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– Supporting Information –

Electrophilic Reactivities of α,β-Unsaturated Iminium Ions

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General

Analytics. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3CN on 300, 400 or 600 MHz NMR spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent as the internal standard ($CDCl_3$: δ_C = 77.23; CD_3CN = 1.39). The following abbreviations were used to designate chemical shift mutiplicities: br s = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet. The assignments of invidual NMR signals were based on additional 2D-NMR. Please note that for technical reasons the listing of NMR chemical shifts above the original spectra is not complete (pp S8–S21). For complete listings of NMR signals see pp S3–S6. HRMS were recorded on a Finnigan MAT 95 Q mass spectrometer.

Chemicals. Solvents were distilled or dried prior to use over the indicated drying agents: Dichloromethane (calcium hydride), diethyl ether (sodium/benzophenone).

Ketene acetals **4a** and **4b** were prepared by the reported methods.[S1] Cinnamylaldehyde (**1**) was purified by distillation before usage and stored under nitrogen. Amines **2a–e** were purchased from Aldrich and used as received, whereas **2f** and **2g** were prepared according to literature procedures.[S2]

Kinetics. The kinetics of the reactions of (**3a–g**)-OTf with ketene acetals **4a** and **4b** were followed by UV/vis spectroscopy in CH_2Cl_2 (Table S1) by using a stopped-flow spectrophotometer system (Applied Photophysics SX.18MV-R). The kinetic runs were initiated by mixing equal volumes of dichloromethane solutions of the ketene acetals and the iminium salts. Concentrations and rate constants for the individual kinetic experiments for the reactions of ketene acetals with iminium ions are given in page S22–S35. The temperature of the solutions during the kinetic studies was maintained to within ± 0.2 °C by using circulating bath cryostats.

Table S1. Molar absorption coefficients ε of the iminium triflates (**3a-g**)-OTf in CH_2Cl_2.

Ar_2CH^+	λ_{max} (nm)	ε (M^{-1} cm^{-1})
3a	360	7.52×10^4
3b	348	4.80×10^4
3c	349	4.65×10^4
3d	342 [a]	3.39×10^4 [a]
3e	342	1.03×10^5
3f	370	1.62×10^4
3g	365	4.32×10^4

[a] Data for **3d**-BF_4 in dichloromethane from ref. [S3].

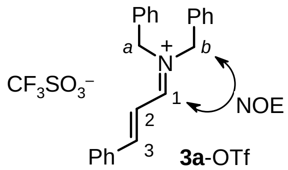
[S1] K. Oisaki, Y. Suto, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2003**, *125*, 5644–5645.

[S2] a) K. C. Ahrendt, C. J. Borths, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2000**, *122*, 4243–4244; b) M. Marigo, T. C. Wabnitz, D. Fielenbach, K. A. Jørgensen, *Angew. Chem. Int. Ed.* **2005**, *44*, 794–797.

[S3] M. Fischer, H. J. Veith, *Helv. Chim. Acta* **1981**, *64*, 1083–1091.

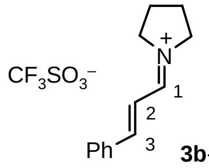
Typical Procedure[S4] for the Preparation of (3a-e)-OTf. A mixture of 1-(trimethylsilyl)pyrrolidine (1.62 g, 11.3 mmol) and trimethylsilyl triflate (2.49 g, 11.3 mmol) in Et_2O (5.0 mL) was added dropwise to (30 min) an Et_2O solution (25 mL) of **1** (1.42 g, 10.7 mmol) at room temperature over 30 min. Then, the reaction mixture was stirred for another 1.5 h. The precipitated crystals were collected by filtration under nitrogen atmosphere, and washed with dry Et_2O. Recrystallization from CH_2Cl_2-Et_2O gave **3b**-OTf (2.6 g, 77 %).

3a-OTf (preparation according to the Typical Procedure): yield: 52 %; mp 91–92 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.90 (s, 2 H, NC^aH_2), 4.92 (s, 2 H, NC^bH_2), 7.02–7.11 (m, 2 H), 7.17–7.39 (m, 11 H), 7.39–7.48 (m, 1 H), 7.63 (d, J = 7.5 Hz, 2 H), 8.32 (d, J = 15.0 Hz, 1 H, 3-H), 9.28 ppm (d, J = 10.8 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 54.6 (t, NCH_2), 63.2 (t, NCH_2), 115.7 (d, C-2), 120.5 (q, $J_{C,F}$ = 318 Hz, CF_3), 127.8, 129.7, 129.7, 129.8, 129.9, 130.2, 131.1, 131.1, 131.2, 133.6, 134.6, 166.0 (d, C-3), 171.9 ppm (d, C-1); HRMS (ESI positive) m/z: Calcd for $C_{23}H_{22}N$ [M^+] 312.1752, found 312.1751.



3a-OTf

3b-OTf (as described in the Typical Procedure): yield: 77 %; mp 120–121 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.89–2.16 (m, 4 H, 2 × CH_2), 3.88–4.16 (m, 4 H, 2 × NCH_2), 7.05 (dd, J = 15.2 Hz, 10.5 Hz, 1 H, 2-H), 7.27–7.53 (m, 3 H), 7.58–7.74 (m, 2 H), 7.91 (d, J = 15.3 Hz, 1 H, 3-H), 8.75 ppm (d, J = 10.5 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 24.4 (t), 24.6 (t), 52.0 (t), 57.3 (t), 117.5 (d, C-2), 120.9 (q, $J_{C,F}$ = 319 Hz, CF_3), 129.5, 130.5, 133.6, 133.7, 161.0 (d, C-3), 166.6 ppm (d, C-1); HRMS (ESI positive) m/z: Calcd for $C_{14}H_{18}N$ [M^+] 168.1277, found 186.1280.

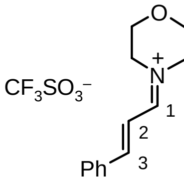


3b-OTf

3c-OTf (preparation according to the Typical Procedure): yield: 43 %; mp 111–112 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ 3.90–3.98 (m, 4 H, 2 × OCH_2), 3.98–4.14 (m, 4 H, 2 × NCH_2), 7.39 (dd, J = 15.2 Hz, 10.4 Hz, 1 H, 2-H), 7.51–7.69 (m, 3 H, Ph), 7.82–7.87 (m, 2 H, Ph),

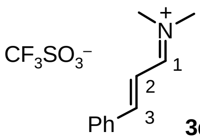
[S4] a) W. Schroth, U. Jahn, D. Ströhl, *Chem. Ber.* **1994**, *127*, 2013–2022; b) W. Schroth, U. Jahn, *J. Prakt. Chem.* **1998**, *340*, 287–299.

7.98 (d, J = 15.2 Hz, 1 H, 3-H), 8.45 ppm (d, J = 10.8 Hz, 1 H, 1-H); ^{13}C NMR (CD_3CN, 100.6 MHz): δ 52.1 (t, NCH_2), 59.2 (t, NCH_2), 67.0 (t, OCH_2), 67.5 (t, OCH_2), 117.3 (d, C-2), 122.2 (q, $J_{C,F}$ = 321 Hz, CF_3), 130.6 (d), 131.4 (d), 134.75 (s), 134.81 (d), 162.1 (d, C-3), 169.4 ppm (d, C-1); HRMS (ESI positive) m/z: Calcd for $C_{13}H_{16}NO$ [M^+] 202.1232, found 202.1236.



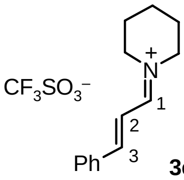
3c-OTf

3d-OTf (preparation according to the Typical Procedure): yield: 89 %. ^{1}H NMR (CD_3CN, 400 MHz): δ 3.55 (s, 3 H, NMe), 3.62 (s, 3 H, NMe), 7.28 (dd, J = 15.3, 10.5 Hz, 1 H, 2-H), 7.52–7.63 (m, 3 H, Ph), 7.83–7.92 (m, 2 H, Ph), 7.91 (d, J = 15.4 Hz, 1 H, 3-H), 8.37 ppm (d, J = 10.5 Hz, 1 H, 1-H); ^{13}C NMR (CD_3CN, 100.6 MHz): δ 42.3 (q, NMe), 50.0 (q, NMe), 118.0 (d, C-2), 122.2 (q, $J_{C,F}$ = 321 Hz, CF_3), 130.5 (d), 131.2 (d), 134.6 (d), 134.7 (s), 161.2 (d, C-3), 171.1 ppm (d, C-1). Anal. Calcd for $C_{12}H_{14}F_3NO_3S$: C, 46.60: H, 4.56: N, 4.53. Found: C, 46.47: H, 4.54: N, 4.47.



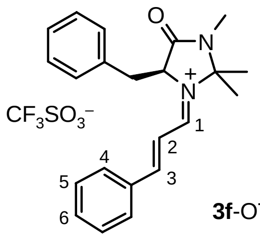
3d-OTf

3e-OTf (preparation according to the Typical Procedure): yield: 66 %; mp 163–164 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.68–1.95 (m, 6 H), 3.86–4.08 (m, 4 H), 7.26–7.54 (m, 4 H), 7.72 (d, J = 6.9 Hz, 2 H), 8.04 (d, J = 15.0 Hz, 1 H, 3-H), 8.73 ppm (d, J = 10.8 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 23.0 (t), 26.7 (t), 27.3 (t), 51.7 (t), 60.0 (t), 115.6 (d, C-2), 120.9 (q, $J_{C,F}$ = 320 Hz, CF_3), 129.6 (d), 130.7 (d), 133.7 (s), 133.9 (d), 162.6 (d, C-3), 168.2 ppm (d, C-1); HRMS (ESI positive) m/z: Calcd for $C_{14}H_{18}N$ [M^+] 200.1439, found 200.1436.



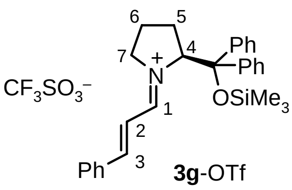
3e-OTf

3f-OTf. An aqueous solution of CF_3SO_3H (4.0 g in 20 ml of water) was added to a solution of (E)-**1** (3.56 g, 27.0 mmol) and **2f** (5.89 g, 27.0 mmol) in diethyl ether (25 mL). After 1 h, the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (15 mL). The organic layers were combined, washed with brine, and dried ($MgSO_4$). After evaporation of the solvent under vacuum, the residue was mixed with Et_2O. The solvent was then removed under vacuum, then the residue was remixed with Et_2O. This cycle was repeated several times until **3f**-OTf was obtained as a pale yellow solid (3.2 g, 24 %); mp decomposition. ^1H NMR ($CDCl_3$, 600 MHz): δ 0.73 (s, 3 H, Me), 1.69 (s, 3 H, Me), 2.73 (s, 3 H, NMe), 3.46–3.55 (m, 2 H, PhC*H*$_2$), 5.33 (br s, 1 H, $^+$N-CH), 6.95 (d, *J* = 6.6 Hz, 2 H), 7.16–7.23 (m, 3 H, 5-H and 6-H), 7.38 (dd, *J* = 14.4 Hz, 10.2 Hz, 1 H, 2-H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.55 (t, *J* = 7.8 Hz, 1 H), 7.88 (d, *J* = 7.8, 2 H, 4-H), 8.59 (d, *J* = 15.0 Hz, 1 H, 3-H), 9.31 ppm (d, *J* = 10.8, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 24.2 (q, CH_3), 25.7 (q, CH_3), 27.5 (q, NMe), 36.6 (t, Ph*C*H$_2$), 64.2 (d, $^+$N-CH), 85.6 (s), 117.2 (d, C-2), 120.8, (q, $J_{C,F}$ = 320 Hz, CF_3), 128.6 (d), 129.4 (d), 129.8 (d), 130.0 (d), 132.1 (d), 133.3 (s), 133.6 (s), 135.4 (d), 164.5 (s, CO), 167.9 (d, C-3), 168.1 ppm (d, C-1); HRMS (ESI positive) *m*/*z*: Calcd for $C_{22}H_{25}N_2O$ [M^+] 300.1967, found 300.1966.



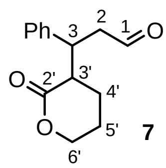
3f-OTf

3g-OTf (preparation as described above for **3f**-OTf). Obtained as a *E*/*Z*-mixture in a ratio of 10:1. Only the signals of (*E*)-**3g**-OTf are given. ^1H NMR ($CDCl_3$, 600 MHz): δ –0.19 (s, 9 H), 1.20–1.30 (m, 1 H, 6-H), 1.82–1.89 (m, 1 H, 6-H), 2.02–2.11 (m, 1 H, 5-H), 2.53–2.62 (m, 1 H, 5-H), 2.62–2.69 (m, 1 H, 7-H), 3.89–3.96 (m, 1 H, 7-H), 5.54 (d, *J* = 8.5 Hz, 1 H, 4-H), 6.94 (dd, *J* = 15.0 Hz, 10.8 Hz, 1 H, 2-H), 7.28 (d, *J* = 7.2 Hz, 2 H), 7.33–7.43 (m, 8 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 7.51–7.57 (m, 1 H), 7.71 (d, *J* = 7.4 Hz, 2 H), 7.76 (d, *J* = 15.0 Hz, 1 H, 3-H), 8.60 ppm (d, *J* = 10.8 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 150.7 MHz): δ 1.65 (q, $OSiMe_3$), 22.7 (t, C-6), 26.3 (t, C-5), 52.6 (t, C-7), 76.5 (d, C-4), 83.6 (s), 117.2 (d, C-2), 121.0 (q, $J_{C,F}$ = 321 Hz, CF_3), 128.4, 128.8, 128.9, 129.01, 129.2, 129.6, 129.7, 130.7, 133.6, 134.0, 140.2, 140.4, 161.6 (d, C-3), 168.5 ppm (d, C-1); HRMS (ESI positive) *m*/*z*: Calcd for $C_{29}H_{34}NOSi$ [M^+] 440.2410, found 440.2410.



3g-OTf

3-(2-Oxotetrahydropyran-3-yl)-3-phenylpropionaldehyde (7). Silyl ketene acetal **4a** (176 mg, 1.02 mmol) was added to a mixture of **3d**-OTf (212 mg, 0.685 mmol) and $Bu_4N^+BF_4^-$ (323 mg, 0.981 mmol) in CH_2Cl_2 (20 mL) under nitrogen atmosphere. After stirring for 15 min, the reaction mixture was poured into 20 mL of phosphate buffer (pH 7) and extracted with Et_2O (2 × 20 mL). The combined organic phases were washed with brine, dried ($MgSO_4$) and filtered. After evaporation of the solvent under reduced pressure, the quaternary ammonium salt was removed by dissolving the residue in Et_2O (15 mL) and washing with H_2O (15 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O (15 mL). The organic phases were combined and washed with brine, dried ($MgSO_4$), and filtred. After evaporation of solvent under reduced pressure, components were separated by column chromatography (silica gel, toluene-ether 90/10 v/v): **7** (105 mg, 66%); viscous liquid; 2:1 mixture of diastereoisomers. ^{1}H NMR: δ 1.32–1.46 (m, 0.33 H, 4’-H), 1.58–1.70 (m, 0.67 H, 4’-H), 1.70–1.93 (m, 3 H; 1 H from 4’-H and 2 H from 5’-H), 2.77 (ddd, *J* = 11.6, 7.9, 7.1 Hz, 0.33 H, 3’-H), 2.83–2.91 (m, 1 H; 0.33 H from 2-H and 0.67 H from 3’-H), 3.00 (ddd, *J* = 17.4, 9.1 and 2.2 Hz, 0.67 H, 2-H), 3.10-3.21 (m, 1 H, 2-H), 3.79 (td, *J* = 8.5 and 5.4 Hz, 0.33H, 3-H), 3.90 (ddd, *J* = 9.3, 5.8 and 3.6 Hz, 0.67H, 3-H), 4.06 (ddd, *J* = 11.1, 7.2 and 5.6 Hz, 0.67 H, 6’-H), 4.16 (dt, *J* = 11.3 and 5.4 Hz, 0.33 H, 6’-H), 4.21-4.30 (m, 1 H, 6’-H), 7.21–7.34 (m, 5 H, Ph), 9.64 (dd, *J* = 2.0 and 1.4 Hz, 0.33 H, 1-H), 9.67 ppm (dd, *J* = 2.0 and 1.1 Hz, 0.67 H, 1-H); ^{13}C NMR: δ 21.9 (t, C-4’), 22.5 (t, C-5’), 40.4 (d, C-3), 45.15 (t, C-2), 45.17 (d, C-3’), 68.8 (t, C-6’), 127.3 (d, Ph), 128.5 (d, Ph), 128.8 (d, Ph), 140.5 (s, Ph), 172.5 (s, 2’-C), 201.20 ppm (d, C-1); additional ^{13}C NMR signals were assigned to the minor isomer: δ 21.5 (t, C-5’), 22.5 (t, C-4’), 40.4 (d, C-3), 44.2 (d, C-3’), 48.2 (t, C-2), 68.0 (t, C-6’), 128.4 (d, Ph), 128.8 (d, Ph), 140.6 (s, Ph), 173.4 (s, C-2’), 200.7 ppm (d, C-1); HRMS (EI) *m*/*z*: Calcd for $C_{14}H_{17}O_3$ 233.1178 [$(M + H)^+$], Found 233.1172.

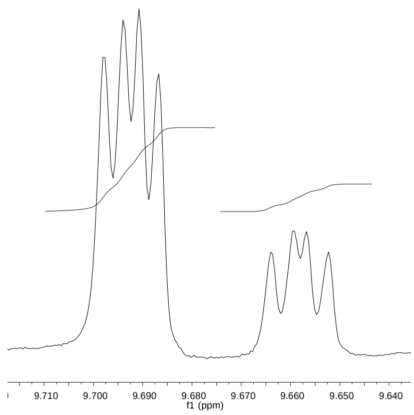


7

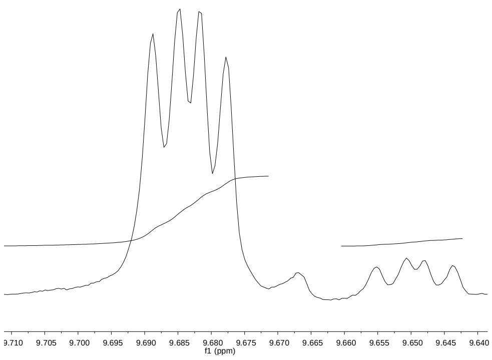
The yields of **7** obtained from the reactions of **4a** with other iminium triflates as well as the ratio of diastereoisomers (Schemes S1 and S2) are given in Table S2.

Table S2. Yields and ratios of diastereoisomers **7** from the reactions of ketene acetal **4a** with the iminium triflates (**3a–g**)-OTf in CH_2Cl_2.

iminium ion	yield (%)	ratio of diastereomers (from ^{1}H NMR)
3a-OTf	22	4 : 1
3b-OTf	63	3 : 1
3c-OTf	51	2 : 1
3d-OTf	66	2 : 1
3e-OTf	50	3 : 1
3f-OTf	38	9 : 1

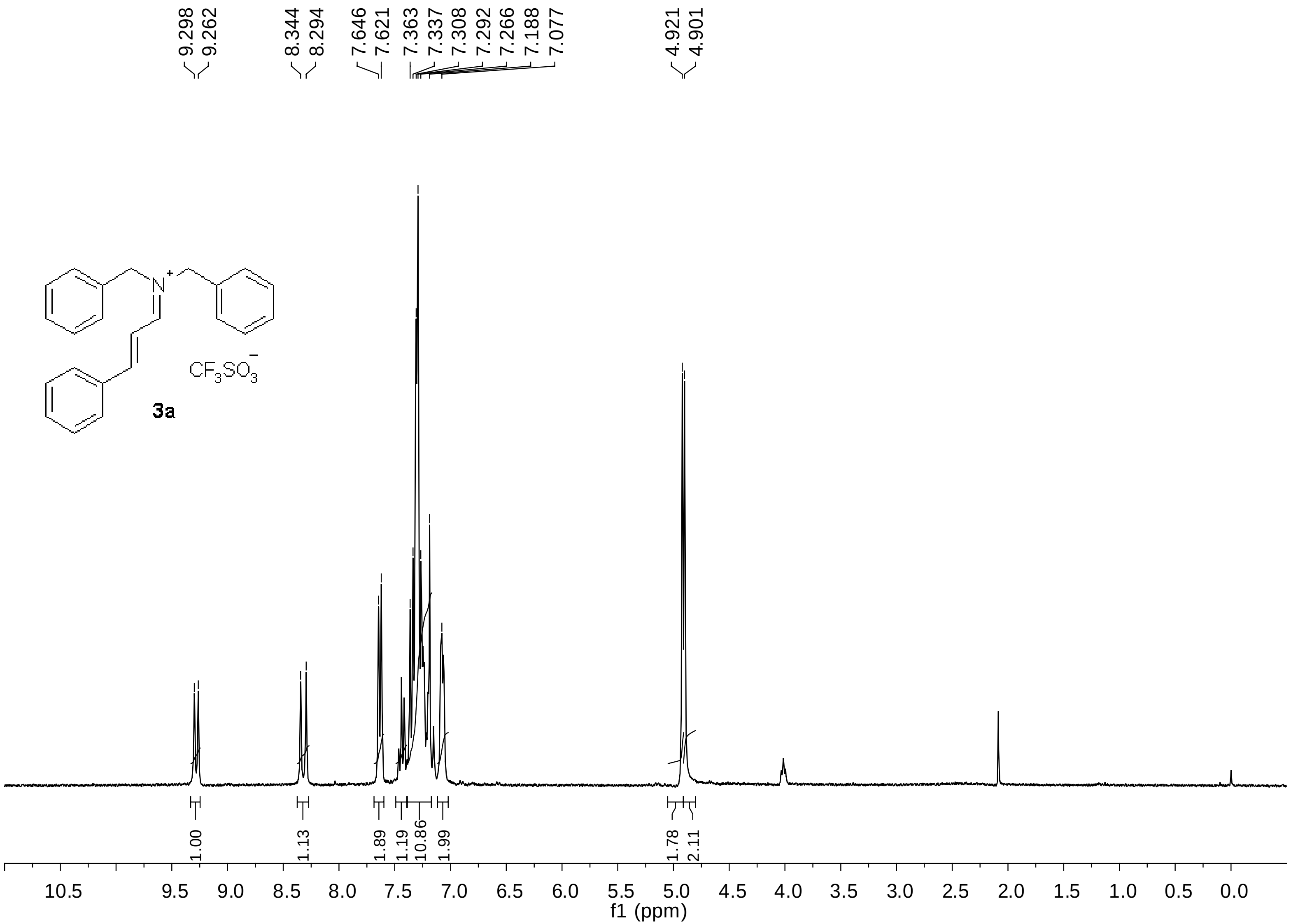


Scheme S1. ^{1}H NMR spectroscopic determination of the ratio of diastereomers **7** (the -CHO region of the product mixture obtained from the reaction of **3b**-OTf with **4a** is shown).

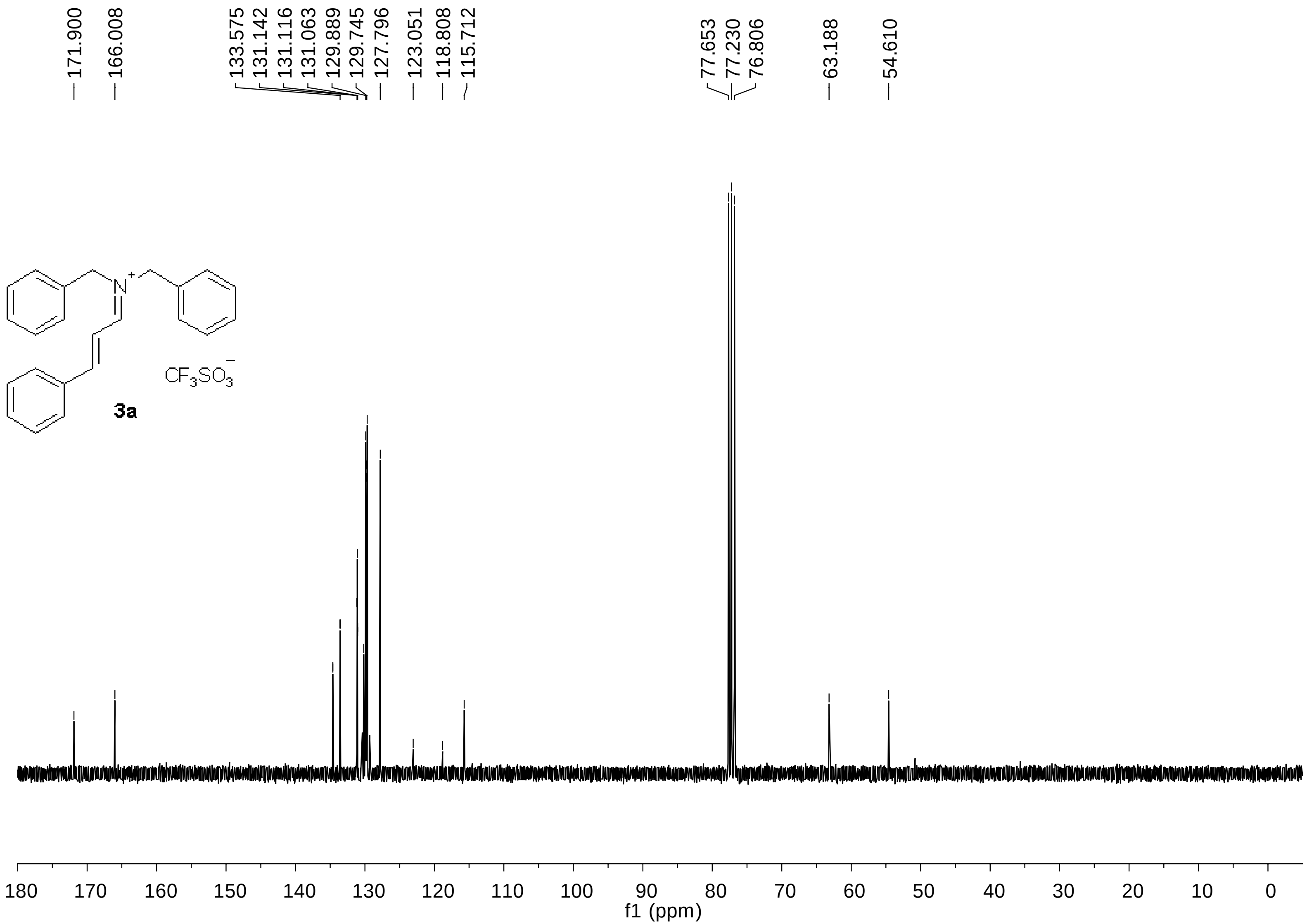


Scheme S2. ^{1}H NMR spectroscopic determination of the ratio of diastereomers **7** (the -CHO region of the product mixture obtained from the reaction of **3f**-OTf with **4a** is shown).

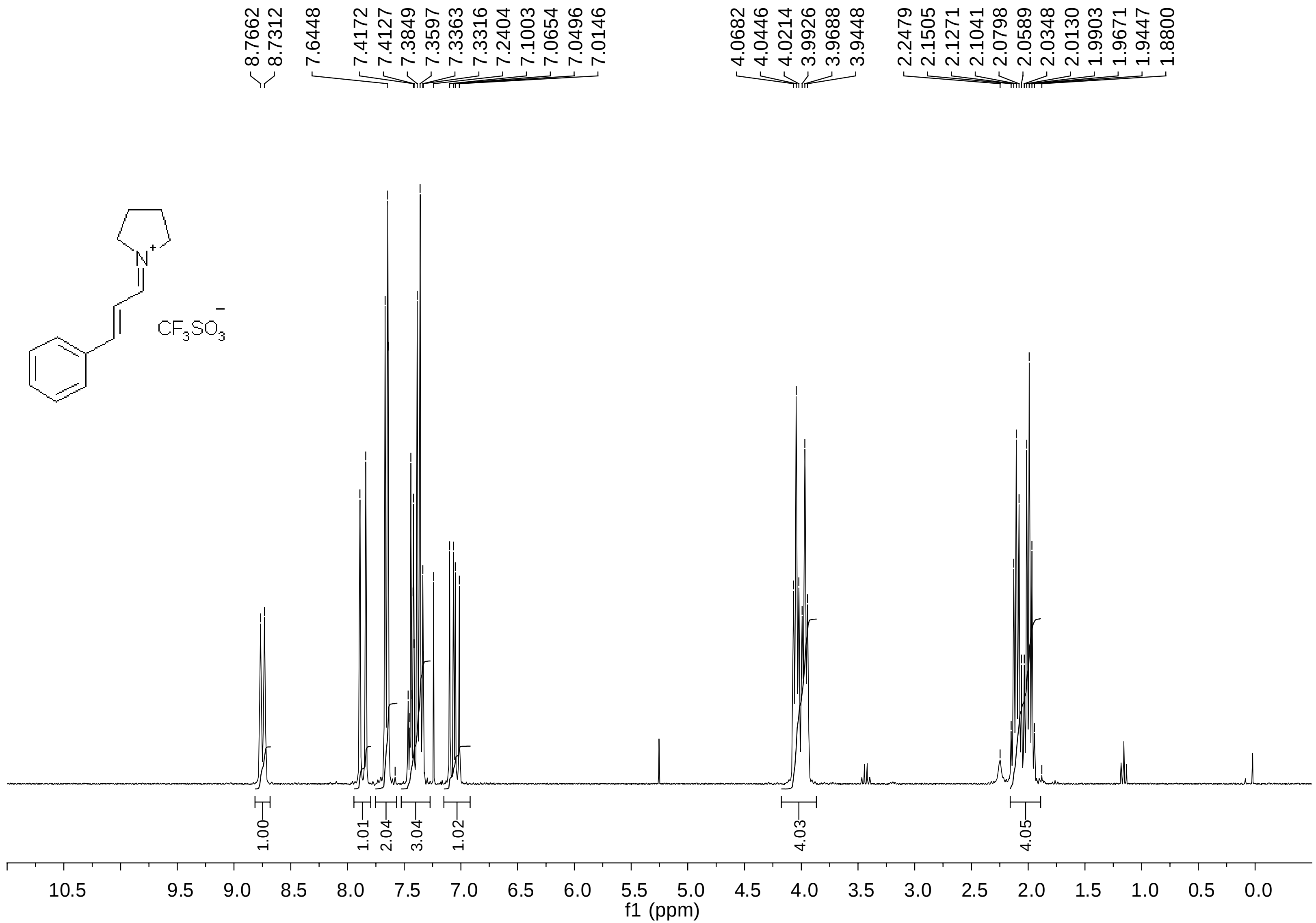
^{1}H NMR, 300 MHz, $CDCl_3$



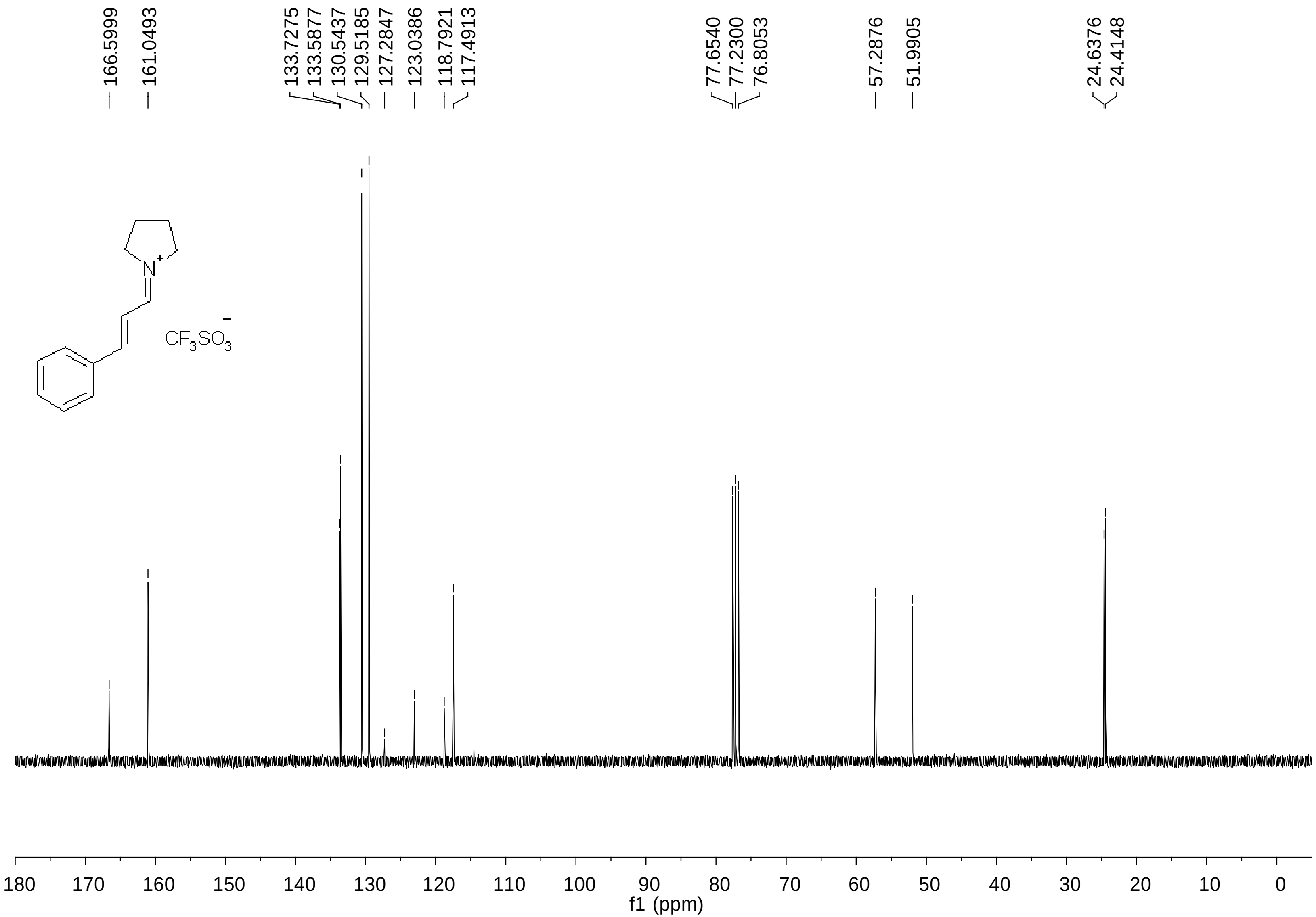
^{13}C NMR, 75.5 MHz, $CDCl_3$



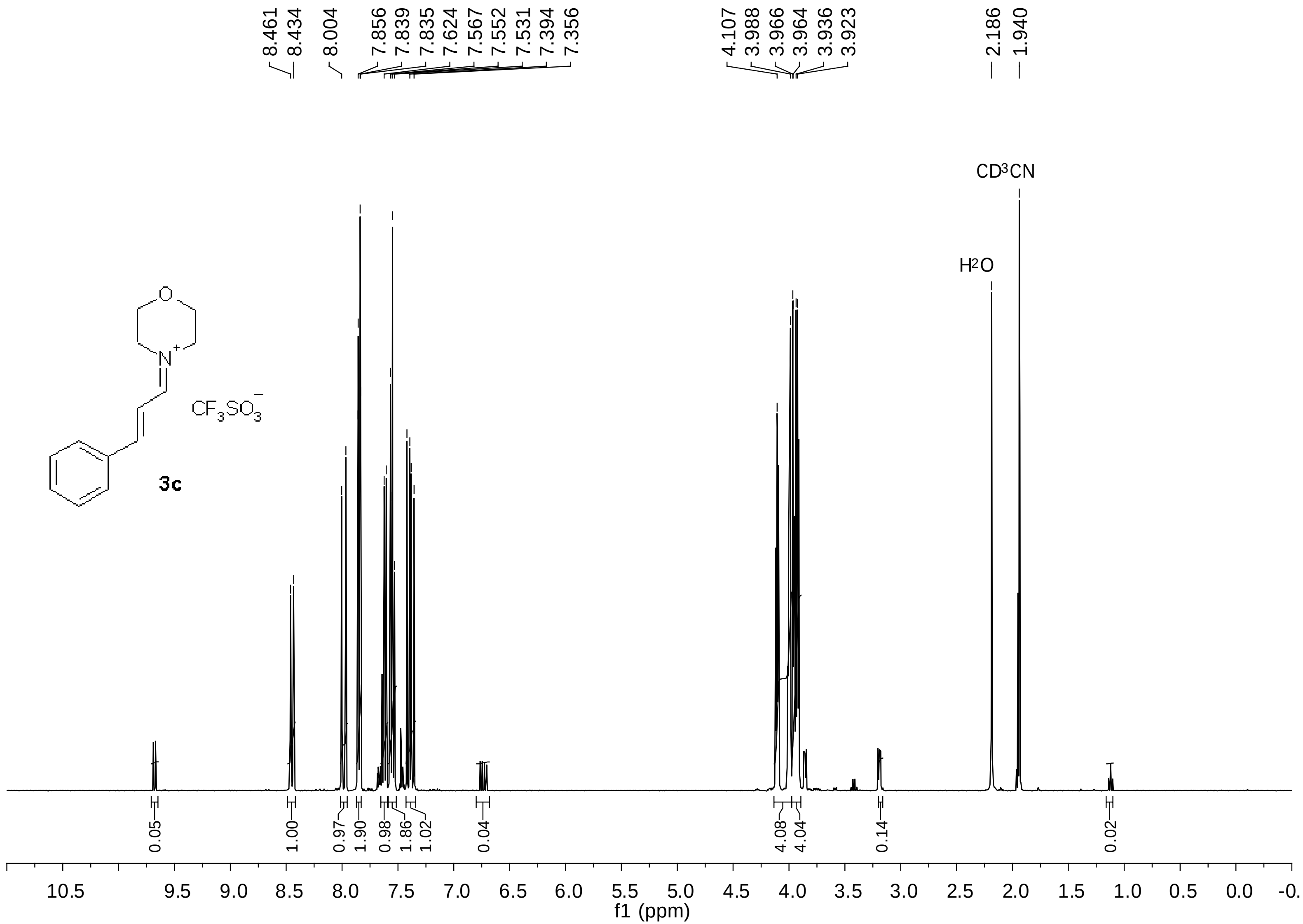
^{1}H NMR, 300 MHz, $CDCl_3$



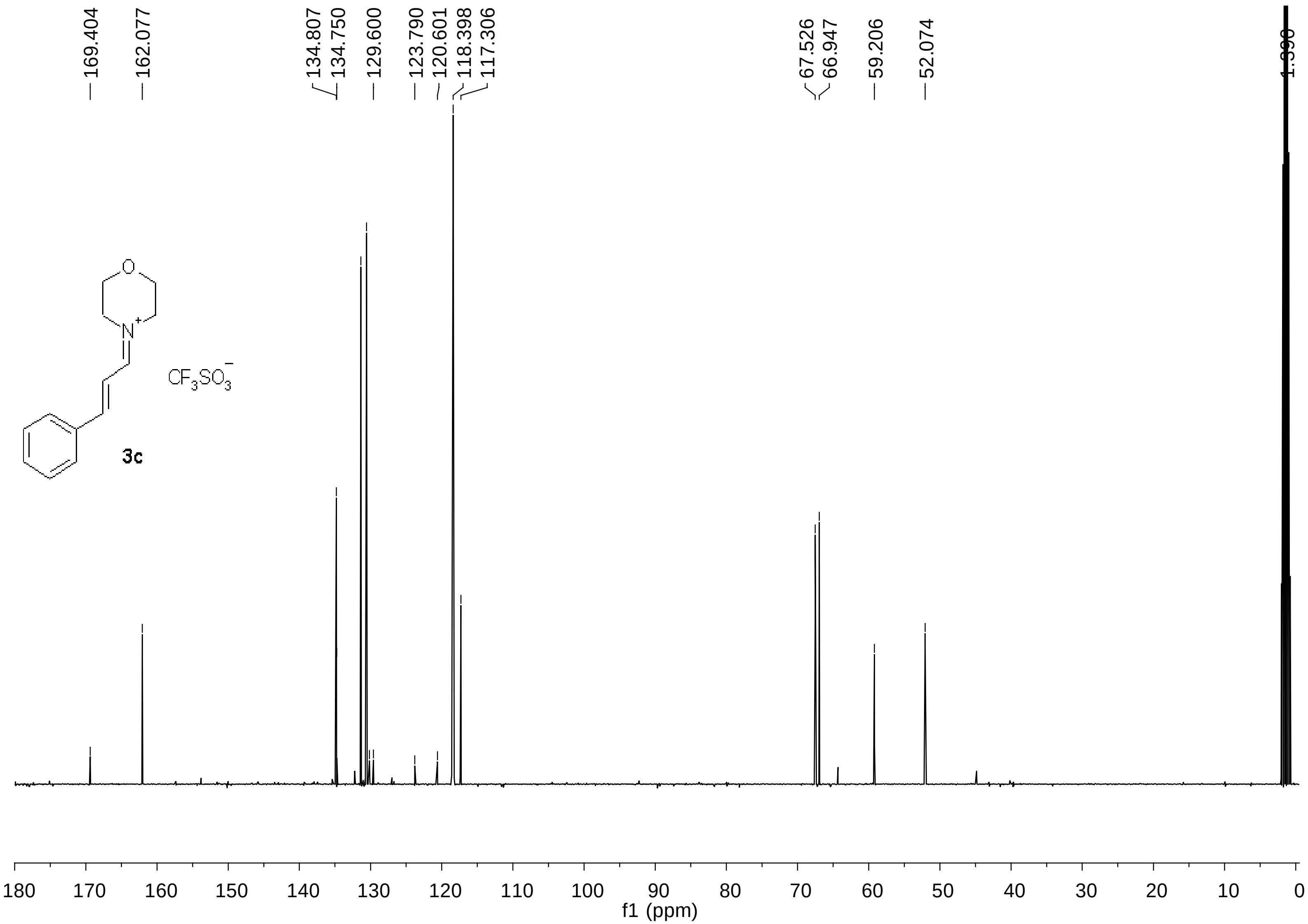
^{13}C NMR, 75.5 MHz, $CDCl_3$



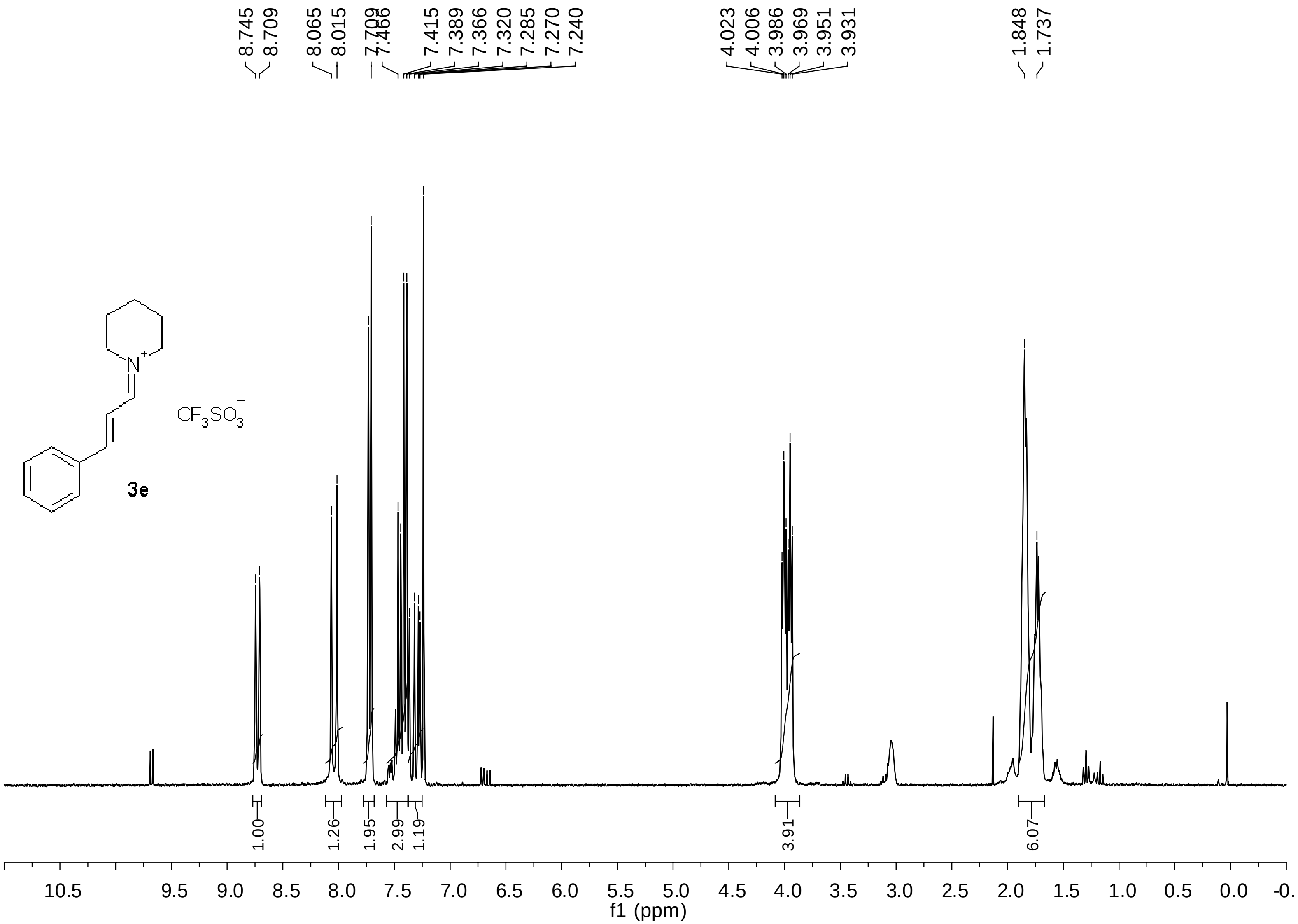
^{1}H NMR, 400 MHz, CD_3CN



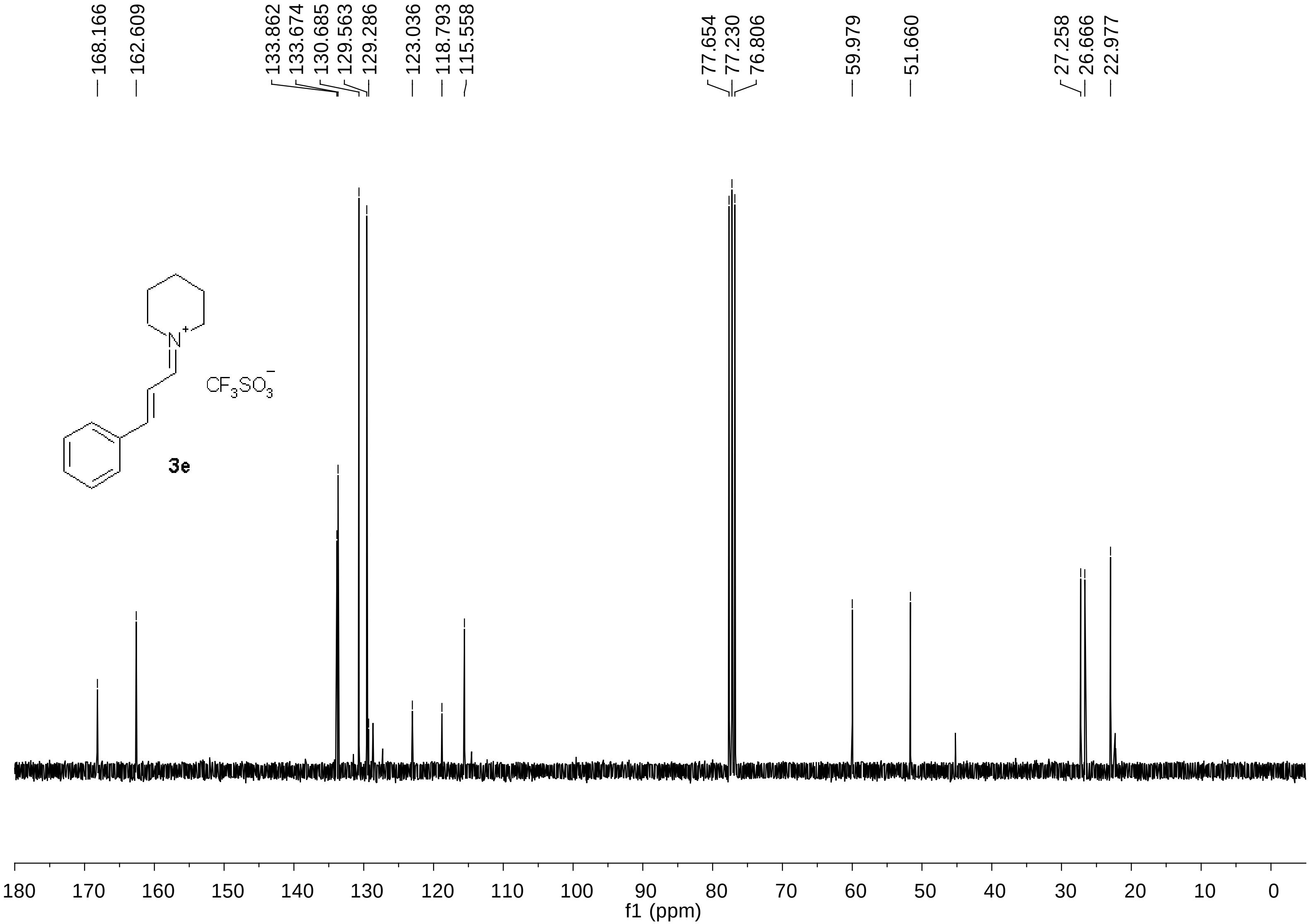
^{13}C NMR, 100.6 MHz, CD_3CN



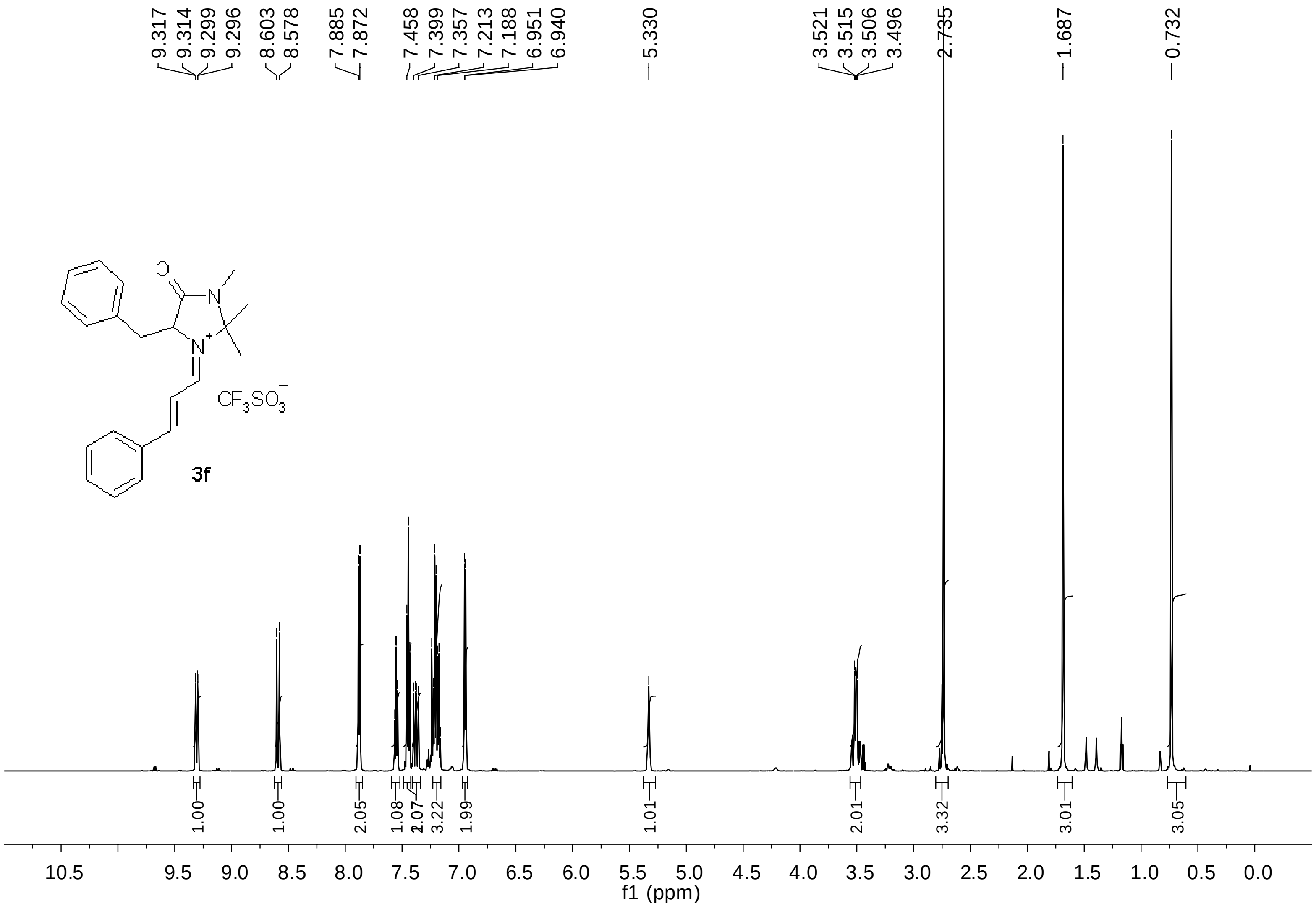
^{1}H NMR, 300 MHz, $CDCl_3$



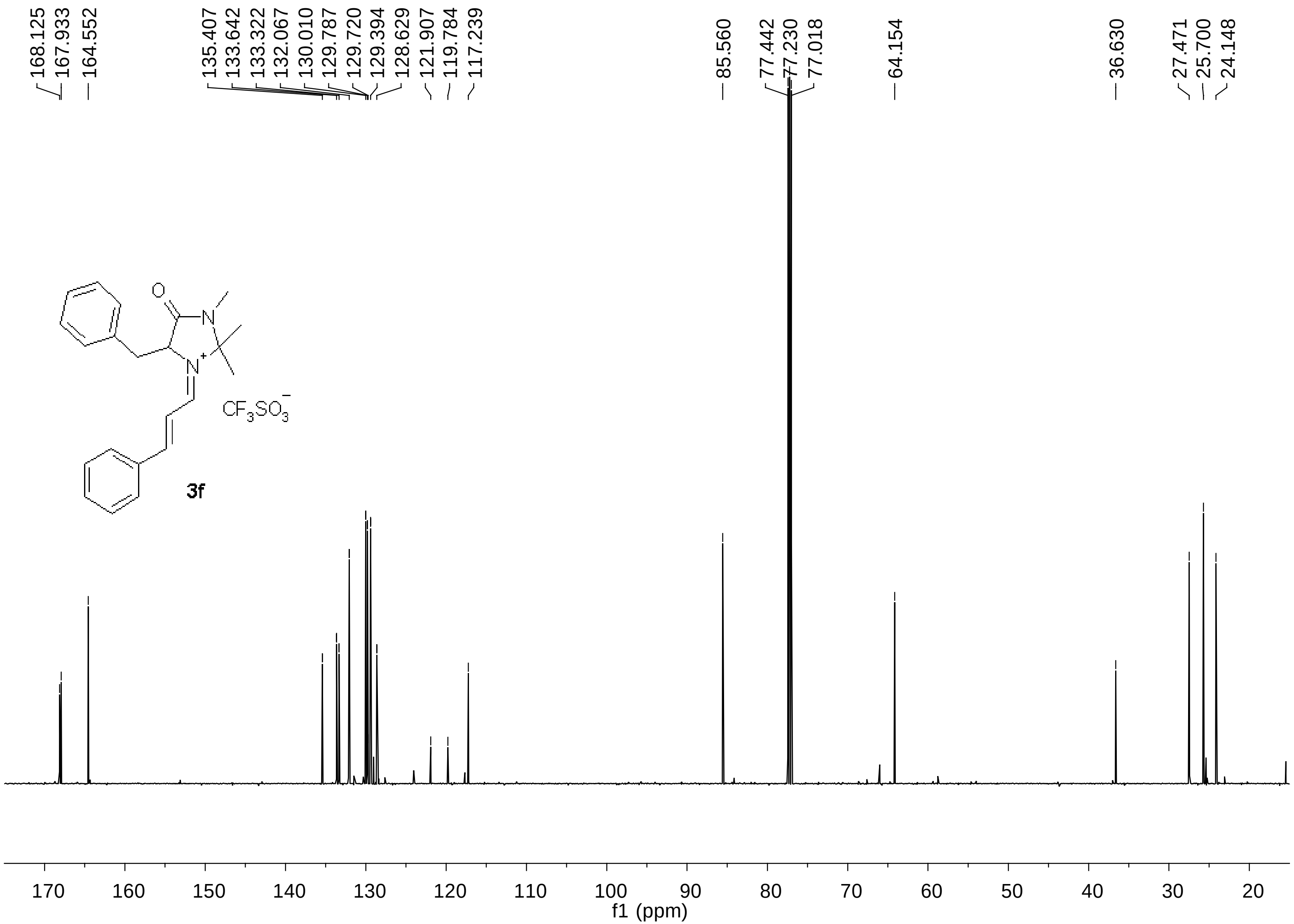
^{13}C NMR, 75.5 MHz, $CDCl_3$

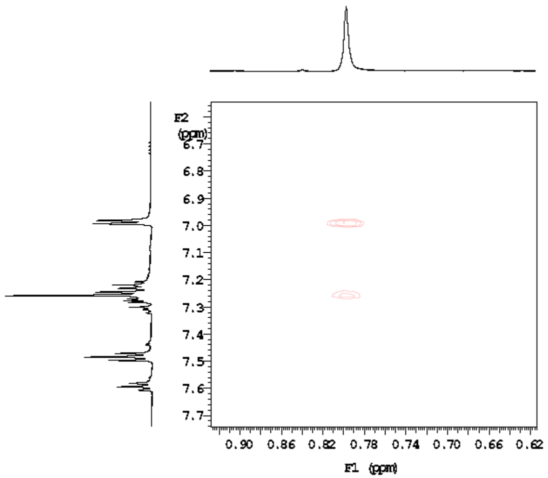


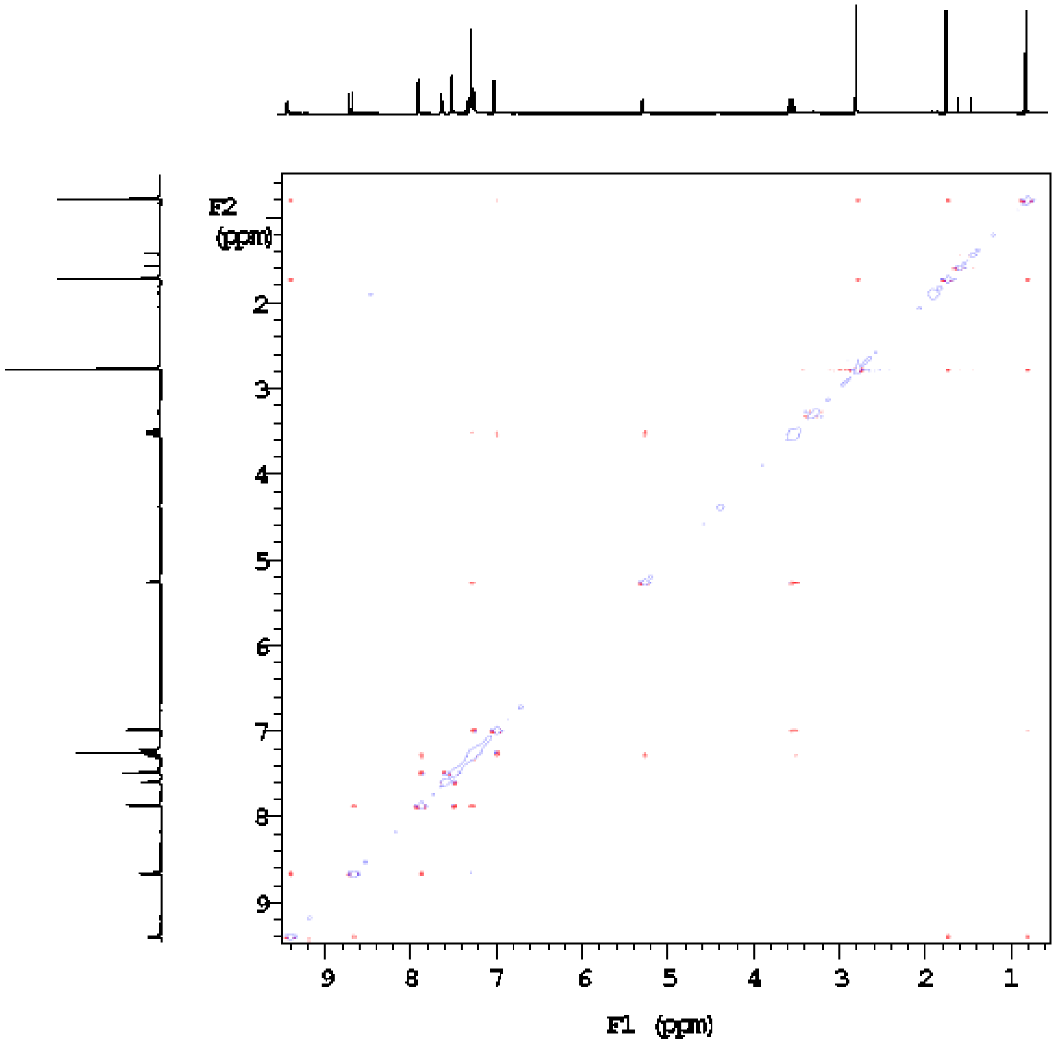
^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 150.7 MHz, $CDCl_3$

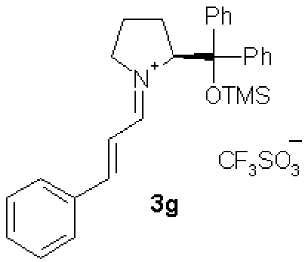




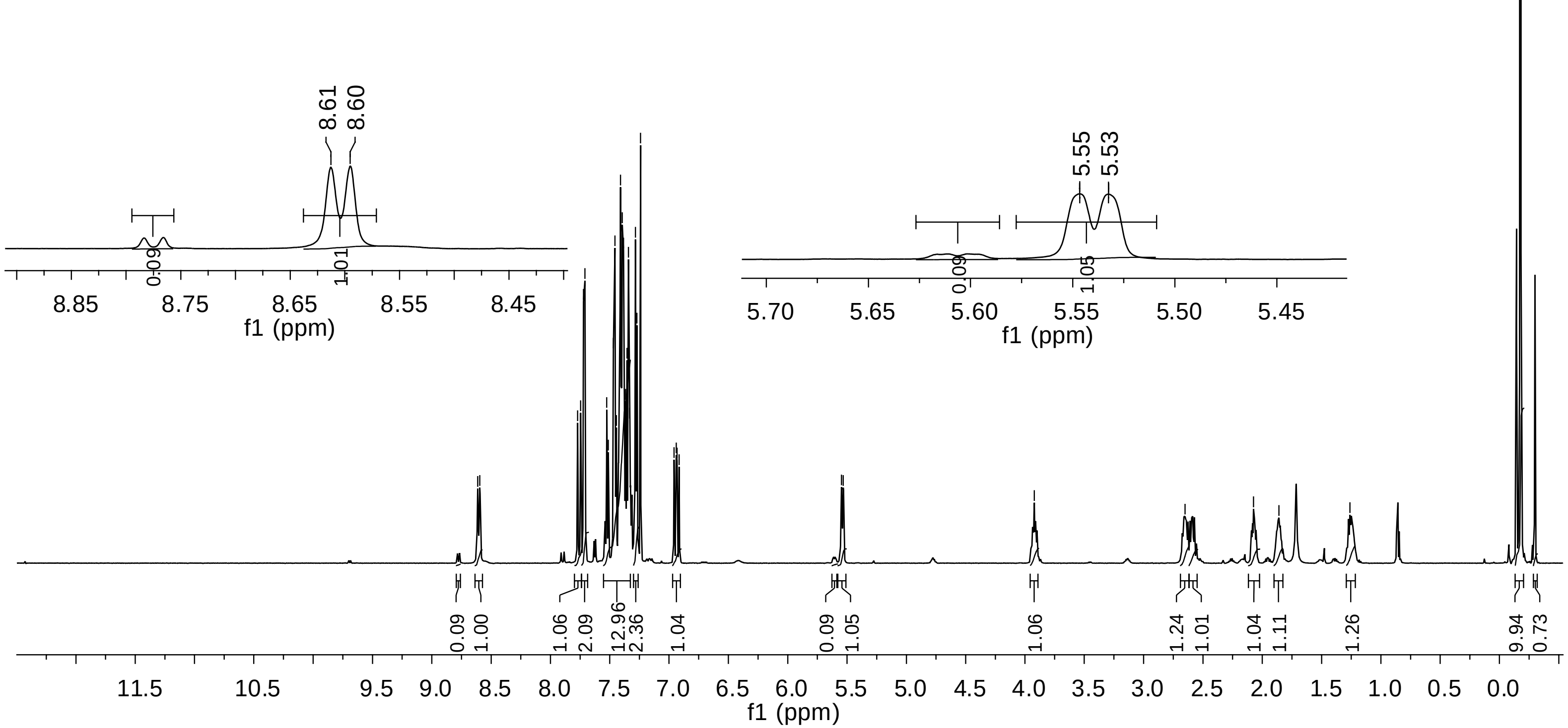


/home/var600/Mayr/Lakhdar/MacMillanIminium/MacMillanIminium_NOESY_601.fid

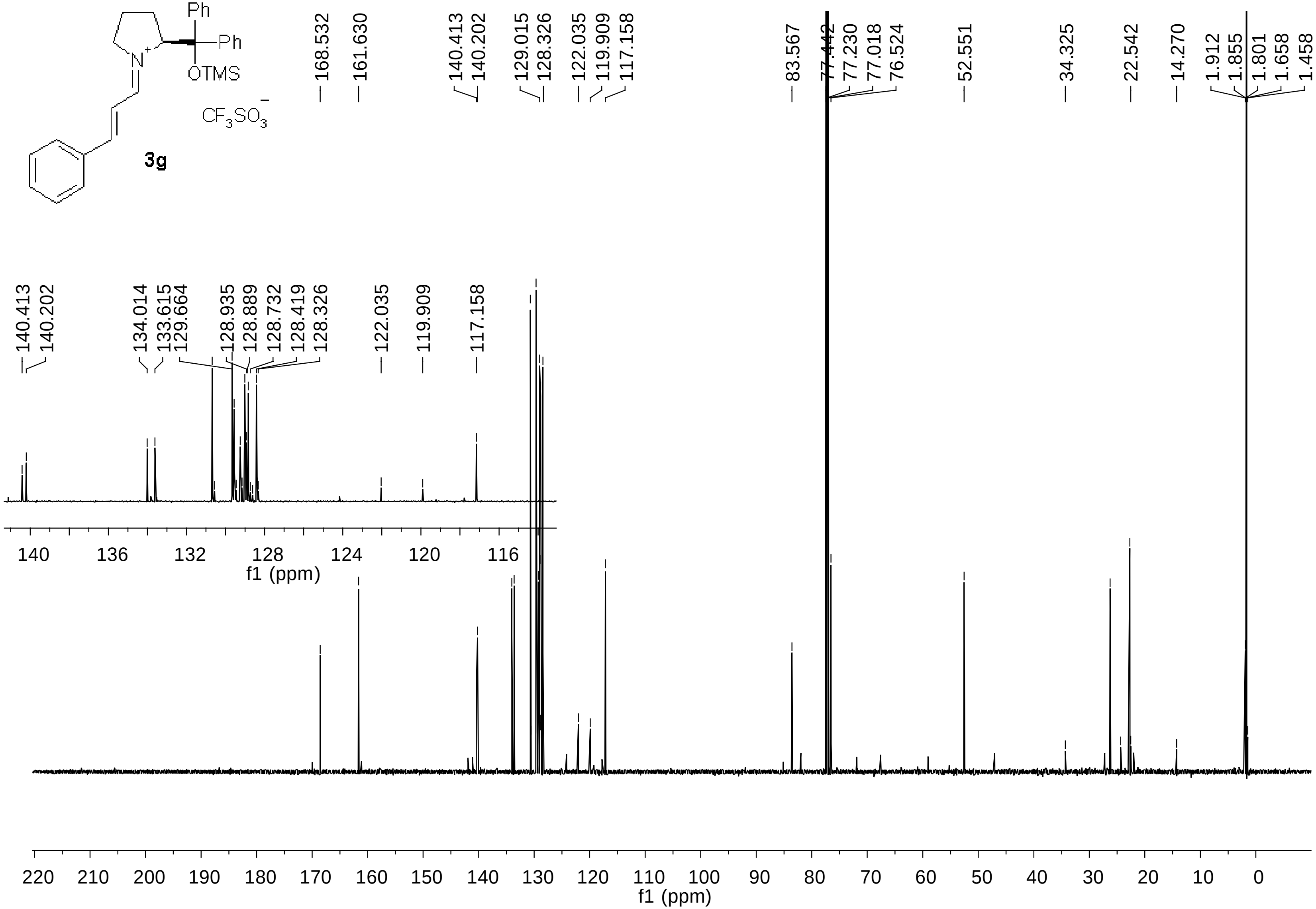
^1H NMR, 600 MHz, $CDCl_3$

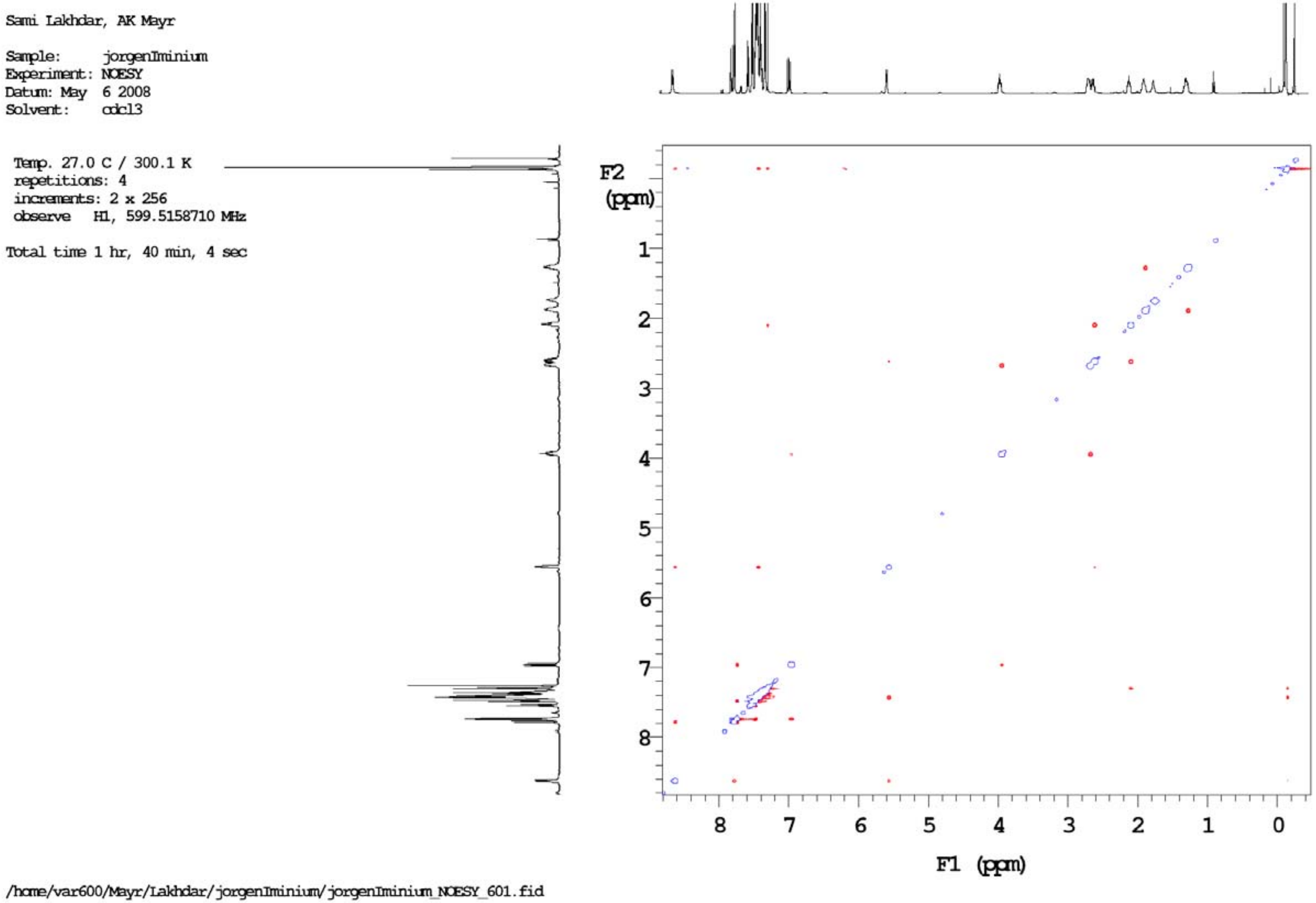


3g



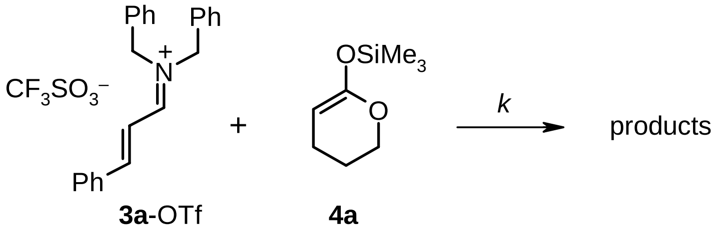
^{13}C NMR, 150.7 MHz, $CDCl_3$



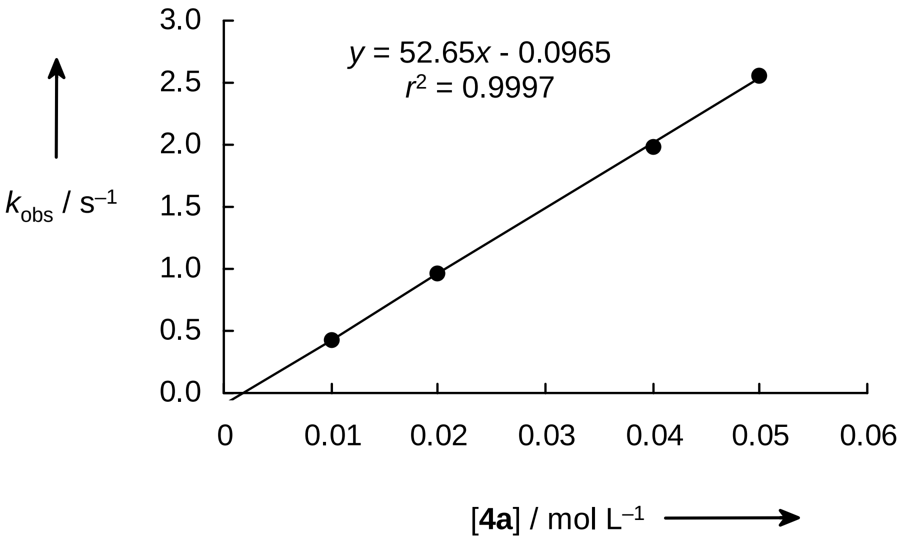

Sami Lakhdar, AK Mayr
Sample: jorgenIminium
Experiment: NOESY
Datum: May 6 2008
Solvent: cdcl3
Temp. 27.0 C / 300.1 K
repetitions: 4
increments: 2 x 256
observe H1, 599.5158710 MHz
Total time 1 hr, 40 min, 4 sec
F2 (ppm)
F1 (ppm)
/home/var600/Mayr/Lakhdar/jorgenIminium/jorgenIminium_NOESY_601.fid

Kinetics of the reaction of the iminium triflate 3a-OTf with silyl ketene acetal 4a

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 360 nm)



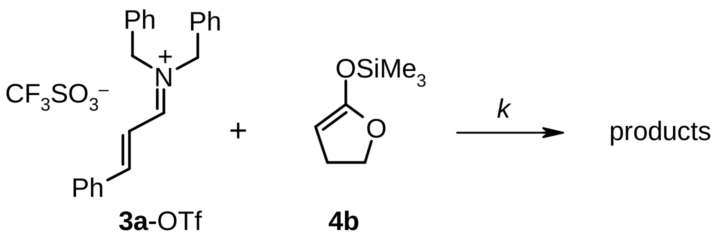
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
1.25×10^{-5}	1.00×10^{-2}	8.00×10^{2}	4.33×10^{-1}
1.25×10^{-5}	2.00×10^{-2}	1.60×10^{3}	9.59×10^{-1}
1.25×10^{-5}	4.00×10^{-2}	3.20×10^{3}	1.99
1.25×10^{-5}	5.00×10^{-2}	4.00×10^{3}	2.55



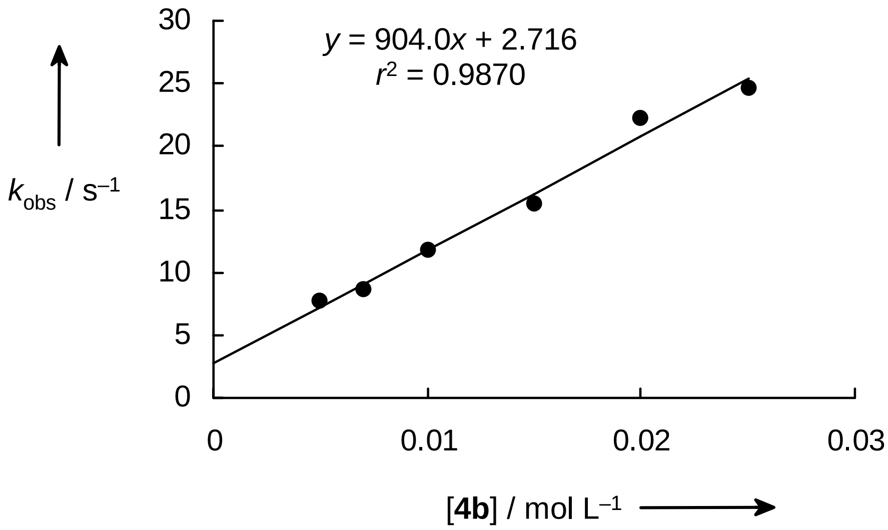
$k_2 = 5.26 \times 10^{1}$ M^{-1} s^{-1}

Kinetics of the reaction of the iminium triflate 3a-OTf with silyl ketene acetal 4b

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 360 nm)



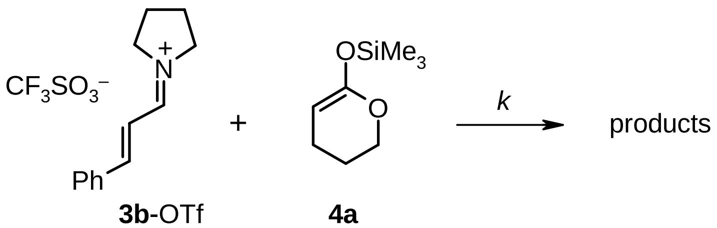
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
1.60×10^{-5}	5.00×10^{-3}	3.12×10^{2}	7.65
1.60×10^{-5}	7.00×10^{-3}	4.37×10^{2}	8.67
1.60×10^{-5}	1.00×10^{-2}	6.25×10^{2}	1.17×10^{1}
1.60×10^{-5}	1.50×10^{-2}	9.37×10^{2}	1.55×10^{1}
1.60×10^{-5}	2.00×10^{-2}	1.25×10^{3}	2.22×10^{1}
1.60×10^{-5}	2.50×10^{-2}	1.56×10^{3}	2.47×10^{1}



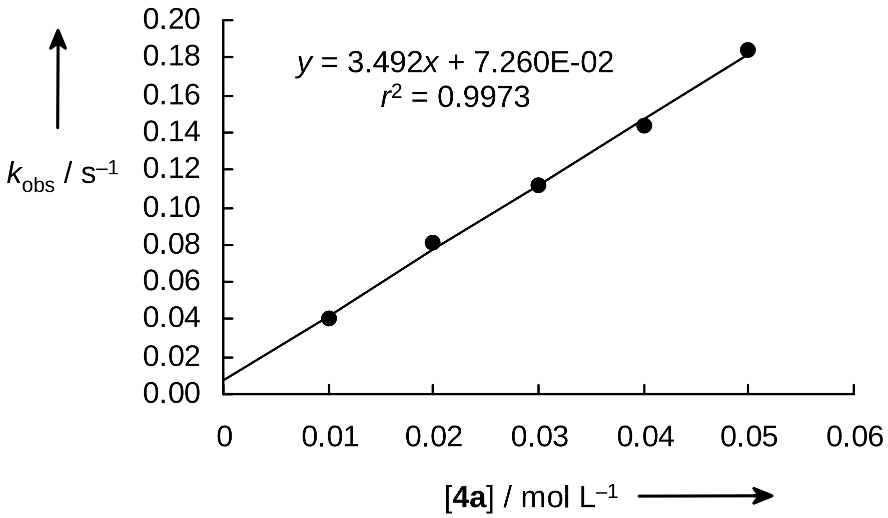
$k_2 = 9.04 \times 10^{2}$ M^{-1} s^{-1}

Kinetics of the reaction of the iminium triflate 3b-OTf with silyl ketene acetal 4a

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 348 nm)



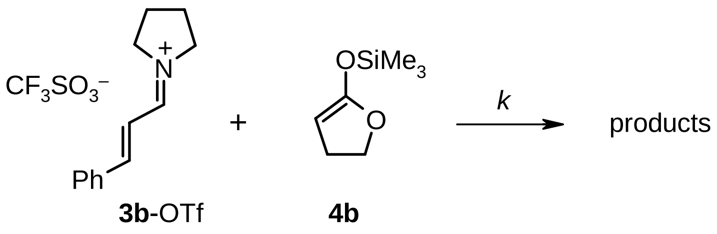
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
2.00×10^{-5}	1.00×10^{-2}	5.00×10^{2}	4.07×10^{-2}
2.00×10^{-5}	2.00×10^{-2}	1.00×10^{3}	8.04×10^{-2}
2.00×10^{-5}	3.00×10^{-2}	1.50×10^{3}	1.12×10^{-1}
2.00×10^{-5}	4.00×10^{-2}	2.00×10^{3}	1.43×10^{-1}
2.00×10^{-5}	5.00×10^{-2}	2.50×10^{3}	1.84×10^{-1}



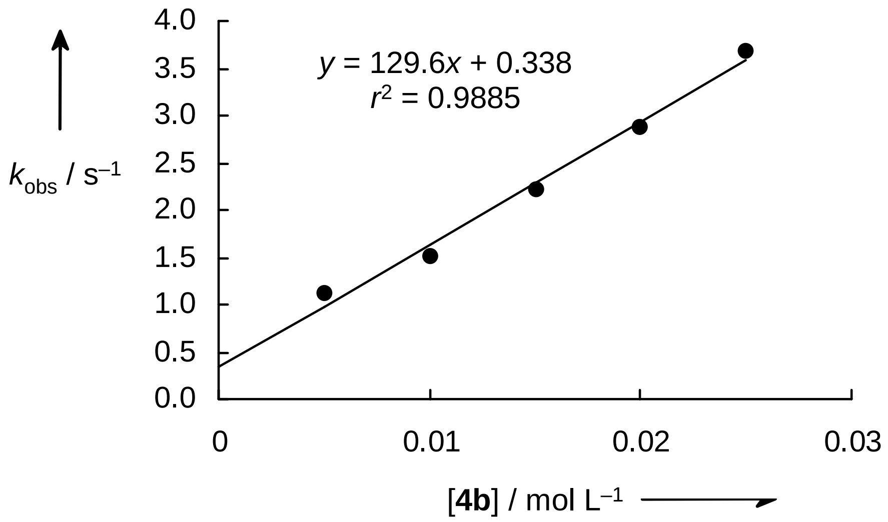
k_2 = 3.49 M^{-1} s^{-1}

Kinetics of the reaction of the iminium triflate 3b-OTf with silyl ketene acetal 4b

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 348 nm)



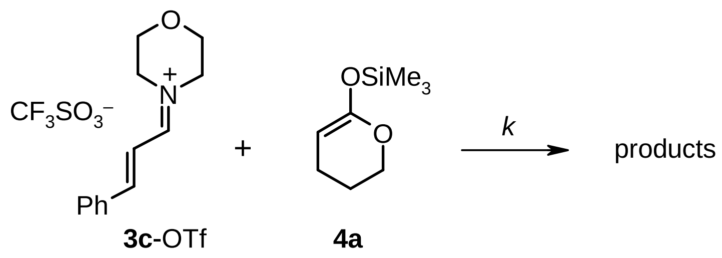
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
8.00×10^{-5}	5.00×10^{-3}	6.25×10^{1}	1.12
8.00×10^{-5}	1.00×10^{-2}	1.25×10^{2}	1.52
8.00×10^{-5}	1.50×10^{-2}	1.88×10^{2}	2.21
8.00×10^{-5}	2.00×10^{-2}	2.50×10^{2}	2.88
8.00×10^{-5}	2.50×10^{-2}	3.13×10^{2}	3.68



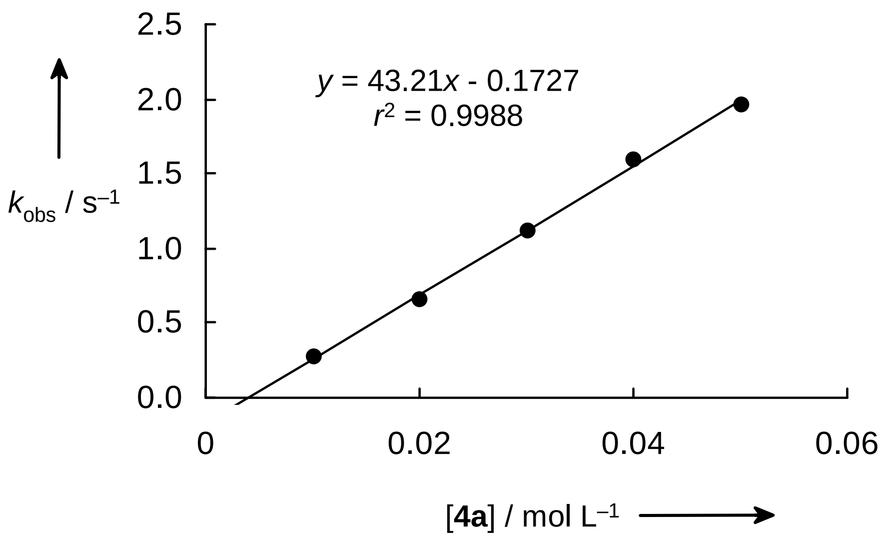
$k_2 = 1.30 \times 10^{2}$ M^{-1} s^{-1}

Kinetics of the reaction of the iminium triflate 3c-OTf with silyl ketene acetal 4a

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 349 nm)



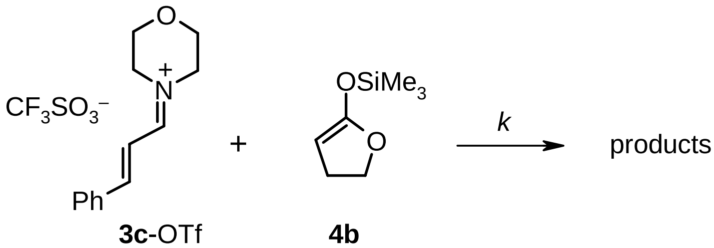
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
1.80×10^{-5}	1.00×10^{-2}	5.55×10^{2}	2.71×10^{-1}
1.80×10^{-5}	2.00×10^{-2}	1.11×10^{3}	6.67×10^{-1}
1.80×10^{-5}	3.00×10^{-2}	1.66×10^{3}	1.12
1.80×10^{-5}	4.00×10^{-2}	2.22×10^{3}	1.59
1.80×10^{-5}	5.00×10^{-2}	2.78×10^{3}	1.97



$k_2 = 4.32 \times 10^{1}$ M^{-1} s^{-1}

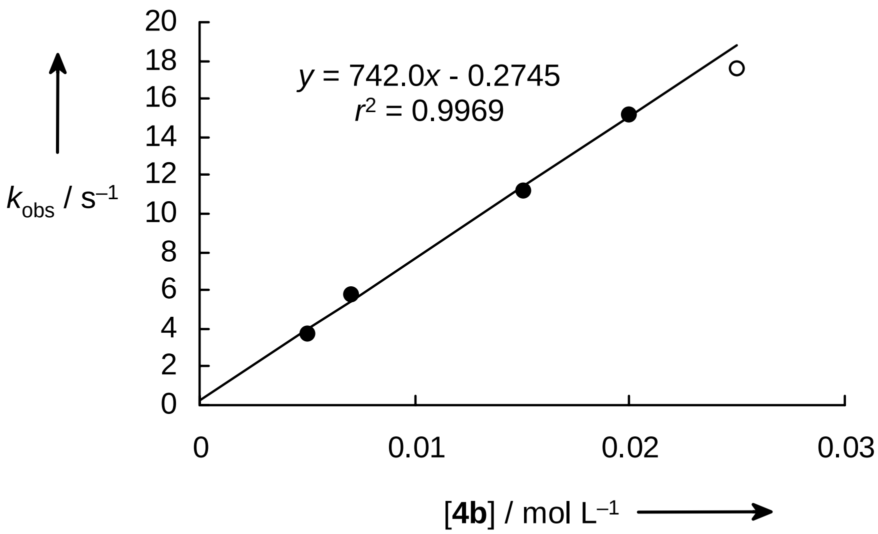
Kinetics of the reaction of the iminium triflate 3c-OTf with silyl ketene acetal 4b

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 349 nm)



[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
2.60×10^{-5}	5.00×10^{-3}	1.92×10^{2}	3.73
2.60×10^{-5}	7.00×10^{-3}	2.69×10^{2}	5.84
2.60×10^{-5}	1.50×10^{-2}	5.77×10^{2}	1.12×10^{1}
2.60×10^{-5}	2.00×10^{-2}	7.69×10^{2}	1.52×10^{1}
2.60×10^{-5}	2.50×10^{-2}	9.61×10^{2}	(1.76×10^{1})[a]

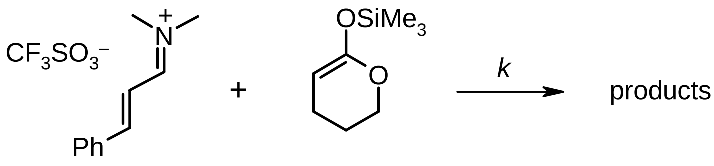
[a] This k_{obs} value was not used for the determination of the second-order rate constant k_2.



$k_2 = 7.42 \times 10^{2}$ M^{-1} s^{-1}

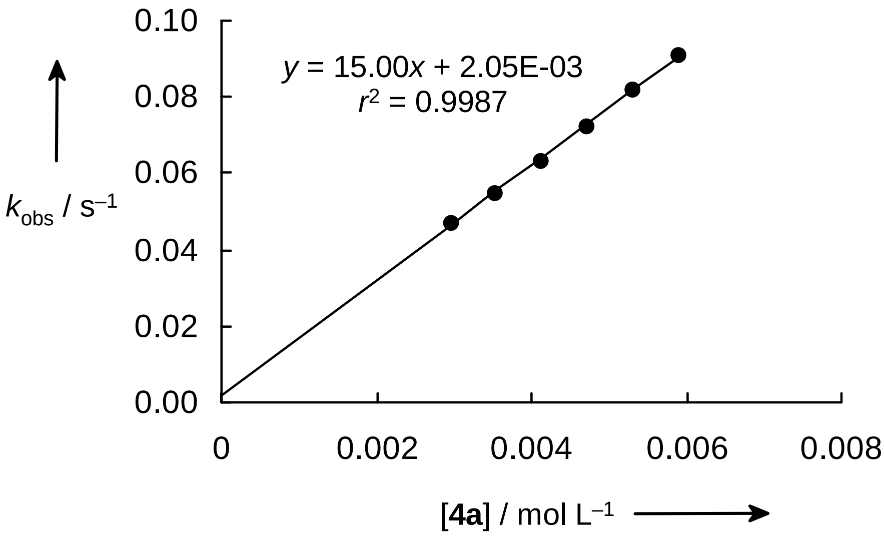
Kinetics of the reaction of the iminium triflate 3d-OTf with silyl ketene acetal 4a

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 341 nm)



3d-OTf **4a**

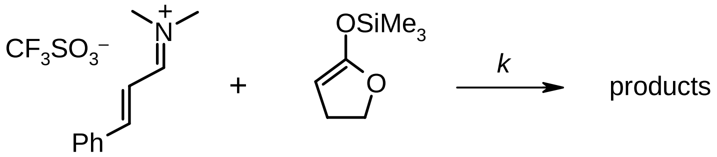
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
2.51×10^{-5}	2.95×10^{-3}	1.18×10^{2}	4.70×10^{-2}
2.51×10^{-5}	3.54×10^{-3}	1.41×10^{2}	5.51×10^{-2}
2.51×10^{-5}	4.13×10^{-3}	1.65×10^{2}	6.30×10^{-2}
2.51×10^{-5}	4.72×10^{-3}	1.88×10^{2}	7.25×10^{-2}
2.51×10^{-5}	5.31×10^{-3}	2.12×10^{2}	8.20×10^{-2}
2.51×10^{-5}	5.90×10^{-3}	2.35×10^{2}	9.09×10^{-2}



$k_2 = 1.50 \times 10^{1}$ M^{-1} s^{-1}

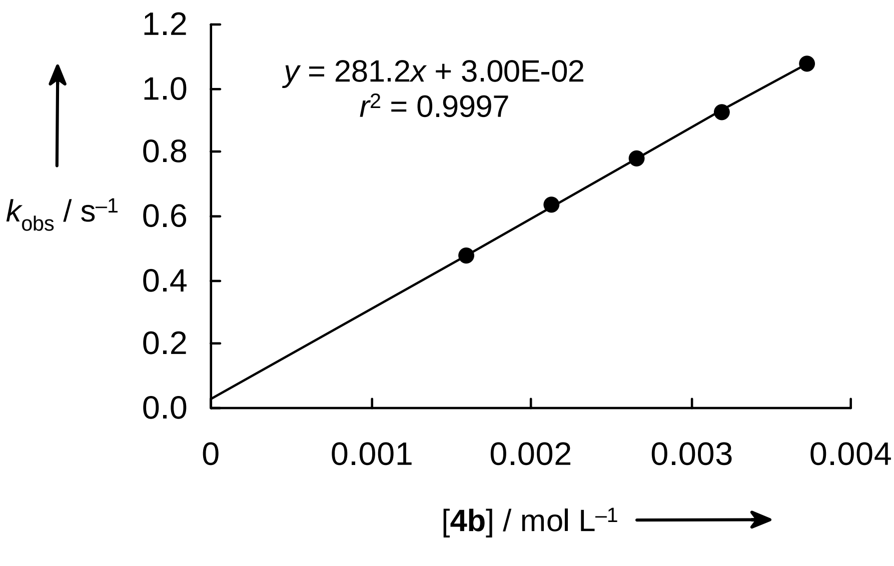
Kinetics of the reaction of the iminium triflate 3d-OTf with silyl ketene acetal 4b

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 341 nm)



3d-OTf **4b**

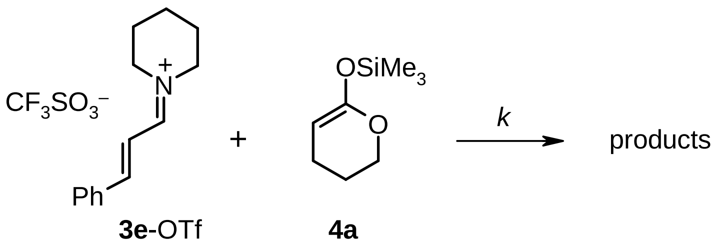
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
3.49×10^{-5}	1.60×10^{-3}	4.58×10^{1}	4.76×10^{-1}
3.49×10^{-5}	2.13×10^{-3}	6.10×10^{1}	6.34×10^{-1}
3.49×10^{-5}	2.66×10^{-3}	7.63×10^{1}	7.81×10^{-1}
3.49×10^{-5}	3.20×10^{-3}	9.15×10^{1}	9.25×10^{-1}
3.49×10^{-5}	3.73×10^{-3}	1.07×10^{2}	1.08



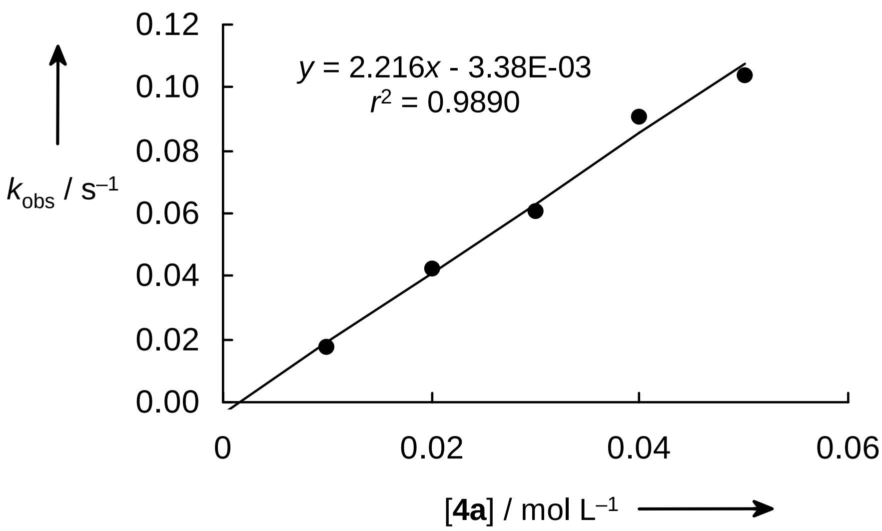
$k_2 = 2.81 \times 10^{2}\ M^{-1}\ s^{-1}$

Kinetics of the reaction of the iminium triflate 3e-OTf with silyl ketene acetal 4a

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 342 nm)



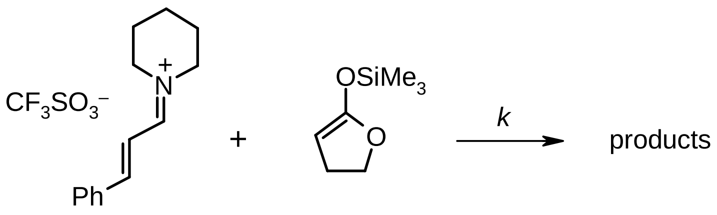
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
1.16×10^{-5}	1.00×10^{-2}	8.62×10^{2}	1.75×10^{-2}
1.16×10^{-5}	2.00×10^{-2}	1.72×10^{3}	4.24×10^{-2}
1.16×10^{-5}	3.00×10^{-2}	2.58×10^{3}	6.06×10^{-2}
1.16×10^{-5}	4.00×10^{-2}	3.45×10^{3}	9.10×10^{-2}
1.16×10^{-5}	5.00×10^{-2}	4.31×10^{3}	1.04×10^{-1}



k_2 = 2.22 M^{-1} s^{-1}

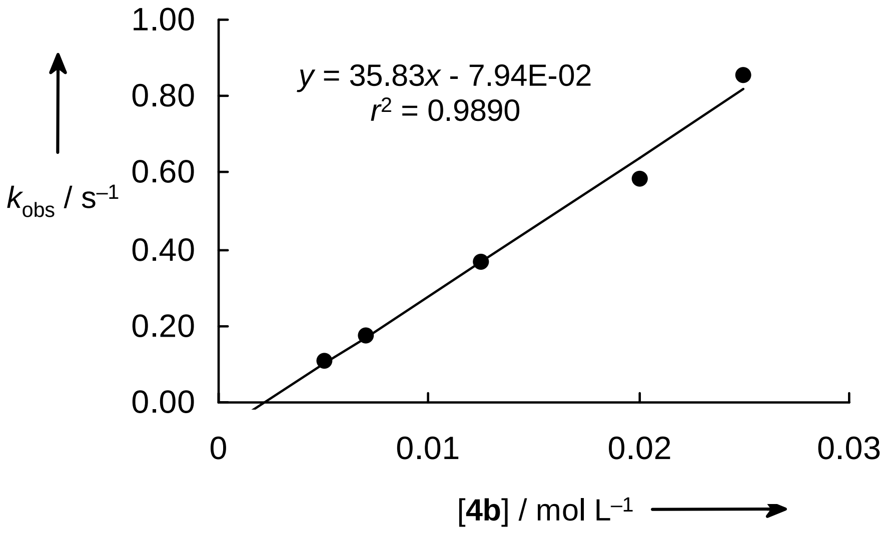
Kinetics of the reaction of the iminium triflate 3e-OTf with silyl ketene acetal 4b

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 342 nm)



3e-OTf **4b**

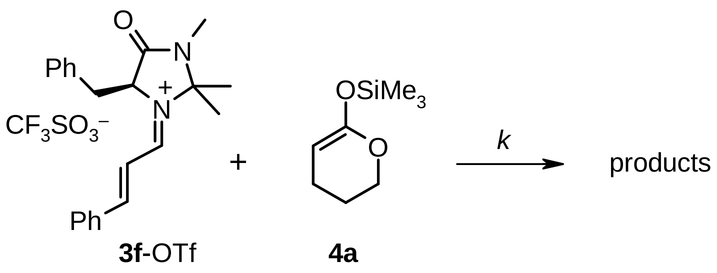
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
4.75×10^{-5}	5.00×10^{-3}	1.05×10^{2}	1.1×10^{-1}
4.75×10^{-5}	7.00×10^{-3}	1.47×10^{2}	1.8×10^{-1}
4.75×10^{-5}	1.25×10^{-2}	2.63×10^{2}	3.7×10^{-1}
4.75×10^{-5}	2.00×10^{-2}	4.21×10^{2}	5.9×10^{-1}
4.75×10^{-5}	2.50×10^{-2}	5.26×10^{2}	8.5×10^{-1}



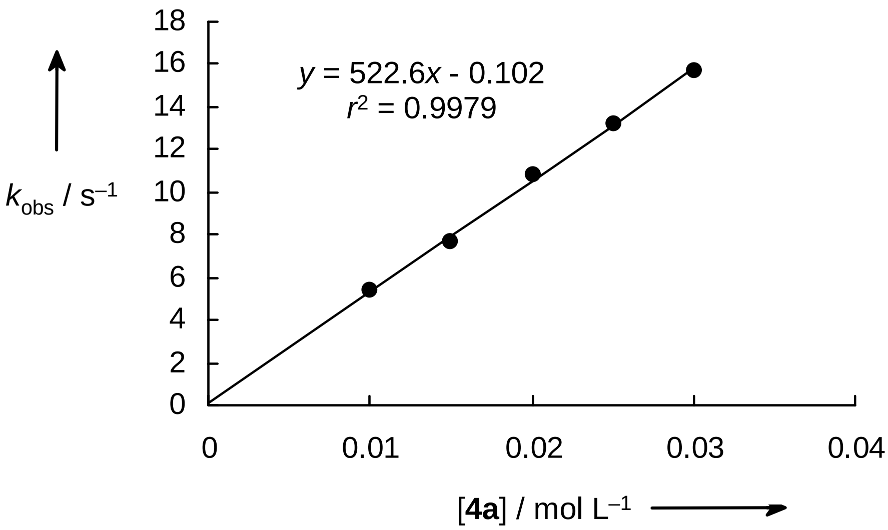
$k_2 = 3.6 \times 10^{1}$ M^{-1} s^{-1}

Kinetics of the reaction of the iminium triflate 3f-OTf with silyl ketene acetal 4a

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 370 nm)



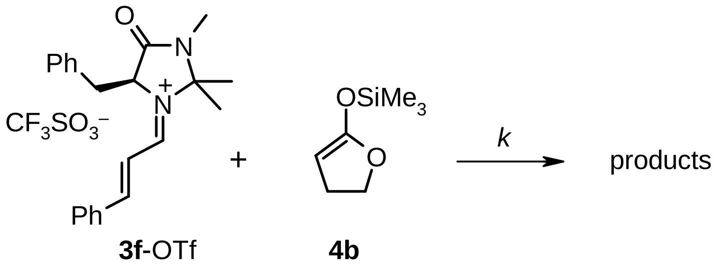
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
4.50×10^{-5}	1.00×10^{-2}	2.22×10^{2}	5.40
4.50×10^{-5}	1.50×10^{-2}	3.33×10^{2}	7.67
4.50×10^{-5}	2.00×10^{-2}	4.44×10^{2}	1.08×10^{1}
4.50×10^{-5}	2.50×10^{-2}	5.55×10^{2}	1.32×10^{1}
4.50×10^{-5}	3.00×10^{-2}	6.67×10^{2}	1.57×10^{1}



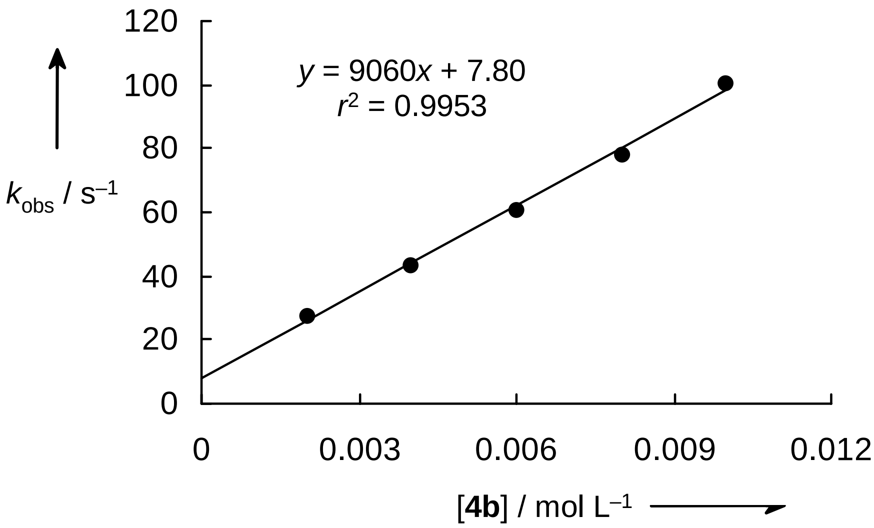
$k_2 = 5.23 \times 10^{2}$ M^{-1} s^{-1}

Kinetics of the reaction of the iminium triflate 3f-OTf with silyl ketene acetal 4b

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 370 nm)



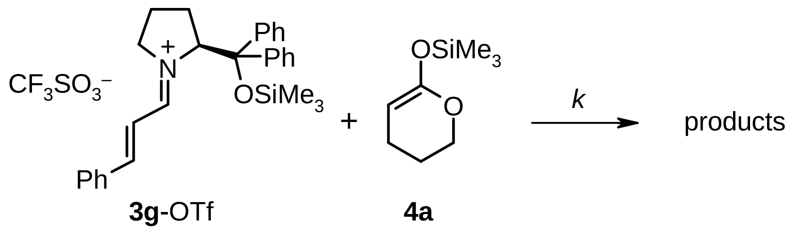
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
4.00×10^{-5}	2.00×10^{-3}	5.00×10^{1}	2.77×10^{1}
4.00×10^{-5}	4.00×10^{-3}	1.00×10^{2}	4.33×10^{1}
4.00×10^{-5}	6.00×10^{-3}	1.50×10^{2}	6.07×10^{1}
4.00×10^{-5}	8.00×10^{-3}	2.00×10^{2}	7.83×10^{1}
4.00×10^{-5}	1.00×10^{-2}	2.50×10^{2}	1.01×10^{2}



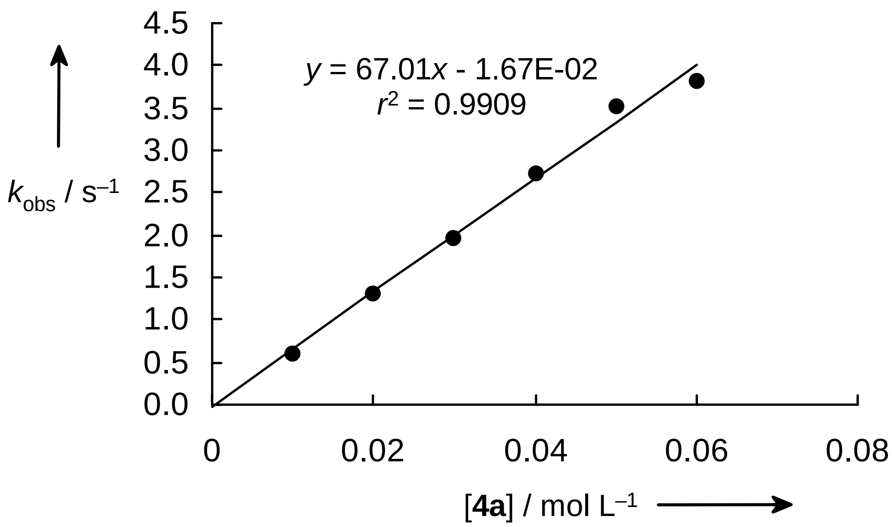
$k_2 = 9.06 \times 10^{3}$ M^{-1} s^{-1}

Kinetics of the reaction of the iminium triflate 3g-OTf with silyl ketene acetal 4a

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 365 nm)



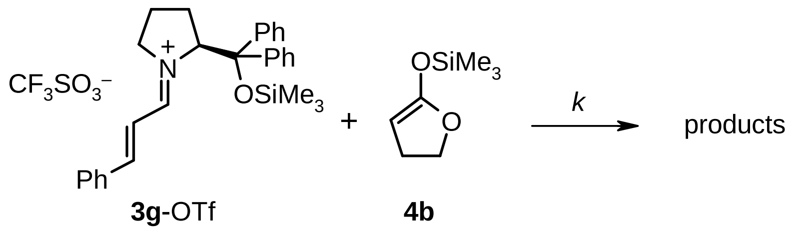
[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
8.00×10^{-5}	1.00×10^{-2}	1.25×10^{2}	6.13×10^{-1}
8.00×10^{-5}	2.00×10^{-2}	2.50×10^{2}	1.32
8.00×10^{-5}	3.00×10^{-2}	3.75×10^{2}	1.96
8.00×10^{-5}	4.00×10^{-2}	5.00×10^{2}	2.73
8.00×10^{-5}	5.00×10^{-2}	6.25×10^{2}	3.52
8.00×10^{-5}	6.00×10^{-2}	7.50×10^{2}	3.83



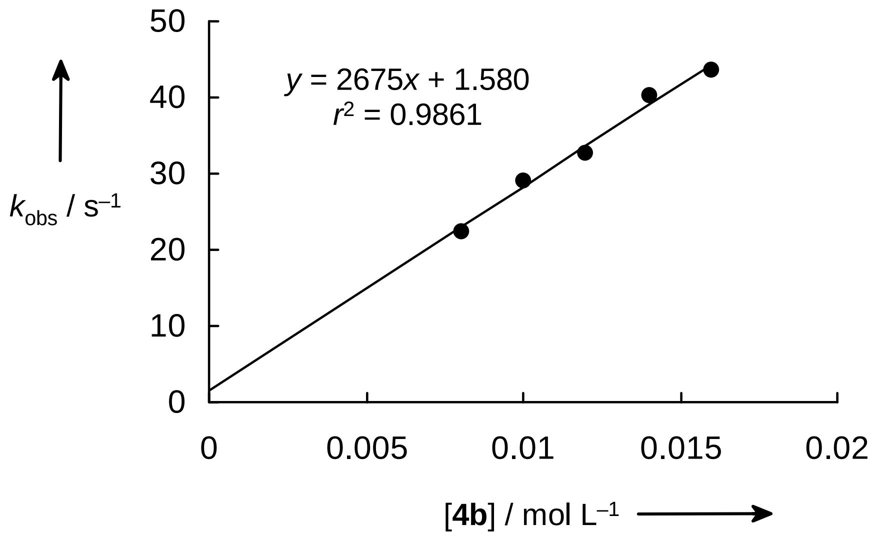
$k_2 = 6.70 \times 10^{1}$ M^{-1} s^{-1}

Kinetics of the reaction of the iminium triflate 3g-OTf with silyl ketene acetal 4b

(in CH_2Cl_2, 20 °C, stopped-flow method, detection at 365 nm)



[El]/ mol L^{-1}	[Nu]/ mol L^{-1}	[Nu]/[El]	k_{obs} / s^{-1}
1.00 × 10^{-5}	8.00 × 10^{-3}	8.00 × 10^{2}	2.25 × 10^{1}
1.00 × 10^{-5}	1.00 × 10^{-2}	1.00 × 10^{3}	2.92 × 10^{1}
1.00 × 10^{-5}	1.20 × 10^{-2}	1.20 × 10^{3}	3.27 × 10^{1}
1.00 × 10^{-5}	1.40 × 10^{-2}	1.40 × 10^{3}	4.03 × 10^{1}
1.00 × 10^{-5}	1.60 × 10^{-2}	1.60 × 10^{3}	4.37 × 10^{1}



$k_2 = 2.68 \times 10^3$ M^{-1} s^{-1}

Correlation between the electrophilicity *E* and the absorption maximum (λ_{max}) of iminium triflates (3a-g)-OTf in CH_2Cl_2

Ar_2CH^+	λ_{max} (nm)	*E*
3a	360	–8.5
3b	348	–9.8
3c	349	–8.6
3d	342[a]	–9.2
3e	342	(–10.3)
3f	370	–7.2
3g	365	–8.2

[a] Data for **3d**-BF_4 in dichloromethane from ref. [S3].