

Supplementary Information

A versatile iodo(III)etherification of terminal ethynylsilanes using $\text{BF}_3\text{-O}^i\text{Pr}_2$ and alkyl benzyl ether

Takuya Matsumoto,^a Hiroshi Hagiyama,^b Kanetsugu Kuribayashi,^a Kazuhito Hioki,^b
Hikaru Fujita,^a Masahito Ochiai^c and Munetaka Kunishima^{*a}

^a Faculty of Pharmaceutical Sciences, Institute of Medical, Pharmaceutical, and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

^b Faculty of Pharmaceutical Sciences, Kobe Gakuin University, 1-1-3 Minatojima, Chuo-ku, Kobe 650-8586, Japan

^c Graduate School of Pharmaceutical Sciences, Tokushima University, 1-78 Shomachi, Tokushima 770-8505, Japan

Table of Contents

1. General	S2
2. Preparation of boron trifluoride diisopropyl etherate ($\text{BF}_3\text{-O}^i\text{Pr}_2$)	S2
3. Procedure for the reactions in Table 1	S2–3
4. Procedure for the reactions in Tables 2, 3, 4	S3
5. Characterization Data of λ^3 -iodonium salts	S4–6
6. References	S7
7. ^1H and ^{13}C NMR spectra	S8–25

General

Unless otherwise noted, all reactions were performed under an atmosphere of dinitrogen. Solvents were dehydrated according to standard methods. Materials were obtained from common commercial suppliers, stored under dinitrogen, and used as received. ^1H and ^{13}C NMR spectra were recorded on a BRUKER DPX400 spectrometer (^1H : 400 MHz; ^{13}C : 100.5 MHz) or a JEOL JNM-ECS400 (^1H : 400 MHz; ^{13}C : 100.5 MHz) in CDCl_3 . Chemical shift values (δ ppm) for ^1H and ^{13}C are referenced to the resonances of the residual non-deuterated solvent as the internal standard (^1H : CDCl_3 , δ 7.26; ^{13}C : CDCl_3 , δ 77.16). NMR data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. Mass spectra were recorded on a JEOL D-300 mass spectrometer (FAB-MS) or a JMS-T100TD (ESI+). IR spectra were recorded on JEOL JIR-100 FT-IR or HORIBA FT-IR 720 spectrometer. GC data were obtained from a HITACHI 263-50 gas chromatograph (column: 10% SE-30 2 mm \times 2 m). Melting points were measured on a Yanaco MP-J3 apparatus.

Iodosylbenzene was prepared from iodobenzene diacetate according to a reported procedure.¹ Benzyl isopropyl ether,² benzyl *tert*-butyl ether,² benzyl 2-phenylethyl ether,³ and benzyl 3-phenylpropyl ether⁴ were prepared according to reported procedures. Benzyl cyclohexylmethyl ether was prepared using a method similar to that of other alkyl benzyl ethers. The spectra of the thus obtained product were in good agreement with reported values.⁵

Preparation of boron trifluoride diisopropyl etherate ($\text{BF}_3\text{-O}^i\text{Pr}_2$)

An ice-cooled solution of $^i\text{Pr}_2\text{O}$ (7.00 g, 68.5 mmol) in CH_2Cl_2 (30 mL) was aerated with BF_3 gas generated from a mixture of NaBF_4 (30.0 g, 273 mmol), B_2O_3 (6.00 g, 86.2 mmol), and conc. H_2SO_4 (30 mL) heated to $180\text{ }^\circ\text{C}$ ⁶ for approximately 10 min. Removal of all volatiles under reduced pressure afforded $\text{BF}_3\text{-O}^i\text{Pr}_2$ (7.90 g, 68% yield) as a colorless, hygroscopic, crystalline solid. ^1H NMR (400 MHz, CDCl_3) δ 1.43 (d, J = 6.5 Hz, 6H), 4.47–4.61 (m, 1H). ^{13}C NMR (100.5 MHz, CDCl_3) δ 21.2, 76.1.

Procedure for the reactions in Table 1

A solution of the BF_3 -ether complex (1.6–3.2 eq.) in CH_2Cl_2 (3.5 mL) was added dropwise to an ice-cooled suspension of trialkylethynylsilane (0.50 mmol, 1.0 eq.) and iodosylbenzene (1.6–3.2 eq.) in CH_2Cl_2 (3.5 mL). The reaction mixture was allowed to warm to room temperature. After the disappearance of trialkylethynylsilane was confirmed by GC, the reaction was quenched with a saturated aqueous solution of NaBF_4 (2 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 \times 3 mL). The combined organic phases were washed with water (2 mL), filtered, and the solvent was removed under reduced pressure. Trituration of the residue with hexane afforded spectroscopically pure products. Recrystallization was performed for data collection.

The procedure was slightly modified for entry 6: The reaction was quenched with cold water. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 \times 3 mL). The combined organic phase was washed with a cold saturated aqueous solution of NaBr (3 \times 2 mL), followed by a saturated aqueous solution of

NaBF₄ (3 × 2 mL), and water (2 mL). The organic phase was filtered, and all volatiles were removed under reduced pressure. Trituration of the residue with hexane afforded spectroscopically pure products. Recrystallization was performed for data collection.

Procedure for the reactions in Tables 2, 3, 4

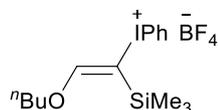
Method A: A solution of the BF₃–ether complex (1.5 mmol, 3.0 eq.) and the dialkylether (5.1 mmol, 10 eq.) in CH₂Cl₂ (3.5 mL) was added dropwise to an ice-cooled suspension of ethynyltrimethylsilane (50 mg, 0.51 mmol, 1.0 eq.) and iodosylbenzene (336 mg, 1.5 mmol, 3.0 eq.) in CH₂Cl₂ (3.5 mL). The reaction solution was allowed to warm to room temperature. After the disappearance of ethynyltrimethylsilane was confirmed by GC, the reaction was quenched with a saturated aqueous solution of NaBF₄ (2 mL). The organic phase was separated and the aqueous phase was extracted by CH₂Cl₂ (3 × 3 mL). The combined organic phase was washed with water (2 mL), filtered, and the solvent was removed under reduced pressure. Trituration of the residue with hexane afforded the iodonium salts. In the cases where the product was a mixture, the yield was calculated based on the ¹H NMR integration values. Recrystallization was performed for data collection.

Method B: A solution of the BF₃–ether complex (1.5 mmol, 3.0 eq.) and the dialkylether (5.1 mmol, 10 eq.) in CH₂Cl₂ (3.5 mL) was heated to 50 °C under a dinitrogen atmosphere at ambient pressure until all CH₂Cl₂ was evaporated. Another portion of CH₂Cl₂ (3.5 mL) was added to the residue and removed again. More CH₂Cl₂ (3.5 mL) was added to the residue, and this solution was added dropwise to an ice-cold mixture of ethynyltrimethylsilane (50 mg, 0.51 mmol, 1.0 eq.) and iodosylbenzene (336 mg, 1.5 mmol, 3.0 eq.) in CH₂Cl₂ (3.5 mL). The subsequent operations were the same as in Method A.

Characterization Data of λ^3 -iodanes

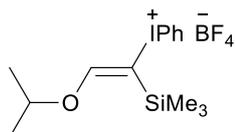
(*E*)-(2-Ethoxy-1-(trimethylsilyl)vinyl)(phenyl)iodonium tetrafluoroborate (**1a**)⁷ and (*E*)-(2-Phenylethoxy-1-(trimethylsilyl)vinyl)(phenyl)iodonium tetrafluoroborate (**1b**)⁸ are known compounds.

(*E*)-(2-Butoxy-1-(trimethylsilyl)vinyl)(phenyl)iodonium tetrafluoroborate (**1c**)



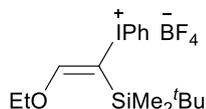
colorless crystalline solid (CH₂Cl₂ / hexane); **mp** 118.5–119°C; ¹H NMR (400 MHz, CDCl₃) δ 0.17 (s, 9H), 0.95 (t, *J* = 7.4 Hz, 3H), 1.36–1.46 (m, 2H), 1.67–1.74 (m, 2H), 4.28 (t, *J* = 6.5 Hz, 2H), 7.42–7.47 (m, 2H), 7.55–7.59 (m, 1H), 7.90–7.93 (m, 2H), 8.22 (s, 1H); ¹³C NMR (100.5 MHz, CDCl₃) δ 0.0, 13.6, 18.8, 31.7, 76.6, 94.4, 110.7, 132.0, 132.2, 133.8, 176.1; **IR** (KBr) 1577, 1083, 842 cm⁻¹; **HRMS-FAB** (*m/z*) Calcd for C₁₅H₂₄OSi [(M-BF₄)⁺] 375.0641, Found 375.0643; **Anal.** Calcd for C₁₅H₂₄BF₄IOSi: C, 38.98; H, 5.23; I, 27.46. Found: C, 38.68; H, 5.26; I, 27.49.

(*E*)-(2-Isopropoxy-1-(trimethylsilyl)vinyl)(phenyl)iodonium tetrafluoroborate (**1d**)



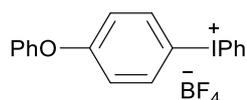
colorless crystalline solid (CH₂Cl₂ / hexane); **mp** 154–155°C (decomp.); ¹H NMR (400 MHz, CDCl₃) δ 0.17 (s, 9H), 1.36 (d, *J* = 6.2 Hz, 6H), 4.56–4.62 (m, 1H), 7.43–7.48 (m, 2H), 7.56–7.61 (m, 1H), 7.88–7.92 (m, 2H), 8.26 (s, 1H); ¹³C NMR (100.5 MHz, CDCl₃) δ 0.0, 22.5, 80.6, 94.5, 110.6, 132.0, 132.2, 133.7, 174.8; **IR** (KBr) 1577, 1083, 842 cm⁻¹; **HRMS-FAB** (*m/z*) Calcd for C₁₄H₂₂OSi [(M-BF₄)⁺] 361.0485, Found 361.0485; **Anal.** Calcd for C₁₄H₂₂BF₄IOSi: C, 37.52; H, 4.95; I, 28.32. Found: C, 37.23; H, 4.93; I, 28.30.

(*E*)-(1-(*tert*-Butyldimethylsilyl)-2-ethoxyvinyl)(phenyl)iodonium tetrafluoroborate (**1e**)



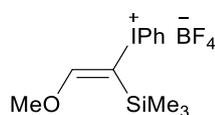
colorless crystalline solid (CH₂Cl₂ / hexane); **mp** 164–165°C (decomp.); ¹H NMR (400 MHz, CDCl₃) δ 0.19 (s, 6H), 0.80 (s, 9H), 1.37 (t, *J* = 7.1 Hz, 3H), 4.36 (q, *J* = 7.1 Hz, 2H), 7.45–7.49 (m, 2H), 7.59–7.62 (m, 1H), 7.91–7.93 (m, 2H), 8.38 (s, 1H); ¹³C NMR (100.5 MHz, CDCl₃) δ -3.5, 15.3, 18.5, 26.6, 72.6, 93.3, 111.5, 132.0, 132.3, 134.3, 177.2; **IR** (KBr) 1573, 1216, 1051, 844, 825 cm⁻¹; **HRMS-FAB** (*m/z*) Calcd for C₁₆H₂₆OSi [(M-BF₄)⁺] 389.07976, Found 389.07916.

Phenyl(4-phenoxyphenyl)iodonium tetrafluoroborate (3)



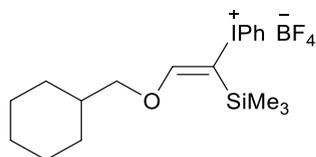
colorless crystalline solid (CH₂Cl₂ / Et₂O); **mp** 136–137°C; ¹H NMR (400 MHz, CDCl₃) δ 6.96–7.00 (m, 2H), 7.02–7.06 (m, 2H), 7.21–7.26 (m, 1H), 7.38–7.43 (m, 2H), 7.43–7.48 (m, 2H), 7.58–7.63 (m, 1H), 7.95–7.98 (m, 2H), 7.99–8.03 (m, 2H); ¹³C NMR (100.5 MHz, CDCl₃) δ 102.0, 112.9, 120.6, 121.0, 125.6, 130.4, 132.5, 132.7, 134.9, 137.8, 154.4, 162.2; **HRMS-FAB** (*m/z*) Calcd for C₁₈H₁₄OI [(M-BF₄)⁺] 373.0089, Found 373.0045.

(E)-(2-Methoxy-1-(trimethylsilyl)vinyl)(phenyl)iodonium tetrafluoroborate (1f)



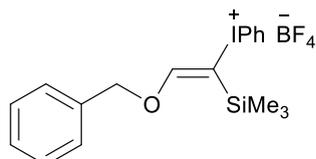
colorless crystalline solid (CH₂Cl₂ / hexane); **mp** 131–133°C; ¹H NMR (400 MHz, CDCl₃) δ 0.16 (s, 9H), 4.05 (s, 3H), 7.42–7.47 (m, 2H), 7.55–7.60 (m, 1H), 7.90–7.94 (m, 2H), 8.17 (s, 1H); ¹³C NMR (100.5 MHz, CDCl₃) δ 0.1, 63.2, 95.3, 110.6, 132.1, 132.3, 133.9, 177.0; **IR** (KBr) 1573, 1083, 844 cm⁻¹; **HRMS-FAB** (*m/z*) Calcd for C₁₂H₁₈OSiI [(M-BF₄)⁺] 333.0172, Found 333.0173.

(E)-(2-Cyclohexylmethoxy-1-(trimethylsilyl)vinyl)(phenyl)iodonium tetrafluoroborate (1g)



colorless crystalline solid (CH₂Cl₂ / hexane); **mp** 134–136°C (decomp.); ¹H NMR (400 MHz, CDCl₃) δ 0.19 (s, 9H), 0.97–1.07 (m, 2H), 1.13–1.32 (m, 3H), 1.66–1.79 (m, 6H), 4.09 (d, *J* = 6.0 Hz, 2H), 7.44–7.49 (m, 2H), 7.58–7.62 (m, 1H), 7.87–7.91 (m, 2H), 8.18 (s, 1H); ¹³C NMR (100.5 MHz, CDCl₃) δ 0.0, 25.6, 26.2, 29.2, 82.2, 94.2, 110.7, 132.0, 132.2, 133.7, 176.3; **IR** (KBr) 1577, 1083, 842 cm⁻¹; **HRMS-FAB** (*m/z*) Calcd for C₁₈H₂₈OSiI [(M-BF₄)⁺] 415.0954, Found 415.0965.

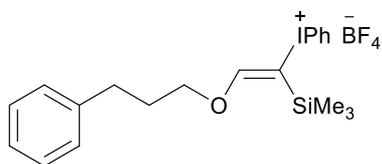
(E)-(2-Benzyloxy-1-(trimethylsilyl)vinyl)(phenyl)iodonium tetrafluoroborate (1h)



orange oil (CH₂Cl₂ / hexane); ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 9H), 5.27 (s, 2H), 7.31–7.41 (m, 7H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 2H), 8.27 (s, 1H); ¹³C NMR (100.5 MHz, CDCl₃) δ 0.0, 77.6, 95.9, 110.8, 128.4, 128.8, 128.9, 131.9, 132.1, 133.8, 135.4, 175.3; **IR** (neat) 1571, 1066, 848 cm⁻¹; **HRMS-FAB**

(*m/z*) Calcd for C₁₈H₂₂OSi [(M-BF₄)⁺] 409.0485, Found 409.0499.

(*E*)-(2-(3-Phenylpropoxy)-1-(trimethylsilyl)vinyl)(phenyl)iodonium tetrafluoroborate (1i)

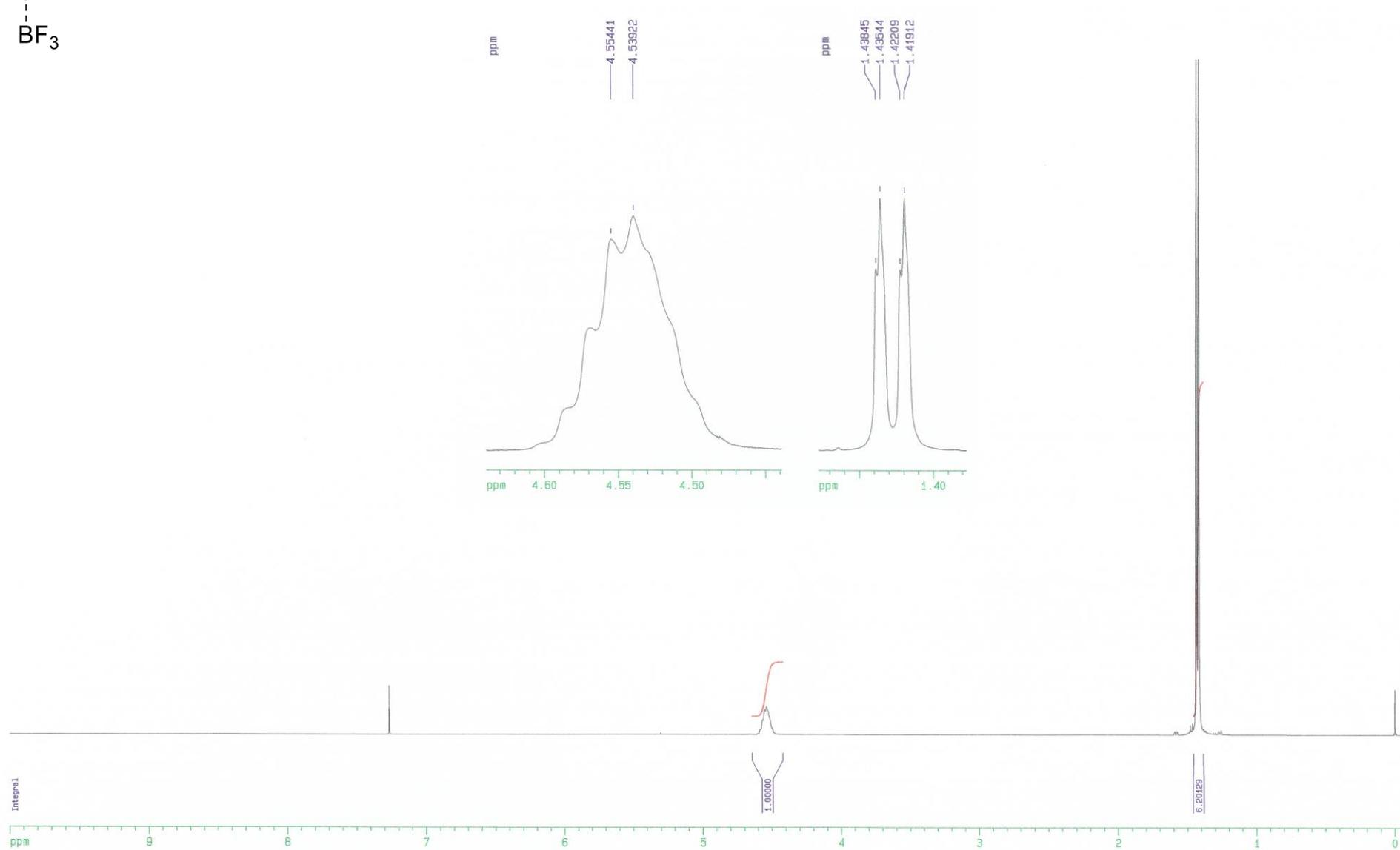
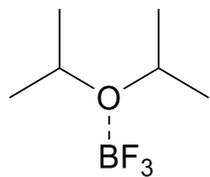


orange oil (CH₂Cl₂ / hexane); ¹H NMR (400 MHz, CDCl₃) δ 0.20 (s, 9H), 1.99–2.06 (m, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 7.16–7.21 (m, 3H), 7.26–7.31 (m, 2H), 7.39–7.44 (m, 2H), 7.51–7.56 (m, 1H), 7.90–7.94 (m, 2H), 8.23 (s, 1H); ¹³C NMR (100.5 MHz, CDCl₃) δ 0.1, 31.5, 31.8, 75.8, 94.6, 110.9, 126.2, 128.5, 128.6, 132.0, 132.2, 133.9, 141.0, 175.8; **HRMS-FAB** (*m/z*) Calcd for C₂₀H₂₆OSi [(M-BF₄)⁺] 437.0798, Found 437.0772.

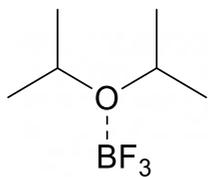
References

- (1) H. Shalzman and J. G. Sharefskin, *Org. Synth.*, 1963, **43**, 60.
- (2) N. Yasukawa, T. Kanie, M. Kuwata, Y. Monguchi, H. Sajiki and Y. Sawama, *Chem. Eur. J.*, 2017, **23**, 10974–10977.
- (3) G. Urgoitia, R. SanMartin, M. T. Herrero and E. Domínguez, *Adv. Synth. Catal.*, 2016, **358**, 3307–3312.
- (4) T. Kurita, K. Hattori, S. Seki, T. Mizumoto, F. Aoki, Y. Yamada, K. Ikawa, T. Maegawa, Y. Monguchi and H. Sajiki, *Chem. Eur. J.*, 2008, **14**, 664–673.
- (5) A. Gellert, N. Kahlcke, M. Feurer and S. Roth, *Chem. Eur. J.*, 2011, **17**, 12203–12209.
- (6) W. Kwasnik, *Handb. Prep. Inorg. Chem.*, 1963, 150–271.
- (7) M. Ochiai, M. Kunishima, K. Fuji, M. Shiro and Y. Nagao, *J. Chem. Soc., Chem. Commun.*, 1988, 1076–1077.
- (8) K. Miyamoto, T. Okubo, M. Hirobe, M. Kunishima and M. Ochiai, *Tetrahedron*, 2010, **66**, 5819–5826.

^1H NMR; $\text{BF}_3\text{-O}^i\text{Pr}_2$ (CDCl_3)

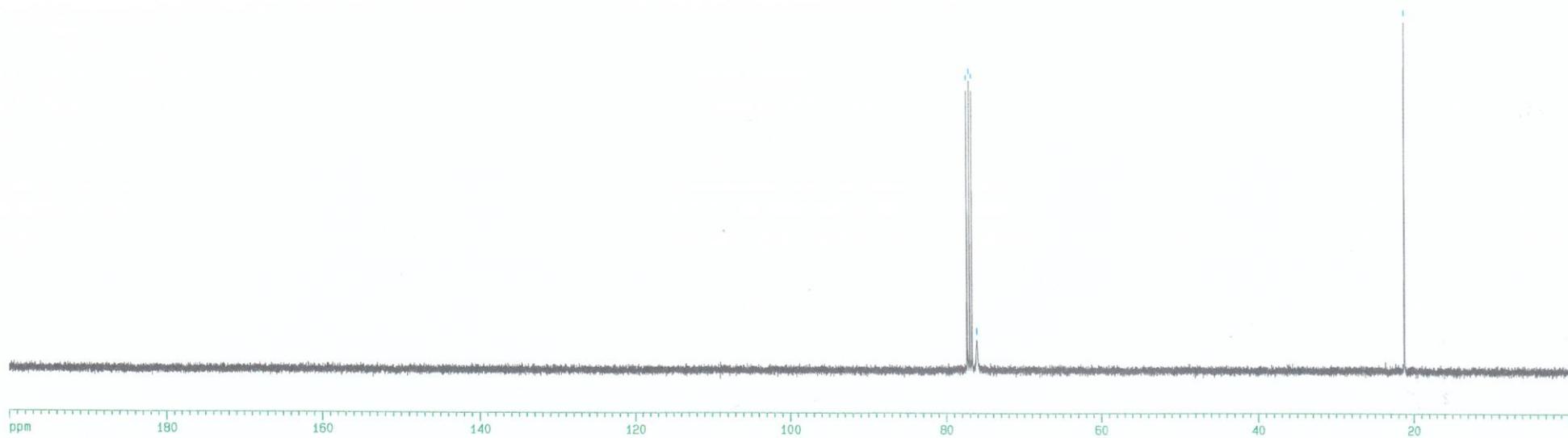


^{13}C NMR; $\text{BF}_3\text{-O}^i\text{Pr}_2$ (CDCl_3)

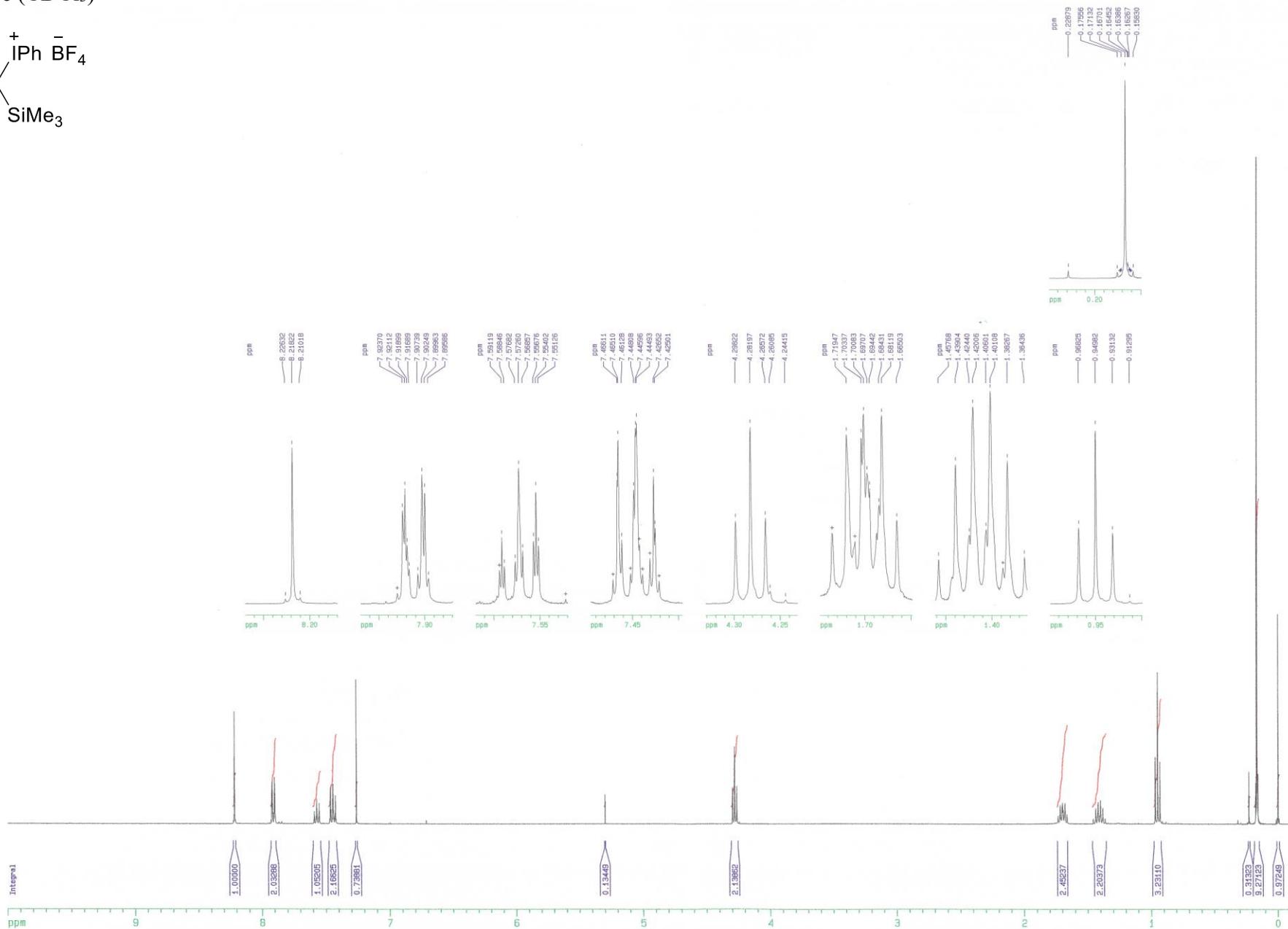
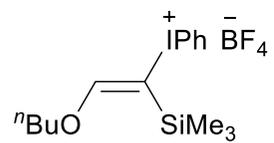


77.3445
77.0266
76.7092
76.1369
76.1065
76.0381

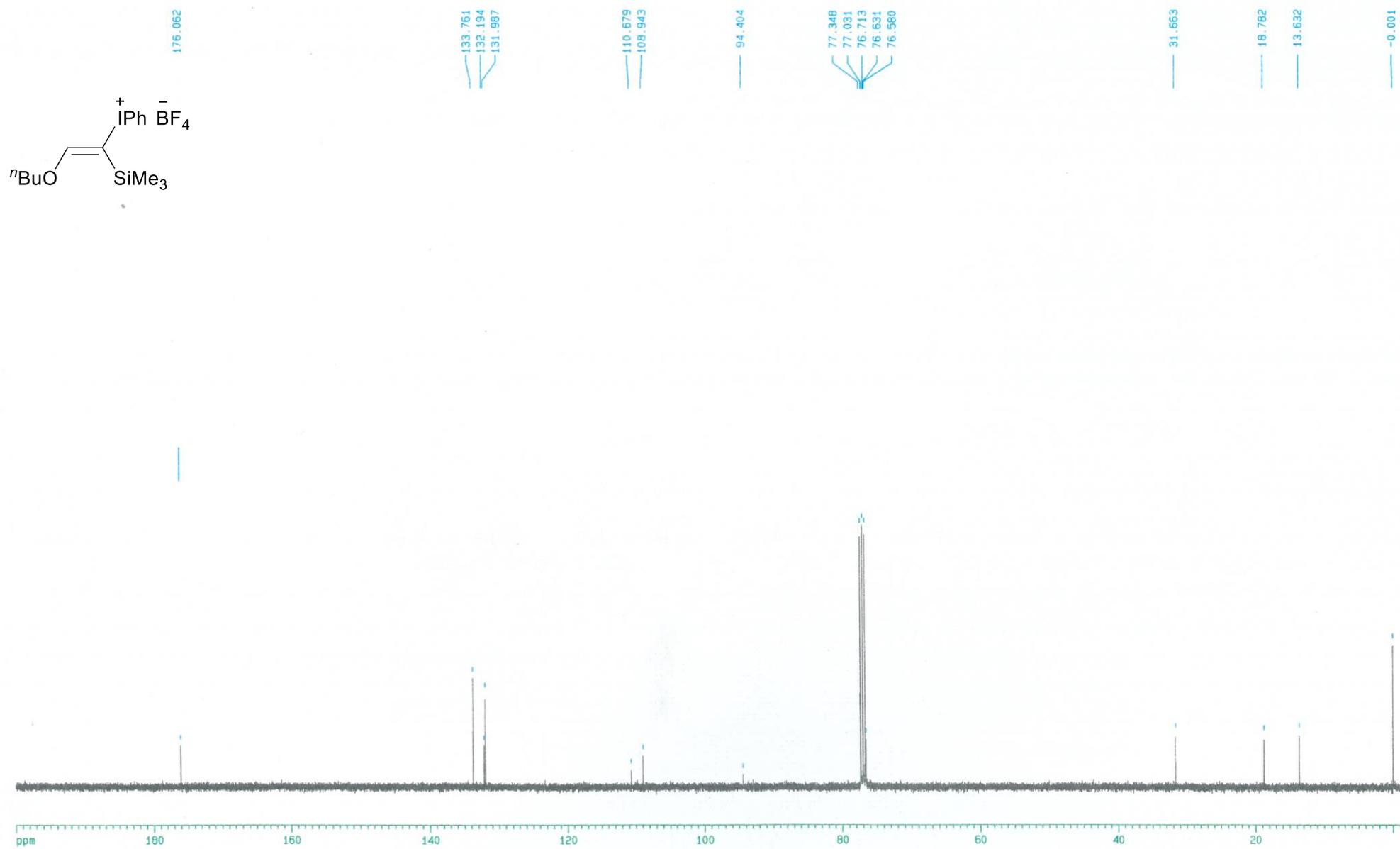
21.2081
21.1867



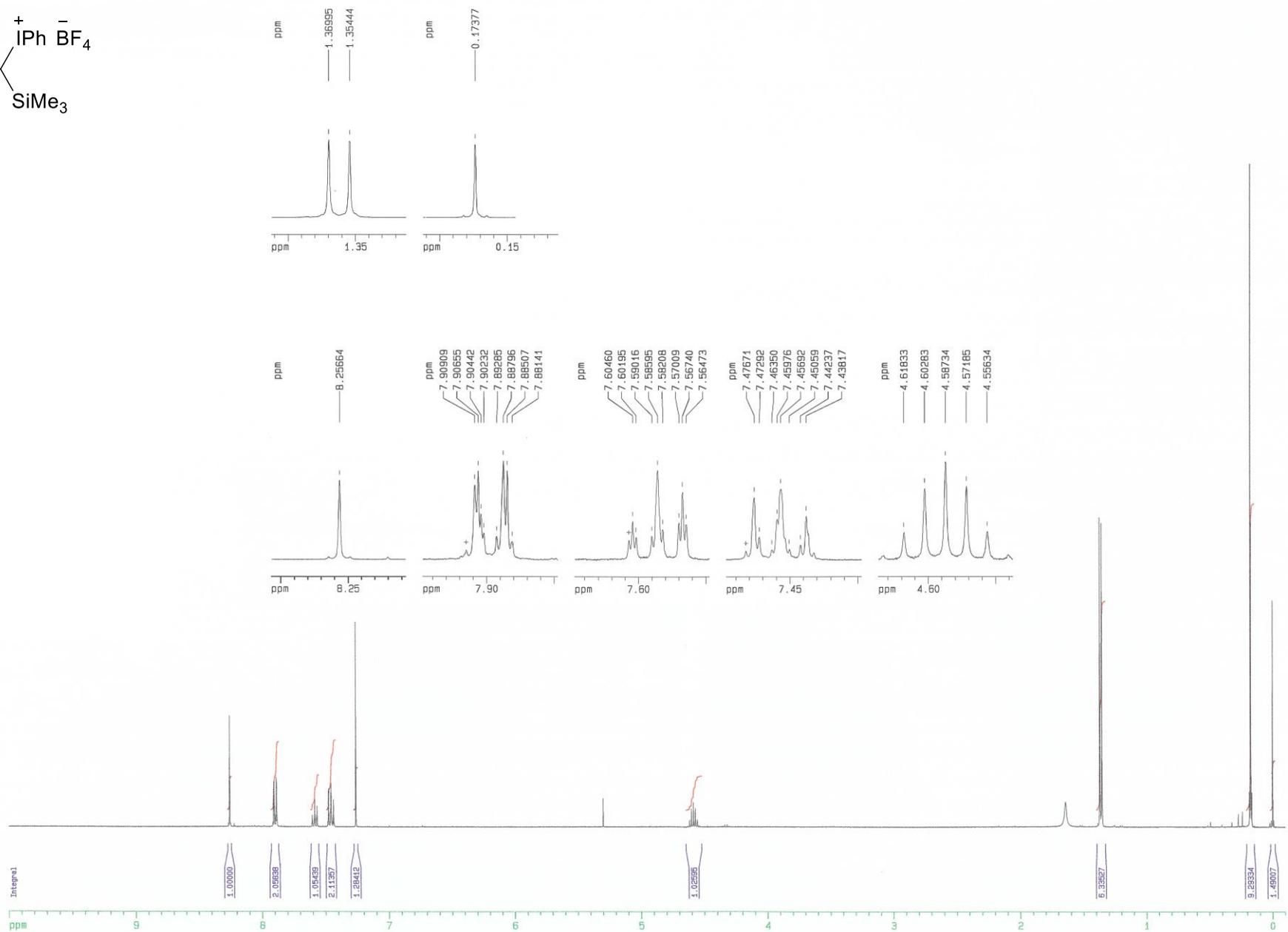
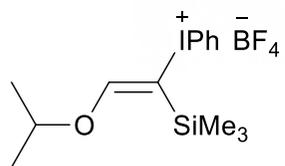
^1H NMR; **1c** (CDCl_3)



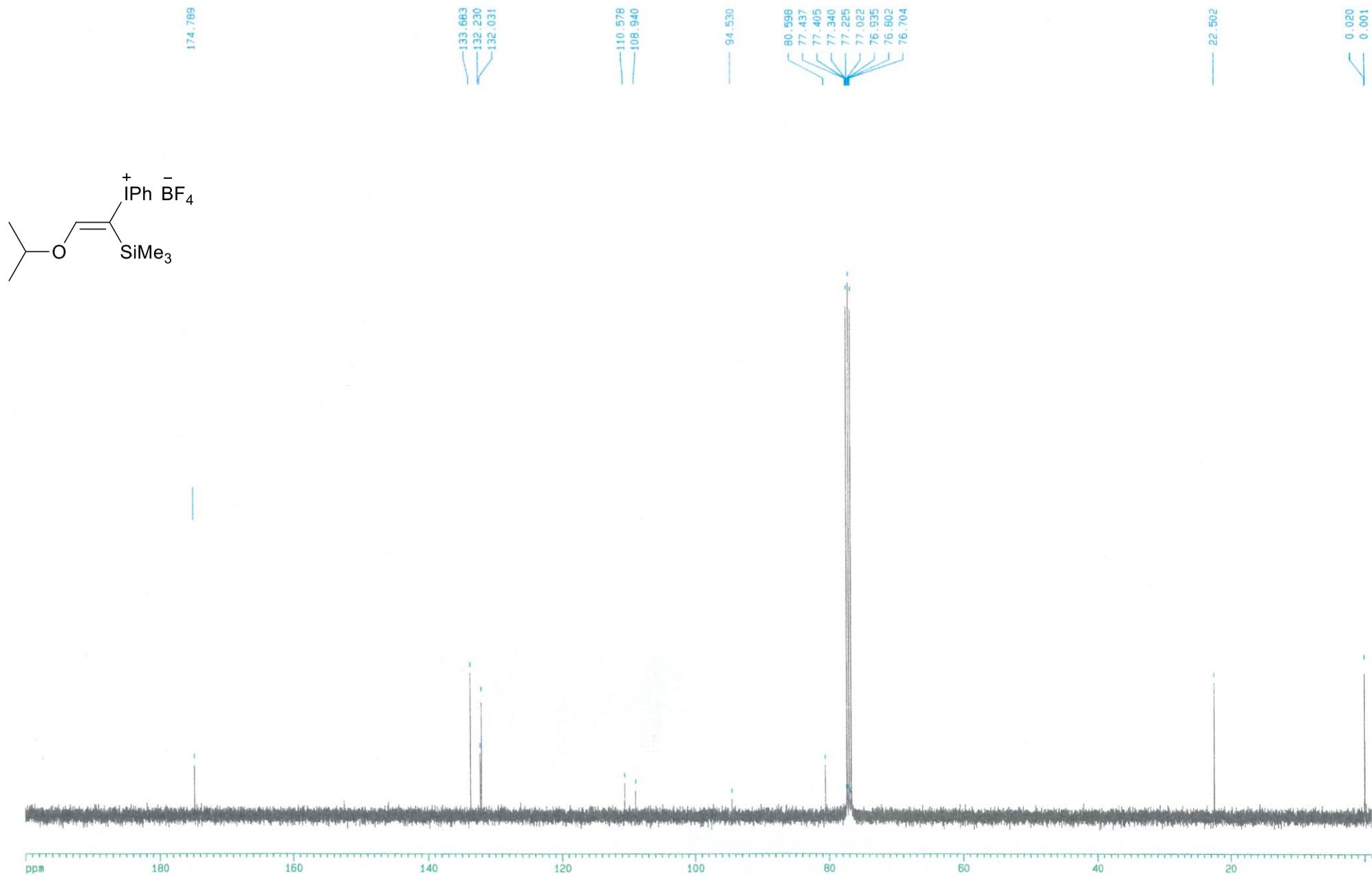
^{13}C NMR: **1c** (CDCl_3)



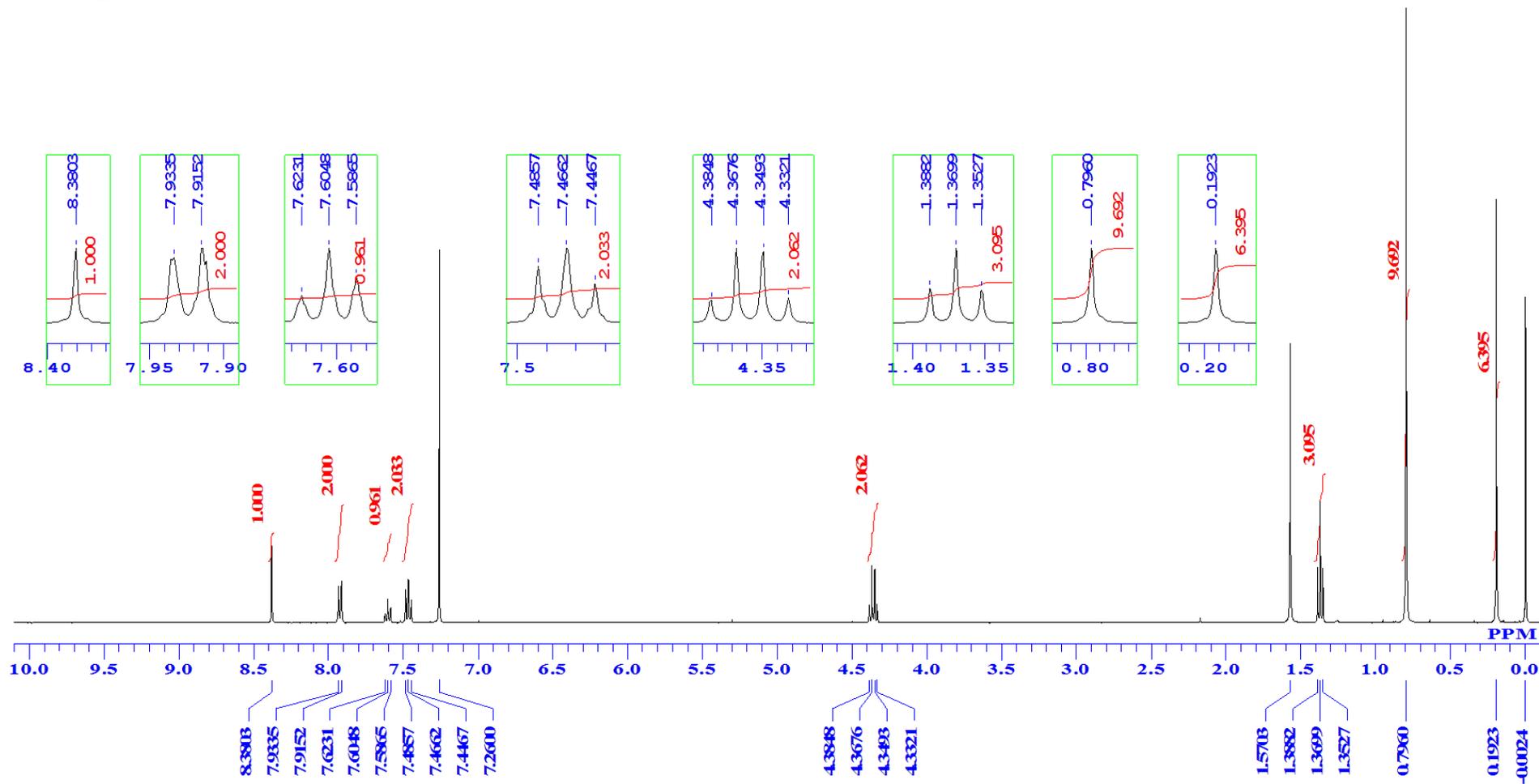
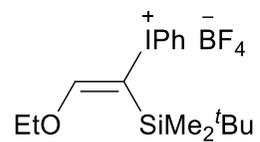
^1H NMR: **1d** (CDCl_3)



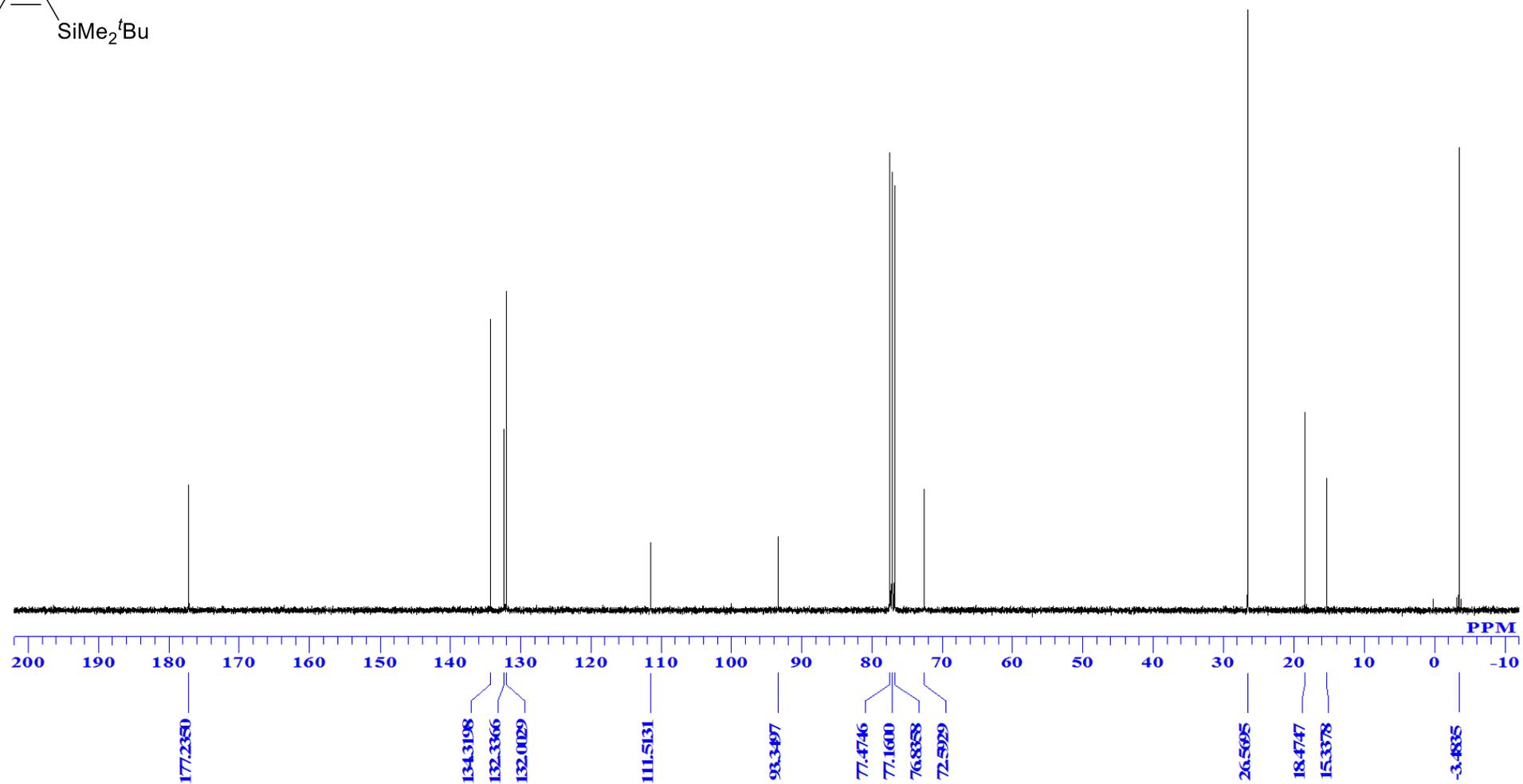
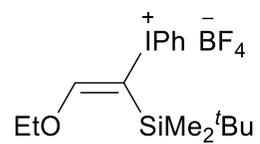
^{13}C NMR: **1d** (CDCl_3)



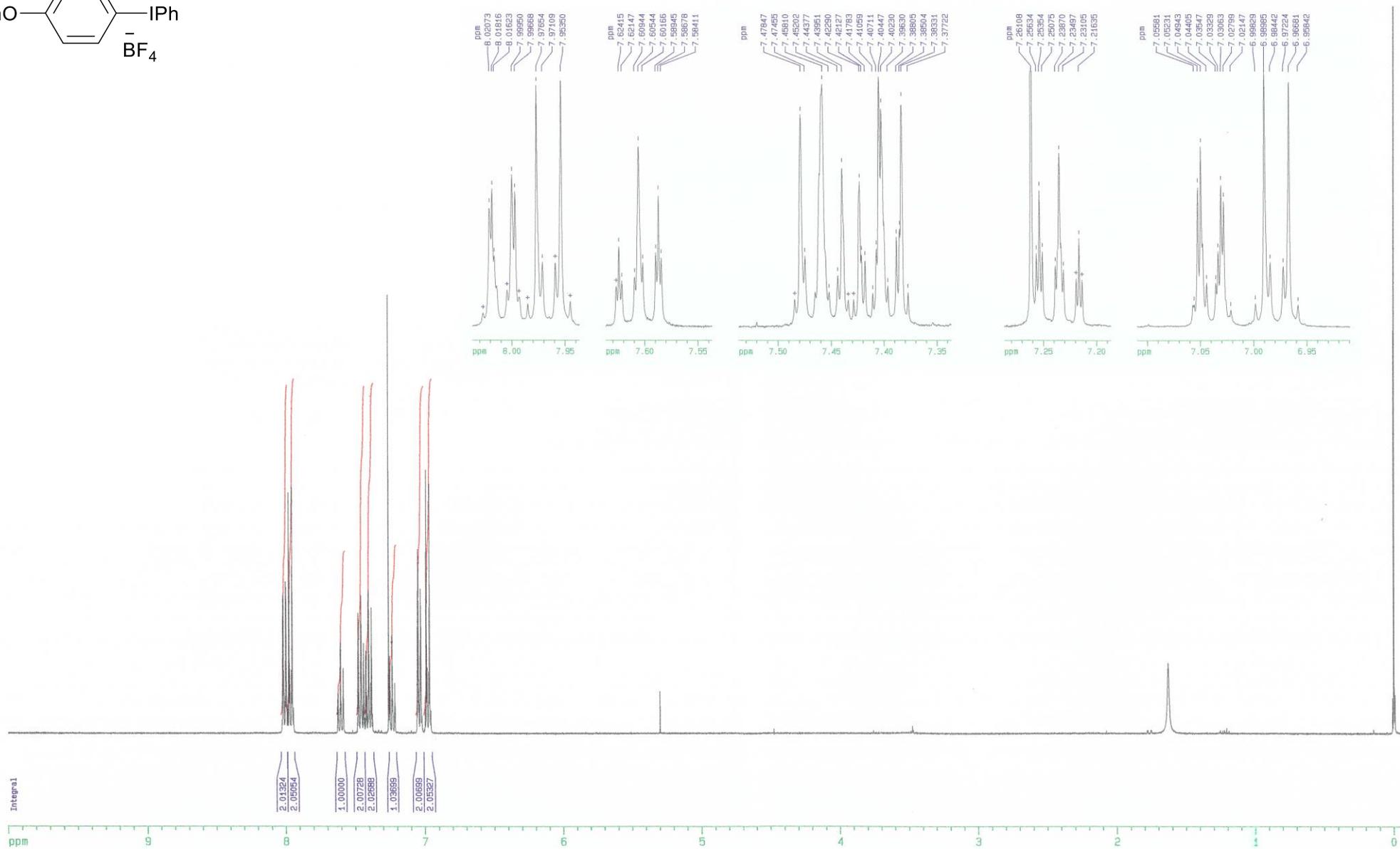
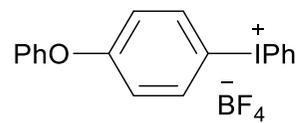
^1H NMR: **1e** (CDCl_3)



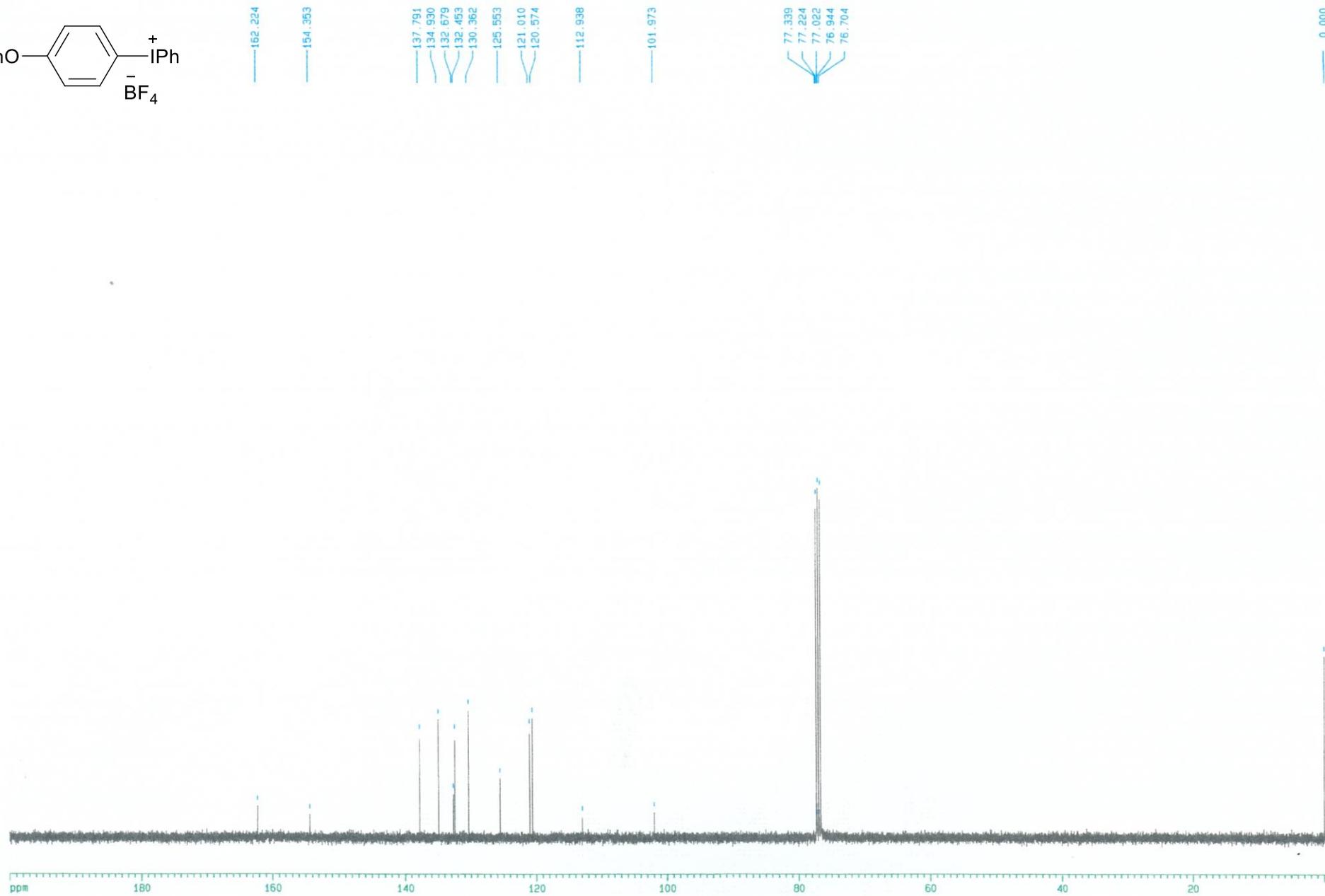
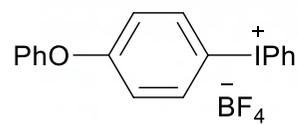
^{13}C NMR: **1e** (CDCl_3)



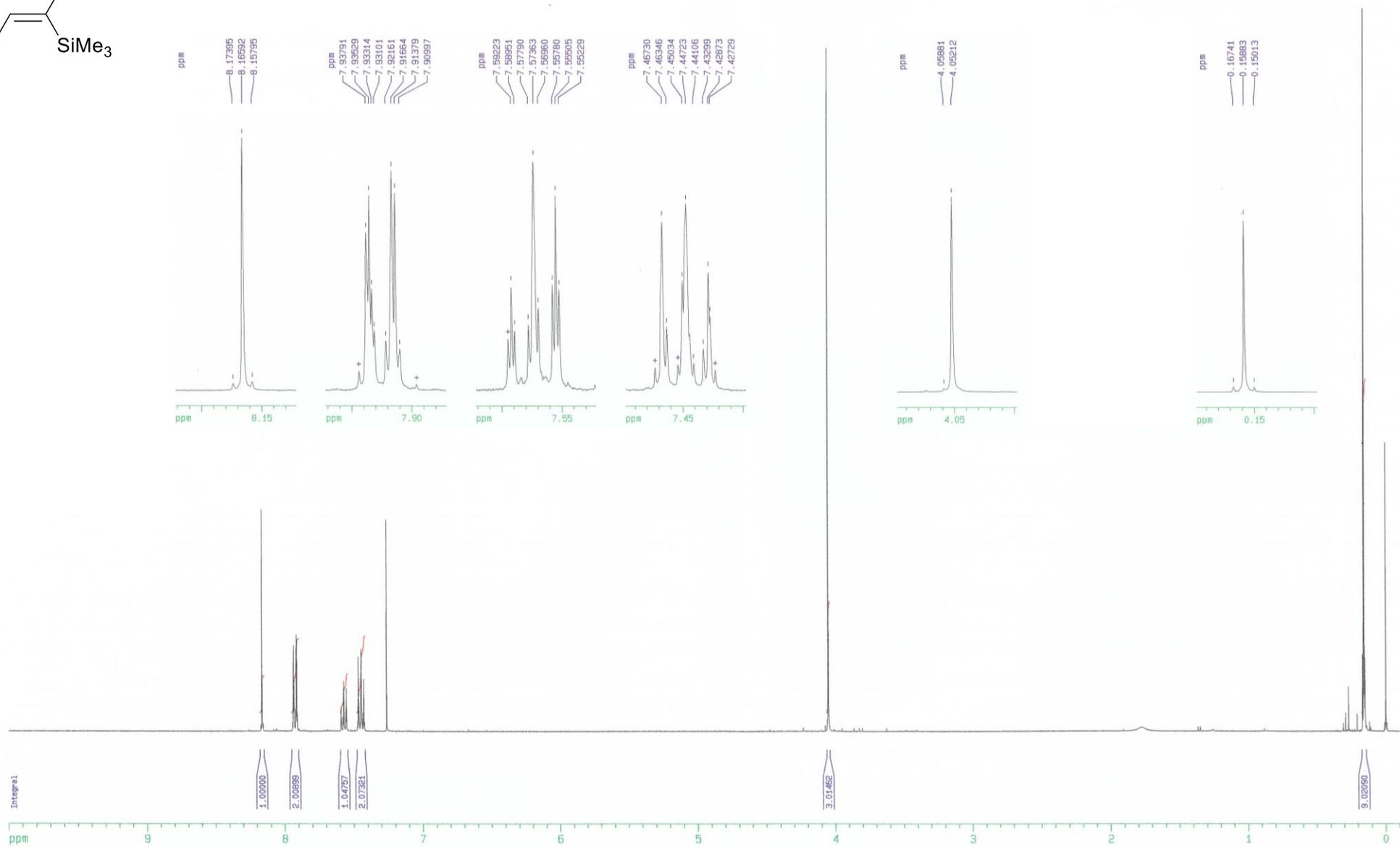
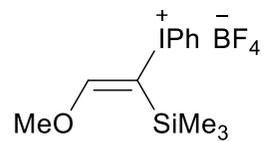
^1H NMR: **3** (CDCl_3)



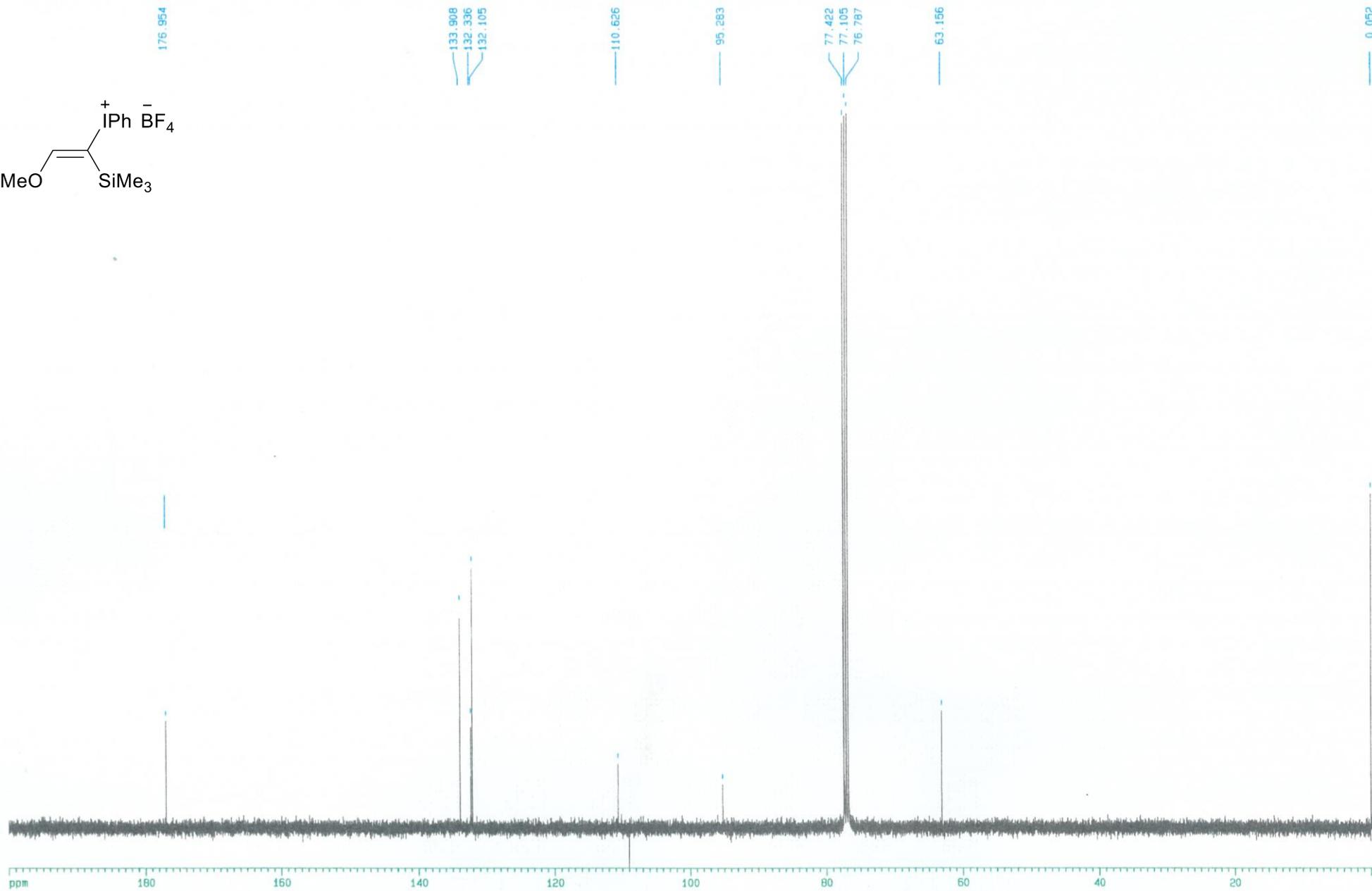
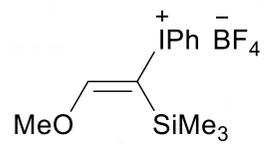
^{13}C NMR: **3** (CDCl_3)



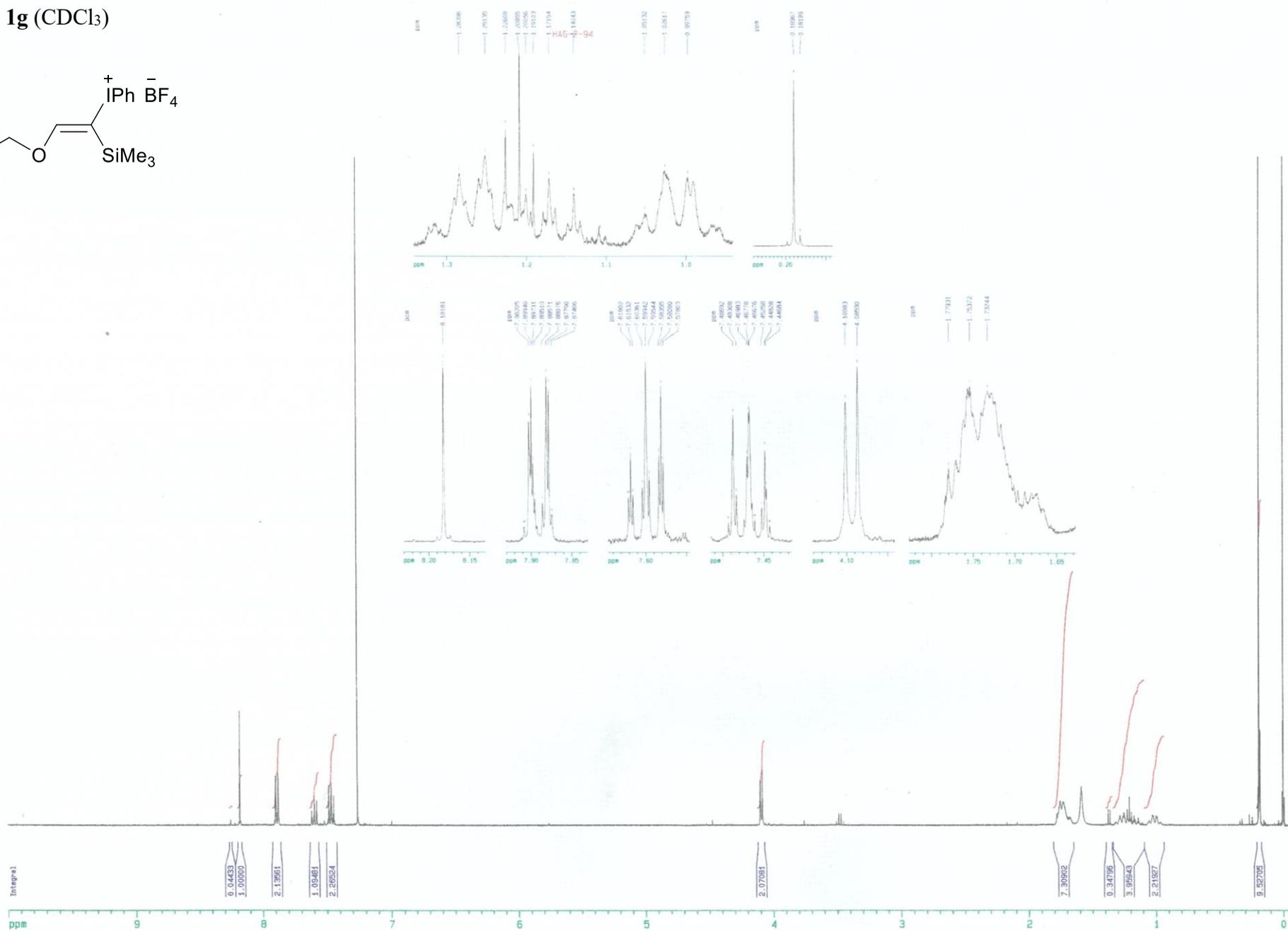
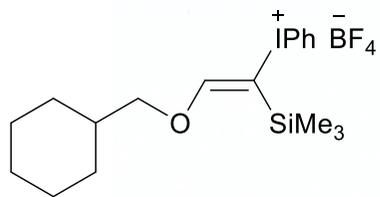
^1H NMR: **1f** (CDCl_3)



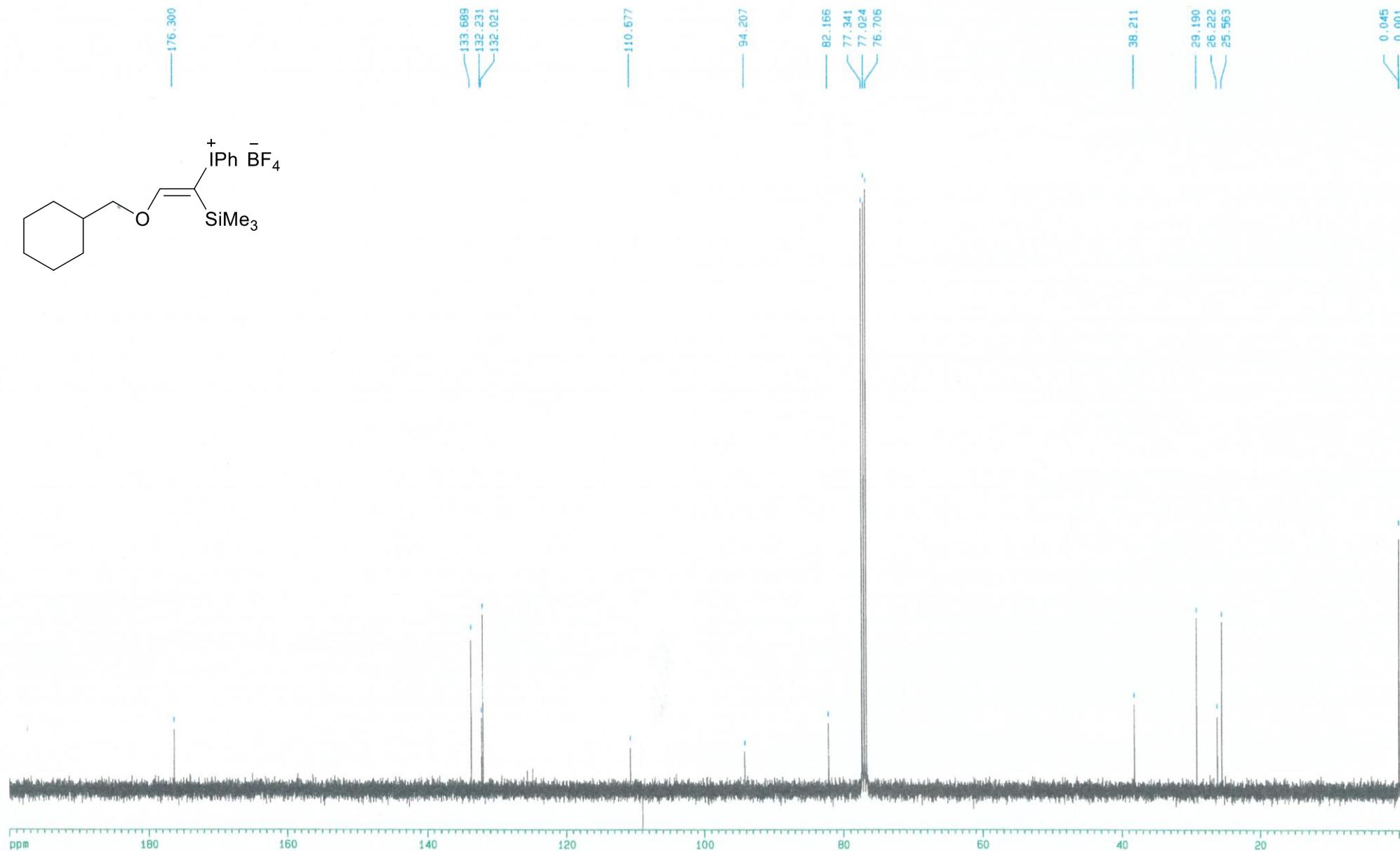
^{13}C NMR: **1f** (CDCl_3)



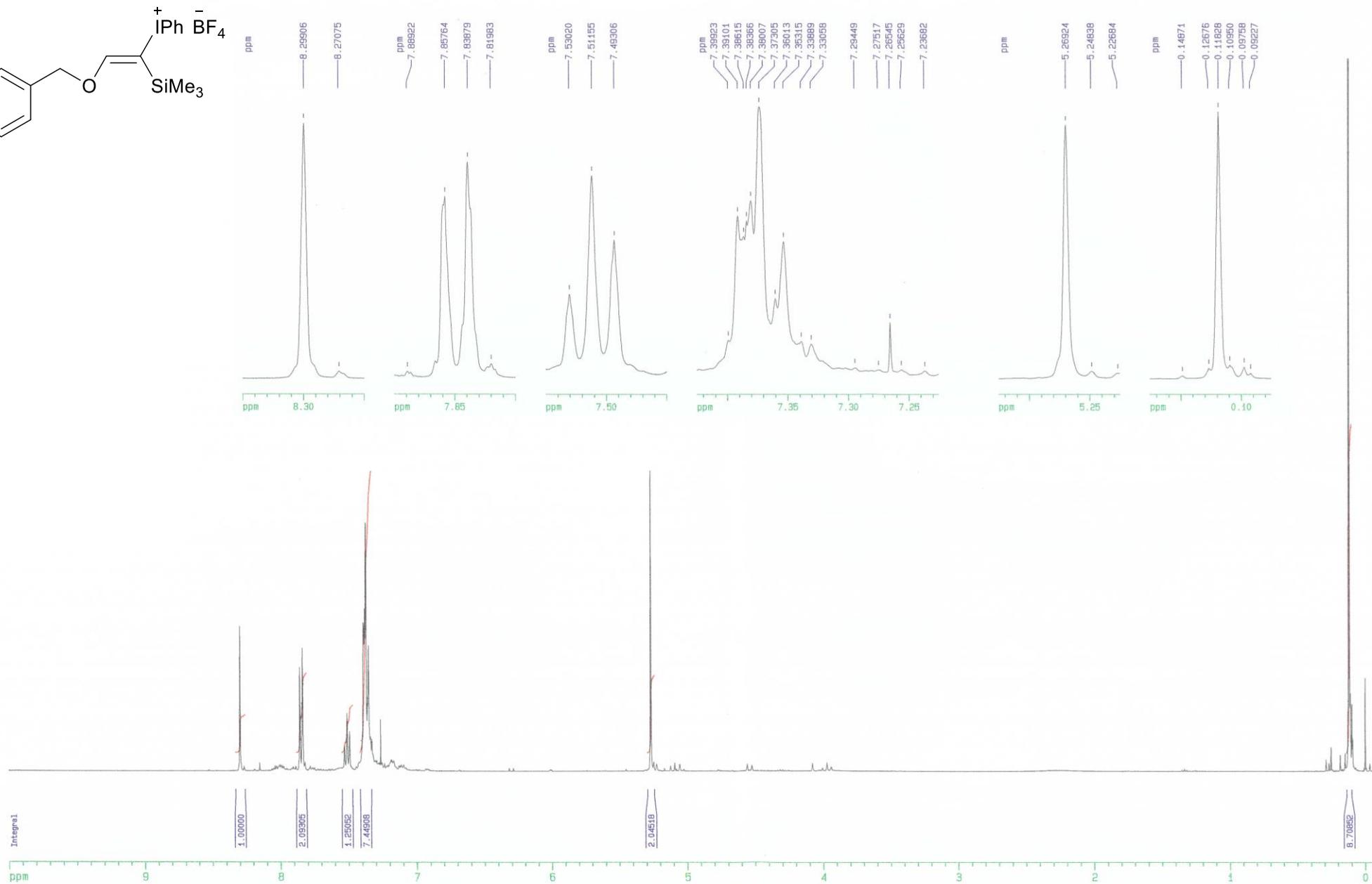
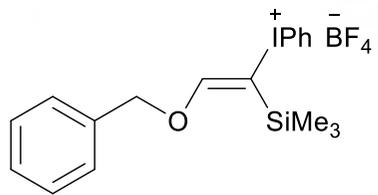
$^1\text{H NMR}$: **1g** (CDCl_3)



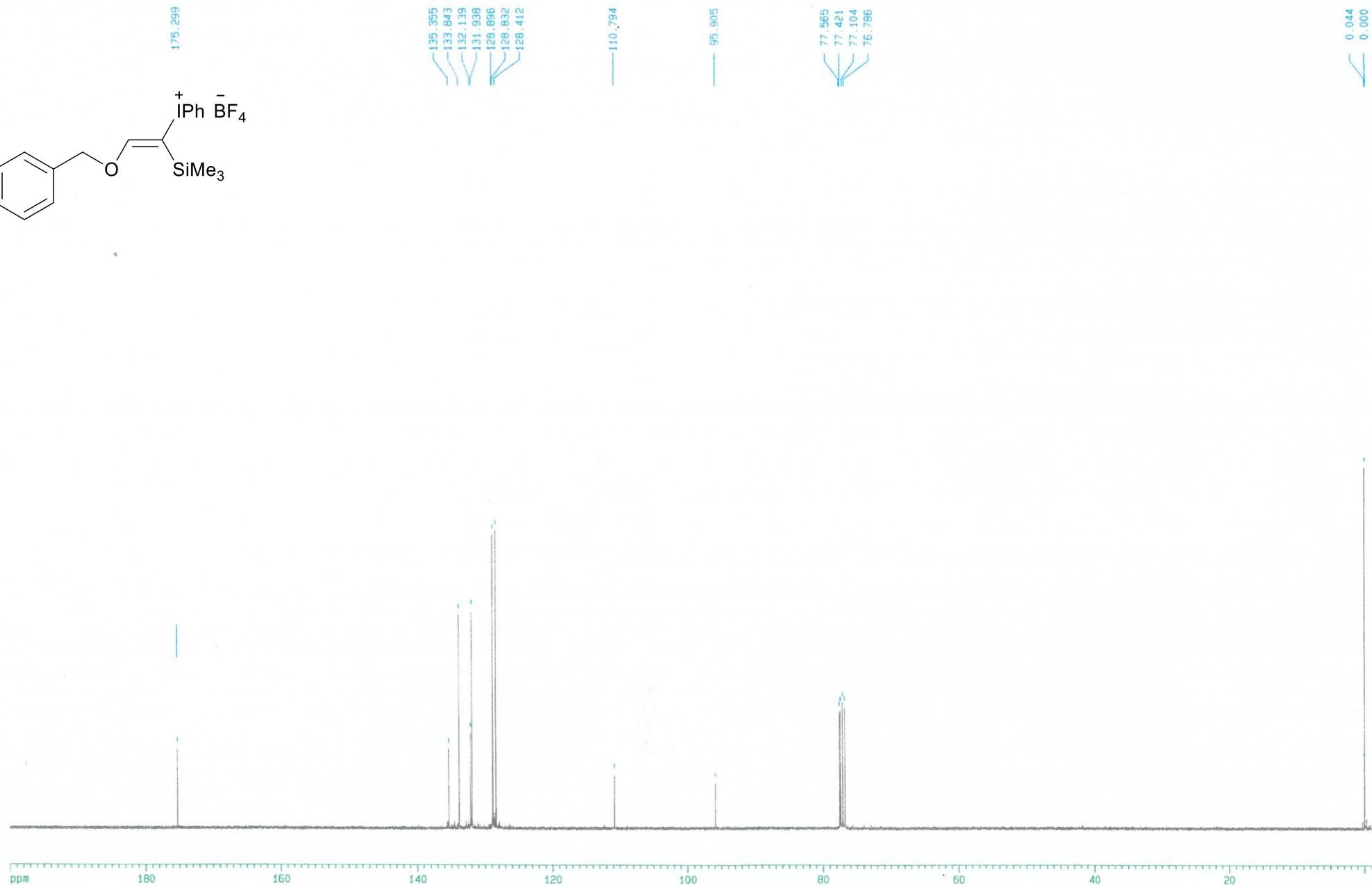
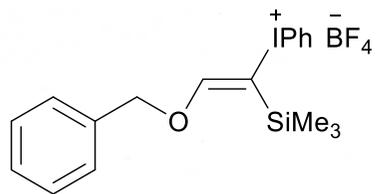
^{13}C NMR: **1g** (CDCl_3)



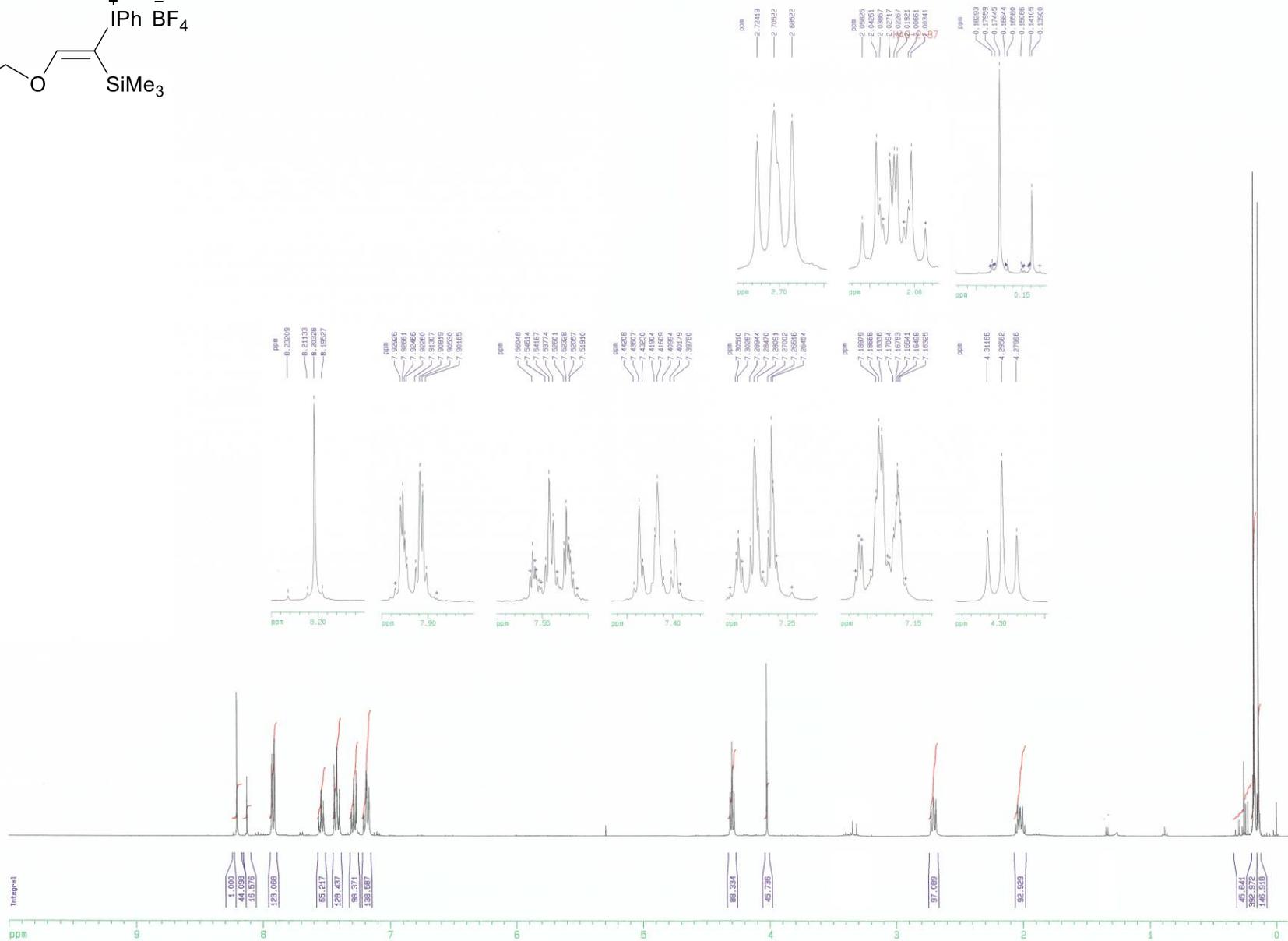
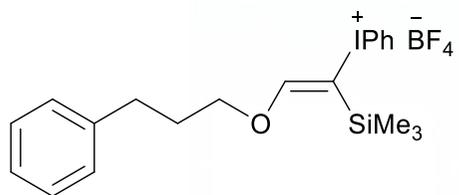
¹H NMR: **1h** (CDCl₃)



^{13}C NMR: **1h** (CDCl_3)



^1H NMR: **1i** (CDCl_3)



^{13}C NMR: **1i** (CDCl_3)

