Supporting Information

Continuous photo-flow synthesis of heterohelicenes

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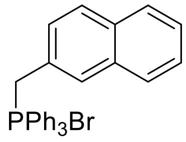
Materials and Methods

Reagents were purchased and used without further purification (unless otherwise stated) from Sigma-Aldrich, Fluorochem, Apollo, Thermo-Fisher or TCI. Copper powder (625 mesh, 0.50-1.5 micron, 99% (metals basis)) was purchased from Thermo-Fisher (product number 041205.30). 'Dry' solvents were purchased from Thermo-Fisher in AcroSeal™ packaging. Flash chromatographic purification of products was carried out using Fluochem silica gel (60 Å, 40-63 µm) using a forced flow of eluent at 0.3–0.5 bar pressure. Further purifications were performed on a LaboACE LC-5060 Plus II recycling HPLC with JAIGEL-HR Plus 2 + 2.5HR size exclusion (gel permeation chromatography, GPC) columns in sequence with chloroform or THF as eluents. Thin layer chromatography was performed using Merck pre-coated silica gel GF254and was visualised under UV light (254 nm and 365 nm).[1] The ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated chloroform (purchased from Cambridge Isotope Laboratories) or deuterated THF (purchased from Fluorochem) on Bruker AVANCE III HD at 400 Hz and 101Hz respectively. Chemical shifts (δ) were given in parts per million (ppm) and coupling constants (J) were given in Hertz (Hz). TMS is used as reference for the NMR peaks. Concentration under reduced pressure was performed by rotary evaporation at 25–30 °C at appropriate pressure. Purified compounds were further dried under high vacuum (0.1–0.01 mbar). HRMS was performed on an Waters Synapt G2Si HDMS or in collaboration with NMSF at Swansea University. Photo-flow reactions were performed in air on a Vapourtec E- or R-Series system with a UV-150 photochemical reactor and high-power 150 W LED lamp (365nm) or a 60 W LED lamp (365 nm).

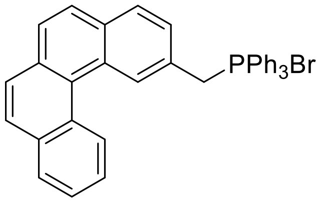
Experimental Data

Table S1 Structures not pictured in main text:

Wittig Salts

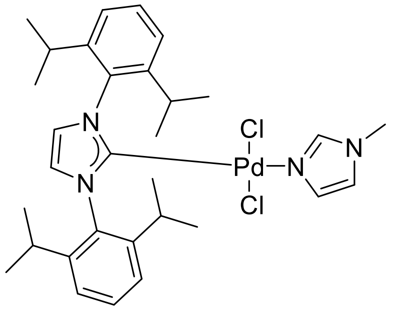


S5a

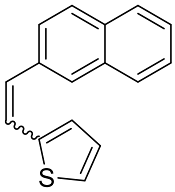


S5b

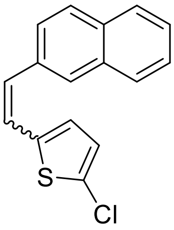
NHC-Pd(II)-Im



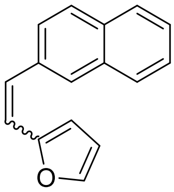
Heterostilbenes and precursors



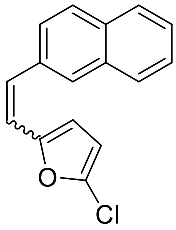
1a



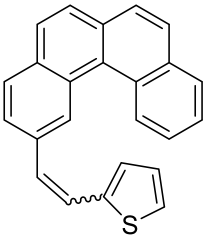
1b



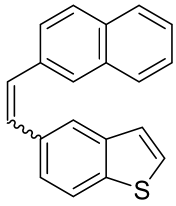
1c



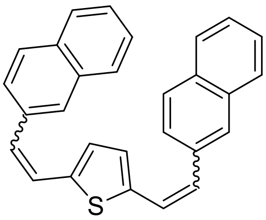
1d



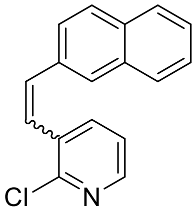
1e



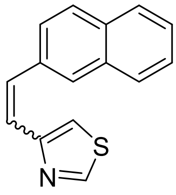
1f



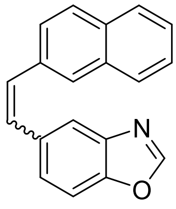
1g



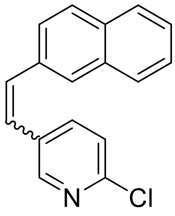
1h



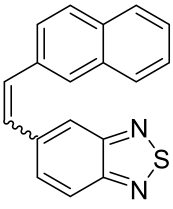
1i



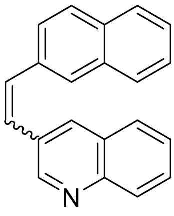
1k



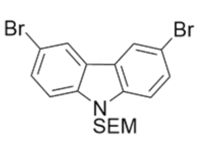
1m



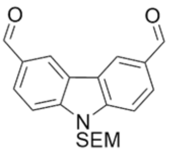
1n



1o

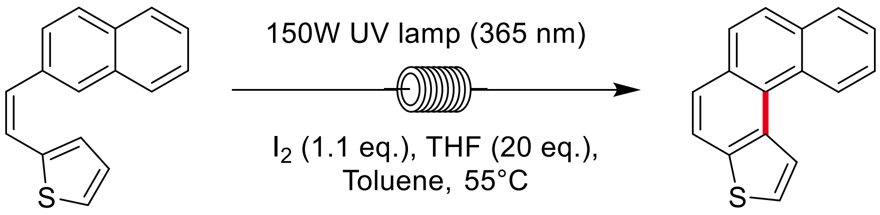


1qa



1qb

Table S2 Optimisation of thia[4]helicene **2a** synthesis:



1a **2a**

Entry	Concentration (mM)	Flow rate (mL/min)	Residence time (s)	Average Peak Integration
1	2	8	75	0.989
2	**2**	**6**	**100**	**0.997**
3	2	5	120	0.965
4	2	4	150	1.010
5	2	3	200	0.951
6	2	2	300	0.914
7	4	6	100	0.955
8	4	2	300	0.874

Optimisation of the Mallory photocyclisation

A stock solution of stilbene **1a** (1.0 equiv), I_2 (1.1 equiv) and THF (20 equiv) was made in Toluene to a concentration of 2 or 4mM. For each test run, 20 mL of stock solution was passed through the Vapourtec E-series flow reactor fitted with a 150 W 365 nm LED lamp at 55 °C with a reactor coil volume of 10 ml. The collected crude mixture was washed with 2 mL each of $Na_2S_2O_3$ (15% in water) and brine. The crude product was dried with $MgSO_4$ and concentrated in vacuo. Trimethoxybenzene (1 equiv) was added to the crude mixture as an internal standard. The proton NMR spectrum was used to determine an approximate yield for the product **2a**.

General Procedures

General procedure A: Synthesis of hetero-stilbenes *via* a Wittig reaction

Wittig salt **S5a** or **S5b** (1.0 equiv) and aldehyde (1.0 equiv) were dissolved in dry MeOH (0.1M) and the reaction solution was sparged by bubbling N_2 through the reaction mixture. KO^tBu (3.0 equiv) was added to the reaction mixture and refluxed for 2 h or until completion (determined by TLC). The mixture was left to cool to room temperature and then was quenched with distilled water (10mL). The crude product was extracted with DCM (3 x 10 ml) and the combined organic layers were washed with brine, dried under $MgSO_4$ (Na_2SO_4 for nitrogen containing compounds) and concentrated in vacuo. The crude product was purified by column chromatography.

General Procedure B: Synthesis of heterohelicenes *via* a Mallory photocyclisation

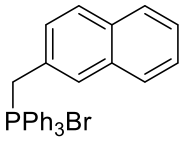
Stilbene (1.0 equiv), I_2 (1.1 equiv) and THF (20 equiv) were dissolved in Toluene or Toluene/MeCN (1:1) to a concentration of 2mM. The reaction was run on the Vapourtec E-series flow reactor fitted with a 150 W 365 nm LED lamp at 55 °C and 6 ml/min with a reactor coil volume of 10 ml. The collected reaction mixture was washed with 10mL each of NaOH (1M) (only for nitrogen-containing compounds), $Na_2S_2O_3$ (15%) and brine. The crude product was dried with $MgSO_4$ or Na_2SO_4 and concentrated in vacuo and purified by column chromatography.

General Procedure C: Synthesis of heterohelicenes *via* a Mallory photocyclisation (catalytic iodine)

Stilbene (1.0 equiv) and I_2 (0.1 equiv) were dissolved in Toluene/THF (9:1). The reaction was run through the Vapourtec E-series flow reactor fitted with a 150 W 365 nm LED lamp at 55 °C and 6 ml/min with a reactor coil length of 10 ml. The collected reaction mixture was washed with 10mL each of NaOH (1M) (only for nitrogen-containing compounds), $Na_2S_2O_3$ (15%) and brine. The crude product was dried with $MgSO_4$ or Na_2SO_4 and concentrated in vacuo and purified by column chromatography.

Synthetic Data

Bromo(naphthalen-2-ylmethyl)triphenyl-λ5-phosphane (**S5a**)

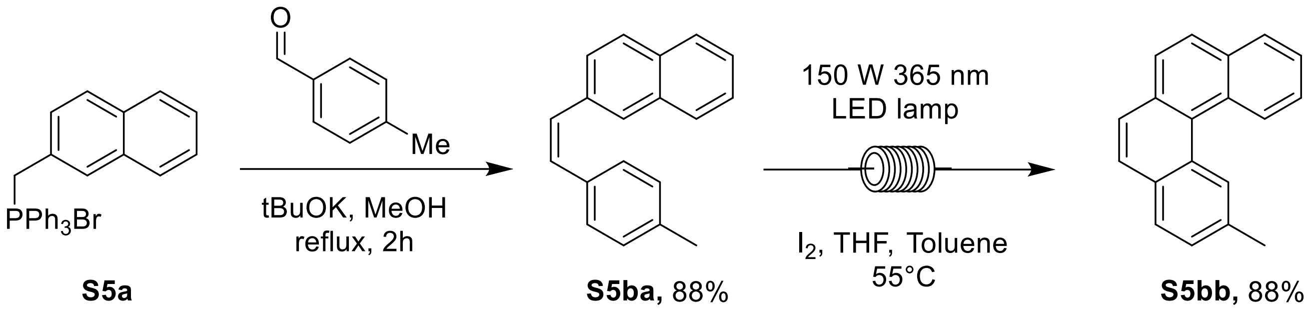


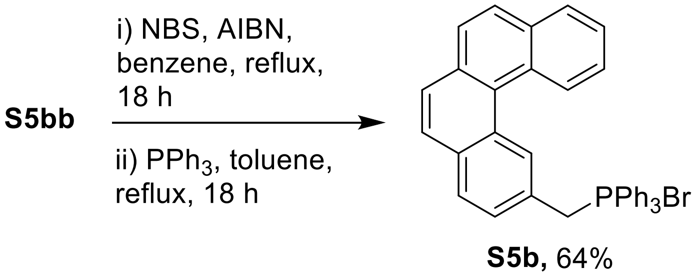
2-(Bromomethyl)naphthalene (22 mmol, 1.0 equiv) and Triphenylphosphine (33 mmol, 1.5 equiv) were dissolved in dry toluene (66mL). The reaction mixture was purged with N_2, then refluxed for 18h. The reaction mixture was left to cool to room temperature and the precipitate was collected by vacuum filtration and washed with toluene to give the product **S5a** as an off-white solid in 90% yield (9.52g, 19.7 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.66 (m, 1H), 7.58 (ddd, *J* = 21.2, 12.8, 6.0 Hz, 1H), 7.45 – 7.35 (m, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 5.62 (d, *J* = 14.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.0 (d, *J* = 3.0 Hz), 134.6 (d, *J* = 9.8 Hz), 133.1 (s), 132.8 (s), 130.2 (d, *J* = 12.5 Hz), 128.8 (d, *J* = 4.3 Hz), 128.5 (s), 128.0 (s), 127.7 (s), 126.7 (s), 126.5 (s), 124.7 (d, *J* = 9.1 Hz), 118.5 (s), 117.7 (s), 31.2 (d, *J* = 46.5 Hz).

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{29}H_{24}BrP$ 483.0877; Found 483.0868.

(Benzo[c]phenanthren-2-ylmethyl)bromotriphenyl- λ5-phosphane (**S5b**)





4-methylbenzaldehyde was subjected to general procedure A on a scale of 10 mmol and purified by column chromatography (Pentane) to give stilbene **S5ba** as a solid in 88% yield (2.15 g, 8.76 mmol). This material was carried forward and subjected to general procedure B and purified by column chromatography (2.5:97.5 EtOAc:Pentane) to give **S5bb** as a solid in 88% yield (1.77g, 7.30 mmol).

[4]-Methylhelicene **S5bb** (1.77g, 7.30 mmol), AIBN (120.0mg, 0.73 mmol) and NBS (1.37g, 7.67 mmol) was dissolved in benzene (70 ml) and refluxed under N_2 for 18h. The reaction mixture was filtered to remove solids, washed with sodium thiosulfate solution and water, dried with sodium sulfate and concentrated *in vacuo*. The unpurified crude was dissolved in dry toluene (20 ml) alongside PPh3 (2.87g, 11.0 mmol), purged with N_2 and refluxed for 18h. The reaction mixture was left to cool to room temperature and the precipitate was collected by vacuum filtration and washed with toluene to give product **S5b** as a light brown solid in 64% yield (2.73 g, 4.68 mmol).

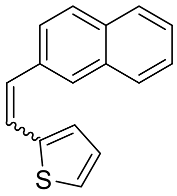
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.60 (s, 1H), 8.33 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.86 – 7.71 (m, J = 13.9, 8.6 Hz, 12H), 7.67 (t, J = 7.4 Hz, 3H), 7.60 – 7.52 (m, J = 11.0, 5.6 Hz, 7H), 7.51 – 7.41 (m, 2H), 5.76 (d, J = 14.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 134.9, 134.9, 134.4, 134.3, 133.2, 132.6, 132.6, 131.1, 130.2, 130.1, 129.8, 129.8, 129.7, 129.0, 129.0, 128.3, 127.7, 127.6, 127.5, 127.0, 126.7, 126.5, 126.5, 125.9, 125.1, 125.0, 118.2, 117.4, 31.3, 30.8.

HRMS (ASAP) m/z: $[M-Br]^+$ calcd. for $C_{37}H_{28}P$ 503.1929; Found 503.1927.

IR (ν_{max}/cm^{-1}): 3038, 2855, 2762, 1439, 1107, 846.

The procedure was adapted from a previous report.[2] Proton NMR spectra of compounds **S5ba**,[3] and **S5bb**[4] matched those reported in literature.

2-(2-(naphthalen-2-yl)vinyl)thiophene (**1a**)



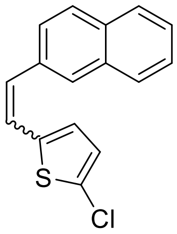
Thiophene-2-carbaldehyde was subjected to general procedure A on a scale of 5 mmol and purified by column chromatography (Pentane) to give product **1a** as a light brown solid in 42% yield (498 mg, 2.11 mmol).

Mixture (1:1.9 E:Z): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.76 (m, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.37 (d, *J* = 16.1 Hz, 1H), 7.23 (d, *J* = 5.1 Hz, 1H), 7.15 – 6.98 (m, 1H), 6.89 (dd, *J* = 4.8, 3.9 Hz, 1H), 6.76 (dd, *J* = 27.4, 12.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.1, 140.0, 135.0, 134.6, 133.9, 133.7, 133.2, 133.0, 131.8, 128.9, 128.6, 128.5, 128.2, 128.1, 128.1, 128.1, 127.9, 127.9, 127.8, 127.0, 126.6, 126.6, 126.5, 126.3, 126.2, 126.2, 126.1, 125.7, 124.6, 123.8, 123.4, 122.3.

HRMS (ES) m/z: $[M+H]^+$ calcd. for $C_{16}H_{13}S$ 237.0738; Found 237.0781.

IR (ν_{max}/cm^{-1}): E/Z mix: 3053 ,3012, 1502, 820, 693.

2-chloro-5-(2-(naphthalen-2-yl)vinyl)thiophene (**1b**)



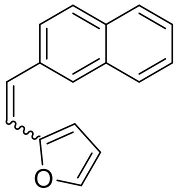
5-Chloro-2-thiophenecarboxaldehyde was subjected to general procedure A on a scale of 10 mmol and purified by column chromatography (Hexane) to product **1b** as a light yellow (*E*) or oily brown (*E*/*Z* mix) solid in 64% yield (1.73 g, 6.39 mmol).

E isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 – 7.75 (m, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.51 – 7.41 (m, 1H), 7.21 (d, *J* = 16.1 Hz, 1H), 6.96 (d, *J* = 16.1 Hz, 1H), 6.85 (dd, *J* = 12.1, 3.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.8, 134.1, 133.7, 133.1, 128.8, 128.6, 128.4, 128.0, 127.7, 126.8, 126.6, 126.5, 126.1, 125.5, 123.1, 121.7.

Mixture (1:1.9 *E*:*Z*): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.77 (m, 1H), 7.65 (d, *J* = 9.7 Hz, 1H), 7.55 – 7.40 (m, 1H), 7.21 (d, *J* = 16.1 Hz, 1H), 6.96 (d, *J* = 16.1 Hz, 1H), 6.85 (dd, *J* = 9.9, 3.8 Hz, 1H), 6.78 (d, *J* = 3.8 Hz, 1H), 6.74 – 6.68 (m, 1H), 6.65 (d, *J* = 11.9 Hz, 1H). **^{13}C NMR (101 MHz, CDCl3)** δ 141.9, 138.7, 134.5, 134.2, 133.8, 133.6, 133.2, 133.0, 130.01, 129.1, 128.9, 128.7, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 126.9, 126.8, 126.7, 126.6, 126.3, 126.2, 125.6, 125.5, 123.6, 123.3, 121.8.

HRMS (ASAP) m/z: $[M]^{+\cdot}$ calcd. for $C_{16}H_{11}ClS$ 270.0270; Found 270.0262.

2-(2-(naphthalen-2-yl)vinyl)furan (**1c**)



Furfural was subjected to general procedure A on a scale of 3.0 mmol and purified by column chromatography (100% Pentane) to give product **1c** as a solid in 83% yield (550.0 mg, 2.50 mmol).

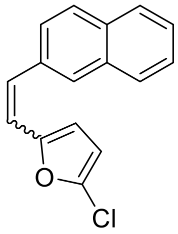
E isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 – 7.77 (m, 1H), 7.67 (dd, J = 8.6, 1.5 Hz, 1H), 7.51 – 7.40 (m, 1H), 7.21 (d, J = 16.2 Hz, 1H), 7.03 (d, J = 16.2 Hz, 1H), 6.49 – 6.36 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.5, 142.4, 134.7, 133.9, 133.2, 128.5, 128.1, 127.8, 127.4, 126.6, 126.5, 126.0, 123.4, 117.0, 111.9, 108.9.

Z isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (s, 1H), 7.85 – 7.77 (m, 3H), 7.58 (dd, J = 8.5, 1.4 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.31 (d, J = 1.2 Hz, 1H), 6.64 (d, J = 12.6 Hz, 1H), 6.46 (d, J = 12.6 Hz, 1H), 6.35 – 6.25 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.3, 141.8, 135.1, 133.5, 132.9, 128.2, 128.1, 127.9, 127.8, 127.6, 127.0, 126.2, 126.1, 118.5, 111.4, 110.3.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{16}H_{13}O$ 221.0966; Found 221.0964.

IR (ν_{max}/cm^{-1}): *E*/*Z* mixture: 3049, 1487, 1152, 954, 820, 738.

2-chloro-5-(2-(naphthalen-2-yl)vinyl)furan (**1d**)



5-Chloro-2-furaldehyde was subjected to general procedure A on a scale of 4.0 mmol and purified by column chromatography (5:95 EtOAc:Pentane) to product **1d** as a grey solid in 69% yield (705 mg, 2.77 mmol).

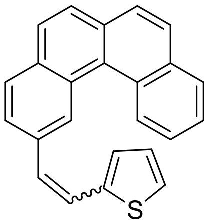
E isomer: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 – 7.76 (m, 4H), 7.64 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.18 (d, *J* = 16.2 Hz, 1H), 6.90 (d, *J* = 16.2 Hz, 1H), 6.35 (d, *J* = 3.3 Hz, 1H), 6.22 (d, *J* = 3.4 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 153.1, 136.3, 134.3, 133.8, 133.2, 128.5, 128.2, 127.9, 127.7, 126.9, 126.6, 126.2, 123.3, 116.0, 110.6, 108.5.

Z isomer: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 (s, 1H), 7.85 – 7.78 (m, 3H), 7.57 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.51 – 7.45 (m, 2H), 6.63 (d, *J* = 12.6 Hz, 1H), 6.40 – 6.33 (m, 1H), 6.23 (d, *J* = 3.4 Hz, 1H), 6.08 (d, *J* = 3.4 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 151.9, 135.6, 134.6, 133.5, 133.0, 131.3, 131.2, 128.6, 128.2, 127.8, 127.8, 127.8, 126.7, 126.3, 126.3, 117.7, 112.0, 108.1.

HRMS (ASAP) m/z: [M]$^{+\cdot}$ calcd. for $C_{16}H_{11}ClO$ 254.0498; Found 254.0495.

IR (ν_{max}/cm^{-1}): E/Z mixture: 3053, 1491, 1014, 950, 906, 783, 731.

2-(2-(benzo[*c*]phenanthren-2-yl)vinyl)thiophene (**1e**)



Thiophene-2-carbaldehyde was subjected to general procedure A (Wittig salt **S5b** was used instead of **S5a**) on a scale of 2.0 mmol and purified by column chromatography (1:99 EtOAc:Hexane) to give product 1e as a solid in 78% yield (525.8 mg, 1.56 mmol).

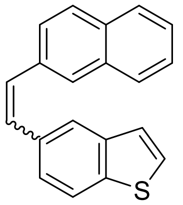
E isomer: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.04 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.81 (t, J = 8.6 Hz, 3H), 7.76 (t, J = 7.7 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.43 (d, J = 16.0 Hz, 1H), 7.25 – 7.19 (m, J = 10.4 Hz, 2H), 7.16 (d, J = 3.1 Hz, 1H), 7.05 (t, J = 4.3 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.14, 134.98, 133.70, 133.2, 131.5, 130.8, 130.5, 129.1, 129.1, 128.8, 128.0, 127.9, 127.8, 127.5, 127.3, 127.0, 127.0, 127.0, 126.5, 126.4, 126.1, 124.7, 123.2, 122.4.

Mixture (1:1.1 *E*:*Z*): **1H NMR (400 MHz, CDCl$_3$)** δ 9.17 (d, J = 8.5 Hz, 1H), 9.13 (s, 1H), 9.12 (s, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.06 (dd, J = 7.9, 1.1 Hz, 1H), 8.01 (dd, J = 8.0, 2.1 Hz, 2H), 7.98 (d, J = 8.4 Hz, 1H), 7.94 – 7.89 (m, 3H), 7.87 (d, J = 8.5 Hz, 1H), 7.85 – 7.75 (m, 6H), 7.71 – 7.65 (m, 2H), 7.63 – 7.59 (m, 1H), 7.55 (ddd, J = 8.3, 7.0, 1.5 Hz, 1H), 7.45 (d, J = 16.0 Hz, 1H), 7.25 (d, J = 21.0 Hz, 2H), 7.17 (d, J = 3.6 Hz, 1H), 7.15 (d, J = 5.1 Hz, 1H), 7.12 (dd, J = 3.6, 0.9 Hz, 1H), 7.08 (dd, J = 5.0, 3.6 Hz, 1H), 6.96 (dd, J = 5.0, 3.6 Hz, 1H), 6.87 (s, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.1, 140.0, 135.4, 134.9, 133.6, 133.5, 133.1, 132.9, 131.5, 131.3, 130.7, 130.6, 130.4, 130.4, 130.0, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 127.0, 127.0, 126.9, 126.8, 126.7, 126.4, 126.4, 126.3, 126.0, 125.9, 125.7, 124.6, 123.8, 123.1, 122.3.

HRMS (ASAP) m/z: [M+H]$^+$ calcd. for $C_{24}H_{16}S$ 337.1051; Found 337.1043.

IR (ν_{max}/cm^{-1}): *E* isomer: 3049, 3012, 1603, 1215, 947, 839, 749, 693. *E*/*Z* mixture: 3049, 3012, 1603, 1215, 947, 839, 745, 693.

5-(2-(naphthalen-2-yl)vinyl)benzo[*b*]thiophene (**1f**)



Benzo[*b*]thiophene-5-carbaldehyde was subjected to general procedure A on a scale of 6.0 mmol and purified by column chromatography (2.5/97.5 EtOAc/Hexane) to give product **1f** as the (*E*) or (*Z*)-isomer in 50% combined yield (856.1 mg, 2.99 mmol).

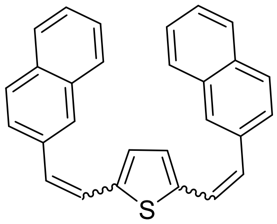
E isomer: **^{1}H NMR (400 MHz, THF)** δ 8.02 (d, J = 1.5 Hz, 1H), 7.92 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.85 – 7.79 (m, 4H), 7.66 (dd, J = 8.5, 1.6 Hz, 1H), 7.57 (d, J = 5.4 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.38 (dd, J = 5.5, 0.6 Hz, 1H). Carbon NMR unable to be obtained due to the insolubility of the sample in all common NMR solvents.

Z isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 – 7.77 (m, 1H), 7.76 – 7.72 (m, J = 5.9, 3.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.43 – 7.38 (m, 1H), 7.30 (dd, J = 8.4, 1.6 Hz, 1H), 7.23 (dd, J = 5.4, 0.6 Hz, 1H), 6.82 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.9, 138.7, 135.1, 133.6, 133.6, 132.7, 130.7, 130.1, 128.2, 128.1, 127.8, 127.6, 127.1, 126.7, 126.2, 126.0, 125.5, 124.1, 122.2.

HRMS (ASAP) m/z: [M]$^{+\cdot}$ calcd. for $C_{20}H_{14}S$ 286.0816; Found 286.0808.

IR (v_{max}/cm^{-1}): *Z* isomer: 3053, 3004, 1502, 1047, 898, 820, 693.

2,5-bis(2-(naphthalen-2-yl)vinyl)thiophene (**1g**)

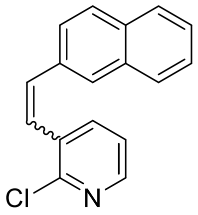


Thiophene-2,5-dicarboxaldehyde was subjected to general procedure A on a scale of 3.0 mmol (Wittig salt **S5a** in excess by 2.5 equiv). Due to the insolubility of the product, after the quench with distilled water, the crude was instead washed with a small quantity of cold methanol and dried under vacuum filtration to give product **1g** as a bright yellow solid in 46% yield (538.1 mg, 1.38 mmol).

EZ:EE Mixture (2:18): **^{1}H NMR (400 MHz, THF)** δ 7.92 (s, 1H), 7.89 (s, 8H), 7.87 – 7.72 (m, 38H), 7.70 – 7.64 (m, 1H), 7.53 (dd, J = 8.5, 1.7 Hz, 1H), 7.49 (s, 4H), 7.48 – 7.36 (m, 24H), 7.32 (d, J = 16.1 Hz, 1H), 7.13 (d, J = 16.1 Hz, 8H), 7.08 (s, 8H), 6.97 (s, J = 4.3 Hz, 2H), 6.90 (d, J = 16.1 Hz, 1H), 6.76 (d, J = 12.0 Hz, 1H), 6.70 (d, J = 11.9 Hz, 1H). Due to the low solubility of **1g**, no suitable ^{13}C-NMR data was obtained.

HRMS (ASAP) m/z: [M+H]$^+$ calcd. for $C_{28}H_{21}S$ 389.1364; Found 389.1357.

2-chloro-3-(2-(naphthalen-2-yl)vinyl)pyridine (**1h**)



2-Chloronicotinaldehyde was subjected to general procedure A on a scale of scale 2 mmol and purified by column chromatography (10:90 EtOAc:Pentane) to give product **1m** as a yellow solid in 85% yield (452 mg, 1.70 mmol).

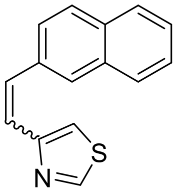
E isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.03 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.91 – 7.80 (m, 4H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.55 (s, 1H), 7.53 – 7.45 (m, 3H), 7.27 (dd, *J* = 15.1, 7.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.4, 148.3, 134.7, 134.1, 133.7, 133.6, 133.5, 132.4, 128.7, 128.3, 127.9, 127.8, 126.7, 126.6, 123.6, 123.6, 122.9.

Z isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.73 – 7.68 (m, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.41 (m, 3H), 7.21 (d, *J* = 9.6 Hz, 1H), 6.98 (dd, *J* = 12.1, 6.8 Hz, 2H), 6.71 (d, *J* = 12.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.0, 148.5, 139.5, 133.5, 133.5, 133.5, 132.9, 132.6, 128.6, 128.2, 128.1, 127.8, 126.6, 126.5, 126.5, 125.7, 122.2.

HRMS (ES) m/z: [M+H]$^+$ calcd. for $C_{17}H_{13}ClN$ 266.0736; Found 266.0749.

IR (ν_{max}/cm^{-1}): *Z* isomer: 3049, 3019, 1554, 1379, 1066, 723.

4-(2-(naphthalen-2-yl)vinyl)thiazole (**1i**)



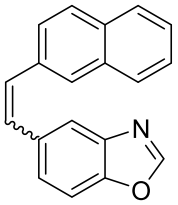
Thiazole-4-carbaldehyde was subjected to general procedure A on a scale of 4.0 mmol and purified by column chromatography (1:9 EtOAc:Hexane) to give product **1i** as a yellow waxy solid (*E*/*Z* mixture) in 84% yield (796.4 mg, 3.36 mmol).

E/Z mixture: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.85 (dd, J = 2.0, 0.5 Hz, 1H), 8.74 (d, J = 2.0 Hz, 2H), 7.90 (s, 1H), 7.86 – 7.73 (m, 12H), 7.70 (d, J = 16.0 Hz, 1H), 7.51 – 7.42 (m, 8H), 7.30 (d, J = 16.0 Hz, 1H), 7.02 (dd, J = 2.0, 0.5 Hz, 2H), 6.91 (d, J = 12.3 Hz, 2H), 6.83 (d, J = 12.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.1, 153.2, 153.1, 151.6, 134.8, 134.5, 133.7, 133.5, 133.3, 132.8, 132.0, 131.8, 128.4, 128.2, 128.1, 127.9, 127.9, 127.8, 127.7, 127.2, 126.8, 126.4, 126.2, 126.2, 126.1, 123.9, 123.6, 121.4, 116.6, 114.9.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{15}H_{11}NS$ 238.0690; Found 238.0693.

IR (ν_{max}/cm^{-1}): *E*/*Z* isomer: 3053, 3012, 1424, 962, 820, 745.

5-(2-(naphthalen-2-yl)vinyl)benzo[*d*]oxazole (**1k**)



Benzo[*d*]oxazole-5-carbaldehyde was subjected to general procedure A on a scale of 6.8 mmol and purified by column chromatography (2:8 EtOAc:Hexane) to give product **1k** as pink solid (*E*) or pink oil (*Z*) in 55% yield (1.02g, 3.77 mmol).

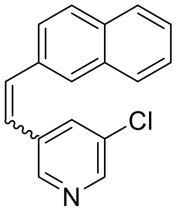
E isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (s, 1H), 7.97 (d, J = 1.5 Hz, 1H), 7.89 (s, 1H), 7.83 (dd, J = 12.2, 4.8 Hz, 3H), 7.77 (dd, J = 8.6, 1.7 Hz, 1H), 7.63 (dd, J = 8.5, 1.7 Hz, 1H), 7.58 (dd, J = 8.5, 0.5 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.33 (dd, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.2, 149.8, 140.9, 134.8, 134.8, 133.9, 133.2, 129.2, 128.6, 128.5, 128.2, 127.9, 126.8, 126.5, 126.1, 124.7, 123.6, 118.4, 111.2.

Z isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (s, 1H), 7.79 – 7.68 (m, 4H), 7.64 (d, J = 8.5 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.40 (d, J = 8.6 Hz, 1H), 7.31 (ddd, J = 8.5, 2.9, 1.7 Hz, 2H), 6.81 (dd, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.0, 149.3, 140.4, 134.6, 134.3, 133.6, 132.7, 130.6, 130.1, 128.2, 128.0, 127.8, 127.8, 127.1, 126.9, 126.2, 126.1, 121.0, 110.7.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{19}H_{14}NO$ 272.1075; Found 272.1067.

IR (ν_{max}/cm^{-1}): Z isomer: 3053, 3008, 1517, 1062, 753. E isomer: 3112, 1510, 1059, 965, 898, 816, 738.

3-chloro-5-(2-(naphthalen-2-yl)vinyl)pyridine (**1m**)



5-Chloronicotinaldehyde was subjected to general procedure A on a scale of 2 mmol and purified by column chromatography (10:90 EtOAc:Pentane) to give product **1m** as a yellow solid in 88% yield (467 mg, 1.76 mmol).

E isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 – 7.80 (m, 5H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.34 (d, *J* = 16.4 Hz, 1H), 7.14 (d, *J* = 16.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.4, 146.4, 134.5, 133.8, 133.7, 133.6, 132.6, 132.4, 132.3, 128.8, 128.3, 127.9, 127.7, 126.8, 126.7, 123.7, 123.4.

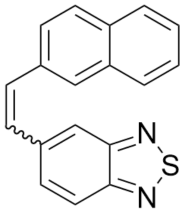
Z isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.41 – 8.34 (m, 2H), 7.83 – 7.76 (m, 1H), 7.76 – 7.68 (m, 3H), 7.56 (s, 1H), 7.47 (dt, *J* = 5.3, 4.0 Hz, 2H), 7.28 (s, *J* = 7.1 Hz, 1H), 6.96 (d, *J* = 12.2 Hz, 1H), 6.57 (d, *J* =

12.2 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 148.1, 147.1, 135.6, 134.4, 134.1, 133.6, 133.6, 133.0, 131.7, 128.4, 128.3, 128.2, 127.9, 126.6, 126.5, 126.3, 125.2.

HRMS (ES) m/z: [M+H]$^+$ calcd. for $C_{17}H_{13}ClN$ 266.0736; Found 266.0749.

IR (v_{max}/cm^{-1}): Z isomer: 3049, 1416, 1103, 1021, 861, 820, 738, 701. E isomer: 3030, 1573, 1424, 1114, 962, 816, 745, 697.

5-(2-(naphthalen-2-yl)vinyl)benzo[*c*][1,2,5]thiadiazole (**1n**)



1n was prepared according to the literature with **S5a** (2.94 g, 6.08 mmol).[5] The crude product was instead purified by column chromatography via 85:15 to 0:100 pentane/DCM elution gradient to afford the E isomer as a yellow solid (913 mg, 3.17 mmol, 52%) and a Z/E-isomeric mixture (7:1) as a yellow solid (504 mg, 1.75 mmol, 29%).

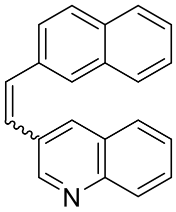
E isomer: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.03 – 7.92 (m, 4H), 7.90 – 7.77 (m, 4H), 7.54 – 7.43 (m, 3H), 7.38 (d, *J* = 16.3 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.8, 154.8, 138.9, 134.2, 133.8, 133.5, 132.0, 128.7, 128.3, 128.1, 127.9, 127.8, 127.6, 126.7, 126.5, 123.5, 121.6, 119.1.

HRMS (ESI$^+$) calculated for $C_{18}H_{13}N_2S$ [M+H]$^+$ 289.0799, found 289.0794.

Z/E isomers (~7:1)**:** **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.03 – 7.93 (m, 0.58H), 7.92 (s, 1H), 7.89 – 7.83 (m, 0.42H), 7.82 – 7.65 (m, 5.07H), 7.52 – 7.40 (m, 3.42H), 7.33 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.98 (d, *J* = 12.2 Hz, 1H), 6.83 (d, *J* = 12.2 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.4, 154.3, 139.2, 134.2, 133.5, 133.0, 133.0, 131.5, 129.2, 128.5, 128.1, 128.1, 127.8, 126.9, 126.5, 126.4, 121.1, 120.7, 77.5, 77.2, 76.8.

HRMS (ESI$^+$) calculated for $C_{18}H_{13}N_2S$ [M+H]$^+$ 289.0799, found 289.0780.

3-(2-(naphthalen-2-yl)vinyl)quinoline (**1o**)



3-Quinoline carboxaldehyde was subjected to general procedure A on a scale of 1.5 mmol and purified by column chromatography (10:90 EtOAc:Pentane) to give product **1o** as a yellow-orange solid in 79% yield (334.9 mg, 1.19 mmol).

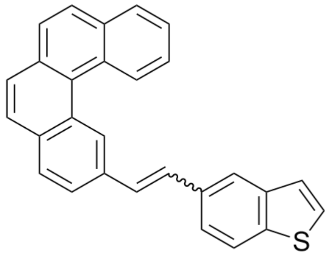
E isomer: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.18 (d, *J* = 1.9 Hz, 1H), 8.21 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.90 – 7.76 (m, 5H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.45 (m, 4H), 7.36 (d, *J* = 16.4 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 149.6, 147.7, 134.4, 133.8, 133.5, 132.4, 131.1, 130.5, 129.5, 129.4, 128.7, 128.3, 128.3, 128.0, 127.9, 127.4, 127.2, 126.7, 126.4, 125.7, 123.4.

Z isomer: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.79 (d, *J* = 1.8 Hz, 1H), 8.07 – 8.01 (m, 2H), 7.79 – 7.75 (m, 2H), 7.73 – 7.69 (m, 1H), 7.69 – 7.62 (m, 3H), 7.51 – 7.41 (m, 3H), 7.34 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 12.2 Hz, 1H), 6.79 (d, *J* = 12.1 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 151.6, 147.1, 135.1, 134.3, 133.7, 133.0, 132.9, 130.6, 129.4, 129.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.0, 126.9, 126.5, 126.4, 126.4.

HRMS (ASAP) m/z: [M+H]$^+$ calcd. for $C_{21}H_{16}N$ 282.1283; Found 282.1276.

IR (v_{max}/cm^{-1}): *Z* isomer: 3049, 3012, 1491, 954, 917, 861, 734.

5-(2-(benzo[*c*]phenanthren-2-yl)vinyl)benzo[*b*]thiophene (**1p**)

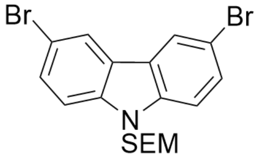


To a solution of S5b (500 mg, 0.857 mmol, 1.00 equiv) and benzo[b]thiophene-5-carbaldehyde (152 mg, 0.937 mmol, 1.09 equiv) in dry MeOH (25 ml), was added KOtBu (288 mg, 2.57 mmol, 2.99 equiv) portion wise under air-free conditions. The reaction mixture was refluxed for 4 hours, followed by subsequent stirring at room temperature overnight. The reaction mixture was quenched with water and the organic layer was extracted with DCM 3 times. The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated *invacuo*. The crude product was purified by column chromatography via 100:0 to 95:5 hexane/EtOAc elution gradient to afford **1p** as afforded as a pale yellow solid (221 mg) containing 5 mol% benzo[b]thiophene-5-carbaldehyde, 4 mol% MeOH and 8 mol% toluene. The corrected quantity of product was 211 mg (0.545 mmol, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 – 9.17 (m, 1H), 8.96 (s, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.07 – 8.00 (m, 4.35H), 7.96 – 7.87 (m, 8.95H), 7.87 – 7.73 (m, 9.65H), 7.70 – 7.64 (m, 2.91H), 7.57 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.51 – 7.37 (m, 9.03H), 7.29 (dd, *J* = 5.4, 0.6 Hz, 1H), 6.91 (s, 2H), 6.73 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 140.2, 139.2, 138.8, 135.5, 135.4, 134.0, 133.9, 133.7, 133.5, 133.2, 132.6, 131.5, 131.3, 131.0, 130.8, 130.5, 130.4, 130.2, 129.5, 129.2, 129.1, 129.1, 128.8, 128.7, 128.5, 128.4, 128.0, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 127.3, 127.2, 127.0, 127.0, 127.0, 126.8, 126.4, 126.0, 126.0, 125.9, 125.9, 124.2, 124.2, 124.2, 123.4, 122.8, 122.8, 122.6, 122.2.

HRMS (APCI$^+$) calculated for $C_{28}H_{19}S$ $[M+H]^+$ 387.1207, found 387.1192.

3,6-dibromo-9-((2-(trimethylsilyl)ethoxy)methyl)-9*H*-carbazole (**1qa**)

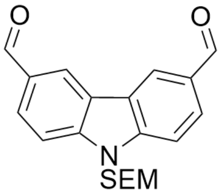


To a solution of 3,6-dibromocarbazole (3.20 g, 9.85 mmol, 1.00 equiv) in DMF (10 ml), was added sodium hydride (60 wt% in mineral oil) (1.20 g, 30.0 mmol, 3.00 equiv) under anhydrous conditions and stirred at room temperature for 20 minutes. SEM-Cl (3.50 ml, 19.8 mmol, 2.00 equiv) was added dropwise and stirred overnight at room temperature. The reaction mixture was quenched with distilled water and the crude product was extracted with DCM three times. The combined organic layers were washed with brine, dried under Na_2SO_4. The crude product was purified by column chromatography via 100:0 to 20:1 hexane/EtOAc elution gradient to afford **1qa** as a white solid (2.75 g) containing 30 mol% SEM-Cl. The corrected quantity of product is 2.48 g (5.45 mmol, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 1.9, 0.4 Hz, 2H), 7.56 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 5.62 (s, 2H), 3.52 – 3.46 (m, 2H), 0.91 – 0.84 (m, 2H), -0.10 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.7, 129.5, 124.1, 123.4, 113.2, 111.1, 72.7, 66.4, 17.9, -1.3.

HRMS (APCI$^+$) calculated for C18H21Br2NOSi $[M]^+$ 452.9759, found 452.9740.

9-((2-(trimethylsilyl)ethoxy)methyl)-9*H*-carbazole-3,6-dicarbaldehyde (**1qb**)

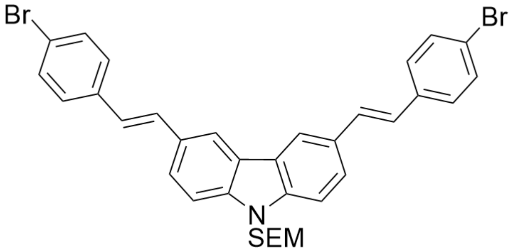


To a solution of **1qa** (4.00 g, 8.79 mmol, 1.00 equiv) in THF (50 ml), was added n-BuLi in hexanes (1.6 M, 13.8 ml, 22.1 mmol, 2.50 equiv) dropwise at – 78 °C under anhydrous conditions and stirred for 1 hour. DMF (4.0 ml) was added dropwise to the reaction mixture at – 78 °C and stirred for 1 hour at – 78 °C, followed 2 hours at room temperature. The reaction mixture was quenched with distilled water and the crude product was extracted with DCM three times. The combined organic layers were washed with brine, dried under Na_2SO_4. The crude product was purified by column chromatography via 8:2 to 7:3 hexane/EtOAc elution gradient to afford **1qb** as a white solid (2.61 g, 7.38 mmol, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 2H), 8.64 (d, *J* = 1.2 Hz, 2H), 8.08 (dd, *J* = 8.5, 1.6 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 5.77 (s, 2H), 3.61 – 3.55 (m, 2H), 0.94 – 0.88 (m, 2H), -0.10 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.6, 145.0, 130.5, 128.3, 124.1, 123.7, 110.5, 72.9, 66.9, 17.9, -1.4.

HRMS (ESI$^+$) calculated for $C_{20}H_{24}NO_3Si$ $[M+H]^+$ 354.1525, found 354.1522.

3,6-bis((*E*)-4-bromostyryl)-9-((2-(trimethylsilyl)ethoxy)methyl)-9*H*-carbazole (**1q**)

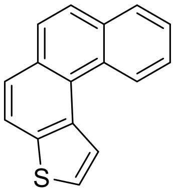


To a solution of diethyl (4-bromobenzyl)phosphonate (2.5 ml, 11 mmol, 3.0 equiv) in THF (30 ml), was added sodium hydride (60 wt% in mineral oil) (500 mg, 12.5 mmol, 3.30 equiv) under air-free and anhydrous conditions and stirred for 40 min at 45 °C. To the reaction mixture was added **1qb** (1.33 g, 3.76 mmol, 1.00 equiv) in THF (20 ml) at room temperature. The reaction mixture was heated under reflux overnight. The reaction mixture was quenched with distilled water and the crude product was extracted with DCM three times. The combined organic layers were washed with brine, dried under Na_2SO_4. The crude product was purified by column chromatography via 92:8 to 86:14 hexane/EtOAc elution gradient to afford **1q** as a white solid (2.05 g, 3.12 mmol, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.5 Hz, 2H), 7.65 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.53 – 7.46 (m, 6H), 7.45 – 7.38 (m, 4H), 7.28 (d, *J* = 15.7 Hz, 2H), 7.09 (d, *J* = 16.3 Hz, 2H), 5.67 (s, 2H), 3.59 – 3.53 (m, 2H), 0.94 – 0.88 (m, 2H), -0.08 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.1, 136.9, 131.9, 130.2, 129.6, 127.9, 125.5, 125.2, 123.9, 120.9, 118.8, 109.9, 72.7, 66.4, 18.0, -1.3.

HRMS (ESI$^+$) calculated for $C_{34}H_{33}Br_2NOSi$ $[M]^+$ 657.0698, found 657.0698.

Thia[4]helicene (**2a**)

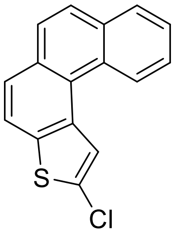


1a was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (Pentane) to give product **2a** as a white solid in 94% yield (44.1 mg, 0.188 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.16 (d, *J* = 8.5 Hz, 1H), 8.65 (d, *J* = 5.6 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.91 – 7.80 (m, 3H), 7.77 – 7.70 (m, 2H), 7.65 (t, *J* = 7.2 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 140.3, 135.1, 133.2, 130.6, 130.6, 128.9, 127.6, 126.8, 126.6, 126.5, 126.5, 126.5, 126.3, 125.8, 125.7, 121.6.

HRMS (ASAP) m/z: [M]$^{+\cdot}$ calcd. for $C_{16}H_{10}S$ 234.0503; Found 234.0479.

2-Chlorothia[4]helicene (**2b**)



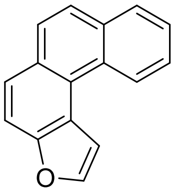
1b was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (Hexane) to give product **2b** as a white solid in 77% yield (41.3 mg, 0.154 mmol). When scaled up to 9.8 mmol, product **2b** was achieved in 79% yield (2.06 g, 7.66 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.95 (d, *J* = 8.4 Hz, 1H), 8.44 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.76 (m, 3H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.2, 134.0, 133.2, 132.1, 130.8, 130.3, 129.0, 127.5, 127.0, 126.7, 126.5, 126.1, 126.0, 125.0, 120.7.

HRMS (ASAP) m/z: [M]$^{+\cdot}$ calcd. for $C_{16}H_9ClS$ 268.0113; Found 268.0105.

IR (ν_{max}/cm^{-1}): 3049, 1510, 1480, 1442, 1163, 906, 734.

Oxa[4]helicene (**2c**)



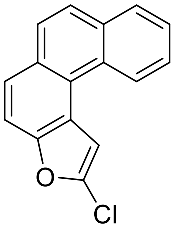
1c was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (2.5:97.5 EtOAc:Hexane) to give product **2c** as a solid in 74% yield (32.2 mg, 0.147 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.03 (d, J = 8.4 Hz, 1H), 8.00 (dd, J = 7.9, 1.4 Hz, 1H), 7.91 (d, J = 2.3 Hz, 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.87 – 7.82 (m, 3H), 7.80 (d, J = 8.7 Hz, 1H), 7.75 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 7.66 (ddd, J = 8.0, 7.0, 1.2 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 154.4, 144.9, 132.9, 130.9, 129.4, 128.9, 127.9, 126.5, 126.3, 126.2, 125.7, 125.5, 125.2, 122.2, 112.4, 108.6.

HRMS (ASAP) m/z: [M+H]$^+$ calcd. for $C_{16}H_{11}O$ 219.0810; Found 219.0814.

IR (ν_{max}/cm^{-1}): 2922, 1327, 1252, 1215, 1144, 835, 738.

2-chlorooxa[4]helicene (**2d**)



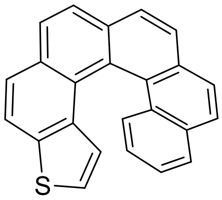
1d was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (100% Hexane) to give product **2d** as a solid in 48% yield (24.2 mg, 0.096 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.83 (d, J = 8.3 Hz, 1H), 8.00 – 7.94 (m, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.79 (t, J = 9.2 Hz, 2H), 7.74 – 7.69 (m, J = 8.4, 6.0, 2.1 Hz, 2H), 7.68 – 7.61 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 153.4, 141.2, 132.9, 130.6, 129.6, 128.9, 127.8, 126.7, 126.5, 126.2, 126.0, 125.2, 124.3, 123.2, 111.6, 105.4.

HRMS (ASAP) m/z: $[M]^{+\cdot}$ calcd. for $C_{16}H_9ClO$ 252.0342; Found 252.0337.

IR (ν_{max}/cm^{-1}): 3049, 1316, 1215, 924, 827, 775, 734.

Thia[6]helicene (**2e**)

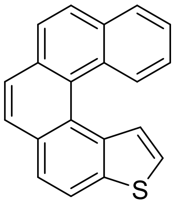


1e was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (1:99 EtOAc:Hexane) to give product **2e** as a pale yellow solid in 71% yield (47.2 mg, 0.141 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (t, J = 8.7 Hz, 1H), 7.98 – 7.89 (m, 3H), 7.87 (d, J = 8.6 Hz, 1H), 7.38 – 7.32 (m, 1H), 6.90 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 6.86 (d, J = 5.6 Hz, 1H), 6.63 (dd, J = 5.6, 0.6 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 138.1, 135.8, 132.8, 131.8, 131.8, 130.8, 130.6, 127.8, 127.8, 127.8, 127.6, 127.4, 127.4, 127.4, 126.9, 126.7, 126.3, 125.9, 125.6, 125.2, 124.7, 124.7, 123.6, 121.8.

HRMS (ES) m/z: $[M+H]^+$ calcd. for $C_{24}H_{15}S$ 335.0894; Found 335.0893.

Thia[5]helicene (**2f**)

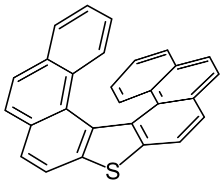


1f was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (2.5:97.5 EtOAc:Hexane) to give product **2f** as a white solid in 56% yield (31.7 mg, 0.111 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.64 (d, J = 8.2 Hz, 1H), 8.09 (dd, J = 8.5, 0.7 Hz, 1H), 8.00 (dd, J = 8.0, 1.2 Hz, 1H), 7.98 – 7.93 (m, J = 8.4, 3.1 Hz, 2H), 7.91 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 5.6 Hz, 1H), 7.58 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 7.44 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.39 (d, J = 5.5 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.3, 136.3, 133.0, 131.9, 131.6, 130.3, 129.1, 127.9, 127.8, 127.7, 127.4, 127.0, 126.5, 126.4, 126.0, 126.0, 125.1, 124.6, 123.6, 121.6.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{20}H_{12}S$ 285.0738; Found 285.0737.

Thia[7]helicene (**2g**)

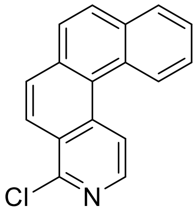


1g was subjected to general procedure B (at a concentration of 0.5 mM) on a scale of 0.2 mmol and purified by column chromatography (5:95 EtOAc/Hexane) to give product **2g** as a yellow solid in 73% yield (55.9 mg, 0.145 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.32 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.6, 131.4, 130.9, 130.2, 129.9, 128.7, 127.6, 126.8, 126.5, 126.5, 126.4, 126.3, 123.7, 121.2.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{28}H_{17}S$ 385.1051; Found 385.1046.

4-chloroaza[4]helicene (**2h**)



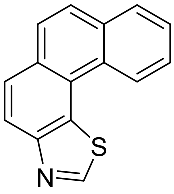
1h was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (10:90 EtOAc/Hexane) to give product **2h** as a white solid in 58% yield (30.7 mg, 0.116 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.99 (d, *J* = 8.4 Hz, 1H), 8.85 (d, *J* = 5.9 Hz, 1H), 8.49 (d, *J* = 5.9 Hz, 1H), 8.44 (d, *J* = 8.8 Hz, 1H), 8.09 – 8.00 (m, 3H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.79 – 7.67 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.2, 142.7, 136.4, 133.8, 133.6, 130.4, 130.2, 129.8, 129.1, 127.5, 127.3, 126.9, 126.6, 126.5, 125.9, 124.3, 120.8.

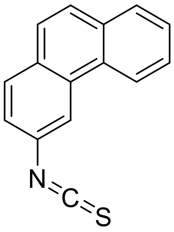
HRMS (ES) m/z: $[M+H]^+$ calcd. for $C_{17}H_{10}ClN$ 264.0580; Found 264.0628.

IR (v_{max}/cm^{-1}): 3053, 1379, 1334, 984, 842, 753.

Thiaza[4]helicene (**2i**)



2i



2i'

1i was subjected to general procedure C on a scale of 0.8 mmol and purified by column chromatography (1:99 EtOAc:Hexane) to give product **2i** as a white solid in 35% yield (66.1 mg, 0.281 mmol) and ring-opened side product **2i'** as a white solid in 26% yield (49.4 mg, 0.210 mmol).

2i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.90 (dd, J = 8.4, 0.6 Hz, 1H), 8.37 (d, J = 8.5 Hz, 1H), 8.05 – 8.00 (m, 2H), 7.90 (q, J = 8.8 Hz, 2H), 7.83 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.70 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.5, 153.1, 132.9, 131.2, 129.4, 129.1, 128.5, 128.3, 127.6, 127.3, 126.7, 126.0, 125.3, 122.9.

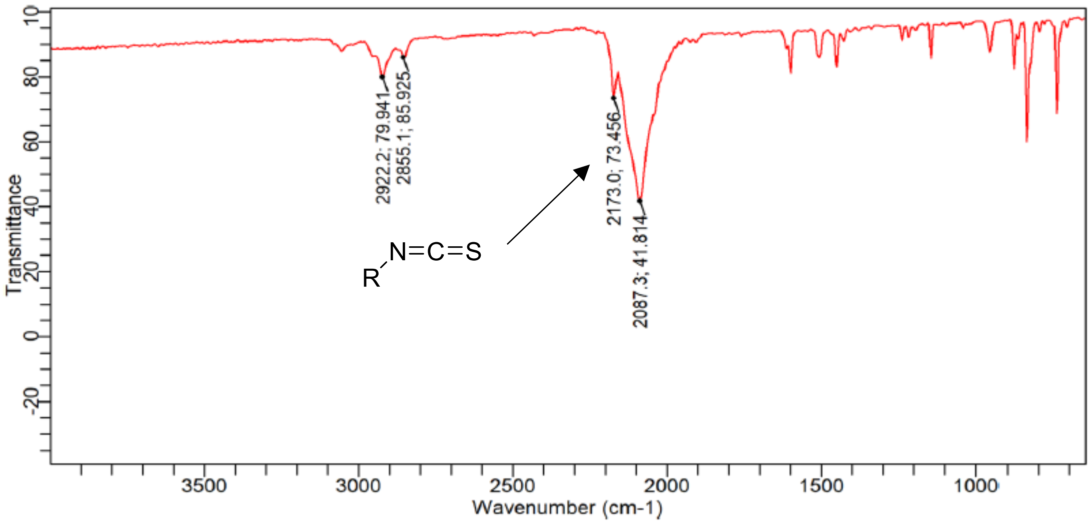
HRMS (ASAP) m/z: $[M]^{+\cdot}$ calcd. for $C_{15}H_9NS$ 235.0456; Found 235.0450.

2i': **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.53 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 1.7 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.71 – 7.61 (m, 3H), 7.41 (dd, J = 8.4, 2.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.6, 132.4, 131.0, 130.8, 130.1, 129.5, 129.4, 128.9, 128.0, 127.6, 127.2, 126.3, 124.2, 122.8, 119.8.

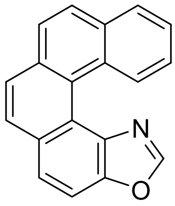
HRMS (ASAP) m/z: $[M]^{+\cdot}$ calcd. for $C_{15}H_9NS$ 235.0456; Found 235.0452.

IR (v_{max}/cm^{-1}): 2922, 2855, 2173, 2087.

The structure of **2i'** was identified by the characteristic strong, broad band at 2087 cm^{-1} and smaller shoulder at 2173 cm^{-1}, which is characteristic of the isothiocyanate group.[6]



Oxaza[5]helicene (**2k**)



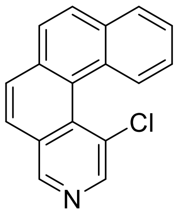
1k was subjected to general procedure C on a scale of 0.2 mmol and purified by column chromatography (1:9 EtOAc:Hexane) to give product **2k** as a beige solid in 40% yield (21.3 mg, 0.079 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.95 (d, J = 8.4 Hz, 1H), 8.22 (s, 1H), 8.07 – 7.97 (m, 4H), 7.90 (d, J = 8.7 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.69 – 7.63 (m, 1H), 7.59 (ddd, J = 8.3, 6.9, 1.5 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 149.6, 148.6, 136.8, 133.2, 132.3, 131.8, 130.5, 130.1, 128.9, 127.8, 127.5, 127.4, 126.8, 126.4, 126.3, 126.2, 124.2, 123.7, 111.1.

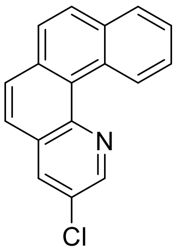
HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{19}H_{12}NO$ 270.0919; Found 270.0922.

IR (ν_{max}/cm^{-1}): 3049, 1417, 1252, 1070, 839.

1-chloroaza[4]helicene (**2m**) and 3-chloroaza[4]helicene (**2m'**)



2m



2m'

1m was subjected to general procedure C on a scale of 0.8 mmol and purified by column chromatography (2.5:97.5 to 2:8 EtOAc/Hexane) to give major product **2m** as a solid in 51% yield (107.7 mg, 0.408 mmol) and minor product **2m'** as a solid in 17% yield (36.8 mg, 0.140 mmol)

2m: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.26 (s, 1H), 8.75 (s, 1H), 8.17 – 8.13 (m, 1H), 8.10 (d, J = 8.5 Hz, 1H), 8.05 – 8.00 (m, 1H), 7.95 (s, 2H), 7.89 – 7.84 (m, 1H), 7.69 – 7.63 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 149.9, 145.6, 134.7, 132.7, 131.4, 131.3, 130.8, 130.0, 128.9, 128.8, 128.7, 127.6, 126.8, 125.6, 125.2, 125.1, 124.4.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{17}H_{11}ClN$ 264.0580; Found 264.0574.

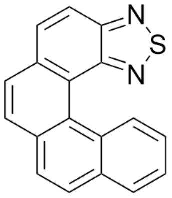
IR (ν_{max}/cm^{-1}): 1379, 1223, 1185, 839, 745, 671.

2m': **^{1}H NMR (400 MHz, CDCl$_3$)** δ 11.03 (dd, J = 8.8, 0.5 Hz, 1H), 9.11 (d, J = 2.6 Hz, 1H), 8.26 (d, J = 2.6 Hz, 1H), 8.02 (dd, J = 11.8, 5.1 Hz, 2H), 7.98 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.83 (ddd, J = 8.7, 6.9, 1.6 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.69 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.3, 146.4, 134.7, 134.1, 133.9, 131.5, 130.6, 130.3, 130.2, 128.7, 128.7, 128.4, 127.6, 126.9, 126.7, 126.5, 125.7.

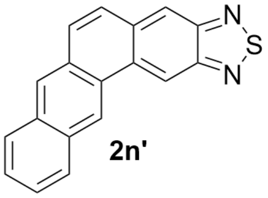
HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{17}H_{11}ClN$ 264.0580; Found 264.0575.

Thiadiazo[5]helicene (**2n**) and tetrapheno[2,3-c][1,2,5]thiadiazole (**2n'**)

A solution of **1n** (E-isomer) (108 mg, 0.375 mmol, 1.0 equiv), I_2 (18 mg, 0.071 mmol, 0.19 equiv), THF (1.8 ml, 22 mmol, 59 equiv) in toluene (360 ml, 1 mM) was pumped through a Vapourtec photoflow reactor (E series, 150 W lamp) at 3.3 ml/min (3 minutes residence time) and 65 °C. The product mixture was concentrated *in vacuo* and the crude product was purified by column chromatography via 9:1 to



2n



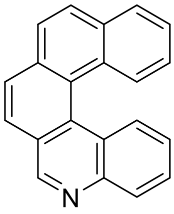
2n'

2:1 pentane/DCM elution gradient to afford helicene **2n** as a yellow solid (58 mg, 0.20 mmol, 54%) and linear product **2n’** as a yellow solid (18 mg, 0.063 mmol, 17%).

2n: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.81 (d, *J* = 8.5 Hz, 1H), 8.09 – 8.01 (m, 3H), 8.00 – 7.93 (m, 3H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 155.1, 153.8, 133.9, 133.6, 133.2, 133.0, 129.9, 129.8, 129.8, 129.1, 128.6, 127.7, 127.6, 127.3, 126.1, 124.0, 123.3, 120.0. Spectral data matched those reported in the literature.[5]

2n’: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 11.03 (s, 1H), 8.52 (s, 1H), 8.35 – 8.30 (m, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.11 – 8.07 (m, 2H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.57 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.5, 153.8, 133.4, 132.9, 132.9, 131.9, 131.3, 131.1, 129.7, 128.3, 128.2, 127.9, 127.1, 126.5, 126.4, 126.1, 122.6, 120.4. Spectral data matched those reported in the literature.[5]

Aza[5]helicene (**2o**)



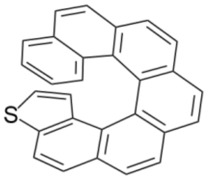
1o (1.0 equiv), I$_2$ (1.1 equiv) and THF (20 equiv) was dissolved in Toluene (100 ml, 2 mM). The reaction was run on the Vapourtec E-series flow reactor fitted with a 60 W 365 nm LED lamp at 40 °C and 6 ml/min with a reactor coil volume of 10 ml. The collected reaction mixture was washed with 10mL each of NaOH (1M), Na$_2$S$_2$O$_3$ (15% in water) and brine. The crude product was concentrated *in vacuo* and purified by column chromatography (1:29:70 Et$_3$N:EtOAc:Hexane) to give product **2o** as a solid in 44% yield (24.5 mg, 0.088 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.40 (s, 1H), 8.61 (d, J = 8.5 Hz, 1H), 8.57 – 8.49 (m, 1H), 8.26 (dd, J = 8.3, 1.1 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.99 – 7.94 (m, 3H), 7.89 – 7.85 (m, 1H), 7.69 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.58 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.34 (dddd, J = 8.4, 6.9, 4.3, 1.4 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 152.7, 145.8, 134.8, 132.9, 130.6, 130.6, 129.6, 129.6, 128.7, 128.7, 128.5, 128.1, 127.8, 127.1, 126.4, 126.3, 126.1, 125.9, 125.0, 125.0, 124.9.

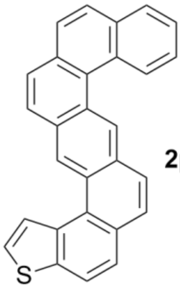
HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{21}H_{14}N$ 280.1126; Found 280.1122.

IR (ν_{max}/cm^{-1}): 1577, 1364, 1122, 1025, 958, 839.

Thia[7]helicene (**2p**) and naphtho[1',2':8,9]tetrapheno[2,1-b]thiophene (**2p’**)



2p



2p'

A solution of the previously reported mixture of **1p** (122 mg) (corrected to 116 mg, 0.301 mmol, 1.00 equiv), I$_2$ (88 mg, 0.347 mmol, 1.15 equiv) and THF (510 uL, 6.3 mmol, 21 equiv) in toluene (160 ml, 1.9 mM) was pumped through a Vapourtec photoflow reactor (E series, 60 W lamp) at 3.3 ml/min (3 minutes residence time) and 80 °C. The product mixture was concentrated *in vacuo* and the crude product was purified by column chromatography via hexane/toluene (9:1) to afford an unseparated mixture of **2p** and **2p'**. The mixture was purified by recycling GPC in chloroform to afford **2p** as a yellow solid (65 mg, 0.17 mmol, 56%) and **2p'** as a yellow solid (21 mg, 0.055 mmol, 18%).

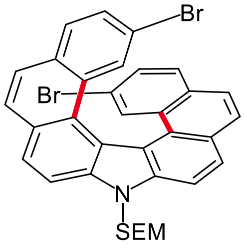
2p: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.09 – 7.98 (m, 5H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.71 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.02 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.55 (d, *J* = 5.6 Hz, 1H), 6.45 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 6.23 (dd, *J* = 5.6, 0.7 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 138.2, 135.6, 132.6, 132.2, 131.8, 130.8, 130.0, 129.4, 128.7, 128.1, 127.7, 127.6, 127.5, 127.1, 126.9, 126.9, 126.8, 126.1, 125.7, 125.5, 125.5, 124.9, 124.8, 124.4, 123.5, 123.5, 123.2, 121.1.

HRMS (APCI$^+$) calculated for $C_{28}H_{17}S$ $[M+H]^+$ 385.1051, found 385.1033.

2p': **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.66 (s, 2H), 9.35 (d, *J* = 8.5 Hz, 1H), 8.85 (d, *J* = 5.5 Hz, 1H), 8.10 – 8.13 (m, 2H), 8.10 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.02 (app. t, *J* = 8.5 Hz, 2H), 7.93 – 7.84 (m, 5H), 7.79 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.69 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 140.3, 135.6, 133.7, 132.0, 131.4, 131.2, 130.6, 130.4, 129.1, 128.9, 128.8, 128.3, 128.1, 127.9, 127.8, 127.7, 127.3, 127.2, 127.2, 127.2, 127.0, 126.8, 126.6, 126.2, 126.0, 125.7, 125.4, 122.0.

HRMS (APCI$^+$) calculated for $C_{28}H_{17}S$ $[M+H]^+$ 385.1051, found 385.1036.

Dibromoaza[7]helicene (**2q**)

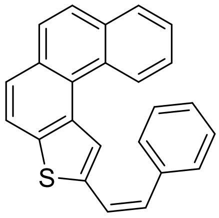


A solution of **1q** (265 mg, 0.400 mmol, 1.00 equiv) and I_2 (55 mg, 0.22 mmol, 0.50 equiv) in toluene/THF (9:1, 100 ml, 4 mM) was pumped through a Vapourtec photoflow reactor (E series, 60 W lamp) at 1 ml/min (10 minutes residence time) and 80 °C. The product mixture was concentrated *in vacuo* and purified by column chromatography via hexane/EtOAc (10:1) to afford **2q** as a yellow solid (187 mg, 0.280 mmol, 71%). The reaction was repeated on a larger (4.28-fold) scale to afford (788 mg, 1.20 mmol, 71% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 – 8.05 (m, 6H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 1.9 Hz, 2H), 7.33 (dd, *J* = 8.5, 2.0 Hz, 2H), 6.12 (s, 2H), 3.71 (dd, *J* = 8.4, 7.8 Hz, 2H), 0.98 (td, *J* = 7.7, 1.7 Hz, 2H), -0.08 (s, 9H). **^{13}C** NMR (101 MHz, CDCl$_3$) δ 139.8, 130.9, 130.8, 130.2, 129.1, 128.6, 127.7, 127.3, 127.3, 125.6, 124.5, 117.1, 116.9, 110.6, 76.8, 72.9, 66.7, 18.0, -1.3.

HRMS (ESI$^+$) calculated for $C_{34}H_{29}Br_2NOSiNa$ $[M+Na]^+$ 676.0283, found 676.0274.

(*Z*)-2-styrylphenanthro[3,4-*b*]thiophene (**3a**)



To a Schlenk tube under N_2 was charged **2b** (806.3 mg, 3 mmol), NHC-Pd(II)-Im (19.4 mg, 1 mol%), Cs_2CO_3 (2.54 g, 7.8 mmol), TBAB (7.95 g, 24.75 mmol) and styrene (0.41 ml, 3.6 mmol). The Schlenk tube was sealed and stirred at 140 °C for 18 h. The resulting mixture was extracted with EtOAc and washed with $HCl_{(aq)}$ and brine, then the organic layers were collected, dried under sodium sulfate and concentrated *in vacuo*. The crude was purified by column chromatography (100% Hexane) to give product **3a** as a yellow solid in 51% yield (518.9 mg, 1.54 mmol).

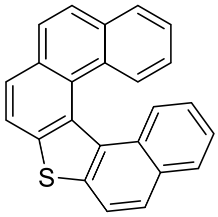
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (dd, J = 8.5, 0.4 Hz, 1H), 8.51 (s, 1H), 7.99 (dd, J = 7.9, 1.4 Hz, 1H), 7.95 (dd, J = 8.4, 0.7 Hz, 1H), 7.80 (dt, J = 8.5, 6.9 Hz, 3H), 7.74 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.66 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.51 (dd, J = 16.0, 0.5 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.35 – 7.29 (m, 1H), 7.10 (d, J = 16.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.2, 139.5, 136.8, 135.5, 133.2, 130.7, 130.7, 130.6, 128.9, 128.8, 128.1, 127.6, 126.7, 126.6, 126.4, 126.4, 126.4, 126.2, 126.2, 125.4, 122.7, 121.3.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{24}H_{17}S$ 337.1051; Found 1041.

IR (ν_{max}/cm^{-1}): 3019, 1592, 1439, 1208, 1144, 827, 738, 686.

Procedure adapted from previous literature.[7]

Thia[6]helicene (**4a**)

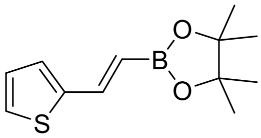


3a was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (5:95 EtOAc:Hexane) to give product **4a** as a yellow solid in 80% yield (46.7 mg, 0.160 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.06 (m, 1H), 8.03 (dt, J = 8.6, 2.0 Hz, 2H), 7.98 (dd, J = 8.1, 0.9 Hz, 2H), 7.94 (ddd, J = 14.0, 8.8, 6.4 Hz, 4H), 7.58 (d, J = 8.5 Hz, 1H), 7.50 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.42 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.04 (dddd, J = 8.4, 7.0, 5.7, 1.3 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.8, 138.8, 132.3, 132.0, 131.5, 131.1, 129.7, 129.6, 129.5, 129.2, 128.3, 128.1, 128.1, 127.8, 127.5, 126.8, 126.7, 126.7, 126.5, 125.0, 124.8, 124.8, 121.2, 121.0.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{24}H_{15}S$ 335.0894; Found 335.0892.

(*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane



A Schlenk tube with a stirrer bar was charged with B_2Pin_2 (1.27 g, 5.0 mmol, 1.0 equiv), -625 mesh copper powder (31.8 mg, 10 mol%) and NaOMe (135.1 mg, 2.5 mmol, 0.5 equiv). The vessel was evacuated under vacuum and refilled with N_2 three times. EtOH (20 mL) was sparged with N_2 and added to the vessel, followed by 2-ethynylthiophene (0.47 mL, 5.0 mmol, 1.0 equiv). The Schlenk tube was sealed and stirred at 40 °C for 24 h. The reaction was diluted with water (10 mL) and the crude was extracted with DCM (2 x 20 mL). The combined organic layers were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (Hexane) to give the title compound as a brown in 45% yield (530.5 mg, 2.25 mmol).

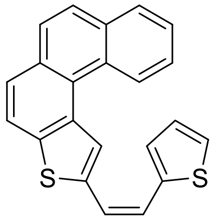
1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 18.1 Hz, 1H), 7.24 (dt, J = 5.0, 0.8 Hz, 1H), 7.09 – 7.07 (m, 1H), 6.99 (dd, J = 5.1, 3.6 Hz, 1H), 5.91 (d, J = 18.1 Hz, 1H), 1.30 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.0, 141.9, 127.8, 127.7, 126.4, 83.4, 24.9.

HRMS (ASAP) m/z: $[M]^{+\cdot}$ calcd. for $C_{12}H_{17}BO_2S$ 235.1079; Found 235.1083.

IR (ν_{max}/cm^{-1}): 2974, 1614, 1372, 1319, 1141.

Procedure adapted from previous literature.[8]

2-(2-(thiophen-2-yl)vinyl)phenanthro[3,4-*b*]thiophene (**3b**)



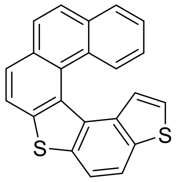
A Schlenk tube with a stirrer bar was charged with $Pd(OAc)_2$ (16.8 mg, 5 mol%), XPhos (42.9 mg, 6 mol%), **2b** (403.1 mg, 1.5 mmol, 1.0 equiv) and (*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (425.0 mg, 1.8 mmol, 1.2 equiv). The vessel was evacuated under vacuum and refilled with N_2 three times. Nitrogen sparged *n*-BuOH (8.4 mL) was added to the reaction vessel and the reaction was pre-stirred at room temperature for 15 mins. CsOH $\cdot H_2O$ (0.25 mL, 1.68 equiv, 50 wt.% in water) was added to the reaction vessel. The Schlenk tube was sealed and stirred at 45 °C for 18 h. The reaction was diluted with water (10 mL) and extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, concentrated *in vacuo*, purified by column chromatography (5:95 EtOAc:Hexane) and triturated in Et_2O and hexane to give **3b** as a yellow solid in 80% yield (408.7 mg, 1.19 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, J = 8.5 Hz, 1H), 8.49 (s, 1H), 7.98 (dd, J = 7.9, 1.4 Hz, 1H), 7.95 (dd, J = 8.4, 0.7 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.79 (d, J = 8.5 Hz, 1H), 7.74 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.65 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.33 (d, J = 15.7 Hz, 1H), 7.26 (d, J = 5.0 Hz, 1H), 7.22 (d, J = 15.8 Hz, 1H), 7.14 (d, J = 3.5 Hz, 1H), 7.05 (dd, J = 5.1, 3.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.7, 142.3, 139.5, 135.6, 133.2, 130.8, 130.6, 128.9, 128.0, 127.6, 126.9, 126.6, 126.5, 126.5, 126.4, 126.3, 126.3, 125.3, 125.2, 123.8, 122.3, 121.3.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{22}H_{15}S_2$ 343.0615; Found 343.0608.

IR (ν_{max}/cm^{-1}): 3008, 1442, 1401, 1338, 1077, 1044.

Dithia[6]helicene (**4b**)



3b was subjected to general procedure B on a scale of 0.2 mmol and purified by column chromatography (5:95 EtOAc:Hexane) to give product **4b** as a yellow solid in 87% yield (59.4 mg, 0.174 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, J = 8.4, 0.4 Hz, 1H), 8.05 – 8.01 (m, 2H), 8.00 – 7.95 (m, 2H), 7.93 – 7.89 (m, 3H), 7.55 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.23 – 7.16 (m, 2H), 6.72 (d, J = 5.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.8, 137.3, 137.2, 135.1, 132.4, 132.1, 130.9, 129.5, 129.5, 128.9, 128.0, 127.5, 127.1, 126.9, 126.7, 126.7, 126.5, 125.0, 124.1, 121.2, 121.1, 119.2.

HRMS (ASAP) m/z: $[M+H]^+$ calcd. for $C_{22}H_{13}S_2$ 341.0459; Found 341.0449.

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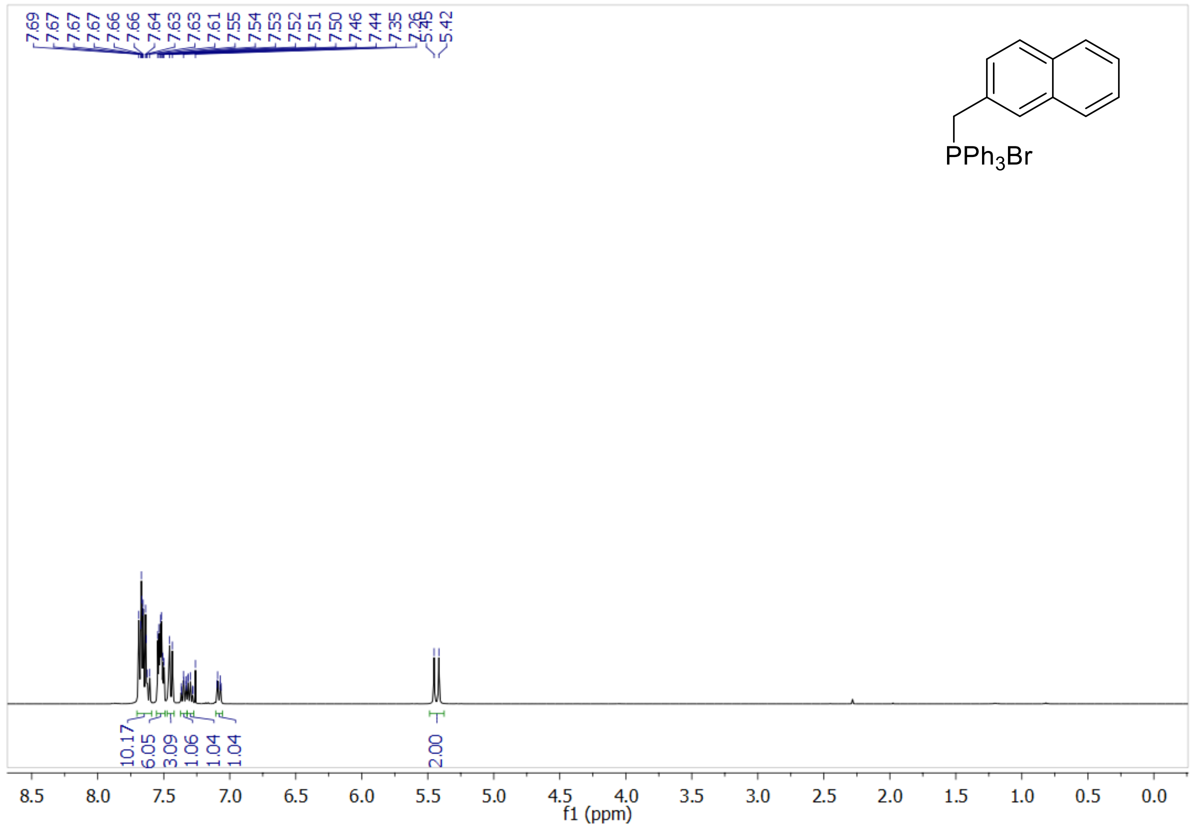
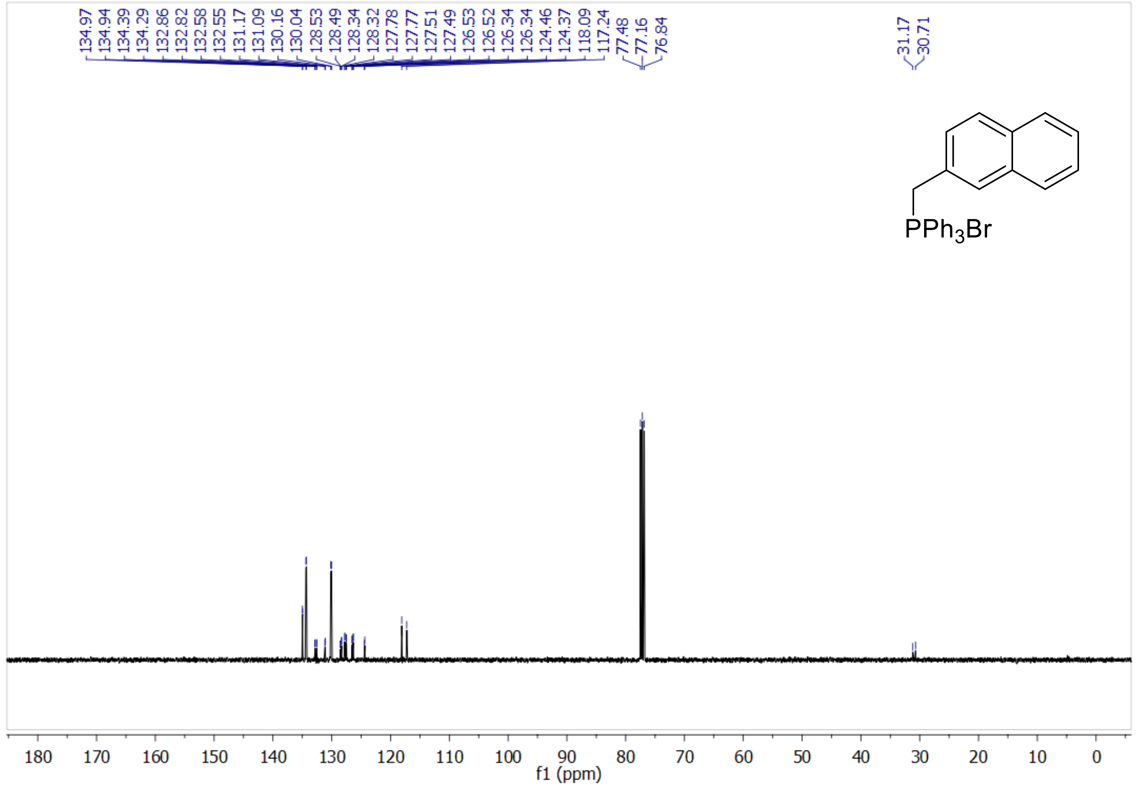
NMR spectra

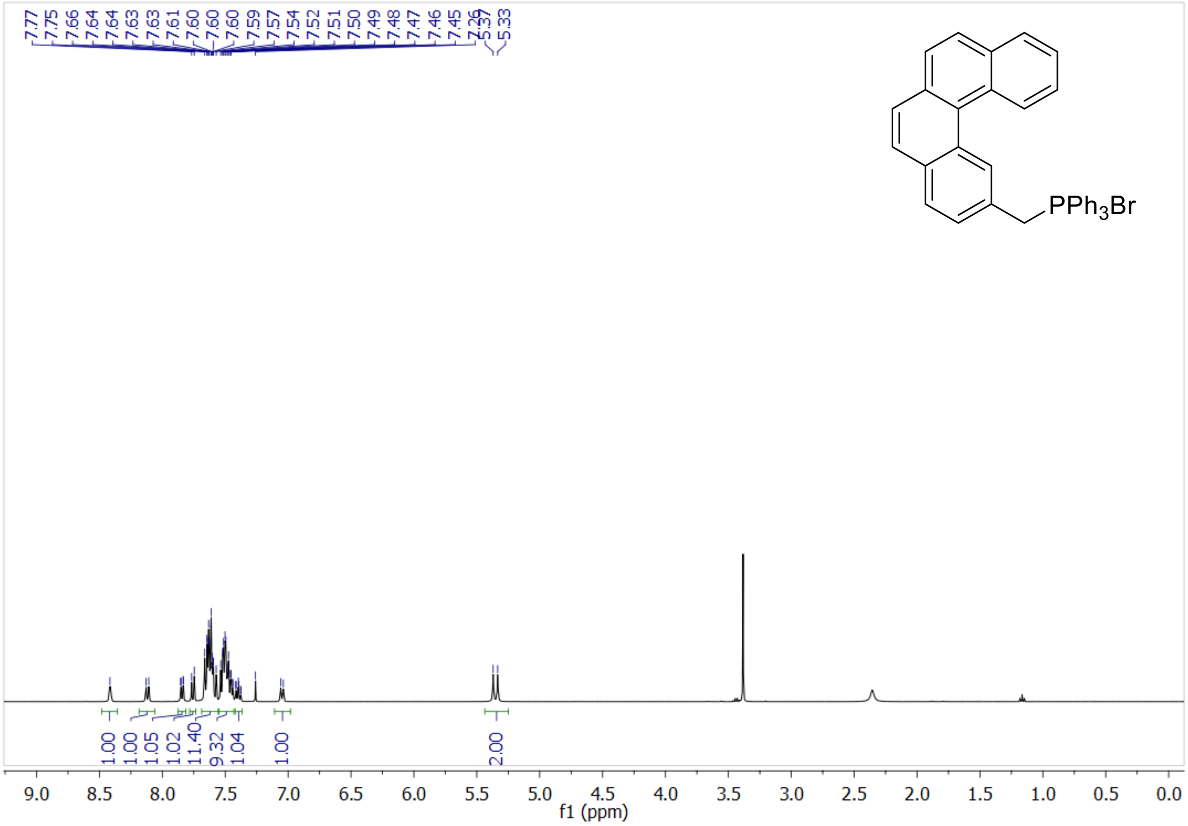
*^{1}H-NMR of Bromo(naphthalen-2-ylmethyl)triphenyl-λ5-phosphane (**S5a**)*



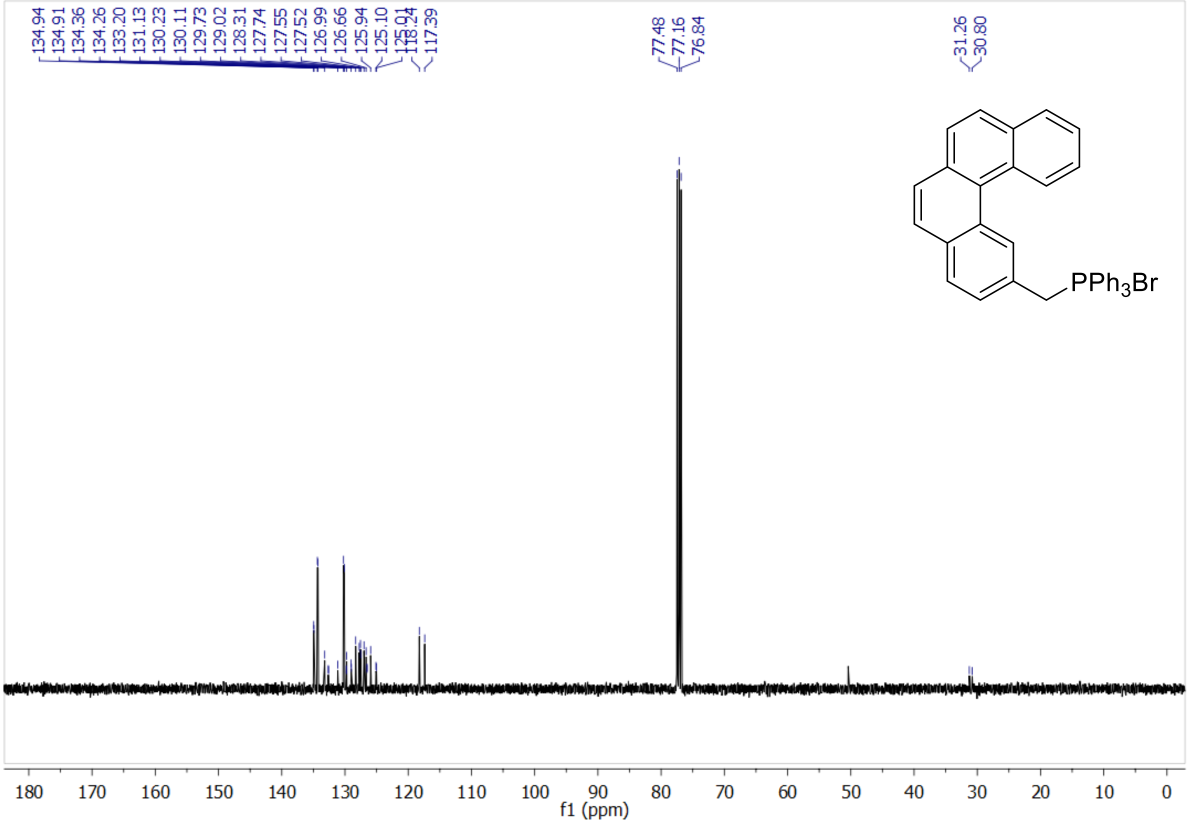
^{13}C-NMR of Bromo(naphthalen-2-ylmethyl)triphenyl-λ5-phosphane (S5a)



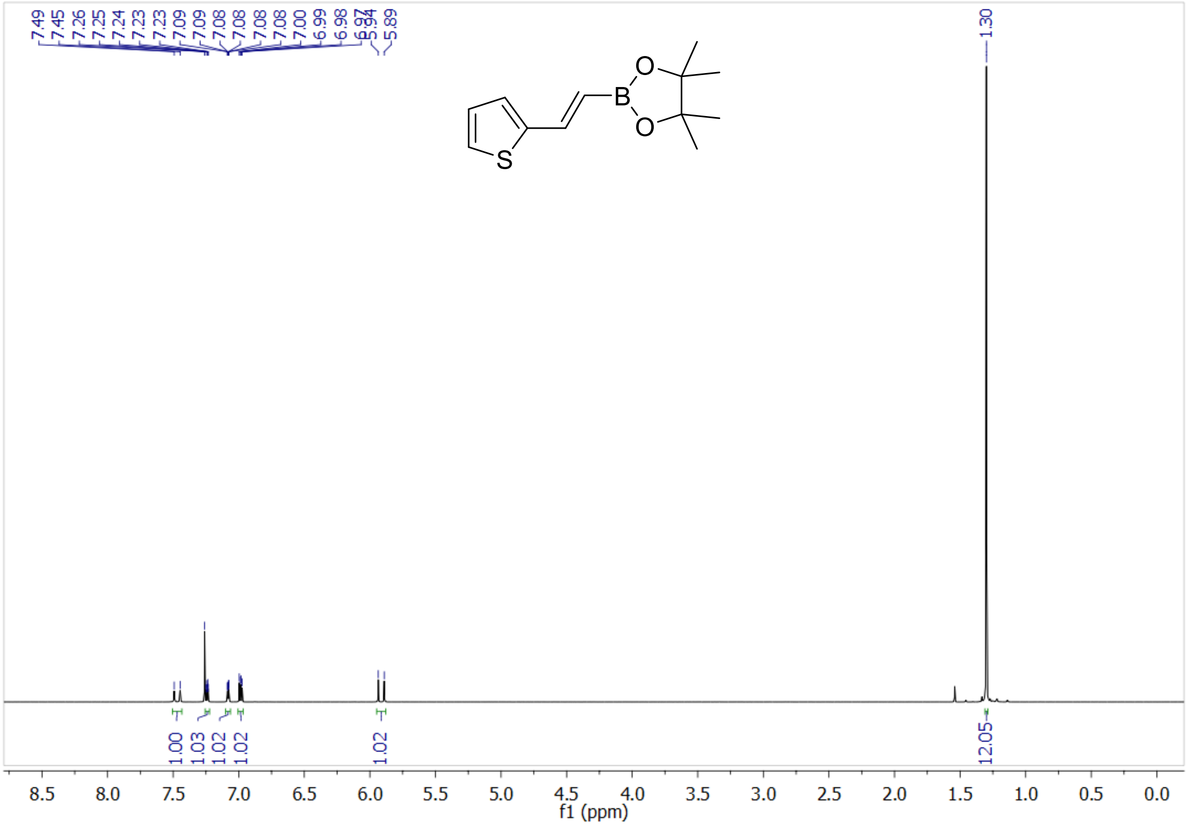
*^{1}H-NMR of (Benzo[c]phenanthren-2-ylmethyl)bromotriphenyl- λ5-phosphane (**S5b**)*



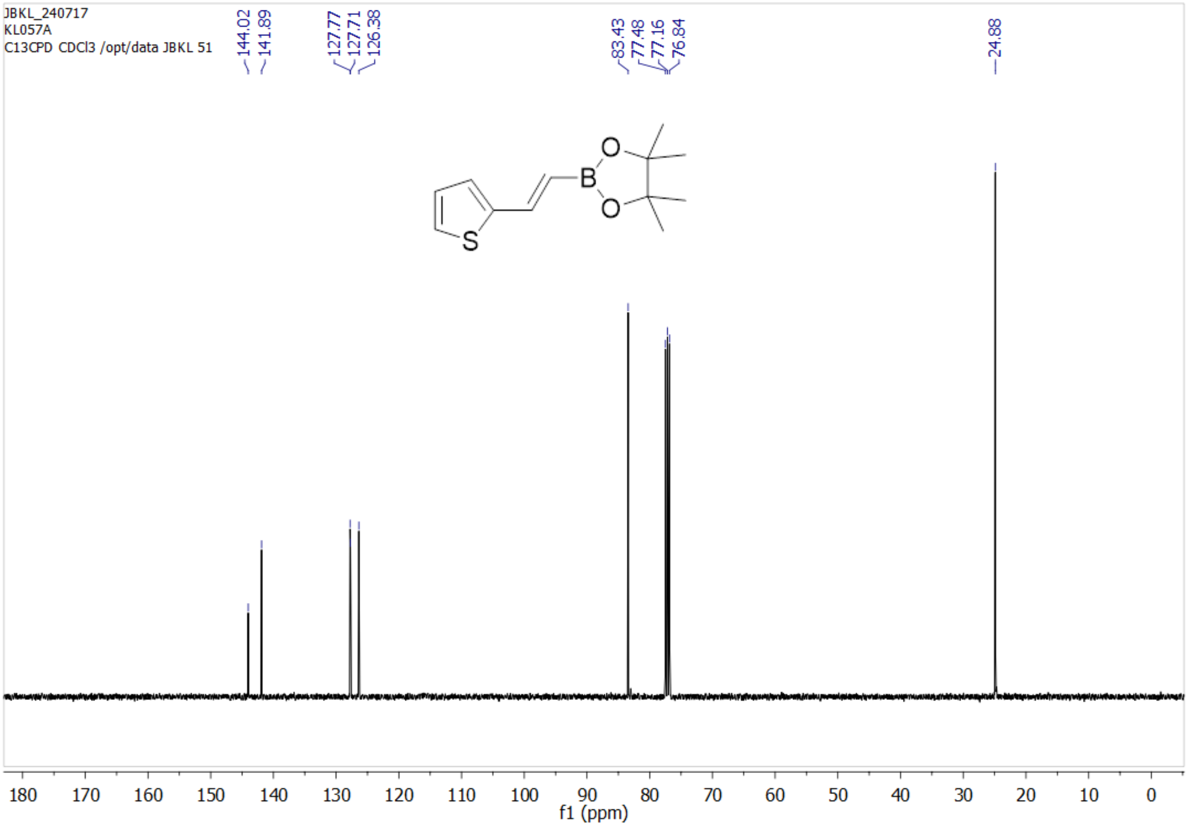
*^{13}C-NMR of (Benzo[c]phenanthren-2-ylmethyl)bromotriphenyl- λ5-phosphane (**S5b**)*



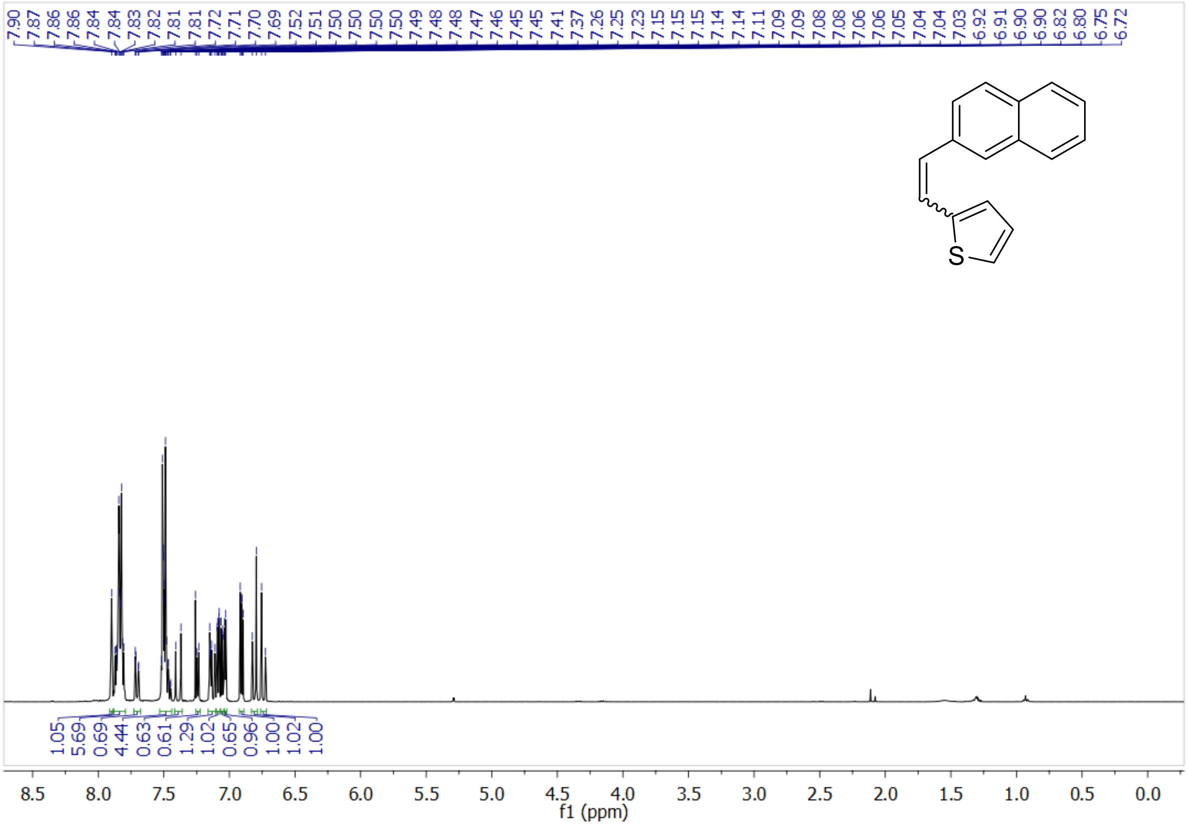
^{1}H-NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane



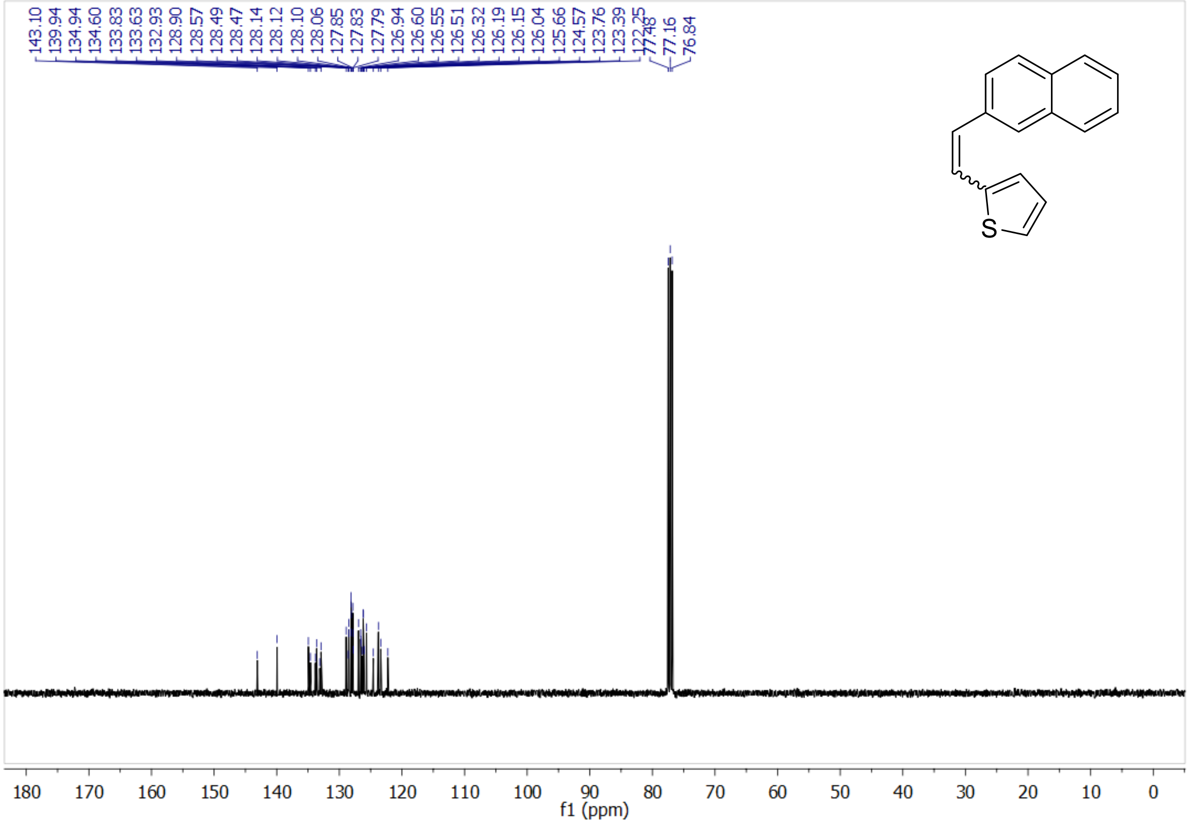
^{13}C-NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane



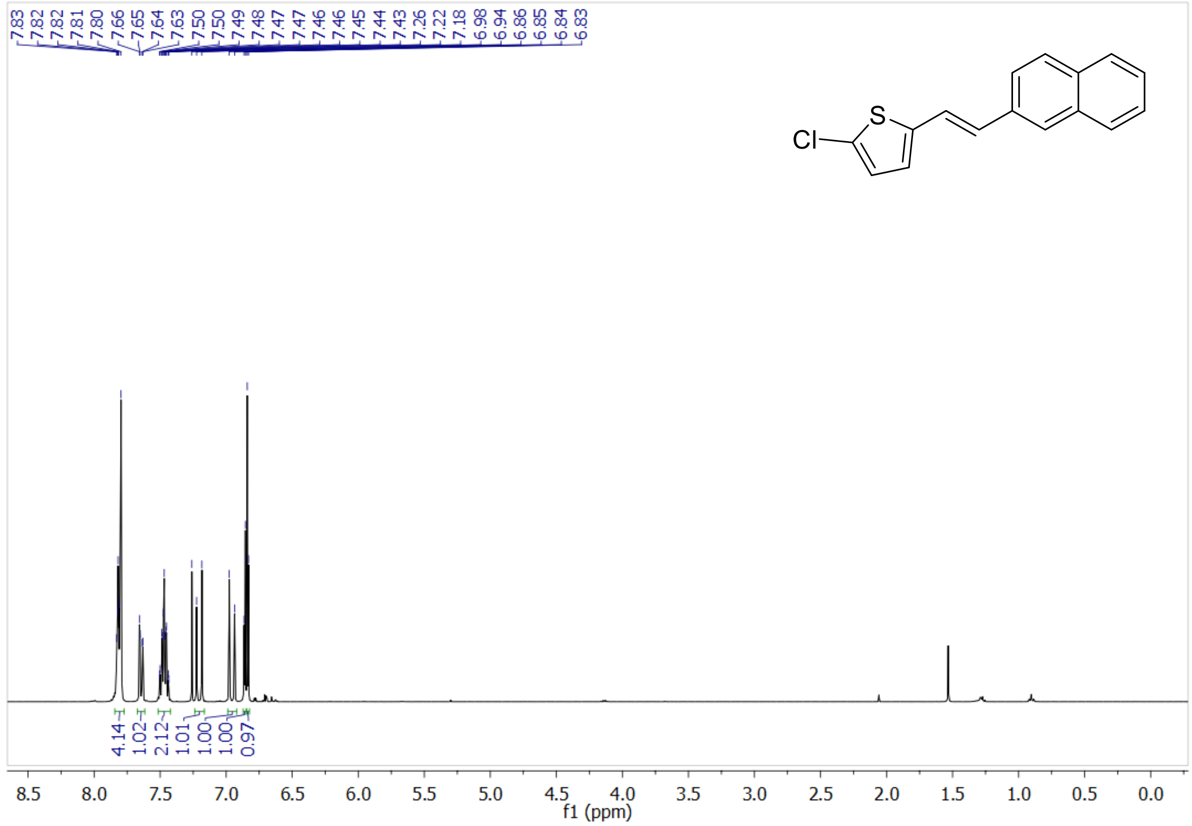
*^{1}H-NMR of 2-(2-(naphthalen-2-yl)vinyl)thiophene (**1a**)*



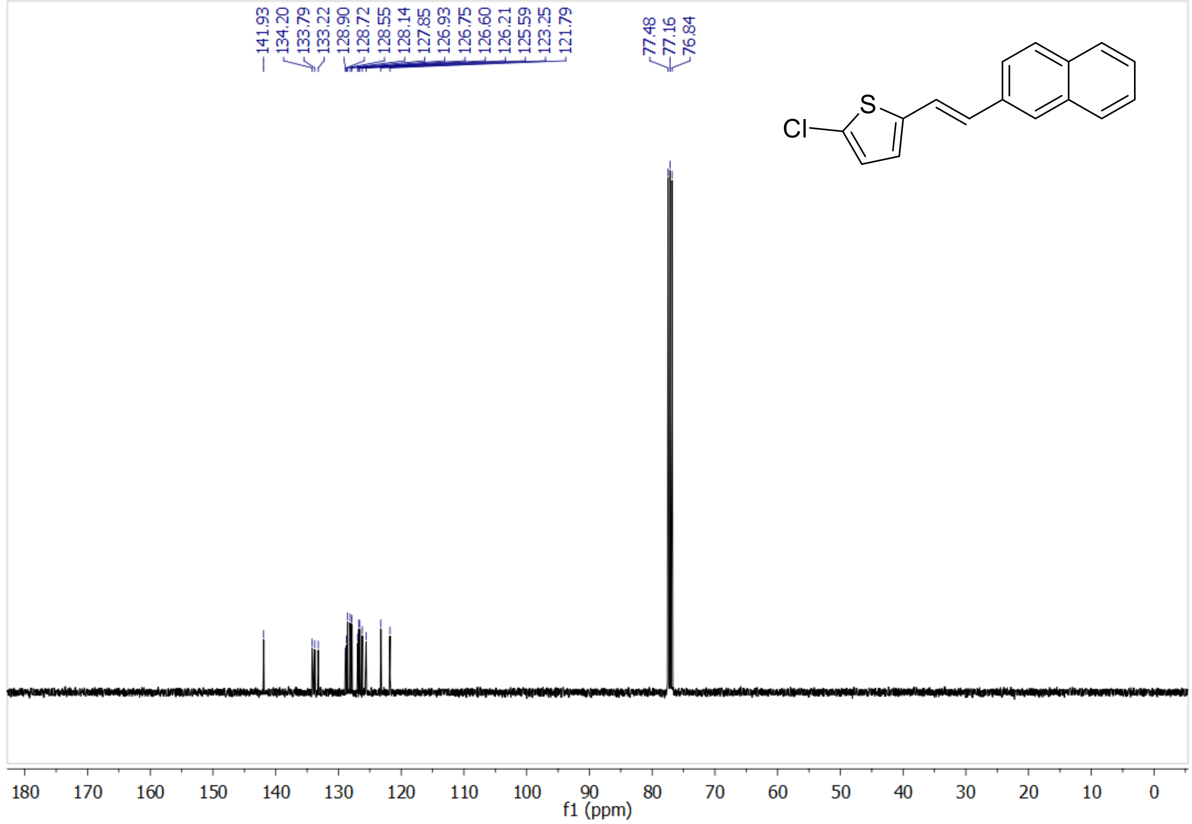
*^{13}C-NMR of 2-(2-(naphthalen-2-yl)vinyl)thiophene (**1a**)*



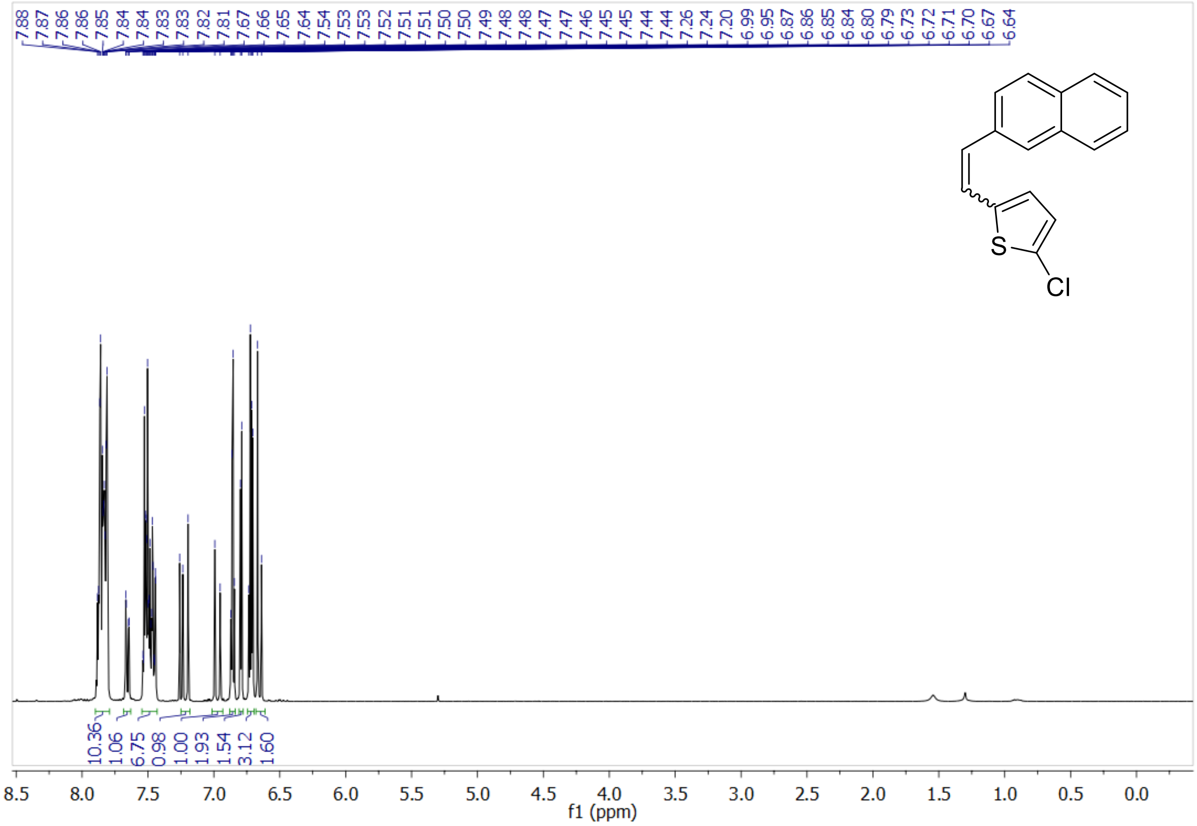
^{1}H-NMR of (E)-2-chloro-5-(2-(naphthalen-2-yl)vinyl)thiophene (**1b**)



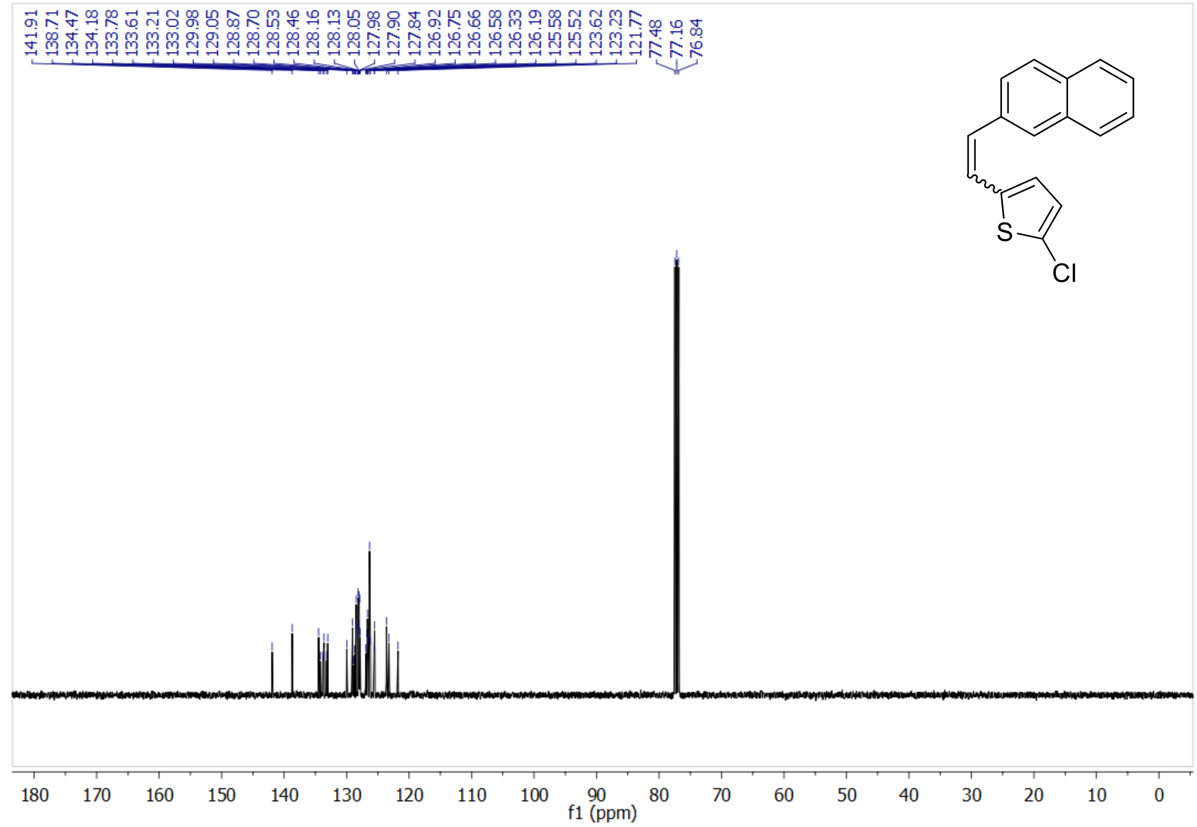
^{13}C-NMR of (E)-2-chloro-5-(2-(naphthalen-2-yl)vinyl)thiophene (**1b**)



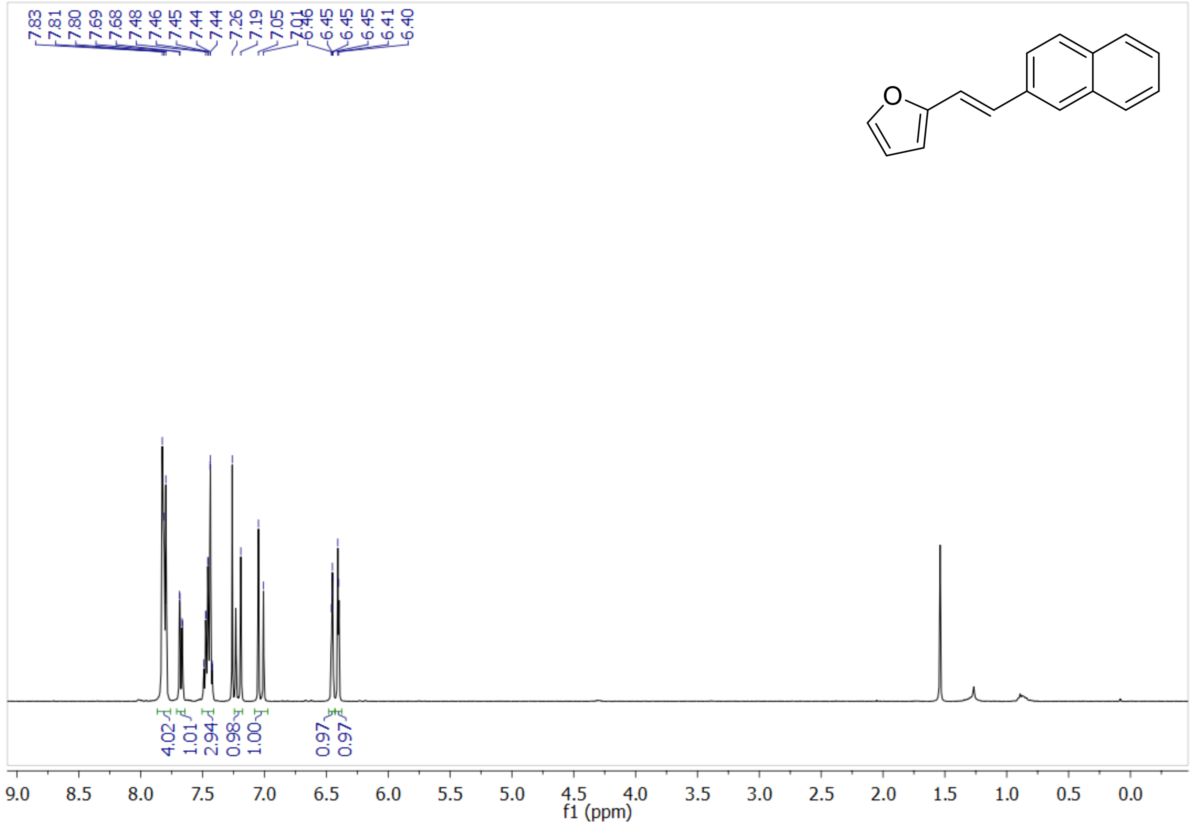
^{1}H-NMR of (E/Z)-2-chloro-5-(2-(naphthalen-2-yl)vinyl)thiophene (**1b**)



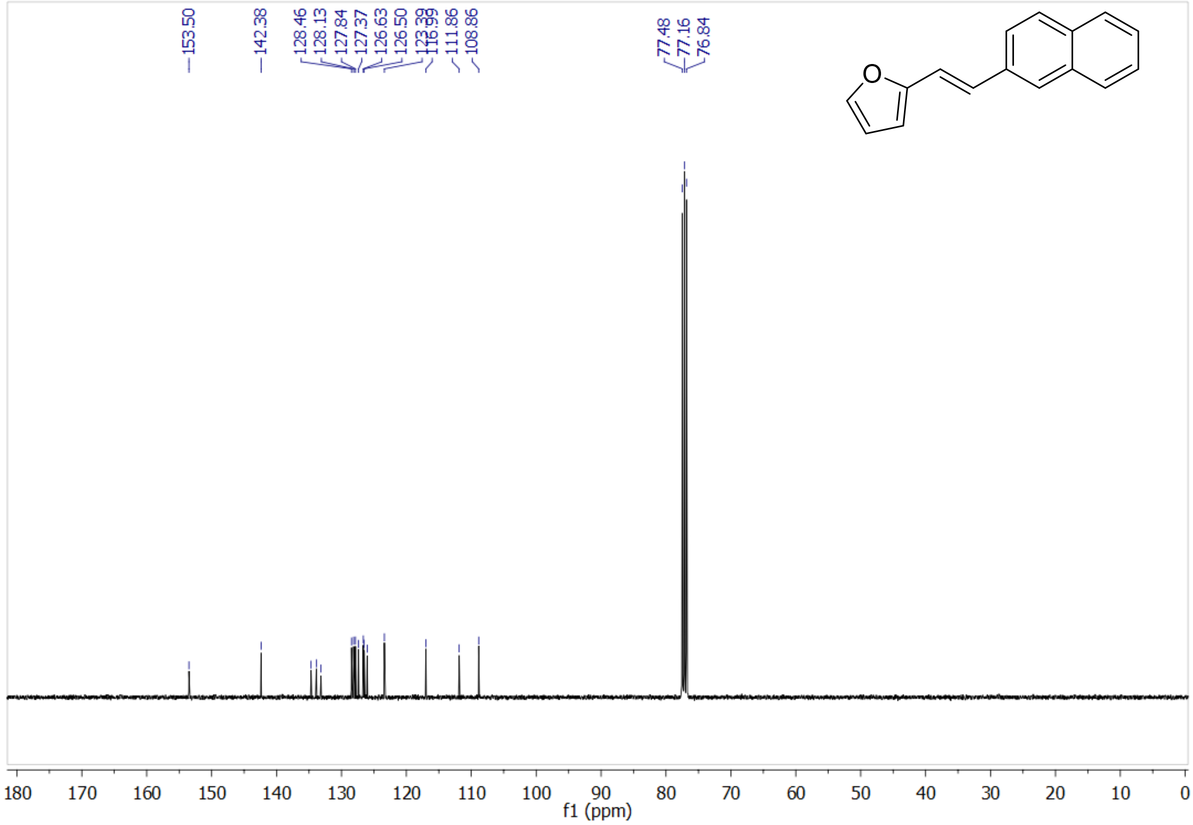
^{13}C-NMR of (E/Z)-2-chloro-5-(2-(naphthalen-2-yl)vinyl)thiophene (**1b**)



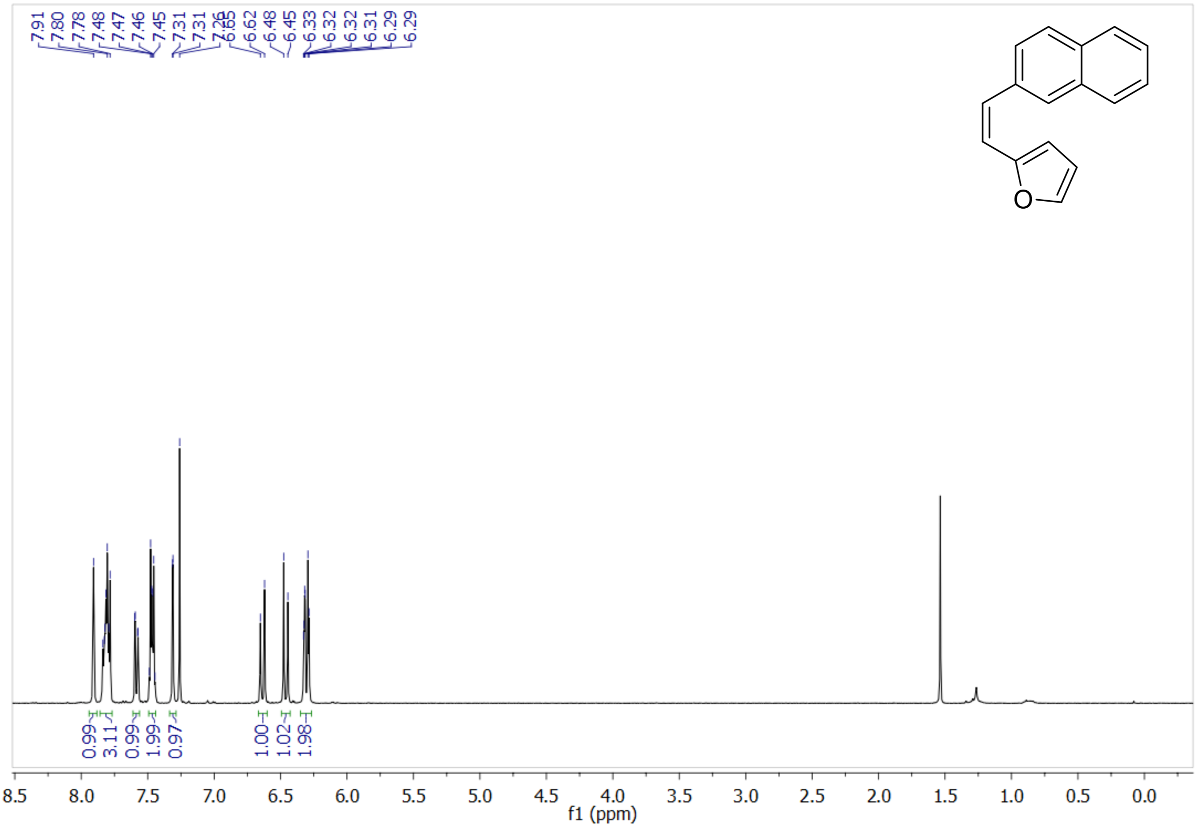
^{1}H-NMR of (E)*-2-(2-(naphthalen-2-yl)vinyl)furan (**1c**)*



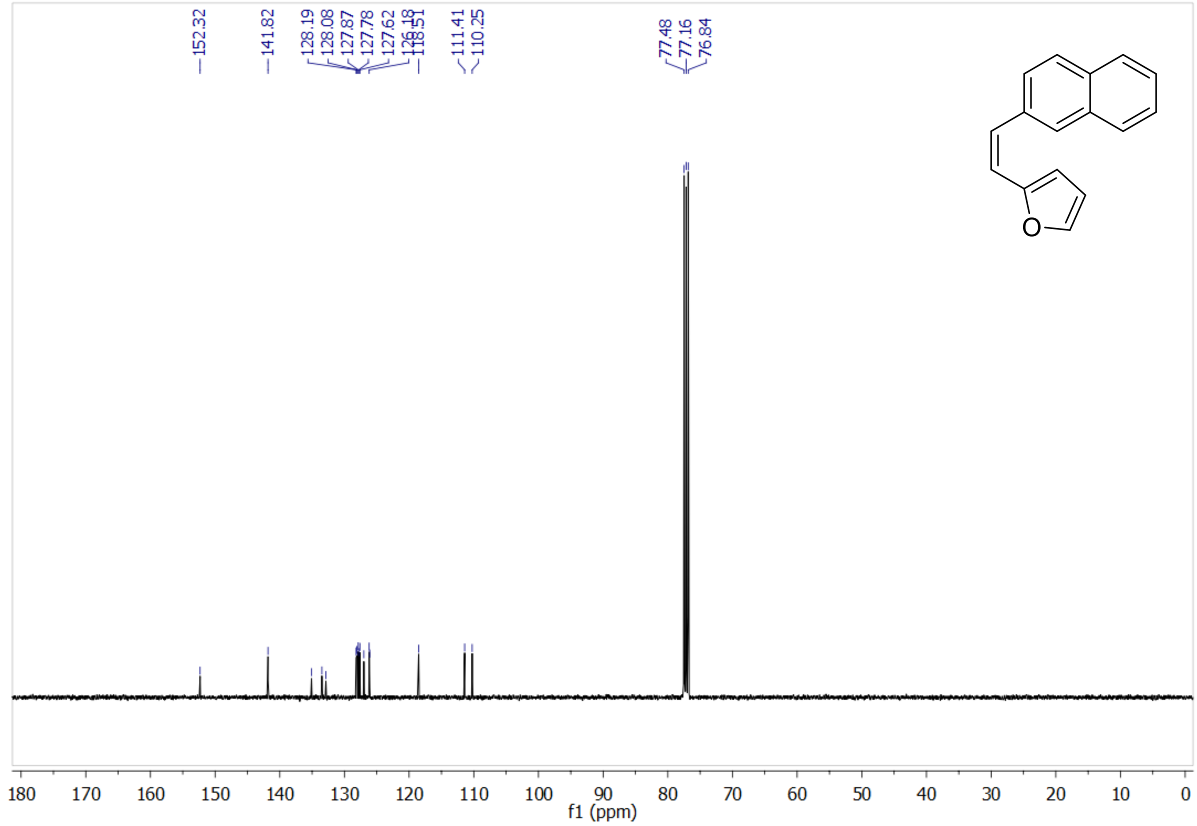
^{13}C-NMR of (E)*-2-(2-(naphthalen-2-yl)vinyl)furan (**1c**)*



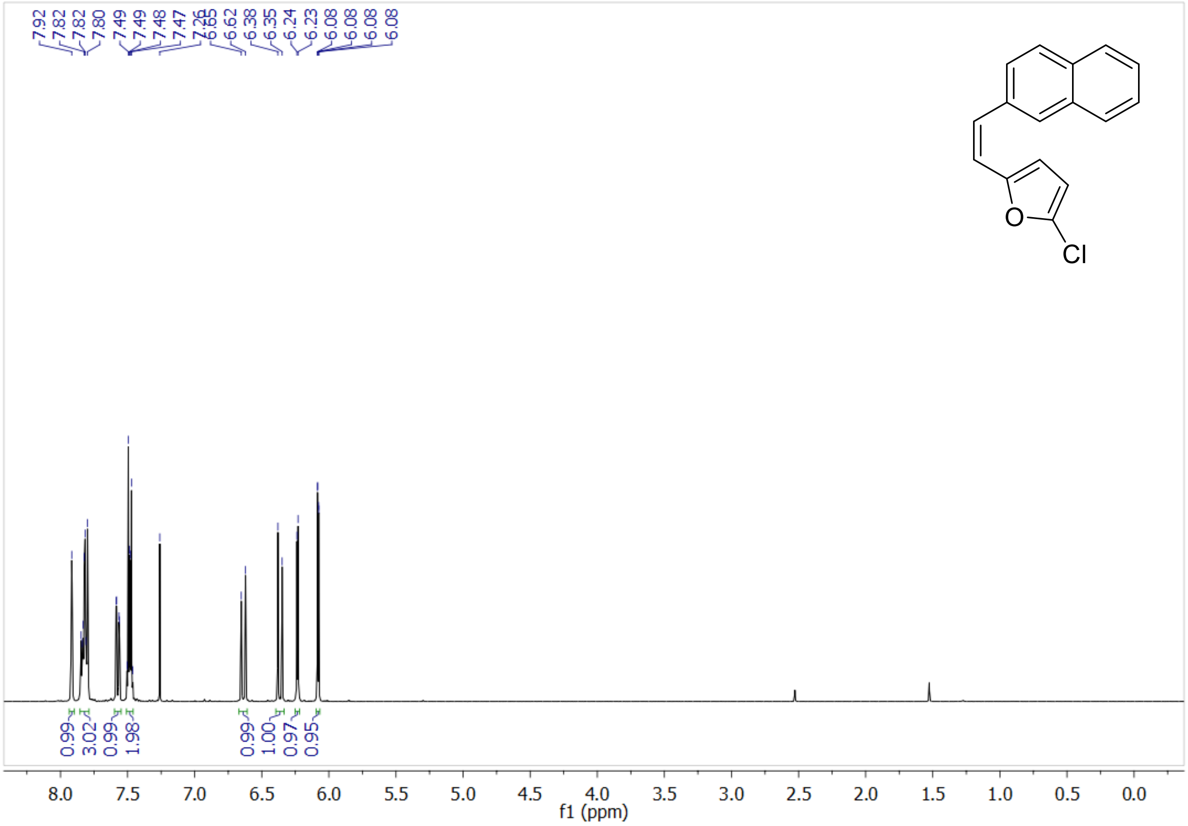
*^{1}H-NMR of (Z)-2-(2-(naphthalen-2-yl)vinyl)furan (**1c**)*



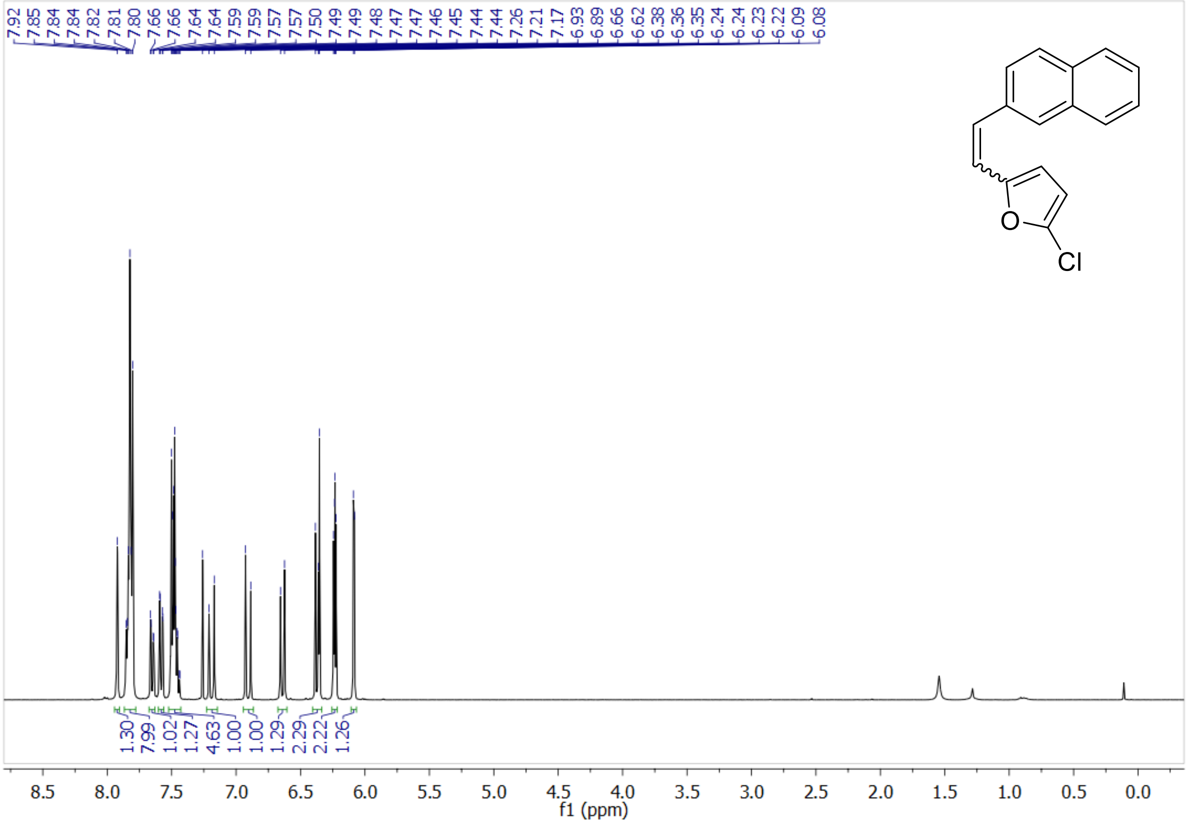
*^{13}C-NMR of (Z)-2-(2-(naphthalen-2-yl)vinyl)furan (**1c**)*



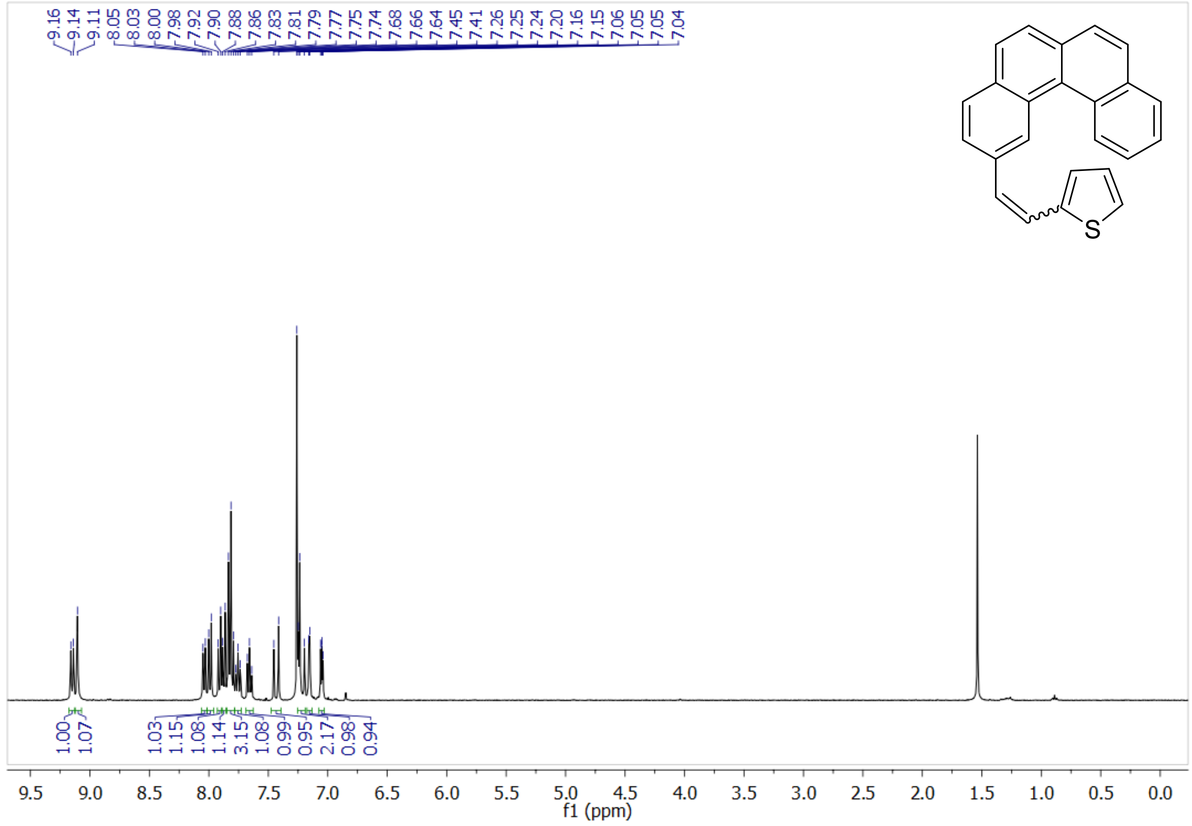
*^{1}H-NMR of (Z)-2-chloro-5-(2-(naphthalen-2-yl)vinyl)furan (**1d**)*



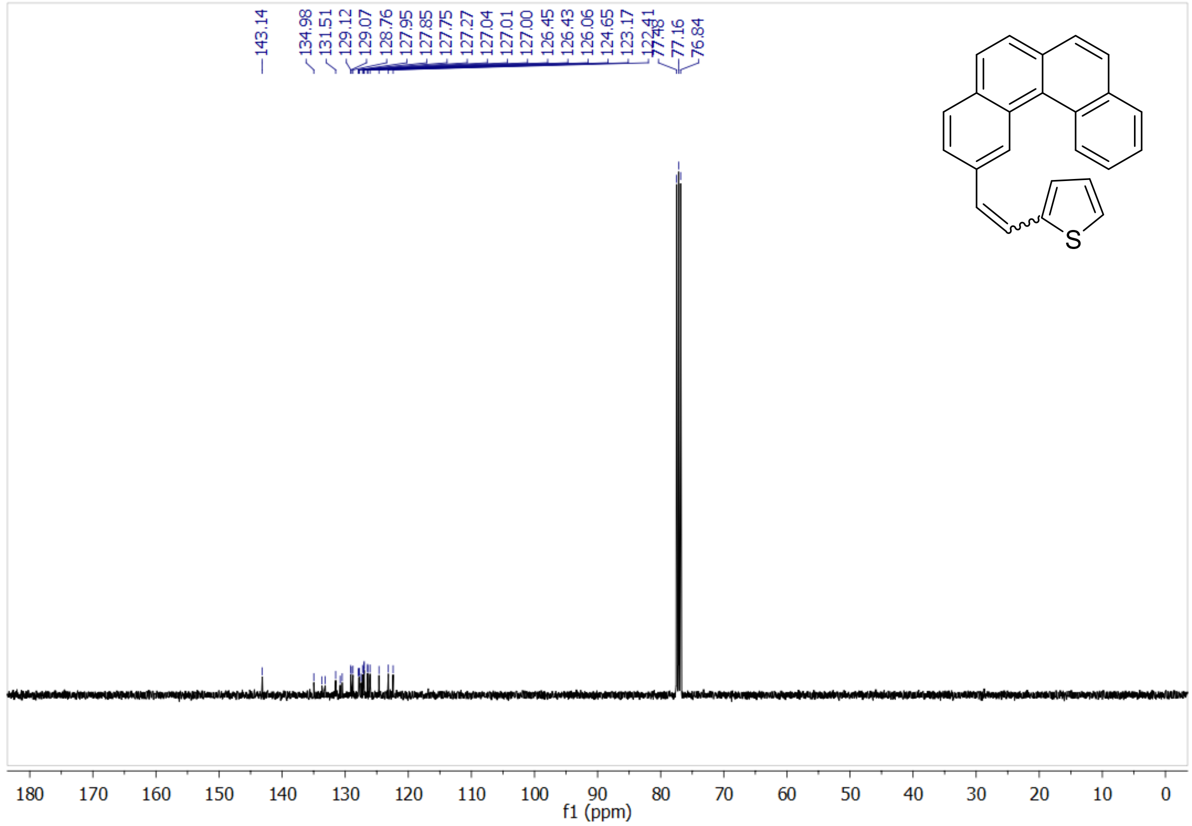
*^{1}H-NMR of (E/Z)-2-chloro-5-(2-(naphthalen-2-yl)vinyl)furan (**1d**)*



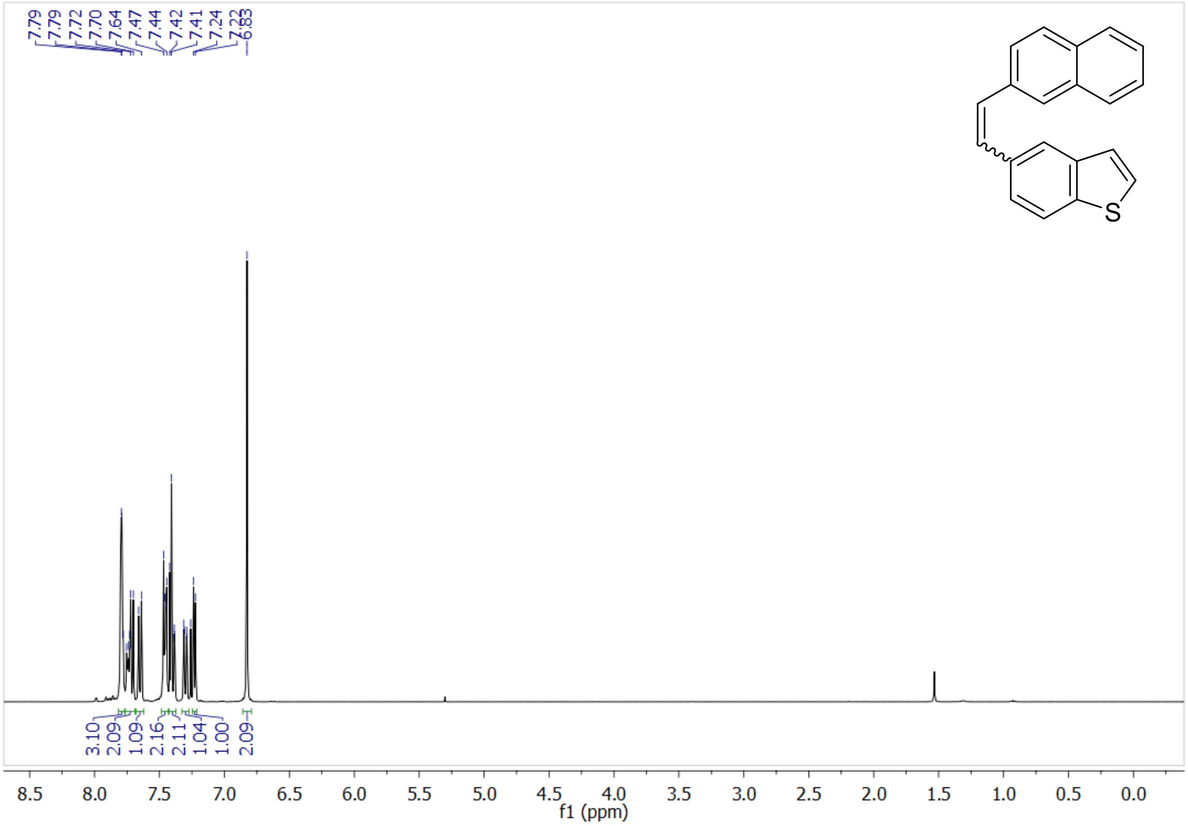
^{1}H-NMR of 2-(2-(benzo[c]phenanthren-2-yl)vinyl)thiophene (**1e**)



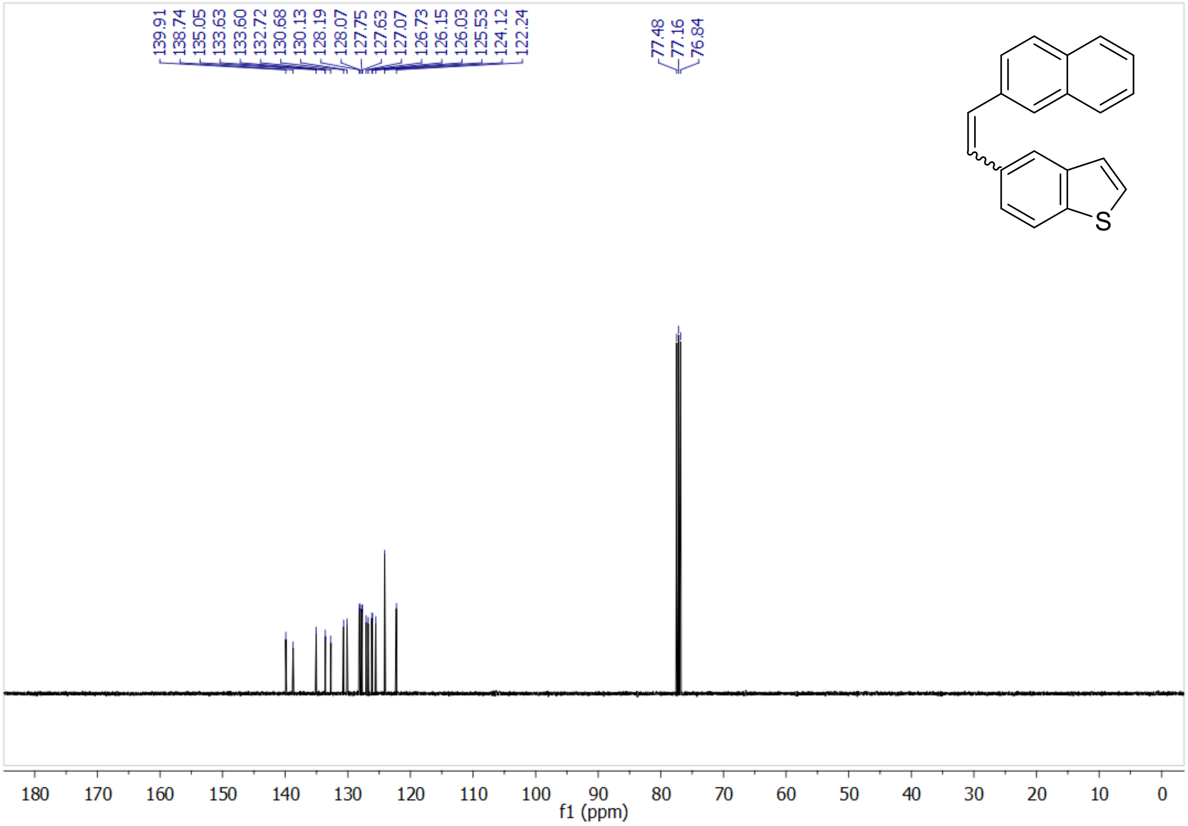
^{13}C-NMR of 2-(2-(benzo[c]phenanthren-2-yl)vinyl)thiophene (**1e**)



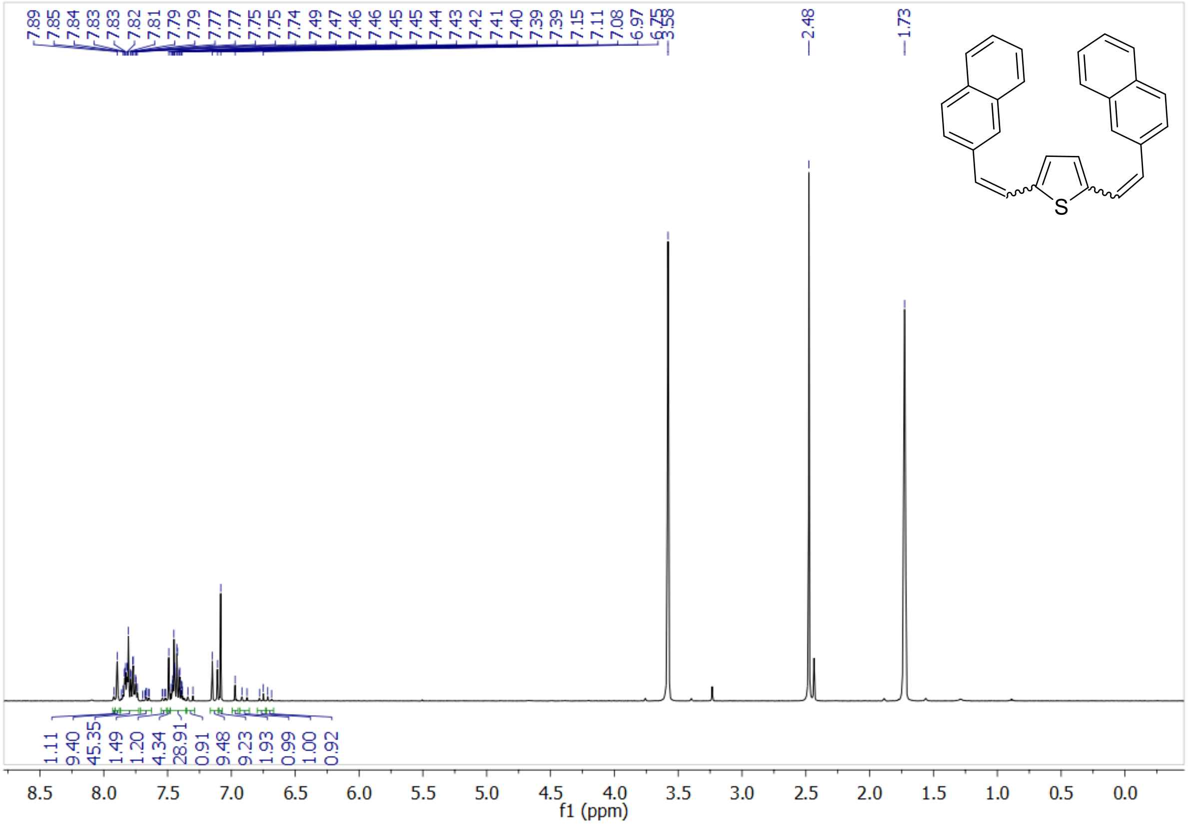
^{1}H-NMR of 5-(2-(naphthalen-2-yl)vinyl)benzo[b]thiophene (**1f**)

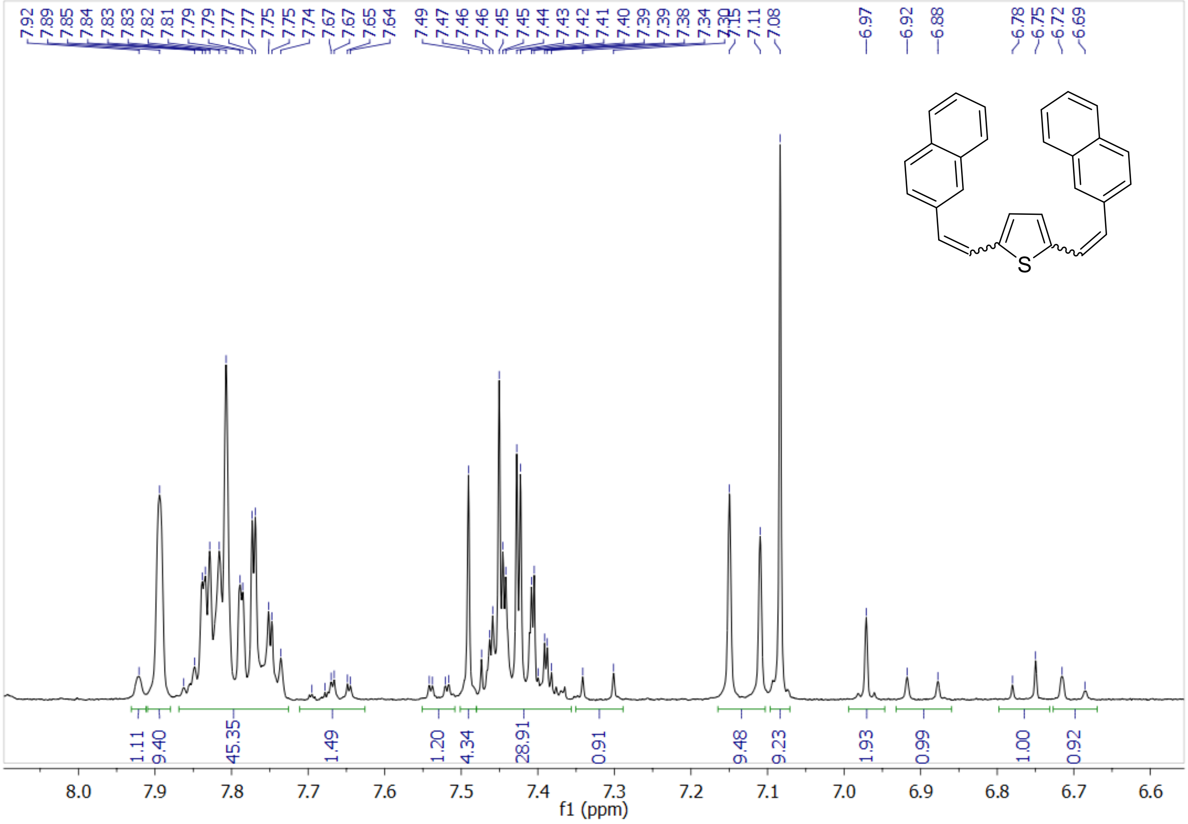


^{13}C-NMR of 5-(2-(naphthalen-2-yl)vinyl)benzo[b]thiophene (**1f**)

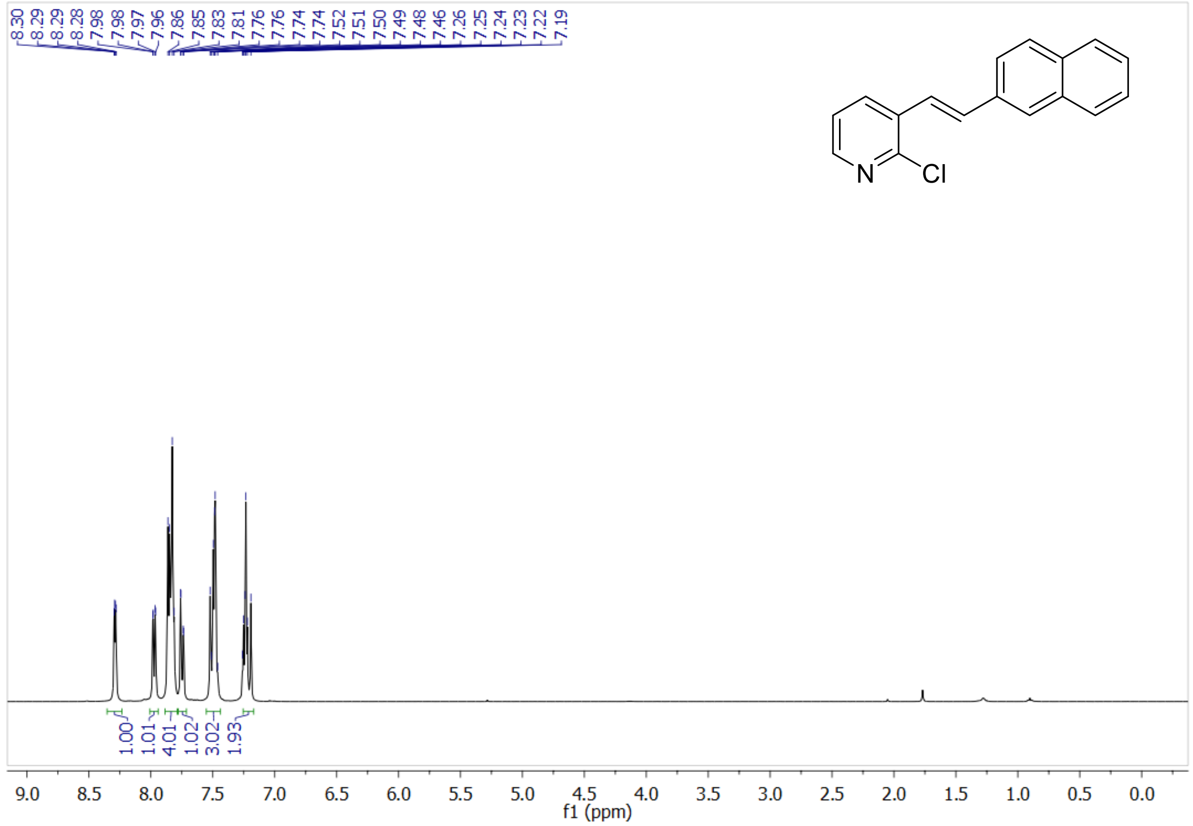


*^{1}H-NMR of 2,5-bis(2-(naphthalen-2-yl)vinyl)thiophene (**1g**)*

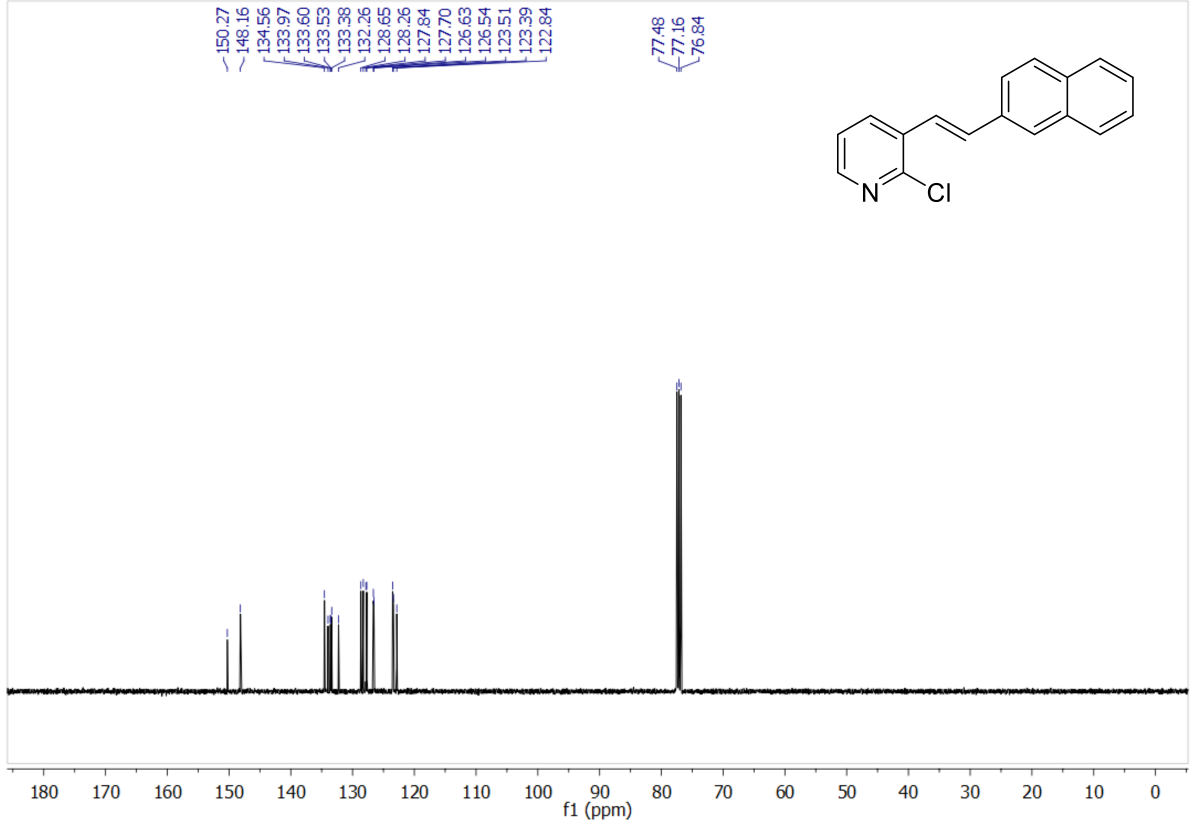




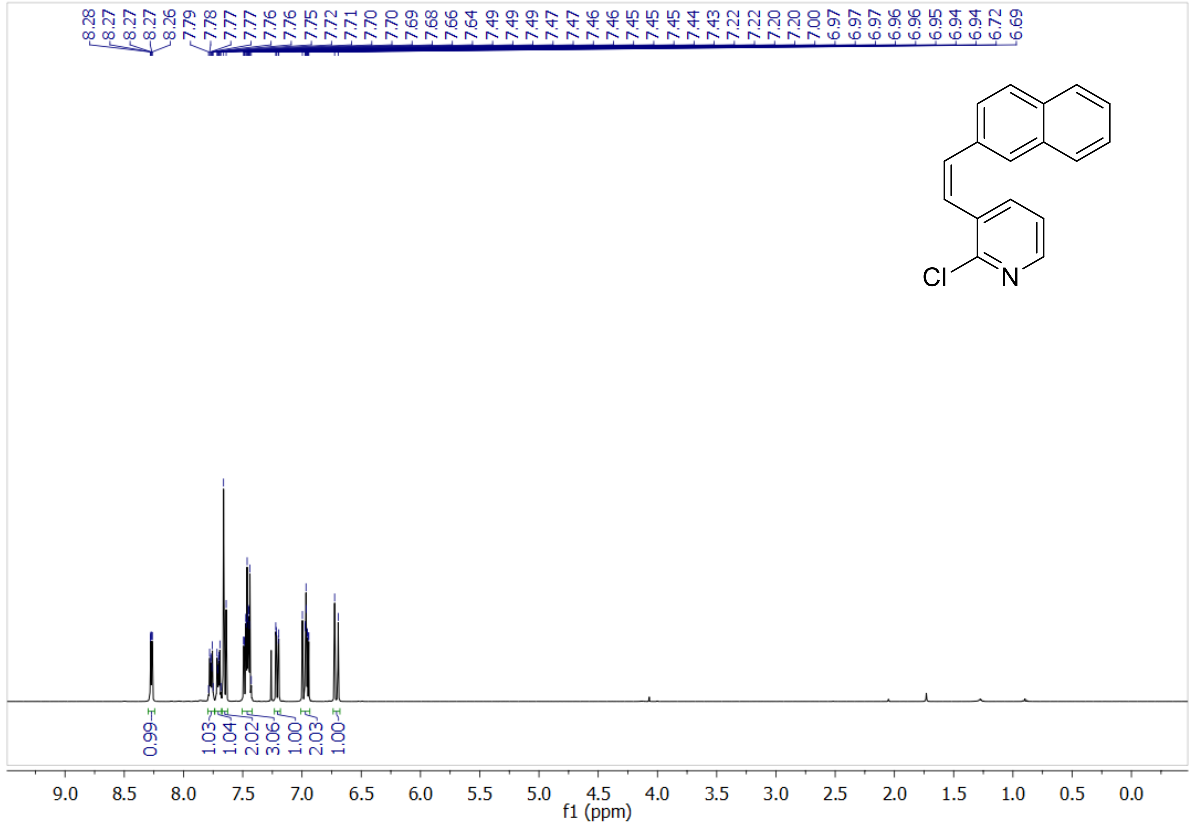
^{1}H-NMR of (E)-2-chloro-3-(2-(naphthalen-2-yl)vinyl)pyridine (**1h**)



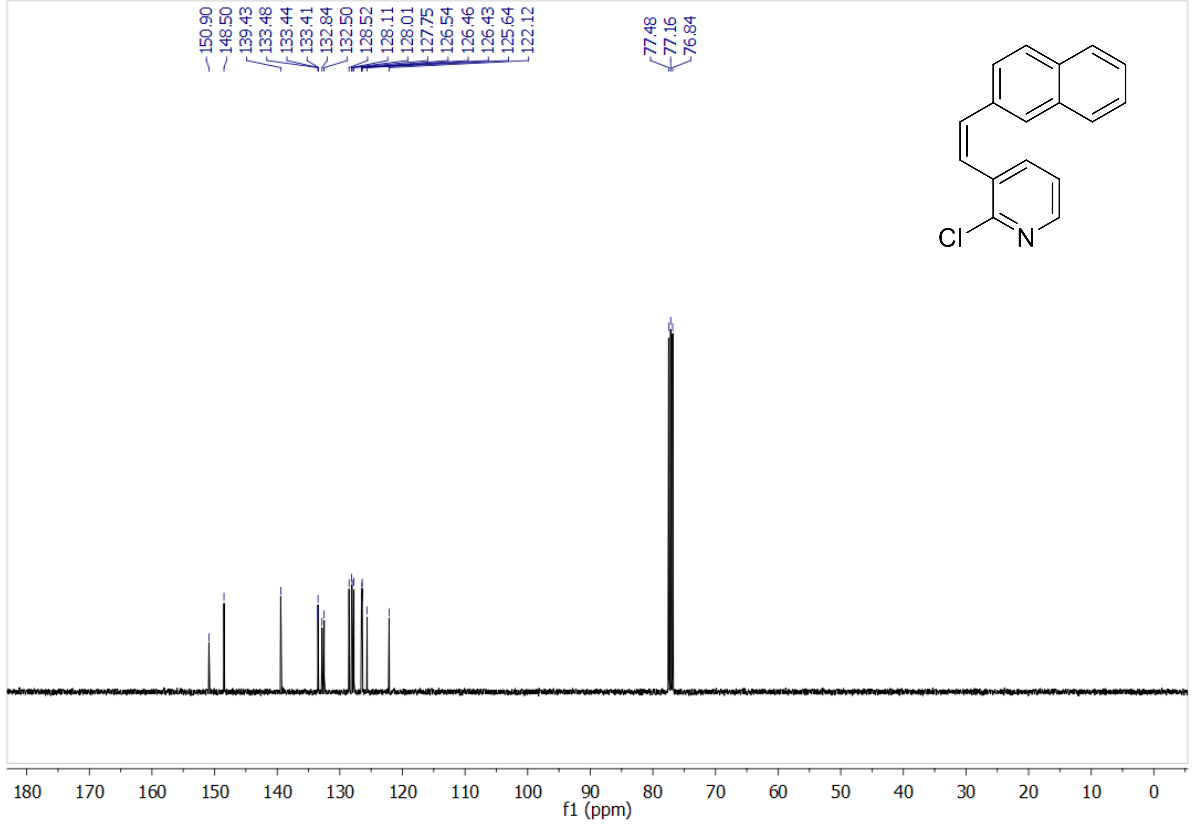
^{13}C-NMR of (E)-2-chloro-3-(2-(naphthalen-2-yl)vinyl)pyridine (**1h**)



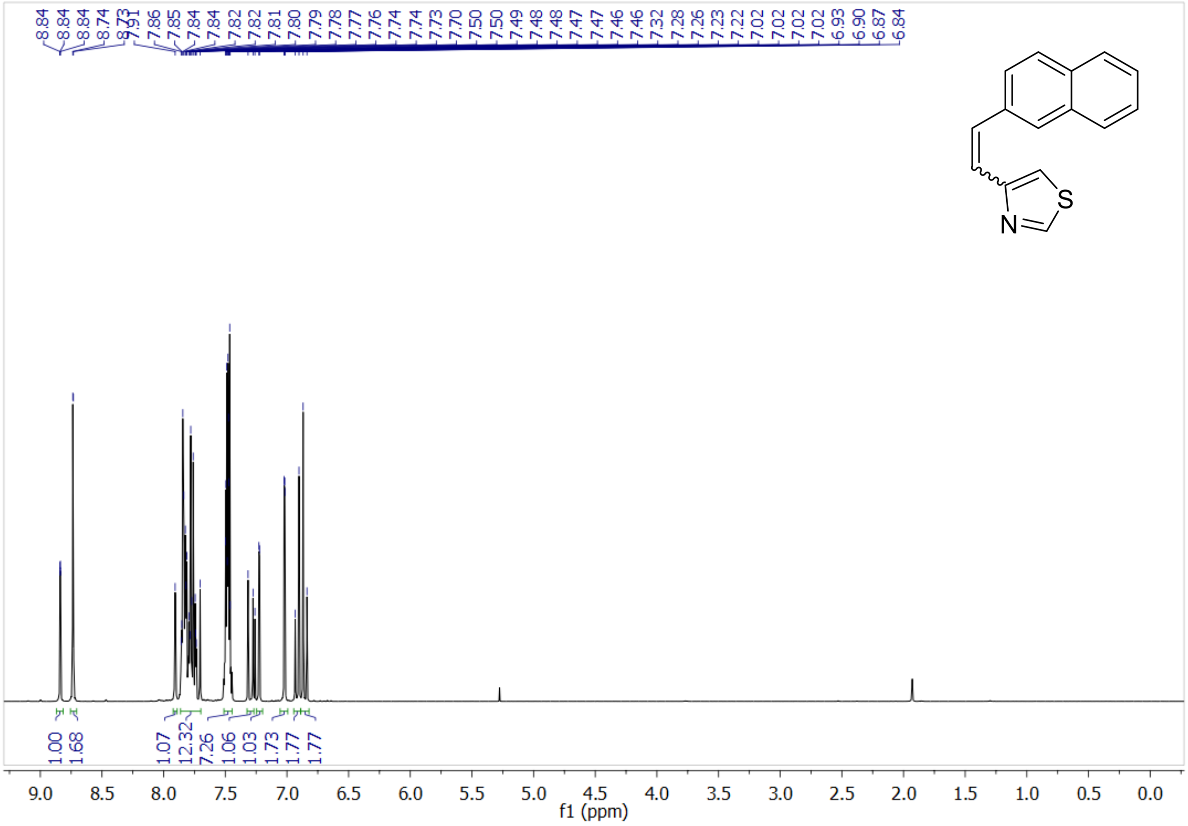
*^{1}H-NMR of (Z)-2-chloro-3-(2-(naphthalen-2-yl)vinyl)pyridine (**1h**)*



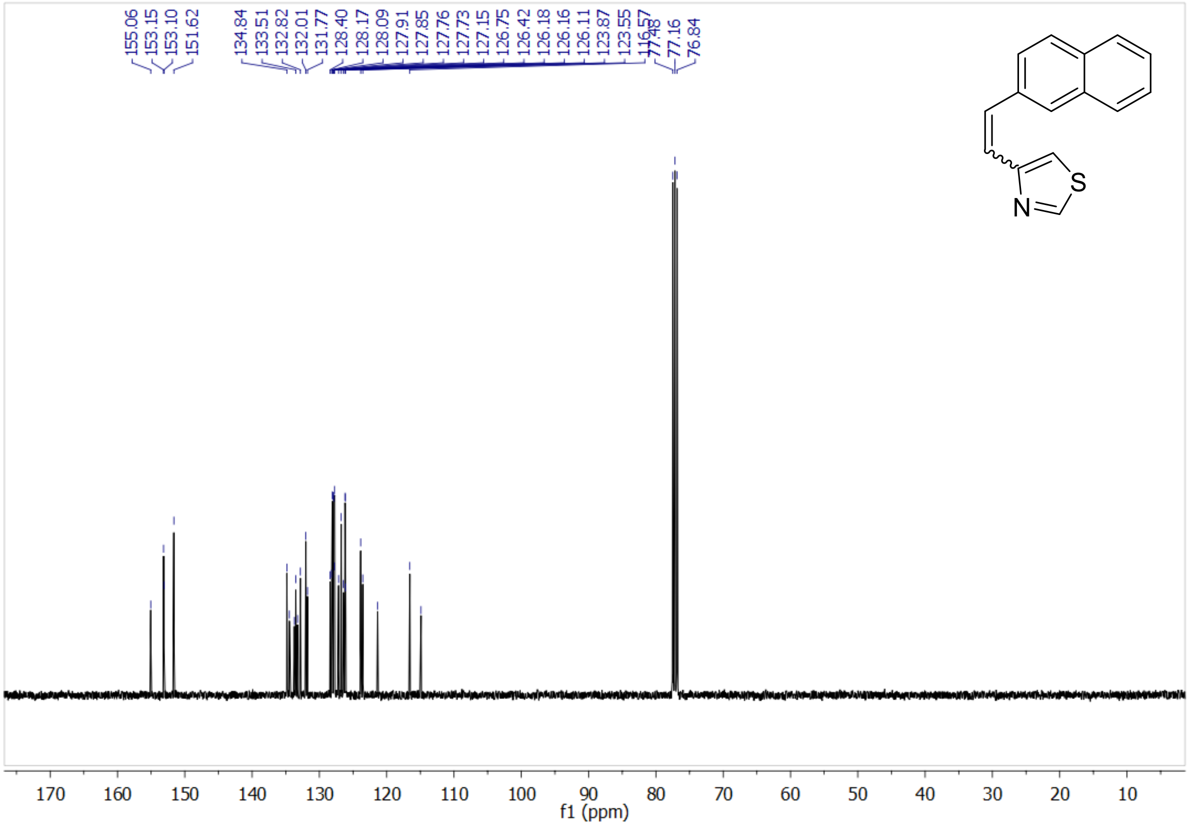
*^{13}C-NMR of (Z)-2-chloro-3-(2-(naphthalen-2-yl)vinyl)pyridine (**1h**)*



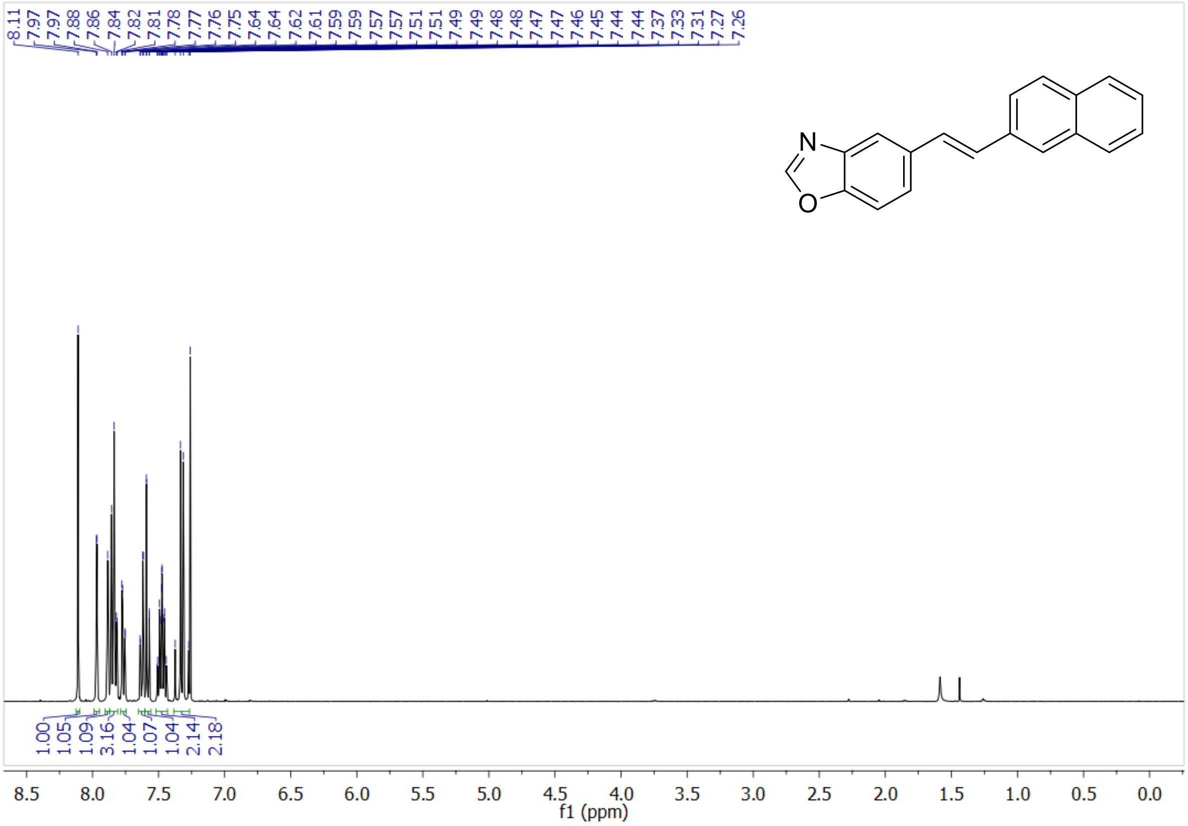
*^{1}H-NMR of 4-(2-(naphthalen-2-yl)vinyl)thiazole (**1i**)*



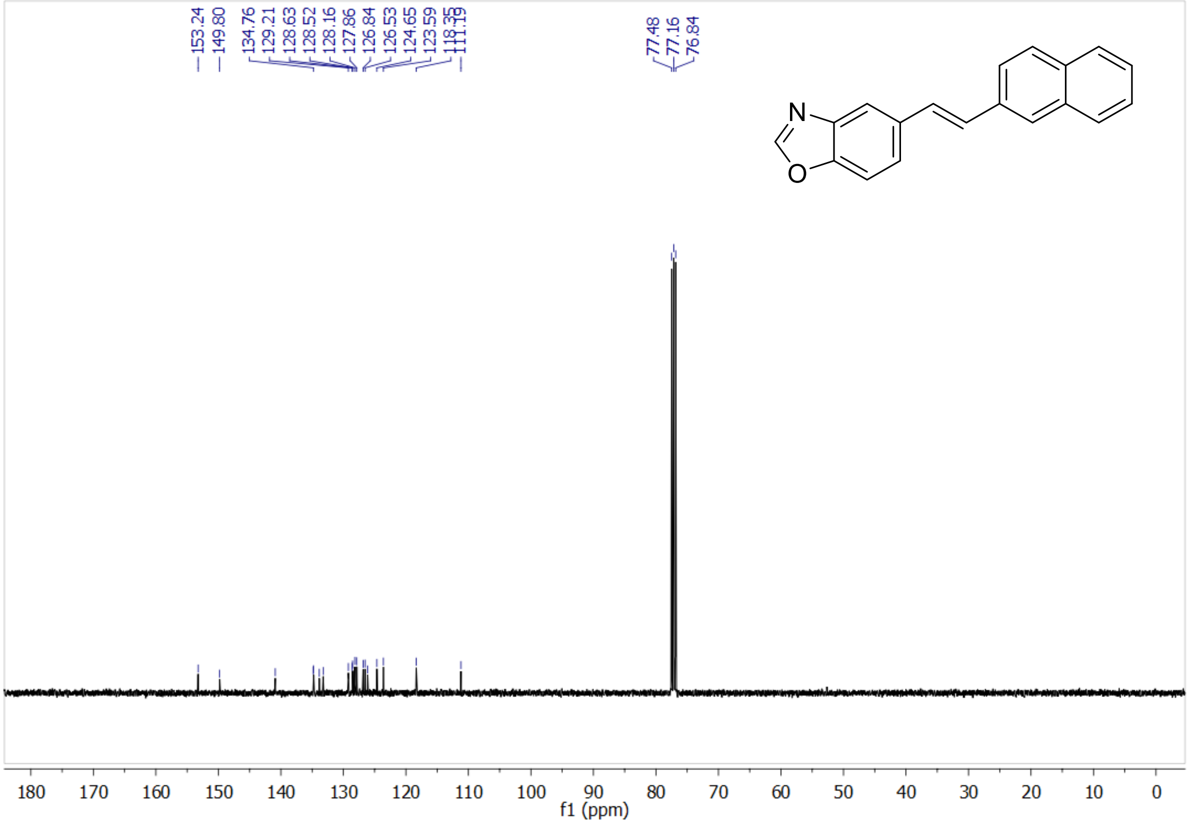
*^{13}C-NMR of 4-(2-(naphthalen-2-yl)vinyl)thiazole (**1i**)*



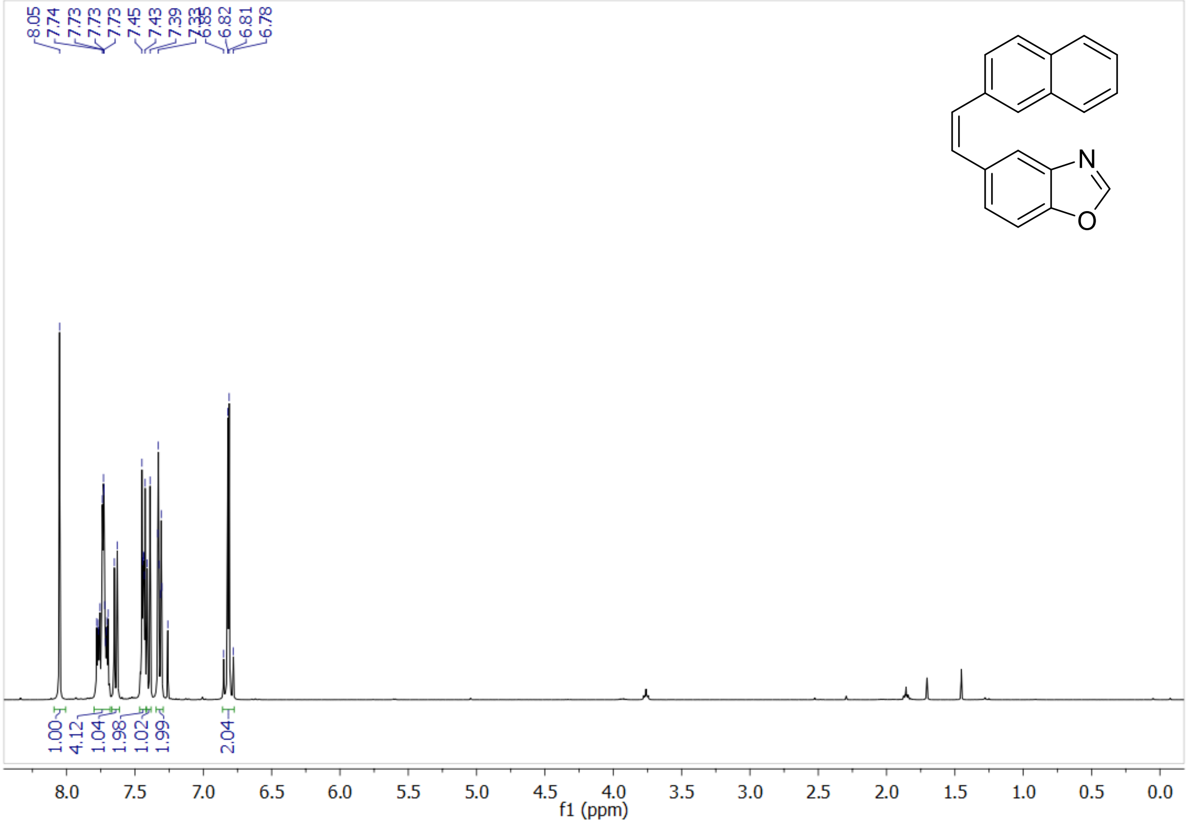
*^{1}H-NMR of (E)-5-(2-(naphthalen-2-yl)vinyl)benzo[d]oxazole (**1k**)*



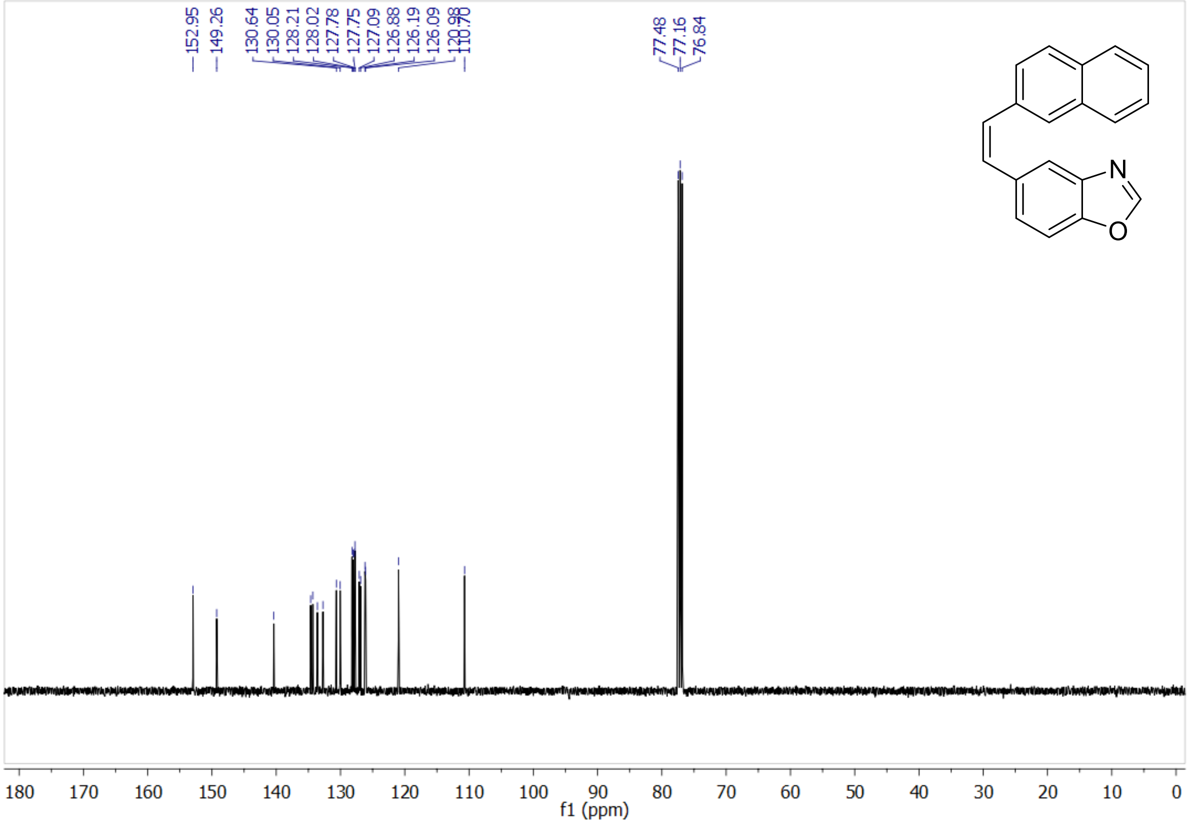
*^{13}C-NMR of (E)-5-(2-(naphthalen-2-yl)vinyl)benzo[d]oxazole (**1k**)*



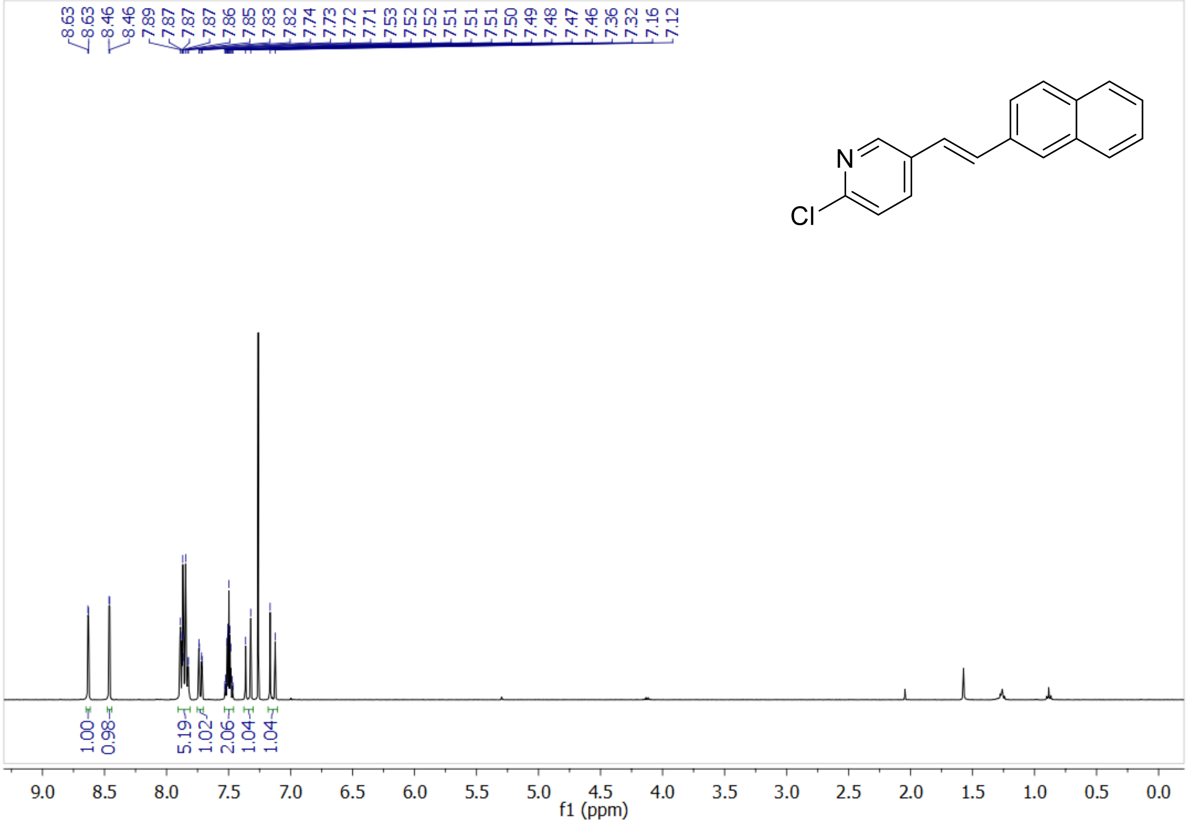
*^{1}H-NMR of (Z)-5-(2-(naphthalen-2-yl)vinyl)benzo[*d*]oxazole (**1k**)*



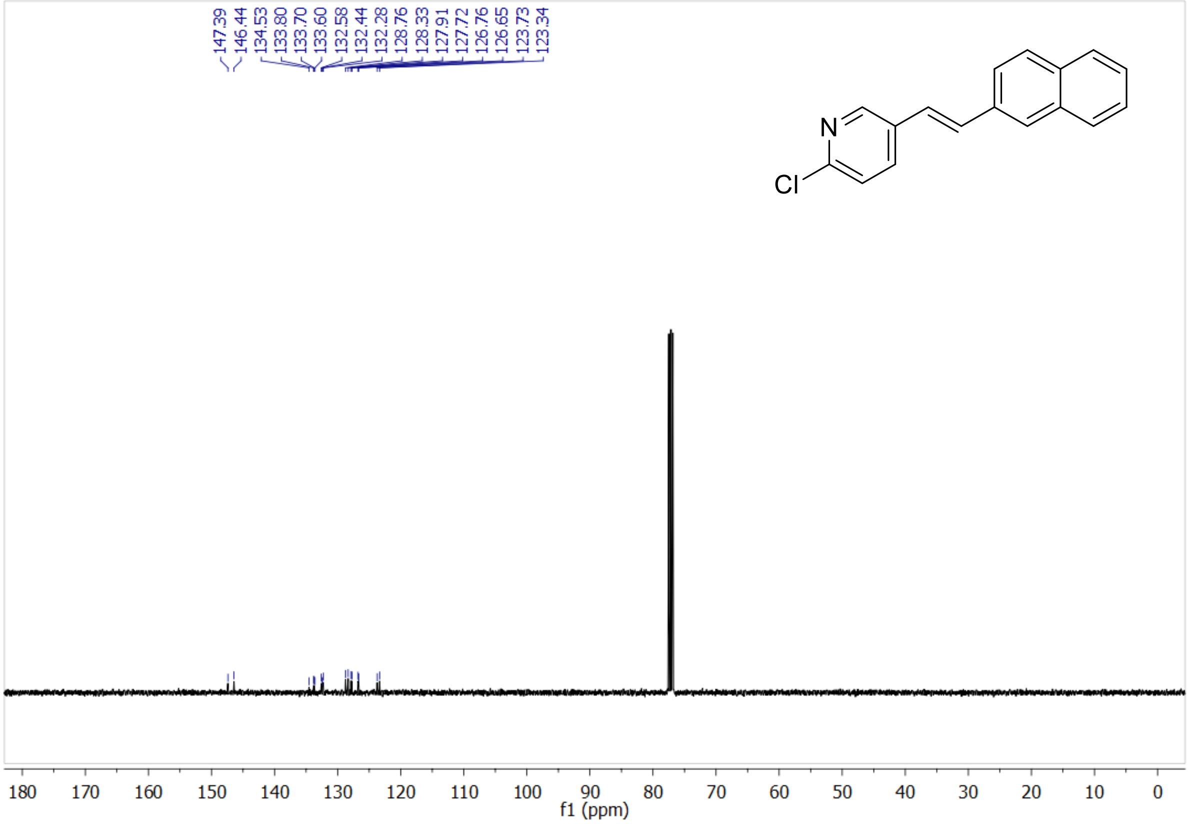
*^{13}C-NMR of (Z)-5-(2-(naphthalen-2-yl)vinyl)benzo[*d*]oxazole (**1k**)*



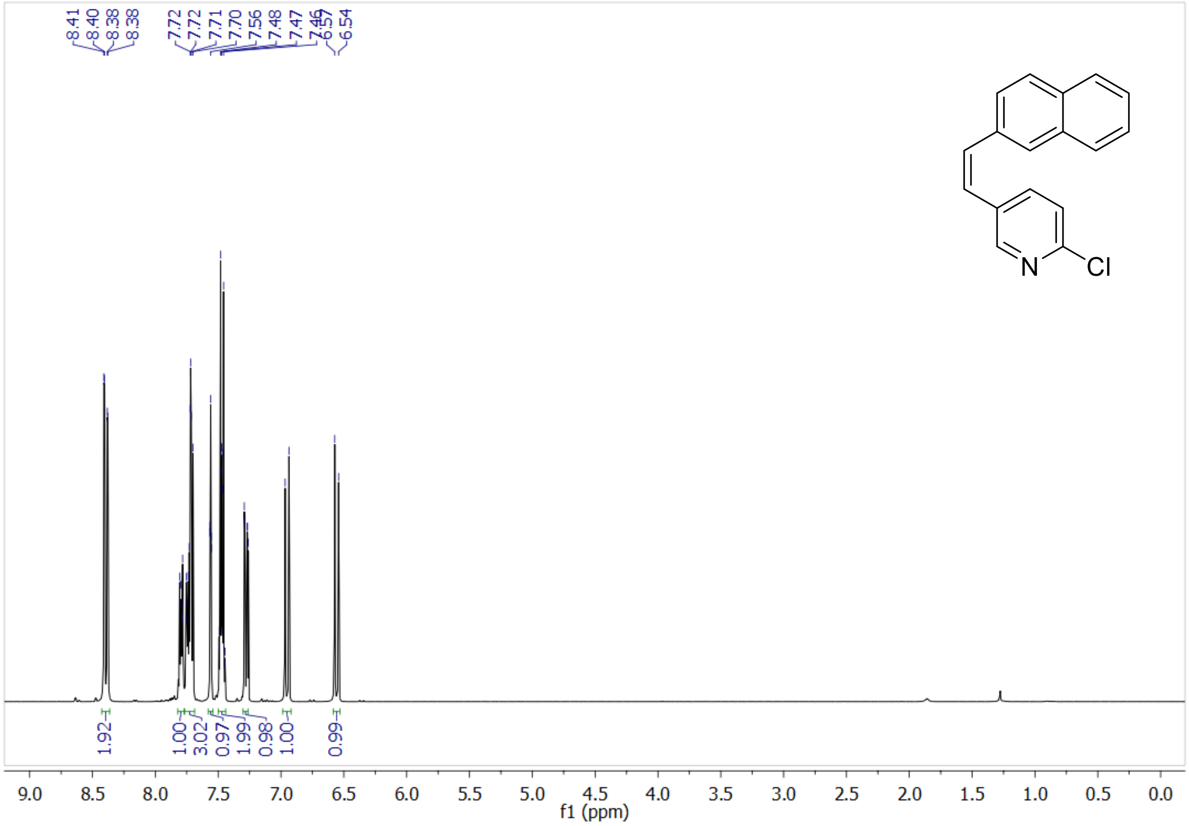
*^{1}H-NMR of (E)-3-chloro-5-(2-(naphthalen-2-yl)vinyl)pyridine (**1m**)*



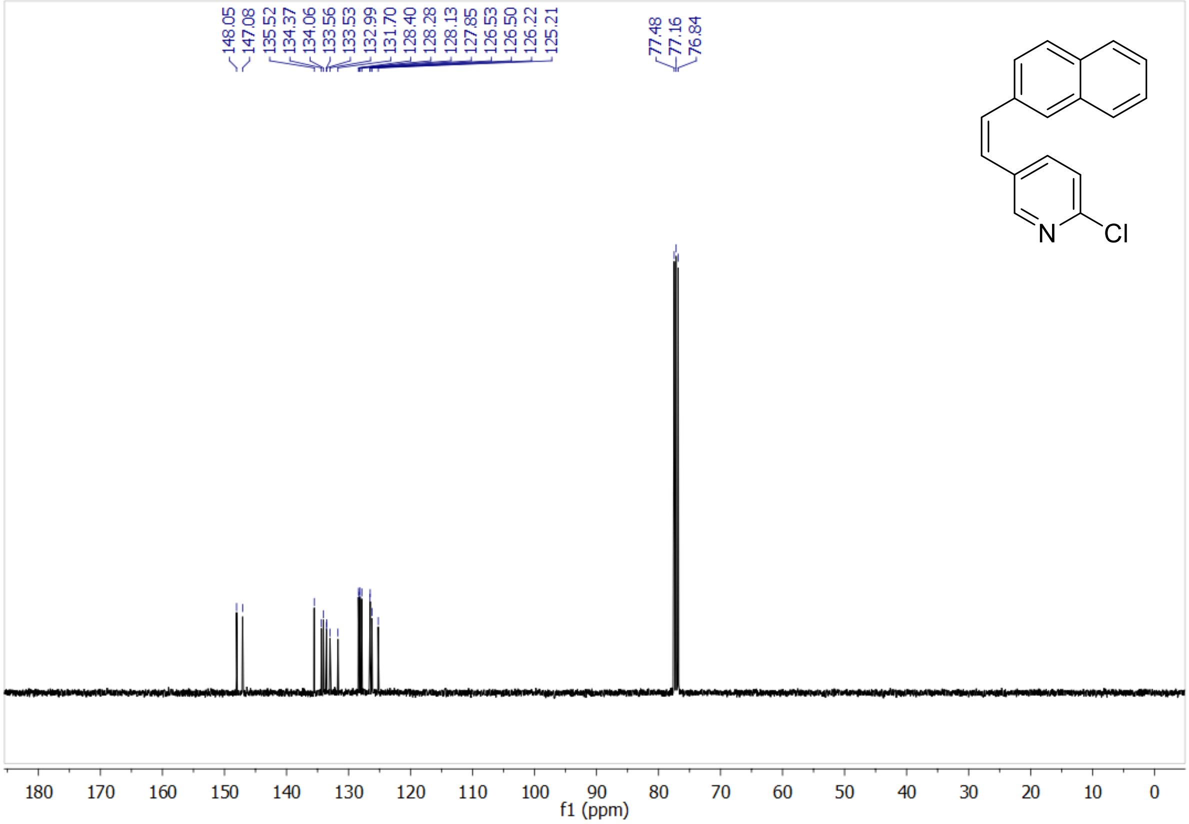
*^{13}C-NMR of (E)-3-chloro-5-(2-(naphthalen-2-yl)vinyl)pyridine (**1m**)*



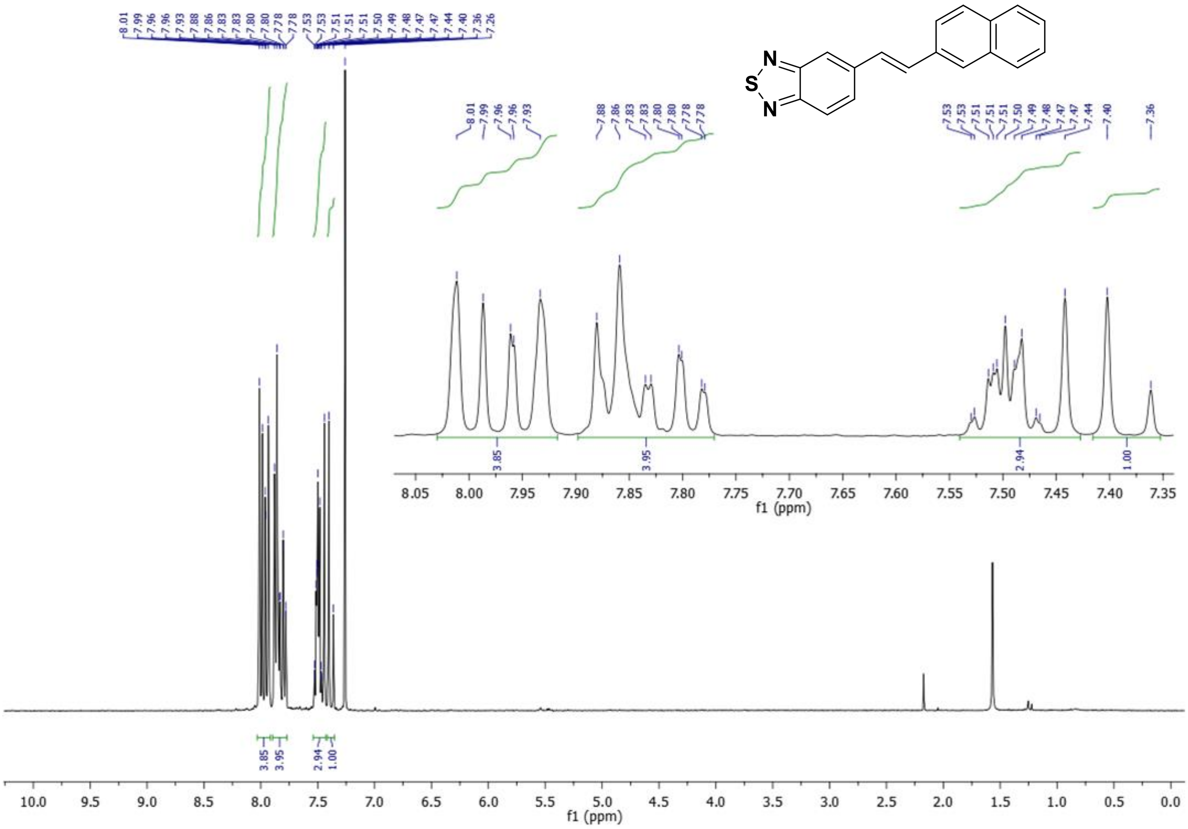
*^{1}H-NMR of (Z)-3-chloro-5-(2-(naphthalen-2-yl)vinyl)pyridine (**1m**)*



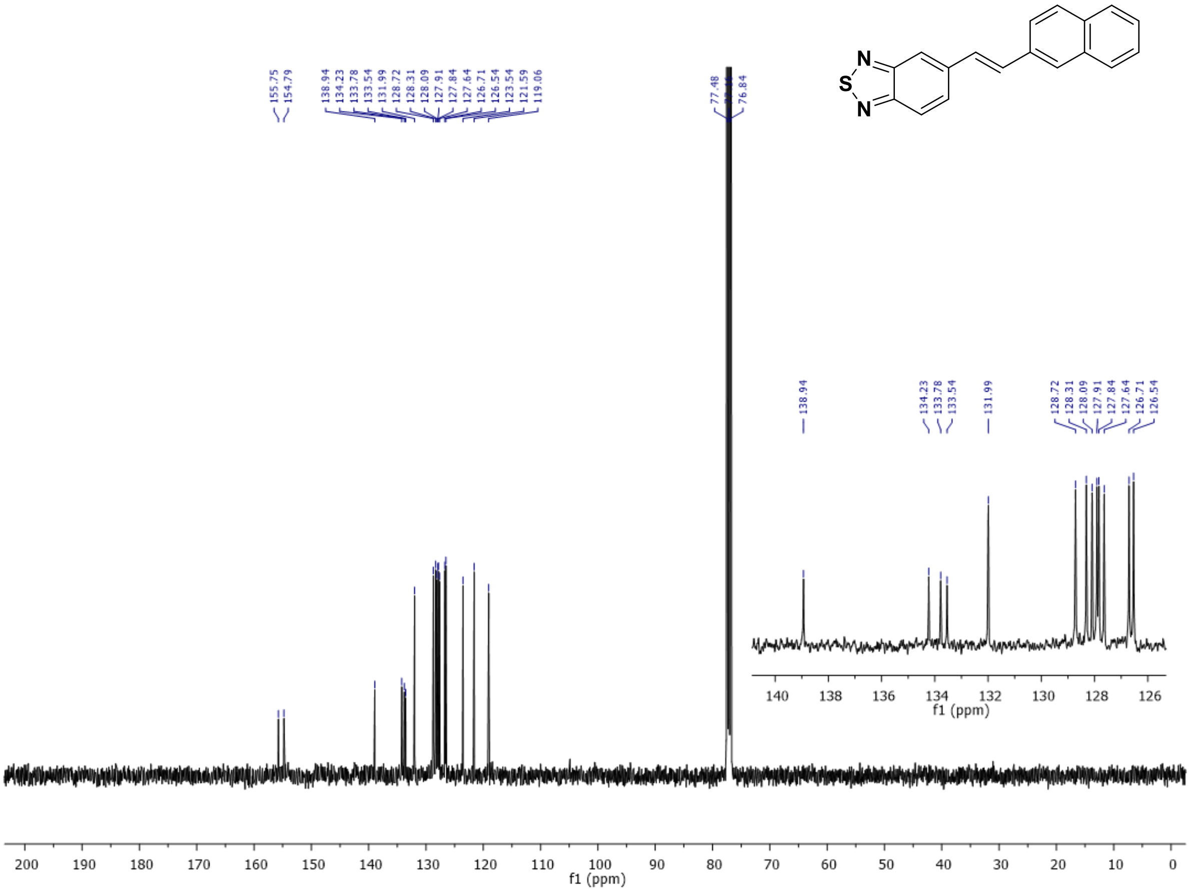
*^{13}C-NMR of (Z)-3-chloro-5-(2-(naphthalen-2-yl)vinyl)pyridine (**1m**)*



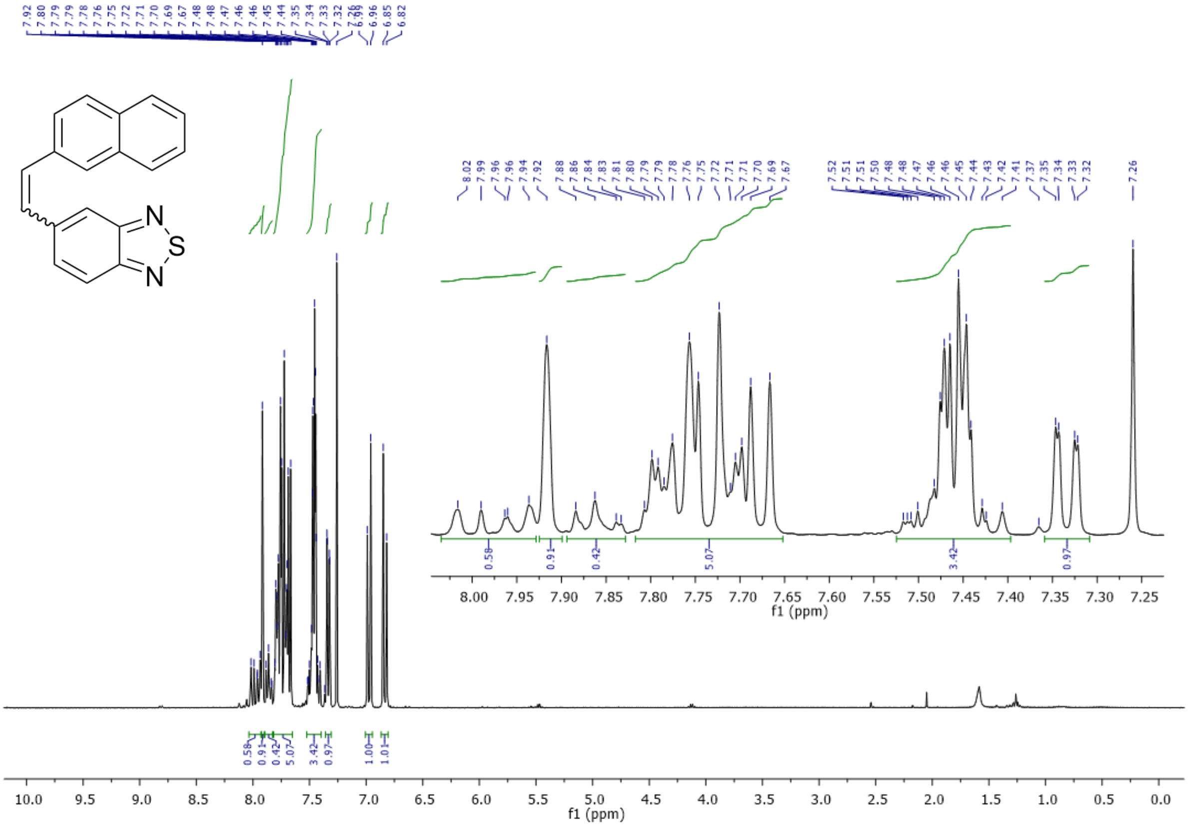
*^{1}H-NMR of (E)-5-(2-(naphthalen-2-yl)vinyl)benzo[c][1,2,5]thiadiazole (**1n**)*



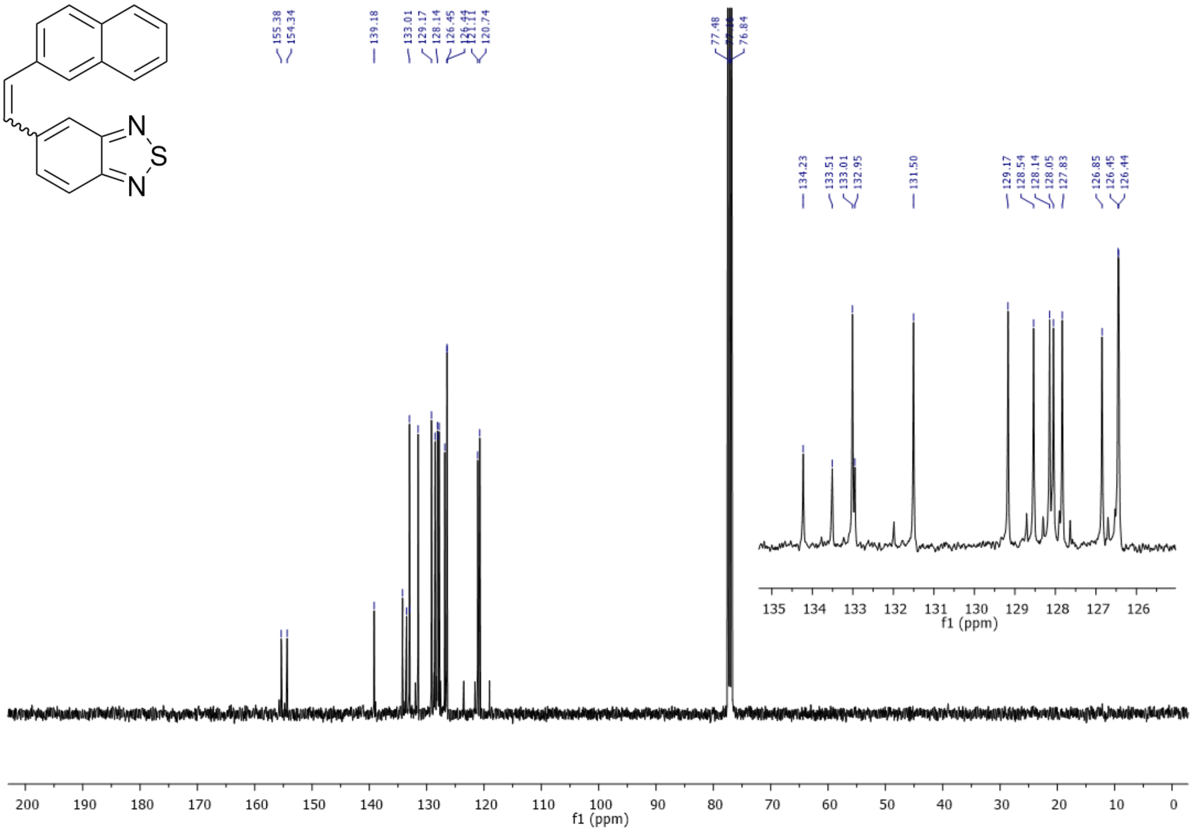
*^{13}C-NMR of (E)-5-(2-(naphthalen-2-yl)vinyl)benzo[c][1,2,5]thiadiazole (**1n**)*



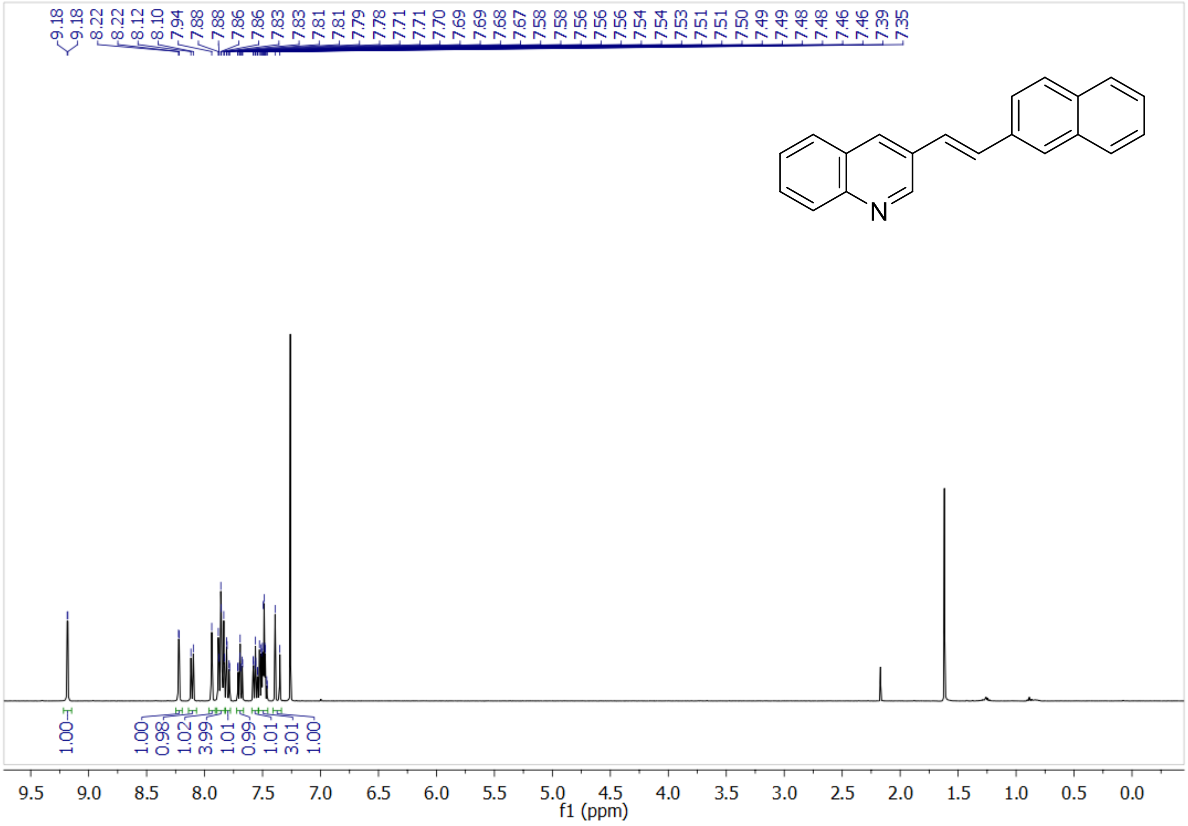
*^{1}H-NMR of (Z/E)-5-(2-(naphthalen-2-yl)vinyl)benzo[c][1,2,5]thiadiazole (**1n**)*



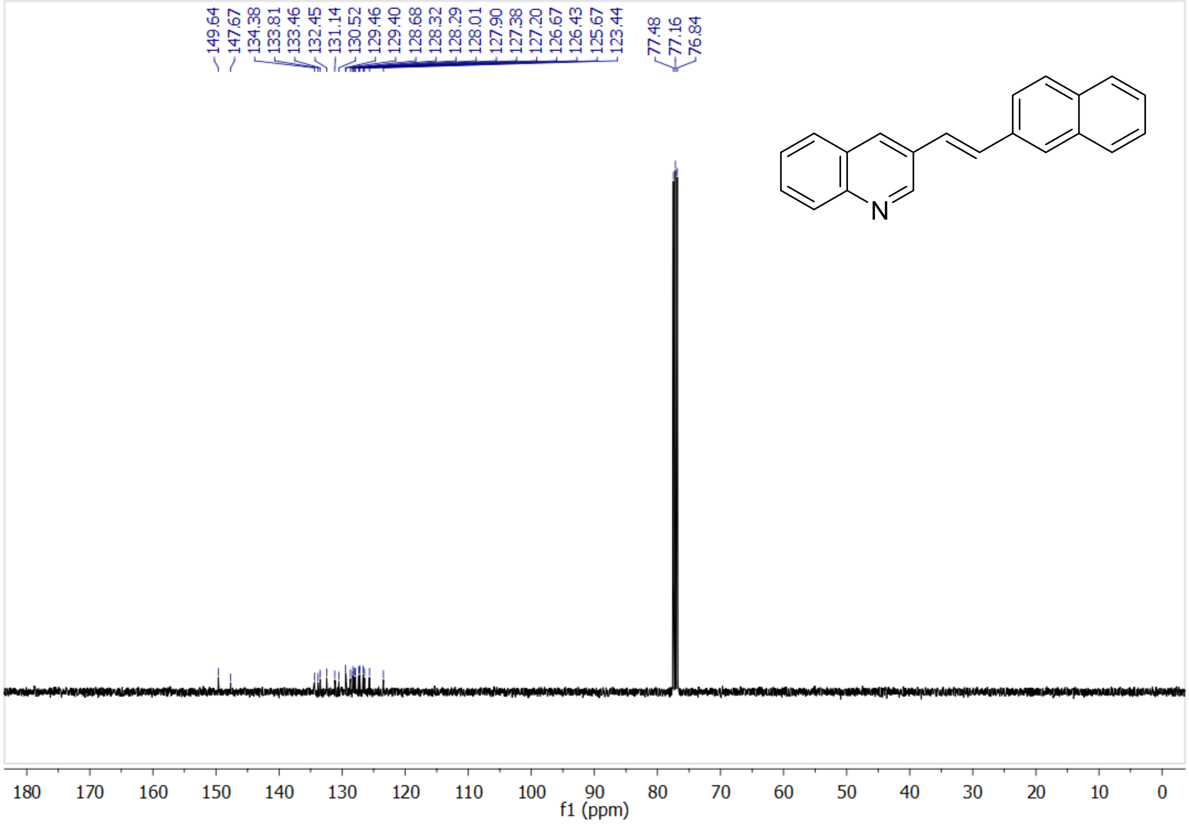
*^{13}C-NMR of (Z/E)-5-(2-(naphthalen-2-yl)vinyl)benzo[c][1,2,5]thiadiazole (**1n**)*



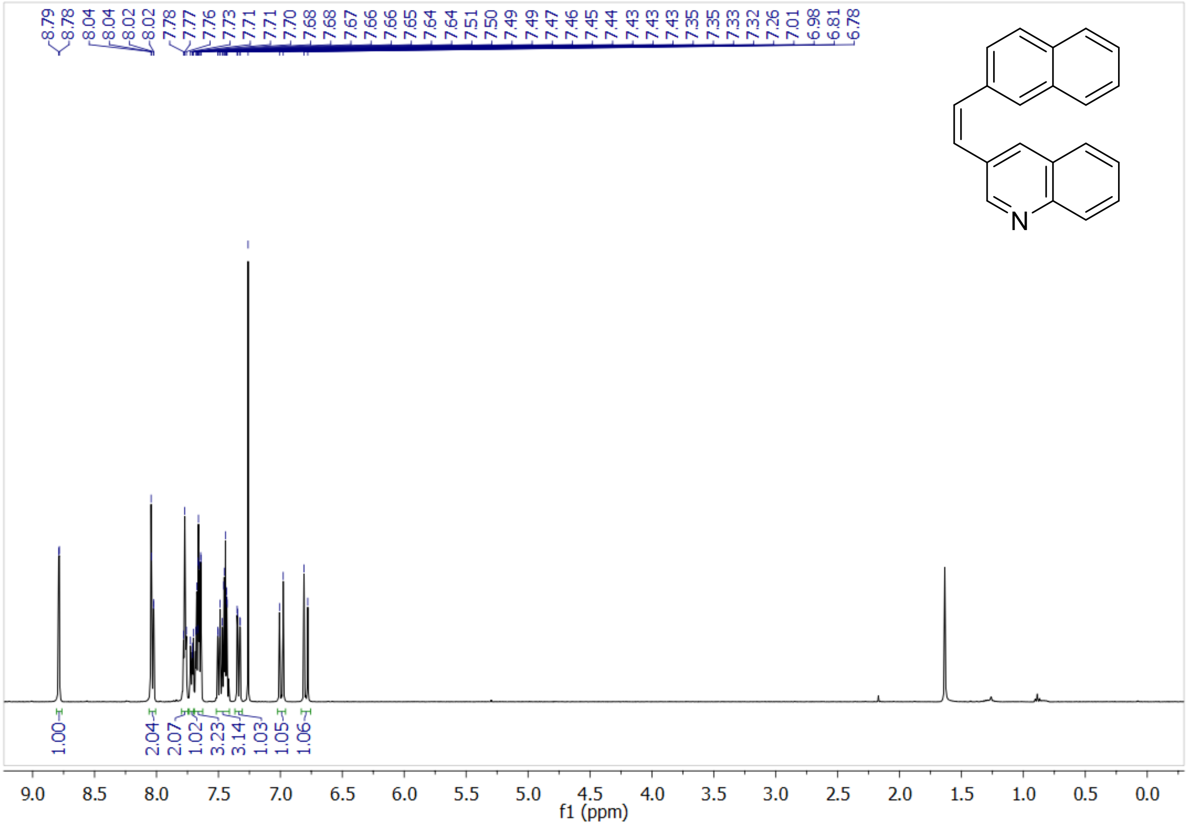
*^{1}H-NMR of (E)-3-(2-(naphthalen-2-yl)vinyl)quinoline (**1o**)*



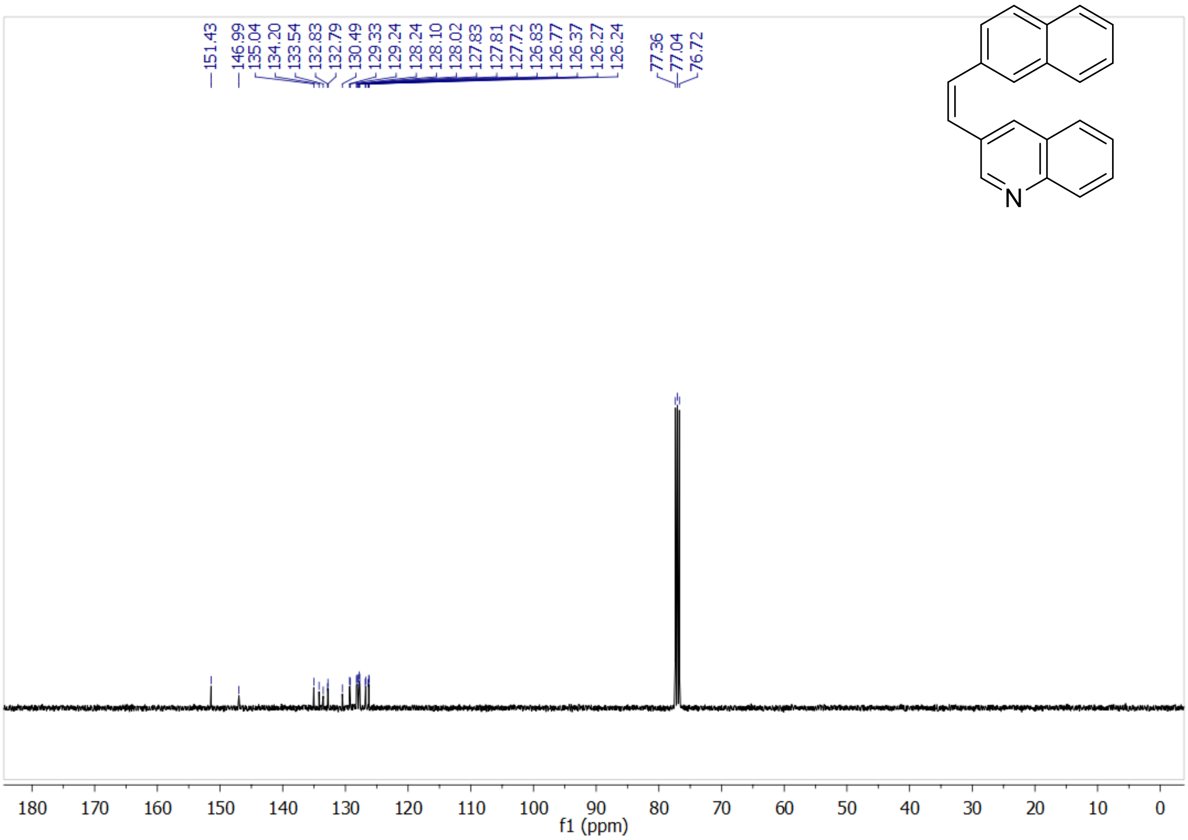
*^{13}C-NMR of (E)-3-(2-(naphthalen-2-yl)vinyl)quinoline (**1o**)*



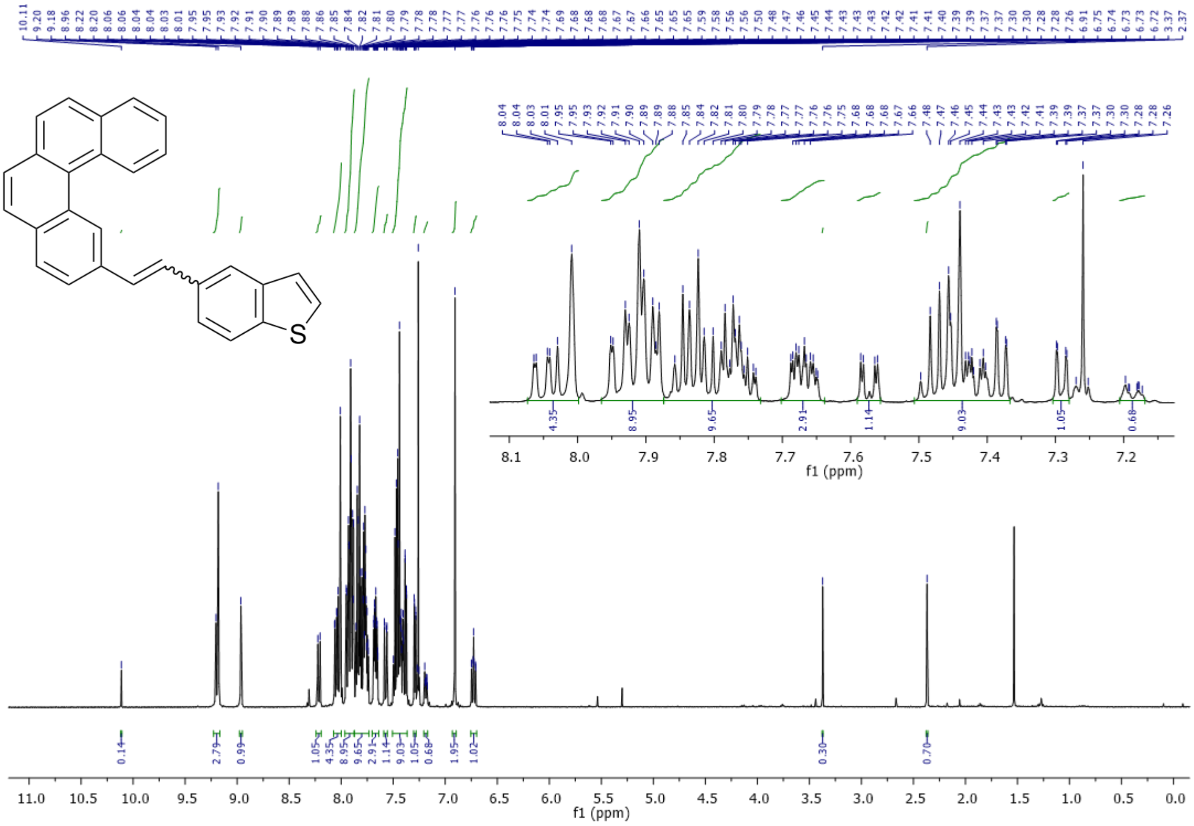
*^{1}H-NMR of (Z)-3-(2-(naphthalen-2-yl)vinyl)quinoline (**1o**)*



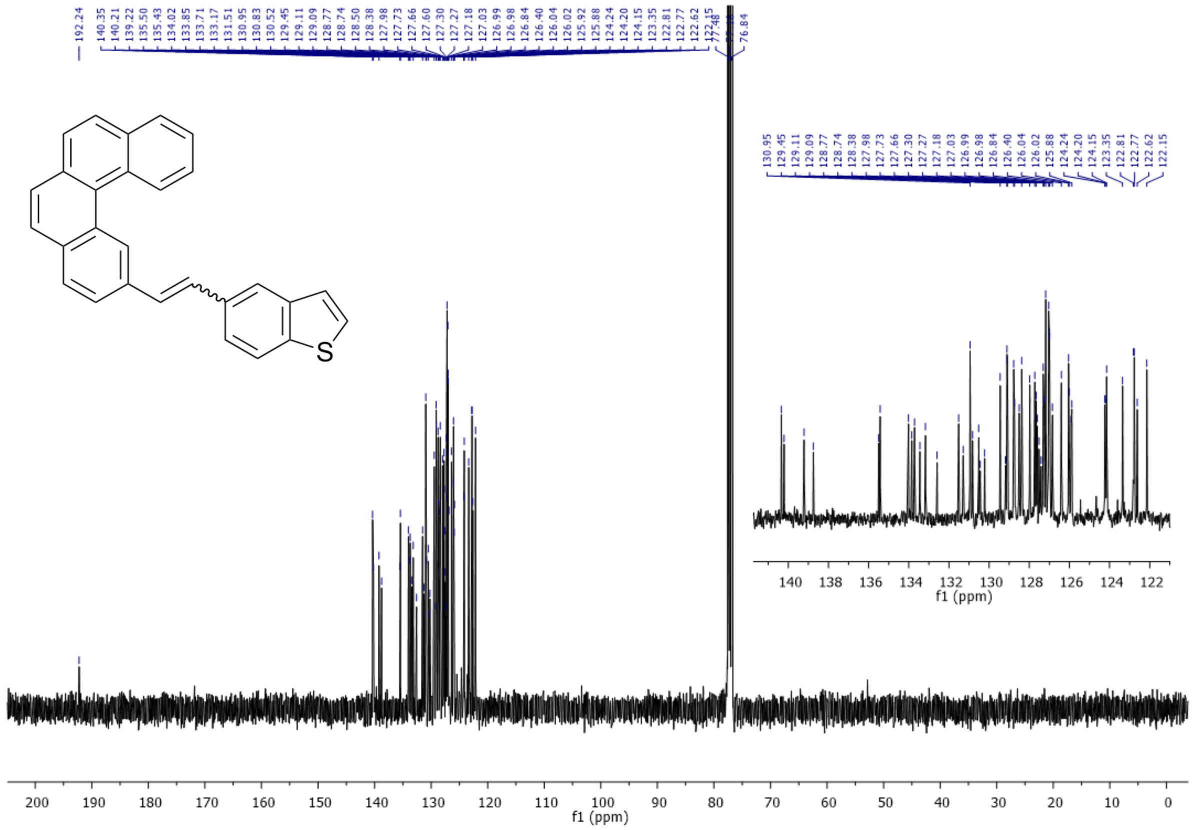
*^{13}C-NMR of (Z)-3-(2-(naphthalen-2-yl)vinyl)quinoline (**1o**)*



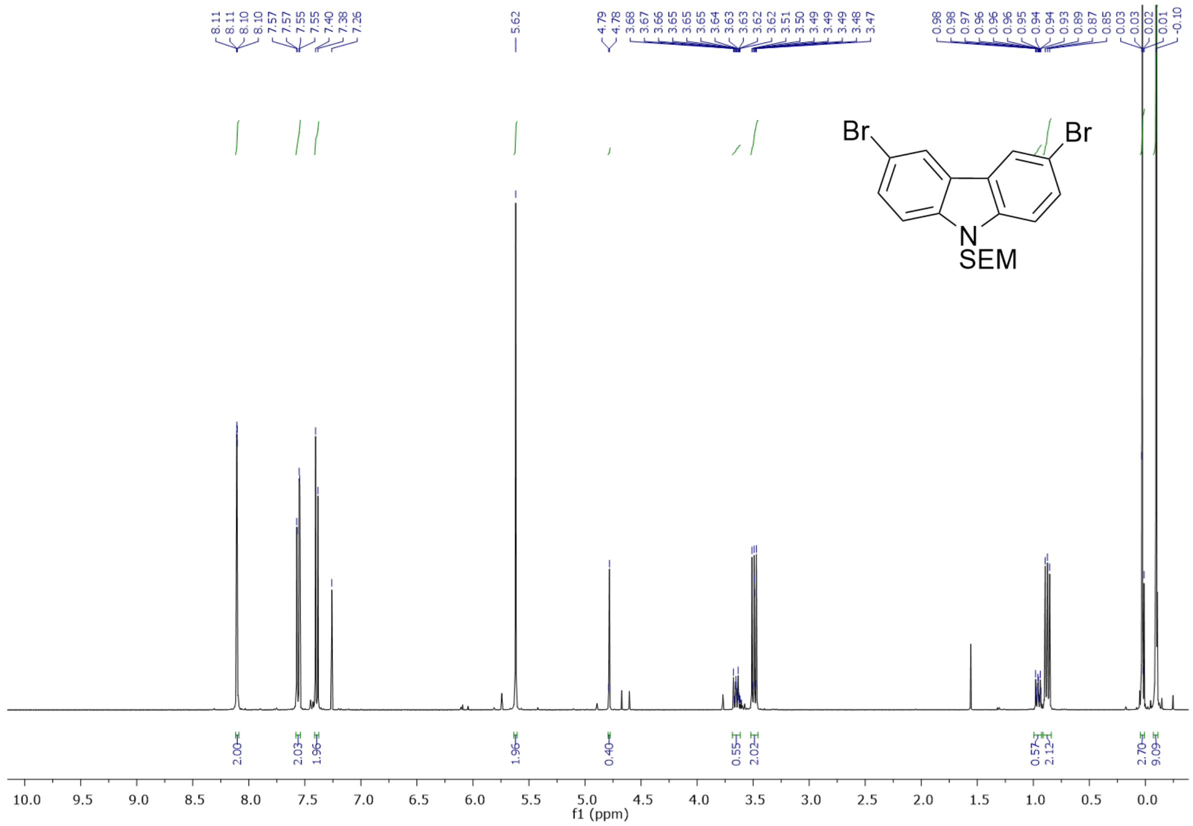
*^{1}H-NMR of 5-(2-(benzo[c]phenanthren-2-yl)vinyl)benzo[b]thiophene (**1p**)*



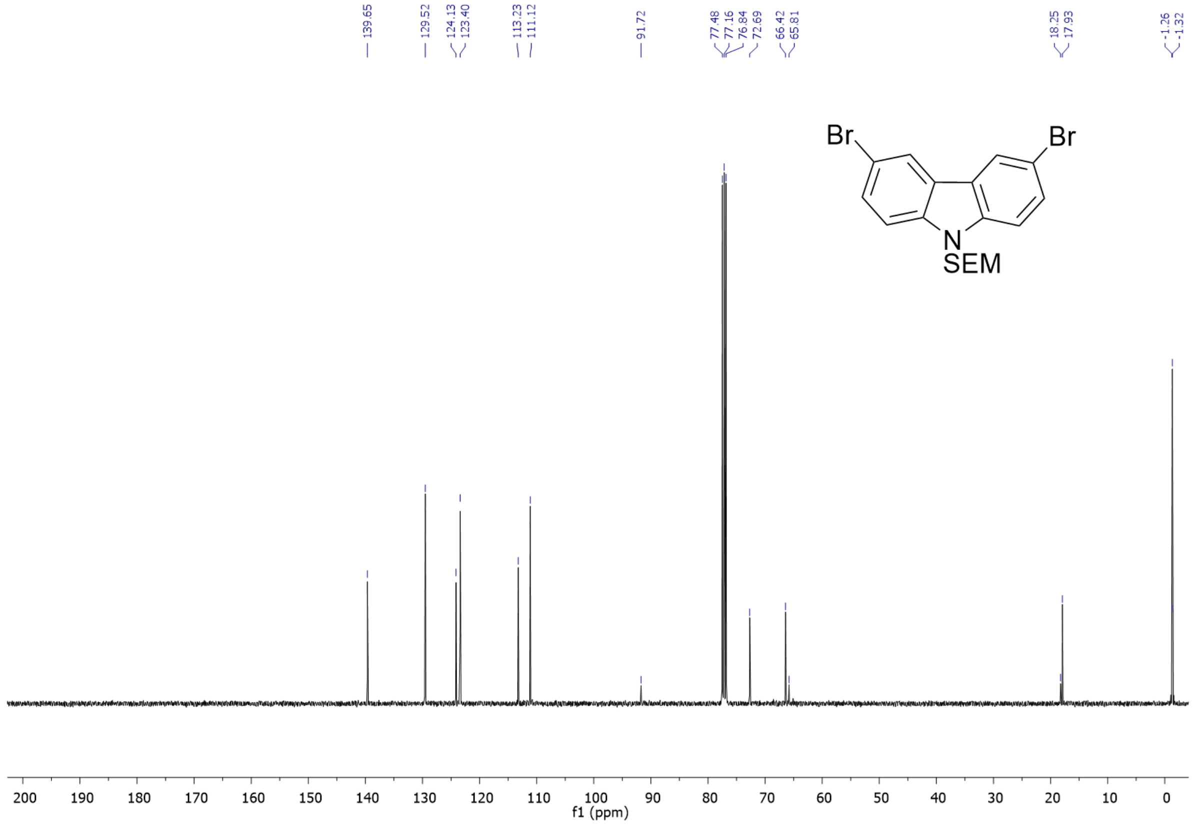
*^{13}C-NMR of 5-(2-(benzo[c]phenanthren-2-yl)vinyl)benzo[b]thiophene (**1p**)*



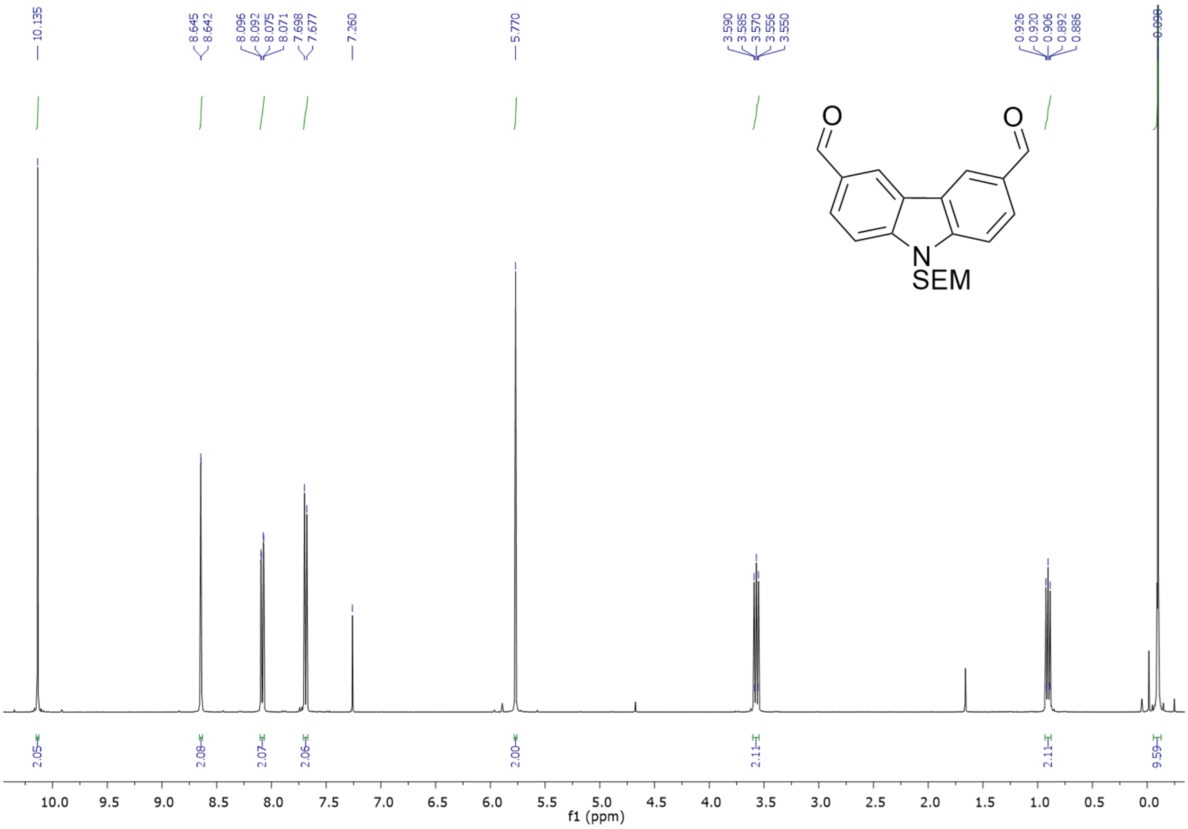
*^{1}H-NMR of 3,6-dibromo-9-((2-(trimethylsilyl)ethoxy)methyl)-9*H*-carbazole (**1qa**)*



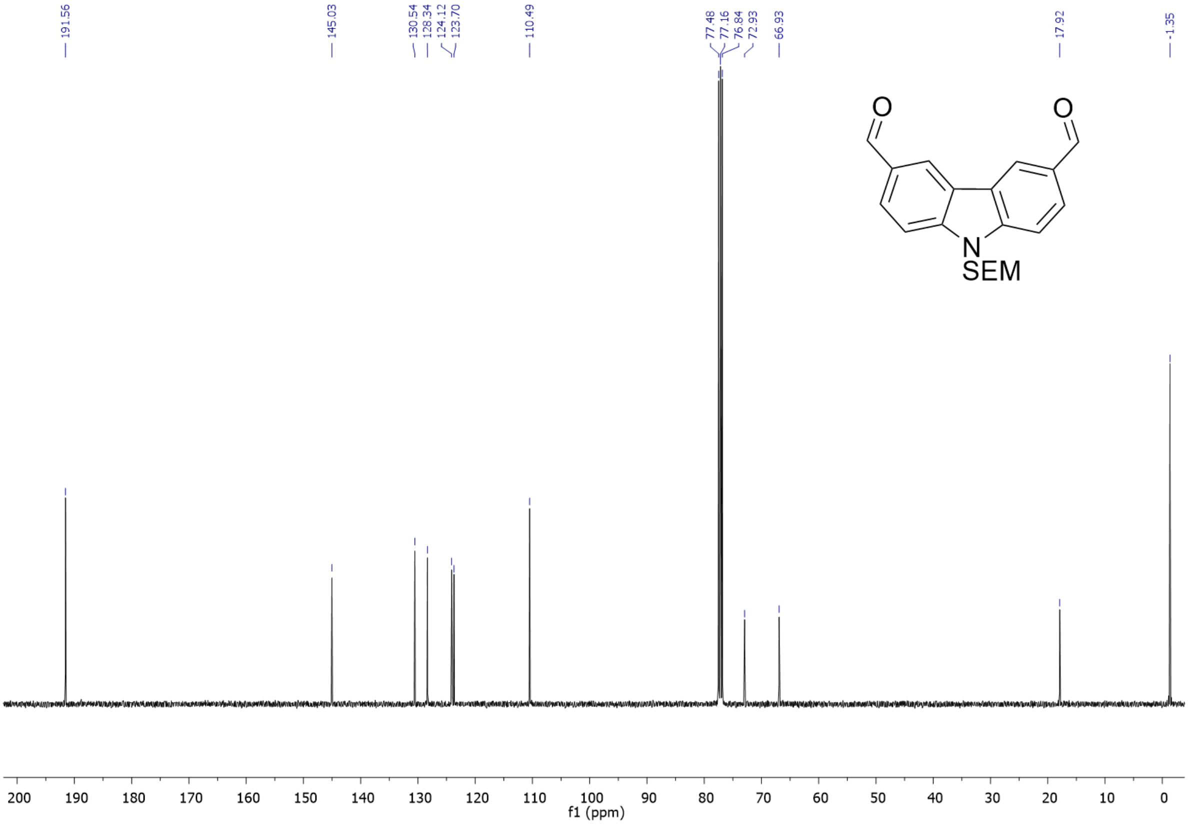
*^{13}C-NMR of 3,6-dibromo-9-((2-(trimethylsilyl)ethoxy)methyl)-9*H*-carbazole (**1qa**)*



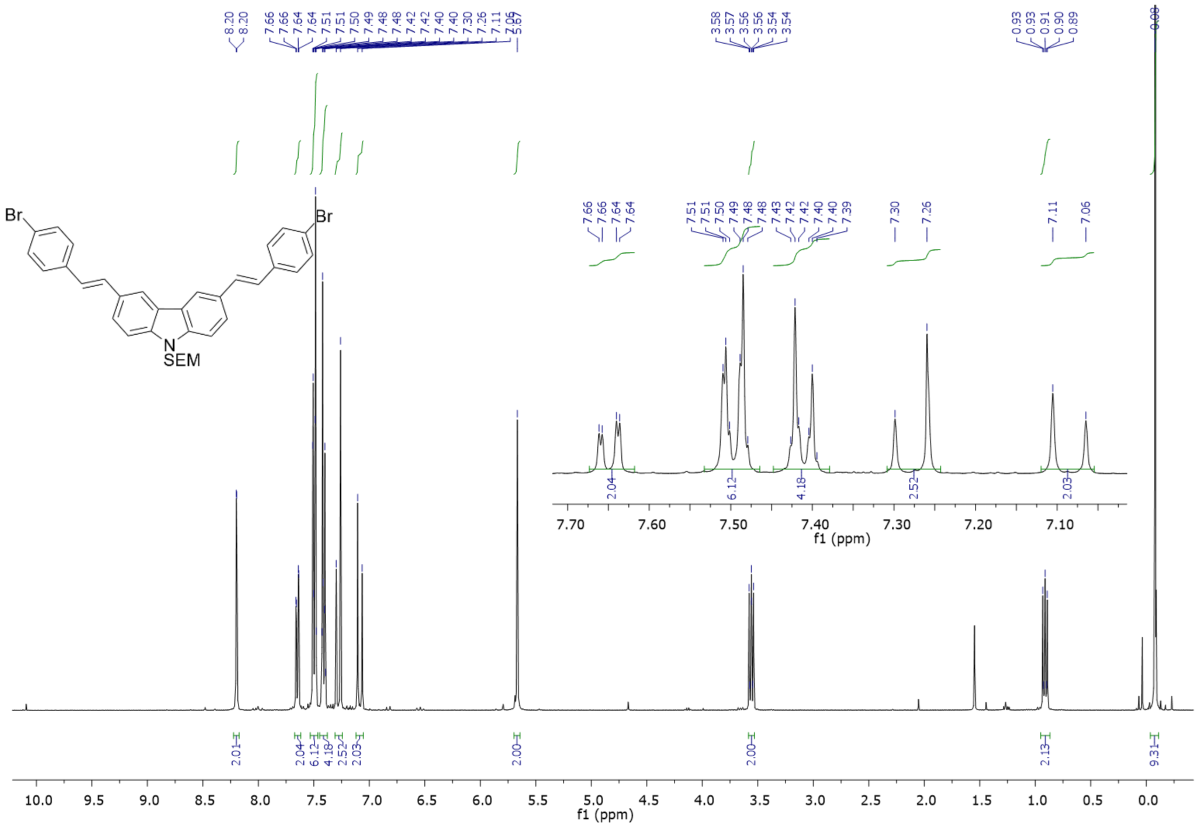
*^{1}H-NMR of 9-((2-(trimethylsilyl)ethoxy)methyl)-9H-carbazole-3,6-dicarbaldehyde (**1qb**)*



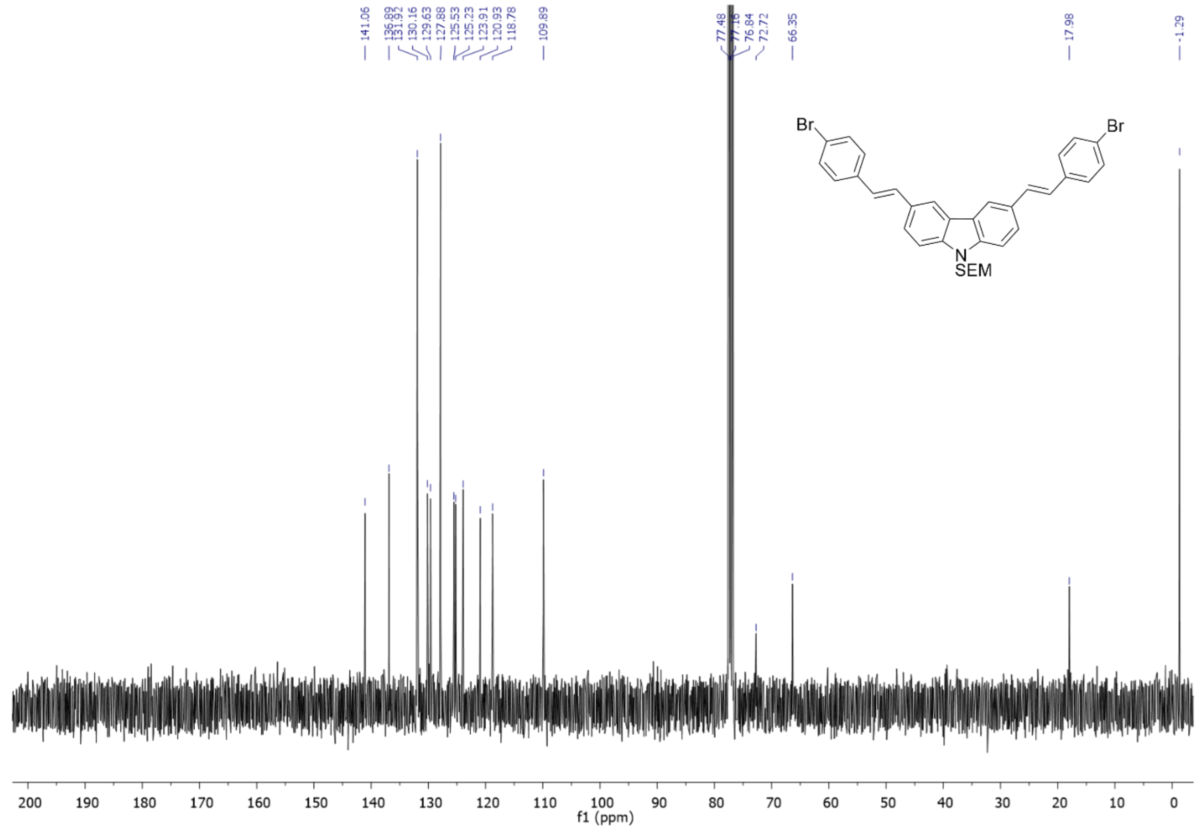
*^{13}C-NMR of 9-((2-(trimethylsilyl)ethoxy)methyl)-9H-carbazole-3,6-dicarbaldehyde (**1qb**)*



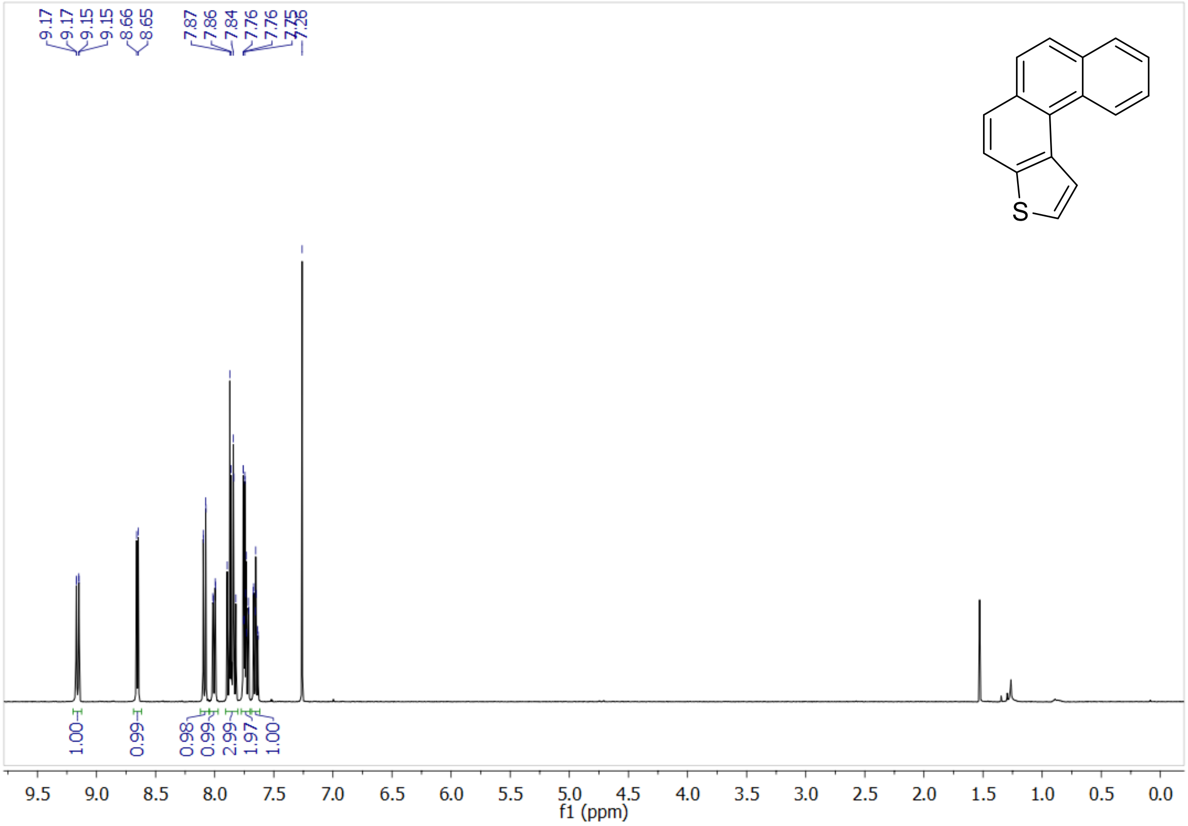
^{1}H-NMR of 3,6-bis((E)-4-bromostyryl)-9-((2-(trimethylsilyl)ethoxy)methyl)-9H-carbazole (**1q**)



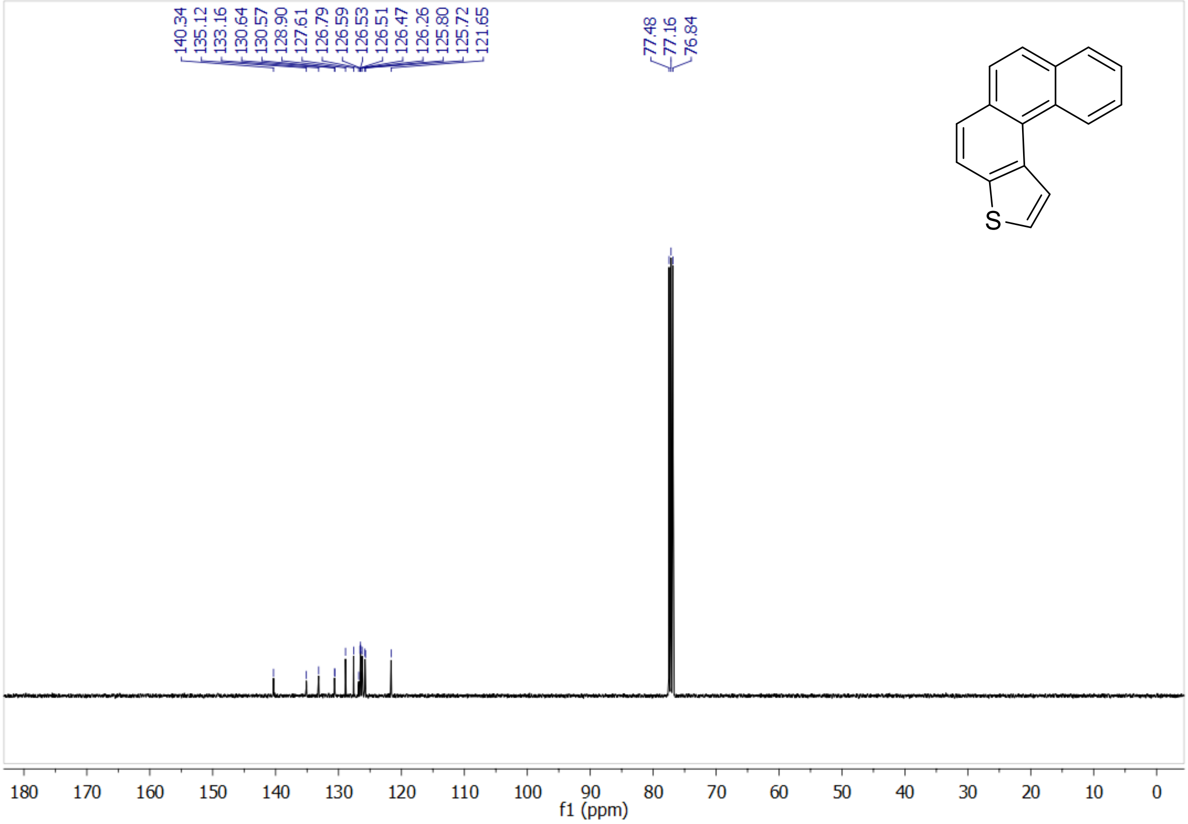
^{13}C-NMR of 3,6-bis((E)-4-bromostyryl)-9-((2-(trimethylsilyl)ethoxy)methyl)-9H-carbazole (**1q**)



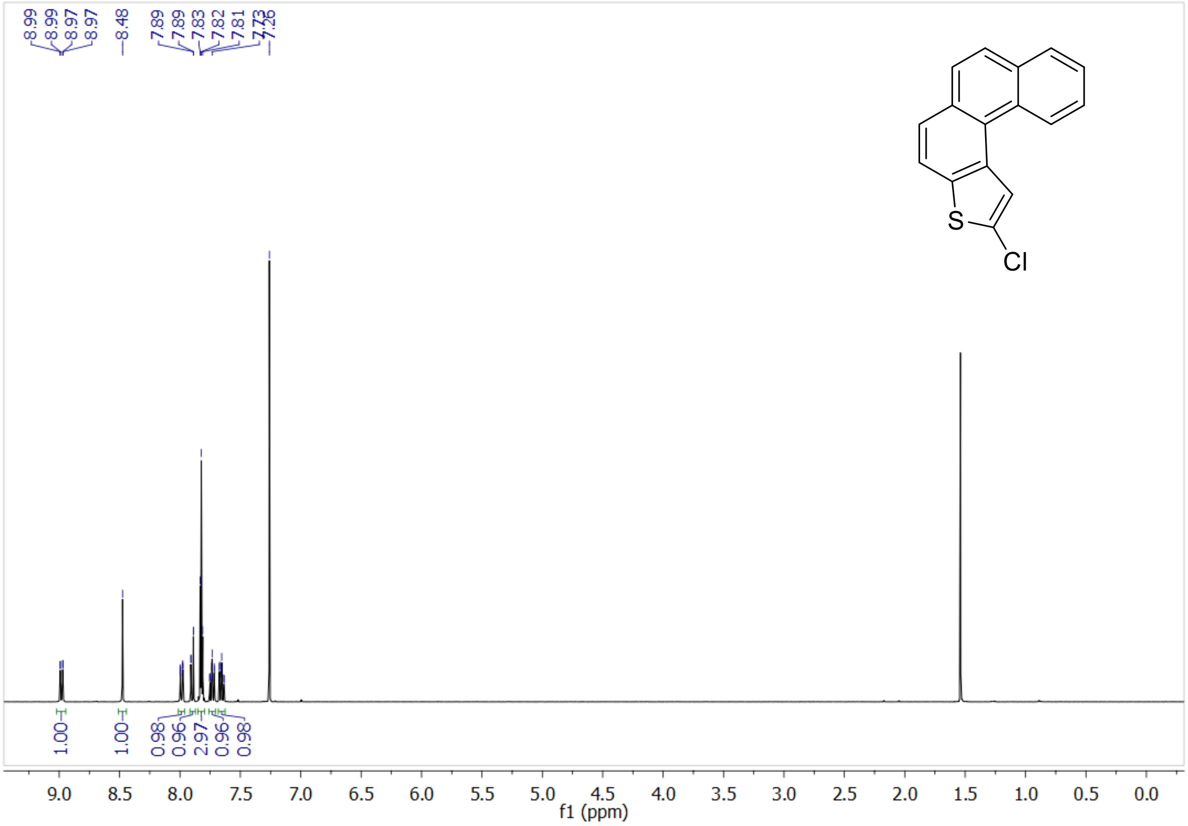
^{1}H-NMR of thia[4]helicene (**2a**)



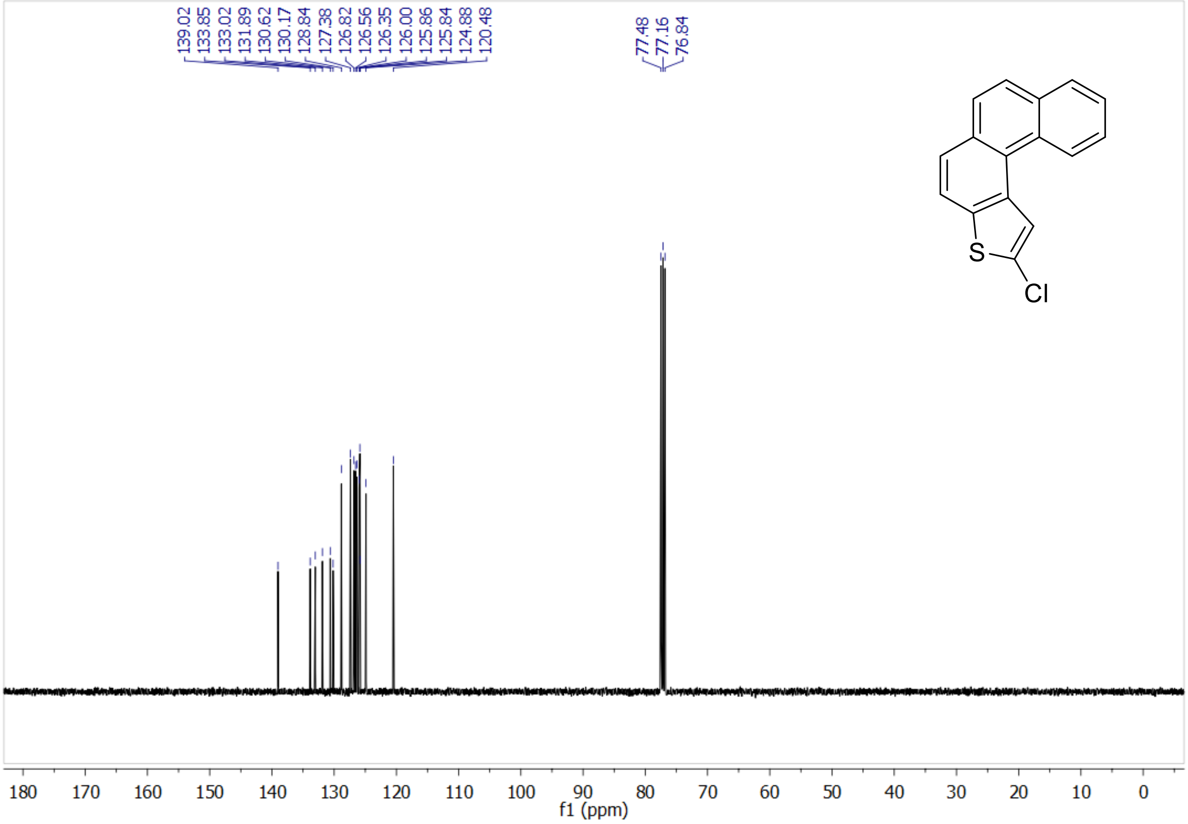
^{13}C-NMR of thia[4]helicene (**2a**)



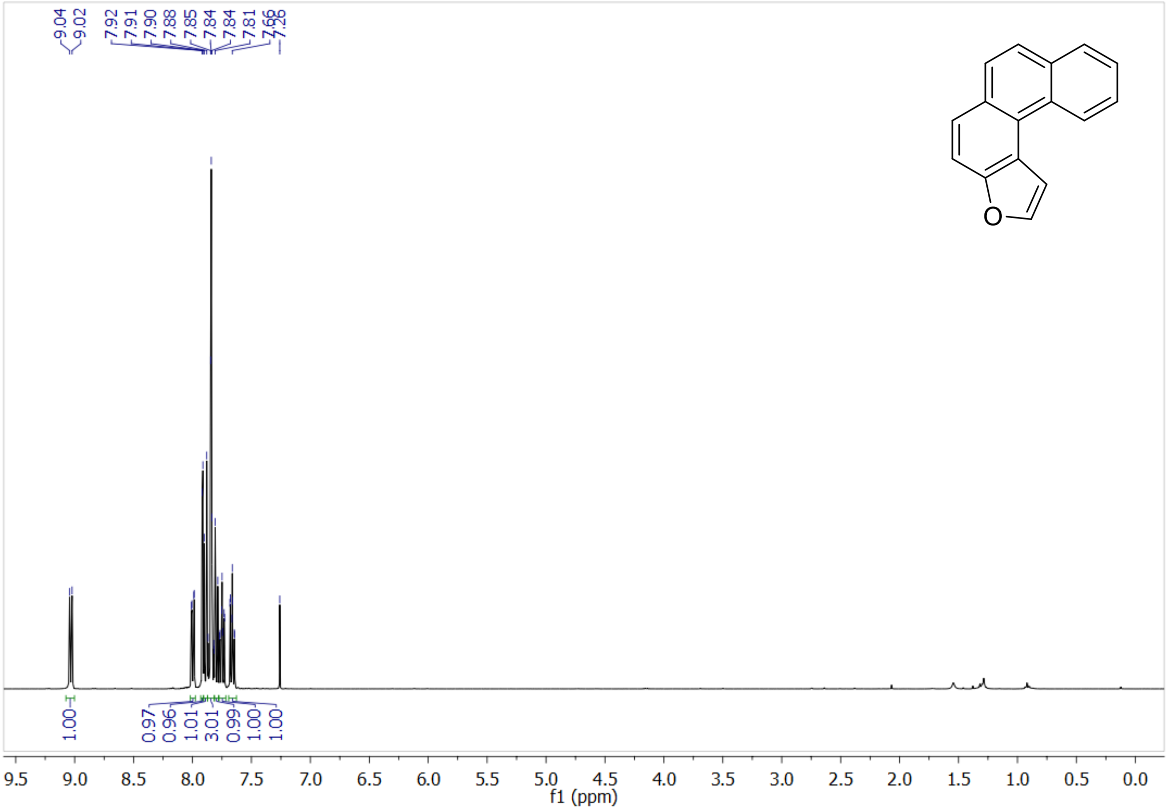
*^{1}H-NMR of 2-chlorothia[4]helicene (**2b**)*



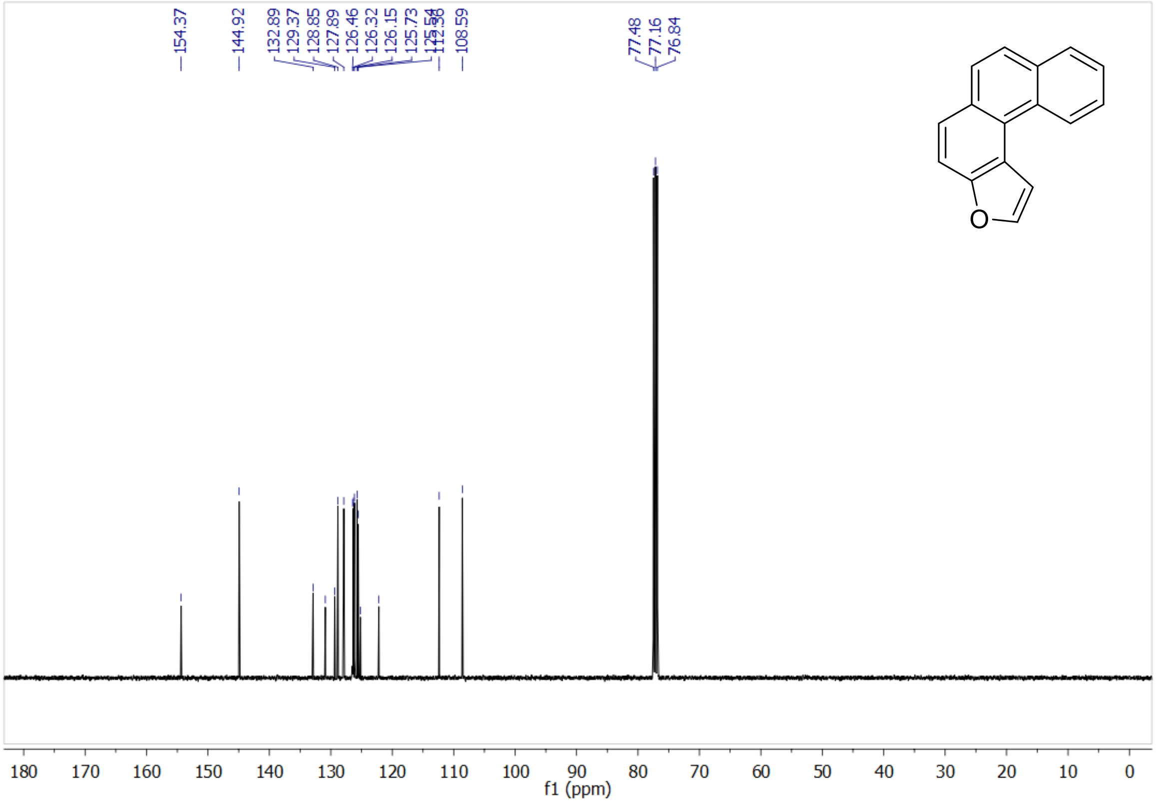
*^{13}C-NMR of 2-chlorothia[4]helicene (**2b**)*



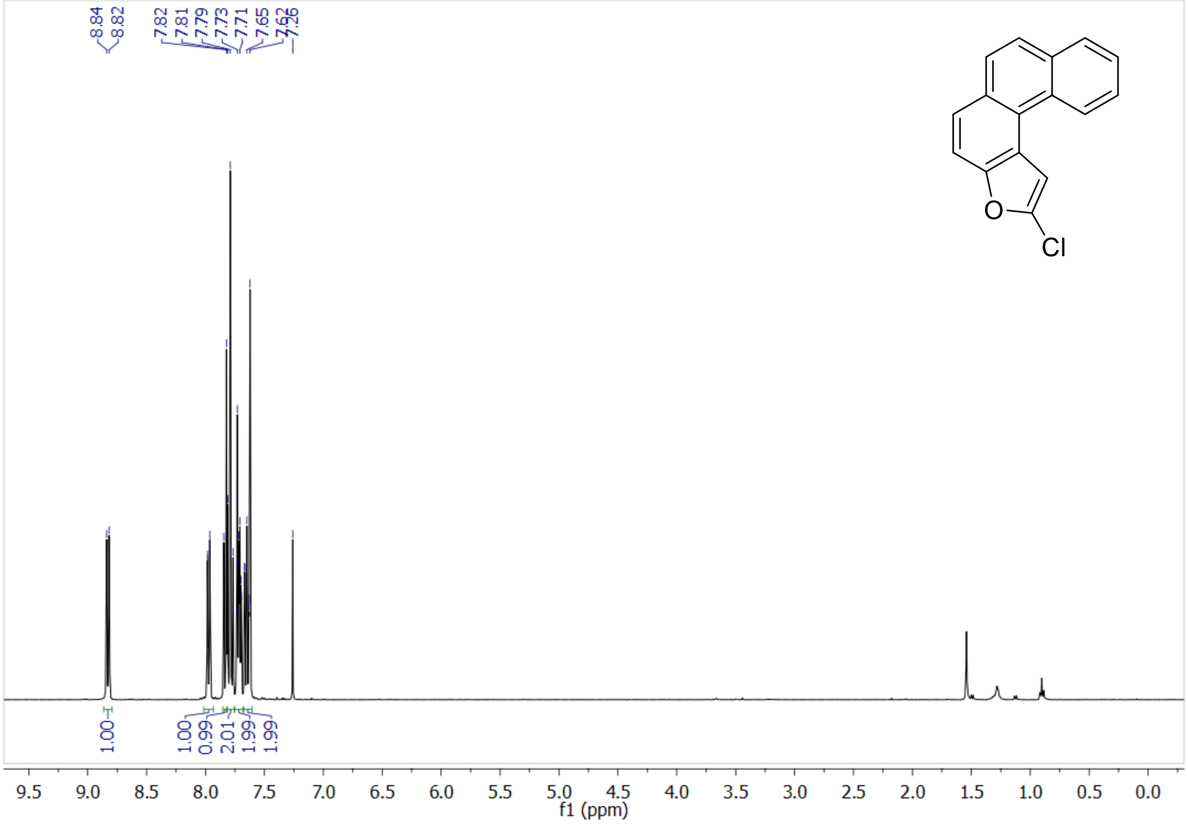
^{1}H-NMR of oxa[4]helicene (**2c**)



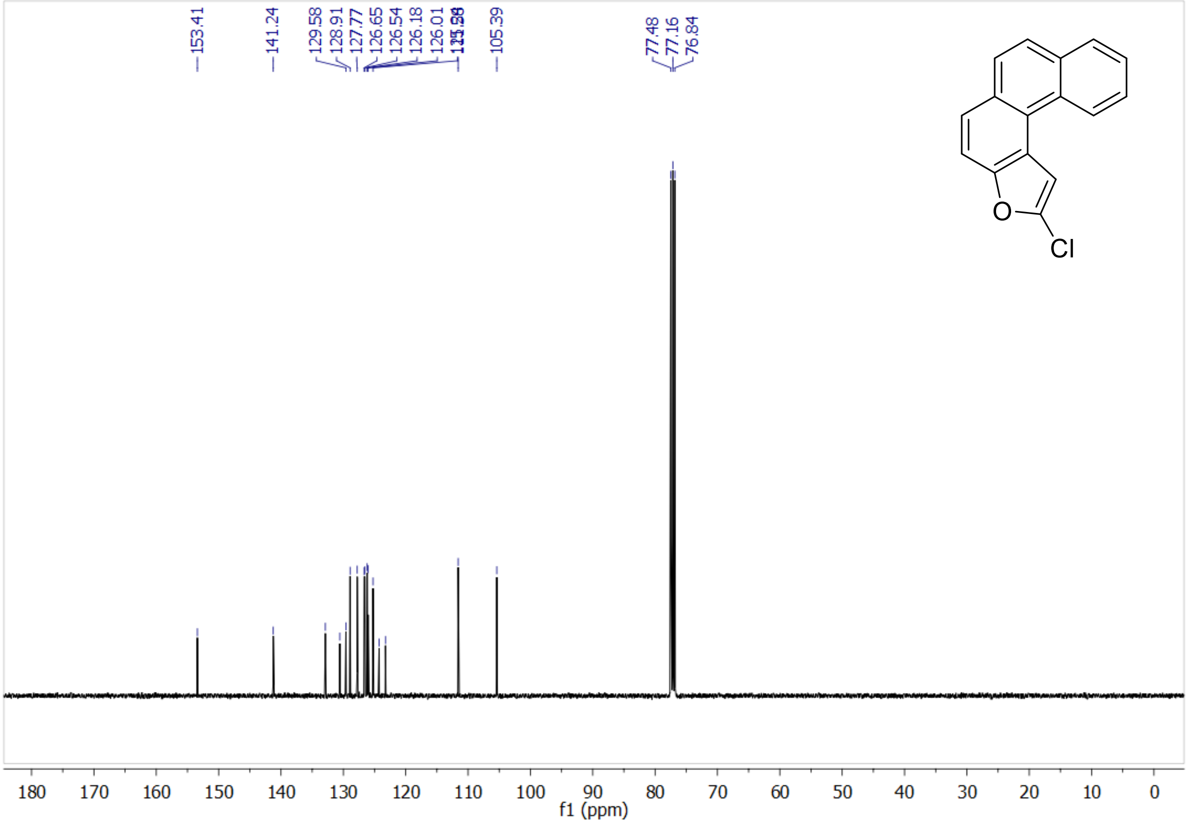
^{13}C-NMR of oxa[4]helicene (**2c**)



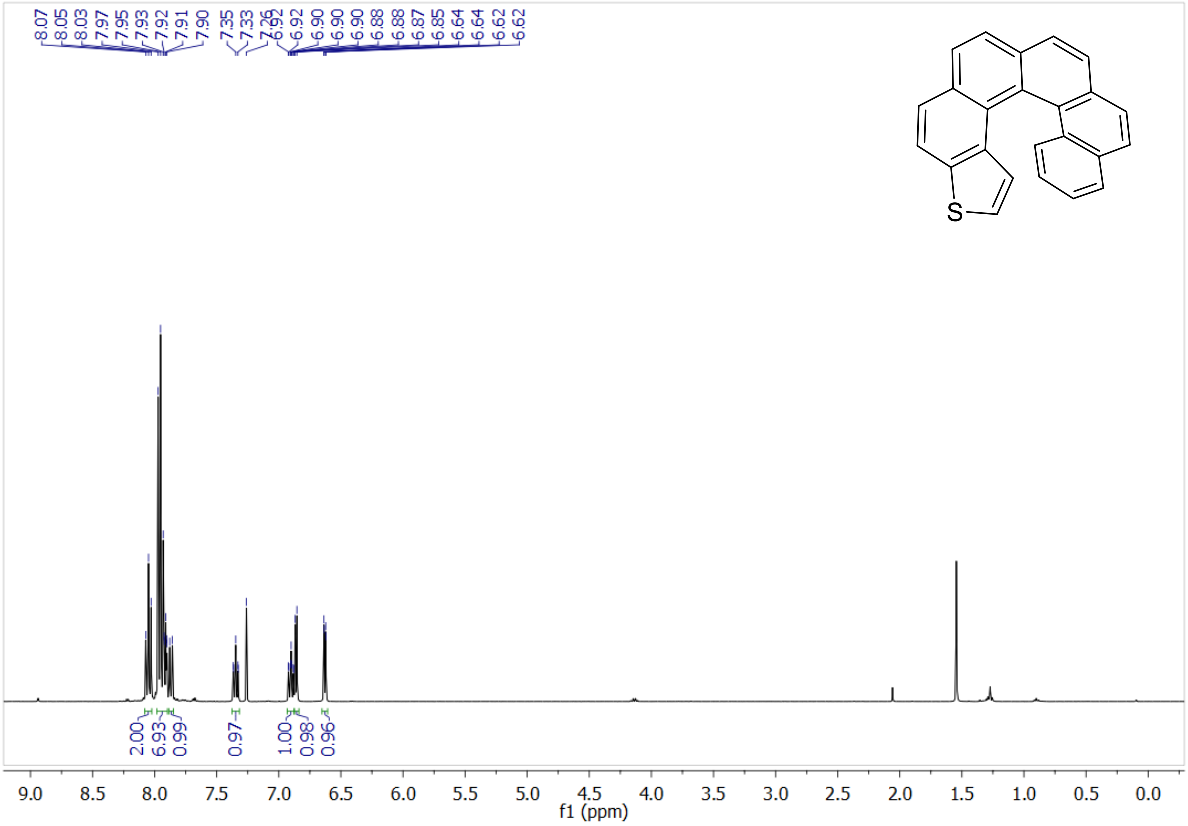
*^{1}H-NMR of 2-chlorooxa[4]helicene (**2d**)*



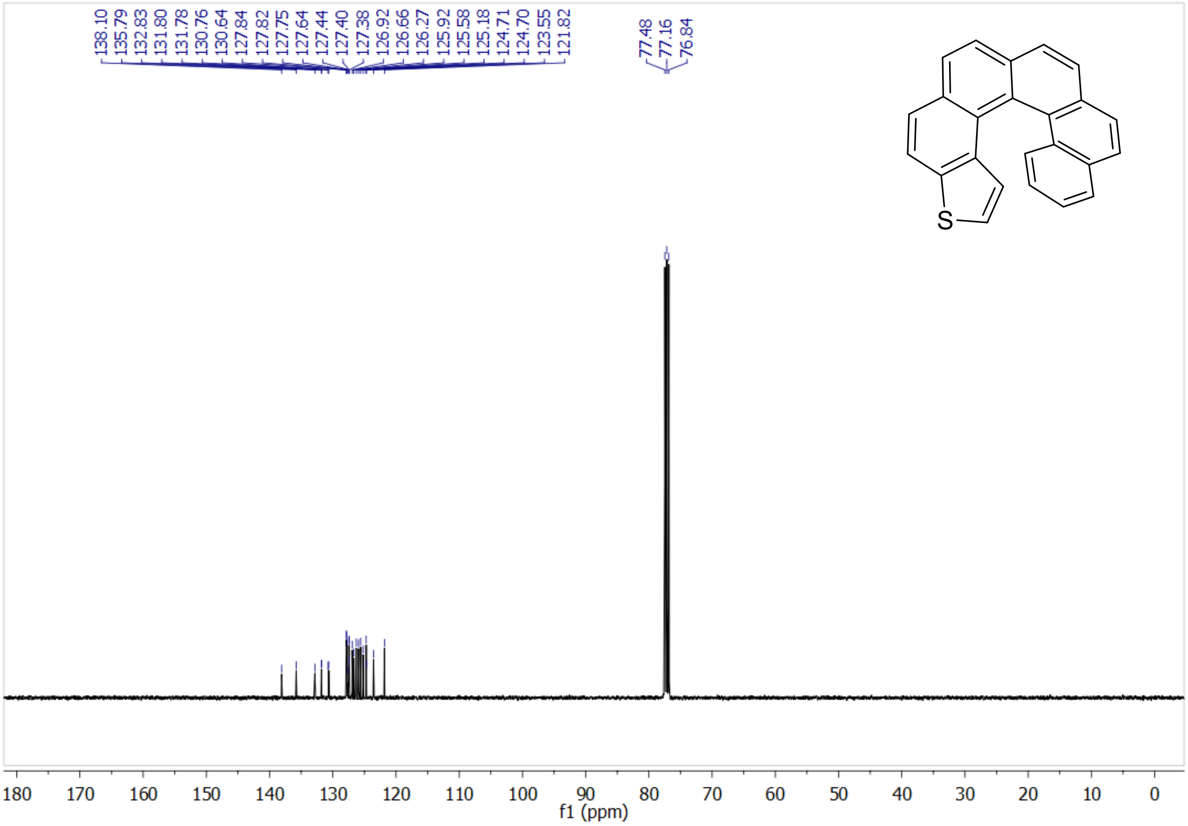
*^{13}C-NMR of 2-chlorooxa[4]helicene (**2d**)*



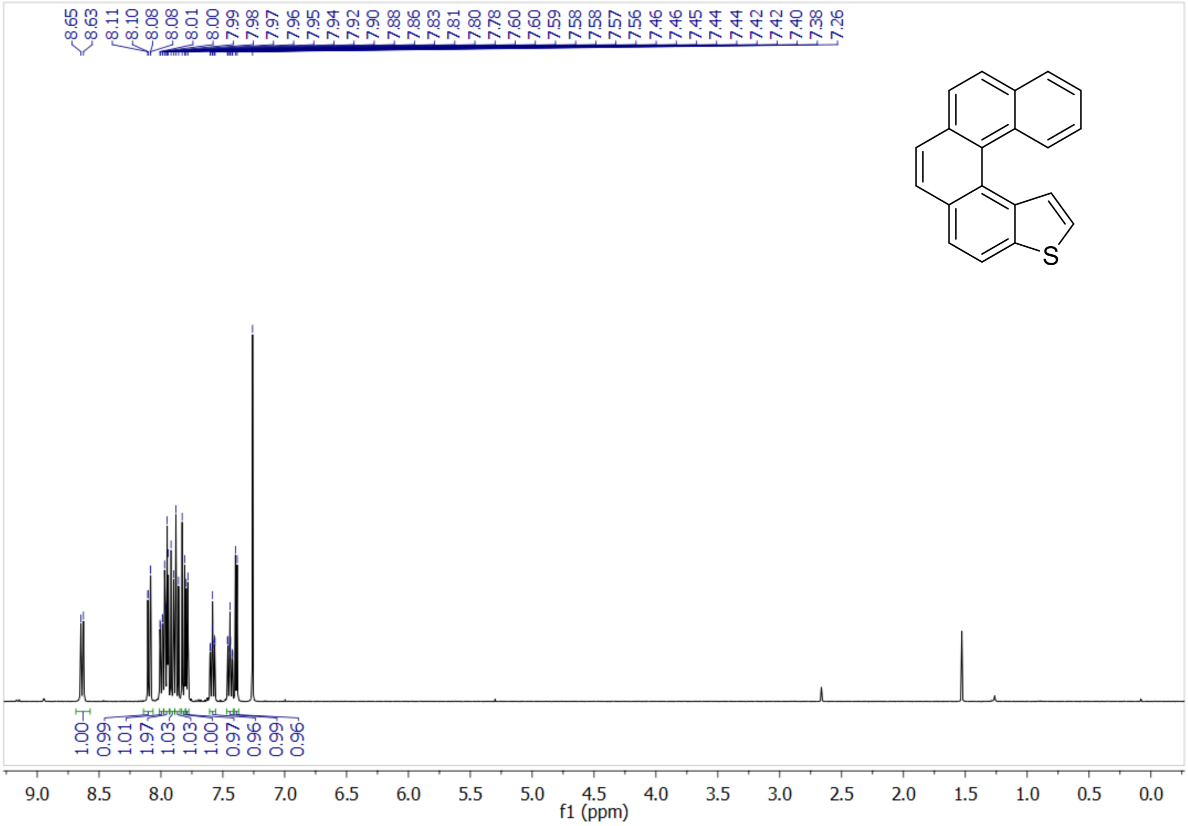
*^{1}H-NMR of thia[6]helicene (**2e**)*



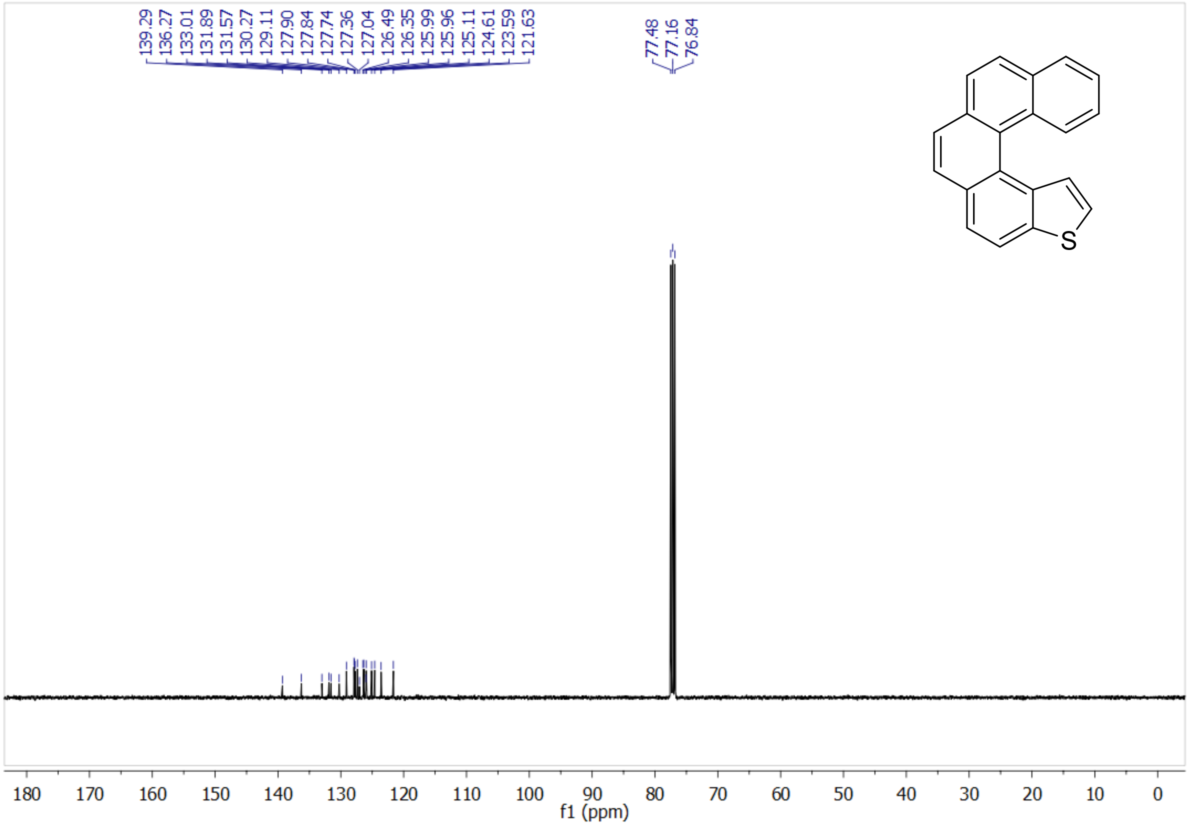
*^{13}C-NMR of thia[6]helicene (**2e**)*



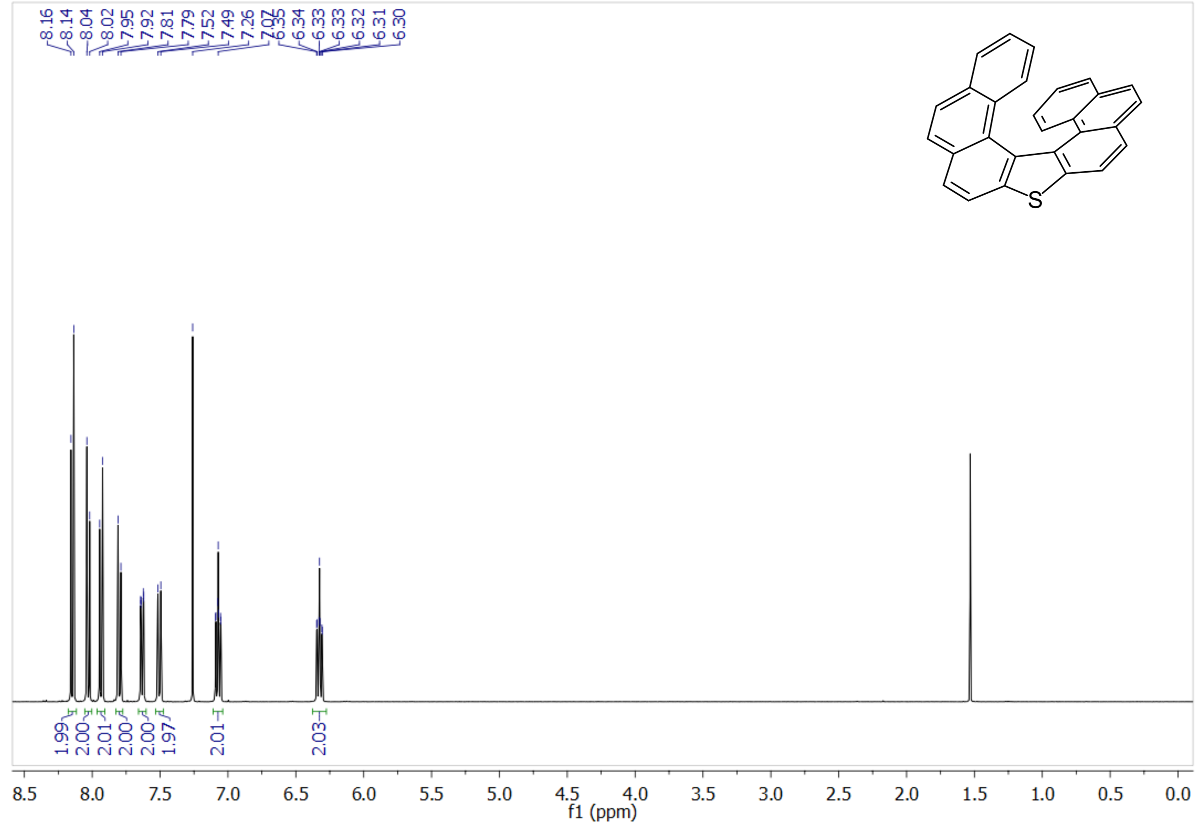
^{1}H-NMR of thia[5]helicene (**2f**)



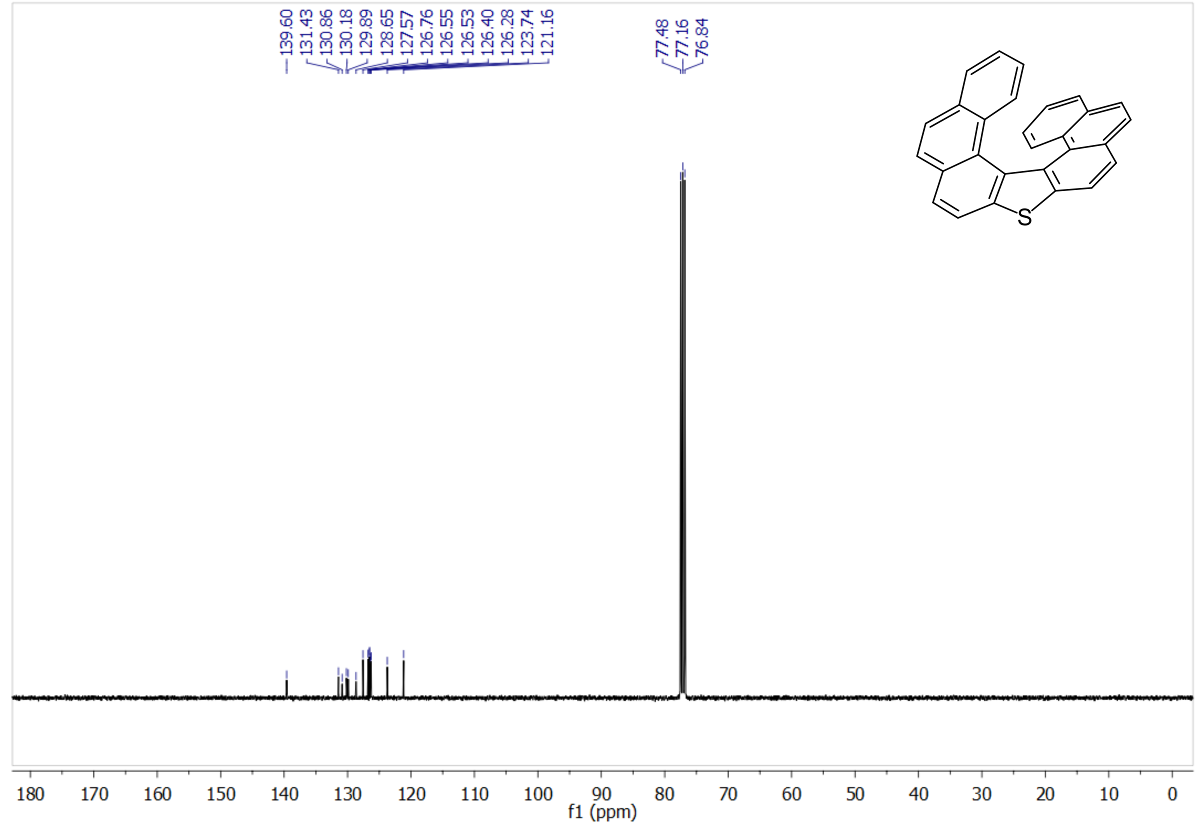
^{13}C-NMR of thia[5]helicene (**2f**)



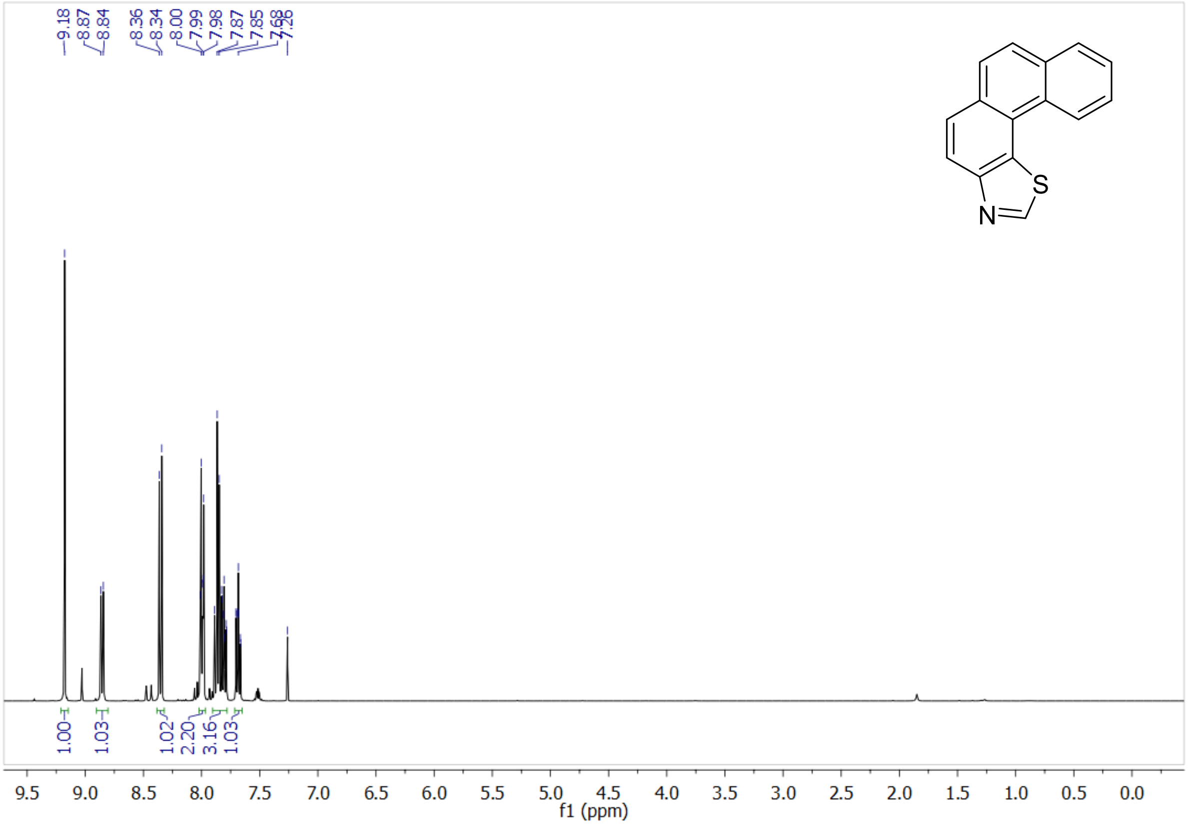
*^{1}H-NMR of thia[7]helicene (**2g**)*



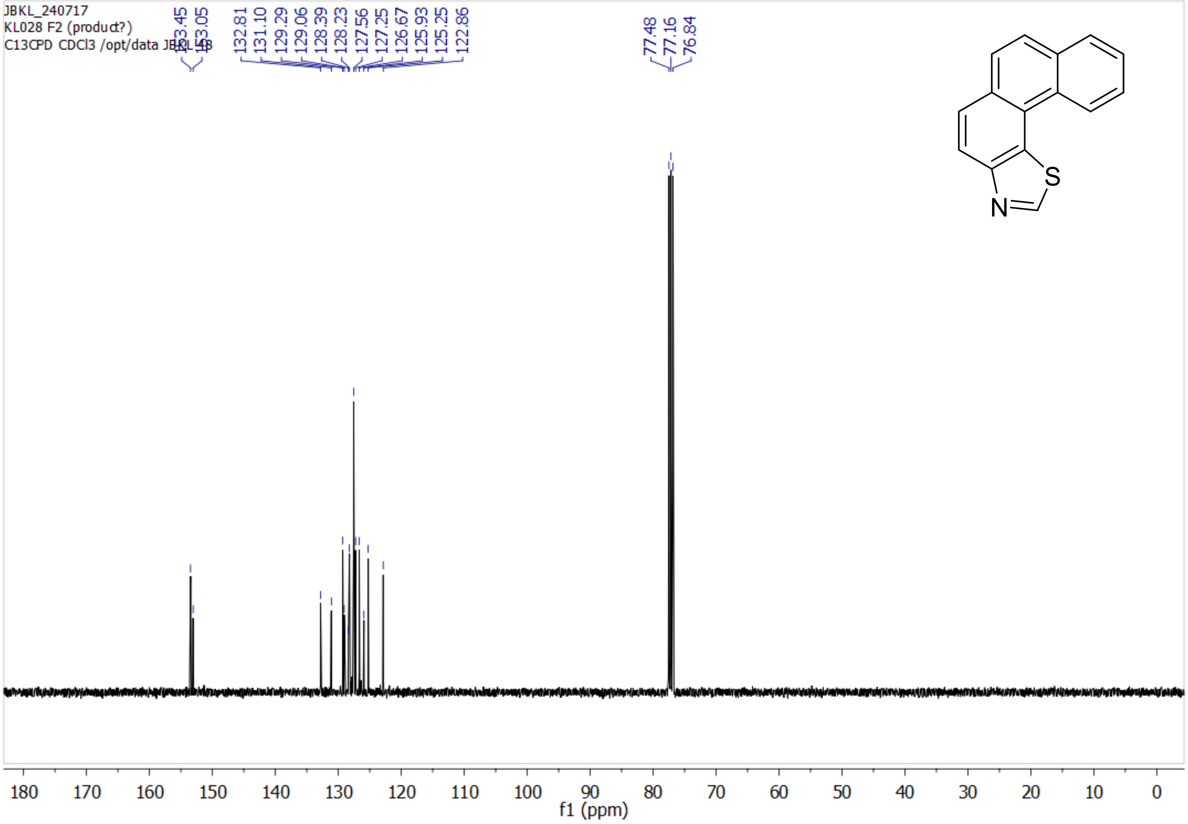
*^{13}C-NMR of thia[7]helicene (**2g**)*



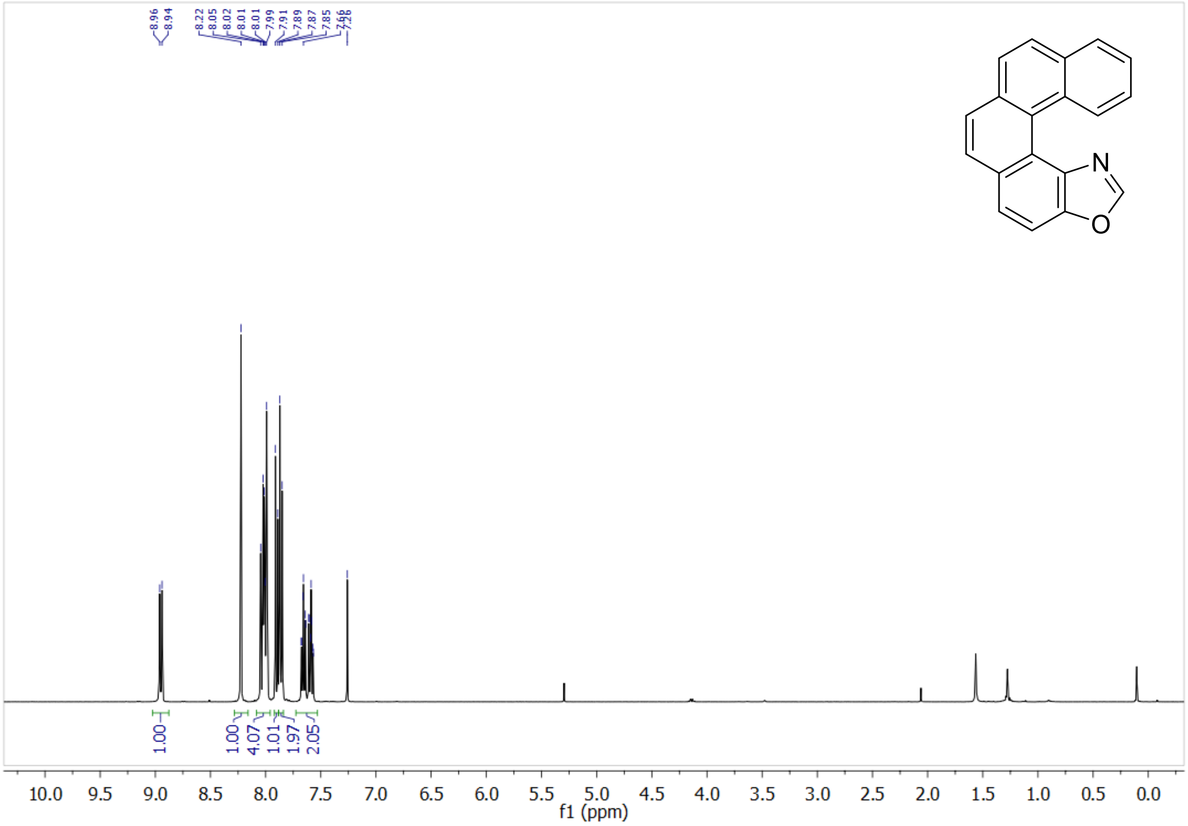
*^{1}H-NMR of thiaza[4]helicene (**2i**)*



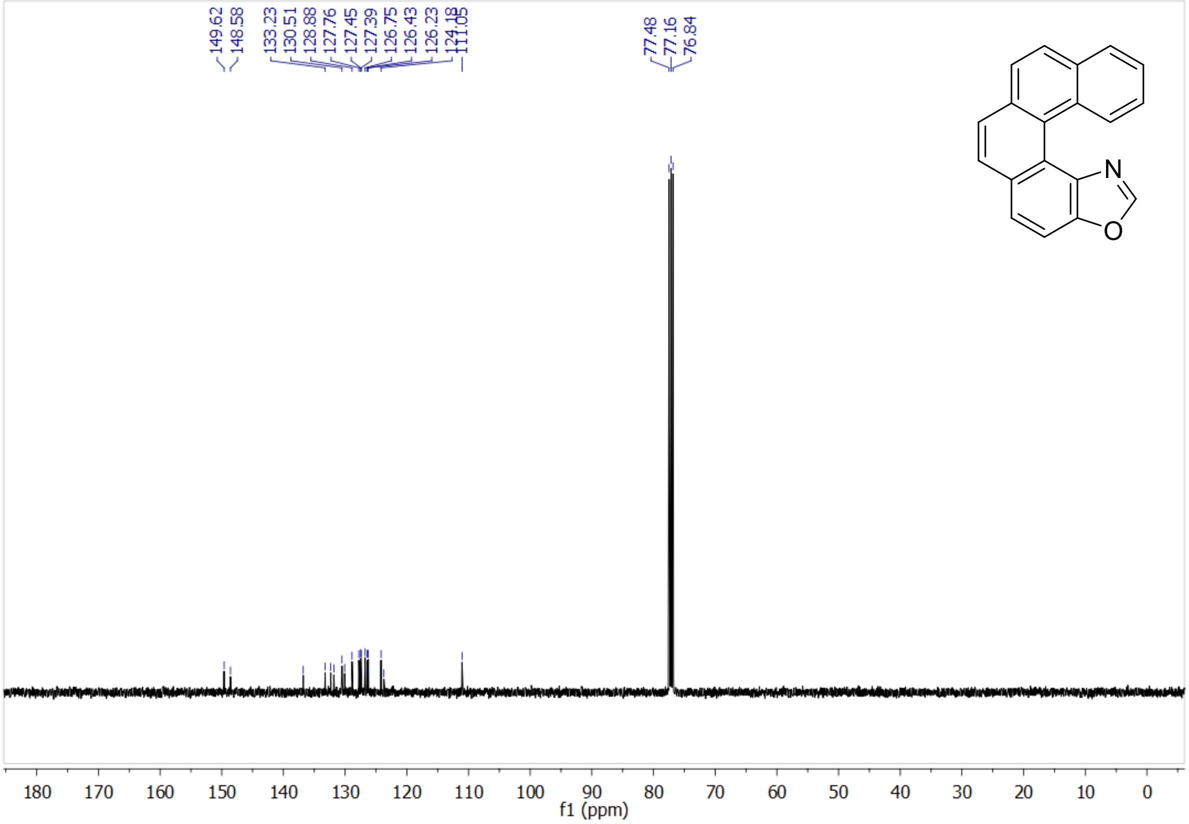
*^{13}C-NMR of thiaza[4]helicene (**2i**)*



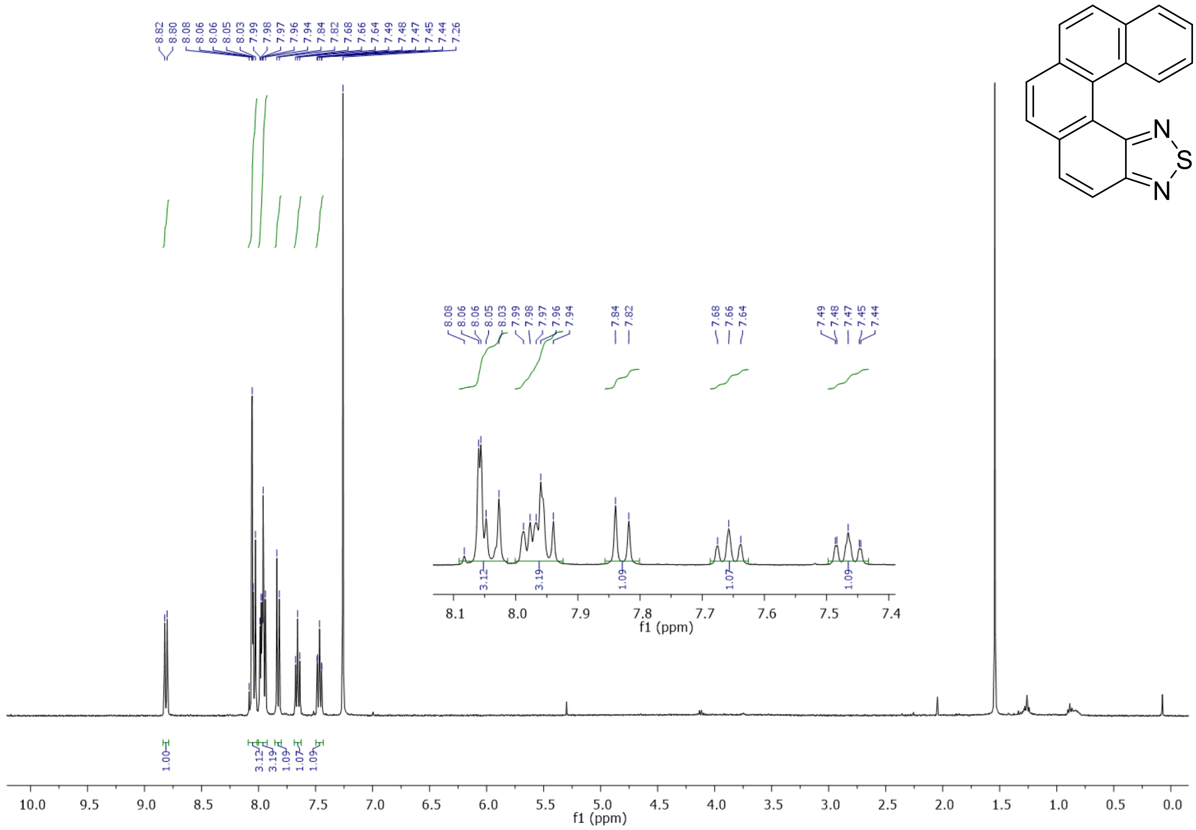
*^{1}H-NMR of oxaza[5]helicene (**2k**)*



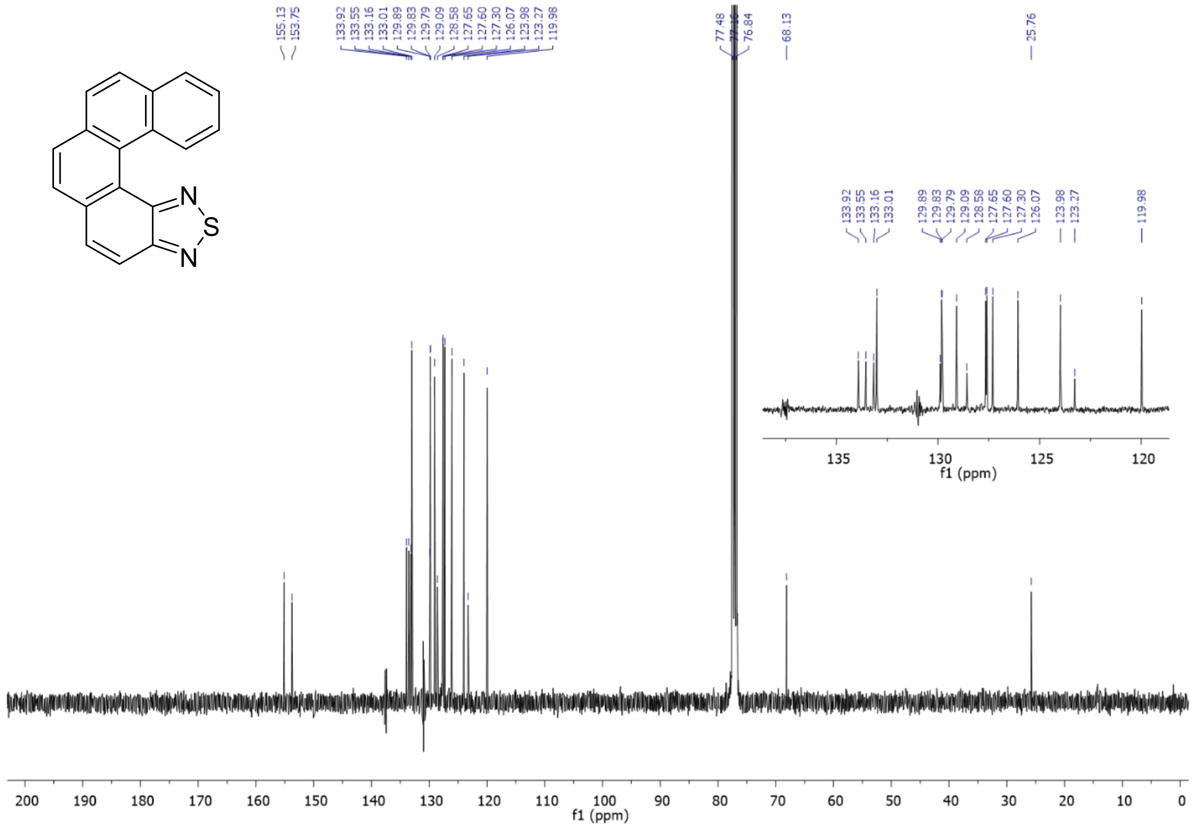
*^{13}C-NMR of oxaza[5]helicene (**2k**)*



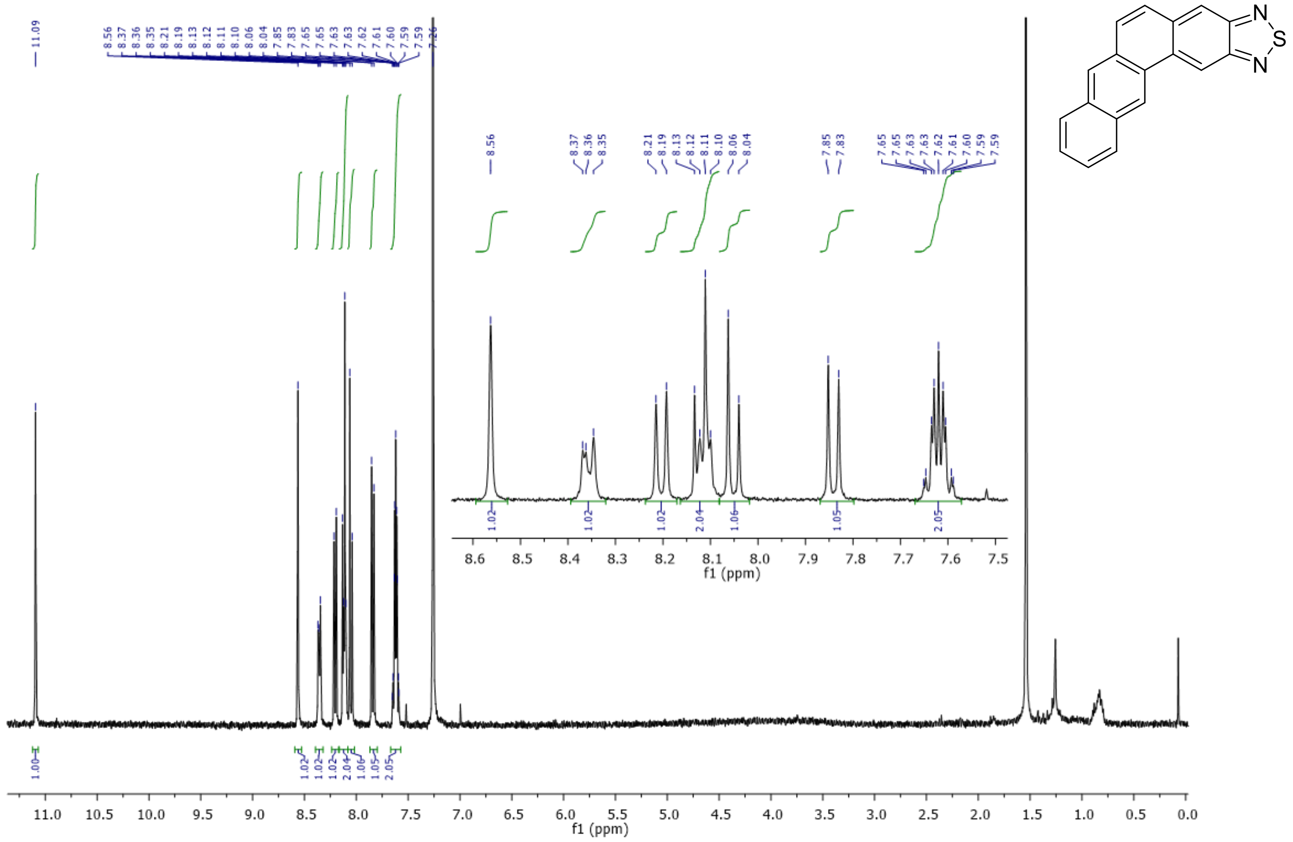
^{1}H-NMR of thiadiazo[5]helicene (**2n**)



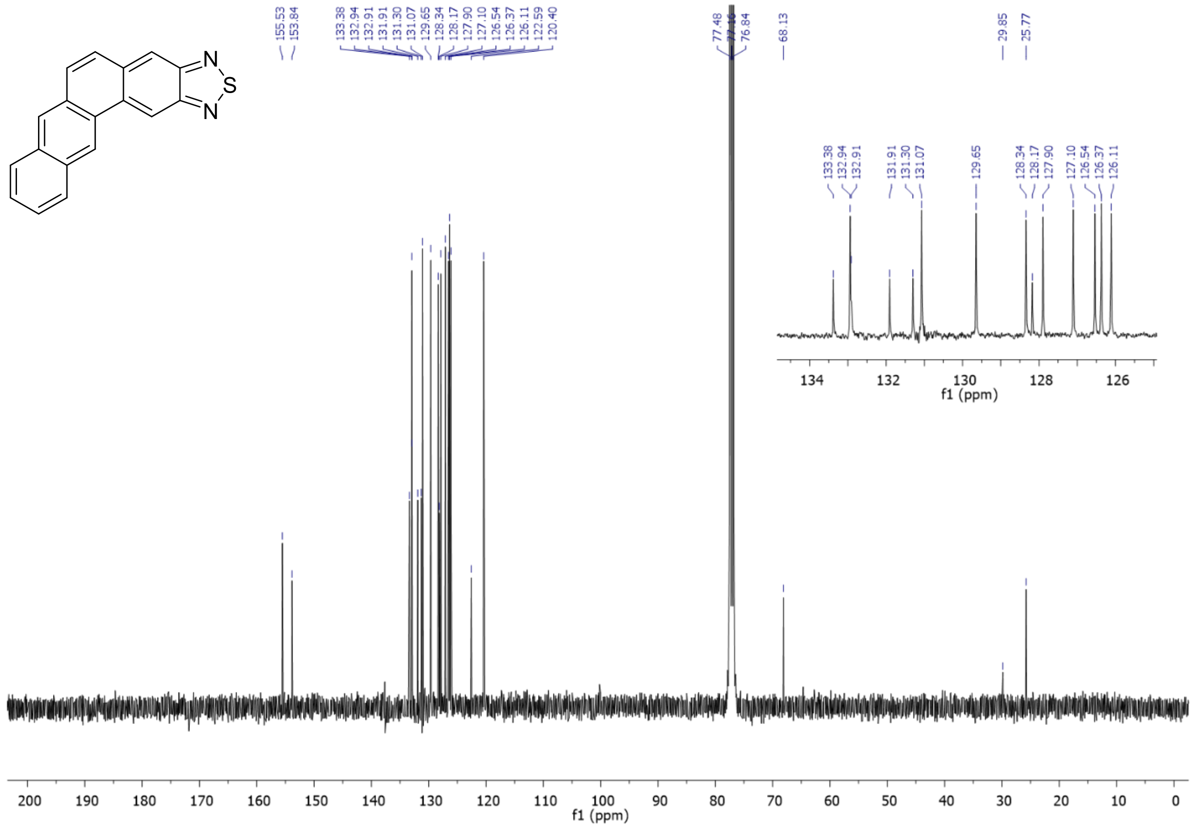
^{13}C-NMR of thiadiazo[5]helicene (**2n**)



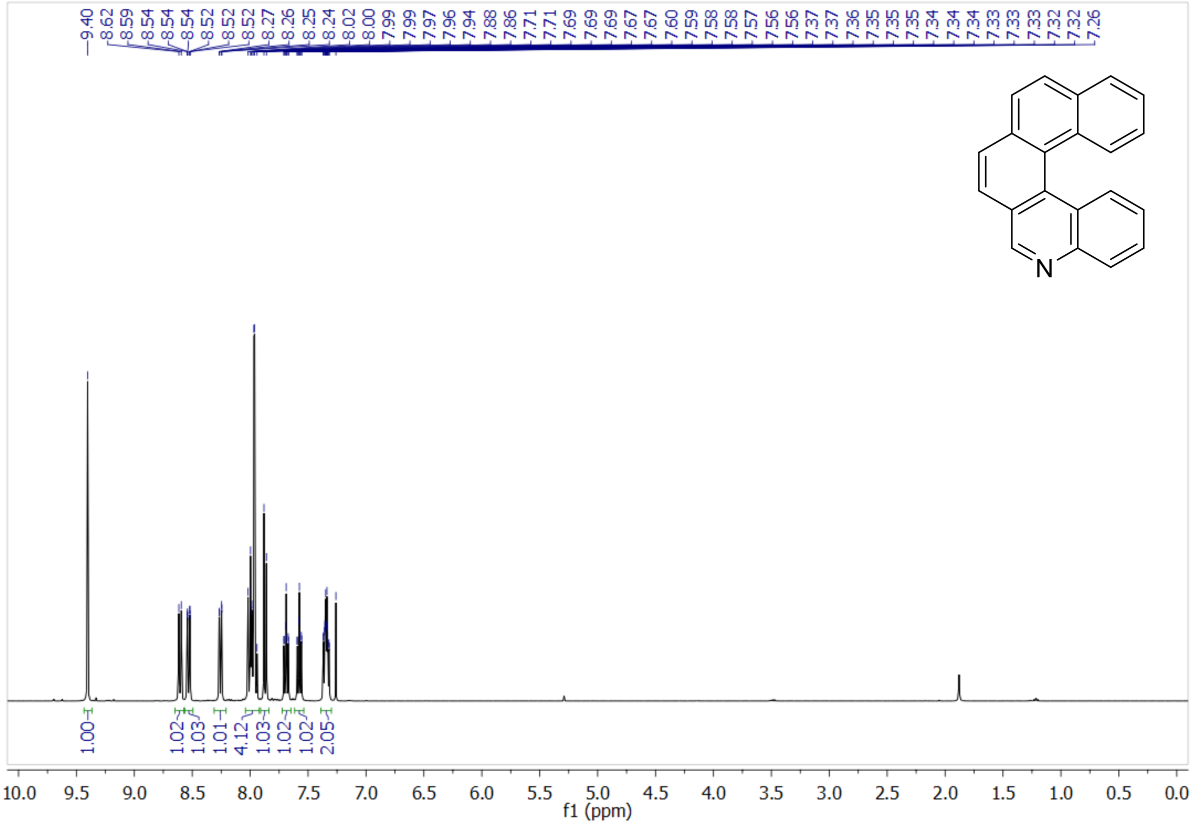
^{1}H-NMR of tetrapheno[2,3-c][1,2,5]thiadiazole (**2n’**)



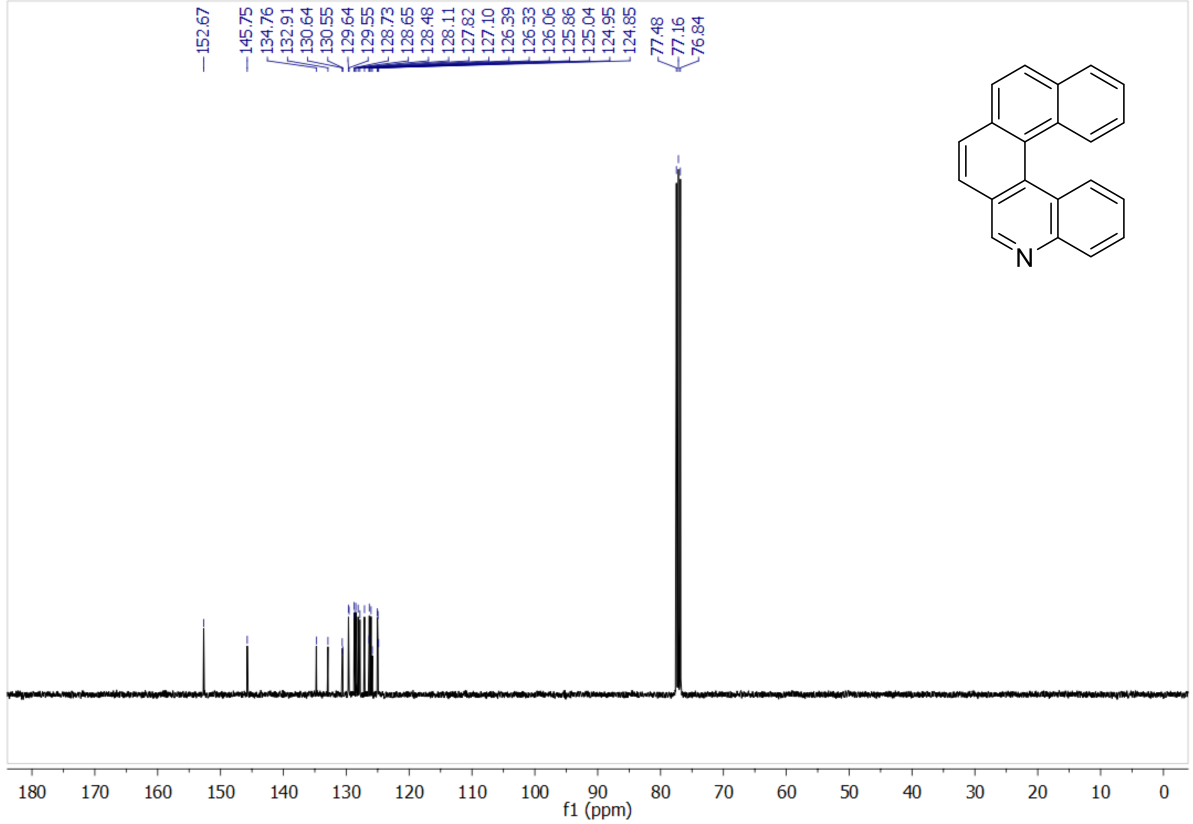
^{13}C-NMR of tetrapheno[2,3-c][1,2,5]thiadiazole (**2n’**)



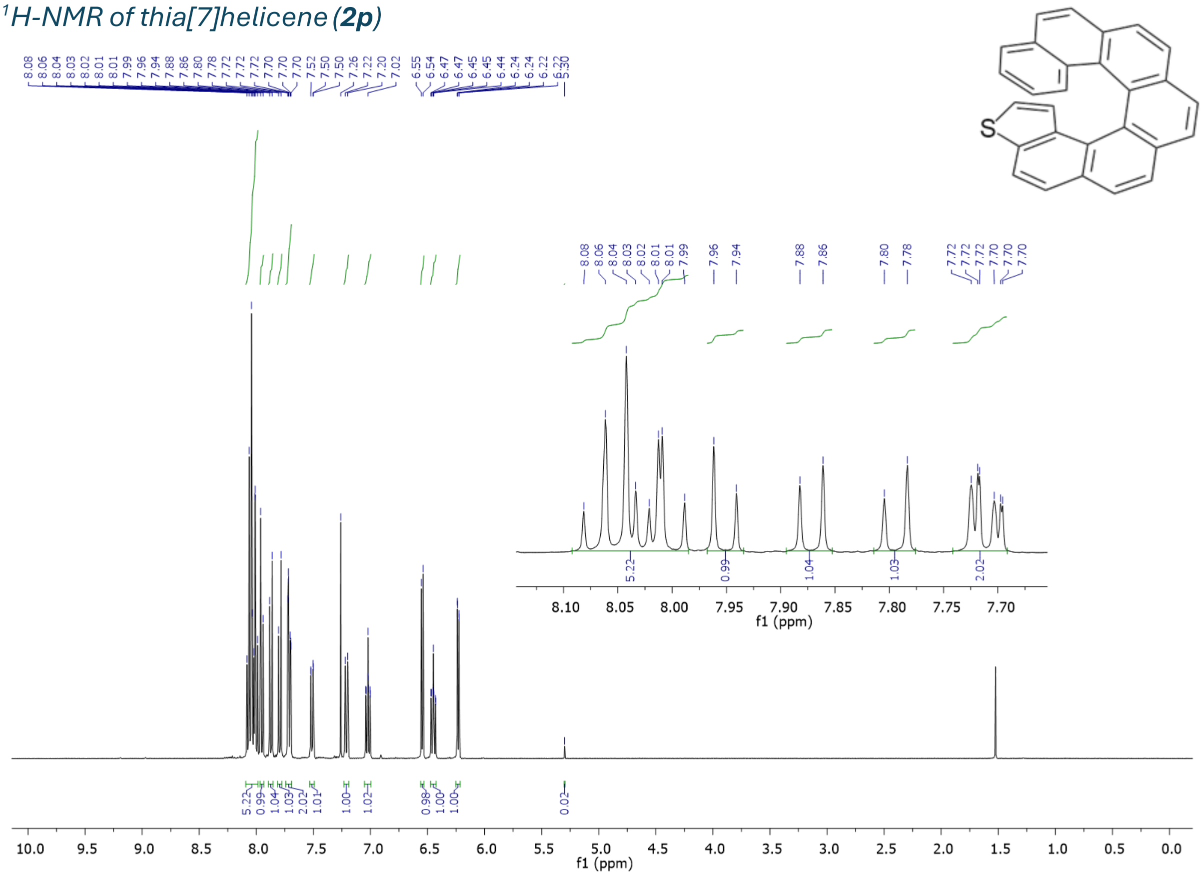
*^{1}H-NMR of aza[5]helicene (**2o**)*



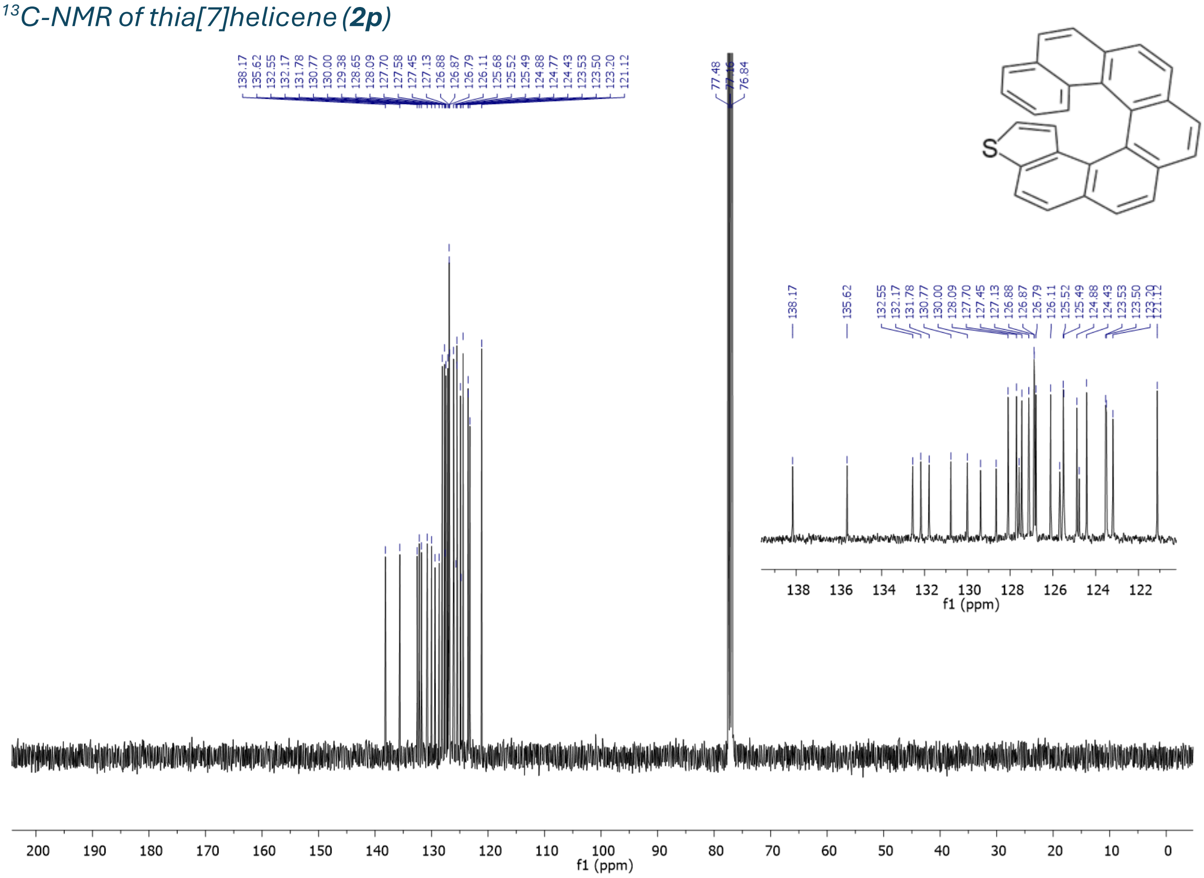
*^{13}C-NMR of aza[5]helicene (**2o**)*



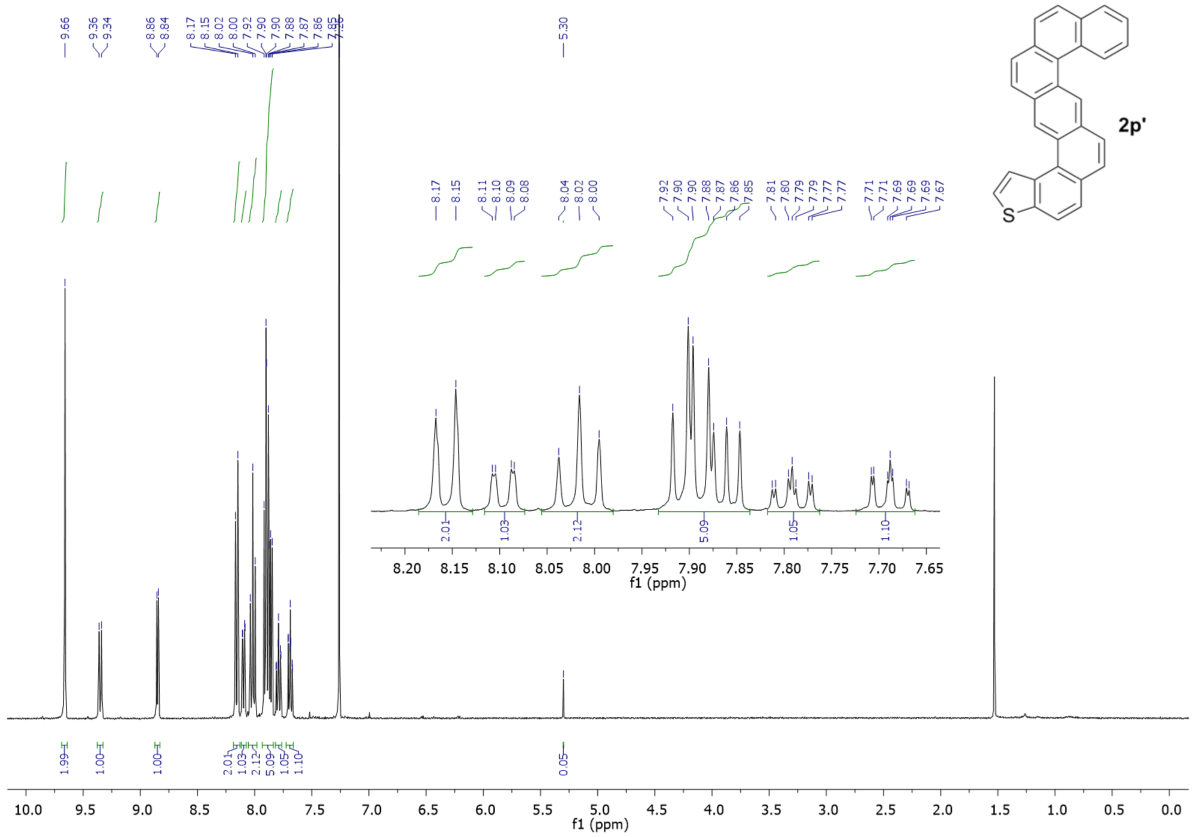
^{1}H-NMR of thia[7]helicene (**2p**)



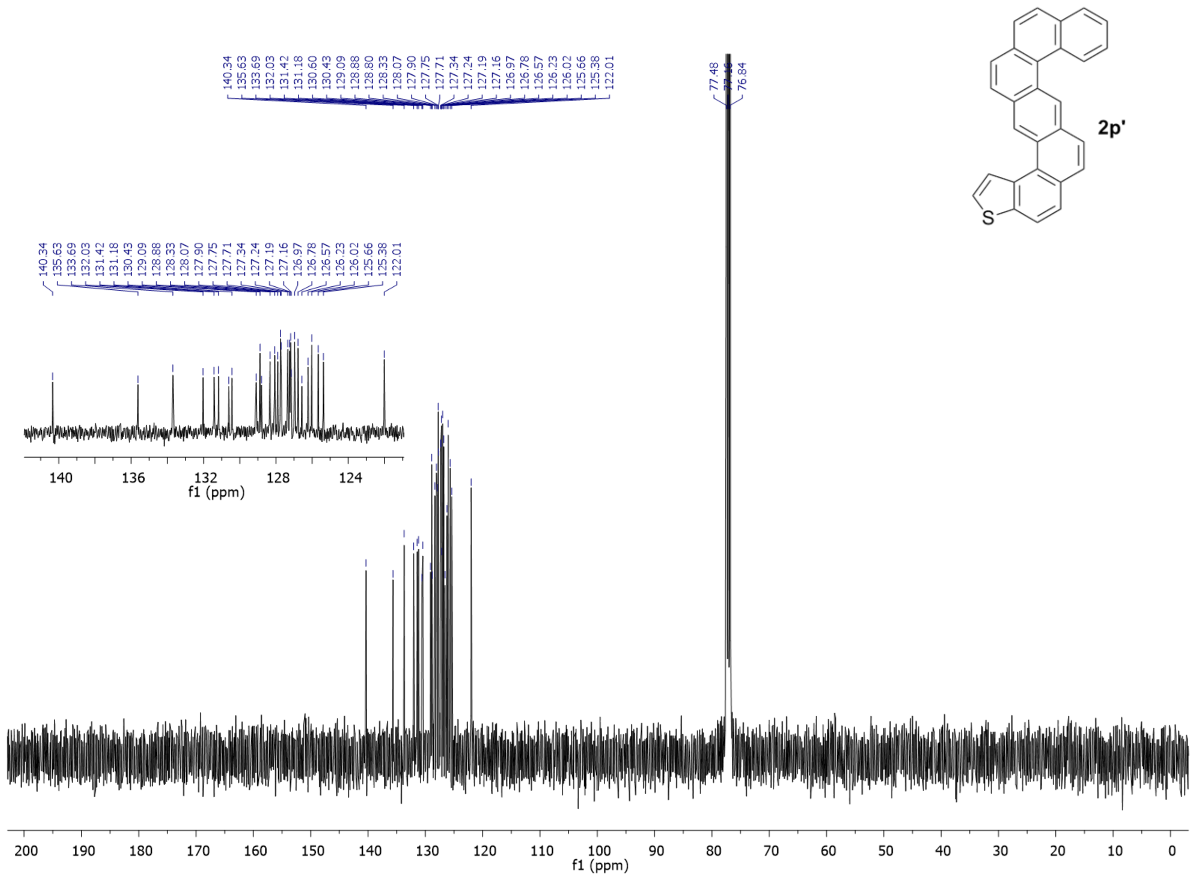
^{13}C-NMR of thia[7]helicene (**2p**)



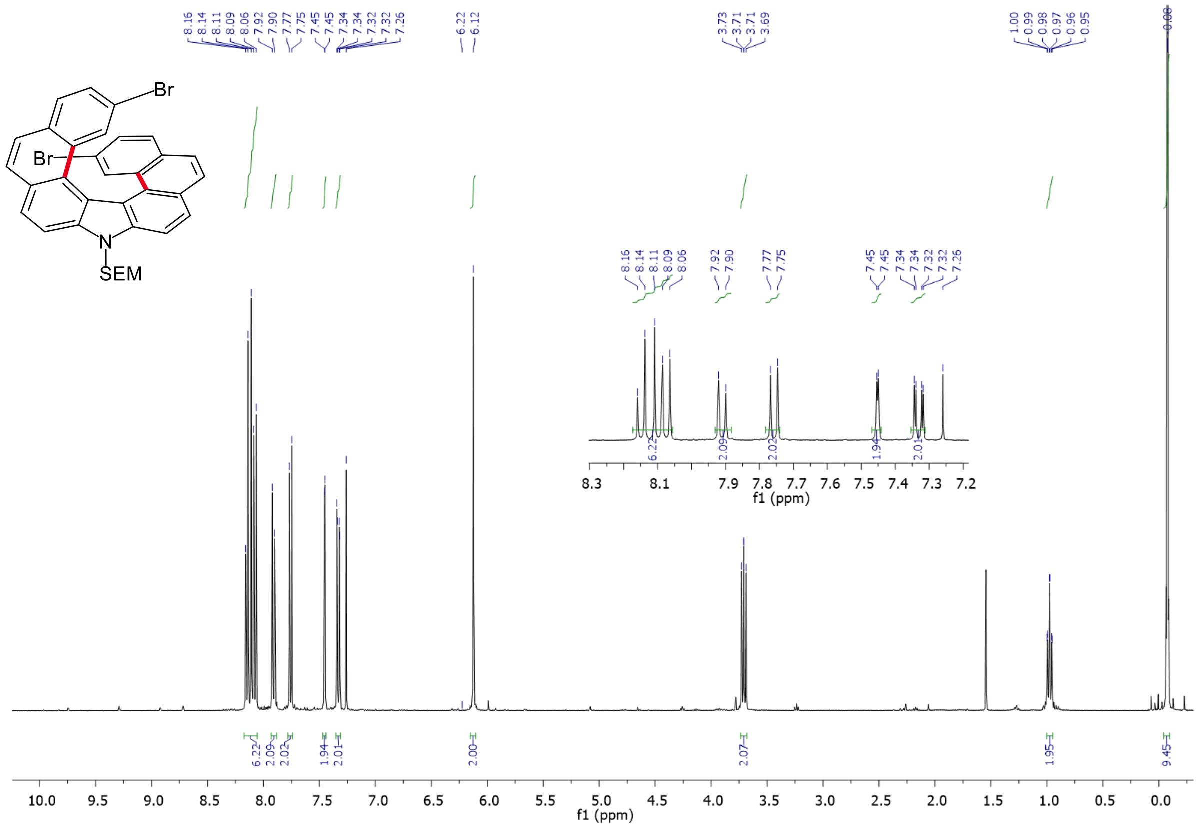
*^{1}H-NMR of naphtho[1',2':8,9]tetrapheno[2,1-*b*]thiophene (**2p'**)*



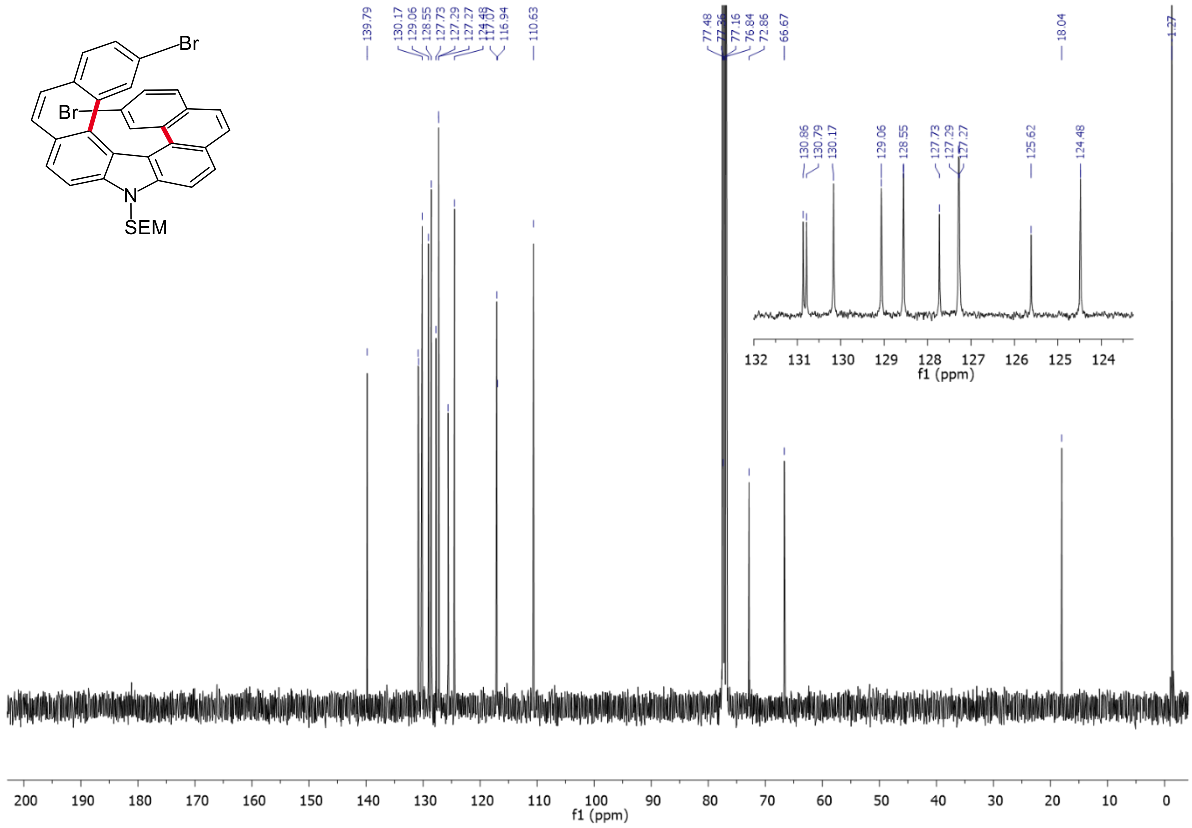
*^{13}C-NMR of naphtho[1',2':8,9]tetrapheno[2,1-*b*]thiophene (**2p'**)*



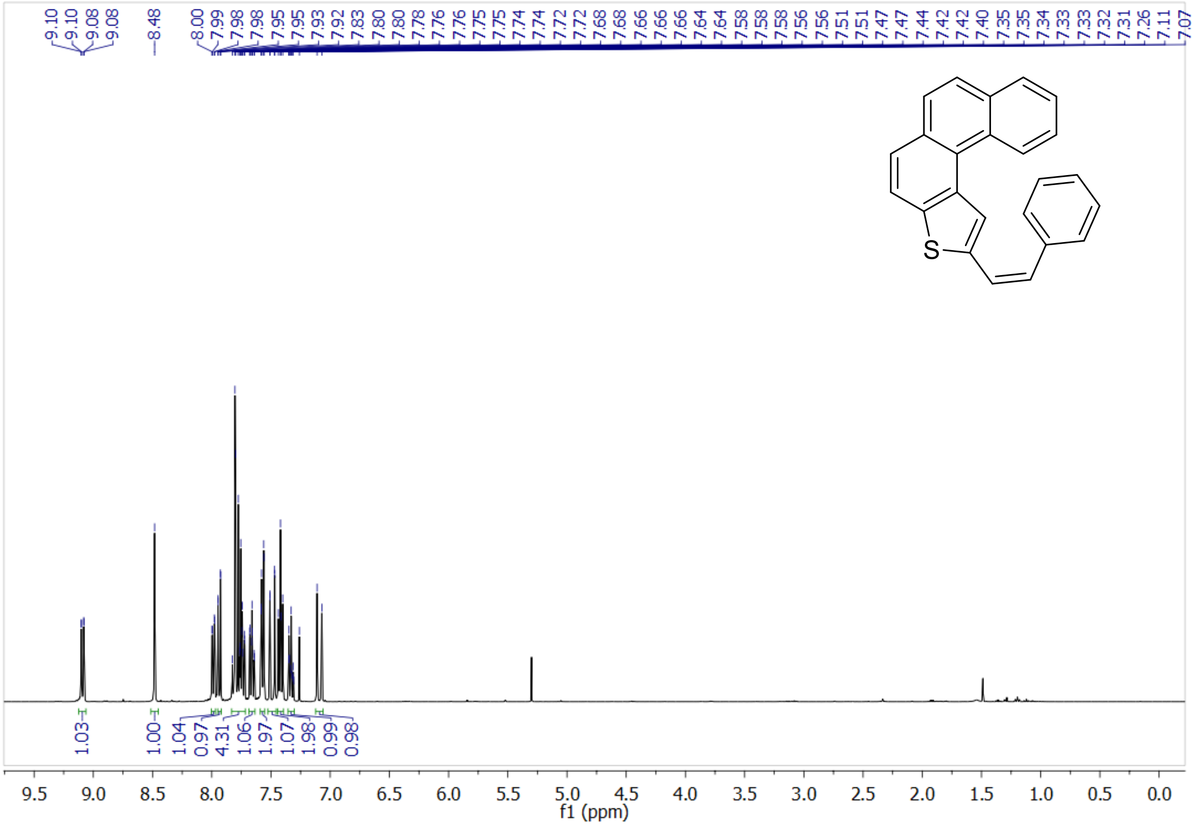
^{1}H-NMR of dibromoaza[7]helicene (**2q**)



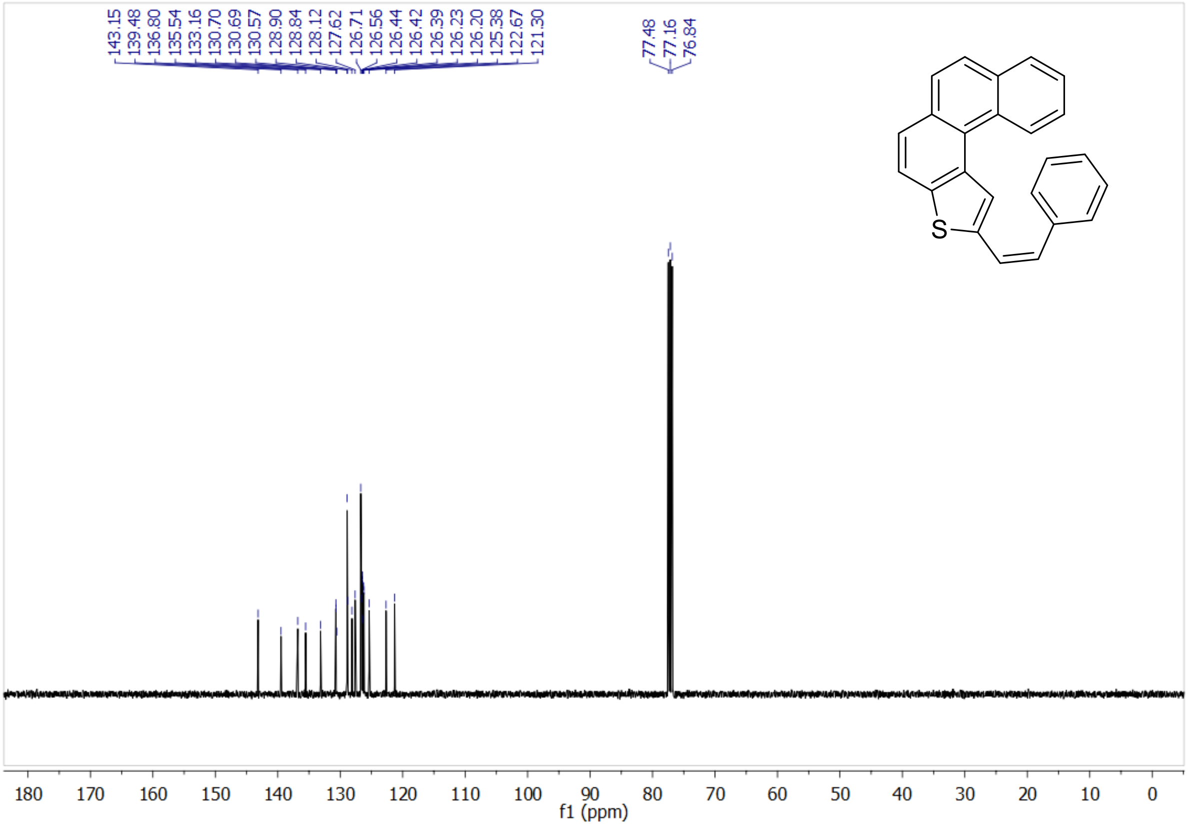
^{13}C-NMR of dibromoaza[7]helicene (**2q**)



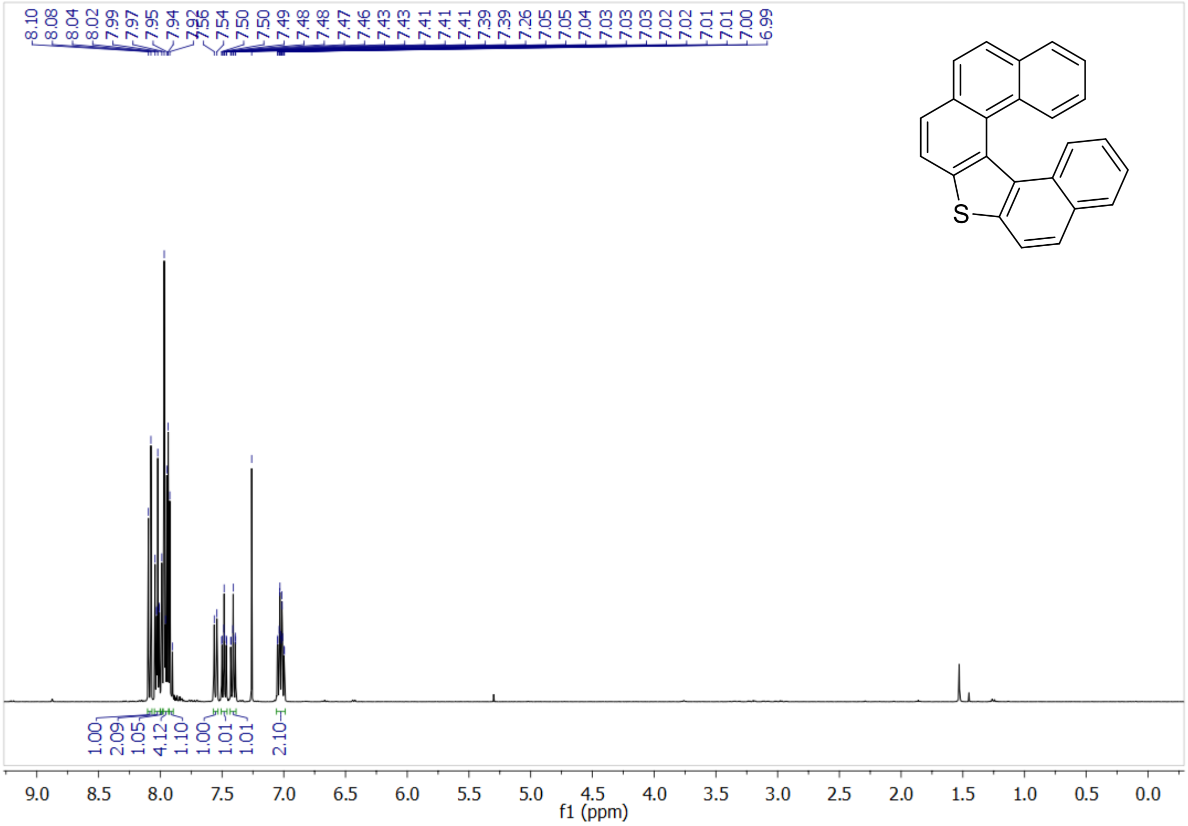
*^{1}H-NMR of (Z)-2-styrylphenanthro[3,4-b]thiophene (**3a**)*



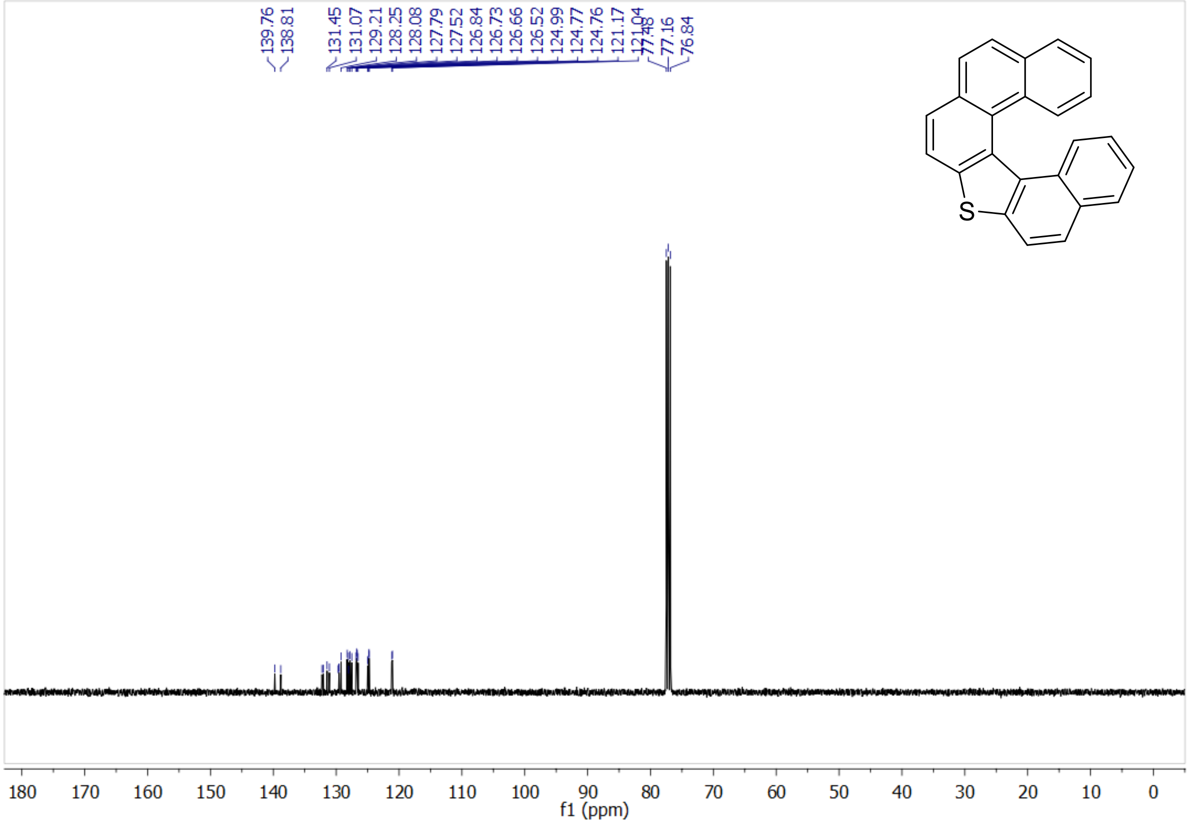
*^{13}C-NMR of (Z)-2-styrylphenanthro[3,4-b]thiophene (**3a**)*



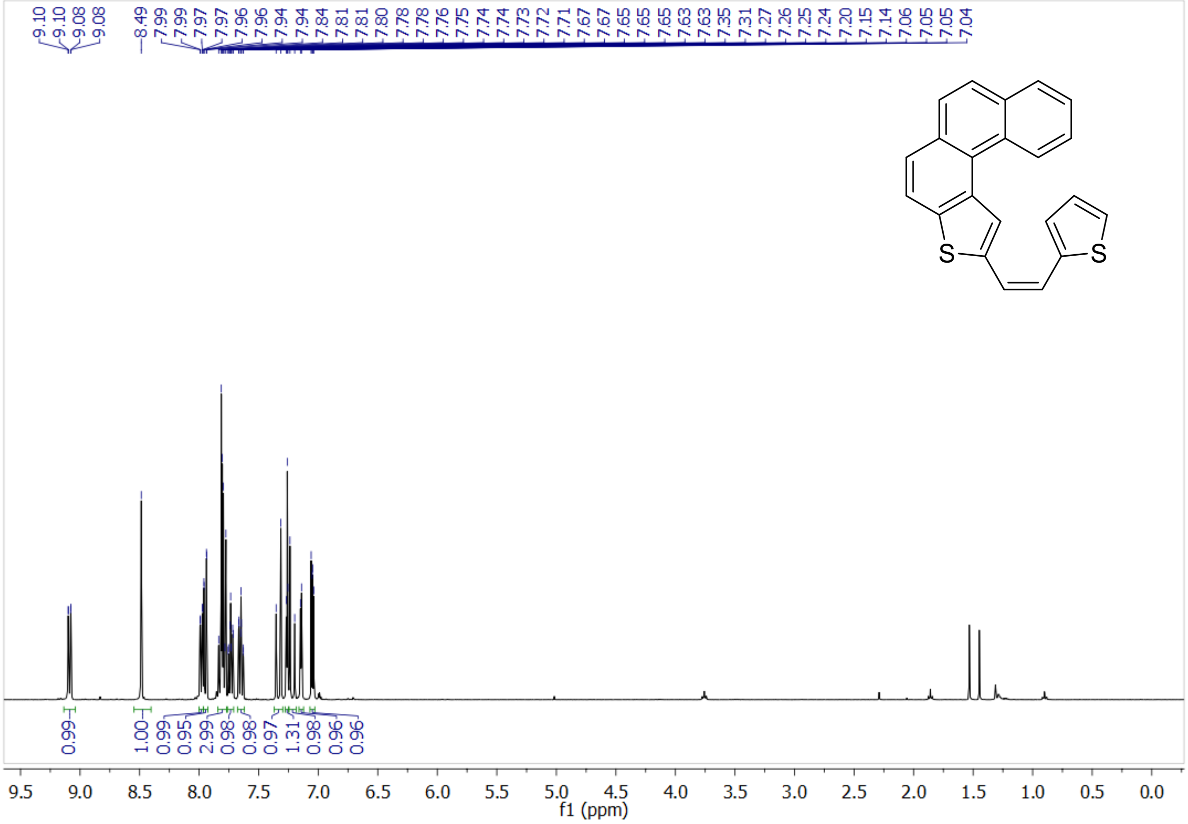
*^{1}H-NMR of thia[6]helicene (**4a**)*



*^{13}C-NMR of thia[6]helicene (**4a**)*



*^{1}H-NMR of 2-(2-(thiophen-2-yl)vinyl)phenanthro[3,4-*b*]thiophene (**3b**)*



*^{13}C-NMR of 2-(2-(thiophen-2-yl)vinyl)phenanthro[3,4-*b*]thiophene (**3b**)*