Supplementary Information

Cobalt-catalyzed conjugate addition of silylacetylenes to α,β-unsaturated ketones

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Contents of Supplementary Information:

1. General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, 202 MHz for ^{31}P). Chemical shifts are reported in δ (ppm) referenced to the residual peaks of $CDCl_3$ (δ 7.26) for ^{1}H NMR and $CDCl_3$ (δ 77.00) for ^{13}C NMR. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, sext: sextet, sept: septet, m: multiplet. Optical rotations were measured on a JASCO P-2200 polarimeter. High-resolution mass spectra were obtained with a Bruker micrOTOF spectrometer.

2. Materials

MeCN and DMSO were distilled over CaH_2 under N_2. 1,4-Dioxane and toluene were purified by passing through a neutral alumina column under N_2. $Co(OAc)_2{\cdot}4H_2O$ (99.0%) and zinc powder were purchased from Kanto Chemical Co., Inc. and used as received. The starting enone **1a** was purchased and purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1). Enones **1b** [97060-29-2],[1] **1c** [95826-96-3],[2] **1d** [131323-45-0],[1] **1e** [91897-73-3],[3] **1f** [61752-66-7],[1] **1g** [36597-08-7],[4] **1h** [3102-33-8],[5] **1i** [167645-81-0],[6] **1k** [769-60-8][7,8] were prepared according to the reported procedures. All other chemicals were purchased from commercial suppliers and used as received.

3. A general procedure for cobalt-catalyzed conjugate addition of (triisopropylsilyl)acetylene to enone (Table 2)

A mixture of $Co(OAc)_2{\cdot}4H_2O$ (3.7 mg, 0.015 mmol), dppe (6.0 mg, 0.015 mmol), Zn powder (9.8 mg, 0.15 mmol), enone **1** (0.30 mmol), and (triisopropylsilyl)acetylene (**2m**) (135 μL, 0.60 mmol) in DMSO (0.5 mL) was stirred at 80 °C for 20 h under N_2. The mixture was passed through a short column of silica gel with diethyl ether as eluent. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with hexane/ethyl acetate to give compound **3**.

1 D. A. Oare, M. A. Henderson, M. A. Sanner and C. H. Heathcock, *J. Org. Chem.,* 1990, **55**, 132.
2 M. Bandini, M. Fagioli, M. Garavelli, A. Melloni, V. Trigari and A. Umani-Ronchi, *J. Org. Chem.,* 2004, **69**, 7511.
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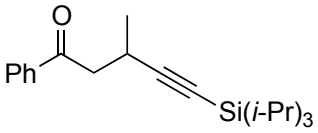
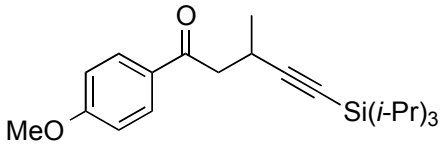
8 J. Yin, C. E. Gallis and J. D. Chisholm, *J. Org. Chem.,* 2007, **72**, 7054.

4. Characterization of the products



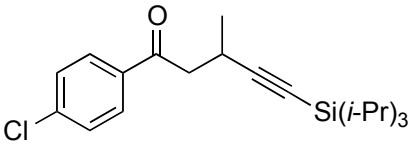
3am

Compound 3am ([CAS: 1008533-93-4]; 97% yield): ^{1}H NMR ($CDCl_3$) δ 0.80–1.05 (m, 21H), 1.28 (d, *J* = 6.6 Hz, 3H), 3.00 (dd, *J* = 14.5, 8.5 Hz, 1H), 3.19–3.29 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H).



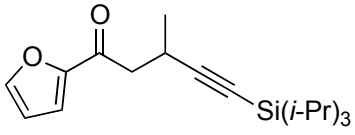
3bm

Compound 3bm ([CAS: 1008533-94-5]; 92% yield): ^{1}H NMR ($CDCl_3$) δ 0.94–1.04 (m, 21H), 1.26 (d, *J* = 6.4 Hz, 3H), 2.95 (dd, *J* = 17.3, 9.5 Hz, 1H), 3.17–3.24 (m, 1H), 3.20 (dd, *J* = 17.3, 5.9 Hz, 1H), 3.85 (s, 3H), 6.92 (d, *J* = 8.7 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 2H).



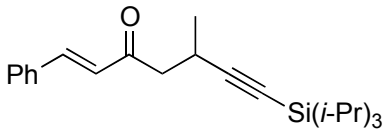
3cm

Compound 3cm (74% yield): ^{1}H NMR ($CDCl_3$) δ 0.92–1.04 (m, 21H), 1.28 (d, *J* = 6.6 Hz, 3H), 2.92–3.00 (m, 1H), 3.19 (dd, *J* = 12.9, 6.5 Hz, 1H), 3.23 (dd, *J* = 12.9, 6.2 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.2, 18.6, 21.3, 23.2, 45.4, 80.6, 112.2, 128.9, 129.6, 135.4, 139.6, 196.8. HRMS (ESI) calcd for $C_{21}H_{31}ClNaOSi$ $(M+Na)^+$ 385.1725, found 385.1724.



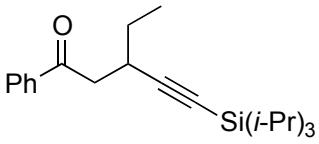
3dm

Compound 3dm ([CAS: 1008533-95-6]; 93% yield): ^{1}H NMR ($CDCl_3$) δ 0.93–1.05 (m, 21H), 1.27 (d, *J* = 6.8 Hz, 3H), 2.85 (dd, *J* = 15.4, 7.5 Hz, 1H), 3.10 (dd, *J* = 15.4, 6.7 Hz, 1H), 3.19 (dqd, *J* = 7.5, 6.8, 6.7 Hz, 1H), 6.53 (dd, *J* = 3.6, 1.7 Hz, 1H), 7.21 (dd, *J* = 3.6, 0.7 Hz, 1H), 7.58 (dd, *J* = 1.7, 0.7 Hz, 1H).



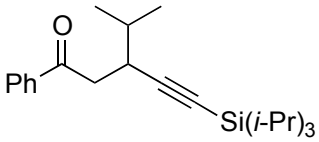
3em

Compound 3em ([CAS: 1008533-96-7]; 80% yield): ^{1}H NMR ($CDCl_3$) δ 0.94–1.10 (m, 21H), 1.26 (d, *J* = 6.9 Hz, 3H), 2.70 (dd, *J* = 15.7, 7.5 Hz, 1H), 2.94 (dd, *J* = 15.7, 6.6 Hz, 1H), 3.13 (dqd, *J* = 7.5, 6.9, 6.6 Hz, 1H), 6.78 (d, *J* = 16.1 Hz, 1H), 7.30–7.45 (m, 3H), 7.50–7.57 (m, 2H), 7.56 (d, *J* = 16.1 Hz, 1H).



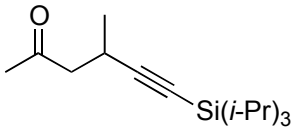
3fm

Compound 3fm ([CAS: 1008533-99-0]; 88% yield): ^{1}H NMR ($CDCl_3$) δ 0.95–1.05 (m, 21H), 1.08 (t, *J* = 7.4 Hz, 3H), 1.43–1.53 (m, 1H), 1.60–1.70 (m, 1H), 3.02 (dd, *J* = 15.7, 7.1 Hz, 1H), 3.05–3.12 (m, 1H), 3.25 (dd, *J* = 15.7, 6.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.52–7.58 (m, 1H), 7.93–7.99 (m, 2H).



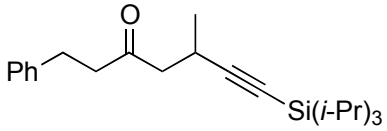
3gm

Compound 3gm (65% yield): ^{1}H NMR ($CDCl_3$) δ 0.90–1.05 (m, 24H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.81 (sept d, *J* = 6.8, 4.9 Hz, 1H), 2.99 (dd, *J* = 15.7, 6.2 Hz, 1H), 3.12 (ddd, *J* = 7.7, 6.2, 4.9 Hz, 1H), 3.25 (dd, *J* = 15.7, 7.7 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.52–7.58 (m, 1H), 7.92–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.2, 17.8, 18.6, 21.3, 31.2, 35.5, 41.8, 82.7, 109.1, 128.2, 128.5, 133.0, 137.3, 198.6. HRMS (ESI) calcd for $C_{23}H_{36}ONaSi$ $(M+Na)^+$ 379.2428, found 379.2426.



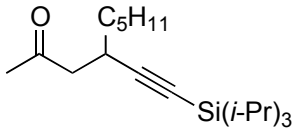
3hm

Compound 3hm ([CAS: 1008533-97-8]; 92% yield): ^{1}H NMR ($CDCl_3$) δ 0.95–1.08 (m, 21H), 1.19 (d, *J* = 6.9 Hz, 3H), 2.16 (s, 3H), 2.48 (dd, *J* = 16.1, 7.1 Hz, 1H), 2.66 (dd, *J* = 16.1, 7.0 Hz, 1H), 2.98 (ddq, *J* = 7.1, 7.0, 6.9 Hz, 1H).



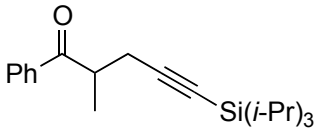
3im

Compound 3im (87% yield): ^{1}H NMR ($CDCl_3$) δ 0.95–1.07 (m, 21H), 1.18 (d, *J* = 7.0 Hz, 3H), 2.45 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.65 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.72–2.84 (m, 2H), 2.84–2.95 (m, 2H), 3.02 (sext, *J* = 7.0 Hz, 1H), 7.15–7.21 (m, 3H), 7.27 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.2, 18.6, 21.1, 22.9, 29.5, 45.0, 49.9, 80.5, 112.2, 126.1, 128.3, 128.5, 141.0, 207.6. HRMS (ESI) calcd for $C_{23}H_{36}ONaSi$ $(M+Na)^+$ 379.2428, found 379.2427.



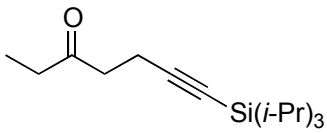
3jm

Compound 3jm ([CAS: 1008534-00-6]; 67% yield): ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3H), 0.94–1.08 (m, 21H), 1.20–1.56 (m, 8H), 2.17 (s, 3H), 2.48 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.63 (dd, *J* = 16.0, 7.7 Hz, 1H), 2.85–2.93 (m, 1H).



3km

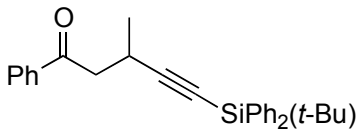
Compound 3km (73% yield): ^{1}H NMR ($CDCl_3$) δ 0.96–1.05 (m, 21H), 1.33 (d, *J* = 7.0 Hz, 3H), 2.48 (dd, *J* = 17.0, 8.2 Hz, 1H), 2.67 (dd, *J* = 17.0, 5.9 Hz, 1H), 3.63–3.73 (m, 1H), 7.44–7.49 (m, 2H), 7.56 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.96 (dd, *J* = 8.1, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.2, 17.3, 18.55, 18.56, 23.9, 40.6, 82.1, 106.4, 128.4, 128.6, 133.0, 136.2, 202.5. HRMS (ESI) calcd for $C_{21}H_{32}ONaSi$ $(M+Na)^+$ 351.2115, found 351.2110.



3lm

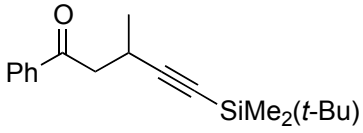
Compound 3lm (77% yield): ^{1}H NMR ($CDCl_3$) δ 0.96–1.10 (m, 24H), 2.45 (q, *J* = 7.3 Hz, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 7.6, 11.2, 14.7, 18.5,

36.1, 41.4, 80.8, 107.4, 209.2. HRMS (ESI) calcd for $C_{16}H_{30}ONaSi$ $(M+Na)^+$ 289.1958, found 289.1955.



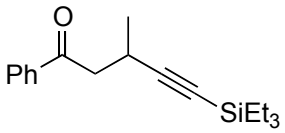
3an

Compound 3an (95% yield): ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.40 (d, *J* = 6.6 Hz, 3H), 3.12 (dd, *J* = 18.4, 9.3 Hz, 1H), 3.35–3.44 (m, 2H), 7.30–7.40 (m, 6H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.73–7.78 (m, 4H), 7.97–8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.4, 21.0, 23.2, 27.0, 45.2, 79.8, 114.9, 127.6, 128.1, 128.6, 129.3, 133.1, 133.7, 135.5, 137.0. 197.7. HRMS (ESI) calcd for $C_{28}H_{30}ONaSi$ $(M+Na)^+$ 433.1958, found 433.1955.



3ao

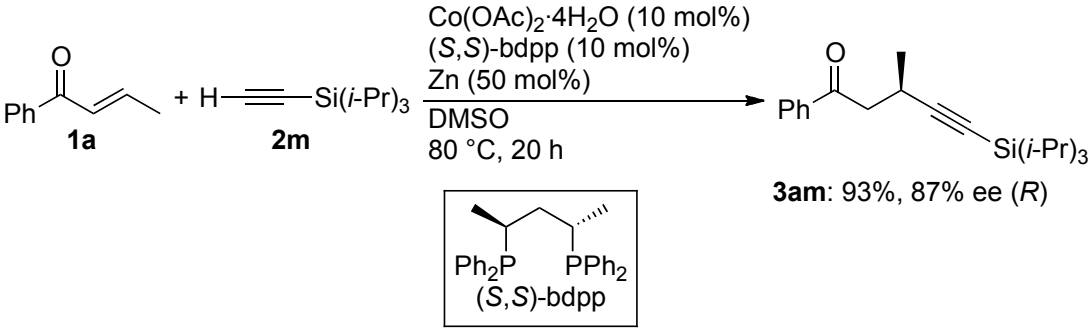
Compound 3ao ([CAS: 960318-62-1]; 70% yield): ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.27 (d, *J* = 6.8 Hz, 3H), 3.01 (dd, *J* = 15.8, 7.3 Hz, 1H), 3.21 (dqd, *J* = 7.3, 6.8, 5.8 Hz, 1H), 3.26 (dd, *J* = 15.8, 5.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.3 Hz, 2H).



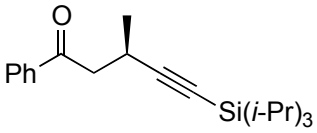
3ap

Compound 3ap ([CAS: 1008534-03-9]; 40% yield): ^{1}H NMR ($CDCl_3$) δ 0.53 (q, *J* = 7.8 Hz, 6H), 0.94 (t, *J* = 7.8 Hz, 9H), 1.27 (d, *J* = 6.7 Hz, 3H), 3.02 (dd, *J* = 15.6, 7.1 Hz, 1H), 3.17–3.30 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 2H).

5. Asymmetric addition of (triisopropylsilyl)acetylene (2m) to enone 1a (Scheme 1 and Table 3)

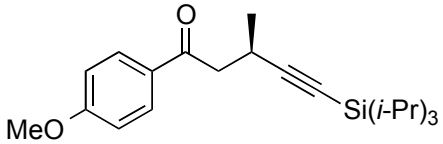


A mixture of $Co(OAc)_2 \cdot 4H_2O$ (7.5 mg, 0.030 mmol), (*S*,*S*)-bdpp (13.2 mg, 0.030 mmol), Zn powder (9.8 mg, 0.15 mmol), enone **1a** (43.9 mg, 0.30 mmol), and (triisopropylsilyl)acetylene (**2m**) (135 μL, 0.60 mmol) in DMSO (0.5 mL) was stirred at 80 °C for 20 h under N_2. The mixture was passed through a short column of silica gel with diethyl ether as eluent. After evaporation of the solvent, the residue was subjected to preparative TLC (silica gel, hexane/ethyl acetate = 10/1) to give compound **3am** (91.2 mg, 0.28 mmol, 93%).



3am

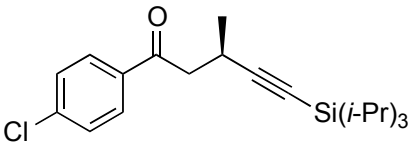
Compound 3am (Table 3, entry 1): The ee was measured by HPLC (Chiralcel OJ-H column × 2, flow 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm, t_1 = 40.8 min (*S*), t_2 = 44.0 min (*R*)); $[\alpha]^{20}_D$ +2 (*c* 0.99, $CHCl_3$) for 87% ee (*R*). The absolute configuration of (*R*)-(+)-**3am** produced by (*S*,*S*)-bdpp was determined by comparison of the specific rotation and the retention time of the chiral HPLC analysis with the values reported previously.[9]



3bm

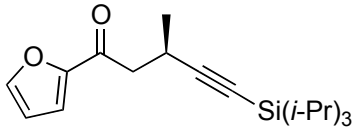
Compound 3bm (Table 3, entry 2): The ee was measured by HPLC (Chiralcel OJ-H column × 2, flow 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm, t_1 = 61.6 min (*S*), t_2 = 83.2 min (*R*)); $[\alpha]^{20}_D$ +12 (*c* 0.60, $CHCl_3$) for 79% ee (*R*).

9 T. Nishimura, X.-X. Guo, N. Uchiyama, T. Katoh and T. Hayashi, *J. Am. Chem. Soc.*, 2008, **130**, 1576.



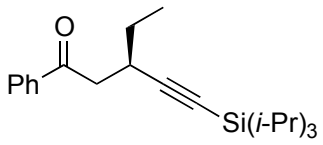
3cm

Compound 3cm (Table 3, entry 3): The ee was measured by HPLC (Chiralcel OJ-H column × 2, flow 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm, t_1 = 41.9 min (*S*), t_2 = 45.1 min (*R*)); $[\alpha]^{20}_{D}$ +5 (*c* 0.88, $CHCl_3$) for 90% ee (*R*).



3dm

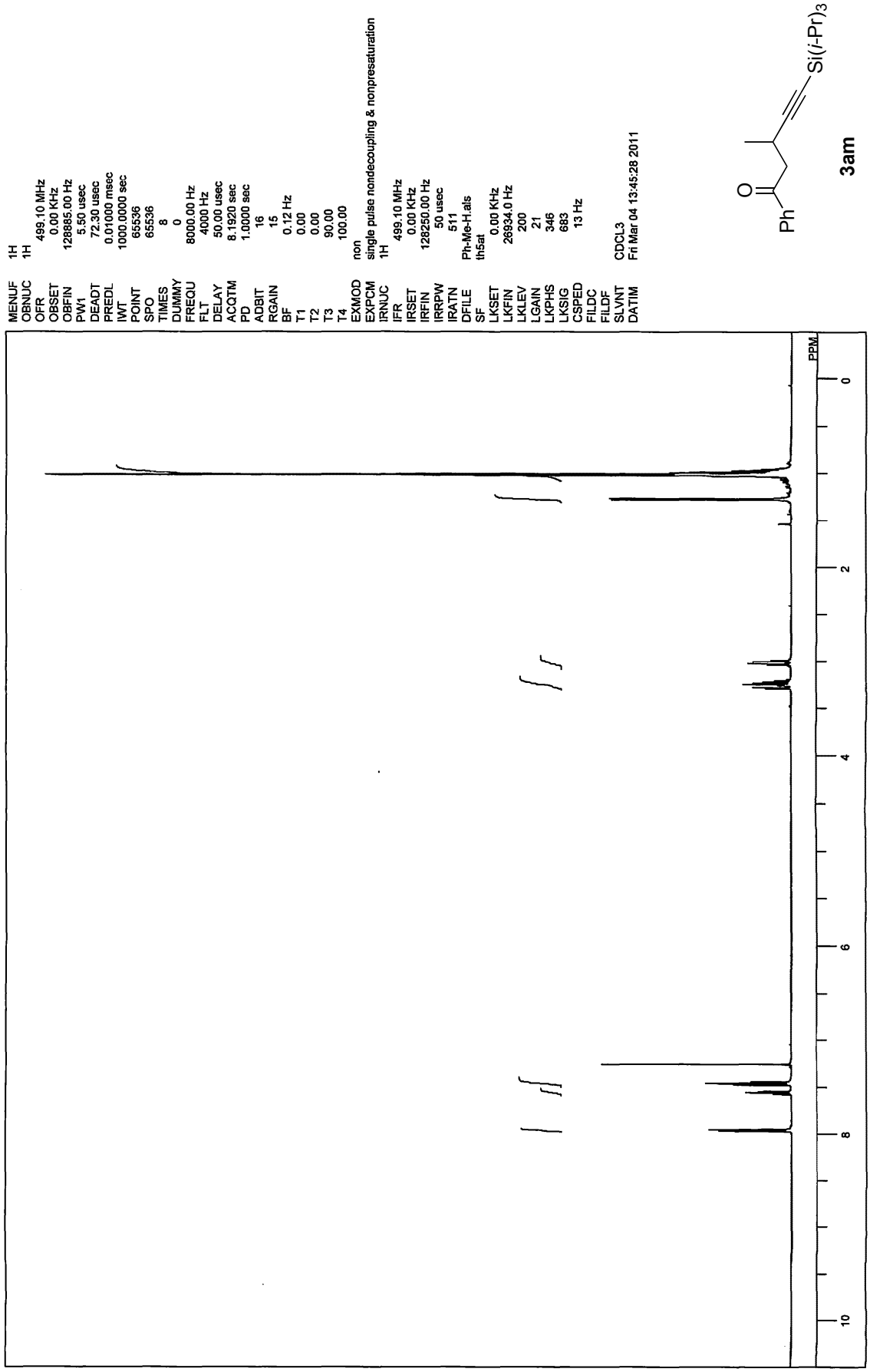
Compound 3dm (Table 3, entry 4): The ee was measured by HPLC (Chiralcel OJ-H column × 2, flow 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm, t_1 = 67.7 min (*S*), t_2 = 71.7 min (*R*)); $[\alpha]^{20}_{D}$ +13 (*c* 0.63, $CHCl_3$) for 81% ee (*R*).

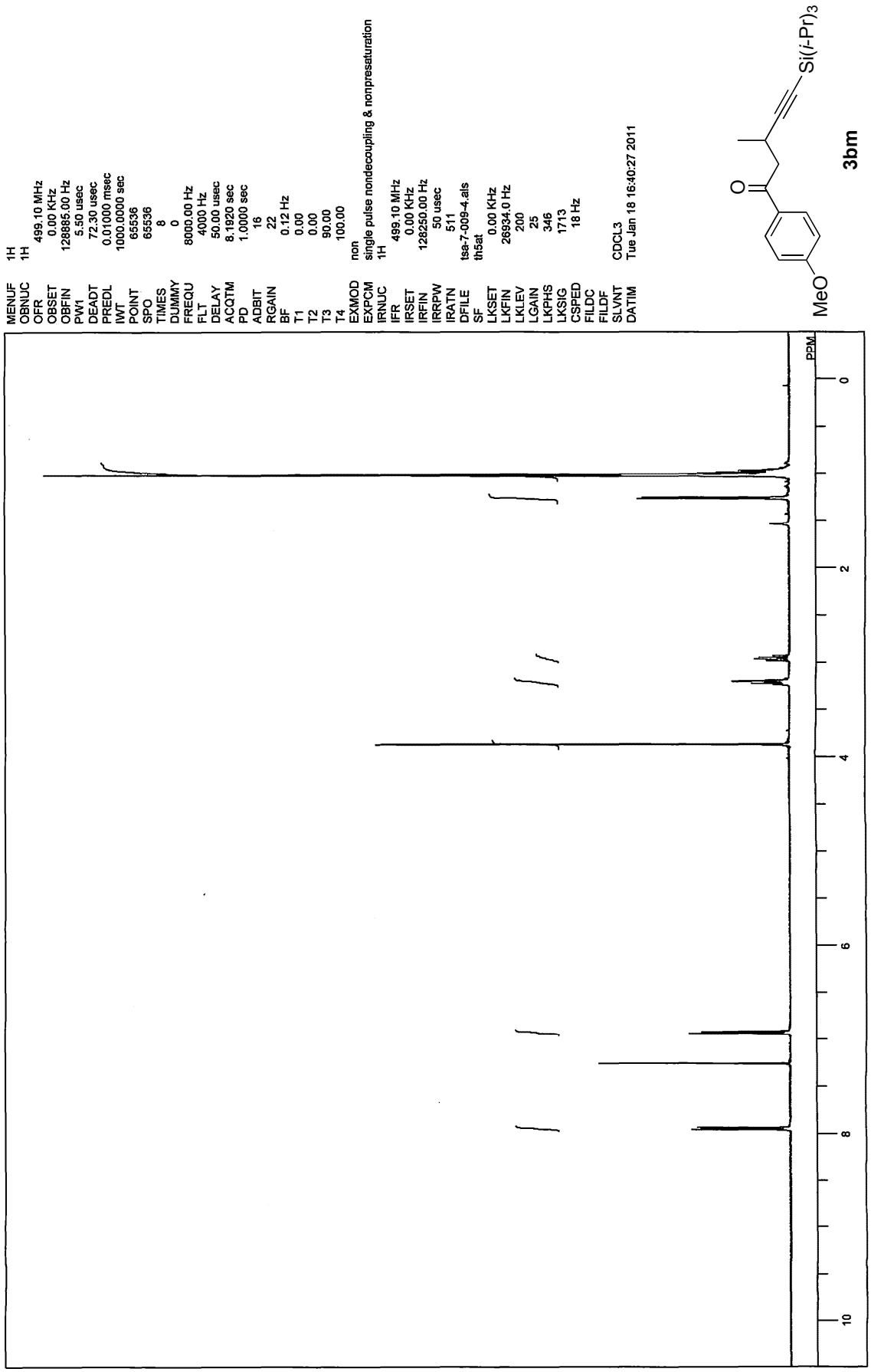


3fm

Compound 3fm (Table 3, entry 5): The ee was measured by HPLC (Chiralcel OJ-H column × 2, flow 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm, t_1 = 40.6 min (*S*), t_2 = 43.4 min (*R*)); $[\alpha]^{20}_{D}$ +3 (*c* 0.79, $CHCl_3$) for 91% ee (*R*).

6. ^{1}H and ^{13}C NMR spectra

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OFR 499.10 MHz
OBSET 0.00 KHz
OBFIN 128885.00 Hz
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DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 22
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-009-4.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 25
LKPHS 346
LKSIG 1713
CSPED 18 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Tue Jan 18 16:40:27 2011
Si(i-Pr)3
O
MeO
3bm
PPM
0
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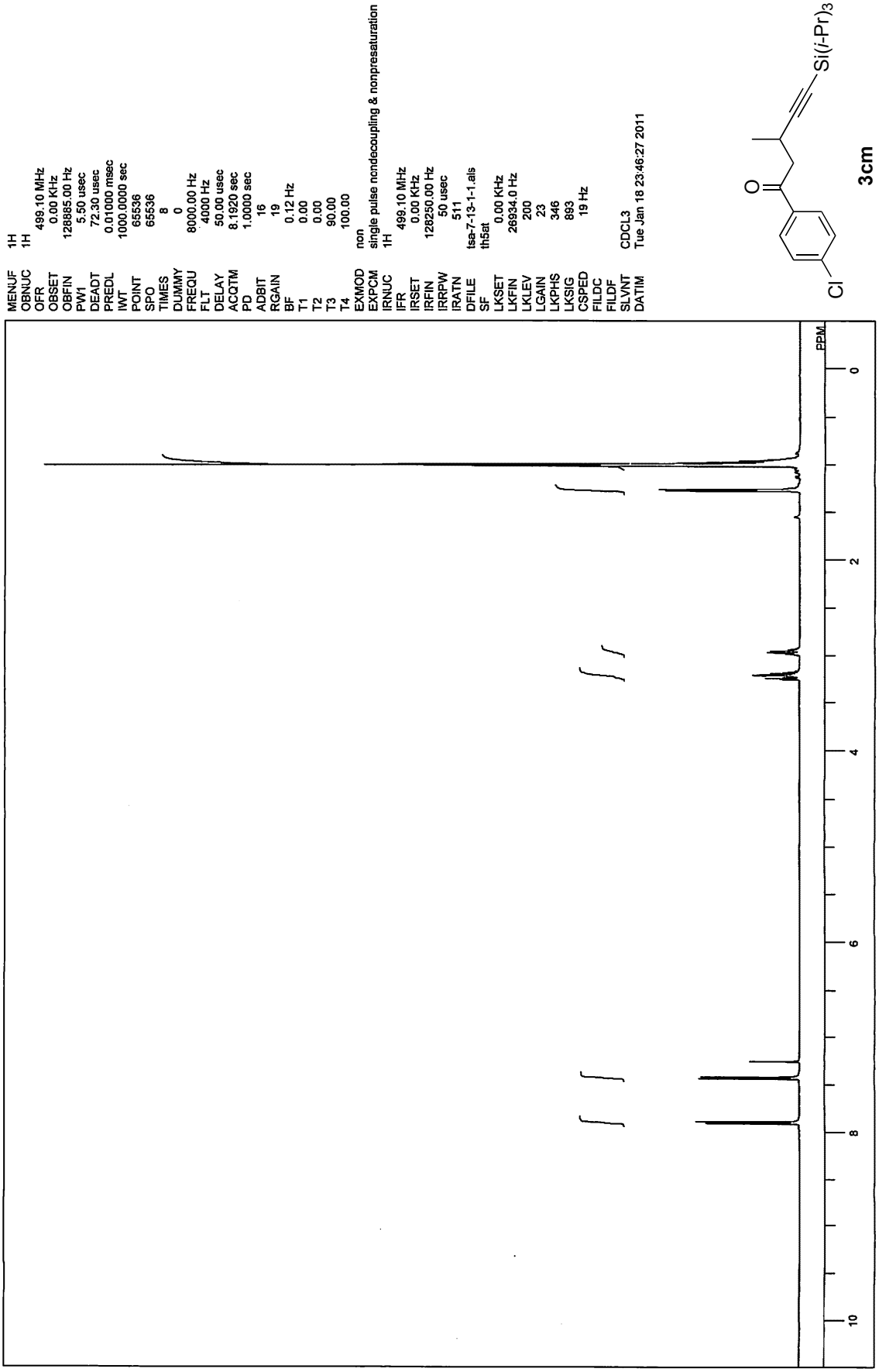
8
10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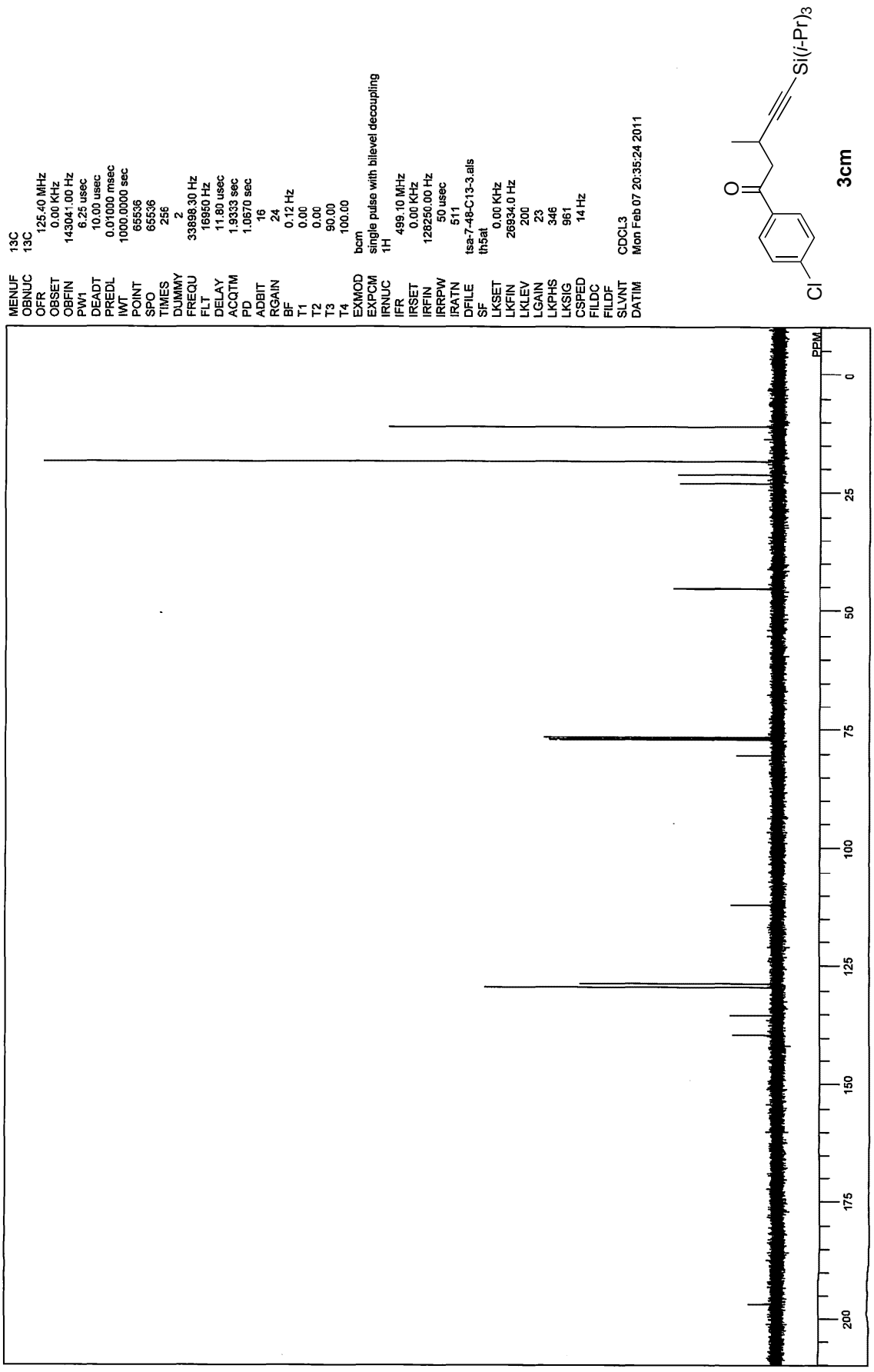
OFR 499.10 MHz
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 19
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-13-1-1.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 23
LKPHS 346
LKSIG 893
CSPED 19 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Tue Jan 18 23:46:27 2011
Si(i-Pr)3
O
Cl
3cm
PPM
0
2
4
6
8
10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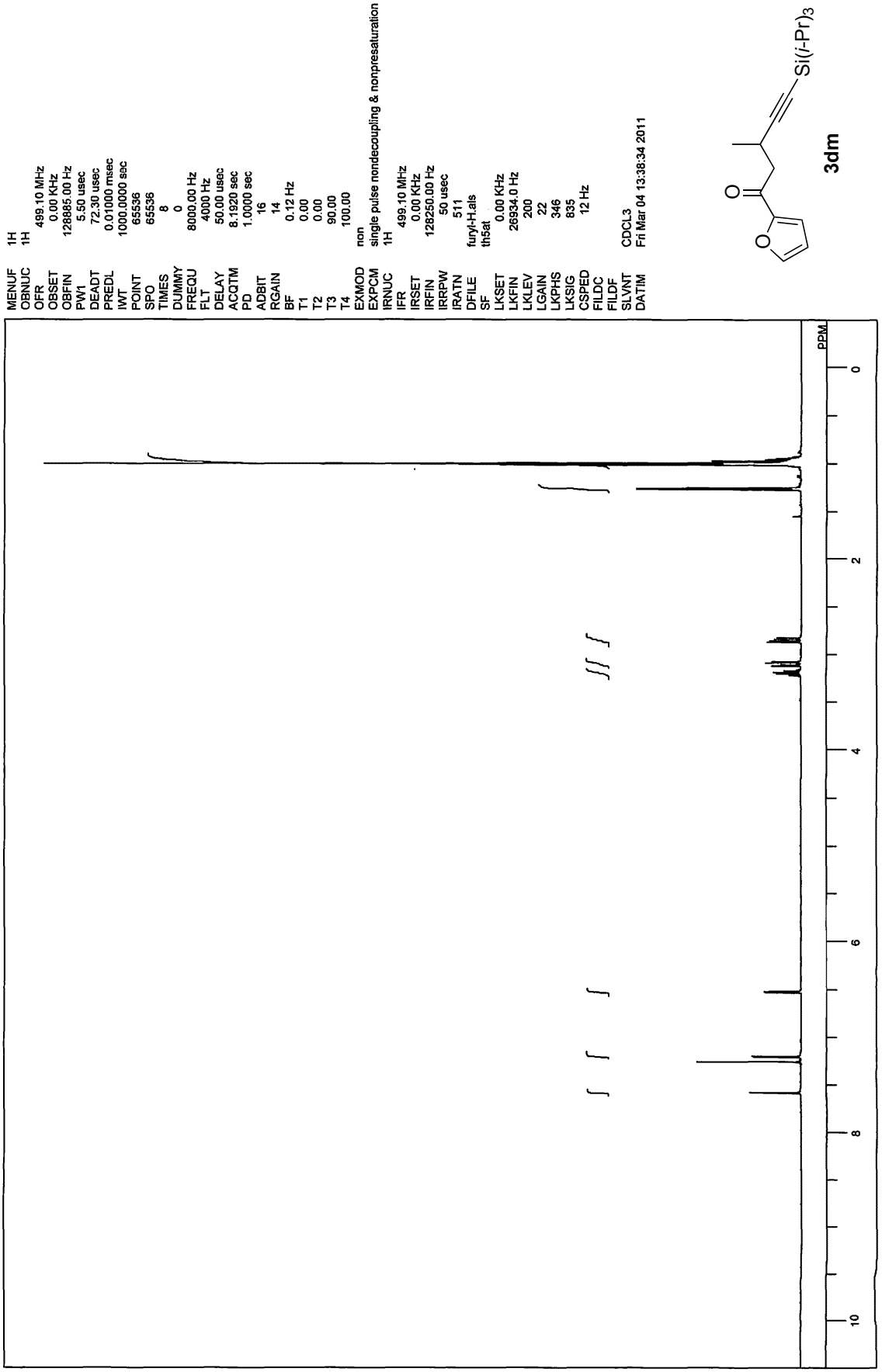
OBFIN 143041.00 Hz
PW1 6.25 usec
DEADT 10.00 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 256
DUMMY 2
FREQU 33898.30 Hz
FLT 16950 Hz
DELAY 11.80 usec
ACQTM 1.9333 sec
PD 1.0670 sec
ADBIT 16
RGAIN 24
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD bcm
EXPCM single pulse with bilevel decoupling
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-48-C13-3.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 23
LKPHS 346
LKSIG 961
CSPED 14 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Mon Feb 07 20:35:24 2011
O
Si(i-Pr)3
Cl
3cm
PPM
0
25
50
75
100
125
150
175
200


MENUF 1H
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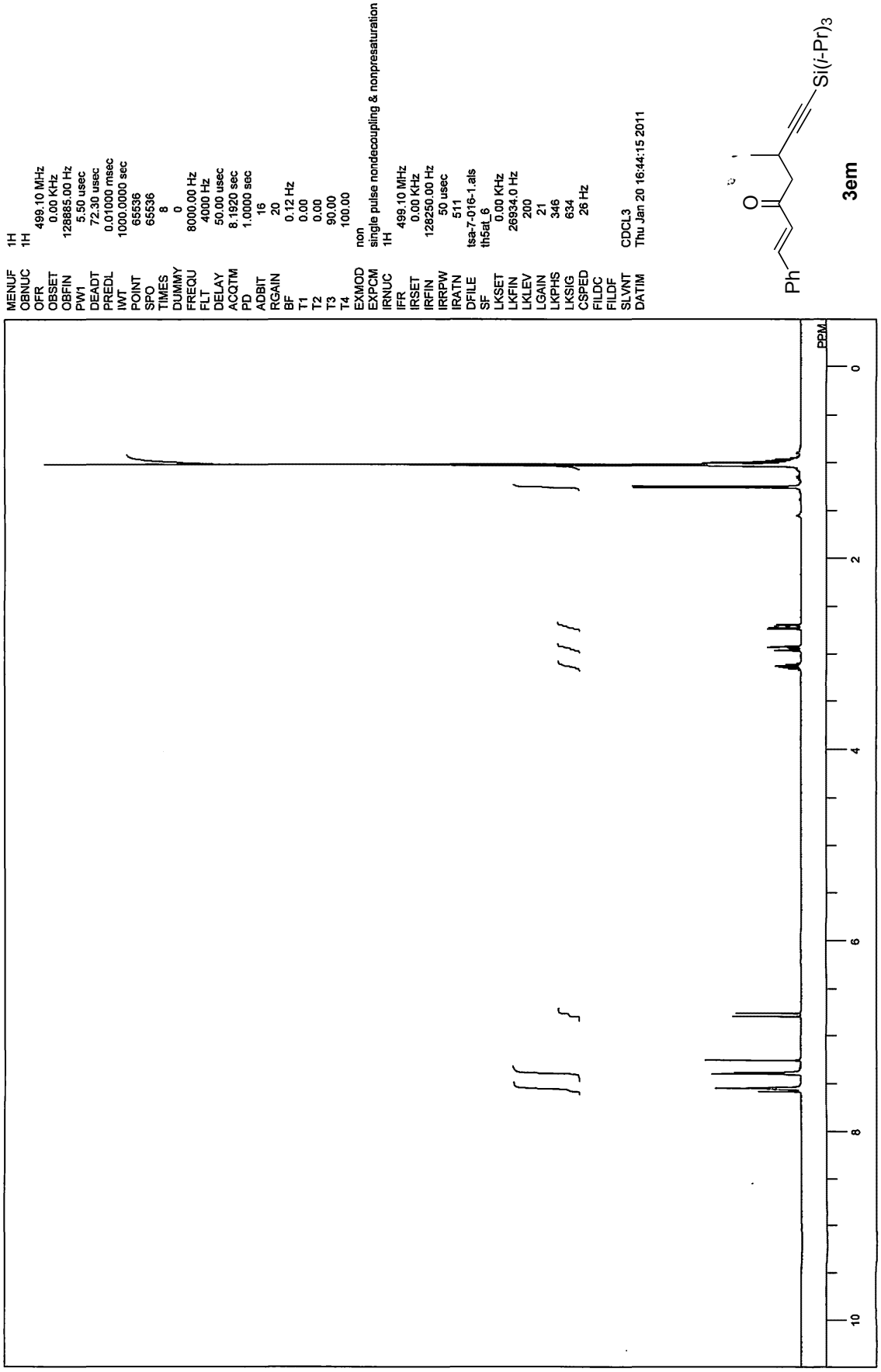
OFR 499.10 MHz
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 14
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE furyl-H.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 22
LKPHS 346
LKSIG 835
CSPED 12 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Fri Mar 04 13:38:34 2011
O
O
Si(i-Pr)3
3dm
PPM
0
2
4
6
8
10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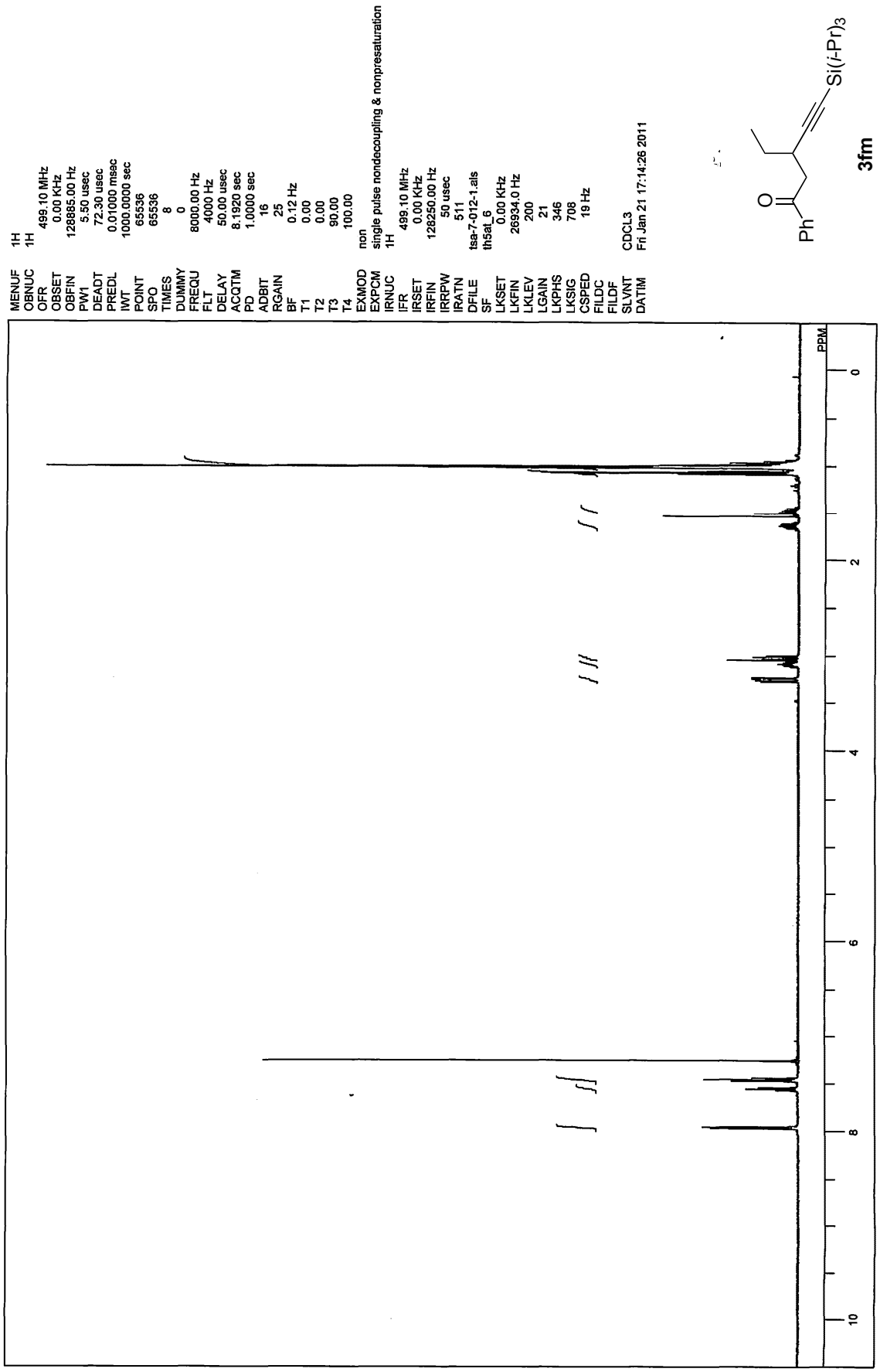
OFR 499.10 MHz
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 20
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-016-1.als
SF th5at_6
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 21
LKPHS 346
LKSIG 634
CSPED 26 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Thu Jan 20 16:44:15 2011
Si(i-Pr)3
O
Ph
3em
PPM
0
2
4
6
8
10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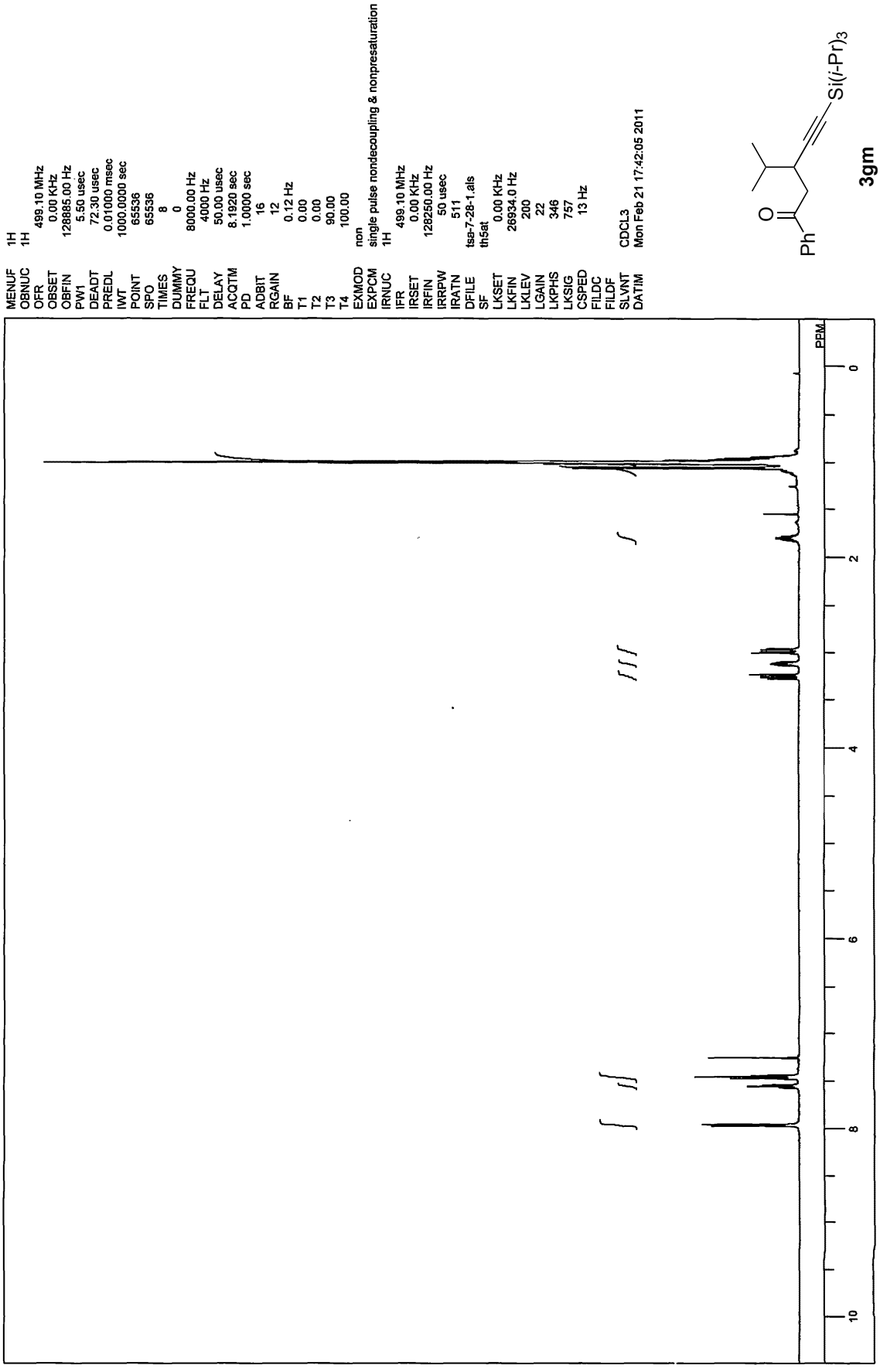
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 25
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-012-1.als
SF tn5at_6
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 21
LKPHS 346
LKSIG 708
CSPED 19 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Fri Jan 21 17:14:26 2011
Ph
O
Si(i-Pr)3
3fm
PPM
0
2
4
6
8
10


MENUF 1H
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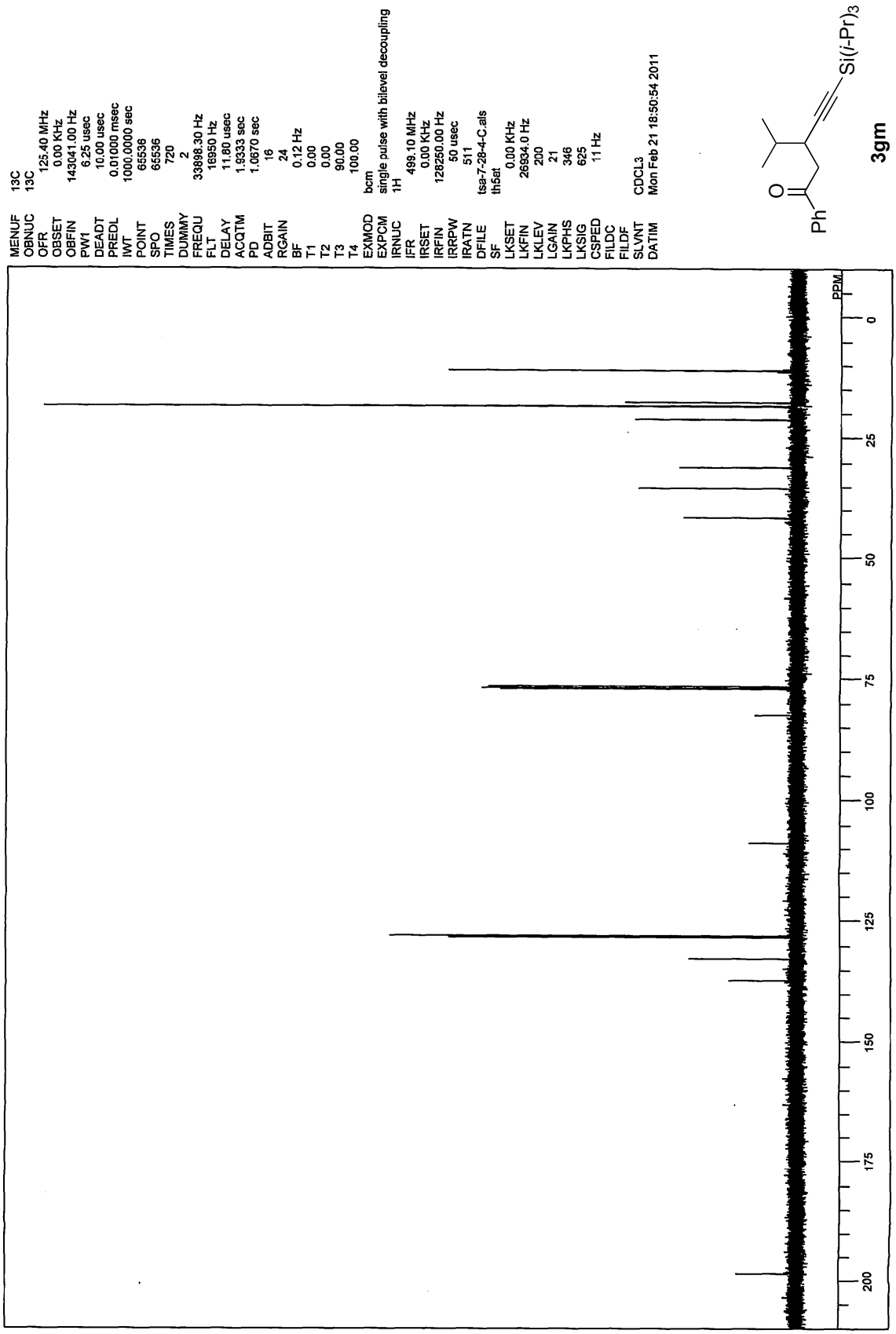
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 12
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-28-1.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 22
LKPHS 346
LKSIG 757
CSPED 13 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Mon Feb 21 17:42:05 2011
O
Ph
Si(i-Pr)3
3gm
PPM
10
8
6
4
2
0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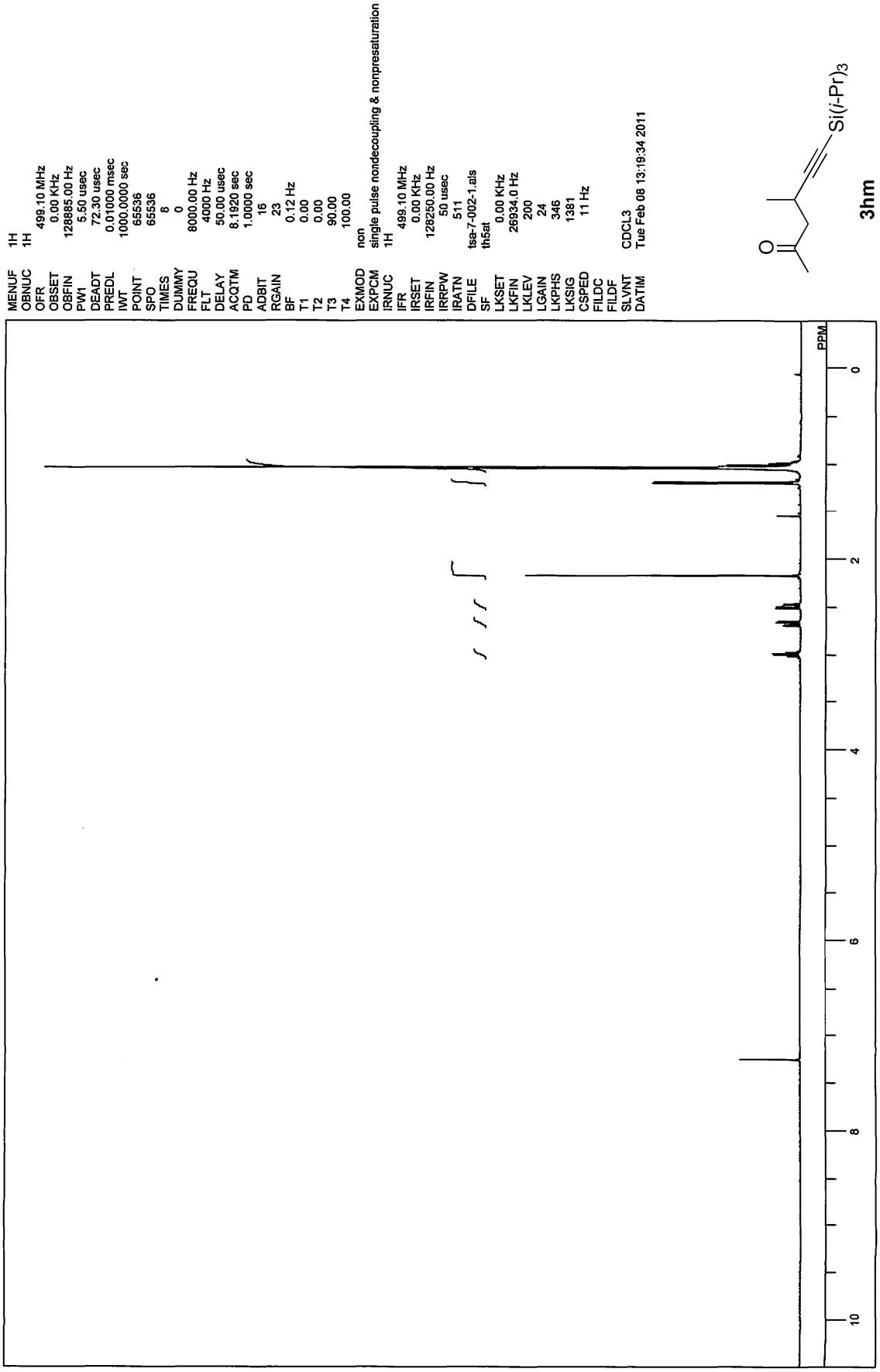
OFR 125.40 MHz
OBSET 0.00 KHz
OBFIN 143041.00 Hz
PW1 6.25 usec
DEADT 10.00 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 720
DUMMY 2
FREQU 33898.30 Hz
FLT 16950 Hz
DELAY 11.80 usec
ACQTM 1.9333 sec
PD 1.0670 sec
ADBIT 16
RGAIN 24
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD bcm
EXPCM single pulse with bilevel decoupling
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-28-4-C.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 21
LKPHS 346
LKSIG 625
CSPED 11 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Mon Feb 21 18:50:54 2011
Si(i-Pr)3
O
Ph
3gm
PPM
0
25
50
75
100
125
150
175
200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OFR 499.10 MHz
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 23
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-002-1.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 24
LKPHS 346
LKSIG 1381
CSPED 11 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Tue Feb 08 13:19:34 2011
PPM
0
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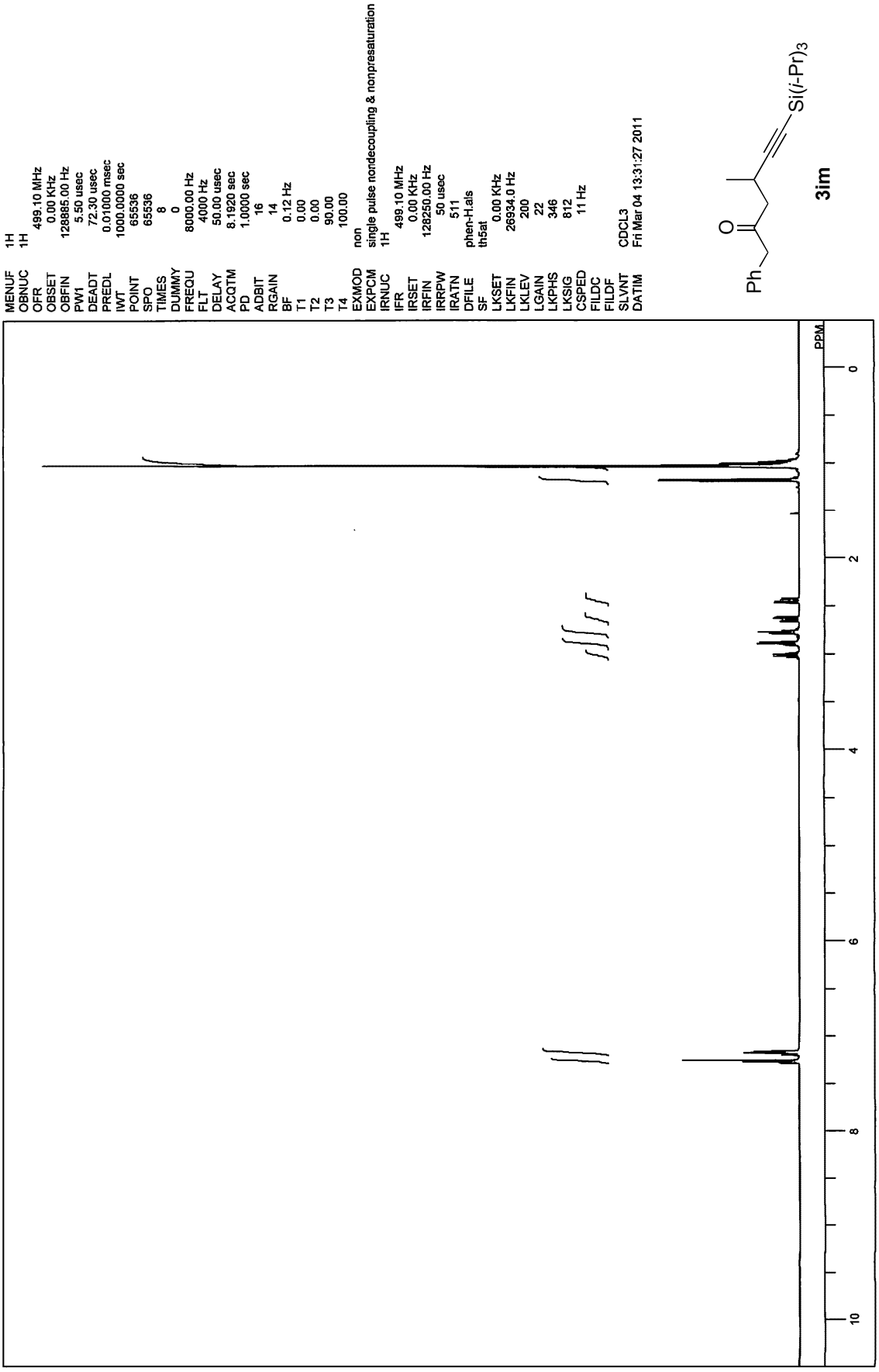
O
Si(i-Pr)3
3hm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PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 14
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE phen-H.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 22
LKPHS 346
LKSIG 812
CSPED 11 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Fri Mar 04 13:31:27 2011
O
Ph
Si(i-Pr)3
3im
PPM
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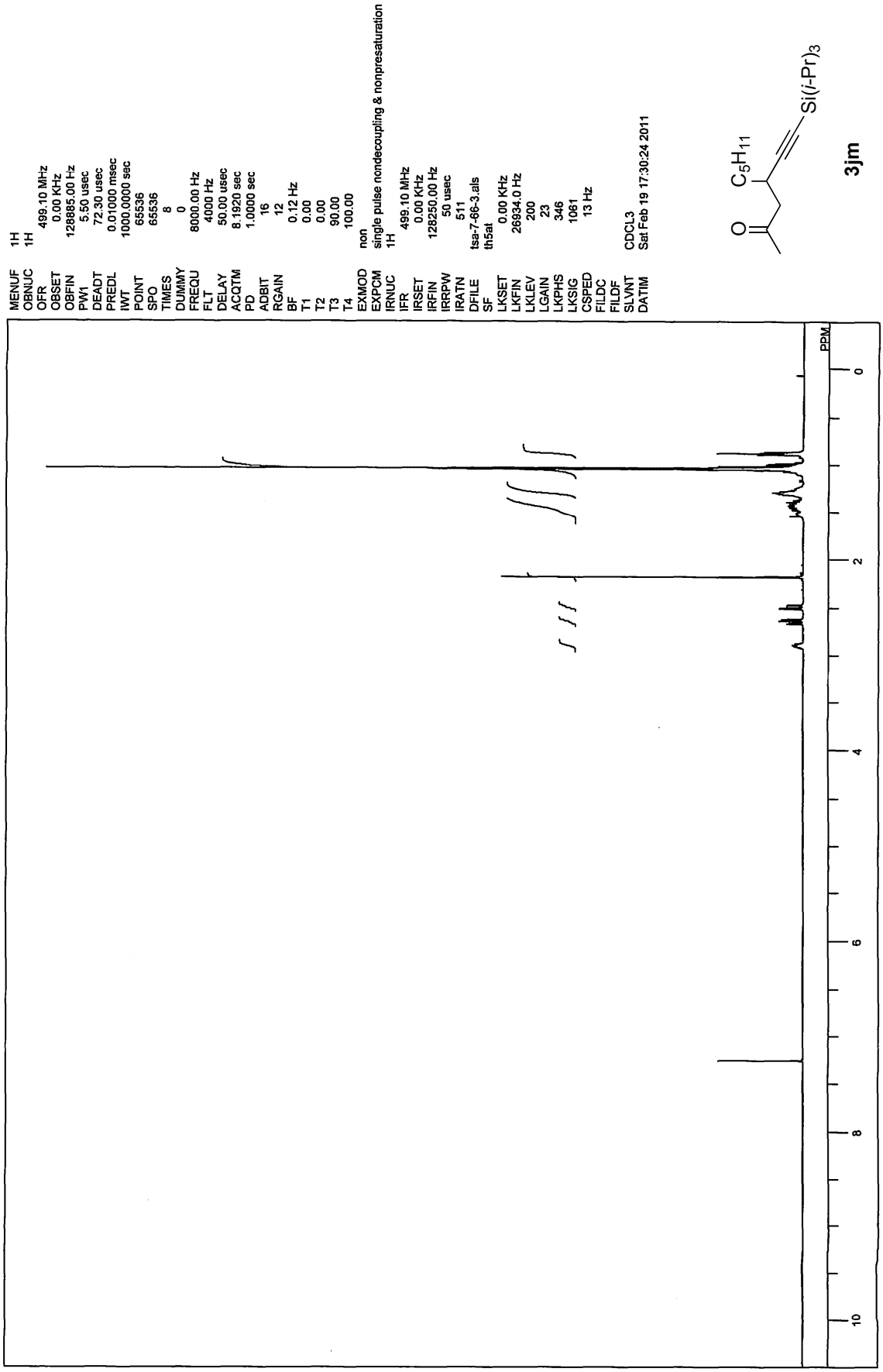
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OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 12
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-66-3.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 23
LKPHS 346
LKSIG 1061
CSPED 13 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Sat Feb 19 17:30:24 2011
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C5H11
Si(i-Pr)3
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PPM
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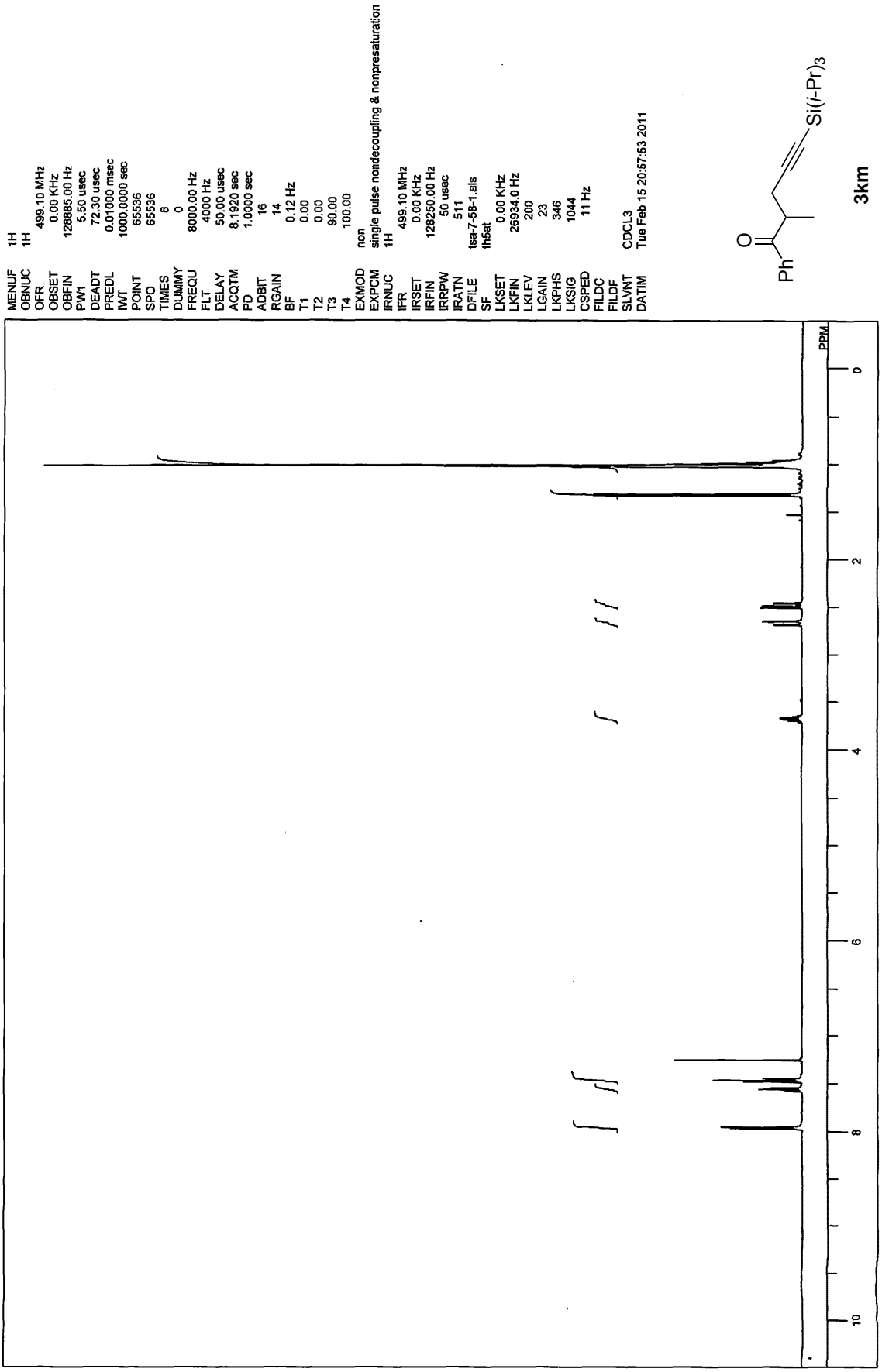
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OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 14
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-58-1.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 23
LKPHS 346
LKSIG 1044
CSPED 11 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Tue Feb 15 20:57:53 2011
O
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Si(i-Pr)3
3km
PPM
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8
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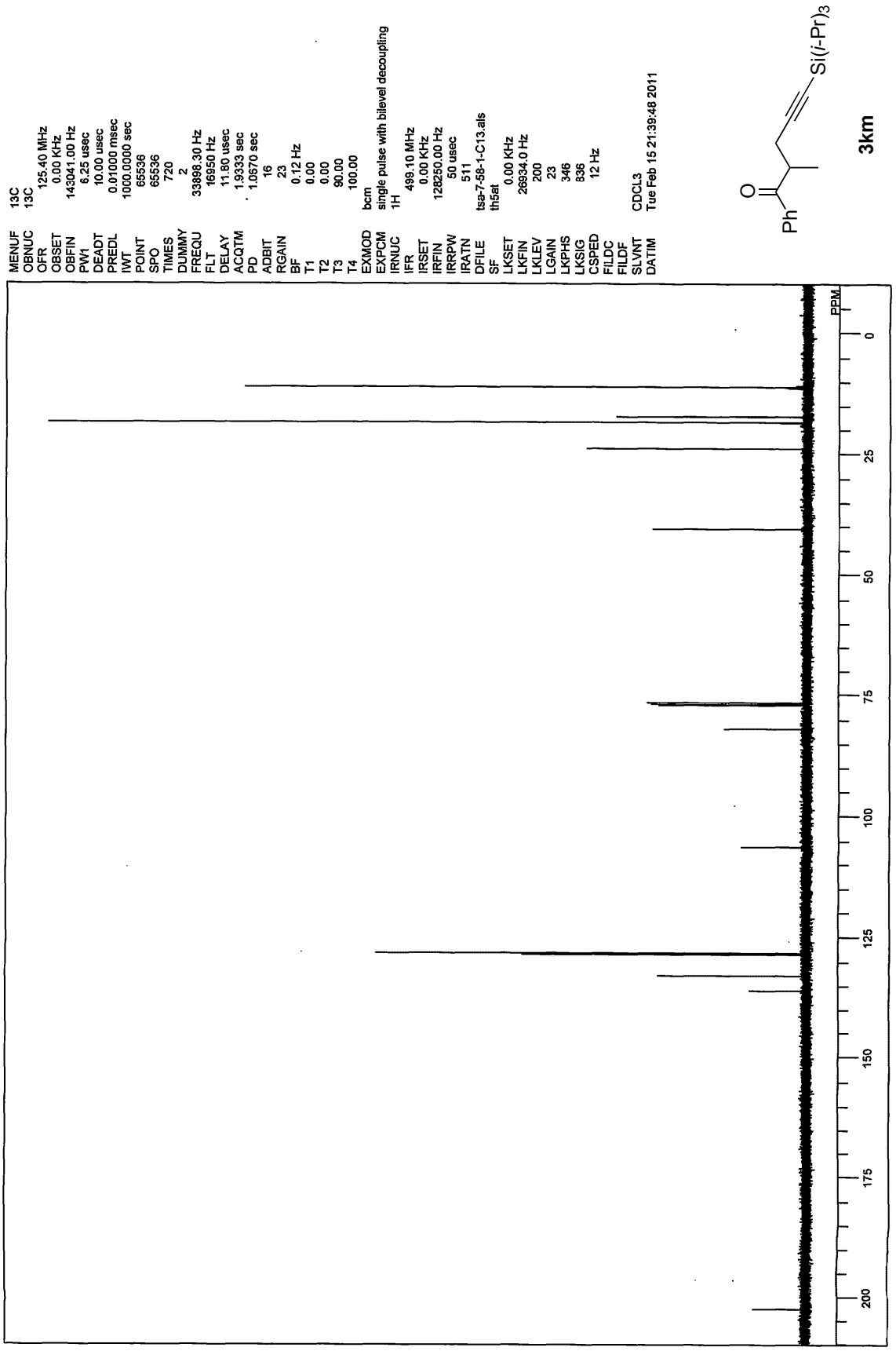
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OBFIN 143041.00 Hz
PW1 6.25 usec
DEADT 10.00 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 720
DUMMY 2
FREQU 33898.30 Hz
FLT 16950 Hz
DELAY 11.80 usec
ACQTM 1.9333 sec
PD 1.0670 sec
ADBIT 16
RGAIN 23
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD bcm
EXPCM single pulse with bilevel decoupling
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-58-1-C13.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 23
LKPHS 346
LKSIG 836
CSPED 12 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Tue Feb 15 21:39:48 2011
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Si(i-Pr)3
3km
PPM
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50
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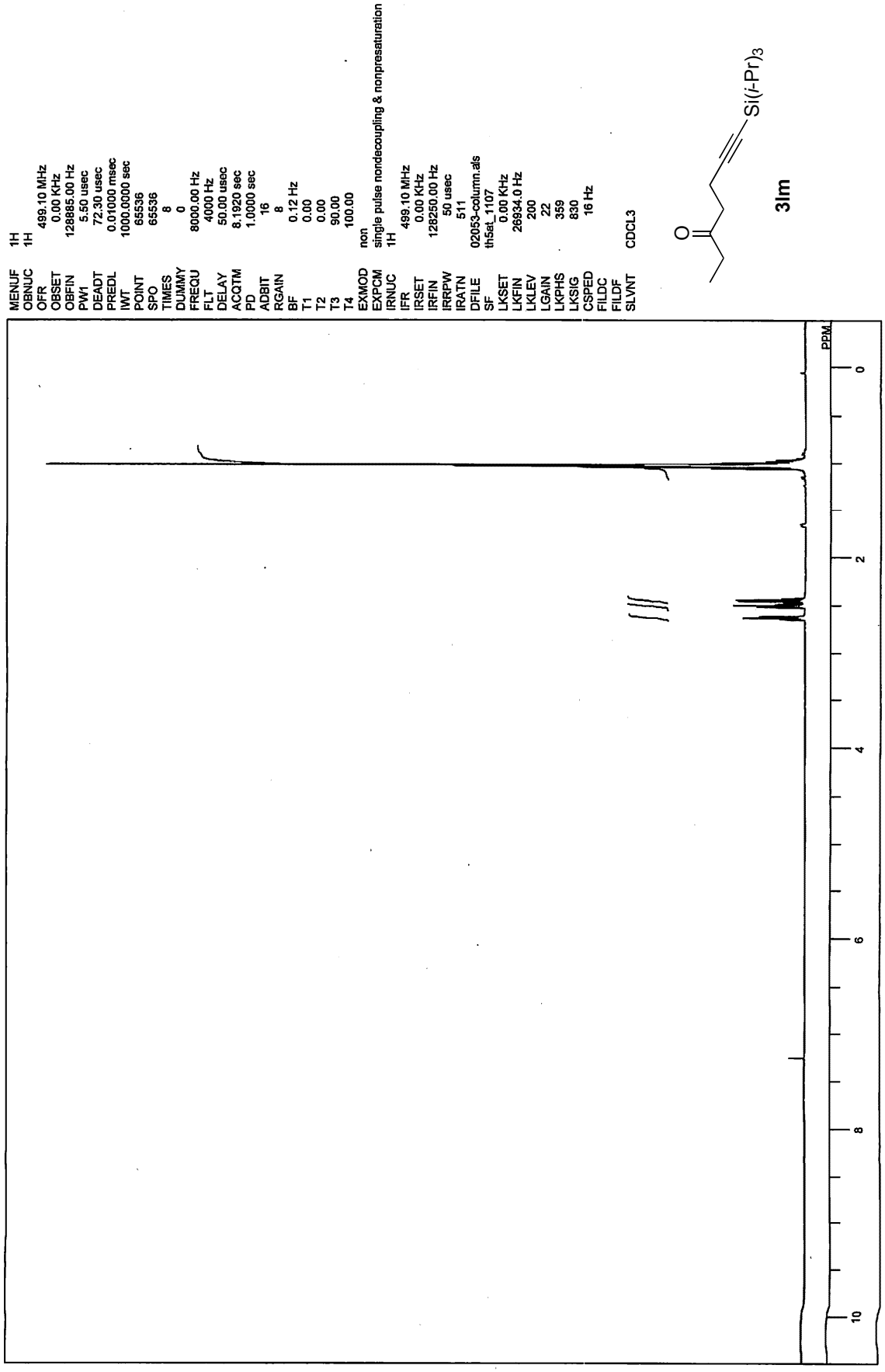
100
125
150
175
200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OFR 499.10 MHz
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 8
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE 02053-column.als
SF th5at_1107
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 22
LKPHS 359
LKSIG 830
CSPED 16 Hz
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FILDF
SLVNT CDCL3
O
Si(i-Pr)3
3lm
PPM
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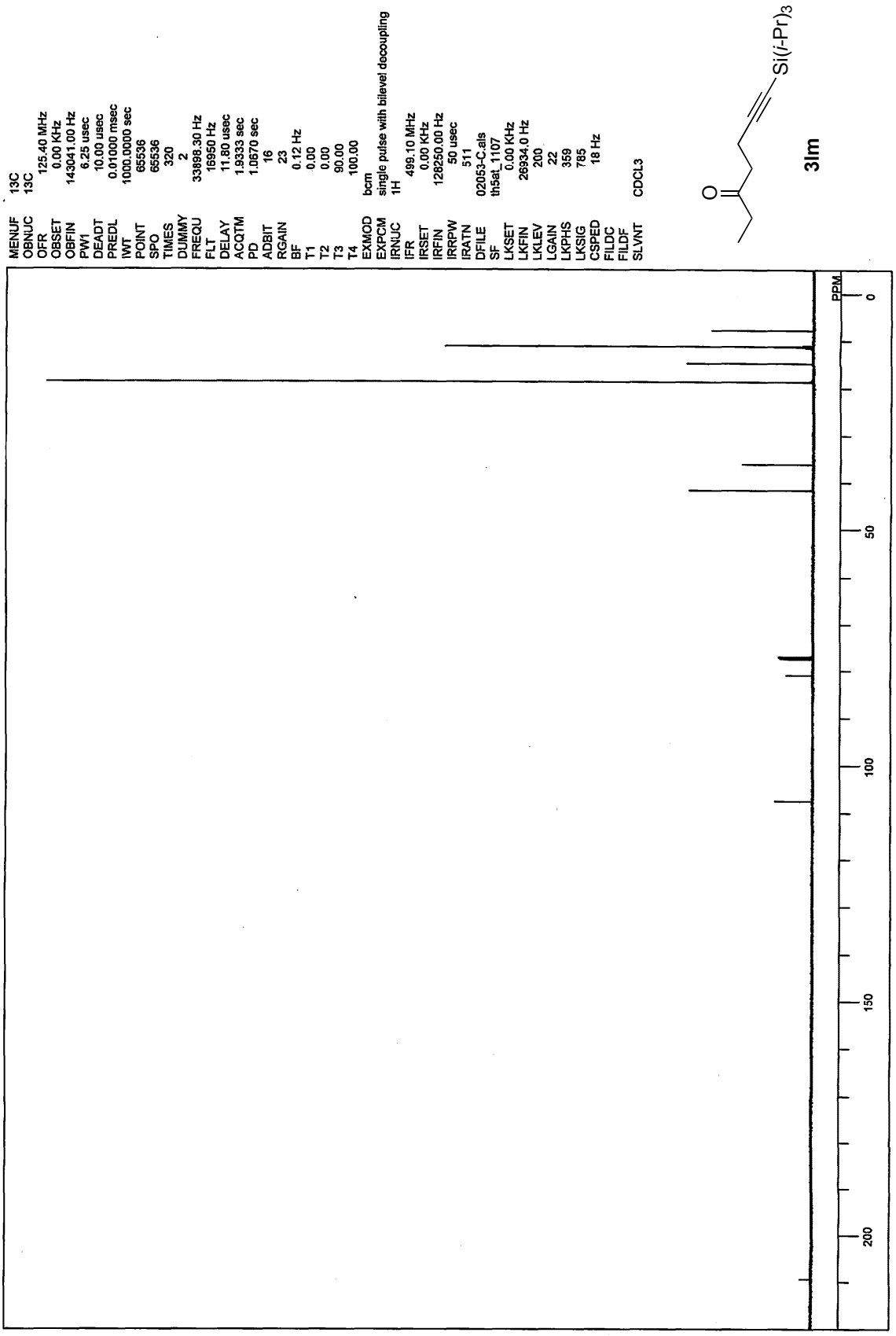
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OBFIN 143041.00 Hz
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DEADT 10.00 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 320
DUMMY 2
FREQU 33698.30 Hz
FLT 16950 Hz
DELAY 11.80 usec
ACQTM 1.9333 sec
PD 1.0670 sec
ADBIT 16
RGAIN 23
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD bcm
EXPCM single pulse with bilevel decoupling
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE 02053-C.als
SF th5at_1107
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 22
LKPHS 359
LKSIG 785
CSPED 18 Hz
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FILDF
SLVNT CDCL3
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3lm
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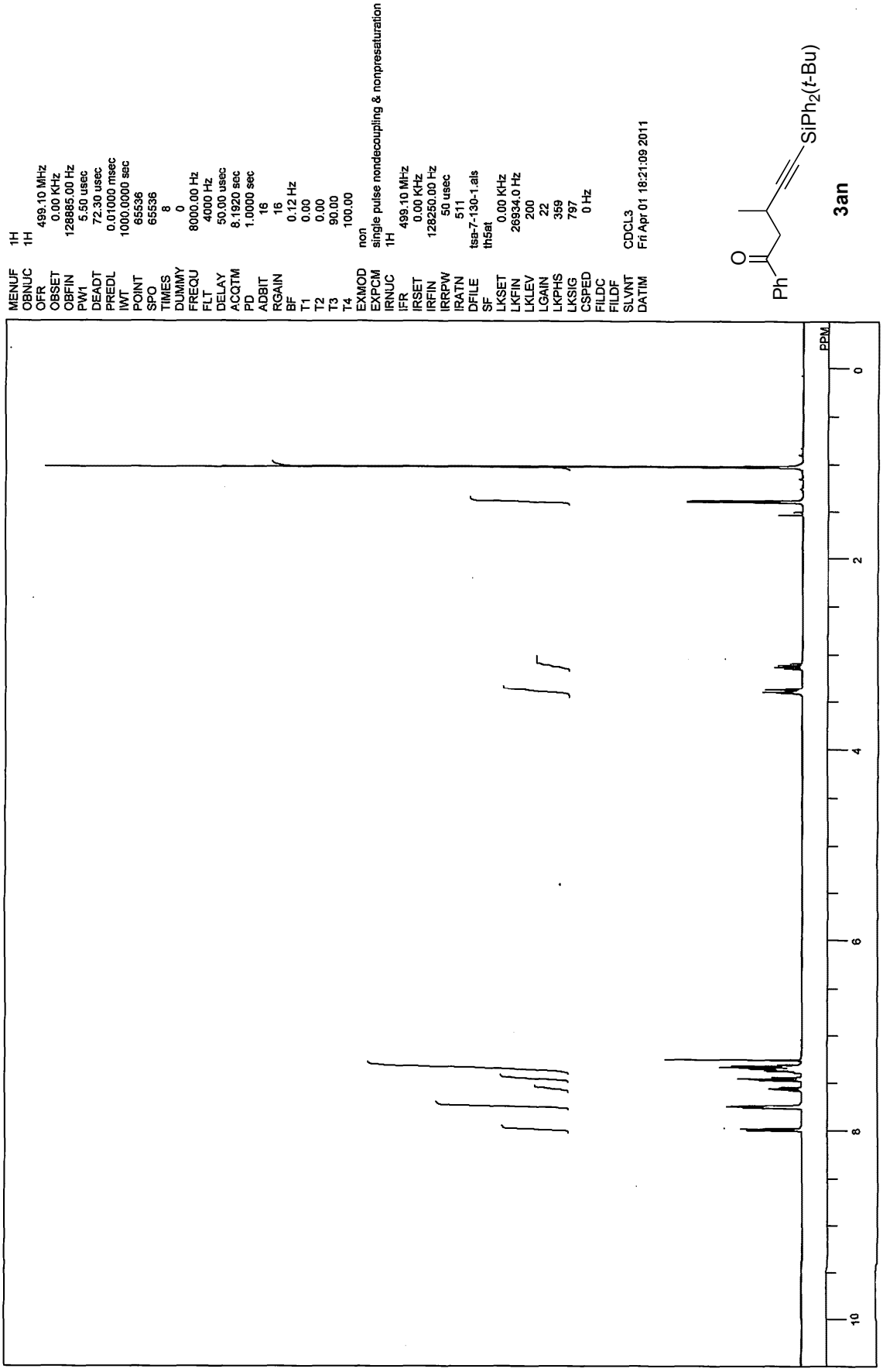
0
50
100
150
200


MENUF 1H
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OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 16
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-130-1.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 22
LKPHS 359
LKSIG 797
CSPED 0 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Fri Apr 01 18:21:09 2011
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3an
PPM
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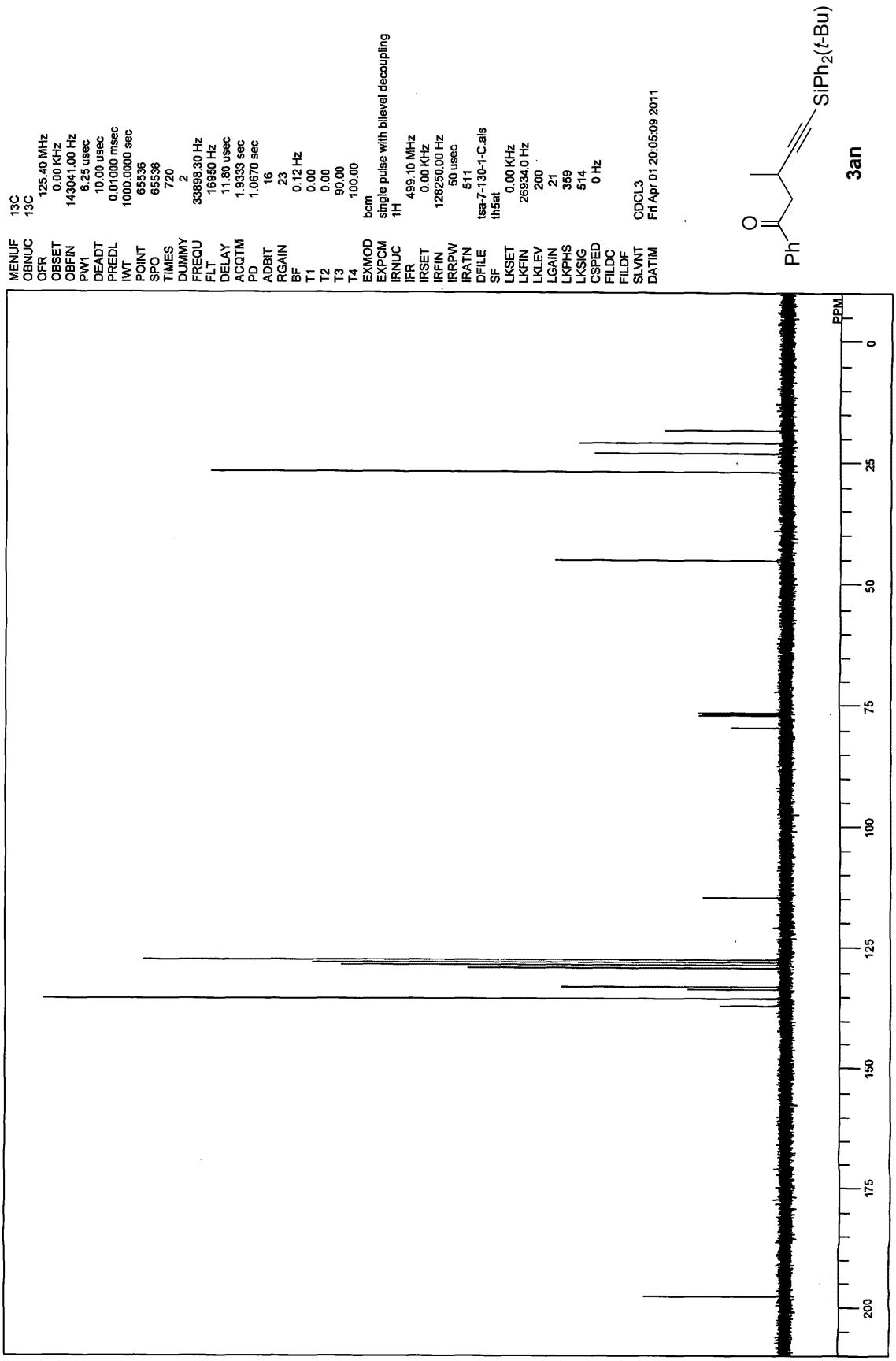
MENUF 13C
OBNUC 13C
OFR 125.40 MHz
OBSET 0.00 KHz
OBFIN 143041.00 Hz
PW1 6.25 usec
DEADT 10.00 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 720
DUMMY 2
FREQU 33898.30 Hz
FLT 16950 Hz
DELAY 11.80 usec
ACQTM 1.9333 sec
PD 1.0670 sec
ADBIT 16
RGAIN 23
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD bcm
EXPCM single pulse with bilevel decoupling
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-130-1-C.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 21
LKPHS 359
LKSIG 514
CSPED 0 Hz
FILDC
FILDF
SLVNT CDCL3
DATIM Fri Apr 01 20:05:09 2011
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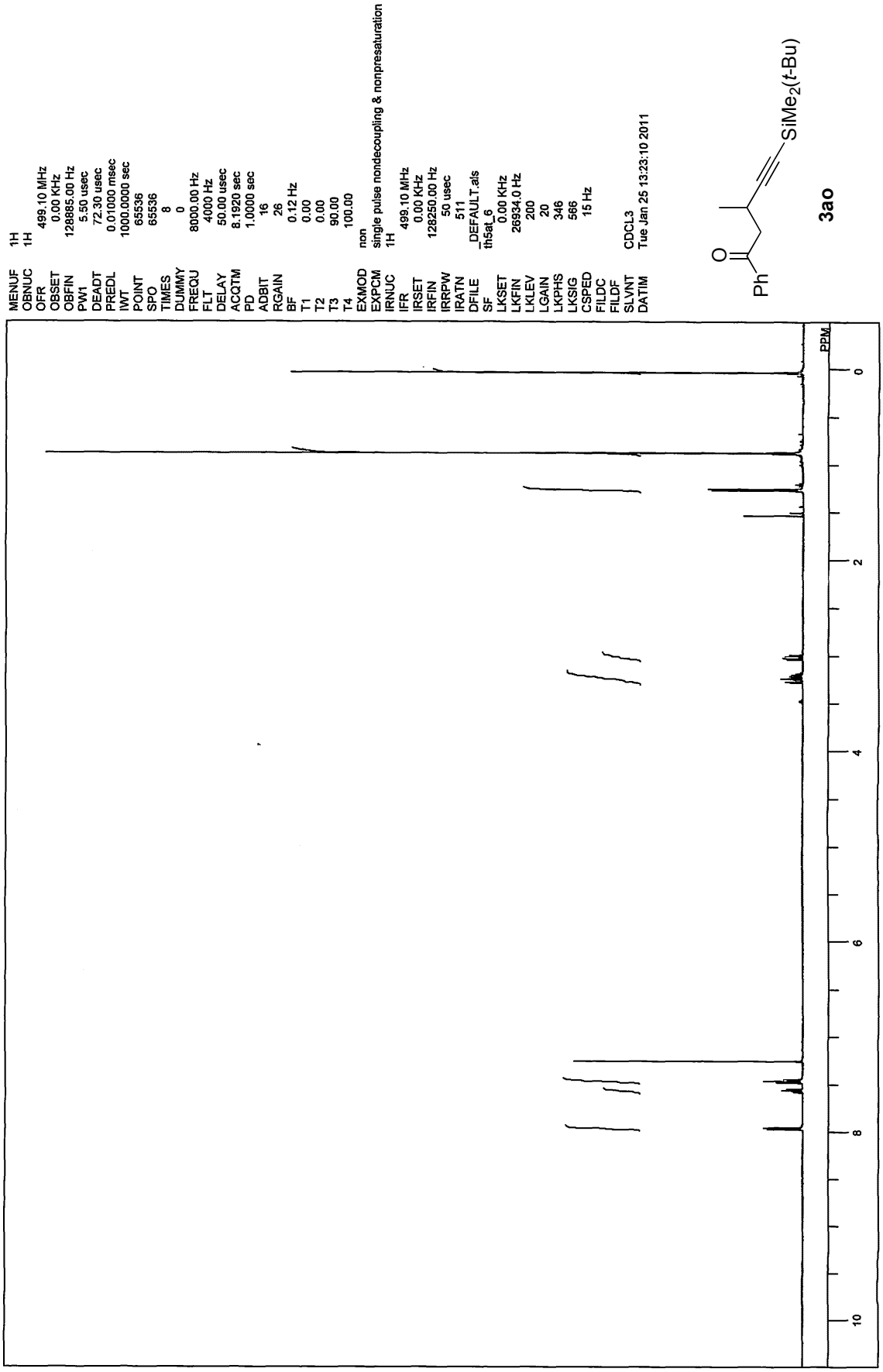
75
100
125
150
175
200


MENUF 1H
OBNUC 1H
OFR 499.10 MHz
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 26
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE _DEFAULT.als
SF thSat_6
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 20
LKPHS 346
LKSIG 586
CSPED 15 Hz
FILDC
FILDF
SLVNT CDCL3
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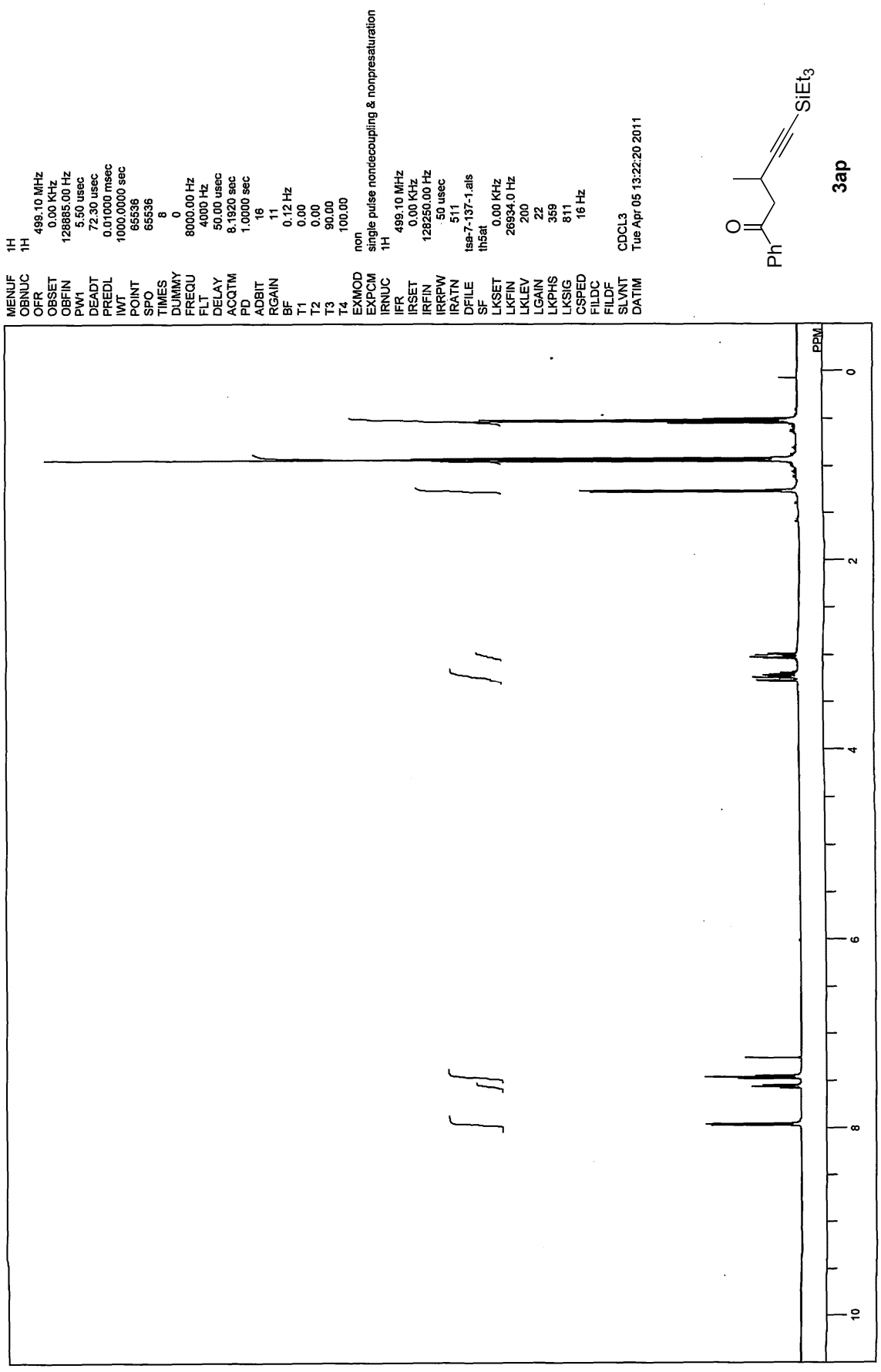
MENUF 1H
OBNUC 1H
OFR 499.10 MHz
OBSET 0.00 KHz
OBFIN 128885.00 Hz
PW1 5.50 usec
DEADT 72.30 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 0
FREQU 8000.00 Hz
FLT 4000 Hz
DELAY 50.00 usec
ACQTM 8.1920 sec
PD 1.0000 sec
ADBIT 16
RGAIN 11
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD non
EXPCM single pulse nondecoupling & nonpresaturation
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE tsa-7-137-1.als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 22
LKPHS 359
LKSIG 811
CSPED 16 Hz
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SLVNT CDCL3
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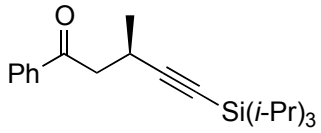
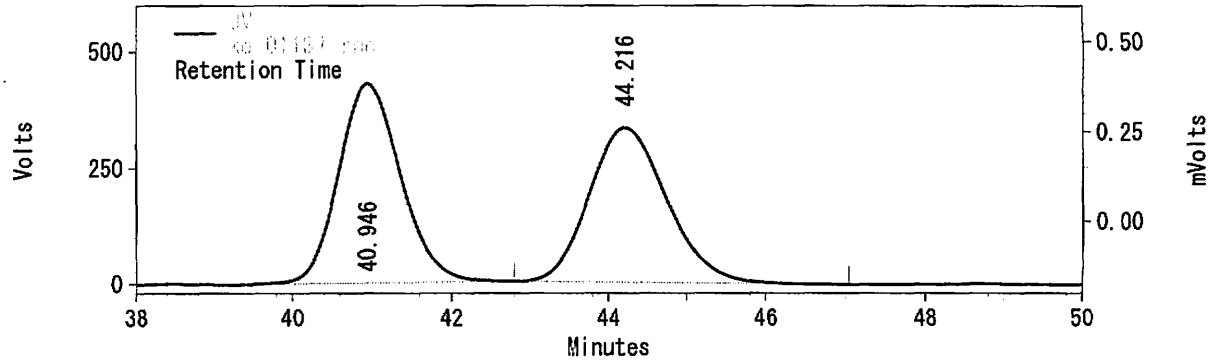
7. Chiral HPLC charts for Table 3

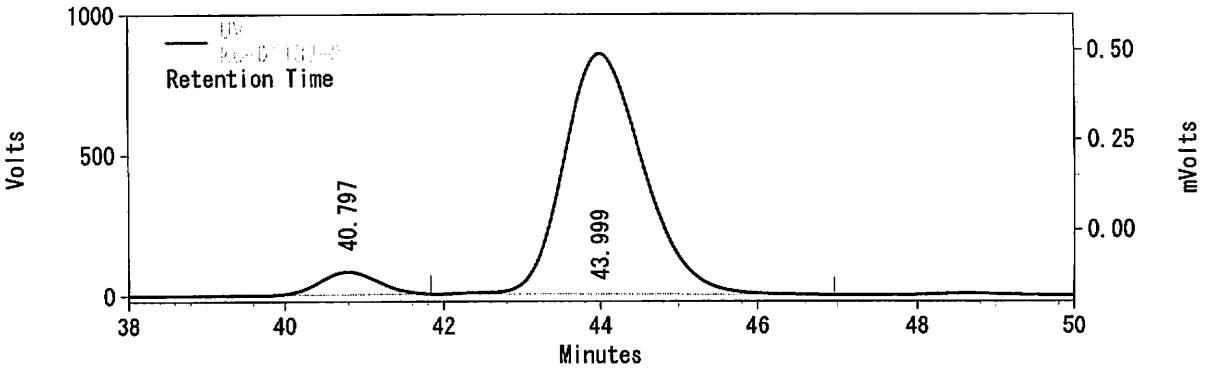


3am



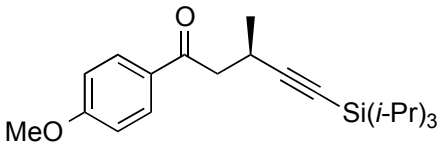
UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	40.946	23309089	50.248	429493
2	44.216	23079175	49.752	333672
Totals		46388264	100.000	763165

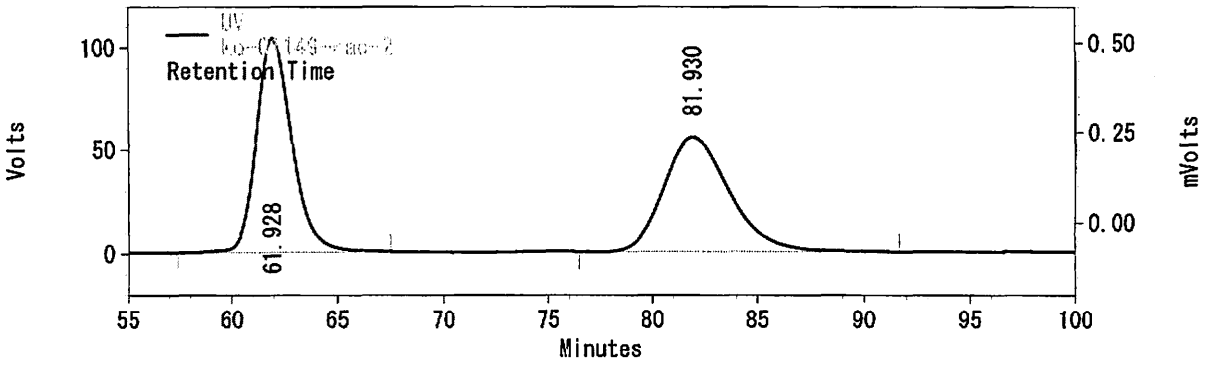


UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	40.797	4100233	6.392	81128
2	43.999	60047837	93.608	853452
Totals		64148070	100.000	934580

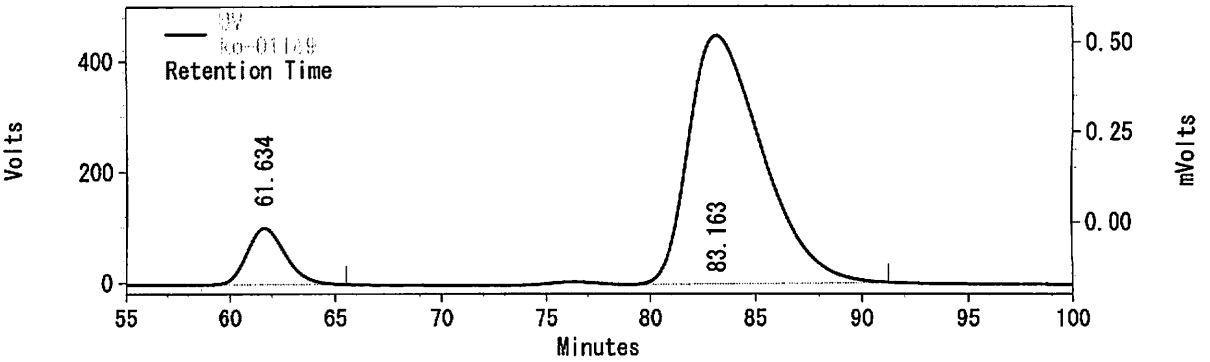


3bm



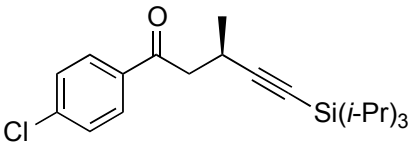
UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	61.928	12189604	50.368	103659
2	81.930	12011415	49.632	55023
Totals		24201019	100.000	158682

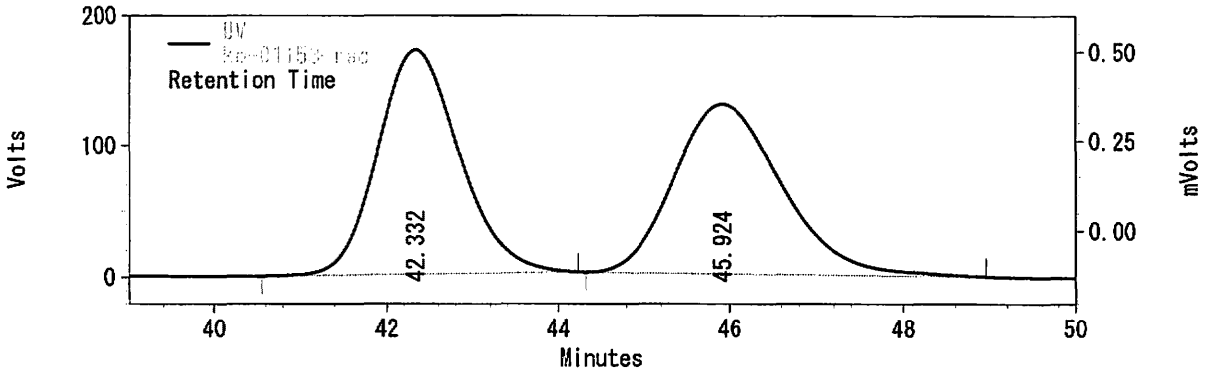


UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	61.634	12958209	10.657	101984
2	83.163	108632716	89.343	448670
Totals		121590925	100.000	550654



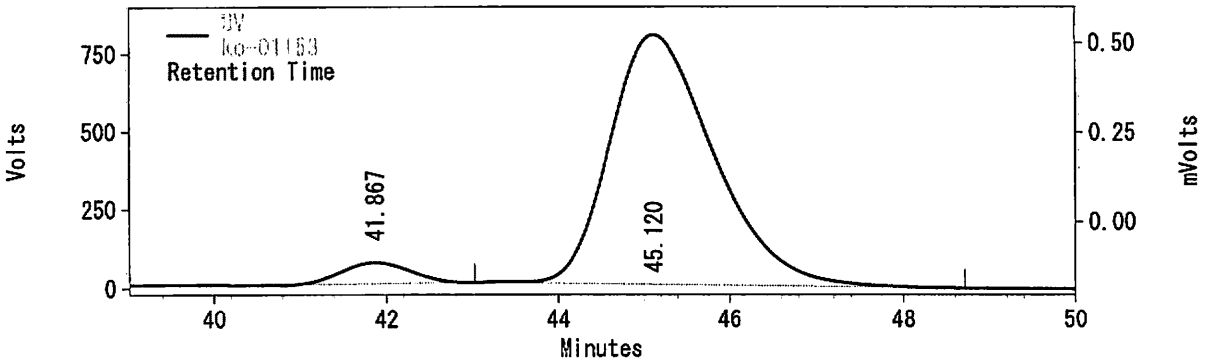
3cm



UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	42.332	11241032	50.160	171521
2	45.924	11169307	49.840	129492

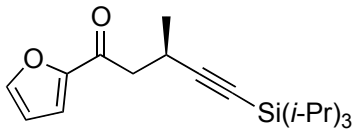
Totals		22410339	100.000	301013



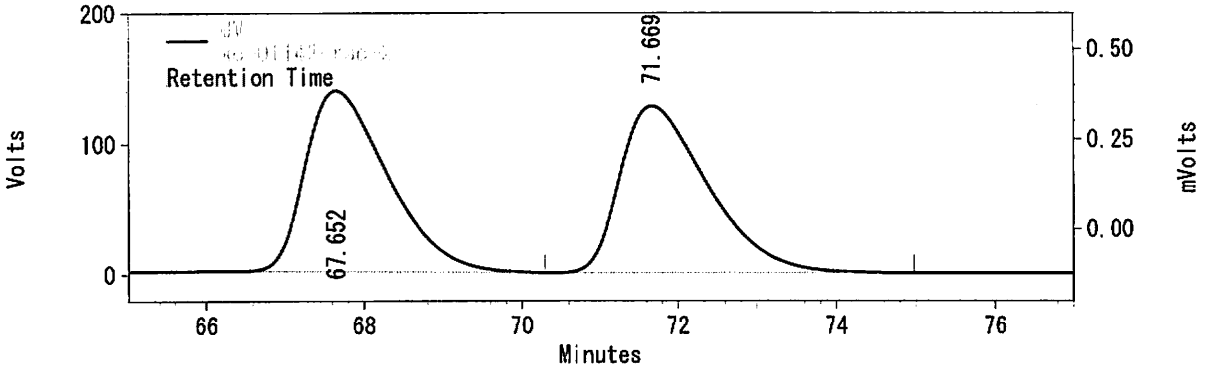
UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	41.867	3663391	5.175	66697
2	45.120	67129404	94.825	798616

Totals		70792795	100.000	865313



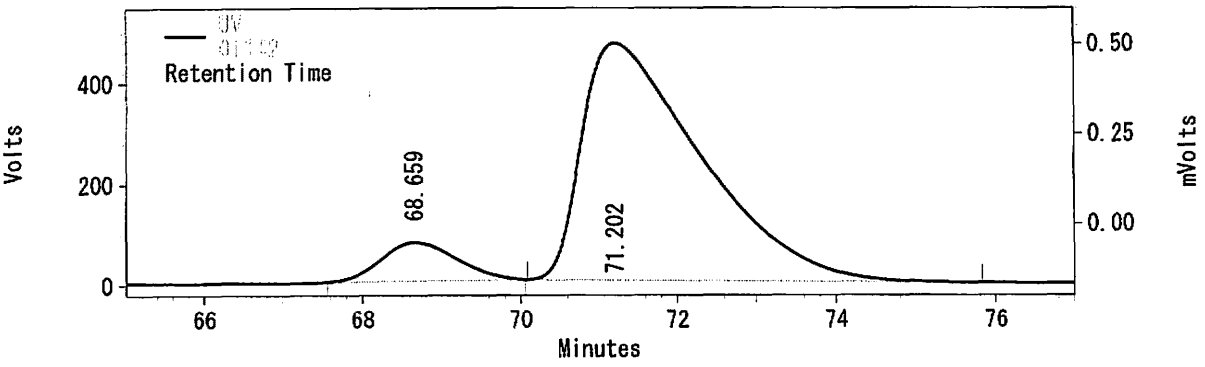
3dm



UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	67.652	10021544	50.244	138231
2	71.669	9924166	49.756	127296

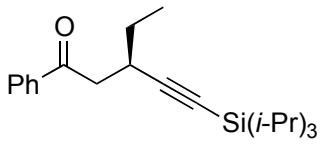
Totals				
		19945710	100.000	265527



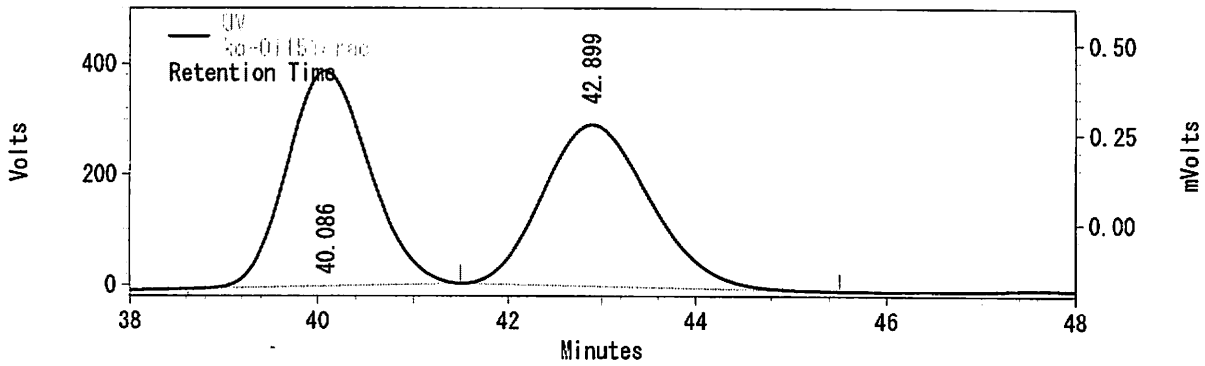
UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	68.659	5092078	9.348	76977
2	71.202	49380192	90.652	469628

Totals				
		54472270	100.000	546605

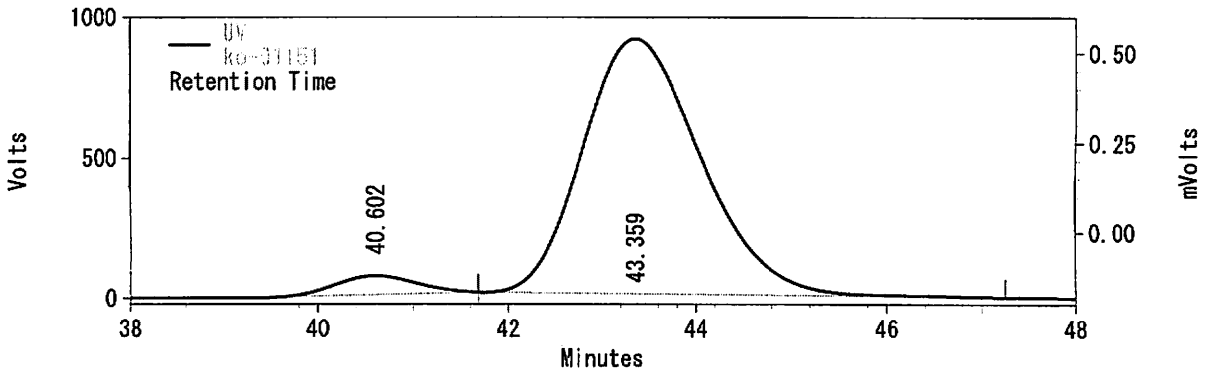


3fm



UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	40.086	23259529	50.201	389842
2	42.899	23073161	49.799	291865
Totals		46332690	100.000	681707



UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	40.602	3885939	4.680	67169
2	43.359	79140026	95.320	907088
Totals		83025965	100.000	974257