Supplementary Material (ESI) for Chemical Communications

Copper-Catalyzed Hydride Transfer from $LiAlH_4$ for the Formation of Alkylidenecyclopropane Derivatives

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Supporting Information

General Remarks:

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were analytical grade. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was carried out using silica gel Grace (particle size 0.040- 0.063 mm).

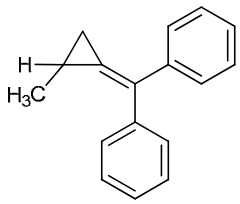
^{1}H NMR, ^{13}C NMR were recorded on a Bruker AV 300 spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated as *bs* (broadened singlet), *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet); coupling constants (*J*) are in Hertz (Hz).

General Procedure for the Preparation of Alkylidenecyclo-propane Derivatives:

1 mmol of cyclopropenylcarbinol **3** was added to a dry three necked flask containing 0.2 mmol of CuI in 20 mL of dry ether. The temperature was lowered to -50 ^{o}C and 1.0 mL of 1M solution of $LiAlH_4$ in THF was added.

The reaction mixture was heated slowly to room temperature over night. After quenching with an aqueous saturated solution of ammonium chloride, the aqueous layer was extracted with ether (3×20 mL), the organic phases were combined and washed with brine (1×20 mL), separated, dried and evaporated. The crude product was purified by column chromatography, eluent: hexane.

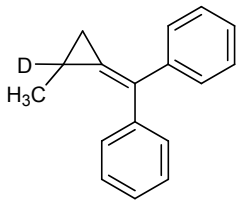
1,1-Diphenylmethylene-2-methylcyclopropane 6a:



6a

Colorless oil isolated in 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (*dd*, J_1 = 9.0 Hz, J_2 = 9.0 Hz 1H), 1.23 (*d*, *J* = 6.0 Hz, 3H), 1.56 (*dd*, J_1 = 9.0 Hz, J_2 = 5.9 Hz 1H), 1.71-1.80 (*m*, 1H), 7.20-7.49 (*m*, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.7, 11.1, 17.7, 126.7, 126.8, 128.0, 128.3, 128.3, 131.2, 140.8.

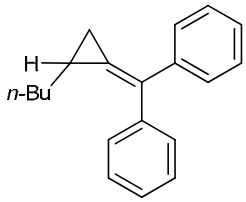
1,1-Diphenylmethylene-2-deuterio-2-methylcyclopropane 6a(D):



6a(D)

Colorless oil isolated in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (*d*, *J* = 9.3 Hz, 1H), 1.18 (*s*, 3H), 1.51 (*d*, *J* = 9.0 Hz, 1H), 7.19-7.40 (*m*, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.7, 11.1, 17.7, 126.7, 126.8, 128.0, 128.3, 128.3, 131.2, 140.9.

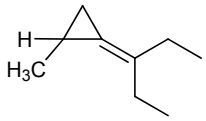
1,1-Diphenylmethylene-2-butylcyclopropane 6b:



6b

Colorless oil isolated in 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79-0.92 (*m*, 3H), 1.05-1.09 (*m*, 1H), 1.23-1.34 (*m*, 5H), 1.48 (*dd*, J_1 = 9.0 Hz, J_2 = 9.0 Hz 1H), 1.61- 1.74 (*m*, 2H), 7.14-7.44 (*m*, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.1, 14.0, 16.2, 22.5, 31.2, 32.5, 126.1, 126.7, 128.0, 128.2, 128.4, 128.5, 128.9, 130.4, 141.0.

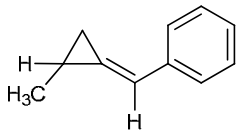
2-Ethylpropylidene-2-methylcyclopropane 6c:



6c

Colorless oil isolated in 40% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56-0.58 (*m*, 1H), 1.11 (*d*, *J* = 3.6 Hz, 3H), 1.12-1.15 (*m*, 1H), 1.28-1.41 (*m*, 1H), 1.52-1.55 (*m*, 6H), 2.21-2.23 (*m*, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.5, 18.0, 26.7, 27.9, 28.1, 33.3, 33.5, 118.8, 128.2.

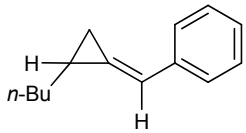
Benzylidene-2-methylcyclopropane 6d:



6d

Colorless oil isolated in 60% yield, *E/Z* = 91:9. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94-1.04 (*m*, 1H), 1.18 (*d*, *J* = 5.7 Hz, 3H for *E* isomer 2H), 1.19 (*d*, *J* = 6.0 Hz, 3H for *Z* isomer 2H), 1.44-1.60 (*m*, 2H), 6.65 (*m*, 1H for *Z* isomer), 6.74 (*q*, *J* = 2.1 Hz, 1H for *E* ismoer), 7.18 (*t*, *J* = 7.2 Hz, 1H), 7.30 (*t*, *J* = 7.5 Hz, 2H), 7.52 (*d*, *J* = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.7, 8.8, 11.8, 17.2, 17.9, 117.4, 126.5, 126.6, 128.4, 128.5, 131.4, 138.3.

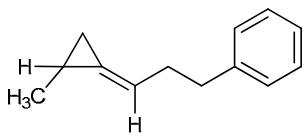
Benzylidene-2-butylcyclopropane 6e:



6e

Colorless oil isolated in 61% yield, *E/Z* = 58:42. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.87 (*m*, 1H), 0.91-0.97 (*m*, 6H), 1.02-1.10 (*m*, 2H), 1.27-1.60 (*m*, 15H), 1.74-1.78 (*m*, 1H), 1.96-2.05 (*m*, 1H), 6.70 (*q*, *J* = 1.8 Hz, 1H for *Z* isomer), 6.77 (*s*, 1H for *E* isomer), 7.20 (*t*, *J* = 7.2 Hz, 2H for *E* isomer), 7.33 (*t*, *J* = 7.1 Hz, 2H for *Z* isomer), 7.47 (*d*, *J* = 7.2 Hz, 2H for *Z* isomer), 7.56 (*d*, *J* = 7.2 Hz, 2H for *E* isomer). ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.5, 10.8, 13.3, 14.1, 17.1, 22.5, 22.6, 31.0, 31.6, 31.7, 32.8, 117.4, 118.6, 126.5, 126.5, 126.6, 126.7, 130.4, 130.6, 138.1, 138.3.

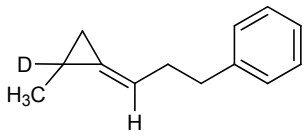
3-Phenylpropylidene-2-methylcyclopropane 6f:



6f

Colorless oil isolated in 68% yield, *E/Z* = 86:14. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.58-0.63 (*m*, 1H), 1.17 (*d*, *J* = 11.1 Hz, 3H), 1.21-1.22 (*m*, 1H), 1.42-1.47 (*m*, 1H), 2.53-2.60 (*m*, 2H), 2.81-2.87 (*m*, 2H), 5.82-5.84 (*m*, 1H for *Z* isomer), 5.86-5.93 (*m*, 1H for *E* isomer), 7.22-7.35 (*m*, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.4, 9.6, 10.0, 17.9, 18.1, 33.5. 33.8, 35.8, 36.0, 116.4, 117.4, 125.6, 125.7, 128.1, 128.2, 128.4, 128.5, 129.1,

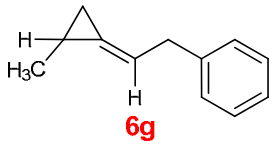
3-Phenylpropylidene-2-deuterio-2-methylcyclopropane 6f(D):



6f(D)

Colorless oil isolated in 70% yield, *E/Z* = 60:40. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.54 (*dd*, J_1 = 7.2 Hz, J_2 = 17.4 Hz, 1H), 1.04 (*s*, 3H), 1.1 (*dd*, J_1 = 7.2 Hz, J_2 = 17.4 Hz, 1H), 2.41-2.48 (*m*, 2H), 2.68-2.76 (*m*, 2H), 5.67-5.81 (*m*, 2H for *E* and *Z* isomers), 5.86-5.93 (*m*, 1H for *E* isomer), 7.14-7.25 (*m*, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.3, 9.4, 9.6, 9.9, 10.1, 17.8, 17.9, 18.1, 33.5, 33.8, 35.8, 36.0, 116.4, 117.4, 125.6, 125.7, 126.1, 128.2, 128.2, 128.5, 128.5, 128.8, 129.1, 142.3.

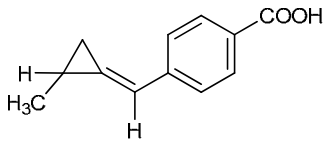
2-Phenylethylidene-2-methylcyclopropane 6g:



6g

Colorless oil isolated in 76% yield, *E/Z* = 93:7. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.52-0.62 (*m*, 1H), 1.06 (*d*, *J* = 6.3 Hz, 3H), 1.12-1.20 (*m*, 1H), 1.37-1.39 (*m*, 1H), 3.44 (*d*, *J* = 6.9 Hz, 2H), 5.85-5.91 (*m*, 1H), 7.10-7.25 (*m*, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ9.4, 9.6, 10.0, 17.9, 18.1, 33.5. 33.8, 35.8, 36.0, 116.4, 117.4, 125.6, 125.7, 128.1, 128.2, 128.4, 128.5, 129.1, 142.2.

4-((2-methylcyclopropylidene)methyl)benzoic acid 6h:



6h

Colorless oil isolated in 83% yield, *E/Z* = 93:7. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10-1.06 (*m*, 1H), 1.16 (*d*, *J* = 5.7 Hz, 3H for *E* isomer), 1.23 (*d*, *J* = 6.3 Hz, 3H for *Z* isomer), 1.48-1.63 (*m*, 2H), 6.70 (*q*, *J* = 1.5 Hz, 1H for *Z* isomer), 6.77 (*q*, *J* = 1.8 Hz, 1H for *E* isomer), 7.46 (*d*, *J* = 8.1 Hz, 2H for *Z* isomer), 7.55 (*d*, *J* = 8.4 Hz, 2H for *E* isomer), 8.01 (*d*, *J* = 8.4 Hz, 2H for *E* isomer), 8.02 (*d*, *J* = 8.1 Hz, 2H for *Z* isomer). ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.1, 9.1, 11.6, 12.0, 17.0, 17.7, 116.9, 118.1, 126.4, 126.5, 127.1, 130.5, 130.6, 135.9, 143.8, 172.2.

Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6a**

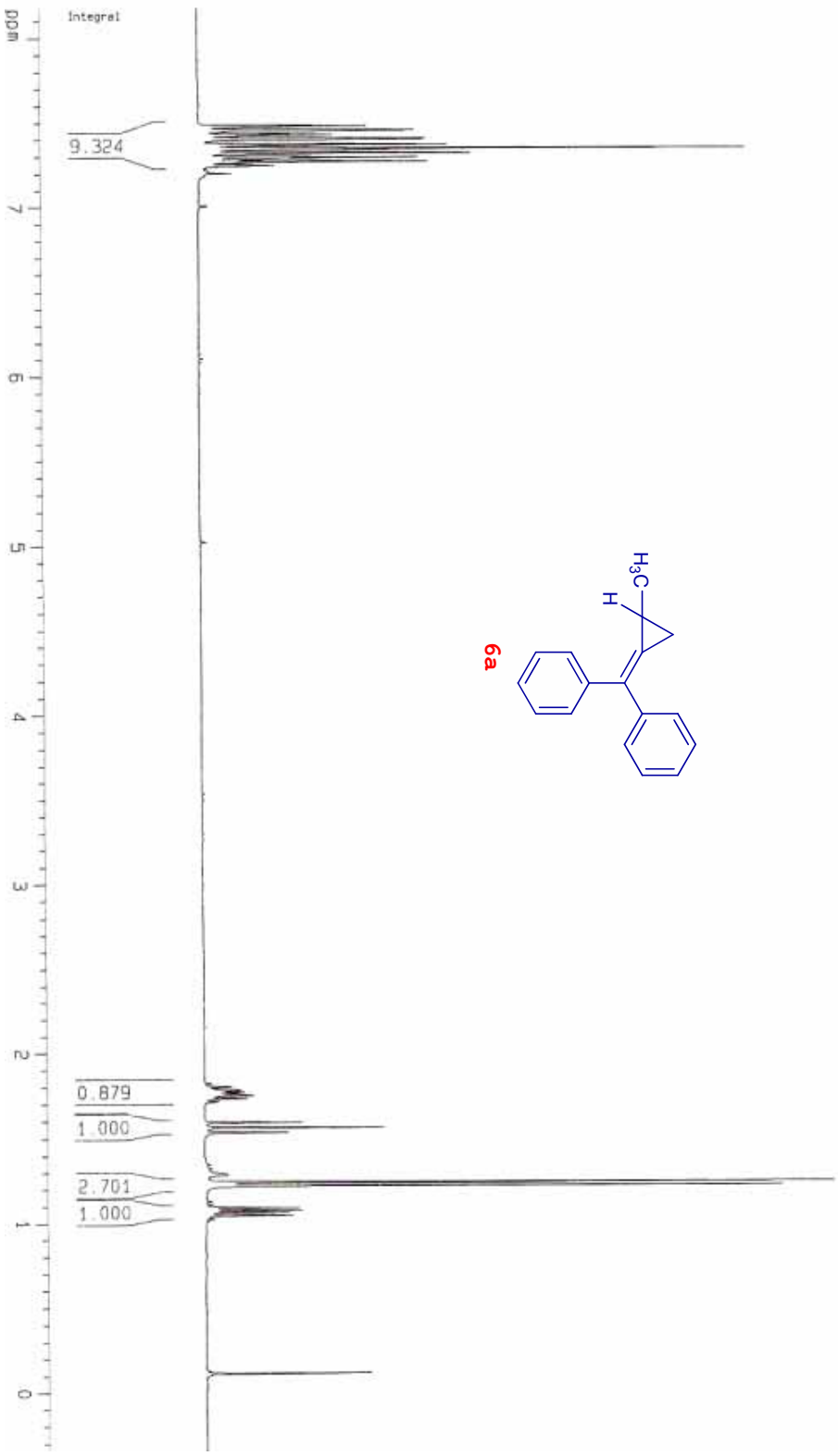


Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6a**

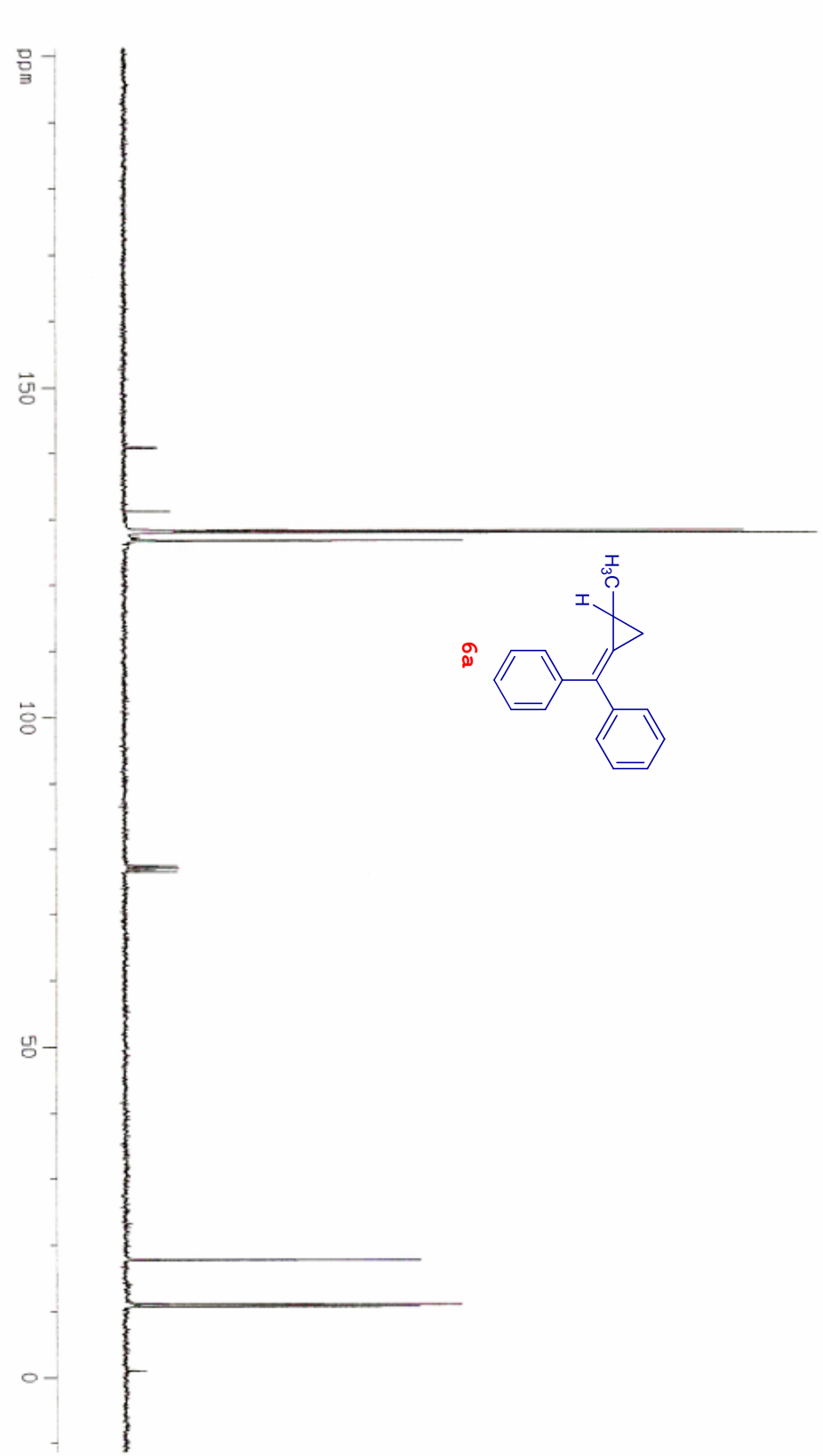


Figure S3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6a(D)**

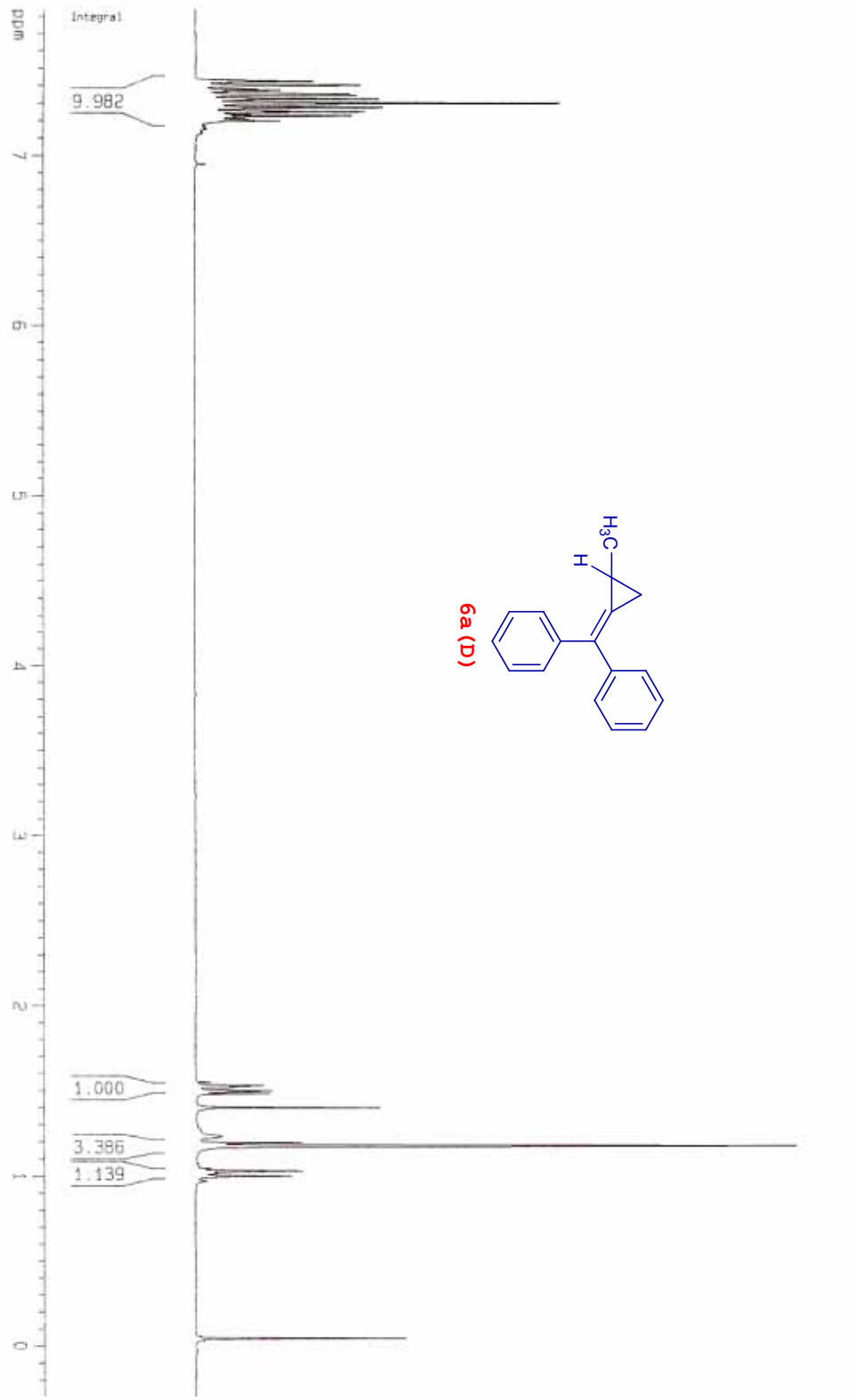


Figure S4. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6a(D)**

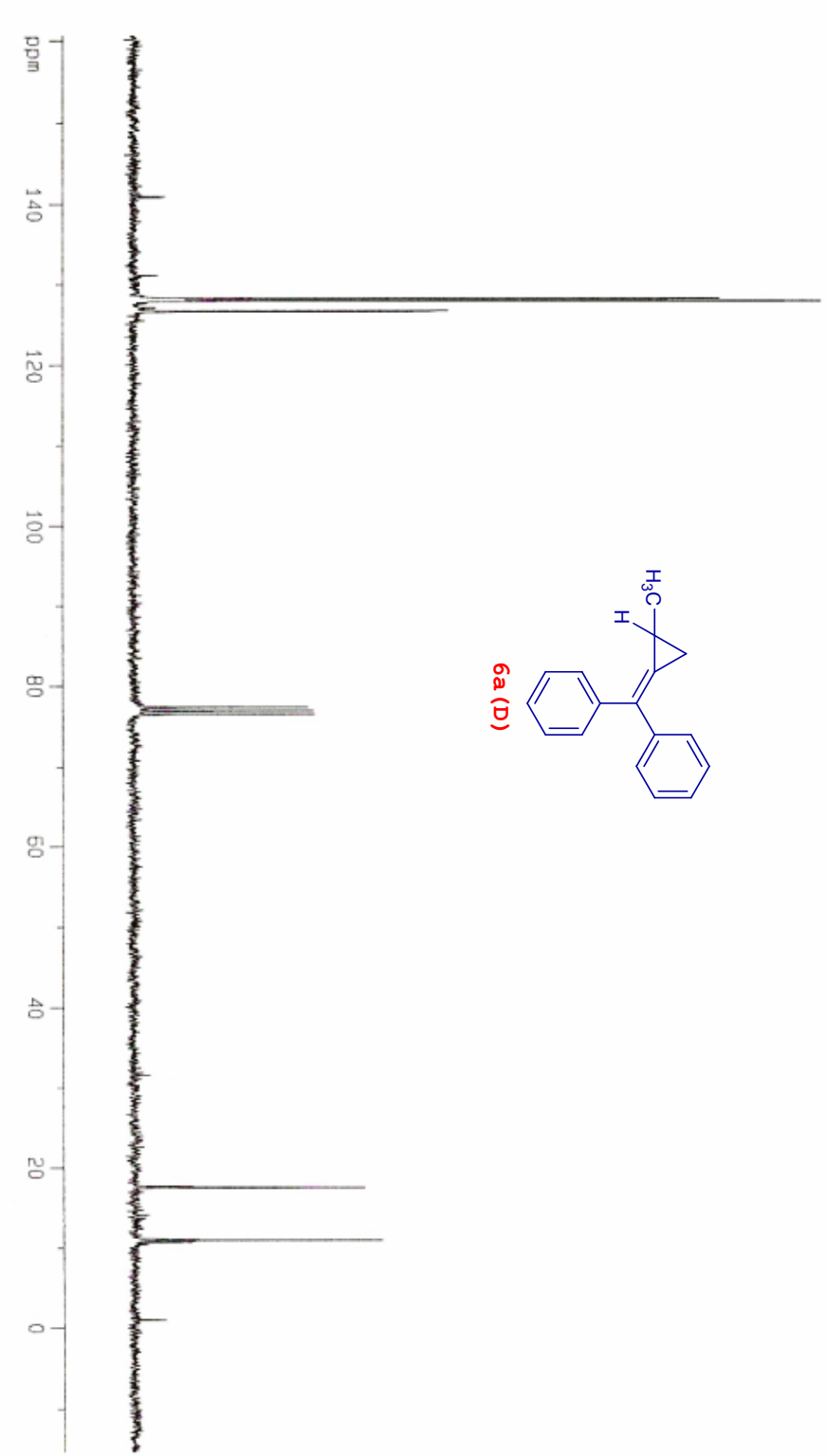


Figure S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6b**

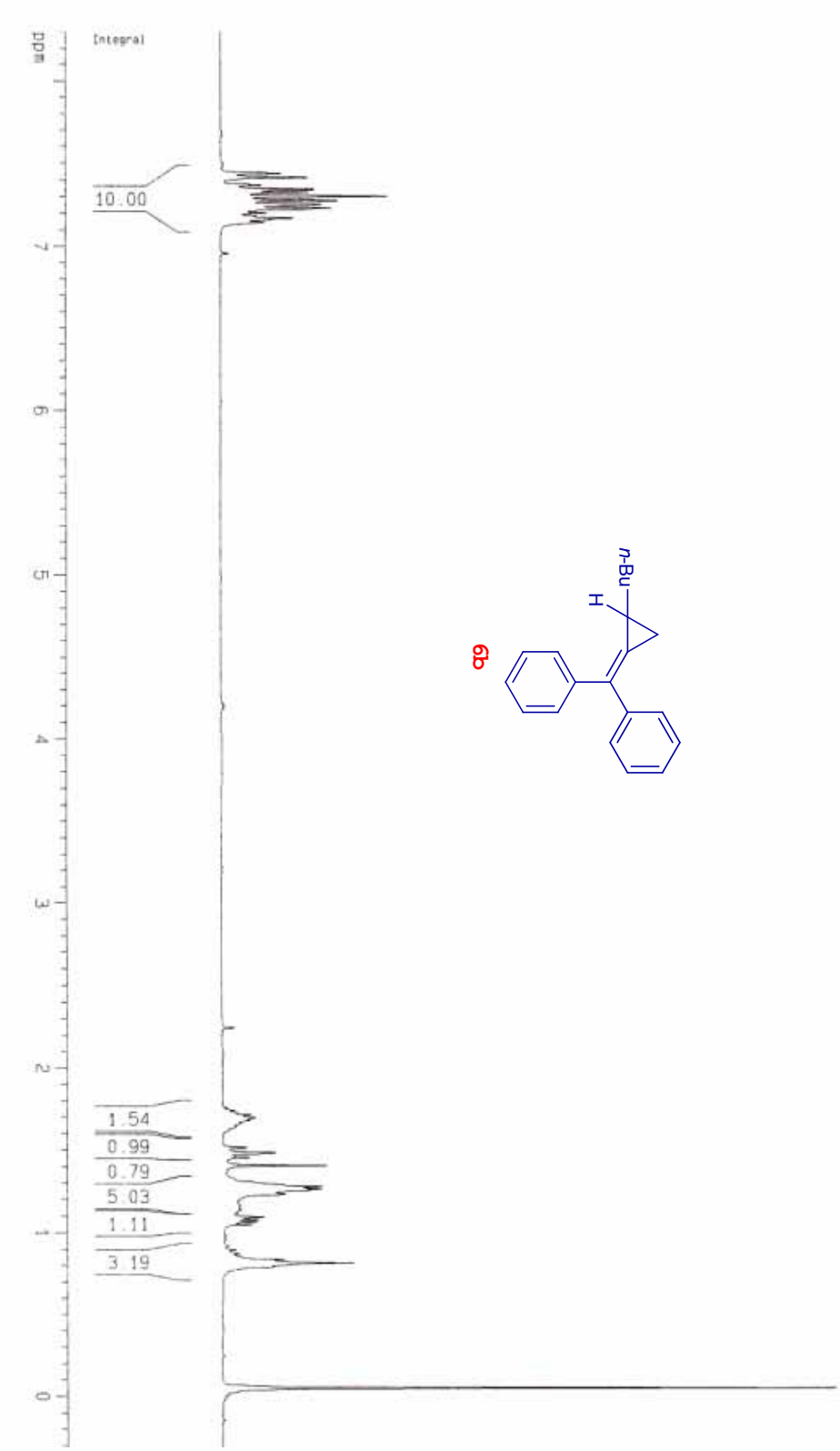


Figure S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6b**

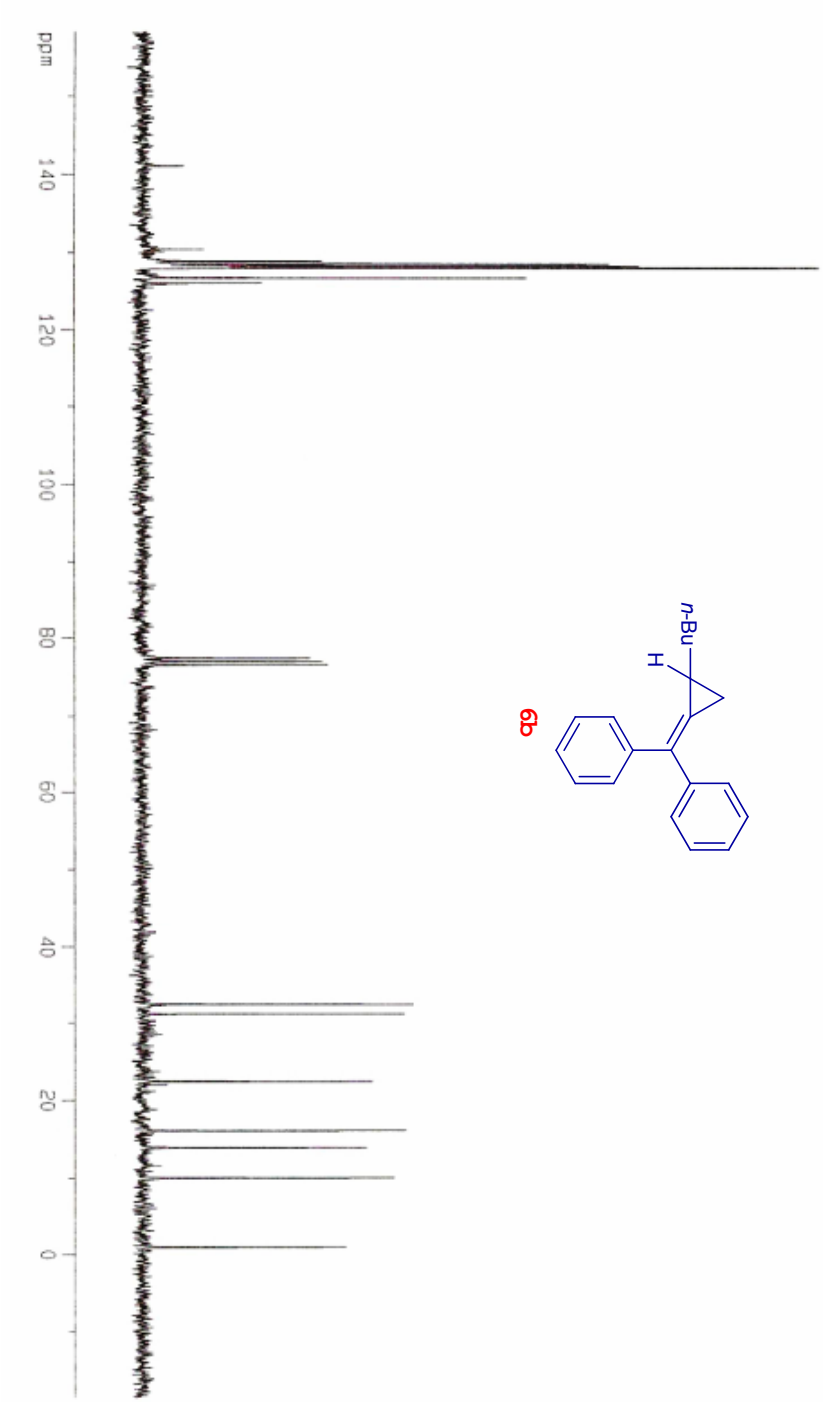


Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6c**

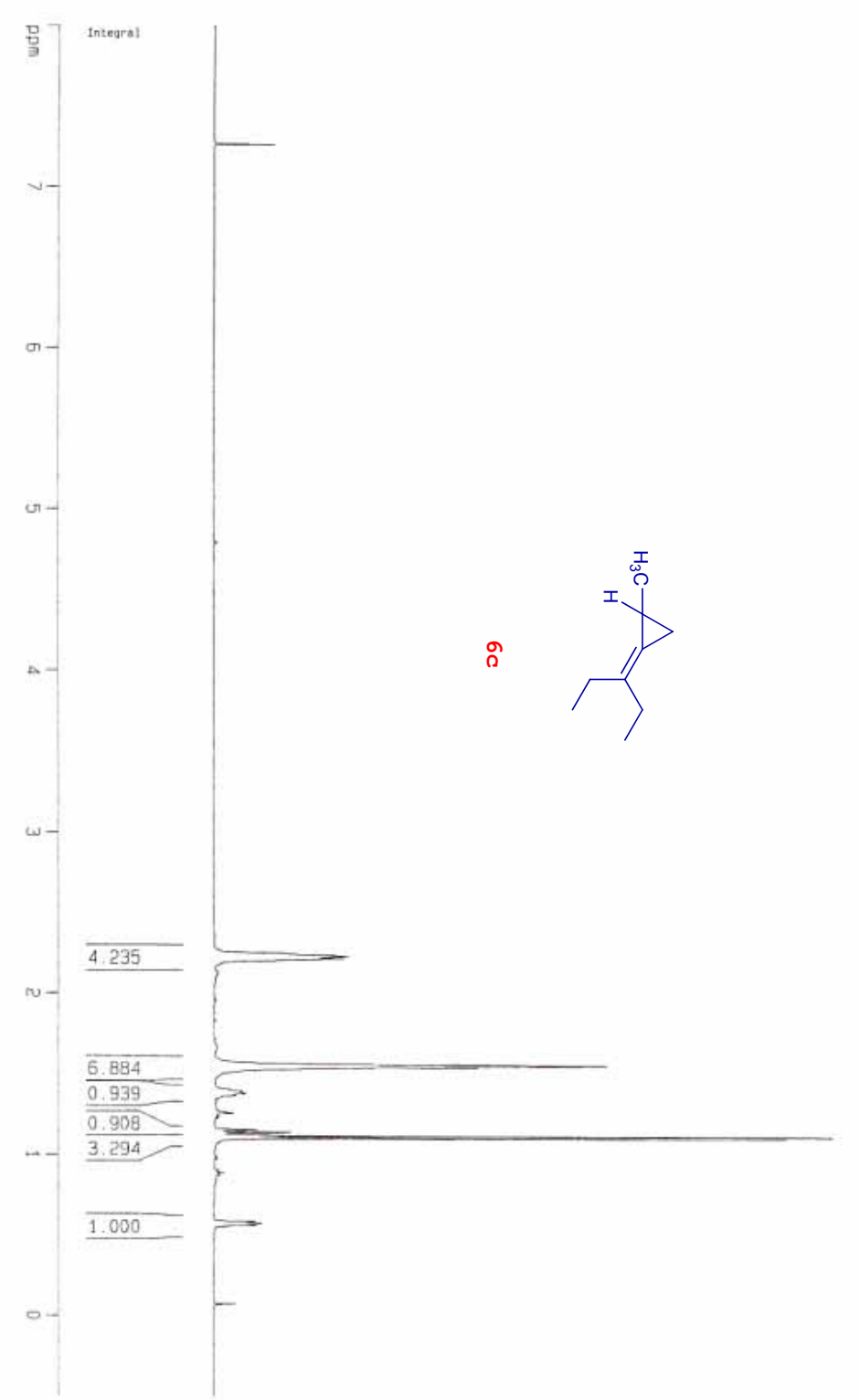


Figure S8. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6c**

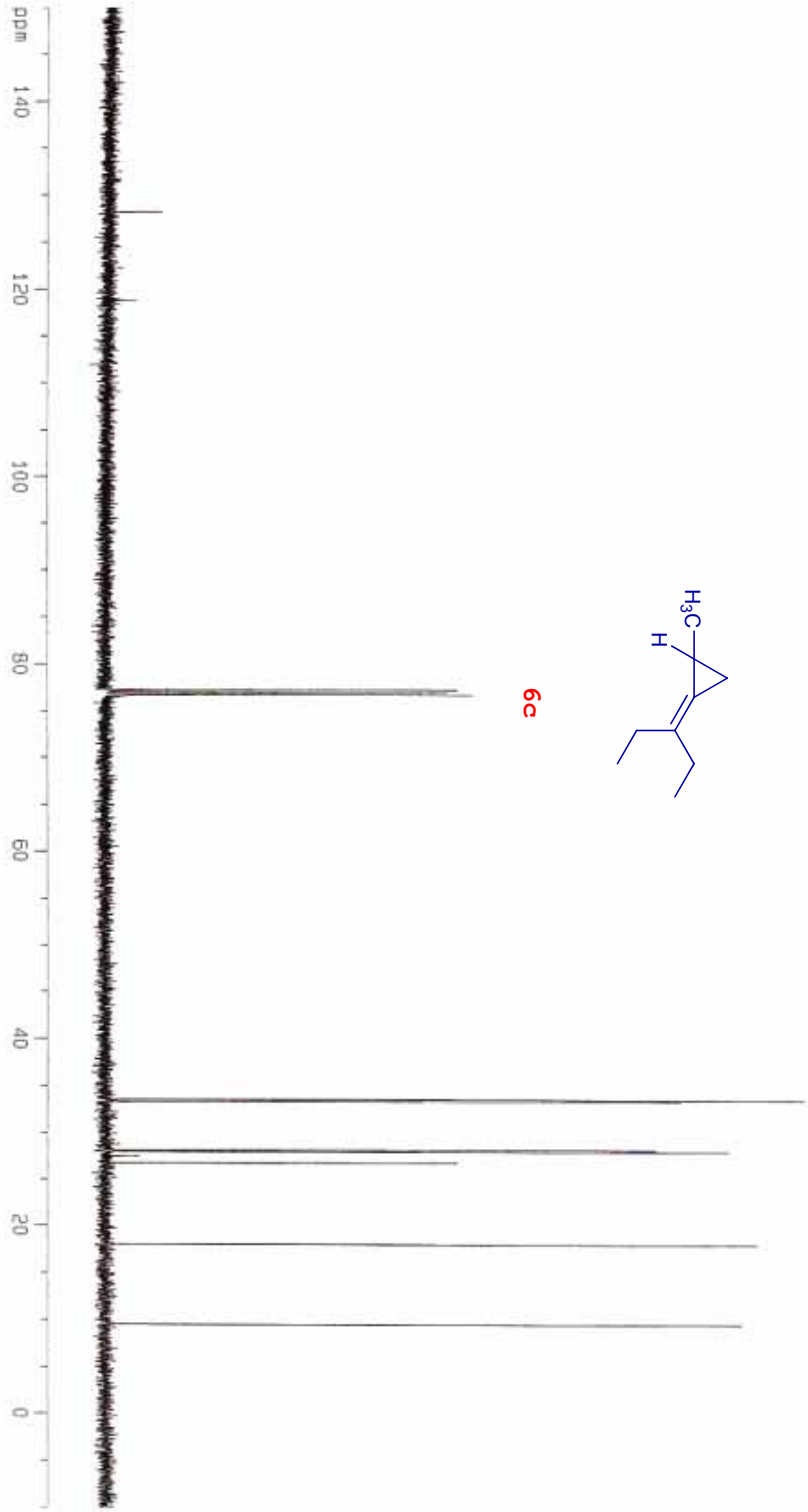


Figure S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6d**

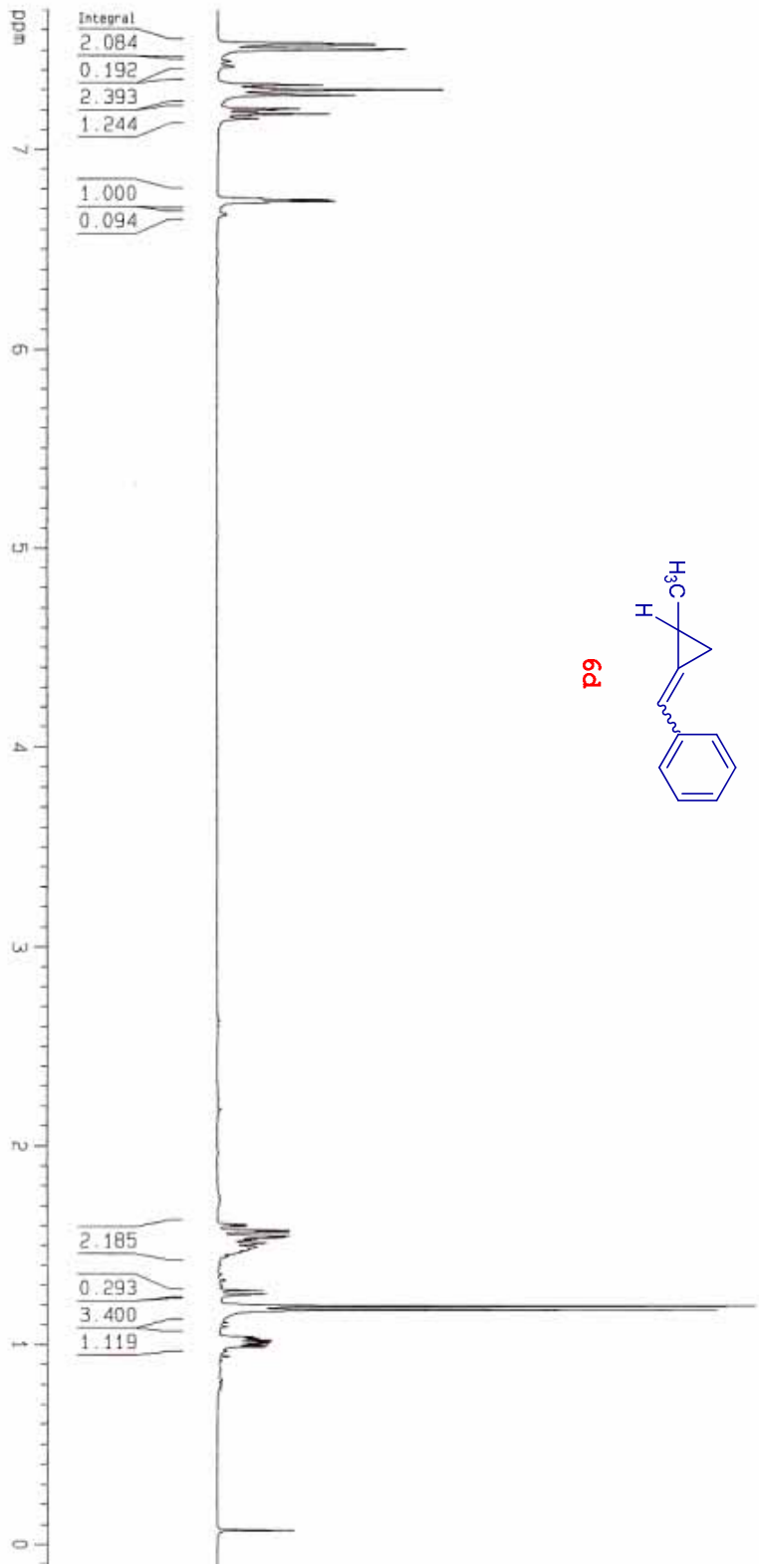


Figure S10. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6d**

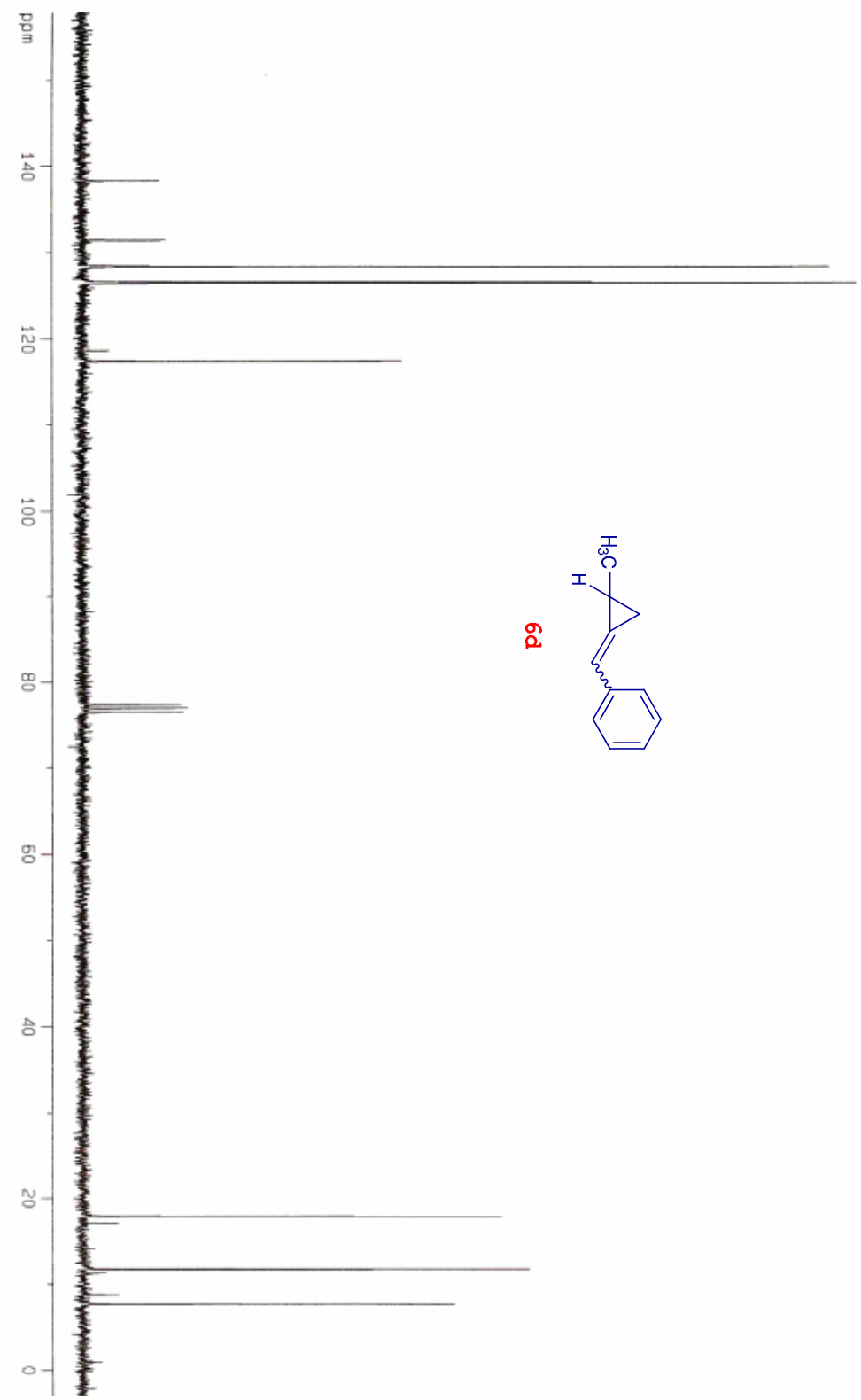


Figure S11. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6e**

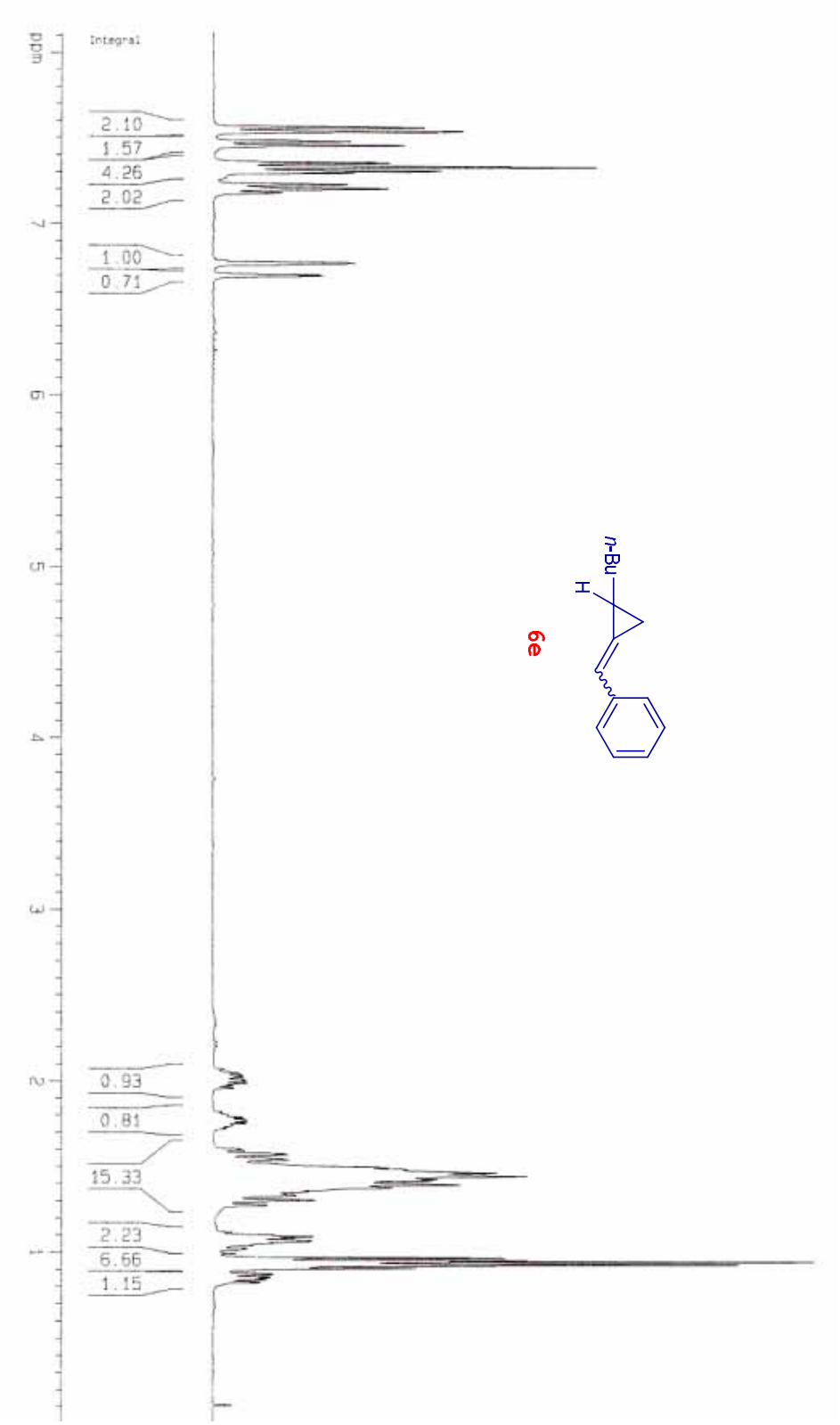


Figure S12. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6e**

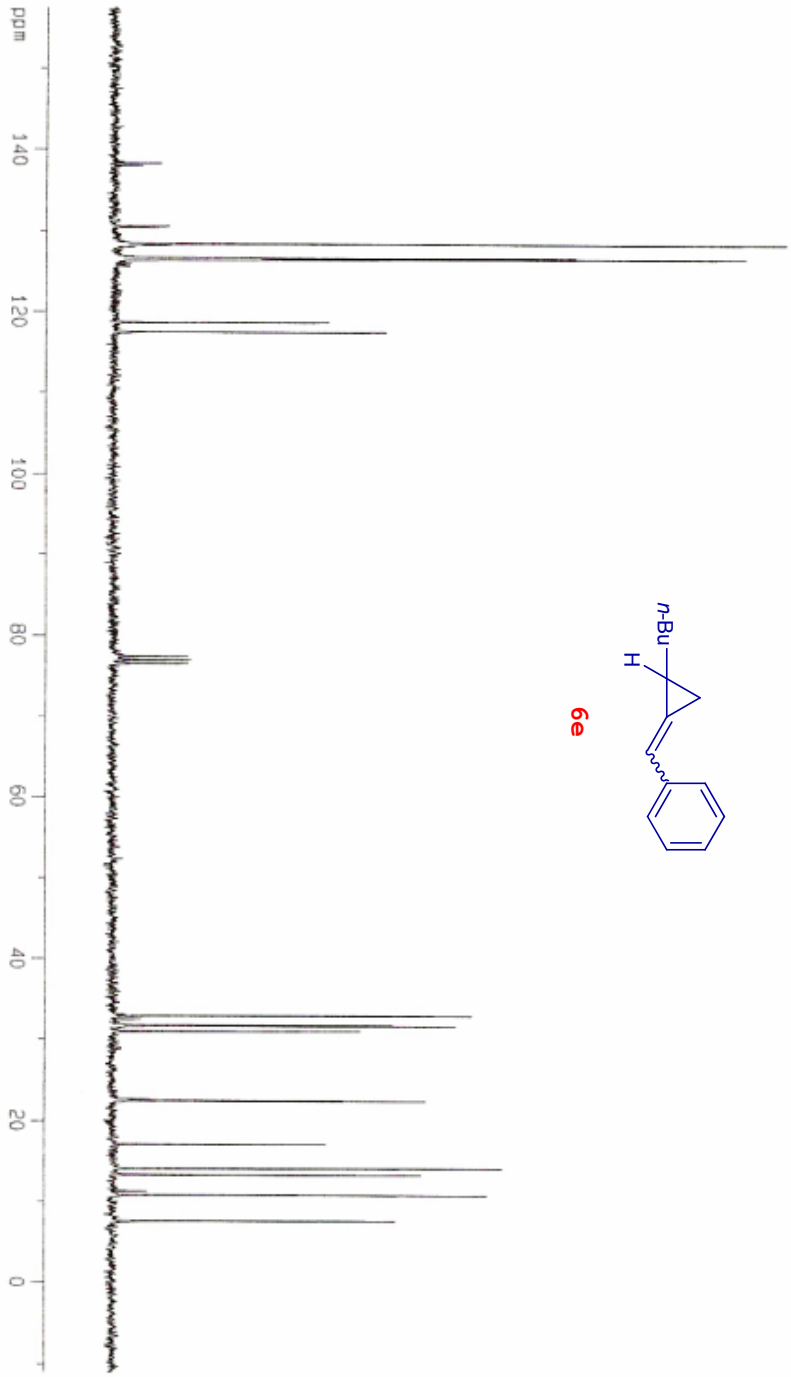


Figure S13. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6f**

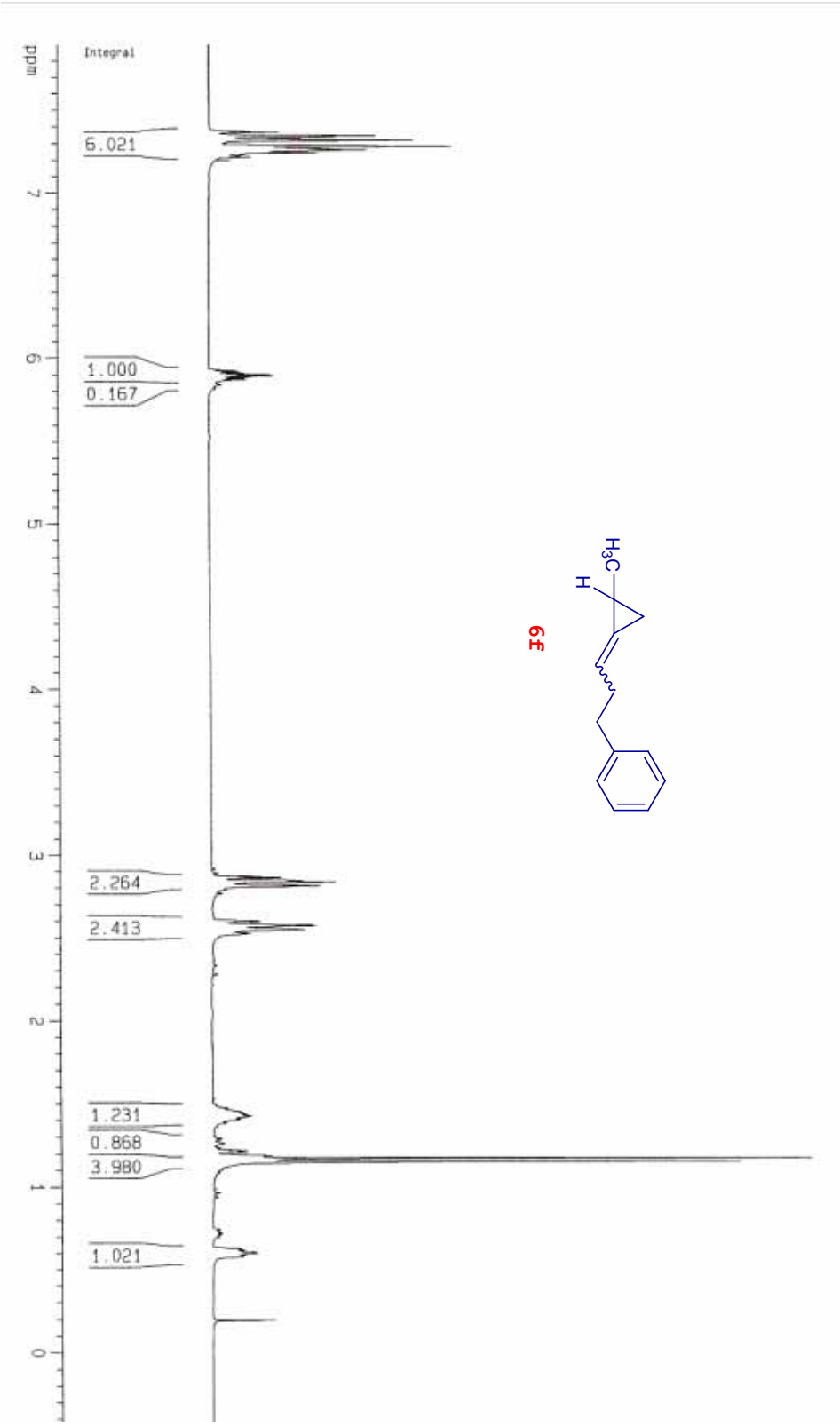


Figure S14. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6f**

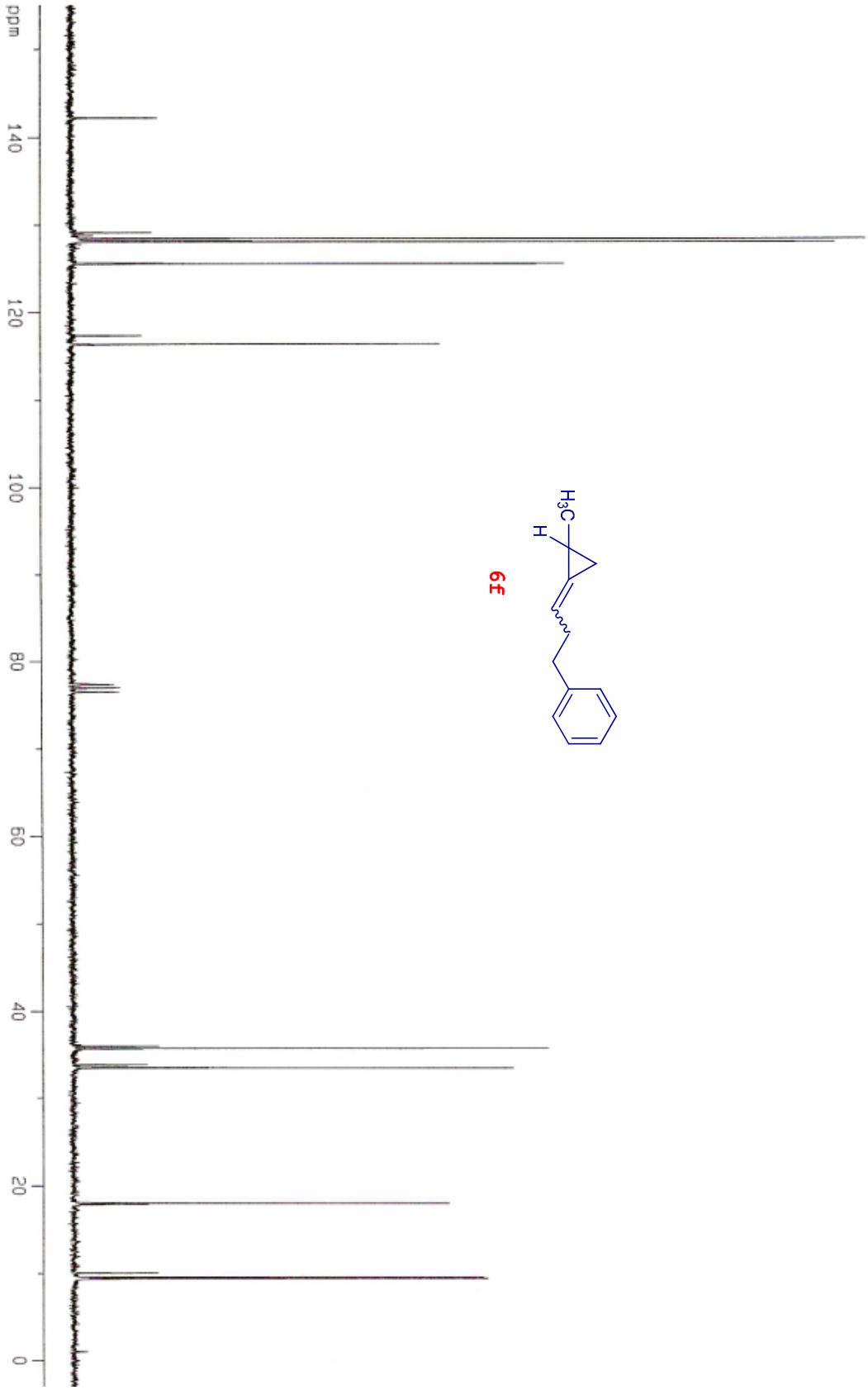


Figure S15. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6f(D)**

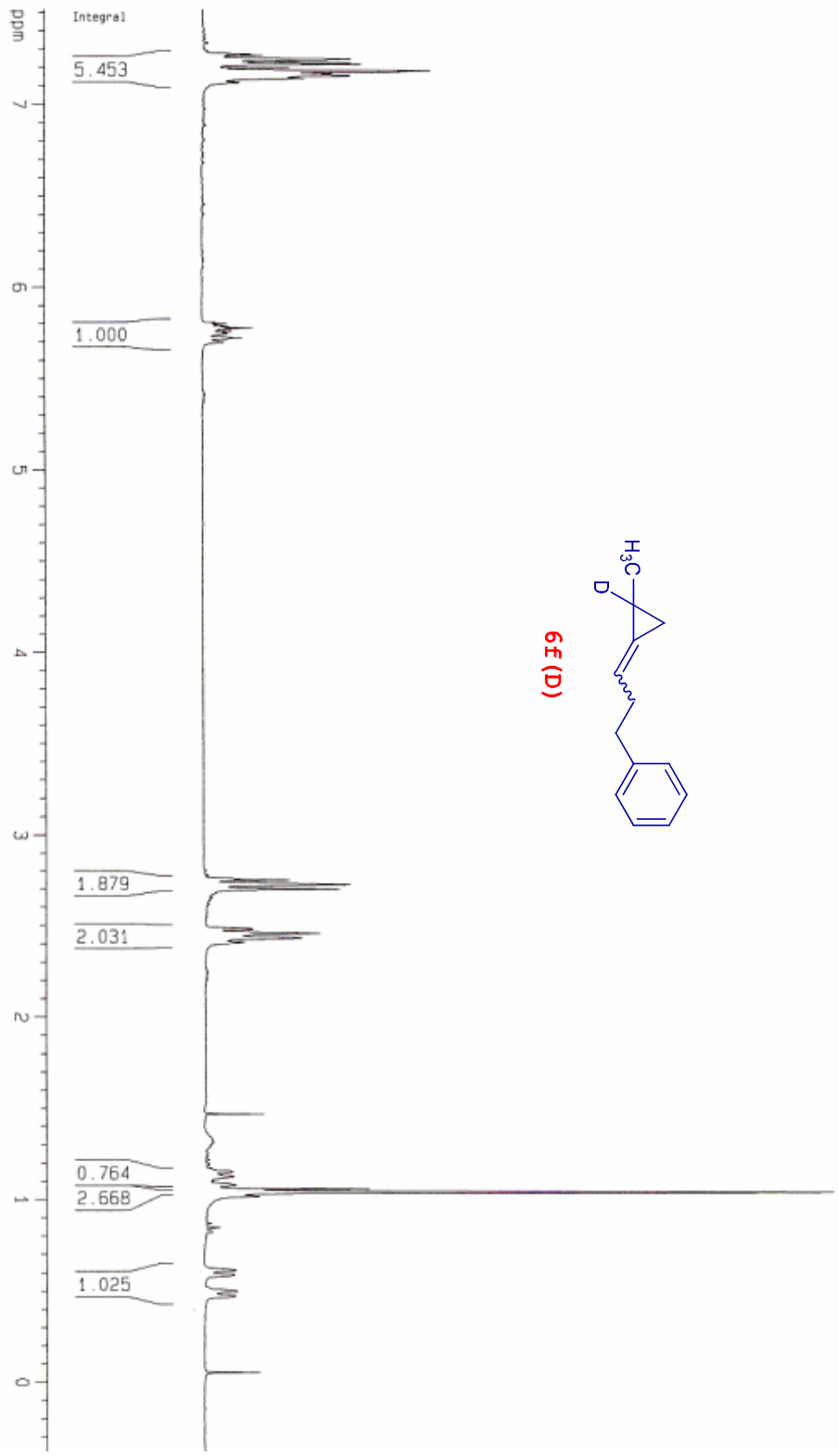


Figure S16. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6f(D)**

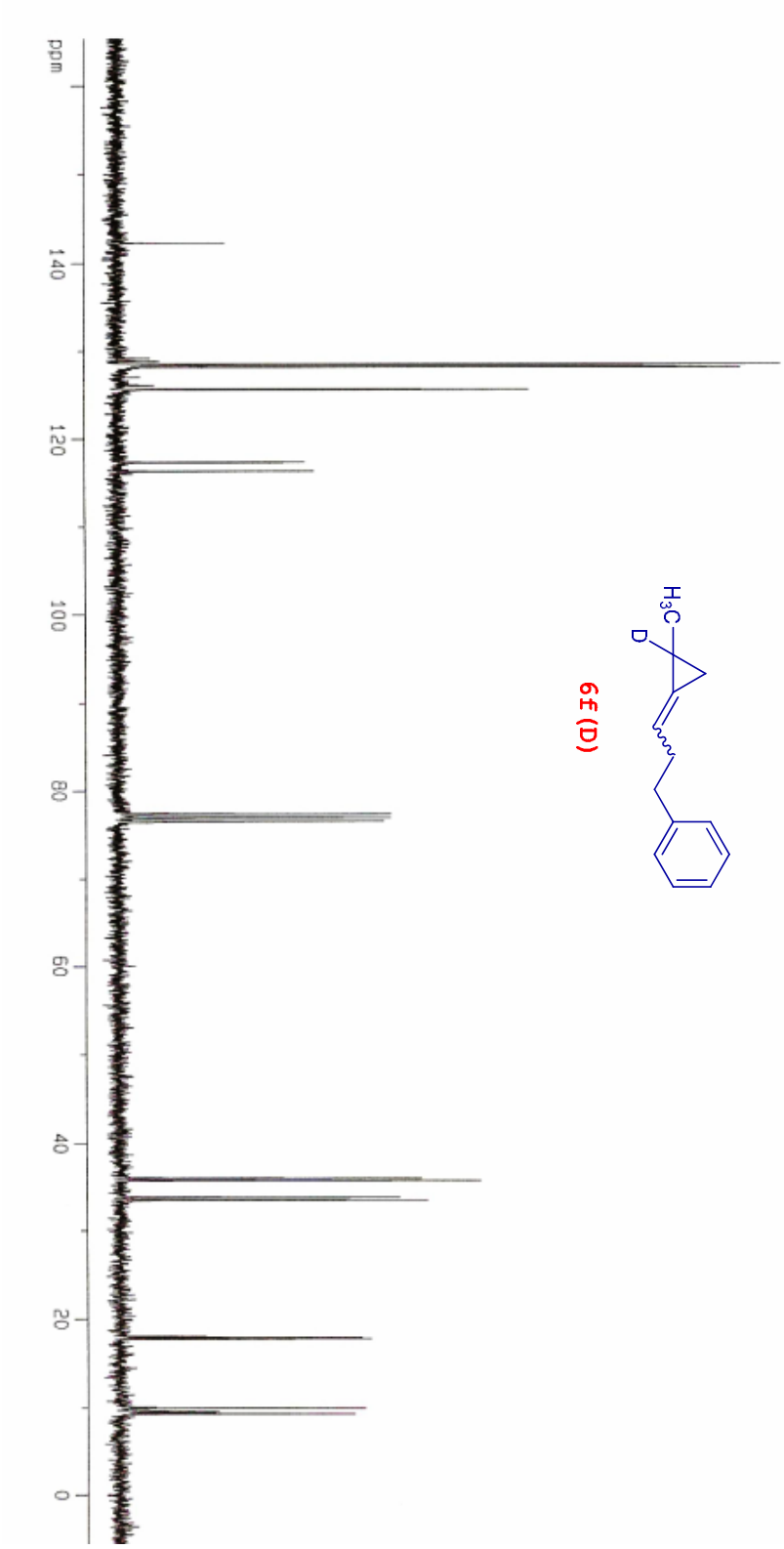


Figure S17. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6g**

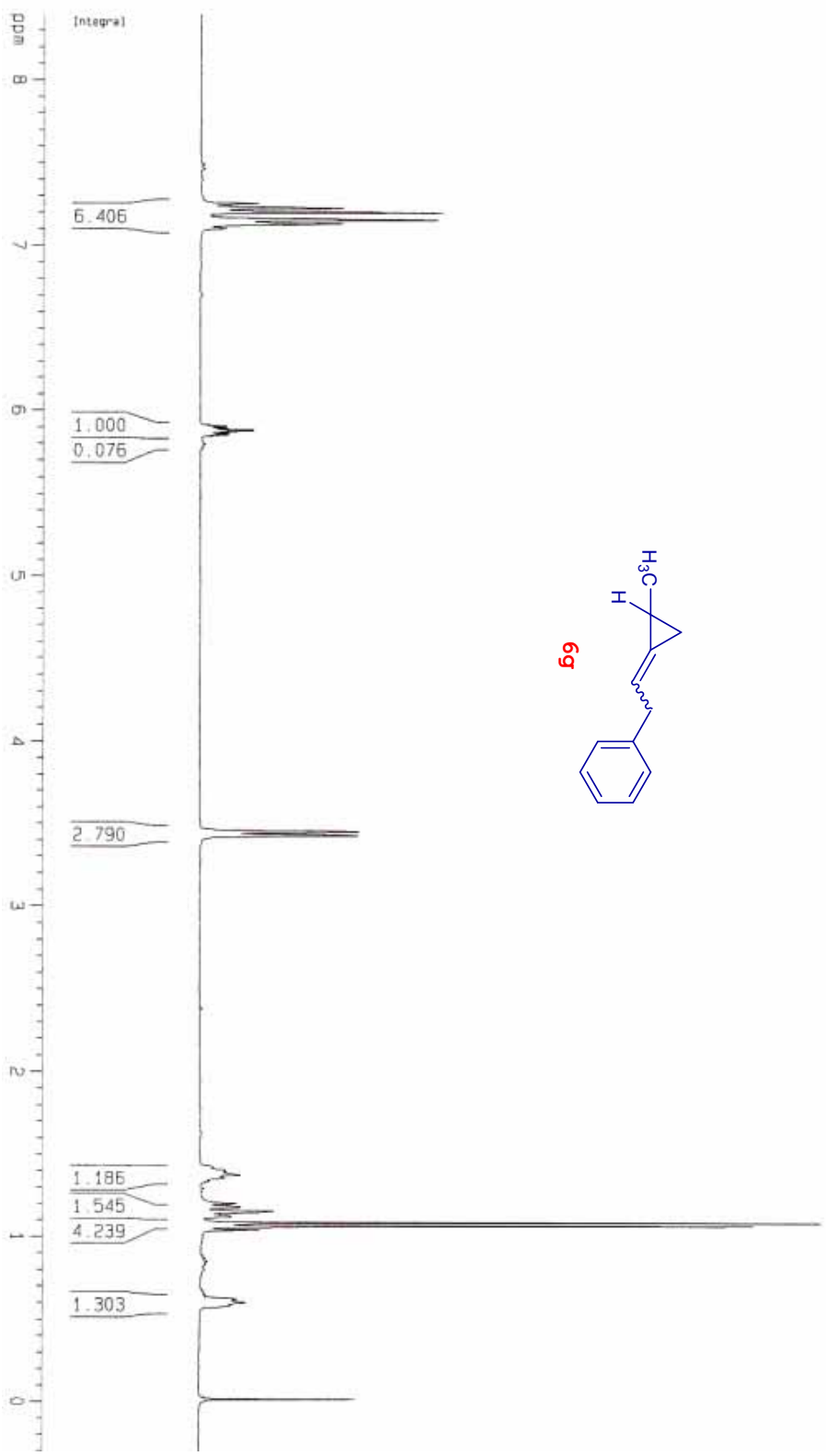


Figure S18. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6g**

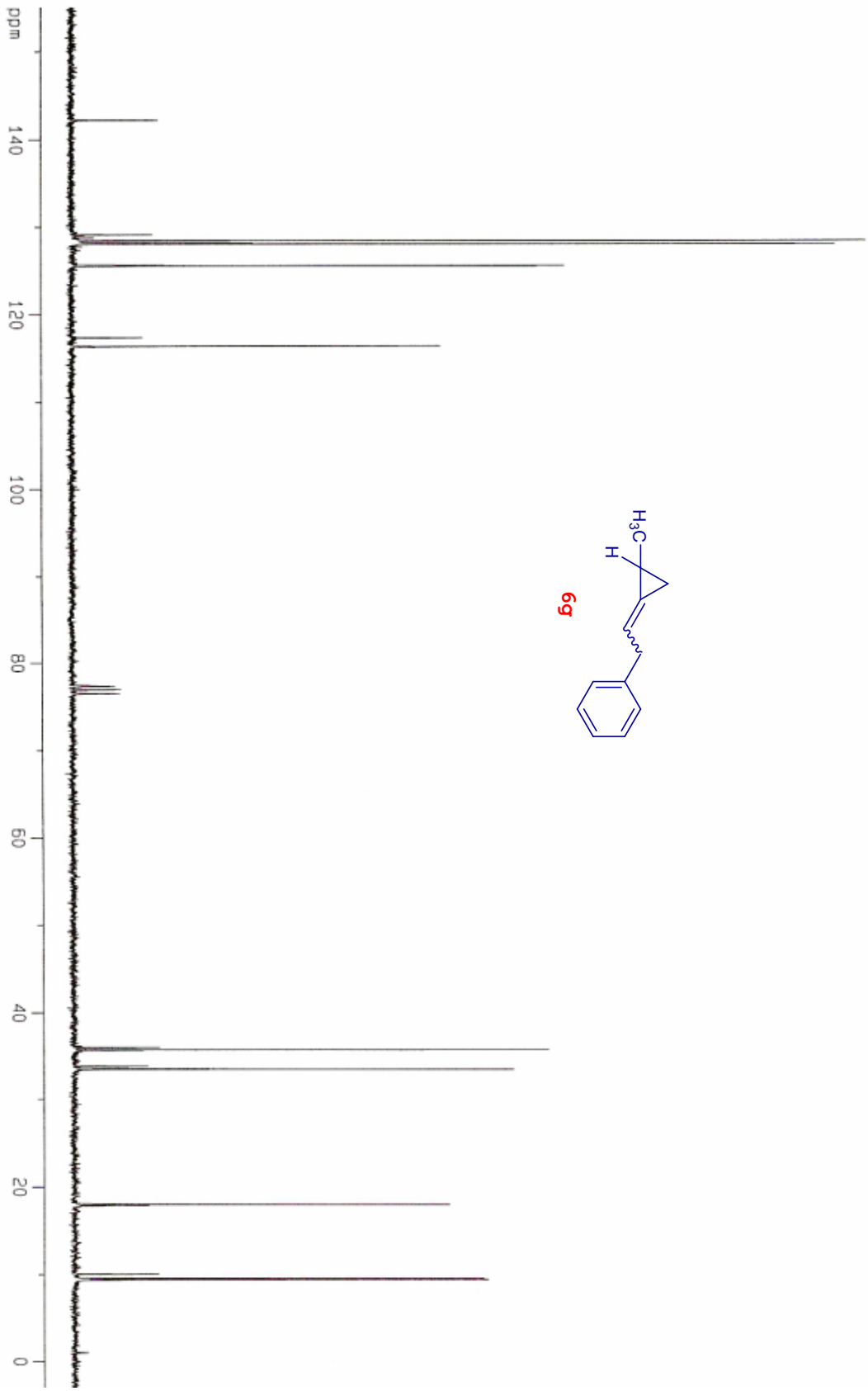


Figure S19. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6h**

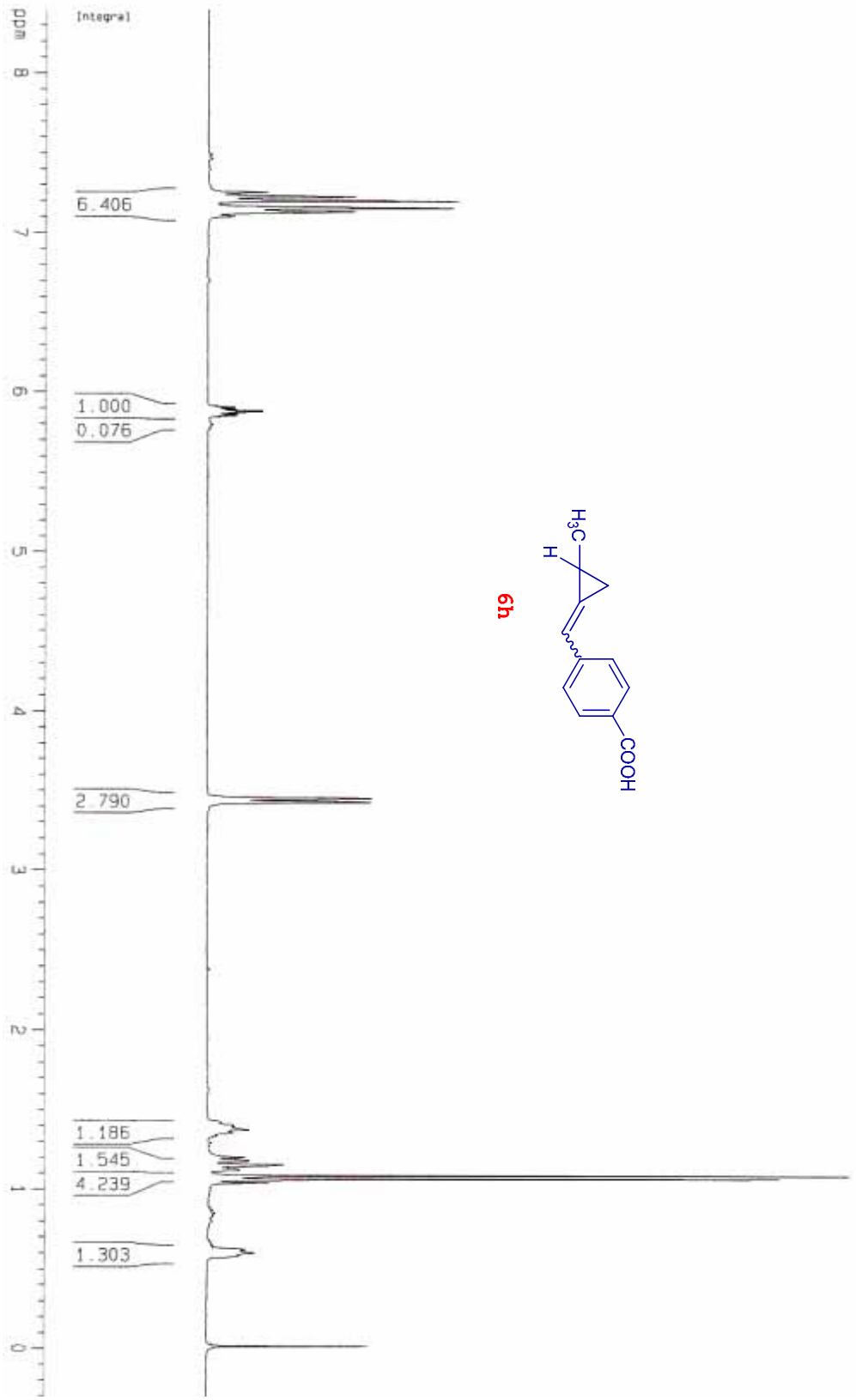


Figure S20. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6h**