Supporting information for

Sequential Click Modification of Lithium-ion Endohedral Fullerene Connecting Small Molecules through A Dieneazide Linker

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Table of Contents

1. General Procedure

All reactions were carried out under an argon atmosphere with dehydrated solvents under anhydrous conditions, unless otherwise noted. For reactions that require heating, oil bath was used as the heat source. Dehydrated THF and CH_2Cl_2 were purchased from Kanto Chemical Co., Inc. Other solvents were dehydrated and distilled according to standard protocols. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials unless otherwise stated. Reagents were obtained from commercial suppliers and used without further purification, unless otherwise noted.

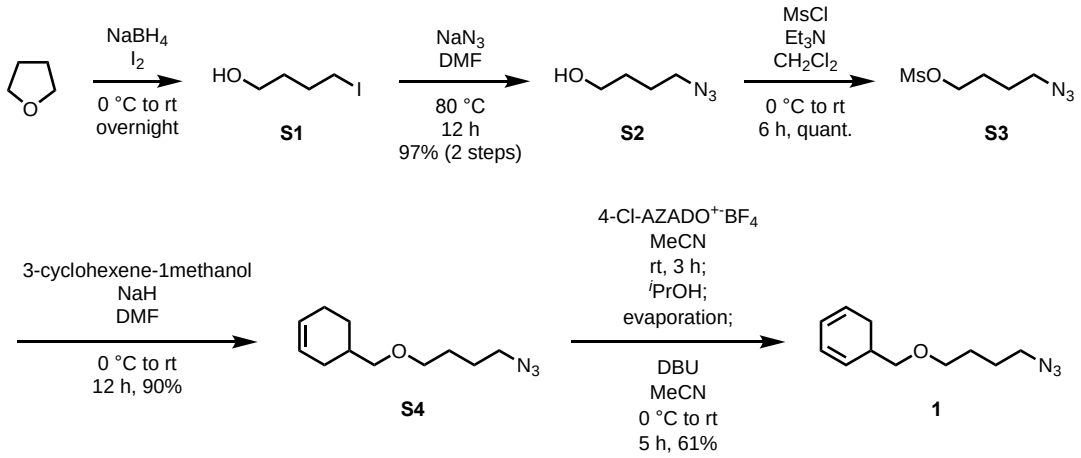
Reactions were monitored by thin-layer chromatography (TLC) carried out on Silica gel plates (Merck Kieselgel 60 F254) or Silica gel plates (Fuji Silysia Chemical Co., Ltd.). Column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 μm) or flash column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 40-50 μm). The eluents employed are reported as volume: volume percentages. Gel permeation chromatography (GPC) was performed on a JAI LC-908 equipped with JAIGEL-2H using $CHCl_3$ as an eluent.

Melting points (mp) were taken with Yazawa BY-2 and are reported uncorrected. In parentheses after melting point, the recrystallization solvents are shown. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using JEOL JMN-AL400 (400 MHz) and a JEOL ECA-600 (600 MHz) spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS). Coupling constants (J) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; m, multiplet; br s, broad singlet; br d, broad doublet; dd, double doublet; dt, double triplet; td, triple doublet; dq, double quartet; sept, septet. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded using JEOL JMN-AL400 (100 MHz) and a JEOL

ECA-600 (150 MHz) spectrometers. Chemical shift is reported in ppm relative to the center line of the triplet of $CDCl_3$ (77.10 ppm). Lithium-7 nuclear magnetic resonance (^{7}Li NMR) spectra were recorded using a JEOL ECA-600 (233 MHz) spectrometer. $LiCl/D_2O$ was used as an external standard (0 ppm).

Infrared spectra (IR) were obtained on a JASCO FT-IR-410 at 4.0 cm^{-1} resolution and are reported in wavenumbers. High resolution mass spectra (HRMS) were recorded on a JMS-AX500, JMS-700 or Thermo Scientific Exactive Mass Spectrometers using electron impact (EI), fast atom bombardment (FAB) and electrospray ionization (ESI), respectively. Low resolution mass spectra (MS) were recorded on JEOL JMS-DX303 or JMS-700. HPLC was performed by Hitachi L-7610 as a degasser, Hitachi L-7100 as a pump, Hitachi L-7300 as a column oven and Hitachi L-7400 as an UV/Vis detector at 370 nm using Inertsil® CX column (GL Sciences) for monitoring reaction mixture, π-NAP column (Nacalai Tesque) or Buckyprep-M column (Nacalai Tesque) for separating, and Buckyprep column (Nacalai Tesque) for confirming purity.

2. Synthesis of dieneazide 1



*4-azidobutan-1-ol (**S2**)*

To a suspension of $NaBH_4$ (680 mg, 18 mmol) in THF (72 mL) was added I_2 (9.1 g, 36 mmol) in THF (30 mL) slowly at 0 °C. The reaction mixture was allowed to reach room

temperature and stirred overnight. The solution was quenched with H_2O (50 mL) sat. $Na_2S_2O_3$ aq. (50 mL). The mixture was extracted with Et_2O (50 mL × 3), washed with brine (50 mL), and dried over $MgSO_4$. The organic layer was concentrated under vacuum to give alcohol **S1**. The product was used in the following step without further purification.

To a solution of alcohol **S1** in DMF (84 mL) was added NaN_3 (10 g, 154 mmol) at room temperature. The reaction mixture was heated to reflux and stirred for 12 h. The solution was quenched with sat. H_2O (50 mL). The mixture was extracted with Et_2O (50 mL × 3), washed with brine (50 mL), and dried over $MgSO_4$. The organic layer was concentrated under vacuum to give alcohol **S2**. (4.04 g, 35.1 mmol, 97% for 2 steps). Characterization data were in agreement with previously reported values[1].

*4-azidobutyl methanesulfonate (**S3**)*

To a solution of alcohol **S2** (4.04 g, 35.1 mmol) and Et_3N (9.9 mL, 70.1 mmol) in CH_2Cl_2 (58 mL) was added MsCl (4.1 mL, 52.6 mmol) at 0 °C. The mixture was stirred at room temperature for 6 h. The mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 times). The organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified with flash column chromatography (AcOEt : hexane = 1 : 4 to 1:2) to afford azide **S3** (7.17 g, quant.) as a yellow oil. Characterization data were in agreement with previously reported values[2].

*4-((4-azidobutoxy)methyl)cyclohex-1-ene (**S4**)*

To a suspension of NaH (60%, 8.9 g, 44 mmol) in DMF (100 mL), 3-cyclohexene-1-methanol (5.18 mL, 44 mmol) was added slowly at 0 °C. The suspension was stirred for 30 min at room temperature. azide **S3** (7.0 g, 37 mmol) in DMF (23 mL) was added to the suspension slowly at the same temperature. The mixture

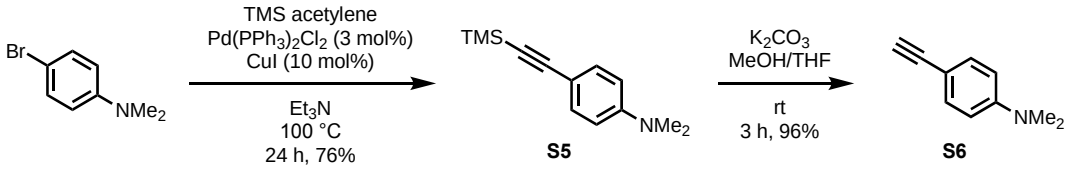
was stirred for 12 h at room temperature. The mixture was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 times). The organic layer was washed with brine and dried over $MgSO_4$ and evaporated. The residue was purified with column chromatography (AcOEt : hexane = 1 : 20) to afford azide **S4** (6.6 g, 31.5 mmol, 90%) as a colorless oil. Characterization data were in agreement with previously reported values[2].

*5-((4-azidobutoxy)methyl)cyclohexa-1,3-diene (**1**)*

To a solution of azide **S4** (209 mg, 0.1 mmol) in MeCN (2 mL) was added 4-Cl-AZADO$^+BF_4^-$[2] (328 mg, 1.2 mmol) at ambient temperature. The reaction mixture was stirred at the same temperature for 3 h. ^{i}PrOH (0.92 mL, 12 mmol) was added to the reaction mixture and the mixture was stirred for 5 min (The color of the reaction mixture was changed from yellow to colorless). The mixture was concentrated at reduced pressure and the resulting residue was dissolved in MeCN (4 mL). DBU (0.45 mL, 3.0 mmol) was added to the reaction mixture at 0 °C and stirred for 5 h at room temperature. The mixture was quenched with sat. $NaHCO_3$ aq. and extracted with $CHCl_3$ (3 times). The organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified with flash column chromatography (AcOEt : hexane = 1 : 50) to dieneazide linker **1** (126.9 mg, 0.61 mmol, 61%) as a colorless oil. Characterization data were in agreement with previously reported values[2].

3. Preparation of alkynes

Phenylacetylene and 4-methoxyphenylacetylene were purchased from commercial suppliers and used as received. Alkyne **S6**, **S8**, **S11**, **S12**, **S16**, **S20**, **S23**, and **S26** were prepared according to the previous literatures as follows.

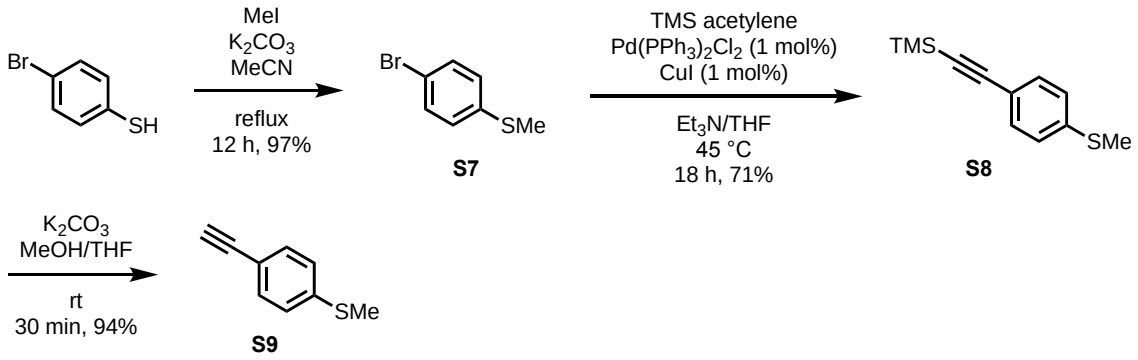


*N,N-dimethyl-4-((trimethylsilyl)ethynyl)aniline (**S5**)*

To a solution of 4-bromo-*N*,*N*-dimethylaniline (1.00 g, 5.00 mmol) and TMS acetylene (1.06 mL, 7.49 mmol) in Et_3N (20 mL) was added $Pd(Ph_3)_2Cl_2$ (105 mg, 0.150 mmol), CuI (95.2 mg, 0.500 mmol), and PPh_3 (13.1 mg, 0.500 mmol). The reaction mixture was stirred at 100 ºC for 24 h. After reaction was completed the catalyst was removed by filtration through Celite (AcOEt : hexane = 1 : 1) and the filtrate was evaporated. The residue was purified with flash column chromatography (CH_2Cl_2 : hexane = 1 : 5) to afford 4-ethynyl-*N*,*N*-dimethylaniline **S5** (732 mg, 3.80 mmol, 76%) as a yellow solid. Characterization data were in agreement with previously reported values[3].

*4-ethynyl-N,N-dimethylaniline (**S6**)*

To solution of *N*,*N*-dimethyl-4-((trimethylsilyl)ethynyl)aniline **S5** (52.2 mg, 0.240 mmol) in MeOH (1 mL) was added K_2CO_3 (35 mg, 0.253 mmol) and stirred at room temperature for 2 h. The insoluble precipitate was removed by filtration and filtrate was poured into saturated aqueous NH_4Cl. The mixture was extracted AcOEt (three times), washed brine (once), and dried over Na_2SO_4. The solution was separated by filtration and the filtrate was concentrated under vacuum. The residue was purified with flash column chromatography (CH_2Cl_2 : hexane = 1 : 4) to afford 4-ethynyl-*N*,*N*-dimethylaniline **S6** (32.2 mg, 0.222 mmol, 93%) as a yellow solid. Characterization data were in agreement with previously reported values[3].



*(4-bromophenyl)(methyl)sulfane (**S7**)*

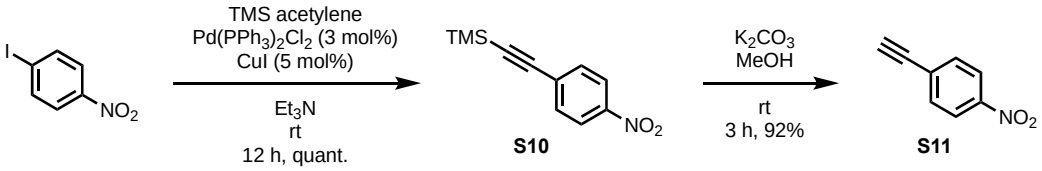
To a solution 4-bromobenzenethiol (1.50 g, 7.93 mmol) and iodemethane (989 μL, 15.9 mmol) in MeCN (13 mL) was added K_2CO_3 (2.12 g, 15.9 mmol). The reaction mixture was stirred reflux for 12 h. the reaction mixture was cooled to room temperature, extracted with AcOEt (three times), washed water (once) and brine (once), and dried over $MgSO_4$. After removing the solvent under vacuum, (4-bromophenyl)(methyl)sulfane **S7** (1566 mg, 7.71 mmol, 97%) was obtained as a yellow oil. Characterization data were in agreement with previously reported values[4].

*trimethyl((4-(methylthio)phenyl)ethynyl)silane (**S8**)*

To a solution of (4-bromophenyl)(methyl)sulfane **S7** (494 mg, 2.43 mmol) and TMS acetylene (521 μL, 3.69 mmol) in Et_3N/THF (1:1) (5.5 mL) was added $Pd(Ph_3)_2Cl_2$ (28.4 mg, 24.6 μmol) and CuI (4.69 mg, 24.6 μmol). The reaction mixture was stirred at 45 ºC for 18 h. After reaction was completed the catalyst was removed by filtration through Celite (AcOEt : hexane = 1 : 1) and the filtrate was evaporated. The residue was dissolved in AcOEt and water. The mixture was extracted with AcOEt (three times), washed water (once) and brine (once), and dried over $MgSO_4$. The residue was purified with flash column chromatography (AcOEt : hexane = 1 : 10) to afford trimethyl((4-(methylthio)phenyl)ethynyl)silane **S8** (386 mg, 1.75 mmol, 72%) as a brown oil. Characterization data were in agreement with previously reported values[4].

*(4-ethynylphenyl)(methyl)sulfane (**S9**)*

To solution of trimethyl((4-(methylthio)phenyl)ethynyl)silane **S8** (100 mg, 0.453 mmol) in MeOH/THF (1:1) (1 mL) was added K_2CO_3 (125 mg, 0.907 mmol) and stirred at room temperature for 30 min. The insoluble precipitate was removed by filtration. The mixture was extracted AcOEt (three times), washed brine (once), and dried over Na_2SO_4. The solution was separated by filtration and the filtrate was concentrated under vacuum. The residue was purified with flash column chromatography (CH_2Cl_2 : hexane = 1 : 4) to afford (4-ethynylphenyl)(methyl)sulfane **S9** (63.5 mg, 0.428 mmol, 94%) as a colorless solid. Characterization data were in agreement with previously reported values[4].



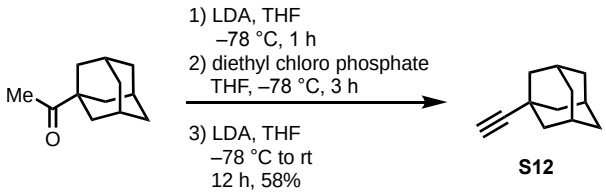
*trimethyl((4-nitrophenyl)ethynyl)silane (**S10**)*

To a solution of 1-iodo-4-nitrobenzene (1.00 g, 4.02 mmol) and TMS acetylene (850 μL, 6.02 mmol) in Et_3N (13 mL) was added $Pd(Ph_3)_2Cl_2$ (84.6 mg, 0.121 mmol) and CuI (38.3 mg, 0.201 mmol). The reaction mixture was stirred at room temperature for 12 h. After reaction was completed the catalyst was removed by filtration through Celite (AcOEt : hexane = 1 : 1) and the filtrate was evaporated. The residue was purified with flash column chromatography (CH_2Cl_2 : hexane = 1 : 2) and recrystallized ($CHCl_3$) to afford trimethyl((4-nitrophenyl)ethynyl)silane **S10** (944 mg, quant.) as a yellow solid. Characterization data were in agreement with previously reported values[5].

1-ethynyl-4-nitrobenzene S11

To solution of trimethyl((4-nitrophenyl)ethynyl)silane **S10** (265 mg, 1.12 mmol) in

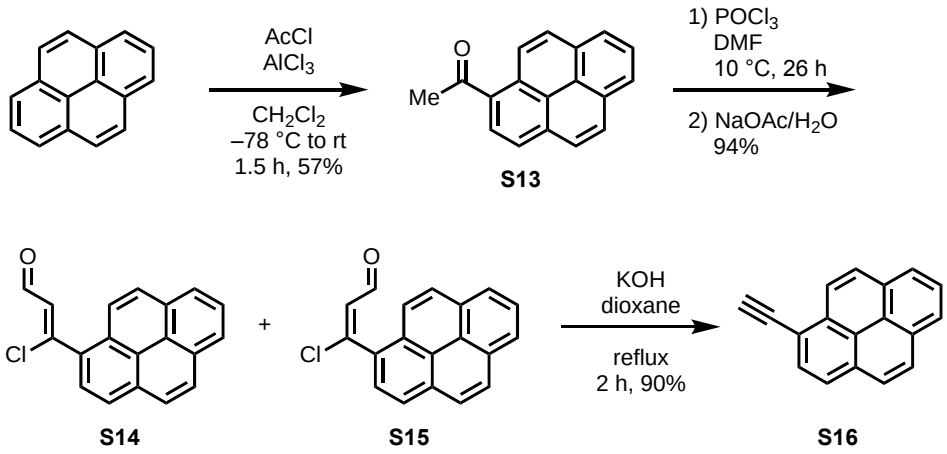
MeOH (12 mL) was added K_2CO_3 (150 mg, 1.09 mmol) and stirred at room temperature for 3 h. The reaction mixture was evaporated under vacuum. The solids were dissolved in AcOEt, washed 10% HCl and brine, and dried over $MgSO_4$. The solution was concentrated under vacuum. The residue was purified with flash column chromatography (CH_2Cl_2 : hexane = 1 : 2) and recrystallized ($CHCl_3$) to afford 1-ethynyl-4-nitrobenzene **S11**(165 mg, 1.11 mmol, 92%) as a yellow solid. Characterization data were in agreement with previously reported values[5].



*1-ethynyladamantane (**S12**)*

In a heat gun-dried three-necked round-bottom flask, diisopropyl amine (943 μL, 6.73 mmol) in THF (6 mL) was –78 ºC followed by dropwise addition of ^{n}BuLi (3.95 mL, 6.17 mmol) in hexane (1.56 M). After 1 h of stiring the LDA was ready-for use. A solution of adamantly methyl ketone (1.00 g, 5.61 mmol) in THF (3 mL) was added dropewise at –78 ºC to LDA a solution as a prepared above. After stirring 1 h chloro diethyl phosphate (834 μL, 5.78 mmol) was added dropwise via syringe pump. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature. After 3 h of stiring the reaction mixture was added dropwise to a second LDA solution as prepared above form diisopropyl amine (1.52 mL, 10.9 mmol) and ^{n}BuLi in hexane (1.56 M) at –78 ºC. The cooling bath was removed and solution was stired for 12 h. The reaction was quenched by addition of water (20 mL). The mixture was extracted with hexane (four times). The combained organic extracts were washed with ice-cold aqueous HCl (1 M) (twice) and saturated $NaHCO_3$ (twice). After drying over Na_2SO_4 and filtration over Celite, solvents were removed under vacuum. The crude

product was obtained as slightly yellow oil. The residue was purified with flash column chromatraphy (AcOEt : hexane = 1 : 50) to afford 1-ethynyladamantane **S12** (527 mg, 3.29 mmol, 58%) as a white solid. Characterization data were in agreement with previously reported values[6].



*1-acetylpyrene (**S13**)*

To a solution of Pyrene (500 mg, 2.47 mmol) and $AlCl_3$ in CH_2Cl_2 (100 mL) was added AcCl (439 μL, 6.18 mmol) slowly at –78 ºC. The mixture was stirred for 1.5 h at the room temperature. After the reaction, it was poured into ice water, stirred well, separated, and the aqueous phase was extracted CH_2Cl_2 (three times). The organic phase was washed with 1M HCl (twice), dried over $MgSO_4$ and evaporated. The residue was purified with flash column chromatography (AcOEt : hexane = 1 : 4) to afford 1-(pyren-1-yl)ethan-1-one **S13** (348 mg, 1.42 mmol, 58%) as a yellow solid. Characterization data were in agreement with previously reported values[7].

*3-(1-Pyrenyl)-3-chloro-2-propenal (**S14**) and (**S15**)*

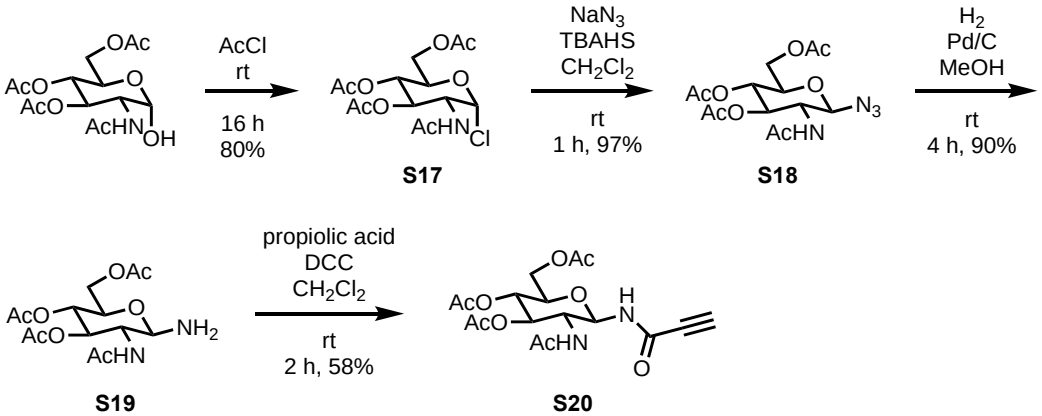
The Vilsmeier reagent prepared from DMF (1.6 mL) and $POCl_3$ (730 μL, 7.86 mmol) upon cooling with a water bath was added dropwise under argon to a stirred solution of 1-acetylpyrene **S13** (398 mg, 1.63 mmol) in DMF (2.4 mL) within 20 min. The mixture

was strirred for 20 h at room temperature. After the reaction, it was poured on ice, pH was adjusted to 6 by adding $AcONa \cdot 3H_2O$ and extracted with CH_2Cl_2 (three times). The organic phase was washed with water (six times), dried $MgSO_4$, and evaporated. The residue was purified with flash column chromatography (AcOEt : hexane = 1 : 4) to afford 3-(1-Pyrenyl)-3-chloro-2-propenal **S14** and **S15** (550 mg, 1.55 mmol, 94%) as a yellow solid. Characterization data were in agreement with previously reported values[8].

*1-ethynylpyrene (**S16**)*

To a solution of 1-ethynylpyrene **S14** and **S15** (154 mg, 0.516 mmol) in dioxane (2.6 mL) was added finely powdered KOH (31.8 mg, 0.568 mmol) at room temperature. The mixture was refluxed for 2 h, cooled to room tempature, diluted with 5% aqueous solution of citric acid, and evaporated. The residue was distributed between water and CH_2Cl_2, the organic phase was washed with water, dried $MgSO_4$, and evaporated. The residue was purified with flash column chromatography (CH_2Cl_2 : hexane = 1 : 6) to afford 1-ethynylpyrene **S16** (69.0 mg, 0.308 mmol, 90%) as a yellow solid. Characterization data were in agreement with previously reported values[8].

Alkyne **S20**, **S23** and **S26** were newly prepared as follows.



*2-acetamido-2-deoxy-3, 4, 6-tri-O-acetyl-α-D-glucopyranosyl chloride (**S17**)*

N-Acetyl glucosamine (10.0 g, 45.2 mmol) was added to stirring acetyl chloride (20 mL) and resulting suspension was stirred magnetically for 16 h. Chloroform was then added to the amber solution and the resulting solution was poured into ice and water with stirring. The organic layer was immediately separated and run into saturated aqueous $NaHCO_3$ and ice with stirring, the neutralization being completed in separating funnel. The organic layer was then separated and dried for 10 min. the organic layer was then filtered with suction and the residue washed thoroughly with dichloromethane. The resulting organic solution was concentrated approximately under vacuum. Anhydrous ether was then added and the product crystallized out immediately. The product was stoppered and left to stand at room temperature for 16 h. The pale yellow solid was then filtered with suction, washed with anhydrous ether, and allowed to dry for 5 min to afford the crude product which is subsequently purified by flash chromatography (AcOEt only) to afford 2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-α-D-glucopyranosyl chloride **S17** (13.2 g, 36.2 mmol, 80%) as a colorless solid. Characterization data were in agreement with previously reported values[9].

*2-acetamido-2-deoxy-3, 4, 6-tri-O-acetyl-β-D-glucopyranosyl azide (**S18**)*

To solution of the 2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-α-D-glucopyranosyl chloride **S17** (5.0 g, 13.7 mmol), TBAHS (4.65 g, 13.7 mmol), and sodium azide (2.67 g, 41.1 mmol) in dichloromethane (50.0 mL) was added saturated aqueous $NaHCO_3$ (50.0 mL). The resulting biphasic solution was stirred vigorously at room temperature for 1 h. Ethyl acetate was added and the organic layer was separated and washed saturated aqueous $NaHCO_3$ (once), water (twice), and brine (once). The organic phase was then dried over Na_2SO_4 and solvent removed under vacuum to afford 2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-α-D-glucopyranosyl azide **S18** (4.95 g, 13.3 mmol, 97%) as a white

solid. Characterization data were in agreement with previously reported values[9].

*2-acetamido-2-deoxy-3, 4, 6-tri-O-acetyl-β-D-glucopyranosyl amine (**S19**)*

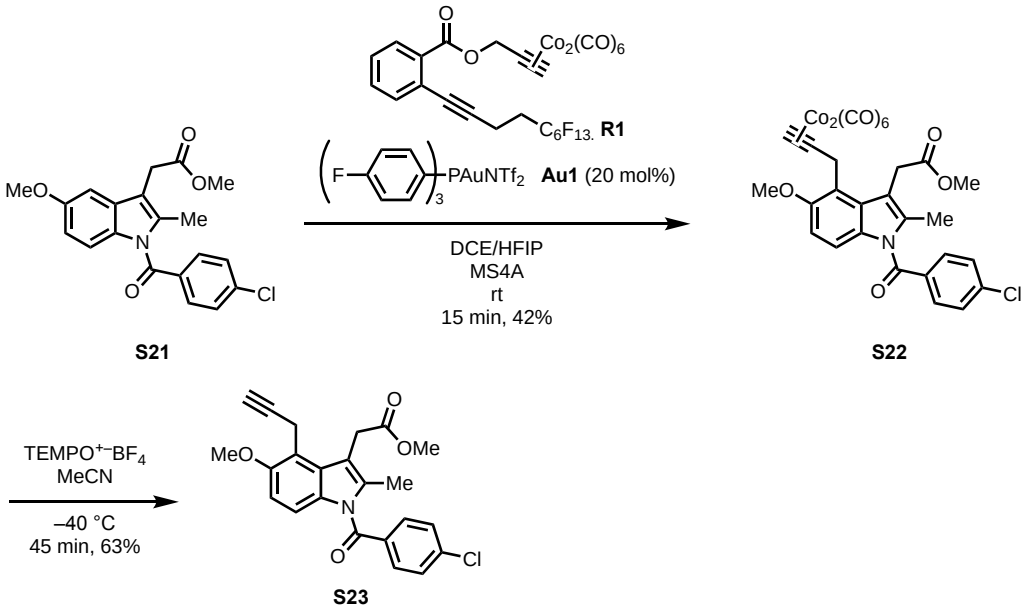
A solution of the 2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-α-D-glucopyranosyl azide **S18** (303 mg, 0.806 mmol) in anhydrous MeOH (5.0 mL) was catalytically hydrogenated with Pd/C (30 mg) under the hydrogen balloon for 4 h. The catalyst was removed by filtration through Celite and the filtrate was evaporated to dryness under vacuum to afford 2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-α-D-glucopyranosyl amine **S19** (252 mg, 0.728 mmol, 90%) as a white amorphous. Characterization data were in agreement with previously reported values[9].

*5-acetamido-2-(acetoxymethyl)-6-propiolamidotetrahydro-2H-pyran-3,4-diyl diacetate (**S20**)*

To a solution of 2-Acetamido-2-Deoxy-3, 4, 6-tri-*O*-acetyl-α-D-glucopyranosyl amine **S19** (23.2 mg, 0.0670 mmol) and propiolic acid (9.38 µl, 0.134 mmol) in dichloromethane (0.67 mL) was added slowly DCC (15.2 mg, 0.0737 mmol) in dichloromethane (0.67 mL) at 0 ºC. The mixture was stirred for 2 h at room temperature. After the reaction, it was poured into water, stirred well, separated, and the aqueous phase was extracted AcOEt (three times). The organic phase was washed with water (twice), brine (once), dried over $MgSO_4$ and evaporated. The residue was purified with flash column chromatography (AcOEt only) to afford 5-acetamido-2-(acetoxymethyl)-6-propiolamidotetrahydro-2*H*-pyran-3,4-diyl diacetate **S20** (15.6 mg, 0.0392 mmol, 58%) as a white amorphous.

IR (neat) 3271, 3062, 2118, 1747, 1650 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.3 Hz, 1H), 6.13 (d, *J* = 8.0 Hz, 1H), 5.15-5.03 (m, 3H), 4.30 (dd, *J* = 12.4, 4.6 Hz, 1H), 4.20-4.13 (m, 1H), 4.10 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.76 (ddd, *J* = 9.5, 4.4, 2.2 Hz,

1H), 2.89 (s, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H). $^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$): δ 172.2, 172.0, 170.7, 169.2, 152.5, 80.0, 76.4, 75.3, 73.6, 72.8, 67.6, 61.6, 53.2, 23.1, 20.70, 20.67, 20.6. HRMS (FAB) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{23}N_2O_9$ 399.1391, found: 399.1404.



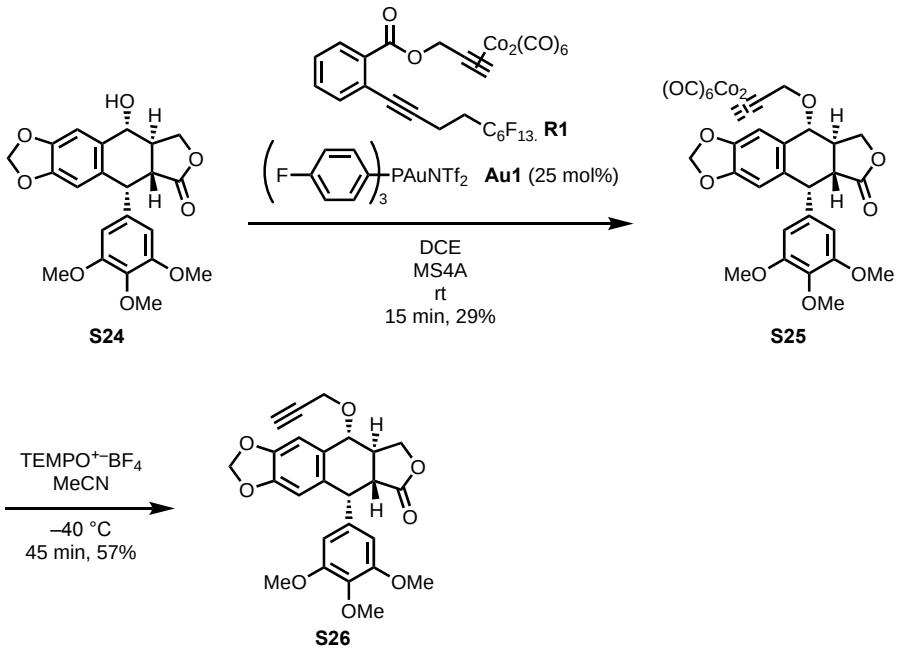
*Functionalized indomethacin methyl ester **S22***

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuum and then cooled to room temperature. After done heating and cooling three times, in the flask was added indomethacin methyl ester **S21** (50 μmol), reagent **R1** (61 mg, 75 μmol), DCE (1.0 mL), and HFIP (0.1 mL) at room temperature. To the reaction mixture was added gold catalyst **Au1** (20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (2 mL), and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (AcOEt : hexane = 1 : 50 to AcOEt : hexane = 1 : 20) to give the desired product **S22** (14.52 mg, 20.9 μmol, 42%). Characterization data were in agreement with previously reported values[10].

*Propargylated indomethacin methyl ester **S23***

To a solution of **S22** (33 mg, 48 μmol) in MeCN (5 mL) was added $TEMPO^{+-}BF_4$ (0.5 eq × 9) every 5 min at –40 °C. After completion of the reaction, the reaction was quenched with sat. $NaHCO_3$ aq. (2 mL) and extracted with AcOEt (4 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (AcOEt : hexane = 1 : 10 to AcOEt : hexane = 1 : 4) to give the desired product. **S23** (12.32 mg, 30.1 μmol, 63%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 1H), 4.03 (s, 2H), 3.95 (d, *J* = 2.4 Hz, 2H), 3.86 (s, 3H), 3.72 (s, 3H), 2.34 (s, 3H), 2.07 (t, *J* = 2.4 Hz, 1H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 172.1, 168.2, 152.9, 139.4, 137.1, 133.9, 131.8, 131.3, 129.1, 128.5, 115.8, 113.3, 112.1, 108.4, 83.6, 69.1, 57.1, 52.2, 31.1, 14.6, 13.2. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{23}ClH_{20}NO_4$ 409.1081, found: 409.1076.



*Functionalized podophyllotoxin **S25***

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuum and then cooled to room temperature. After done heating and cooling three times, in the flask was added podophyllotoxin **S24** (50 μmol), reagent **R1** (61 mg, 75 μmol), DCE (1.0 mL) at room temperature. To the reaction mixture was added gold catalyst **Au1** (25 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (2 mL), and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (AcOEt : hexane = 1 : 20 to AcOEt : hexane = 1 : 4) to give a desired product **S25** (10.72 mg, 14.5 μmol, 29%). Characterization data were in agreement with previously reported values[10].

*Propargylated podophyllotoxin **S26***

To a solution of **S25** (10.7 mg, 14.5 μmol) in MeCN (1.5 mL) was added $TEMPO^{+}{}^{-}BF_4$ (0.5 eq × 9) every 5 min at –40 °C. After completion of the reaction, the reaction was quenched with sat. $NaHCO_3$ aq. (2 mL) and extracted with AcOEt (4 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (AcOEt : hexane = 1 : 8 to AcOEt : hexane = 1 : 2) to give a desired product. **S26** (3.75 mg, 8.29 μmol, 57%).

IR (neat) 1774, 1715 cm^{-1}.^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H), 6.51 (s, 1H), 6.38 (s, 2H), 5.98 (s, 1H), 6.38 (s, 1H), 4.85 (d, *J* = 9.2 Hz, 1H), 4.66 (t, *J* = 7.2 Hz, 1H), 4.58 (d, *J* = 4.3 Hz, 1H), 4.39 (dd, *J* = 15.9, 2.4 Hz, 1H), 4.21-4.15 (m, 2H), 3.81 (s, 3H), 3.75 (s, 6H), 3.02-2.91 (m, 1H), 2.84 (dd, *J* = 14.5, 4.8 Hz, 1H), 2.53 (t, *J* = 2.4 Hz, 1H). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ 173.9, 152.7, 147.9, 147.6, 137.2, 135.2, 132.1,

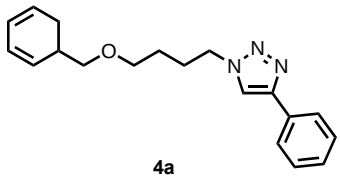
130.4, 109.6, 108.1, 107.3, 101.4, 79.5, 78.9, 75.6, 71.4, 60.7, 56.22, 56.15, 45.6, 44.0, 38.0. HRMS (EI) *m/z*: [M^+] Calcd. for $C_{25}H_{24}O_8$ 452.1471, found: 452.1472.

4. Huisgen annulation

General procedure 1: Huisgen annulation

To solution of dieneazide **1** in ^{t}BuOH/H_2O (1:1, 0.07 M) was added alkyne (1.2 eq of dieneazide **1**), $CuSO_4 \cdot 5H_2O$ (5 mol%), Ca-ascorbate (10 mol%) at room temperature. The reaction mixture was stirred at room temperature for 24–60 h. After the reaction was completed, the mixture was concentrated under vacuum. The residue was purified with silica gel column chromatography to afford corresponding diene derivatives **4**.

*1-(4-(cyclohexa-2,4-dien-1-ylmethoxy)butyl)-4-phenyl-1H-1,2,3-triazole (**4a**)*



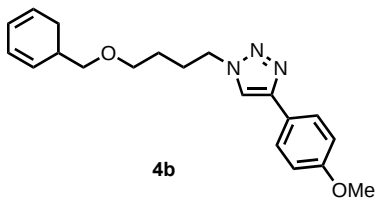
4a

The reaction was conducted based on General procedure 1 using dieneazide **1** (30.2 mg, 0.146 mmol) and phenylacetylene and the reaction time was 24 h. The mixture was concentrated under vacuum and the residue was purified with silica gel column chromatography (AcOEt : hexane = 1 : 4) to afford the desired product **4a** (39.2 mg, 0.127 mmol, 87%) as a colorless oil.

IR (neat) 3131, 3034, 2937, 2859, 1609 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.77 (s, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32(t, *J* = 7.3 Hz, 1H), 5.95-5.91 (m, 1H), 5.89-5.85 (m, 1H), 5.75 (dt, *J* = 9.3, 4.5 Hz, 1H), 5.67 (dd, *J* = 9.8, 4.3 Hz, 1H), 4.45 (t, *J* = 7.1 Hz, 2H), 3.47 (t, *J* = 6.1 Hz, 2H), 3.38 (t, *J* = 8.3 Hz, 1H), 3.34 (dd, *J* = 8.8, 6.3 Hz, 1H), 2.59 (br s, 1H), 2.25 (dddd, *J* = 17.4, 8.6, 4.7, 1.6 Hz 1H), 2.16-2.14 (m, 1H), 2.10-2.02 (m, 2H), 1.63 (quin, *J* = 5.8 Hz, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ147.7, 130.7, 128.8, 128.0, 127.5, 125.7, 125.5, 124.9, 123.9, 119.5, 73.1, 70.1, 50.2, 33.5, 27.5, 26.5, 25.5. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{19}H_{23}N_3O$ 309.1841,

found: 309.1871.

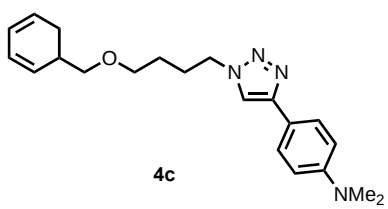
*1-(4-(cyclohexa-2,4-dien-1-ylmethoxy)butyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazole (**4b**)*



4b

The reaction was conducted based on General procedure 1 using dieneazide **1** (14.7 mg, 0.0709 mmol) and 1-ethynyl-4-methoxybenzene and the reaction time was 24 h. The mixture was concentrated under vacuum and the residue was purified with silica gel column chromatography (AcOEt : hexane = 1 : 4) to afford the desired product **47** (22.9 mg, 0.0675 mmol, 95%) as a colorless oil. IR (neat) 3132, 3036, 2940, 2859, 2045, 1721 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.69 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.95-5.91 (m, 1H), 5.89-5.85 (m, 1H), 5.76 (dt, *J* = 9.3, 3.4 Hz, 1H), 5.67 (dd, *J* = 9.5, 3.7 Hz, 1H), 4.43 (t, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.46 (t, *J* = 6.1 Hz, 2H), 3.38 (t, *J* = 8.0 Hz, 1H), 3.34 (dd, *J* = 9.0, 6.1 Hz, 1H), 2.59 (br s, 1H), 2.25 (dddd, *J* = 17.4, 8.5, 4.6, 1.6 Hz 1H), 2.16-2.14 (m, 1H), 2.06 (quin, *J* = 5.5 Hz, 2H), 1.63 (quin, *J* = 5.6 Hz, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 159.5, 147.6, 127.0, 125.5, 124.9, 123.5, 118.8, 114.2, 73.1, 70.1, 55.3, 50.1, 33.4, 27.5, 26.5, 25.4. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{20}H_{25}N_3O_2$ 339.1947, found: 339.1929.

*4-(1-(4-(cyclohexa-2,4-dien-1-ylmethoxy)butyl)-1H-1,2,3-triazol-4-yl)-N,N-dimethylaniline (**4c**)*



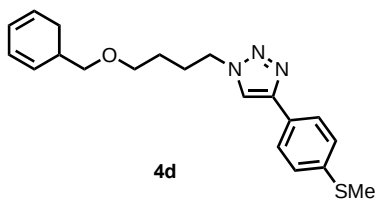
4c

The reaction was conducted based on General procedure 1 using dieneazide **1** (15.0 mg, 0.0724 mmol) and 4-ethynyl-*N*,*N*-dimethylaniline (**S6**) and the reaction time was 24 h. The mixture was concentrated under

vacuum and the residue was purified with silica gel column chromatography (AcOEt : hexane = 1 : 4) to afford the desired product **4c** (22.5 mg, 0.0638 mmol, 88%) as a brown oil.

IR (neat) 3035, 2935, 2864, 2361, 1618 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.63 (s, 1H), 6.77 (d, *J* = 9.3 Hz, 2H), 5.95-5.91 (m, 1H), 5.88 - 5.85 (m, 1H), 5.76 (dt, *J* = 9.3, 4.4 Hz, 1H), 5.67 (dd, *J* = 9.2, 3.9 Hz, 1H), 4.46 (t, *J* = 7.1 Hz, 2H), 3.45 (t, *J* = 6.1 Hz, 2H), 3.37 (t, *J* = 7.8 Hz, 1H), 3.34 (dd, *J* = 9.0, 6.1 Hz, 1H), 2.99 (s, 6H), 2.59 (br s, 1H), 2.26 (dddd, *J* = 17.5, 8.7, 4.7, 1.6 Hz 1H), 2.15-2.11 (m, 1H), 2.10-2.00 (m, 2H), 2.04 (quin, *J* = 6.4 Hz, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 150.3, 148.1, 128.4, 127.5, 126.6, 125.5, 124.8, 123.9, 118.1, 112.5, 73.0, 70.1, 50.0, 40.5, 33.4, 27.5, 26.5, 25.4. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{21}H_{28}N_4O$ 352.2263, found: 352.2259.

1-(4-(cyclohexa-2,4-dien-1-ylmethoxy)butyl)-4-(4-(methylthio)phenyl)-1H-1,2,3-triazole ***(4d)***



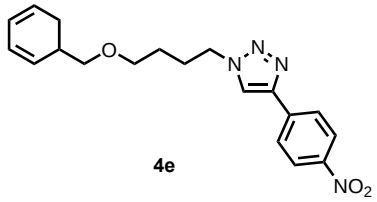
4d

The reaction was conducted based on General procedure 1 using dieneazide **1** (14.8 mg, 0.0714 mmol) and (4-ethynylphenyl)(methyl)sulfane (**S9**) and the reaction time was 24 h. The mixture was concentrated under vacuum and the residue was purified with silica gel column chromatography (AcOEt : hexane = 1 : 4) to afford the desired product **4d** (18.3 mg, 0.0545 mmol, 76%) as a yellow oil.

IR (neat) 3083, 3036, 2858, 1718 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.74 (s, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 5.95-5.92 (m, 1H), 5.89 - 5.85 (m, 1H), 5.76 (dt, *J* = 9.8, 4.4 Hz, 1H), 5.66 (dd, *J* = 9.3, 3.9 Hz, 1H), 4.44 (t, *J* = 7.3 Hz, 2H), 3.46 (t, *J* = 6.1 Hz, 2H), 3.40-3.32 (m, 2H), 2.59 (brs, 1H), 2.51 (s, 3H), 2.25 (dddd, *J* =

17.2, 8.7, 4.9, 1.6 Hz 1H), 2.16-2.15 (m, 1H), 2.05 (quin, *J* = 7.3 Hz, 2H), 1.63 (quin, *J* = 6.4 Hz, 2H). $^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$): δ 147.3, 138.4, 127.56, 127.49, 126.8, 126.0, 125.5, 124.9, 123.9, 119.3, 73.1, 70.1, 50.2, 33.5, 27.5, 26.5, 25.4, 15.8. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{20}H_{25}N_3OS$ 355.1718, found: 355.16944.

*1-(4-(cyclohexa-2,4-dien-1-ylmethoxy)butyl)-4-(4-nitrophenyl)-1H-1,2,3-triazole (**4e**)*

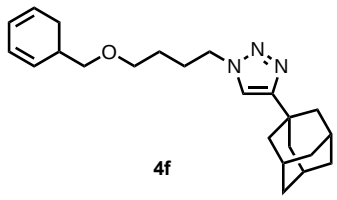


4e

The reaction was conducted based on General procedure 1 using dieneazide **1** (15.1 mg, 0.0728 mmol) and 1-ethynyl-4-nitrobenzene (**S11**) and the reaction time was 24 h. The mixture was concentrated under vacuum and the residue was purified with silica gel column chromatography (AcOEt : hexane = 1 : 4) to the desired product **4e** (20.2 mg, 0.0545 mmol, 78%) as a brown oil.

IR (neat) 3132, 3035, 2939, 2860, 1606, 1518 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.95 (s, 1H), 5.96-5.92 (m, 1H), 5.90-5.86 (m, 1H), 5.77 (dt, *J* = 9.3, 4.5 Hz, 1H), 5.67 (dd, *J* = 9.5, 3.7 Hz, 1H), 4.50 (t, *J* = 7.1 Hz, 2H), 3.49 (t, *J* = 5.9 Hz, 2H), 3.40 (t, *J* = 8.3 Hz, 1H), 3.36 (dd, *J* = 9.0, 6.1 Hz, 1H), 2.60 (br s, 1H), 2.26 (dddd, *J* = 17.4, 8.7, 4.6, 1.6 Hz 1H), 2.17-2.16 (m, 1H), 2.14-2.06 (m, 2H), 1.65 (quin, *J* = 6.3 Hz, 2H). $^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$): δ 180.0, 137.0, 127.5, 126.1, 125.6, 125.0, 124.3, 124.0, 122.2, 121.2, 73.2, 70.2, 50.4, 33.5, 27.6, 26.5, 25.5. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{19}H_{22}N_4O_3$ 353.1636, found: 354.1634.

*4-((1s,3s)-adamantan-1-yl)-1-(4-(cyclohexa-2,4-dien-1-ylmethoxy)butyl)-1H-1,2,3-triazole (**4f**)*



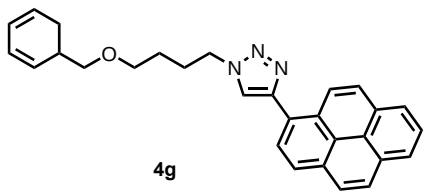
4f

The reaction was conducted based on General procedure 1 using dieneazide **1** (15.0 mg, 0.0724 mmol) and 1-ethynyladamantane (**S12**) and the reaction time was 24 h.

The mixture was concentrated under vacuum and the residue was purified with silica gel column chromatography (AcOEt : hexane = 1 : 4) to afford the desired product **4f** (25.0 mg, 0.0680 mmol, 94%) as a colorless oil.

IR (neat) 3130, 3034, 2904, 2849, 1680 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 1H), 5.95-5.91 (m, 1H), 5.89-5.86 (m, 1H), 5.76 (dt, *J* = 9.7, 4.6 Hz, 1H), 5.67 (dd, *J* = 9.7, 3.9 Hz, 1H), 4.35 (t, *J* = 7.2 Hz, 2H), 3.45 (d, *J* = 6.3 Hz, 1H), 3.43 (d, *J* = 6.2 Hz, 1H), 3.37 (t, *J* = 7.7 Hz, 1H), 3.33 (dd, *J* = 8.4, 5.6 Hz, 1H), 2.58 (br s, 1H), 2.26 (dddd, *J* = 16.4, 9.1, 4.8, 1.6 Hz 1H), 2.16-2.11 (m, 1H), 2.07-2.02 (m, 2H), 1.98-1.84 (m, 8H), 1.78-1.75 (m, 7H), 1.60 (quin, *J* = 6.8 Hz, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 157.9, 127.50, 125.5, 124.8, 123.9, 118.1, 73.1, 70.1, 49.9, 42.6, 36.7, 33.4, 32.6, 28.5, 27.5, 26.6, 25.5. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{23}H_{32}N_3O$ 366.2546, found: 366.2552.

*1-(4-(cyclohexa-2,4-dien-1-ylmethoxy)butyl)-4-(pyren-1-yl)-1H-1,2,3-triazole (**4g**)*



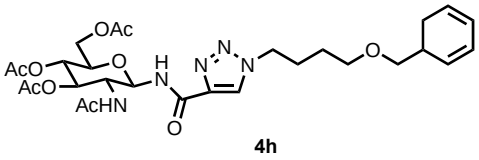
4g

The reaction was conducted based on General procedure 1 using dieneazide **1** (15.0 mg, 0.0724 mmol) and 1-ethynylpyrene (**S16**). The solvent was changed to MeOH/CH_2Cl_2/H_2O (1:8:1) and the reaction time was 24 h. The mixture was concentrated under vacuum and the residue was purified with silica gel column chromatography solvent (AcOEt : hexane = 1 : 4) to afford the desired product **4g** (23.2 mg, 0.0535 mmol, 74%) as a yellow oily solid.

IR (neat) 3132, 3038, 2938, 2860, 2242, 2095, 1925, 1798, 1723, 1605 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 9.3 Hz, 1H), 8.27-7.93 (m, 8H), 7.93 (s, 1H), 5.95-5.91 (m, 1H), 5.88-5.85 (m, 1H), 5.75 (dt, *J* = 9.3, 4.5 Hz, 1H), 5.69 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.58 (t, *J* = 7.0 Hz, 2H), 3.52 (t, *J* = 6.1 Hz, 2H), 3.41 (t, *J* = 8.3 Hz, 1H), 3.37 (dd, *J* = 8.8, 5.9 Hz, 1H), 2.61 (brs, 1H), 2.27 (dddd, *J* = 20.1, 9.1, 5.1, 2.7 Hz 1H),

2.20-2.11 (m, 3H), 1.73 (quin, *J* = 5.7 Hz, 2H). $^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$): δ 147.4, 131.4, 131.3, 130.9, 128.6, 128.1, 127.8, 127.7, 127.5, 127.4, 127.2, 126.1, 125.6, 125.41, 125.37, 125.1, 124.94, 124.87, 124.83, 124.79, 123.9, 122.9, 73.1, 70.2, 50.4, 33.5, 27.7, 26.7, 25.5. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{29}H_{27}N_3O$ 433.2154, found: 433.2162.

*(2R,3S,4R,5R,6R)-5-acetamido-2-(acetoxymethyl)-6-(1-(4-(cyclohexa-2,4-dien-1-ylmeth oxy)butyl)-1H-1,2,3-triazole-4-carboxamido)tetrahydro-2H-pyran-3,4-diyl diacetate (**4h**)*

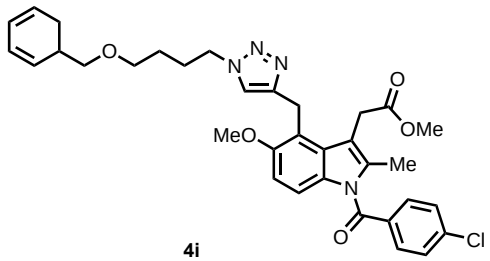


4h

The reaction was conducted based on General procedure 1 using dieneazide **1** (7.38 mg, 35.6 μmol) and acetylated glucosamine derivative **S20** and the reaction time was 24 h. The mixture was concentrated under vacuum and the residue was purified with silica gel column chromatography (AcOEt only) to afford the desired product **4h** (13.2 mg, 21.8 μmol, 61%) as a white oil.

IR (neat) 3302, 3130, 2949, 2854, 2451, 1795, 1743, 1638 cm^{-1}. ^{1}H-NMR (600 MHz, CD_3OD): δ 8.32 (s, 1H), 5.81-5.79 (m, 1H), 5.76-5.74 (m, 1H), 5.64 (dt, *J* = 9.6, 4.6 Hz, 1H), 5.56 (dd, *J* = 9.6, 3.4 Hz, 1H), 5.33 (d, *J* = 9.6 Hz, 1H), 5.20 (dd, *J* = 10.6, 9.2 Hz, 1H), 4.96 (dd, *J* = 9.6 Hz, 1H), 4.39 (t, *J* = 7.2 Hz, 2H), 4.19 (dd, *J* = 10.9, 3.4 Hz, 1H), 4.13 (dd, *J* = 10.3 Hz, 1H), 4.02 (dd, *J* = 12.3, 1.4 Hz, 1H), 3.84-3.81 (m, 1H), 3.37-3.35 (m, 2H), 3.24-3.21 (m, 2H), 2.43 (br s, 1H), 2.12 (dddd, *J* = 17.4, 8.5, 4.8, 1.7 Hz 1H), 2.02-1.99 (m, 1H), 1.93-1.90 (m, 11H), 1.75 (s, 3H), 1.49 (quin, *J* = 5.3 Hz, 2H). $^{13}C\{^{1}H\}$-NMR (100 MHz, CD_3OD): δ 174.0, 172.4, 171.8, 171.3, 162.8, 143.0, 128.6, 127.8, 126.4, 125.9, 125.0, 119.7, 81.8, 79.8, 74.7, 74.5, 74.0, 71.1, 70.0, 63.3, 54.0, 51.4, 34.7, 28.4, 27.5, 26.4, 22.5, 20.6. HRMS (FAB) *m/z*: $[M]^+$ Calcd. for $C_{28}H_{40}N_5O_{10}$ 606.2775, found: 606.2767.

*Huisgen annulated indomethacin derivative **4i***

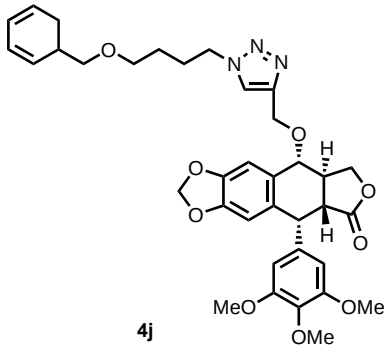


4i

The reaction was conducted based on General procedure 1 using dieneazide **1** (7.5 mg, 36 μmol) and propargylated indomethacin methyl ester **S23**. The solvent was changed to ^{t}BuOH/MeOH/$CHCl_3$/H_2O (2:1:1:1, 0.03 M) and the reaction time was 60 h. The mixture was concentrated under vacuum and the residue was purified with silica gel column chromatography (AcOEt : hexane = 1 : 4 to AcOEt : hexane = 1 : 1) to afford the desired product **4i** (15.55 mg, 25.2 μmol, 84%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.06 (s, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 2H), 5.92-5.83 (m, 2H), 5.75-5.70 (m, 1H), 5.63 (dd, *J* = 9.7, 3.9 Hz, 1H), 4.43 (s, 2H), 4.25 (d, *J* = 7.2 Hz, 2H), 3.97 (s, 2H), 3.82 (s, 3H), 3.67 (s, 3H), 3.40 (t, *J* = 6.3 Hz, 2H), 3.36-3.28 (m, 2H), 2.62-2.47 (m, 1H), 2.29-2.18 (m, 1H), 2.26 (s, 3H), 2.12-2.06 (m, 1H), 1.02 (quin, *J* = 7.2 Hz, 2H), 1.59-1.52 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 172.1, 168.3, 153.4, 147.9, 139.4, 136.8, 134.0, 131.8, 131.3, 129.1, 128.8, 127.5, 125.5, 124.9, 123.9, 121.6, 118.4, 112.9, 112.6, 107.9, 73.0, 70.1, 56.7, 52.1, 50.0, 33.4, 31.1, 27.4, 26.6, 25.4, 13.3. HRMS (EI): $[M]^+$ Calcd. for $C_{34}H_{37}ClN_4O_5$ 616.2452, found: 616.2433.

*Huisgen annulated podophyllotoxin derivative **4j***



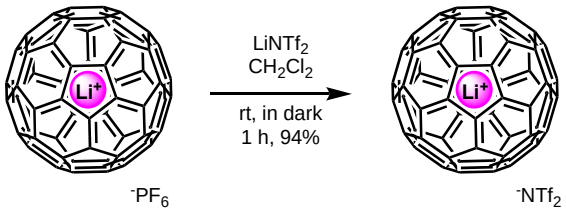
4j

The reaction was conducted based on General procedure 1 using dieneazide **1** (2.1 mg, 11 μmol) and propargylated podophyllotoxin **S26**. and the reaction time was 48 h. The mixture was concentrated under vacuum and the residue was purified with silica gel

column chromatography (AcOEt : hexane = 1 : 3 to AcOEt : hexane = 2 : 1) to afford the desired product **4j** (3.93 mg, 5.96 μmol, 72%) as a colorless oil.

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.63 (s, 1H), 6.99 (s, 1H), 6.51 (s, 1H), 6.40 (s, 2H), 5.96 (d, *J* = 1.2 Hz, 1H), 5.95 (d, *J* = 1.2 Hz, 1H), 5.94-5.91 (m, 1H), 5.88-5.85 (m, 1H), 5.77-5.73 (m, 1H), 5.66 (dd, *J* = 9.7, 3.9 Hz, 1H), 4.82 (d, *J* = 9.2 Hz, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.69 (d, *J* = 11.8 Hz, 1H), 4.59-4.55 (m, 2H), 4.43 (t, *J* = 7.2 Hz, 2H), 4.15 (td, *J* = 9.4, 1.4 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 6H), 3.46 (t, *J* = 5.8 Hz, 2H), 3.40-3.32 (m, 2H), 3.03-2.92 (m, 1H), 2.84 (dd, *J* = 14.5, 4.8 Hz, 1H), 2.65-2.52 (m, 1H), 2.26 (dddd, *J* = 17.4, 8.7, 4.8, 1.4 Hz 1H), 2.16-2.10 (m, 1H), 2.04 (quin, *J* = 7.2 Hz, 2H), 1.65-1.58 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 174.0, 152.6, 147.8, 147.6, 144.5, 137.2, 135.3, 131.9, 130.6, 127.5, 125.5, 124.9, 123.9, 122.5, 110.0, 108.2, 107.2, 101.4, 79.2, 73.1, 71.3, 70.1, 62.0, 60.7, 56.2, 50.3, 45.6, 44.0, 38.0, 33.5, 27.6, 26.6, 25.5. HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{36}H_{41}N_3O_9$ 659.2843, found: 659.2837.

5. Preparation of Li^+@C_{60} bis(trifleoromethanesulfonyl)imide ($^-NTf_2$) salt 2



S27 **2**

To a solution of Li^+@C_{60} hexafluorophosphate (PF_6) salt **S27** (20.3 mg, 23.2 μmol) in CH_2Cl_2 (10 mL) was added $LiNTf_2$ (33.3 mg, 116 μmol) at room temperature. The reaction mixture was sonication for 1 min and stirred for 1 h under darkness. After the color of reaction mixture was changed from dark black to purple, the solution was concentrated in vacuum. To the black residue was added CH_2Cl_2. Then, recrystallized by vapor diffusion of Et_2O to afford Li^+@C_{60} bis (trifluoromethane sulfonyl) imide (NTf_2) salt **2** (22.2 mg, 21.9 μmol, 94%) as a black solid. Characterization data were in

agreement with previously reported values[11].

6. Diels-Alder reactions

General procedure 2: Diels-Alder reaction

To solution of $Li^+@C_{60}$ **2** (5.0 μmol) in CH_2Cl_2 (2.5 mL) was slowly added the solution of diene (4.0 μmol) in CH_2Cl_2 (2.5 mL) at 0 ºC. The reaction mixture was stirred at room temperature for 24 h under darkness. The mixture was concentrated under vacuum. Purification of the product was performed by HPLC. From the collected fraction, solvent was evaporated in vacuum. To the black residue containing white solid $LiNTf_2$ was added CH_2Cl_2 (ca. 0.5 mL). Reprecipitation by addition of Et_2O afforded $Li^+@C_{60}$ derivatives as a black solid. Note that, most of obtained products were containing Et_2O (see ^{1}H-NMR charts) due to coordination to $Li^+@C_{60}$ unit. Protons of obtained products **5a-j** were assigned putatively (see ^{1}H-NMR charts). $^{13}C\{^1H\}$-NMR spectra were not provided because of the paucity of obtained compounds except for **5a**.

<HPLC conditions>

column: π-NAP (0.46 cm × 25 cm)

Eluent: 2.5 mM in $LiNTf_2$ PhCl-CH_3CN (1:3)

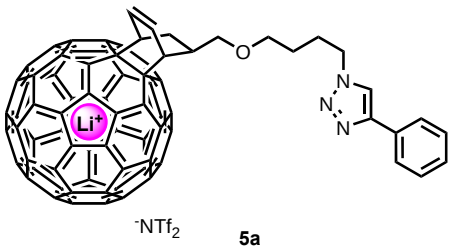
Flow rate: 1.0 mL/min

Detection: UV 350 nm

Temperature: 35 ºC

Injection: 10 μL (reaction tracking), 200 μL (preparative)

*Li^+@C_{60}–phenyl derivative (**5a**)*

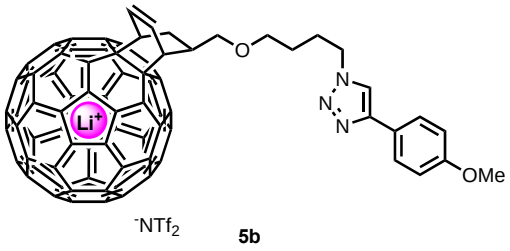


5a

The reaction was conducted based on General procedure 2 using $Li^+@C_{60}$ **2** and diene **4a**. Reprecipitation by addition of Et_2O afforded $Li^+@C_{60}$-phenyl derivative **5a** (2.49 mg, 1.89 μmol, 46%) as a black solid.

^{1}H-NMR (700 MHz, CD_2Cl_2): δ 7.85 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.42-7.38 (m, 3H), 7.31 (dd, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 4.50-4.46 (m, 3H), 4.31-4.30 (m, 1H), 3.70-3.56 (m, 5H), 3.26 (ddd, *J* = 14.1, 10.0, 2.6, 1H), 2.14-2.10 (m, 2H), 1.81 (ddd, *J* = 14.2, 4.9, 3.1 Hz, 1H), 1.74 (quin, *J* = 8.9 Hz, 2H). ^{13}C{^{1}H}-NMR (175 MHz, CD_2Cl_2): δ 157.9, 157.8, 157.1, 156.9, 147.8, 147.5, 147.4, 146.52, 146.49, 146.42, 146.35, 146.3, 146.21, 146.18, 146.16, 146.1, 145.80, 145.76, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 144.6, 144.44, 144.41, 144.2, 143.3, 143.0, 142.9, 142.8, 142.2, 142.0, 141.81, 141.79, 141.7, 142.6, 141.5, 140.1, 140.0, 139.8, 137.6, 137.4, 136.5, 136.4, 134.0., 131.3, 129.3, 128.4, 125.9, 121.3, 120.3, 119.5, 77.7, 77.5, 74.6, 71.7, 71.4, 70.9, 50.6, 45.8, 44.5, 38.4, 29.8, 28.0, 27.0. (Carbon signal of Tf group is too small to detect in this measurement.) ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –13.6 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{79}H_{23}LiN_3O^+$ 1036.1996, found: 1036.1995.

*Li^+@C_{60}–4-anisolyl derivative (**5b**)*



5b

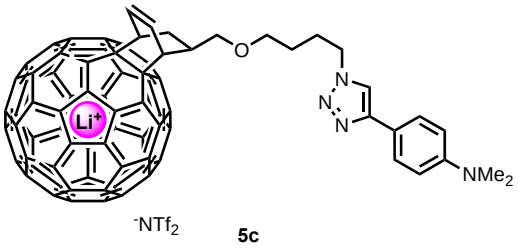
The reaction was conducted based on General procedure 2 using $Li^+@C_{60}$ **2** and diene **4b**. Reprecipitation by addition of Et_2O afforded $Li^+@C_{60}$-4-anisolyl derivative **5b** (1.58 mg, 1.17 μmol, 27%) as a black solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 7.68 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.2

Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 4.40-4.37 (m, 3H), 4.22 (t, *J* = 3.4 Hz, 1H), 3.73 (s, 3H), 3.60-3.49 (m, 5H), 3.18 (td, *J* = 11.9, 1.7 Hz, 1H), 2.03 (quin, *J* = 3.8 Hz, 2H), 1.72 (dt, *J* = 14.0, 4.1 Hz, 1H), 1.65 (quin, *J* = 7.0 Hz, 2H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –13.6 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{80}H_{25}LiN_3O^+$ 1166.2101, found:1166.2097.

$^{13}C\{^{1}H\}$-NMR data was not provided because of the paucity of the compound.

*$Li^+@C_{60}$– N,N-dimethylaniline derivative (**5c**)*



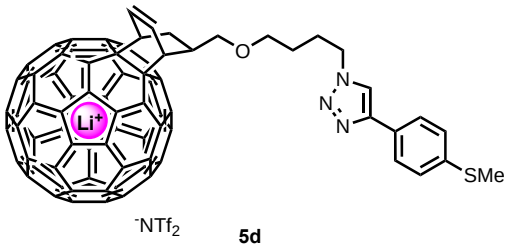
5c

The reaction was conducted based on General procedure 2 using $Li^+@C_{60}$ **2** and diene **4c**. Reprecipitation by addition of Et_2O afforded $Li^+@C_{60}$-*N*,*N*-dimethylaniline derivative **5c** (3.67 mg, 2.70 μmol, 66%) as a black solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 7.72 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 2H), 4.47-4.44 (m, 3H), 4.29 (t, *J* = 3.4 Hz, 1H), 3.68-3.55 (m, 5H), 3.25 (td, *J* = 12.0, 1.0 Hz, 1H), 2.97 (s, 6H), 2.14-2.06 (m, 2H), 1.79 (dt, *J* = 14.2, 3.6 Hz, 1H), 1.74 (quin, *J* = 6.7 Hz, 2H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –13.6 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{81}H_{28}LiN_4O^+$ 1079.2418, found: 1079.2411.

$^{13}C\{^{1}H\}$-NMR data was not provided because of the paucity of the compound.

*$Li^+@C_{60}$–4-(methylthio)phenyl derivative (**5d**)*



5d

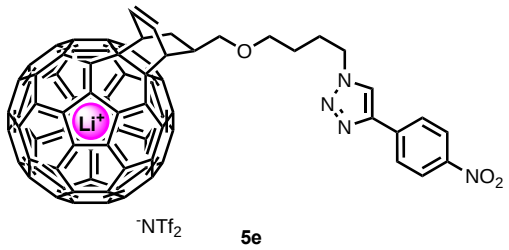
The reaction was conducted based on General procedure 2 using $Li^+@C_{60}$ **2** and diene **4d**. Reprecipitation by addition of Et_2O afforded $Li^+@C_{60}$-4-(methylthio)phenyl

derivative **5d** (3.32 mg, 2.44 μmol, 64%) as a black solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 7.83 (s, 1H), 7.71 (d, *J* = 8.9 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.27-7.23 (m, 3H), 4.48 (t, *J* = 7.2 Hz, 2H), 4.44 (d, *J* = 6.2 Hz, 1H), 4.30 (t, *J* = 3.4 Hz, 1H), 3.67-3.57 (m, 5H), 3.25 (td, *J* = 11.6, 1.0 Hz, 1H), 2.49 (s, 3H), 2.14-2.09 (m, 2H), 1.80 (dt, *J* = 14.0, 3.8 Hz, 1H), 1.74 (quin, *J* = 6.8 Hz, 2H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –13.6 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{80}H_{25}LiN_3O^+$ 1082.1873, found: 1082.1834.

^{13}C{^{1}H}-NMR data was not provided because of the paucity of the compound.

*Li^+@C_{60}–4-nitrophenyl derivative (**5e**)*



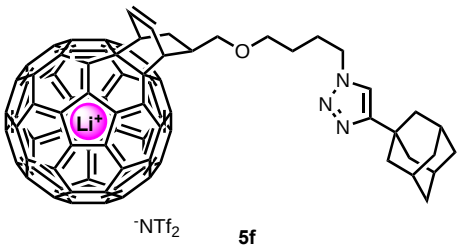
5e

The reaction was conducted based on General procedure 2 using Li^+@C_{60} **2** and diene **4e**. Reprecipitation by addition of Et_2O afforded Li^+@C_{60}-4-nitrophenyl derivative **5e** (2.66 mg, 1.95 μmol, 52%) as a black solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 8.26 (d, *J* = 8.9 Hz, 2H), 8.05 (s, 1H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 4.53 (t, *J* = 7.2 Hz, 2H), 4.46 (d, *J* = 6.2 Hz, 1H), 4.31 (t, *J* = 2.7 Hz, 1H), 3.70-3.58 (m, 5H), 3.27 (td, *J* = 11.3 Hz, 1H), 2.14 (quin, *J* = 6.8 Hz, 2H), 1.82 (dt, *J* = 14.2, 3.9 Hz, 1H), 1.74 (quin, *J* = 6.8 Hz, 2H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –13.6 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{79}H_{22}LiN_4O^+$ 1081.1846, found: 1081.1800.

^{13}C{^{1}H}-NMR data was not provided because of the paucity of the compound.

*Li^+@C_{60}–adamantyl derivative (**5f**)*



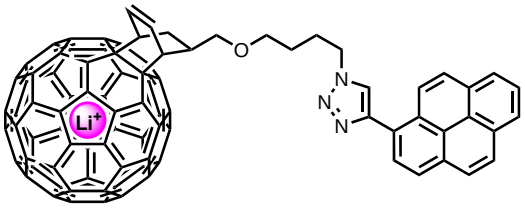
5f

The reaction was conducted based on General procedure 2 using Li^+@C_{60} **2** and diene **4f**. Reprecipitation by addition of Et_2O afforded Li^+@C_{60}-adamantyl derivative **5f** (2.36 mg, 1.72 μmol, 42%) as a black solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 7.42-7.39 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 4.47 (d, *J* = 6.0 Hz, 1H), 4.42 (t, *J* = 7.2 Hz, 2H), 4.32 (t, *J* = 3.1 Hz, 1H), 3.71 (s, 2H), 3.63-3.45 (m, 5H), 3.28 (ddd, *J* = 14.0, 9.9, 2.7 Hz, 1H), 2.12-2.06 (m, 5H), 2.00 (s, 6H), 1.85-1.76 (m, 7H), 1.69 (quin, *J* = 7.0 Hz, 2H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –13.6 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{83}H_{33}LiN_3O^+$ 1094.2771, found: 1094.2778.

$^{13}C\{^1H\}$-NMR data was not provided because of the paucity of the compound.

*Li^+@C_{60}–pyrenyl derivative (**5g**)*



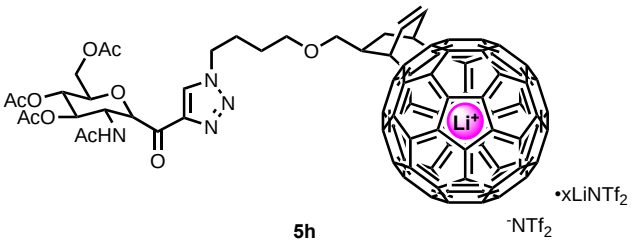
5g

The reaction was conducted based on General procedure 2 using Li^+@C_{60} **2** and diene **4g**. Reprecipitation by addition of Et_2O afforded Li^+@C_{60}-pyrenyl derivative **5g** (3.68 mg, 2.55 μmol, 64%) as a black solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 8.60 (d, *J* = 8.9 Hz, 1H), 8.15-8.08 (m, 4H), 8.03-7.92 (m, 5H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 4.58 (quin d, *J* = 9.6, 5.2 Hz, 2H), 4.26 (d, *J* = 6.8 Hz, 1H), 4.11 (t, *J* = 3.1 Hz, 1H), 3.64 (ddd, *J* = 19.3, 9.7, 5.3 Hz, 2H), 3.54-3.49 (m, 3H), 3.08 (ddd, *J* = 13.6, 8.8, 2.5 Hz, 1H), 2.17 (quin, *J* = 7.3 Hz, 2H), 1.79-1.78 (m, 2H), 1.66 (dt, *J* = 14.5, 3.6 Hz, 1H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –14.0 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{89}H_{27}LiN_3O^+$ 1160.2309, found: 1160.2274.

$^{13}C\{^{1}H\}$-NMR data was not provided because of the paucity of the compound.

*Li^{+}@C_{60}–glucosamine derivative (**5h**)*



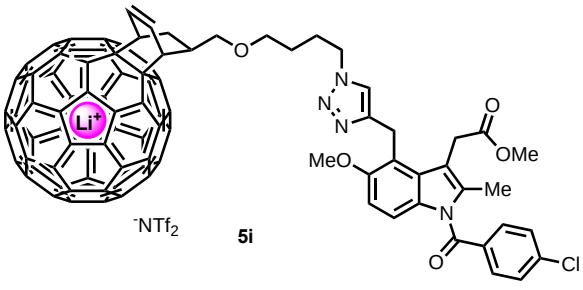
5h

The reaction was conducted based on General procedure 2 using Li^{+}@C_{60} **2** and diene **4h**. Reprecipitation by addition of Et_2O afforded Li^{+}@C_{60}-glucosamine derivative **5h** (5.68 mg, 3.50 μmol, 68%) as a black solid. Yield was calculated as a mono $LiNTf_2$ adduct.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 8.25-8.24 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 5.38 (t, *J* = 9.2 Hz, 1H), 5.24 (t, *J* = 9.9 Hz, 1H), 5.10 (t, *J* = 9.9 Hz, 1H), 4.51 (t, *J* = 7.2 Hz, 2H), 4.46 (d, *J* = 6.1 Hz, 1H), 4.31 (t, *J* = 3.4 Hz, 1H), 4.22-4.15 (m, 2H), 4.10 (d, *J* = 12.3 Hz, 1H), 3.86 (dt, *J* = 9.7, 3.2 Hz, 1H), 3.71 (brs, 1H), 3.63-3.58 (m, 5H), 3.28 (td, *J* = 12.3, 3.8 Hz, 1H), 2.12-2.09 (m, 2H), 2.05-2.03 (m, 9H), 1.90 (s, 3H), 1.69 (quin, *J* = 6.5 Hz, 2H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –0.28 (s), –13.6 (s). HRMS (ESI) *m/z*: $[M–LiNTf_2–NTf_2]^{+}$ Calcd. for $C_{88}H_{39}LiN_5O_{10}^{+}$ 1332.2851, found: 1332.2800.

$^{13}C\{^{1}H\}$-NMR data was not provided because of the paucity of the compound.

*Li^{+}@C_{60}–indomethacin derivative (**5i**)*

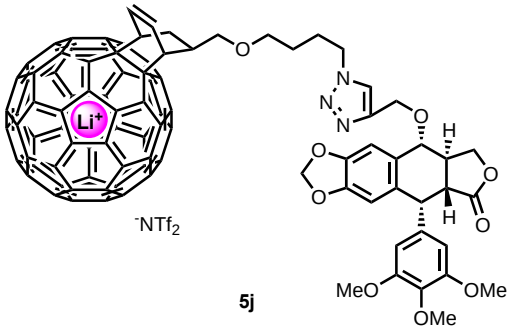


5i

The reaction was conducted based on General procedure 2 using Li^{+}@C_{60} **2** and diene **4i**. Reprecipitation by addition of Et_2O afforded Li^{+}@C_{60}-indomethacin derivative **5i** (5.82 mg, 2.97 μmol, 74%) as a black solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.22 (s, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.73 (d, *J* = 9.0 Hz, 1H), 4.48 (d, *J* = 6.0 Hz, 1H), 4.33-4.29 (m, 5H), 3.99 (d, *J* = 2.5 Hz, 2H), 3.82 (s, 3H), 3.72-3.66 (m, 1H), 3.65 (s, 3H), 3.63-3.54 (m, 4H), 3.24 (td, *J* = 9.5, 2.5 Hz, 1H), 2.23 (s, 3H), 2.01 (quin, *J* = 7.0 Hz, 2H), 1.79 (dt, *J* = 14.5, 4.5 Hz, 1H), 1.67 (quin, *J* = 6.5 Hz, 2H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ –13.6 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{94}H_{37}ClLiN_4O_5^+$ 1343.2607, found: 1343.2622. ^{13}C{^{1}H}-NMR data was not provided because of the paucity of the compound.

*$Li^+@C_{60}$– podophyllotoxin derivative (**5j**)*



5j

The reaction was conducted based on General procedure 2 using $Li^+@C_{60}$ **2** and diene **4i**. Purification of the product was performed by Buckyprep-M column instead of π-NAP column. Reprecipitation by addition of Et_2O afforded $Li^+@C_{60}$-podophyllotoxin derivative **5i** (1.12 mg, 0.672 μmol, 17%) as a black solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ 7.72 (s, 1H), 7.39 (dd, *J* = 7.5, 4.8 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 3.4 Hz, 1H), 6.47 (s, 1H), 6.36 (s, 2H), 5.95 (s, 2H), 4.81 (d, *J* = 8.9 Hz, 1H), 4.74 (d, *J* = 11.6, 1H), 4.70 (d, *J* = 11.6, 1H), 4.55 (d, *J* = 4.8 Hz, 1H), 4.50-4.47 (m, 4H), 4.31 (d, *J* = 5.5 Hz, 1H), 4.08 (t, *J* = 9.6 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 6H), 3.67-3.57 (m, 5H), 3.28 (t, *J* = 11.6 Hz, 1H), 2.98-2.91 (m, 1H), 3.24 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.11 (quin, *J* = 6.8 Hz, 2H), 1.83 (dt, *J* = 14.4, 4.1 Hz, 1H), 1.71 (quin, *J* = 6.8 Hz, 2H). ^{7}Li-NMR (233 MHz, CD_2Cl_2): δ -13.6 (s). HRMS (ESI) *m/z*: $[M–NTf_2]^+$ Calcd. for $C_{96}H_{41}LiN_3O_9^+$ 1386.2997, found: 1386.2985.

^{13}C{^{1}H}-NMR data was not provided because of the paucity of the compound.

7. Purity of $Li^+@C_{60}$-small molecule adducts

<HPLC conditions for confirming purity>

column: Buckyprep (0.46 cm × 25 cm)

Eluent: 30 mM in $LiNTf_2$ PhCl-CH_3CN (19:1)

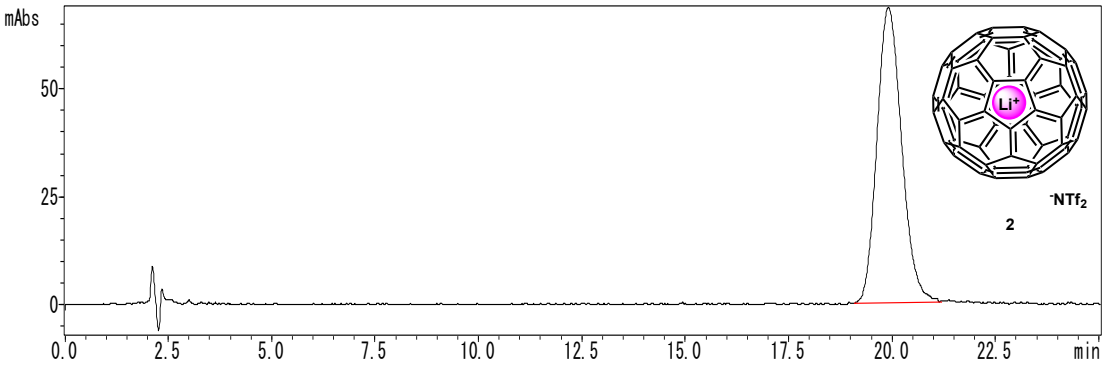
Flow rate: 1.0 mL/min

Detection: UV 337 nm

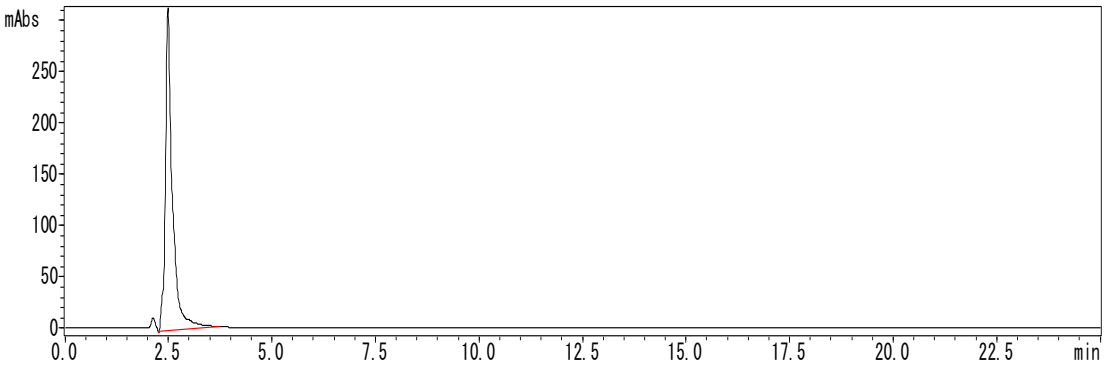
Temperature: 50 ºC

Injection: 10 μL

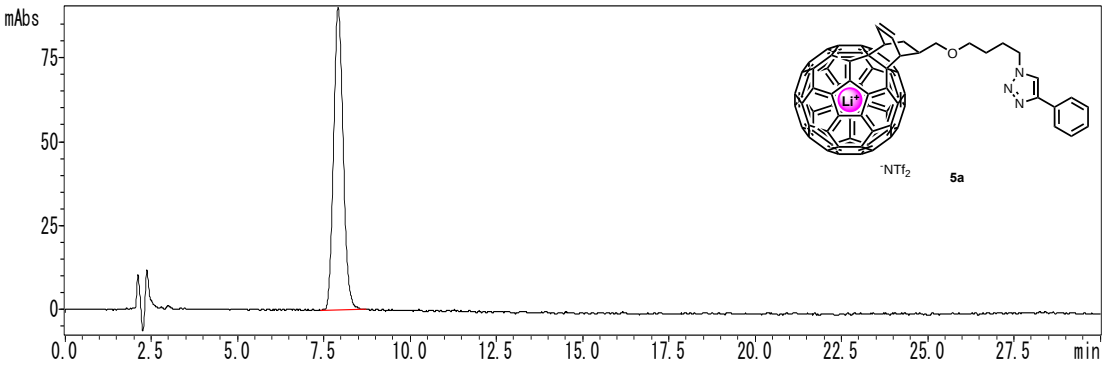
HPLC chart of $Li^+@C_{60}$ 2



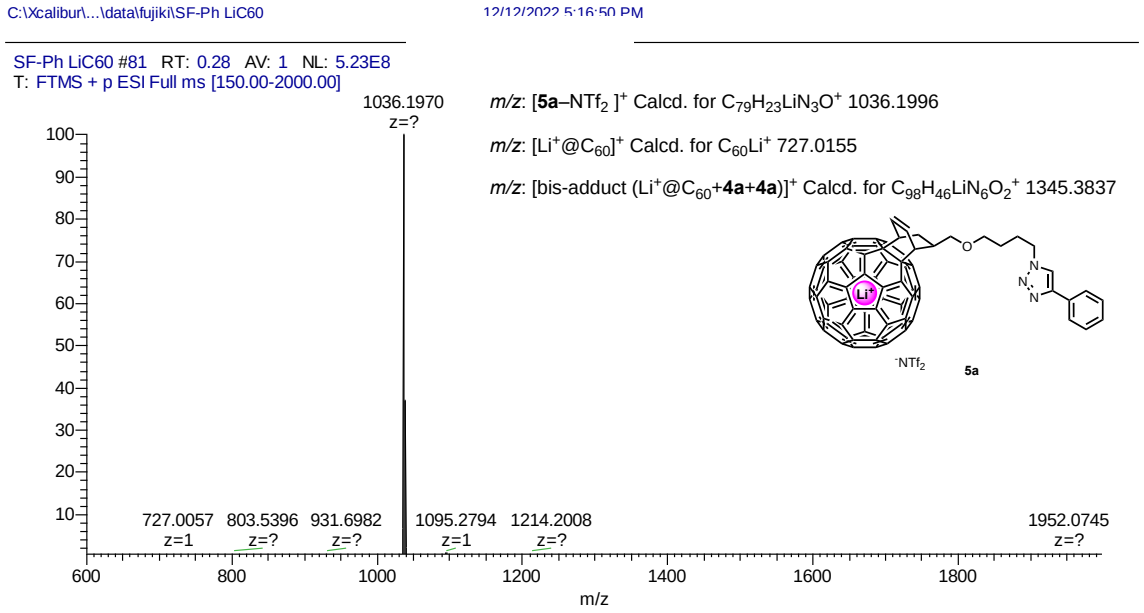
HPLC chart of bis-adduct of $Li^+@C_{60}$ 2 and diene 4a



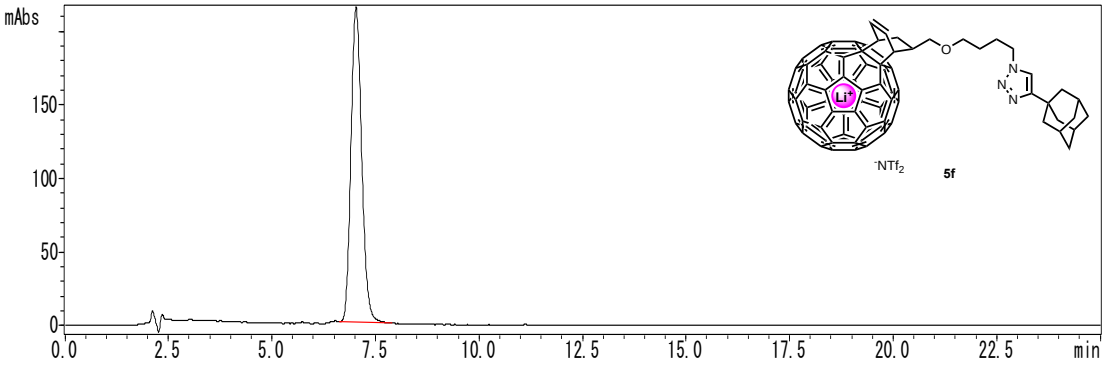
HPLC chart of $Li^+@C_{60}$-small molecule adduct 5a



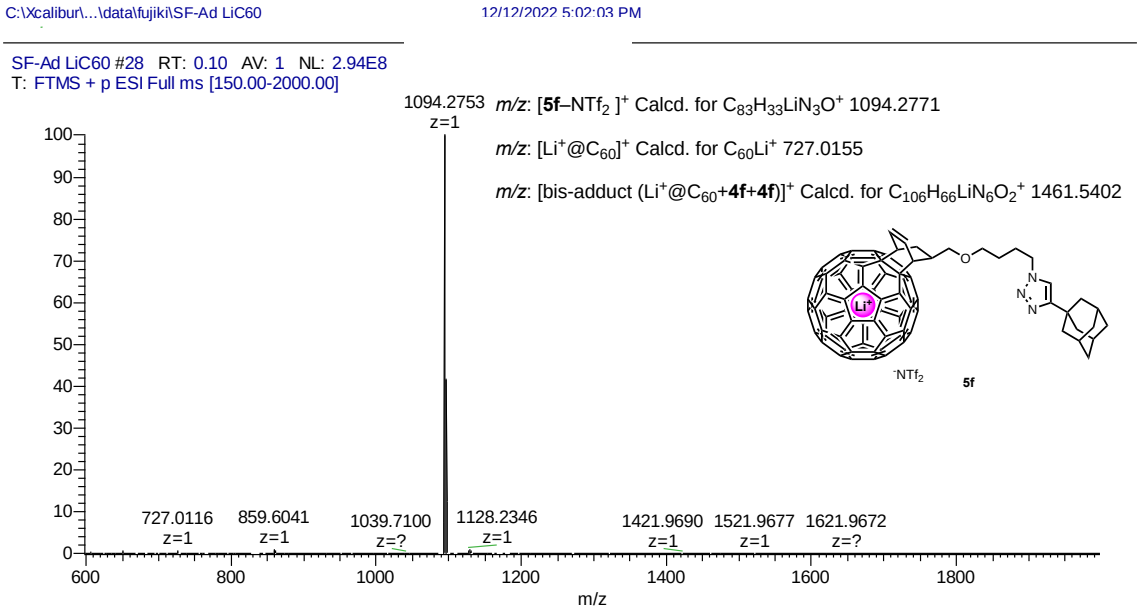
ESI-MS spectrum of $Li^+@C_{60}$-small molecule adduct 5a



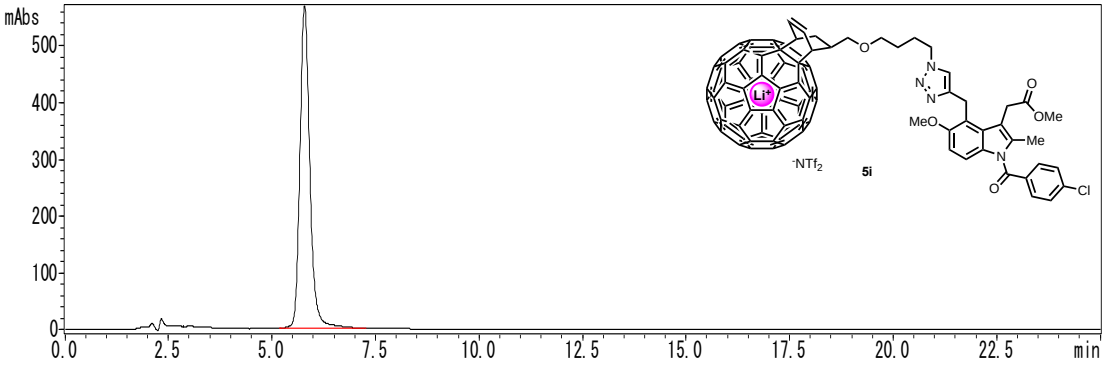
HPLC chart of $Li^+@C_{60}$-small molecule adduct 5f



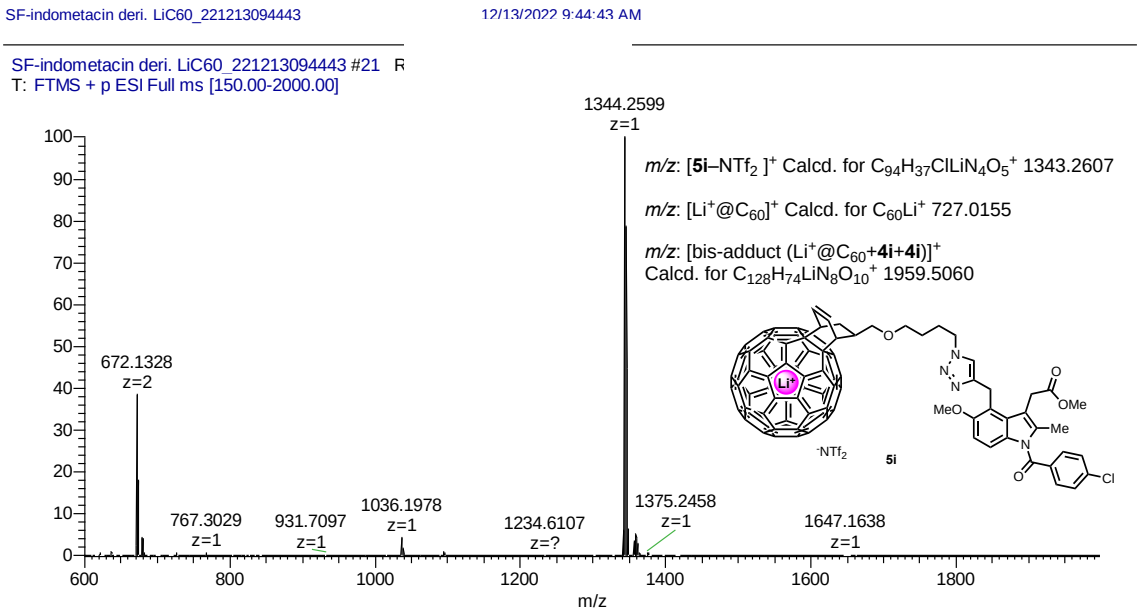
ESI-MS spectrum of $Li^+@C_{60}$-small molecule adduct 5f



HPLC chart of $Li^+@C_{60}$-small molecule adduct 5i



ESI-MS spectrum of $Li^+@C_{60}$-small molecule adduct 5i



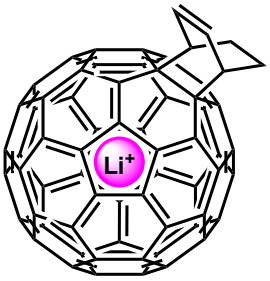
Purified $Li^+@C_{60}$-small molecule adducts were pure form by confirming HPLC, ESI-MS, ^{1}H-NMR, and ^{7}Li-NMR (NMR spectra are shown in section 10. NMR spectra.).

8. Table of ^{7}Li-NMR

^{7}Li-NMR spectra of lithium-ion endohedral fullerenes showed high-field signals due to the shielding effect of the π-conjugated system of C_{60}.

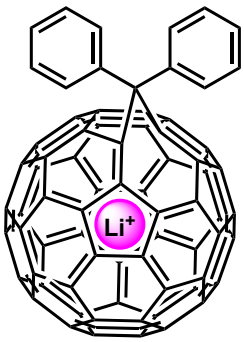
compound	solvent	^{7}Li-NMR (ppm)[a]
5a-f, 5i, 5j	CD_2Cl_2	–13.6
5g	CD_2Cl_2	–0.28, –14.0
5h	CD_2Cl_2	–14.0
$Li^+@C_{60}(^-NTf_2)$ 2	CD_2Cl_2	–10.1[b]
$Li^+@C_{60}(C_6H_8)(^-PF_6)$	CD_2Cl_2	–13.5[c]
[5,6]-$Li^+@C_{61}Ph_2(^-NTf_2)$	d_4-*o*-dichlorobenzene	–10.6[d]
[6,6]-$Li^+@C_{61}Ph_2(^-NTf_2)$	d_4-*o*-dichlorobenzene	–12.4[d]
LiCl	THF	0.48[e]
LiBr	THF	0.59[e]
LiHMDS	THF	0.78[e]
$Li^{+-}CPh_3$	THF	–0.45[e]

[a]LiCl/D_2O was used as an external standard (0 ppm).; [b]see ref 11.; [c]see ref 12.; [d]see ref 13.;[e]see ref 14.



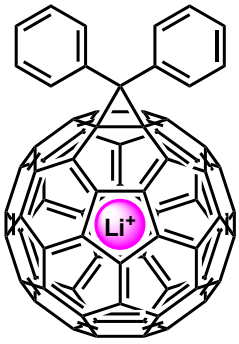
$^{-}PF_6$

$[Li^+@C_{60}(C_6H_8)]PF_6^-$



$^{-}NTf_2$

[5,6]-$Li^+@C_{61}Ph_2(^-NTf_2)$



$^{-}NTf_2$

[6,6]-$Li^+@C_{61}Ph_2(^-NTf_2)$

9. References

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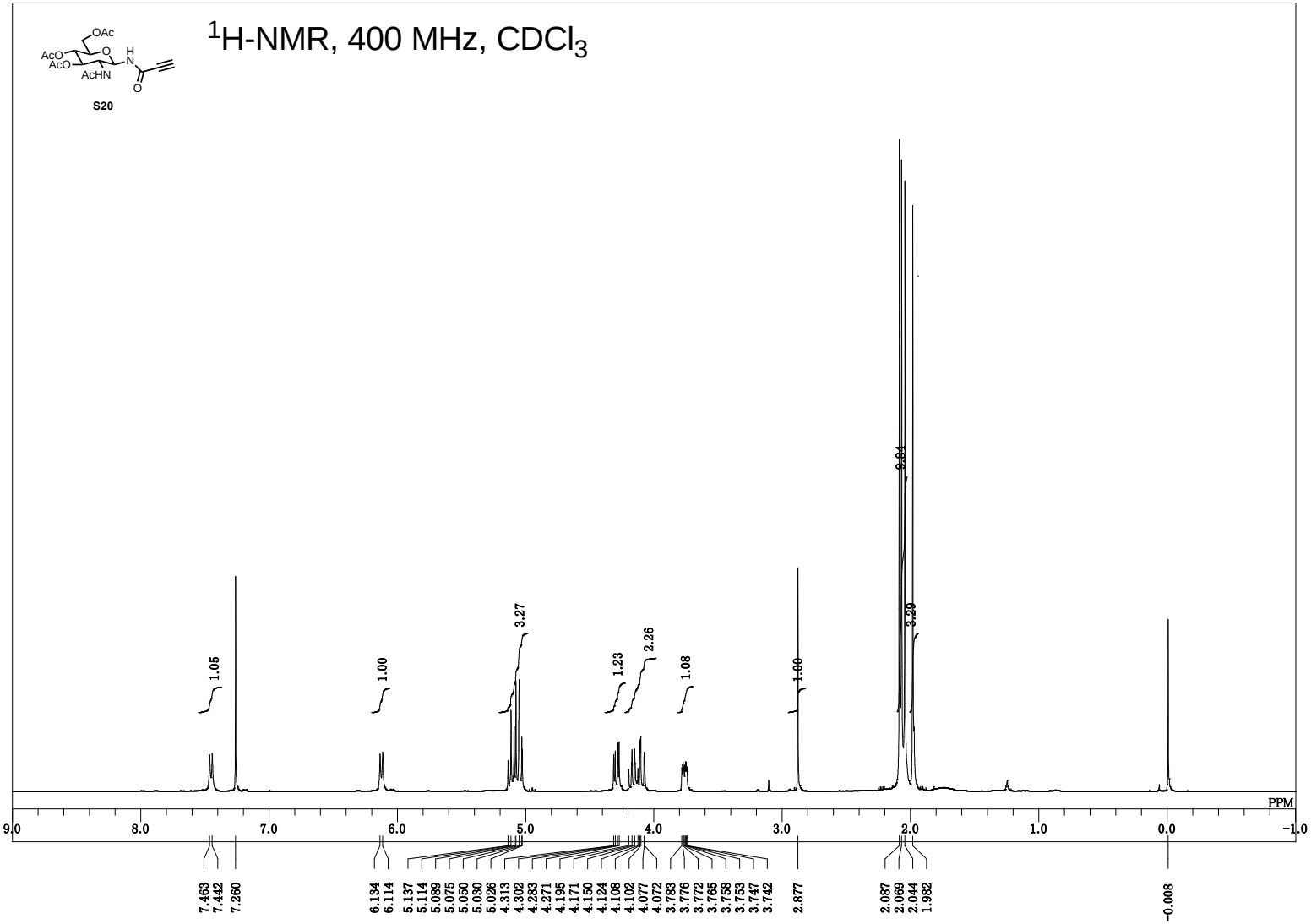
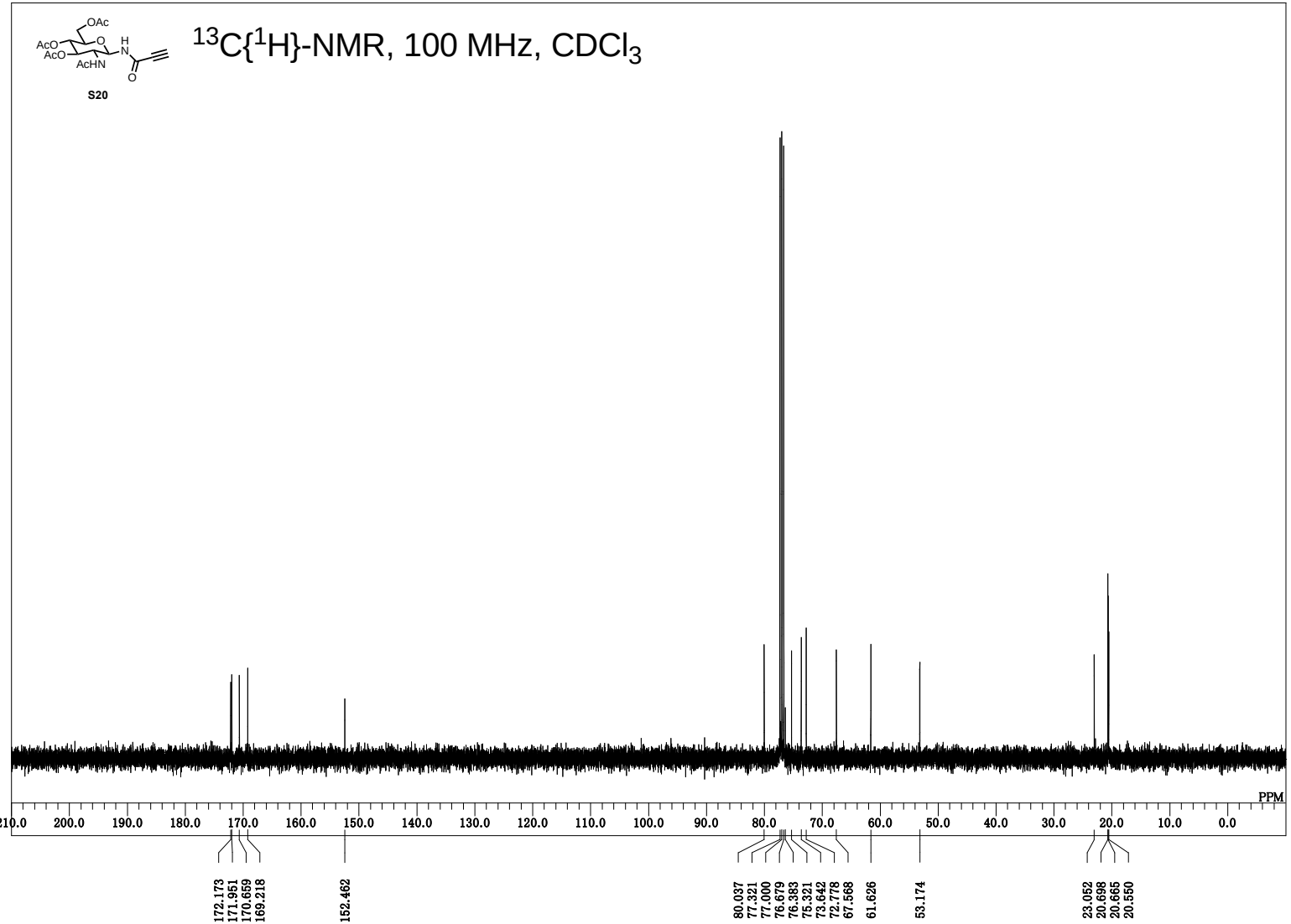
10. NMR spectra

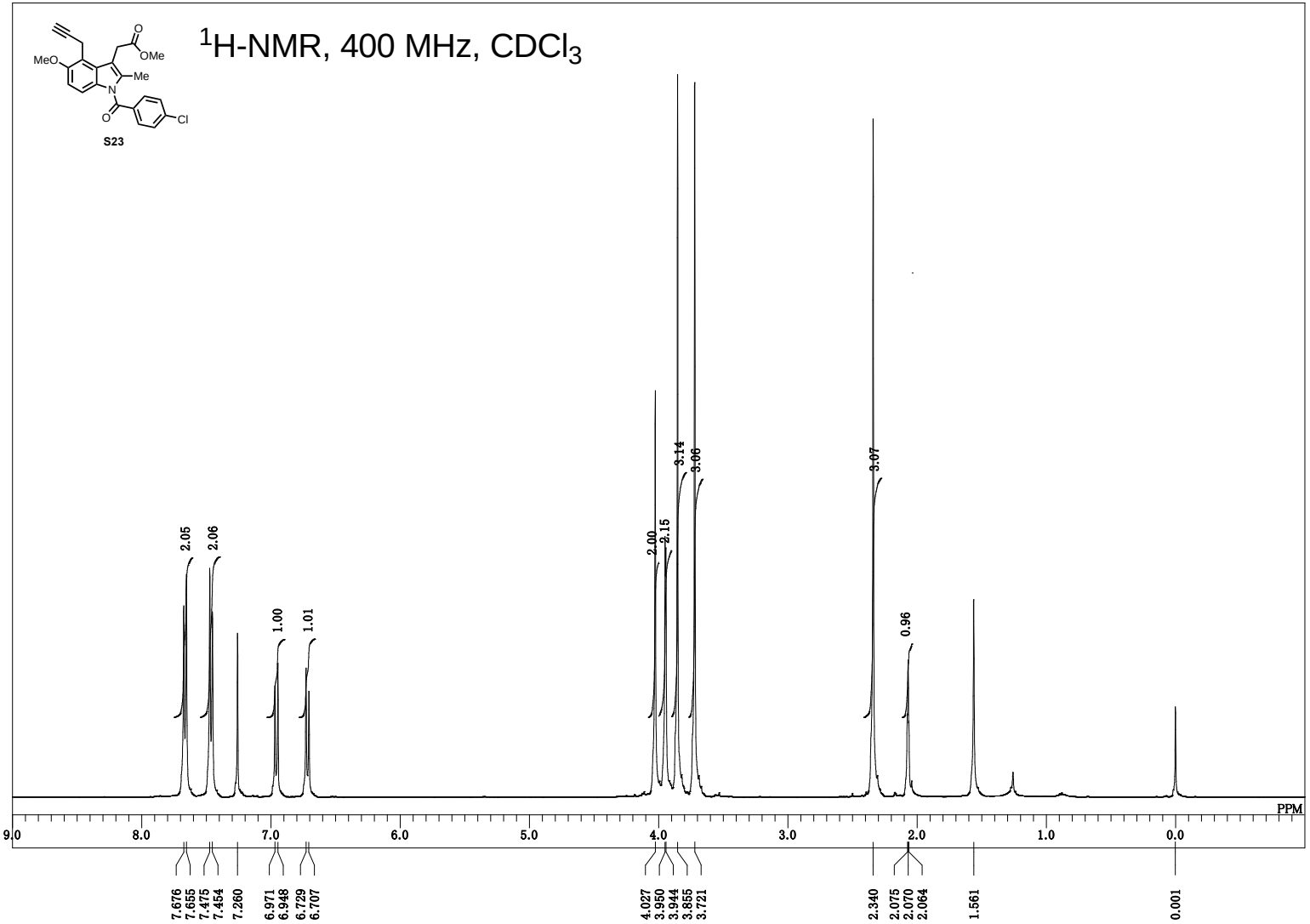
S20_H


OAc
AcO
AcO
O
H
N
AcHN
O
S20
1H-NMR, 400 MHz, CDCl3
1.05
1.00
3.27
1.23
2.26
1.08
1.00
9.84
3.59
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.463
7.442
7.260
6.134
6.114
5.137
5.114
5.089
5.075
5.050
5.030
5.026
4.313
4.302
4.283
4.271
4.195
4.171
4.150
4.124
4.108
4.102
4.077
4.072
3.783
3.776
3.772
3.765
3.758
3.753
3.747
3.742
2.877
2.087
2.069
2.044
1.982
-0.008

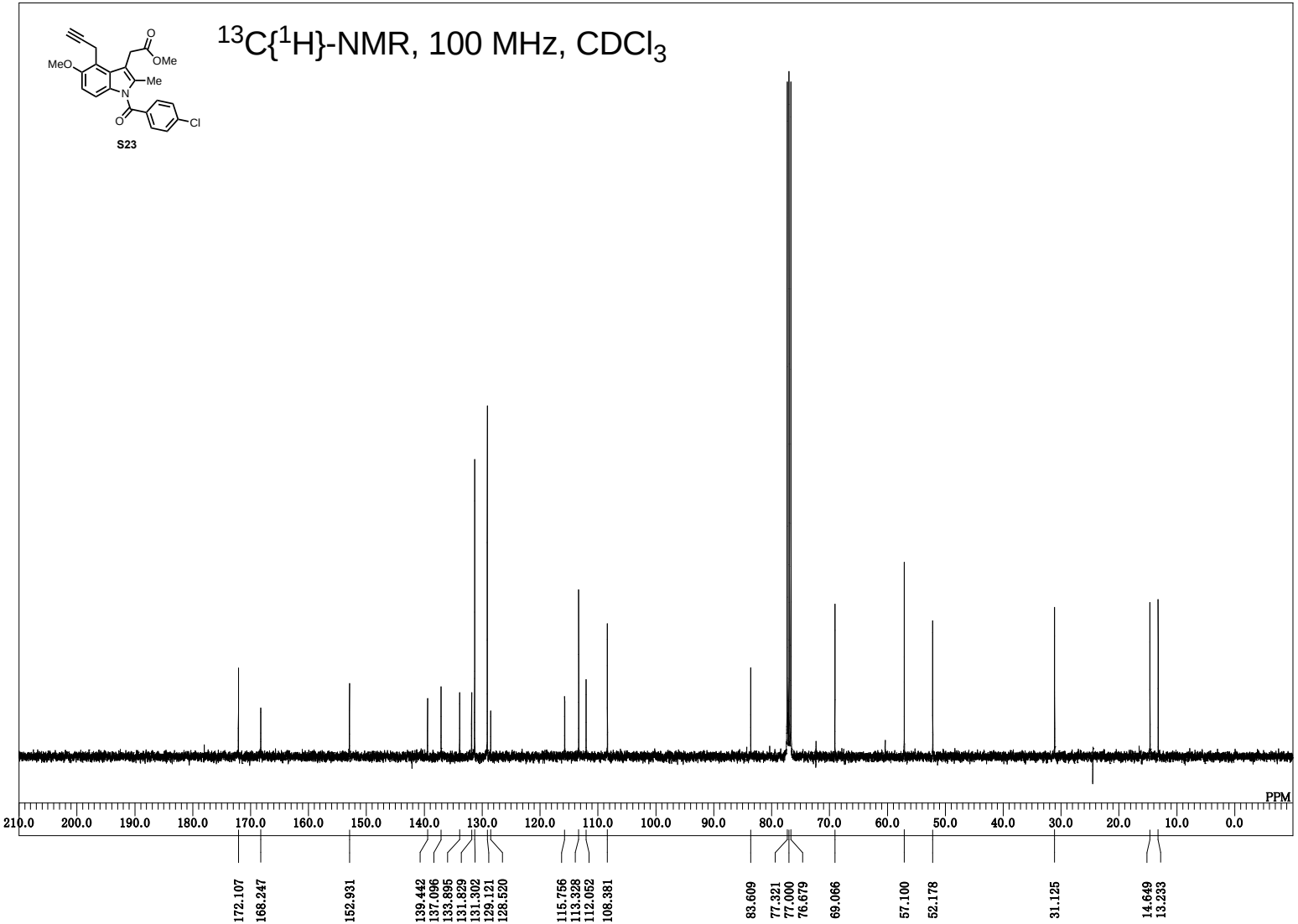
S20_C


OAc
AcO
AcO
O
H
N
AcHN
O
S20
13C{1H}-NMR, 100 MHz, CDCl3
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
172.173
171.951
170.659
169.218
152.462
80.037
77.321
77.000
76.679
76.383
75.321
73.642
72.778
67.568
61.626
53.174
23.052
20.698
20.665
20.550

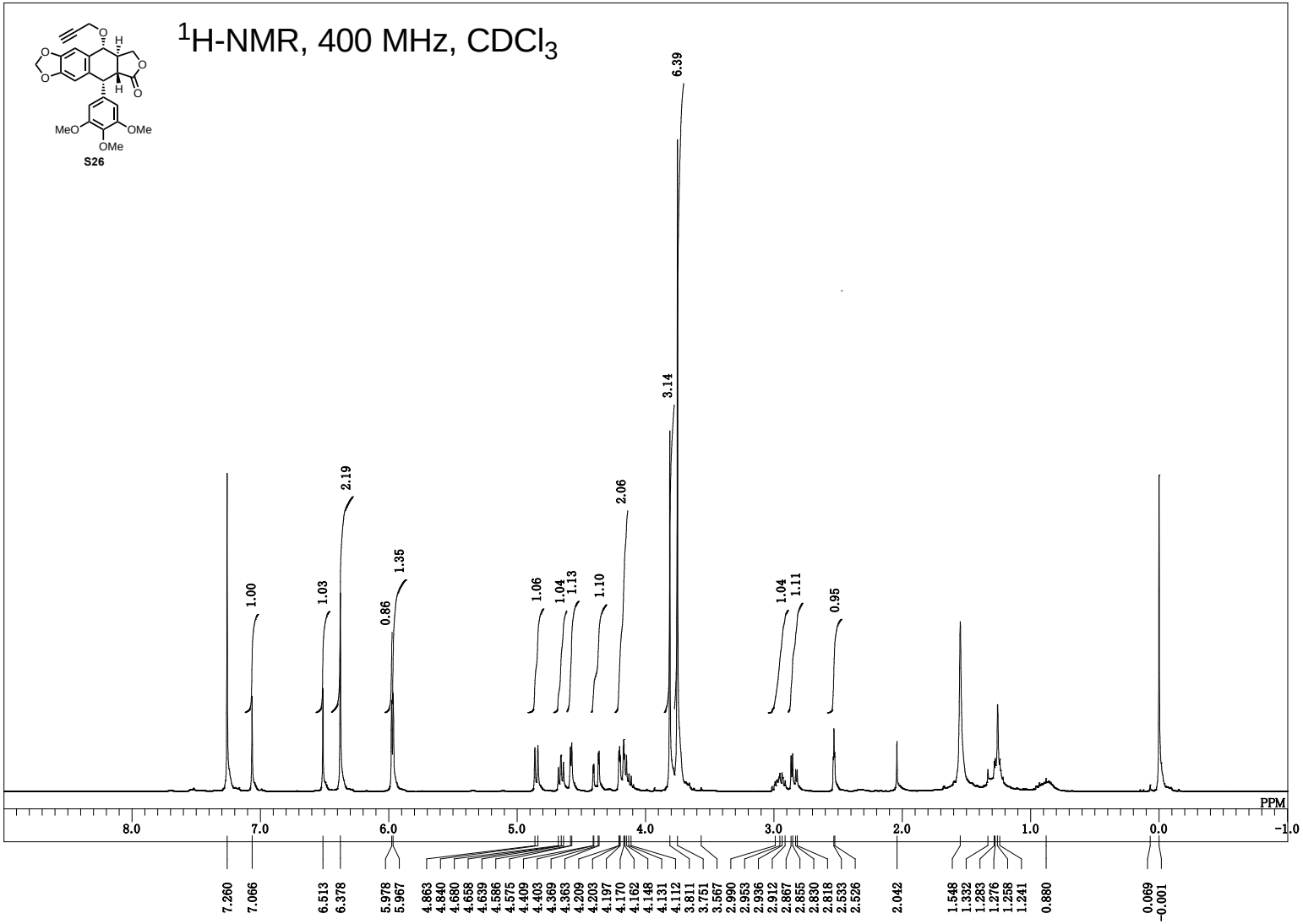
S23_H


^{1}H-NMR, 400 MHz, $CDCl_3$
MeO
OMe
Me
N
O
Cl
S23
2.05
2.06
1.00
1.01
2.00
2.15
3.14
3.06
3.07
0.96
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.676
7.655
7.475
7.454
7.260
6.971
6.948
6.729
6.707
4.027
3.950
3.944
3.855
3.721
2.340
2.075
2.070
2.064
1.561
0.001

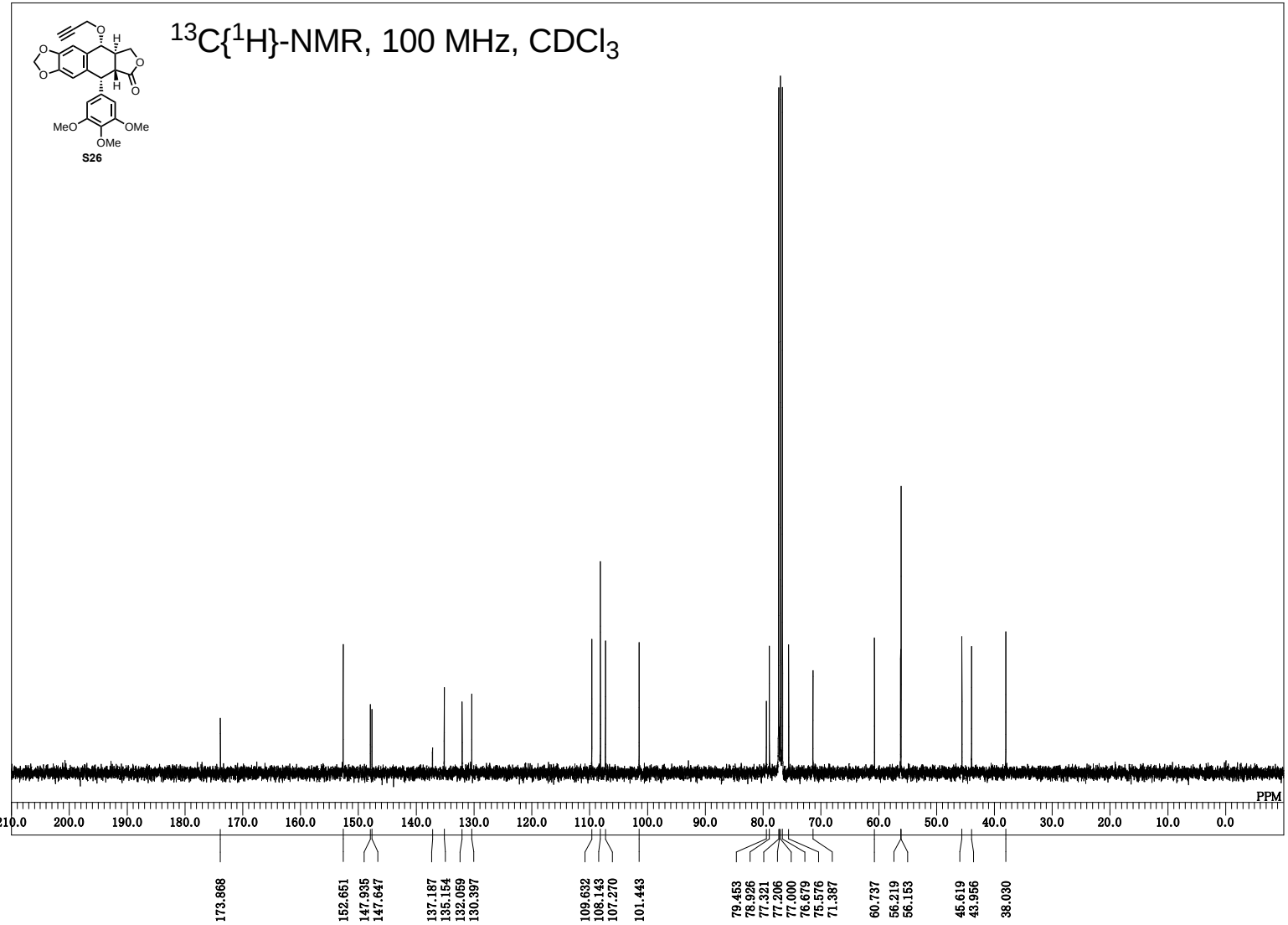
S23_C


$^{13}C\{^{1}H\}$-NMR, 100 MHz, $CDCl_3$
MeO
OMe
Me
N
O
O
Cl
S23
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
172.107
168.247
152.931
139.442
137.096
133.895
131.829
131.302
129.121
128.520
115.756
113.328
112.052
108.381
83.609
77.321
77.000
76.679
69.066
57.100
52.178
31.125
14.649
13.233

S26_H


^{1}H-NMR, 400 MHz, $CDCl_3$
S26
MeO
OMe
OMe
6.39
3.14
2.19
2.06
1.35
1.00
1.03
0.86
1.06
1.04
1.13
1.10
1.04
1.11
0.95
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.260
7.066
6.513
6.378
5.978
5.967
4.863
4.840
4.680
4.658
4.639
4.586
4.575
4.409
4.403
4.369
4.363
4.209
4.203
4.197
4.170
4.162
4.148
4.131
4.112
3.811
3.751
3.567
2.990
2.953
2.936
2.912
2.867
2.855
2.830
2.818
2.533
2.526
2.042
1.548
1.332
1.283
1.276
1.258
1.241
0.880
0.069
-0.001

S26_C


13C{1H}-NMR, 100 MHz, CDCl3
S26
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
173.868
152.651
147.935
147.647
137.187
135.154
132.059
130.397
109.632
108.143
107.270
101.443
79.453
78.926
77.321
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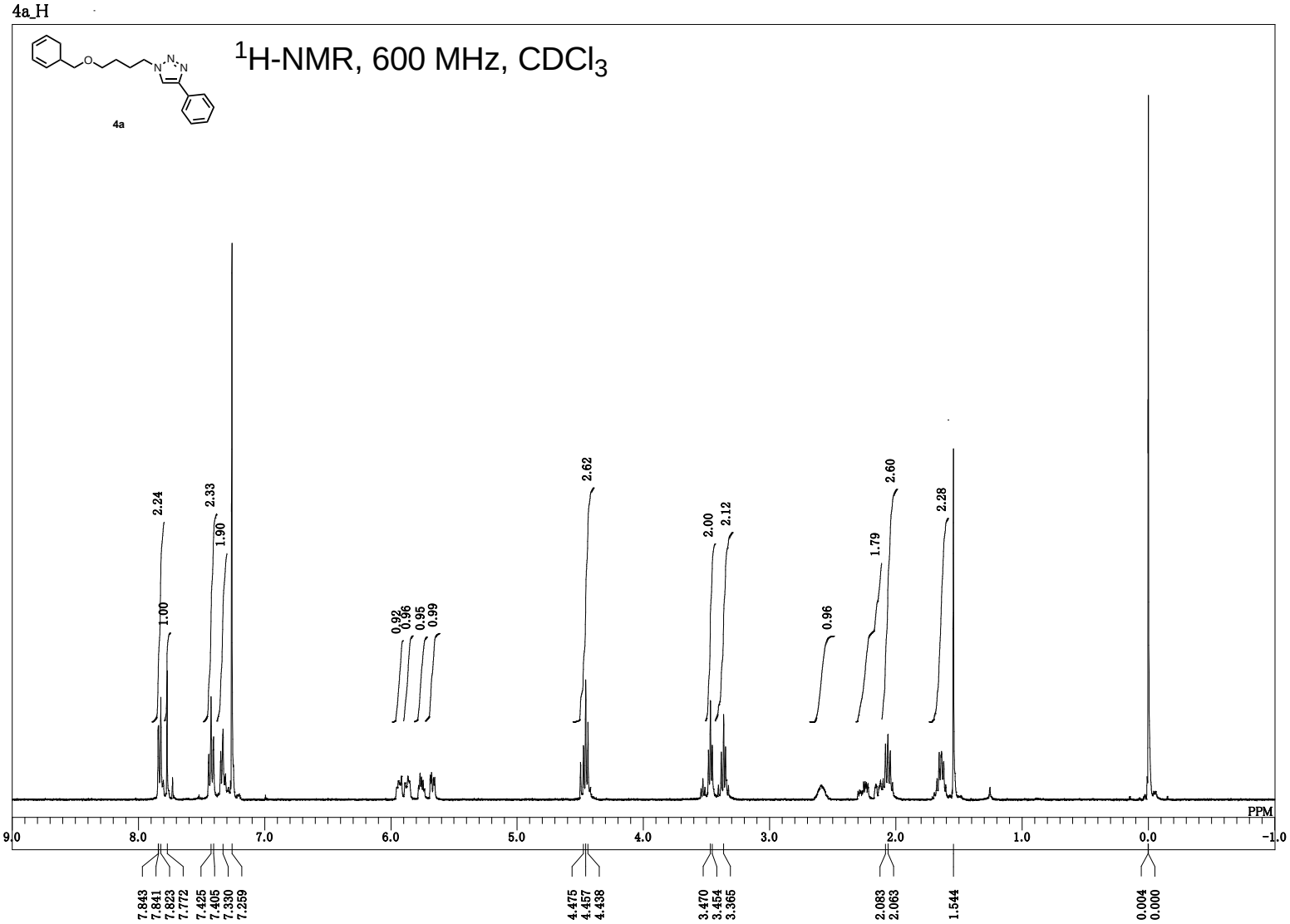
38.030


4a_H
^{1}H-NMR, 600 MHz, $CDCl_3$
4a
2.24
1.00
2.33
1.90
0.92
0.96
0.95
0.99
2.62
2.00
2.12
0.96
1.79
2.60
2.28
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.843
7.841
7.823
7.772
7.425
7.405
7.330
7.259
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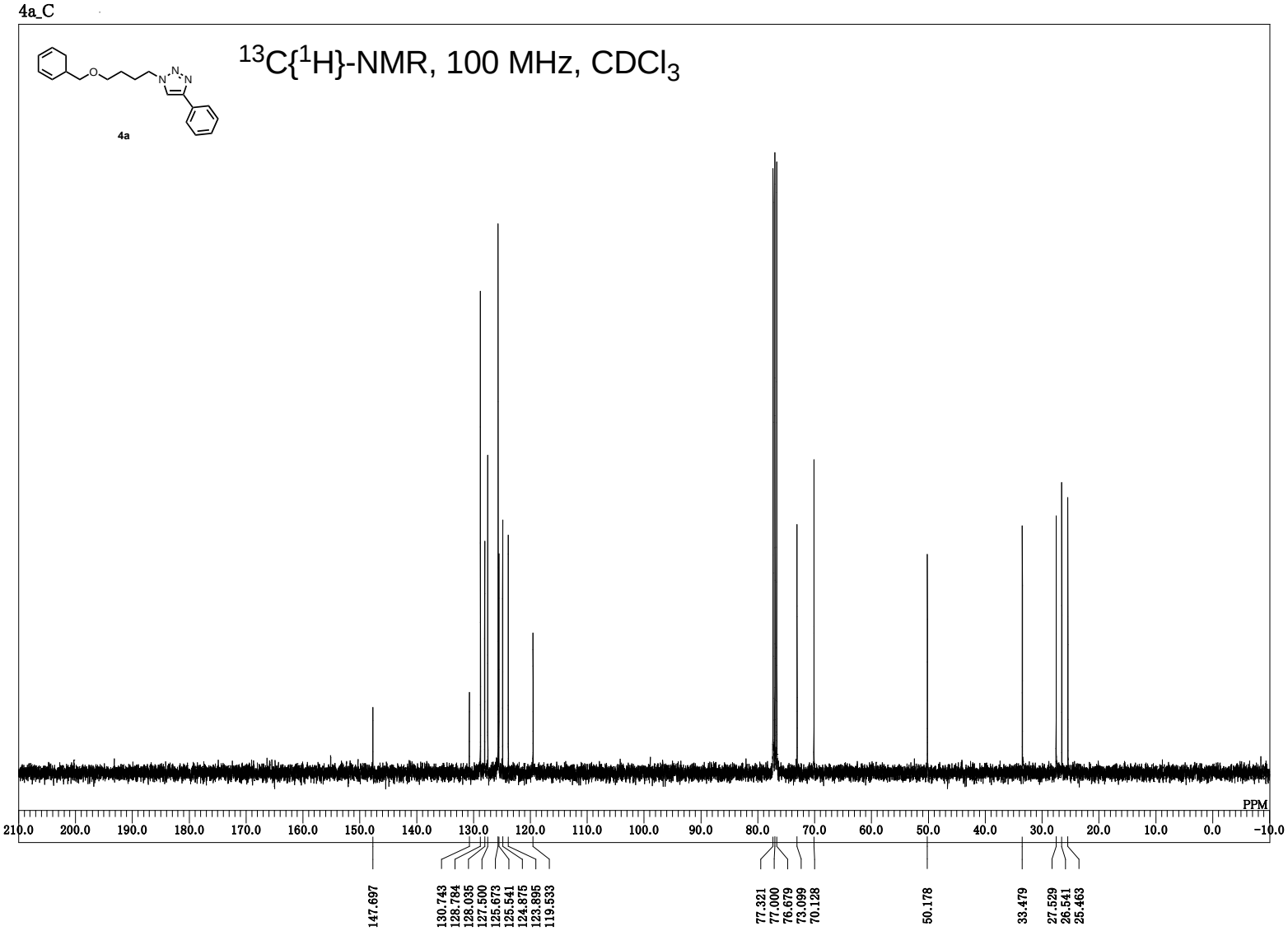
3.365
2.083
2.063
1.544
0.004
0.000


4a_C
$^{13}C\{^{1}H\}$-NMR, 100 MHz, $CDCl_3$
4a
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
147.697
130.743
128.784
128.035
127.500
125.673
125.541
124.875
123.895
119.533
77.321
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76.679
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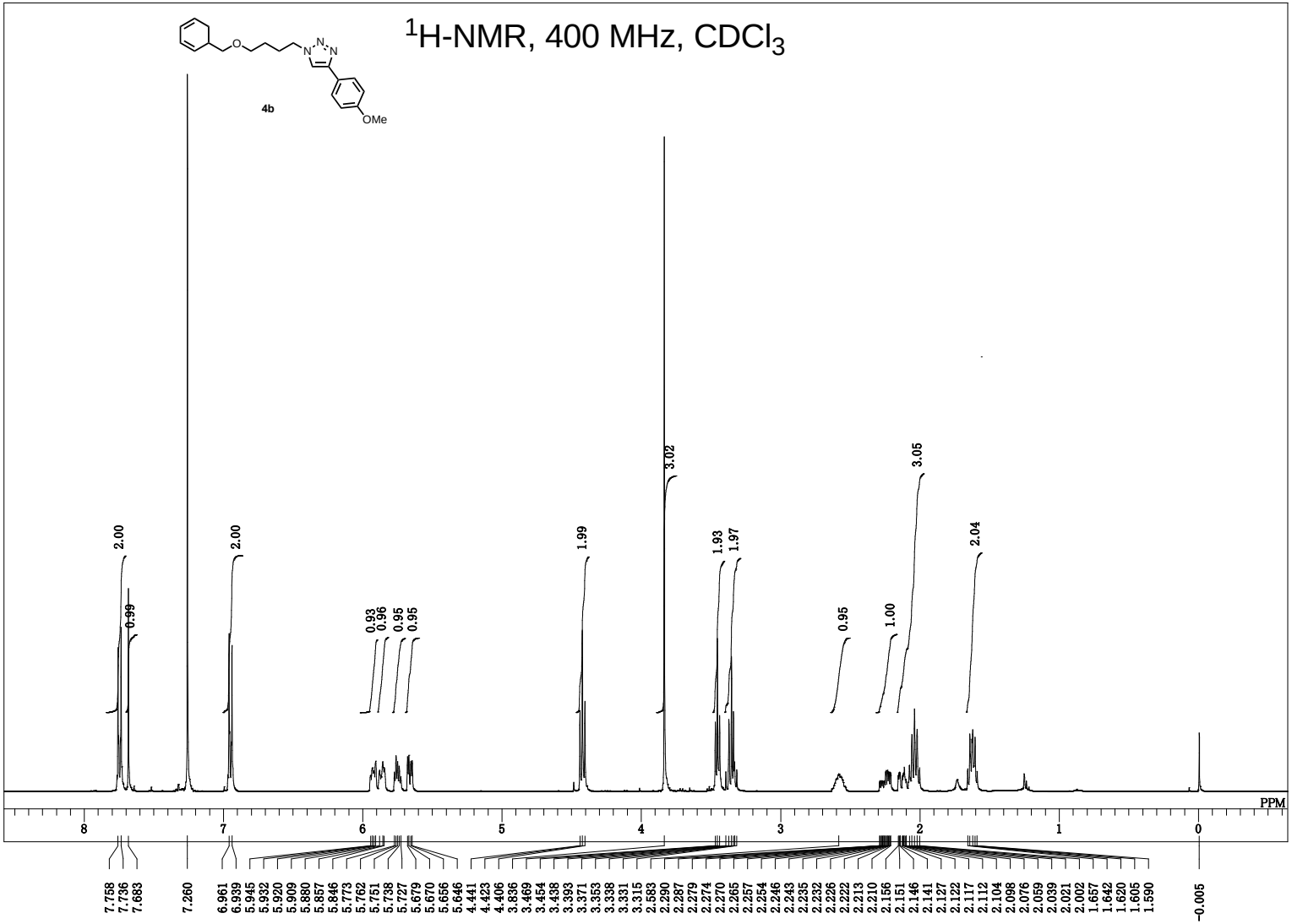
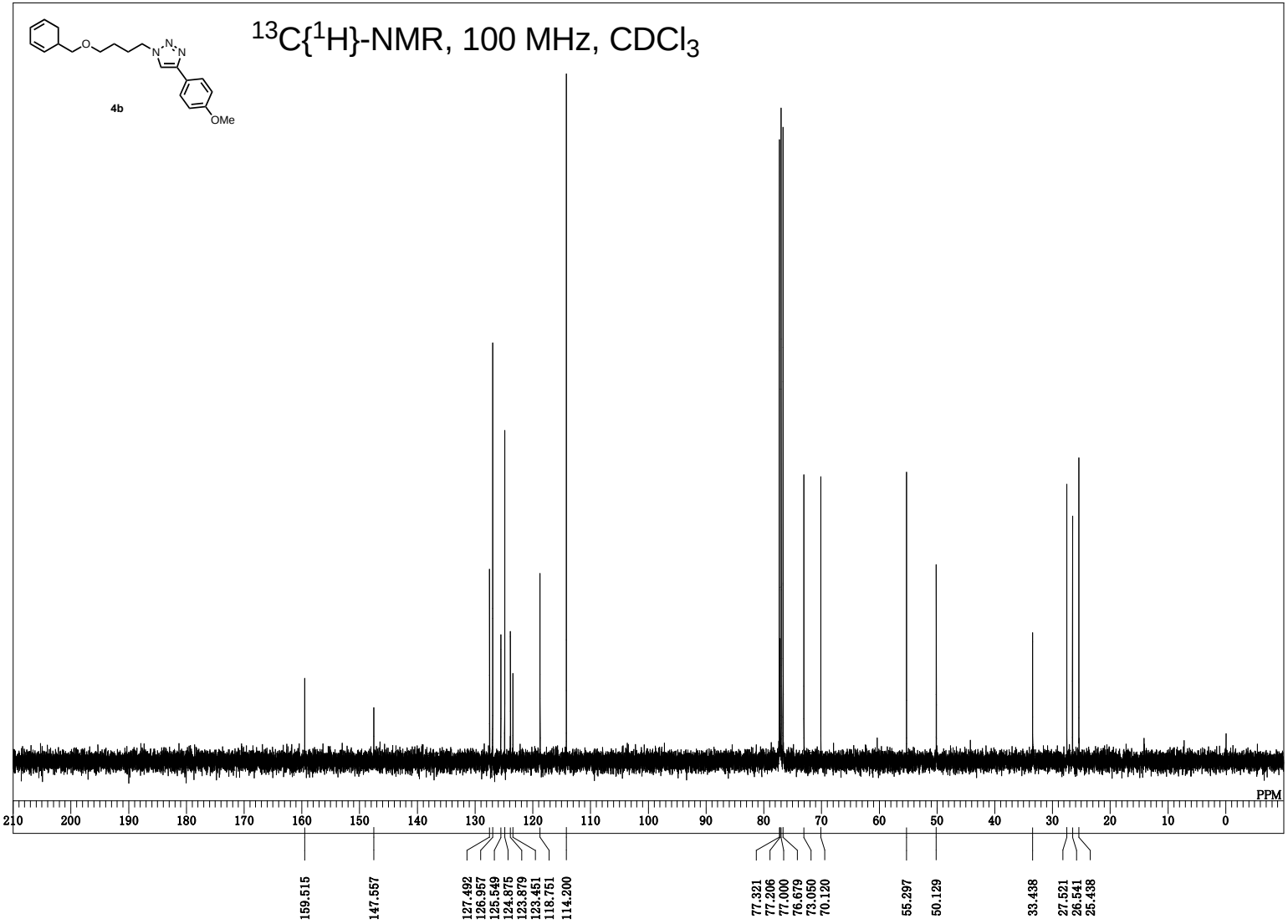
33.479
27.529
26.541
25.463

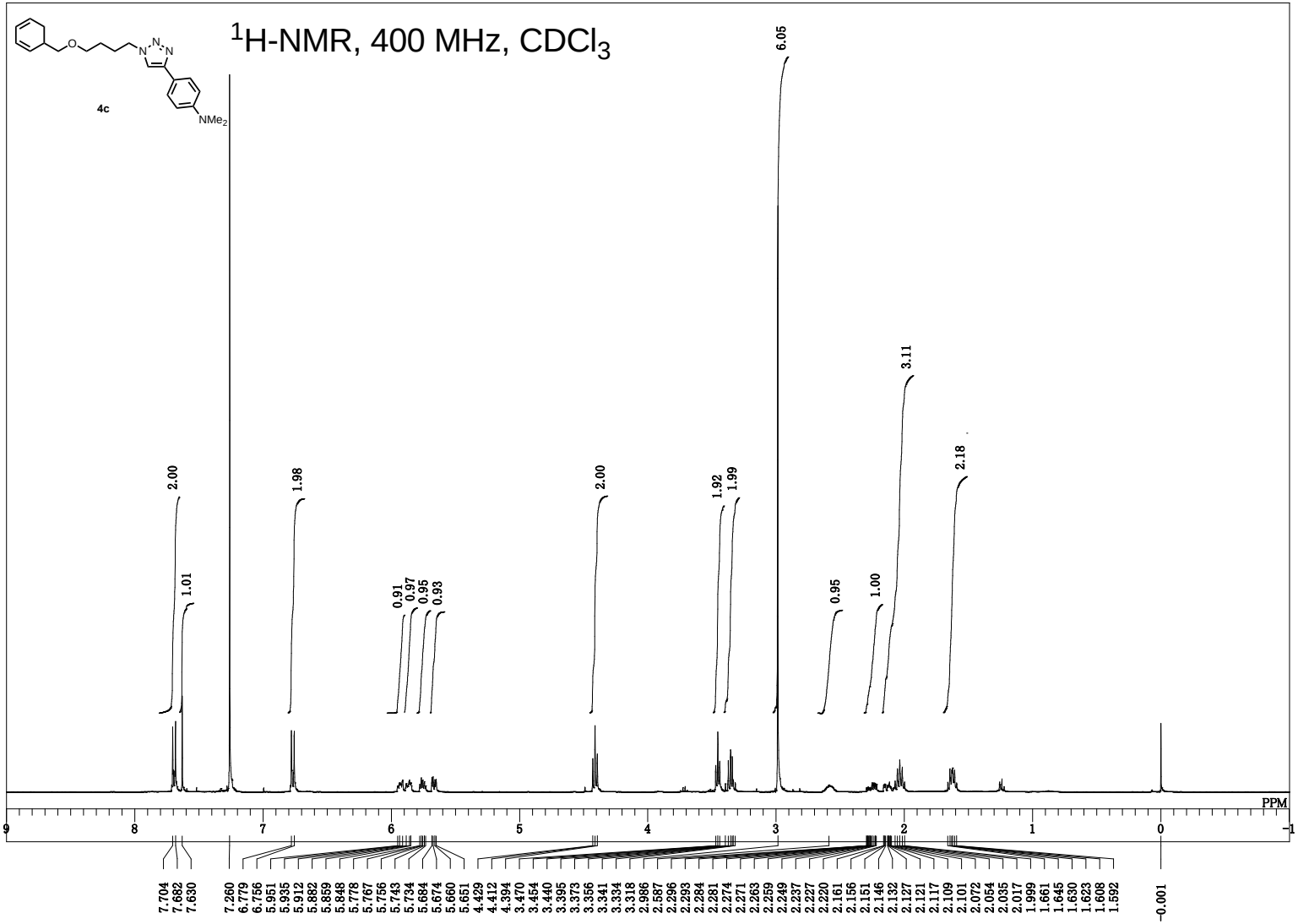
4b_H


1H-NMR, 400 MHz, CDCl3
4b
OMe
2.00
0.99
2.00
0.93
0.96
0.95
0.95
1.99
3.02
1.93
1.97
0.95
1.00
3.05
2.04
PPM
8
7
6
5
4
3
2
1
0
7.758
7.736
7.683
7.260
6.961
6.939
5.945
5.932
5.920
5.909
5.880
5.857
5.846
5.773
5.762
5.751
5.738
5.727
5.679
5.670
5.656
5.646
4.441
4.423
4.406
3.836
3.469
3.454
3.438
3.393
3.371
3.353
3.338
3.331
3.315
2.583
2.290
2.287
2.279
2.274
2.270
2.265
2.257
2.254
2.246
2.243
2.235
2.232
2.226
2.222
2.213
2.210
2.156
2.151
2.146
2.141
2.127
2.122
2.117
2.112
2.104
2.098
2.076
2.059
2.039
2.021
2.002
1.657
1.642
1.620
1.605
1.590
-0.005

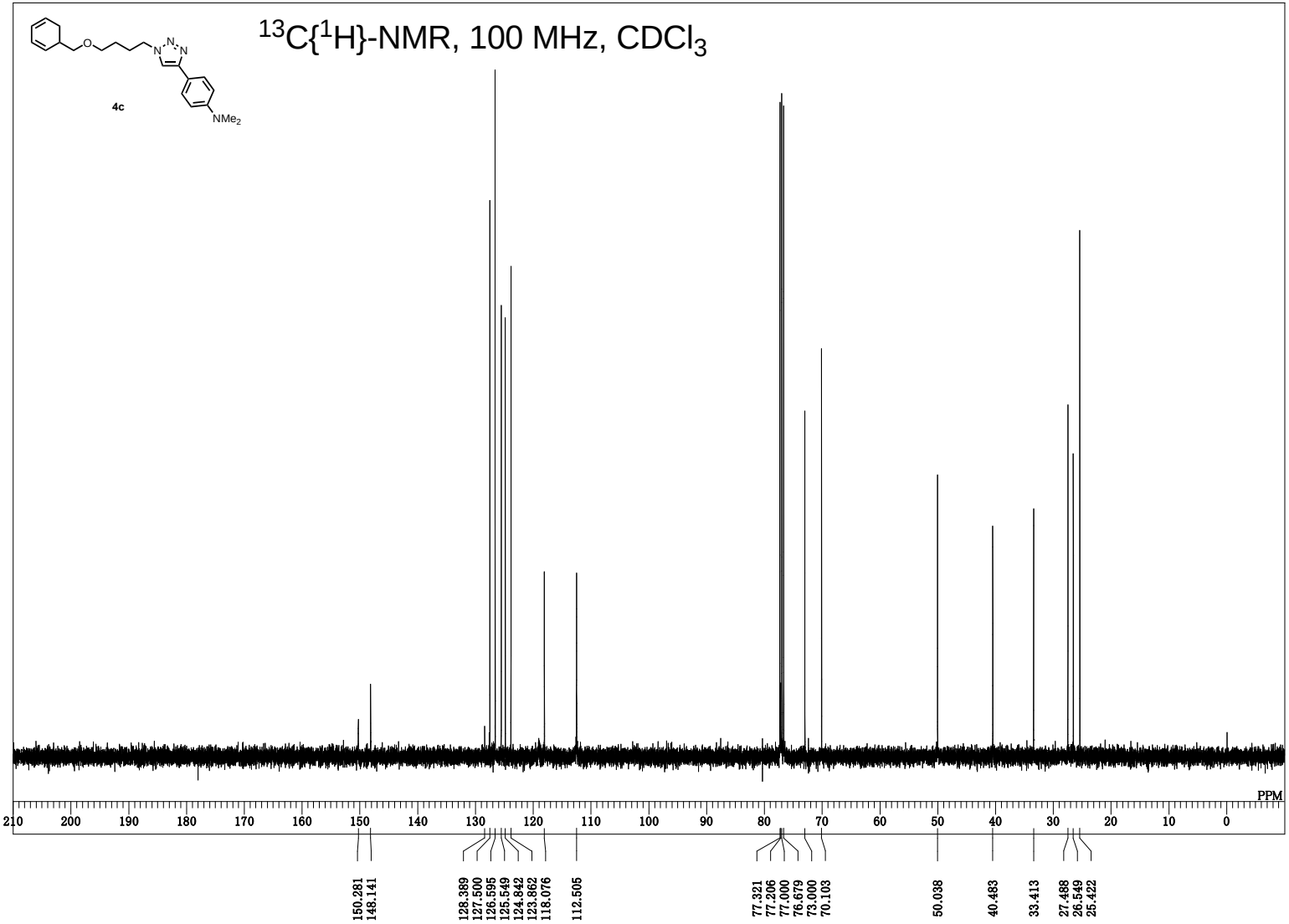
4b_C


13C{1H}-NMR, 100 MHz, CDCl3
4b
OMe
PPM
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
159.515
147.557
127.492
126.957
125.549
124.875
123.879
123.451
118.751
114.200
77.321
77.206
77.000
76.679
73.050
70.120
55.297
50.129
33.438
27.521
26.541
25.438

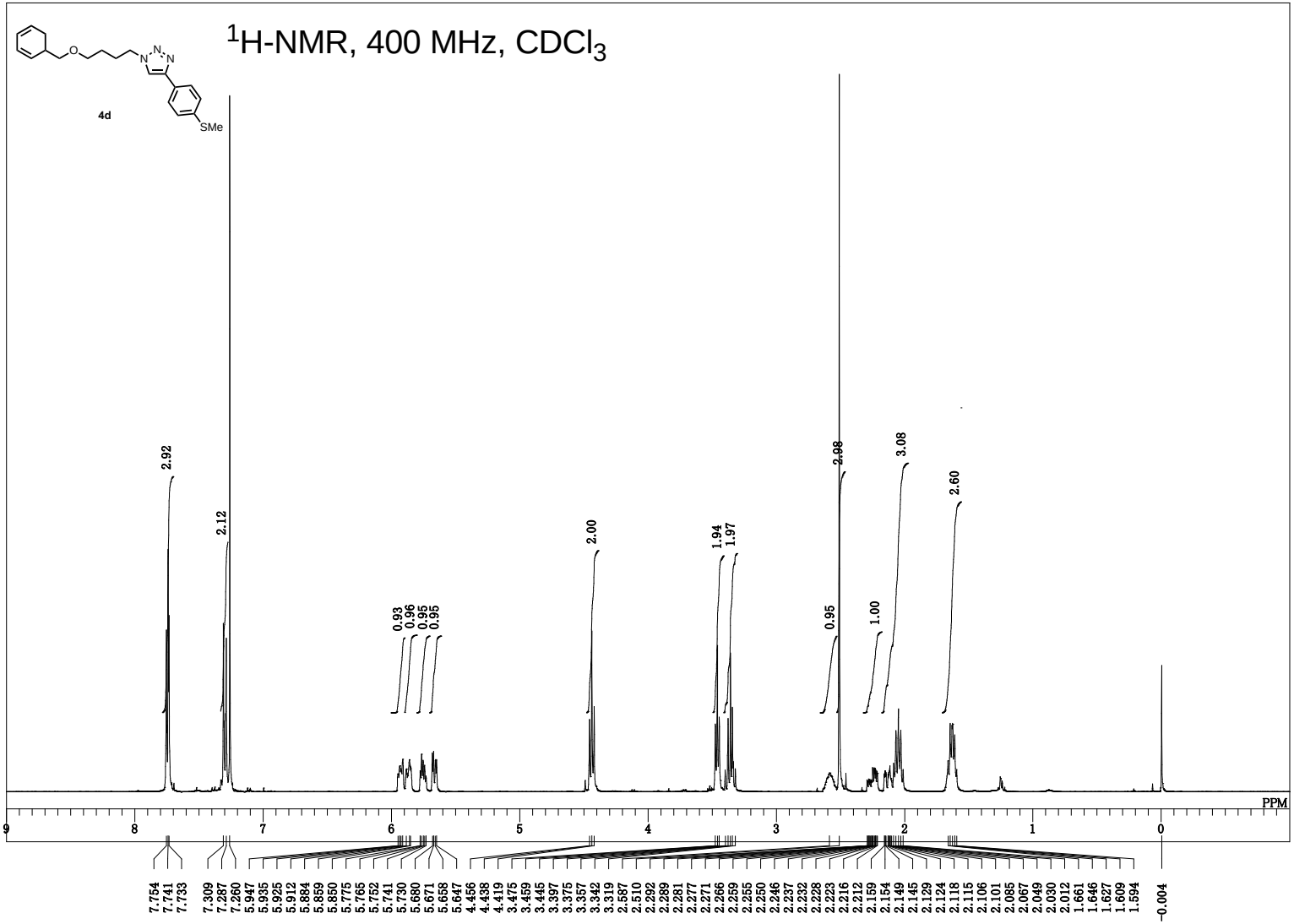
4c_H


^{1}H-NMR, 400 MHz, $CDCl_3$
4c
NMe2
6.05
3.11
2.18
2.00
1.98
2.00
1.92
1.99
1.01
0.91
0.97
0.95
0.93
0.95
1.00
PPM
9
8
7
6
5
4
3
2
1
0
−1
7.704
7.682
7.630
7.260
6.779
6.756
5.951
5.935
5.912
5.882
5.859
5.848
5.778
5.767
5.756
5.743
5.734
5.684
5.674
5.660
5.651
4.429
4.412
4.394
3.470
3.454
3.440
3.395
3.373
3.356
3.341
3.334
3.318
2.986
2.587
2.296
2.293
2.284
2.281
2.274
2.271
2.263
2.259
2.249
2.237
2.227
2.220
2.161
2.156
2.151
2.146
2.132
2.127
2.121
2.117
2.109
2.101
2.072
2.054
2.035
2.017
1.999
1.661
1.645
1.630
1.623
1.608
1.592
−0.001

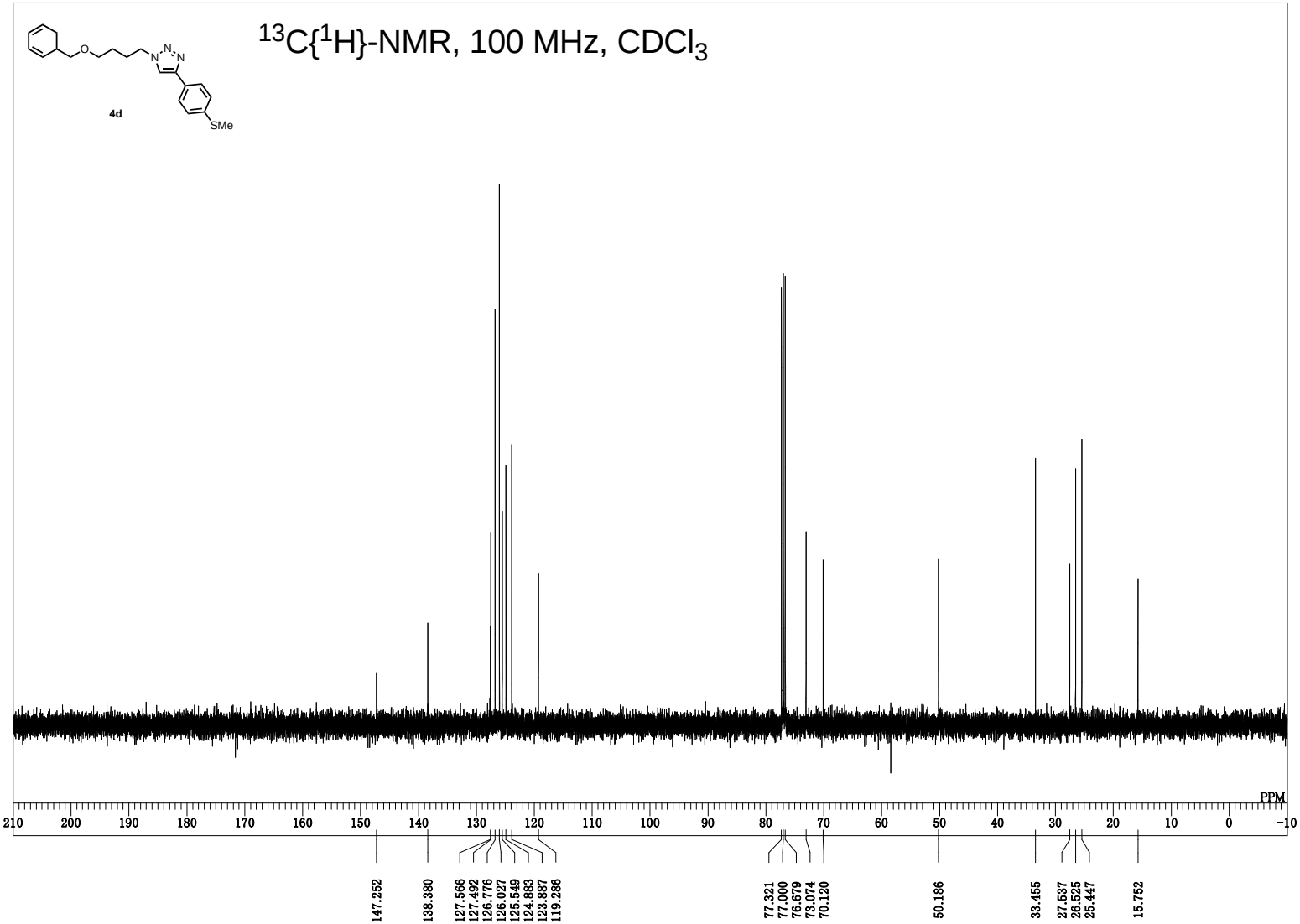
4c_C

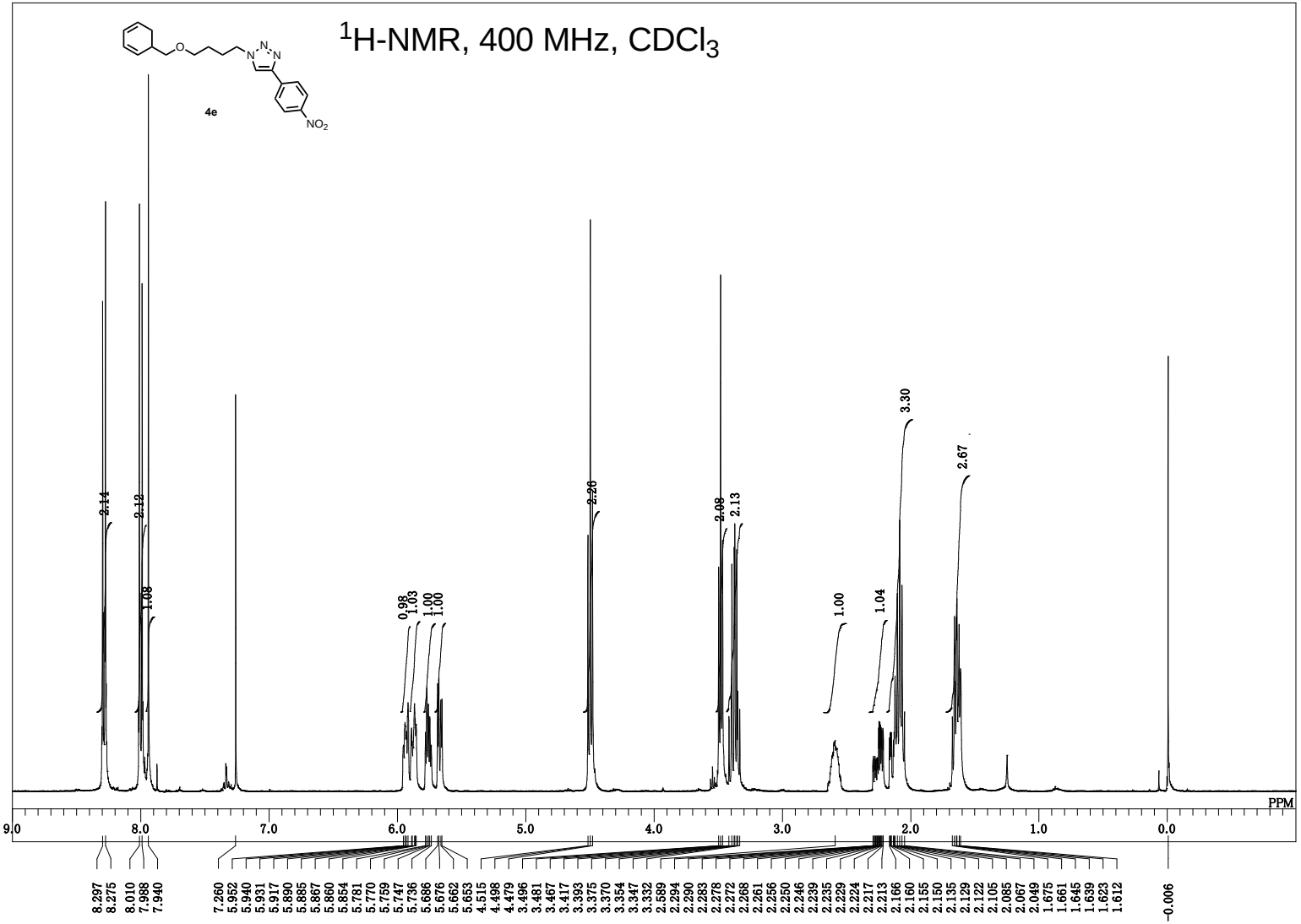

$^{13}C\{^{1}H\}$-NMR, 100 MHz, $CDCl_3$
4c
NMe2
PPM
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
150.281
148.141
128.389
127.500
126.596
125.549
124.842
123.862
118.076
112.505
77.321
77.206
77.000
76.679
73.000
70.103
50.038
40.483
33.413
27.488
26.549
25.422

4d_H

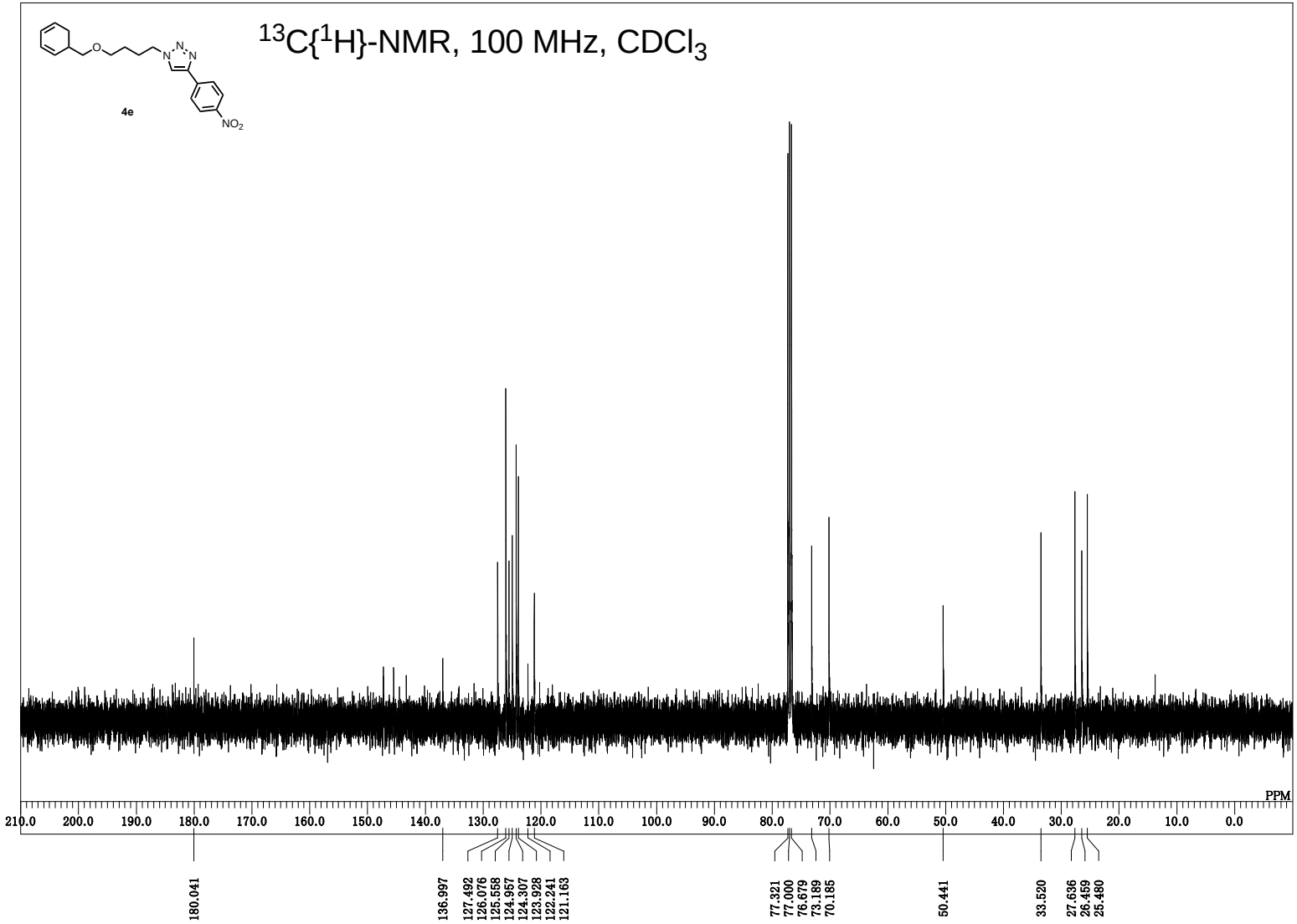

^{1}H-NMR, 400 MHz, $CDCl_3$
4d
SMe
2.92
2.12
0.93
0.96
0.95
0.95
2.00
1.94
1.97
0.95
2.98
1.00
3.08
2.60
PPM
9
8
7
6
5
4
3
2
1
0
7.754
7.741
7.733
7.309
7.287
7.260
5.947
5.935
5.925
5.912
5.884
5.859
5.850
5.775
5.765
5.752
5.741
5.730
5.680
5.671
5.658
5.647
4.456
4.438
4.419
3.475
3.459
3.445
3.397
3.375
3.357
3.342
3.319
2.587
2.510
2.292
2.289
2.281
2.277
2.271
2.266
2.259
2.255
2.250
2.246
2.237
2.232
2.228
2.223
2.216
2.212
2.159
2.154
2.149
2.145
2.129
2.124
2.118
2.115
2.106
2.101
2.085
2.067
2.049
2.030
2.012
1.661
1.646
1.627
1.609
1.594
-0.004

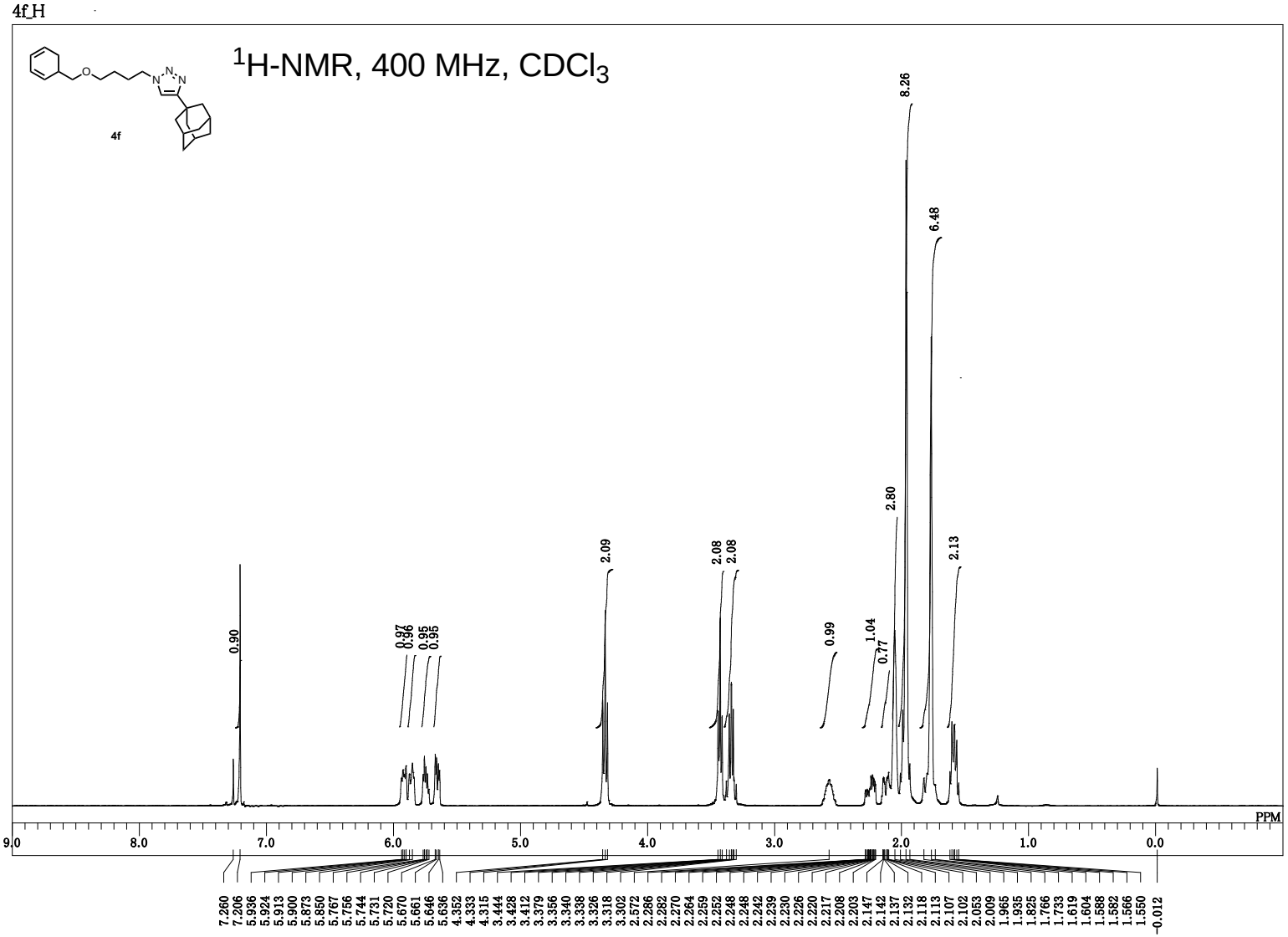
4d_C

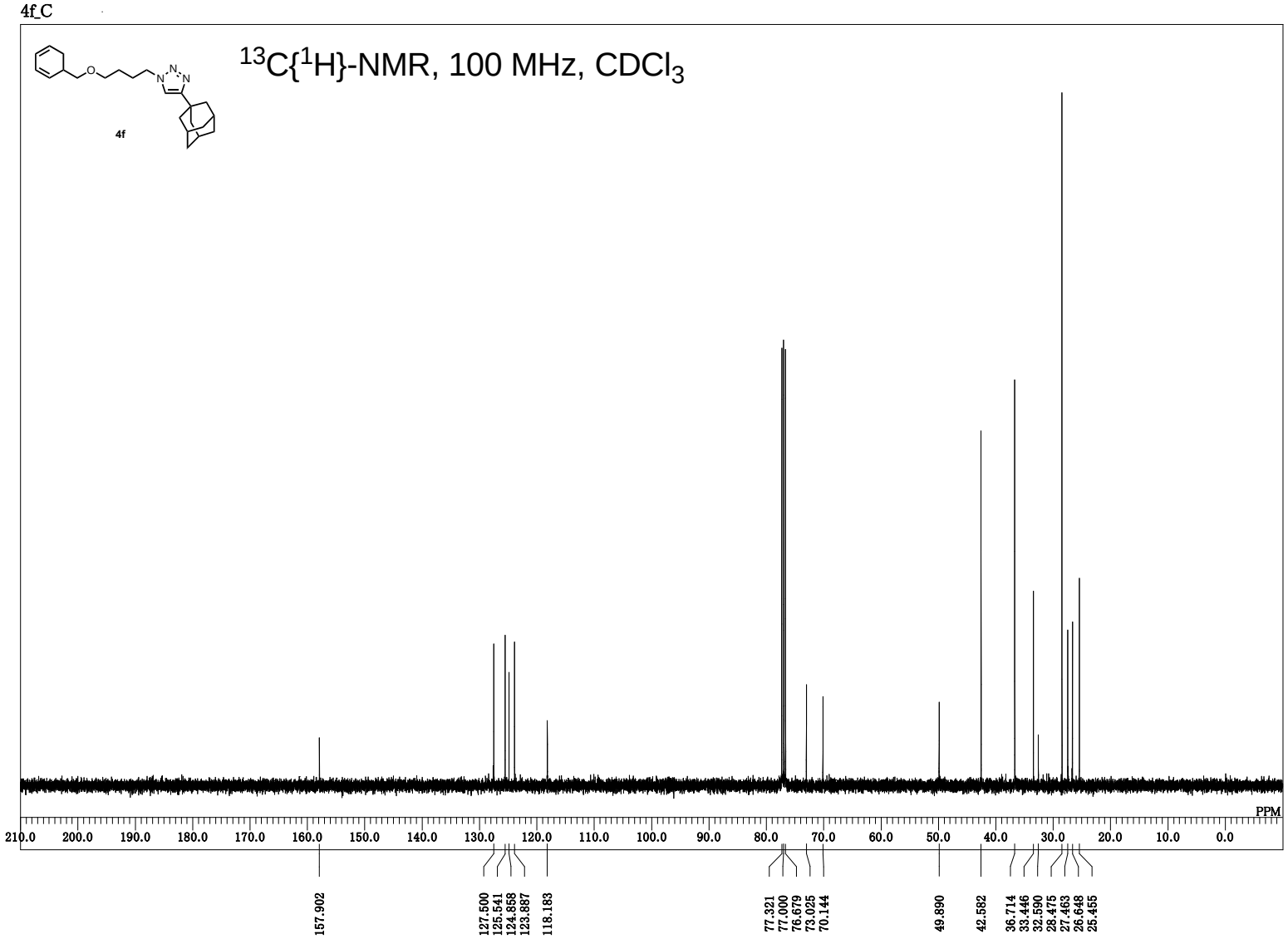

13C{1H}-NMR, 100 MHz, CDCl3
4d
SMe
PPM
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
147.252
138.380
127.566
127.492
126.776
126.027
125.549
124.883
123.887
119.286
77.321
77.000
76.679
73.074
70.120
50.186
33.455
27.537
26.525
25.447
15.752


4e_H
^{1}H-NMR, 400 MHz, $CDCl_3$
4e
NO_2
2.14
2.12
1.08
0.98
1.03
1.00
1.00
2.20
2.08
2.13
1.00
1.04
3.30
2.67
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.297
8.275
8.010
7.988
7.940
7.260
5.952
5.940
5.931
5.917
5.890
5.885
5.867
5.860
5.854
5.781
5.770
5.759
5.747
5.736
5.686
5.676
5.662
5.653
4.515
4.498
4.479
3.496
3.481
3.467
3.417
3.393
3.375
3.370
3.354
3.347
3.332
2.589
2.294
2.290
2.283
2.278
2.272
2.268
2.261
2.256
2.250
2.246
2.239
2.235
2.229
2.224
2.217
2.213
2.166
2.160
2.155
2.150
2.135
2.129
2.122
2.105
2.085
2.067
2.049
1.675
1.661
1.645
1.639
1.623
1.612
-0.006

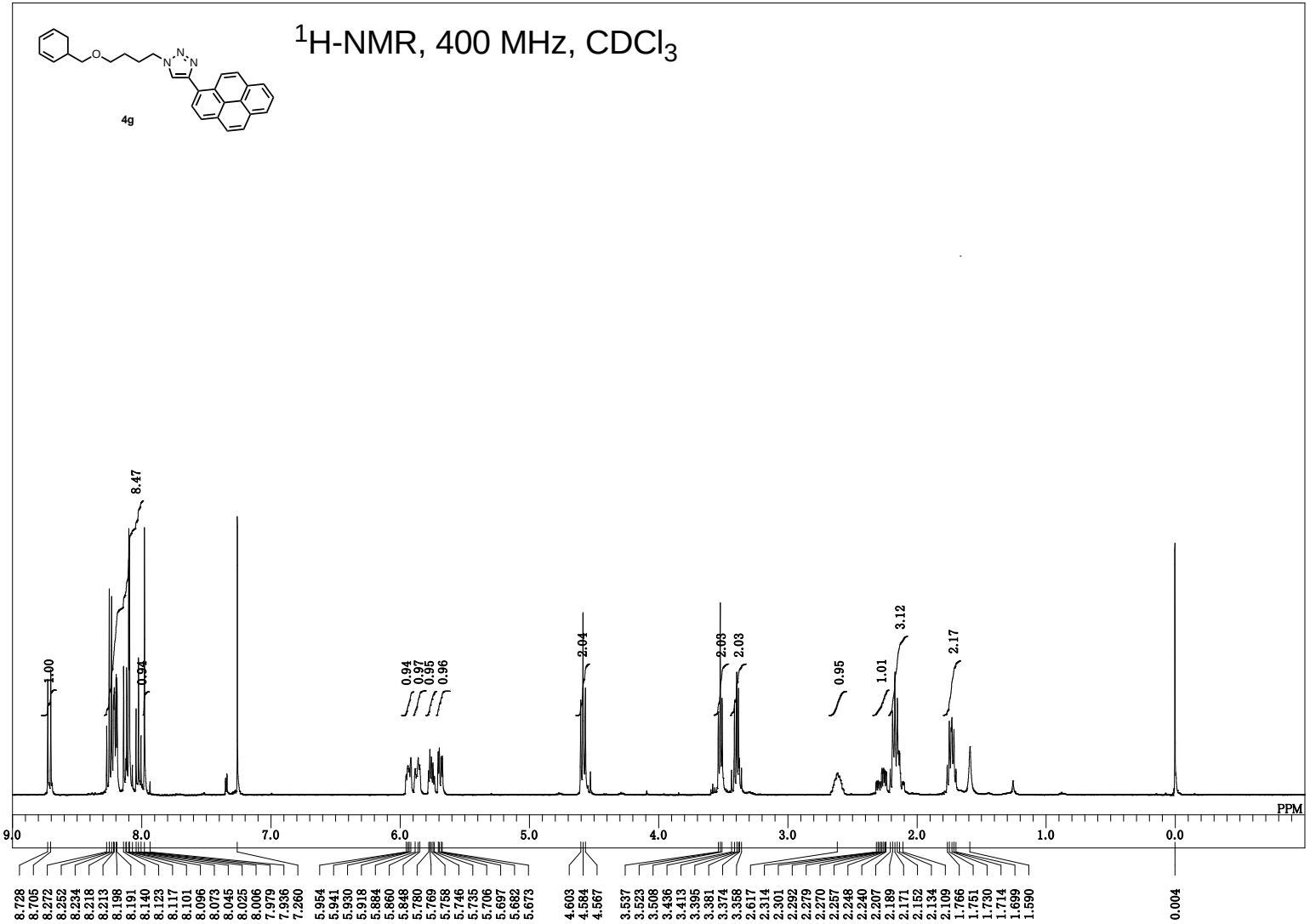
4e_C


$^{13}C\{^{1}H\}$-NMR, 100 MHz, $CDCl_3$
4e
NO_2
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
180.041
136.997
127.492
126.076
125.558
124.957
124.307
123.928
122.241
121.163
77.321
77.000
76.679
73.189
70.185
50.441
33.520
27.636
26.459
25.480

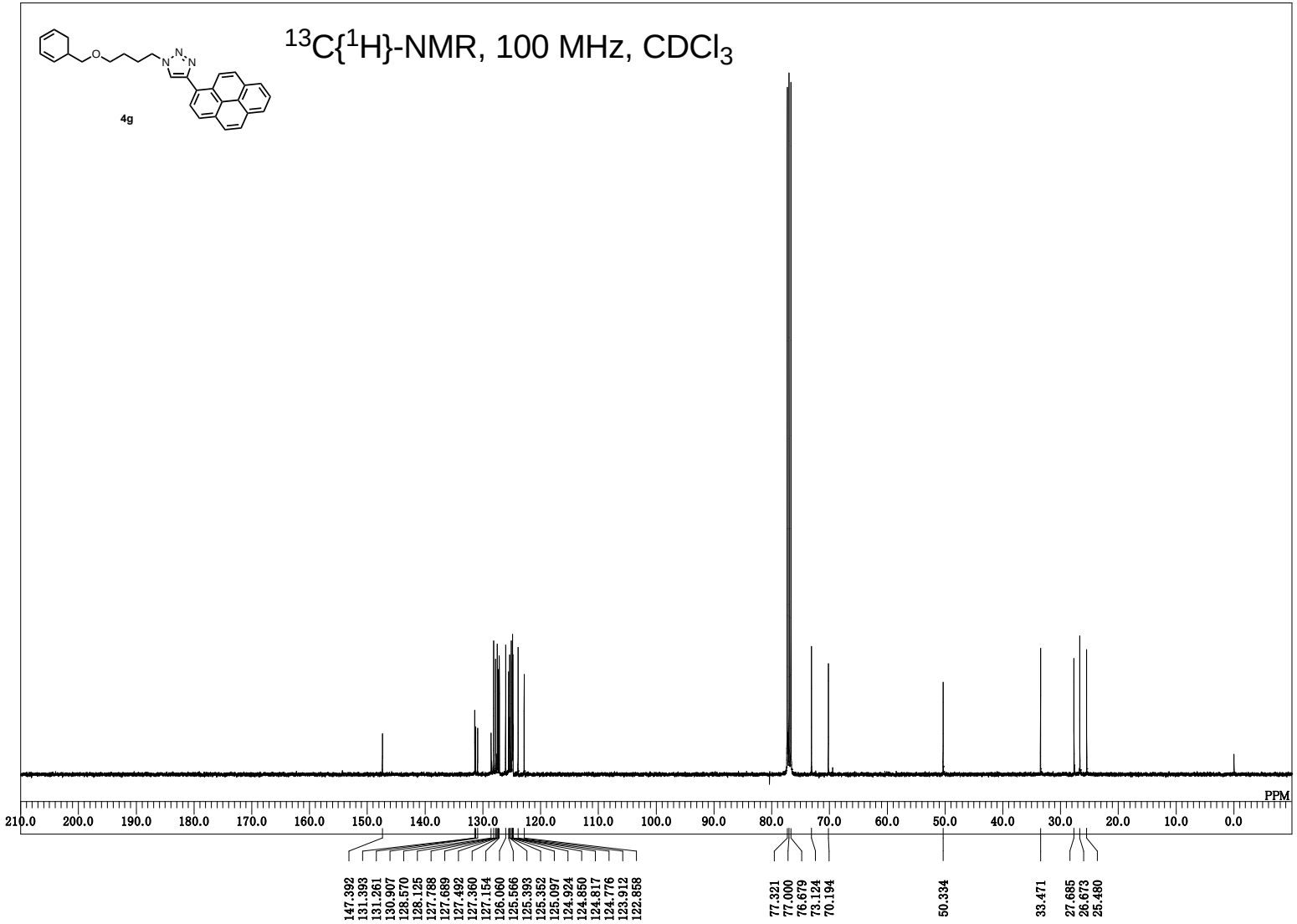

4f_H
^{1}H-NMR, 400 MHz, $CDCl_3$
4f
8.26
6.48
2.80
2.13
2.09
2.08
2.08
1.04
0.99
0.90
0.97
0.96
0.95
0.95
0.77
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.260
7.206
5.936
5.924
5.913
5.900
5.873
5.850
5.767
5.756
5.744
5.731
5.720
5.670
5.661
5.646
5.636
4.352
4.333
4.315
3.444
3.428
3.412
3.379
3.356
3.340
3.338
3.326
3.318
3.302
2.572
2.286
2.282
2.270
2.264
2.259
2.252
2.248
2.248
2.242
2.239
2.230
2.226
2.220
2.217
2.208
2.203
2.147
2.142
2.137
2.132
2.118
2.113
2.107
2.102
2.053
2.009
1.965
1.935
1.825
1.766
1.733
1.619
1.604
1.588
1.582
1.566
1.550
-0.012


4f_C
$^{13}C\{^{1}H\}$-NMR, 100 MHz, $CDCl_3$
4f
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
157.902
127.500
125.541
124.858
123.887
118.183
77.321
77.000
76.679
73.025
70.144
49.890
42.582
36.714
33.446
32.590
28.475
27.463
26.648
25.455

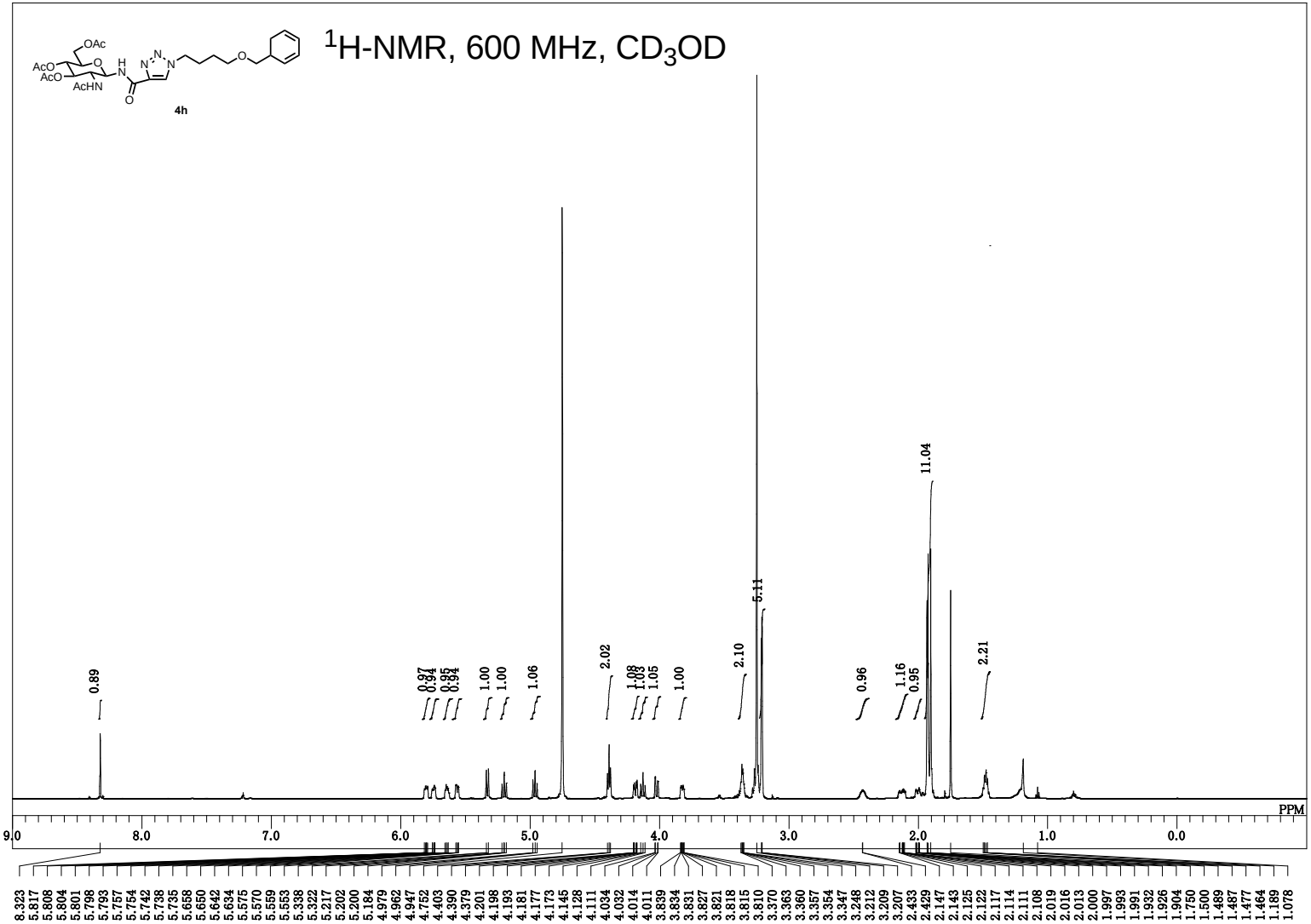
4g_H


4g
1H-NMR, 400 MHz, CDCl3
1.00
8.47
0.94
0.94
0.97
0.95
0.96
2.04
2.03
2.03
0.95
1.01
3.12
2.17
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.728
8.705
8.272
8.252
8.234
8.218
8.213
8.198
8.191
8.140
8.123
8.117
8.101
8.096
8.073
8.045
8.025
8.006
7.979
7.936
7.260
5.954
5.941
5.930
5.918
5.884
5.860
5.848
5.780
5.769
5.758
5.746
5.735
5.706
5.697
5.682
5.673
4.603
4.584
4.567
3.537
3.523
3.508
3.436
3.413
3.395
3.381
3.374
3.358
2.617
2.314
2.301
2.292
2.279
2.270
2.257
2.248
2.240
2.207
2.189
2.171
2.152
2.134
2.109
1.766
1.751
1.730
1.714
1.699
1.590
0.004

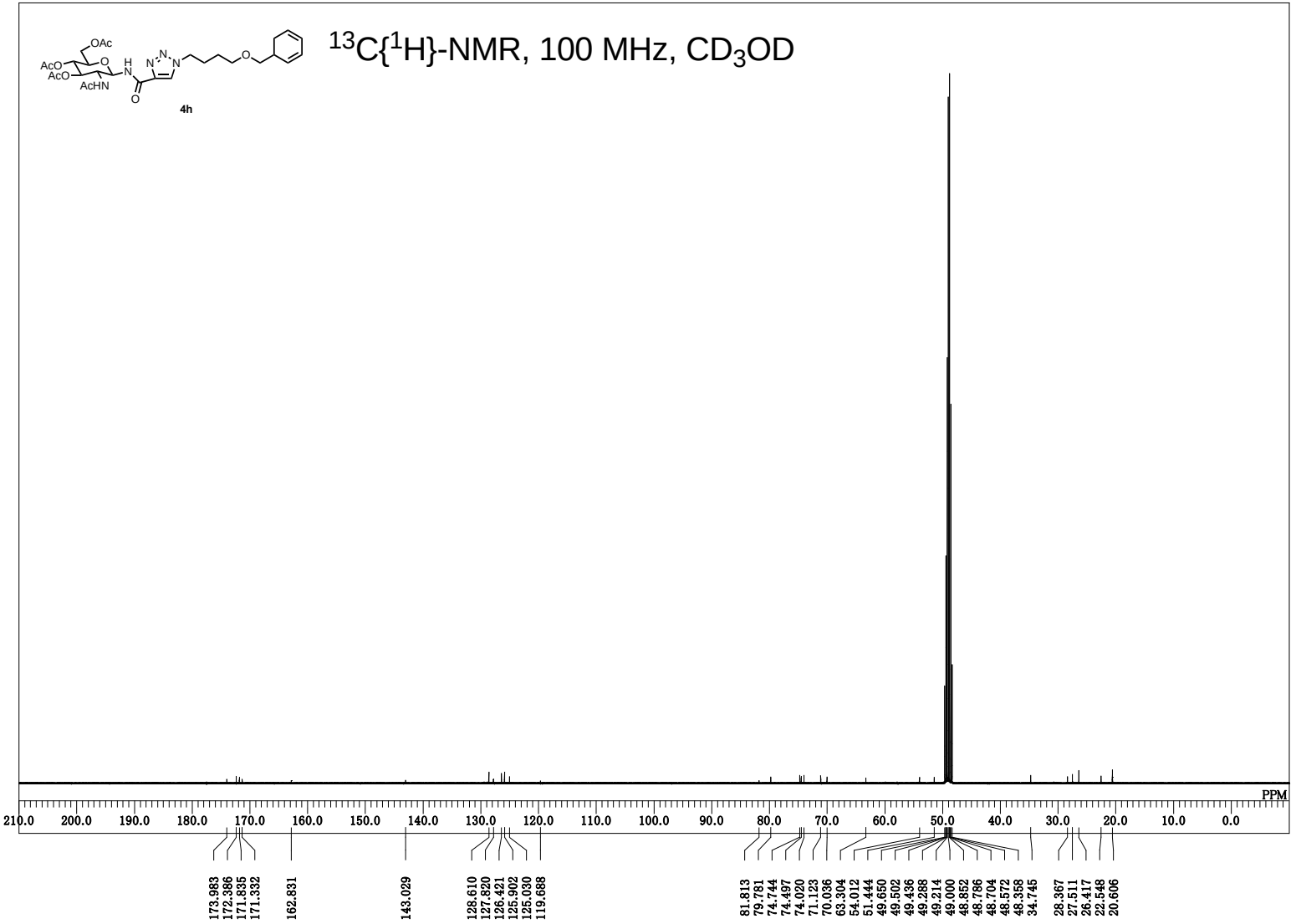
4g_C


$^{13}C\{^{1}H\}$-NMR, 100 MHz, $CDCl_3$
4g
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
147.392
131.393
131.261
130.907
128.570
128.125
127.788
127.689
127.492
127.360
127.154
126.060
125.566
125.393
125.352
125.097
124.924
124.850
124.817
124.776
123.912
122.858
77.321
77.000
76.679
73.124
70.194
50.334
33.471
27.685
26.673
25.480

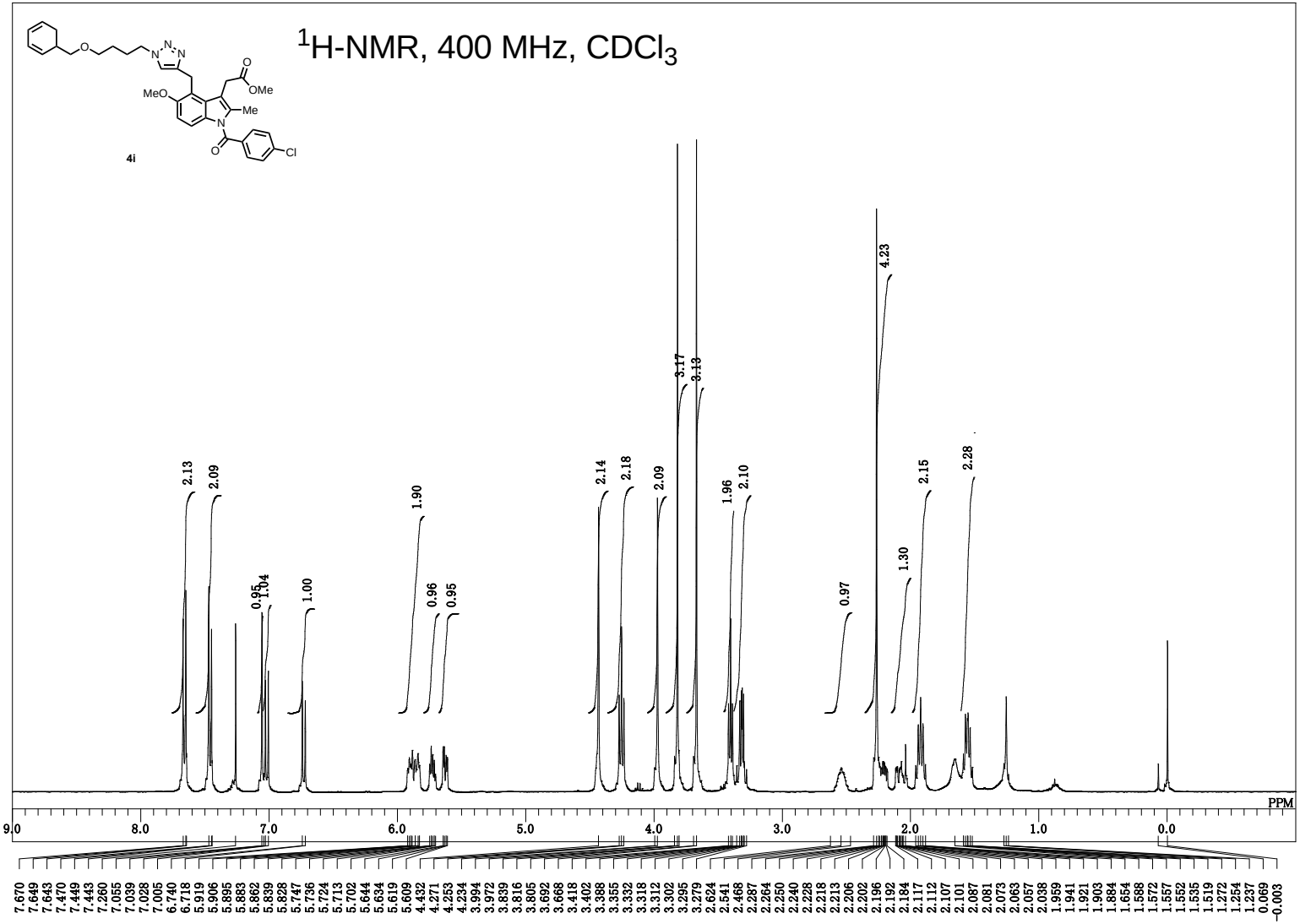
4h_H


4h
1H-NMR, 600 MHz, CD3OD
0.89
1.00
1.00
1.06
2.02
1.00
2.10
5.11
0.96
1.16
0.95
11.04
2.21
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

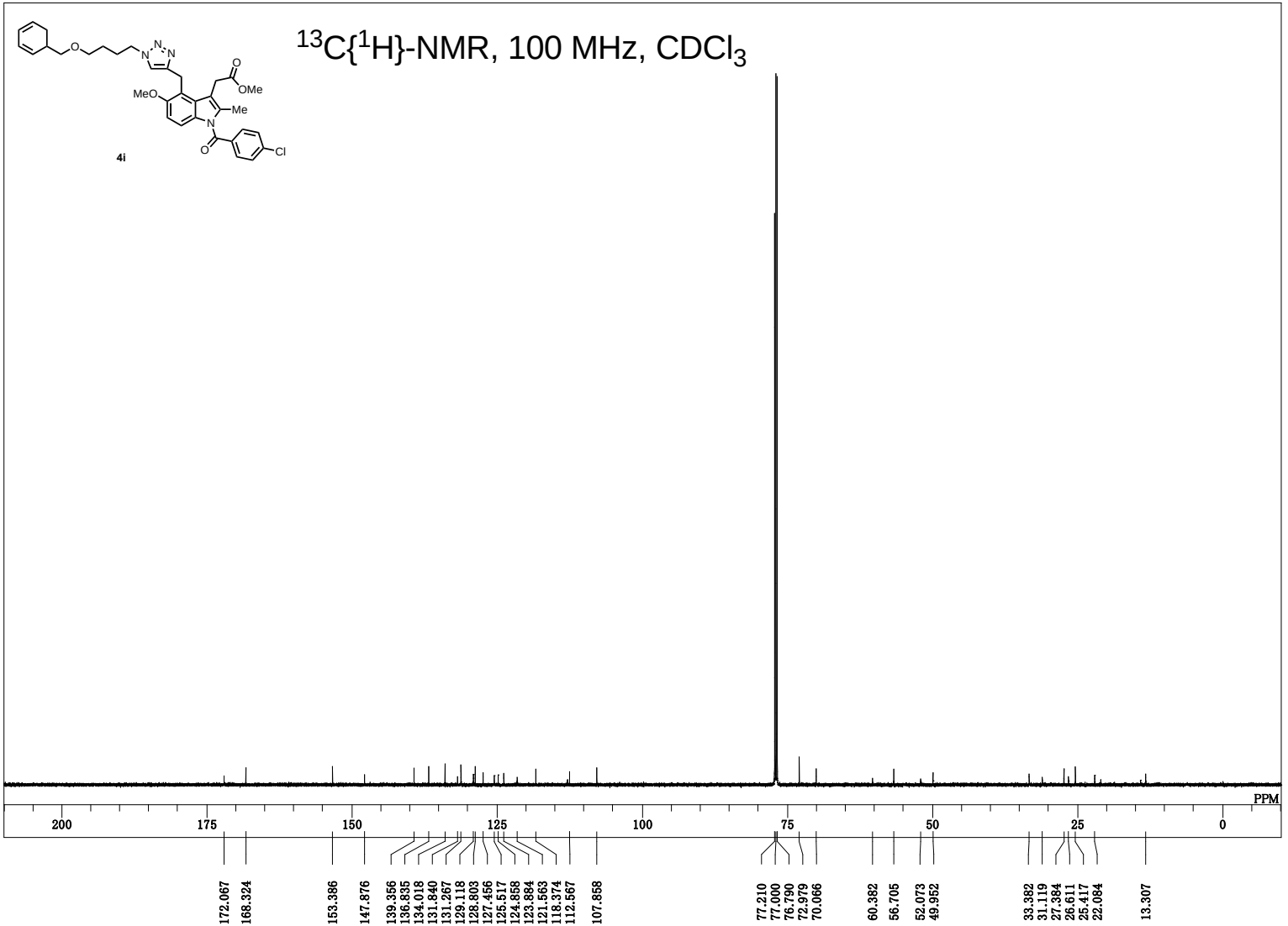
4h_C


4h
$^{13}C\{^{1}H\}$-NMR, 100 MHz, CD_3OD
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
173.983
172.386
171.835
171.332
162.831
143.029
128.610
127.820
126.421
125.902
125.030
119.688
81.813
79.781
74.744
74.497
74.020
71.123
70.036
63.304
54.012
51.444
49.650
49.502
49.436
49.288
49.214
49.000
48.852
48.786
48.704
48.572
48.358
34.745
28.367
27.511
26.417
22.548
20.606

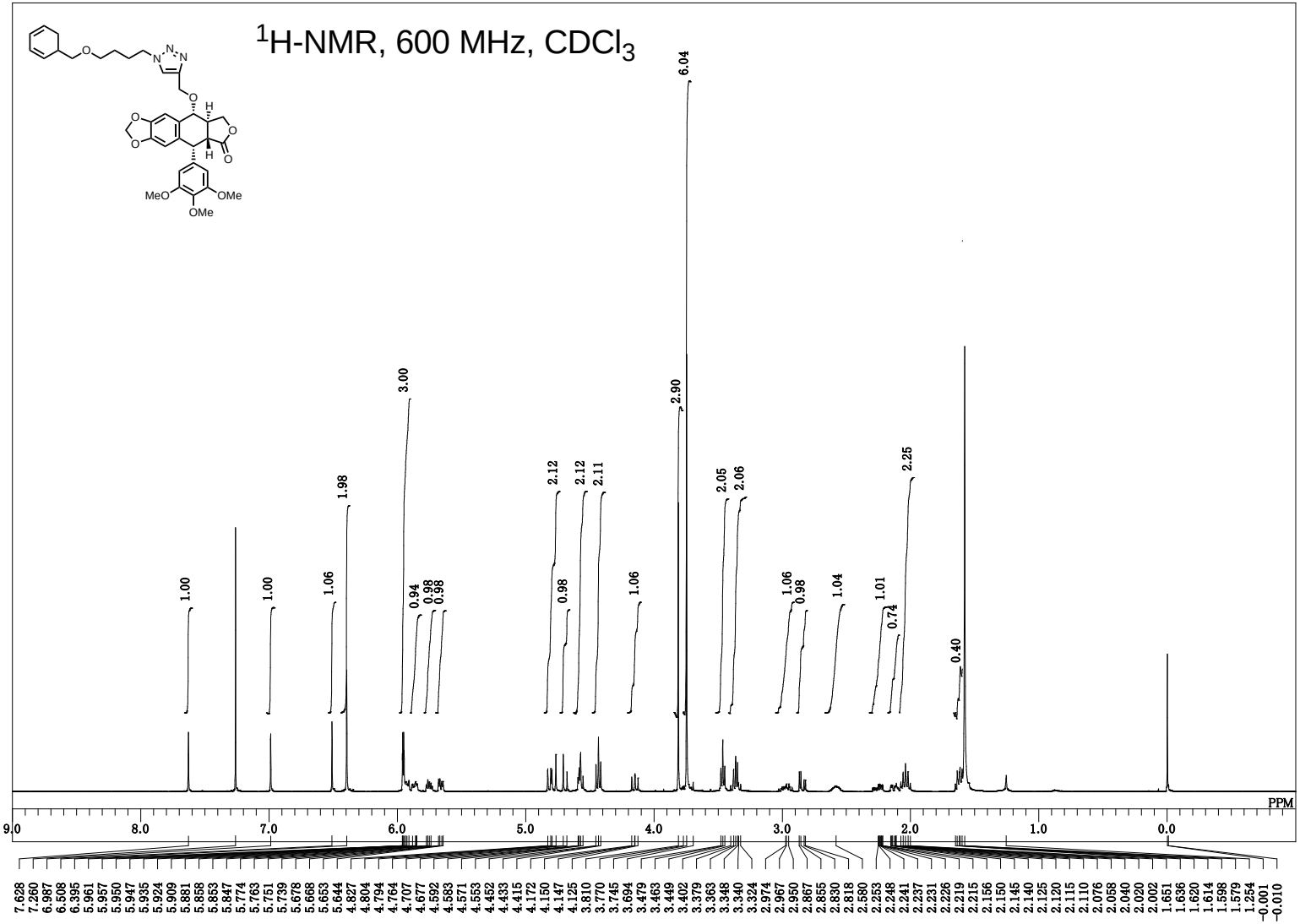
4i_H


^{1}H-NMR, 400 MHz, $CDCl_3$
4i
MeO
OMe
Me
Cl
2.13
2.09
0.95
1.04
1.00
1.90
0.96
0.95
2.14
2.18
2.09
3.17
3.18
1.96
2.10
0.97
4.23
1.30
2.15
2.28
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

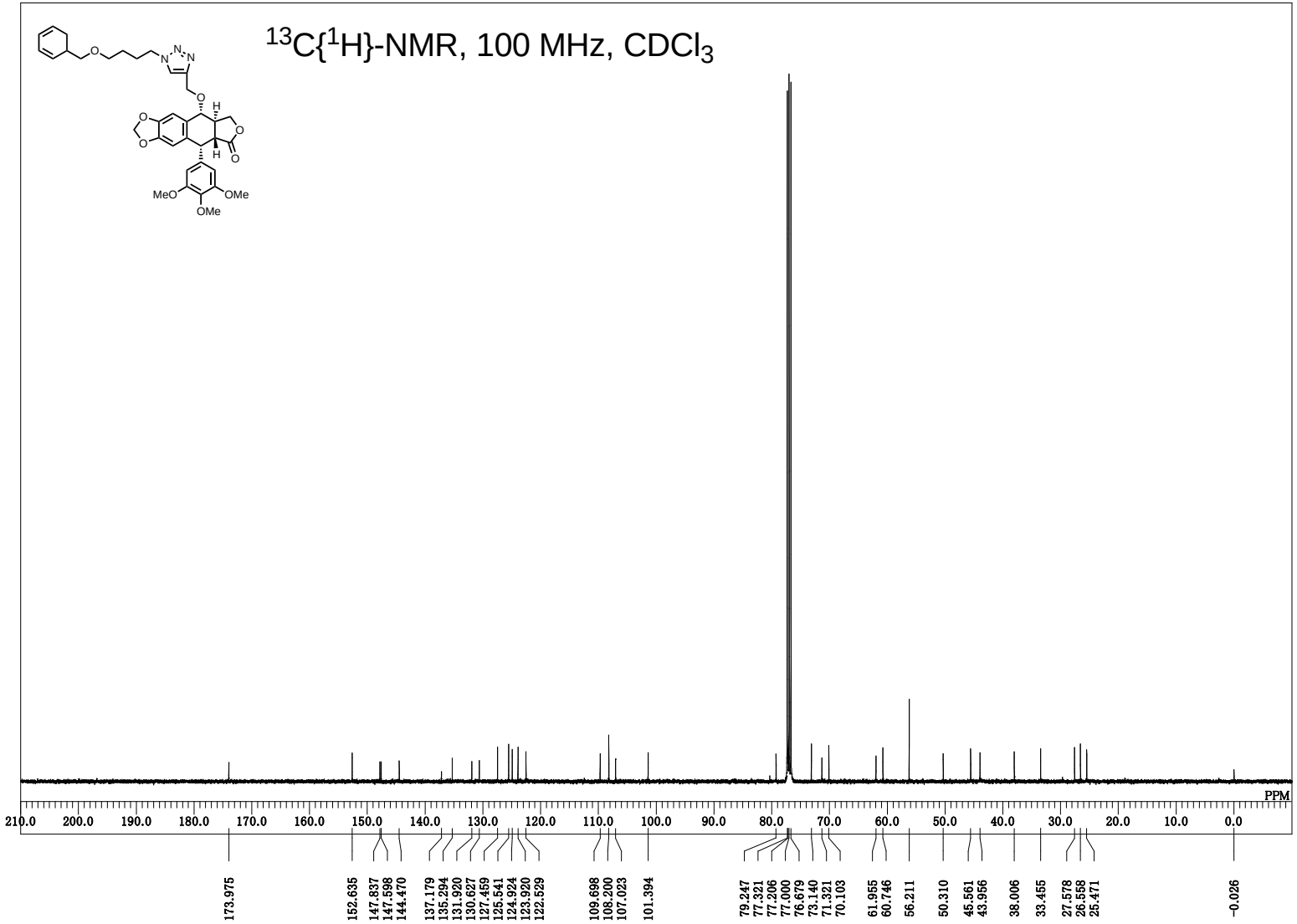
4i_C


13C{1H}-NMR, 100 MHz, CDCl3
MeO
OMe
Me
Cl
4i
PPM
200
175
150
125
100
75
50
25
0
172.067
168.324
153.386
147.876
139.356
136.835
134.018
131.840
131.267
129.118
128.803
127.456
125.517
124.858
123.884
121.563
118.374
112.567
107.858
77.210
77.000
76.790
72.979
70.066
60.382
56.705
52.073
49.952
33.382
31.119
27.384
26.611
25.417
22.084
13.307

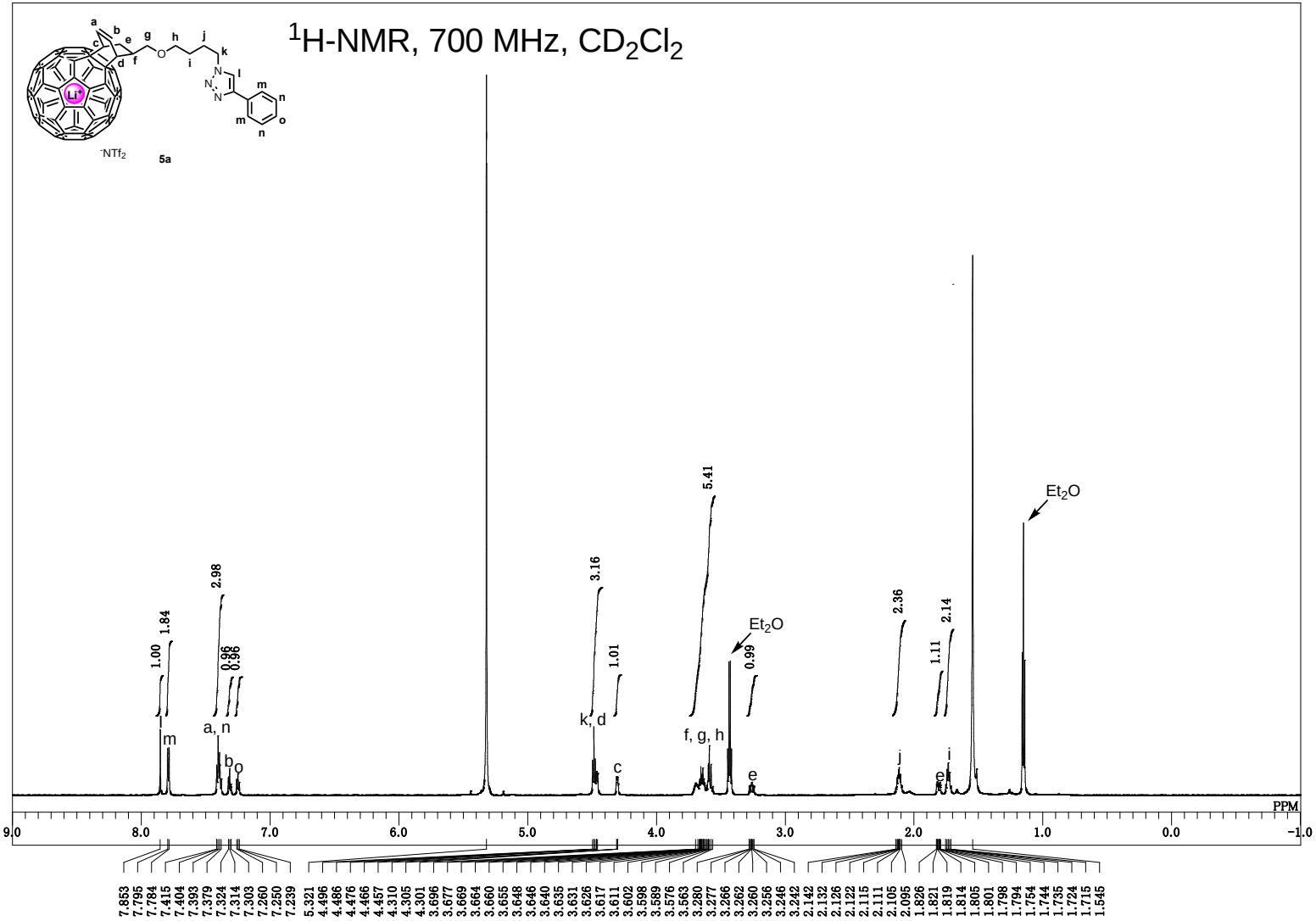
4j_H



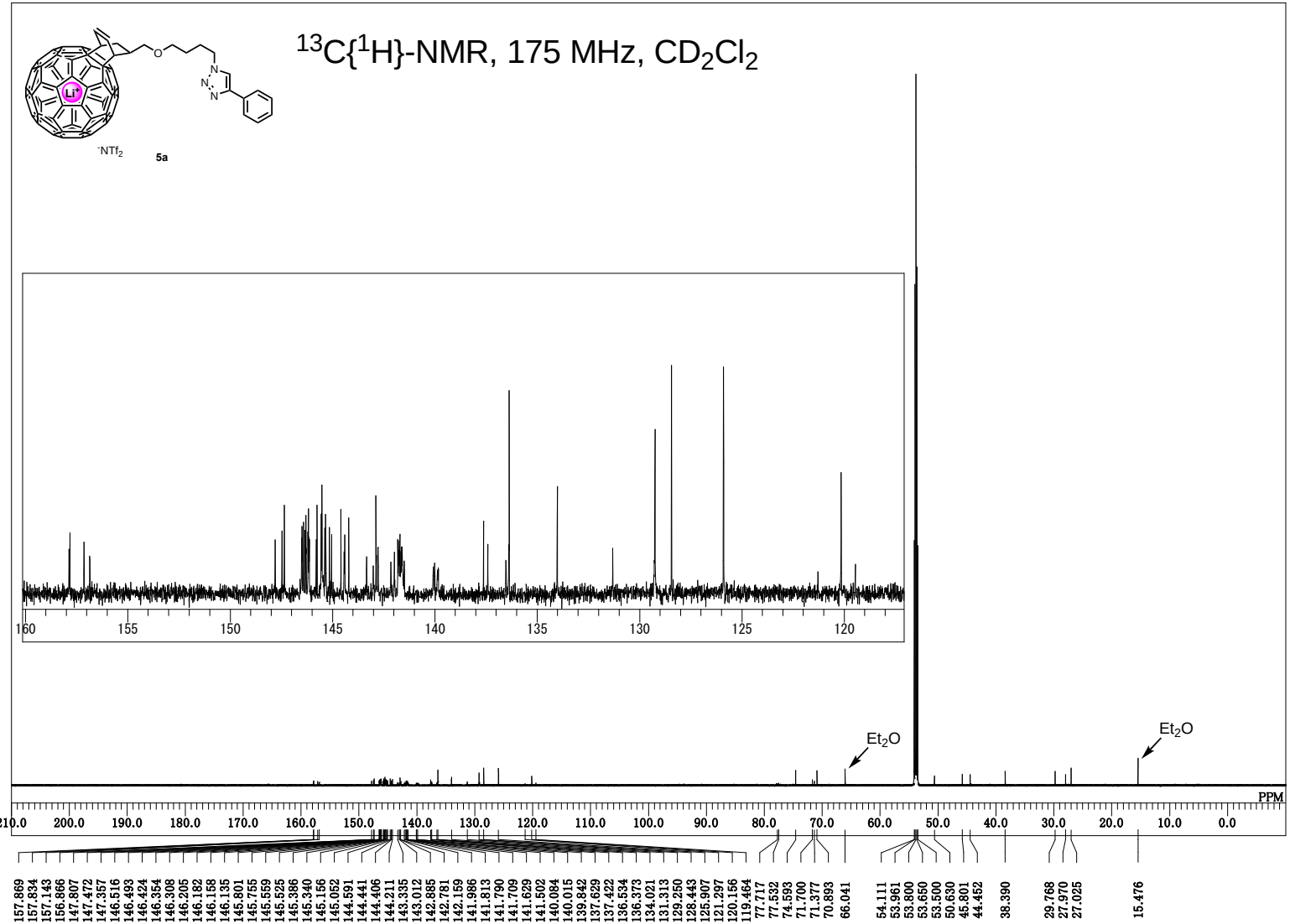
4j_C


13C{1H}-NMR, 100 MHz, CDCl3
MeO
OMe
OMe
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
173.975
152.635
147.837
147.598
144.470
137.179
135.294
131.920
130.627
127.459
125.541
124.924
123.920
122.529
109.698
108.200
107.023
101.394
79.247
77.321
77.206
77.000
76.679
73.140
71.321
70.103
61.955
60.746
56.211
50.310
45.561
43.956
38.006
33.455
27.578
26.558
25.471
-0.026

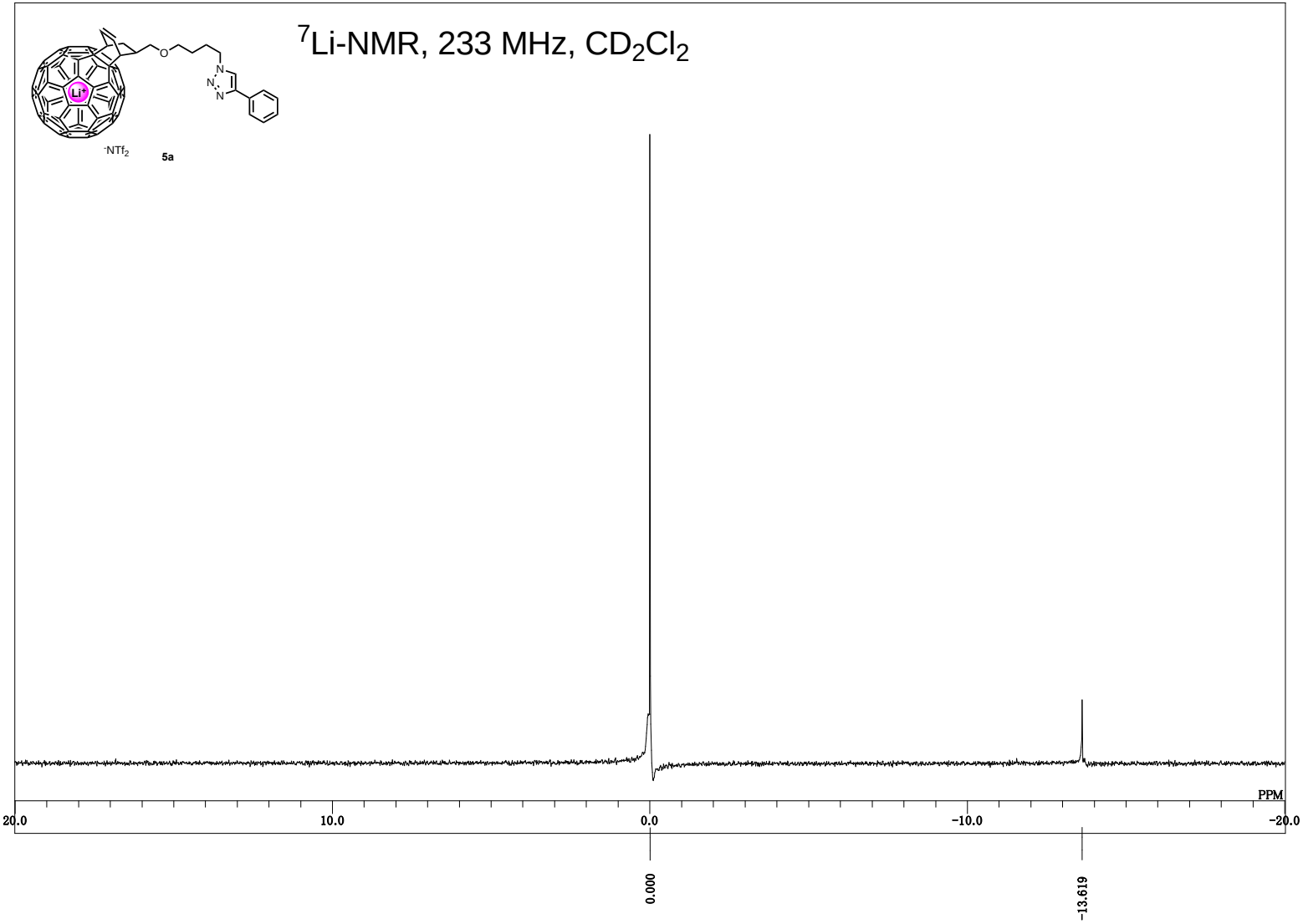
5a_H


1H-NMR, 700 MHz, CD2Cl2
5a
-NTf2
Et2O
Et2O
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

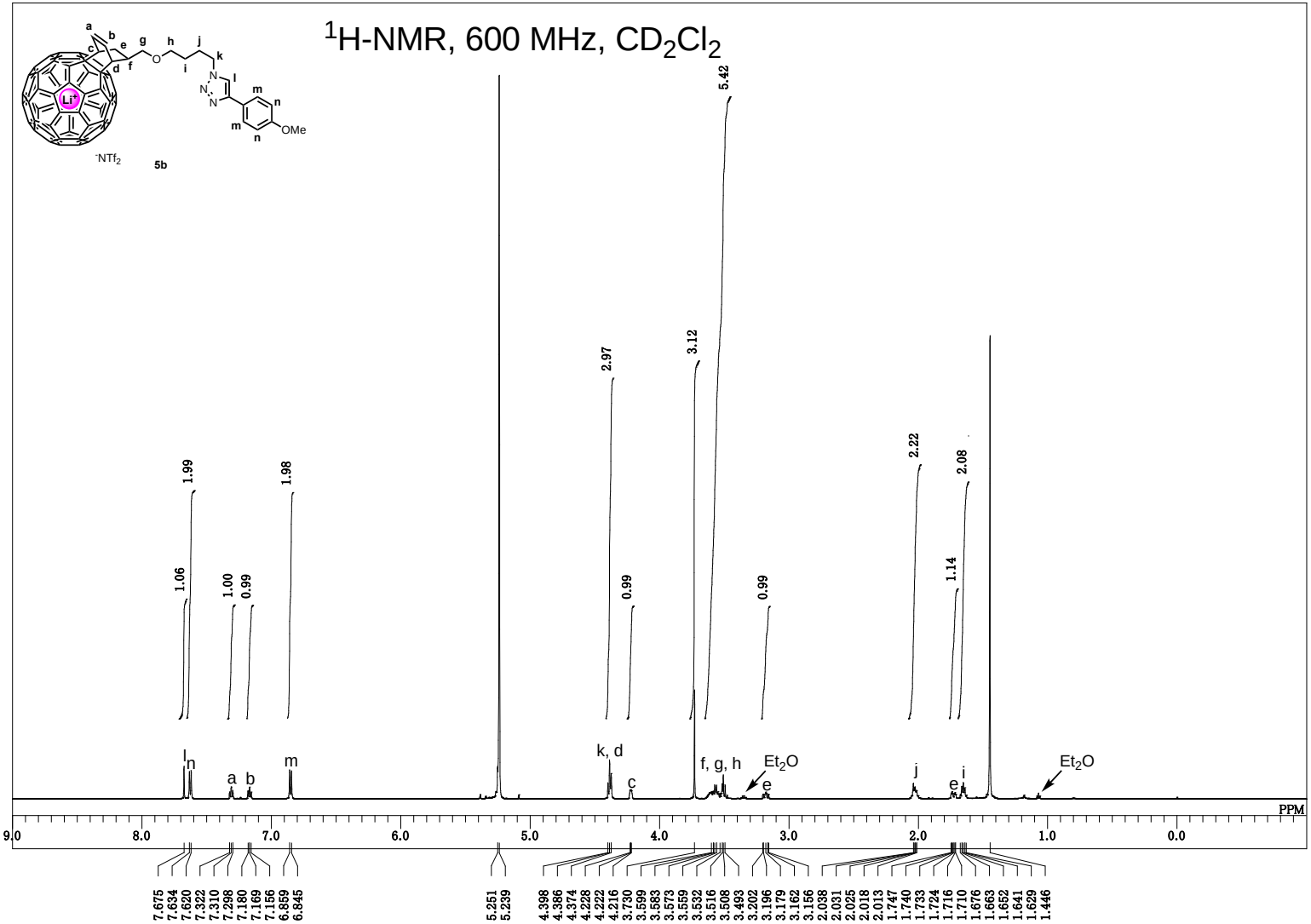
5a_C



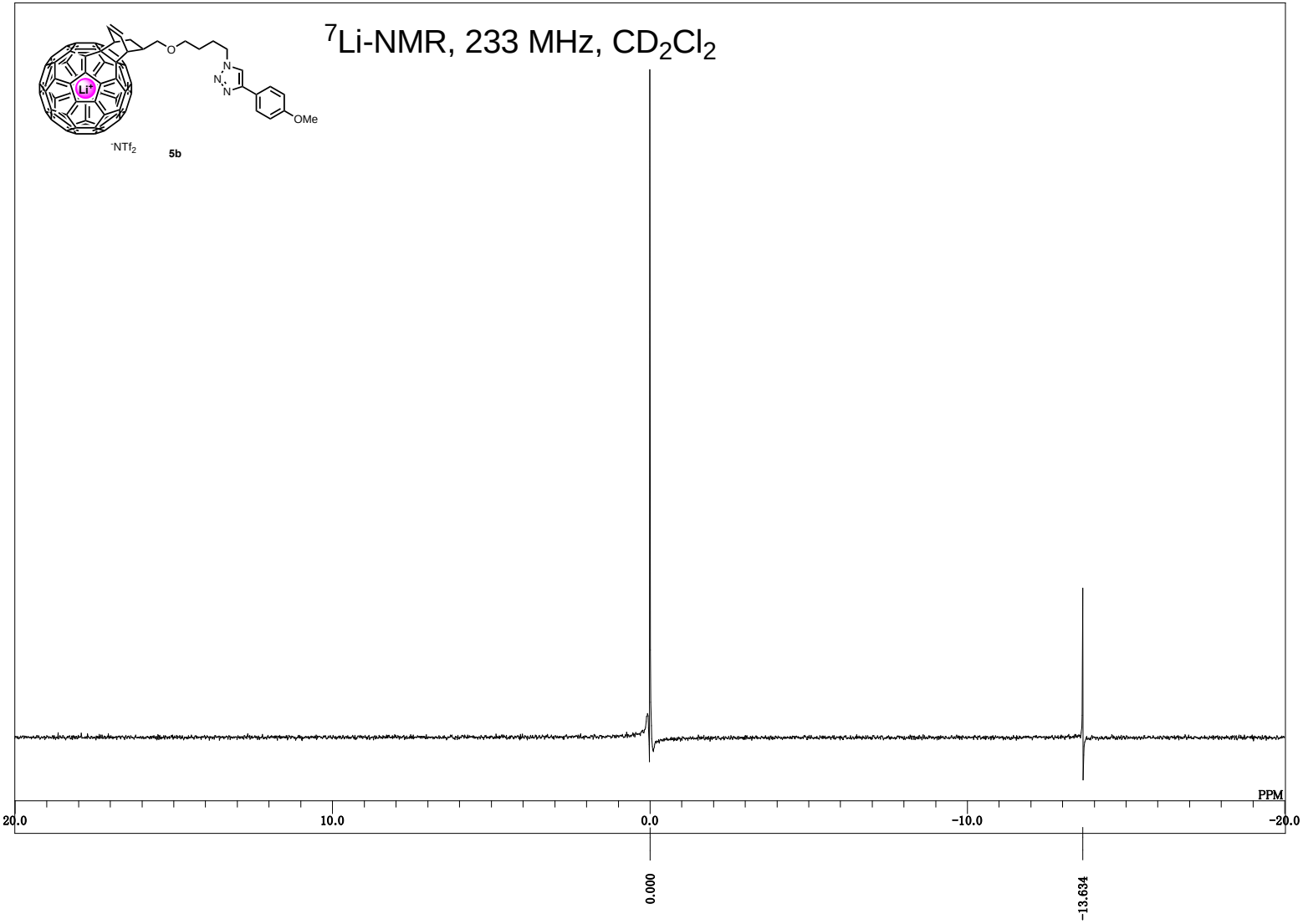
5a_Li


7Li-NMR, 233 MHz, CD2Cl2
Li+
-NTf2
5a
PPM
20.0
10.0
0.0
-10.0
-20.0
0.000
-13.619

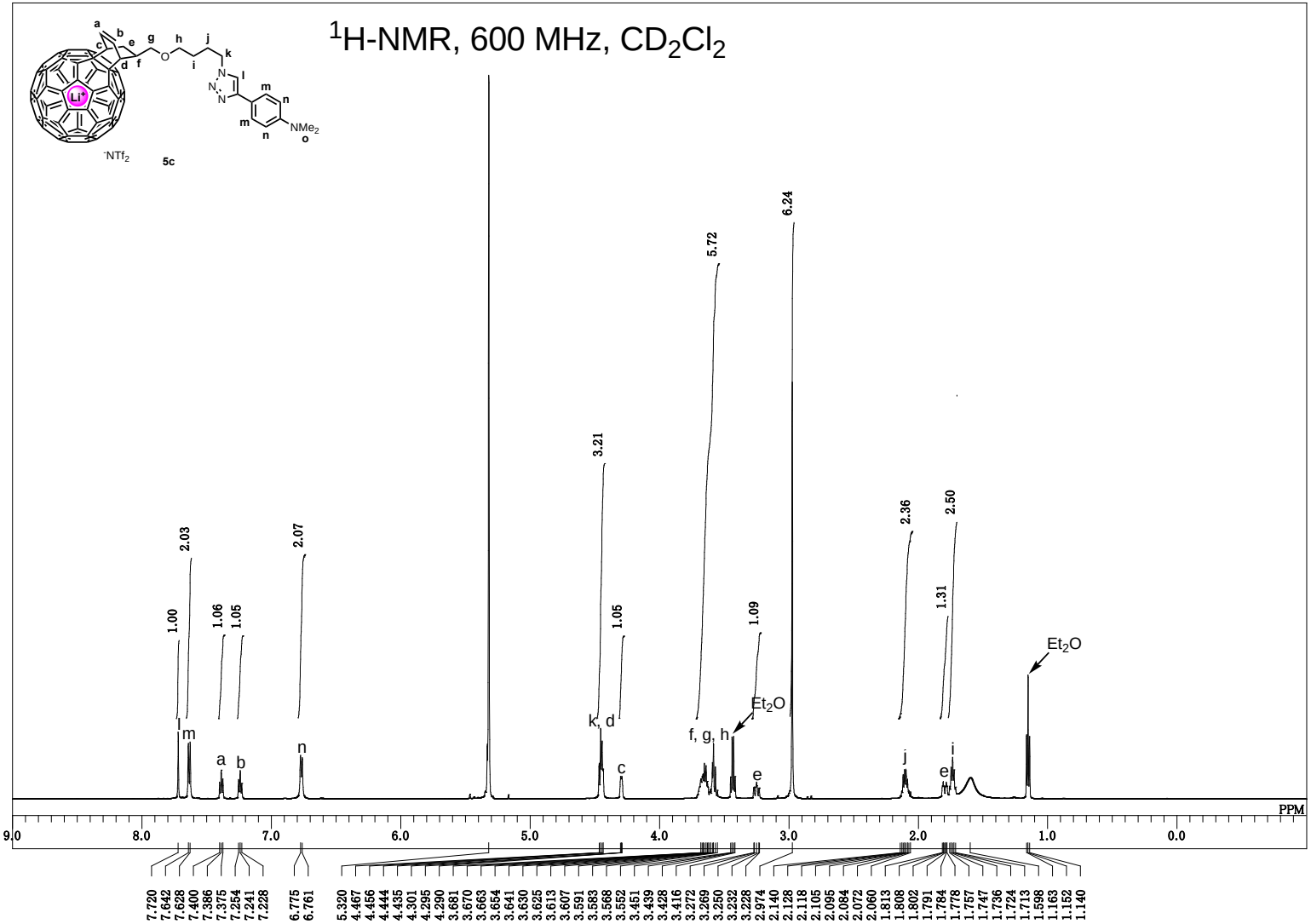
5b_H


1H-NMR, 600 MHz, CD2Cl2
5b
NTf2
1.06
1.99
1.00
0.99
1.98
2.97
0.99
3.12
5.42
0.99
2.22
1.14
2.08
l
n
a
b
m
k, d
c
f, g, h
Et2O
e
j
e
i
Et2O
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.675
7.634
7.620
7.322
7.310
7.298
7.180
7.169
7.156
6.859
6.845
5.251
5.239
4.398
4.386
4.374
4.228
4.222
4.216
3.730
3.599
3.583
3.573
3.559
3.532
3.516
3.508
3.493
3.202
3.196
3.179
3.162
3.156
2.038
2.031
2.025
2.018
2.013
1.747
1.740
1.733
1.724
1.716
1.710
1.676
1.663
1.652
1.641
1.629
1.446

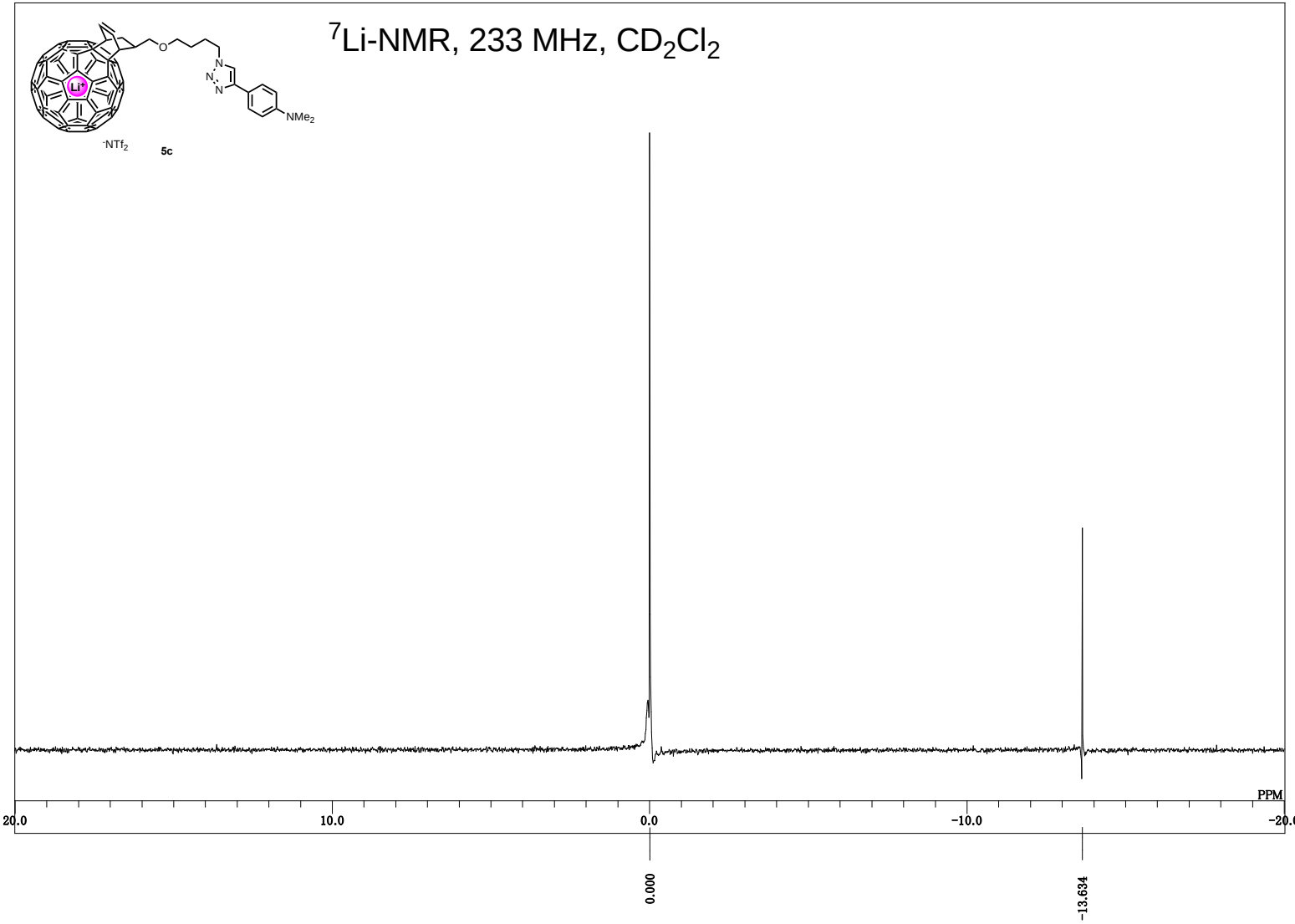
5b_Li


7Li-NMR, 233 MHz, CD2Cl2
Li+
NTf2
5b
OMe
PPM
20.0
10.0
0.0
−10.0
−20.0
0.000
−13.634

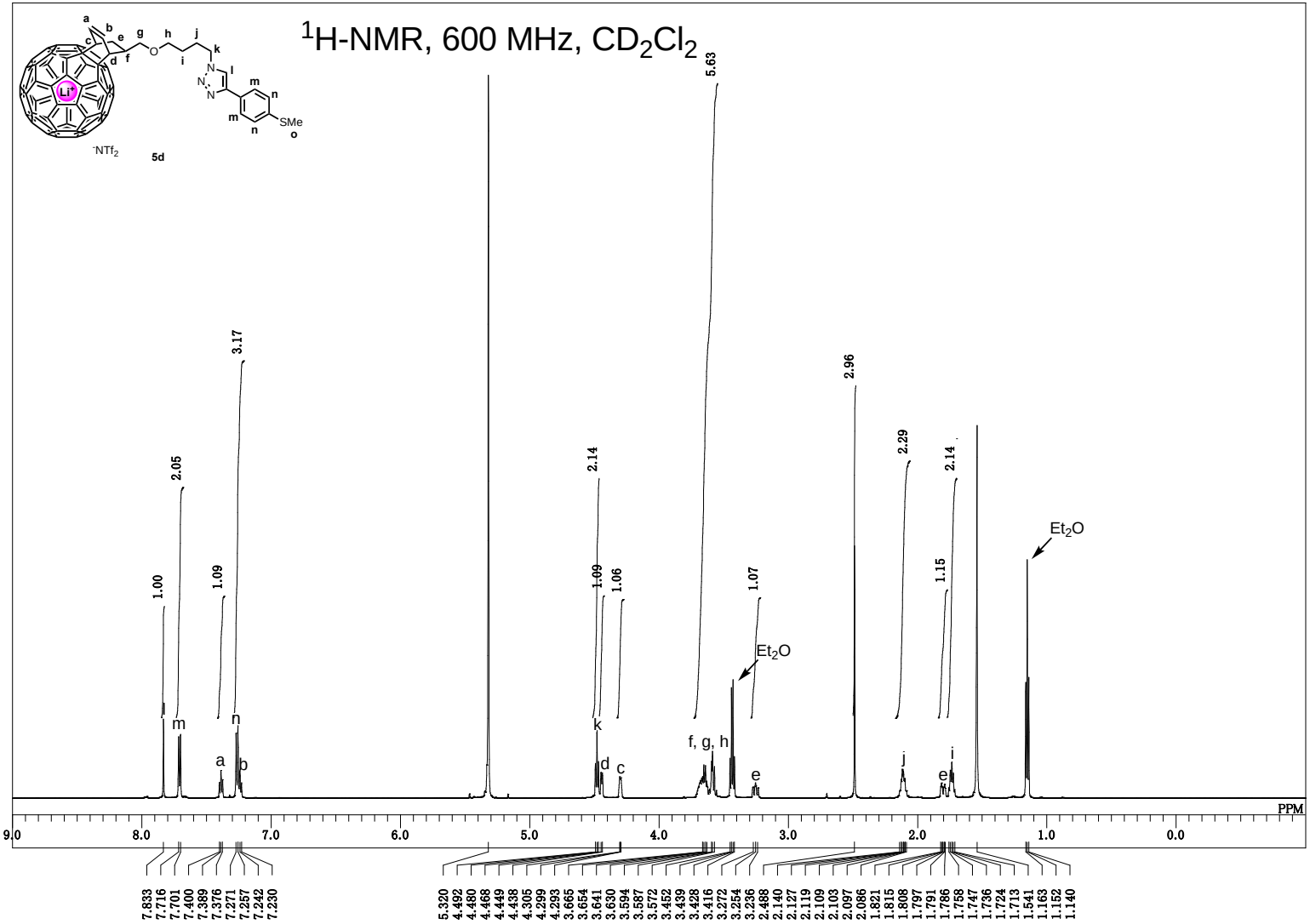
5c_H


1H-NMR, 600 MHz, CD2Cl2
5c
NTf2
Li+
NMe2
1.00
2.03
1.06
1.05
2.07
3.21
1.05
5.72
1.09
6.24
2.36
1.31
2.50
Et2O
Et2O
l
m
a
b
n
k, d
c
f, g, h
e
j
i
e
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.720
7.642
7.628
7.400
7.386
7.375
7.254
7.241
7.228
6.775
6.761
5.320
4.467
4.456
4.444
4.435
4.301
4.295
4.290
3.681
3.670
3.663
3.654
3.641
3.630
3.625
3.613
3.607
3.591
3.583
3.568
3.552
3.451
3.439
3.428
3.416
3.272
3.269
3.250
3.232
3.228
2.974
2.140
2.128
2.118
2.105
2.095
2.084
2.072
2.060
1.813
1.808
1.802
1.791
1.784
1.778
1.757
1.747
1.736
1.724
1.713
1.598
1.163
1.152
1.140

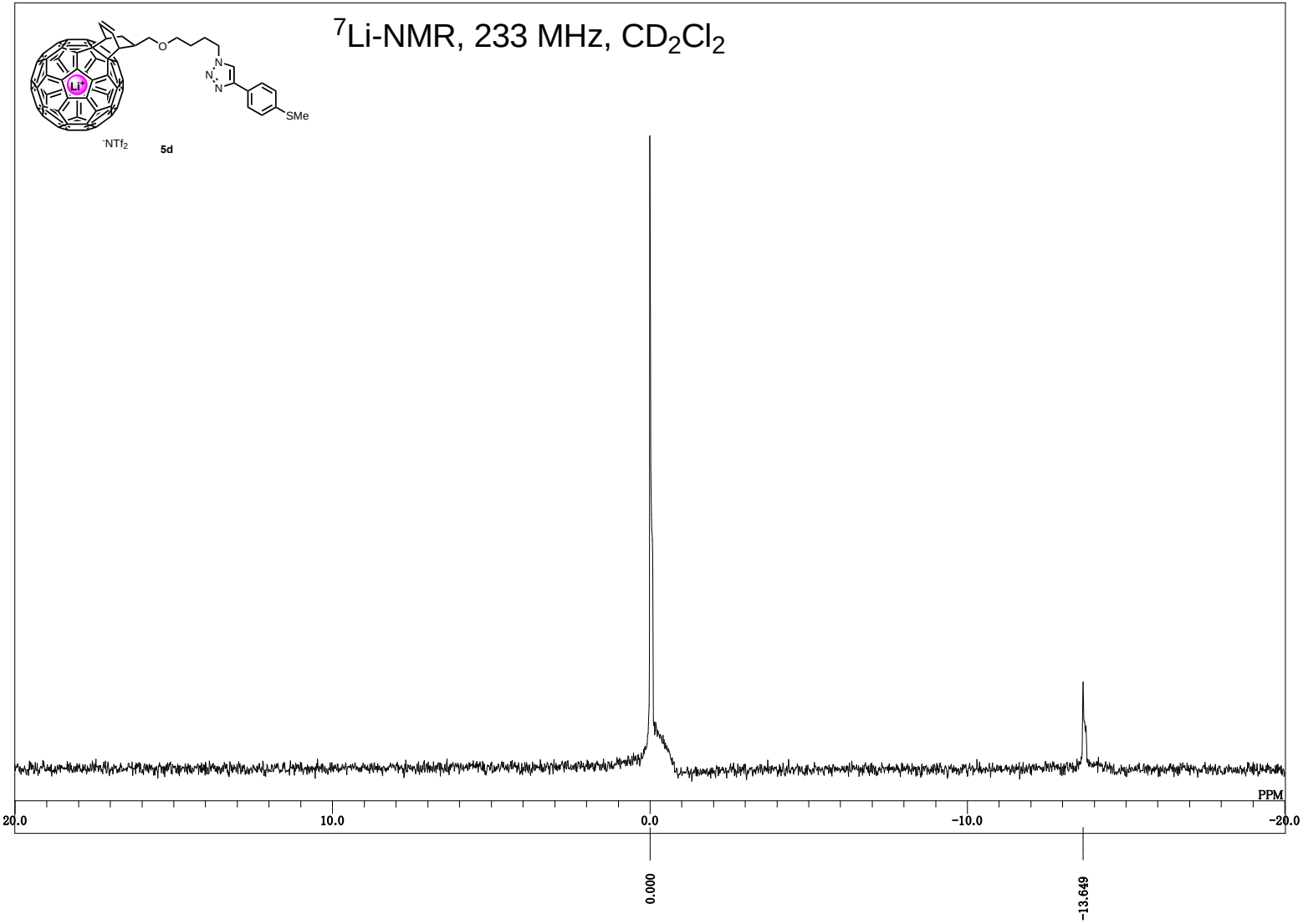
5c_Li


7Li-NMR, 233 MHz, CD2Cl2
Li+
NMe2
·NTf2
5c
PPM
20.0
10.0
0.0
−10.0
−20.0
0.000
−13.634

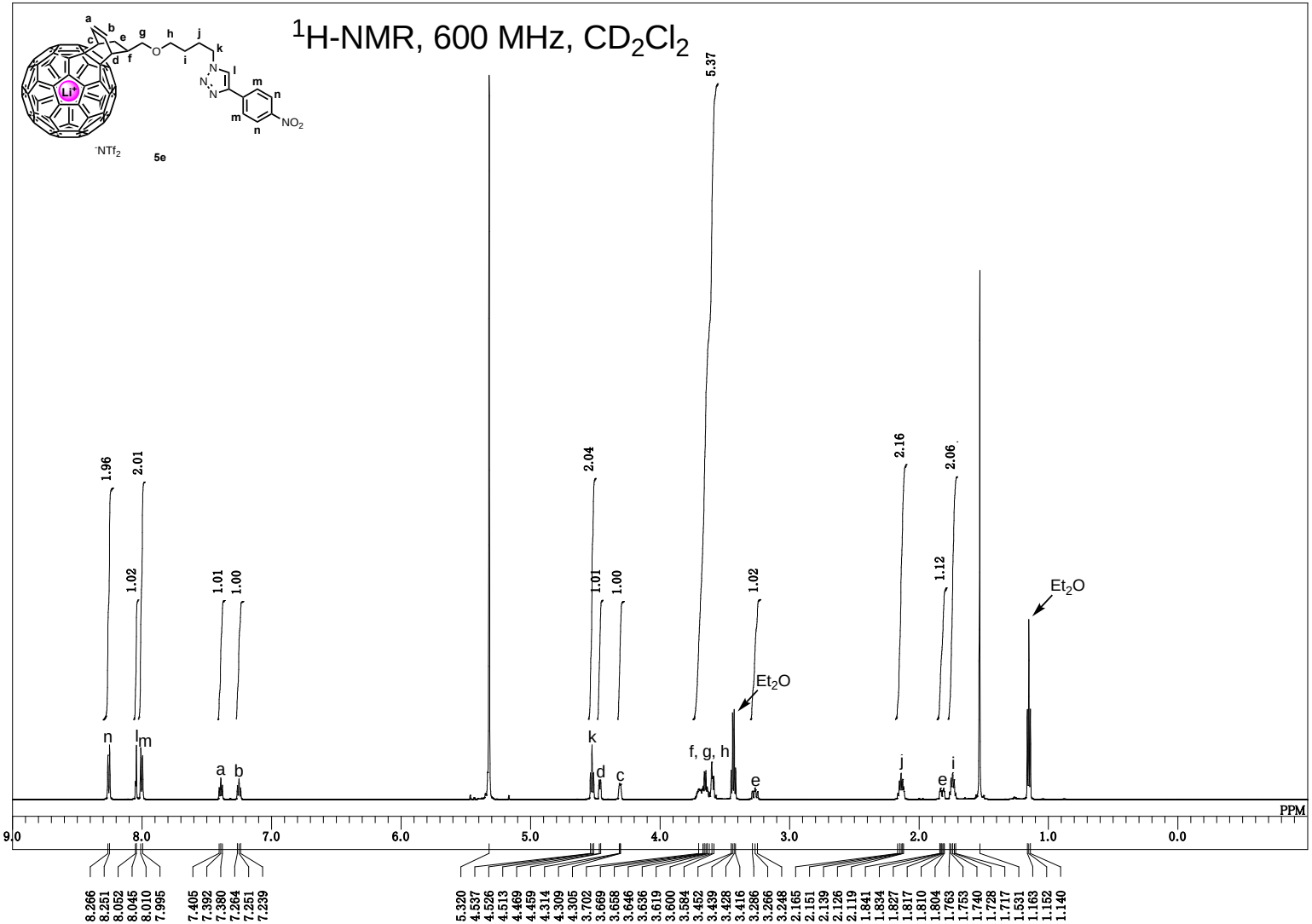
5d_H



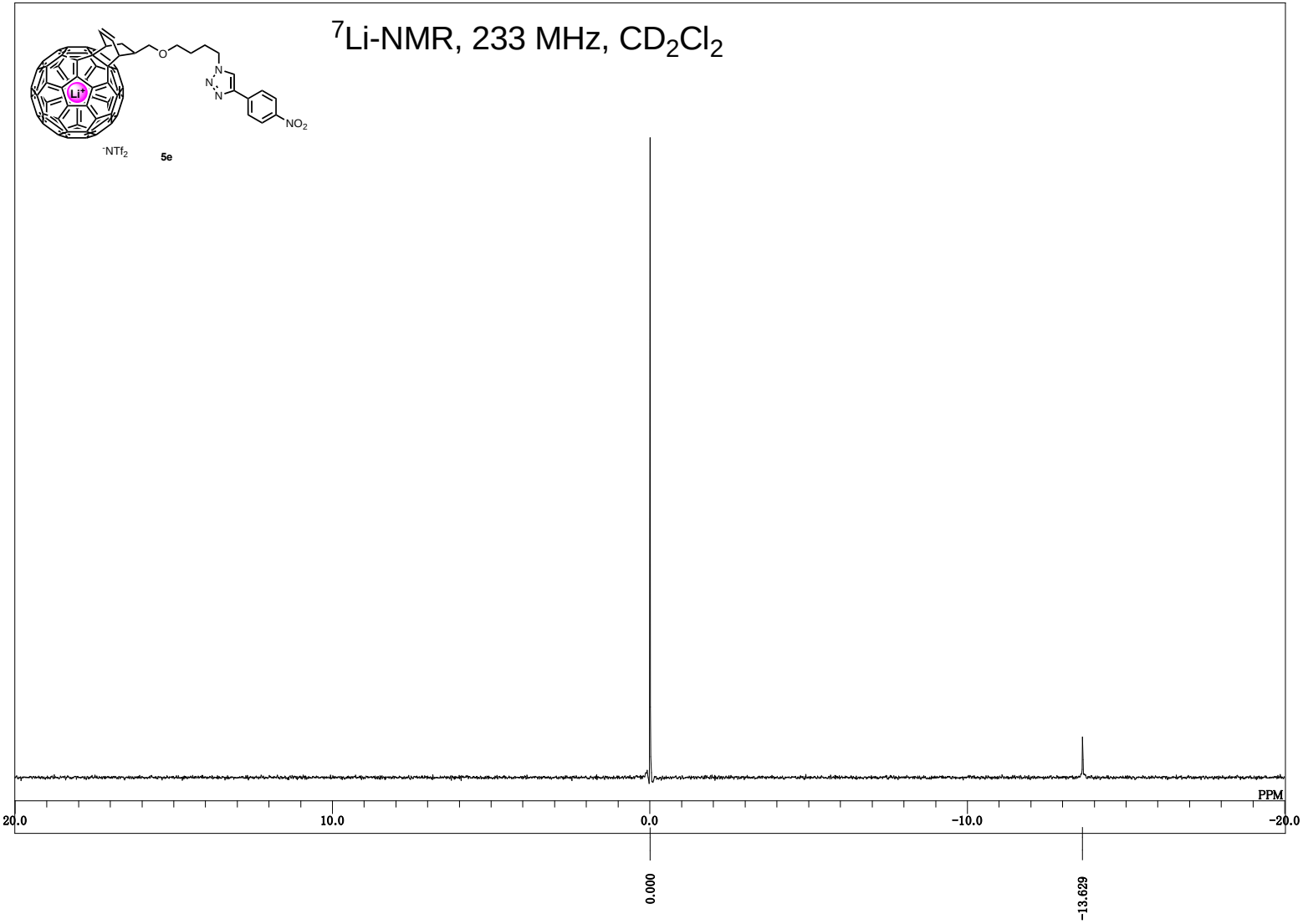
5d_Li


7Li-NMR, 233 MHz, CD2Cl2
Li+
O
N
N
N
SMe
NTf2
5d
PPM
20.0
10.0
0.0
−10.0
−20.0
0.000
−13.649

5e_H


1H-NMR, 600 MHz, CD2Cl2
5e
NTf2
Et2O
Et2O
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

5e_Li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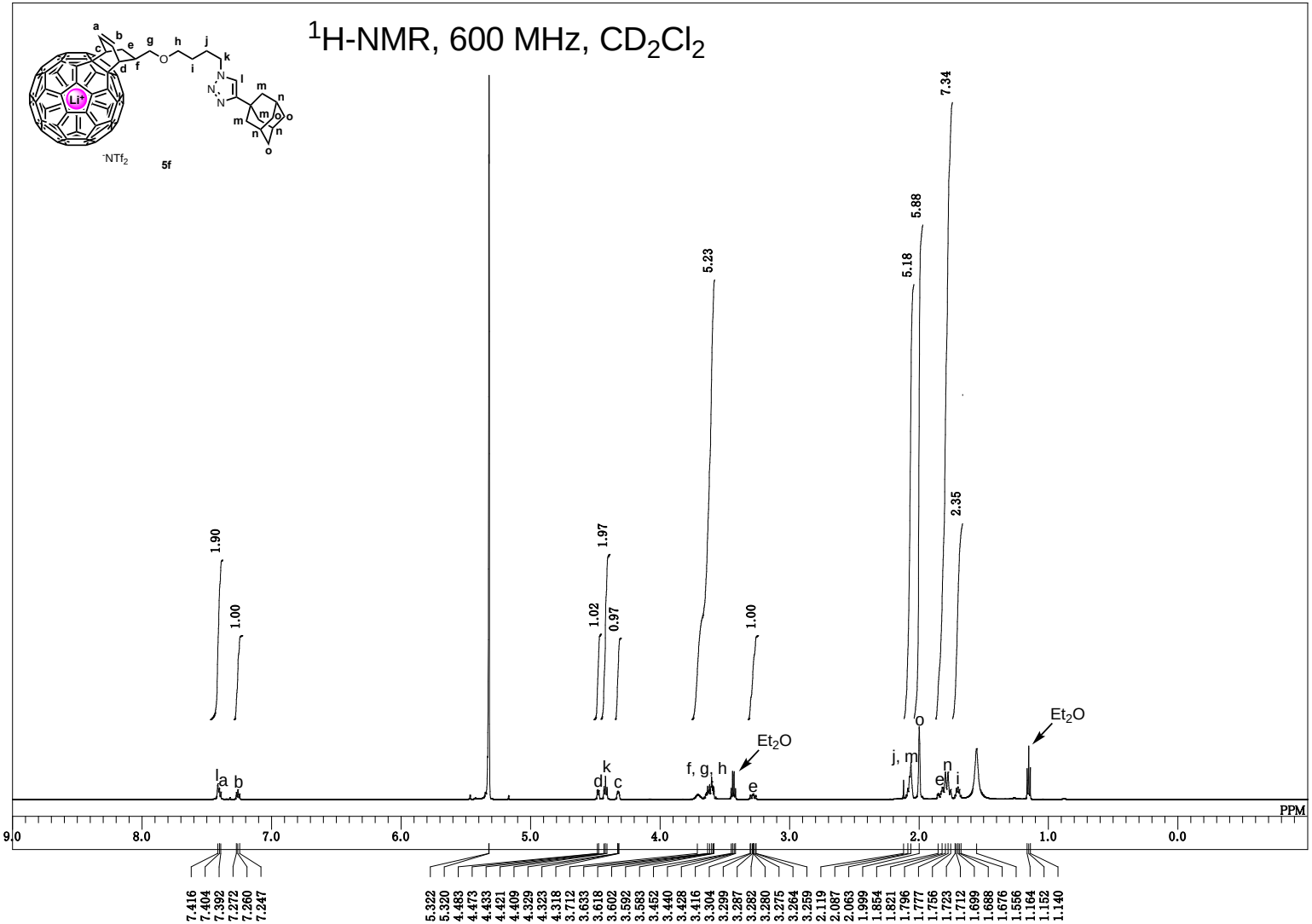
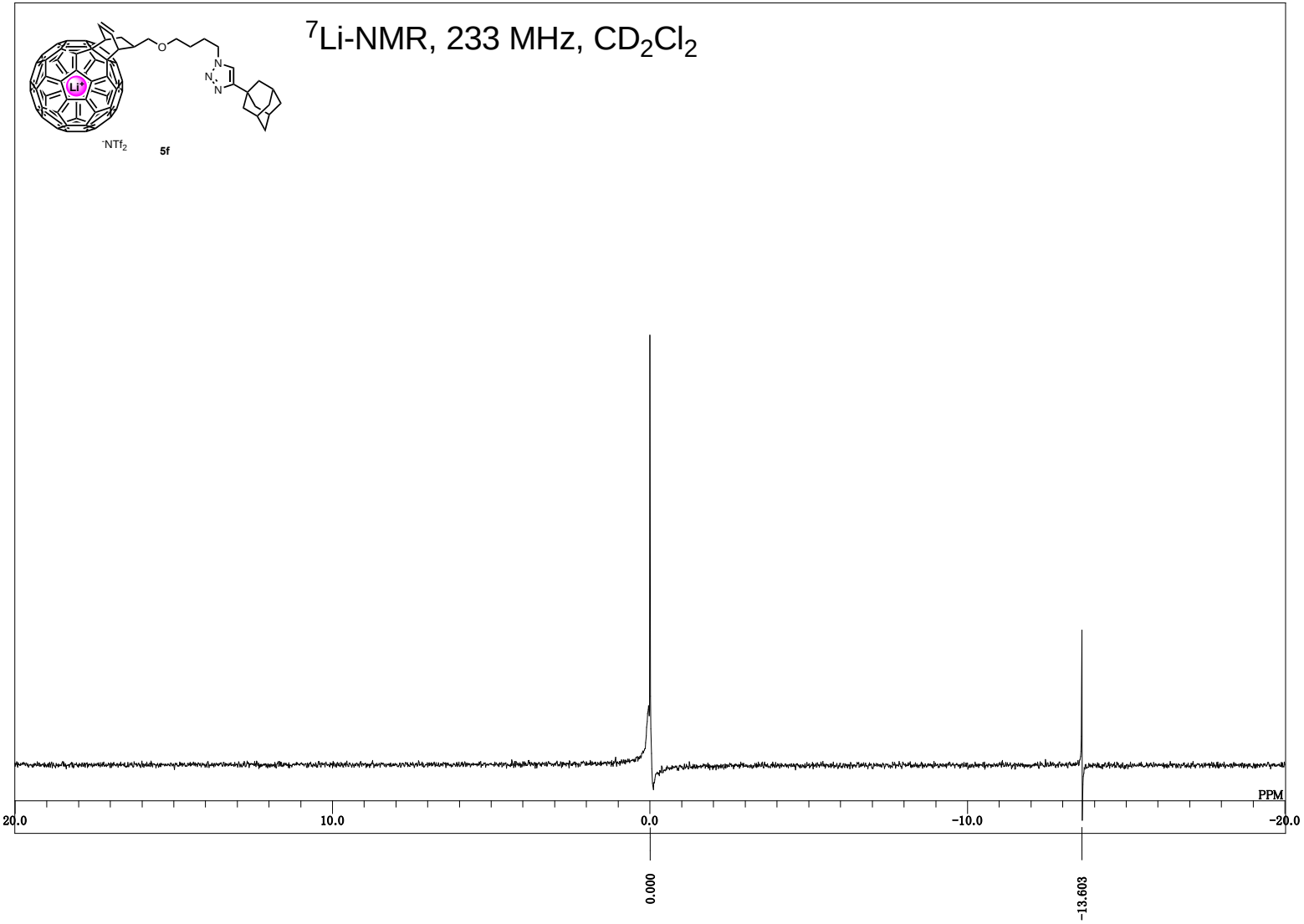
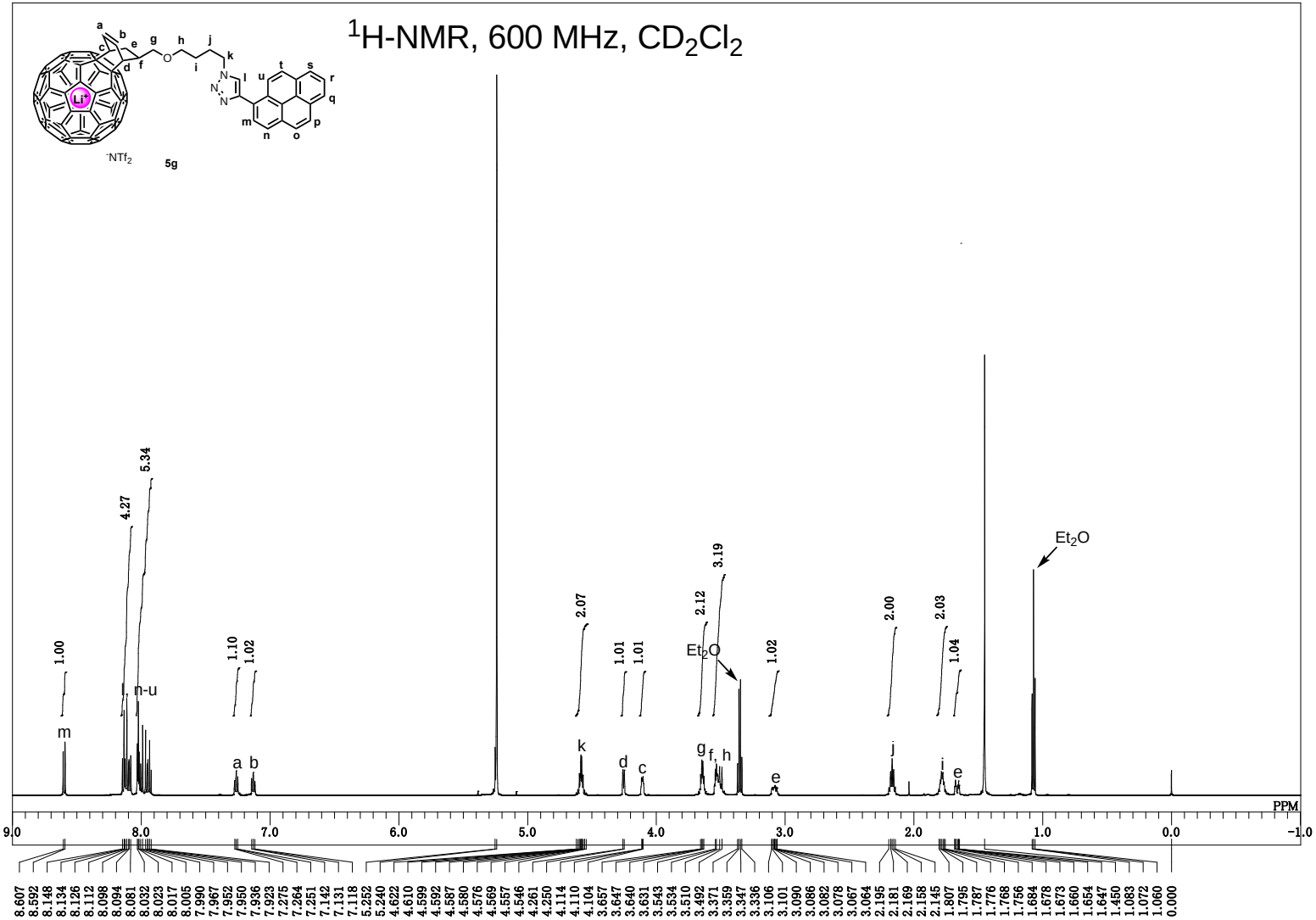
Li+
NTf2
5e
NO2
PPM
20.0
10.0
0.0
−10.0
−20.0
0.000
−13.629


5f_H
1H-NMR, 600 MHz, CD2Cl2
5f
7.34
5.88
5.18
5.23
2.35
1.97
1.90
1.00
1.02
0.97
1.00
Et2O
Et2O
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

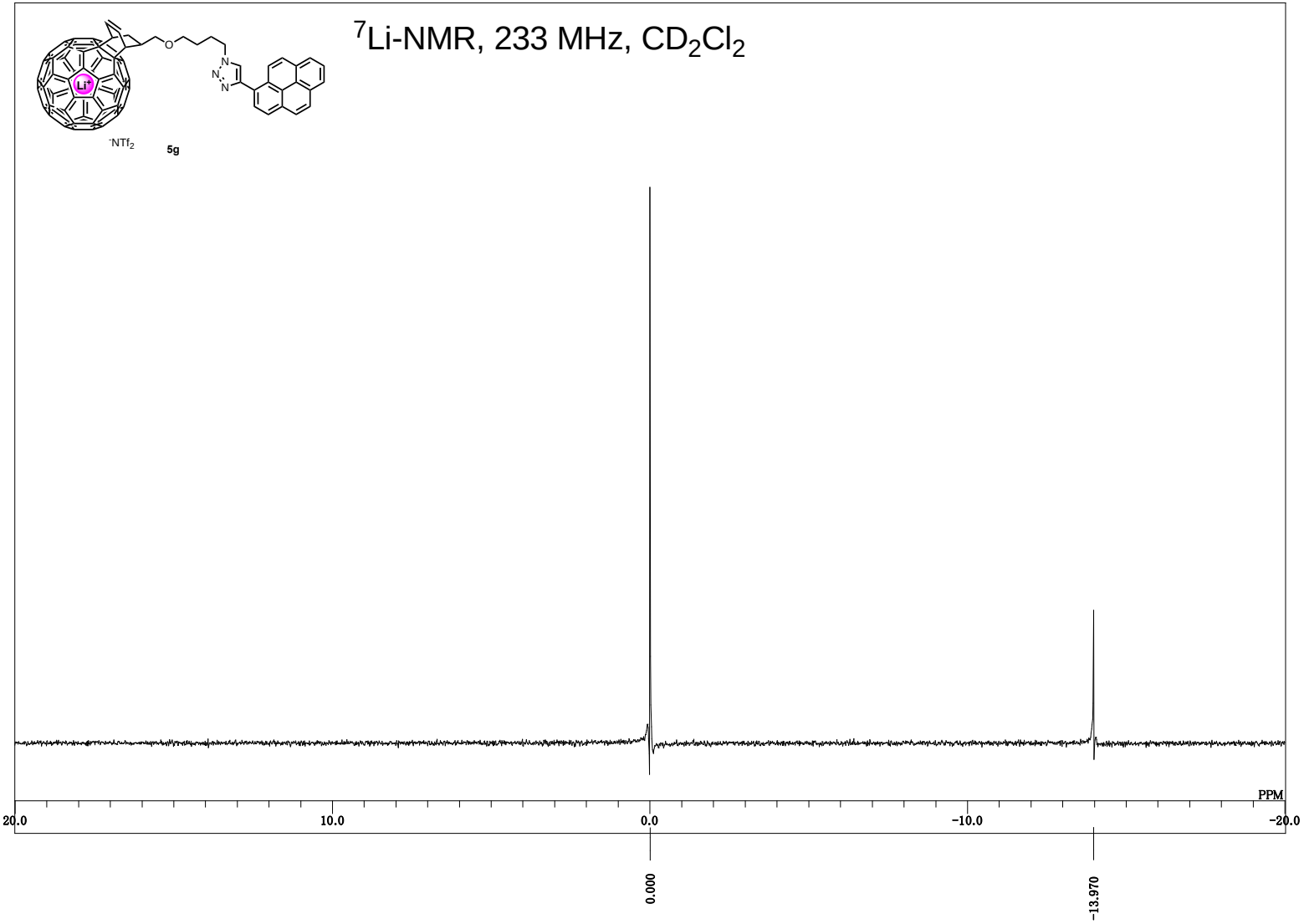
5f_Li

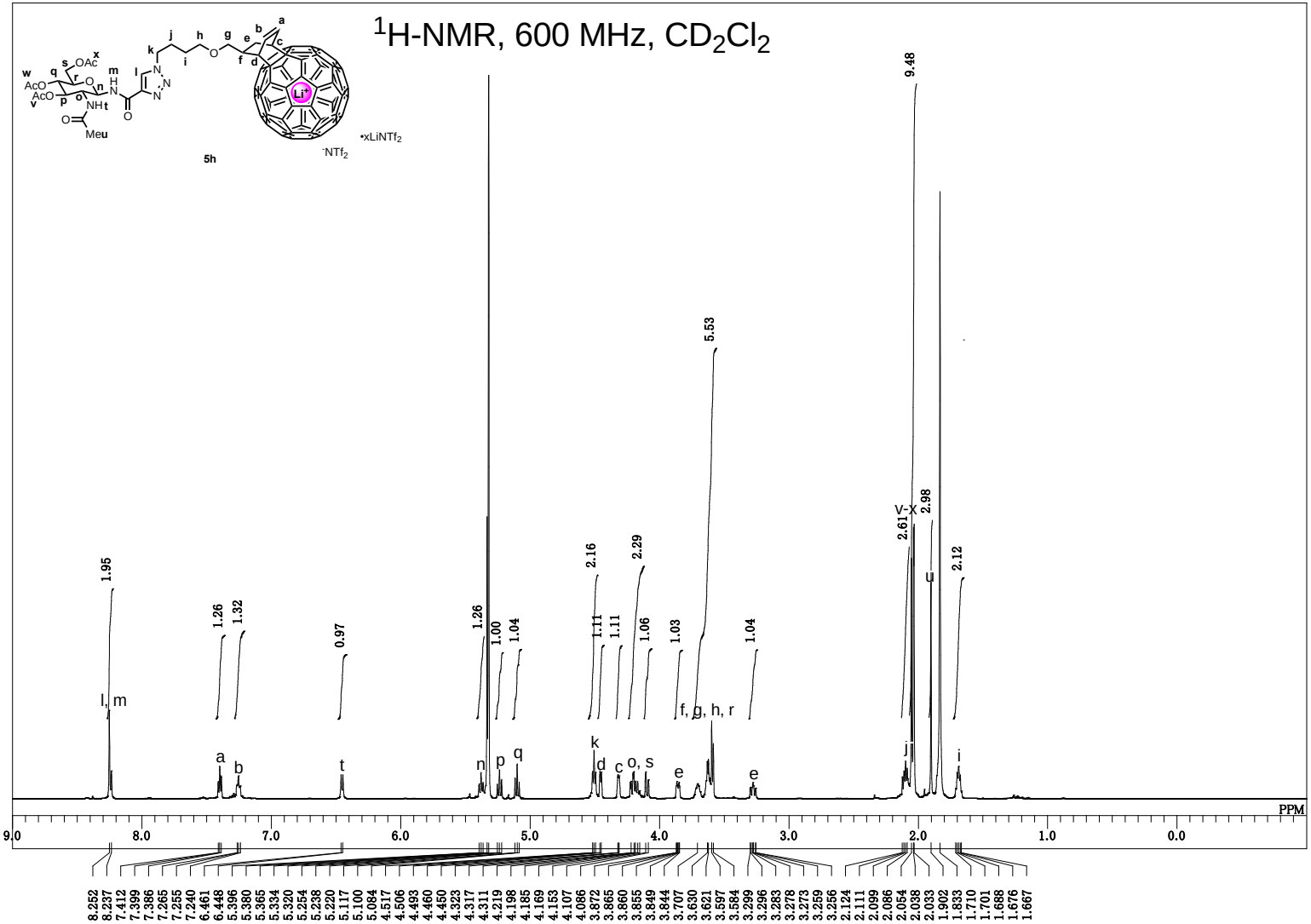

7Li-NMR, 233 MHz, CD2Cl2
Li+
NTf2
5f
PPM
20.0
10.0
0.0
−10.0
−20.0
0.000
−13.603

5g_H

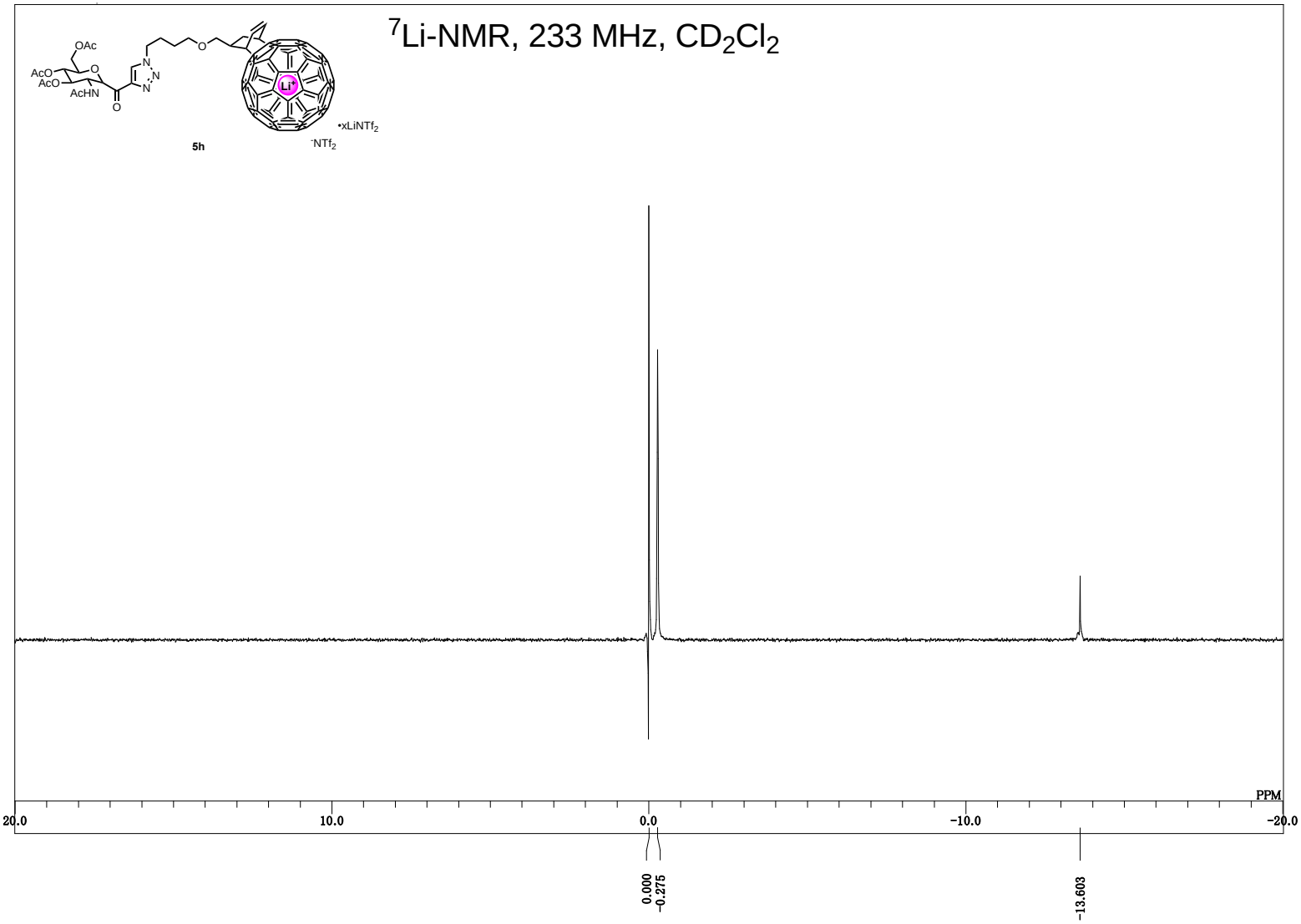

1H-NMR, 600 MHz, CD2Cl2
Li+
-NTf2
5g
1.00
5.34
4.27
n-u
m
1.10
1.02
a b
2.07
1.01
1.01
k
d
c
2.12
3.19
Et2O
g
f, h
1.02
e
2.00
2.03
1.04
j
i
e
Et2O
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

5g_Li

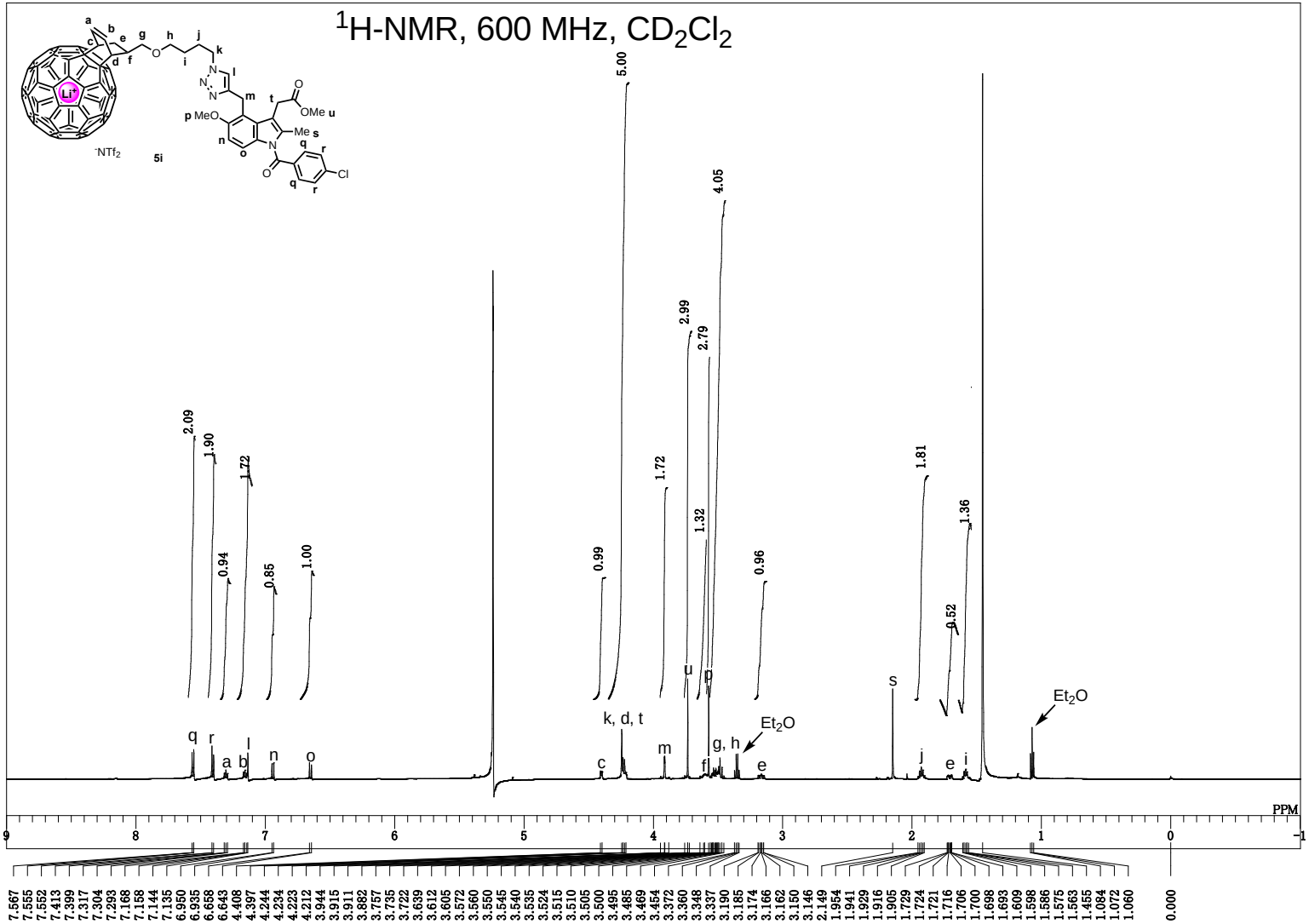

7Li-NMR, 233 MHz, CD2Cl2
Li+
O
N
N
N
-NTf2
5g
PPM
20.0
10.0
0.0
-10.0
-20.0
0.000
-13.970


5h_H
1H-NMR, 600 MHz, CD2Cl2
5h
•xLiNTf2
-NTf2
PPM

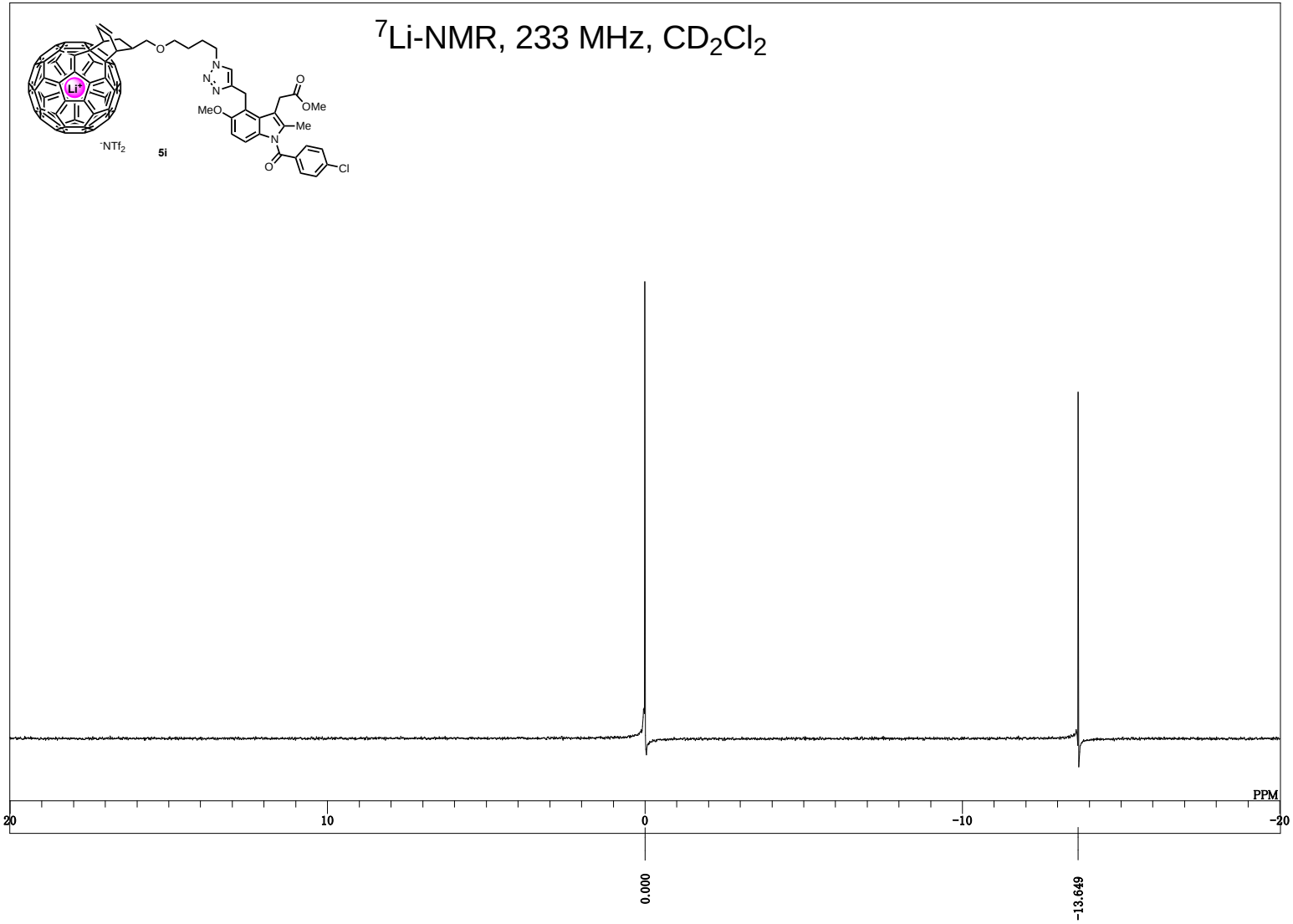
5h_Li


7Li-NMR, 233 MHz, CD2Cl2
OAc
AcO
AcO
AcHN
O
N
N
N
O
Li+
•xLiNTf2
-NTf2
5h
PPM
20.0
10.0
0.0
−10.0
−20.0
0.000
−0.275
−13.603

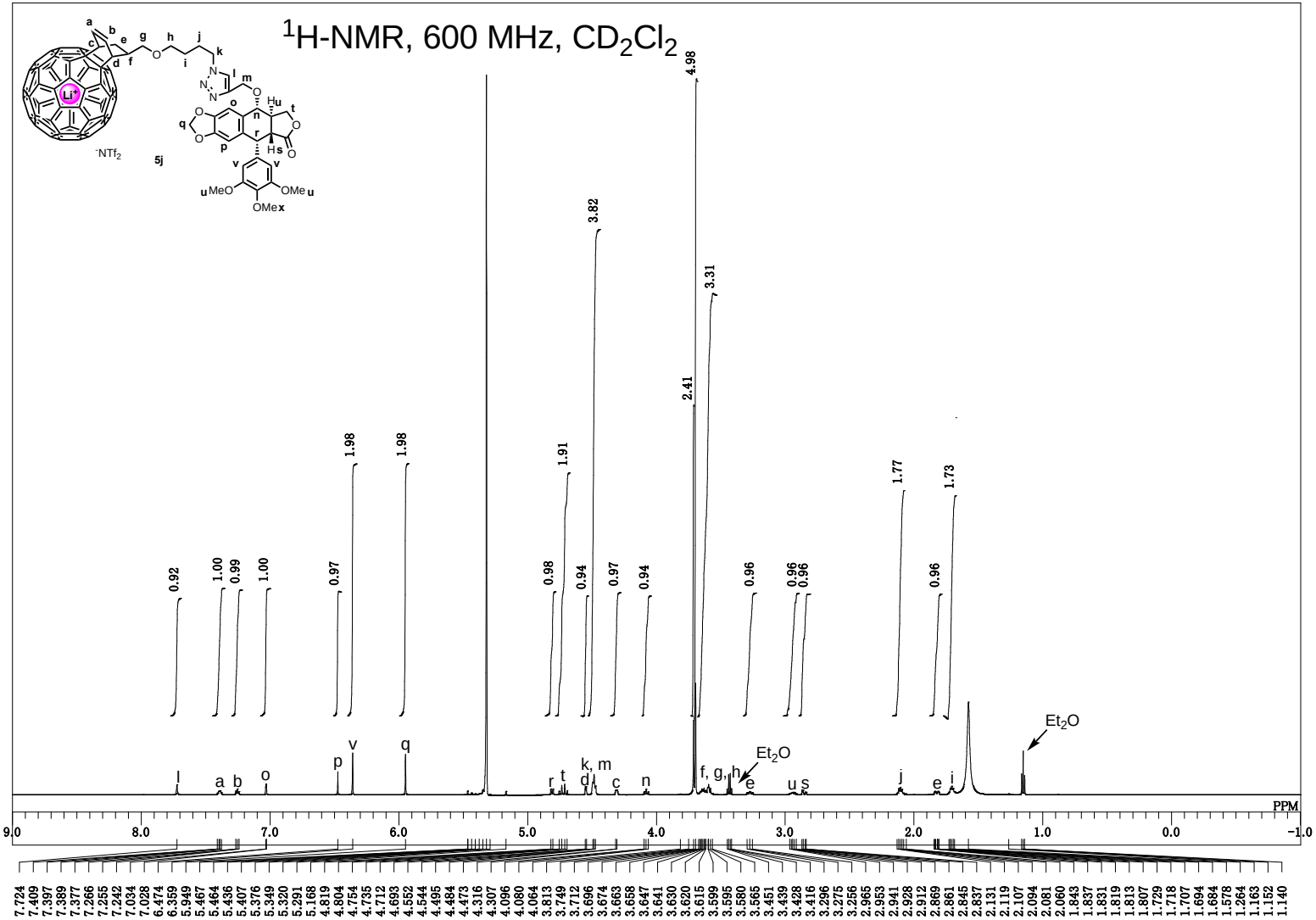
5i_H



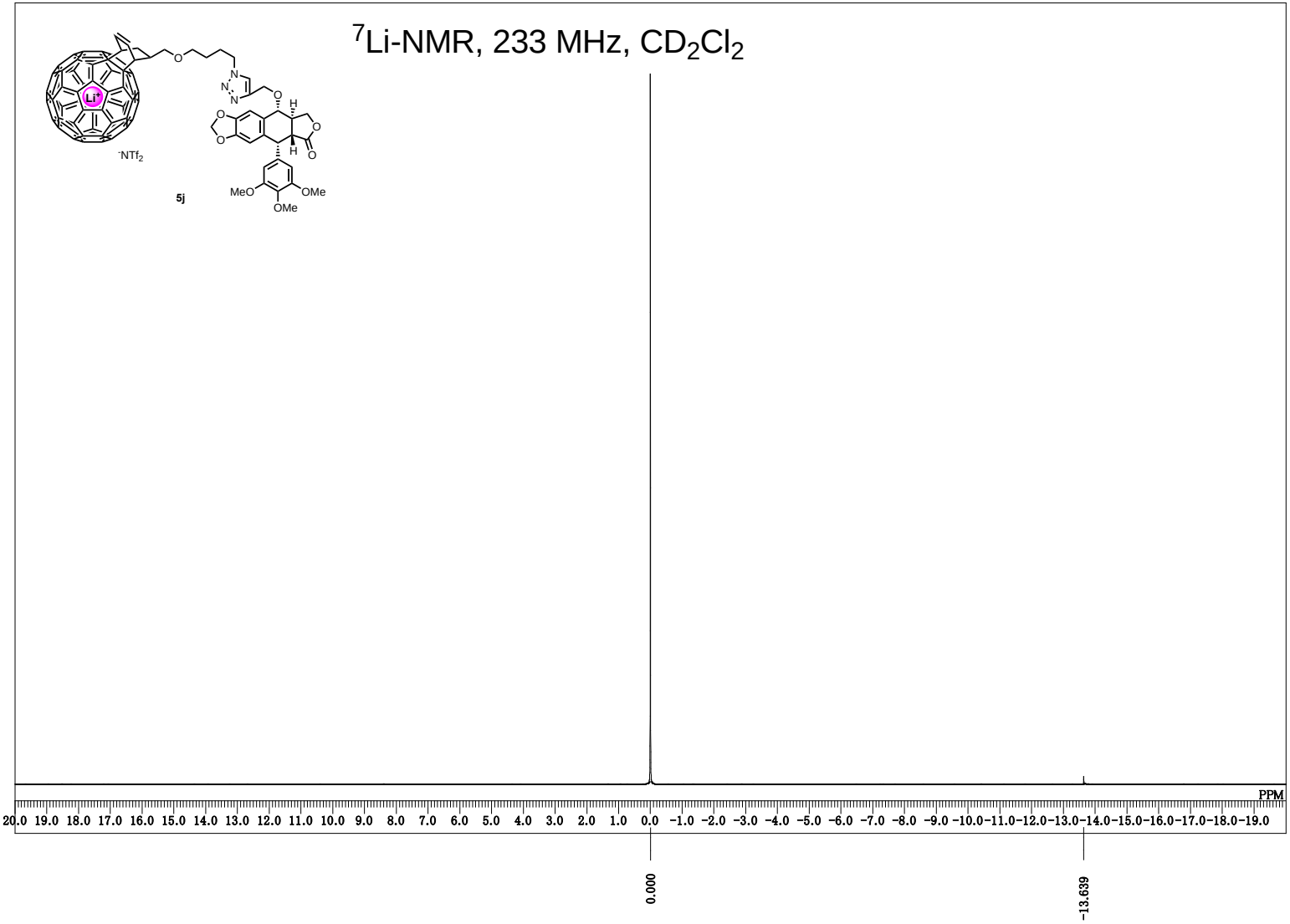
5i_Li


7Li-NMR, 233 MHz, CD2Cl2
Li+
-NTf2
5i
MeO
OMe
Me
Cl
PPM
20
10
0
-10
-20
0.000
-13.649

5j_H



5j_Li


7Li-NMR, 233 MHz, CD2Cl2
Li+
-NTf2
5j
MeO
OMe
OMe
PPM
20.0 19.0 18.0 17.0 16.0 15.0 14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0 -3.0 -4.0 -5.0 -6.0 -7.0 -8.0 -9.0 -10.0 -11.0 -12.0 -13.0 -14.0 -15.0 -16.0 -17.0 -18.0 -19.0
0.000
-13.639