Supporting Information

Dihydropyranone Formation by *Ipso* C–H Activation in a Glucal 3-Carbamate-Derived Rhodium Acyl Nitrenoid

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General: NMR spectra were recorded at 300 MHz for ^{1}H spectra and 75 MHz for ^{13}C spectra. ^{1}H chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS, δ 0.00), using as a reference either added TMS or an appropriate signal for residual solvent protons. ^{13}C NMR chemical shifts are reported in parts per million, using the center peak of the solvent signal as a reference (e.g., δ 77.0 for $CDCl_3$). ^{13}C NMR peak multiplicities, where reported, were inferred using either DEPT 135 or edited HSQC experiments. The designation "o" (for odd number of attached hydrogens) denotes a CH or CH_3 carbon. Where ^{1}H and ^{13}C NMR peak assignments are given, these were made unambiguously by a combination of $^{1}H/^{1}H$ COSY and $^{1}H/^{13}C$ HSQC experiments. Infrared spectra were recorded on an FT-IR spectrometer. Melting points were obtained using a capillary melting point apparatus and are uncorrected.

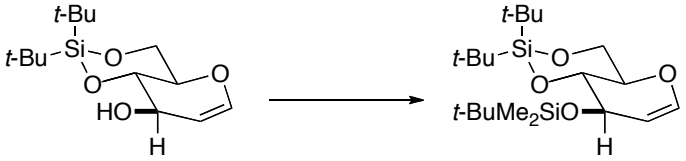
Iodosobenzene (PhIO) was prepared according to the literature procedure[1] and was stored at –20 °C under dry argon or nitrogen. Oven-dried (135 °C) 4 Å molecular sieves were further activated by flame-drying under vacuum (0.5 mmHg) just prior to use. Methylene chloride was either distilled from CaH_2 or used as received from Sigma-Aldrich (anhydrous, Sure Seal). Anhydrous dimethylformamide and tetrahydrofuran (Sure Seal) were purchased from Sigma-Aldrich and used as received. Other reagents were obtained commercially and were used as received. Reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry nitrogen. The amidoglycosylation products were sometimes difficult to visualize on TLC. A useful system to char the TLC plates involved pre-warming the eluted TLC plate, dipping the plate in a solution of Coleman's Permanganate [$KMnO_4$ (3 g), K_2CO_3 (20 g), 5% NaOH (5 mL), H_2O (300 mL)], and then gently heating the TLC plate.

We have reported spectroscopic data for **1**,[5] **2-α**,[5] **2-β**,[5] **3**,[5] **14**,[5b,6] and **17**[5,6a,7] previously, and ^{1}H NMR spectra of authentic samples of those materials were used for comparison in this study.

[1] Saltzman, H.; Sharefkin, J. G. In *Organic Syntheses*; Baumgarten, H. E., Ed.; John Wiley & Sons: New York, 1973; Coll. Vol. 5, pp 658–659.

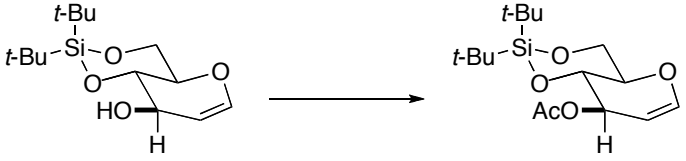
Experimental Procedures and Characterization Data

Part 1. Synthesis of compounds 7 for control experiments



8 **7a**

3-*O*-*tert*-Butyldimethylsilyl-4,6-*O*-di-*tert*-butylsilylene-D-glucal (7a). To a solution of di-*tert*-butylsilylene-protected D-glucal **8**[2] (101.3 mg, 0.354 mmol) in DMF (1.5 mL) was added imidazole (73.9 mg, 1.09 mmol), followed by *tert*-butyldimethylsilyl chloride (81.3 mg, 0.539 mmol). After stirring 4 h at 23 °C, the mixture was poured into satd aq $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (25 mL). The organic layer was further washed with satd aq $NaHCO_3$ (15 mL) and brine (15 mL), dried ($MgSO_4$), filtered, and concentrated on the rotovap and then under high vacuum overnight to remove residual DMF. The crude material was chromatographed (4% EtOAc/hexanes, 50 mL SiO_2), affording *tert*-butyldimethylsilyl ether **7a** (134.0 mg, 95%) as a clear, colorless oil. R_f = 0.73 (15% EtOAc/hexanes); IR (thin film) 1650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.23 (dd, J = 6.0, 1.6 Hz, 1H), 4.60 (dd, J = 6.1, 1.9 Hz, 1H), 4.28 (ddd, J = 7.0, 1.8, 1.8 Hz, 1H), 4.16 (dd, J = 10.3, 4.9 Hz, 1H), 3.97 (dd, J = 10.3, 7.1 Hz, 1H), 3.95 (dd, J = 10.3, 10.3 Hz, 1H), 3.81 (ddd, J = 10.2, 10.2, 4.8 Hz, 1H), 1.06 (s, 9H), 1.00 (s, 9H), 0.92 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9 (o), 105.1 (o), 77.06 (o),* 72.8 (o), 70.7 (o), 66.0 (t), 27.5 (o), 27.0 (o), 25.8 (o), 22.8 (s), 19.8 (s), 18.2 (s), -4.4 (o), -4.7 (o); *the ^{13}C NMR resonance at δ 77.06 was distinguished from the solvent peak by reprocessing the FID with lb = 0 and was also visible in the DEPT 135 spectrum; HRMS (FAB) *m/z* calcd for $C_{20}H_{39}O_4Si_2$ $(M-H)^+$ 399.2387, found 399.2393.

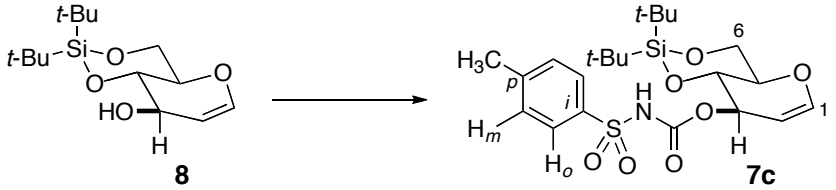


8 **7b**

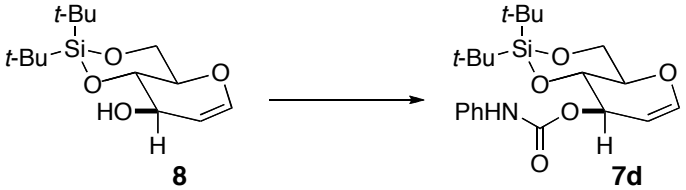
3-*O*-Acetyl-4,6-*O*-di-*tert*-butylsilylene-D-glucal[2] **(7b).** To a room-temperature solution of di-*tert*-butylsilylene-protected D-glucal **8**[2] (49.9 mg, 0.174 mmol) in CH_2Cl_2 (3.0 mL) were added, sequentially, pyridine (56 μL, 0.70 mmol), acetic anhydride (33 μL, 0.35 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (2.4 mg, 0.020 mmol). After 3 h, satd aq $NaHCO_3$ (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were washed with satd aq $CuSO_4$ (15 mL), dried ($MgSO_4$), filtered, and concentrated. Chromatography (8% EtOAc/hexanes, 15 mL SiO_2) afforded acetate ester **7b** as a yellowish syrup (53.1 mg, 93%). R_f = 0.60 (20% EtOAc/hexanes); IR (thin film)

[2] Hoberg, J. O. *Carbohydr. Res.* **1997**, *300*, 365–367.

1744, 1648 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.32 (dd, J = 6.0, 1.6 Hz, 1H), 5.38 (ddd, J = 7.6, 1.8, 1.8 Hz, 1H), 4.73 (dd, J = 6.1, 2.1 Hz, 1H), 4.19 (dd, J = 9.5, 4.3 Hz, 1H), 4.15 (dd, J = 10.0, 7.5 Hz, 1H), 3.99 (dd, J = 9.9, 9.9 Hz, 1H), 3.91 (ddd, J = 10.0, 10.0, 4.4 Hz, 1H), 2.11 (s, 3H), 1.06 (s, 9H), 0.99 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 145.0, 100.6, 73.6, 72.9, 72.3, 65.7, 27.4, 26.8, 22.7, 21.2, 19.8; HRMS (FAB) m/z calcd for $C_{16}H_{27}O_5Si$ $(M-H)^+$ 327.1628, found 327.1635.



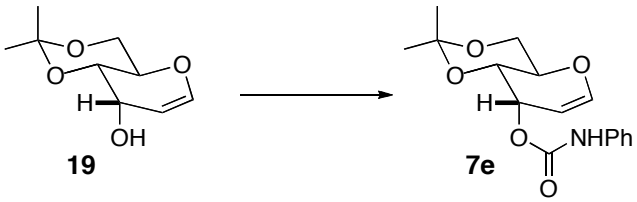
4,6-*O*-Di-*tert*-butylsilylene-3-*O*-(*N*-tosyl)carbamoyl-D-glucal (7c). A solution of 4,6-*O*-di-*tert*-butylsilylene-D-glucal **8**[2] (301.5 mg, 1.053 mmol) in CH_2Cl_2 (1.0 mL) was cooled to 0 ºC, followed by addition of *p*-toluenesulfonyl isocyanate (176 μL, 1.16 mmol). The solution was stirred 10 min at 0 ºC then 25 min at room temperature, diluted with H_2O (15 mL), and extracted with CH_2Cl_2 (15 mL). The aqueous layer was further extracted with CH_2Cl_2 (10 mL) and the combined organic layers were washed with H_2O (15 mL), dried (Na_2SO_4), and concentrated to leave the crude as a white foamy oil. Column chromatography (20→25→30% EtOAc/hexanes, 175 mL SiO_2) gave carbamate **7c** as an oil (313 mg, 61%). R_f = 0.57 (40% EtOAc/hexanes); IR (thin film) 3240, 1757, 1646, 1598 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (apparent d, J = 8.4 Hz, 2H, H_o), 7.61 (br, 1H, NH), 7.32 (apparent d, J = 8.1 Hz, 2H, H_m), 6.29 (dd, J = 6.0, 1.5 Hz, 1H, H1), 5.31 (ddd, J = 7.5, 1.8, 1.8 Hz, 1H, H3), 4.66 (dd, J = 6.1, 2.0 Hz, 1H, H2), 4.15 (dd, J = 9.6, 4.3 Hz, 1H, $H6_{eq}$), 4.03 (dd, J = 10.1, 7.6 Hz, 1H, H4), 3.94 (dd, J = 9.9, 9.9 Hz, 1H, $H6_{ax}$), 3.85 (ddd, J = 10.1, 10.1, 4.4 Hz, 1H, H5), 2.43 (s, 3H, Ar-C**H**$_3$), 0.97 (s, 9H, $SiC(CH_3)_3$), 0.91 (s, 9H, $SiC(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1 (s), 145.5 (o, C1), 145.0 (s), 135.5 (s), 129.6 (o, C_m), 128.4 (o, C_o), 99.5 (o, C2), 74.8 (o, C3), 73.5 (o, C4), 72.7 (o, C5), 65.5 (t, C6), 27.2 (o, $SiC(\mathbf{C}H_3)_3$), 26.7 (o, $SiC(\mathbf{C}H_3)_3$), 22.6 (s, $Si\mathbf{C}(CH_3)_3$), 21.7 (o, Ar-$\mathbf{C}H_3$), 19.7 (s, $Si\mathbf{C}(CH_3)_3$); HRMS (FAB) m/z calcd for $C_{22}H_{32}NO_7SiS$ $(M-H)^+$ 482.1669, found 482.1690.



4,6-*O*-Di-*tert*-butylsilylene-3-*O*-(*N*-phenyl)carbamoyl-D-glucal[3] **(7d).** Glucal derivative **8**[2] (54.5 mg, 0.190 mmol) was dissolved in CH_2Cl_2 (2.5 mL) at room temperature and phenyl isocyanate (23 μL, 0.21 mmol) was added, followed by DBU (3.0 μL, 0.019 mmol). After 2.5 h, brine (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried

[3] (a) Nicolaou, K. C.; Baran, P. S.; Zhong, Y.-L.; Vega, J. A. *Angew. Chem. Int. Ed.* **2000**, *39*, 2525–2529. (b) Nicolaou, K. C.; Baran, P. S.; Zhong, Y.-L.; Barluenga, S.; Hunt, K. W.; Kranich, R.; Vega, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 2233–2244.

($MgSO_4$), filtered, and concentrated. The crude material was chromatographed (10% EtOAc/hexanes, 15 mL SiO_2), providing *N*-phenyl carbamate **7d** as a syrup (77.0 mg, quant). R_f = 0.58 (30% EtOAc/hexanes); IR (thin film) 3327, 1724, 1647, 1602 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.20 (m, 4H), 7.07 (apparent t, J = 7.3 Hz, 1H), 6.75 (s, 1H), 6.33 (dd, J = 6.0, 1.2 Hz, 1H), 5.36 (ddd, J = 7.6, 1.6, 1.6 Hz, 1H), 4.87 (dd, J = 6.0, 1.8 Hz, 1H), 4.28-4.12 (m, 2H), 4.06-3.88 (m, 2H), 1.07 (s, 9H), 1.00 (s, 9H); there was evidence of a minor rotamer (~6%) from ^1H NMR signals just upfield of the signals at δ 6.33, 5.36, and 4.87; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 144.9, 137.8, 129.0, 123.5, 118.8, 100.9, 73.7, 73.4, 72.9, 65.7, 27.4, 26.9, 22.7, 19.8; the ^{13}C resonances at δ 118.8 and 73.4 were appreciably broadened; HRMS (FAB) *m/z* calcd for $C_{21}H_{32}NO_5Si$ $(M+H)^+$ 406.2050, found 406.2055.



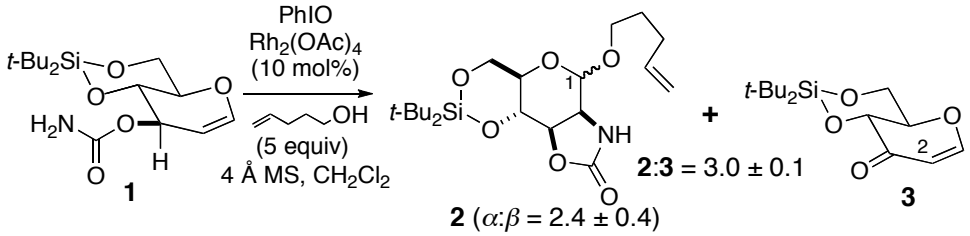
4,6-*O*-Isopropylidene-3-*O*-(*N*-phenyl)carbamoyl-D-allal (7e). To a room-temperature solution of isopropylidene-protected allal **19**[4] (101.2 mg, 0.544 mmol) in CH_2Cl_2 (3.0 mL) was added DBU (24 μL, 0.16 mmol), followed by phenyl isocyanate (119 μL, 1.09 mmol). After 50 min, the reaction mixture was diluted with CH_2Cl_2 and washed with satd aq $NaHCO_3$ (15 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was chromatographed (20→30→40% EtOAc/hexanes, 50 mL SiO_2), affording *N*-phenyl carbamate **11e** as a white solid (118.5 mg, 71%). mp 144-146 °C, R_f = 0.50 (40% EtOAc/hexanes); IR (thin film) 3379, 3334, 1729, 1711, 1631, 1601 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43-7.23 (m, 4H), 7.15-6.90 (m, 2H), 6.46 (d, J = 6.0 Hz, 1H), 5.24 (dd, J = 5.8, 3.1 Hz, 1H), 5.08 (dd, J = 6.0, 6.0 Hz, 1H), 4.16-4.00 (m, 3H), 3.95-3.80 (m, 1H), 1.54 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 147.2, 137.9, 128.9, 123.2, 118.6, 100.0, 98.8, 69.2, 65.7, 63.4, 61.8, 28.7, 18.9; HRMS (FAB) *m/z* calcd for $C_{16}H_{19}NO_5$ (M^+) 305.1263, found 305.1266.

Part 2. Experiments with compounds 1 and 7

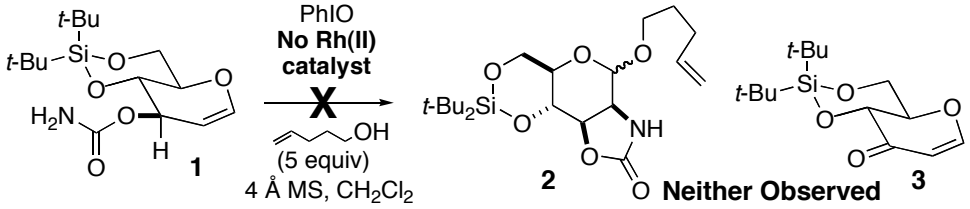
General Procedure: The glycal substrate (~50 mg), activated 4Å molecular sieves (300 wt % relative to the glycal), catalyst (0.1 equiv when included), and PhIO (1.8 equiv) were combined in a 10 mL round-bottom flask at room temperature. Introduction of 4-penten-1-ol (5.0 equiv) was followed immediately by addition of CH_2Cl_2 (2.0 mL) and the mixture was well stirred for >3 h and in most cases for ~24 h (reactions of **1** under these conditions, with catalyst included, were complete in under 3 h). The reaction mixture was filtered through a plug of tightly packed Celite (2 cm x 2 cm in a medium porosity fritted glass filter funnel), rising with EtOAc (75 mL). The filtrate was concentrated on the rotovap and kept under high vacuum (~0.5 mmHg) overnight to remove excess 4-penten-1-ol. The

[4] Kan, C.; Long, C. M.; Paul, M.; Ring, C. M.; Tully, S. E.; Rojas, C. M. *Org. Lett.* **2001**, *3*, 381–384.

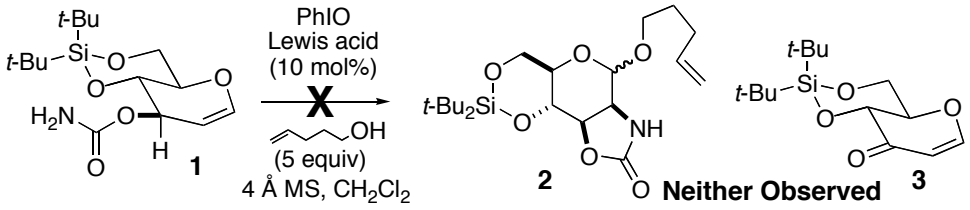
crude was analyzed by ^{1}H NMR, comparing with spectra of authentic samples of **2**,[5] **3**,[5] **14**,[5b,6] and **17**.[5,6a,7] Where appropriate, the crude material was chromatographed (SiO_2, EtOAc/hexanes) to isolate pure recovered starting material.



Product ratios for amidoglycosylation with primary carbamate 1. The amidoglycosylation shown above was conducted according to the general procedure given above and as described previously.[5] We have also reported spectroscopic data for the anomers of **2** and dihydropyranone **3**.[5] The ratios **2**:**3** and **2-*α***:**2-*β*** were determined by integration of the ^{1}H NMR ($CDCl_3$) signals for H1 of **2-*α*** and **2-*β*** (δ 4.81 and δ 4.69, respectively) and H2 of **3** (δ 5.42). The ratios reported in the scheme above are the average of five separate runs ± std dev.



Control experiment with 1 omitting the catalyst. Reaction time: 18 h. Neither the amidoglycosylation product **2** nor the dihydropyranone **3** was observed when comparing the ^{1}H NMR spectrum of the crude product to the spectra of authentic **2** (both anomers) and **3**. Remaining starting material **1** (86%) was evident by ^{1}H NMR analysis of the crude material versus mesitylene as an internal standard.



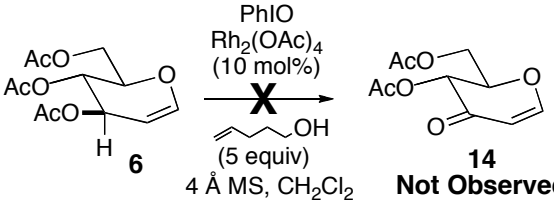
Control experiments with 1 and Lewis acid catalysts. Separate experiments were conducted using $Sm(OTf)_3$, $La(OTf)_3$, and $Zn(OTf)_2$ as possible catalysts. Reaction time for each experiment: 17 h. In each case, neither the amidoglycosylation product **2** nor the dihydropyranone **3** was observed when

[5] (a) Bodner, R.; Marcellino, B. K.; Severino, A.; Smenton, A. L.; Rojas, C. M. *J. Org. Chem.* **2005**, *70*, 3988–3996. (b) Gupta, R.; Sogi, K. M.; Bernard, S. E.; Decatur, J. D.; Rojas, C. M. *Org. Lett.* **2009**, *11*, 1527–1530.

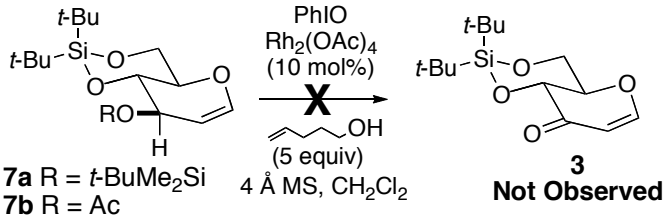
[6] (a) Fetizon, M.; Do Khac, D.; Nguyen Dinh, T. *Tetrahedron Lett.* **1986**, *27*, 1777–1780. (b) Czernecki, S.; Vijayakumaran, K.; Ville, G. *J. Org. Chem.* **1986**, *51*, 5472–5475. (c) Bouillot, A.; Do Khac, D.; Fétizon, M.; Guir, F.; Memoria, Y. *Synth. Commun.* **1993**, *23*, 2071–2081.

[7] Fraser-Reid, B.; Walker, D. L.; Tam S. Y.-K.; Holder, N. L. *Can. J. Chem.* **1973**, *51*, 3950–3954.

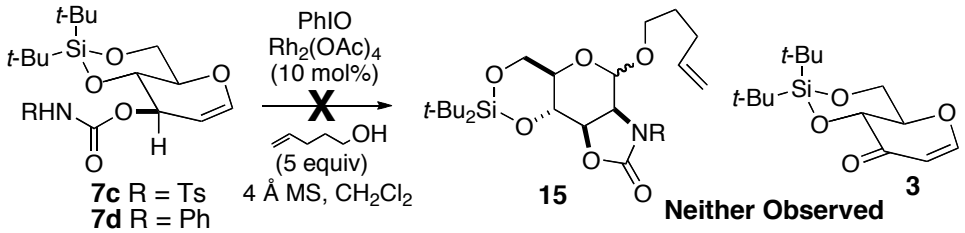
comparing the ^{1}H NMR spectrum of the crude product to the spectra of authentic **2** (both anomers) and **3**. Remaining starting material **1** was evident by ^{1}H NMR analysis of the crude material versus mesitylene as an internal standard [94% with $Sm(OTf)_3$, 93% with $La(OTf)_3$, and 92% with $Zn(OTf)_2$].



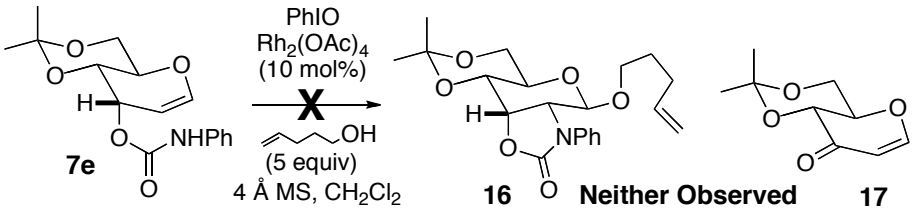
Control experiment with 6. Reaction time: 24 h. None of dihydropyranone **14**[5b,6] was observed when comparing the ^{1}H NMR spectrum of the crude product to the spectrum of authentic **14**.[5b] Starting material **6** (87%) was recovered by chromatography (30% EtOAc/hexanes, SiO_2).



Control experiments with 7a and 7b. Reaction time with **7a**: 5 h. Reaction time with **7b**: 20 h. None of dihydropyranone **3** was observed in the ^{1}H NMR spectrum of the crude product from either reaction; only the starting glycals were evident. Glucal **7a** (83%) was recovered by chromatography (5→10→15% EtOAc/hexanes, SiO_2), while the amount of remaining **7b** was measured by ^{1}H NMR (80% versus mesitylene as an internal standard).

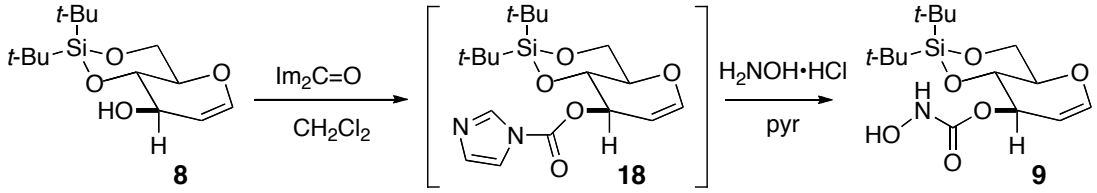


Control experiments with 7c and 7d. With **7c**, we conducted two experimental runs, one for 5 h and the other for 26 h. In neither case was **3** observed in the crude reaction mixture, nor did we detect signs of **15** (R = Ts). Recovered **7c** (71% after 5h and 61% after 26 h) was purified by chromatography (15→20→25% EtOAc/hexanes, 50 mL SiO_2). With **7d**, the reaction time was 19 h, and dihydropyranone **3** was not formed, as judged by comparison of the ^{1}H NMR spectrum of crude material with the spectrum of authentic **3**. Neither were signals attributable to oxidative cyclization products **15** (R = Ph) observed in the reaction with **7d**. Unreacted *N*-phenyl carbamate **7d** (70%) was recovered.



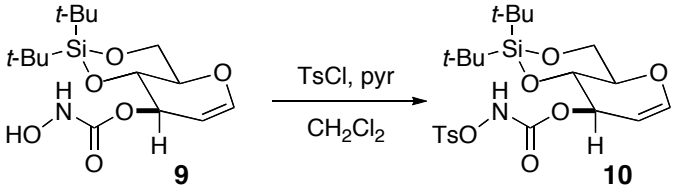
Control experiment with 7e. Reaction time: 26 h. None of dihydropyranone **17**[5,6a,7] was observed when comparing the ^{1}H NMR spectrum of the crude product to the spectrum of authentic **17**.[5a] Neither were signals attributable to amidoglycosylation product **16** observed. Starting material **7e** (94%) was recovered by chromatography (30→40% EtOAc/hexanes, SiO_2).

Part 3. Synthesis of *N*-tosyloxycarbamate 10 and glucal 3-azidoformate 11

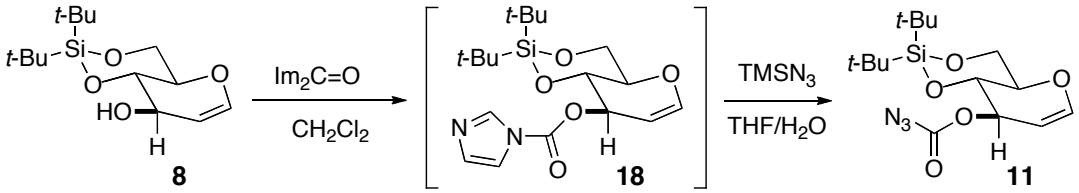


4,6-*O*-Di-*tert*-butylsilylene-3-*O*-(*N*-hydroxy)carbamoyl-D-glucal (9). To a solution of alcohol **8**[2] (0.5009 g, 1.75 mmol) in CH_2Cl_2 (20 mL) was added 1,1'-carbonyl diimidazole (0.4252 g, 2.62 mmol). After 2 h at room temperature, the mixture was diluted with CH_2Cl_2 (80 mL) and washed with satd aq NH_4Cl (3 x 80 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated, providing the carbonyl imidazole product **18** as a light yellow foam. Without further purification, *N*-acyl imidazole **18** (assumed 1.75 mmol) was dissolved in pyridine (4.0 mL) and hydroxylamine hydrochloride (0.3648 g, 5.25 mmol) was added. After stirring 60 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (80 mL) and washed with water (2 x 80 mL) and brine (80 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. The crude product was chromatographed (30% EtOAc/hexanes, 100 mL SiO_2), yielding hydroxycarbamate **9** as a white solid (0.4697 g, 78%). Data for hydroxycarbamate **9**: mp 110.0 °C; R_f = 0.21 (30% EtOAc/hexanes); IR (thin film) 3315, 1731, 1649 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 1H), 6.92 (very br s, 1H), 6.33 (dd, J = 6.0, 1.5 Hz, 1H), 5.34 (ddd, J = 7.5, 1.8, 1.8 Hz, 1H), 4.80 (dd, J = 6.1, 2.1 Hz, 1H), 4.25-4.10 (m, 2H), 4.04-3.85 (m, 2H), 1.05 (s, 9H), 0.99 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0 (s), 145.2 (o), 100.3 (o), 74.4 (o), 73.6 (o), 72.8 (o), 65.6 (t), 27.4 (o), 26.8 (o), 22.7 (s), 19.8 (s); HRMS (FAB) *m/z* calcd for $C_{15}H_{28}NO_6Si$ $(M+H)^+$ 346.1686, found 346.1688.

Data for intermediate *N*-acyl imidazole **18**: R_f = 0.41 (30% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.45 (br s, 1H), 7.10 (m, 1H), 6.42 (dd, J = 6.0, 1.5 Hz, 1H), 5.56 (ddd, J = 7.5, 1.8, 1.8 Hz, 1H), 4.88 (dd, J = 6.1, 2.1 Hz, 1H), 4.37-4.19 (m, 2H), 4.09-3.93 (m, 2H), 1.05 (s, 9H), 1.00 (s, 9H).



4,6-*O*-Di-*tert*-butylsilylene-3-*O*-(*N*-tosyloxy)carbamoyl-D-glucal (10). The *N*-hydroxycarbamate **9** (105.1 mg, 0.3042 mmol) was dissolved in CH_2Cl_2 (1.5 mL) and pyridine (74 μL, 0.915 mmol) was added, followed by *p*-toluenesulfonyl chloride (89.3 mg, 0.468 mmol). The solution was stirred at 25 °C during 4.5 h, diluted with CH_2Cl_2 (25 mL), and washed with water (2 x 20 mL) and brine (1 x 20 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. The crude material was immediately chromatographed (20→25→30% EtOAc/Hexanes, 50 mL SiO_2). Because **10** was prone to decomposition when kept neat for extended periods of time, the yield was determined by weight after concentration on the rotovap, followed by 5 min on the vacuum line. The resulting product **10**, a colorless foam (~120 mg, 80%), consequently contained traces of solvent, and the reported yield is an upper-limit estimate. After weighing, **10** was dissolved in CH_2Cl_2 (1.0 mL) and used immediately. R_f = 0.52 (30% EtOAc/hexanes); IR (thin film) 3281, 1775, 1736, 1647, 1597 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 8.20 (s, 1H), 7.86 (apparent d, J = 8.4 Hz, 2H), 7.37 (apparent d, J = 8.0 Hz, 2H), 6.31 (dd, J = 6.0, 1.4 Hz, 1H), 5.21 (ddd, J = 7.4, 1.8, 1.8 Hz, 1H), 4.53 (dd, J = 6.1, 2.0 Hz, 1H), 4.16 (dd, J = 9.6, 4.4 Hz, 1H), 4.03 (dd, J = 10.2, 7.4 Hz, 1H), 3.95 (dd, J = 9.9, 9.9 Hz, 1H), 3.87 (ddd, J = 10.1, 10.1, 4.5 Hz, 1H), 2.45 (s, 3H), 1.05 (s, 9H), 0.96 (s, 9H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.9 (s), 147.0 (s), 146.1 (o), 131.0 (s), 130.4 (o), 130.0 (o), 100.0 (o), 75.7 (o), 73.9 (o), 73.4 (o), 66.2 (t), 27.7 (o), 27.2 (o), 23.1 (s), 22.1 (o), 20.2 (s); HRMS (FAB) *m/z* calcd for $C_{22}H_{34}NO_8SiS$ $(M+H)^+$ 500.1774, found 500.1760.



4,6-*O*-Di-*tert*-butylsilylene-3-*O*-carbonylazido-D-glucal (11). The *N*-acyl imidazole **18** was prepared from glucal **8** (529 mg, 1.85 mmol) as described above. After aqueous workup but without further purification, the intermediate **18** was dissolved in THF (5.0 mL) and $TMSN_3$ (1.0 mL, 7.5 mmol) was added. The solution was stirred at 25 °C during 69 h, at which point TLC indicated partial conversion to the upper R_f product **11**, but considerable amounts of unreacted **18** still remained. As suggested by the work of Yoshimitsu and Tanaka,[8] H_2O (500 μL) was added and stirring continued at room temperature for 2 h. Remarkably, all the *N*-acyl imidazole **18** reacted within this period of time. The mixture was poured into satd aq $NaHCO_3$ (30 mL) and extracted with Et_2O (50 mL). The organic layer was washed with satd aq $NaHCO_3$ (2 x 30 mL), dried ($MgSO_4$), filtered, and concentrated. The crude material was

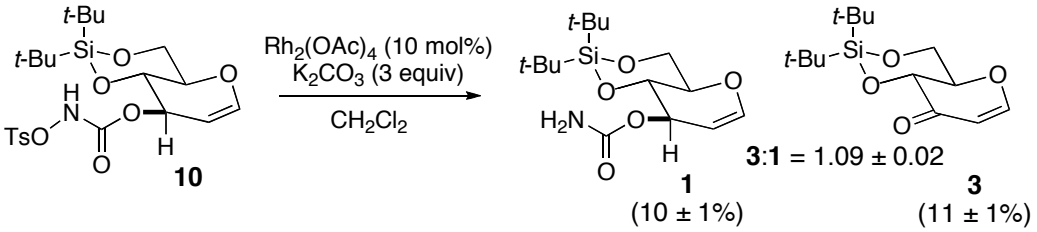
[8] Yoshimitsu, T.; Ino, T.; Futamura, N.; Kamon, T.; Tanaka, T. *Org. Lett.* **2009**, *11*, 3402–3405.

chromatographed (4% EtOAc/Hexanes, 125 mL SiO_2), providing **11** as a clear, colorless oil (385 mg, 59% for the two steps from alcohol **8**). The azidoformate **11** exhibited signs of decomposition on SiO_2-coated TLC plates (lower R_f spots appeared), but showed clean NMR spectra and was stable to storage over at least several weeks.

CAUTION: Azidoformates are potentially explosive. While we did not experience any problems with the preparation, storage, and use of 11, proper precautions should be taken in handling this material.[9]

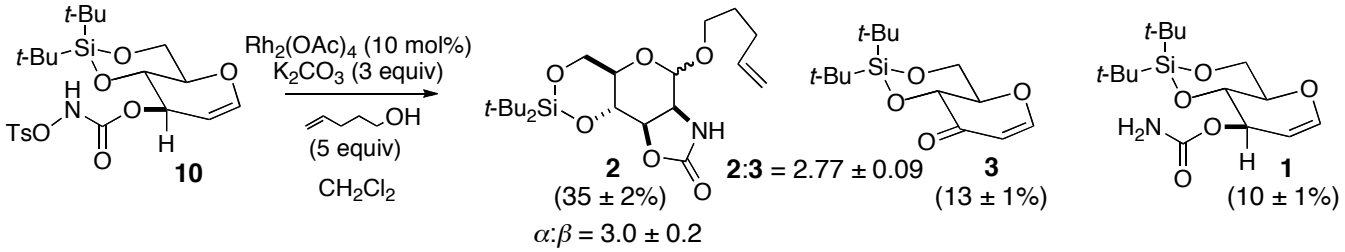
Data for **11**: R_f = 0.66 (30% EtOAc/hexanes); IR (thin film) 2180, 2140, 1755 (shoulder), 1733, 1648 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.36 (dd, J = 6.1, 1.5 Hz, 1H), 5.35 (ddd, J = 7.4, 1.8, 1.8 Hz, 1H), 4.78 (dd, J = 6.1, 2.1 Hz, 1H), 4.24-4.14 (m, 2H), 3.99 (dd, J = 9.9, 9.9 Hz, 1H), 3.91 (ddd, J = 10.1, 10.1, 4.4 Hz, 1H), 1.06 (s, 9H), 0.99 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4 (s), 145.9 (o), 99.2 (o), 76.8 (o), 73.3 (o), 72.8 (o), 65.6 (t), 27.3 (o), 26.8 (o), 22.7 (s), 19.8 (s); HRMS (FAB) m/z calcd for $C_{15}H_{25}N_3O_5Si$ (M^+) 355.1563, found 355.1560.

Part 4. Investigations with *N*-tosyloxycarbamate 10



Reaction of 10 in the absence of alcohol with $Rh_2(OAc)_4$ catalysis. Potassium carbonate (102.3 mg, 0.740 mmol) and $Rh_2(OAc)_4$ (10.8 mg, 0.0244 mmol) were combined in a 10 mL round-bottom flask and a solution of freshly prepared *N*-tosyloxycarbamate **10** (~120 mg, 0.242 mmol) in CH_2Cl_2 (1.0 mL) was added. The carbamate-containing pear-shaped flask was rinsed with CH_2Cl_2 (2 x 1.0 mL) with the rinsings being added to the reaction mixture. The reaction mixture was initially green, becoming blue-grey and then purplish over a period of 1 h. The mixture was well stirred during 16.5 h then filtered through a tightly packed pad of Celite, rising with EtOAc (80 mL). The filtrate was concentrated and the crude material analyzed by ^1H NMR ($CDCl_3$), which identified dihydropyranone **3** and carbamate **1** by comparison with ^1H NMR spectra of authentic samples. The **3**:**1** ratio was determined by integration of the H3 signal for **1** (δ 5.27) and the H2 signal of **3** (δ 5.42). The ratio reported in the scheme above is the average of three separate runs ± std dev. NMR yields of **1** and **3** were determined by including mesitylene as an internal standard; here, too, the reported values are the average of three separate runs ± std dev.

[9] For a report on the violent decomposition of *tert*-butylazidoformate ($BocN_3$) during distillation, see: Feyen, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 115.



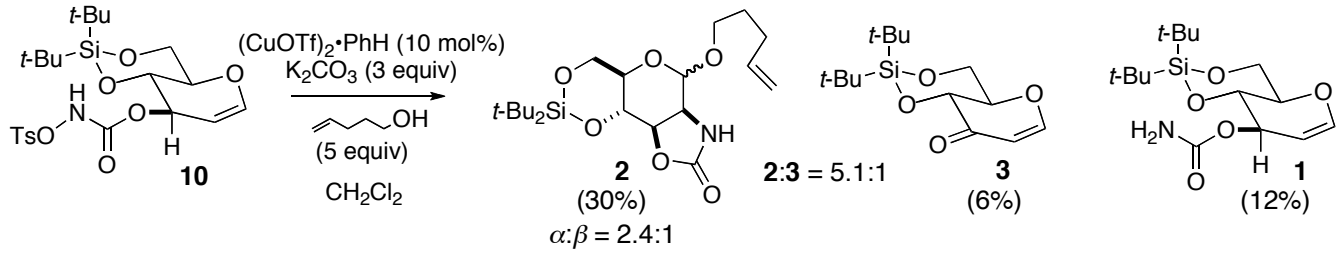
Reaction of 10 in the presence of 4-penten-1-ol with $Rh_2(OAc)_4$ catalysis. Potassium carbonate (95.8 mg, 0.693 mmol) and $Rh_2(OAc)_4$ (11.1 mg, 0.0251 mmol) were combined in a 10 mL round-bottom flask and 4-penten-1-ol (125 μL, 1.23 mmol) was added, followed immediately by a solution of freshly prepared *N*-tosyloxycarbamate **10** (~114 mg, 0.228 mmol) in CH_2Cl_2 (1.0 mL). The carbamate-containing pear-shaped flask was rinsed with CH_2Cl_2 (2 x 1.0 mL) with the rinsings being added to the reaction mixture. The well stirred mixture turned from a blue-green-grey to a purple color within 20–30 min. Stirring was continued 16 h and the purple mixture was filtered through a tightly packed pad of Celite, rising with EtOAc (80 mL). The filtrate was concentrated (rotovap → vacuum line to remove excess 4-penten-1-ol) and the crude material analyzed by ^{1}H NMR (separately in $CDCl_3$ and acetone-d_6), comparing to authentic samples of **1**, **2**, and **3**. The **2**:**3** and **2-α**:**2-β** ratios were best measured in acetone-d_6 from the resonances for H3 of **2-α** (δ 4.56), H1 of **2-β** (δ 4.86), and H2 of **3** (δ 5.33). The ratios reported in the scheme above are the average of three separate runs ± std dev. The yields were determined by ^{1}H NMR analysis of the crude in $CDCl_3$ using the H1 signals for **2-α** and **2-β** (δ 4.81 and δ 4.69, respectively), the H2 signal for **3** (δ 5.42), and the H3 signal for **1** (δ 5.27) versus mesitylene added as an internal standard. The reported values are the average of three experiments ± std dev.

Statistical comparison of results from iodine(III) mediated amidoglycosylation of 1 with results from amidoglycosylation of 10 using $Rh_2(OAc)_4$ catalysis). The mean values of the **2-α**:**2-β** ratio were compared using a Student's t-test. The t-value (6 degrees of freedom) = 2.380, and the p-value = 0.054,[10] indicating a near-95% confidence level that the difference between the means was statistically significant. The mean values of the **2**:**3** ratio were also compared. For this comparison, the t-value (6 degrees of freedom) = 3.614, and the p-value = 0.011, indicating a greater than 98% confidence level that the difference between the means was statistically significant. We attribute these small but nevertheless statistically significant differences in the product ratios to the impact of the different reaction conditions (4 Å molecular sieves in the iodine(III)-mediated reactions of **1** versus K_2CO_3 in reactions of **10**) on trapping of the glycosyl aziridine or oxocarbenium ion formed upon nitrenoid insertion into the glucal C=C.

[10] P-values were calculated using a two-tail, equal variance t-test, as implemented in Microsoft Excel 2008 for Macintosh.

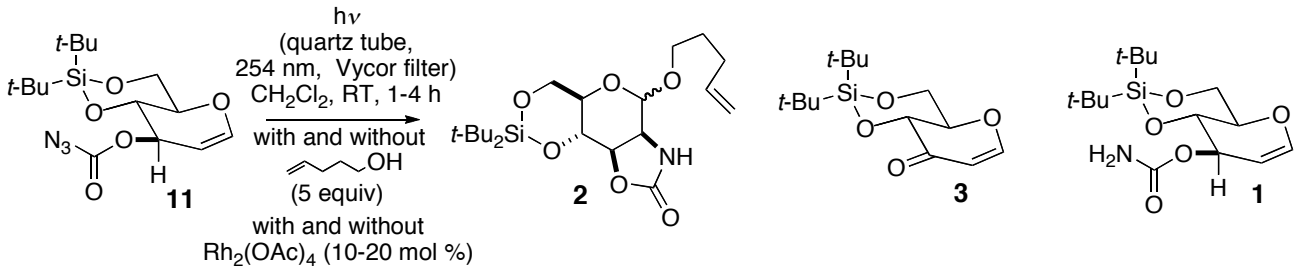
Control experiments using 10 in the absence of rhodium or base. Following the same procedures outlined above, the control experiments were conducted as shown in the table below. The crude reaction mixtures were analyzed by ^{1}H NMR and TLC, comparing with authentic samples of **1**, **2**, and **3**:[11]

Entry	4-penten-1-ol	$Rh_2(OAc)_4$	K_2CO_3	**1** observed?	**2** observed?	**3** observed?
1	–	–	+	no	N/A	no
2	+	–	+	no	no	no
3	+	+	–	no	no	no



Reaction of 10 in the presence of 4-penten-1-ol with $(CuOTf)_2$•PhH catalysis. Potassium carbonate (94.7 mg, 0.685 mmol) and $(CuOTf)_2$•PhH (11.3 mg, 0.0225 mmol) were combined in a 10 mL round-bottom flask and 4-penten-1-ol (120 μL, 1.18 mmol) was added, followed immediately by a solution of freshly prepared *N*-tosyloxycarbamate **10** (~114 mg, 0.228 mmol) in CH_2Cl_2 (1.5 mL). The carbamate-containing pear-shaped flask was rinsed with CH_2Cl_2 (2 x 1.0 mL) and the rinsings were added to the reaction mixture. The mixture was stirred 18 h at room temperature and filtered through a tightly packed pad of Celite, rising with CH_2Cl_2 (75 mL). The filtrate was concentrated (rotovap → vacuum line to remove excess 4-penten-1-ol) and the crude material analyzed by ^{1}H NMR (separately in $CDCl_3$ and acetone-d_6), comparing to authentic samples of **1**, **2**, and **3** as described above for the rhodium(II)-catalyzed reaction, except that yields were determined versus mesitylene in acetone-d_6 instead of in $CDCl_3$.

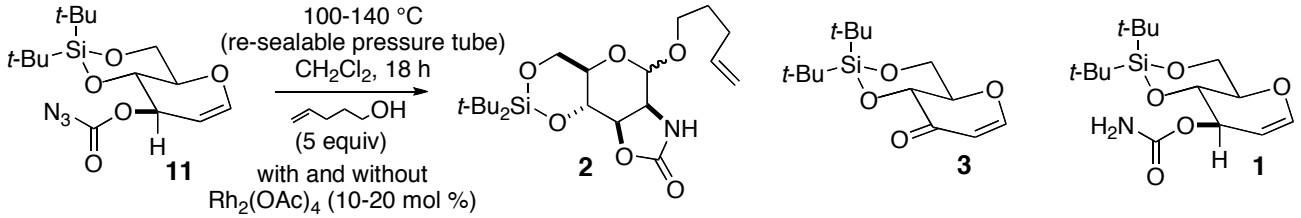
Part 5. Investigations with glucal 3-azidoformate 11



General photolysis procedure. A solution of azidoformate **11** (~22 mg, 0.062 mmol) in CH_2Cl_2 (4–10 mL) in a quartz reaction tube was irradiated during 1–4 h with a low-pressure 254 nm lamp through a

[11] Because the crude reaction products in the control experiments consisted of complex mixtures, we cannot completely rule out formation of the merest traces of **1**, **2**, or **3**.

Vycor filter in a Rayonet merry-go-round apparatus. The solution was concentrated and the crude reaction mixture analyzed by ^{1}H NMR in both $CDCl_3$ and acetone-d_6, using diagnostic resonances as described above in the *N*-tosyloxycarbamate reactions. Yields were determined by ^{1}H NMR versus mesitylene as an internal standard, either in acetone-d_6 or $CDCl_3$. Photolysis experiments were also conducted with added 4-penten-1-ol and $Rh_2(OAc)_4$ as summarized in the table below. In photochemical reactions run for varying lengths of time and to varying amounts of starting material consumption, we did not in any case detect formation of dihydropyranone **3**. The dihydropyranone is photo-labile to an appreciable extent (see the description of control experiments on the following page), but we expect that if **3** had formed in the photochemical reactions of **11**, we would have detected at least some of it.



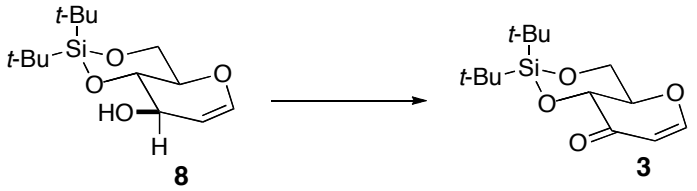
General thermolysis procedure. A solution of azidoformate **11** (~20 mg, 0.056 mmol) and 4-penten-1-ol (~29 μL, 0.285 mmol) in CH_2Cl_2 (4–6 mL) was heated in a thick-walled re-sealable pressure tube at ~100 °C-140 °C) as summarized in the table below. Thermolysis was also conducted in the presence of $Rh_2(OAc)_4$. The reaction mixture was concentrated and analyzed by ^{1}H NMR as described above. Below 90 °C, the azidoformate **11** did not undergo appreciable thermal reaction either in the absence or presence of $Rh_2(OAc)_4$ over periods of 2–15 h.

Tabular summary of results for reactions of 11.

hν	Δ	OH	$Rh_2(OAc)_4$	%**2** (α:β)	%**3**	%**1**
1 h				N/A	None	Formed but yield nd[a]
1 h		+		44 (1.5:1)	None	-*b*-
1.5 h		+	+	20 (2.4)	None	-*b*-
4 h		+	+	34 (2.5)	None	-*b*-
	110 °C, 1 h → 140 °C 1 h	+		Formed but yield nd[a]	None	-*b*-
	110 °C, 18 h	+		2 of β (nd[a])	None	None
	23 °C, 15 h → 55 °C, 2 h → 90 °C, 17 h	+	+	8 (3.0)	2	5

[a]nd = not determined. [b]Not detected, but regions in ^{1}H NMR spectra of the crude reaction mixture that would have contained resonances for **1** were obscured by other signals.

Part 6. Stability of dihydropyranone 3 under the reaction conditions



Independent preparation of dihydropyranone 3. To a solution of alcohol **12** (100.6 mg, 3.54 mmol) in CH_2Cl_2 (2.0 mL) was added pyridinium dichromate (199.9 mg, 5.44 mmol) and the solution was stirred 4 h at room temperature. Additional PDC (91.6 mg, 2.49 mmol) was added and the solution stirred overnight. The reaction mixture was diluted with Et_2O (10 mL) and filtered through Celite. The solution was dried ($MgSO_4$), filtered, and concentrated. Chromatography (25% EtOAc/hexanes, 50 mL SiO_2) yielded dihydropyranone **3** as a white solid (55.1 mg, 55%). The identity of this material with that prepared in our previous studies was confirmed by ^{1}H NMR analysis.

Control experiments with dihydropyranone 3. To a solution of dihydropyranone **3** (35.6 mg, 0.125 mmol) in CD_2Cl_2 (1.00 mL) was added 4-penten-1-ol (64 μL, 0.63 mmol), followed immediately by K_2CO_3 (52.6 mg, 0.380 mmol) and $Rh_2(OAc)_4$ (6.0 mg, 0.14 mmol). The mixture was stirred at room temperature, and aliquots (100 μL) were taken after 15 min, 1 h, and 18 h. The aliquots were mixed with a stock solution of mesitylene in CD_2Cl_2 (500 μL of a 0.0250 M solution, 0.0125 mmol mesitylene), and the resulting solution was analyzed by ^{1}H NMR. No decomposition of the dihydropyranone was noted after 18 h as measured against the mesitylene internal standard.

In a separate experiment, the same procedure was followed, but in the absence of 4-penten-1-ol. Again, no decomposition of the dihydropyranone was noted.

To assess the stability of dihydropyranone **3** under the conditions used for photolysis reactions of **11**, a solution of **3** (22 mg, 0.0773 mmol) in CH_2Cl_2 (10 mL) in a quartz reaction tube was irradiated (254 nm low-pressure lamp, Vycor filter, Rayonet merry-go-round apparatus) during 1 h. The solution was concentrated and analyzed by ^{1}H NMR. While no identifiable byproducts were observed, the amount of remaining **3** was 42% versus mesitylene added as an internal standard. When the photochemical control was repeated in the presence of added 4-penten-1-ol (5 equiv), 34% of the original **3** remained after 1 h photolysis.

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PROCNO 1

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I-AS-3
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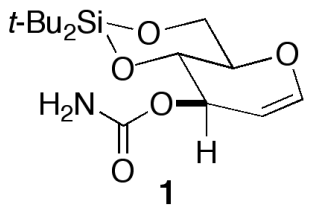
By CMR on 12/21/2007



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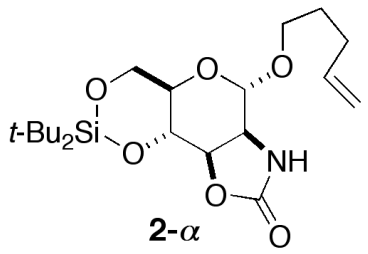
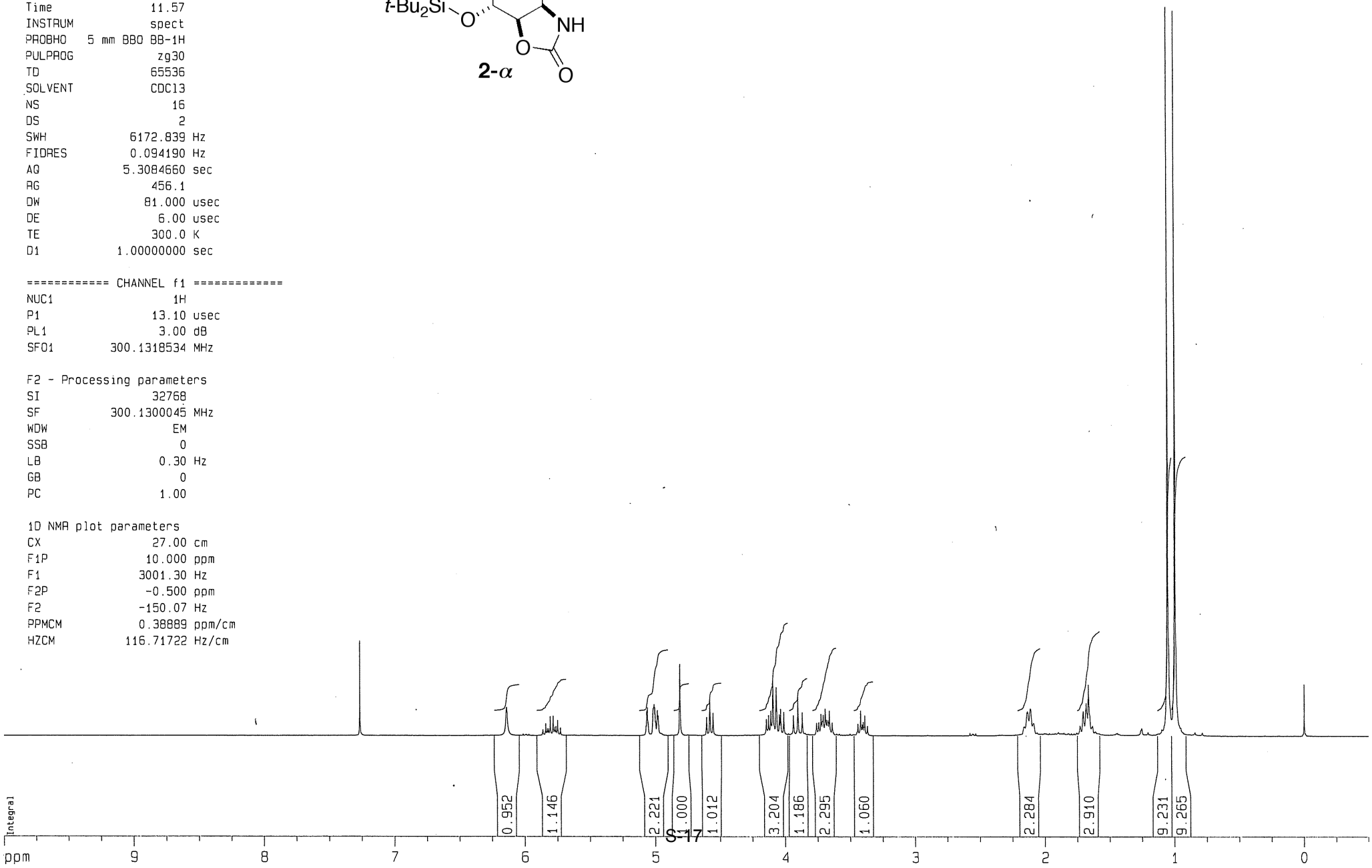


2-α



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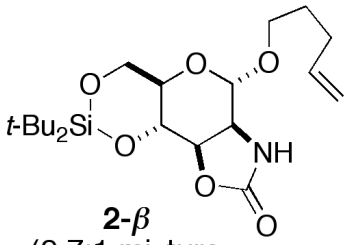
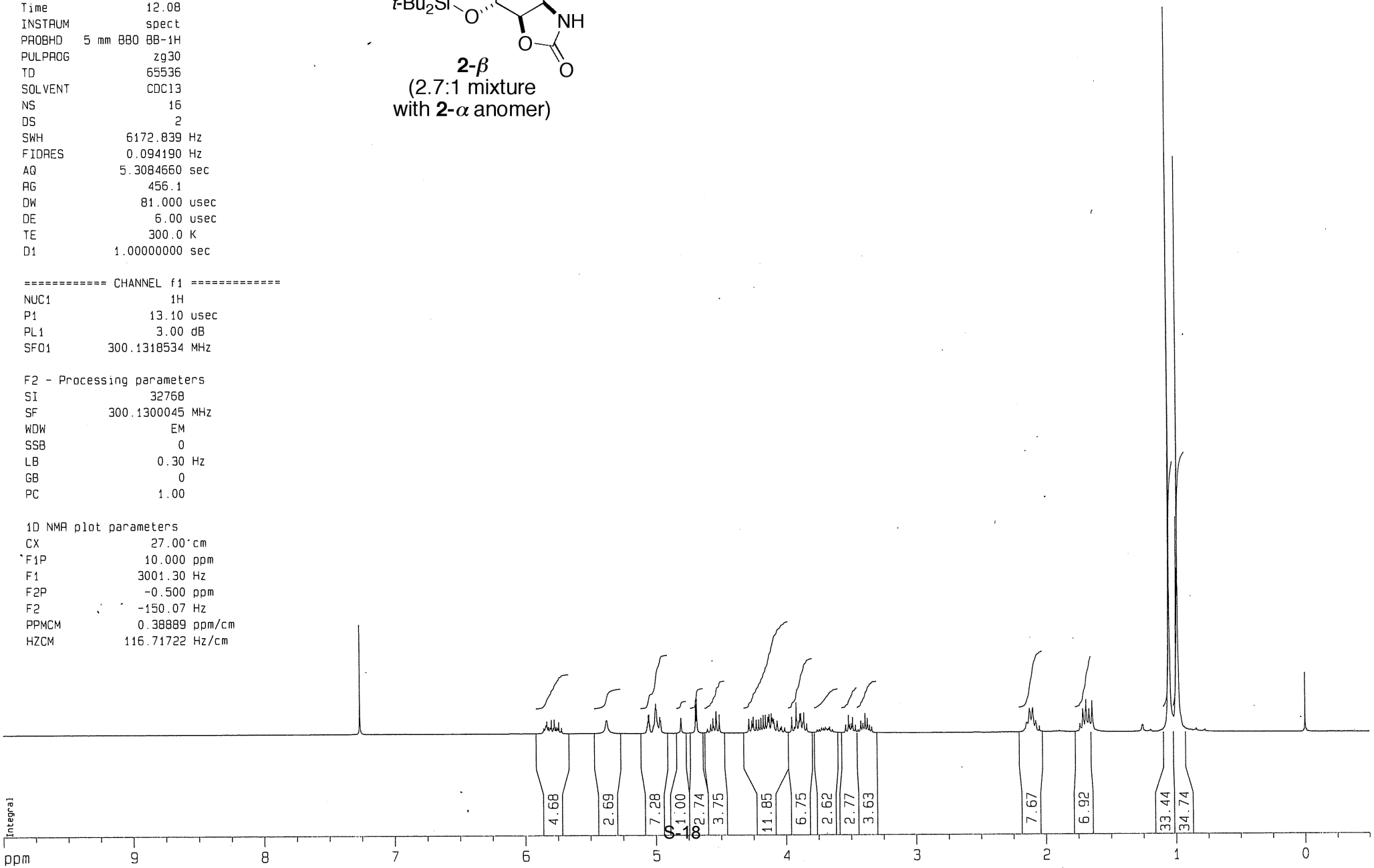
II-CMR-255-F22-27



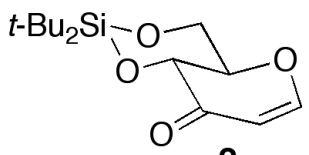
2-β
(2.7:1 mixture
with **2-α** anomer)



II-BKM-31

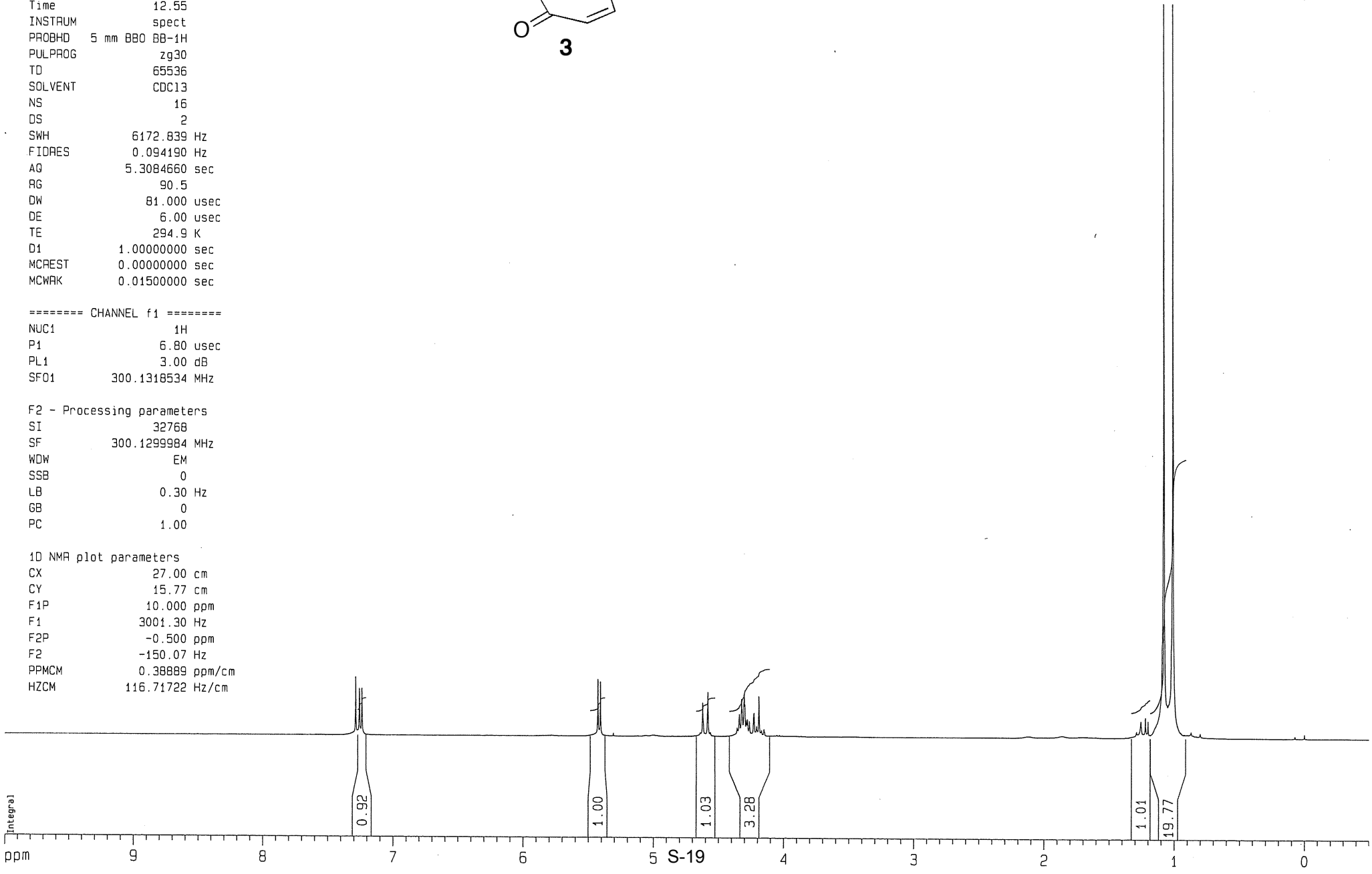
carbamate treated with iodosobenzene, Rh2(OAc)4, 4-penten-1-ol 4A Molecular Sieves by-product

F29-37



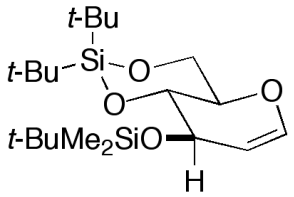
3

```
Current Data Parameters
NAME          II-BKM-31
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20040902
Time              12.55
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ             5.3084660 sec
RG                  90.5
DW                81.000 usec
DE                 6.00 usec
TE                294.9 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 6.80 usec
PL1                3.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1299984 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                27.00 cm
CY                15.77 cm
F1P              10.000 ppm
F1             3001.30 Hz
F2P              -0.500 ppm
F2             -150.07 Hz
PPMCM          0.38889 ppm/cm
HZCM         116.71722 Hz/cm
```

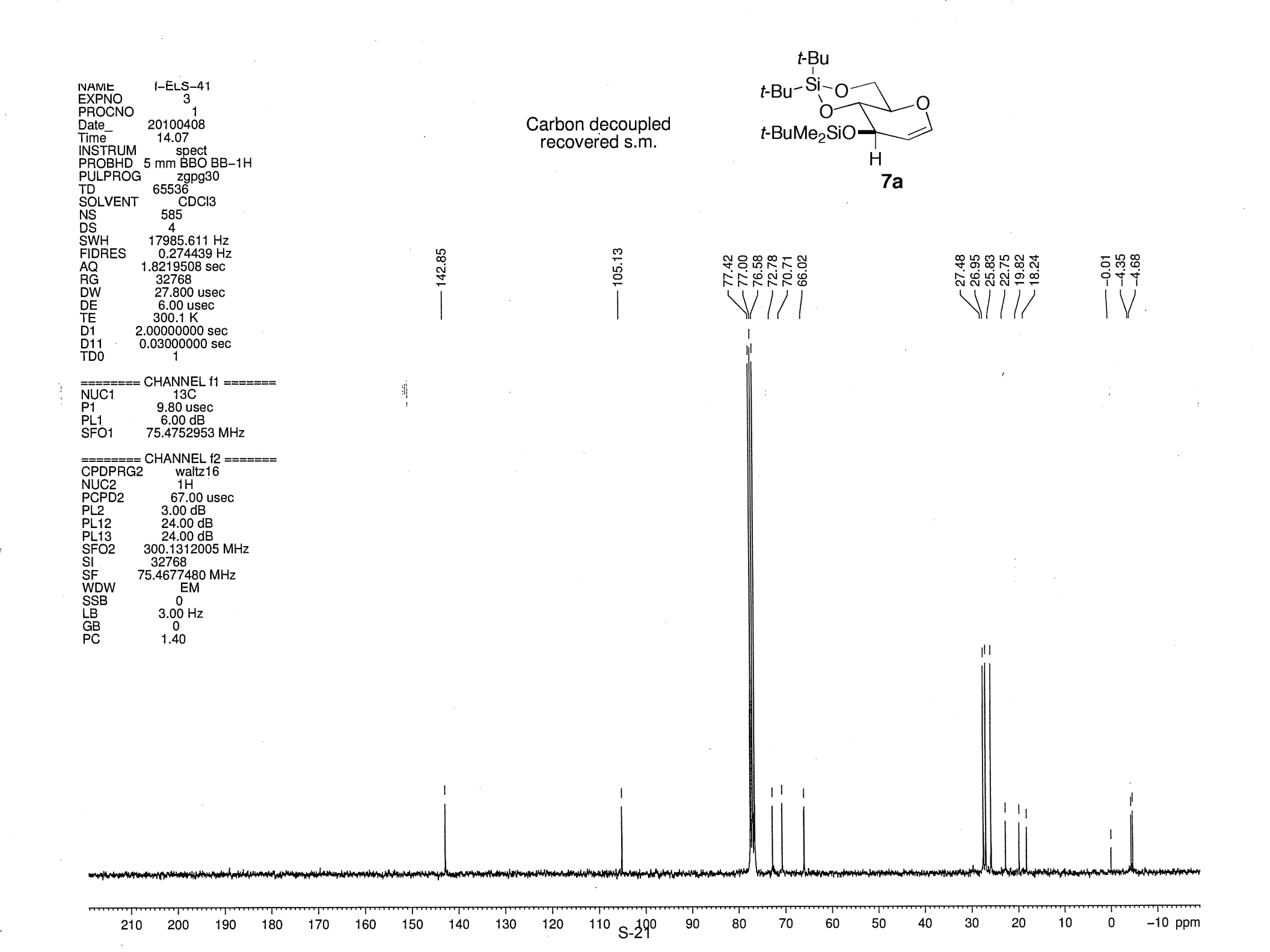


NAME	I–ELS–37
EXPNO	1
PROCNO	1
Date_	20100218
Time	15.15
INSTRUM	spect
PROBHD	5 mm BBO BB–1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	574.7
DW	81.000 usec
DE	6.50 usec
TE	294.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	6.90 usec
PL1	3.00 dB
SFO1	300.1318534 MHz
SI	32768
SF	300.1300056 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

I–ELS–37
1H NMR chromatographed pdt



7a


NAME I-ELS-41
EXPNO 3
PROCNO 1
Date_ 20100408
Time 14.07
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 585
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 300.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.80 usec
PL1 6.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 67.00 usec
PL2 3.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677480 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
Carbon decoupled
recovered s.m.
t-Bu
t-Bu
Si
O
O
O
t-BuMe2SiO
H
7a
142.85
105.13
77.42
77.00
76.58
72.78
70.71
66.02
27.48
26.95
25.83
22.75
19.82
18.24
-0.01
-4.35
-4.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

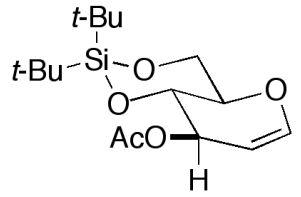
Current Data Parameters
NAME I-VB-23
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050727
Time 15.52
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 294.3 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 6.80 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300033 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

I-VB-23
Chromatographed 3-Acylated D-glucal



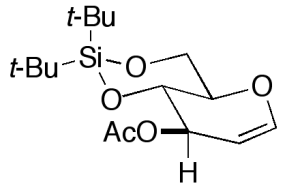
7b

NAME I-VB-23
EXPNO 3
PROCNO 2
Date_ 20050727
Time 20.16
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 18518.518 Hz
FIDRES 0.282570 Hz
AQ 1.7695220 sec
RG 1290.2
DW 27.000 usec
DE 6.00 usec
TE 295.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

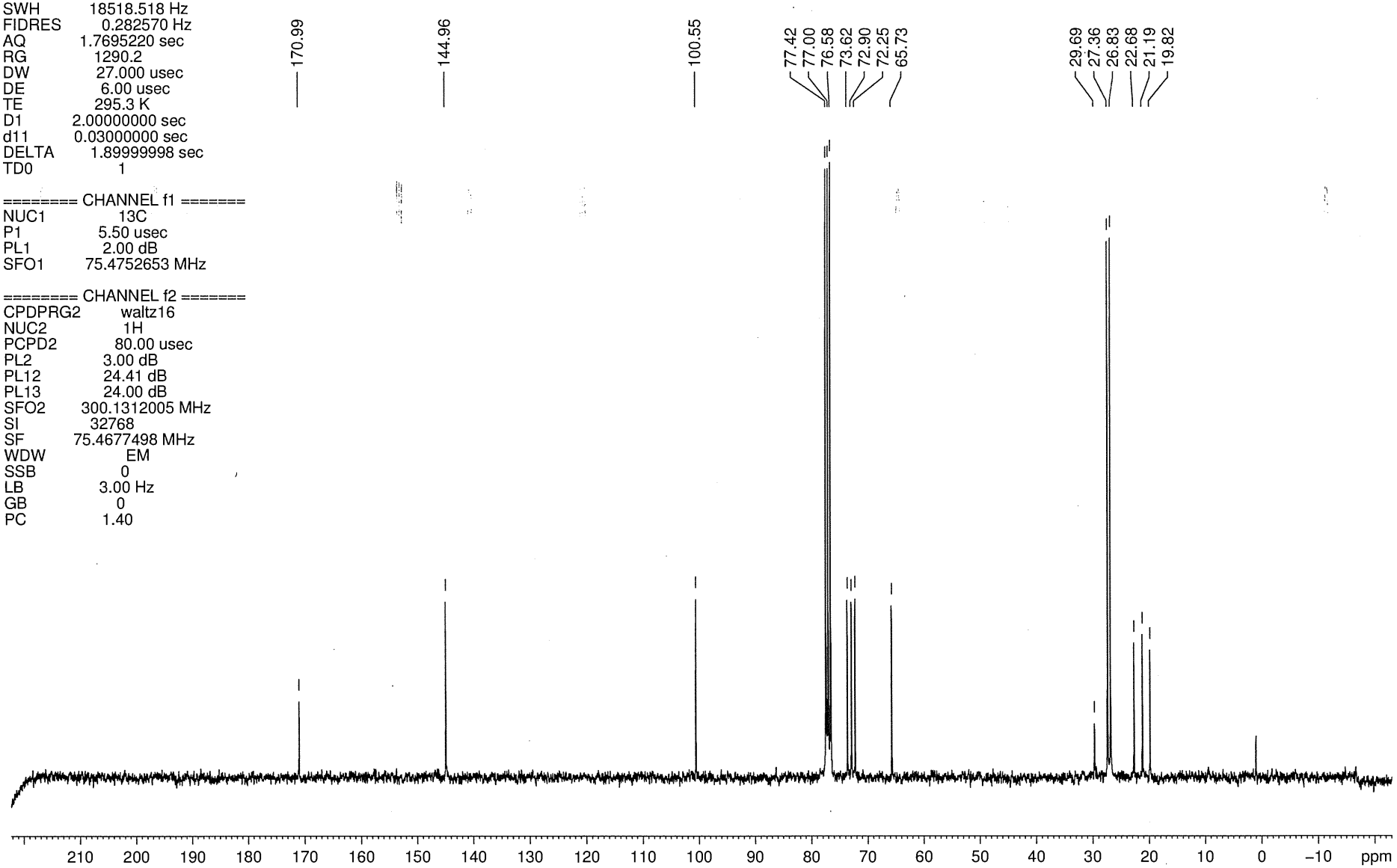
======== CHANNEL f1 =======
NUC1 13C
P1 5.50 usec
PL1 2.00 dB
SFO1 75.4752653 MHz

======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 3.00 dB
PL12 24.41 dB
PL13 24.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677498 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

I-VB-23
Chromatographed 3-Acylated D-glucal CNMR
LB = 3 by CMR



7b



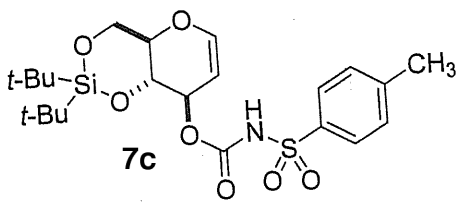
II-LR-3
Silyl-proctected N-tosylated D-glucal 3-carbamate
1H NMR

Current Data Parameters
NAME II-LR-3
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080218
Time 12.54
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 228.1
DW 81.000 usec
DE 6.00 usec
TE 294.4 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 6.56 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300046 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



7c

Current Data Parameters
NAME II-LR-3
EXPNO 8
PROCNO 1

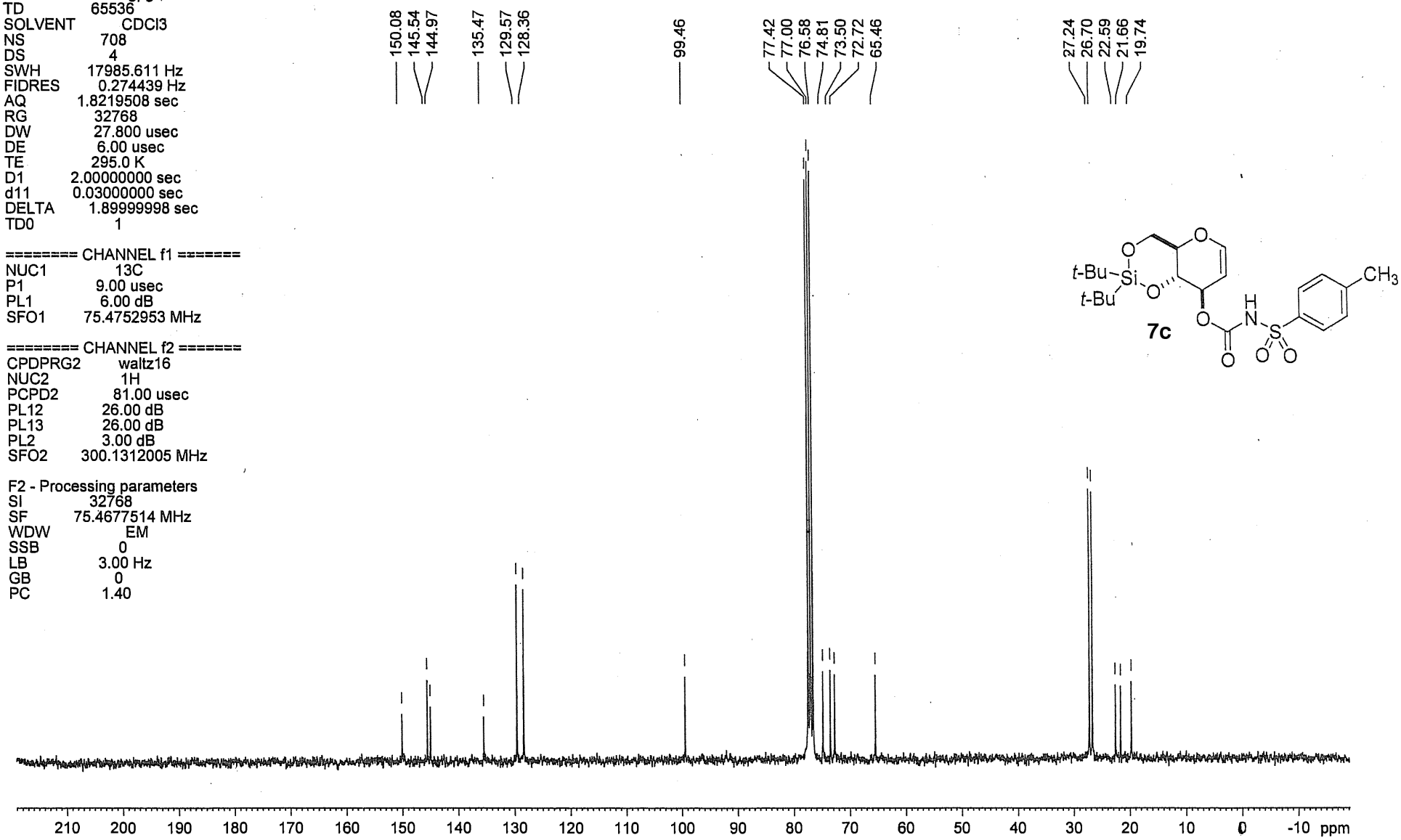
F2 - Acquisition Parameters
Date_ 20080218
Time 13.15
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 708
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 295.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 9.00 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 81.00 usec
PL12 26.00 dB
PL13 26.00 dB
PL2 3.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677514 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

II-LR-3
Silyl-protected N-tosylated D-glucal 3-carbamate
13C NMR



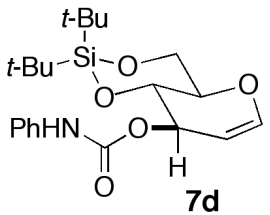
Current Data Parameters
NAME I-VB-31
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050811
Time 13.12
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 90.5
DW 81.000 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 6.80 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

I-VB-31□
Chrom. Product: Phenyl Carbamate



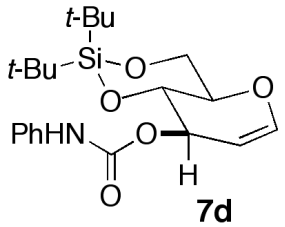
7d

NAME I-VB-31
EXPNO 4
PROCNO 2
Date_ 20050811
Time 18.29
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 18518.518 Hz
FIDRES 0.282570 Hz
AQ 1.7695220 sec
RG 2580.3
DW 27.000 usec
DE 6.00 usec
TE 295.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

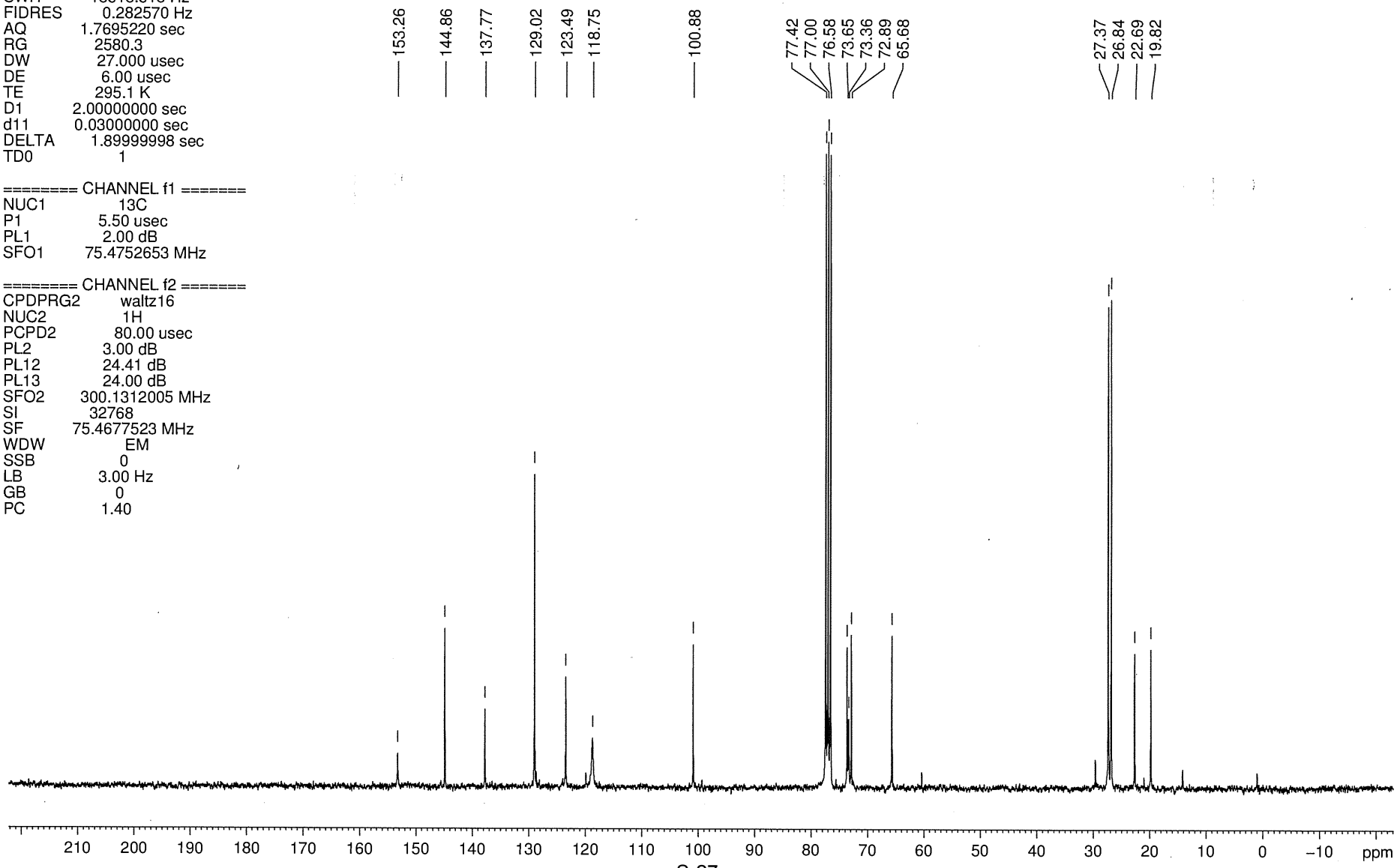
======== CHANNEL f1 =======
NUC1 13C
P1 5.50 usec
PL1 2.00 dB
SFO1 75.4752653 MHz

======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 3.00 dB
PL12 24.41 dB
PL13 24.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677523 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

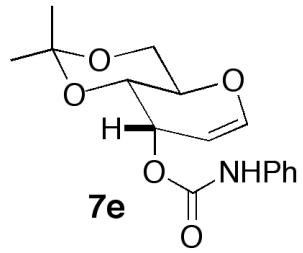
I-VB-31
Chrom Pdt CNMR: Phenyl Carbamate
LB = 3 by CMR



7d



I-AS-95
Rechromatographed by CMR
June 9, 2003



7e

Current Data Parameters

NAME	I-AS-95
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20030609
Time	14.23
INSTRUM	spect
PROBHD	5 mm B80 B8-1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	90.5
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ==========

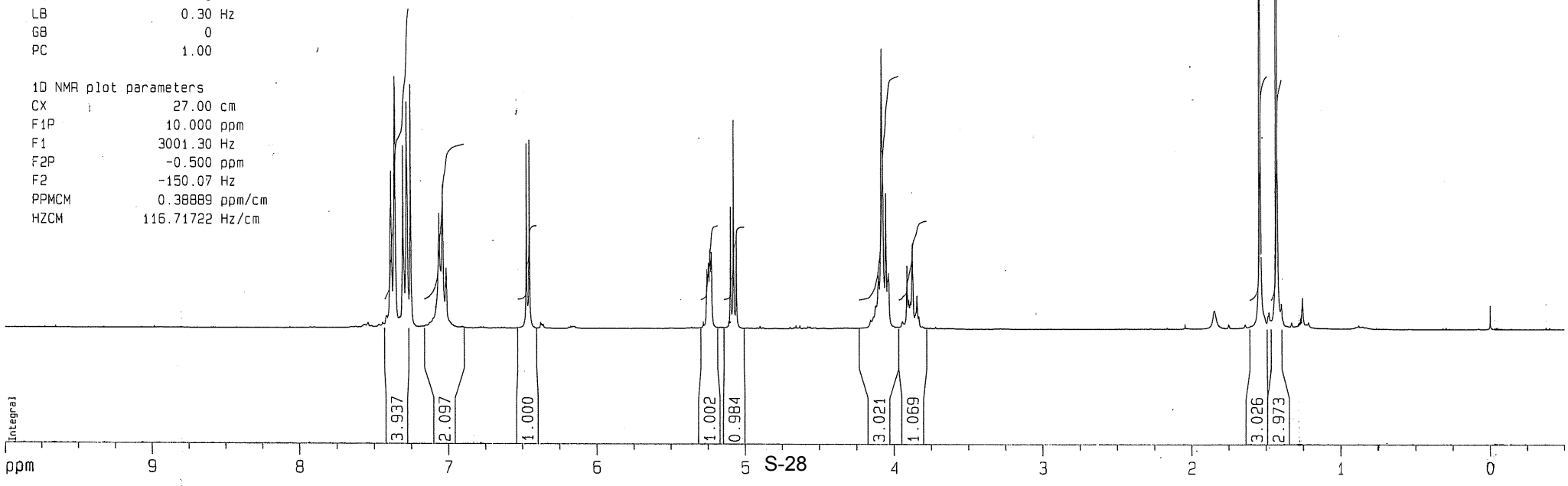
NUC1	1H
P1	21.25 usec
PL1	3.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

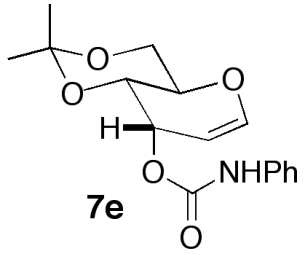
SI	32768
SF	300.1300071 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

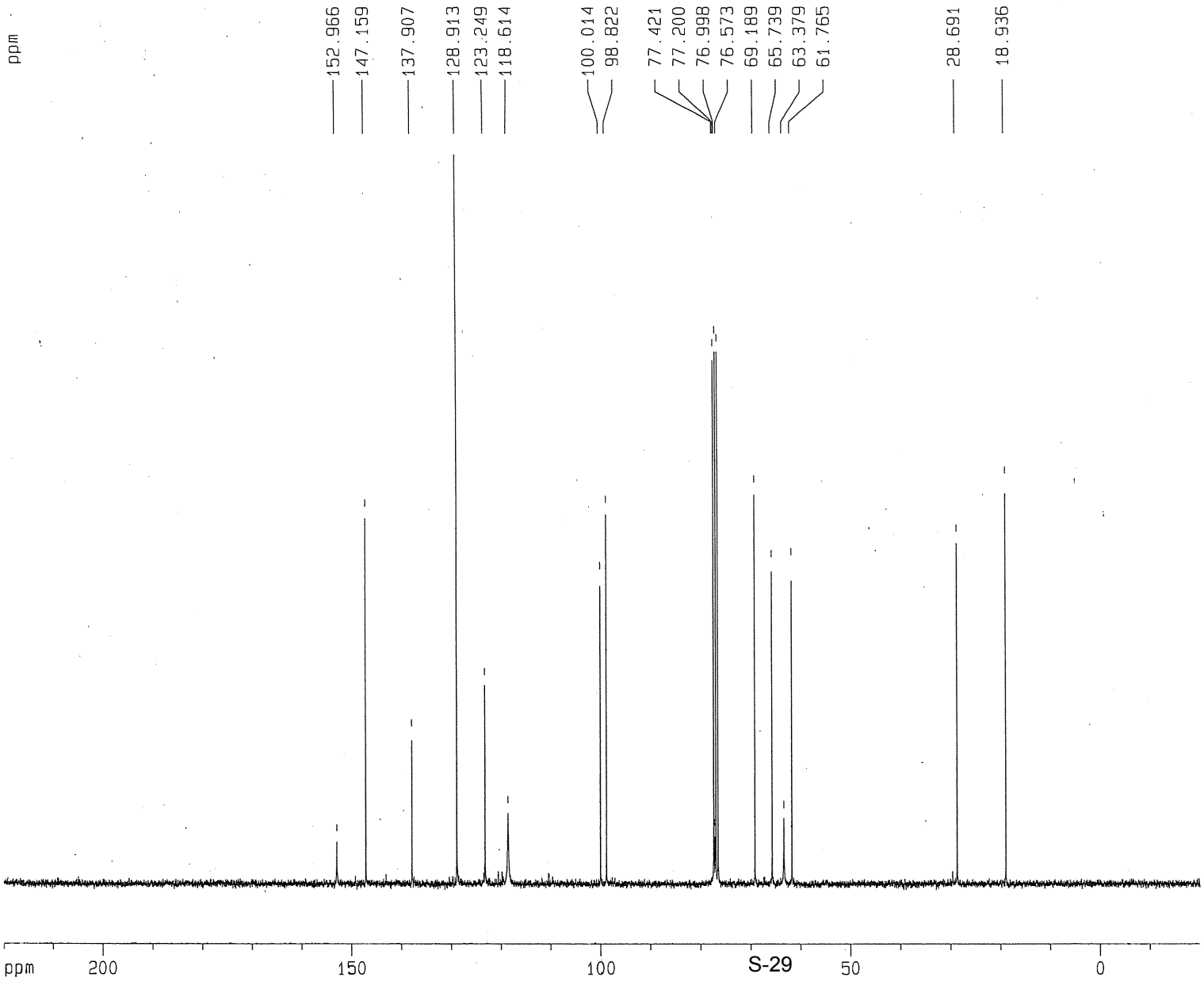
CX	27.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.38889 ppm/cm
HZCM	116.71722 Hz/cm



I-AS-95
Rechromatographed by CMR
13C NMR, June 9, 2003



7e



Current Data Parameters

NAME	I-AS-95
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20030609
Time	15.09
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	18518.518 Hz
FIDRES	0.282570 Hz
AQ	1.7695220 sec
RG	1149.4
DW	27.000 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	23.13 usec
PL1	6.00 dB
SFO1	75.4752653 MHz

========== CHANNEL f2 ==========

CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	3.00 dB
PL12	14.75 dB
PL13	24.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	75.4677561 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

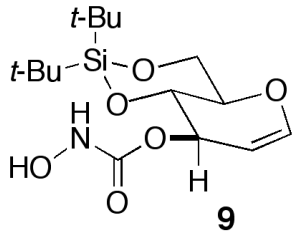
CX	20.00 cm
F1P	220.000 ppm
F1	16602.91 Hz
F2P	-20.000 ppm
F2	-1509.35 Hz
PPMCM	12.00000 ppm/cm
HZCM	905.61310 Hz/cm

NAME	I–BH–7
EXPNO	4
PROCNO	1
Date_	20090617
Time	18.13
INSTRUM	spect
PROBHD	5 mm BBO BB–1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	181
DW	81.000 usec
DE	6.50 usec
TE	294.8 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	7.00 usec
PL1	3.00 dB
SFO1	300.1318534 MHz
SI	32768
SF	300.1300042 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

I–BH–7
Proton (purified)



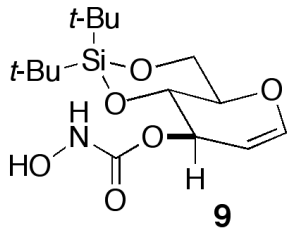
9

NAME I-BH-7
EXPNO 5
PROCNO 1
Date_ 20090617
Time 14.59
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 526
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

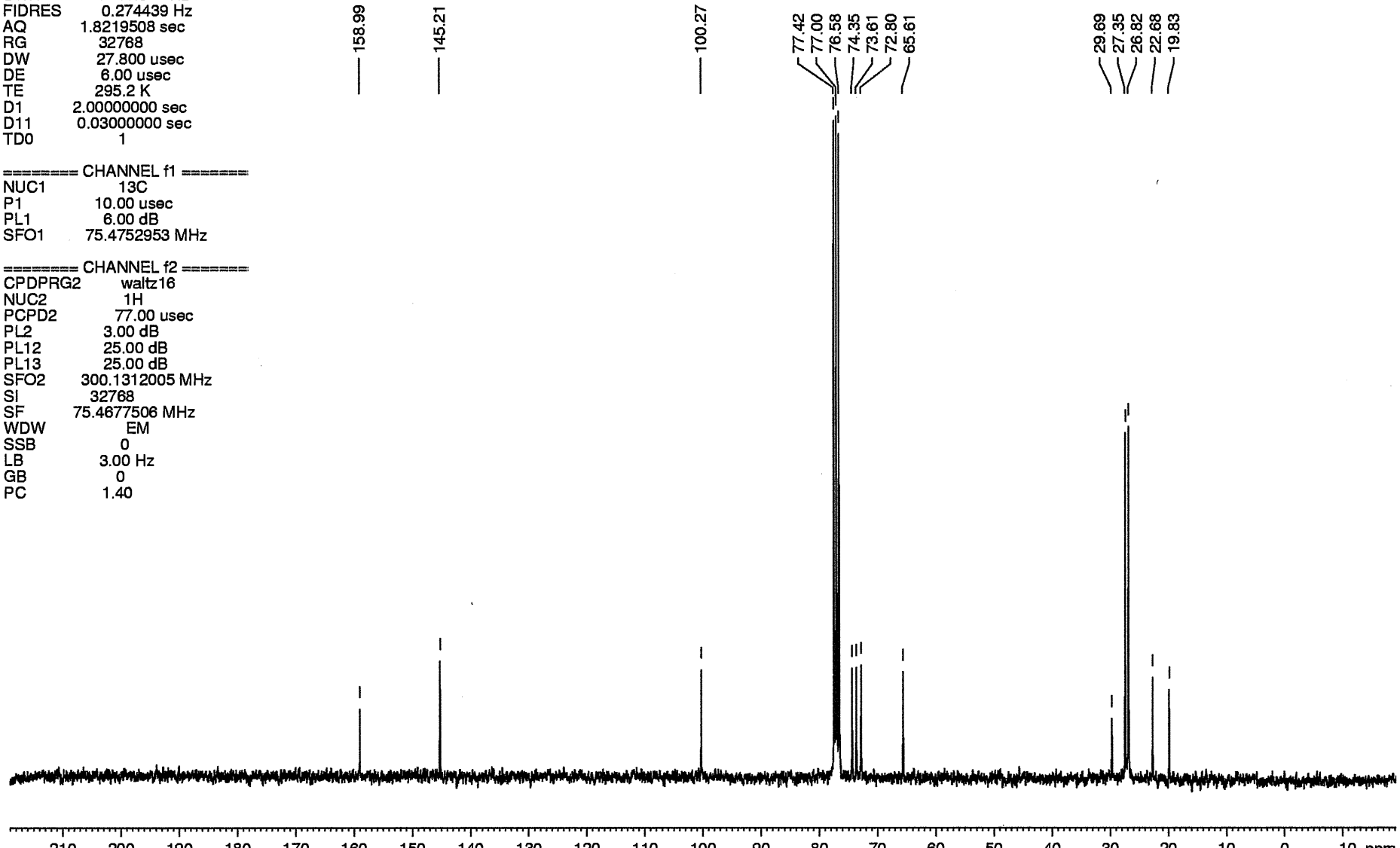
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 77.00 usec
PL2 3.00 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677506 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

I-BH-7
Carbon (purified)



9

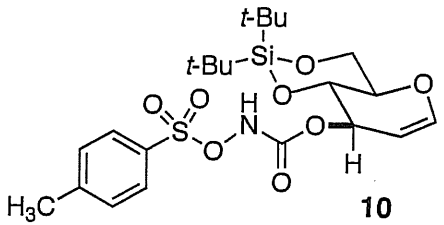


NAME	IV-CMR-107
EXPNO	1
PROCNO	1
Date_	20100910
Time	11.43
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	65536
SOLVENT	CD2Cl2
NS	4
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	71.8
DW	81.000 usec
DE	6.50 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	6.90 usec
PL1	3.00 dB
SFO1	300.1318534 MHz
SI	32768
SF	300.1300103 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

IV-CMR-107
N-Tosyloxycarbamate in CD2Cl2



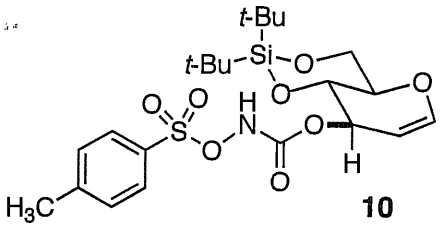
10

NAME IV–CMR–107
EXPNO 2
PROCNO 1
Date_ 20100910
Time 11.48
INSTRUM spect
PROBHD 5 mm BBO BB–1H
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 258
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 10.00 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 68.00 usec
PL2 3.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677034 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

IV–CMR–107
N–Tosyloxycarbamate in CD2Cl2
13C NMR



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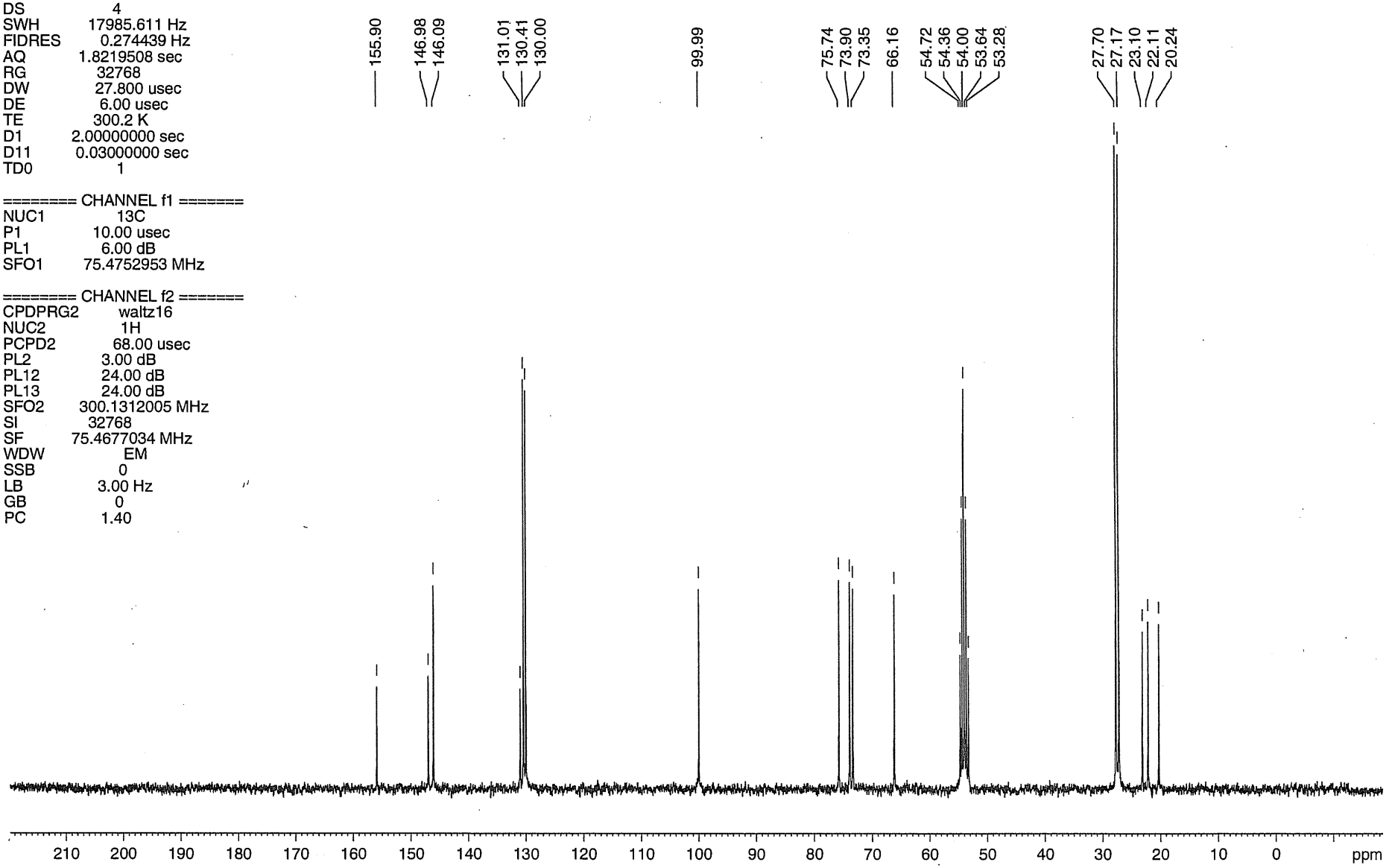
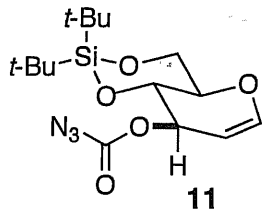


NAME	IV-CMR-151
EXPNO	1
PROCNO	1
Date_	20101118
Time	6.39
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	128
DW	81.000 usec
DE	6.50 usec
TE	300.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	6.90 usec
PL1	3.00 dB
SFO1	300.1318534 MHz
SI	32768
SF	300.1300051 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

IV-CMR-151
F22-23



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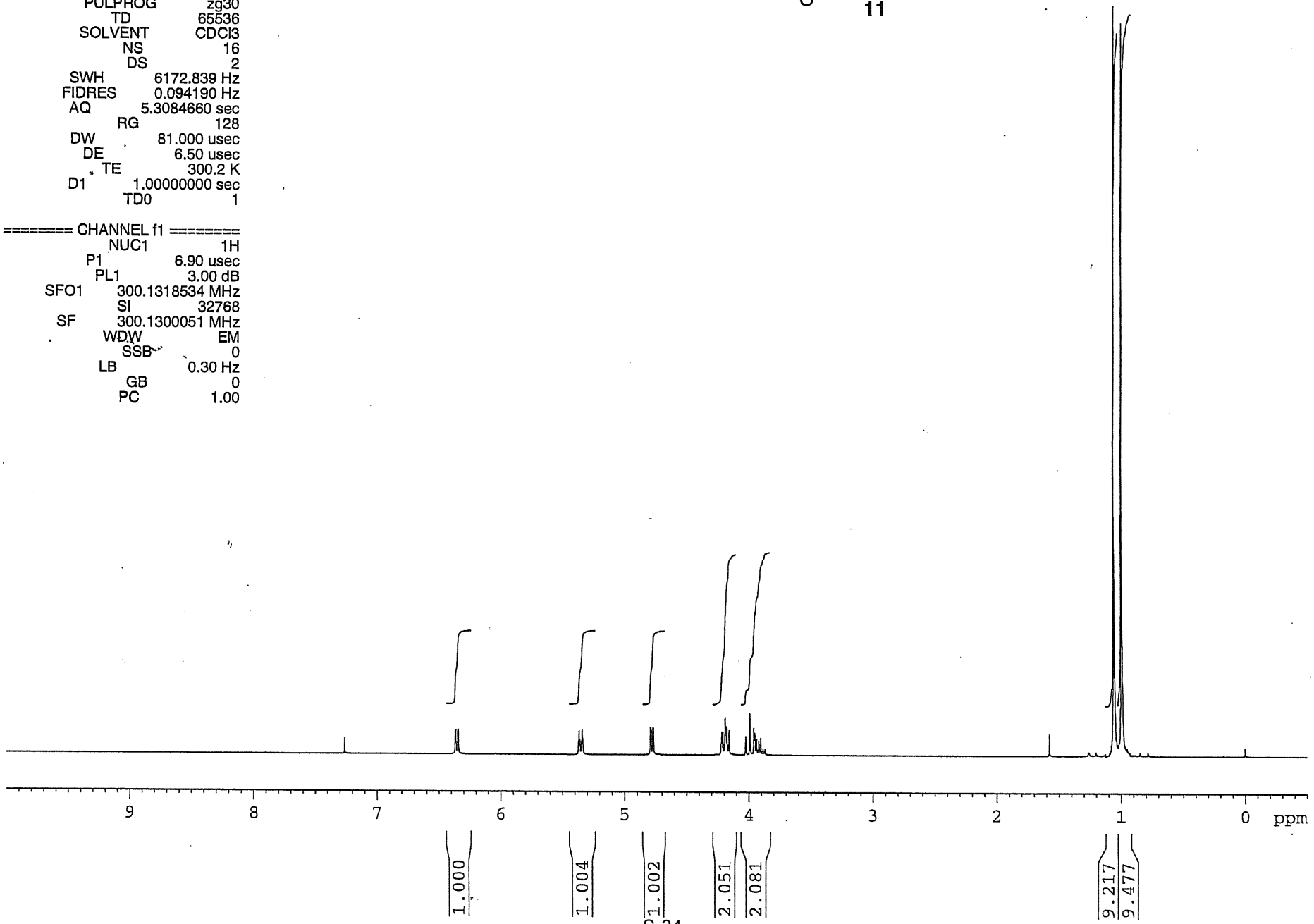
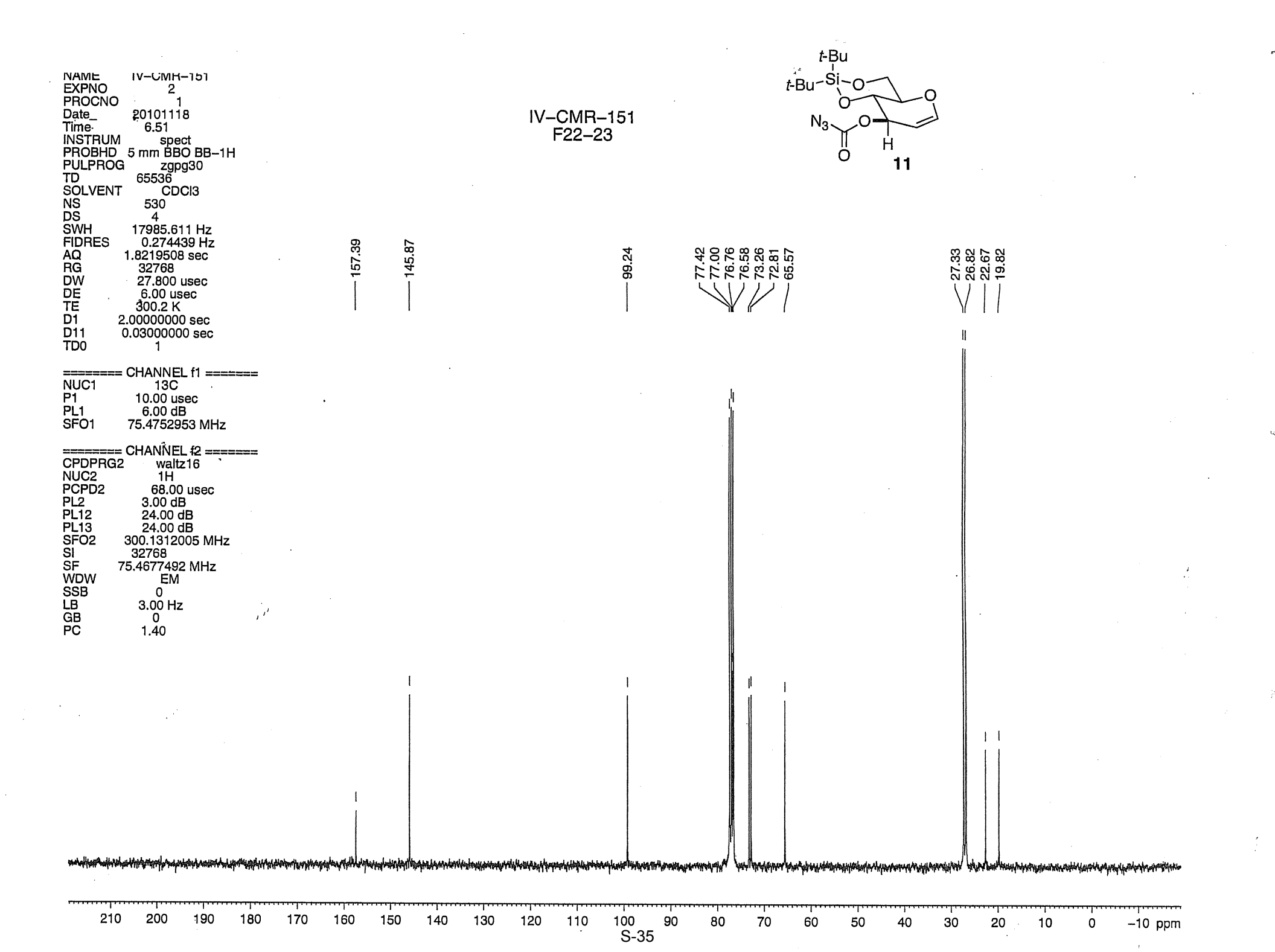


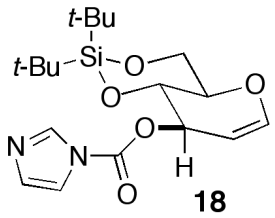

NAME IV-CMR-151
EXPNO 2
PROCNO 1
Date_ 20101118
Time 6.51
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 530
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 68.00 usec
PL2 3.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677492 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
IV-CMR-151
F22-23
t-Bu
t-Bu
Si
O
O
O
N3
O
O
H
11
157.39
145.87
99.24
77.42
77.00
76.76
76.58
73.26
72.81
65.57
27.33
26.82
22.67
19.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

NAME	I-BH-5
EXPNO	1
PROCNO	1
Date_	20090612
Time	19.20
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	574.7
DW	81.000 usec
DE	6.50 usec
TE	673.2 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	7.00 usec
PL1	3.00 dB
SFO1	300.1318534 MHz
SI	32768
SF	300.1300048 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1-BH-5
Proton



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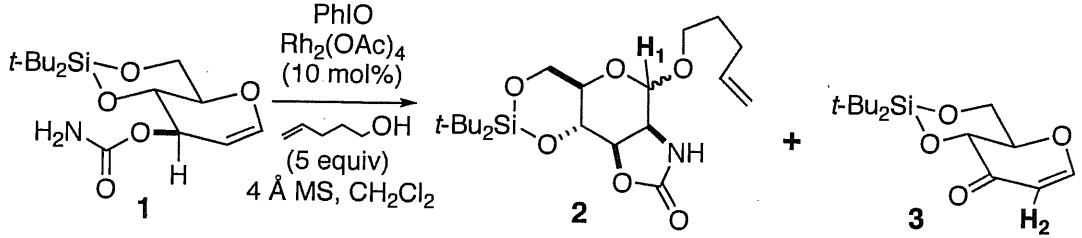
NAME	II–CMR–255
EXPNO	1
PROCNO	3
Date_	20030411
Time	14.11
INSTRUM	spect
PROBHD	5 mm BBO BB–1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	287.4
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

==== CHANNEL f1 ==========	
NUC1	1H
P1	13.10 usec
PL1	3.00 dB
SFO1	300.1318534 MHz
SI	32768
SF	300.1300035 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

II–CMR–255
Crude in CDCl3



1 **2** **3**

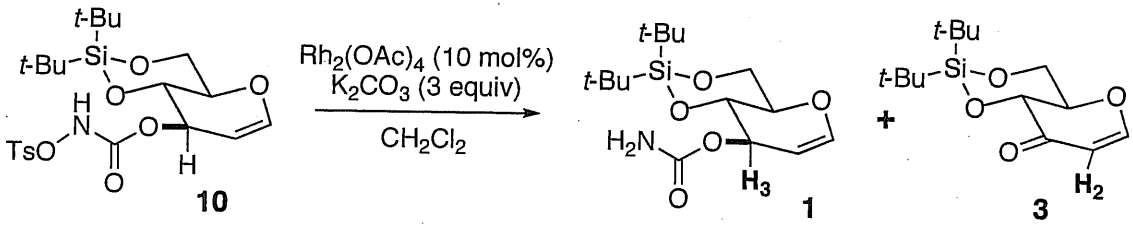
Crude reaction mixture; one of five runs

NAME	IV–CMR–71
EXPNO	1
PROCNO	2
Date_	20100623
Time	12.30
INSTRUM	spect
PROBHD	5 mm BBO BB–1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	64
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	362
DW	81.000 usec
DE	6.50 usec
TE	300.2 K
D1	1.00000000 sec
TD0	1

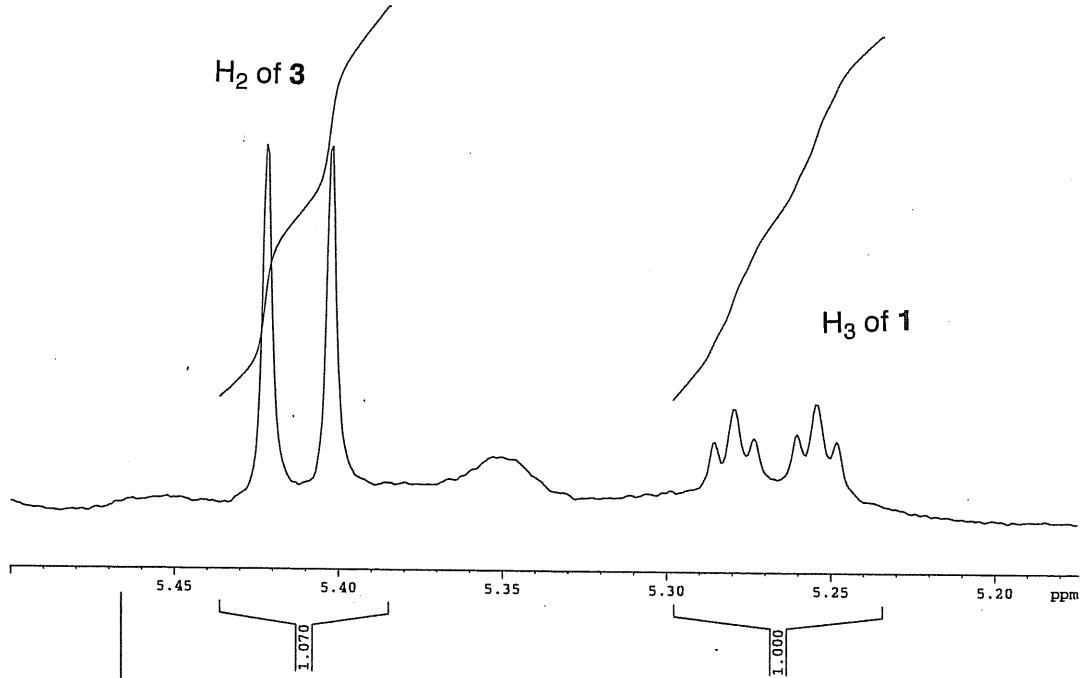
======== CHANNEL f1 ========

NUC1	1H
P1	6.90 usec
PL1	3.00 dB
SFO1	300.1318534 MHz
SI	32768
SF	300.1300054 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

IV–CMR–71
Crude in CDCl3



Crude reaction mixture; one of three runs

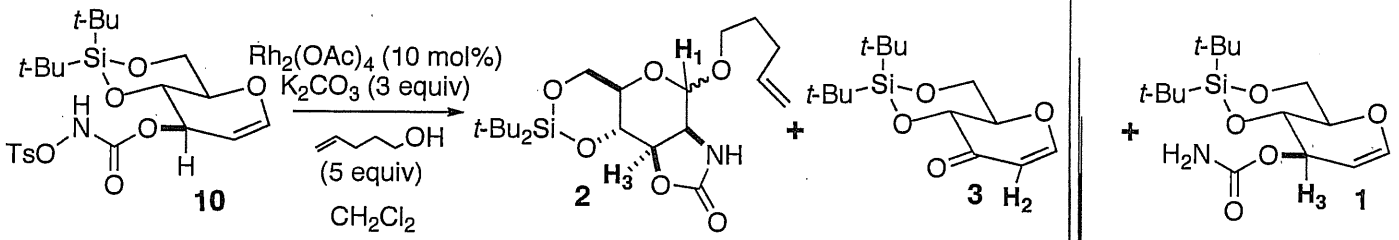


NAME	IV–CMR–67
EXPNO	2
PROCNO	1
Date_	20100623
Time	9.37
INSTRUM	spect
PROBHD	5 mm BBO BB–1H
PULPROG	zg30
TD	65536
SOLVENT	Acetone
NS	64
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	228.1
DW	81.000 usec
DE	6.50 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	6.90 usec
PL1	3.00 dB
SFO1	300.1318534 MHz
SI	32768
SF	300.1300032 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

IV–CMR–67
Crude in Acetone–d6



Crude reaction mixture; one of three runs