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JUL 27 1998

Supporting Information

Journal of

Nickel and Zinc-Promoted [2+2+2] Cycloaddition of Diynes and α,β -Enones

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Spectral data for **2e-i**, ^{13}C NMR spectral data for **3**, **7-10**, **12a**, and **13-17**, and the copies of ^{13}C NMR spectra for **14-17** and the aromatized compounds of **14** and **15**.

2e: a colorless oil; bp 100 °C (20 mmHg); ^1H NMR (270 MHz, CDCl_3) δ 0.12 (s, 9 H), 2.44 (t, $J = 2.0$ Hz, 2 H), 4.21–4.26 (m, 4 H); GC/MS (EI, 70 eV) m/z (rel int) 166 (M^+ , 0), 151 ($\text{M}^+ - \text{Me}$, 9), 121 (100); HRMS for $\text{C}_8\text{H}_{11}\text{OSi}$ ($\text{M}^+ - \text{Me}$): calcd 151.0579, found 151.0574.

2f: a colorless oil; $R_f = 0.40$ (hexane); ^1H NMR (500 MHz, CDCl_3) δ 0.12 (s, 3 H), 0.15 (s, 9 H), 0.15 (s, 3 H), 0.90 (s, 9 H), 1.02 (s, 3 H), 1.04 (s, 3 H), 2.19 (d, $J = 16.7$ Hz, 1 H), 2.34 (d, $J = 16.7$ Hz, 1 H), 2.36 (d, $J = 2.1$ Hz, 1 H), 4.23 (d, $J = 2.1$ Hz, 1 H); GC/MS (EI, 70 eV) m/z (rel int) 322 (M^+ , 1), 265 (100); HRMS for $\text{C}_{18}\text{H}_{34}\text{OSi}_2$ (M^+): calcd, 322.2148; found, 322.2144.

2g: a colorless oil; $R_f = 0.40$ (hexane); ^1H NMR (500 MHz, CDCl_3) δ 0.11 (s, 3 H), 0.15 (s, 3 H), 0.15 (s, 9 H), 0.90 (s, 9 H), 1.02 (s, 3 H), 1.04 (s, 3 H), 1.96 (t, $J = 2.8$ Hz, 1 H), 2.18 (dd, $J = 16.7, 2.8$ Hz, 1 H), 2.31 (dd, $J = 16.7, 2.8$ Hz, 1 H), 4.18 (s, 1 H); GC/MS (EI, 70 eV) m/z (rel int) 322 (M^+ , 0), 265 (100); HRMS for $\text{C}_{17}\text{H}_{31}\text{OSi}_2$ ($\text{M}^+ - \text{Me}$), calcd: 307.1913, found: 307.1887.

2h: a colorless oil; $R_f = 0.37$ (hexane); ^1H NMR (400 MHz, CDCl_3) δ -0.05 (s, 3 H),

−0.01 (s, 3 H), 0.00 (s, 9 H), 0.75 (s, 9 H), 0.83 (s, 3 H), 0.85 (s, 3 H), 1.64 (t, J = 2.6 Hz, 3 H), 1.93 (dq, J = 16.3, 2.6 Hz, 1 H), 2.09 (dq, J = 16.3, 2.6 Hz, 1 H), 4.03 (s, 1 H); GC/MS (EI, 70 eV) m/z (rel int) 336 (M^+ , 0), 279 (20), 147 (100); HRMS for $C_{18}H_{33}OSi_2$ (M^+ − Me) calcd 321.2070; found 321.2057.

2i: a colorless oil; R_f = 0.14 (hexane:AcOEt = 19:1); 1H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 3 H), 0.15 (s, 9 H), 0.16 (s, 3 H), 0.91 (s, 9 H), 0.95 (s, 3 H), 0.99 (s, 3 H), 1.98 (t, J = 2.7 Hz, 1 H), 2.13 (d, J = 16.8 Hz, 1 H), 2.21 (ddd, J = 17.4, 5.5, 2.7 Hz, 1 H), 2.29 (t, J = 16.8 Hz, 1 H), 2.49 (ddd, J = 17.4, 5.5, 2.7 Hz, 1 H), 3.74 (t, J = 5.5 Hz, 1 H); GC/MS (EI, 70 eV) m/z (rel int) 336 (M^+ , 0), 279 (M^+ − t Bu, 83), 73 (100); HRMS for $C_{15}H_{27}OSi$ (M^+ − t Bu): calcd, 279.1600; found, 279.1599.

3: ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 13.96, 26.63, 40.11, 40.45, 60.38, 61.83, 124.12, 124.22, 127.64, 136.44, 140.70, 145.82, 171.23, 197.77.

7: ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 26.65, 73.10, 73.26, 120.85, 120.97, 127.98, 136.78, 139.84, 144.46, 197.45.

8: ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 22.77, 22.91, 26.45, 29.31, 29.56, 125.36, 129.15, 129.24, 134.68, 137.36, 143.13, 198.11.

9: ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 13.93, 23.25, 29.80, 39.07, 39.77, 40.42, 60.31, 61.74, 122.73, 124.33, 131.79, 138.76, 143.72, 146.33, 171.23, 198.08.

10: ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 14.00, 20.99, 31.23, 38.24, 38.69, 47.32, 58.98, 61.60, 116.28, 117.36, 135.69, 140.04, 171.07, 171.18, 201.51.

12a: ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 14.48, 24.49, 29.88, 72.53, 73.80, 117.96, 129.13, 136.78, 138.04, 139.65, 142.47, 201.33.

13: ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −1.08, 26.26, 27.84, 48.86, 69.92, 70.87, 114.61, 123.47, 136.86, 147.24, 210.28.

5-Acetyl-4-(trimethylsilyl)isobenzofuran: ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 1.82, 28.50, 72.54, 74.84, 120.99, 127.73, 134.36, 141.92, 145.19, 146.63, 202.42.

14: ^{13}C NMR (100.5 MHz, $CDCl_3$) δ −4.65, −4.27, −0.65, 18.19, 20.40, 25.90, 26.17, 28.16, 41.35, 43.88, 49.49, 80.88, 117.14, 125.07, 143.38, 147.35, 211.57.

5-Acetyl-1-[(*tert*-butyldimethylsilyl)oxy]-2,2-dimethyl-4-(trimethylsilyl)-

indan: ^{13}C NMR (100.5 MHz, CDCl_3) δ -4.62, -4.14, 2.09, 18.20, 21.01, 25.92, 26.44, 28.95, 42.50, 47.50, 82.48, 123.95, 126.05, 136.48, 146.31, 148.33, 148.44, 203.99.

15: ^{13}C NMR (127.5 MHz, CDCl_3) δ [-3.87 (major), -3.59 (minor)], [-3.35 (minor), -2.97 (major)], [-2.67 (major), -2.51 (minor)], [0.23 (minor), 0.82 (major)], [18.68 (major), 18.71 (minor)], [22.62 (major), 22.86 (minor)], 24.93, [25.97 (minor), 26.08 (major)], [26.97 (minor), 27.22 (major)], [28.03 (major), 28.23 (minor)], [40.52 (minor), 41.93 (major)], [42.46 (major), 43.96 (minor)], [49.51 (minor), 51.53 (major)], [81.12 (major), 82.26 (minor)], [115.43 (minor), 118.53 (major)], [139.16 (major), 141.14 (minor)], [153.93 (major), 154.59 (minor)], [210.08 (minor), 212.35 (major)].

6-Acetyl-1-[(*tert*-butyldimethylsilyl)oxy]-2,2-dimethyl-7-(trimethylsilyl)-

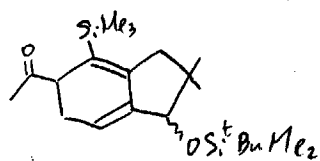
indan: ^{13}C NMR (100.4 MHz, CDCl_3) δ -3.34, -2.52, 3.58, 18.69, 22.76, 25.46, 26.13, 26.60, 28.86, 43.97, 84.76, 125.71, 128.95, 139.16, 144.52, 148.31, 153.02, 202.74.

16: ^{13}C NMR (100 MHz, CDCl_3) δ [-4.13 (minor), -3.26 (major)], [-3.11 (major), -2.99 (minor)], [0.00 (major), 0.67 (minor)], 18.36, [19.24 (major), 19.35 (minor)], [22.36 (minor), 22.63 (major)], 25.02, [25.66 (major), 25.77 (minor)], [27.47 (major), 27.50 (minor)], [32.40 (minor), 32.59 (major)], [38.84 (major), 39.15 (minor)], [41.13 (minor), 42.00 (major)], [50.19 (major), 52.37 (minor)], [81.07 (minor), 82.43 (major)], [123.40 (minor), 124.90 (major)], [126.34 (major), 126.55 (minor)], [132.59 (minor), 134.14 (major)], [154.48 (minor), 154.93 (major)], [210.54 (minor), 212.38 (major)].

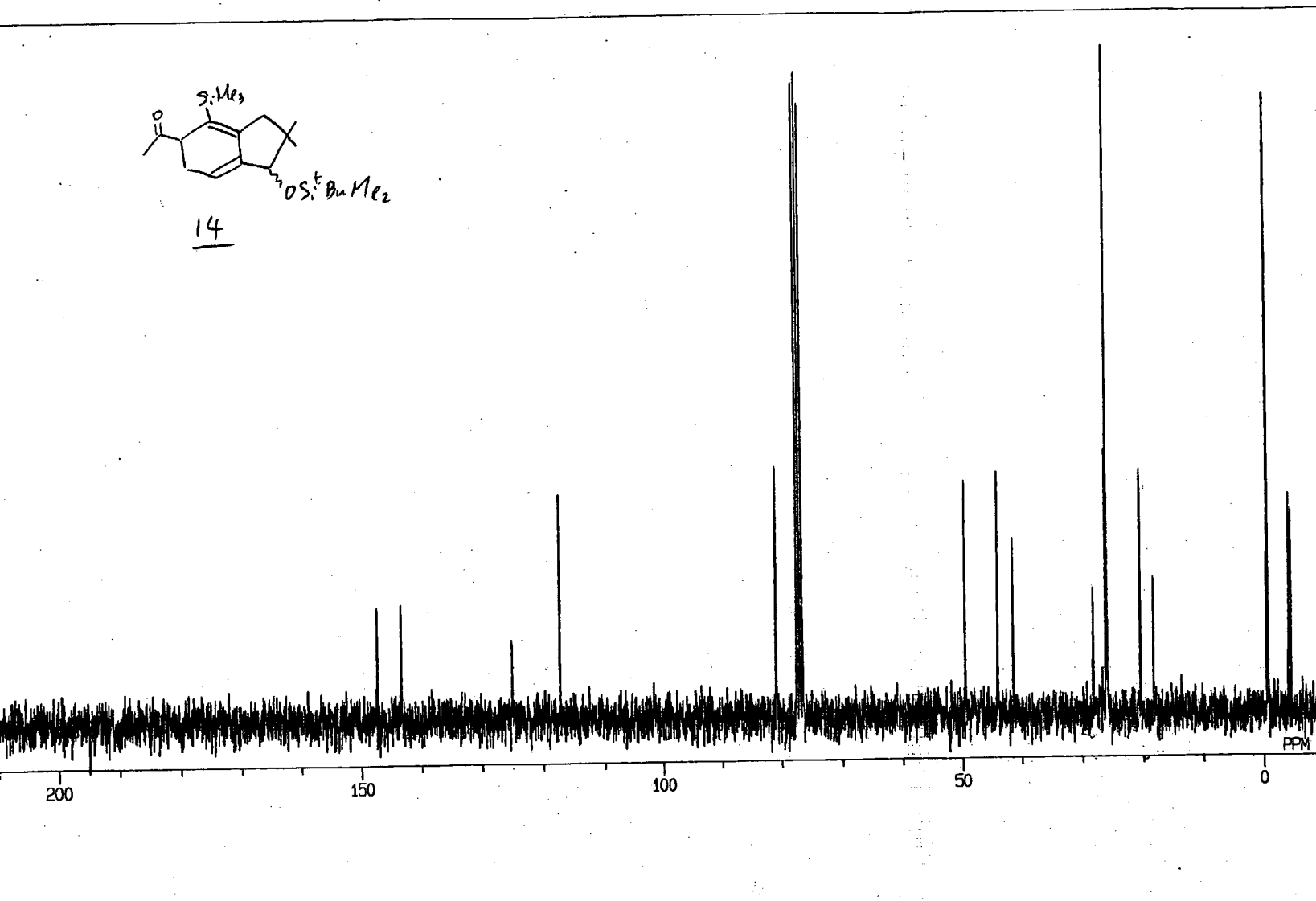
17: ^{13}C NMR (67.8 MHz, CDCl_3) δ -4.90, -4.08, -2.30, 0.63, [17.88 (major), 18.01 (minor)], [25.81 (major), 26.00 (minor)], 28.61, 29.08, 36.64, 37.83, 44.78, 48.91, 75.44, 122.70, 129.43, 135.24, 145.53, 211.71.

14

25-NOV-96 16:30:02
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 PD 2.181 sec
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 CTEMP 28.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.22 Hz
 RGAIN 24
 OPERATOR : _____

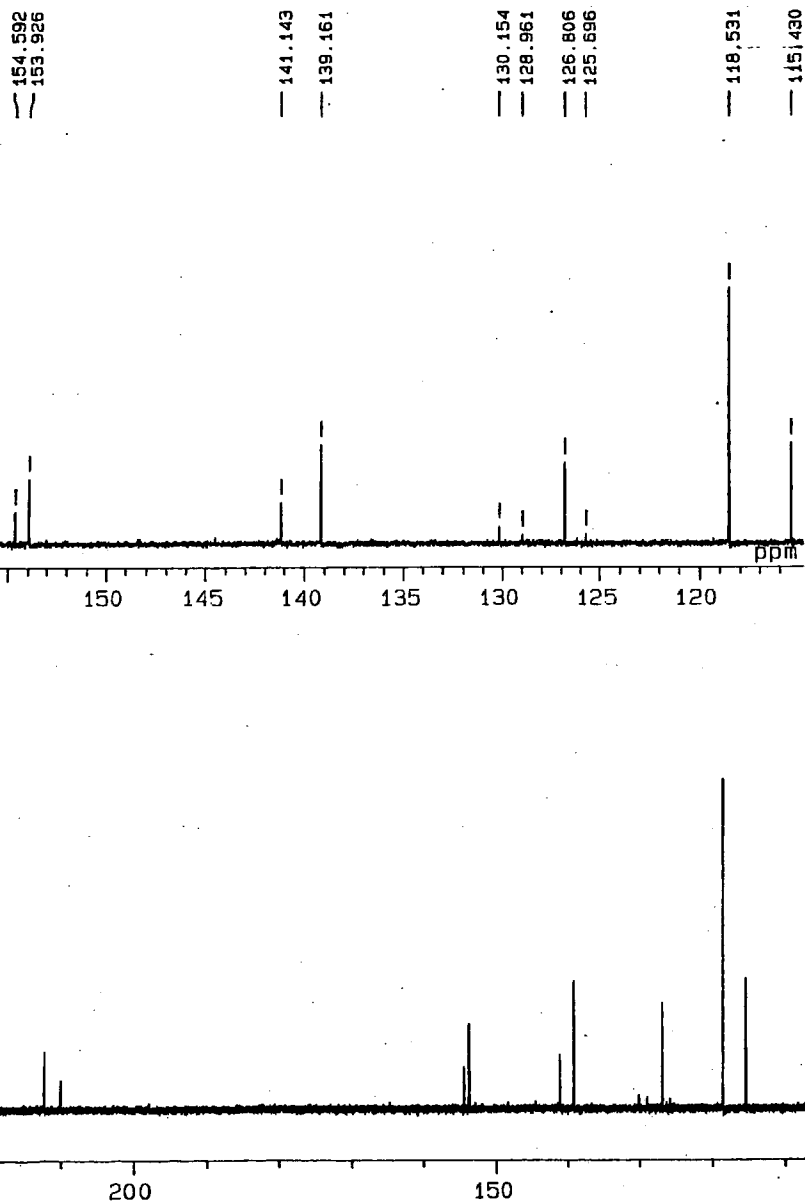


14



15

109-117



22-APR-1997 10:12:51.22

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SCANS : 1000
DUMMY : 4
ACQTM : 0.9667 sec
PD : 1.5000 sec
RGAIN : 23

PW1 : 4.00 usec

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OBFRQ : 125.65 MHz
OBSET : 129418.71 Hz

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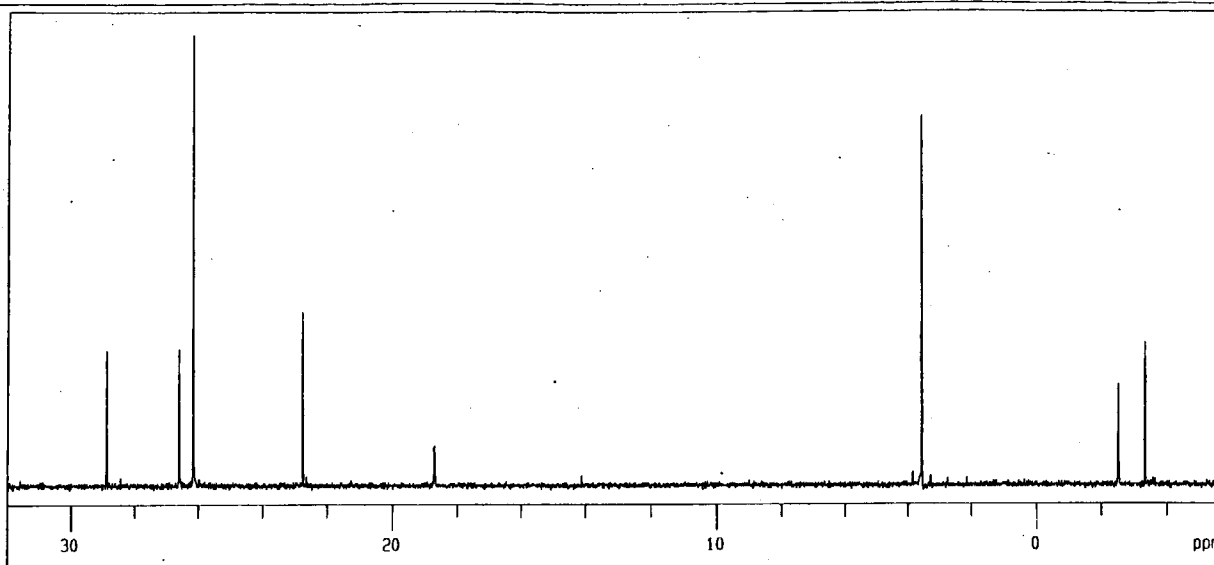
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BF : 0.50 Hz
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T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
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XE : 28295.48 Hz
XS : 589.66 Hz
operator

19

15 (aromatized)

bcm



Date : Thu Apr 24 14: 47: 38 1997

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DUMMY : 1 times
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IRFRQ : 399.65 MHz
IRSET : 134300.00 Hz
IRRPW : 43.0 usec
IRRNS : 0

SCANS : 695 times

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SPINNING : 14 Hz
TEMP : 26.5 C

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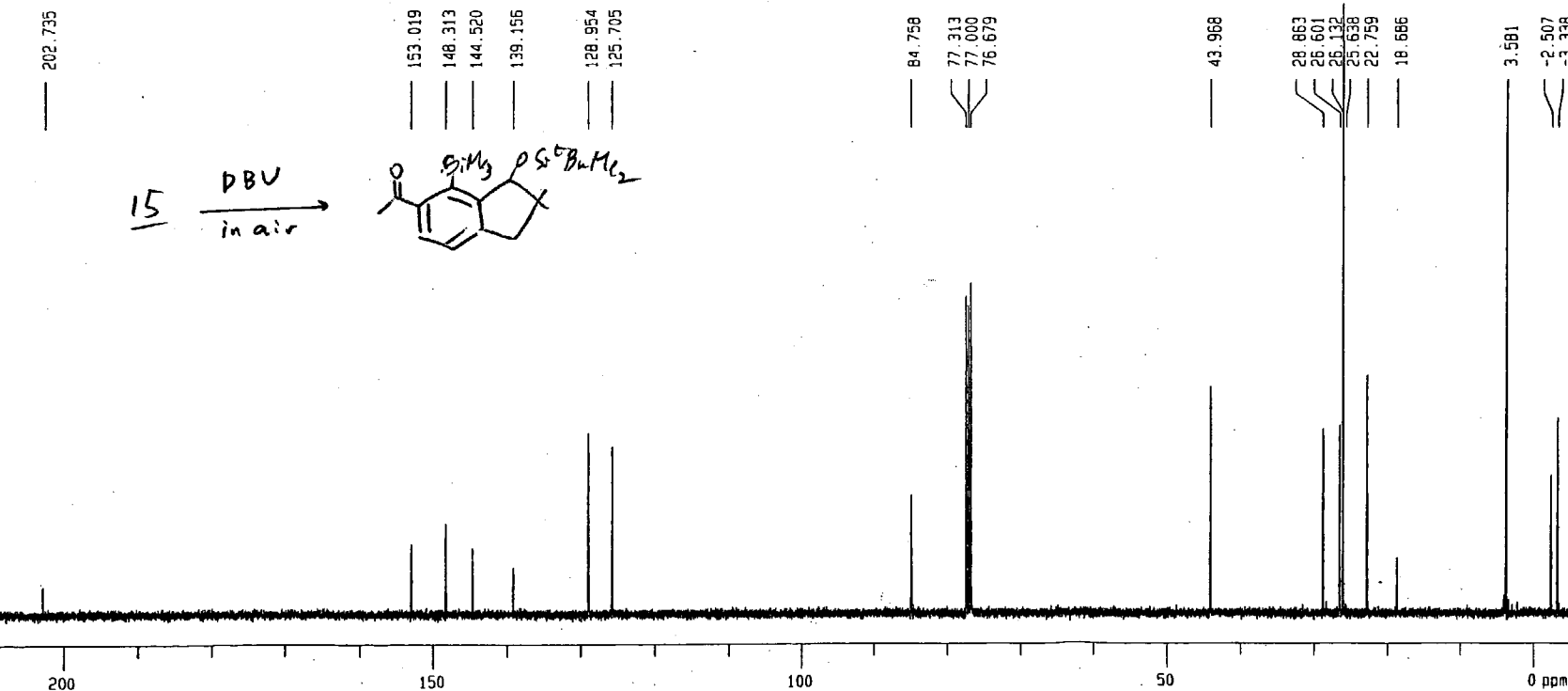
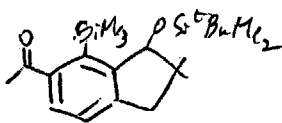
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3.581
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-3.338

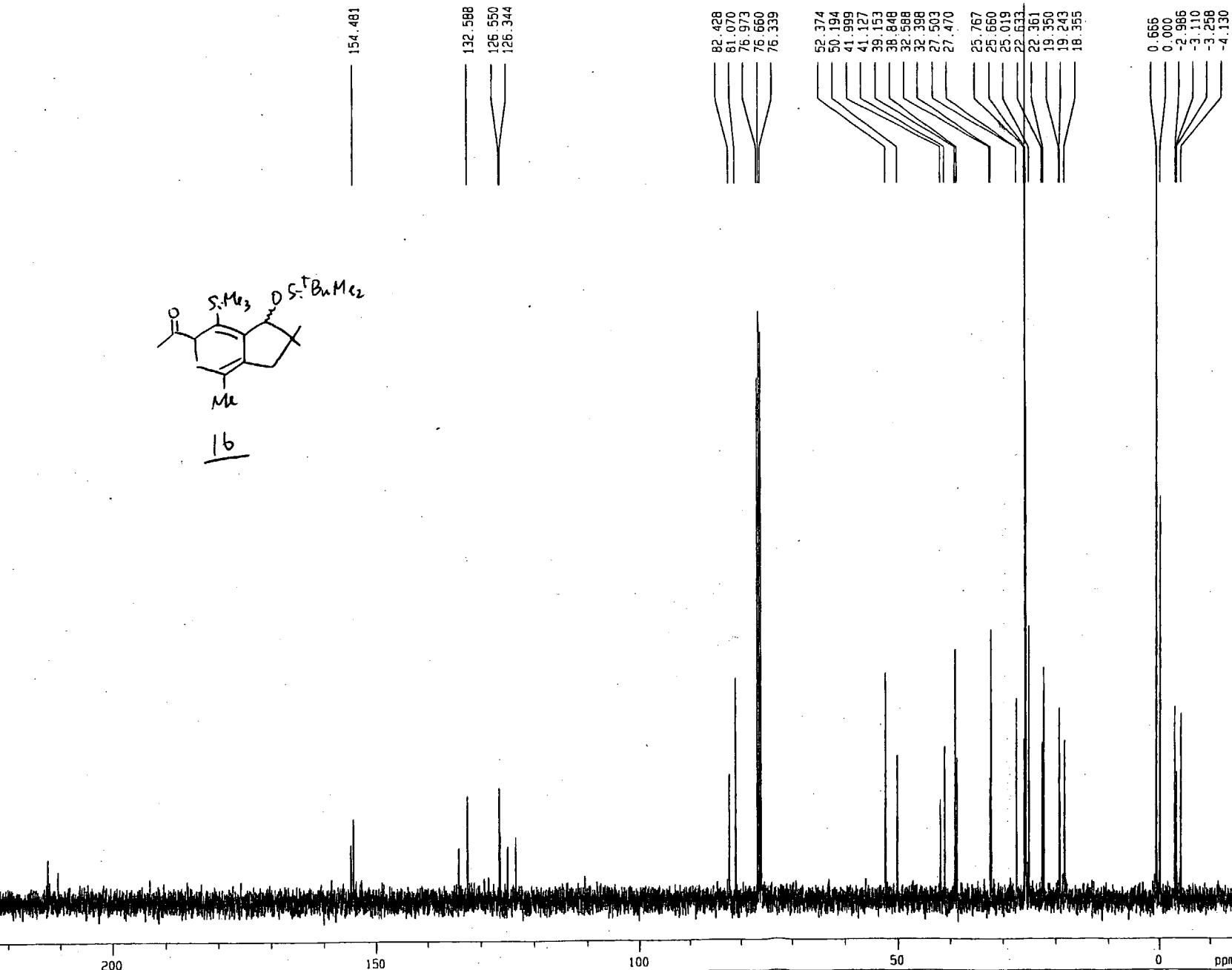
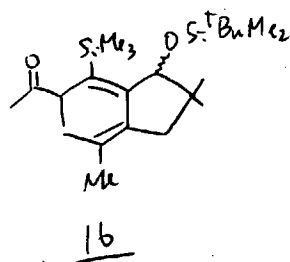
15 $\xrightarrow[\text{in air}]{\text{DBU}}$



7/9

8/9

109_139



Date : Fri Jul 4 15:18:55 1997

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 INTVL : 36.9 usec
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 DUMMY : 1 times
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 INIWT : 10.0000 msec
 RESOL : 0.83 Hz
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OBNUC : 13C
 OBFRQ : 100.40 MHz
 OBSET : 135500.00 Hz
 RGAIN : 29

1H
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 IRFRO : 134300.00 Hz
 IRSET : 43.0 usec
 IRRPW : 0

SCANS : 128 times

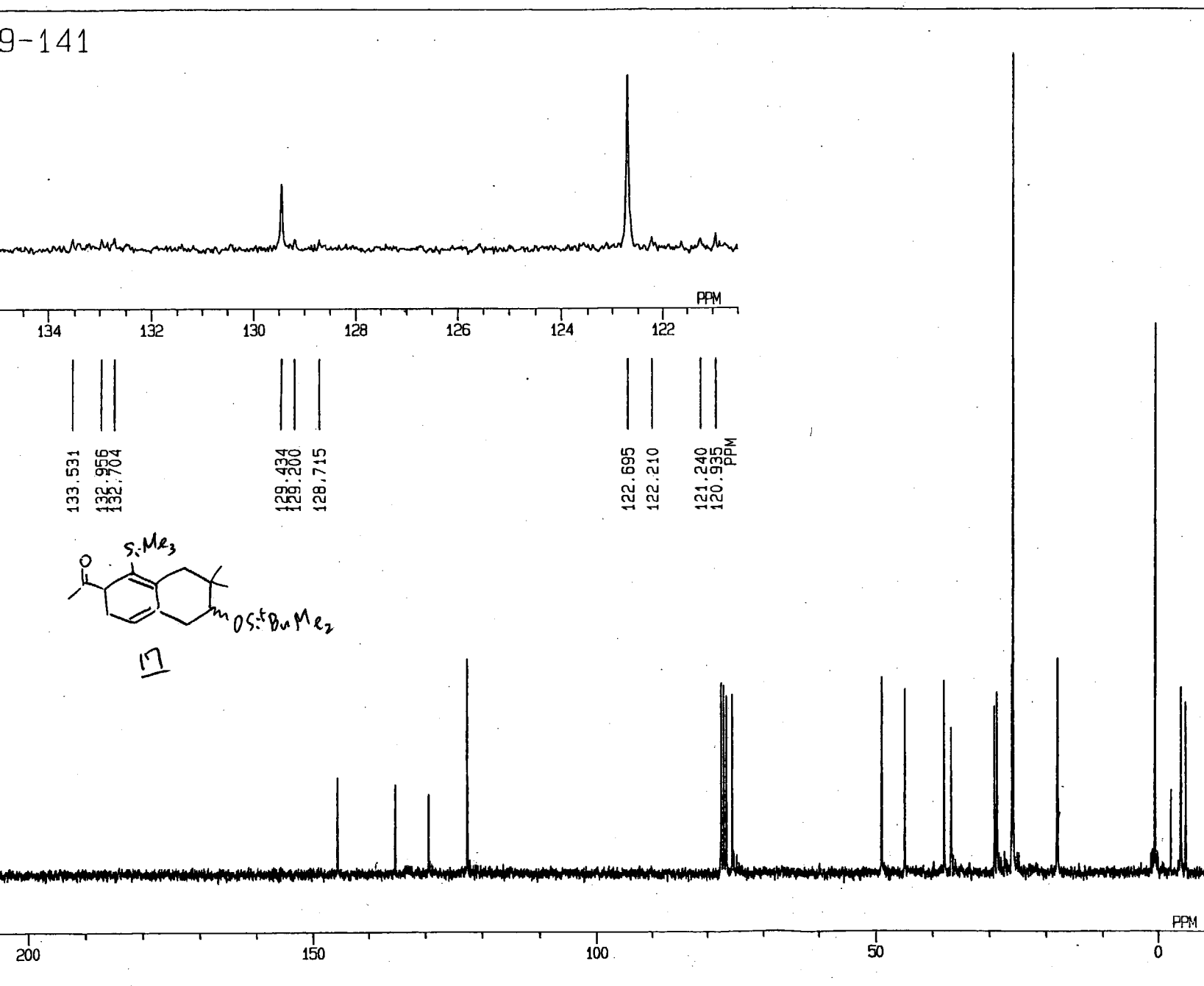
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 SPINNING : 10 Hz
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16

17

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 PD 2.181 sec
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 EXREF 77.00 ppm
 BF 1.22 Hz
 RGAIN 28
 OPERATOR :

9-141



19