Supporting Information for

Self-Assembled Dehydro[24]annnulene Monolayers at the Liquid/Solid Interface: Towards On-Surface Synthesis of Tubular π-Conjugated Nanowires

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1. Synthesis

1.1. General

All reactions were carried out under argon unless otherwise noted. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were acquired on a Bruker ARX-500 or DRX-500 spectrometer at 297–300 K, and chemical shifts were calculated using the solvent resonances as internal standards (^{1}H: 7.26 ppm for $CHCl_3$, 2.05 ppm for acetone; $^{13}C\{^{1}H\}$: 77.00 ppm for $CDCl_3$, 29.92 ppm for acetone-d_6). Infrared spectra were recorded on a Jasco FT/IR-420 spectrometer, and wavenumbers are reported in cm^{-1} with peak descriptions: s (strong), m (medium), w (weak), br (broad), sh (shoulder). UV–vis absorption spectra were measured on a Shimadzu UV-3101PC spectrometer and absorption peak wavelengths were reported in nm with molar absorptivities in $M^{-1}\cdot cm^{-1}$. Mass spectra were acquired on an Applied Biosystems Voyager-DE-STR MALDI-TOF instrument. Column chromatography was performed on silica gel purchased from Sorbent Technologies (standard grade, 60 Å, 40–63 μm). Analytical thin layer chromatography (TLC) was performed on Whatman 250 μm-thick silica gel 60 plates with a fluorescent indicator. Visualization of TLC spots was accomplished with UV light at 254 nm.

1.2. Materials

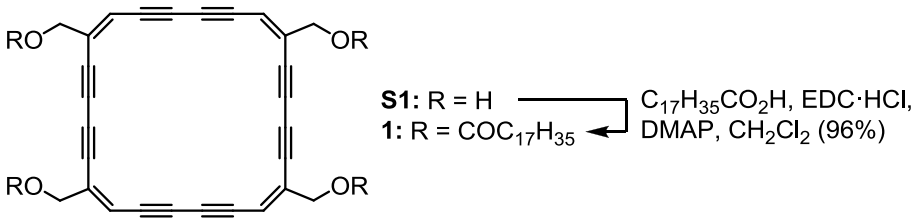
CH_2Cl_2, THF, and toluene were distilled under argon immediately before use over drying agents (CaH_2 for CH_2Cl_2, sodium and benzophenone for THF and toluene). DMF was distilled under vacuum over $MgSO_4$ and stored on molecular sieve 4Å. Et_3N, *i*-Pr_2NEt, and piperidine were distilled over CaH_2 and stored under argon. TMEDA was stored on molecular sieve 4Å for at least 3 days before use. Other solvents and reagents were obtained from commercial sources and used without further purification.

1.3. Procedures and Characterization

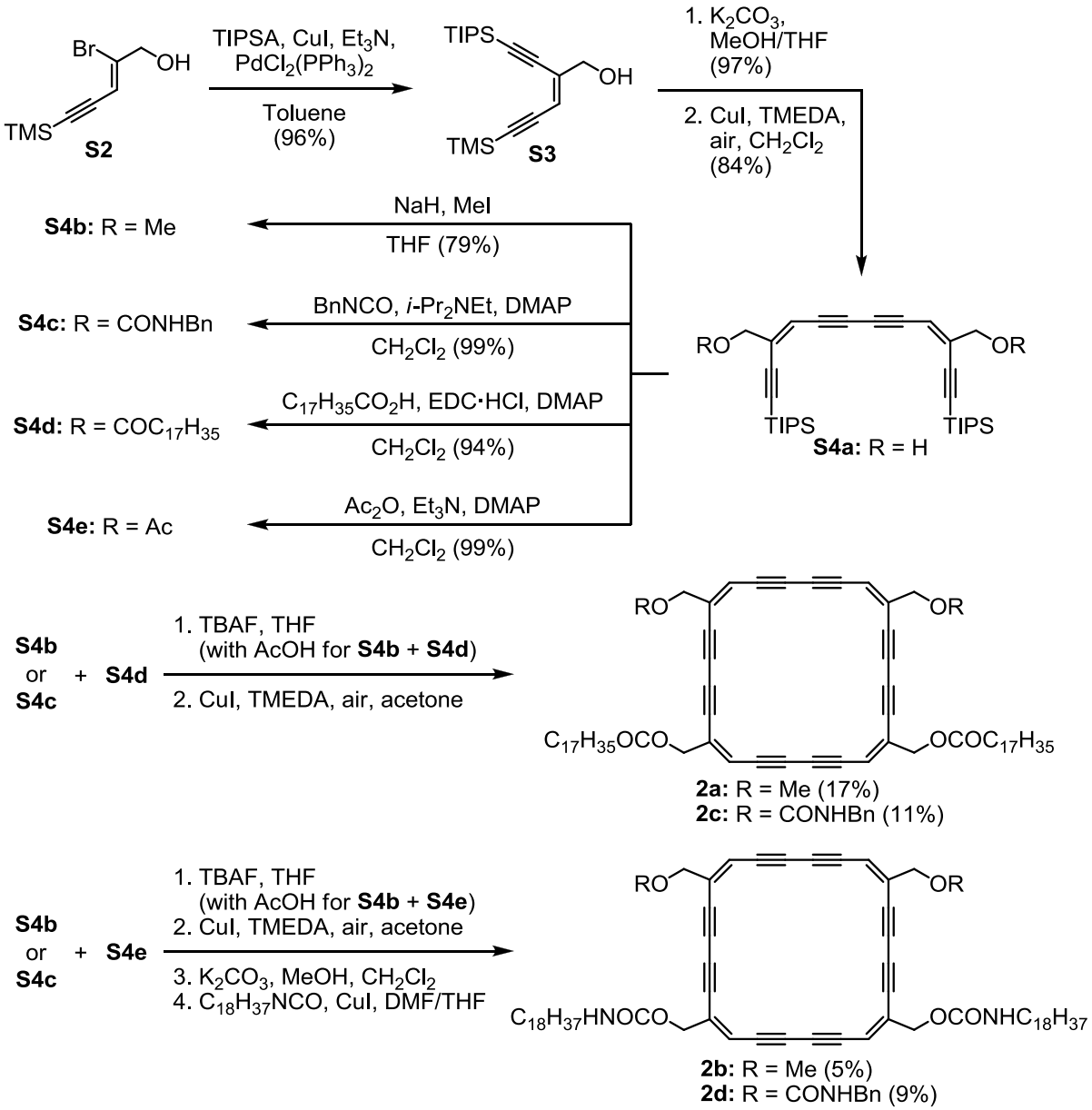
Tetrasterate **1** was obtained by fourfold esterification of the corresponding tetraol **S1**[1] (Scheme S1). A series of nonsymmetrically substituted derivatives **2a–2d** were synthesized from the known trimethylsilyl-protected bromoenyne derivative **S2**[2] (Scheme S2). The other series of nonsymmetrically substituted dehydro[24]annulenes **3a–3c** were synthesized via derivatization of **S5a**[1] followed by Hay

coupling, hydrolytic removal of acetyl moieties, and introduction of long alkyl chains through ester or carbamate linkages (Scheme S3).

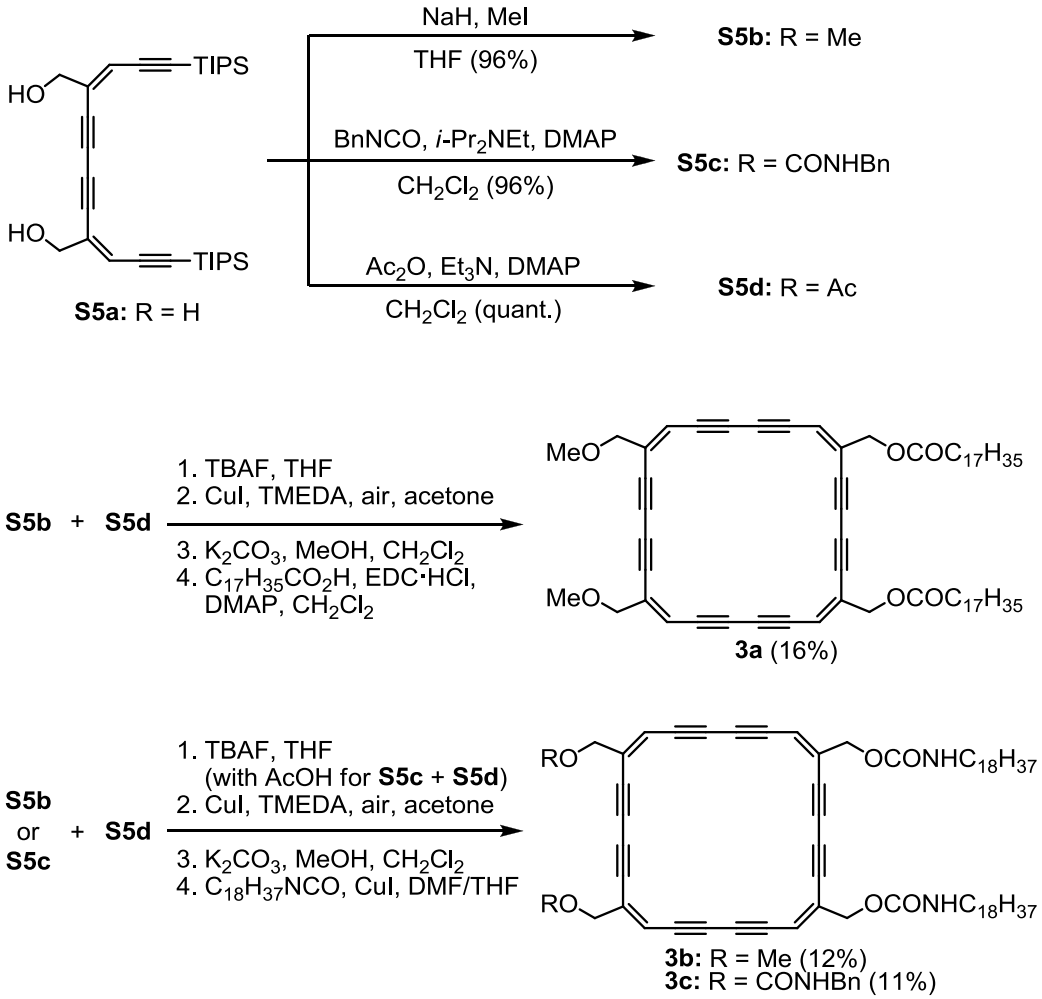
Scheme S1. Synthesis of tetrastearate **1**.



Scheme S2. Synthesis of nonsymmetrically substituted derivatives **2a**–**2d**.

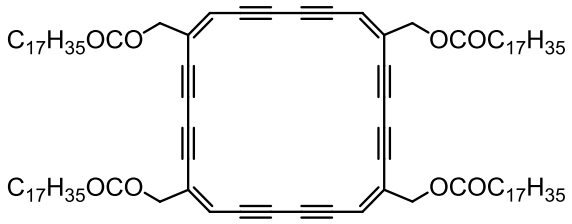


Scheme S3. Synthesis of nonsymmetrically substituted derivatives **3a**–**3c**.



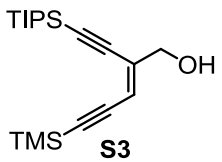
(1*E*,6*E*,12*E*,18*E*)-Cyclotetracosa-6,12,18,24-tetraen-2,4,8,10,14,16,20,22-octayne-1,6,13,18-tetrayltetrakis(methylene) tetrastearate (1). EDC·HCl (79.6 mg, 415 μmol) was added to a mixture of tetraol **S1**[1] (33.0 mg, 79.2 μmol), stearic acid (110 mg, 385 μmol), and DMAP (7.81 mg, 64.8 μmol) in a mixture of THF (5 mL) and CH_2Cl_2 (5 mL) at 0 °C. The reaction was stirred for 10 min at 0 °C and allowed to warm up. After stirred for 12 h at 25 °C, the solution was evaporated to dryness to provide an orange solid, which was then subjected to flash silica gel column chromatography (CH_2Cl_2). The resulting solid was further purified by precipitating from a CH_2Cl_2 solution by adding MeOH to afford **1** (113 mg, 96%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 0.88 (t, J = 7.0 Hz, 12H), 1.25–1.29 (m, 112H), 1.63 (quintet, J = 7.3 Hz, 8H), 2.36 (t, J = 7.6 Hz, 8H), 4.65 (s, 8H), 6.16 (s, 4H); ^{13}C{^{1}H} NMR

(126 MHz, $CDCl_3$), [ppm]: 14.1, 22.7, 24.8, 29.1, 29.2, 29.4, 29.4, 29.6, 29.6, 29.7, 31.9, 34.0, 64.4, 81.3, 81.8, 82.6, 82.7, 118.6, 131.3, 172.8; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3032 (w), 2954 (m), 2918 (s), 2850 (s), 2185 (w), 2125 (w), 1734 (s), 1466 (m), 1387 (m), 1171 (m), 1155 (m); UV–vis (cyclohexane), λ_{max} [nm] (ε [$M^{-1}\cdot cm^{-1}$]): 252 (53 100), 333 (44 300), 356 (52 800); HRMS (ESI) *m*/*z* calcd for $C_{100}H_{152}O_8Na$ [M + Na]$^+$: 1504.1379, found: 1504.1394.



1

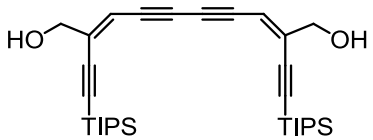
(*E*)-2-((Triisopropylsilyl)ethynyl)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (S3). (*Z*)-2-bromo-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (**S2**)[2] (2.50 g, 10.7 mmol) was dissolved in 25 mL of toluene. Piperidine (2.12 mL, 1.82 g, 21.4 mmol), triisopropylsilylacetylene (4.81 mL, 3.91 g, 21.4 mmol), $PdCl_2(PPh_3)_2$ (38.0 mg, 54.1 μmol), and CuI (31.4 mg, 0.164 mmol) were subsequently added. After stirred at 25 °C for 2 h, the solution was poured into a separatory funnel containing Et_2O (20 mL) and HCl aq. (10%, 20 mL). The organic phase was separated, washed with 20 mL of water, dried over $MgSO_4$, filtered, and evaporated. The resulting crude product was subjected to flash silica gel column chromatography (hexanes/AcOEt, 10/1) to afford **S3** (3.46 g, 96%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 0.18 (s, 18H), 1.10 (s, 42H), 1.97 (br s, 2H), 4.18 (d, J = 6.5 Hz, 4H), 5.99 (s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), [ppm]: −0.20, 11.1, 18.7, 65.0, 100.8, 102.0, 102.1, 102.6, 114.2, 135.1; IR (neat film), $\bar{\nu}_{max}$ [cm^{-1}]: 3351 (br m), 2948 (s), 2944 (s), 2892 (s), 2865 (s), 2752 (w), 2720 (w), 2181 (w), 2139 (m), 1578 (w), 1463 (m), 1250 (s), 1092 (m), 1057 (m), 878 (s), 843 (s).



S3

(2*E*,8*E*)-2,9-Bis(triisopropylsilylethynyl)deca-2,8-dien-4,6-diyne-1,10-diol (S4a). Protected enediyne **S3** (3.40 g, 10.1 mmol) was dissolved in a mixture of THF (10 mL) and MeOH (30 mL), to which anhydrous K_2CO_3 (140 mg, 1.01 mmol) was added. After stirred at 25 °C for 25 min under air, the mixture was poured into a separatory funnel containing Et_2O (70 mL) and NaCl aq. (10%, 70 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (35 mL × 2). All the organic phases were combined, washed with brine (35 mL), dried over $MgSO_4$, filtered, and evaporated. The resulting crude product was subjected to flash silica gel column chromatography (hexanes/AcOEt, 5:1) to afford (*E*)-2-(triisopropylsilylethynyl)pent-2-en-4-yn-1-ol (2.57 g, 97%) as a brown-yellow oil. The complete removal of the trimethylsilyl group was confirmed by NMR: ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 1.10 (s, 42H), 2.03 (t, *J* = 5.9 Hz, 2H), 3.26 (d, *J* = 1.8 Hz, 2H), 4.20 (d, *J* = 6.1 Hz, 4H), 5.96 (d, *J* = 1.6 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 11.1, 18.6, 64.7, 80.9, 84.0, 100.9, 102.3, 113.3, 136.5.

The compound obtained above (2.51 g, 9.57 mol) was dissolved in CH_2Cl_2 (95 mL), to which CuI (365 mg, 1.91 mmol) and TMEDA (2.90 mL, 2.23 g, 192 mmol) were sequentially added. After stirred at 25 °C for 5 h under air, the solvents were removed under vacuum and subjected to flash silica gel column chromatography (CH_2Cl_2, then CH_2Cl_2/AcOEt, 25/1) to afford **S4a** (2.11 g, 84%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 1.10 (s, 42H), 1.84 (br s, 2H), 4.23 (d, *J* = 3.5 Hz, 4H), 6.08 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 11.1, 18.6, 64.8, 80.8, 81.1, 102.4, 102.4, 113.4, 137.7; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3253 (br s), 3032 (w), 2941 (s), 2874 (m), 2863 (s), 2198 (w), 2137 (m), 1688 (w), 1585 (w), 1462 (m), 1059 (s), 1015 (s), 880 (s), 850 (m), 676 (m), 659 (m); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 545.3 (100, $[M + Na]^+$), 659.3 (60, $[M + C_7H_4O_3]^+$)[a]. ([a]Formed by a reaction with the matrix compound, 2,5-dihydroxybenzoic acid.)



S4a

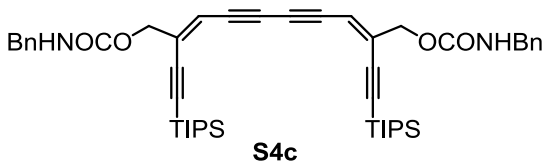
((3*E*,9*E*)-3,10-Bis(methoxymethyl)-1,12-bis(triisopropylsilyl)dodeca-3,9-dien-1,5,7,11-tetrayne

(S4b). Compound **S4a** (250 mg, 0.478 mmol) was dissolved in THF (15 mL), to which NaH (116 mg, 2.90 mmol) and MeI (0.30 mL, 0.68 g, 4.8 mmol) were added. Upon the addition of NaH, the yellow solution turned brown. The mixture was stirred at 25 °C for 1 h, then the reaction was terminated by adding water (7.5 mL) dropwise. The products were extracted with Et_2O (15 mL × 2). The Et_2O phases were combined, dried over $MgSO_4$, filtered, and evaporated to give a brown oil. The crude product was purified by flash silica gel column chromatography (hexanes/CH_2Cl_2, 3/2) to afford **S4b** (209 mg, 79%) as a brown-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 1.10 (s, 42H), 3.39 (s, 6H), 4.01 (s, 4H), 6.04 (s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), [ppm]: 11.2, 18.6, 58.5, 73.7, 80.8, 81.3, 101.5, 102.9, 114.0, 135.2; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3043 (w), 3005 (w), 2949 (sh), 2937 (s), 2873 (m), 2863 (s), 2844 (sh), 2825 (sh), 2144 (m), 2078 (w), 1668 (w), 1575 (m), 1466 (m), 1384 (m), 1198 (s), 1111 (s), 983 (m), 978 (m), 880 (s), 674 (s), 610 (s); UV–vis (cyclohexane), λ_{max} [nm] (ε [$M^{-1}\cdot cm^{-1}$]): 270 (15 800), 284 (16 600), 300 (19 000), 323 (19 100), 347 (23 400), 374 (22 000); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 519.5 (33, $[M - OCH_3]^+$), 551.5 (25, $[M + H]^+$), 573.5 (100, $[M + Na]^+$).

S4b

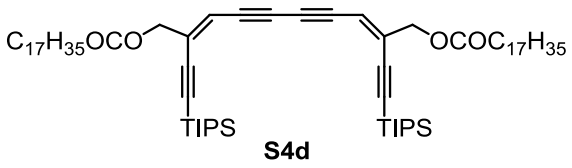
(2*E*,8*E*)-2,9-Bis((triisopropylsilyl)ethynyl)deca-2,8-dien-4,6-diyne-1,10-diylbis(benzylcarbamate) (S4c). Compound **S4a** (0.253 g, 0.484 mmol) and DMAP (12.1 mg, 99.0 μmol) were dissolved in CH_2Cl_2 (5 mL), to which *i*-Pr_2NEt (0.30 mL, 0.22 g, 1.7 mmol) and benzyl isocyanate (210 μL, 228 mg, 1.71 mmol) were sequentially added. The solution was stirred at 25 °C overnight, then poured into a separatory funnel containing 25 mL of AcOEt and 10 mL of 10% NH_4Cl. The organic phase was isolated, washed with water (10 mL × 3) and brine (10 mL), dried over $MgSO_4$, filtered, and evaporated to give a pale yellow solid. The crude product was purified by flash silica gel column chromatography (CH_2Cl_2/AcOEt, 50:1 then 25:1) to afford **S4c** (0.379 g, 99%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]:

1.11 (s, 42H), 4.38 (d, J = 5.8 Hz, 4H), 4.69 (s, 4H), 4.97, 5.13 (two s, 2H in total), 5.84−5.99 (two s, 2H in total), 7.28−7.36 (m, 10H (overlapping with $CHCl_3$)); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), [ppm]: 11.0, 18.6, 45.1, 65.5, 81.1, 81.1, 102.3, 102.3, 114.9, 127.5, 127.6, 128.7, 133.4, 138.1, 155.5; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3298 (m), 3070 (w), 3060 (w), 3023 (w), 2949 (sh), 2944 (s), 2890 (m), 2865 (s), 2146 (w), 2127 (w), 1706 (m), 1695 (s), 1547 (s), 1462 (m), 1267 (s), 1244 (s), 1148 (m), 1043 (m), 993 (m), 881 (m), 676 (m), 660 (m); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 811.7 (100, $[M + Na]^+$), 828.7 (15, $[M + K]^+$).



S4c

(2*E*,8*E*)-2,9-Bis(triisopropylsilylethynyl)deca-2,8-dien-4,6-diyne-1,10-diyl distearate (S4d). Compound **S4a** (307 mg, 0.587 mmol), DMAP (29.8 mg, 0.244 mmol), and stearic acid (411 mg, 1.44 mmol) were dissolved in CH_2Cl_2 (20 mL). After addition of EDC·HCl (303 mg, 1.58 mmol), the solution was stirred for 18 h at 25 °C, and evaporated to provide an orange-brown oil. The crude product was purified by flash silica gel column chromatography (CH_2Cl_2/hexanes, 2:1) to afford **S4d** (568 mg, 94 %) as a pale yellow solid. ^1H NMR (500 MHz, $CDCl_3$), [ppm]: 0.87 (t, J = 6.7 Hz, 6H), 1.10 (s, 42H), 1.25 (s, 56H), 1.63 (t, J = 6.9 Hz, 4H), 2.34 (t, J = 7.5 Hz, 4H), 4.65 (s, 4H), 5.98 (s, 2.0 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), [ppm]: 11.1, 14.1, 18.5, 22.7, 24.9, 29.1, 29.2, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9, 34.1, 64.8, 81.1, 81.2, 102.3, 102.3, 115.3, 132.9, 172.8; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3003 (sh), 2918 (s), 2850 (s), 2191 (w), 2142 (w), 2125 (w), 1749 (s), 1577 (w), 1467 (m), 1383 (m), 1143 (s), 880 (m), 678 (m), 660 (m); UV–vis (cyclohexane), λ_{max} [nm] (ε [$M^{-1}\cdot cm^{-1}$]): 271 (17 300), 284 (18 000), 300 (20 400), 323 (20 200), 350 (26 000), 377 (23 900); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 771.5 (50, $[M - OCOC_{17}H_{35}]^+$), 1077.8 (100, $[M + Na]^+$).



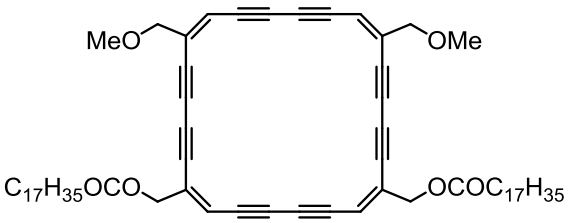
S4d

(2*E*,8*E*)-2,9-Bis(triisopropylsilylethynyl)deca-2,8-dien-4,6-diyne-1,10-diyl diacetate (S4e). Compound **S4a** (0.514 g, 0.982 mmol) and DMAP (26.4 mg, 0.216 mmol) were dissolved in CH_2Cl_2 (10 mL), to which Et_3N (0.55 mL, 0.40 g, 3.9 mmol) and Ac_2O (0.28 mL, 0.30 mg, 3.0 mmol) were sequentially added. The solution was stirred at 25 °C for 1 h, and then poured into a separatory funnel containing of NH_4Cl aq. (10%, 10 mL). The organic phase was isolated, and the aqueous phase was extracted with CH_2Cl_2 (5 mL × 3). All the organic phases were combined, washed with brine (10 mL), dried over $MgSO_4$, filtered, and evaporated to give a brown oil. The crude product was purified by flash silica gel column chromatography (hexanes/AcOEt, 4:1) to afford **S4e** (0.589 g, 99%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 1.08, (s, 42H), 2.08 (s, 6H), 4.64 (s, 4H), 5.97 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 11.1, 18.5, 20.6, 64.9, 81,0, 81.2, 102.2, 102.4, 115.3, 132.8, 167.0; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3020 (w), 2942 (s), 2876 (m), 2865 (s), 2191 (w), 2143 (w), 1751 (s), 1575 (w), 1461 (m), 1374 (m), 1218 (s), 1048 (m), 1025 (m), 881 (s), 678 (m), 596 (m); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 547.3 (100, $[M - OAc]^+$), 629.3 (100, $[M + Na]^+$).

S4e

((1*E*,7*E*,13*E*,19*E*)-13,20-Bis(methoxymethyl)cyclotetracosa-1,7,13,19-tetraen-3,5,9,11,15,17,21,23-octayne-1,8-diyl)bis(methylene) distearate (2a). Compound **S4b** (178 mg, 0.323 mmol) and **S4d** (342 mg, 0.324 mmol) were dissolved in THF (15 mL), to which a small amount of water (0.05 mL) and a solution of TBAF in THF (1.0 M, 65.0 μL, 65.0 μmol) were sequentially added. After

stirred for 90 min at 25 °C, the solution was poured into a separatory funnel containing Et_2O (50 mL) and NH_4Cl aq. (10%, 15 mL). The organic phase was isolated, washed with water (15 mL × 3) then brine (15 mL), dried over $MgSO_4$, filtered, and concentrated to about 5 mL. The solution was diluted with 50 mL of acetone, concentrated to about 5 mL, and diluted again with acetone to 650 mL (*ca.* 1.0×10^{-3} M of the deprotected enediynes). After sequential addition of TMEDA (0.48 mL, 0.37 g, 3.2 mmol) and CuI (247 mg, 1.30 mmol), the solution was stirred for 40 h at 25 °C, then concentrated to a small volume (ca. 5 mL), and filtered through a pad of silica gel with the aid of CH_2Cl_2/acetone (4:1) as eluent. The filtrate was concentrated to dryness and purified by flash silica gel column chromatography (hexanes/AcOEt, 10:1) to give **2a** (26.9 mg , 9%) as a yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 0.88 (t, J = 6.7 Hz, 6H), 1.25–1.31 (m, 56H), 1.63 (quintet, J = 7.3 Hz, 4H), 2.35 (t, J = 7.6 Hz, 4H), 3.37 (s, 6H), 4.02 (d, J = 1.3 Hz, 4H), 4.64 (d, J = 0.8 Hz, 4H), 6.14, 6.19 (two singlets, 4H in total); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 14.1, 22.7, 24.8, 29.1, 29.2, 29.4, 29.4, 29.6, 29.6, 29.7, 31.9, 34.1, 58.6, 64.5, 73.4, 81.1, 81.8, 81.8, 82.0, 82.3, 82.3, 82.7, 82.8, 117.2, 118.4, 131.4, 133.5, 172.8; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3013 (w), 2925 (s), 2847 (s), 2187 (w), 2169 (w), 2121 (w), 1742 (s), 1469 (m), 1160 (s), 1110 (s); UV–vis (cyclohexane), λ_{max} [nm] (ε [$M^{-1}\cdot cm^{-1}$]): 249 (48 000), 334 (39 900), 355 (47 400); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 999.8 (100, $[M + Na]^+$).

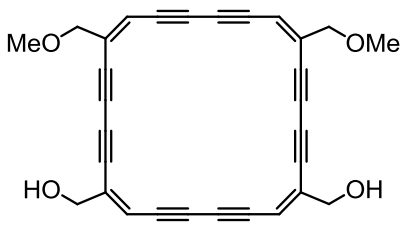


2a

((1*E*,7*E*,13*E*,19*E*)-13,20-Bis(methoxymethyl)cyclotetracosa-1,7,13,19-tetraen-3,5,9,11,15,17,21,23-octayne-1,8-diyl)bis(methylene) bis(octadecylcarbamate) (2b). Compound **S4b** (152 mg, 0.275 mmol) and **S4e** (152 mg, 0.251 mmol) were dissolved in THF (15 mL), to which a small amount of water (0.05 mL) and a solution of TBAF in THF (1.0 M, 52.0 µL, 52.0 µmol) were sequentially added. After the reaction was stirred for 1 h at 25 °C, the TLC analysis (hexanes/AcOEt, 4:1) indicated

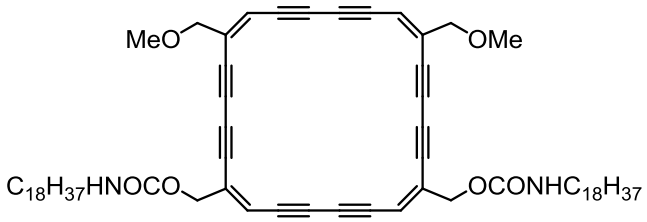
the incompletion of the deprotection. An additional portion of the solution of TBAF in THF (52.0 μL, 52.0 μmol) was added, and the reaction was further stirred for 1 h. At this point, the complete deprotection was confirmed by TLC (two spots were observed at R_f = 0.12 and 0.30 with hexanes/AcOEt, 4:1), and the solution was poured into a separatory funnel containing 50 mL of Et_2O and NH_4Cl aq. (10%, 15 mL). The organic phase was isolated, washed with water (15 mL × 3) then brine (15 mL), dried over $MgSO_4$, filtered, and concentrated to a small volume (about 20 mL). The solution was diluted with acetone (50 mL), concentrated again to a small volume (about 20 mL), and diluted again with acetone (525 mL, *ca.* 1.0×10^{-3} M). After sequential addition of TMEDA (0.40 mL, 0.31 g, 2.7 mmol) and CuI (306 mg, 1.60 mmol), the solution was stirred at 25 °C for 30 h under air, then concentrated to a small volume (20 mL), and filtered through a pad of silica gel (CH_2Cl_2/acetone, 4:1). The filtrate was concentrated to dryness, and purified by flash silica gel column chromatography (CH_2Cl_2, then CH_2Cl_2/acetone, gradient up to 4:1) to give a dark brown amorphous solid (66.2 mg) containing multiple dehydro[24]annulenes formed by homo- and heterocoupling.

The dark brown solid obtained above was dissolved in a mixture of CH_2Cl_2 (5 mL) and MeOH (3 mL), and then K_2CO_3 (66.9 mg, 0.484 mmol) was added to the solution. After stirred for 30 min at 25 °C in air, the mixture was filtered to remove insoluble material, and acidified by adding TFA (less than 3 drops). The filtrate was evaporated to dryness and purified by flash silica gel column chromatography (CH_2Cl_2/THF, 4:1). The solid material thus obtained was further purified by reprecipitation seven times from a CH_2Cl_2 solution by adding pentanes. After drying in vacuo, diol **S6** (13.1 mg, 12%) was obtained as a yellow powder. ^{1}H NMR (500 MHz, acetone-d_6), [ppm]: 3.35 (s, 6H), 4.09 and 4.24 (two s, 8H in total), 4.73 (br s, 2H), 6.38 and 6.43 (two s, 4H in total); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6), [ppm]: 58.6, 64.3, 73.9, 81.7, 81.8, 82.3, 82.4, 82.6, 82.6, 82.9, 82.9, 116.3, 118.2, 135.8, 139.4.



S6

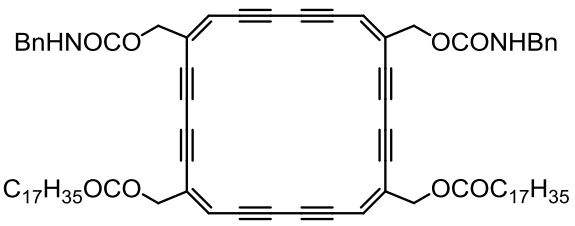
The intermediate **S6** (13.1 mg, 29.5 μmol) and CuI (16.9 mg, 88.7 μmol) were dissolved in a mixture of DMF (1 mL) and THF (1 mL). Octadecyl isocyanate (62.5 μL, 52.9 mg, 179 μmol) was added to the solution, which was then stirred for 30 min at 25 °C. The reaction was terminated by adding MeOH (1 mL). The mixture was diluted with acetone (8 mL), and the white precipitate was removed by centrifuging and decantation. The precipitate was further rinsed with acetone (8 mL × 2), and the rinse solutions were combined with the decanted supernatant. The combined solution was evaporated to a small volume to remove most of acetone, THF, and MeOH, then diluted with AcOEt (20 mL). The insoluble white-brown solid was removed by filtration. The filtrate was diluted with THF (1 mL), washed with water (10 mL × 3) then brine (10 mL), dried over $MgSO_4$, filtered, and evaporated to give a yellow solid. The solid was subjected to flash silica gel column chromatography (CH_2Cl_2/AcOEt, 25/1) and further purified by precipitating three times from a CH_2Cl_2 solution by adding pentanes to afford 12.2 mg of **2b** (40% from **S6**, 5% from **S4b** and **S4e**) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 0.88 (t, J = 6.4 Hz, 6H), 1.25 (s, 60H), 1.49 (s, 4H), 3.17 (q (not well resolved), J = 6.1 Hz, 4H), 3.37 (s, 6H), 4.02 (s, 4H), 4.62–4.79 (four singlets, 6H in total), 6.14, 6.19 (two singlets, 4H in total); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 14.1, 22.7, 26.7, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 29.9, 31.9, 41.2, 58.5, 65.1, 73.5, 81.3, 81.7, 81.8, 81.9, 82.2, 82.4, 82.6, 82.7, 117.2, 118.2, 132.0, 133.5, 155.3; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3426 (s), 3289 (m), 3055 (s), 3020 (s), 2918 (s), 2849 (s), 2173 (w), 2166 (w), 2121 (w), 1692 (s), 1543 (m), 1465 (m), 1259 (m), 1142 (m), 1112 (m), 843 (w); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 1057.8 (100, $[M + Na]^+$), 1073.8 (97, $[M + K]^+$).



2b

((1*E*,7*E*,13*E*,19*E*)-13,20-Bis(benzylcarbamoyloxymethyl)cyclotetracosa-1,7,13,19-tetraen-3,5,9,11,15,17,21,23-octayne-1,8-diyl)bismethylene distearate (2c). Compounds **S4c** (116 mg, 0.197

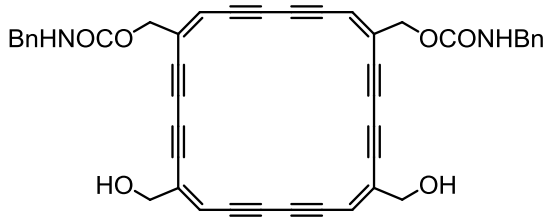
mmol) and **S4d** (209 mg, 0.197 mmol) were dissolved in THF (15 mL), to which a small amount of water (0.10 mL), a solution of AcOH in THF (1.0 M, 0.86 mL, 0.86 mmol), and a THF solution of TBAF (1.0 M, 0.86 mL, 0.86 mmol) were sequentially added at 0 °C. After stirred for 70 min at 0 °C, the solution was poured to a separatory funnel containing Et_2O (50 mL) and NH_4Cl aq. (10%, 15 mL). The organic phase was isolated, washed with water (15 mL × 3) then brine (15 mL), dried over $MgSO_4$, filtered, and concentrated to a small volume (about 5 mL). The solution was diluted with acetone (50 mL), concentrated to a small volume (about 5 mL), and diluted again with acetone (400 mL, *ca.* 1.0×10^{-3} M). After sequential addition of TMEDA (0.30 mL, 0.23 g, 2.0 mmol) and CuI (151 mg, 0.793 mmol), the solution was stirred for 41 h at 25 °C, then concentrated to a small volume (about 5 mL), and filtered through a pad of silica gel with the aid of CH_2Cl_2/acetone (4/1) as eluent. The filtrate was concentrated to dryness and purified by repetitive flash silica gel column chromatography (1st, CH_2Cl_2 → CH_2Cl_2/AcOEt, 25:1; 2nd, hexanes/AcOEt, 8:3) to give **2c** (26.9 mg, 11%) as a yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 0.88 (t, J = 6.9 Hz, 6H), 1.25 (s, 56H), 1.63 (quintet, J = 7.2 Hz, 4H), 2.35 (t, J = 7.5 Hz, 4H), 4.38 (d, J = 5.8 Hz, 4H), 4.64, 4.68 (two singlets, 8H in total), 4.95, 5.16 (two br s, 2H in total), 6.01, 6.16, 6.17 (three singlets, 4H in total), 7.25–7.36 (m, 10H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 14.1, 22.7, 24.8, 29.1, 29.2, 29.3, 29.4, 29.6, 29.6, 29.7, 31.9, 34.0, 45.2, 64.4, 65.2, 81.2, 81.4, 81.8, 81.8, 82.5, 82.6, 82.7, 82.7, 118.6, 127.5, 127.6, 128.7, 131.4, 131.8, 138.0, 155.3, 172.8; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3308 (br m), 3063 (w), 3030 (w), 2922 (s), 2851 (s), 2189 (w), 2166 (w), 2123 (w), 1735 (s), 1695 (s), 1542 (m), 1455 (m), 1256 (m), 1158 (m); UV–vis (cyclohexane), λ_{max} [nm] (ε [$M^{-1}\cdot cm^{-1}$]): 249 (56 800), 334 (46 000), 356 (54 300); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 1237.9 (100, $[M + Na]^+$), 1253.9 (9, $[M + K]^+$).



2c

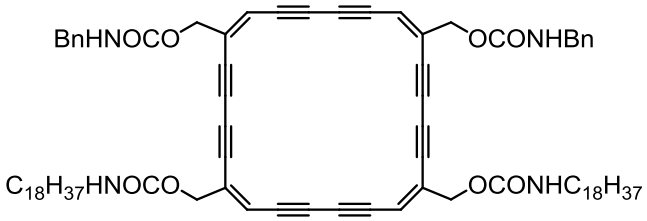
(1*E*,6*E*,12*E*,18*E*)-1,18-Bis(benzylcarbamoyloxymethyl)-6,13-bis(octadecyl-carbamoyloxymethyl)cyclotetracosa-6,12,18,24-tetraen-2,4,8,10,14,16,20,22-octayne (2d). Compounds **S4c** (153 mg, 0.251 mmol) and **S4e** (198 mg, 0.251 mmol) were dissolved in THF (15 mL), to which a small amount of water (0.1 mL) was added. At 0 °C, a solution of AcOH in THF (1.0 M, 1.10 mL, 1.10 mmol) and a solution of TBAF in THF (1.0 M, 1.10 mL, 1.10 mmol) were added. After stirred for 10 minutes at 0 °C, the solution was poured into a separatory funnel containing Et_2O (50 mL) and of NH_4Cl aq. (10%, 15 mL). The organic phase was isolated, washed with water (15 mL × 3) then brine (15 mL), dried over $MgSO_4$, filtered, and concentrated to a small volume (about 10 mL). The solution was diluted with acetone (50 mL), concentrated to a small volume (about 10 mL), and diluted again with acetone (500 mL, *ca.* 1.0×10^{-3} M). After sequential addition of TMEDA (0.38 mL, 0.29 g, 2.5 mmol) and CuI (192 mg, 1.00 mmol), the solution was stirred for 17 h at 25 °C in air, then concentrated to a small volume (about 10 mL), and filtered through a pad of silica gel with the aid of CH_2Cl_2/acetone (4:1) as eluent. The filtrate was concentrated to dryness, and purified by flash silica gel column chromatography (gradient, CH_2Cl_2 →CH_2Cl_2/acetone, 10:1) to give a brown-yellow amorphous solid (48.8 mg) containing multiple dehydro[24]annulenes formed by homo- and hetero-coupling.

The brown-yellow solid obtained above was dissolved in a mixture of CH_2Cl_2 (5 mL) and MeOH (3 mL), and K_2CO_3 (48.8 mg, 0.353 mmol) was added to the solution. After stirred for 30 min at 25 °C in air, the solution was filtered to remove insoluble material, and acidified by adding TFA (~5 drops). The filtrate was evaporated to dryness, subjected to flash silica gel column chromatography (CH_2Cl_2/THF, 4/1), and further purified by precipitating three times from CH_2Cl_2/acetone (6/1) solutions by adding pentanes. After drying in vacuo, diol **S7** (21.0 mg, 12 %) was obtained as a yellow powder. ^{1}H NMR (500 MHz, acetone-d_6), [ppm]: 4.24 (s, 4H), 4.34 (s, 4H), 4.73 (s, 5H), 6.20, 6.43, 6.45 (three singlets, 4H in total), 6.71, 7.04 (two singlets, 2H in total), 7.23–7.32 (m, 10H); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6), [ppm]: 45.2, 64.2, 65.4, 81.7, 82.1, 82.2, 82.3, 82.6, 82.8, 82.8, 82.9, 116.5, 119.0, 127.9, 128.2, 129.3, 134.5, 139.4, 140.5, 156.5.



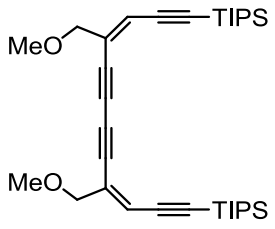
S7

Octadecyl isocyanate (65.0 μL, 55.0 mg, 186 μmol) was added to a mixture of **S7** (21.0 mg, 30.8 μmol) and CuI (17.7 mg, 92.9 μmol) in a mixture of DMF (1 mL) and THF (1 mL). The reaction was stirred at 25 °C for 30 min, then quenched with MeOH (1 mL) and diluted with acetone (8 mL). The white precipitate was removed by centrifuging and decantation. The precipitate was further rinsed with acetone (8 mL ×2), and the rinsed solutions were combined with the decanted supernatant obtained earlier. The combined solution was evaporated to remove most of the solvents, then diluted with AcOEt (20 mL), and filtered to remove the insoluble material. The filtrate was washed with water (10 mL × 3) then brine (10 mL), dried over $MgSO_4$, filtered, and evaporated to give a yellow brown solid. The product was reprecipitated three times from CH_2Cl_2 solutions by adding MeOH. Finally, the product was subjected to flash silica gel column chromatography (CH_2Cl_2/Acetone, 25:1) to afford **2d** (22.1 mg, 72% from **S7**, 9% from **S4b** and **S4e**) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 0.88 (t, J = 6.9 Hz, 6H), 1.25 (s, 60H), 1.48 (quitet (not well resolved), J = 6.3 Hz, 4H), 3.16 (q, J = 6.6 Hz, 4H), 4.38 (d, J = 5.9 Hz, 4 H), 4.62, 4.67, 4.83 (three singlets, 10H in total), 4.99, 5.22 (two singlets, 2H in total), 6.00, 6.15, 6.16 (three singlets, 4H in total), 7.28–7.36 (m, 10H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 14.1, 22.7, 26.7, 29.3, 29.3, 29.5, 29.6, 29.6, 29.7, 29.8, 31.9, 41.2, 45.2, 65.0, 65.3, 81.3, 81.5, 81.8, 82.5, 82.6, 82.6, 82.7, 118.4, 118.5, 127.5, 127.6, 128.7, 131.9, 132.0, 138.0, 155.3, 155.4; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3302 (m), 3061 (s), 3026 (s), 2920 (s), 2850 (s), 2175 (w), 2167 (w), 2122 (w), 1690 (s), 1544 (s), 1457 (m), 1455 (m), 1262 (s), 1140 (m), 1076 (m), 981 (m), 842 (w), 695 (m); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 1296.9 (97, [M + Na]$^+$), 1311.9 (100, [M + K]$^+$).



2d

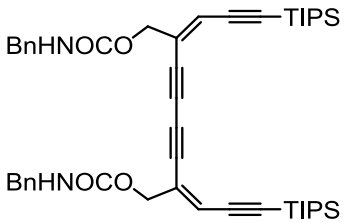
((3*E*,9*E*)-4,9-Bis(methoxymethyl)-1,12-bis(triisopropylsilyl)dodeca-3,9-dien-1,5,7,11-tetrayne (S5b). A solution of compound **S5a** (0.463 g, 0.885 mmol) in THF (8 mL) was added to a suspension of NaH (218 mg as a 60% dispersion in oil, 5.37 mmol) in THF (22 mL), to which MeI (0.55 mL, 1.3 g, 8.8 mmol) and a drop of water were sequentially added. After stirred at 25 °C for 30 min, the reaction was terminated by adding water (15 mL) dropwise. The mixture was extracted with Et_2O (15 mL × 2). The organic phases were combined, dried over $MgSO_4$, filtered, and evaporated to provide a brown waxy solid. The crude product was purified by flash silica gel chromatography (CH_2Cl_2/hexanes, 1/1 then 3/1) to afford **S5b** (0.468 g, 96%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 1.10 (s, 42H), 3.36 (s, 6H), 3.97 (d, J = 1.6 Hz, 4H), 6.10 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 11.2, 18.6, 58.4, 73.4, 81.0, 81.4, 100.9, 103.6, 119.0, 131.2; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3045(w), 2997 (w), 2956 (sh), 2943 (s), 2924 (sh), 2889 (m), 2864 (s), 2723 (w), 2183 (w), 2139 (sh), 2127 (m), 1664 (w), 1464 (m), 1109 (s); UV–vis (MeCN), λ_{max} [nm] (ε [M^{-1}·cm^{-1}]): 282 (18 800), 298 (22 800), 318 (23 100), 341 (21 800), 378 (19 300). MS (MALDI-TOF, reflector mode, 2,5-dehydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 529.1 (100, [M – CH_2OMe + H + Na]$^+$), 573.0 (32, [M + Na]$^+$).



S5b

(2*E*,7*E*)-2,7-Bis(3-(triisopropylsilyl)prop-2-ynylidene)octa-3,5-diyne-1,8-diyl

bis(benzylcarbamate) (S5c). Diol **S5a** (200 mg, 0.382 mmol) and DMAP (9.37 mg, 76.7 μmol) were dissolved in CH_2Cl_2 (5 mL), to which *i*-Pr_2NEt (235 μL, 1.35 mmol) and benzyl isocyanate (165 μL, 1.35 mmol) were sequentially added. After stirred at 25 °C for 17.5 h, the solution was poured to a separatory funnel containing AcOEt (25 mL) and NH_4Cl aq. (10%, 10 mL). The organic phase was washed with water (10 mL × 3) then brine (10 mL), dried over $MgSO_4$, and evaporated. The resulting oil was purified by flash silica gel column chromatography (CH_2Cl_2/AcOEt, 200/3 then 50/1) to afford **S5c** (290 mg, 96%) as a light yellow oil, which gradually turned into a pale yellow waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 1.10 (s, 42H), 4.38 (d, J = 5.8 Hz, 4 H), 4.65 (s, 4H), 4.97 and 5.13 (two br s, 2H in total), 5.96, 6.10 (two singlets, 2H in total), 7.26–7.35 (m, 10H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 11.1, 18.5, 45.1, 65.2, 80.6, 81.3, 102.1, 103.0, 120.4, 127.4, 127.5, 128.6, 129.1, 138.0, 155.4; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3305 (s), 3090 (w), 3067 (w), 3033 (w), 2942 (s), 2890 (m), 2846 (s), 2193 (w), 2139 (w), 1696 (s), 1530 (m), 1459 (m), 1241 (s), 1048 (m); UV–vis (cyclohexane), λ_{max} [nm] (ε [$M^{-1}\cdot cm^{-1}$]): 299 (19 300), 319 (21 000), 343 (24 300), 369 (22 400); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 811.7 (100, $[M + Na]^+$), 827.7 (53, $[M + K]^+$).

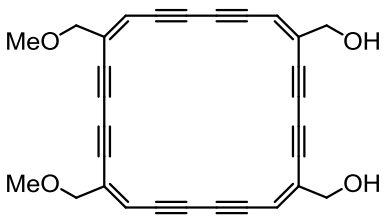


S5c

((1*E*,6*E*,12*E*,18*E*)-13,18-Bis(methoxymethyl)cyclotetracosa-6,12,18,24-tetraen-2,4,8,10,14,16,20,22-octayne-1,6-diyl)bis(methylene) distearate (3a). Compound **S5b** (111 mg, 0.202 mmol) and **S5d** (122 mg, 0.201 mmol) were dissolved in THF (15 mL), to which water (0.05 mL) and a solution of TBAF in THF (1.0 M, 40.0 μL, 40.0 μmol) were sequentially added. After stirred at 25 °C for 30 min, the solution was poured into a separatory funnel containing Et_2O (40 mL) and NH_4Cl aq. (10%, 15 mL). The organic phase was isolated, washed with water (10 mL × 3) then brine (10 mL), dried over $MgSO_4$, filtered, and concentrated to a small volume (about 10 mL). The solution was diluted with acetone

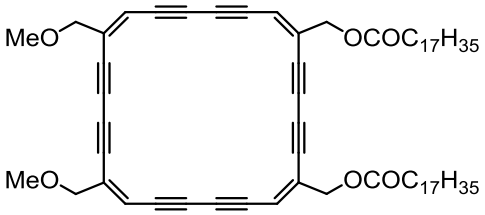
(50 mL), concentrated to a small volume (about 10 mL), and diluted again with acetone to 400 mL (*ca.* 1.0×10^{-3} M of the enediynes). After sequential addition of TMEDA (0.30 mL, 0.23 g, 2.0 mmol) and CuI (152 mg, 0.800 mmol), the solution was stirred at 25 °C for 20 h in air, concentrated to small volume (about 5 mL), and filtered through a pad of silica gel with CH_2Cl_2/acetone (4:1) as eluent. The filtrate was concentrated to dryness, and purified by flash silica gel column chromatography (CH_2Cl_2, then CH_2Cl_2/acetone, gradient up to 50/3) to give a brown solid (51.5 mg) containing multiple dehydro[24]annulenes formed by homo- and heterocoupling.

The solid obtained above was dissolved in a mixture of CH_2Cl_2 (5 mL) and MeOH (3 mL), to which K_2CO_3 (51.5 mg, 0.372 mmol) was added. After the solution was stirred at 25 °C for 40 min in air, TLC analysis indicated complete hydrolysis of the acetyl groups (R_f = 0.02, 0.05 and 0.44 with CH_2Cl_2/acetone, 25:1). The solution was diluted with THF (8 mL), filtered to remove insoluble material, and acidified by adding TFA (~3 drops). The resulting solution was evaporated to dryness and purified by flash silica gel column chromatography (CH_2Cl_2/THF, 4:1). The product was further purified by precipitating three times from CH_2Cl_2 solutions by adding petroleum ether. After drying in vacuo, diol **S8** (15.3 mg, 17 %) was obtained as an orange powder. ^{1}H NMR (500 MHz, acetone-d_6), [ppm]: 3.35 (s, 6H), 4.09 (d, J = 1.1 Hz, 4H), 4.24 (s, 4H), 4.72 (br s, 1.4H[a]), 6.38, 6.43 (two s, 4H in total); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6), [ppm]: 58.6, 64.4, 73.9, 81.5, 82.0, 82.2, 82.5, 82.5, 82.6, 82.7, 83.3, 116.1, 118.3, 135.6, 139.7; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3302 (br, m), 3321 (w), 2981 (w), 2913 (w), 2872 (w), 2818 (w), 2167 (w), 2166 (w), 2116 (w), 1650 (w), 1569 (w), 1444 (m), 1364 (m), 1350 (m), 1331 (m), 1268 (w), 1205 (w), 1191 (m), 1104 (s), 1046 (s), 832 (s); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 445.2 (8, $[M + H]^+$), 467.1 (100, $[M + Na]^+$), 483.1 (10, $[M + K]^+$). ([a]Smaller than the expected value of 2H because of H–D exchange with acetone-d_6.)



S8

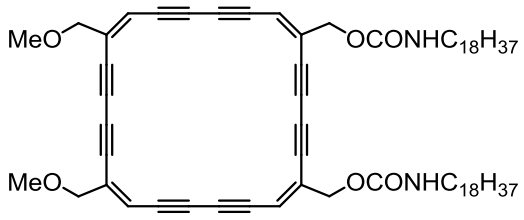
The intermediate **S8** (32.9 mg, 74.0 μmol), steric acid (53.9 mg, 189.5 μmol), and DMAP (4.51 mg, 36.9 μmol) were dissolved in CH_2Cl_2 (5 mL). The solution was cooled to 0 °C before EDC·HCl (38.2 mg, 199.2 μmol) was added in one portion. The solution was allowed to warm up to 25 °C and stirred overnight before washed with water (5 mL × 2) then brine (5 mL), dried over $MgSO_4$, filtered, and evaporated to yield a yellow powder. The mixture was purified by flash silica gel column chromatography (CH_2Cl_2) to yield **3a** (10.8 mg, 15%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$), [ppm]: 0.88 (t, J = 6.4 Hz), 1.63 (quintet, unresolved, J = 6.8 Hz), 2.36 (quintet, unresolved, J = 5.6 Hz), 2.44 (t, J = 7.2 Hz), 3.37 (s, 6 H), 4.02 (d, J = 1.5 Hz, 4H), 4.65 (d, J = 0.8 Hz, 4H), 6.16 (s, 2H), 6.18 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 14.1, 22.7, 24.8, 29.1, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9, 34.1, 58.6, 64.5, 73.5, 81.3, 81.3, 81.5, 81.9, 82.5, 82.5, 82.6, 83.0, 116.8, 118.8, 131.0, 133.9, 172.9; IR (ATR), $\bar{\nu}_{max}$ [cm^{-1}]: 2956 (m), 2915 (s), 2850 (s), 1740 (m), 1473 (m), 1170 (m), 1112 (m); MS (MALDI-TOF, reflector mode) *m*/*z* (% relative intensity, ion): 999.6 (100, $[M + Na]^+$), 1016.1 (10, $[M + K]^+$).



3a

((1*E*,6*E*,12*E*,18*E*)-13,18-Bis(methoxymethyl)cyclotetracosa-6,12,18,24-tetraen-2,4,8,10,14,16,20,22-octayne-1,6-diyl)bis(methylene) bis(octadecyl-carbamate) (3b). The precursor **S8** was prepared as described in the synthesis of **3a**. Compound **S8** (15.3 mg, 34.4 μmol) and CuI (20.0 mg, 105 μmol) were dissolved in DMF (1 mL). After addition of octadecyl isocyanate (72.5 μL, 61.4 mg, 208 μmol), the solution was stirred at 25 °C for 1.5 h. The resulting yellow powder was mostly dissolved by adding THF (2 mL), and the solution was further stirred for additional 4 h before quenching with MeOH (1 mL). The mixture was evaporated to remove most MeOH and THF, diluted with AcOEt (20 mL), and filtered to remove white precipitate, washed with water (5 mL × 3) then brine (5 mL), dried over $MgSO_4$, filtered again, and evaporated. The isolated product was further purified by precipitating three times from a CH_2Cl_2 solution by adding petroleum ether. After drying in vacuo, **3b** (24.5 mg, 69 %) was

obtained as a yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 0.87 (t, J = 6.8 Hz, 6H), 1.25–1.28 (m, 60H), 1.49 (quintet (not well resolved), J = 6.4 Hz, 4H), 3.17 (q, J = 6.5 Hz, 4H), 3.37 (s, 6H), 4.01 (s, 4H), 4.63, 4.68, 4.81 (three singlets, 6H in total), 6.14, 6.17 (two singlets, 4H in total); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 14.1, 22.7, 26.7, 29.3, 29.3, 29.5, 29.6, 29.6, 29.7, 29.7, 29.9, 31.9, 41.2, 58.5, 65.0, 73.5, 81.4, 81.5, 81.5, 82.0, 82.3, 82.5, 82.5, 82.8, 116.9, 118.5, 131.7, 133.8, 155.3; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3420 (sh), 3294 (m), 3020 (w), 2914 (s), 2847 (s), 2173 (w), 2167 (sh), 2121 (w), 1689 (s), 1543 (s), 1467 (m), 1269 (s), 1110 (s); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 1057.7 (100, $[M + Na]^+$), 1073.7 (10, $[M + K]^+$).

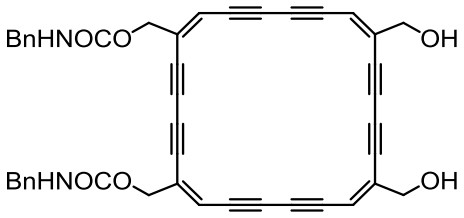


3b

(1*E*,6*E*,12*E*,18*E*)-1,6-Bis(benzylcarbamoyloxymethyl)-13,18-bis(octadecylcarbamoyloxymethyl)cyclotetracosa-6,12,18,24-tetraen-2,4,8,10,14,16,20,22-octayne (3c). Compound **S5c** (134 mg, 0.170 mmol) and **S5d** (104 mg, 0.171 mmol) were dissolved in THF (12 mL), to which a THF solution of AcOH (1.0 M, 0.75 mL, 0.75 mmol) and a solution of TBAF in THF (1.0 M, 0.75 mL, 0.75 mmol) were sequentially added. After stirred at 0 °C for 30 min, the solution was poured into a separatory funnel containing Et_2O (50 mL) and NH_4Cl aq. (10%, 15 mL). The organic phase was separated, washed with water (15 mL × 3) then brine (15 mL), dried over $MgSO_4$, filtered, and concentrated to small volume (about 10 mL). The solution was diluted with acetone (50 mL), concentrated to small volume (about 10 mL), and diluted again with acetone (340 mL , *ca.* 1.0 × 10^{-3} M). After sequential addition of TMEDA (0.26 mL, 0.20 g, 1.7 mmol) and CuI (130 mg, 0.680 mmol), the solution was stirred at 25 °C for 20 h in air, concentrated to small volume (about 5 mL), and filtered through a pad of silica gel with the aid of CH_2Cl_2/acetone (4/1) as eluent. The filtrate was concentrated to dryness, and purified by flash silica gel column chromatography (CH_2Cl_2, then CH_2Cl_2/acetone, gradient up to 10/1)

to give a brown solid (44.5 mg) containing multiple dehydro[24]annulenes formed by homo- and heterocoupling.

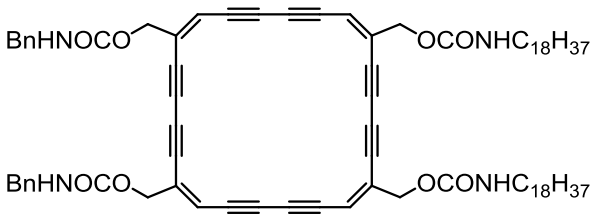
The solid obtained above was dissolved in a mixture of CH_2Cl_2 (5 mL) and MeOH (3 mL), to which K_2CO_3 (44.7 mg, 0.323 mmol) was added. After stirred at 25 °C for 1 h in air, the solution was diluted with THF (8 mL), filtered to remove insoluble material, and acidified by adding TFA (~3 drops). The resulting solution was evaporated to dryness and purified by flash silica gel column chromatography (CH_2Cl_2/THF, 4:1 then 8:3). The product was further purified by precipitating three times from acetone solutions by adding petroleum ether. After drying in vacuo, diol **S9** (14.1 mg, 12%) was obtained as a yellow powder. ^{1}H NMR (500 MHz, acetone-d_6), [ppm]: 4.24, 4.34 (two d, J = 4.2 and 6.1 Hz, 8H in total), 4.73 (s, 6H), 6.22, 6.44 (two s, 4H in total), 6.67, 7.02 (two s, 2H in total), 7.23–7.25, 7.31, 7.32 (overlapping peaks, 10H in total); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6), [ppm]: 45.4, 64.4, 65.4, 81.3, 82.1, 82.3, 82.4, 82.5, 82.6, 82.7, 83.7, 116.0, 119.5, 127.9, 128.2, 129.3, 134.1, 139.9, 140.5, 156.6; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3385 (sh), 3295 (br m), 3069 (w), 3045 (w), 3025 (w), 2918 (w), 2845 (w), 2172 (w), 2167 (w), 2118 (w), 1698 (s), 1518 (m), 1452 (m), 1250 (s), 1132 (m), 1043 (m), 1026 (m), 697 (m); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 705.3 (100, $[M + Na]^+$), 721.2 (35, $[M + K]^+$).



S9

Compound **S9** (14.1 mg, 20.7 μmol) and CuI (12.0 mg, 63.0 μmol) were dissolved in a mixture of DMF (1 mL) and THF (1 mL). After adding octadecyl isocyanate (45.0 μL, 38.1 mg, 129 μmol), the solution was stirred at 25 °C for 3.5 h, and then quenched with of MeOH (1 mL). The mixture was diluted with acetone (7 mL), and the white precipitate was removed by centrifuging and decantation. The precipitate was further rinsed with acetone (7 mL × 2) and the rinse solutions were combined with the supernatant obtained above. Acetone was evaporated off in vacuo and the resulting solution was diluted with AcOEt

(20 mL), washed with water (10 mL × 3) then brine (10 mL), diluted with THF (10 mL), dried over $MgSO_4$, filtered again, and evaporated to dryness. The solid thus obtained was further purified by precipitating three times from CH_2Cl_2 solutions by adding MeOH. After drying in vacuo, **3c** (23.4 mg, 89 % from **S9**, 11% from **S5c** and **S5d**) was obtained as a yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$), [ppm]: 0.89 (t, J = 6.9 Hz, 6H), 1.25–1.29 (m, 60H), 1.49 (quintet, not well-resolved, J = 6.7 Hz, 4H), 3.17 (q, J = 6.7 Hz, 4H), 4.36 (d, J = 5.8 Hz, 4H), 4.63, 4.66, 4.83 (overlapping peaks, 10H in total), 4.97, 5.20 (two broad singlets, 2H in total), 6.00, 6.15, 6.16 (three singlets, 4H in total), 7.26–7.35 (m, 10H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), [ppm]: 14.1, 22.7, 26.7, 29.3, 29.3, 29.5, 29.6, 29.6, 29.7, 29.9, 31.9, 41.2, 45.2, 65.0, 65.3, 81.4, 81.8, 81.9, 82.6, 82.6, 82.7, 118.3, 118.6, 127.5, 127.6, 128.7, 131.8, 132.0, 138.0, 155.3, 155.4; IR (KBr), $\bar{\nu}_{max}$ [cm^{-1}]: 3299 (m), 3059 (w), 3027 (w), 2917 (s), 2849 (s), 2173 (w), 2165 (w), 2121 (w), 1692 (s), 1541 (s), 1257 (s), 1136 (m), 695 (m); MS (MALDI-TOF, reflector mode, 2,5-dihydroxybenzoic acid), *m*/*z* (% relative intensity, ion): 1296.3 (100, [M + Na]$^+$), 1312.2 (40, [M + K]$^+$).



3c

1.4. References

(1) Suzuki, M.; Comito, A.; Khan, S. I.; Rubin, Y. Nanochannel Array within a Multilayered Network of a Planarized Dehydro[24]annulene. *Org. Lett.* **2010**, *12*, 2346–2349.

(2) Myers, A. G.; Dragovich, P. S. Synthesis of Functionalized Enynes by Palladium/Copper-Catalyzed Coupling Reactions of Acetylenes with (Z)-2,3-Dibromopropenoic Acid Ethyl Ester: (Z)-2-Bromo-5-(trimethylsilyl)-2-penten-4-ynoic Acid Ethyl Ester. *Org. Synth. Coll.* **1995**, *9*, 117–121.

2. Additional STM Images.

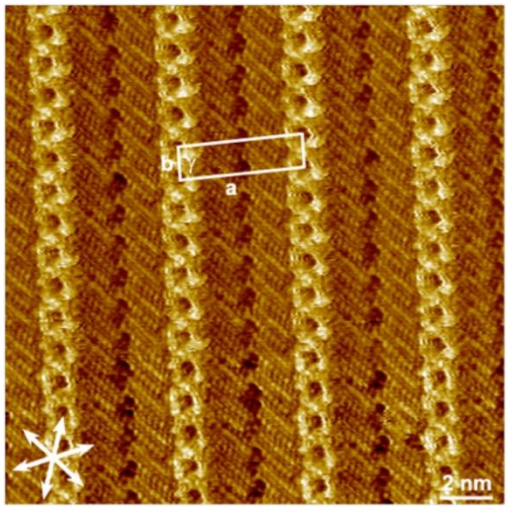


Figure S1. STM image of a monolayer (pattern A) formed by **1** at the 1-phenyloctane/graphite interface (saturated (less than 1×10^{-4} M), tunneling conditions, $I_{set} = 0.14$ nA, $V_{set} = -0.99$ V). Unit cell parameters are $a = 4.68 \pm 0.07$ nm, $b = 1.23 \pm 0.03$ nm, $\gamma = 87 \pm 1°$.

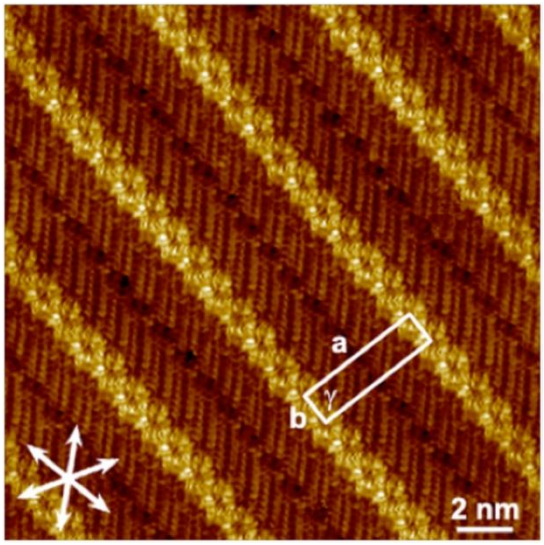


Figure S2. STM image of a monolayer (pattern A) formed by **1** at the octanoic acid/graphite interface (saturated (less than 1×10^{-4} M), tunneling conditions, $I_{set} = 0.35$ nA, $V_{set} = -0.91$ V). Unit cell parameters are $a = 4.83 \pm 0.06$ nm, $b = 1.24 \pm 0.03$ nm, and $\gamma = 88 \pm 1°$.

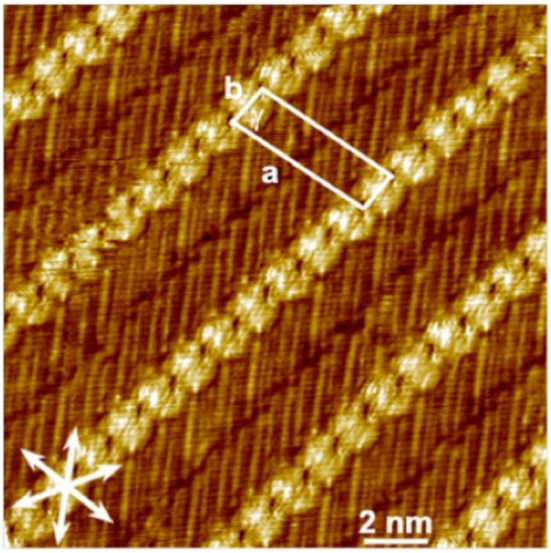


Figure S3. STM image of a monolayer (pattern A) formed by **1** at the octanoic acid/graphite interface (1.0×10^{-5} M, tunneling conditions, I_{set} = 0.20 nA, V_{set} = –0.75 V). Unit cell parameters are a = 4.68 ± 0.07 nm, b = 1.23 ± 0.03 nm, and γ = 87 ± 1°.

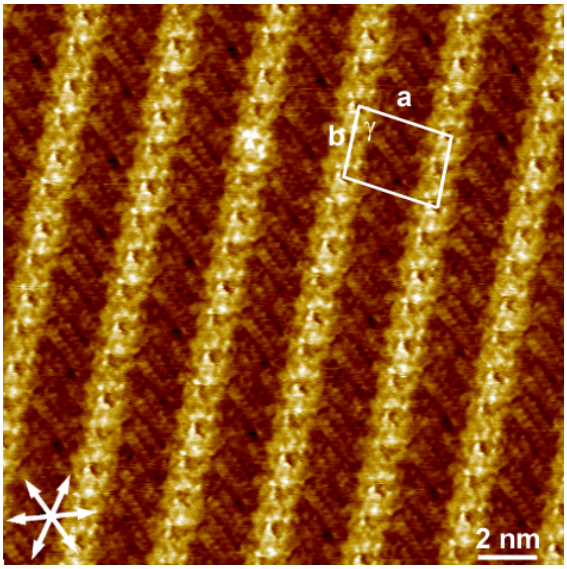


Figure S4. STM image of a monolayer formed by **2a** at the octanoic acid/graphite interface (pattern B, 1.0×10^{-5} M, tunneling conditions, I_{set} = 0.15 nA, V_{set} = –0.81 V). Unit cell parameters are a = 3.26(5) nm, b = 2.40(5) nm, and γ = 82 ± 1°.

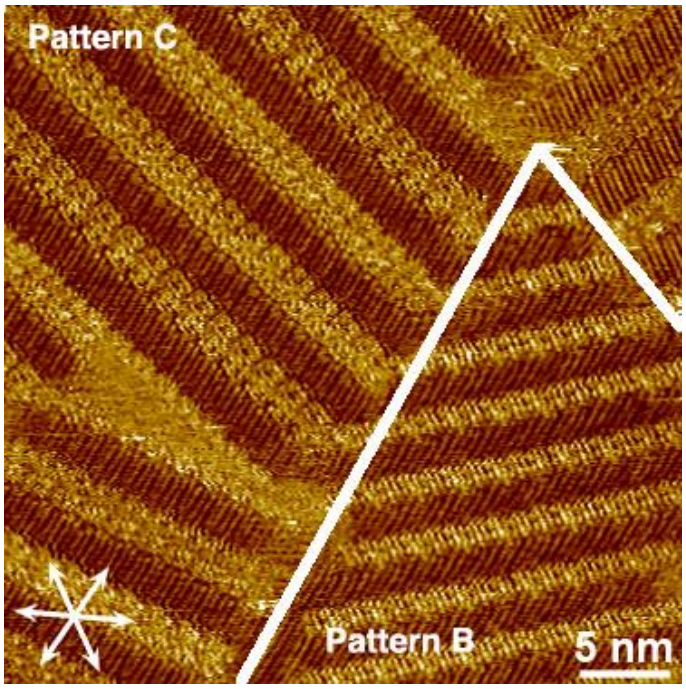


Figure S5. STM image of a monolayer (both patterns B and C) formed by **2a** at the 1-phenyloctane/graphite interface (1.0×10^{-3} M, tunneling conditions, $I_{set} = 0.25$ nA, $V_{set} = -0.89$ V). White lines correspond to the domain boundaries between the patterns B and C.

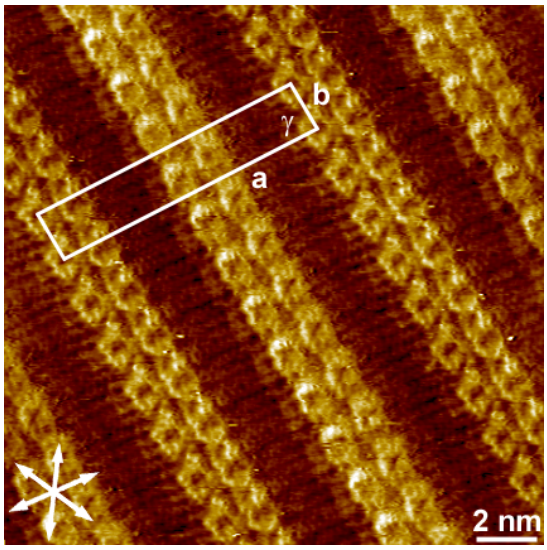


Figure S6. STM image of a monolayer (pattern C) formed by **2a** at the 1-phenyloctane/graphite interface (1.0×10^{-3} M, tunneling conditions, $I_{set} = 0.20$ nA, $V_{set} = -1.1$ V). Unit cell parameters are $a = 9.78 \pm 0.08$ nm, $b = 1.76 \pm 0.05$ nm, and $\gamma = 85 \pm 1°$.

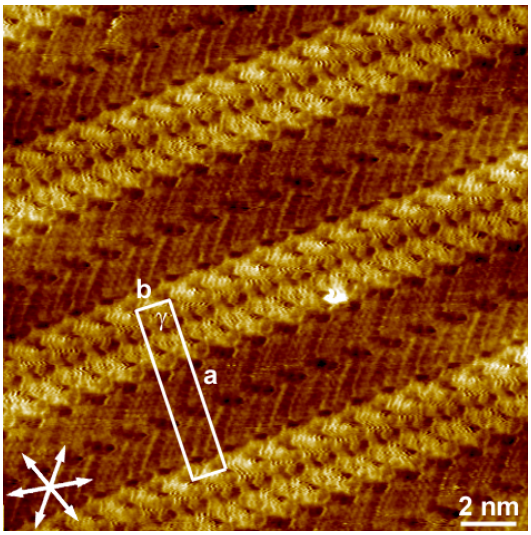


Figure S7. STM image of a monolayer (pattern D) formed by **3a** at the 1-phenyloctane/graphite interface (1.0×10^{-5} M, tunneling conditions, I_{set} = 0.10 nA, V_{set} = –0.50 V). Unit cell parameters are a = 6.57 ± 0.04 nm, b = 1.25 ± 0.03 nm, and γ = 88 ± 1°.

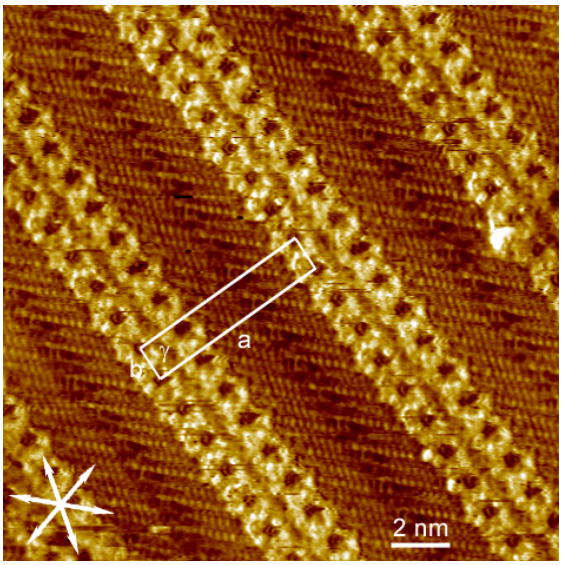


Figure S8. STM image of a monolayer (pattern D) formed by **3a** at the octanoic acid/graphite interface (1.0×10^{-5} M, tunneling conditions, I_{set} = 0.22 nA, V_{set} = –0.22 V). Unit cell parameters are a = 6.40 ± 0.06 nm, b = 1.28 ± 0.04 nm, and γ = 76 ± 1°.

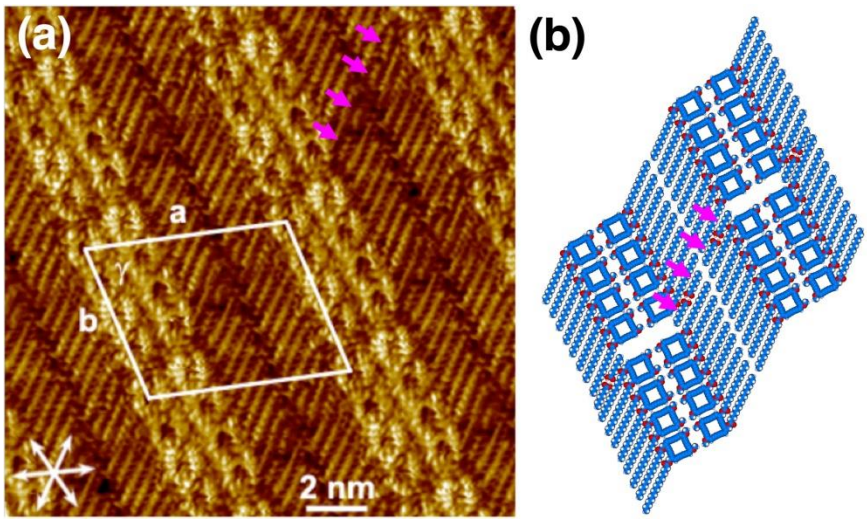


Figure S9. STM image and a molecular model of a monolayer formed by **3a** at the octanoic acid/graphite interface (1.0×10^{-5} M, tunneling conditions, I_{set} = 0.22 nA, V_{set} = –0.4 V). Unit cell parameters are $a = 6.77 \pm 0.04$ nm, $b = 5.51 \pm 0.07$ nm, and $\gamma = 72 \pm 1°$. Pink arrows indicate co-adsorbed octanoic acid molecules.

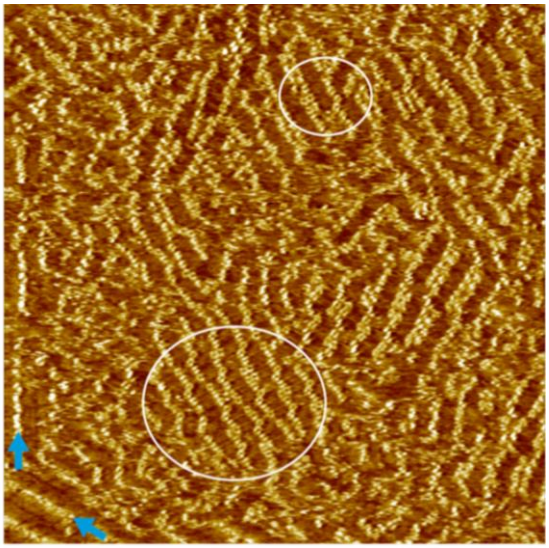


Figure S10. STM image of a monolayer formed by **2b** at the octanoic acid/graphite interface (1.1×10^{-4} M, tunneling conditions, I_{set} = 0.14 nA, V_{set} = –0.43 V). White ellipsoids in (a) indicate the molecules of **2b** lying flat on the graphite surface (recognizable by the characteristic "doughnut" shape of the π-core). Blue arrows indicate the linear bight lines.

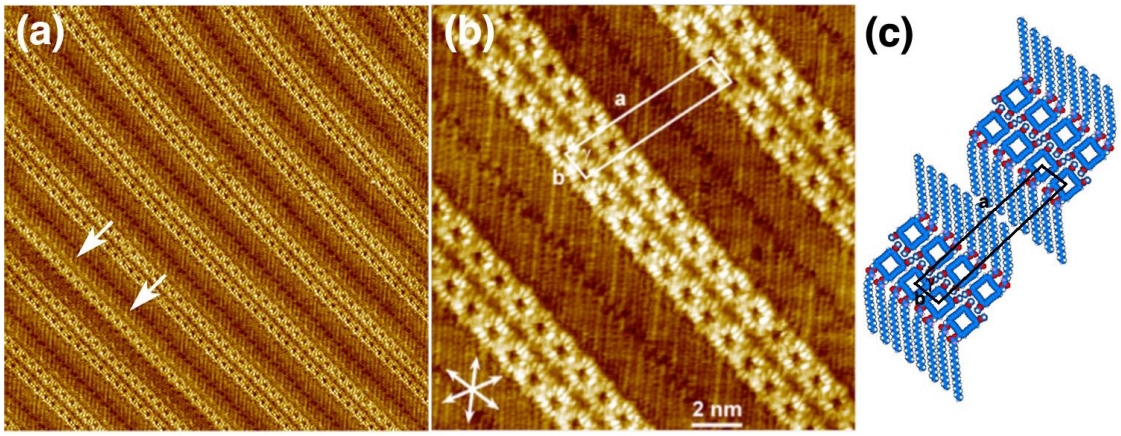


Figure S11. STM images (a, b) and a molecular model (c) of monolayers (pattern D) of compound **3b** at the octanoic acid/graphite interface (1.1×10^{-5} M, I_{set} = 0.21 nA, V_{bias} = –0.57 V for both images). Unit cell parameters are a = 7.1 ± 0.2 nm, b = 1.3 ± 0.1 nm, and γ = 89 ± 2° (plane group: $p2$). Single-row structures are occasionally observed as indicated with the white arrows in (a). Structural parameters of the model (c) are a = 6.95 nm, b = 1.25 nm, and γ = 89.4°.

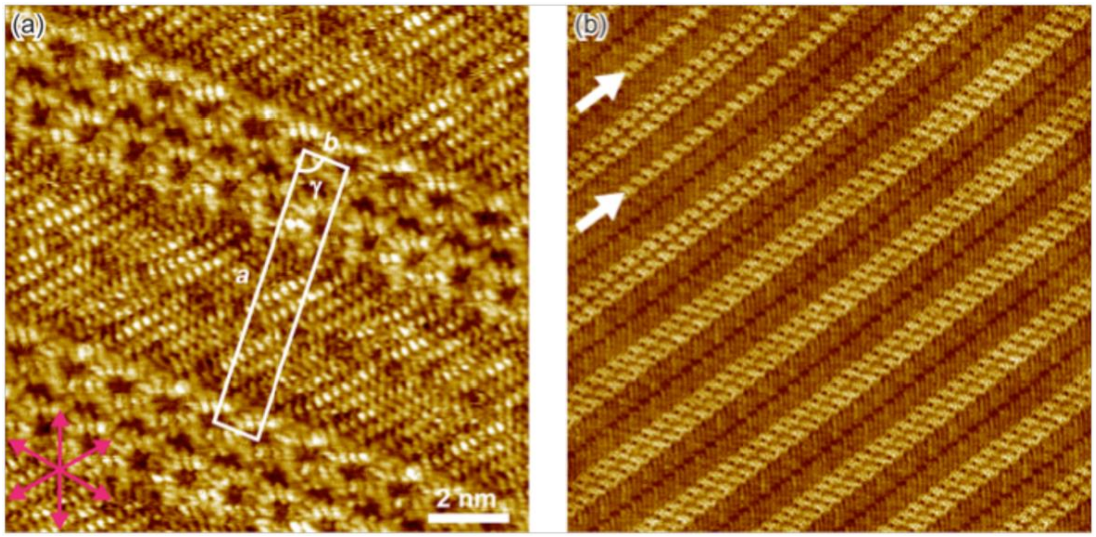


Figure S12. STM images (a, b) of monolayers formed by **3b** at the 1-phenyloctane/graphite interface (1.2×10^{-5} M, tunneling conditions, I_{set} = 0.18 nA, V_{set} = –0.31 V for image (a) and I_{set} = 0.19 nA, V_{set} = –0.37 V for image (b)). Unit cell parameters are a = 7.4 ± 0.1 nm, b = 1.3 ± 0.1 nm, and γ = 85 ± 2°. Single-chain structures are occasionally observed as indicated by white arrows in image (b).

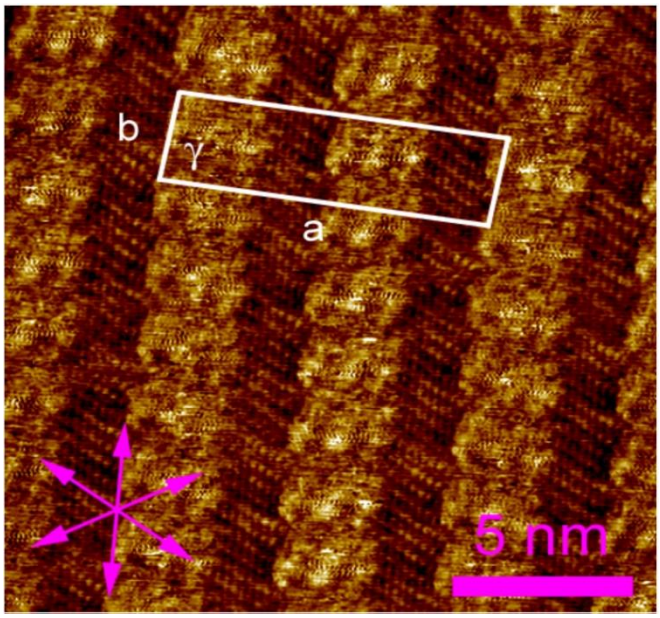


Figure S13. STM image of a monolayer formed by **2c** at the octanoic acid/graphite interface (1.0×10^{-3} M, tunneling conditions, I_{set} = 0.30 nA, V_{set} = –0.51 V). Unit cell parameters are a = 9.1 ± 0.2 nm, b = 2.2 ± 0.2 nm, and γ = 89 ± 2°.

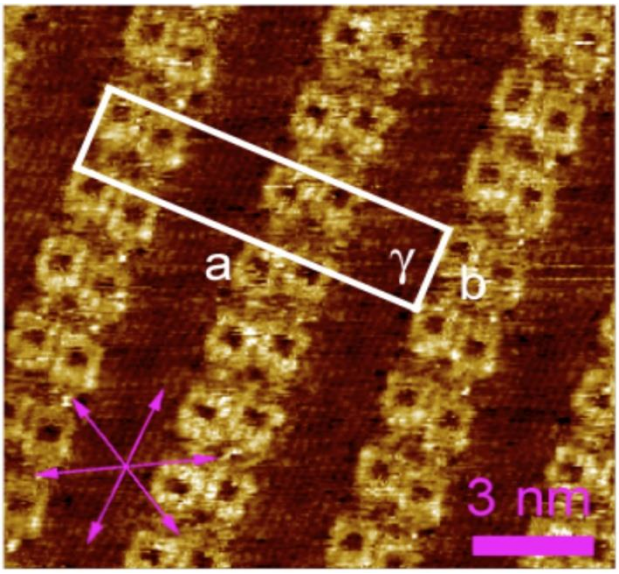


Figure S14. STM image of a monolayer formed by **2c** at the 1-phenyloctane/graphite interface (1.0×10^{-3} M, tunneling conditions, I_{set} = 0.24 nA, V_{set} = –0.73 V). Unit cell parameters are a = 9.3 ± 0.1 nm, b = 2.2 ± 0.2 nm, γ = 86 ± 2°.

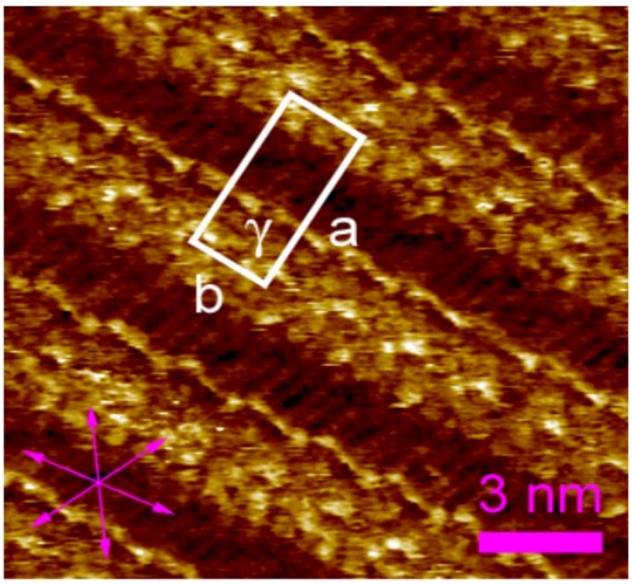


Figure S15. STM image of a monolayer formed by **2c** at the 1-phenyloctane/graphite interface (1.0×10^{-5} M, tunneling conditions, I_{set} = 0.30 nA, V_{set} = –0.69 V). Unit cell parameters are a = 5.0 ± 0.2 nm, b = 2.1 ± 0.1 nm, γ = 76 ± 3°.

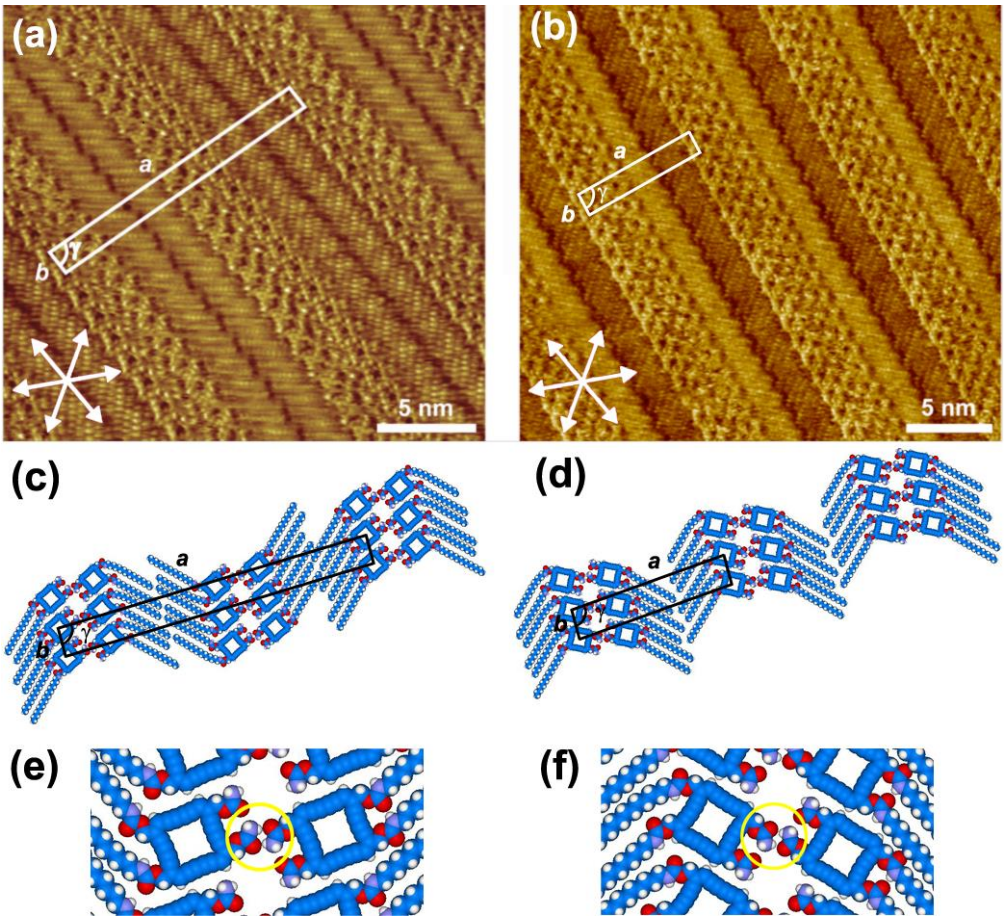


Figure S16. STM images of self-assembled monolayers of compound **3c** at the 1-phenyloctane/graphite interface. (a) Pattern F (1.0×10^{-5} M, I_{set} = 0.15 nA, V_{bias} = –0.31 V). Unit cell parameters are a = 14.8 ± 0.3 nm, b = 1.3 ± 0.1 nm, γ = 88 ± 1° (plane group: *p2gg*). (b) Pattern G (1.0×10^{-5} M, I_{set} = 0.24 nA, V_{bias} = –0.49 V). Unit cell parameters asre a = 7.39 ± 0.12 nm, b = 1.28 ± 0.06 nm, and γ = 88 ± 2° (plane group: *p*2). (c, e) Molecular models for pattern F. Structural parameters in (c) are a = 14.1 nm, b = 1.4 nm, and γ = 90.5° (d, f) Molecular models for pattern G. Structural parameters in (d) are a = 7.32 nm, b = 1.39 nm, and γ = 86.5°. In these models, benzyl groups are omitted for clarity. The yellow circles in (c) and (f) show hydrogen bonded pairs of the benzyl carbamate groups.

3. DFT simulations of dehydro[24]annulene with four methoxymethyl groups.

To estimate the inter-chain distances of the substituents attached to the macrocyclic core of the [24]annulene derivatives, density functional theory (DFT) calculation of the model compound having four methoxyl methyl groups were performed with a Gaussian 09 package. The M062X calculations with the 6-311g(d,p) bases sets were used for the geometry optimization of model compounds. The symmetry of the model compound was fixed to D_{2h} during the optimization. The distances were estimated as shown in Figure S15.

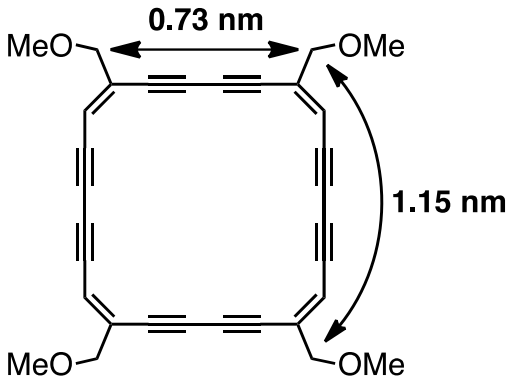


Figure S17. The interatomic distances between the carbon atoms in the methylene units.

4. Estimation of π-π interactions by theoretical simulations.

DFT simulations of dehydro[24]annulene and its dimers were performed with a Gaussian 09 package to estimate energies of π-π interactions. The DFT calculations with M062X/6-311g(d,p) and M06/6-311g(d,p) levels of theory and Hartree-Fock calculations followed by a Møller-Plesset correlation energy correction with MP2/6-311g(d,p) level of theory were used for the geometry optimizations of the monomers and dimmers with different symmetric constraints. Dehydro[24]annulene was optimized with D_{4h} (planar) and D_{2d} (puckered) symmetric constraints to know the energy minimum geometries (Table 1). Coronene was optimized with D_{6h} (planar) symmetric constraint. Geometries of the dimers consisting of the planar or non-planar dehydro[24]annulenes were optimized for a offset geometry (C_{2h} symmetric constraint in a initial geometry) and overlapped geometry (D_{2d} symmetric constraint in a initial geometry), respectively. After optimizations, the symmetry of resulting geometries of the dimers was reduced to C_1. An offset configuration of the non-planar monomers and overlapped dimer of the planar molecules were excluded because the former is not sterically adoptable and the latter is known to be unstable due to a repulsive force (Figures S18). Similarly, the dimers of coronene were optimized in an offset geometry (C_{2h} symmetric constraint in a initial geometry). The energies of intermolecular interactions (E_{inter}) were calculated by the following equation.

E_{inter} = (total energy of dimer) – (total energy of monomer) × 2

Basis set superposition error (BSSE) was corrected for all calculations using the counterpoise method. Table 2 summarizes calculated relative energies of the dimers and the energies of intermolecular interactions.

Relative positions of the centroids of each molecule in the dimers were described as Cartesian coordinates (Figure S18). The x,y-axes and z-axis in the coordinates correspond the molecular plane and stacking direction, respectively.

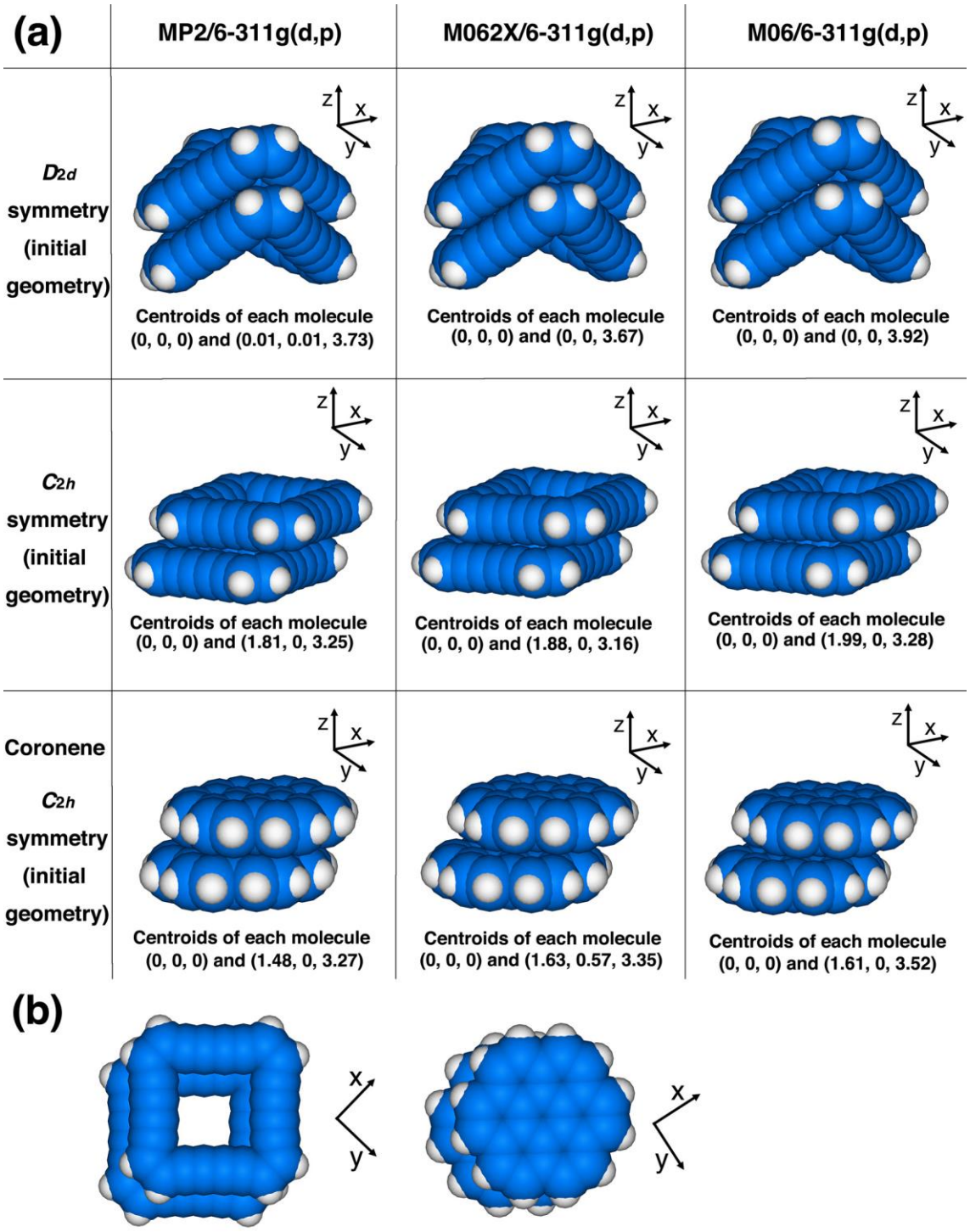


Figure S18. (a) Optimized geometries of the dimers of dehydro[24]annulene and coronene by MP2/6-311g(d,p), M062X/6-311g(d,p), and M06/6-311g(d,p) levels of theory. Cartesian coordinates of centorids of each molecule are shown in parentheses. (b) Top views of MP2 optimized geometries. Black arrows in (a, b) correspond x,y,z-axes in the coordinates.

5. NMR spectra.

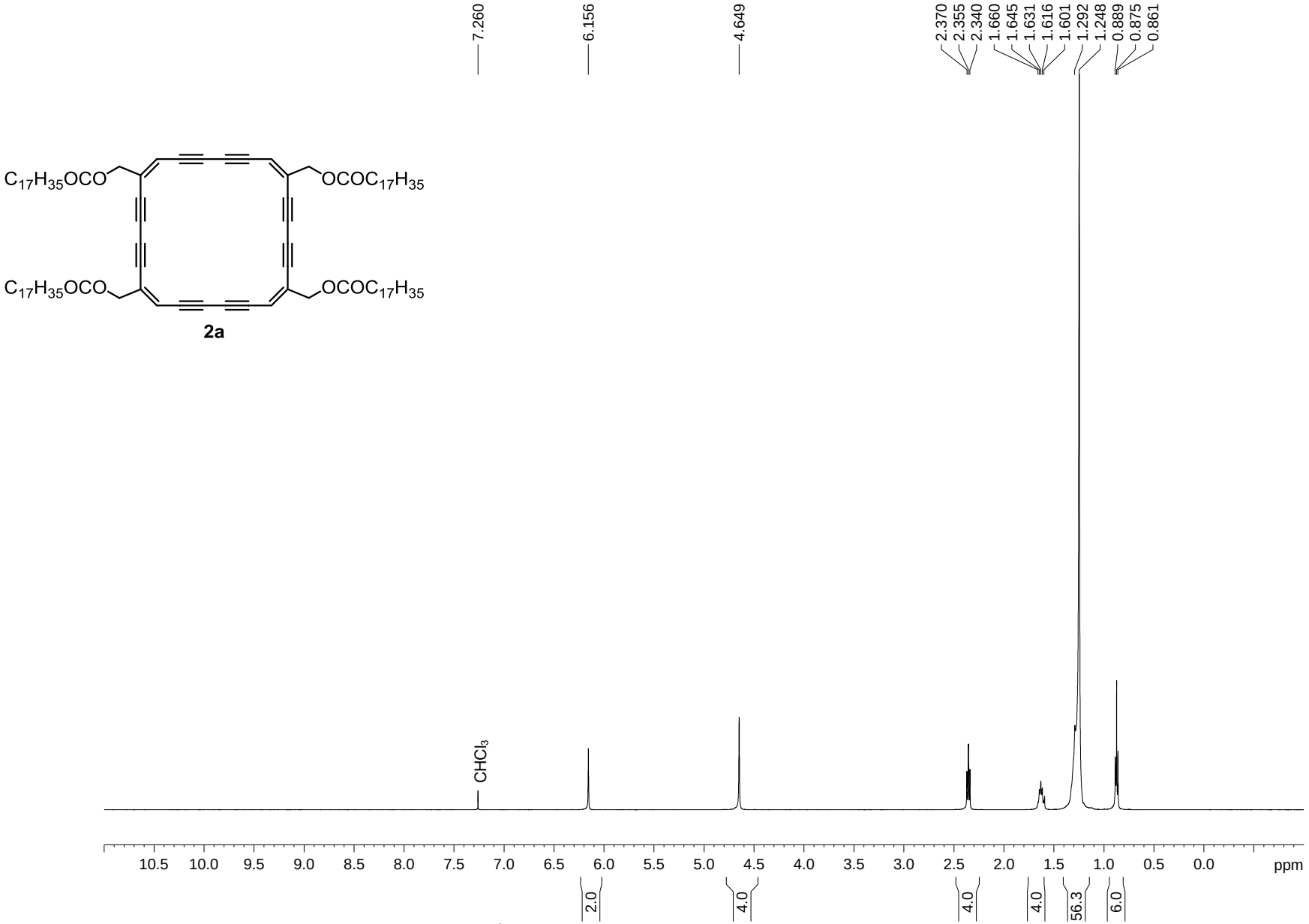


Figure S19. ^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 500 MHz).

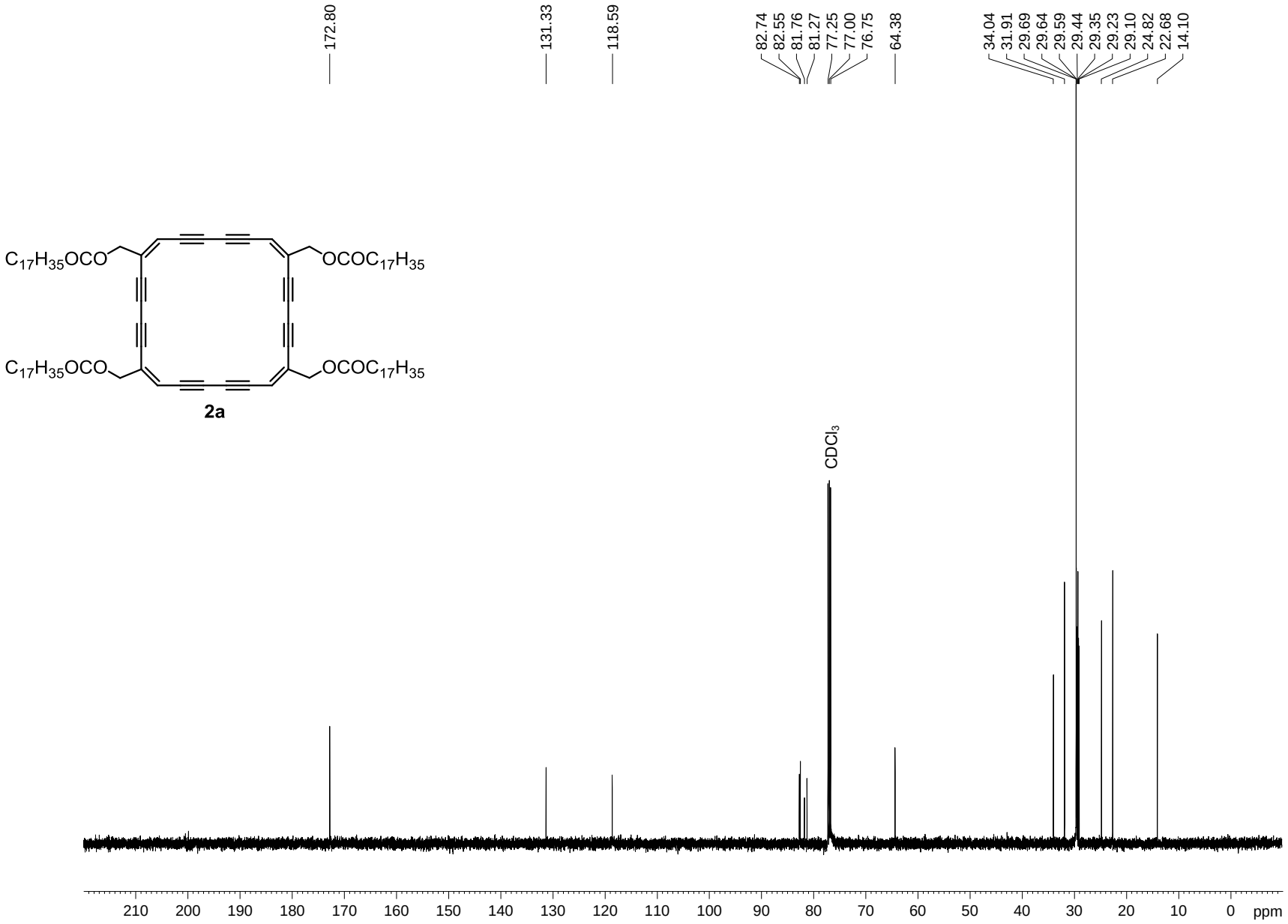


Figure S20. ^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 126 MHz).

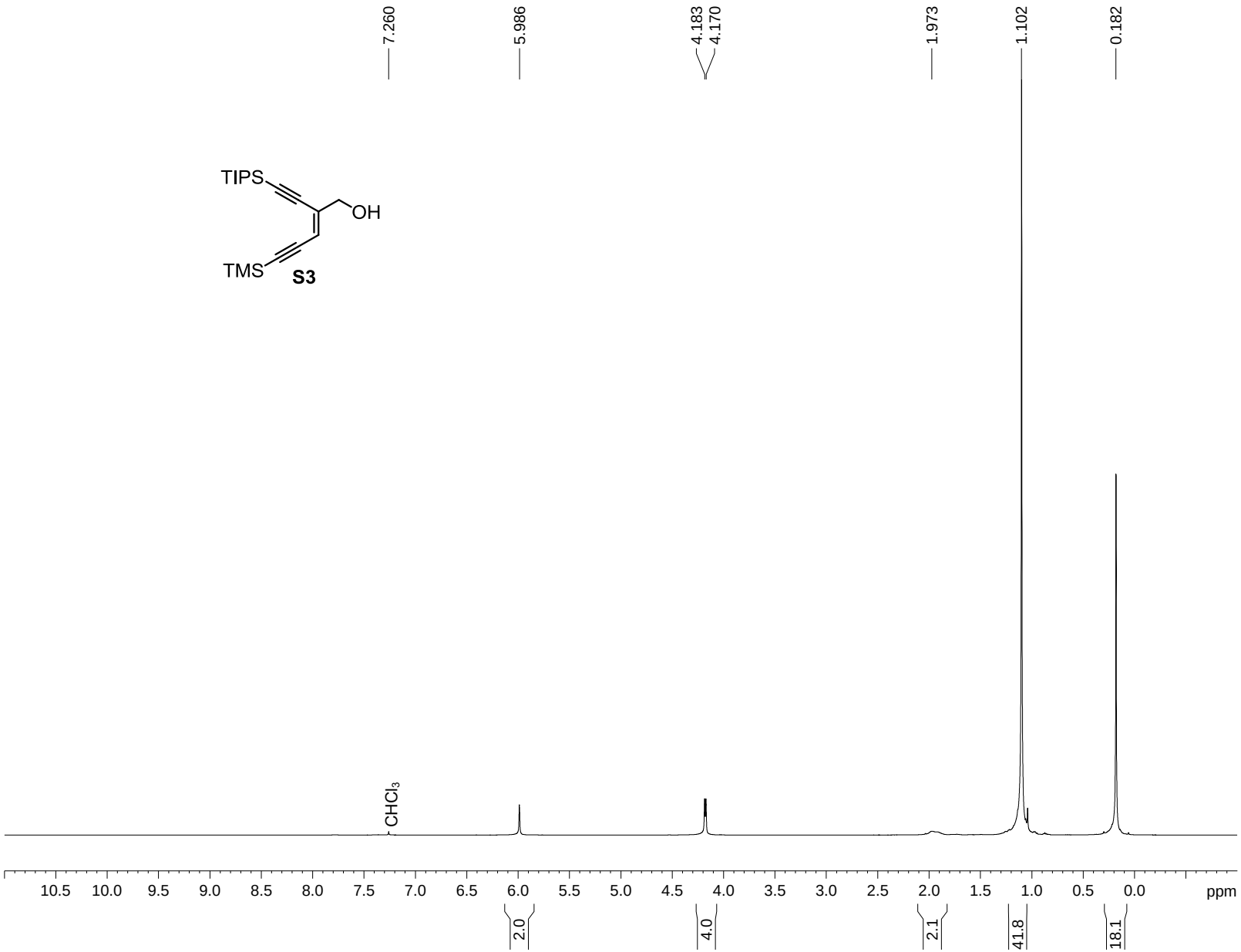


Figure S21. ^{1}H NMR spectrum of compound **S3** ($CDCl_3$, 500 MHz).

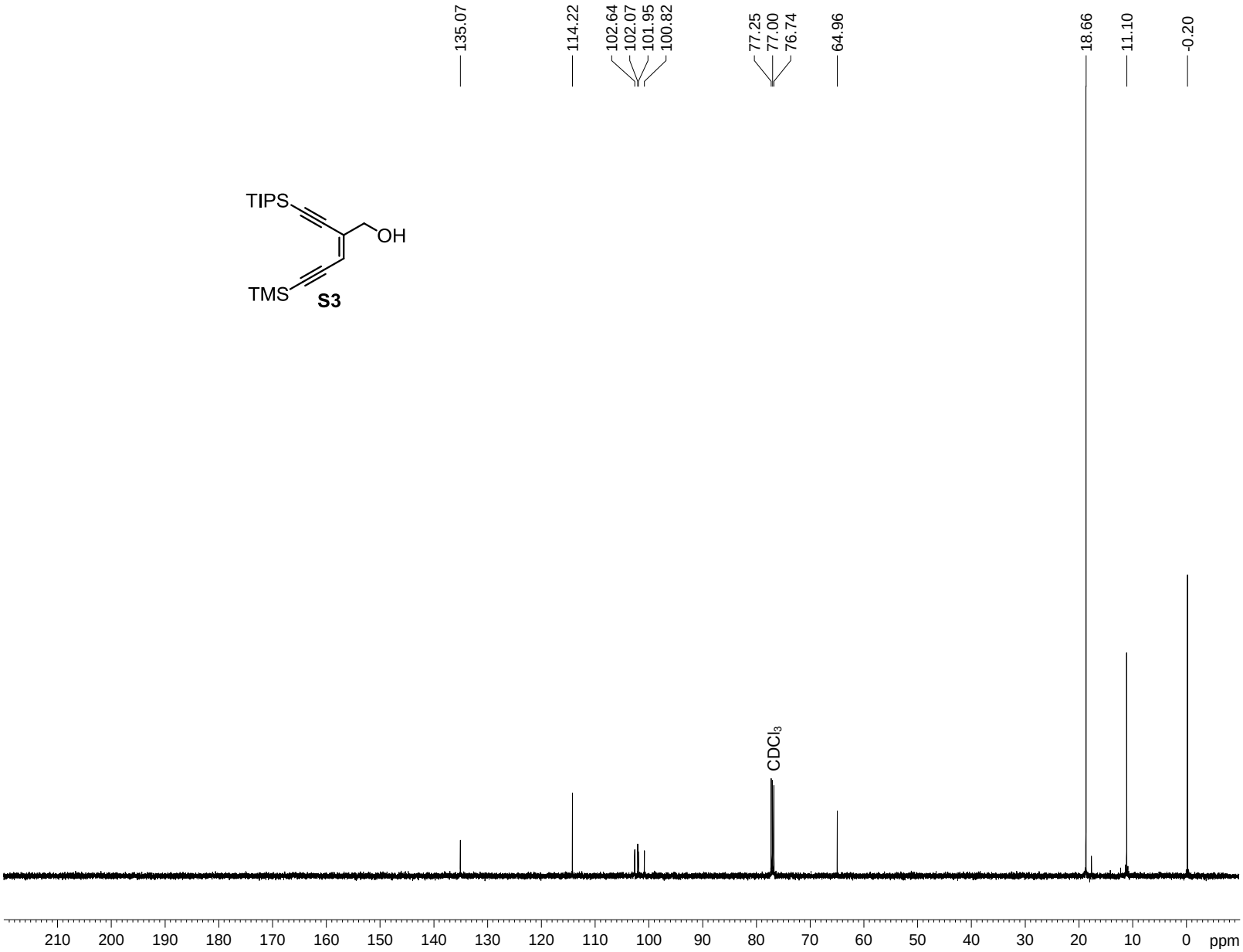


Figure S22. ^{13}C NMR spectrum of compound **S3** ($CDCl_3$, 126 MHz).

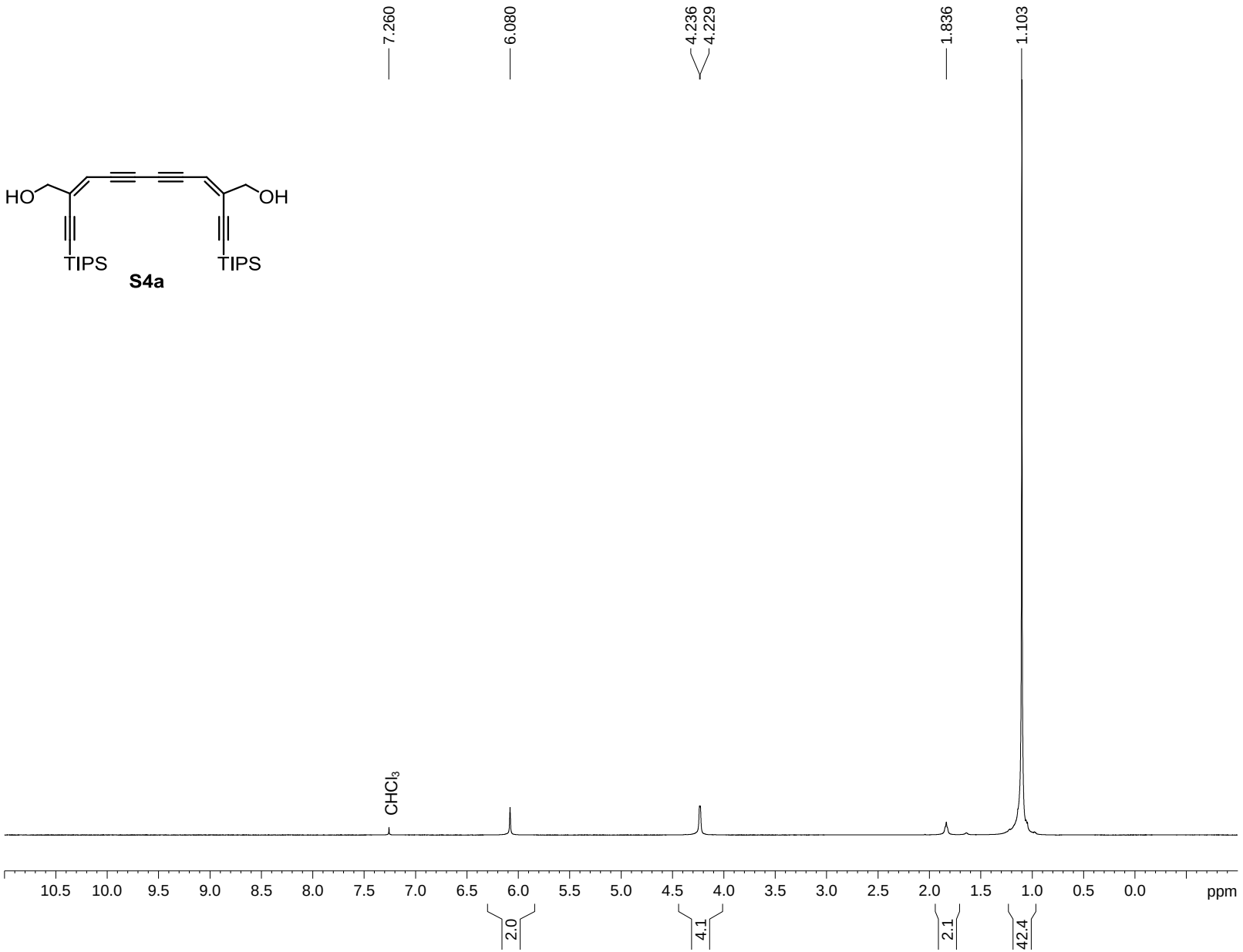


Figure S23. ^{1}H NMR spectrum of compound **S4a** ($CDCl_3$, 500 MHz).

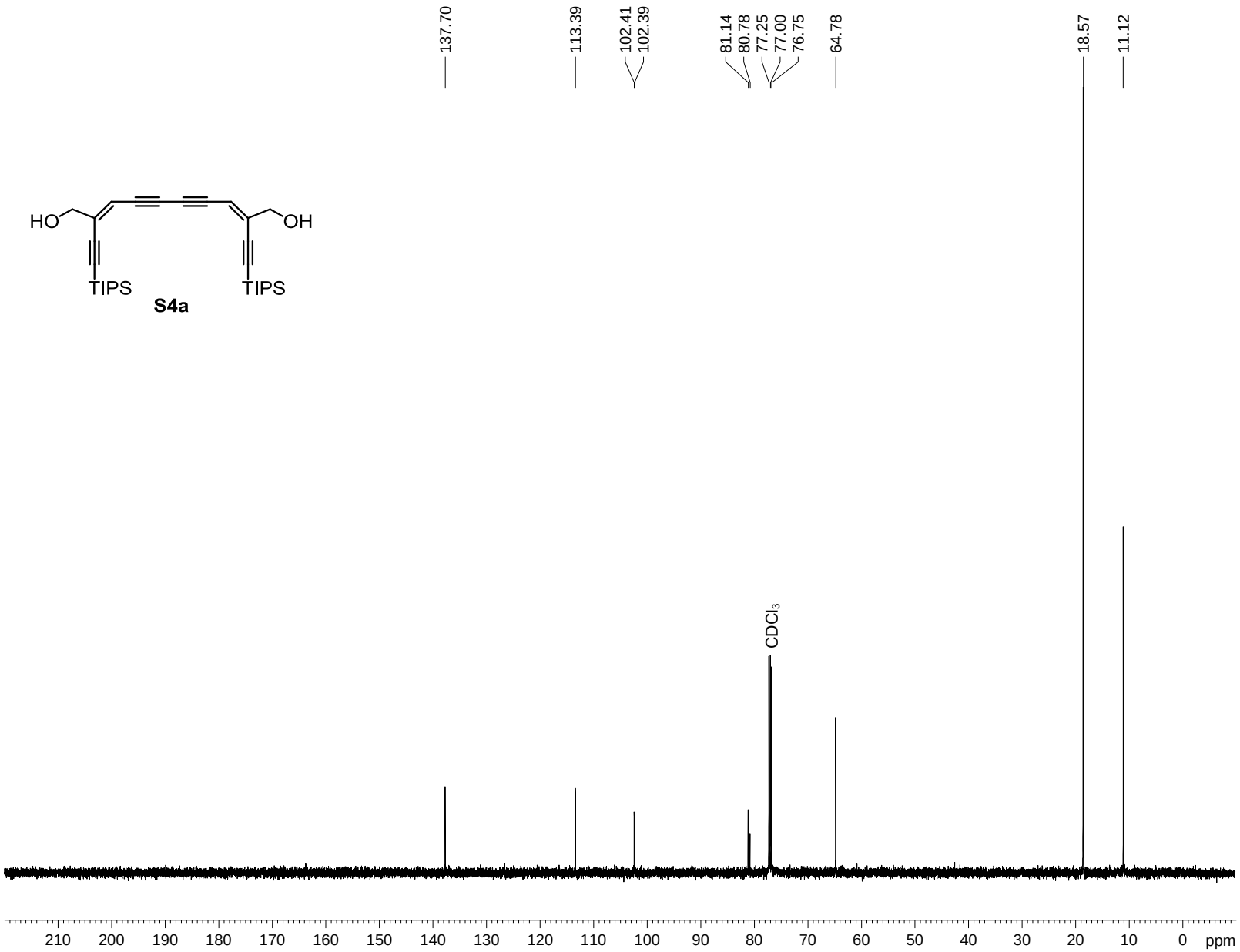


Figure S24. ^{13}C NMR spectrum of compound **S4a** ($CDCl_3$, 126 MHz).

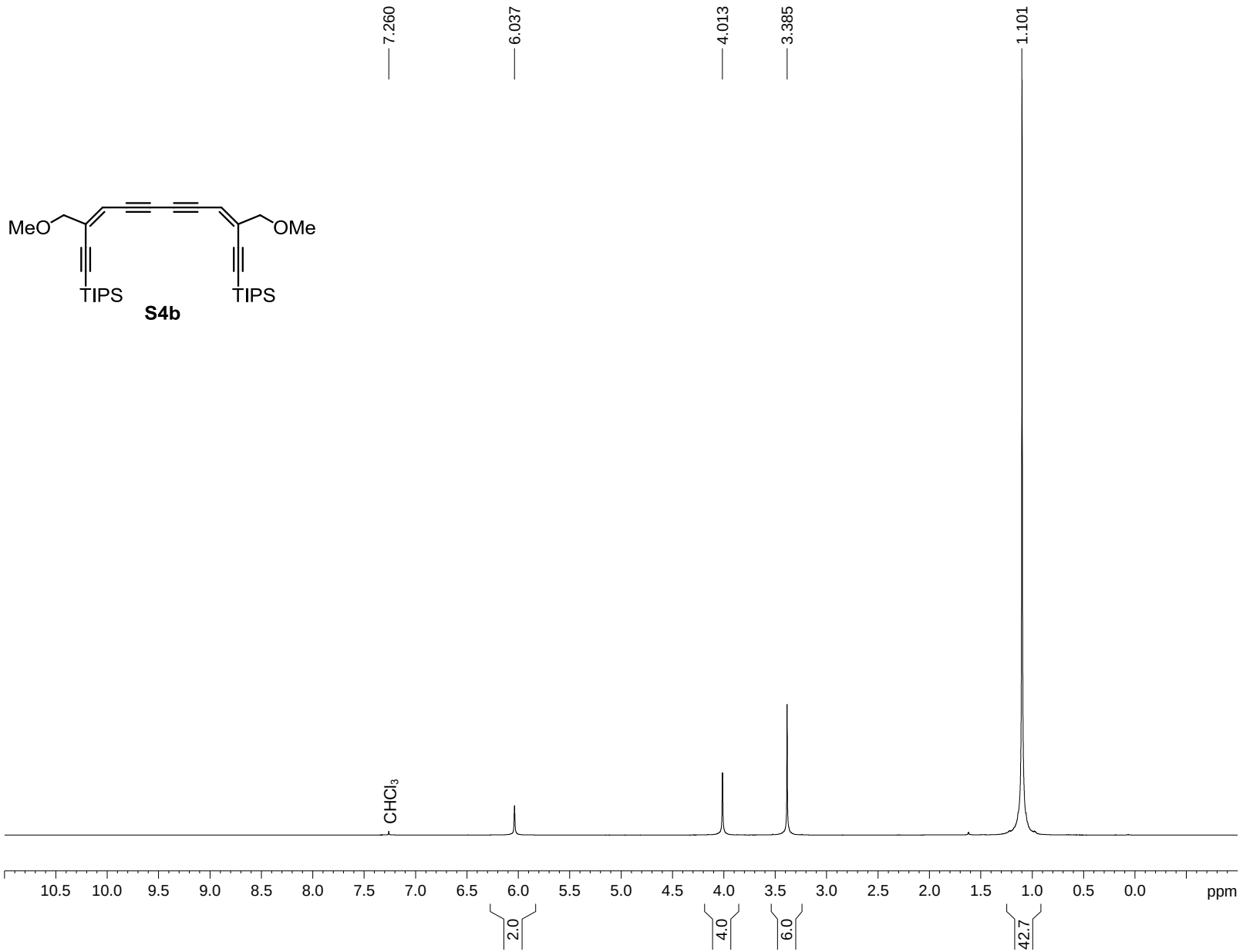


Figure S25. ^{1}H NMR spectrum of compound **S4b** ($CDCl_3$, 500 MHz).

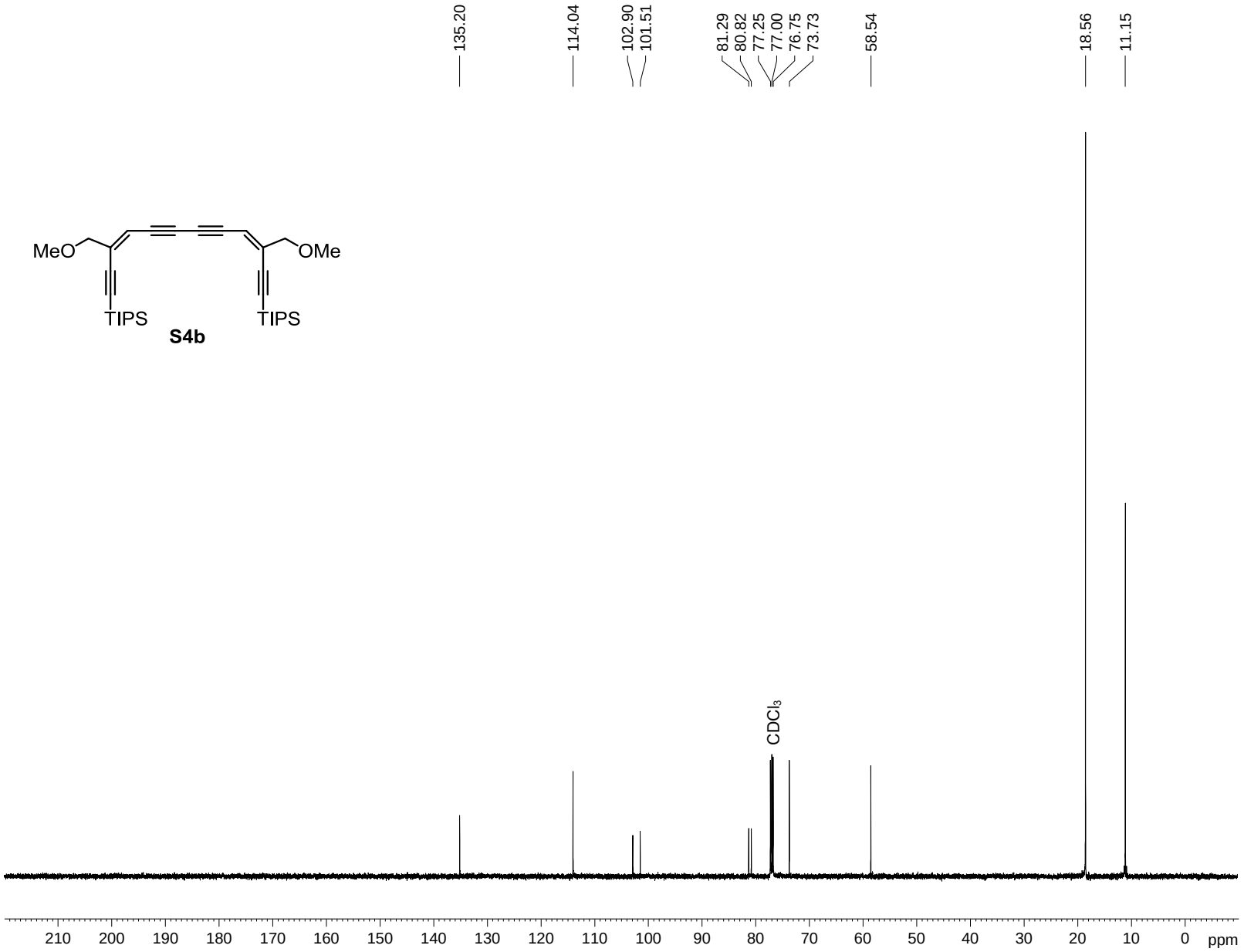


Figure S26. ^{13}C NMR spectrum of compound **S4b** ($CDCl_3$, 126 MHz).

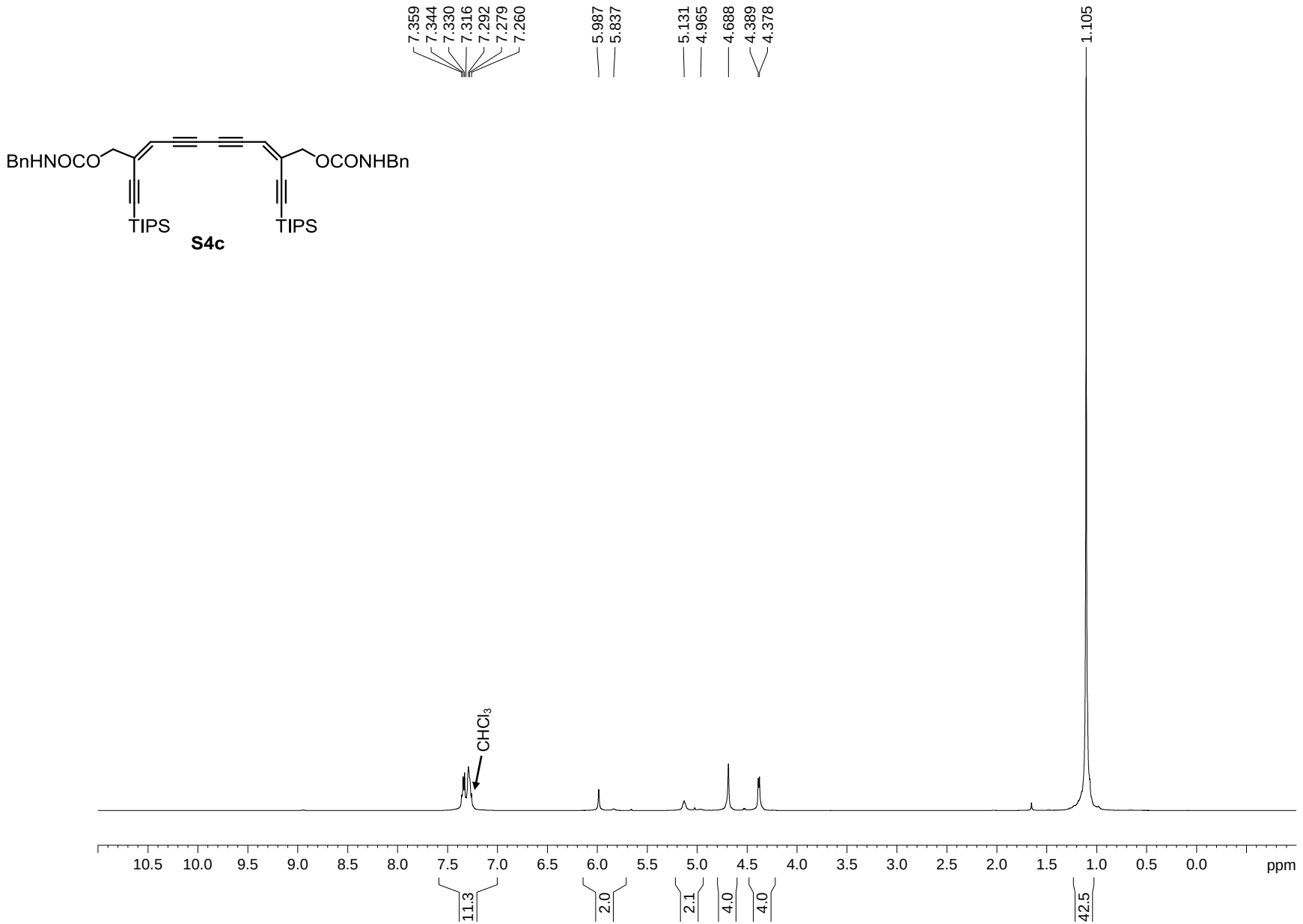


Figure S27. ^{1}H NMR spectrum of compound **S4c** ($CDCl_3$, 500 MHz).

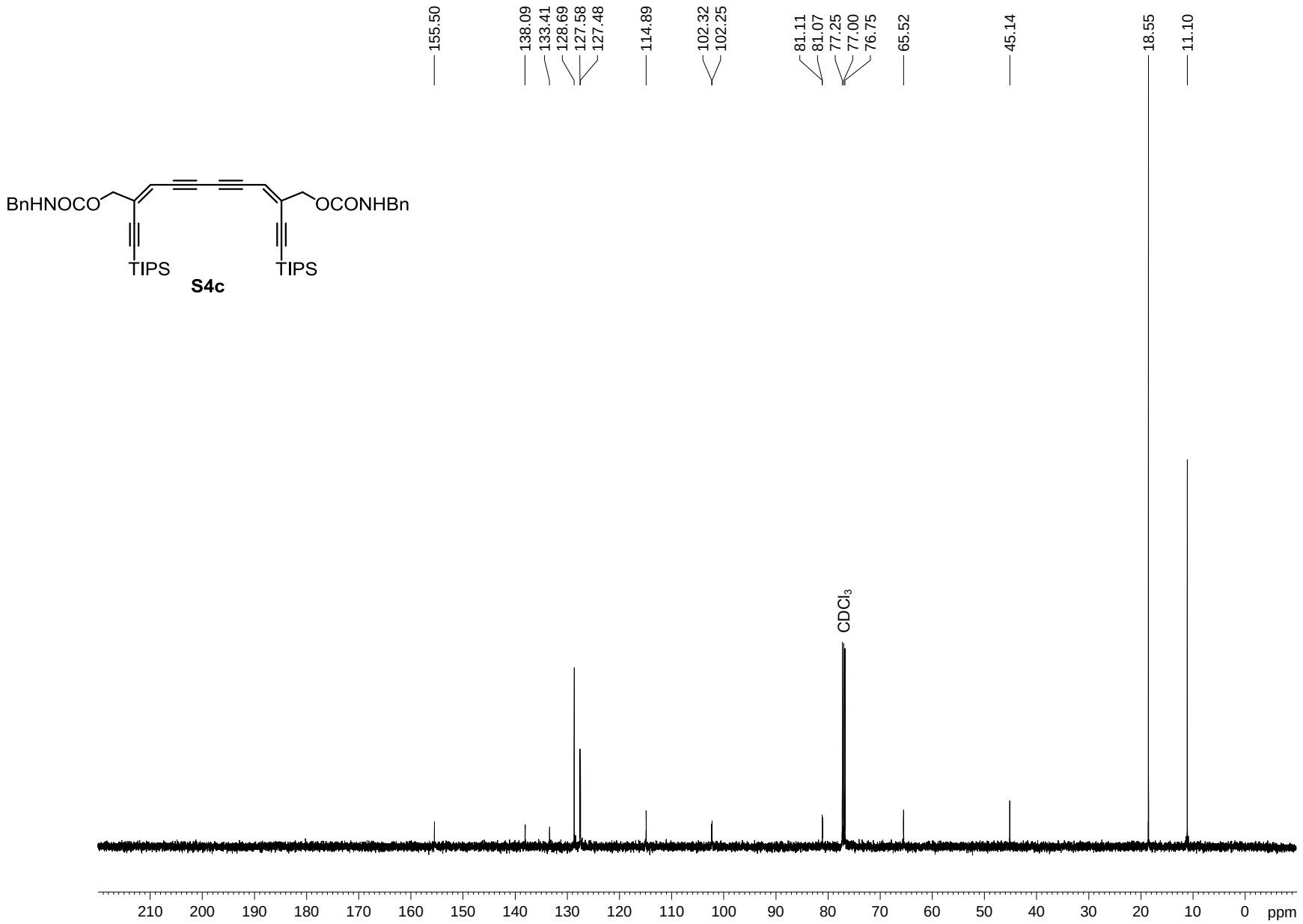


Figure S28. ^{13}C NMR spectrum of compound **S4c** ($CDCl_3$, 126 MHz).

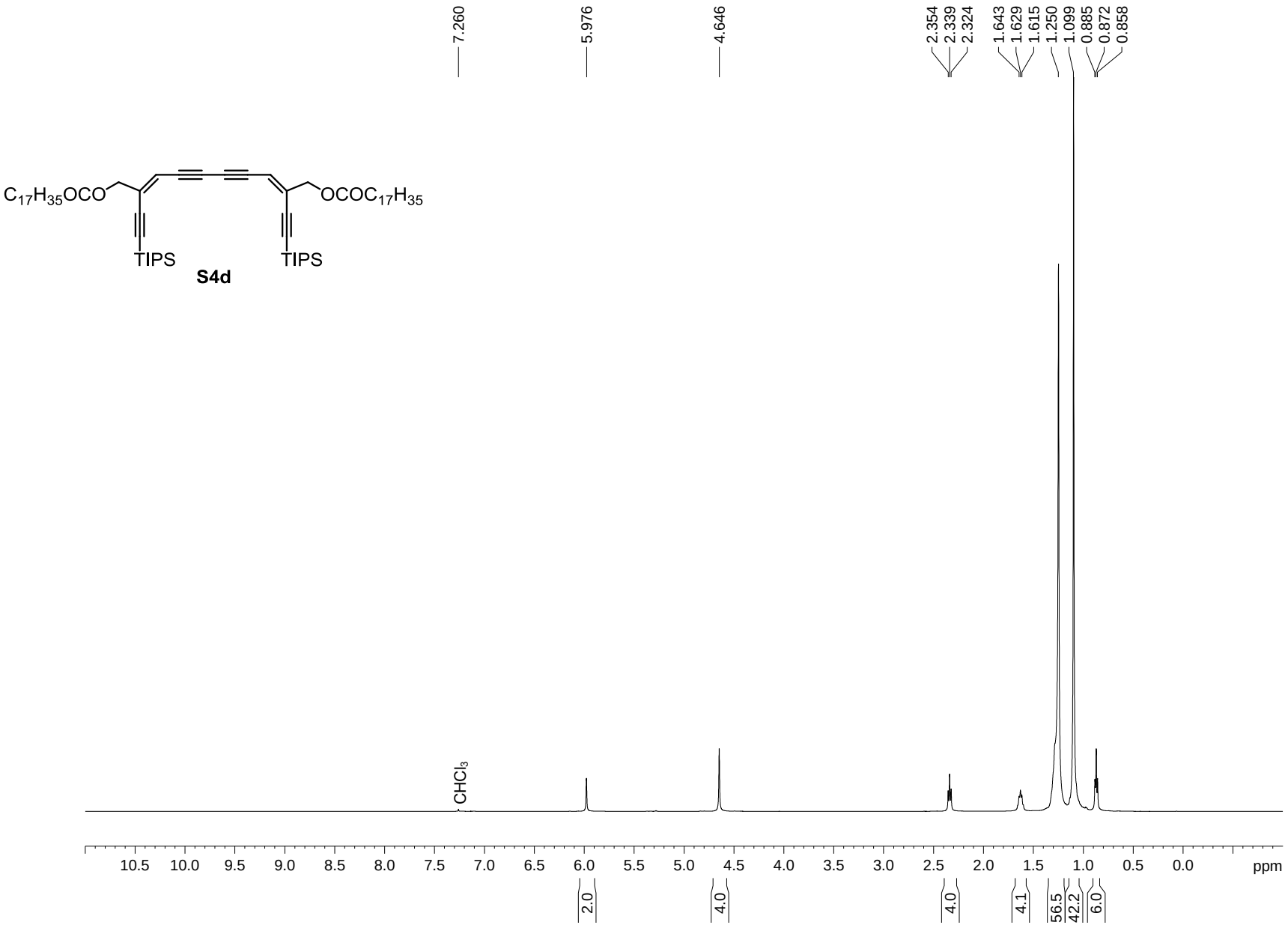


Figure S29. ^{1}H NMR spectrum of compound **S4d** ($CDCl_3$, 500 MHz).

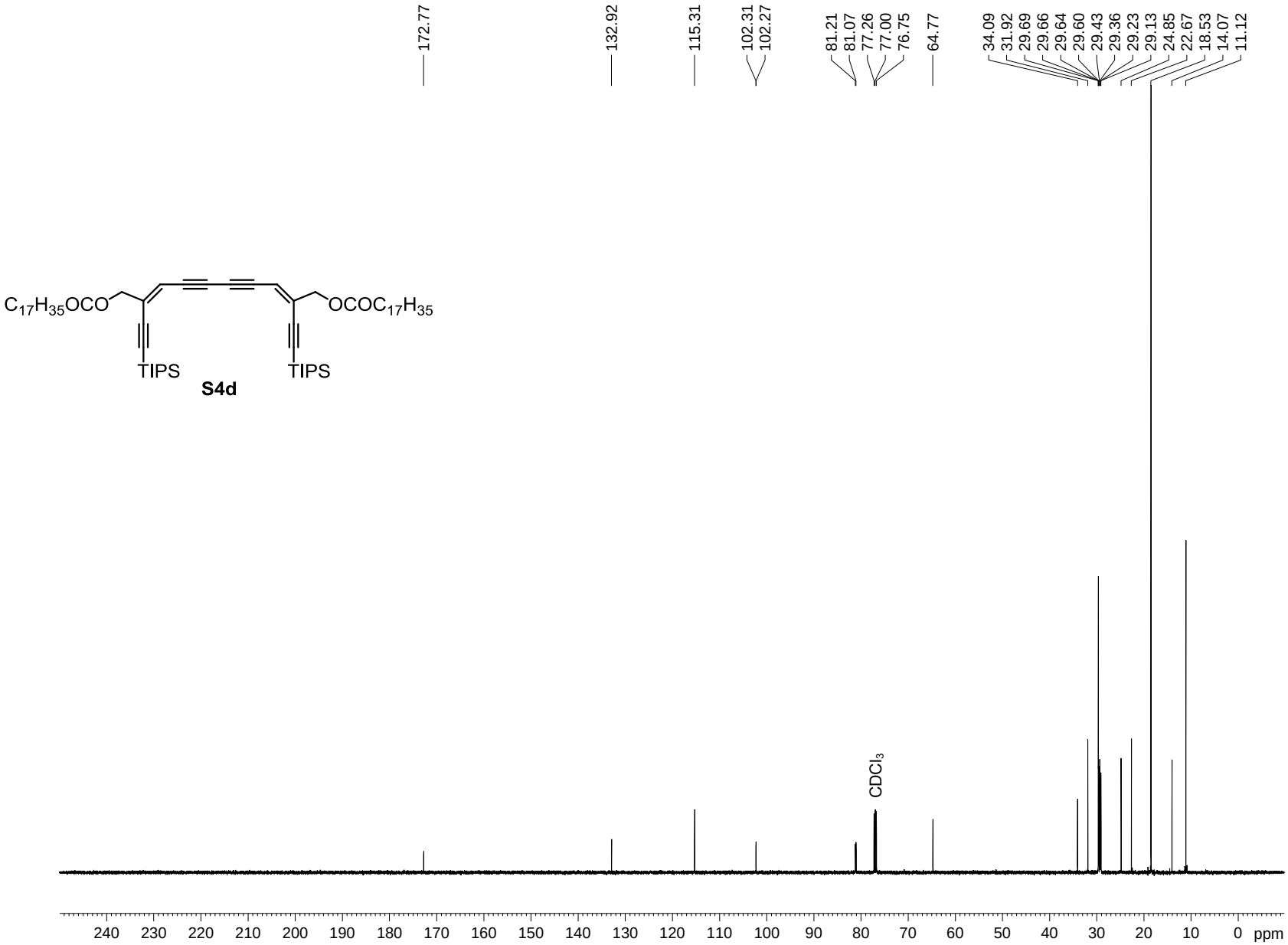


Figure S30. ^{13}C NMR spectrum of compound **S4d** ($CDCl_3$, 126 MHz).

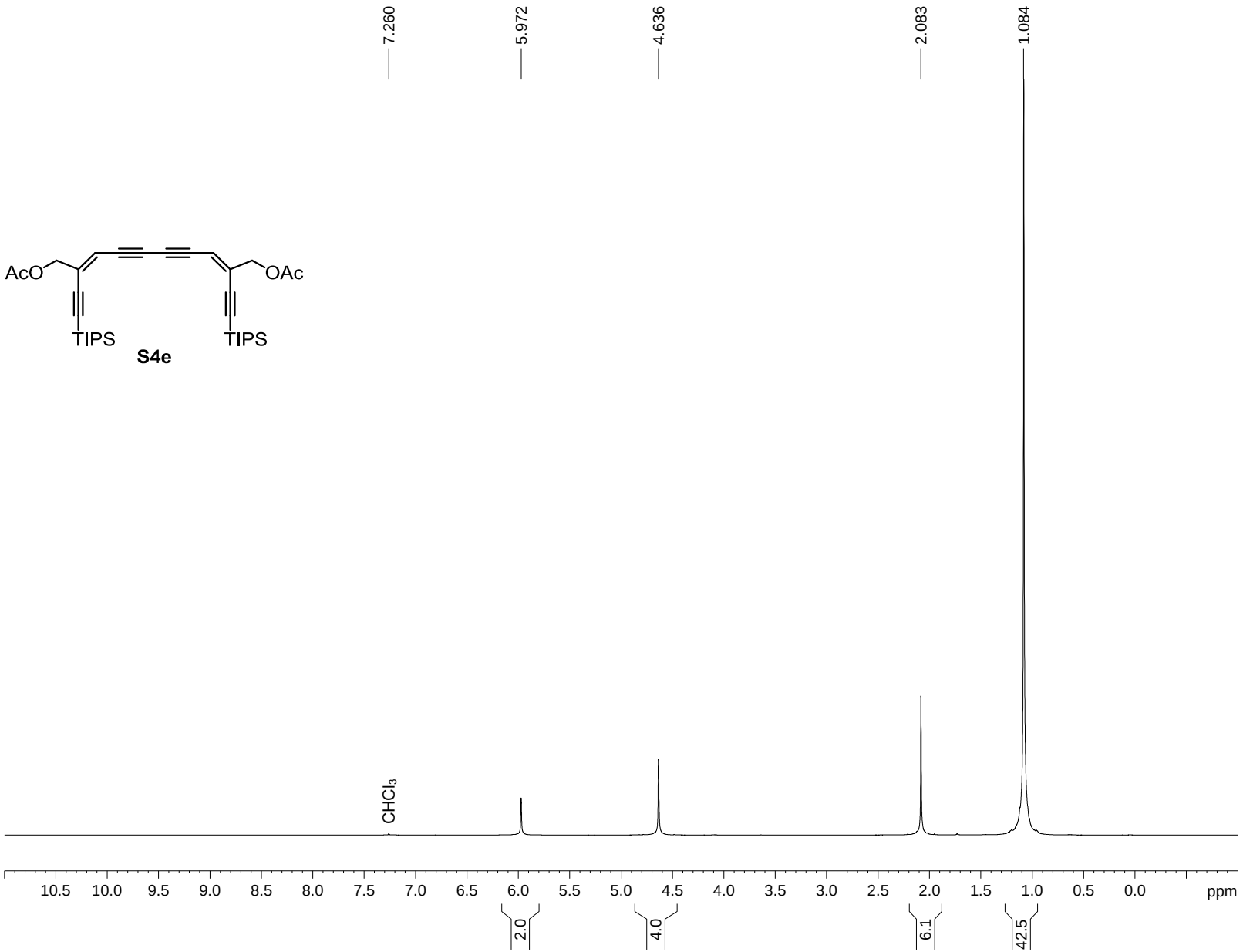


Figure S31. ^{1}H NMR spectrum of compound **S4e** ($CDCl_3$, 500 MHz).

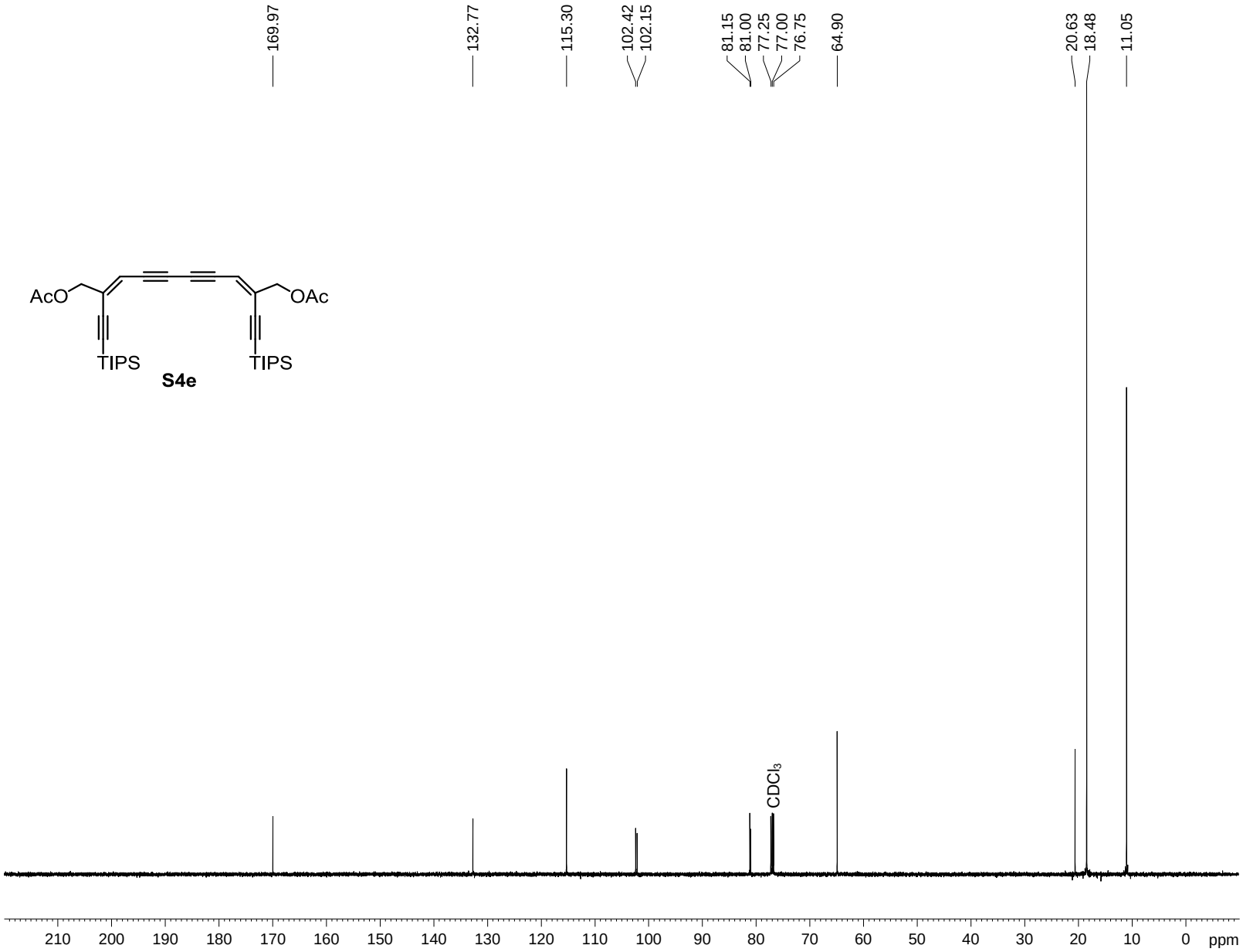


Figure S32. ^{13}C NMR spectrum of compound **S4e** ($CDCl_3$, 126 MHz).

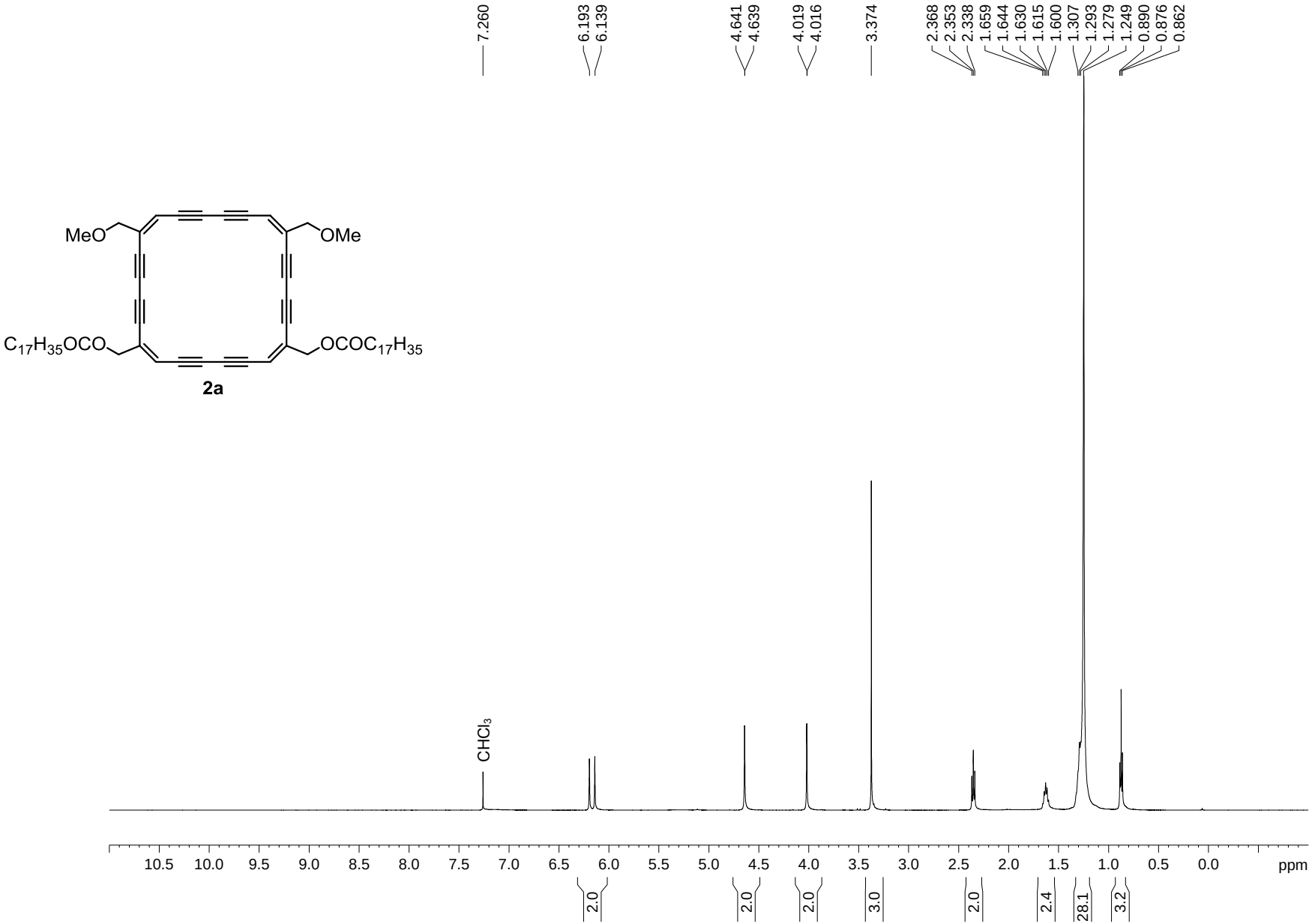


Figure S33. ^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 500 MHz).

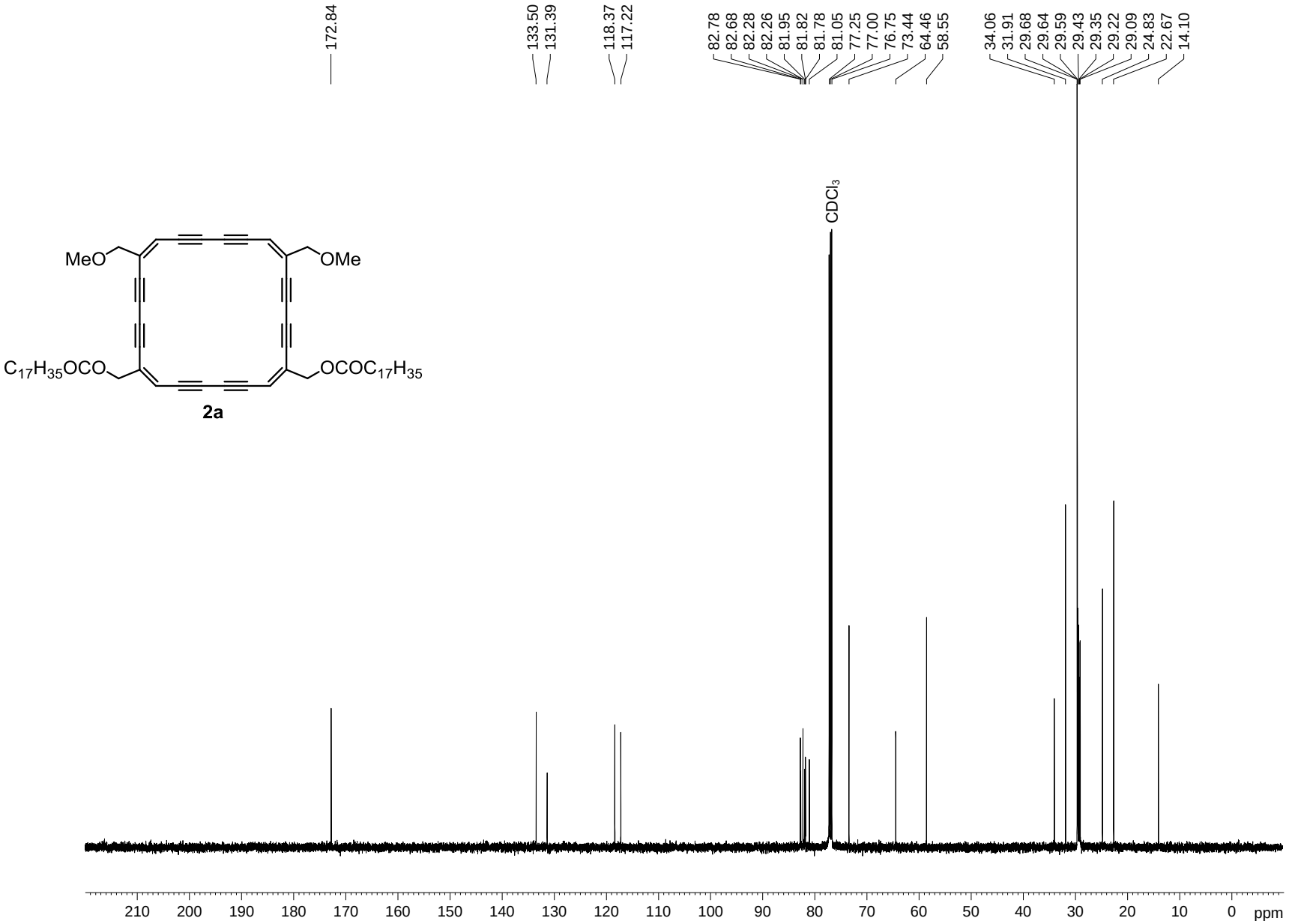


Figure S34. ^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 126 MHz).

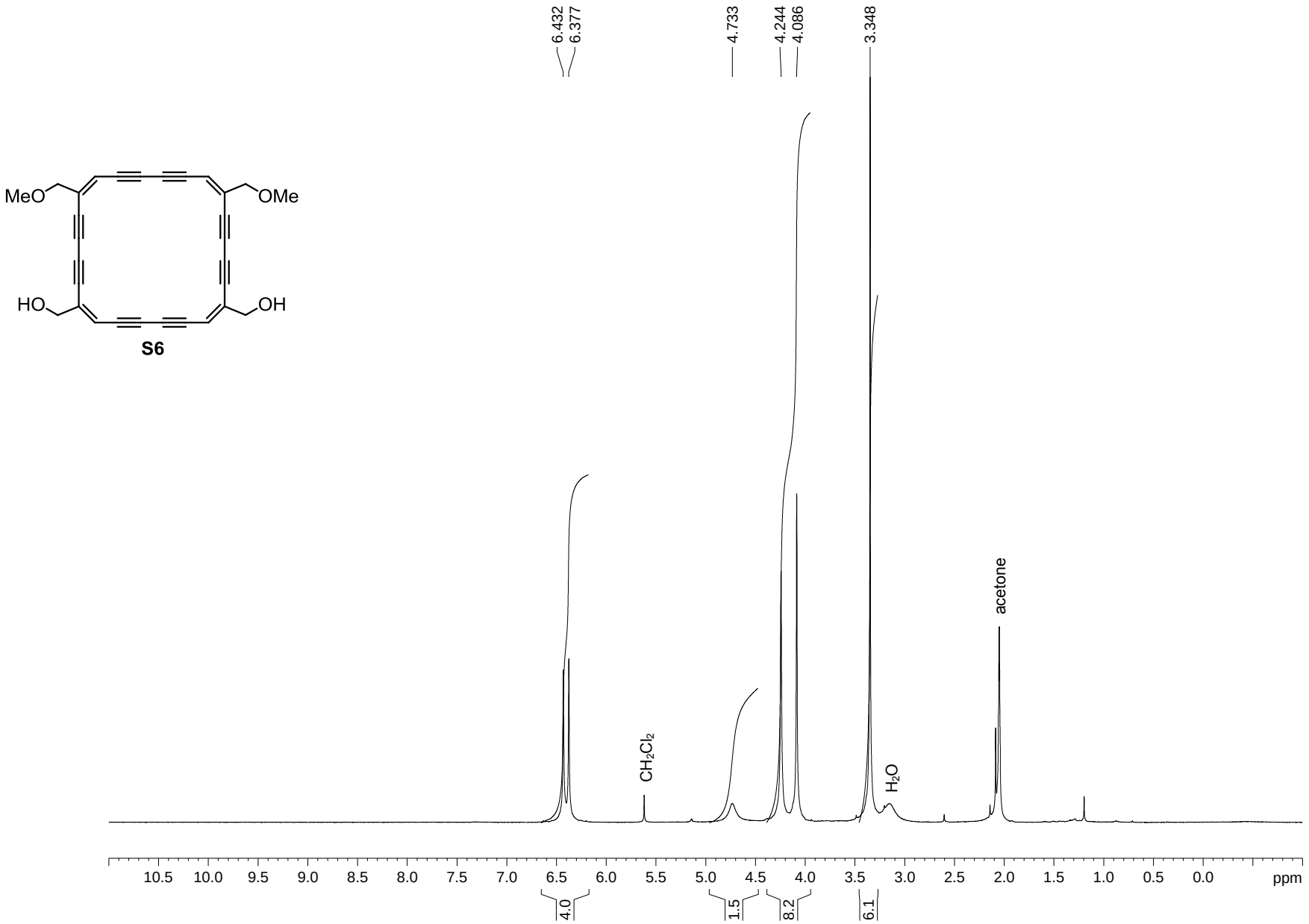


Figure S35. ^{1}H NMR spectrum of compound **S6** (acetone-d_6, 500 MHz).

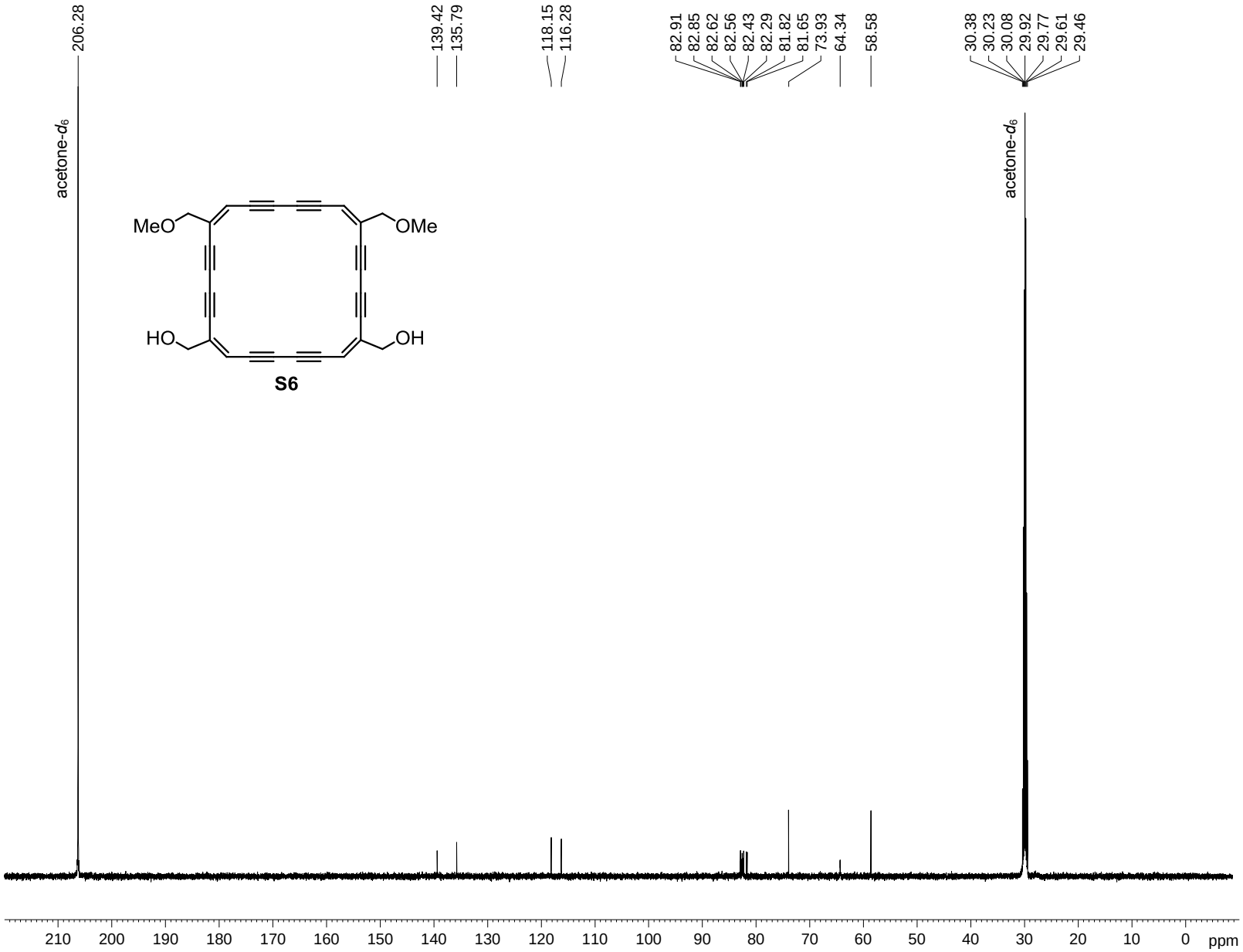


Figure S36. ^{13}C NMR spectrum of compound **S6** (acetone-d_6, 126 MHz).

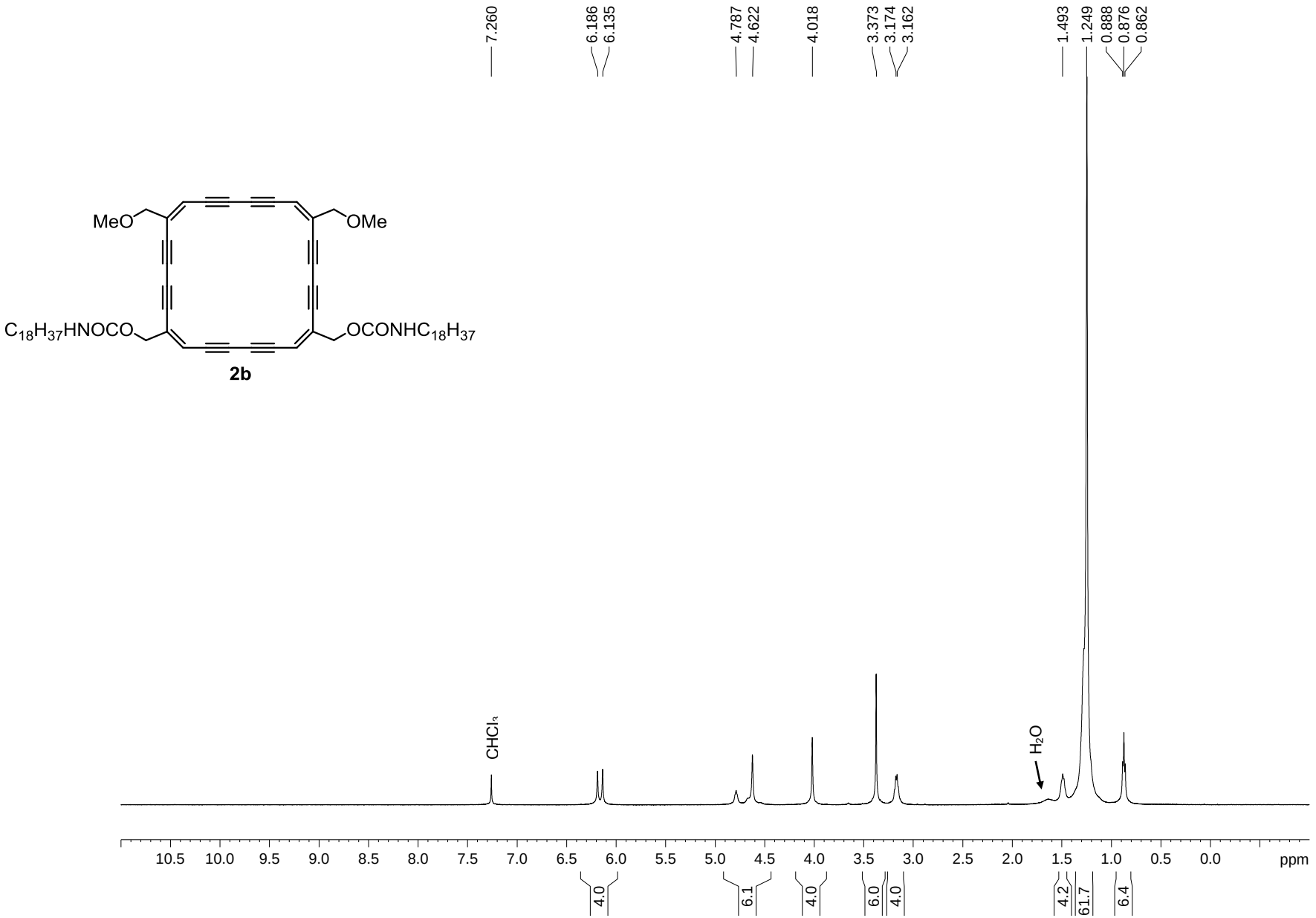


Figure S37. ^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 500 MHz).

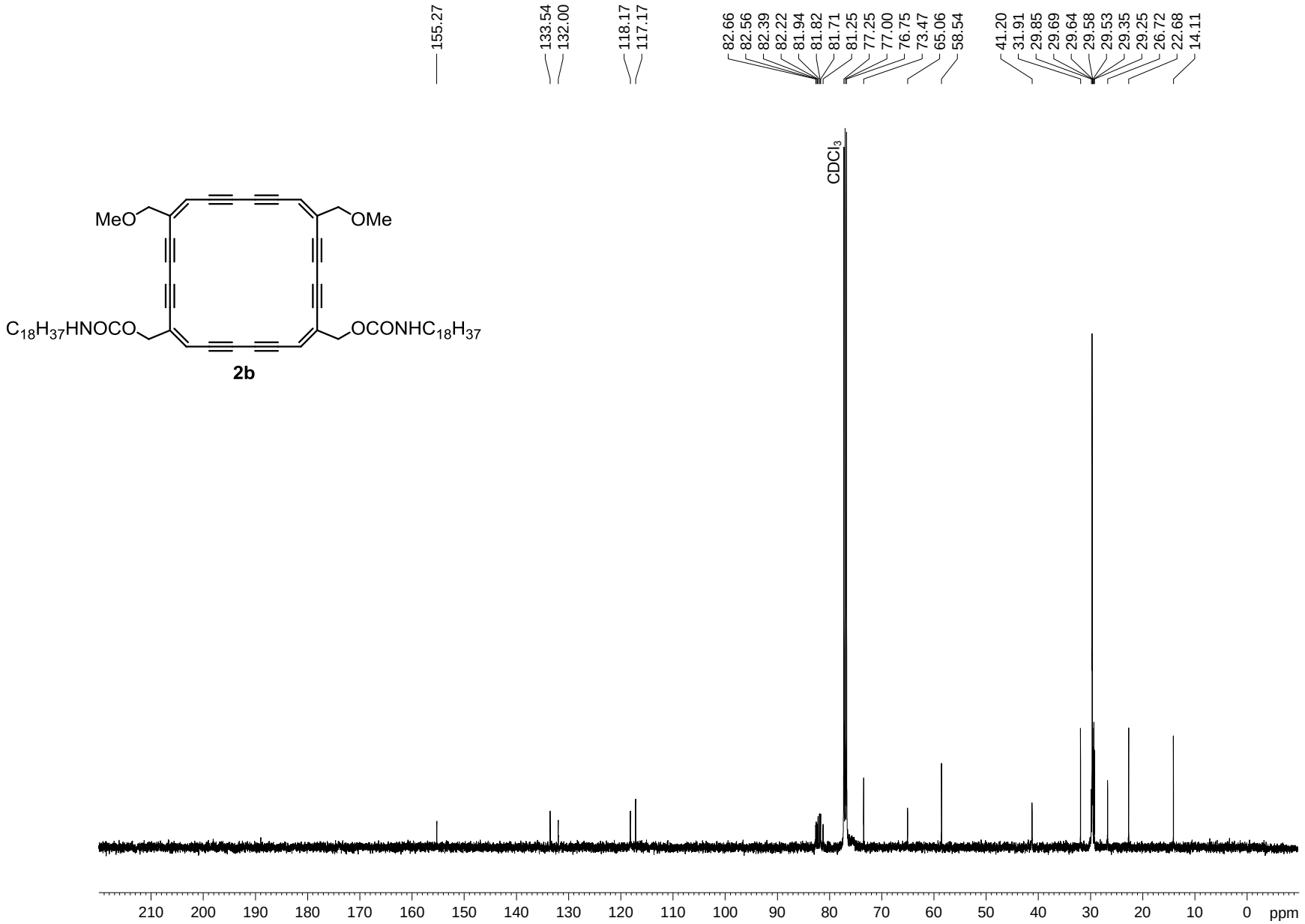


Figure S38. ^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 126 MHz).

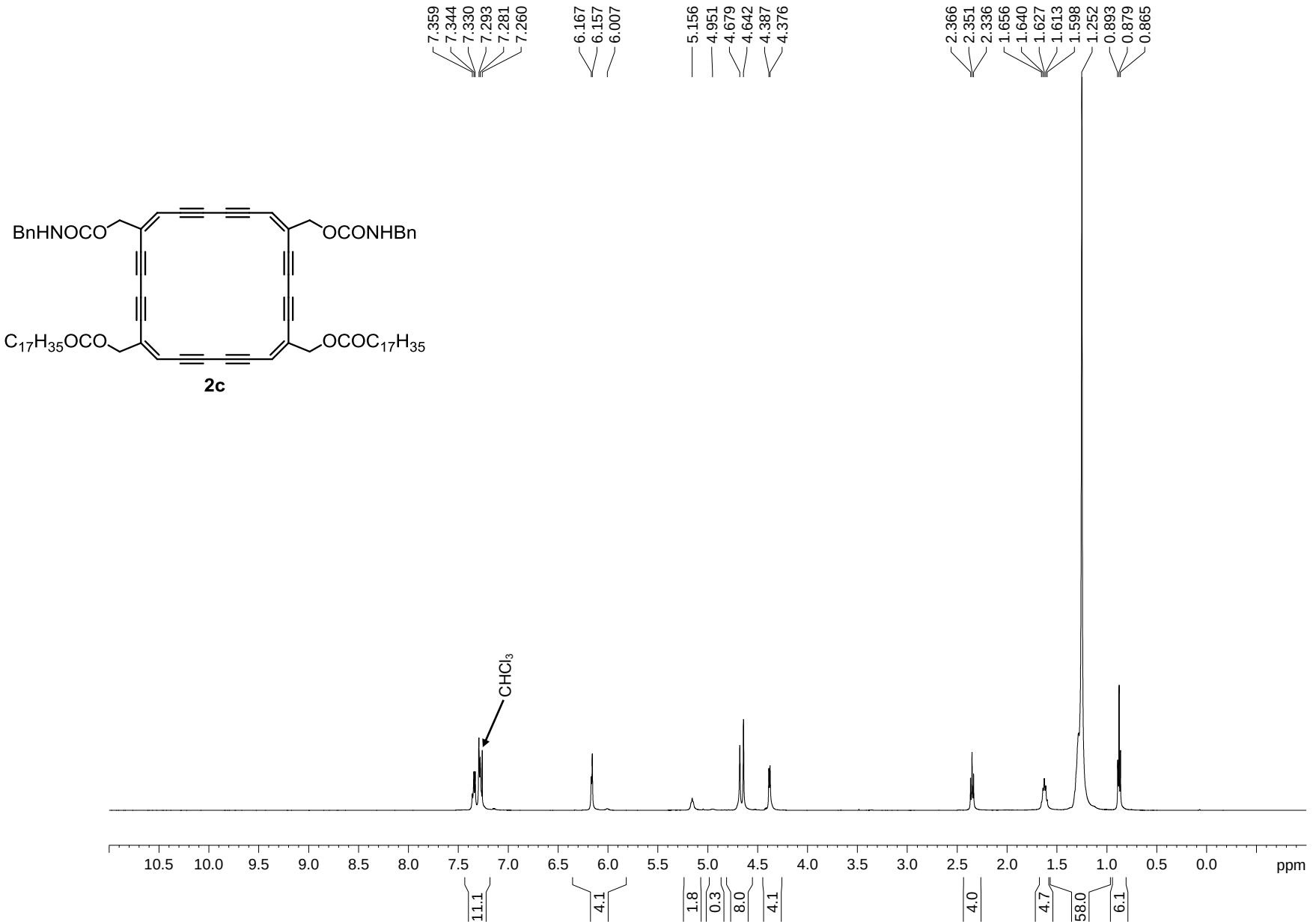


Figure S39. ^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 500 MHz).

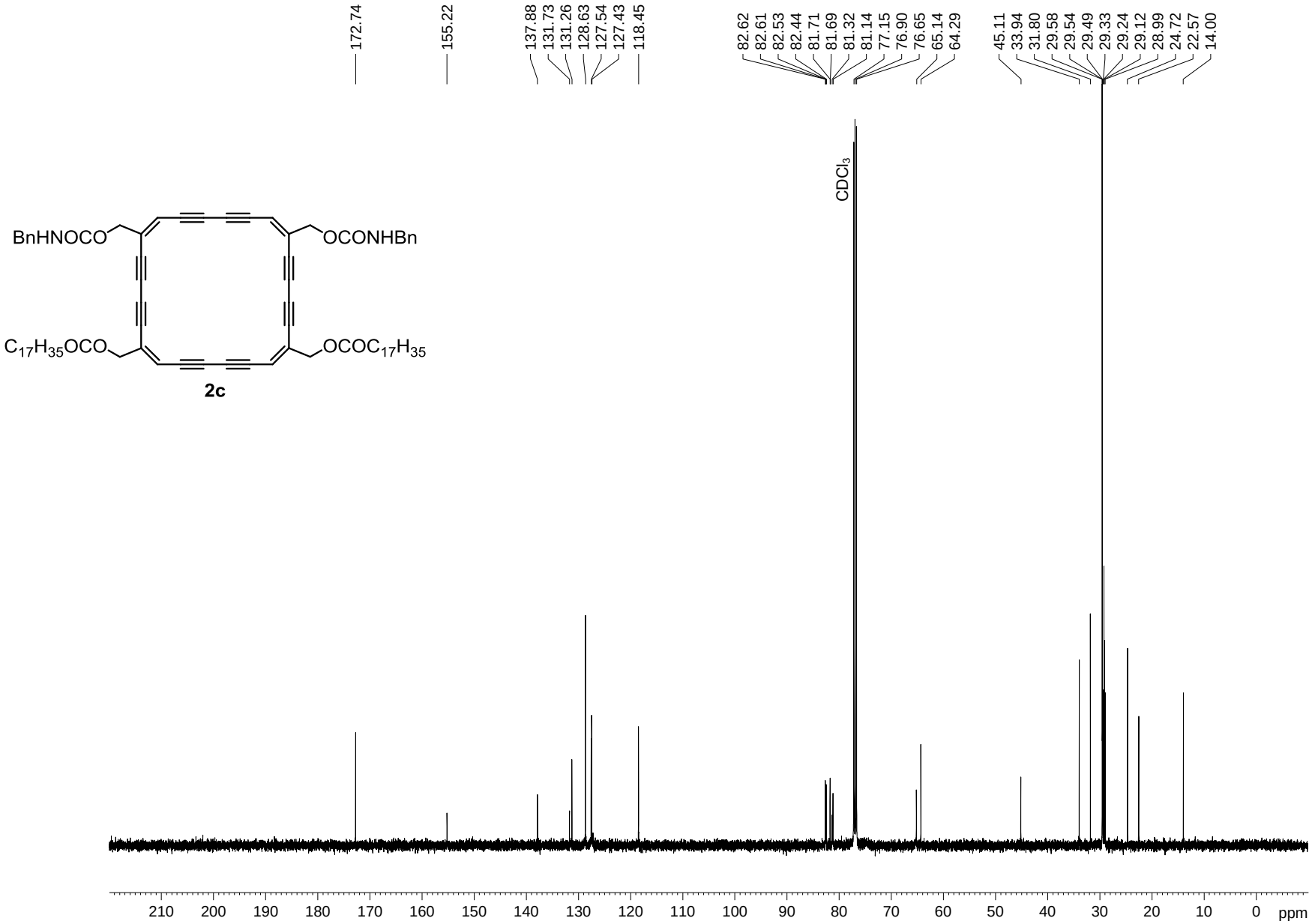


Figure S40. ^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 126 MHz).

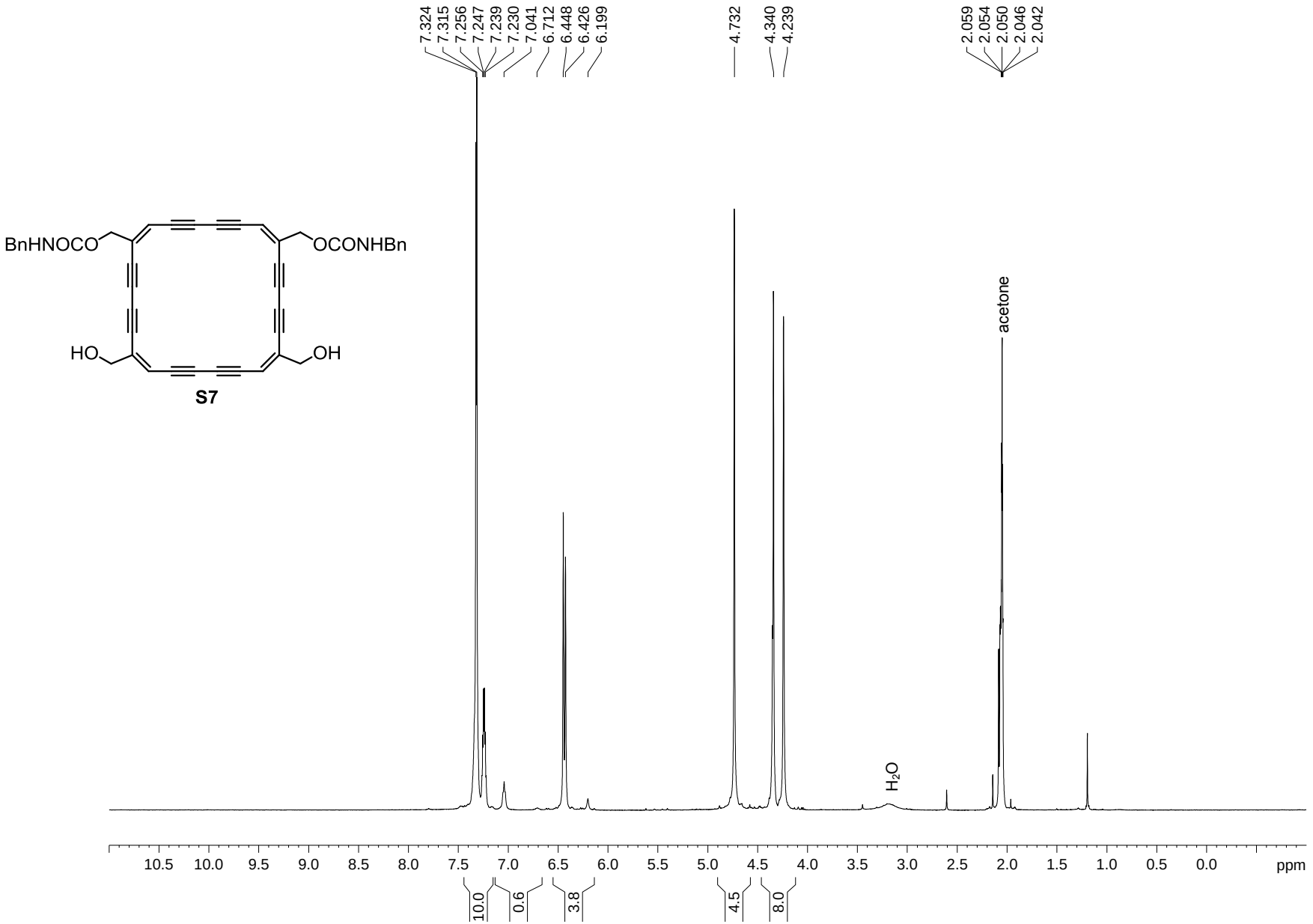


Figure S41. ^{1}H NMR spectrum of compound **S7** (acetone-d_6, 500 MHz).

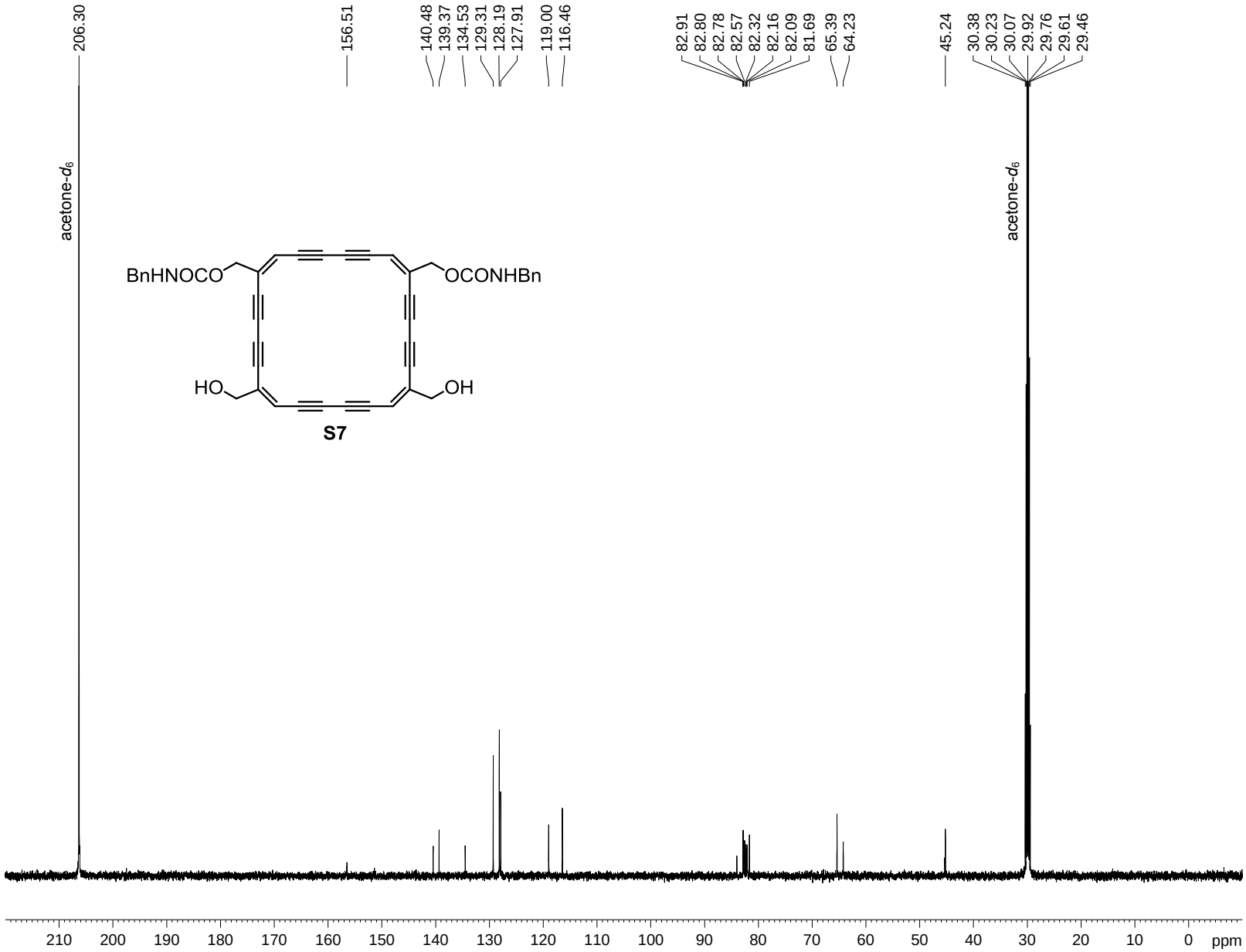


Figure S42. ^{13}C NMR spectrum of compound **S7** (acetone-d_6, 126 MHz).

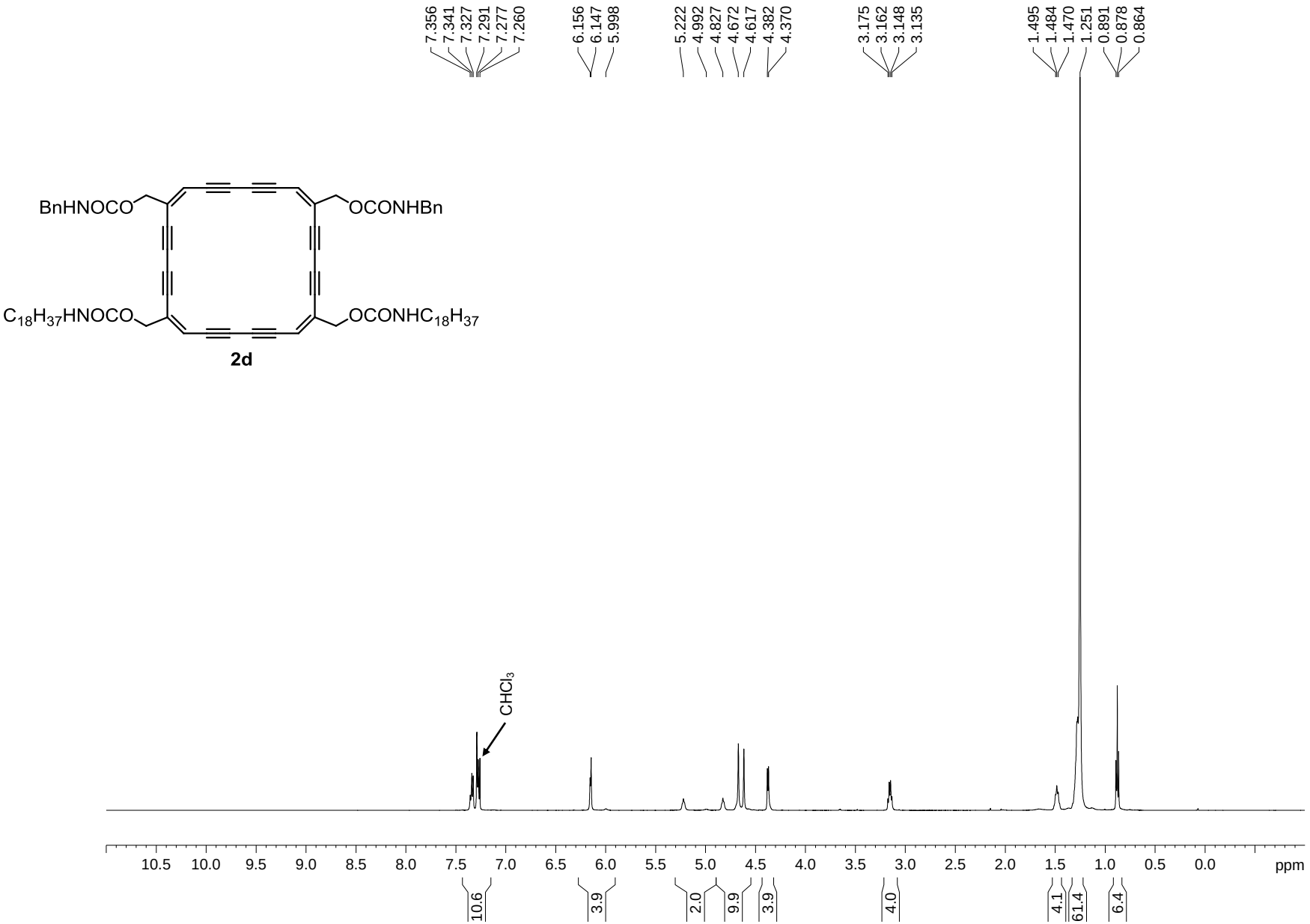


Figure S43. ^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 500 MHz).

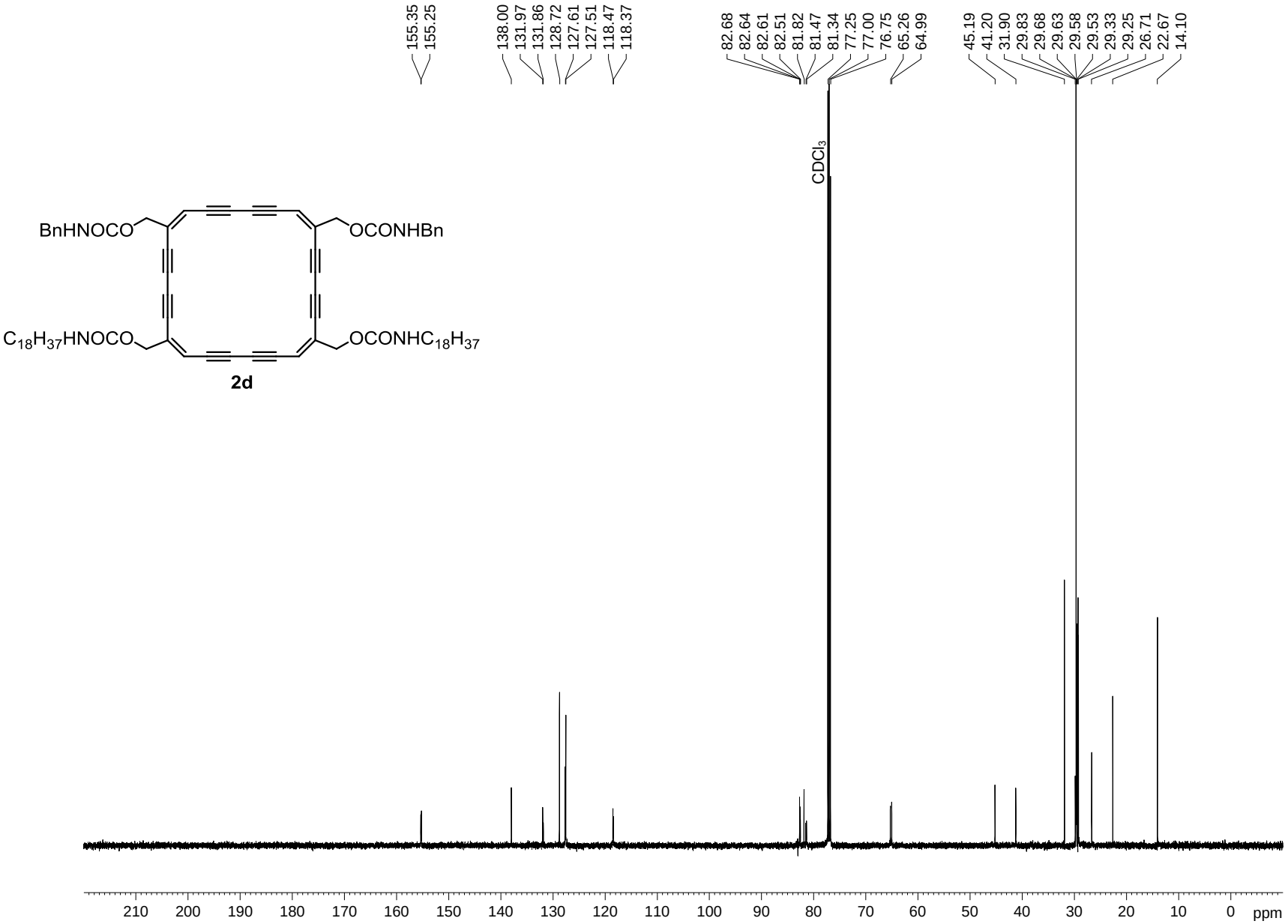


Figure S44. ^{13}C NMR spectrum of compound **13b** ($CDCl_3$, 126 MHz).

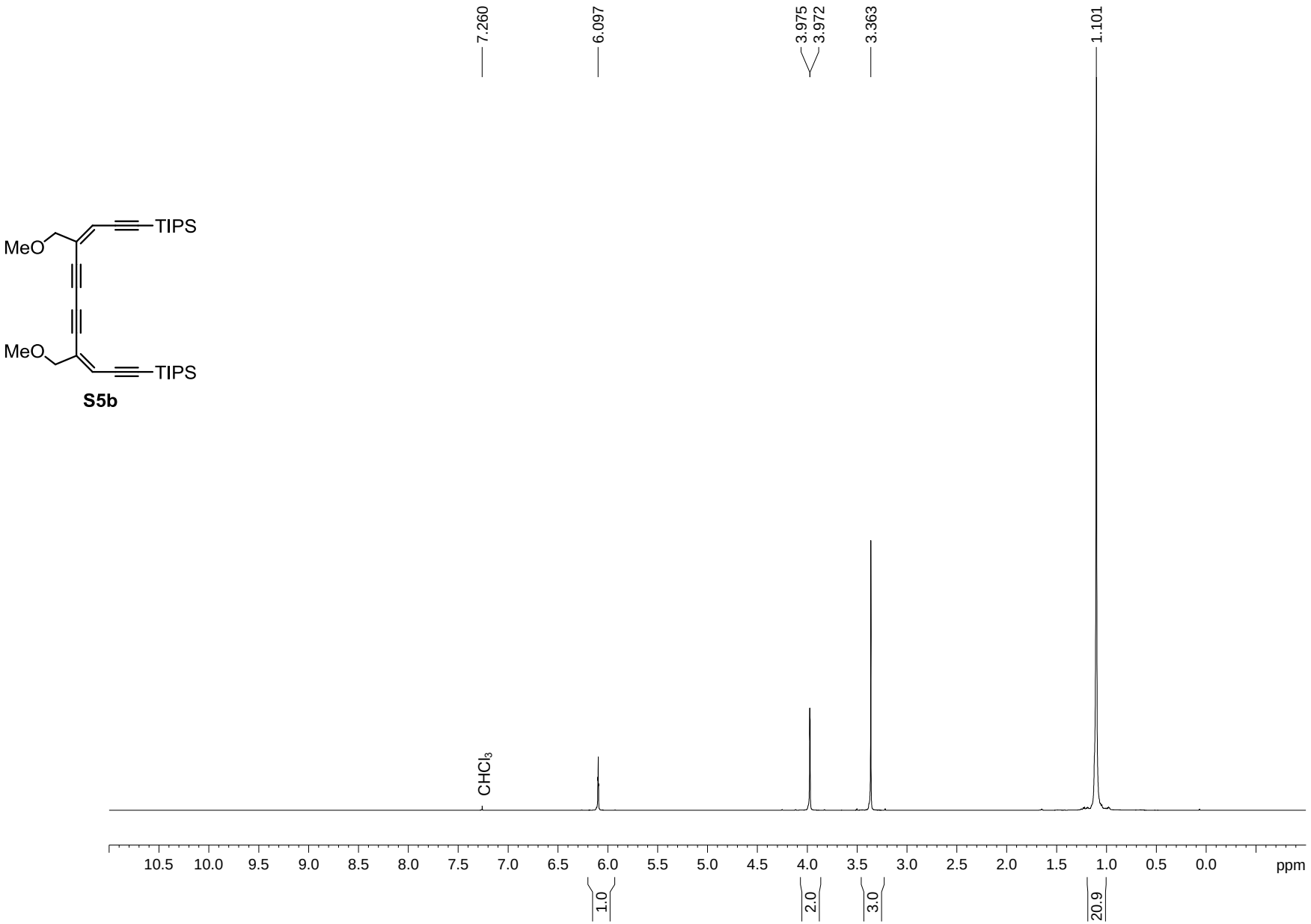


Figure S45. ^{1}H NMR spectrum of **S5b** ($CDCl_3$, 500 MHz).

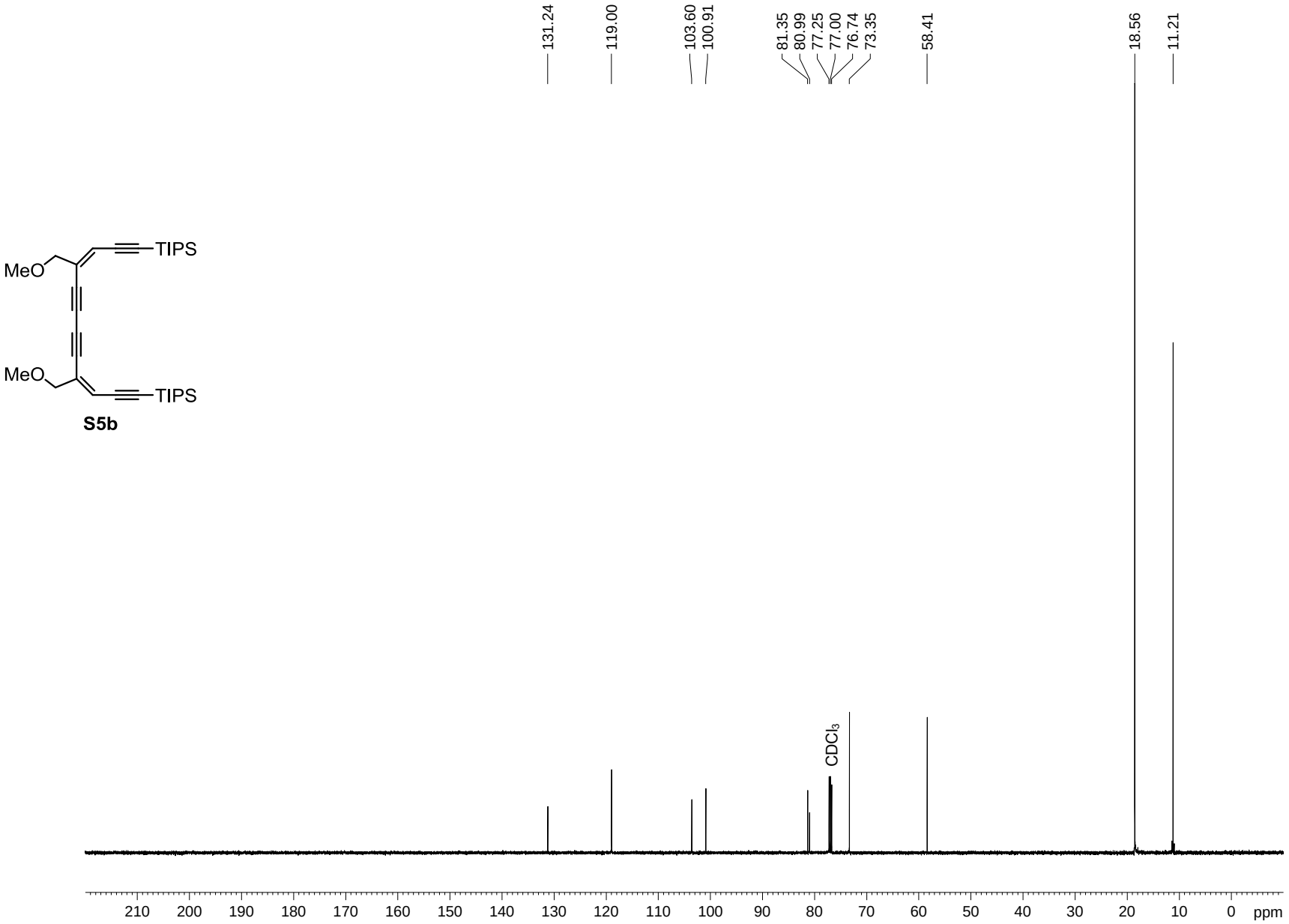


Figure S46. ^{13}C NMR spectrum of **S5b** ($CDCl_3$, 126 MHz).

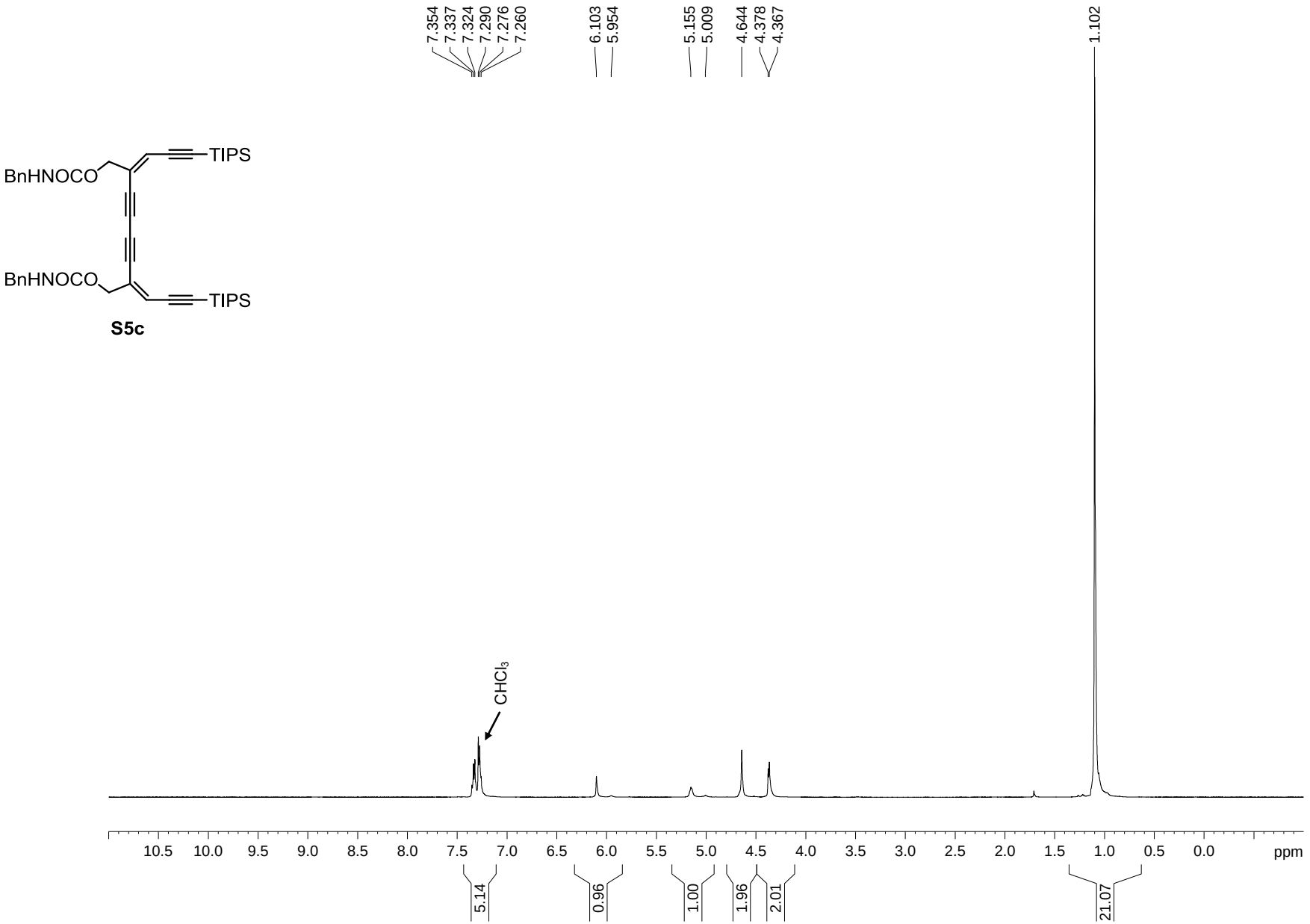


Figure S47. ^{1}H NMR spectrum of **S5c** ($CDCl_3$, 500 MHz).

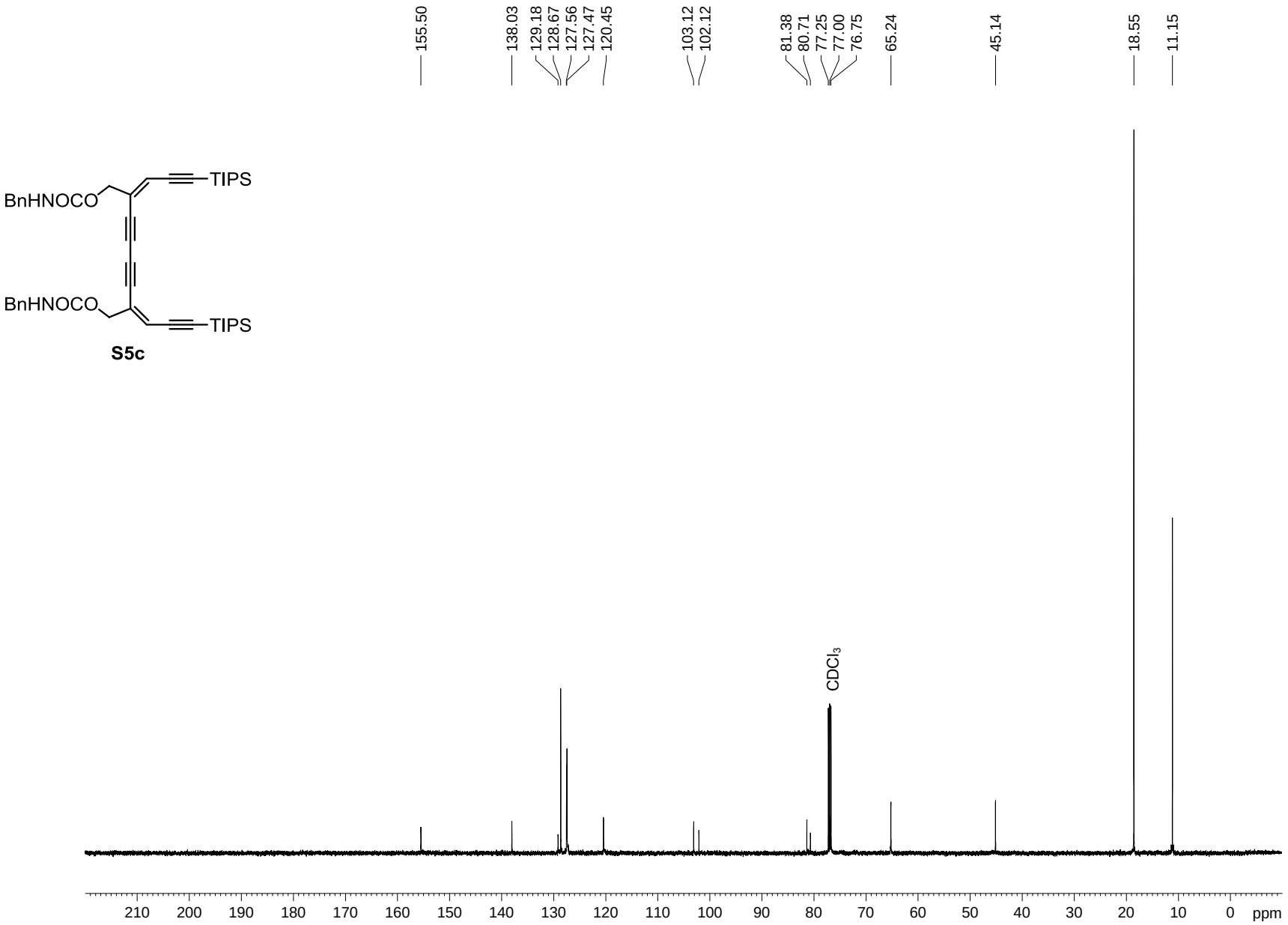


Figure S48. ^{13}C NMR spectrum of **S5c** ($CDCl_3$, 126 MHz).

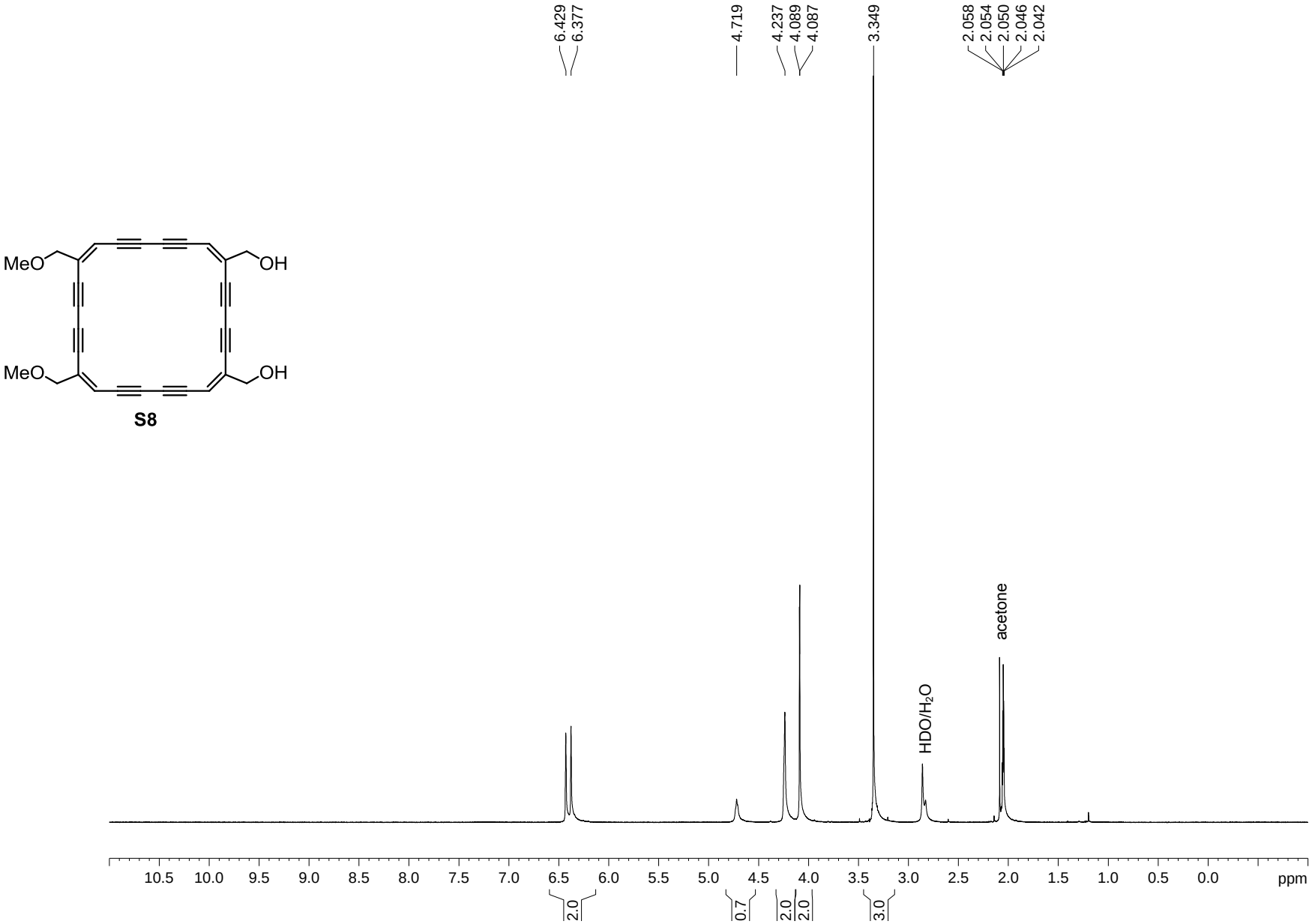


Figure S49. ^{1}H NMR of compound **S8** (acetone-d_6, 500 MHz).

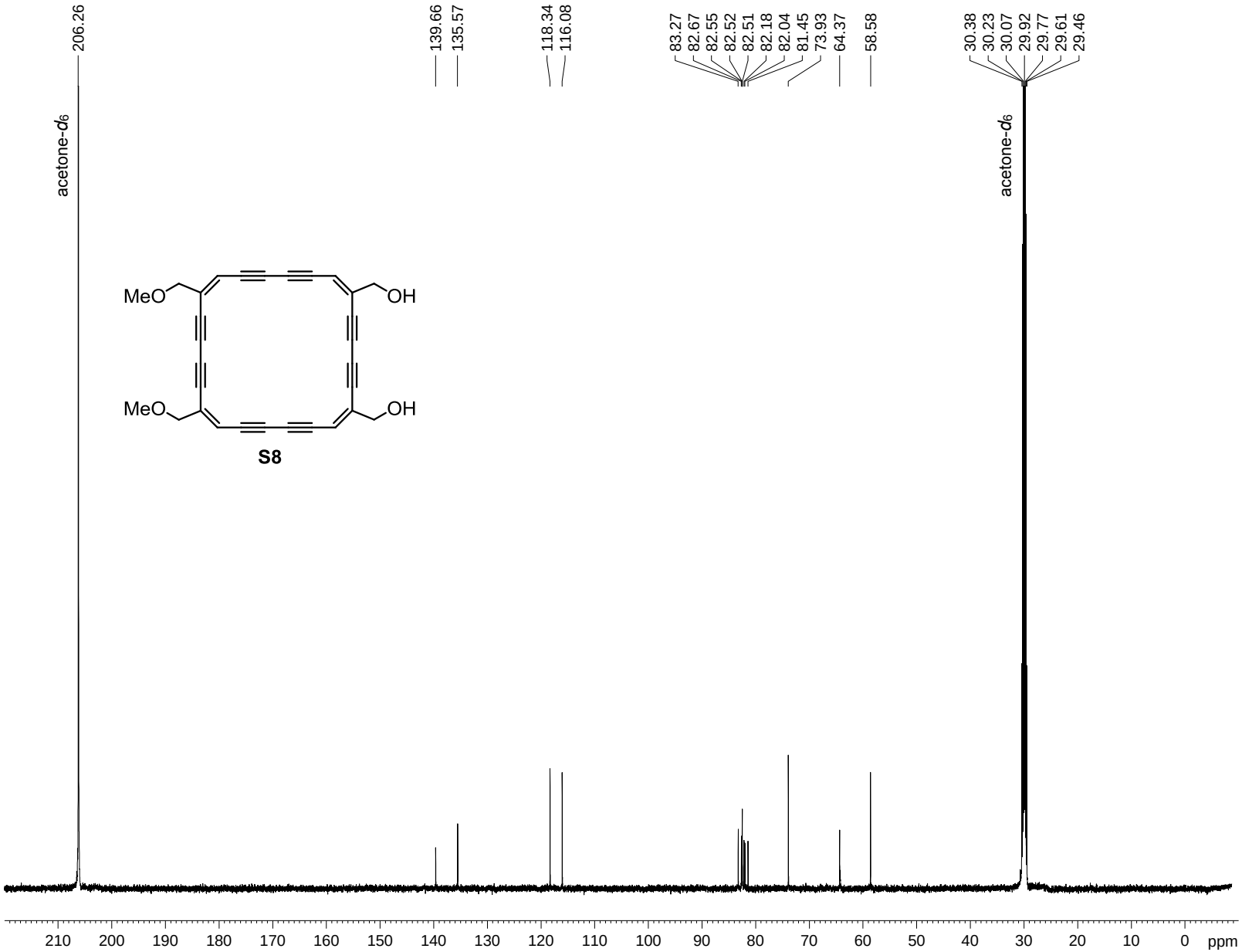


Figure S50. ^{13}C NMR of compound **S8** (acetone-d_6, 126 MHz).

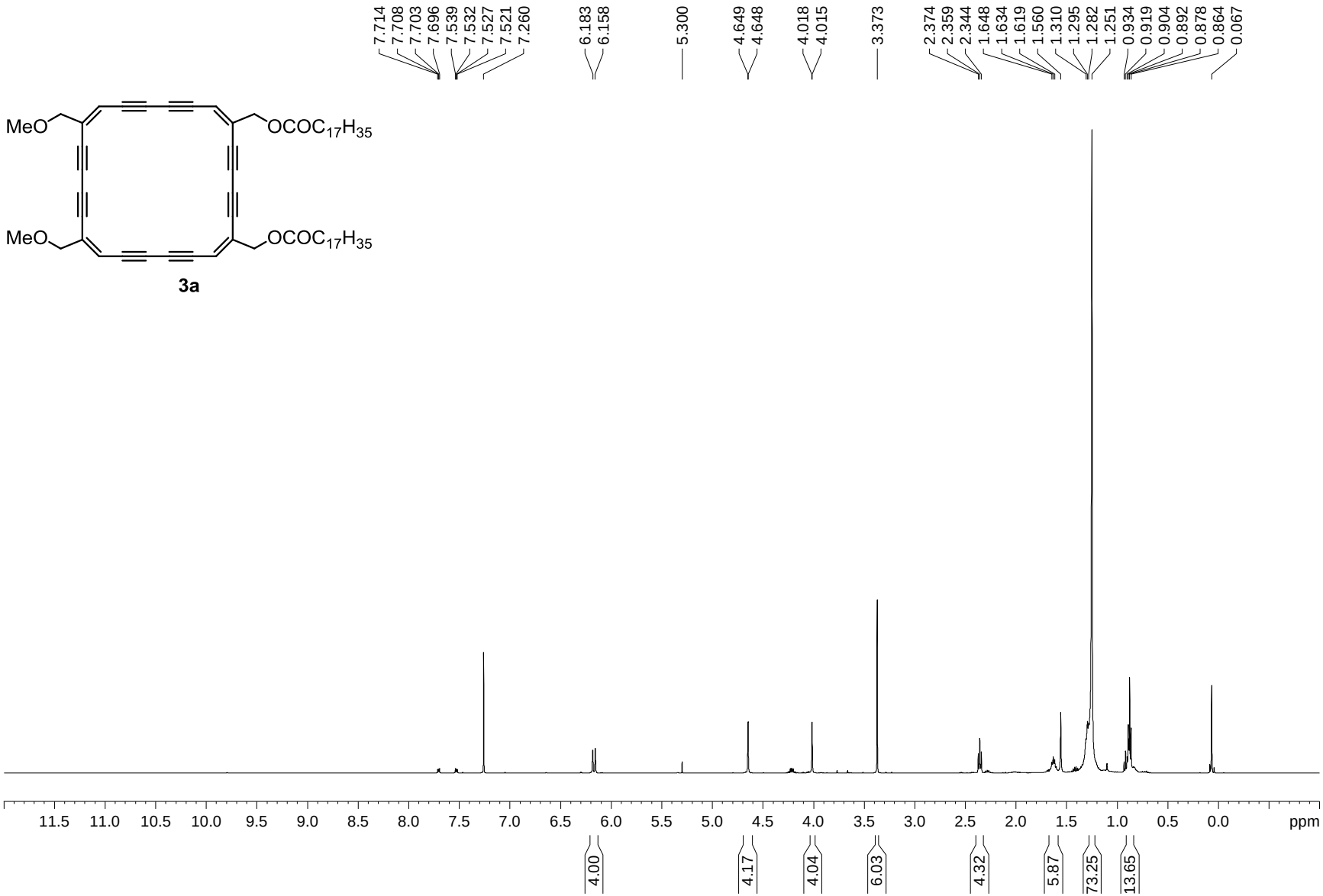


Figure S51. ^{1}H NMR of compound **3a** ($CDCl_3$, 500 MHz).

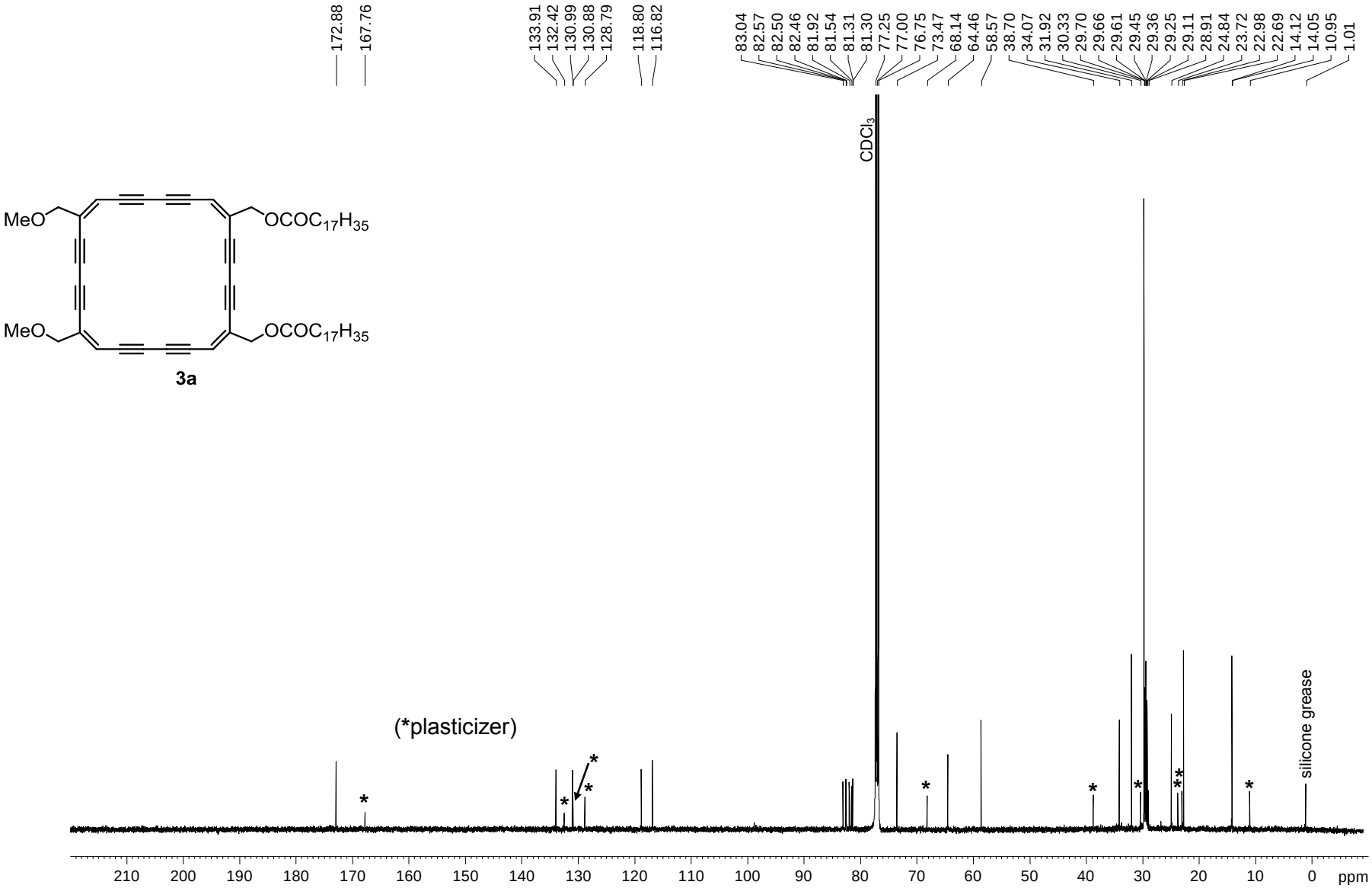


Figure S52. ^{13}C NMR of compound **3a** ($CDCl_3$, 126 MHz).

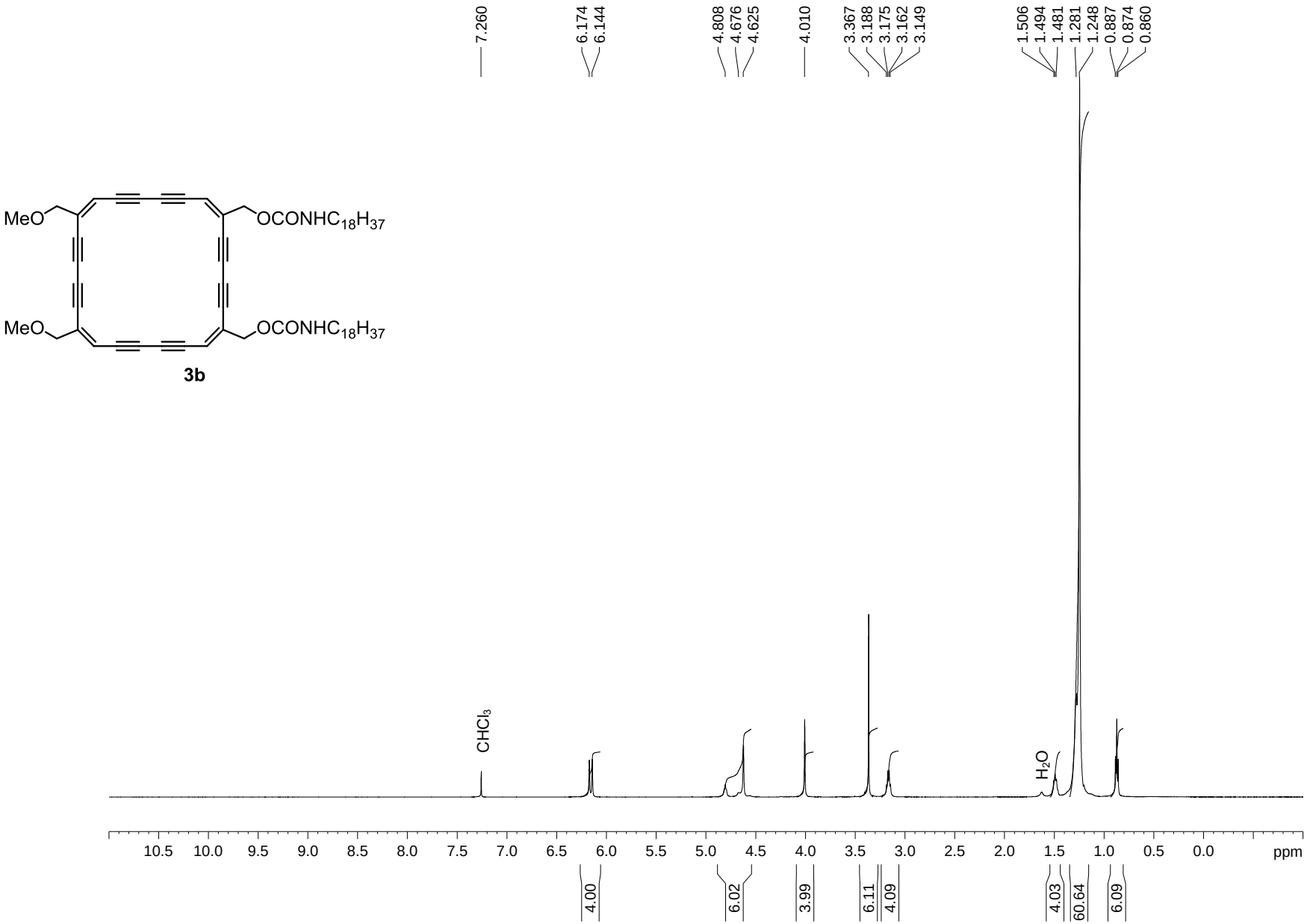


Figure S53. ^{1}H NMR of compound **3b** ($CDCl_3$, 500 MHz).

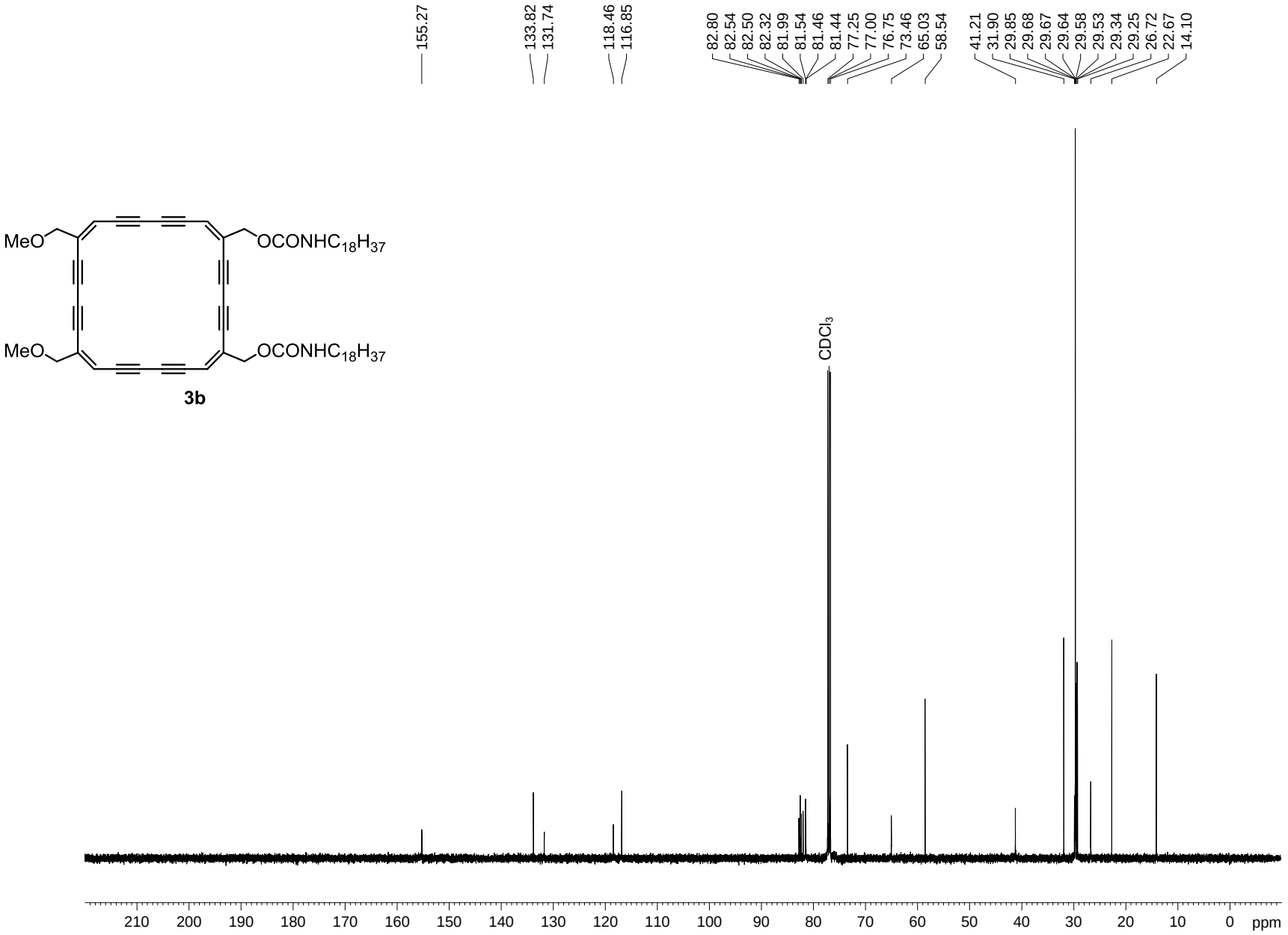


Figure S54. ^{13}C NMR of compound **3b** ($CDCl_3$, 126 MHz).

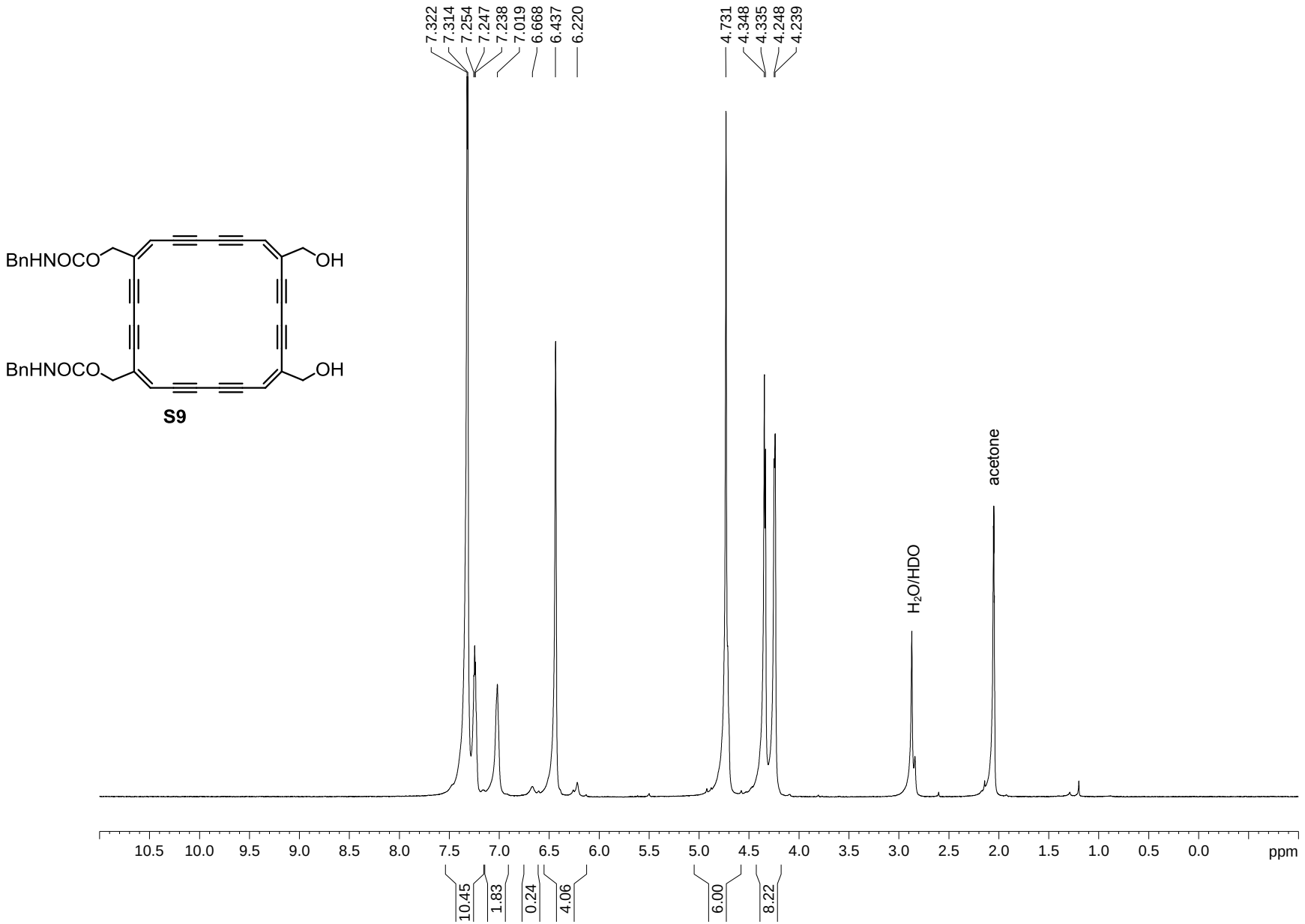


Figure S55. ^{1}H NMR of compound **S9** (acetone-d_6, 500 MHz).

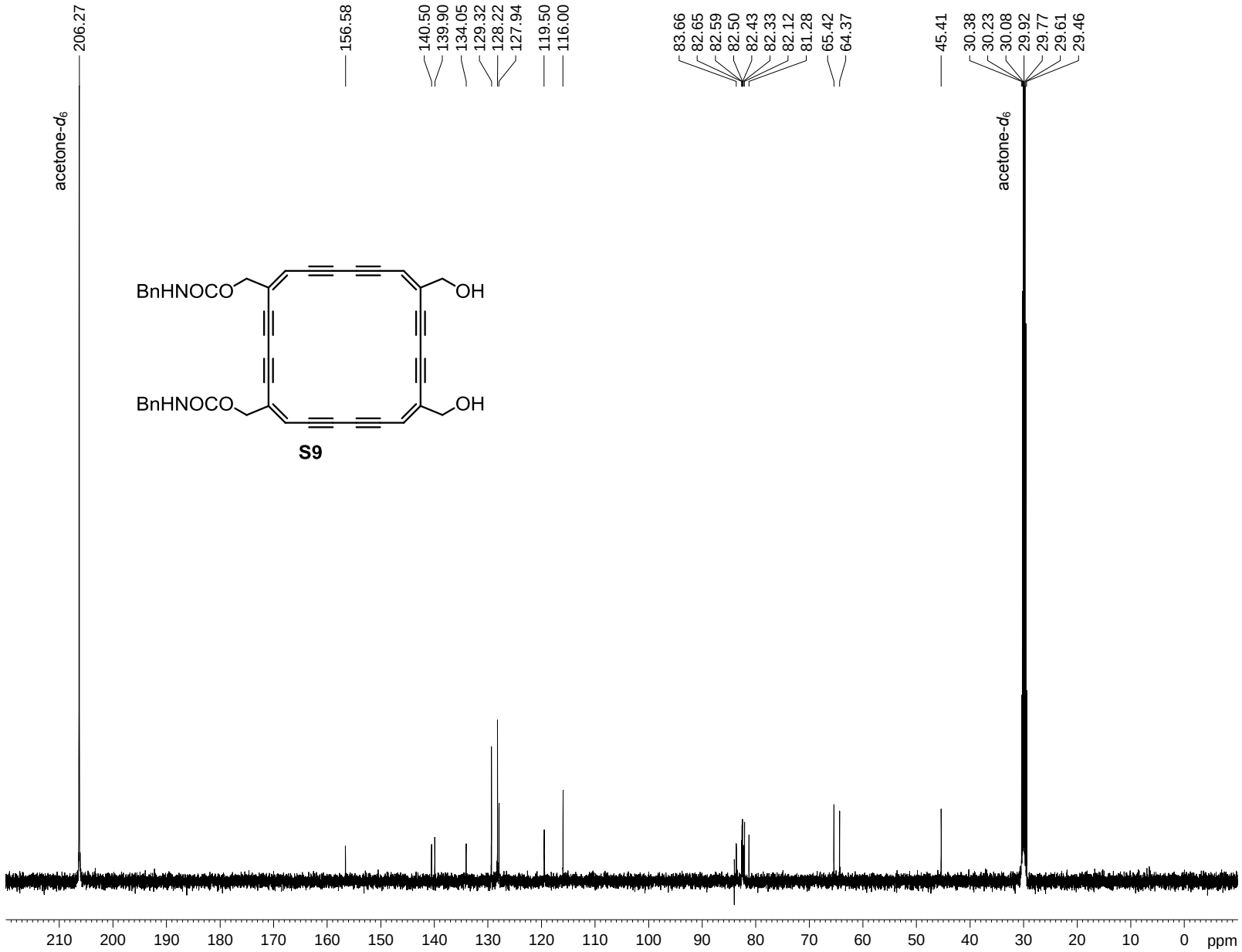


Figure S56. ^{13}C NMR of compound **S9** (acetone-d_6, 126 MHz).

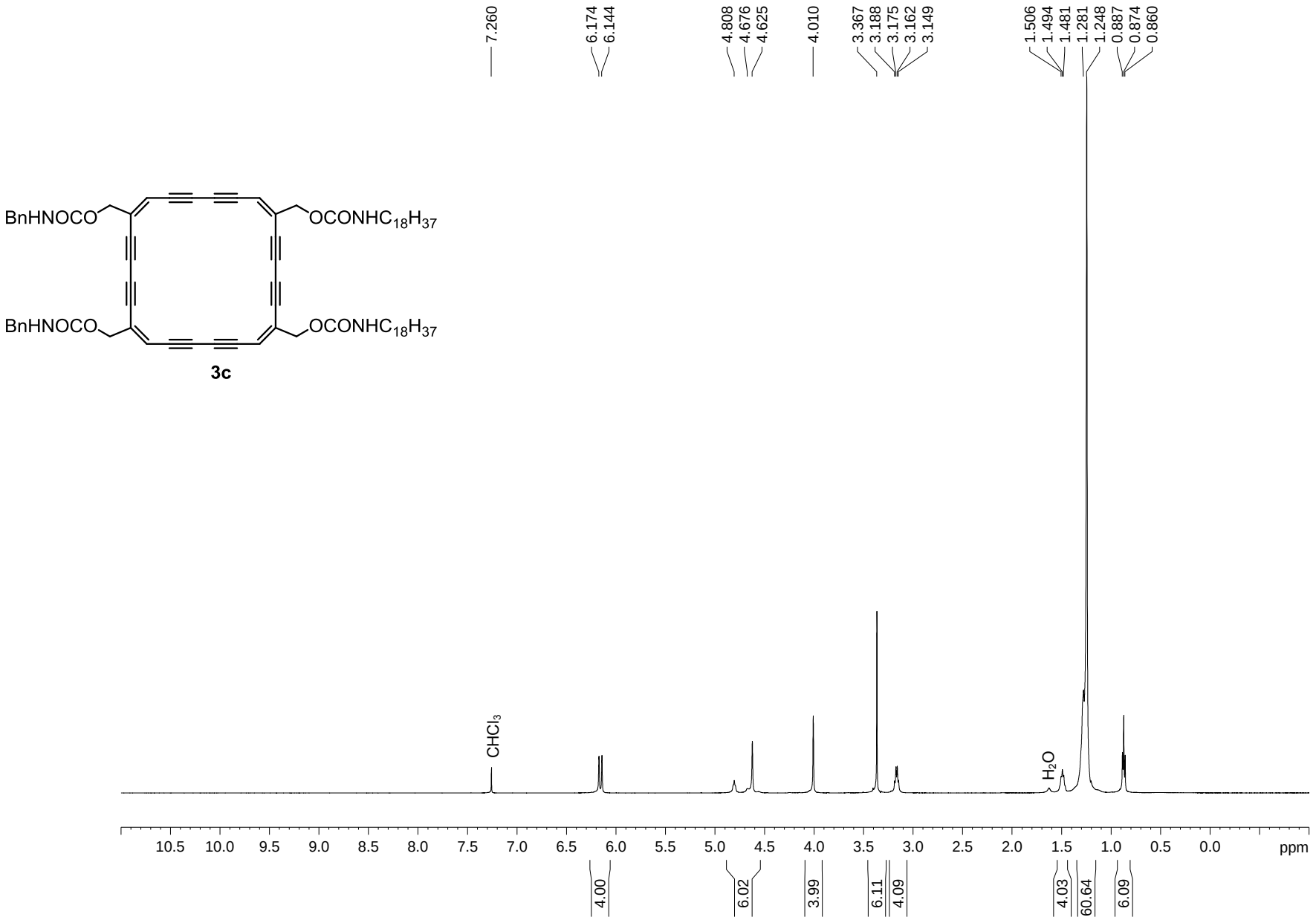


Figure S57. ^{1}H NMR of compound **3c** ($CDCl_3$, 500 MHz).

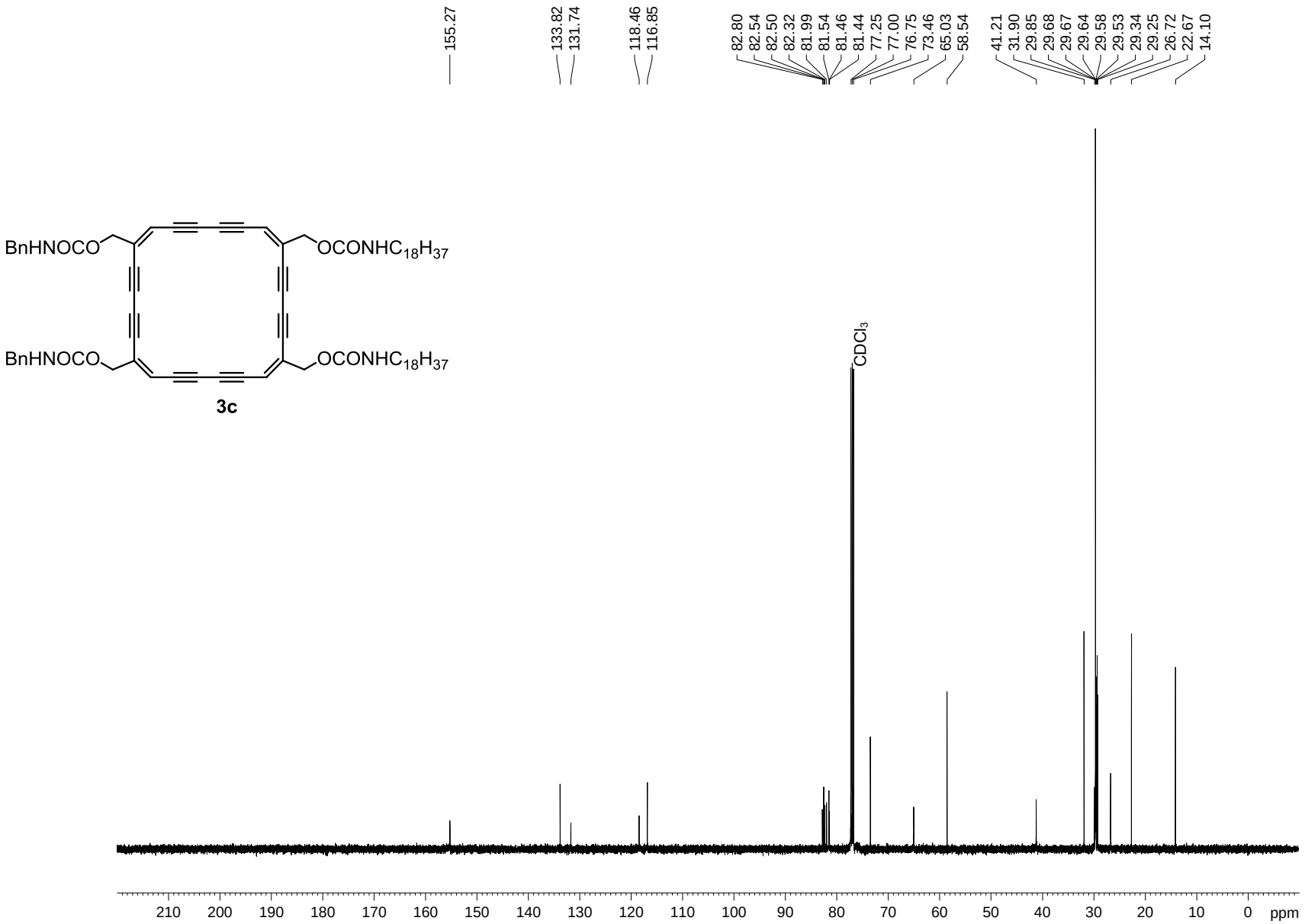


Figure S58. ^{13}C NMR of compound **3c** ($CDCl_3$, 126 MHz).