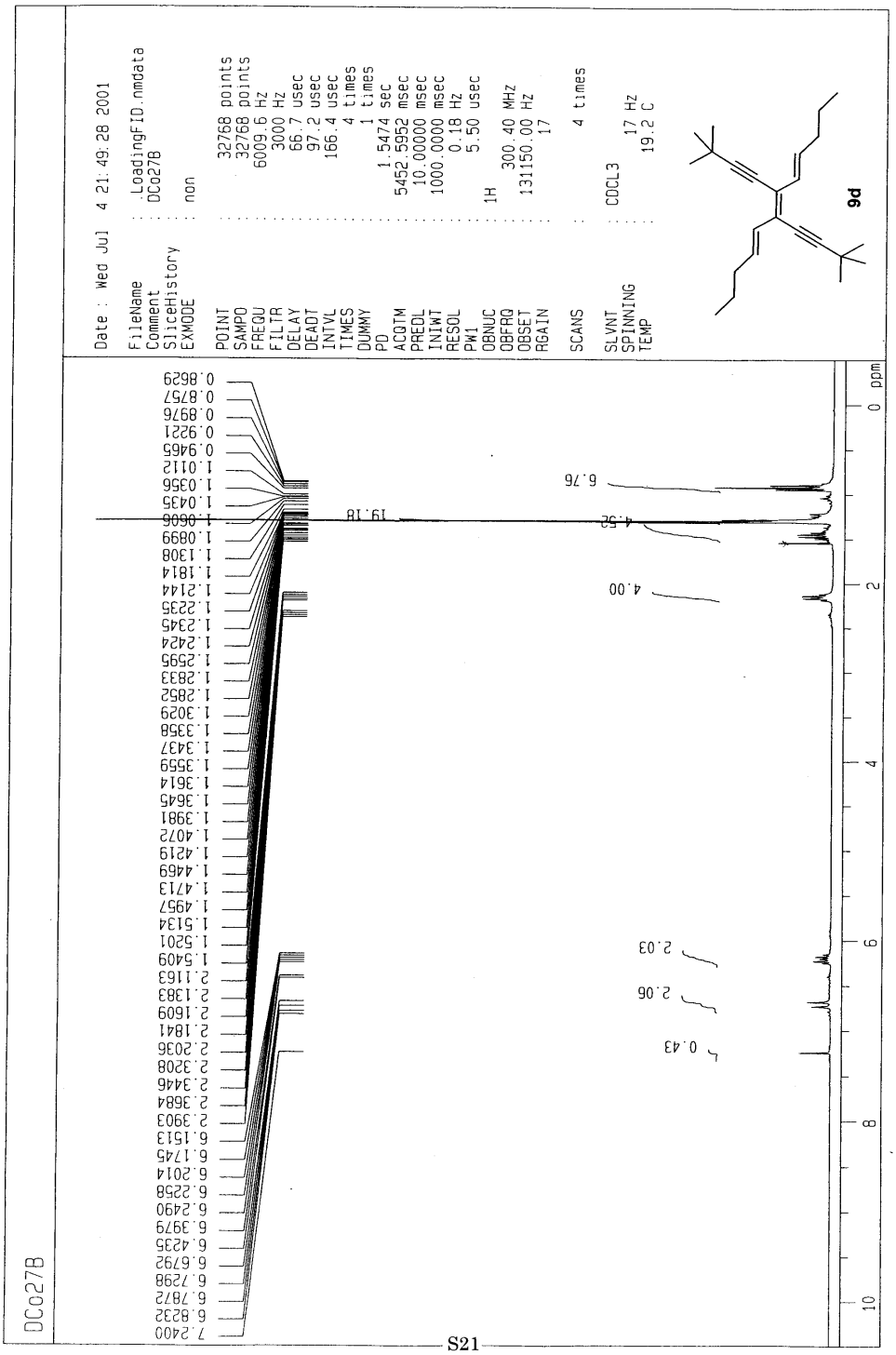
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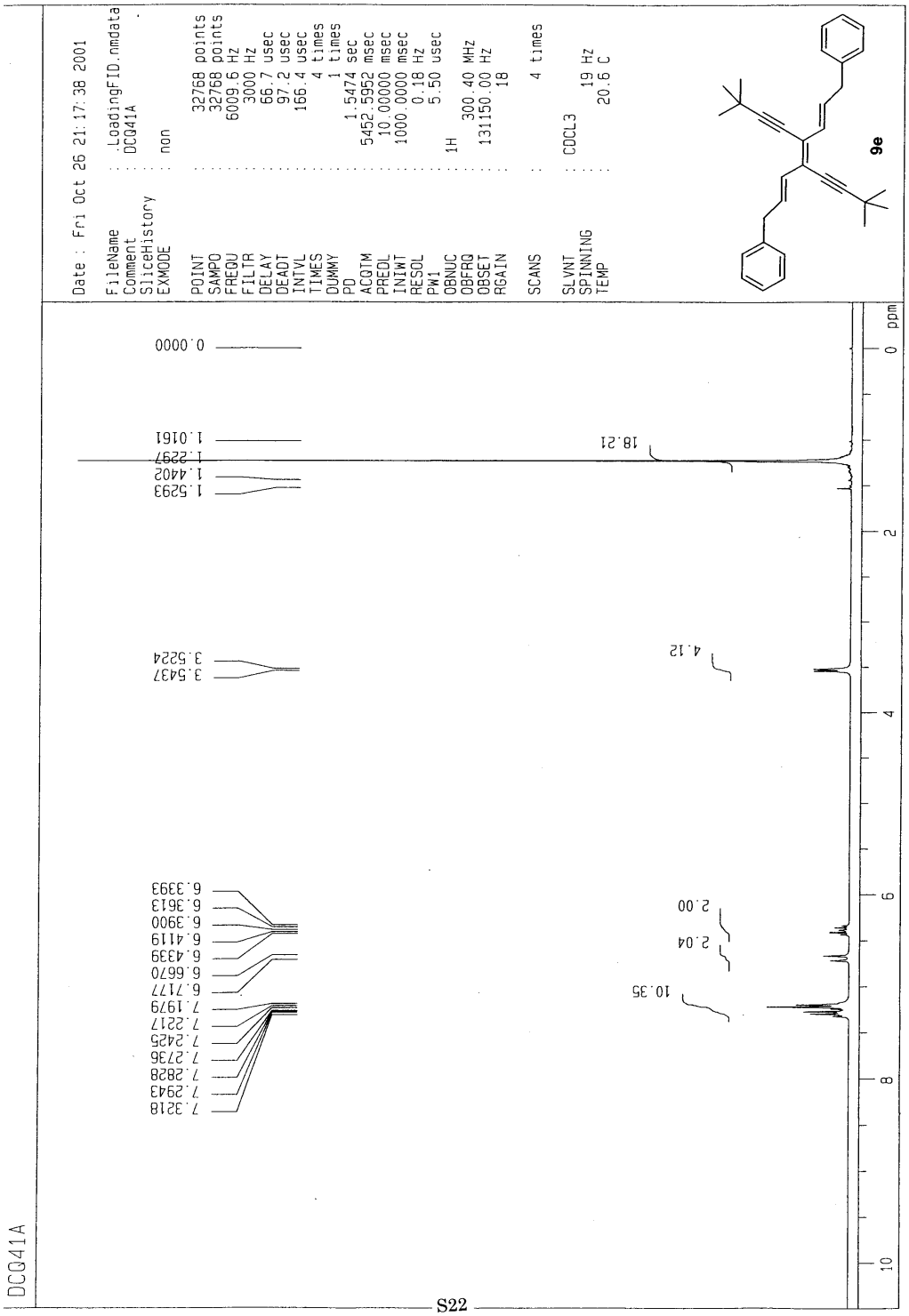
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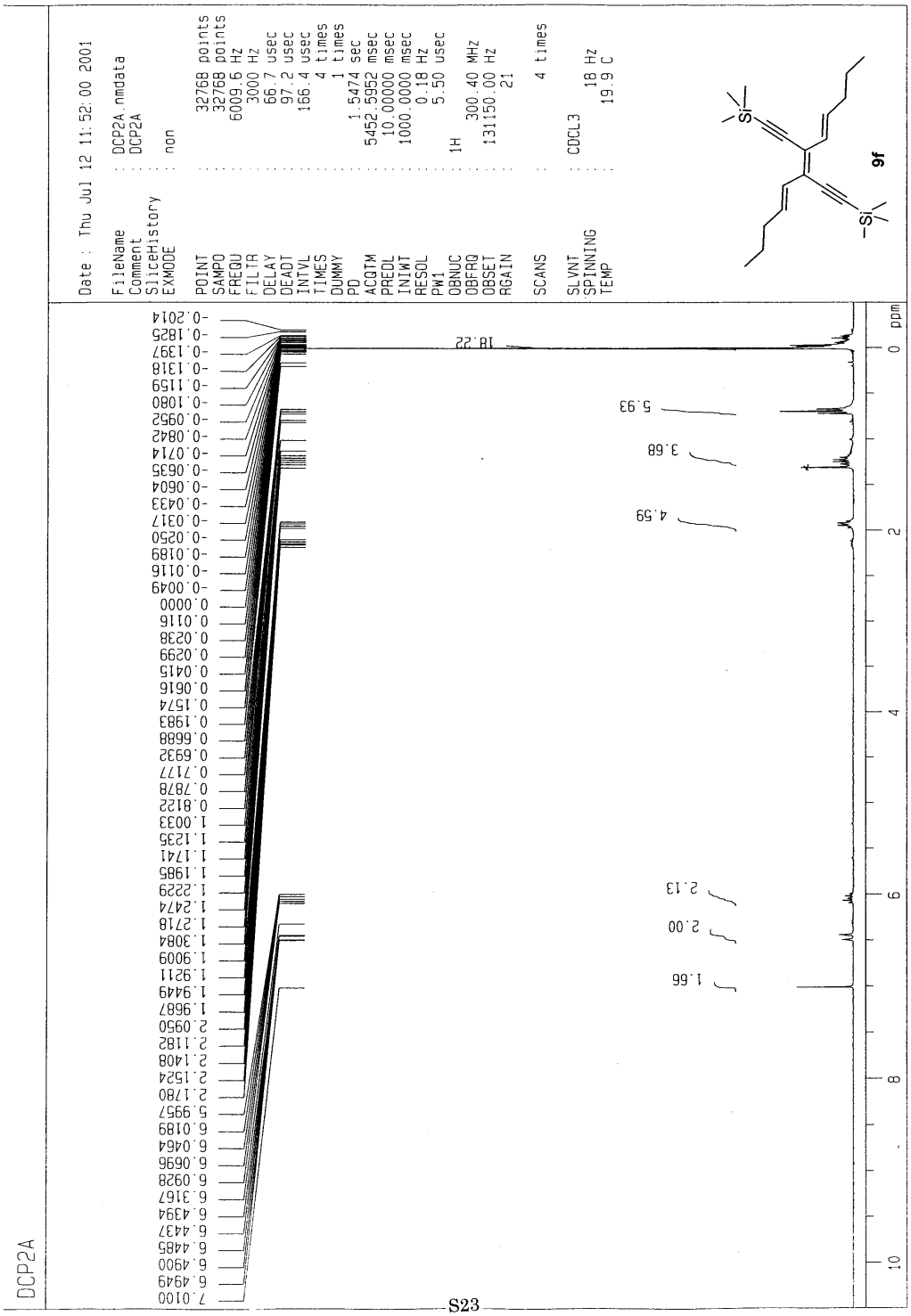
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ppm
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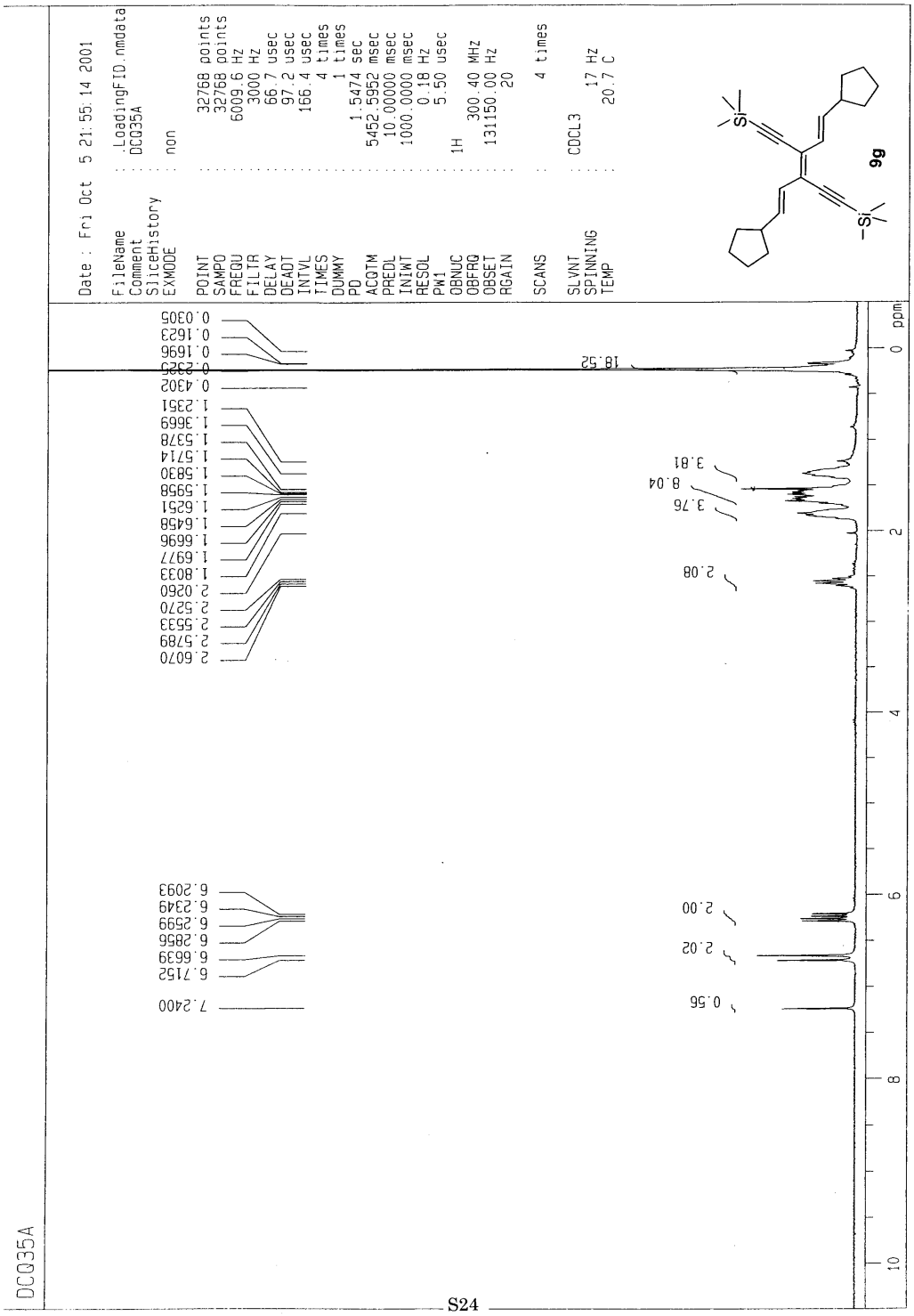
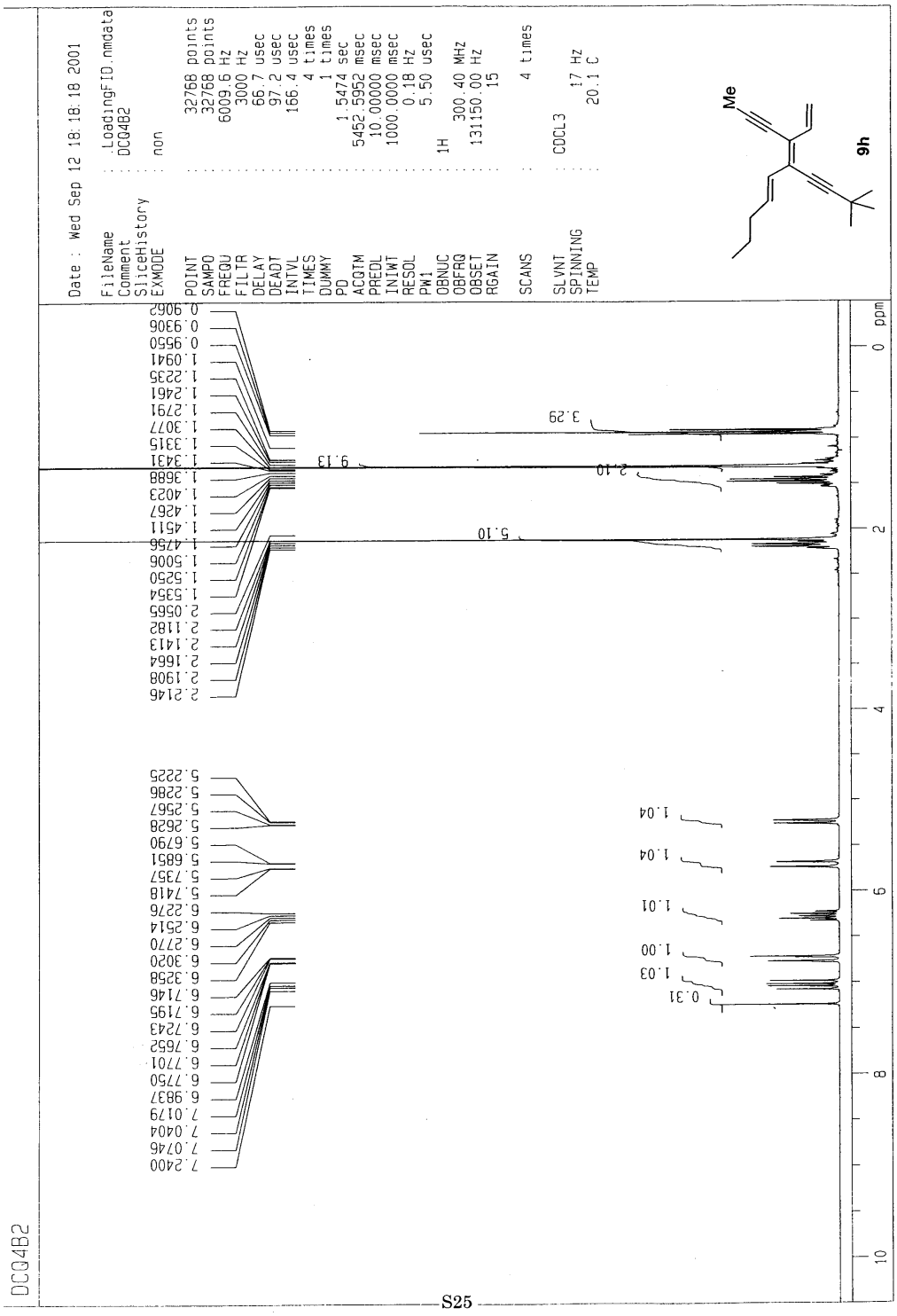
4
6
8
10


Date : Fri Oct 5 21:55:14 2001
FileName : .LoadingFID.nmdata
Comment : DC035A
SliceHistory :
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 6009.6 Hz
FILTR : 3000 Hz
DELAY : 66.7 usec
DEADT : 97.2 usec
INTVL : 166.4 usec
TIMES : 4 times
DUMMY : 1 times
PD : 1.5474 sec
ACQTM : 5452.5952 msec
PREDL : 10.00000 msec
INIWT : 1000.0000 msec
RESOL : 0.18 Hz
PW1 : 5.50 usec
OBNUC : 1H
OBFRQ : 300.40 MHz
OBSET : 131150.00 Hz
RGAIN : 20
SCANS : 4 times
SLVNT : CDCL3
SPINNING : 17 Hz
TEMP : 20.7 C
Si
Si
9g
0.0305
0.1623
0.1696
0.2329
0.4302
1.2351
1.3669
1.5378
1.5714
1.5830
1.5958
1.6251
1.6458
1.6696
1.6977
1.8033
2.0260
2.5270
2.5533
2.5789
2.6070
6.2093
6.2349
6.2599
6.2856
6.6639
6.7152
7.2400
18.52
3.81
8.04
3.76
2.08
2.00
2.02
0.56
ppm
0
2
4
6
8
10
DC035A


Date : Wed Sep 12 18:18:18 2001
FileName : LoadingFID.nmdata
Comment : DCQ4B2
SliceHistory : .
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 6009.6 Hz
FILTR : 3000 Hz
DELAY : 66.7 usec
DEADT : 97.2 usec
INTVL : 166.4 usec
TIMES : 4 times
DUMMY : 1 times
PD : 1.5474 sec
ACQTM : 5452.5952 msec
PREDL : 10.00000 msec
INIWT : 1000.0000 msec
RESOL : 0.18 Hz
PW1 : 5.50 usec
1H
OBNUC : 300.40 MHz
OBFRQ : 131150.00 Hz
OBSET : 15
AGAIN : 4 times
SCANS :
SLVNT : CDCL3
SPINNING : 17 Hz
TEMP : 20.1 C
Me
9h
DCQ4B2
ppm
3.29
9.13
2.10
5.10
1.04
1.04
1.01
1.00
1.03
0.31

S25