

SUPPORTING INFORMATION

for

Room Temperature Syntheses of Entirely Diverse Substituted β -Fluorofurans

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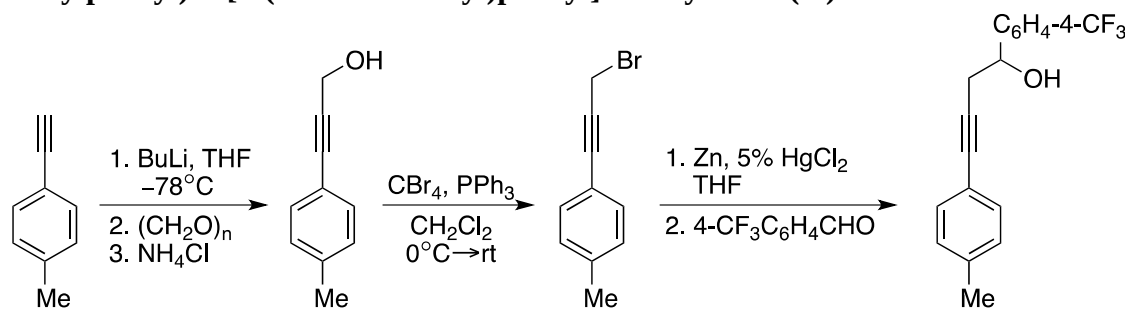
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4-(4-Methylphenyl)-1-[4-(trifluoromethyl)phenyl]but-3-yn-1-ol (5f).



A 250-mL three-necked flask was charged with 4-ethynyltoluene (12.0 g, 0.100 mol) and anhydrous THF (100 mL). The solution was cooled to -78°C and BuLi (2.5 M, 44 mL, 0.11 mol) was added during 1 h. Paraformaldehyde (3.6 g, 0.12 mol) was added portionwise under nitrogen. The reaction was stirred at ambient temperature for 12 h and acidified with HCl (1 N, 120 mL) at 0°C . Most of the organic solvent was removed under vacuum. The residue was extracted with Et₂O (2 $\times$ 200 mL). Brine (100 mL) was added to the aqueous layer which was then extracted with Et₂O (100 mL). The combined organic layer was washed with brine (2 $\times$ 50 mL), dried over MgSO₄, filtered, and concentrated under vacuum. The crude **3-(4-methylphenyl)prop-2-yn-1-ol** (white solid) was kept for a few hours under vacuum and used for next step without further purification. NMR (δ , ppm): ¹H (CDCl₃) 7.37 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 4.73 (d, J = 6.0 Hz, 2H), 2.36 (s, 3H), 1.94 (t, J = 6.0 Hz, 1H); ¹³C (CDCl₃) 138.8, 131.7, 129.2, 119.6, 86.7.^{S1}

The propargyl alcohol (estimated as 0.10 mol) in anhydrous CH₂Cl₂ (200 mL) was loaded into a 500-mL three-necked flask equipped with septum and nitrogen inlet adapter. Carbon tetrabromide (40 g, 0.12 mol) was added under nitrogen. The homogeneous solution was cooled to 0°C and PPh₃ (32 g, 0.12 mol) was added in small portions under nitrogen (highly exothermic). The reaction mixture was stirred at ambient temperature for 16 h. EtOH (5 mL) was added to quench the reaction, followed by ice-water (50 mL). The organic layer was separated, dried over MgSO₄, filtered, and concentrated. The residue was distilled under vacuum to give the **1-(3-bromoprop-1-yn-1-yl)-4-methylbenzene** as a yellow or colorless oil (8.5 g, 0.041 mol). NMR (δ , ppm): ¹H (CDCl₃) 7.65 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.18 (s, 2H), 2.36 (s, 3H).^{S2}

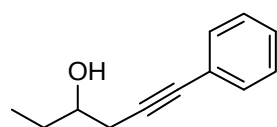
Zinc dust (0.384 g, 6.00 mmol), HgCl₂ (0.082 g, 0.30 mmol) in anhydrous THF (2.0 mL) was stirred vigorously under nitrogen at ambient temperature for 1 h. The aldehyde (0.900 g, 5.00 mmol) and propargyl bromide (1.16 g, 5.50 mmol) in anhydrous THF (23 mL) were to the mixture

S1) Köllhofer, A.; Plenio, H. *Adv. Synth. Catal.* **2005**, 347, 1295–1300.

S2) (a) Bird, T. G. C.; Bruneau, P.; Crawley, G. C.; Edwards, M. P.; Foster, S. J.; Girodeau, J. M.; Kingston, J. F.; McMillan, R. M. *J. Med. Chem.* **1991**, 34, 2176–2186. (b) Kleinbeck, F.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, 131, 9178–9179.

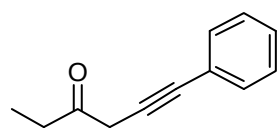
via syringe. The reaction was stirred at ambient temperature for 72 h (monitored by TLC). Saturated NH_4Cl solution (30 mL) and Et_2O (100 mL) were added and the mixture was filtered through celite pad. The organic layer was separated, dried over MgSO_4 , filtered and concentrated. The residue was purified via silica gel column chromatography (hexanes/ethyl acetate 10:1). The 4-(4-methylphenyl)-1-[4-(trifluoromethyl)phenyl]but-3-yn-1-ol (**5f**) was separated as the major product (0.660 g, 2.17 mmol, 43%) along the isomeric product, buta-2,3-dien-1-ol (0.530 g, 1.74 mol) which arose from the dual reactivity of propargyl-metal reagent. Data for **5f**: White solid, mp 138-140 °C. Calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{O}$: C, 71.04; H, 4.97. Found: C, 70.64; H, 4.87. IR (ν , cm^{-1} , KBr) 3376, 2927, 1327, 1119. UV-vis (ϵ , $\text{M}^{-1}\text{cm}^{-1}$; ether; 3.9×10^{-5} M) 243 (22000), 254 (20000). MS (EI, m/z): 304 (4%, M^+), 130 (100%). NMR (δ , ppm): ^1H (CDCl_3) 7.65 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 5.02 (t, $J = 5.6$ Hz, 1H), 2.90 (dd, $J = 5.2, 16.8$ Hz, 1H), 2.84 (dd, $J = 7.3, 16.8$ Hz, 1H), 2.53 (bd, $J = 2.7$ Hz, 1H), 2.35 (s, 3H); ^{13}C (CDCl_3) 146.8, 138.6, 131.8, 130.3 (q, $J = 32.3$ Hz), 129.3, 126.4, 125.6 (q, $J = 3.8$ Hz), 124.4 (q, $J = 272.0$ Hz), 120.1, 84.4, 72.2, 30.9, 21.7.

6-Phenylhex-5-yn-3-ol (**5g**).



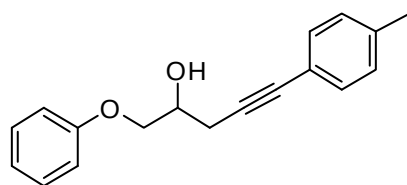
White solid, mp 37-38 °C. IR (ν , cm^{-1} , KBr) 2929, 1700, 1653, 1119. MS (EI, m/z): 174 (10%, M^+), 116 (100%). NMR (δ , ppm, CDCl_3): ^1H 7.46-7.39 (m, 2H), 7.32-7.28 (m, 3H), 3.84-3.74 (m, 1H), 2.68 (dd, $J = 16.8, 4.8$ Hz, 1H), 2.57 (dd, $J = 16.8, 6.7$ Hz, 1H), 1.95 (d, $J = 5.0$ Hz, 1H), 1.74-1.59 (m, 2H), 1.02 (t, $J = 7.4$ Hz, 3H); ^{13}C 131.9, 128.5, 128.1, 123.6, 86.4, 83.2, 29.5, 28.2, 10.2.

6-Phenylhex-5-yn-3-one (**3g**).



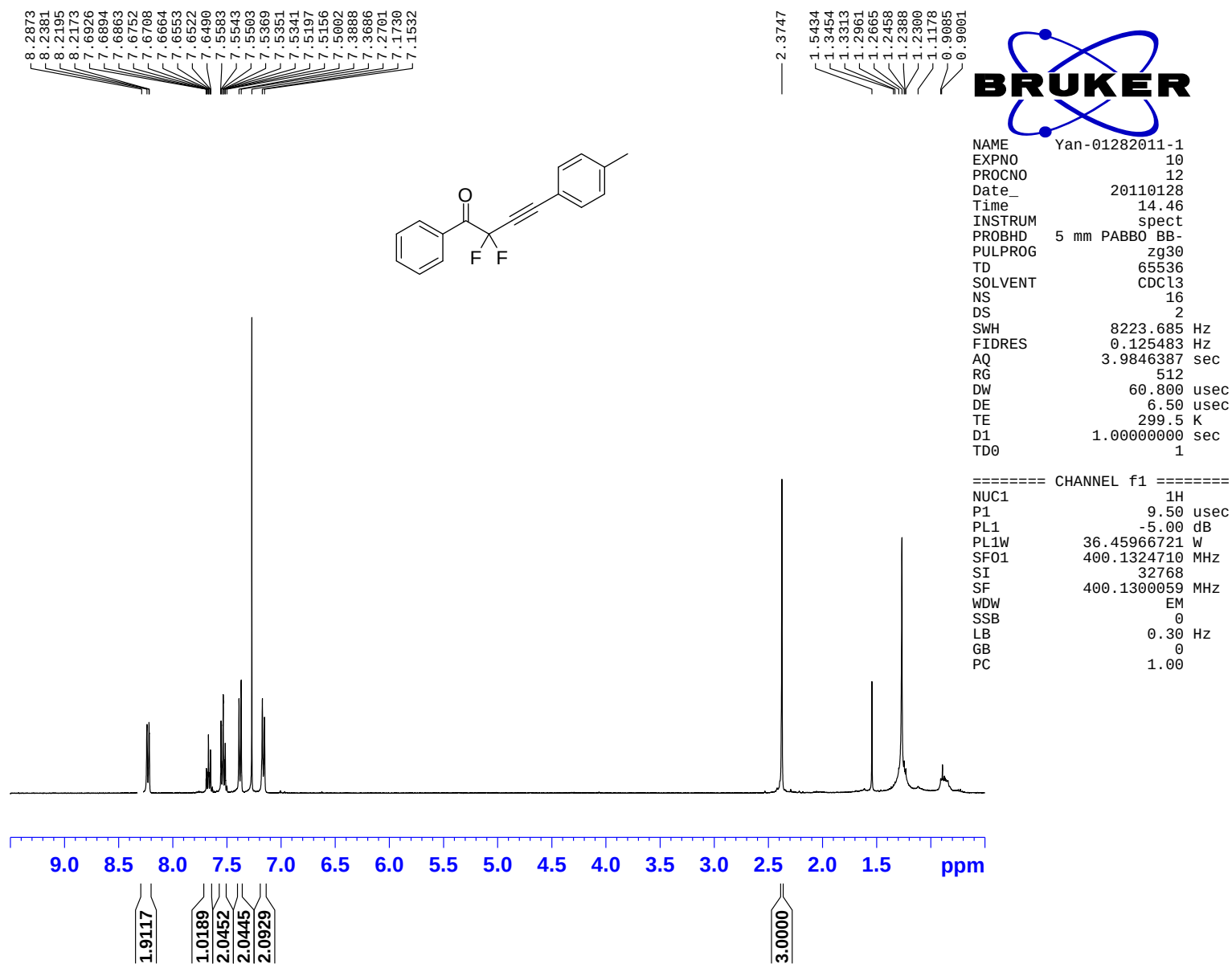
Unstable yellow oil. IR (ν , cm^{-1} , film) 2979, 2940, 2190, 1719, 1491, 758. MS (EI, m/z): 172 (20%, M^+), 57 (100%). NMR (δ , ppm, CDCl_3): ^1H 7.45-7.41 (m, 2H), 7.34-7.29 (m, 3H), 3.48 (s, 2H) 2.73 (q, $J = 7.3$ Hz, 2H), 1.13 (t, $J = 7.3$ Hz, 3H); ^{13}C 205.4, 131.8, 128.5, 128.4, 123.2, 84.8, 82.4, 35.0, 34.7, 7.9.

5-(4-Methylphenyl)-1-phenoxy-pent-4-yn-2-ol (**5h**).

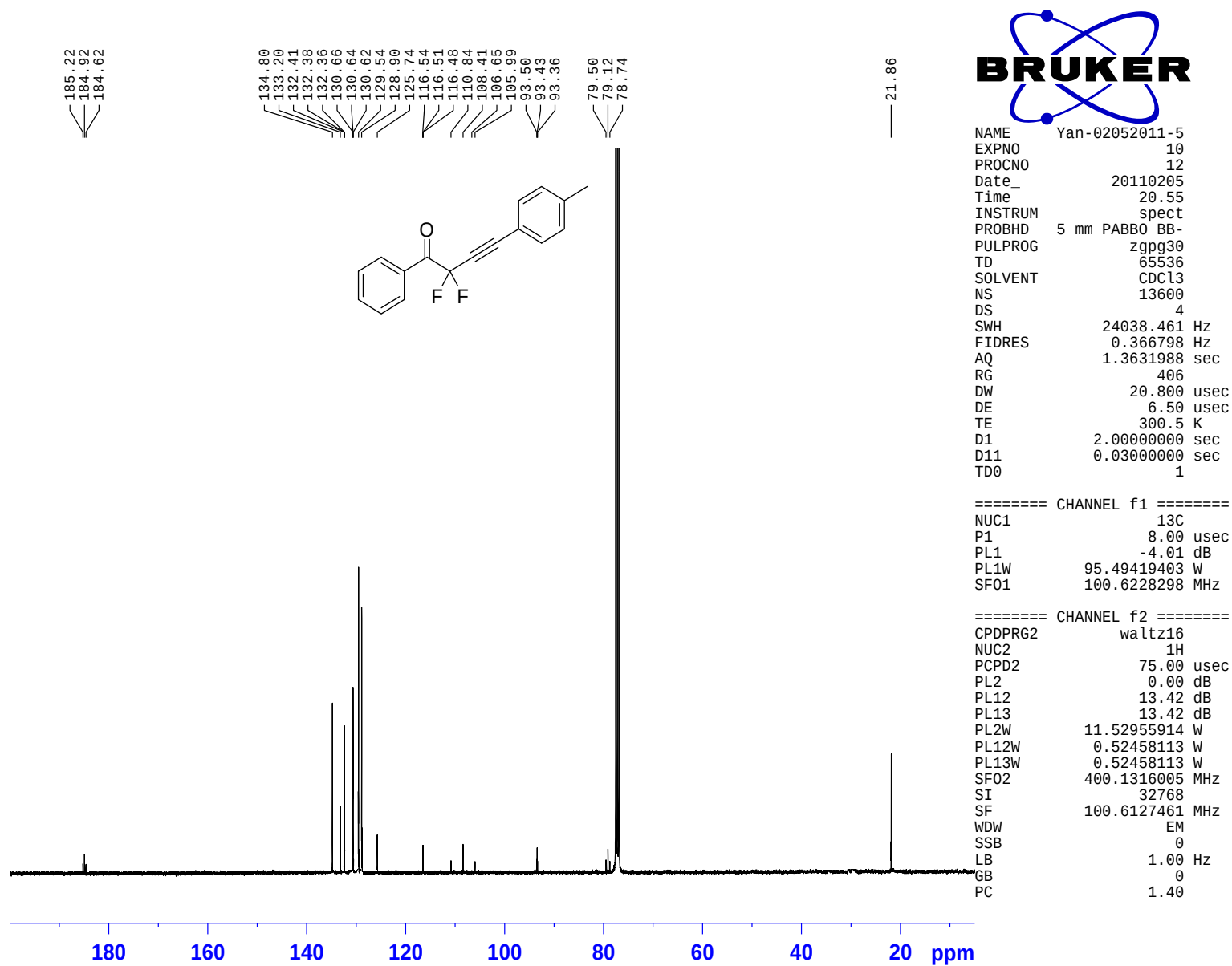


White solid, mp 63-64 °C. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 81.17; H, 6.81. Found: C, 81.13; H, 6.89. IR (ν , cm^{-1} , KBr) 3460, 2916, 2332, 1599, 1500, 1251. UV-vis (ϵ , $\text{M}^{-1}\text{cm}^{-1}$; ether; 3.3×10^{-5} M) 242 (24000), 253 (23000). MS (EI, m/z): 266 (30%, M^+), 155 (100%). NMR (δ , ppm): ^1H (CDCl_3) 7.35-7.25 (m, 4H), 7.11 (d, $J = 7.8$ Hz, 2H), 7.02-6.93 (m, 3H), 4.30-4.22 (m, 1H), 4.18 (dd, $J = 9.4, 4.1$ Hz, 1H), 4.08 (dd, $J = 9.4, 6.4$ Hz, 1H), 2.81 (d, $J = 6.2$ Hz, 2H), 2.50 (d, $J = 5.0$ Hz, 1H), 2.35 (s, 3H); ^{13}C (CDCl_3) 158.7, 138.3, 131.7, 129.8, 129.2, 121.4, 120.3, 114.8, 84.4, 83.5, 70.8, 69.0, 24.8, 21.6.

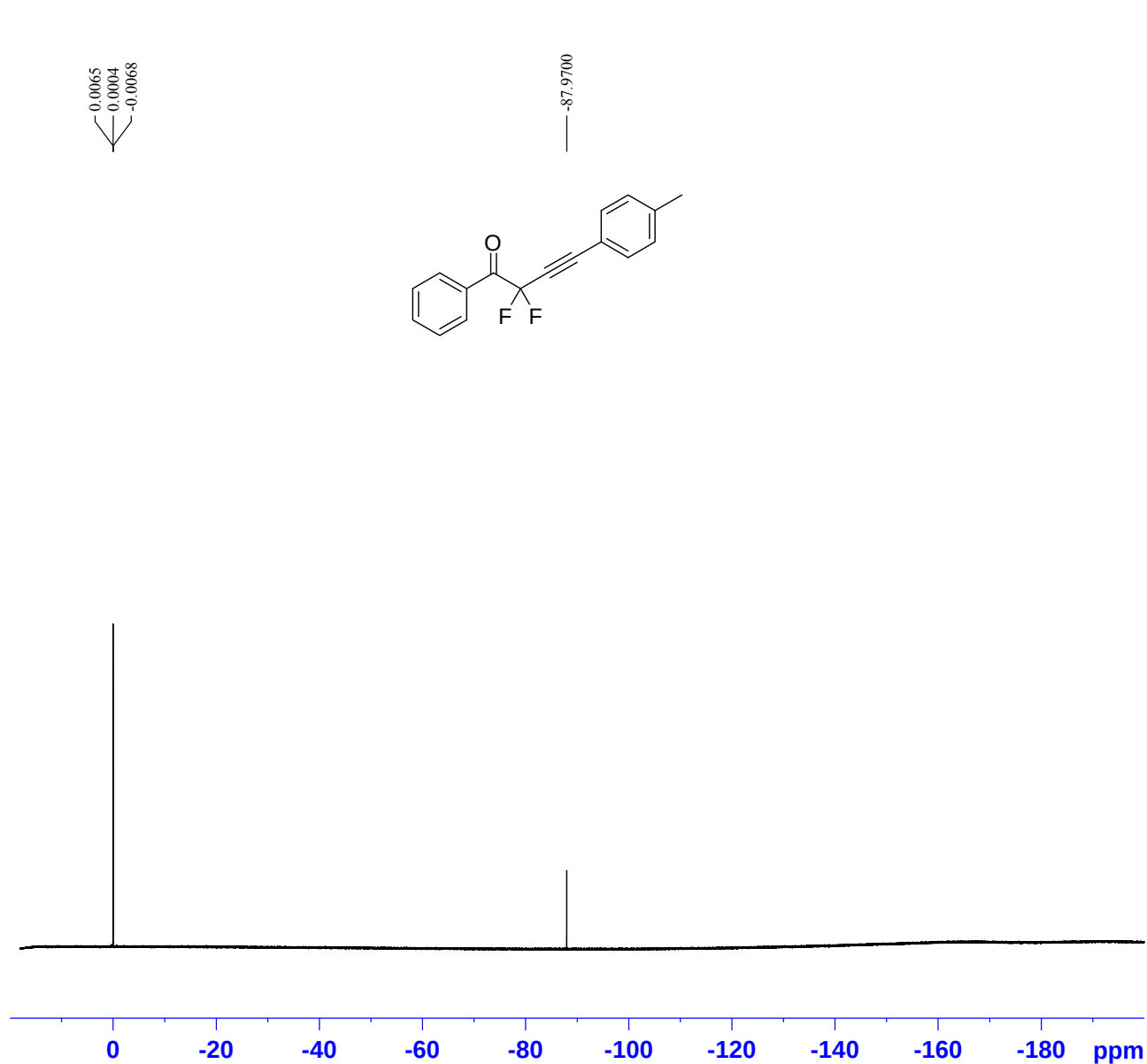
^1H NMR spectrum for **4a** (CDCl_3)



^{13}C NMR spectrum for **4a** (CDCl_3)



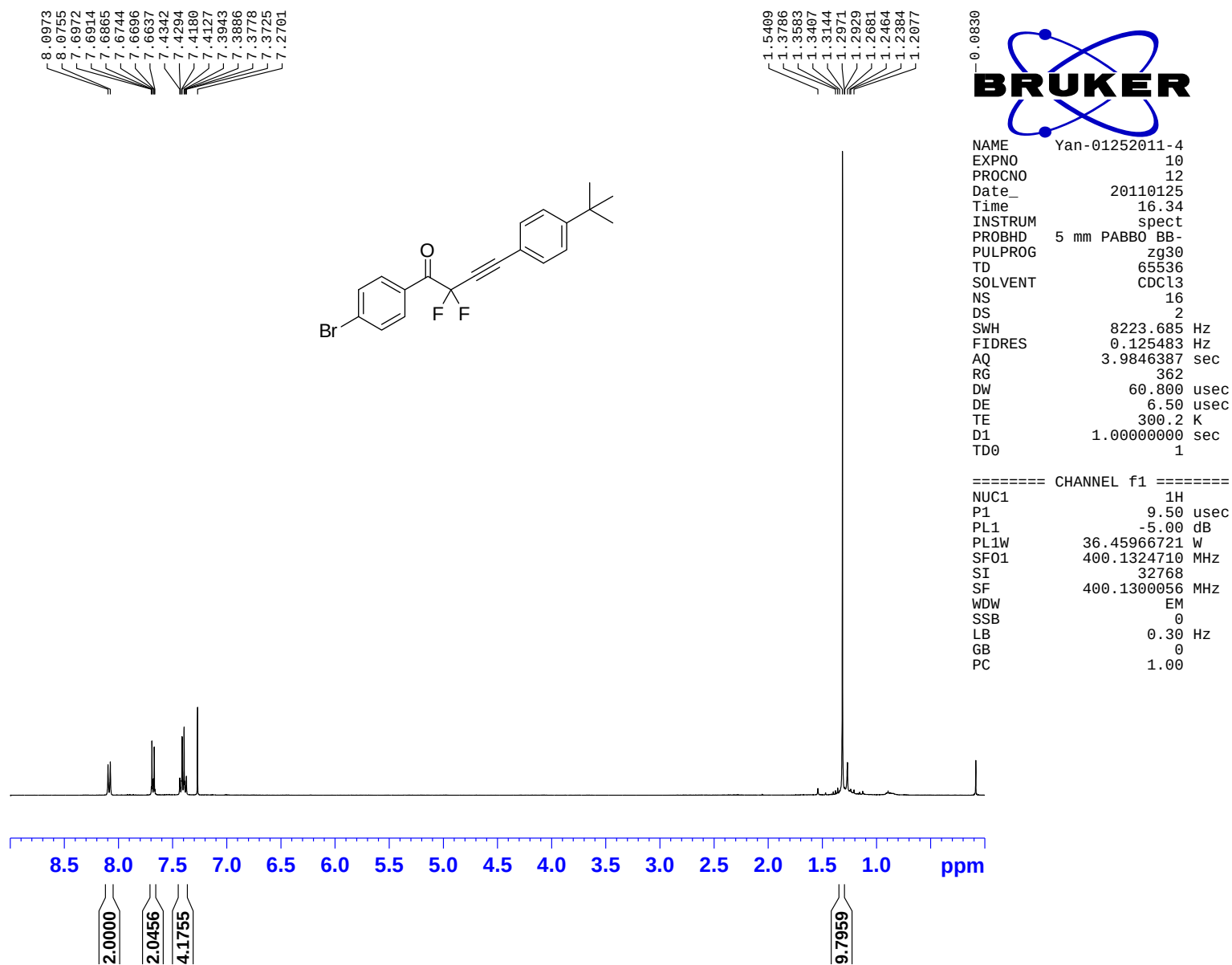
^{19}F NMR spectrum for **4a** (CDCl_3)



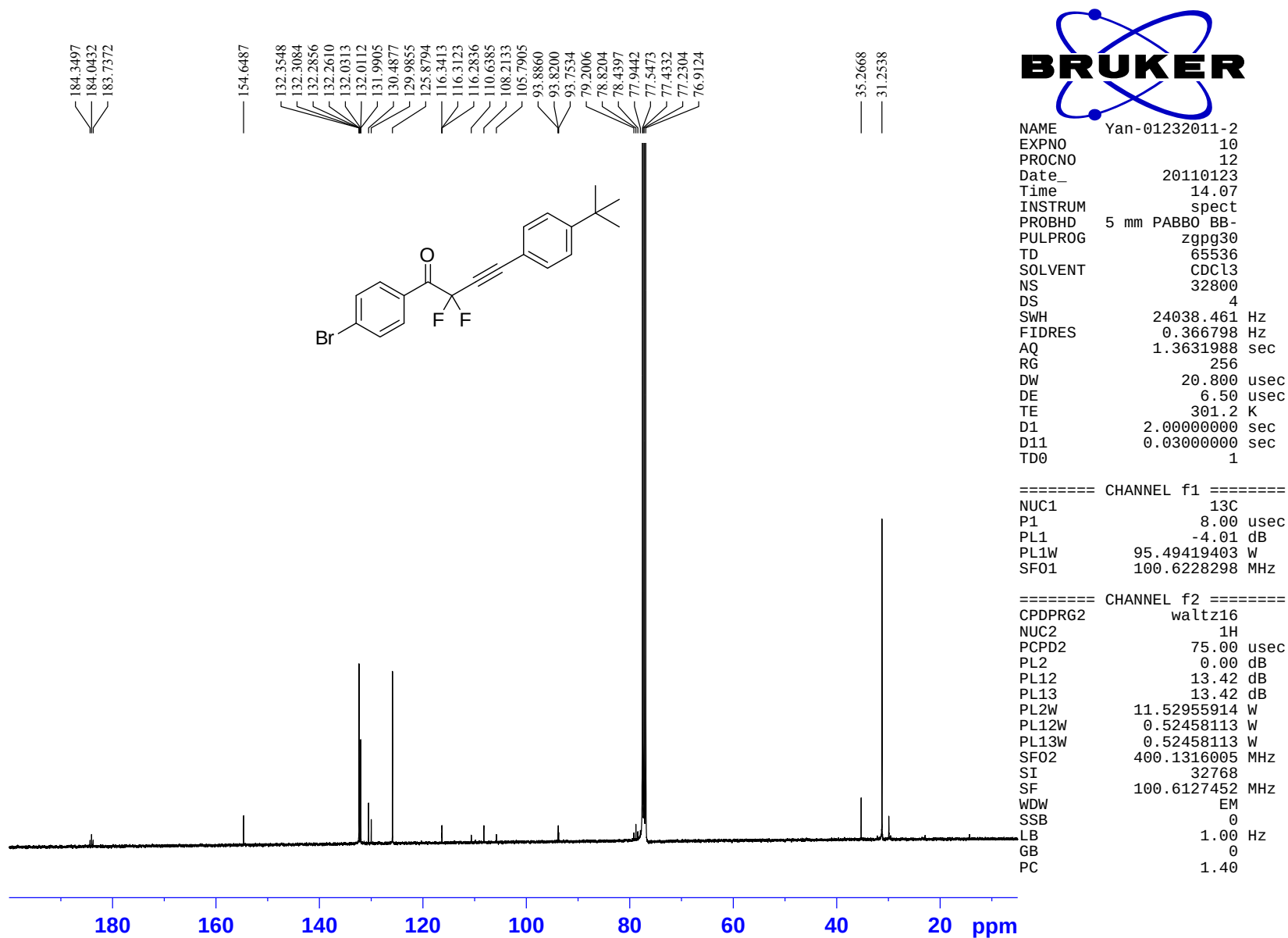
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DE 6.50 usec
TE 299.6 K
D1 1.00000000 sec
TD0 1

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SF01 376.4607164 MHz
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WDW EM
SSB 0
LB 0.30 Hz
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PC 1.00

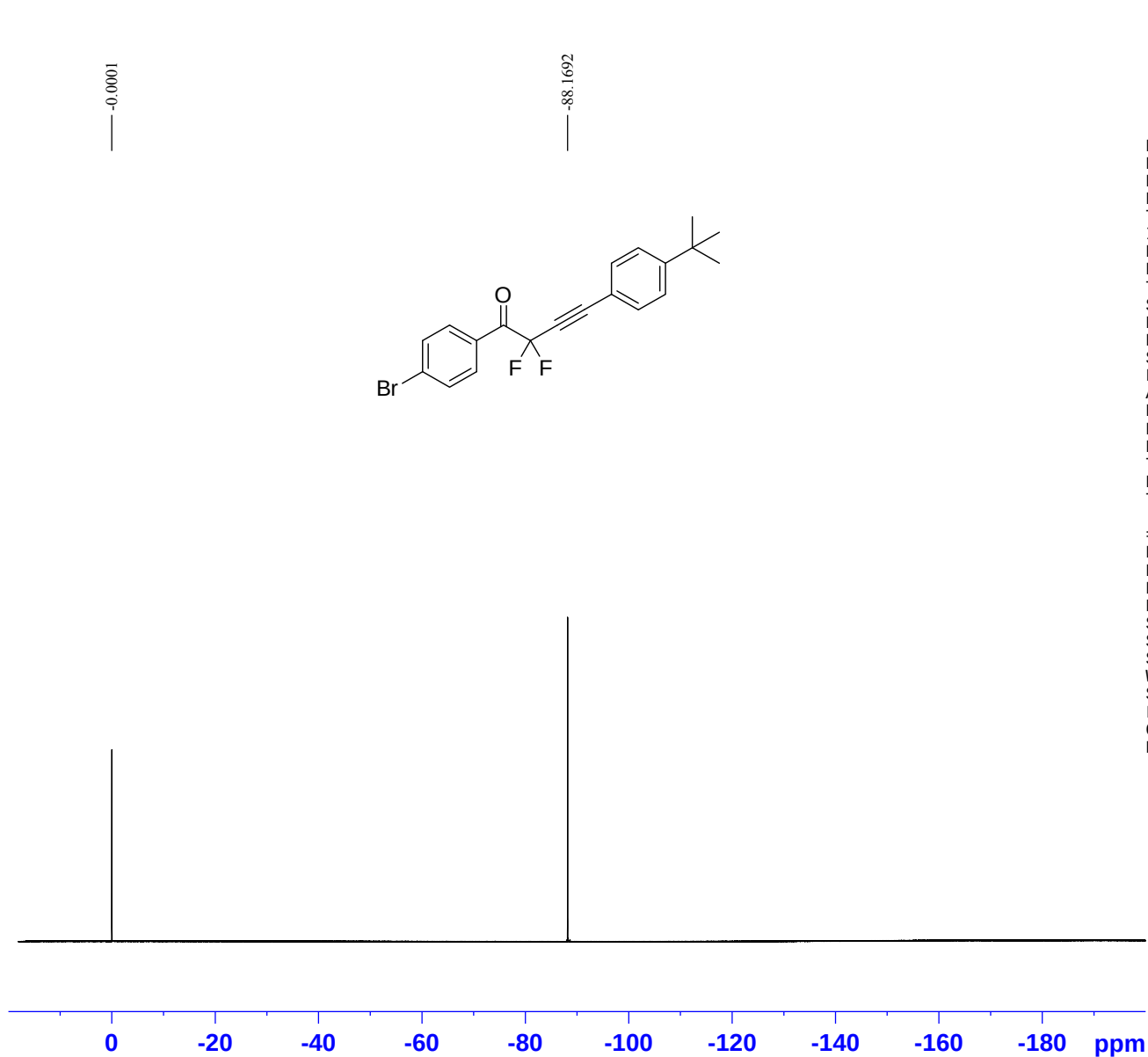
^1H NMR spectrum for **4e** (CDCl_3)



^{13}C NMR spectrum for **4e** (CDCl_3)

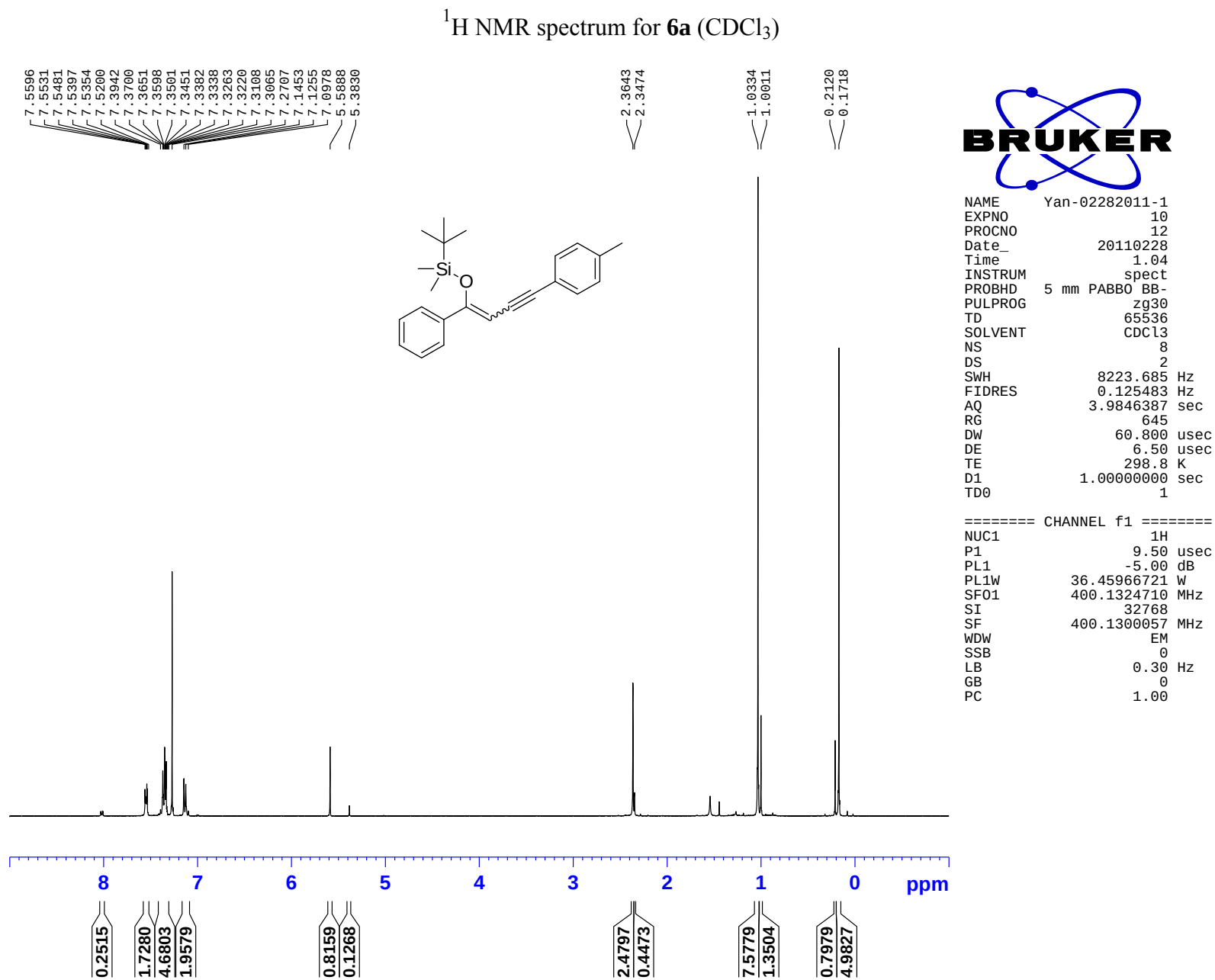


^{19}F NMR spectrum for **4e** (CDCl_3)

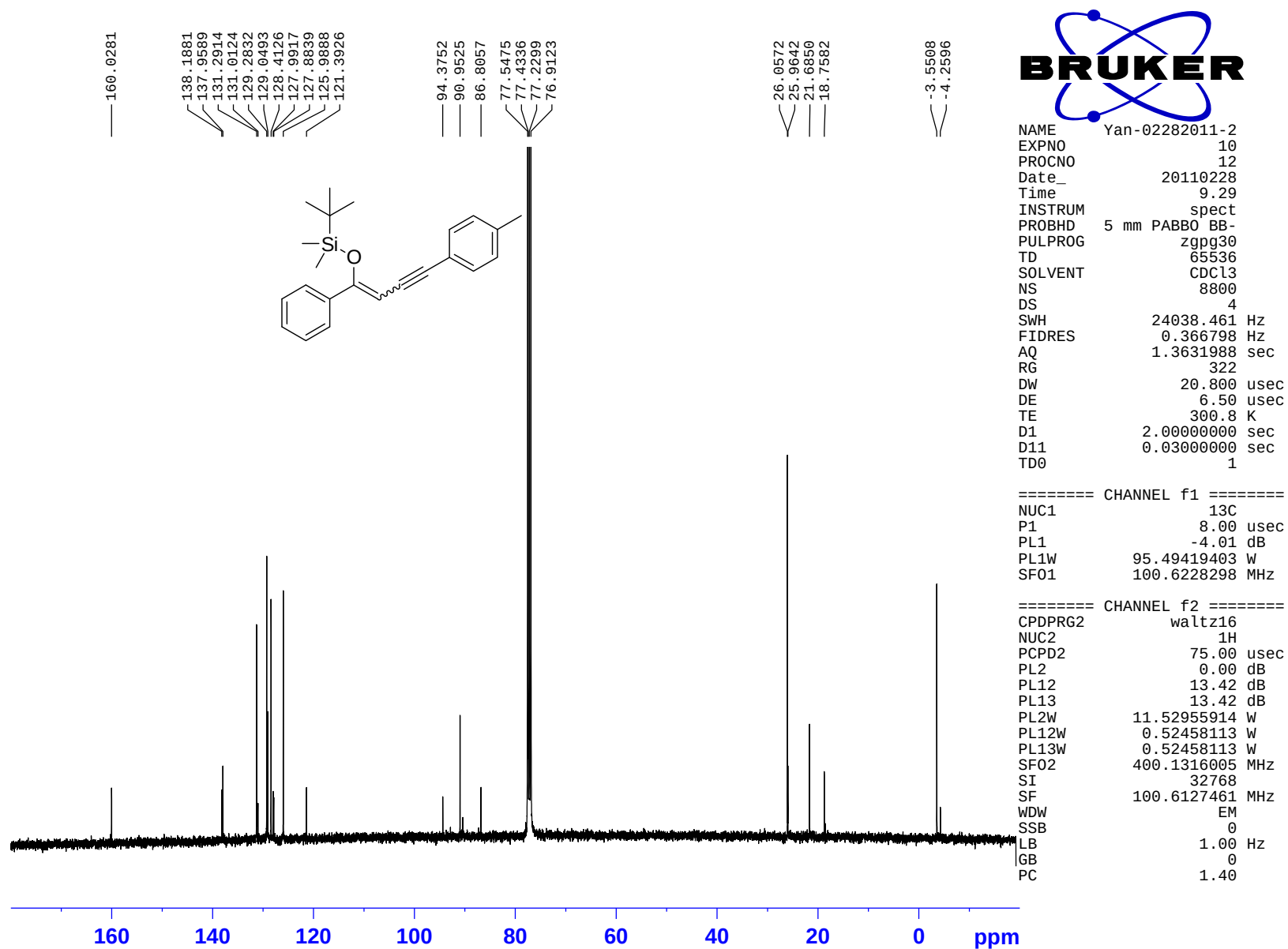


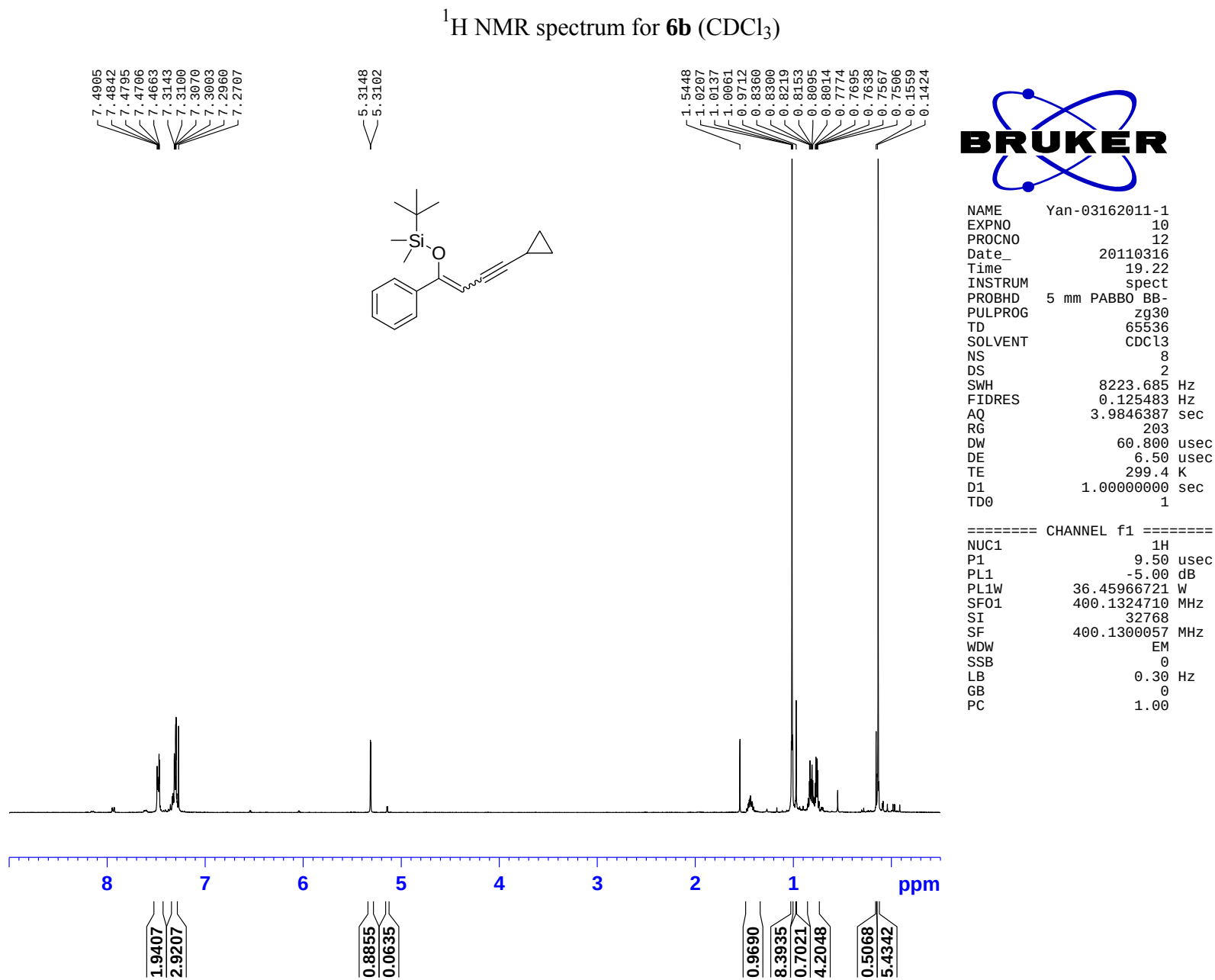
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DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
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PL1 -3.00 dB
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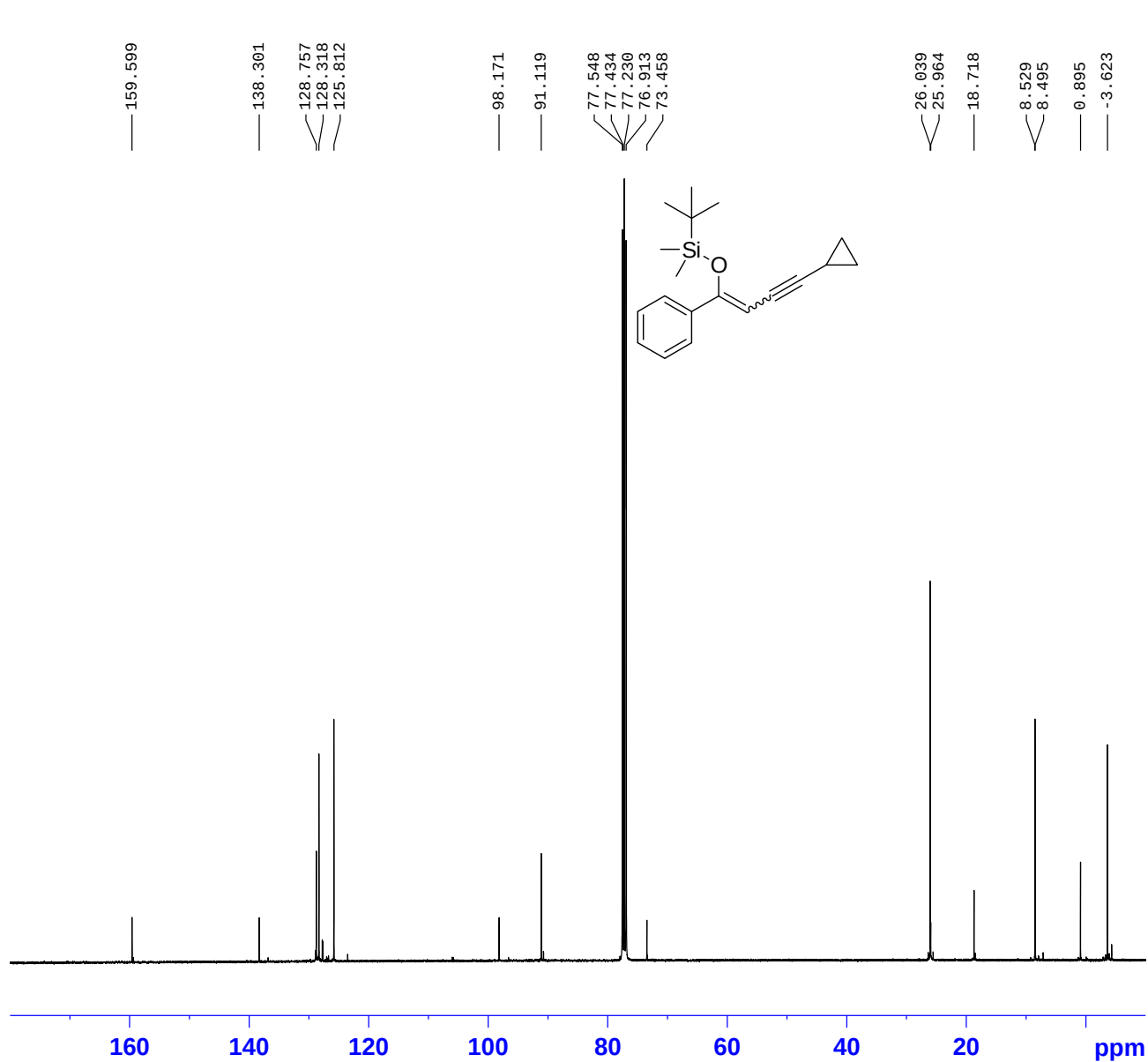


^{13}C NMR spectrum for **6a** (CDCl_3)





^{13}C NMR spectrum for **6b** (CDCl_3)

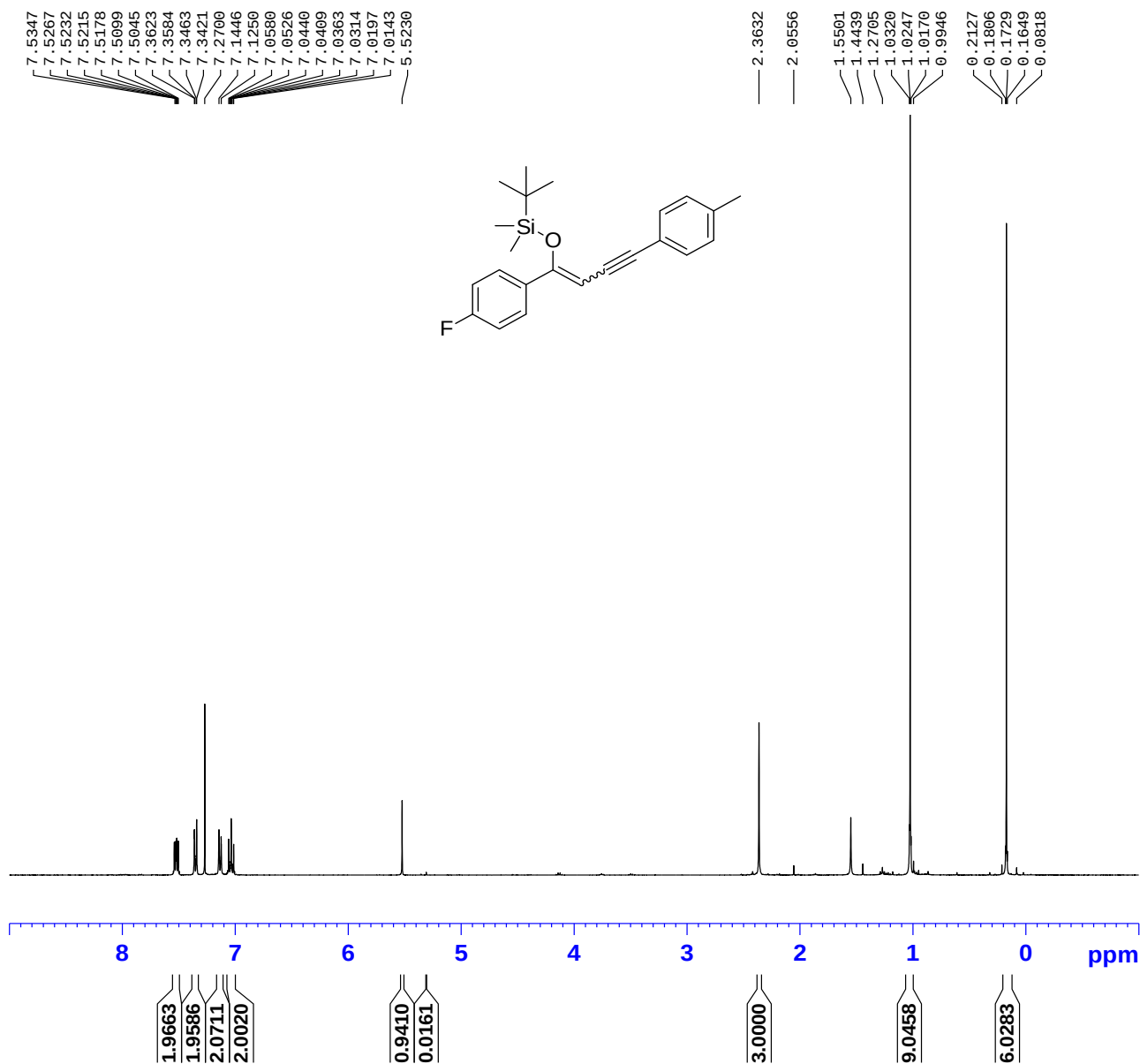


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FIDRES 0.366798 Hz
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RG 322
DW 20.800 usec
DE 6.50 usec
TE 300.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

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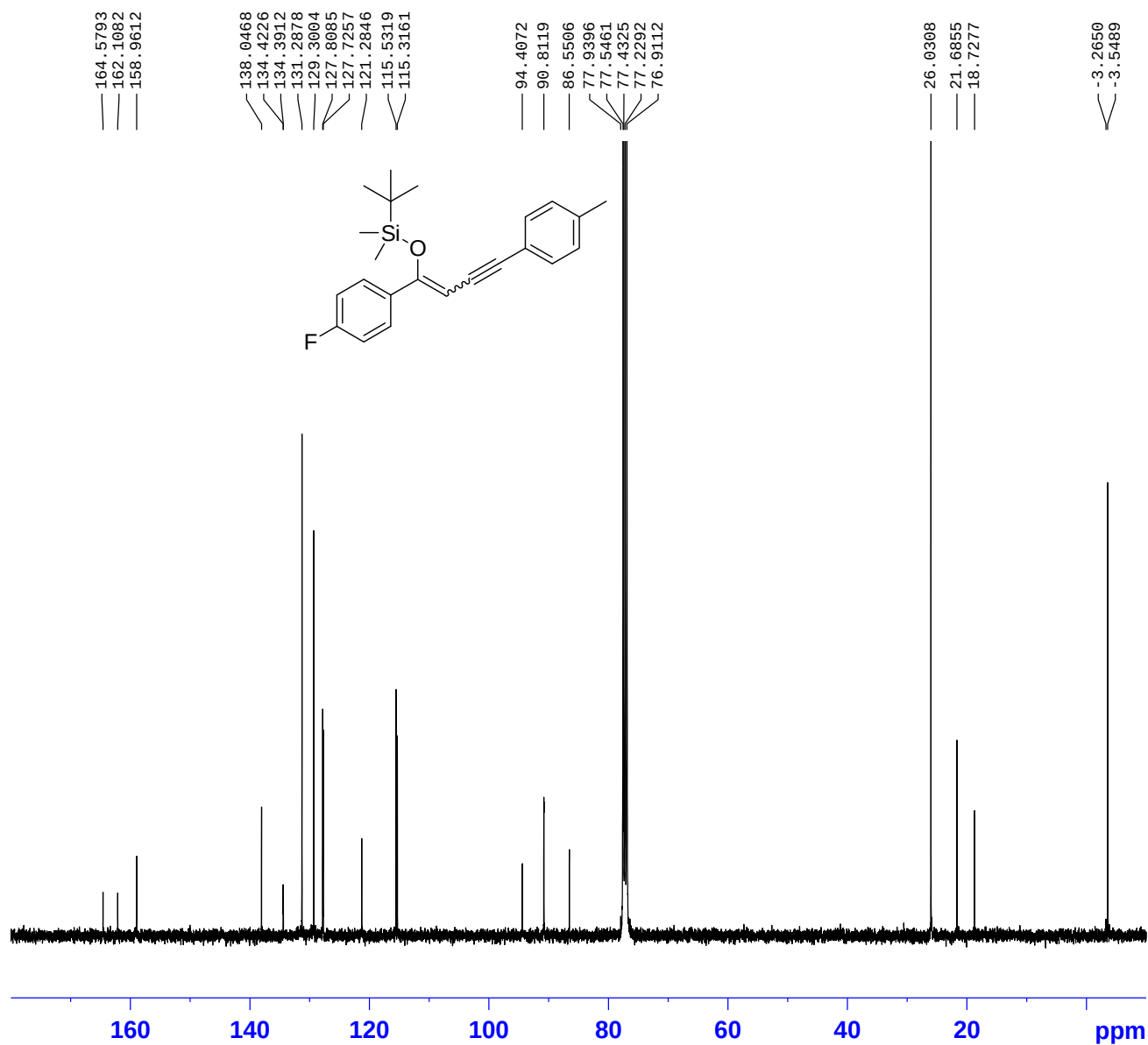
^1H NMR spectrum for **6c** (CDCl_3)



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D1 1.00000000 sec
TD0 1

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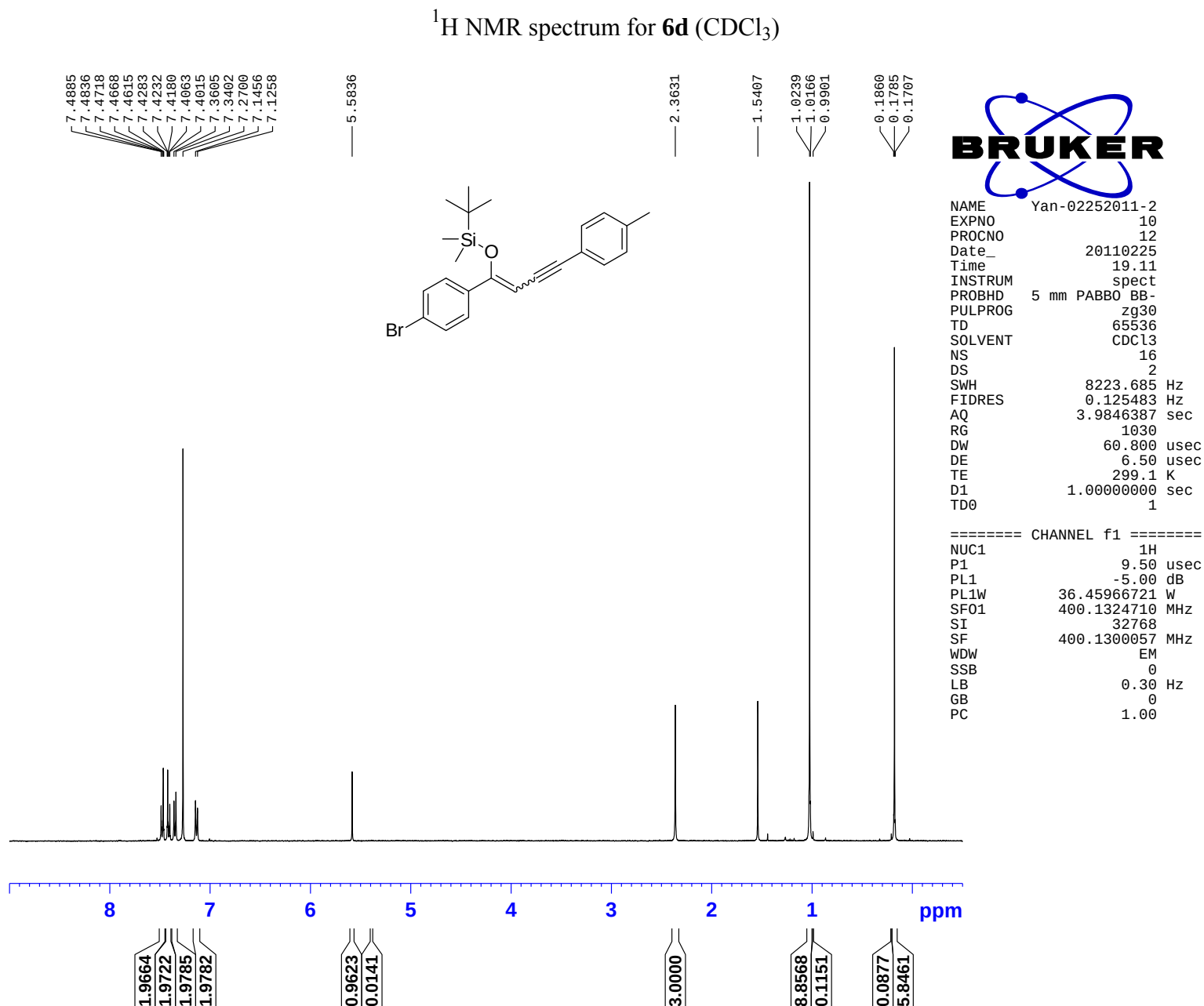
^{13}C NMR spectrum for **6c** (CDCl_3)

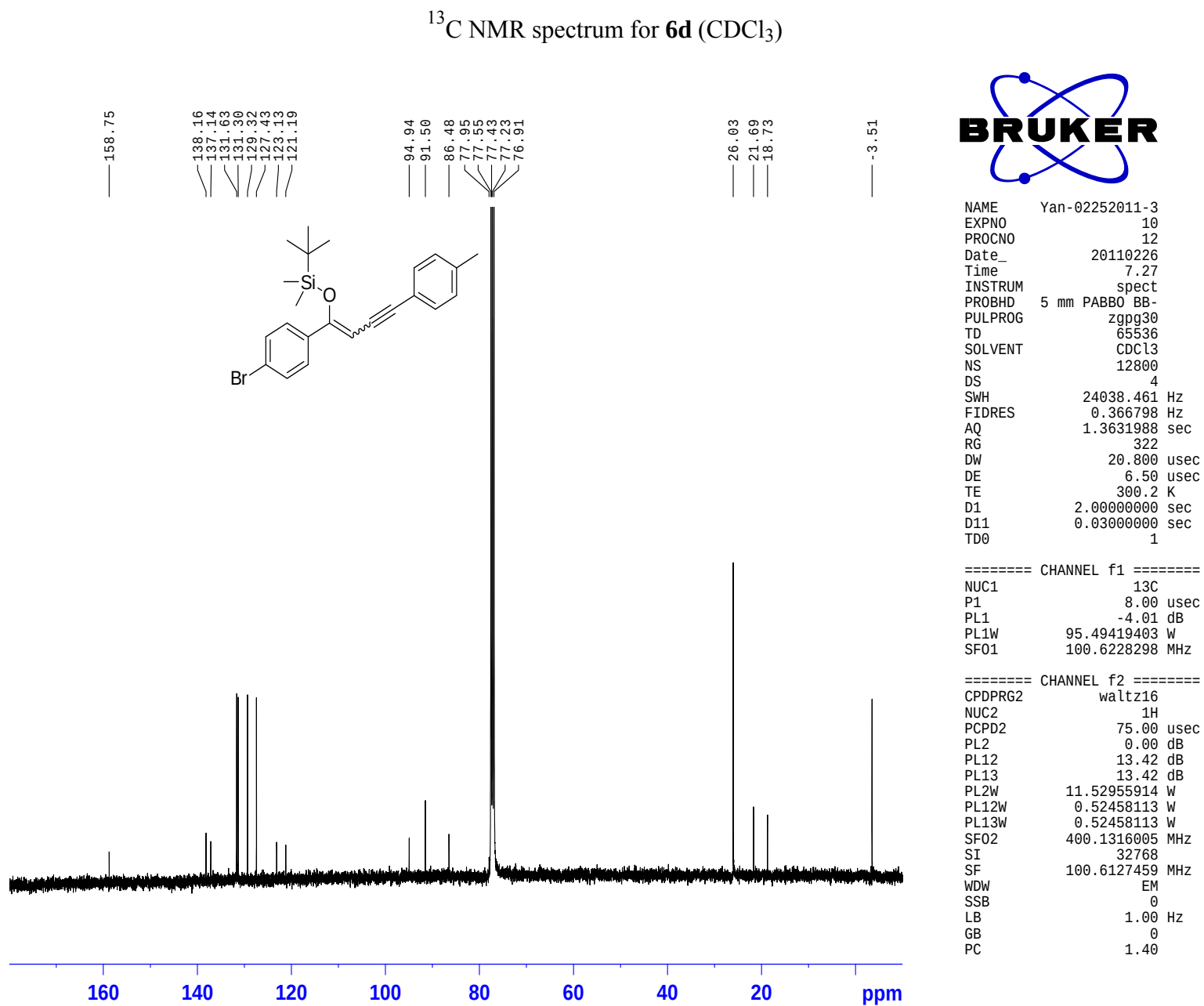


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FIDRES 0.366798 Hz
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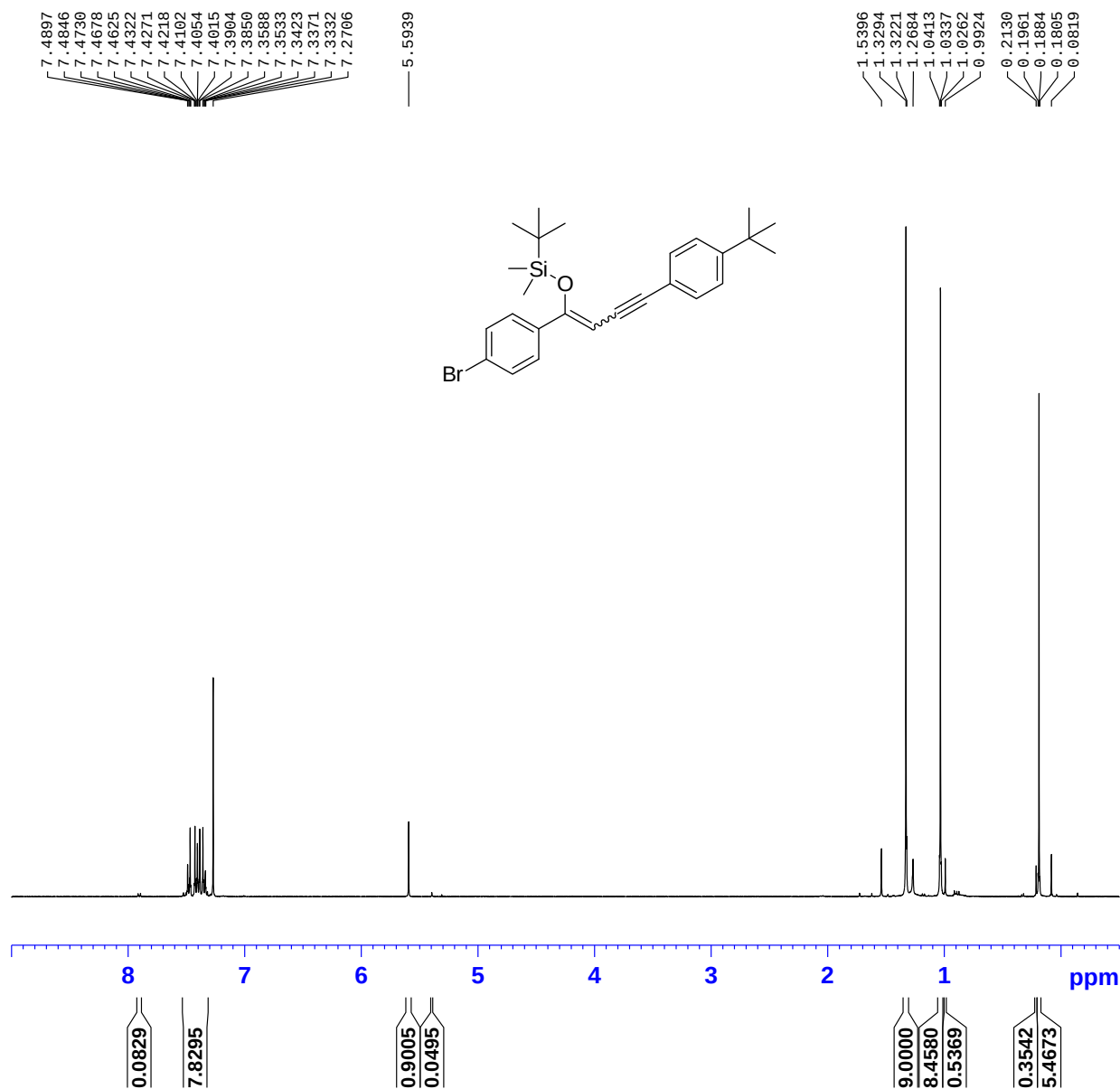
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PL13 13.42 dB
PL2W 11.52955914 W
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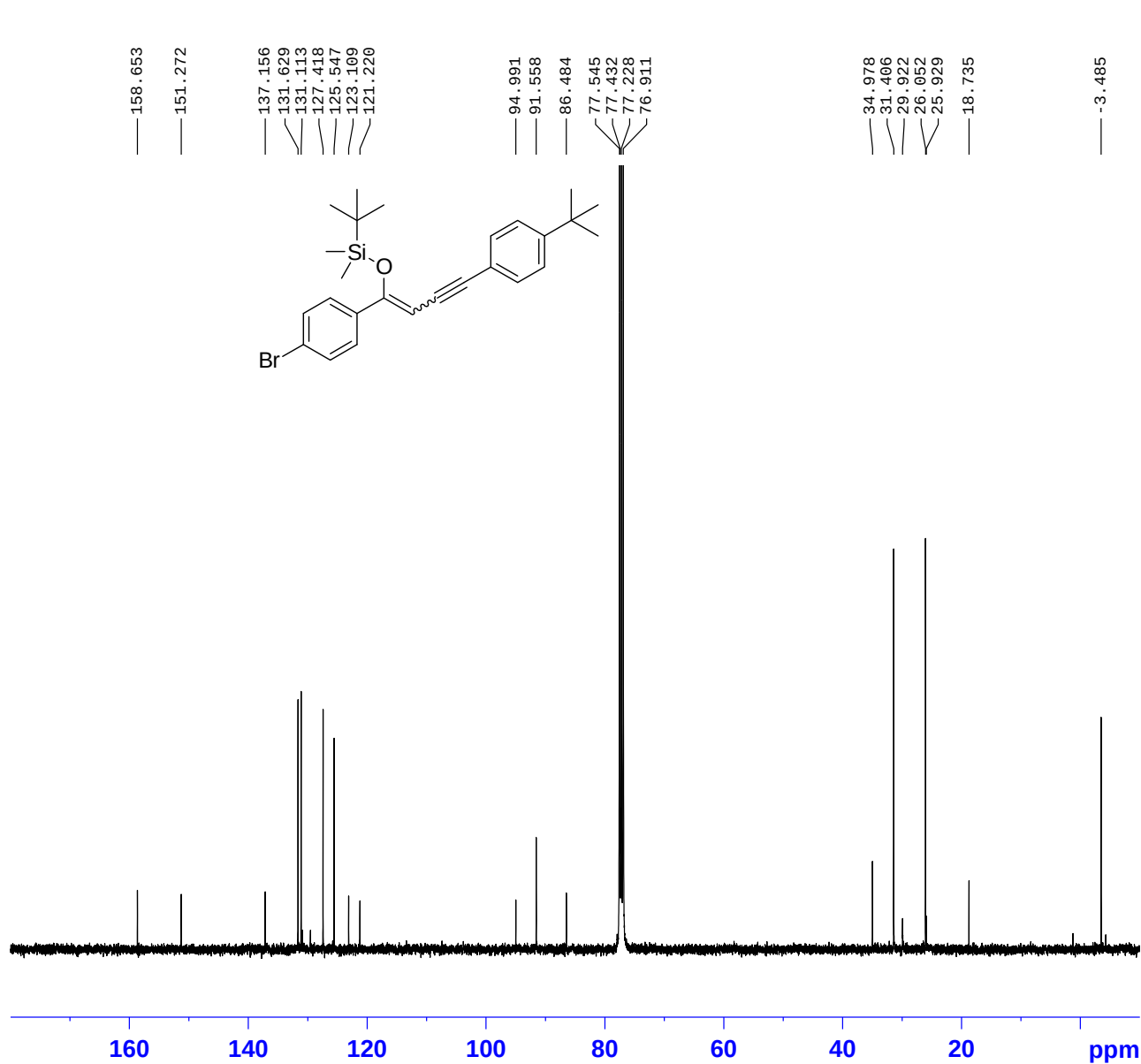
^1H NMR spectrum for **6e** (CDCl_3)



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PROCNO 12
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FIDRES 0.125483 Hz
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RG 645
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DE 6.50 usec
TE 299.3 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
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SF 400.1300057 MHz
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LB 0.30 Hz
GB 0
PC 1.00

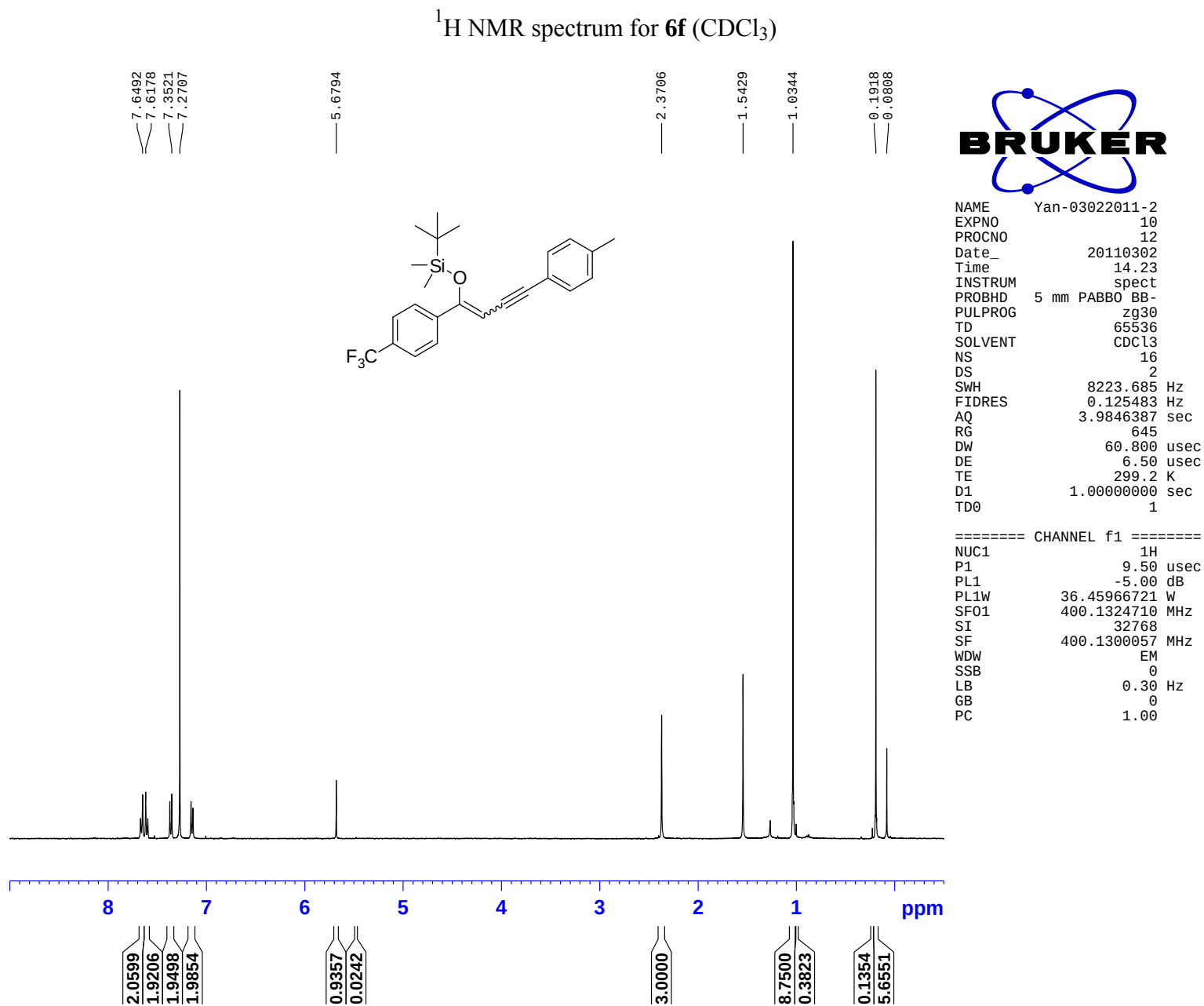
^{13}C NMR spectrum for **6e** (CDCl_3)

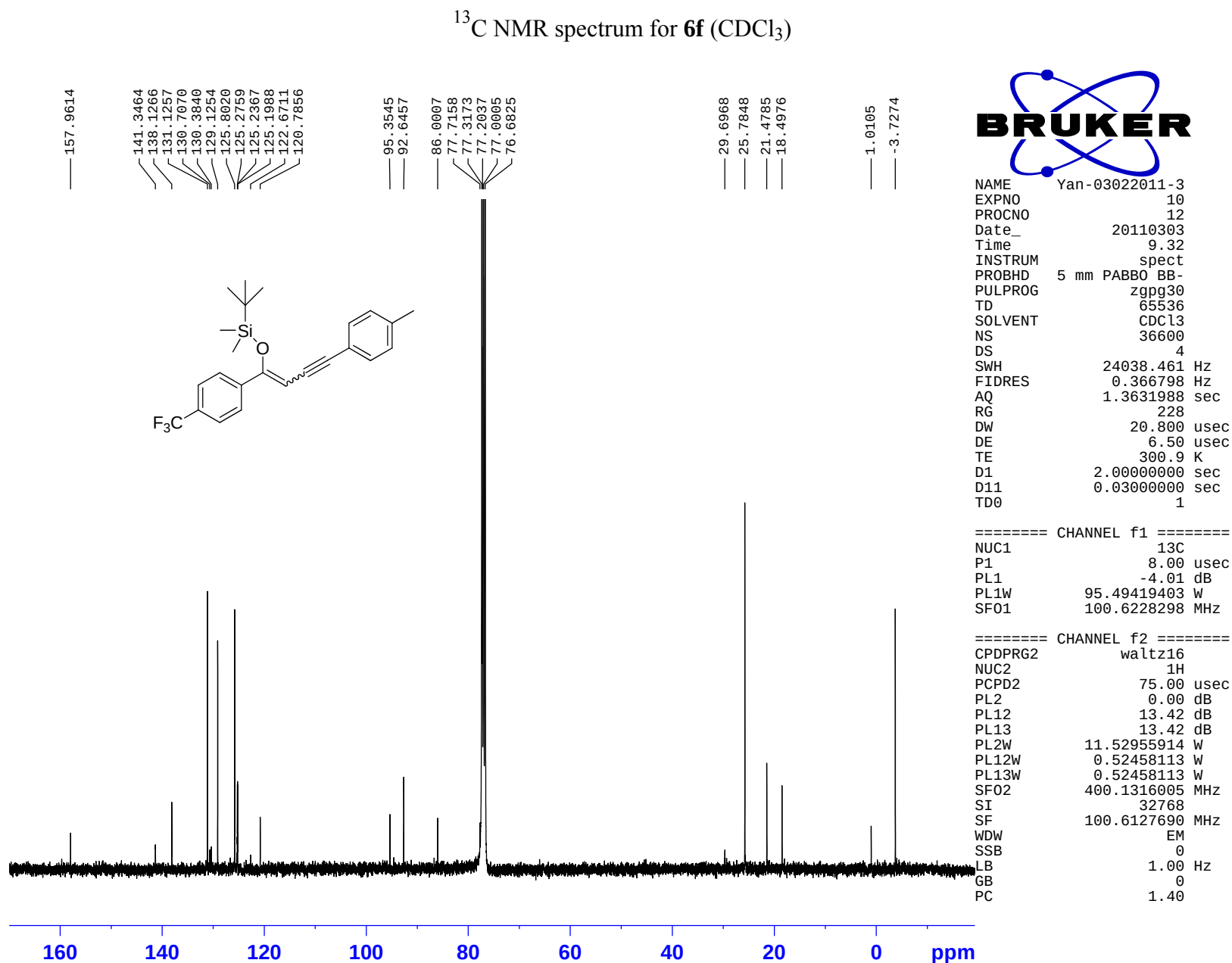


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FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 322
DW 20.800 usec
DE 6.50 usec
TE 301.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

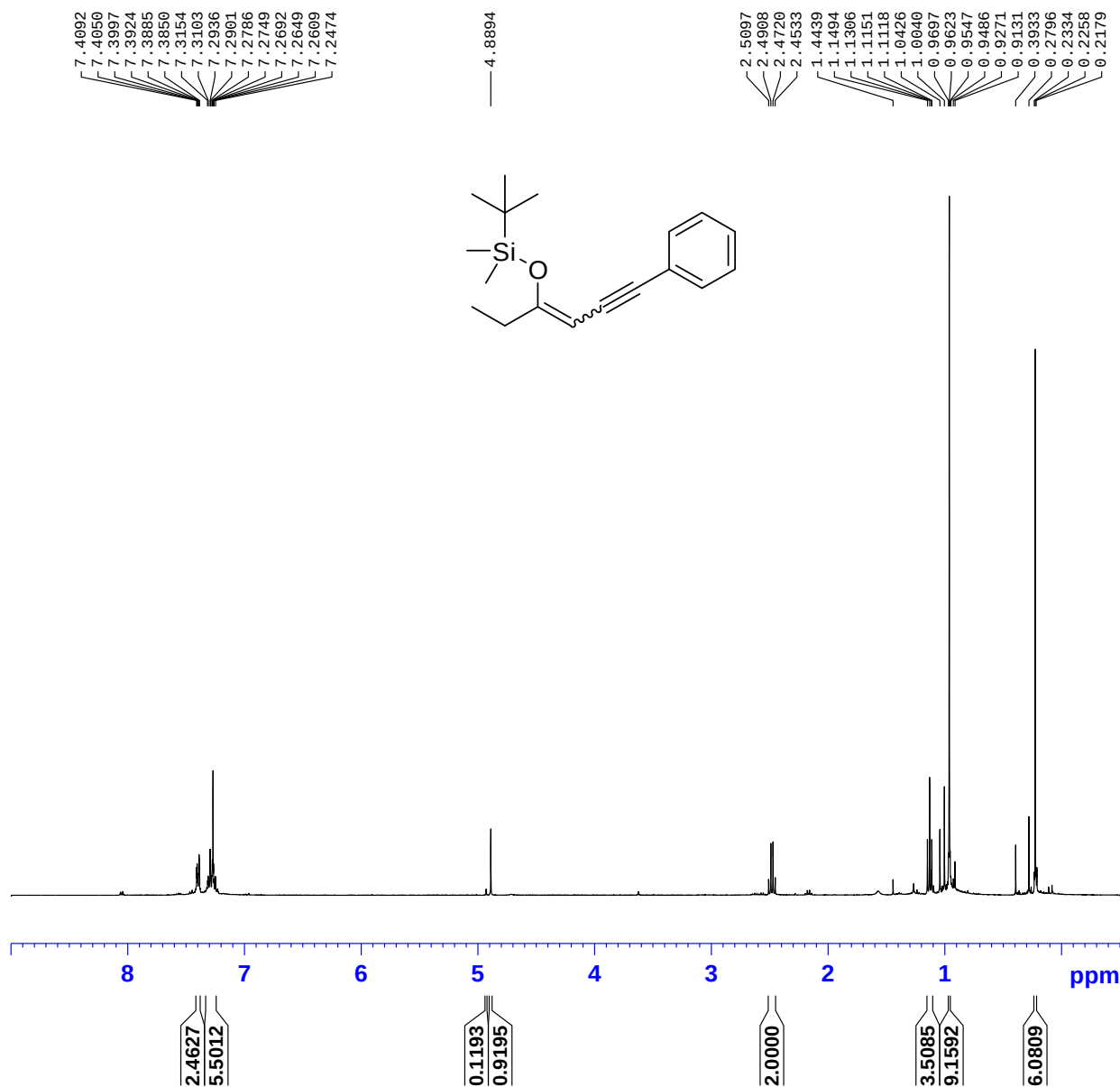
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P1 8.00 usec
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PL1W 95.49419403 W
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===== CHANNEL f2 =====
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NUC2 1H
PCPD2 75.00 usec
PL2 0.00 dB
PL12 13.42 dB
PL13 13.42 dB
PL2W 11.52955914 W
PL12W 0.52458113 W
PL13W 0.52458113 W
SF02 400.1316005 MHz
SI 32768
SF 100.6127461 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



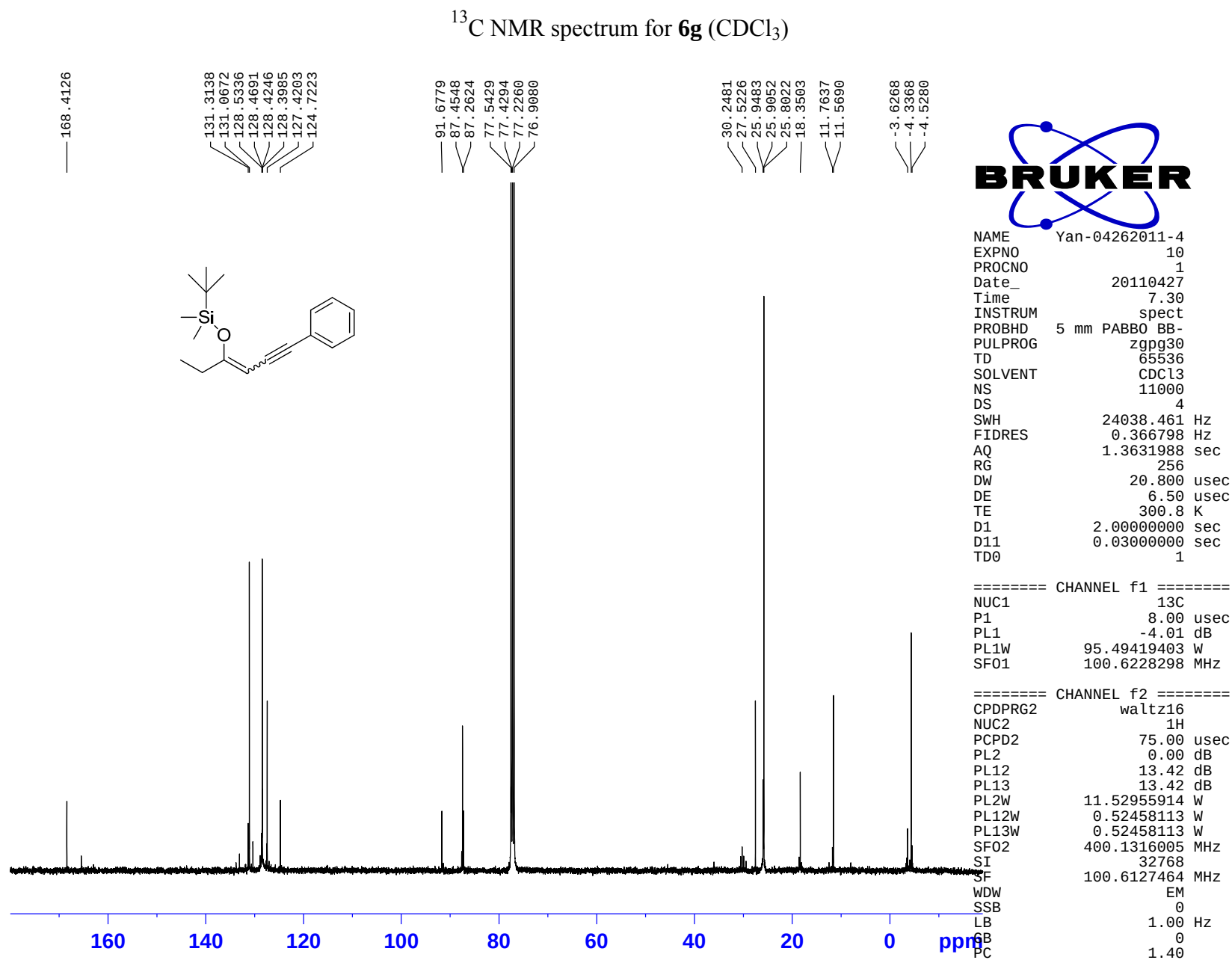


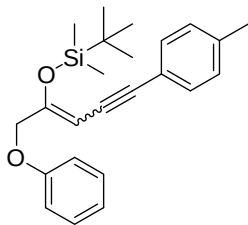
^1H NMR spectrum for **6g** (CDCl_3)



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SOLVENT CDCl_3
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DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 287
DW 60.800 usec
DE 6.50 usec
TE 299.4 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 ^1H
P1 9.50 usec
PL1 -5.00 dB
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WDW EM
SSB 0
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GB 0
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[illegible]

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FIDRES        0.125483 Hz
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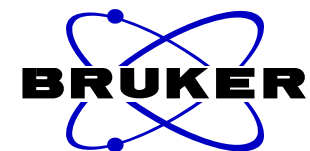
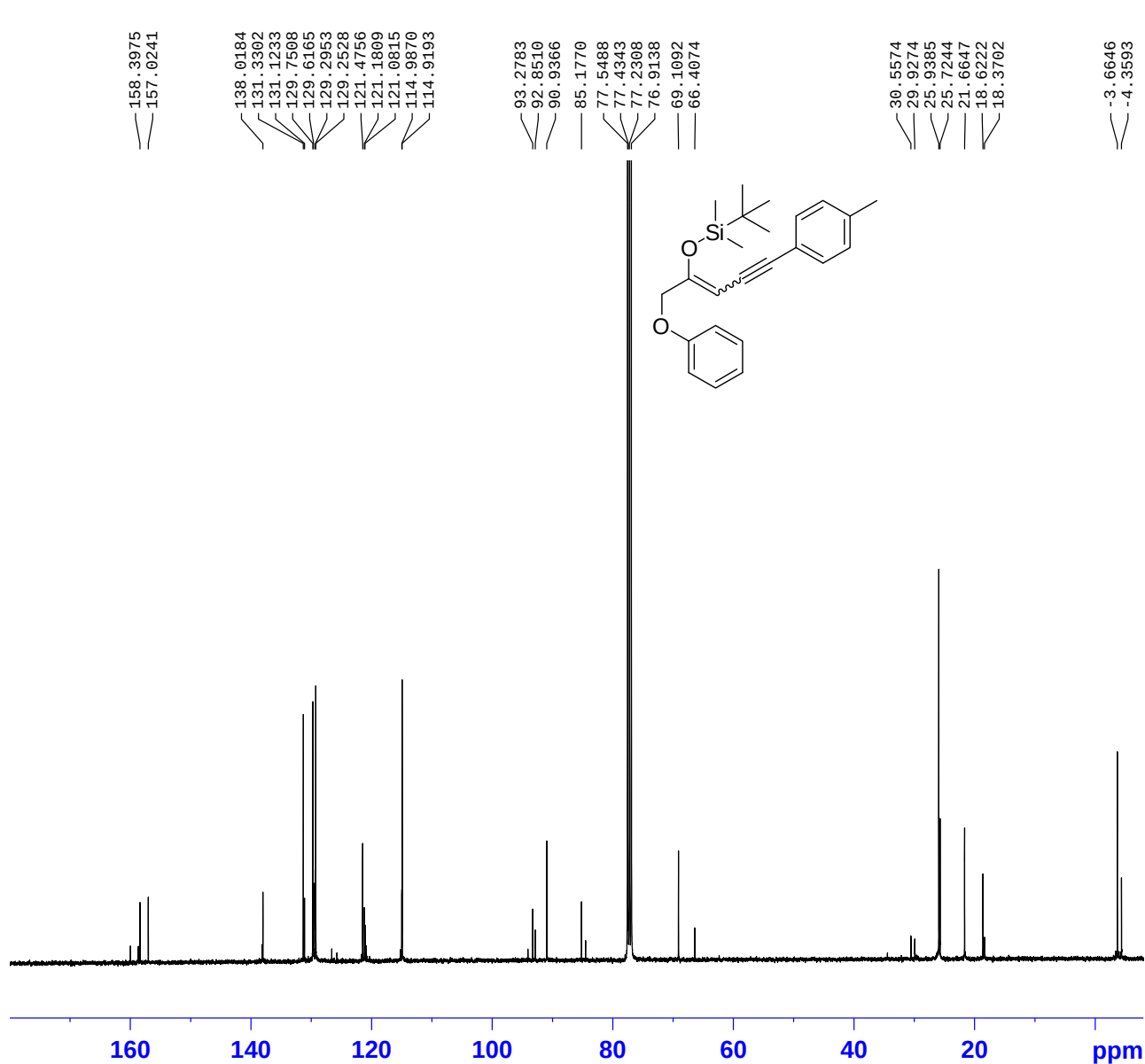
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SI                  32768
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WDW                 EM
SSB                  0
LB                   0.30 Hz
GB                   0
PC                   1.00

```


^{13}C NMR spectrum for **6h** (CDCl_3)

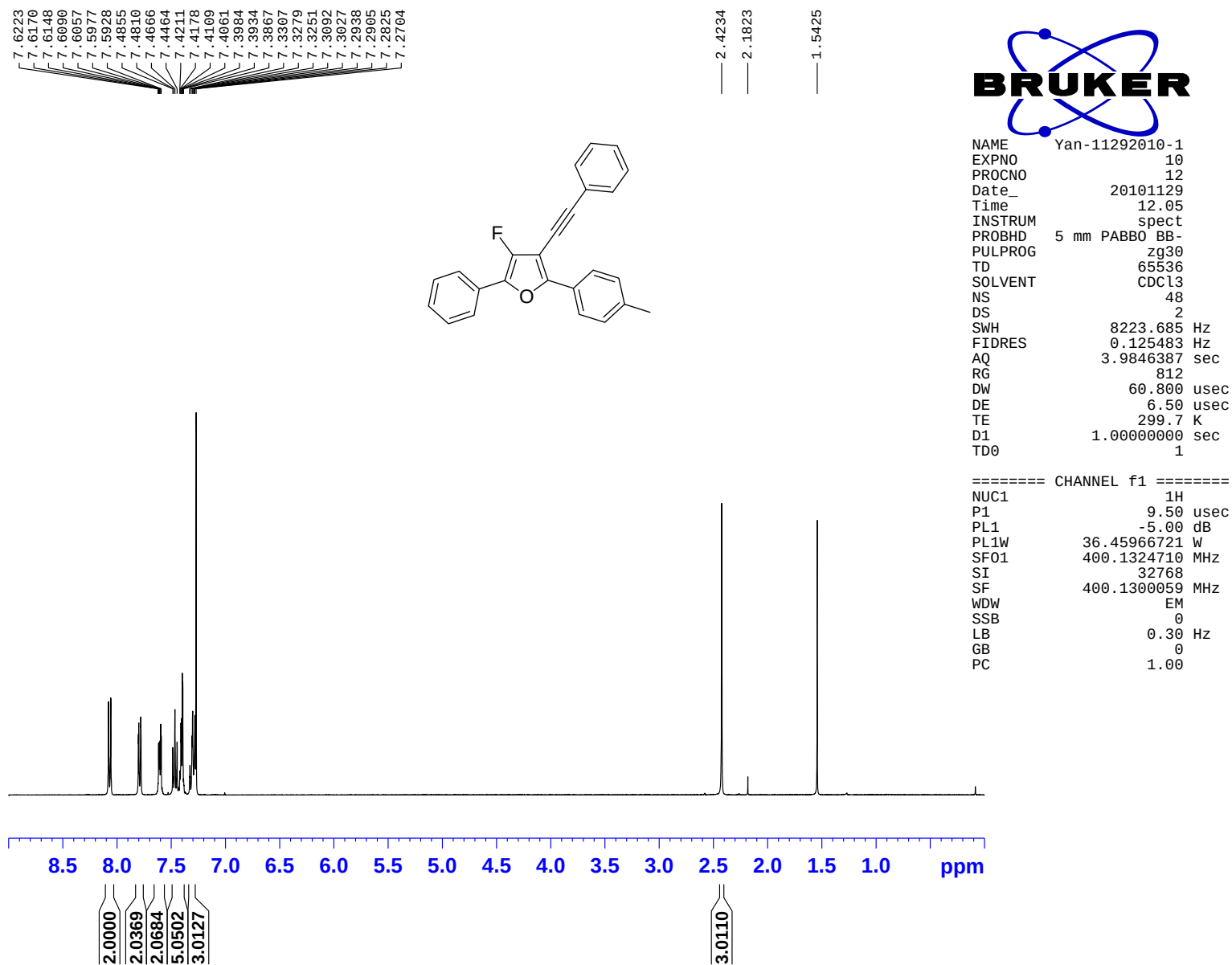


NAME Yan-04082011-2
EXPNO 10
PROCNO 1
Date_ 20110408
Time 9.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl_3
NS 8000
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 256
DW 20.800 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

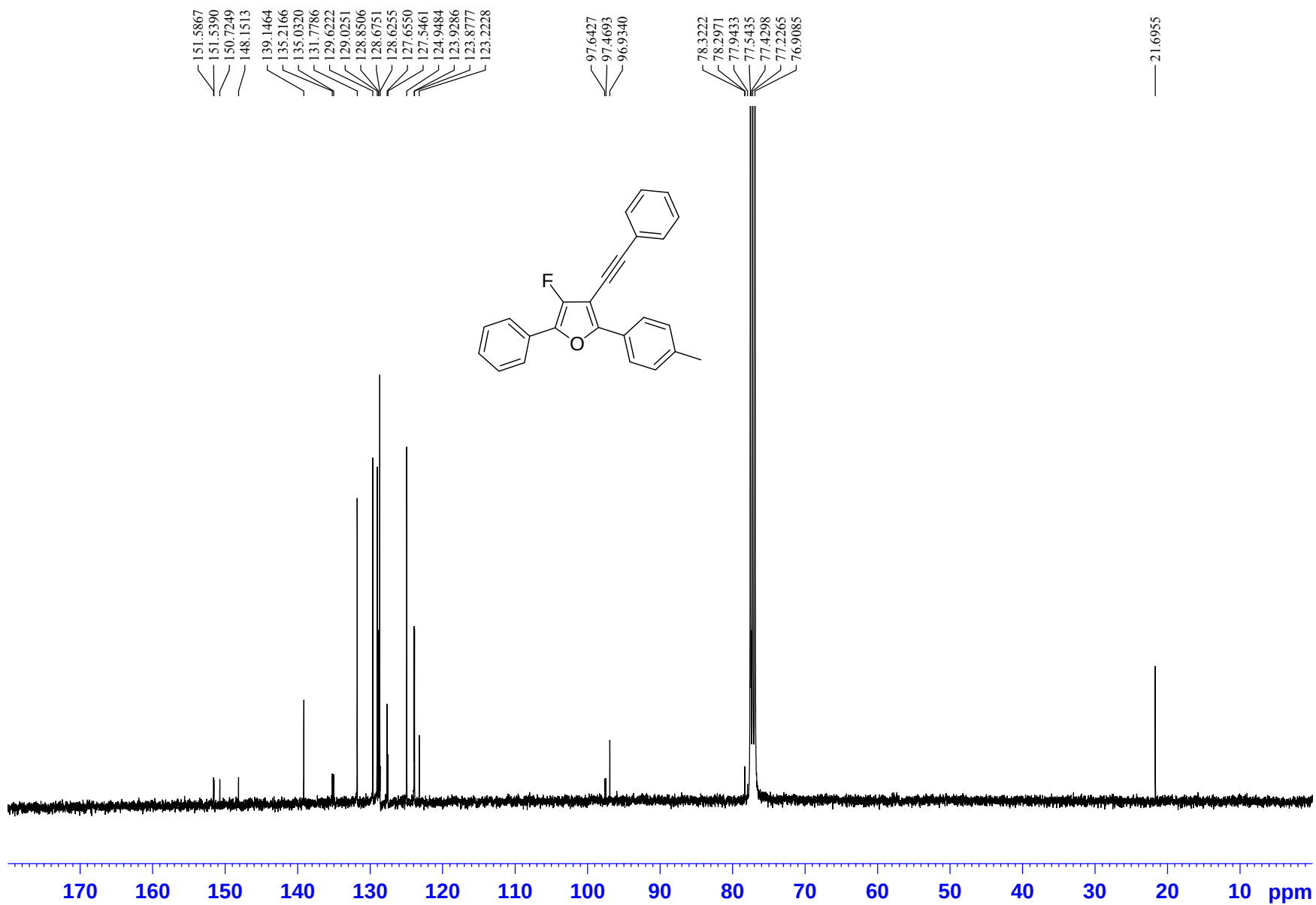
===== CHANNEL f1 =====
NUC1 ^{13}C
P1 8.00 usec
PL1 -4.01 dB
PL1W 95.49419403 W
SF01 100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ^1H
PCPD2 75.00 usec
PL2 0.00 dB
PL12 13.42 dB
PL13 13.42 dB
PL2W 11.52955914 W
PL12W 0.52458113 W
PL13W 0.52458113 W
SF02 400.1316005 MHz
SI 32768
SF 100.6127468 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

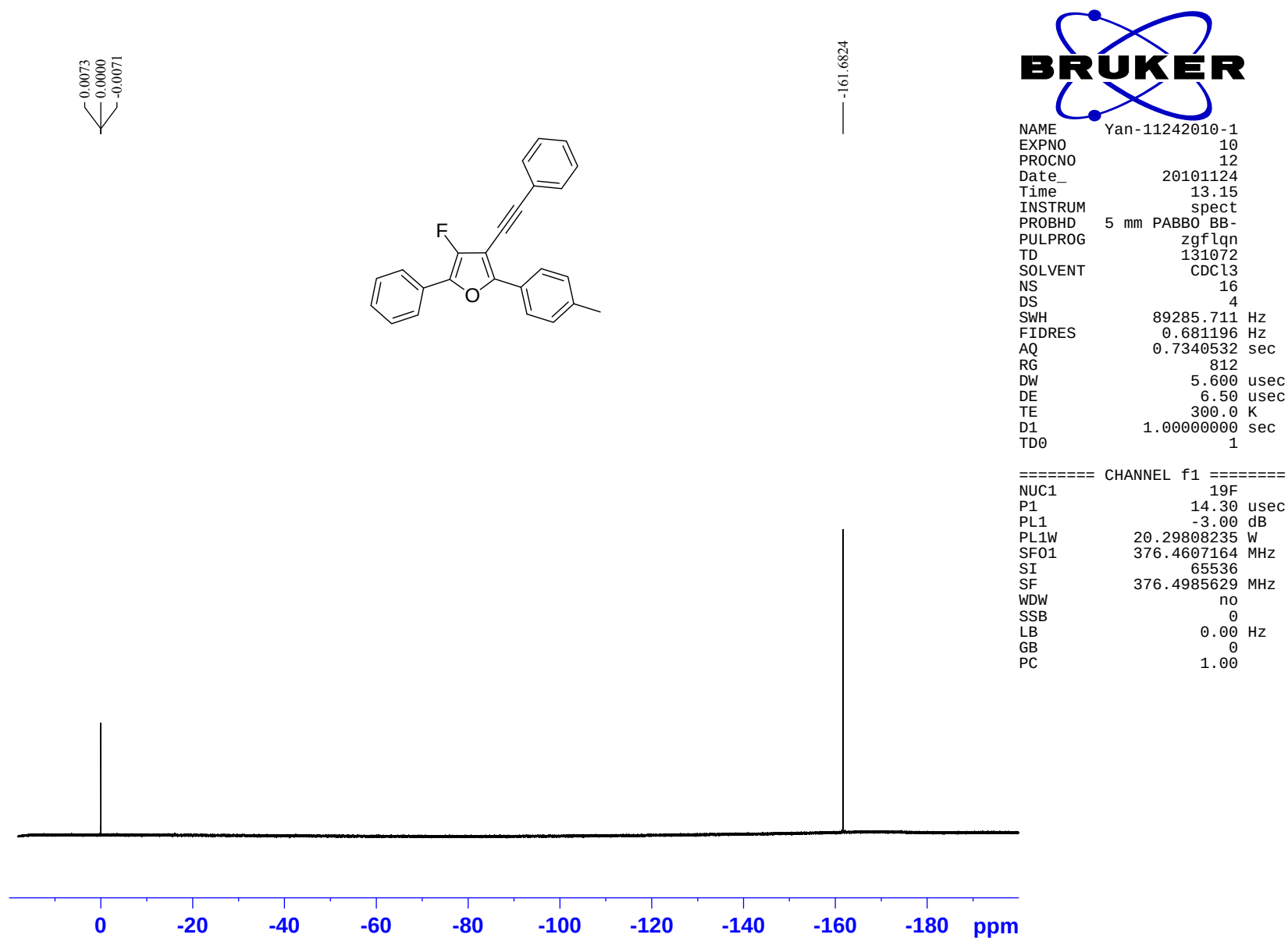
^1H NMR spectrum for **10** (CDCl_3)



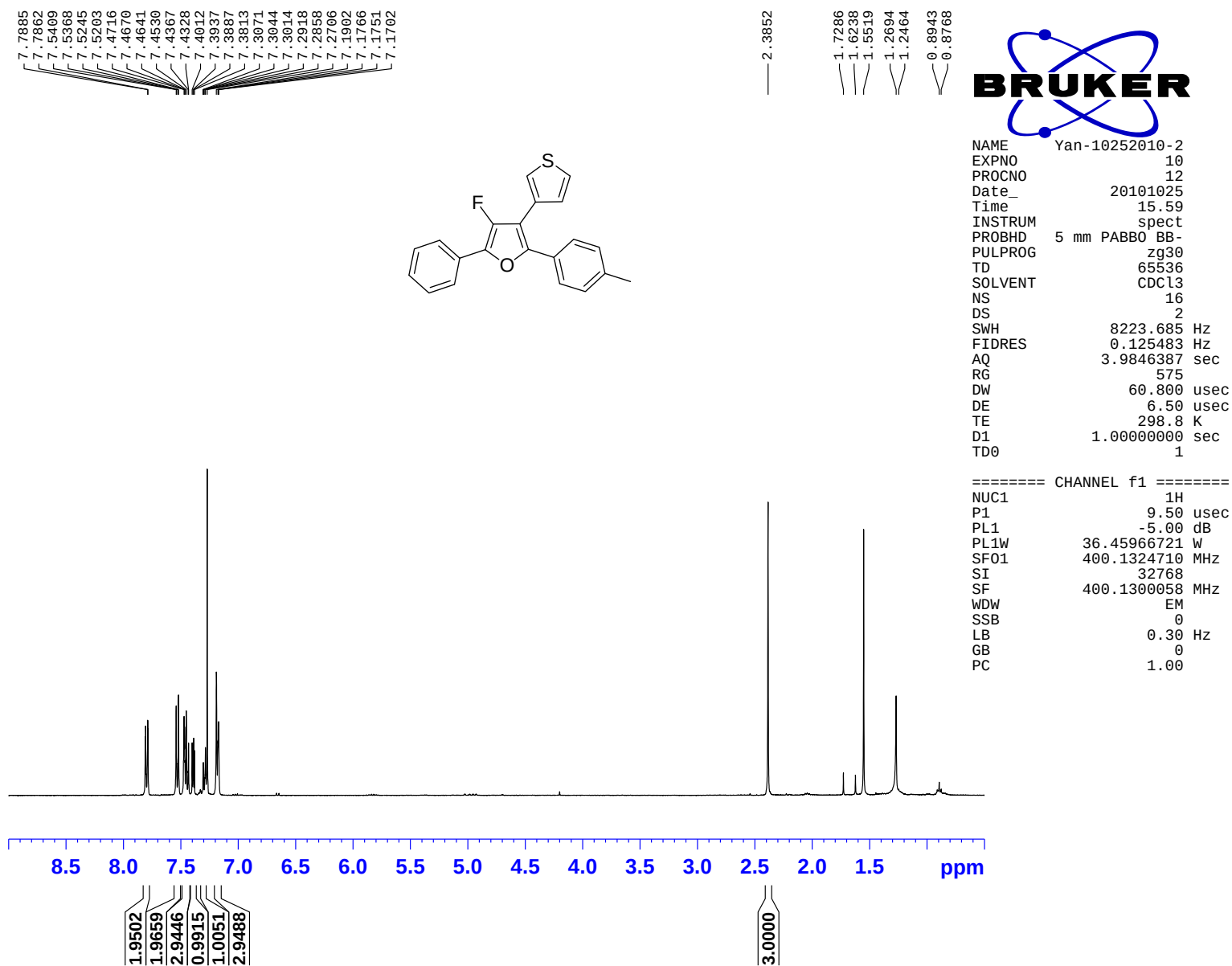
^{13}C NMR spectrum for **10** (CDCl_3)



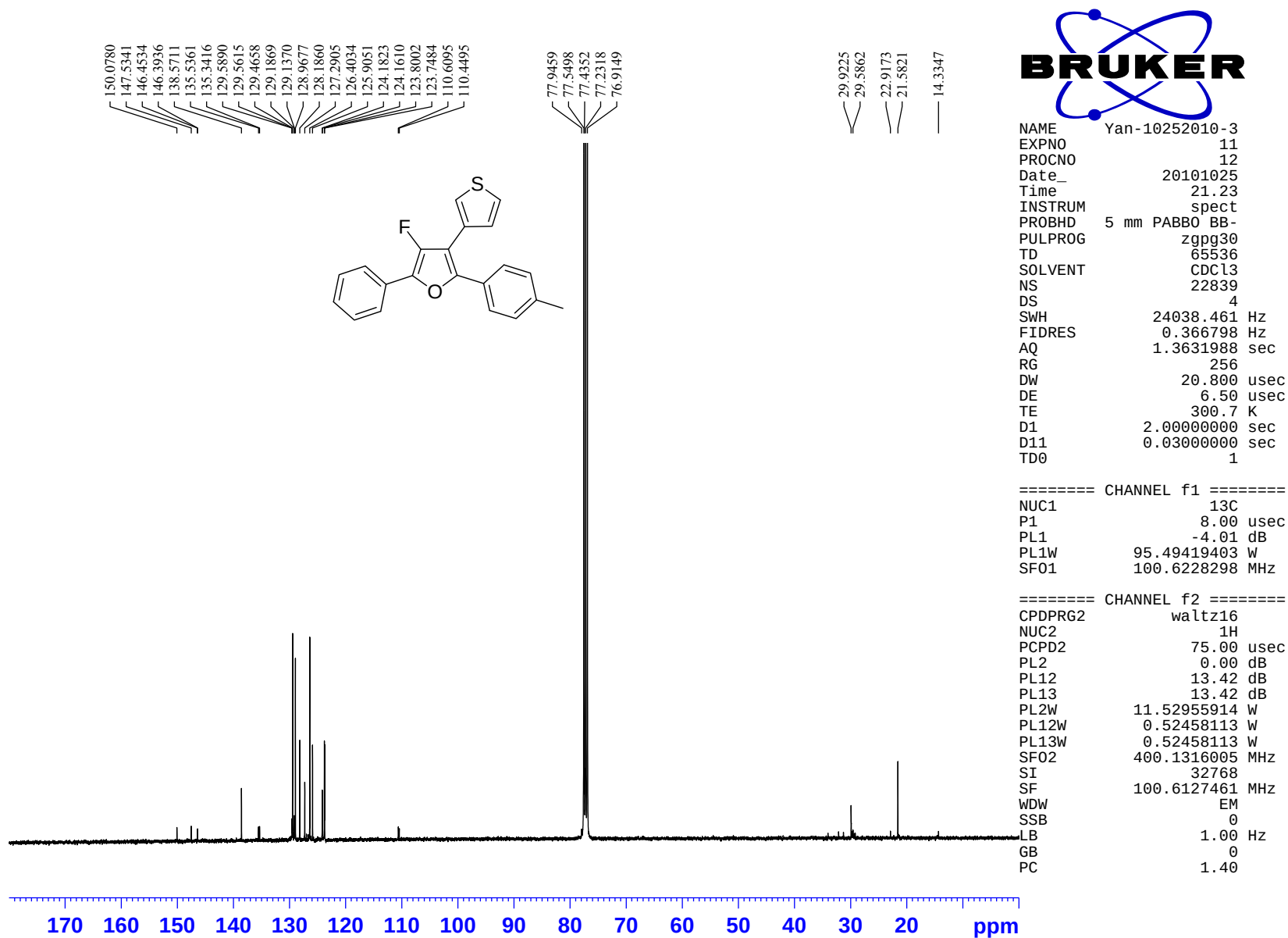
^{19}F NMR spectrum for **10** (CDCl_3)



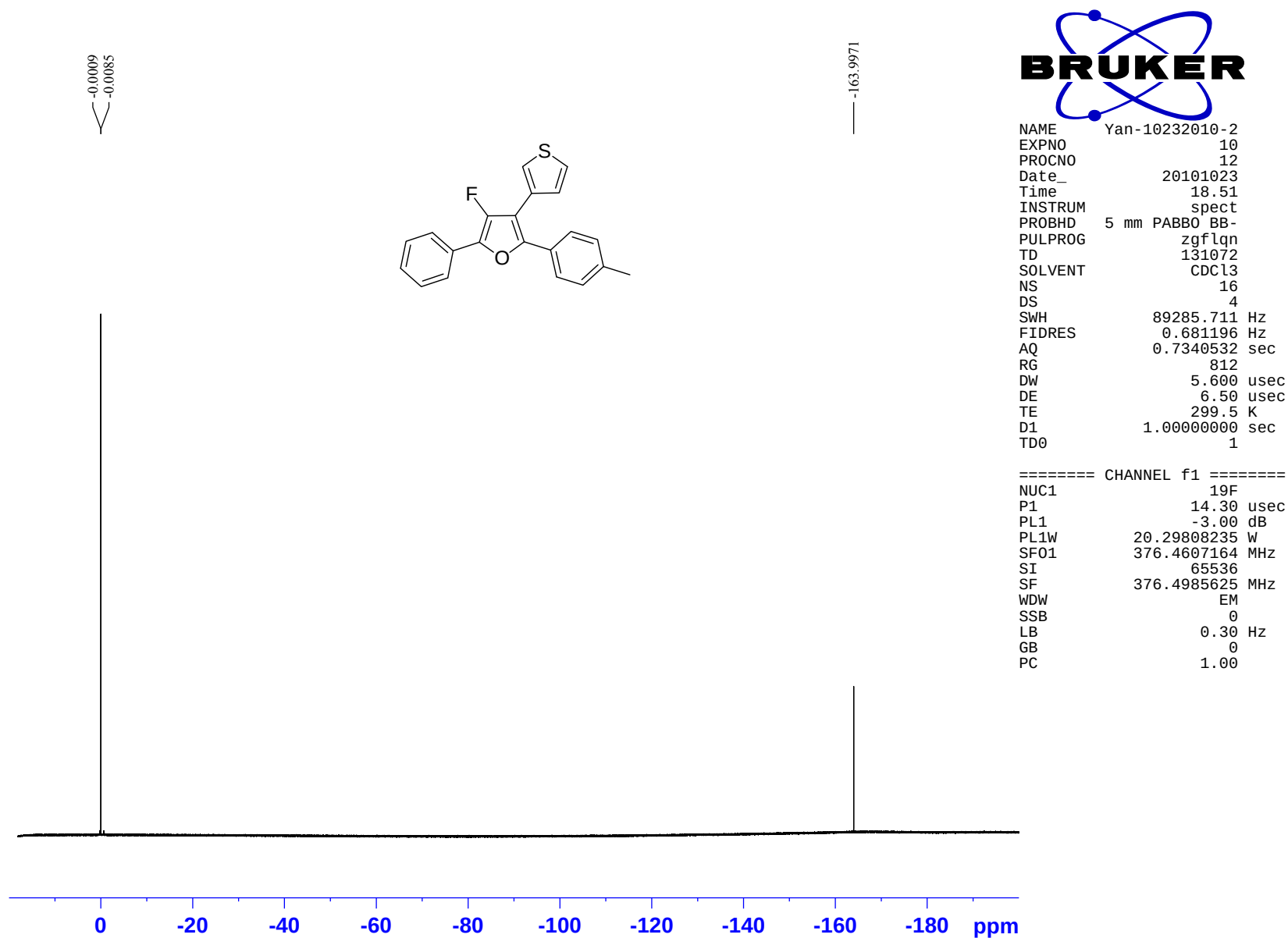
^1H NMR spectrum for **11** (CDCl_3)

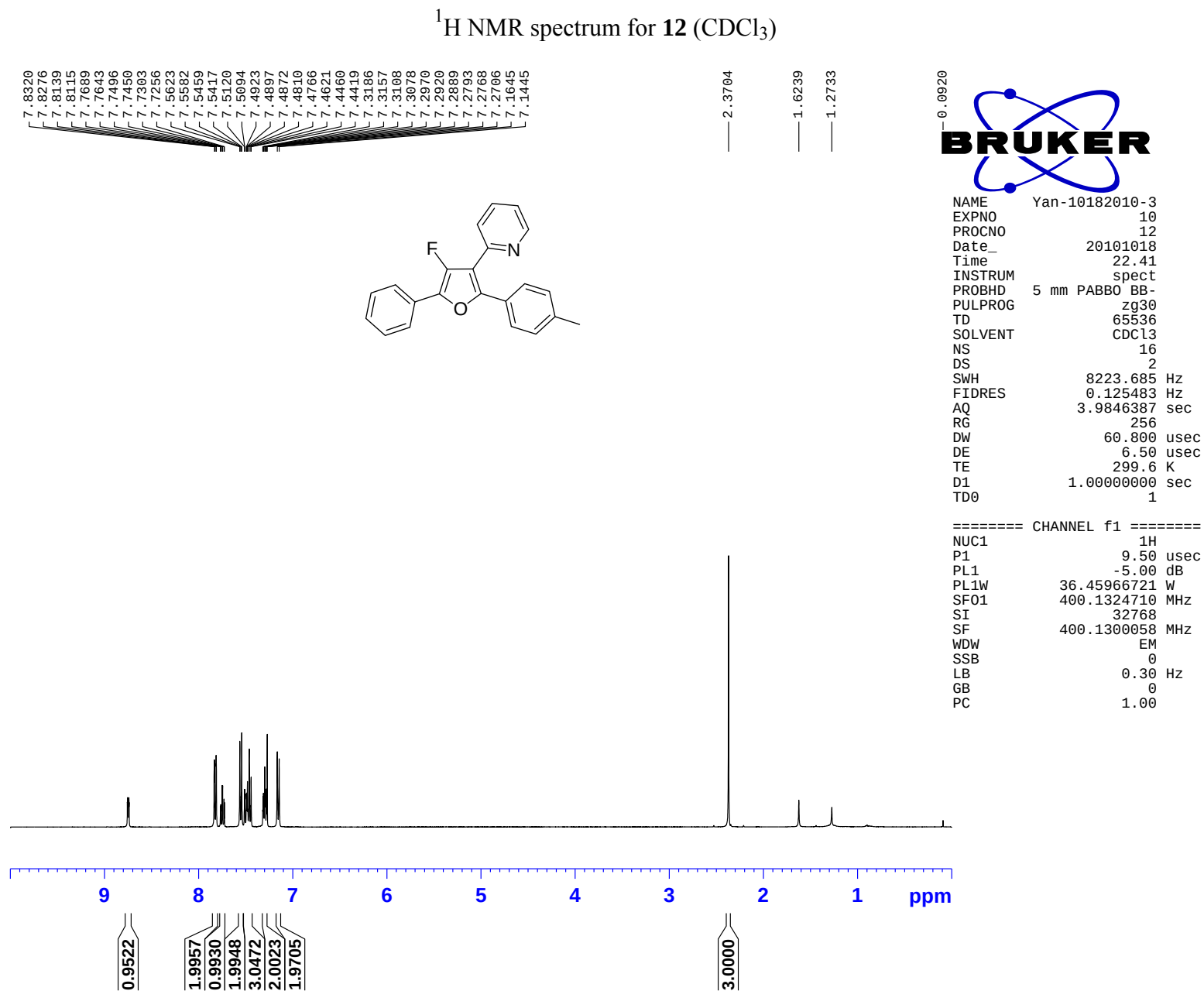


^{13}C NMR spectrum for **11** (CDCl_3)

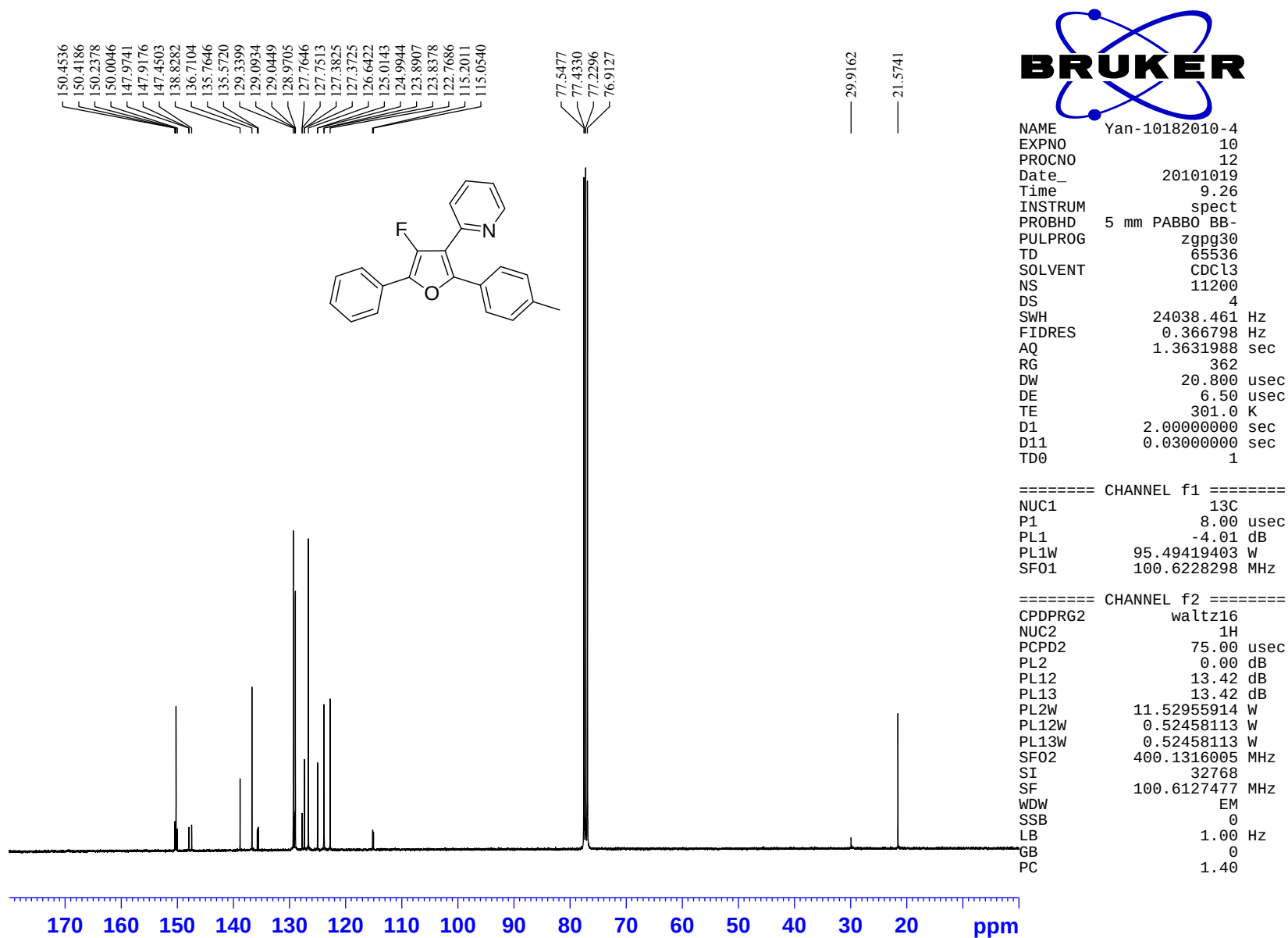


^{19}F NMR spectrum for **11** (CDCl_3)

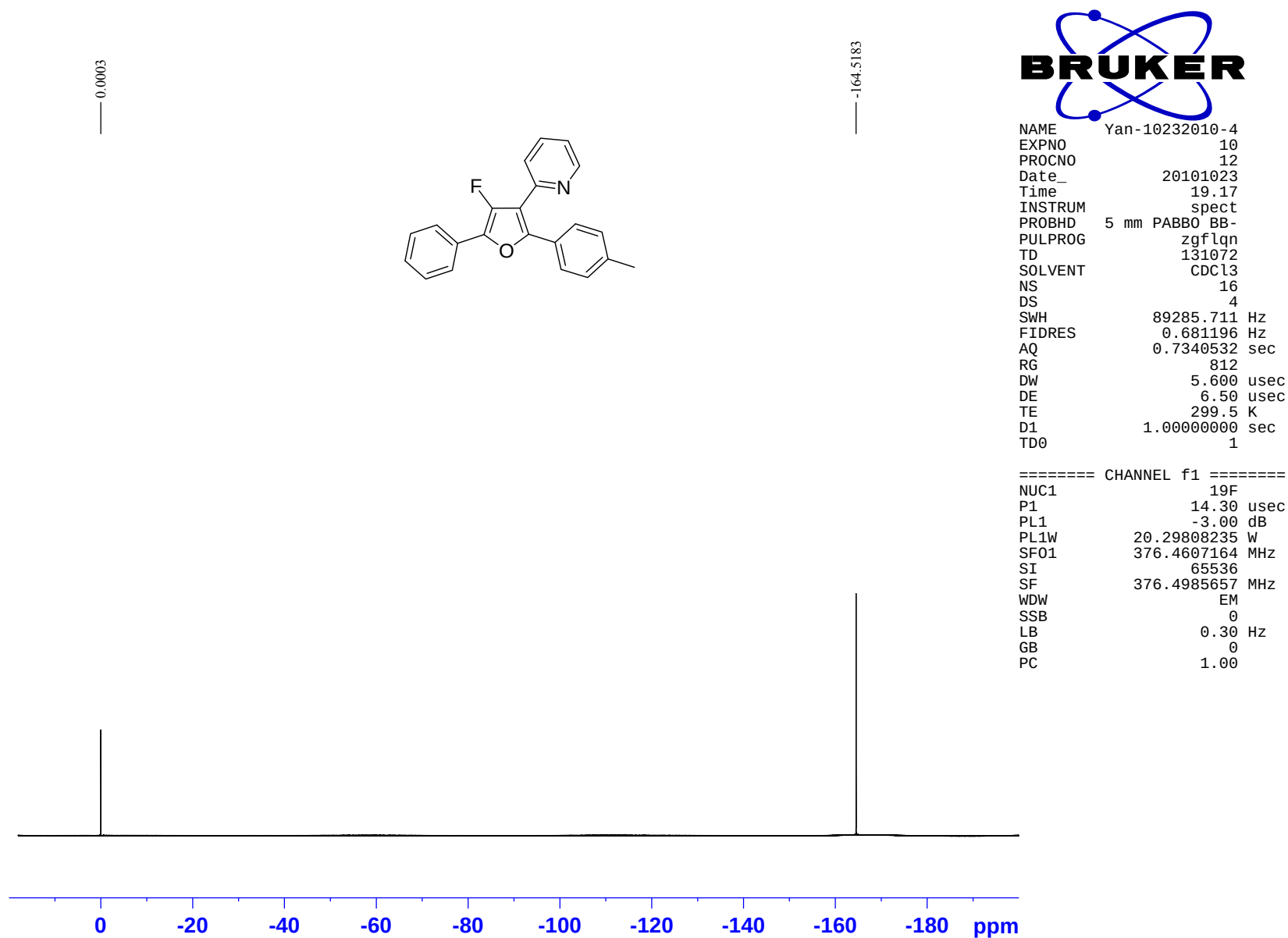




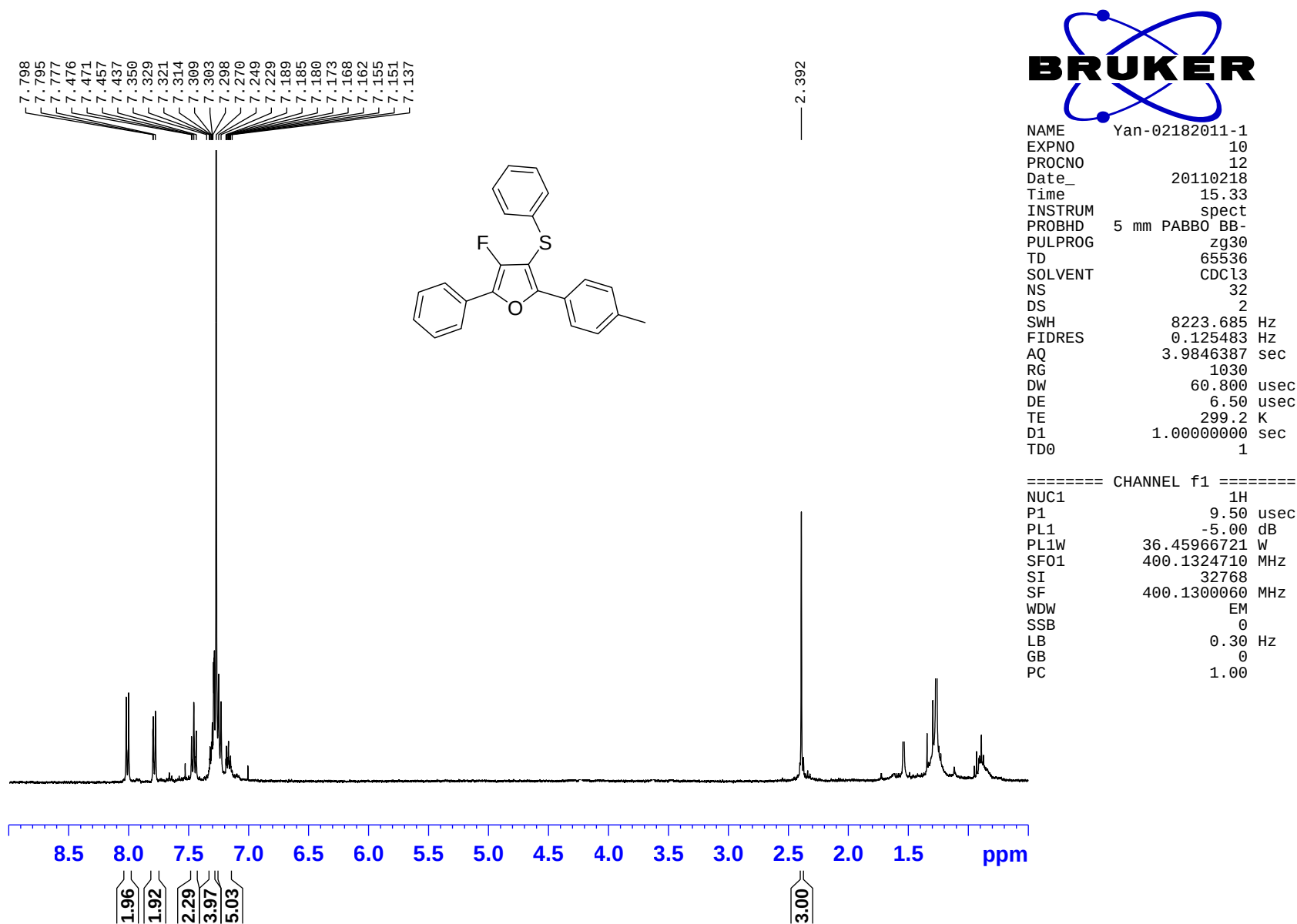
^{13}C NMR spectrum for **12** (CDCl_3)

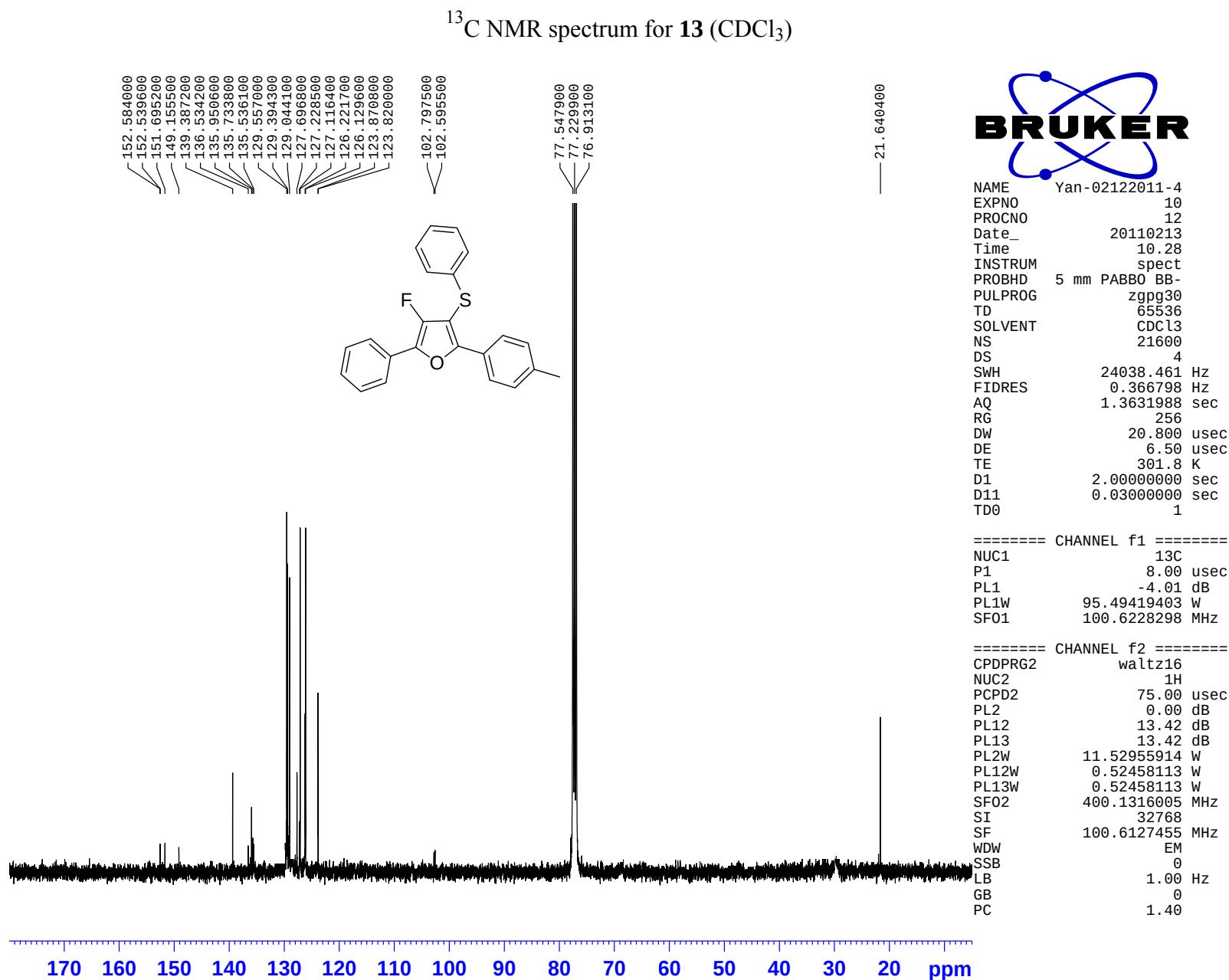


^{13}F NMR spectrum for **12** (CDCl_3)

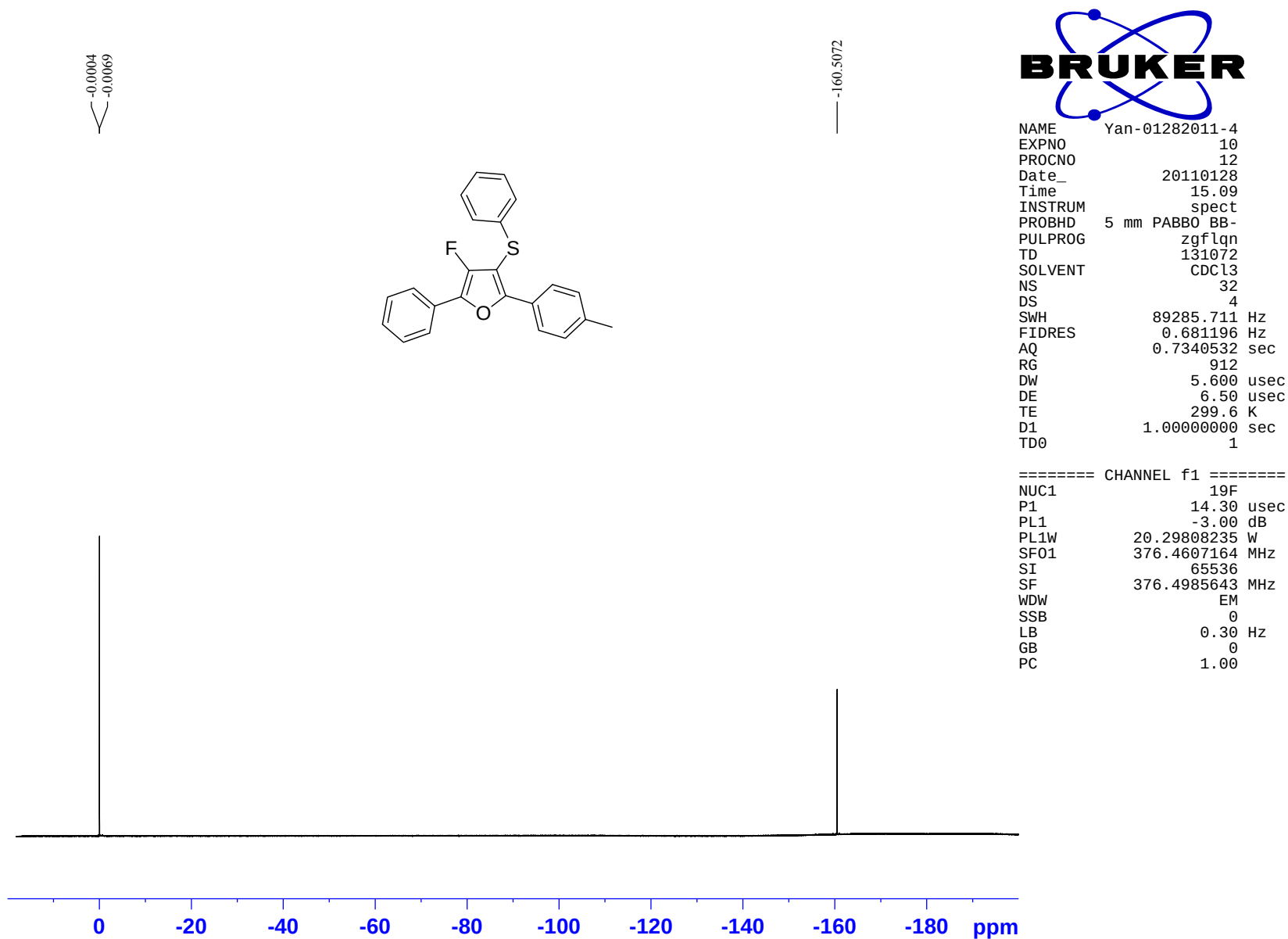


^1H NMR spectrum for **13** (CDCl_3)

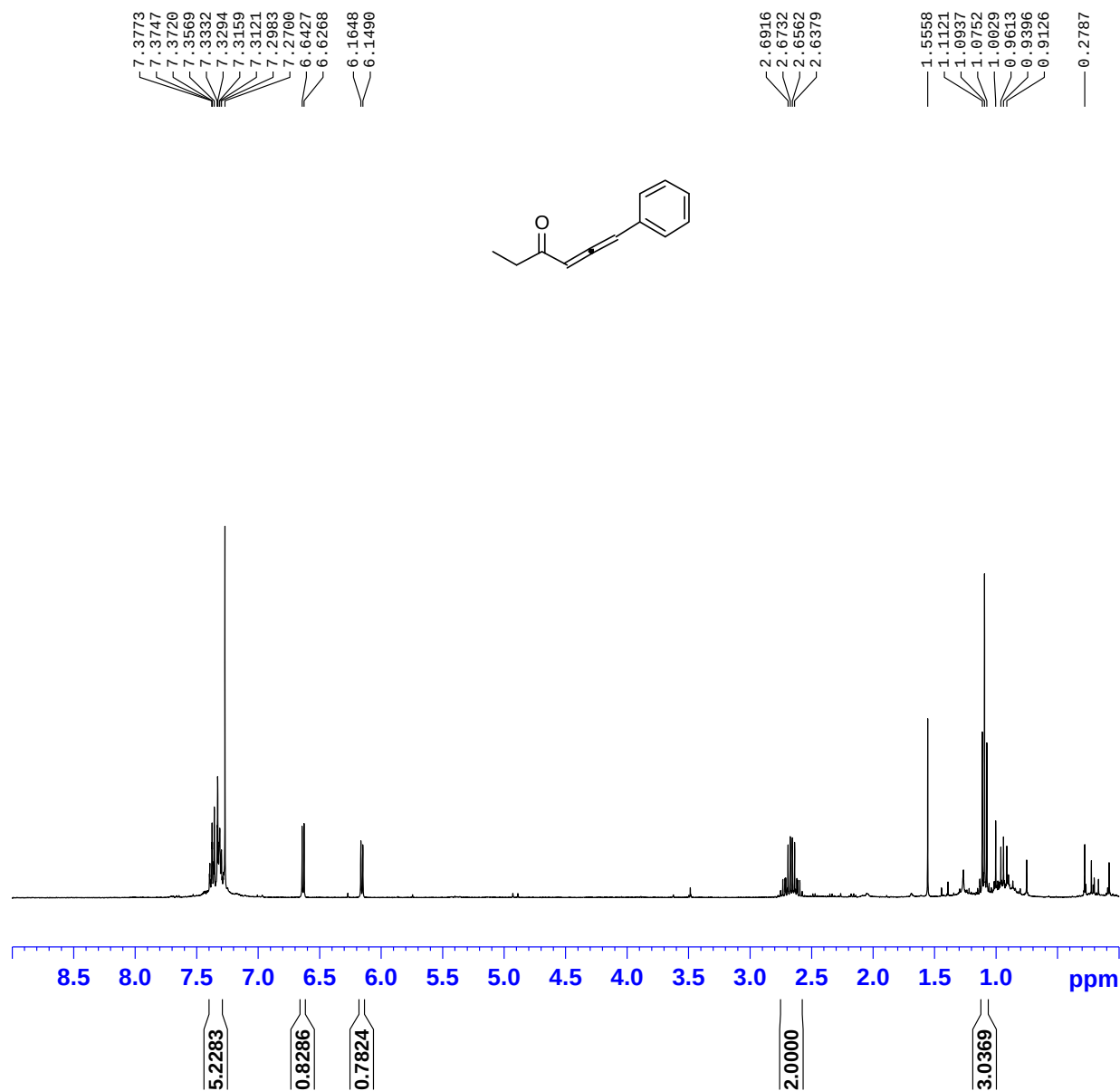




^{19}F NMR spectrum for **13** (CDCl_3)



^1H NMR spectrum for **Allenylketone** (CDCl_3)



NAME Yan-04062011-1
EXPNO 10
PROCNO 1
Date_ 20110406
Time 1.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl_3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 362
DW 60.800 usec
DE 6.50 usec
TE 298.5 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 ^1H
P1 9.50 usec
PL1 -5.00 dB
PL1W 36.45966721 W
SF01 400.1324710 MHz
SI 32768
SF 400.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR spectrum for **Allenylketone** (CDCl_3)

