Electronic supplementary information:

Halogen-, oxidant- and directing group-free synthesis of donor–acceptor type conjugated polymers

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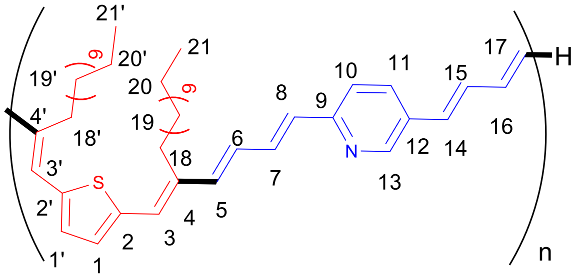
1. General procedures

All procedures described in this paper were performed under a nitrogen or argon atmosphere by use of Schlenk, glovebox and vacuum line techniques or a personal organic synthesiser (EYELA ChemStation PPM-5512). Benzene and tetrahydrofuran (thf) were dried and purified using the Nikko-Hansen Glass Contour Ultimate Solvent System. MeCN was dried over Drierite and distilled under nitrogen. Benzene-d_6 and thf-d_8 were dried over sodium wire and stored under vacuum, and it was directly transferred into an NMR tube or a 25 ml Schlenk tube by vacuum distillation prior to use. [Ru(η^6-naphthalene)(η^4-1,5-cod)] (**1a**: cod = cyclooctadiene),[1] [Ru(η^6-naphthalene)(η^4-oxa-bnd)] (**1b**: oxa-bnd = 9-oxabicyclo[3.3.1]nona-2,6-diene),[2] 2,5-dialkynylthiophenes (**2a-c**),[3] 2,5-dialkynyl-3-methylthiophene (**2d**),[3] 1,4-di(tetradec-1-yn-1-yl)benzene (**2e**)[3] and 2,5- and 2,6-di(buta-1,3-diene-1yl)pyridines (**3a-b**)[4] were prepared according to the literature procedures. Other reagents were purchased from commercial suppliers and were used as received. ^{1}H, ^{13}C{^{1}H}, and 2-dimensional NMR spectra were measured on a JEOL ECX-400P spectrometer (400 MHz for ^{1}H). MALDI-TOF MS were performed on Bruker Daltonics autoflex III smartbeam or Bruker Ultraflextreme-TK2. UV-Vis analyses were performed on a JASCO V-650 spectrophotometer. The fluorescence analyses were performed on a JASCO FP-6500 fluorescence spectrophotometer. The CV analyses were performed on a TOHO polarisation unit PS-07. The GPC analyses were performed on a TOSOH HLC-8320 GPC using tetrahydrofuran as an eluent monitored by refractive index detector.

2. Reaction of 2,5-di(tetradec-1-yn-1-yl)thiophene (2a) with 2,5-di(buta-1,3-dien-1-yl)pyridine (3a)



4aa

2a (70.0 mg, 0.149 mmol) and **3a** (27.4 mg, 0.150 mmol) in thf (1.8 ml) were added to a test tube under a nitrogen atmosphere. To the solution was added [Ru(η^6-naphthalene)(η^4-oxa-bnd)] (**1b**) (5.2 mg, 0.015 mmol; 10 mol%) as a catalyst. The test tube was capped with a silicone septum and the mixture was allowed to react at 30 °C for 3 d using a personal organic synthesiser. The reaction mixture was then concentrated and purified by reprecipitation with methanol to obtain a purple powder (72.2 mg) in 74% yield. This product was soluble to thf and was characterised by ^{1}H NMR (Fig. S1) ^{1}H-^{1}H

COSY experiment (Fig. S3), ^{13}C{^{1}H} NMR (Fig. S4) and MALDI-TOF MS (Fig. S5). The dominant product was characterised as **4aa** but small amount of isomer **4aa'** was observed in the ^{1}H NMR (**4aa**/**4aa'** = 8/1). Although the detailed structure of **4aa'** is less clear, we tentatively characterised as a regioisomer based on the unsymmetric **3a**. ^{1}H NMR showed no traces of Ru complexes such as diene complex and cyclooctadienyl complex, but no further analysis of Ru contamination was carried out.

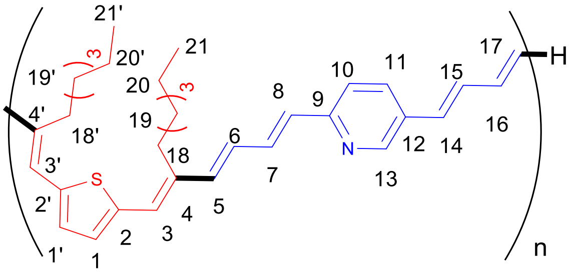
In the ^{1}H NMR spectrum, very small amount of resonances assignable to the terminal protons have been observed (Fig. S1-2). For comparison, a ^{1}H NMR spectrum of the same region of **3a** is shown in Fig. S2. In Fig. S1-2, the terminal proton at 2-butadienyl group has almost disappeared and only the terminal protons at 5-butadienyl group were observed at 5.16 and 5.35 ppm. This polymer has the mass number of multiple of repeating units (MS = 652.08) with the pyridyl end (MS = 182.25) by MALDI-TOF MS spectroscopy (Fig. S5). From this fact, we have considered the terminal chain end group of polymer **4a** is the 5-butadienyl group on pyridyl ring.

4aa: ^{1}H NMR (400 MHz, thf-d_8, r.t.): δ 0.80-1.00 (br.m, 6H, 21- and 21'-CH_3), 1.20-1.68 (br.m, 40H, 19- and 19'-CH_2, 20- and 20'-CH_2, overlapped with thf), 2.40-2.80 (br.m, 4H, 18- and 18'-CH_2, overlapped with contaminated H_2O), 5.16 (d, $^{3}J_{\mathrm{H\text{-}H}}$ = 8 Hz, trace amount, terminal 17-CH_2), 5.35 (d, $^{3}J_{\mathrm{H\text{-}H}}$ = 16 Hz, trace amount, terminal 17-CH_2), 6.45-6.80 (m, 8H, 3-, 3'-, 5-, 6-, 8-, 14-, 16- and 17-C*H*), 6.98-7.14 (m, 1H, 15-C*H* overlapped with 1- and 1'-C*H*), 7.04 (br.s, 2H, 1- and 1'-C*H*, overlapped with 15-C*H*), 7.25 (br.d, $^{3}J_{\mathrm{H\text{-}H}}$ = 7 Hz, 1H, 10-C*H*), 7.42-7.55 (m, 1H, 7-C*H*), 7.74 (br.d, $^{3}J_{\mathrm{H\text{-}H}}$ = 7 Hz, 1H, 11-C*H*), 8.55 (br.s, 1H, 13-C*H*).

4aa': ^{1}H NMR (400 MHz, thf-d_8, r.t.): δ 0.80-1.00 (br.m, 6H, CH_3, overlapped with **4aa**), 1.20-1.68 (br.m, 40H, CH_2 overlapped with thf and **4aa**), 2.40-2.80 (br.m, 4H, CH_2, overlapped with contaminated H_2O and **4aa**), 6.45-6.80 (m, 8H, =C*H*, overlapped with **4aa**), 6.90-7.05 (m, 3H, =C*H* and thienyl ring protons overlapped with **4aa**), 7.14-7.20 (1H, pyridyl ring proton), 7.35-7.48 (m, 1H, =C*H*), 7.66-7.72 (1H, pyridyl ring proton overlapped with **4aa**), 8.49 (br.s, 1H, pyridyl ring proton).

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, r.t.): δ 14.3, 20.1, 23.4, 30.2, 30.5, 32.7, 120.2, 122.32, 129.1, 129.2, 129.5, 130.0, 130.2, 131.7, 132.2, 132.7, 138.9, 139.8, 139.9, 140.0, 140.2, 140.3, 140.4, 141.5, 142.36, 142.42, 149.3, 155.1.
MALDI-TOF MS m/z = 8006.785 (n = 12).

3. Reaction of 2,5-di(oct-1-yn-1-yl)thiophene (2b) with 2,5-di(hexyl-1,3-dien-1-yl)pyridine (3a)



4ba

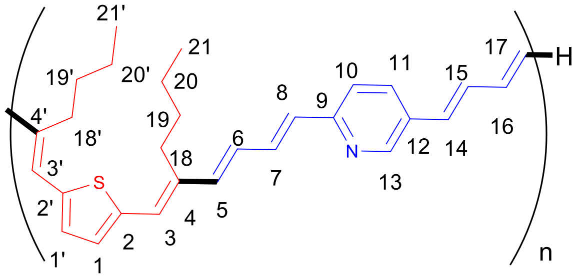
2b (19.0 mg, 0.0609 mmol) and **3a** (11.0 mg, 0.601 mmol) in thf (0.5 ml) were added to a test tube under a nitrogen atmosphere. To the solution was added **1b** (2.5 mg, 0.071 mmol; 12 mol%). The mixture was allowed to react at 30 °C for 3 d. The reaction mixture was concentrated and purified by reprecipitation with methanol to obtain a red solid of **4ba** (14.9 mg) in 51% yield. This product was characterised by NMR and MALDI-TOF MS.

^{1}H NMR (400 MHz, thf-d_8, r.t.): δ 0.90-1.00 (m, 6H, 21- and 21'-CH_3), 1.25-1.65 (br.m, 16H, 19-, 19'-, 20- and 20'-CH_2, overlapped with thf), 2.42-2.80 (m. 4H, 18- and 18'-CH_2, overlapped with H_2O), 5.17 (d, $^3J_{H\text{-}H}$ = 10 Hz, trace amount, terminal 17-CH_2), 5.22 (d, $^3J_{H\text{-}H}$ = 10 Hz, trace amount, regioisomer, terminal proton of 2-butadienyl proton), 5.35 (d, $^3J_{H\text{-}H}$ = 17 Hz, trace amount, terminal 17-CH_2), 5.41 (d, $^3J_{H\text{-}H}$ = 17 Hz, trace amount, regioisomer, terminal proton of 2-butadienyl proton), 6.30-6.80 (m, 4H, 3-, 3'-, 5- and 17-C*H*, overlapped with 6-, 8-, 14- and 16-C*H*), 6.50-6.60 (m, 2H, 6- and 16-C*H*, overlapped with 8- or 14-C*H*), 6.63 (d, $J_{H\text{-}H}$ = 15.6 Hz, 1H, 8- or 14-C*H*, overlapped with 6- and 16-C*H*), 6.67 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H, 14- or 8-C*H*, overlapped with 8- or 14-C*H*), 7.00-7.45 (2H, 1- and 1'-C*H*, overlapped with 15-C*H*), (7.08, dd, $^3J_{H\text{-}H}$ = 16, 10 Hz, 1H, 15-C*H*, overlapped with 1- and 1'-C*H*), 7.26 (br.d, $^3J_{H\text{-}H}$ = 9 Hz, 1H, 10-C*H*), 7.48 (dd, $^3J_{H\text{-}H}$ = 15, 9 Hz 1H, 7-C*H*), 7.74 (br.d, $^3J_{H\text{-}H}$ = 9 Hz, 1H, 11-C*H*), 8.55 (br.s, 1H, 13-C*H*).

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, r.t.): δ 14.4, 20.1, 23.3, 23.5, 29.4, 30.8, 32.2, 32.5, 32.7, 118.2 (terminal 17-*C*H), 122.3, 125.4, 125.7, 126.1, 126.5, 129.2, 129.4, 129.5, 130.1, 131.5, 132.2, 132.7, 134.1, 134.2, 138.1, 138.9, 139.9, 140.2, 141.5, 142.4, 149.3, 155.2, 155.7.

MALDI-TOF MS m/z = 2231.967 (n = 4).

4. Reaction of 2,5-di(hex-1-yn-1-yl)thiophene (2c) with 2,5-di(buta-1,3-dien-1-yl)pyridine (3a)



4ca

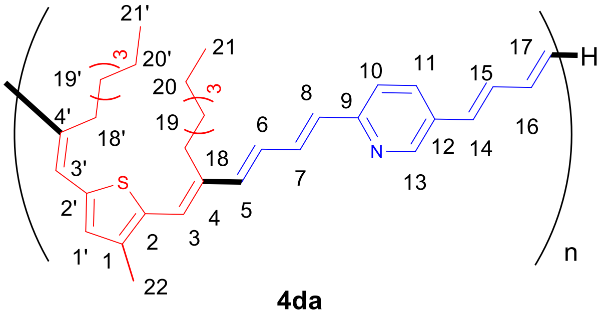
4ca: reddish brown solid. 47% yield.

^{1}H NMR (400 MHz, thf-d_8, r.t.): δ 0.95 (t, $^3J_{\text{H-H}}$ = 7 Hz, chain end protons assignable to terminal 21'-CH_3), 0.97-1.08 (br.s, 6H, 21- and 21'-CH_3), 1.50-1.70 (br.m, 8H, 19-, 19'-, 20- and 20'-CH_2, overlapped with thf), 2.42-2.50 (m, 1H, 18- or 18'-CH_2), 2.60-2.80 (br.m, 3H, 18- and 18'-CH_2, overlapped with H_2O), 5.17 (d, $^3J_{\text{H-H}}$ = 10 Hz, terminal 17-CH_2), 5.35 (d, $^3J_{\text{H-H}}$ = 18 Hz, terminal 17-CH_2), 6.40-6.80 (m, 8H, 3-, 3'-, 5-, 6-, 8-, 14-, 16- and 17-CH), 6.95-7.14 (br.m, 3H, 1-, 1'- and 15-CH), 7.26 (br.d, $^3J_{\text{H-H}}$ = 8 Hz, 1H, 10-CH), 7.48 (br.dd, $^3J_{\text{H-H}}$ = 16, 9 Hz, 1H, 7-CH), 7.74 (br.d, $^3J_{\text{H-H}}$ = 8 Hz, 1H, 11-CH), 8.55 (br.s, 1H, 13-CH).

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, r.t.): δ 14.4, 20.1, 23.3, 23.5, 29.4, 30.8, 32.2, 32.5, 32.7, 118.2 (17-CH), 122.3, 125.4, 125.7, 126.1, 126.5, 129.2, 129.4, 129.5, 130.1, 131.5, 132.2, 132.7, 134.1, 134.2, 138.1, 138.9, 139.9, 140.2, 141.5, 142.4, 149.3, 155.3.

MALDI-TOF MS m/z = 2379.886 (n = 5).

5. Reaction of 2,5-di(oct-1-yn-1-yl)-3-methylthiophene (2d) with 2,5-di(buta-1,3-dien-1-yl)pyridine (3a)



4da

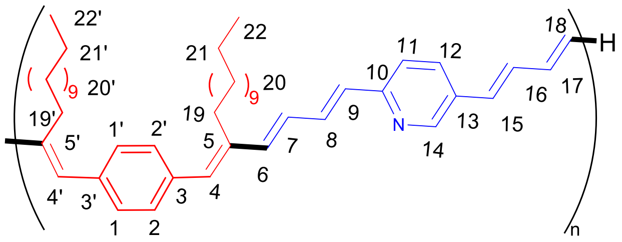
4da: red powder. 13% yield.

^{1}H NMR (400 MHz, thf-d_8, r.t.): δ 0.88-1.00 (br.m, 6H, 21- and 21'-CH_3), 1.25-1.65 (br.m, 16H, 19-, 19'-, 20- and 20'-CH_2, overlapped with thf), 2.21 (s, 3H, 22-CH_3), 2.27 (s, minor regioisomer assignable to 22-CH_3: major/minor = 4/1), 2.42-2.80 (br, 4H, 18- and 18'-CH_2, overlapped with H_2O), 5.17 (d, $^3J_{\text{H-H}}$ = 10 Hz, terminal 17-CH_2), 5.35 (d, $^3J_{\text{H-H}}$ = 17 Hz, terminal 17-CH_2), 6.40-6.80 (m, 8H, 3-, 3’-, 5-, 6-, 8-, 14-, 16- and 17-C*H*), 6.81 (s, 1H, 1’-C*H*), 6.82 (s, 1H, 1’-C*H* of isomer), 6.90 (s, terminal 1’-C*H*), 6.92 (s, terminal 1’-C*H* of isomer), 7.06 (dd, $^3J_{\text{H-H}}$ = 15, 11 Hz, 1H, 15-C*H*, overlapped with 1’-C*H*), 7.24 (br.d, $^3J_{\text{H-H}}$ = 8 Hz, 1H, 10-C*H*), 7.45 (dd, $^3J_{\text{H-H}}$ = 15, 10 Hz, 1H, 7-C*H*), 7.73 (br.d, $^3J_{\text{H-H}}$ = 8 Hz, 1H, 11-C*H*), 8.54 (br.s, 1H, 13-C*H*).

$^{13}C\{^1H\}$ NMR (100 MHz, thf-d_8, r.t.): δ 14.2, 14.3, 14.4, 14.5, 20.2, 23.3, 23.4, 29.3, 29.5, 30.5, 30.6, 30.1, 32.5, 32.7, 122.4, 126.0, 128.9, 129.2, 131.5, 131.6, 132.3, 132.7, 133.1, 134.0, 138.7, 139.6, 140.0, 141.8, 144.9, 149.3, 155.3. This $^{13}C\{^1H\}$ NMR spectrum of this compound was measured twice, but it was difficult to measure the spectrum with sufficient resolution.

MALDI-TOF MS m/z = 5789.253 (n = 11).

6. Reaction of 1,4-di(tetradec-1-yn-1-yl)benzene (2e) with 2,5-di(buta-1,3-dien-1-yl)pyridine (3a)



4ea

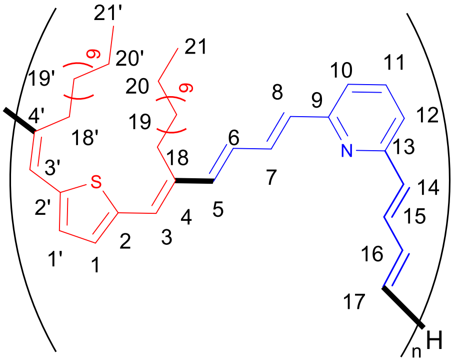
4ea, yellow brown solid. 64% yield.

^1H NMR (400 MHz, thf-d_8, r.t.): 0.89 (br.t, $^3J_{\text{H-H}}$ = 7 Hz, 6H, 22- and 22’-CH_3), 1.10-1.70 (br, 40H, 20-, 20’-, 21- and 21’-CH_2), 2.30-2.70 (m, 4H, 19- and 19’-CH_2, overlapped with H_2O), 5.17 (d, $^3J_{\text{H-H}}$ = 10 Hz, terminal 18-C*H*), 5.37 (d, $^3J_{\text{H-H}}$ = 17 Hz, terminal 18-C*H*), 6.40-6.70 (m, 6- or 9-, 7- or 8-, 15- and 7-C*H*), 6.56 (s, 2H, 4- and 4’-C*H*, overlapped), 6.66 (d, $^3J_{\text{H-H}}$ = 8 Hz, 1H, 9- or 6-C*H*), 6.94 (dd, $^3J_{\text{H-H}}$ = 16, 10 Hz, 1H, 16-C*H*), 7.20-7.40 (m, 1H, 18-C*H*, overlapped), 7.26 (d, $^3J_{\text{H-H}}$ = 6 Hz, 1H, 11-C*H*, overlapped), 7.26 (d, $^3J_{\text{H-H}}$ = 8.0 Hz, 2H, 1- and 1’ or 2- and 2’-C*H*, overlapped), 7.33 (d, $^3J_{\text{H-H}}$ = 8 Hz, 2H, 1’- and 1 or 2’- and 2-C*H*), 7.46 (dd, $^3J_{\text{H-H}}$ = 15, 10 Hz, 1H, 7- or 8-C*H*), 7.74 (d, $^3J_{\text{H-H}}$ = 6 Hz, 1H, 12-C*H*), 8.55 (s, 1H, 14-C*H*).

$^{13}C\{^1H\}$ NMR (100 MHz, thf-d_8, r.t.): 14.3, 23.4, 29.5, 29.6, 29.7, 29.9, 30.0, 30.1, 30.4, 30.5, 30.7, 32.7, 118.1, 122.2, 129.3, 129.6, 130.1, 131.4, 131.9, 132.0, 132.3, 132.6, 133.1, 134.1, 137.7, 137.9, 138.1, 140.3, 140.5, 142.3, 149.4, 155.7.

MALDI-TOF MS m/z = 2576.434.

7. Reaction of 2,5-di(tetradec-1-yn-1-yl)thiophene (2a) with 2,6-di(buta-1,3-dien-1-yl)pyridine (3b)



4ab

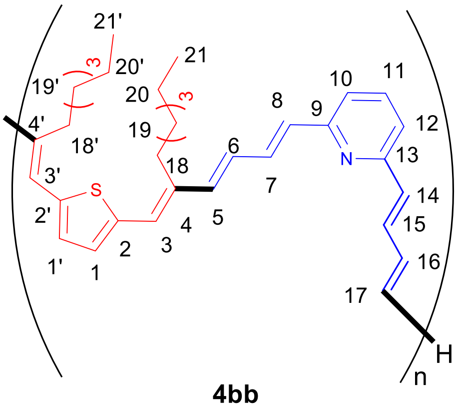
4ab: red powder. 88% yield.

^{1}H NMR (400 MHz, thf-d$_8$, r.t.): δ 0.89 (br, 6H, 21- and 21’-CH_3), 1.20-1.70 (br.m, 40H, 19-, 19’-, 20- and 20’-CH_2, overlapped), 2.40-2.50 (m, 1H, 18- or 18’-CH_2, overlapped with H$_2$O), 2.60-2.83 (br.m, 3H, 18- and 18’-CH_2), 5.24 (d, $^3J_{\text{H-H}}$ = 11 Hz, terminal 17-CH_2), 5.45 (d, $^3J_{\text{H-H}}$ = 17 Hz, terminal 17-CH_2), 6.55-6.90 (m, 8H , 3-, 3’-, 5-, 6-, 8-, 14-, 16- and 17-CH), 7.00-7.10 (br.s, 2H, 1- and 1’-CH), 7.10-7.20 (m, 2H, 11- and 10- or 12-CH), 7.30-7.65 (3H, 7-, 12- or 10- and 15-CH).

^{13}C{^{1}H} NMR (100 MHz, thf-d$_8$, r.t.): 14.3, 23.4, 30.2, 30.5, 30.6, 31.1, 32.8, 120.8, 126.4, 129.1, 130.1, 132.6, 134.3, 137.1, 137.2, 137.9, 139.9, 140.3, 142.4, 156.3.

MALDI-TOF MS m/z = 5868.287 (n = 9).

8. Reaction of 2,5-di(oct-1-yn-1-yl)thiophene (2b) with 2,6-di(buta-1,3-dien-1-yl)pyridine (3b)



4bb

4bb: red solid. 33% yield.

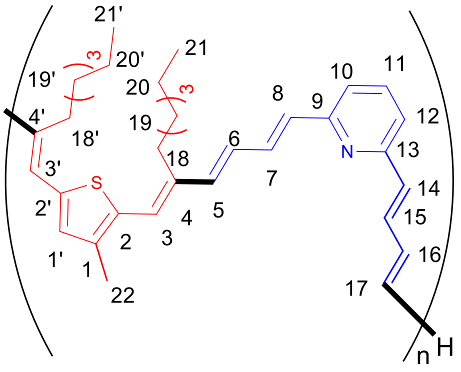
^{1}H NMR (400 MHz, thf-d$_8$, r.t.): δ 0.85-1.05 (m, 6H, 21- and 21’-CH_3), 1.20-1.70 (br.m, 16H, 19-, 19’-, 20- and 20’-CH_2, overlapped), 2.40-2.50 (m, 2H, 18 or 18’-CH_2, overlapped with H$_2$O), 2.60-

2.80 (br.m, 2H, 18, 18’-CH_2), 5.25 (d, $^{3}J_{\text{H-H}}$ = 10 Hz, terminal 17-CH_2), 5.45 (d, $^{3}J_{\text{H-H}}$ = 16 Hz, terminal 17-CH_2), 6.50-6.65 (m, 1H, 16-C*H*), 6.55-6.80 (m, 7H, 3-, 3’-, 5-, 6-, 8-, 14-, 16- and 17-C*H*), 6.94 (d, $^{3}J_{\text{H-H}}$ = 4 Hz, 1H, 1- or 1’-C*H*), 7.02 (d, $^{3}J_{\text{H-H}}$ = 4 Hz, 1H, 1’- or 1-C*H*), 7.04 (d, 1H, $^{3}J_{\text{H-H}}$ = 9 Hz, 10- or 12-C*H*), 7.10-7.20 (m, 1H, 11-C*H*), 7.50-7.65 (3H, 7-, 10- or 12-, 15-C*H*).

^{13}C{^{1}H} NMR (100 MHz, thf-d$_8$, r.t.): 14.2, 14.29, 14.34, 23.3, 23.46, 23.53, 29.4, 29.5, 30.5, 30.6, 30.8, 32.2, 32.5, 32.7, 119.4, 125.5, 125.9, 126.4, 129.4, 130.1, 131.6, 132.8, 133.9, 134.1, 134.3, 137.1, 137.3, 139.9, 140.2, 141.6, 142.4, 156.3.

MALDI-TOF MS m/z = 2422.999.

9. Reaction of 2,5-di(oct-1-yn-1-yl)-3-methylthiophene (2d) with 2,6-di(buta-1,3-dien-1-yl)pyridine (3b)



4db

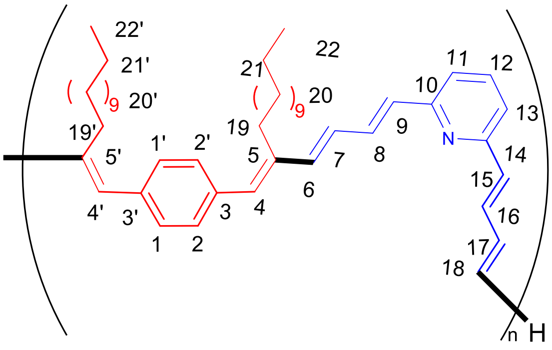
4db: orange solid. 98% yield.

^{1}H NMR (400 MHz, thf-d$_8$, r.t.): δ 0.85-1.05 (m, 6H, 21- and 21’-CH_3), 1.20-1.70 (br.m, 16H, 19-, 19’-, 20- and 20’-CH_2, overlapped), 2.20-2.24 (br.s, 1.2H, a regioisomer of 1-CH_3), 2.26-2.33 (br.s, 1.7H, a regioisomer of 1-CH_3), 2.40-2.50 (m, 1H, 18 or 18’-CH_2, overlapped with H_2O), 2.60-2.80 (br.m, 4H, 18- and 18’-CH_2), 6.50-6.85 (m, 8H, 3-, 3’-, 5-, 6-, 7-, 8-, 16- and 17-C*H*), 6.92 (br.s, 1H, 1’-C*H*), 7.05-7.15 (br.m, 2H, 11- and 14-C*H*), 7.45-7.65 (m, 3H, 10-, 12- and 15-C*H*).

^{13}C{^{1}H} NMR (100 MHz, thf-d$_8$, r.t.): 14.3, 14.4, 23.4, 23.5, 23.6, 29.3, 33.8, 32.5, 32.7, 120.8, 121.2, 126.3, 128.6, 129.0, 131.6, 132.3, 133.2, 134.4, 136.2, 137.1, 138.3, 139.1, 139.8, 140.0, 140.3, 140.7, 156.2.

MALDI-TOF MS m/z = 5972.95 (n = 12).

10. Reaction of 1,4-di(tetradec-1-yn-1-yl)benzene (2e) with 2,6-di(buta-1,3-dien-1-yl)pyridine (3b)



4eb

4eb: yellow brown powder. 91% yield.

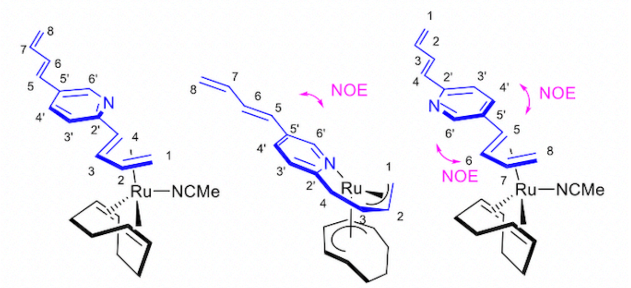
^{1}H NMR (400 MHz, thf-d_8, r.t.): 0.87 (br, 6H, 22- and 22’-CH_3), 1.10-1.70 (br, 40H, 20-, 20’-, 21- and 21’-CH_2), 2.30-2.70 (m, 4H, 19- and 19’-CH_2, overlapped), 6.40-6.80 (m, 7H, 4-, 4’-, 6-, 9-, 15-, 7- or 8- or 16-, and 18-C*H*), 7.10-7.20 (m, 1H, 7- or 8- or 16-C*H*), 7.13 (br.d, $^{3}J_{\text{H-H}}$ = 7 Hz, 2H, 1-, 1’- or 2-, 2’-C*H*), 7.20-7.50 (br.m, 4H, 1-, 1’- or 2-, 2’-, 12- and 15-C*H*), 7.50-7.70 (br.m, 3H, 11-, 13- and 17-C*H*).

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, r.t.): 14.3, 23.4, 29.9, 30.2, 30.5, 30.8, 32.7, 120.65, 120.72, 120.8, 129.1, 129.4, 129.6, 130.2, 132.0, 132.6, 132.8, 134.2, 137.1, 140.7, 142.0, 156.3.

MALDI-TOF MS m/z = 5814.467 (n = 9).

11. Reaction of 1a with 3a in the presence of MeCN

3a (3.52 mg, 0.0192 mmol) in C_6D_6 (600 µl) was added to an NMR tube under nitrogen atmosphere. To the solution was added MeCN (2.0 µl, 0.038 mmol) by a hypodermic syringe at room temperature. Complex **1a** (6.47 mg, 0.0192 mmol) was added to the solution. The mixture was allowed to react at room temperature for 1 h, during which the reaction was monitored by ^{1}H NMR spectroscopy. The formation of **5a** (8%), **5b** (42%) and **6a** (22%) was characterised according to our previous paper.[5] An acetonitrile complex coordinated 2-butadienyl group, and a complex coordinated 2-butadienyl group and pyridine were formed within 5 minutes.



5a **5b** **6a**

5a: 0.74 (d, $^{3}J_{\text{H-H}}$ = 8.0 Hz, 1H, 1-*endo*-C*H*), 0.94 (s, 3H, *Me*CN), 1.74 (d, $^{3}J_{\text{H-H}}$ = 8.0 Hz, 1H, 1-*exo*-

C*H*). 2.40 (d, $^{3}J_{\text{H-H}}$ = 8.0 Hz, 1H, 4-C*H*), 5.04-5.15 (m, 1H, 2-C*H*, overlapped with 8-CH), 5.15 (d, $^{3}J_{\text{H-H}}$ = 16.8 Hz, 1H, 8-C*H*), 5.15 (d, $^{3}J_{\text{H-H}}$= 16.8 Hz, 1H, 8-C*H*), 6.24-6.35 (m, 1H, 7-C*H*, overlapped with **5b**), 6.40-6.52 (m, 1H, 6-C*H,* overlapped with **5b**), 6.78 (dd, $^{3}J_{\text{H-H}}$ = 12.4, 8.0 Hz, 1H, 3-C*H*), 6.81 (d, $^{3}J_{\text{H-H}}$ = 8.0 Hz, 1H, 3'-C*H*), 7.10-7.20 (1H, 4'-C*H,* overlapped with C_6HD_5), 8.49 (br.s, 1H, 6'-C*H*), and the resonances assigned to the 1,5-cod ligand were obscured in the mixture of **5b** and **6a**.

5b:0.66-0.67 (1H, 1-1-*endo*-C*H*, overlapped with free MeCN), 1.72 (d, $^{3}J_{\text{H-H}}$ = 12.0 Hz, 1H, 1-*exo*-C*H*), 2.86 (d, $^{3}J_{\text{H-H}}$ = 19.2 Hz, 1H, 4-CH_2), 3.07 (dd, $^{3}J_{\text{H-H}}$ = 19.2, 8.0 Hz, 1H, 4-CH_2), 4.55-4.65 (m, 1H, 3-C*H*), 4.90-5.05 (m, 1H, 2-C*H*), 4.95-5.10 (1H, 8-C*H*, overlapped with **5a**), 5.17 (d, $^{3}J_{\text{H-H}}$ = 16.4 , Hz, 1H, 8-C*H*), 6.06 (d, $^{3}J_{\text{H-H}}$ = 16.0 Hz, 1H, 5-C*H*), 6.17 (d, $^{3}J_{\text{H-H}}$ = 7.6 Hz, 1H, 3'-C*H*), 6.30 (dt, $^{3}J_{\text{H-H}}$ = 16.8, 10.4 Hz 1H, 7-C*H*), 6.47 (dd, $^{3}J_{\text{H-H}}$ = 14.8, 9.6 Hz, 1H, 6-C*H*), 6.73 (d, $^{3}J_{\text{H-H}}$ = 8.4 Hz, 1H, 4'-C*H*), 9.42 (br.s, 1H, 6'-C*H*), and the resonances assigned to the cyclooctadienyl ligand were obscured in the mixture of **5b** and **6a**.

6a: 0.66-0.67 (1H, 8-*endo*-C*H*, overlapped with free MeCN), 0.94 (s, 3H, *Me*CN), 1.74 (d, $^{3}J_{\text{H-H}}$ = 8.0 Hz, 1H, 8-*exo*-C*H*), 2.86 (d, $^{3}J_{\text{H-H}}$ = 19.2 Hz, 1H, 5-C*H*), overlapped with **5a**), 4.90-5.05 (m, 1H, 7-C*H*), 5.08 (d, $^{3}J_{\text{H-H}}$ = 8.4 Hz, 1H, 1-C*H*), 5.28 (d, $^{3}J_{\text{H-H}}$ = 16.8 Hz, 1H, 1-C*H*), 6.10-6.22 (m, 1H, 6-CH, overlapped with **5a**), 6.40-6.55 (m, 1H, 2- C*H*), 6.73 (d, $^{3}J_{\text{H-H}}$ = 8.4 Hz, 1H, 3'-C*H*), 7.20-7.30 (1H, 4'-C*H,* overlapped with naphthalene), 7.56 (dd, $^{3}J_{\text{H-H}}$ = 15.6, 11.2 Hz, 1H, 3-C*H*), 8.44 (br.s, 1H, 6'-C*H*), and the resonances assigned to the 1,5-cod ligand were obscured in the mixture of **5b** and **6a**.

12. Reaction of 2,5-di(oct-1-yn-1-yl)thiophene (2b) with 2,6-di(buta-1,3-dien-1-yl)pyridine (3b)

This experiment was conducted to check whether the reaction could be further progressed by adding new monomers after the reaction had finished. **2b** (2.4 μl, 0.013 mmol) and **3b** (4.0 μl, 0.013 mmol) in thf-d_8 (600 μl) were added in an NMR tube under nitrogen atmosphere. Complex **1b** (0.89 mg, 0.0025 mmol; 20 mol%) was added in the solution. The mixture was allowed to react at 30 °C for 2d, during which the reaction was monitored by ^{1}H NMR spectroscopy. The mixture (20 μl) of **2b** (4.8 μl, 0.026 mmol) and **3b** (8.0 μl, 0.026 mmol) in C_6D_6 (87 μl) was added in reaction mixture. No further polymerization was observed.

13. Reaction of 2,5-di(hex-1-yn-1-yl)thiophene (2c) with 2,5-di(buta-1,3-dien-1-yl)pyridine (3a)

This experiment was conducted for observation of the initial stage of polymerisation. **2c** (7.1 μl, 0.028 mmol) and **3a** (5.24 mg, 0.0286 mmol) in C_6D_6 (600 μl) was added in an NMR tube under nitrogen atmosphere. Complex **1b** (1.29 mg, 0.00367 mmol; 13 mol%) was added in the solution. The mixture was allowed to react at 23 °C for 1d, during which the reaction was monitored by ^{1}H NMR spectroscopy. Dimers were predominantly produced within 5 minutes, where the butadienyl group at the 2 position preferentially reacted to give the dimer.

14. Stoichiometric Reaction of 1b with 3b in the presence of MeCN

3b (2.9 μl, 0.015 mmol) in C_6D_6 (500 μl) was added in an NMR tube under nitrogen atmosphere. To the solution was added MeCN (1.60 μl, 0.030 mmol) by a hypodermic syringe at room temperature. Complex **1b** (5.36 mg, 0.0153 mmol) was added to the solution. The mixture was allowed to react at room temperature for 80 min, during which the reaction was monitored by ^{1}H NMR spectroscopy. The solution was added 2,5-di(oct-1-yn-1-yl)thiophene (**2b**) (4.7 μl, 0.015 mmol) by a hypodermic syringe at room temperature. Reaction of complex with alkyne did not proceed even at 50 °C and the mixture was allowed to react at 70 °C for 1d, the solution became a complex mixture. Although detailed characterisation was difficult, we assumed the formation of a complex similar to **5a** and **5b** in an approximately 1/1 ratio.

15. UV-Vis measurements

The UV-Vis spectra of **4aa**, **4ab** and **7**[5] were measured in a spectroscopic grade thf solution (or acetone) using a quartz cell (cell length = 1.0 cm) at the concentration of 0.010 mM.

16. Fluorescence measurements

The fluorescence spectra of **4aa**, **4ab** and trimer **7** were measured in a spectroscopic grade thf solution using a quartz cell (cell length = 1.0 cm) at the concentration of 0.10 mM at room temperature. Although the excitation spectra of **4aa**, **4ab** and **7** were measured, no peaks were observed due to poor signal-to-nose ratio. These optimum excitation wavelengths were therefore screened for wavelengths giving the strongest fluorescence intensity in the range of 350-550 nm at room temperature. As the result, the optimum excitation wavelengths for **4ab** and **7** were found to be 400 nm. On the other hand, no significant fluorescence was observed for **4aa** by excitation in these wavelength range but that excited at 400 nm was depicted in Figure 3.

17. Cyclic voltammetry

The CV spectra of **4aa**, **4ab** and **7** (1.0 mM) were recorded in a spectroscopic grade thf solution at the Pt electrodes with $[Bu_4N][ClO_4]$ (0.1 M) as the supporting electrolyte at a sweep rate of 10 mVs^{-}

[1]. Pt was employed as the working electrode, and the potential scale was corrected with the standard redox potential of ferrocene (E˚ = +0.380 V).

18. MALDI-TOF MS

The MALDI-TOF MS of conjugated compounds were measured with trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DTCB) by linier positive mode.

19. GPC measurements

The GPC measurements of **4aa** and **4ab** were performed at 40 ˚C using tetrahydrofuran as the eluent at a flow rate of 0.35 ml/min. The polymer solution was prepared at the saturation concentration of tetrahydrofuran (approx. 2 mg in 2 ml) followed by filtration through a polytetrafluoroethylene filter. The calibration was made by use of polystyrene standard (Tosoh Corporation).

20. References

(1) M. A. Bennett, H. Neumann, M. Thomas, X.-Q. Wang, P. Pertici, P. Salvadori and G. Vitulli, *Organometallics* 1991, **10**, 3237.
(2) Y. Hiroi, N. Komine, S. Komiya and M. Hirano, *Organometallics*, 2014, **33**, 6604.
(3) C. A. Busacca, E. Farber, J. DeYoung, S. Campbell, N. C. Gonnella, N. Grinberg, N. Haddad, H. Lee, S. Ma, D. Reeves, S. Shen and C. H. Senanayake, *Org. Lett.*, 2009, **11**, 5594.
(4) V. T. Nguyen, H. T. Dang, H. H. Pham, V. D. Nguyen, C. Flores-Hansen, H. D. Arman and O. V. Larionov, *J. Am. Chem. Soc.*, 2018, **140**, 8434.
(5) S. Kiyota, K. Kamakura, N. Komine and M. Hirano, *Org. Biomol. Chem.*, 2023, **17**, 3588.

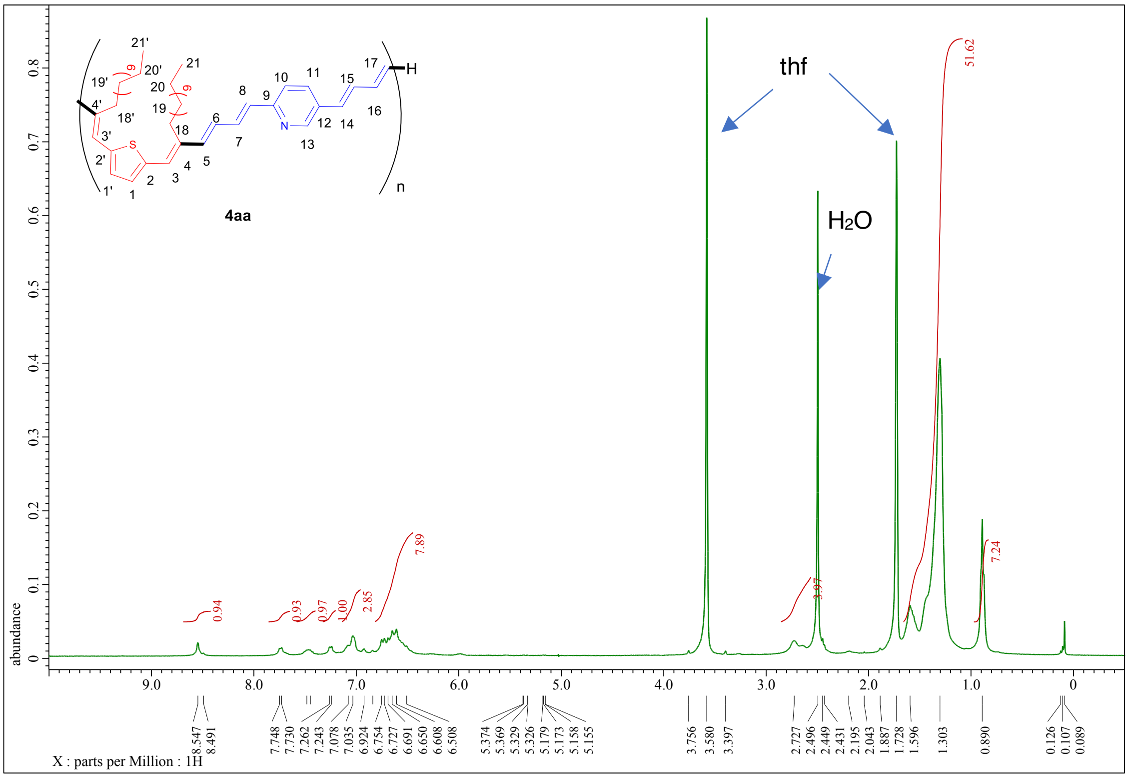


Figure S1. ^{1}H NMR Spectrum of 4aa in thf-d_8.

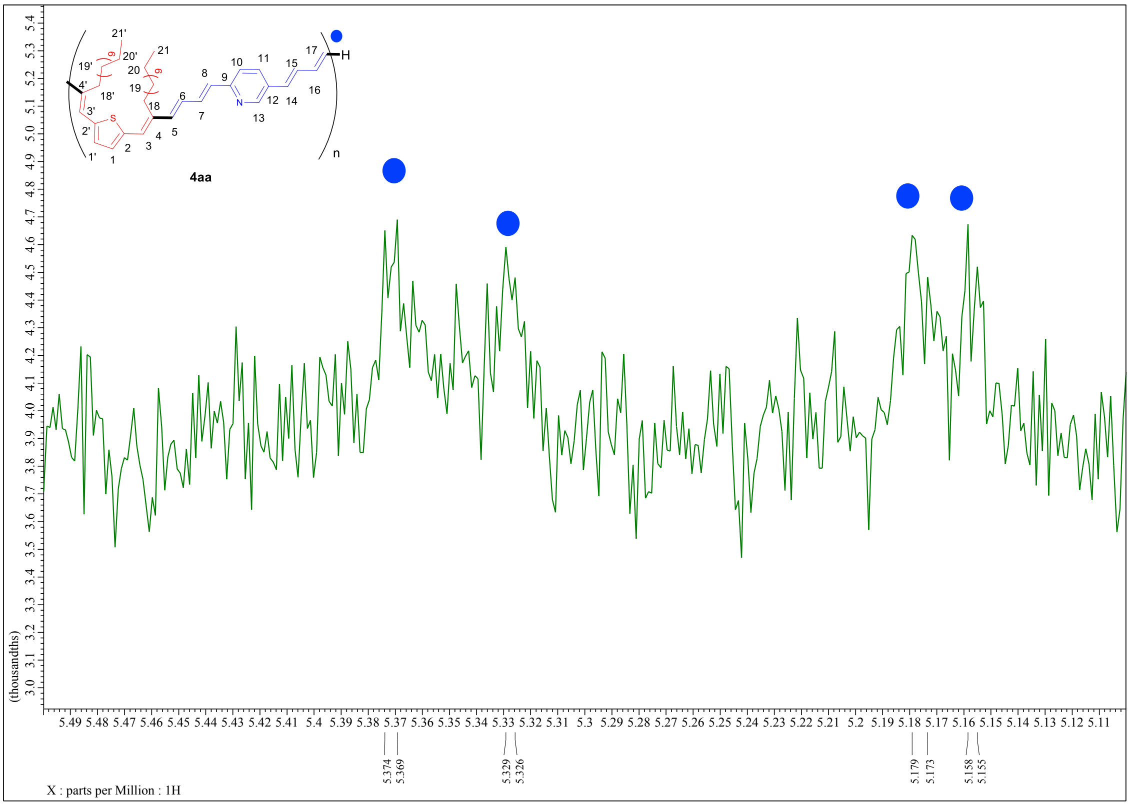


Figure S1-2. ^{1}H NMR Spectrum (5.1-5.5 ppm) of 4aa in thf-d_8.

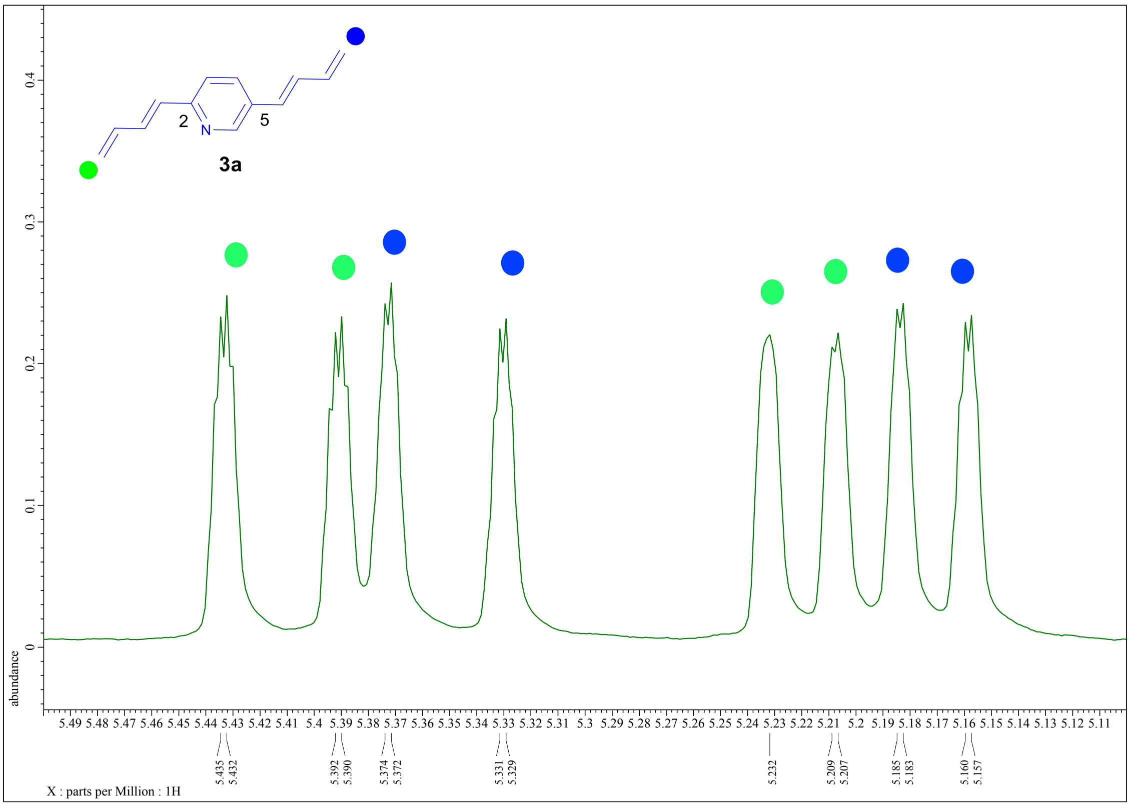


Figure S2. ^{1}H NMR Spectrum (5.1-5.5 ppm) of 3a in thf-d_8.

Figure S3 .^{1}H-^{1}H COSY NMR Spectrum of 4aa in thf-d_8.

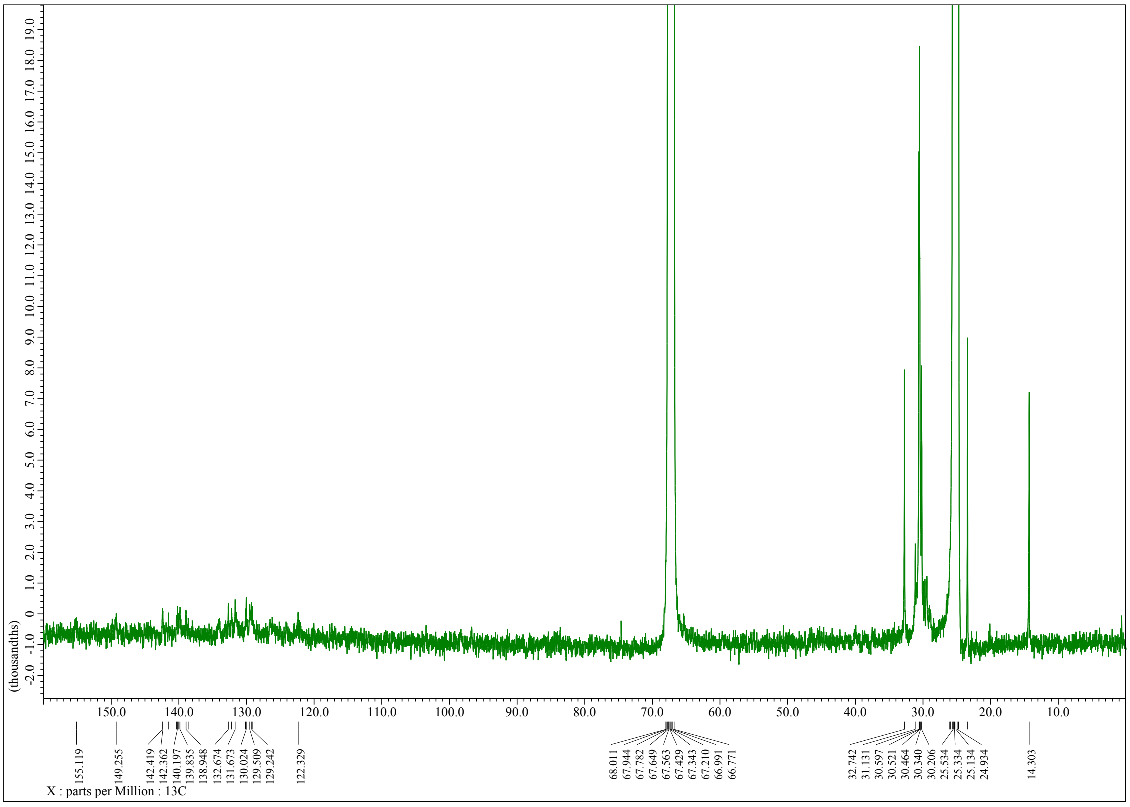


Figure S4. $^{13}C\{^1H\}$ **NMR Spectrum of 4aa in thf-d**$_8$**.**

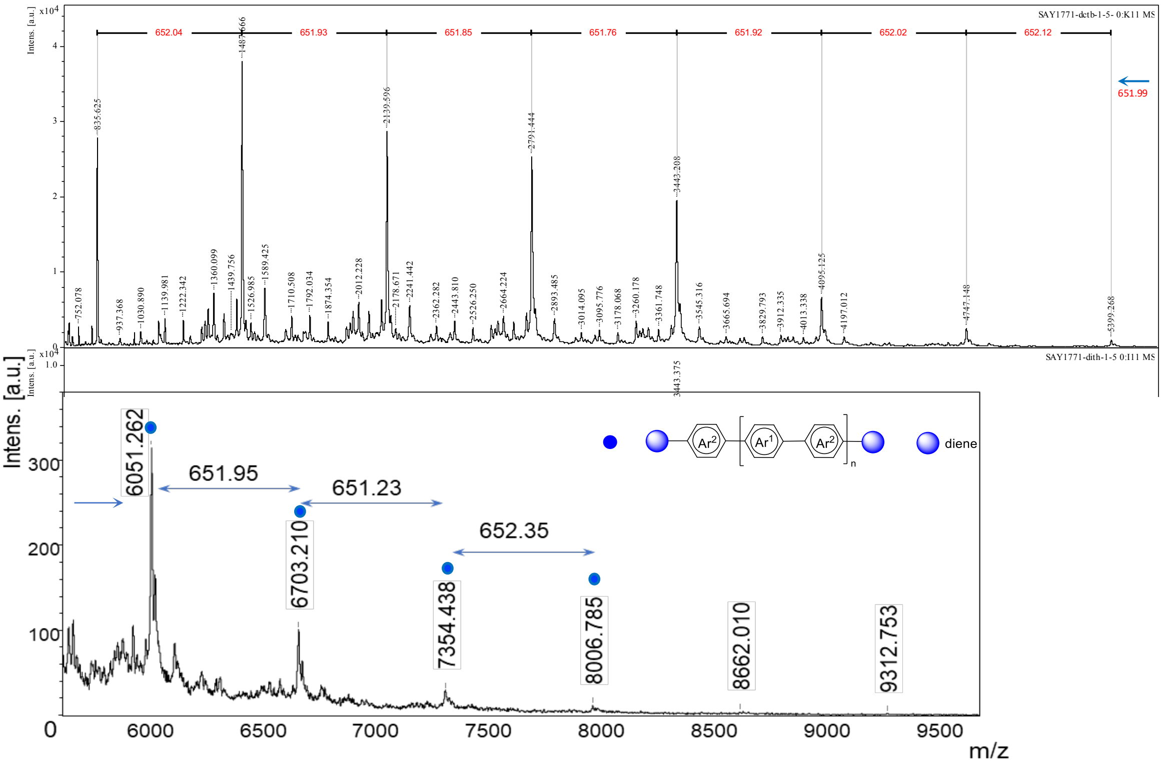
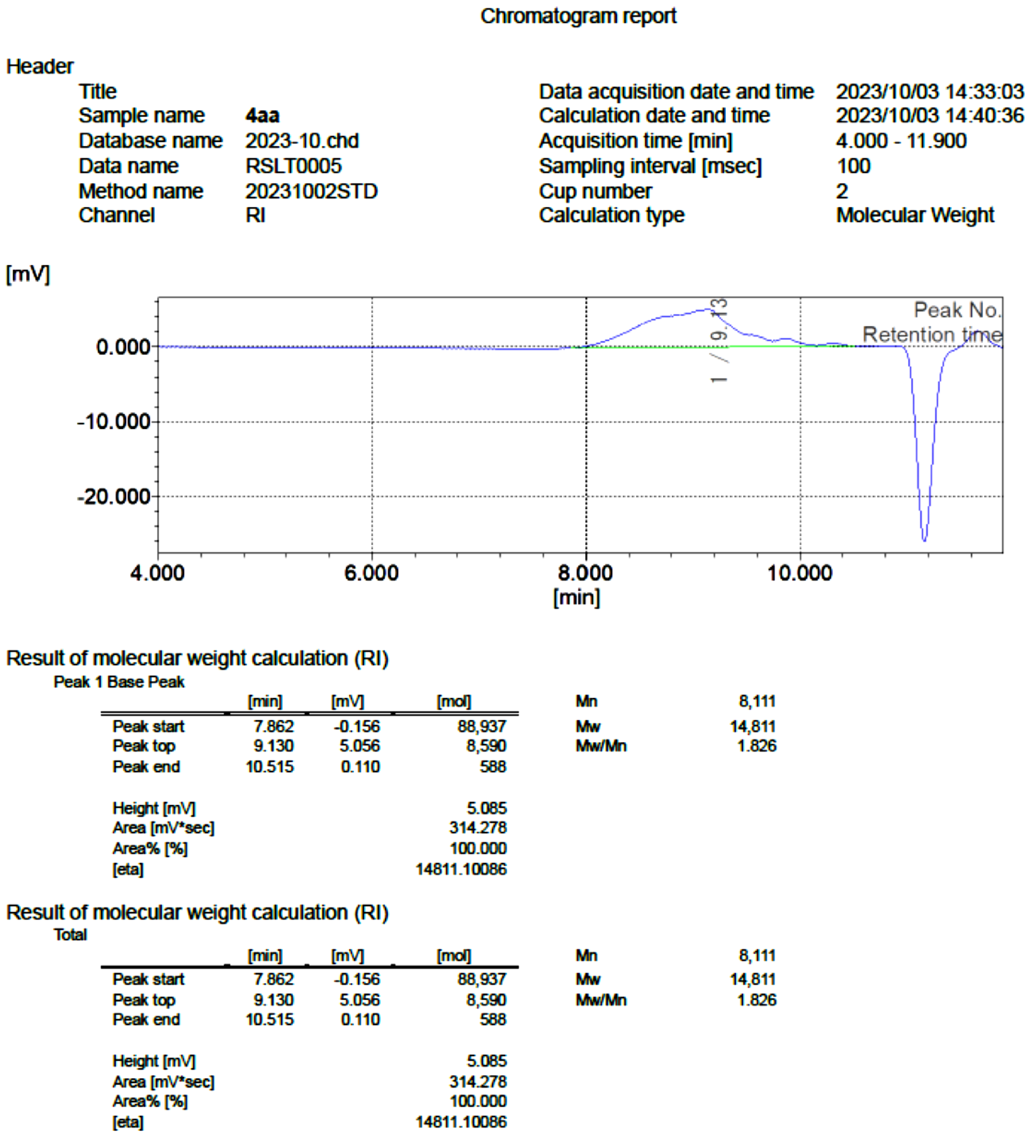


Figure S5. MALDI-TOF MS of 4aa. Ar^1: thienyl fragment. Ar^2: pyridyl fragment. The conjugated trienyl fragments were omitted in the structure drawing.



Chromatogram report

Header

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Database name	2023-10.chd	Acquisition time [min]	4.000 - 11.900
Data name	RSLT0005	Sampling interval [msec]	100
Method name	20231002STD	Cup number	2
Channel	RI	Calculation type	Molecular Weight

Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	7.862	-0.156	88,937	Mn	8,111
Peak top	9.130	5.056	8,590	Mw	14,811
Peak end	10.515	0.110	588	Mw/Mn	1.826
Height [mV]			5.085		
Area [mV*sec]			314.278		
Area% [%]			100.000		
[eta]			14811.10086		

Result of molecular weight calculation (RI)

Total

	[min]	[mV]	[mol]		
Peak start	7.862	-0.156	88,937	Mn	8,111
Peak top	9.130	5.056	8,590	Mw	14,811
Peak end	10.515	0.110	588	Mw/Mn	1.826
Height [mV]			5.085		
Area [mV*sec]			314.278		
Area% [%]			100.000		
[eta]			14811.10086		

Figure S6. GPC Calculation result of 4aa.

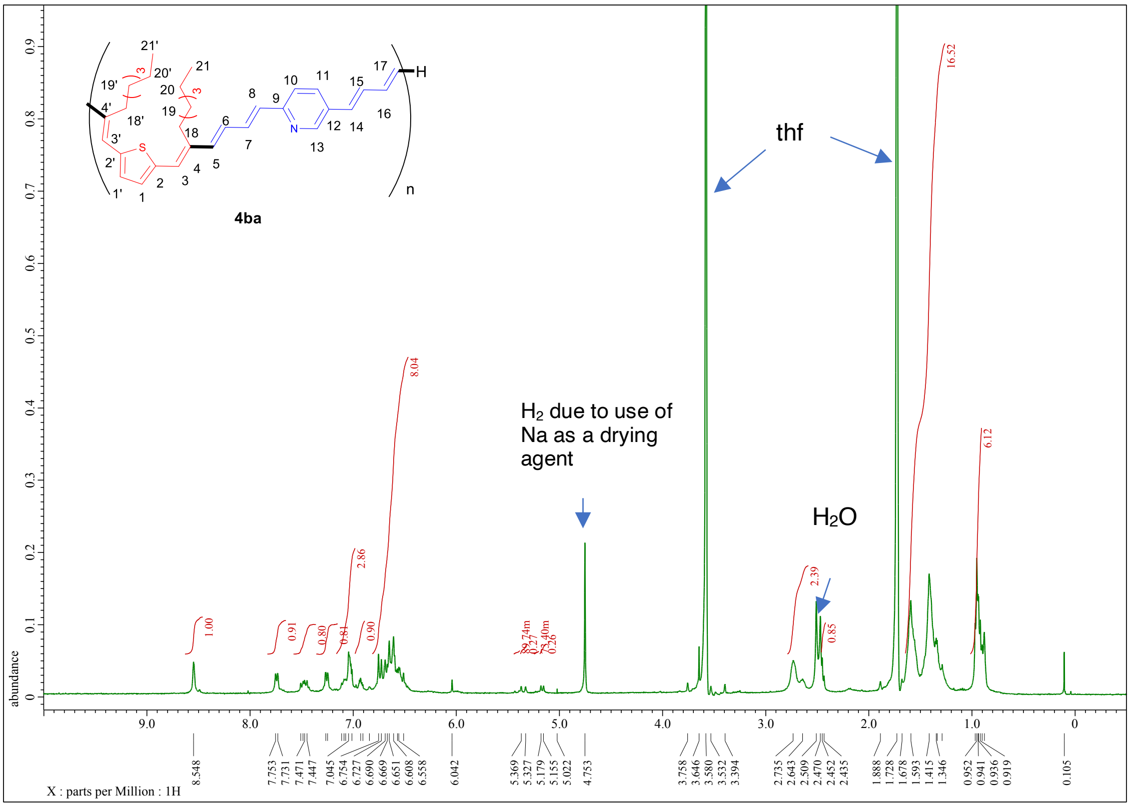


Figure S7. ^{1}H NMR Spectrum of 4ba in thf-d_8.

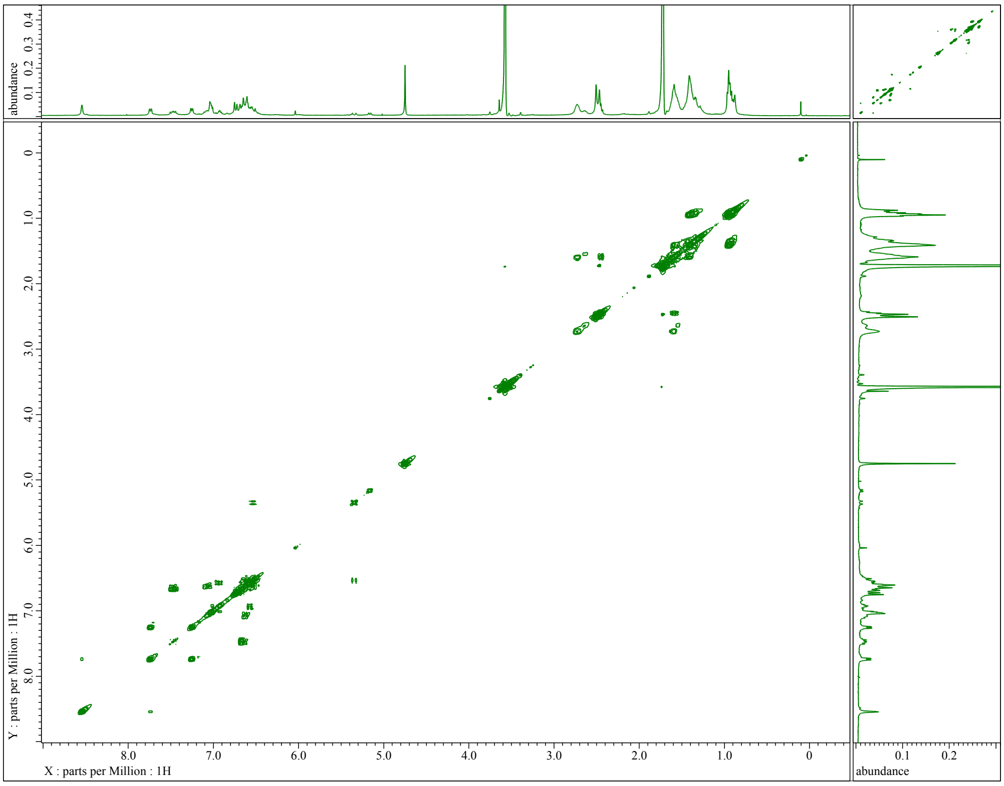


Figure S8. ^{1}H-^{1}H COSY NMR Spectrum of 4ba in thf-d_8.

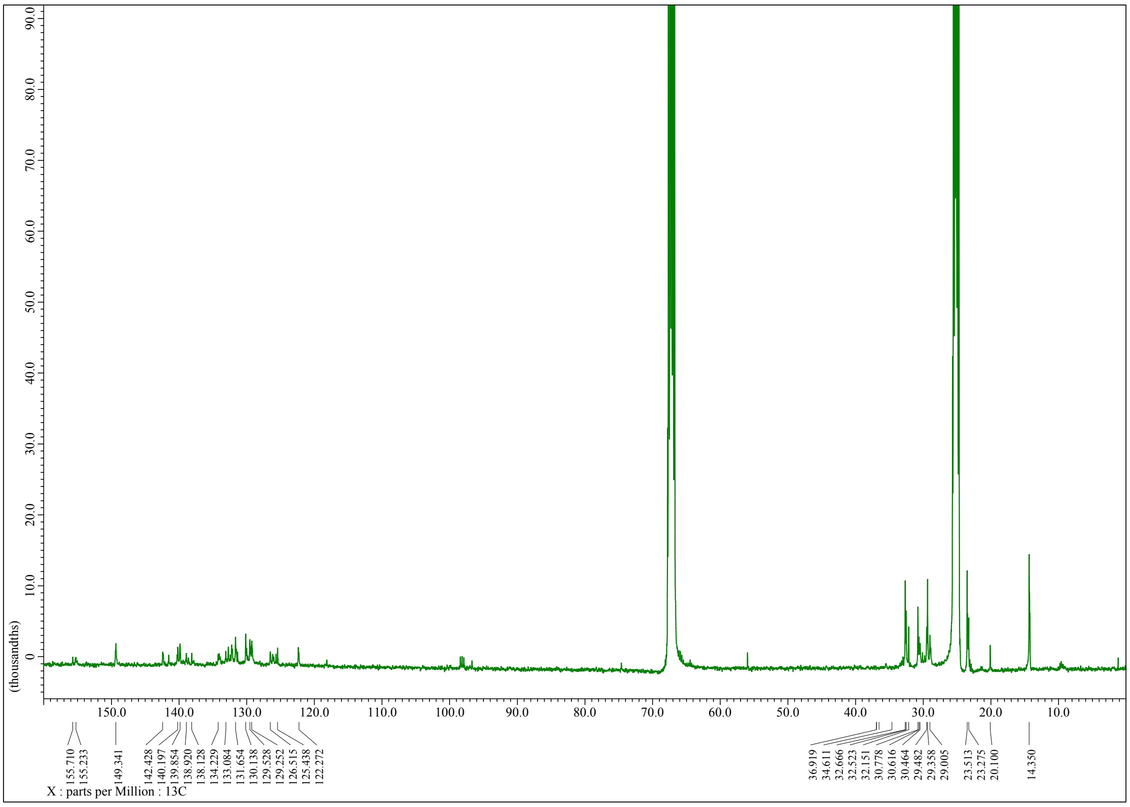


Figure S9. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ba in thf-d_8

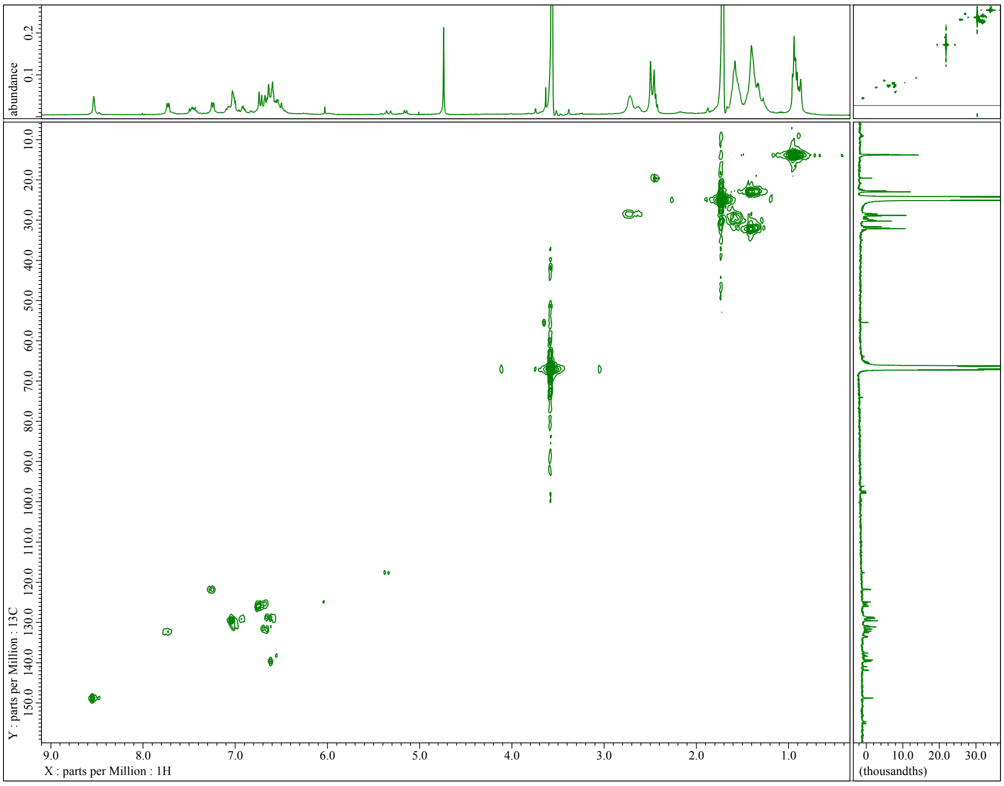


Figure S10. ^{13}C-^{1}H Correlation Spectrum of 4ba in thf-d_8 (HMQC).

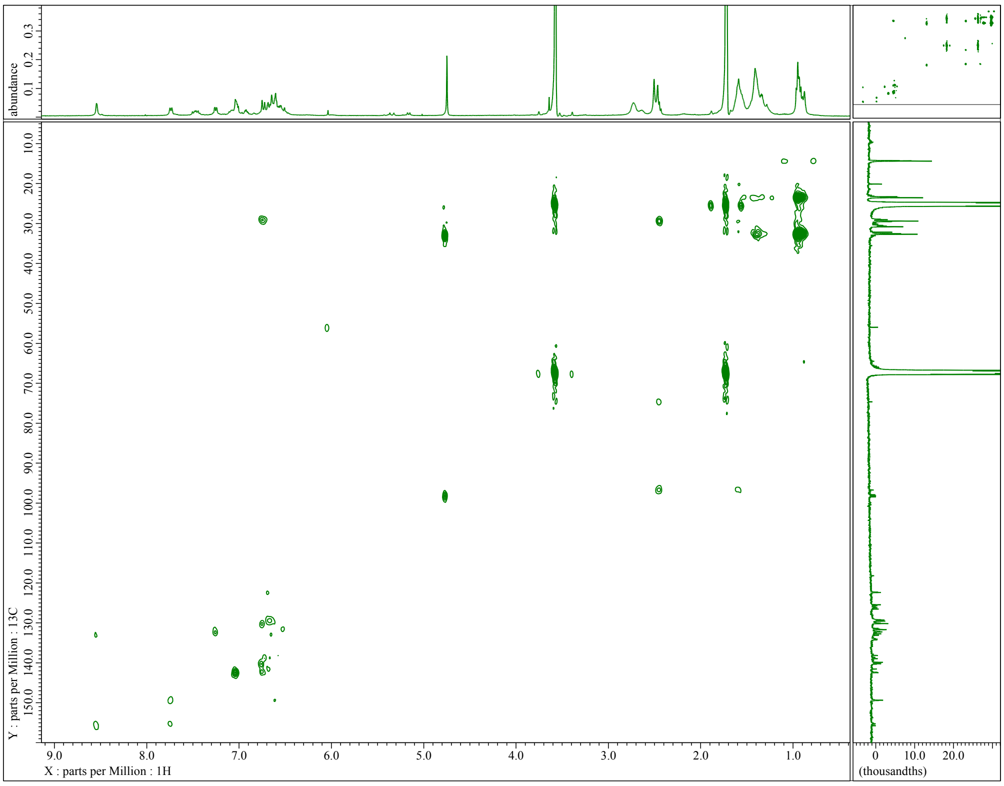


Figure S11. ^{13}C-^{1}H **Correlation Spectrum of 4ba in thf-d_8 (HMBC).**

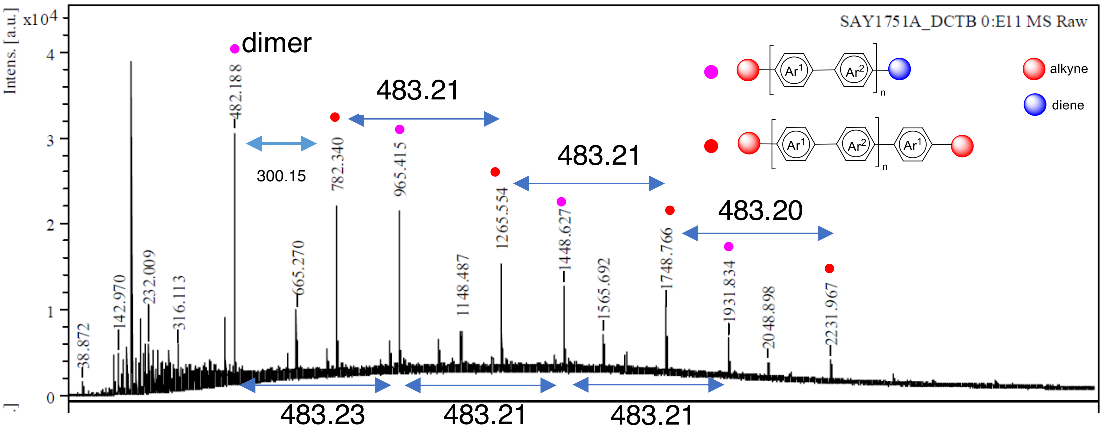


Figure S12. MALDI-TOF MS of 4ba. Ar^1: thienyl fragment. Ar^2: pyridyl fragment. The conjugated trienyl fragments were omitted in the structure drawing.

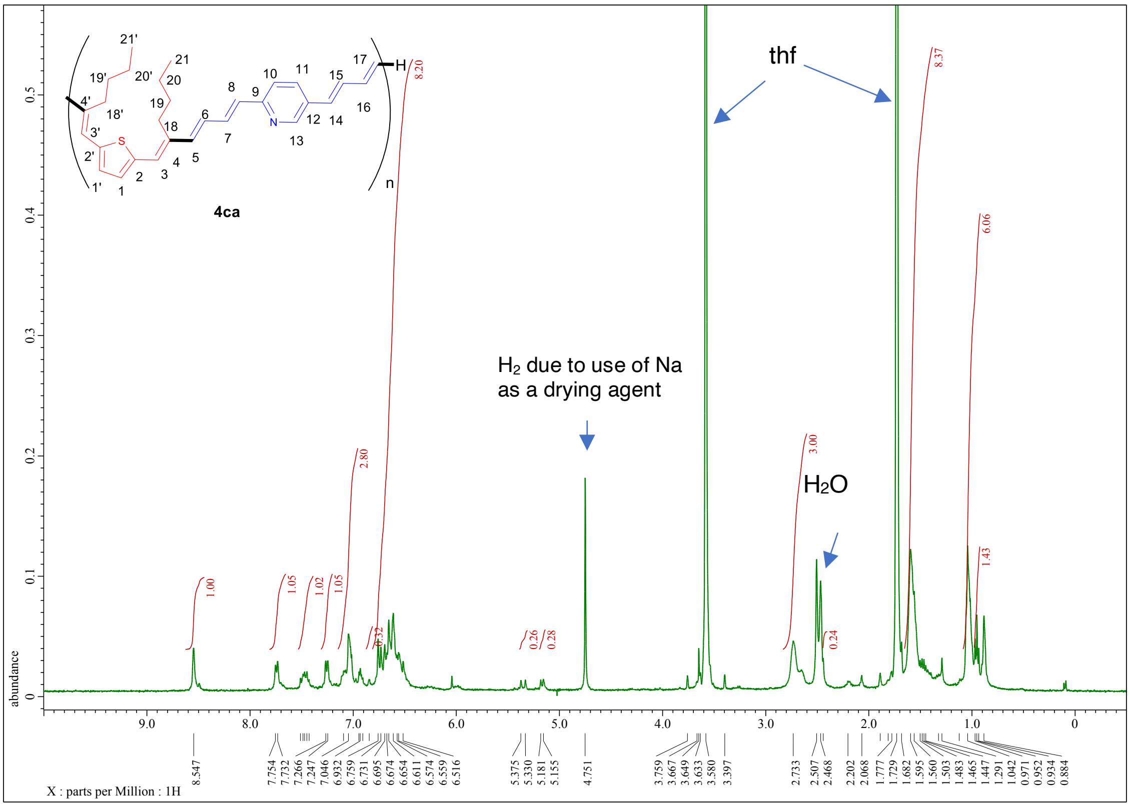


Figure S13. ^{1}H NMR Spectrum of 4ca in thf-d_8.

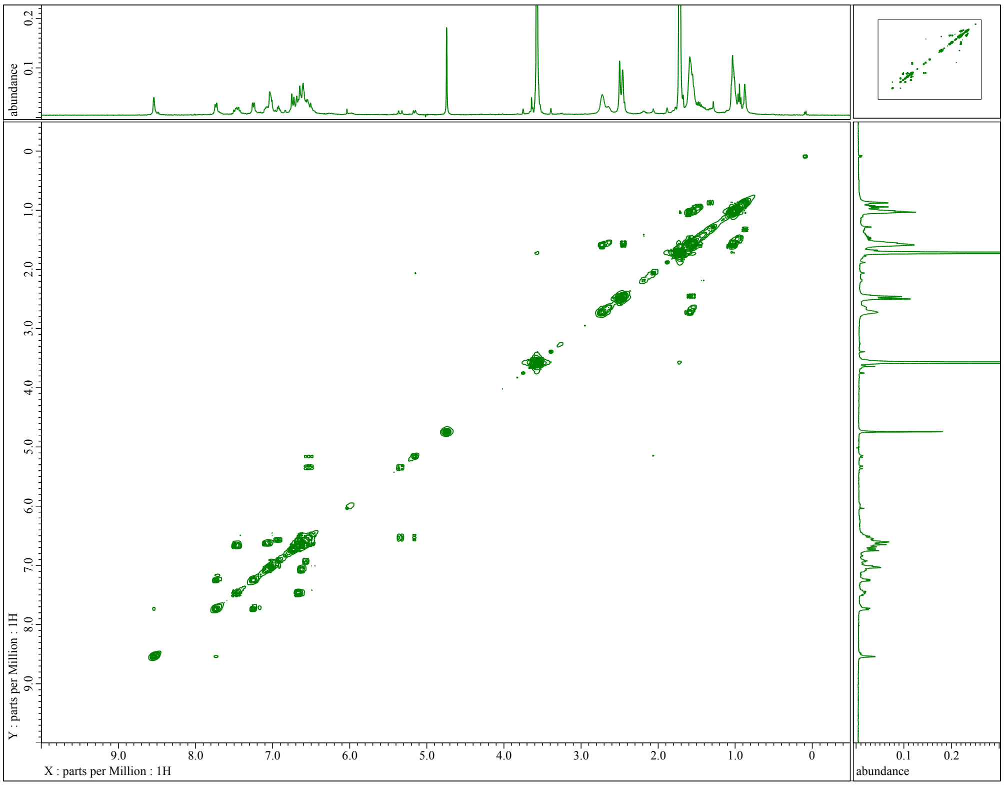


Figure S14. ^{1}H-^{1}H COSY NMR Spectrum of 4ca in thf-d_8.

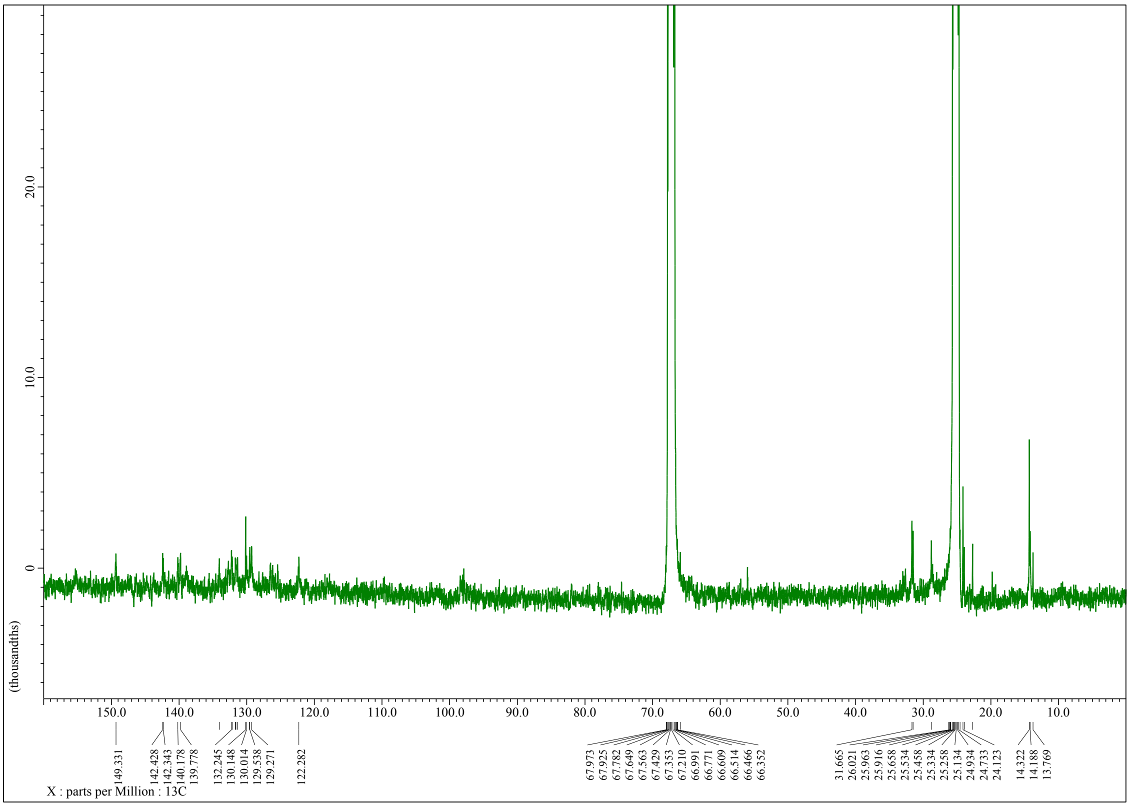


Figure S15. $^{13}C\{^{1}H\}$ **NMR Spectrum of 4ca in thf-d$_8$.**

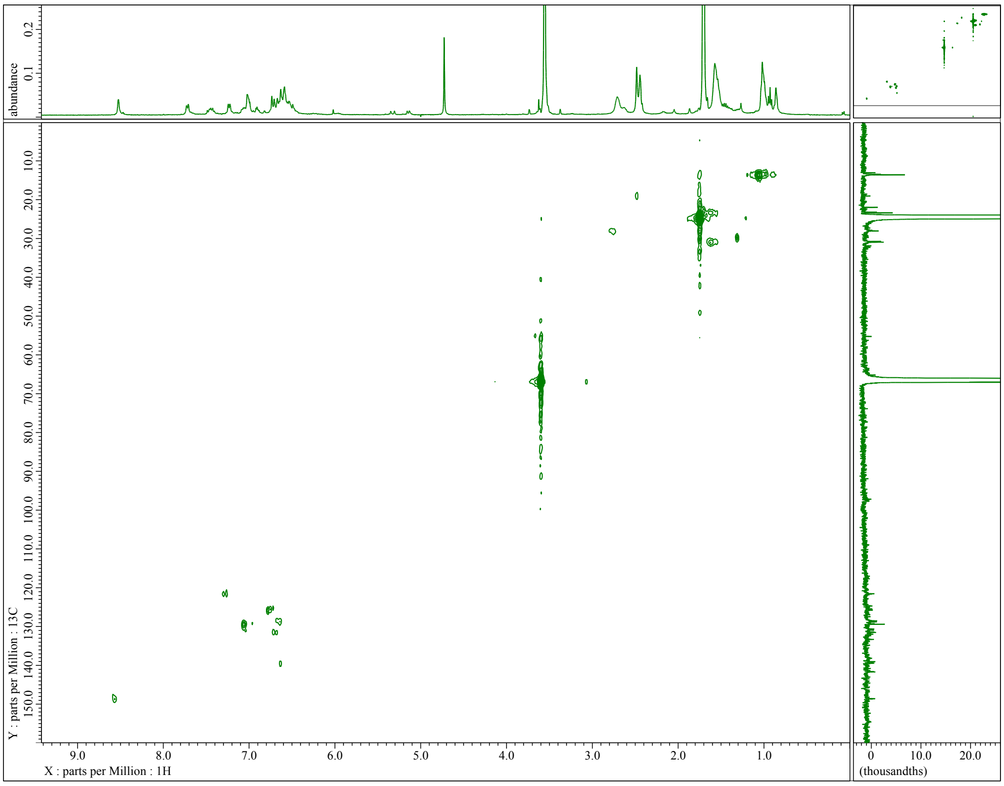
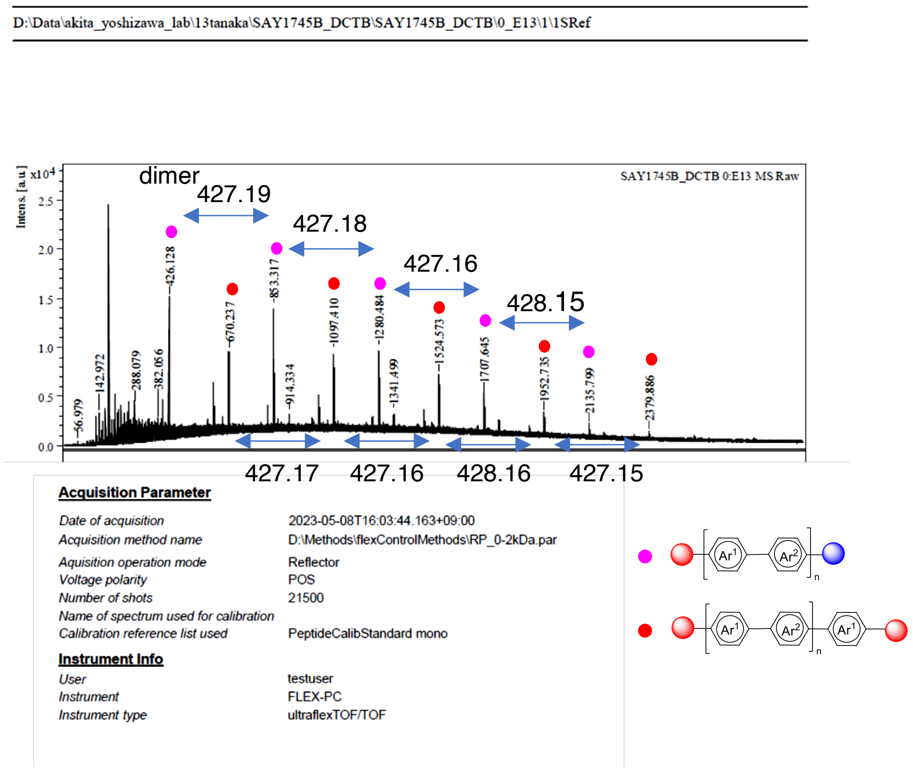


Figure S16. ^{13}C-^{1}H **Correlation Spectrum of 4ca in thf-d$_8$. (HMQC).**



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Name of spectrum used for calibration	
Calibration reference list used	PeptideCalibStandard mono

Instrument Info

User	testuser
Instrument	FLEX-PC
Instrument type	ultraflexTOF/TOF

Figure S17. MALDI-TOF MS of 4ca. Ar^1: thienyl fragment. Ar^2: pyridyl fragment. The conjugated trienyl fragments were omitted in the structure drawing.

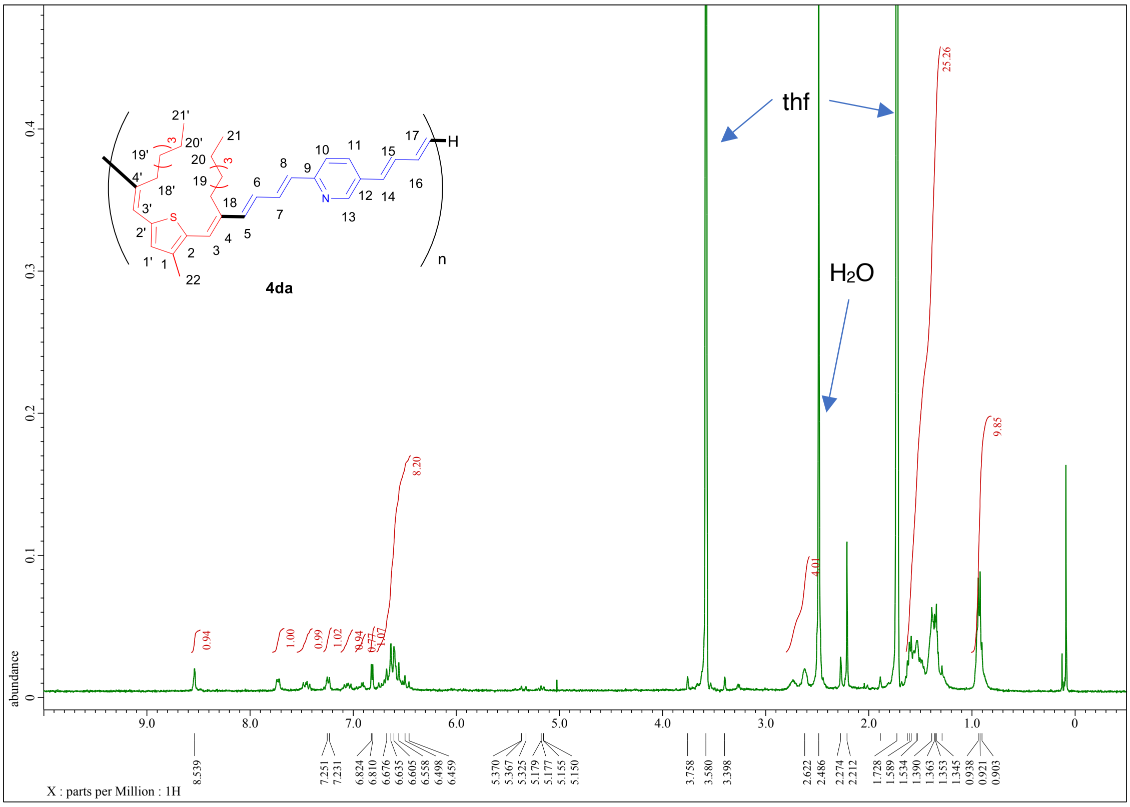


Figure S18. ^{1}H NMR Spectrum of 4da in thf-d_8.

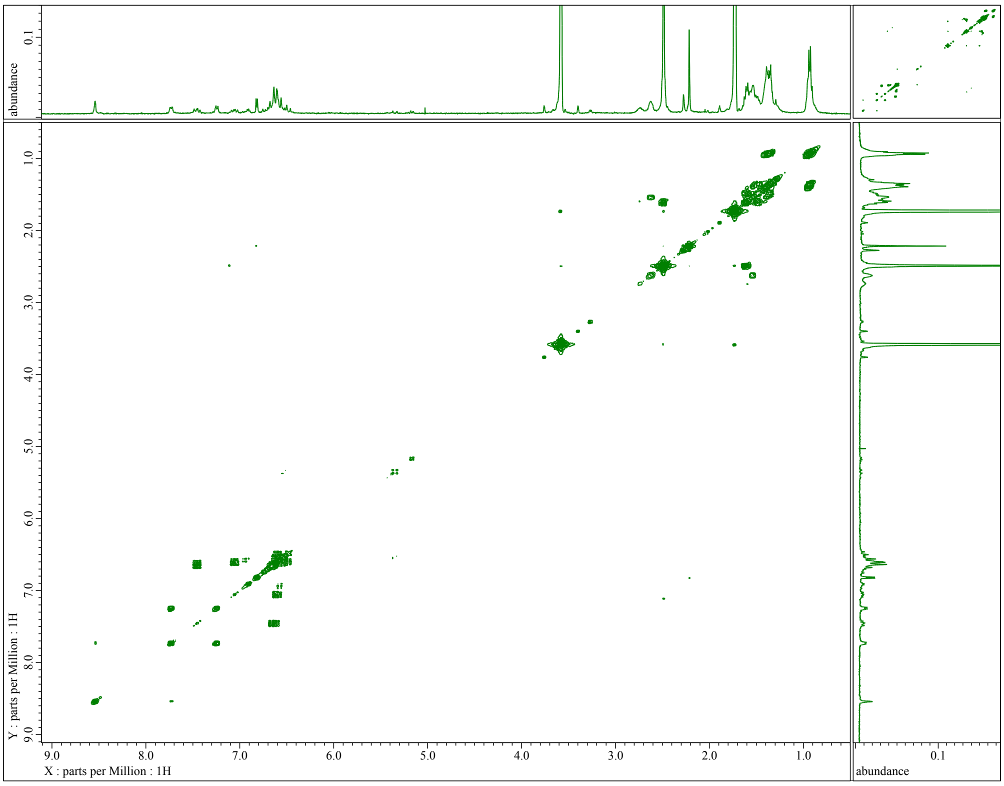


Figure S19. ^{1}H-^{1}H COSY NMR Spectrum of 4da in thf-d$_8$.

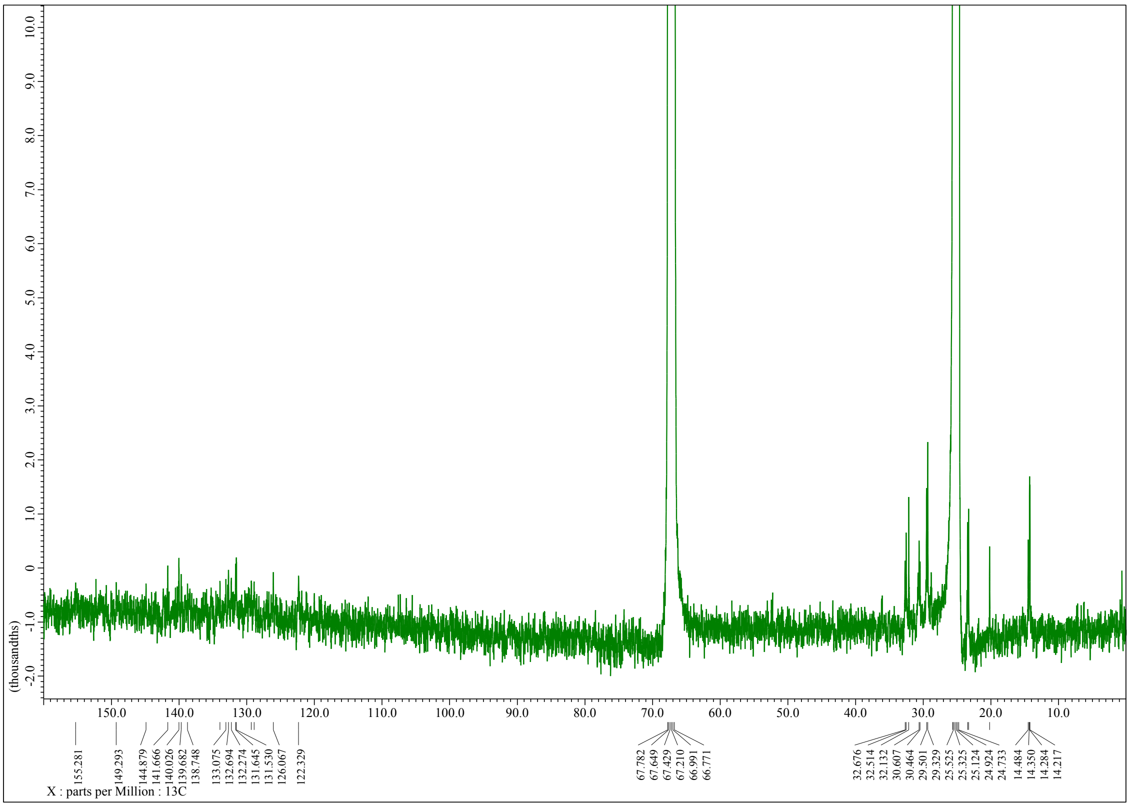


Figure S20. ^{13}C{^{1}H} NMR Spectrum of 4da in thf-d$_8$.

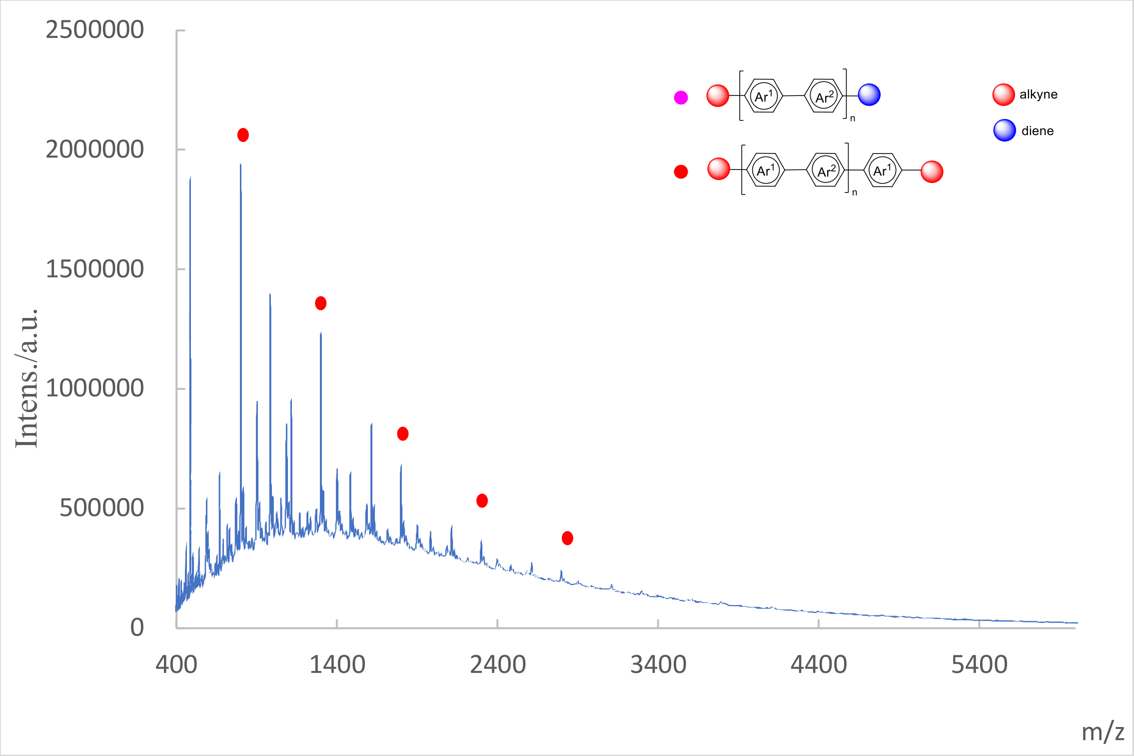


Figure S21-1. MALDI-TOF MS of 4da. Ar^1: thienyl fragment. Ar^2: pyridyl fragment. The conjugated trienyl fragments were omitted in the structure drawing.

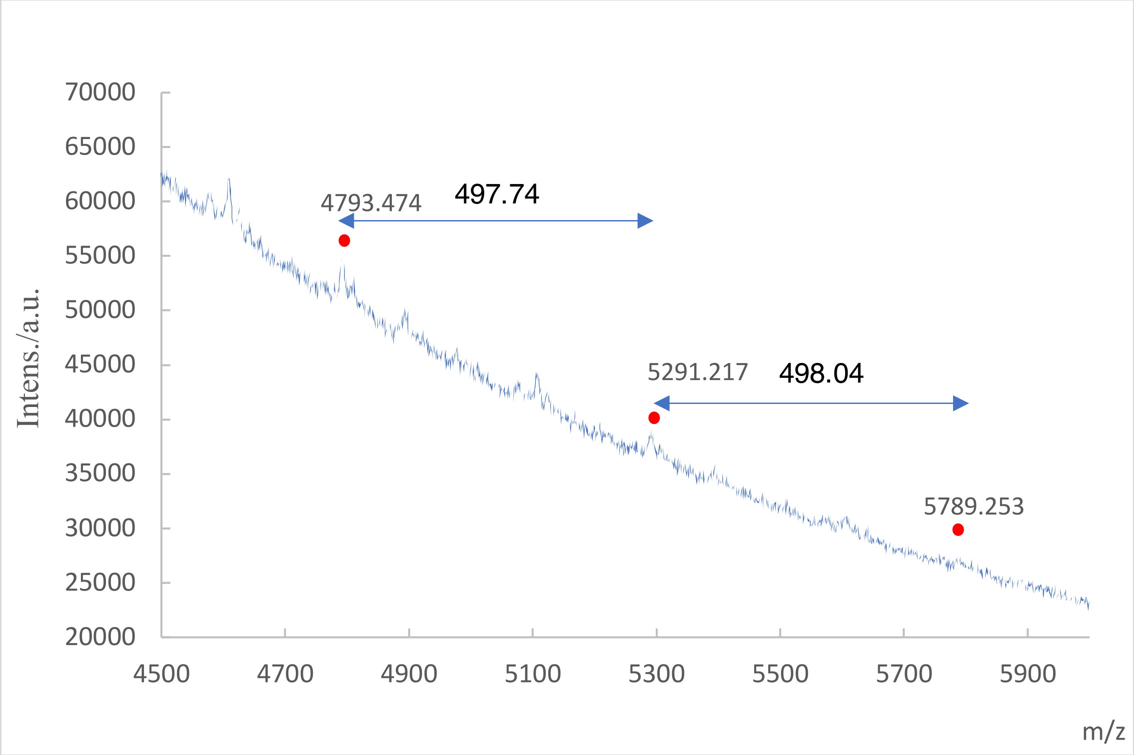


Figure S21-2. MALDI-TOF MS of 4da.

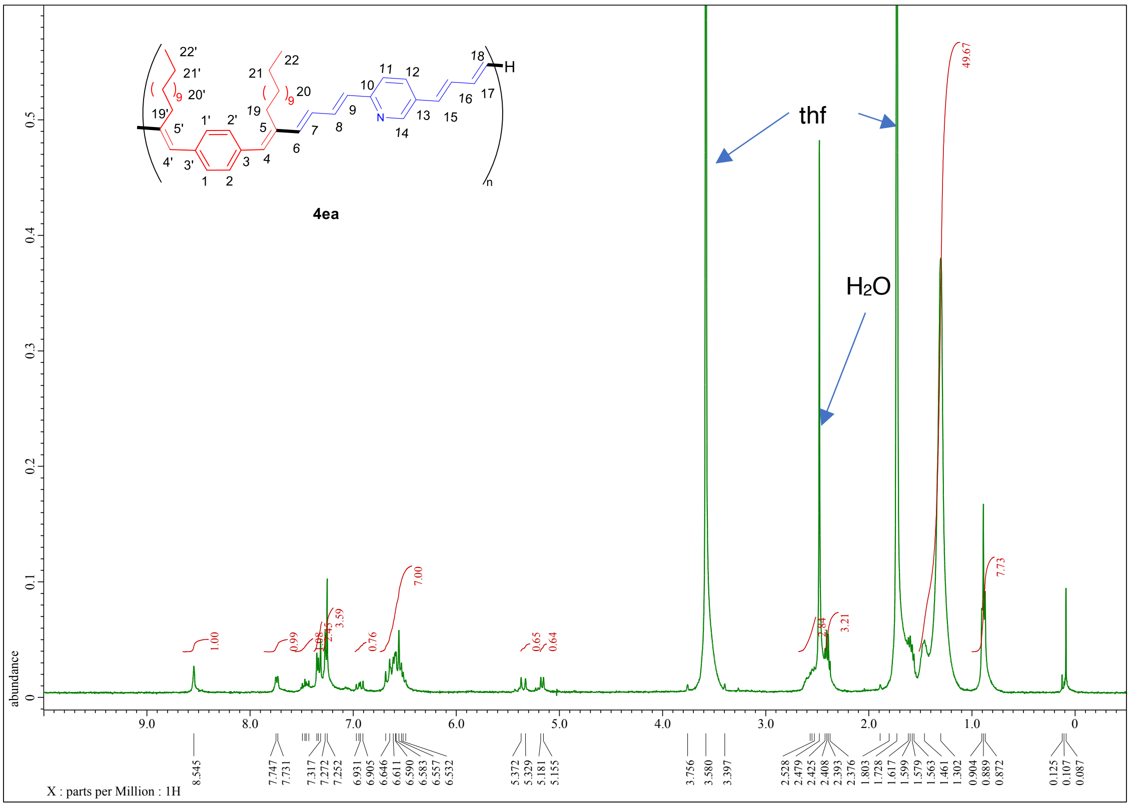


Figure S22. ^{1}H NMR Spectrum of 4ea in thf-d_8.

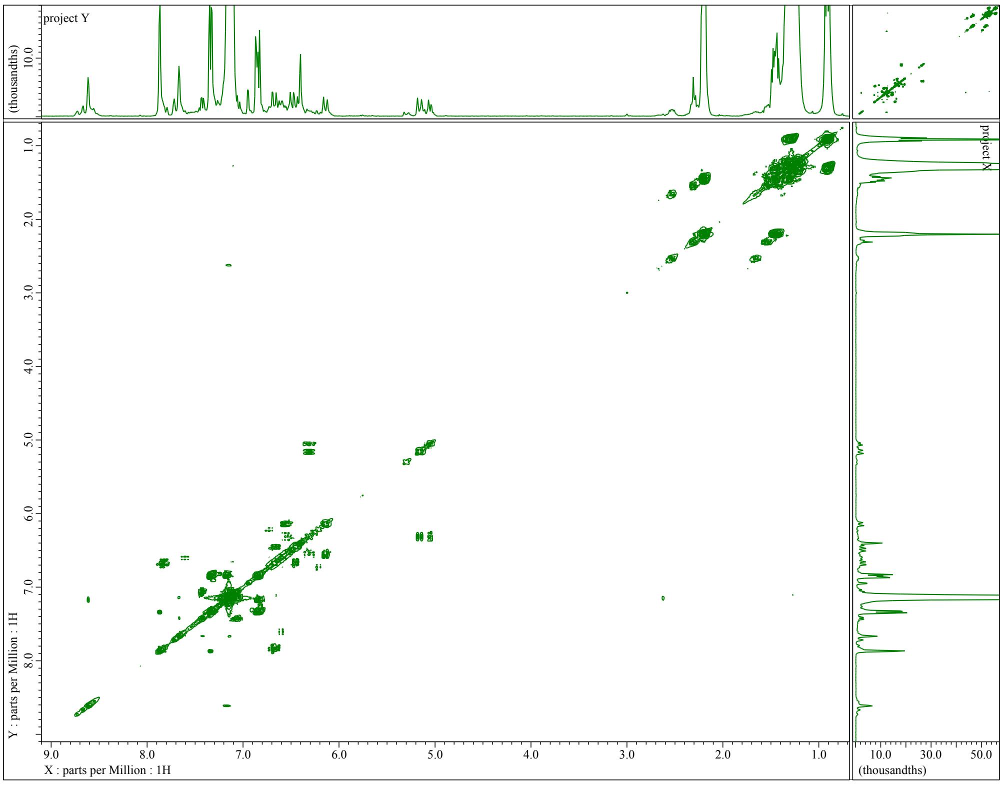


Figure S23. ^{1}H-^{1}H COSY NMR Spectrum of 4ea in thf-d_8.

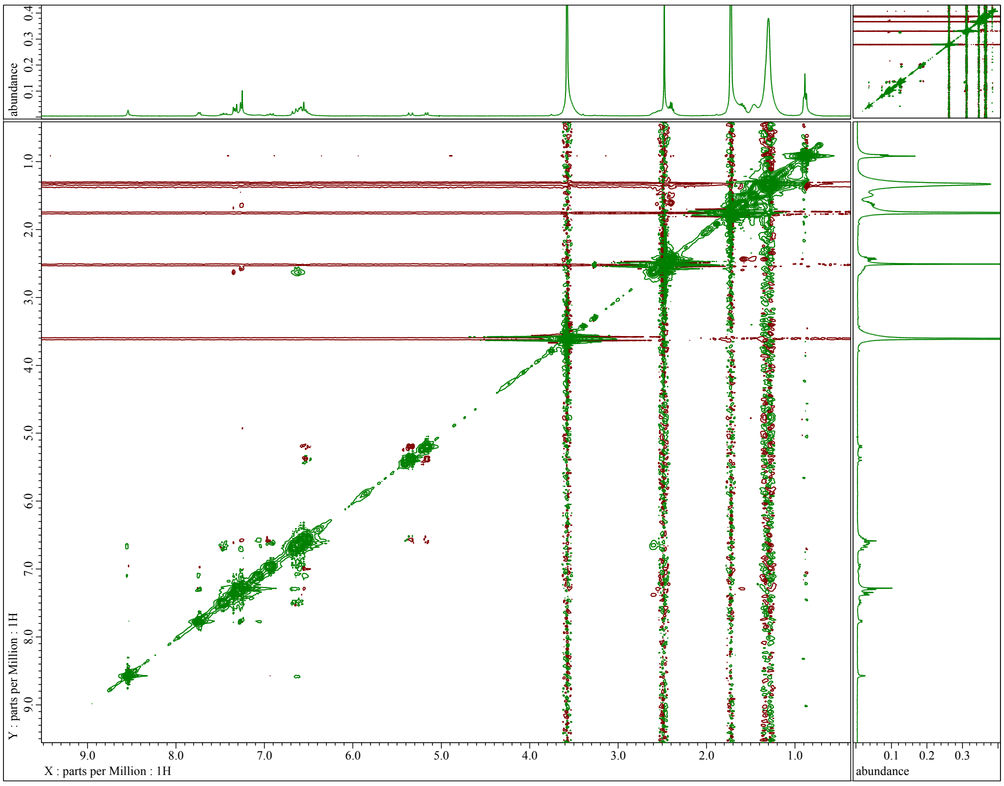


Figure S24. ^{1}H-^{1}H NOESY NMR Spectrum of 4ea in thf-d_8.

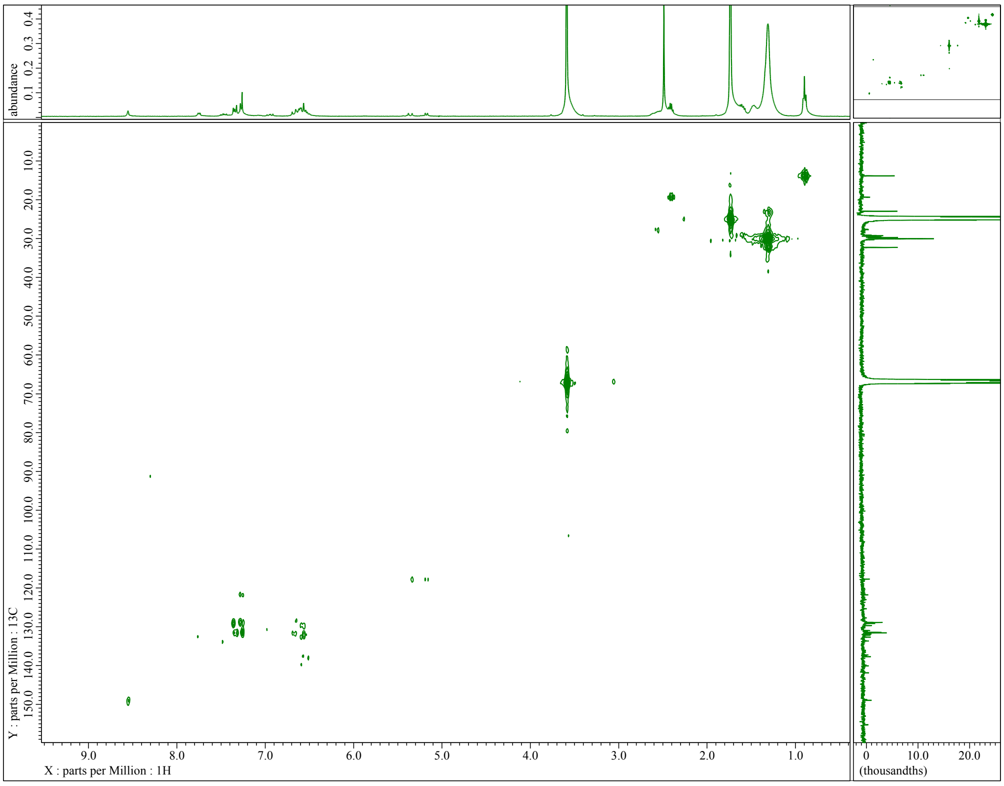


Figure S25. ^{13}C-^{1}H Correlation Spectrum of 4ea in thf-d_8 (HMQC).

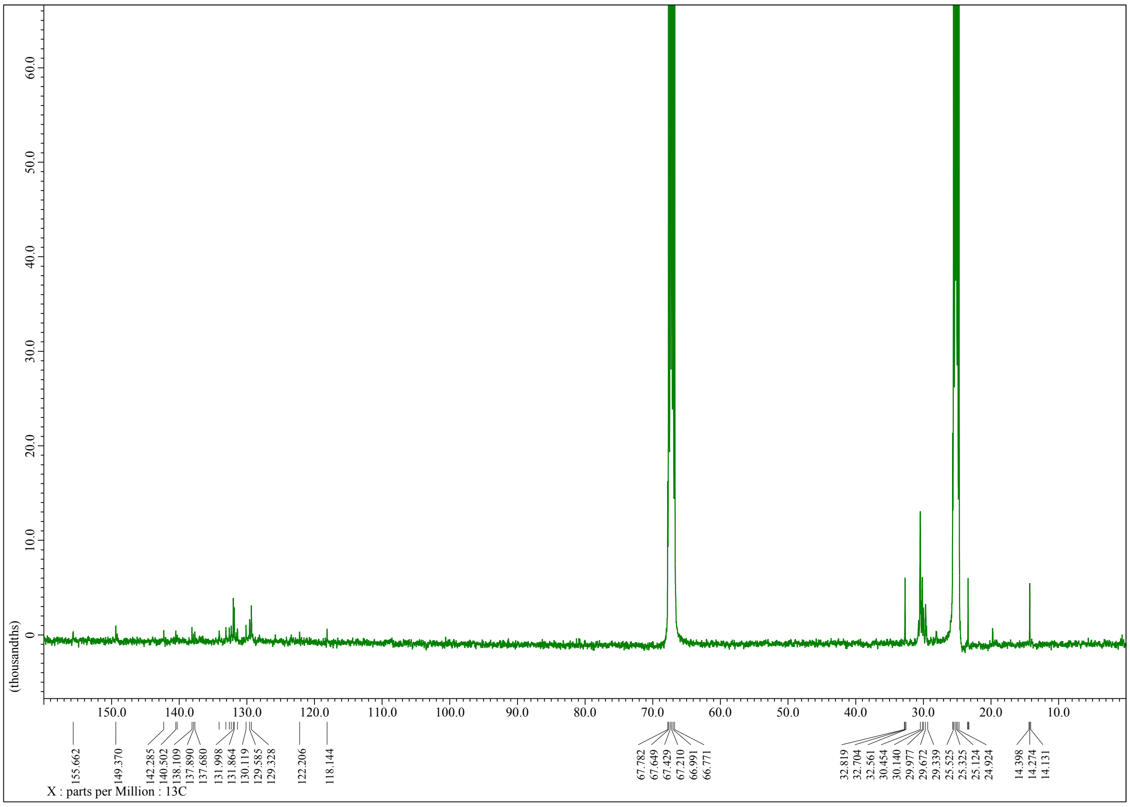


Figure S26. $^{13}C\{^1H\}$ NMR Spectrum of 4ea in thf-d_8.

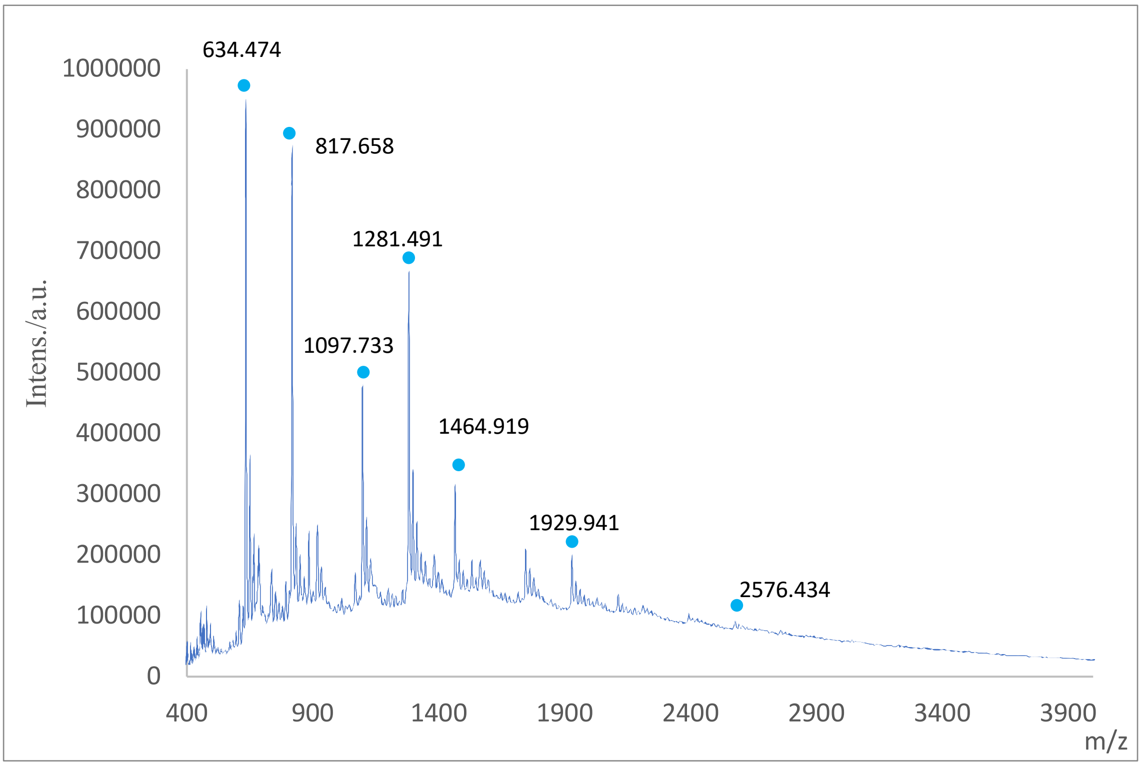


Figure S27. MALDI-TOF MS of 4ea.

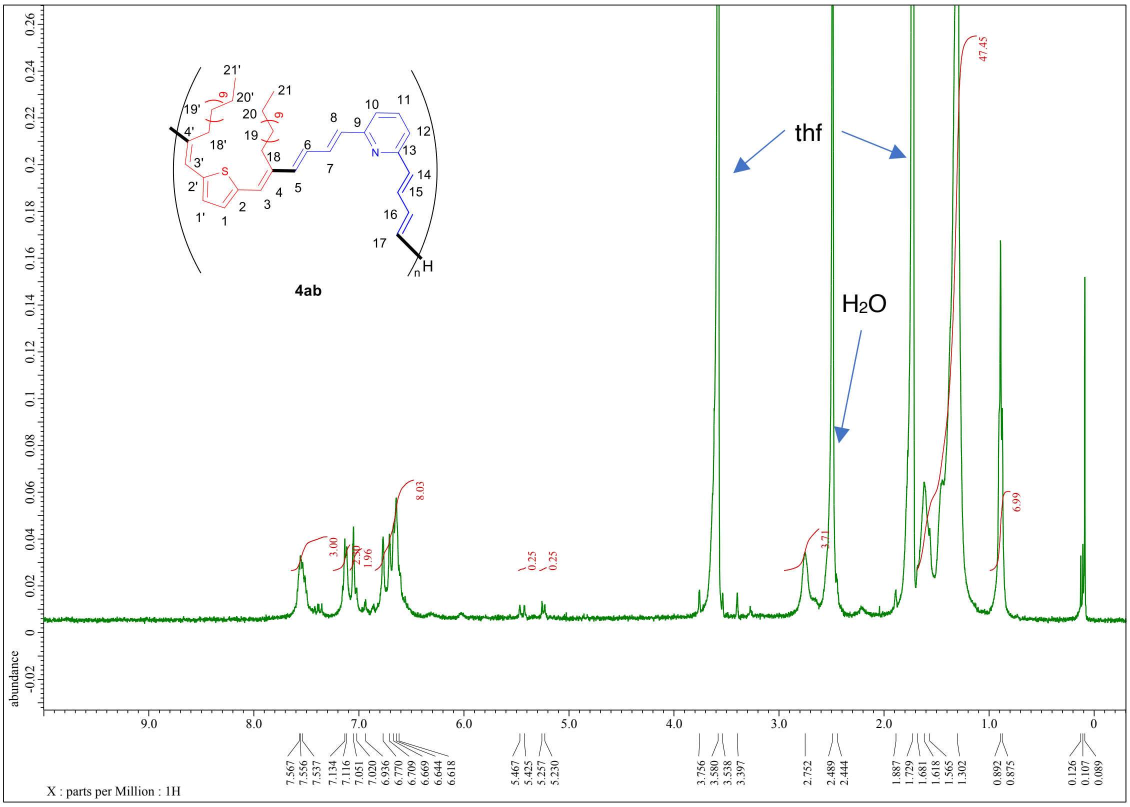


Figure S28. ^{1}H NMR Spectrum of 4ab in thf-d_8.

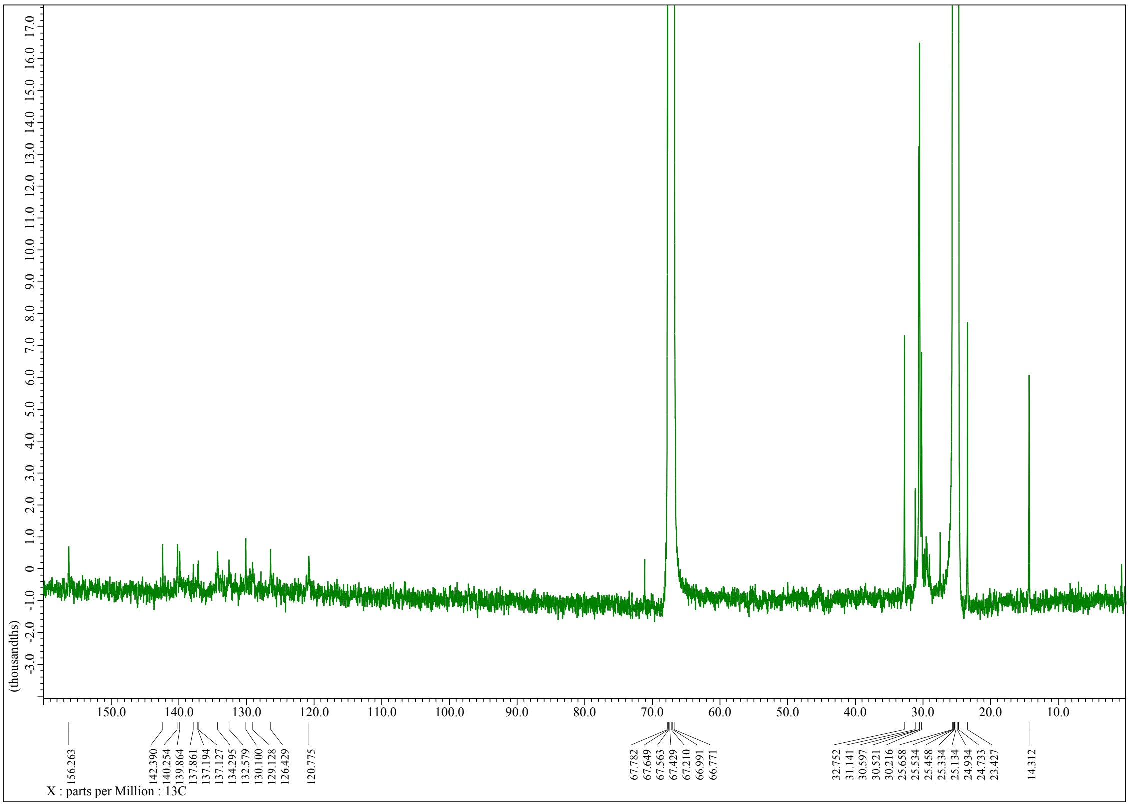


Figure S29. ^{13}C{^{1}H} NMR Spectrum of 4ab in thf-d_8.

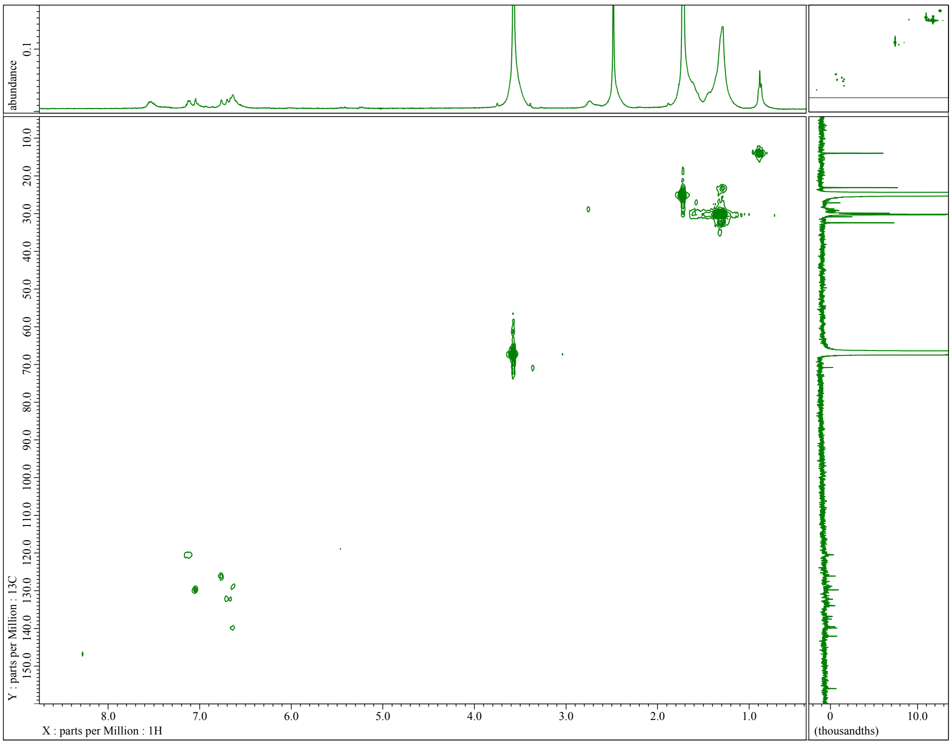


Figure S30. ^{13}C-^{1}H **Correlation Spectrum of 4ab in thf-d$_8$ (HMQC).**

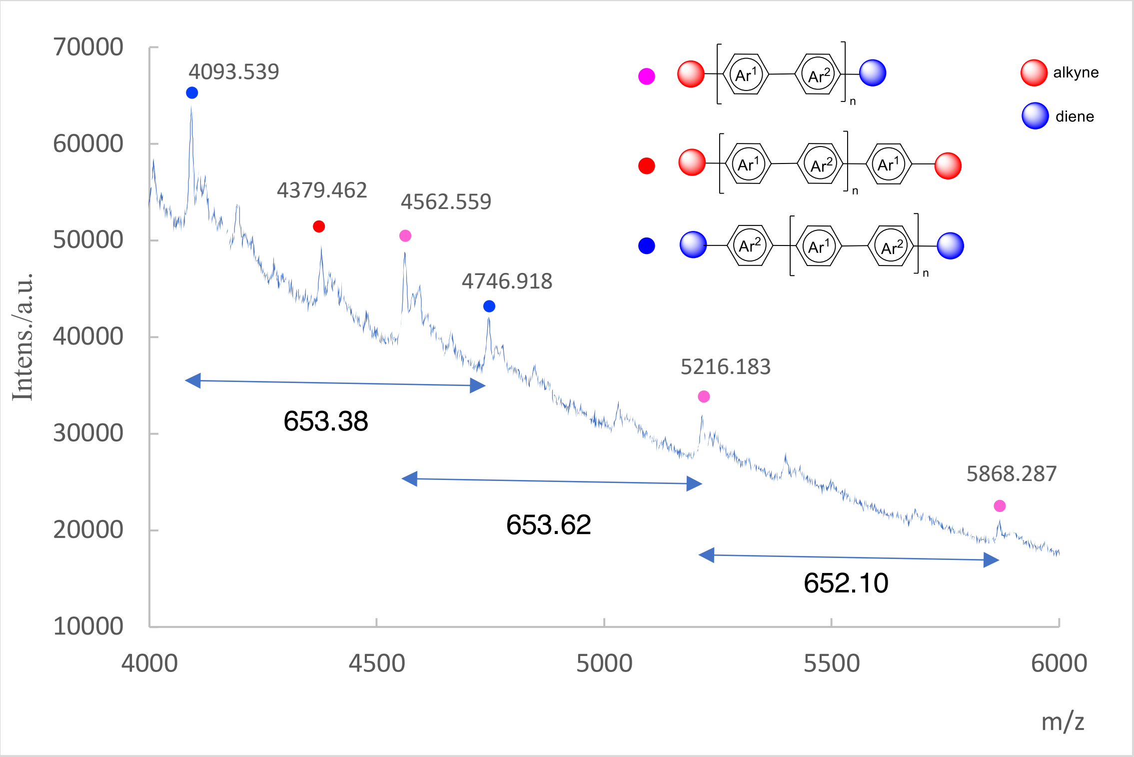
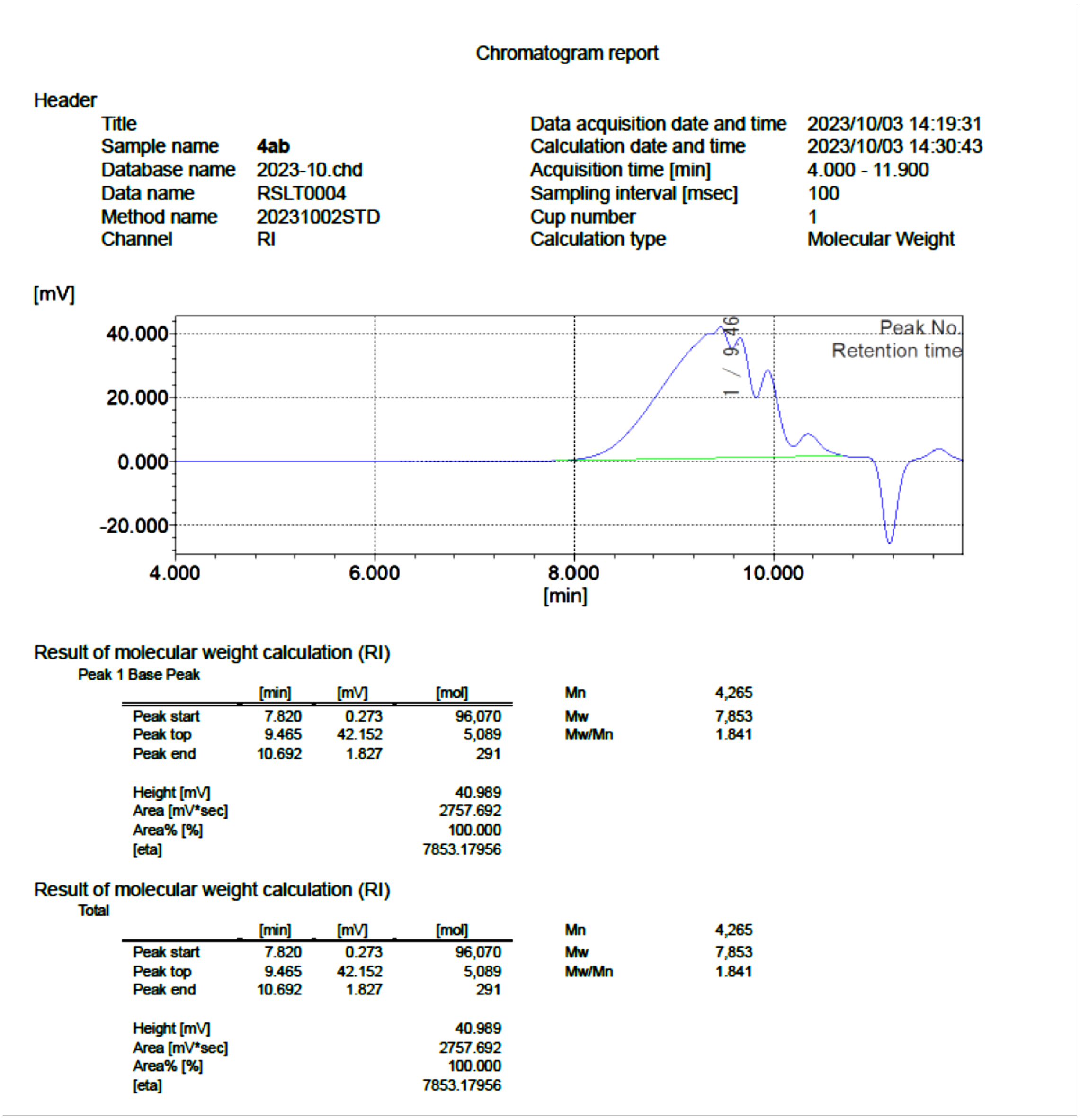


Figure S31. MALDI-TOF MS of 4ab. Ar^{1}: thienyl fragment. Ar^{2}: pyridyl fragment. The conjugated trienyl fragments were omitted in the structure drawing.



Chromatogram report

Header

Title		Data acquisition date and time	2023/10/03 14:19:31
Sample name	**4ab**	Calculation date and time	2023/10/03 14:30:43
Database name	2023-10.chd	Acquisition time [min]	4.000 - 11.900
Data name	RSLT0004	Sampling interval [msec]	100
Method name	20231002STD	Cup number	1
Channel	RI	Calculation type	Molecular Weight

Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	7.820	0.273	96,070	Mn	4,265
Peak top	9.465	42.152	5,089	Mw	7,853
Peak end	10.692	1.827	291	Mw/Mn	1.841
Height [mV]			40.989		
Area [mV*sec]			2757.692		
Area% [%]			100.000		
[eta]			7853.17956		

Result of molecular weight calculation (RI)

Total

	[min]	[mV]	[mol]		
Peak start	7.820	0.273	96,070	Mn	4,265
Peak top	9.465	42.152	5,089	Mw	7,853
Peak end	10.692	1.827	291	Mw/Mn	1.841
Height [mV]			40.989		
Area [mV*sec]			2757.692		
Area% [%]			100.000		
[eta]			7853.17956		

Figure S32. GPC Calculation result of 4ab.

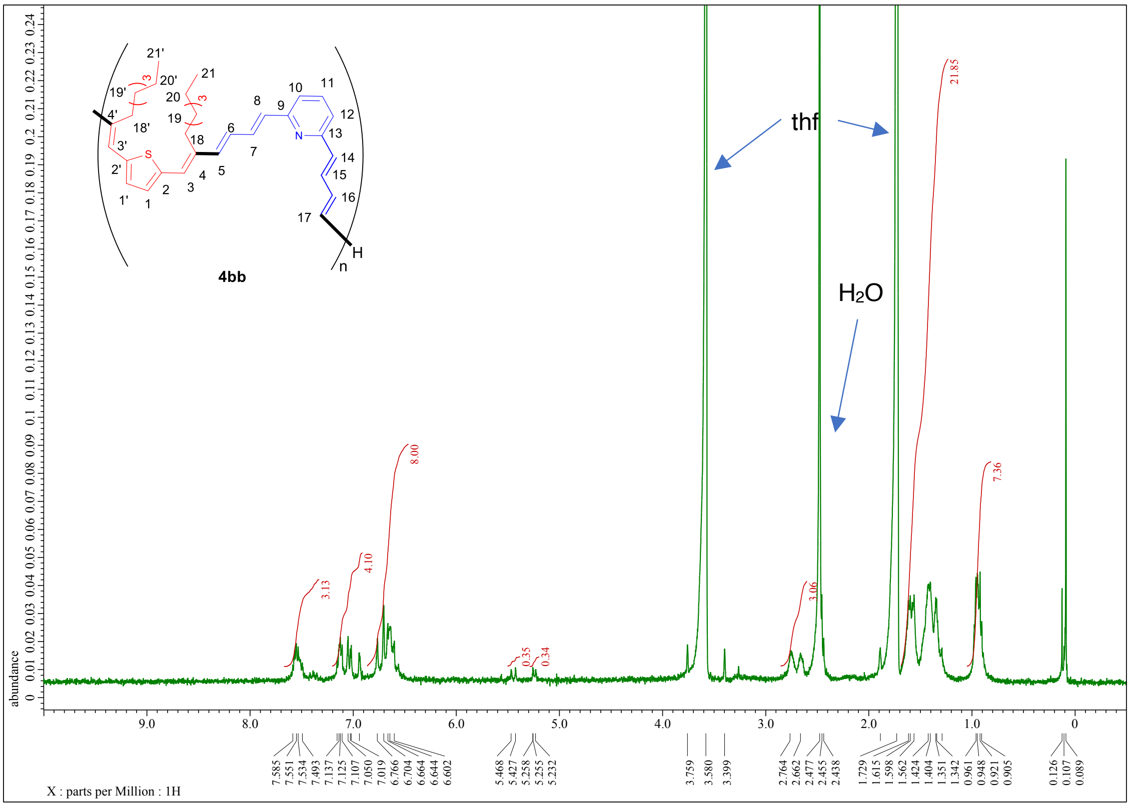


Figure S33. ^{1}H NMR Spectrum of 4bb in thf-d_8.

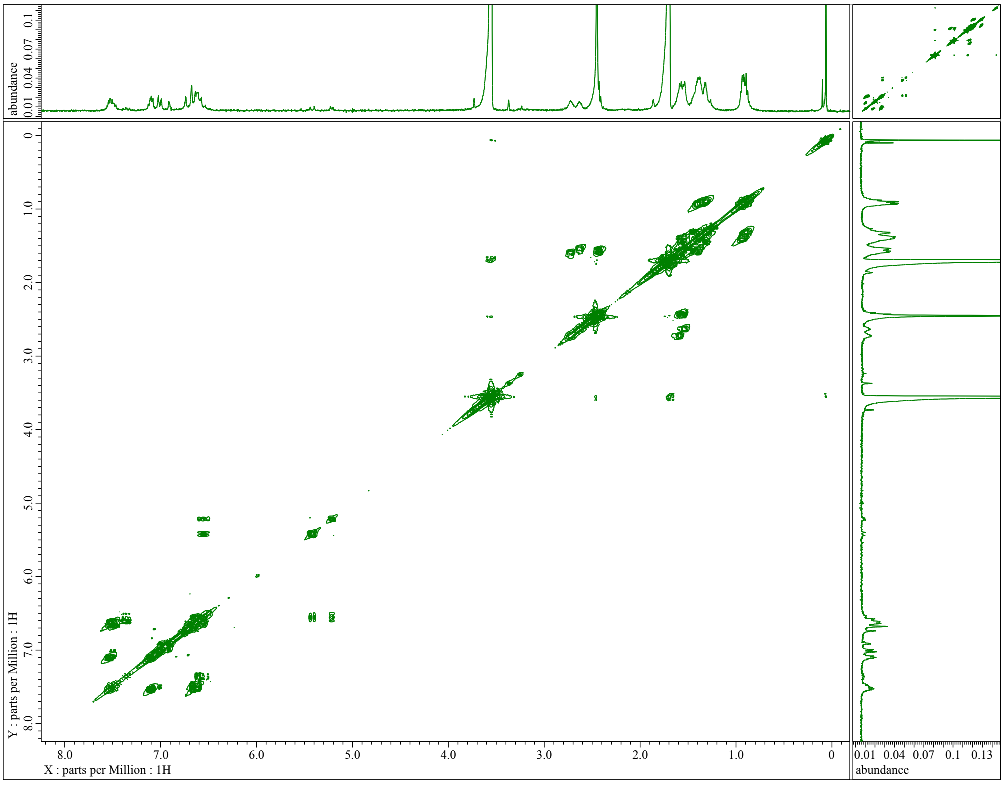


Figure S34. ^{1}H-^{1}H COSY NMR Spectrum of 4bb in thf-d_8.

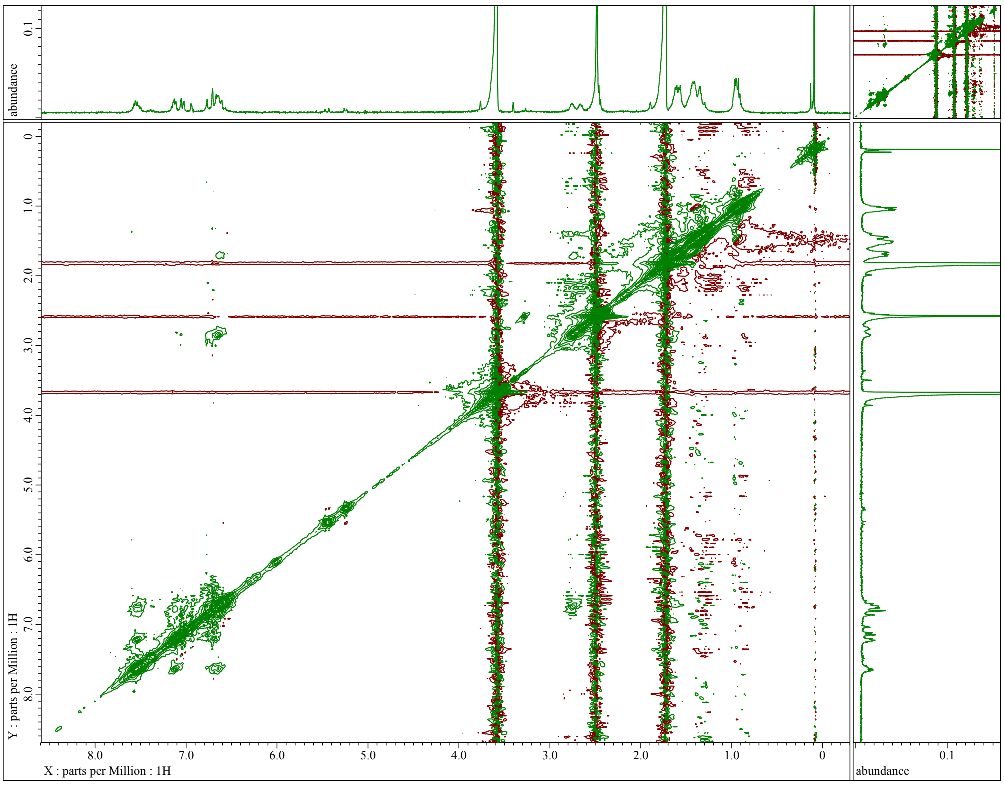


Figure S35. ^{1}H-^{1}H NOESY NMR Spectrum of 4bb in thf-d_8.

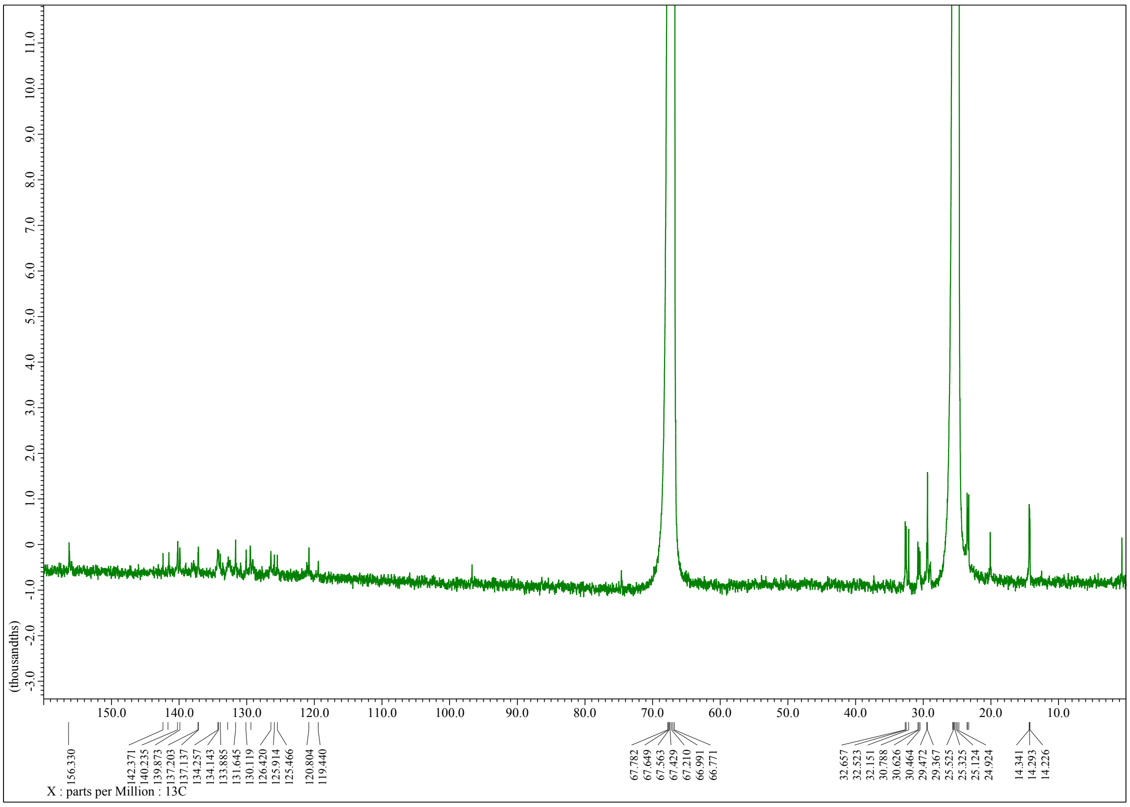


Figure S36. $^{13}C\{^{1}H\}$ NMR Spectrum of 4bb in thf-d_8.

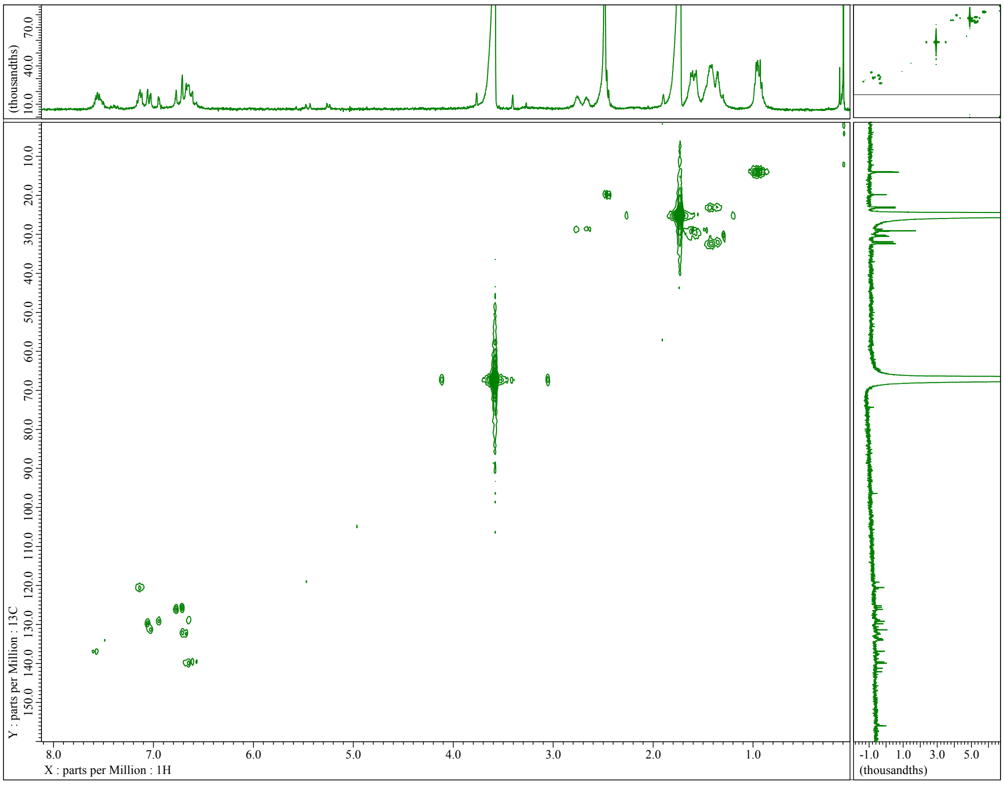


Figure S37. ^{13}C-^{1}H Correlation Spectrum of 4bb in thf-d_8 (HMQC).

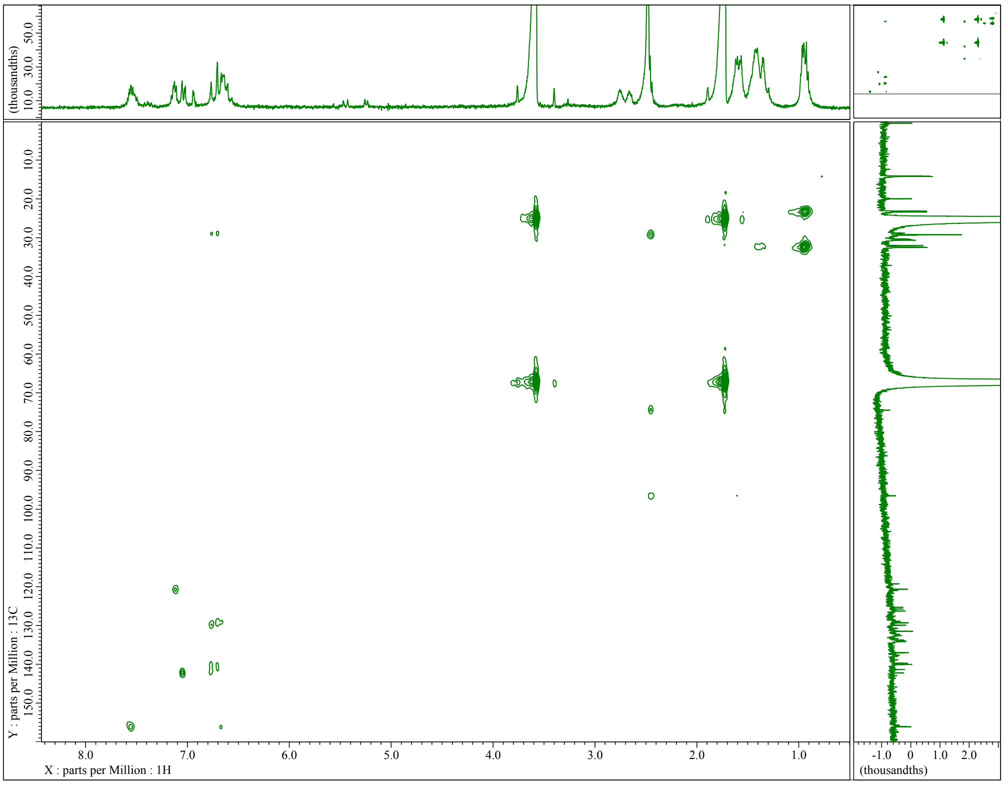


Figure S38. ^{13}C-^{1}H Correlation Spectrum of 4bb (HMBC).

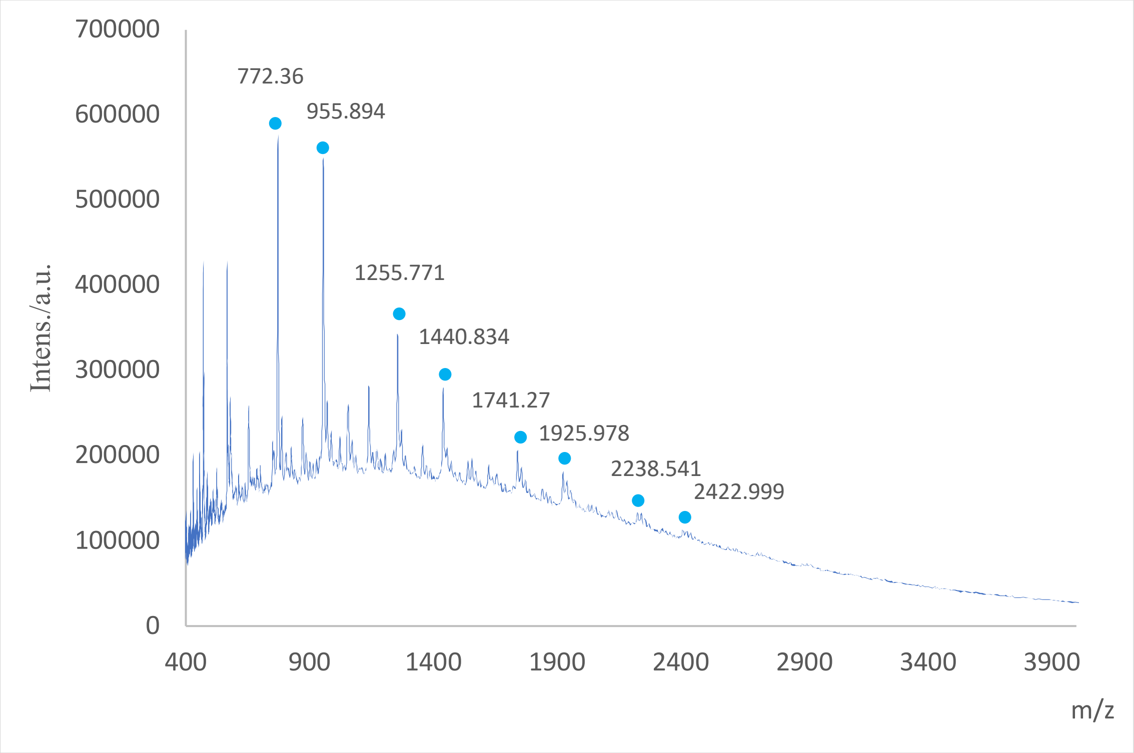


Figure S39. MALDI-TOF MS of 4bb.

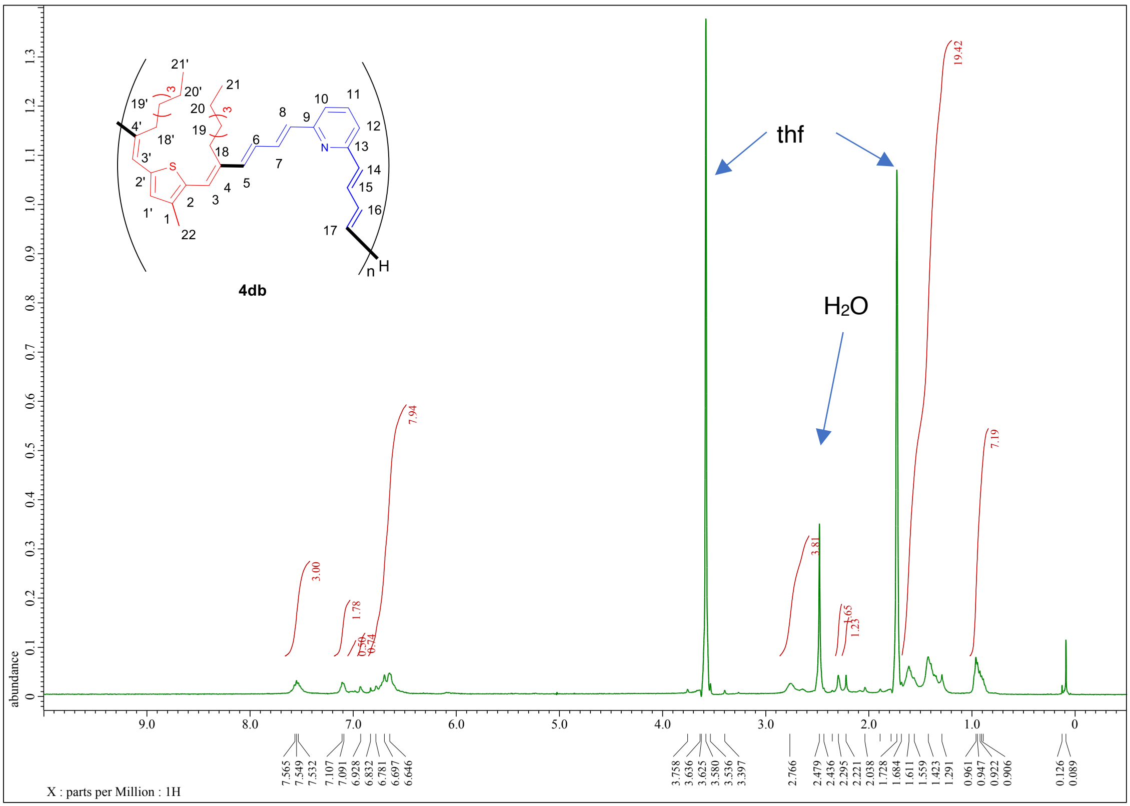


Figure S40. ^{1}H NMR Spectrum of 4db in thf-d$_8$.

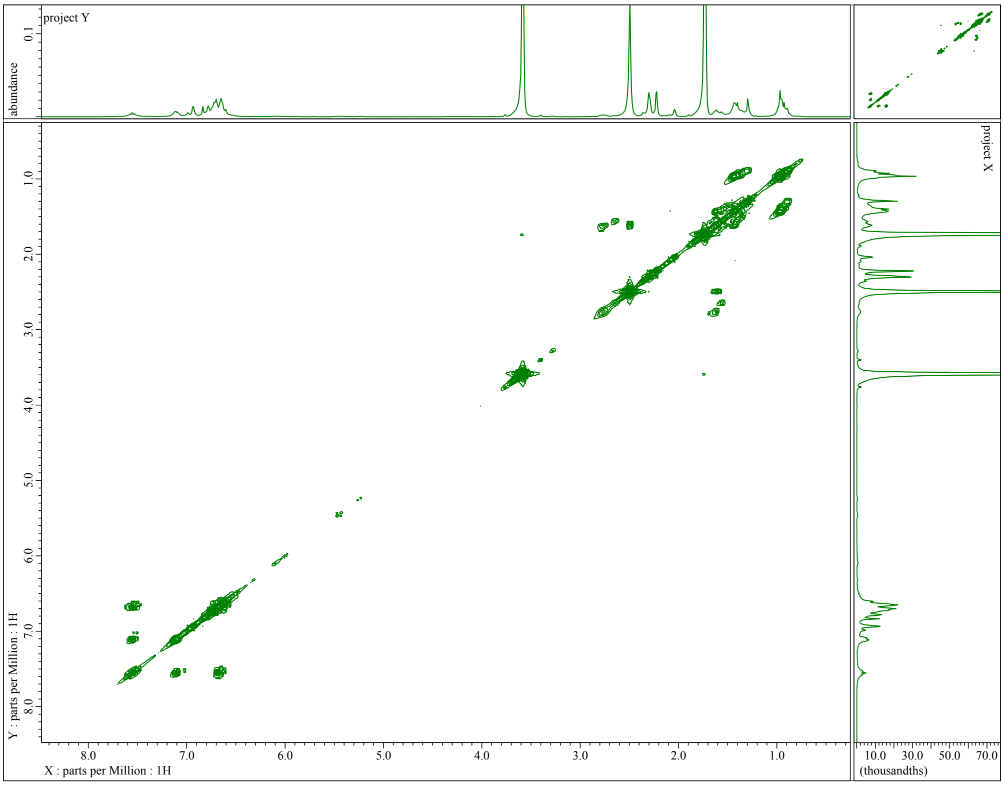


Figure S41. ^{1}H-^{1}H COSY NMR Spectrum of 4db in thf-d_8.

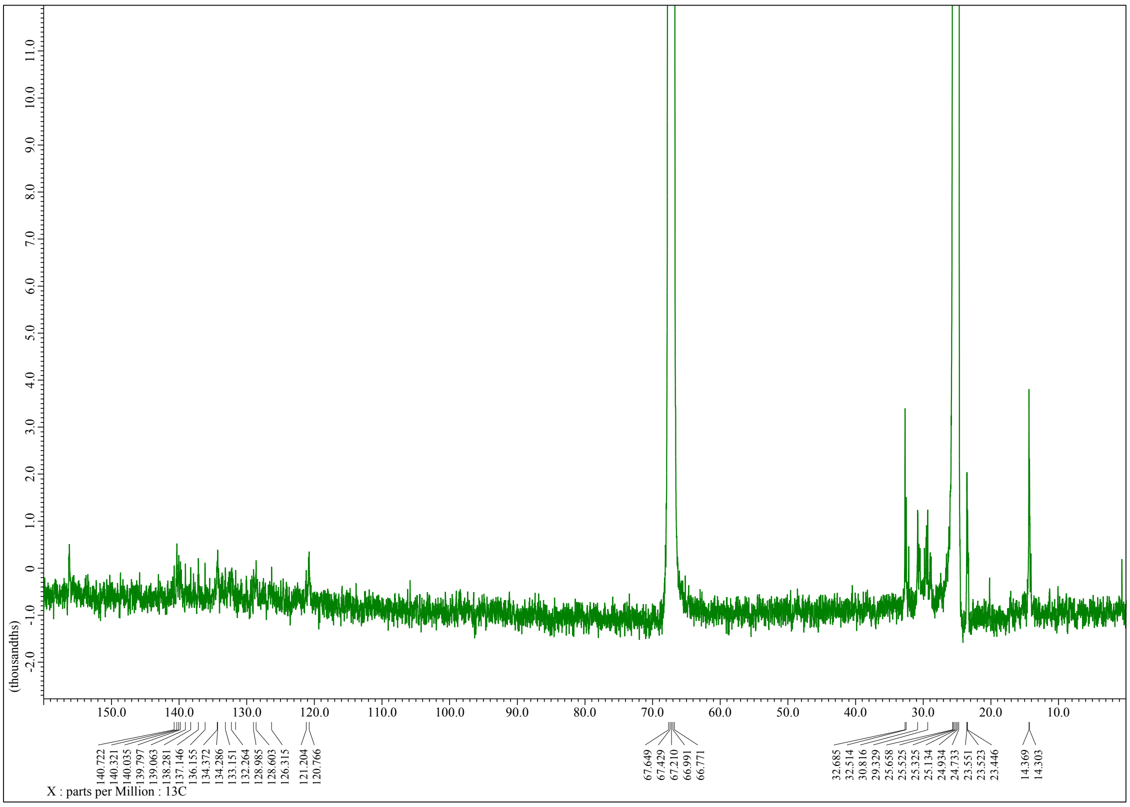


Figure S42. $^{13}C\{^{1}H\}$ NMR Spectrum of 4db in thf-d_8.

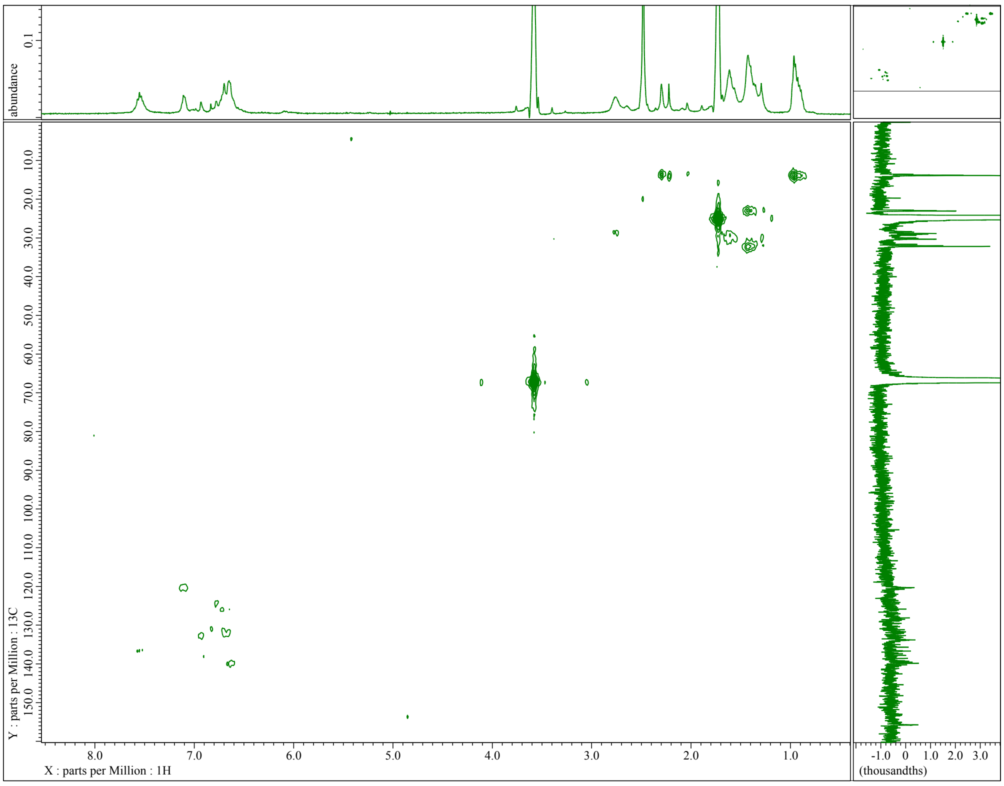


Figure S43. ^{13}**C-**^{1}**H Correlation Spectrum of 4db in thf-d**$_8$ **(HMQC).**

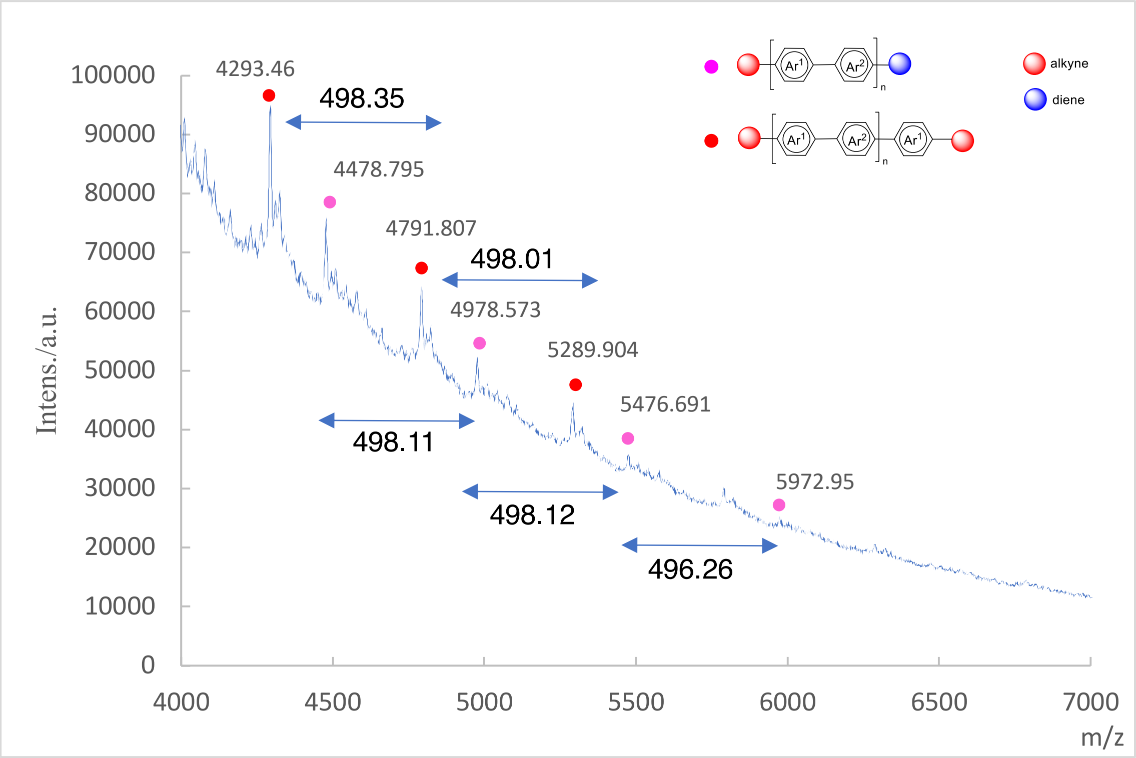


Figure S44. MALDI-TOF MS of 4db. Ar^{1}**: thienyl fragment. Ar**^{2}**: pyridyl fragment. The conjugated trienyl fragments were omitted in the structure drawing.**

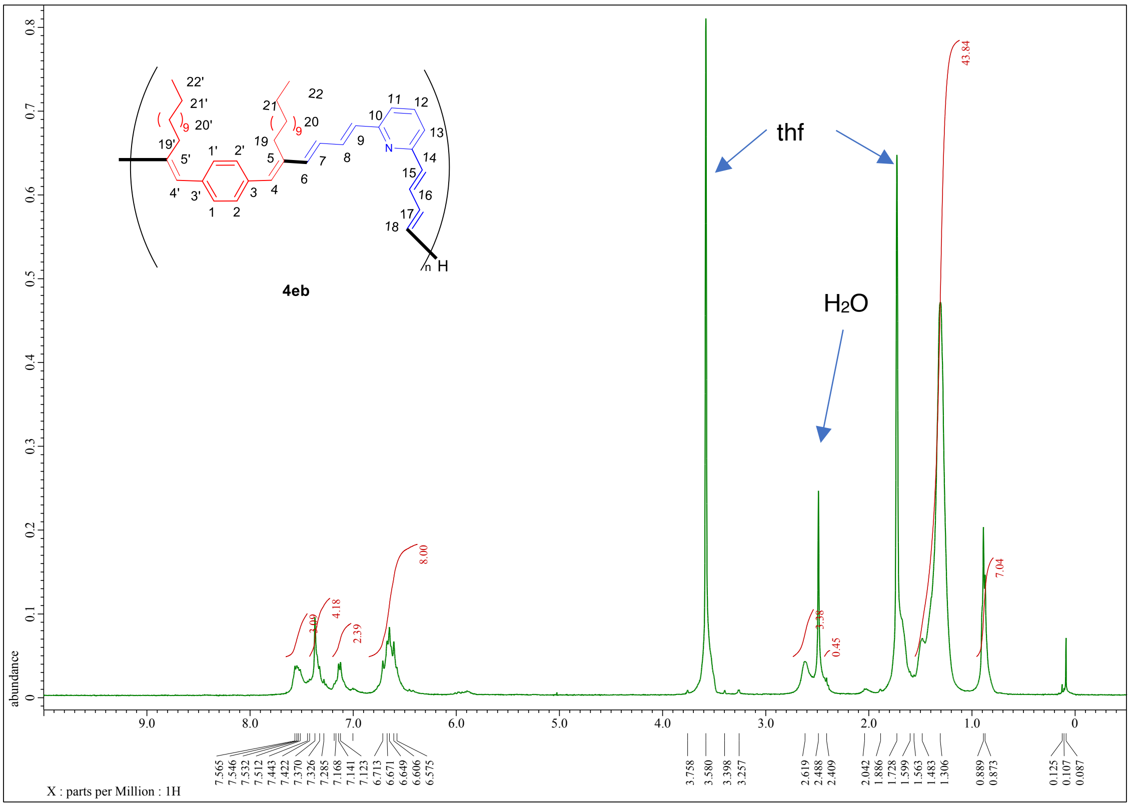


Figure S45. ^{1}H NMR Spectrum of 4eb in thf-d_8.

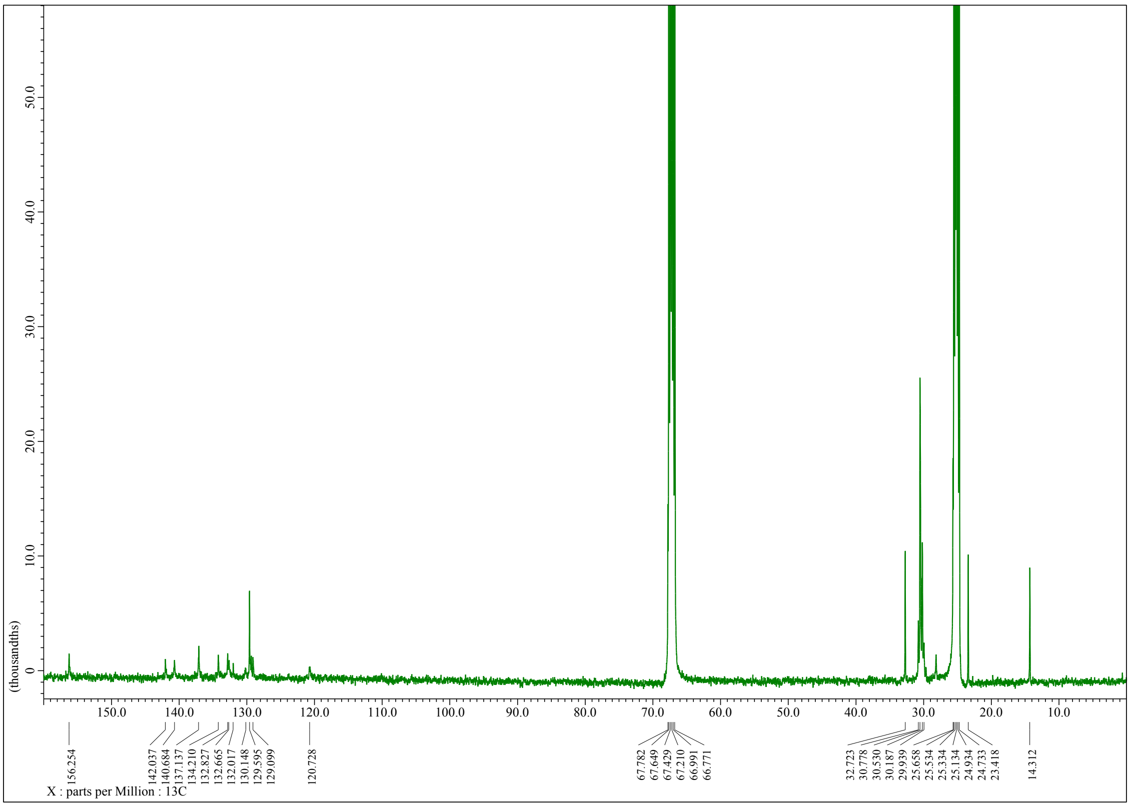


Figure S46. ^{13}C{^{1}H} NMR Spectrum of 4eb in thf-d_8.

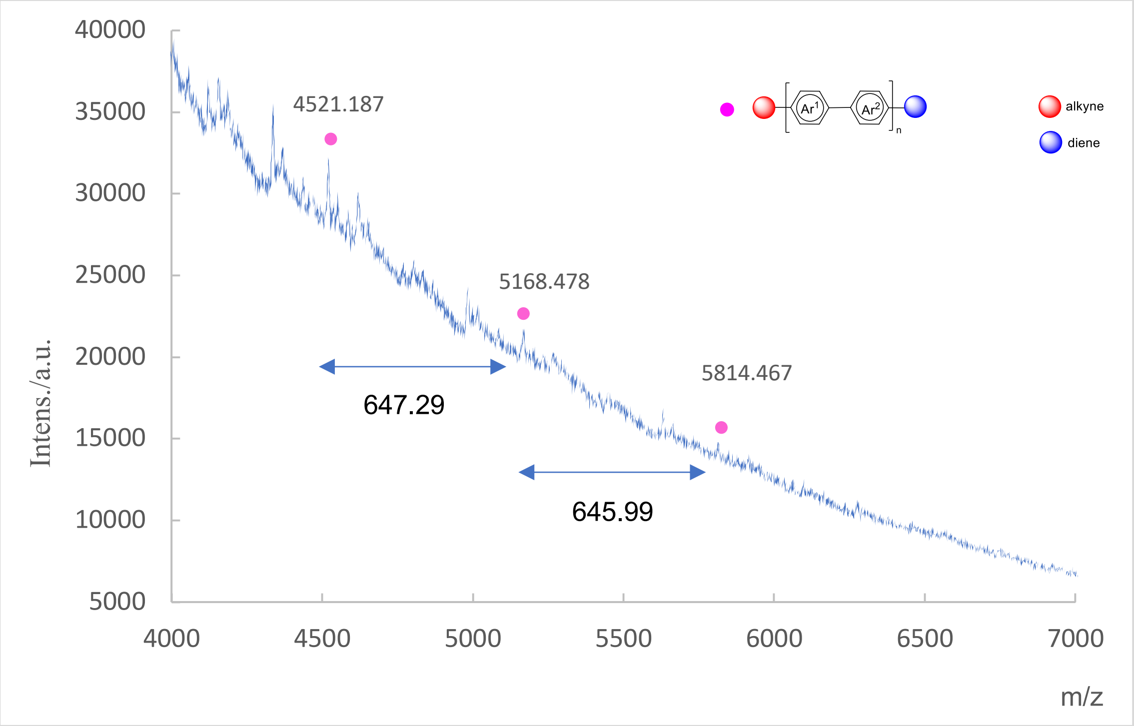


Figure S47. MALDI-TOF MS of 4eb. Ar^1: thienyl fragment. Ar^2: pyridyl fragment. The conjugated trienyl fragments were omitted in the structure drawing.

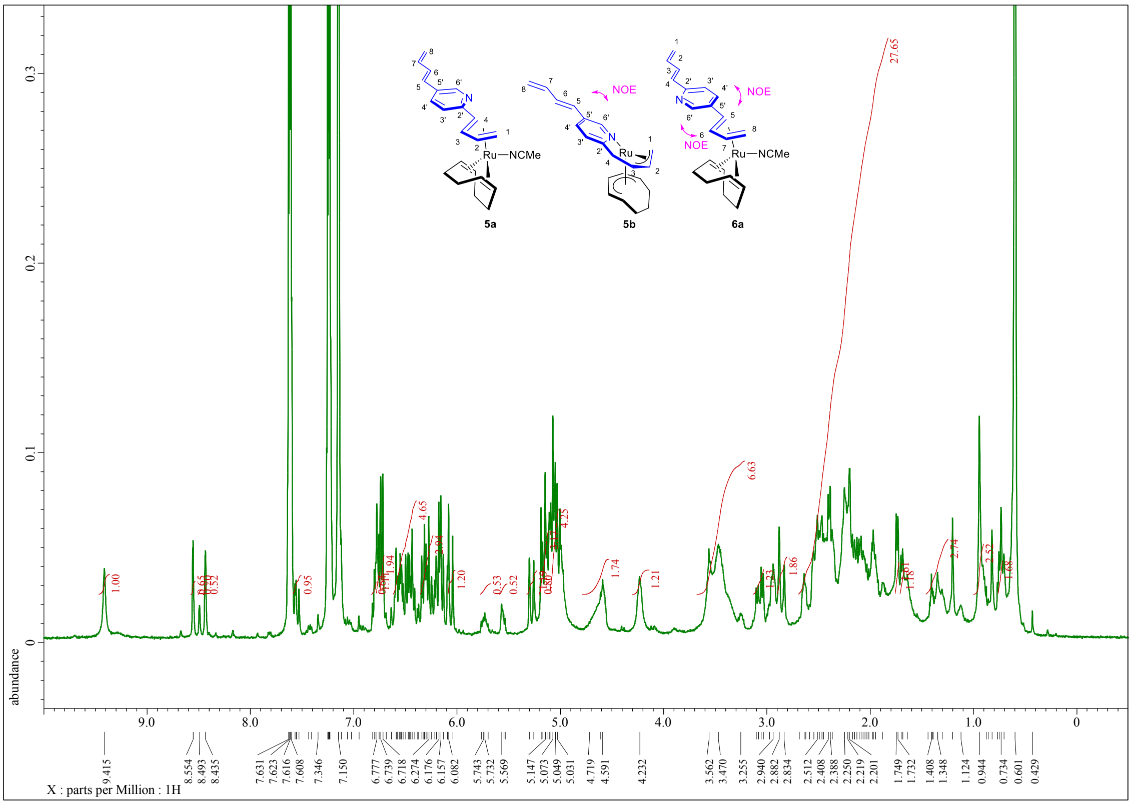


Figure S48. ^{1}H NMR Spectrum of reaction between 3a and 1a in C_6D_6.

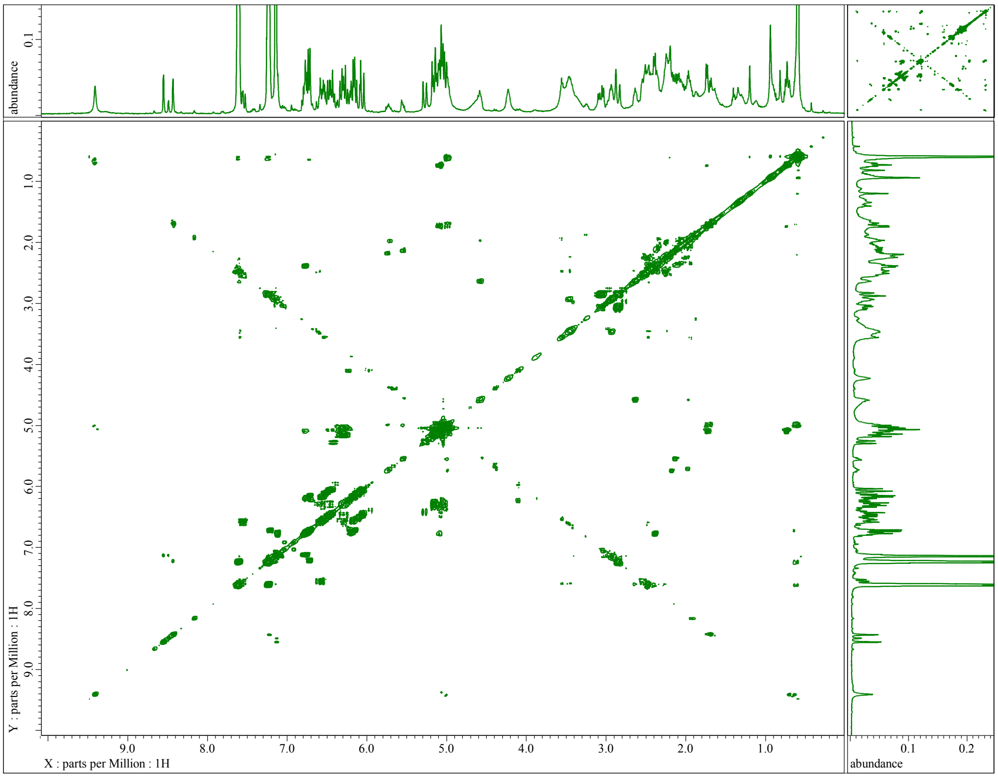


Figure S49. ^{1}H-^{1}H COSY NMR Spectrum of reaction between 3a and 1a in C_6D_6.

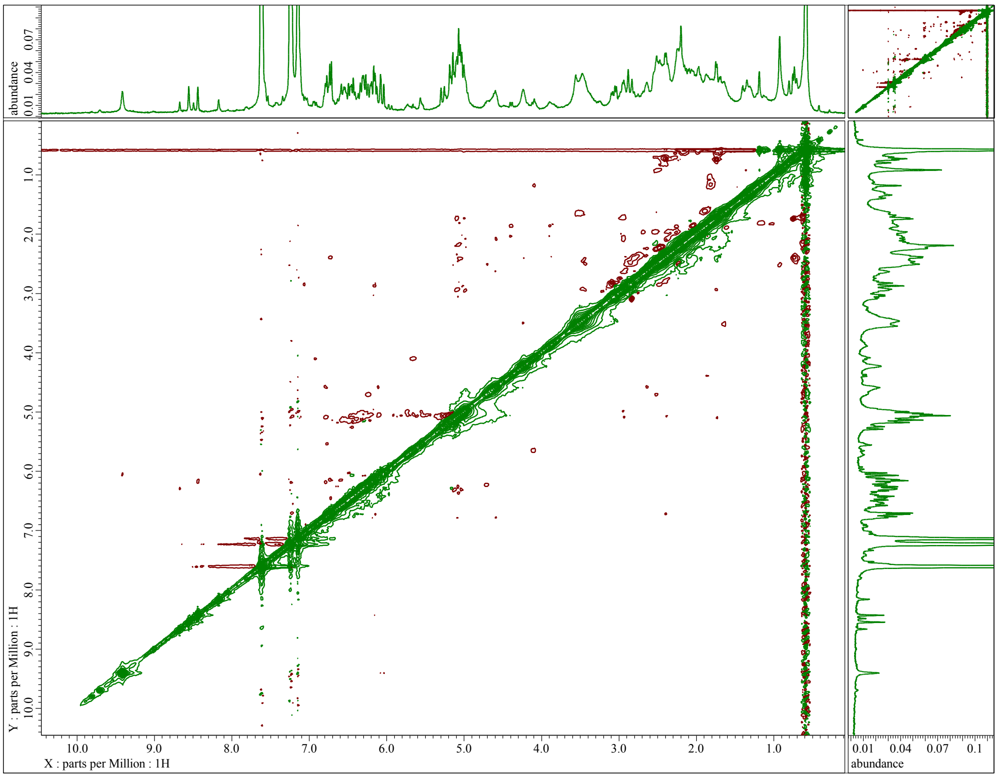


Figure S50. ^{1}H-^{1}H NOESY NMR Spectrum of reaction between 3a and 1a in C_6D_6.