

Supporting information

Tetracationic bis-triarylborane tetraynes as dual fluorescence and SERS sensors for DNA, RNA and proteins

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Synthesis

General information:

Unless otherwise noted, all reactions were performed using standard Schlenk or glovebox (Innovative Technology Inc.) techniques under argon. Reagent grade solvents were argon saturated, dried using an Innovative Technology Inc. Pure-Solv Solvent Purification System, and further deoxygenated by using the freeze-pump-thaw method. All starting materials were purchased from commercial sources and used without further purification.

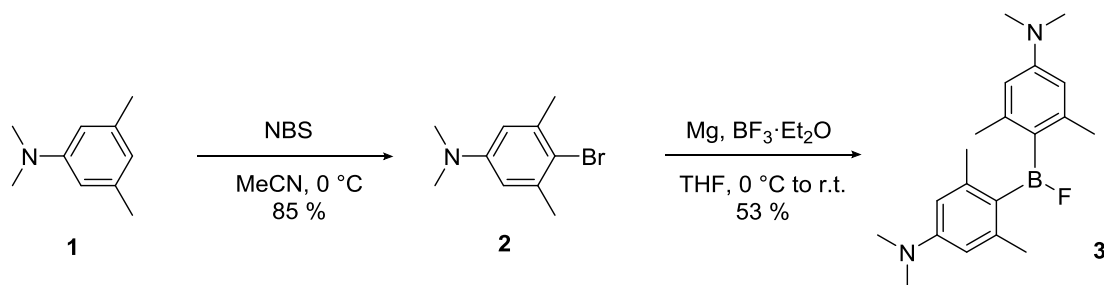
Automated flash chromatography was performed using a Biotage® Isolera Four system on silica gel or NH-silica. Commercially available, precoated TLC plates (Polygram® Sil G/UV₂₅₄ and Polygram® Alox N/UV₂₅₄) were purchased from Macherey-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 45 °C.

GC-MS analyses were performed using an Agilent 7890A gas chromatograph equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. High resolution mass spectrometry was obtained using a Thermo Scientific Exactive Plus MS System with either an atmospheric-pressure chemical ionization (APCI) or a heated-electrospray ionization (HESI) probe.

NMR spectra were recorded at ambient temperature on a Bruker DRX-300 (¹H, 300 MHz; ¹³C{¹H}, 75 MHz; ¹¹B{¹H}, 96 MHz), Bruker Avance 500 NMR (¹H, 500 MHz; ¹³C{¹H}, 125 MHz; ¹¹B{¹H}, 160 MHz) or on Bruker Avance Neo I 600 (¹H: 600 MHz, ¹¹B: 192 MHz, ¹³C: 150 MHz) spectrometers. NMR chemical shifts for ¹H and ¹³C are reported relative to TMS and were referenced *via* carbon signals or residual proton resonances of the corresponding deuterated solvent. The ¹¹B{¹H} NMR spectra are reported relative to the external standard BF₃·Et₂O.

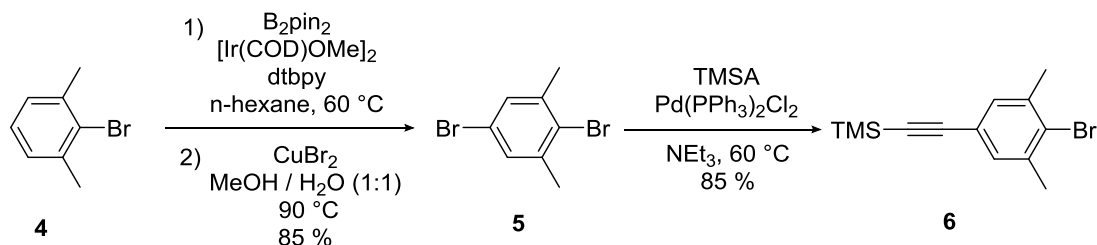
Elemental analyses were performed with an Elementar vario micro cube device. Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer as solids by using an ATR unit with a resolution of 4 cm⁻¹ and are reported in cm⁻¹. Raman spectra were recorded as solids at room temperature with a MultiRAM FT-Raman spectrometer in melting point capillaries.

In the first step, N,N,3,5-tetramethylaniline **1** was brominated with NBS to obtain **2**. Next, fluoroborane **3** was synthesized *via* a Grignard reaction with BF₃·Et₂O (Scheme S1).



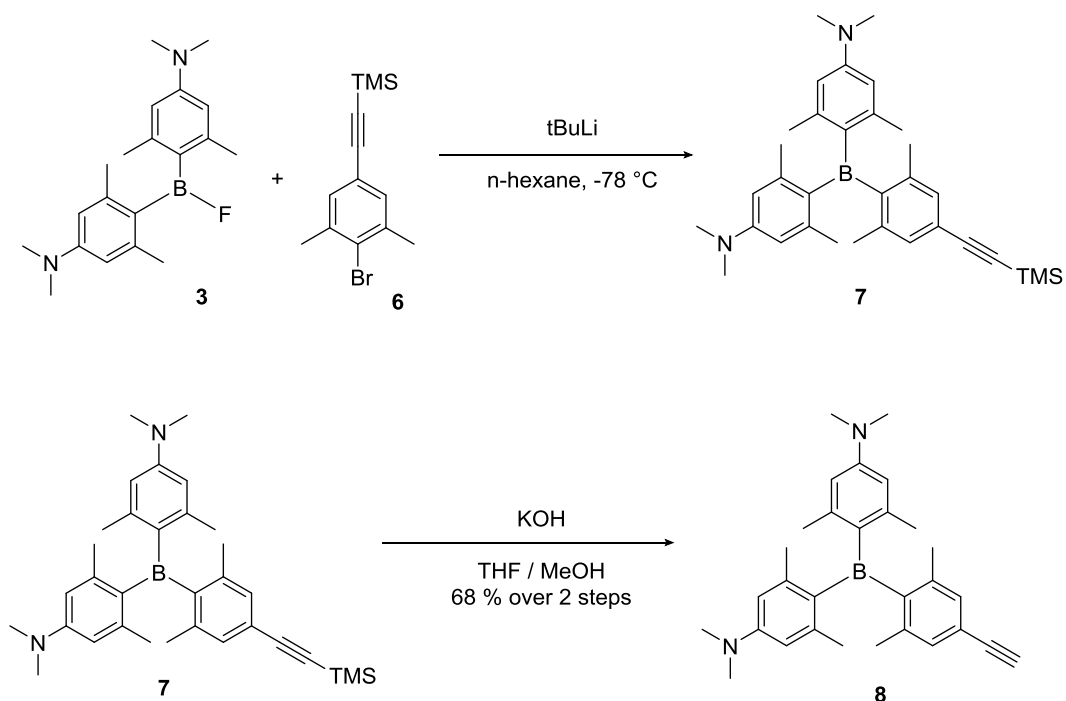
Scheme S1: Grignard-based synthesis of the fluoroborane **3**.

To prepare precursor **6**, first 2-bromo-*m*-xylene, **4**, was subjected to Ir-catalyzed C-H borylation, followed by conversion of the Bpin moiety to bromine to obtain **5**. In a Sonogashira reaction, this aryl dibromide was selectively coupled with trimethylsilylacetylene (TMSA) at the less sterically hindered position (Scheme 2).



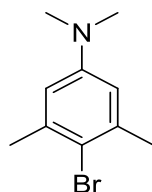
Scheme S2: Synthesis of **6** by a series of borylation, bromination, and Sonogashira reactions.

Triarylborane **7** was prepared by lithiation with *t*BuLi followed by reaction with fluoroborane **3**. The crude triarylborane product **7** was deprotected with KOH to obtain the terminal alkyne **8** (Scheme 3). The synthetic strategy for the preparation of ethynyl precursor **8** followed the route reported by our group in 2020.



Scheme S3: Synthesis of triarylborane **7**, followed by alkaline deprotection yielding **8**.

4-Bromo-N,N,3,5-tetramethylaniline 2



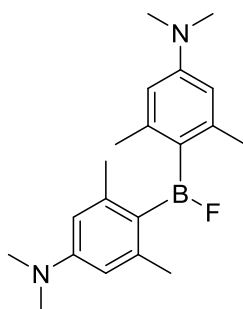
N,N,3,5-tetramethylaniline (25.5 g, 171 mmol) was dissolved in MeCN (600 mL) and cooled to 0 °C. NBS (30.4 g, 171 mmol) was slowly added. After stirring at 0 °C for 2 h, the solution was warmed to r.t.. To the solution, water (150 mL) was added, and the aqueous phase was extracted with hexane (3 x 80 mL). The organic phases were combined and dried over MgSO₄. The reaction mixture was filtered, and the solvent was removed under reduced pressure.

The procedure and NMR data are similar to those reported previously.^{1,2}

Yield: 33.0 g (145 mmol, 85%) of a yellow liquid.

¹H NMR (300 MHz, CDCl₃): δ [ppm] = 6.50 (m, 2H), 2.92 (s, 6H), 2.40 (m, 6H).

4,4'-(Fluoroboranediy)l)-bis-(N,N,3,5-tetramethylaniline) 3



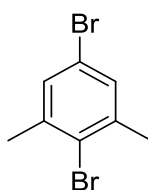
Compound **2** (33.0 g, 145 mmol) was reacted with Mg (4.12 g, 170 mmol) in THF (180 mL) under reflux for 5 h. After cooling to r.t., the reaction mixture was filtered, and the filtrate was slowly added to a solution of BF₃·Et₂O (8.60 mL, 68.0 mmol) in THF (50 mL) at 0 °C with the exclusion of light. The reaction mixture was stirred for 2 h at 0 °C and then overnight at r.t., also under exclusion of light. The solvent was removed under reduced pressure and the residue was extracted with hexane (2 x 250 mL) under an argon atmosphere. The hexane fractions were combined, and the solvent was removed under reduced pressure. The product was stored under argon.

The procedure and NMR data are similar to those reported previously.^{3,4}

Yield: 12.3 g (37.7 mmol, 55%) of a yellow powder.

¹H NMR (300 MHz, C₆D₆): δ [ppm] = 6.37 (m, 4H), 2.53 (s, 12H), 2.50 (m, 12H).

2,5-Dibromo-1,3-dimethylbenzene 5



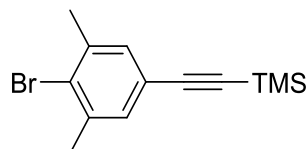
B₂pin₂ (15.0 g, 59.0 mmol), [Ir(COD)(OMe)]₂ (180 mg, 272 μmol) and 4,4'-di-^t-butyl-2,2'-dipyridyl (dtbpy) (149 mg, 555 μmol) were dissolved in dry and degassed hexane (80 mL). The solution was stirred at r.t. for 2 h. Then, 2-bromo-1,3-dimethylbenzene (10.1 g, 54.6 mmol) was added and the mixture was stirred at 60 °C for 16 h. After cooling to r.t., the solvent was removed under reduced pressure. The crude borylated intermediate was dissolved in MeOH (300 mL) and CuBr₂ (36.6 g, 164 mmol) in water (300 mL) was added. The mixture was stirred at 90 °C for 4 days. The mixture was cooled to 0 °C, and the precipitate was collected by filtration and then extracted with hexane (3 x 100 mL). The combined organic fractions were filtered through a short silica plug and the solvent was removed under reduced pressure.

The procedure and NMR data are similar to those reported previously.^{5,6}

Yield: 12.2 g (46.2 mmol, 85%) of a colorless liquid.

¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.21 (s, 2H), 2.38 (s, 6H).

(4-Bromo-3,5-dimethylphenyl)ethynyl)trimethylsilane 6



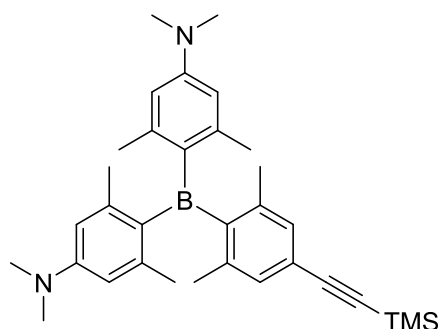
The compounds Pd(PPh₃)₂Cl₂ (617 mg, 877 μmol) and CuI (472 mg, 2.48 mmol) were dissolved in dry, degassed NEt₃ (350 mL). Trimethylsilylacetylene (5.09 g, 51.9 mmol) and **5** (12.2 g, 46.2 mmol) were added and the mixture was stirred at 80 °C overnight. Afterwards the solvent was removed under reduced pressure. The residue was suspended in hexane (450 mL) and passed through a silica plug. The solvent was removed under reduced pressure. The crude product contained a small amount of the homo-coupled dimer of trimethylsilylacetylene, which was removed by kugelrohr distillation.

The procedure and NMR data are similar to those reported previously.^{6,7}

Yield: 11.0 g (39.1 mmol, 85%) of a brown liquid.

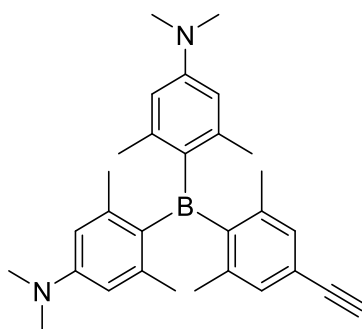
¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.18 (m, 2H), 2.37 (m, 6H), 2.42 (s, 9H).

4,4'-((2,6-dimethyl-4-((trimethylsilyl)ethynyl)phenyl)boranediyl)bis(N,N,3,5-tetramethylaniline) 7



Compound **6** (2.67 g, 9.49 mmol) was dissolved in dry and degassed hexane (60 mL) and cooled to $-70\text{ }^{\circ}\text{C}$. Then $t\text{BuLi}$ (18.7 mmol, 11 mL, 2 eq., 1.7 M in hexane) was added *via* syringe. The solution was stirred for 30 min. Then, the cooling bath was removed, and the solution was stirred for 18 h at r.t. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$, and a solution of the fluoroborane **3** (2.40 g, 7.36 mmol) in THF (60 mL) was added *via* cannula. The resulting solution was allowed to warm to r.t. and stirred for additional 18 h. Water and brine were added, and the product was extracted with dichloromethane. The combined organic phases were dried over MgSO_4 , and the solvent was removed under reduced pressure. The crude product was directly used in the deprotection step without further purification.

4,4'-((4-ethynyl-2,6-dimethylphenyl)boranediyl)bis(N,N,3,5-tetramethylaniline) 8



Crude **7** (~3.8 g) was dissolved in THF (180 mL), and MeOH (180 mL) was added, followed by powdered KOH (2.50 g, 45.0 mmol). The solution was stirred overnight at r.t. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (50 mL) and then washed with water (5 x 50 mL). The organic layer was dried over MgSO_4 , and the solvent was removed under reduced pressure. The residue was suspended in MeOH, filtered and the resulting precipitate was dried on a glass frit to obtain the product.

The procedure and NMR data are similar to those reported previously.⁶

Yield (based on **3** over two steps): 2.18 g (5.00 mmol, 68%) of a bright yellow solid.

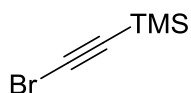
^1H NMR (300 MHz, CDCl_3): δ [ppm] = 7.04 (s, 2H), 6.29 (s, 4H), 3.02 (s, 1H), 2.96 (s, 12H), 2.01 (s, 12H), 1.91 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3) δ [ppm] = 151.32, 143.27, 142.74, 140.32, 130.81, 121.29, 111.64, 84.74, 40.11, 24.17, 23.81, 22.80.

$^{11}\text{B}\{^1\text{H}\}$ (96 MHz, CDCl_3) δ [ppm] = 73.5.

HRMS (APCI+): m/z calculated: 437.3128 [M+H], m/z found: 437.3116.

(bromoethynyl)trimethylsilane



Trimethylsilylacetylene (1.96 g, 20.0 mmol) was dissolved in acetone (40 mL) and AgNO_3 (340 mg, 2.00 mmol) and NBS (4.27 g, 24.0 mmol) were added. The solution was stirred for 4 h at r.t., after which a white solid precipitated. The solution was filtered through a silica plug and the solvent was removed under reduced pressure from the filtrate. The residue was dissolved in pentane and filtered again. The product was obtained after removing the solvent under reduced pressure from the filtrate. It is critical to remove the solvent gently because of the low boiling point of the product.

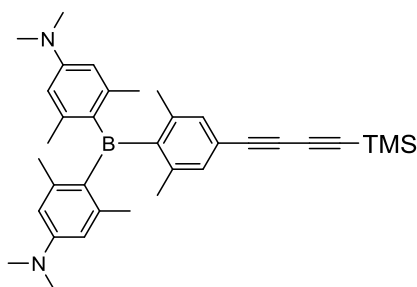
The procedure and NMR data are similar to those reported previously.⁸

Yield: 2.80 g (15.9 mmol, 80%) of an off-white liquid.

^1H NMR (300 MHz, CDCl_3): δ [ppm] = 0.19 (s, 9H)

GC-MS (EI): m/z calcd.: 176 [M], found 176.

4,4'-((2,6-dimethyl-4-((trimethylsilyl)buta-1,3-diyne-1-yl)phenyl)boranediyl)bis(N,N,3,5-tetramethylaniline) **9**



In a Schlenk flask, **8** (1.04 g, 2.39 mmol, 1 eq.) was dissolved in 15 mL of THF and cooled to $-45\text{ }^{\circ}\text{C}$ in an *m*-xylene dry ice bath. Then, *n*BuLi (1.05 mL, 2.63 mmol, 1.1 eq, 2.5 M in hexane) was added dropwise. After 30 min, CuI (501 mg, 2.63 mmol, 1.1 eq.) was added and the reaction was stirred for 30 min at $-45\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to $-10\text{ }^{\circ}\text{C}$ in an acetone/ice bath. The mixture was again cooled to $-45\text{ }^{\circ}\text{C}$, and 7.20 mL *n*BuNH₂ was added, followed by (bromoethynyl)trimethylsilane (673 mg, 3.80 mmol, 1.6 eq.). After 10 min, the cooling bath was removed, and the mixture was stirred at r.t. for 1 h. The solvent was removed under reduced pressure and the mixture was filtered through a 5 cm silica plug CH₂Cl₂/hexane (1:9). After removal of the solvent under reduced pressure, the compound was isolated as a yellow solid. The crude product was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95/5%).

Yield: 1.08 g, 2.03 mmol, 85%

Rf: (12.5% EtOAc in cyclohexane): 0.5

¹H NMR (300 MHz, CDCl₃) δ [ppm] = 7.03 (s, 2H), 6.29 (s, 4H), 2.96 (s, 12H), 2.01 (m, 12H), 1.90 (s, 6H), 0.23 (s, 6H)

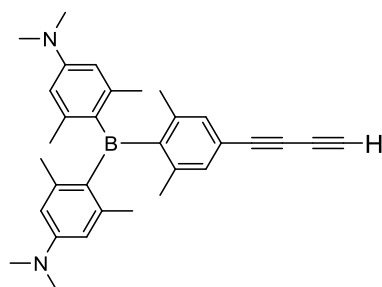
¹³C{¹H} NMR (75 MHz, CDCl₃) δ [ppm] = 151.35, 143.32, 142.73, 140.39, 135.55, 131.26, 120.48, 111.65, 90.16, 88.41, 78.16, 73.77, 40.09, 24.18, 23.81, 22.80, -0.17.

¹¹B{¹H} (192 MHz, CDCl₃) δ [ppm] = 71.9.

Elem. anal. calcd. (%) for C₃₅H₄₅BN₂Si: C, 78.92; H, 8.52; N, 5.26 found: C, 78.18; H, 8.76; N, 4.86.

HRMS (APCI+): *m/z* calculated: 533.3518 [M+H], *m/z* found: 533.3514.

4,4'-((4-(buta-1,3-diyne-1-yl)-2,6-dimethylphenyl)boranediyl)bis(N,N,3,5-tetramethylaniline) **10**



A mixture of **9** (1.69 g, 3.17 mmol) and KOH (890 mg, 15.9 mmol, 5 eq.) in 100 mL of THF and 100 mL of MeOH was stirred for 2 h at r.t.. After removal of most of the solvent, 200 mL of water and 200 mL of CH₂Cl₂ were added. The organic layer was separated and washed 2 times with water. After addition of ca. 5 mL of acetone, the volatiles were removed *in vacuo* to obtain a yellow solid, while maintaining the temperature below 40 °C.

The product is quite unstable and was stored in a freezer or, used immediately in further reactions.

Yield: 1.45 g, 3.16 mmol, 99%

¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.06 (m, 2H), 6.29 (m, 4H), 2.96 (s, 12H), 2.45 (s, 1H), 2.04-1.88 (m, 18 H).

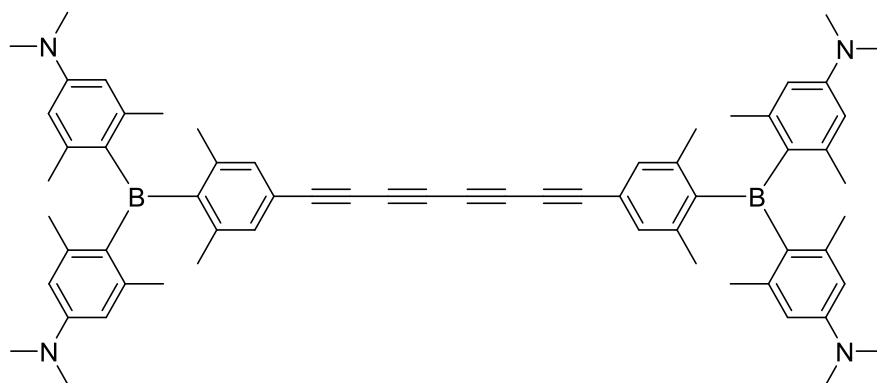
¹³C{¹H} NMR (75 MHz, CDCl₃): δ [ppm] = 151.36, 143.35, 142.72, 140.44, 131.34, 120.07, 111.64, 73.03, 70.95, 68.64, 68.12, 40.09, 25.76, 24.19, 23.80, 22.79.

¹¹B{¹H} (96 MHz, CDCl₃) δ [ppm] = *signal too weak to observe*.

Elem. anal. calcd. (%) for C₃₂H₃₇BN₂: C, 83.47; H, 8.10; N, 6.08 Found: C, 82.07; H, 8.61; N 5.72.

HRMS (APCI+): m/z calculated: 461.3113 [M+H], m/z found: 461.3123.

4,4',4'',4'''-((octa-1,3,5,7-tetrayne-1,8-diylbis(2,6-dimethyl-4,1-phenylene))bis(boranetriyl))tetrakis(N,N,3,5-tetramethylaniline) **11**



A mixture of **10** (1.45 g, 3.16 mmol, 1 eq.), iodine (401 mg, 1.58 mmol, 0.5 eq. I₂), Pd(PPh₃)₂Cl₂ (44 mg, 63.3 μmol, 0.02 eq.), and CuI (30 mg, 158 μmol, 0.05 eq.) in

150 mL of THF and 50 mL of MeOH was stirred at r.t. for 1 d. The solvent was removed under reduced pressure, then the mixture was filtrated through a silica plug with Et₂O to give a yellow crude product. The mixture was then flash-chromatographed on silica (4-10% EtOAc + 3% NEt₃ in cyclohexane).

Yield: 1.01 g, 1.10 mmol, 70%.

¹H NMR (500 MHz, CD₂Cl₂): δ [ppm] = 7.09 (m, 4H), 6.30 (m, 8H), 2.94 (s, 24H), 2.01-1.85 (m, 36H).

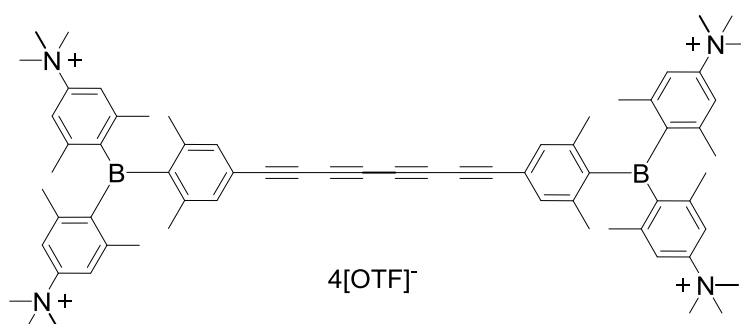
¹³C{¹H} NMR (125 MHz, CD₂Cl₂): δ [ppm] = 153.44, 151.83, 143.53, 142.92, 140.9202, 135.45, 131.93, 119.58, 111.84, 79.47, 73.96, 67.20, 64.26, 40.09, 24.09, 23.79, 22.74.

¹¹B{¹H} NMR (192 MHz, CDCl₃) δ [ppm] = 71.2 ppm.

Elem. anal. calcd. (%) for C₆₄H₇₂B₂N₄: C, 83.65; H, 7.90; N, 6.10 found: C, 83.13; H, 8.63; N 5.60.

HRMS (APCI+): m/z calculated: 919.5971 [M+H], m/z found: 919.6020.

4,4',4'',4'''-((octa-1,3,5,7-tetrayne-1,8-diylbis(2,6-dimethyl-4,1-phenylene))bis(boranetriyl))tetrakis(N,N,N,3,5-pentamethylbenzenaminium)tetratriflate **12**



In a soda-lime glass vial, tetrayne **11** (32 mg, 35.0 μmol, 1 eq.) was dissolved in 5 mL of CH₂Cl₂ and MeOTf (69 mg, 0.42 mmol, 12 eq.) was added slowly. The mixture was stirred overnight at r.t. in the absence of light. The solid product was collected by filtration on a glass frit and was then washed with Et₂O in an ultrasonic bath.

Yield: 34 mg, 21.6 μmol, 62%.

¹H NMR (300 MHz, MeOD) δ [ppm] = 7.75 (m, 8H), 7.25 (m, 4H), 3.65 (s, 36H), 2.30-1.87 (m, 36H).

¹³C{¹H} NMR (75 MHz, MeOD): δ [ppm] = 149.91, 148.90, 148.67, 144.89, 144.74, 142.47, 133.49, 123.91, 123.65, 120.31, 119.68, 78.92, 75.41, 67.83, 64.50, 57.46, 23.47, 23.04.

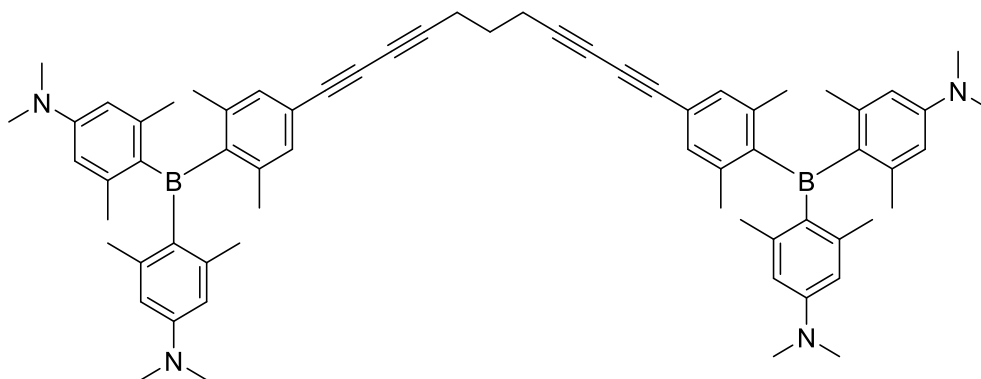
¹¹B{¹H} NMR (96 MHz, MeOD) δ [ppm] = *signal too weak to observe*.

Elem. anal. calcd. (%) for C₇₂H₈₄B₂F₁₂N₄O₁₂S₄: C, 54.90; H, 5.37; N, 3.56; S, 8.14. Found: C, 54.70; H, 5.89; N, 3.26; S, 8.23.

HRMS of the cation (ESI+): m/z calculated: 244.6715 (M), m/z found: 244.6715.

HRMS of the anion (ESI-): m/z calculated: 148.9515 (M), m/z found: 148.9515.

4,4',4'',4'''-((undeca-1,3,8,10-tetrayne-1,11-diylbis(2,6-dimethyl-4,1-phenylene))bis(boranetriyl))tetrakis(N,N,3,5-tetramethylaniline) (13)



A Schlenk flask was charged with 20 mL of a degassed aqueous solution of n-butyl amine (40 % v/v). The solution was cooled to 0 °C and then CuCl (5 mg, 52 μmol) and NH₂OH·HCl (15 mg, 0.22 mmol) were added. To this solution was added a degassed solution of compound **8** (23 mg, 52.0 μmol) in CH₂Cl₂ (3 mL) at 0 °C. After stirring for 30 min, a degassed solution of **8** (250 mg, 0.57 mmol) and 1,7-dibromohepta-1,6-diyne (65 mg, 0.26 mmol) in MeOH/CH₂Cl₂ [30 ml (1:14)] was added at 0 °C. The resulting yellow solution was stirred for 2 h at 0 °C and 12 h at r.t. Then, a saturated aqueous solution of NH₄Cl (20 ml) was added. The reaction mixture was extracted with CH₂Cl₂ (150 mL) dried over Na₂SO₄ and filtered. The solvent was removed from the filtrate. The residue was washed with MeOH (25 mL) and dried *in vacuo* to give the product as a yellow powder.

Yield: 225 mg, 0.23 mmol, 90%.

¹H NMR (300 MHz, CD₂Cl₂) δ [ppm] = 7.02 (s, 4H), 6.30 (m, 8H), 2.94 (s, 24H, H), 2.53 (m, 4H), 1.99 (s, 24H), 1.89 (s, 12H), 1.84 (m, 2H).

¹³C{¹H} NMR (75 MHz, CD₂Cl₂) δ [ppm] = 151.78, 151.77, 143.43, 142.92, 140.69, 135.67, 131.31, 121.28, 111.84, 83.34, 76.39, 73.86, 66.32, 40.12, 27.50, 24.06, 23.77, 22.74, 19.15.

¹¹B{¹H} NMR (96 MHz, CD₂Cl₂) δ [ppm] = 73.0.

HRMS (APCI⁺): *m/z* calc. for [M+H]: 961.6491; found: 961.6467.

Elem. anal. calc. (%) for C₆₇H₇₈B₂N₄: C 83.74, H 8.18, N 5.83; found: C 82.72, H 8.62, N 6.17.

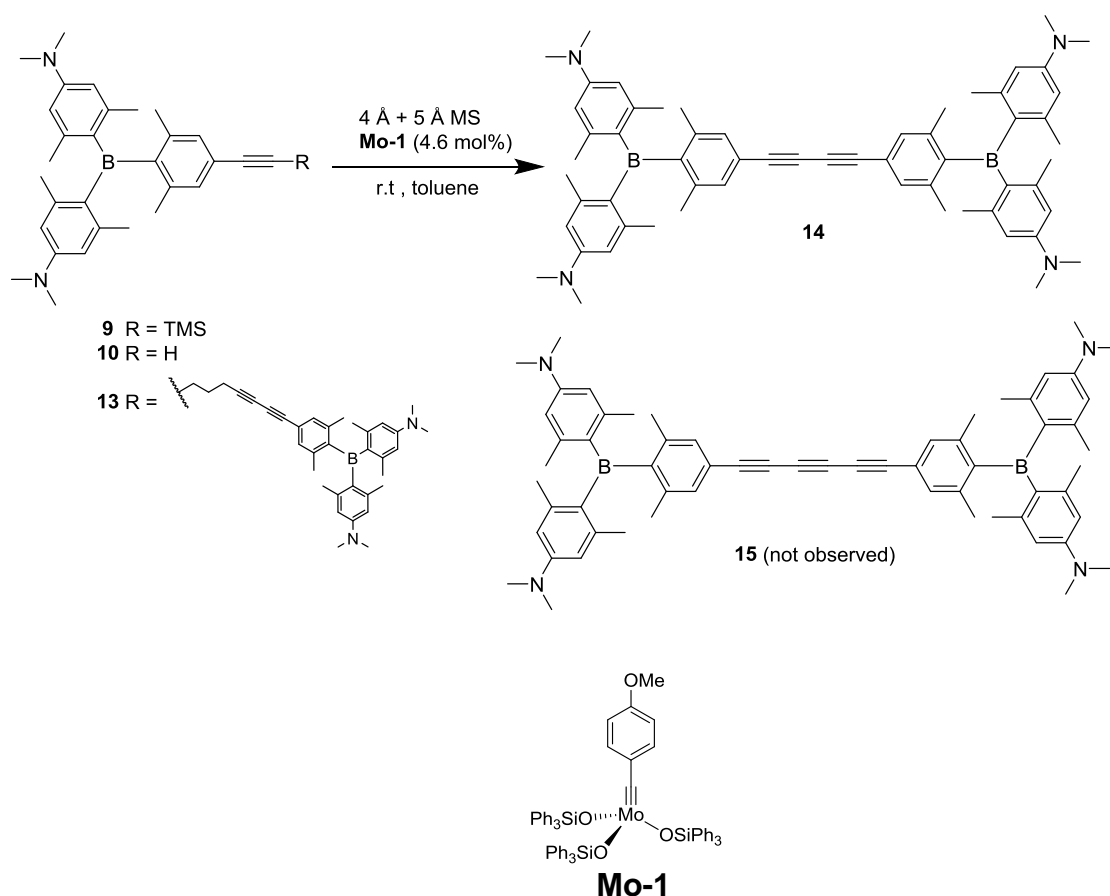
Alkyne metathesis experiments using substituted TAB diynes with Mo-1

General information

All manipulations were carried out in an argon-filled glovebox. Glassware was dried in an oven overnight at 135 °C or flame dried prior to use. Toluene and THF were purified using MBraun Solvent Purification Systems. Toluene used for metathesis

was freeze-pump-thaw degassed prior to use. Molecular sieves (4 Å and 5 Å) were purchased from Sigma-Aldrich and activated with a heat gun under vacuum for 24 h prior to use. **Mo-1** complex was generously donated by A. Fürstner whom we sincerely acknowledge. The highly sensitive complex was stored in an argon-filled glove box at -20 °C. Column chromatography was performed with silica gel (spherical, particle size 40 µm, neutral) purchased from Sigma-Aldrich. The eluents employed are reported as volume (volume percentages). Multinuclear NMR spectra were recorded at 298 on a Bruker ARX400 400 MHz spectrometer (¹H 400 MHz, ¹³C 101 MHz, ¹¹B 128 MHz). For nuclei other than ¹H, spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃ = 7.27 ppm for ¹H; 77.1 ppm for ¹³C / CD₂Cl₂ = 5.32 ppm for ¹H; 54.0 ppm for ¹³C). HRMS were recorded on a Bruker MaXis 4G spectrometer using ASAP as the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1.

Alkyne metathesis general procedure



Scheme S4. Presentation of attempted preparation of **15**.

The diyne substrate (2 equiv) was placed in an oven-dried vial and transferred into an argon-filled glove box. Molecular sieves (4 Å and 5 Å, 40 mg of each) were added followed by toluene (0.1 mL). A fresh solution of the **Mo-1** catalyst was prepared (8.0 mg in 0.8 mL of toluene) and (4.6 mol%) was added to the reaction mixture. The

mixture was stirred 4 h at r.t. Conversions were determined by ^1H NMR spectroscopy after filtration of aliquots using a syringe filter. Aliquots were collected and volatiles were removed under vacuum. The diyne configuration was confirmed by ^{13}C NMR spectroscopy of the crude mixture and the targeted triyne was not observed. The product was purified by column chromatography (eluent: pentane:Et₂O 98/2 to 96/4) yielding the symmetrical diyne **14** as a yellow solid.

^1H NMR (400 MHz, CD₂Cl₂) δ [ppm] = 7.07 (s, 4H) 6.31 (m, 8H), 2.95 (s, 24H), 2.01 (m, 24H), 1.91 (s, 12H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD₂Cl₂) δ [ppm] = 151.7, 151.6, 143.4, 142.9, 140.7, 135.6, 131.2, 121.2, 112.0, 111.8, 82.7, 73.8, 40.1, 24.0, 23.8, 22.7. Analytical data for this compound match those in the literature.⁶¹

Detailed procedure for each substrate

With 9: The general procedure was applied with **9** (14.0 mg, 0.026 mmol) and 61 μL of **Mo-1** solution (0.6 μmol , 4.6 mol%). After 1 h, 55% conv. of **9** was observed. No further reaction occurred during the following 3 . After purification, the symmetrical diyne was isolated (6.0 mg, 53% yield).

With 10: The general procedure was applied with **10** (10.0 mg, 0.022 mmol) and 51 μL of **Mo-1** solution (0.5 μmol , 4.6 mol%). After 4 h, only starting material was detected by ^1H NMR spectroscopy.

With 13: The general procedure was applied with **13** (10.0 mg, 0.010 mmol) and 46 μL of **Mo-1** solution (0.46 μmol , 4.6 mol%). After 1 h, 45% conv. of **13** was observed. No further reaction occurred during the following 3 h. After purification, the symmetrical diyne was isolated (3.8 mg, 44% yield).

Single-crystal X-ray diffraction

Data was collected from a shock-cooled single crystal at 173 K on an XtaLAB Synergy, Dualflex, HyPix four-circle diffractometer with a micro-focus sealed X-ray tube using a mirror monochromator and a HyPix detector. The diffractometer was equipped with a low temperature device and Cu- K_{α} radiation ($\lambda = 1.54184 \text{ \AA}$) was used. All data were integrated with CrysAlis^{pro} and a Gaussian absorption correction using SCALE3 ABSPACK was applied. The structure was solved by intrinsic phasing method using SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL software.^{9,10} All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.¹¹ The CIF file was generated using FinalCif, the images were generated with Olex2.^{12,13} Full structural information has been deposited with the Cambridge Crystallographic Data Centre. CCDC-2250177.

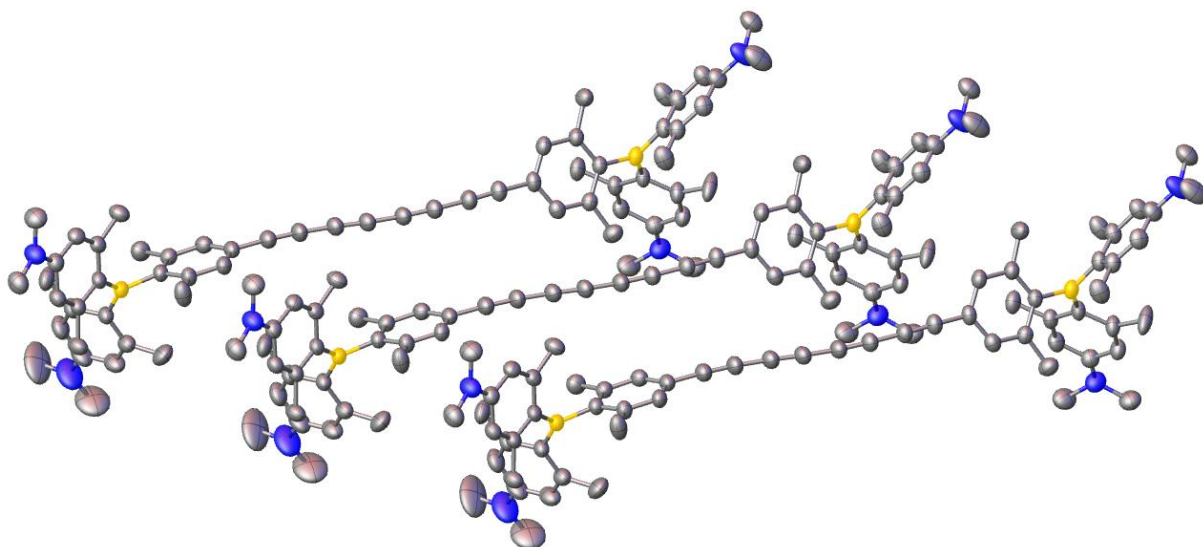


Figure S 1. Excerpt of the crystal structure of **11**, depicting the staggered arrangement of the rods; viewed along the [111] direction.

Crystal data for 11

CCDC	2250177
Empirical formula	C ₆₄ H ₇₂ B ₂ N ₄ [+ Acetone]
Formula weight [<i>M</i> / g·mol ⁻¹]	918.87
Temperature [K]	173(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> [Å]	23.3558(2)
<i>b</i> [Å]	8.39130(10)
<i>c</i> [Å]	30.5505(3)
α [°]	90
β [°]	90.5770(10)
γ [°]	90
Volume [Å ³]	5987.14(11)
<i>Z</i>	4
ρ_{calc} [g·cm ⁻³]	1.019
μ [mm ⁻¹]	0.439
<i>F</i> (000)	1976
Crystal size [mm ³]	0.272 × 0.170 × 0.123
Crystal color	orange
Crystal shape	block
Radiation (wavelength [Å])	Cu- <i>K</i> α (1.54184)
2 θ range [°] (resolution [Å])	3.78 – 160.28 (0.78)
Index ranges	-29 ≤ <i>h</i> ≤ 26 -10 ≤ <i>k</i> ≤ 10 -39 ≤ <i>l</i> ≤ 38
Reflections collected	56261
Independent reflections	12849
<i>R</i> _{int}	0.0322
<i>R</i> _{sigma}	0.0303
Completeness [%] to $\theta = 74.33^\circ$	99.8
Parameters	651
Goodness-of-fit on <i>F</i> ²	1.055
Final <i>R</i> indexes [$\geq 2\sigma(I)$]	<i>R</i> ₁ = 0.0455 <i>wR</i> ₂ = 0.1257
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0574 <i>wR</i> ₂ = 0.1340
Max. / min. residual electron density [e·Å ⁻³]	0.24/-0.21

Photophysical characterization

General information

All measurements were performed in standard quartz cuvettes (1 cm x 1 cm cross-section). UV-visible absorption spectra were recorded using an Agilent 8453 diode array UV-visible spectrophotometer. Emission spectra were recorded using an Edinburgh Instruments FLSP920 spectrometer equipped with a double monochromator for both excitation and emission, operating in right-angle geometry mode, and all spectra were fully corrected for the spectral response of the instrument. All solutions used in photophysical measurements had concentrations lower than $5 \cdot 10^{-6}$ M to minimize inner filter effects during fluorescence measurements.

Fluorescence quantum yield measurements. The fluorescence quantum yields were measured using a calibrated integrating sphere (inner diameter: 150 mm) from Edinburgh Instruments combined with the FLSP920 spectrometer described above. For solution-state measurements, the longest-wavelength absorption maximum of the compound in the respective solvent was chosen as the excitation wavelength, unless stated otherwise.

Lifetime measurements. Fluorescence lifetimes were recorded using the time-correlated single-photon counting (TCSPC) method using an Edinburgh Instruments FLS980 spectrometer equipped with a high-speed photomultiplier tube positioned after a single emission monochromator. Measurements were made in right-angle geometry mode, and the emission was collected through a polarizer set to the magic angle. The full-width-at-half-maximum (FWHM) of the pulse from the diode laser was ca. 75-90 ps with an instrument response function (IRF) of ca. 230 ps FWHM. The IRFs were measured from the scatter of an aqueous suspension of Ludox at the excitation wavelength. Decays were recorded to 10000 counts in the peak channel with a record length of 8192 channels. The band pass of the emission monochromator and a variable neutral density filter on the excitation side were adjusted to give a signal count rate of <60 kHz. Iterative reconvolution of the IRF with one decay function and non-linear least-squares analysis were used to analyze the data. The quality of all decay fits was judged to be satisfactory, based on the calculated values of the reduced χ^2 and Durbin-Watson parameters and visual inspection of the weighted residuals.

Due to technical limitations of our spectrometer (temporal resolution/ detector response time), only lifetimes >1 ns were accurately determined..

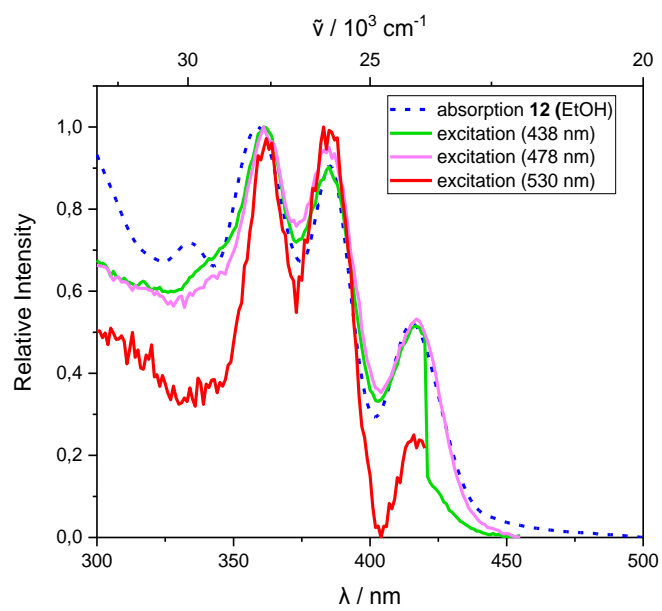


Figure S 2. Absorption and excitation spectra of **12** in EtOH solution.

Interactions with ds-DNA, ds-RNA, and protein (BSA)

General information

The solvents, sodium cacodylate buffer ($I = 0.05 \text{ mol dm}^{-3}$, pH = 7.0), dimethyl sulfoxide (DMSO, Alfa Aesar), and toluene (Sigma-Aldrich) were used without further purification.

Polynucleotides were purchased as noted: poly A–poly U (Sigma), calf thymus (*ct*)-DNA (Aldrich) and dissolved in sodium cacodylate buffer ($I = 0.05 \text{ mol dm}^{-3}$, pH = 7.0). The *ct*-DNA was additionally sonicated and filtered through a 0.45 mm filter to obtain mostly short (ca. 100 base pairs) rod-like B-helical DNA fragments. Polynucleotide concentrations were determined spectroscopically as the concentration of phosphates (corresponds to $c(\text{nucleobase})$).¹⁴²

All measurements of interactions with ds-DNA/RNA were performed in aqueous buffer solution (pH = 7.0, sodium cacodylate buffer, $I = 0.05 \text{ mol dm}^{-3}$). The UV-Vis spectra were recorded on a Varian Cary 100 Bio spectrometer, fluorescence spectra were recorded on a Varian Cary Eclipse fluorimeter, and CD spectra were recorded on JASCO J815 spectropolarimeter at 25.0 °C, equipped with a thermostating device, using appropriate quartz cuvettes (Hellma Suprasil QX, path length:1 cm).

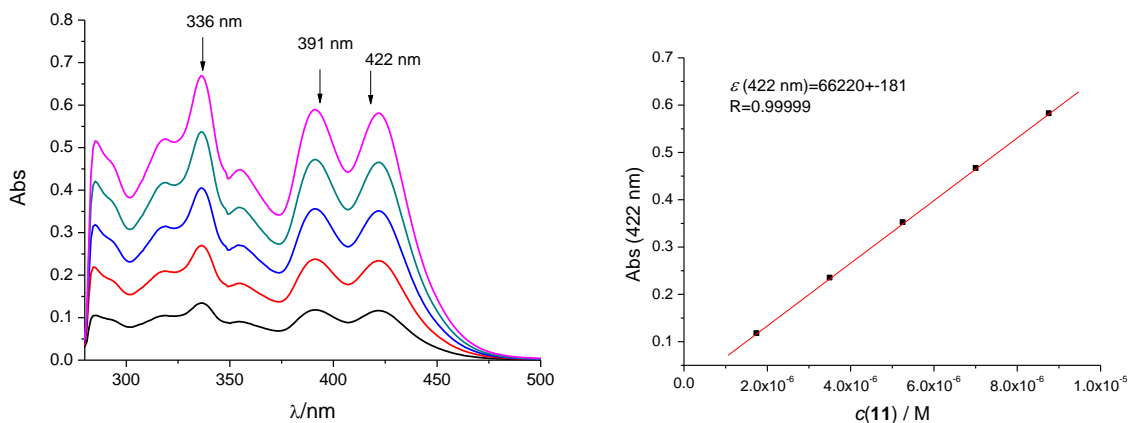
The absorption spectral changes of **11** and **12** were recorded upon stepwise addition of DNA/RNA or BSA stock solutions into the cuvette. The absorbances were sampled at 1 nm intervals, with an integration time of 10 s.

Fluorimetric titrations at λ_{exc} were performed by adding aliquots of polynucleotide or BSA stock solutions to a solution of the compound.

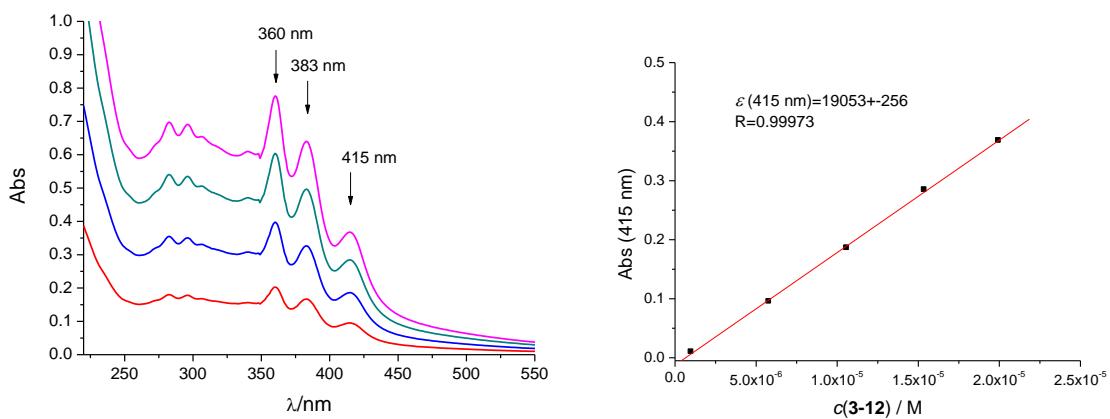
The obtained UV and fluorimetric data were corrected for the dilution and used for calculation of binding constants by fitting to 1:1 stoichiometry of complex formed.

Thermal melting curves for ds-DNA, ds-RNA, and their complexes with studied compounds were determined as previously described¹⁵ by monitoring the absorption change at 260 nm as a function of temperature. The absorbance of the ligands was subtracted from every curve, and the absorbance scale was normalized. T_m values are the midpoints of the transition curves determined from the maximum of the first derivative and checked graphically by the tangent method. The ΔT_m values were calculated subtracting T_m of the free nucleic acid from T_m of the complex. Every ΔT_m value here reported was the average of at least two measurements. The error in ΔT_m is $\pm 0.5 \text{ }^\circ\text{C}$.

CD experiments were performed by adding portions of the compound stock solution into the solution of the polynucleotide. The spectra were recorded as an average of three accumulations with a scanning speed of 200 nm/min and a buffer background was subtracted from each spectrum.



a)



b)

Figure S 3. a) Absorption spectrum of **11** (left) and the absorbance dependence on concentration ($c(\mathbf{11}) = 1.76 \times 10^{-6} - 8.77 \times 10^{-6}$ M) at $\lambda_{\text{max}} = 422$ nm (right) (done in toluene, $l = 1$ cm); b) absorption spectrum of **12** (left) and the absorbance dependence on concentration ($c(\mathbf{12}) = 1 \times 10^{-6} - 2 \times 10^{-5}$ M) at $\lambda_{\text{max}} = 415$ nm (right) (done in sodium cacodylate buffer, $l = 0.05$ M, pH = 7, $l = 1$ cm).

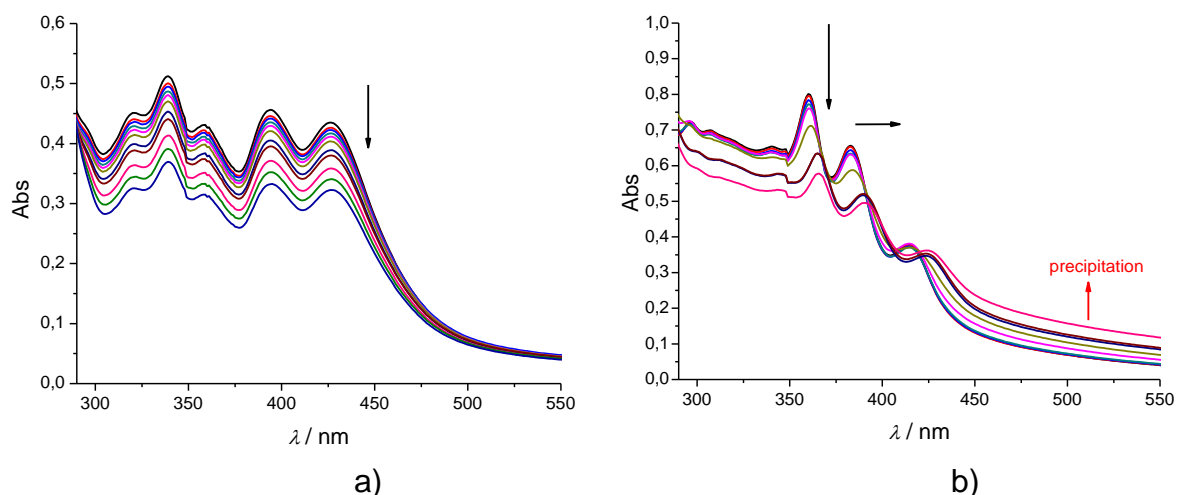


Figure S 4. Spectrophotometric titration of: a) **11** ($c = 9 \times 10^{-6} \text{ M}$), and b) **12** ($c = 1 \times 10^{-5} \text{ M}$) with ct-DNA ($c = 1 \times 10^{-6} - 1 \times 10^{-4} \text{ M}$) (done in sodium cacodylate buffer, $I = 0.05 \text{ M}$, $\text{pH} = 7$, $l = 1 \text{ cm}$).

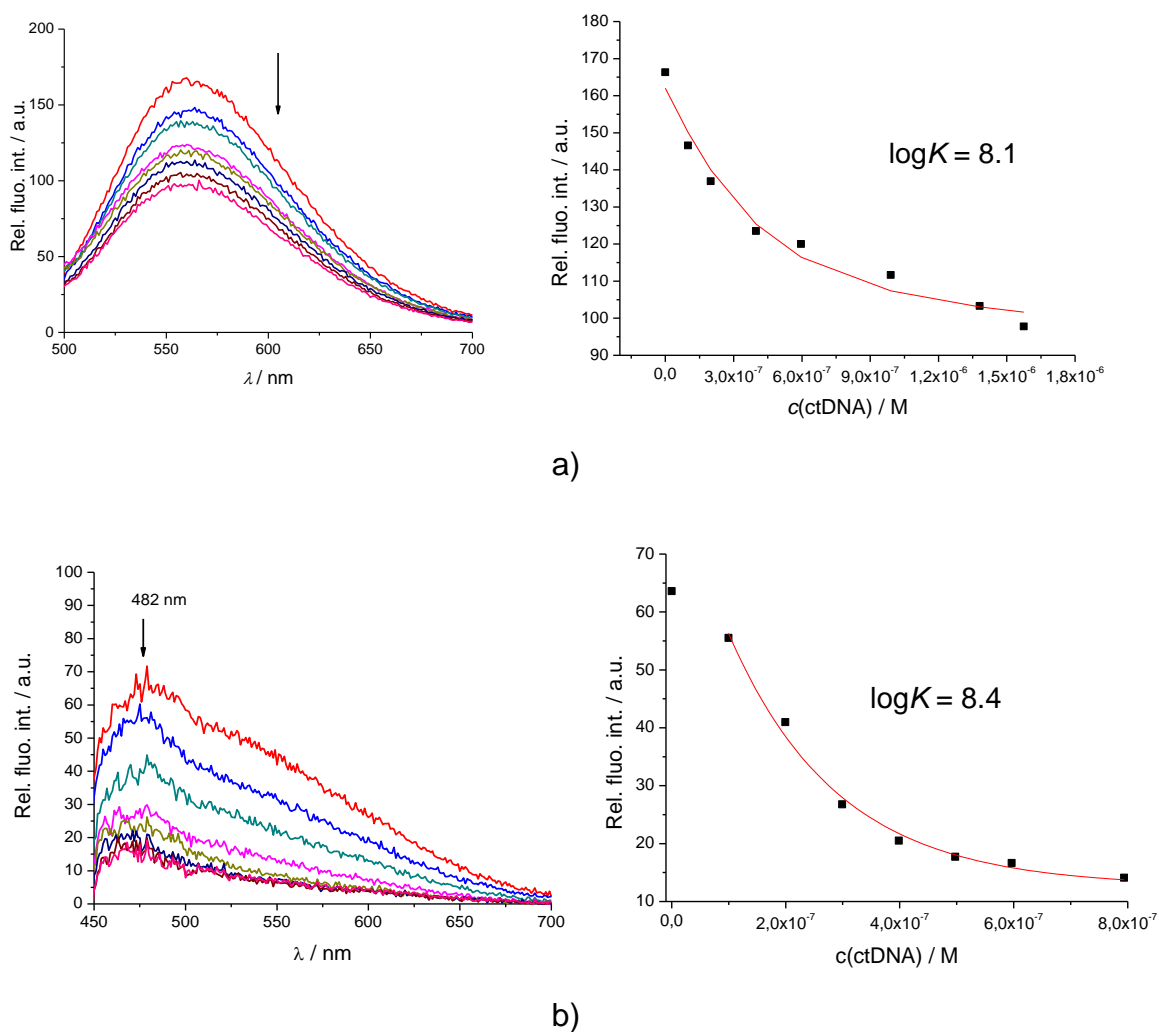


Figure S 5. Fluorimetric titration of: a) **11** ($c = 3.51 \times 10^{-7} \text{ M}$, $\lambda_{\text{exc}} = 420 \text{ nm}$) with ctDNA ($c = 1 \times 10^{-7} - 1.6 \times 10^{-6} \text{ M}$), slit: 20-20 (left), and dependence of **11** emission

at $\lambda_{\max} = 561$ nm on $c(\text{ctDNA})$; b) **12** ($c = 5 \times 10^{-7}$ M, $\lambda_{\text{exc}} = 415$ nm) with ctDNA ($c = 1 \times 10^{-7} - 8 \times 10^{-7}$ M), slit: 20-20 (left), and dependence of **12** emission at $\lambda_{\max} = 482$ nm on $c(\text{ctDNA})$ (done in sodium cacodylate buffer, $I = 0.05$ M, $\text{pH} = 7$, $l = 1$ cm).

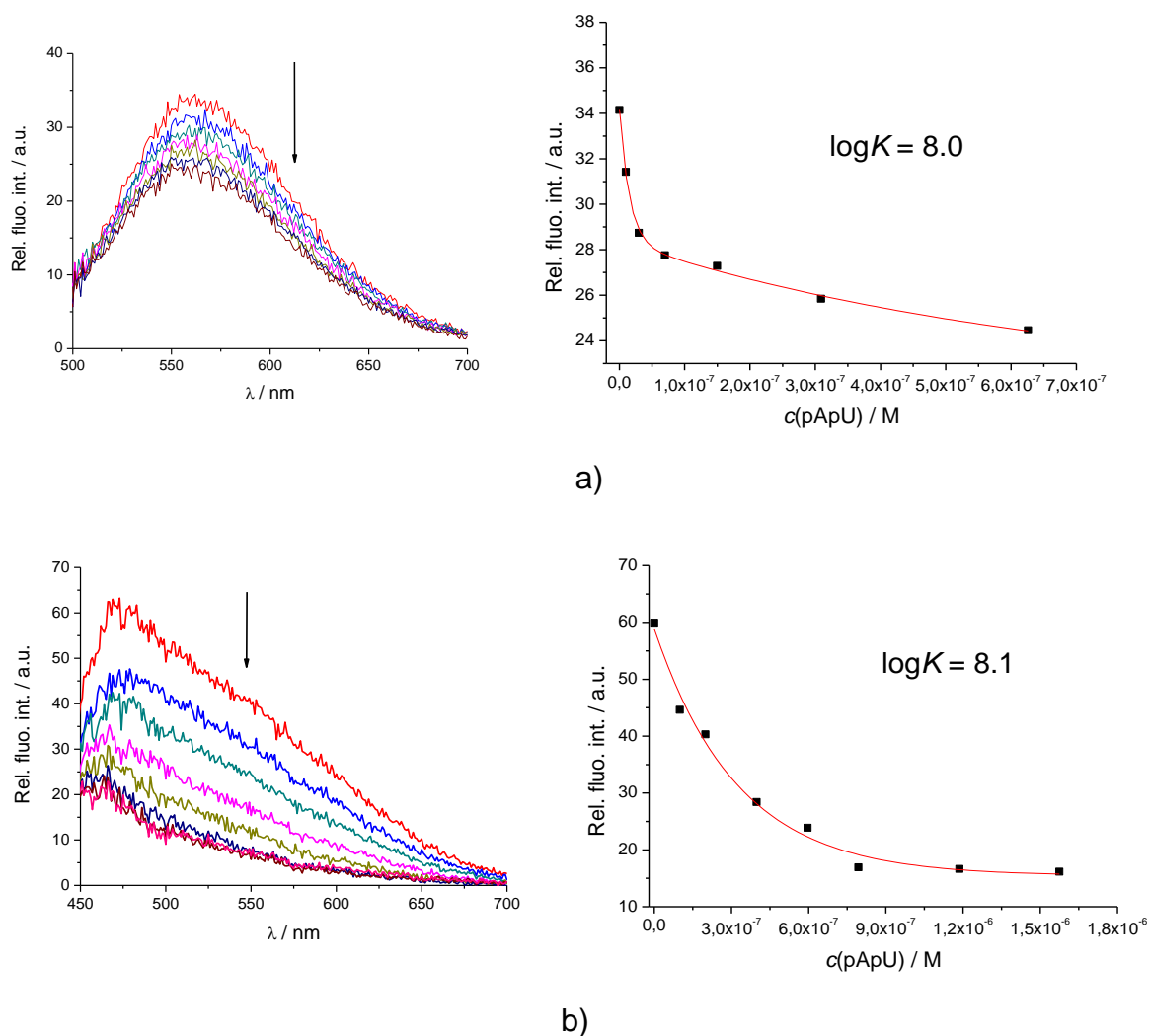


Figure S6. Fluorimetric titration of: a) **11** ($c = 5 \times 10^{-7}$ M, $\lambda_{\text{exc}} = 420$ nm) with poly A – poly U, and dependence of **11** emission at $\lambda_{\max} = 561$ nm on $c(\text{poly A – poly U})$; b) **12** ($c = 5 \times 10^{-7}$ M, $\lambda_{\text{exc}} = 415$ nm) with poly A – poly U, and dependence of **12** emission at $\lambda_{\max} = 482$ nm on $c(\text{poly A – poly U})$. Done at $\text{pH} = 7$, sodium cacodylate buffer, $I = 0.05$ M.

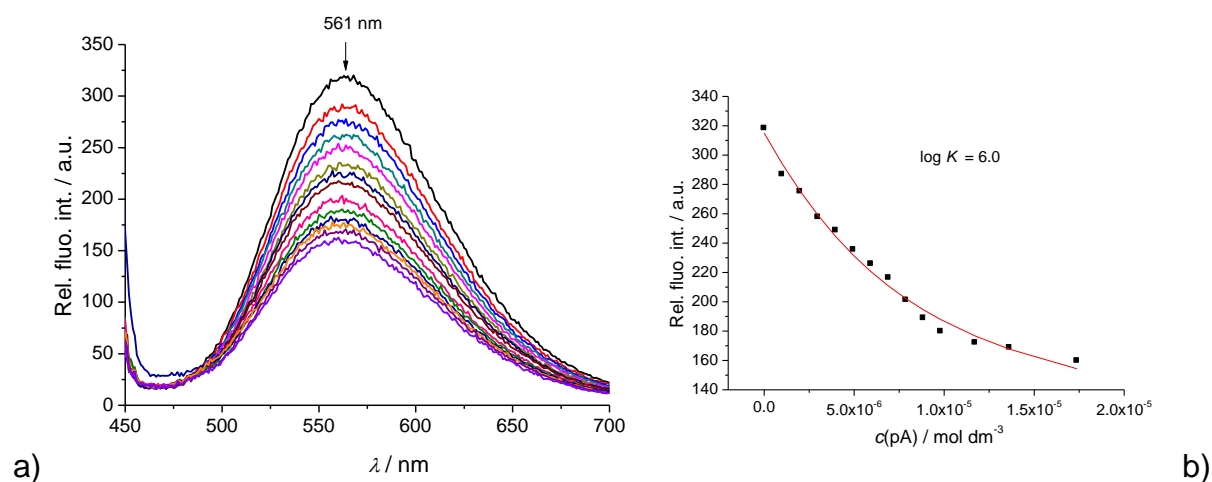


Figure S7. a) Fluorimetric titration of **11** ($c = 1 \times 10^{-6}$ M, $\lambda_{\text{exc}} = 420$ nm) with poly A ($c = 1 \times 10^{-6} - 1.7 \times 10^{-5}$ M), and b) dependence of **11** emission at $\lambda_{\text{max}} = 561$ nm on $c(\text{poly A})$, (right). Done in sodium cacodylate buffer, $I = 0.05$ M, pH = 7.

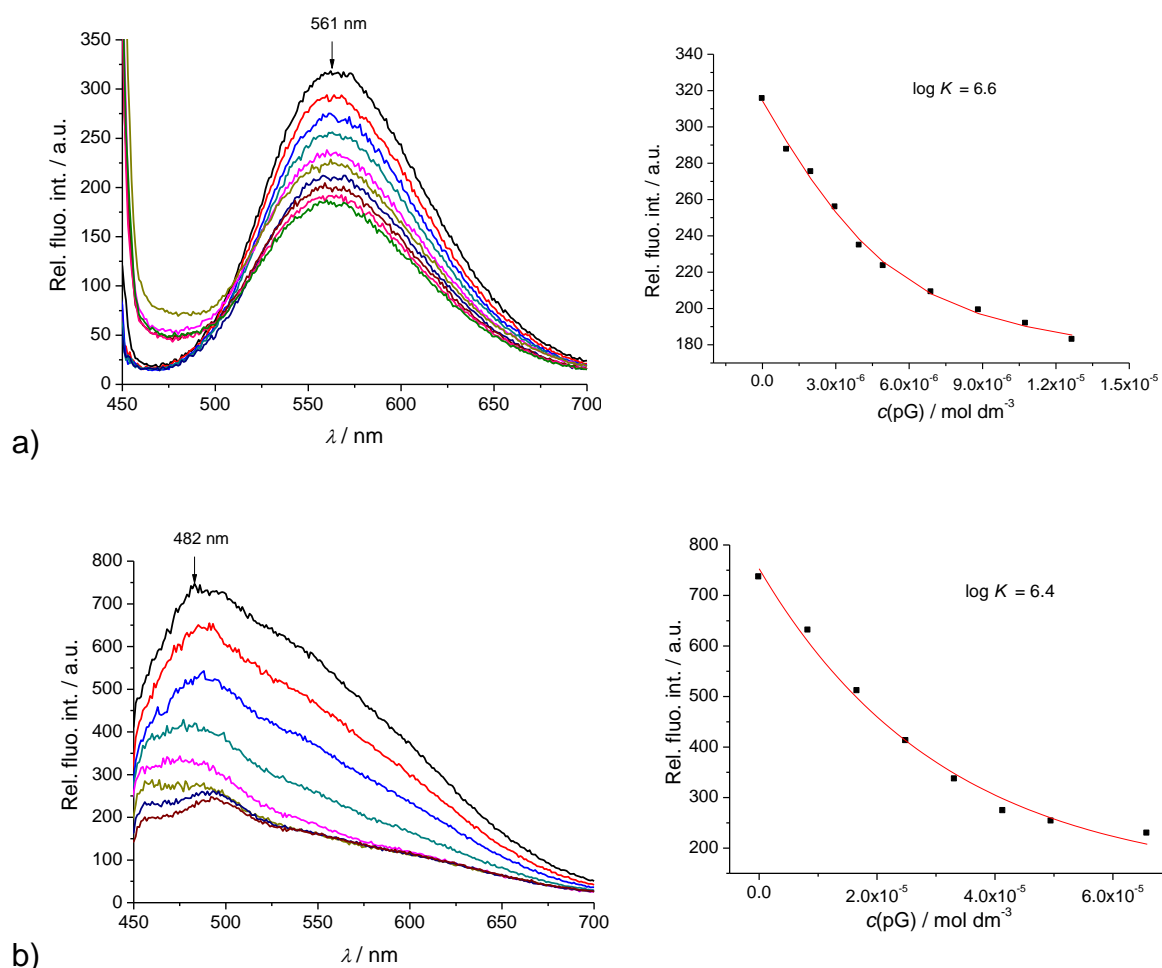


Figure S8. Fluorimetric titration of: a) **11** ($c = 1 \times 10^{-6}$ M, $\lambda_{\text{exc}} = 420$ nm) with poly G ($c = 1 \times 10^{-6} - 1.3 \times 10^{-5}$ M), slit: 20-20 (left), and dependence of **11** emission at $\lambda_{\text{max}} = 561$ nm on $c(\text{poly G})$; b) **12** ($c = 1 \times 10^{-5}$ M, $\lambda_{\text{exc}} = 415$ nm) with poly G ($c = 8.4 \times 10^{-6}$

– 6.6×10^{-5} M), slit: 20-20 (left), and dependence of **12** emission at $\lambda_{\max} = 482$ nm on $c(\text{poly G})$. Done at pH = 7, sodium cacodylate buffer, $I = 0.05$ M.

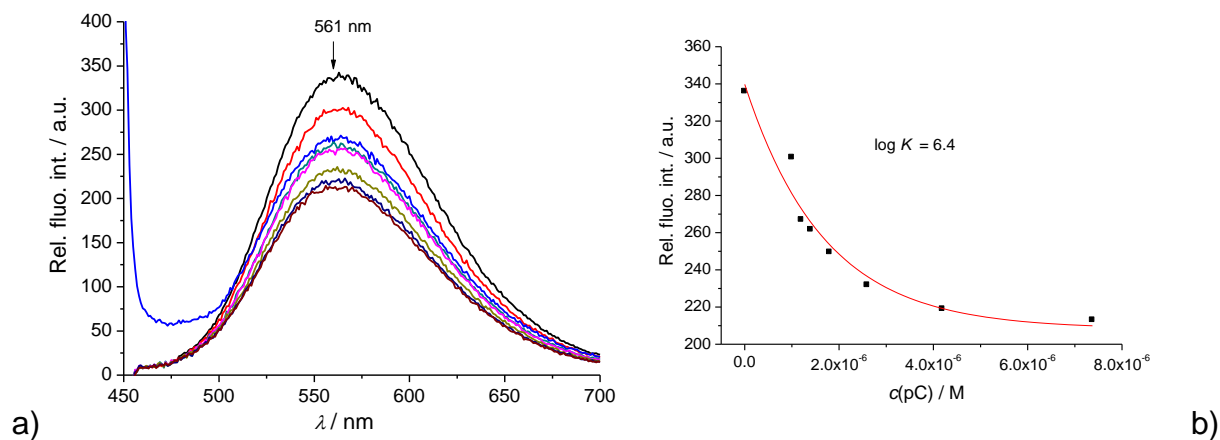


Figure S9. Fluorimetric titration of: a) **11** ($c = 1 \times 10^{-6}$ M, $\lambda_{\text{exc}} = 420$ nm) with poly C ($c = 1 \times 10^{-6} - 7.4 \times 10^{-6}$ M), and b) dependence of **11** emission at $\lambda_{\max} = 561$ nm on $c(\text{poly C})$; Done at pH = 7, sodium cacodylate buffer, $I = 0.05$ M.

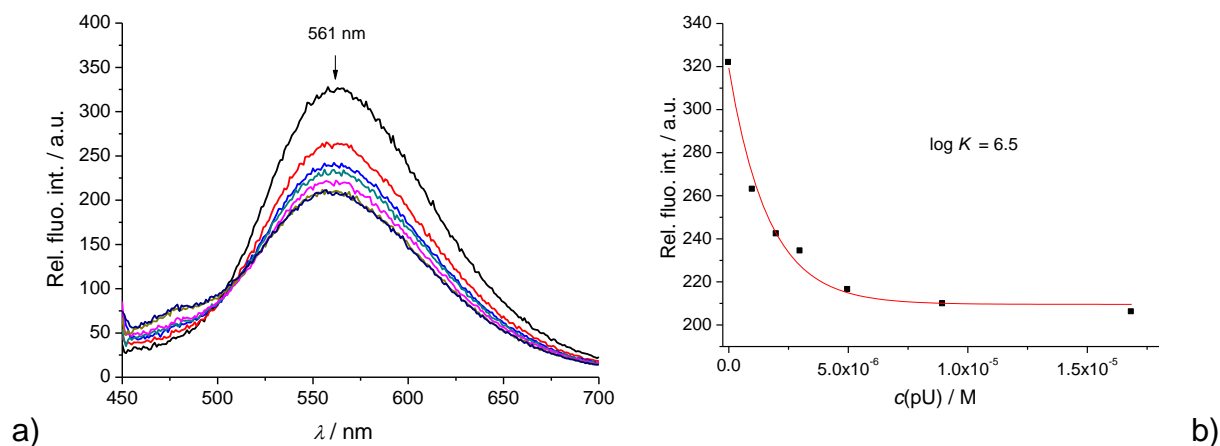


Figure S10. Fluorimetric titration of: a) **11** ($c = 1 \times 10^{-6}$ M, $\lambda_{\text{exc}} = 420$ nm) with poly U ($c = 1 \times 10^{-6} - 1.7 \times 10^{-5}$ M), slit: 20-20 (left), and b) dependence of **11** emission at $\lambda_{\max} = 561$ nm on $c(\text{poly U})$. Done at pH = 7, sodium cacodylate buffer, $I = 0.05$ M.

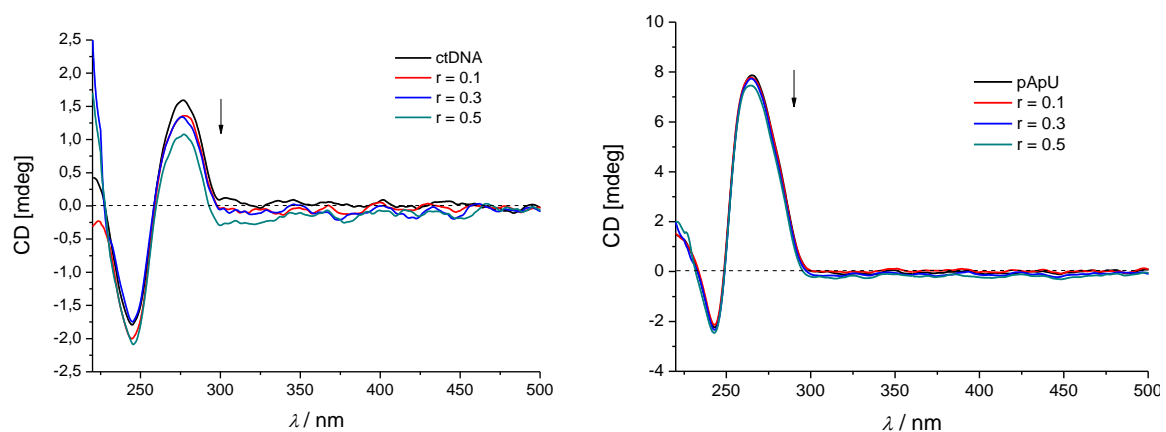


Figure S 11. CD titration of ctDNA ($c = 3 \times 10^{-5}$ M) and poly A – poly U ($c = 3 \times 10^{-5}$ M) with **11** at molar ratios $r = [\text{compound}] / [\text{polynucleotide}]$ (done in sodium cacodylate buffer, $I = 0.05$ M, pH = 7, $l = 1$ cm).

Thermal denaturation experiments

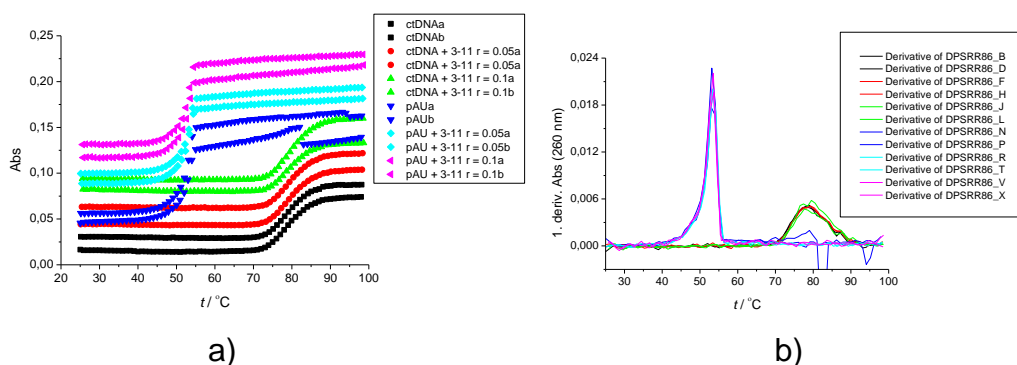


Figure S12. a) Melting curves of ctDNA and poly A – poly U upon addition of $r = 0.05$ or 0.1 ([compound/ [polynucleotide)] of **11** at pH 7.0 (buffer sodium cacodylate, $I = 0.05$ M); b) the first derivation of absorbance (fitted to sigmoidal eq.) on temperature.

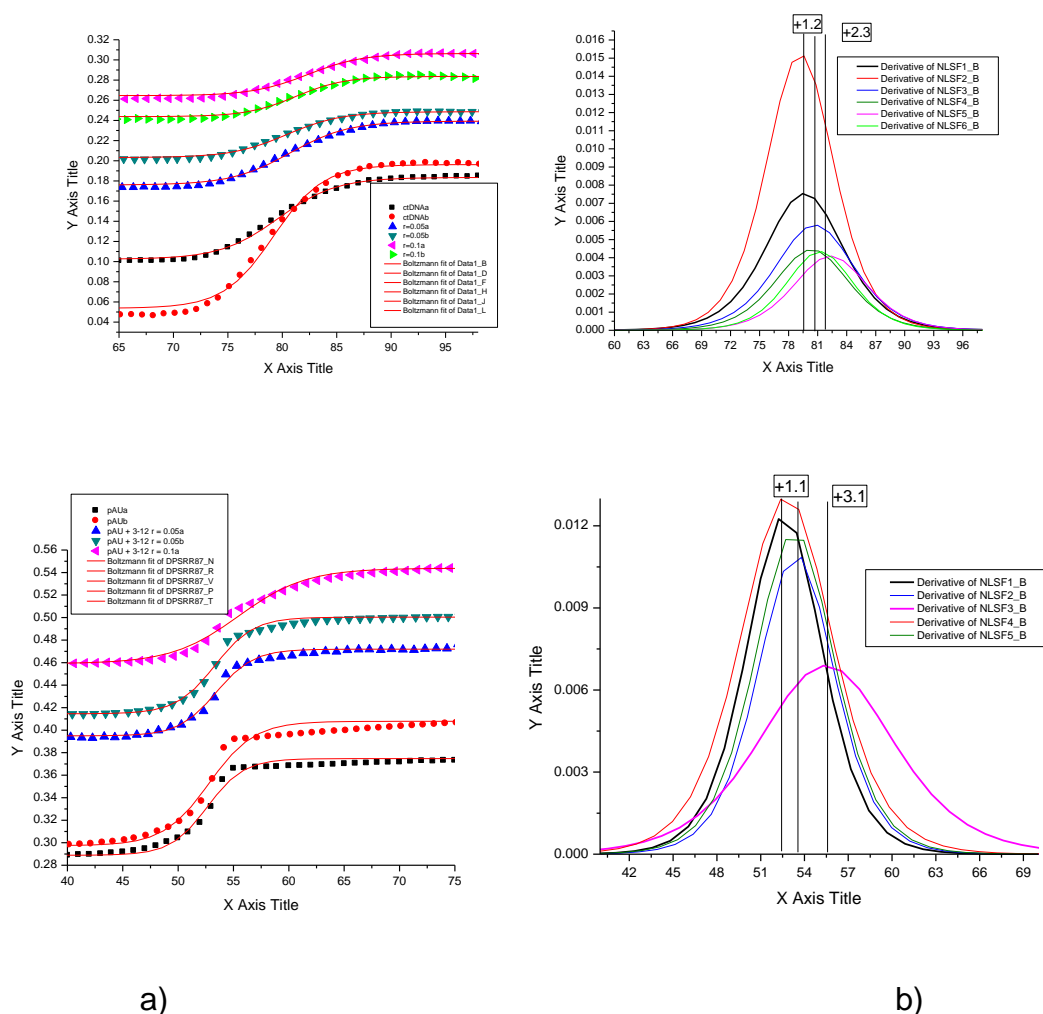


Figure S13. a) Melting curves of ctDNA and poly A – poly U upon addition of $r = 0.05$ or 0.1 ([compound/ [polynucleotide)] of **12** at pH 7.0 (buffer sodium cacodylate, $I = 0.05$ M); b) the first derivation of absorbance (fitted to sigmoidal eq.) on temperature.

SERS analysis

General information

SERS spectra upon excitation at 1064 nm were measured using a Bruker Equinox 55 interferometer equipped with FRA 106/S Raman module and Nd-YAG laser of 500 mW power. Quartz cuvettes with the back placed mirror were used for handling colloidal samples. The spectra were recorded in the 3500–100 cm^{-1} spectral range at a resolution of 4 cm^{-1} and averaged over 128 scans.

A Renishaw inVia Raman microscope was used for measurements of SERS spectra upon excitation at 785 nm. Laser radiation of 15 mW power was focused on the colloidal sample placed in a 40- μL aluminum pan using a 5 \times microscopic objective (NA = 0.12). The spectra were recorded in the 3200–100 cm^{-1} spectral range at a resolution of 1 cm^{-1} with exposure time of 10 s.

Metal substrate synthesis

Colloidal suspension of silver nanoparticles was prepared by reduction of silver nitrate with trisodium citrate using modified Lee and Meisel method.¹⁶ The UV/Vis absorption maximum of the silver colloid was 412 nm, and the pH value of the colloidal suspension was 6.9. The prepared suspension of silver nanoparticles was centrifuged at 5000 rpm for 15 min. The supernatant (85 % of the initial colloidal suspension) was removed, and the residue containing silver nanoparticles (15 % volume of the initial colloidal suspension) was used as the SERS substrate.

Working samples for concentration dependent SERS measurements were prepared by dissolution of:

- a) **11** stock solution ($c = 1 \times 10^{-4}$ M in DMSO) in an appropriate volume of DMSO, followed by addition of 400 μL of the silver colloid. The total sample volume was 500 μL , while DMSO volume ratio (v/v) was 20% in all the samples. The final concentrations of **11** in the samples were 5×10^{-6} M and 1×10^{-5} M.
- b) **12** stock solution ($c = 1 \times 10^{-4}$ M in water) in an appropriate volume of water, followed by addition of 400 μL of the silver colloid. The total sample volume was 500 μL . For the concentration dependent measurements, the final concentrations of **12** in the Ag colloid were 1×10^{-7} M, 5×10^{-7} M, 1×10^{-6} M, 5×10^{-6} M and 1×10^{-5} M.

Table S 1. Assignment of the bands observed in the SERS spectra of **11** and DMSO.

Wavenumber / cm^{-1}				Assignment
$c(\mathbf{11}) = 1 \times 10^{-5} \text{ M}$		DMSO		
785 nm	1064 nm	785 nm	1064 nm	
	3011		3009	$\nu \text{ C-H}$
2931	2926	2933	2926	$\nu \text{ C-H}$
	2861		2861	$\nu \text{ C-H}$
1422	1419	1425	1418	$\delta \text{ CH}_3$
1024		1019		$\nu \text{ S=O}$
957		958		$\delta \text{ CH}_3$
683	678	683	678	$\nu \text{ C-S}$
240		235		$\nu \text{ Ag-O}$

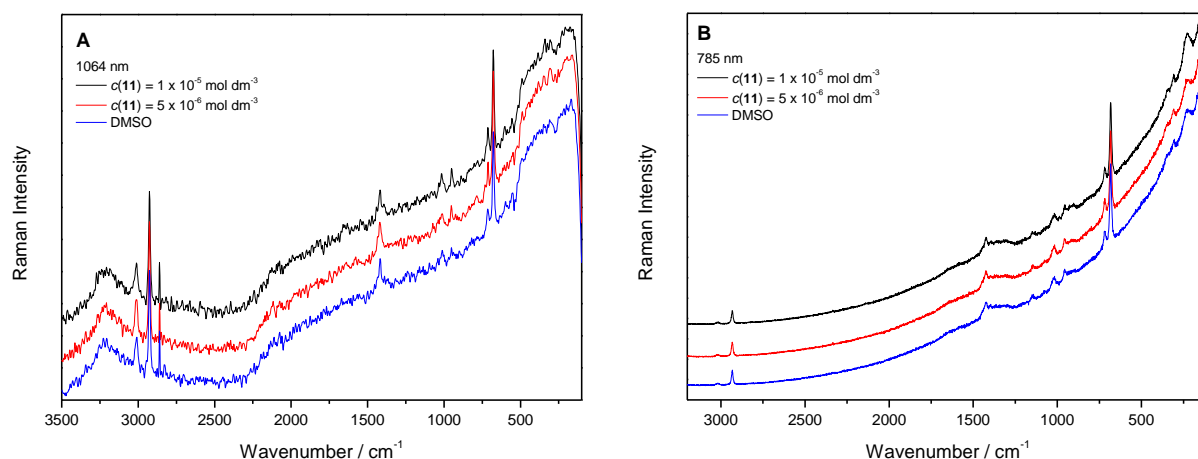


Figure S 14. Raman spectrum of the silver colloid containing DMSO (blue) and concentration dependent SERS spectra of **11** in the silver colloid, $c(\mathbf{11}) = 5 \times 10^{-6} \text{ M}$ (red) and $1 \times 10^{-5} \text{ M}$ (black). A) Excitation wavelength 1064 nm, laser power 500 mW; B) Excitation wavelength 785 nm, laser power 300 mW. The spectra are displaced for visual clarity.

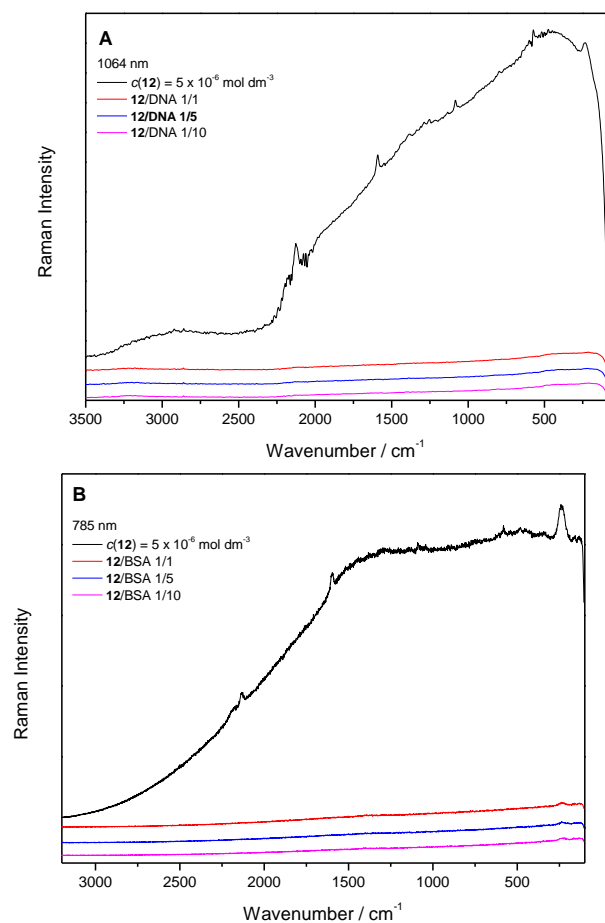
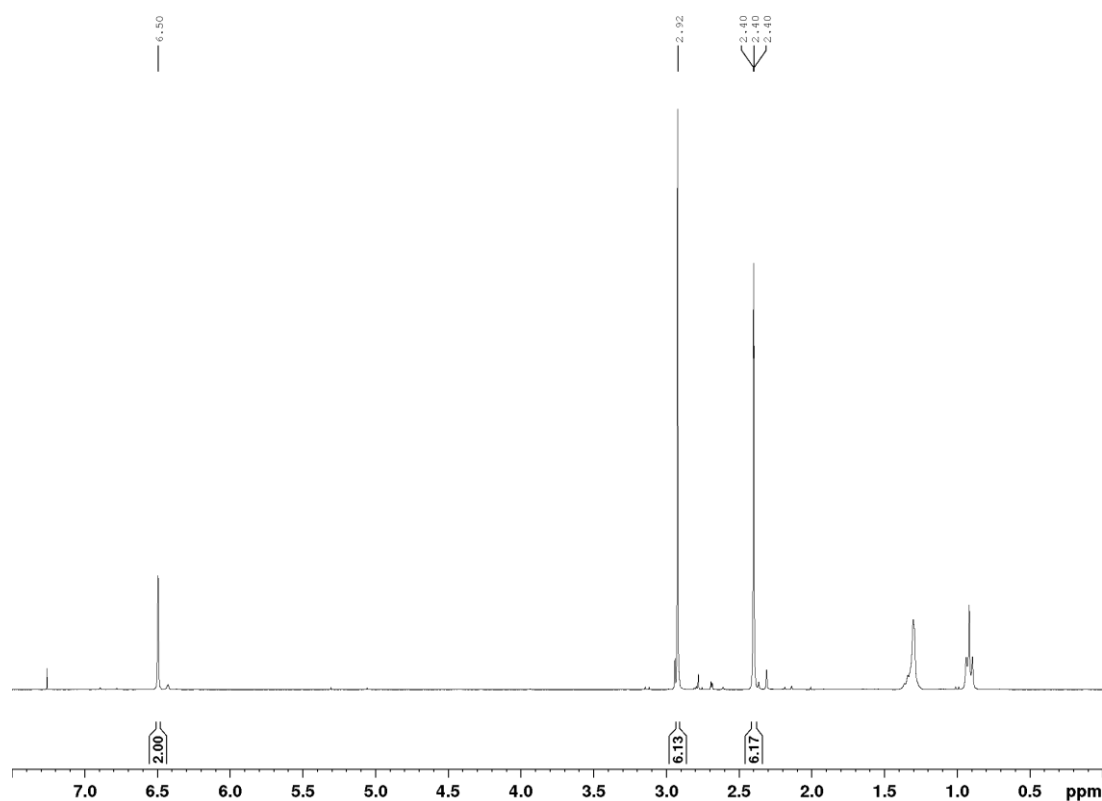
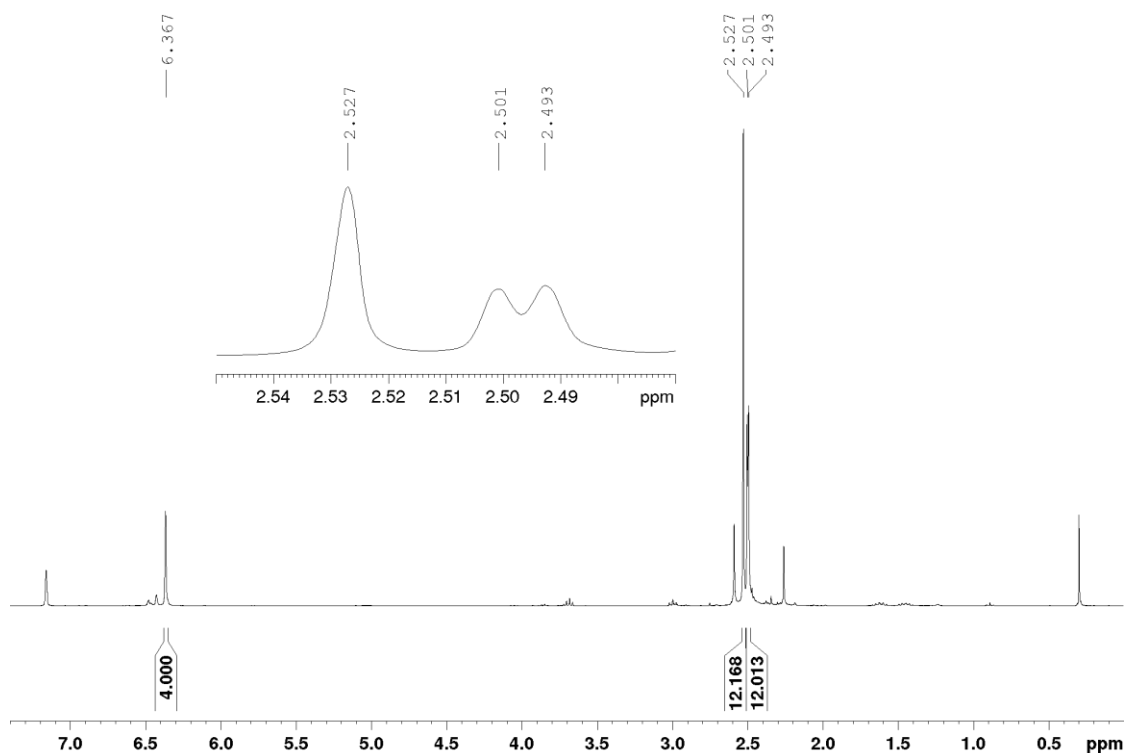


Figure S15. SERS spectra of **12** in Na-cacodylate buffer (black); **12**/BSA complexes: 1/1 (red), 1/5 (blue) and 1/10 (magenta). A) Excitation wavelength 1064 nm, laser power 500 mW; B) Excitation wavelength 785 nm, laser power 300 mW. The spectra are displaced for visual clarity.

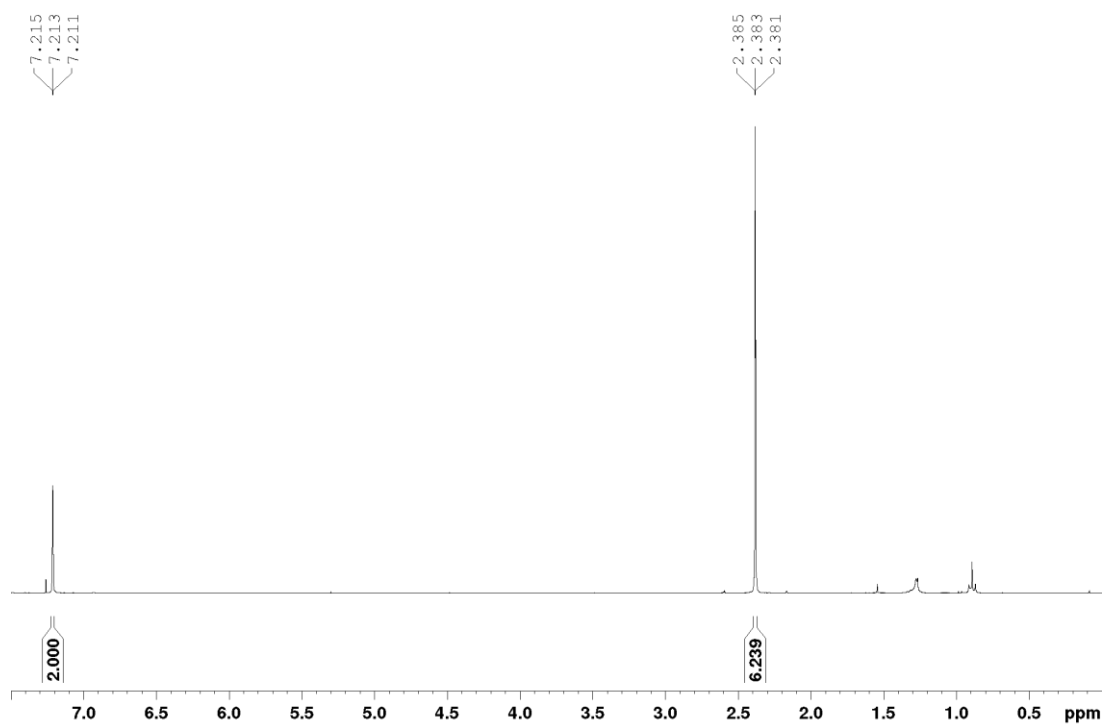
NMR Spectra



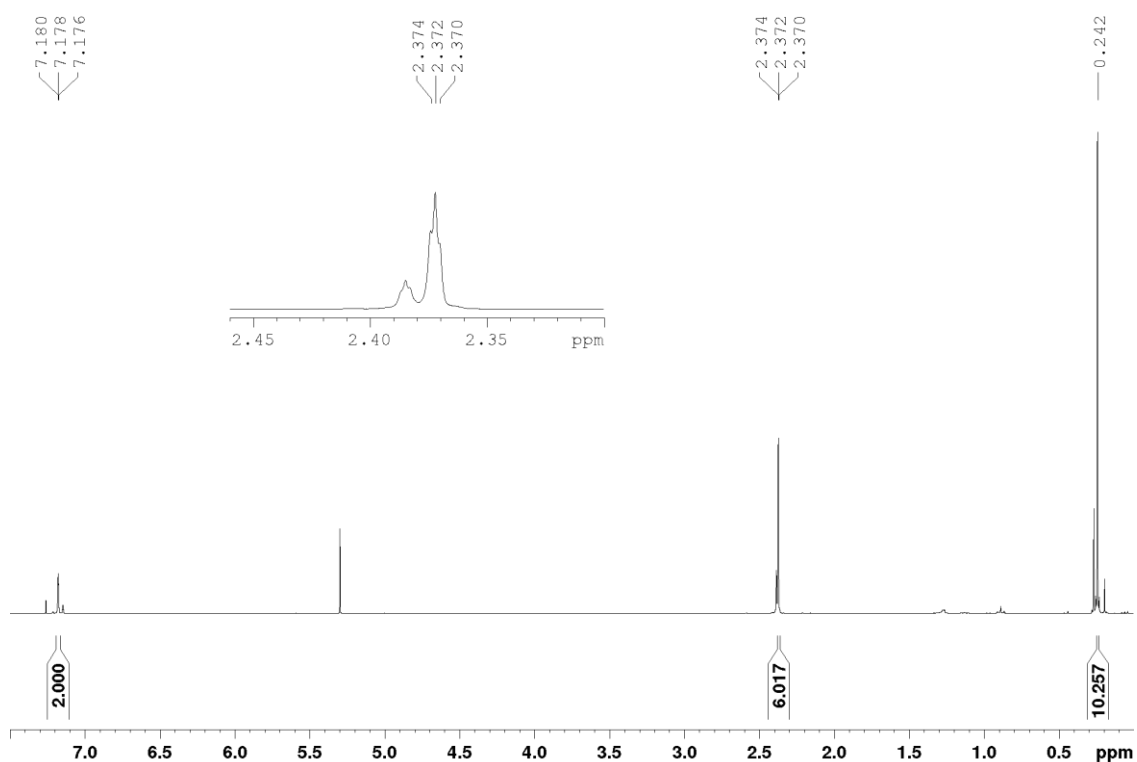
^1H NMR spectrum (300 MHz) of **2** in CDCl_3 . The spectrum was recorded of the crude material and contains solvent & grease signals.



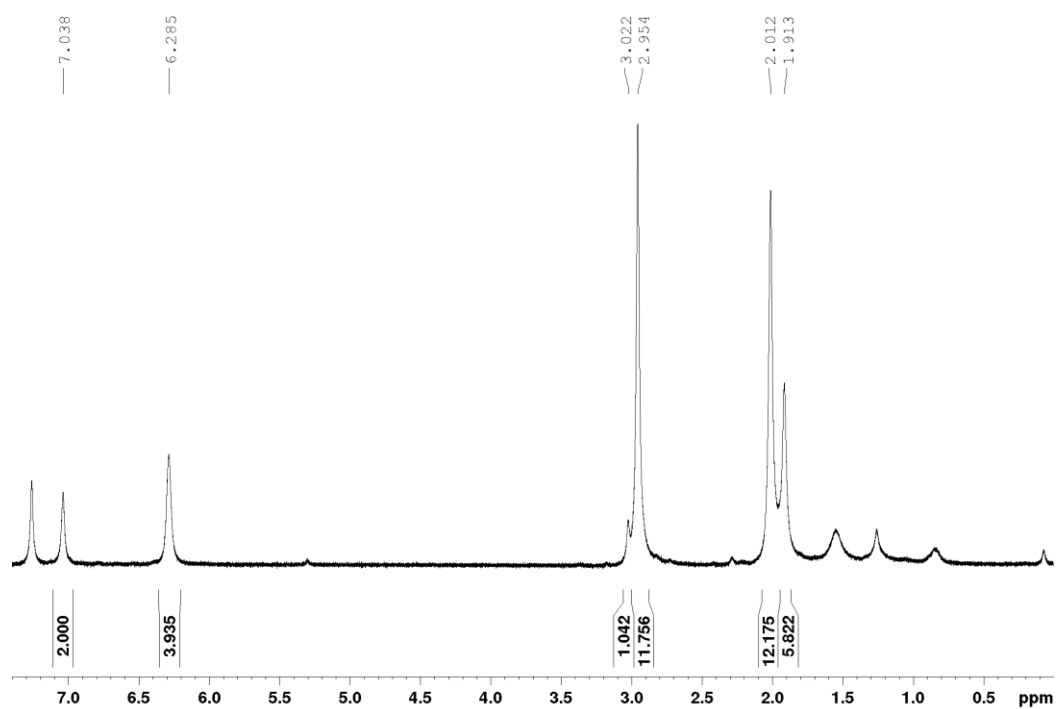
^1H NMR spectrum (300 MHz) of **3** in C_6D_6 . The spectrum was recorded of the crude material and contains solvent & grease signals.



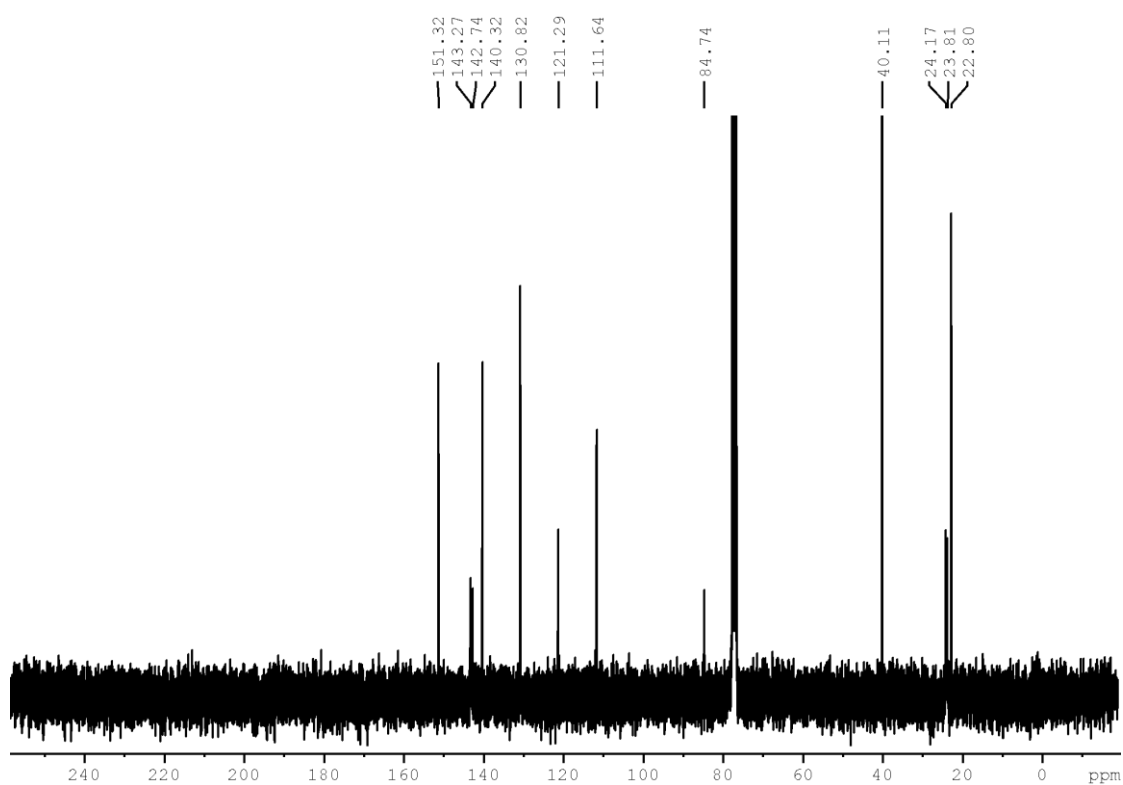
^1H NMR spectrum (300 MHz) of **5** in CDCl_3 . The spectrum was recorded of the crude material and contains solvent signals.



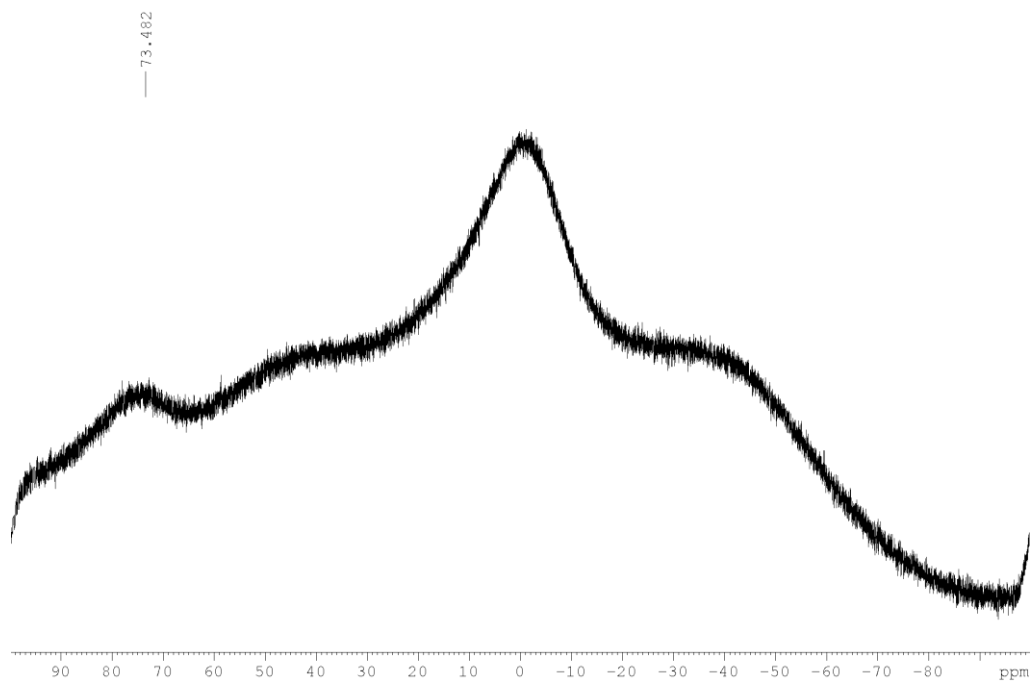
^1H NMR spectrum (300 MHz) of **6** in CDCl_3 . The spectrum was recorded of the crude material and contains solvent signals.



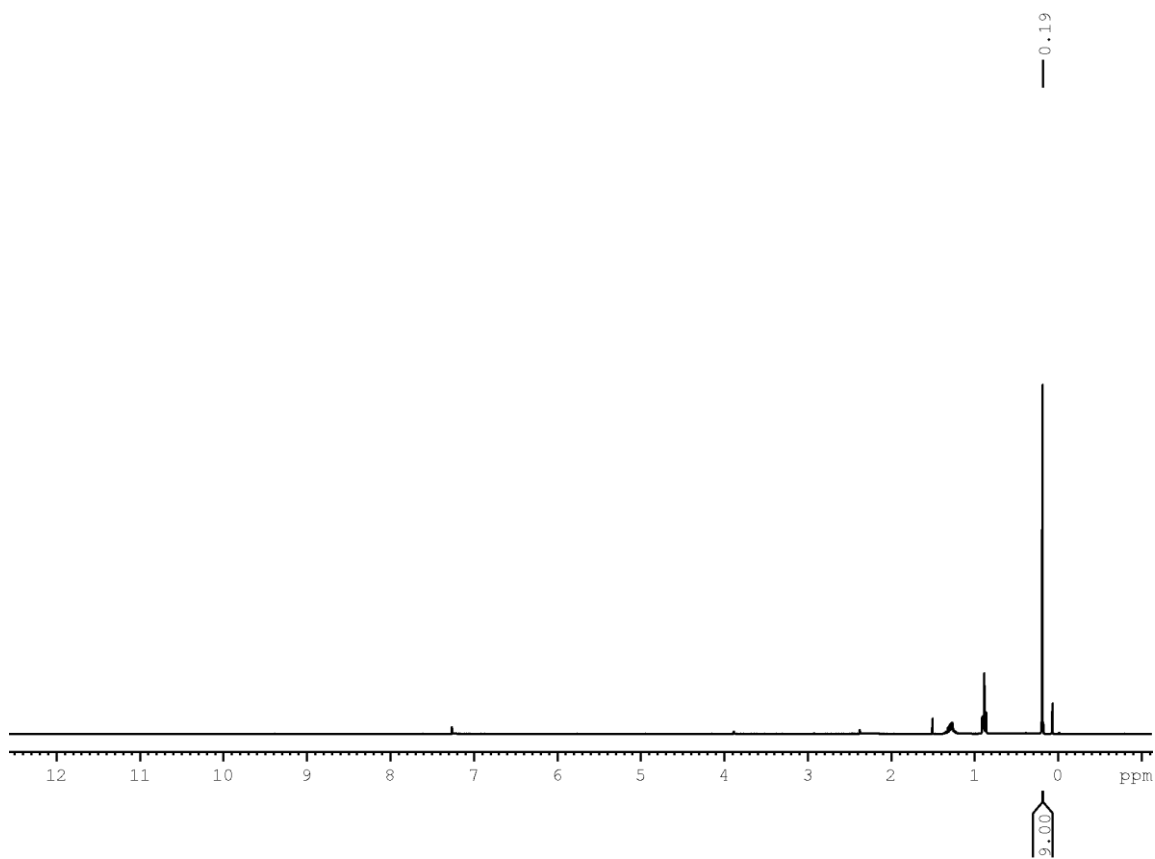
^1H NMR spectrum (300 MHz) of **8** in CDCl_3 . The spectrum was recorded of the crude material and contains solvent signals.



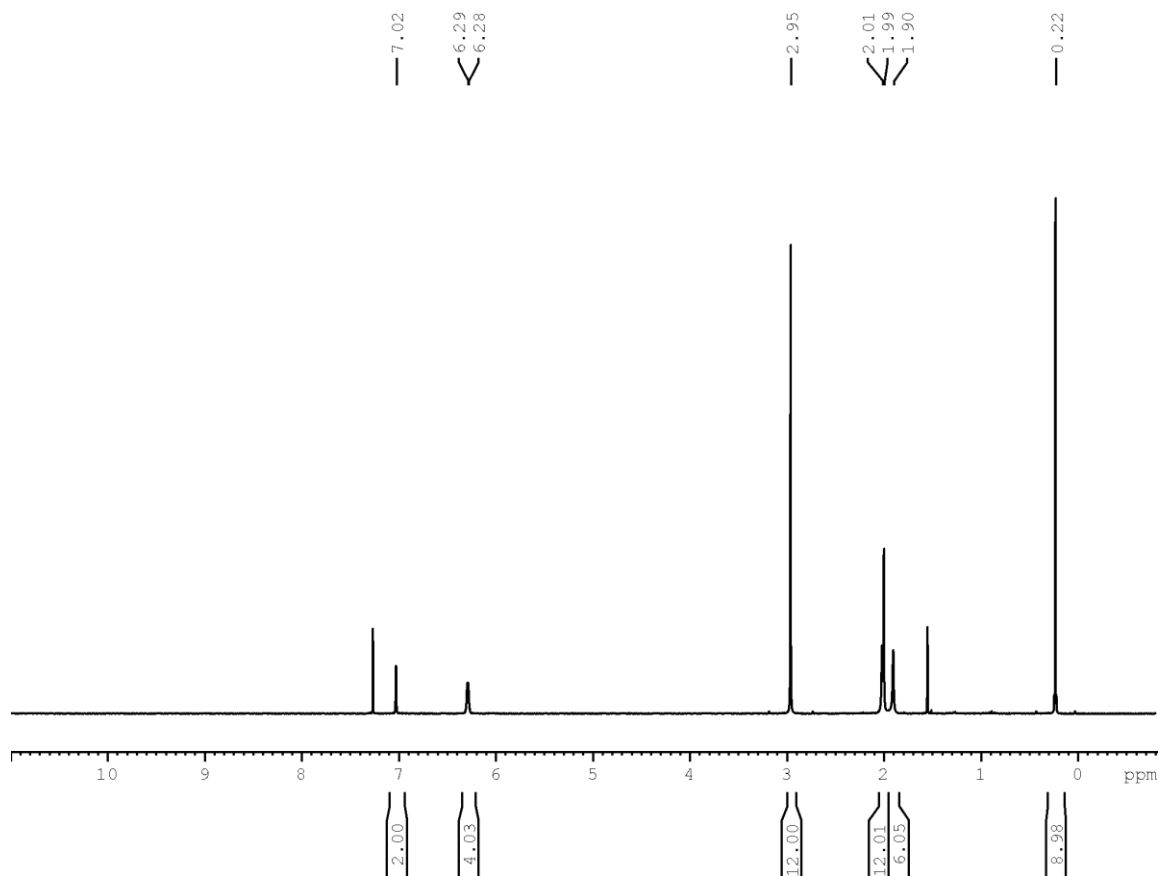
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz) of **8** in CDCl_3 .



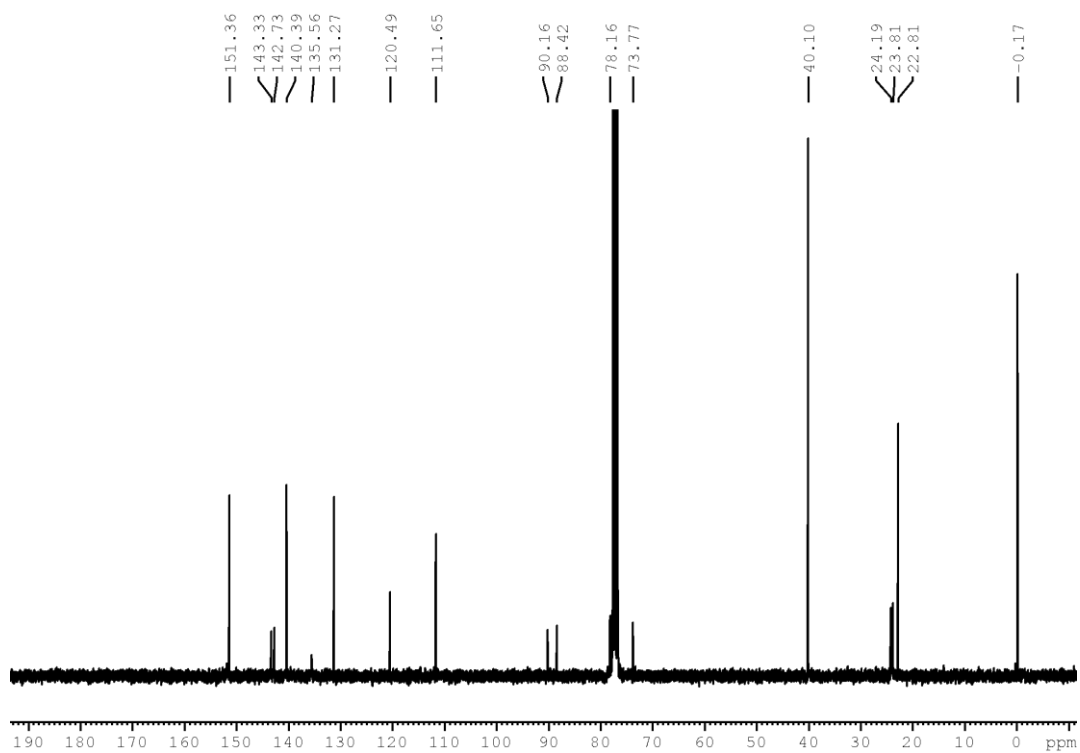
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (96 MHz) of **8** in CDCl_3 .



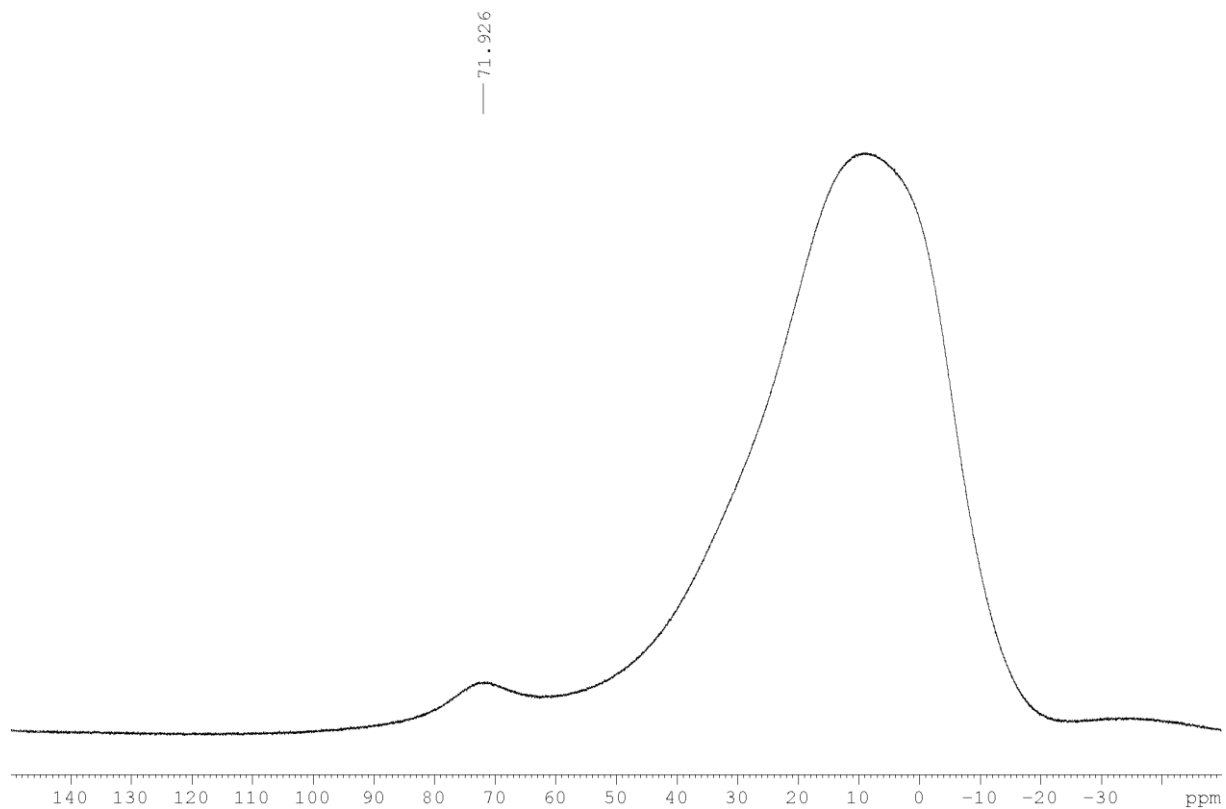
^1H NMR spectrum (300 MHz) of (bromoethynyl)trimethylsilane in CDCl_3 . The spectrum was recorded of the crude material and contains solvent signals.



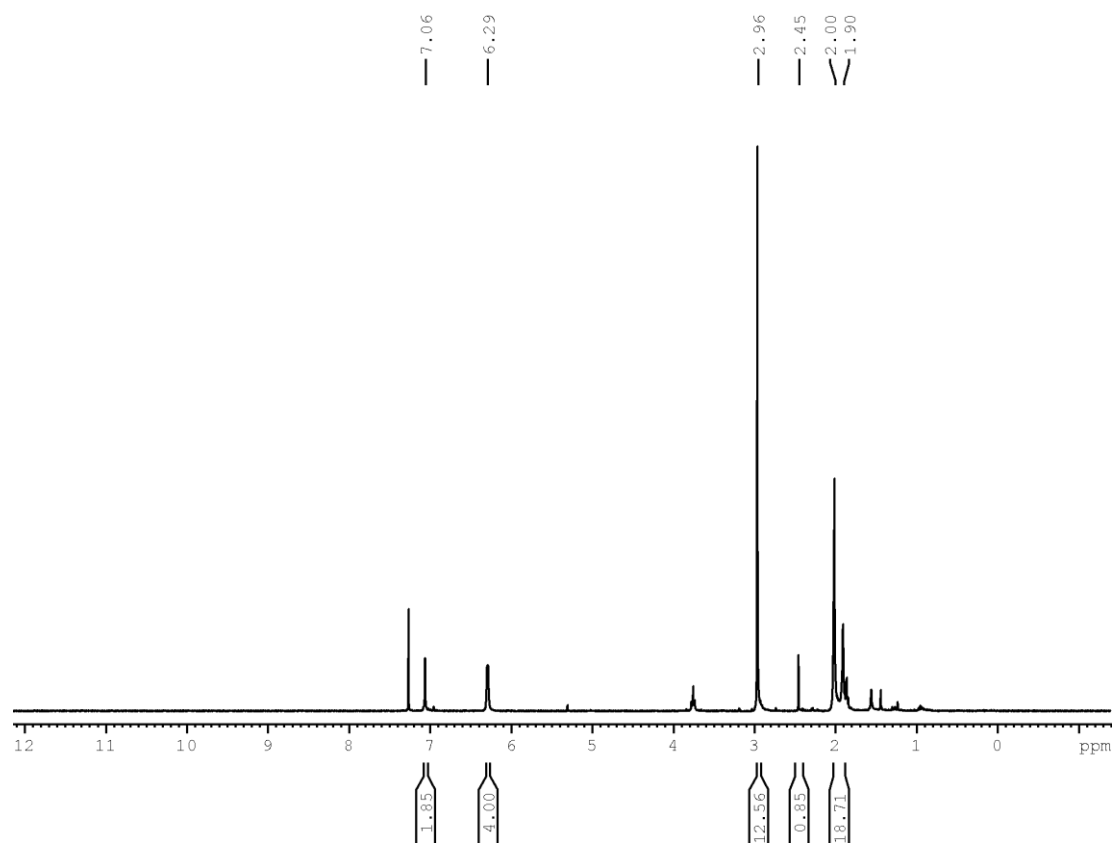
^1H NMR spectrum (300 MHz) of **9** in CDCl_3 .



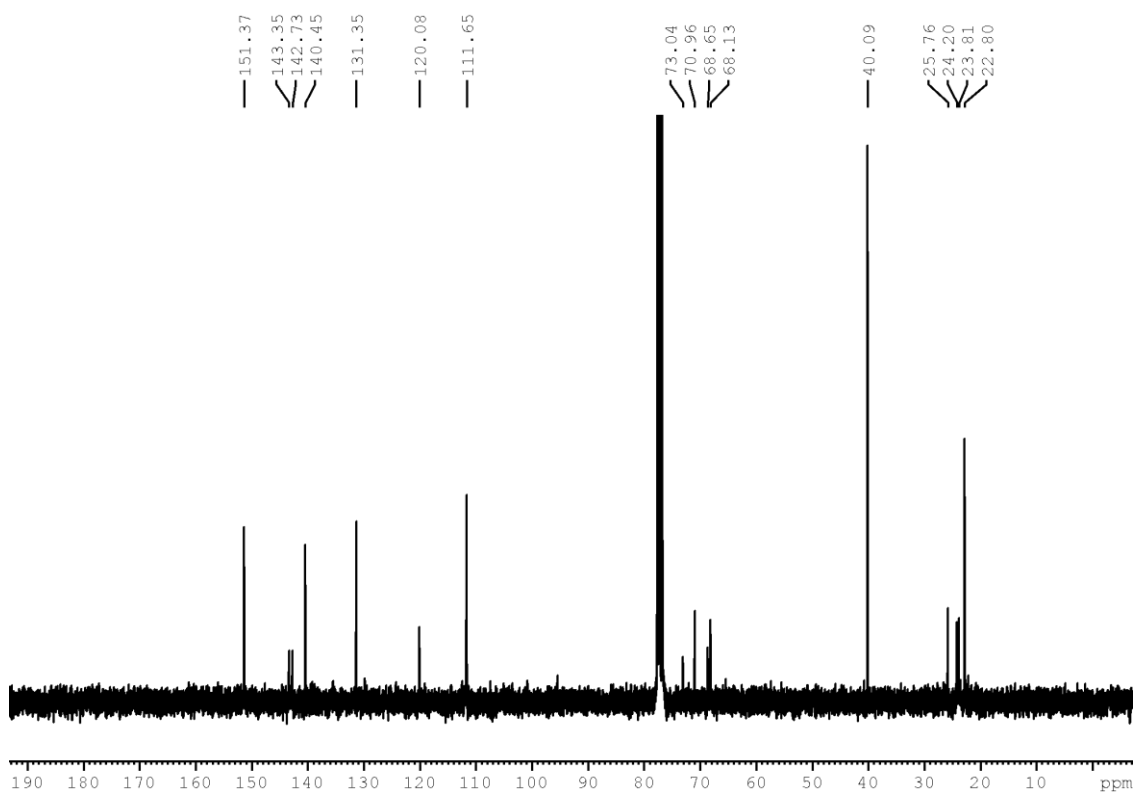
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz) of **9** in CDCl_3 .



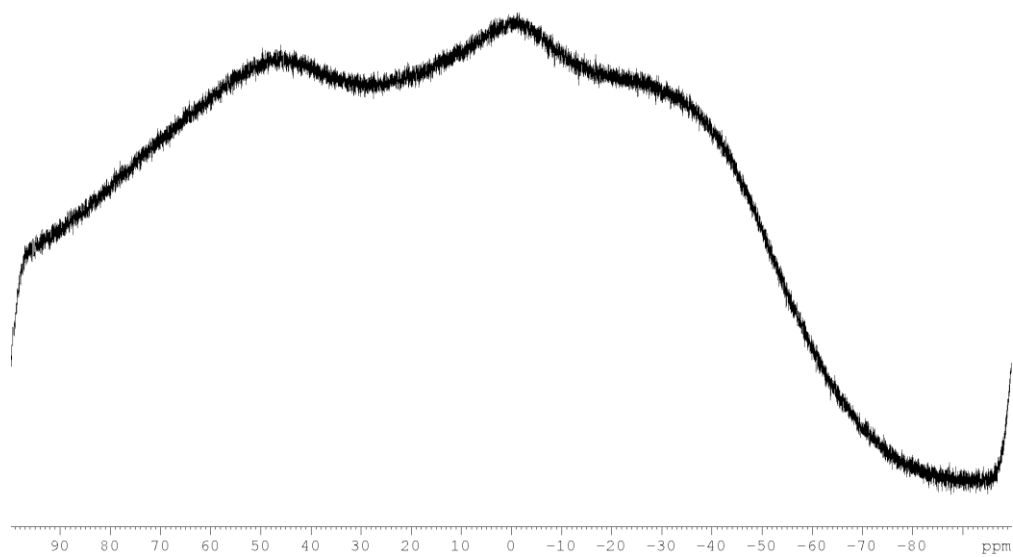
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (192 MHz) of **9** in CDCl_3 .



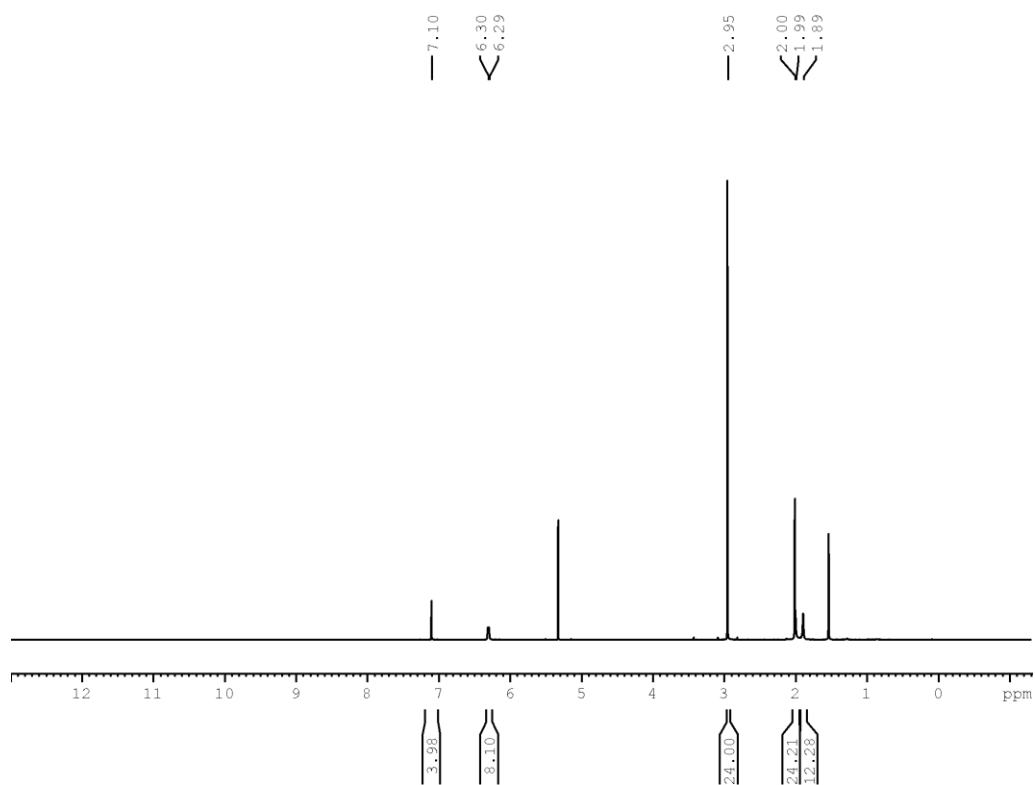
^1H NMR spectrum (300 MHz) of **10** in CDCl_3 .



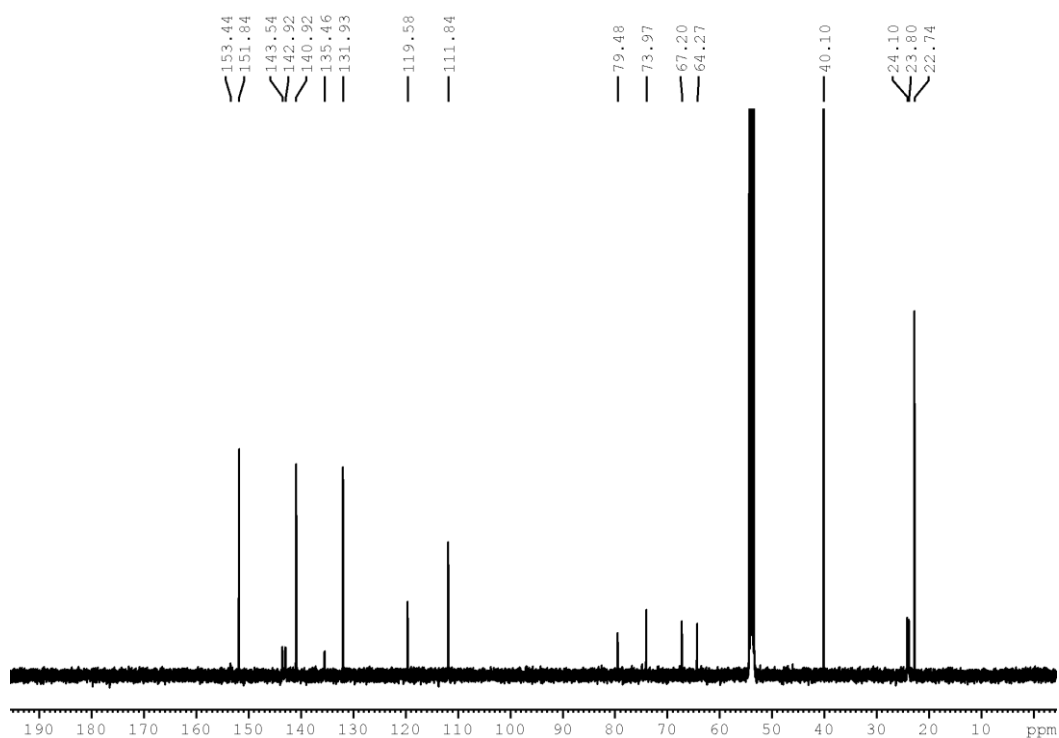
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz) of **10** in CDCl_3 .



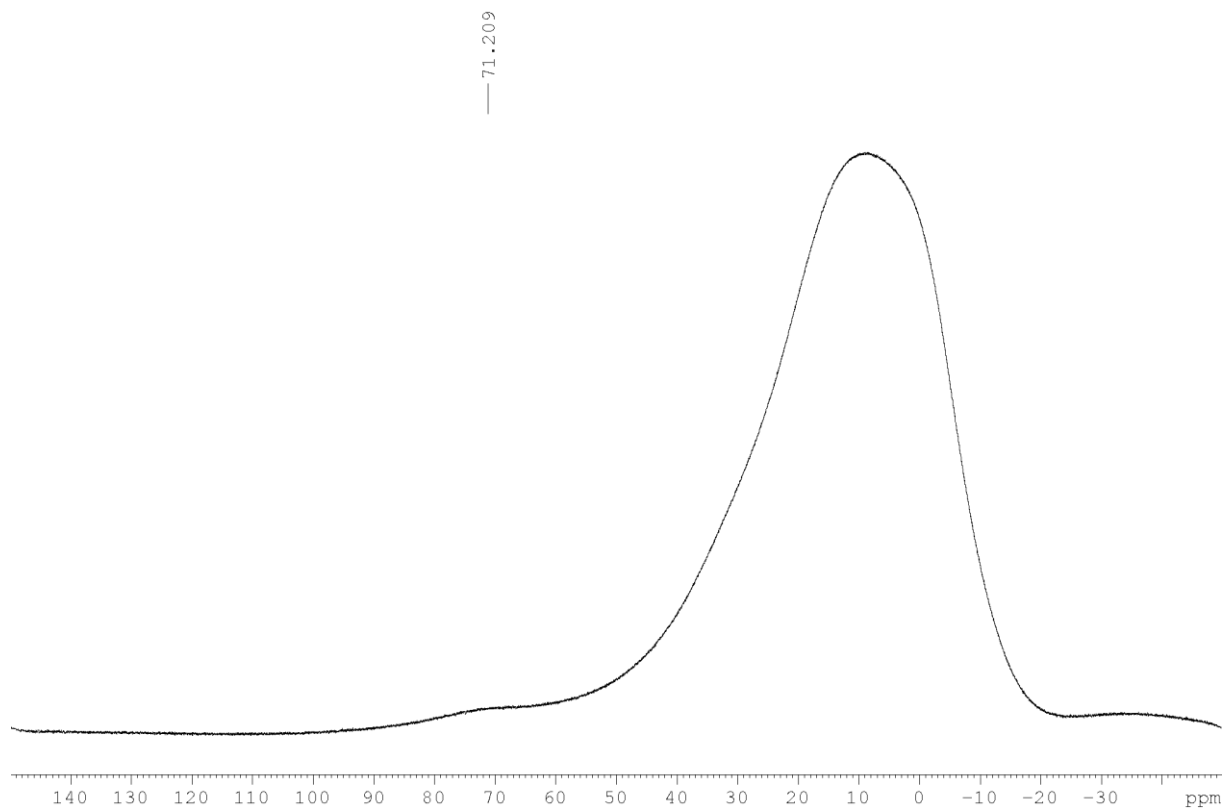
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (96 MHz) of **10** in CDCl_3 . The signal was too weak and could not be observed.



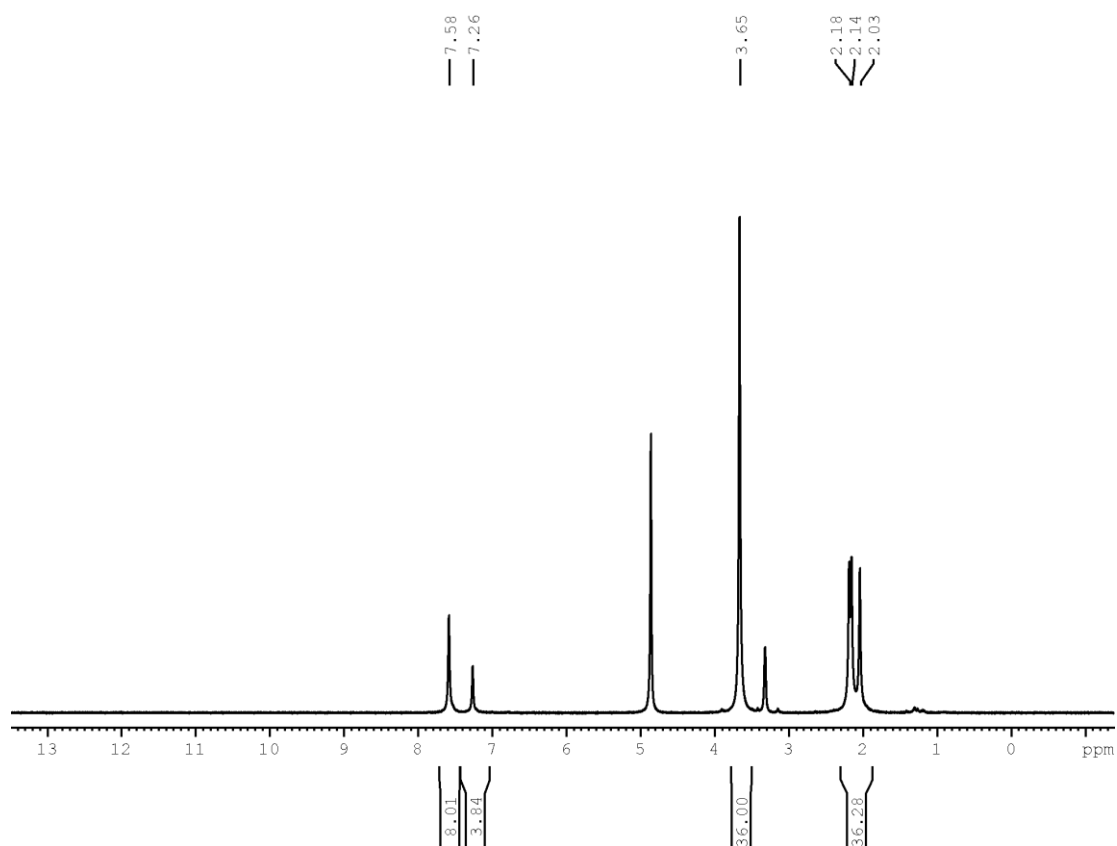
^1H NMR spectrum (500 MHz) of **11** in CD_2Cl_2 .



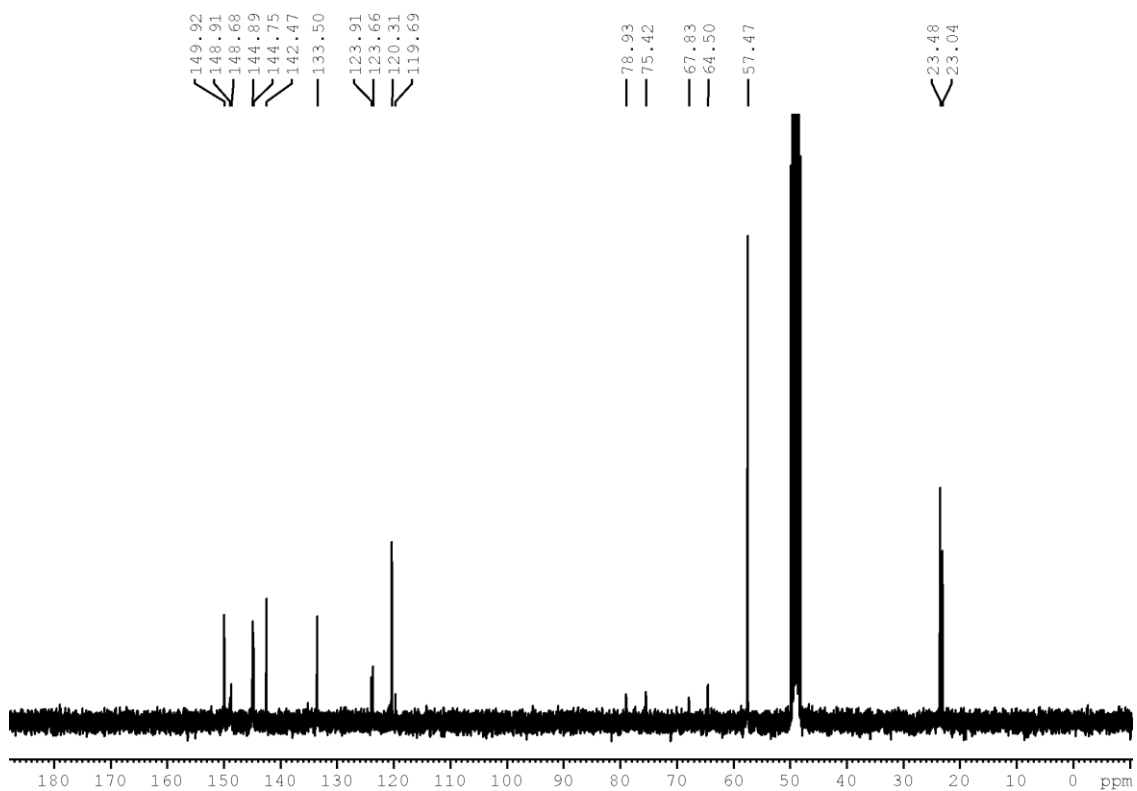
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) of **11** in CD_2Cl_2 .



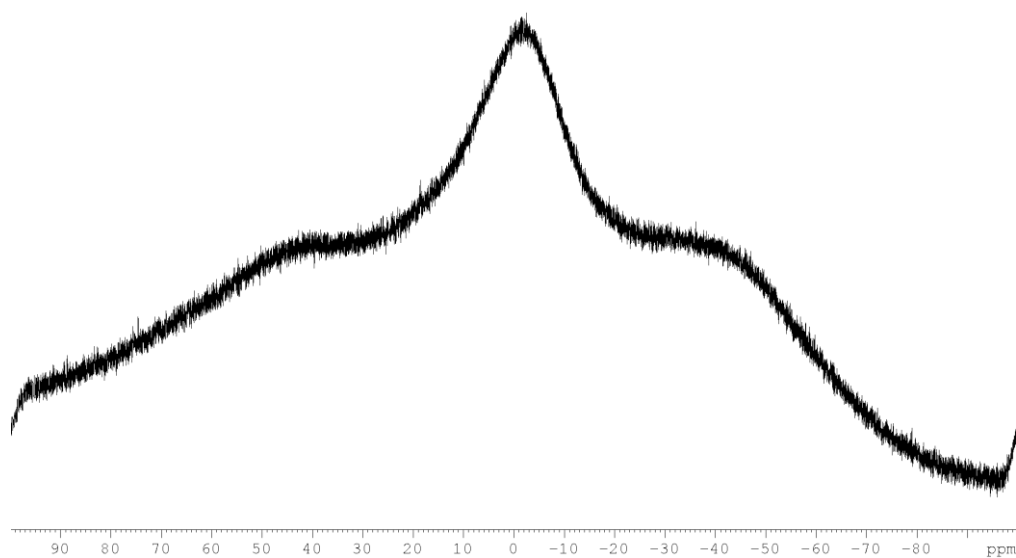
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (192 MHz) of **11** in CDCl_3 .



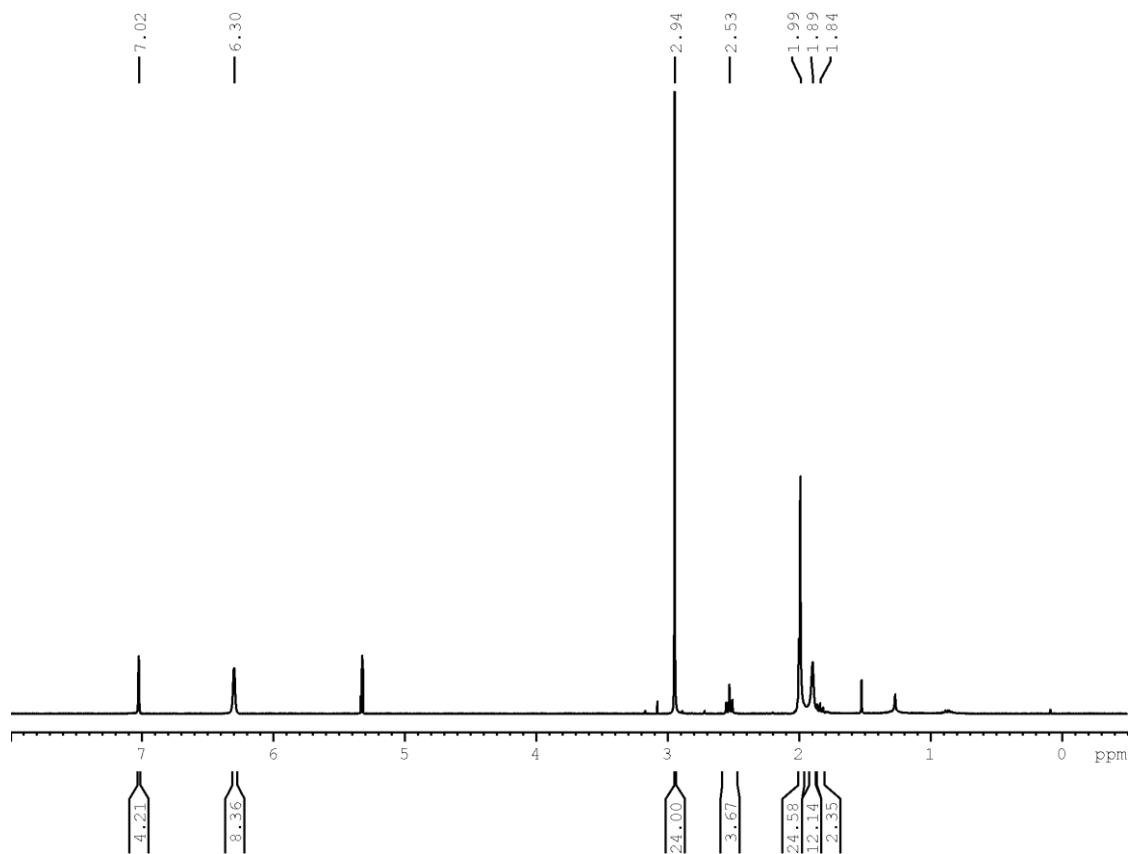
^1H NMR spectrum (300 MHz) of **12** in MeOD.



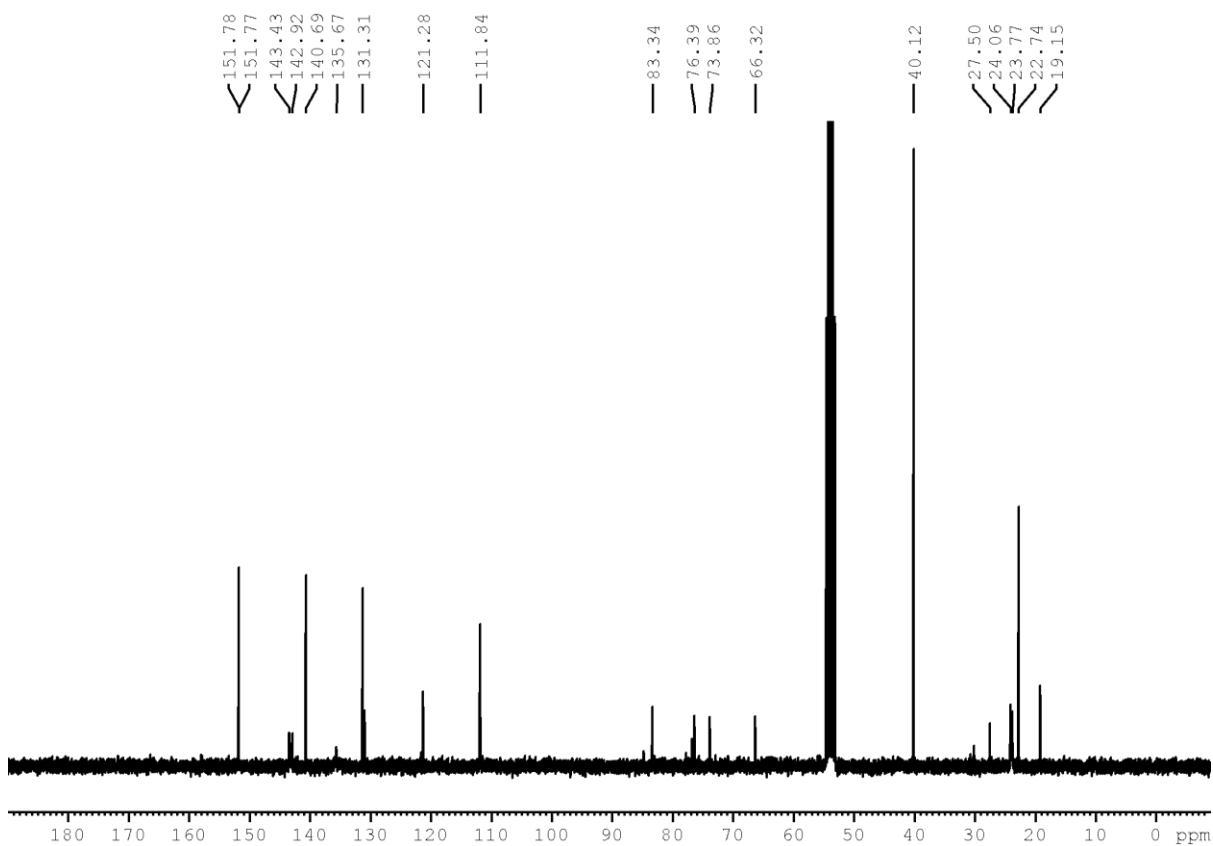
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz) of **12** in MeOD.



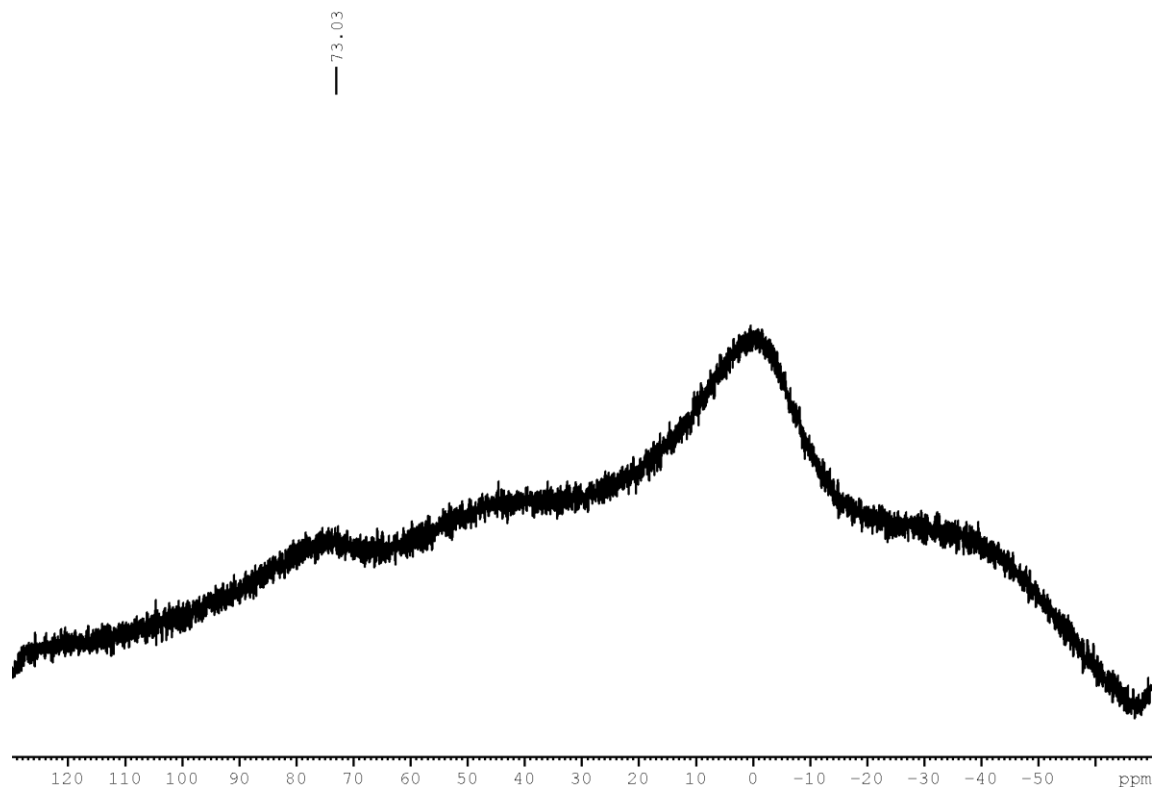
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (96 MHz) of **12** in MeOD. The signal was too weak and could not be observed.



^1H NMR spectrum (300 MHz) of **13** in CD_2Cl_2 .



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz) of **13** in CD_2Cl_2 .



$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (96 MHz) of **13** in CD_2Cl_2 .

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