Supplementary Information

Trifluoromethanesulfonyloxy-Group-Directed Regioselective (3+2) Cycloadditions of Benzynes for the Synthesis of Functionalized Benzo-Fused Heterocycles

Takashi Ikawa,* Hideki Kaneko, Shigeaki Masuda, Erika Ishitsubo, Hiroaki Tokiwa, Shuji Akai*

Graduate School of Pharmaceutical Sciences, Osaka University, Yamadaoka, Suita, Osaka, Japan

Department of Chemistry, Reseach Center for Smart Molecules, Rikkyo University, Nishi-Ikebukuro, Toshimaku, Tokyo 171-8501, Japan

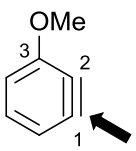
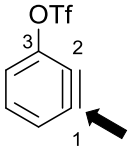
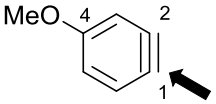
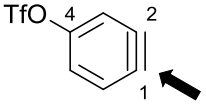
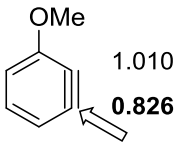
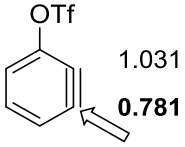
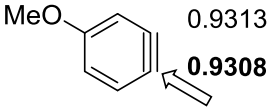
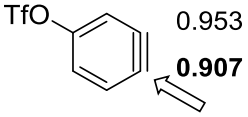
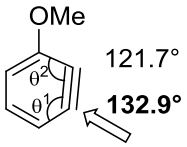
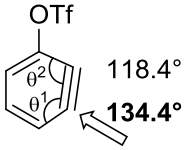
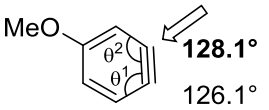
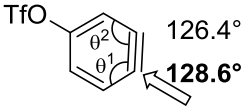
E-mail: ikawa@phs.osaka-u.ac.jp, akai@phs.osaka-u.ac.jp

Table of Contents

Comparison between distortion and NBO analyses of benzynes 3c–f:

The experimental results, electron densities of the reacting π-orbitals (by NBO analysis), and internal angles of C1 and C2 of benzynes **3c**–**f** are summarized in Table S1. The internal angles represent that the C1 position of **3c**–**e** are more electrophilic (for details of the distortion analysis, see Ref 19), which is accountable for the experimental results. However, in regard to **3f**, the distortion analysis indicates that the C2 position is more electrophilic, which has little correspondence with the experimental result. Meanwhile, the electron density analysis is in good agreement with all experimental results.

Table S1. More electrophilic sites of benzynes **3c**–**f** based on experimental results and theoretical analyses.

Table or Ref.	Ref 4g	Table 1, Entry 2	Table 2, Entry 1	Table 2, Entry 3
Compound	**3c**	**3d**	**3f**	**3e**
The more electrophilic site based on experimental results[a]				
Product ratio[b]	>98 : 2	>98 : 2	52 : 48	77 : 23
NBO analysis[c]				
C2–C1	0.184	0.250	0.0005	0.046
Electron densities by NBO analysis[c]				
$\theta^2 - \theta^1$	–11.2°	–16.0°	+2.0°	–2.2°

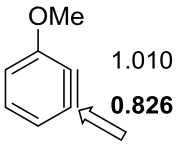
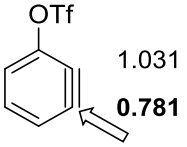
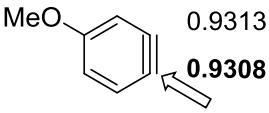
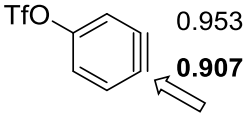
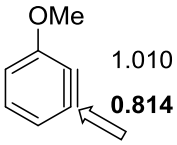
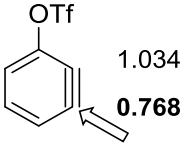
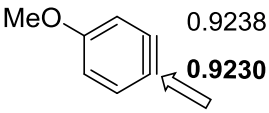
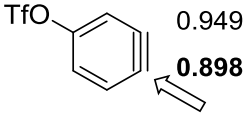
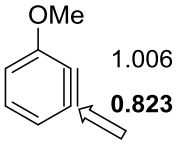
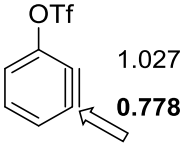
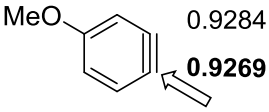
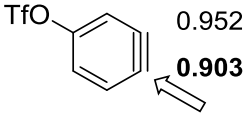
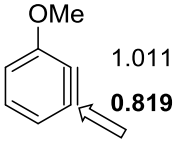
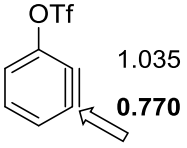
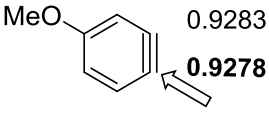
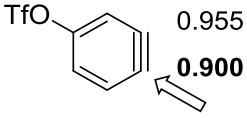
[a]The black filled arrow shows the more nucleophilic site of each benzyne based on the reaction with benzyl azide **2b**. [b]The ratio of two regioisomeric products obtained by the reaction of each benzyne with benzyl azide **2b**. [c]The hollowed arrow shows the theoretically more electrophilic site. The optimized structure was calculated by density functional theory (DFT) calculation and natural bond orbital (NBO) was analyzed by NBO6 [B3LYP/6-31G(d)].

Therefore, we propose that the NBO analysis may be suitable to discuss the reaction mechanism and origin of the regioselectivity more extensively than the distortion analysis, although more examples and theoretical studies are acquired for complete clarification.

Validation of basis-set independency of NBO analyses of benzynes 3c–f:

We have performed validation of the independency for our NBO results by using some DFT methods with more flexible basis sets (B3LYP/6-31G(d), B3LYP/6-311+G(d,p), M06-2X/aug-cc-pVDZ). These results indicate that actual computational levels would hardly affect the results of NBO analysis.

Table S2. Validation of basis set independency of electron densities of benzynes **3c**–**f**.

NLMO[a]//Opt[b]	**3c**	**3d**	**3f**	**3e**
B3LYP/6-31G(d)//B3LYP/6-31G(d)				
C2–C1	0.184	0.250	0.0005	0.046
B3LYP/6-311+G(d,p)//B3LYP/6-31G(d,p)				
C2–C1	0.196	0.266	0.0008	0.051
M06-2X/aug-cc-pVDZ//B3LYP/6-31G(d)				
C2–C1	0.183	0.249	0.0015	0.049
M06-2X/aug-cc-pVDZ//M06-2X/aug-cc-pVDZ				
C2–C1	0.192	0.265	0.0005	0.055

[a]Basis set for Natural Localized Molecular Orbital (NLMO) calculation. [b]Basis set for structure optimization.

Detailed information for reference 14:

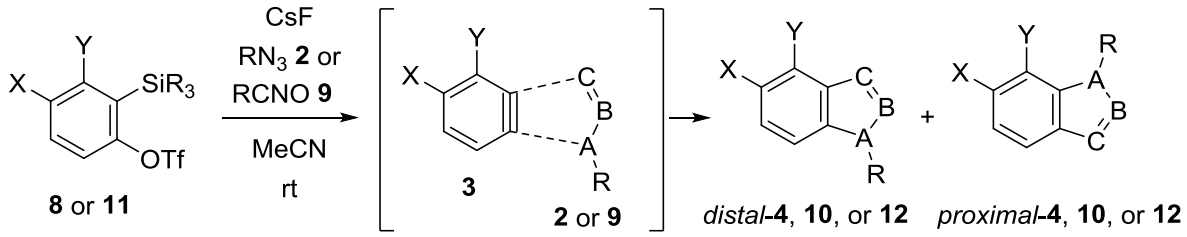
All calculations were performed using the Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

General considerations:

Reagents: All reactions were carried out under an argon or nitrogen atmosphere. A round-bottomed flask containing a stir-bar with a three-way stopcock was used as a reactor. 1.6 and 2.3 M solutions of *n*-BuLi in hexane were purchased from Kanto Chemical. Anhydrous THF, CH_2Cl_2 and MeCN were obtained from Wako Pure Chemical Industries or Kanto Chemical and used without further purification. Anhydrous DMF was purchased from Kanto Chemicals, and purified by Glass Contour solvent dispensing system (Nikko Hansen & Co., Ltd., Osaka, Japan) using two packed columns of activated molecular sieves and an isocyanate column. 4-Methoxyphenyl azide **4a**,[1] 4-nitrophenylmethyl azide **2c**,[2] cyclohexyl azide **2d**,[3] and 2,4,6-trimethylbenzonitrile oxide **9a**[4] were prepared according to the literatures.[5] CsF was dried over a flame under reduced pressure before use. All other reagents were purchased from Wako Pure Chemical Industries, Tokyo Chemical Industry, Aldrich Chemical, and Kishida Chemical and used without further purification. Flash chromatography[6] was performed with Silica gel 60N, spherical neutral (40–50 μm), purchased from Kanto Chemical.

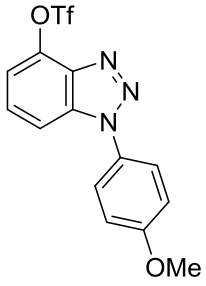
Analytical methods: Elemental analyses were performed by YANACO CHN CORDER MT-5 instrument. Melting points were recorded on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were obtained on a SHIMADZU FTIR-8400S. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-ECA-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) or a JEOL JMN-ECS-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or a JEOL AL-300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) instrument with chemical shifts reported in ppm relative to the residual deuterated solvent. GC spectra were taken on SHIMADZU GC-2010. The mass spectra were recorded on a JEOL JMS-S3000 (MALDI), or a JMS-T100TD (APCI) spectrometer. Yield refers to isolated yields of compounds greater than 95% purity as determined by ^{1}H NMR analysis. ^{1}H NMR and melting points (where applicable) of all known compounds were taken. All new products were further characterized by high resolution mass spectrum (HRMS) or Elemental analysis. Each regiochemistry of representative cycloaddition products (*distal*-**4e**, *distal*-**12c**, and *distal*-**12d**) was confirmed by NOESY or dNOE experiment and that of *proximal*-**10a** was confirmed by NOESY experiment of **16**. The regiochemistries of all other cycloaddition products were predicted by the similarity of ^{1}H NMR data.

Experimental details, NMR and numerical data:



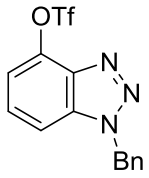
General Procedure I: CsF (3.0 equiv) was flame-dried under reduced pressure in a flask equipped with a three-way stopcock, and back-filled with Ar. Azide **2** or nitrile oxide **9** (3.0 equiv) with a stir bar was loaded into the flask and evacuated and backfilled with Ar (This process was repeated three times). MeCN (One-fifth of its total volume) was added into the flask via a syringe. A solution of precursor **8**, or **11** (1.0 equiv) in anhydrous MeCN (one-fifth of its total volume) was added to the flask through a cannula and washed with MeCN (three-fifth of its total volume). The mixture was stirred at rt for 3 h. H_2O and EtOAc were added to the reaction mixture, and the aqueous phase was extracted thrice with EtOAc. The combined organic phase was washed with a saturated aqueous NaCl solution (brine). The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to ^{1}H NMR analysis for calculating the ratio of the two regioisomers (*distal*- and *proximal*-**4**, **10**, or **12**). The crude product was purified by flash column chromatography on silica gel (hexane, a mixture of hexane and EtOAc, or CH_2Cl_2) to afford *distal*- and *proximal*-**4**, **10**, or **12**.

Reaction of 3-triflyloxybenzyne 3d with azide 2 (Table 1):



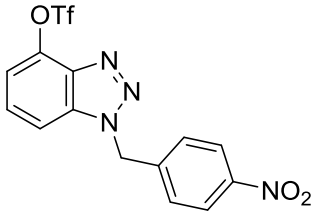
distal-**4d**

1-(4-Methoxyphenyl)-4-(trifluoromethanesulfonyloxy)benzotriazole (*distal*-4d) (Table 1, Entry 1): Following General Procedure I, a mixture of CsF (46 mg, 0.30 mmol), 4-methoxyphenyl azide **2a**[2] (45 mg, 0.30 mmol) and 2-(*tert*-butyldimethylsilyl)-1,3-bis(trifluoromethanesulfonyloxy)benzene **8** (50 mg, 0.10 mmol) was stirred in MeCN (1.0 mL, 0.10 M) for 3 h at rt. The crude product (*distal*-**4d**/*proximal*-**4d** = >98:2, determined by 300 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 3:1) to provide the titled compound, *distal*-**4d** (18 mg, 48%) as a colourless solid. Mp: 109–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.92 (3 H, s), 7.13 (2 H, d, *J* = 8.0 Hz), 7.36 (1 H, d, *J* = 7.0 Hz), 7.54–7.70 (4 H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.7, 110.9, 115.1, 116.5 118.8 (q, *J* = 318 Hz), 124.9, 128.3, 129.1, 135.2, 139.0, 139.6, 160.3. ^{19}F NMR (280MHz, $CDCl_3$) δ: –72.4. IR (neat): 1423 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{11}N_3O_4F_3S$ $[M+H]^+$: 374.0417, found 374.0416.



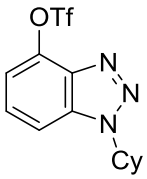
distal-**4e**

1-Benzyl-4-(trifluoromethanesulfonyloxy)benzotriazole (*distal*-4e) (Table 1, Entry 2): Following General Procedure I, a mixture of CsF (46 mg, 0.30 mmol), benzyl azide **2b** (37 μL, 0.30 mmol) and 2-(*tert*-butyldimethylsilyl)-1,3-bis(trifluoromethanesulfonyloxy)benzene **8** (50 mg, 0.10 mmol) was stirred in MeCN (1.0 mL) for 3 h at rt. The crude product (*distal*-**4e**/*proximal*-**4e** = >98:2, determined by 300 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 4:1) to provide the titled compound, *distal*-**4e** (26 mg, 74%) as a colourless solid, and its regiochemistry was determined by dNOE experiments. Mp: 84–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.86 (2 H, s), 7.25–7.44 (8 H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 52.8, 110.4, 116.2, 118.8 (q, *J* = 318 Hz), 127.7, 127.7, 128.8, 129.1, 133.8, 135.3, 139.1, 139.6. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –72.6. IR (neat): 1427 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{11}N_3O_3F_3S$ $[M+H]^+$: 358.0468, found 358.0471.



distal-**4f**

1-(4-Nitrobenzyl)-4-(trifluoromethanesulfonyloxy)benzotriazole (*distal*-4f) (Table 1, Entry 3): Following General Procedure I, a mixture of CsF (46 mg, 0.30 mmol), 4-nitrobenzyl azide **2c** (53 mg, 0.30 mmol), and 2-(*tert*-butyldimethylsilyl)-1,3-bis(trifluoromethanesulfonyloxy)benzene **8** (50 mg, 0.10 mmol) was stirred in MeCN (1.0 mL) for 3 h at rt. The crude product (*distal*-**4f**/*proximal*-**4f** = >98:2, determined by 500 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to provide the titled compound, *distal*-**4f** (28 mg, 70%) as a colourless solid. Mp: 106–109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.98 (2 H, s), 7.32 (1 H, d, *J* = 4.0 Hz), 7.34–7.45 (3 H, m), 7.51 (1 H, t, *J* = 7.5 Hz), 8.21 (2 H, d, *J* = 9.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 51.6, 109.7, 116.7, 118.8 (q, *J* = 320 Hz), 124.4, 128.4, 128.5, 135.1, 139.2, 139.8, 140.8, 148.1. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –72.5. IR (neat): 1424, 1522 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{10}N_4O_5F_3S$ $[M+H]^+$: 403.0319, found 403.0321.

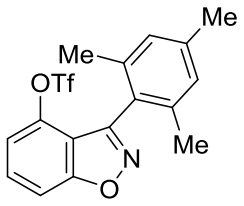


distal-**4g**

1-Cyclohexyl-4-(trifluoromethanesulfonyloxy)benzotriazole (*distal*-4g) (Table 1, Entry 4): Following General Procedure I, a mixture of CsF (46 mg, 0.30 mmol), cyclohexyl azide **2d**[2] (38 mg, 0.30 mmol), and 2-(*tert*-butyldimethylsilyl)-1,3-bis(trifluoromethanesulfonyloxy)benzene **8** (50 mg, 0.10 mmol) was stirred in MeCN (1.0 mL) for 3 h at rt. The crude product (*distal*-**4g**/*proximal*-**4g** = >98:2, determined by 500 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 6:1) to provide the titled compound, *distal*-**4g** (22 mg, 63%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.32–1.61 (4 H, m), 1.81–2.20 (6 H, m), 4.62–4.73 (1 H, m), 7.28 (1 H, d, *J* = 8.0 Hz), 7.49 (1 H, t, *J* = 8.0 Hz), 7.61 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ:

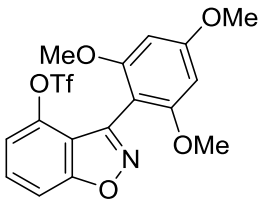
25.1, 25.4, 32.5, 59.7, 110.4, 116.0, 118.8 (q, J = 320 Hz), 127.0, 134.8, 138.8, 139.7. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –72.6. IR (neat): 1427 cm^{-1}. HRMS (MALDI) Calcd for $C_{13}H_{15}N_3O_3F_3S$ $[M+H]^+$: 350.0781, found 350.0783.

Reaction of 3-triflyloxybenzyne 3d with nitrile oxide 9 (Scheme 3):



proximal-**10a**

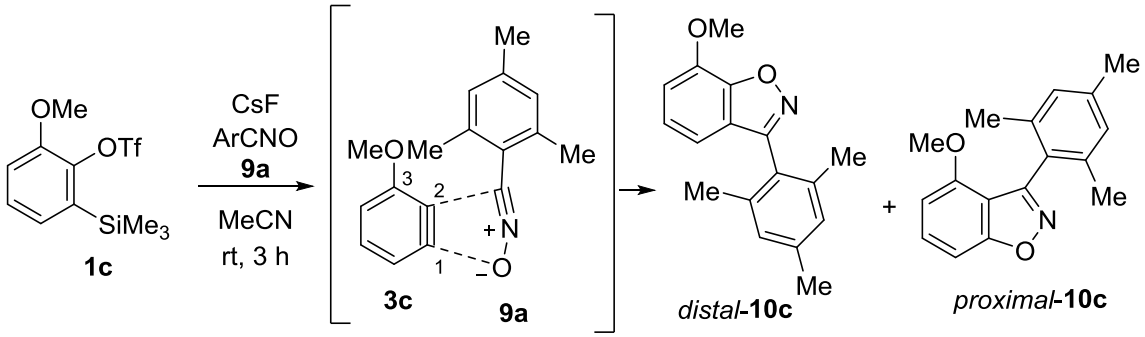
3-(2,4,6-Trimethylphenyl)-4-(trifluoromethanesulfonyloxy)-1,2-benzisoxazole (*proximal*-10a) (Scheme 3): Following General Procedure I, a mixture of CsF (30 mg, 0.20 mmol), 2,4,6-trimethylphenylnitrileoxide **9a** (48 mg, 0.30 mmol), and 2-(*tert*-butyldimethylsilyl)-1,3-bis(trifluoromethanesulfonyloxy)benzene **8** (50 mg, 0.10 mmol) was stirred in MeCN (2.0 mL) for 3 h at rt. The crude product (*distal*-**10a**/*proximal*-**10a** = 2:>98, determined by 500 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 5:2) to provide the titled compound, *proximal*-**10a** (30 mg, 77%) as a colourless solid. Mp: 102–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.12 (6 H, s), 2.38 (3 H, s), 7.03 (2 H, s), 7.23 (1 H, d, J = 8.5 Hz), 7.65 (1 H, t, J = 8.5 Hz), 7.72 (1 H, d, J = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 19.9, 21.1, 110.6, 115.7, 116.1, 118.4 (q, J = 320 Hz), 122.8, 128.5, 130.9, 137.7, 139.9, 142.0, 155.5, 164.9. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –73.2. IR (neat): 1435, 1626 cm^{-1}. HRMS (MALDI) Calcd for $C_{17}H_{15}NO_4F_3S$ $[M+H]^+$: 386.0668, found 386.0668.



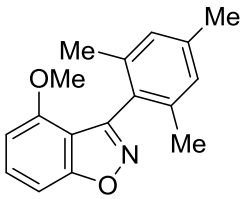
proximal-**10b**

3-(2,4,6-Trimethoxyl)phenyl-4-(trifluoromethanesulfonyloxy)-1,2-benzisoxazole (*proximal*-10b) (Scheme 3): Following General Procedure I, a mixture of CsF (30 mg, 0.20 mmol), 2,4,6-trimethoxyphenylnitrileoxide **9b** (63 mg, 0.30 mmol), and 2-(*tert*-butyldimethylsilyl)-1,3-bis(trifluoromethanesulfonyloxy)benzene **8** (50 mg, 0.10 mmol) was stirred in MeCN (2.0 mL) for 3 h at rt. The crude product (*distal*-**10b**/*proximal*-**10b** = 2:>98, determined by 500 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to provide the titled compound, *proximal*-**10b** (30 mg, 69%) as a colourless solid. Mp: 108–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.73 (6 H, s), 3.87 (3 H, s), 6.25 (2 H, s), 7.16 (1 H, d, *J* = 8.5 Hz), 7.55 (1 H, t, *J* = 8.5 Hz), 7.62 (1 H, d, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.4, 55.7, 90.8, 97.0, 110.2, 115.2, 116.6, 118.4 (q, *J* = 318 Hz), 130.0, 142.4, 150.6, 159.8, 163.5, 164.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ: –73.3. IR (neat): 1340, 1429 cm^{-1}. HRMS (MALDI) Calcd for $C_{17}H_{15}NO_7F_3S$ $[M+H]^+$: 434.0516, found 434.0521.

Reaction of 3-methoxybenzyne 3c with nitrile oxide 9a:



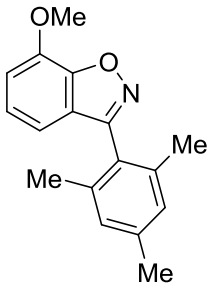
distal-**10c**:*proximal*-**10c** = 15:85 (57%)



proximal-**10c**

3-(2,4,6-Trimethyl)phenyl-4-(methoxy)-1,2-benzisoxazole (*proximal*-10c): Following General Procedure I, a mixture of CsF (93 mg, 0.61 mmol), 2,4,6-trimetylphenylnitrileoxide **9a** (74 mg, 0.46

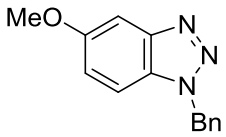
mmol), and 1-methoxy-2-(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene[7] (50 mg, 0.15 mmol) was stirred in MeCN (1.5 mL) for 3 h at rt. The crude product (*distal*-**10c**/*proximal*-**10c** = 15:85, determined by 500 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 15:1) to provide the titled compound, *proximal*-**10c** (23 mg, 57%) as a colourless solid. Mp: 140–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.10 (6 H, s), 2.35 (3 H, s), 3.73 (3 H, s), 6.62 (1 H, d, *J* = 8.5 Hz), 6.95 (2 H, s), 7.22 (1 H, d, *J* = 8.5 Hz), 7.48 (1 H, t, *J* = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.0, 21.2, 55.7, 102.6, 103.3, 112.4, 125.6, 128.0, 131.3, 137.4, 138.5, 155.1, 156.5, 165.1. IR (neat): 1283, 1360, 1501 cm^{-1}. HRMS (MALDI) Calcd for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332, found 268.1331.



distal-**10c**

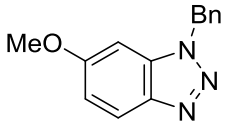
3-(2,4,6-Trimethyl)phenyl-7-(methoxy)-1,2-benzisoxazole (*distal*-10c) was obtained from the above-mentioned reaction mixture by column chromatography on silica gel (3.8 mg, 9.5%) as a colourless solid. Mp: 116–119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.08 (6 H, s), 2.36 (3 H, s), 4.10 (3 H, s), 6.94 (1 H, d, *J* = 7.5 Hz), 6.99 (2 H, s), 7.01 (1 H, d, *J* = 7.5 Hz), 7.20 (1 H, t, *J* = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.0, 21.2, 56.5, 111.0, 113.4, 124.0, 124.1, 124.7, 128.4, 137.7, 139.2, 144.7, 153.7, 158.1. IR (neat): 1273, 1371, 1505 cm^{-1}. HRMS (MALDI) Calcd for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332, found 268.1328.

Reaction of 4-substituted benzyne 3e–g with azide 2b (Table 2):



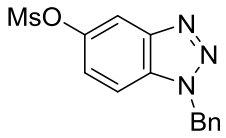
distal-**12a**

1-Benzyl-5-methoxybenzotriazole (*distal*-12a) (Table 2, Entry 1): Following General Procedure I, a mixture of CsF (91 mg, 0.60 mmol), benzyl azide **2b** (56 μL, 0.45 mmol) and 1-methoxy-4-(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene **11a** (50 mg, 0.15 mmol) was stirred in MeCN (1.5 mL, 0.10 M) for 3 h at rt. The crude product (*distal*-**12a**/*proximal*-**12a** = 52:48, determined by 500 MHz ^{1}H NMR analysis) was purified by preparative TLC (toluene/EtOAc = 5:1) to provide the titled compound, *distal*-**12a** (15 mg, 42%) as a colourless solid. Mp: 135–137 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.87 (3 H, s), 5.80 (2 H, s), 7.05 (1 H, dd, *J* = 2.0, 9.0 Hz), 7.19–7.37 (7 H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 52.4, 55.7, 98.7, 110.4, 120.3, 127.5, 128.3, 128.5, 129.0, 134.7, 147.3, 157.2. IR (neat): 1205 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{14}N_3O$ $[M+H]^+$: 240.1131, found 240.1131.



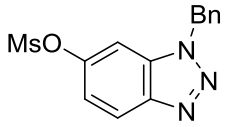
proximal-**12a**

1-Benzyl-6-methoxybenzotriazole (*proximal*-12a) (Table 2, Entry 1) was obtained from the above-mentioned reaction mixture by preparative TLC (14 mg, 38%) as a colourless solid. Mp: 91–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.72 (3 H, s), 5.72 (2 H, s), 6.53 (1 H, d, *J* = 2.0 Hz), 6.91 (1 H, dd, *J* = 2.0, 9.0 Hz), 7.18–7.28 (5 H, m), 7.85 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 51.9, 55.7, 90.0, 116.1, 120.7, 127.4, 128.4, 129.0, 133.9, 134.8, 141.7, 159.9. IR (neat): 1232 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{14}N_3O$ $[M+H]^+$: 240.1131, found 240.1134.



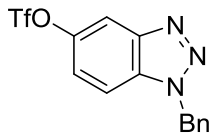
distal-**12b**

1-Benzyl-5-(methanesulfonyloxy)benzotriazole (*distal*-12b) (Table 2, Entry 2): Following General Procedure I, a mixture of CsF (58 mg, 0.38 mmol), benzyl azide **2b** (47 μL, 0.38 mmol) and 1-methanesulfonyloxy-4-(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene **11b** (50 mg, 0.13 mmol) was stirred in MeCN (1.3 mL) for 3 h at rt. The crude product (*distal*-**12b**/*proximal*-**12b** = 72:28, determined by 300 MHz ^{1}H NMR analysis) was purified by preparative TLC (only CH_2Cl_2) to provide the titled compound, *distal*-**12b** (18 mg, 47%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.19 (3 H, s), 5.86 (2 H, s), 7.27–7.37 (7 H, m), 7.97 (1 H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 37.4, 52.7, 111.0, 112.9, 123.0, 127.6, 128.8, 129.2, 131.6, 134.1, 145.4, 146.3. IR (neat): 1364 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{14}N_3O_3S$ $[M+H]^+$: 304.0750, found 304.0756.



proximal-**12b**

1-Benzyl-6-(methanesulfonyloxy)benzotriazole (*proximal*-12b) (Table 2, Entry 2) was obtained from the above-mentioned reaction mixture by preparative TLC (7.0 mg, 18%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.14 (3 H, s), 5.85 (2 H, s), 7.24–7.38 (7 H, m), 8.11 (2 H, d, J = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 37.7, 52.6, 103.6, 119.0, 121.6, 127.7, 128.8, 129.2, 132.9, 134.0, 144.8, 148.0. IR (neat): 1364 cm^{-1}. HRMS (MALDI) Calcd for$C_{14}H_{14}N_3O_3S$ $[M+H]^+$: 304.0750, found 304.0745.

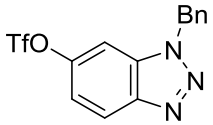


distal-**12c**

1-Benzyl-5-(trifluoromethanesulfonyloxy)benzotriazole (*distal*-12c) (Table 2, Entries 3 and 4): For Entry 3: Following General Procedure I, a mixture of CsF (50 mg, 0.33 mmol), benzyl azide **2b**

(41 μL, 0.33 mmol), and 1,4-bis(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene **11c** (50 mg, 0.11 mmol) was stirred in MeCN (1.0 mL) for 3 h at rt. The crude product (*distal*-**12c**/*proximal*-**12c** = 77:23, determined by 500 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/Et_2O = 5:3) to provide the titled compound, *distal*-**12c** (14 mg, 36%) as a colourless solid, and its regiochemistry was determined by dNOE experiments. Mp: 108–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.82 (2 H, t, *J* = 7.5 Hz), 7.24–7.40 (7 H, m), 7.93 (1 H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 52.7, 111.3, 112.7, 118.6 (q, *J* = 318 Hz), 121.5, 127.6, 128.8, 129.1, 131.8, 133.8, 145.7, 145.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ: –72.5. IR (neat): 1421 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{11}N_3O_3F_3S$ $[M+H]^+$: 358.0468, found 358.0470.

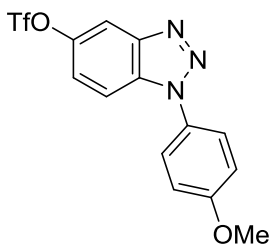
For Entry 4: Following General Procedure I, a mixture of CsF (50 mg, 0.33 mmol), benzyl azide **2b** (0.16 mL, 1.3 mmol), and 1,4-bis(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene **11c** (50 mg, 0.11 mmol) was stirred in MeCN (1.0 mL) for 3 h at rt. The crude product (*distal*-**12c**/*proximal*-**12c** = 75:25, determined by 500 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/Et_2O = 5:3) to provide the titled compound, *distal*-**12c** (18 mg, 45%) as a colourless solid



proximal-**12c**

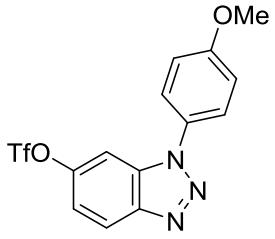
1-Benzyl-6-(trifluoromethanesulfonyloxy)benzotriazole (*proximal*-12c) (Table 2, Entries 3 and 4) was obtained from the above-mentioned reaction mixture by column chromatography on silica gel (4.3 mg, 11%, Entry 3; 5.8 mg, 15%, Entry 4) as a colourless solid. Mp: 88–90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.86 (2 H, s), 7.23–7.39 (7 H, m), 8.14 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 52.8, 103.3, 118.0, 118.6 (q, *J* = 318 Hz), 122.0, 127.7, 129.0, 129.3, 132.6, 133.6, 145.1, 148.2. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –72.4. IR (neat): 1219, 1427 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{11}N_3O_3F_3S$ $[M+H]^+$: 358.0468, found 358.0468.

Reaction of 4-triflyloxybenzyne 3e with azide 2 (Table 3):



distal-**12d**

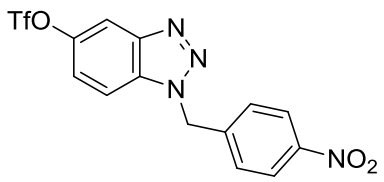
1-(4-Methoxyphenyl)-5-(trifluoromethanesulfonyloxy)benzotriazole (*distal*-12d) (Table 3, Entry 1): Following General Procedure I, a mixture of CsF (50 mg, 0.33 mmol), 4-methoxyphenyl azide **2a** (0.19 g, 1.3 mmol), and 1,4-bis(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene **11c** (50 mg, 0.11 mmol) was stirred in MeCN (1.0 mL) for 3 h at rt. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4:1) to provide the titled compound, *distal*-**12d** (19 mg, 46%) as a colourless solid and its regiochemistry was determined by NOESY spectra. Mp: 94–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.91 (3 H, s), 7.12 (2 H, d, *J* = 7.5 Hz), 7.45 (1 H, d, *J* = 9.0 Hz), 7.62 (2 H, d, *J* = 7.5 Hz), 7.73 (1 H, d, *J* = 9.0 Hz), 8.05 (1 H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.7, 111.8, 112.9, 115.1, 118.7 (q, *J* = 318 Hz), 122.1, 124.7, 129.1, 131.8, 145.8, 145.9, 160.3. ^{19}F NMR (280MHz, $CDCl_3$) δ: –72.4. IR (neat): 1209, 1427 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{11}N_3O_4FS$ $[M+H]^+$: 374.0417, found 374.0417.



proximal-**12d**

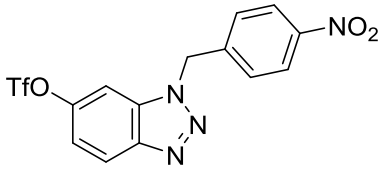
1-(4-Methoxyphenyl)-6-(trifluoromethanesulfonyloxy)benzotriazole (*proximal*-12d) (Table 3, Entry 1) was obtained from the above-mentioned reaction mixture by column chromatography on silica gel (6.1 mg, 15%) as a colourless solid (*distal*-**12d**:*proximal*-**12d** = 76:24, determined by isolated product yield). Mp: 91–94 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.92 (3 H, s), 7.15 (2 H, d, *J* = 9.0 Hz), 7.34 (2 H, dd, *J* = 2.0, 9.0 Hz), 7.61–7.63 (3 H, m), 8.22 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.7, 103.9, 115.3, 118.3, 118.7 (q, *J* = 320 Hz), 122.1, 124.7, 129.0, 132.6,

145.0, 148.8, 160.4. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –72.4. IR (neat): 1211, 1425 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{11}N_3O_4F_3S$ $[M+H]^+$: 374.0417, found 374.0416.



distal-**12e**

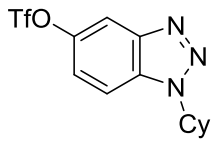
1-(4-Nitrobenzyl)-5-(trifluoromethanesulfonyloxy)benzotriazole (*distal*-12e) (Table 3, Entry 2): Following General Procedure I, a mixture of CsF (50 mg, 0.33 mmol), 4-nitrobenzyl azide **2c** (0.23 g, 1.3 mmol), and 1,4-bis(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene **11c** (50 mg, 0.11 mmol) was stirred in MeCN (1.1 mL) for 3 h at rt. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to provide the titled compound, *distal*-**12e** (17 mg, 39%) as a colourless solid. Mp: 80–82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.98 (2 H, s), 7.38–7.46 (4 H, m), 8.02 (1 H, d, *J* = 2.5 Hz), 8.21 (2 H, d, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 51.5, 110.7, 113.1, 118.6 (q, *J* = 320 Hz), 122.1, 124.3, 128.3, 131.8, 140.9, 145.9, 145.9, 148.0. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –72.4. IR (neat): 1348, 1424, 1526 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{10}N_4O_5F_3S$ $[M+H]^+$: 403.0319, found 403.0315.



proximal-**12e**

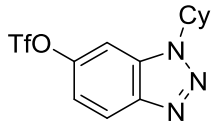
1-(4-Nitro)benzyl-6-(trifluoromethanesulfonyloxy)benzotriazole (*proximal*-12e) (Table 3, Entry 2) was obtained from the above-mentioned reaction mixture by column chromatography on silica gel (5.9 mg, 13%) as a colourless solid (*distal*-**12e**:*proximal*-**12e** = 75:25, determined by isolated product yield). Mp: 121–123 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.97 (2 H, s), 7.29–7.33 (2 H, m), 7.43 (2 H, d, *J* = 9.0 Hz), 8.19 (1 H, d, *J* = 9.0 Hz), 8.23 (2 H, d, *J* = 9.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 51.4, 102.7, 118.4, 118.6 (q, *J* = 320 Hz), 122.4, 124.4, 128.4, 132.6, 140.7, 145.0, 148.1,

148.6. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –72.4. IR (neat): 1348, 1424, 1524 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{10}N_4O_5F_3S$ $[M+H]^+$: 403.0319, found 403.0321.



distal-**12f**

1-Cyclohexyl-5-(trifluoromethanesulfonyloxy)benzotriazole (*distal*-12f) (Table 3, Entry 3): Following General Procedure I, a mixture of CsF (50 mg, 0.33 mmol), cyclohexyl azide **2d**[2] (0.16 g, 1.3 mmol), and 1,4-bis(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene **11c** (50 mg, 0.11 mmol) was stirred in MeCN (1.1 mL) for 3 h at rt. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:1) to provide the titled compound *distal*-**12f** (18 mg, 46%) as a colourless solid. Mp: 98–101 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.32–2.19 (10 H, m), 4.61–4.72 (1 H, m), 7.39 (1 H, brd, *J* = 9.0 Hz), 7.65 (1 H, d, *J* = 9.0 Hz), 7.98 (1 H, brs). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.1, 25.4, 32.6, 59.6, 111.2, 112.8, 118.7 (q, *J* = 319 Hz), 121.0, 131.4, 145.6, 145.7. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –72.4. IR (neat): 1223, 1416 cm^{-1}. HRMS (MALDI) Calcd for $C_{13}H_{15}N_3O_3F_3S$ $[M+H]^+$: 350.0781, found 350.0783.

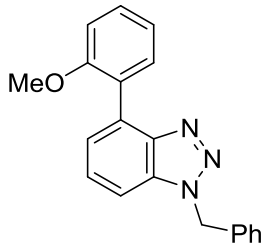


proximal-**12f**

1-Cyclohexyl-6-(trifluoromethanesulfonyloxy)benzotriazole (*proximal*-12f) (Table 3, Entry 3) was obtained from the above-mentioned reaction mixture by column chromatography on silica gel (5.6 mg, 15%) as a colourless oil (*distal*-**12f**:*proximal*-**12f** = 76:24, determined by isolated product yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.33–2.20 (10 H, m), 4.58–4.68 (1 H, m), 7.27 (1 H, dd, *J* = 2.5, 8.5 Hz), 7.52 (1 H, d, *J* = 2.5 Hz), 8.14 (1 H, d, *J* = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.1, 25.4, 32.6, 59.5, 103.2, 117.7, 118.7 (q, *J* = 318 Hz), 121.9, 132.1, 144.8, 147.9. ^{19}F NMR (280MHz, $CDCl_3$) δ: –72.4. IR (neat): 1425 cm^{-1}. HRMS (MALDI) Calcd for $C_{13}H_{15}N_3O_3F_3S$ $[M+H]^+$: 350.0781, found 350.0781.

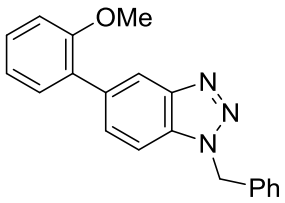
Transformation of cycloaddition adducts, *distal*-4e, *distal*-12c, and *proximal*-10a (Scheme 4):

General Procedure II: An oven dried Schlenk tube was charged with *distal*-**4e**, or **12c** (1.0 equiv), 2-methoxyphenylboronic acid **13a** (1.5 equiv), $Pd(OAc)_2$ (0.10 equiv), PCy_3 (0.20 equiv), K_3PO_4 (2.0 equiv) and evacuated and back-filled with argon. Anhydrous *n*-BuOH (0.56 mL) was added via syringes, and the reaction mixture was stirred at 100 °C for 14 h and filtered through a pad of silica gel cake using EtOAc. The eluent was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc) to provide the biaryl compound **14** or **15**.



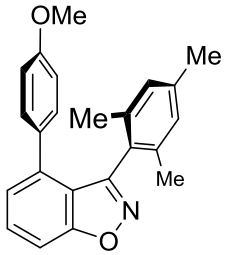
14

1-Benzyl-4-(2-methoxyphenyl)-benzotriazole (14) (Scheme 4): Following General Procedure II, a mixture of $Pd(OAc)_2$ (1.3 mg, 5.6 μmol), PCy_3 (3.1 mg, 11 μmol), 2-methoxyphenylboronic acid **13a** (13 mg, 84 μmol), K_3PO_4 (23 mg, 0.11 mmol) and *distal*-**4e** (20 mg, 56 μmol) was stirred in *n*-BuOH (0.56 mL) for 14 h at 100 °C. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 3:1) to provide the titled compound **14** (13 mg, 75%) as a colourless solid. Mp: 92–94 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.82 (3 H, s), 5.87 (2 H, s), 7.08 (1 H, d, J = 8.5 Hz), 7.12 (1 H, t, J = 7.5 Hz), 7.30–7.50 (9 H, m), 7.68 (1 H, dd, J = 1.5, 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 52.3, 55.7, 108.4, 111.5, 120.7, 125.0, 125.8, 127.1, 127.6, 128.4, 128.9, 129.6, 130.9, 132.2, 133.1, 134.9, 145.1, 156.9. IR (neat): 1244, 1489 cm^{-1}. HRMS (MALDI) Calcd for $C_{20}H_{18}N_3O$ $[M+H]^+$: 316.1444, found 316.1446.



15

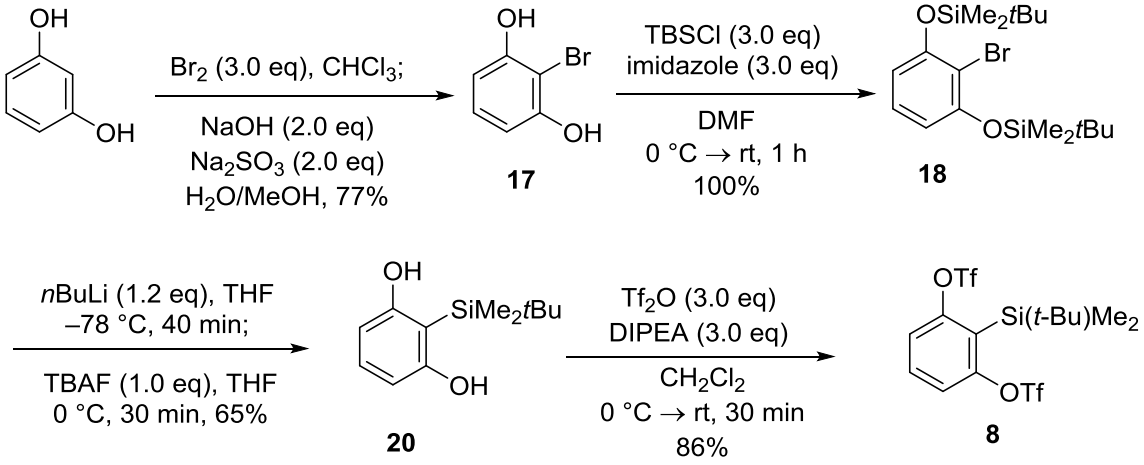
1-Benzyl-5-(2-methoxyphenyl)-benzotriazole (15) (Scheme 4): Following General Procedure II, a mixture of $Pd(OAc)_2$ (1.3 mg, 5.6 μmol), PCy_3 (3.1 mg, 11 μmol), 2-methoxyphenyboronic acid **13a** (13 mg, 84 μmol), K_3PO_4 (23 mg, 0.11 mmol) and *distal*-**12c** (20 mg, 56 μmol) was stirred in *n*-BuOH (0.56 mL) for 11 h at 100 °C. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4:1) to provide the titled compound **15** (16 mg, 88%) as a colourless solid. Mp: 104–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.81 (3 H, s), 5.86 (2 H, s), 7.03 (1 H, t, *J* = 8.5 Hz), 7.06 (1 H, t, *J* = 6.0 Hz), 7.33–7.38 (8 H, m), 7.61 (1 H, dd, *J* = 1.0, 8.5 Hz), 8.19 (1 H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 52.3, 55.5, 108.9, 111.2, 120.3, 121.0, 127.6, 128.5, 129.0, 129.0, 129.8, 129.9, 131.1, 131.9, 134.8, 146.7, 156.4. IR (neat): 1244, 1456 cm^{-1}. HRMS (MALDI) Calcd for $C_{20}H_{18}N_3O$ $[M+H]^+$: 316.1444, found 316.1444.



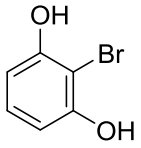
16

3-(2,4,6-Trimethylphenyl)-4-(4-methoxyphenyl)-1,2-benzisoxazole (16) (Scheme 4): An oven dried Schlenk tube was charged with *proximal*-**10a** (20 mg, 52 μmol), 4-methoxyphenylboronic acid **13b** (16 mg, 0.10 mmol), $Pd(PPh_3)_4$ (6.0 mg, 5.2 μmol), K_2CO_3 (22 mg, 0.16 mmol) and evacuated and back-filled with argon. Anhydrous DMF (0.15 mL) was added via syringes and stirred at 100 °C for 10 h. The reaction mixture was filtered through a pad of silica gel cake using EtOAc. The mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc) to provide the titled compound **16** (14 mg, 76%) as a colourless solid and its regiochemistry was determined by NOESY spectra. Mp: 116–118°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.89 (6 H, s), 2.25 (3 H, s), 3.71 (3 H, s), 6.51 (2 H, d, *J* = 8.5 Hz), 6.70 (2 H, s), 6.89 (2 H, d, *J* = 8.5 Hz), 7.22 (1 H, dd, *J* = 2.5, 5.0 Hz), 7.60–7.62 (2 H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.0, 21.0, 55.2, 108.4, 112.5, 119.5, 124.1, 125.7, 127.9, 129.1, 129.7, 129.8, 137.0, 138.5, 138.6, 157.3, 158.9, 163.8. IR (neat): 1252, 1518 cm^{-1}. HRMS (MALDI) Calcd for $C_{23}H_{22}NO_2$ $[M+H]^+$: 344.1645, found 344.1648.

Synthesis of benzyne precursors 8, 11b and 11c:

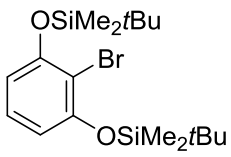


Scheme S1



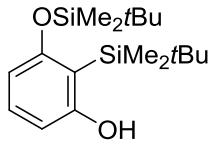
17

2-Bromoresorcinol (17):[8,9] To a solution of resorcinol (11 g, 0.10 mol) in $CHCl_3$ (63 mL, 0.50 M) was added Br_2 (15 mL, 0.30 mol) at 0 °C. After stirring for 10 h at rt, the mixture was concentrated in vacuo. The residue was recrystallized from $CHCl_3$ to give 2,4,6-tribromoresorcinol (27 g, 77%). To a solution of 2,4,6-tribromoresorcinol (17 g, 50 mmol) in H_2O/MeOH (0.35 L, H_2O/MeOH = 6:1, 0.14 M) were added NaOH (15 mL, 0.30 mol) and Na_2SO_3 at rt. After stirring for 10 h at rt, the reaction was stopped by adding 1N HCl aq. and the mixture was extracted with EtOAc three times. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was recrystallized from $CHCl_3$ to give the titled compound **17** (7.3 g, 78%) as a colourless solid. Mp: 101–102 °C (Lit. 101–102 °C).[9] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.39 (2 OH, s), 6.60 (2 H, d, J = 8.5 Hz), 7.11 (1 H, t, J = 8.5 Hz).



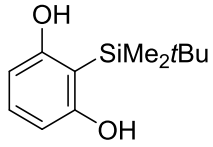
18

1,3-Bis(*tert*-butyldimethylsilyloxy)-2-bromobenzene (18): To a solution of **17** (6.0 g, 32 mmol) in DMF (63 mL, 0.50 M) were added imidazol (6.5 g, 95 mmol) and TBSCl (14 g, 95 mmol) at 0 °C. After stirring for 1 h at rt, the reaction was stopped by adding a saturated aqueous solution of NH_4Cl and the mixture was extracted with hexane. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to provide the titled compound **18** (13 g, quant) as a colourless solid. Mp: 40–42 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.23 (12 H, s), 1.04 (18 H, s), 6,51 (2 H, d, J = 8.5 Hz), 6.99 (1 H, t, J = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: –4.22, 18.4, 25.8, 109.3, 113.0, 127.3, 154.1. IR (neat): 1252, 1464 cm^{-1}. HRMS (MALDI) Calcd for $C_{18}H_{34}O_2Si_2Br$ $[M+H]^+$: 417.1275, found 417.1257.



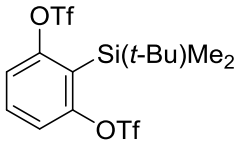
19

2-(*tert*-Butyldimethylsilyl)-3-[(*tert*-butyldimethylsilyl)oxy]phenol (19): To a solution of **18** (10 g, 24 mmol) in THF (0.12 L, 0.20 M) was added 1.6 M *n*-BuLi in hexane (18 mL, 29 mmol) slowly at –78 °C. After stirring for 40 min, the reaction was stopped by adding a saturated aqueous solution of NH_4Cl and the mixture was extracted with hexane. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 15:1) to provide the titled compound **19** (8.1 g, 85%) as a colourless solid. Mp: 57–60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.31 (6 H, s), 0.37 (6 H, s), 0.93 (9 H, s), 1.00 (9 H, s), 4.87 (OH, s), 6.30 (1 H, d, J = 8.0 Hz), 6.40 (1 H, d, J = 8.0 Hz), 7.05 (1 H, t, J = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –2.95, –1.37, 18.6, 19.5, 26.9, 27.0, 107.8, 110.5, 112.0, 130.6, 162.3, 162.3. IR (neat): 1254, 1437, 3512 cm^{-1}. HRMS (MALDI) Calcd for $C_{18}H_{35}O_2Si_2$ $[M+H]^+$:339.2170, found 339.2170.



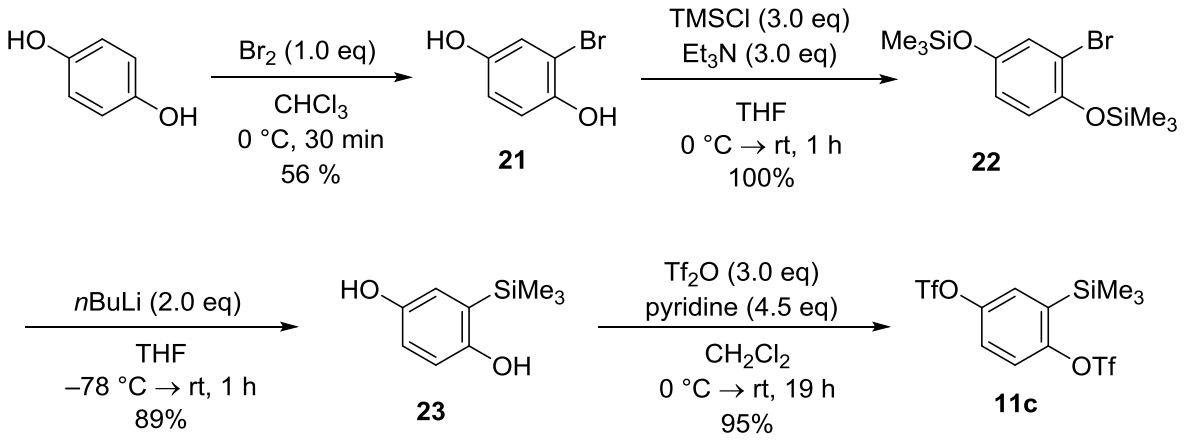
20

2-(*tert*-Butyldimethylsilyl)benzene-1,3-diol (20): To a solution of **19** (2.0 g, 5.0 mmol) in THF (50 mL, 0.10 M) was added TBAF (5.0 mL, 5.0 mmol) slowly at 0 °C. After stirring for 0.5 h, the reaction was stopped by adding a saturated aqueous solution of NH_4Cl and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was recrystallized from $CHCl_3$ to provide the titled compound **20** (0.86 g, 77%) as a colourless solid. Mp: 128–131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.41 (6 H, s), 0.94 (9 H, s), 4.90 (2 OH, s), 6.29 (2 H, d, J = 8.0 Hz), 7.07 (1 H, t, J = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –2.09, 18.4, 26.8, 107.7, 108.0, 131.4, 162.1. IR (neat): 1263, 1327, 1445, 3518 cm^{-1}. HRMS (MALDI) Calcd for $C_{12}H_{21}O_2Si$ $[M+H]^+$: 225.1305, found 225.1298.

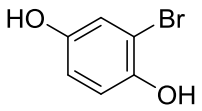


8

2-(*tert*-Butyldimethylsilyl)-1,3-bis(trifluoromethanesulfonyloxy)benzene (8): To a solution of **20** (0.20 g, 0.89 mmol) in CH_2Cl_2 (4.5 mL, 0.20 M) were added DIPEA (0.47 mL, 2.7 mmol) and Tf_2O (0.45 mL, 2.7 mmol) at 0 °C. After stirring for 0.5 h at rt, the reaction was stopped by adding $NaHCO_3$ aq. and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to provide the titled compound **8** (0.37 g, 86%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.53 (6 H, s), 0.98 (9 H, s), 7.49 (2 H, d, J = 9.0 Hz), 7.56 (1 H, t, J = 9.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –2.00, 18.6, 26.5, 117.9, 118.6 (q, J = 318 Hz), 122.4, 132.3, 156.0. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –73.8. IR (neat): 1215, 1424 cm^{-1}. Anal. Calcd for $C_{14}H_{18}F_6O_6S_2Si$: C, 34.42; H, 3.71. Found: C, 34.54; H, 3.72.

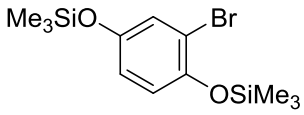


Scheme S2



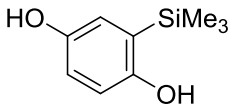
21

2-Bromohydroquinone (21):[10,11] To a solution of hydroquinone (6.4 g, 58 mmol) in $CHCl_3$ (0.29 L, 0.20 M) was added Br_2 (3.0 mL, 58 mmol) at 0 °C. After stirring for 0.5 h at rt, the mixture was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 3:1) to provide the titled compound **21** (6.0 g, 56%) as a colourless solid. Mp: 111–114 °C (Lit. 112 °C).[11] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.12 (2 OH, brs), 6.73 (1 H, dd, J = 3.0, 9.0 Hz), 6.90 (1 H, d, J = 9.0 Hz), 6.99 (1 H, d, J = 3.0 Hz).



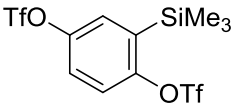
22

1,4-Bis(trimethylsilyloxy)-2-bromobenzene (22): To a solution of **21** (2.5 g, 13 mmol) in THF (65 mL, 0.20 M) were added Et_3N (5.4 mL, 39 mmol) and TMSCl (4.9 mL, 39 mmol). After stirring for 1 h at rt, the mixture was concentrated in vacuo. The residue was filtered through Celite pad (washed with hexane) and concentrated in vacuo as a colourless oil (4.3 g, quant). This compound **22** was used for next reaction without purification due to the instability on silica gel column chromatography.



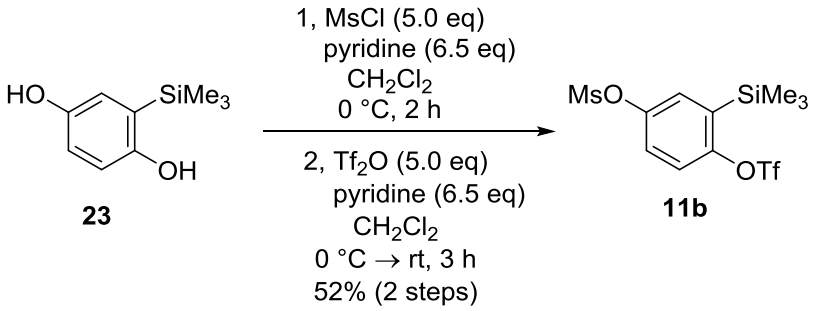
23

2-(Trimethylsilyl)hydroquinone (23):[12] To a solution of **22** (4.3 g, 13 mmol) in THF (65 mL, 0.20 M) was added 2.3 M *n*-BuLi in hexane (11 mL, 26 mmol) slowly at –78 °C. After stirring for 1 h at rt, the reaction was stopped by adding a saturated aqueous solution of NH_4Cl and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide the titled compound **23** (2.1 g, 89%) as a colourless solid. Mp: 126–127 °C (Lit. 126–127 °C).[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.30 (9 H, s), 4.49 (OH, s), 4.54 (OH, s), 6.57 (1 H, d, *J* = 8.5 Hz), 6.70 (1 H, dd, *J* = 3.5, 8.5 Hz), 6.82 (1 H, d, *J* = 3.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –1.08, 115.5, 116.2, 117.0, 121.4, 149.0, 154.2. IR (neat): 1362, 3349 cm^{-1}. HRMS (MALDI) Calcd for $C_9H_{14}O_2Si$ $[M+H]^+$: 182.0758, found 182.0759.

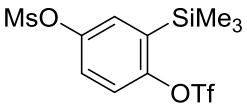


11c

1,4-Bis(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)benzene (11c): To a solution of **23** (1.0 g, 5.5 mmol) in CH_2Cl_2 (28 mL, 0.20 M) were added pyridine (2.0 mL, 25 mmol) and Tf_2O (2.8 mL, 17 mmol) at 0 °C. After stirring for 19 h at rt, the reaction was stopped by adding a saturated aqueous solution of NH_4Cl and the mixture was extracted with Et_2O. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 15:1) to provide the titled compound **11c** (2.3 g, 95%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.39 (9 H, s), 7.34 (1 H, dd, *J* = 3.0, 9.0 Hz), 7.38 (1 H, d, *J* = 3.0 Hz), 7.44 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: –1.21, 118.4 (q, *J* = 318 Hz), 118.7 (q, *J* = 319 Hz), 121.5, 123.9, 128.6, 136.7, 147.9, 153.3. ^{19}F NMR (280 MHz, $CDCl_3$) δ: –73.7, –72.6. IR (neat): 1427 cm^{-1}. HRMS (APCI) Calcd for $C_{12}H_{13}F_6O_6S_2Si$ $[M+H]^+$: 446.98270, found 446.98508.



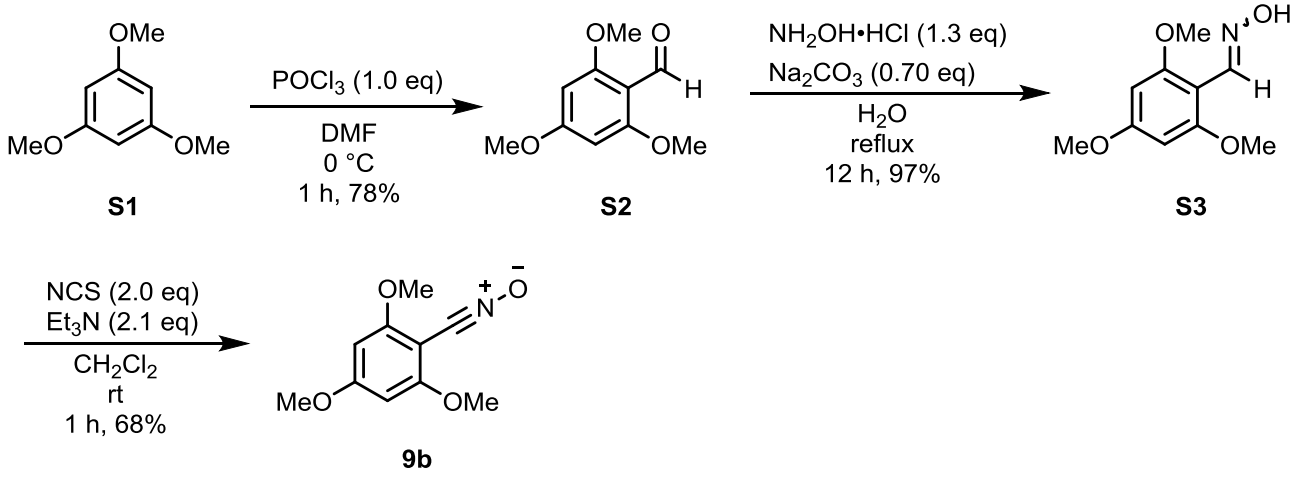
Scheme S3



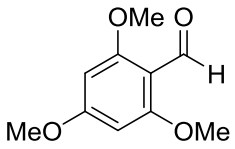
11b

1-(Methanesulfonyloxy)-3-(trimethylsilyl)-4-(trifluoromethanesulfonyloxy)benzene (11b): To a solution of **23** (0.90 g, 4.9 mmol) in CH_2Cl_2 (25 mL, 0.20 M) were added pyridine (2.6 mL, 32 mmol) and MsCl (1.9 mL, 25 mmol) at 0 °C. After stirring for 2 h at rt, the reaction was stopped by adding H_2O and the mixture was extracted with Et_2O. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (toluene/EtOAc = 6:1) to provide the mixture of 3-(trimethylsilyl)-4-(methansulfonyloxy)phenol and 1,4-bis(methansulfonyloxy)-3-(trimethylsilyl)benzene (1.3 g). To a solution of the mixture in CH_2Cl_2 (14 mL) was added pyridine (1.9 mL, 24 mmol) and Tf_2O (3.1 mL, 18 mmol) at 0 °C. After stirring for 3 h at rt, the reaction was stopped by adding H_2O and the mixture was extracted with Et_2O. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide the titled compound [1.0 g, 52% (2 steps)] as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.38 (9 H, s), 3.18 (3 H, s), 7.36 (1 H, dd, J = 3.0, 8.5 Hz), 7.21 (1 H, d, J = 8.5 Hz), 7.40 (1 H, d, J = 3.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –1.21, 37.6, 118.3 (q, J = 317 Hz), 121.2, 124.5, 129.3, 135.9, 147.5, 152.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ: –73.8. IR (neat): 1373, 1420 cm^{-1}. HRMS (APCI) Calcd for $C_{11}H_{16}F_3O_6S_2Si$ $[M+H]^+$: 393.01097, found 393.01356.

Synthesis of 2,4,6-trimethoxybenzonitrile oxide (9b):

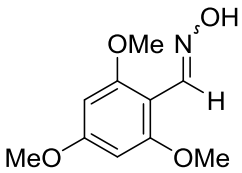


Scheme S4



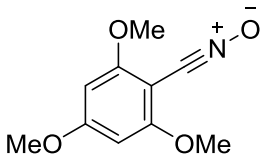
S2

2,4,6-Trimethoxybenzaldehyde (S2):[13,14] To a solution of **S1** (0.80 mg, 4.8 mmol) in DMF (15 mL, 0.30 M) was added $POCl_3$ (0.45 mL, 4.8 mmol) at 0 °C. After stirring for 1 h at 0 °C, the reaction was stopped by adding a saturated aqueous solution of NH_4Cl and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 1:1) to provide the titled compound **S2** (0.73 g, 78%) as a colourless solid. Mp: 119–120 °C (Lit. 119–121 °C).[14] ^{1}H NMR (300 MHz,$CDCl_3$) δ: 3.87 (9 H, s), 6.06 (2 H, s), 10.3 (1 H, s).



S3

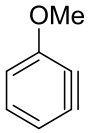
2,4,6-Trimethoxybenzaldehyde oxime (S3):[15] To a solution of **S2** (0.69 g, 3.5 mmol) in H_2O (35 mL, 0.10 M) was added Na_2CO_3 (0.27 g, 2.5 mmol) and $NH_2OH{\cdot}HCl$ (0.32 g, 4.6 mmol) at rt. After stirring for 12 h at rt, the reaction was stopped by adding a saturated aqueous solution of NH_4Cl and the mixture was extracted with Et_2O. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 15:1) to provide the titled compound **S3** (0.72 g, 97%) as a colourless solid. Mp: 216–218 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.77 (6 H, s), 3.80 (3 H, s), 6.26 (2 H, s), 8.13 (OH, s), 10.8 (1 H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 55.4, 55.8, 91.0, 102.4, 142.4, 159.2, 161.6. IR (neat): 1464, 1611, 3181 cm^{-1}. HRMS (MALDI) Calcd for $C_{10}H_{14}NO_4$ $[M+H]^+$: 212.0917, found 212.0919.



9b

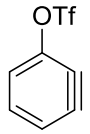
2,4,6-Trimethoxyphenylnitrile oxide (9b): To a solution of **S3** (0.22 g, 1.1 mmol) in CH_2Cl_2 (11 mL, 0.10 M) was added Et_3N (0.30 mL, 2.2 mmol) and *N*-chlorosuccinimide (0.28 g, 2.1 mmol) at rt. After stirring for 1 h at rt, the reaction was stopped by adding H_2O and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 1:2) to provide the titled compound **9b** (0.15 g, 68%) as a colourless solid. Mp: 164–167 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.83 (9 H, s), 6.06 (2 H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.6, 55.9, 84.3, 90.4, 163.4, 163.7. IR (neat): 1333, 1582 cm^{-1}. HRMS (MALDI) Calcd for $C_{10}H_{11}NO_4$ $[M+H]^+$: 209.0683, found 209.0683.

Cartesian coordinates of benzynes 3c–7f optimized by DFT [B3LYP/6-31G(d)]:



3c

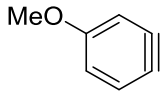
1	C	-1.4012340	-1.9820040	0.0000000
2	C	-1.9158900	-0.7017010	0.0000000
3	C	-1.3844100	0.4289210	0.0000000
4	C	0.0000000	0.5868860	0.0000000
5	C	0.6889330	-0.6532870	0.0000000
6	C	0.0065520	-1.8841970	0.0000000
7	O	0.5727830	1.8141540	0.0000000
8	C	1.9923020	1.8880390	0.0000000
9	H	-1.9371320	-2.9231500	0.0000000
10	H	1.7741190	-0.6693630	0.0000000
11	H	0.5924200	-2.8015940	0.0000000
12	H	2.2351920	2.9518010	0.0000000
13	H	2.4178110	1.4165660	0.8952410
14	H	2.4178110	1.4165660	-0.8952410



3d

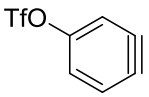
1	C	4.3439170	-0.2734480	0.1237090
2	C	3.6576610	0.8861480	-0.3087160
3	C	3.4306290	-1.2899530	0.2561410
4	C	2.2733950	0.8935130	-0.5421010
5	C	2.1922790	-1.3843920	0.0853730
6	C	1.4991100	-0.2667160	-0.3443450

7	O	0.1273570	-0.2625480	-0.6436730
8	S	-0.8790360	0.4800390	0.4392730
9	O	-0.6407650	-0.0237720	1.7819550
10	O	-0.9431840	1.9058860	0.1551360
11	C	-2.4299840	-0.3205410	-0.2419350
12	F	-2.5560360	-0.0344860	-1.5332930
13	F	-2.3725230	-1.6356990	-0.0688780
14	F	-3.4608530	0.1810980	0.4358830
15	H	5.4112710	-0.3017160	0.3051570
16	H	4.2260420	1.7989860	-0.4693410
17	H	1.7826580	1.7996830	-0.8836890



3f

1	C	-0.0432360	-2.0214650	0.0000000
2	C	-1.4114160	-1.8134740	0.0000000
3	C	0.6633850	-0.8007590	0.0000000
4	C	-1.9883820	-0.7032780	0.0000000
5	C	-1.4185880	0.5496390	0.0000000
6	C	0.0000000	0.4510130	0.0000000
7	O	0.6476630	1.6538600	0.0000000
8	C	2.0659780	1.6683100	0.0000000
9	H	0.4687220	-2.9788100	0.0000000
10	H	1.7473430	-0.8334450	0.0000000
11	H	-1.9064250	1.5181370	0.0000000
12	H	2.3537110	2.7213890	0.0000000
13	H	2.4744510	1.1809660	0.8953100
14	H	2.4744510	1.1809660	-0.8953100



3e

1	C	4.1542530	0.1867320	0.0374970
2	C	3.5231410	1.2591820	0.1528490
3	C	3.6682440	-1.0721760	-0.2749900
4	C	2.1624450	1.4323430	-0.0206410
5	C	2.2777630	-1.0170790	-0.4805580
6	C	1.5721070	0.1972860	-0.3554460
7	O	0.1882850	0.1985220	-0.6399990
8	S	-0.8166170	-0.3014280	0.5746410
9	O	-0.7760820	-1.7512270	0.6944780
10	O	-0.6777500	0.5676940	1.7326400
11	C	-2.3795120	0.1685260	-0.3456610
12	F	-2.3990000	1.4792340	-0.5627340
13	F	-2.4395190	-0.4861010	-1.5001040
14	F	-3.4078130	-0.1779310	0.4257360
15	H	4.2368590	-1.9912340	-0.3644410
16	H	1.5776020	2.3405960	0.0703910
17	H	1.7221380	-1.9121290	-0.7415520

Experimental references:

[1] H. Ankati and E. R. Biehl, *Tetrahedron*, 2009, **50**, 4677–4682.

[2] C. Rossy, J. Majimel, M. T. Delapierre, E. Fouquet and F. X. Felpin, *J. Organomet. Chem.*, 2014, **755**, 78–85.

[3] M. Juricek, M. Felici, P. C. Carballada, J. Lauko, S. R. Bou, P. H. J. Kouwer, A, M. Brouwer and A, E. Rowan, *J. Mater. Chem.*, 2011, **21**, 2104–2111.

[4] A. R. Evans and G. A. Taylor, *J. Chem, Soc., Perkin Trans. 1*, 1983, 979–983.

[5] K. Asano and S. Matsubara, *Org. Lett.*, 2010, **12**, 4988–4991.

[6] W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923–2925.

[7] C. Zhou, J. Wang, J. Jin, P. Lu and Y. Wang, *Eur. J. Org. Chem.*, 2014, 1832–1835.

[8] E. Kiehlmann and R. W. Lauener, *Can. J. Chem.*, 1989, **67**, 335–344.

[9] U. Lüning, M. Abbass and F. Fahrenkrug, *Eur. J. Org. Chem.*, 2002, 3294–3303.

[10] G. Viault, D. Grée, S. Das, J. S. Yadav and R. Grée, *Eur. J. Org. Chem.*, 2011, 1233–1241.

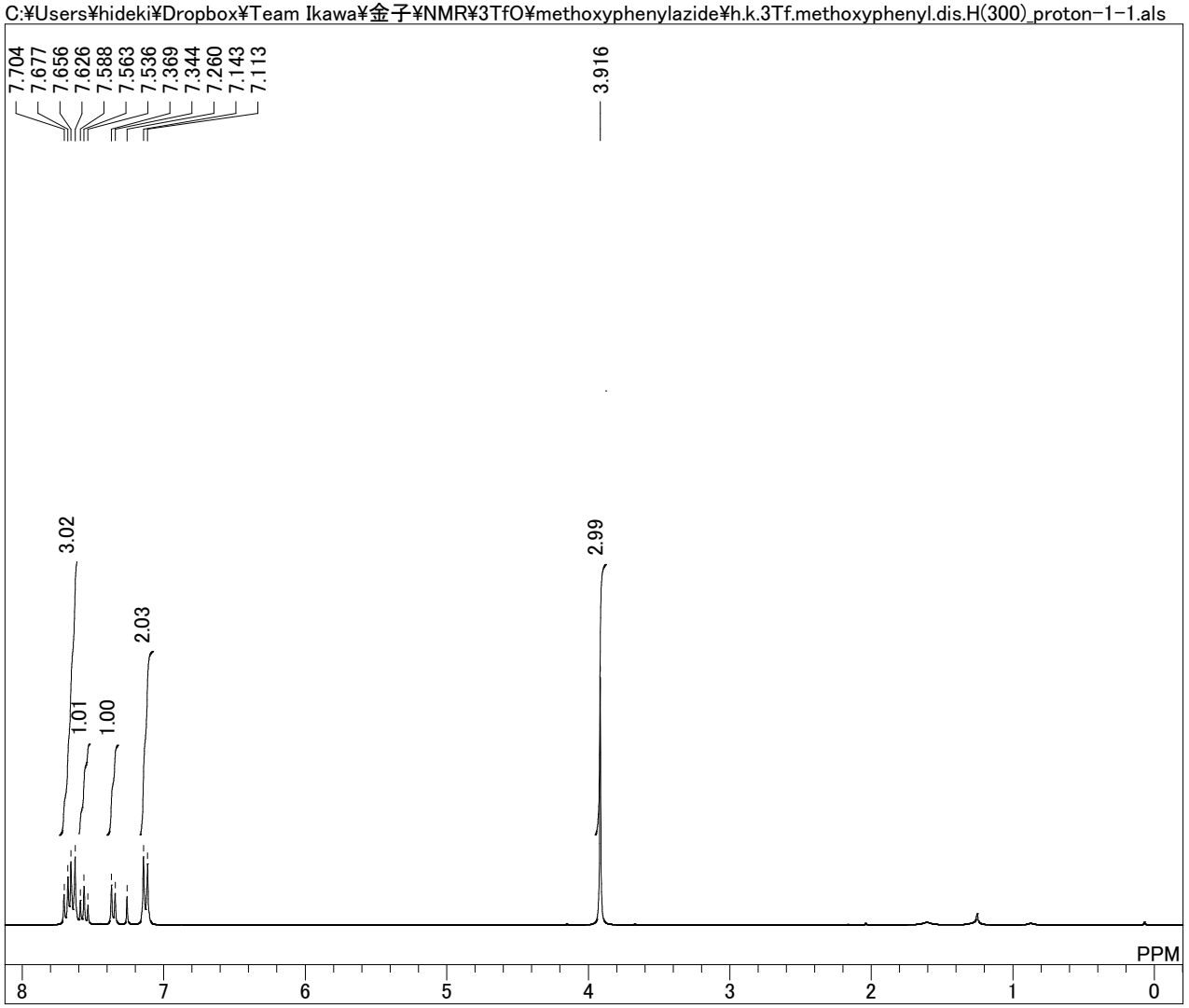
[11] D. A. M. Egbe, C. Bader, E. Klemn, L. Ding, F. E. Karasz, U. W. Grummt and E. Birckner, *Macromolecules*, 2003, **36**, 9303–9312.

[12] G. Cooper, B. Williams and C. Lape, *J. Org. Chem.*, 1961, **26**, 4171–4173.

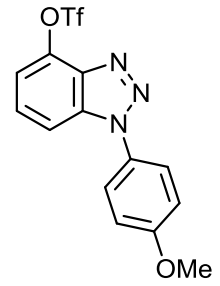
[13] M. Tobisu, S. Yamaguchi and N. Chatani, *Org. Lett.*, 2007, **9**, 3351–3353.

[14] A. G. Godoy, A. Fierro, T. H. Mclean, M. Castillo, B. K. Cassels, M. R. Parada and D. E. Nichols, *J. Med. Chem.*, 2005, **48**, 2407–2419.

[15] Y. Hou, S. Lu and G. Liu, *J. Org. Chem.*, 2013, **78**, 8386–8395.



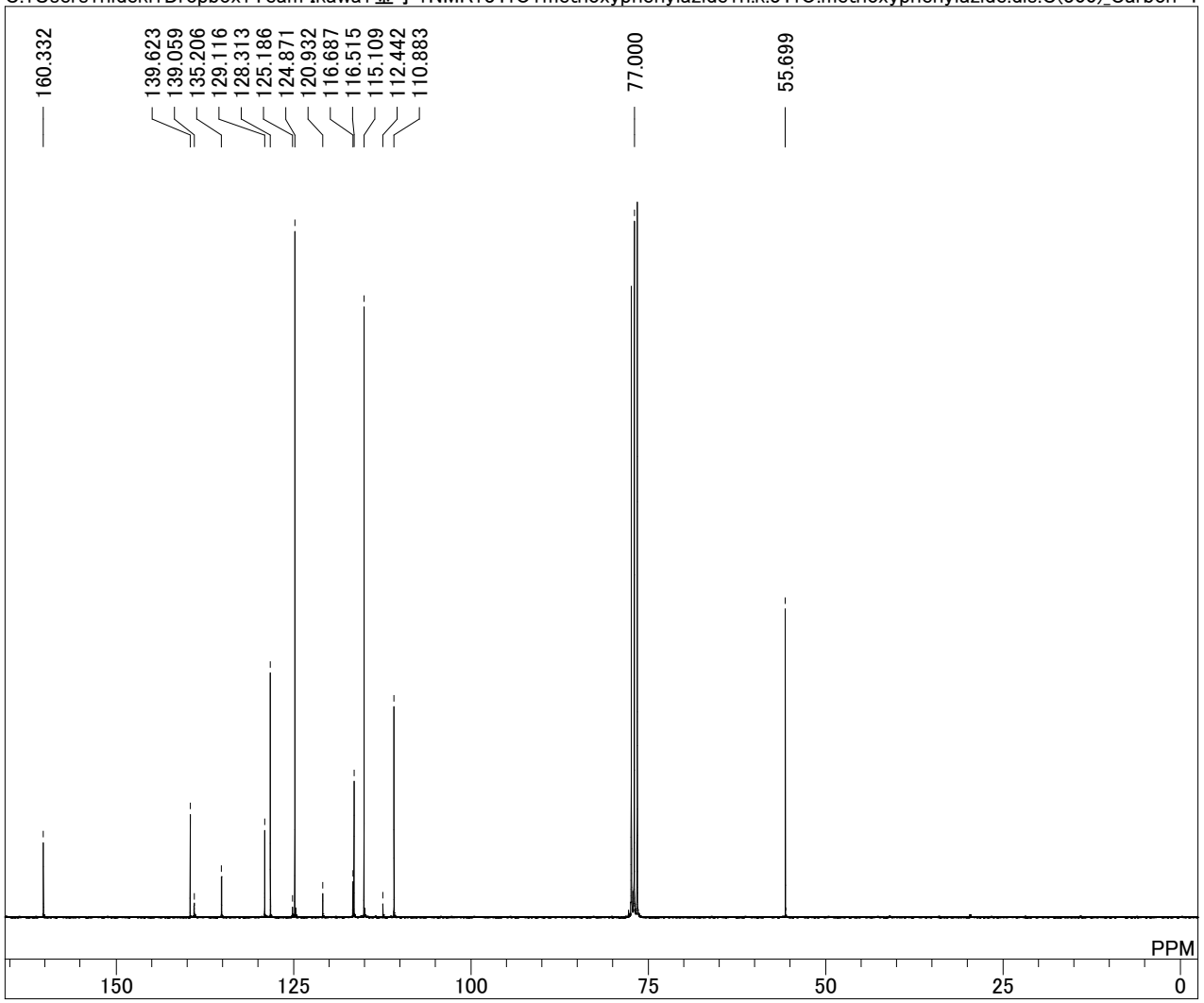
DFILE	h.k.3Tf.methoxyphenyl.dis.H(
COMNT	
DATIM	16-05-2014 17:18:56
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	42



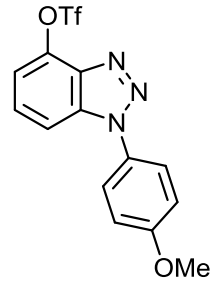
distal-**4d** (Table 1, Entry 1)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥methoxyphenylazide¥h.k.3TfO.methoxyphenylazide.dis.C(300)_Carbon-1-1.als



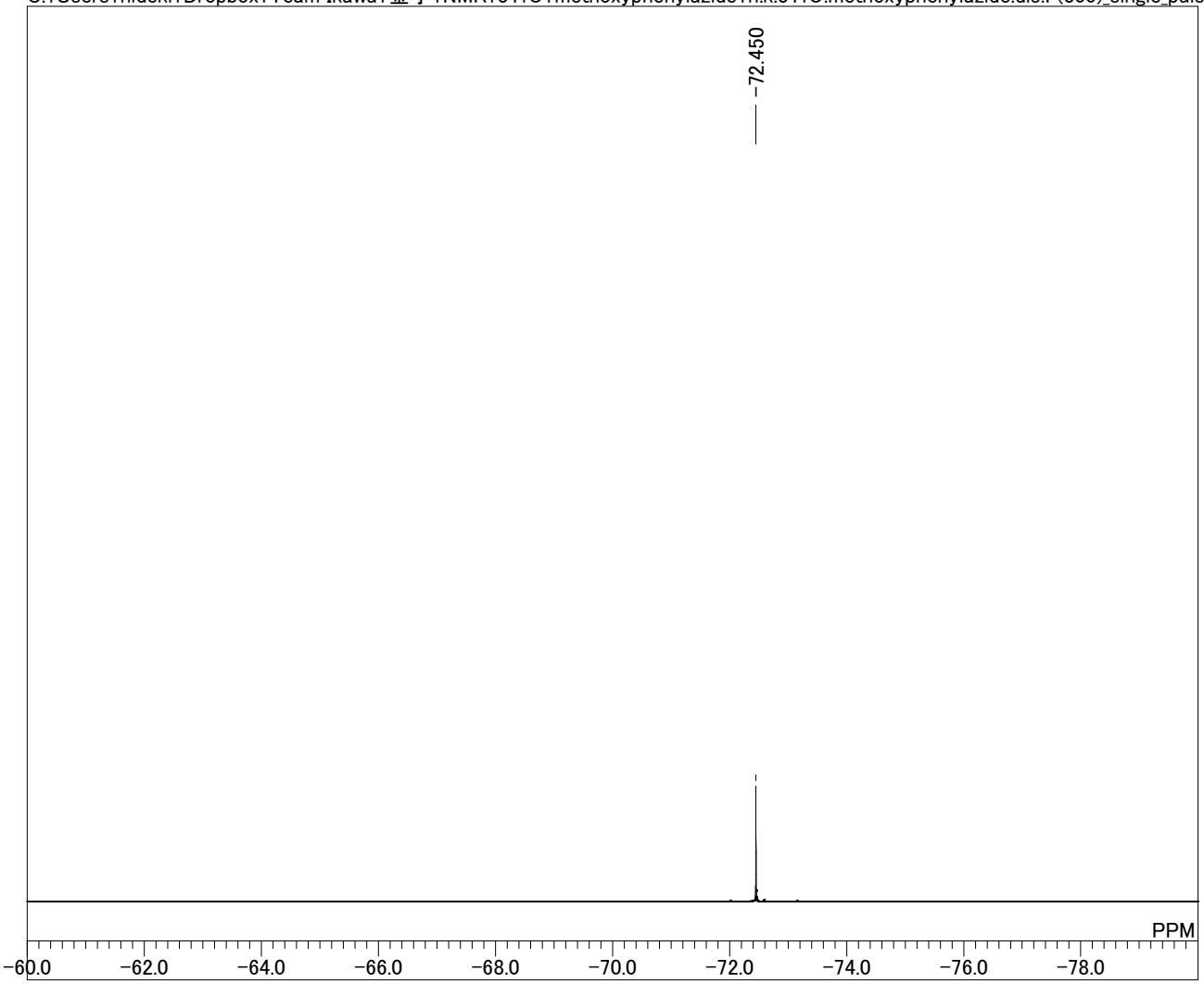
DFILE	h.k.3TfO.methoxyphenylazide
COMNT	single pulse decoupled gated
DATIM	17-05-2014 22:04:49
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.39 Hz
SCANS	12500
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



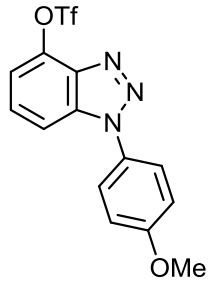
distal-**4d** (Table 1, Entry 1)

single_pulse

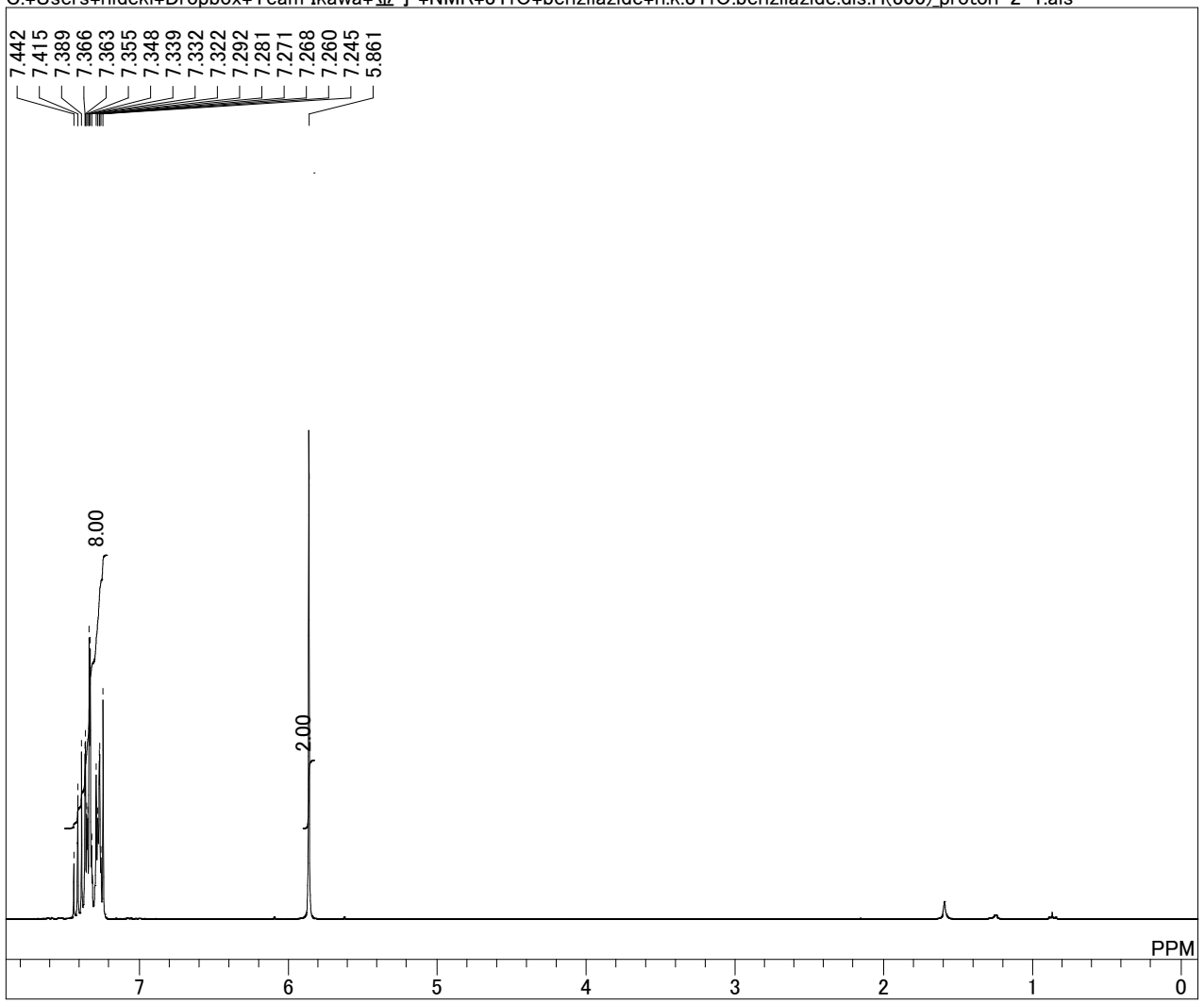
C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥methoxyphenylazide¥h.k.3TfO.methoxyphenylazide.dis.F(300)_single_pulse-1-1.als



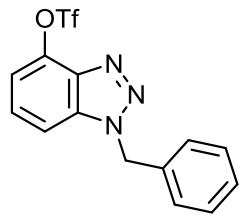
DFILE	h.k.3TfO.methoxyphenylazide
COMNT	single_pulse
DATIM	09-06-2014 18:19:22
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	52428
FREQU	5656.11 Hz
SCANS	8
ACQTM	9.2694 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	24.8 c
SLVNT	CDCL3
EXREF	-72.45 ppm
BF	0.12 Hz
RGAIN	38



distal-**4d** (Table 1, Entry 1)



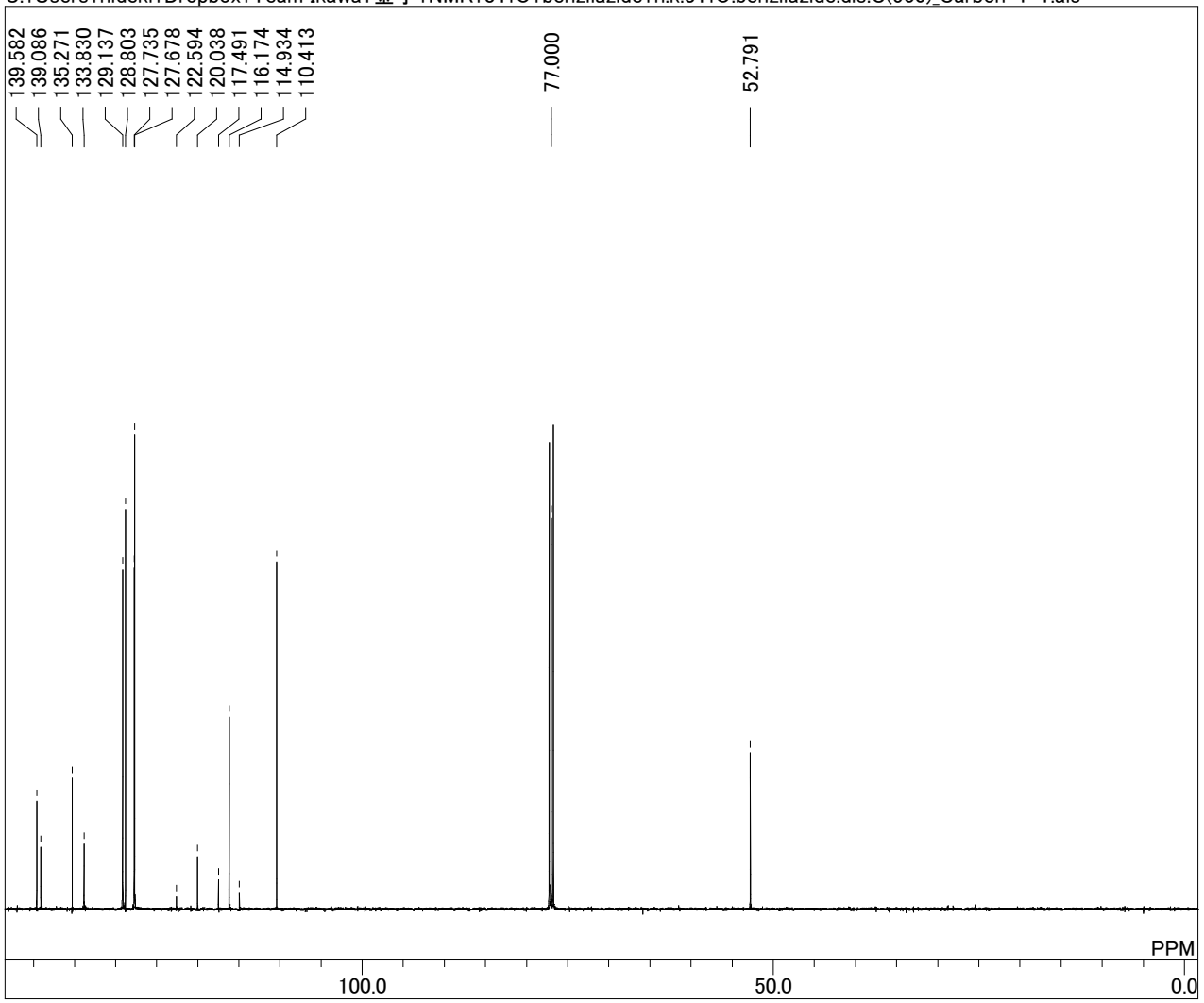
DFILE	h.k.3TfO.benzilazide.dis.H(30(
COMNT	
DATIM	14-05-2014 14:26:29
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	42



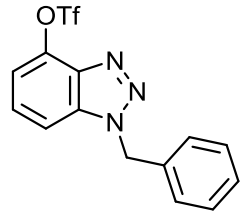
distal-**4e** (Table 1, Entry 2)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥benzilazide¥h.k.3TfO.benzilazide.dis.C(500)_Carbon-1-1.als



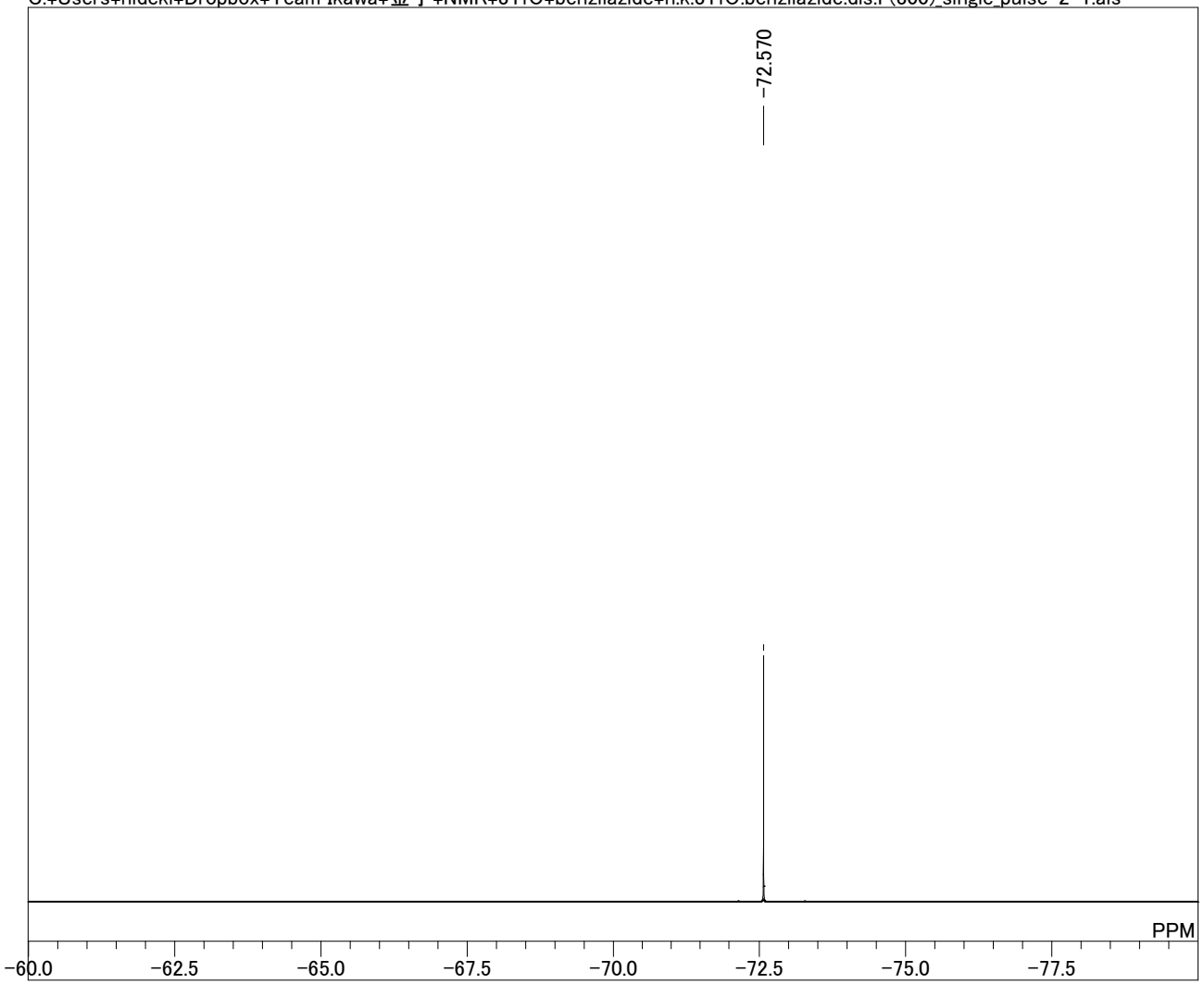
DFILE	h.k.3TfO.benzilazide.dis.C(50(
COMNT	single pulse decoupled gated
DATIM	09-06-2014 18:45:27
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	419
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



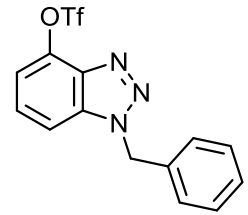
distal-**4e** (Table 1, Entry 2)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥benzilazide¥h.k.3TfO.benzilazide.dis.F(300)_single_pulse-2-1.als



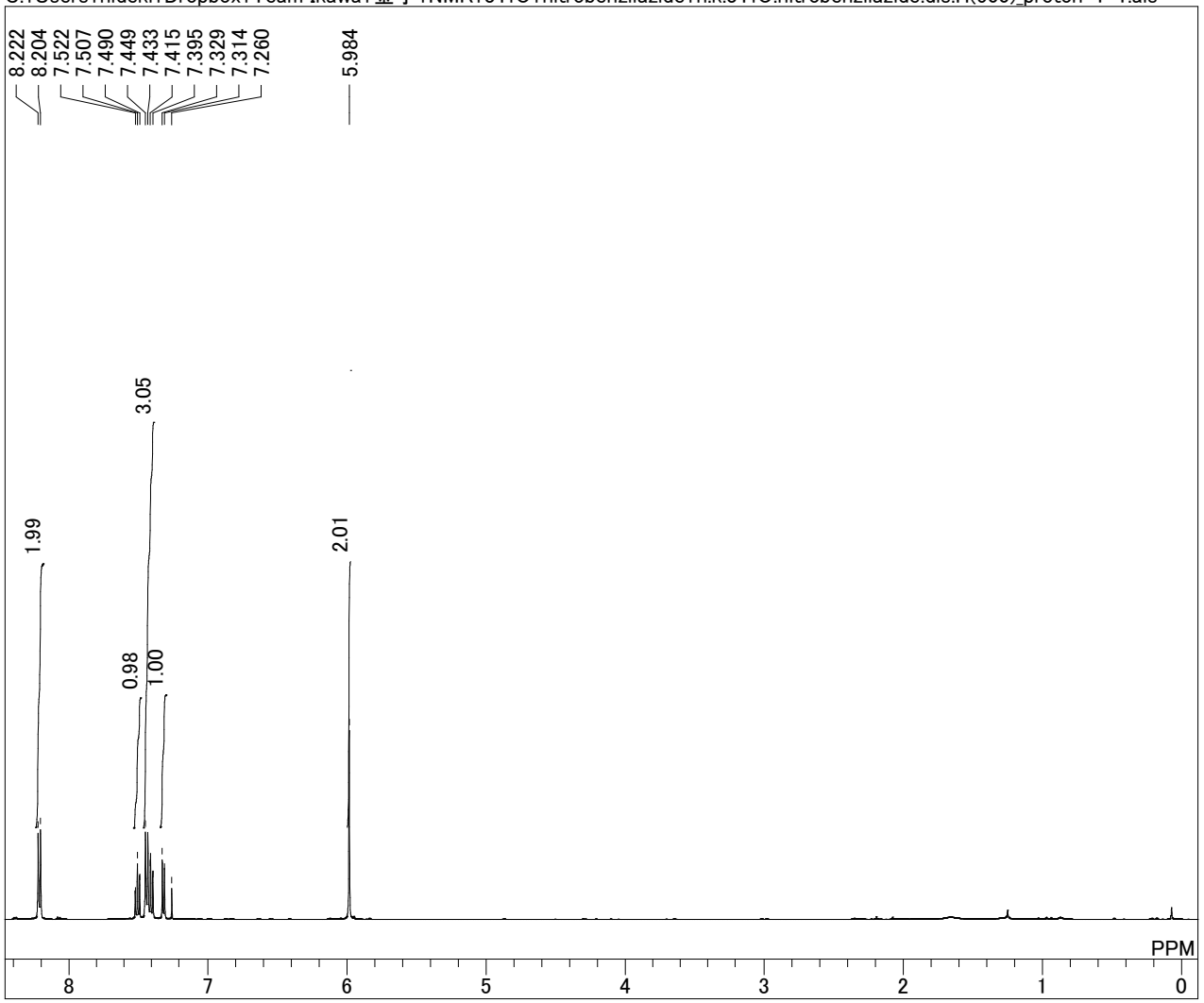
DFILE	h.k.3TfO.benzilazide.dis.F(30(
COMNT	single_pulse
DATIM	14-05-2014 14:22:38
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	13107
FREQU	5656.11 Hz
SCANS	8
ACQTM	2.3174 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	−72.57 ppm
BF	0.12 Hz
RGAIN	40



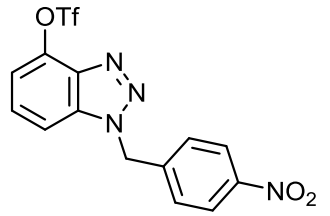
distal-**4e** (Table 1, Entry 2)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrobenzilazide¥h.k.3TfO.nitrobenzilazide.dis.H(500)_proton-1-1.als



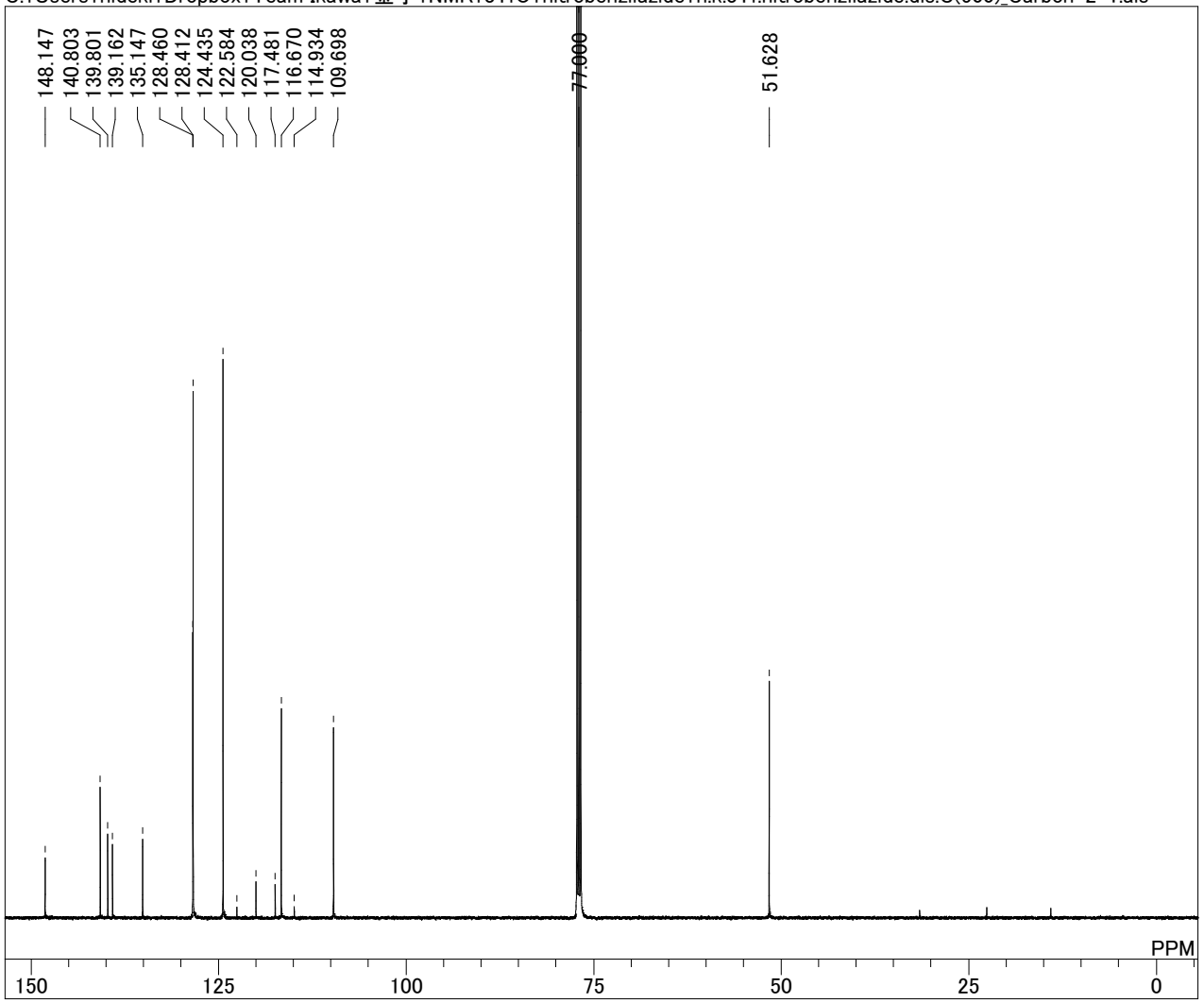
DFILE	h.k.3TfO.nitrobenzilazide.dis.H
COMNT	single_pulse
DATIM	15-05-2014 12:36:20
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



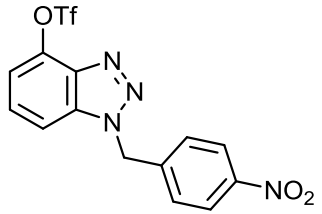
distal-**4f** (Table 1, Entry 3)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrobenzilazide¥h.k.3Tf.nitrobenzilazide.dis.C(500)_Carbon-2-1.als



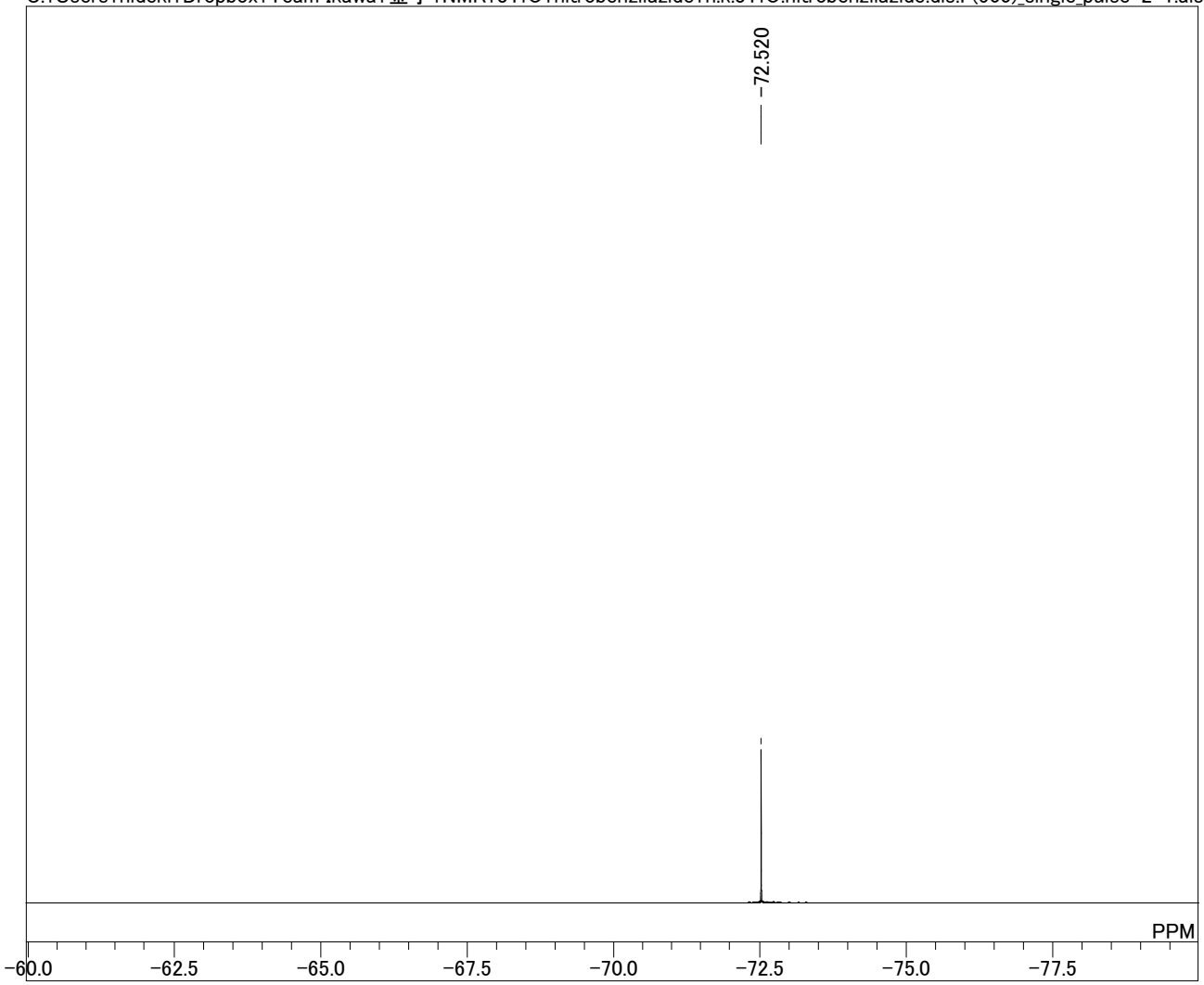
DFILE	h.k.3Tf.nitrobenzilazide.dis.C(
COMNT	single pulse decoupled gated
DATIM	11-06-2014 23:52:17
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	13115
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



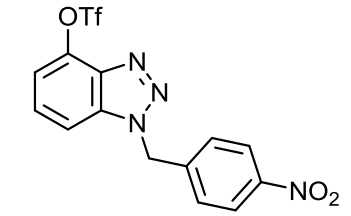
distal-**4f** (Table 1, Entry 3)

single_pulse

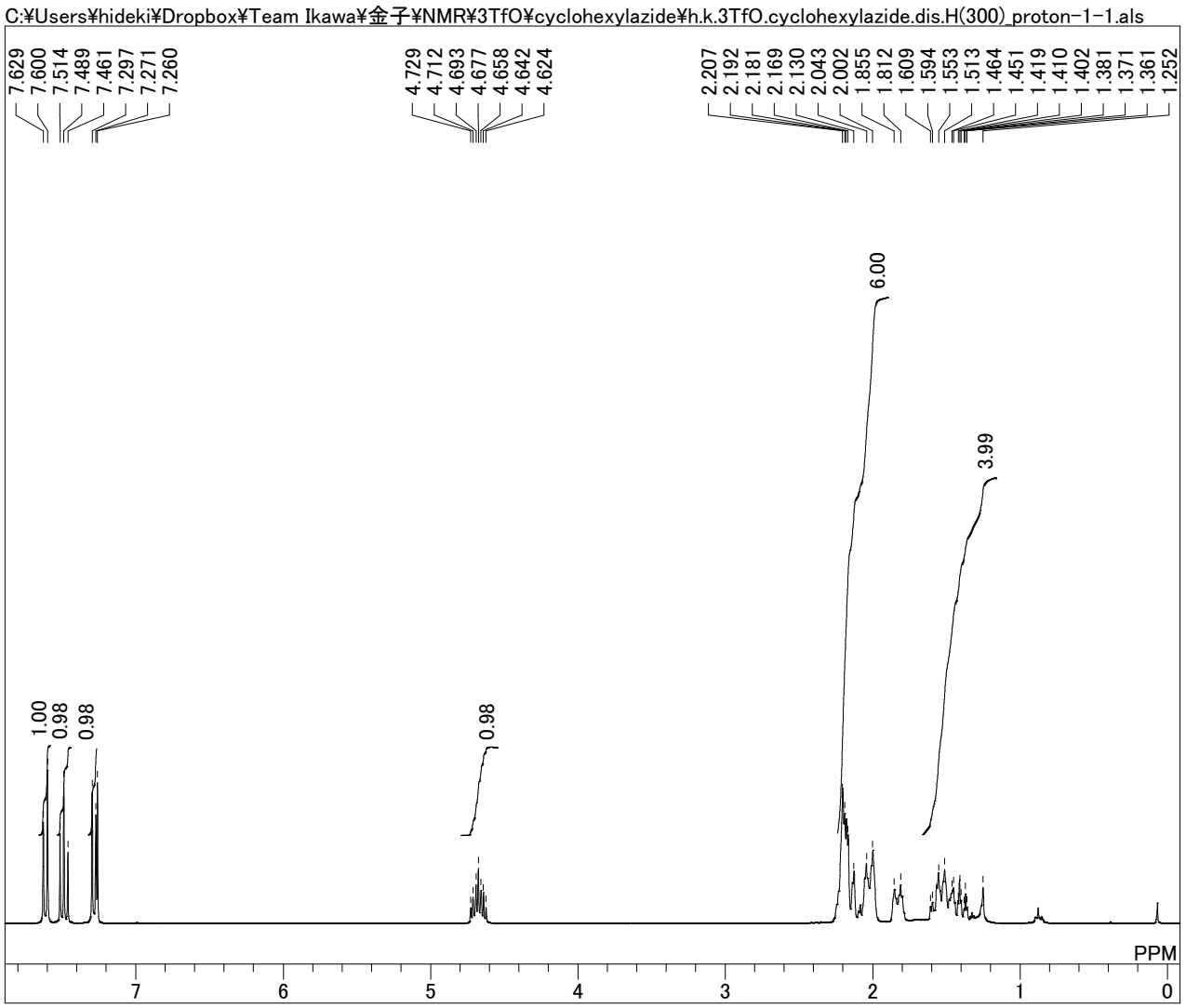
C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrobenzilazide¥h.k.3TfO.nitrobenzilazide.dis.F(500)_single_pulse-2-1.als



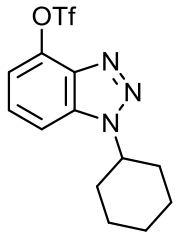
DFILE	h.k.3TfO.nitrobenzilazide.dis.F
COMNT	single_pulse
DATIM	15-05-2014 12:32:60
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	470.58 MHz
OBSET	7.51 KHz
OBFIN	7.41 Hz
POINT	13107
FREQU	9416.20 Hz
SCANS	8
ACQTM	1.3920 sec
PD	5.0000 sec
PW1	5.80 usec
IRNUC	19F
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	-72.52 ppm
BF	0.12 Hz
RGAIN	50



distal-**4f** (Table 1, Entry 3)



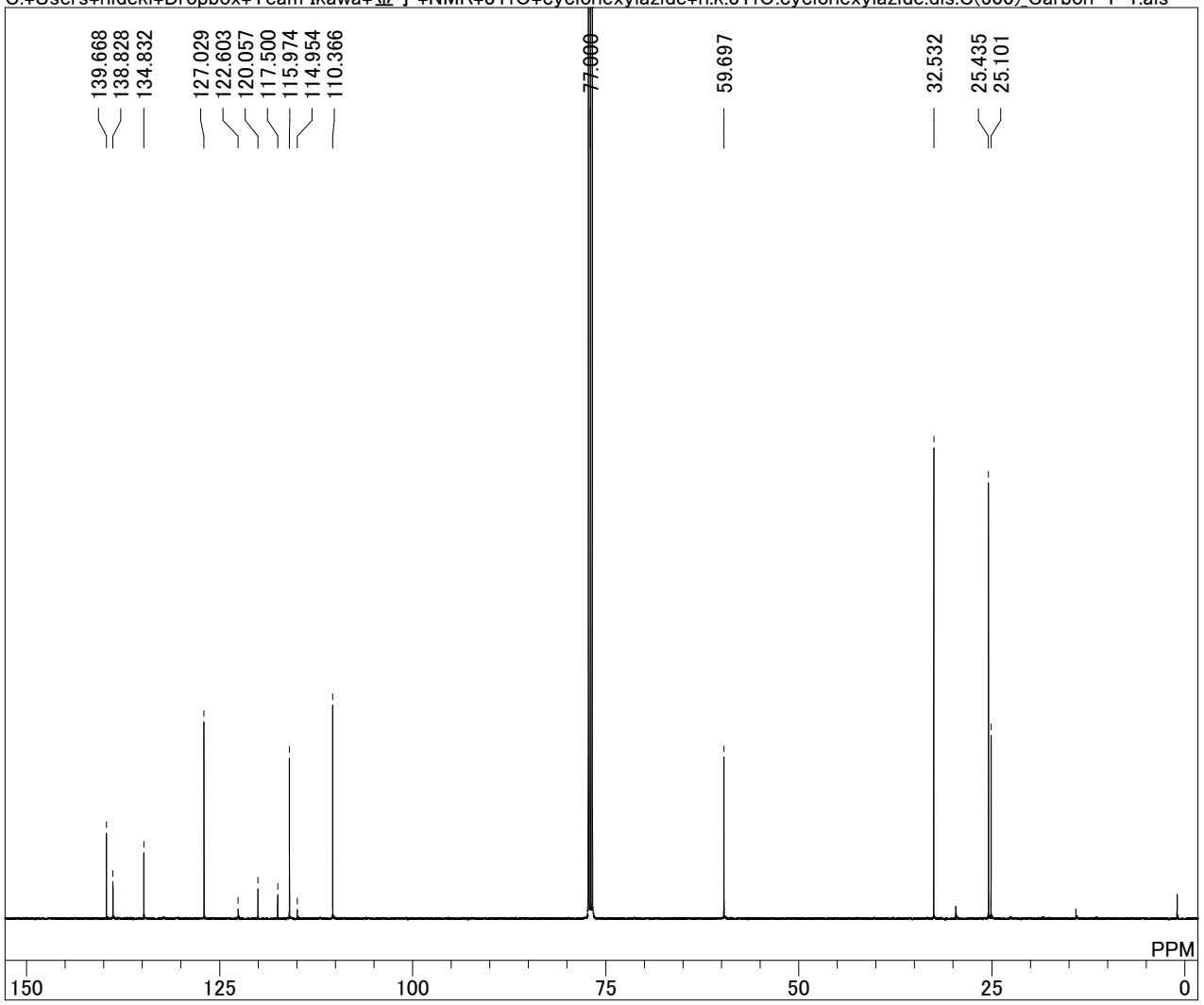
DFILE	h.k.3TfO.cyclohexylazide.dis.l
COMNT	
DATIM	14-05-2014 12:06:02
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



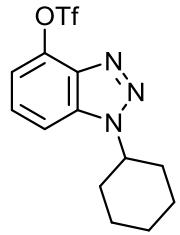
distal-**4g** (Table 1, Entry 4)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥cyclohexylazide¥h.k.3TfO.cyclohexylazide.dis.C(500)_Carbon-1-1.als



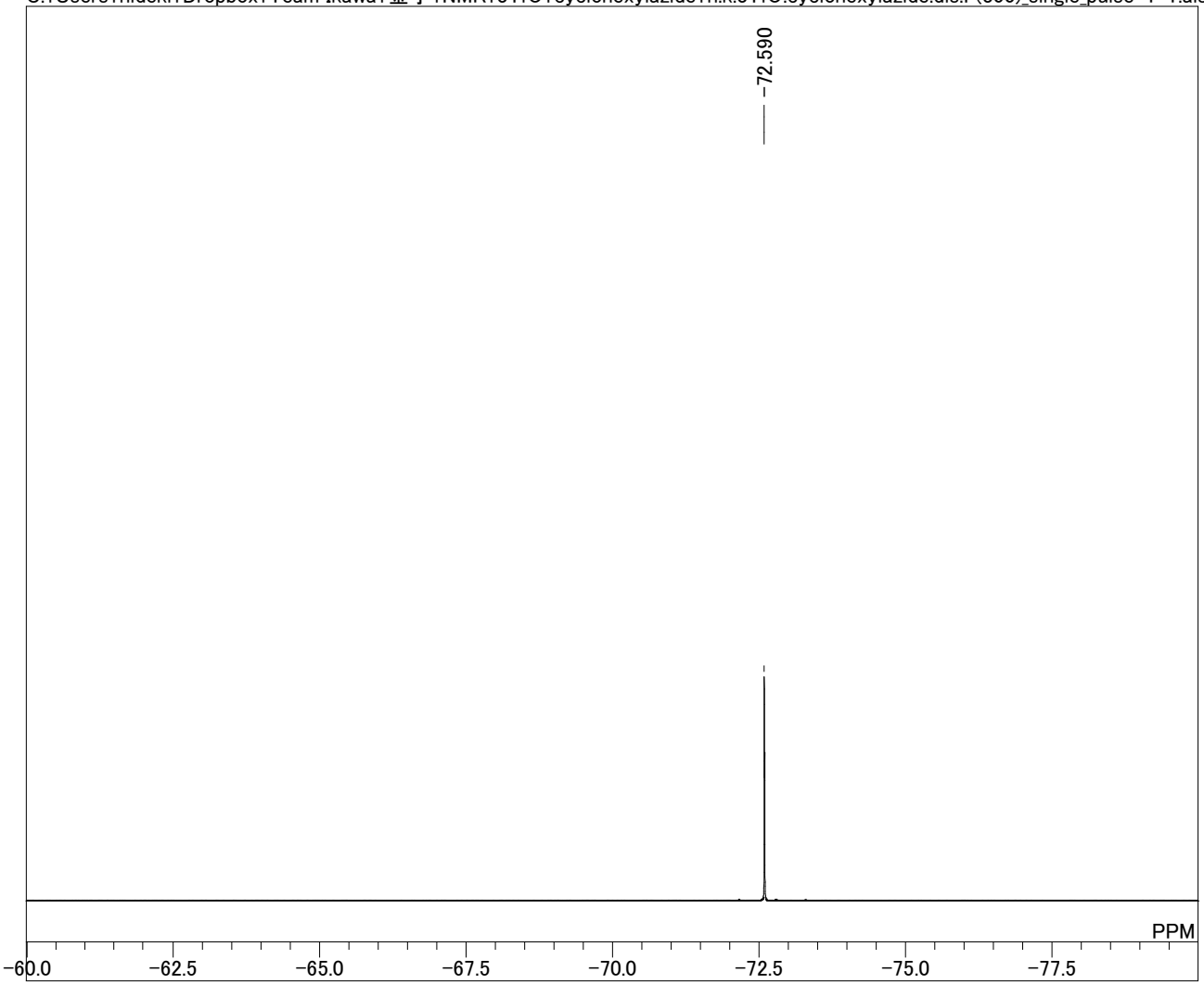
DFILE	h.k.3TfO.cyclohexylazide.dis.(
COMNT	single pulse decoupled gated
DATIM	18-05-2014 14:44:14
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	3385
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



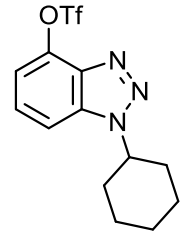
distal-**4g** (Table 1, Entry 4)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥cyclohexylazide¥h.k.3TfO.cyclohexylazide.dis.F(300)_single_pulse-1-1.als

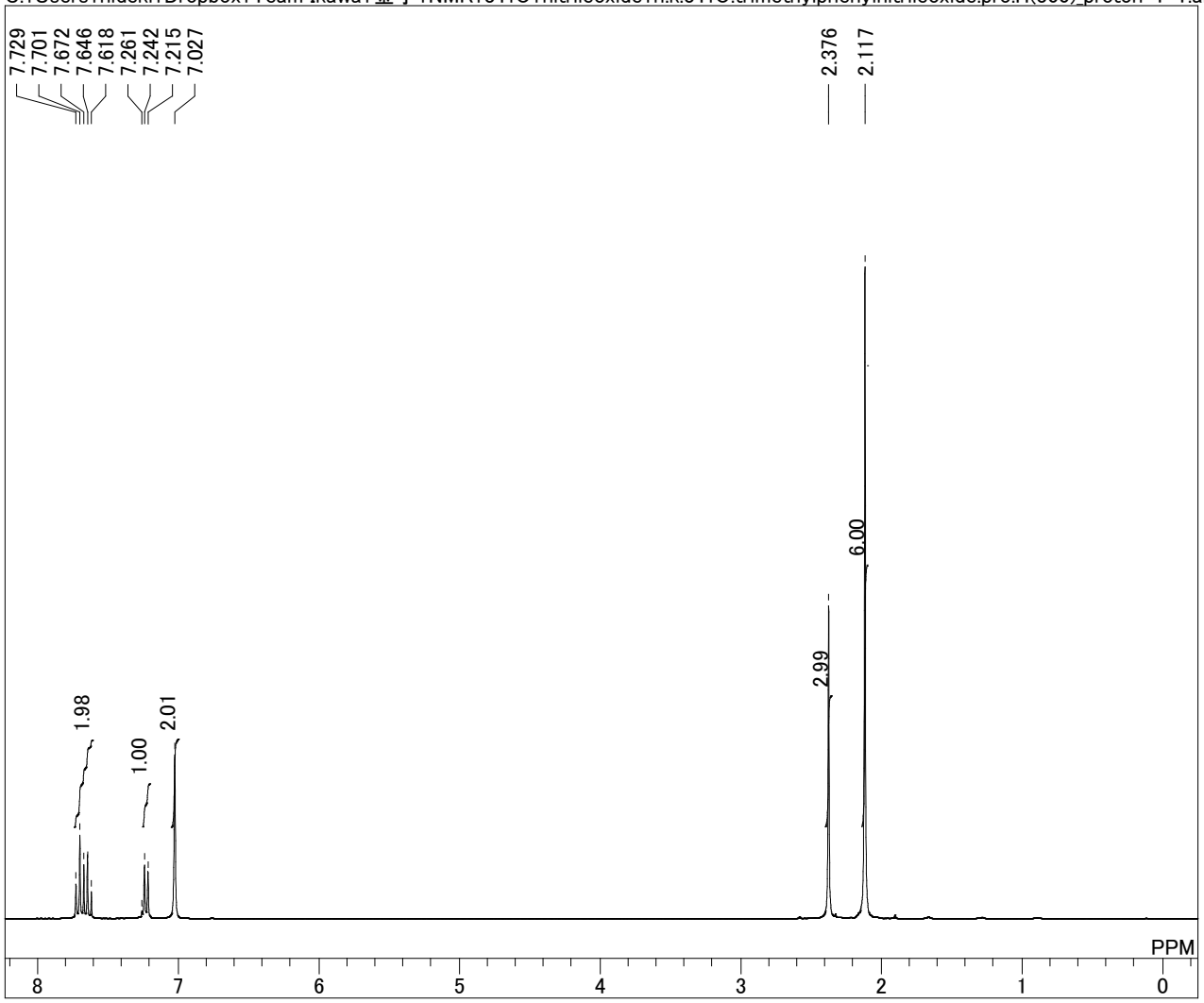


DFILE	h.k.3TfO.cyclohexylazide.dis.l
COMNT	single_pulse
DATIM	14-05-2014 12:09:39
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	13107
FREQU	5656.11 Hz
SCANS	8
ACQTM	2.3174 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	-72.59 ppm
BF	0.12 Hz
RGAIN	40

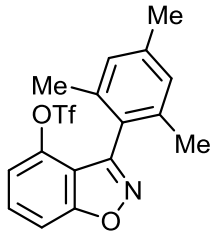


distal-**4g** (Table 1, Entry 4)

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrileoxide¥h.k.3TfO.trimethylphenylnitrileoxide.pro.H(300)_proton-1-1.als



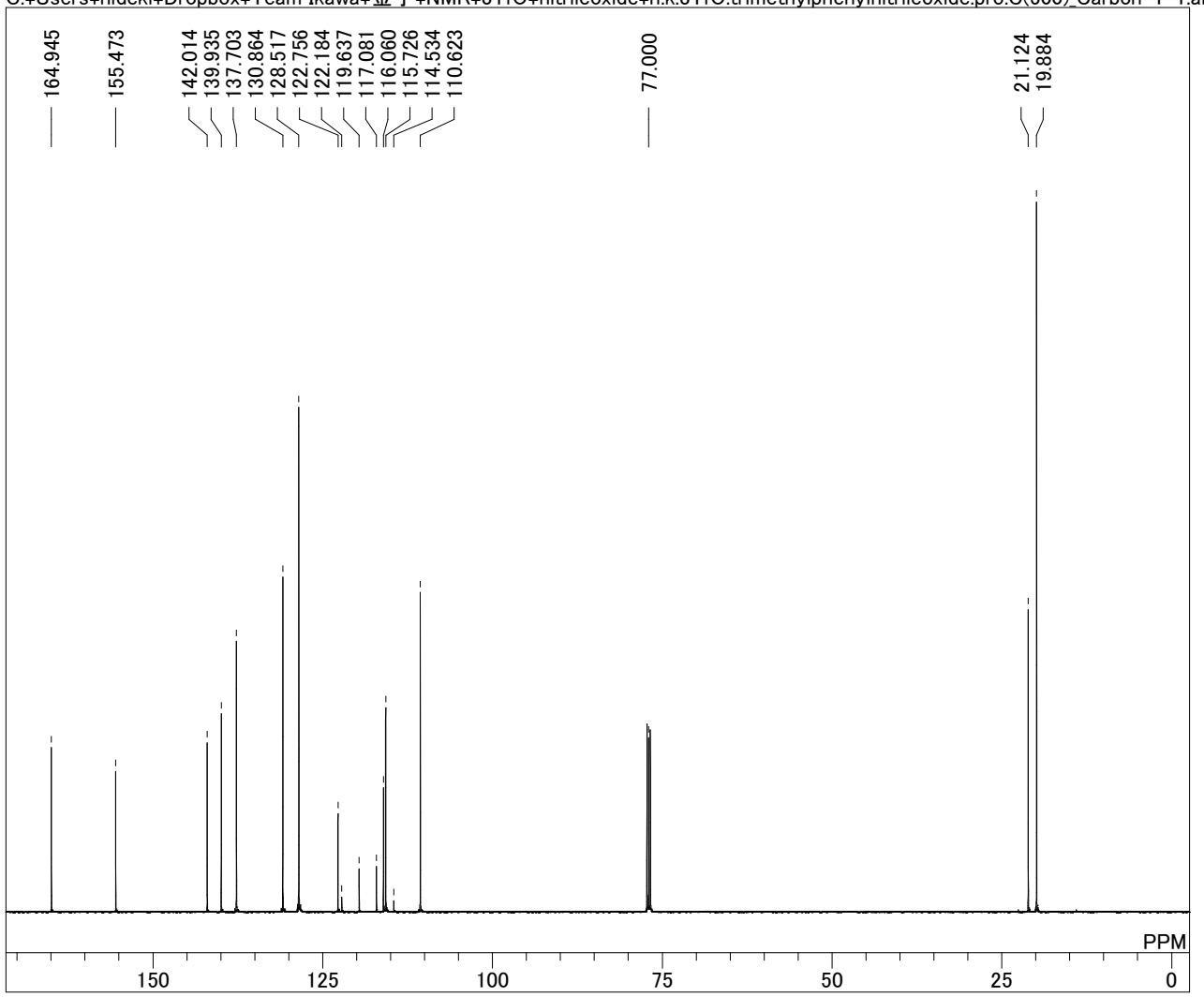
DFILE	h.k.3TfO.trimethylphenylnitril
COMNT	
DATIM	15-05-2014 14:28:14
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	4
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	28



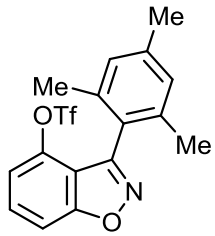
proximal-**10a** (Scheme 3)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrileoxide¥h.k.3TfO.trimethylphenylnitrileoxide.pro.C(500)_Carbon-1-1.als



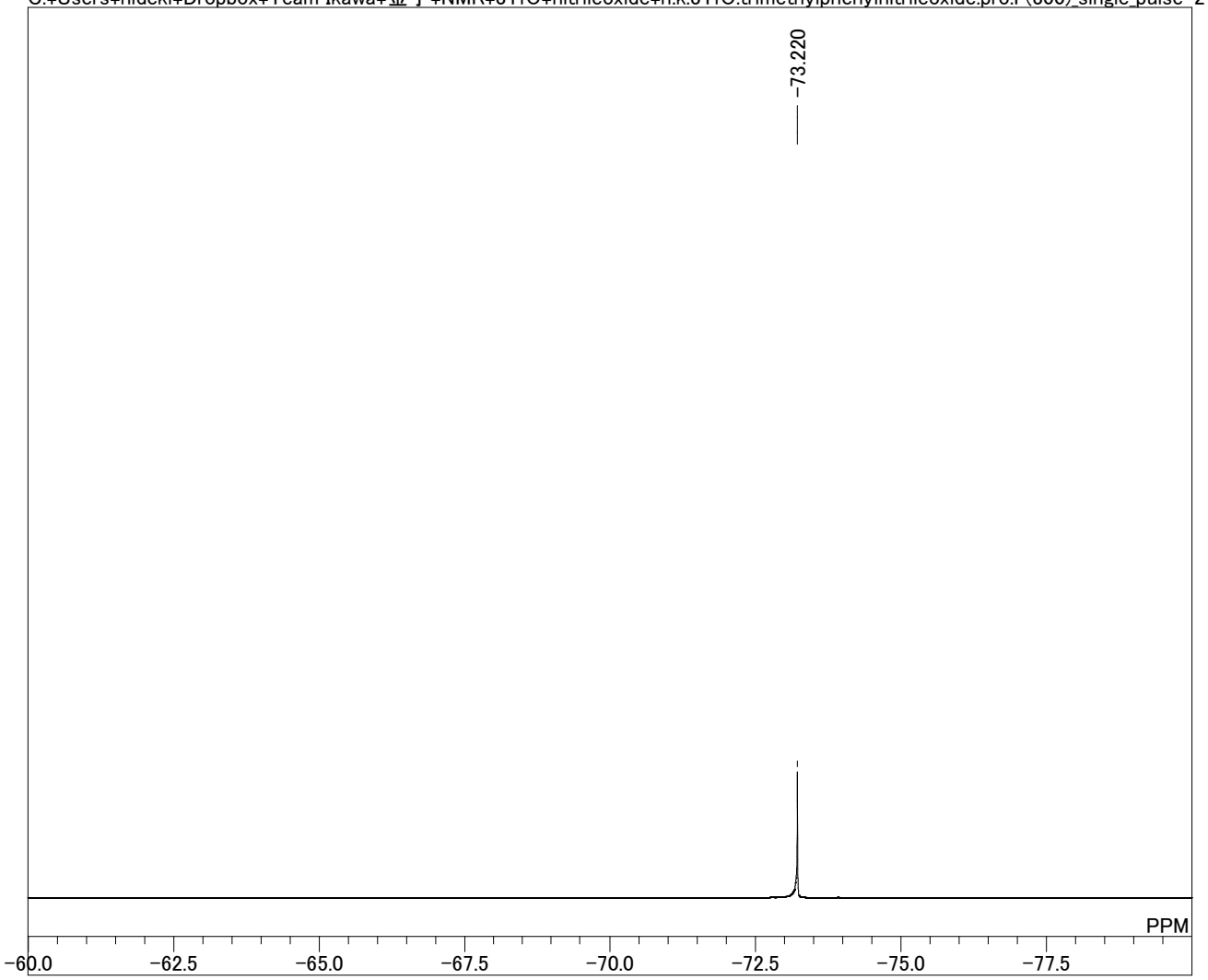
DFILE	h.k.3TfO.trimethylphenylnitril
COMNT	single pulse decoupled gated
DATIM	15-05-2014 15:43:48
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	778
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



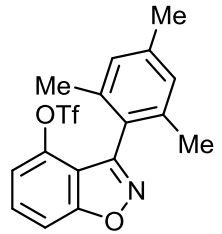
proximal-**10a** (Scheme 3)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrileoxide¥h.k.3TfO.trimethylphenylnitrileoxide.pro.F(300)_single_pulse-2-1.als



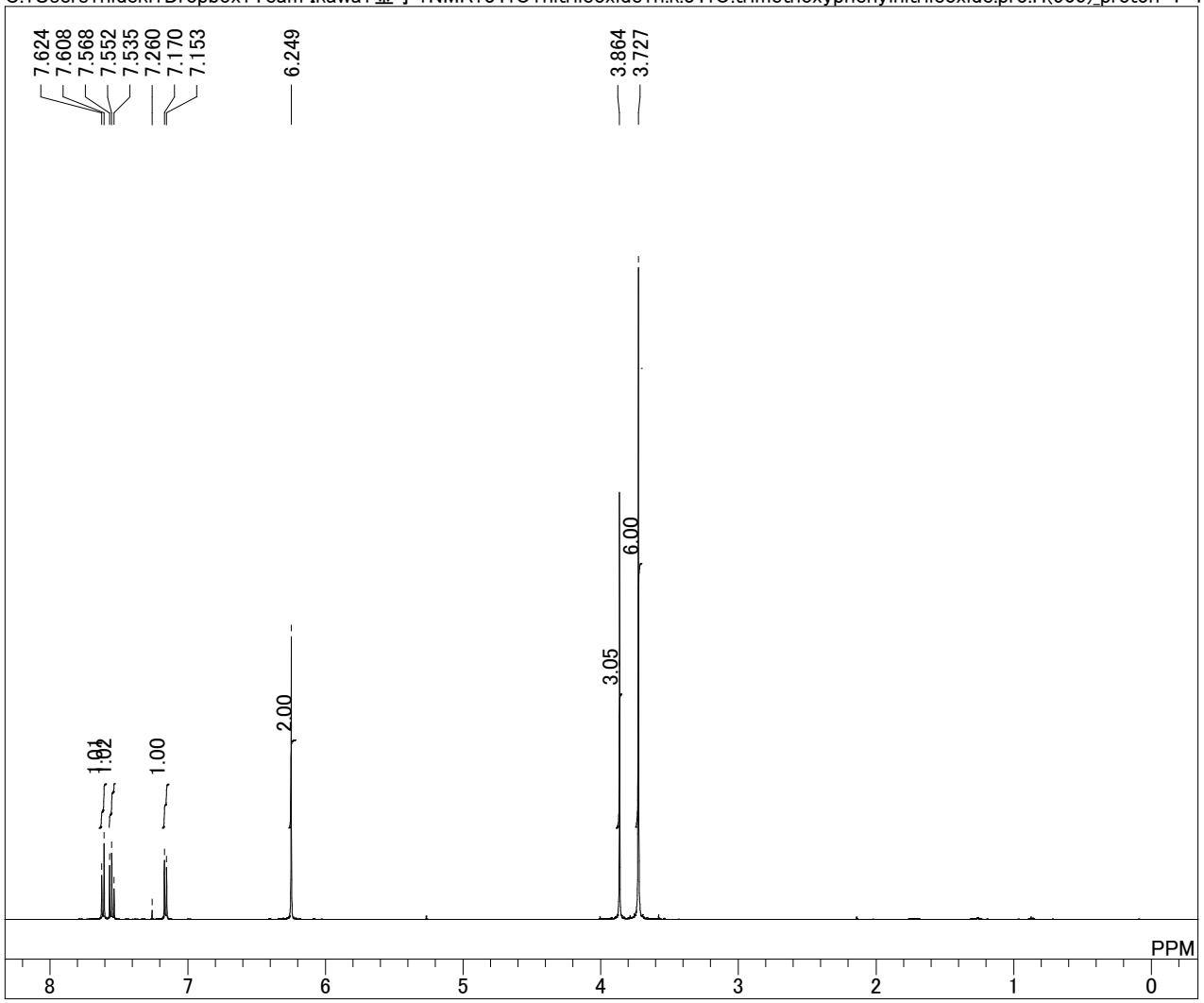
DFILE	h.k.3TfO.trimethylphenylnitril
COMNT	single_pulse
DATIM	15-05-2014 14:16:33
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	13107
FREQU	5656.11 Hz
SCANS	8
ACQTM	2.3174 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	22.1 c
SLVNT	CDCL3
EXREF	-73.22 ppm
BF	0.12 Hz
RGAIN	38



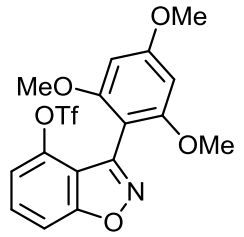
proximal-**10a** (Scheme 3)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrileoxide¥h.k.3TfO.trimethoxyphenylnitrileoxide.pro.H(500)_proton-1-1.als



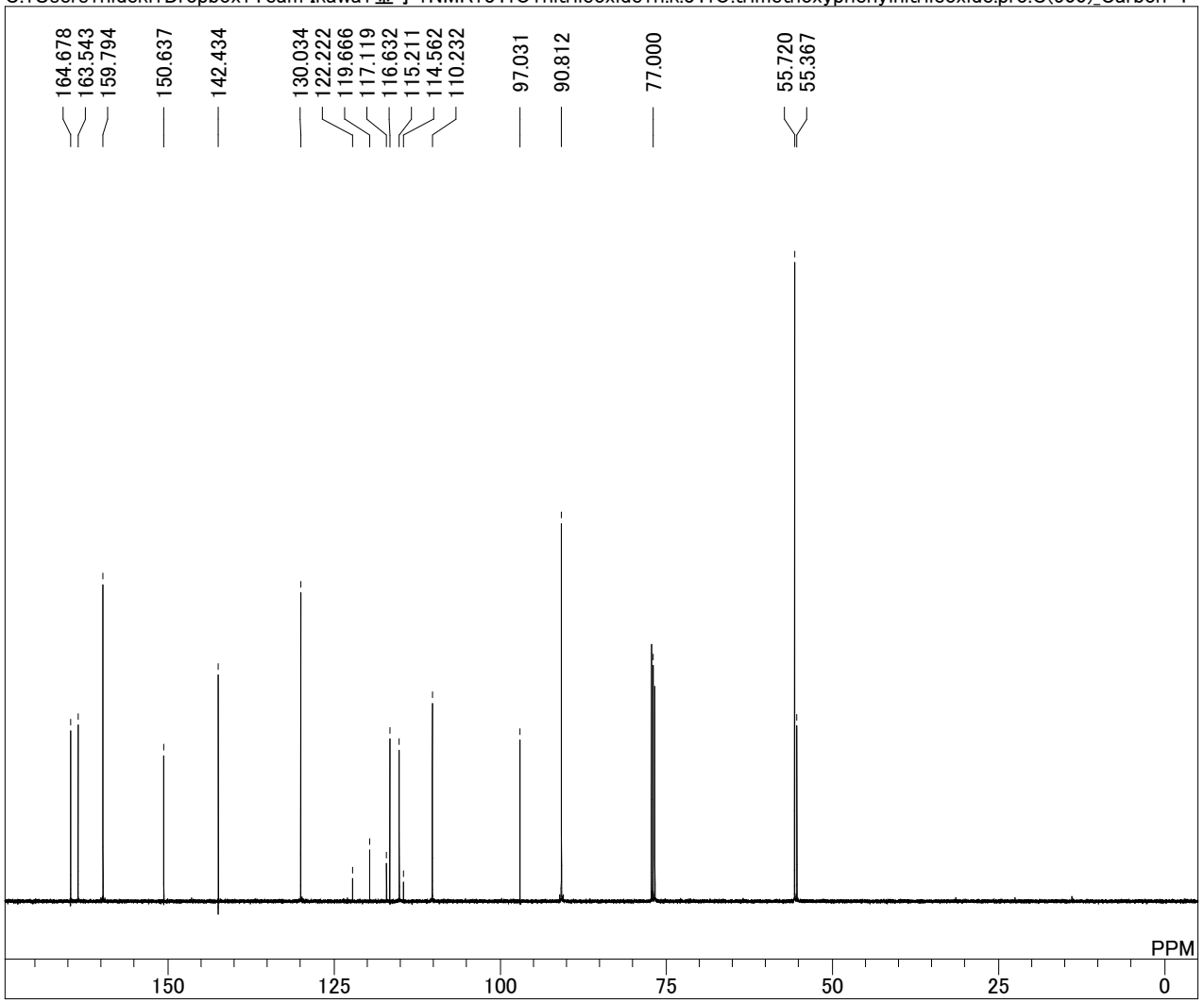
DFILE	h.k.3TfO.trimethoxyphenylnit
COMNT	single_pulse
DATIM	15-05-2014 10:57:46
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	26



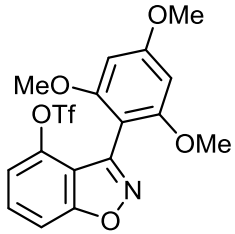
proximal-**10b** (Scheme 3)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrileoxide¥h.k.3TfO.trimethoxyphenylnitrileoxide.pro.C(500)_Carbon-1-1.als



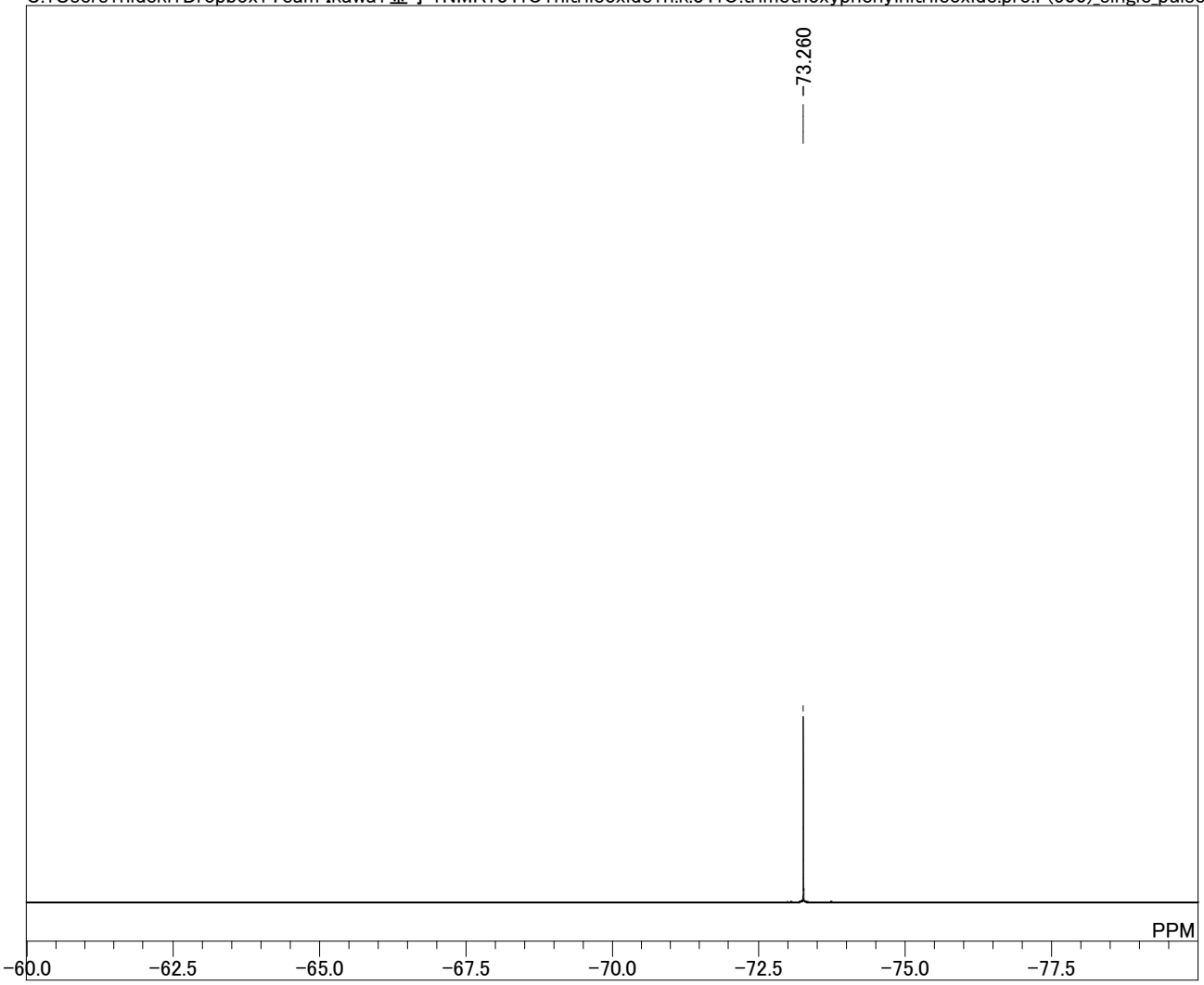
DFILE	h.k.3TfO.trimethoxyphenylnit
COMNT	single pulse decoupled gated
DATIM	15-05-2014 10:23:33
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	545
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



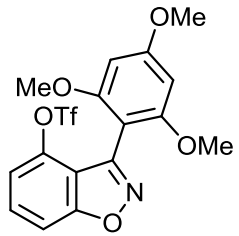
proximal-**10b** (Scheme 3)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥nitrileoxide¥h.k.3TfO.trimethoxyphenylnitrileoxide.pro.F(500)_single_pulse-2-1.als



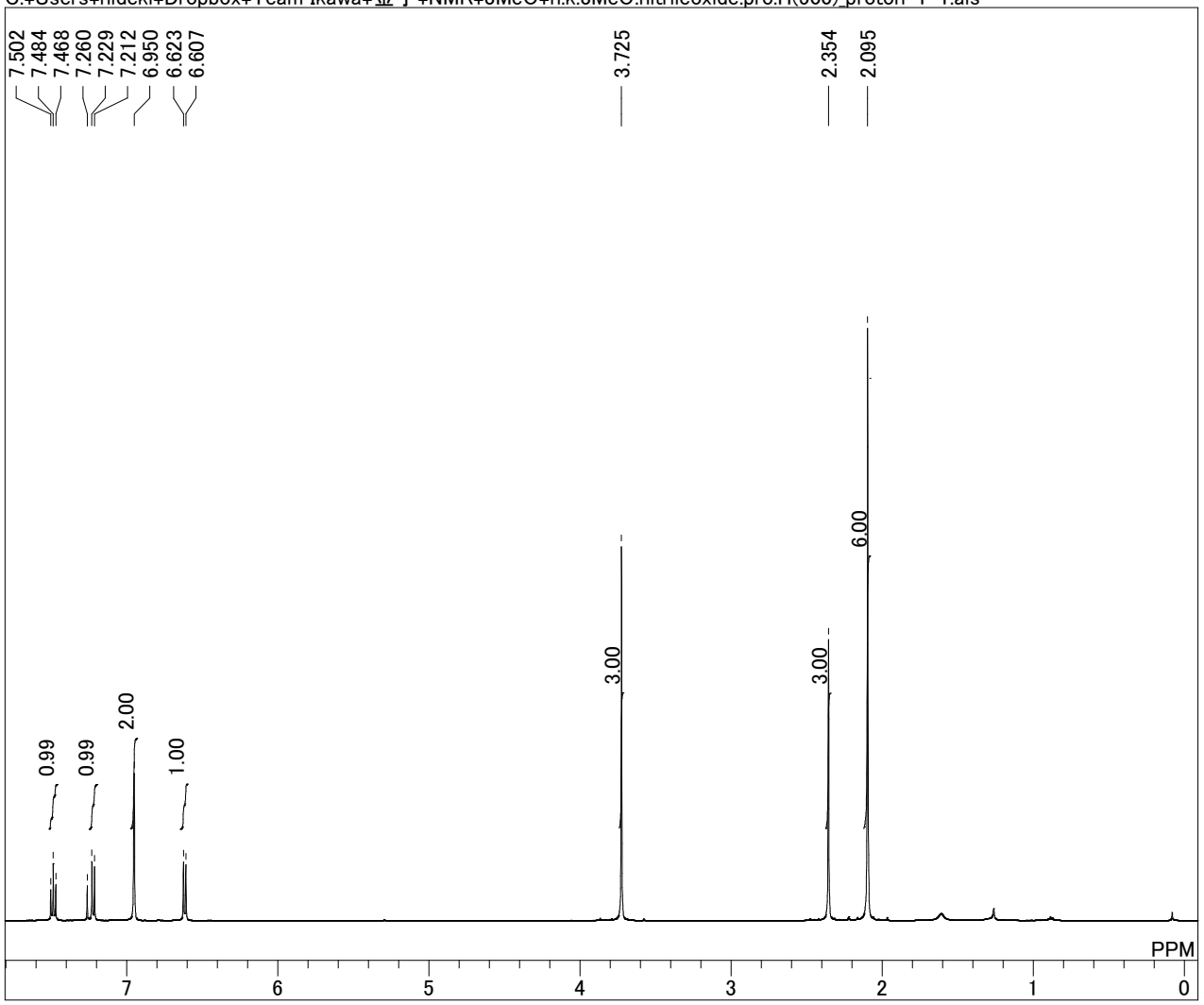
DFILE	h.k.3TfO.trimethoxyphenylnit
COMNT	single_pulse
DATIM	15-05-2014 10:54:19
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	470.58 MHz
OBSET	7.51 KHz
OBFIN	7.41 Hz
POINT	13107
FREQU	9416.20 Hz
SCANS	8
ACQTM	1.3920 sec
PD	5.0000 sec
PW1	5.80 usec
IRNUC	19F
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	-73.26 ppm
BF	0.12 Hz
RGAIN	38



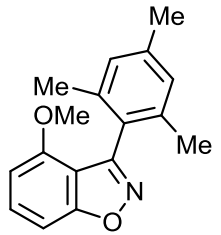
proximal-**10b** (Scheme 3)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3MeO¥h.k.3MeO.nitrileoxide.pro.H(500)_proton-1-1.als



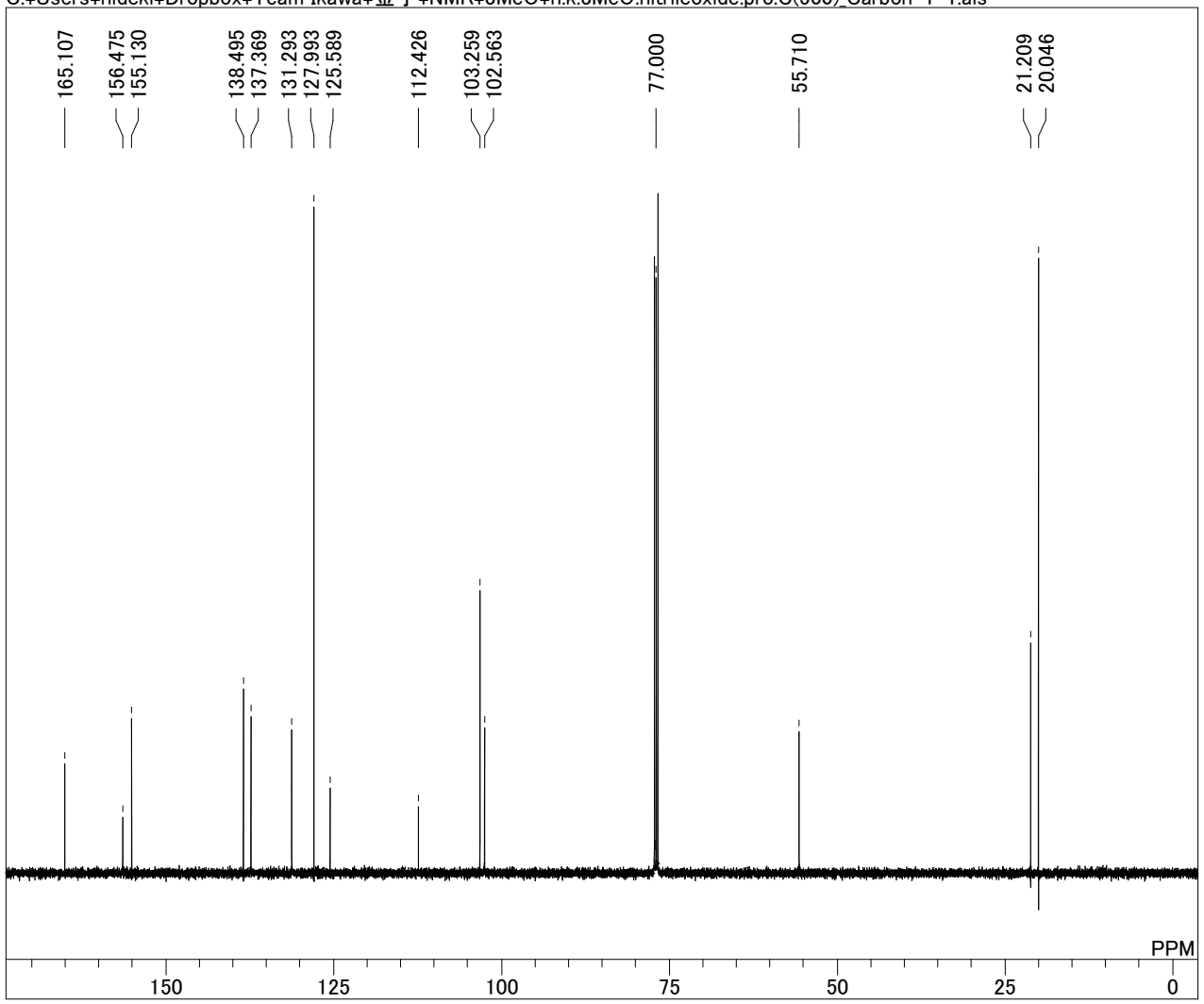
DFILE	h.k.3MeO.nitrileoxide.pro.H(5(
COMNT	single_pulse
DATIM	04-06-2014 18:04:42
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



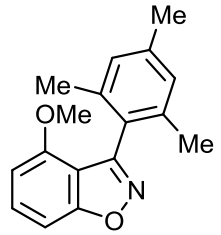
proximal-**10c**

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3MeO¥h.k.3MeO.nitrileoxide.pro.C(500)_Carbon-1-1.als



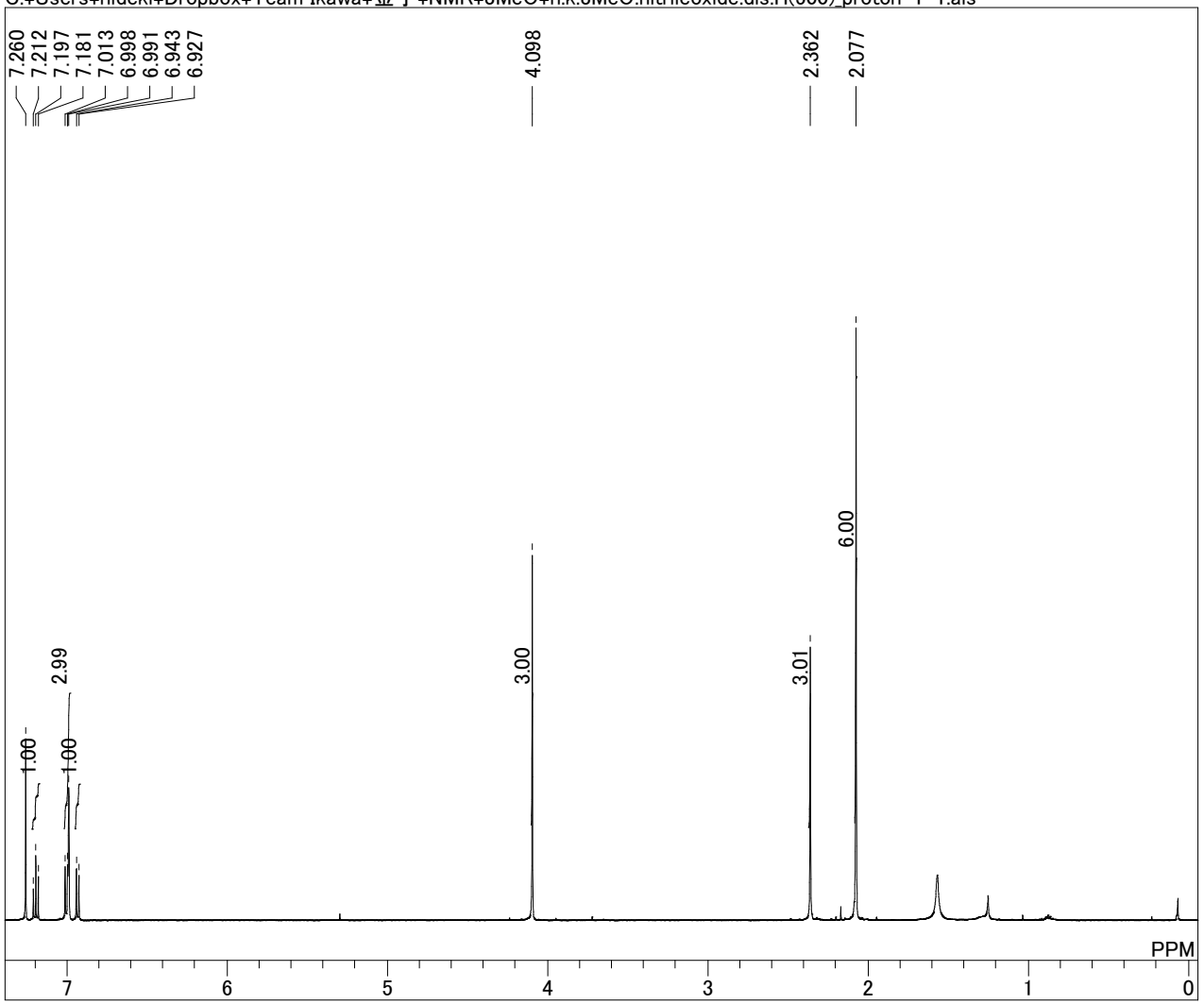
DFILE	h.k.3MeO.nitrileoxide.pro.C(5(
COMNT	single pulse decoupled gated
DATIM	04-06-2014 21:02:50
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	412
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



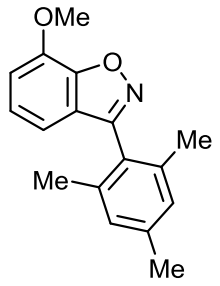
proximal-**10c**

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3MeO¥h.k.3MeO.nitrileoxide.dis.H(500)_proton-1-1.als



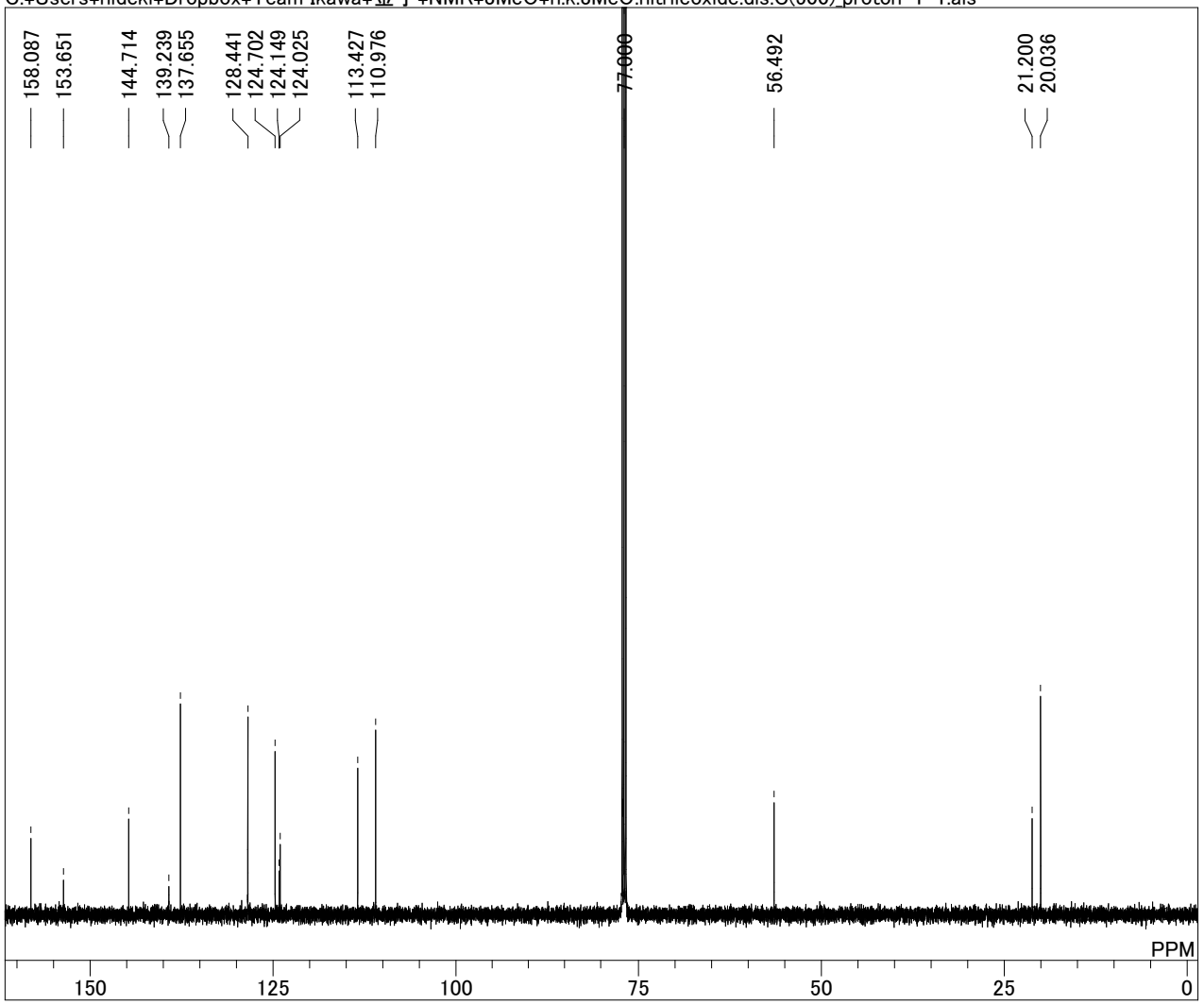
DFILE	h.k.3MeO.nitrileoxide.dis.H(5C
COMNT	single_pulse
DATIM	05-06-2014 00:44:32
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	21.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	50



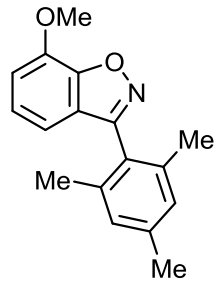
distal-**10c**

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3MeO¥h.k.3MeO.nitrileoxide.dis.C(500)_proton-1-1.als



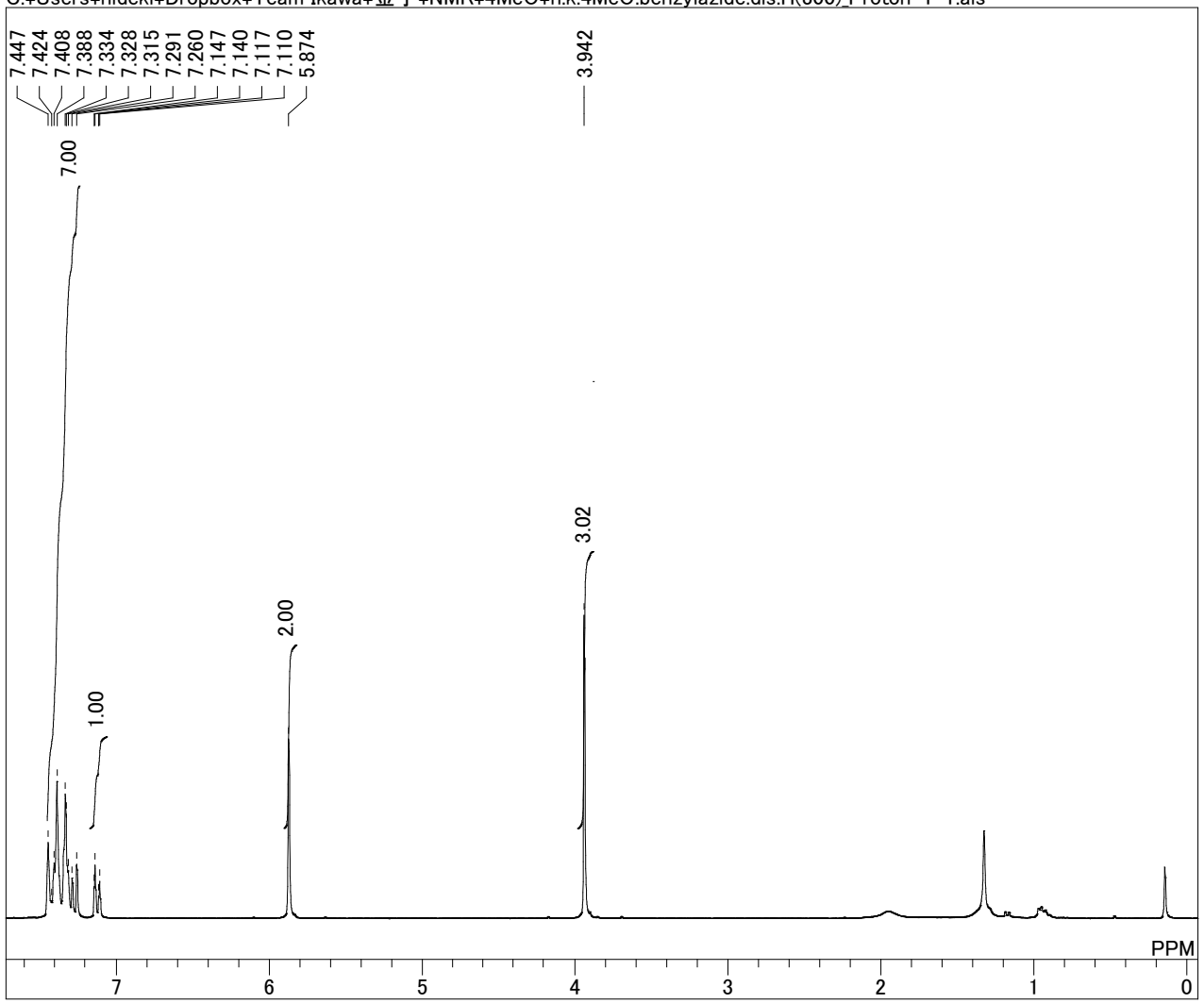
DFILE	h.k.3MeO.nitrileoxide.dis.C(5(
COMNT	single pulse decoupled gated
DATIM	05-06-2014 00:48:24
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	2159
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



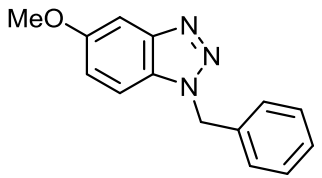
distal-**10c**

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4MeO¥h.k.4MeO.benzylazide.dis.H(300)_Proton-1-1.als



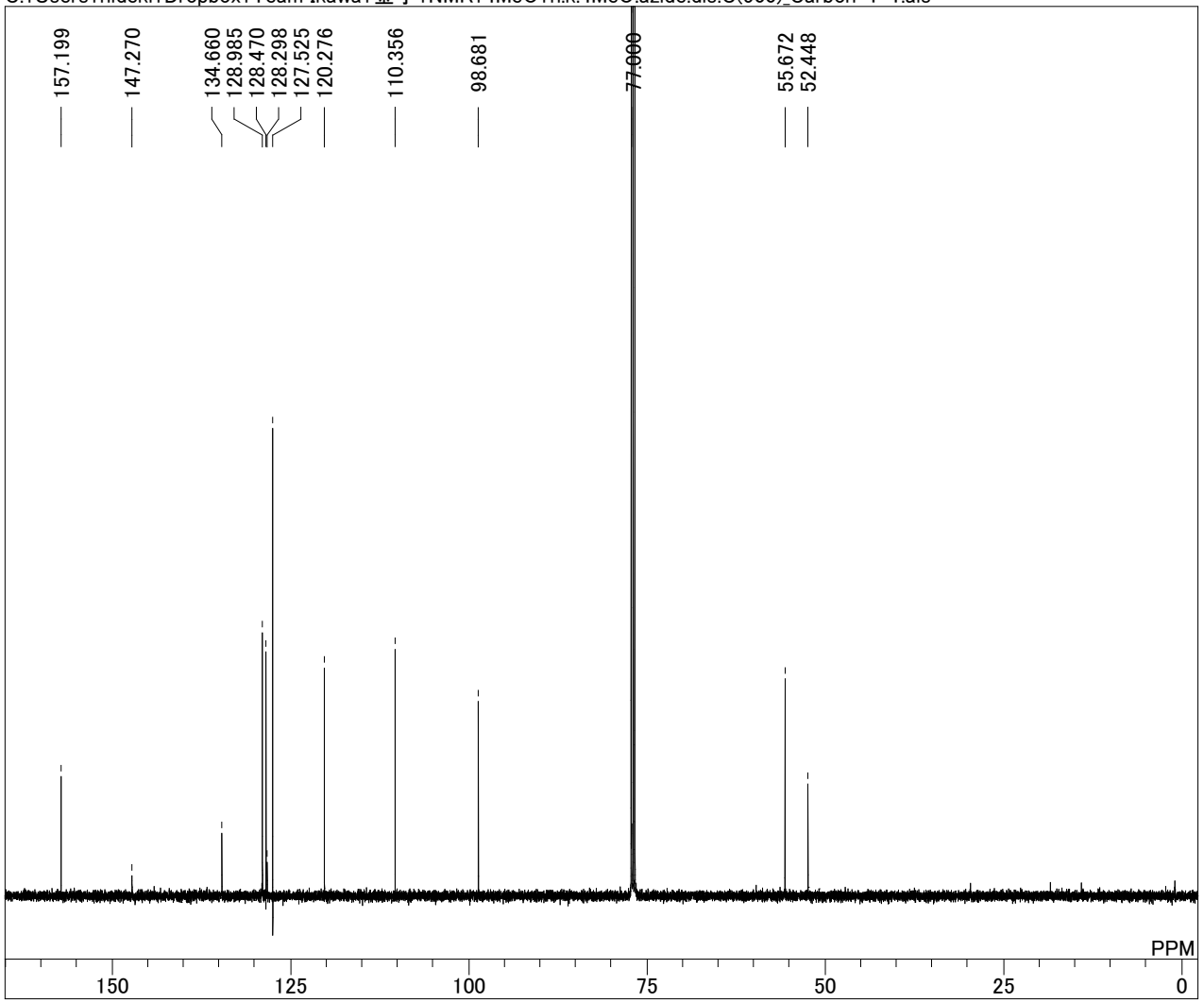
DFILE	h.k.4MeO.benzylazide.dis.H(3
COMNT	single_pulse
DATIM	30-06-2014 14:16:12
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	42



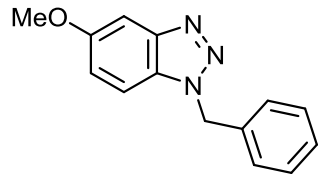
distal-**12a** (Table 2, Entry 1)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4MeO¥h.k.4MeO.azide.dis.C(500)_Carbon-1-1.als



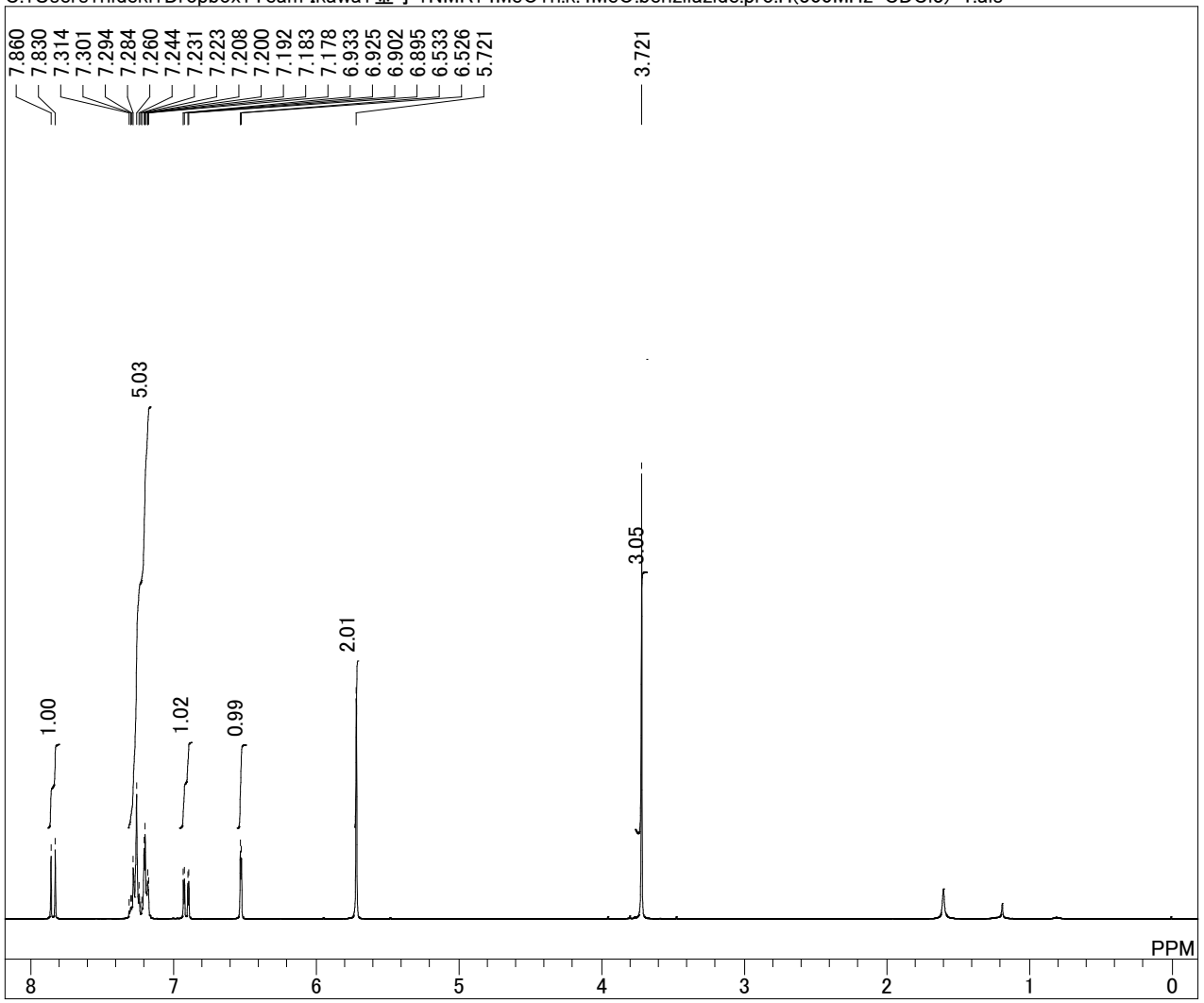
DFILE	h.k.4MeO.azide.dis.C(500)_Ca
COMNT	single pulse decoupled gated
DATIM	10-06-2014 20:36:37
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1674
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



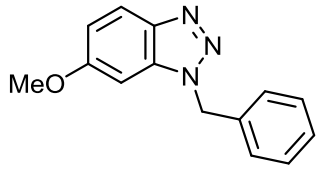
distal-**12a** (Table 2, Entry 1)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4MeO¥h.k.4MeO.benzilazide.pro.H(300MHz-CDCl3)-1.als



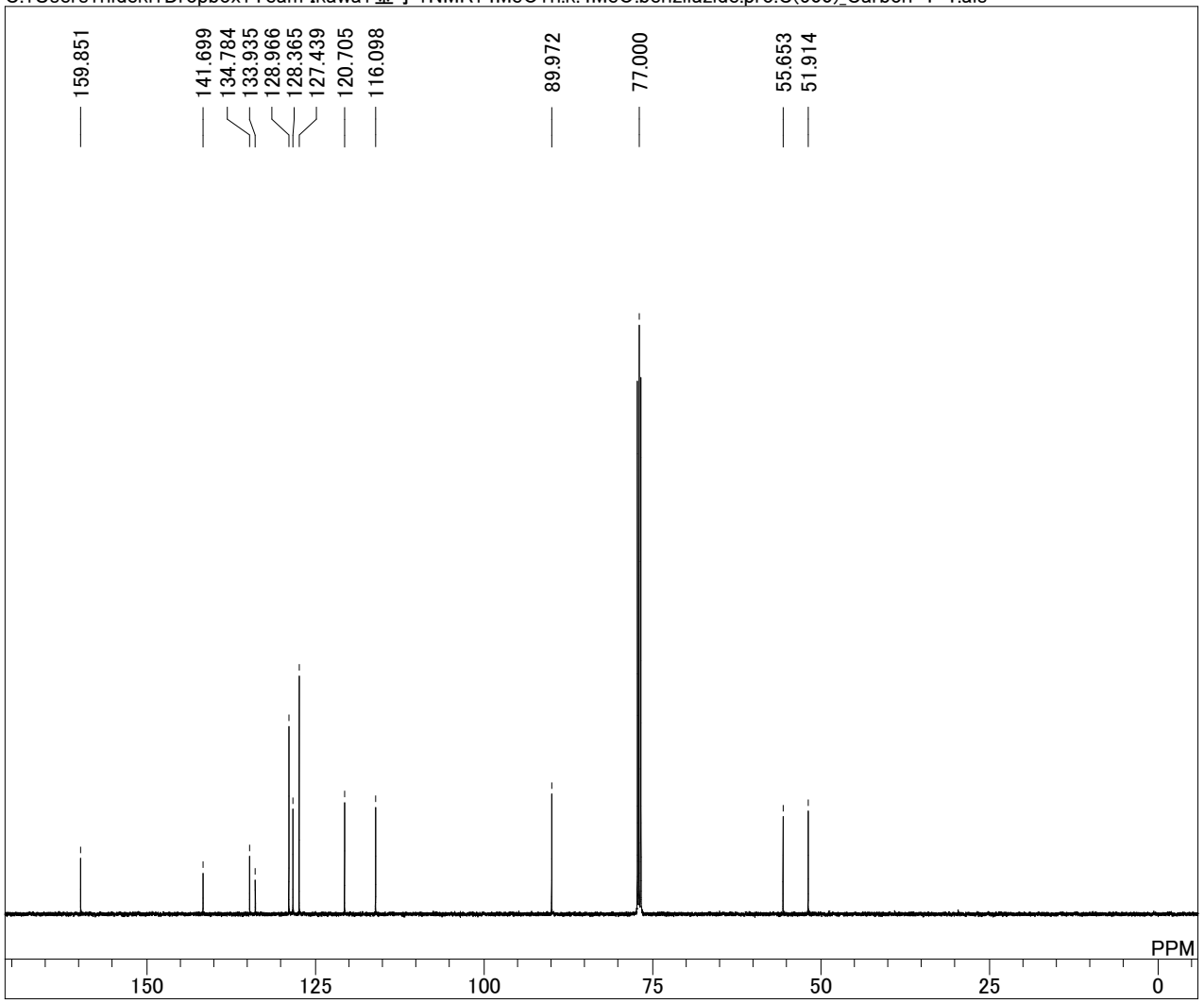
DFILE	h.k.4MeO.benzilazide.pro.H(3(
COMNT	single_pulse
DATIM	06-08-2013 10:48:45
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



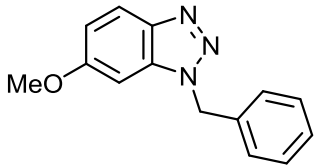
proximal-**12a** (Table 2, Entry 1)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4MeO¥h.k.4MeO.benzilazide.pro.C(500)_Carbon-1-1.als



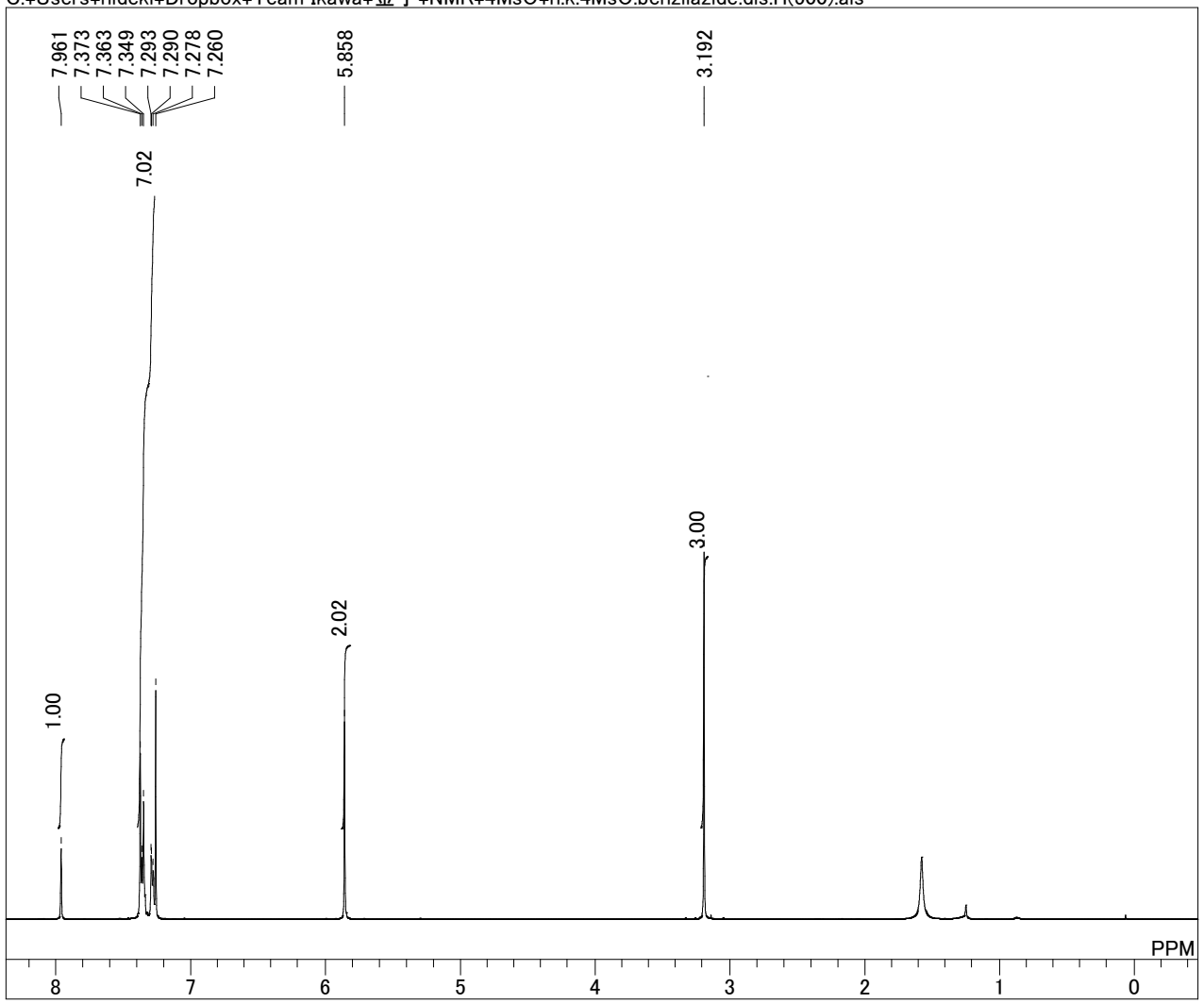
DFILE	h.k.4MeO.benzilazide.pro.C(5(
COMNT	single pulse decoupled gated
DATIM	06-08-2013 13:15:00
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	900
ACQTM	0.8336 sec
PD	2.5000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



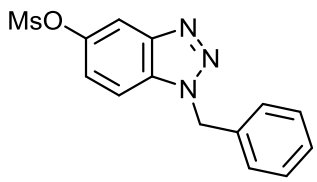
proximal-**12a** (Table 2, Entry 1)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4MsO¥h.k.4MsO.benzilazide.dis.H(500).als



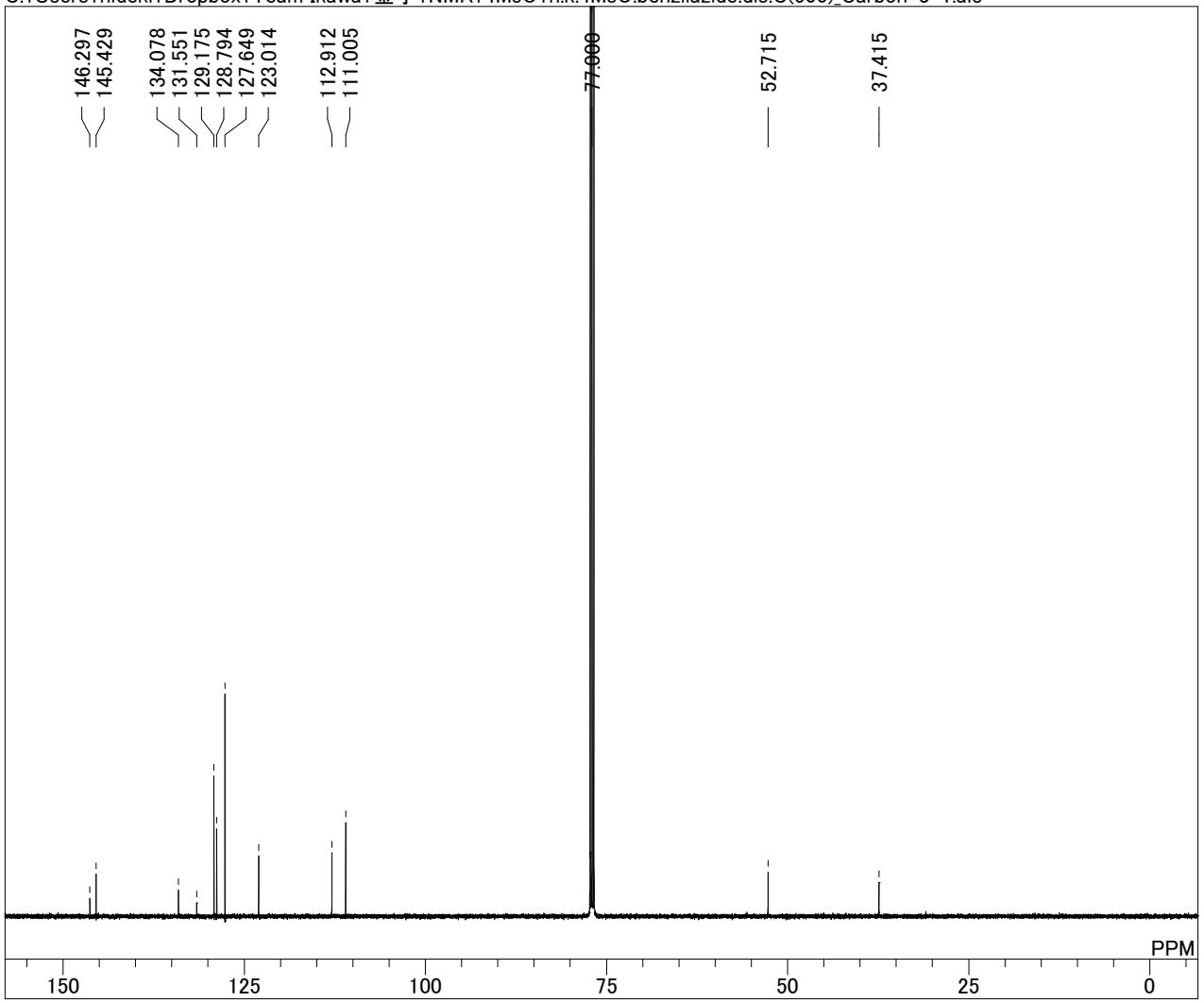
DFILE	h.k.4MsO.benzilazide.dis.H(50
COMNT	single_pulse
DATIM	23-06-2014 09:54:25
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	19.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	52



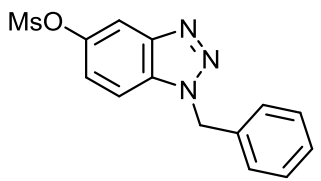
distal-**12b** (Table 2, Entry 2)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4MsO¥h.k.4MsO.benzilazide.dis.C(500)_Carbon-3-1.als



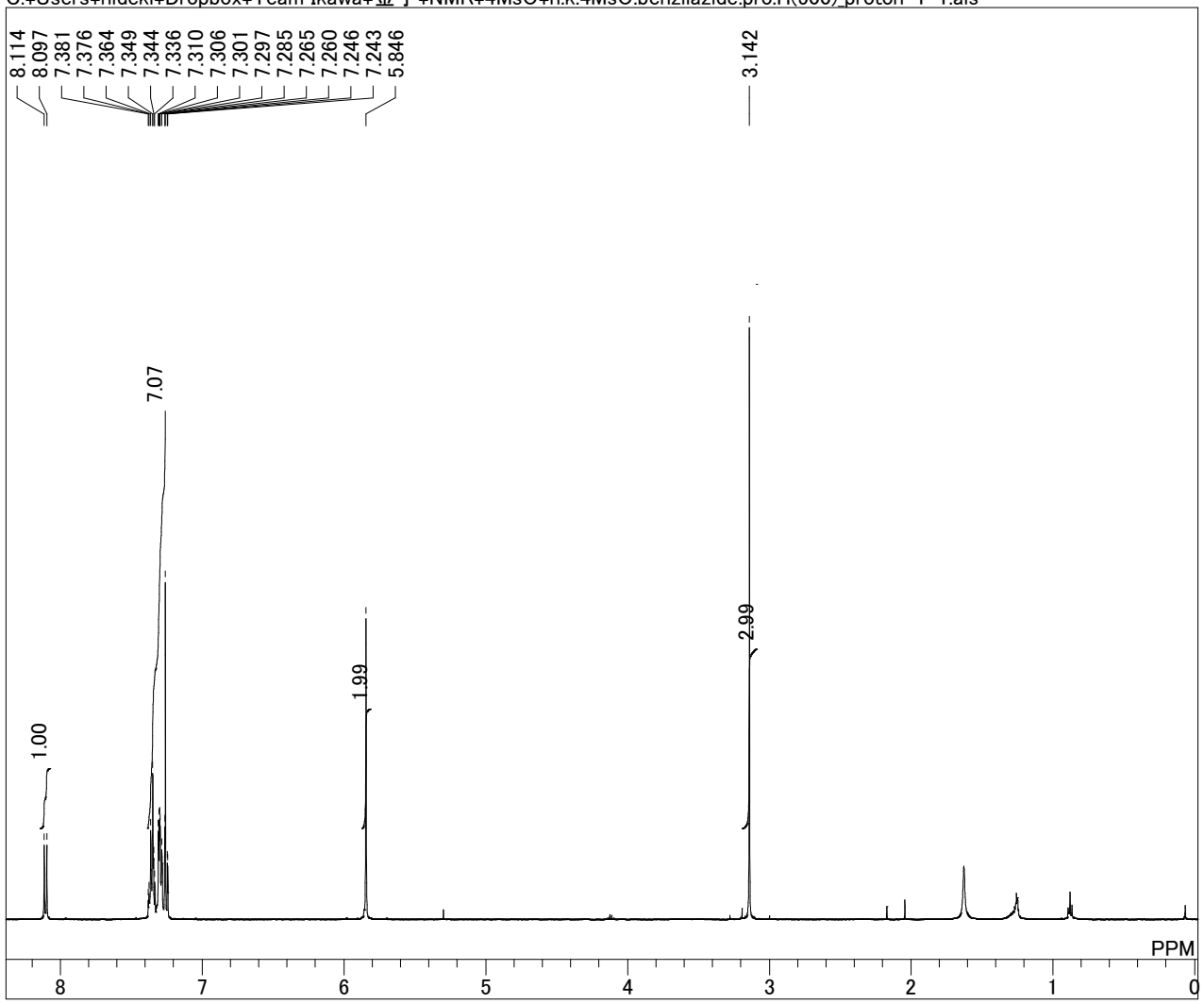
DFILE	h.k.4MsO.benzilazide.dis.C(5(
COMNT	single pulse decoupled gated
DATIM	22-06-2014 00:03:03
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	13000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



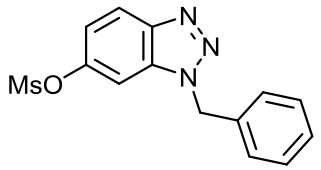
distal-**12b** (Table 2, Entry 2)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4MsO¥h.k.4MsO.benzilazide.pro.H(500)_proton-1-1.als



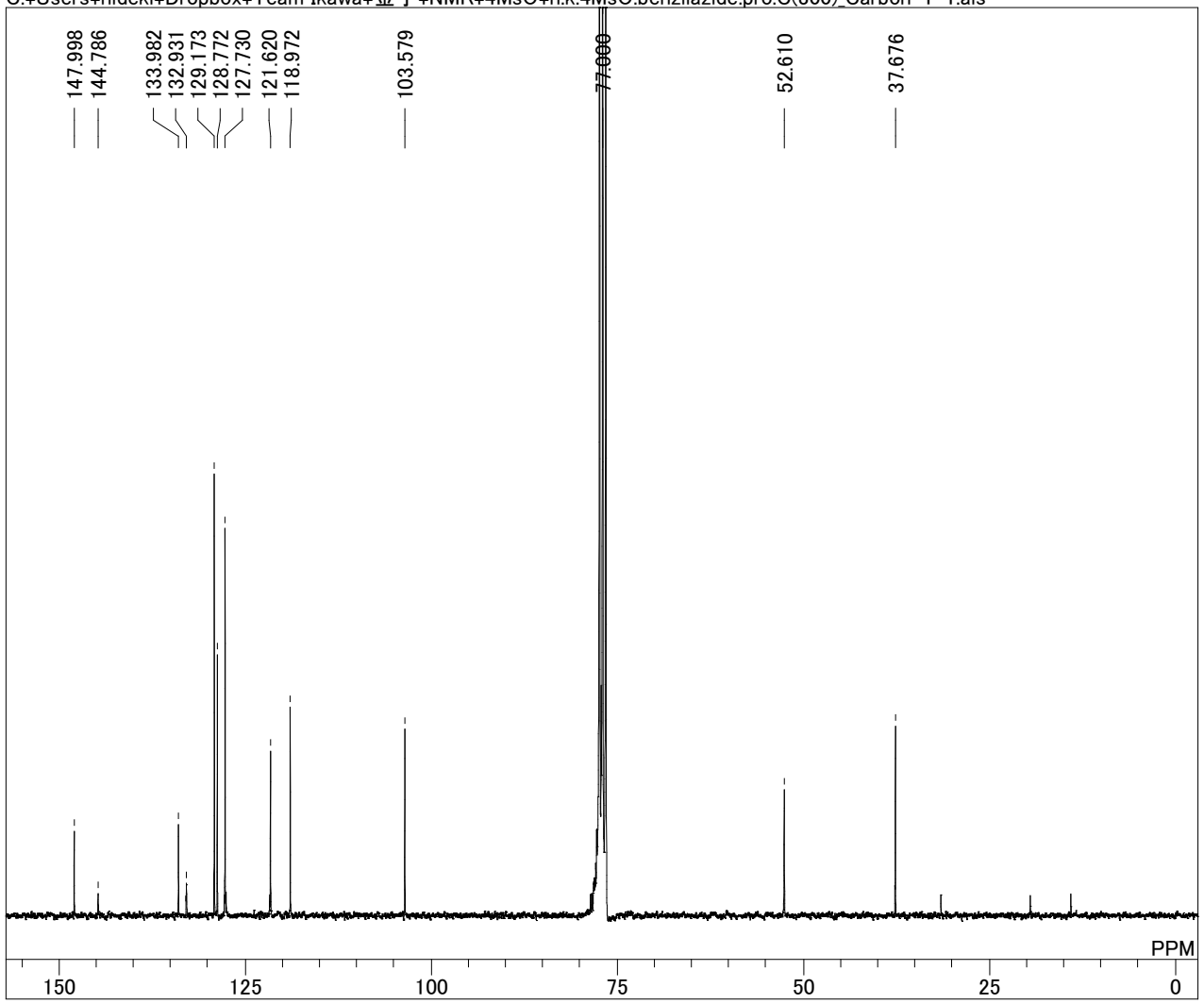
DFILE	h.k.4MsO.benzilazide.pro.H(5(
COMNT	single_pulse
DATIM	19-06-2014 10:40:49
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	46
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	19.2 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	50



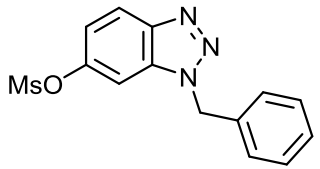
proximal-**12b** (Table 2, Entry 2)

single pulse decoupled gated NOE

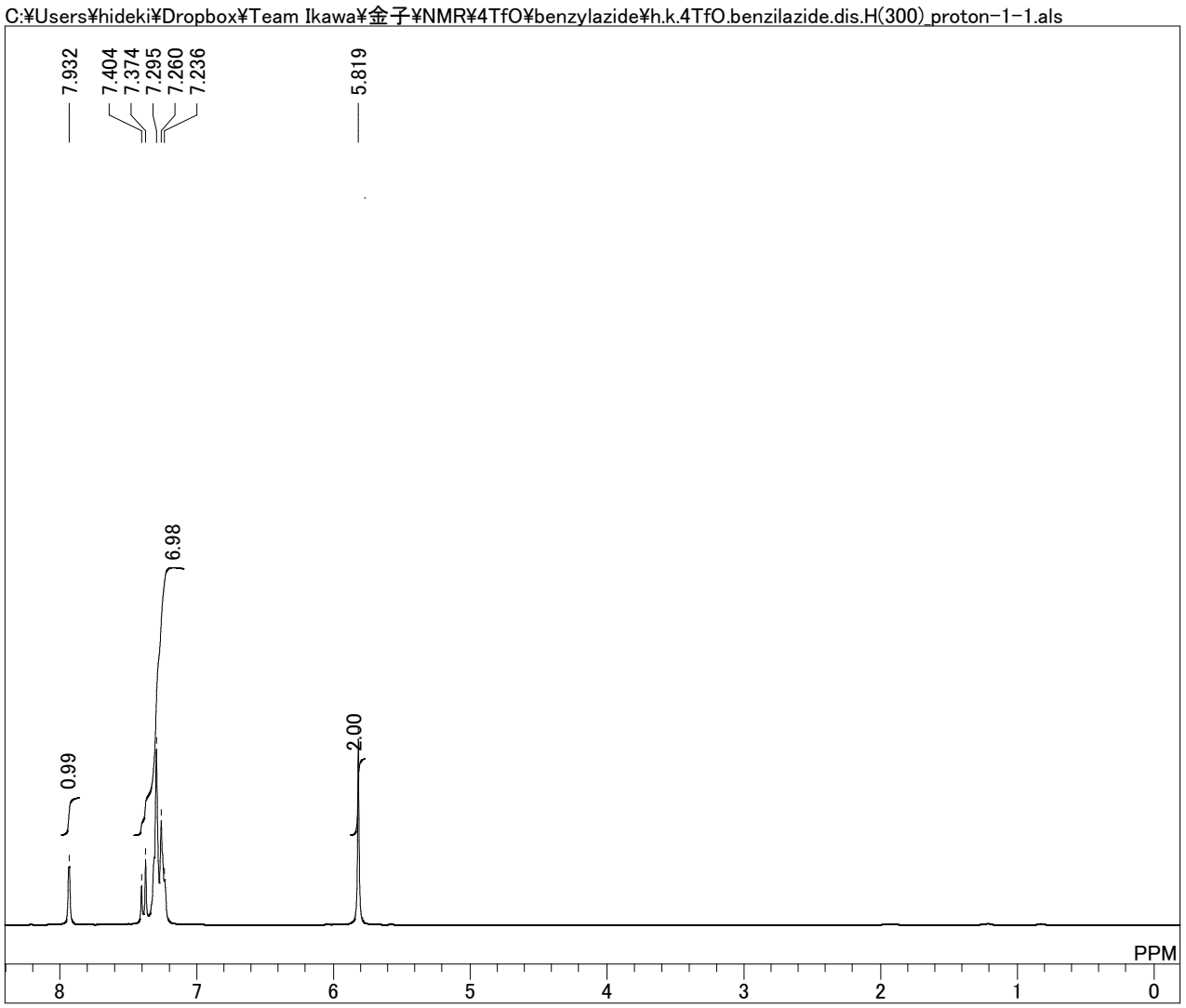
C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4MsO¥h.k.4MsO.benzilazide.pro.C(300)_Carbon-1-1.als



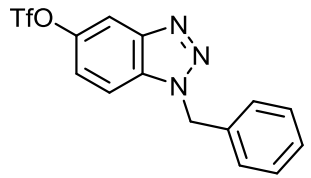
DFILE	h.k.4MsO.benzilazide.pro.C(3(
COMNT	single pulse decoupled gated
DATIM	20-06-2014 00:27:41
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.39 Hz
SCANS	7310
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



proximal-**12b** (Table 2, Entry 2)



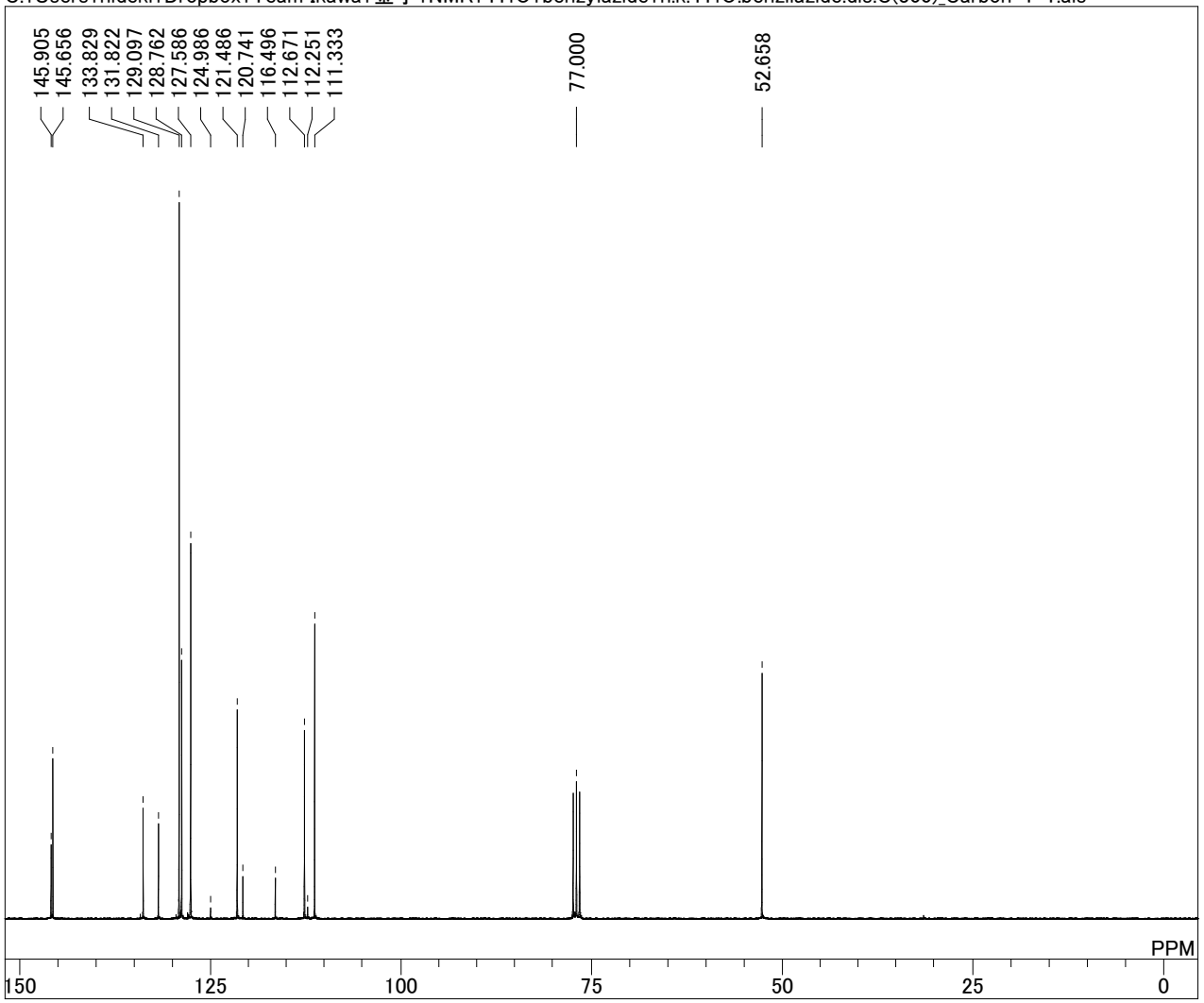
DFILE h.k.4TfO.benzilazide.dis.H(30(
COMNT
DATIM 14-05-2014 18:15:38
OBNUC 1H
EXMOD proton.jxp
OBFRQ 300.53 MHz
OBSET 1.15 KHz
OBFIN 8.57 Hz
POINT 13107
FREQU 4508.57 Hz
SCANS 8
ACQTM 2.9072 sec
PD 2.0000 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 32



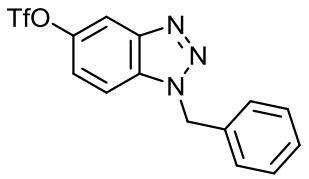
distal-**12c** (Table 2, Entry 3, 4)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥benzylazide¥h.k.4TfO.benzilazide.dis.C(300)_Carbon-1-1.als



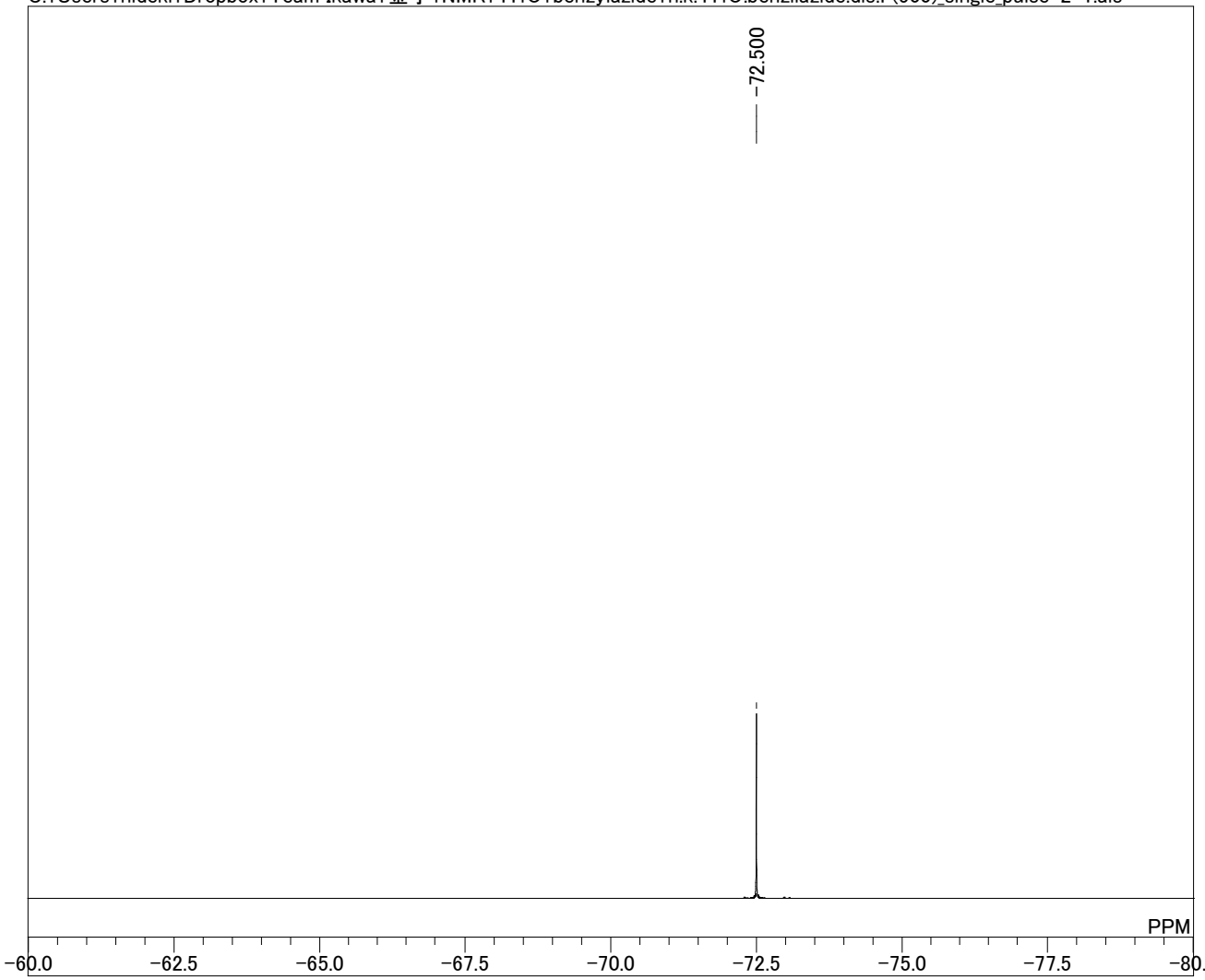
DFILE	h.k.4TfO.benzilazide.dis.C(30(
COMNT	single pulse decoupled gated
DATIM	15-05-2014 05:13:45
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.39 Hz
SCANS	3381
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



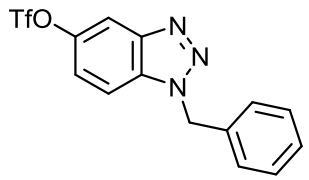
distal-**12c** (Table 2, Entry 3, 4)

single_pulse

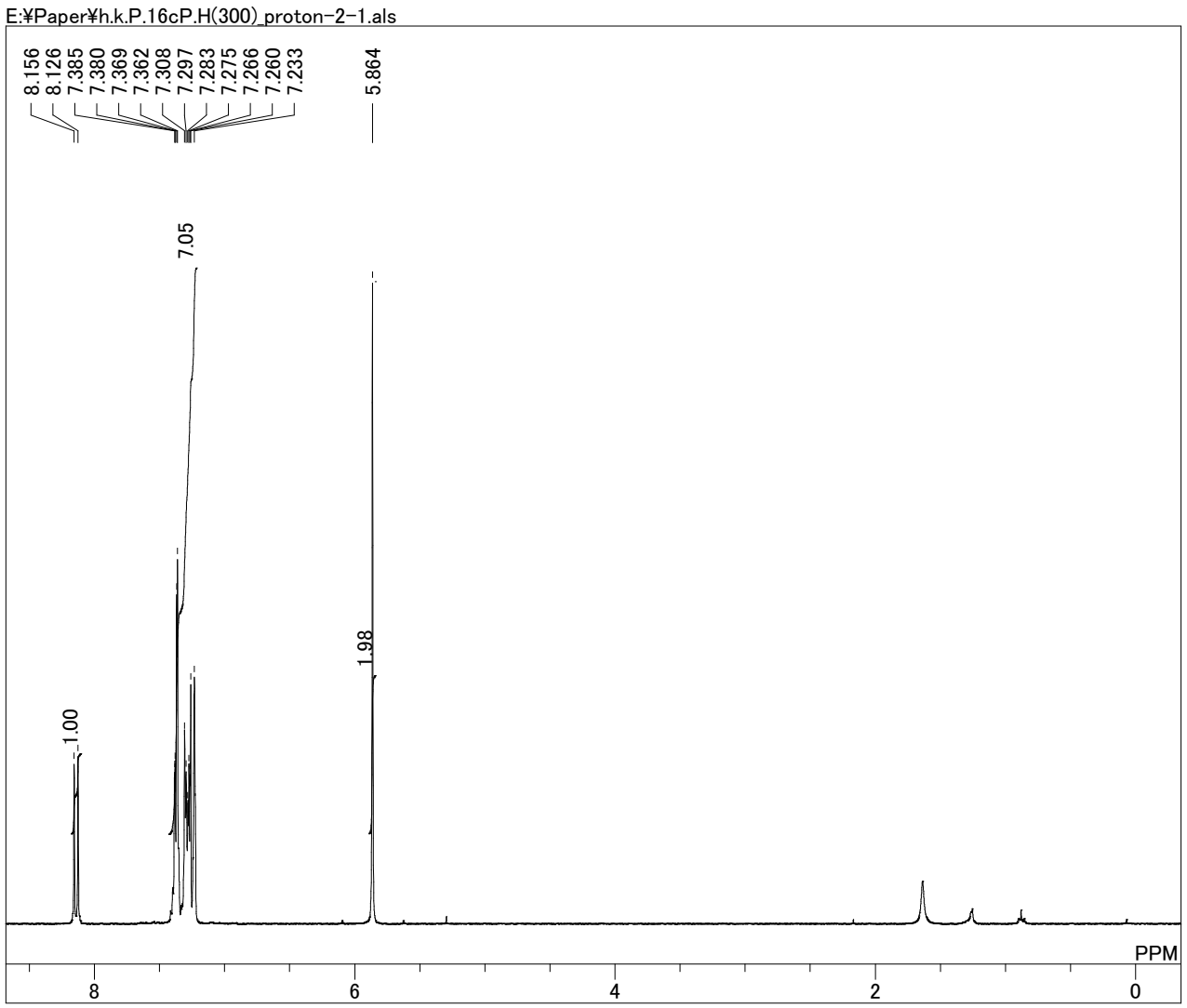
C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥benzylazide¥h.k.4TfO.benzilazide.dis.F(500)_single_pulse-2-1.als



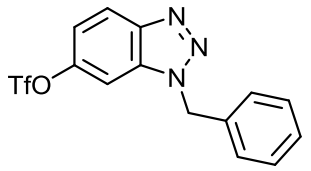
DFILE	h.k.4TfO.benzilazide.dis.F(500
COMNT	single_pulse
DATIM	14-05-2014 18:23:36
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	470.58 MHz
OBSET	7.51 KHz
OBFIN	7.41 Hz
POINT	13107
FREQU	9416.20 Hz
SCANS	8
ACQTM	1.3920 sec
PD	5.0000 sec
PW1	5.80 usec
IRNUC	19F
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	-72.50 ppm
BF	1.20 Hz
RGAIN	38



distal-**12c** (Table 2, Entry 3, 4)



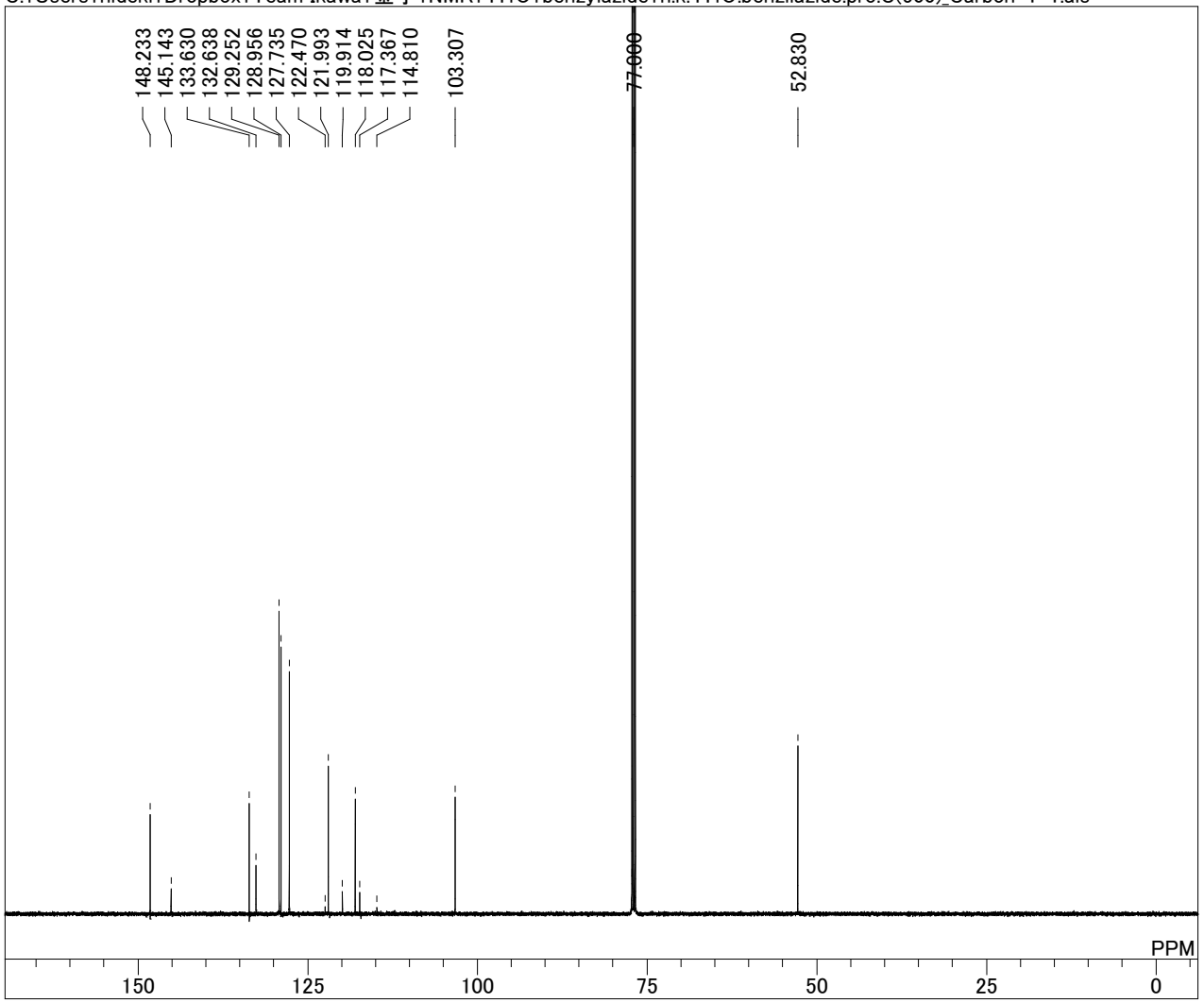
DFILE	h.k.P.16cP.H(300)_proton-2-
COMNT	
DATIM	20-05-2014 11:22:26
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	42



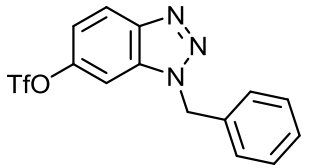
proximal-**12c** (Table 2, Entry 3, 4)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥benzylazide¥h.k.4TfO.benzilazide.pro.C(500)_Carbon-1-1.als



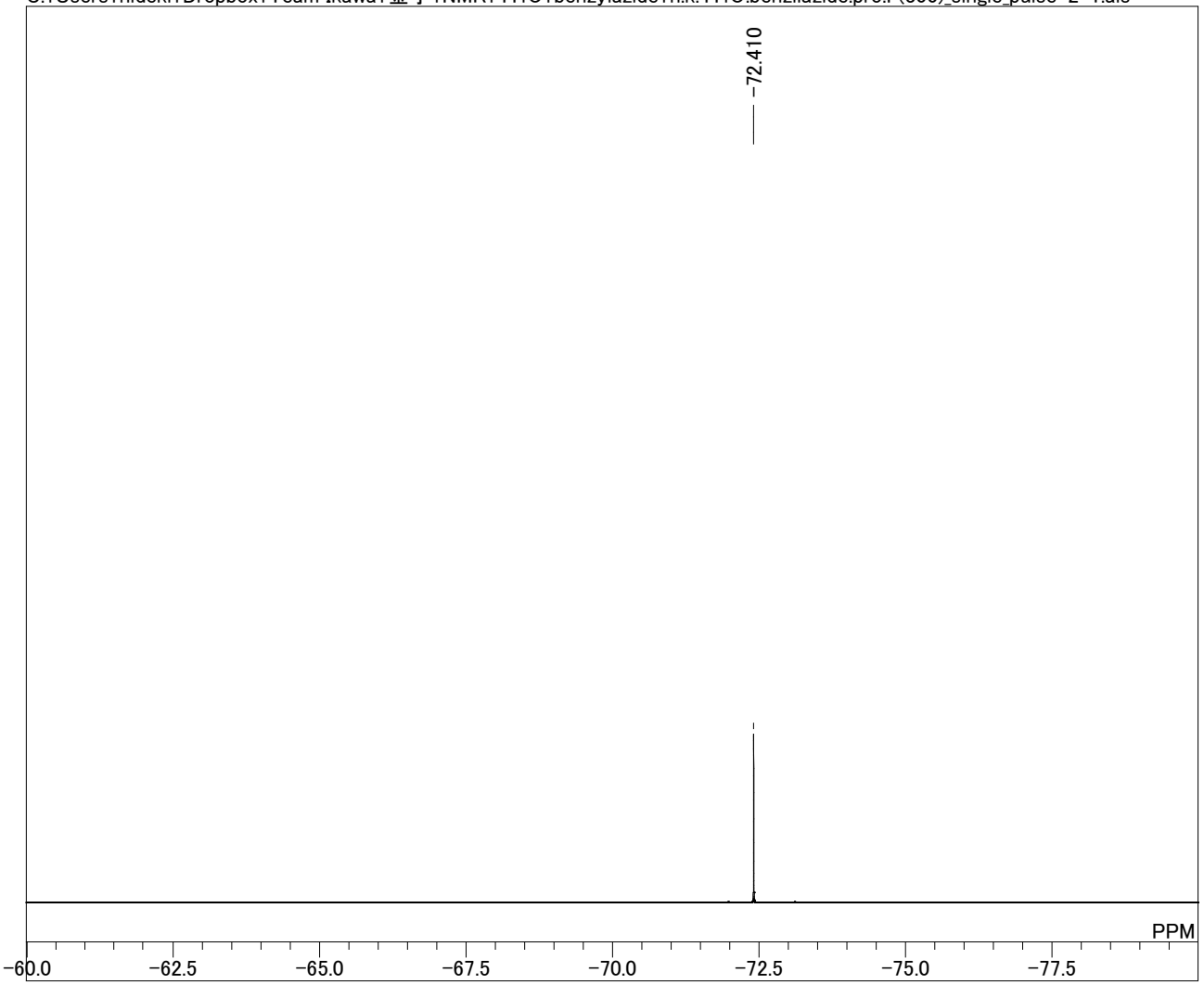
DFILE	h.k.4TfO.benzilazide.pro.C(50
COMNT	single pulse decoupled gated
DATIM	20-05-2014 14:58:29
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1134
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



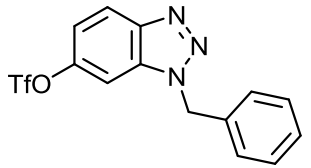
proximal-**12c** (Table 2, Entry 3, 4)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥benzylazide¥h.k.4TfO.benzilazide.pro.F(300)_single_pulse-2-1.als



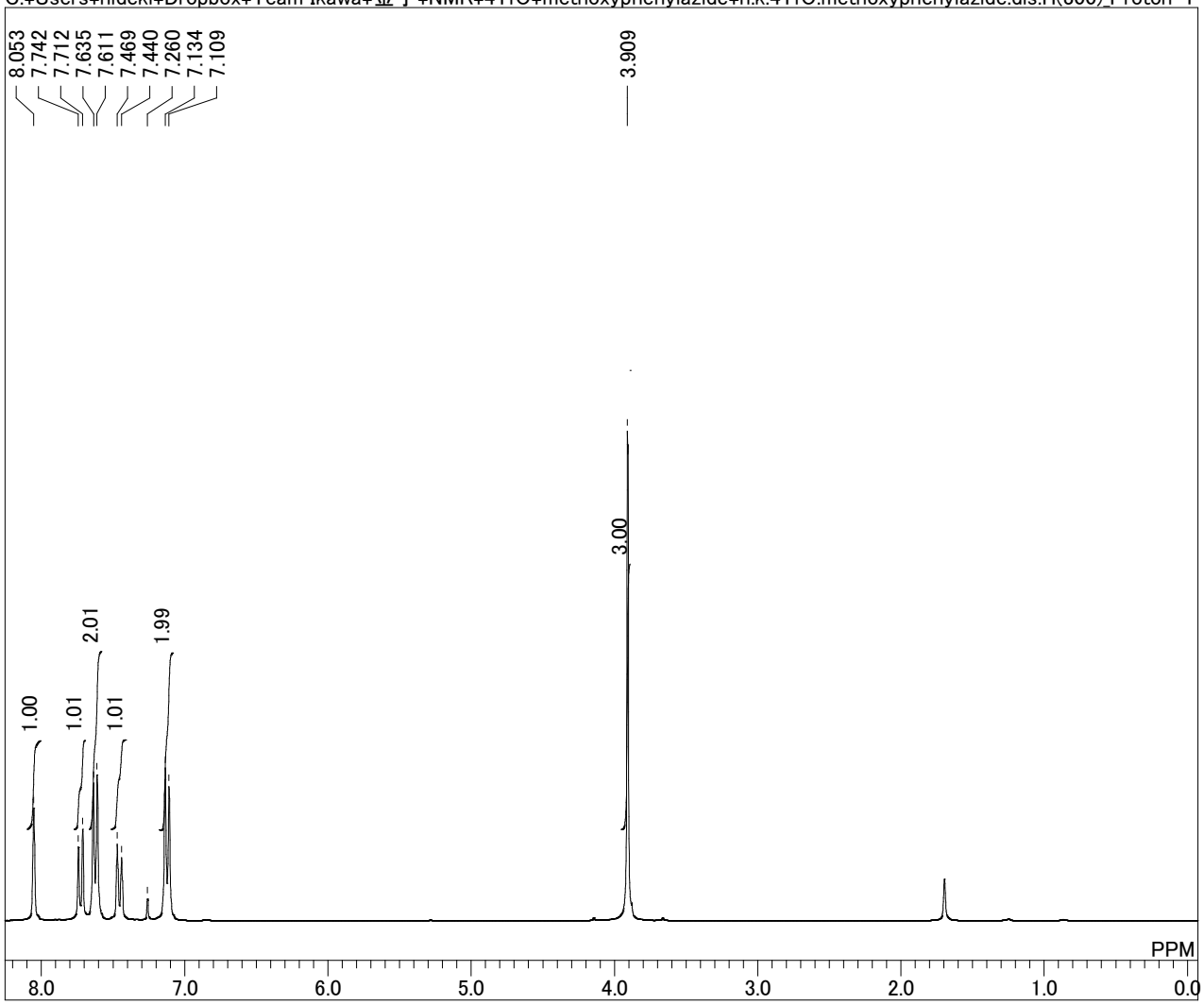
DFILE	h.k.4TfO.benzilazide.pro.F(30
COMNT	single_pulse
DATIM	21-05-2014 21:44:10
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	52428
FREQU	5656.11 Hz
SCANS	8
ACQTM	9.2694 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	-72.41 ppm
BF	0.12 Hz
RGAIN	38



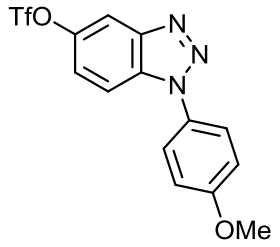
proximal-**12c** (Table 2, Entry 3, 4)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥methoxyphenylazide¥h.k.4TfO.methoxyphenylazide.dis.H(300)_Proton-1-1.als



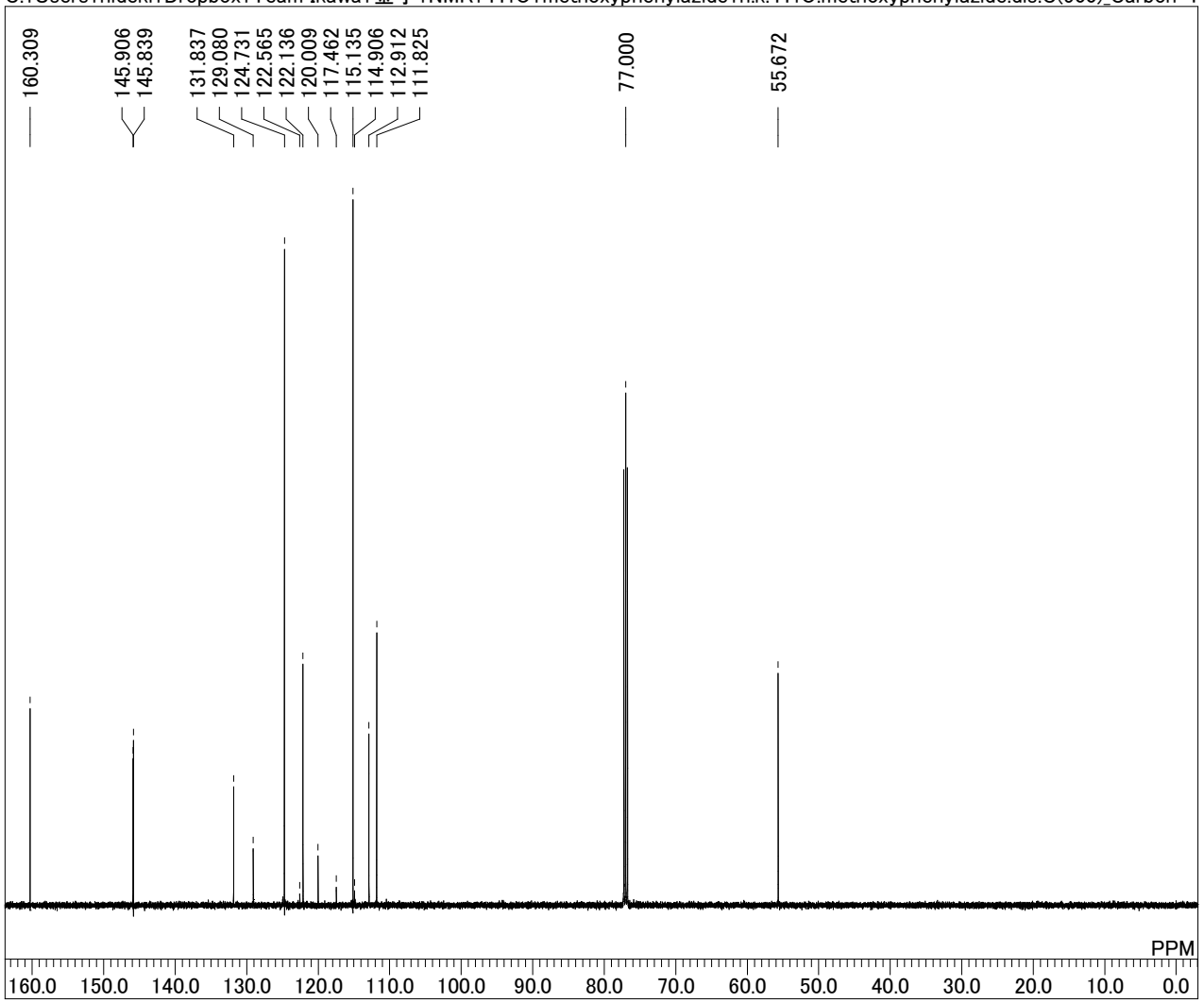
DFILE	h.k.4TfO.methoxyphenylazide
COMNT	single_pulse
DATIM	04-06-2014 08:48:27
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	24.2 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



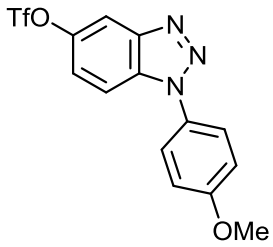
disal-**12d** (Table 3, Entry 1)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥methoxyphenylazide¥h.k.4TfO.methoxyphenylazide.dis.C(500)_Carbon-1-1.als



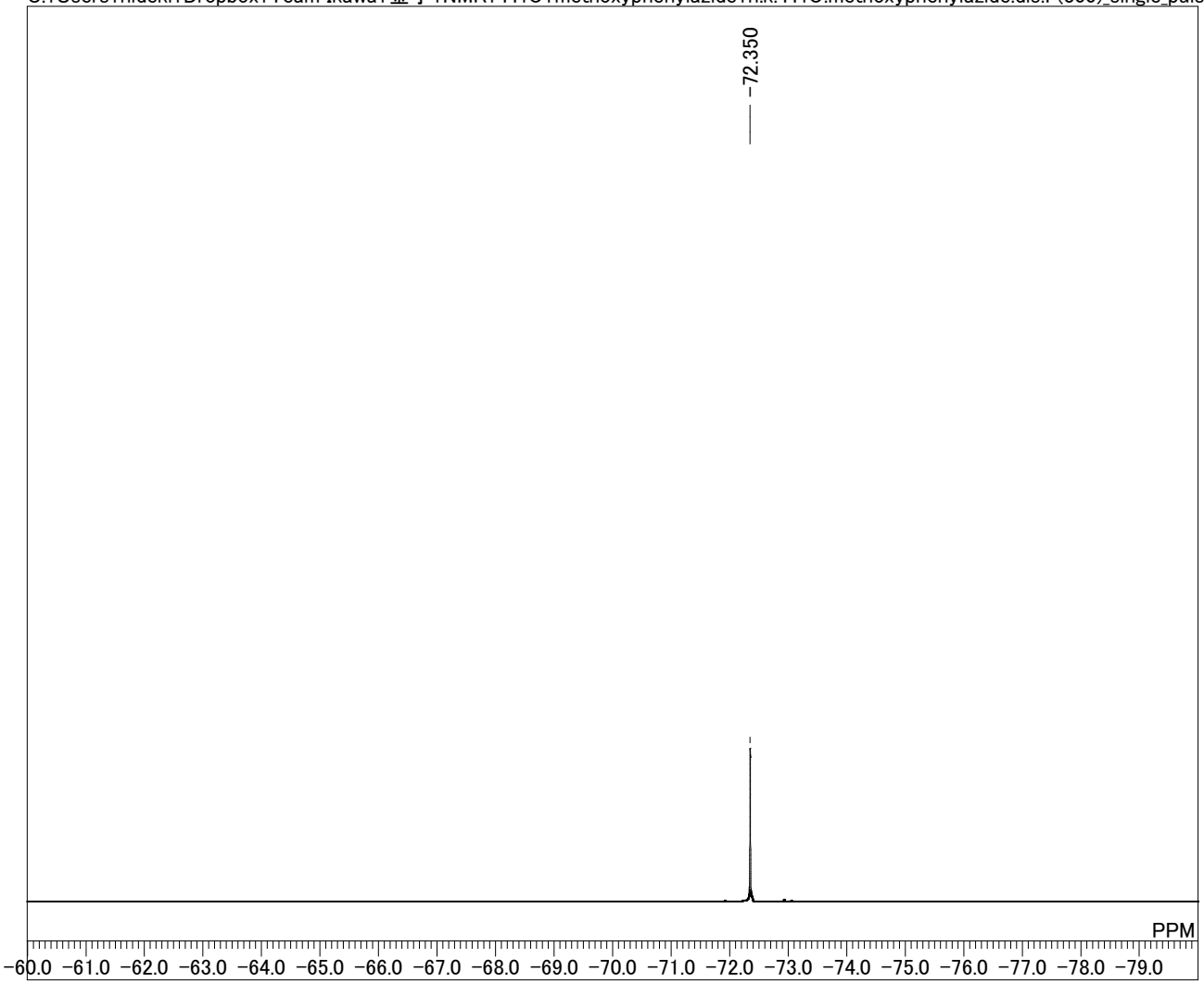
DFILE	h.k.4TfO.methoxyphenylazide
COMNT	single pulse decoupled gated
DATIM	04-06-2014 12:34:03
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	647
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



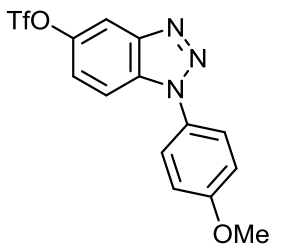
disal-**12d** (Table 3, Entry 1)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥methoxyphenylazide¥h.k.4TfO.methoxyphenylazide.dis.F(300)_single_pulse-1-1.als



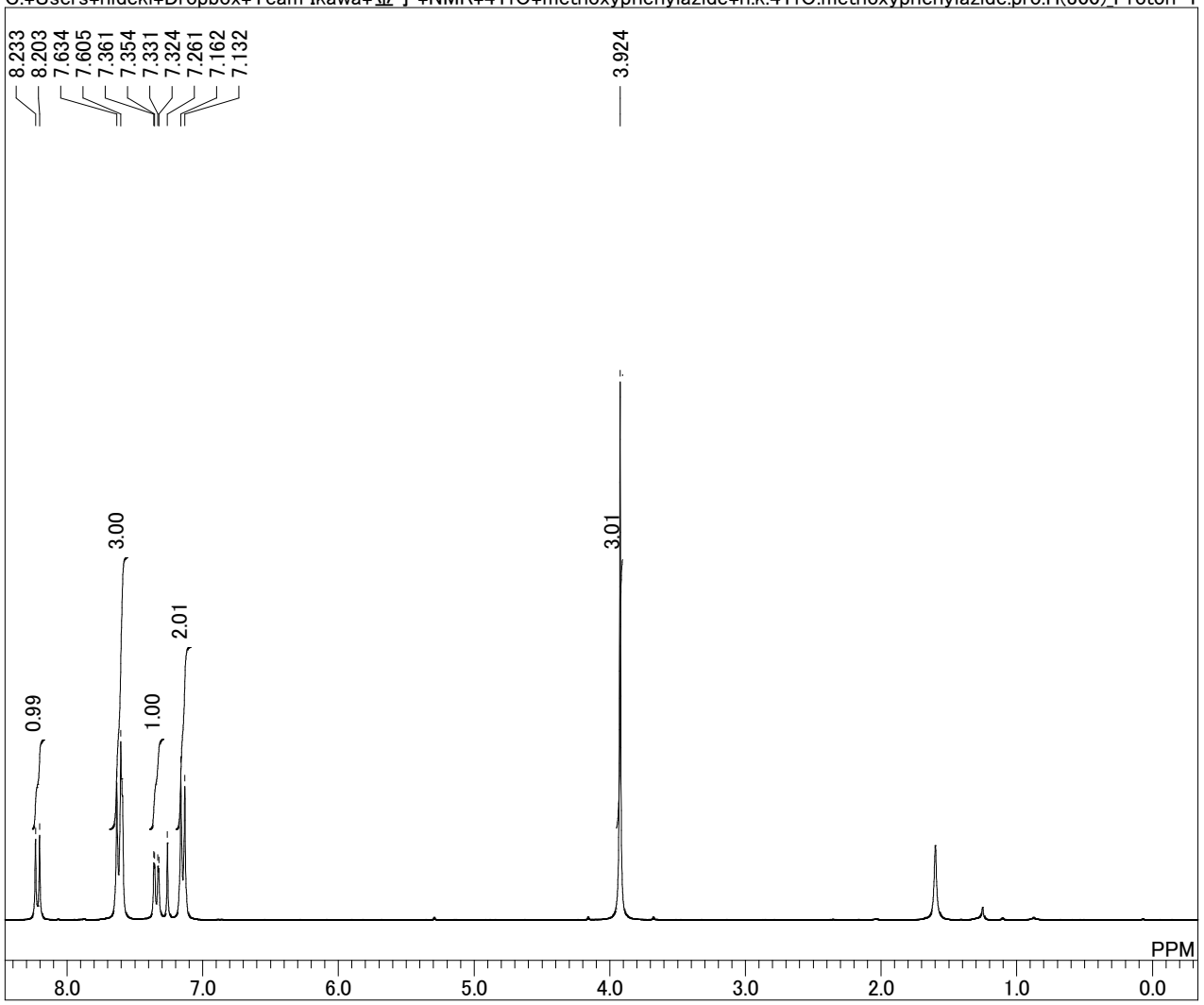
DFILE	h.k.4TfO.methoxyphenylazide
COMNT	single_pulse
DATIM	04-06-2014 08:52:15
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	52428
FREQU	5656.11 Hz
SCANS	8
ACQTM	9.2694 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	-72.35 ppm
BF	0.12 Hz
RGAIN	40



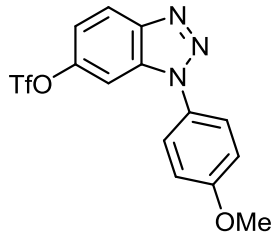
disal-**12d** (Table 3, Entry 1)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥methoxyphenylazide¥h.k.4TfO.methoxyphenylazide.pro.H(300)_Proton-1-1.als



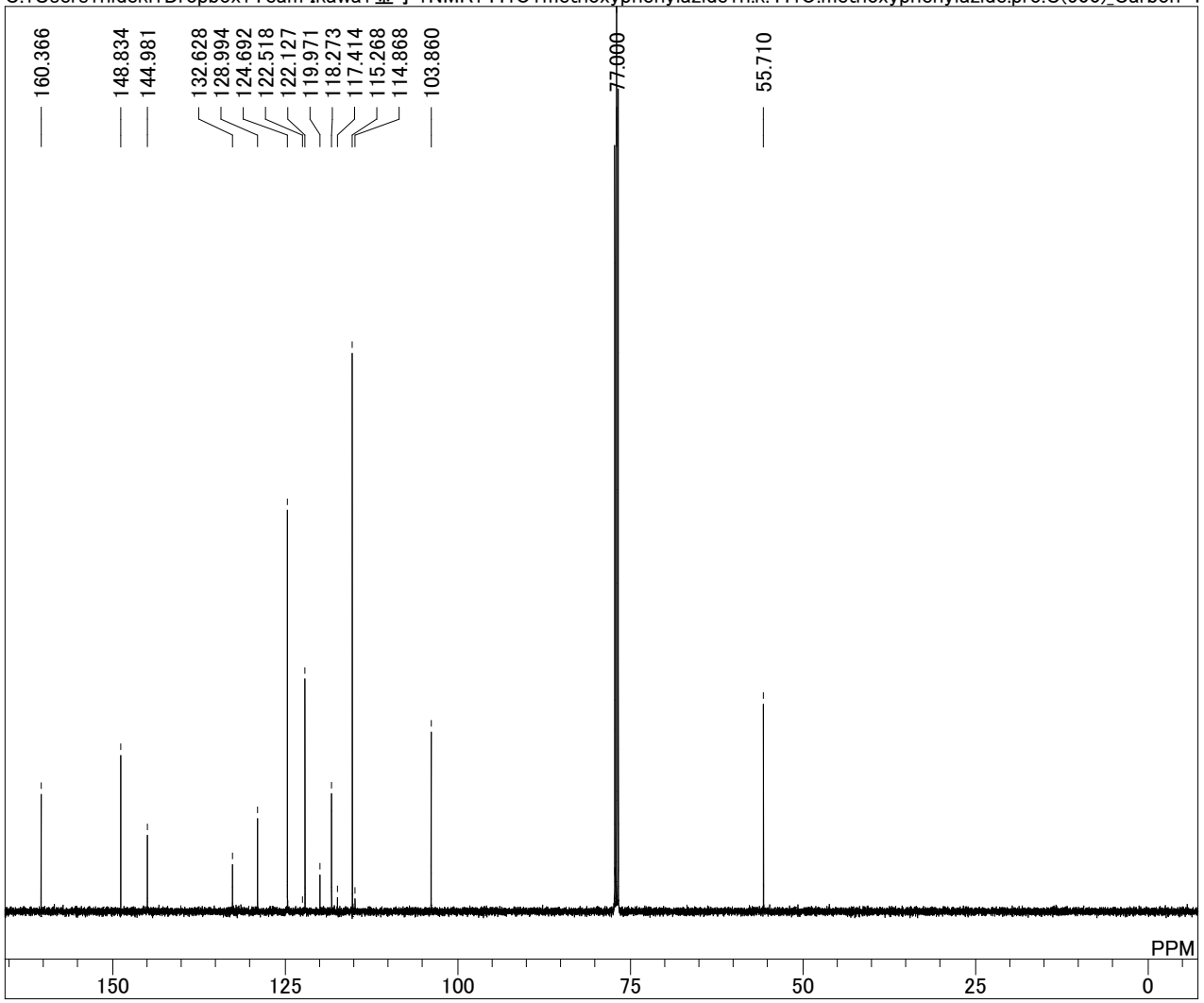
DFILE	h.k.4TfO.methoxyphenylazide
COMNT	single_pulse
DATIM	04-06-2014 14:12:40
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	16
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	24.3 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	42



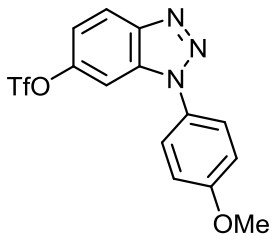
proximal-**12d** (Table 3, Entry 1)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥methoxyphenylazide¥h.k.4TfO.methoxyphenylazide.pro.C(500)_Carbon-1-1.als



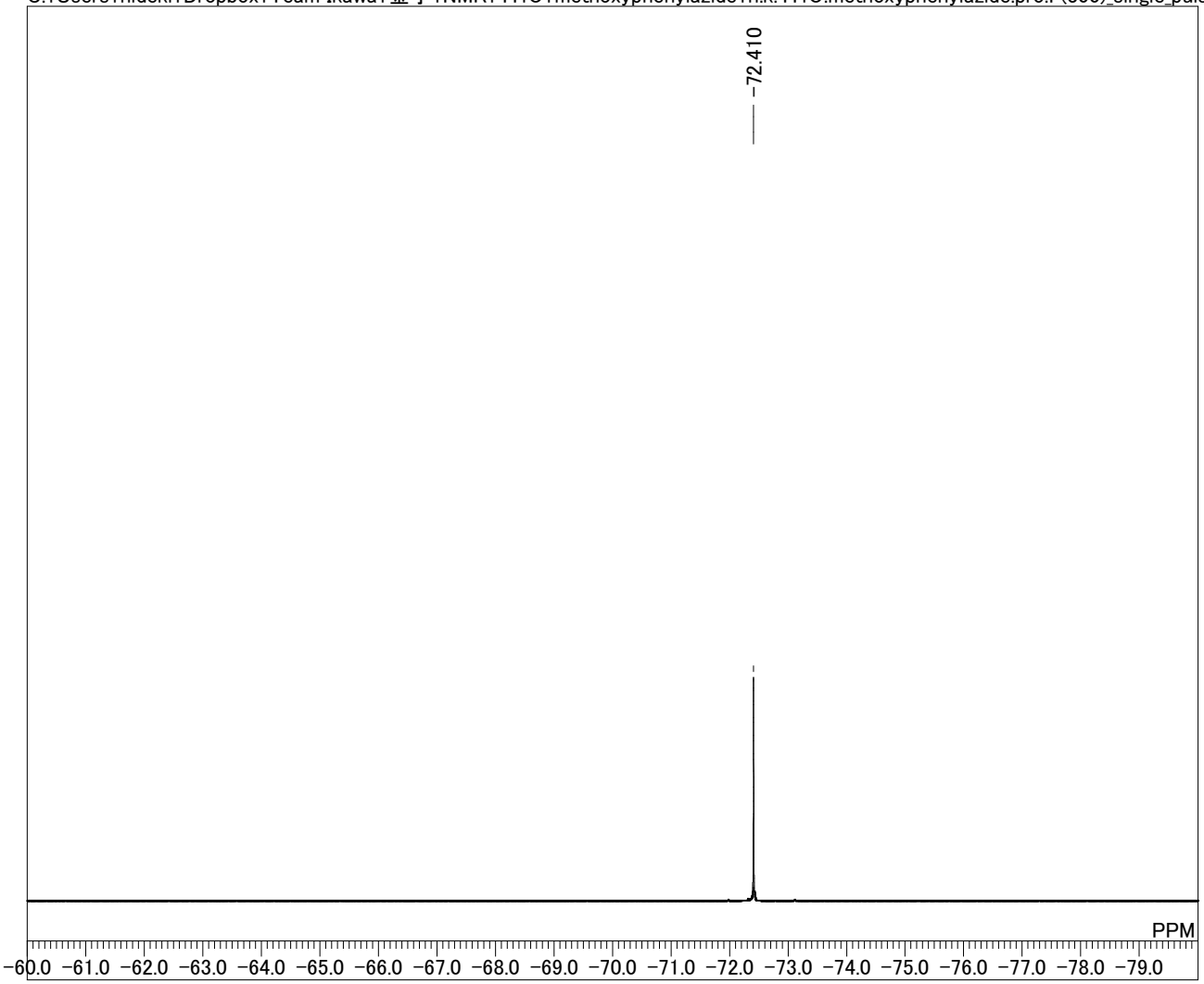
DFILE	h.k.4TfO.methoxyphenylazide
COMNT	single pulse decoupled gated
DATIM	04-06-2014 22:42:49
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1400
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



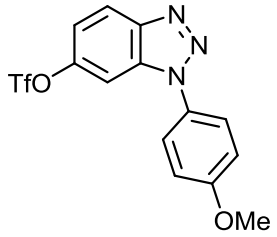
proximal-**12d** (Table 3, Entry 1)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥methoxyphenylazide¥h.k.4TfO.methoxyphenylazide.pro.F(300)_single_pulse-2-1.als



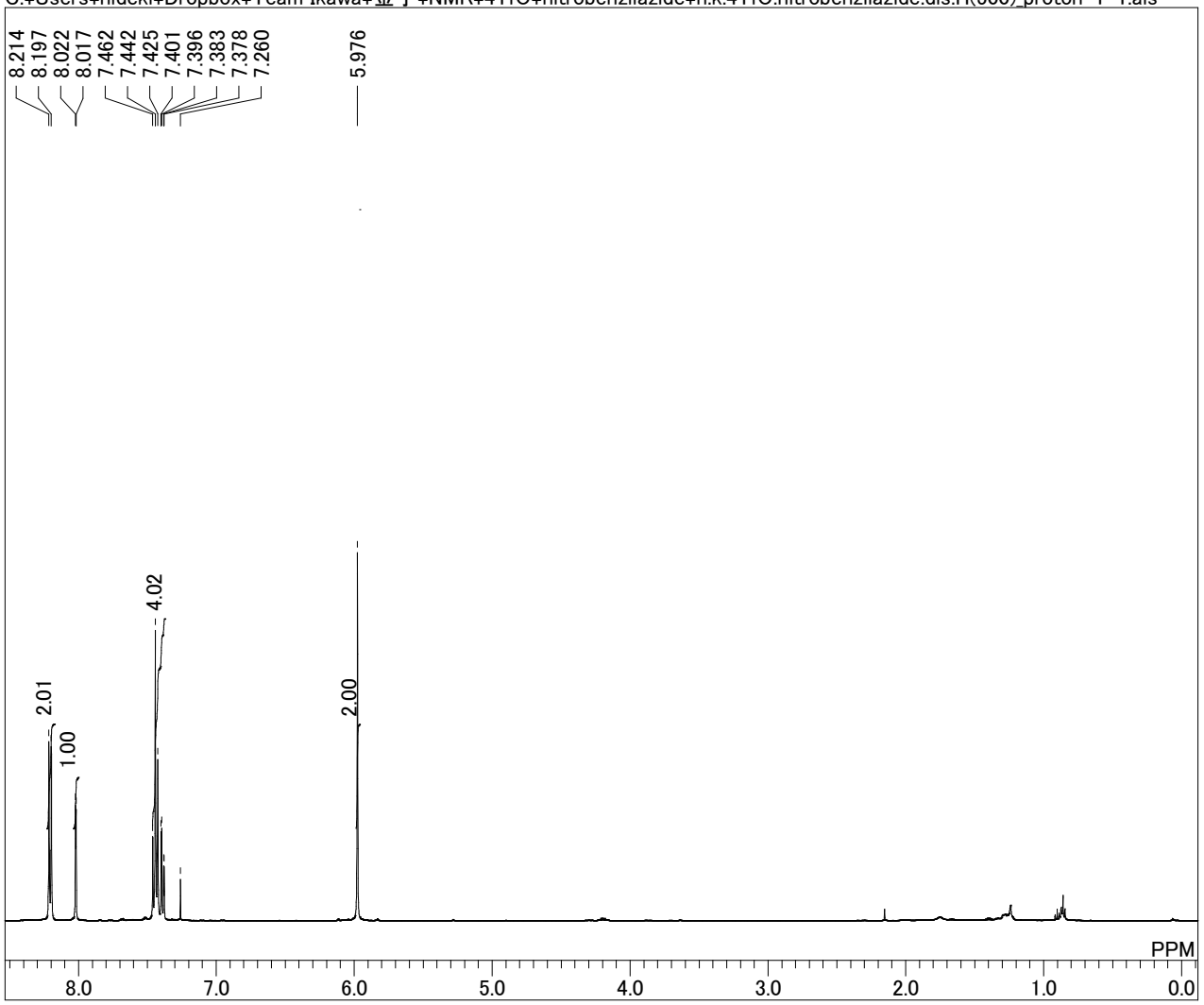
DFILE	h.k.4TfO.methoxyphenylazide
COMNT	single_pulse
DATIM	04-06-2014 14:19:48
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	52428
FREQU	5656.11 Hz
SCANS	8
ACQTM	9.2694 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	-72.41 ppm
BF	0.12 Hz
RGAIN	38



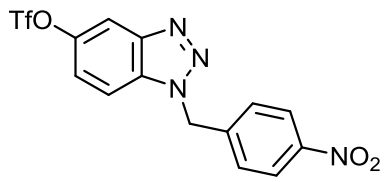
proximal-**12d** (Table 3, Entry 1)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥nitrobenzilazide¥h.k.4TfO.nitrobenzilazide.dis.H(500)_proton-1-1.als



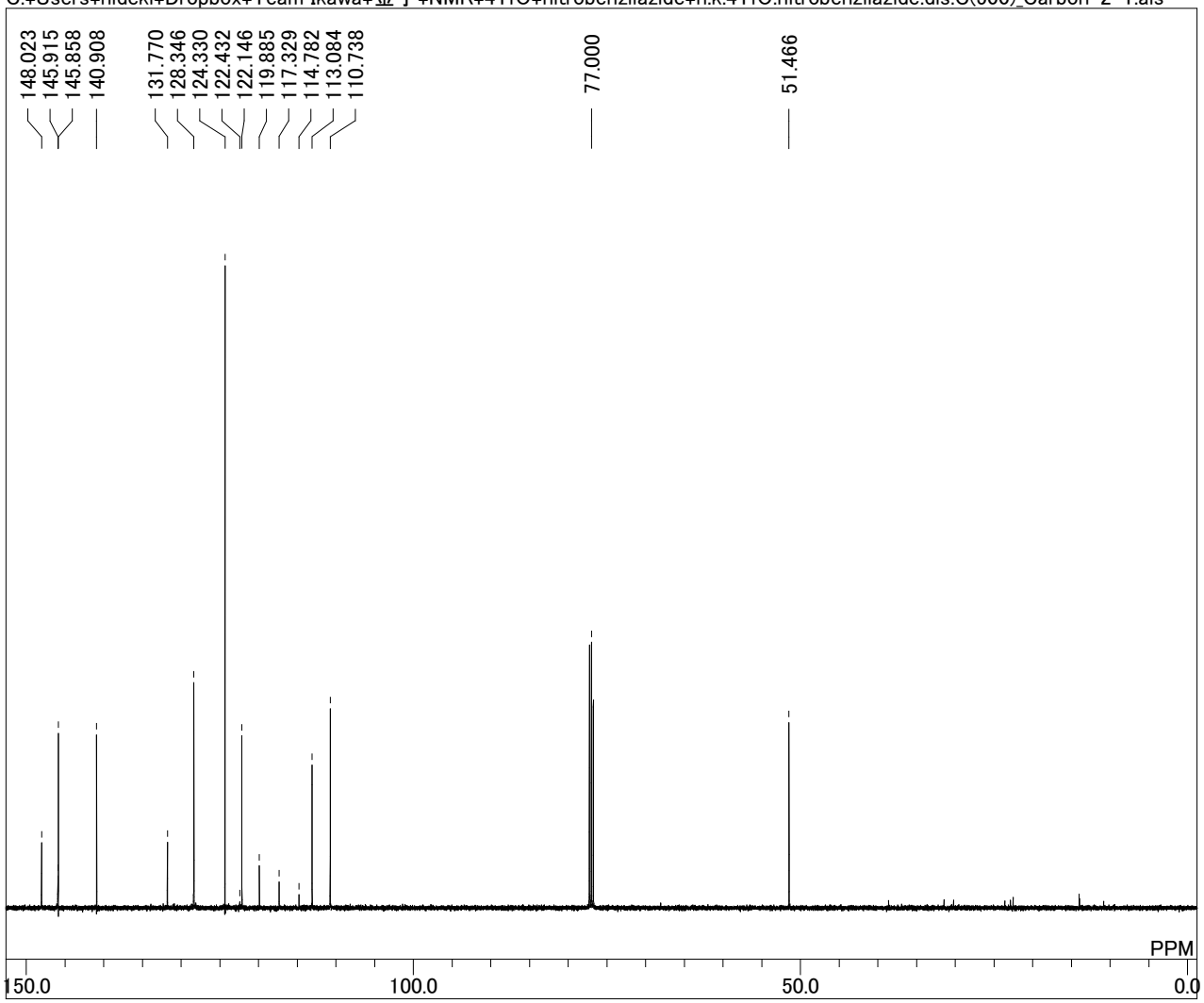
DFILE	h.k.4TfO.nitrobenzilazide.dis.H
COMNT	single_pulse
DATIM	27-05-2014 18:17:19
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	36



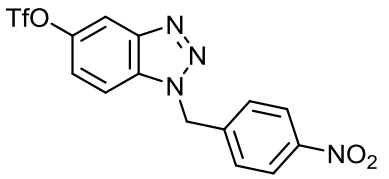
distal-**12e** (Table 3, Entry 2)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥nitrobenzilazide¥h.k.4TfO.nitrobenzilazide.dis.C(500)_Carbon-2-1.als



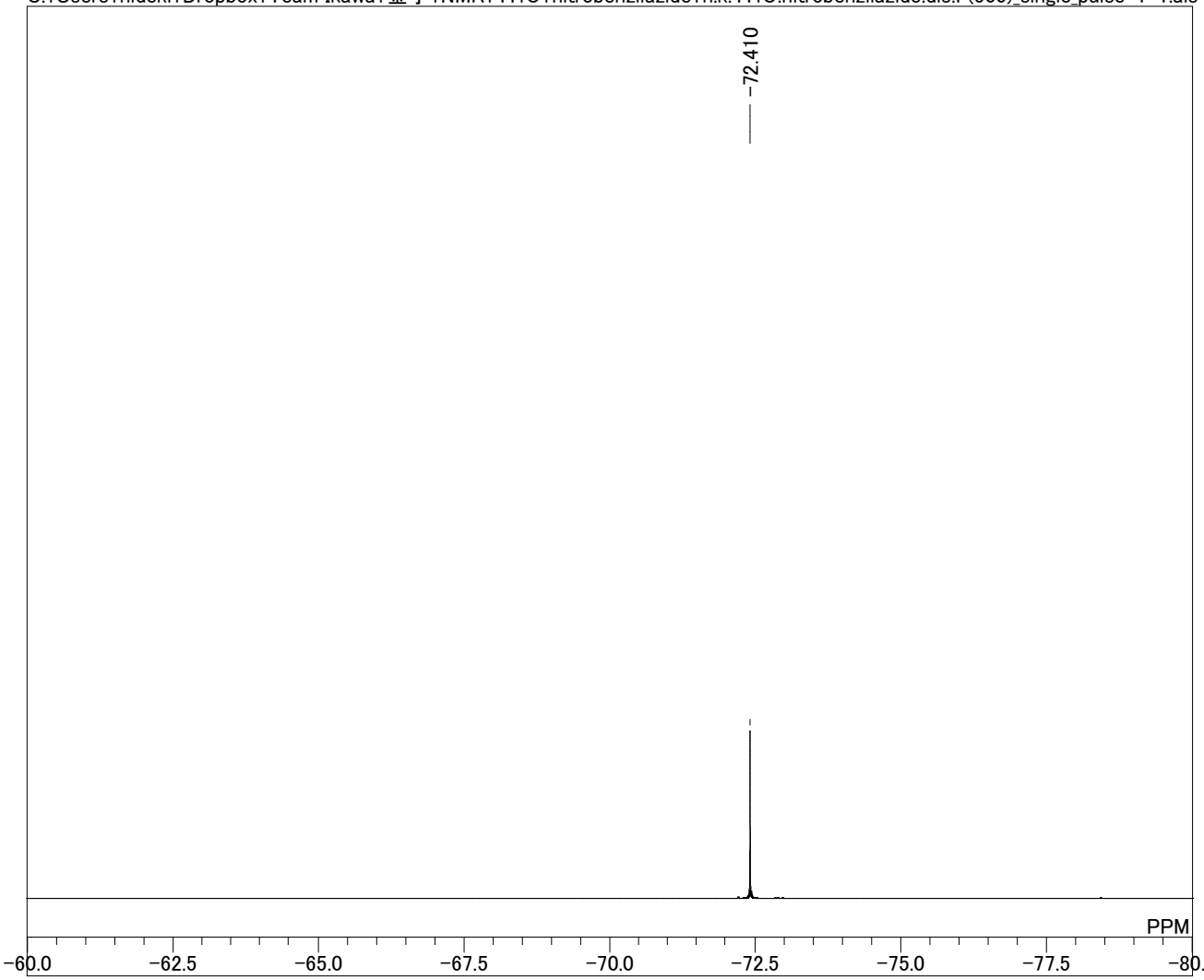
DFILE	h.k.4TfO.nitrobenzilazide.dis.C
COMNT	single pulse decoupled gated
DATIM	27-05-2014 22:31:48
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	267
ACQTM	0.8336 sec
PD	2.5000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



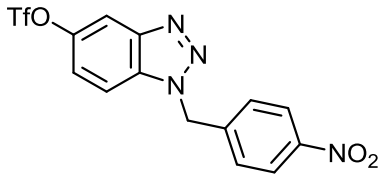
distal-**12e** (Table 3, Entry 2)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥nitrobenzilazide¥h.k.4TfO.nitrobenzilazide.dis.F(500)_single_pulse-1-1.als



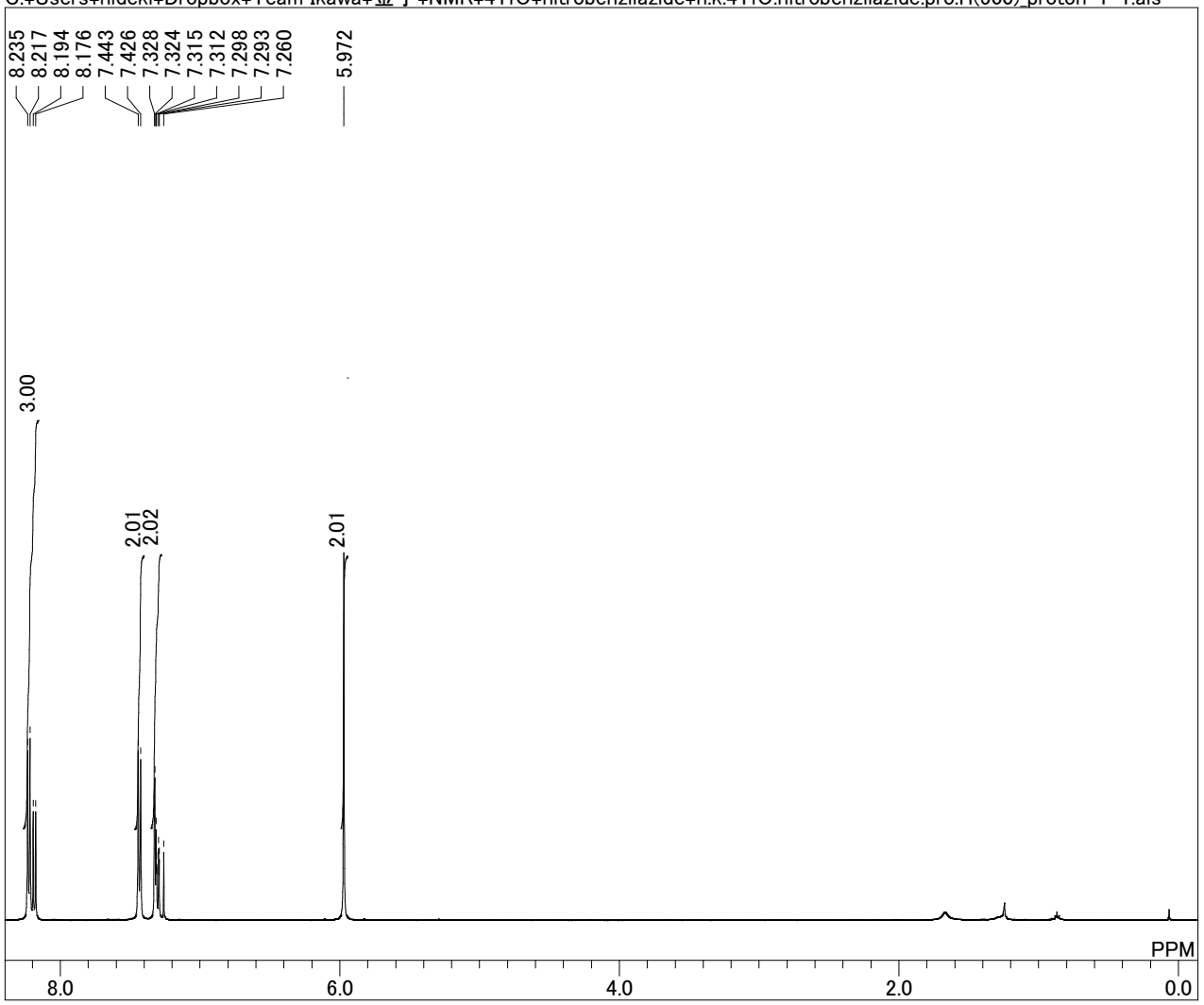
DFILE	h.k.4TfO.nitrobenzilazide.dis.F
COMNT	single_pulse
DATIM	27-05-2014 18:20:18
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	470.58 MHz
OBSET	7.51 KHz
OBFIN	7.41 Hz
POINT	52428
FREQU	9416.20 Hz
SCANS	8
ACQTM	5.5679 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	19F
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	-72.41 ppm
BF	1.20 Hz
RGAIN	46



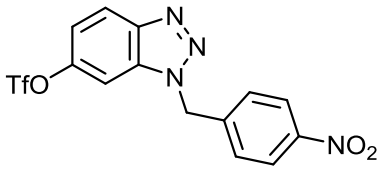
distal-**12e** (Table 3, Entry 2)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥nitrobenzilazide¥h.k.4TfO.nitrobenzilazide.pro.H(500)_proton-1-1.als



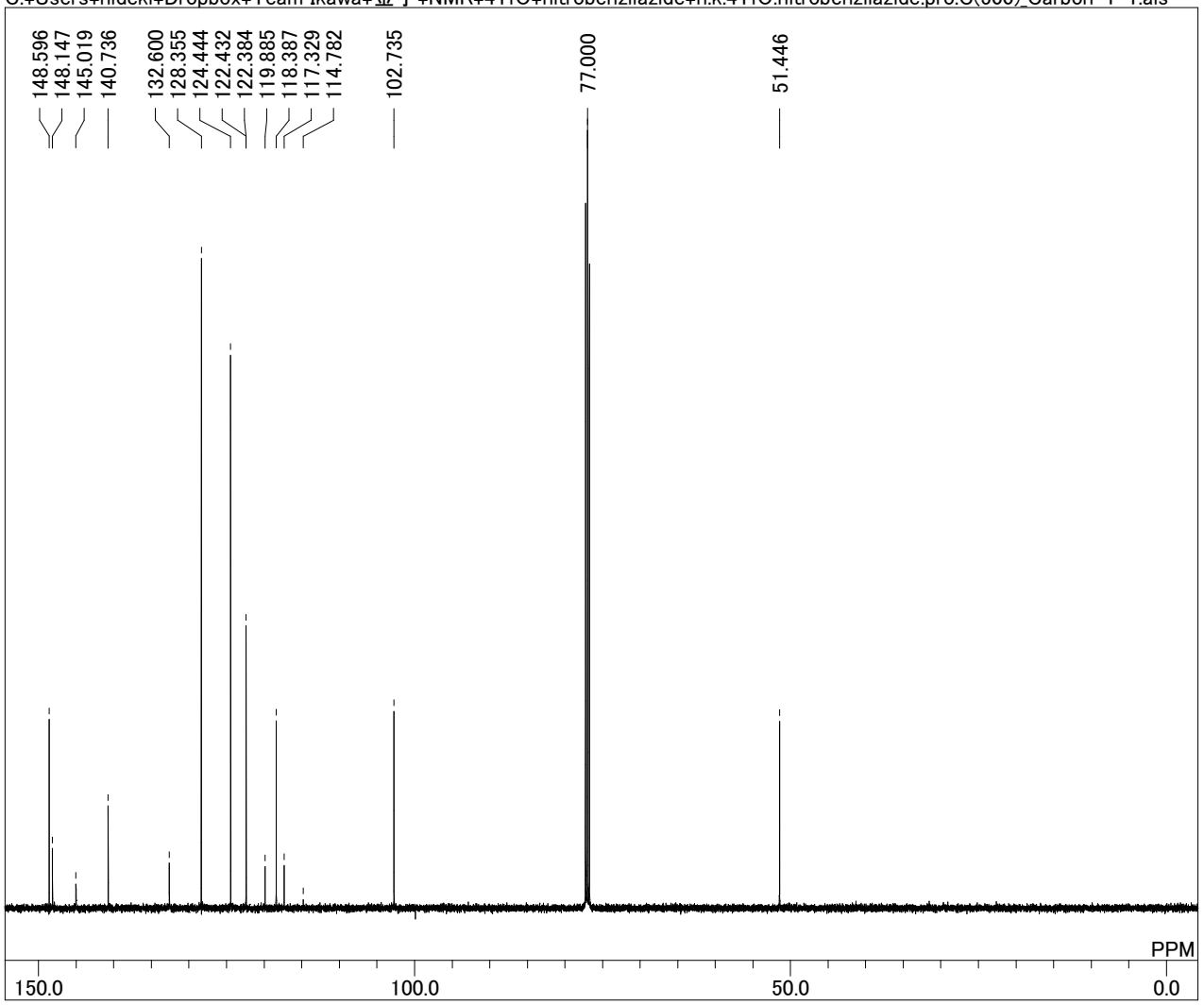
DFILE	h.k.4TfO.nitrobenzilazide.pro.
COMNT	single_pulse
DATIM	27-05-2014 22:52:46
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



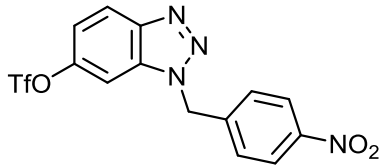
proximal-**12e** (Table 3, Entry 2)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥nitrobenzilazide¥h.k.4TfO.nitrobenzilazide.pro.C(500)_Carbon-1-1.als



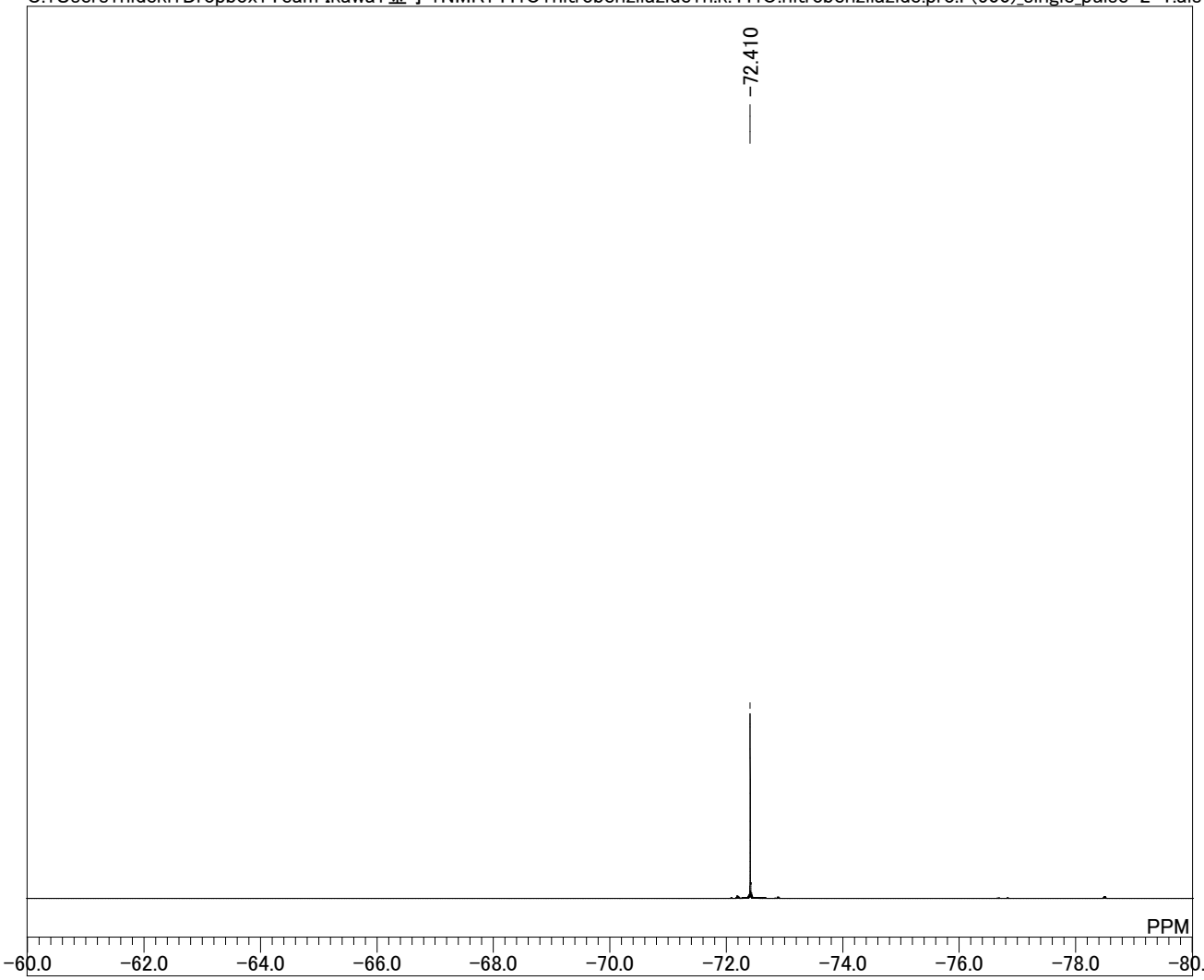
DFILE	h.k.4TfO.nitrobenzilazide.pro.
COMNT	single pulse decoupled gated
DATIM	27-05-2014 23:02:17
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	958
ACQTM	0.8336 sec
PD	2.5000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



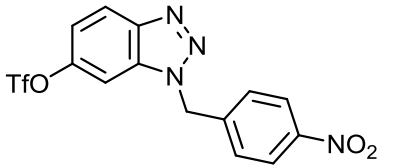
proximal-**12e** (Table 3, Entry 2)

single_pulse

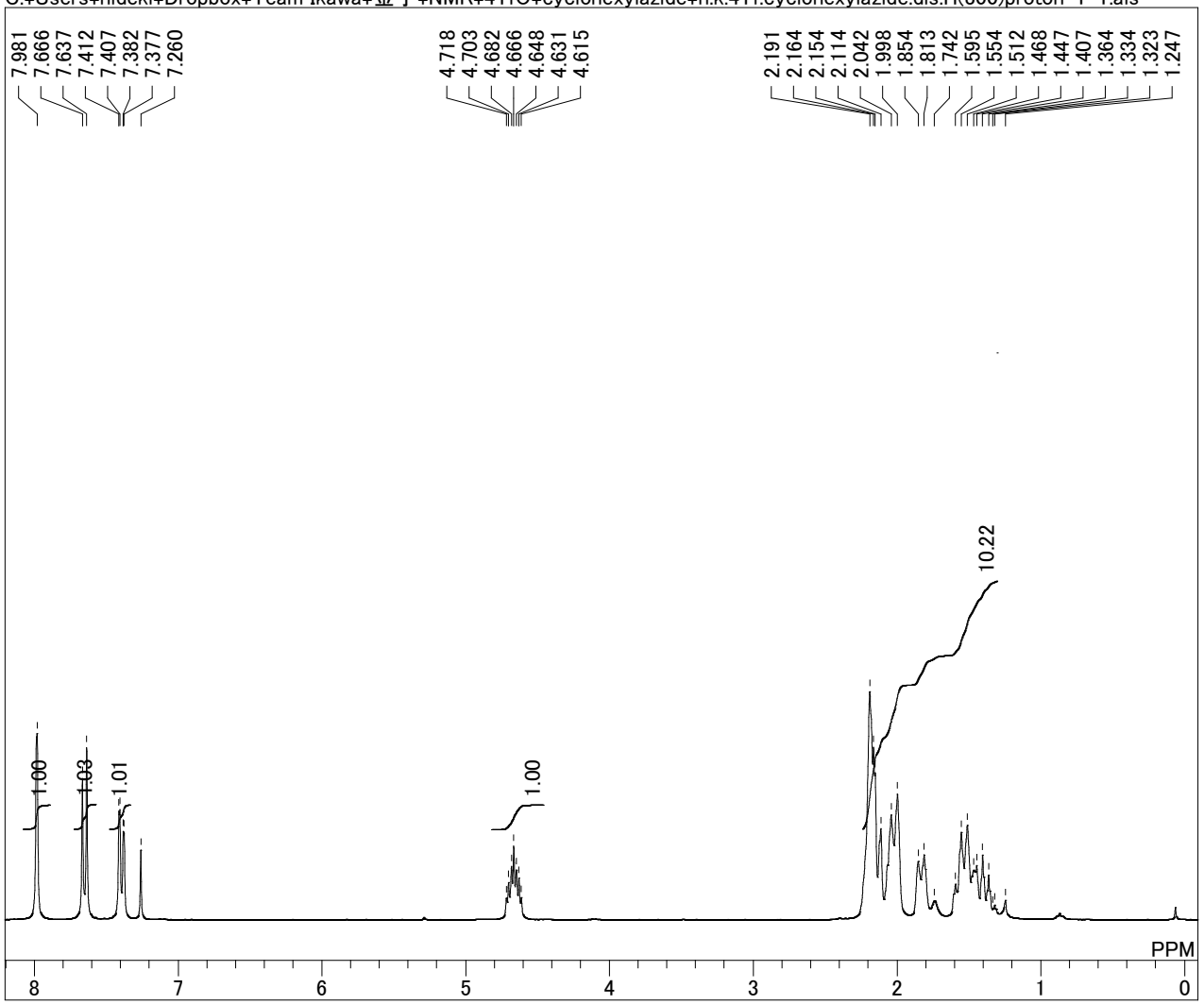
C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥nitrobenzilazide¥h.k.4TfO.nitrobenzilazide.pro.F(500)_single_pulse-2-1.als



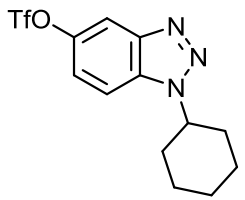
DFILE	h.k.4TfO.nitrobenzilazide.pro.
COMNT	single_pulse
DATIM	27-05-2014 22:58:07
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	470.58 MHz
OBSET	7.51 KHz
OBFIN	7.41 Hz
POINT	52428
FREQU	9416.20 Hz
SCANS	8
ACQTM	5.5679 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	19F
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	-72.41 ppm
BF	0.12 Hz
RGAIN	50



proximal-**12e** (Table 3, Entry 2)



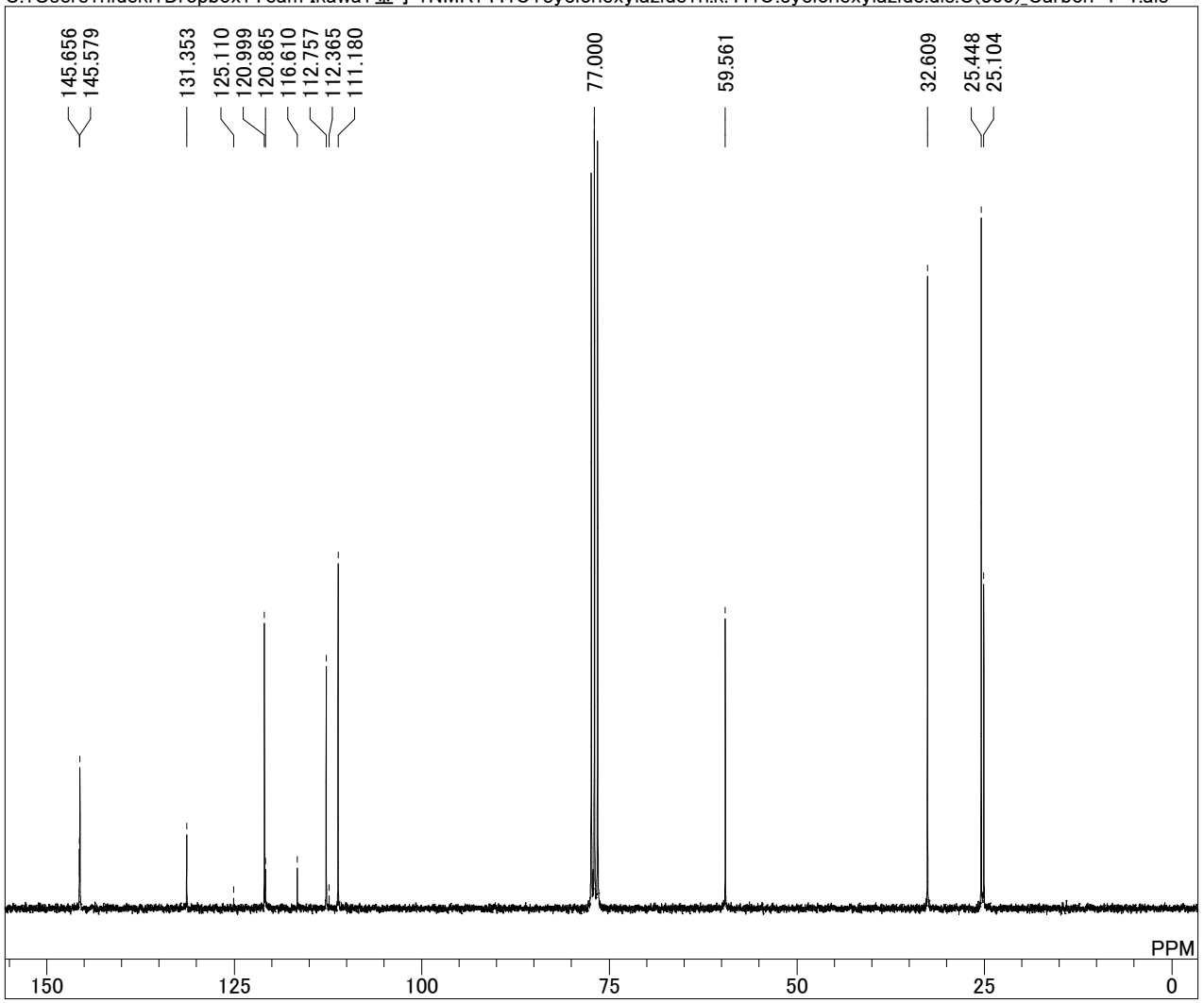
DFILE	h.k.4Tf.cyclohexylazide.dis.H(
COMNT	
DATIM	21-05-2014 13:40:45
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	38



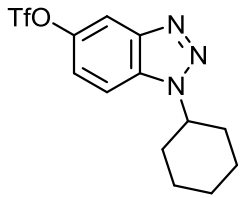
distal-**12f** (Table 3, Entry 3)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥cyclohexylazide¥h.k.4TfO.cyclohexylazide.dis.C(300)_Carbon-1-1.als



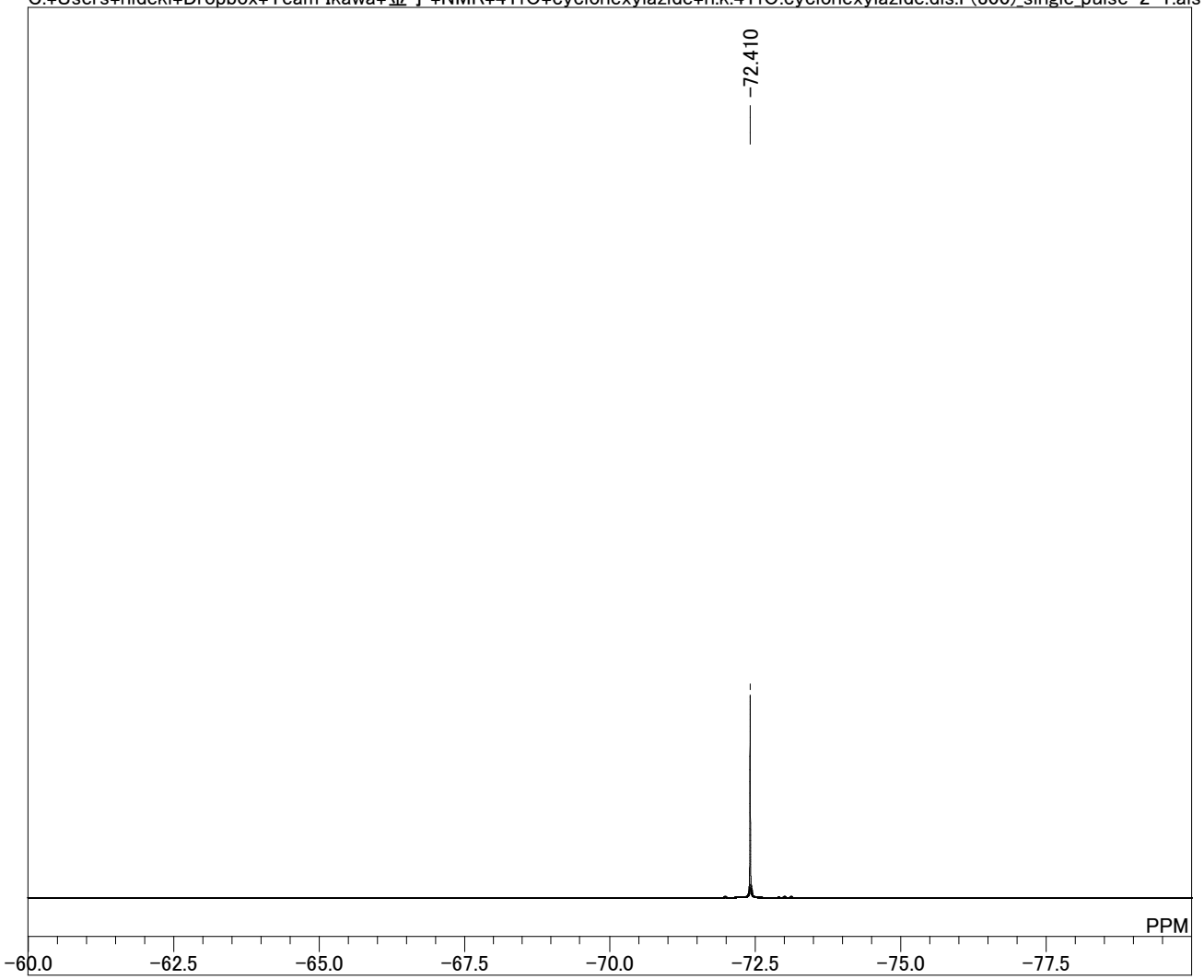
DFILE	h.k.4TfO.cyclohexylazide.dis.(
COMNT	single pulse decoupled gated
DATIM	22-05-2014 02:07:09
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.39 Hz
SCANS	2124
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



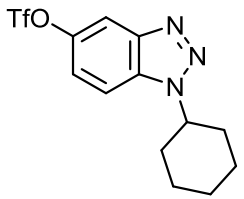
distal-**12f** (Table 3, Entry 3)

single_pulse

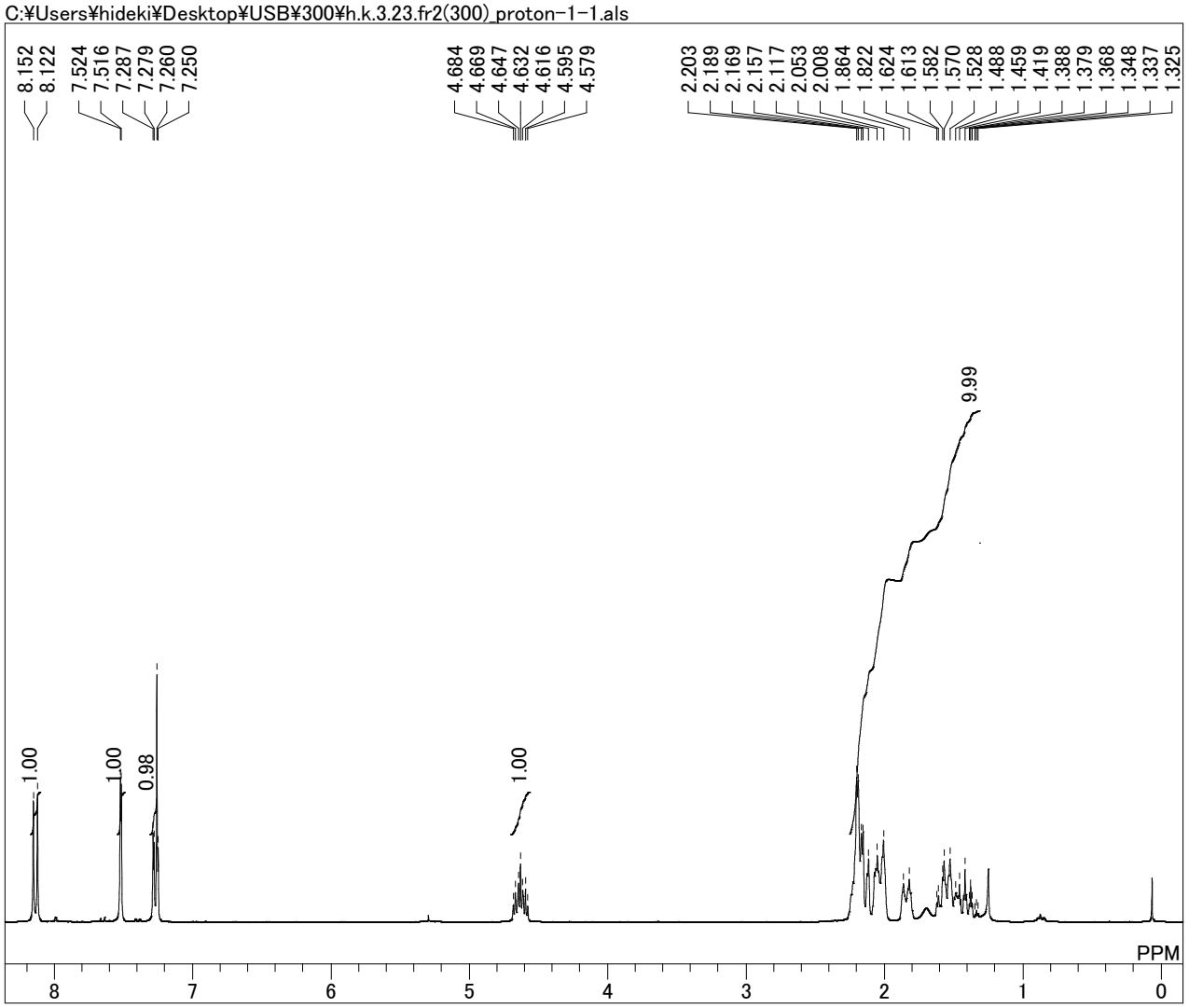
C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥cyclohexylazide¥h.k.4TfO.cyclohexylazide.dis.F(300)_single_pulse-2-1.als



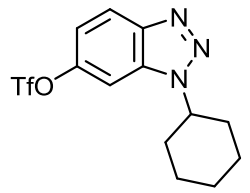
DFILE	h.k.4TfO.cyclohexylazide.dis.l
COMNT	single_pulse
DATIM	22-05-2014 04:13:18
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	52428
FREQU	5656.11 Hz
SCANS	8
ACQTM	9.2694 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	-72.41 ppm
BF	1.20 Hz
RGAIN	40



distal-**12f** (Table 3, Entry 3)



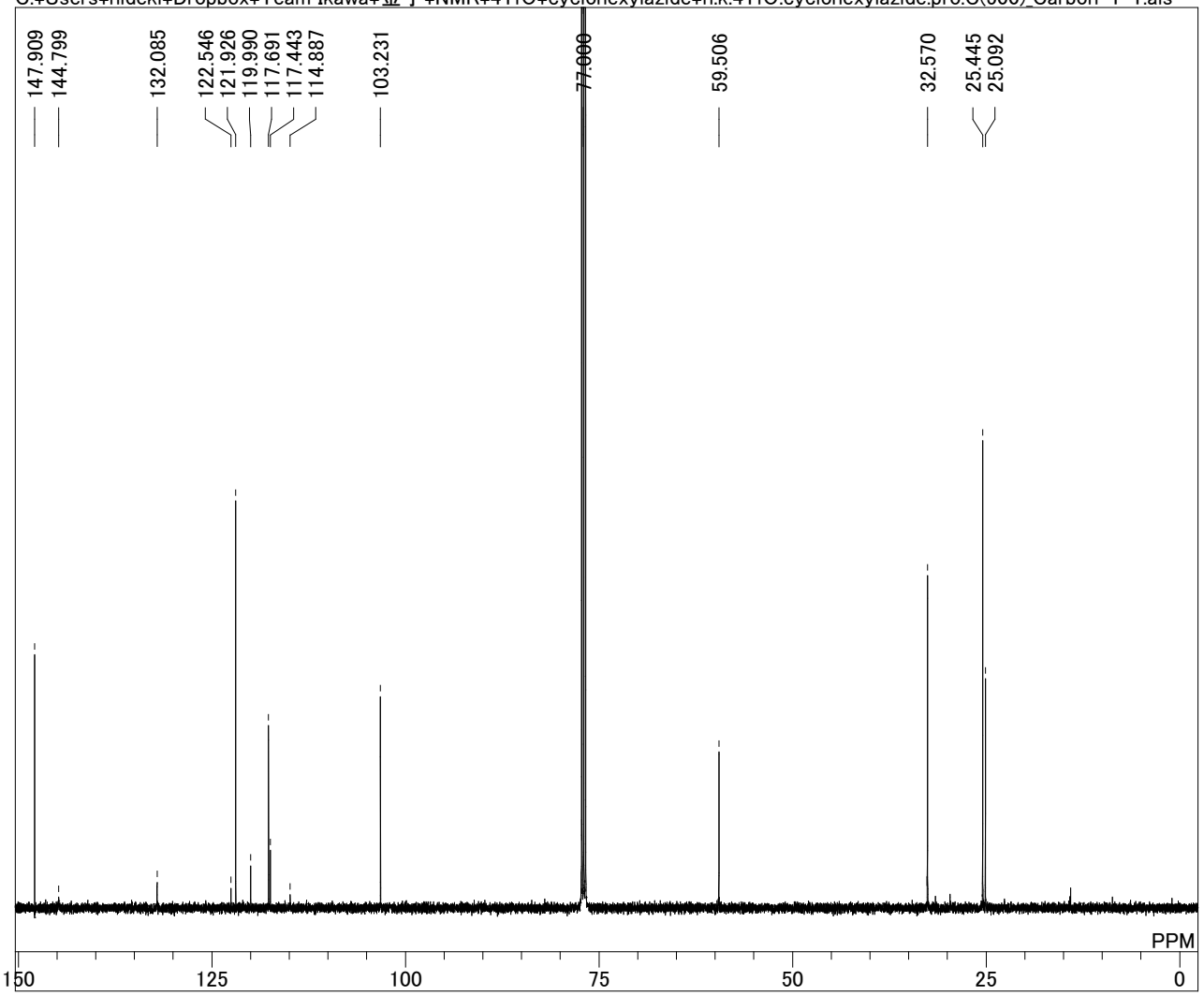
DFILE	h.k.3.23.fr2(300)_proton-1-1.a
COMNT	
DATIM	22-05-2014 00:22:47
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	22.2 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	42



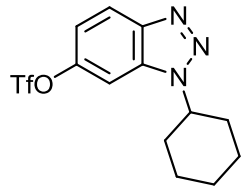
proximal-**12f** (Table 3, Entry 3)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥cyclohexylazide¥h.k.4TfO.cyclohexylazide.pro.C(500)_Carbon-1-1.als



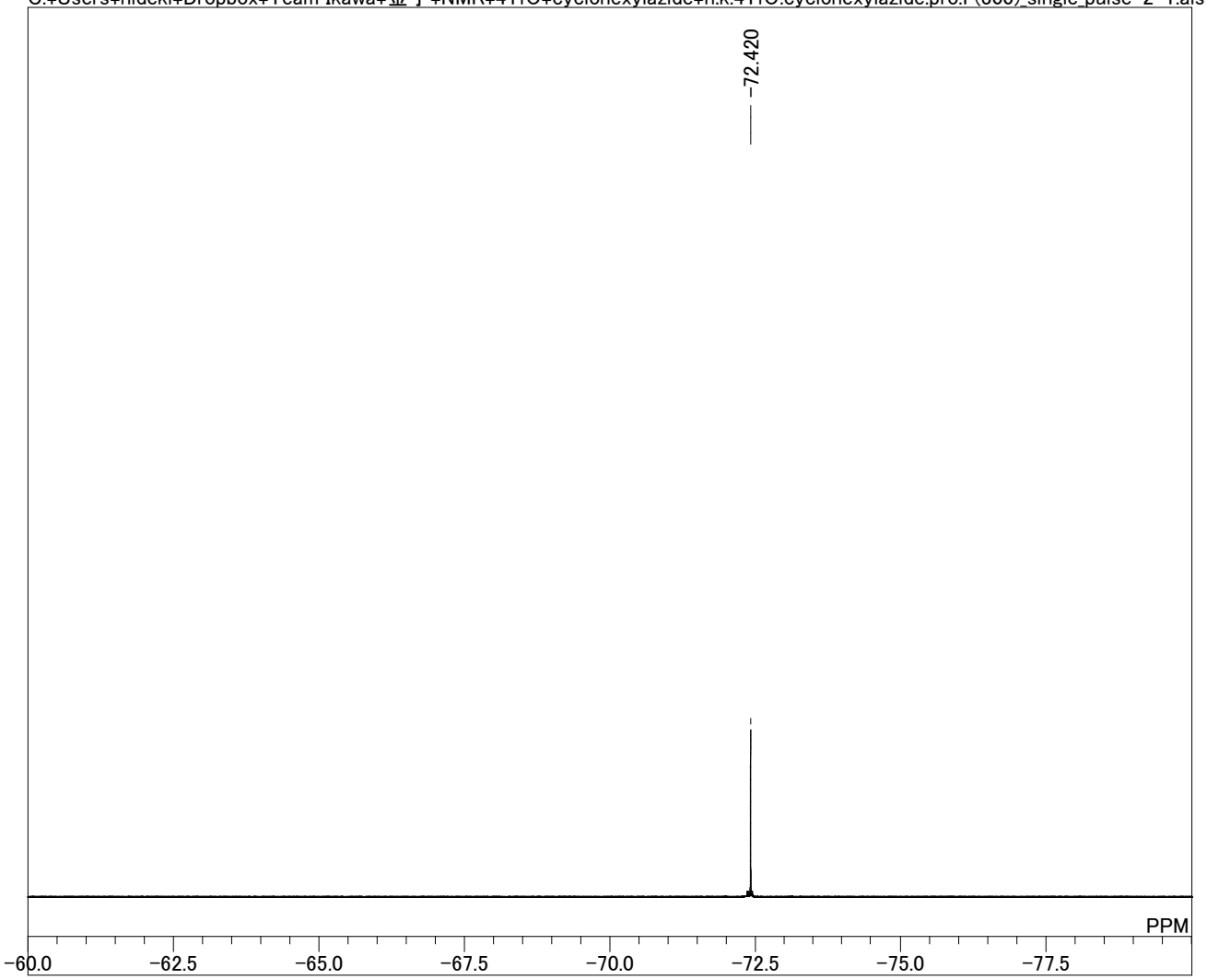
DFILE	h.k.4TfO.cyclohexylazide.pro.
COMNT	single pulse decoupled gated
DATIM	09-06-2014 22:59:24
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	3472
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



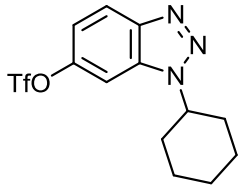
proximal-**12f** (Table 3, Entry 3)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥cyclohexylazide¥h.k.4TfO.cyclohexylazide.pro.F(300)_single_pulse-2-1.als



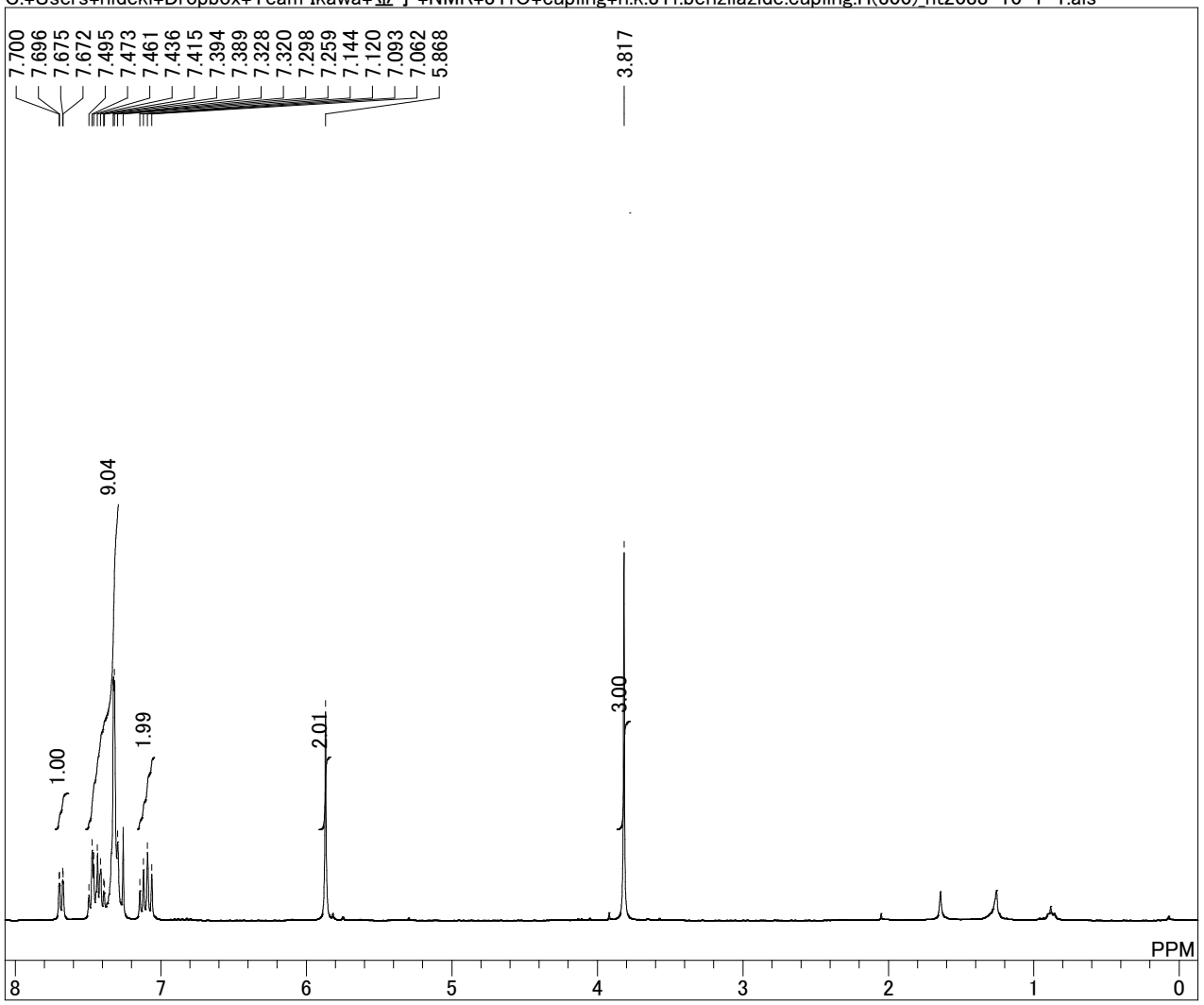
DFILE	h.k.4TfO.cyclohexylazide.pro.
COMNT	single_pulse
DATIM	09-06-2014 22:50:18
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	52428
FREQU	5656.11 Hz
SCANS	8
ACQTM	9.2694 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	24.7 c
SLVNT	CDCL3
EXREF	-72.42 ppm
BF	0.12 Hz
RGAIN	38



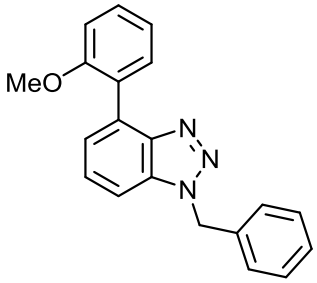
proximal-**12f** (Table 3, Entry 3)

1H 300MHz CDCl3

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥cupling¥h.k.3Tf.benzilazide.cupling.H(300)_ht2088-10-1-1.als



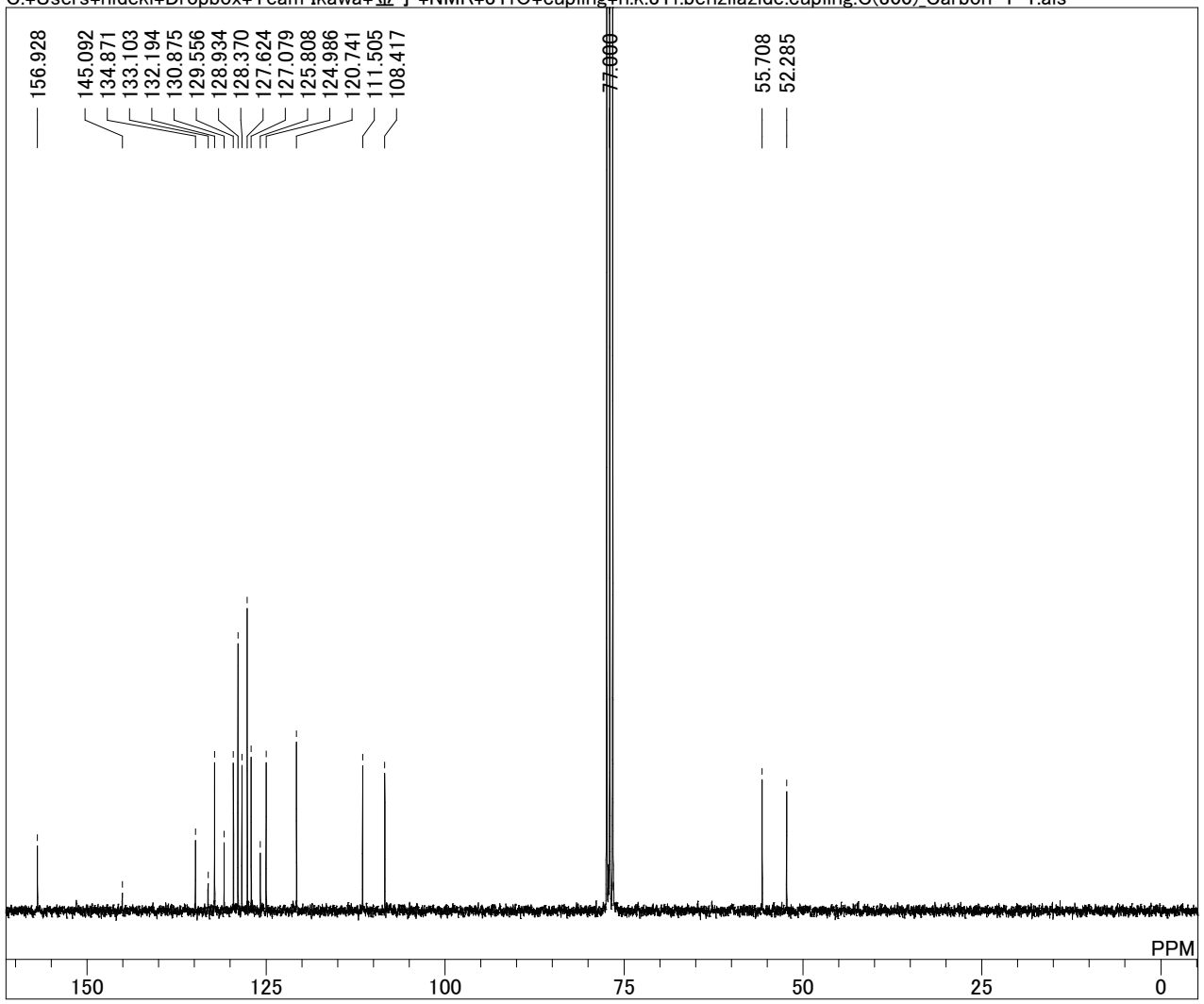
DFILE	h.k.3Tf.benzilazide.cupling.H(3
COMNT	1H 300MHz CDCl3
DATIM	21-03-2014 10:55:25
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	32
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	16.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	40



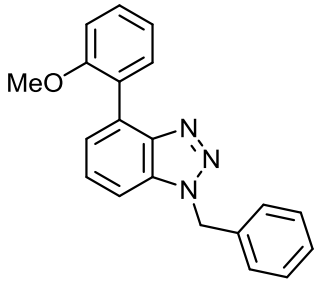
14 (Scheme 4)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥cupling¥h.k.3Tf.benzilazide.cupling.C(300)_Carbon-1-1.als



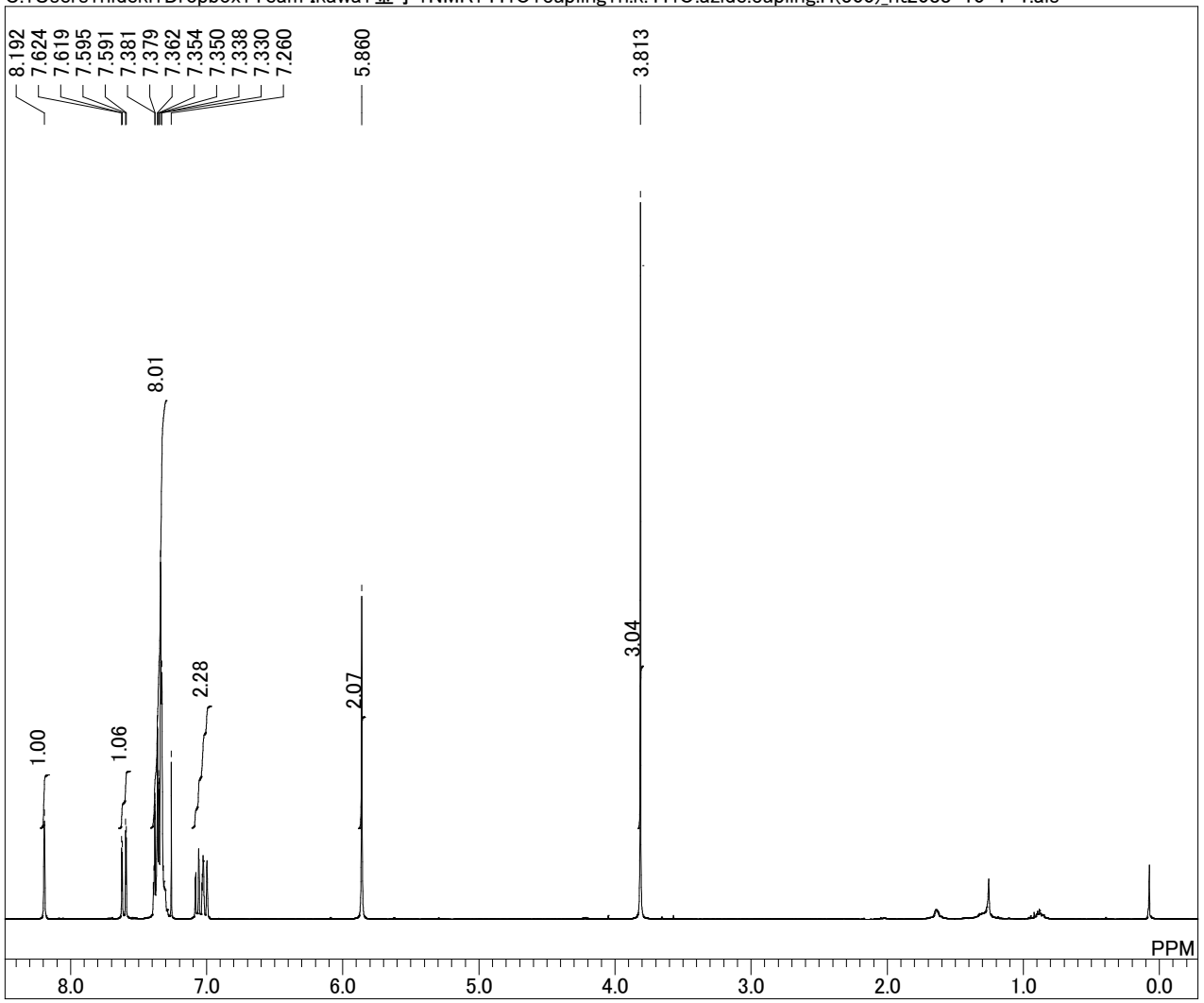
DFILE	h.k.3Tf.benzilazide.cupling.C(
COMNT	single pulse decoupled gated
DATIM	20-05-2014 01:54:08
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.39 Hz
SCANS	402
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



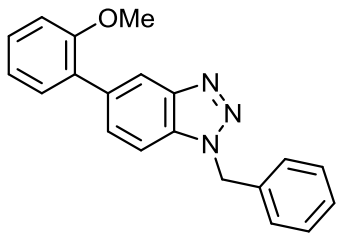
14 (Scheme 4)

1H 300MHz CDCl3

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥cupling¥h.k.4TfO.azide.cupling.H(300)_ht2088-10-1-1.als



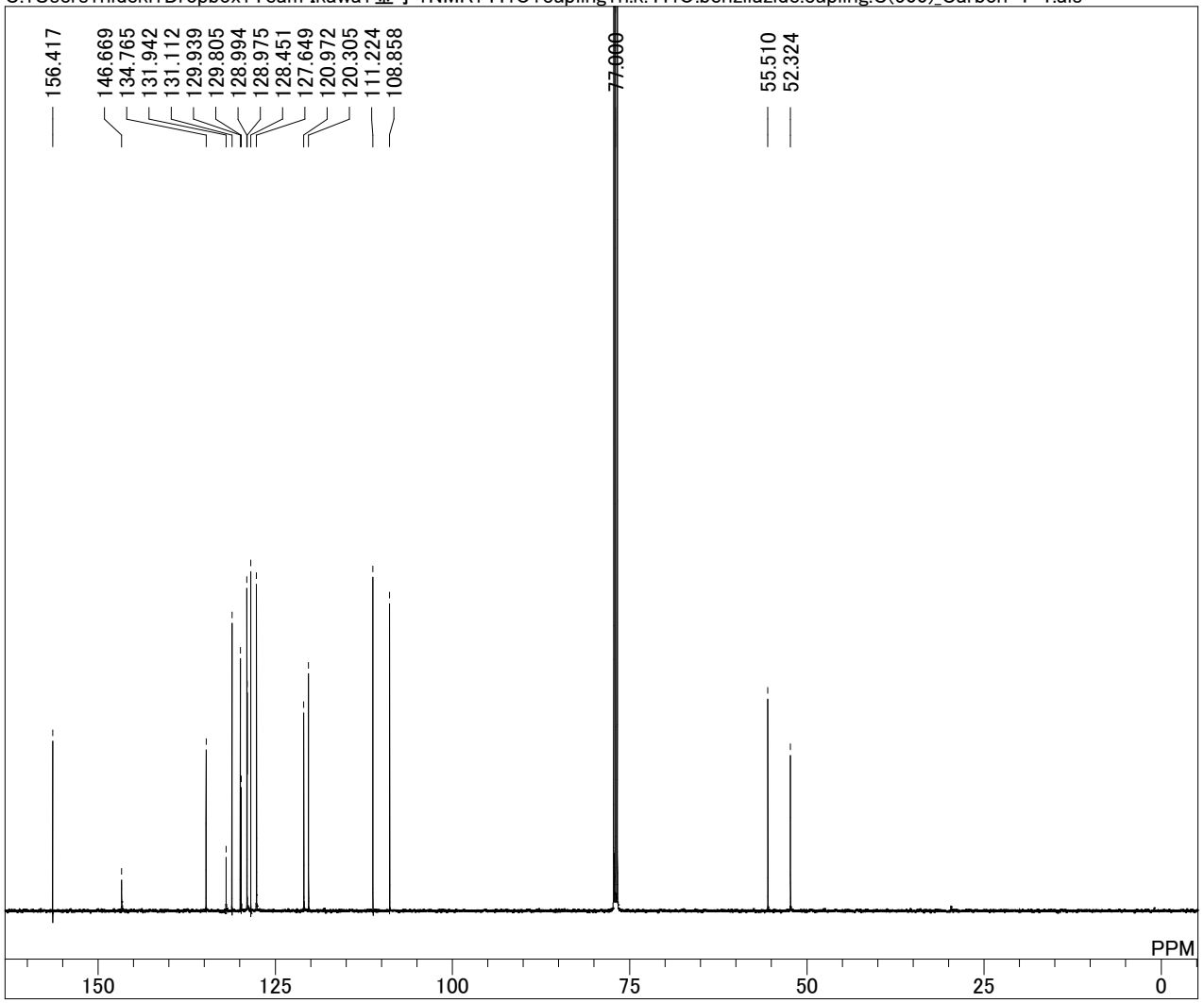
DFILE	h.k.4TfO.azide.cupling.H(300)
COMNT	1H 300MHz CDCl3
DATIM	21-03-2014 10:46:56
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	32
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	17.3 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



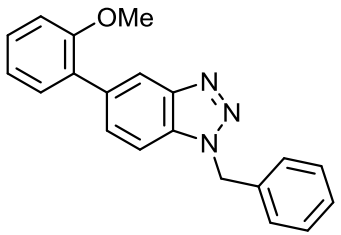
15 (Scheme 4)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO¥cupling¥h.k.4TfO.benzilazide.cupling.C(500)_Carbon-1-1.als



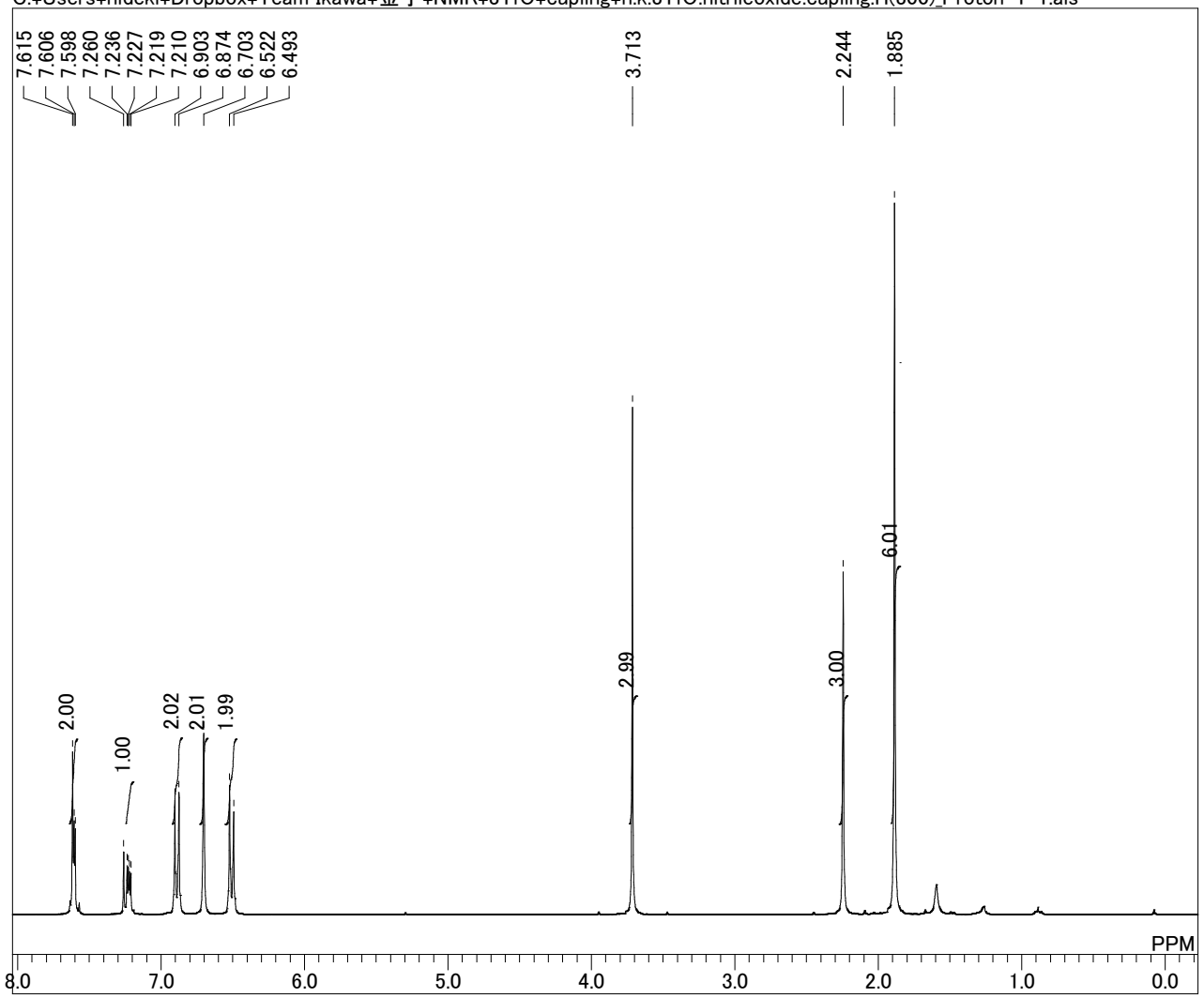
DFILE	h.k.4TfO.benzilazide.cupling.C
COMNT	single pulse decoupled gated
DATIM	15-05-2014 17:11:01
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1200
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



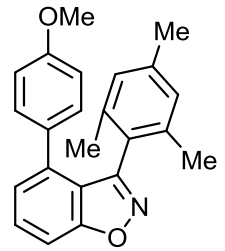
15 (Scheme 4)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥cupling¥h.k.3TfO.nitrileoxide.cupling.H(300)_Proton-1-1.als



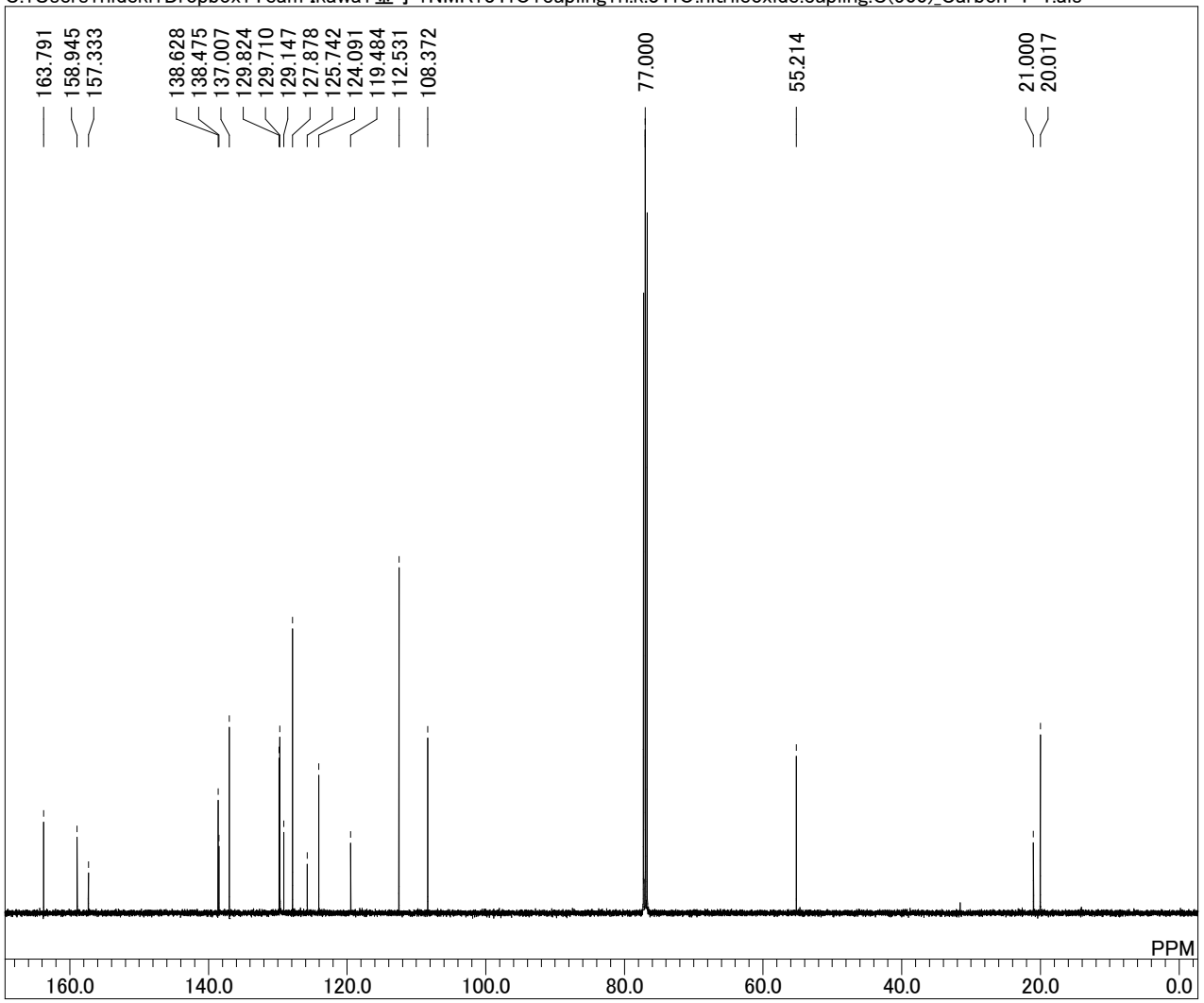
DFILE	h.k.3TfO.nitrileoxide.cupling.H
COMNT	single_pulse
DATIM	30-05-2014 22:32:50
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	23.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



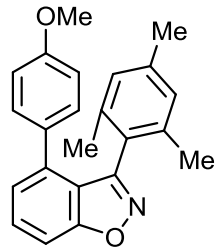
16 (Scheme 4)

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO¥cupling¥h.k.3TfO.nitrileoxide.cupling.C(500)_Carbon-1-1.als



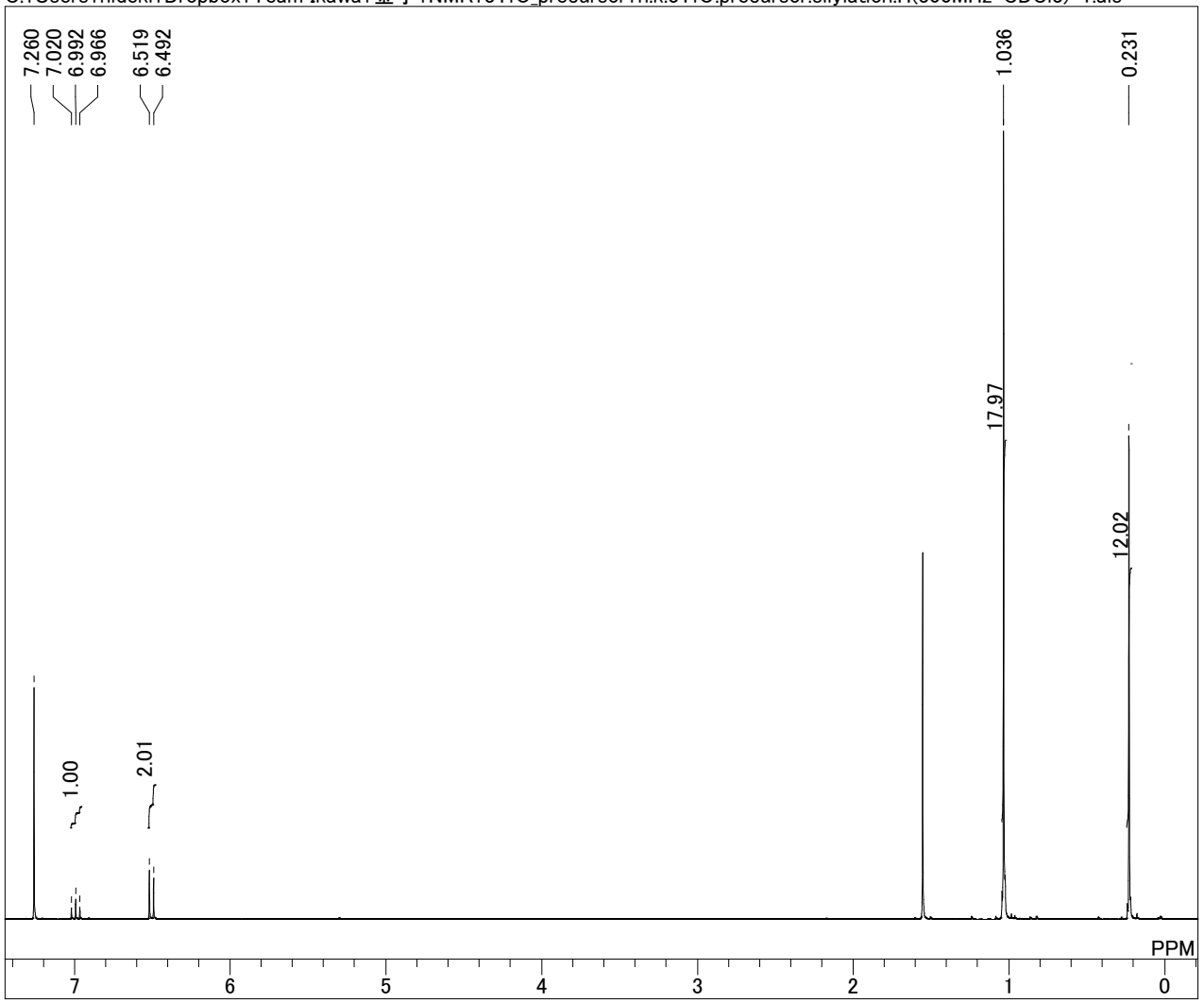
DFILE	h.k.3TfO.nitrileoxide.cupling.C
COMNT	single pulse decoupled gated
DATIM	31-05-2014 00:46:03
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1475
ACQTM	0.8336 sec
PD	2.5000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



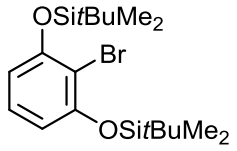
16 (Scheme 4)

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.silylation.H(300MHz-CDCl3)-1.als



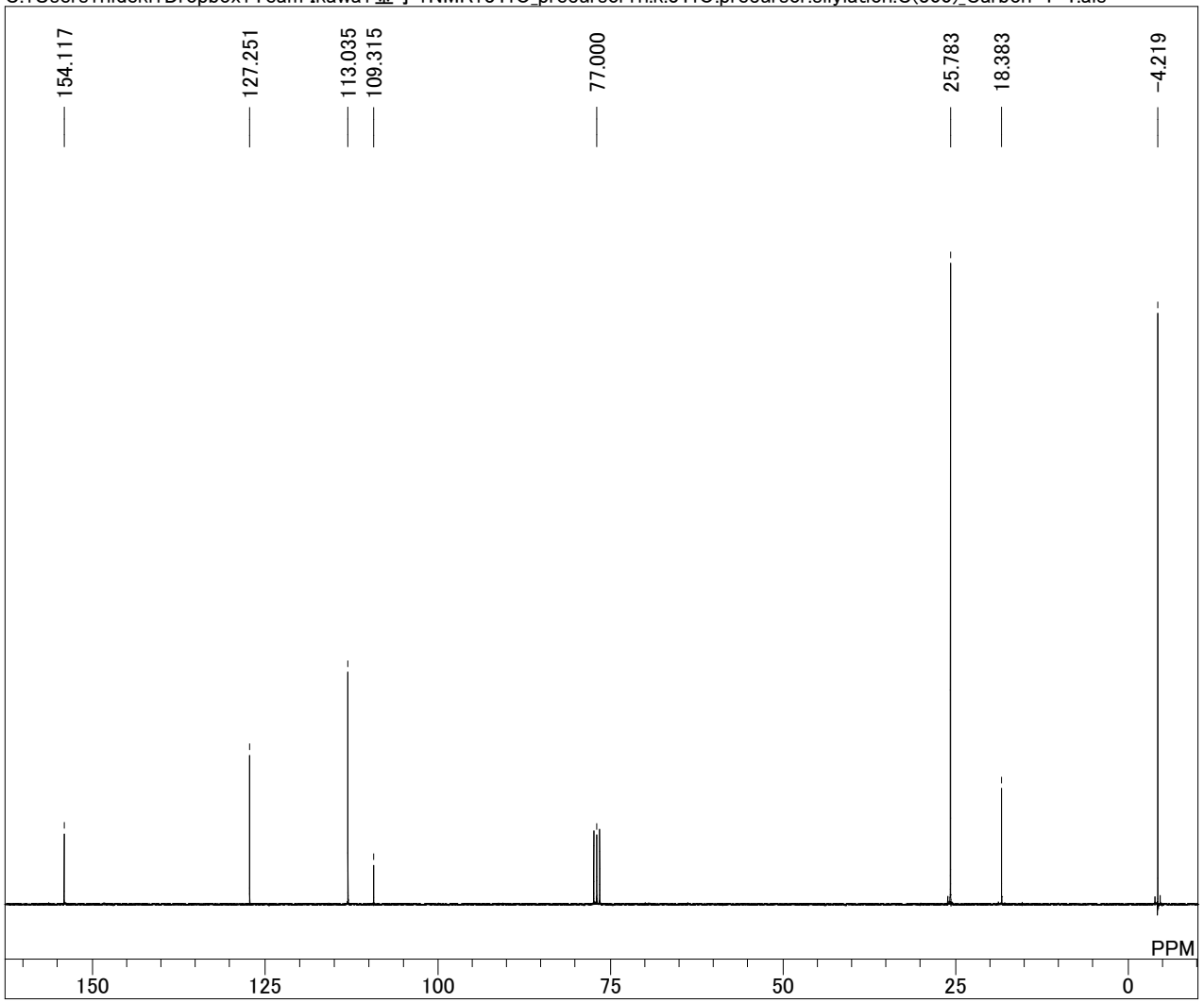
DFILE	h.k.3TfO.precursor.silylation.H
COMNT	single_pulse
DATIM	14-05-2013 20:43:38
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	18.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	44



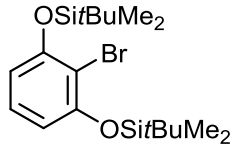
18

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.silylation.C(300)_Carbon-1-1.als



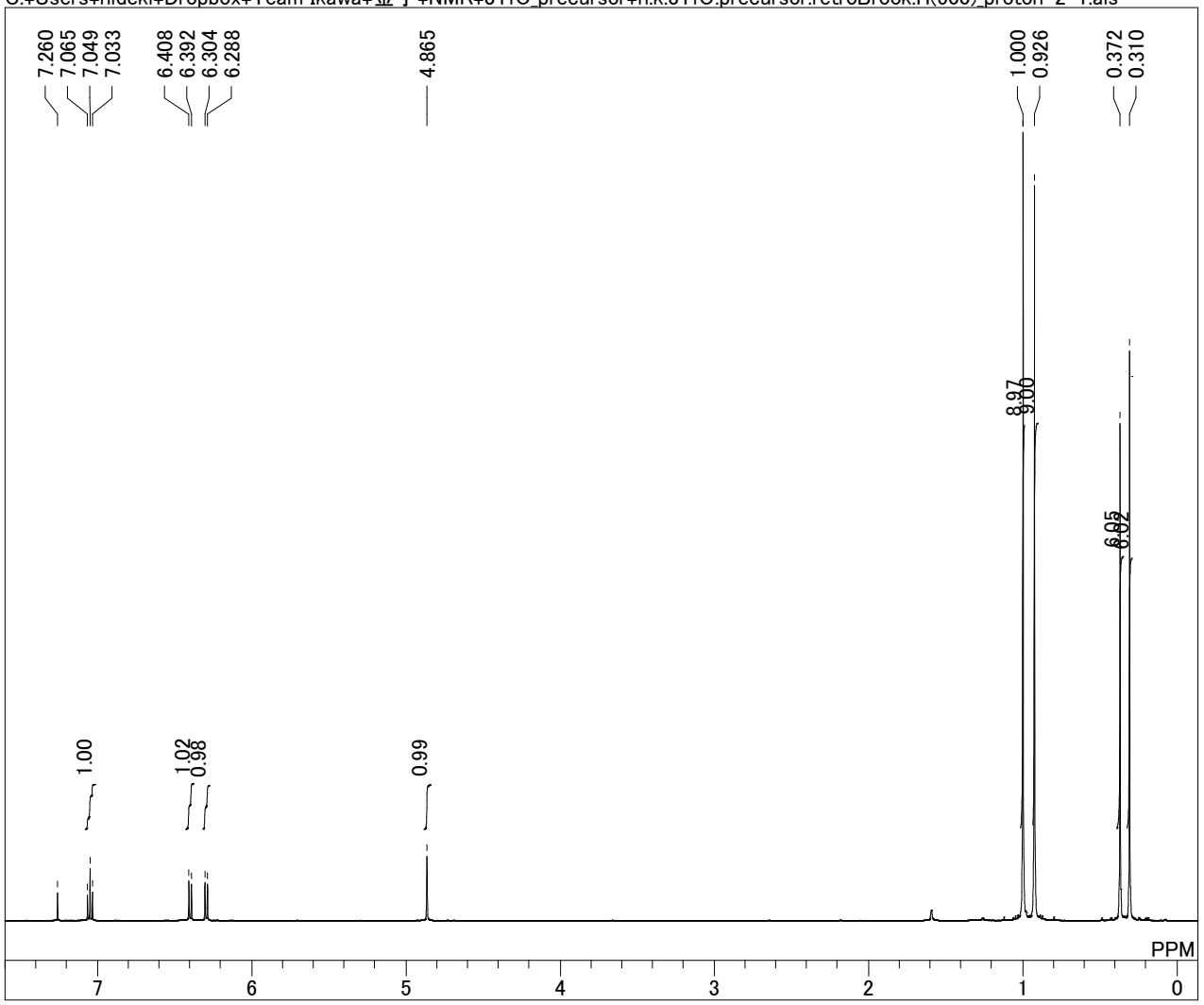
DFILE	h.k.3TfO.precursor.silylation.C
COMNT	single pulse decoupled gated
DATIM	17-05-2014 13:28:36
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.39 Hz
SCANS	142
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



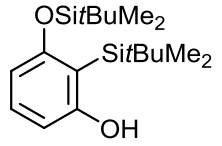
18

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.retroBrook.H(500)_proton-2-1.als



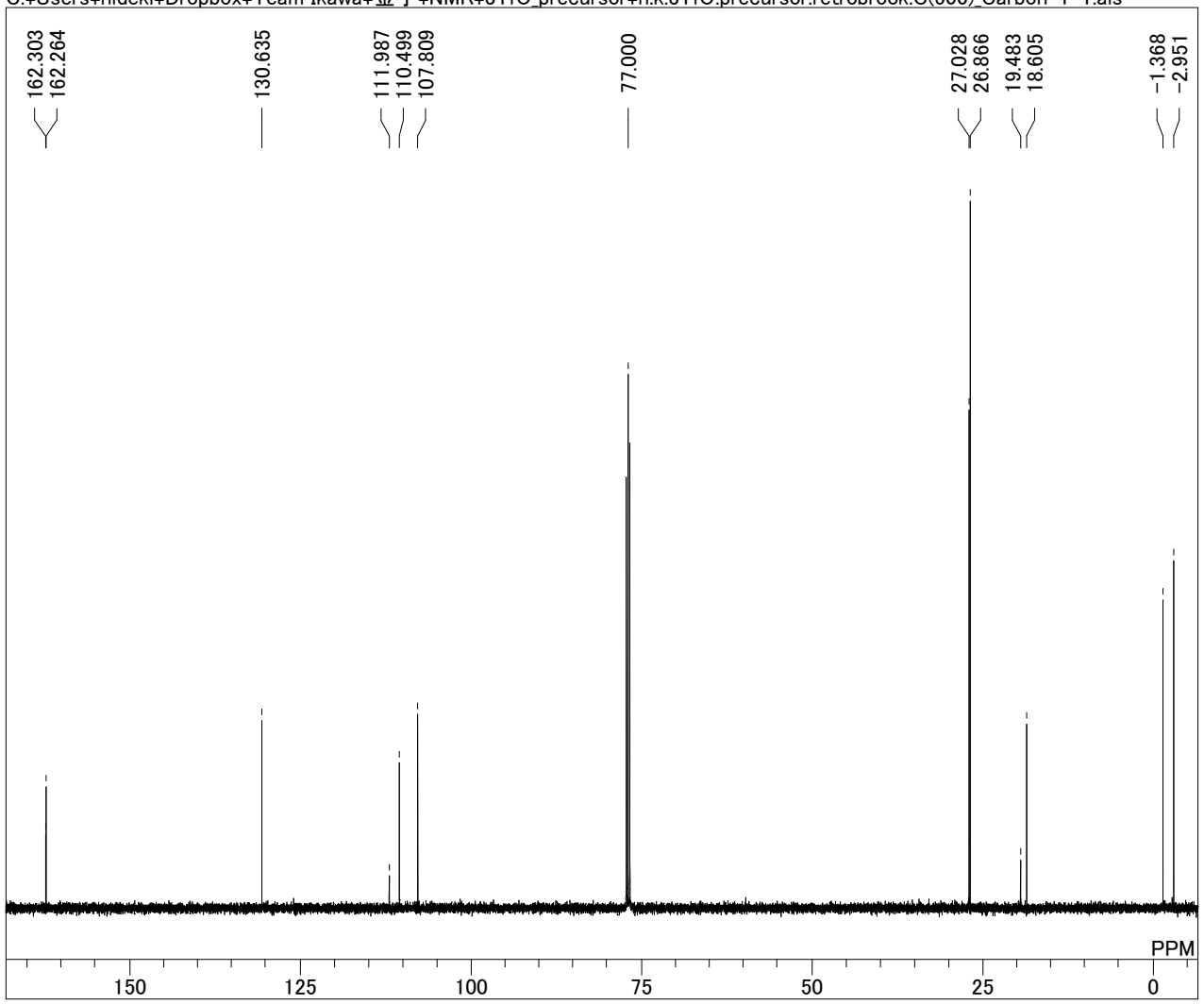
DFILE	h.k.3TfO.precursor.retroBroo
COMNT	single_pulse
DATIM	21-06-2014 21:47:35
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	32



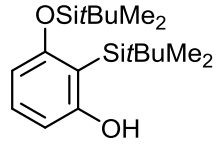
19

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.retrobrook.C(500)_Carbon-1-1.als



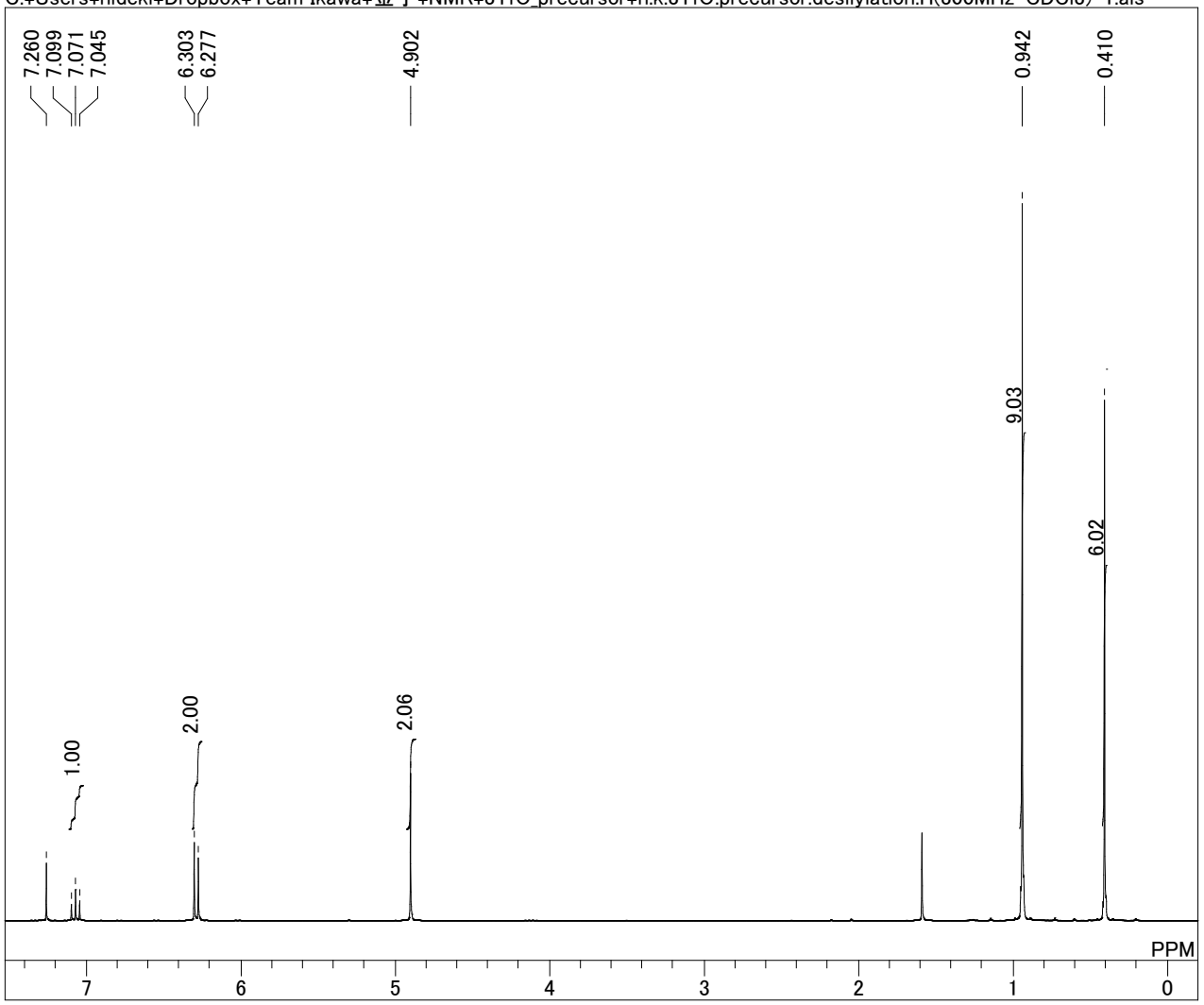
DFILE	h.k.3TfO.precursor.retrobrool
COMNT	single pulse decoupled gated
DATIM	21-06-2014 21:50:43
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	244
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



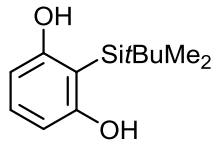
19

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.desilylation.H(300MHz-CDCl3)-1.als



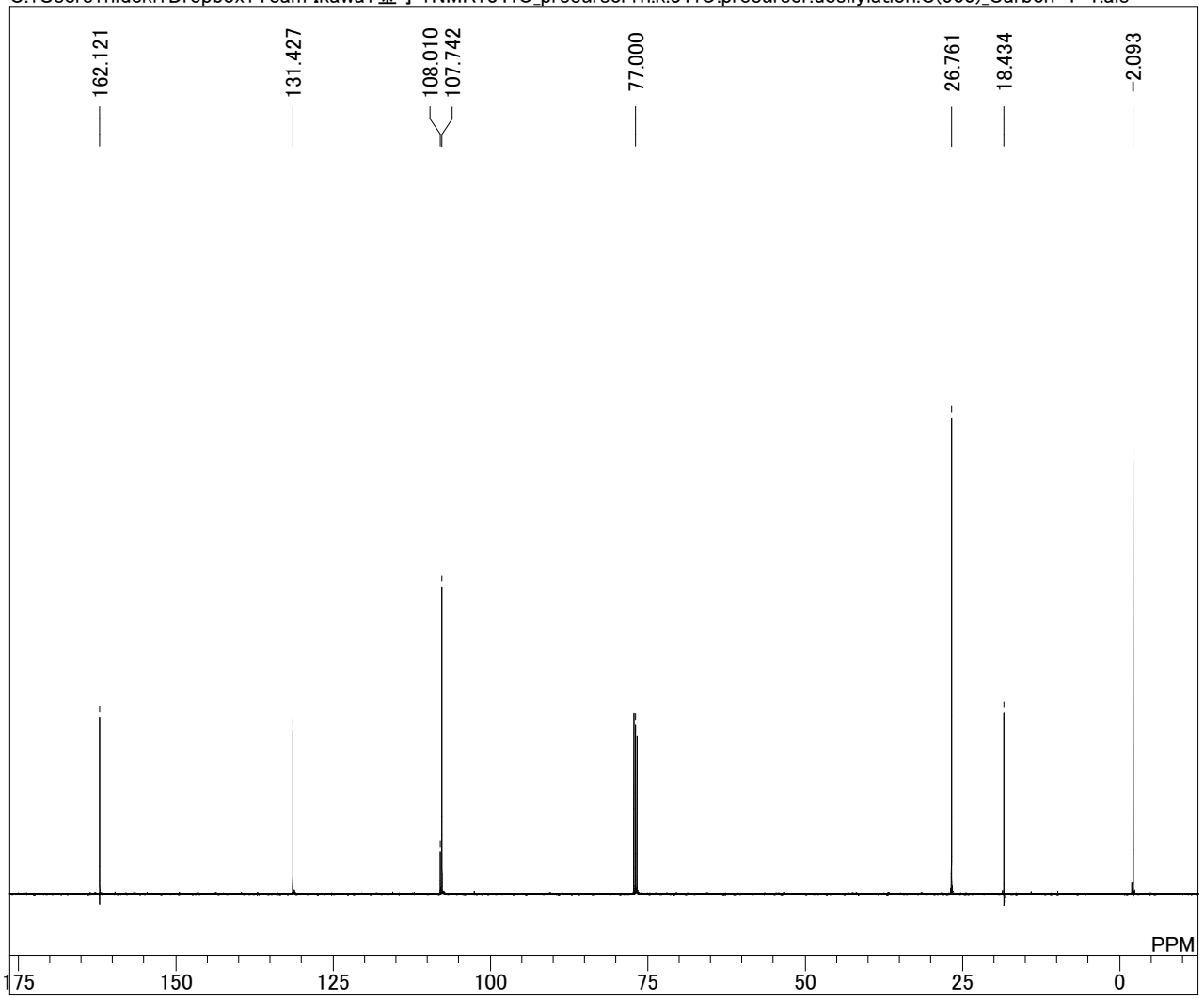
DFILE	h.k.3TfO.precursor.desilylatio
COMNT	single_pulse
DATIM	18-05-2013 13:01:03
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	32
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	18.3 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	42



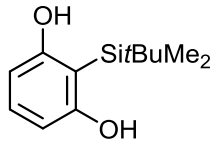
20

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.desilylation.C(500)_Carbon-1-1.als



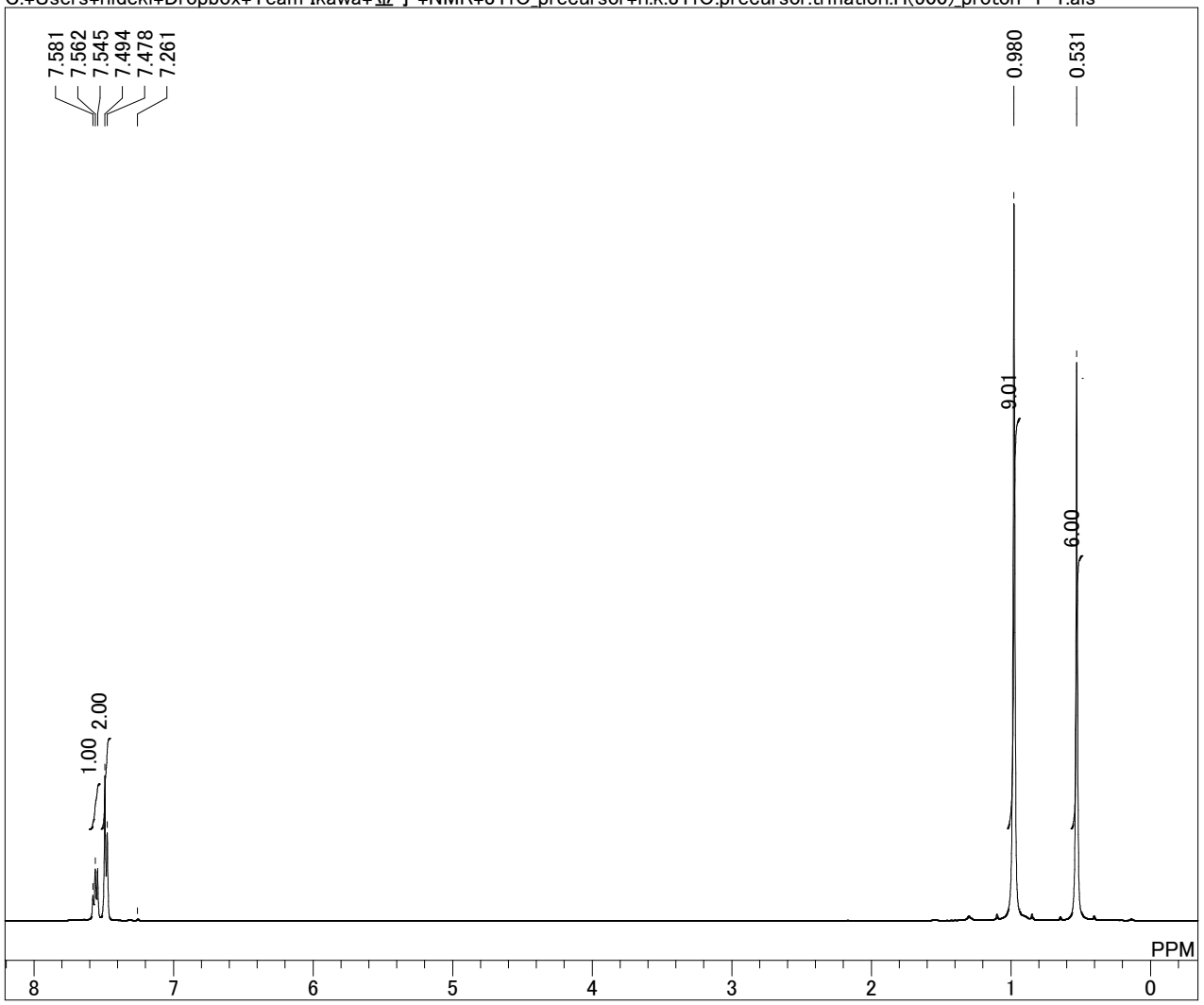
DFILE	h.k.3TfO.precursor.desilylatio
COMNT	single pulse decoupled gated
DATIM	17-05-2014 12:18:56
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	256
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



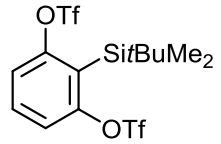
20

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.triflation.H(500)_proton-1-1.als



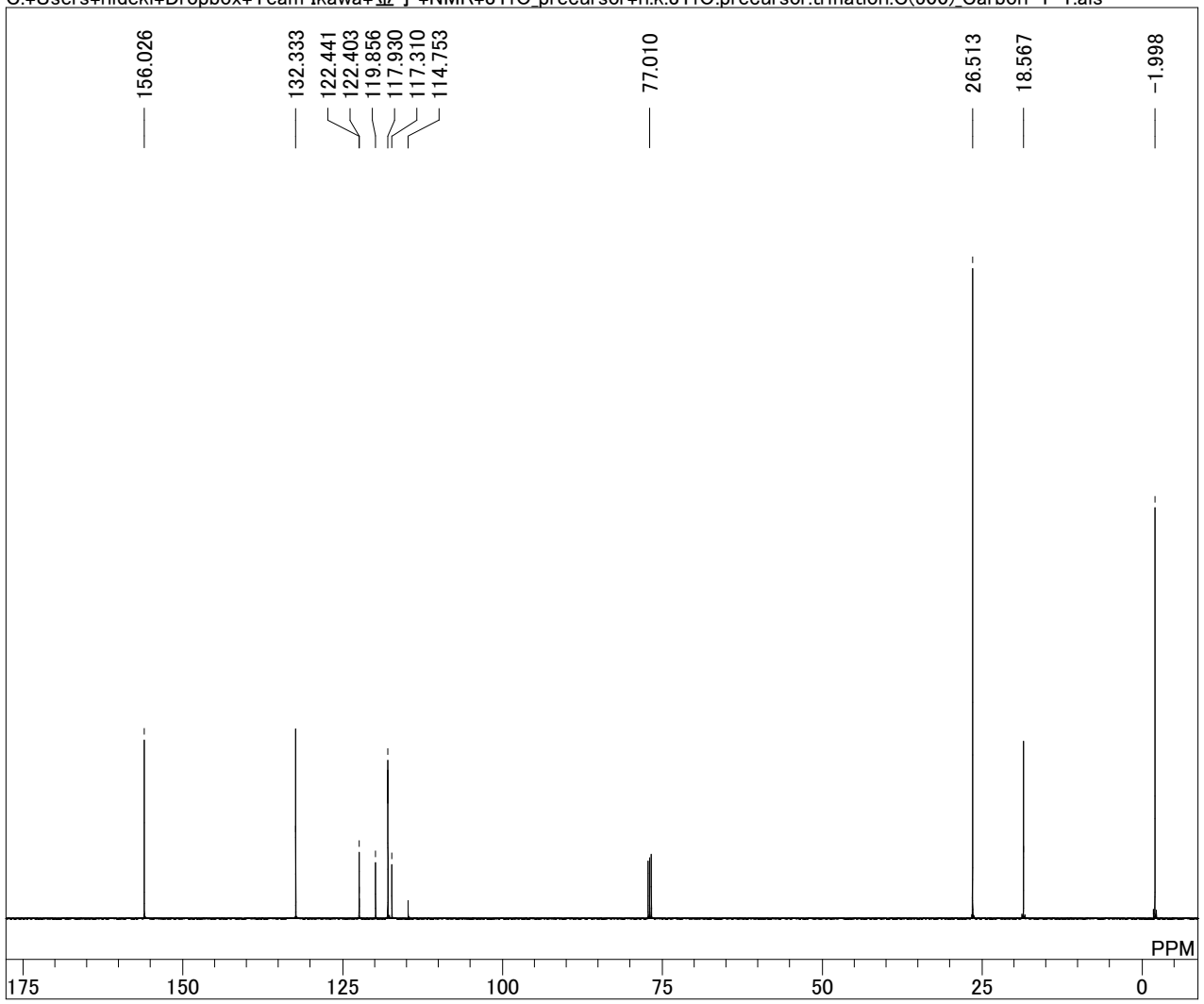
DFILE	h.k.3TfO.precursor.triflation.H
COMNT	single_pulse
DATIM	17-05-2014 18:54:28
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	20.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	16



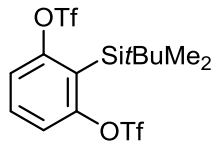
8

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.triflation.C(500)_Carbon-1-1.als



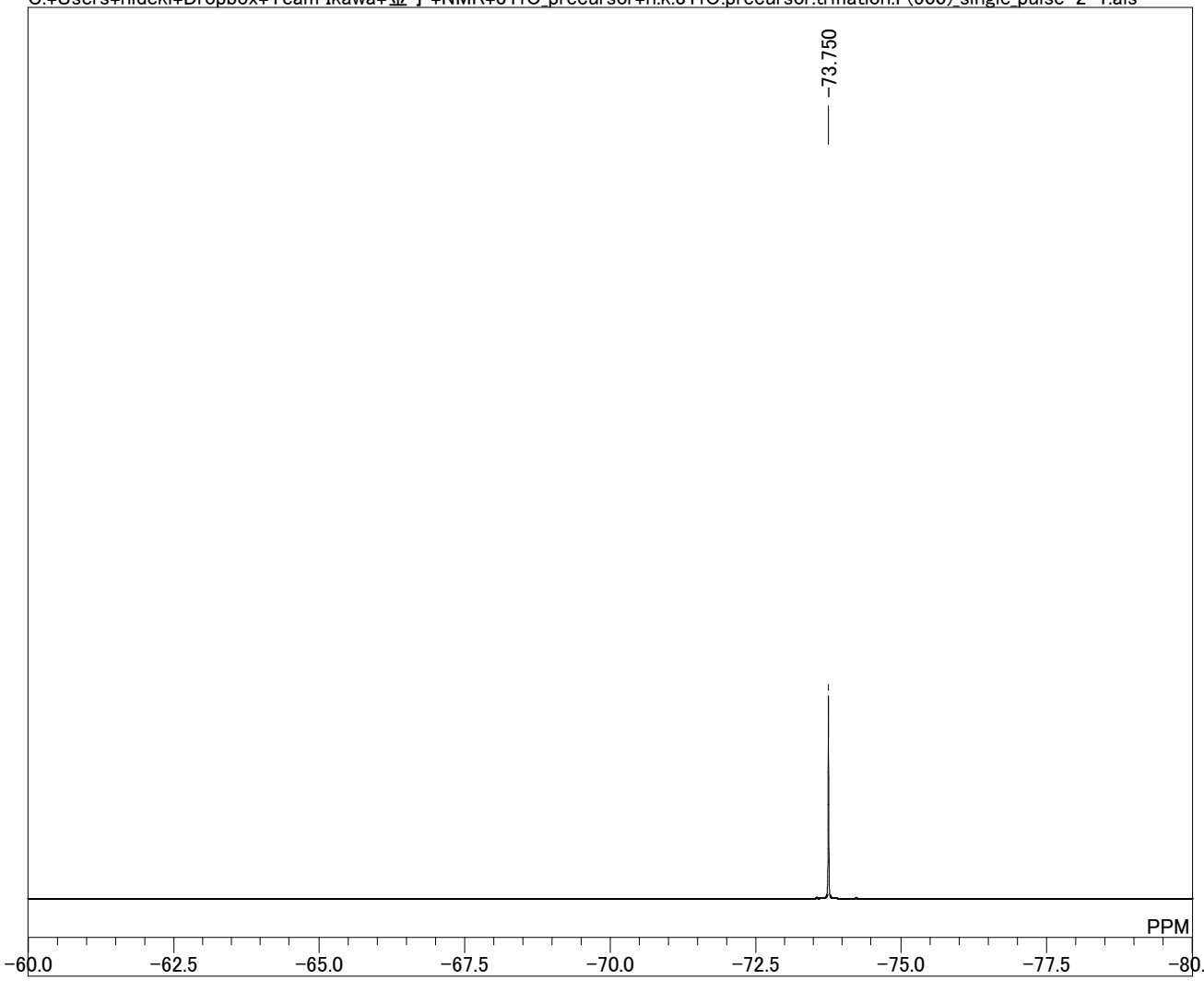
DFILE	h.k.3TfO.precursor.triflation.C
COMNT	single pulse decoupled gated
DATIM	17-05-2014 18:38:16
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	166
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



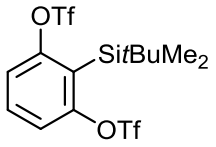
8

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥3TfO_precursor¥h.k.3TfO.precursor.triflation.F(500)_single_pulse-2-1.als



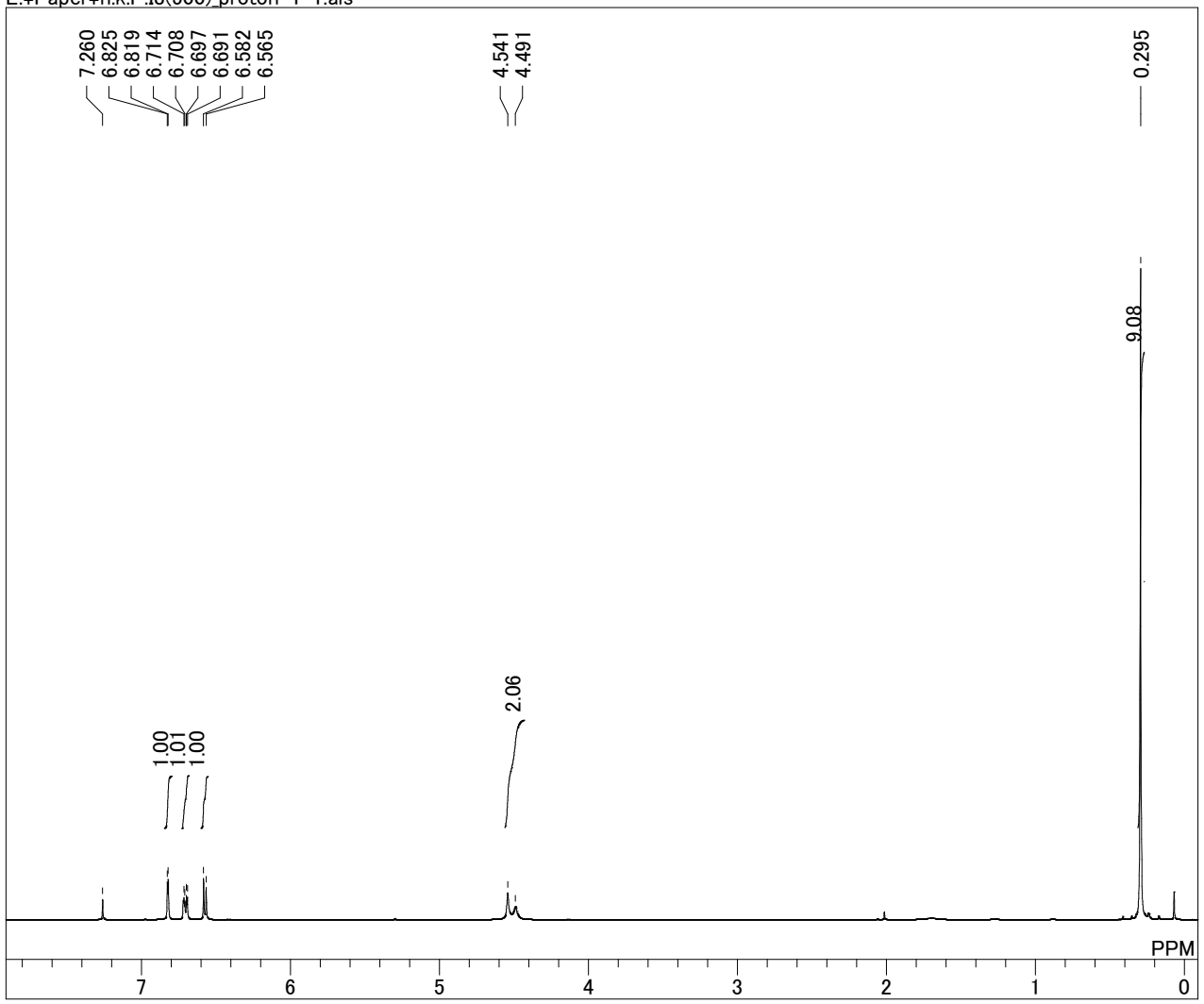
DFILE	h.k.3TfO.precursor.triflation.F
COMNT	single_pulse
DATIM	17-05-2014 18:51:14
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	470.58 MHz
OBSET	7.51 KHz
OBFIN	7.41 Hz
POINT	13107
FREQU	9416.20 Hz
SCANS	8
ACQTM	1.3920 sec
PD	5.0000 sec
PW1	5.80 usec
IRNUC	19F
CTEMP	20.0 c
SLVNT	CDCL3
EXREF	-73.75 ppm
BF	0.12 Hz
RGAIN	24



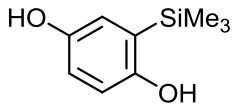
8

single_pulse

E:¥Paper¥h.k.P.I8(500)_proton-1-1.als



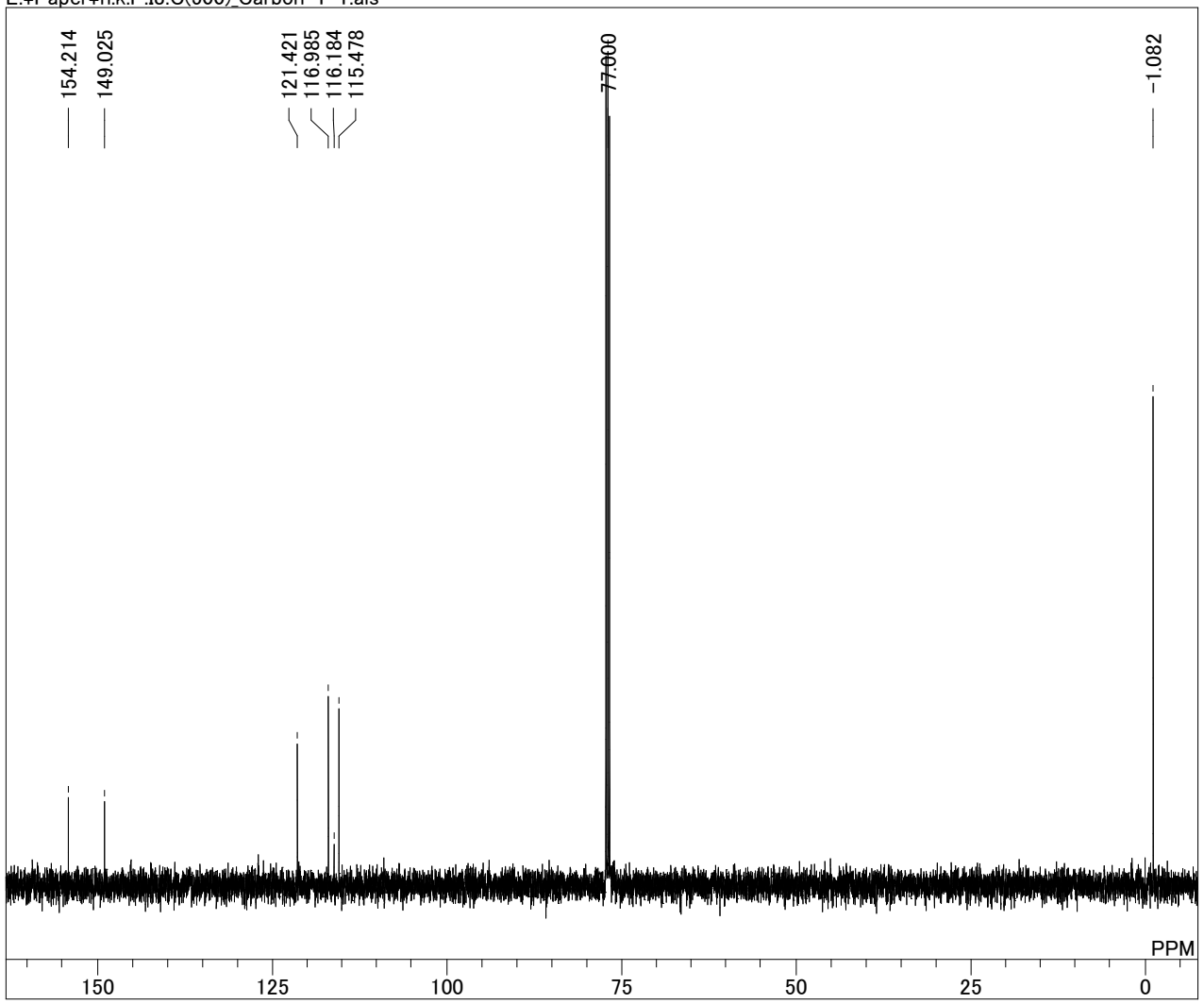
DFILE	h.k.P.I8(500)_proton-1-1.als
COMNT	single_pulse
DATIM	26-05-2014 12:17:55
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	42



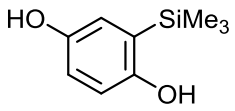
23

single pulse decoupled gated NOE

E:¥Paper¥h.k.P.I8.C(500)_Carbon-1-1.als



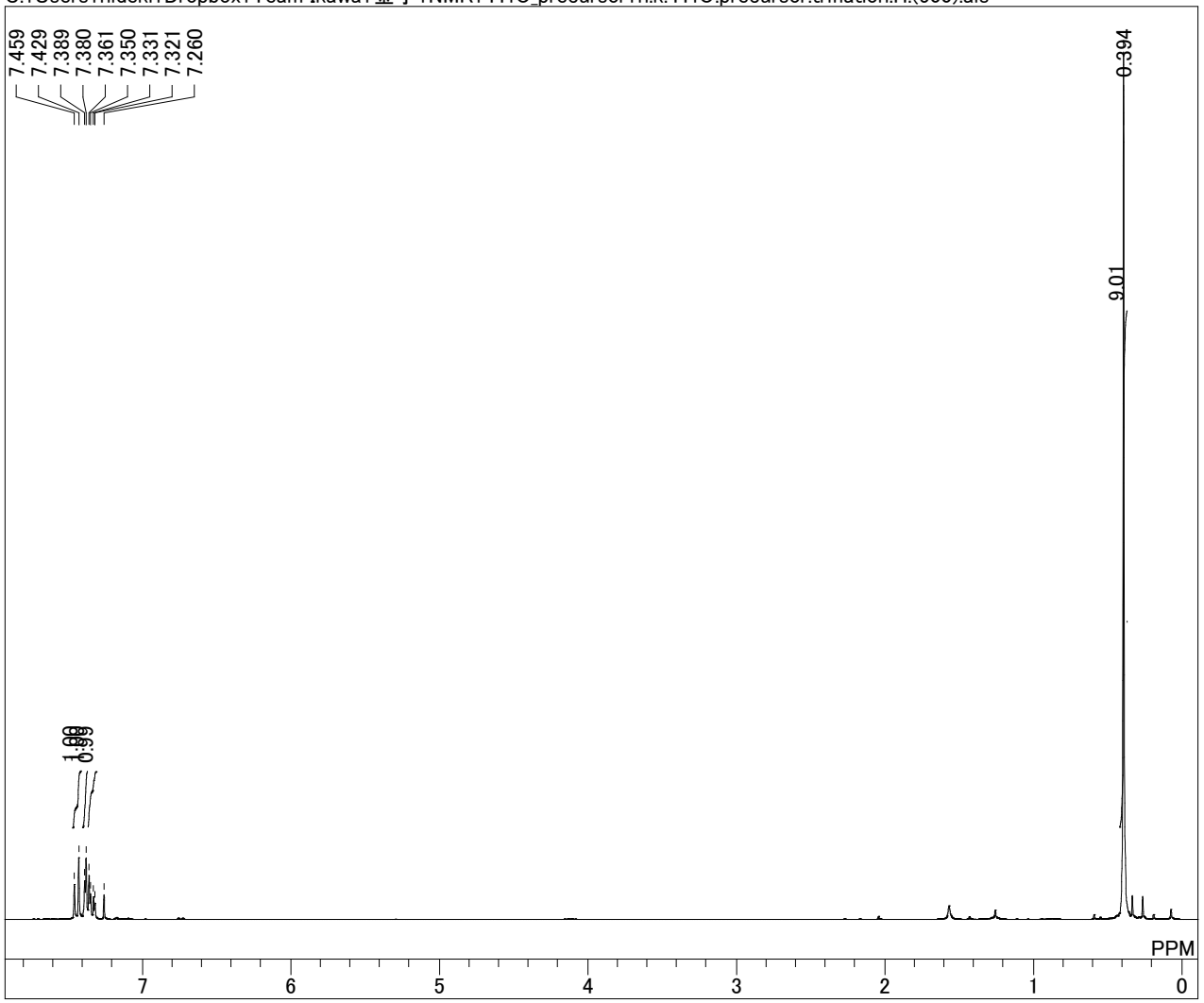
DFILE	h.k.P.I8.C(500)_Carbon-1-1.a
COMNT	single pulse decoupled gated
DATIM	26-05-2014 12:27:31
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	24
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



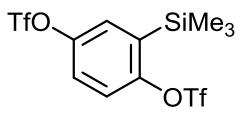
23

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO_precursor¥h.k.4TfO.precursor.triflation.H.(500).als



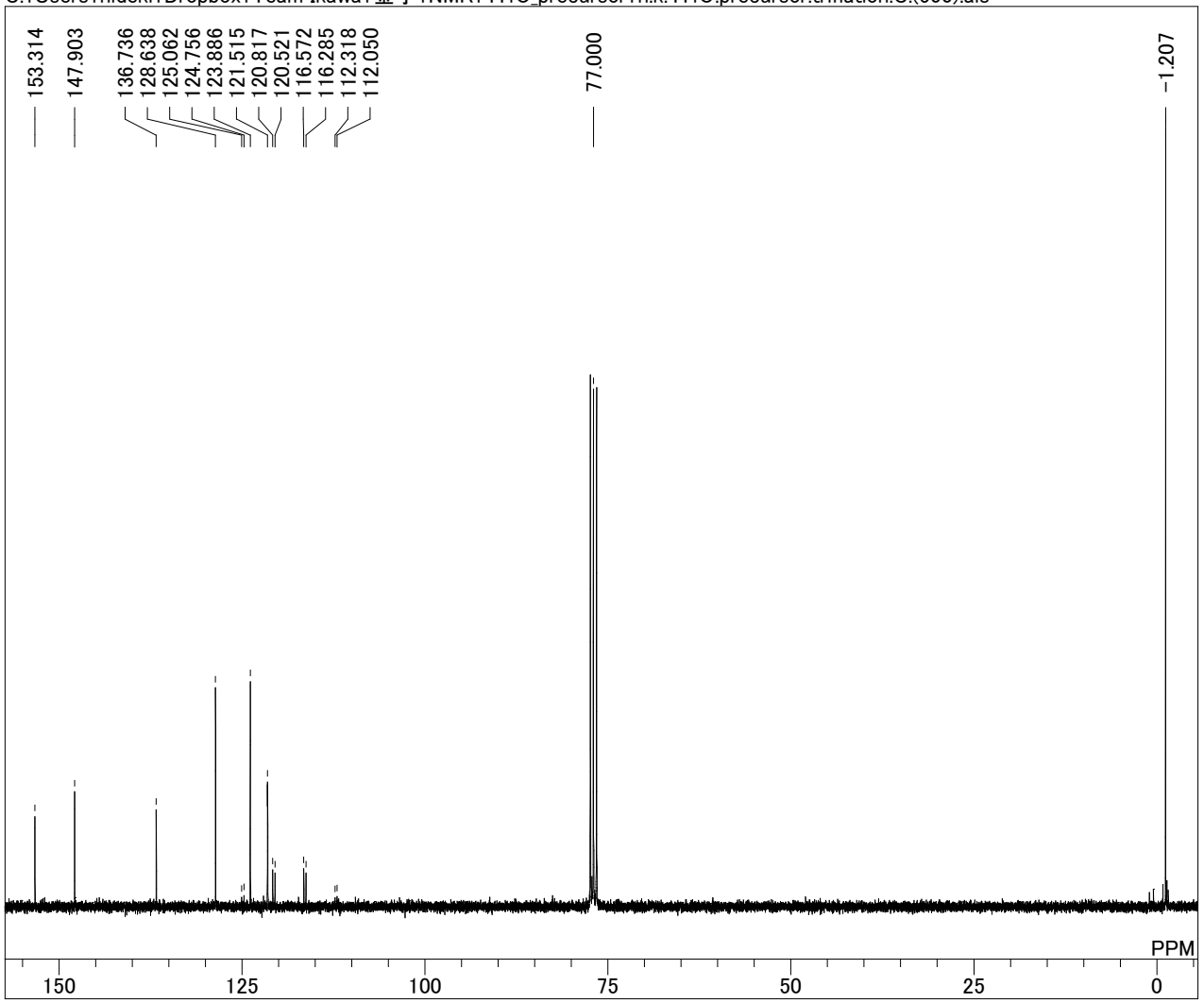
DFILE	h.k.4TfO.precursor.triflation.H
COMNT	single_pulse
DATIM	27-06-2014 01:26:46
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



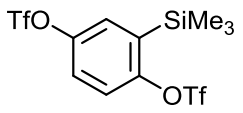
11c

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO_precursor¥h.k.4TfO.precursor.triflation.C.(500).als



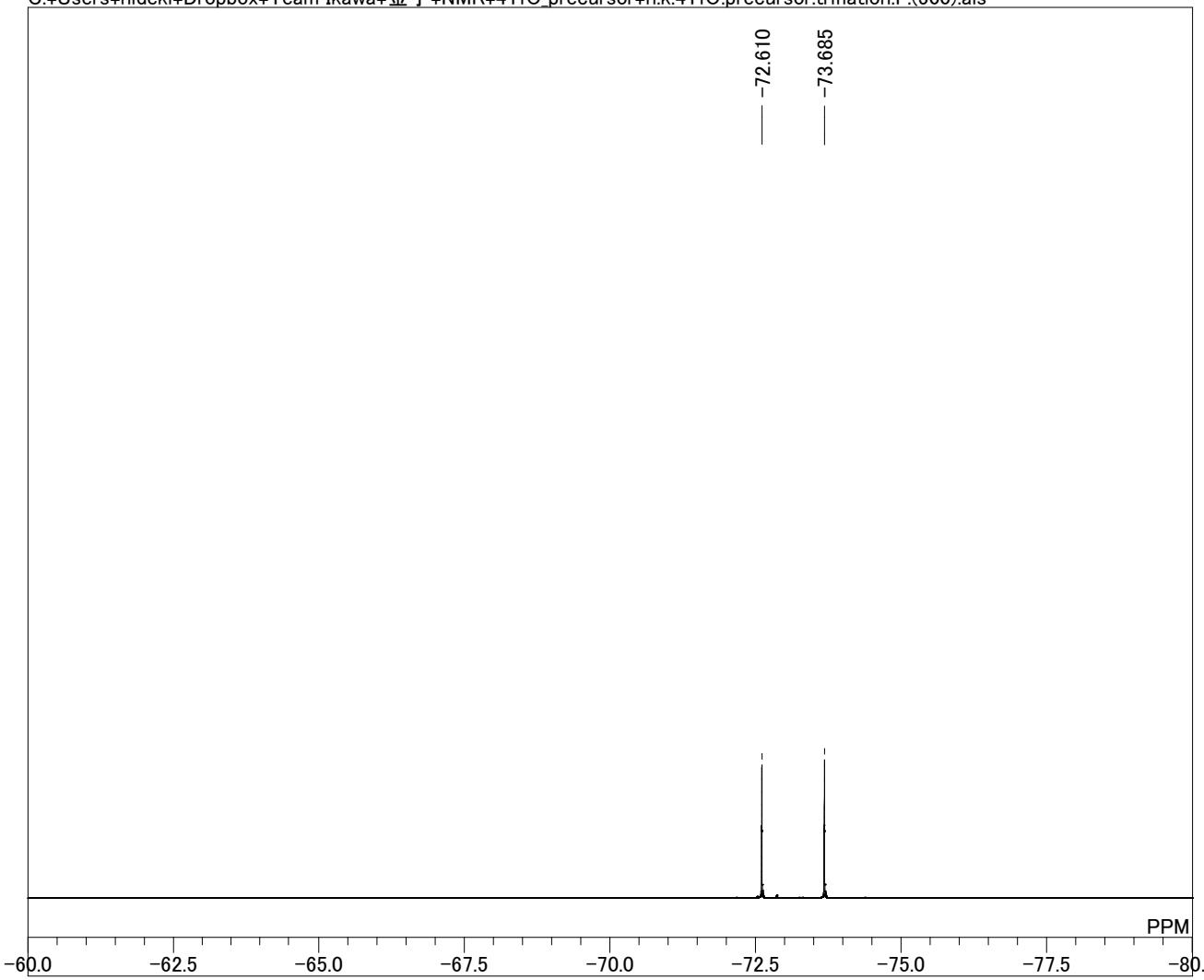
DFILE	h.k.4TfO.precursor.triflation.C
COMNT	single pulse decoupled gated
DATIM	27-06-2014 01:53:36
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.39 Hz
SCANS	2445
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



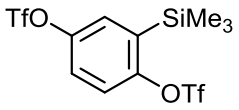
11c

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥NMR¥4TfO_precursor¥h.k.4TfO.precursor.triflation.F.(500).als



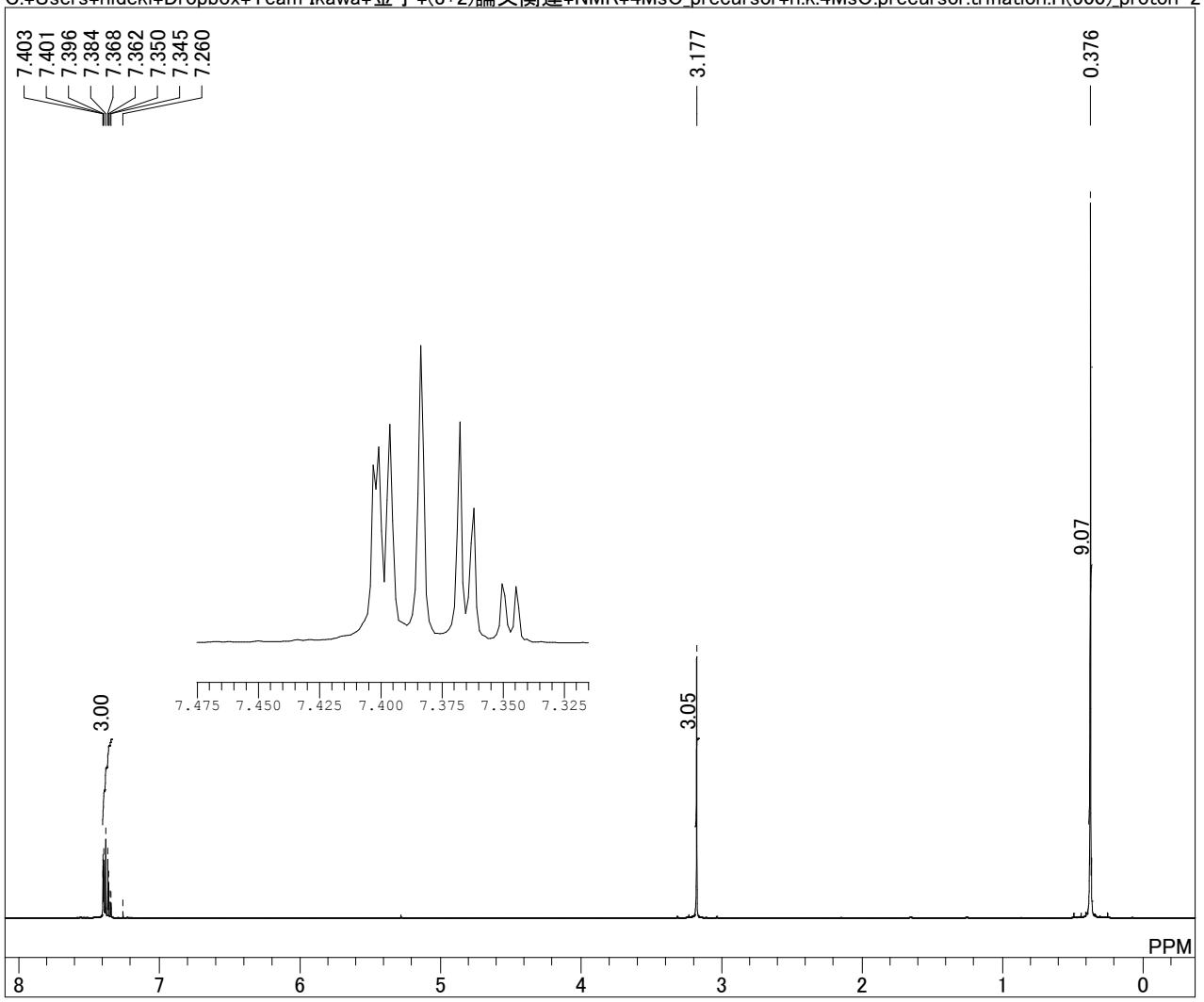
DFILE	h.k.4TfO.precursor.triflation.F
COMNT	single_pulse
DATIM	27-06-2014 01:19:31
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	282.76 MHz
OBSET	0.57 KHz
OBFIN	3.94 Hz
POINT	52428
FREQU	5656.11 Hz
SCANS	8
ACQTM	9.2694 sec
PD	5.0000 sec
PW1	6.00 usec
IRNUC	19F
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	−72.61 ppm
BF	0.12 Hz
RGAIN	40



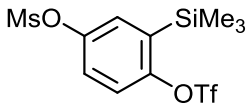
11c

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥(3+2)論文関連¥NMR¥4MsO_precursor¥h.k.4MsO.precursor.triflation.H(500)_proton-2-1.als



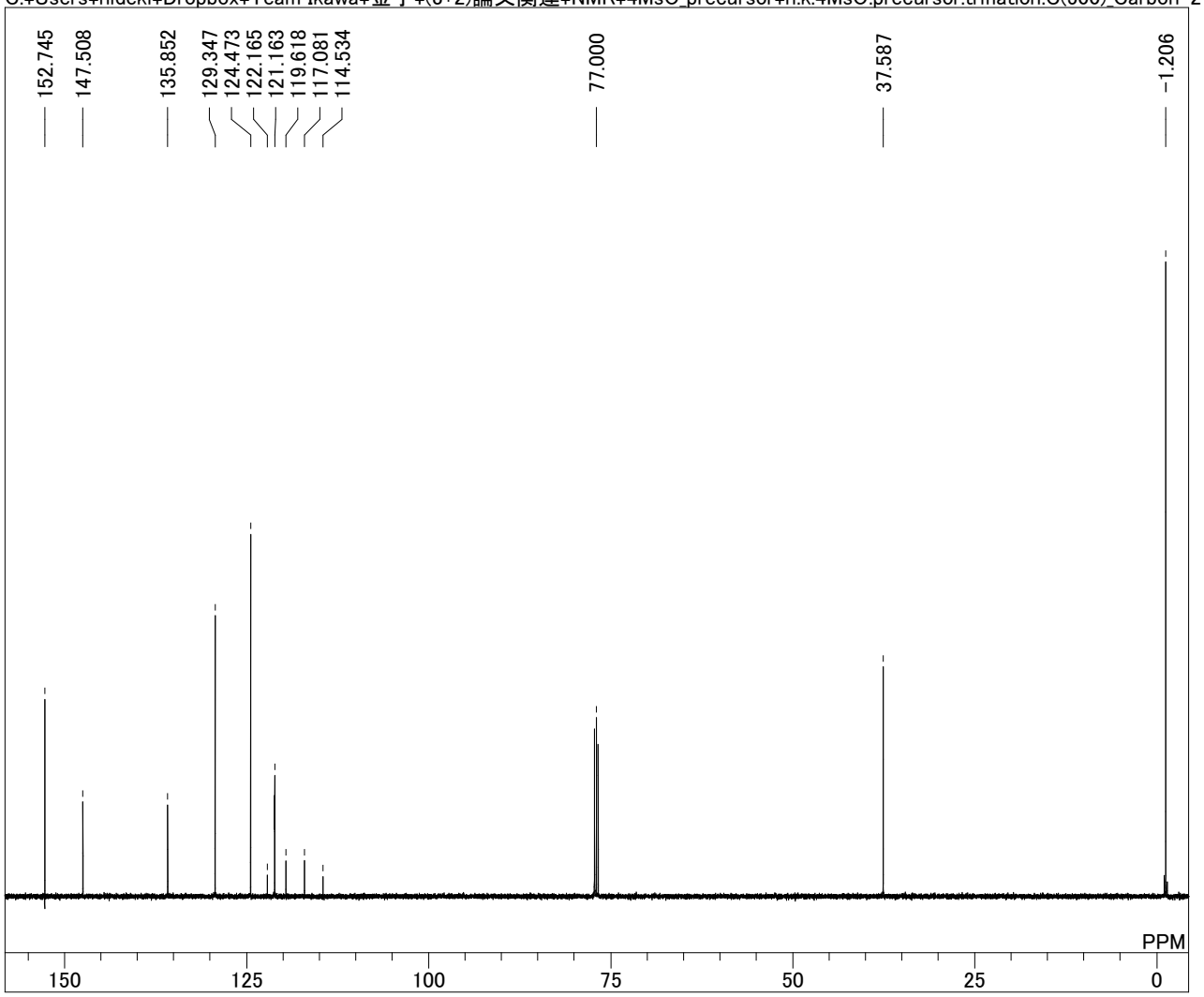
DFILE	h.k.4MsO.precursor.triflation.
COMNT	single_pulse
DATIM	19-05-2014 18:19:57
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	24



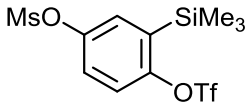
11b

single pulse decoupled gated NOE

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥(3+2)論文関連¥NMR¥4MsO_precursor¥h.k.4MsO.precursor.triflation.C(500)_Carbon-2-1.als



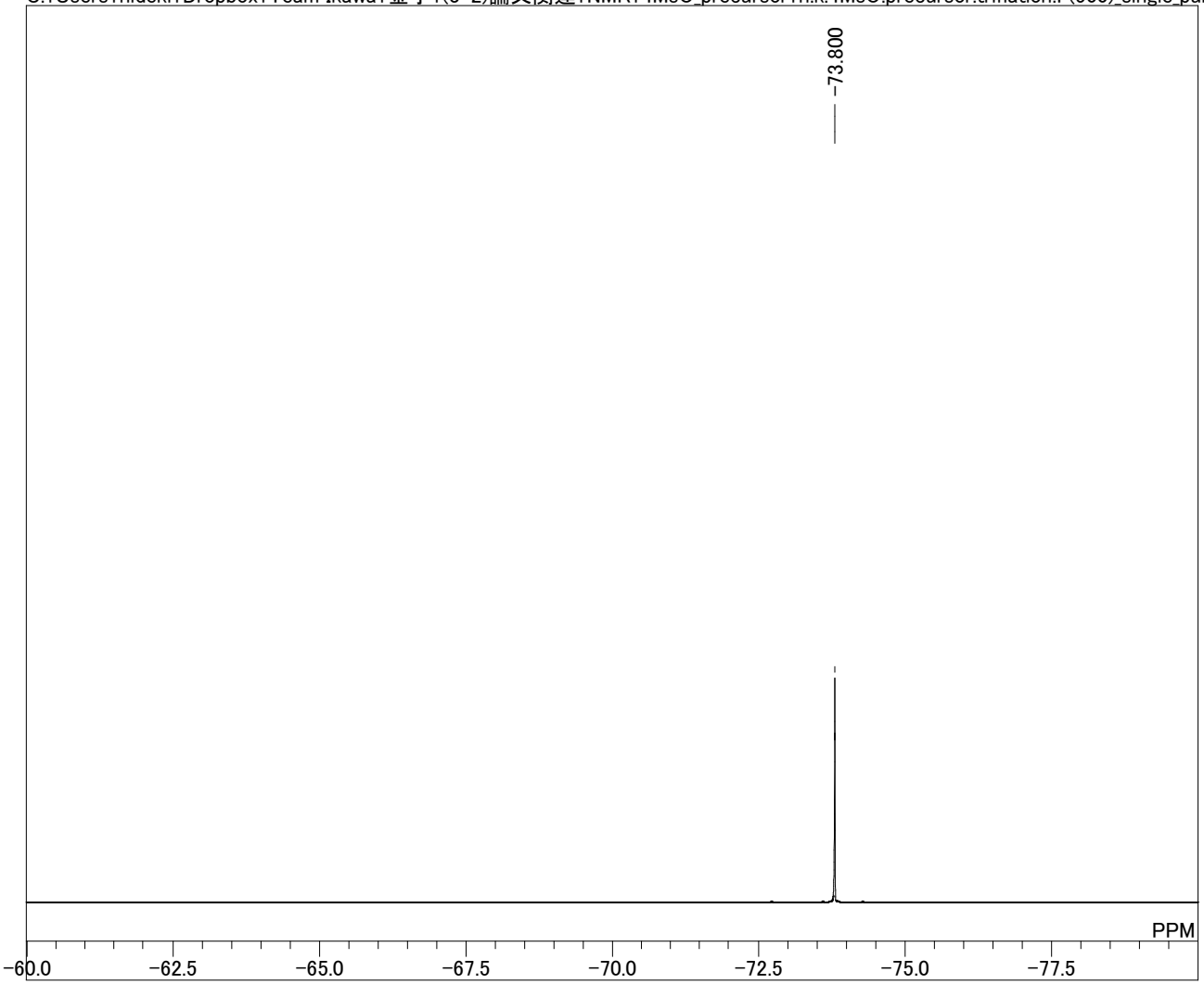
DFILE	h.k.4MsO.precursor.triflation.
COMNT	single pulse decoupled gated
DATIM	19-05-2014 18:05:00
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	140
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



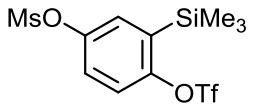
11b

single_pulse

C:¥Users¥hideki¥Dropbox¥Team Ikawa¥金子¥(3+2)論文関連¥NMR¥4MsO_precursor¥h.k.4MsO.precursor.triflation.F(500)_single_pulse-4-1.als



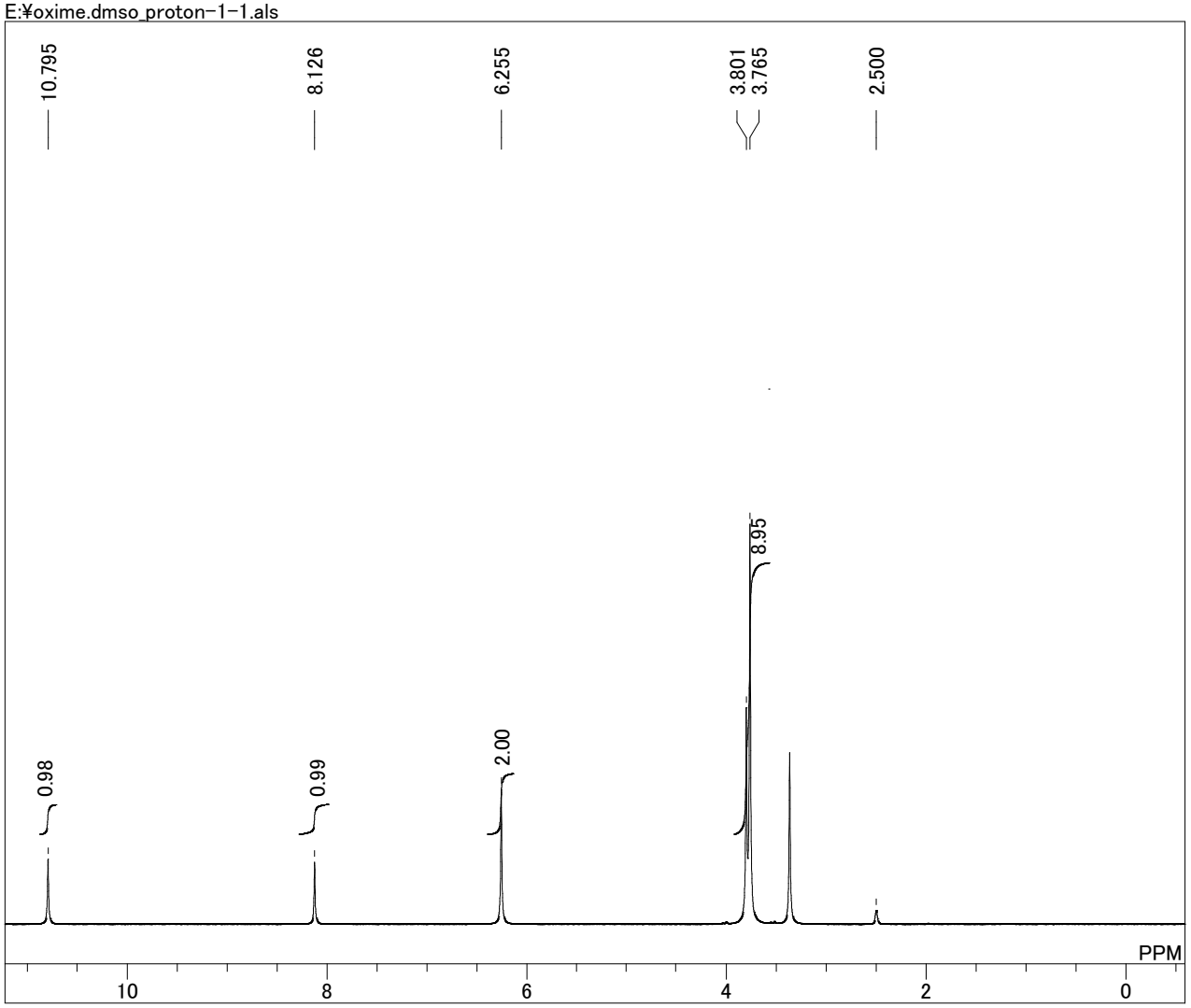
DFILE	h.k.4MsO.precursor.triflation.
COMNT	single_pulse
DATIM	19-05-2014 18:16:32
OBNUC	19F
EXMOD	single_pulse.jxp
OBFRQ	470.58 MHz
OBSET	7.51 KHz
OBFIN	7.41 Hz
POINT	13107
FREQU	9416.20 Hz
SCANS	8
ACQTM	1.3920 sec
PD	5.0000 sec
PW1	5.80 usec
IRNUC	19F
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	-73.80 ppm
BF	0.12 Hz
RGAIN	36



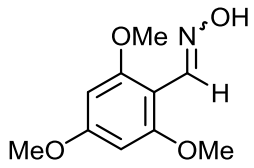
11b

single_pulse

E:¥oxime.dmso_proton-1-1.als



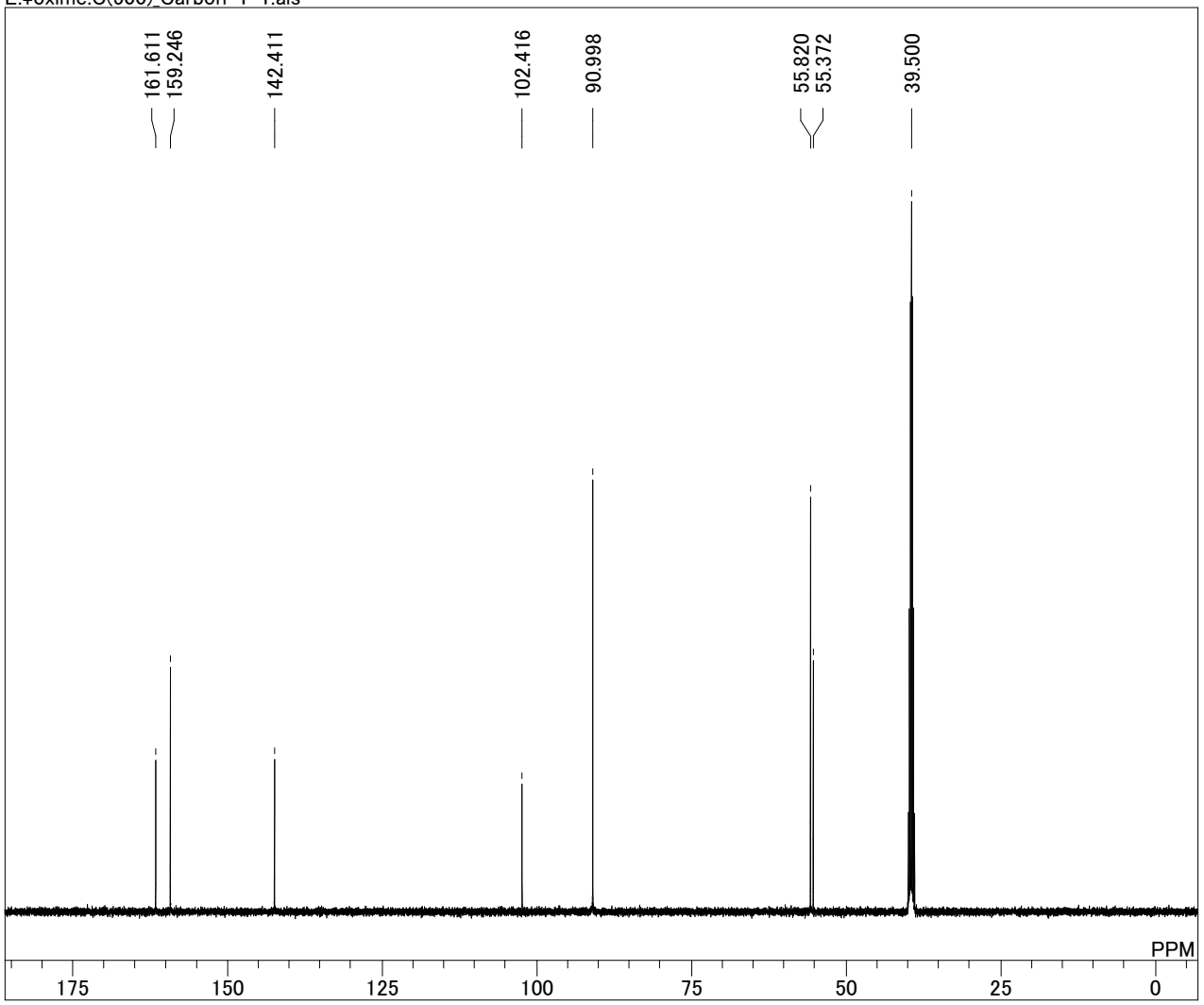
DFILE	oxime.dmso_proton-1-1.als
COMNT	single_pulse
DATIM	14-07-2014 20:43:26
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	4
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	23.4 c
SLVNT	DMSO
EXREF	2.50 ppm
BF	0.12 Hz
RGAIN	34



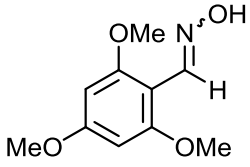
S3

single pulse decoupled gated NOE

E:¥oxime.C(500)_Carbon-1-1.als



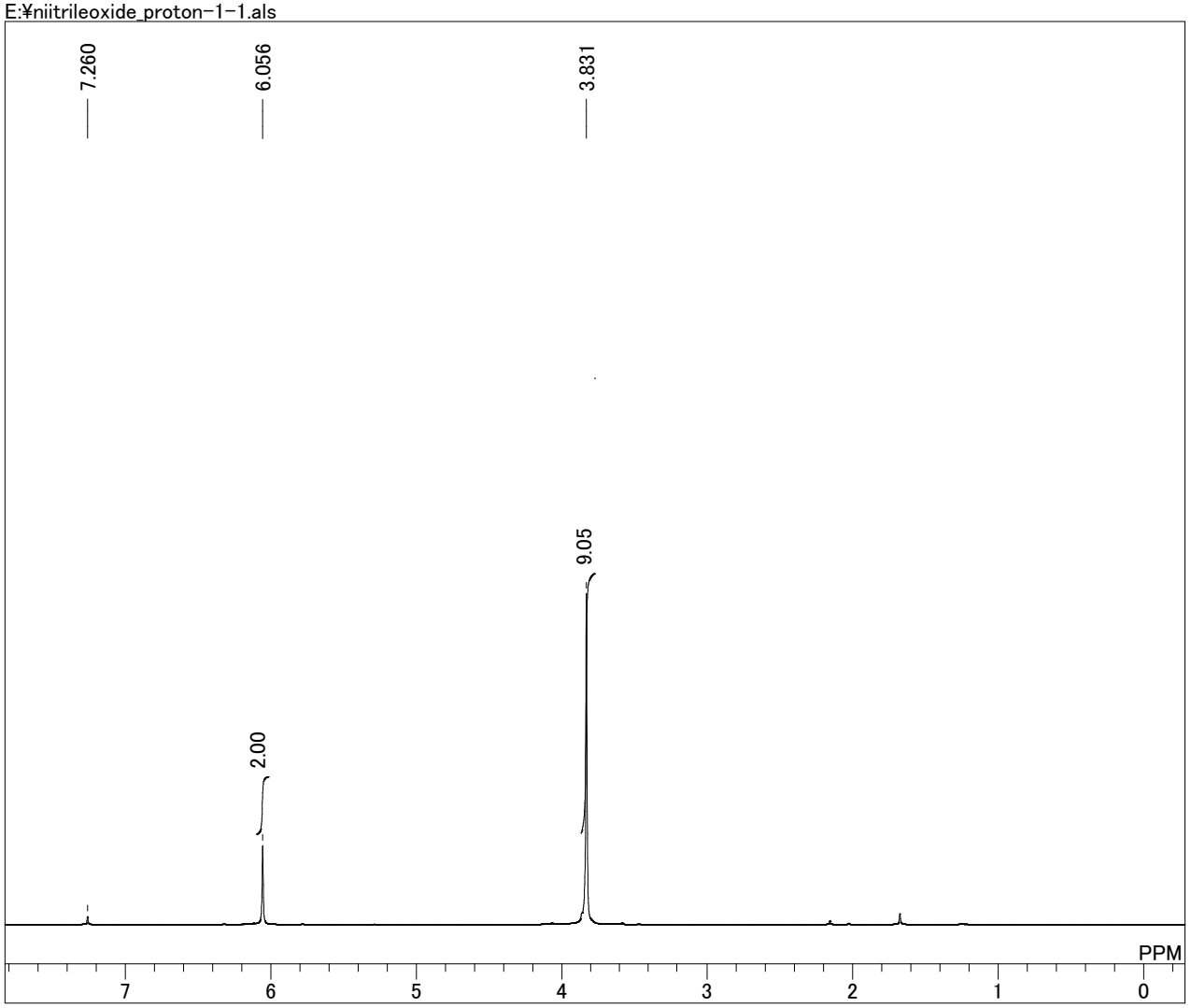
DFILE	oxime.C(500)_Carbon-1-1.als
COMNT	single pulse decoupled gated
DATIM	14-07-2014 22:12:59
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	310
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.4 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	60



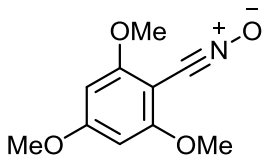
S3

single_pulse

E:¥niitrileoxide_proton-1-1.als



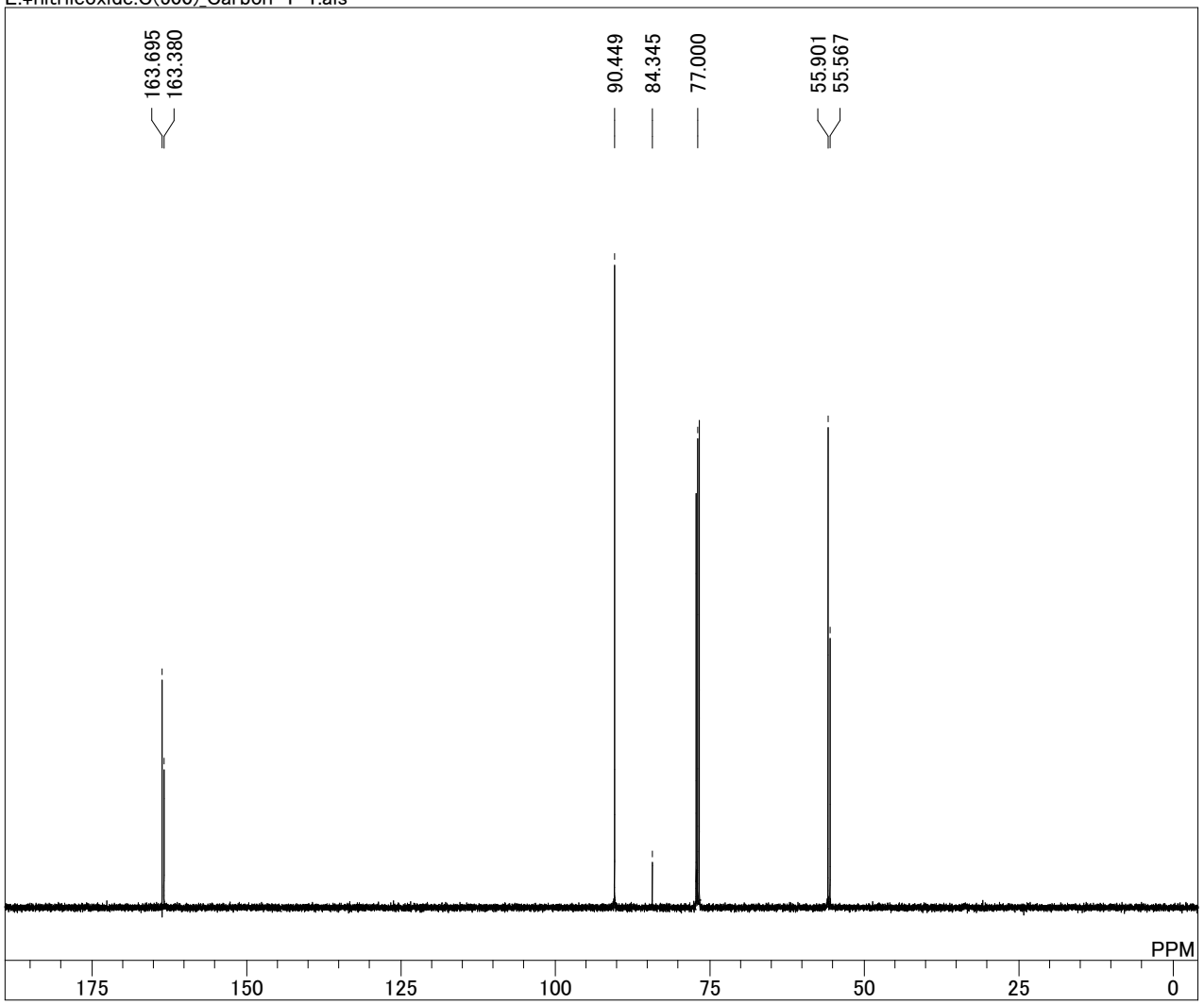
DFILE	niitrileoxide_proton-1-1.als
COMNT	single_pulse
DATIM	15-07-2014 11:44:07
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	8
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	36



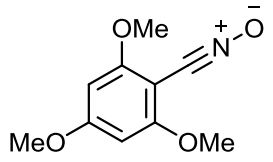
9b

single pulse decoupled gated NOE

E:¥nitrileoxide.C(500)_Carbon-1-1.als



DFILE	nitrileoxide.C(500)_Carbon-1-
COMNT	single pulse decoupled gated
DATIM	15-07-2014 11:55:58
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	578
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



9b