SUPPORTING INFORMATION

RECOMPENSE: A Student-Led Open Science Initiative for Sustainable Polystyrene Waste Upcycling in Academic Labs

Victoria Lageard,[1] YuHan Yan,[1] Jiayin Liu,[1] Yueze Gong,[1] Shuoxi Liu,[1] Bob C. Schroeder,[1] David Palomas[1,2*]

1. Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, London UK
2. Manufacturing Futures Lab, Marshgate Building, 7 Sidings Street, E20 2AE, London, UK.

*Corresponding author, email: d.palomas@ucl.ac.uk

TABLE OF CONTENTS

1. Links to video recorded protocols and resources from the RECOMPENSE project

RECOMPENSE project introduction:
https://recompenseproject.com/2025/10/20/introducing-the-recompense-project/

Synthesis of u-PSSA

https://recompenseproject.com/2025/10/24/synthesis-of-polystyrene-sulfonic-acid-from-waste-expanded-polystyrene/

Determination of acidic sites of u-PSSA by Titration

https://recompenseproject.com/2025/10/24/titration-of-polystyrene-sulfonic-acid-prepared-from-waste-polystyrene/

Detailed synthesis of a precursor of biodiesel from furfural and 2-Methylfuran using u-PSSA as catalyst

https://recompenseproject.com/2025/10/25/synthesis-of-biofuel-precursor-with-a-polystyrene-sulfonic-acid-resin-from-waste-polystyrene/

Database of applications of polystyrene sulfonic acid (PSSA) in organic chemistry

https://recompenseproject.com/pssa-in-the-literature/

RECOMPENSE project YouTube Channel

https://www.youtube.com/@RECOMPENSEproject

2. General Experimental Information

General: Reagents and solvents were used as supplied from the vendor without further purification. Expanded polystyrene waste was collected from our teaching wet labs at UCL East.

Chromatography was performed on silica gel for flash chromatography (Sigma Aldrich, 40-63 µm particle size, 60 Å pore size). Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with Silica Gel 60 F254 and visualized using a UV lamp (254 nm) or $KMnO_4$ stain.

Nuclear Magnetic Resonance Spectroscopy: Products were characterised by ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra where applicable obtained from an Avance III 400 Spectrometer (Bruker, Germany) in $CDCl_3$ (dH 400 MHz, dC 101 MHz) at 300 K. Chemical shifts for ^{1}H-NMR spectra are recorded in parts per million from tetramethylsilane with the residual protic solvent resonance as the internal standard (chloroform: $\delta = 7.27$ ppm). Data are reported as follows: chemical shift, multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublet (dd), doublet of quartet (dq), doublet of doublet of doublet (ddd), triplet of doublet (td), multiplet (m)], coupling constant in Hz and integration. ^{13}C-NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($^{13}CDCl_3$: $\delta = 77.0$ ppm).

Infrared (IR) spectroscopy: Infrared spectra were obtained on a Bruker Alpha II compact FTIR Spectrometer operating in ATR mode and are reported in wavenumbers (cm^{-1}) to the nearest integer.

High Resolution Mass Spectrometry (HRMS) was performed using a Thermo Vanquish LC connected to Q Exactive Plus Hybrid Quadrupole-Orbitrap mass spectrometer operating in ESI mode.

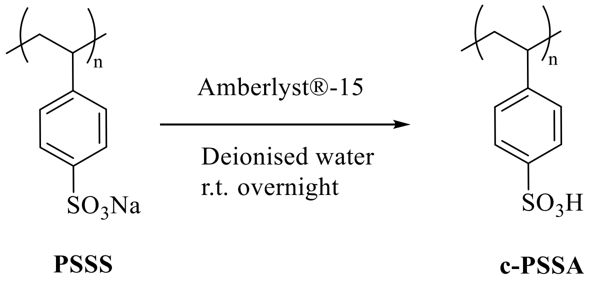
Thermogravimetric analysis (TGA) was carried out on a TA Instruments TGA 5500 under a N2 or air atmosphere and a heating rate of 10 °C min^{-1}

Differential Scanning Calorimetry (DSC) was carried out on a TA Instruments DSC2500 with a TA LN2P Pump attached. DSC measurements were carried out at a heating rate of 10 °C min^{-1} under a He atmosphere, using Tzero Aluminium pans and lids.

3. Experimental Data

3.1. Standard procedure for the preparation of c-PSSA

Note: This procedure was adapted from other protocol previously reported[1]



A 50 mL solution of PSSNa in water (25 wt%) was added to a mixture of 60 g of ground Amberlyst®-15 and 250 mL of deionised water. The mixture was stirred at room temperature overnight and then filtered to separate Amberlyst®-15 from the c-PSSA solution. The filtrate was evaporated to dryness at 60 °C to recover c-PSSA. The recovered c-PSSA was ground into small pieces and dried for an additional 24 h at 80 °C in an oven to minimise water content. To determine the number of acidic sites, 20 mg of c-PSSA were dissolved in 10 mL of deionised water and titrated against a 0.01 M NaOH solution using phenolphthalein as an indicator. The maximum theoretical number of acidic sites is 5.4 mmol H^+ g^{-1} of resin. The titration results showed an acidity of 4.86 mmol H^+ g^{-1}, indicating a 90% degree of sulfonation measured as mmol H^+ g^{-1}.

3.2. Detailed procedure for the preparation of u-PSSA

Note: Working with expanded PS presents some practical difficulties. A small mass occupies a disproportionately large volume, and cutting it into smaller pieces generates static charge, causing fragments to cling to surfaces and create considerable mess. PS dissolves readily in certain organic solvents. While dichloromethane is highly effective, we recommend using a greener alternative such as ethyl acetate, which also dissolves PS efficiently. After dissolution and solvent evaporation, the PS occupies significantly less volume, making it much easier to handle (**Figure S1**).

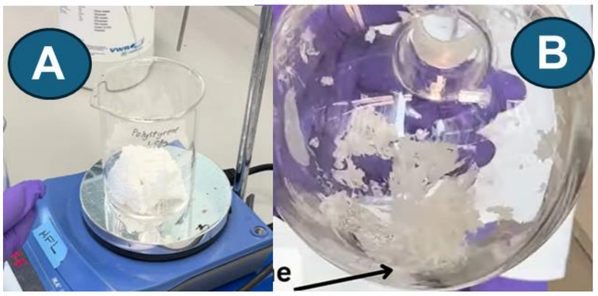
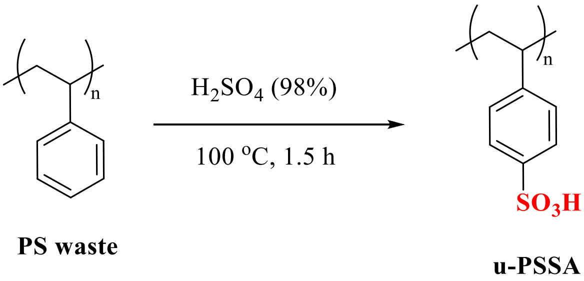


Figure S1. A) Volume of 1 g of expanded PS in a 400 mL beaker. B) Volume of the same amount of PS in a 250 mL round-bottom flask after dissolution in ethyl acetate and solvent evaporation.



1g of expanded polystyrene (PS) waste was dissolved in the minimum amount of ethyl acetate in a beaker (~5 mL). The resulting solution was transferred to a round-bottom flask, and the solvent was evaporated using a rotary evaporator with a water bath set at 35 °C. The flask was left connected to the rotavapor for an additional 20–30 min to ensure complete removal of the solvent. The reduced PS was scraped from the flask walls and evenly distributed across the bottom to minimise volume and maximise contact with sulfuric acid during the reaction. The flask was clamped to a stand, and 10 mL of concentrated sulfuric acid (98%) was added along with a Teflon-coated magnetic stirring bar. The reaction mixture was heated at 100 °C for 1.5 h using a heating block. After completion, the mixture was cooled in an ice-water bath, and 100 mL of ice-cold water was slowly added. A rubbery solid precipitated, which was filtered under vacuum and washed thoroughly with deionised water until the filtrate reached pH 7 (**Figure S2**). The solid was dried overnight in an oven at 70 °C, yielding a yellowish-white product (**Figure S3A**). The resulting u-PSSA was insoluble in deuterated solvents and characterised by FTIR spectroscopy, TGA and DSC. The number of acidic sites was determined by titration against a standard 0.01 M NaOH solution using phenolphthalein as an indicator (**Figure S3B**). Typical yields ranged from 0.9 to 1.2 g of u-PSSA, with degrees of sulfonation between 30% and 45%.

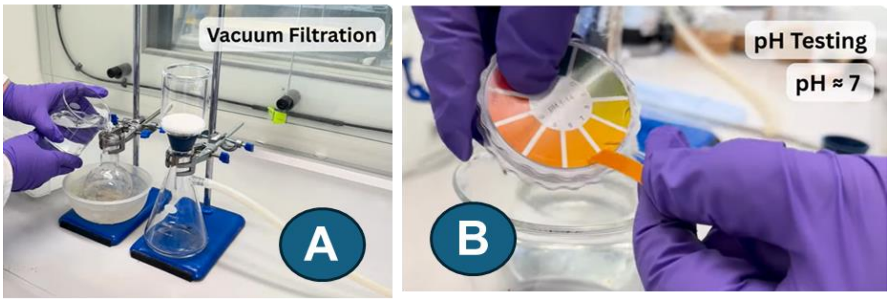


Figure S2. A) Typical setup for vacuum filtration of u-PSSA. B) pH testing of filtrate.

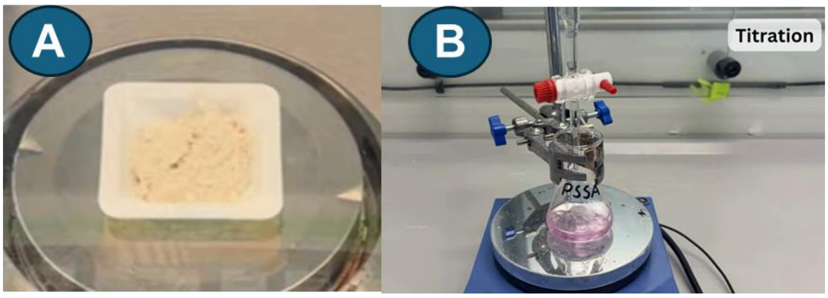


Figure S3. A**)** Appearance of an isolated sample of u-PSSA obtained from waste expanded PS**.** B) Typical setup for the determination of acidic sites of u-PSSA by titration.

3.3. Detailed explanation of the calculation of acidic sites of u-PSSA

An approximation to the degree of sulfonation of u-PSSA can be calculated by determining the number of acidic protons from the sulfonic acid (–SO_3H) groups present in the polymer. While this method provides a useful estimate, the precise sulfur content should ideally be determined by elemental analysis. Nevertheless, calculating the number of active acid sites allows us to evaluate the catalytic potential of u-PSSA in organic synthesis.

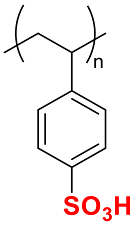
The degree of sulfonation is determined by titrating a sample of u-PSSA with a 0.01 M NaOH solution in water, using phenolphthalein as an indicator. Since u-PSSA is not soluble in water, the titration is performed as a suspension in deionised water. The colour change can be slow and may lead to false positives, so the titration should only be considered complete if the pink colour (typical of phenolphthalein in basic solution) persists for 15–20 minutes. For better visibility, it is recommended to place a piece of white paper under the conical flask during titration.

To calculate the degree of sulfonation, we consider the mass of the repeating unit of a fully para-sulfonated polystyrene resin. The molar mass of this unit is 184.02 g/mol, meaning that 1 g of fully sulfonated PS contains:

1000 mg / (184.02 mg/mmol) ~ 5.4 mmol.

$$1000\,mg\ x\ 1\frac{mmol}{184.02\,mg} \sim 5.4\,mmol$$

Meaning that a fully sulfonated resin has 5.4 mmol of H^+ in 1g of resin.



Repeating unit of PSSA

(mass of 184.02 g/mol, $C_8H_8O_3S_2$)

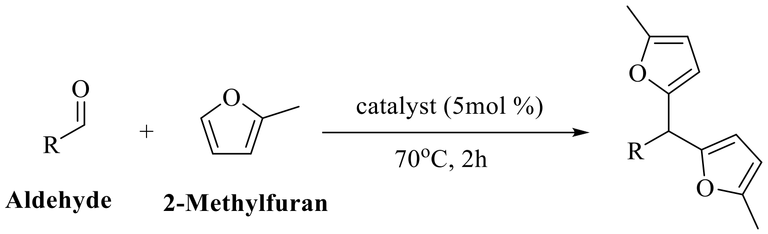
In a typical protocol, 20 mg of u-PSSA are suspended in 20 mL of distilled water in a small conical flask. Two drops of phenolphthalein solution are added as an indicator, and the resin is titrated with 0.01 M NaOH. If the titration endpoint is reached at 4.75 mL of NaOH, the degree of sulfonation is calculated as:

$$0.01\frac{mmol}{mL}x\;4.75\;mL\;x\frac{1}{0{,}02}g = 2{,}37\;mmol\;of\;H + per\;gram\;of\;resin$$

Given the theoretical maximum of 5.4 mmol/g, then the percentage of sulfonation is:

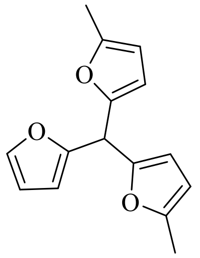
$$\frac{2.37}{5.4}\;x\;100 = 43.8 \sim \mathbf{44\%}\;\boldsymbol{sulfonation}$$

3.4. Standard procedure for the Friedel-Crafts reaction of aldehydes with MF



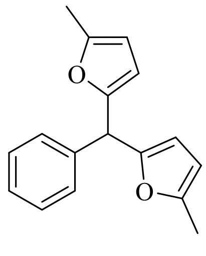
A 9 mL pressure tube was charged with 0.5 mL of 2-methylfuran (used as both solvent and reactant), aldehyde (0.5 mmol), and catalyst (0.025 mmol based on acidic sites, 5 mol%). The reaction mixture was stirred at 70 °C for 2 h and monitored by TLC (hexane: ethyl acetate). Upon completion, the mixture was filtered under vacuum to recover the catalyst. The filtrate was transferred to a round-bottom flask, diluted with ethyl acetate, and concentrated using a rotary evaporator. The crude product was purified by column chromatography using hexane: ethyl acetate as the eluent. Fractions containing the product were collected, transferred to a tared round-bottom flask, and the solvent was removed. The flask was then placed on a Schlenk line for further drying. The product was analysed by FTIR and NMR spectroscopy.

5,5'-(furan-2-ylmethylene)bis(2-methylfuran) (3a)[2,3]



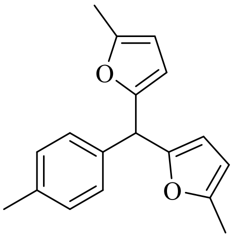
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 4:1) afforded the title compound as a light-yellow oil (121 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3107, 2981, 2951, 2922, 2883, 1451, 1195, 1073, 934, 886, 816 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.33 (s, 1H), 6.29 (d, *J*=3.1 Hz, 1H), 6.10 (m, 1H), 5.97 (d, *J*=3.1 Hz, 2H), 5.89-5.88 (m, 2H), 5.42(s, 1H), 2.23 (d, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 152.6, 151.6, 150.4, 141.9, 110.4, 108.0, 107.2, 106.4, 39.1, 13.6. Data obtained were consistent with reported literature.

5,5'-(phenylmethylene)bis(2-methylfuran) (5a)[3]



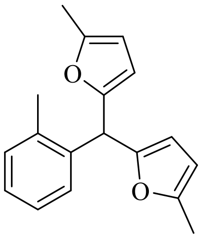
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 24:1) afforded the title compound as a brown oil (126 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3104, 3064, 3028, 2978, 2949, 2922, 2883, 1603, 1495, 1452, 1185 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.34-7.21 (m, 5H), 5.87-5.85 (m, 4H), 5.36 (s, 1H), 2.28 (s, 6H)). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 152.9, 151.5, 140.1, 128.6, 128.4, 127.1, 108.3, 106.1, 45.2, 13.6. Data obtained were consistent with reported literature.

5,5'-(*p*-tolylmethylene)bis(2-methylfuran) (5b)[3]



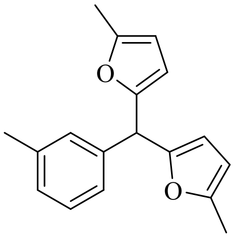
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 25:1) afforded the title compound as a brown oil (125 mg, 0.47 mmol, 94% yield). **IR (oil)** ν 3106, 3023, 2979, 2922, 2869, 1612, 1560, 1450, 1164, 963, 833 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.05-6.99 (m, 4H), 5.78-5.76 (m, 4H), 5.20 (s, 1H), 2.21(s, 3H), 2.12 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 153.2, 151.4, 137.2, 136.4, 129.2, 128.3, 108.2, 106.2, 44.9, 21.2, 13.7. Data obtained were consistent with reported literature.

5,5'-(*o*-tolylmethylene)bis(2-methylfuran) (5c)



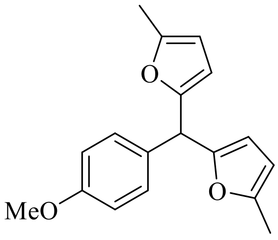
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (133 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3104, 3021, 2948, 2922, 1606, 1560, 1450, 1218, 1001, 963, 950 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.28-7.22 (m, 1H), 7.21-7.18 (m, 3H), 6.00 (d, *J* = 3.25 Hz, 2H), 5.93 (d, *J* = 3.25 Hz, 2H), 5.67 (s, 1H), 2.45 (s, 3H), 2.37 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 152.7, 151.4, 138.3, 136.2, 130.5, 128.2, 127.0, 126.1, 108.6, 106.2, 41.7, 19.4, 13.7. **HRMS (ESI)** [M+H]$^+$ calcd. For C$_{18}$H$_{19}$O$_2$ 267.1380, found 267.1376.

5,5'-(*m*-tolylmethylene)bis(2-methylfuran) (5d)[4]



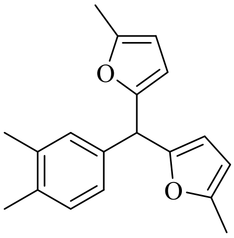
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (133 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 2921, 1607, 1561, 1488, 1455, 1383, 1218, 1149, 1002, 965, 951 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.31 (t, *J*= 7.5 Hz, 1H), 7.25-7.20 (m, 3H), 6.02-5.98 (m, 4H), 5.43 (s, 1H), 2.44 (s, 3H), 2.36 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 153.1,151.4, 140.0, 138.1, 129.2, 128.4, 127.8, 125.5, 108.2, 106.2, 45.2, 21.5, 13.7. Data obtained were consistent with reported literature.

5,5'-((4-methoxyphenyl)methylene)bis(2-methylfuran) (5e)[3]



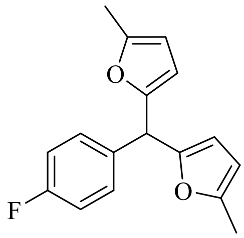
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (141 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3104, 2952, 2922, 2836, 1612, 1585, 1462, 1452, 1442, 1109, 856 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.07 (d, J= 8.25 Hz, 2H), 6.74 (d, J= 8.25 Hz, 2H), 5.76-5.75 (m, 4H), 5.19 (s, 1H), 3.65 (s, 3H), 2.13 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 158.6, 153.9, 151.4, 132.2, 129.4, 113.8, 108.1, 106.1, 55.2, 44.4, 13.6. Data obtained were consistent with reported literature.

5,5'-((3,4-dimethylphenyl)methylene)bis(2-methylfuran) (5f)[3]



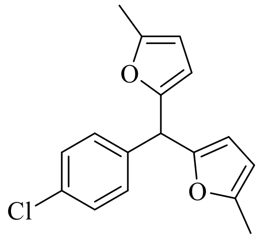
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (140 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3105, 2921, 2884, 1613, 1560, 1449, 1218, 1020, 1002, 965, 949 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.11-7.00 (m, 3H), 5.90 (d, 4H), 5.29 (s, 1H), 2.27 (m, 12H) **^{13}C NMR (100 MHz, CDCl$_3$) δ** 153.3, 151.4, 137.6, 136.6, 135.3, 129.8, 129.7, 125.9, 108.1, 106.2, 44.9, 19.9, 19.5, 13.7. Data obtained were consistent with reported literature.

5,5'-((4-fluorophenyl)methylene)bis(2-methylfuran) (5g)[3]



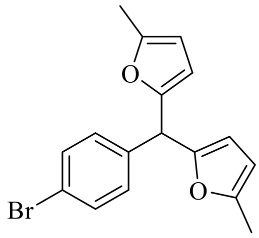
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (135 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3106, 2981, 2951, 2922, 2885, 1605, 1560, 1451, 1187, 1096, 859 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.31-7.22 (m, 2H), 7.08-7.04 (m, 2H), 5.96-5.94 (m, 4H), 5.40 (s, 1H), 2.3 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 163.2, 160.7, 152.7, 151.6, 130.0, 130.0, 129.9 115.4, 115.2, 108.3, 106.2, 44.4, 13.6. Data obtained were consistent with reported literature.

5,5'-((4-chlorophenyl)methylene)bis(2-methylfuran) (5h)[5]



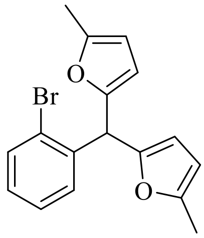
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (143 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3106, 2979, 2951, 2922, 2882, 1610, 1560, 1089, 1003, 963, 942 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.17 (d, *J* = 8.18 Hz, 2H), 7.08 (d, *J* = 8.18 Hz, 2H), 5.79-5.75 (m, 4H), 5.21 (s, 1H), 2.14 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 152.3, 151.7, 138.6, 132.8, 129.8, 128.6, 108.4, 106.2, 44.5, 13.6. Data obtained were consistent with reported literature.

5,5'-((4-bromophenyl)methylene)bis(2-methylfuran) (5i)[3]



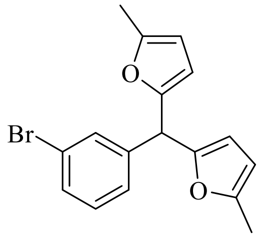
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (165 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3106, 2978, 2921, 2883, 1610, 1560, 1450, 1404, 1382, 1167, 963 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.32 (d, *J* = 8.00 Hz, 2H), 7.02 (d, *J* = 8.00 Hz, 2H), 5.80-5.76 (m, 4H), 5.19 (s, 1H), 2.14 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 152.2, 151.7, 139.2, 130.9, 121.0, 108.4, 106.2, 44.6, 13.6. Data obtained were consistent with reported literature.

5,5'-((2-bromophenyl)methylene)bis(2-methylfuran) (5j)[3]



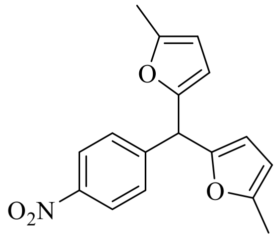
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (165 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3106, 2978, 2921, 2883, 1610, 1560, 1450, 1404, 1382, 1167, 963 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.43 (d, *J* = 7.88 Hz, 1H), 7.12-7.08 (m, 2H), 7.22 (d, *J* = 7.55 Hz, 1H), 7.01-6.92 (m, 1H), 5.84-5.62 (m, 4H), 5.72 (s, 1H), 2.28 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 151.7, 151.6, 139.2, 133.0, 130.2, 128.6, 127.5, 124.6, 108.9, 106.2, 44.5, 13.7. Data obtained were consistent with reported literature.

5,5'-((3-bromophenyl)methylene)bis(2-methylfuran) (5k)[3]



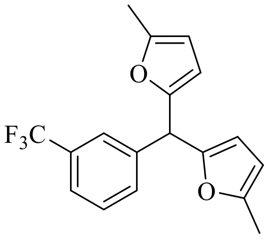
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (134 mg, 0.42 mmol, 83% yield). **IR (oil)** ν 3104, 2979, 2949, 2921, 2883, 1610, 1590, 1560, 1450, 1382, 1184 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.38-7,34 (m, 2H), 7.24-7.19 (m, 2H), 5.94-5.90 (m, 4H), 5.32 (s, 1H), 2.28 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 152.0, 151.8, 142.4, 131.5, 130.2, 130.0, 127.1, 122.6, 108.5, 106.2, 44.8, 13.7. Data obtained were consistent with reported literature.

5,5'-((4-nitrophenyl)methylene)bis(2-methylfuran) (5l)[3]



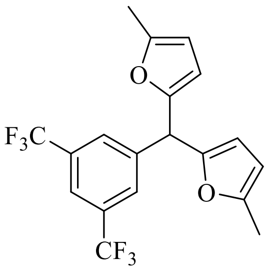
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a yellow solid (140 mg, 0.47 mmol, 94% yield). **IR (solid)** ν 3129, 3103, 3076, 2977, 2955, 2869, 1608, 1596, 1559, 1450 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.20 (d, J = 8.32 Hz, 2H), 7.45 (d, J = 8.32 Hz, 2H), 5.98-5,96 (m, 4H), 5.47 (s, 1H), 2.29 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 152.1, 151.0, 147.5, 147.0, 129.3, 123.7, 108.9, 106.3, 44.9, 13.6. Data obtained were consistent with reported literature.

5,5'-((3-(trifluoromethyl)phenyl)methylene)bis(2-methylfuran) (5m)



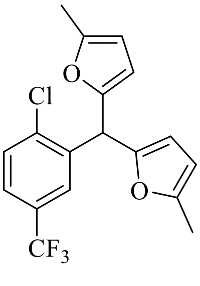
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (160 mg, 0.5 mmol, >99% yield). **IR (oil)** ν 3108, 2924, 1614, 1560, 1449, 1328, 1218, 1162, 1096, 965, 951 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.65-7.56 (m, 2H), 7.55-7.44 (m, 2H), 5.98-5,96 (m, 4H), 5.48 (s, 1H), 2.32 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 151.9, 141.1, 131.9, 130.8 (q, $J_{C\text{-}F}$= 32.18 Hz), 128.9, 125.2 (q, $J_{C\text{-}F}$= 3.85 Hz), 124.3 (q, $J_{C\text{-}F}$= 273.71 Hz), 123.9 (q, $J_{C\text{-}F}$=3.75 Hz), 108.6, 106.2, 44.9, 13.5. **HRMS (ESI)** [M+H]$^+$ calcd. For $C_{18}H_{16}O_2F_3$ 321.1097, found 321.1091.

5,5'-((3,5-bis(trifluoromethyl)phenyl)methylene)bis(2-methylfuran) (5n)



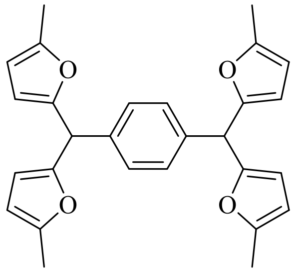
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (194 mg, 0.5 mmol, >99% yield). **IR (oil)** 3109, 2979, 2886, 1613, 1560, 1452, 1372, 1276, 1004, 950, 850 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.81 (s, 1H), 7.74 (s, 2H), 5.98-5.96 (m, 4H), 5.48 (s, 1H), 2.29 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 152.3, 150.8, 142.8,131.8 (q, $J_{C\text{-}F}$= 33.25 Hz), 128.8-128.6 (m), 123.4 (q, $J_{C\text{-}F}$= 273.71 Hz), 121.17 (hep, $J_{C\text{-}F}$= 4.03 Hz), 109.1, 106.4, 44.8, 13.4. **HRMS (ESI)** [M-H]$^-$ calcd. For $C_{19}H_{13}O_2F_6$ 387.0825, found 387.0828.

5,5'-((2-chloro-5-(trifluoromethyl)phenyl)methylene)bis(2-methylfuran) (5o)



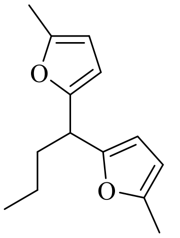
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 24:1) afforded the title compound as a brown oil (165 mg, 0.46 mmol, 93% yield). **IR (oil)** 3106, 2923, 2883, 1610, 1560, 1451, 1327, 1276, 1218, 964, 910 cm^{-1}. **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.41-7,32 (m, 3H), 5.81-5.79 (m, 4H), 5.78 (s, 1H), 2.14 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 152.1, 150.5, 138.7, 137.6, 130.18, 129.3 (q, $J_{C\text{-}F}$= 32.32 Hz), 126.9 (hep, $J_{C\text{-}F}$= 4.04 Hz), 125.1 (hep, $J_{C\text{-}F}$= 3.03 Hz), 124.1 (q, $J_{C\text{-}F}$= 273.71 Hz), 109.2, 106.3, 41.6, 13.6. **HRMS (ESI)** [M+H]$^+$ calcd. For $C_{18}H_{15}ClO_2F_3$ 355.0707, found 355.0700.

1,4-bis(bis(5-methylfuran-2-yl)methyl)benzene (5p)[3]



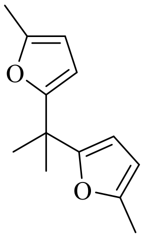
Prepared according to the standard procedure. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a light brown solid (213 mg, 0.5 mmol, >99% yield). **IR (solid)** ν 3106, 2921, 2880, 1718, 1609, 1510, 1450, 1421, 1381, 1089 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.10 (s, 4H), 5.78 (s, 8H), 5.23 (s, 2H), 2.15 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 152.9, 151.4, 138.7, 128.4, 108.2, 106.1, 44.8, 13.6. Data obtained were consistent with reported literature.

5,5'-(butane-1,1-diyl)bis(2-methylfuran) (7a)[2]



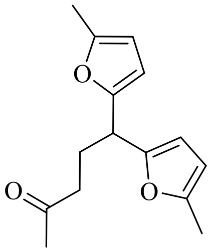
Prepared according to the standard procedure except that 0.5 mL of 2-Methylfuran were combined with 0.166 mL of butanal and 10 mg of c-PSSA at 60 °C for 6 h. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a brown oil (292 mg, 1.34 mmol, 71% yield). **IR (oil)** ν 3104, 2958, 2925, 1563, 1452, 1218, 1020, 998, 964, 950, 935 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.98 (d, *J* = 3.13 Hz, 2H), 5.91 (d, *J* = 3.00 Hz, 2H), 3.99 (t, *J* = 7.45 Hz, 1H), 2.30 (s, 6H), 1.95 (ddd, *J* = 9.13, 8.00, 6.13 Hz, 2H), 1.35-1.41 (m, 2H), 0.98 (t, *J* = 7.45 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 154.2, 150.6, 105.9, 38.8, 35.2, 20.6, 13.9, 13.6. Data obtained were consistent with reported literature.

5,5'-(propane-2,2-diyl)bis(2-methylfuran) (7b)[6]



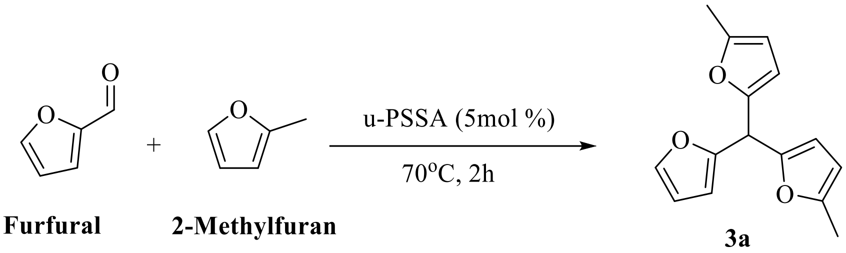
Prepared according to the standard procedure except that 0.5 mL of 2-Methylfuran were combined with 0.135 mL of acetone and 10 mg of c-PSSA at 60 °C for 6 h. Purification via flash column chromatography (Hex/EtOAc 23:2) afforded the title compound as a light brown oil (257 mg, 1.26 mmol, 67% yield). **IR (oil)** ν 3106, 2977, 2923, 2872, 1612, 1451, 1382, 1235, 1135, 1102, 958 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.89-5.87 (m, 4H), 2.27 (s, 6H), 1.62 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.7, 150.6, 105.9, 104.7, 37.3, 26.6, 13.6. Data obtained were consistent with reported literature.

5,5-bis(5-methylfuran-2-yl)pentan-2-one (7c)[2]



Prepared according to the standard procedure except that 0.5 mL of 2-Methylfuran were combined with 0.5 ml of a solution 18 wt.% PSSA catalyst in water at 60 °C for 24h. Purification via flash column chromatography (Hex/EtOAc 4:1) afforded the title compound as a light brown oil (1.2 g, 4.54 mmol, 82% yield). **IR (oil)** ν 3106, 2923, 2890, 1613, 1412, 1310, 1096, 998, 963, 947, 935 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.81 (d, *J* = 3.13 Hz,2H), 5.73-5.71 (m, 2H), 3.84 (t, *J* =7.44 Hz, 1H), 2.31 (t, *J* = 3.05 Hz, 2H), 2.15-2.07 (m, 2H), 2.10 (s, 6H), 1.93 (s, 3H)). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 207.9, 153.1, 150.7, 106.6, 106.0, 41.0, 38.0, 29.8, 26.8, 13.4. Data obtained were consistent with reported literature.

3.5. Detailed procedure for the synthesis of biofuel precursor 3a with u-PSSA



A 9 mL pressure tube was charged with 0.5 mL of 2-methylfuran (serving as both solvent and reactant), furfural (41.4 µL, 0.5 mmol, 1 equiv.), and u-PSSA catalyst (44% sulfonation, 10 mg, 5 mol%). An example of the standard reaction setup, using a hotplate with a heating block and a coupled thermometer, is shown in **Figure S4a**. Initially, the reaction mixture appeared yellow when the reagents and u-PSSA catalyst were combined, and it turned red upon heating (**Figures S4b and S4c**).

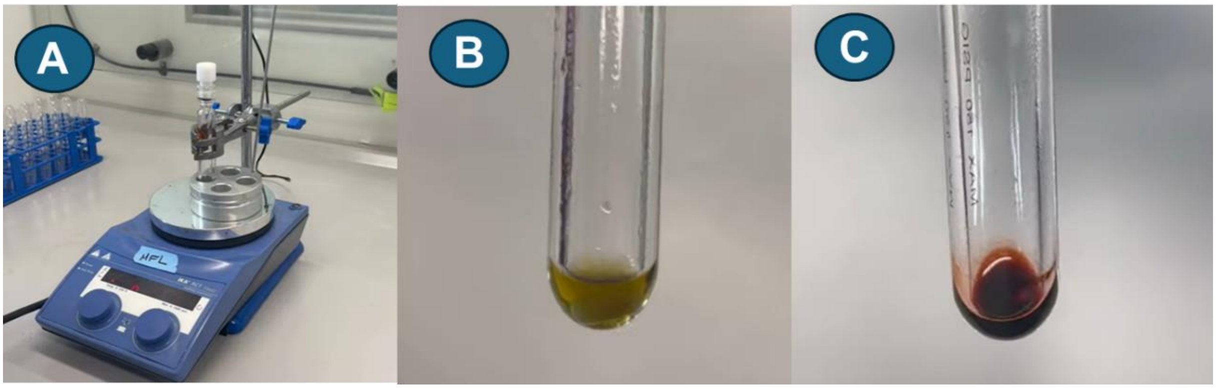


Figure S4. A) Standard reaction setup for the synthesis of 3a. B) Initial yellow colour of the reaction mixture. C) Red colour of the reaction mixture upon heating to 70 °C.

The mixture was stirred at 70 °C for 2 hours and monitored by TLC (hexane: ethyl acetate, 4:1). A representative TLC plate (under UV light) after reaction completion is shown in **Figure S5a**. Since u-PSSA is insoluble, it can be easily recovered by vacuum filtration. After completion, the reaction mixture was filtered under vacuum to recover the u-PSSA catalyst (**Figure 5b**).

The filtrate was transferred to a round-bottom flask, diluted with ethyl acetate, and concentrated using a rotary evaporator. The crude product was purified by column chromatography with a 19:1 mixture of hexane: ethyl acetate as the eluent. Fractions containing the product were collected, transferred to a tared round-bottom flask, and the solvent was removed. Finally, the flask was placed on a Schlenk line for further drying.

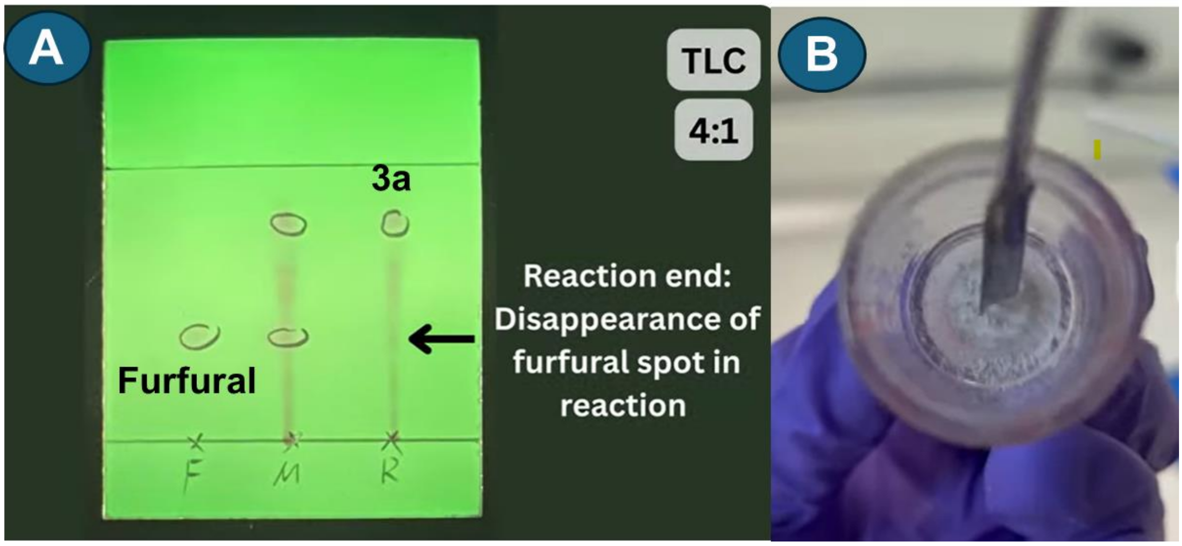


Figure S5. A) A representative TLC plate (under UV light) using hexane: Ethyl Acetate (4:1) after reaction completion. B) Recovery of u-PSSA catalyst under vacuum filration.

4. References

1 H. Abedsoltan, I. S. Omodolor, A. C. Alba-Rubio and M. R. Coleman, *Polymer (Guildf)*, 2021, 222, 123620.

2 A. Corma, O. de la Torre, M. Renz and N. Villandier, *Angewandte Chemie International Edition*, 2011, 50, 2375–2378.

3 Z. Li, X. Liu, Y. Yin, Y. Li, J. Wang and X. Yu, *ChemistrySelect*, 2018, 3, 599–601.

4 H.-E. Qu, C. Xiao, N. Wang, K.-H. Yu, Q.-S. Hu and L.-X. Liu, *Molecules*, 2011, 16, 3855–3868.

5 S. Genovese, F. Epifano, C. Pelucchini and M. Curini, *European J Org Chem*, 2009, 2009, 1132–1135.

6 S. Dutta, A. Bohre, W. Zheng, G. R. Jenness, M. Núñez, B. Saha and D. G. Vlachos, *ACS Catal*, 2017, 7, 3905–3915.

5. FTIR, TGA and DSC of PS, c-PSSA and u-PSSA

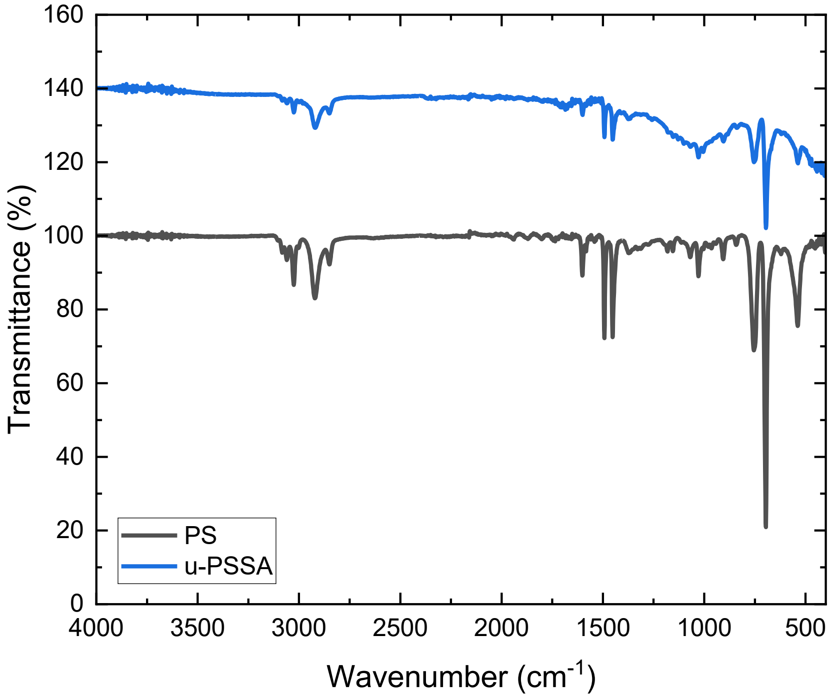


Figure S6. FTIR spectra of PS and u-PSSA. The u-PSSA spectrum was offset by 40% on the y-axis for clarity.

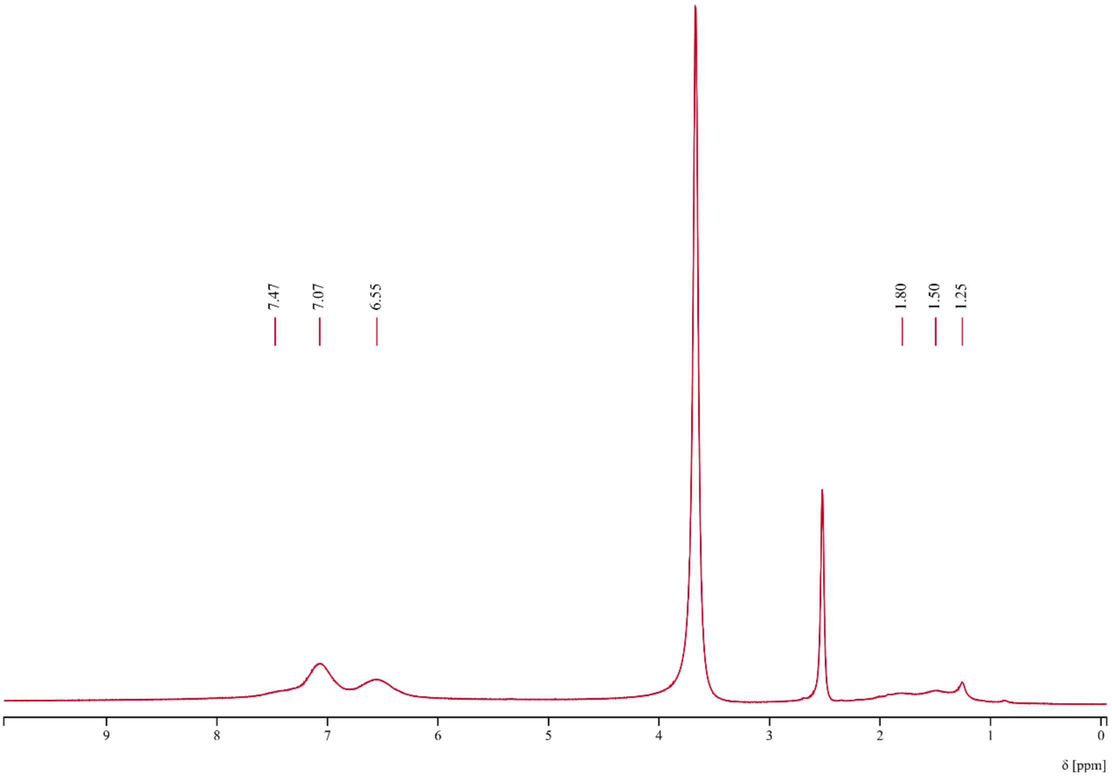


Figure S7. ^{1}H-NMR of u-PSSA in DMSO-d_6

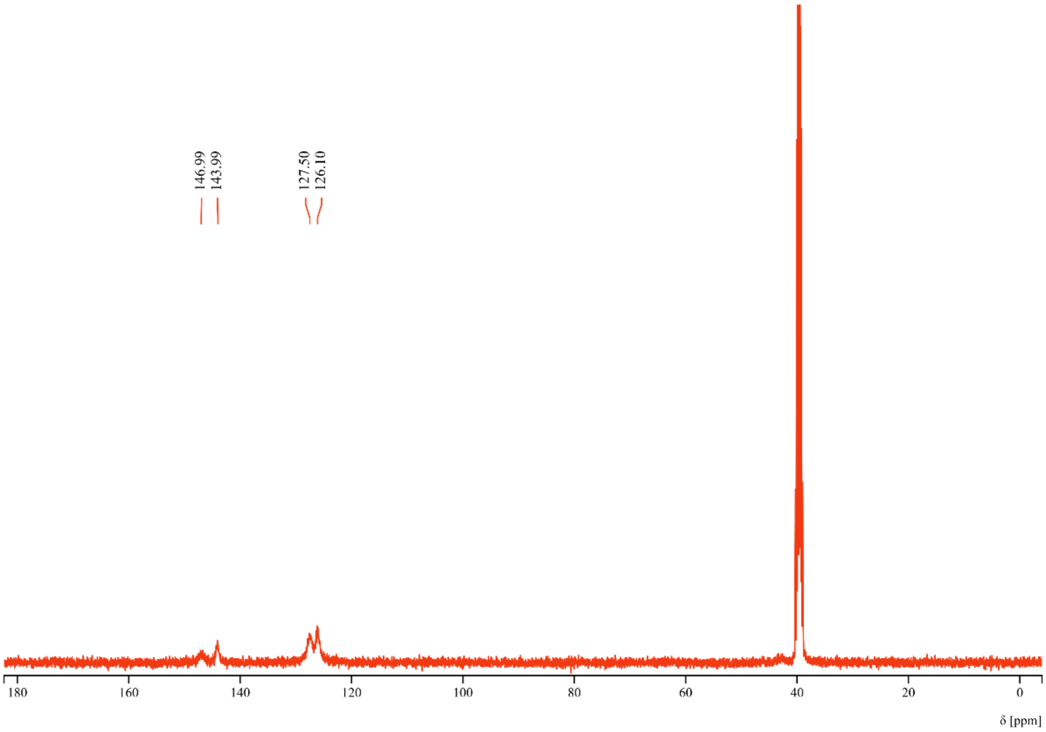


Figure S8. ^{13}C-NMR of u-PSSA in DMSO-d_6. The aliphatic carbon peaks are not shown, as they are obscured by the residual DMSO-d_6 peak at around 40 ppm.

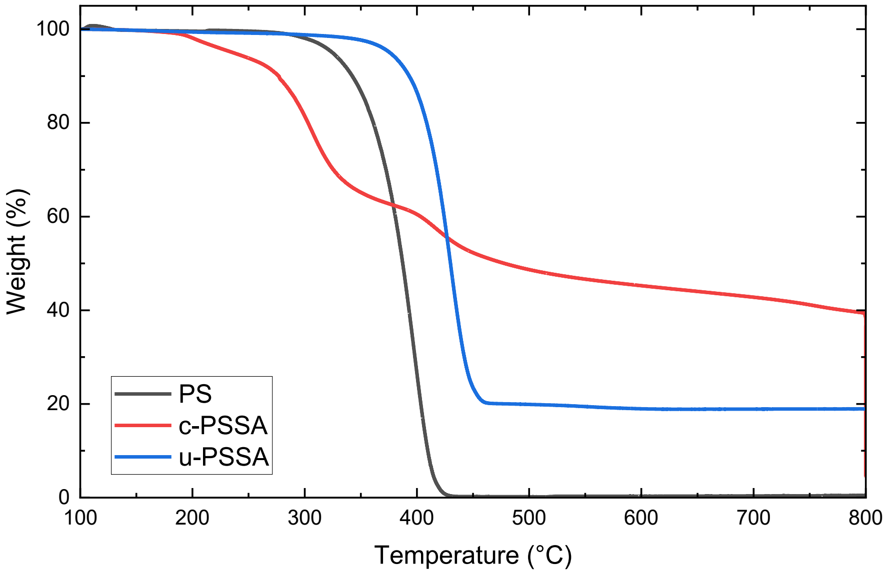


Figure S9. TGA thermograms of all three polymers, heated at a heating rate of 10 °C min^{-1} from 100 to 800 °C under a nitrogen atmosphere (flow rate: 25 mL min^{-1}).

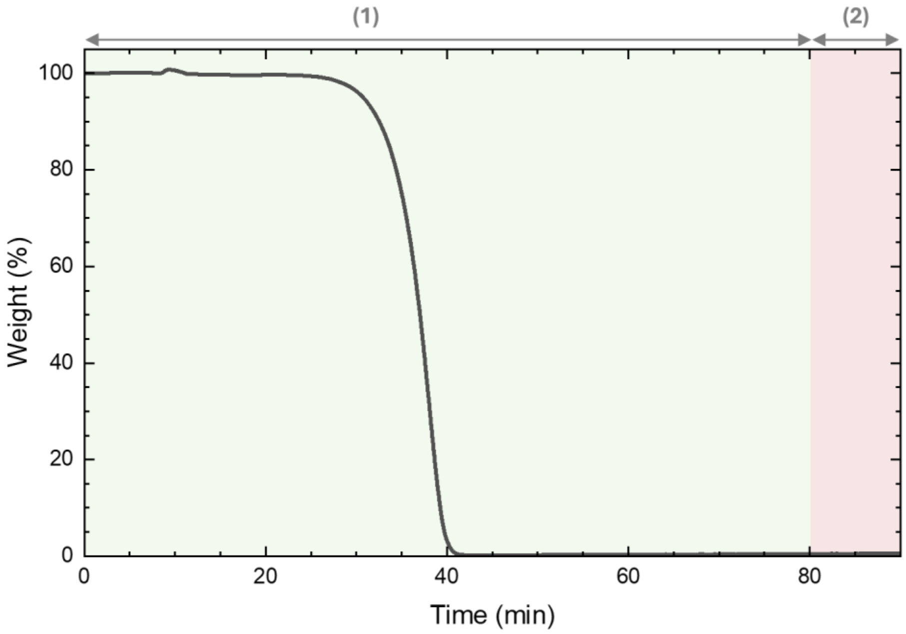


Figure S10. TGA thermogram of PS sample weight as a function of time. In a first step (1), the sample was heated at a heating rate of 10 °C min-1 from 40 to 800 °C, (2) before being kept at that temperature for 10 minutes. The area shaded in green represents the time the sample was heated under a nitrogen atmosphere, before changing to air (red shaded area) to burn off any residual organic compounds. The flow rate for both gases was 25 mL min^{-1}.

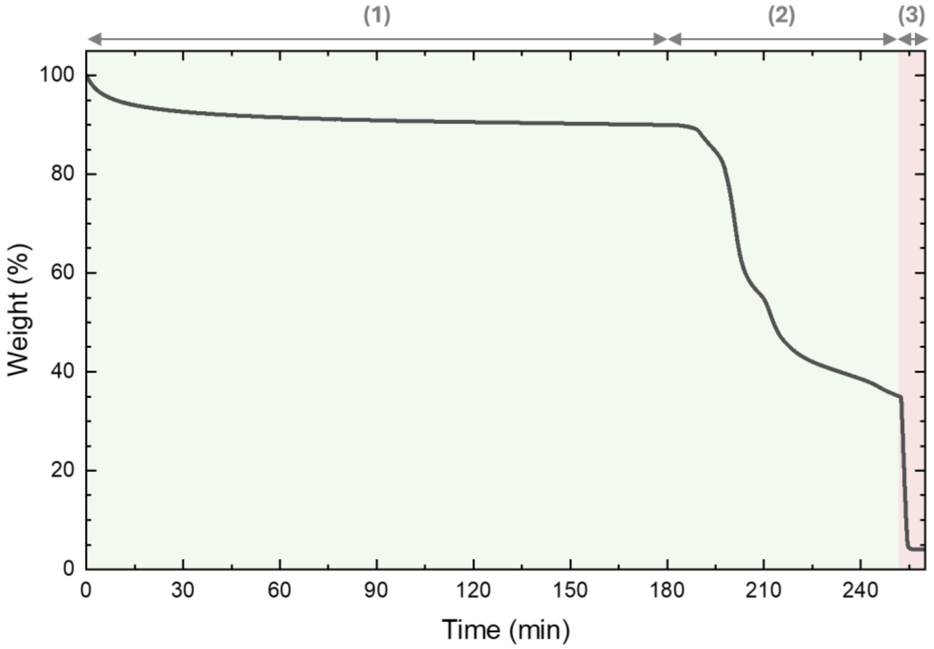


Figure S11. TGA thermogram of c-PSSA sample weight as a function of time. In a first step (1), the sample was heated to 100 °C and ket isothermal for 180 minutes to allow complete removal of any residual water from the sample. During this time, around 10 percent of water (by weight) were removed, and the thermogram plateaued. After drying (2) the sample was heated at a heating rate of 10 °C min^{-1} from 100 to 800 °C, (3) before being kept at that temperature for 10 minutes. The area shaded in green represents the time the sample was heated under a nitrogen atmosphere, before changing to air (red shaded area) to burn off any residual organic compounds. The flow rate for both gases was 25 mL min^{-1}.

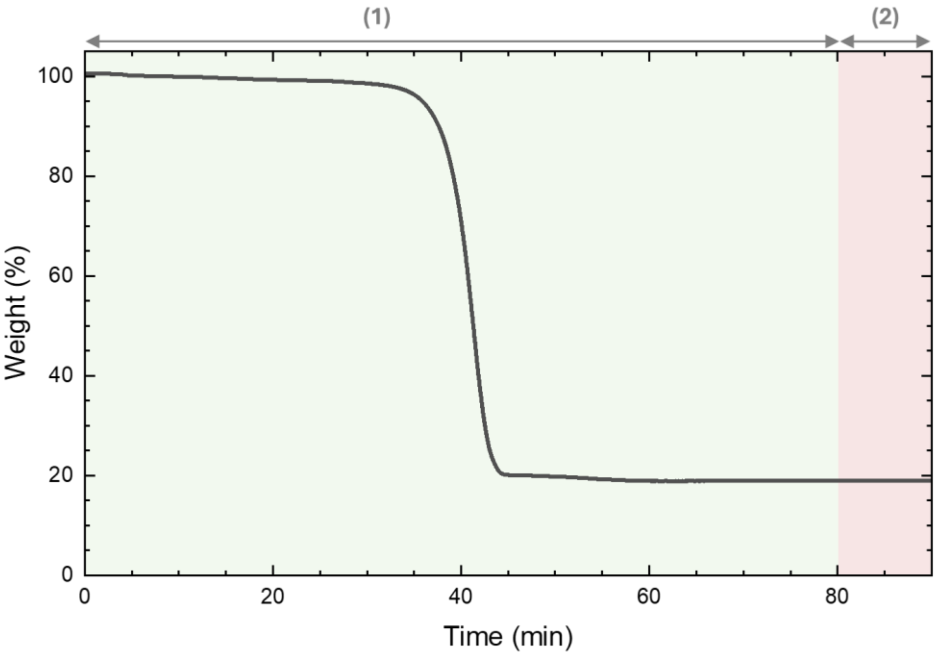


Figure S12. TGA thermogram of u-PSSA sample weight as a function of time. In a first step (1), the sample was heated at a heating rate of 10 °C min^{-1} from 40 to 800 °C, (2) before being kept at that temperature for 10 minutes. The area shaded in green represents the time the sample was heated under a nitrogen atmosphere, before changing to air (red shaded area) to burn off any residual organic compounds. The flow rate for both gases was 25 mL min^{-1}.

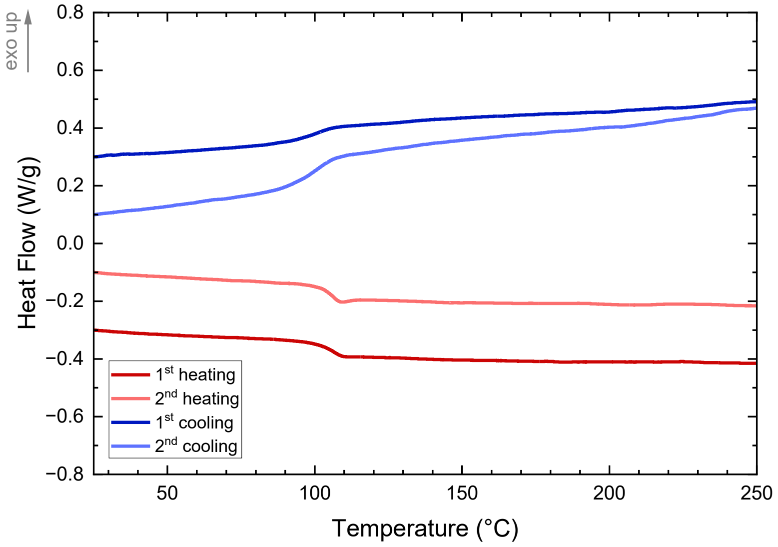


Figure S13. DSC thermograms showing two heating and two cooling cycles of PS. The curves have been offset on the y-axis for clarity.

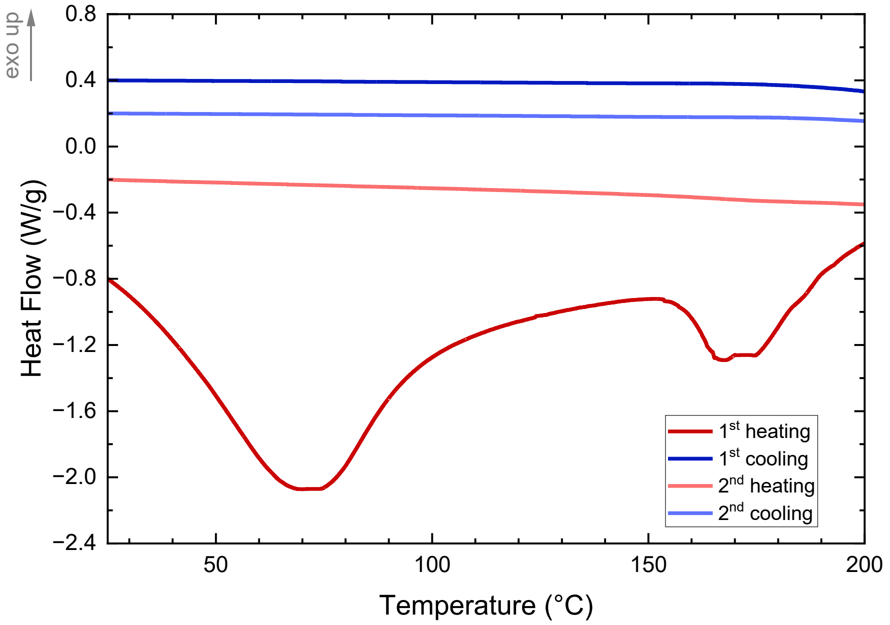


Figure S14. DSC thermograms showing two heating and two cooling cycles of c-PSSA. The curves have been offset on the y-axis for clarity.

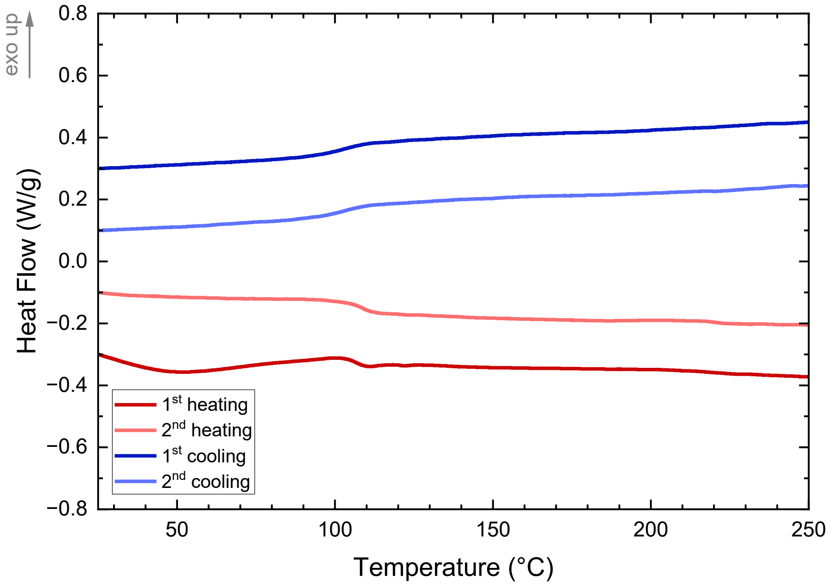
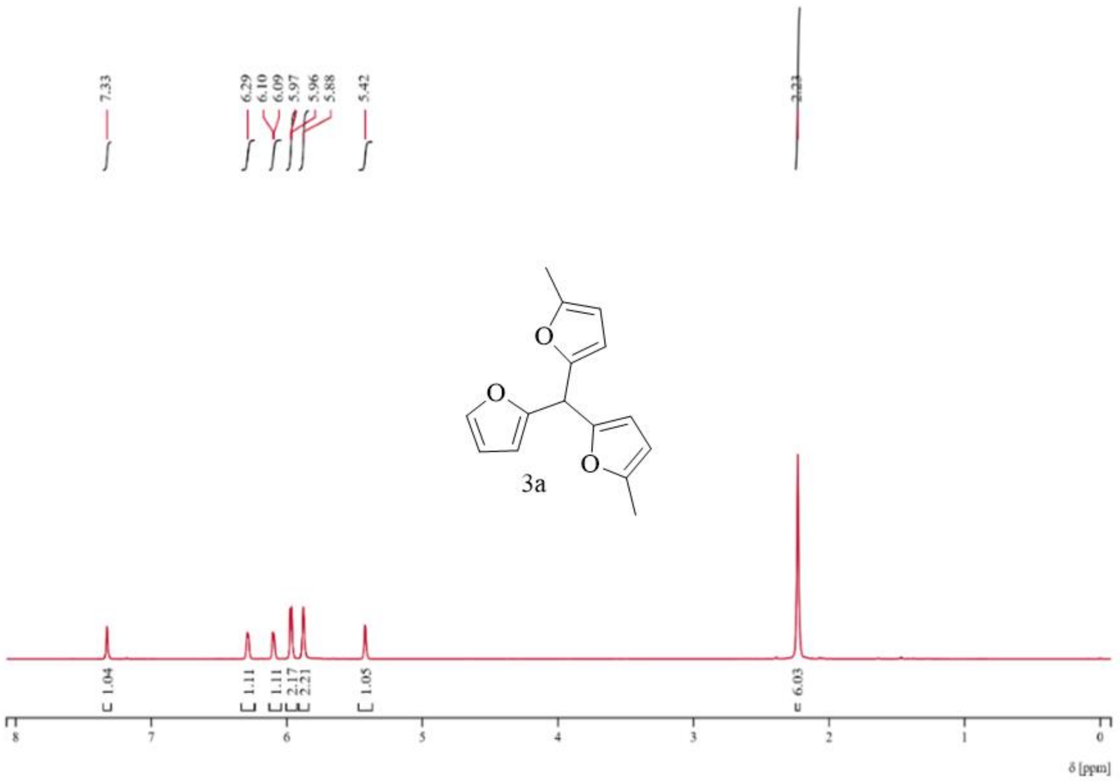
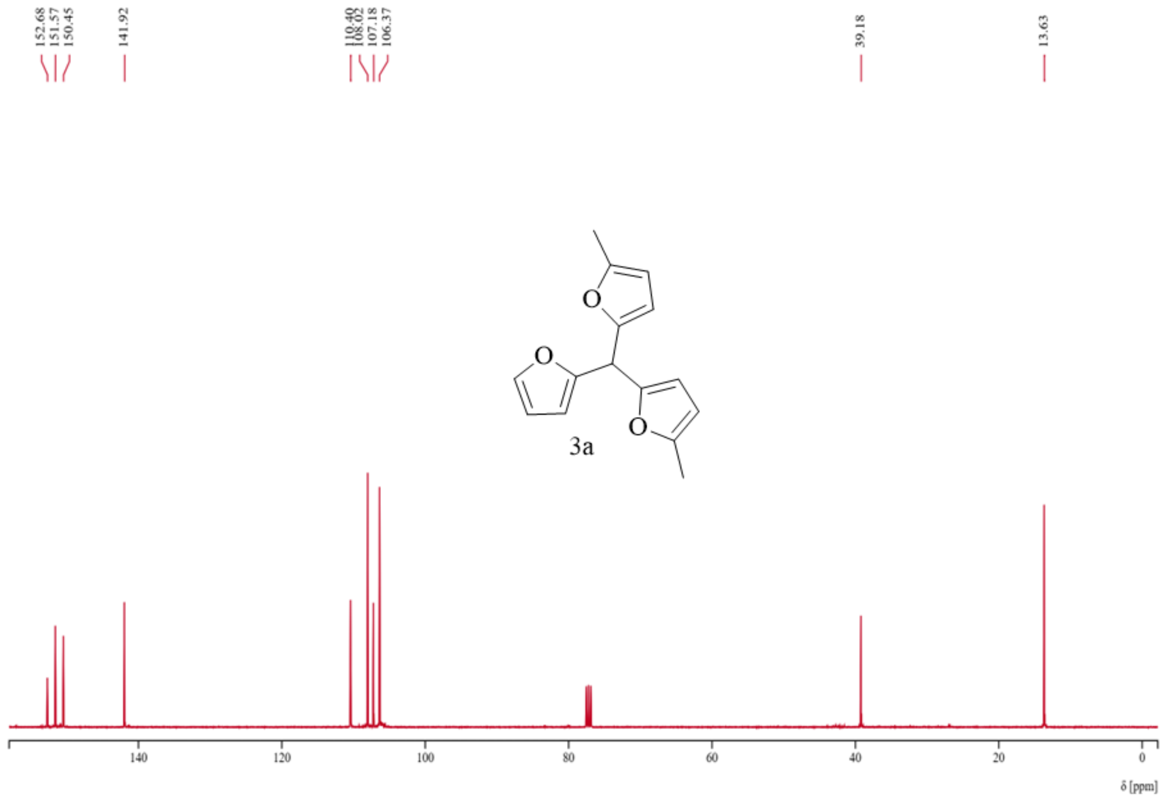
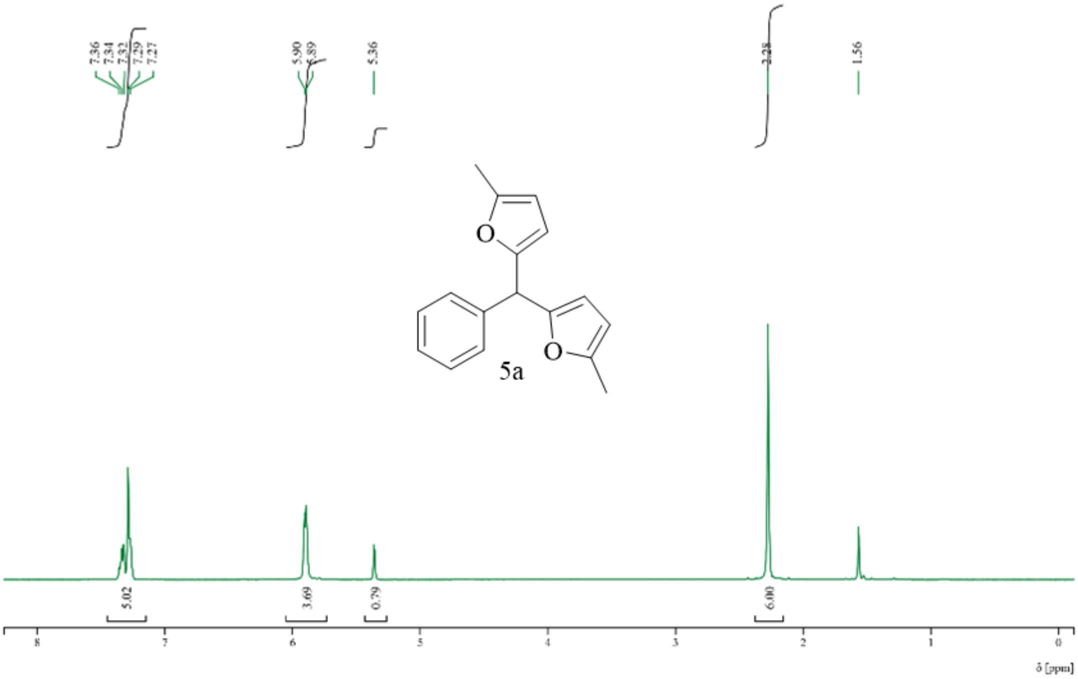


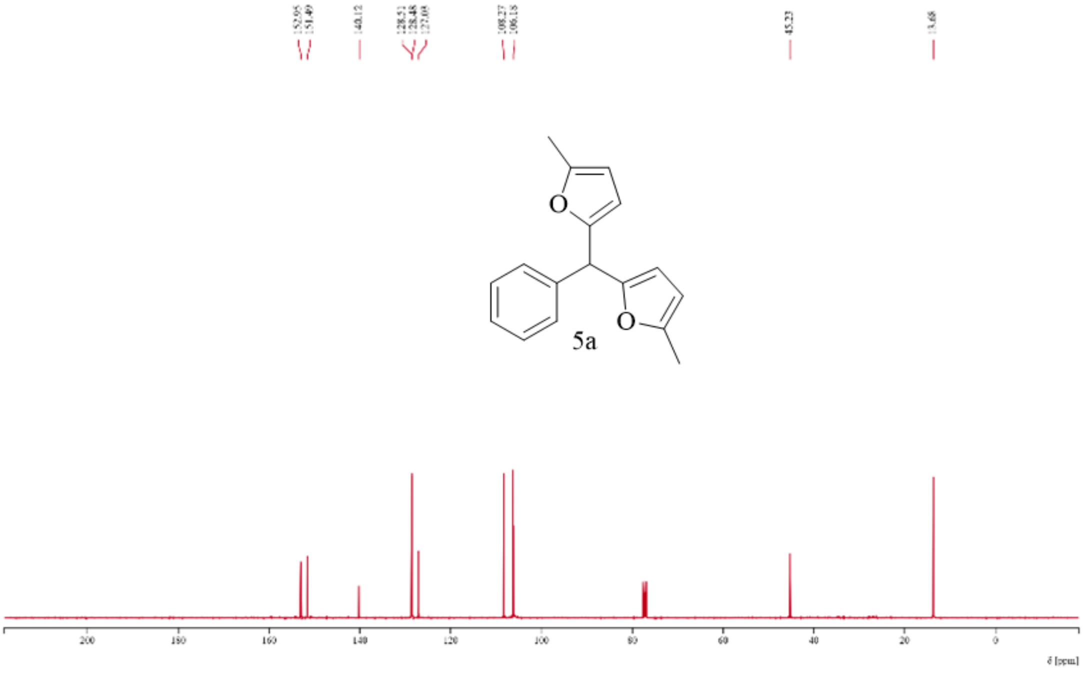
Figure S15. DSC thermograms showing two heating and two cooling cycles of u-PSSA. The curves have been offset on the y-axis for clarity.

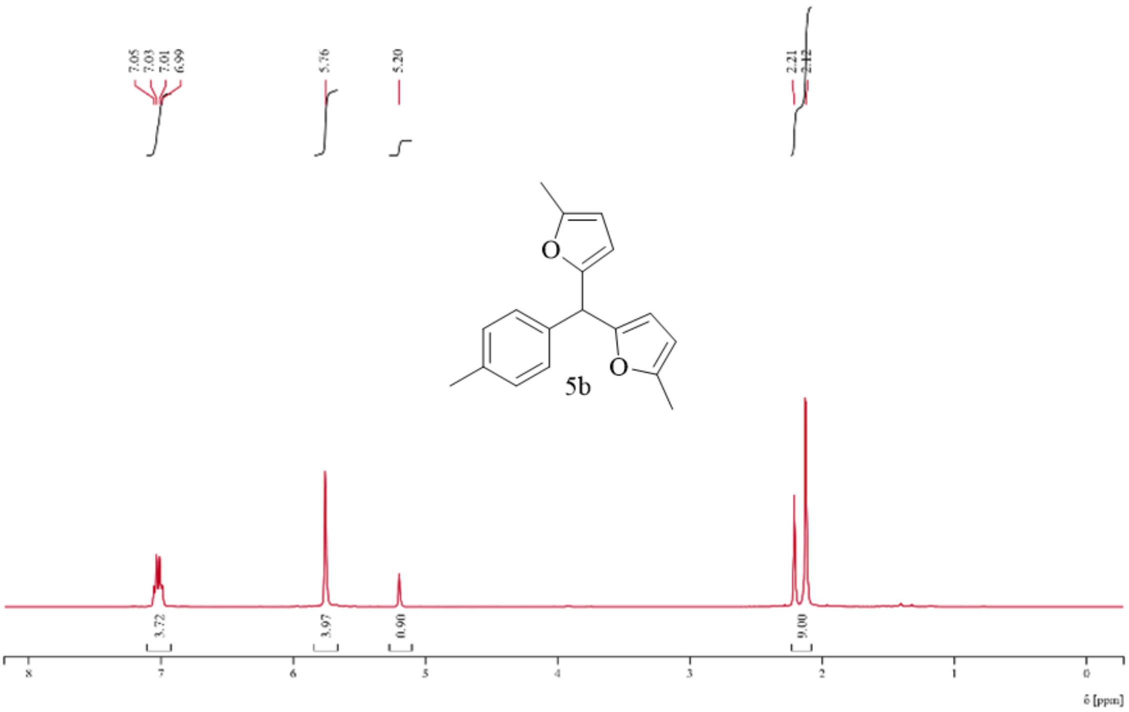
6. ^{1}H ,^{13}C NMR and HRMS Spectra

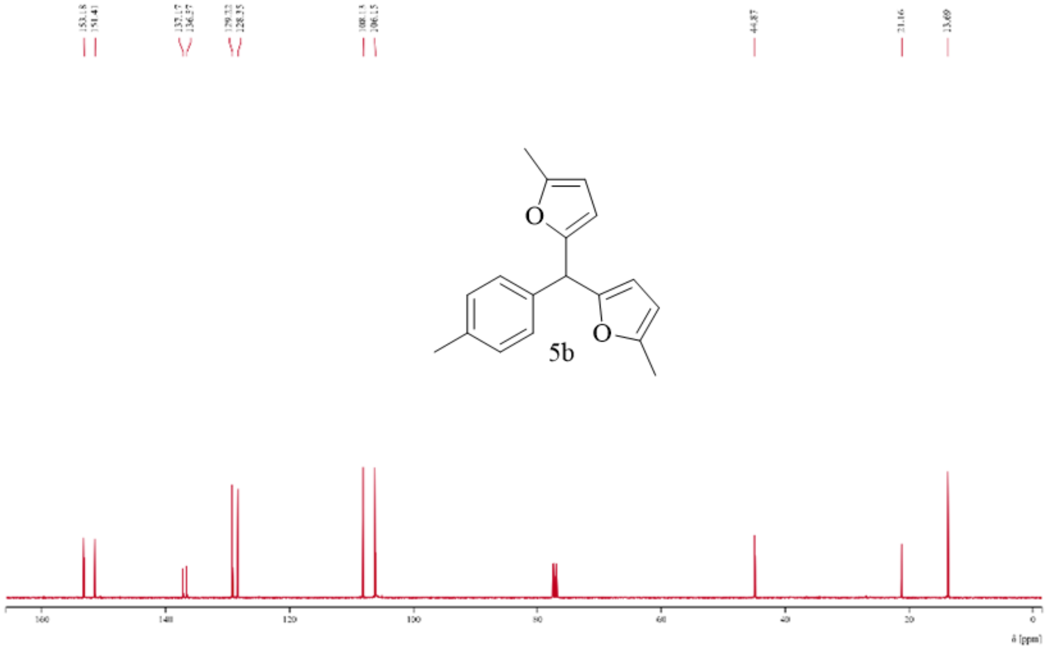


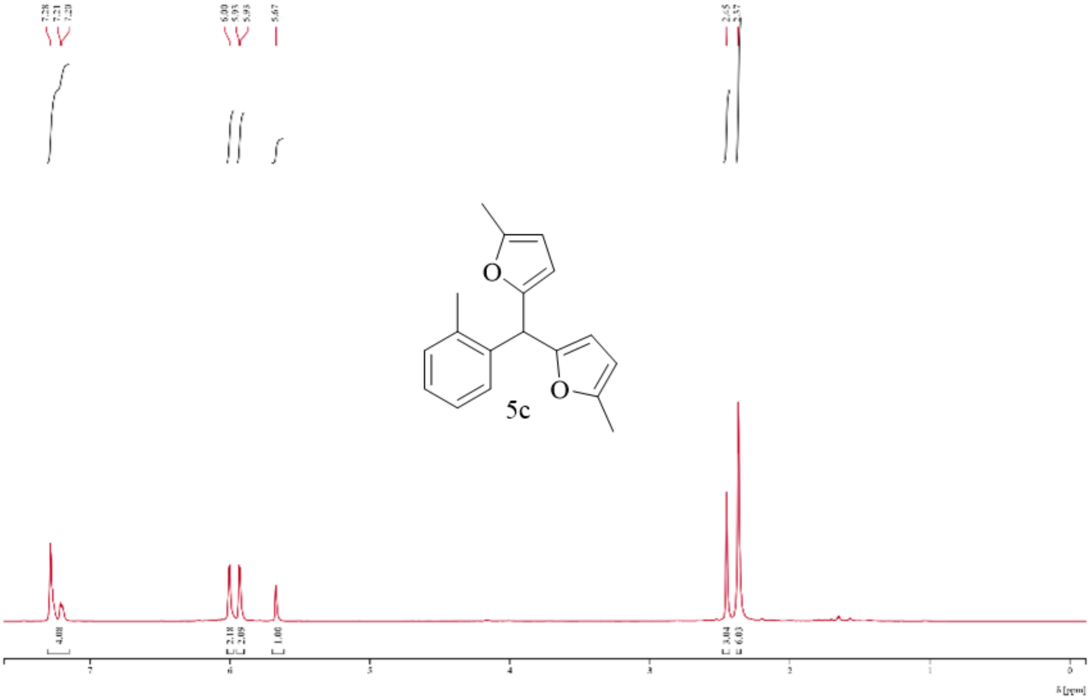


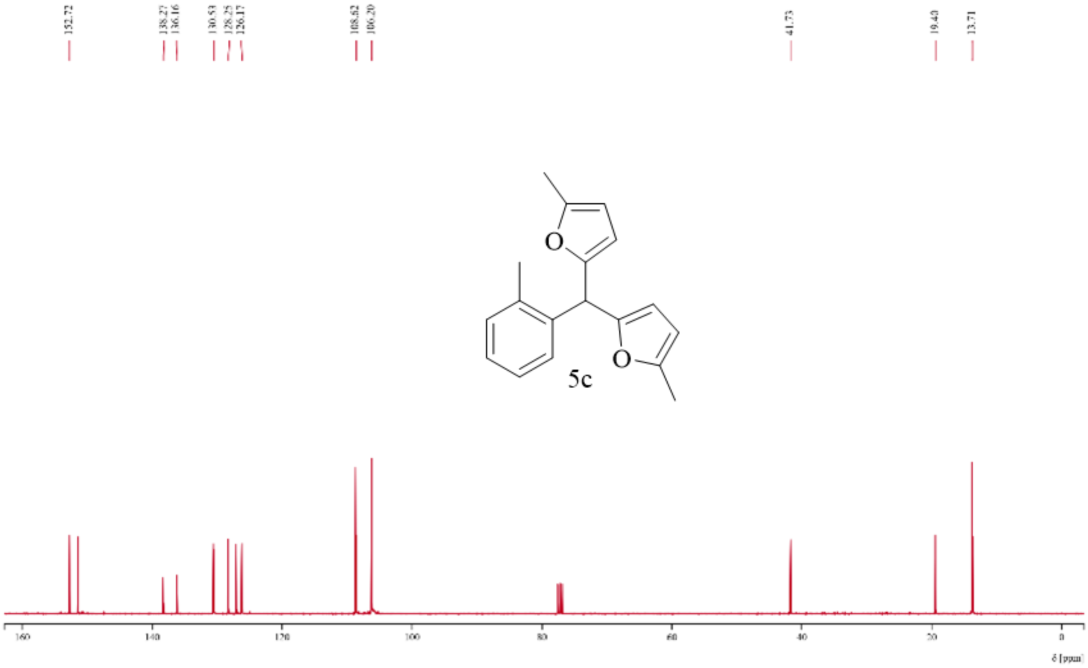

7.36
7.34
7.32
7.29
7.27
5.90
5.89
5.36
2.28
1.56
O
O
5a
5.02
3.69
0.79
6.00
8
7
6
5
4
3
2
1
0
δ [ppm]

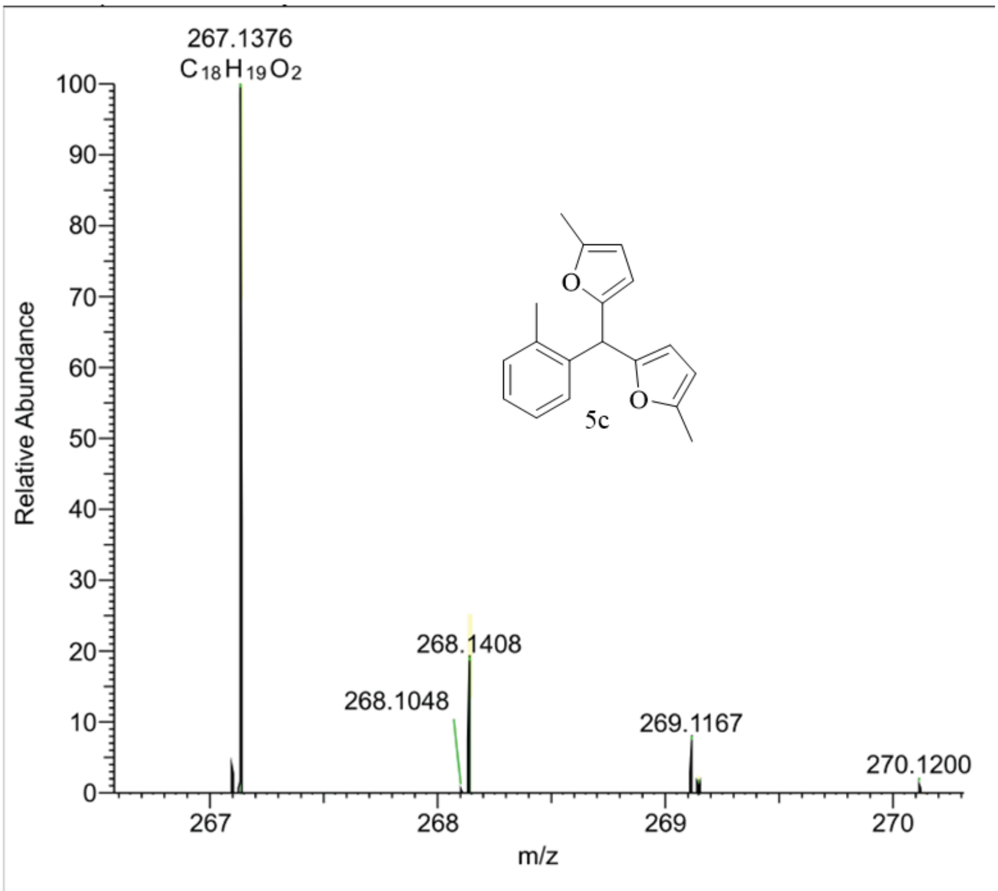

152.95
151.49
140.12
128.51
128.48
127.09
108.27
106.18
45.23
13.68
O
O
5a
200
180
160
140
120
100
80
60
40
20
0
δ [ppm]

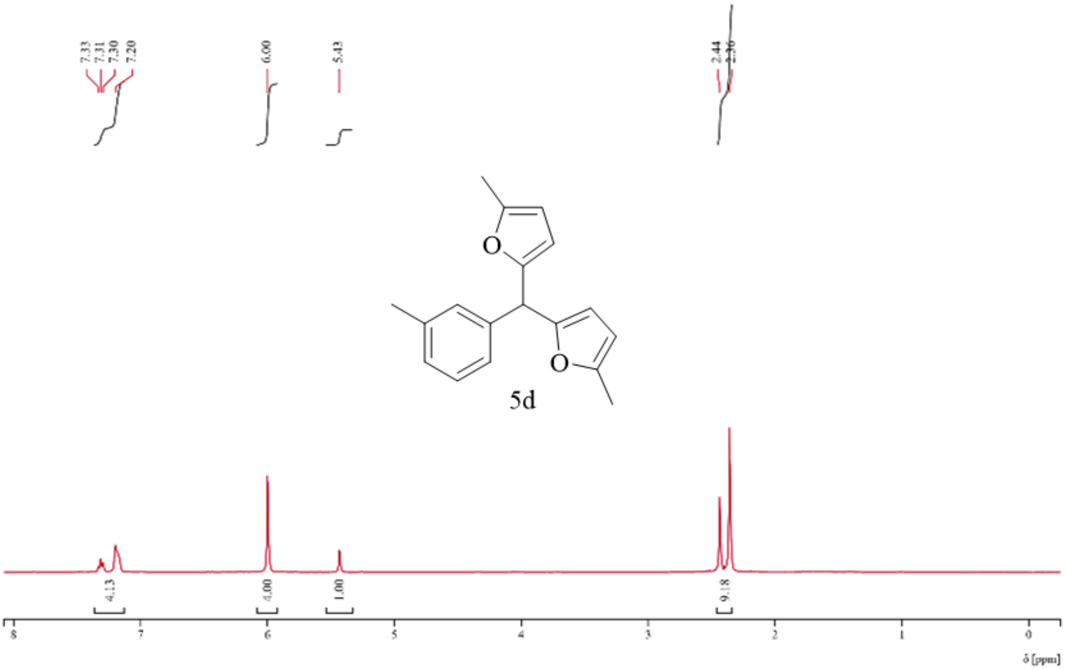

7.05
7.03
7.01
6.99
5.76
5.20
2.21
2.12
O
O
5b
3.72
3.97
0.90
9.00
8
7
6
5
4
3
2
1
0
δ [ppm]

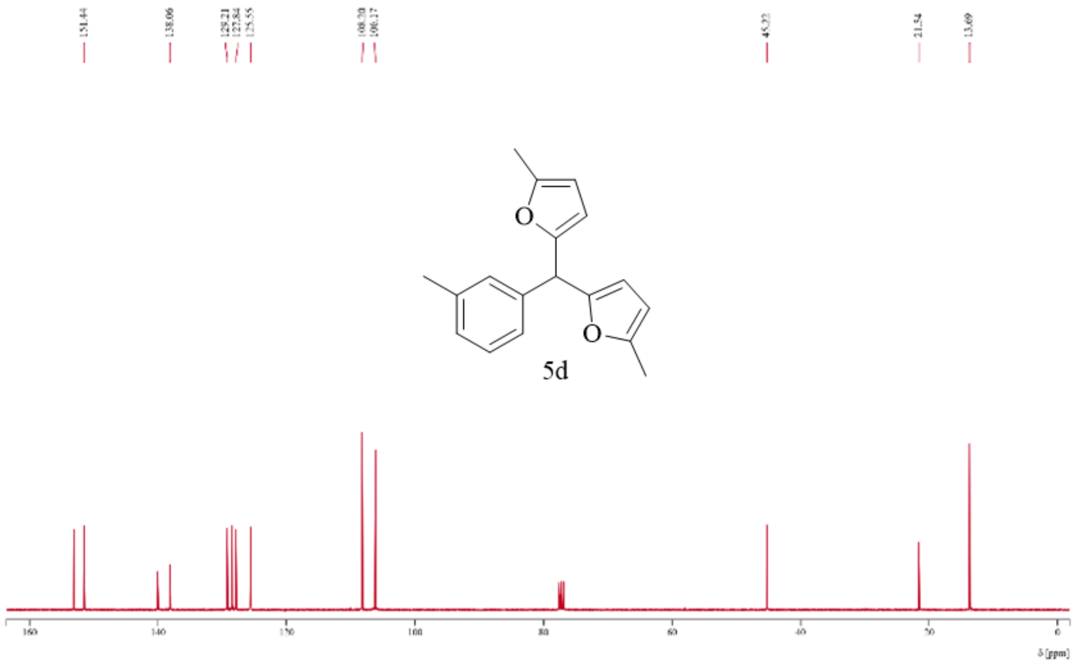

153.18
151.41
137.17
136.37
129.32
128.35
108.13
106.15
44.87
21.16
13.69
O
O
5b
160
140
120
100
80
60
40
20
0
δ [ppm]


7.28
7.21
7.20
6.00
5.95
5.93
5.67
2.45
2.37
O
O
5c
4.08
2.18
2.09
1.00
3.04
6.03
7
6
5
4
3
2
1
0
δ [ppm]

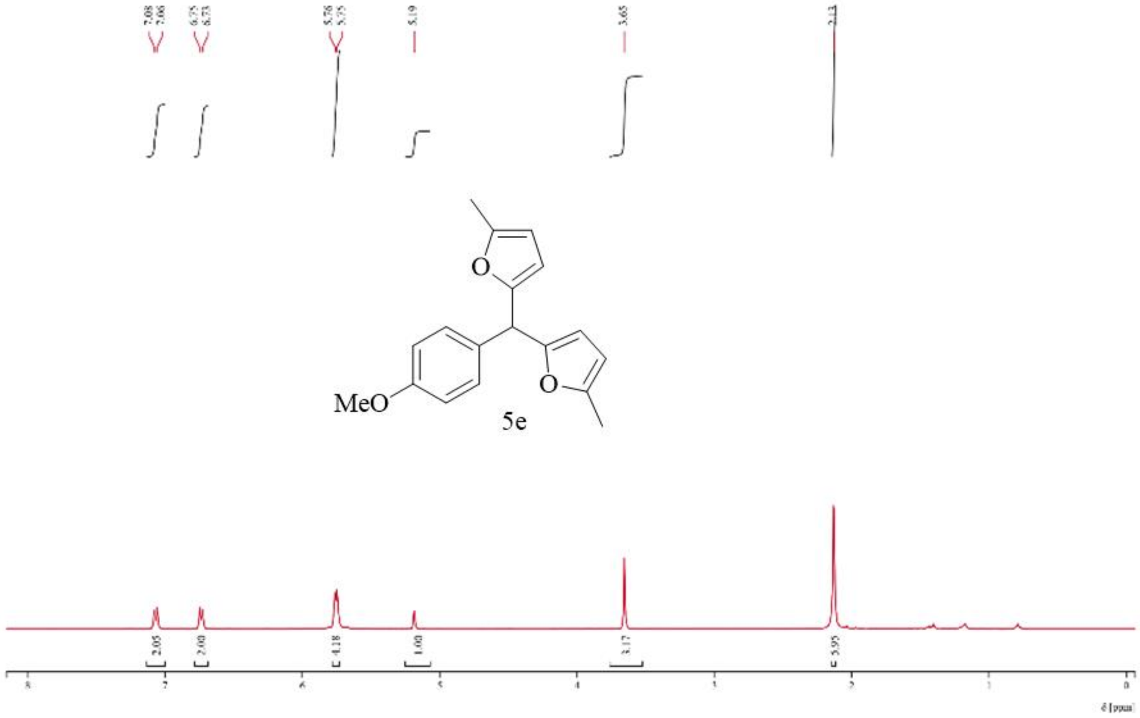

152.72
138.27
136.16
130.53
128.25
126.17
108.62
106.20
41.73
19.40
13.71
O
O
5c
160
140
120
100
80
60
40
20
0
δ [ppm]


267.1376
$C_{18}H_{19}O_2$
Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
268.1408
268.1048
269.1167
270.1200
267
268
269
270
m/z
O
O
5c

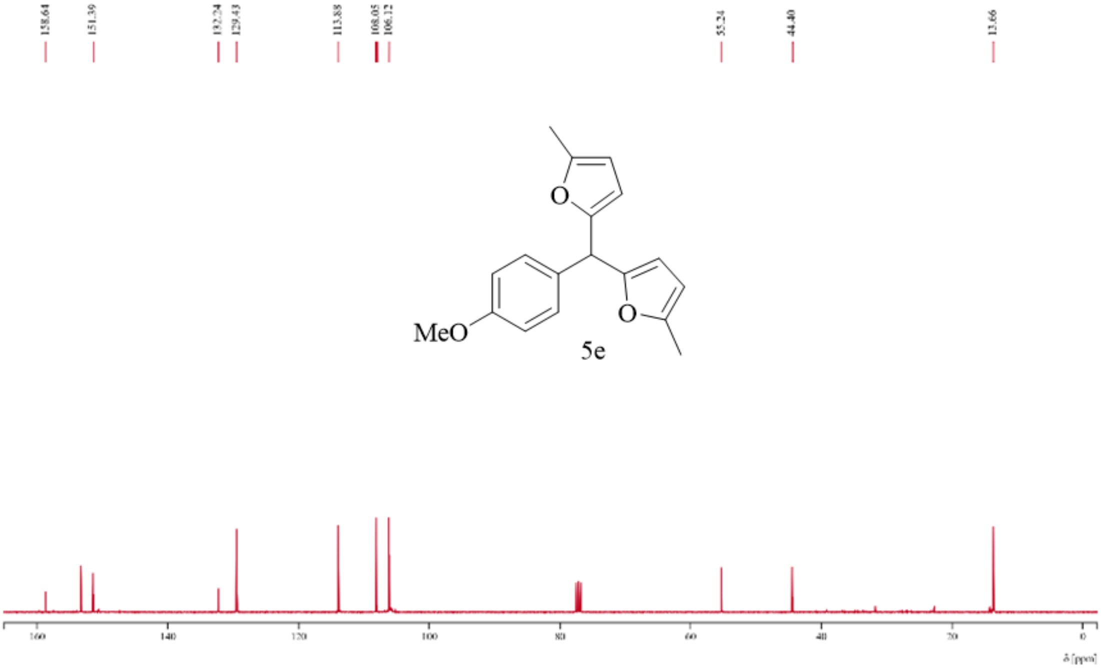

7.33
7.31
7.30
7.20
6.00
5.43
2.44
2.36
O
O
5d
4.13
4.00
1.00
9.18
8
7
6
5
4
3
2
1
0
δ [ppm]

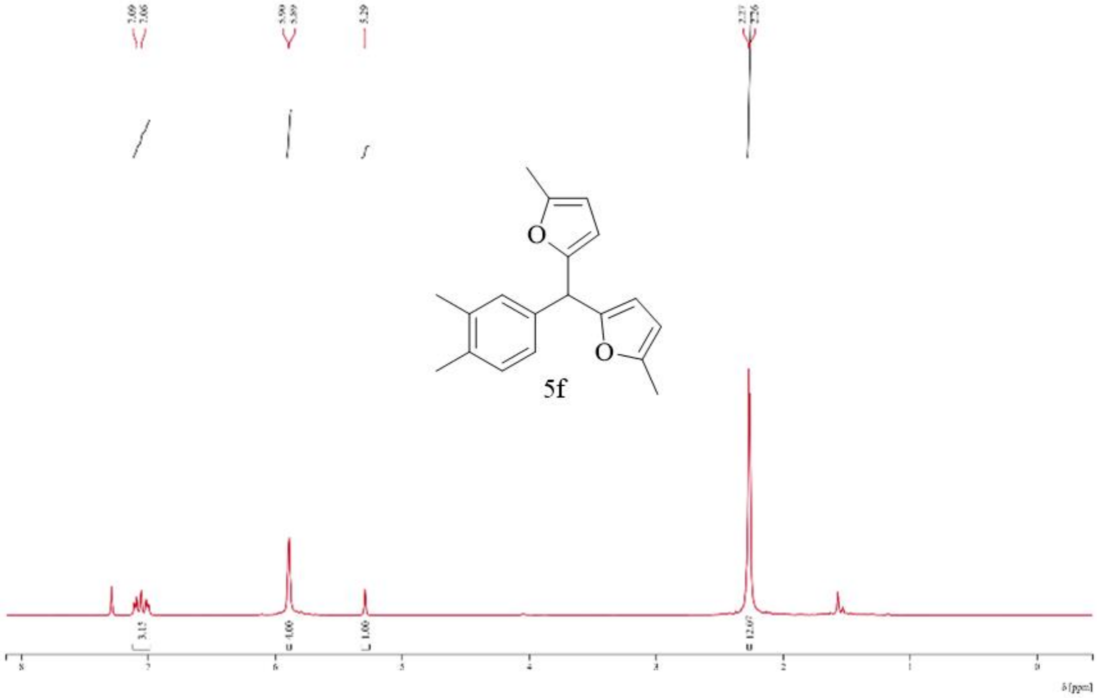

5d

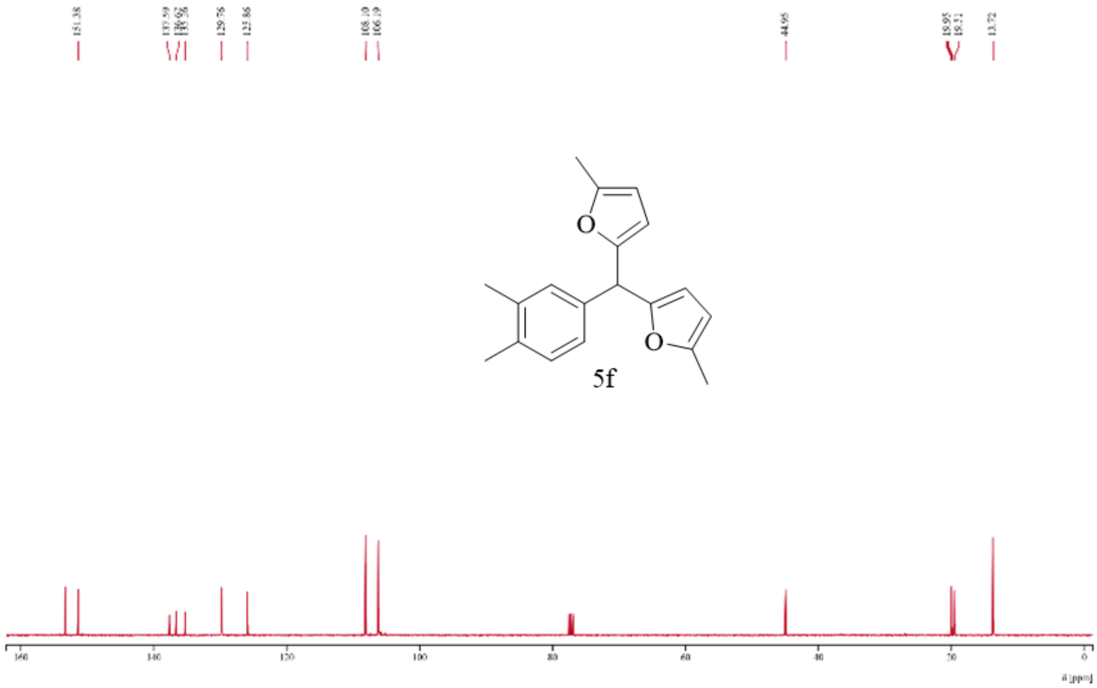
151.44
138.06
129.21
127.84
125.55
108.20
106.17
45.22
21.54
13.69
160
140
120
100
80
60
40
20
0
δ [ppm]

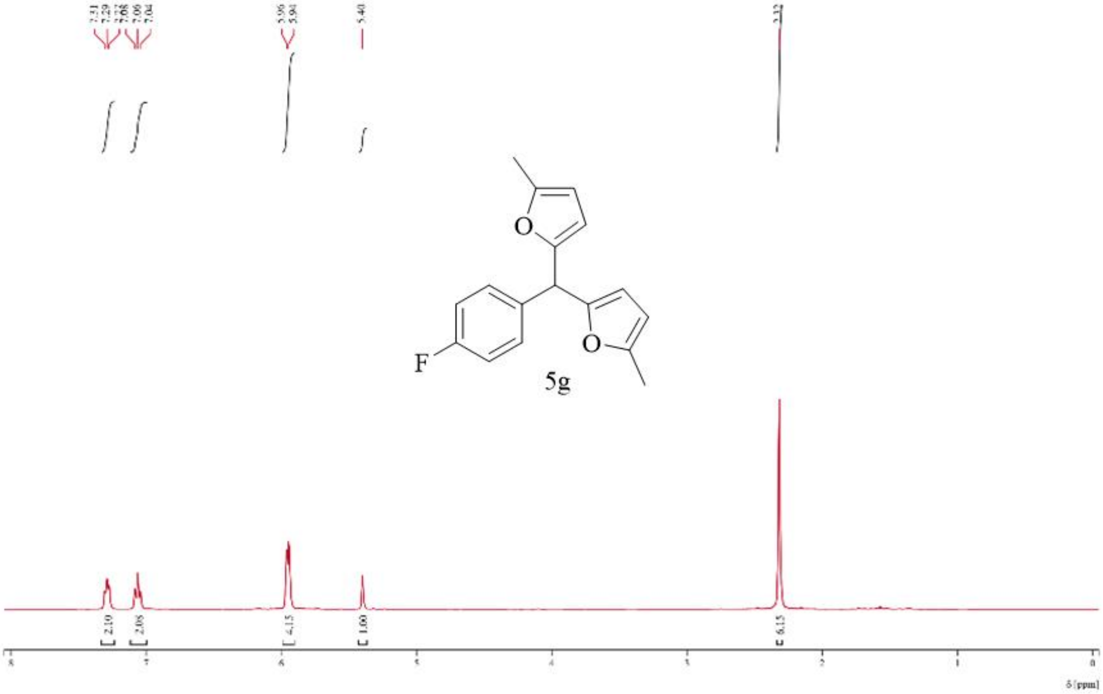

5e

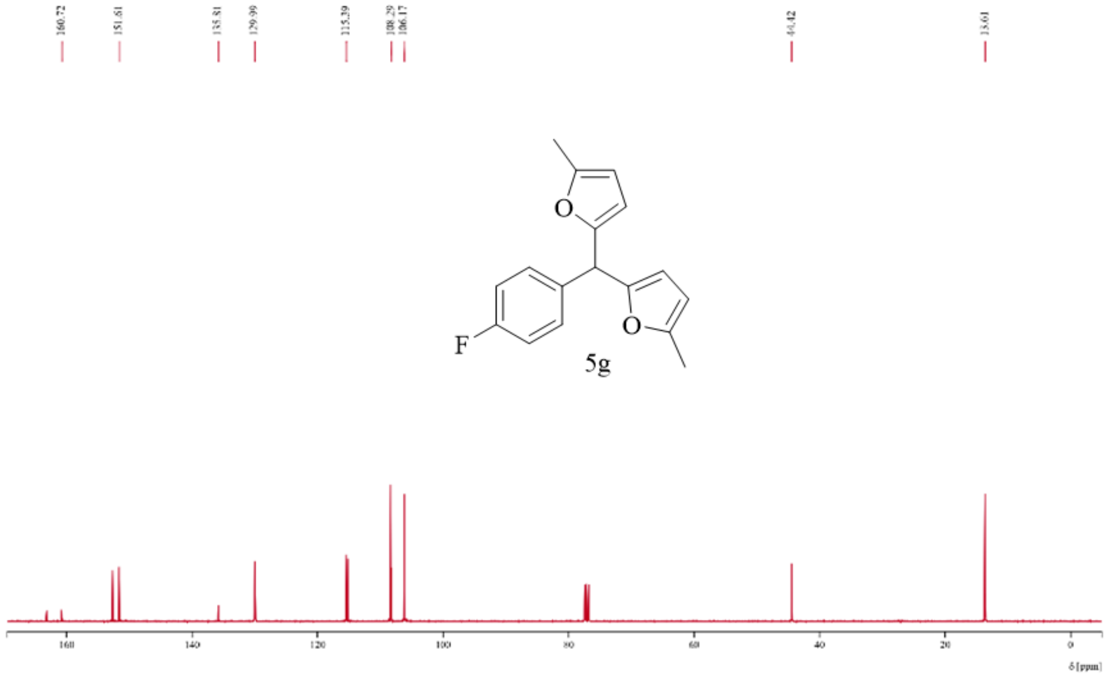
7.08
7.06
6.75
6.73
5.76
5.75
5.19
3.65
2.13
MeO
2.05
2.00
4.18
1.00
3.17
5.95
8
7
6
5
4
3
2
1
0
δ [ppm]

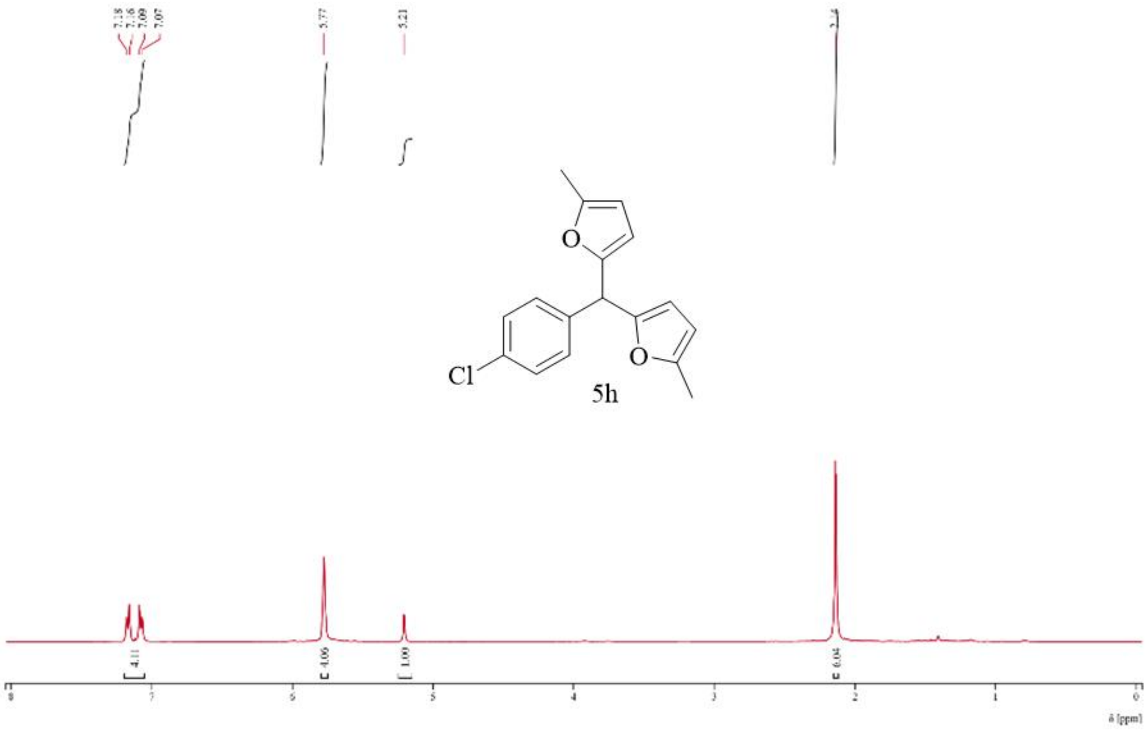

158.64
151.39
132.24
129.43
113.88
108.05
106.12
55.24
44.40
13.66
O
O
MeO
5e
160
140
120
100
80
60
40
20
0
δ [ppm]

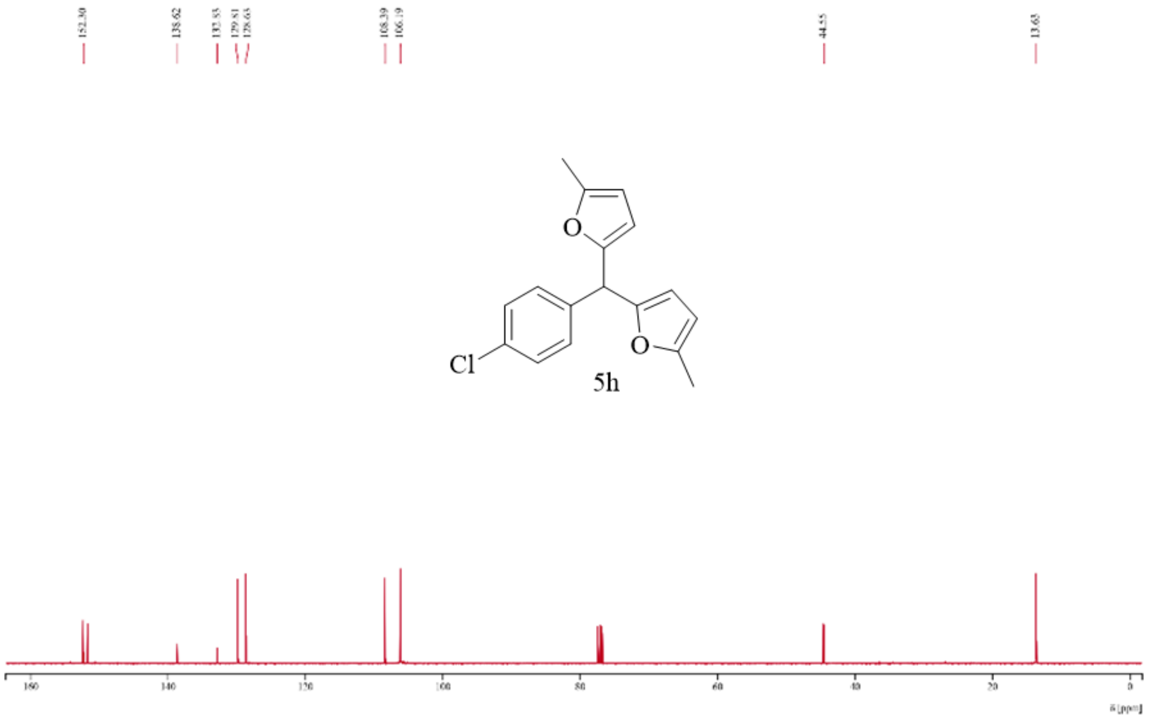

7.09
7.06
5.90
5.89
5.29
2.27
2.26
O
O
5f
3.15
4.00
1.00
12.07
8
7
6
5
4
3
2
1
0
δ [ppm]

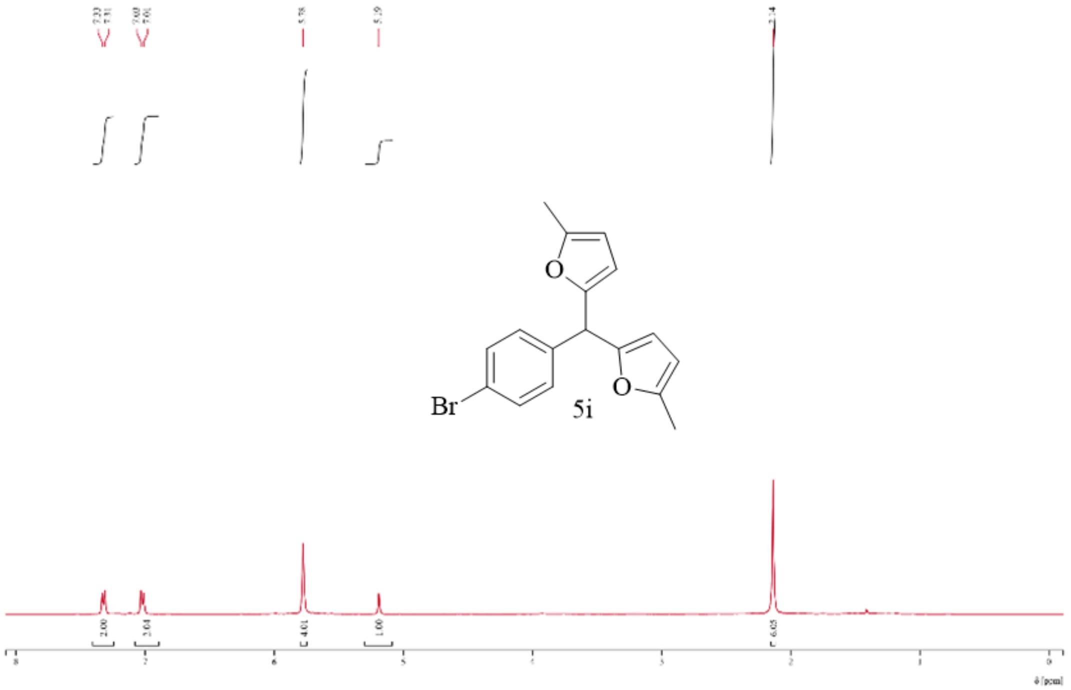

151.38
137.59
136.92
135.56
129.76
125.86
108.10
106.19
44.95
19.95
19.51
13.72
O
O
5f
160
140
120
100
80
60
40
20
0
δ [ppm]

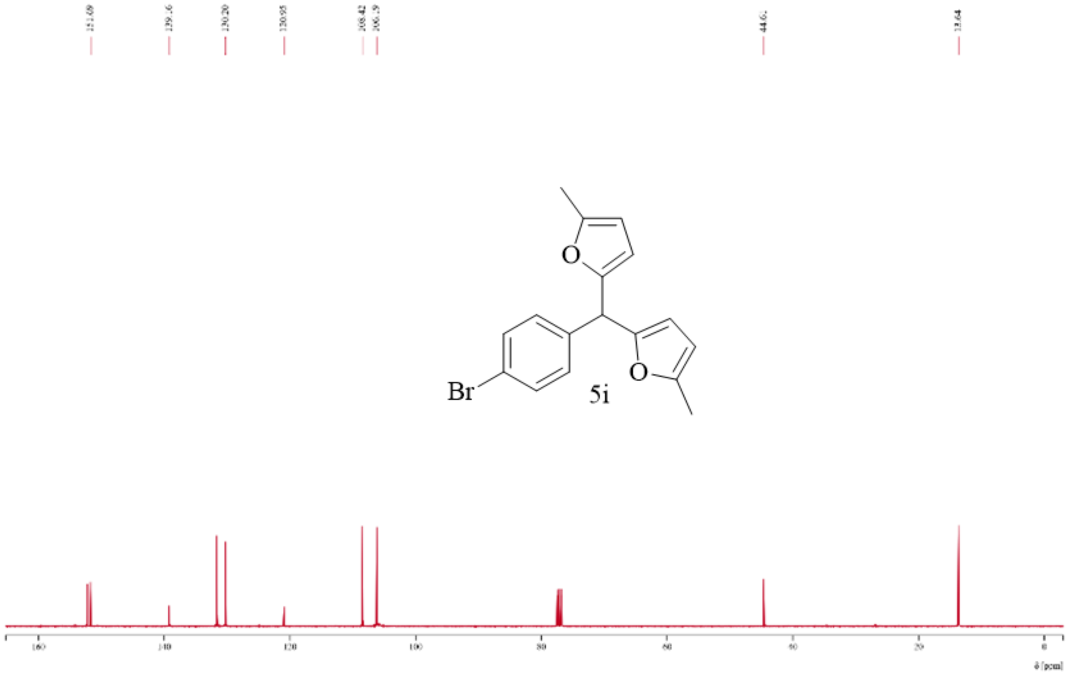

7.31
7.29
7.27
7.08
7.06
7.04
5.96
5.94
5.40
2.32
O
O
F
5g
2.10
2.08
4.15
1.00
6.15
8
7
6
5
4
3
2
1
0
δ [ppm]


160.72
151.61
135.81
129.99
115.39
108.29
106.17
44.42
13.61
O
O
F
5g
160
140
120
100
80
60
40
20
0
δ [ppm]

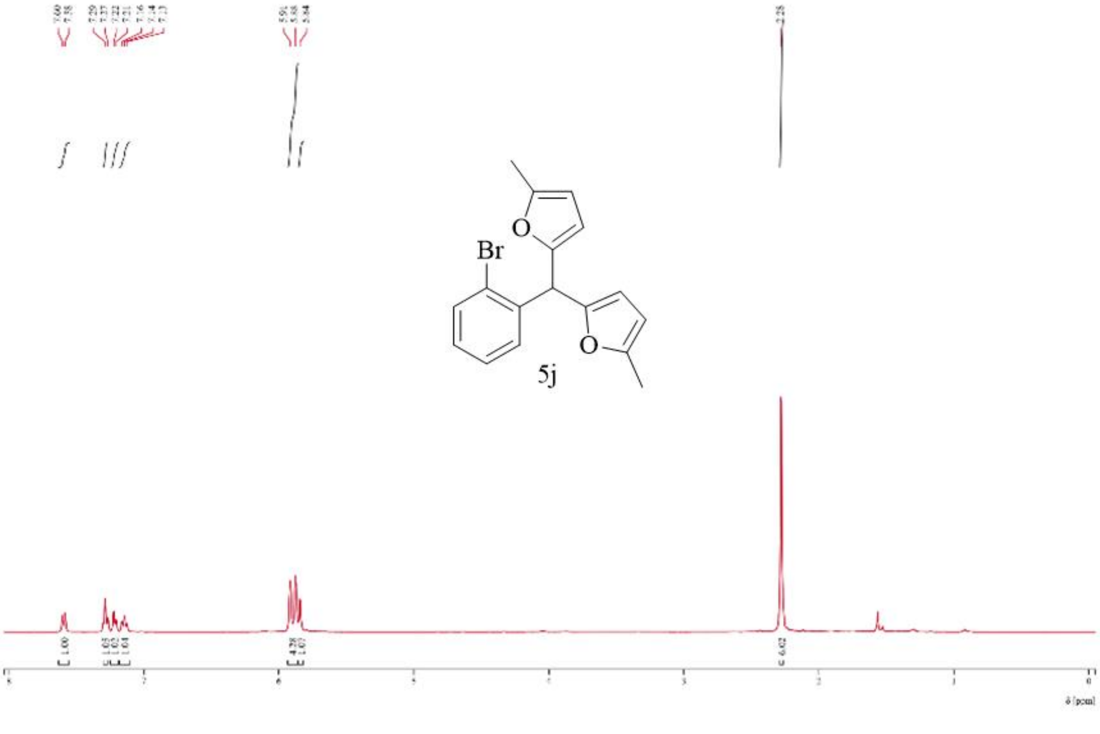

7.18
7.16
7.09
7.07
5.77
5.21
O
O
Cl
5h
4.11
4.06
1.00
6.04
8
7
6
5
4
3
2
1
0
δ [ppm]


5h
152.30
138.62
132.53
129.81
128.63
108.39
106.19
44.55
13.63
O
O
Cl
160
140
120
100
80
60
40
20
0
δ [ppm]

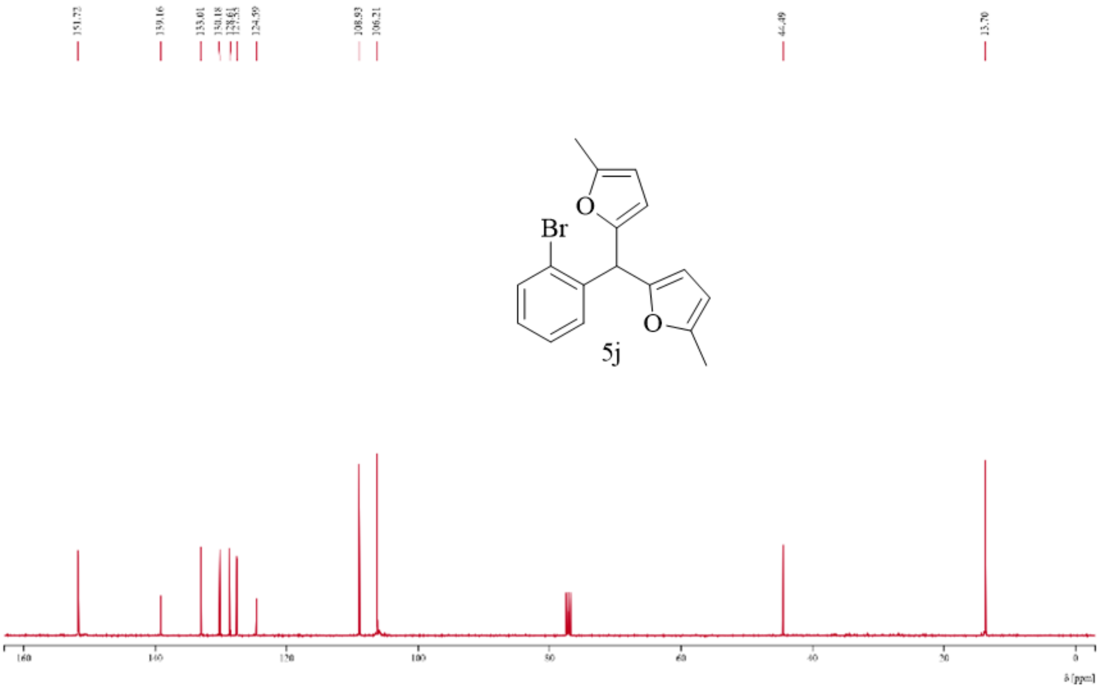

5i
7.33
7.31
7.03
7.01
5.78
5.19
2.14
O
O
Br
2.00
2.04
4.01
1.00
6.05
8
7
6
5
4
3
2
1
0
δ [ppm]

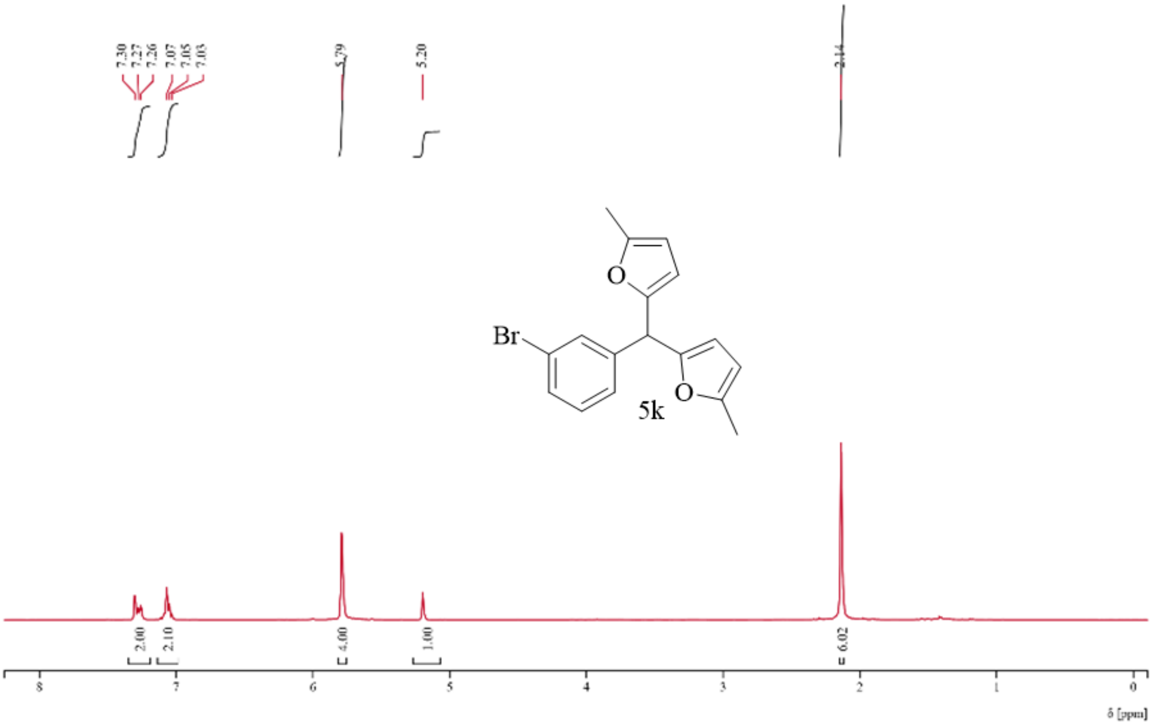

5i

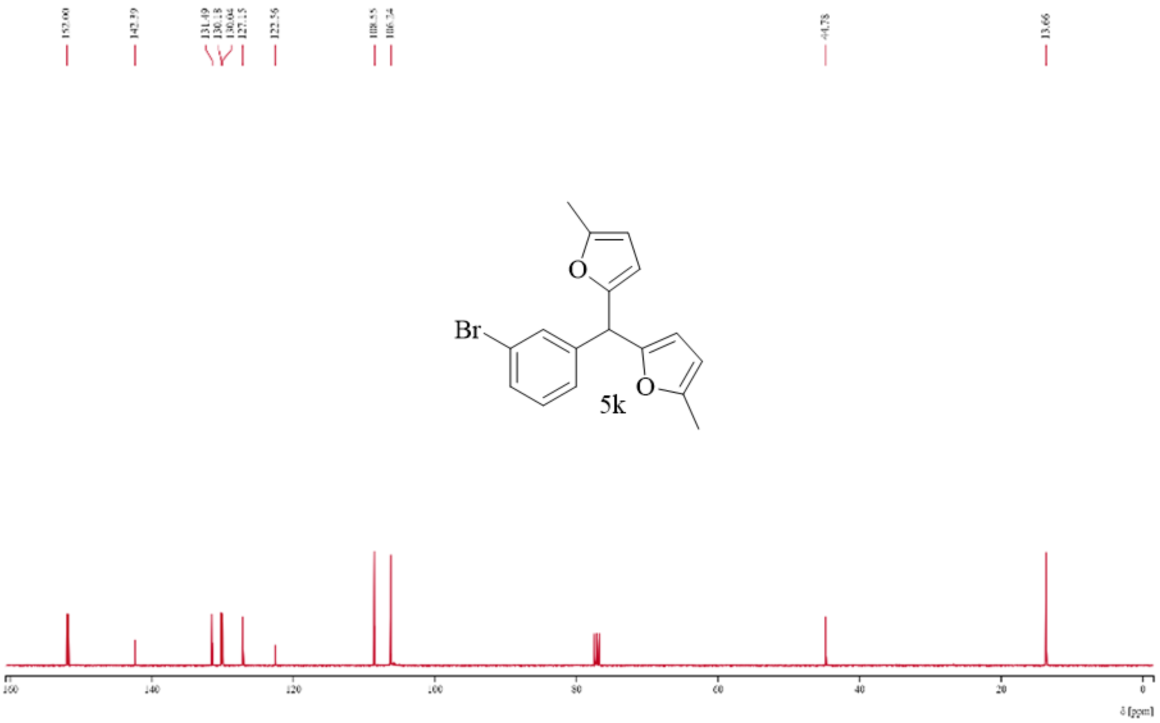
151.69
139.16
130.20
130.95
108.42
106.19
44.62
13.64
Br
O
O
160
140
120
100
80
60
40
20
0
δ [ppm]

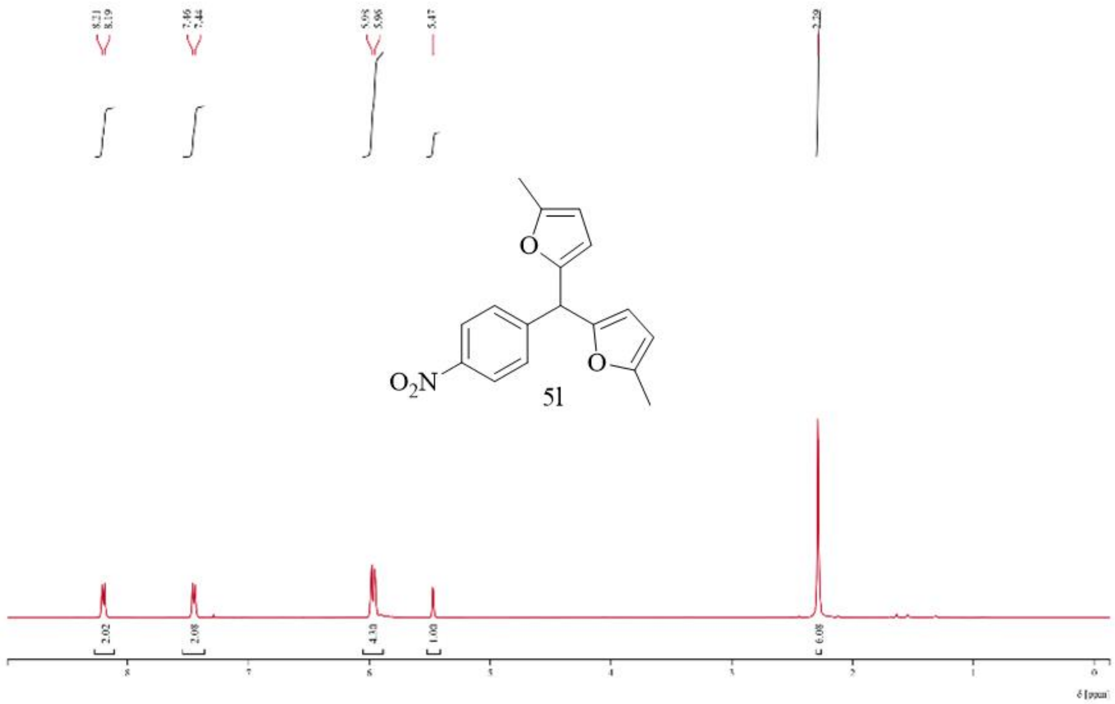

5j

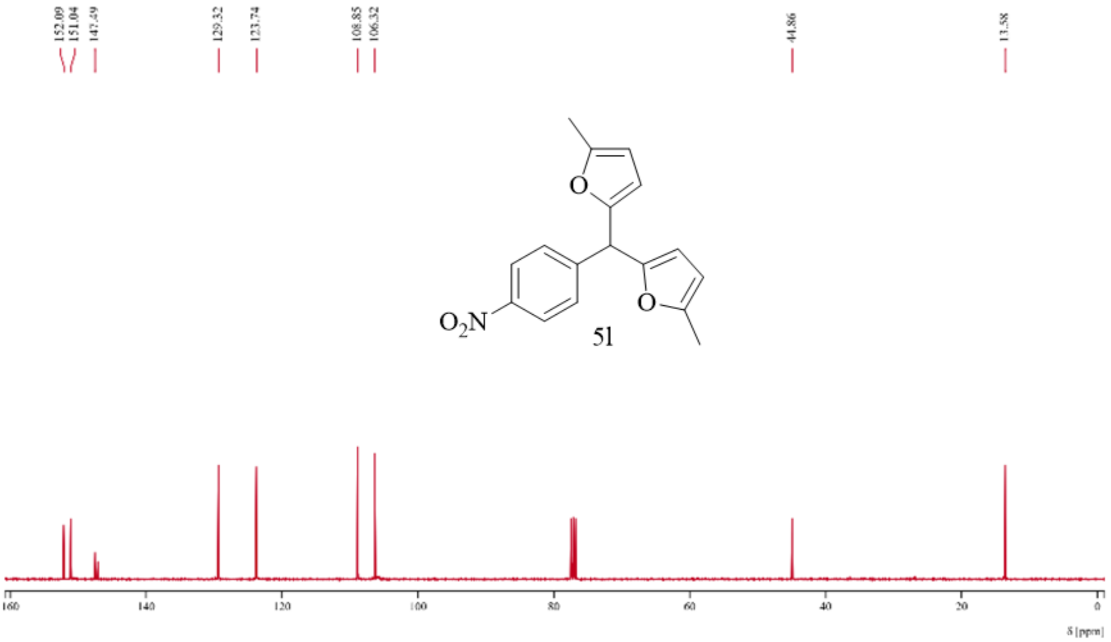
7.60
7.58
7.29
7.27
7.22
7.21
7.16
7.14
7.13
5.91
5.88
5.84
2.25
Br
O
O
1.00
1.05
1.02
1.04
4.28
1.07
6.02
8
7
6
5
4
3
2
1
0
δ [ppm]


5j
151.72
139.16
133.01
130.18
128.61
127.55
124.59
108.93
106.21
44.49
13.70
Br
O
O
160
140
120
100
80
60
40
20
0
δ [ppm]

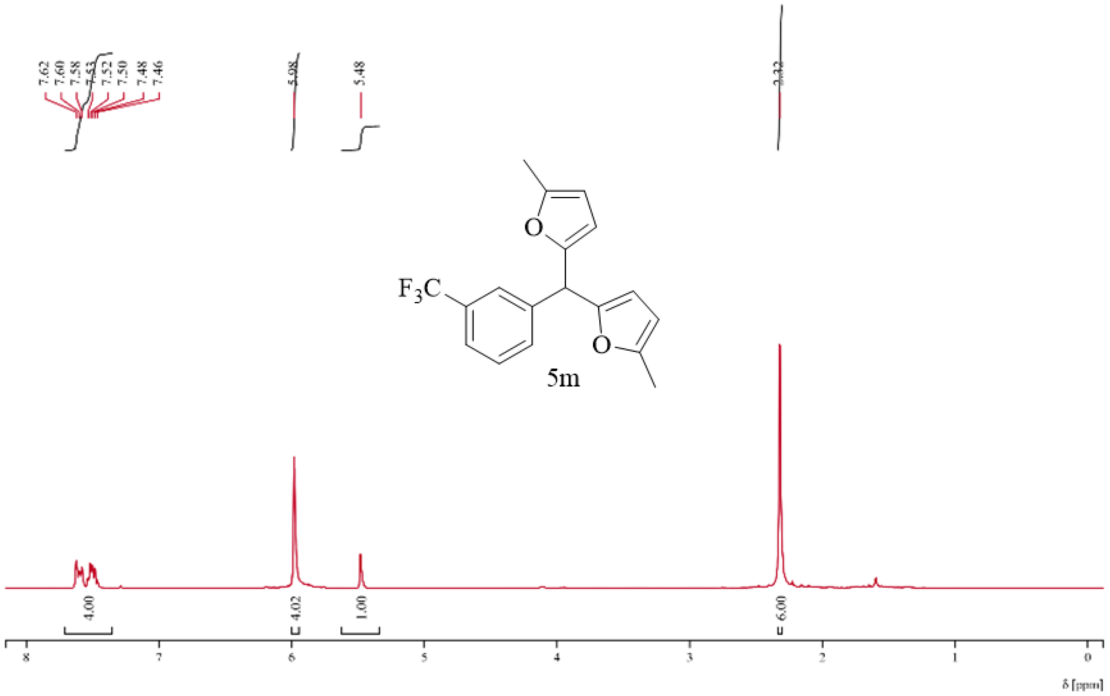

5k
7.30
7.27
7.26
7.07
7.05
7.03
5.79
5.20
2.14
Br
O
O
2.00
2.10
4.00
1.00
6.02
8
7
6
5
4
3
2
1
0
δ [ppm]


152.00
142.39
131.49
130.18
130.04
127.15
122.56
108.55
106.34
44.78
13.66
Br
O
O
5k
160
140
120
100
80
60
40
20
0
δ [ppm]

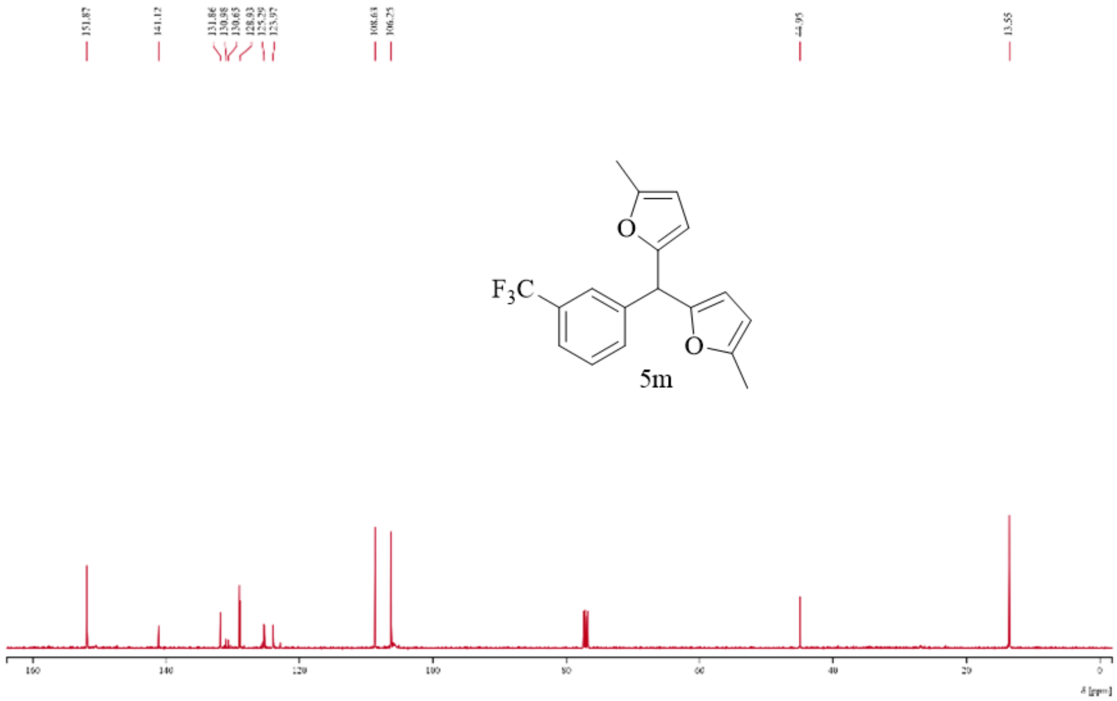

8.21
8.19
7.46
7.44
5.98
5.96
5.47
2.29
O
O
O₂N
5l
2.02
2.08
4.10
1.00
6.08
8
7
6
5
4
3
2
1
0
δ [ppm]

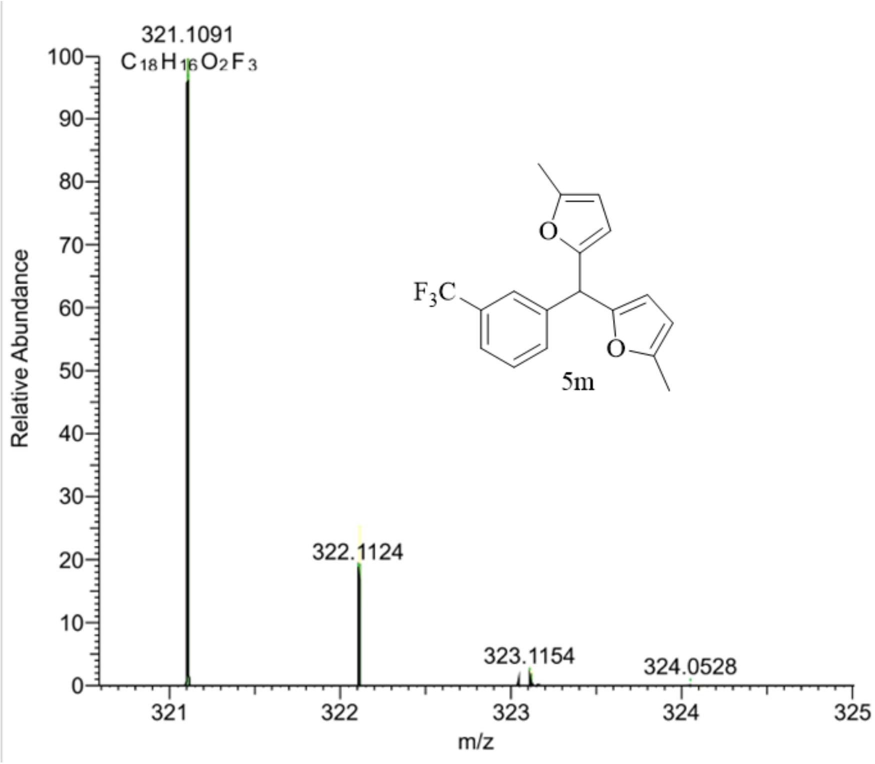

152.09
151.04
147.49
129.32
123.74
108.85
106.32
44.86
13.58
O
O
O_2N
160
140
120
100
80
60
40
20
0
δ [ppm]

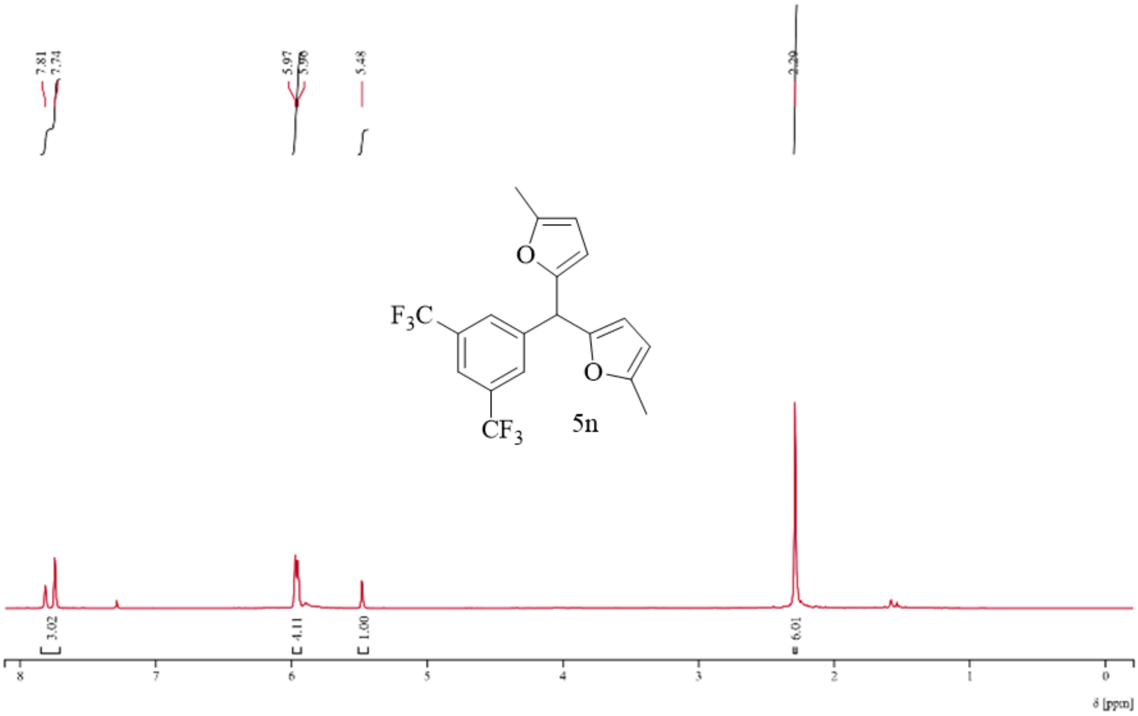
5l

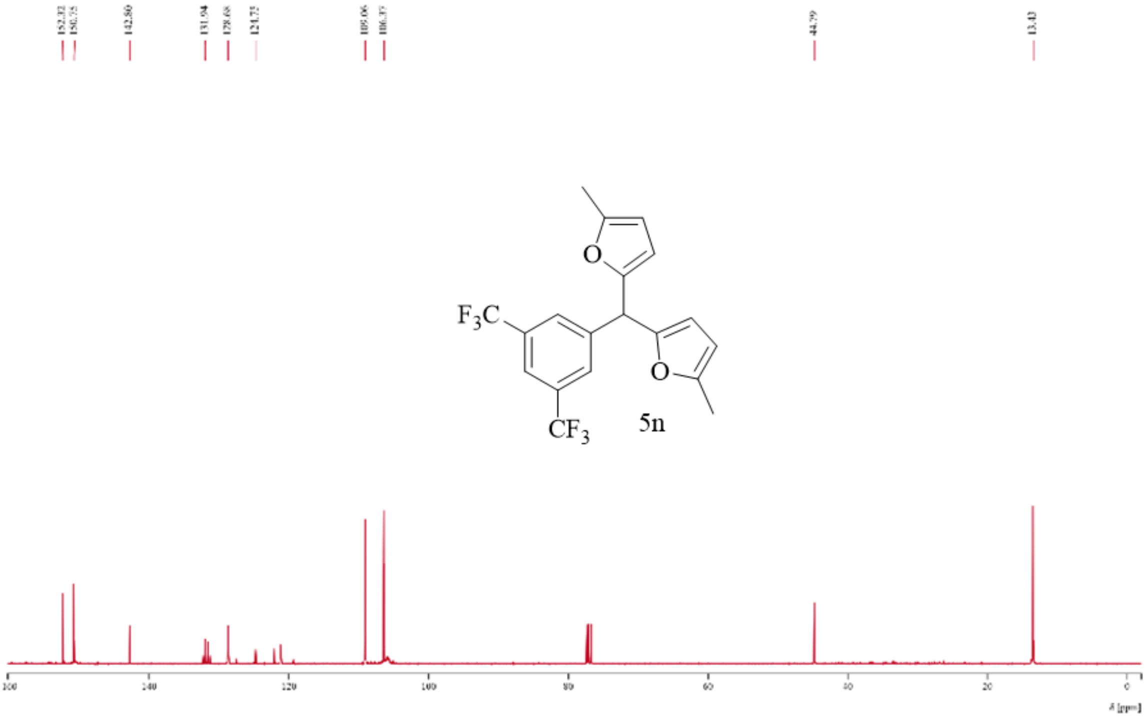

7.62
7.60
7.58
7.53
7.52
7.50
7.48
7.46
5.98
5.48
2.32
O
O
F_3C
4.00
4.02
1.00
6.00
8
7
6
5
4
3
2
1
0
δ [ppm]

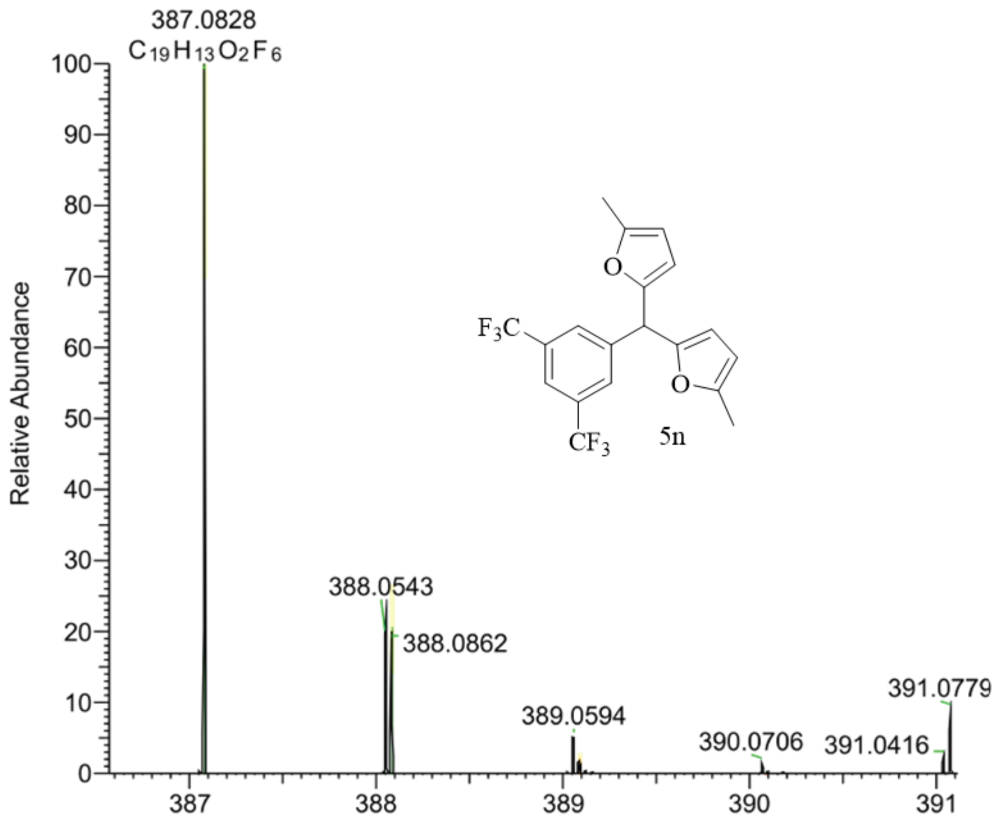
5m

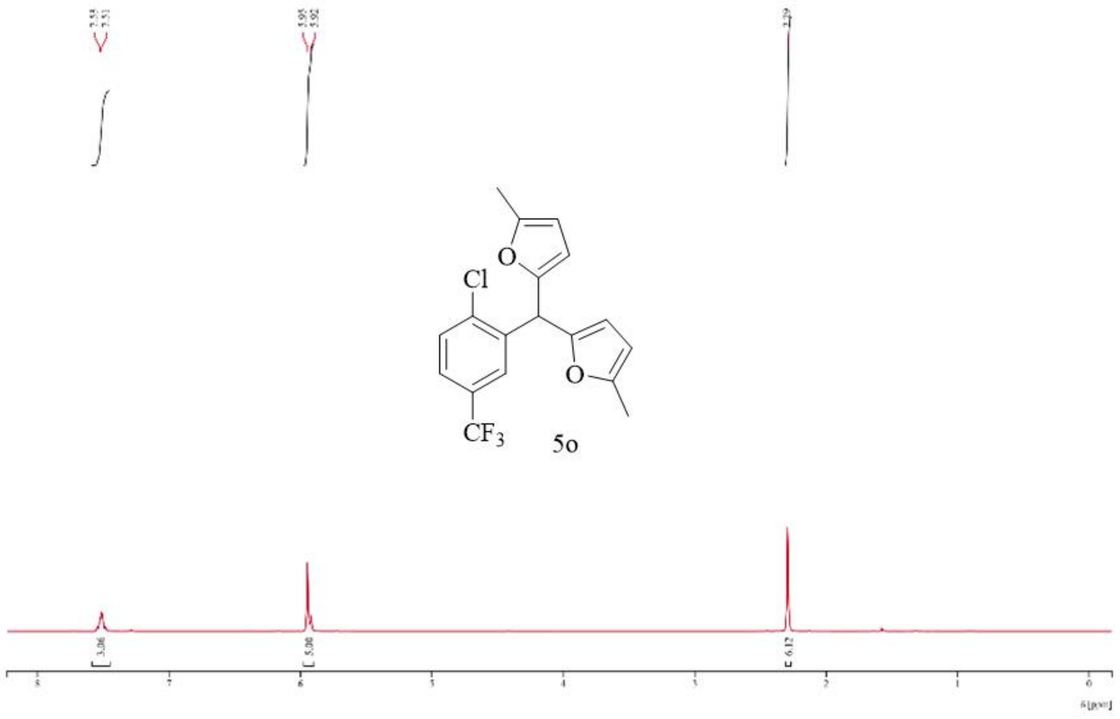

151.87
141.12
131.86
130.98
130.63
128.93
125.29
123.97
108.63
106.25
44.95
13.55
F3C
O
O
5m
160
140
120
100
80
60
40
20
0
δ [ppm]

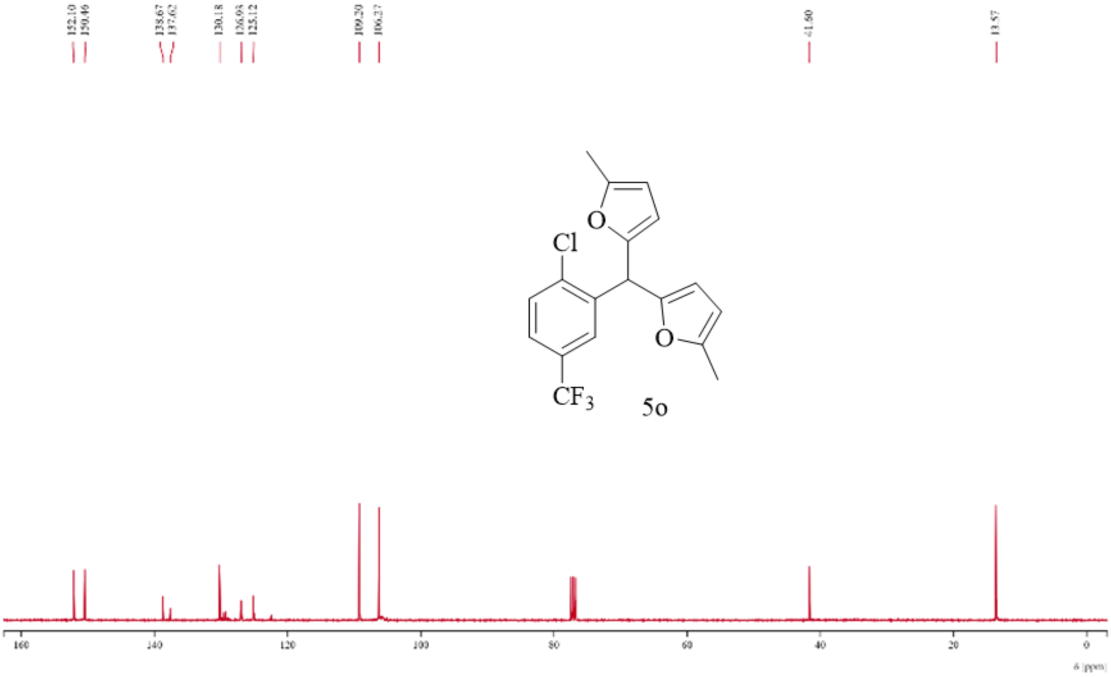

321.1091
C18H16O2F3
322.1124
323.1154
324.0528
Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
321
322
323
324
325
m/z
F3C
O
O
5m

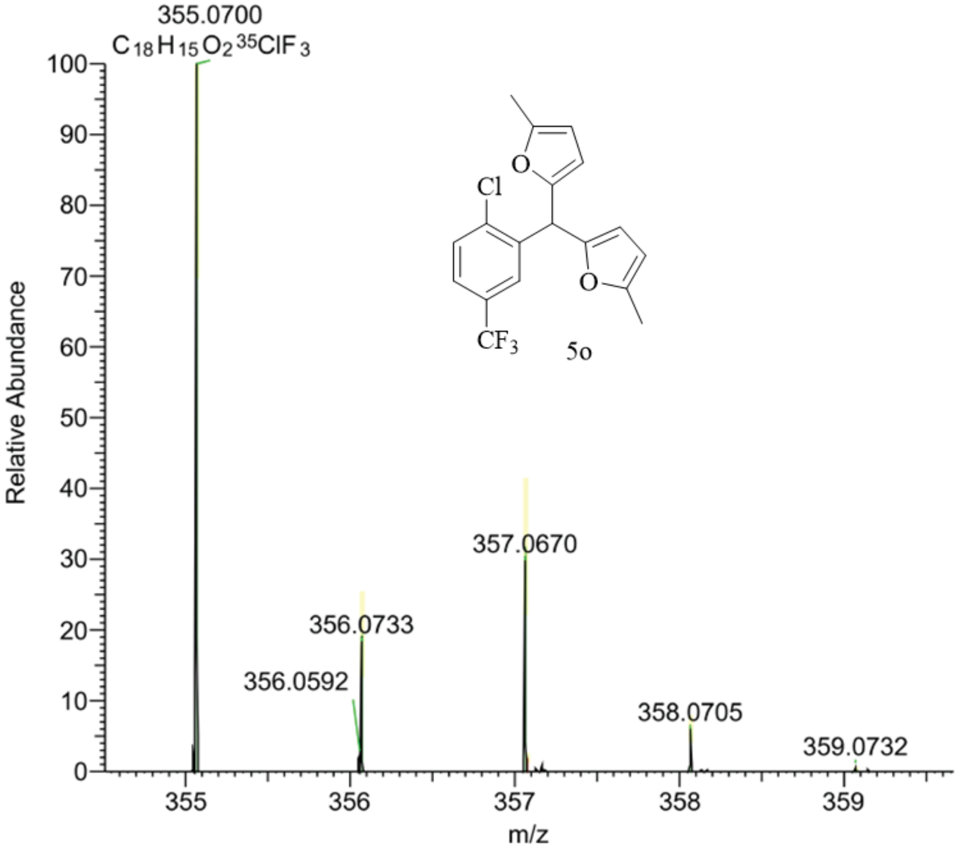

7.81
7.74
5.97
5.96
5.48
2.29
F3C
CF3
O
O
5n
3.02
4.11
1.00
6.01
8
7
6
5
4
3
2
1
0
δ [ppm]

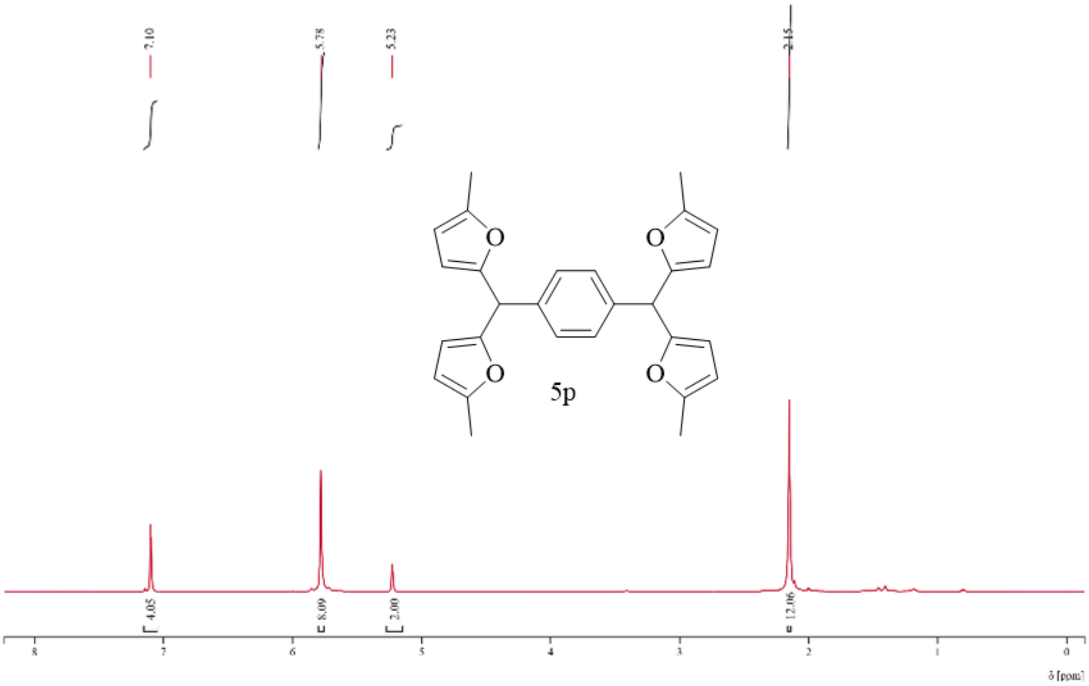

152.32
150.75
142.80
131.94
128.68
124.75
109.06
106.37
44.79
13.43
F3C
CF3
O
O
5n
160
140
120
100
80
60
40
20
0
δ [ppm]

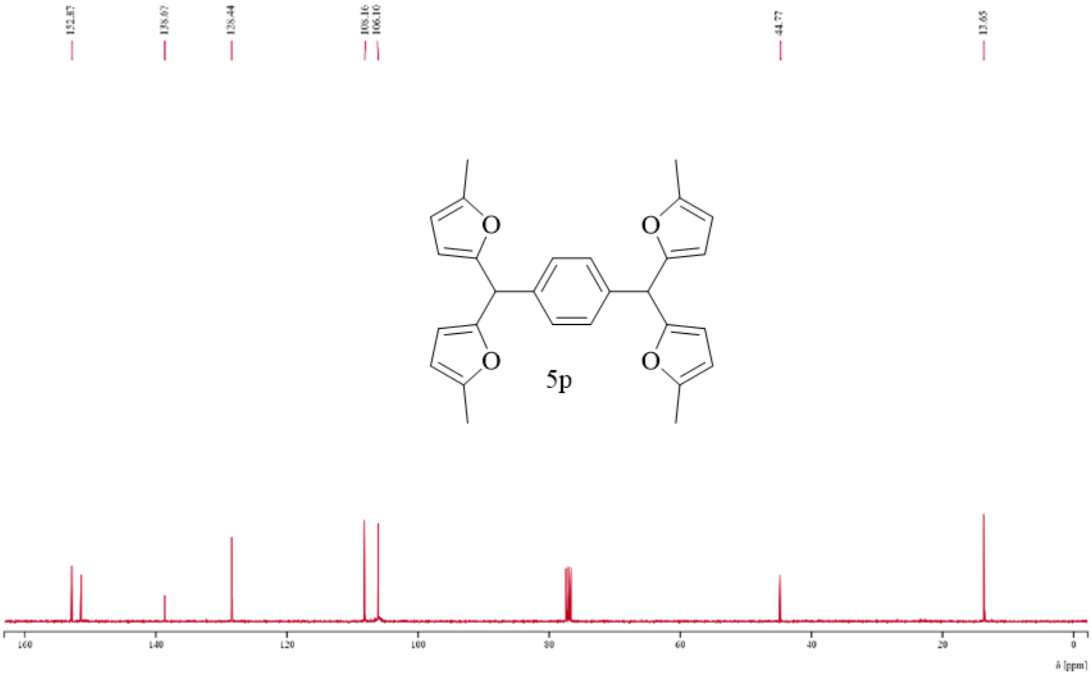

387.0828
$C_{19}H_{13}O_2F_6$
100
90
80
70
60
50
40
30
20
10
0
Relative Abundance
388.0543
388.0862
389.0594
390.0706
391.0416
391.0779
387
388
389
390
391
F₃C
CF₃
O
O
5n

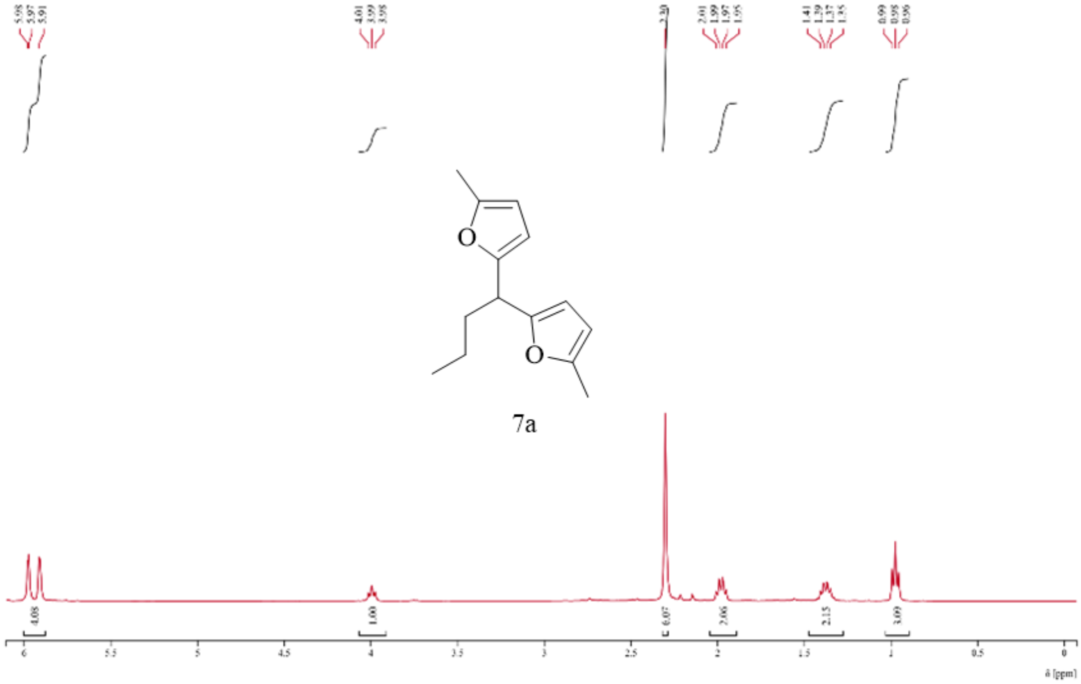

7.53
7.51
5.95
5.92
2.29
Cl
CF₃
O
O
5o
3.06
5.00
6.12
8
7
6
5
4
3
2
1
0
δ [ppm]


152.10
150.46
138.67
137.62
130.18
126.93
125.12
109.20
106.27
41.60
13.57
Cl
O
O
CF3
5o
160
140
120
100
80
60
40
20
0
δ (ppm)

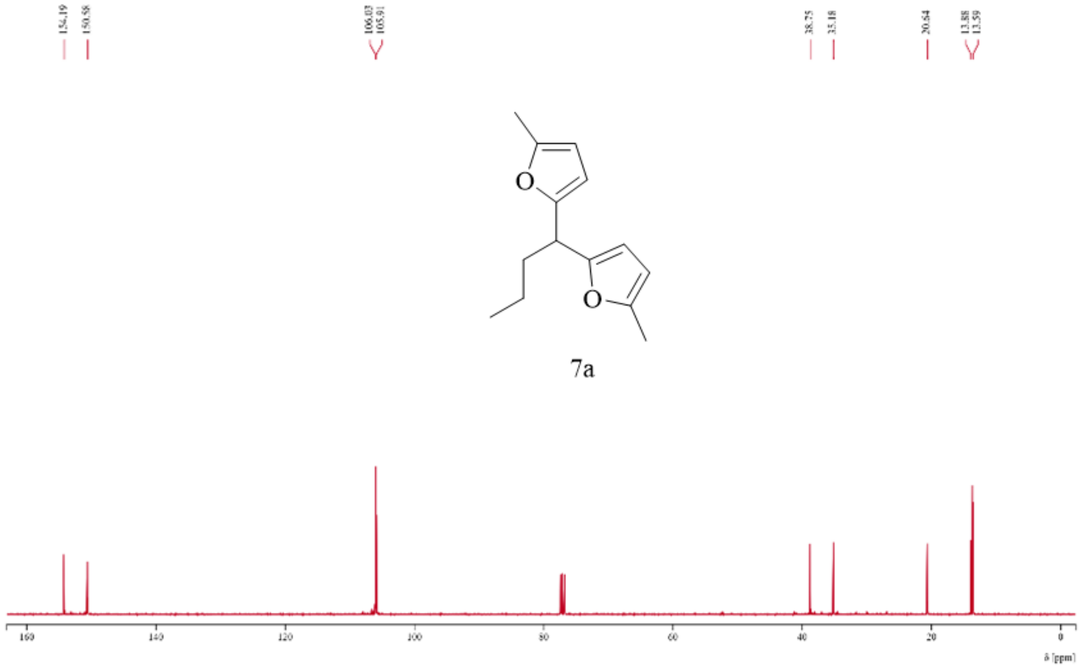

355.0700
C18H15O2 35ClF3
356.0592
356.0733
357.0670
358.0705
359.0732
Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
355
356
357
358
359
m/z
Cl
O
O
CF3
5o


7.10
5.78
5.23
2.15
O
O
O
O
5p
4.05
8.09
2.00
12.06
8
7
6
5
4
3
2
1
0
δ [ppm]

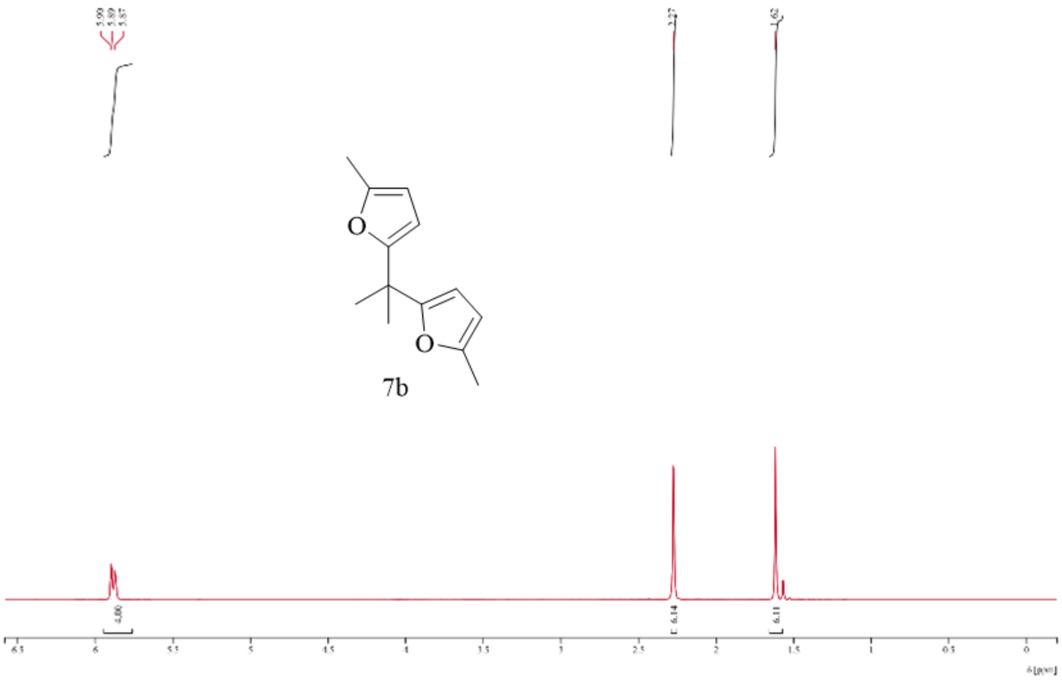

152.87
138.67
128.44
108.16
106.10
44.77
13.65
O
O
O
O
5p
160
140
120
100
80
60
40
20
0
δ [ppm]

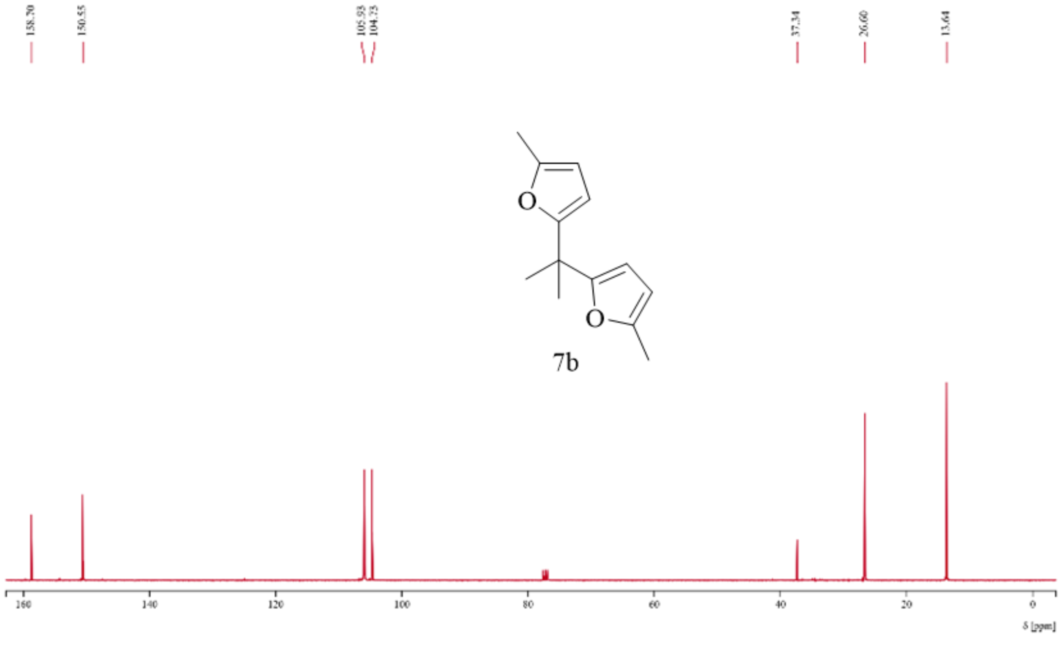

5.98
5.97
5.91
4.01
3.99
3.98
2.30
2.01
1.99
1.97
1.95
1.41
1.39
1.37
1.35
0.99
0.98
0.96
O
O
4.08
1.00
6.07
2.06
2.15
3.09
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
δ [ppm]

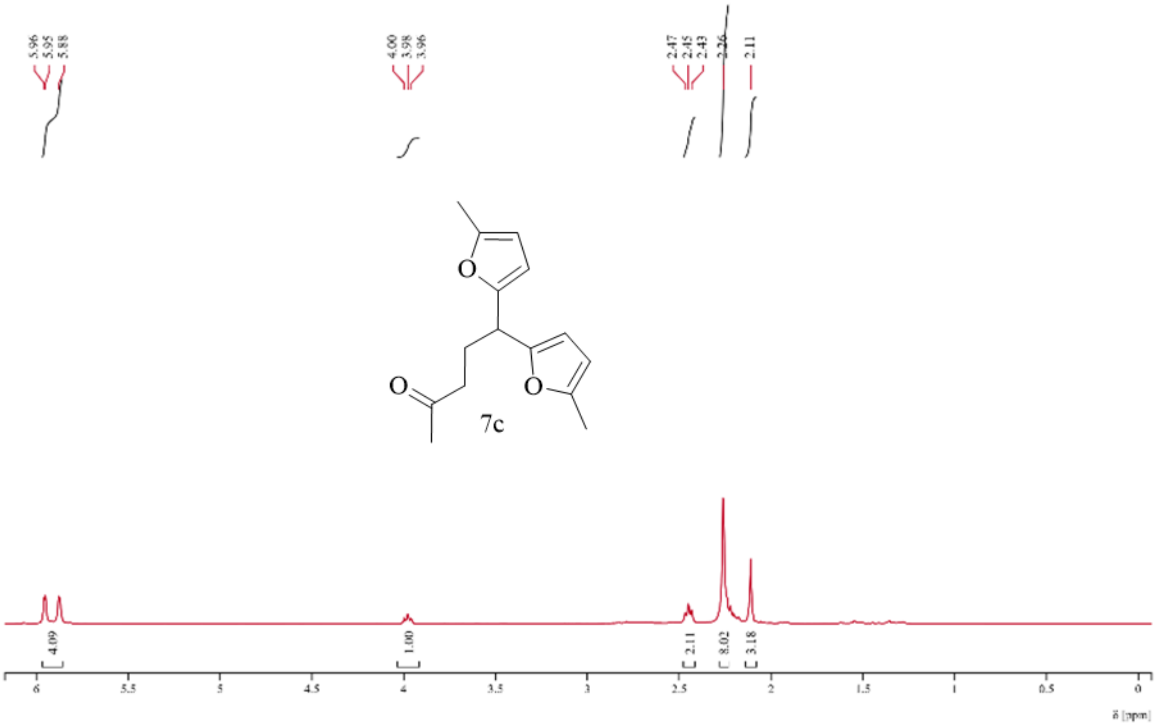
7a


154.19
150.58
106.03
105.91
38.75
35.18
20.64
13.88
13.59
O
O
160
140
120
100
80
60
40
20
0
δ [ppm]

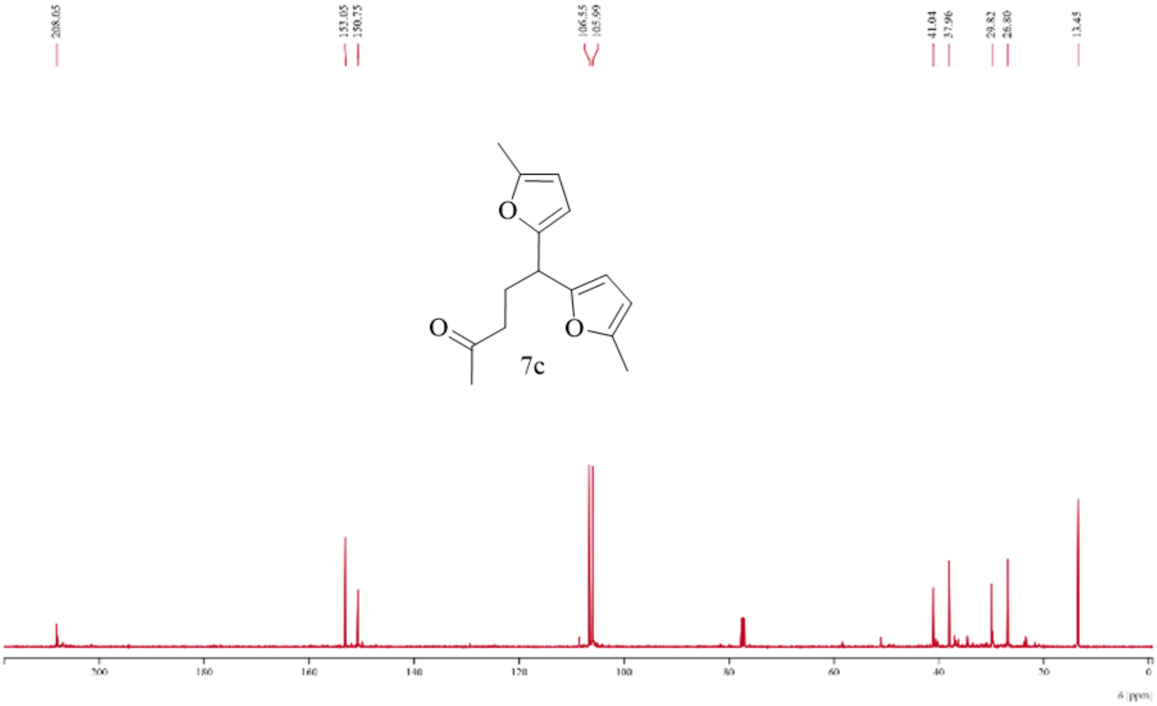
7a


5.90
5.89
5.87
2.27
1.62
7b
4.00
6.14
6.11
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
δ [ppm]


158.70
150.55
105.93
104.73
37.34
26.60
13.64
7b
160
140
120
100
80
60
40
20
0
δ [ppm]


5.96
5.95
5.88
4.00
3.98
3.96
2.47
2.45
2.43
2.26
2.11
O
O
O
4.09
1.00
2.11
8.02
3.18
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
δ [ppm]

7c


208.05
153.05
150.75
106.55
105.99
41.04
37.96
29.82
26.80
13.45
O
O
O
200
180
160
140
120
100
80
60
40
20
0
δ [ppm]

7c