

Supporting Information

Rhodium-Catalyzed Annulation Reactions of 2-Cyanophenylboronic Acid with Alkynes and Strained Alkenes

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General. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300 MHz and ^{13}C at 75 MHz) spectrometer using CHCl_3 (^1H , $\delta=7.26$) and CDCl_3 (^{13}C , $\delta=77.0$) as an internal standard. High resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under a nitrogen atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck).

Materials. Unless otherwise noted, all reagents and anhydrous solvents were obtained from commercial suppliers and used as received. 1,4-Dioxane was distilled from sodium–benzophenone ketyl. $[\text{Rh}(\text{OH})(\text{cod})]_2$ was prepared according to the reported procedure.¹ 2-Cyanophenylboronic acid, 4-octyne, 1-phenyl-1-propyne, and 2,2,7,7-tetramethyl-3,5-octadiyne were purchased from Aldrich Chemical Co. Diphenylacetylene was purchased from Tokyo Kasei Kogyo Co., Ltd. 1-(Trimethylsilyl)-1-propyne and 1-phenyl-2-(trimethylsilyl)acetylene were purchased from Wako Pure Chemical Industries, Ltd. 2-Norbornene was purchased from Nacalai Tesque, Inc. 2-Methoxycarbonylphenylboronic acid was purchased from Boron Molecular, Ltd. Ethyl 2-hexynoate was purchased from Lancaster Synthesis, Inc. Benzonorbornadiene was prepared according to the reported procedure.²

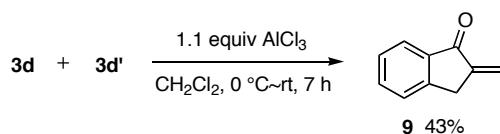
¹ Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg, Synth.* **1985**, 23, 129.

² Fernandez, F.; Garcia-Mera, X.; Morales, M.; Rodriguez-Borges, J. E.; De Clercq, E. *Synthesis.* **2002**, 8, 1084.

General procedure for the rhodium-catalyzed formation of indenones or indanones. To an oven-dried, N₂-purged flask were added a solution of substrate **1** (0.35 mmol, 1.0 equiv) in 1,4-dioxane/H₂O [3.5 mL/88 μL (40:1)], 2-cyanoboronic acid (**2**) (205 mg, 1.4 mmol, 4.0 equiv) and [Rh(OH)(cod)]₂ (8.0 mg, 0.0175 mmol, 0.1 equiv of Rh). The reaction mixture was stirred at 100 °C for 2 days. Then, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate three times. The combined organic extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate) to give the product **3**.

Product. Compounds **3a**,³ **3b**,⁴ **3c**,⁵ the minor regioisomer **3c'**,⁵ **3e**,⁶ the minor regioisomer **3e'**,³ the minor regioisomer **3f'**,³ **3g**,⁷ **3h**⁸ are known and their spectral data were compared with those of authentic specimens. The analytical data of other products **3d**, **3d'** and **3f** are as follows.

2-Methyl-3-trimethylsilylinden-1-one (3d) and 3-Methyl-2-trimethylsilylinden-1-one (3d'). The reaction mixture was chromatographed using 10:1 hexane/EtOAc to yield a 3:1 mixture as a yellow oil. When the mixture of **3d** and **3d'** was desilylated, compound **9** was obtained as the major product. Thus, the regiochemistry was determined.



A mixture of **3d** and **3d'**; IR (neat): 2955, 1701, 1561, 1283, 1250 cm⁻¹; ¹H NMR: **3d** δ = 0.29 (s, 9H), 2.30 (s, 3H), 7.07–7.43 (m, 4H); **3d'** δ = 0.38 (s, 9H), 1.94 (s 3H), 7.20–7.68 (m, 4H); HRMS (EI⁺): Calcd for C₁₃H₁₆OSi, M⁺ 216.0970. Found m/z 216.0974.

3-tert-Butyl-2-(tert-butylethynyl)inden-1-one (3f).

IR (neat): 2969, 1725, 1592, 1458, 1258, 1204 cm⁻¹; ¹H NMR: δ = 1.31 (s, 9H), 1.53 (s, 9H), 7.17–7.48 (m, 4H); ¹³C NMR: δ = 28.8, 29.8, 30.8, 36.8, 72.6, 110.7, 117.6, 122.7, 123.9, 128.5, 131.3, 133.6, 145.0, 168.8, 194.9; HRMS (EI⁺): Calcd for C₁₉H₂₂O, M⁺ 266.1671. Found m/z 266.1670.

³ Larock, R. C.; Doty, M. J.; Cacchi, S. *J. Org. Chem.* **1993**, *58*, 4579.

⁴ Pouchert, C.; Behnke, J. *Aldrich Library of ¹³C and ¹H FT-NMR Spectra*, Aldrich Chemical Co., 1992.

⁵ Liebeskind, L. S.; South, M. S. *J. Org. Chem.* **1980**, *45*, 5426.

⁶ Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. *J. Org. Chem.* **1996**, *61*, 6941.

⁷ Pletnev, A. A.; Tian, Q.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 9276.

⁸ Larock, R. C.; Tian, Q.; Pletnev, A. A. *J. Am. Chem. Soc.* **1999**, *121*, 3238.

Rhodium-catalyzed asymmetric cyclization of 2 with 1h. To an oven-dried, N₂-purged flask were added [RhCl(C₂H₄)₂] (7.1 mg, 0.0182 mmol, 0.15 equiv of Rh), KOH (6.9 mg, 0.123 mmol, 0.5 equiv), and 2-cyanoboronic acid (**2**) (1.23 mmol, 5.0 equiv). A solution of **1h** (0.246 mmol, 1.0 equiv) and Carreira ligand, prepared from *S*-(+)-Carvone, in dioxane/H₂O [2.5 mL/65 μ L (40:1)] was added to the reaction mixture at room temperature, and then the mixture was stirred at 100 °C for 2 days. Then, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate=10:1) to give **3h** (37.6 mg, 0.153 mmol) as a colorless oil. The ee was determined on a Daicel Chiralpak OD-H column with hexane:isopropanol=90:10, flow rate=0.6 mL/min. Retention times: 9.99 min, 14.24 min. 80% ee. $[\alpha]_D^{30} +178.8$ (*c* 1.0, CHCl₃) of 80% ee.

Rhodium-catalyzed synthesis of benzotropone derivative 8. To an oven-dried, N₂-purged flask were added a solution of ethyl 2-hexynoate (**7**) (34.8 mg, 0.238 mmol, 1.0 equiv) in 1,4-dioxane/H₂O [2.5 mL/65 μ L (40:1)], 2-cyanoboronic acid (**2**) (143.4 mg, 0.979 mmol, 2.0 equiv), and [Rh(OH)(cod)]₂ (5.5 mg, 0.012 mmol, 0.1 equiv of Rh). The reaction mixture was stirred at 80 °C for 2 days. Then, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate three times. The combined organic extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate=4:1) to give **8** (29.1 mg, 0.076 mmol) as a colorless oil.

6,8-Diethoxycarbonyl-7,9-dipropylbenzotropone (8)

IR (neat): 2965, 1728, 1466, 1213, 1192 cm⁻¹; ¹H NMR: δ = 0.72 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.20–1.50 (m, 4H), 2.43–2.51 (m, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 7.48–7.73 (m, 4H); ¹³C NMR: δ = 13.6, 13.9, 14.0, 14.1, 22.7, 22.9, 34.6, 37.5, 61.5, 61.6, 126.6, 127.1, 129.9, 130.7, 132.8, 133.6, 136.2, 143.7, 143.8, 144.4, 165.3, 168.5, 192.9; HRMS (EI⁺): Calcd for C₂₃H₂₈O₅, M⁺ 384.1937. Found *m/z* 384.1937.

TM-Pr, Pr

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300BB "varian2"

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Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5000.0 Hz

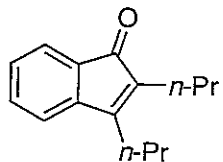
16 repetitions

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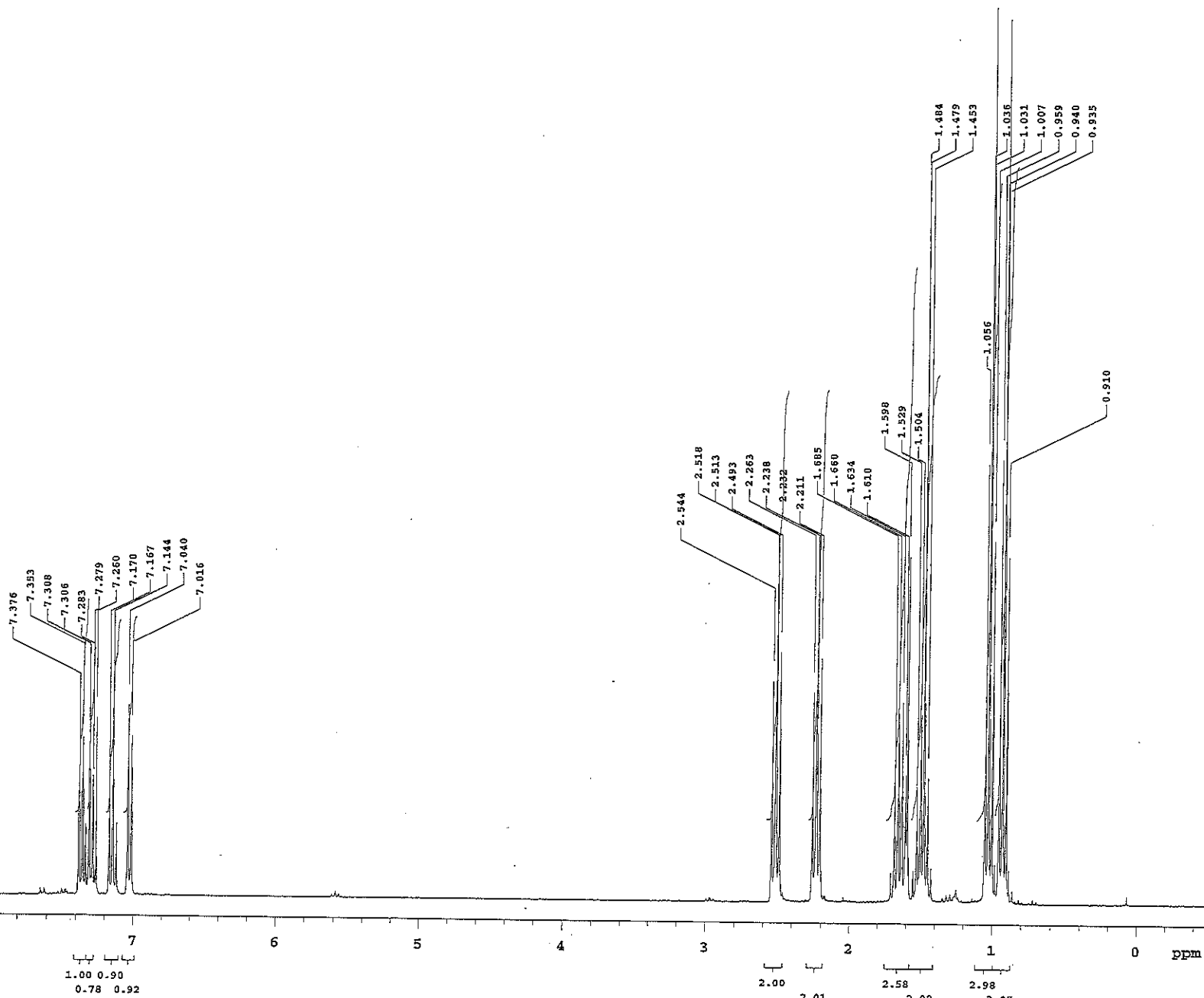
DATA PROCESSING

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Total time 1 min, 24 sec



3a



TM-Ph, Ph

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300BB "varian2"

Relax. delay 1.502 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5000.0 Hz

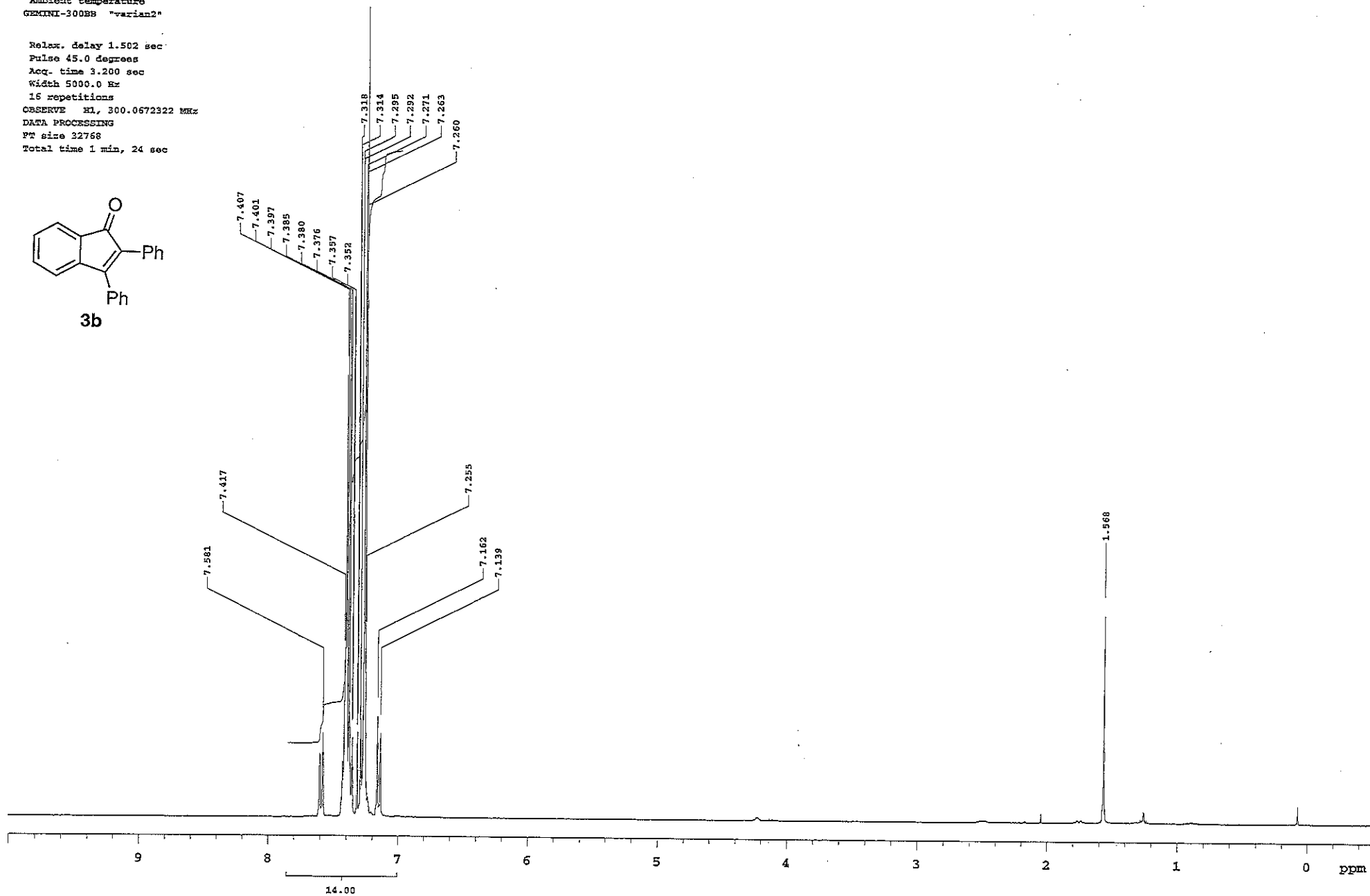
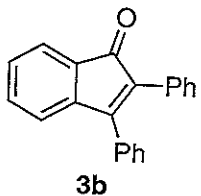
16 repetitions

OBSERVE H1, 300.0672322 MHz

DATA PROCESSING

FT size 32768

Total time 1 min, 24 sec



TM-mix.Ph,Me

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

GEMINI-300BB "varian2"

Relax. delay 1.502 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5000.0 Hz

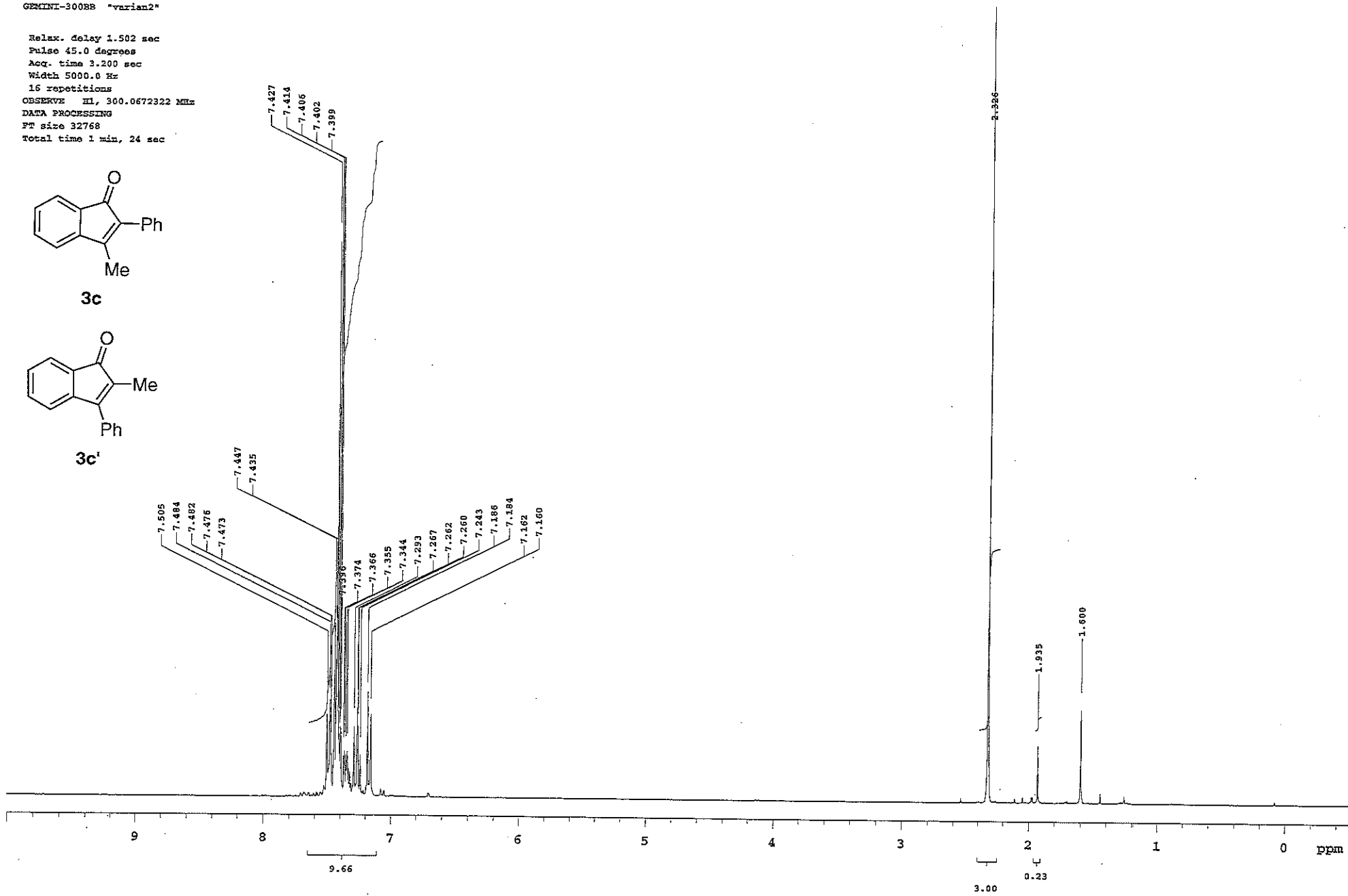
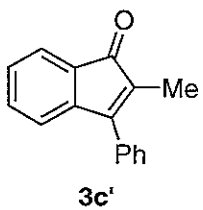
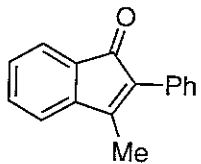
16 repetitions

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DATA PROCESSING

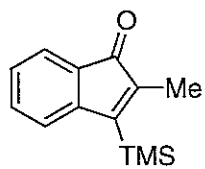
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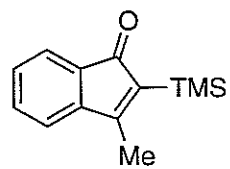


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Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

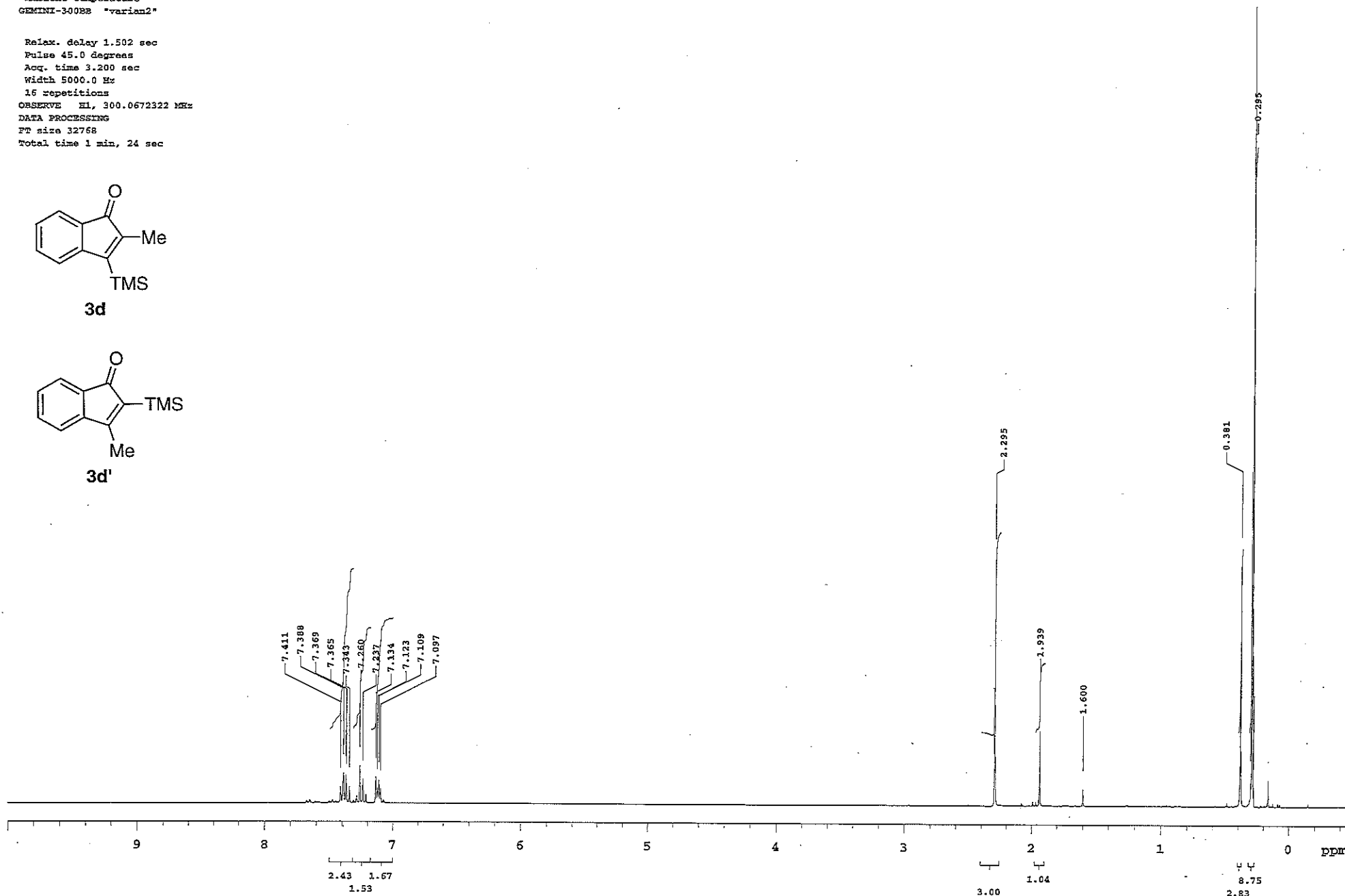
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Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5000.0 Hz
16 repetitions
OBSERVE E1, 300.0672322 MHz
DATA PROCESSING
F2 size 32758
Total time 1 min, 24 sec



3d

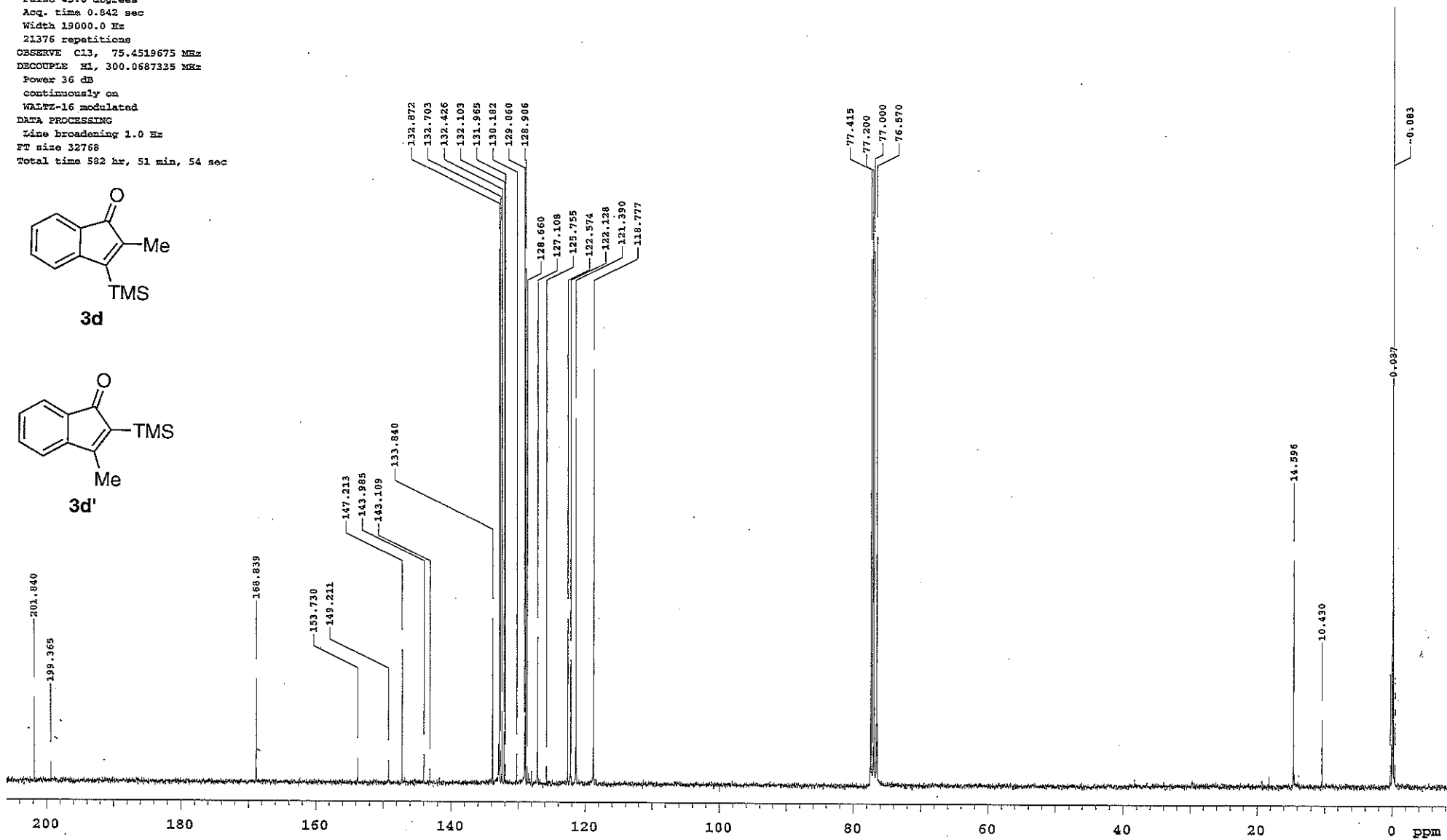
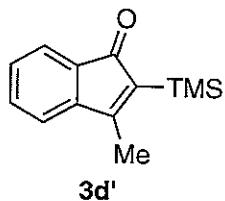
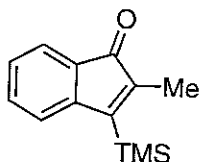


3d'



Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
21376 repetitions
OBSERVE C13, 75.4519675 MHz
DECOUPLE H1, 300.0687335 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 582 hr, 51 min, 54 sec



TM-Ph,TMS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300BS "varian2"

Relax. delay 1.502 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5000.0 Hz

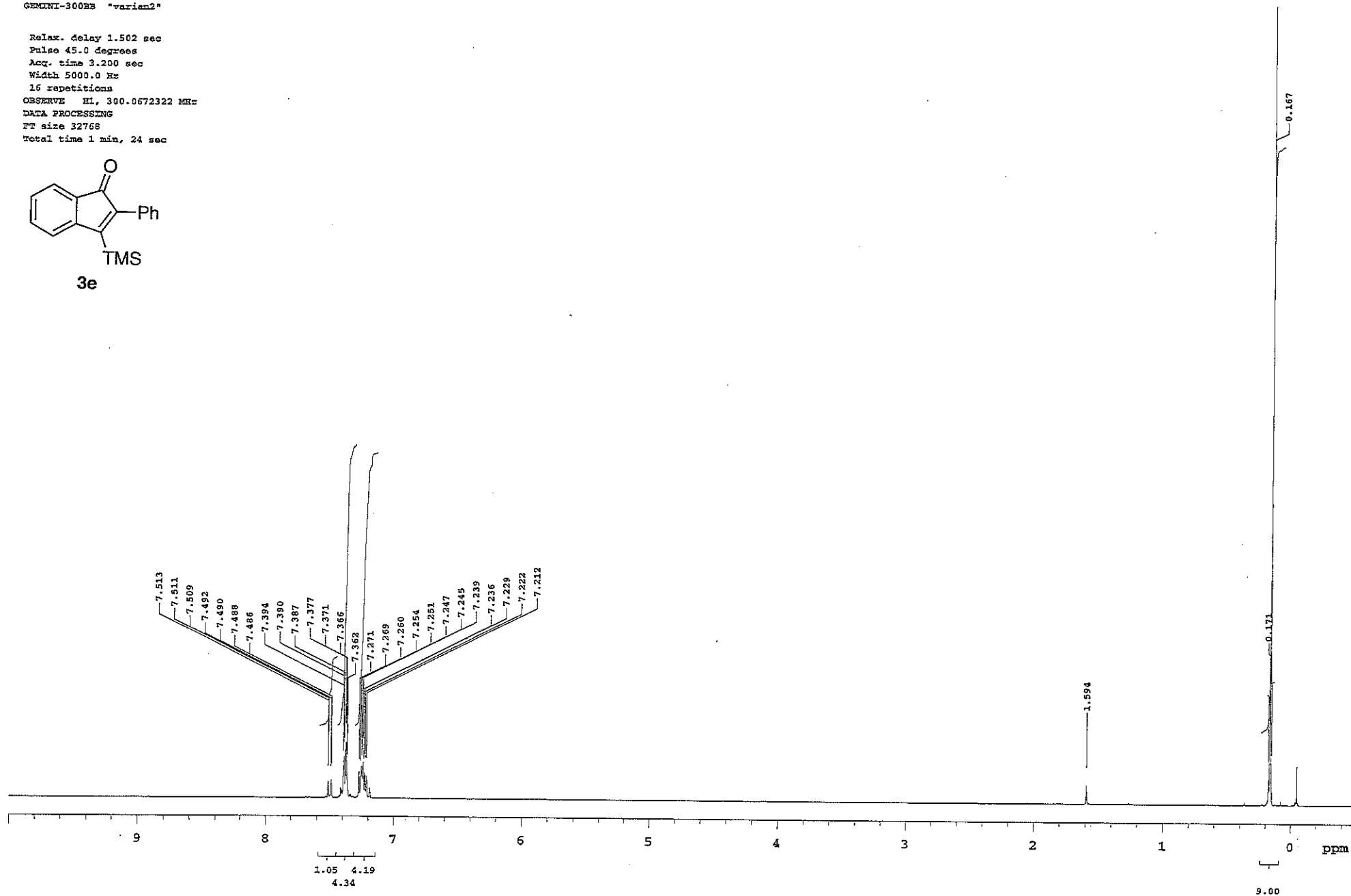
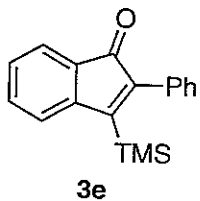
15 repetitions

OBSERVE H1, 300.0672322 MHz

DATA PROCESSING

FT size 32768

Total time 1 min, 24 sec



TM-TMS, Ph

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300BS "varian2"

Relax. delay 1.502 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5000.0 Hz

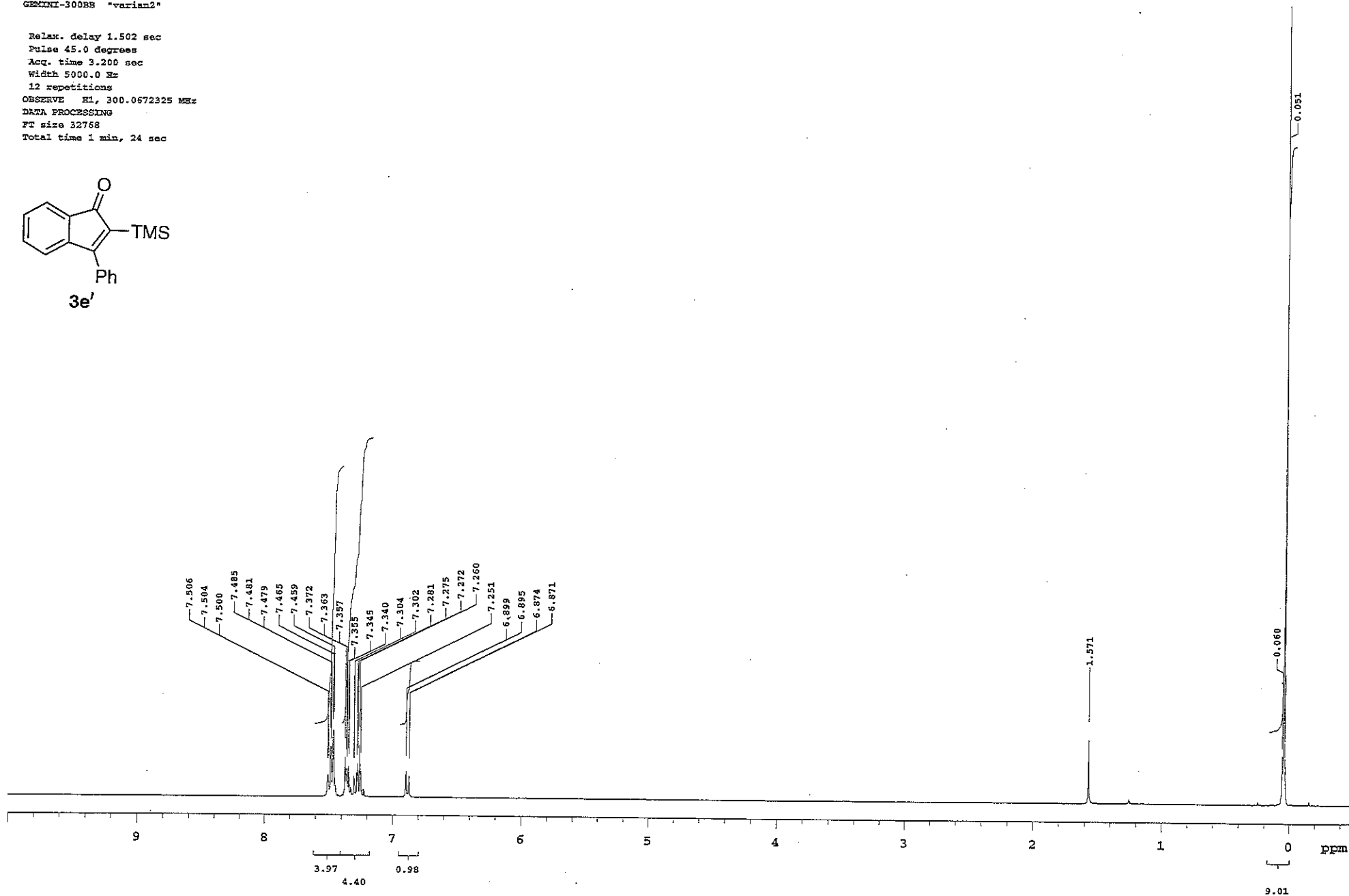
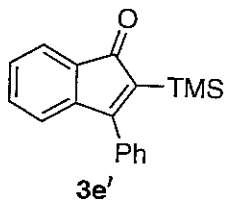
12 repetitions

OBSERVE H1, 300.0672325 MHz

DATA PROCESSING

FT size 32768

Total time 1 min, 24 sec



TM-CC,t-Bu

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient Temperature

GEMINI-300BB "varian2"

Relax. delay 1.502 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5000.0 Hz

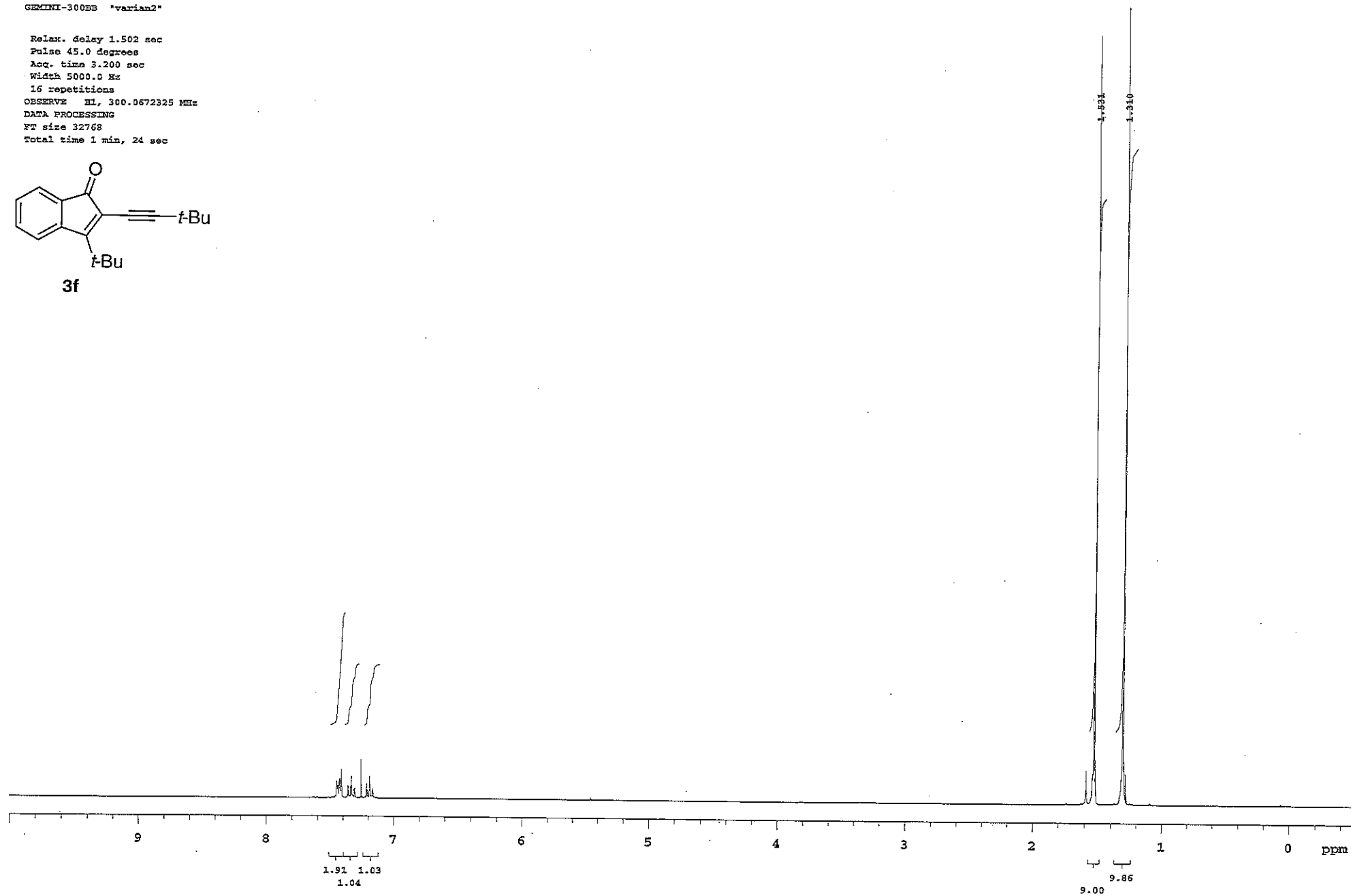
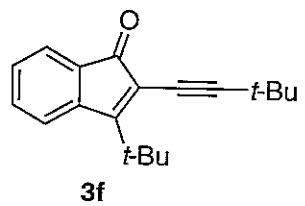
16 repetitions

OBSERVE H1, 300.0672325 MHz

DATA PROCESSING

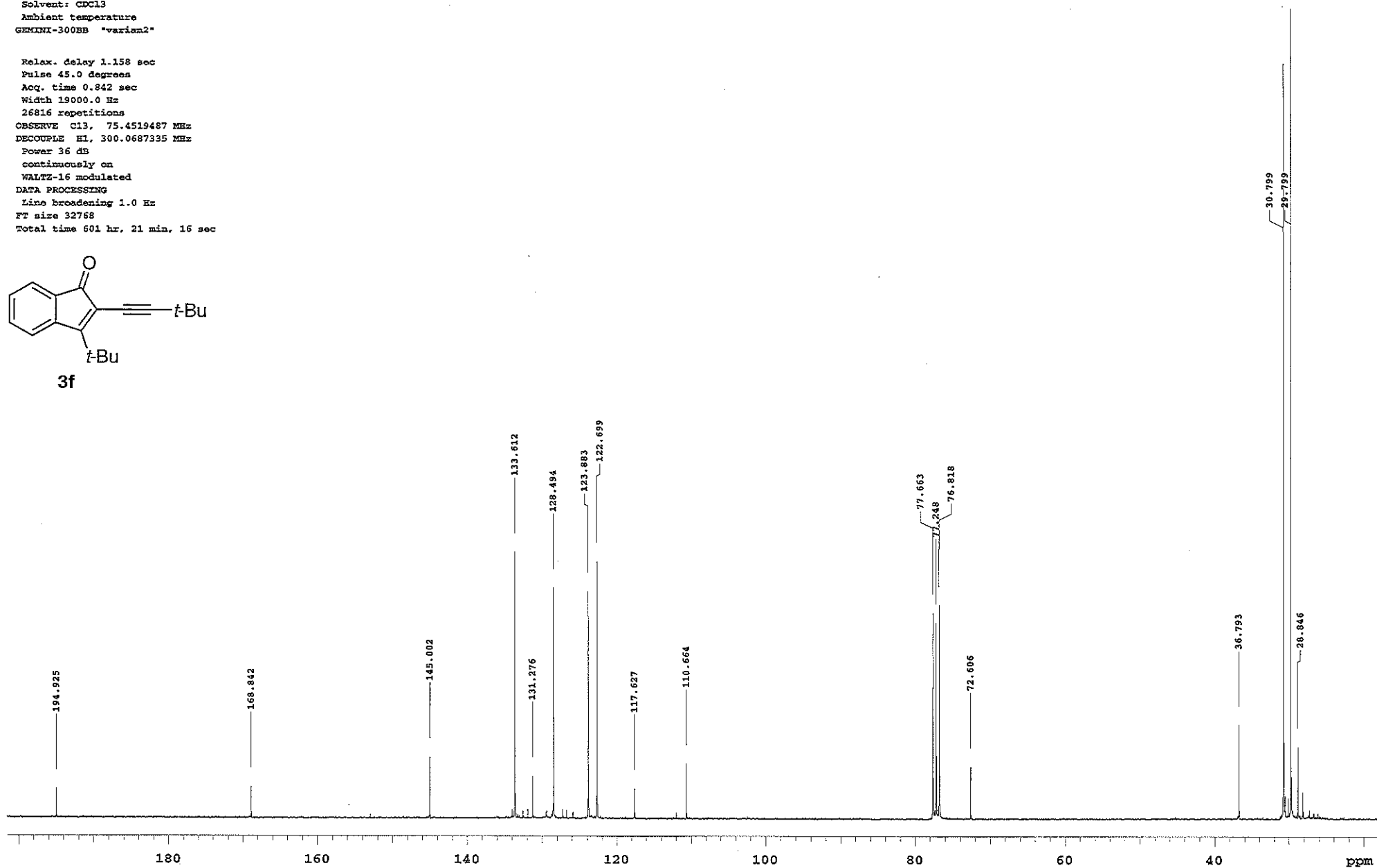
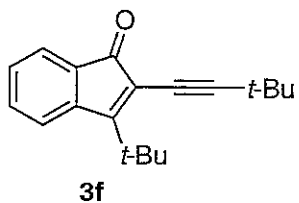
FT size 32768

Total time 1 min, 24 sec



Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
26816 repetitions
OBSERVE C13, 75.4519487 MHz
DECUPLE H1, 300.0687335 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 601 hr, 21 min, 16 sec



TM-tBu,CC

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300SB "varian2"

Relax. delay 1.502 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5000.0 Hz

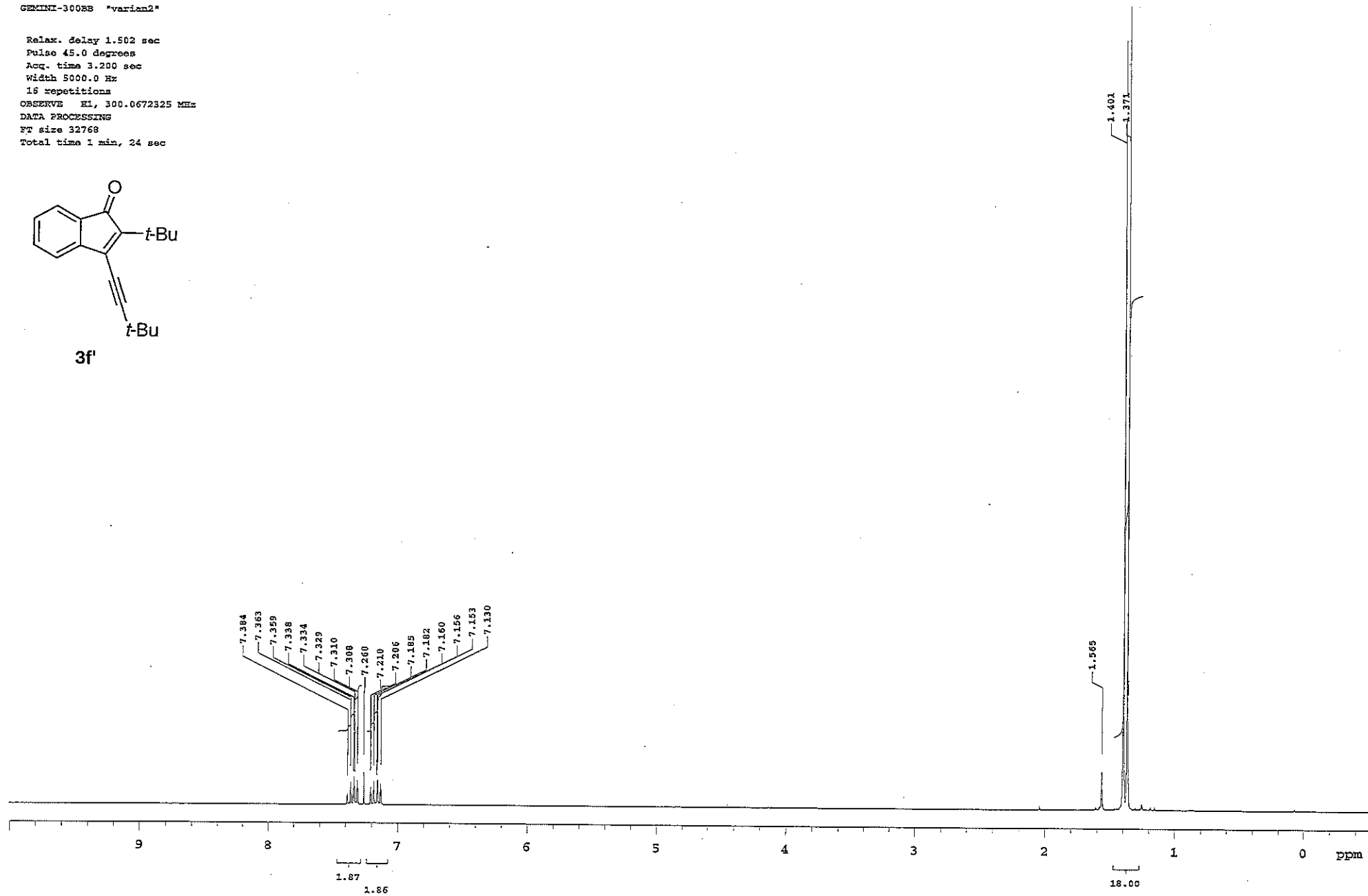
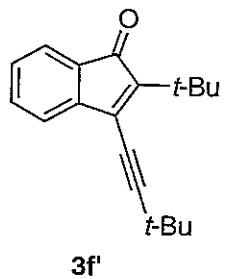
15 repetitions

OBSERVE E1, 300.0672325 MHz

DATA PROCESSING

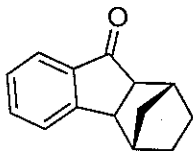
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Total time 1 min, 24 sec

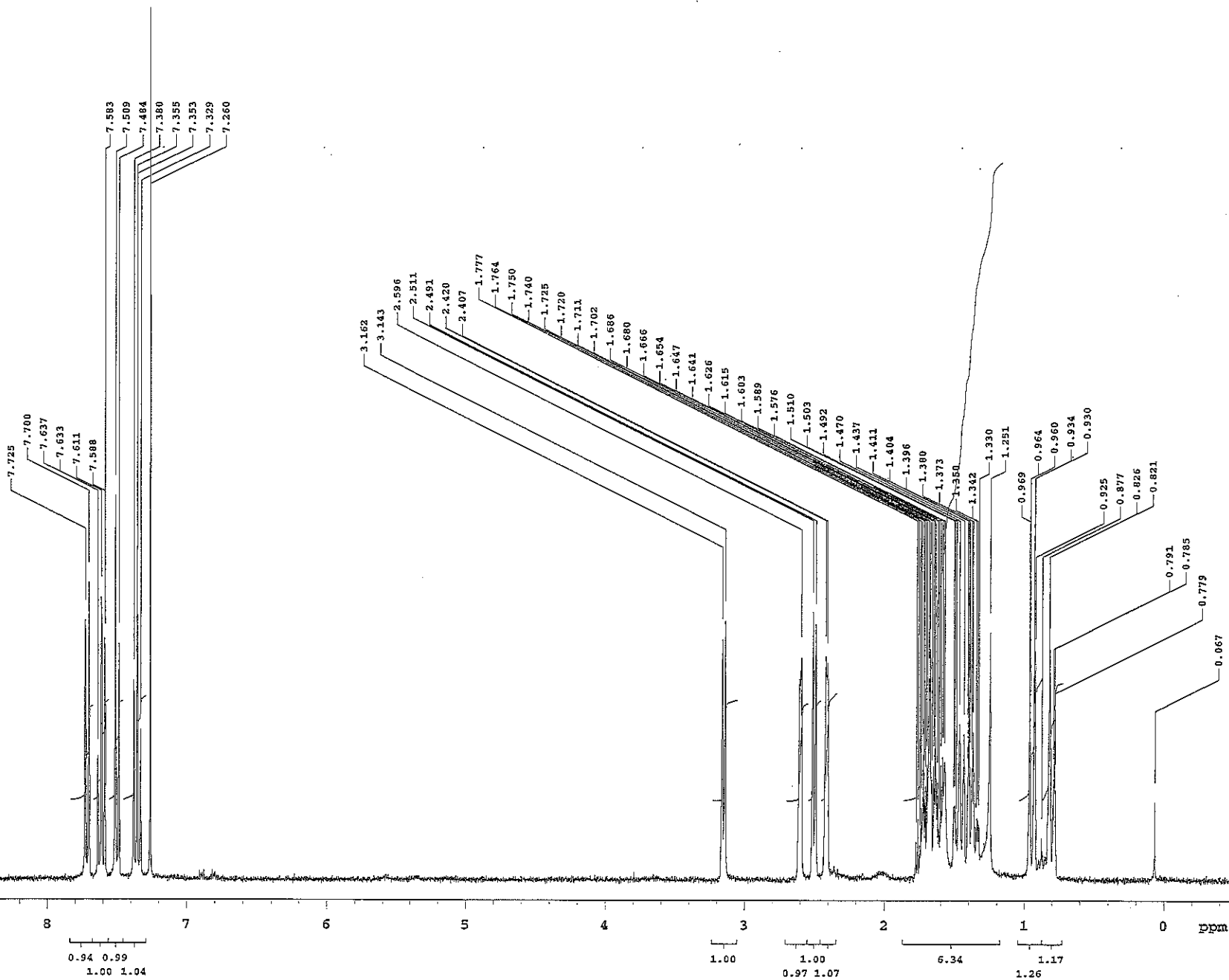


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.502 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5000.0 Hz
16 repetitions
OBSERVE H1, 300.0672331 MHz
DATA PROCESSING
FT size 32758
Total time 1 min, 24 sec

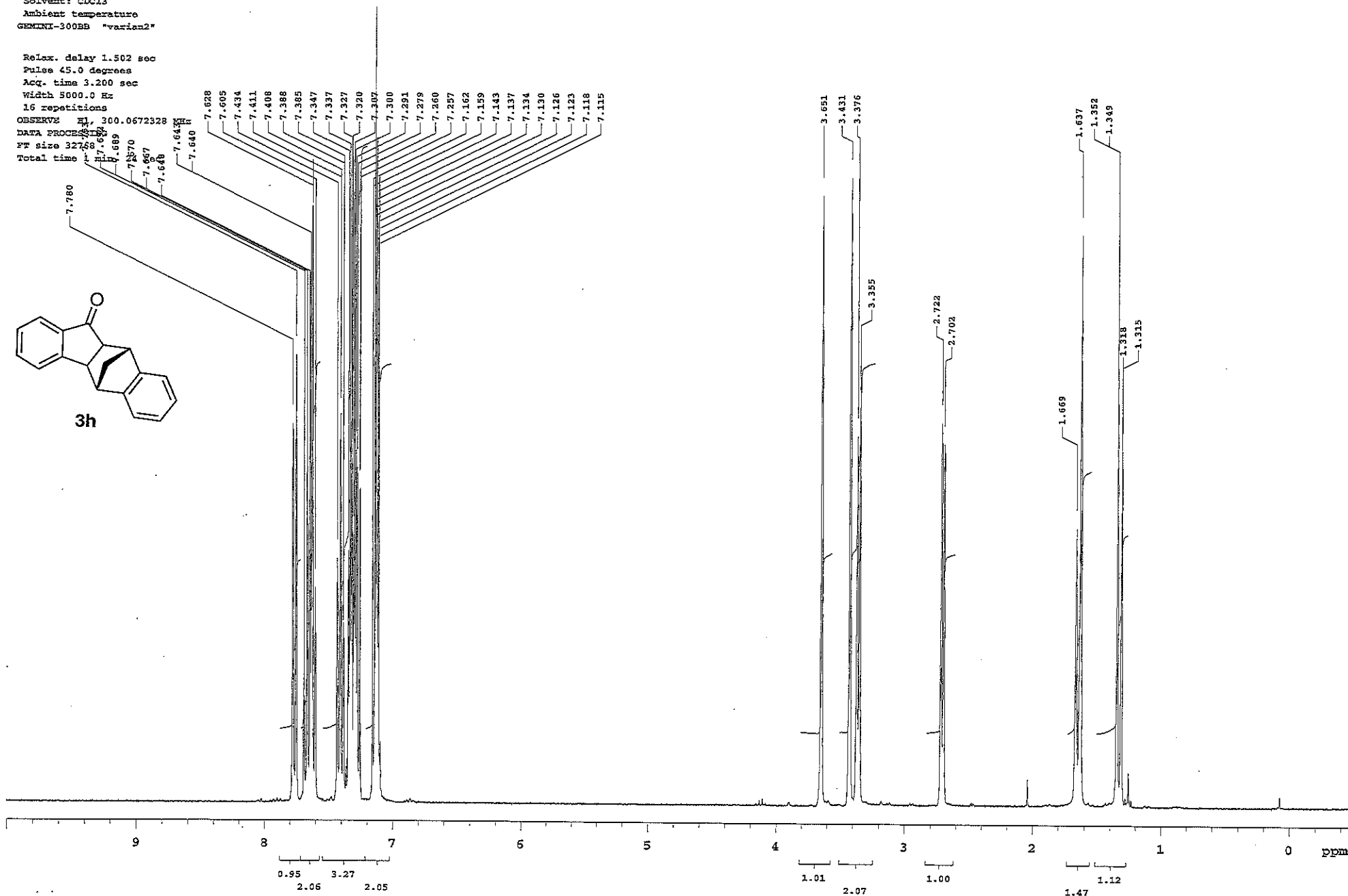
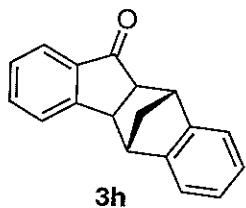


3g



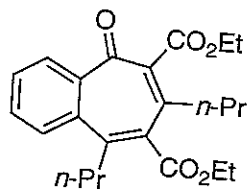
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Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

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Width 5000.0 Hz
16 repetitions
OBSERVE F1 300.0672328
DATA PROCESSING
FF size 32768
Total time 1.000

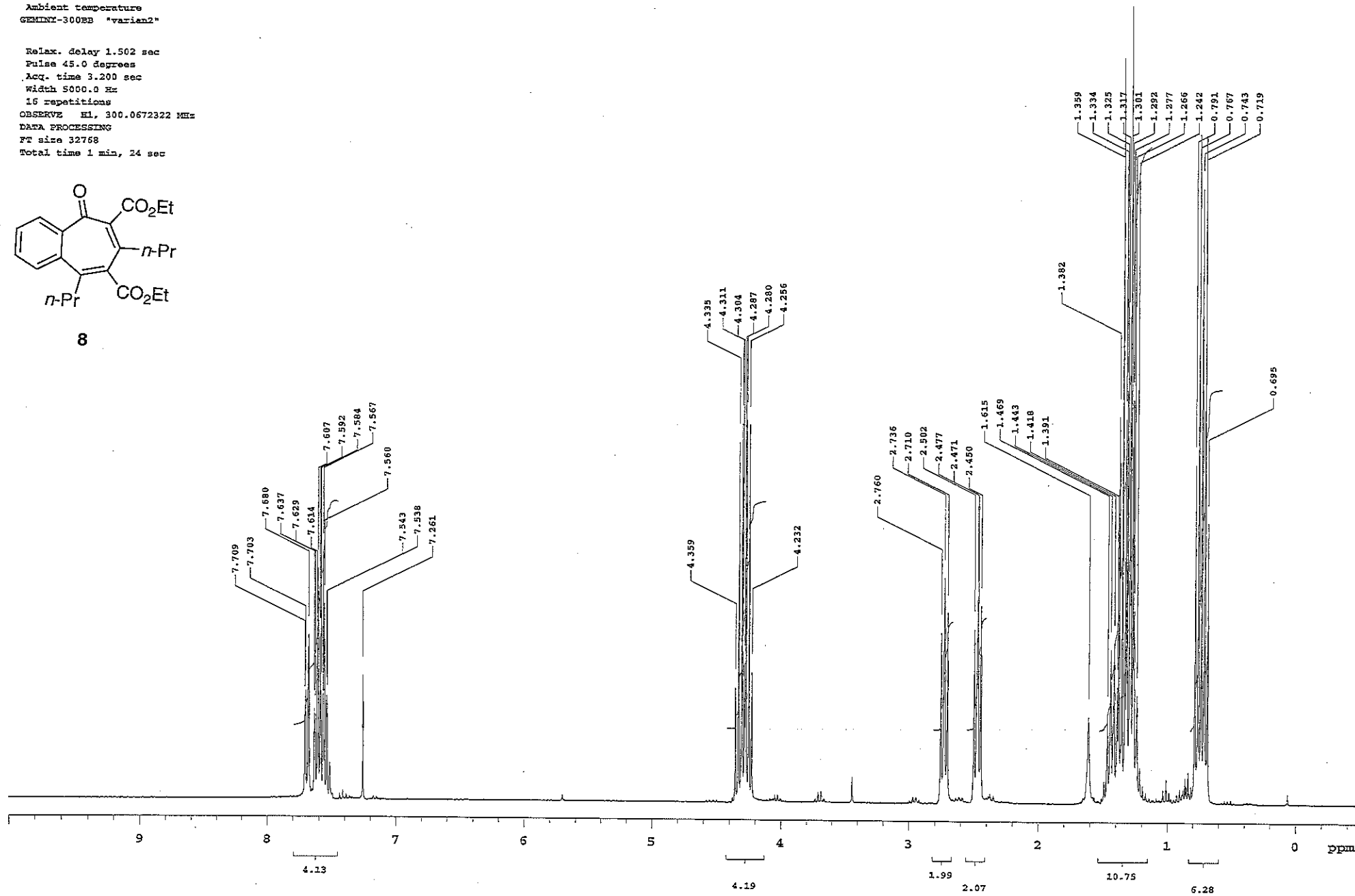


Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
GEMINI-300EB "varian2"

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Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5000.0 Hz
15 repetitions
OBSERVE HL, 300.0672322 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 24 sec

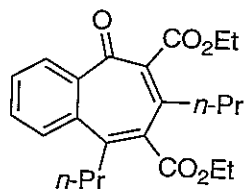


8



Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BE "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
672 repetitions
OBSERVE C13, 75.4519663 MHz
DECOUPLE H1, 300.0687335 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 6 hr, 48 sec



8

