Electronic Supplementary Information

Development of 3-Triazenylaryne and Its Application to Iterative Aryne Reactions via *o*-Triazenylarylboronic Acids

Motoki Ito,* Yuta Takishima, Rinto Ishikawa, Mao Kamimura, Hana Watanabe, Takehiro Konishi, Kazuhiro Higuchi, and Shigeo Sugiyama*

Meiji Pharmaceutical University, 2-522-1 Noshio Kiyose, Tokyo 204-8588, Japan

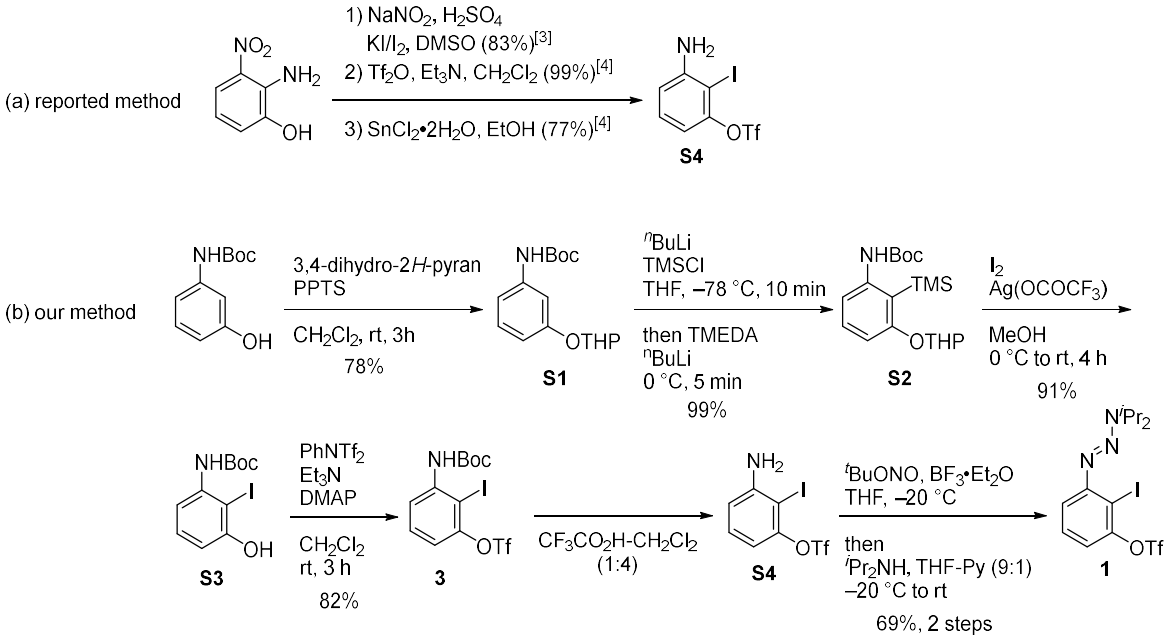
mito@my-pharm.ac.jp
sugiyama@my-pharm.ac.jp

Experimental Section

General. All melting points were measured on a Yanagimoto micro melting point apparatus. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer and absorbance bands are reported in wavenumber (cm^{-1}). ^{1}H NMR spectra were recorded on JEOL JNM-AL 300 (300 MHz) spectrometer or JEOL JNM-ECA 400 (400 MHz) spectrometer or JEOL JNM-ECZ 500 (500 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane at δ_H 0.00, $CDCl_3$ at δ_H 7.26, CD_3CN at δ_H 1.94, CD_3OD at δ_H 3.31). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration. ^{13}C NMR spectra were recorded on JEOL JNM-ECA 400 (100 MHz) spectrometer or JEOL JNM-ECZ 500 (125 MHz) spectrometer. Chemical shifts are reported relative to internal standard ($CDCl_3$ at δ 77.00, CD_3CN at δ 118.26, CD_3OD at δ 49.00,). Mass spectra were recorded on JEOL JMS 700 (EI) or JEOL JMS-T100LC (ESI) instrument with a direct inlet system. Column chromatography was carried out on Kanto silica gel 60 N (spherical, neutral, particle size 40–50 μm) or MP Alumina N Super I (neutral, particle size 50–200 μm). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. All non-aqueous reactions were carried out in flame-dried glassware under Ar atmosphere unless otherwise noted. Reagents and solvents were used without purification. *N*-Boc-3-aminophenol was synthesized from 3-aminophenol by a conventional *N*-Boc protection procedure. 3,17-*O*-Bis(*tert*-butyldimethylsilyl)-17α-ethynylestradiol (**6d**)[1] and 6-phenylhexa-1,3-diyne (**6e**)[2] were synthesized according to the literature procedures. $TMSCH_2MgCl$ (1.0 M in THF) was purchased from FUJIFILM Wako Pure Chemical Co. For aryne generation from *o*-triazenilarylboronic acids **2**, silica gel, which was the same as that used for column chromatography, was used after dryness under vacuum at 200 °C.

1. Preparation of 3-triazenylaryne precursor (1).

In the literature, the synthesis of 3-amino-2-iodotriflate (**S4**) from 2-amino-3-nitrophenol was reported through three step transformations including Sandmeyer reaction, triflation, and reduction of nitro group (Scheme S1a).[3,4] On the other hand, we prepared **S4** from *N*-Boc-amide **3**, which was prepared from *N*-Boc-3-aminophenol in four steps (Scheme S1b). 3-Triazenylaryne precursor **1** was obtained from **3** via removal of Boc group and triazene formation. The experimental procedure of our method (Scheme S1b) is described below.



Scheme S1

To a solution of *N*-Boc-3-aminophenol (6.01 g, 28.7 mmol) in CH_2Cl_2 (287 mL) was added 3,4-dihydro-2*H*-pyran (3.11 mL, 34.4 mmol) and PPTS (1.44 g, 5.74 mmol) at 0 °C. After stirring at room temperature for 3 hours, the reaction mixture was concentrated in vacuo, and the crude product was purified by column chromatography (silica gel, 5:1 *n*-hexane/AcOEt) to give **S1** (6.11 g, 78%) as a colorless solid: mp 104–106 °C; IR (KBr) ν 2930, 1714, 1605, 1539, 1159, 911 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 9H, *t*-Bu), 1.59−1.70 (m, 3H, THP), 1.82−1.86 (m, 2H, THP), 1.95−2.05 (m, 1H, THP), 3.57−3.63 (m, 1H, −OC*H*H−), 3.90 (ddd, J = 3.2, 10.0, 11.2 Hz, 1H, −OCH*H*−), 5.42 (t, J = 3.2 Hz, 1H, −OC*H*O−), 6.44 (brs, 1H, N*H*Boc), 6.73 (dd, J = 2.4, 8.2 Hz, 1H, Ar*H*), 6.92 (d, J = 6.8 Hz, 1H, Ar*H*), 7.15−7.19 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5 (CH_2), 25.1 (CH_2), 28.2 (CH_3), 30.2 (CH_2), 61.7 (CH_2), 80.2 (C), 96.1 (CH), 106.9 (CH), 110.8 (CH), 111.6 (CH), 129.4 (CH), 139.4 (C), 152.6 (C), 157.6 (C=O); HRMS (EI) calcd for $C_{16}H_{23}NO_4$ $[M]^+$ 293.1627, found 293.1625.

To a solution of **S1** (5.33 g, 18.2 mmol) in THF (73 mL) was added ^{n}BuLi (1.6 M in *n*-hexane, 25.0 mL, 40.0 mmol) at –78 °C. After stirring at the same temperature for 10 min, TMSCl (5.05 mL, 40.0 mmol) was added. After stirring at the same temperature for 10 min, TMEDA (6.50 mL, 43.6 mmol) and ^{n}BuLi (1.6 M in *n*-hexane, 27.3 mL, 43.6 mmol) were added, and dry ice/MeOH bath was replaced by ice water bath. After stirring at 0 °C for 5 min, the reaction was quenched with 1 M HCl, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give **S2** (6.64 g, 99%) as a colorless solid: mp 81–83 °C; IR (KBr) *v* 2941, 1732, 1220, 1157, 983 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.40 (s, 9H, Si(C*H*$_3$)$_3$), 1.50 (s, 9H, *t*-Bu), 1.59−1.74 (m, 3H, THP), 1.85−2.02 (m, 3H, THP), 3.61−3.65 (m, 1H, −OC*H*H−), 3.85−3.91 (m, 1H, −OCH*H*−), 5.39 (t, *J* = 3.2 Hz, 1H, −OC*H*O−), 6.71 (brs, 1H, N*H*Boc), 6.91 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.25 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.36 (d, *J* = 8.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.9 (CH_3), 19.0 (CH_2), 25.1 (CH_2), 28.4 (CH_3), 30.3 (CH_2), 62.0 (CH_2), 79.9 (C), 96.8 (CH), 109.2 (CH), 116.3 (CH), 117.9 (C), 131.0 (CH), 143.4 (C), 153.3 (C), 162.8 (C=O); HRMS (EI) calcd for $C_{19}H_{31}NO_4Si$ $[M]^+$ 365.2022, found 365.2020.

To a solution of **S2** (6.13 g, 16.7 mmol) in CH_2Cl_2 (56 mL) was added $Ag(OCOCF_3)$ (4.45 g, 20.0 mmol) and I_2 (5.09 g, 20.0 mmol) at 0 °C. After stirring at the same temperature for 1 hour and then at room temperature for 3 hours, the reaction was quenched with aqueous 10% $Na_2S_2O_3$ solution, and the whole mixture was filtered through a pad of Celite. The filtrate was extracted with Et_2O and the combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give **S3** (5.14 g, 91%) as a beige solid: mp 113–115 °C; IR (KBr) *v* 2980, 1698, 1525, 1466, 1157 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (s, 9H, *t*-Bu), 5.65 (brs, 1H, O*H*), 6.66 (dd, *J* = 1.2, 8.0 Hz, 1H, Ar*H*), 6.75 (brs, 1H, N*H*Boc), 7.15 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.54 (dd, *J* = 1.2, 8.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2 (CH_3), 81.2 (C), 81.4 (C), 109.9 (CH), 112.7 (CH), 129.8 (CH), 139.4 (C), 152.6 (C), 155.1 (C=O); HRMS (EI) calcd for $C_{11}H_{14}INO_3$ $[M]^+$ 335.0018, found 335.0017.

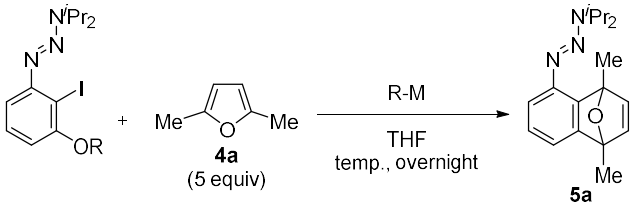
To a solution of **S3** (4.80 g, 14.3 mmol) in CH_2Cl_2 (57 mL) was added $PhNTf_2$ (5.61 g, 15.7 mmol), Et_3N (5.98 mL, 42.9 mmol), and DMAP (175 mg, 1.43 mmol) at room temperature. After stirring at the same temperature for 3 hours, the reaction mixture was concentrated in vacuo, and the crude product was purified by column chromatography (silica gel, 5:1 *n*-hexane/AcOEt) to give **3** (5.49 g, 82%) as a colorless solid: mp 103–105 °C; IR

(KBr) *v* 1738, 1514, 1410, 1220, 1154 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.55 (s, 9H, *t*-Bu), 7.01 (dd, *J* = 1.2, 8.2 Hz, 1H, Ar*H*), 7.04 (brs, 1H, N*H*Boc), 7.38 (t, *J* = 8.2 Hz, 1H, Ar*H*), 8.13 (dd, *J* = 1.2, 8.2 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2 (CH_3), 81.9 (C), 84.6 (C), 115.8 (CH), 118.6 (q, *J* = 319 Hz, CF_3), 118.9 (CH), 130.2 (CH), 141.7 (C), 150.1 (C), 152.2 (C=O); HRMS (EI) calcd for $C_{12}H_{13}F_3INO_5S$ $[M]^+$ 466.9511, found 466.9514.

To a solution of **3** (4.64 g, 9.93 mmol) in CH_2Cl_2 (20 mL) was added CF_3CO_2H (5.0 mL) at 0 °C. After stirring at room temperature for 3 hours, the reaction mixture was concentrated in vacuo, and the crude amine **S4** was used without further purification. To a solution of crude amine **S4** in THF (5.0 mL) was added BF_3•Et_2O (1.88 mL, 14.9 mmol) and ^{t}BuONO (1.77 mL, 14.9 mmol) at –20 °C. After stirring at the same temperature overnight, the formed precipitates were collected by suction and washed with Et_2O to give crude diazonium salt. The crude diazonium salt was added to a solution of ^{i}Pr$_2$NH (4.18 mL, 29.7 mmol) in THF–pyridine (9:1, 13.2 mL) at –20 °C, and the mixture was allowed to warm to room temperature. After stirring overnight, the reaction was quenched with saturated aqueous NH_4Cl, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give triazene **1** (3.30 g, 69%) as a yellow oil: IR (KBr) *v* 2978, 1403, 1213, 1140, 967 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.33 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$) 1.38 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 4.05 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 5.18 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 7.02 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.28 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.35 (dd, *J* = 1.2, 8.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9 (CH_3), 23.6 (CH_3), 48.3 (CH), 50.4 (CH), 92.1 (C), 116.3 (CH), 117.0 (CH), 118.8 (q, *J* = 319 Hz, CF_3), 129.3 (CH), 151.0 (C), 153.7 (C); HRMS (EI) calcd for $C_{13}H_{17}F_3IN_3O_3S$ $[M]^+$ 478.9987, found 478.9986.

2. Optimization of Reaction Conditions for 3-Triazenylaryne Generation from 1

Table S1



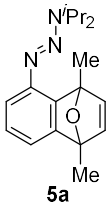
entry	substrate	R-M	temp (°C)	yield (%)
1	R = Tf (**1**)	^{n}BuLi (2.0 equiv)	–78	9
2	R = Tf (**1**)	^{i}PrMgCl (1.5 equiv)	–30	16
3	R = Tf (**1**)	$TMSCH_2MgCl$ (1.5 equiv)	–30	17
4	R = Tf (**1**)	$TMSCH_2MgCl$ (3.0 equiv)	–30	34
5	R = Tf (**1**)	$TMSCH_2MgCl$ (5.0 equiv)	–30	64
6	R = Tf (**1**)	$TMSCH_2MgCl$ (5.0 equiv)	rt	91
7	R = Ts (**S5**)	$TMSCH_2MgCl$ (5.0 equiv)	rt	trace
8	R = 4-$ClC_6H_4SO_2$ (**S6**)	$TMSCH_2MgCl$ (5.0 equiv)	rt	59
9	R = 4-$O_2NC_6H_4SO_2$ (**S7**)	$TMSCH_2MgCl$ (5.0 equiv)	rt	ND*

* Removal of arylsulfonyl group occured, and 2-Iodo-3-triazenylphenol was obtained in 74% yield.

2. General Procedure for Reactions of 1 and Arynophiles using $TMSCH_2MgCl$

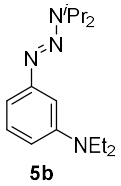
To a solution of **1** (1.00 equiv.) in THF (0.10 M) was added arynophile **4** (5 equiv.) and $TMSCH_2MgCl$ (1.0 M in THF, 5–10 equiv.) at room temperature. After stirring at the same temperature overnight, the reaction was quenched with water, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography.

1-(1,4-Dimethyl-1,4-dihydro-1,4-epoxynaphthalen-5-yl)-3,3-diisopropyltriaz-1-ene (5a)



The reaction was performed using **1** (47.9 mg, 0.100 mmol), 2,5-dimethylfuran (**4a**, 49.0 μL, 0.500 mmol) and $TMSCH_2MgCl$ (1.0 M in THF, 0.50 mL, 0.500 mmol), and **5a** (27.2 mg, 91%) was obtained as a yellow oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): IR (KBr) *ν* 2974, 1600, 1408, 1245, 1152, 858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.30 (broad doublet, 12H, $CH(CH_3)_2$), 1.87 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 4.12 (broad, 1H, $CH(CH_3)_2$), 4.99 (broad, 1H, $CH(CH_3)_2$), 6.72 (d, J = 5.2 Hz, 1H, C*H*=CH), 6.82−6.91 (m, 3H, CH=C*H* and Ar*H*), 7.11(d, J = 8.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3 (CH_3), 18.3 (CH_3), 20.6 (CH_3), 22.9 (CH_3), 47.3 (CH×2), 88.2 (C), 90.0 (C), 114.4 (CH), 114.7 (CH), 125.5 (CH), 143.9 (C), 145.0 (C), 146.4 (CH), 147.3 (CH), 154.4 (C); HRMS (EI) calcd for $C_{18}H_{25}N_3O$ $[M]^+$ 299.1998, found 299.2000.

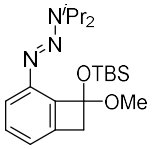
3-(3,3-Diisopropyltriaz-1-en-1-yl)-*N*,*N*-diethylaniline (5b)



5b

The reaction was performed using **1** (95.8 mg, 0.200 mmol), diethylamine (**4b**, 104 μL mg, 1.00 mmol) and $TMSCH_2MgCl$ (1.0 M in THF, 2.0 mL, 2.00 mmol), and **5b** (31.8 mg, 58%) was obtained as a yellow oil after purification by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt): IR (KBr) *v* 2971, 1596, 1422, 1224, 1153, 1022 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (t, *J* = 7.2 Hz, 6H, CH_2CH_3), 1.30 (d, *J* = 6.6 Hz, 12H, $CH(CH_3)_2$), 3.37 (q, *J* = 7.2 Hz, 4H, CH_2CH_3), 4.63 (broad, 2H, $CH(CH_3)_2$), 6.48 d(d, *J* = 2.7, 8.1 Hz, 1H, Ar*H*), 6.75–6.80 (m, 2H, Ar*H*), 7.16 (t, *J* = 8.1 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.7 (CH_3), 21.7 (CH_3), 44.5 (CH_2), 47.2 (CH), 105.3 (CH), 108.1 (CH), 109.4 (CH), 129.3 (CH), 148.8 (C), 153.0 (C); HRMS (EI) calcd for $C_{16}H_{28}N_4$ $[M]^+$ 276.2314, found 276.2311.

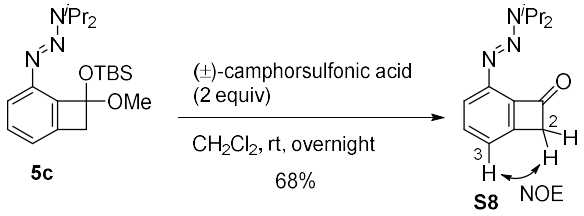
1-[(*tert*-Butyldimethylsilyl)oxy]-6-(3,3-diisopropyltriaz-1-en-1-yl)-1-methoxy benzocyclobutene (5c)



5c

The reaction was performed using **1** (479 mg, 1.00 mmol), 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**4c**, 1.08 mL, 5.00 mmol) and $TMSCH_2MgCl$ (1.0 M in THF, 10 mL, 10.0 mmol), and **5c** (248 mg, 63%) was obtained as a yellow oil after purification by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt): IR (KBr) *v* 2930, 1600, 1403, 1247, 1137 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −0.08 (s, 3H, $Si(CH_3)(CH_3)$), −0.06 (s, 3H, $Si(CH_3)(CH_3)$), 0.85 (s, 9H, *t*-Bu), 1.19 (broad, 6H, $CH(CH_3)_2$), 1.33 (broad, 6H, $CH(CH_3)_2$), 3.28 (d, *J* = 14.0 Hz, 1H, ArC*H*H), 3.44 (d, *J* = 14.0 Hz, 1H, ArCH*H*), 3.53 (s, 3H, OCH_3), 3.94 (broad, 1H, $CH(CH_3)_2$), 5.22 (broad, 1H, $CH(CH_3)_2$), 6.86−6.90 (m, 1H, Ar*H*), 7.18−7.22 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.10 (CH_3), −3.82 (CH_3), 18.0 (C), 19.3 (CH_3), 23.8 (CH_3), 25.7 (CH_3), 46.0 (CH), 47.8 (CH_2), 49.1 (CH), 52.8 (CH_3), 103.3 (C), 116.3 (CH), 119.4 (CH), 130.4 (CH), 139.8 (C), 141.8 (C), 144.9 (C); HRMS (EI) calcd for $C_{21}H_{37}N_3O_2Si$ $[M]^+$ 391.2655, found 391.2656.

The regioselectivity was verified by NOE correlation between C2–H and C3–H of corresponding benzocyclobuten-1-one **S8**.

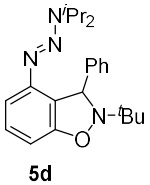


5c **S8**

To a solution of **5c** (29.5 mg, 0.0750 mmol) in CH_2Cl_2 (0.75 mL) was added (±)-

camphorsulfonic acid (35.0 mg, 0.150 mmol) at room temperature. After stirring at the same temperature overnight, the reaction was quenched with aqueous sat. $NaHCO_3$ solution, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt) to give benzocyclobuten-1-one **S8** (12.6 mg, 68%) as a colorless oil: IR (KBr) *v* 2970, 1764, 1375, 1248, 1152 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.25 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.49 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 3.88 (s, 2H, ArC*H*$_2$O), 4.06 (septet, 1H, *J* = 6.8 Hz, C*H*(CH$_3$)$_2$), 5.41 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 7.14 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.29 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.46 (t, *J* = 8.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3 (CH_3), 23.3 (CH_3), 46.5 (CH), 49.9 (CH), 51.5 (CH_2), 118.1 (CH), 121.7 (CH), 136.2 (CH), 137.1 (C), 146.4 (C), 151.4 (C), 186.4 (C=O); HRMS (EI) calcd for $C_{14}H_{19}N_3O$ $[M]^+$ 245.1528, found 245.1527.

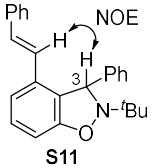
2-(*tert*-Butyl)-4-(3,3-diisopropyltriaz-1-en-1-yl)-3-phenyl-2,3-dihydrobenzo[*d*]isoxazole (5d)



5d

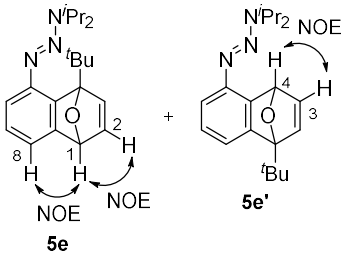
The reaction was performed using **1** (479 mg, 1.00 mmol), *N*-*tert*-butyl-α-phenylnitrone (**4d**, 886 mg, 5.00 mmol) and $TMSCH_2MgCl$ (1.0 M in THF, 10 mL, 10.0 mmol), and **5d** (217 mg, 57%) was obtained as a red-brown solid after purification by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt): mp 78–81 °C ; IR (KBr) *v* 2972, 1594, 1407, 1240, 1007 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ 1.16 (s, 9H, *t*-Bu), 1.22 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 4.13 (broad, 1H, C*H*(CH$_3$)$_2$), 4.93 (broad, 1H, C*H*(CH$_3$)$_2$), 5.84 (s, 1H, ArC*H*N), 6.56 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.90 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.13–7.19 (m, 2H, Ar*H*), 7.22–7.29 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, CD_3OD): δ 19.3 (CH_3), 24.0 (CH_3), 25.8 (CH_3), 47.4 (CH), 50.2 (CH), 62.7 (C), 67.4 (CH), 103.1 (CH), 112.1 (CH), 122.1 (C), 128.2 (CH), 129.2 (CH×2), 130.6 (CH), 144.4 (C), 148.4 (C), 159.9 (C); HRMS (EI) calcd for $C_{23}H_{32}N_4O$ $[M]^+$ 380.2576, found 380.2572.

The regioselectivity was verified by NOE correlation between C3–H and alkenyl proton of compound **S11**. For the synthesis of **S11**, see next section.



S11

1-(1-*tert*-Butyl-1,4-dihydro-1,4-epoxynaphthalen-5-yl)-3,3-diisopropyltriaz-1-ene (5e) and 1-(4-*tert*-Butyl-1,4-dihydro-1,4-epoxynaphthalen-5-yl)-3,3-diisopropyltriaz-1-ene (5e')



The reaction was performed using **1** (95.8 mg, 0.200 mmol), 2-*tert*-butylfuran (**4e**, 143 μL, 1.00 mmol) and $TMSCH_2MgCl$ (1.0 M in THF, 2.0 mL, 2.00 mmol), and **5e** (24.5 mg, 37%) and **5e'** (16.1 mg, 25%) were obtained after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt then silica gel, CH_2Cl_2).

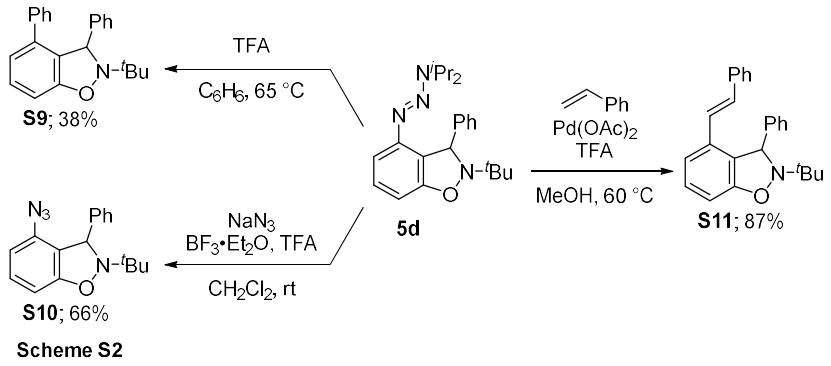
5e: a colorless oil; IR (KBr) *v* 2973, 1409, 1225, 1155, 912, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.29 (broad, 21H, $CH(CH_3)_2$ and *t*-Bu), 4.04 (broad, 1H, $CH(CH_3)_2$), 5.28 (broad, 1H, $CH(CH_3)_2$), 6.03 (d, *J* = 2.0 Hz, 1H, -CH=CH-C*H*-), 6.94 (dd, *J* = 7.0, 8.0 Hz, 1H, Ar*H*), 6.98 (d, *J* = 5.5 Hz, 1H, -C*H*=CH-CH-), 7.01 (dd, *J* = 1.0, 8.0 Hz, 1H, Ar*H*), 7.07 (dd, *J* = 2.0, 5.5 Hz, 1H, -CH=C*H*-CH-), 7.17 (d, *J* = 7.0 Hz, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.4 (CH_3), 23.8 (CH_3), 26.6 (CH_3), 32.5 (C), 45.9 (CH), 48.4 (CH), 80.9 (CH), 99.3 (C), 118.2 (CH), 118.7 (CH), 125.0 (CH), 141.9 (C), 142.8 (CH), 144.3 (CH), 144.4 (C), 150.2 (C); HRMS (EI) calcd for $C_{20}H_{29}N_3O$ $[M]^+$ 327.2311, found 327.2313.

The structure of **5e** was verified by NOE correlations between C1–H and C2–H, and C1–H and C8–H.

5e': a colorless oil; IR (KBr) *v* 2975, 1427, 1222, 1154, 909 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.22–1.35 (m, 21H, $CH(CH_3)_2$ and *t*-Bu), 3.96 (broad, 1H, $CH(CH_3)_2$), 5.43 (broad, 1H, $CH(CH_3)_2$), 5.61 (s, 1H, -CH=CH-C*H*-), 6.91 (dd, *J* = 7.0, 8.0 Hz, 1H, Ar*H*), 6.96−6.97 (m, 3H, C*H*=C*H* and Ar*H*), 7.11(dd, *J* = 1.0, 7.0 Hz, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.7 (CH_3), 24.1 (CH_3), 27.2 (CH_3), 32.7 (C), 45.7 (CH), 48.0 (CH), 81.2 (CH), 102.8 (C), 115.8 (CH), 116.3 (CH), 125.6 (CH), 141.1 (C), 143.2 (CH), 143.6 (CH), 144.9 (C), 153.3 (C) ; HRMS (EI) calcd for $C_{20}H_{29}N_3O$ $[M]^+$ 327.2311, found 327.2313.

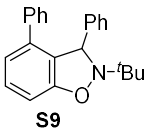
The structure of **5e'** was verified by NOE correlation between C3–H and C4–H.

3. Transformation of triazenyl group of 5d.



Scheme S2

2-(*tert*-Butyl)-3,4-diphenyl-2,3-dihydrobenzo[*d*]isoxazole (S9)

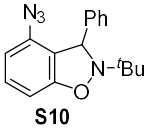


S9

To a solution of **5d** (38.0 mg, 0.100 mmol) in C_6H_6 (1.0 mL) was added CF_3CO_2H (15 μL, 0.200 mmol) at 65 °C. After stirring at the same temperature for 3 hours, the reaction was quenched with aqueous sat. $NaHCO_3$ solution, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give **S9** (12.6 mg, 38%) as an orange oil: IR (KBr) *v* 2971, 1585, 1454, 1207, 756 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ 1.10 (s, 9H, *t*-Bu), 5.67 (s, 1H, ArC*H*N), 6.71−6.78 (m, 4H, Ar*H*), 6.95−6.98 (m, 5H, Ar*H*), 7.12−7.21 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, CD_3OD): δ 25.7 (CH_3), 62.7 (C), 67.7 (CH), 106.4 (CH), 123.1 (CH), 128.2 (CH), 128.3 (CH), 128.4 (C), 128.8 (CH), 129.1 (CH), 129.2 (CH×2), 130.6 (CH), 140.3 (C), 141.0 (C), 144.1 (C), 159.0 (C); HRMS (EI) calcd for $C_{23}H_{23}NO$ $[M]^+$ 329.1780, found 329.1781.

4-Azido-2-(*tert*-butyl)-3-phenyl-2,3-dihydrobenzo[*d*]isoxazole (S10)

[CAUTION! Sodium azido produces explosive species under certain reaction conditions, and azido-containing compounds are presumed to be potentially explosive. Although we have never experienced such an explosion with azido compounds used in this study, all manipulations should be carefully carried out behind a safety shield in a hood.]

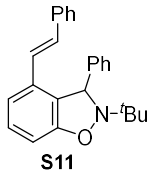


S10

To a solution of **5d** (38.0 mg, 0.100 mmol) and NaN_3 (13.0 mg, 0.200 mmol) in CH_2Cl_2 (1.0 mL) was added BF_3•Et_2O (25 μL, 0.200 mmol) and CF_3CO_2H (15 μL, 0.200 mmol) at room temperature. After stirring at the same temperature overnight, the reaction was quenched with water, and the whole mixture was extracted with Et_2O. The combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo

furnished the crude mixture, which was purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt) to give **S10** (19.6 mg, 68%) as a brown solid: mp 101–103 °C; IR (KBr) *v* 2972, 1602, 1455, 1302, 1200, 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 9H, *t*-Bu), 5.53 (s, 1H, ArC*H*N), 6.62 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.20 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.26−7.32 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.3 (CH_3), 61.5 (C), 65.1 (CH), 103.2 (CH), 110.5 (CH), 120.0 (C), 127.5 (CH), 127.6 (CH), 128.5 (CH), 130.3 (CH), 135.8 (C), 142.5 (C), 158.9 (C); HRMS (EI) calcd for $C_{17}H_{18}N_4O$ $[M]^+$ 294.1481, found 294.1478.

2-(*tert*-Butyl)-3-phenyl-4-styryl-2,3-dihydrobenzo[*d*]isoxazole (S11)



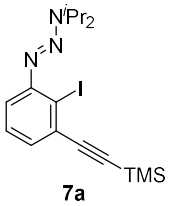
S11

To a solution of **5d** (76.0 mg, 0.200 mmol) in MeOH (2.0 mL) was added $Pd(OAc)_2$ (4.5 mg, 0.0200 mmol, 10 mol%), styrene (46 μL, 0.400 mmol), CF_3CO_2H (31 μL, 0.400 mmol) at room temperature. After stirring at 65 °C for 1 hour, the reaction mixture was concentrated in vacuo, and the crude product was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give **S11** (62.4 mg, 87%) as a colorless solid: mp 142–145 °C; IR (KBr) *v* 2973, 1580, 1453, 1250, 963 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 9H, *t*-Bu), 5.69 (s, 1H, ArC*H*N), 6.76−6.81 (m, 2H, Ar*H* and Ar−C*H*=CH−Ph), 6.93 (d, *J* = 16.0 Hz, 1H, Ar−CH=C*H*−Ph), 7.14 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.20−7.35 (m, 11H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.5 (CH_3), 61.5 (C), 66.5 (CH), 105.6 (CH), 117.5 (CH), 124.7 (CH), 126.5 (CH), 126.9 (C), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.6 (CH), 128.8 (CH), 129.3 (CH), 130.4 (CH), 133.4 (C), 137.0 (C), 143.1 (C), 157.7(C); HRMS (EI) calcd for $C_{25}H_{25}NO$ $[M]^+$ 355.1936, found 355.1937.

4. General Procedure for Iodoalkynylation of 1

To a solution of alkyne **6** (2.10 equiv) in THF (5 mL for 1.00 mmol of **1**) was added ^{n}BuLi (1.6 M in *n*-hexane, 2.0 equiv) at –78 °C. After stirring at the same temperature for 10 min, to the reaction mixture was added a solution of **1** (1.00 equiv.) in THF (5 mL for 1.00 mmol of **1**) via cannula, and dry ice/MeOH bath was replaced by ice water bath. After stirring at 0 °C for 3 hours, the reaction was quenched with water, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography to give **7**.

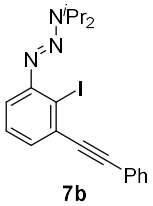
1-{2-Iodo-3-[(trimethylsilyl)ethynyl]phenyl}-3,3-diisopropyltriaz-1-ene (7a)



7a

The reaction was performed using **1** (239 mg, 0.500 mmol), trimethylsilylacetylene (**6a**, 145 μL, 1.05 mmol) and ^{n}BuLi (1.6 M in *n*-hexane, 0.625 mL, 1.00 mmol), and **7a** (144 mg, 68%) was obtained as a brown oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): IR (KBr) *v* 2970, 2156, 1405, 1240, 844 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.30 (s, 9H, Si(C*H*$_3$)$_3$), 1.33 (broad doublet, 6H, CH(C*H*$_3$)$_2$),1.38 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 4.04 (broad, 1H, C*H*(CH$_3$)$_2$), 5.20 (broad, 1H, C*H*(CH$_3$)$_2$), 7.16−7.27 (m, 3H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.00 (CH_3), 19.2 (CH_3), 23.9 (CH_3), 47.9 (CH), 50.0 (CH), 98.0 (C), 103.5 (C), 107.6 (C), 117.2 (CH), 128.1 (CH), 129.2 (CH), 130.7 (C), 151.8 (C); HRMS (EI) calcd for $C_{17}H_{26}IN_3Si$ $[M]^+$ 427.0941, found 427.0939.

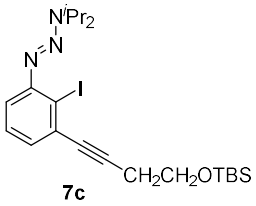
1-[2-Iodo-3-(phenylethynyl)phenyl]-3,3-diisopropyltriaz-1-ene (7b)



7b

The reaction was performed using **1** (95.9 mg, 0.200 mmol), phenylacetylene (**6b**, 46 μL, 0.420 mmol) and ^{n}BuLi (1.6 M in *n*-hexane, 0.250 mL, 0.400 mmol), and **7b** (57.0 mg, 66%) was obtained as a yellow oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): IR (KBr) *v* 2973, 1404, 1240, 1156, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (broad doublet, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.38 (broad doublet, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.03 (broad septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 5.21 (broad septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.21−7.38 (m, 6H, Ar*H*), 7.61−7.64 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1 (CH_3), 23.8 (CH_3), 47.8 (CH), 49.9 (CH), 92.4 (C), 92.6 (C), 103.3 (C), 116.9 (CH), 123.3 (C), 128.1 (CH), 128.3 (CH×2), 128.7 (CH), 130.7 (C), 131.6 (CH), 151.7 (C); HRMS (EI) calcd for $C_{20}H_{22}IN_3$ $[M]^+$ 431.0858, found 431.0863.

1-{3-[4-(*tert*-Butyldimethylsilyloxy)-but-1-yn-1-yl]-2-iodophenyl}-3,3-diisopropyltriaz-1-ene (7c)

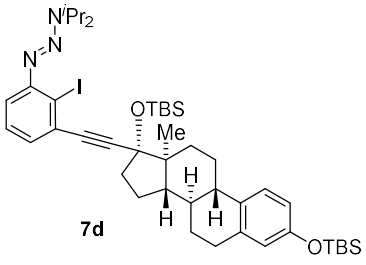


7c

The reaction was performed using **1** (240 mg, 0.500 mmol), 4-(*tert*-Butyldimethylsilyloxy)-1-butyne (**6c**, 230 μL, 1.05 mmol) and ^{n}BuLi (1.6 M in *n*-hexane, 0.625 mL, 1.00 mmol), and **7c** (121 mg, 47%) was obtained as a pale yellow oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt then silica gel, 4:1 *n*-hexane/CH_2Cl_2): IR (KBr) *v* 2939, 1404, 1240, 1103, 837, 778 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.11 (s, 6H, Si(C*H*$_3$)$_2$), 0.92 (s, 9H, *t*-Bu), 1.33 (broad doublet, *J* = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.39 (broad doublet, *J* = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 2.71 (t, *J* = 7.5 Hz, 2H, -

C*H*$_2$CH$_2$O-), 3.89 (t, *J* = 7.5 Hz, 2H, -CH$_2$C*H*$_2$O-), 4.04 (broad, 1H, C*H*(CH$_3$)$_2$), 5.20 (broad, 1H, C*H*(CH$_3$)$_2$), 7.15−7.17 (m, 2H, Ar*H*), 7.22 (dd, *J* = 3.0, 6.0 Hz, 1H, Ar*H*); ^{13}C NMR (125 MHz, CDCl$_3$): δ –5.2 (CH$_3$), 18.4 (C), 19.1 (CH$_3$), 23.8 (CH$_3$), 24.1 (CH$_2$), 25.9 (CH$_3$), 47.7 (CH), 49.8 (CH), 61.9 (CH$_2$), 84.6 (C), 90.7 (C), 103.3 (C), 116.4 (CH), 128.0 (CH), 128.8 (CH), 131.2 (C), 151.6 (C); HRMS (EI) calcd for C$_{22}$H$_{36}$IN$_3$OSi [M]$^+$ 513.1672, found 513.1673.

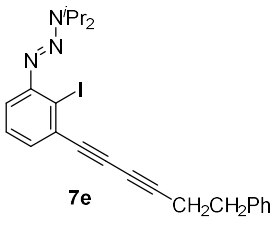
3,17-*O*-Bis(*tert*-butyldimethylsilyl)-17α-[{2-iodo-3-(3,3-diisopropyltriaz-1-en-1-yl)phenyl}ethynyl]estradiol (7d)



7d

The reaction was performed using **1** (95.9 mg, 0.200 mmol), 3,17-*O*-bis(*tert*-butyldimethylsilyl)-17α-ethynylestradiol[1] (**6d**, 220 mg, 0.420 mmol) and ^{n}BuLi (1.6 M in *n*-hexane, 0.250 mL, 0.400 mmol), and **7d** (100 mg, 58%) was obtained as a colorless solid after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): mp 89–91 °C; [α]$_D^{24}$ = –51.9 (c 0.585, CHCl$_3$); IR (KBr) *ν* 2929, 1496, 1406, 1241, 778 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.18 (s, 6H, Si(C*H*$_3$)$_2$), 0.25 (s, 6H, Si(C*H*$_3$)$_2$), 0.90 (s, 3H, CH$_3$), 0.92 (s, 9H, *t*-Bu), 0.97 (s, 9H, *t*-Bu), 1.26−1.53 (m, 16H, CH(C*H*$_3$)$_2$×2 and 4H), 1.71−1.74 (m, 1H), 1.83−1.89 (m, 2H), 2.03 (dt, *J* = 4.0, 14.2 Hz, 1H), 2.11−2.22 (m, 2H), 2.27−2.36 (m, 2H), 2.42−2.49 (m, 1H), 2.74−2.83 (m, 2H, C6-*H*), 4.02 (broad septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 5.14 (broad septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 6.54 (d, *J* = 2.4 Hz, 1H, Ar*H*), 6.60 (dd, *J* = 2.4, 8.4 Hz, 1H, Ar*H*), 7.12−7.25 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$): δ −4.3 (CH$_3$), −2.8 (CH$_3$), 13.4 (CH$_3$), 18.2 (C), 18.3 (C), 19.1 (CH$_3$), 23.3 (CH$_2$), 23.7 (CH$_3$), 25.8 (CH$_3$), 26.0 (CH$_3$), 26.6 (CH$_2$), 27.5 (CH$_2$), 29.8 (CH$_2$), 33.1 (CH$_2$), 39.8 (CH), 40.5 (CH$_2$), 43.7 (CH), 48.2 (CH), 49.0 (C), 50.3 (CH×2), 81.5 (C), 89.3 (C), 97.2 (C), 103.0 (C), 116.7 (CH), 117.1 (CH), 119.9 (CH), 126.2 (CH), 128.1 (CH), 128.6 (CH), 131.2 (C), 133.6 (C), 137.9 (C), 151.9 (C), 153.3 (C); HRMS (ESI) calcd for C$_{44}$H$_{69}$IN$_3$O$_2$Si$_2$ [M+H]$^+$ 854.3973, found 854.3978.

1-[2-Iodo-3-(6-phenylhexa-1,3-diyn-1-yl)phenyl]-3,3-diisopropyltriaz-1-ene (7e)



7e

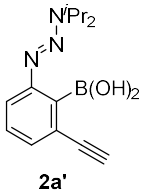
The reaction was performed using **1** (280 mg, 0.584 mmol), 6-phenylhexa-1,3-diyne[2] (**6e**, 189 mg, 1.23 mmol) and ^{n}BuLi (1.6 M in *n*-hexane, 0.73 mL, 1.17 mmol), and **7e** (207 mg, 73%) was obtained as a pale yellow oil after purification by column chromatography (silica gel, 4:1 *n*-hexane/CH$_2$Cl$_2$): IR (KBr) *ν* 2973, 1404, 1240, 1156, 789 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.33 (d, *J* = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.39 (d, *J* = 6.5 Hz,

6H, CH(C*H*$_3$)$_2$), 2.68 (t, *J* = 7.0 Hz, 2H, C*H*$_2$CH$_2$), 2.92 (t, *J* = 7.0 Hz, 2H, CH$_2$C*H*$_2$), 4.04 (broad septet, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 5.19 (broad septet, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 7.17–7.33 (m, 8H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.1 (CH$_3$), 22.0 (CH$_2$), 23.8 (CH$_3$), 34.6 (CH$_2$), 47.9 (CH), 50.0 (CH), 66.0 (C), 77.2 (C), 77.5 (C), 85.0 (C), 103.2 (C), 117.5 (CH), 126.5 (CH), 128.2 (CH), 128.4 (CH), 128.5 (CH), 129.7 (C), 130.1 (CH), 140.1 (C), 151.7 (C); HRMS (ESI) calcd for C$_{24}$H$_{27}$IN$_3$ [M+H]$^+$ 484.1250, found 484.1251.

5. General Procedure for Synthesis of *o*-Triazenylarylboronic acids 2

To a solution of **7** (1.00 equiv) in THF (0.20 M) was added ^{n}BuLi (1.6 M in *n*-hexane, 2.0 equiv) at –78 °C. After stirring at the same temperature for 30 min, a solution of B(OMe)$_3$ (2.00 equiv) in THF (1.0 M) was added, and the mixture was allowed to warm to room temperature. After stirring overnight, the reaction was quenched with water, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with saturated aqueous NH$_4$Cl and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography or reprecipitation to give **2**.

[(3,3-Diisopropyltriaz-1-en-1-yl)-6-ethynylphenyl]boronic acid (2a')

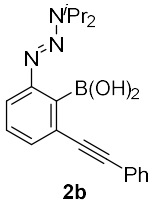


2a'

The reaction was performed using **7a** (230 mg, 0.540 mmol), ^{n}BuLi (1.6 M in *n*-hexane, 0.675 mL, 1.08 mmol) and B(OMe)$_3$ (112 mg, 1.08 mmol). Obtained crude mixture contained **2a** and **2a'**. Therefore, the crude mixture was treated with TBAF (1.0 M in THF, 0.650 mL, 0.650 mmol) in THF (5 mL) at room temperature. After stirring for 1 hour, the reaction was quenched with water, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography (silica gel, 10:1 CH$_2$Cl$_2$/THF (contains no BHT as a stabilizer)) to give **2a'** (68.1 mg, 46%) as a pale brown solid: mp 121–124 °C; IR (KBr) *v* 3296, 2979, 1417, 1240 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.31 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.43 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 3.52 (s, 1H, −C≡C*H*), 4.10 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 4.99 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.33−7.40 (m, 2H, Ar*H*), 7.65 (dd, *J* = 1.2, 7.6 Hz, 1H, Ar*H*), 8.50 (s, 2H, B(O*H*)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.1 (CH$_3$), 24.0 (CH$_3$), 48.1 (CH), 49.8 (CH), 81.7 (C), 85.2 (CH), 117.3 (CH), 126.4 (C), 130.6 (CH), 131.2 (CH), 156.6 (C) (*C*–B was not detected.); HRMS (ESI) calcd for C$_{16}$H$_{24}$BN$_3$O$_2$Na [M+Na]$^+$ 324.1859, found 324.1862 [Molecular ion peak was detected as

dimethyl boronate (Ar-B(OMe)$_2$), because MeOH was used as a solvent for ionization.].

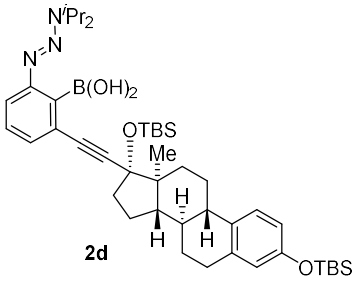
[2-(3,3-Diisopropyltriaz-1-en-1-yl)-6-(phenylethynyl)phenyl]boronic acid (2b)



2b

The reaction was performed using **7b** (266 mg, 0.610 mmol), ^{n}BuLi (1.6 M in *n*-hexane, 0.763 mL, 1.22 mmol) and B(OMe)$_3$ (127 mg, 1.08 mmol), and **2b** (101 mg, 47%) was obtained as a pale brown oil after purification by column chromatography (neutral alumina, 10:1 *n*-hexane/AcOEt): IR (KBr) *v* 3549, 2924, 1559, 1417, 1240, 1099 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.37 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 4.10 (septet, *J* = 6.8 Hz, 1H, CH(C*H*$_3$)$_2$), 5.00 (septet, *J* = 6.8 Hz, 1H, CH(C*H*$_3$)$_2$), 7.36−7.40 (m, 4H, Ar*H*), 7.43 (dd, *J* = 1.2, 7.2 Hz, 1H, Ar*H*), 7.57−7.59 (m, 2H, Ar*H*), 7.64 (dd, *J* = 1.6, 8.4 Hz, 1H, Ar*H*), 8.55 (s, 2H, B(O*H*)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1 (CH_3), 24.0 (CH_3), 48.0 (CH), 49.7 (CH), 90.1 (C), 93.9 (C), 116.8 (CH), 121.9 (C), 127.7 (C), 128.5 (CH), 129.0 (CH), 130.6 (CH×2), 131.6 (CH), 156.6 (C) (C−B was not detected.); HRMS (ESI) calcd for $C_{22}H_{29}BN_3O_2$ $[M+H]^+$ 378.2353, found 378.2357 [Molecular ion peak was detected as dimethyl boronate (Ar-B(OMe)$_2$), because MeOH was used as a solvent for ionization.].

3,17-*O*-Bis(*tert*-butyldimethylsilyl)-17α-[{2-borono-3-(3,3-diisopropyltriaz-1-en-1-yl)phenl}ethynyl]estradiol (2d)

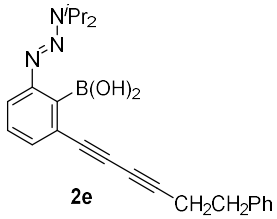


2d

The reaction was performed using **7d** (371 mg, 0.440 mmol), ^{n}BuLi (1.6 M in *n*-hexane, 0.540 mL, 0.880 mmol) and B(OMe)$_3$ (91.4 mg, 0.880 mmol), and **2d** (233 mg, 69%) was obtained as a colorless solid after purification by column chromatography (neutral alumina, 10:1 *n*-hexane/AcOEt): mp 104–106 °C; $[\alpha]_D^{24}$ = –77.7 (c 0.500, $CHCl_3$); IR (KBr) *v* 2929, 1418, 1252, 1090, 838 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 6H, Si(C*H*$_3$)$_2$), 0.19 (s, 3H, Si(C*H*$_3$)(CH$_3$)), 0.20 (s, 3H, Si(CH$_3$)(C*H*$_3$)), 0.90 (s, 9H, *t*-Bu), 0.91 (s, 3H, C*H*$_3$), 0.97 (s, 9H, *t*-Bu), 1.26−1.50 (m, 16H, CH(C*H*$_3$)$_2$×2 and 4H), 1.68−1.76 (m, 1H), 1.80−1.93 (m, 4H), 2.08 (dt, *J* = 4.0, 15.0 Hz, 1H), 2.21 (dt, *J* = 4.0, 10.8 Hz, 1H), 2.32−2.43 (m, 2H), 2.78−2.82 (m, 2H, C6-*H*), 4.09 (septet, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 4.98 (septet, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 6.53 (d, *J* = 2.4 Hz, 1H, Ar*H*), 6.59 (dd, *J* = 2.4, 8.4 Hz, 1H, Ar*H*), 7.11 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.33−7.37 (m, 2H, Ar*H*), 7.59−7.62 (m, 1H, Ar*H*), 8.46 (s, 2H, B(O*H*)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.4 (CH$_3$×2), −3.0 (CH$_3$), −2.9 (CH$_3$), 13.4 (CH$_3$), 18.1 (C), 18.2 (C), 19.2 (CH$_3$), 23.1 (CH$_2$), 24.0 (CH$_3$), 25.7 (CH$_3$), 25.8 (CH$_3$), 26.4 (CH$_2$), 27.3 (CH$_2$), 29.7 (CH$_2$), 33.2 (CH$_2$), 39.5 (CH), 40.2 (CH$_2$), 43.6 (CH), 48.0 (CH), 48.7 (CH), 49.0 (C), 49.7 (CH), 81.4 (C), 87.3 (C), 99.1 (C), 116.7 (CH), 117.1 (CH), 119.9 (CH), 126.2 (CH), 127.8 (C),

130.7 (CH), 130.8 (CH), 133.2 (C), 137.9 (C), 153.2 (C), 156.7 (C) (C−B was not detected.); HRMS (ESI) calcd for $C_{46}H_{75}BN_3O_4Si_2$ $[M+H]^+$ 800.5389, found 800.5394 [Molecular ion peak was detected as dimethyl boronate (Ar-B(OMe)$_2$), because MeOH was used as a solvent for ionization.].

[2-(3,3-Diisopropyltriaz-1-en-1-yl)-6-(6-phenylhexa-1,3-diyn-1-yl)phenyl]boronic acid (2e)



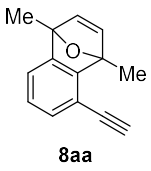
2e

The reaction was performed using **7e** (105 mg, 0.217 mmol), ^{n}BuLi (1.6 M in *n*-hexane, 0.27 mL, 0.434 mmol) and $B(OMe)_3$ (45.1 mg, 0.434 mmol), and **2e** (48.1 mg, 55%) was obtained as a beige solid after reprecipitation from Et_2O–*n*-hexane: mp 106–109 °C; IR (KBr) *ν* 2976, 1417, 1379, 1240, 1128, 1033, 805, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.31 (d, *J* = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.42 (d, *J* = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 2.68 (t, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_2$), 2.91 (t, *J* = 7.5 Hz, 2H, CH$_2$C*H*$_2$), 4.10 (septet, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 4.98 (septet, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 7.23–7.26 (m, 3H, Ar*H*), 7.31–7.34 (m, 3H, Ar*H*), 7.38 (dd, *J* = 1.5, 7.5 Hz, 1H, Ar*H*), 7.63 (dd, *J* = 1.5, 8.0 Hz, 1H, Ar*H*), 8.23 (s, 2H, B(O*H*)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.2 (CH_3), 21.9 (CH_2), 24.0 (CH_3), 34.4 (CH_2), 48.1 (CH), 49.8 (CH), 65.1 (C), 75.4 (C), 78.8 (C), 86.3 (C), 117.3 (CH), 126.6 (CH), 126.7 (C), 128.4 (CH), 128.6 (CH), 130.7 (CH), 132.0 (CH), 139.9 (C), 156.6 (C) (*C*–B was not detected.); HRMS (ESI) calcd for $C_{26}H_{32}BN_3O_2Na$ $[M+Na]^+$ 452.2485, found 452.2483[Molecular ion peak was detected as dimethyl boronate (Ar-B(OMe)$_2$), because MeOH was used as a solvent for ionization.].

6. General Procedure for Reactions of *o*-Triazenylarylboronic acids 2 with arynophiles 4

A suspension of *o*-triazenylarylboronic acid **2** (0.100 mmol), pinacol (11.8 mg, 0.100 mmol), Na_2SO_4 (200 mg) in CH_2Cl_2 (1.0 mL) was stirred at room temperature. After stirring at the same temperature for 4 h, arynophile (**4**, 0.150 mmol) and silica gel (neutral, spherical, 40–50 μm, 200 mg, dried under vacuum at 200 °C) were added to the suspension. After stirring at room temperature for 16 h, silica gel was filtered off, and the eluent was concentrated in vacuo to furnish the crude product, which was purified by column chromatography to give **8**.

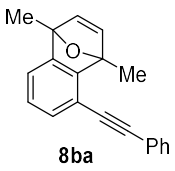
5-Ethynyl-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (8aa)



8aa

The reaction was performed using **2a'** (27.3 mg, 0.100 mmol) and 2,5-dimethylfuran (16 μL, 0.150 mmol), and **8aa** (12.0 mg, 63%) was obtained as a colorless oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): IR (KBr) *v* 3285, 2932, 1382, 1139, 859 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.88 (s, 3H, C*H*$_3$), 2.10 (s, 3H, C*H*$_3$), 3.18 (s, 1H, −C≡C*H*), 6.75 (d, *J* = 5.6 Hz, 1H, −*H*C=CH−), 6.83 (d, *J* = 5.6 Hz, 1H, −HC=C*H*−), 6.93 (dd, *J* = 7.2, 8.0 Hz, 1H, Ar*H*), 7.04 (dd, *J* = 0.8, 8.0 Hz, 1H, Ar*H*), 7.08 (dd, *J* = 0.8, 7.2 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1 (CH_3), 16.5 (CH_3), 80.3 (C), 80.9 (CH), 87.9 (C), 89.8 (C), 114.1 (C), 118.6 (CH), 124.9 (CH), 129.4 (CH), 146.6 (CH), 146.8 (CH), 153.5 (C), 153.9 (C); HRMS (EI) calcd for $C_{14}H_{12}O$ $[M]^+$ 196.0888, found 196.0889.

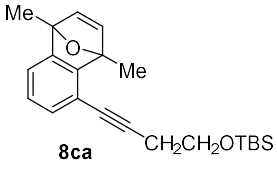
1,4-Dimethyl-5-(phenylethynyl)-1,4-dihydro-1,4-epoxynaphthalene (8ba)



8ba

The reaction was performed using **2b** (34.9 mg, 0.100 mmol) and 2,5-dimethylfuran (**4a**, 16 μL, 0.150 mmol), and **8ba** (17.2 mg, 63%) was obtained as a colorless oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): IR (KBr) *v* 2979, 1491, 1382, 1139, 859, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.90 (s, 3H, C*H*$_3$), 2.19 (s, 3H, C*H*$_3$), 6.77 (d, *J* = 5.2 Hz, 1H, −*H*C=CH−), 6.87 (d, *J* = 5.2 Hz, 1H, −HC=C*H*−), 6.96 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.07−7.10 (m, 2H, Ar*H*), 7.35−7.37 (m, 3H, Ar*H*), 7.51−7.54 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1 (CH_3), 16.7 (CH_3), 86.7 (C), 88.1 (C), 89.9 (C), 92.1 (C), 115.2 (C), 118.2 (CH), 123.2 (C), 124.9 (CH), 128.4 (CH×2), 128.7 (CH), 131.3 (CH), 146.8 (CH×2), 153.2 (C), 153.4 (C) ; HRMS (EI) calcd for $C_{20}H_{16}O$ $[M]^+$ 272.1201, found 272.1199.

5-(4-(*tert*-Butyldimethylsilyloxy)-but-1-yn-1-yl)-1,4-dimethyl--1,4-dihydro-1,4-epoxynaphthalene (8ca)

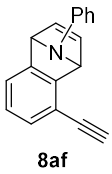


8ca

To a solution of **7c** (107 mg, 0.208 mmol) in THF (2.1 mL) was added ^{n}BuLi (1.6 M in *n*-hexane, 0.261 mL, 0.417 mmmol) at –78 °C. After stirring at the same temperature for 30 min, a solution of $B(OMe)_3$ (43.3 mg, 0.417 mmol) in THF (0.42 mL) was added, and the mixture was allowed to warm to room temperature. After stirring overnight, the reaction was quenched with water, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude **2c**. To a solution of crude **2c**

was added pinacol (24.6 mg, 0.208 mmol), Na_2SO_4 (417 mg) in CH_2Cl_2 (2.1 mL) at room temperature. After stirring at the same temperature for 4 h, 2,5-dimethylfuran (**4a**, 33 μL, 0.312 mmol) and silica gel (417 mg) were added to the suspension. After stirring at room temperature for 16 h, silica gel was filtered off, and the eluent was concentrated in vacuo to furnish the crude product, which was purified by column chromatography to give **8ca** as a pale orange oil (48.9 mg, 66%): IR (KBr) *v* 2931, 1462, 1382, 1301, 1254, 1106, 837, 777 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.09 (s, 6H, Si(C*H*$_3$)$_2$), 0.91 (s, 9H, *t*-Bu), 1.86 (s, 3H, C*H*$_3$), 2.08 (s, 3H, C*H*$_3$), 2.64 (t, *J* = 7.0 Hz, 2H, -C*H*$_2$CH$_2$O-), 3.82 (t, *J* = 7.0 Hz, 2H, -CH$_2$C*H*$_2$O-), 6.73 (d, *J* = 5.5 Hz, 1H, −*H*C=CH−), 6.82 (d, *J* = 5.5 Hz, 1H, −HC=C*H*−), 6.88 (dd, *J* = 6.5, 7.5 Hz, 1H, Ar*H*), 6.95 (dd, *J* = 1.0, 7.5 Hz, 1H, Ar*H*), 7.02 (dd, *J* = 1.0, 6.5 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ –5.3 (CH_3), 15.1 (CH_3), 16.6 (CH_3), 18.3 (C), 23.9 (CH_2), 25.9 (CH_3), 61.8 (CH_2), 78.7 (C), 87.9 (C), 89.8 (C), 90.3 (C), 115.7 (C), 117.6 (CH), 124.8 (CH), 129.0 (CH), 146.7 (CH×2), 152.9 (C), 153.2 (C); HRMS (EI) calcd for $C_{22}H_{30}O_2Si$ $[M]^+$ 354.2015, found 354.2013.

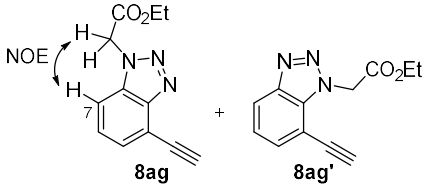
5-Ethynyl-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (8af)



8af

The reaction was performed using **2a'** (27.3 mg, 0.100 mmol) and *N*-phenylpyrrole (**4f**, 21.4 mg, 0.150 mmol), and **8af** (14.4 mg, 59%) was obtained as a colorless oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): IR (KBr) *v* 3283, 1597, 1496, 1306, 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.21 (s, 1H, −C≡C*H*), 5.45 (broad, 1H, ArC*H*N), 5.63 (broad, 1H, ArC*H*N), 6.82−6.90 (m, 4H, Ar*H*), 6.96−7.02 (m, 3H, Ar*H*), 7.16−7.22 (m, 3H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 68.1 (CH), 69.8 (CH), 79.3 (C), 81.0 (CH), 116.0 (C), 117.9 (CH), 121.0 (CH), 121.8 (CH), 125.0 (CH), 128.0 (CH), 128.9 (CH), 141.5 (CH), 142.3 (CH), 146.6 (C), 148.8 (C), 152.1 (C); HRMS (EI) calcd for $C_{18}H_{13}N$ $[M]^+$ 243.1048, found 243.1044.

Ethyl 2-(4-Ethynyl-1,2,3-benzotriazol-1-yl)acetate (8ag) and Ethyl 2-(7-Ethynyl-1,2,3-benzotriazol-1-yl)acetate (8ag')



8ag 8ag'

The reaction was performed using **2a'** (27.3 mg, 0.100 mmol) and ethyl azidoacetate (**4g**, 17 μL, 0.150 mmol), and **8ag** (5.6 mg, 24%) and **8ag'** (4.8 mg, 20%) were obtained as a colorless oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt).

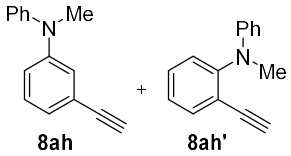
8ag: IR (KBr) *v* 3274, 3072, 1748, 1218, 1014 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.27 (t, *J* = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 3.57 (s, 1H, −C≡C*H*), 4.25 (q, *J* = 7.2 Hz, 2H,

$CO_2CH_2CH_3$), 5.44 (s, 2H, NCH_2CO), 7.48−7.49 (m, 2H, Ar*H*), 7.57 (dd, *J* = 3.6, 4.4 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0 (CH_3), 49.3 (CH_2), 62.4 (CH_2), 78.7 (C), 83.6 (CH), 110.2 (CH), 114.5 (C), 127.6 (CH), 128.7 (CH), 133.4 (C), 146.4 (C), 166.1 (C=O); HRMS (EI) calcd for $C_{12}H_{11}N_3O_2$ $[M]^+$ 229.0851, found 229.0852.

The structure of **8ag** was verified by NOE correlation between C7–H and α-methylene protons.

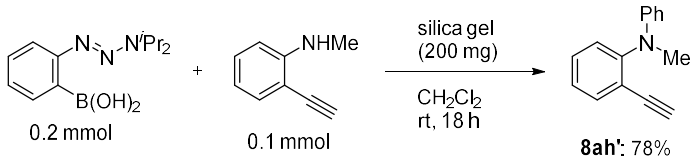
8ag': IR (KBr) *v* 3257, 2984, 1752, 1212, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 3.42 (s, 1H, −C≡C*H*), 4.26 (q, *J* = 7.2 Hz, 2H, $CO_2CH_2CH_3$), 5.73 (s, 2H, NCH_2CO), 7.35 (dd, *J* = 7.2, 8.4 Hz, 1H, Ar*H*), 7.65 (d, *J* = 7.2 Hz, 1H, Ar*H*), 8.10 (d, *J* = 8.4 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 50.0 (CH_2), 62.2 (CH_2), 78.4 (C), 83.0 (CH), 105.0 (C), 121.6 (CH), 124.1 (CH), 133.0 (CH), 133.0 (C), 146.3 (C), 167.0 (C=O); HRMS (EI) calcd for $C_{12}H_{11}N_3O_2$ $[M]^+$ 229.0851, found 229.0850.

3-Ethynyl-*N*-methyl-*N*-phenylaniline (8ah) and 2-Ethynyl-*N*-methyl-*N*-phenylaniline (8ah')



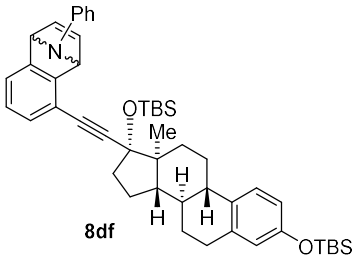
The reaction was performed using **2a'** (27.3 mg, 0.100 mmol) and *N*-methyaniline (**4h**, 16 μL, 0.150 mmol), and a mixture of **8ah** and **8ah'** (9.1 mg, 43%, **8ah**:**8ah'** = 72:28) was obtained as a colorless oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt). IR (KBr) *v* 3292, 1589, 1496, 1344, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.02 (s, 1H, −C≡C*H* for **8ah**), 3.12 (s, 1H, −C≡C*H* for **8ah'**), 3.30 (s, 3H, CH_3 for **8ah**), 3.32 (s, 3H, CH_3, for **8ah'**), 6.71 (d, *J* = 8.8 Hz, 2H, Ar*H* for **8ah'**), 6.77 (t, *J* = 7.4 Hz, 1H, Ar*H* for **8ah'**), 6.93 (dd, *J* = 2.4, 8.4 Hz, 1H, Ar*H* for **8ah**), 7.02−7.34 (m, 8H, Ar*H* for **8ah** and 5H, Ar*H* for **8ah'**), 7.56 (d, *J* = 8.0 Hz, 1H, Ar*H* for **8ah'**); HRMS (EI) calcd for $C_{15}H_{13}N$ $[M]^+$ 207.1048, found 207.1049.

An isomer **8ah'** was synthesized by the reaction of *N*-methyl-2-ethynylaniline[5] with benzyne.[6] It was confirmed that **8ah'** was the minor product by comparing ^1H NMR spectrum of regioisomeric mixture with authentic sample.



8ah': ^1H NMR (400 MHz, $CDCl_3$): δ 3.12 (s, 1H, −C≡C*H*), 3.32 (s, 3H, CH_3), 6.71 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.77 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.15−7.22 (m, 4H, Ar*H*), 7.34 (dt, *J* = 1.6, 7.6 Hz, 1H, Ar*H*), 7.56 (dd, *J* = 2.0, 8.0 Hz, 1H, Ar*H*).

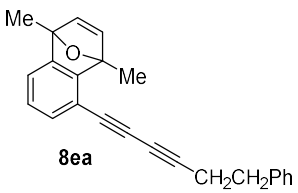
3,17-*O*-Bis(*tert*-butyldimethylsilyl)-17α-{(9-phenyl-1,4-dihydro-1,4-epiminonaphthalen-5-yl)ethynyl}estradiol (8df)



8df

The reaction was performed using **2d** (77.2 mg, 0.100 mmol) and *N*-phenylpyrrole (**4f**, 21.4 mg, 0.150 mmol), and **8df** (31.7 mg, 42%, dr ~1:1) was obtained as a colorless oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): IR (KBr) *ν* 2929, 1600, 1496, 1254, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 6H, Si(C*H*$_3$)$_2$), 0.23−0.25 (s, 6H, Si(C*H*$_3$)$_2$), 0.92 (s, 9H, *t*-Bu), 0.93 (s, 3H, CH_3), 0.98 (s, 9H, *t*-Bu), 1.27−1.57 (m, 4H), 1.80−1.94 (m, 4H), 2.02−2.11 (m, 2H), 2.25−2.30 (m, 1H), 2.34−2.42 (m, 2H), 2.76−2.85 (m, 2H), 5.43 (broad doublet, 1H, ArC*H*N), 5.62 (broad doublet, 1H, ArC*H*N), 6.56 (m, 1H, −C*H*=CH−), 6.61−6.64 (m, 1H, −CH=C*H*−), 6.78−6.80 (m, 3H, Ar*H*), 6.87 (dt, *J* = 1.2, 8.0 Hz, 1H, Ar*H*), 6.93−6.98 (m, 3H, Ar*H*), 7.07−7.18 (m, 4H, Ar*H*); HRMS (ESI) calcd for $C_{48}H_{64}NO_2Si_2$ $[M+H]^+$ 742.4476, found 742.4478.

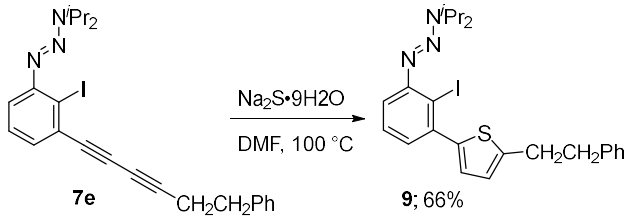
1,4-Dimethyl-5-(6-phenylhexa-1,3-diyn-1-yl)-1,4-dihydro-1,4-epoxynaphthalene (8ea)



8ea

The reaction was performed using **2e** (23.1 mg, 0.0575 mmol) and 2,5-dimethylfuran (**4a**, 9 μL, 0.0863 mmol), and **8ea** (15.9 mg, 85%) was obtained as a colorless oil after purification by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt): IR (KBr) *ν* 2931, 1454, 1382, 1301, 1137, 859, 780 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.87 (s, 3H, C*H*$_3$), 2.08 (s, 3H, C*H*$_3$), 2.67 (t, *J* = 7.5 Hz, 1H, C*H*$_2$CH$_2$), 2.90 (t, *J* = 7.5 Hz, 1H, CH$_2$C*H*$_2$), 6.74 (d, *J* = 5.5 Hz, 1H, -C*H*=CH-), 6.82 (d, *J* = 5.5 Hz, 1H, -CH=C*H*-), 6.91 (dd, *J* = 7.5, 8.0 Hz, 1H, Ar*H*), 7.02 (dd, *J* = 0.5, 8.0 Hz, 1H, Ar*H*), 7.07 (dd, *J* = 0.5, 7.0 Hz, 1H, Ar*H*), 7.23–7.25 (m, 3H, Ar*H*), 7.30–7.33 (m, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.1 (CH_3), 16.5 (CH_3), 21.8 (CH_2), 34.6 (CH_2), 65.8 (C), 72.2 (C), 77.1 (C), 84.2 (C), 88.0 (C), 89.8 (C), 114.0 (C), 118.6 (CH), 125.0 (CH), 126.5 (CH), 128.4 (CH), 128.5 (CH), 129.5 (CH), 140.0 (C), 146.6 (CH), 146.9 (CH), 153.5 (C), 154.9 (C); HRMS (EI) calcd for $C_{24}H_{20}O$ $[M]^+$ 324.1514, found 324.1512.

7. Synthesis of 1-(2-iodo-3-(5-phenethylthiophen-2-yl)phenyl)-3,3-diisopropyltriaz-1-ene (9) from 7e

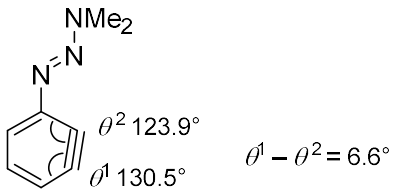


A suspention of **7e** (24.2 mg, 0.0500 mmol), and $Na_2S•9H_2O$ (36.0 mg, 0.150 mmol) in DMF (0.5 mL) was stirred at 100 °C. After stirring at the same temperature for 6 hours, the reaction was quenched with water, and the whole mixture was extracted with Et_2O. The combined organic layers were successively washed with brine and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude mixture, which was purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt) to give **9** (17.0 mg, 66%) as an colorless oil: IR (KBr) *v* 2972, 1403, 1239, 1155, 1010, 793 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (broad doublet, *J* = 7.5 Hz, 6H, $CH(CH_3)_2$), 1.40 (broad doublet, *J* = 7.5 Hz, 6H, $CH(CH_3)_2$), 3.04 (dd, *J* = 6.4, 9.2 Hz, 2H, CH_2CH_2), 3.15 (dd, *J* = 6.4, 9.2 Hz, 2H, CH_2CH_2), 4.06 (broad, 1H, $CH(CH_3)_2$), 5.23 (broad, 1H, $CH(CH_3)_2$), 6.76 (d, *J* = 4.0 Hz, 1H, Ar*H*), 6.96 (d, *J* = 4.0 Hz, 1H, Ar*H*), 7.14 (dd, *J* = 2.5, 9.0 Hz, 1H, Ar*H*), 7.19–7.25 (m, 4H, Ar*H*), 7.27–7.32 (m, 3H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2 (CH_3), 23.8 (CH_3), 32.1 (CH_2), 37.9 (CH_2), 47.7 (CH), 49.8 (CH), 102.8 (C), 116.7 (CH), 123.9 (CH), 126.1 (CH), 127.3 (CH), 127.5 (CH), 128.0 (CH), 128.4 (CH), 128.5 (CH), 140.9 (C), 141.2 (C), 143.7 (C), 144.7 (C), 151.8 (C); HRMS (EI) calcd for $C_{24}H_{28}IN_3S$ $[M]^+$ 517.1049, found 517.1050.

8. DFT calculation

All calculations were performed with the Gaussian 09 program package.[7] The groundstate geometries were optimized at the B3LYP/6-31+G(d,p) basis set without an implicit solvation model.

3-(3,3-dimethyltriaz-1-en-1-yl)benzyne



Cartesian coordinates

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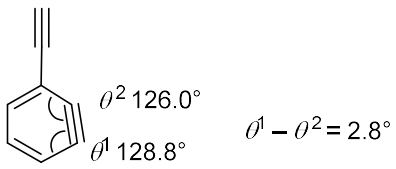
C	1.3690410	-1.1220820	-0.0256810
C	2.5963640	-1.3608100	-0.0181940
C	3.6800810	-0.4979630	0.0081770
C	3.2121720	0.8362300	0.0282130
H	1.5351370	2.1992900	0.0354740
H	4.7319210	-0.7567570	0.0127060
H	3.9401290	1.6440250	0.0497620
N	-0.5146540	0.5674490	-0.0112660
N	-1.3202500	-0.4168040	-0.0328340
N	-2.5999590	-0.0853040	-0.0674330
C	-3.5508480	-1.1759530	0.0633440
H	-3.0035970	-2.1130330	-0.0411340
H	-4.0466600	-1.1571230	1.0431080
H	-4.3142700	-1.1114470	-0.7194740
C	-3.0362330	1.3034880	-0.0057690
H	-2.5675440	1.8792610	-0.8086320
H	-4.1217100	1.3257880	-0.1130080
H	-2.7452450	1.7622210	0.9473240

3-ethinylbenzyne



Cartesian coordinates

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H	-0.3076978	2.0489258	0.0001939
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C	-3.2498929	0.0083661	-0.0001191
H	-4.3156184	0.0445590	-0.0002003

References

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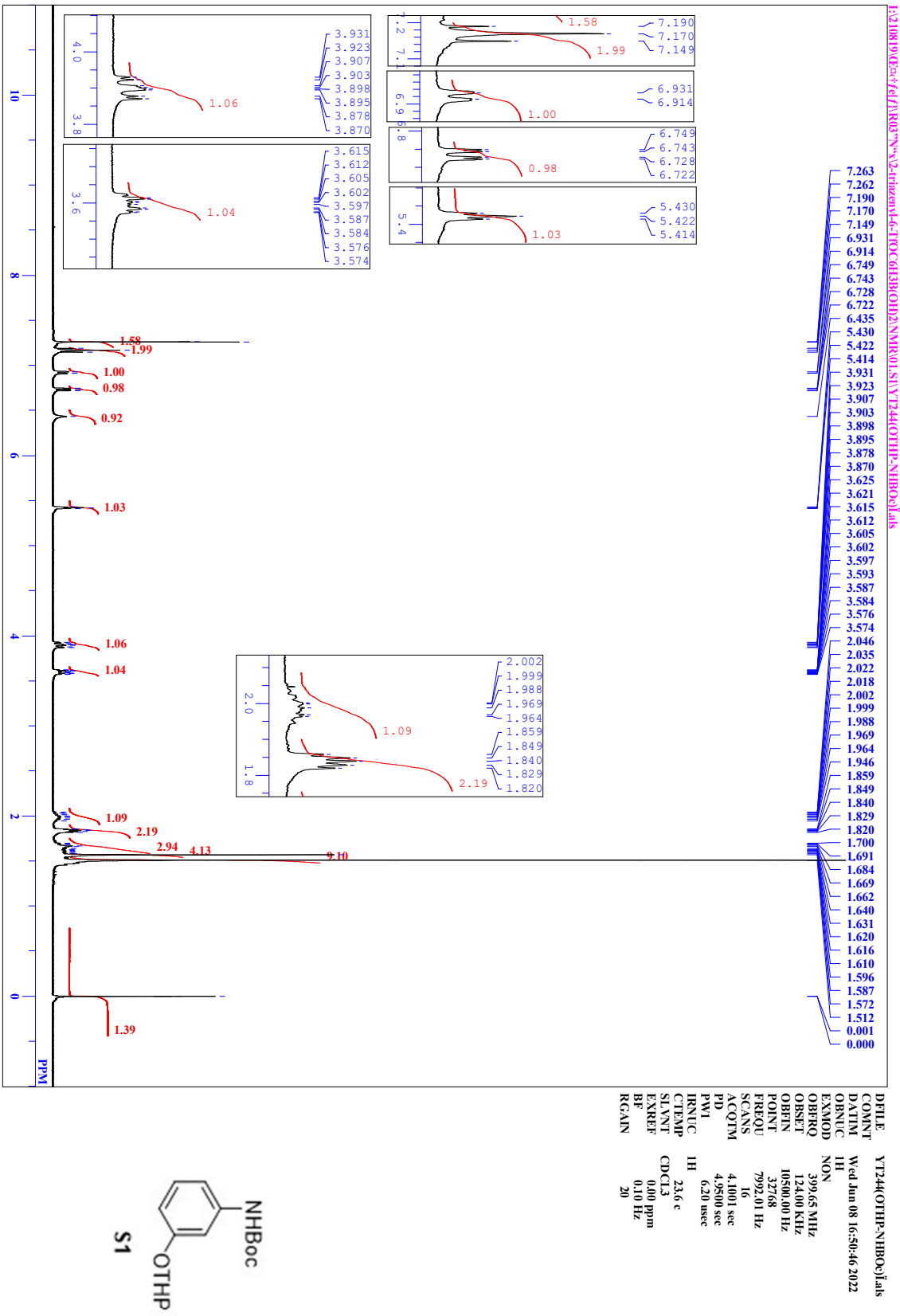
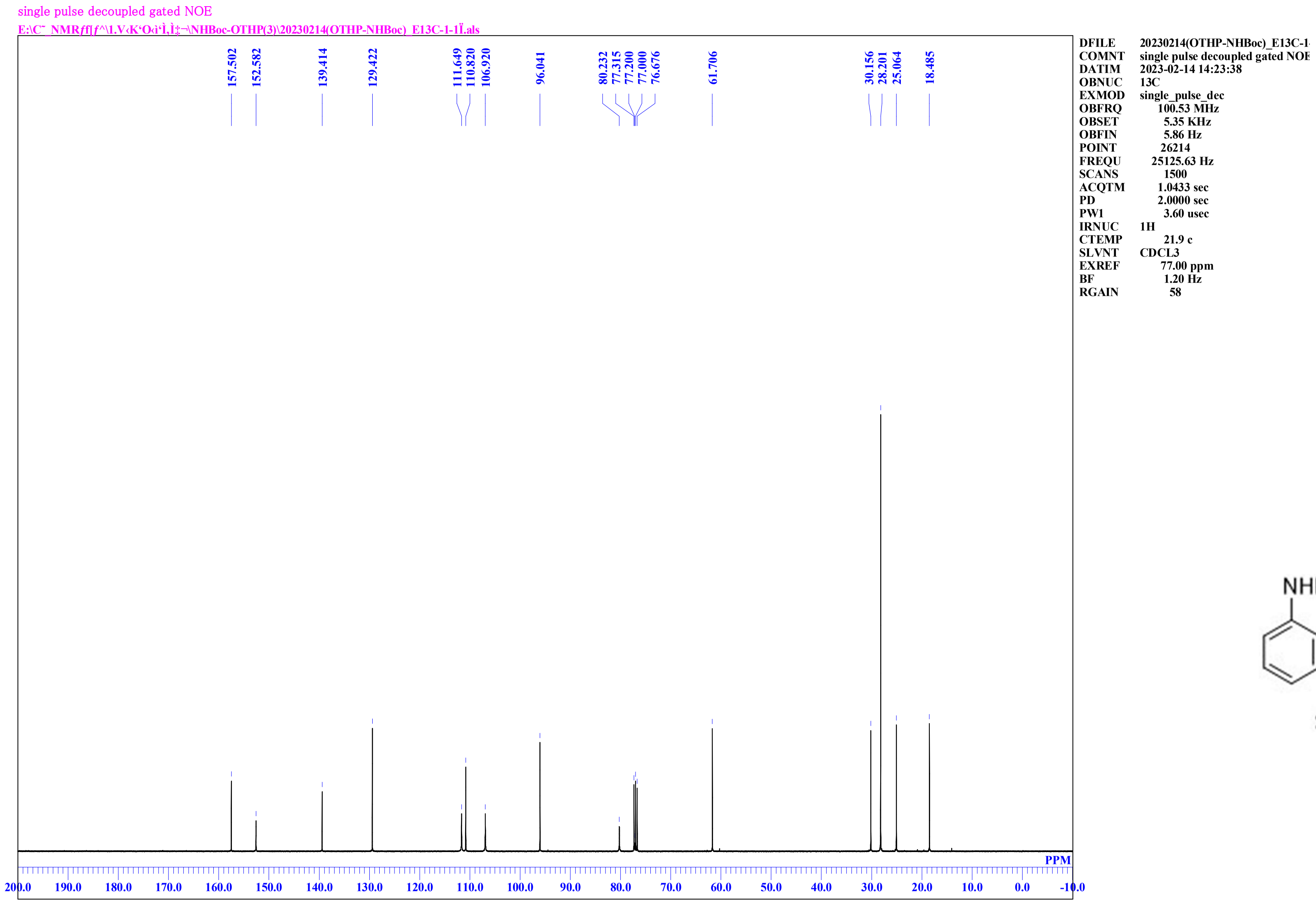
[7] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. 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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

tert-Butyl [3-{(tetrahydro-2*H*-pyran-2-yl)oxy}phenyl]carbamate (S1)

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152.582
139.414
129.422
111.649
110.820
106.920
96.041
80.232
77.315
77.200
77.000
76.676
61.706
30.156
28.201
25.064
18.485
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
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FREQU 25125.63 Hz
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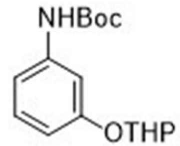
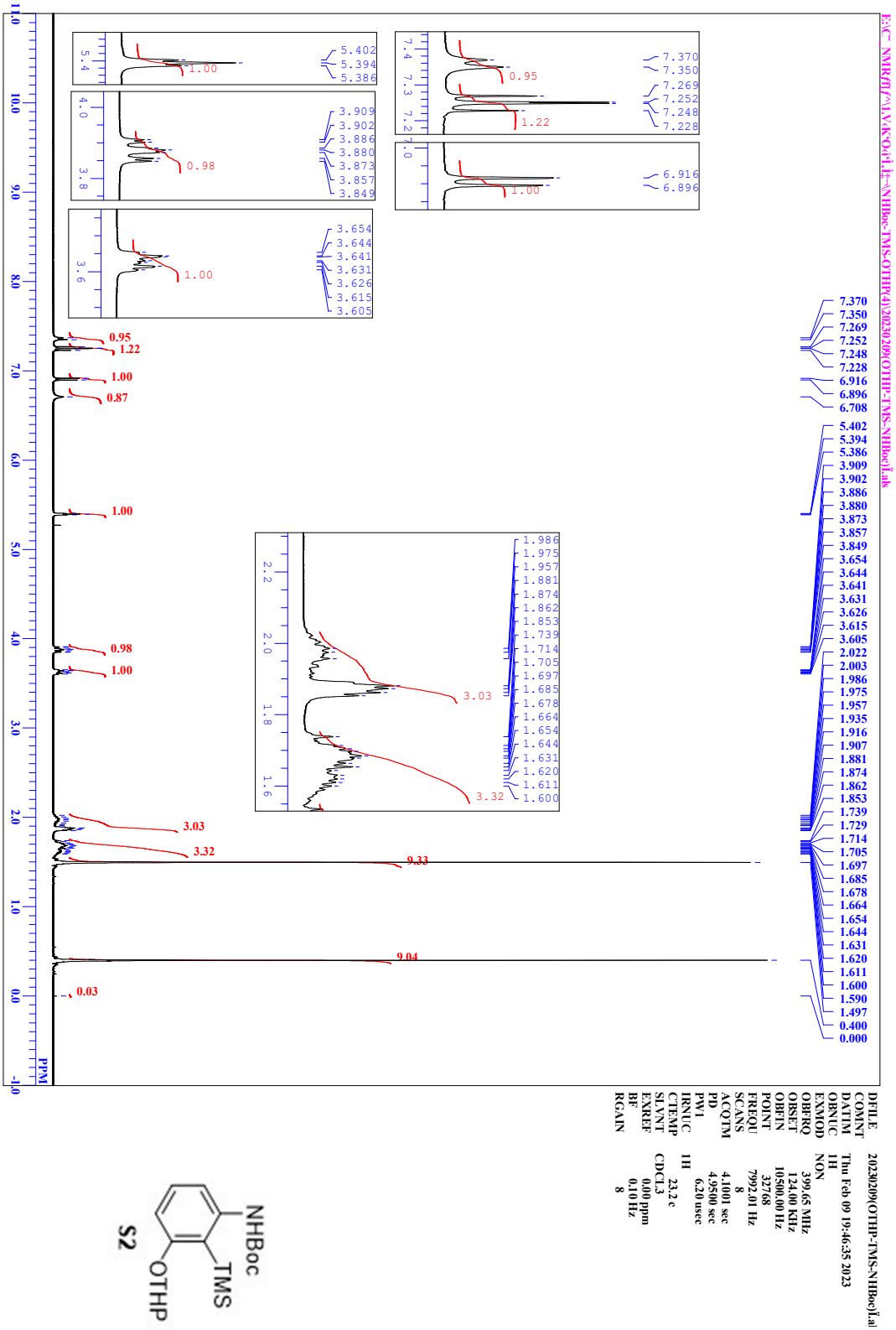
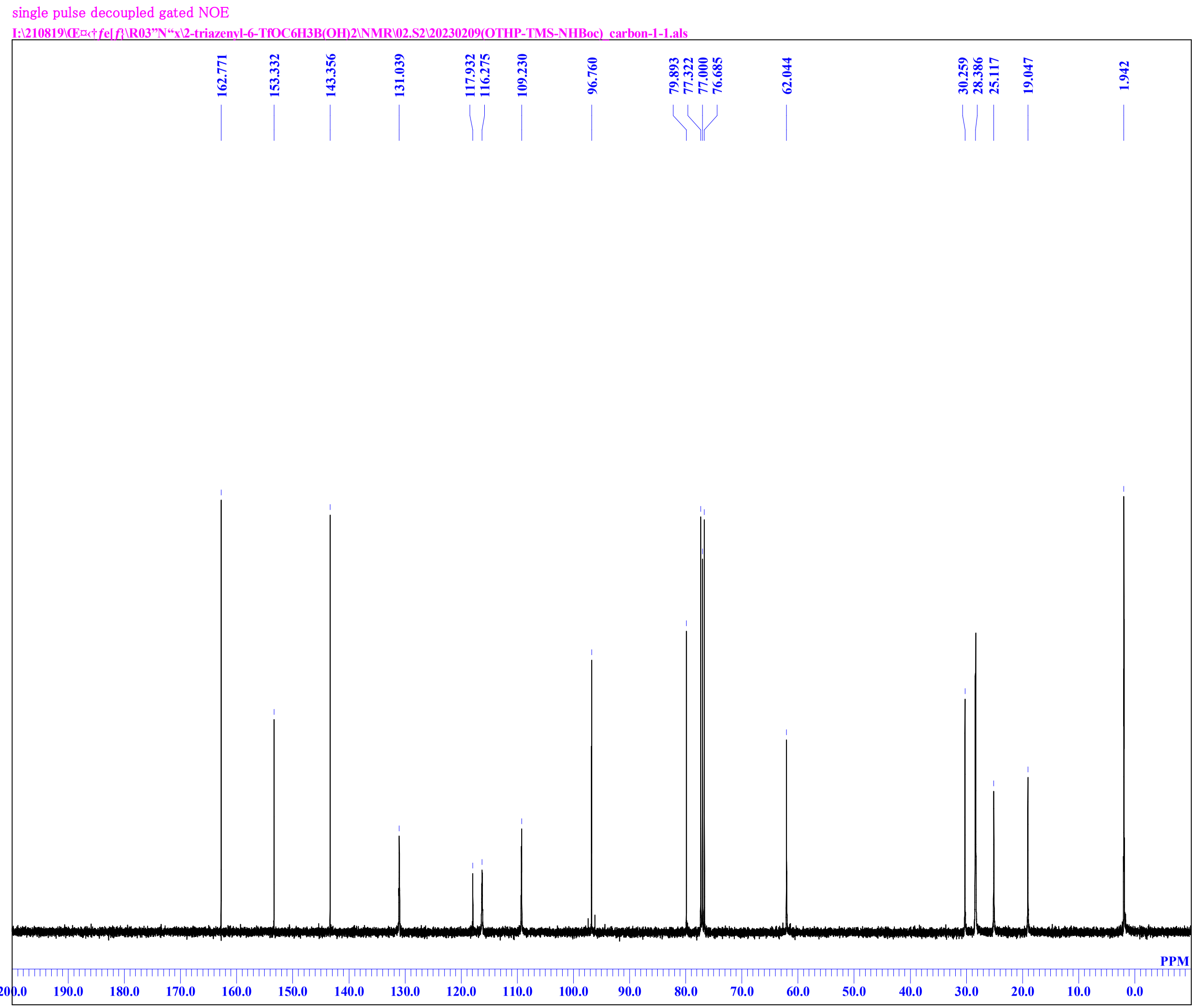

NHBoc
OTHP

S1

tert-Butyl [3-{(tetrahydro-2*H*-pyran-2-yl)oxy}-2-(trimethylsilyl)phenyl]carbamate (S2)

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153.332
143.356
131.039
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77.000
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200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
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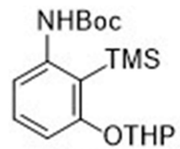
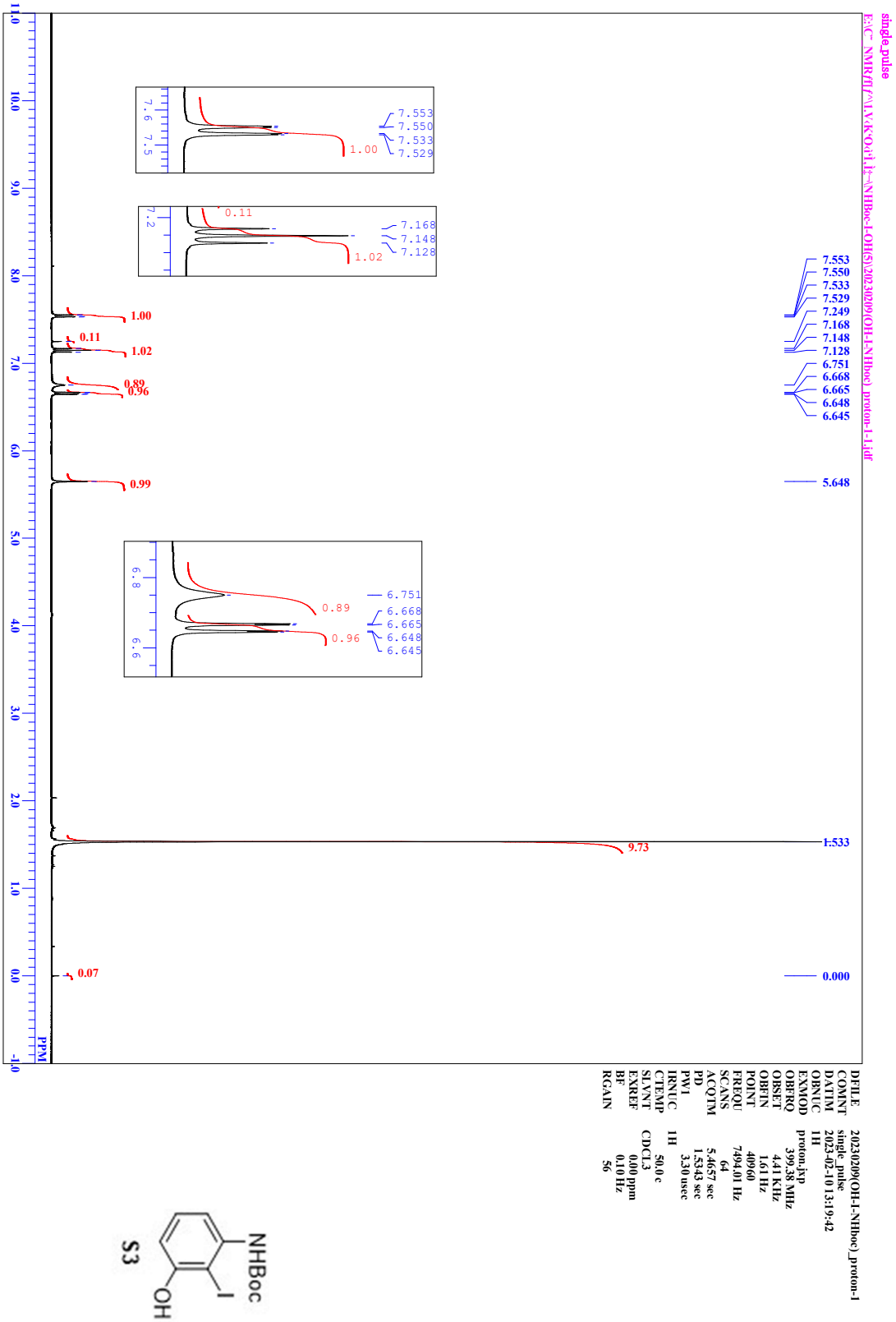
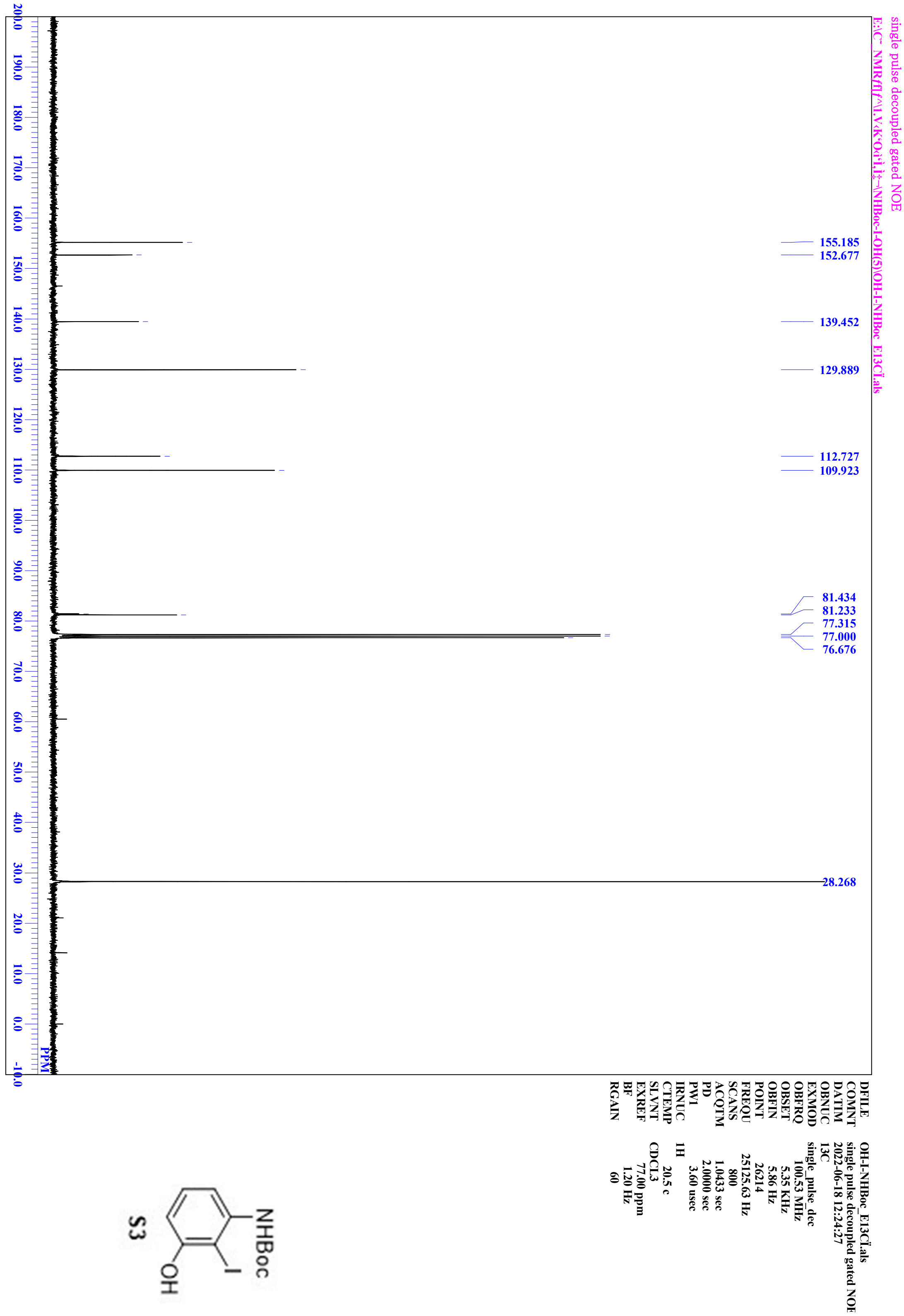
RGAIN 56


NHBoc
TMS
OTHP

S2

tert-Butyl (3-hydroxy-2-iodophenyl)carbamate (S3)

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CTEMP 20.5 c
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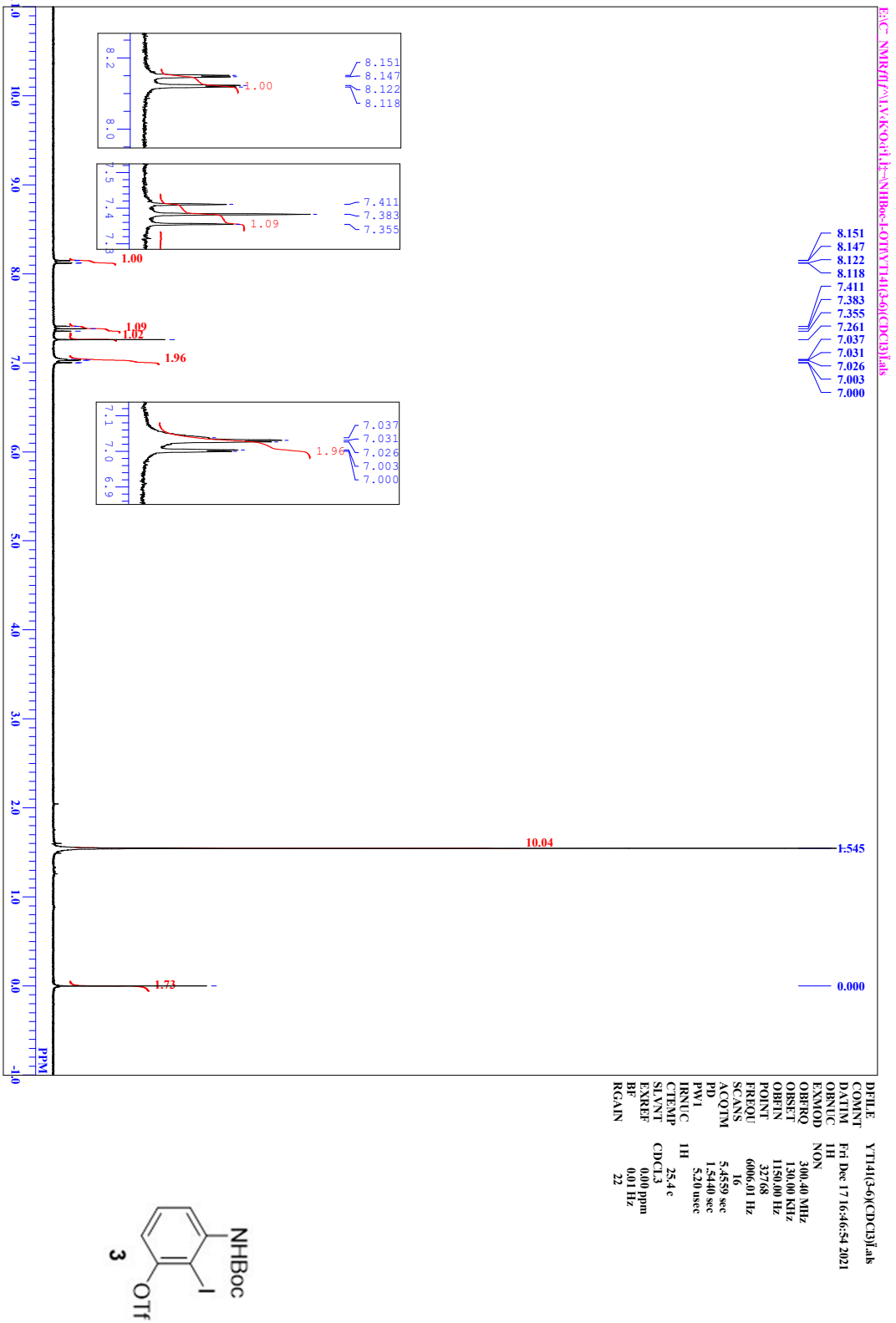
NHBoc
I
OH
S3

3-{(*tert*-Butoxycarbonyl)amino}-2-iodophenyl trifluoromethanesulfonate (3)



single pulse decoupled gated NOE

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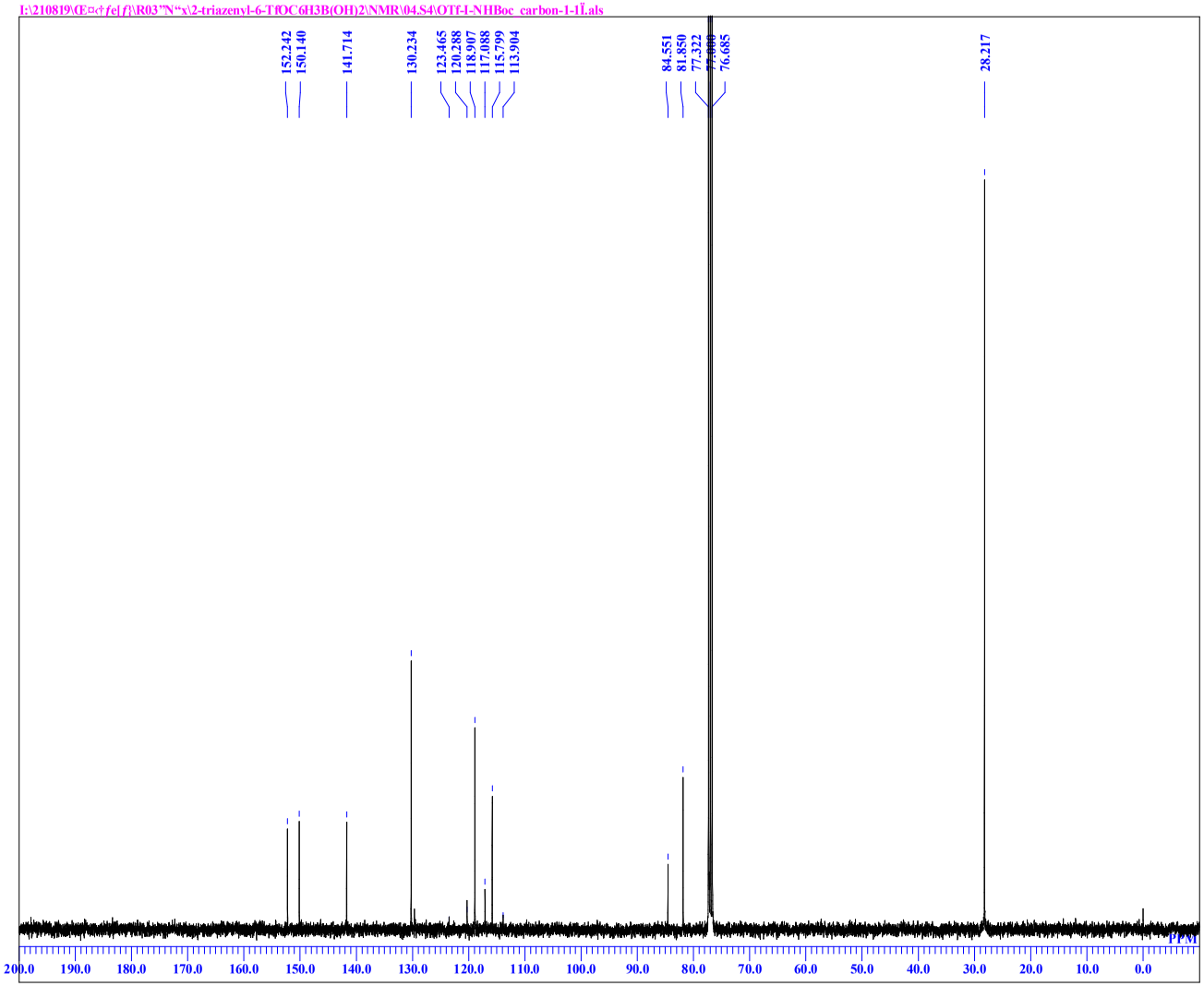

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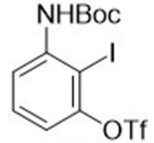
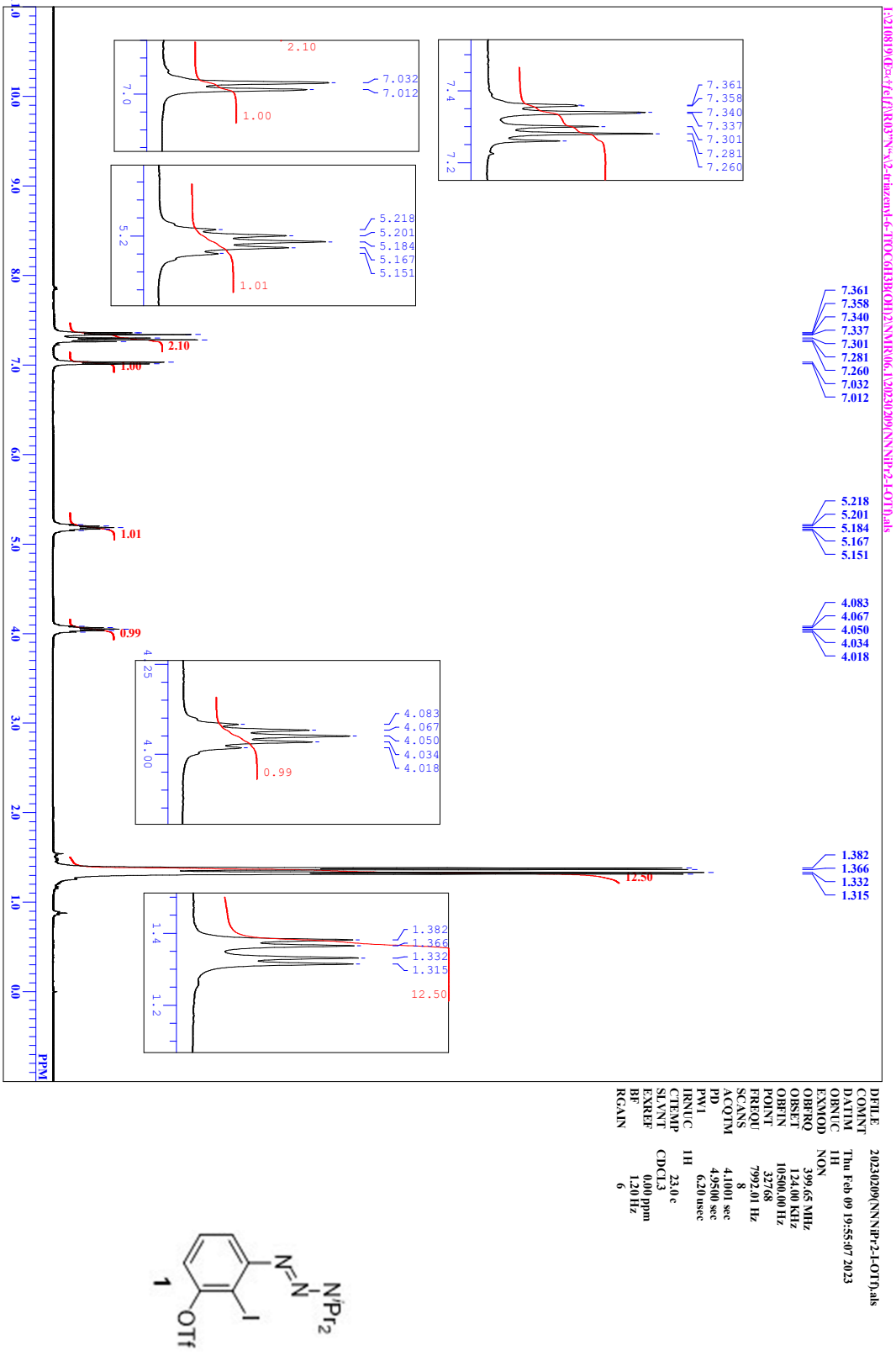
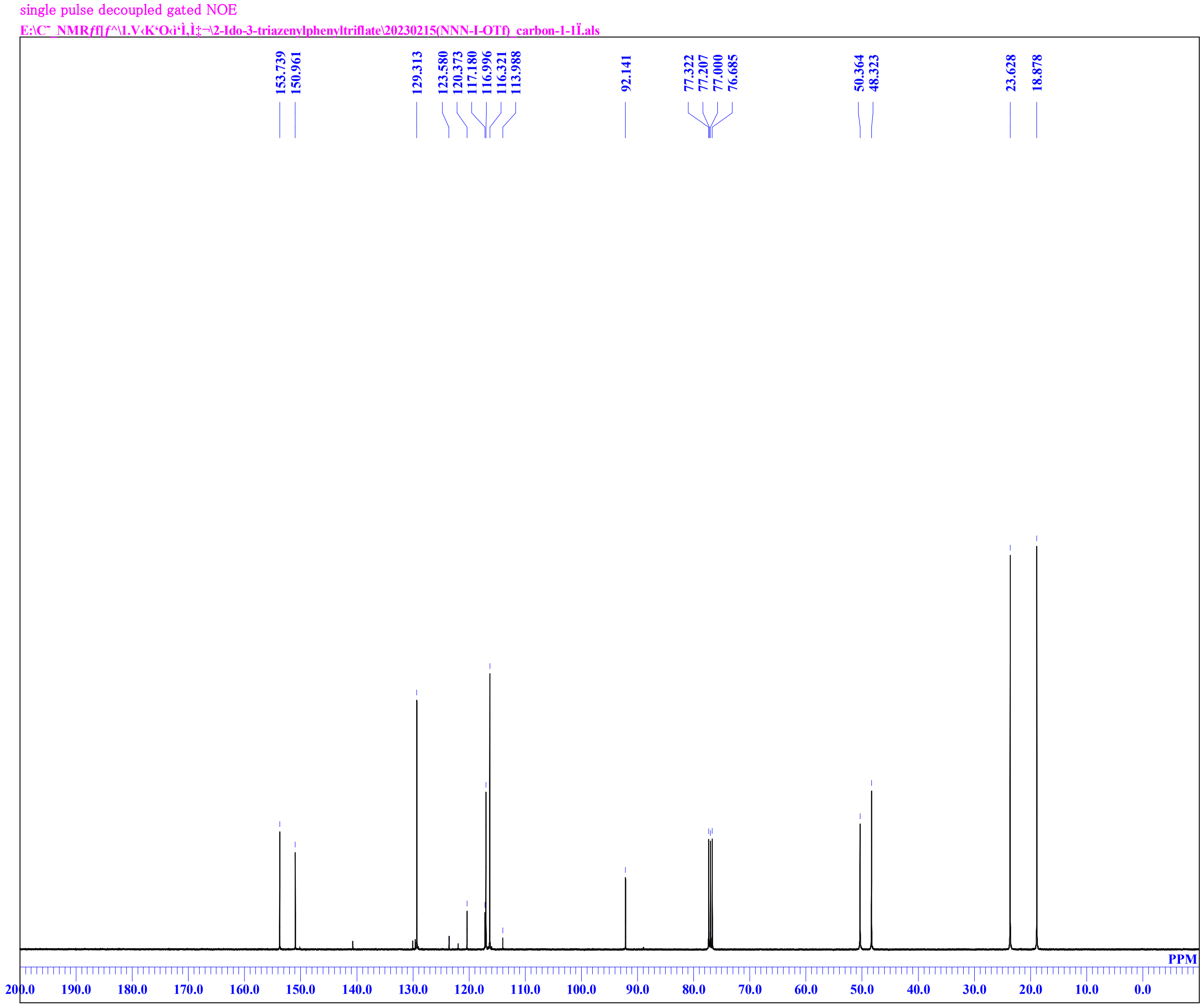
BF	1.20 Hz
RGAIN	56



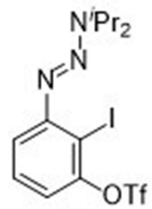
3

3-(3,3-Diisopropyltriaz-1-en-1-yl)-2-iodophenyl trifluoromethanesulfonate (1)



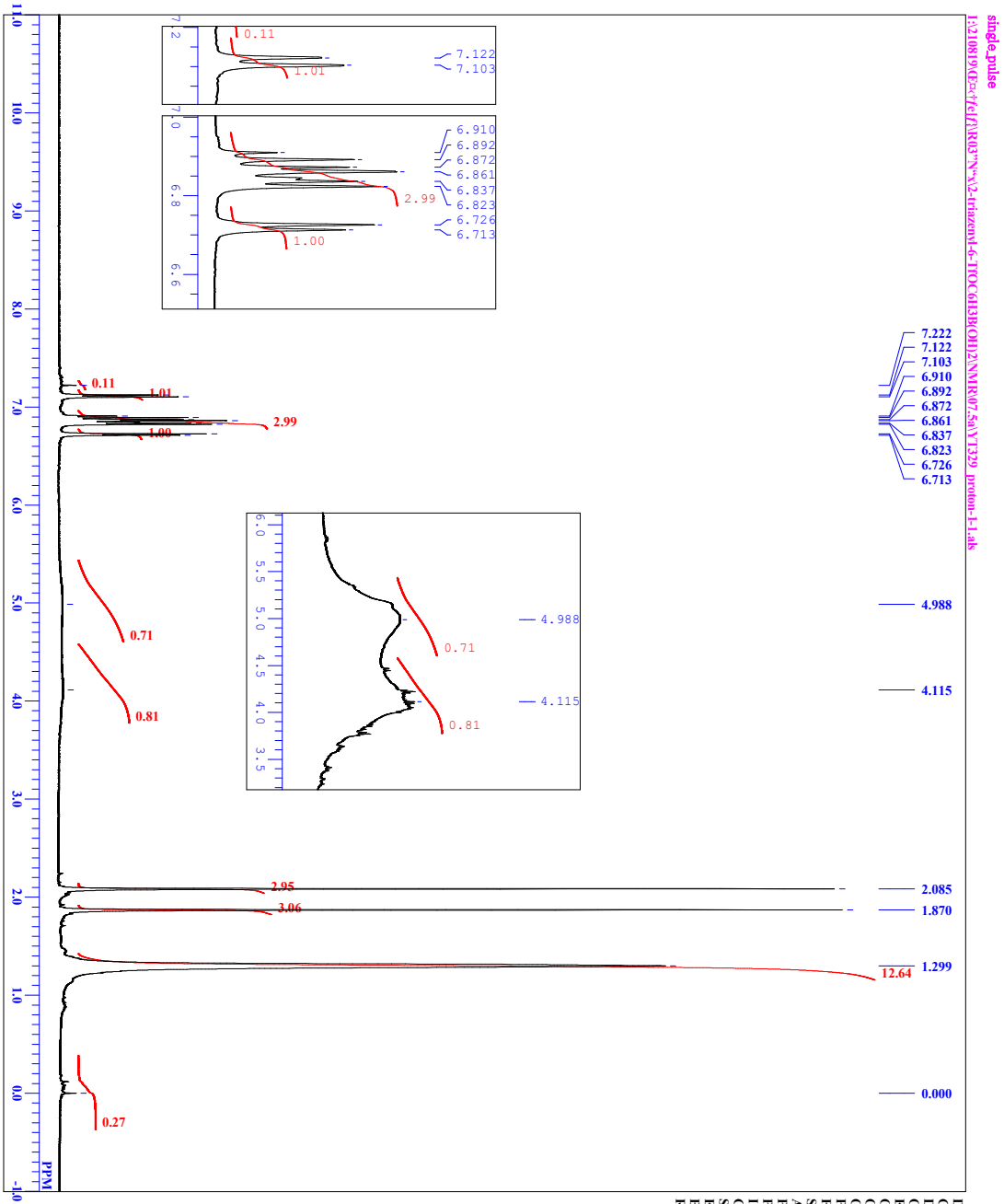


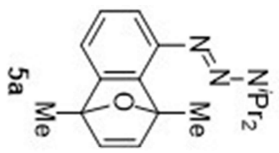
DFILE	20230215(NNN-I-OTf)_carbon-1-1
COMNT	single pulse decoupled gated NOE
DATIM	2023-02-15 11:14:17
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.43 MHz
OBSET	4.82 KHz
OBFIN	0.13 Hz
POINT	32768
FREQU	25252.53 Hz
SCANS	1500
ACQTM	1.2976 sec
PD	1.7024 sec
PW1	3.77 usec
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	56

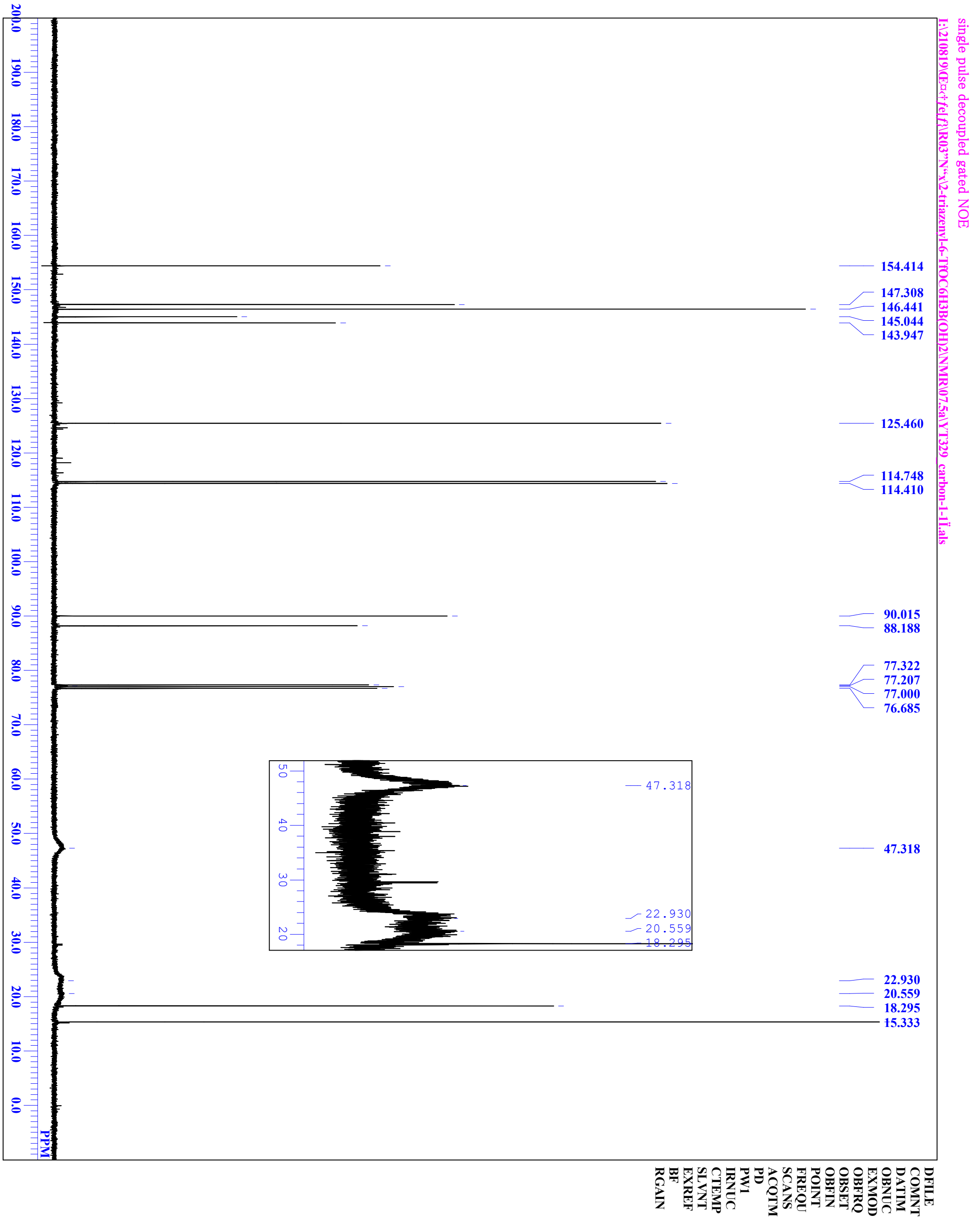


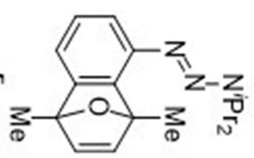
1

1-(1,4-Dimethyl-1,4-dihydro-1,4-epoxynaphthalen-5-yl)-3,3-diisopropyltriaz-1-ene (5a)



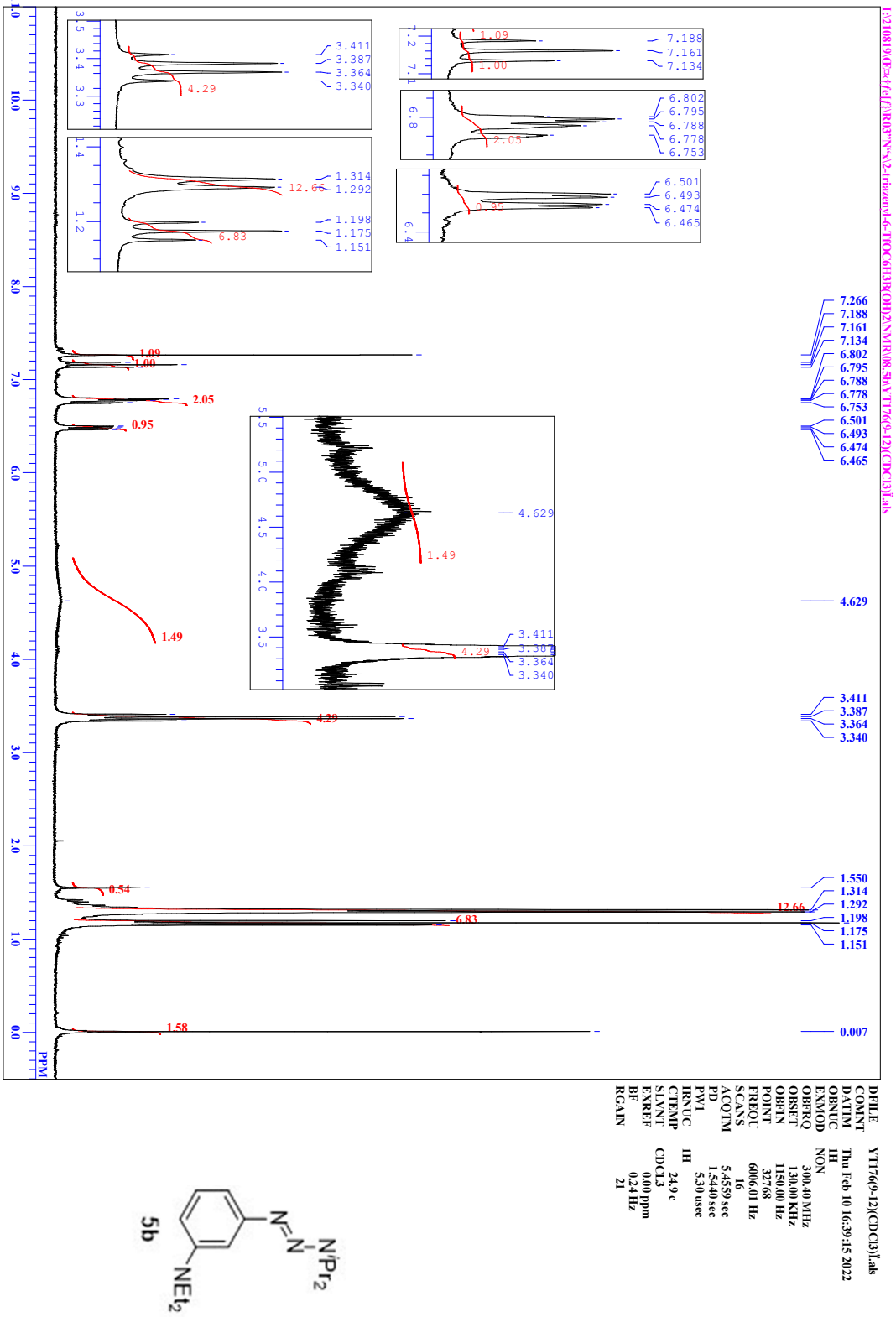



single pulse decoupled gated NOE
154.414
147.308
146.441
145.044
143.947
125.460
114.748
114.410
90.015
88.188
77.322
77.207
77.000
76.685
47.318
22.930
20.559
18.295
15.333
PPM
DFILE YT329_carbon-1-1ï.als
COMNT single pulse decoupled gated NOE
DATIM 2023-02-02 10:14:32
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.43 MHz
OBSET 4.82 KHz
OBFIN 0.13 Hz
POINT 32768
FREQU 25252.53 Hz
SCANS 2000
ACQTM 1.2976 sec
PD 1.7024 sec
PW1 3.75 usec
IRNUC 1H
CTEMP 50.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 56


N^{i}Pr$_2$
N
N
O
Me
Me

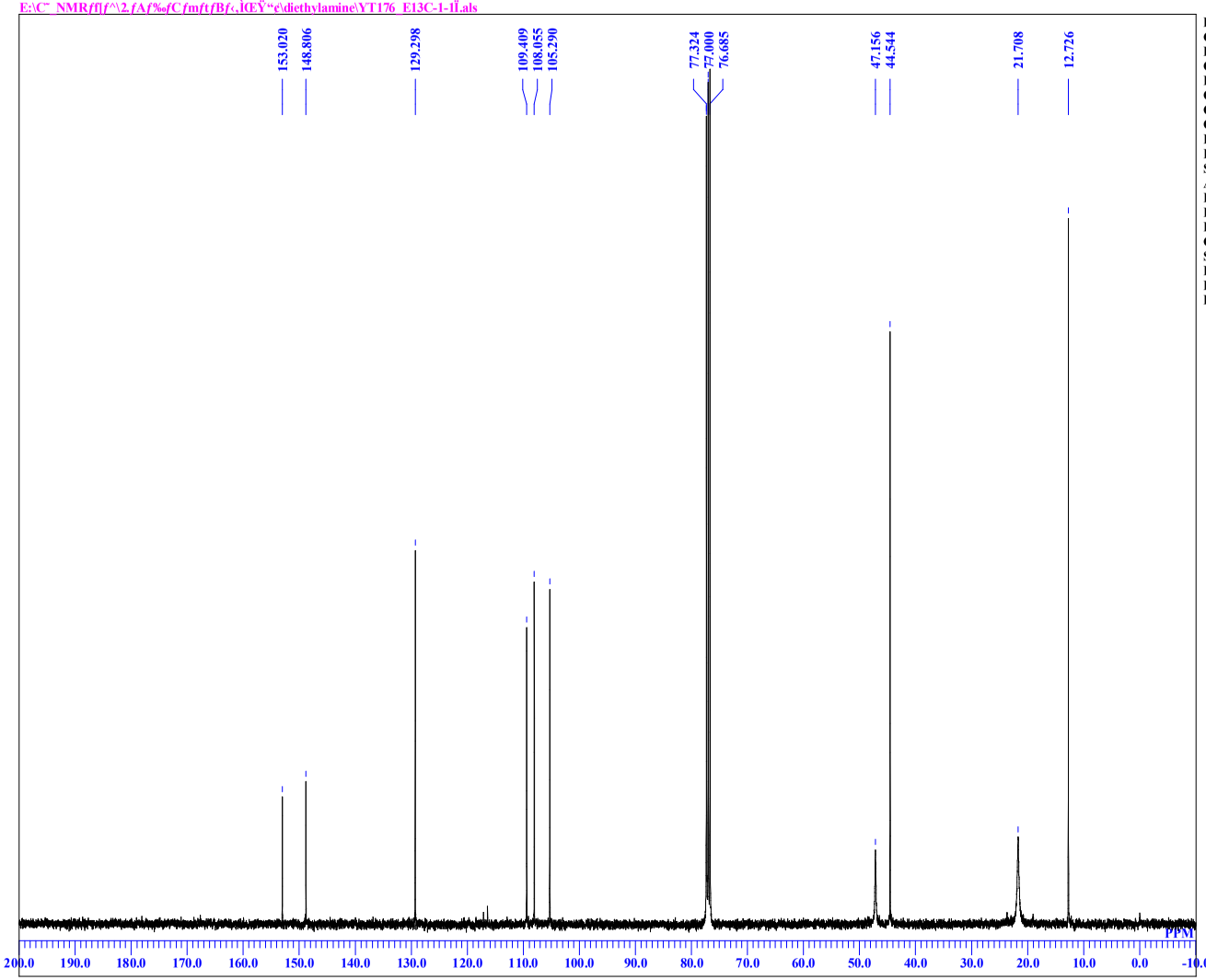
5a

3-(3,3-Diisopropyltriaz-1-en-1-yl)-*N*,*N*-diethylaniline (5b)

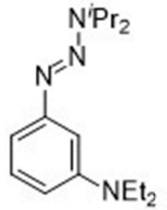


single pulse decoupled gated NOE

E:\C~_NMR\fl\f^\2.fA\f‰\fC\fm\ft\fB\fc\,ìŒÝ“ę\diethylamine\YT176_E13C-1-1Ï.als

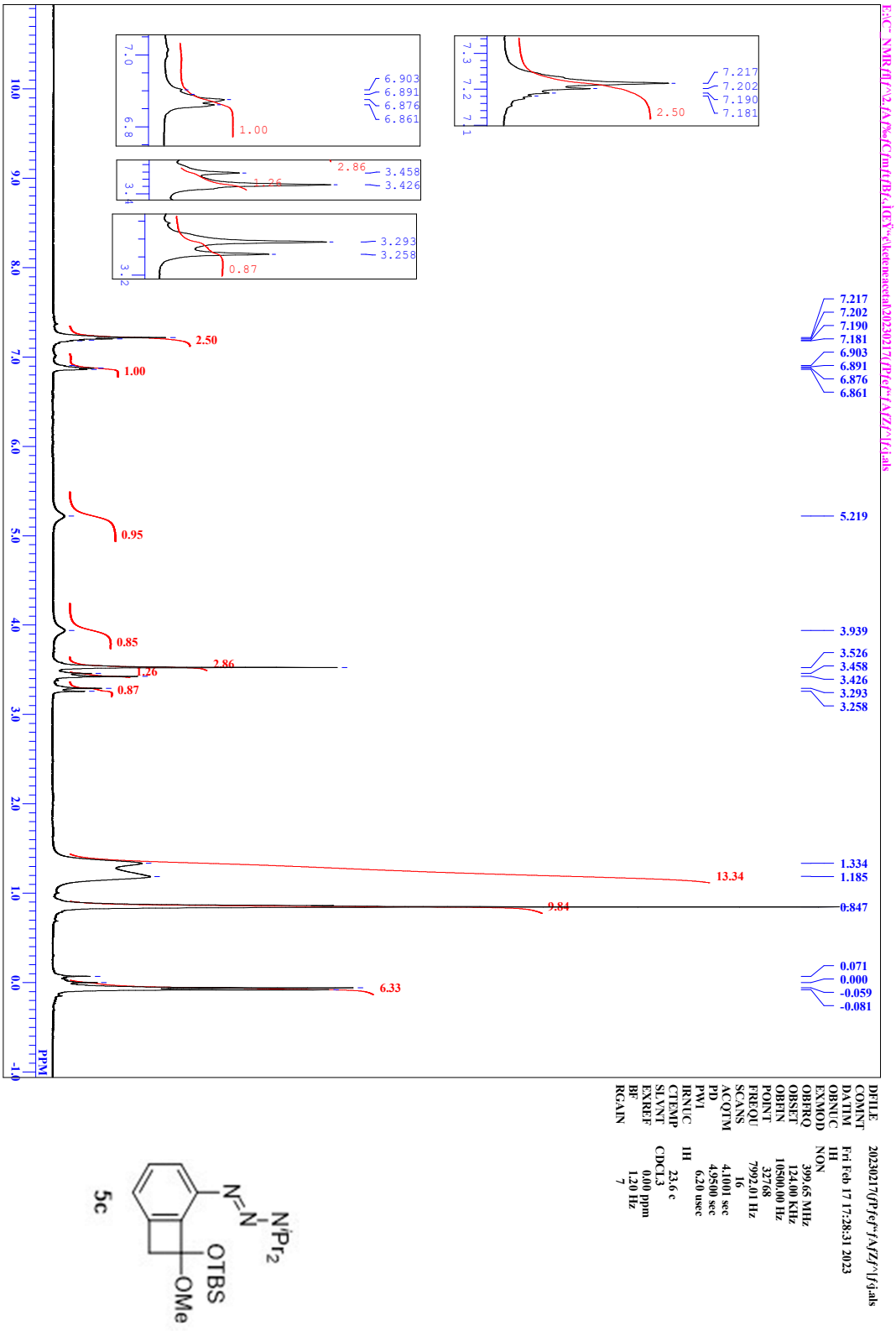


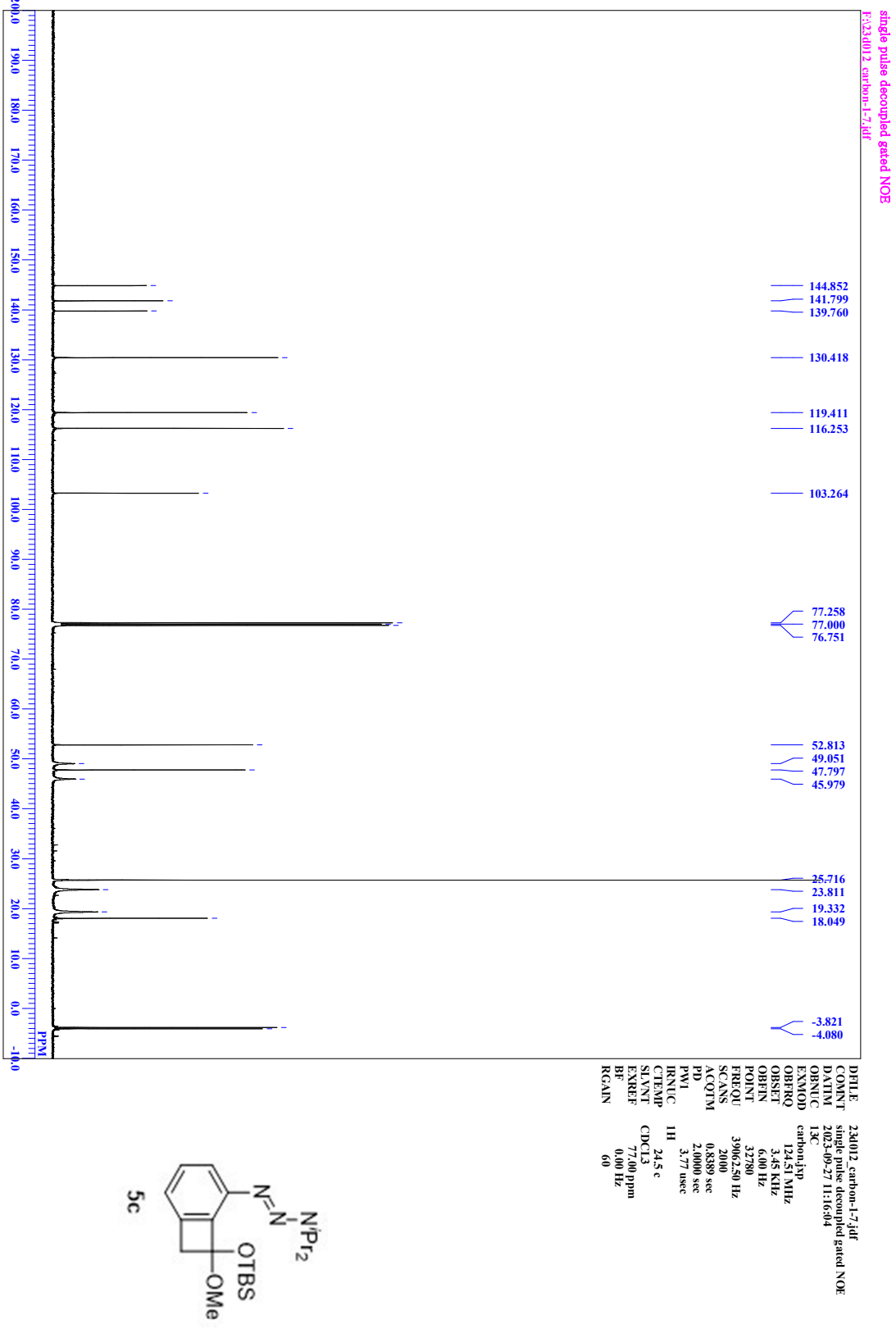
DFILE	YT176_E13C-1-1Ï.als
COMNT	single pulse decoupled gated NOE
DATIM	2023-02-01 13:55:50
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	2000
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	50.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



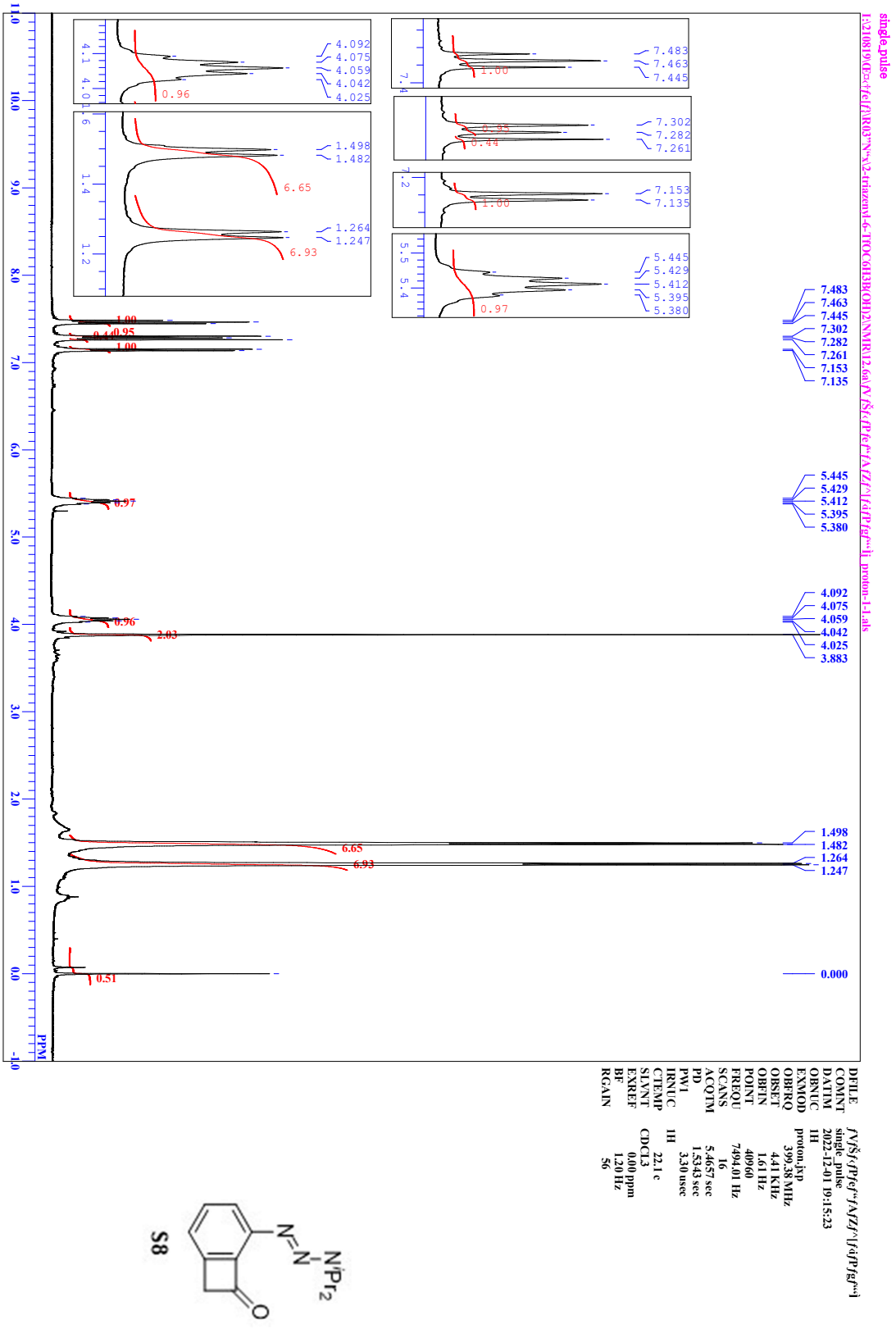
5b

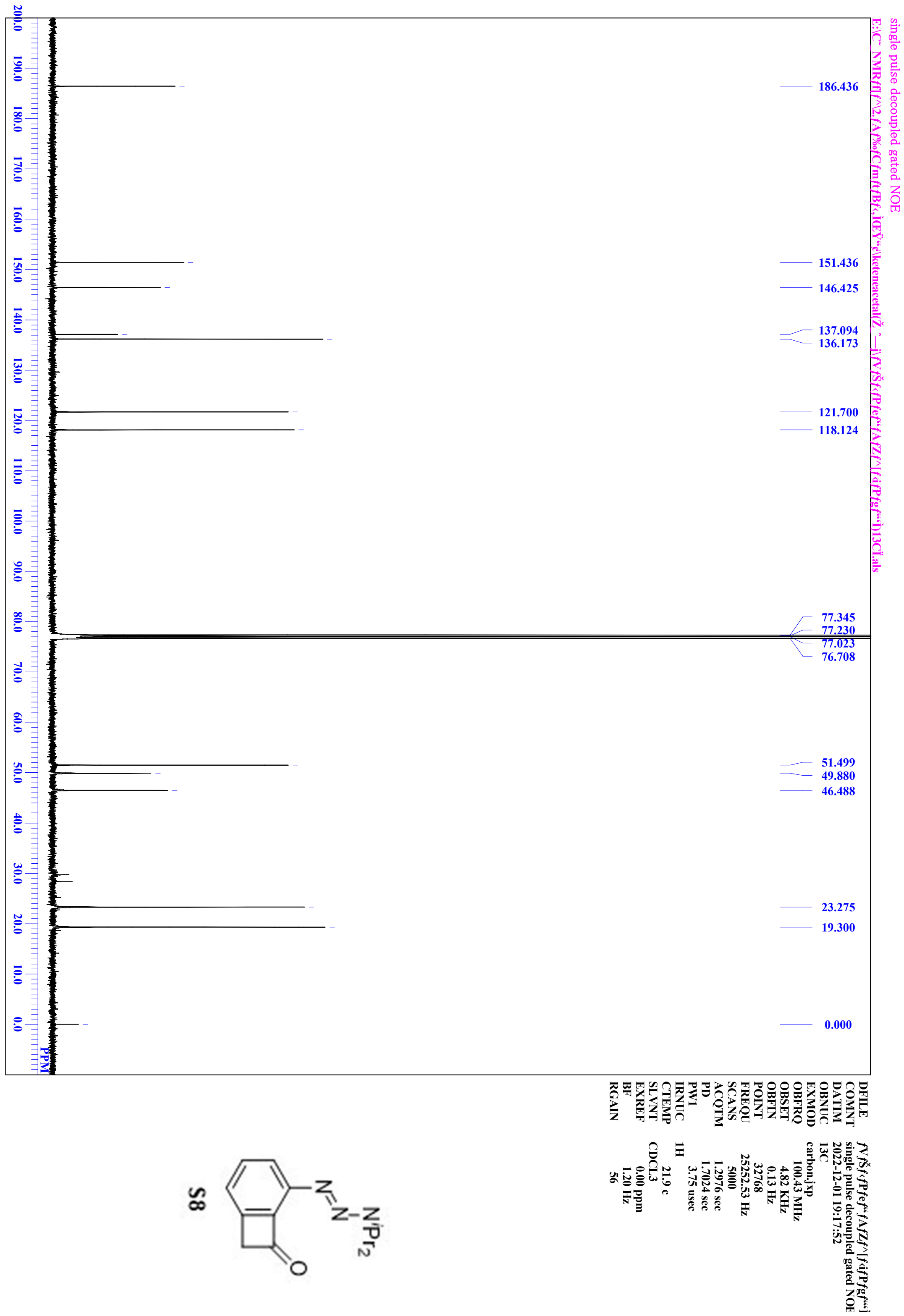
1-[(*tert*-Butyldimethylsilyl)oxy]-6-(3,3-diisopropyltriaz-1-en-1-yl)-1-methoxy benzocyclobutene (5c)



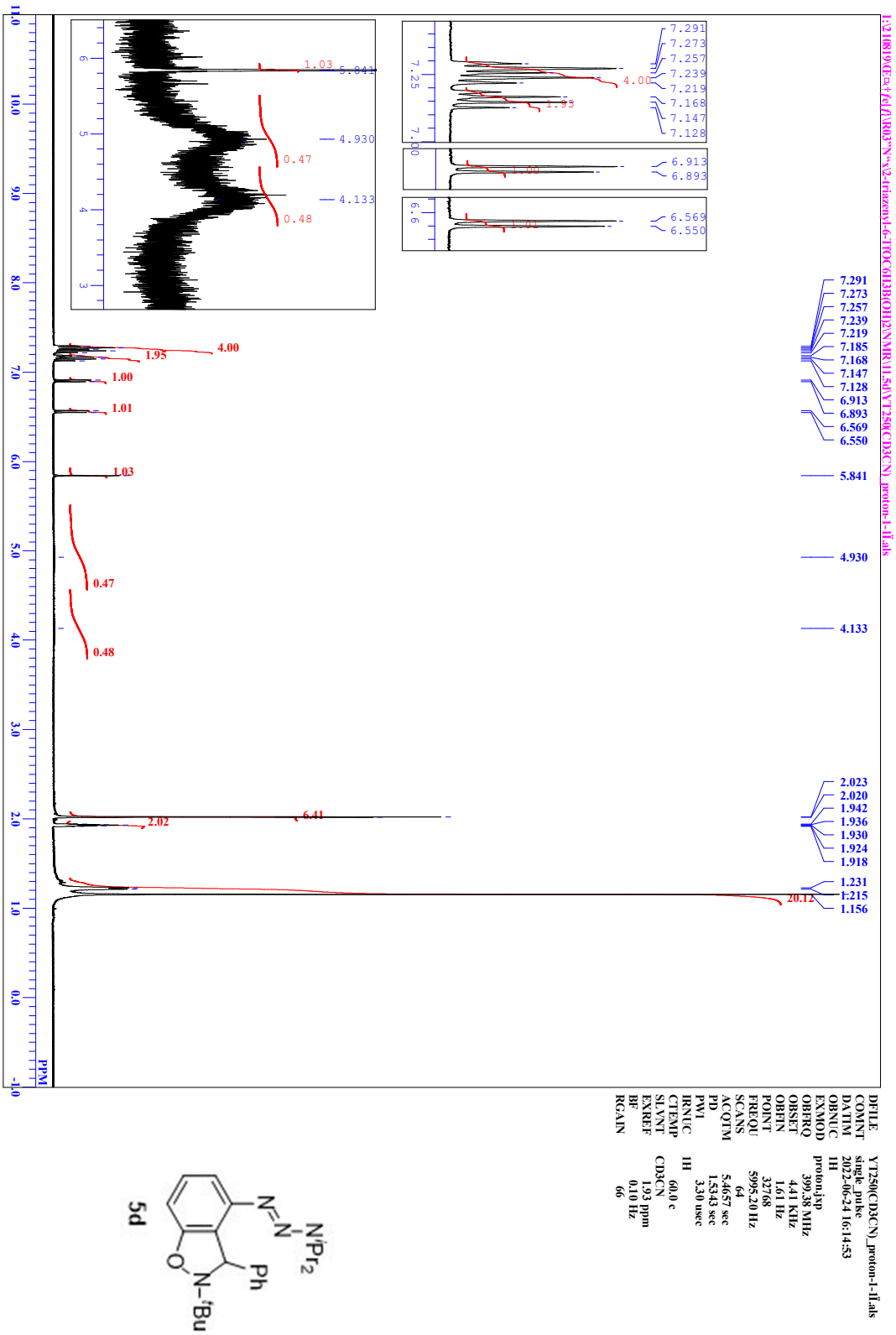

single pulse decoupled gated NOE
F:\23d012_carbon-1-7.jdf
144.852
141.799
139.760
130.418
119.411
116.253
103.264
77.258
77.000
76.751
52.813
49.051
47.797
45.979
25.716
23.811
19.332
18.049
-3.821
-4.080
PPM
DFILE 23d012_carbon-1-7.jdf
COMNT single pulse decoupled gated NOE
DATIM 2023-09-27 11:16:04
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32780
FREQU 39062.50 Hz
SCANS 2000
ACQTM 0.8389 sec
PD 2.0000 sec
PW1 3.77 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 60
5c
N
N
N
iPr2
OTBS
OMe

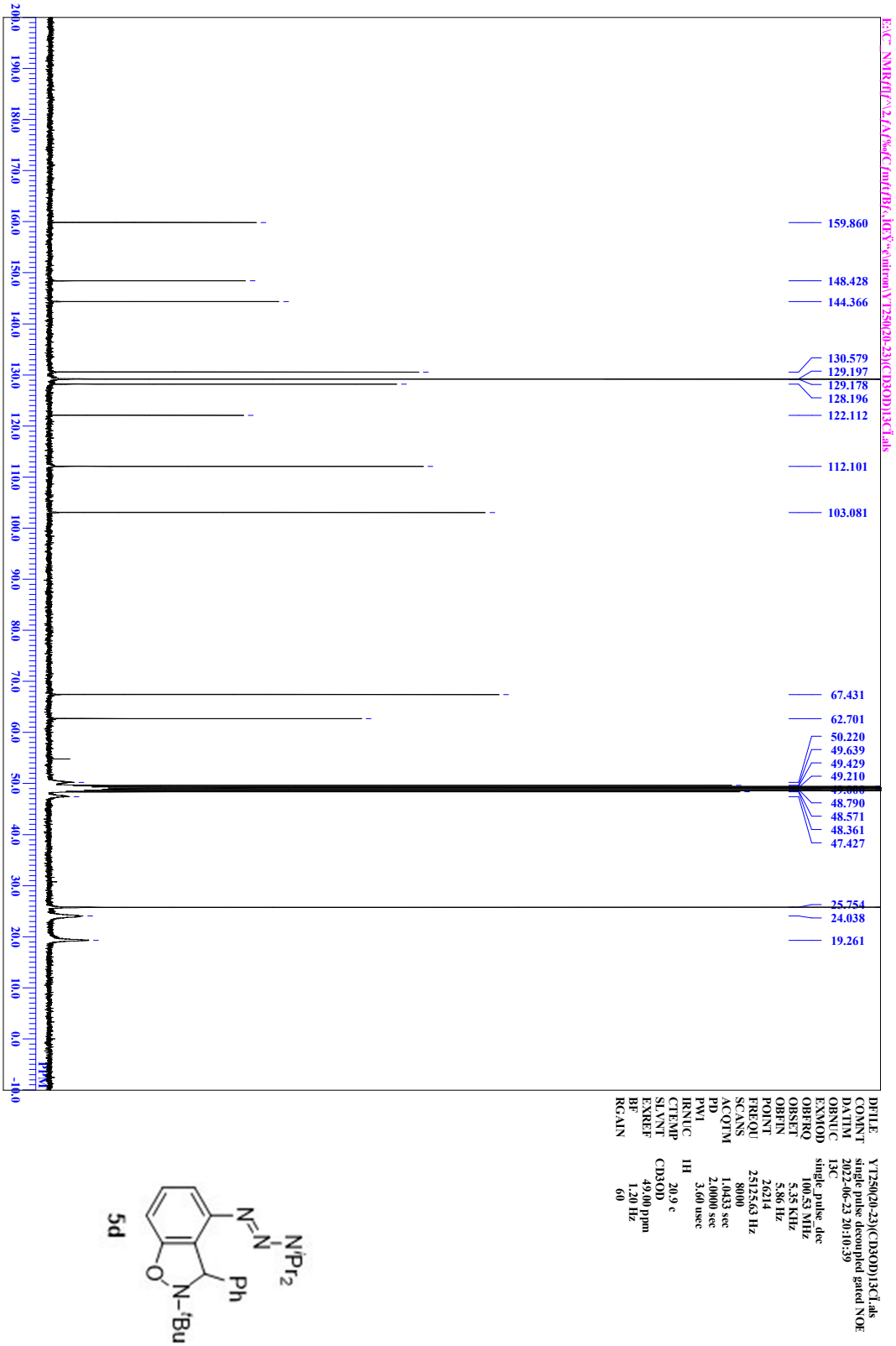
6-(3,3-Diisopropyltriaz-1-en-1-yl)benzocyclobuten-1-one (S8)




single pulse decoupled gated NOE
186.436
151.436
146.425
137.094
136.173
121.700
118.124
77.345
77.230
77.023
76.708
51.499
49.880
46.488
23.275
19.300
0.000
PPM
DFILE
COMNT single pulse decoupled gated NOE
DATIM 2022-12-01 19:17:52
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.43 MHz
OBSET 4.82 KHz
OBFIN 0.13 Hz
POINT 32768
FREQU 25252.53 Hz
SCANS 5000
ACQTM 1.2976 sec
PD 1.7024 sec
PW1 3.75 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 56
S8

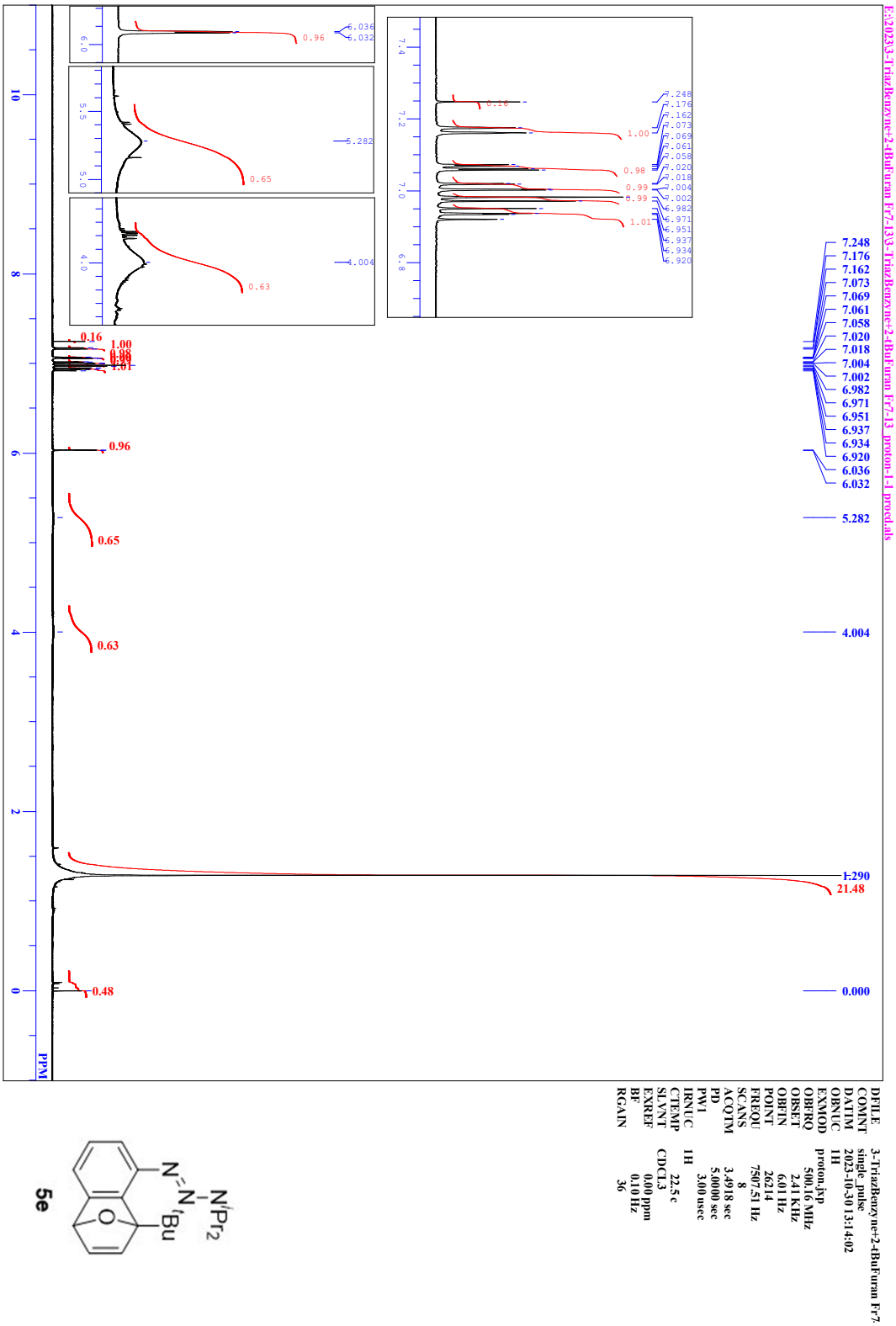
2-(*tert*-Butyl)-4-(3,3-diisopropyltriaz-1-en-1-yl)-3-phenyl-2,3-dihydrobenzo[*d*]isoxazole (5d)




single pulse decoupled gated NOE
159.860
148.428
144.366
130.579
129.197
129.178
128.196
122.112
112.101
103.081
67.431
62.701
50.220
49.639
49.429
49.210
48.790
48.571
48.361
47.427
25.754
24.038
19.261
PPM
DFILE YT250(20-23)(CD3OD)13C1.als
COMNT single pulse decoupled gated NOE
DATIM 2022-06-23 20:10:39
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 8000
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CD3OD
EXREF 49.00 ppm
BF 1.20 Hz
RGAIN 60

5d

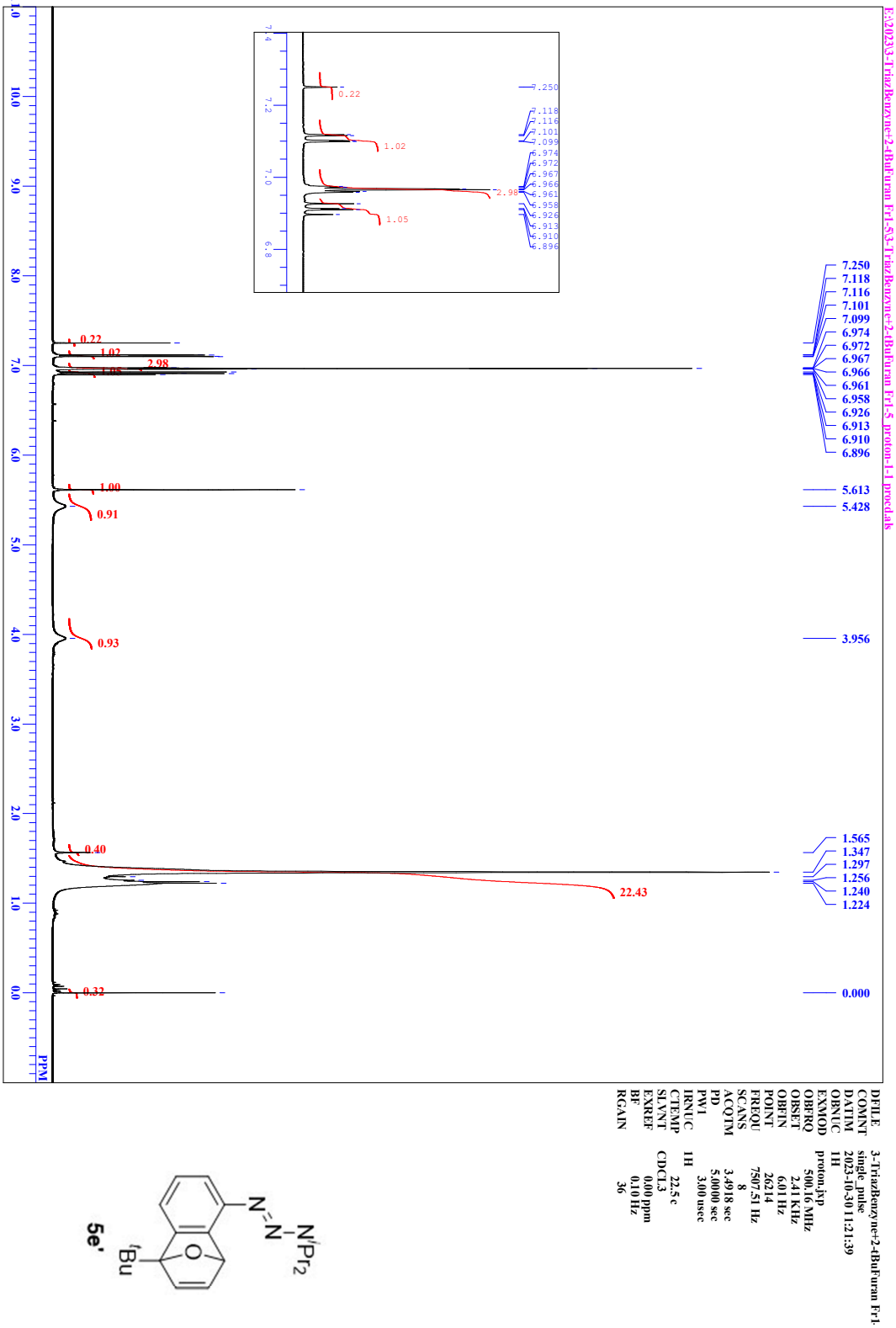
1-(1-*tert*-Butyl-1,4-dihydro-1,4-epoxynaphthalen-5-yl)-3,3-diisopropyltriaz-1-ene (5e)

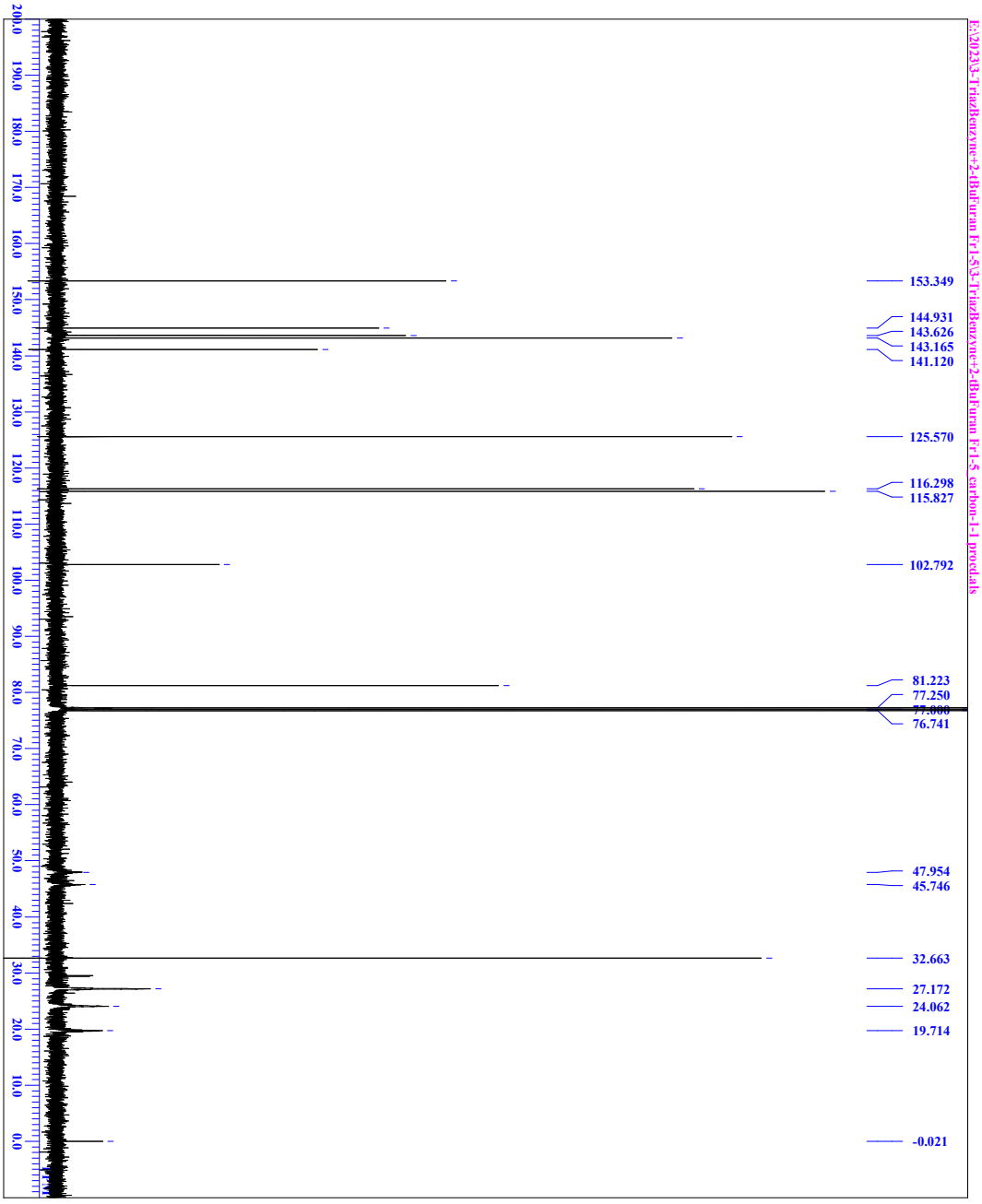



single pulse decoupled gated NOE
F:\2023-TriazBenzyne+2-tBuFuran Fr7-13\3-TriazBenzyne+2-tBuFuran Fr7-13_carbon-1-1.procl.als
48.378
45.940
23.757
19.390
150.155
144.405
144.299
142.840
141.919
125.015
118.661
118.239
99.310
80.880
77.280
77.031
76.772
48.378
45.940
32.492
26.627
23.757
19.390
PPM
DFILE 3-TriazBenzyne+2-tBuFuran Fr7.
COMNT single pulse decoupled gated NOE
DATIM 2023-10-30 13:37:25
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31645.57 Hz
SCANS 2048
ACQTM 0.8284 sec
PD 2.0000 sec
PW1 3.46 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 36

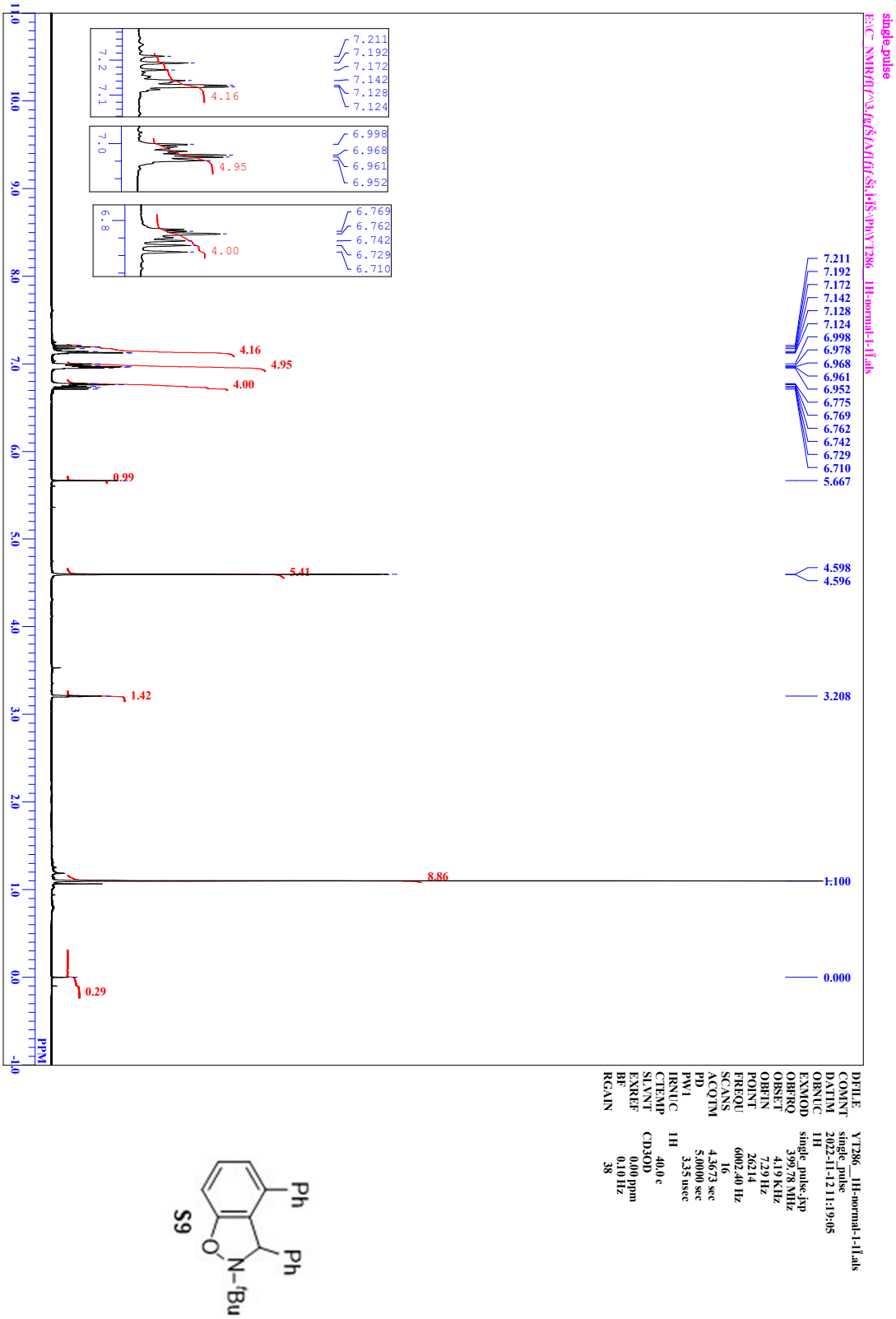
5e

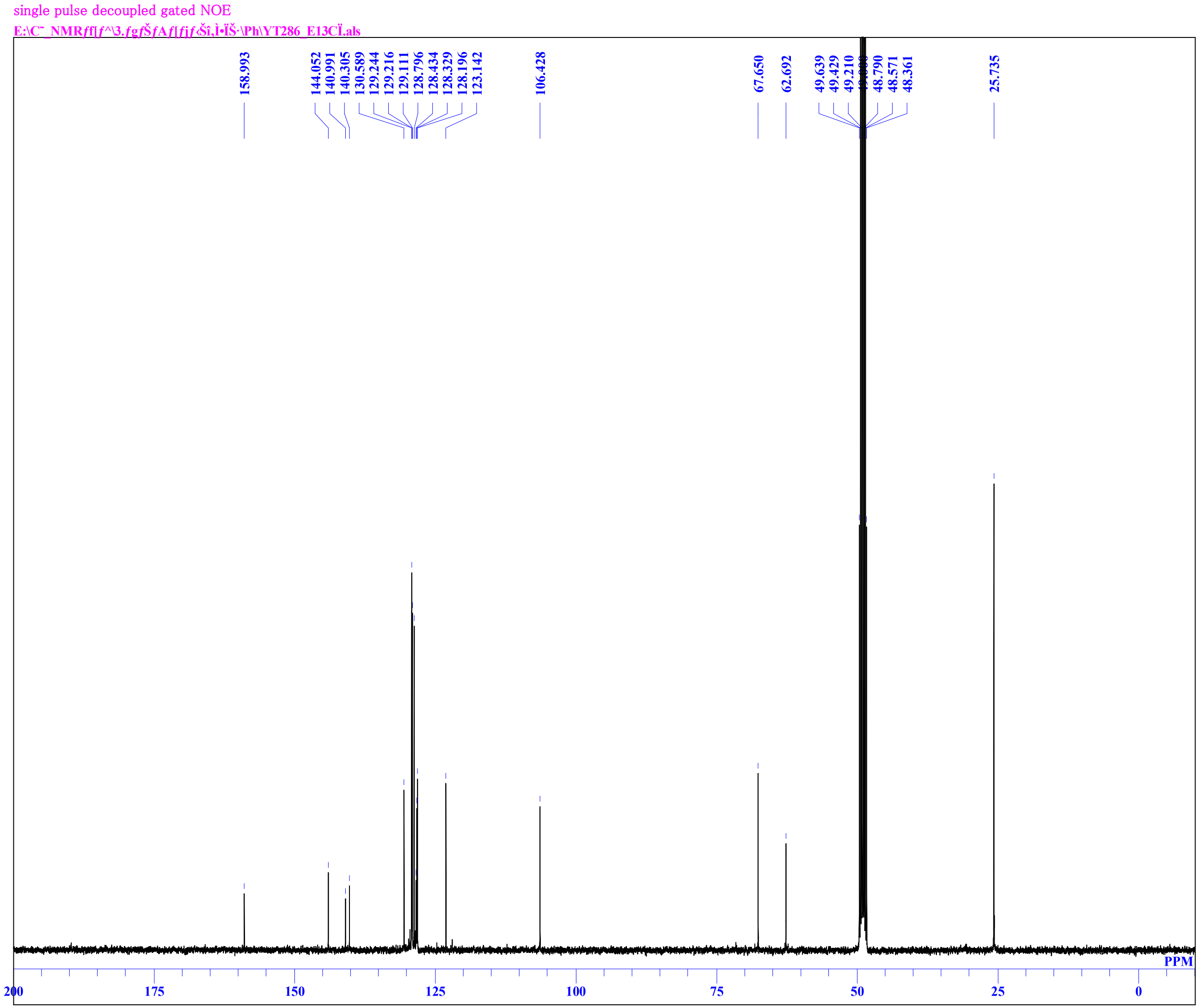
1-(4-*tert*-Butyl-1,4-dihydro-1,4-epoxynaphthalen-5-yl)-3,3-diisopropyltriaz-1-ene (5e')



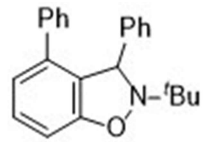

single pulse decoupled gated NOE
F:\2023-TriazBenzyne+2-tButFuran Fr1-5\3-TriazBenzyne+2-tBuFuran Fr1-5_carbon-1-1.procpl.als
153.349
144.931
143.626
143.165
141.120
125.570
116.298
115.827
102.792
81.223
77.250
77.000
76.741
47.954
45.746
32.663
27.172
24.062
19.714
-0.021
DFILE 3-TriazBenzyne+2-tButFuran Fr1-
COMNT single pulse decoupled gated NOE
DATIM 2023-10-30 11:59:36
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 3164.57 Hz
SCANS 600
ACQTM 0.8284 sec
PD 2.0000 sec
PW1 3.46 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 36
5e'
tBu
O
N
N
NiPr2

2-(*tert*-Butyl)-3,4-diphenyl-2,3-dihydrobenzo[*d*]isoxazole (S9)



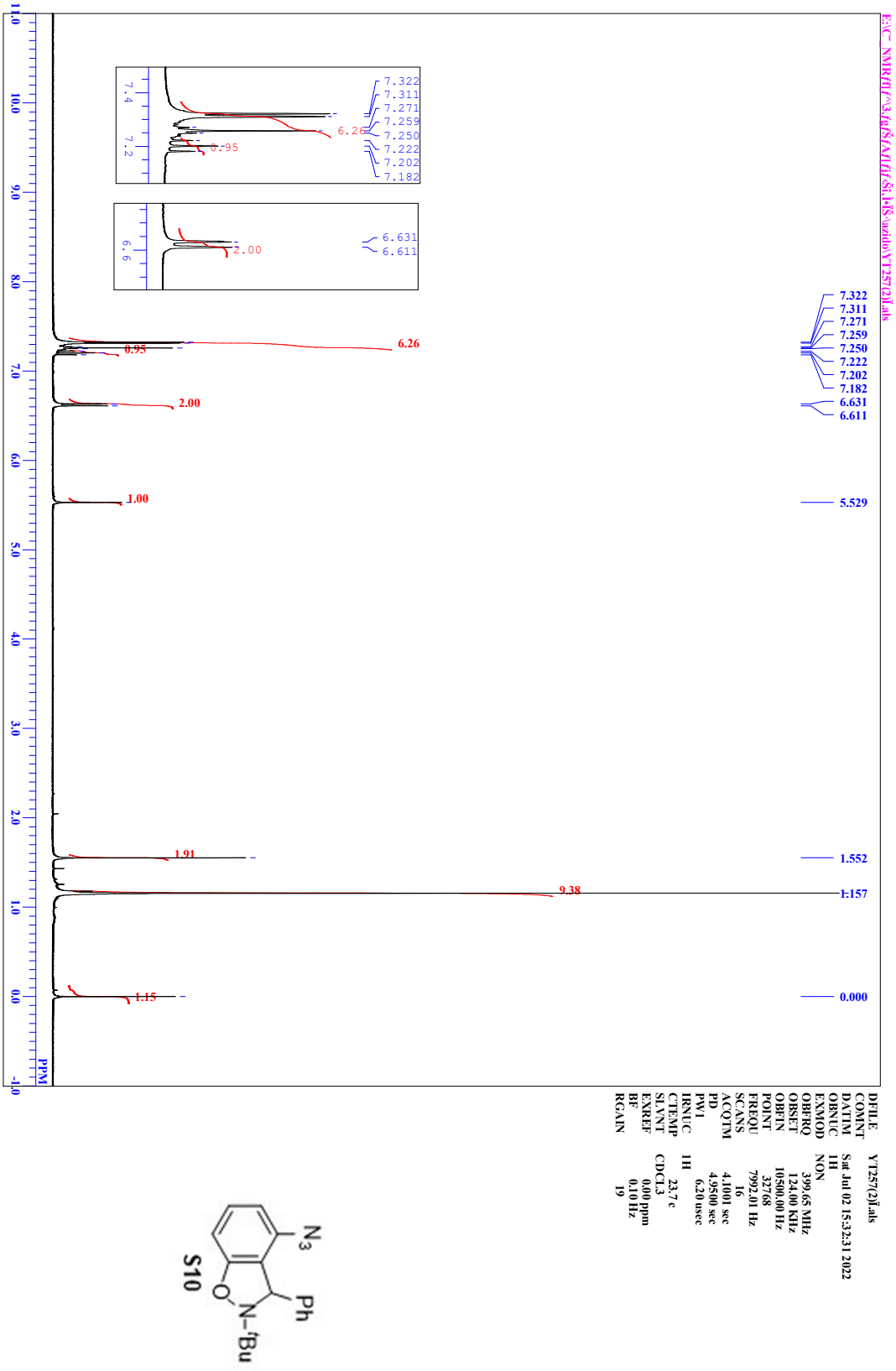


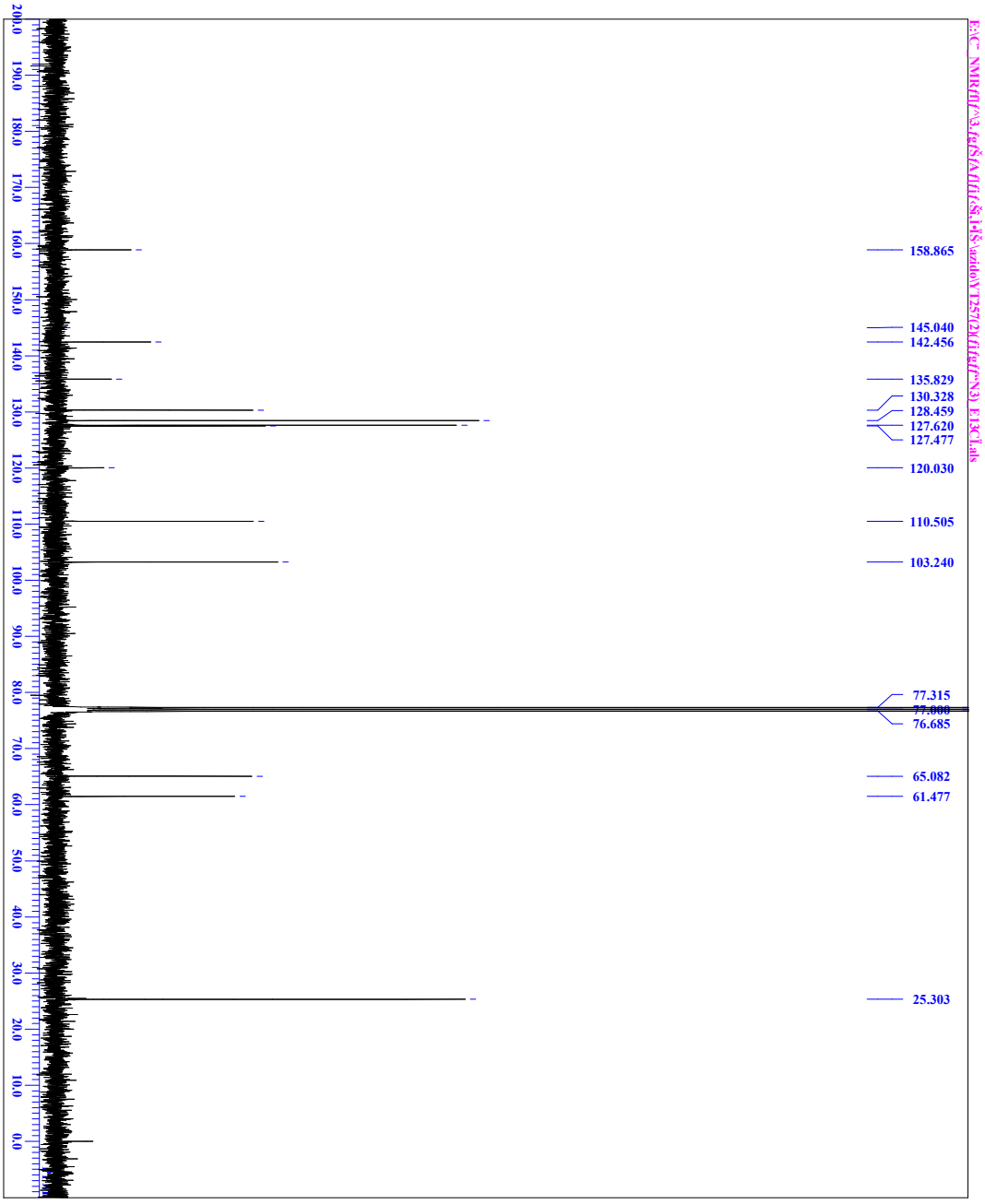
DFILE	YT286_E13CÏ.als
COMNT	single pulse decoupled gated NOE
DATIM	2022-11-12 11:24:18
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	3500
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	40.0 c
SLVNT	CD3OD
EXREF	49.00 ppm
BF	1.20 Hz
RGAIN	60



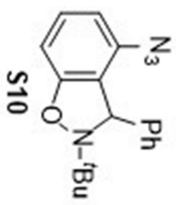
S9

4-Azido-2-(*tert*-butyl)-3-phenyl-2,3-dihydrobenzo[*d*]isoxazole (S10)



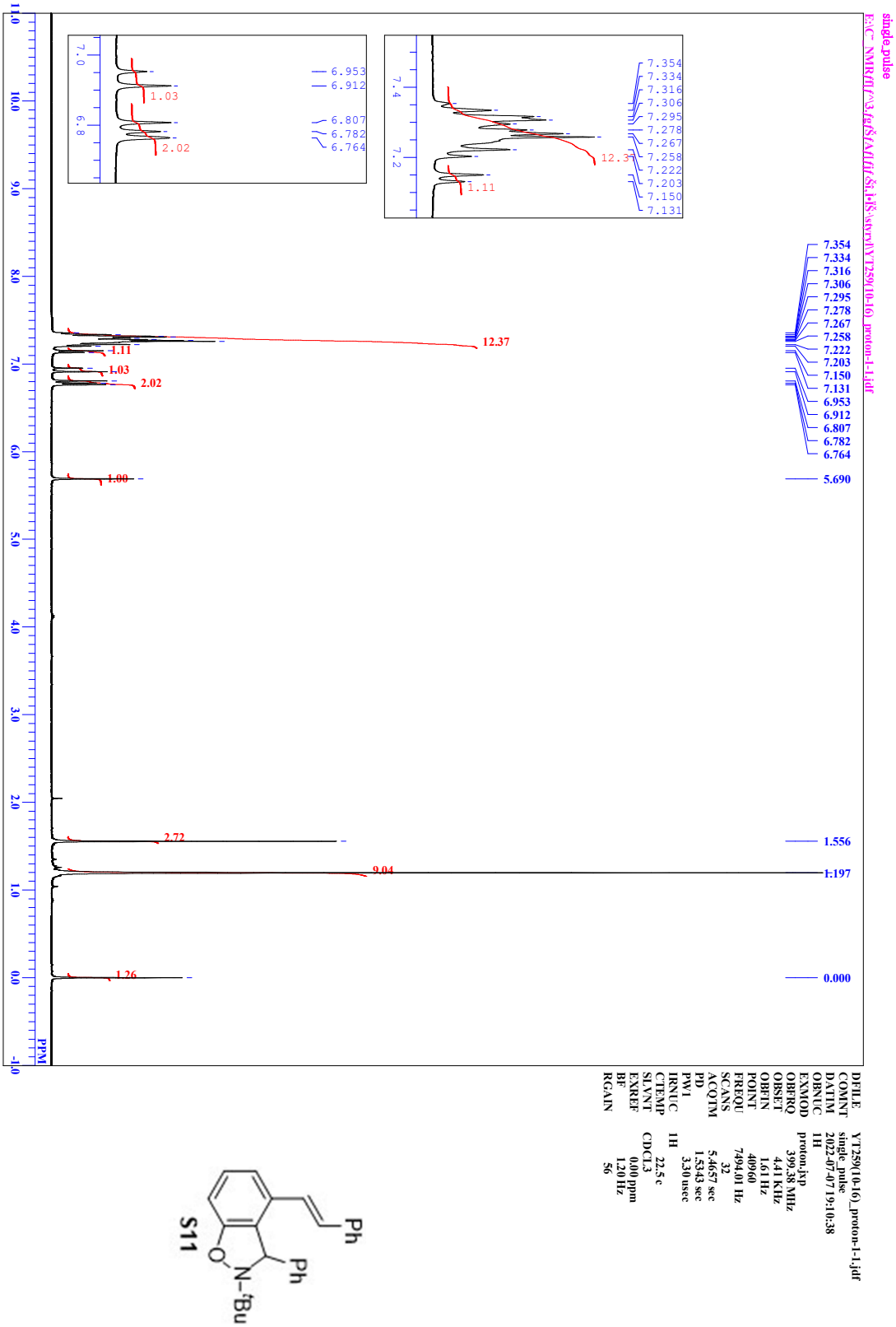


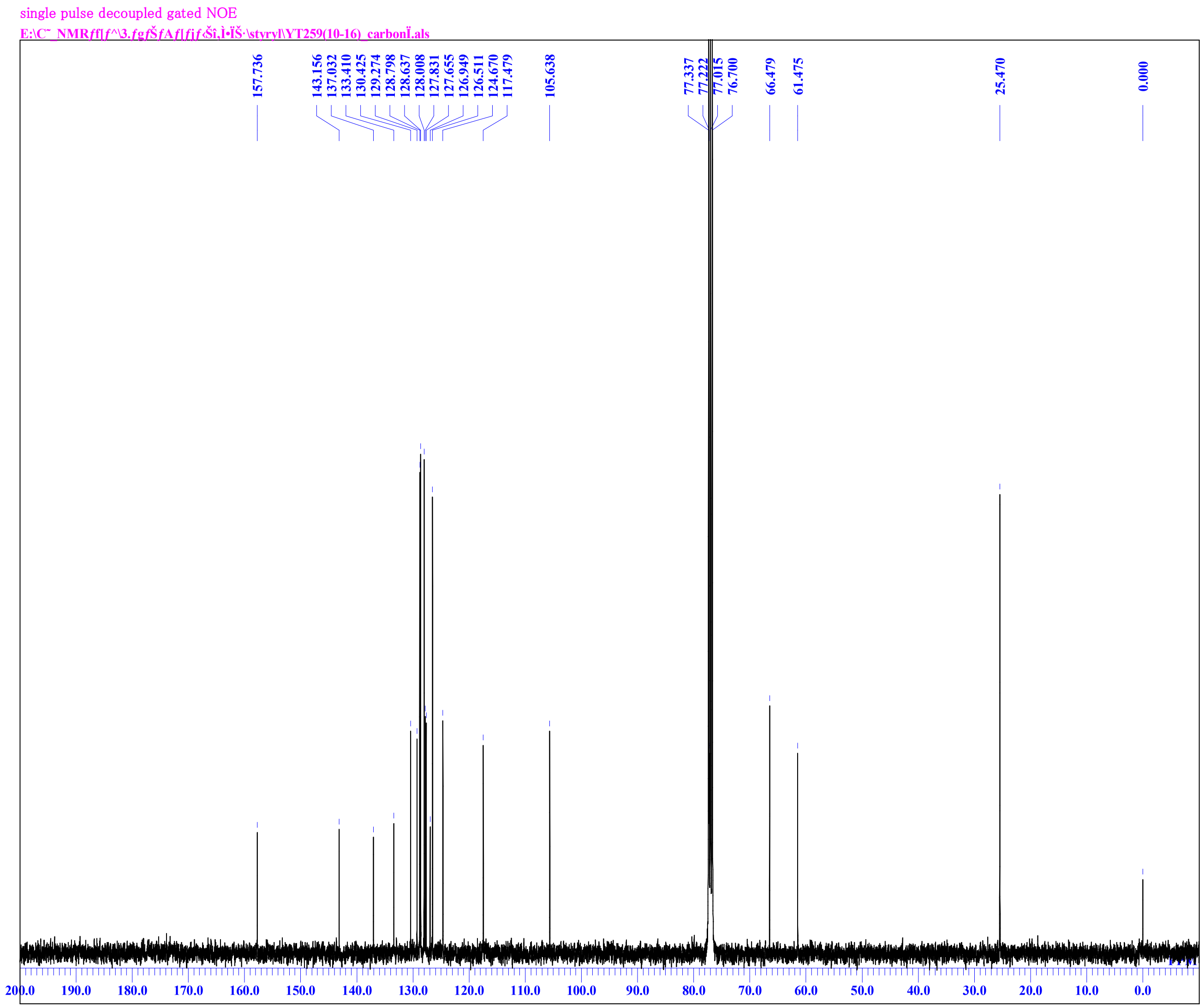
DFILE YT257(2)(fig/f^{cm}N3)_E13Cl.als
COMNT single pulse decoupled gated NOE
DATIM 2022-07-02 16:22:02
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1000
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 21.8 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 58



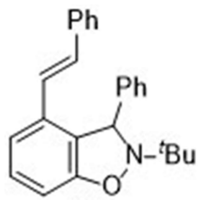
S10

2-(*tert*-Butyl)-3-phenyl-4-styryl-2,3-dihydrobenzo[*d*]isoxazole (S11)



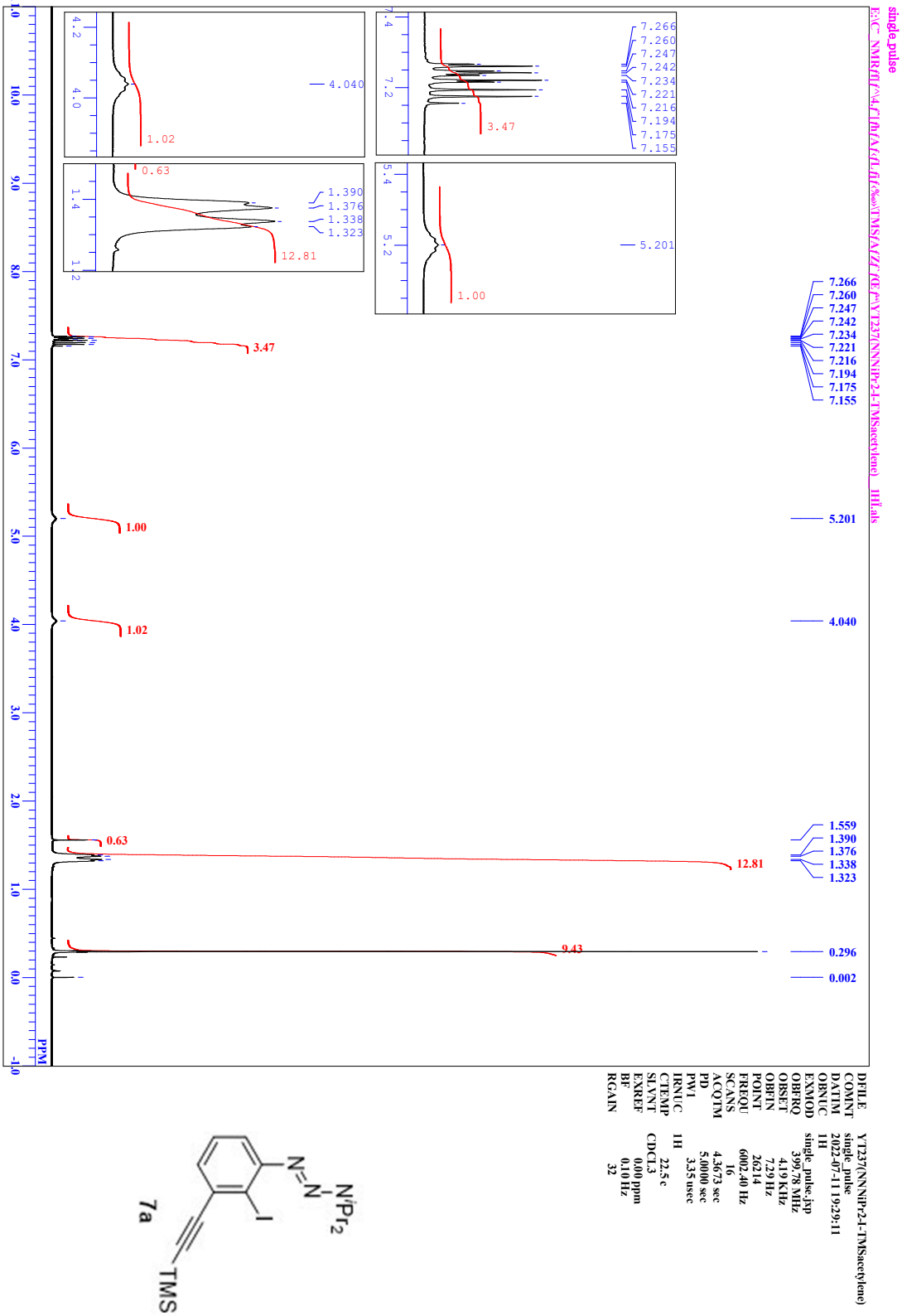


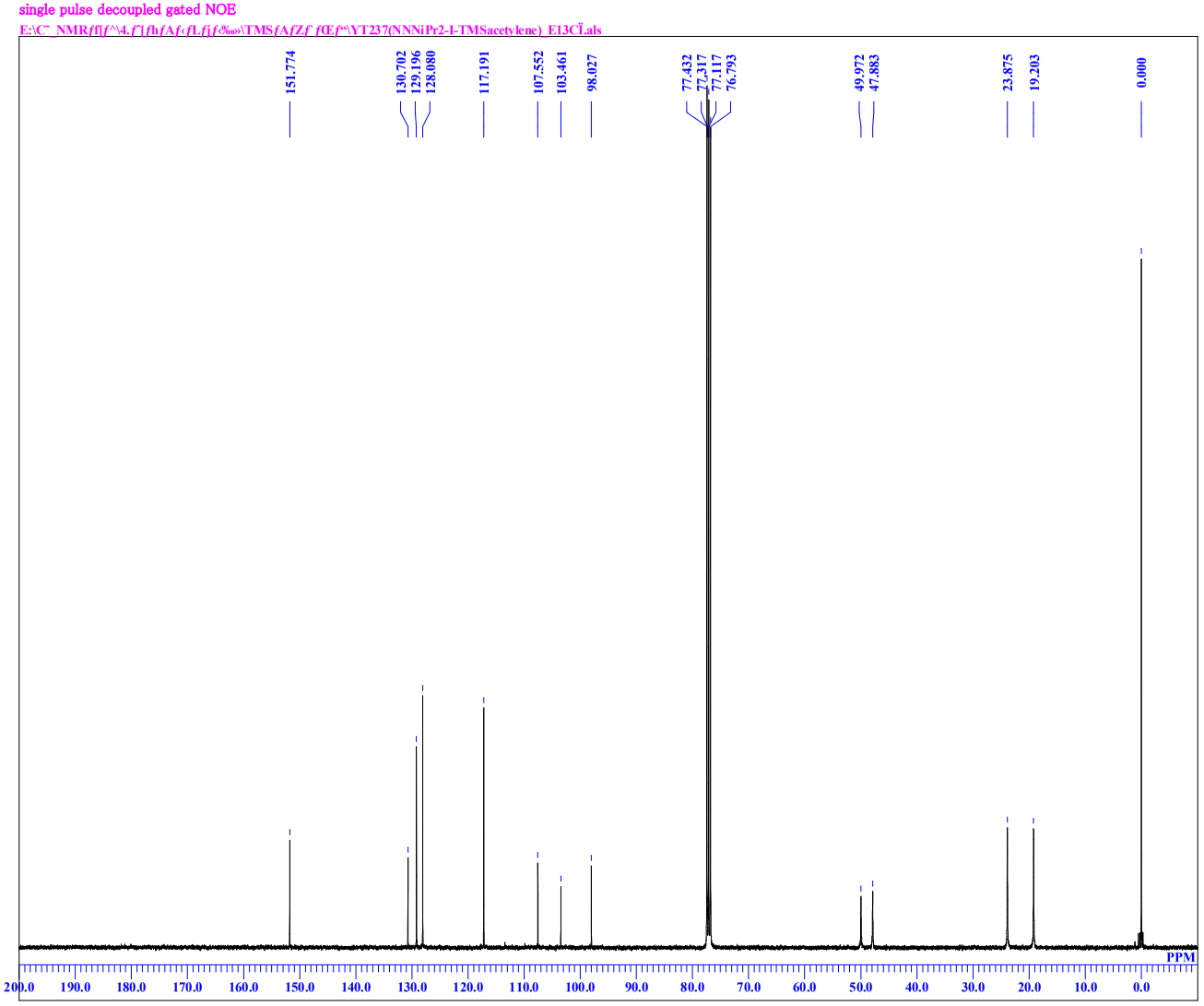
DFILE	YT259(10-16)_carbonÏ.als
COMNT	single pulse decoupled gated NOE
DATIM	2022-07-07 19:15:01
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.43 MHz
OBSET	4.82 KHz
OBFIN	0.13 Hz
POINT	32768
FREQU	25252.53 Hz
SCANS	5000
ACQTM	1.2976 sec
PD	1.7024 sec
PW1	3.75 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	56



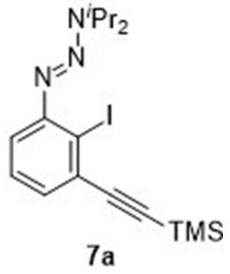
S11

1-{2-Iodo-3-[(trimethylsilyl)ethynyl]phenyl}-3,3-diisopropyltriaz-1-ene (7a)



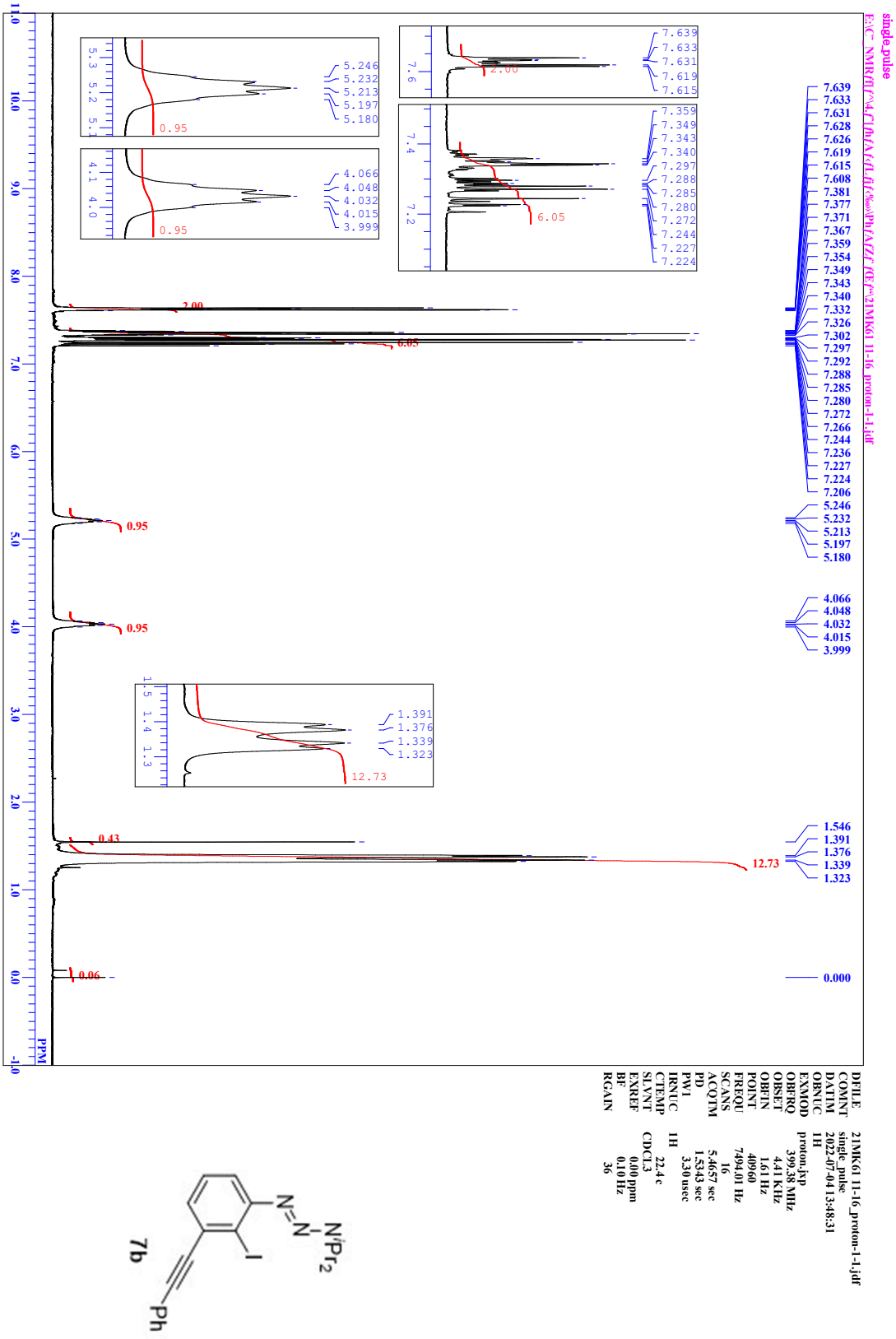


DFILE	YT237(NNNiPr2-I-TMSacetylene)
COMNT	single pulse decoupled gated NOE
DATIM	2022-07-11 19:32:17
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	6000
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	60



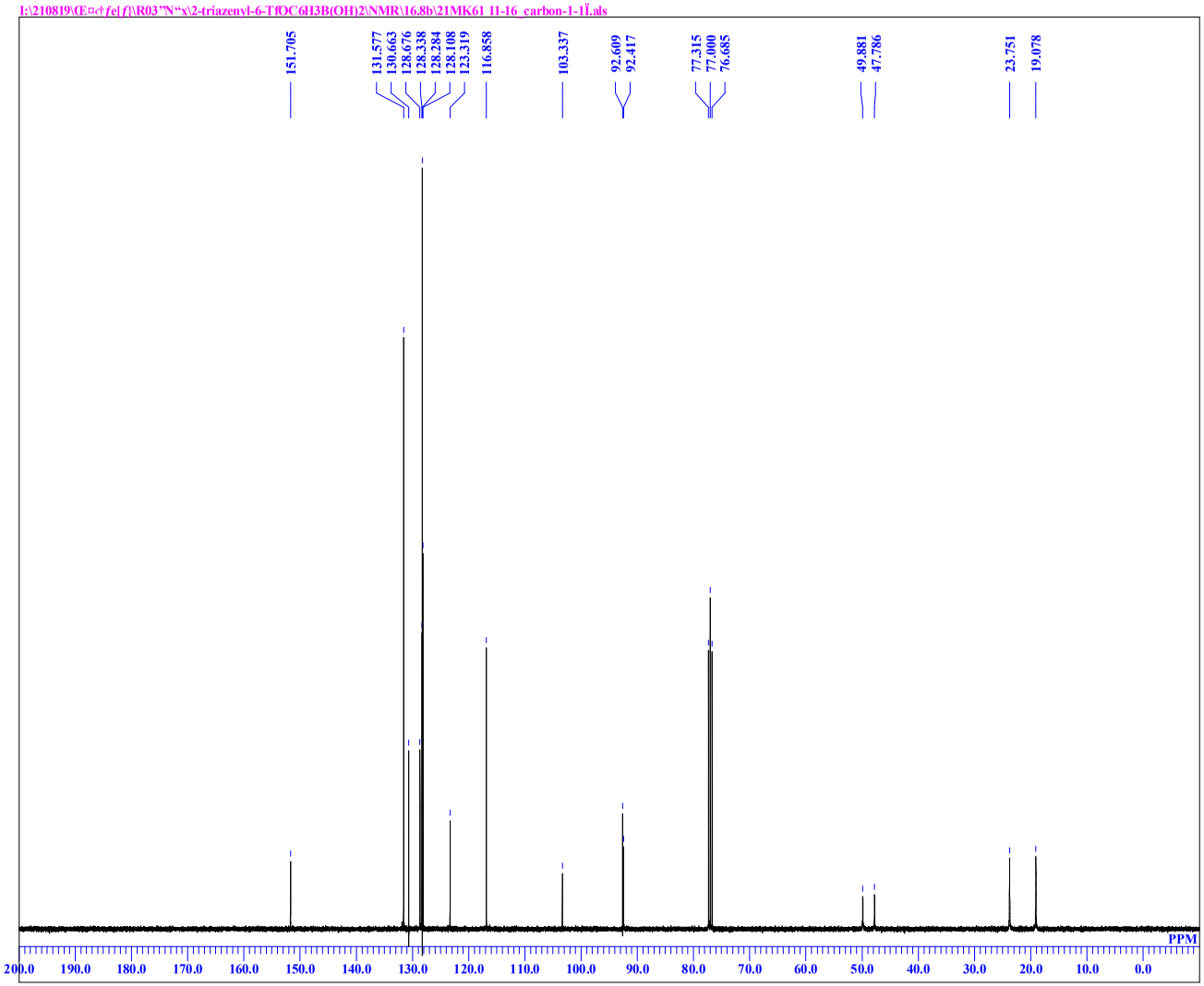
7a

1-[2-Iodo-3-(phenylethynyl)phenyl]-3,3-diisopropyltriaz-1-ene (7b)

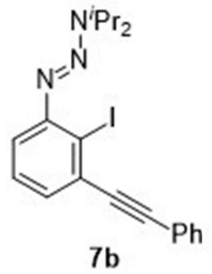


single pulse decoupled gated NOE

I:\210819\CE¤ć†e[ƒ\\R03"N"x\2-triazenyl-6-TfOC6H3B(OH)2\NMR\16.8b\21MK61 11-16_carbon-1-1Ľ.als

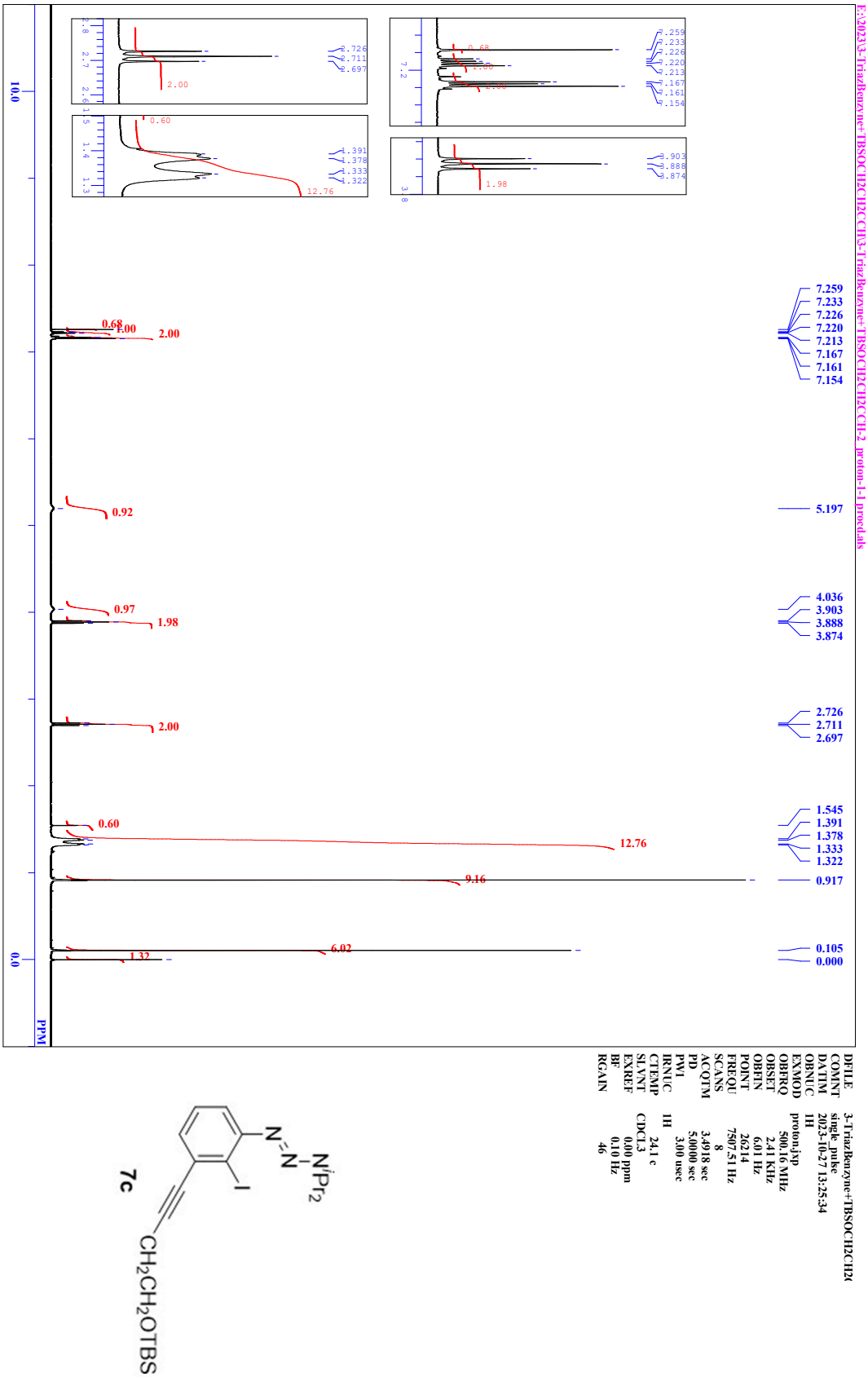


DFILE	21MK61 11-16_carbon-1-1Ľ.als
COMNT	single pulse decoupled gated NOE
DATIM	2022-07-04 13:53:46
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.43 MHz
OBSET	4.82 KHz
OBFIN	0.13 Hz
POINT	32768
FREQU	25252.53 Hz
SCANS	1000
ACQTM	1.2976 sec
PD	1.7024 sec
PW1	3.75 usec
IRNUC	1H
CTEMP	22.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	56



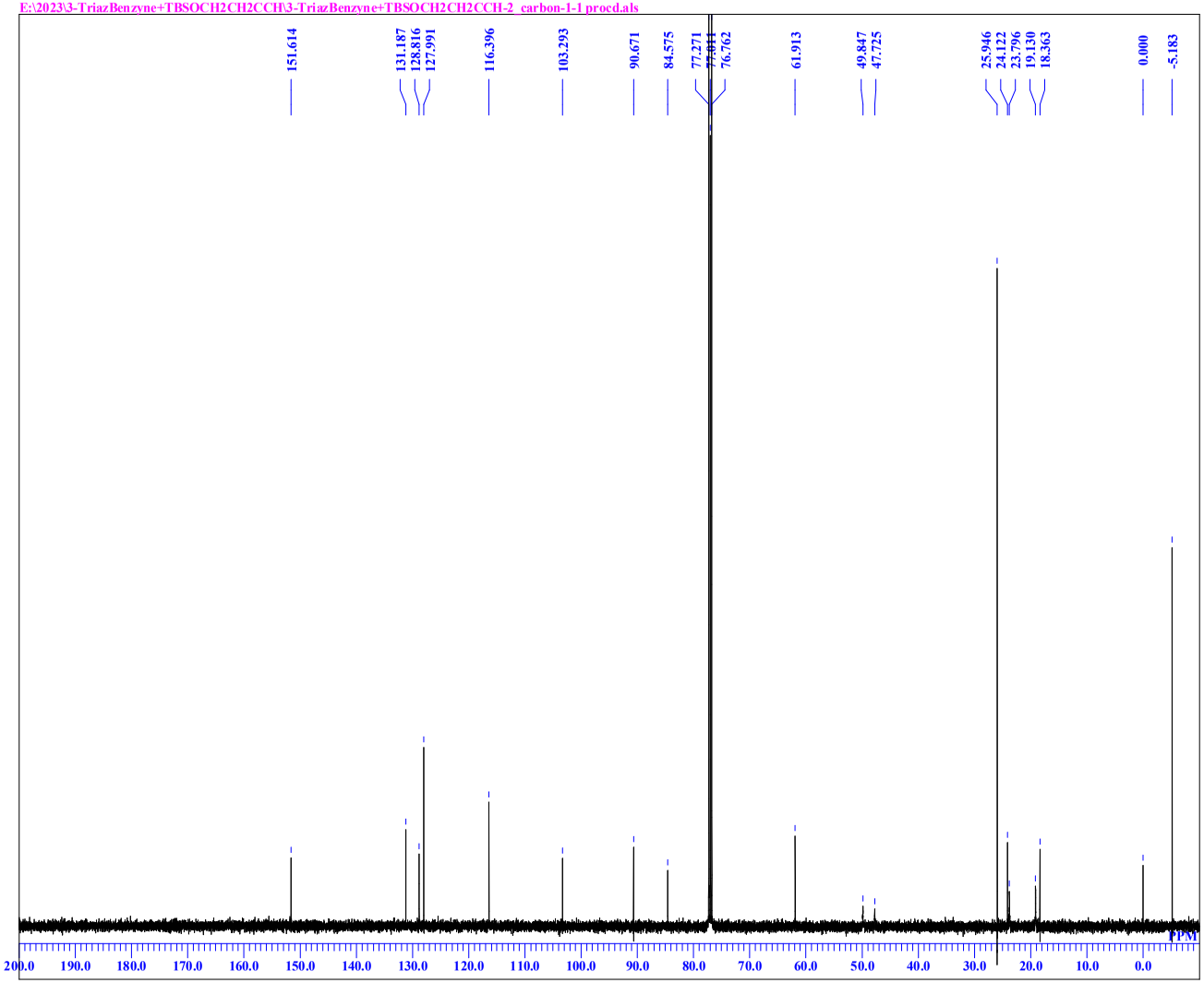
7b

1-{3-[4-(*tert*-Butyldimethylsilyloxy)-but-1-yn-1-yl]-2-iodophenyl}-3,3-diisopropyltriaz-1-ene (7c)

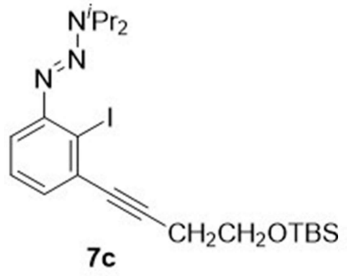


single pulse decoupled gated NOE

E:\2023\3-TriazBenzyne+TBSOCH2CH2CCH\3-TriazBenzyne+TBSOCH2CH2CCH-2_carbon-1-1 procd.als

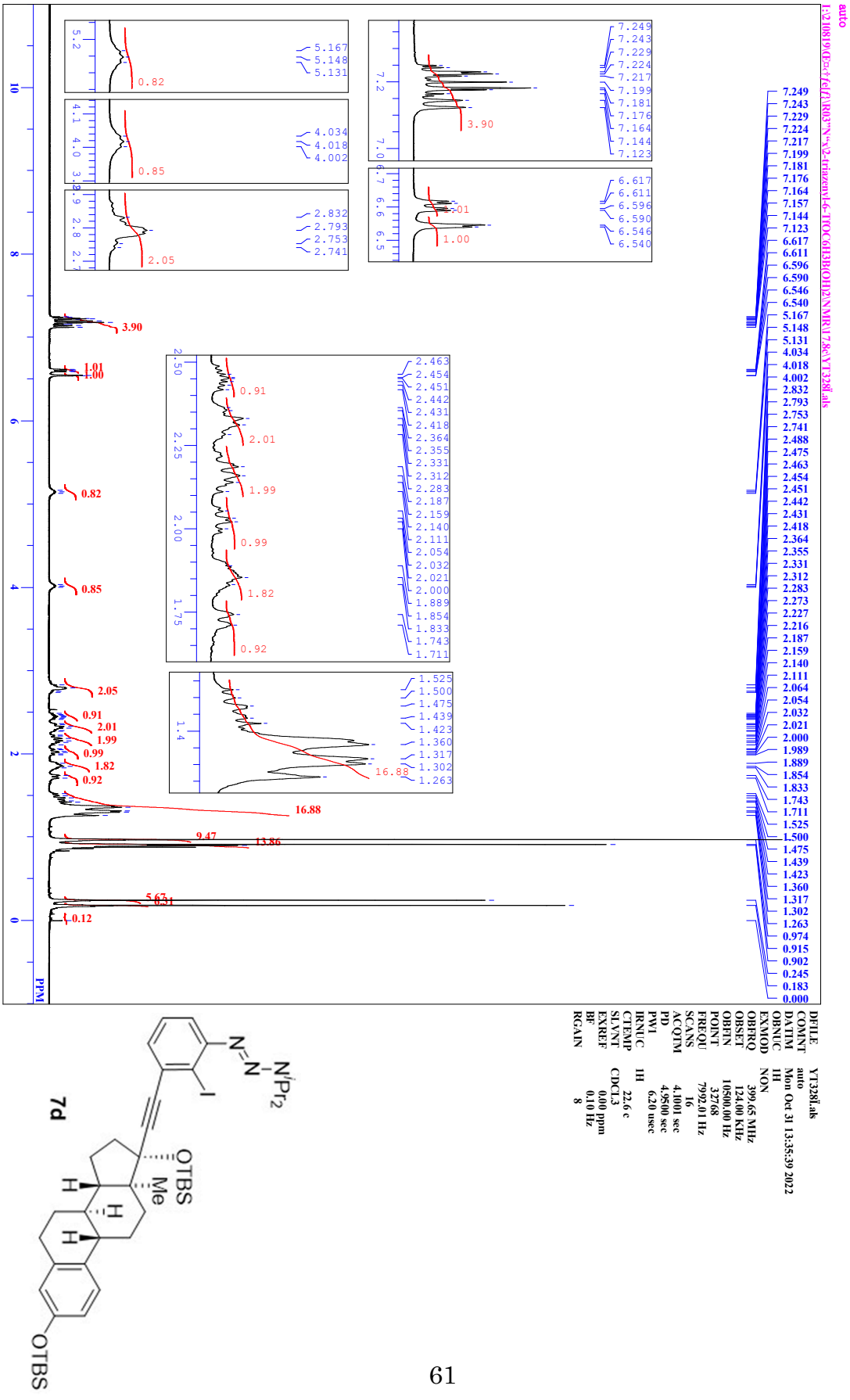


DFILE	3-TriazBenzyne+TBSOCH2CH2(
COMNT	single pulse decoupled gated NOE
DATIM	2023-10-27 13:27:20
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31645.57 Hz
SCANS	1024
ACQTM	0.8284 sec
PD	2.0000 sec
PW1	3.46 usec
IRNUC	1H
CTEMP	24.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	36



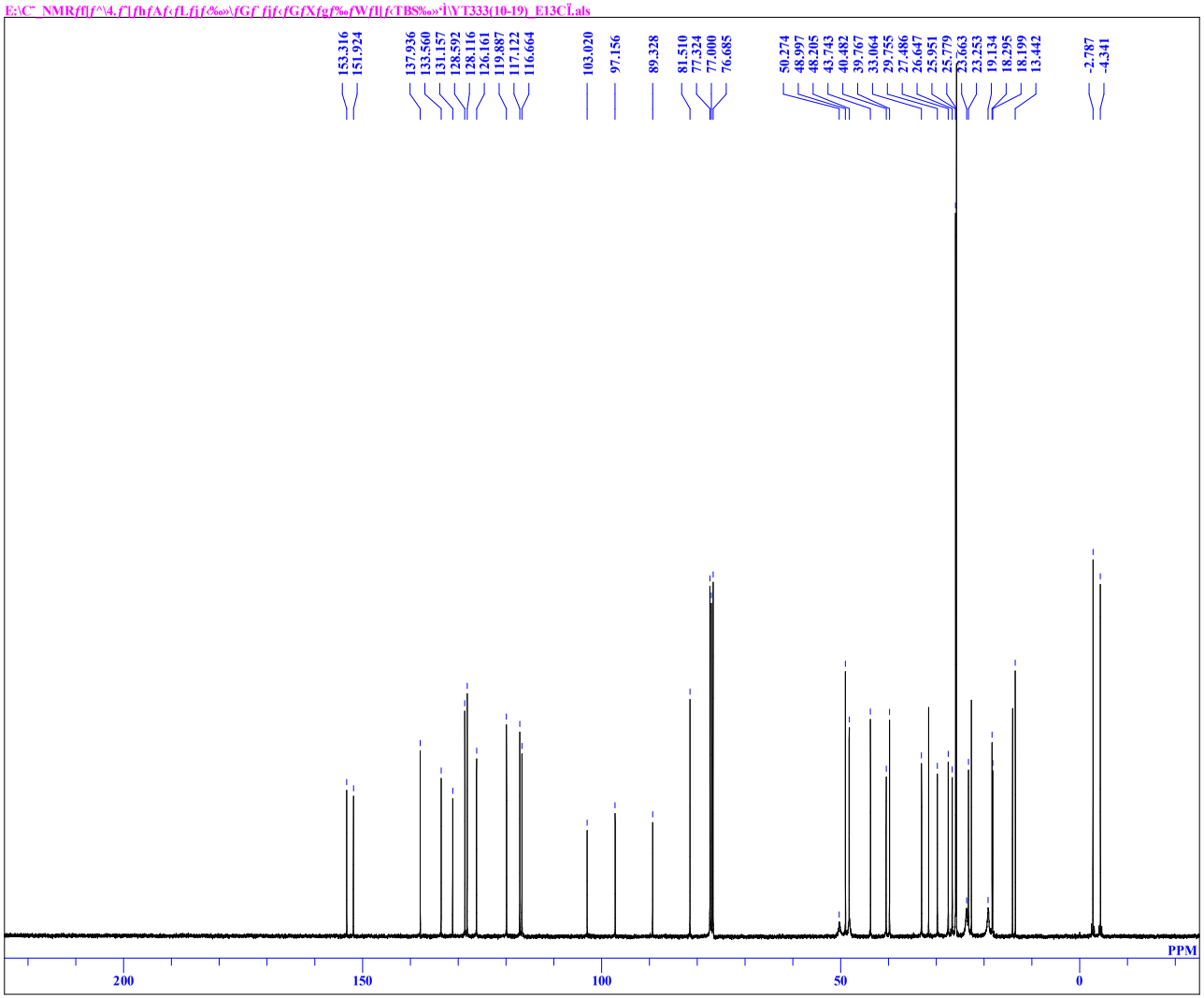
7c

3,17-*O*-Bis(*tert*-butyldimethylsilyl)-17α-[{2-iodo-3-(3,3-diisopropyltriaz-1-en-1-yl)phenyl}ethynyl]estradiol (7d)

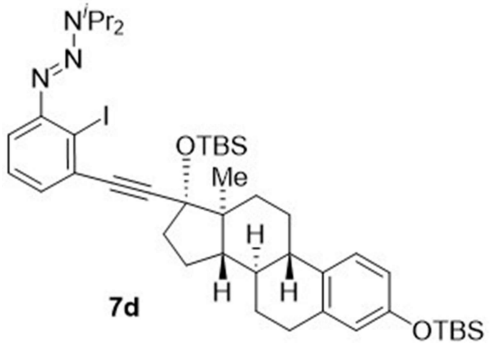


single pulse decoupled gated NOE

E:\C~_NMR\fl\f^\4.f~\fh\fA\f<\fL\fj\f‰»\fG\f~\fj\f<\fG\fX\fg\f‰\fW\fl\\f<TBS‰»'ì\YT333(10-19)_E13CÏ.als

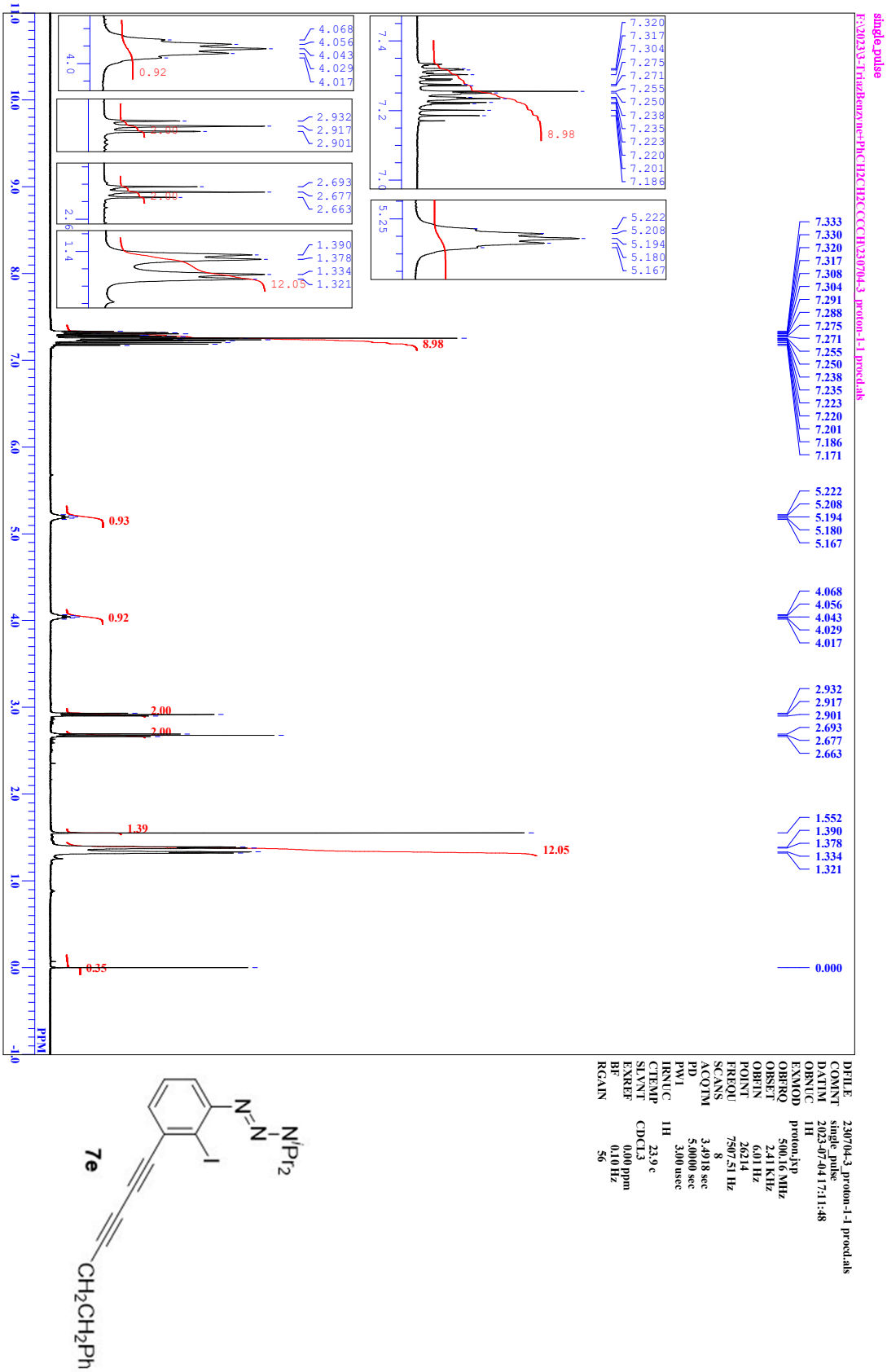


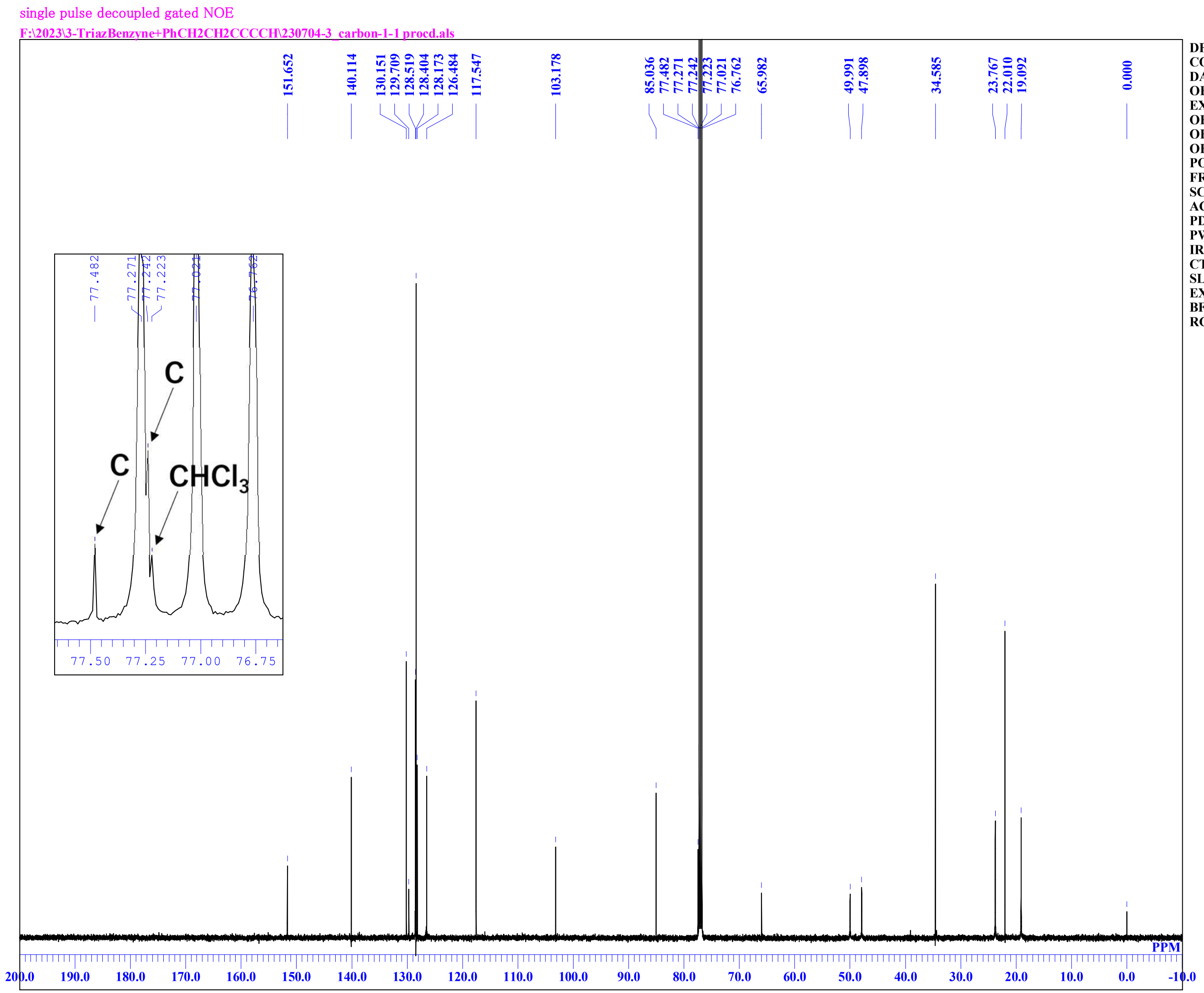
DFILE YT333(10-19)_E13CÏ.als
COMNT single pulse decoupled gated NOE
DATIM 2022-11-04 11:30:12
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 2400
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 50.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60



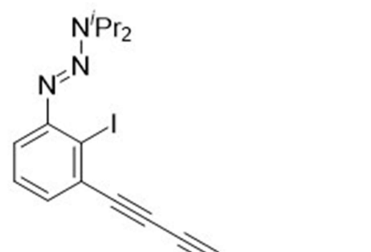
7d

1-[2-Iodo-3-(6-phenylhexa-1,3-diyn-1-y)phenyl]-3,3-diisopropyltriaz-1-ene (7e)



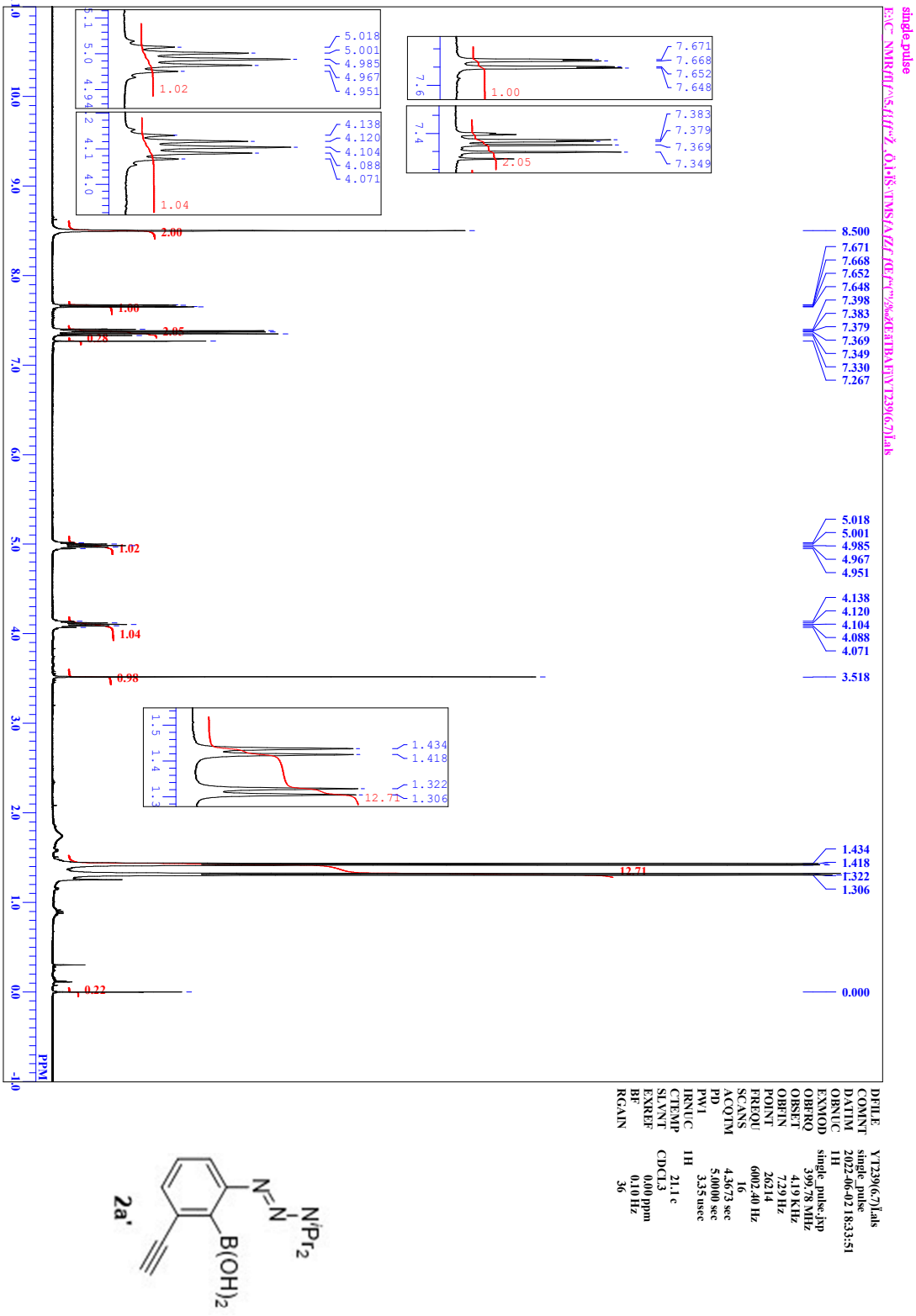


DFILE	230704-3_carbon-1-1 procd.als
COMNT	single pulse decoupled gated NOE
DATIM	2023-07-04 17:16:07
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31645.57 Hz
SCANS	12000
ACQTM	0.8284 sec
PD	2.0000 sec
PW1	3.46 usec
IRNUC	1H
CTEMP	23.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	36



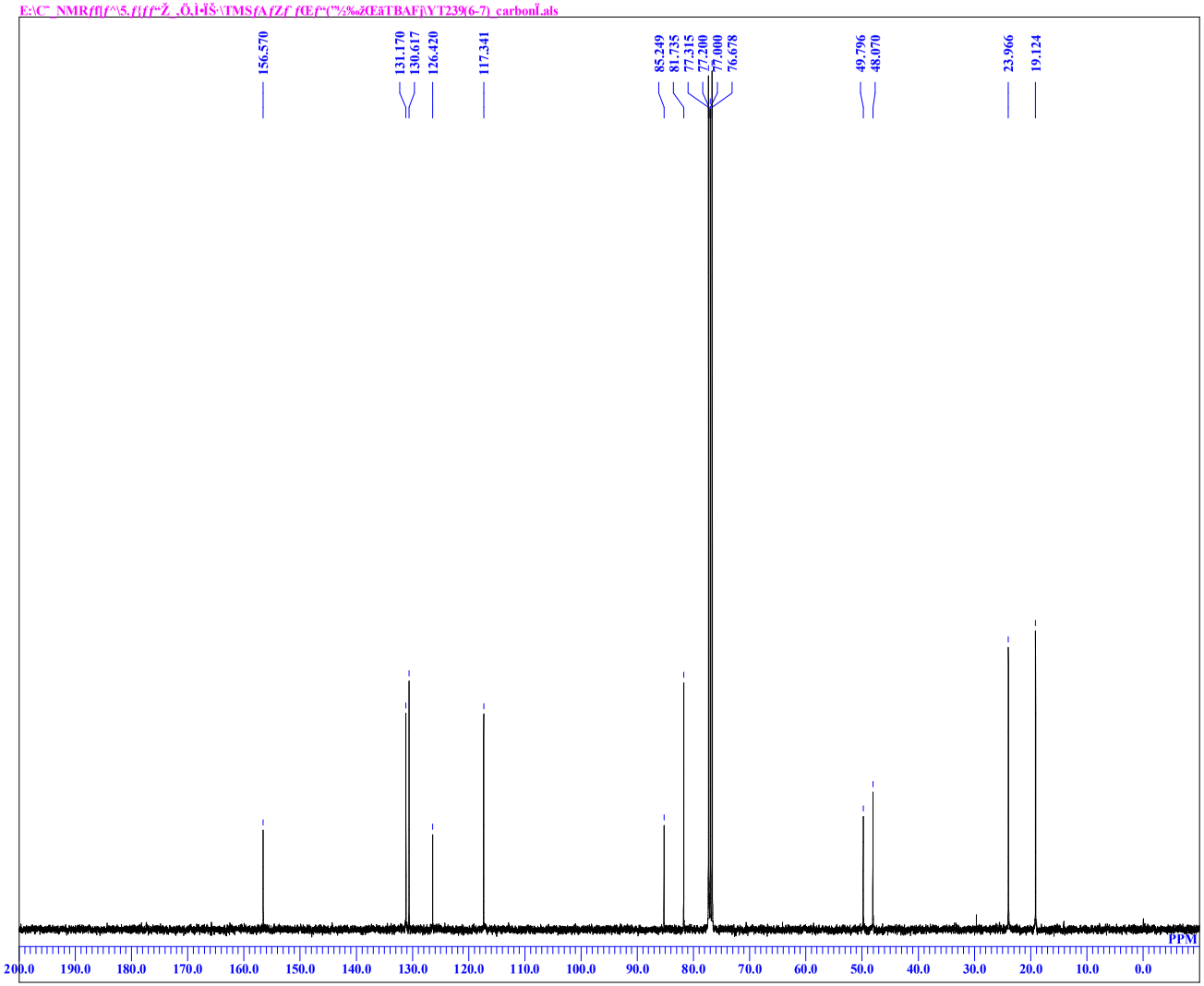
7e

[(3,3-Diisopropyltriaz-1-en-1-yl)-6-ethynylphenyl]boronic acid (2a')

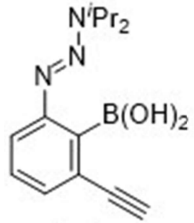


single pulse decoupled gated NOE

E:\C~_NMR\fl\f^\5.f\ff^Ž_,Ö‚Ì•ÏŠ'\TMS\fA\fZ\f-\fŒf^"("½‰žŒãTBAF\YT239(6-7)_carbonÏ.als

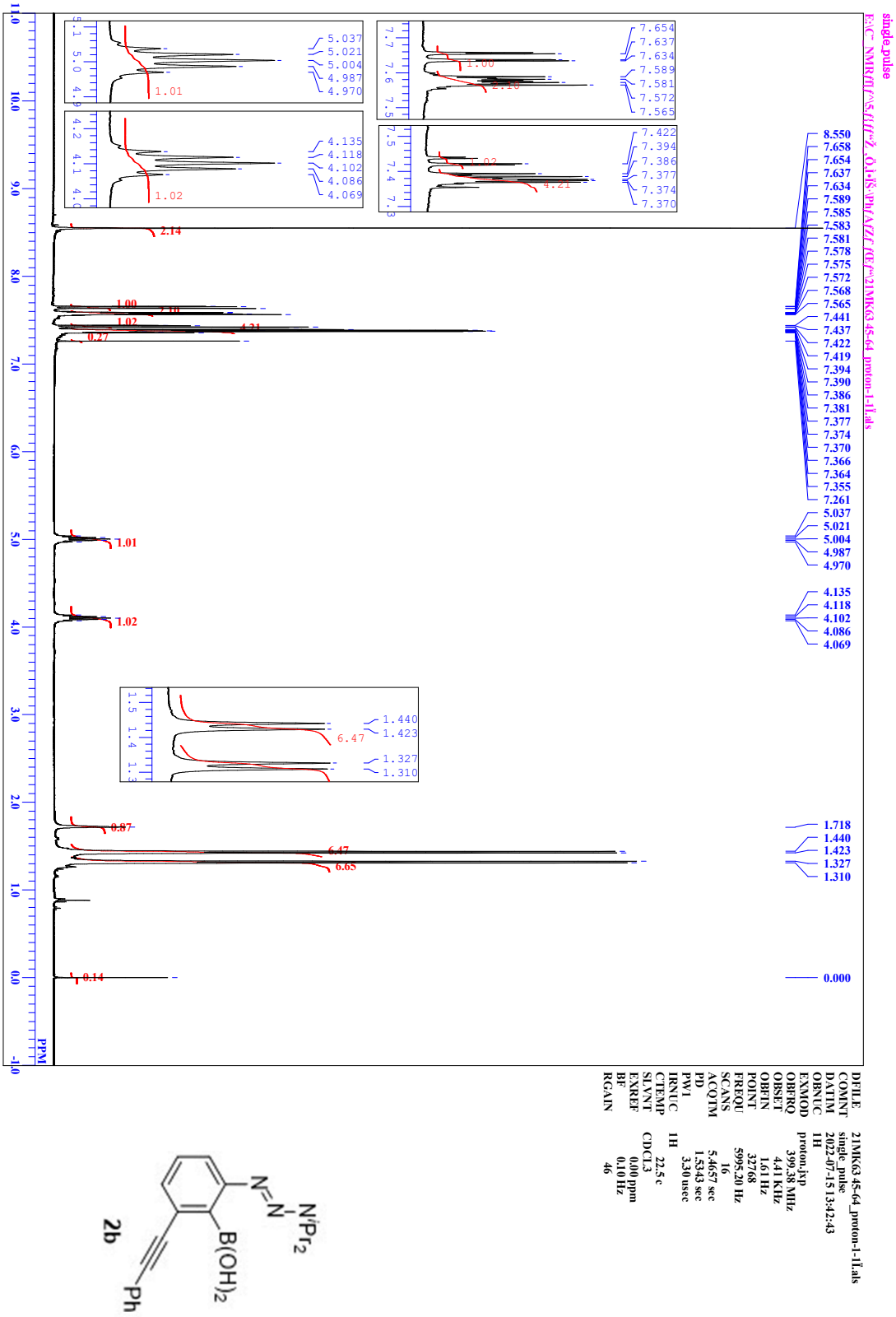


DFILE	YT239(6-7)_carbonÏ.als
COMNT	single pulse decoupled gated NOE
DATIM	2022-06-03 11:55:28
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.43 MHz
OBSET	4.82 KHz
OBFIN	0.13 Hz
POINT	32768
FREQU	25252.53 Hz
SCANS	1000
ACQTM	1.2976 sec
PD	1.7024 sec
PW1	3.75 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	56



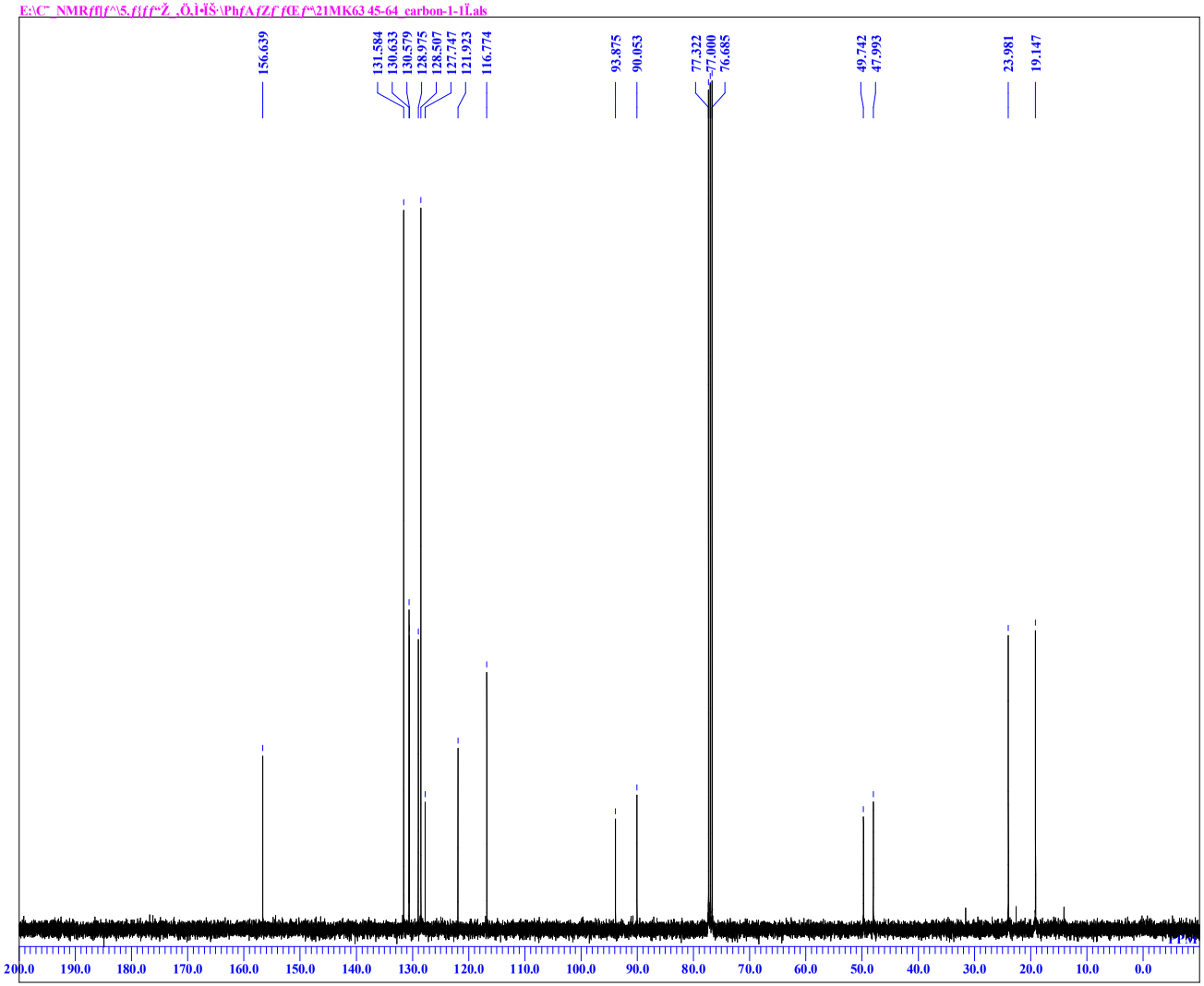
2a'

[2-(3,3-Diisopropyltriaz-1-en-1-yl)-6-(phenylethynyl)phenyl]boronic acid (2b)

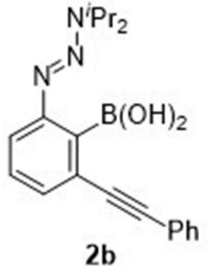


single pulse decoupled gated NOE

E:\C~_NMR\fl\f^\5.f\f\f^Ž_,Ö.ì•ÏŠ\Pbf\fZf.fŒf^%21MK63 45-64_carbon-1-1Ï.als

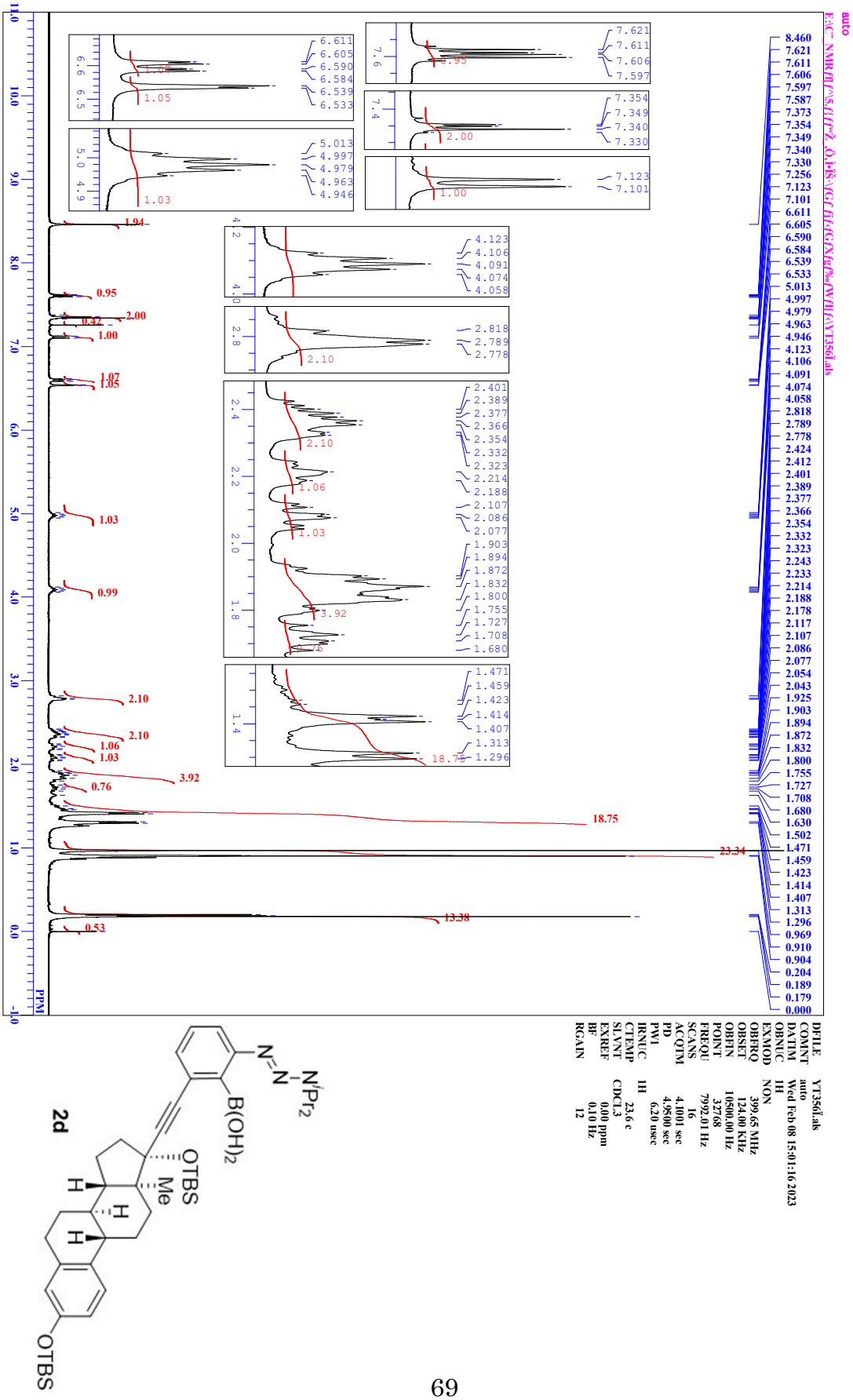


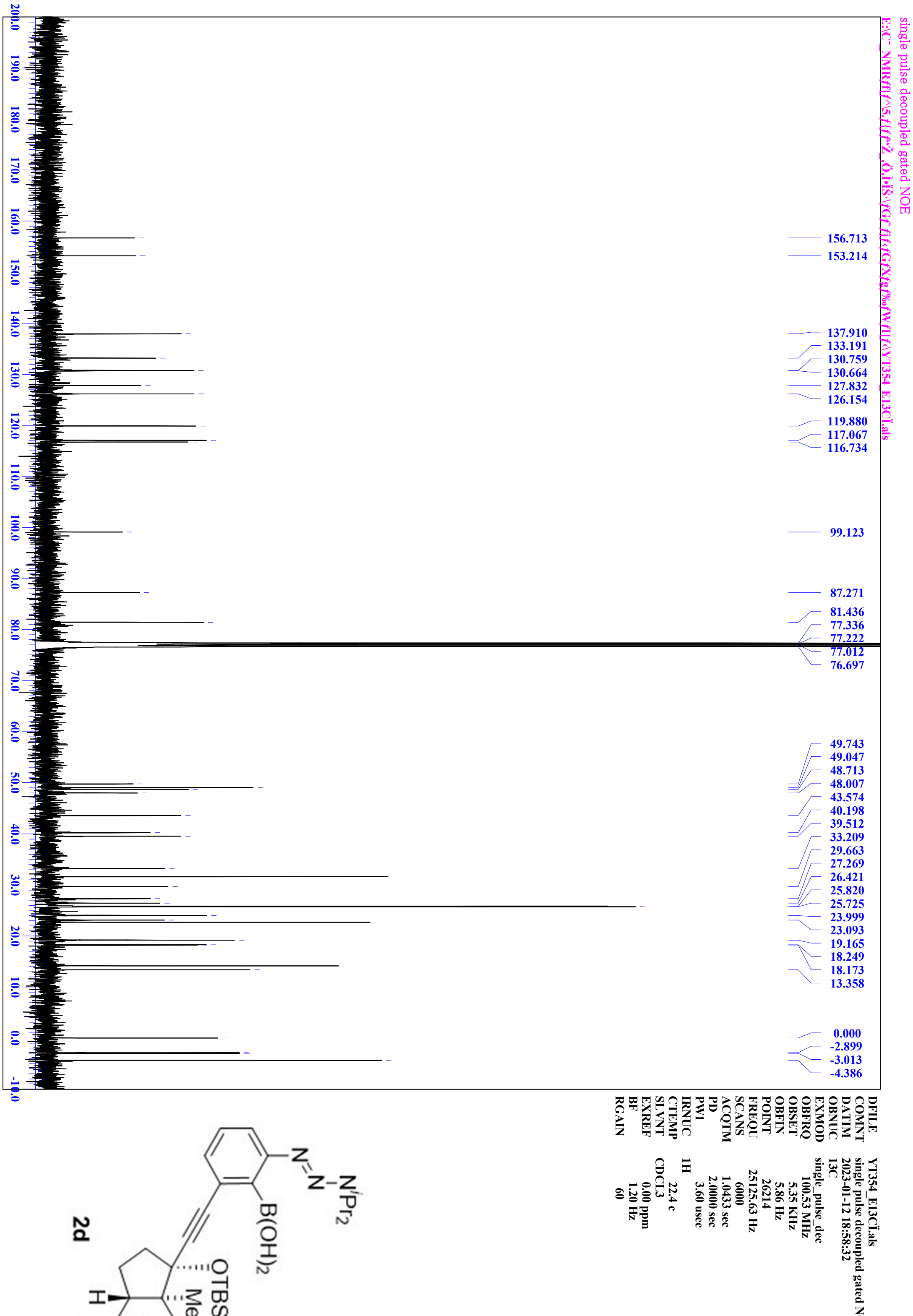
DFILE 21MK63 45-64_carbon-1-1Ï.als
COMNT single pulse decoupled gated NOE
DATIM 2022-07-15 13:45:14
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.43 MHz
OBSET 4.82 KHz
OBFIN 0.13 Hz
POINT 32768
FREQU 25252.53 Hz
SCANS 1000
ACQTM 1.2976 sec
PD 1.7024 sec
PW1 3.75 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 56

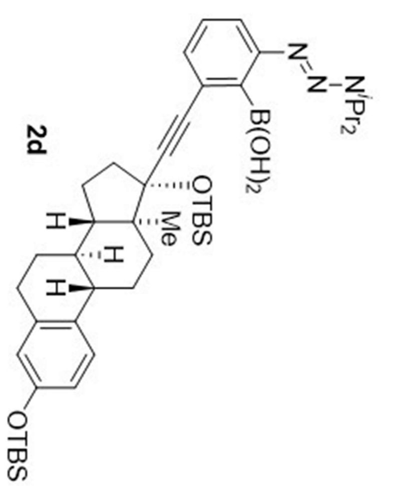


2b

3,17-*O*-Bis(*tert*-butyldimethylsilyl)-17α-[{2-borono-3-(3,3-diisopropyltriaz-1-en-1-yl)phenl}ethynyl]estradiol (2d)

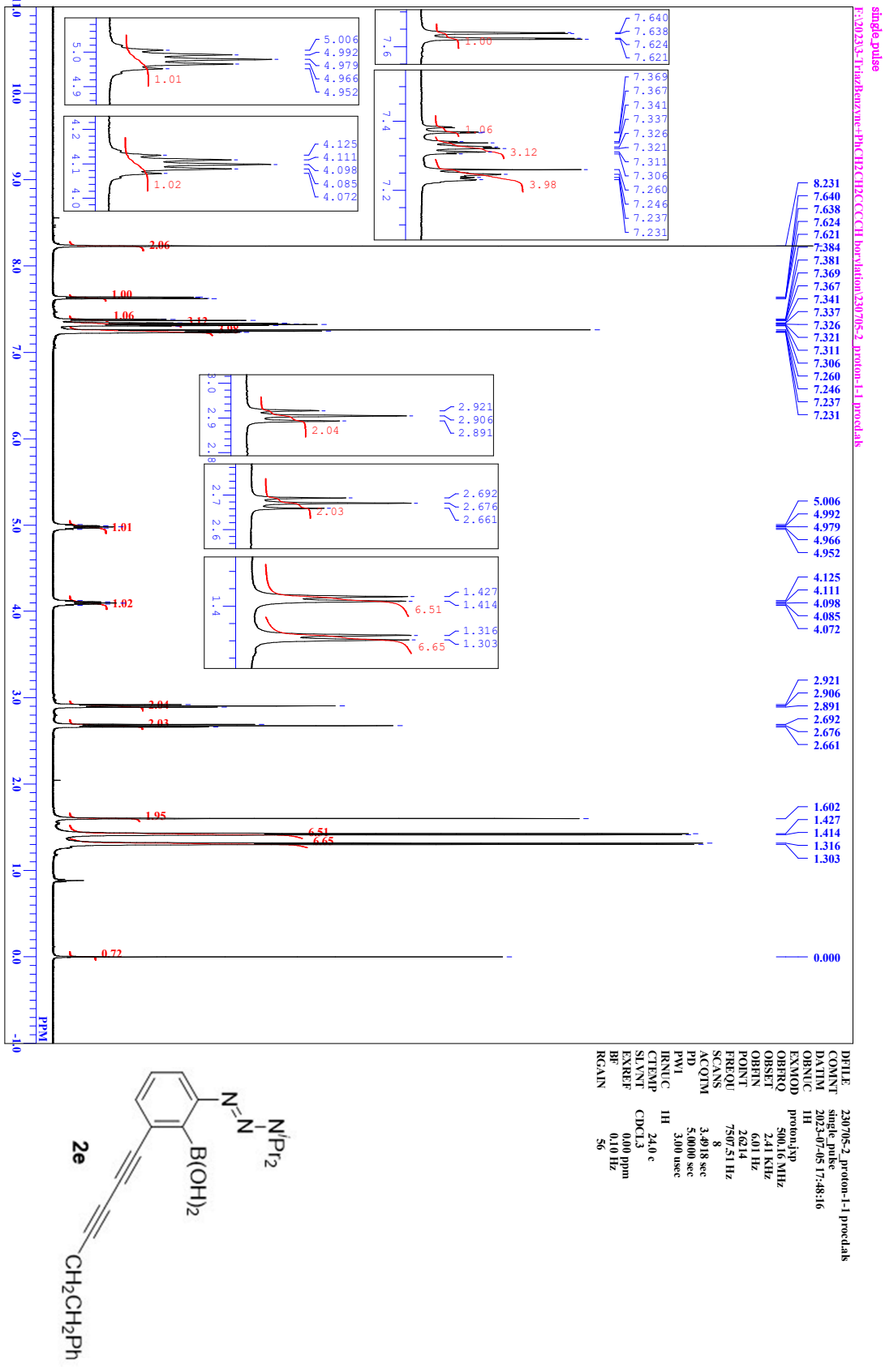



single pulse decoupled gated NOE
156.713
153.214
137.910
133.191
130.759
130.664
127.832
126.154
119.880
117.067
116.734
99.123
87.271
81.436
77.336
77.222
77.012
76.697
49.743
49.047
48.713
48.007
43.574
40.198
39.512
33.209
29.663
27.269
26.421
25.820
25.725
23.999
23.093
19.165
18.249
18.173
13.358
0.000
-2.899
-3.013
-4.386
DFILE YT354_E13C.als
COMNT single pulse decoupled gated NOE
DATIM 2023-01-12 18:58:32
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 6000
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 60
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0


N=N
N^{i}Pr$_2$
B(OH)$_2$
OTBS
Me
H
H
H
OTBS

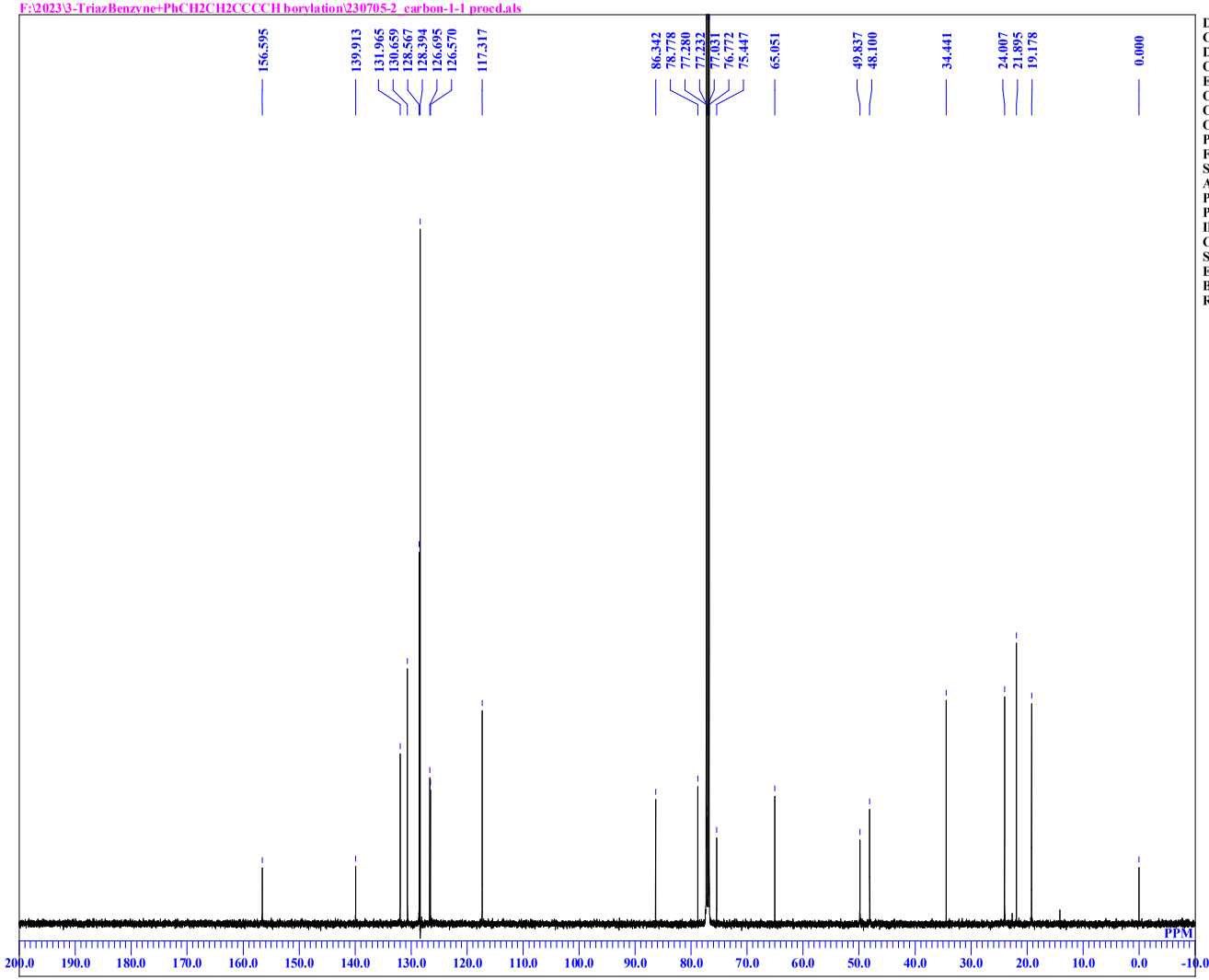
2d

[2-(3,3-Diisopropyltriaz-1-en-1-yl)-6-(6-phenylhexa-1,3-diyn-1-yl)phenyl]boronic acid (2e)

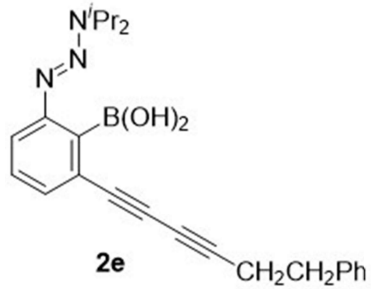


single pulse decoupled gated NOE

F:\2023\3-TriazBenzyne+PhCH2CH2CCCCH borylation\230705-2_carbon-1-1 procd.als

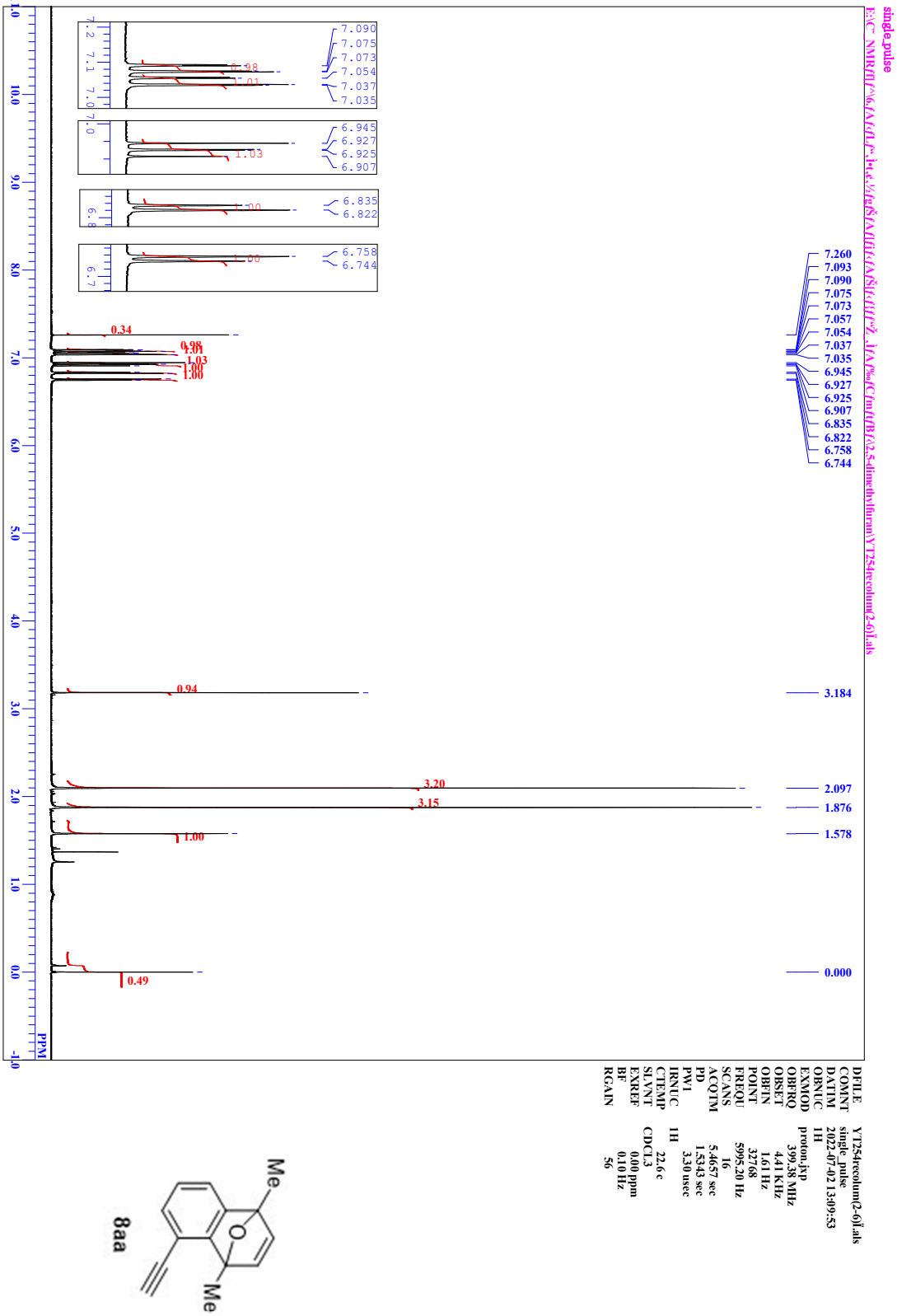


DFILE	230705-2_carbon-1-1 procd.als
COMNT	single pulse decoupled gated NOE
DATIM	2023-07-05 17:51:43
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31645.57 Hz
SCANS	12000
ACQTM	0.8284 sec
PD	2.0000 sec
PW1	3.46 usec
IRNUC	1H
CTEMP	23.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	36



2e

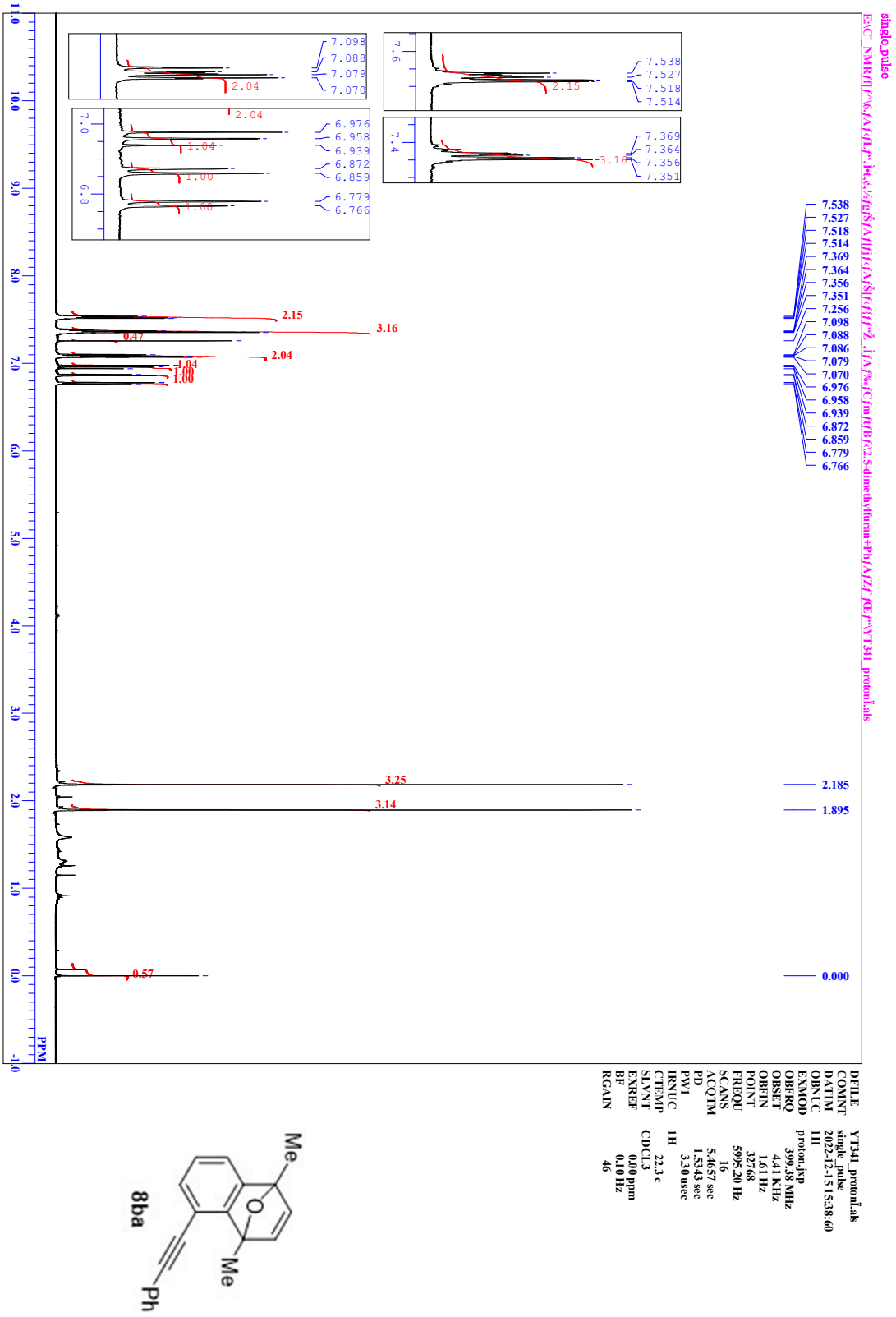
5-Ethynyl-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (8aa)

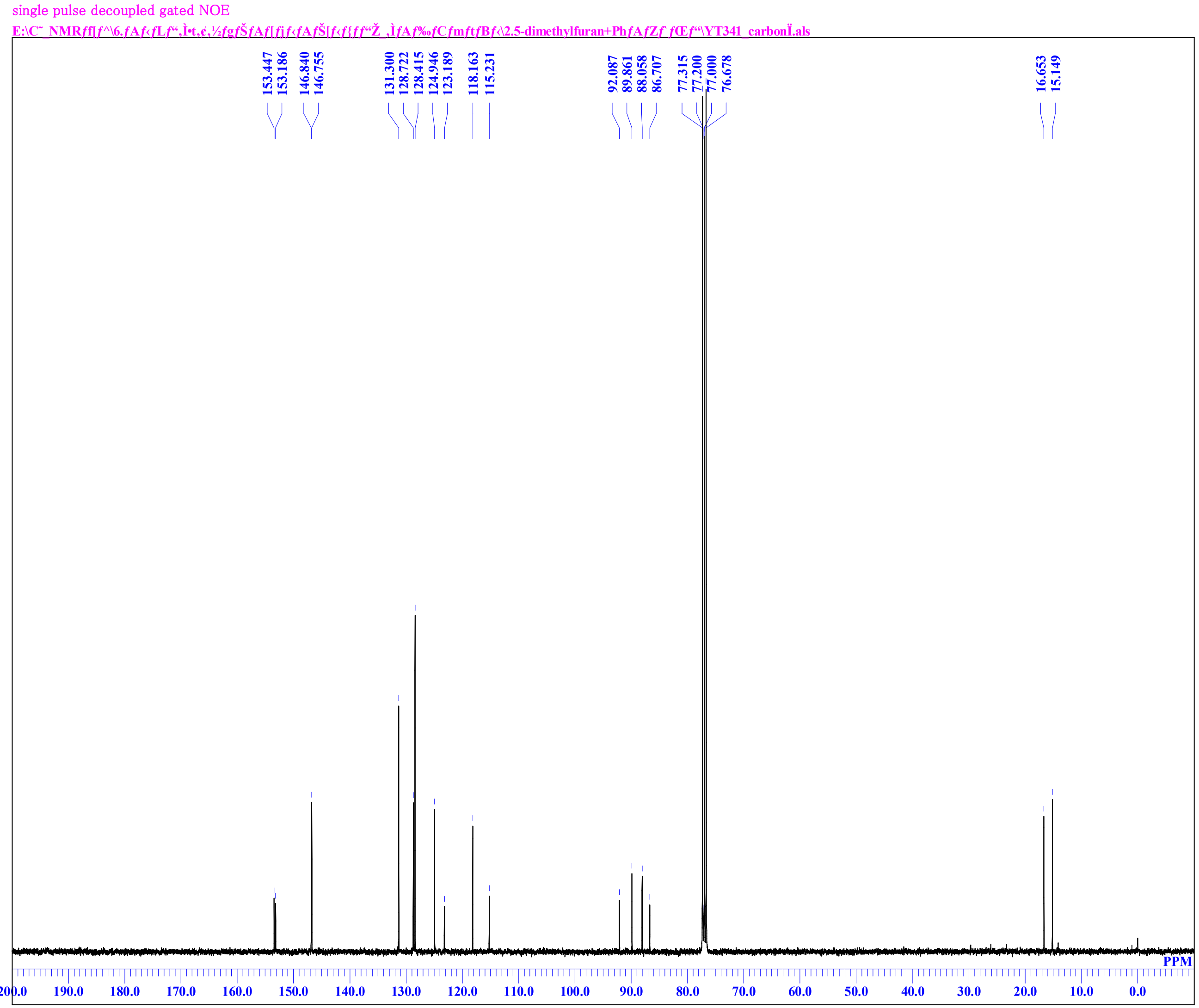



single pulse decoupled gated NOE
153.900
153.462
146.847
146.640
129.351
124.916
118.554
114.065
89.785
87.905
80.883
80.277
77.315
77.200
77.000
76.678
16.461
15.087
DFILE YT254recolumn(2-6)_carbon-1-1i.al
COMNT single pulse decoupled gated NOE
DATIM 2022-07-02 13:12:23
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.43 MHz
OBSET 4.82 KHz
OBFIN 0.13 Hz
POINT 32768
FREQU 25252.53 Hz
SCANS 1200
ACQTM 1.2976 sec
PD 1.7024 sec
PW1 3.75 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 56

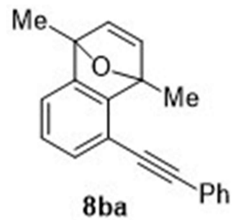
8aa

1,4-Dimethyl-5-(phenylethynyl)-1,4-dihydro-1,4-epoxynaphthalene (8ba)



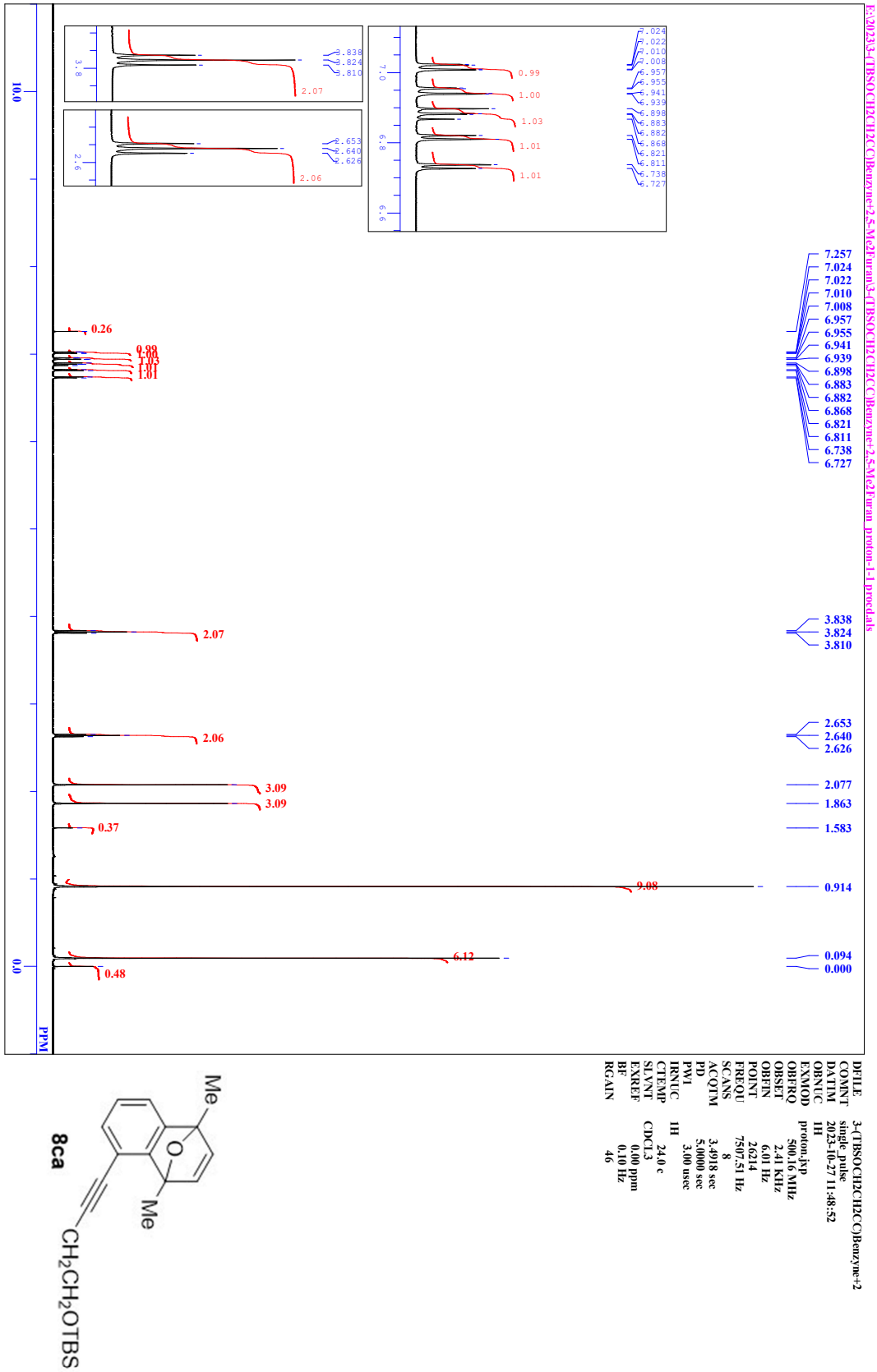


DFILE	YT341_carbonÏ.als
COMNT	single pulse decoupled gated NOE
DATIM	2022-12-15 16:44:27
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.43 MHz
OBSET	4.82 KHz
OBFIN	0.13 Hz
POINT	32768
FREQU	25252.53 Hz
SCANS	2000
ACQTM	1.2976 sec
PD	1.7024 sec
PW1	3.75 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	56



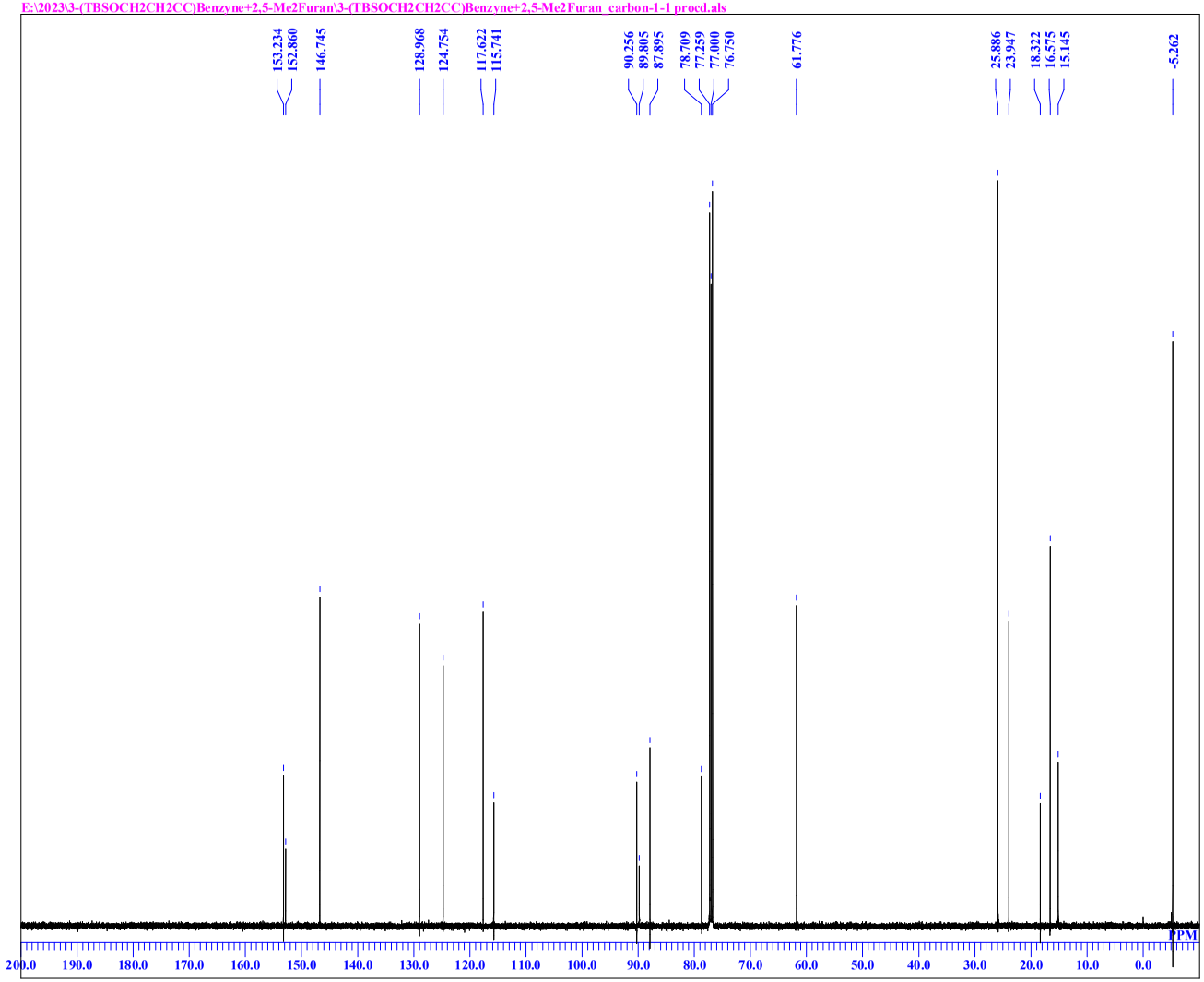
8ba

5-(4-(*tert*-Butyldimethylsilyloxy)-but-1-yn-1-yl)-1,4-dimethyl--1,4-dihydro-1,4-epoxynaphthalene (8ca)

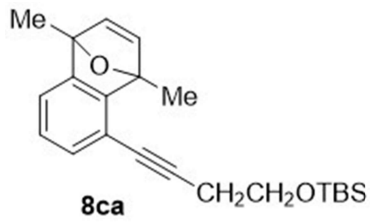


single pulse decoupled gated NOE

E:\2023\3-(TBSOCH2CH2CC)Benzyne+2,5-Me2Furan\3-(TBSOCH2CH2CC)Benzyne+2,5-Me2Furan_carbon-1-1 procd.als

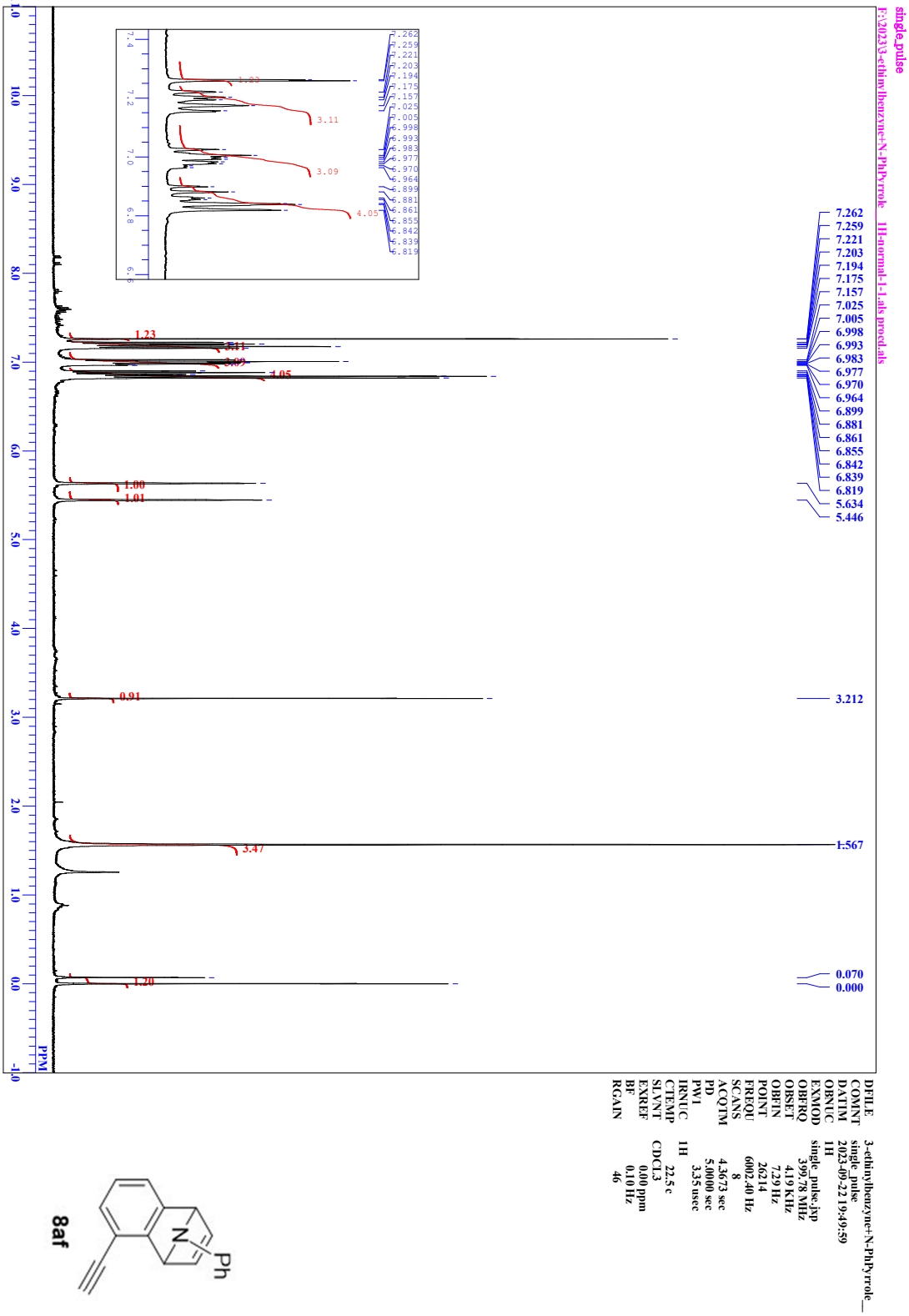


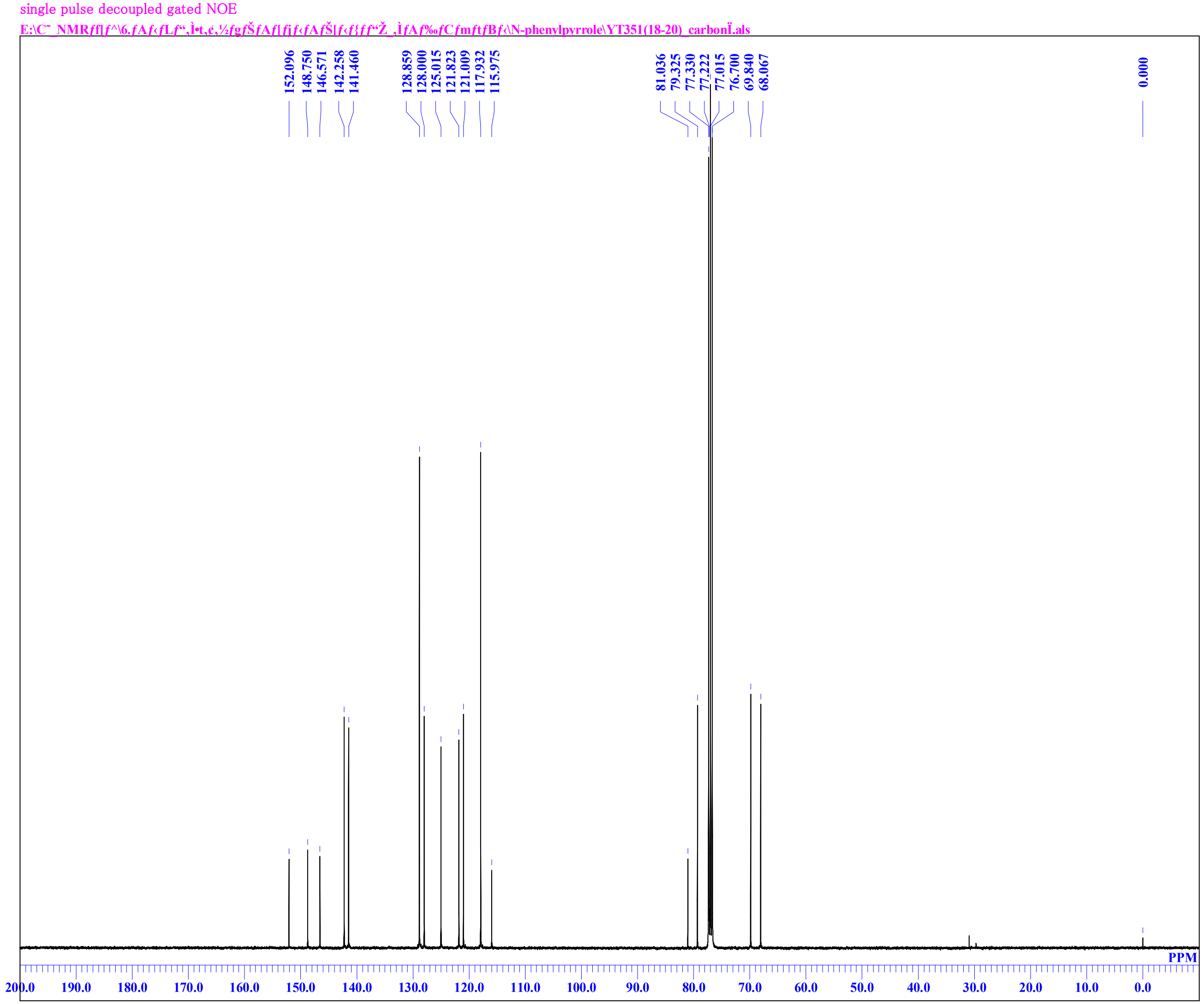
DFILE	3-(TBSOCH2CH2CC)Benzyne+2
COMNT	single pulse decoupled gated NOE
DATIM	2023-10-27 11:50:38
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31645.57 Hz
SCANS	1720
ACQTM	0.8284 sec
PD	2.0000 sec
PW1	3.46 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	36



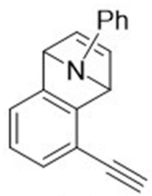
8ca

5-Ethynyl-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (8af)



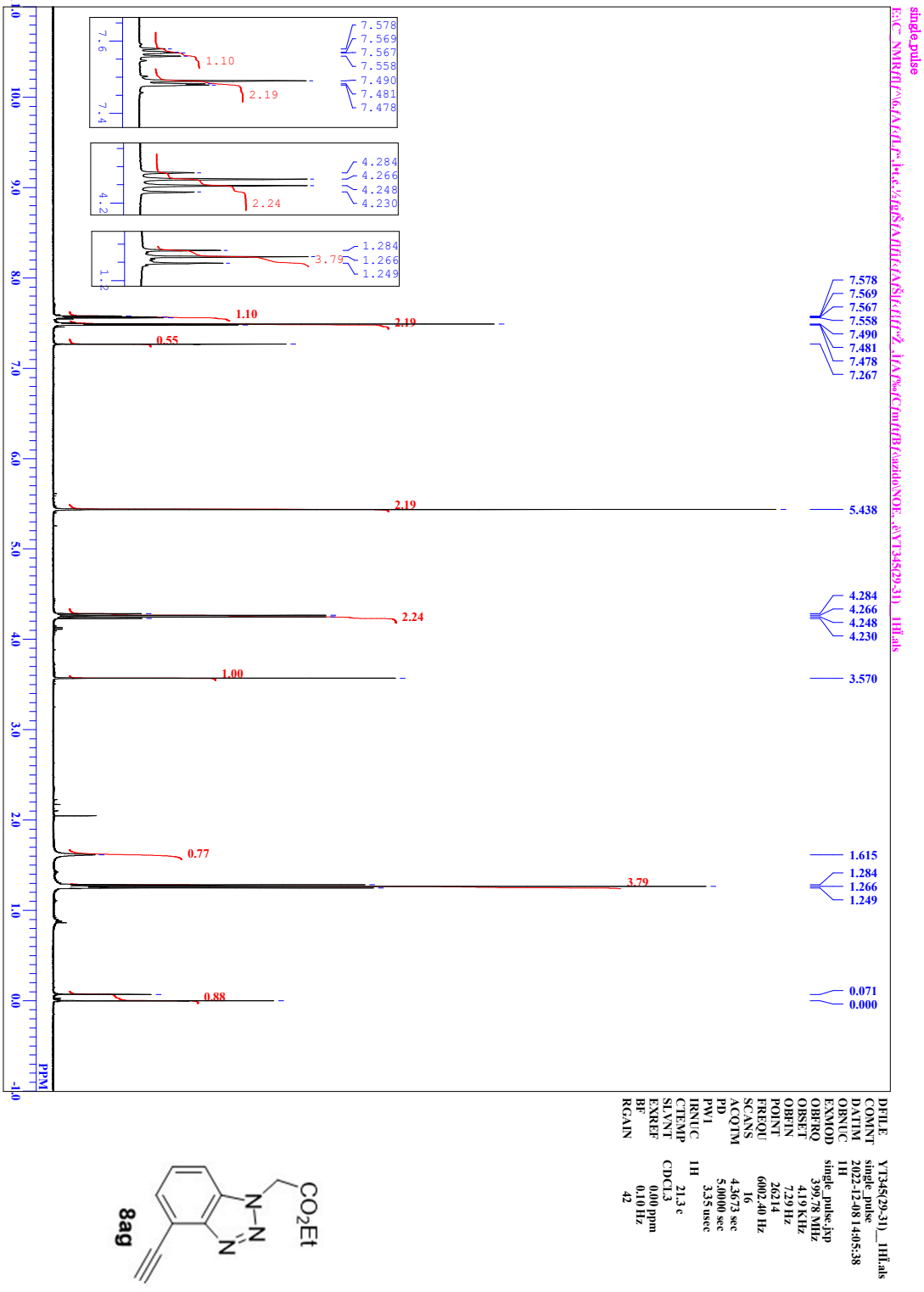


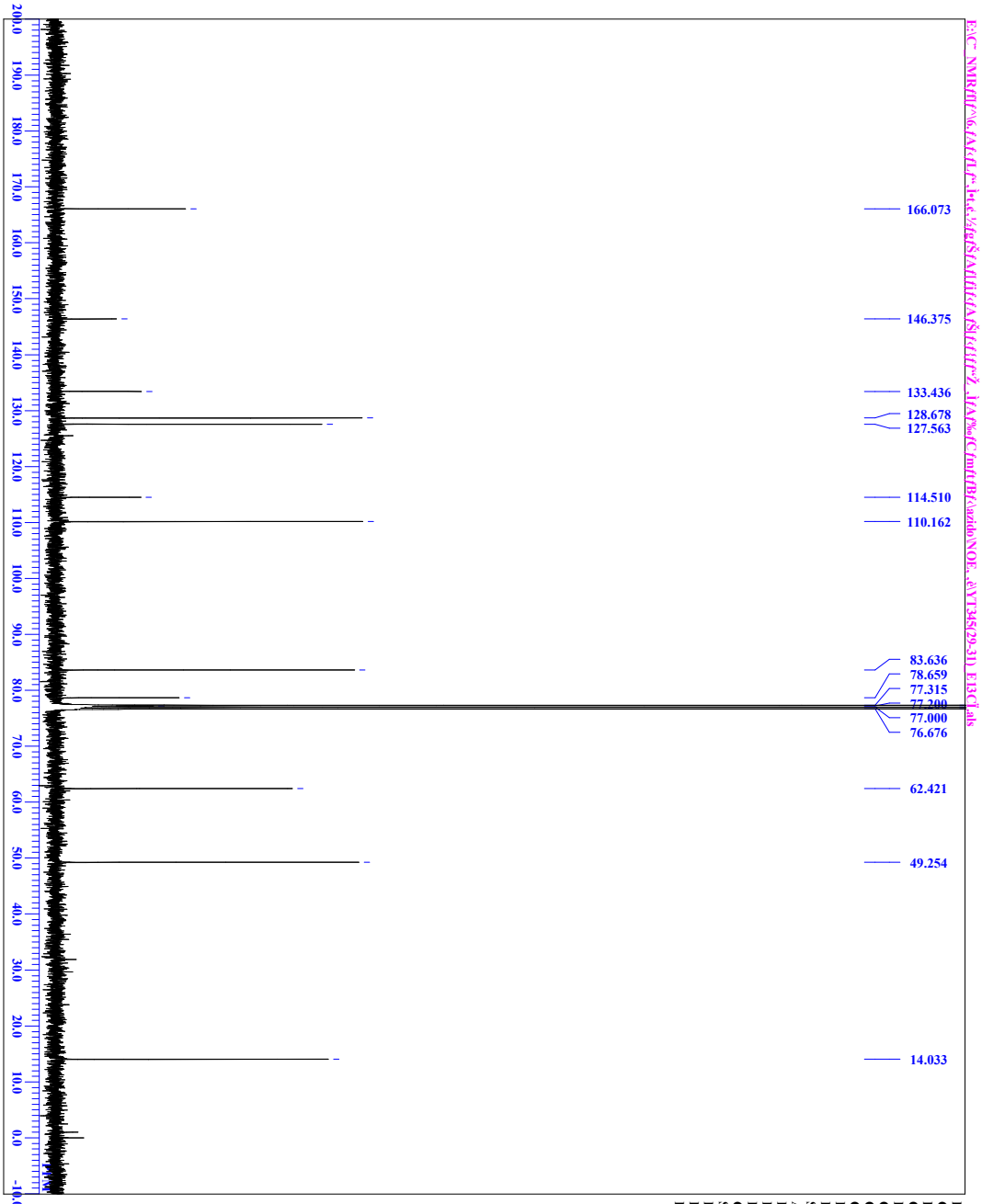
DFILE	YT351(18-20)_carbonÏ.als
COMNT	single pulse decoupled gated NOE
DATIM	2022-12-24 16:15:16
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.43 MHz
OBSET	4.82 KHz
OBFIN	0.13 Hz
POINT	32768
FREQU	25252.53 Hz
SCANS	15000
ACQTM	1.2976 sec
PD	1.7024 sec
PW1	3.75 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	56



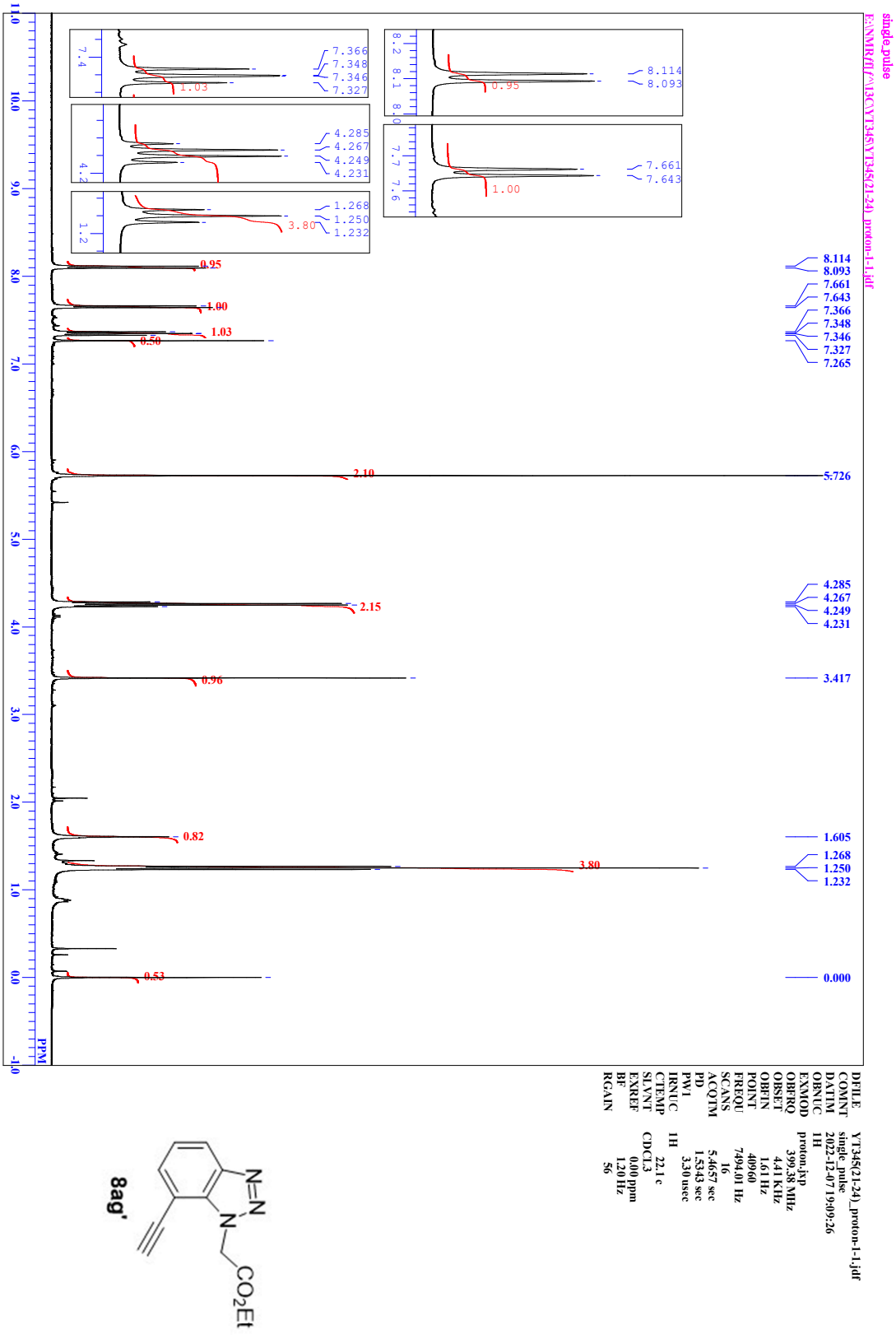
8af

Ethyl 2-(4-Ethynyl-1,2,3-benzotriazol-1-yl)acetate (8ag)




single pulse decoupled gated NOE
166.073
146.375
133.436
128.678
127.563
114.510
110.162
83.636
78.659
77.315
77.000
76.676
62.421
49.254
14.033
DFILE YT345(29-31)_E13Cl.als
COMNT single pulse decoupled gated NOE
DATIM 2022-12-08 14:08:38
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1500
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60
8ag
CO2Et

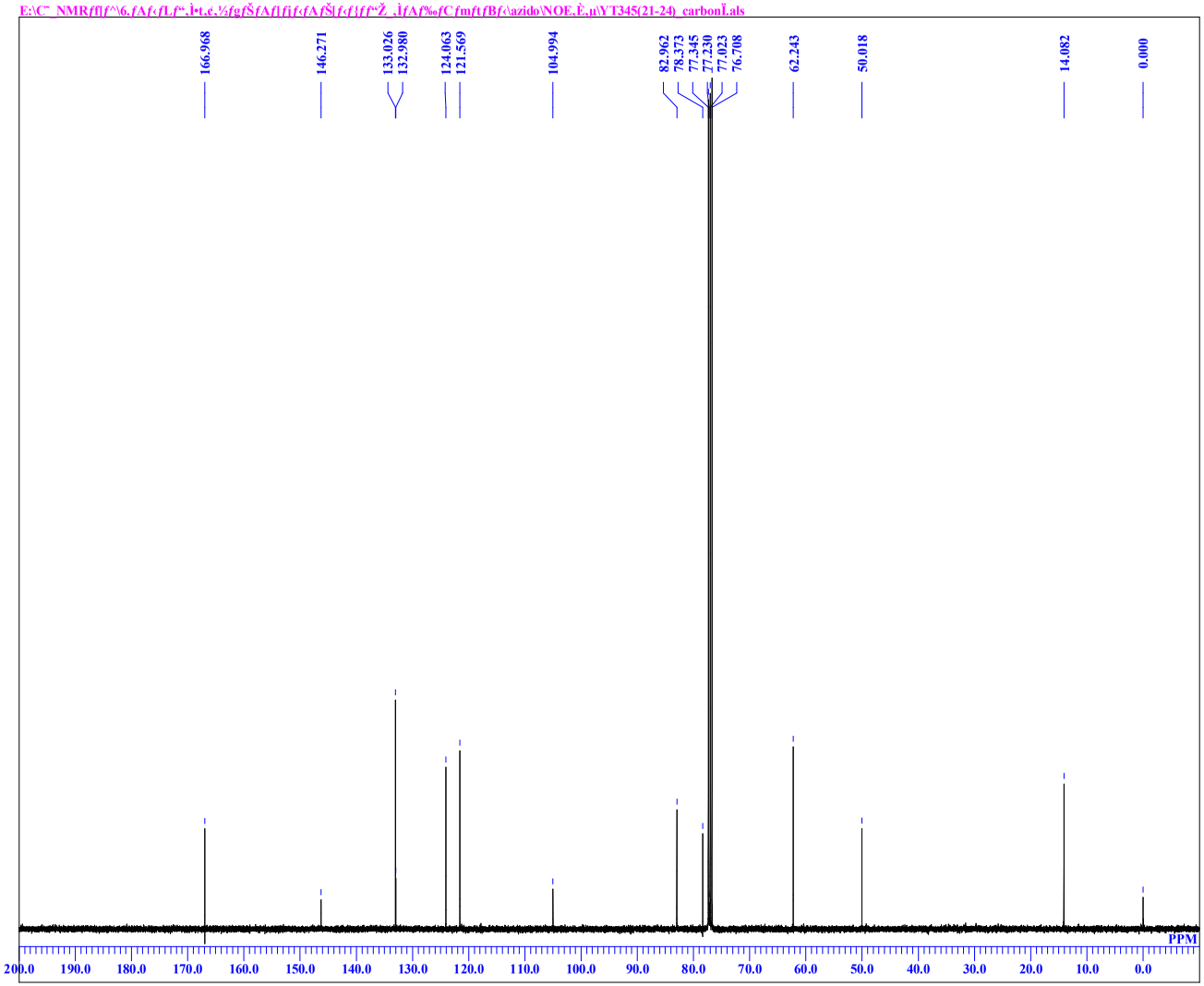
Ethyl 2-(7-Ethynyl-1,2,3-benzotriazol-1-yl)acetate (8ag')



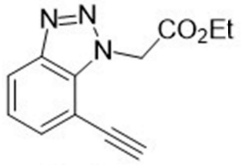
8ag'

single pulse decoupled gated NOE

E:\C~_NMR\fl\f^\6.fA\f‹fL\f“,ì•t,€,½\fg\fŠ\fA\f|\fj\f‹\fA\fŠ|\f‹\f{\f“Ž_,ìfAf‰\fCfmftfBf‹\azido\NOE,È,µ\YT345(21-24)_carbonÏ.als

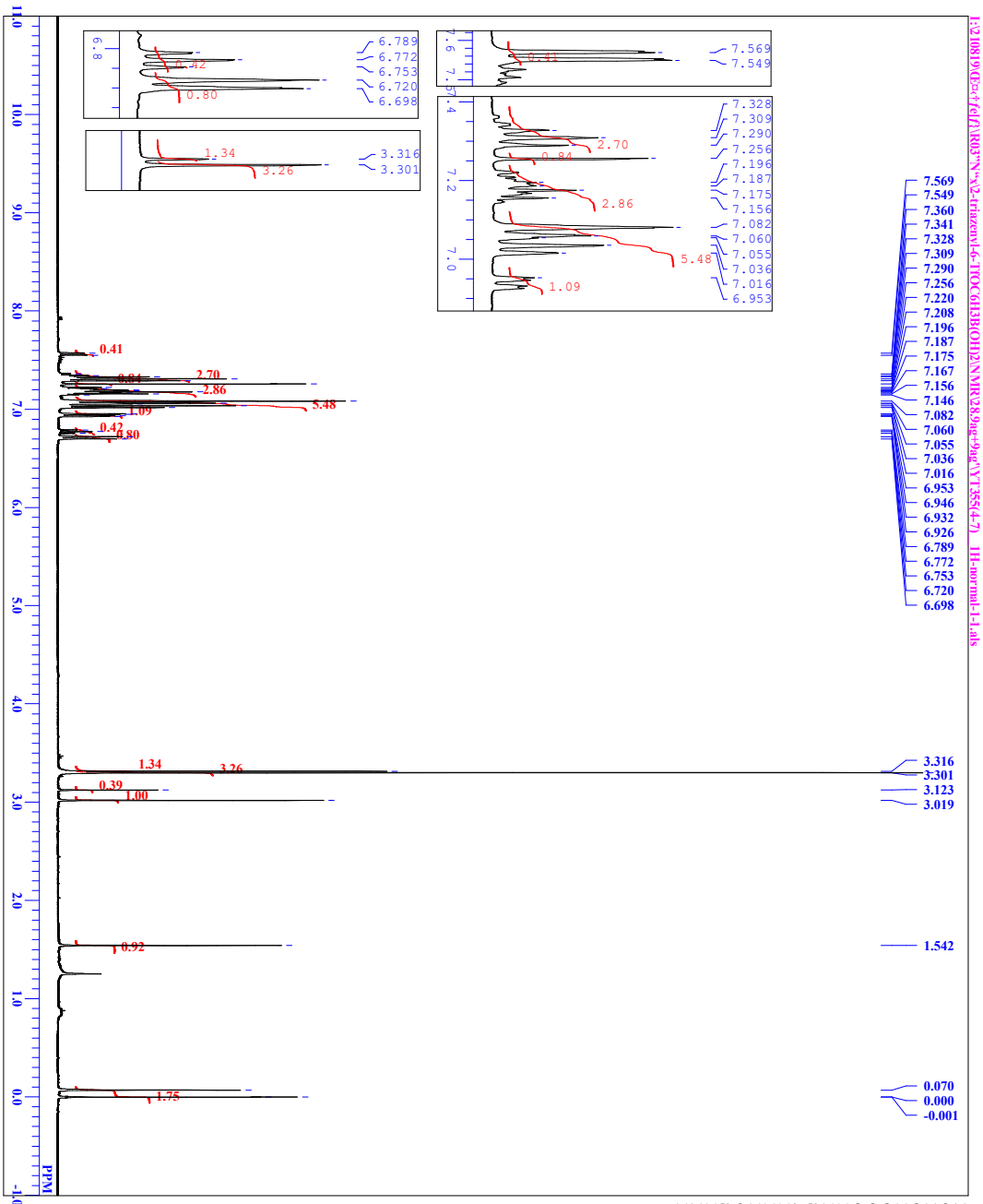


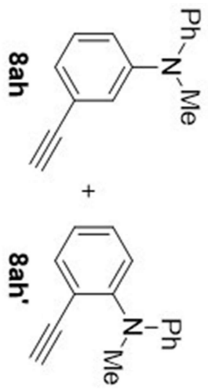
DFILE	YT345(21-24)_carbonÏ.als
COMNT	single pulse decoupled gated NOE
DATIM	2022-12-07 19:23:35
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.43 MHz
OBSET	4.82 KHz
OBFIN	0.13 Hz
POINT	32768
FREQU	25252.53 Hz
SCANS	4000
ACQTM	1.2976 sec
PD	1.7024 sec
PW1	3.75 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	56



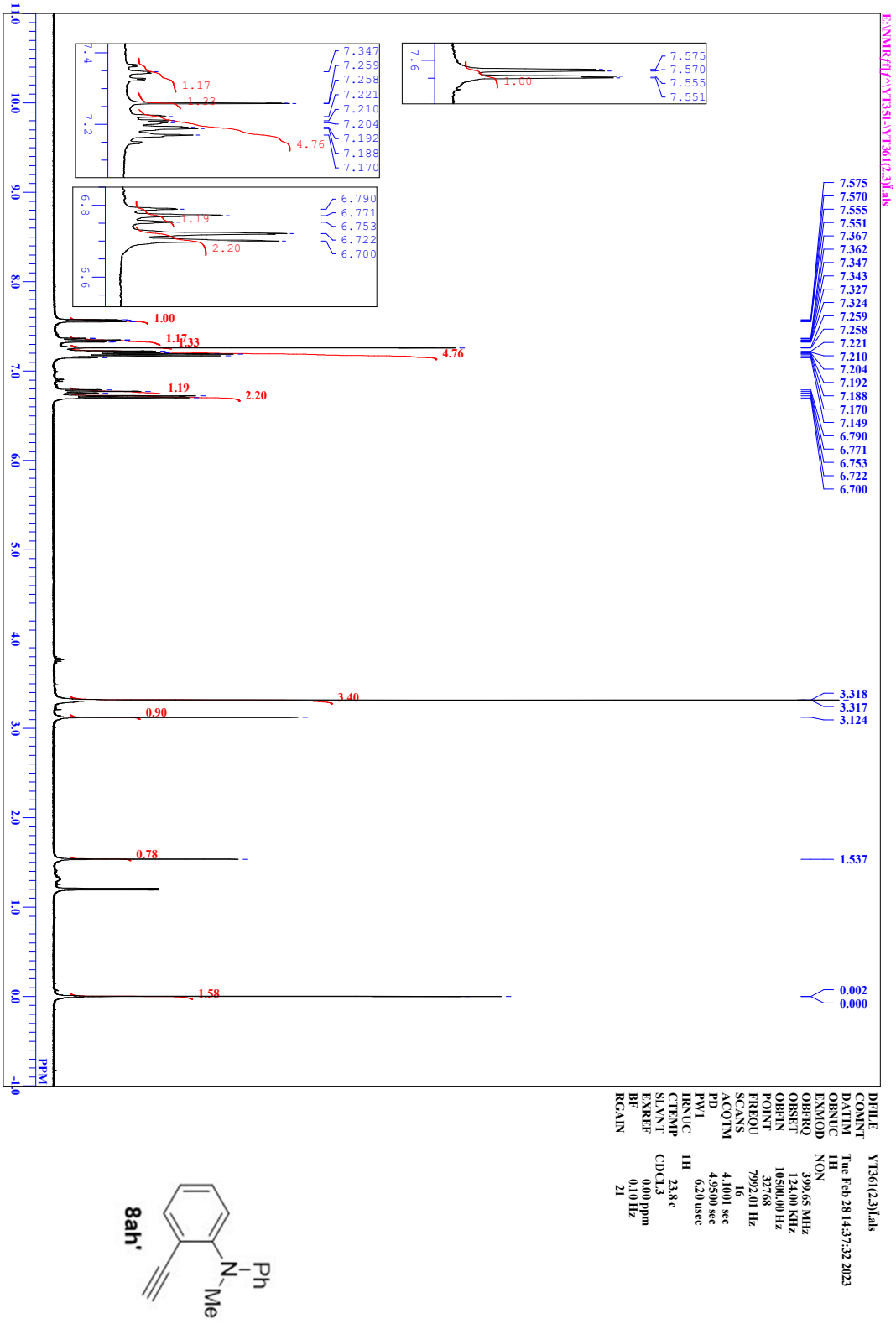
8ag'

3-Ethynyl-*N*-methyl-*N*-phenylaniline (8ah) and 2-Ethynyl-*N*-methyl-*N*-phenylaniline (8ah')

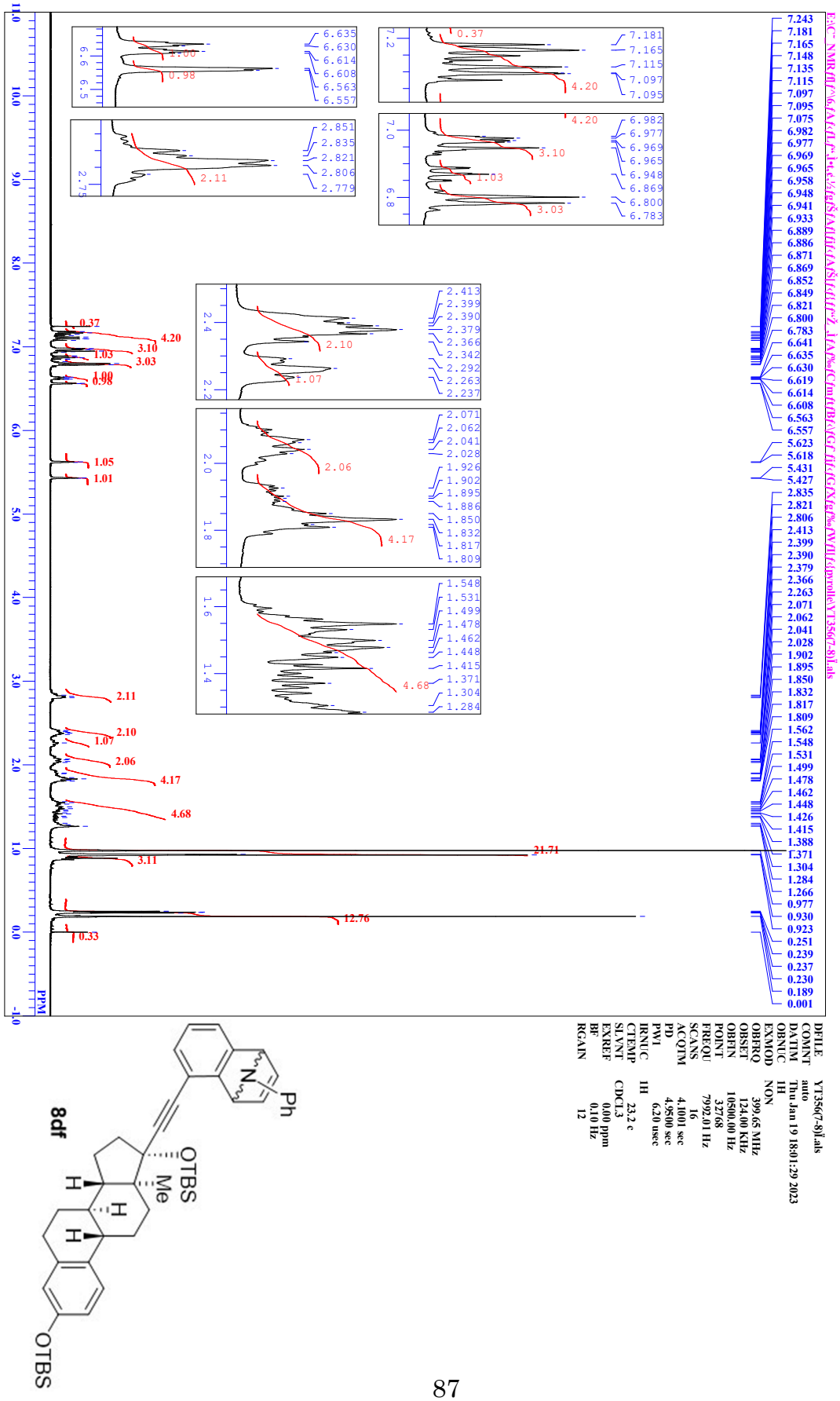




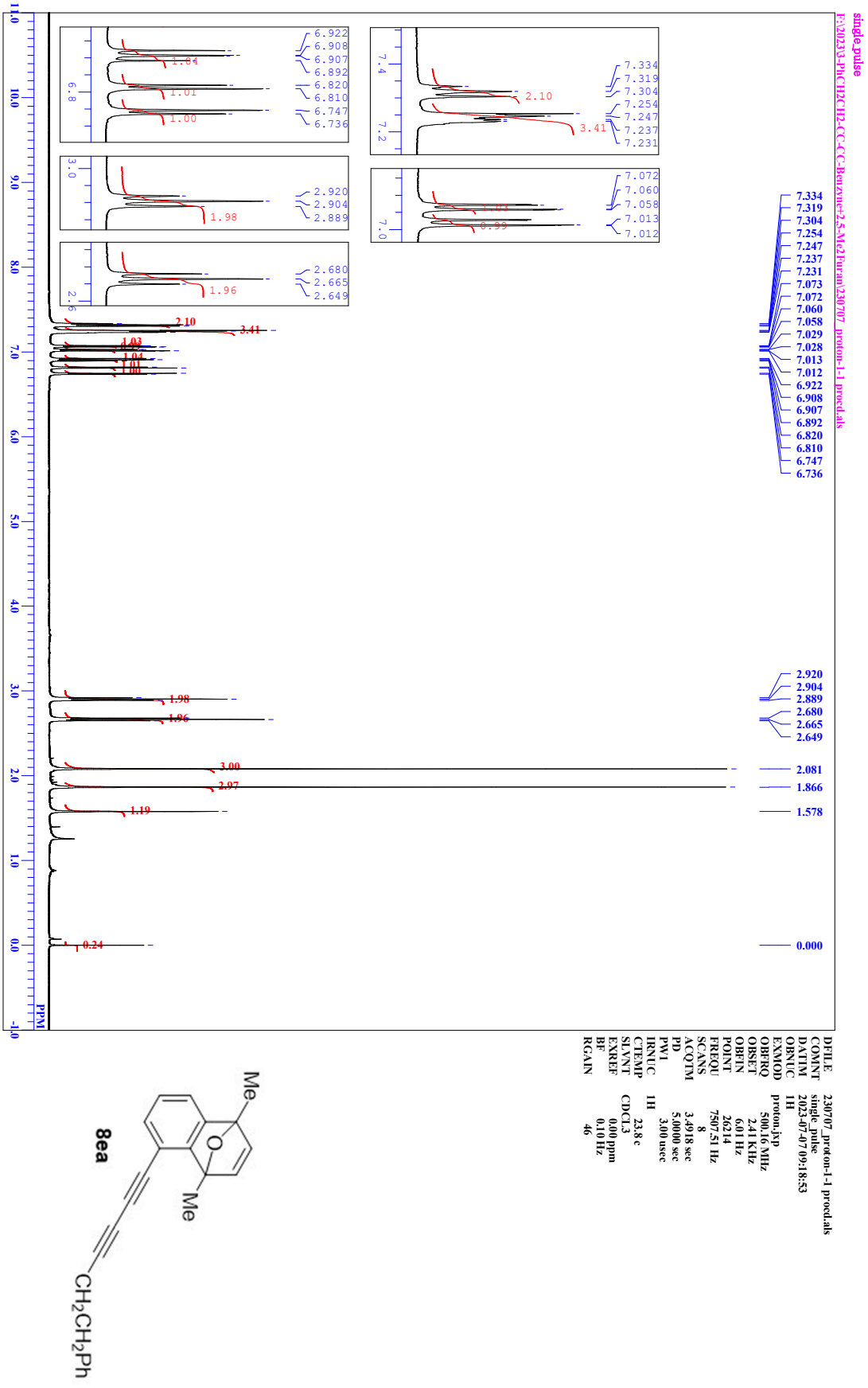
2-Ethynyl-*N*-methyl-*N*-phenylaniline (8ah')



3,17-*O*-Bis(*tert*-butyldimethylsilyl)-17α-{(9-phenyl-1,4-dihydro-1,4-epiminonaphthalen-5-yl)ethynyl}estradiol (8df)

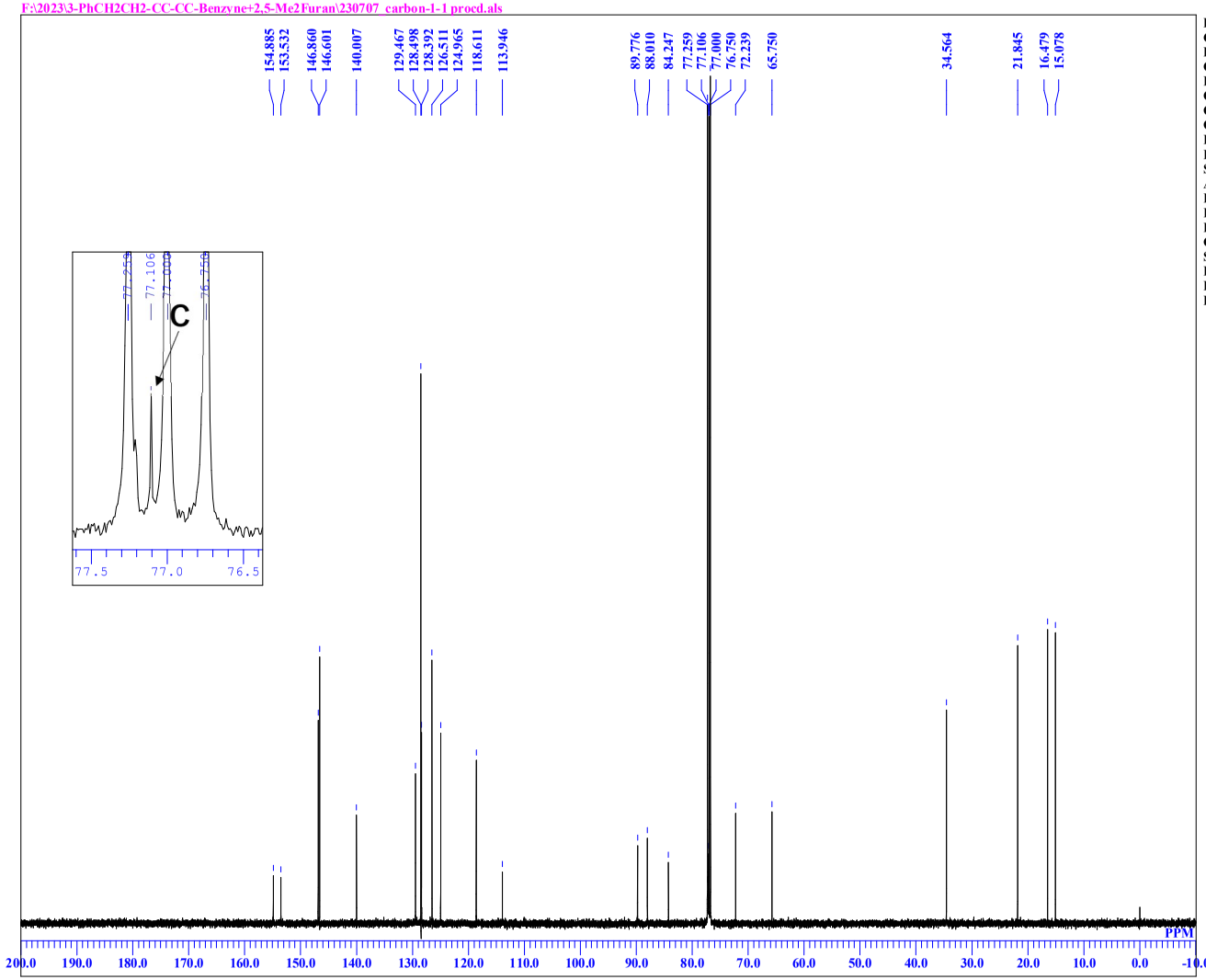


1,4-Dimethyl-5-(6-phenylhexa-1,3-diyn-1-yl)-1,4-dihydro-1,4-epoxynaphthalene (8ea)

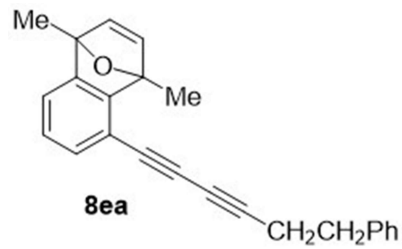


single pulse decoupled gated NOE

F:\2023\3-PhCH2CH2-CC-CC-Benzyne+2,5-Me2Furan\230707_carbon-1-1 procd.als

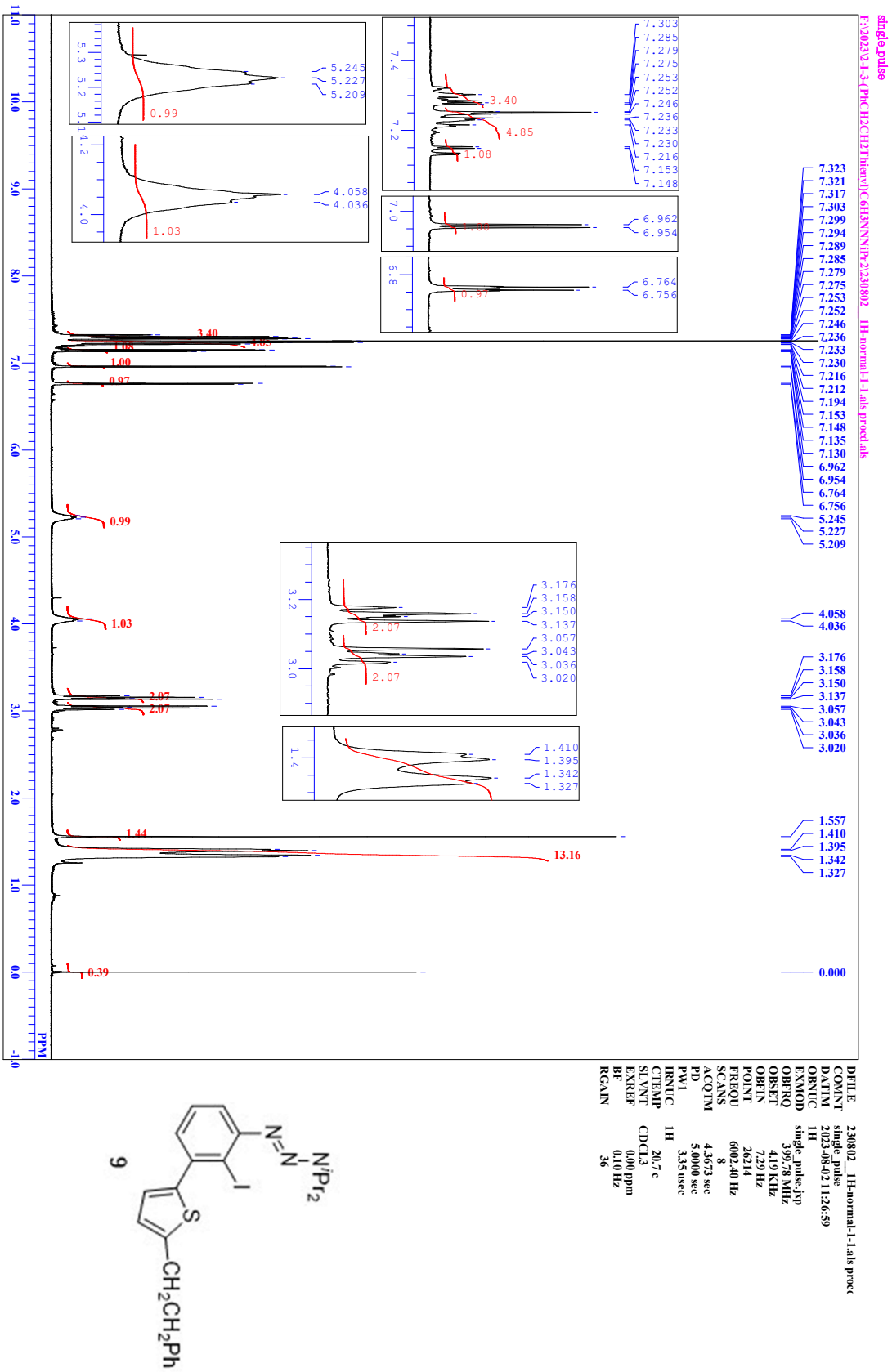


DFILE	230707_carbon-1-1 procd.als
COMNT	single pulse decoupled gated NOE
DATIM	2023-07-07 09:20:54
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31645.57 Hz
SCANS	2400
ACQTM	0.8284 sec
PD	2.0000 sec
PW1	3.46 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	36



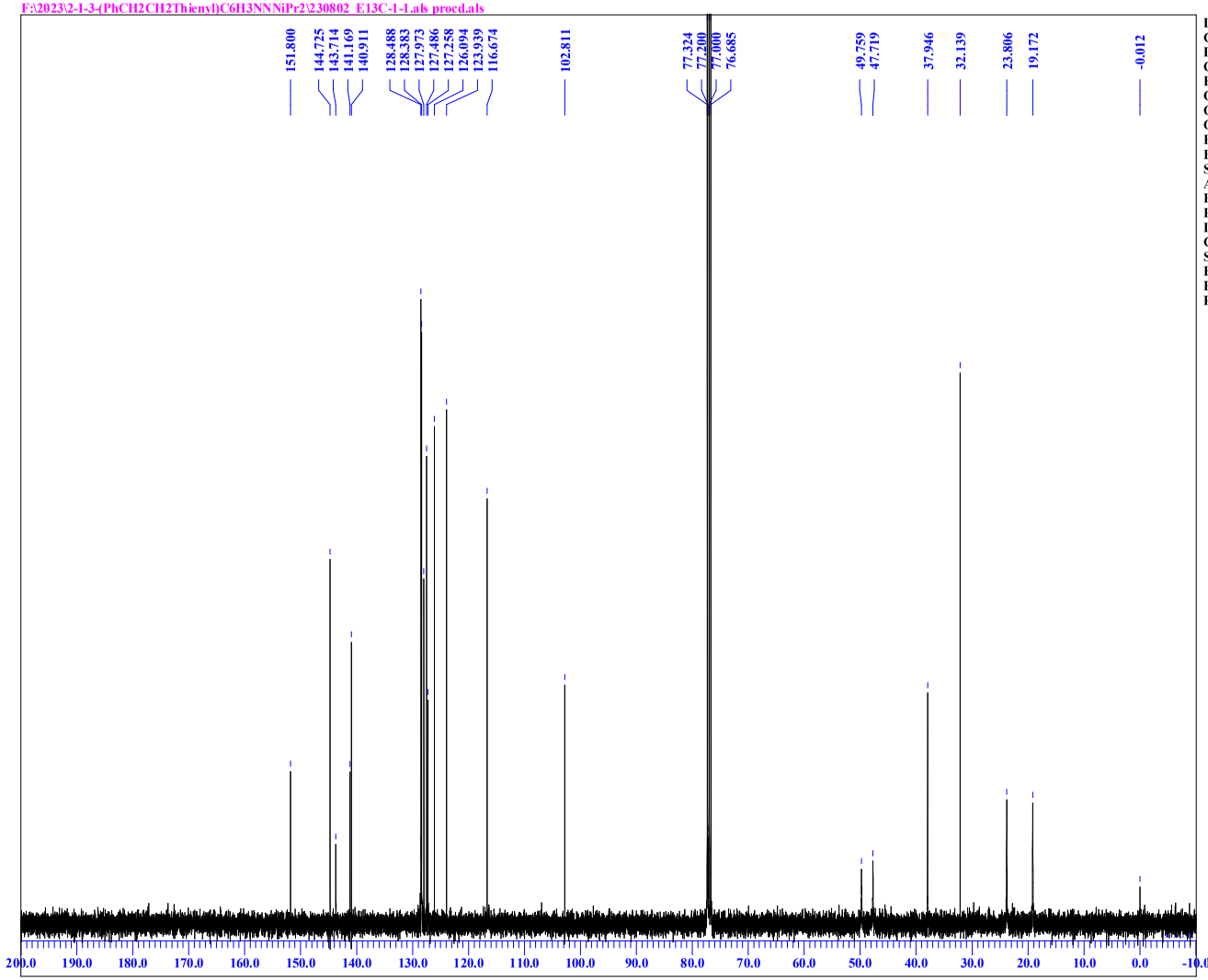
8ea

1-(2-Iodo-3-(5-phenethylthiophen-2-yl)phenyl)-3,3-diisopropyltriaz-1-ene (9)

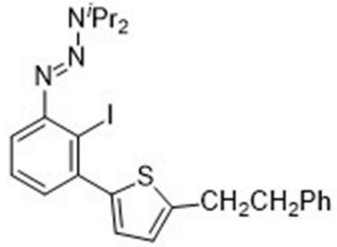


single pulse decoupled gated NOE

F:\2023\2-I-3-(PhCH2CH2Thienyl)C6H3NNiPr2\230802_E13C-1-1.als procd.als



DFILE	230802_E13C-1-1.als procd.als
COMNT	single pulse decoupled gated NOE
DATIM	2023-08-02 11:28:45
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	2048
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60



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