Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Flow-IEG Enables Programmable Thermodynamic Properties in Sequence-Defined Unimolecular Macromolecules

Amanda C. Wicker,[a] Frank A. Leibfarth[b] and T. F. Jamison*[a]

[a] Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA. *Email: tfj@mit.edu
[b] University of North Carolina at Chapel Hill, Department of Chemistry, Chapel Hill, NC 27599, USA.

TABLE OF CONTENTS

Experimental procedures

Materials
See main text.

Sample preparation and setup
See main text.

Copper-catalyzed azide–alkyne cycloaddition optimization
The coupling partners were prepared and mixed in solution at a total concentration of 0.2 M in toluene and loaded into an 8 mL stainless-steel syringe. A mixture of $CuBr_2$, ligand, and solvent was prepared and loaded into an 8 mL stainless-steel syringe. The two reagent streams were allowed to mix in a T-mixer before continuing into a copper-metal tubing reactor. The residence time was varied by adjusting the flow rate. The system was allowed to equilibrate for 3 residence times to reach steady state before the product was collected for analysis. The results of the trials are shown in Table 1.

Ruthenium-catalyzed azide–alkyne cycloaddition optimization
The coupling partners were prepared and mixed in solution at a total concentration of 0.2 M in toluene. The Cp*RuCl(COD) catalyst was weighed out into a vial, capped, evacuated, and backfilled with argon two times before the introduction of toluene. All solvent and reagent solutions were degassed by sparging with argon for 20 min before being loaded into 8 mL stainless-steel syringes. The reagent streams were allowed to mix in a T-mixer before continuing into a PFA tubing reactor. The residence time was varied by adjusting the flow rate. The system was allowed to equilibrate for 3 residence times to reach steady state before the product was collected for analysis. The results of the trials are shown in Table 2.

General notes for running the Flow-IEG reactions
The substrates of interest, TBAF, and TBAA solutions were all pumped using Harvard PHD 2000 pumps equipped with 8 mL stainless-steel syringes at 50 μL/min. The deionized water for the separation was pumped at 300 μL/min using an M6 pump. The organic stream exiting the separator was recorded as flowing at 172 μL/min, and so the catalyst stream was also pumped at 172 μL/min, using an M6 pump. The catalyst loading is calculated from the concentration of the reagent stream post-separation in order to account for the concentrating effect of the separator. The system was allowed to equilibrate for 3 residence times to reach steady state before product was collected for analysis. Reactions generating alkyl ester tetramers were generally conducted at monomer concentrations of 0.15 M in chlorobenzene to maintain solubility in the flow system. For reactions involving the alkyl ester/oligo(ethylene glycol) series, a substrate concentration of 0.32 M in toluene was found to be necessary to ensure reactivity.

Example procedure for running the CuAAC Flow-IEG system
Two 0.32 M solutions of 3-(triisopropylsilyl)prop-2-yn-1-yl 11-bromoundecanoate were prepared by dissolving 1.47 g of 3-(triisopropylsilyl)prop-2-yn-1-yl 11-bromoundecanoate in 5 mL toluene per solution. A 0.35 M (1.1 eq) solution of TBAF was prepared by dissolving 0.55 g TBAF•$3H_2O$ in a 2:1 THF/toluene solution for a total volume of 5 mL. A 0.48 M (1.5 eq)

solution of TBAA was prepared by dissolving 0.68 g TBAA in THF at a total volume of 5 mL, then filtered to remove undissolved particles. A 5 mol% $CuBr_2$/15 mol% Me_6TREN solution was prepared by dissolving 42 mg of $CuBr_2$ and 129 mg of Me_6TREN in 20 mL ACN. The pumps were turned on and the system was allowed to equilibrate for 3 residence times to reach steady state. The product was collected for 2 h. The solvent was evaporated, and the product was loaded directly on a column and run at 10% EtOAc/Hex to remove byproducts, and then ramped to 40% EtOAc/Hex to yield the product as a waxy white solid (70% yield). A photograph of the setup can be seen in Figure 7, and the diagram of the system can be viewed in Scheme 1.

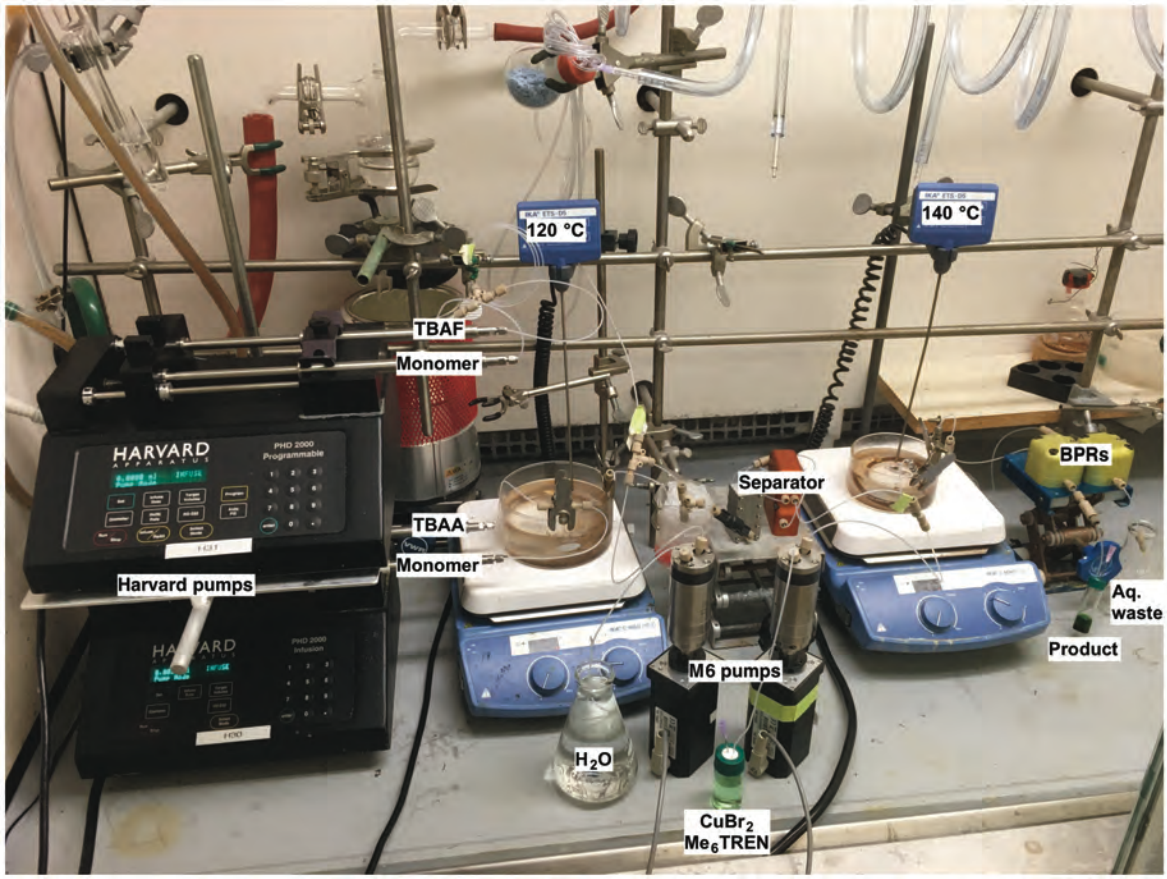


Figure S1. Photograph of CuAAC system with labeled components.

Example procedure for running the RuAAC Flow-IEG system

Two 0.15 M solutions of 3-(triisopropylsilyl)prop-2-yn-1-yl 11-bromoundecanoate were prepared by dissolving 0.69 g of 3-(triisopropylsilyl)prop-2-yn-1-yl 11-bromoundecanoate in 5 mL toluene for each. A 0.165 M (1.1 eq) solution of TBAF was prepared by dissolving 0.26 g TBAF•$3H_2O$ in a 2:1 THF/toluene solution for a total volume of 5 mL. A 0.225 M (1.5 eq) solution of TBAA was prepared by dissolving 0.32 g TBAA in THF at a total volume of 5 mL, then filtered to remove undissolved particles. A 5 mol% solution of Cp*RuCl(COD) was prepared as described above with 33 mg Cp*RuCl(COD) in 20 mL toluene. All reagent and solvent solutions were degassed for 20 min before use. The pumps were turned on, and the system was allowed to equilibrate for 3 residence times to reach steady state. The product was collected for 2 h. The solvent was evaporated, and the product was loaded directly on a column and run at 10% EtOAc/Hex to remove byproducts, and then ramped to 40% EtOAc/Hex to yield

the product as an amber viscous liquid (84% yield). A photograph of the setup can be seen in Figure 8, and a diagram of the system can be viewed in Scheme 1.

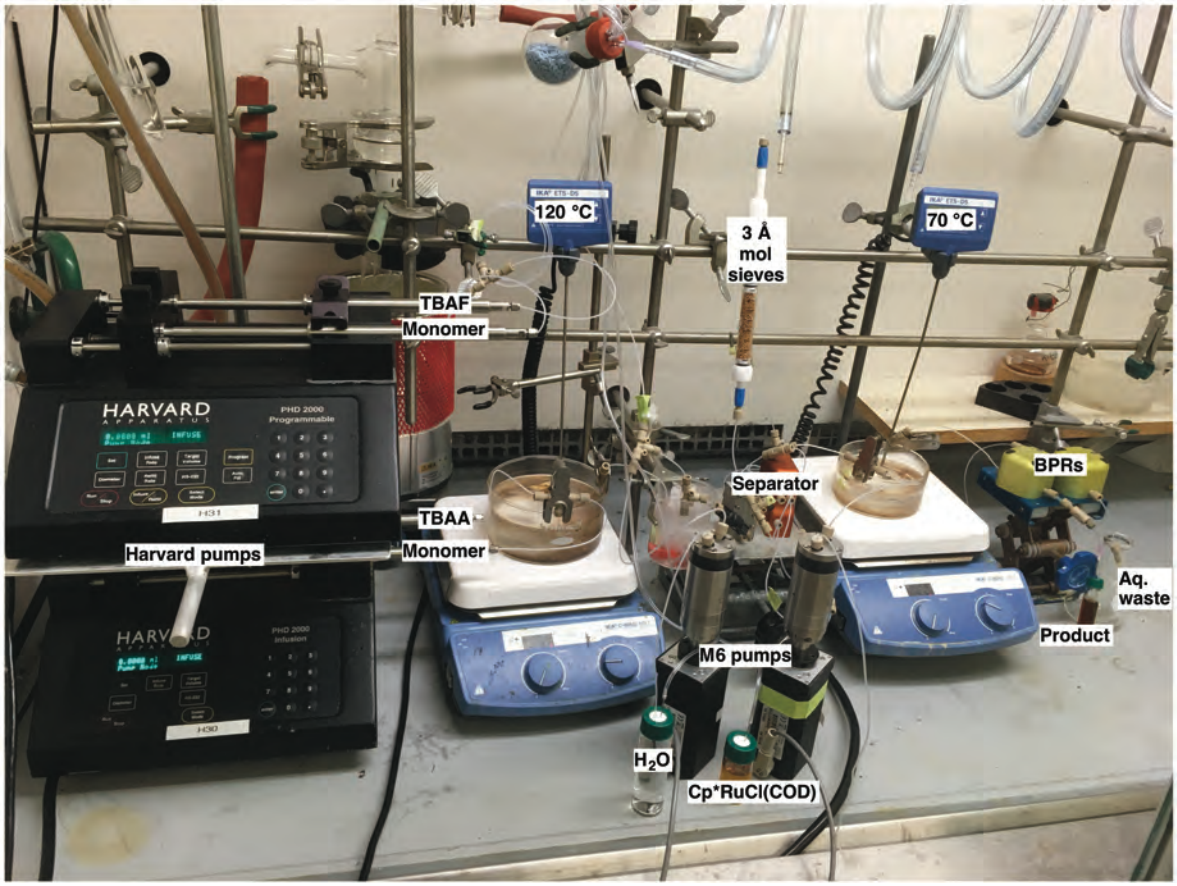
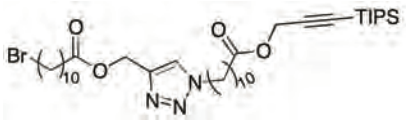


Figure S2. Photograph of the RuAAC system with labeled components.

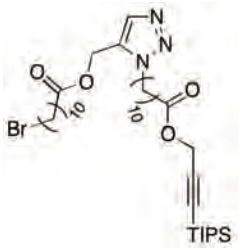
Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 or a JEOL 500 NMR spectrometer. Chemical shifts are reported in δ, parts per million (ppm) relative to the residual solvent peak of $CDCl_3$. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, m = multiplet), coupling constant (*J*) in Hertz (Hz), and integration. GPC was performed in THF on an HP/Agilent series 1100 GPC system and analyzed using a HP/Agilent refractive index detector. TGA was performed on a TA Instruments Discovery TGA. Samples were run in platinum TGA pans at a ramp rate of 10 °C/min from 50 °C to 600 °C. DSC was performed on a TA Instruments Discovery DSC. Samples were run in Tzero aluminum pans with hermetic lids. Data for the alkyl ester oligomers were taken from the third heating cycle of a run where the sample was cycled at a rate of 5 °C/min from –70 °C to 150 °C; data for the alkyl ester/oligo(ethylene glycol) oligomers were taken from the third heating cycle of a run where the sample was cycled at a rate of 5 °C/min from –70 °C to 50 °C. High-resolution mass spectrometry data were acquired in the Department of Chemistry Instrumentation Facility, Massachusetts Institute of Technology on a Bruker Daltonics APEXIV 4.7 Tesla FT-ICR Mass Spectrometer. Water content was calculated with a Mettler Toledo C20 Coulometric KF Titrator.



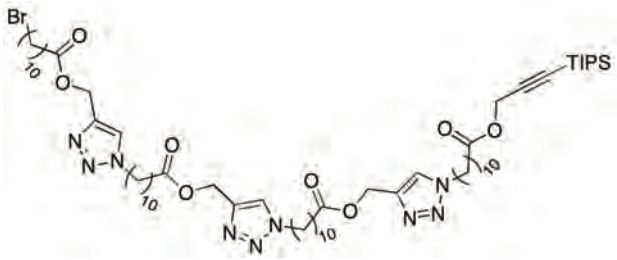
1,4 alkyl ester dimer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 5.21 (s, 2H), 4.70 (s, 2H), 4.33 (t, *J* = 7.4 Hz, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.37 – 2.28 (m, 4H), 1.93 – 1.80 (m, 4H), 1.65 – 1.58 (m, 4H), 1.44 – 1.37 (m, 2H), 1.34 – 1.22 (m, 22H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 173.0, 143.0, 123.6, 101.2, 88.1, 57.6, 52.7, 50.5, 34.2, 34.1, 32.8, 30.4, 29.41, 29.37, 29.2, 29.12, 29.07, 29.0, 28.8, 28.2, 26.5, 24.94, 24.88, 18.6, 11.2. GPC: T_{ret} = 27.4 min, *Đ* = 1.007. HR-MS (m/z) $[M + H]^+$ calcd for $C_{37}H_{66}BrN_3O_4Si$: 726.4082; found: 726.4055.



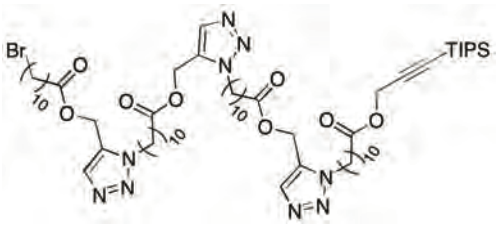
1,5 alkyl ester dimer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 5.16 (s, 2H), 4.70 (s, 2H), 4.33 (t, *J* = 7.4 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.36 – 2.29 (m, 4H), 1.93 – 1.80 (m, 4H), 1.64 – 1.60 (m, 4H), 1.44 – 1.37 (m, 2H), 1.34 – 1.24 (m, 22H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.00, 172.97, 134.8, 131.5, 101.2, 88.1, 53.4, 52.7, 48.5, 34.1, 34.0, 32.8, 30.3, 29.43, 29.40, 29.35, 29.3, 29.2, 29.14, 29.09, 28.8, 28.2, 26.7, 24.9, 24.8, 18.6, 11.1. GPC: T_{ret} = 27.5 min, *Đ* = 1.007. HR-MS (m/z) $[M + H]^+$ calcd for $C_{37}H_{66}BrN_3O_4Si$: 726.4082; found: 726.4053.



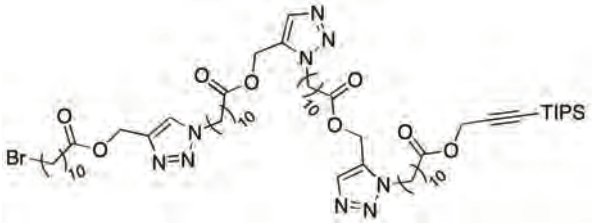
1,4-1,4-1,4 alkyl ester tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 3H), 5.21 (s, 6H), 4.70 (s, 2H), 4.33 (t, *J* = 7.3 Hz, 6H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.36 – 2.28 (m, 8H), 1.92 – 1.81 (m, 8H), 1.65 – 1.58 (m, 8H), 1.44 – 1.37 (m, 2H), 1.32 – 1.23 (m, 46H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.73, 173.70, 172.9, 142.89, 142.86, 123.6, 101.2, 88.1, 57.5, 52.6, 50.4, 34.13, 34.07, 32.8, 30.3, 29.4, 29.3, 29.2, 29.14, 29.06, 29.04, 28.98, 28.9, 28.7, 28.2, 26.49, 26.46, 24.9, 24.8, 18.5, 11.1. GPC: T_{ret} = 26.4 min, *Đ* = 1.011. HR-MS (m/z) $[M + H]^+$ calcd for $C_{65}H_{112}BrN_9O_8Si$: 1256.7673; found: 1256.7712.



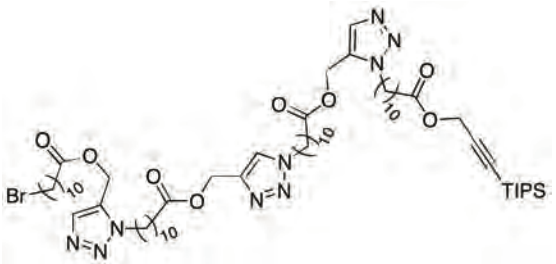
1,5-1,5-1,5 alkyl ester tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 3H), 5.16 (s, 6H), 4.70 (s, 2H), 4.33 (t, *J* = 7.4 Hz, 6H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.36 – 2.28 (m, 8H), 1.92 – 1.79 (m, 8H), 1.62 – 1.56 (m, 8H), 1.44 – 1.36 (m, 2H), 1.34 – 1.22 (m, 46H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 134.8, 131.5, 101.2, 88.1, 53.4, 52.6, 48.4, 34.11, 34.08, 34.0, 32.8, 30.31, 30.28, 29.39, 29.36, 29.3, 29.24, 29.20, 29.10, 29.06, 28.7, 28.2, 26.62, 26.59, 24.9, 24.8, 18.6, 11.1. GPC: T_{ret} = 26.5 min, *Đ* = 1.009. HR-MS (m/z) $[M + H]^+$ calcd for $C_{65}H_{112}BrN_9O_8Si$: 1256.7673; found: 1256.7705.



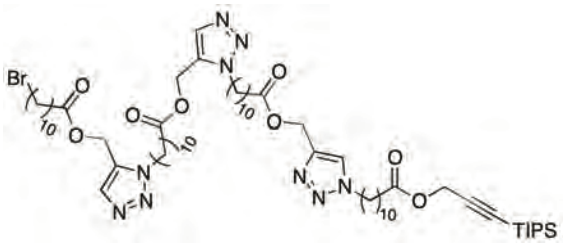
1,4-1,5-1,5 alkyl ester tetramer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.57 (s, 1H), 5.23 – 5.14 (m, 6H), 4.70 (s, 2H), 4.34 (t, *J* = 7.6 Hz, 6H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.37 – 2.28 (m, 8H), 1.95 – 1.80 (m, 8H), 1.67 – 1.57 (m, 8H), 1.45 – 1.16 (m, 48H), 1.07 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 172.9, 142.8, 134.7, 131.4, 123.5, 101.1, 88.0, 57.5, 53.4, 52.5, 50.3, 48.4, 34.1, 34.04, 33.99, 33.9, 32.8, 30.2, 29.3, 29.24, 29.21, 29.15, 29.1, 29.01, 28.96, 28.9, 28.7, 28.1, 26.53, 26.50, 26.4, 24.82, 24.76, 24.7, 18.5, 11.0. GPC: T_{ret} = 26.5 min, *Đ* = 1.009. HR-MS (m/z) $[M + H]^+$ calcd for $C_{65}H_{112}BrN_9O_8Si$: 1256.7673; found: 1256.7700.



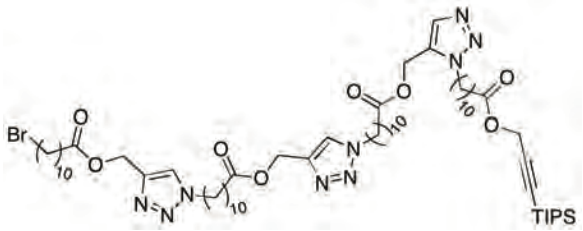
1,5-1,4-1,5 alkyl ester tetramer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.58 (s, 1H), 5.22 – 5.14 (m, 6H), 4.70 (s, 2H), 4.33 (t, *J* = 7.6 Hz, 6H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.36 – 2.28 (m, 8H), 1.95 – 1.80 (m, 8H), 1.65 – 1.58 (m, 8H), 1.45 – 1.20 (m, 48H), 1.07 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 172.97, 172.95, 142.9, 134.8, 131.5, 123.6, 101.2, 88.1, 57.5, 53.4, 52.6, 50.4, 48.5, 34.14, 34.10, 34.07, 34.0, 32.8, 30.3, 29.38, 29.35, 29.3, 29.23, 29.18, 29.1, 29.04, 28.96, 28.7, 28.1, 26.6, 26.5, 24.9, 24.82, 24.78, 18.6, 11.1. GPC: T_{ret} = 26.5 min, *Đ* = 1.010. HR-MS (m/z) $[M + H]^+$ calcd for $C_{65}H_{112}BrN_9O_8Si$: 1256.7673; found: 1256.7637.



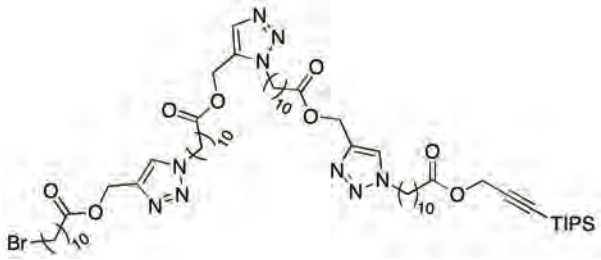
1,5-1,5-1,4 alkyl ester tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.57 (s, 1H), 5.23 – 5.13 (m, 6H), 4.70 (s, 2H), 4.37 – 4.30 (m, 6H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.37 – 2.27 (m, 8H), 1.93 – 1.80 (m, 8H), 1.66 – 1.61 (m, 8H), 1.44 – 1.21 (m, 48H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 173.02, 172.99, 142.9, 134.8, 131.5, 123.6, 101.2, 88.2, 57.6, 53.5, 52.7, 50.5, 48.5, 34.2, 34.1, 34.0, 32.8, 30.33, 30.30, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.2, 26.6, 26.5, 24.93, 24.86, 24.8, 18.6, 11.1. GPC: T_{ret} = 26.5 min, *Đ* = 1.012. HR-MS (m/z) $[M + H]^+$ calcd for $C_{65}H_{112}BrN_9O_8Si$: 1256.7673; found: 1256.7691.



1,4-1,4-1,5 alkyl ester tetramer

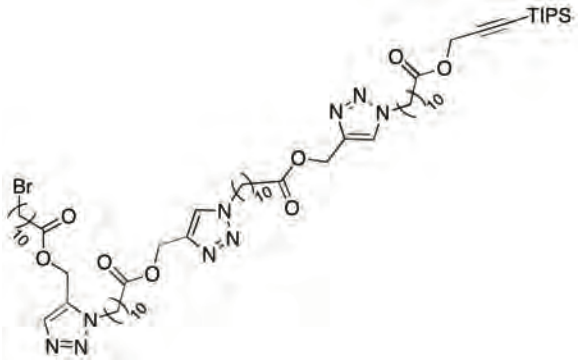
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.57 (s, 2H), 5.23 – 5.14 (m, 6H), 4.70 (s, 2H), 4.33 (t, *J* = 7.4 Hz, 6H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.37 – 2.27 (m, 8H), 1.94 – 1.80 (m, 8H), 1.66 – 1.56 (m, 8H), 1.45 – 1.20 (m, 48H), 1.07 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.68, 173.66, 172.89, 172.87, 142.85, 142.83, 134.7, 131.4, 123.6, 101.1, 88.0, 57.5, 53.4, 52.6, 50.4, 48.4, 34.10, 34.09, 34.06, 34.0, 33.9, 32.8, 30.2, 29.7, 29.4, 29.32, 29.28, 29.27, 29.25, 29.24, 29.19, 29.15, 29.12, 29.05, 29.03, 28.99, 28.9, 28.7, 28.1, 26.6, 26.4, 24.9, 24.80, 24.78, 24.7, 18.5, 11.1. GPC: T_{ret} = 26.5 min, *Đ* = 1.013. HR-MS (m/z) $[M + H]^+$ calcd for $C_{65}H_{112}BrN_9O_8Si$: 1256.7673; found: 1256.7679.



1,4-1,5-1,4 alkyl ester tetramer

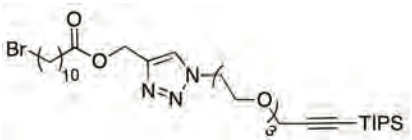
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.57 (d, *J* = 1.8 Hz, 2H), 5.21 (s, 4H), 5.16 (s, 2H), 4.70 (s, 2H), 4.38 – 4.29 (m, 6H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.36 – 2.28 (m, 8H), 1.94 – 1.80 (m, 8H), 1.66 – 1.57 (m, 8H), 1.45 –1.22 (m, 48H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 173.6, 172.9, 142.84, 142.80, 134.7, 131.4, 123.5, 101.1, 88.0, 57.5, 53.4, 52.6, 50.4, 48.4,

34.1, 34.0, 33.9, 32.8, 30.2, 29.3, 29.2, 29.1, 29.01, 28.97, 28.93, 28.90, 28.7, 28.1, 26.5, 26.44, 26.41, 24.85, 24.78, 24.7, 18.5, 11.0. GPC: T_{ret} = 26.5 min, $Đ$ = 1.007. HR-MS (m/z) $[M + H]^+$ calcd for $C_{65}H_{112}BrN_9O_8Si$: 1256.7673; found: 1256.7662.



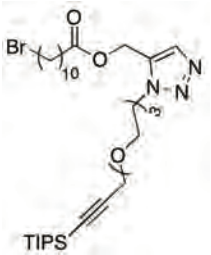
1,5-1,4-1,4 alkyl ester tetramer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.57 (s, 2H), 5.22 – 5.15 (m, 6H), 4.70 (s, 2H), 4.33 (t, *J* = 7.3 Hz, 6H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.36 – 2.27 (m, 8H), 1.94 – 1.80 (m, 8H), 1.65 – 1.57 (m, 8H), 1.45 – 1.19 (m, 48H), 1.07 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 172.93, 172.90, 142.9, 134.7, 131.5, 123.5, 101.2, 88.1, 57.6, 53.4, 52.6, 50.4, 48.5, 34.13, 34.07, 34.05, 34.0, 32.8, 30.3, 29.4, 29.33, 29.29, 29.27, 29.20, 29.17, 29.15, 29.05, 29.02, 28.98, 28.95, 28.7, 28.2, 26.6, 26.49, 26.47, 24.9, 24.82, 24.79, 18.6, 11.1. GPC: T_{ret} = 26.5 min, $Đ$ = 1.011. HR-MS (m/z) $[M + H]^+$ calcd for $C_{65}H_{112}BrN_9O_8Si$: 1256.7673; found: 1256.7699.



1,4 alkyl ester/oligo(ethylene glycol) dimer

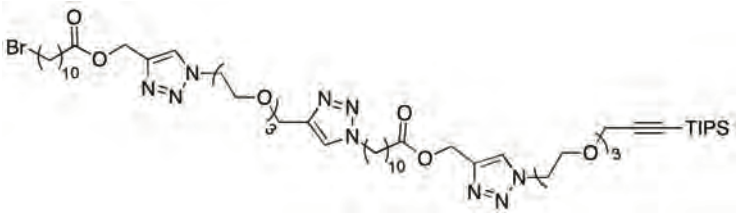
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 5.21 (s, 2H), 4.54 (t, *J* = 5.1 Hz, 2H), 4.24 (s, 2H), 3.87 (t, *J* = 5.0 Hz, 2H), 3.73 – 3.70 (m, 2H), 3.67 – 3.64 (m, 2H), 3.64 – 3.60 (s, 4H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.88 – 1.81 (m, 2H), 1.64 – 1.58 (m, 2H), 1.44 – 1.37 (m, 2H), 1.33 – 1.23 (m, 10H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 142.8, 125.0, 103.2, 87.9, 70.65, 70.58, 70.55, 69.5, 68.8, 59.3, 57.5, 50.4, 34.23, 34.18, 32.9, 29.5, 29.4, 29.3, 29.2, 28.8, 28.3, 24.9, 18.7, 11.2. GPC: T_{ret} = 27.6 min, $Đ$ = 1.004. HR-MS (m/z) $[M + H]^+$ calcd for $C_{32}H_{58}BrN_3O_5Si$: 674.3403; found: 674.3407.



1,5 alkyl ester/oligo(ethylene glycol) dimer

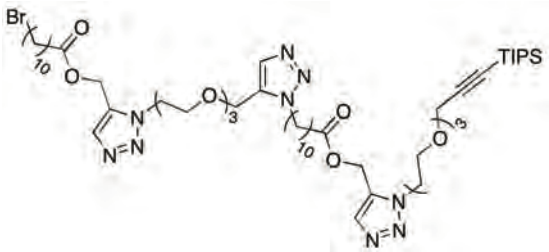
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 5.26 (s, 2H), 4.59 (t, *J* = 5.1 Hz, 2H), 4.23 (s, 2H), 3.87 (t, *J* = 5.2 Hz, 2H), 3.70 – 3.66 (m, 2H), 3.62 – 3.58 (m, 2H), 3.55 (s, 4H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.89 – 1.80 (m, 2H), 1.62 – 1.57 (m, 2H), 1.44 – 1.37 (m, 2H),

1.31 – 1.24 (m, 10H), 1.07 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 134.2, 133.6, 103.2, 87.8, 70.7, 70.5, 70.2, 68.7, 59.2, 54.1, 48.8, 34.2, 34.1, 32.9, 29.45, 29.40, 29.3, 29.1, 28.8, 28.2, 24.9, 18.7, 11.2. GPC: T_{ret} = 27.7 min, $Đ$ = 1.007. HR-MS (m/z) $[M + H]^+$ calcd for $C_{32}H_{58}BrN_3O_5Si$: 674.3403; found: 674.3397.



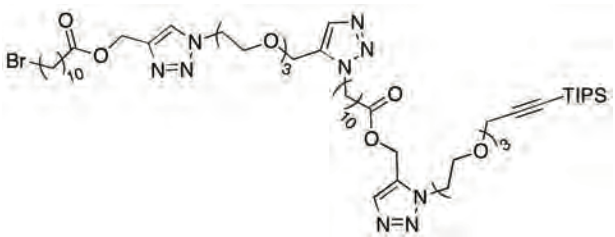
1,4-1,4-1,4 alkyl ester/oligo(ethylene glycol) tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.53 (s, 1H), 5.20 (d, J = 3.0 Hz, 4H), 4.67 (s, 2H), 4.56 – 4.50 (m, 4H), 4.33 (t, J = 7.4 Hz, 2H), 4.23 (s, 2H), 3.87 (t, J = 5.0 Hz, 4H), 3.73 – 3.59 (m, 16H), 3.40 (t, J = 6.9 Hz, 2H), 2.31 (t, J = 7.5 Hz, 4H), 1.92 – 1.80 (m, 4H), 1.64 – 1.59 (m, 4H), 1.44 – 1.37 (m, 2H), 1.33 – 1.22 (m, 22H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 173.6, 144.9, 142.8, 125.0, 124.9, 122.5, 103.2, 87.8, 70.58, 70.55, 70.53, 70.49, 69.7, 69.5, 68.7, 64.6, 59.2, 57.5, 50.4, 50.3, 34.2, 32.9, 30.4, 29.40, 29.35, 29.2, 29.1, 29.0, 28.8, 28.2, 26.6, 24.9, 18.6, 11.2. T_{ret} = 26.6 min, $Đ$ = 1.009. HR-MS (m/z) $[M + Na]^+$ calcd for $C_{55}H_{96}BrN_9O_{10}Si$: 1174.6135; found: 1174.6094.



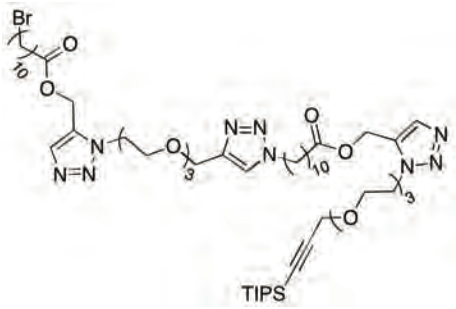
1,5-1,5-1,5 alkyl ester/oligo(ethylene glycol) tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 4.0 Hz, 2H), 7.61 (s, 1H), 5.26 (s, 2H), 5.23 (s, 2H), 4.63 – 4.56 (m, 6H), 4.33 (t, J = 7.4 Hz, 2H), 4.22 (s, 2H), 3.87 (t, J = 5.2 Hz, 4H), 3.71 – 3.66 (m, 2H), 3.62 – 3.48 (m, 14H), 3.40 (t, J = 6.8 Hz, 2H), 2.34 – 2.28 (m, 4H), 1.92 – 1.80 (m, 4H), 1.62 – 1.57 (m, 4H), 1.44 – 1.37 (m, 2H), 1.32 – 1.22 (m, 22H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.08, 173.05, 134.3, 134.1, 133.5, 133.3, 132.8, 103.2, 87.7, 70.60, 70.57, 70.5, 70.4, 70.11, 70.05, 69.5, 68.7, 61.1, 59.2, 54.00, 53.96, 48.7, 48.6, 48.5, 34.1, 34.0, 32.8, 30.1, 29.4, 29.3, 29.2, 29.11, 29.06, 28.7, 28.2, 26.6, 24.8, 18.6, 11.2. GPC: T_{ret} = 26.8 min, $Đ$ = 1.016. HR-MS (m/z) $[M + H]^+$ calcd for $C_{55}H_{96}BrN_9O_{10}Si$: 1152.6316; found: 1152.6324.



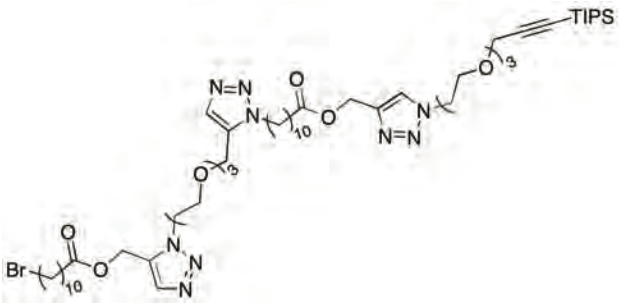
1,4-1,5-1,5 alkyl ester/oligo(ethylene glycol) tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.66 (s, 1H), 7.62 (s, 1H), 5.26 (s, 2H), 5.20 (s, 2H), 4.64 – 4.56 (m, 4H), 4.53 (t, *J* = 5.0 Hz, 2H), 4.34 (t, *J* = 7.3 Hz, 2H), 4.23 (s, 2H), 3.87 (q, *J* = 5.4 Hz, 4H), 3.70 – 3.65 (m, 2H), 3.61 – 3.53 (m, 14H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 4H), 1.93 – 1.80 (m, 4H), 1.63 – 1.58 (m, 4H), 1.43 – 1.37 (m, 2H), 1.34 – 1.22 (m, 22H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 173.0, 142.8, 134.3, 134.2, 133.4, 132.7, 124.8, 103.2, 87.7, 70.6, 70.54, 70.47, 70.4, 70.1, 69.5, 69.4, 68.6, 61.1, 59.2, 57.4, 54.0, 50.3, 48.7, 48.5, 34.2, 34.0, 32.8, 30.1, 29.4, 29.3, 29.2, 29.10, 29.05, 28.7, 28.2, 26.6, 24.85, 24.79, 18.6, 11.2. GPC: T_{ret} = 26.7 min, *Đ* = 1.015. HR-MS (m/z) $[M + H]^+$ calcd for $C_{55}H_{96}BrN_9O_{10}Si$: 1152.6316; found: 1152.6321.



1,5-1,4-1,5 alkyl ester/oligo(ethylene glycol) tetramer

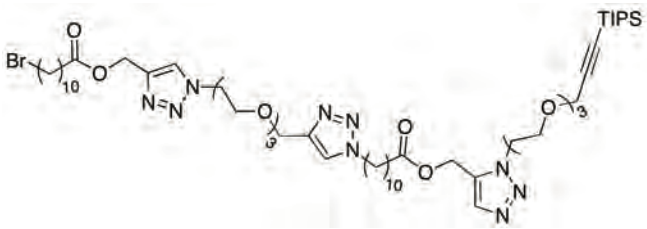
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.3 Hz, 2H), 7.54 (s, 1H), 5.26 (d, *J* = 2.9 Hz, 4H), 4.67 (s, 2H), 4.61 – 4.57 (m, 4H), 4.33 (t, *J* = 7.3 Hz, 2H), 4.23 (s, 2H), 3.87 (t, *J* = 5.1 Hz, 4H), 3.69 – 3.64 (m, 4H), 3.61 – 3.52 (m, 12H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 4H), 1.93 – 1.80 (m, 4H), 1.62 – 1.57 (m, 4H), 1.43 – 1.38 (m, 2H), 1.34 – 1.23 (m, 22H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.01, 172.98, 144.9, 134.2, 133.41, 133.37, 122.4, 103.2, 87.7, 70.60, 70.58, 70.45, 70.42, 70.36, 70.3, 70.1, 69.6, 68.6, 64.6, 59.1, 54.0, 50.3, 48.6, 34.1, 33.9, 32.8, 30.3, 29.32, 29.26, 29.1, 29.00, 28.95, 28.7, 28.1, 26.5, 24.8, 18.6, 11.1. GPC: T_{ret} = 26.7 min, *Đ* = 1.015. HR-MS (m/z) $[M + H]^+$ calcd for $C_{55}H_{96}BrN_9O_{10}Si$: 1152.6316; found: 1152.6357.



1,5-1,5-1,4 alkyl ester/oligo(ethylene glycol) tetramer

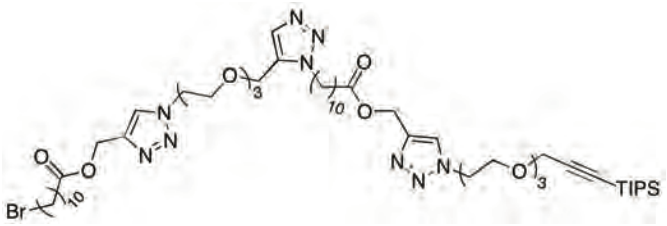
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.65 (s, 1H), 7.61 (s, 1H), 5.23 (s, 2H), 5.20 (s, 2H), 4.61 (s, 2H), 4.58 (t, *J* = 5.1 Hz, 2H), 4.54 (t, *J* = 5.1 Hz, 2H), 4.34 (t, *J* = 7.4 Hz, 2H), 4.24 (s, 2H), 3.89 – 3.85 (m, 4H), 3.74 – 3.69 (m, 2H), 3.68 – 3.64 (m, 2H), 3.62 (s, 4H), 3.56 – 3.49 (m, 8H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 4H), 1.92 – 1.80 (m, 4H), 1.64 – 1.57 (m, 4H), 1.44 – 1.37 (m, 2H), 1.34 – 1.21 (m, 22H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 173.0, 142.7, 134.3, 134.1, 133.2, 132.7, 124.8, 103.1, 87.7, 70.52, 70.45, 70.41, 70.35, 70.0, 69.5, 69.4, 68.6, 61.0, 59.1, 57.5, 53.9, 50.3, 48.6, 48.4, 34.1, 33.9, 32.8, 30.0, 29.4, 29.31, 29.27,

29.2, 29.14, 29.07, 29.0, 28.7, 28.1, 26.6, 24.80, 24.75, 18.6, 11.1. GPC: T_{ret} = 26.8 min, $Đ$ = 1.015. HR-MS (m/z) $[M + H]^+$ calcd for $C_{55}H_{96}BrN_9O_{10}Si$: 1152.6316; found: 1152.6340.



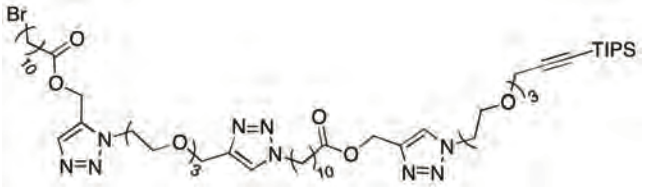
1,4-1,4-1,5 alkyl ester/oligo(ethylene glycol) tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.66 (s, 1H), 7.53 (s, 1H), 5.26 (s, 2H), 5.19 (s, 2H), 4.67 (s, 2H), 4.59 (t, J = 5.1 Hz, 2H), 4.53 (t, J = 5.0 Hz, 2H), 4.33 (t, J = 7.4 Hz, 2H), 4.22 (s, 2H), 3.87 (q, J = 4.7 Hz, 4H), 3.71 – 3.51 (m, 16H), 3.40 (t, J = 6.8 Hz, 2H), 2.31 (t, J = 7.5 Hz, 4H), 1.92 – 1.79 (m, 4H), 1.61 – 1.54 (m, 4H), 1.44 – 1.21 (m, 24H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 173.0, 144.8, 142.7, 134.3, 133.4, 124.9, 122.4, 103.1, 87.7, 70.6, 70.50, 70.46, 70.3, 70.0, 69.6, 69.4, 68.60, 64.59, 59.1, 57.4, 54.0, 50.3, 50.2, 48.6, 34.1, 33.9, 32.8, 30.3, 29.31, 29.27, 29.24, 29.16, 29.1, 29.04, 28.98, 28.9, 28.7, 28.1, 26.5, 24.8, 24.7, 18.6, 11.1. GPC: T_{ret} = 26.7 min, $Đ$ = 1.010. HR-MS (m/z) $[M + H]^+$ calcd for $C_{55}H_{96}BrN_9O_{10}Si$: 1152.6316; found: 1152.6314.



1,4-1,5-1,4 alkyl ester/oligo(ethylene glycol) tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.74 (s, 1H), 7.62 (s, 1H), 5.20 (d, J = 2.2 Hz, 4H), 4.63 (s, 2H), 4.55 – 4.51 (m, 4H), 4.34 (t, J = 7.4 Hz, 2H), 4.23 (s, 2H), 3.89 – 3.84 (m, 4H), 3.73 – 3.69 (m, 2H), 3.68 – 3.64 (m, 2H), 3.63 – 3.56 (m, 12H), 3.40 (t, J = 6.7 Hz, 2H), 2.31 (t, J = 7.6 Hz, 4H), 1.93 – 1.80 (m, 4H), 1.63 – 1.58 (m, 4H), 1.44 – 1.37 (m, 2H), 1.34 – 1.21 (m, 22H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 173.5, 142.8, 142.7, 134.1, 132.7, 124.84, 124.80, 103.1, 87.7, 70.5, 70.43, 70.41, 69.5, 69.4, 68.6, 61.0, 59.1, 57.45, 57.40, 50.3, 50.2, 48.4, 34.1, 32.8, 30.0, 29.34, 29.32, 29.28, 29.2, 29.0, 28.7, 28.1, 26.6, 24.8, 18.6, 11.1. GPC: T_{ret} = 26.7 min, $Đ$ = 1.013. HR-MS (m/z) $[M + H]^+$ calcd for $C_{55}H_{96}BrN_9O_{10}Si$: 1152.6316; found: 1152.6352.



1,5-1,4-1,4 alkyl ester/oligo(ethylene glycol) tetramer

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.65 (s, 1H), 7.54 (s, 1H), 5.25 (s, 2H), 5.20 (s, 2H), 4.67 (s, 2H), 4.59 (t, J = 5.1 Hz, 2H), 4.54 (t, J = 5.0 Hz, 2H), 4.33 (t, J = 7.4 Hz, 2H), 4.24 (s, 2H), 3.90 – 3.84 (m, 4H), 3.74 – 3.69 (m, 2H), 3.68 – 3.52 (m, 14H), 3.40 (t, J = 6.8 Hz, 2H),

2.31 (t, J = 7.5 Hz, 4H), 1.92 – 1.81 (m, 4H), 1.64 – 1.59 (m, 4H), 1.44 – 1.21 (m, 24H), 1.06 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 173.1, 145.0, 142.8, 134.4, 133.4, 124.9, 122.4, 103.2, 87.8, 70.65, 70.58, 70.52, 70.48, 70.1, 69.7, 69.5, 68.7, 64.7, 59.2, 57.5, 54.0, 50.4, 50.3, 48.7, 34.2, 34.0, 32.8, 30.4, 29.4, 29.3, 29.2, 29.12, 29.08, 29.0, 28.8, 28.2, 26.6, 24.9, 24.8, 18.6, 11.2. GPC: T_{ret} = 26.7 min, $Đ$ = 1.010. HR-MS (m/z) $[M + Na]^+$ calcd for $C_{55}H_{96}BrN_9O_{10}Si$: 1174.6135; found: 1174.6125.

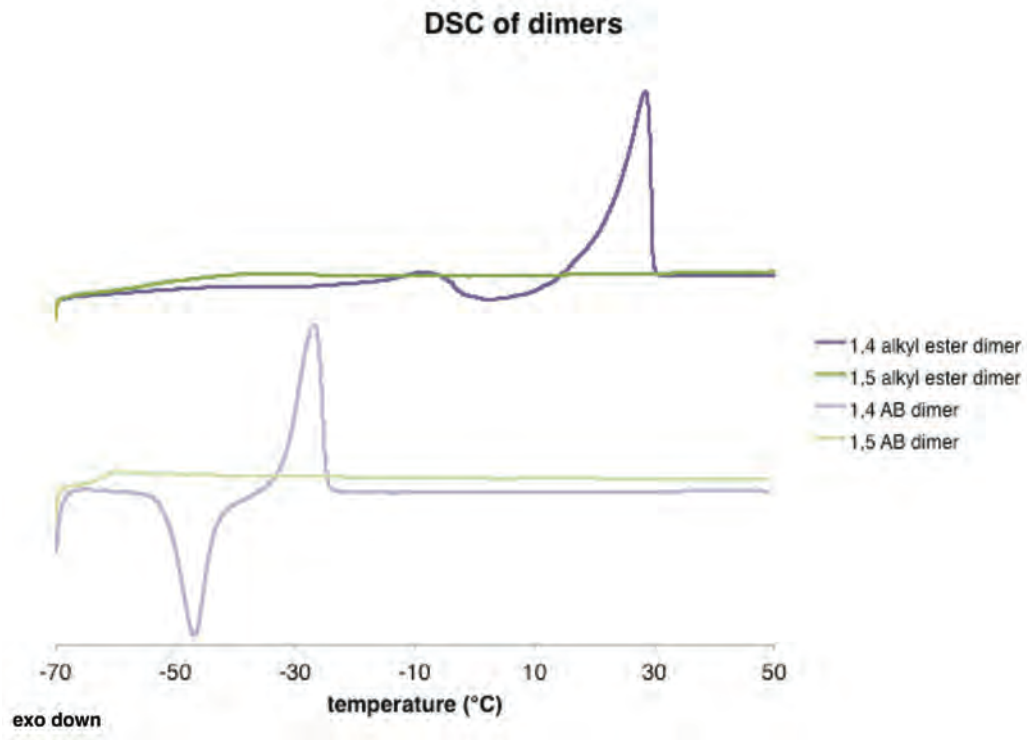


Figure S3. DSC traces of the third heating cycle of alkyl ester and alternating dimers.

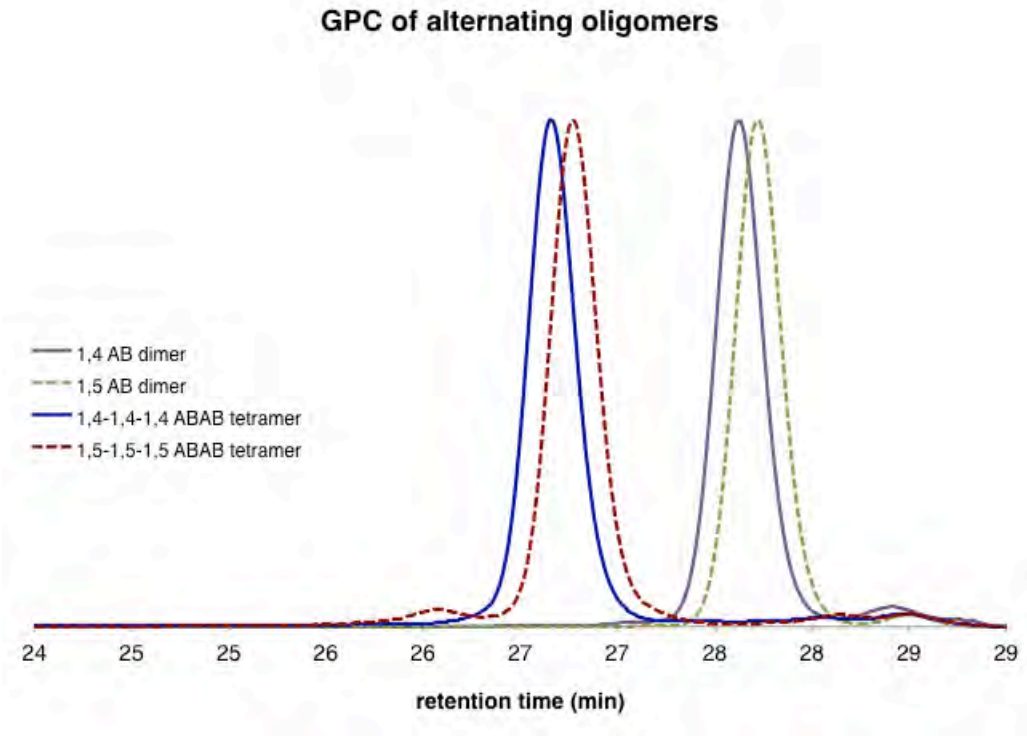


Figure S4. Overlaid GPC traces of 1,4 and 1,5 alternating oligomers.

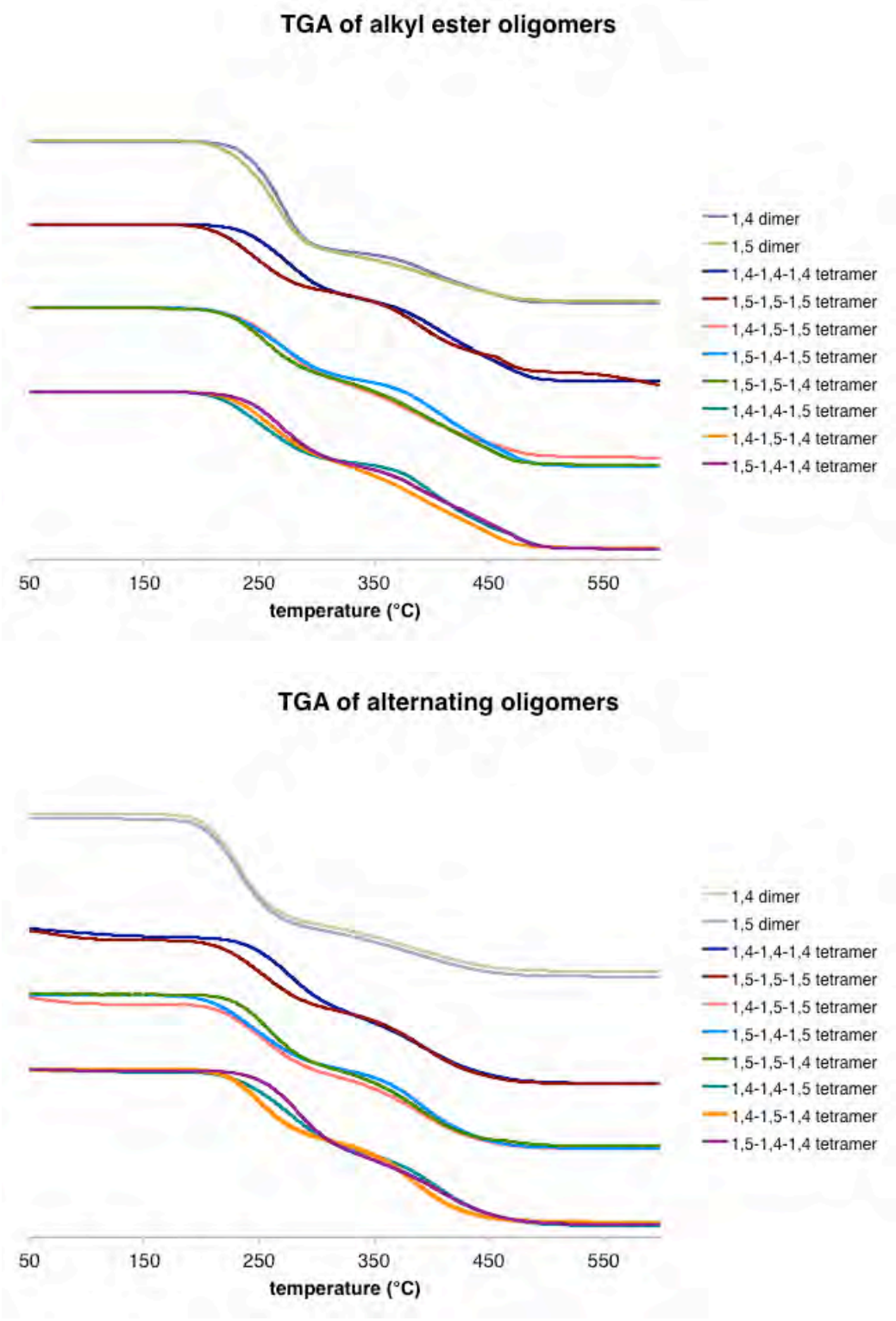
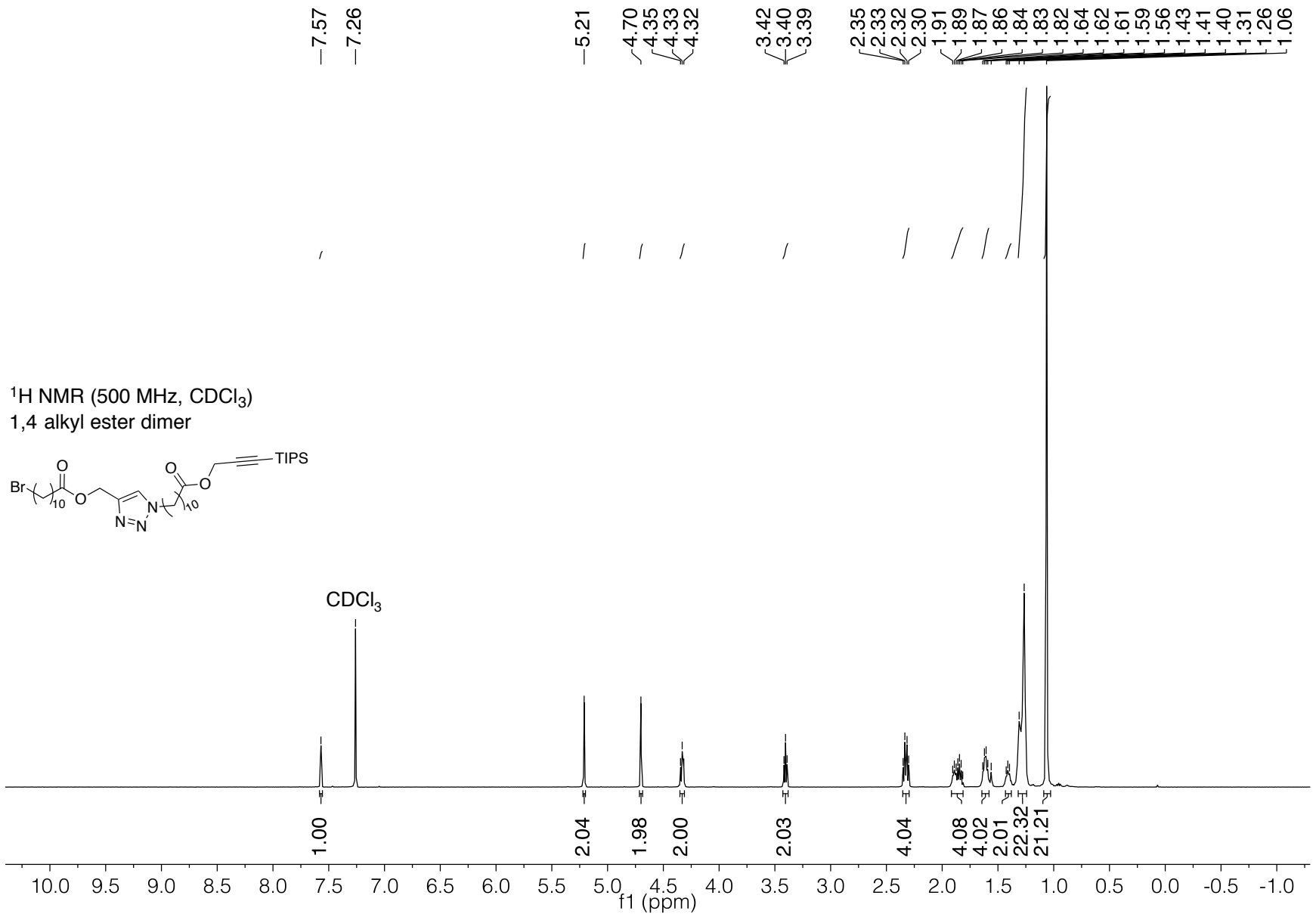
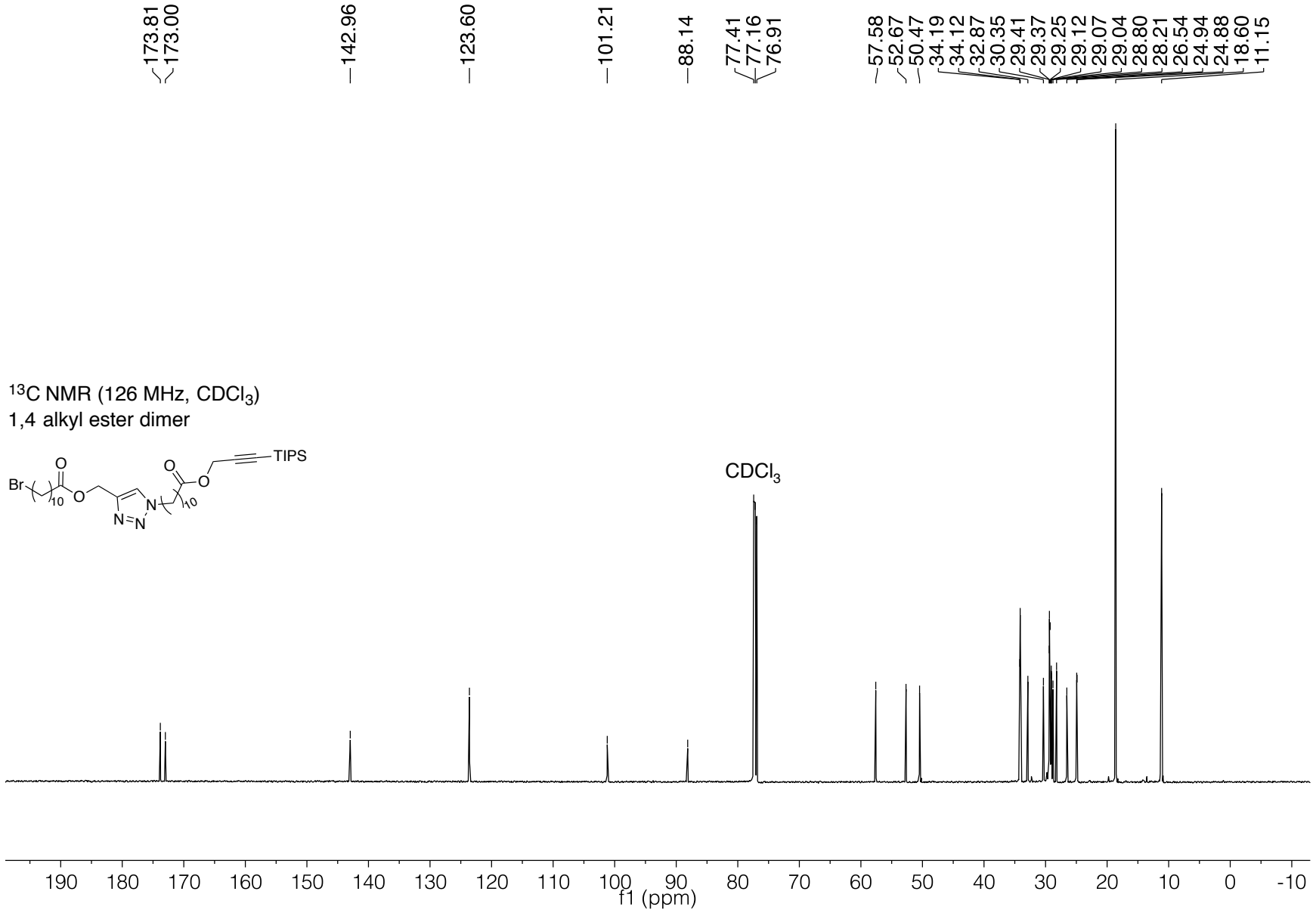
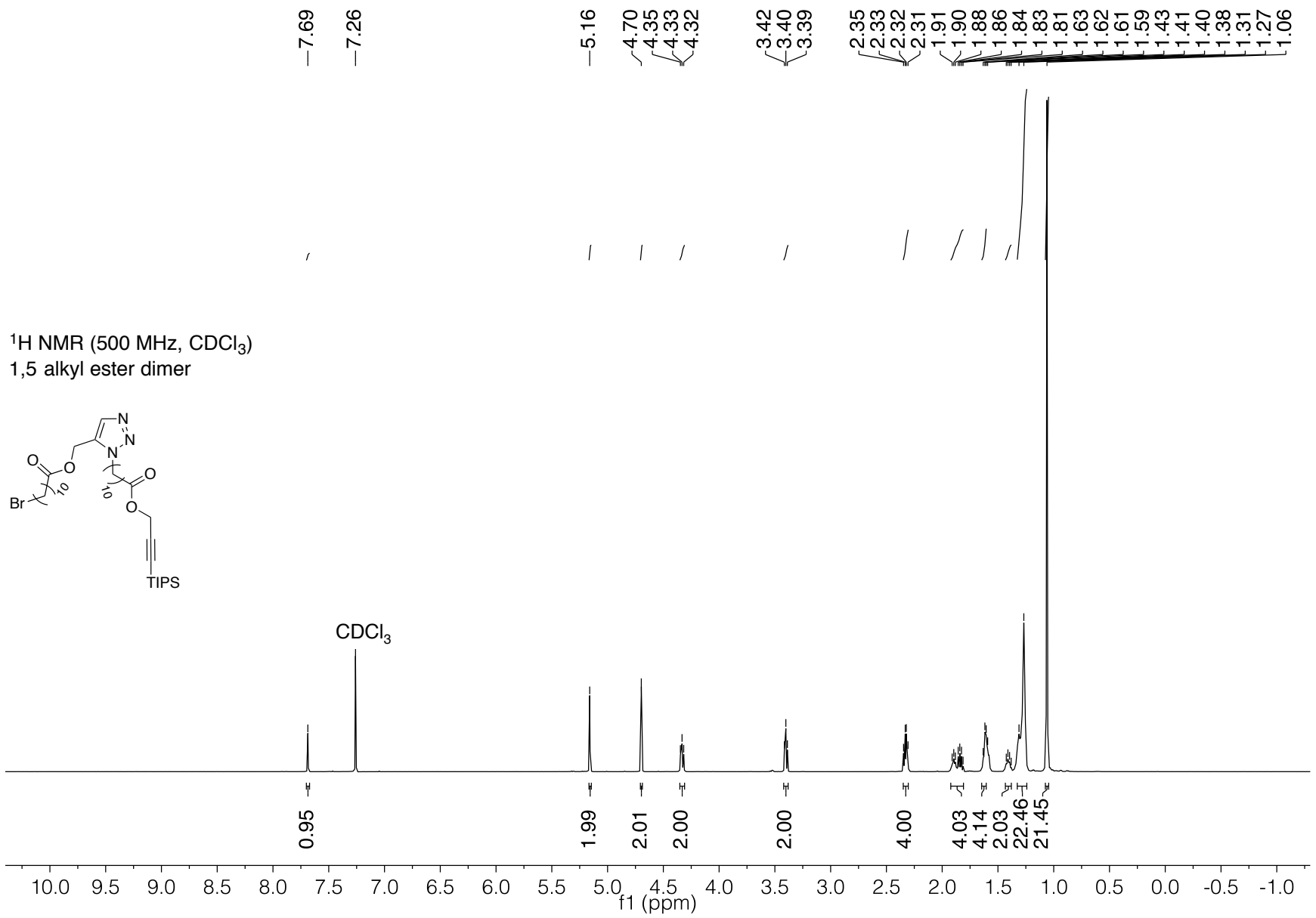
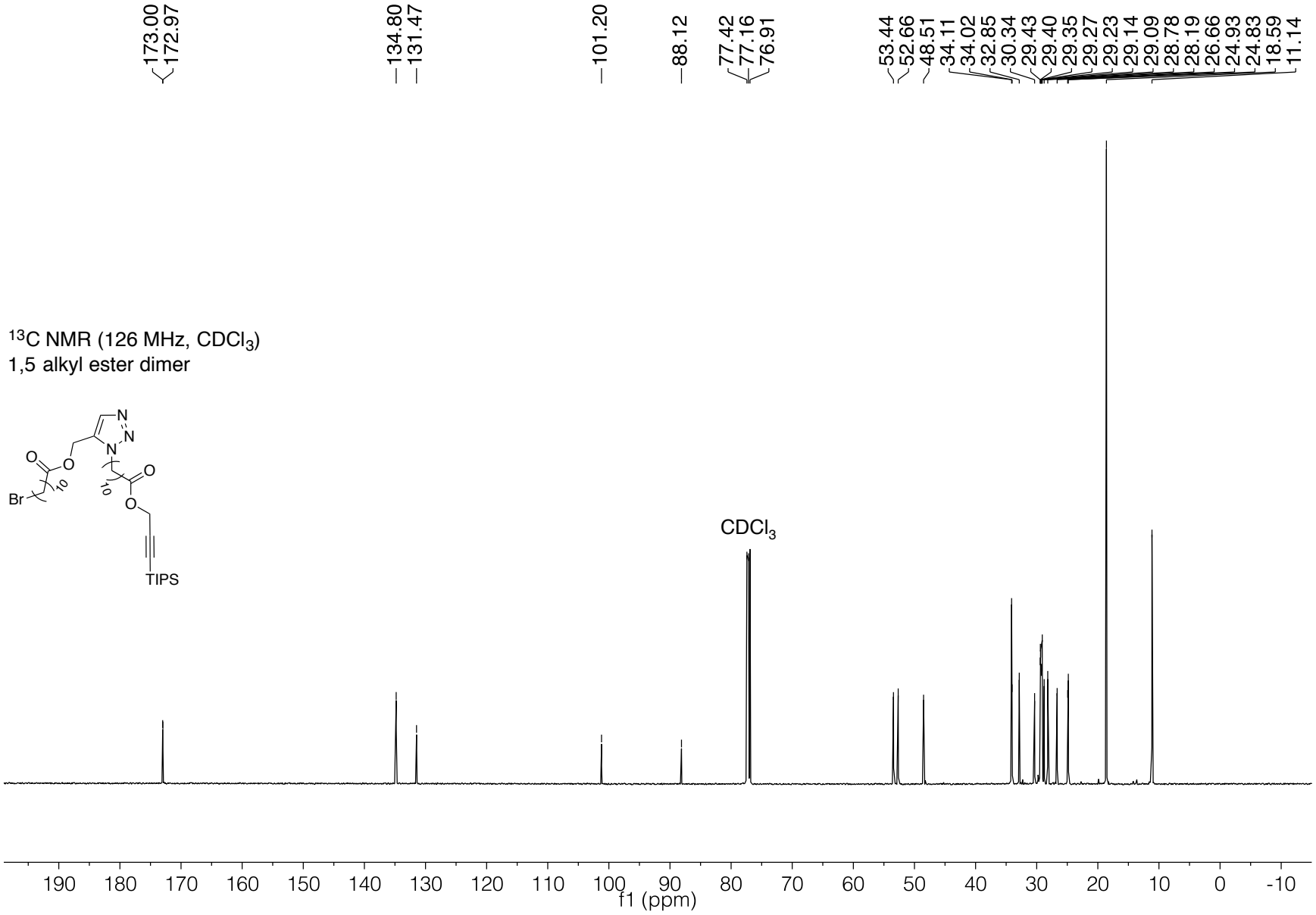


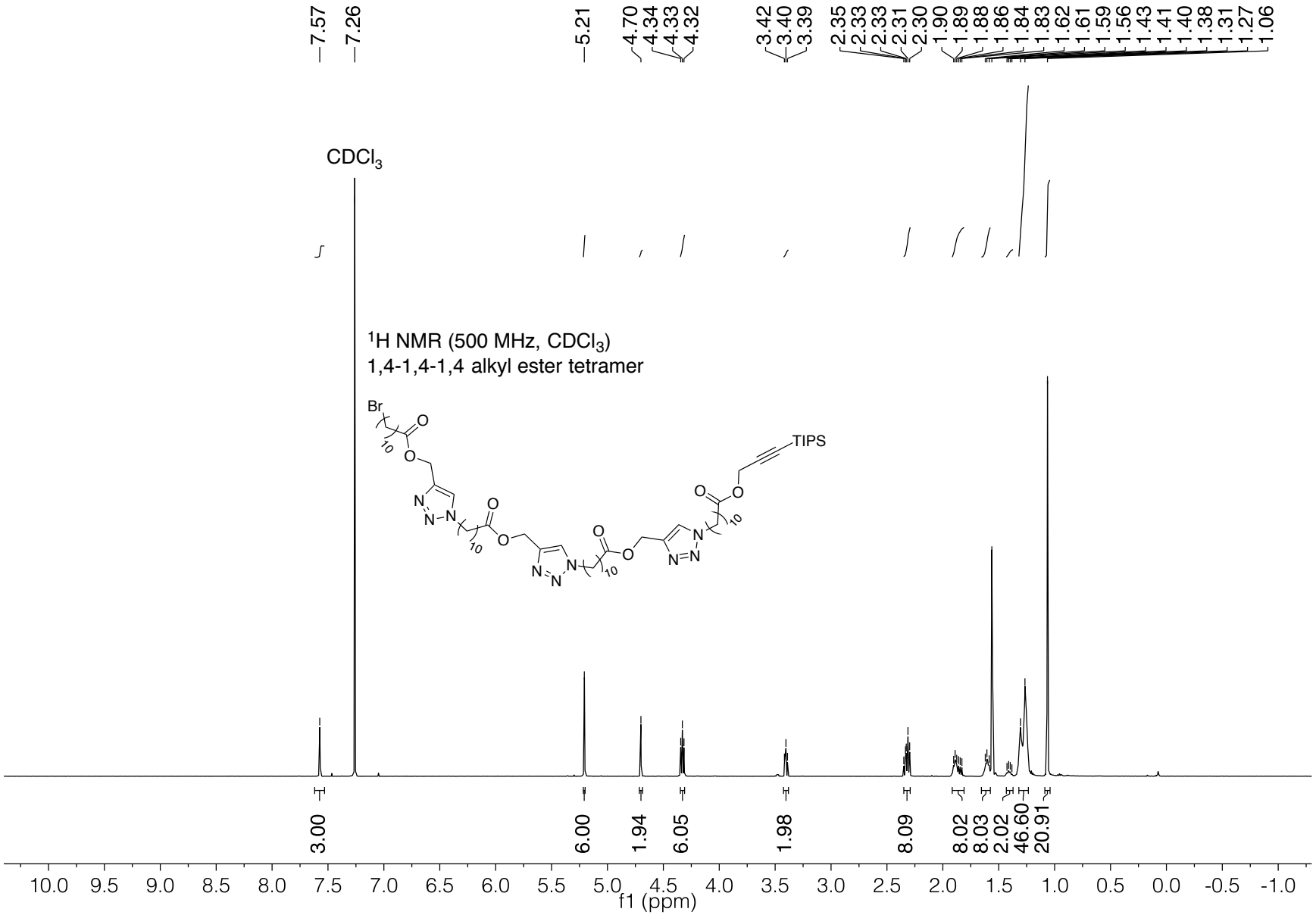
Figure S5. TGA traces of the oligomers studied in this manuscript.

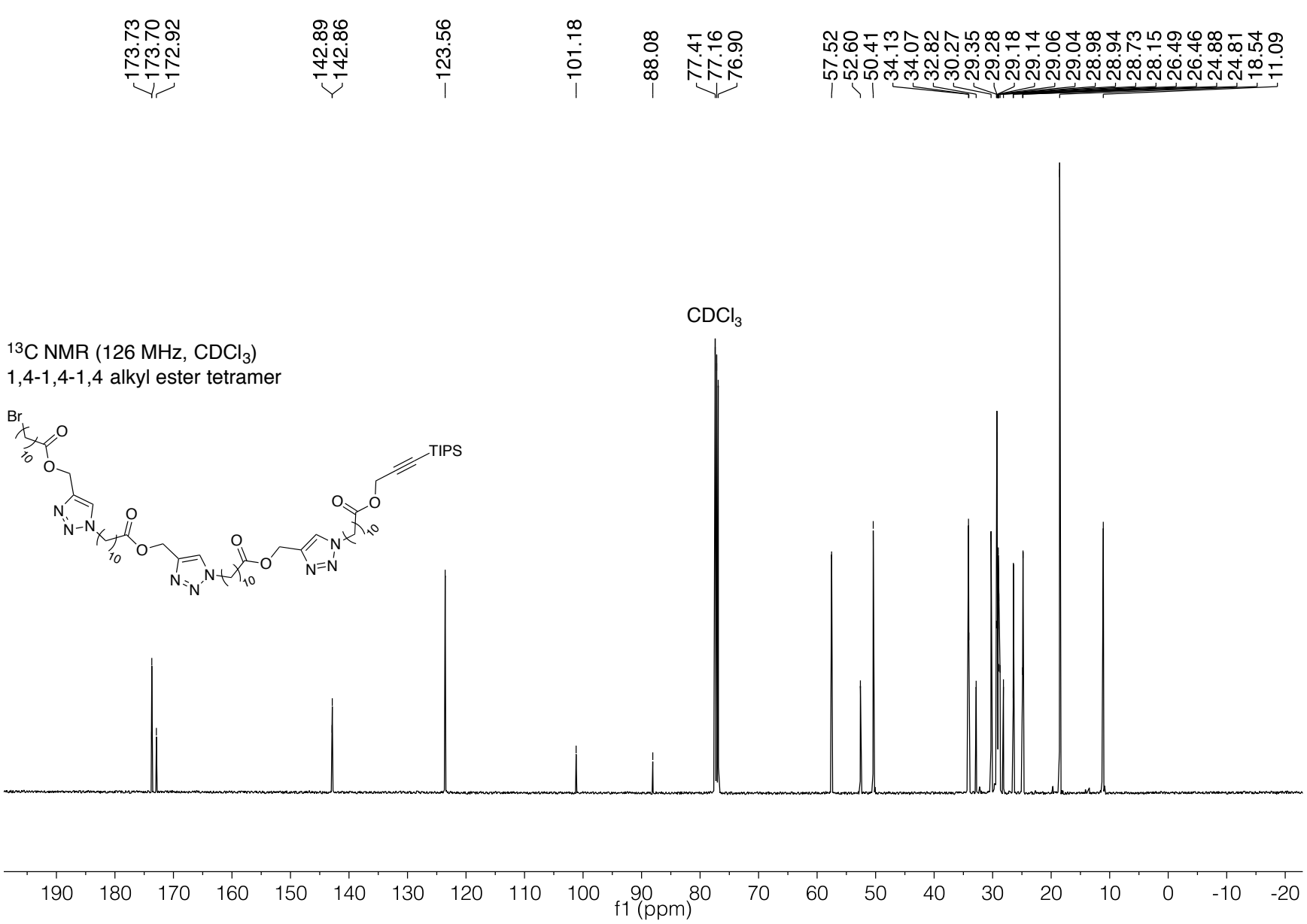

7.57
7.26
5.21
4.70
4.35
4.33
4.32
3.42
3.40
3.39
2.35
2.33
2.32
2.30
1.91
1.89
1.87
1.86
1.84
1.83
1.82
1.64
1.62
1.61
1.59
1.56
1.43
1.41
1.40
1.31
1.26
1.06
1H NMR (500 MHz, CDCl3)
1,4 alkyl ester dimer
Br
O
10
O
N=N
N
O
10
O
O
TIPS
CDCl3
1.00
2.04
1.98
2.00
2.03
4.04
4.08
4.02
2.01
22.32
21.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


173.81
173.00
142.96
123.60
101.21
88.14
77.41
77.16
76.91
57.58
52.67
50.47
34.19
34.12
32.87
30.35
29.41
29.37
29.25
29.12
29.07
29.04
28.80
28.21
26.54
24.94
24.88
18.60
11.15
13C NMR (126 MHz, CDCl3)
1,4 alkyl ester dimer
CDCl3
TIPS
Br
f1 (ppm)


7.69
7.26
5.16
4.70
4.35
4.33
4.32
3.42
3.40
3.39
2.35
2.33
2.32
2.31
1.91
1.90
1.88
1.86
1.84
1.83
1.81
1.63
1.62
1.61
1.59
1.43
1.41
1.40
1.38
1.31
1.27
1.06
1H NMR (500 MHz, CDCl3)
1,5 alkyl ester dimer
Br
TIPS
CDCl3
0.95
1.99
2.01
2.00
2.00
4.00
4.03
4.14
2.03
22.46
21.45
f1 (ppm)


173.00
172.97
134.80
131.47
101.20
88.12
77.42
77.16
76.91
53.44
52.66
48.51
34.11
34.02
32.85
30.34
29.43
29.40
29.35
29.27
29.23
29.14
29.09
28.78
28.19
26.66
24.93
24.83
18.59
11.14
13C NMR (126 MHz, CDCl3)
1,5 alkyl ester dimer
CDCl3
TIPS
Br
f1 (ppm)


7.57
7.26
5.21
4.70
4.34
4.33
4.32
3.42
3.40
3.39
2.35
2.33
2.33
2.31
2.30
1.90
1.89
1.88
1.86
1.84
1.83
1.62
1.61
1.59
1.56
1.43
1.41
1.40
1.38
1.31
1.27
1.06
CDCl3
1H NMR (500 MHz, CDCl3)
1,4-1,4-1,4 alkyl ester tetramer
Br
TIPS
3.00
6.00
1.94
6.05
1.98
8.09
8.02
8.03
2.02
46.60
20.91
f1 (ppm)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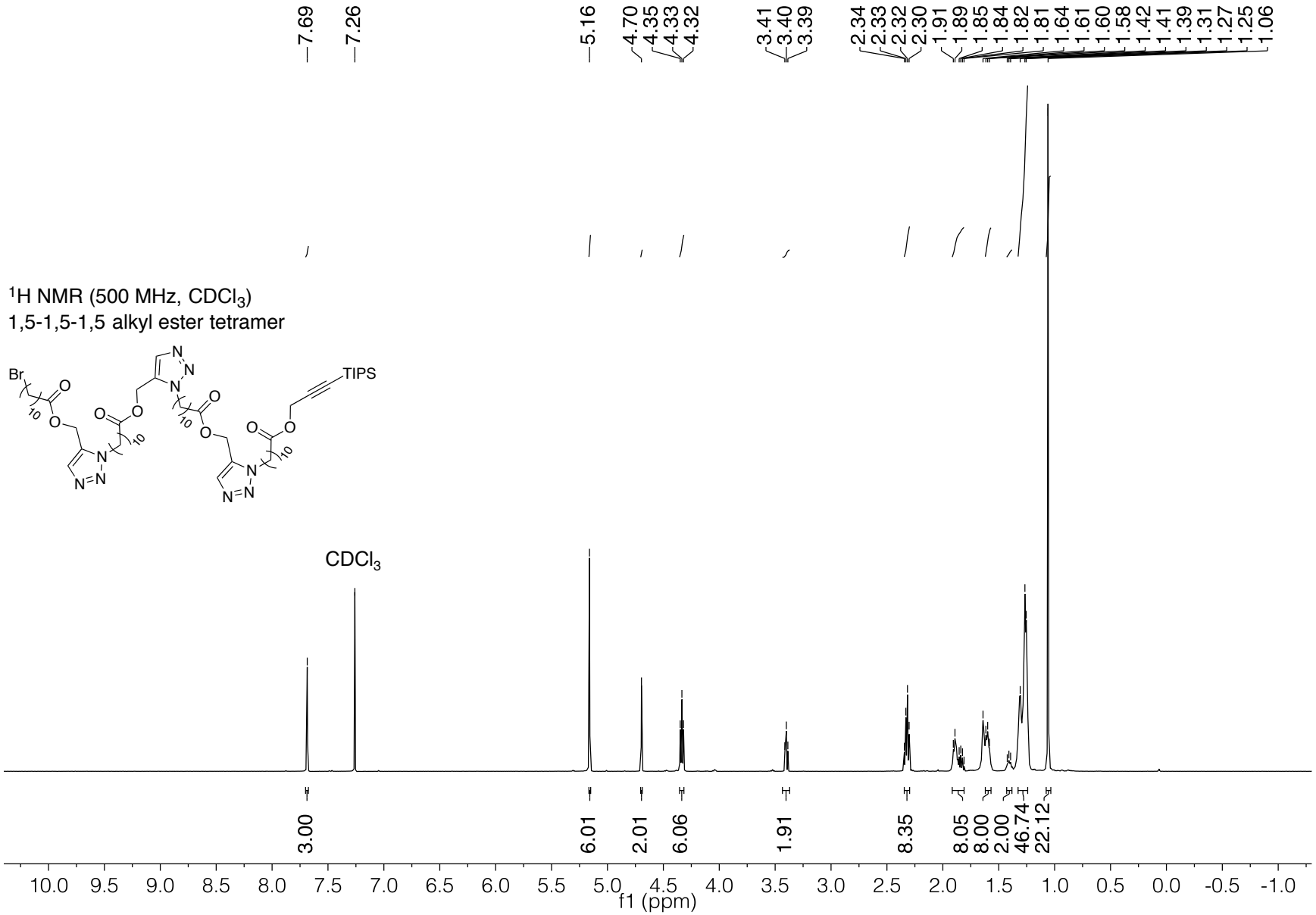
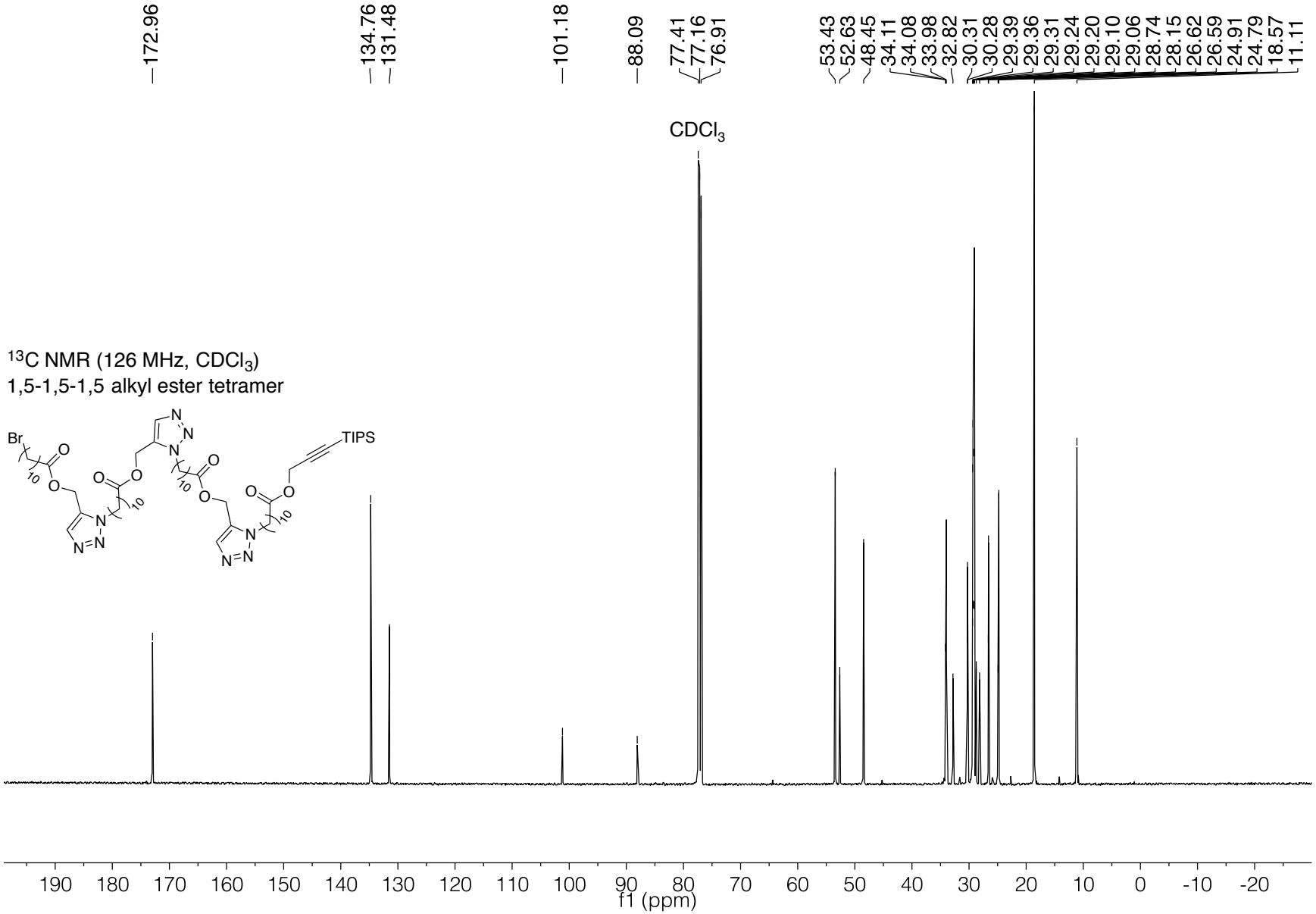
173.70
172.92
142.89
142.86
123.56
101.18
88.08
77.41
77.16
76.90
57.52
52.60
50.41
34.13
34.07
32.82
30.27
29.35
29.28
29.18
29.14
29.06
29.04
28.98
28.94
28.73
28.15
26.49
26.46
24.88
24.81
18.54
11.09
CDCl3
13C NMR (126 MHz, CDCl3)
1,4-1,4-1,4 alkyl ester tetramer
Br
TIPS
f1 (ppm)


7.69
7.26
5.16
4.70
4.35
4.33
4.32
3.41
3.40
3.39
2.34
2.33
2.32
2.30
1.91
1.89
1.85
1.84
1.82
1.81
1.64
1.61
1.60
1.58
1.42
1.41
1.39
1.31
1.27
1.25
1.06
1H NMR (500 MHz, CDCl3)
1,5-1,5-1,5 alkyl ester tetramer
Br
TIPS
CDCl3
3.00
6.01
2.01
6.06
1.91
8.35
8.05
8.00
2.00
46.74
22.12
f1 (ppm)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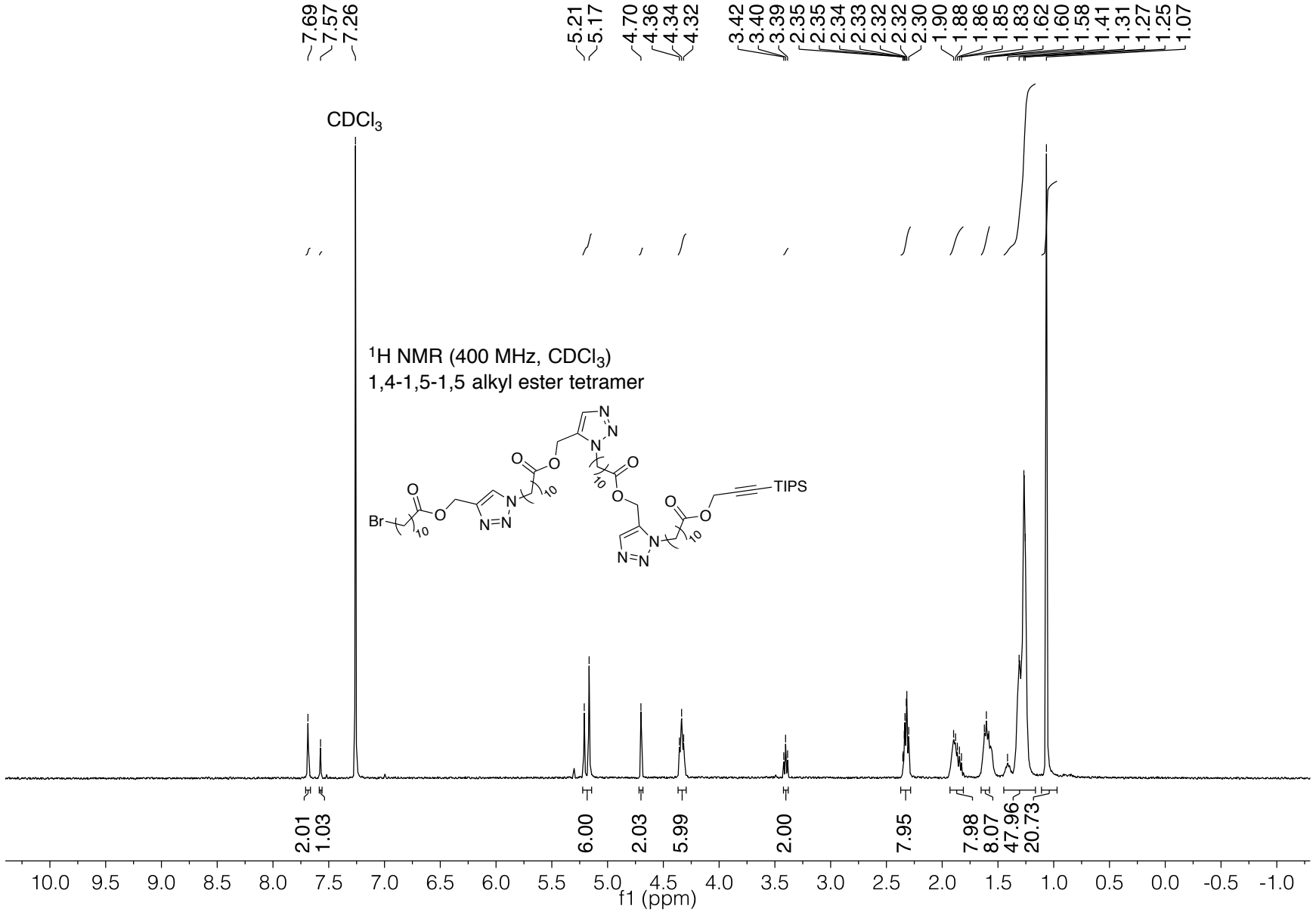
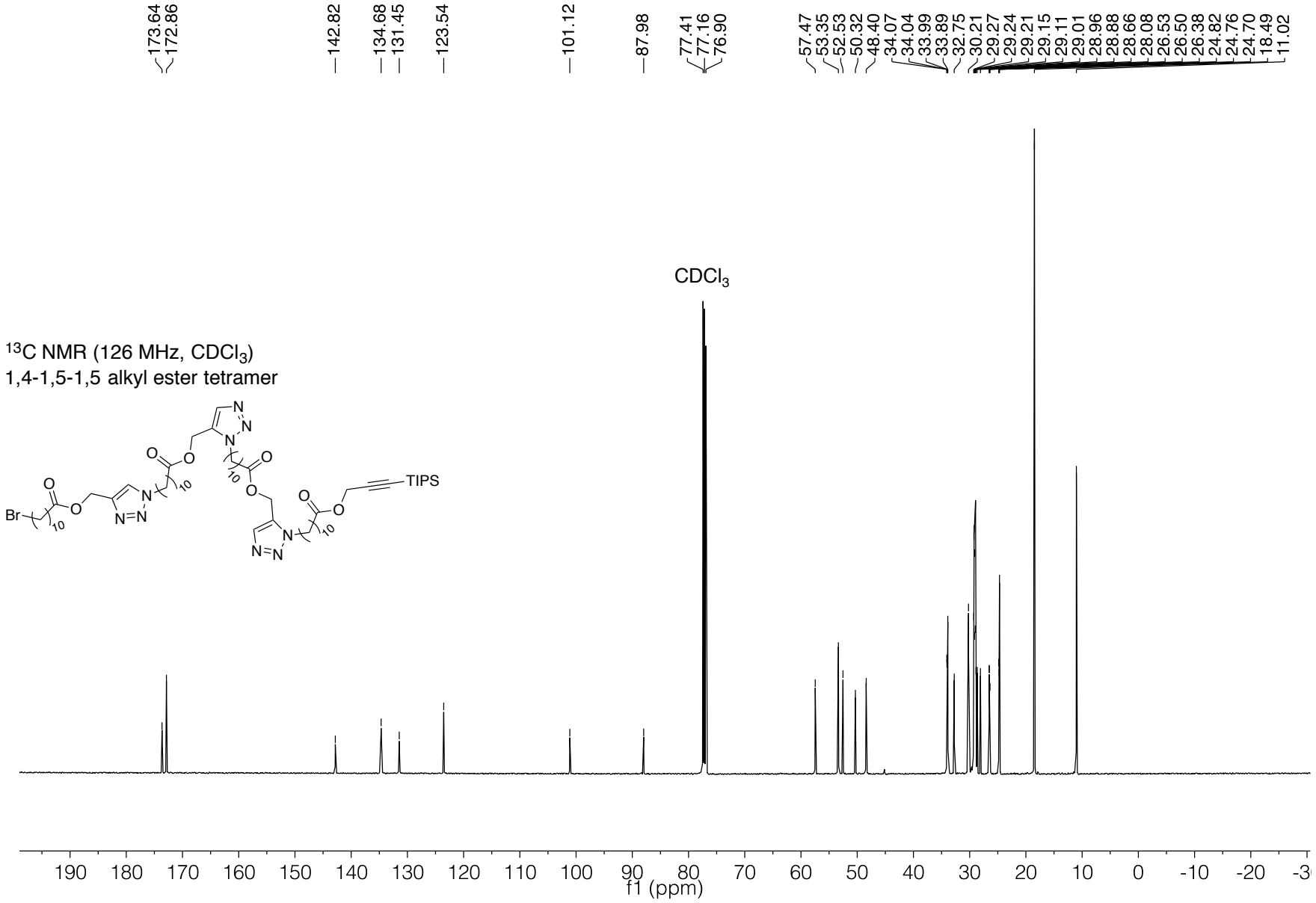
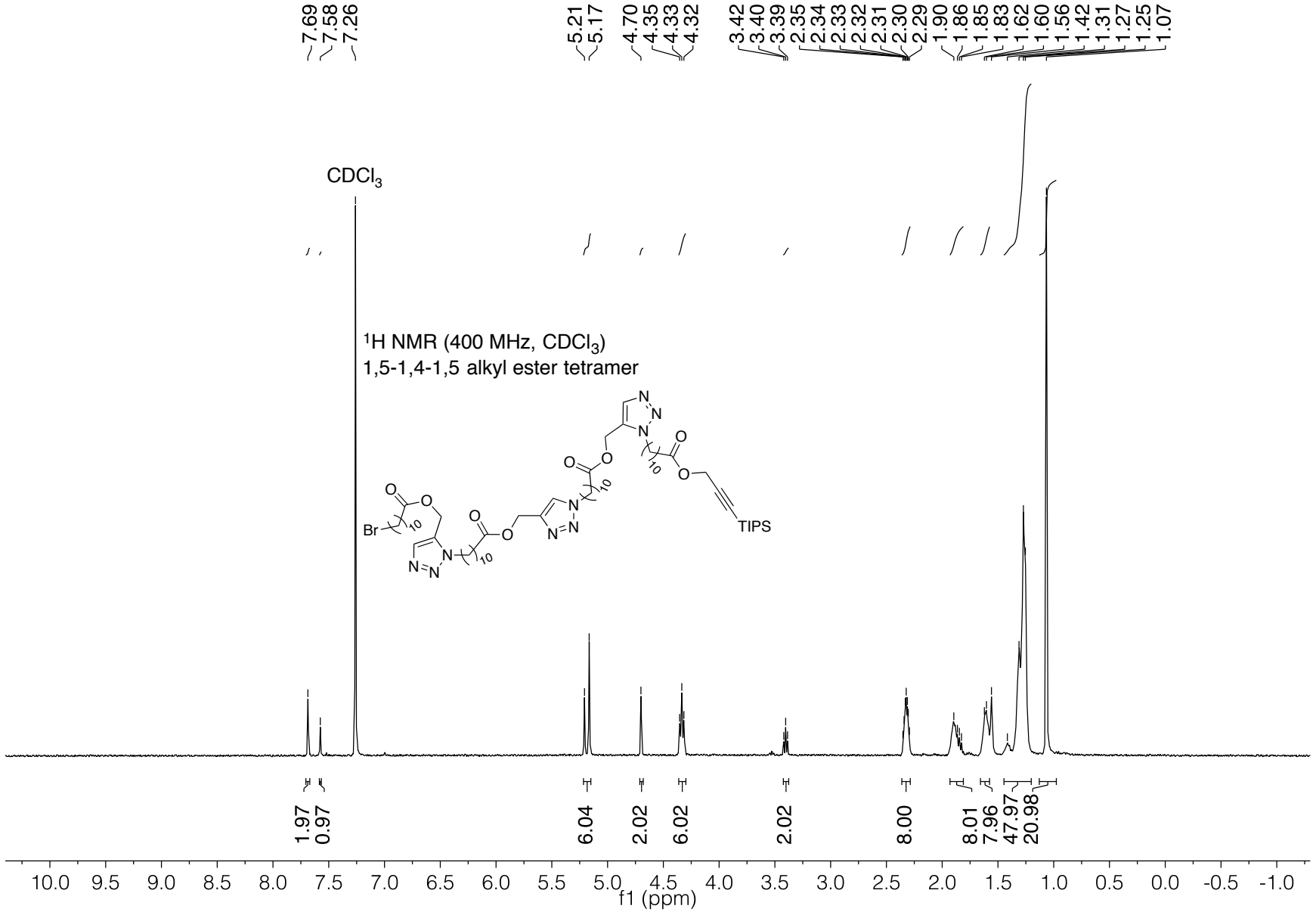
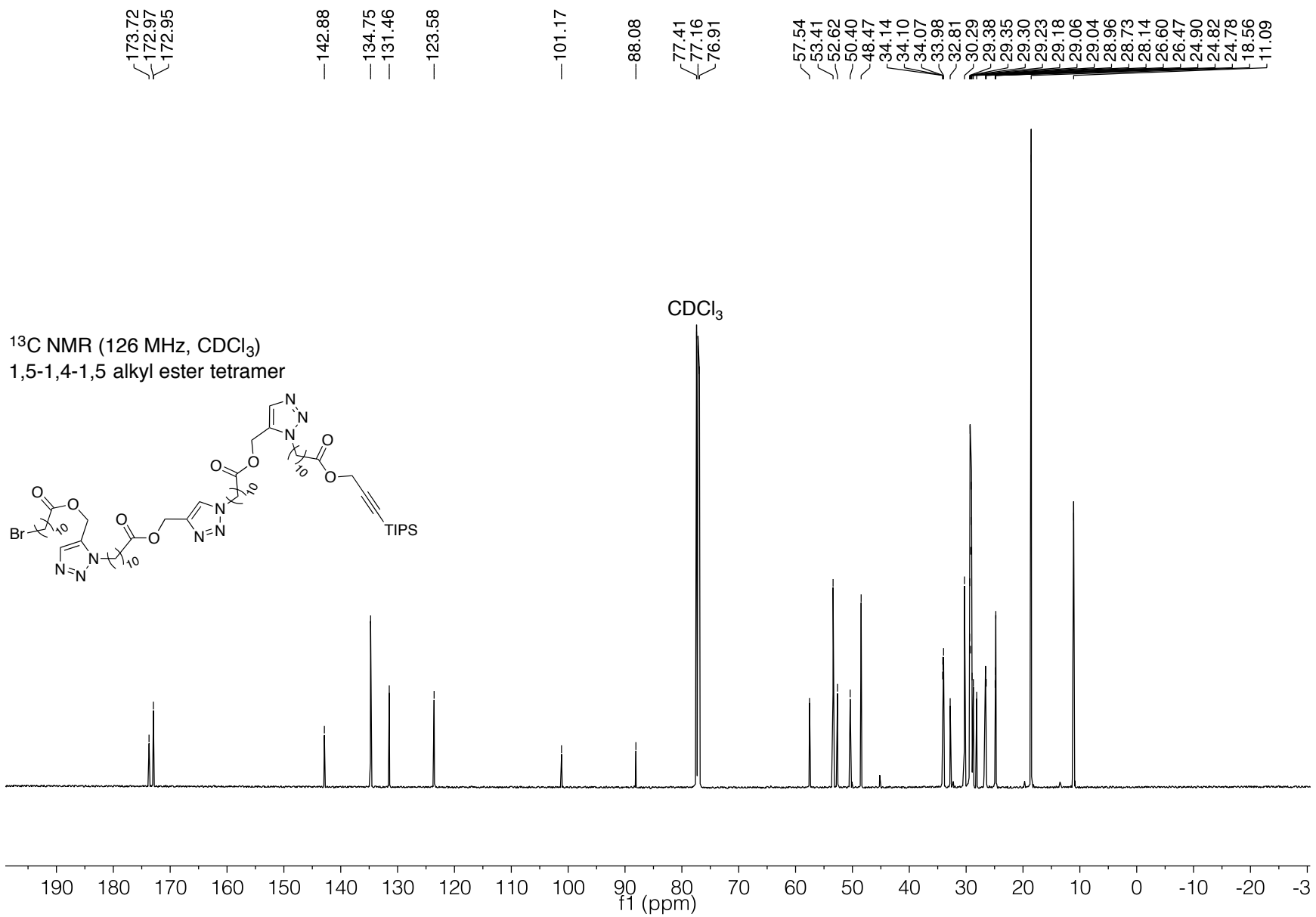
134.76
131.48
101.18
88.09
77.41
77.16
76.91
53.43
52.63
48.45
34.11
34.08
33.98
32.82
30.31
30.28
29.39
29.36
29.31
29.24
29.20
29.10
29.06
28.74
28.15
26.62
26.59
24.91
24.79
18.57
11.11
CDCl3
13C NMR (126 MHz, CDCl3)
1,5-1,5-1,5 alkyl ester tetramer
Br
TIPS
f1 (ppm)


7.69
7.57
7.26
5.21
5.17
4.70
4.36
4.34
4.32
3.42
3.40
3.39
2.35
2.35
2.34
2.33
2.32
2.32
2.30
1.90
1.88
1.86
1.85
1.83
1.62
1.60
1.58
1.41
1.31
1.27
1.25
1.07
CDCl3
1H NMR (400 MHz, CDCl3)
1,4-1,5-1,5 alkyl ester tetramer
TIPS
2.01
1.03
6.00
2.03
5.99
2.00
7.95
7.98
8.07
47.96
20.73
f1 (ppm)


173.64
172.86
142.82
134.68
131.45
123.54
101.12
87.98
77.41
77.16
76.90
57.47
53.35
52.53
50.32
48.40
34.07
34.04
33.99
33.89
32.75
30.21
29.27
29.24
29.21
29.15
29.11
29.01
28.96
28.88
28.66
28.08
26.53
26.50
26.38
24.82
24.76
24.70
18.49
11.02
CDCl3
13C NMR (126 MHz, CDCl3)
1,4-1,5-1,5 alkyl ester tetramer
Br
TIPS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -3
f1 (ppm)


7.69
7.58
7.26
5.21
5.17
4.70
4.35
4.33
4.32
3.42
3.40
3.39
2.35
2.34
2.33
2.32
2.31
2.30
2.29
1.90
1.86
1.85
1.83
1.62
1.60
1.56
1.42
1.31
1.27
1.25
1.07
CDCl3
1H NMR (400 MHz, CDCl3)
1,5-1,4-1,5 alkyl ester tetramer
Br
TIPS
1.97
0.97
6.04
2.02
6.02
2.02
8.00
8.01
7.96
47.97
20.98
f1 (ppm)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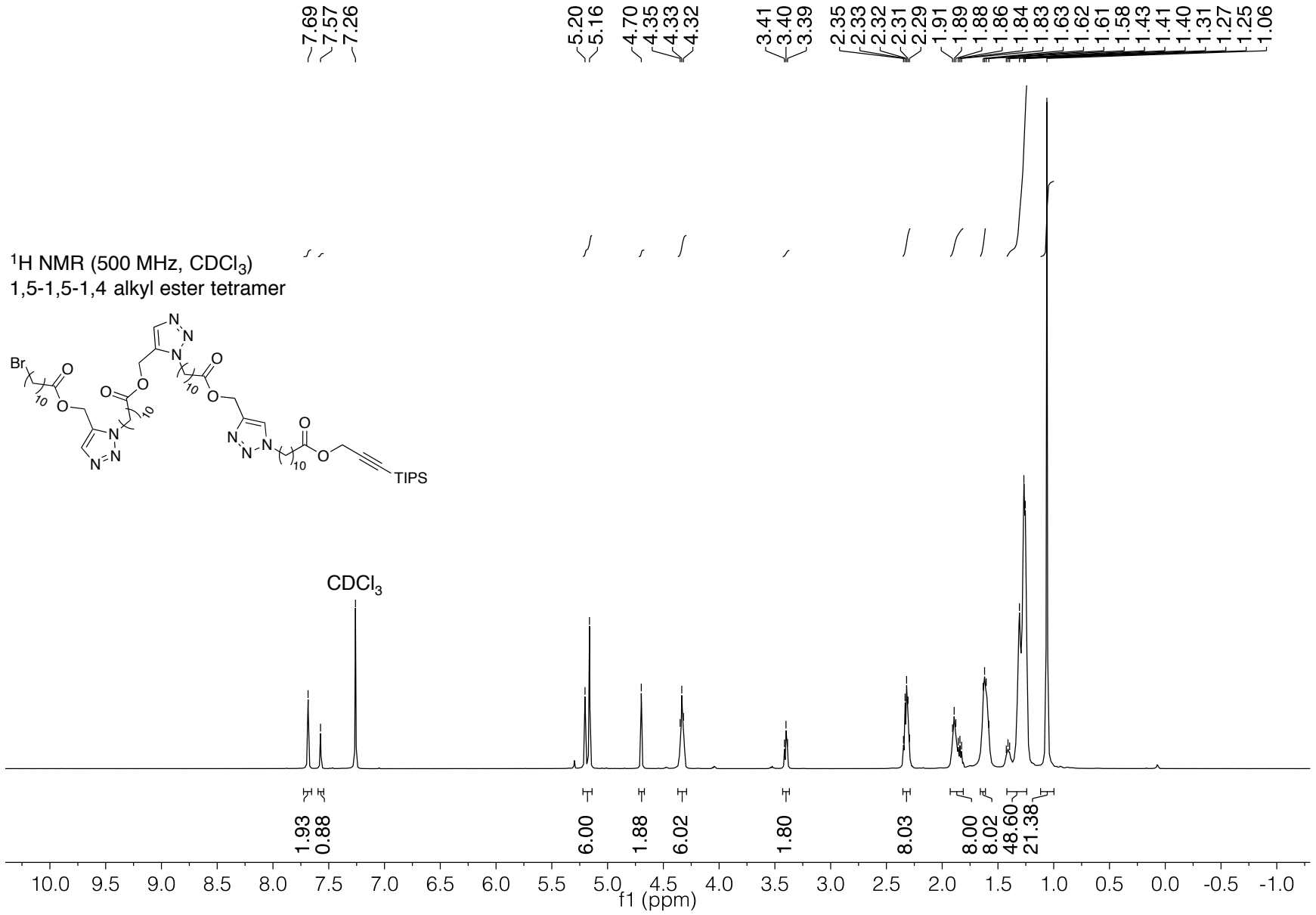
172.97
172.95
142.88
134.75
131.46
123.58
101.17
88.08
77.41
77.16
76.91
57.54
53.41
52.62
50.40
48.47
34.14
34.10
34.07
33.98
32.81
30.29
29.38
29.35
29.30
29.23
29.18
29.06
29.04
28.96
28.73
28.14
26.60
26.47
24.90
24.82
24.78
18.56
11.09
CDCl3
13C NMR (126 MHz, CDCl3)
1,5-1,4-1,5 alkyl ester tetramer
Br
TIPS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-3
f1 (ppm)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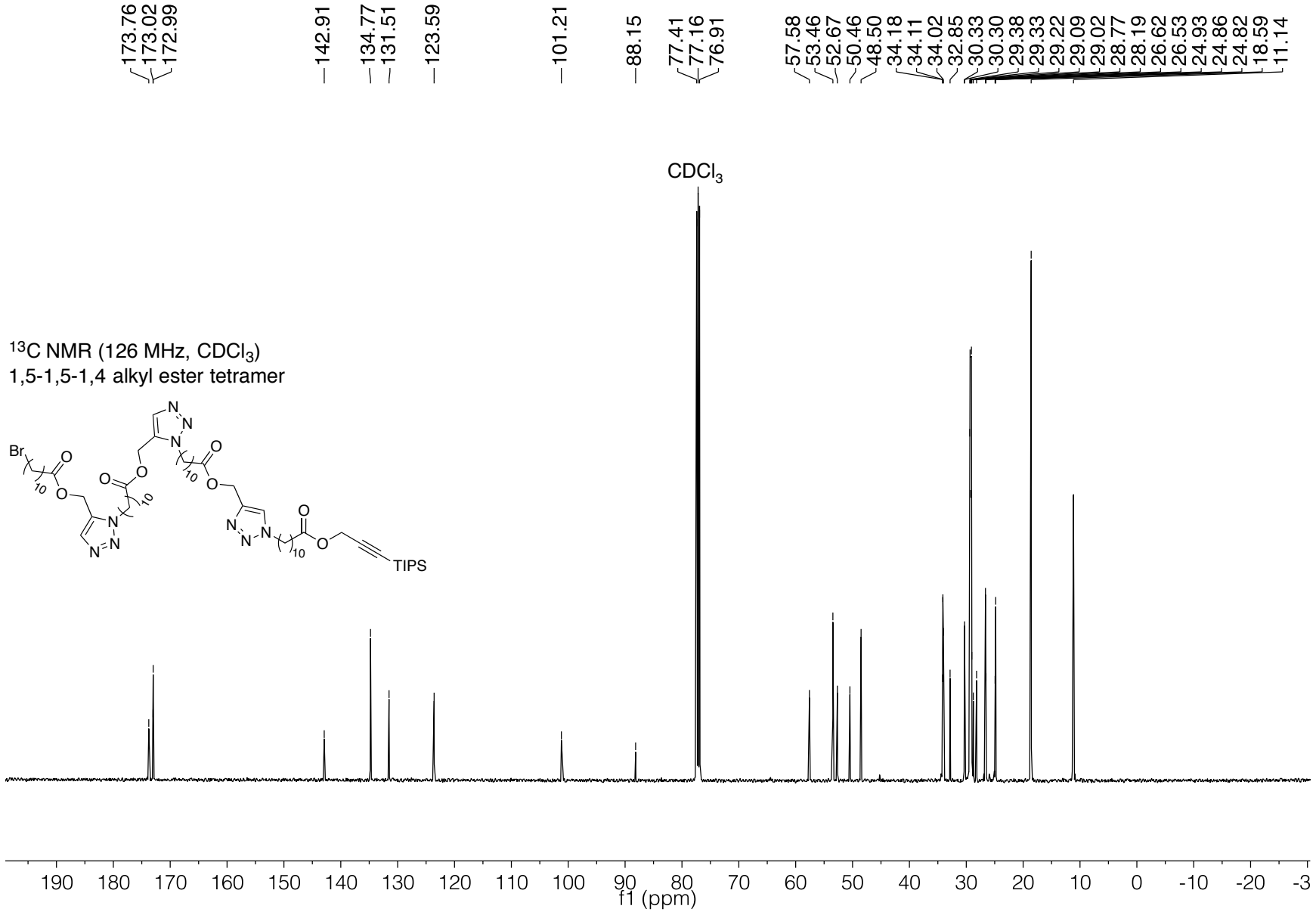
7.57
7.26
5.20
5.16
4.70
4.35
4.33
4.32
3.41
3.40
3.39
2.35
2.33
2.32
2.31
2.29
1.91
1.89
1.88
1.86
1.84
1.83
1.63
1.62
1.61
1.58
1.43
1.41
1.40
1.31
1.27
1.25
1.06
1H NMR (500 MHz, CDCl3)
1,5-1,5-1,4 alkyl ester tetramer
Br
TIPS
CDCl3
1.93
0.88
6.00
1.88
6.02
1.80
8.03
8.00
8.02
48.60
21.38
f1 (ppm)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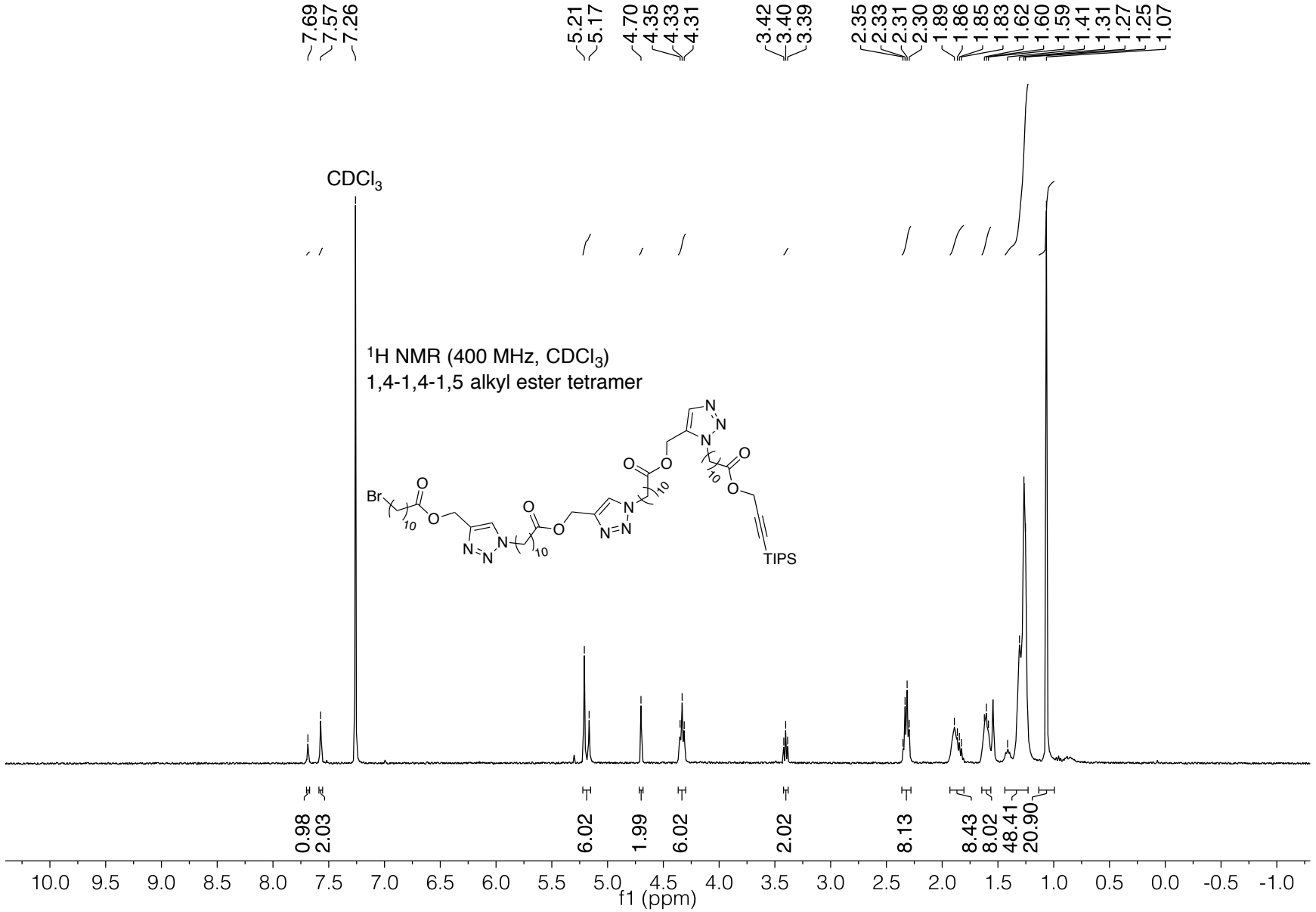
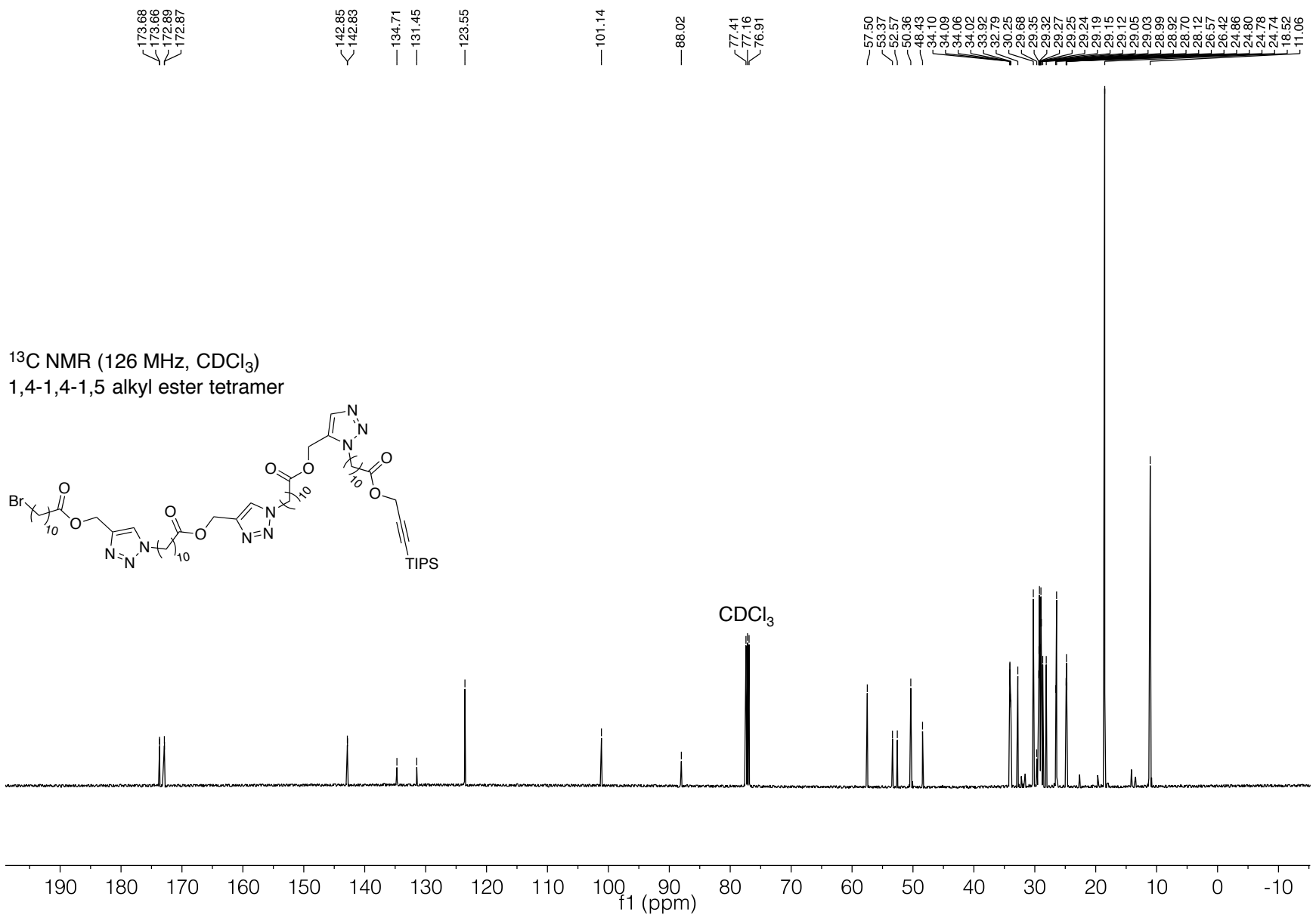
173.02
172.99
142.91
134.77
131.51
123.59
101.21
88.15
77.41
77.16
76.91
57.58
53.46
52.67
50.46
48.50
34.18
34.11
34.02
32.85
30.33
30.30
29.38
29.33
29.22
29.09
29.02
28.77
28.19
26.62
26.53
24.93
24.86
24.82
18.59
11.14
CDCl3
13C NMR (126 MHz, CDCl3)
1,5-1,5-1,4 alkyl ester tetramer
Br
TIPS
f1 (ppm)


7.69
7.57
7.26
5.21
5.17
4.70
4.35
4.33
4.31
3.42
3.40
3.39
2.35
2.33
2.31
2.30
1.89
1.86
1.85
1.83
1.62
1.60
1.59
1.41
1.31
1.27
1.25
1.07
CDCl3
1H NMR (400 MHz, CDCl3)
1,4-1,4-1,5 alkyl ester tetramer
Br
TIPS
0.98
2.03
6.02
1.99
6.02
2.02
8.13
8.43
8.02
48.41
20.90
f1 (ppm)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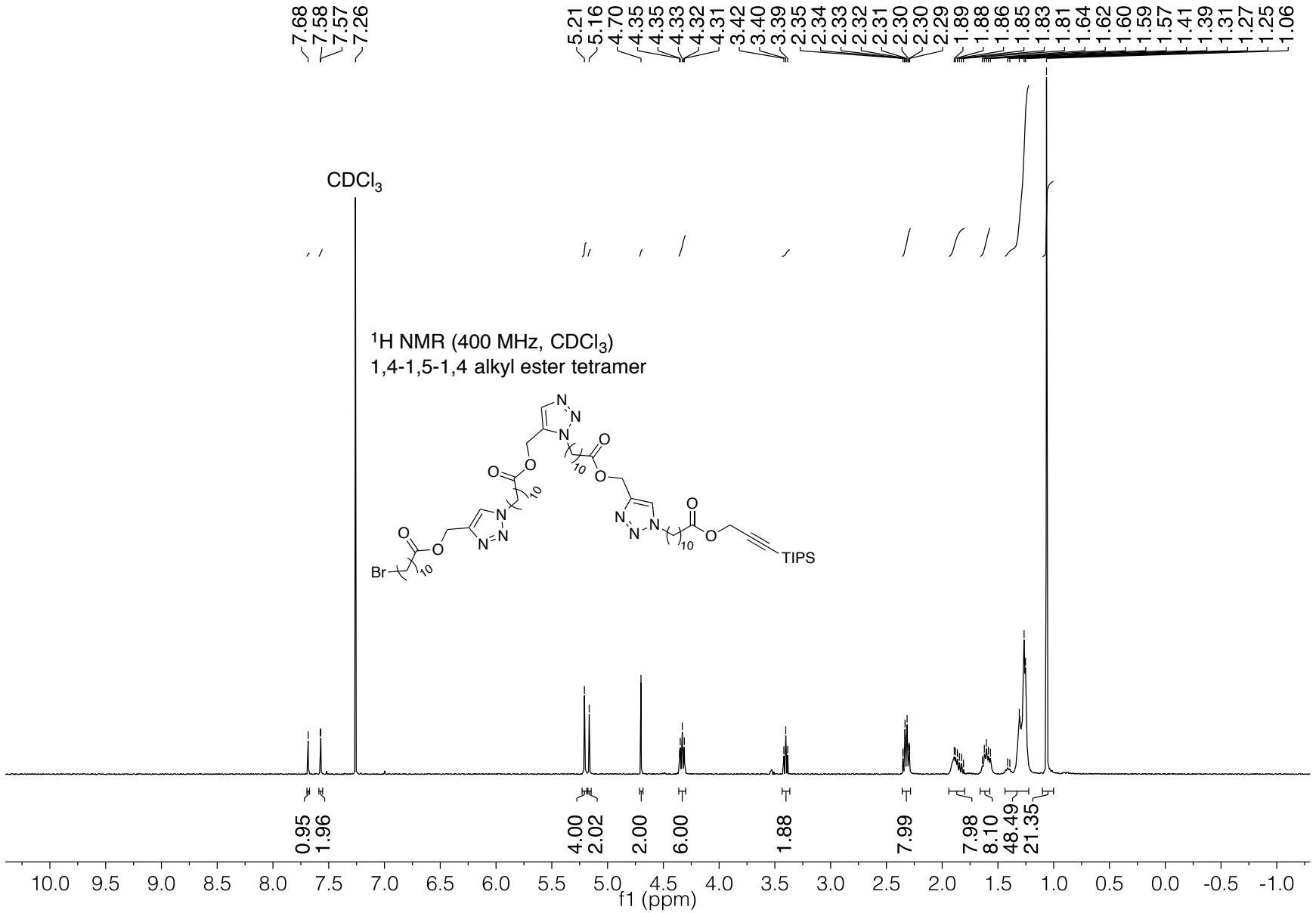
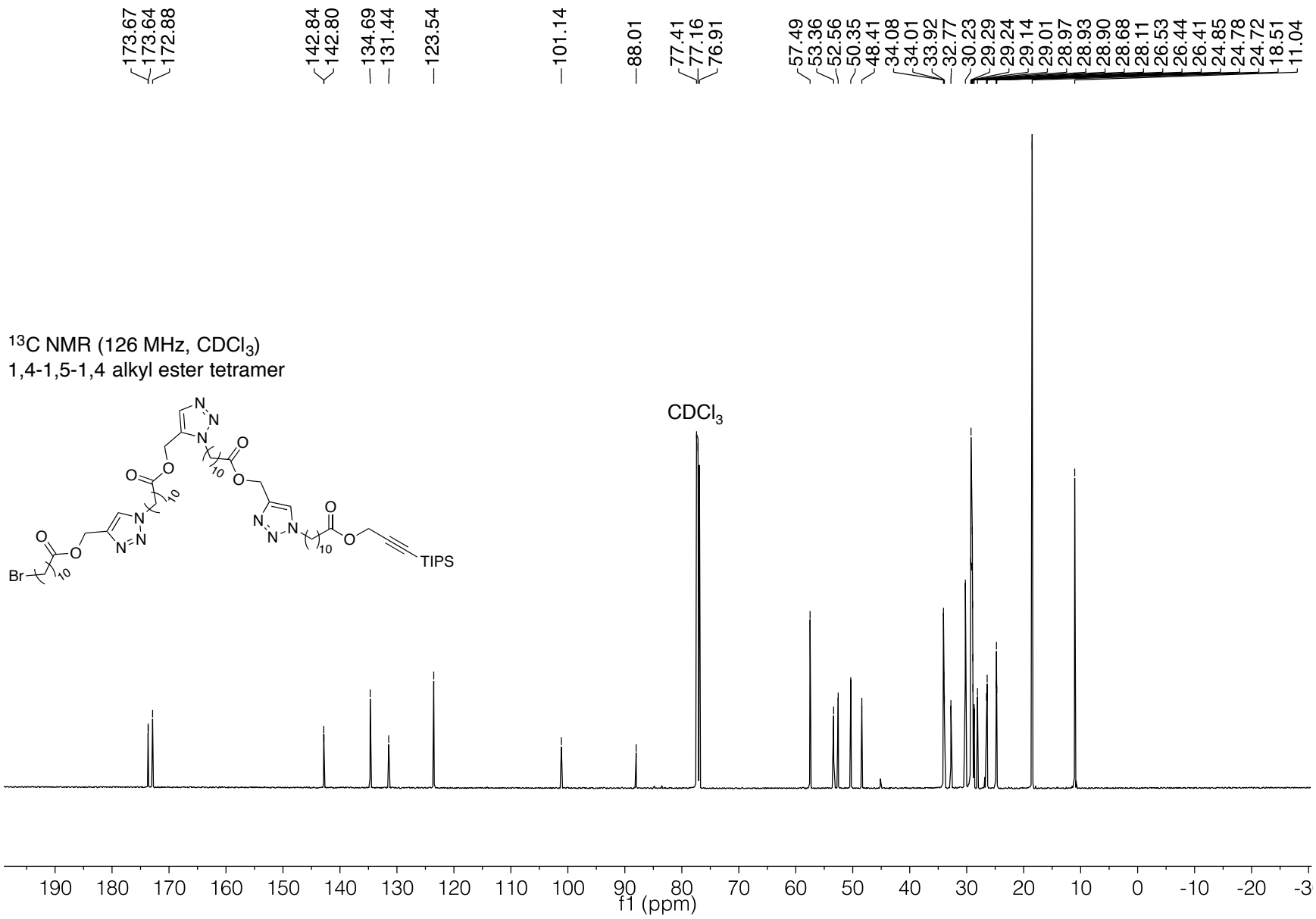
173.66
172.89
172.87
142.85
142.83
134.71
131.45
123.55
101.14
88.02
77.41
77.16
76.91
57.50
53.37
52.57
50.36
48.43
34.10
34.09
34.06
34.02
33.92
32.79
30.25
29.68
29.35
29.32
29.27
29.25
29.24
29.19
29.15
29.12
29.05
29.03
28.99
28.92
28.70
28.12
26.57
26.42
24.86
24.80
24.78
24.74
18.52
11.06
13C NMR (126 MHz, CDCl3)
1,4-1,4-1,5 alkyl ester tetramer
Br
TIPS
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.68
7.58
7.57
7.26
5.21
5.16
4.70
4.35
4.35
4.33
4.32
4.31
3.42
3.40
3.39
2.35
2.34
2.33
2.32
2.31
2.30
2.30
2.29
1.89
1.88
1.86
1.85
1.83
1.81
1.64
1.62
1.60
1.59
1.57
1.41
1.39
1.31
1.27
1.25
1.06
CDCl3
1H NMR (400 MHz, CDCl3)
1,4-1,5-1,4 alkyl ester tetramer
Br
TIPS
0.95
1.96
4.00
2.02
2.00
6.00
1.88
7.99
7.98
8.10
48.49
21.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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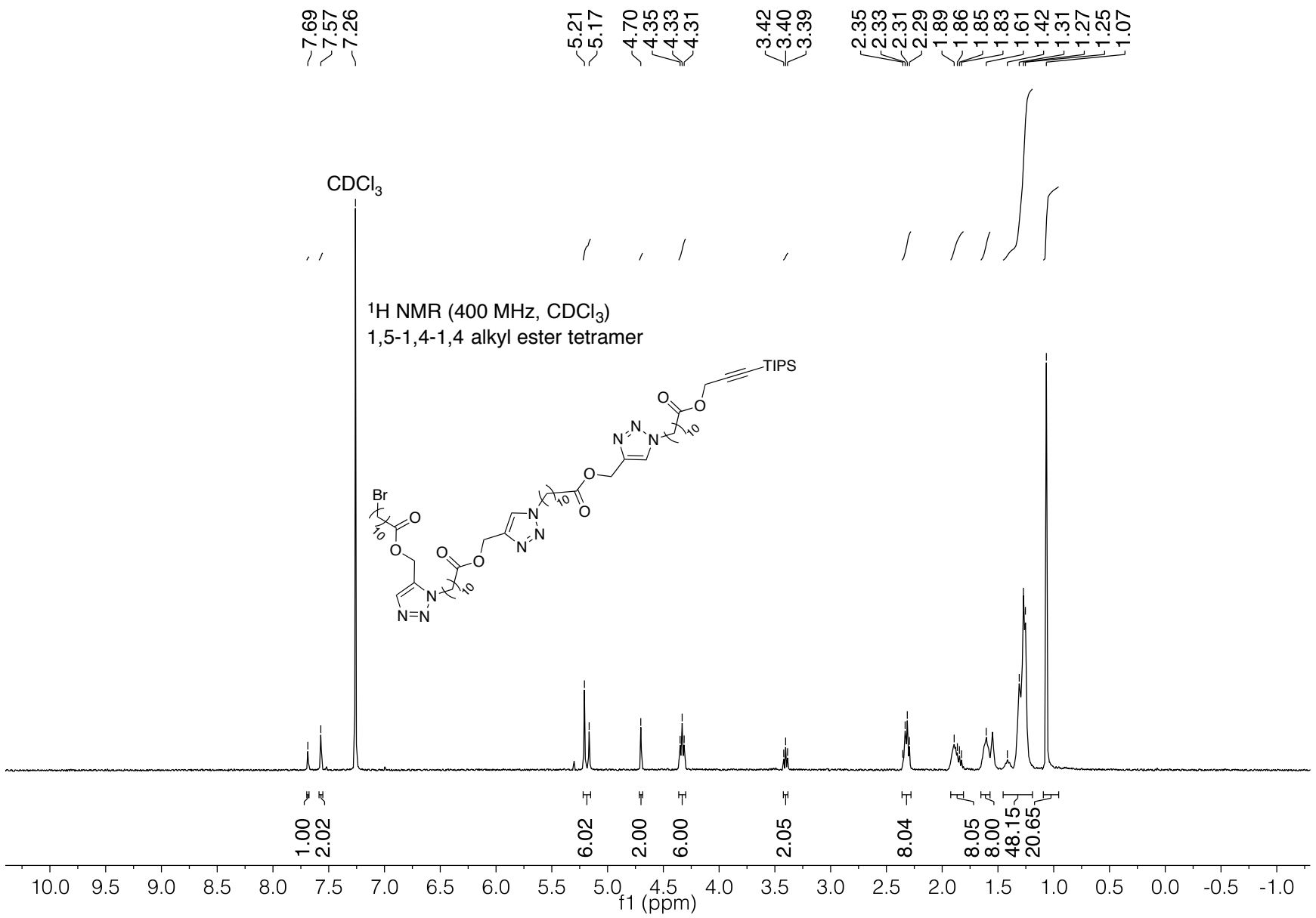
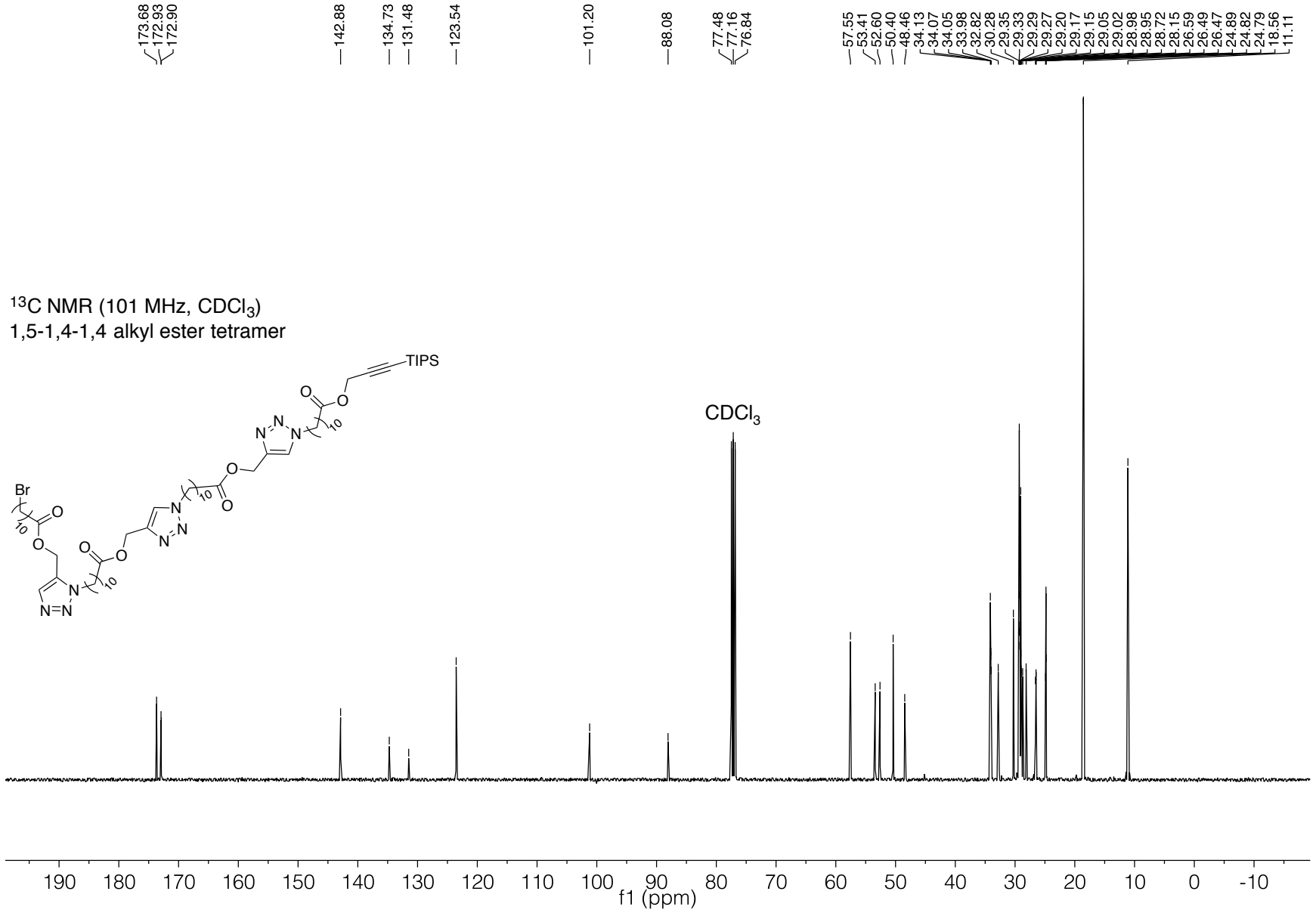
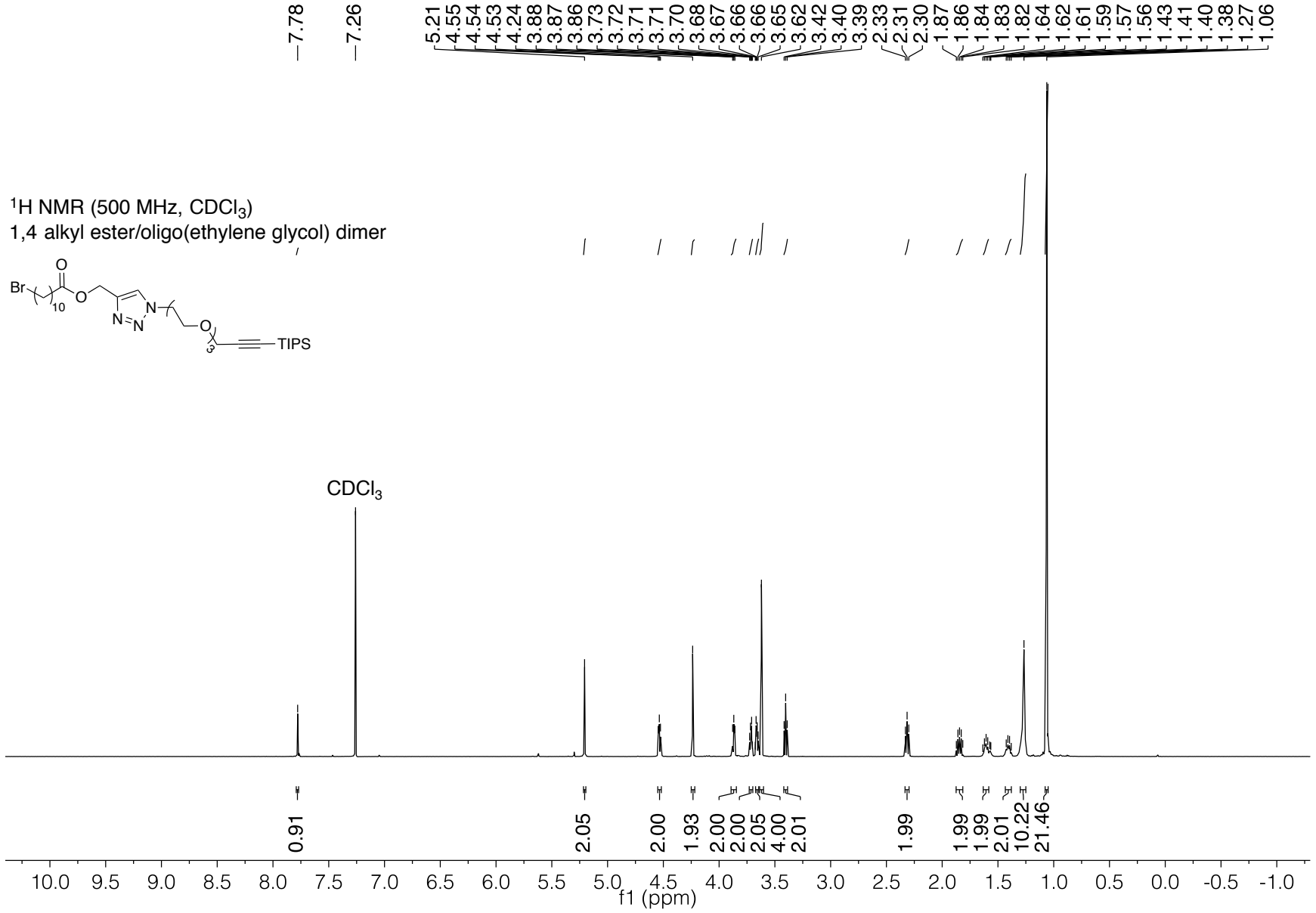
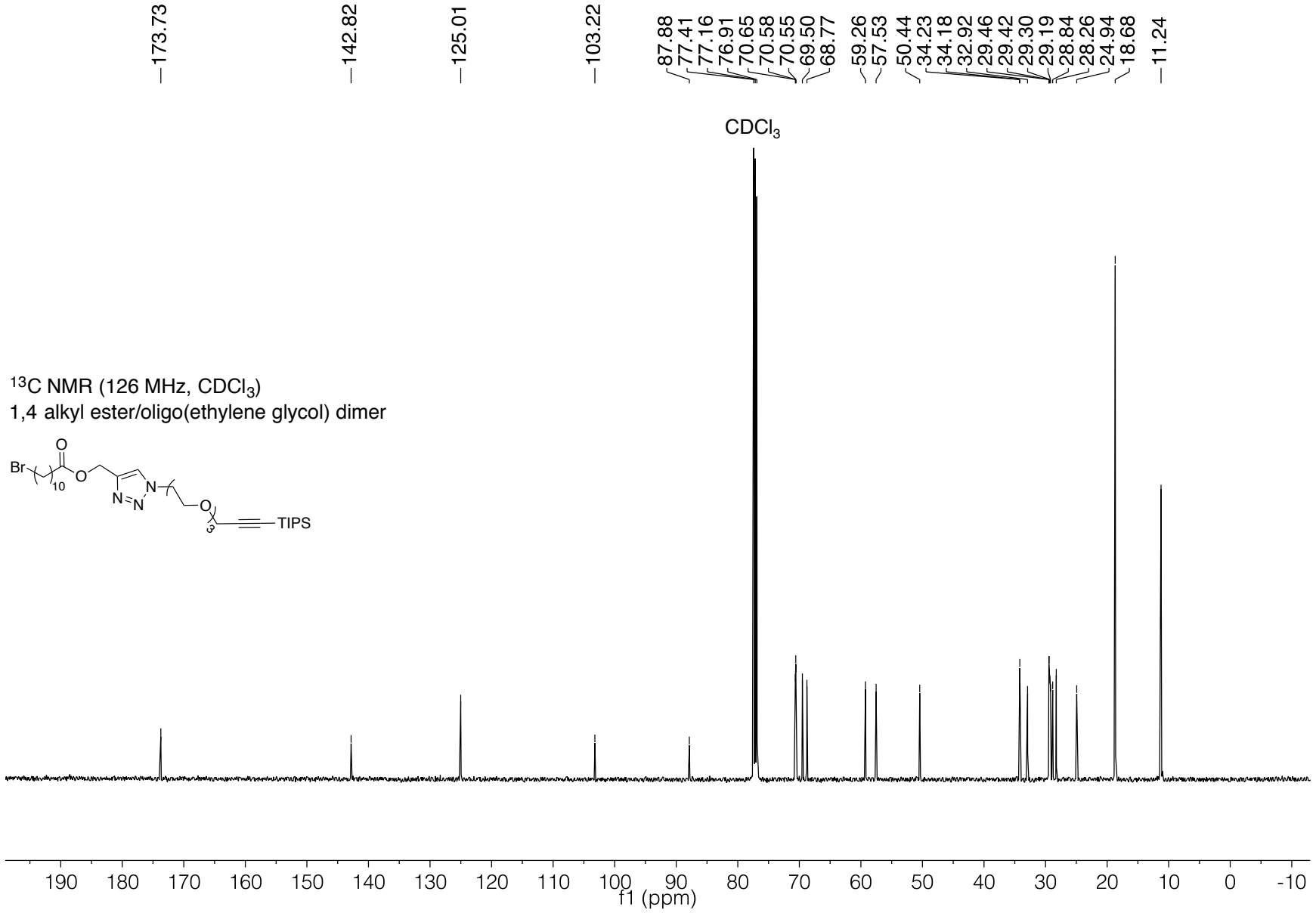
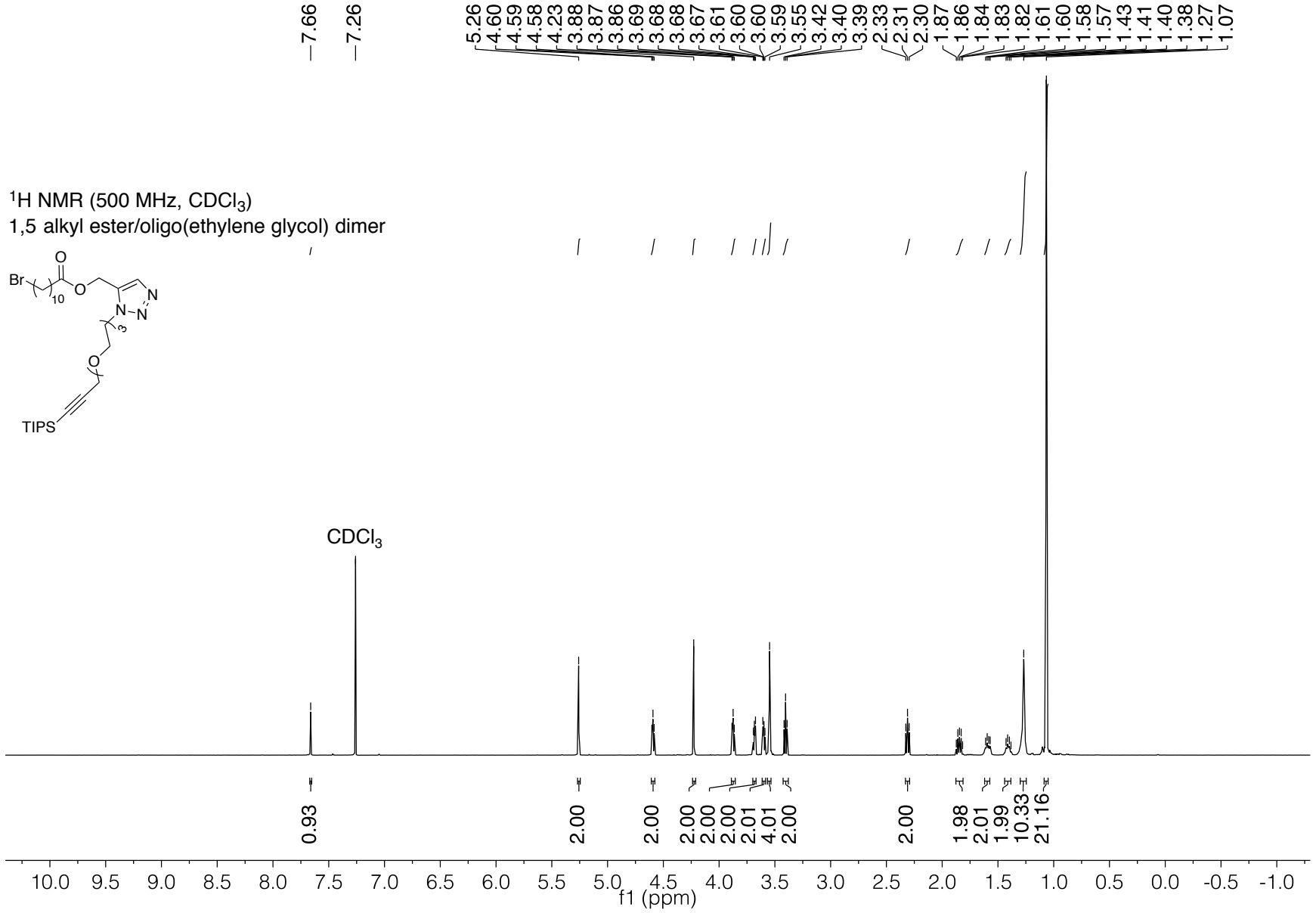
173.64
172.88
142.84
142.80
134.69
131.44
123.54
101.14
88.01
77.41
77.16
76.91
57.49
53.36
52.56
50.35
48.41
34.08
34.01
33.92
32.77
30.23
29.29
29.24
29.14
29.01
28.97
28.93
28.90
28.68
28.11
26.53
26.44
26.41
24.85
24.78
24.72
18.51
11.04
13C NMR (126 MHz, CDCl3)
1,4-1,5-1,4 alkyl ester tetramer
CDCl3
TIPS
Br
f1 (ppm)

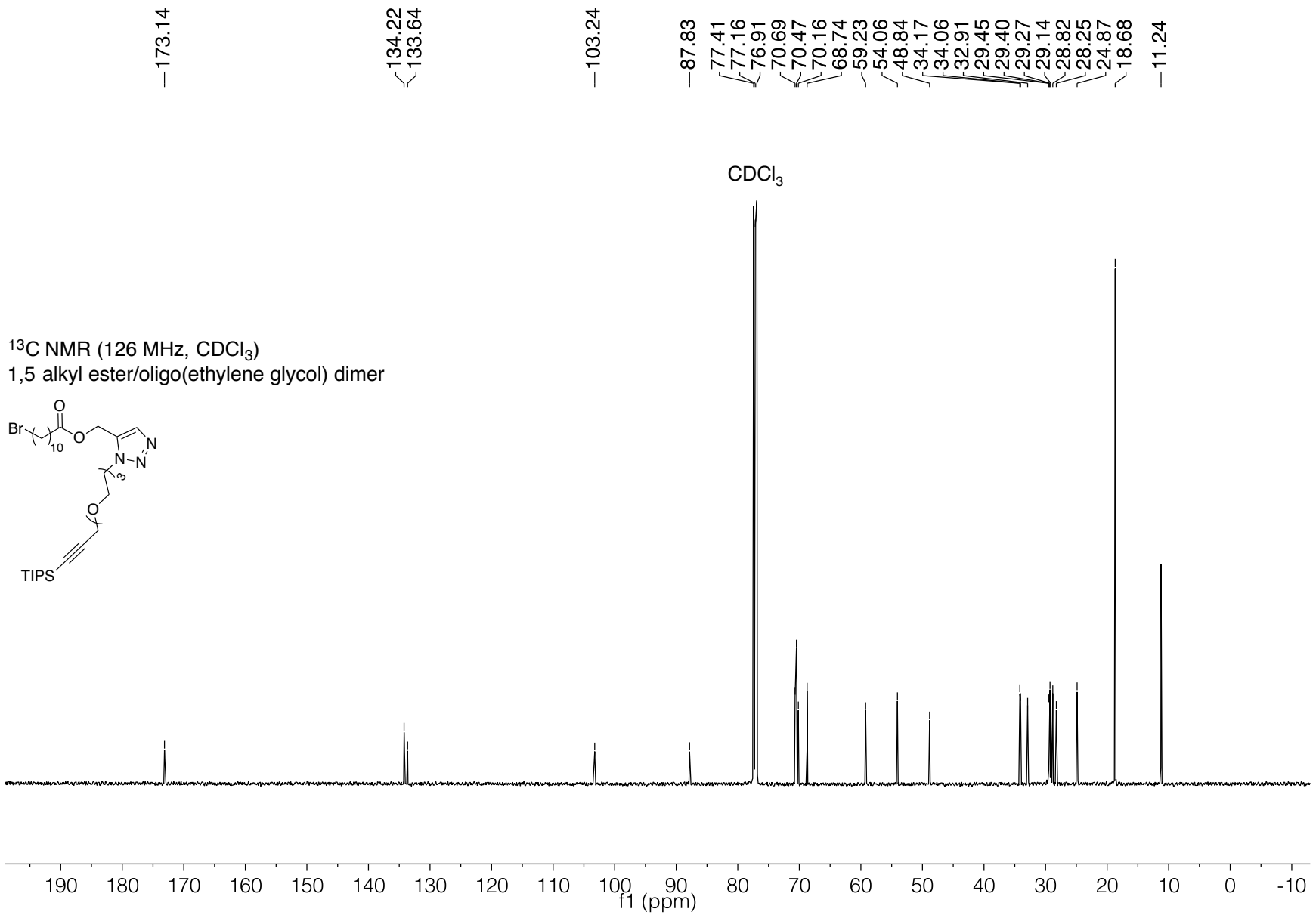

7.69
7.57
7.26
5.21
5.17
4.70
4.35
4.33
4.31
3.42
3.40
3.39
2.35
2.33
2.31
2.29
1.89
1.86
1.85
1.83
1.61
1.42
1.31
1.27
1.25
1.07
CDCl3
1H NMR (400 MHz, CDCl3)
1,5-1,4-1,4 alkyl ester tetramer
TIPS
Br
1.00
2.02
6.02
2.00
6.00
2.05
8.04
8.05
8.00
48.15
20.65
f1 (ppm)

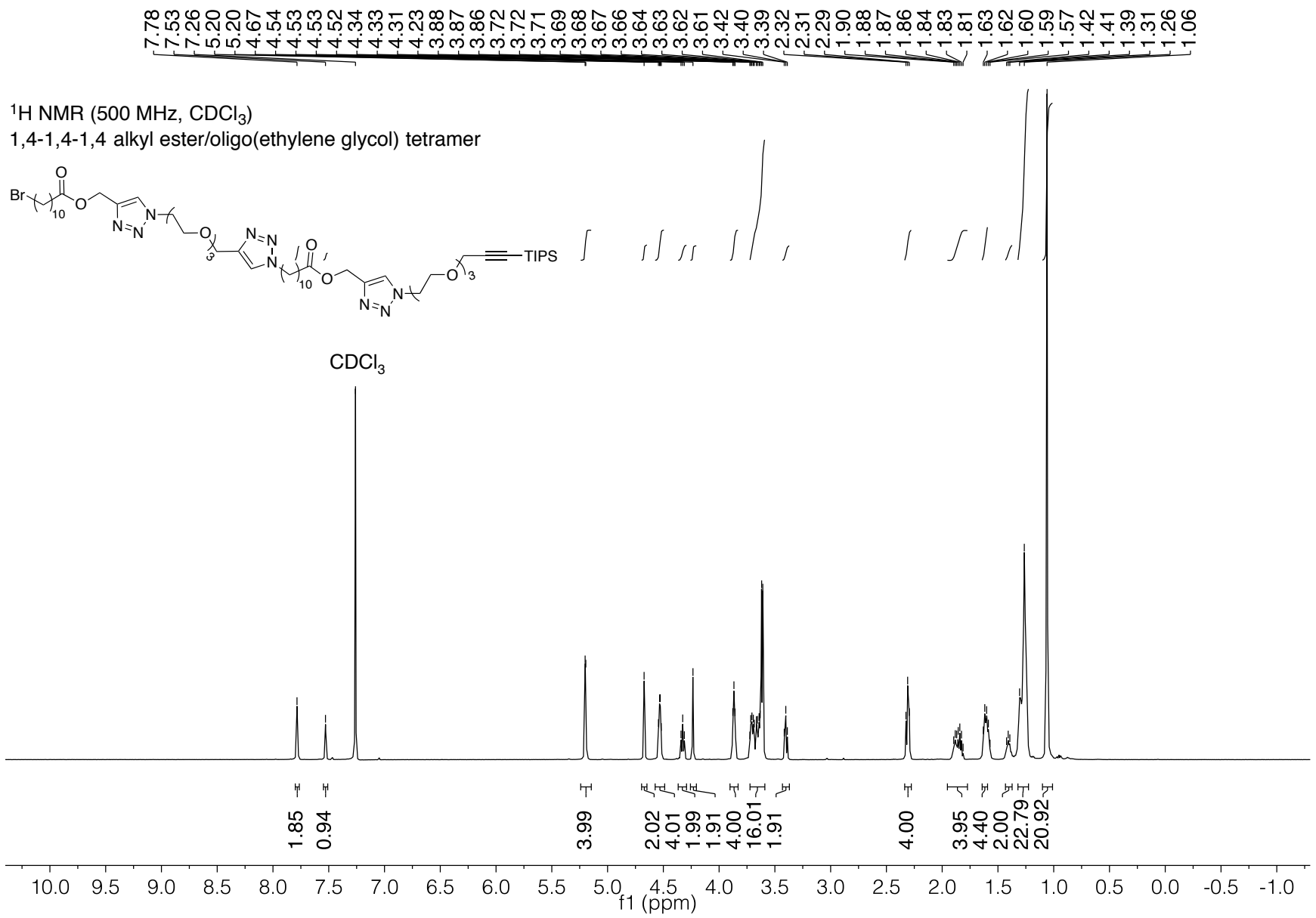

173.68
172.93
172.90
142.88
134.73
131.48
123.54
101.20
88.08
77.48
77.16
76.84
57.55
53.41
52.60
50.40
48.46
34.13
34.07
34.05
33.98
32.82
30.28
29.35
29.33
29.29
29.27
29.20
29.17
29.15
29.05
29.02
28.98
28.95
28.72
28.15
26.59
26.49
26.47
24.89
24.82
24.79
18.56
11.11
13C NMR (101 MHz, CDCl3)
1,5-1,4-1,4 alkyl ester tetramer
CDCl3
TIPS
Br
f1 (ppm)

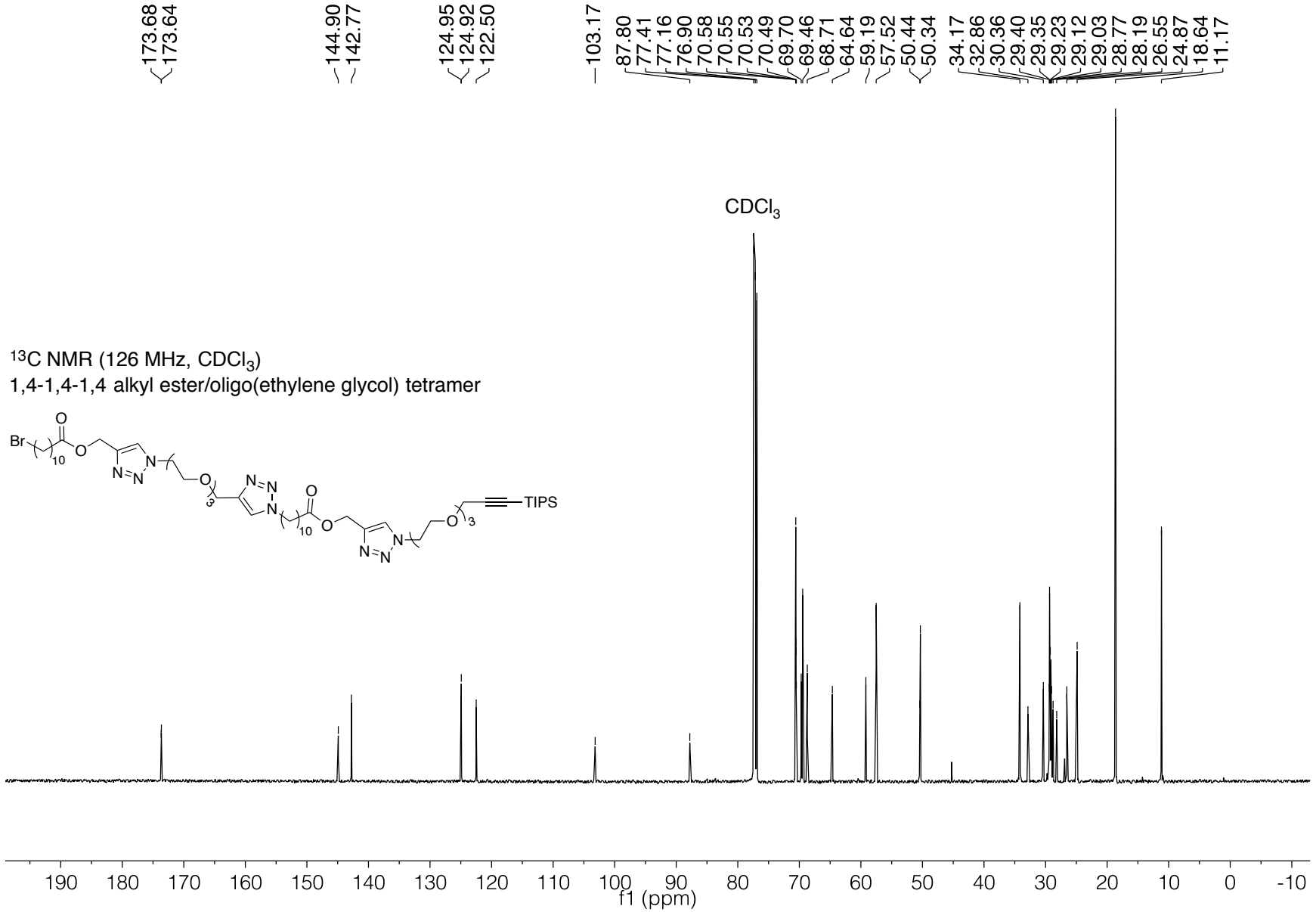

7.78
7.26
5.21
4.55
4.54
4.53
4.24
3.88
3.87
3.86
3.73
3.72
3.71
3.71
3.70
3.68
3.67
3.66
3.66
3.65
3.62
3.42
3.40
3.39
2.33
2.31
2.30
1.87
1.86
1.84
1.83
1.82
1.64
1.62
1.61
1.59
1.57
1.56
1.43
1.41
1.40
1.38
1.27
1.06
1H NMR (500 MHz, CDCl3)
1,4 alkyl ester/oligo(ethylene glycol) dimer
Br
10
O
O
N
N
N
O
3
TIPS
CDCl3
0.91
2.05
2.00
1.93
2.00
2.00
2.05
4.00
2.01
1.99
1.99
1.99
2.01
10.22
21.46
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

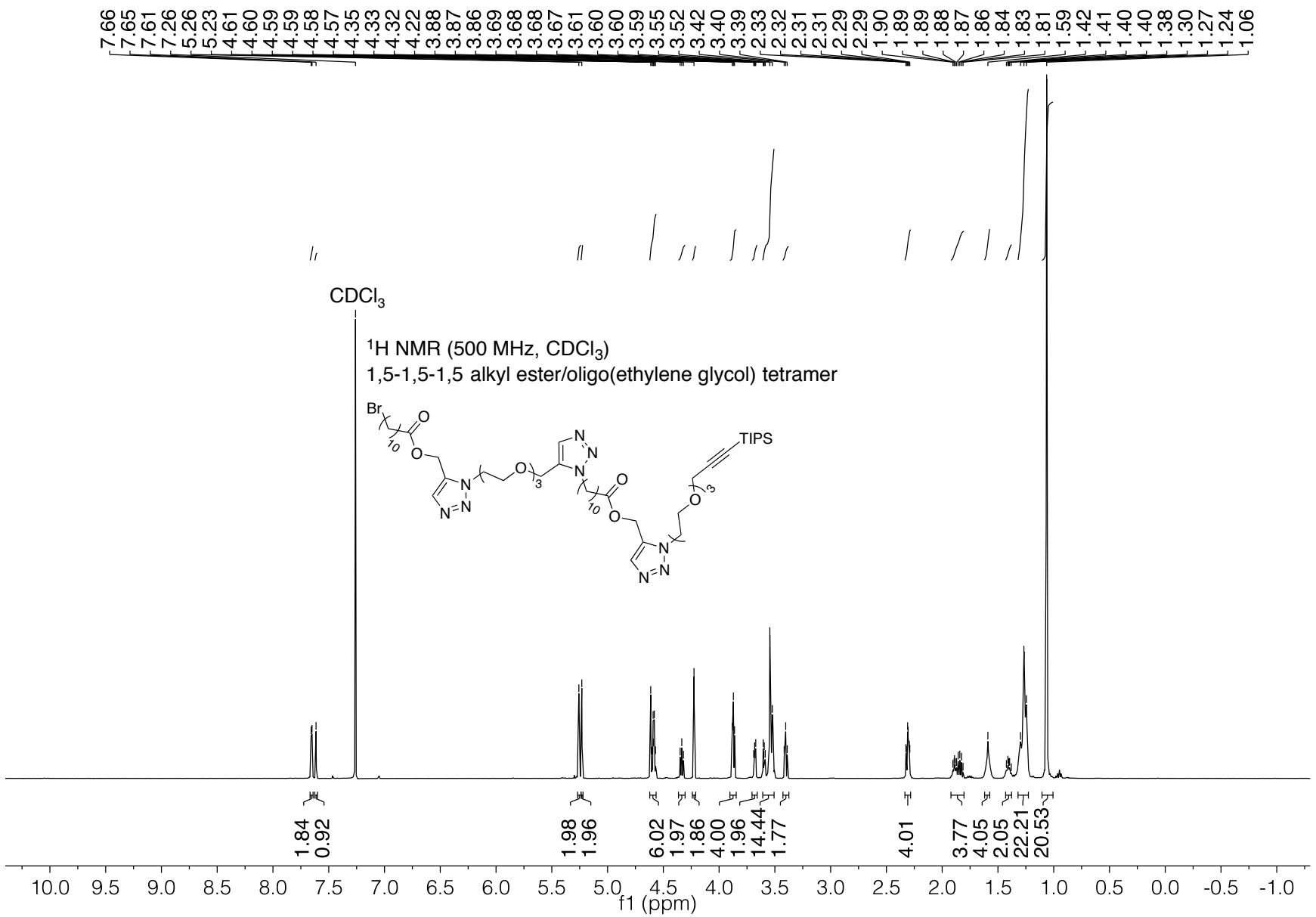

173.73
142.82
125.01
103.22
87.88
77.41
77.16
76.91
70.65
70.58
70.55
69.50
68.77
59.26
57.53
50.44
34.23
34.18
32.92
29.46
29.42
29.30
29.19
28.84
28.26
24.94
18.68
11.24
CDCl3
13C NMR (126 MHz, CDCl3)
1,4 alkyl ester/oligo(ethylene glycol) dimer
Br
10
O
N
N
N
O
3
TIPS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

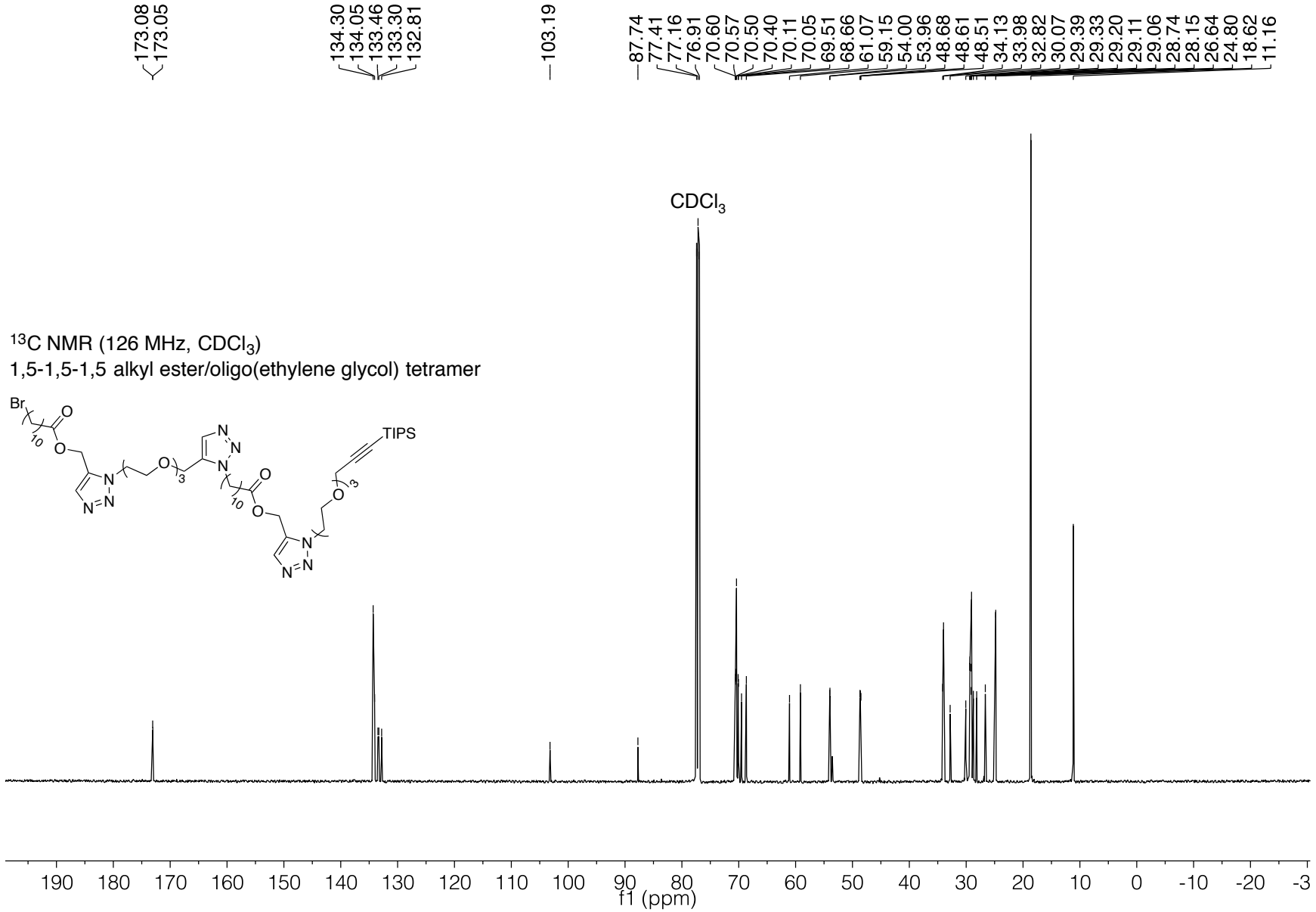

7.66
7.26
5.26
4.60
4.59
4.58
4.23
3.88
3.87
3.86
3.69
3.68
3.68
3.67
3.61
3.60
3.60
3.59
3.55
3.42
3.40
3.39
2.33
2.31
2.30
1.87
1.86
1.84
1.83
1.82
1.61
1.60
1.58
1.57
1.43
1.41
1.40
1.38
1.27
1.07
1H NMR (500 MHz, CDCl3)
1,5 alkyl ester/oligo(ethylene glycol) dimer
Br
10
O
O
N
N
N
3
O
TIPS
CDCl3
0.93
2.00
2.00
2.00
2.00
2.00
2.01
4.01
2.00
2.00
1.98
2.01
1.99
10.33
21.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


173.14
134.22
133.64
103.24
87.83
77.41
77.16
76.91
70.69
70.47
70.16
68.74
59.23
54.06
48.84
34.17
34.06
32.91
29.45
29.40
29.27
29.14
28.82
28.25
24.87
18.68
11.24
CDCl3
13C NMR (126 MHz, CDCl3)
1,5 alkyl ester/oligo(ethylene glycol) dimer
Br
10
O
N
N
N
3
O
TIPS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.78
7.53
7.26
5.20
5.20
4.67
4.54
4.53
4.53
4.52
4.34
4.33
4.31
4.23
3.88
3.87
3.86
3.72
3.72
3.71
3.69
3.68
3.67
3.66
3.64
3.63
3.62
3.61
3.42
3.40
3.39
2.32
2.31
2.29
1.90
1.88
1.87
1.86
1.84
1.83
1.81
1.63
1.62
1.60
1.59
1.57
1.42
1.41
1.39
1.31
1.26
1.06
1H NMR (500 MHz, CDCl3)
1,4-1,4-1,4 alkyl ester/oligo(ethylene glycol) tetramer
Br
O
10
O
N
N
N
O
3
N
N
N
O
10
O
N
N
N
O
3
TIPS
CDCl3
1.85
0.94
3.99
2.02
4.01
1.99
1.91
4.00
16.01
1.91
4.00
3.95
4.40
2.00
22.79
20.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


173.68
173.64
144.90
142.77
124.95
124.92
122.50
103.17
87.80
77.41
77.16
76.90
70.58
70.55
70.53
70.49
69.70
69.46
68.71
64.64
59.19
57.52
50.44
50.34
34.17
32.86
30.36
29.40
29.35
29.23
29.12
29.03
28.77
28.19
26.55
24.87
18.64
11.17
CDCl3
13C NMR (126 MHz, CDCl3)
1,4-1,4-1,4 alkyl ester/oligo(ethylene glycol) tetramer
Br
O
10
O
N
N
N
O
3
N
N
N
O
10
O
N
N
O
3
TIPS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.66 7.65 7.61 7.26 5.26 5.23 4.61 4.60 4.59 4.59 4.58 4.57 4.35 4.33 4.32 4.22 3.88 3.87 3.86 3.69 3.68 3.68 3.67 3.61 3.60 3.60 3.59 3.55 3.52 3.42 3.40 3.39 2.33 2.32 2.31 2.31 2.29 2.29 1.90 1.89 1.89 1.88 1.87 1.86 1.84 1.83 1.81 1.59 1.42 1.41 1.40 1.40 1.38 1.30 1.27 1.24 1.06
CDCl3
1H NMR (500 MHz, CDCl3)
1,5-1,5-1,5 alkyl ester/oligo(ethylene glycol) tetramer
Br
TIPS
1.84 0.92 1.98 1.96 6.02 1.97 1.86 4.00 1.96 14.44 1.77 4.01 3.77 4.05 2.05 22.21 20.53
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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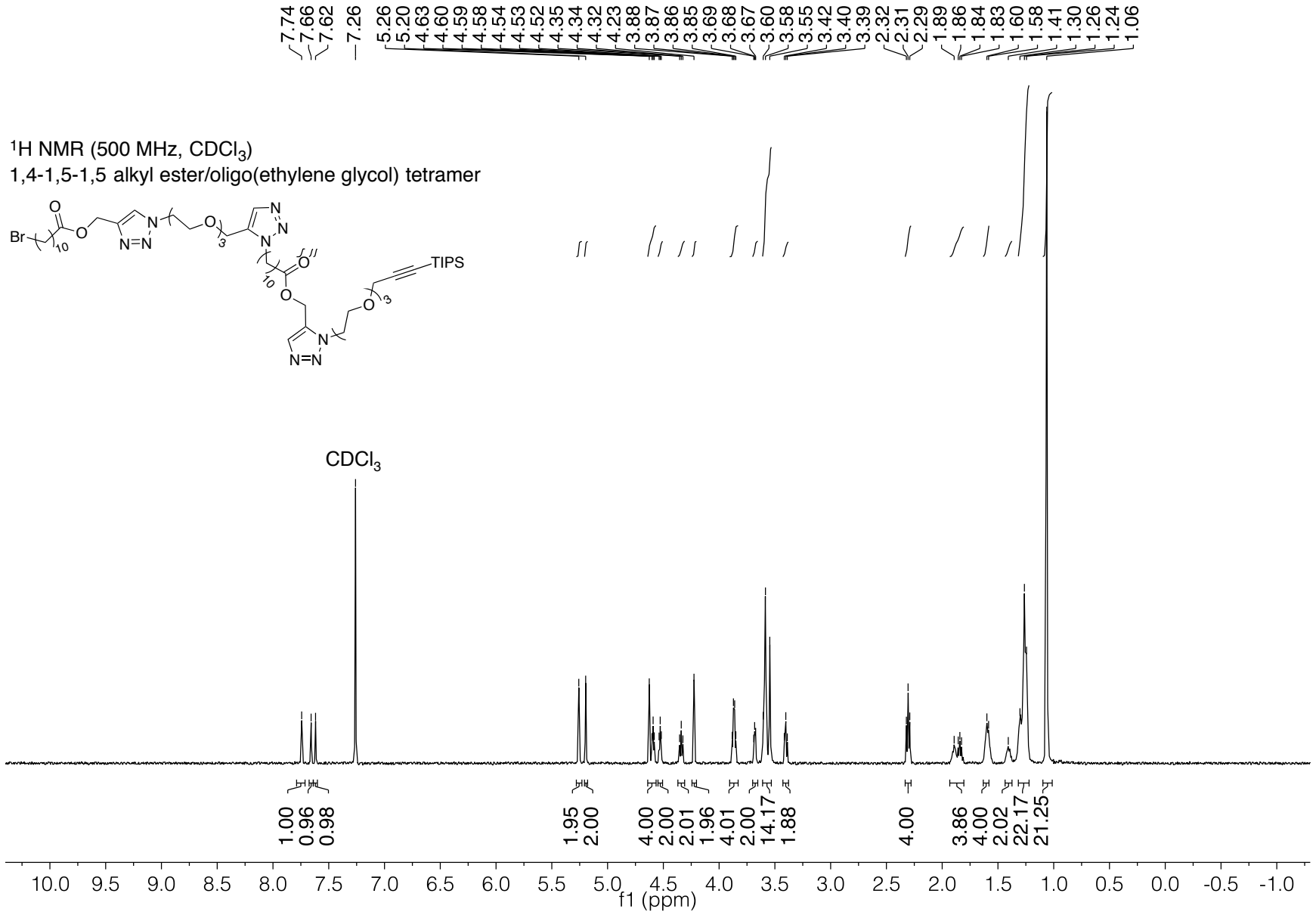
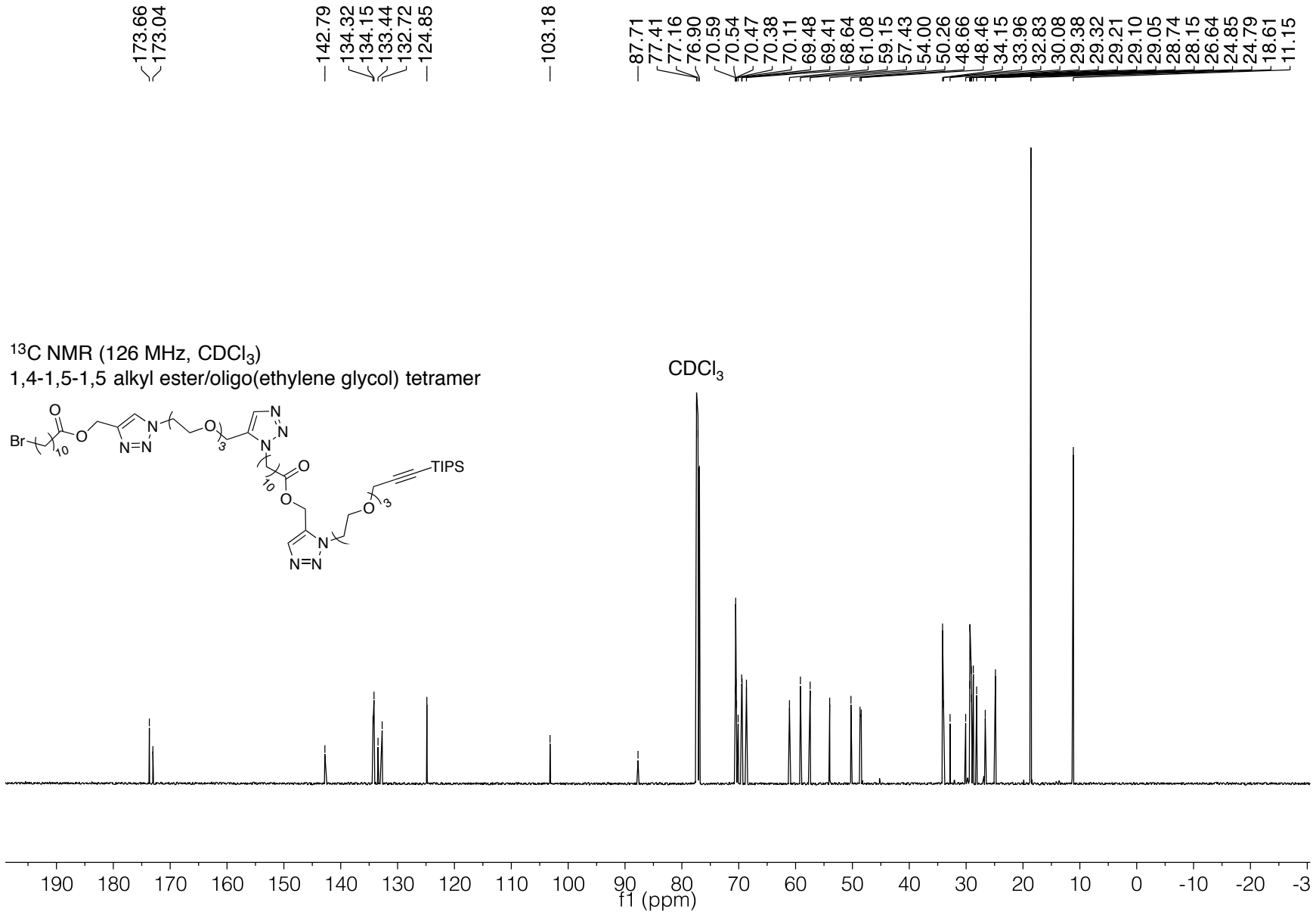
173.05
134.30
134.05
133.46
133.30
132.81
103.19
87.74
77.41
77.16
76.91
70.60
70.57
70.50
70.40
70.11
70.05
69.51
68.66
61.07
59.15
54.00
53.96
48.68
48.61
48.51
34.13
33.98
32.82
30.07
29.39
29.33
29.20
29.11
29.06
28.74
28.15
26.64
24.80
18.62
11.16
CDCl3
13C NMR (126 MHz, CDCl3)
1,5-1,5-1,5 alkyl ester/oligo(ethylene glycol) tetramer
Br
TIPS
f1 (ppm)


7.74
7.66
7.62
7.26
5.26
5.20
4.63
4.60
4.59
4.58
4.54
4.53
4.52
4.35
4.34
4.32
4.23
3.88
3.87
3.86
3.85
3.69
3.68
3.67
3.60
3.58
3.55
3.42
3.40
3.39
2.32
2.31
2.29
1.89
1.86
1.84
1.83
1.60
1.58
1.41
1.30
1.26
1.24
1.06
1H NMR (500 MHz, CDCl3)
1,4-1,5-1,5 alkyl ester/oligo(ethylene glycol) tetramer
Br
TIPS
CDCl3
1.00
0.96
0.98
1.95
2.00
4.00
2.00
2.01
1.96
4.01
2.00
14.17
1.88
4.00
3.86
4.00
2.02
22.17
21.25
f1 (ppm)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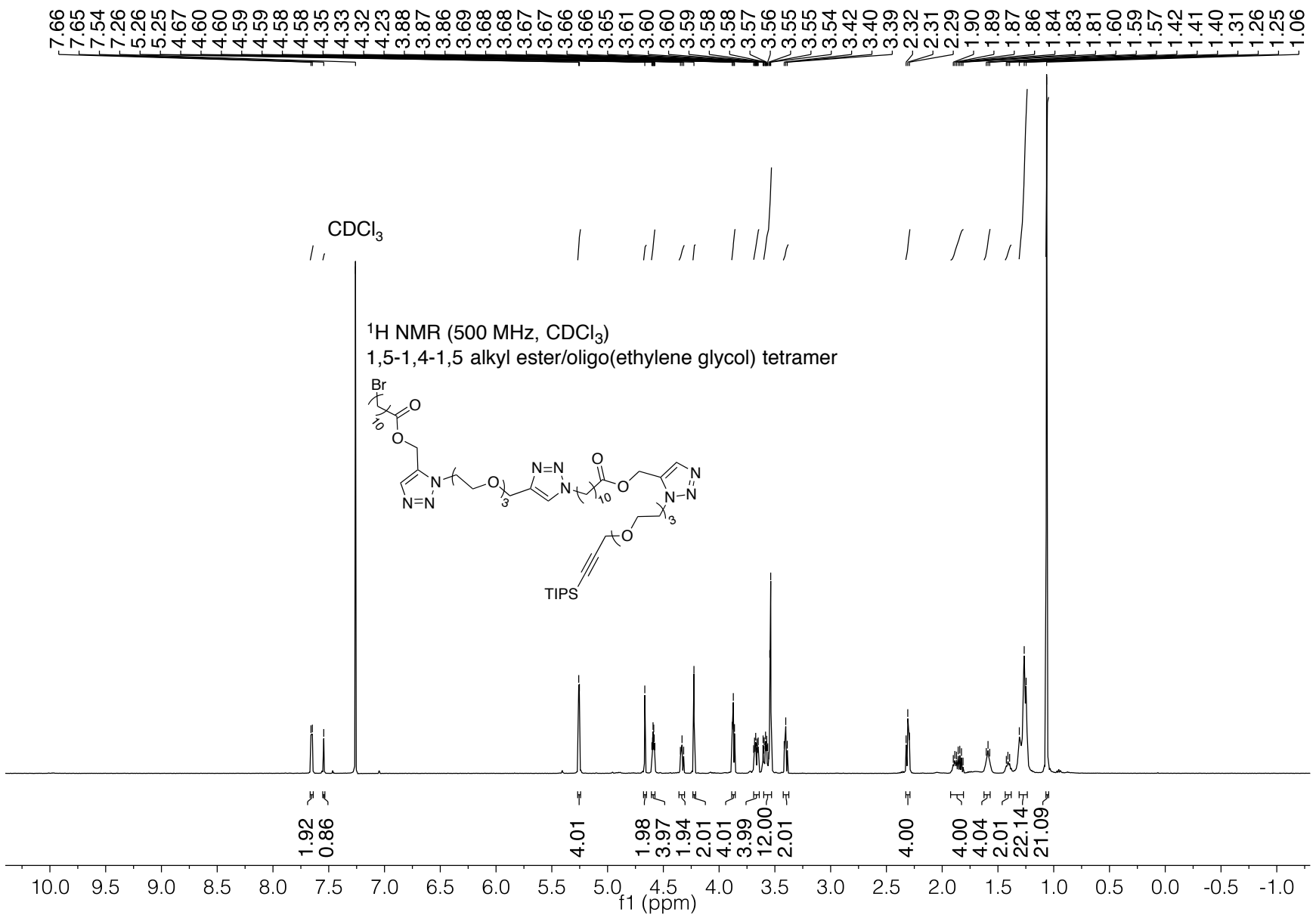
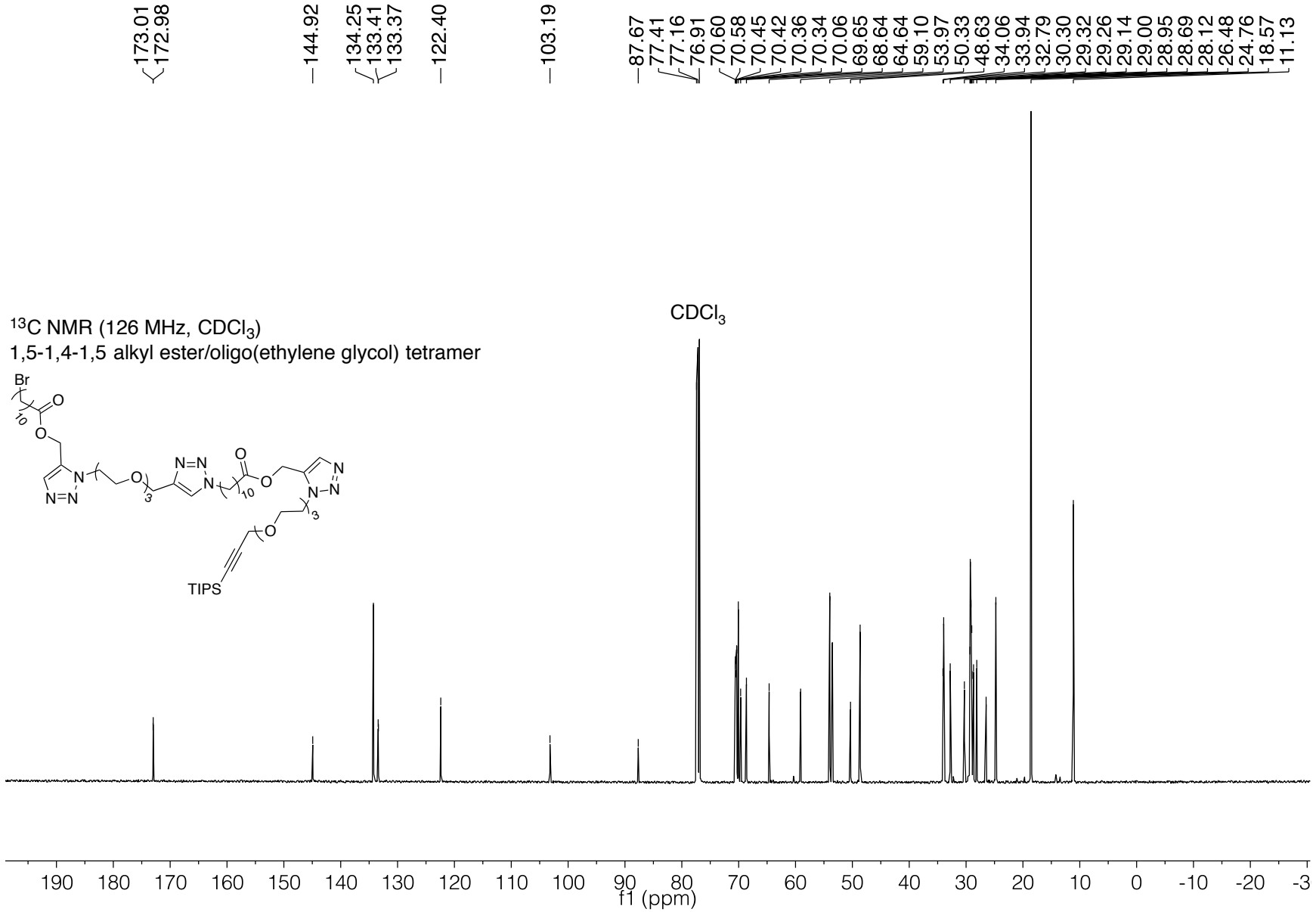
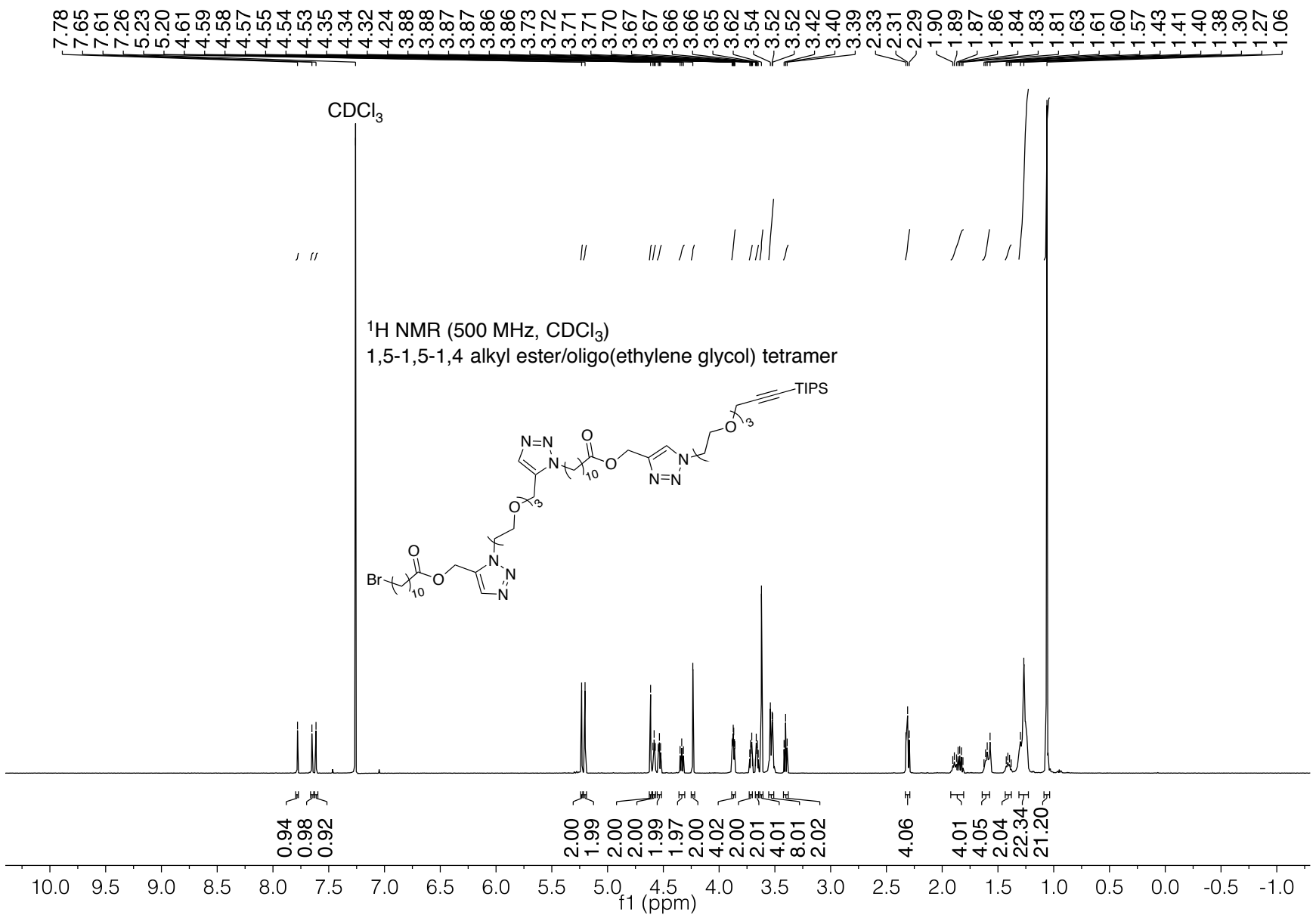
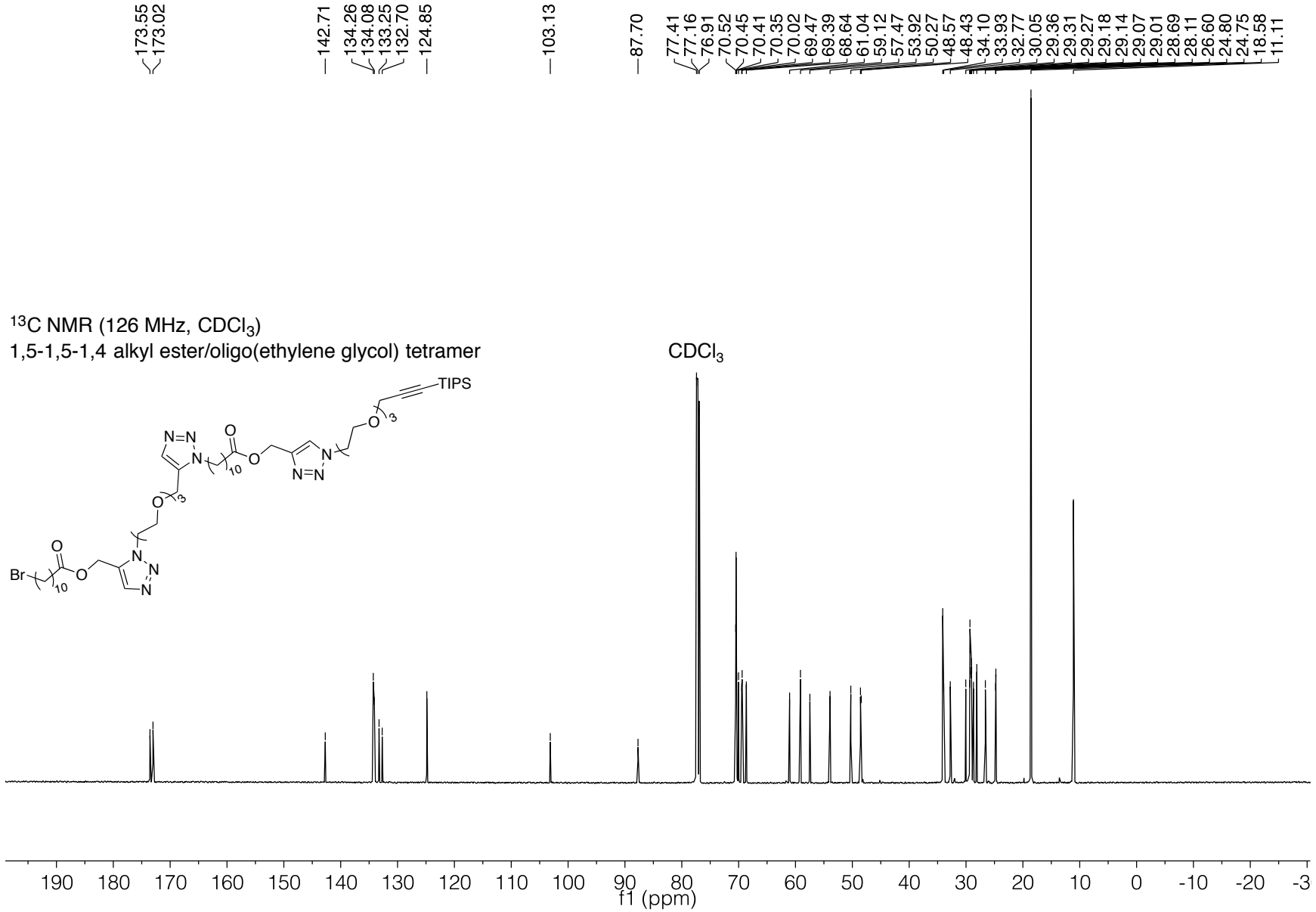
173.04
142.79
134.32
134.15
133.44
132.72
124.85
103.18
87.71
77.41
77.16
76.90
70.59
70.54
70.47
70.38
70.11
69.48
69.41
68.64
61.08
59.15
57.43
54.00
50.26
48.66
48.46
34.15
33.96
32.83
30.08
29.38
29.32
29.21
29.10
29.05
28.74
28.15
26.64
24.85
24.79
18.61
11.15
13C NMR (126 MHz, CDCl3)
1,4-1,5-1,5 alkyl ester/oligo(ethylene glycol) tetramer
CDCl3
Br
O
10
O
N=N
O
3
N
N
N
O
10
O
O
TIPS
3
N
N=N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-3
f1 (ppm)


7.66 7.65 7.54 7.26 5.26 5.25 4.67 4.60 4.60 4.59 4.59 4.58 4.58 4.35 4.33 4.32 4.23 3.88 3.87 3.86 3.69 3.68 3.68 3.67 3.67 3.66 3.65 3.61 3.60 3.60 3.59 3.58 3.58 3.57 3.56 3.55 3.55 3.54 3.42 3.40 3.39 2.32 2.31 2.29 1.90 1.89 1.87 1.86 1.84 1.83 1.81 1.60 1.59 1.57 1.42 1.41 1.40 1.31 1.26 1.25 1.06
CDCl3
1H NMR (500 MHz, CDCl3)
1,5-1,4-1,5 alkyl ester/oligo(ethylene glycol) tetramer
Br
TIPS
1.92 0.86 4.01 1.98 3.97 1.94 2.01 4.01 3.99 12.00 2.01 4.00 4.00 4.04 2.01 22.14 21.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


173.01
172.98
144.92
134.25
133.41
133.37
122.40
103.19
87.67
77.41
77.16
76.91
70.60
70.58
70.45
70.42
70.36
70.34
70.06
69.65
68.64
64.64
59.10
53.97
50.33
48.63
34.06
33.94
32.79
30.30
29.32
29.26
29.14
29.00
28.95
28.69
28.12
26.48
24.76
18.57
11.13
CDCl3
13C NMR (126 MHz, CDCl3)
1,5-1,4-1,5 alkyl ester/oligo(ethylene glycol) tetramer
Br
TIPS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-3
f1 (ppm)


7.78 7.65 7.61 7.26 5.23 5.20 4.61 4.59 4.58 4.57 4.55 4.54 4.53 4.35 4.34 4.32 4.24 3.88 3.88 3.87 3.87 3.86 3.86 3.73 3.72 3.71 3.71 3.70 3.67 3.67 3.66 3.66 3.65 3.62 3.54 3.52 3.52 3.42 3.40 3.39 2.33 2.31 2.29 1.90 1.89 1.87 1.86 1.84 1.83 1.81 1.63 1.61 1.60 1.57 1.43 1.41 1.40 1.38 1.30 1.27 1.06
CDCl3
1H NMR (500 MHz, CDCl3)
1,5-1,5-1,4 alkyl ester/oligo(ethylene glycol) tetramer
TIPS
Br
0.94 0.98 0.92 2.00 1.99 2.00 2.00 1.99 1.97 2.00 4.02 2.00 2.01 4.01 8.01 2.02 4.06 4.01 4.05 2.04 22.34 21.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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173.02
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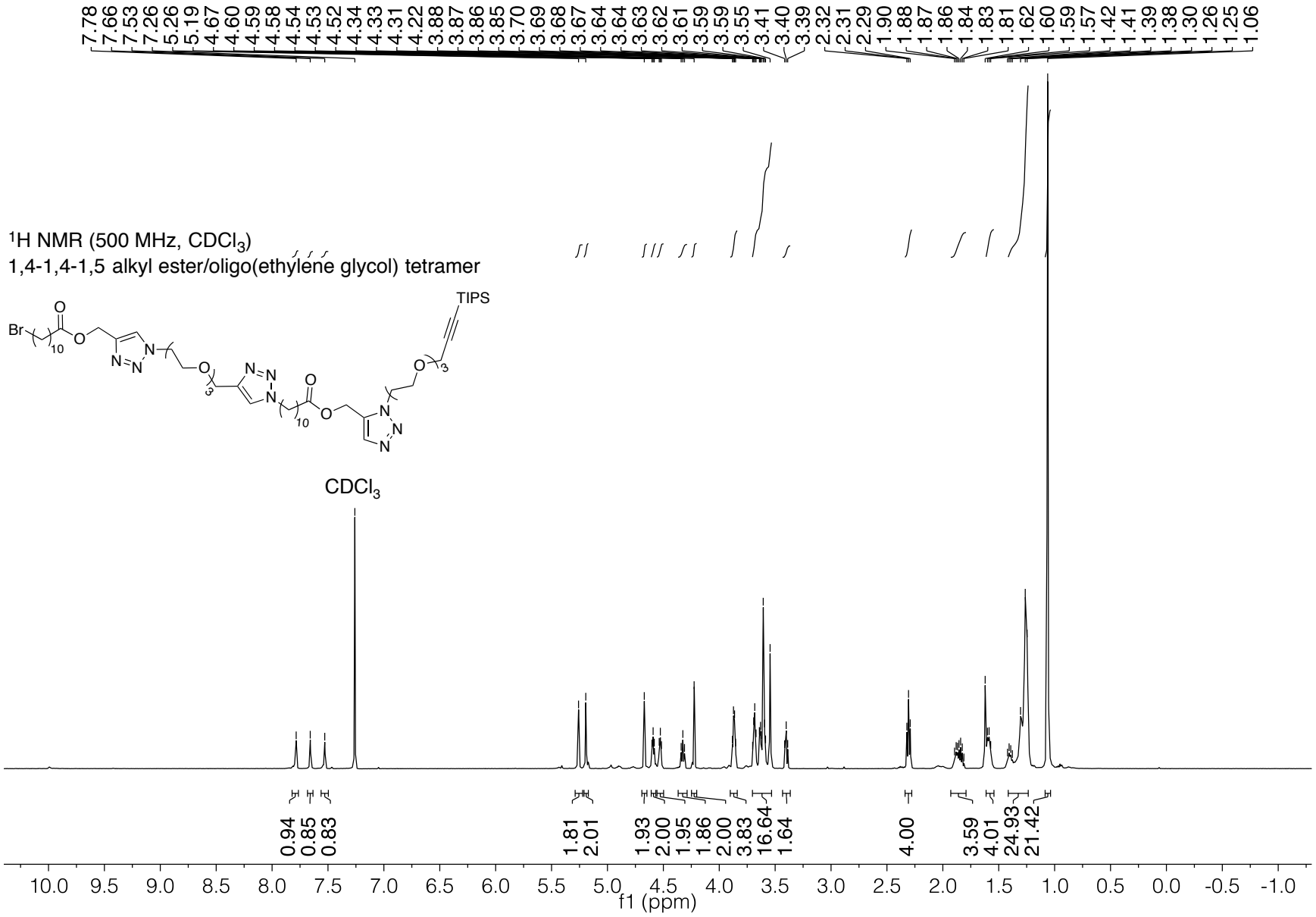
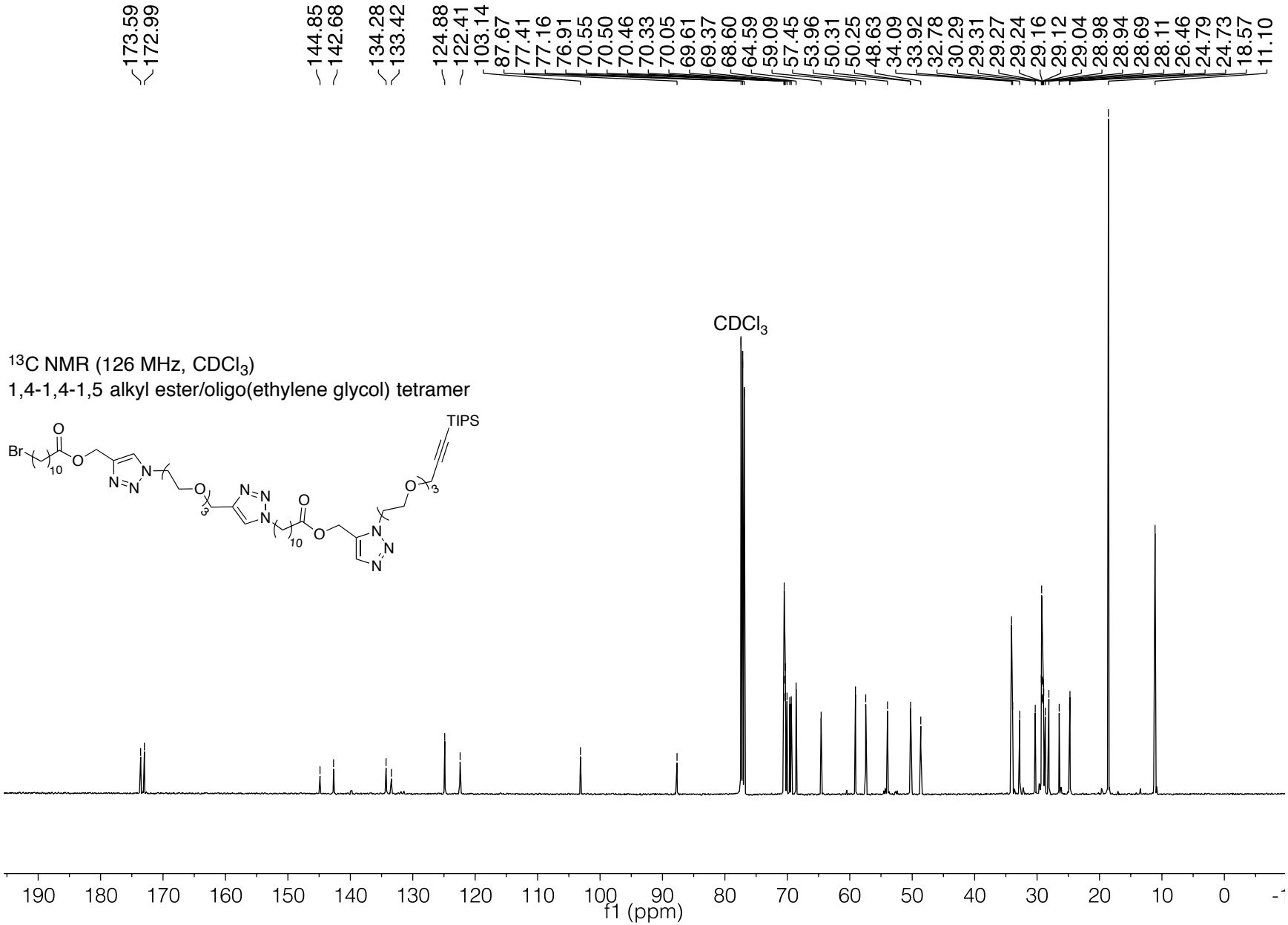
134.08
133.25
132.70
124.85
103.13
87.70
77.41
77.16
76.91
70.52
70.45
70.41
70.35
70.02
69.47
69.39
68.64
61.04
59.12
57.47
53.92
50.27
48.57
48.43
34.10
33.93
32.77
30.05
29.36
29.31
29.27
29.18
29.14
29.07
29.01
28.69
28.11
26.60
24.80
24.75
18.58
11.11
13C NMR (126 MHz, CDCl3)
1,5-1,5-1,4 alkyl ester/oligo(ethylene glycol) tetramer
CDCl3
TIPS
Br
f1 (ppm)


7.78 7.66 7.53 7.26 5.26 5.19 4.67 4.60 4.59 4.58 4.54 4.53 4.52 4.34 4.33 4.31 4.22 3.88 3.87 3.86 3.85 3.70 3.69 3.68 3.67 3.64 3.64 3.63 3.62 3.61 3.59 3.59 3.55 3.41 3.40 3.39 2.32 2.31 2.29 1.90 1.88 1.87 1.86 1.84 1.83 1.81 1.62 1.60 1.59 1.57 1.42 1.41 1.39 1.38 1.30 1.26 1.25 1.06
1H NMR (500 MHz, CDCl3)
1,4-1,4-1,5 alkyl ester/oligo(ethylene glycol) tetramer
TIPS
CDCl3
0.94 0.85 0.83 1.81 2.01 1.93 2.00 1.95 1.86 2.00 3.83 16.64 1.64 4.00 3.59 4.01 24.93 21.42
f1 (ppm)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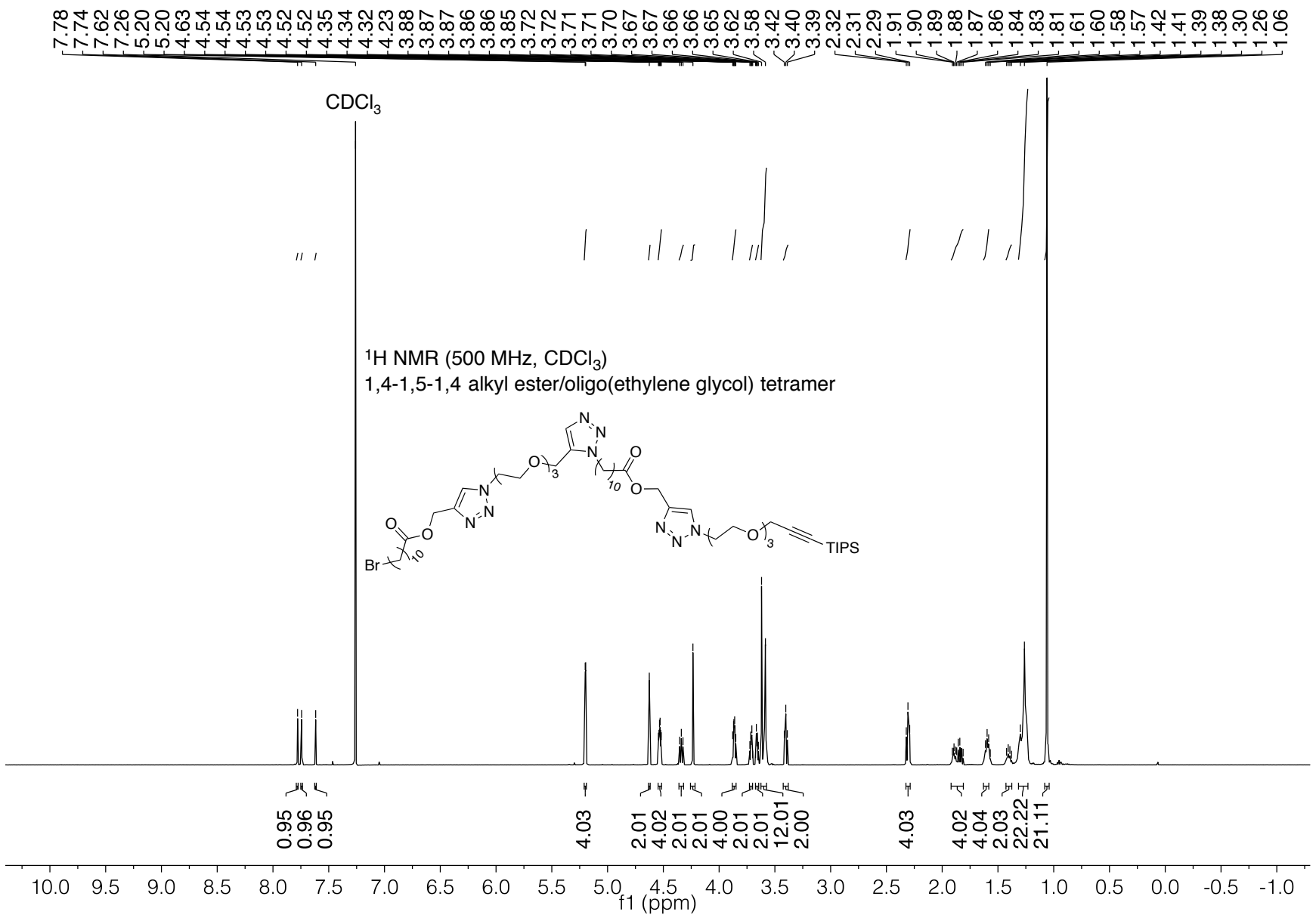
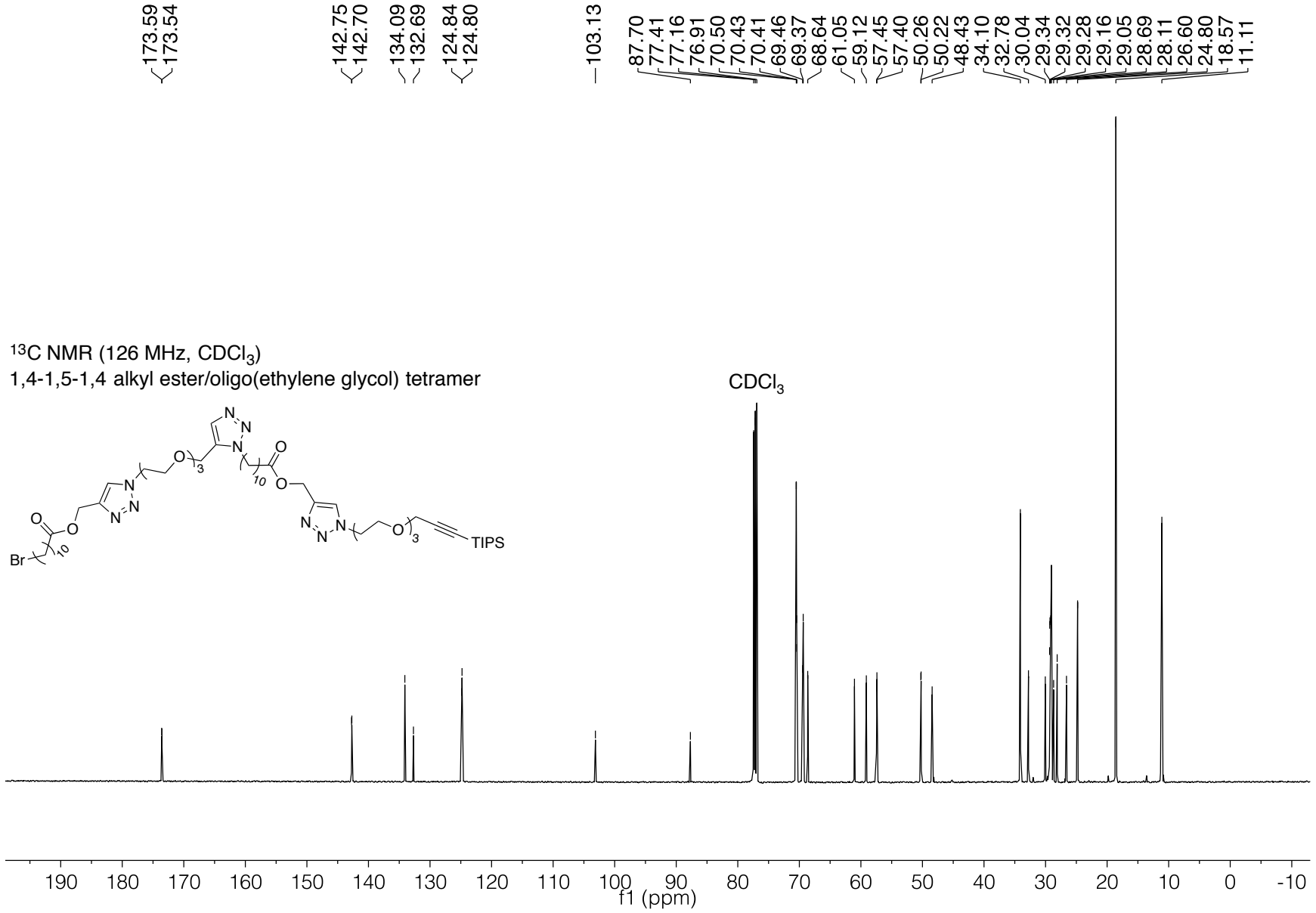
142.68
134.28
133.42
124.88
122.41
103.14
87.67
77.41
77.16
76.91
70.55
70.50
70.46
70.33
70.05
69.61
69.37
68.60
64.59
59.09
57.45
53.96
50.31
50.25
48.63
34.09
33.92
32.78
30.29
29.31
29.27
29.24
29.16
29.12
29.04
28.98
28.94
28.69
28.11
26.46
24.79
24.73
18.57
11.10
CDCl3
13C NMR (126 MHz, CDCl3)
1,4-1,4-1,5 alkyl ester/oligo(ethylene glycol) tetramer
TIPS
Br
f1 (ppm)


7.78 7.74 7.62 7.26 5.20 5.20 4.63 4.54 4.54 4.53 4.53 4.52 4.52 4.35 4.34 4.32 4.23 3.88 3.87 3.87 3.86 3.86 3.85 3.72 3.72 3.71 3.71 3.70 3.67 3.67 3.66 3.66 3.65 3.62 3.58 3.42 3.40 3.39 2.32 2.31 2.29 1.91 1.90 1.89 1.88 1.87 1.86 1.84 1.83 1.81 1.61 1.60 1.58 1.57 1.42 1.41 1.39 1.38 1.30 1.26 1.06
CDCl3
1H NMR (500 MHz, CDCl3)
1,4-1,5-1,4 alkyl ester/oligo(ethylene glycol) tetramer
Br
TIPS
0.95 0.96 0.95 4.03 2.01 4.02 2.01 2.01 4.00 2.01 2.01 12.01 2.00 4.03 4.02 4.04 2.03 22.22 21.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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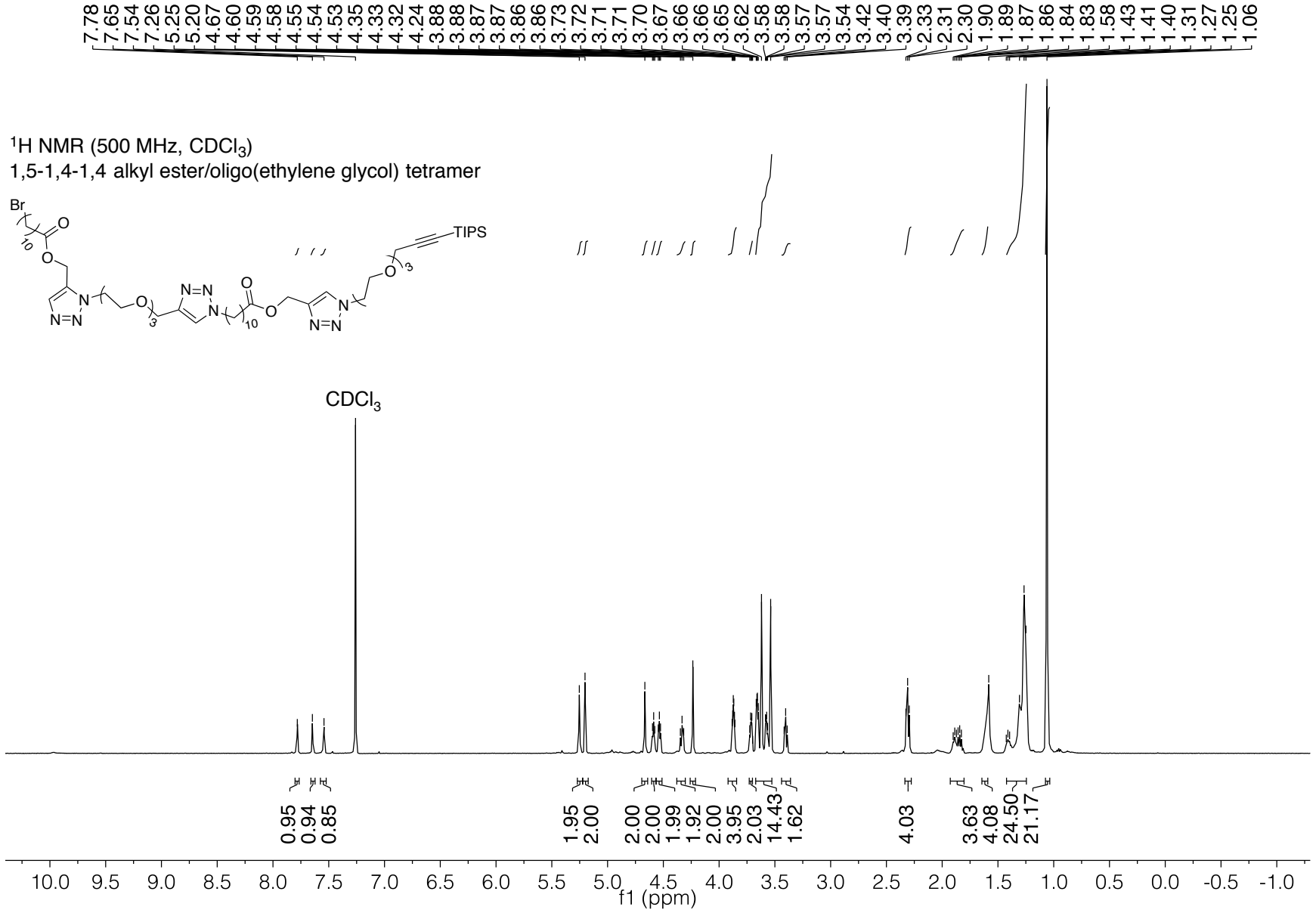
124.84
124.80
103.13
87.70
77.41
77.16
76.91
70.50
70.43
70.41
69.46
69.37
68.64
61.05
59.12
57.45
57.40
50.26
50.22
48.43
34.10
32.78
30.04
29.34
29.32
29.28
29.16
29.05
28.69
28.11
26.60
24.80
18.57
11.11
13C NMR (126 MHz, CDCl3)
1,4-1,5-1,4 alkyl ester/oligo(ethylene glycol) tetramer
CDCl3
Br
TIPS
f1 (ppm)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7.65
7.54
7.26
5.25
5.20
4.67
4.60
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4.58
4.55
4.54
4.53
4.35
4.33
4.32
4.24
3.88
3.88
3.87
3.87
3.86
3.86
3.73
3.72
3.71
3.71
3.70
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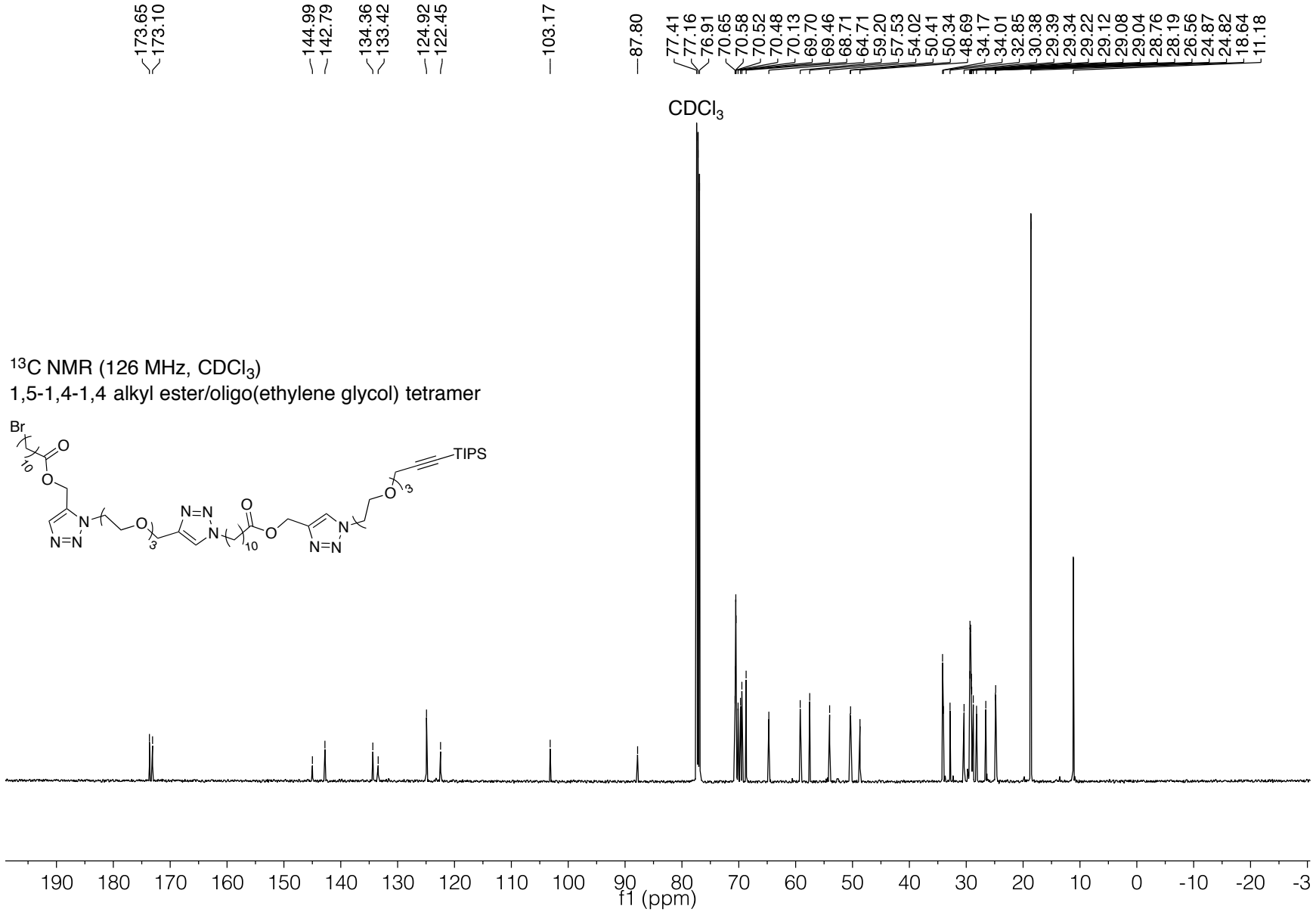
3.66
3.66
3.65
3.62
3.58
3.58
3.57
3.57
3.54
3.42
3.40
3.39
2.33
2.31
2.30
1.90
1.89
1.87
1.86
1.84
1.83
1.58
1.43
1.41
1.40
1.31
1.27
1.25
1.06
1H NMR (500 MHz, CDCl3)
1,5-1,4-1,4 alkyl ester/oligo(ethylene glycol) tetramer
Br
TIPS
CDCl3
0.95
0.94
0.85
1.95
2.00
2.00
2.00
1.99
1.92
2.00
3.95
2.03
14.43
1.62
4.03
3.63
4.08
24.50
21.17
f1 (ppm)


173.65
173.10
144.99
142.79
134.36
133.42
124.92
122.45
103.17
87.80
77.41
77.16
76.91
70.65
70.58
70.52
70.48
70.13
69.70
69.46
68.71
64.71
59.20
57.53
54.02
50.41
50.34
48.69
34.17
34.01
32.85
30.38
29.39
29.34
29.22
29.12
29.08
29.04
28.76
28.19
26.56
24.87
24.82
18.64
11.18
CDCl3
13C NMR (126 MHz, CDCl3)
1,5-1,4-1,4 alkyl ester/oligo(ethylene glycol) tetramer
Br
TIPS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -3
f1 (ppm)