Cover page for Supporting Information

Manuscript Title:

Skeletal rearrangement of all-carbon spiro skeletons mediated by Lewis acid

Authors:

Fei Zhao, Chao Wang, Lantao Liu, Wen-Xiong Zhang, and Zhenfeng Xi*

Affiliations:

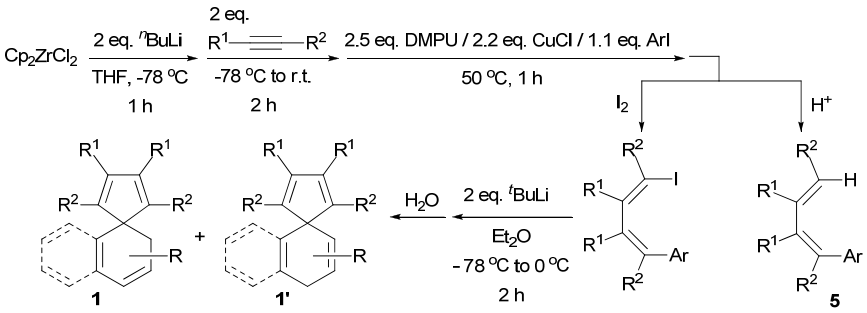
Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China.

Contents

1) Experimental details and characterization data

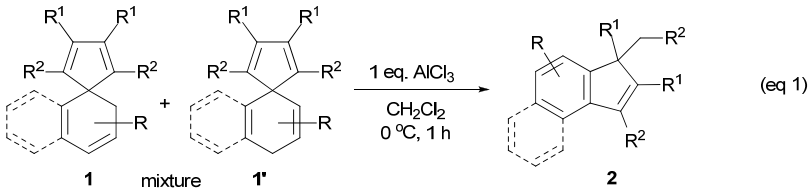
General Methods

All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Dichloromethane were refluxed and distilled from calcium hydride under nitrogen atmosphere. Aluminum trichloride was purified by sublimation under ambient pressure. Spiro compounds **1**[1] and 1-aryl-1,3-diene compounds **5**[2] were prepared according to the literature (Scheme 1). ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ at room temperature unless stated otherwise.



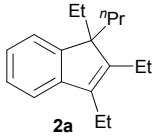
Scheme 1

A typical procedure for synthesis of indene derivatives 2 from spiro compounds 1



(eq 1)

As showed in eq 1, to a solution of a mixture of **1** and **1′** (1 mmol in total) in dichloromethane (5 mL) was added $AlCl_3$ (133 mg, 1 mmol). The reaction mixture was stirred at 0 °C for 1 h. After quenching with water, the mixture was extracted with hexane. The extract was washed with brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo and the residue was purified by column chromatography (silica gel, hexane) to afford the product **2**.

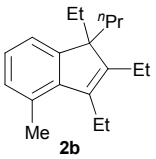


2a

2a: Colorless liquid, isolated yield 80% (194 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ

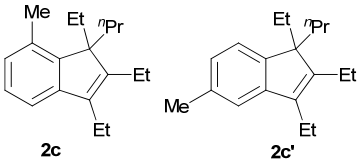
0.28 (t, J = 7.5 Hz, 3H, CH_3), 0.54-0.58 (m, 1H, CH_2), 0.68 (t, J = 6.6 Hz, 3H, CH_3), 0.72-0.78 (m, 1H, CH_2), 1.13 (t, J = 7.5 Hz, 3H, CH_3), 1.16 (t, J = 7.5 Hz, 3H, CH_3), 1.64-1.88 (m, 4H, CH_2), 2.24 (qd, J = 7.5, 1.5 Hz, 2H, CH_2), 2.53 (q, J = 7.5 Hz, 2H, CH_2), 7.08-7.20 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 7.97 (1 CH_3), 13.92 (1 CH_3), 13.99 (1 CH_3), 14.46 (1 CH_3), 16.83 (1 CH_2), 18.21 (1 CH_2), 18.68 (1 CH_2), 30.25 (1 CH_2), 40.00 (1 CH_2), 58.67 (1 quart C), 117.89 (1 CH), 120.92 (1 CH), 123.76 (1 CH), 125.90 (1 CH), 139.56 (1 quart C), 145.89 (1 quart C), 147.28 (1 quart C), 149.63 (1 quart C); HRMS(ESI) calcd for $[C_{18}H_{26}]H^+$: 243.2107; found 243.2102.

Similar results can be obtained by using the pure **1a** or **1a′** as the starting material. In the case of **1a**, indene **2a** can be obtained in 92% isolated yield (223 mg); for **1a′**, indene **2a** can be obtained in 71% isolated yield (172 mg).



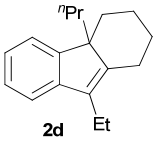
2b

2b: Colorless liquid, isolated yield 64% (164 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.26 (t, J = 7.2 Hz, 3H, CH_3), 0.47-0.58 (m, 1H, CH_2), 0.67 (t, J = 6.0 Hz, 3H, CH_3), 0.72-0.82 (m, 1H, CH_2), 1.13 (t, J = 7.5 Hz, 3H, CH_3), 1.16 (t, J = 7.5 Hz, 3H, CH_3), 1.62-1.83 (m, 4H, CH_2), 2.23 (qd, J = 7.5, 1.5 Hz, 2H, CH_2), 2.55 (s, 3H, CH_3), 2.66 (q, J = 7.5 Hz, 2H, CH_2), 6.90-7.02 (m, 3H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 7.90 (1 CH_3), 14.08 (1 CH_3), 14.45 (1 CH_3), 15.39 (1 CH_3), 16.75 (1 CH_2), 18.03 (1 CH_2), 19.80 (1 CH_3), 20.22 (1 CH_2), 30.58 (1 CH_2), 40.37 (1 CH_2), 57.77 (1 quart C), 118.76 (1 CH), 123.72 (1 CH), 129.10 (1 quart C), 129.25 (1 CH), 141.35 (1 quart C), 143.40 (1 quart C), 147.69 (1 quart C), 150.55 (1 quart C); HRMS(ESI) calcd for $[C_{19}H_{28}]H^+$: 257.2264; found 257.2260.



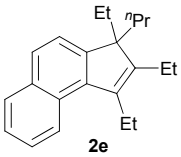
2c and **2c′**: Colorless liquid, isolated yield 73% (187 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) for a mixture of two isomers: δ 0.22-0.32 (m, 3H, CH_3), 0.50-0.62 (m, 1H, CH_2), 0.68 (t, J = 6.6 Hz, 3H, CH_3), 0.72-0.83 (m, 1H, CH_2), 1.10-1.19 (m, 6H, CH_3), 1.60-1.85 (m, 4H, CH_2),

2.17-2.26 (m, 2H, CH_2), 2.37 (s, 3H, CH_3), 2.51 (q, J = 7.5 Hz, 2H, CH_2), 6.81-7.13 (m, 3H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) for one isomer: δ 8.04 (1 CH_3), 13.93 (1 CH_3), 14.01 (1 CH_3), 14.48 (1 CH_3), 16.90 (1 CH_2), 18.24 (1 CH_2), 18.65 (1 CH_2), 21.64 (1 CH_3), 30.22 (1 CH_2), 40.00 (1 CH_2), 58.29 (1 quart C), 118.77 (1 CH), 120.71 (1 CH), 124.46 (1 CH), 135.27 (1 quart C), 139.43 (1 quart C), 146.08 (1 quart C), 146.68 (1 quart C), 147.66 (1 quart C); for the other isomer: δ 7.94 (1 CH_3), 14.11 (1 CH_3), 14.43 (1 CH_3), 16.92 (1 CH_2), 17.74 (1 CH_2), 18.70 (1 CH_2), 18.78 (1 CH_3), 27.35 (1 CH_2), 30.91 (1 CH_3), 37.22 (1 CH_2), 60.27 (1 quart C), 115.56 (1 CH), 126.01 (1 CH), 126.38 (1 CH), 138.07 (1 quart C), 139.60 (1 quart C), 145.72 (1 quart C), 146.32 (1 quart C), 147.10 (1 quart C); HRMS(ESI) calcd for $[C_{19}H_{28}]H^+$: 257.2264; found 257.2258.



2d

2d: Colorless liquid, isolated yield 54% (130 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.48-0.57 (m, 1H, CH_2), 0.69 (t, J = 6.0 Hz, 3H, CH_3), 0.92-1.09 (m, 2H, CH_2), 1.13 (t, J = 7.5 Hz, 3H, CH_3), 1.60-2.08 (m, 7H, CH_2), 2.12-2.19 (m, 1H, CH_2), 2.51 (qd, J = 7.5, 1.5 Hz, 2H, CH_2), 2.68-2.74 (m, 1H, CH_2), 7.07-7.13 (m, 1H, CH), 7.20-7.28 (m, 3H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 14.31 (1 CH_3), 14.62 (1 CH_3), 16.53 (1 CH_2), 18.02 (1 CH_2), 21.96 (1 CH_2), 24.00 (1 CH_2), 28.47 (1 CH_2), 36.22 (1 CH_2), 37.72 (1 CH_2), 53.22 (1 quart C), 118.42 (1 CH), 120.93 (1 CH), 123.38 (1 CH), 125.97 (1 CH), 133.87 (1 quart C), 145.03 (1 quart C), 147.74 (1 quart C), 152.91 (1 quart C); HRMS(ESI) calcd for $[C_{18}H_{24}]H^+$: 241.1951; found 241.1947.

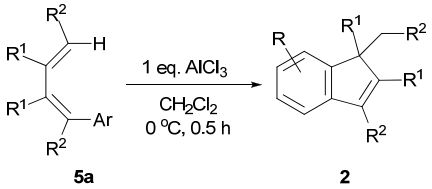


2e

2e: Colorless liquid, isolated yield 59% (172 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.22 (t, J = 7.2 Hz, 3H, CH_3), 0.44-0.47 (m, 1H, CH_2), 0.65 (t, J = 6.9 Hz, 3H, CH_3), 0.71-0.74 (m, 1H, CH_2), 1.17 (t, J = 7.5 Hz, 3H, CH_3), 1.33 (t, J = 7.5 Hz, 3H, CH_3), 1.76-1.92 (m, 4H, CH_2), 2.31-2.34 (m, 2H, CH_2), 2.97 (q, J = 7.5 Hz, 2H, CH_2), 7.33-7.46 (m, 3H, CH), 7.65 (d, J =

8.4 Hz, 1H, CH), 7.86 (dd, *J* = 8.1, 1.5 Hz, 1H, CH), 8.37 (d, *J* = 8.4 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 7.75 (1 CH_3), 14.04 (1 CH_3), 14.41 (1 CH_3), 14.81 (1 CH_3), 16.58 (1 CH_2), 18.19 (1 CH_2), 21.09 (1 CH_2), 29.89 (1 CH_2), 39.61 (1 CH_2), 58.27 (1 quart C), 119.88 (1 CH), 123.86 (1 CH), 124.00 (1 CH), 124.78 (1 CH), 125.21 (1 CH), 128.17 (1 quart C), 129.04 (1 CH), 133.56 (1 quart C), 140.07 (1 quart C), 141.56 (1 quart C), 148.14 (1 quart C), 148.94 (1 quart C); HRMS(ESI) calcd for $[C_{22}H_{28}]H^+$: 293.2264; found 293.2264.

A typical procedure for synthesis of indene derivatives 2 from 5



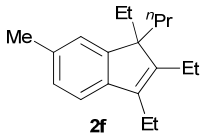
5a **2** (eq 2)

As showed in eq 2, to a solution of **5** (1 mmol) in dichloromethane (5 mL) was added $AlCl_3$ (133 mg, 1 mmol). The reaction mixture was stirred at 0 °C for 0.5 h. After quenching with water, the mixture was extracted with hexane. The extract was washed with brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo and the residue was purified by column chromatography (silica gel, hexane) to afford the product **2**.

2a: Isolated yield 85% (206 mg).

2b: Isolated yield 60% (154 mg).

2c: Isolated yield 78% (200 mg).



2f

2f: Colorless liquid, isolated yield 92% (236 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.29 (t, *J* = 7.5 Hz, 3H, CH_3), 0.49-0.63 (m, 1H, CH_2), 0.68 (t, *J* = 6.6 Hz, 3H, CH_3), 0.72-0.84 (m, 1H, CH_2), 1.12 (t, *J* = 7.5 Hz, 3H, CH_3), 1.15 (t, *J* = 7.5 Hz, 3H, CH_3), 1.60-1.84 (m, 4H, CH_2), 2.22 (qd, *J* = 7.5, 1.5 Hz, 2H, CH_2), 2.37 (s, 3H CH_3), 2.50 (q, *J* = 7.5 Hz, 2H, CH_2), 6.95-7.08 (m, 3H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 8.03 (1 CH_3), 13.99 (2 CH_3), 14.47 (1 CH_3), 16.85 (1 CH_2), 18.16 (1 CH_2), 18.72 (1 CH_2), 21.58 (1 CH_3), 30.30 (1 CH_2), 40.07

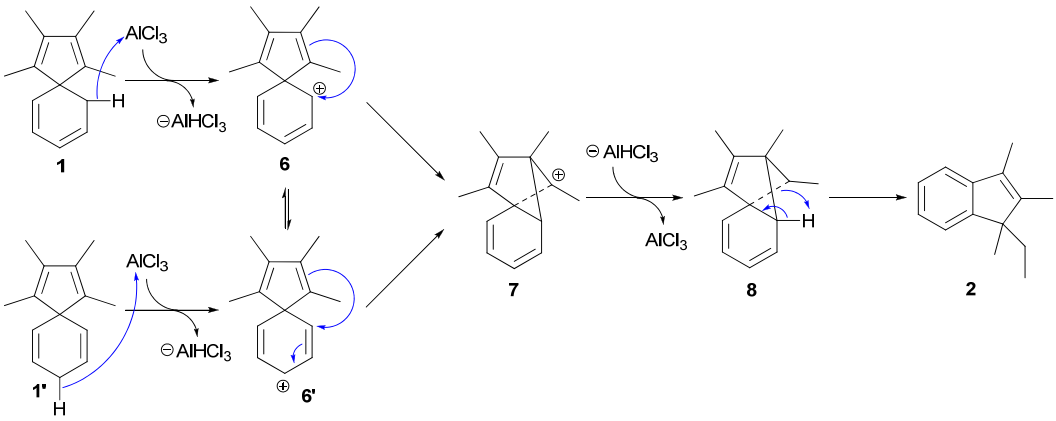
(1 CH_2), 58.47 (1 quart C), 117.49 (1 CH), 121.97 (1 CH), 126.47 (1 CH), 133.18 (1 quart C), 139.37 (1 quart C), 143.33 (1 quart C), 146.20 (1 quart C), 149.91 (1 quart C); HRMS(ESI) calcd for $[C_{19}H_{28}]H^+$: 257.2264; found 257.2260.

References

1. (*a*) Z. Wang and Z. Xi, *Synlett*, 2006, 1275; (*b*) L. Liu, Z. Wang, F. Zhao and Z. Xi, *J. Org. Chem.*, 2007, **72**, 3484.
2. T. Takahashi, W. Sun, C. Xi, H. Ubayama and Z. Xi, *Tetrahedron*, 1998, **54**, 715.

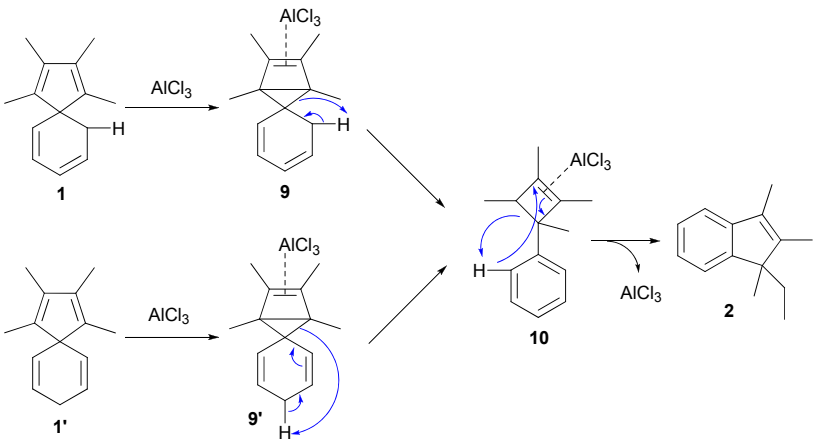
2) Discussion on mechanisms

Alternative mechanism 1 (Scheme 2): Carbon cation species **6** and **6′** can be generated from $AlCl_3$ by abstracting hydride from C–H bond.[1] Therefore, an alternative pathway including hydride transfer is displayed as shown in scheme 2. Cationic intermediate **6,** obtained by removing hydride to $AlCl_3$, would undergo rearrangement to form intermediate **7**. The new cation **7** will accept the hydride to give intermediate **8**, which would successively rearrange into the final product **2** via ring-opening proton transfer process.



Scheme 2

Alternative mechanism 2 (Scheme 3): As shown in Scheme 3, poly-cyclic species **9** and **9′**, generated through Lewis-acid-mediated [2+2] cyclization,[2] can further undergo ring-opening reaction of the three-membered ring, leading to intermediate **10**. Formation of **10** is probably because of aromatization as the driving force. Promoted by $AlCl_3$, the four-membered ring can be cleaved to form the final product **2** via proton transfer.

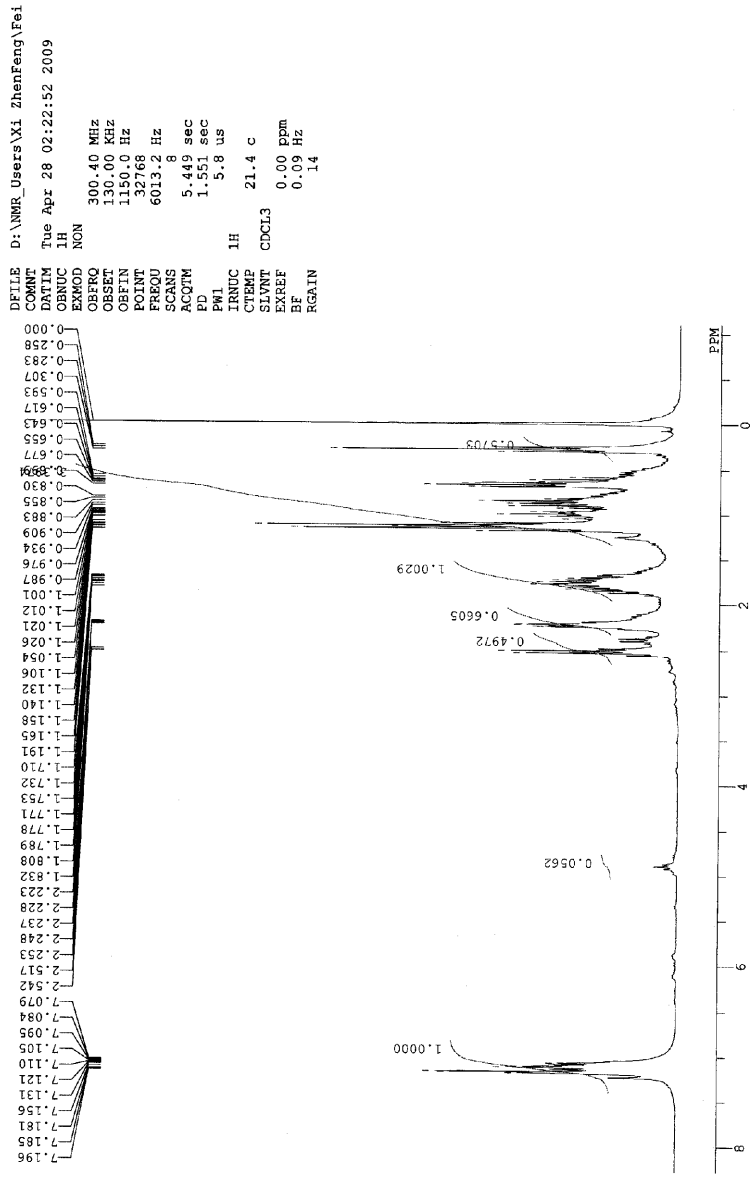


Scheme 3

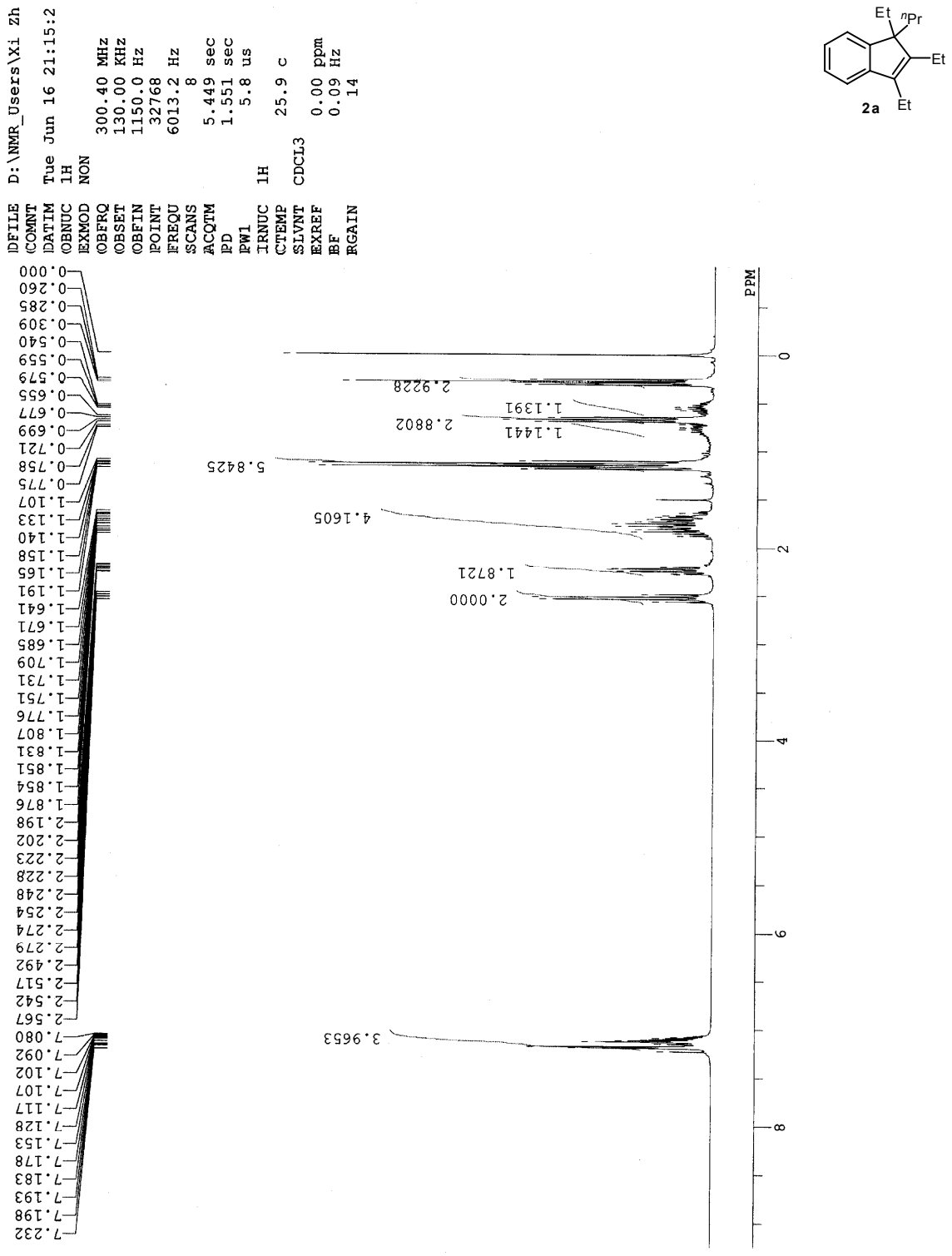
Reference

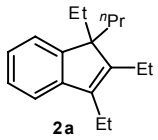
1. K. Kakiuchi, M. Ue, H. Tsukahara, T. Shimizu, T. Miyao, Y. Tobe, Y. Odaira, M. Yasuda and K. Shima, *J. Am. Chem. Soc.*, 1989, **111**, 3707.
2. J. B. Koster, G. J. Timmermans and H. van Bekkum, *Synthesis*, 1971, 139.

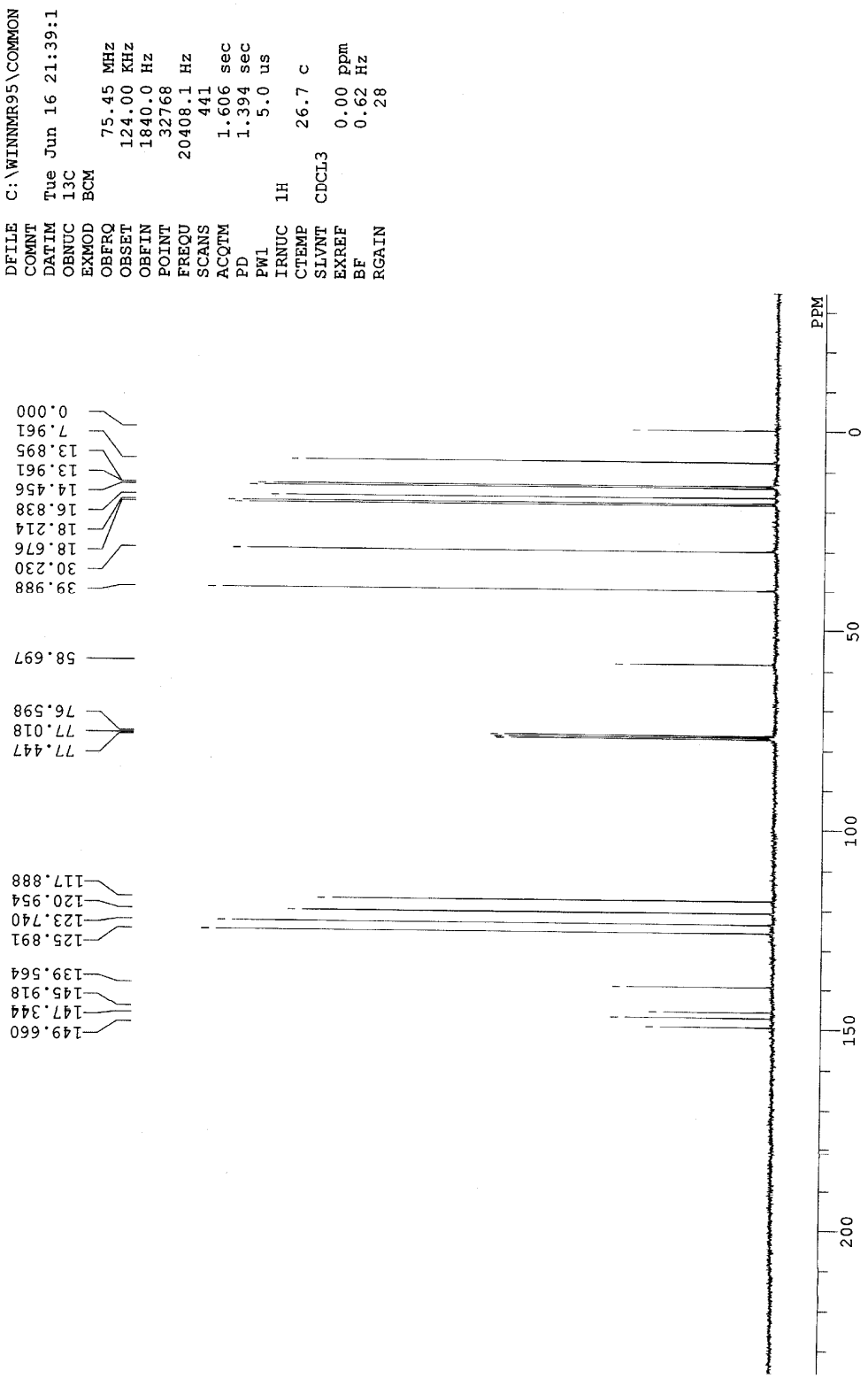
***in-situ* ^{1}H NMR spectrum of the reaction mixture of 1a indicating the formation of 5a.** The formation of **5a** was more clearly verified upon quenching of the reaction mixture before it completed. At this stage, compounds **5a** and **2a** were both observed.

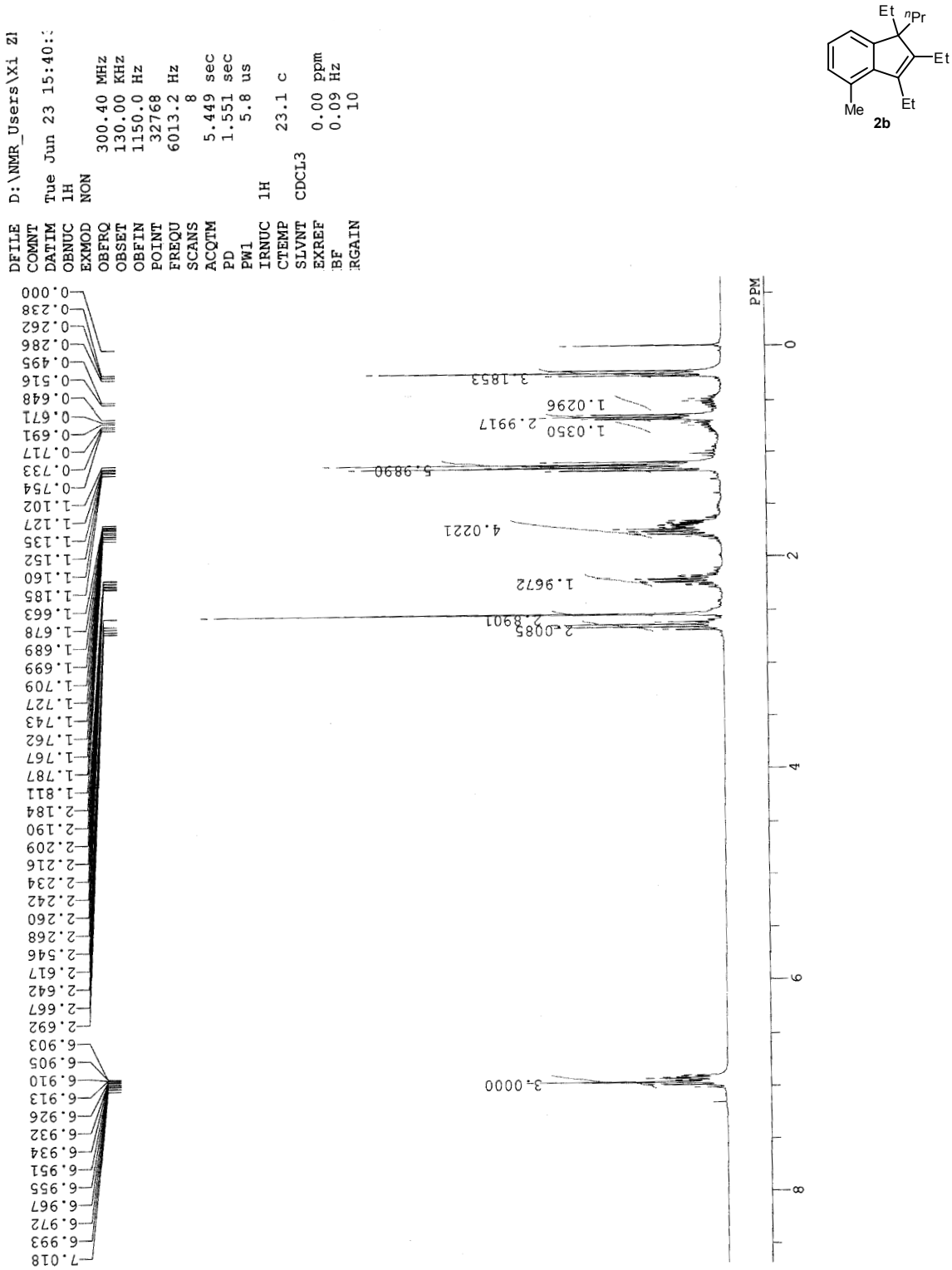


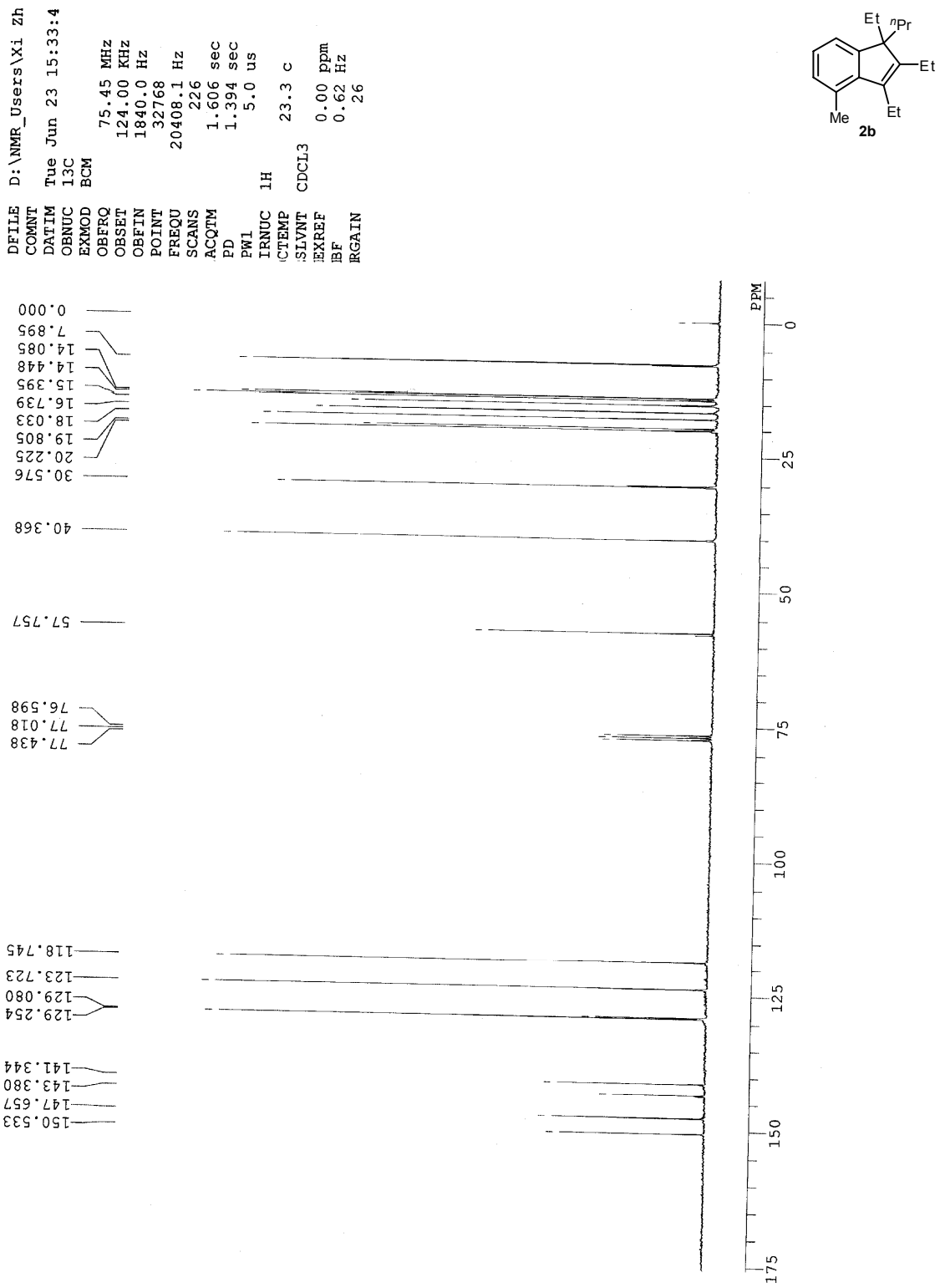
3) Copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds

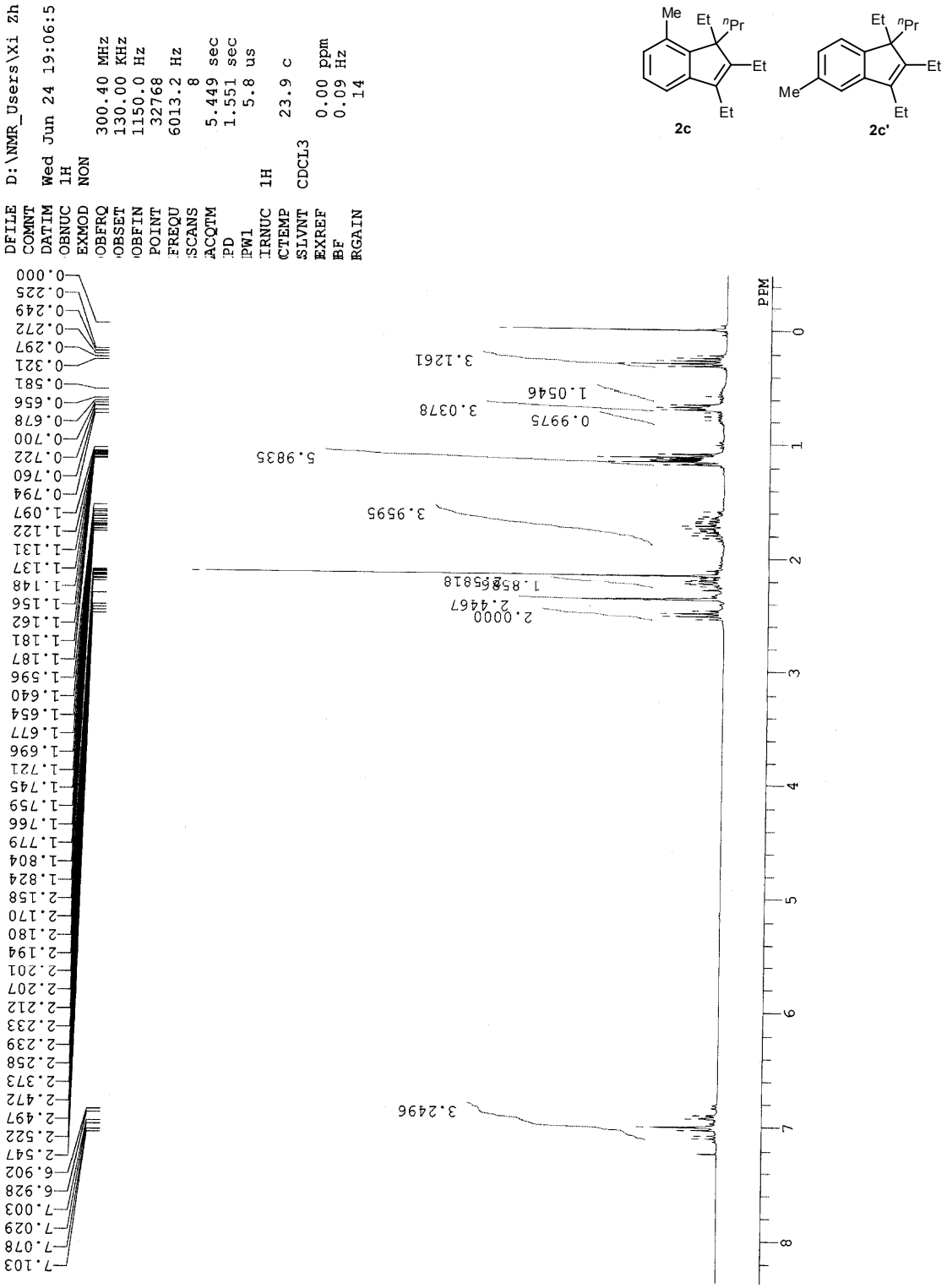

Et
nPr
Et
Et
2a
D:\NMR_Users\Xi Zh
Tue Jun 16 21:15:2
1H
NON
300.40 MHz
130.00 KHz
1150.0 Hz
32768
6013.2 Hz
8
5.449 sec
1.551 sec
5.8 us
1H
25.9 c
CDCL3
0.00 ppm
0.09 Hz
14
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
2.9228
1.1391
2.8802
1.1441
5.8425
4.1605
1.8721
2.0000
3.9653
PPM

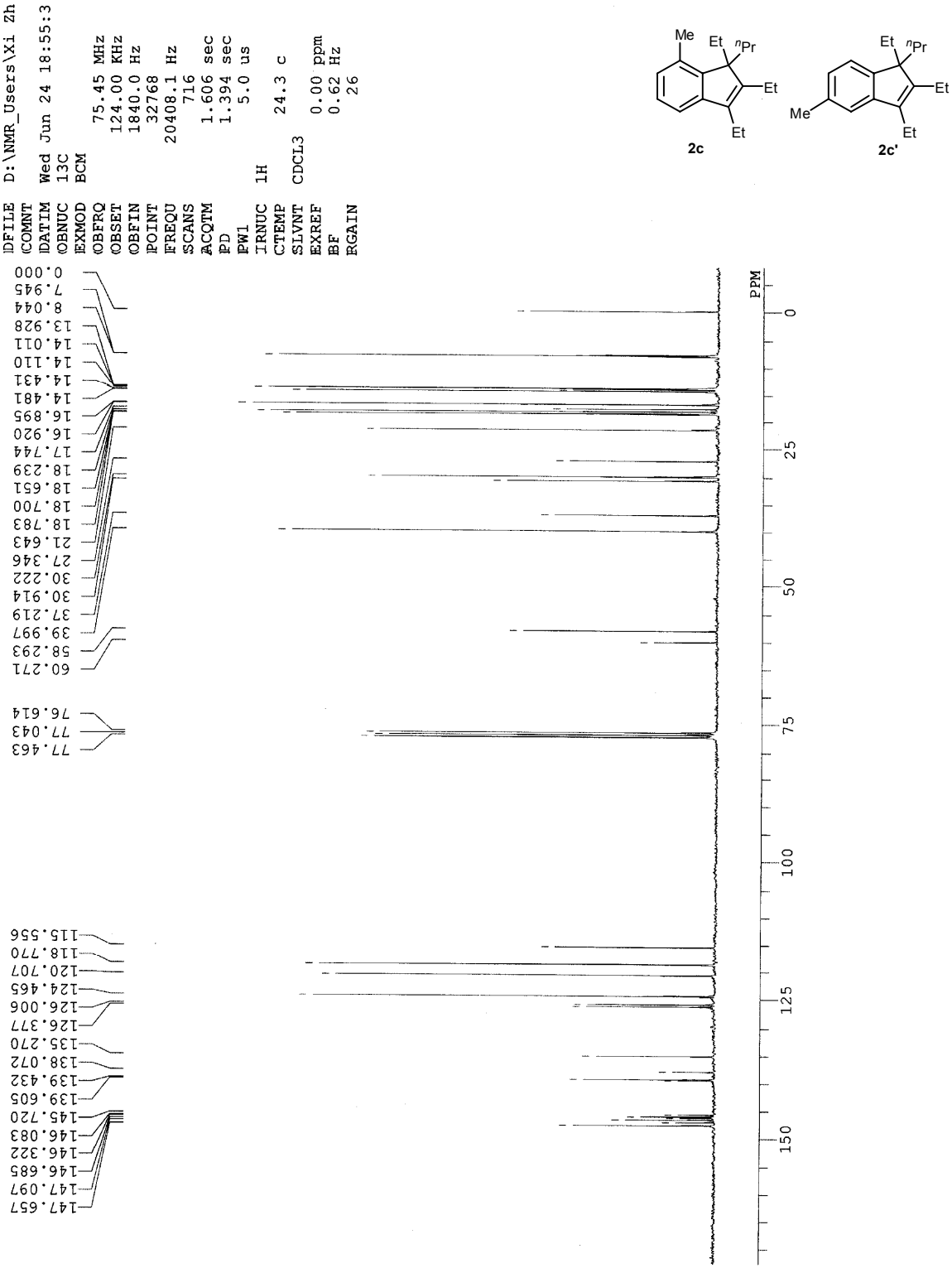

Et
nPr
Et
Et
2a

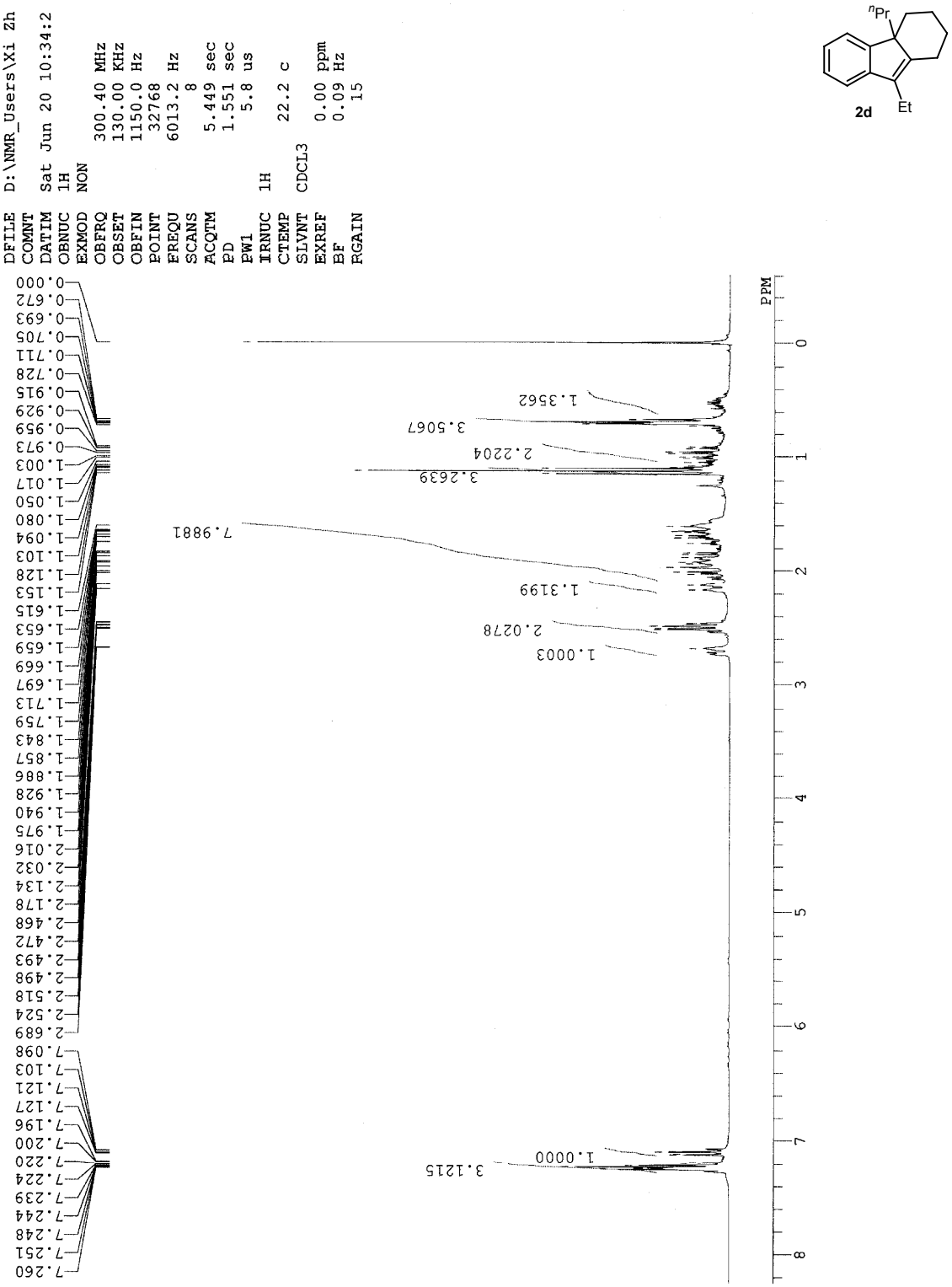

DFILE C:\WINNMR95\COMMON
COMNT
DATIM Tue Jun 16 21:39:1
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 441
ACQTM 1.606 sec
PD 1.394 sec
PW1 5.0 us
IRNUC 1H
CTEMP 26.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 28
0.000
7.961
13.895
13.961
14.456
16.838
18.214
18.676
30.230
39.988
58.697
76.598
77.018
77.447
117.888
120.954
123.740
125.891
139.564
145.918
147.344
149.660
PPM
0
50
100
150
200


Et
nPr
Et
Me
Et
2b
D:\NMR_Users\Xi Zl
Tue Jun 23 15:40:
1H
NON
300.40 MHz
130.00 KHz
1150.0 Hz
32768
6013.2 Hz
8
5.449 sec
1.551 sec
5.8 us
1H
23.1 c
CDCl3
0.00 ppm
0.09 Hz
10
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
3.1853
1.0296
1.0350
2.9917
5.9890
4.0221
1.9672
2.8901
2.0085
3.0000
PPM
0
2
4
6
8

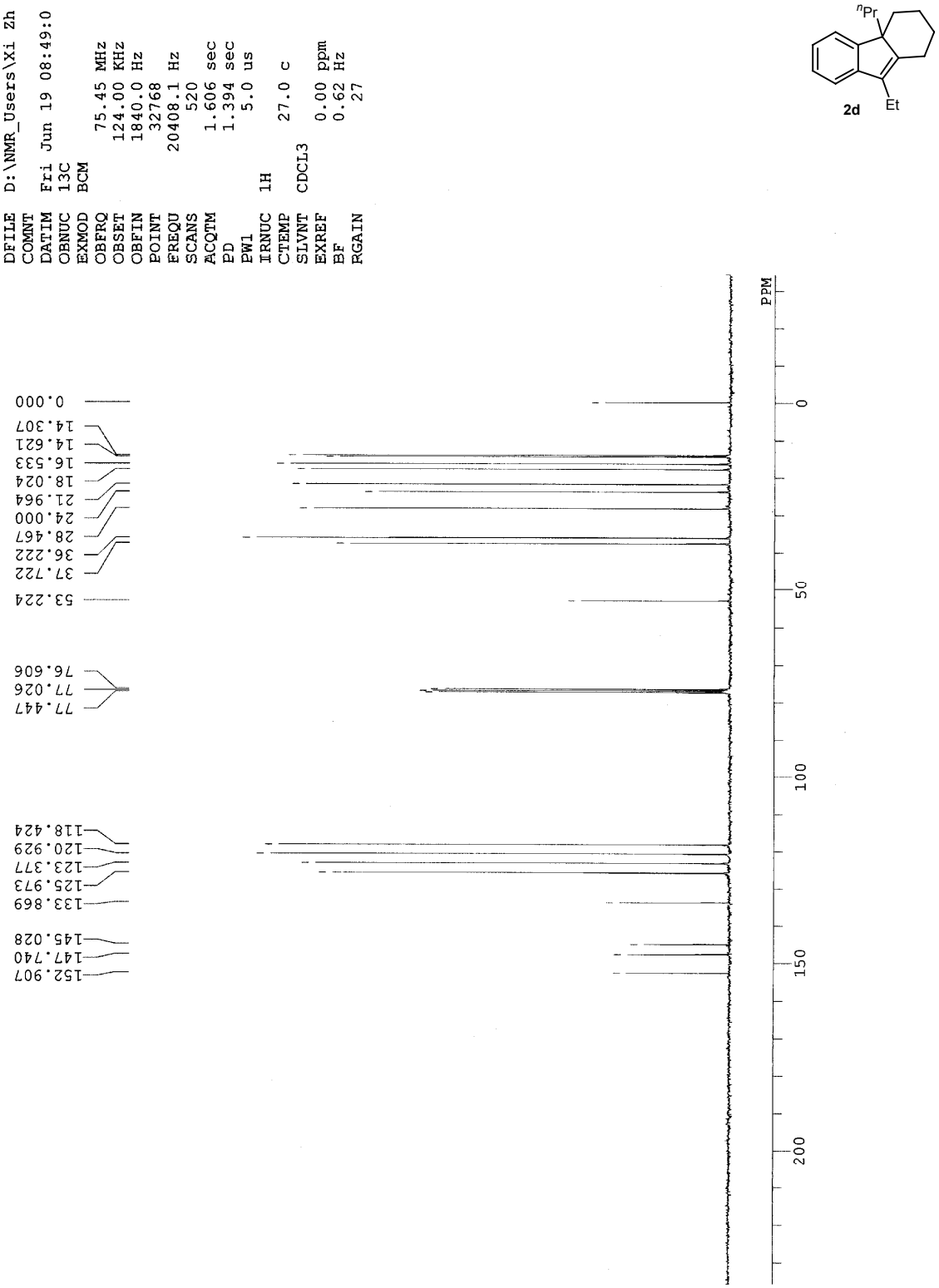

DFILE D:\NMR_Users\Xi Zh
COMNT
DATIM Tue Jun 23 15:33:4
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 226
ACQTM 1.606 sec
PD 1.394 sec
PW1 5.0 us
IRNUC 1H
CTEMP 23.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 26
0.000
7.895
14.085
14.448
15.395
16.739
18.033
19.805
20.225
30.576
40.368
57.757
76.598
77.018
77.438
118.745
123.723
129.080
129.254
141.344
143.380
147.657
150.533
PPM
0
25
50
75
100
125
150
175
Et
nPr
Et
Me
Et
2b

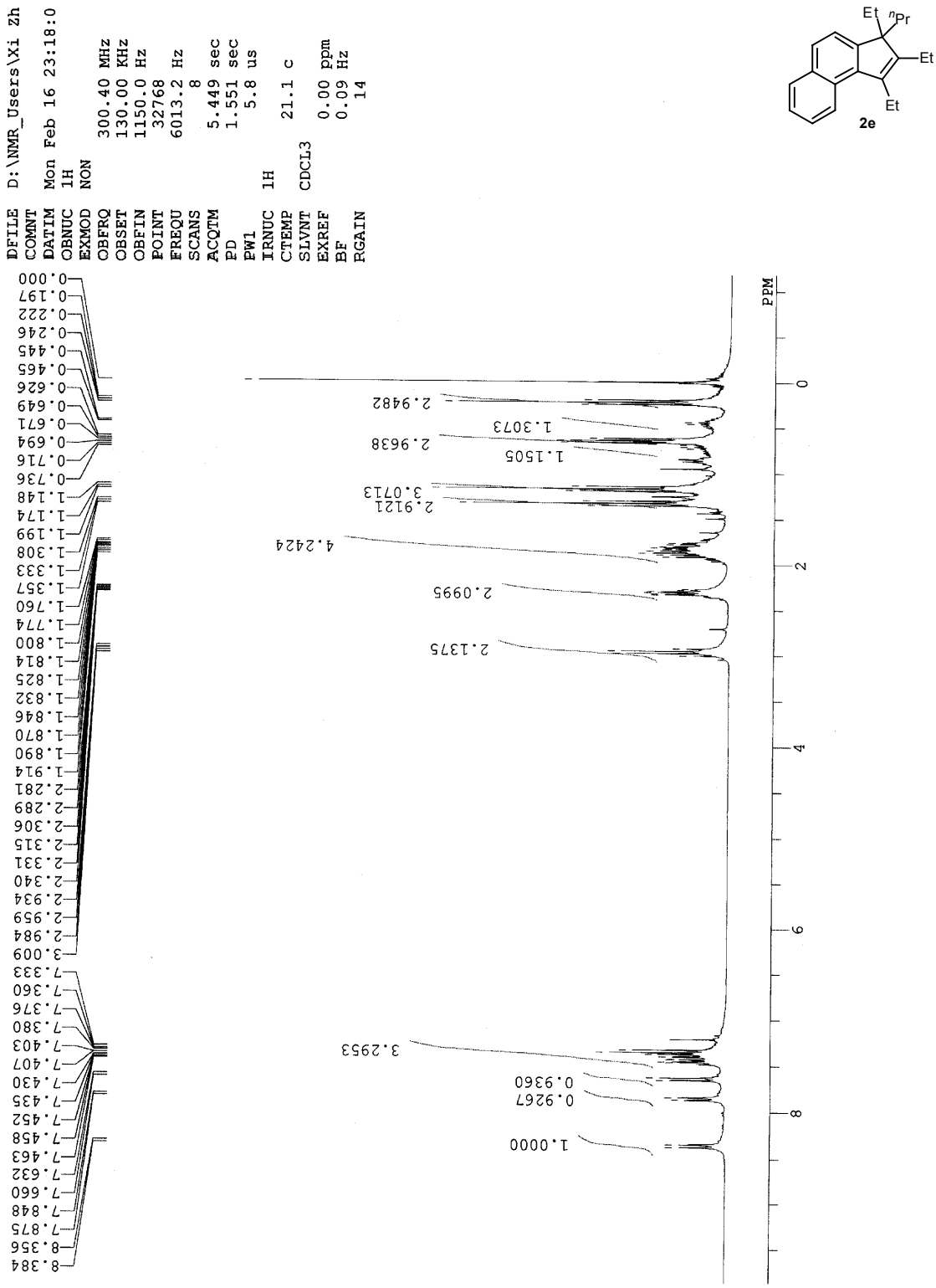

Me
Et
nPr
Et
Et
2c
Et
nPr
Et
Me
Et
2c'
FILE D:\NMR_Users\Xi zh
COMNT
DATIM Wed Jun 24 19:06:5
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 8
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
TRNUC 1H
CTEMP 23.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 14
3.1261
1.0546
3.0378
0.9975
5.9835
3.9595
1.8585
2.4467
2.0000
3.2496
PPM

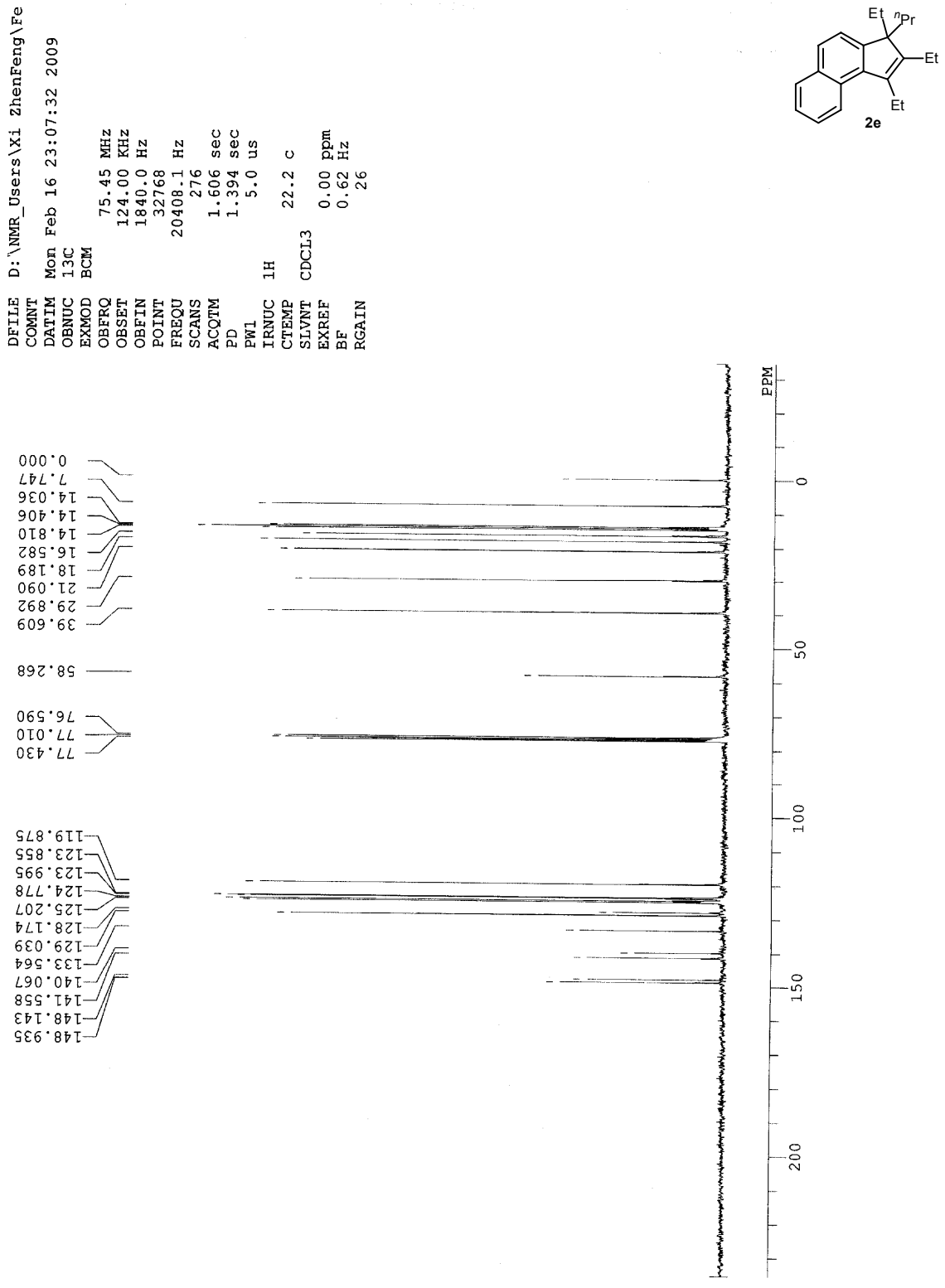

Me
Et
nPr
Et
Et
2c
Et
nPr
Et
Me
Et
2c'
PPM
0
25
50
75
100
125
150

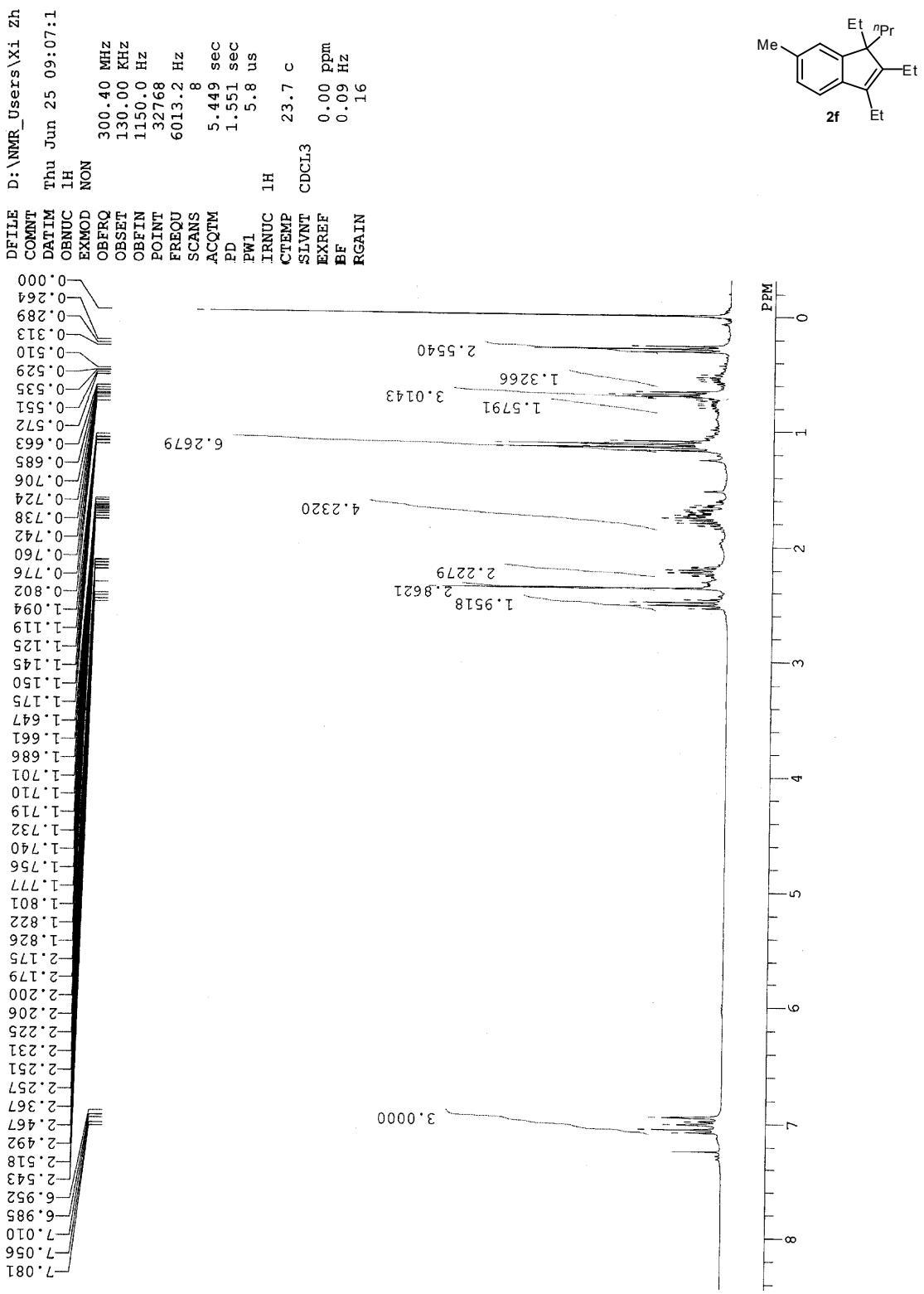

DFILE D:\NMR_Users\Xi Zh
COMNT
DATIM Sat Jun 20 10:34:2
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 8
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 15
7.260
7.251
7.248
7.244
7.239
7.224
7.220
7.200
7.196
7.127
7.121
7.103
7.098
2.689
2.524
2.518
2.498
2.493
2.472
2.468
2.178
2.134
2.032
2.016
1.975
1.940
1.928
1.886
1.857
1.843
1.759
1.713
1.697
1.669
1.659
1.653
1.615
1.153
1.128
1.103
1.094
1.080
1.050
1.017
1.003
0.973
0.959
0.929
0.915
0.728
0.711
0.705
0.693
0.672
0.000
1.3562
3.5067
2.2204
3.2639
7.9881
1.3199
2.0278
1.0003
1.0000
3.1215
PPM
0
1
2
3
4
5
6
7
8

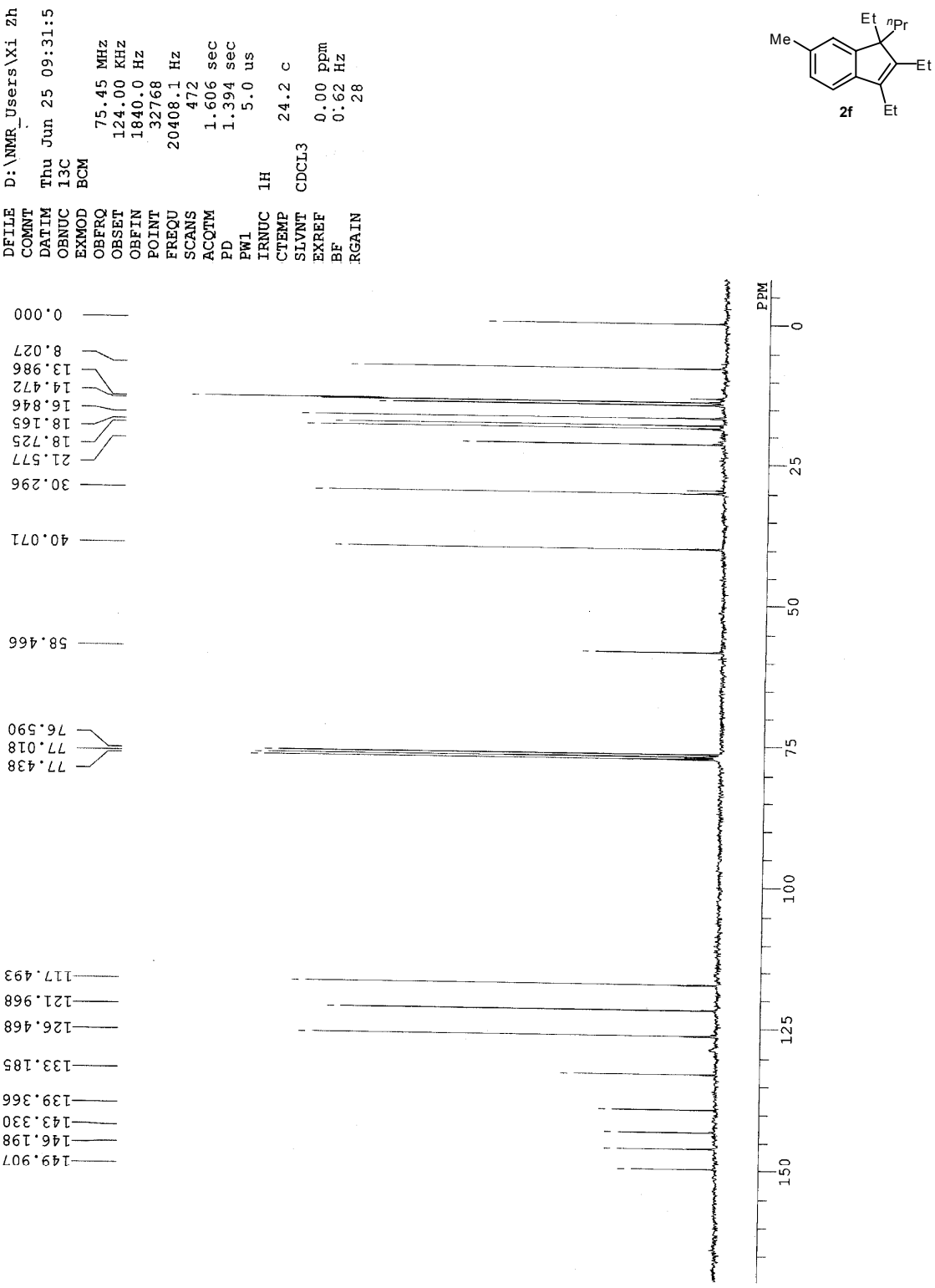
nPr
2d
Et


DFILE D:\NMR_Users\Xi Zh
COMNT
DATIM Fri Jun 19 08:49:0
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 520
ACQTM 1.606 sec
PD 1.394 sec
PW1 5.0 us
IRNUC 1H
CTEMP 27.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 27
0.000
14.307
14.621
16.533
18.024
21.964
24.000
28.467
36.222
37.722
53.224
76.606
77.026
77.447
118.424
120.929
123.377
125.973
133.869
145.028
147.740
152.907
PPM
0
50
100
150
200
nPr
Et
2d


DFILE D:\NMR_Users\Xi Zh
COMNT
DATIM Mon Feb 16 23:18:0
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 8
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 14
2.9482
1.3073
2.9638
1.1505
3.0713
2.9121
4.2424
2.0995
2.1375
3.2953
0.9360
0.9267
1.0000
PPM
0
2
4
6
8
Et
nPr
Et
Et
2e


DFILE D:\NMR_Users\Xi ZhenFeng\Fe
COMNT
DATIM Mon Feb 16 23:07:32 2009
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 276
ACQTM 1.606 sec
PD 1.394 sec
PW1 5.0 us
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 26
0.000
7.747
14.036
14.406
14.810
16.582
18.189
21.090
29.892
39.609
58.268
76.590
77.010
77.430
119.875
123.855
123.995
124.778
125.207
128.174
129.039
133.564
140.067
141.558
148.143
148.935
PPM
0
50
100
150
200
Et
nPr
Et
Et
2e


D:\NMR_Users\Xi Zh
Thu Jun 25 09:07:1
1H
NON
300.40 MHz
130.00 KHz
1150.0 Hz
32768
6013.2 Hz
8
5.449 sec
1.551 sec
5.8 us
1H
23.7 c
CDCL3
0.00 ppm
0.09 Hz
16
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
Me
Et
nPr
Et
Et
2f
2.5540
1.3266
3.0143
1.5791
6.2679
4.2320
2.2279
2.8621
1.9518
3.0000
PPM


DFILE D:\NMR_Users\Xi zh
COMNT
DATIM Thu Jun 25 09:31:5
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 472
ACQTM 1.606 sec
PD 1.394 sec
PW1 5.0 us
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 28
0.000
8.027
13.986
14.472
16.846
18.165
18.725
21.577
30.296
40.071
58.466
76.590
77.018
77.438
117.493
121.968
126.468
133.185
139.366
143.330
146.198
149.907
PPM
0
25
50
75
100
125
150

Me
Et
nPr
Et
Et
2f