The supporting information

Strain-promoted azide-alkyne cycloaddition enhanced by the secondary interactions

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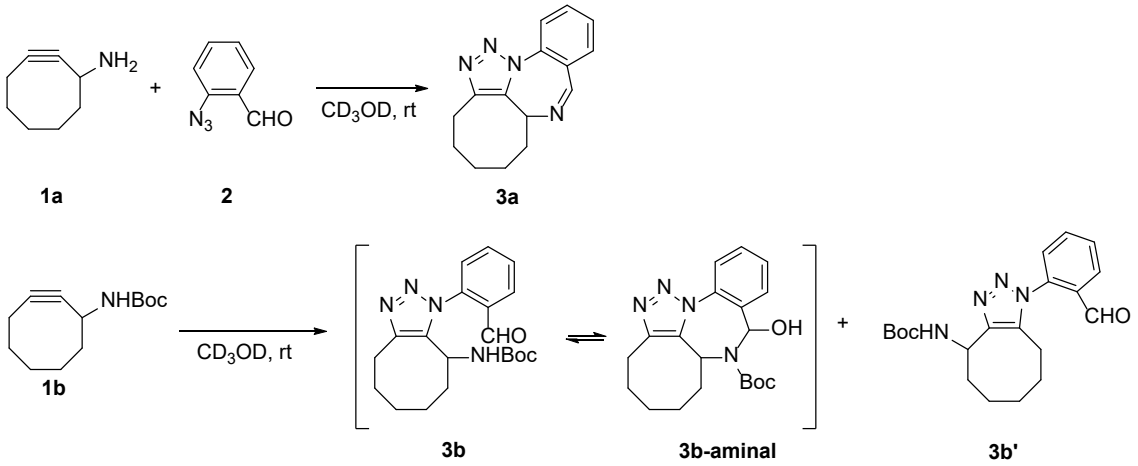
1. General

All melting points were determined on MPA100 Melting Point Apparatus. Infrared spectra (IR) were recorded on Horiba IR-710. ^{1}H NMR spectra were recorded on a JEOL JNM ECA400 (400 MHz) or a JEOL JNM ECA600 (600 MHz) spectrometer at room temperature; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane or residual protic solvent ($CDCl_3$ at 7.26, CD_3OD at 3.31). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM ECS400 (100 MHz) or a JEOL JNM ECA600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts data are given in units δ calibrated with residual protic solvent (e.g., 77.0 ppm for $^{13}CDCl_3$, 49.0 ppm for $^{13}CD_3OD$). High resolution mass spectra (HRMS) data were recorded on JEOL JMS-T100TD. Elemental analysis was performed with J-Science Lab Micro Coder JM-10. Analytical TLC was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica gel column chromatography was carried out on silica gel 60 N (Kanto Kagaku Co., Ltd., spherical, neutral, 63-210 μm).

2. The kinetic study for AAC of 2 with 1a or 1b by ^{1}H NMR



Preparation of a solution of cyclooctyne **1a** and **1b**

Solution 1-**1a**: cyclooctyne **1a** (4.9 mg, 40 μ mol) and diphenylmethane (2.2 mg, 13 μ mol) were dissolved in methanol-d_4 (1.0 mL).

Solution 1-**1b**: cyclooctyne **1b** (8.0 mg, 36 μ mol) and diphenylmethane (2.6 mg, 15 μ mol) were dissolved in methanol-d_4 (1.0 mL).

Preparation of a solution of aldehyde **2**

Solution 2-1: aldehyde **2** (26.5 mg, 180 μ mol) was dissolved in methanol-d_4 (0.5 mL).

Solution 2-2: aldehyde **2** (32.4 mg, 220 μ mol) was dissolved in methanol-d_4 (0.5 mL).

Solution 2-3: aldehyde **2** (38.3 mg, 260 μ mol) was dissolved in methanol-d_4 (0.5 mL).

The experimental procedure

Solution 1 (250 μ L) was added to a NMR tube. Solution 2 (250 μ L) was added with a syringe and the NMR tube was shaken to allow mixing. The reaction progress of the mixture was analyzed by ^{1}H NMR.

$[2]_0$ = 0.18 M		
t (sec)	[3b+3b-aminal+3b'] (mM)	3b+3b-aminal+3b' yield (%)
198	2.10	12
347	3.68	20
490	4.65	26
632	5.40	30
772	5.70	32
1233	7.80	43
1800	8.10	45

$[2a]_0$ = 0.18 M		
t (sec)	[3a] (mM)	3a yield (%)
207	7.28	36
348	11.05	55
489	12.74	64
630	13.52	68
770	13.52	68
1203	13.52	68
1804	13.52	68

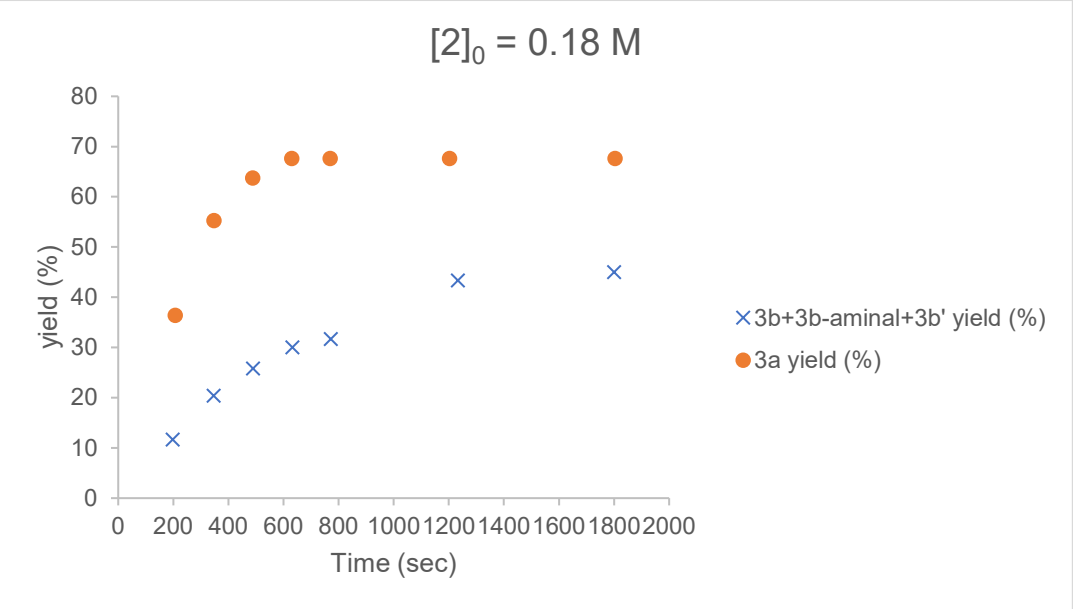


Figure S1a. Reaction of **1a** and **2** ($[2]^0$ = 0.18 M) in CD_3OD.

$[2]_0$ = 0.22 M		
t (sec)	[3b+3b-aminal+3b'] (mM)	3b+3b-aminal+3b' yield (%)
278	2.70	15
439	5.25	29
579	6.45	36
719	8.10	45
858	9.15	51
1200	10.65	59
1800	11.55	64

$[2a]_0$ = 0.22 M		
t (sec)	[3a] (mM)	3a yield (%)
202	8.19	41
341	11.57	58
479	12.09	60
620	12.35	62
759	13.26	66
1204	13.26	66
1802	13.65	68

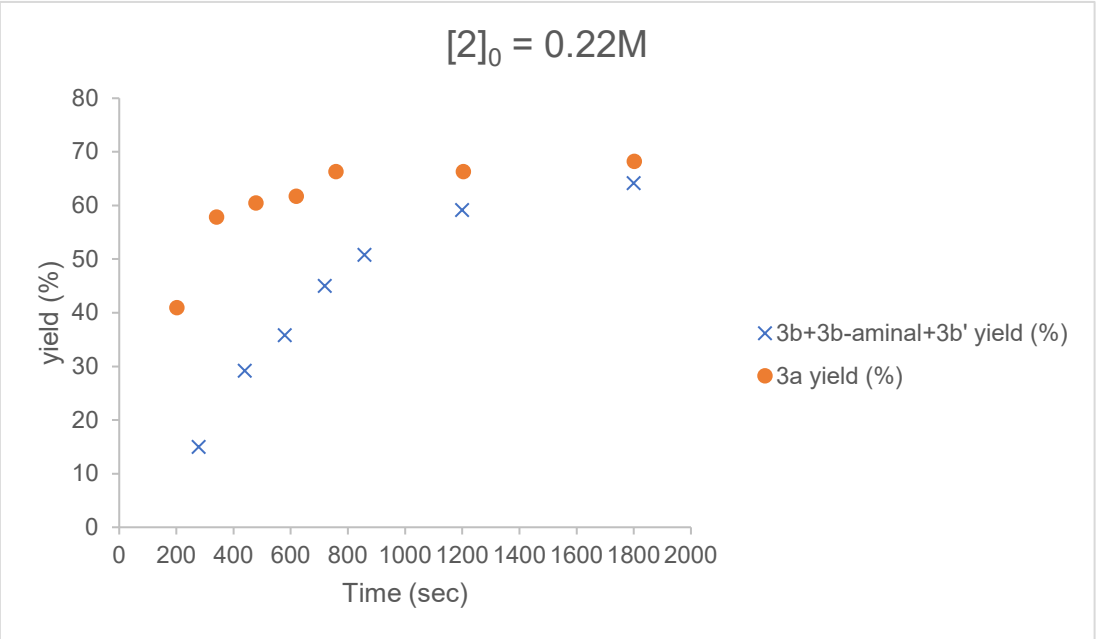


Figure S1b. Reaction of **1a** and **2** ($[2]^0$ = 0.22 M) in CD_3OD.

$[2]_0$ = 0.26 M		
t (sec)	[3b+3b-aminal+3b'] (mM)	3b+3b-aminal+3b' yield (%)
205	4.04	22
346	6.00	33
487	7.50	42
629	8.40	47
771	9.45	53
1185	11.10	62
1787	12.15	68

$[2a]_0$ = 0.26 M		
t (sec)	[3a] (mM)	3a yield (%)
205	8.11	41
345	11.57	58
485	12.22	61
626	12.35	62
767	12.48	62
1202	12.61	63
1801	13.00	65

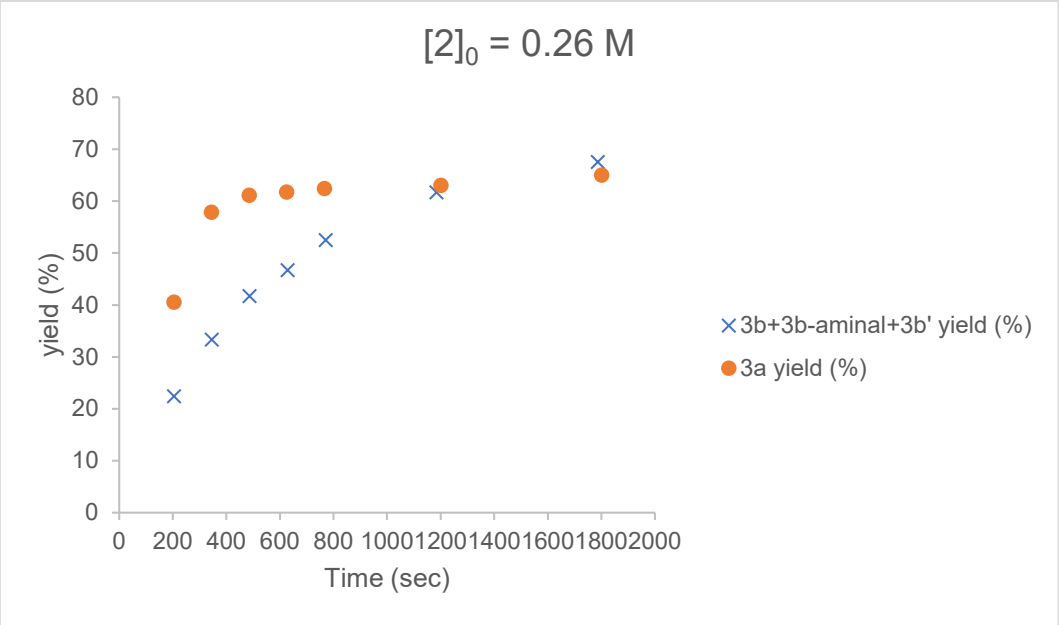
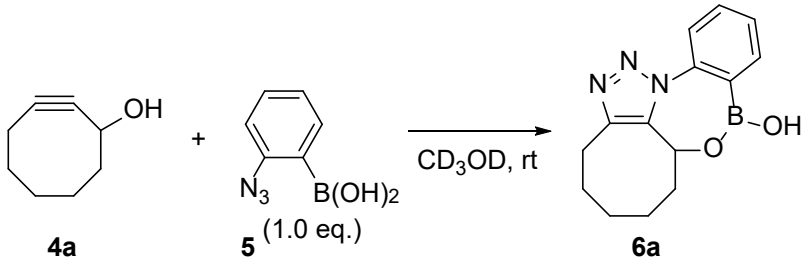
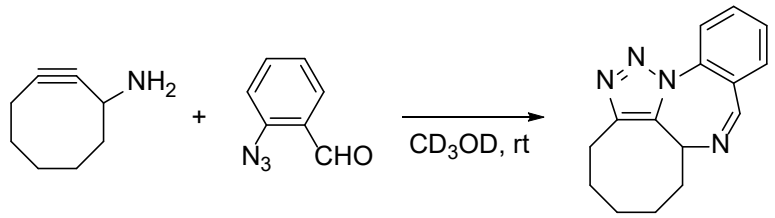


Figure S1c. Reaction of **1a** and **2** ($[2]^0$ = 0.26 M) in CD_3OD.

3. The reaction progress of AAC between 1a and 2 to 3a and that of between 4a and 5 to 6a.





Preparation of a solution of cyclooctynes (Solution 1)

Solution 1-**4a**: cyclooctyne **4a** (4.5 mg, 36 μ mol) and diphenylmethane (an internal standard, 2.4 mg, 14 μ mol) were dissolved in methanol-d_4 (1.0 mL).

Solution 1-**1a**: cyclooctyne **1a** (4.4 mg, 36 μ mol) and diphenylmethane (an internal standard, 2.5 mg, 14.8 μ mol) were dissolved in methanol-d_4 (1.0 mL).

Preparation of a solution of azides (Solution 2)

Solution 2-**5**: azide **5** (5.9 mg, 36 μ mol) was dissolved in methanol-d_4 (1.0 mL).

Solution 2-**2**: azide **2** (5.3 mg, 36 μ mol) was dissolved in methanol-d_4 (1.0 mL).

The experimental procedure

Solution 1 (250 μ L) was added to a NMR tube. Solution 2 (250 μ L) was added with a syringe and the NMR tube shaken to allow mixing. The reaction progress of the mixture was analyzed by ^{1}H NMR.

t (sec)	[6a] (mM)	[3a] (mM)	6a yield (%)	3a yield (%)
240	7.81	0.30	43	2
330	9.51	0.44	53	2
420	9.94	0.59	55	3
510	10.93	0.74	61	4
600	11.79	0.89	66	5
1200	14.63	1.33	81	7
1800	15.05	1.78	84	10

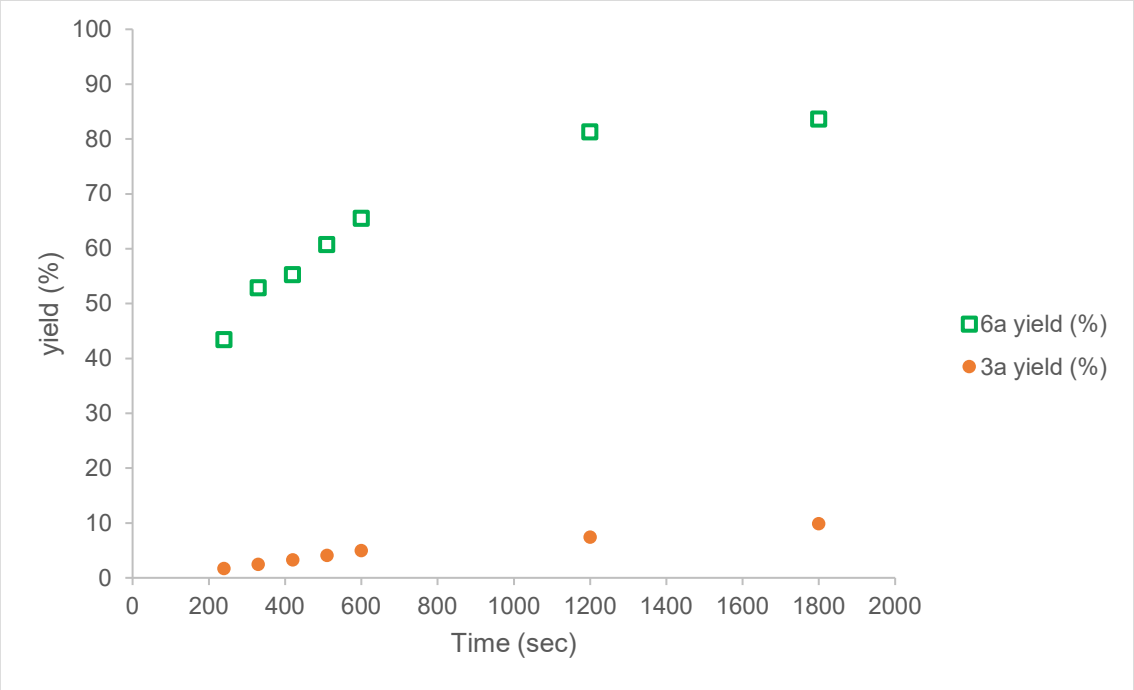
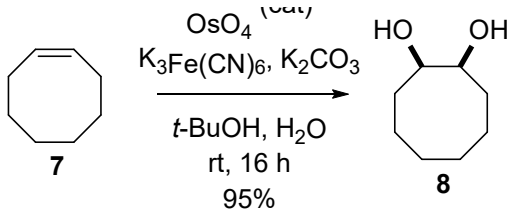


Figure 1. ^{1}H NMR (CD_3OD)-monitoring of the reaction progress between **1a** and **2** to **3a** and between **4a** and **5** to **6a**.

4. Synthesis

cis-Cycloontane-1,2-diol (**8**)



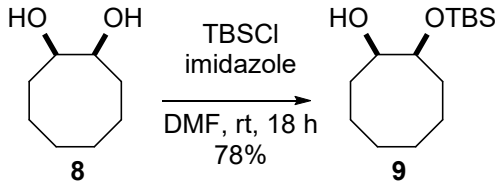
Compound **8** was prepared according to the reported procedure,[1] and was obtained in 95% yield. Characterization data were in accordance with the literature.[2]

mp: 76.6-77.0 °C (ref[3] 75-77 °C)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.92-3.90 (2H, m), 2.07 (1H, br), 1.91-1.86 (2H, m), 1.69-1.66 (4H, m), 1.54-1.48 (6H, m), 0.90 (9H, s)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 73.1, 30.1, 26.2, 23.7

(1*R**,2*S**)-2-((*tert*-Butyldimethylsilyl)oxy)cyclooctanol (**9**)[4]



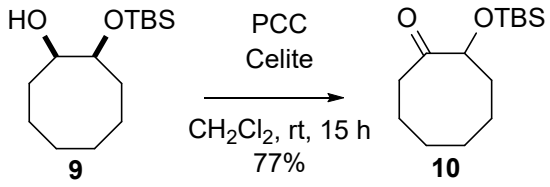
To a solution of diol **8** (1.18 g, 8.18 mmol, 1.0 equiv.) in DMF (16 mL) were added imidazole (613 mg, 9.00 mmol, 1.1 equiv.) and TBSCl (1.36 g, 9.00 mmol, 1.1 equiv.), and the mixture was stirred at room temperature for 19 h. The mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1 to 5:1) to afford **9** (1.65 g, 6.38 mmol, 78%) as a colorless oil.

Characterization data were in accordance with the literature.[4]

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.92-3.90 (1H, m), 3.72-3.71 (1H, m), 2.69 (1H, d, J = 3.2 Hz), 2.05-1.90 (1H, m), 185-1.35 (11H, m), 0.90 (9H, s), 0.08 (6H, s)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 74.5, 73.5, 30.7, 29.0, 26.8, 25.8, 25.5, 25.3, 22.6, 18.1, -4.5, -4.9

2-((*tert*-Butyldimethylsilyl)oxy)cyclooctan-1-one (**10**)[5]



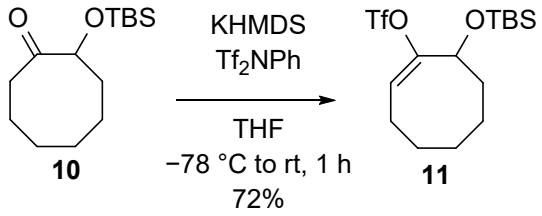
To a solution of **9** (1.37 g, 5.30 mmol, 1.0 equiv.) in DCM (53 mL) were added Celite® (4.57 g), and the solution was cooled to 0 °C. Then, PCC (4.57 g, 21.2 mmol, 4.0 equiv.) was added, and the mixture was stirred at room temperature for 18 h. The precipitate was filtered off through a pad of silica gel, and the filtrate was concentrated. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1) to afford **10** (1.05 g, 4.09 mmol, 77%) as a colorless oil.

Characterization data were in accordance with the literature.[5]

^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.19 (1H, dd, *J* = 6.4, 2.8 Hz), 2.74-2.70 (1H, m), 2.30-2.20 (2H, m), 2.00-1.80 (2H, m), 1.80-1.65 (1H, m), 1.60-1.45 (5H, m), 1.20-1.10 (1H, m), 0.92 (9H, s), 0.06 (3H, s), 0.05 (3H, s)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 218.4, 78.1, 39.3, 35.5, 27.3, 25.7, 25.2, 25.1, 20.8, 18.2, -5.0, -5.1

8-((*tert*-Butyldimethylsilyl)oxy)cyclooct-1-en-1-yl trifluoromethanesulfonate (**11**)



To a solution of **10** (1.60 g, 6.24 mmol, 1.0 equiv.) in THF (31 mL) were added KHMDS (1 M in THF, 7.5 mL, 7.49 mmol, 1.2 equiv.) at −78°C. After 45 min, a solution of Tf_2NPh (2.45 g, 6.86 mmol, 1.1 equiv.) in THF (31 mL) was added, and the mixture was stirred at room temperature for 20 min. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$, and extracted with hexane. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 50:1) to afford **11** (1.76 g, 4.53 mmol, 72%) as a colorless oil.

R_f = 0.54 (hexane/ethyl acetate = 10/1)

^{1}H NMR($CDCl_3$, 400 MHz): δ 5.71 (1H, t, *J* = 9.0 Hz), 4.68 (1H, dd, *J* = 9.6, 6.0 Hz), 2.45-2.35 (1H, m), 2.10-2.00 (1H, m), 1.85-1.70 (4H, m), 1.65-1.60 (1H, m), 1.50-1.40 (2H, m), 1.40-1.30 (1H, m), 0.92 (9H, s), 0.10 (6H, s)

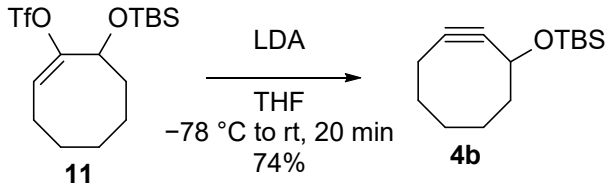
^{13}C NMR($CDCl_3$, 100 MHz): δ 150.4, 120.2, 67.8, 36.7, 29.7, 26.0, 25.8, 24.5, 23.0, 18.3, -4.9, -5.2.

The $\underline{C}F_3$ peaks, which are expected to appear around 118 ppm as quartet ($^1J_{C\text{-}F}$ = around 320 Hz) were not detected in this sample.

IR($CHCl_3$) cm^{-1}: 3739, 3593, 3039, 2939, 2860, 2376, 1680, 1608

HRMS(DART+) *m/z* calcd for $C_{15}H_{28}F_3O_4SSi$ [$(M+H)^+$]: 389.14297, found 389.14197

tert-Butyl(cyclooct-2-yn-1-yloxy)dimethylsilane (**4b**)



To a solution of diisopropylamine (0.57 mL, 2.1 equiv.) in THF (10 mL) was added *n*-BuLi (1.5 M in THF, 2.5 mL, 2.0 equiv.) at −78°C. After 10 min, a solution of **11** (739 mg, 1.90 mmol, 1.0 equiv.) in THF (9 mL) was added at −78°C, and the mixture was stirred at room temperature for 1 h. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with hexane. The combined organic extracts were washed with a saturated aqueous solution of NH_4Cl and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 100:1) to afford **4b** (338 mg, 1.41 mmol, 74%) was a yellow oil.

R_f = 0.63 (hexane/ethyl acetate = 10/1)

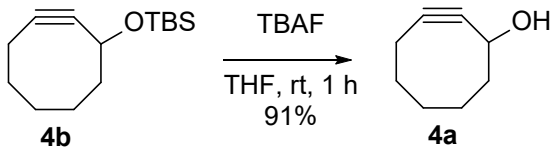
^{1}H NMR($CDCl_3$, 400 MHz): δ 4.46 (1H, m), 2.30-2.20 (1H, m), 2.15-2.05 (2H, m), 2.00-1.73 (5H, m), 1.55-1.50 (1H, m), 1.35-1.25 (1H, m), 0.89 (9H, s), 0.10 (3H, s), 0.08 (3H, s)

^{13}C NMR($CDCl_3$, 100 MHz): δ 98.0, 94.7, 65.5, 46.0, 34.5, 29.8, 26.4, 25.9, 20.7, 18.2, -4.7, -4.9

IR($CHCl_3$) cm^{-1}: 3739, 3676, 3635, 3008, 2939, 2856, 2376, 2314, 1712, 1608, 1550

HRMS(DART+) *m/z* calcd for $C_{14}H_{27}OSi$ [$(M+H)^+$]: 239.18312, found 239.18243

Cyclooct-2-yn-1-ol (**4a**)[6]



To a solution of **4b** (692 mg, 2.90 mmol, 1.0 equiv.) in THF (29 mL) were added TBAF (1 M in THF, 5.8 mL, 2.0 equiv.) and the mixture was stirred at room temperature for 1 h. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with EtOAc. The combined organic

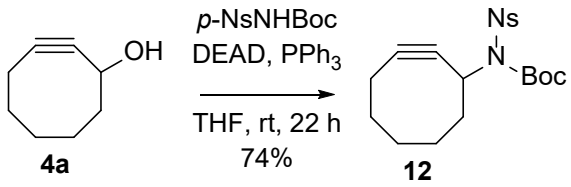
extracts were washed with a saturated aqueous solution of NH_4Cl and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 2:1) to afford **4a** (328 mg, 2.64 mmol, 91%) as a colorless oil.

Characterization data were in accordance with the literature.[6]

^{1}H NMR($CDCl_3$, 400 MHz): δ 4.46 (1H, br), 2.30-2.10 (3H, m), 1.99-1.89 (3H, m), 1.74-1.50 (5H, m)

^{13}C NMR($CDCl_3$, 100 MHz): δ 99.8, 94.1, 64.7, 45.3, 34.4, 29.7, 25.9, 20.7

tert-Butyl *N*-cyclooct-2-yn-1-yl-*N*-((4-nitrophenyl)sulfonyl)carbamate (**12**)



To a solution of **4a** (841 mg, 6.77 mmol, 1.0 equiv.) in THF (27 mL) were added *p*-NsNHBoc (2.57 g, 8.50 mmol, 1.25 equiv.) and PPh_3 (2.31 g, 8.80 mmol, 1.3 equiv.), and the solution was cooled to 0°C. Then, DEAD (2.2 M in toluene, 3.8 mL, 1.25 equiv.) was added, and the solution was warmed to room temperature overnight. The solvent was removed, and the crude mixture was purified column chromatography on silica gel (hexane/ethyl acetate = 40:1 to 10:1) to afford **12** (2.16 g, 5.29 mmol, 78%) as white solids. mp: 154.3-155.1℃

R_f = 0.42 (hexane/ethyl acetate = 4/1)

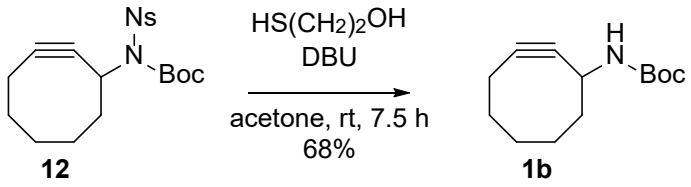
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (2H, d, *J* = 8.8 Hz), 8.17 (2H, d, *J* = 8.8 Hz), 5.40-5.30 (1H, m), 2.51 (1H, q, *J* = 11.6 Hz), 2.35-2.30 (2H, m), 2.20-2.10 (4H, m), 1.80-1.70 (1H, m), 1.41 (9H, s), 1.40-1.30 (1H, m), 1.25-1.15 (1H, m)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2, 150.0, 145.8, 129.1, 123.9, 101.1, 88.8, 85.4, 53.1, 41.8, 34.6, 28.9, 28.8, 28.0, 20.7

IR($CHCl_3$) cm^{-1}: 3685, 3573, 3107, 3035, 2981, 2933, 2858, 2218, 1732, 1606, 1533

Anal. Calcd. for $C_{19}H_{24}N_2O_6S$: C, 55.87; H, 5.92; N, 6.86. found: C, 55.17; H, 5.92; N, 6.81.

tert-Butyl N-cyclooct-2-yn-1-ylcarbamate (**1b**)



To a solution of **12** (1.56 g, 3.82 mmol, 1.0 equiv.) in acetone (13 mL) were added 2-mercaptoethanol (0.53 mL, 7.64 mmol, 2.0 equiv.) and DBU (1.14 mL, 7.64 mmol, 2.0 equiv.), and the mixture was stirred at room temperature for 1 h. The solvent was removed, and the crude mixture was purified column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford **1b** (584 mg, 2.62 mmol, 68%) as white solids. mp: 77.7-78.1 ℃

R_f = 0.5 (hexane/ethyl acetate = 4/1)

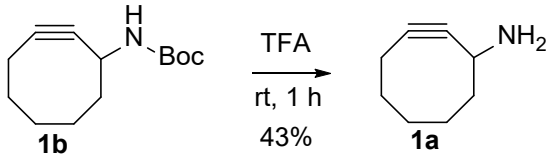
^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.70 (1H, brs), 4.44 (1H, brs), 2.25-2.10 (3H, m), 1.90-1.40 (7H, m), 1.43 (9H, s)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.7, 98.5, 92.2, 79.5, 45.3, 43.5, 34.4, 29.8, 28.3, 26.8, 20.6

IR($CHCl_3$) cm^{-1}: 3689, 3597, 3450, 3016, 2931, 2854, 2366, 2316, 2216, 1707, 1604

HRMS (DART+) *m/z* calcd for $C_{13}H_{22}NO_2$ [$(M+H)^+$]: 224.16505, found 224.16578

Cyclooct-2-yn-1-amine (**1a**)



A round-bottom flask was charged with **1b** (200 mg, 0.896 mmol, 1.0 equiv.) and TFA (1mL), and the mixture was stirred at room temperature for 1 h. The reaction mixture was basified to pH 11 with 2 M NaOH solution, and extracted with DCM. The combined organic extracts were washed with brine, dried over anhydrous K_2CO_3, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexane/isopropylamine = 20:1) to afford **1a** (48 mg, 0.39 mmol, 43%). Further purification of **1a** (48 mg, 0.39 mmol) by Kugelrohr distillation (150 - 160 ℃, 45 mm Hg) gave **1a** (27 mg, 0.22mmol) as a colorless oil.

R_f = 0.38 (hexane/isopropyl amine = 10/1)

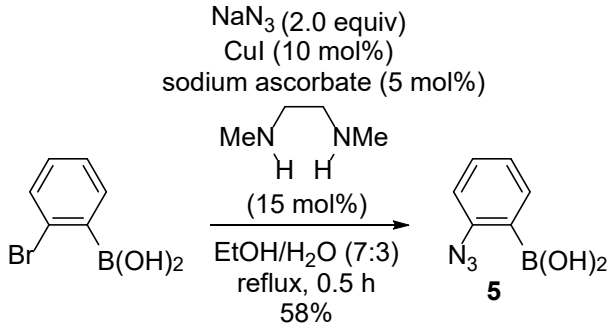
^{1}H NMR($CDCl_3$, 400 MHz): δ 3.70-3.65 (1H, m), 2.25-2.10 (3H, m), 1.95-1.70 (5H, m), 1.60-1.40 (4H, m)

^{13}C NMR($CDCl_3$, 100 MHz): δ 96.4, 95.7, 46.2, 46.1, 34.7, 29.9, 27.0, 20.7

IR($CHCl_3$) cm^{-1}: 3739, 3681, 3635, 3435, 3010, 2935, 2854, 2382, 2301, 1655, 1604, 1562, 1514

HRMS(DART+) *m/z* calcd for $C_8H_{14}N$ [$(M+H)^+$]: 124.11262, found 124.11220

2-Azidophenylboronic acid (**5**)



2-Bromophenylboronic acid (500 mg, 2.49 mmol, 1.0 equiv.), NaN_3 (324 mg, 4.98 mmol, 2.0 equiv.), sodium ascorbate (33 mg, 0.374 mmol, 5 mol%), CuI (47 mg, 0.249 mmol, 10 mol%), *N,N'*-dimethylethylenediamine (33 mg, 0.374 mmol, 15 mmol), EtOH (3.5 mL) and H_2O (1.5 mL) were introduced into a two-necked round bottom flask. The reaction mixture was refluxed for 0.5 h. The mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 4:1) to afford **5** (238 mg, 1.46 mmol, 58%) as white solids.

mp: 82.1-82.6 °C ;

R_f = 0.53 (hexane/ethyl acetate = 1/1)

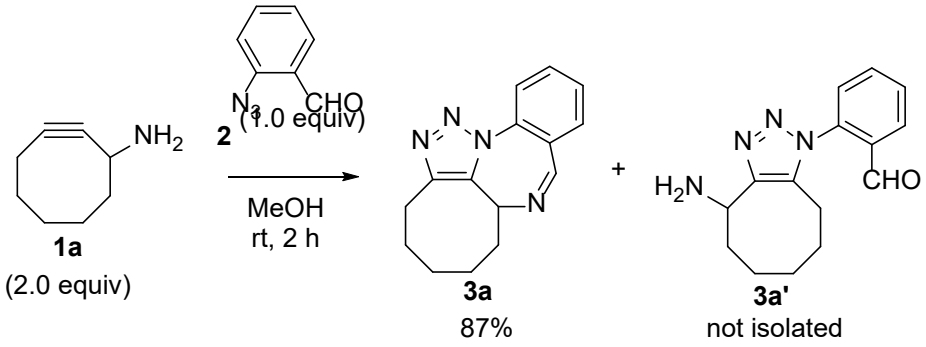
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (1H, d, *J* = 6.8 Hz), 7.54-7.50 (1H, m), 7.23-7.18 (2H, m), 5.68 (2H, s)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 137.2, 132.7, 124.9, 117.3

IR (nujol) cm^{-1}: 2125, 1587, 1566, 1155, 1117, 1012

Anal. calcd for $C_6H_6BN_3O_2$: C, 44.23; H, 3.71; N, 25.79, found C, 43.43; H, 3.76; N, 23.11

5. AAC of 1a and 2 to 3a



To a solution of **1a** (27 mg, 0.218 mmol, 2.0 equiv.) in MeOH (2.2 mL) was added **2** (16 mg, 0.109 mmol, 1.0 equiv.), and the mixture was stirred at room temperature for 2 h. The solvent was removed, and the crude mixture was purified column chromatography on silica gel (hexane/ethyl acetate = 2:1) to afford **3a** (24 mg, 95.1 μmol, 87%) as yellow solids.

mp: 137.8-138.2 °C

R_f = 0.23 (hexane/ethyl acetate = 1/1)

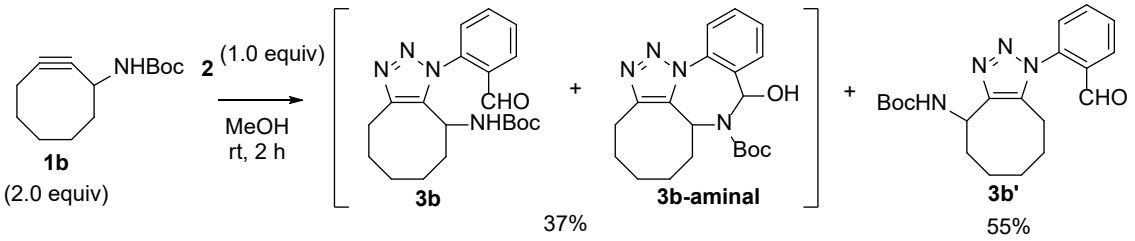
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 (1H, s), 8.18 (1H, d, *J* = 8.0 Hz), 7.68 (1H, t, *J* = 7.6 Hz), 7.59-7.53 (2H, m), 4.28 (1H, d, *J* = 10.4 Hz), 3.18-3.10 (2H, m), 2.80-2.60 (1H, m), 2.45-2.40 (1H, m), 2.10-2.00 (1H, m), 1.90-1.60 (3H, m), 1.55-1.45 (2H, m)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.5, 142.5, 137.4, 135.1, 132.2, 130.3, 128.1, 124.9, 122.6, 54.59, 30.7, 26.9, 24.8, 24.4

IR ($CHCl_3$) cm^{-1}: 3668, 3056, 2989, 2937, 2860, 2472, 2370, 1718, 1630

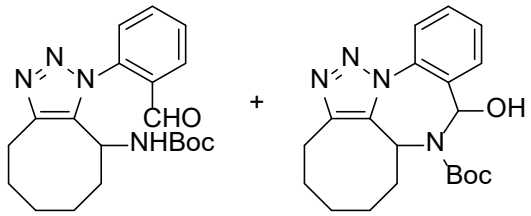
HRMS (DART+) *m/z* calcd for $C_{15}H_{17}N_4$ [$(M+H)^+$]: 253.14532, found 253.14503

6. AAC of 1b and 2 to 3b and 3b'



To a solution of **1b** (49 mg, 0.218 mmol, 2.0 equiv.) in MeOH (2.2 mL) was added **2** (16 mg, 0.109 mmol, 1.0 equiv.), and the mixture was stirred at room temperature for 2 h. The solvent was removed, and the crude mixture was purified column chromatography on silica gel (hexane/ethyl acetate = 4:1 to 2:1) to afford a mixture of **3b** and **3b-aminal** (15 mg, 40.5 μmol, 37%) as yellow solids and **3b'** (23 mg, 60.7 μmol, 55%) as white solids.

Compound **3b** and **3b-aminal**



3b **3b-aminal**

Obtained as an inseparable mixture of **3b** and **3b-aminal** (70:30).

mp: 71.2-72.0 °C

R_f = 0.29 (hexane/ethyl acetate = 1/1)

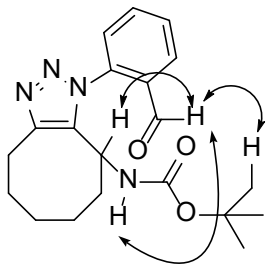
^{1}H NMR (400 MHz, $CDCl_3$, a mixture of **3b** and **3b-aminal**) δ 9.56 (1H, s, **3b**-CHO), 8.07 (1H, d, *J* = 7.2 Hz, **3b**), 8.05 (1H, d, *J* = 7.2 Hz, **3b-aminal**), 7.77 (1H, t, *J* = 7.2 Hz, **3b**), 7.70 (1H, t, *J* = 7.2 Hz, 3b), 7.53 (1H, t, *J* = 7.2 Hz, **3b-aminal**), 7.4-7.3 (1H, m, **3b**), 7.4-7.3 (2H, m, **3b-aminal**), 6.73 (1H, brs, **3b-aminal**), 5.46 (1H, brs, **3b-aminal**), 4.89 (1H, brs, **3b**), 4.58 (1H, brs, **3b**), 3.2-3.1 (2H, m, **3b-aminal**), 3.15-3.05 (2H, m, **3b**), 2.68 (1H, m, **3b-aminal**), 2.1-1.4 (8H, m, **3b**), 2.1-1.4 (8H, m, 3b-aminal), 1.23 (9H, s, **3b**), 1.23 (9H, s, **3b-aminal**)

^{13}C NMR (100 MHz, $CDCl_3$, a mixture of **3b** and **3b-aminal**, the assignments for **3b** are shown) δ 188.3, 153.8, 144.3, 137.7, 136.4, 134.4, 132.2, 130.6, 129.8, 128.0, 79.9, 44.9, 33.2, 28.3, 28.1, 27.7, 24.7, 24.4, 23.6

IR ($CHCl_3$) cm^{-1}: 3676, 3581, 3440, 2979, 2933, 2862, 2374, 1703, 1601

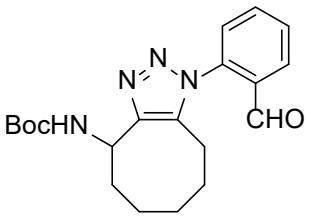
HRMS (DART+) *m/z* calcd for $C_{20}H_{27}N_4O_3$ [$(M+H)^+$]: 371.20831, found 371.21084

NOESY correlations of the aldehyde form **3b** is shown below.



NOESY correlations

Compound **3b'**



3b'

mp: 40.8-41.2 ℃

R_f = 0.34 (hexane/ethyl acetate = 1/1);

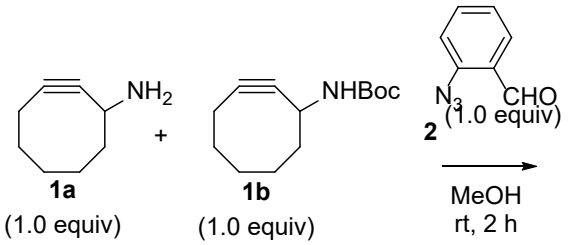
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.57 (1H, s), 8.13 (1H, d, *J* = 7.6 Hz), 7.80 (1H, t, *J* = 7.0 Hz), 7.73 (1H, t, *J* = 7.6 Hz), 7.40 (1H, d, *J* = 7.6 Hz), 5.97 (1H, m), 5.10-5.05 (1H, m), 2.80-2.75 (1H, m), 2.60-2.55 (1H, m), 2.30-2.25 (1H, m), 1.95-1.85 (1H, m), 1.70-1.60 (3H, m), 1.60-1.45 (2H, m), 1.49 (9H, s), 1.32-1.26 (1H, m)

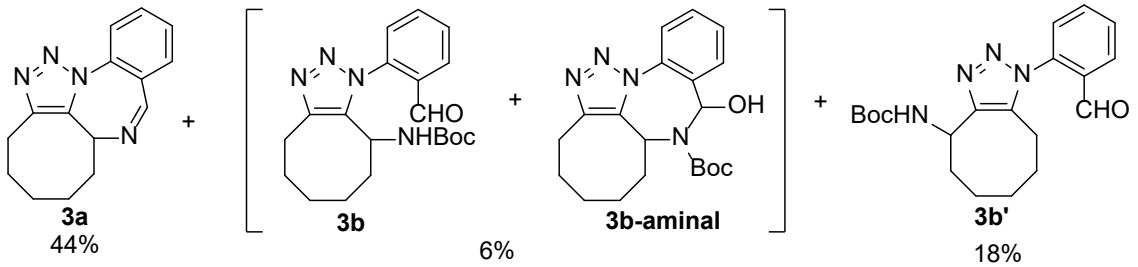
^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.9, 155.5, 144.6, 137.3, 135.5, 134.7, 132.2, 130.8, 129.5, 127.7, 79.5, 46.8, 37.0, 28.4, 27.3, 25.6, 23.4, 21.8

IR($CHCl_3$) cm^{-1}: 3672, 3437, 3010, 2935, 2862, 2756, 2366, 1703, 1599, 1502

HRMS (DART+) *m/z* calcd for $C_{20}H_{27}N_4O_3$ [$(M+H)^+$]: 371.20831, found 371.20896

7. Competitive AAC of 2 with 1a and 1b





3a 44%

3b 6%

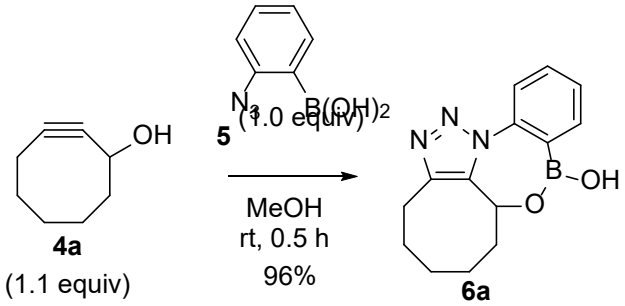
3b-aminal

3b' 18%

To a solution of **1a** (15 mg, 0.12 mmol, 1.0 equiv.) in MeOH (2.5 mL) was added **1b** (27 mg, 0.13 mmol, 1.0 equiv.) and **2** (18 mg, 0.12 mmol, 1.0 equiv.), and the mixture was stirred at room temperature for 2 h. The solvent was removed, and the crude mixture was purified column

chromatography on silica gel (hexane/ethyl acetate = 10:1 to 2:1) to afford **3a** (14 mg, 53.9 μmol, 44%) as yellow solids, a mixture of **3b** and **3b-aminal** (2.9 mg, 7.83 μmol, 6%) as white solids and **3b'** (8.3 mg, 22.4 μmol, 18%) as white solids.

8. AAC of 4a with 5 to 6a



To a solution of **4a** (8 mg, 67.5 μmol, 1.1 equiv.) in MeOH (1.2 mL) was added **5** (10 mg, 61.4 μmol, 1.0 equiv.), and the mixture was stirred at room temperature for 30 min. The solvent was removed, and the crude mixture was purified column chromatography on silica gel (DCM 100% to DCM/MeOH = 99:1) to afford **6a** (17 mg, 65.0 mmol, 96%) as white solids.

mp: 173.3-173.9 °C

R_f = 0.19 (dichloromethane / methanol = 20/1)

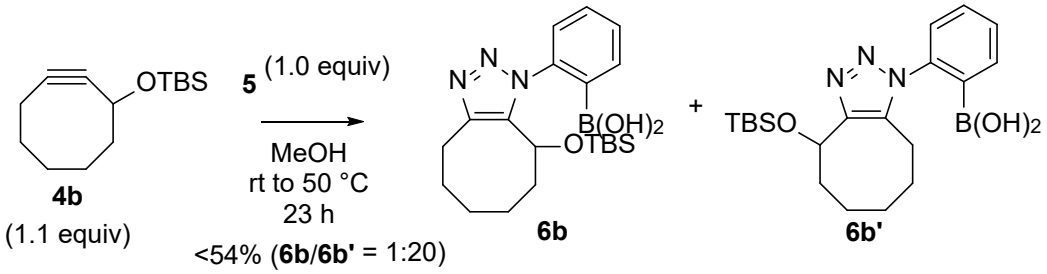
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (1H, d, *J* = 7.6 Hz), 7.92 (1H, d, *J* = 7.6 Hz), 7.67 (1H, t, *J* = 7.2 Hz), 7.47 (1H, t, *J* = 7.6 Hz), 5.09 (1H, d, *J* = 8.0 Hz), 4.95 (1H, br), 3.25-3.16 (1H, m), 3.09-3.05 (1H, m), 2.52-2.45 (1H, m), 2.25-2.15 (1H, m), 1.95-1.35 (6H, m)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 140.8, 135.4, 134.9, 132.8, 128.1, 122.7, 66.5, 30.0, 26.4, 24.7, 23.5

IR (nujol) cm^{-1}: 2723, 1653, 1604, 1568, 1269, 1126, 1082, 1009, 766, 725

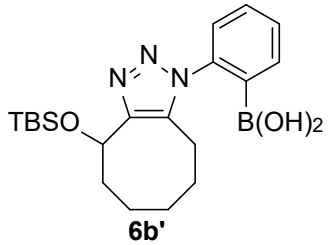
HRMS (DART+) *m/z* calcd for $C_{14}H_{17}BN_3O_2$ [$(M+H)^+$]: 270.14138, found 270.13966

9. AAC of 4b with 5 to 6b and 6b'



To a solution of **4b** (32 mg, 0.135 mmol, 1.1 equiv.) in MeOH (2.5 mL) wa added **5** (20 mg, 0.123

mmol, 1.0 equiv.), and the mixture was stirred for at room temperature 2 h. Then, the solution was warmed to 40 °C for 2 h and to 50 °C for 19 h. The solvent was removed, and the crude mixture was purified column chromatography on silica gel (hexane/ethyl acetate = 20:1 to 10:1) to afford **6b'** (27 mg, 67.2 mmol, 54%) containing some impurities as white solids. The ratio of **6b**/**6b'** was determined by ^{1}H NMR of the crude product.



6b'

mp: 66.9-67.7°C

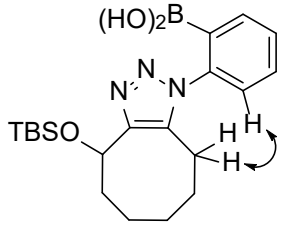
R_f = 0.47 (hexane / ethyl acetate = 1/1)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.51 (2H, m), 7.44-7.42 (2H, m), 5.31-5.30 (1H, m), 3.32-3.24 (1H, m), 2.63-2.59 (1H, m), 2.13-2.08 (1H, m), 1.81-1.78 (4H, m), 1.64-1.59 (2H, m), 1.05-1.00 (1H, m), 0.88 (9H, s), 0.11 (3H, s), −0.06 (3H, s)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.2, 136.4, 134.3, 129.4, 129.4, 125.5, 67.7, 38.5, 28.3, 25.8, 25.1, 20.2, 19.8, 18.1, −4.9, −5.2

IR (nujol) cm^{-1}: 2721, 2675, 1593, 1250, 1165, 1095, 1068, 1024, 768, 729

NOESY correlations of **6b'** are shown below.



NOESY correlations

10. References

1. Minato, M.; Yamamoto, K.; Tsuji, J., *J. Org. Chem.* **1990**, *55* (2), 766.
2. Borrell, M.; Costas, M., *J. Am. Chem. Soc.* **2017**, *139* (36), 12821-12829.
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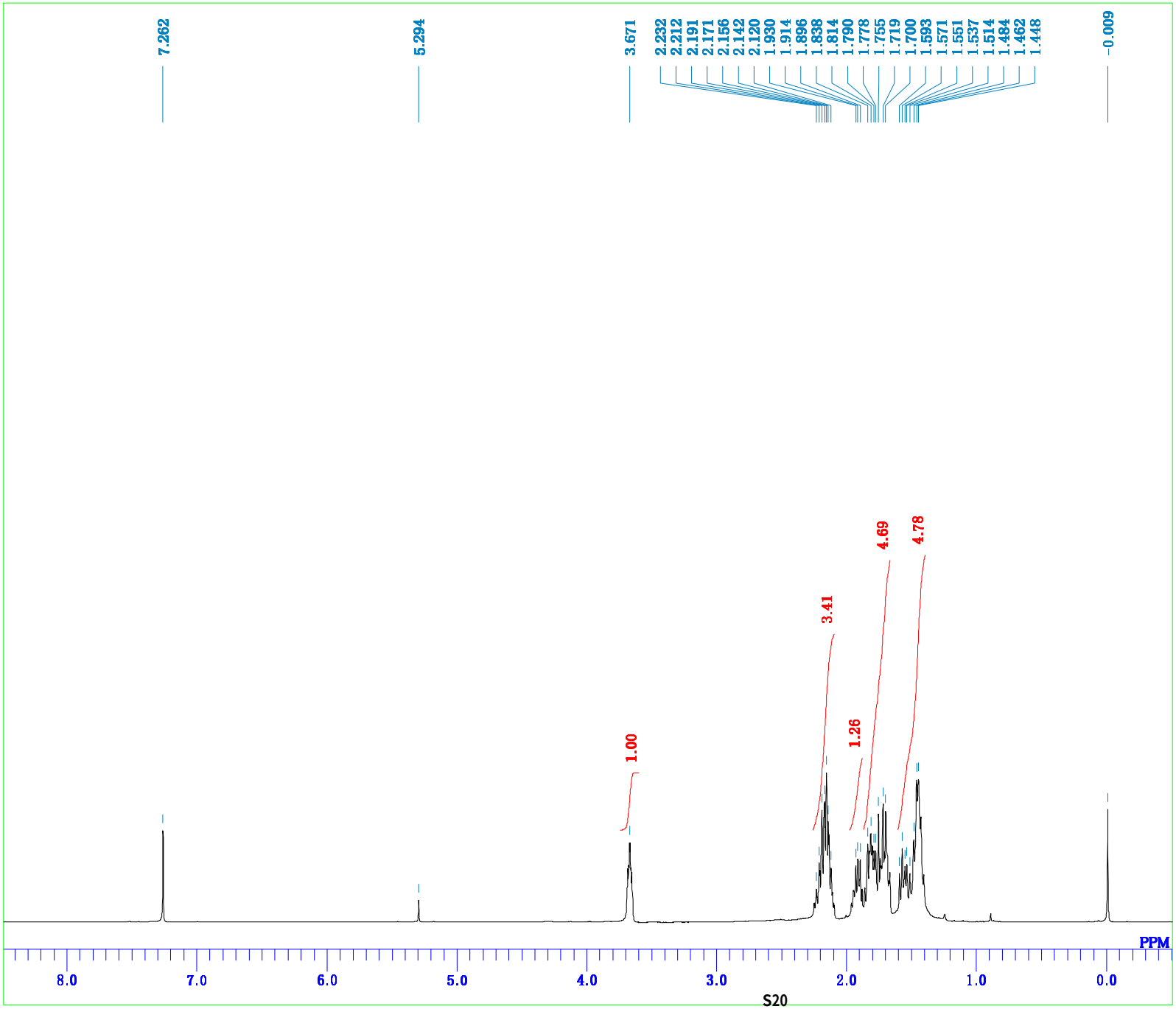
5. Liu, H.; Sun, C.; Lee, N.-K.; Henry, R. F.; Lee, D., *Chem. - Eur. J.* **2012**, *18* (38), 11889.
6. Hagendorn, T.; Braese, S., *Eur. J. Org. Chem.* **2014**, *2014* (6), 1280-1286.

11. ^{1}H and ^{13}C NMR spectra of new compounds



DFILE	RY183-1.als
COMNT	
DATIM	13-12-2023 17:02:33
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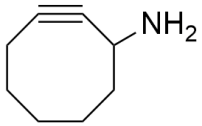
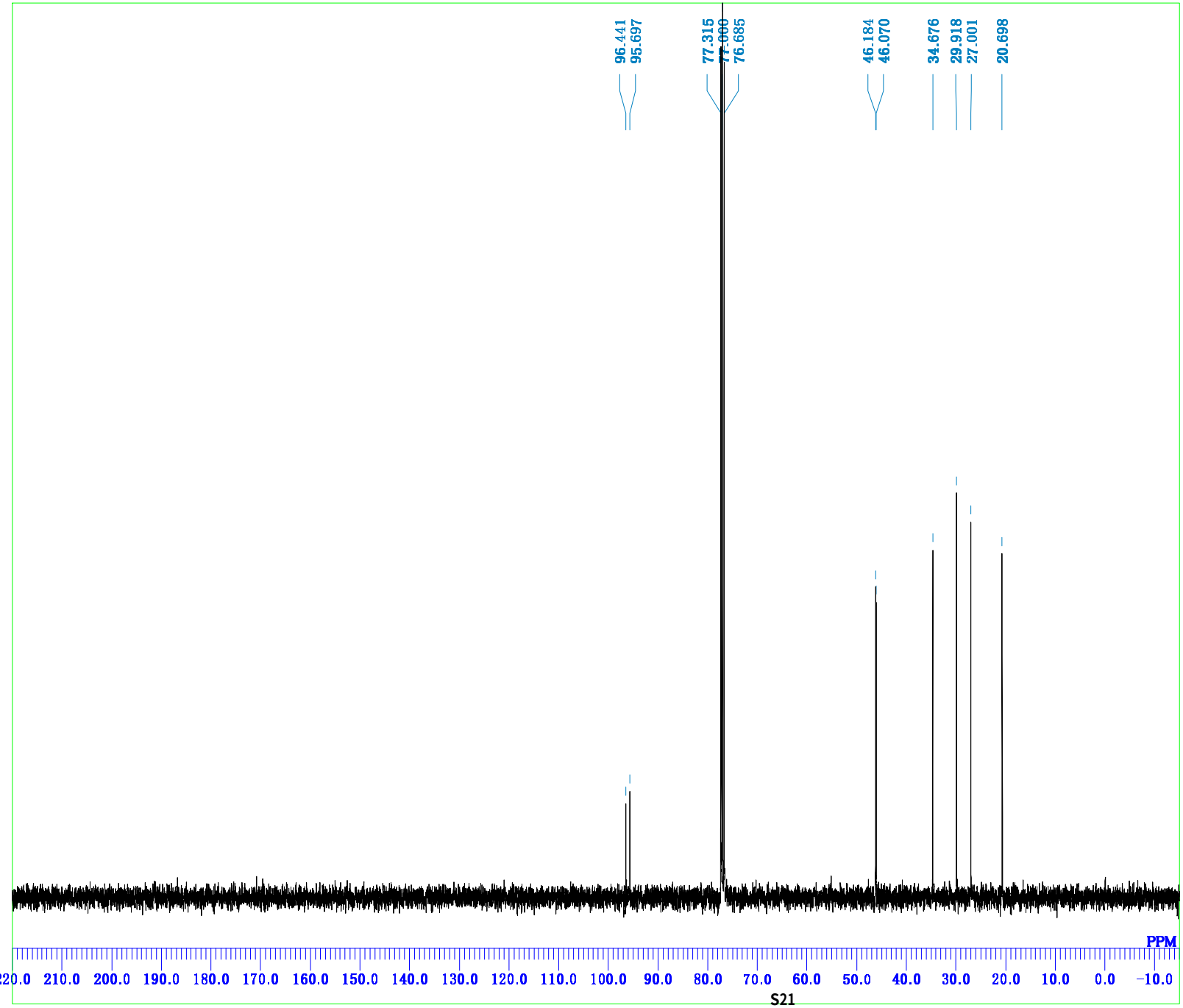
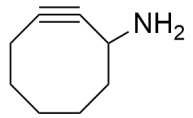
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.40 Hz
RGAIN	34



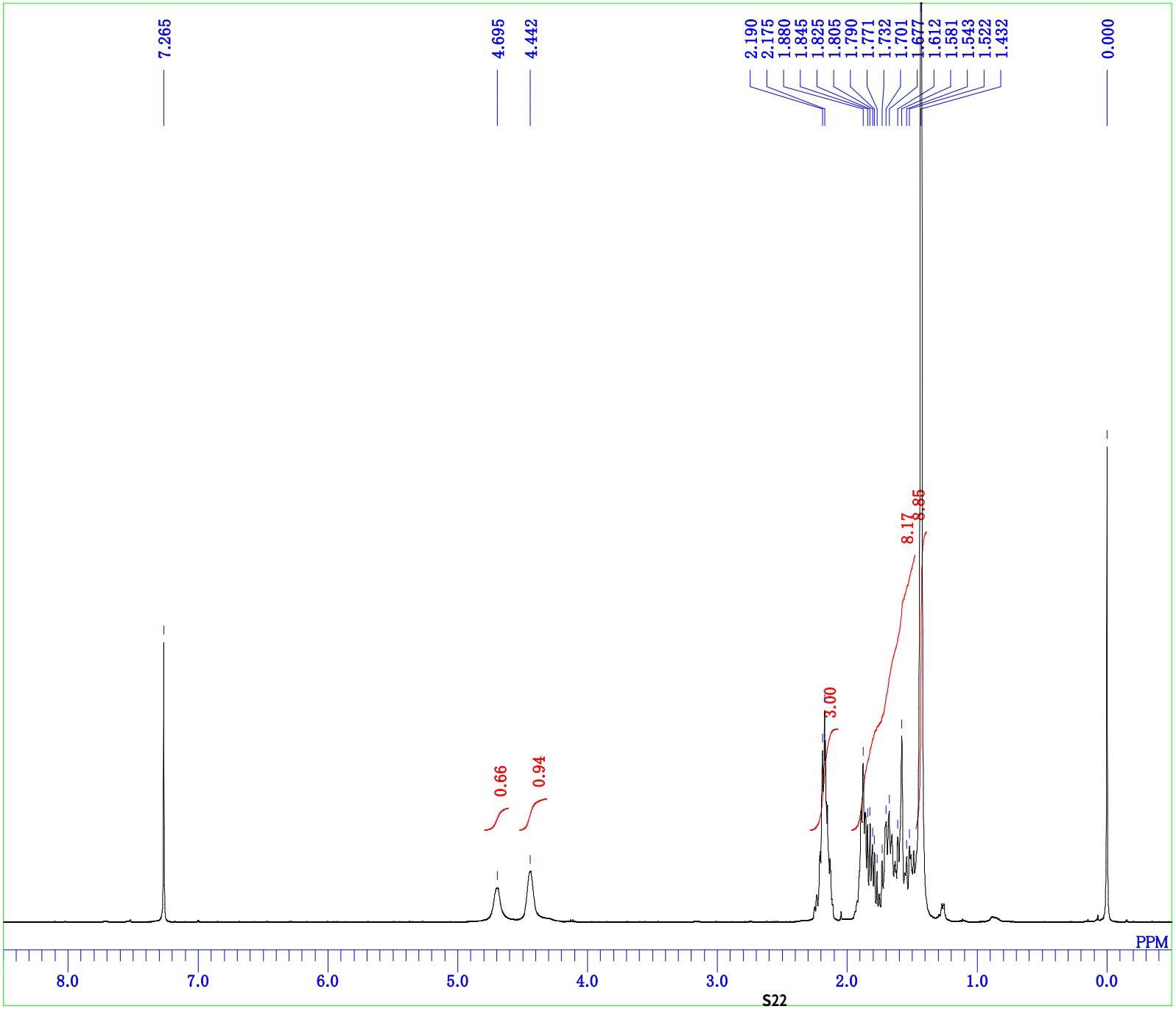
1a



DFILE	RY183 13C-1.als
COMNT	
DATIM	13-12-2023 18:20:46
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	263
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



1a



S22

DFILE	RY cyclooctynyl NHBoc 1H.jdf
COMNT	
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OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	16384
FREQU	7503.00 Hz
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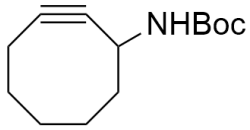
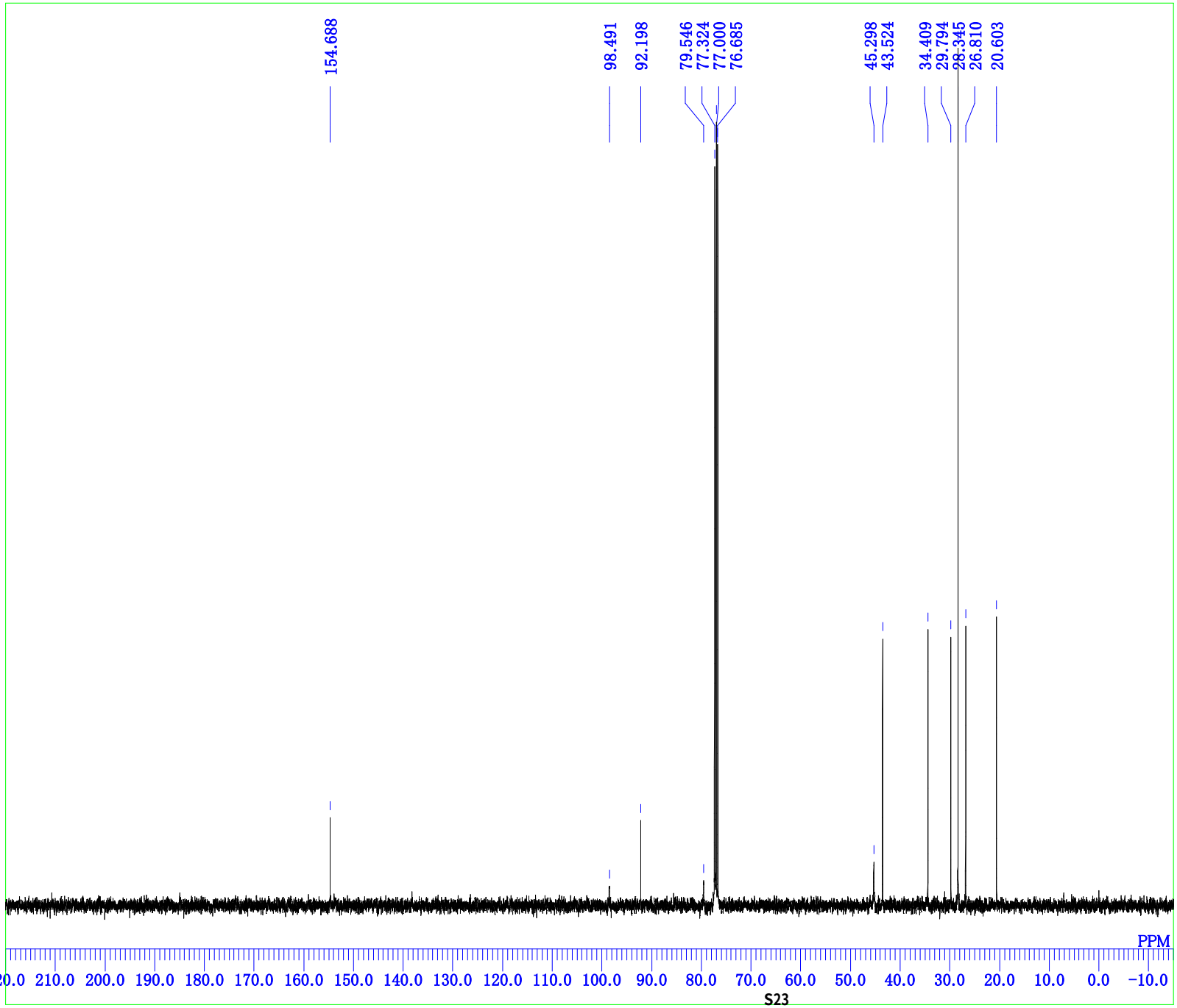
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	44



1b



DFILE	RY cyclooctynyl NHBoc 13C-1.jdf
COMNT	
DATIM	2023-06-26 11:56:28
OBNUC	13C
EXMOD	single_pulse_dec
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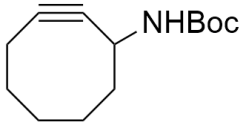
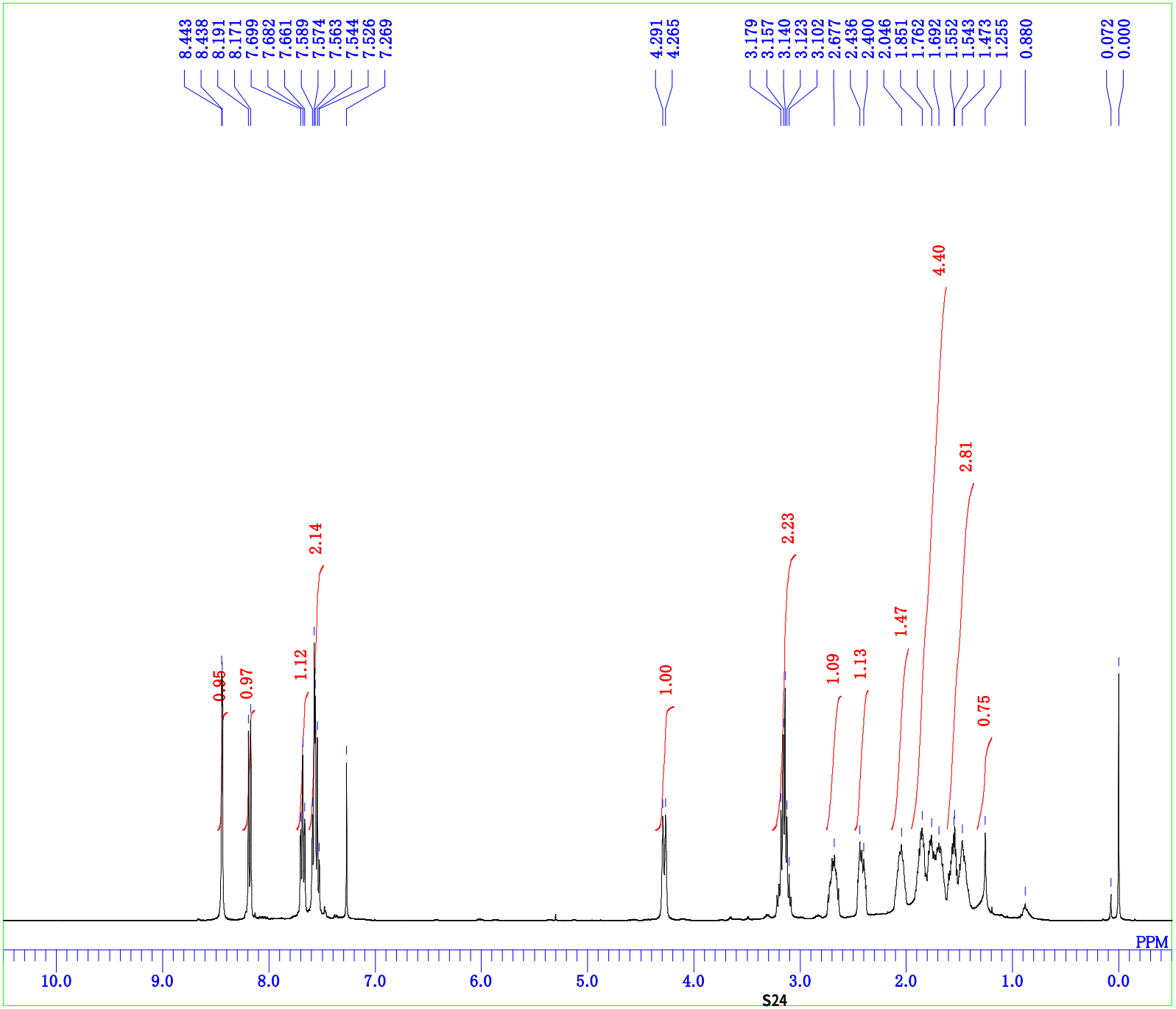
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	563
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.00 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



1b



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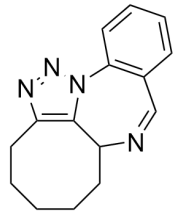
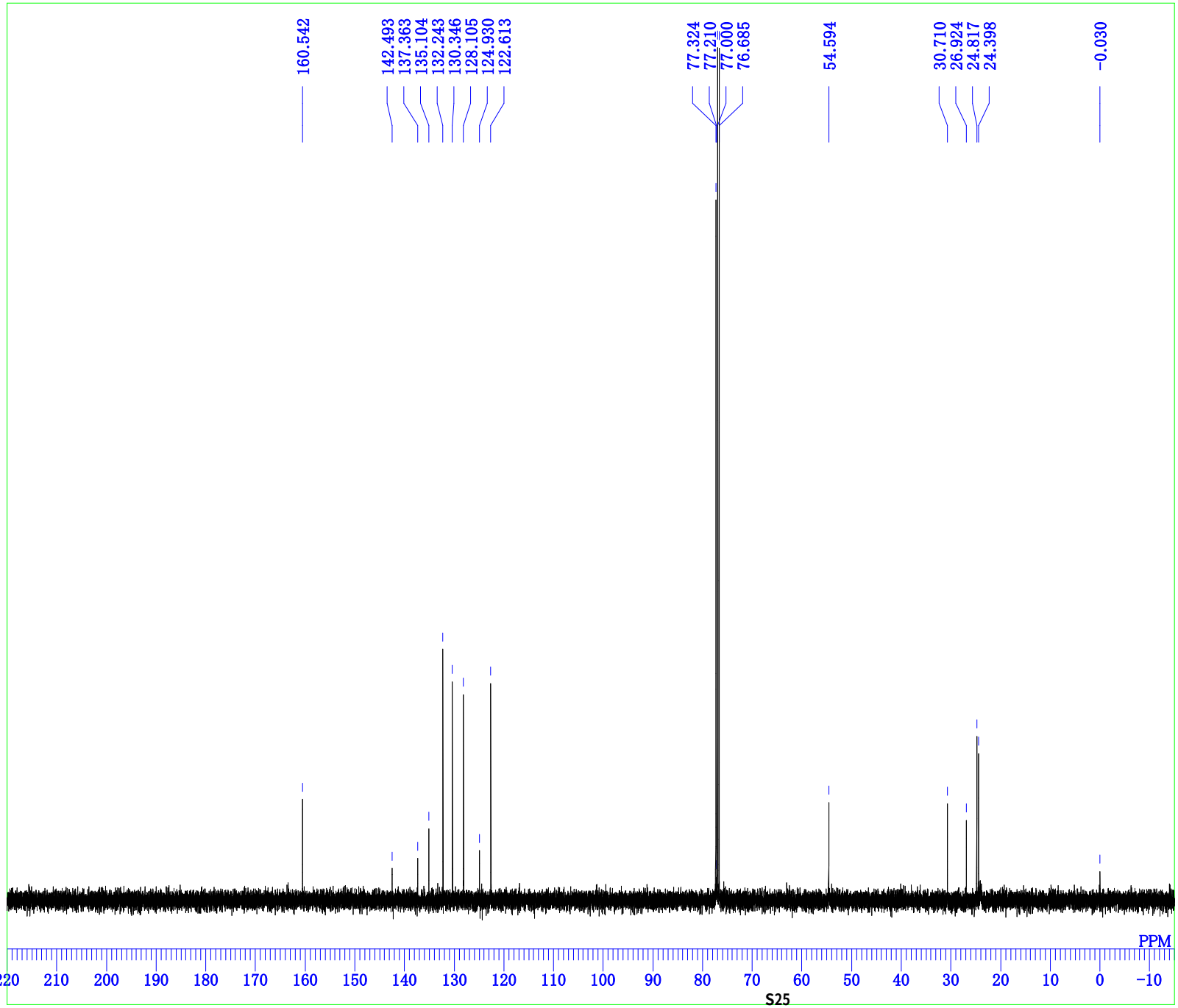
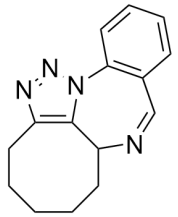
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	40



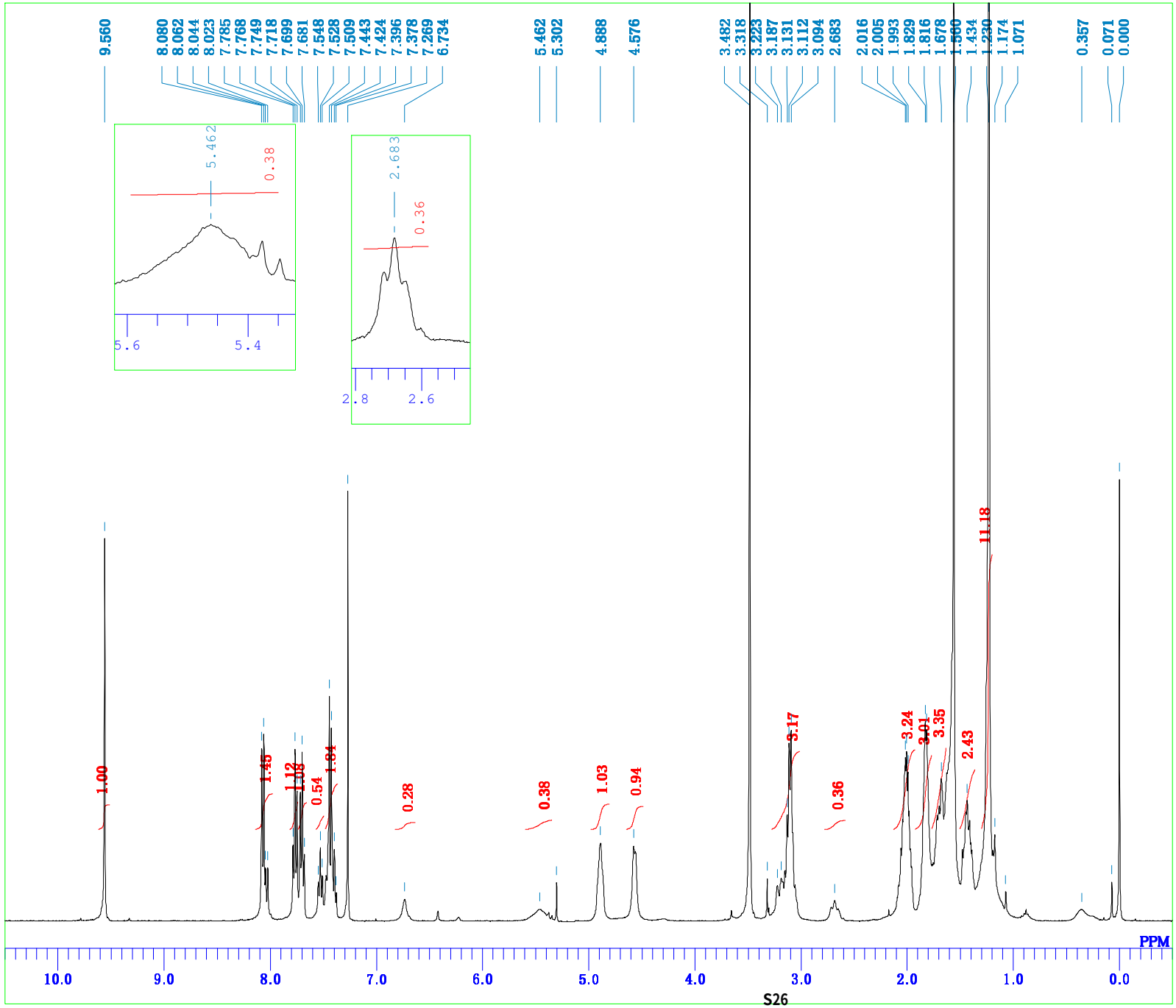
3a



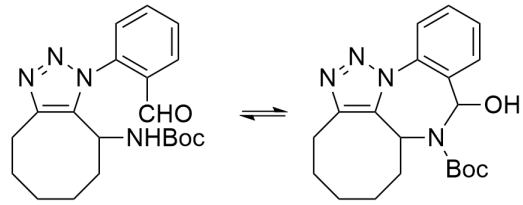
DFILE	RY SPAAC cyclization 13C-1.als
COMNT	
DATIM	2023-06-27 11:31:28
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	474
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.00 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60



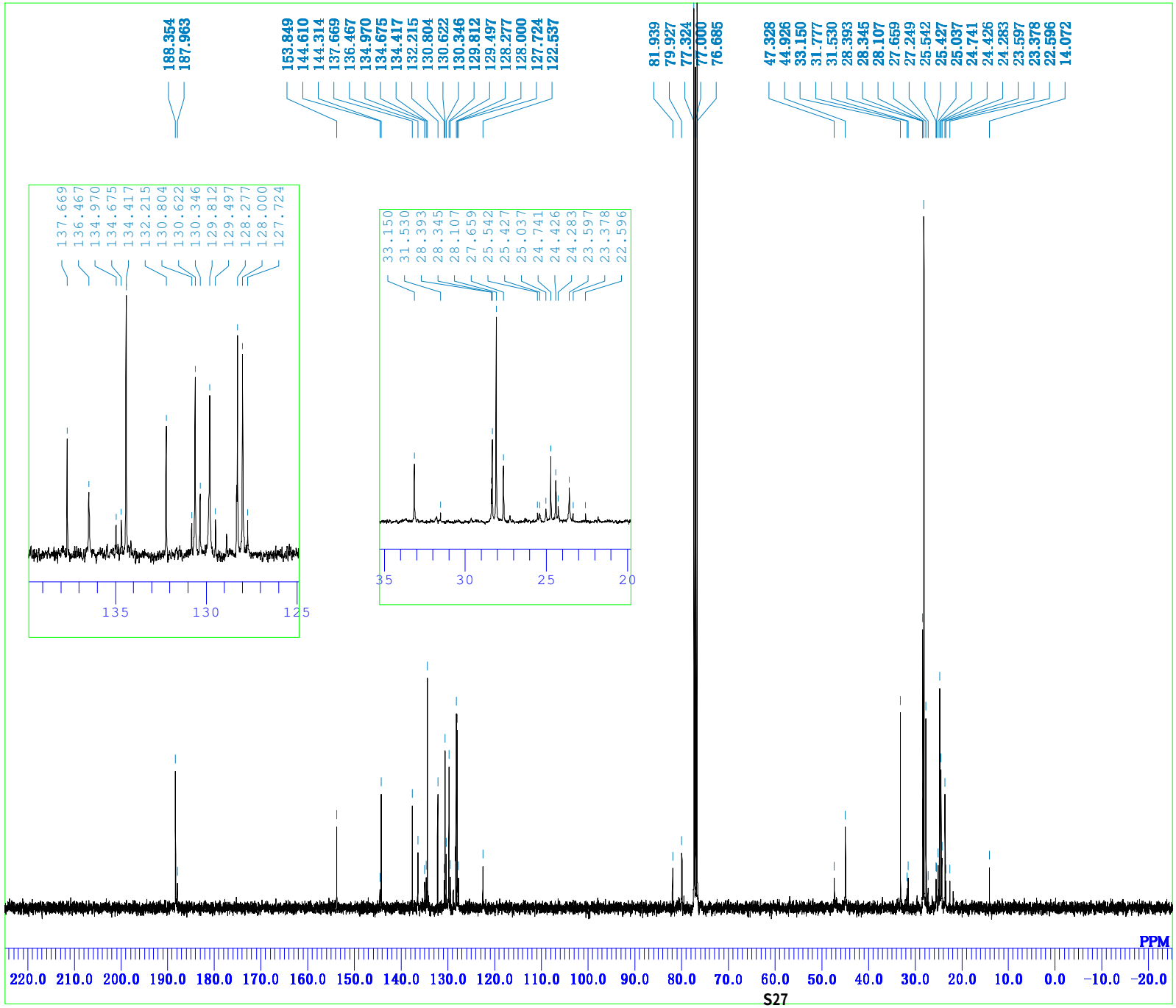
3a



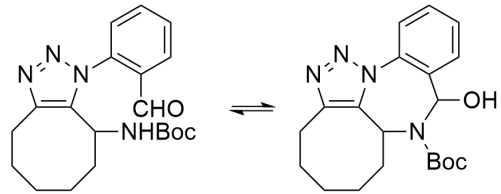
DFILE	RY172 PTLC-m-1.als
COMNT	
DATIM	22-11-2023 12:56:38
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	36



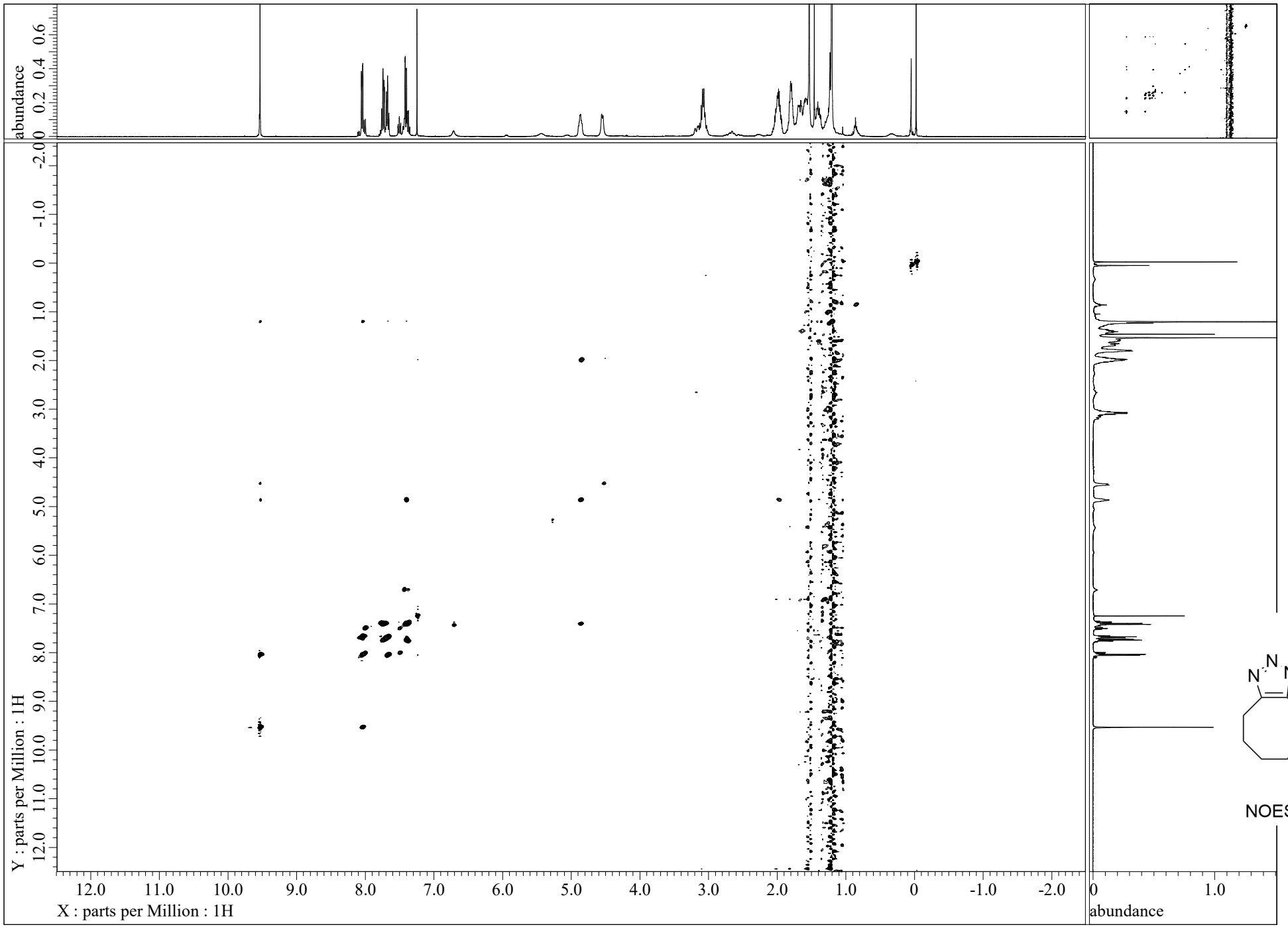
3b **3b-aminal**

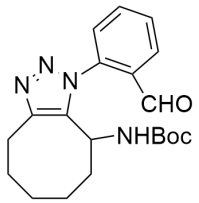


DFILE	RY compound 3b 3b-aminal-1.jdf
COMNT	
DATIM	23-10-2024 09:20:15
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	654
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	23.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



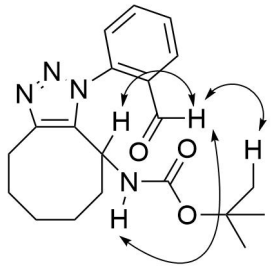
3b **3b-aminal**



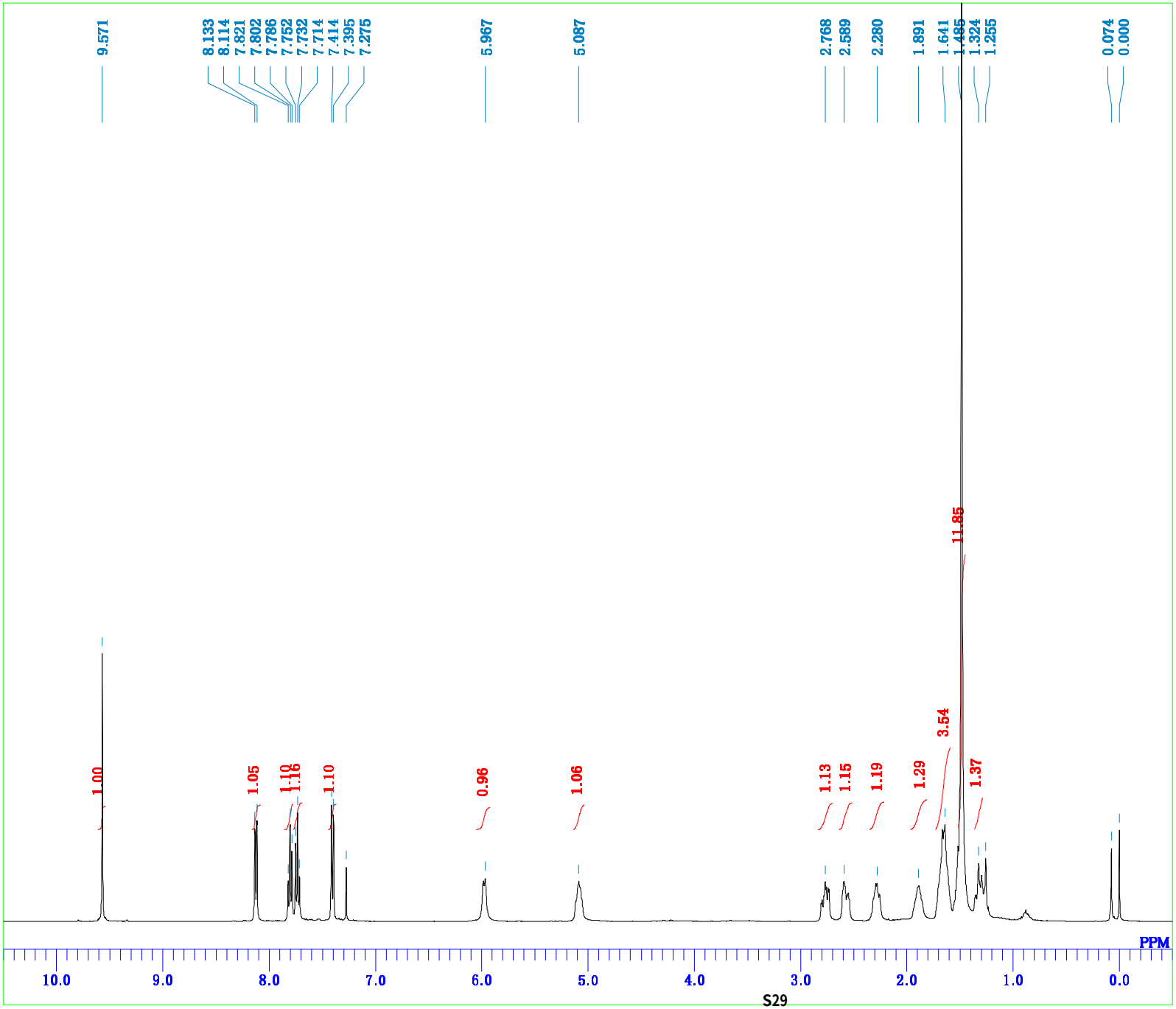


3b

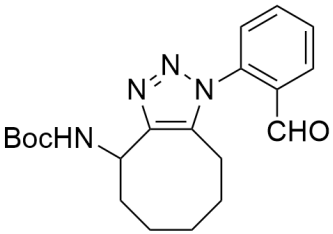
NOESY



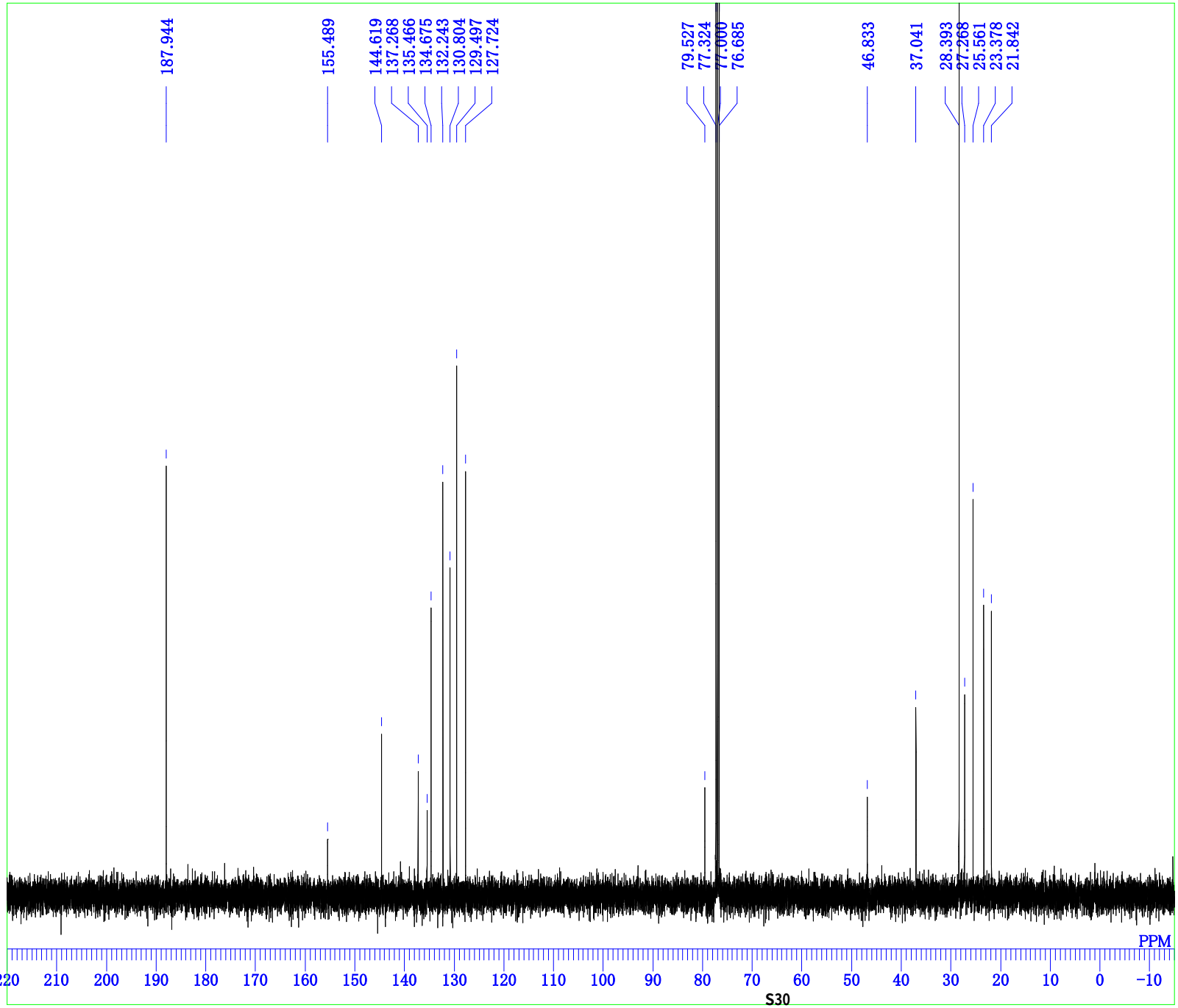
NOESY correlations



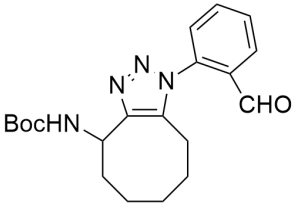
DFILE	RY154fr46-1.jdf
COMNT	
DATIM	20-06-2023 11:16:42
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	16384
FREQU	7503.00 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	22.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	34



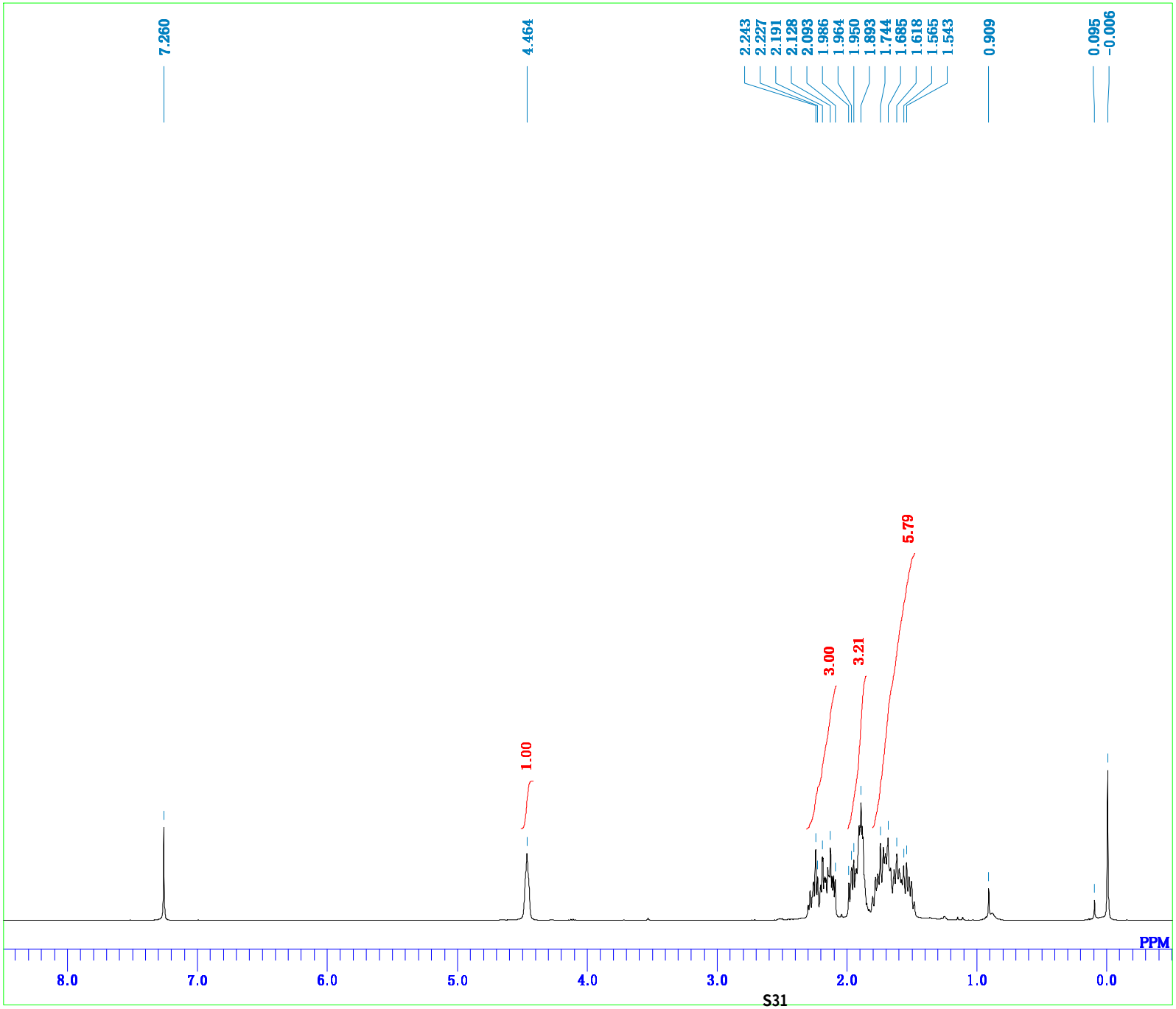
3b'



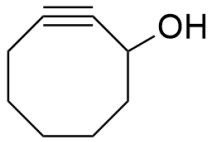
DFILE	RY spaac 1,4-triazole 13C.als
COMNT	
DATIM	2023-06-22 11:36:08
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	356
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.00 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60



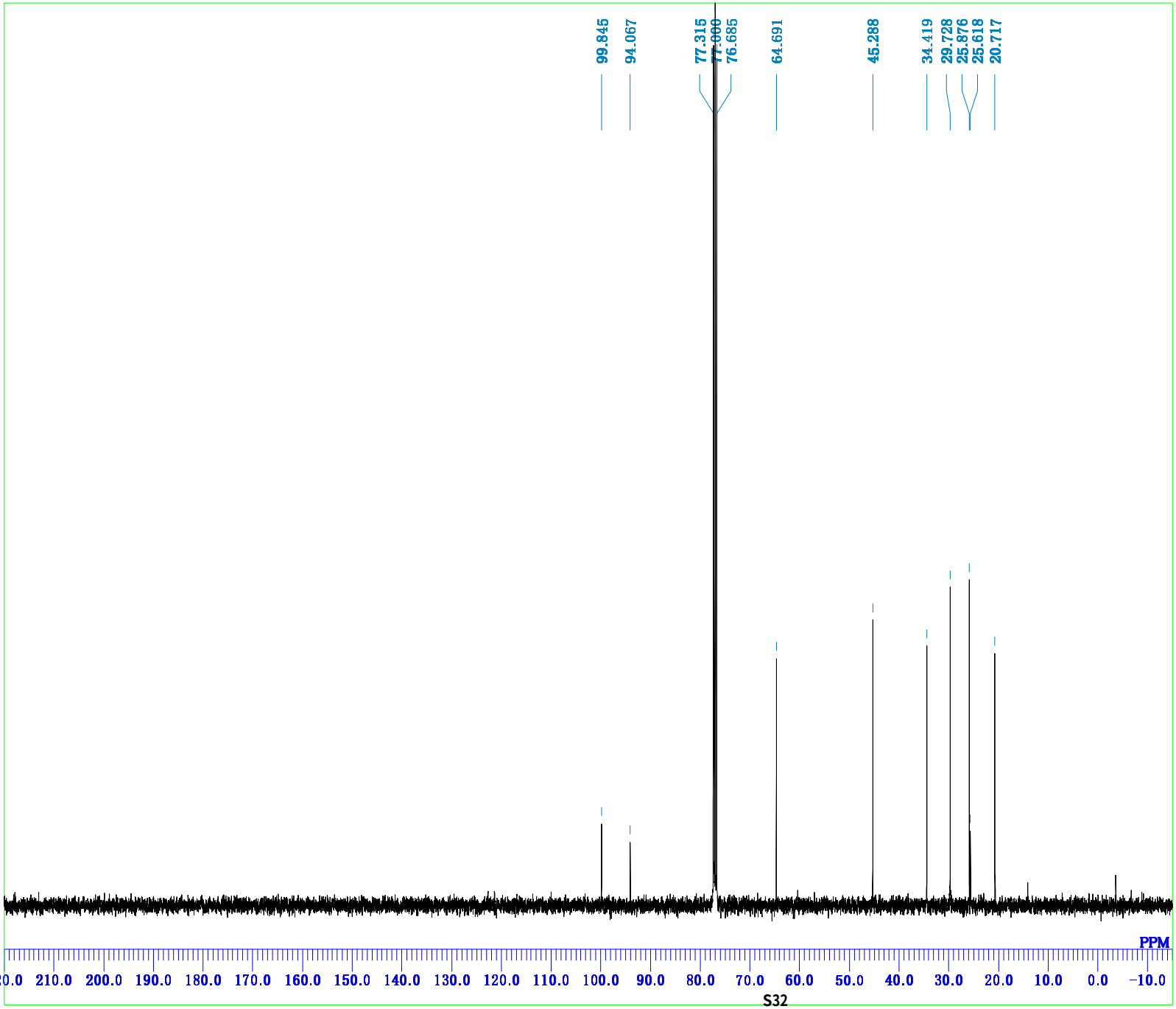
3b'



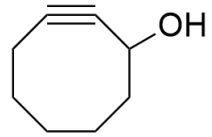
DFILE	RY spaac12.als
COMNT	
DATIM	2023-01-17 08:54:06
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	20.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.40 Hz
RGAIN	44



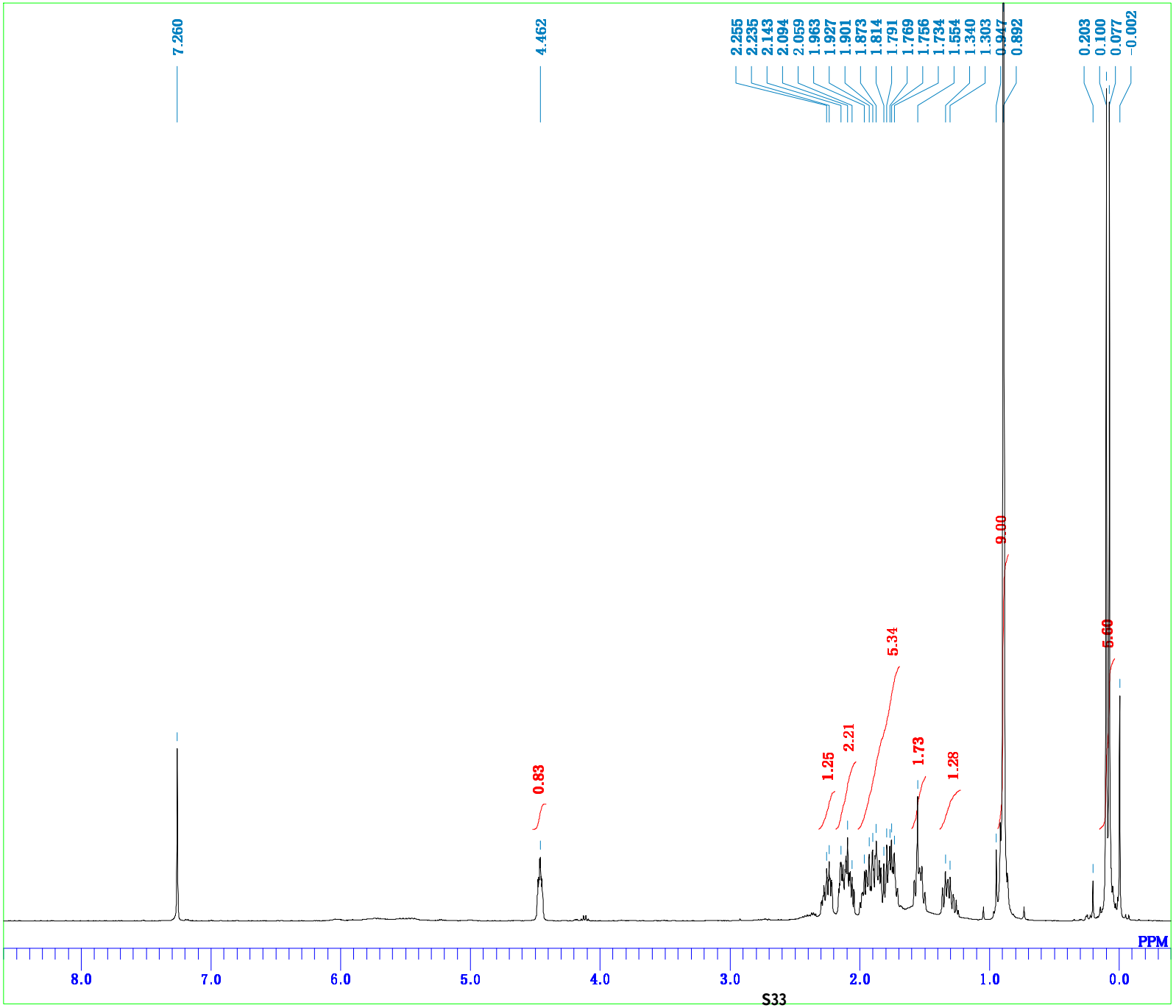
4a



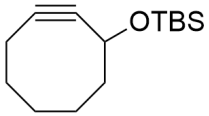
DFILE	RYspaac12 13C.als
COMNT	
DATIM	17-06-2022 13:59:47
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	407
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



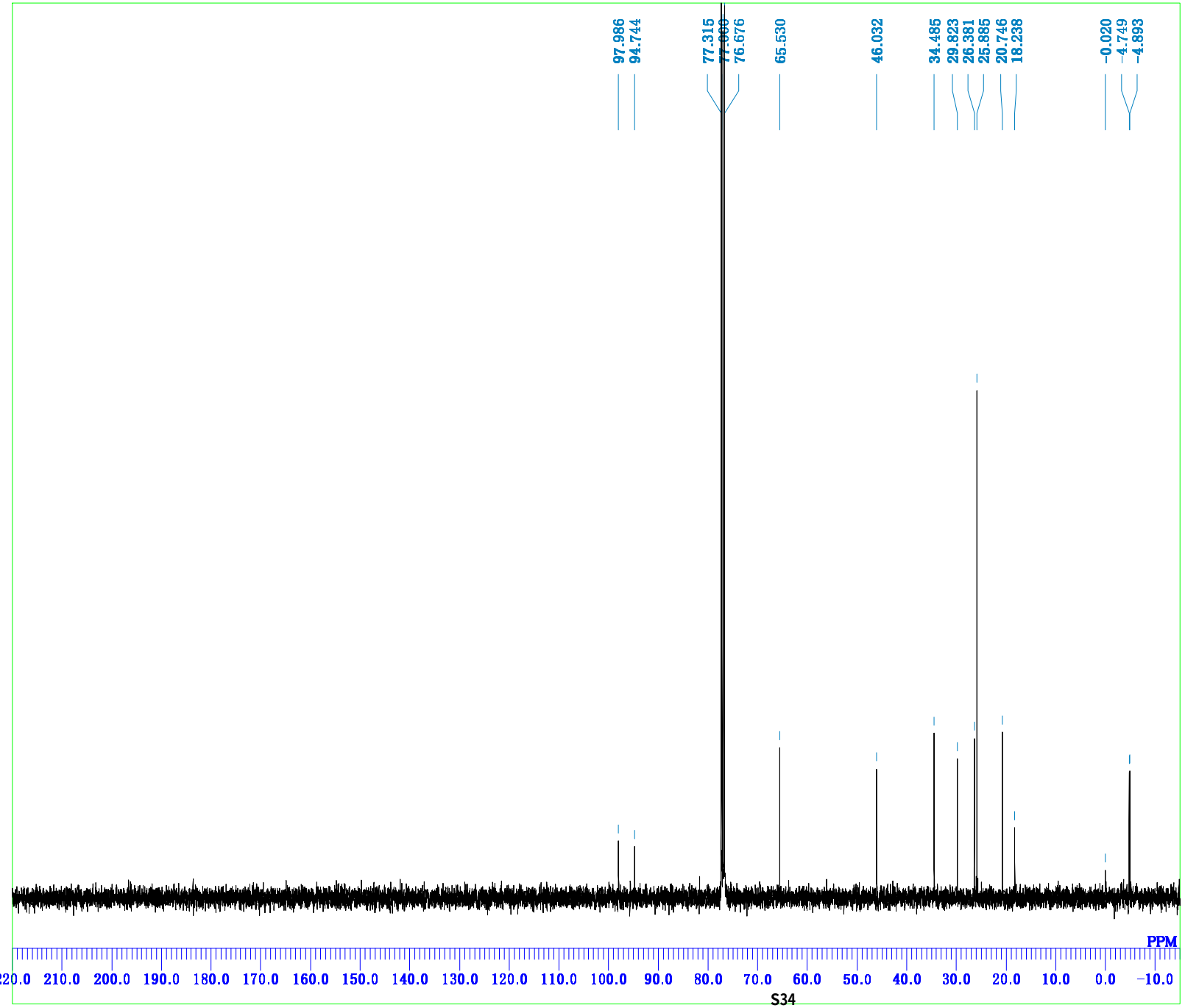
4a



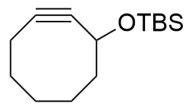
DFILE	RY179-1.als
COMNT	
DATIM	07-12-2023 11:32:08
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.40 Hz
RGAIN	34



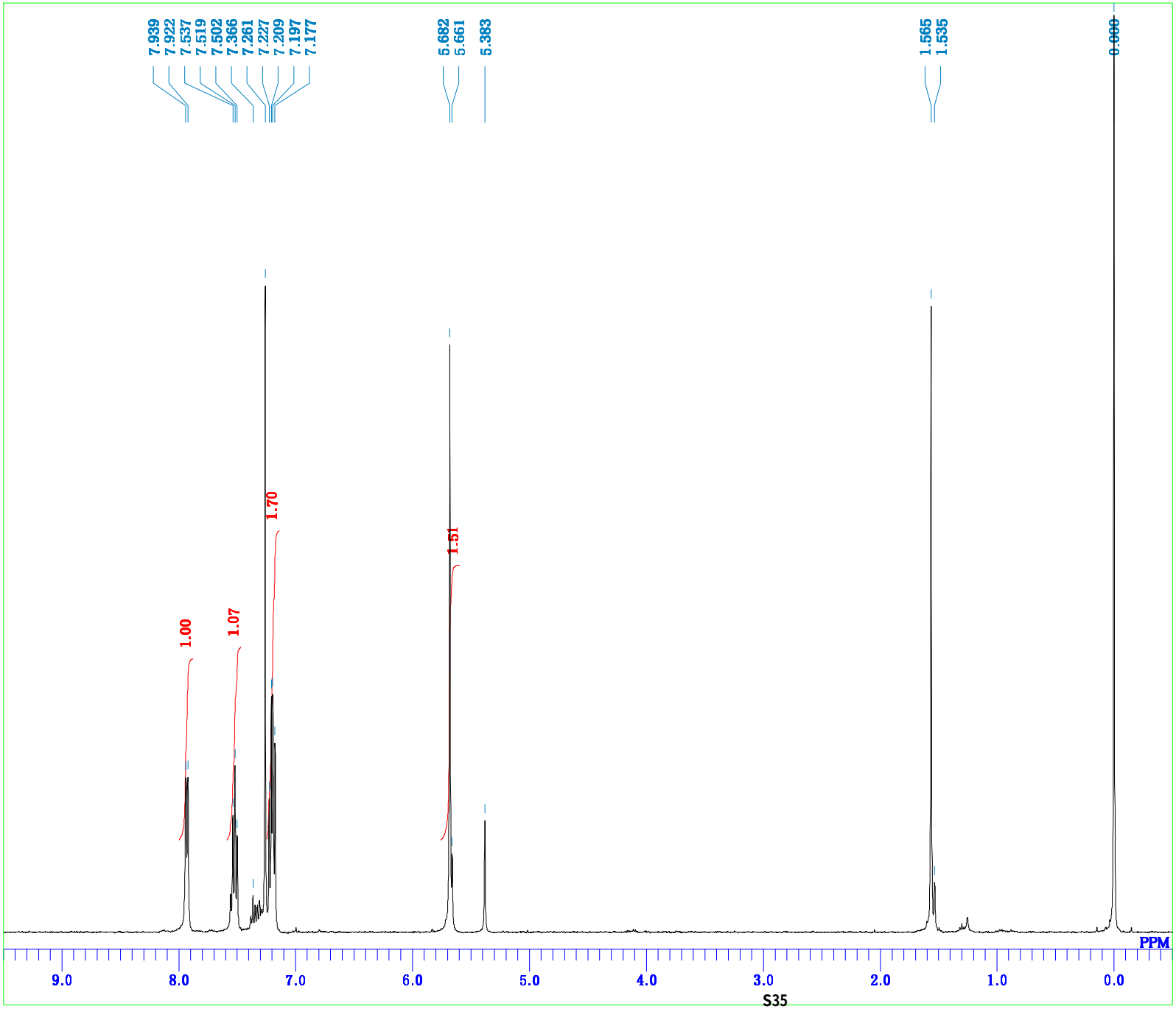
4b



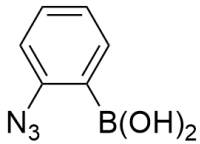
DFILE	RY179 13C-1.als
COMNT	
DATIM	07-12-2023 11:42:38
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	257
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



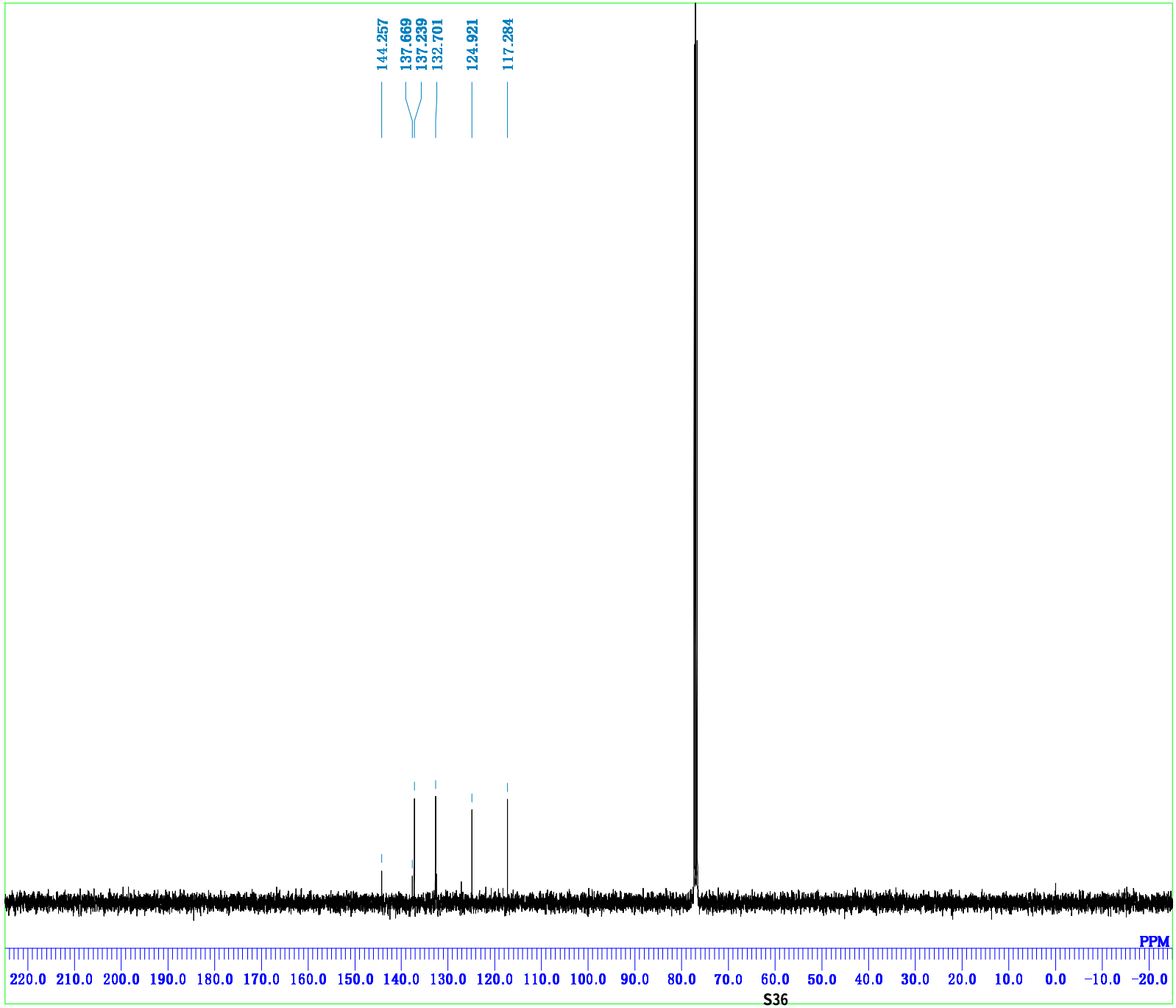
4b



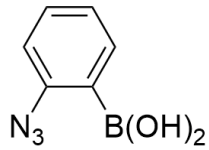
DFILE	RY241-1.als
COMNT	
DATIM	31-05-2024 14:48:27
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	38



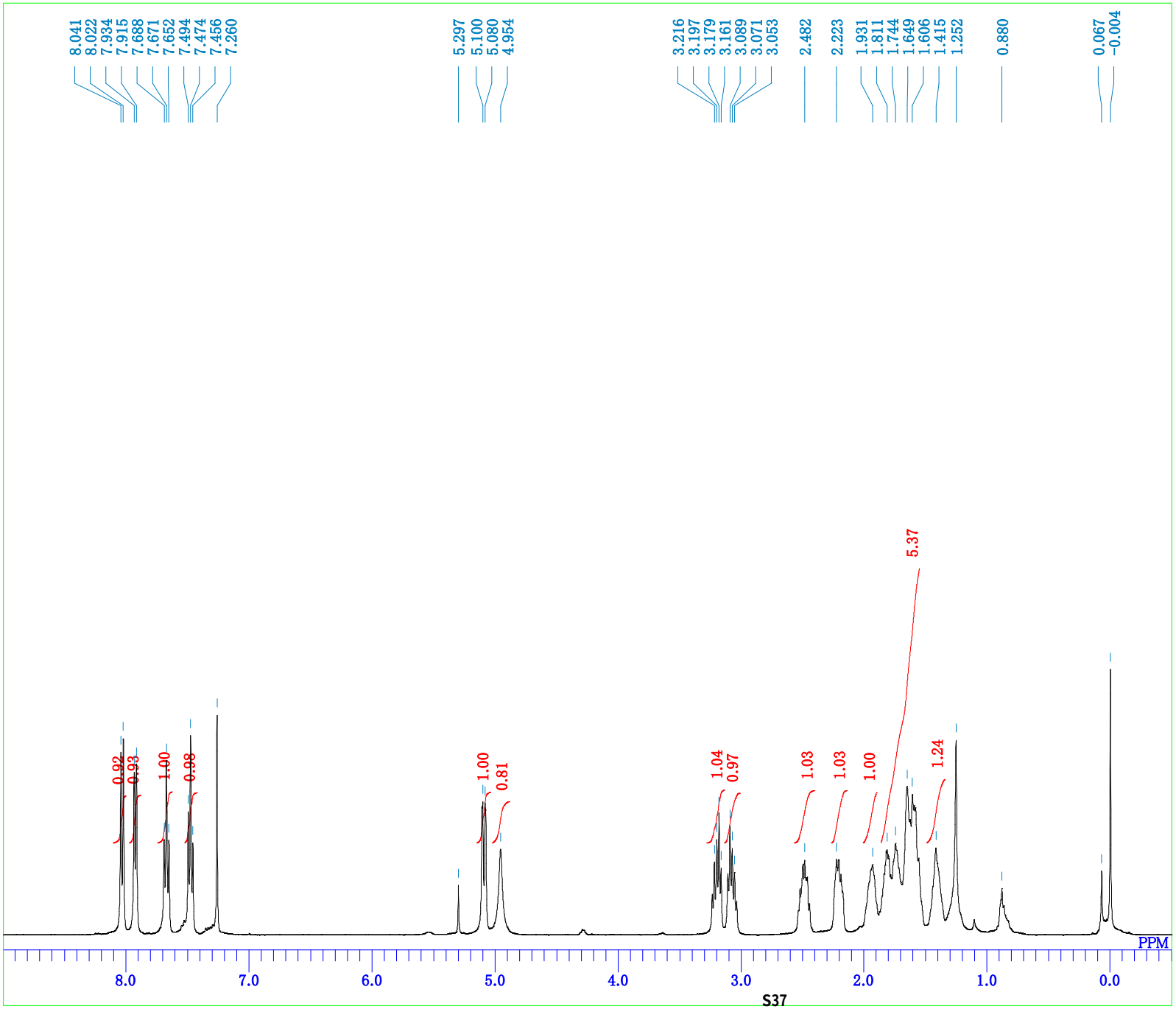
5



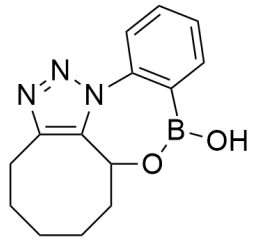
DFILE	RY241 13C-1.als
COMNT	
DATIM	13-06-2024 10:17:08
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	375
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



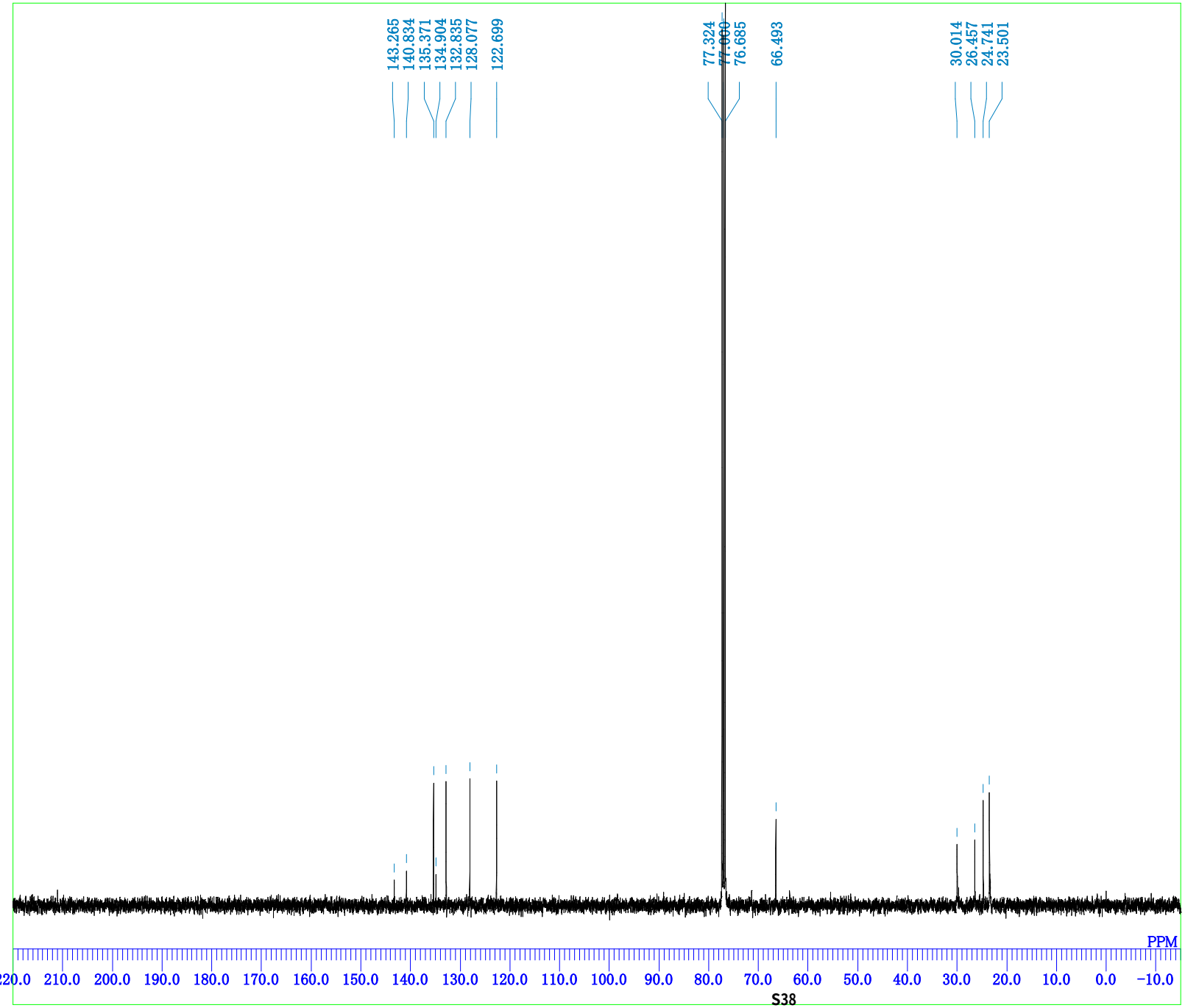
5



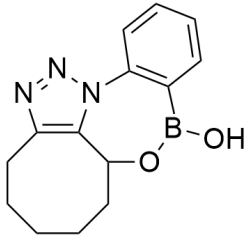
DFILE	RY244-2-1.als
COMNT	
DATIM	14-06-2024 17:23:14
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.40 Hz
RGAIN	34



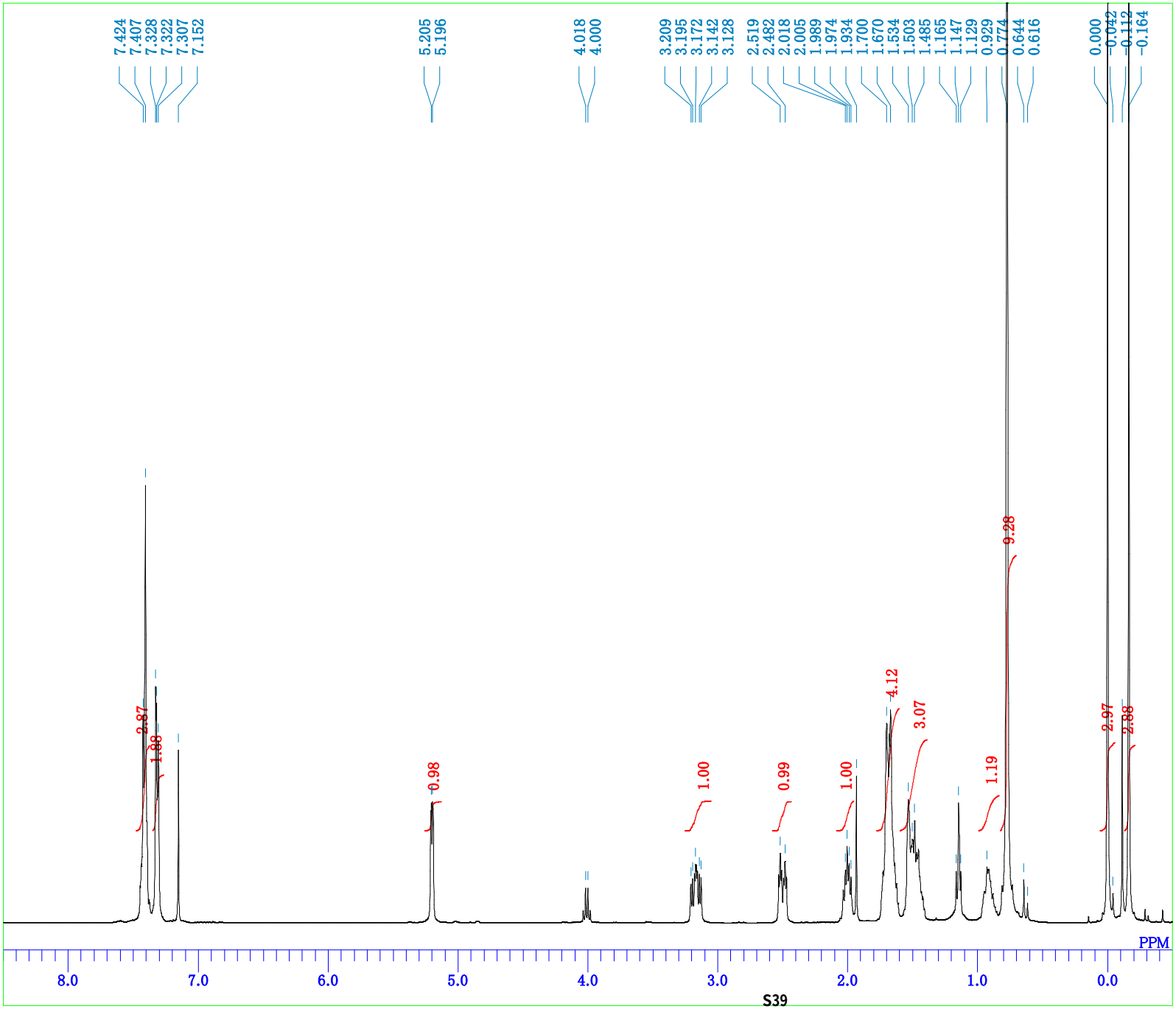
6a



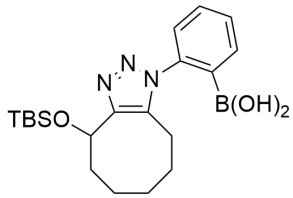
DFILE	RY244-2 13C-1.als
COMNT	
DATIM	14-06-2024 17:48:29
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	650
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



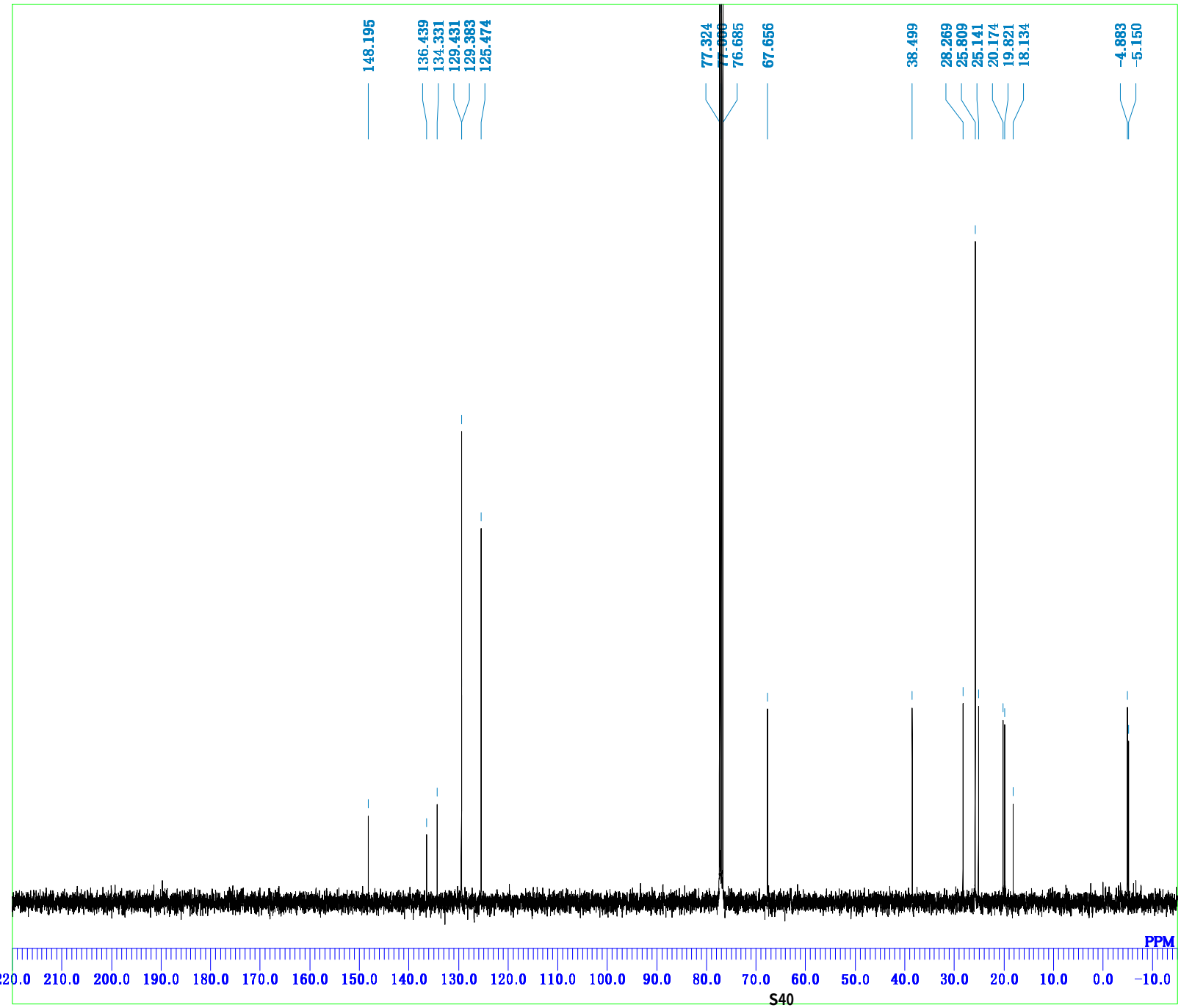
6a



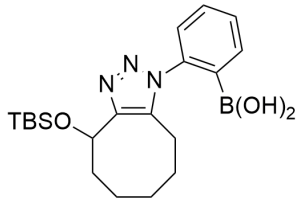
DFILE	RY242 ptlc-t-1.als
COMNT	
DATIM	06-06-2024 17:32:49
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	32



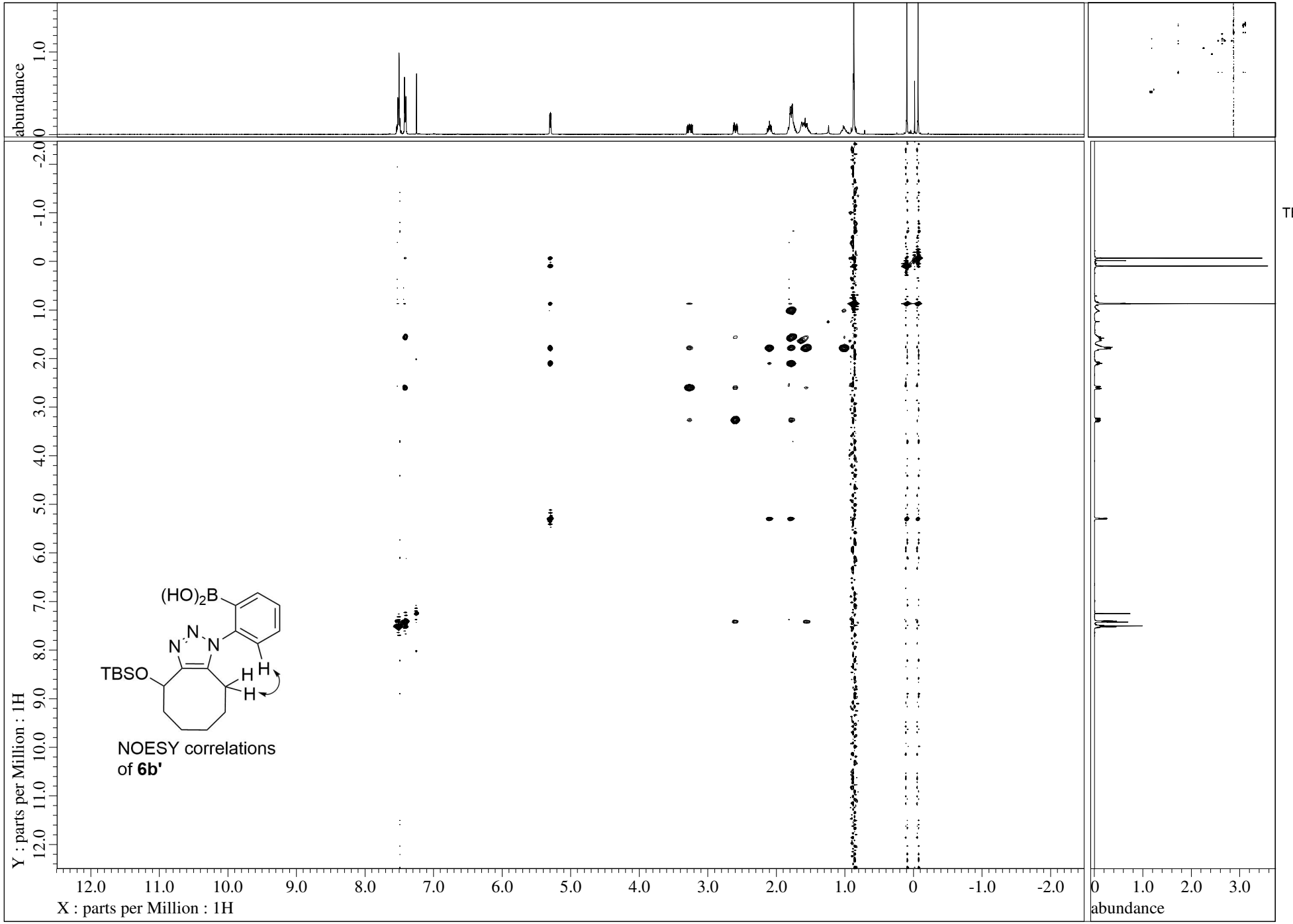
6b'

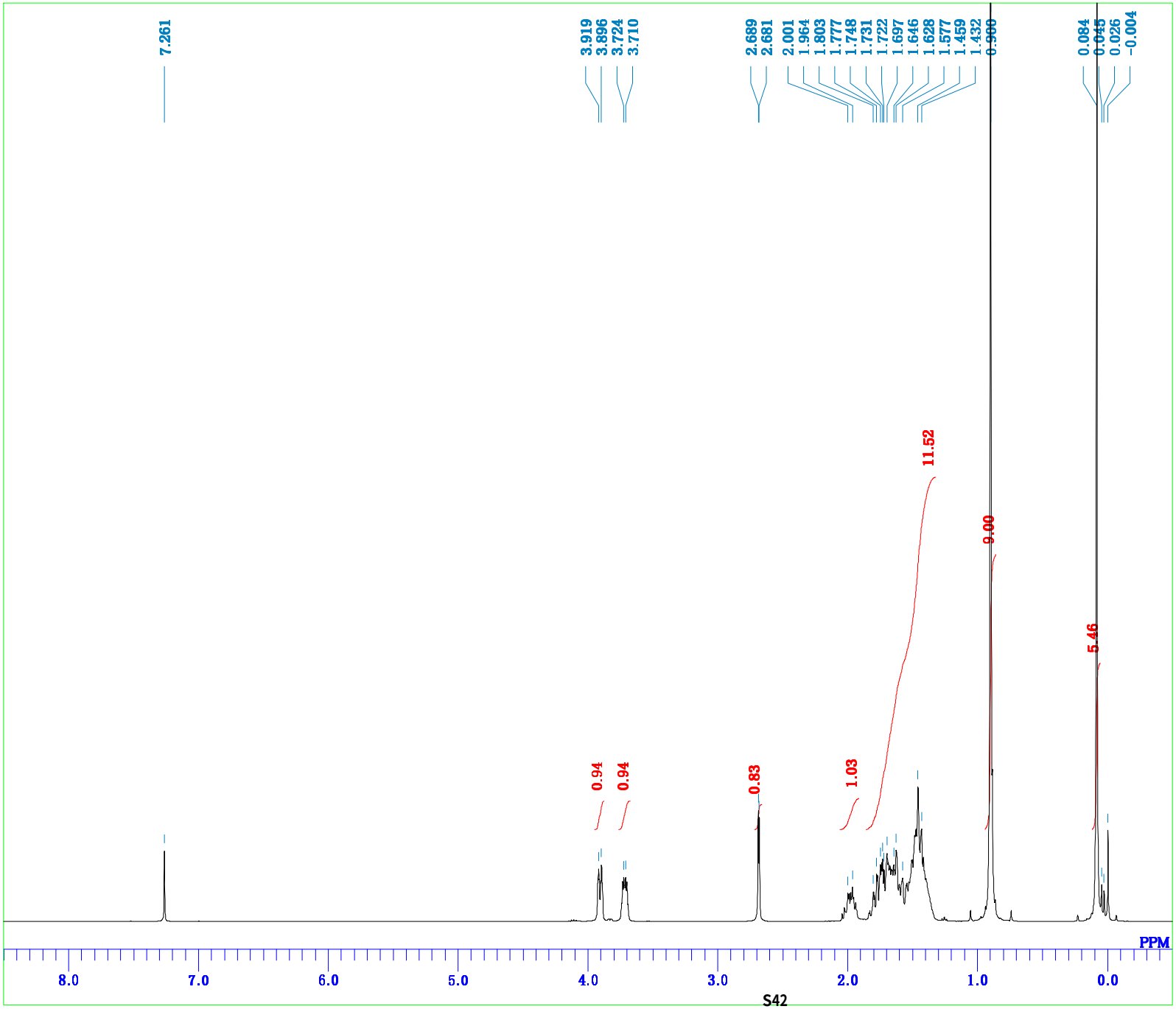


DFILE	RY242 13C-1.als
COMNT	
DATIM	13-06-2024 13:53:01
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	414
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60

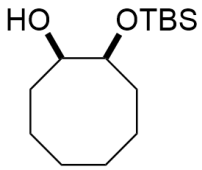


6b'

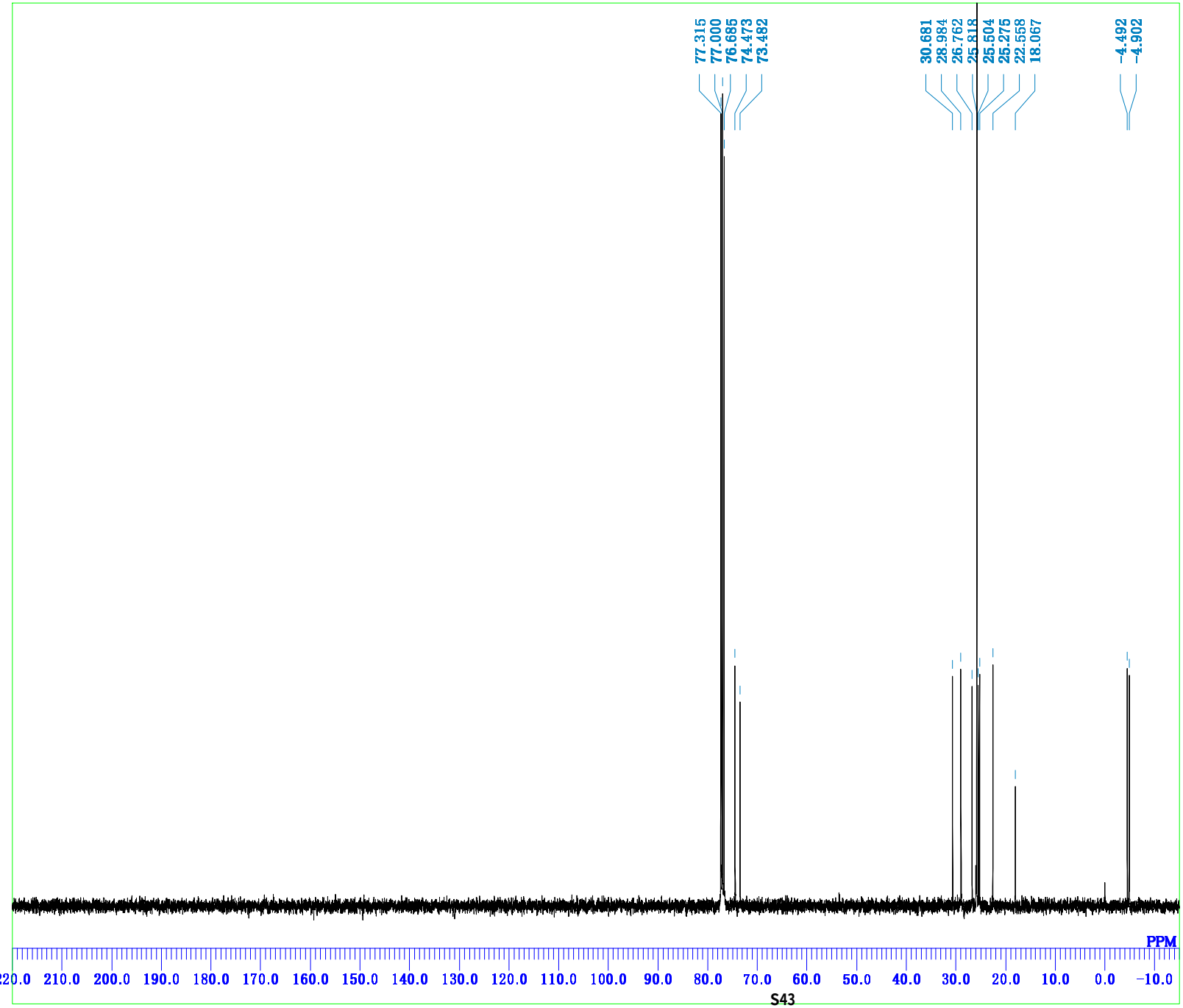

abundance
Y : parts per Million : 1H
X : parts per Million : 1H
abundance
(HO)2B
TBSO
H
H
NOESY correlations
of 6b'
TBSO
B(OH)2
6b'



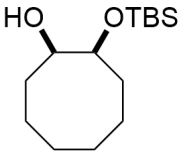
DFILE	RY spaac8-1.als
COMNT	
DATIM	01-12-2023 14:42:06
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.40 Hz
RGAIN	34



9



DFILE	RY spaac8 13C-1.als
COMNT	
DATIM	01-12-2023 15:01:25
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	490
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



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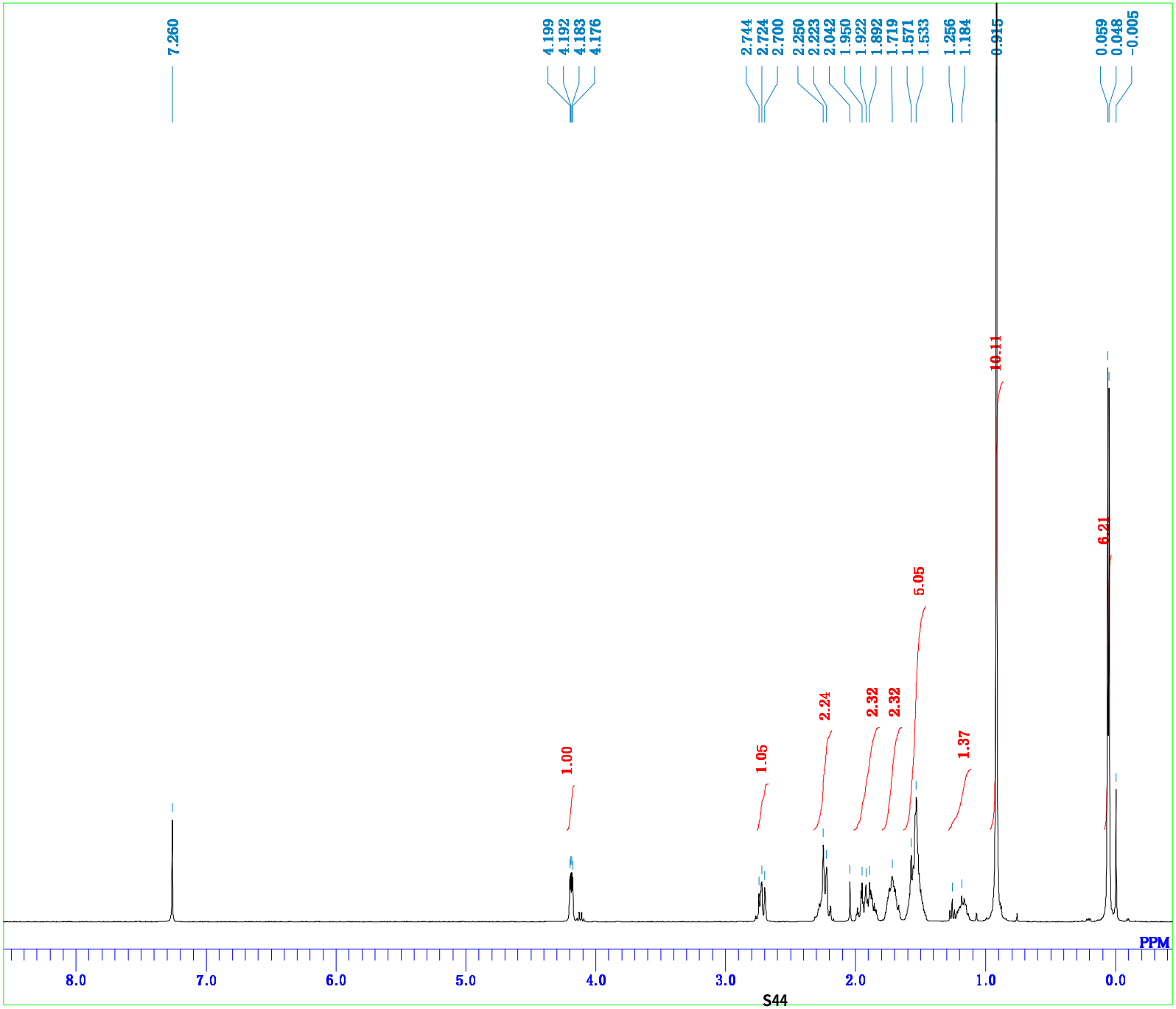
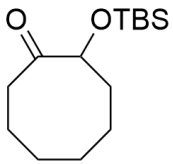


DFILE	RY177-1.als
COMNT	
DATIM	04-12-2023 08:50:53
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.40 Hz
RGAIN	36



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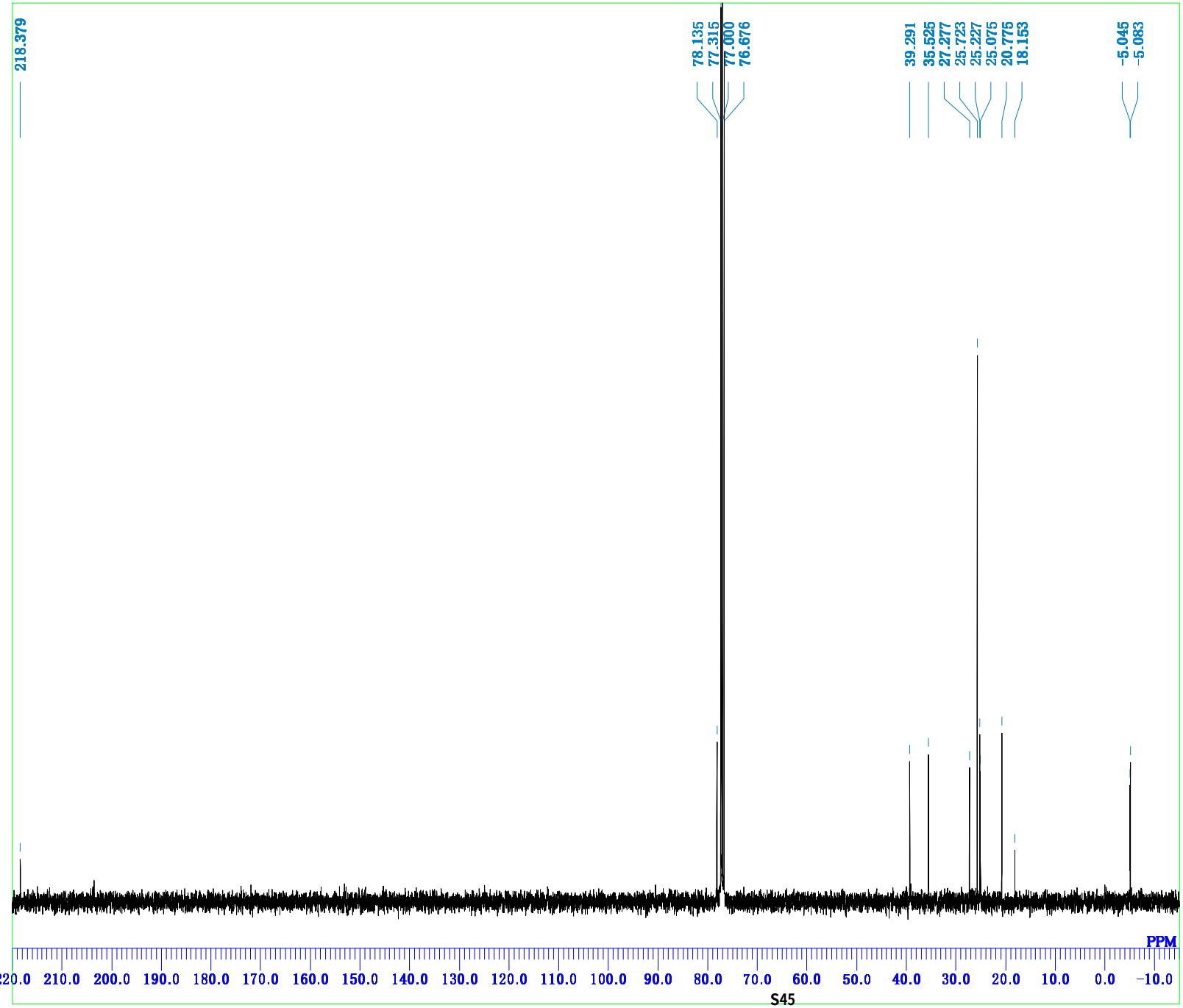
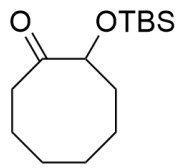


DFILE	RY177 13C-1.als
COMNT	
DATIM	04-12-2023 09:02:24
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	284
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



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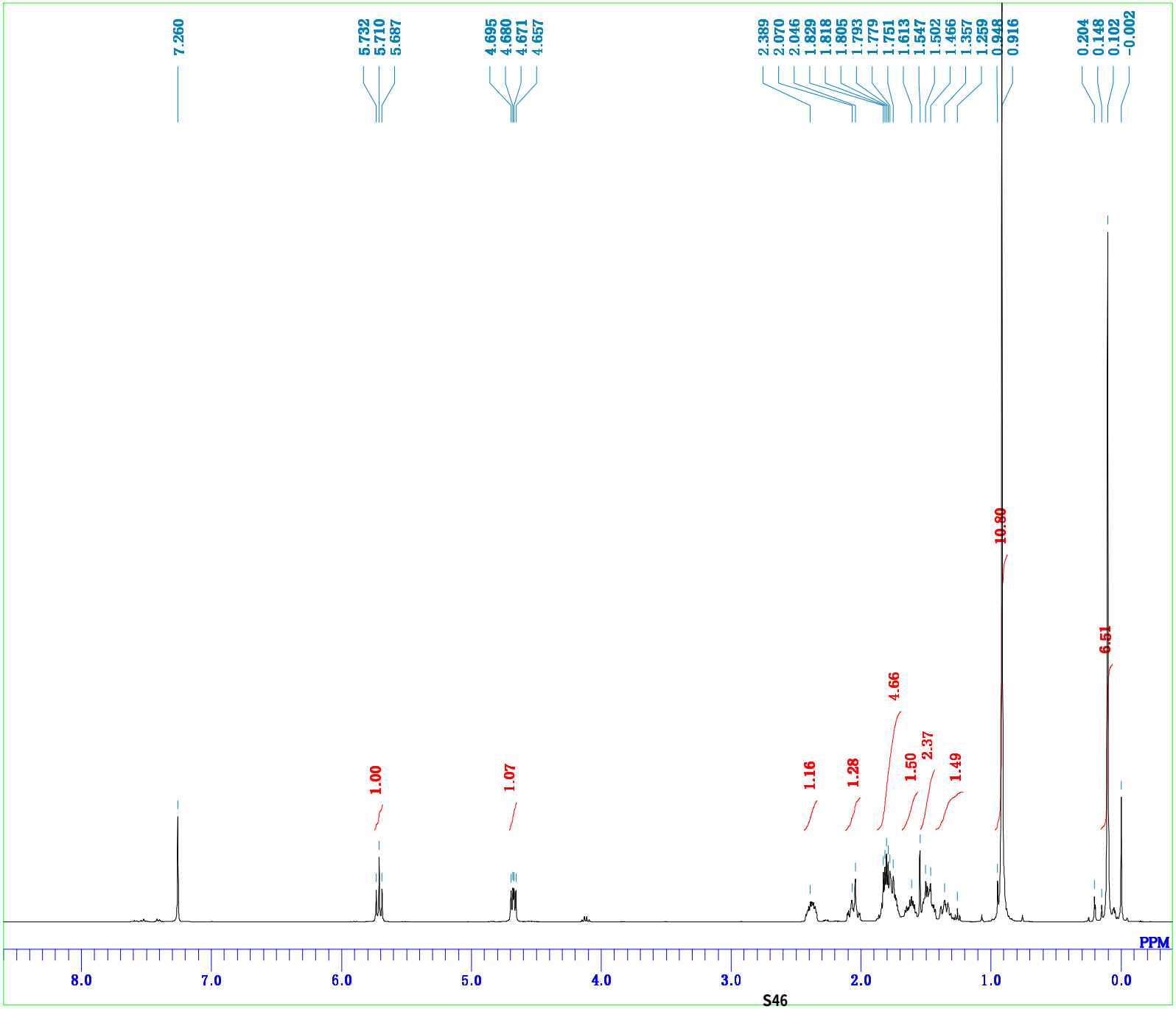
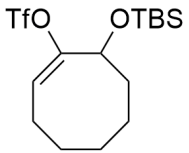


DFILE RY178 fr4-1.als
COMNT
DATIM 05-12-2023 13:21:29
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.40 Hz
RGAIN 36



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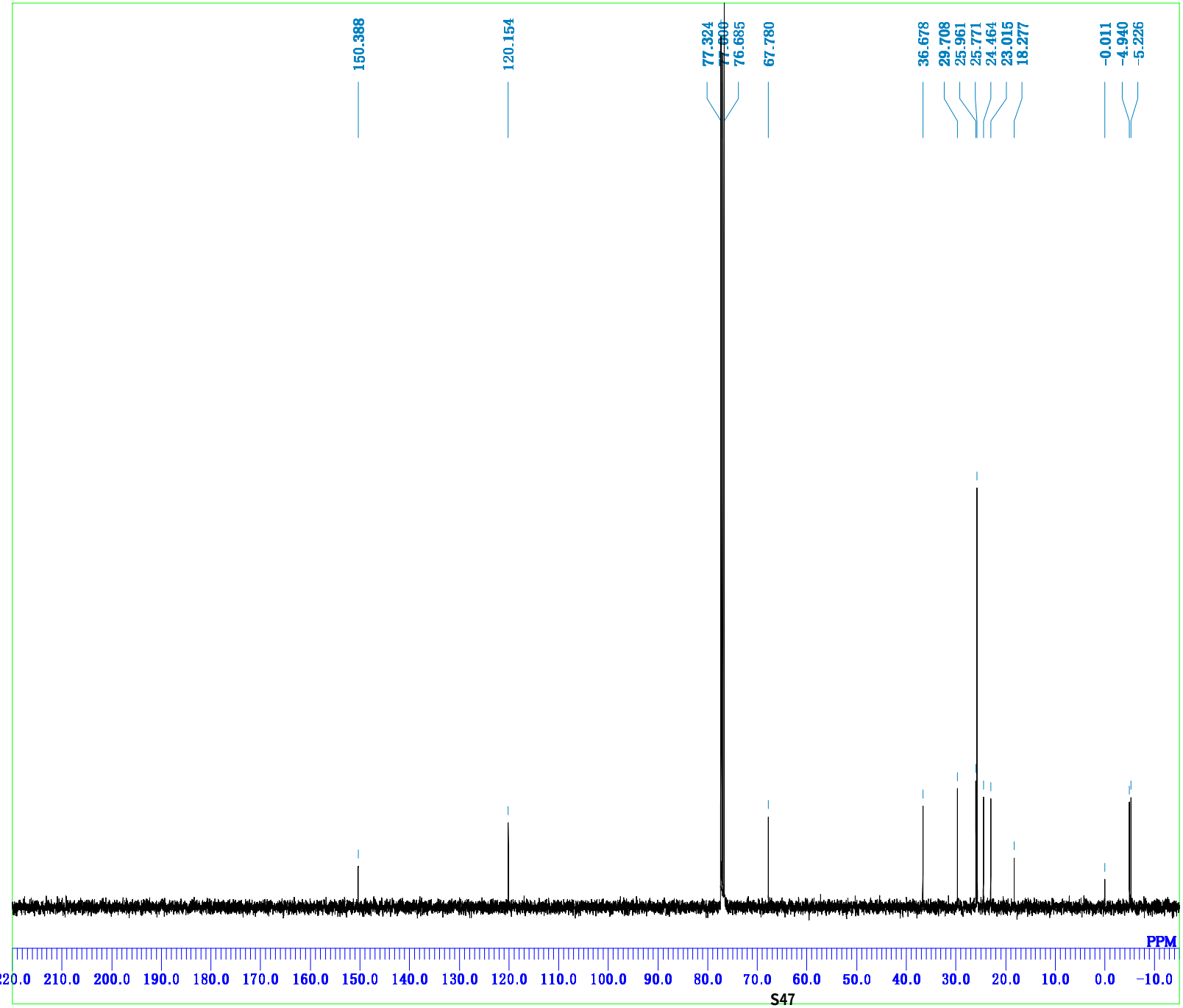
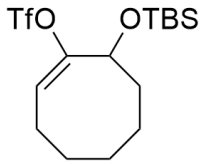


DFILE	RY178 fr4 13C-1.als
COMNT	
DATIM	05-12-2023 13:42:34
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	536
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



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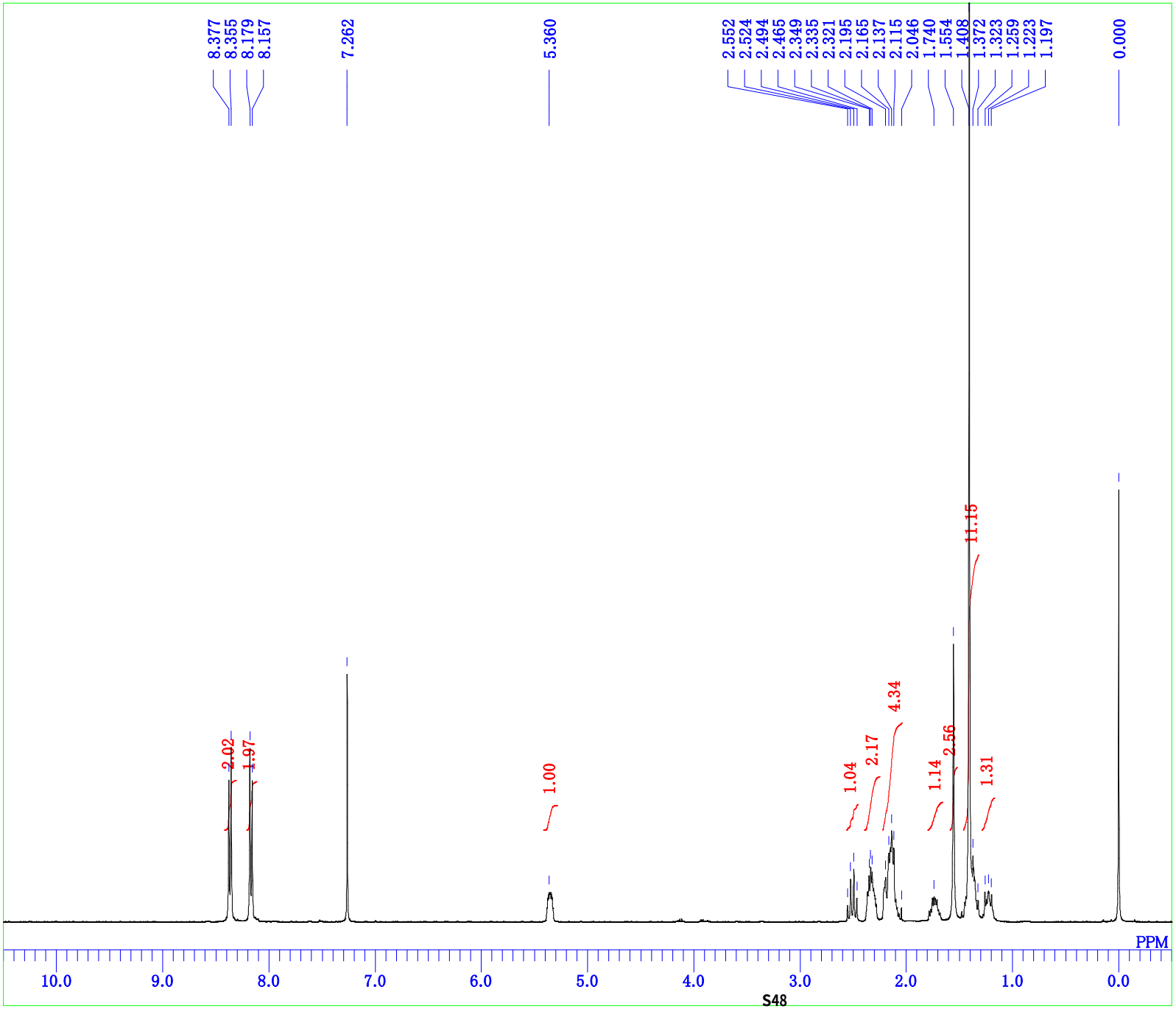
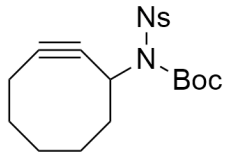
The $\underline{C}F_3$ peaks, which are expected to appear around 118 ppm as q, ($J_{C\text{-}F}$= 320 Hz) were not detected.



DFILE	RY cyclooctynyl NBocNs 1H-1.als
COMNT	
DATIM	2023-07-11 10:13:50
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	48



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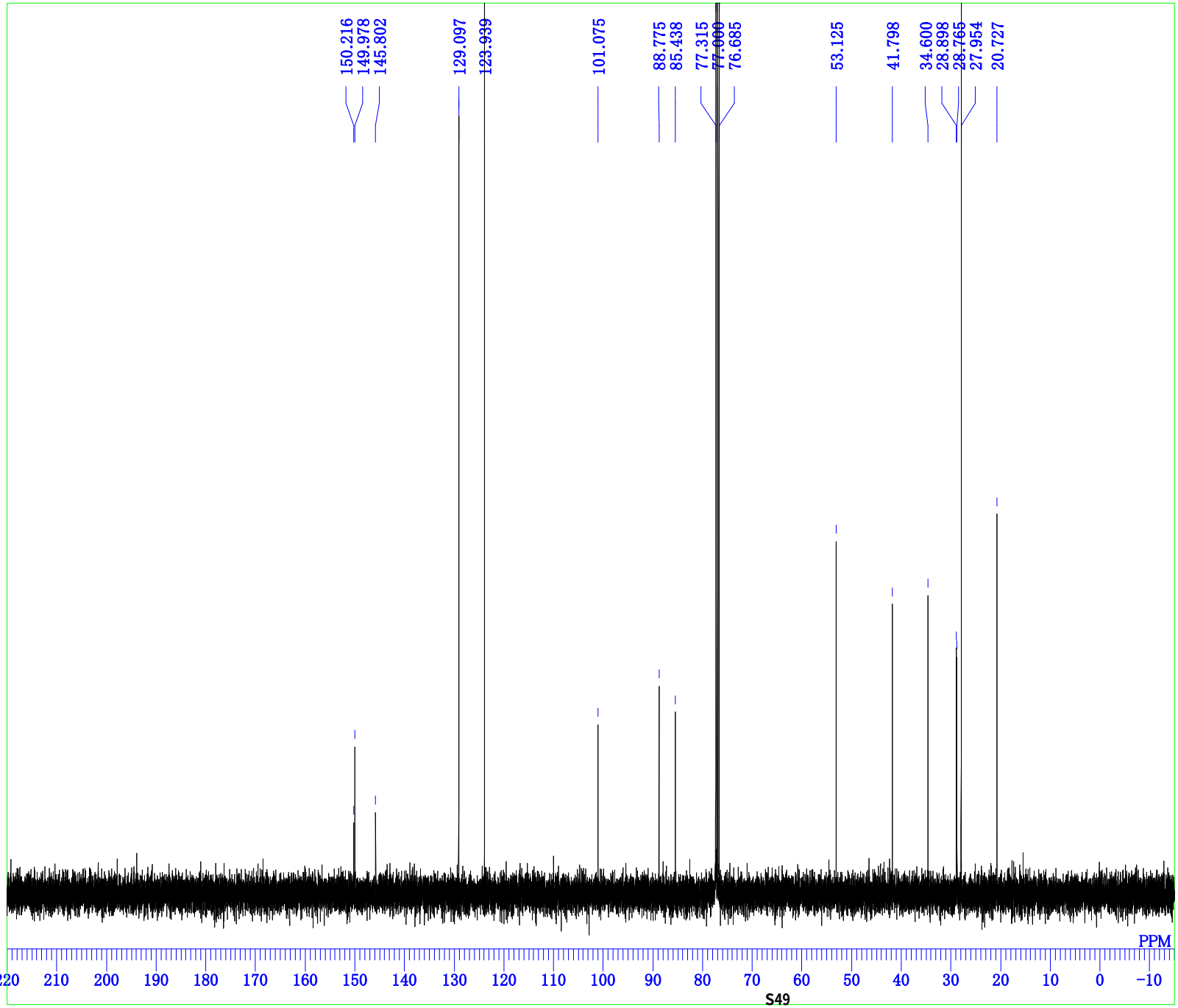
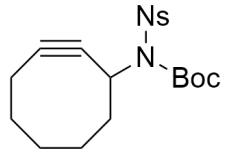


DFILE	RY cyclooctynyl NBocNs 13C-1.als
COMNT	
DATIM	2023-06-26 11:30:33
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	434
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	3.00 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60



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