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ELECTRONIC SUPPLEMENTARY INFORMATION

Gateway-state mediated, long-range tunnelling in molecular wires.

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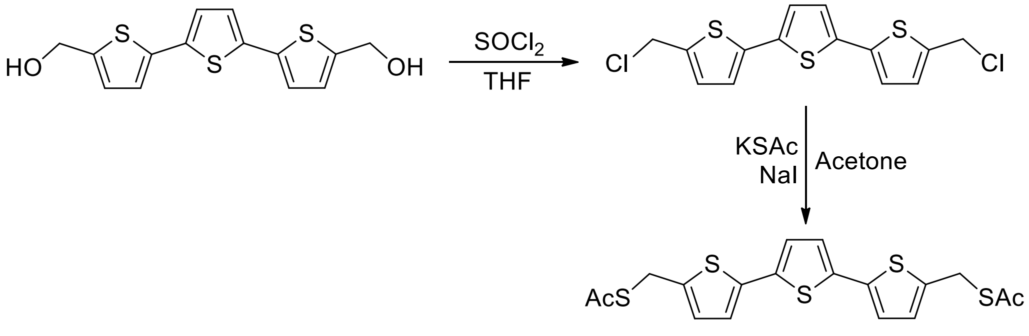
1. Synthetic procedures

The molecular wires used in this paper were synthesised using common preparative chemistry techniques. All reactions that are air or moisture sensitive were performed in degassed or dry solvents, in oven-dried glassware, under Ar. All reagents were purchased from Sigma-Aldrich Chemical Company and used as received except as follows (and elsewhere noted). Tetrahydrofuran (THF) was used after distillation over sodium benzophenone ketyl when needed anhydrous, and stored over 4 Å molecular sieves. *N*-Bromosuccinimide (NBS) was recrystallized from boiling H_2O and dried overnight in vacuum before use, PPh_3 and 1,2-bis(diphenylphosphino)ethane (DPPE) were recrystallized from boiling 95% ethanol, dried in vacuum and stored under Ar. Alkyllithium compounds were titrated against *N*-benzylbenzamide to a blue endpoint before use. Thin layer chromatography was performed on Merck Silica Gel 60 F-254 plates. Flash column chromatography was performed using Sigma-Aldrich technical grade silica (230-400 mesh, pore size 60 Å) using compressed air. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 Ultrashield spectrometer and referenced to internal TMS; chemical shifts are reported as ppm, and coupling constants quoted are in Hz. Mass spectra were recorded using a Carlo Erba 8000 Trio-1000 quadrupole spectrometer in CI positive ion mode (NH_3). High resolution mass spectra were recorded using an Agilent Q-TOF 7200 GC/MS or a Waters Micromass LCT TOF spectrometer.

Molecular wires with thiolate contacts were synthesised as thioacetates to protect against possible oxidation to (polymeric) disulfides. The acetyl protecting group is optimal for single-molecule conductance measurements as it is readily cleaved *in situ* in the presence of the gold substrate[1].

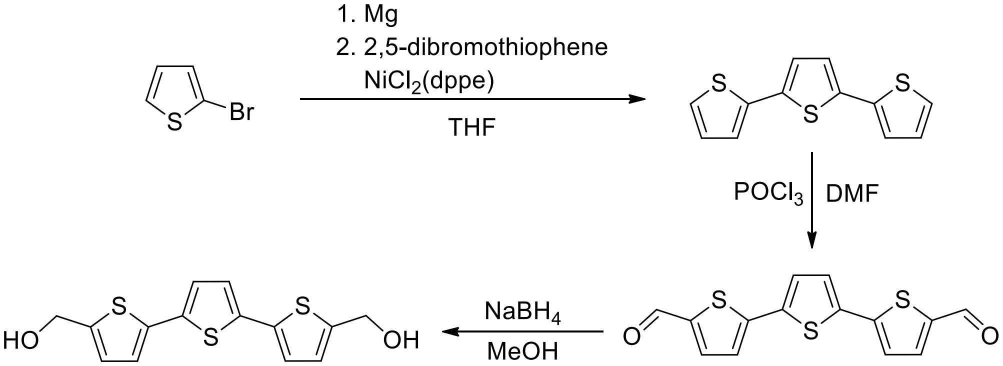
X[T3]X

1[T3]1 was synthesised by substitution of the hydroxyl function of [2,2’:5’,2”-terthiophene]5,5”-dimethanol with a chloride and nucleophilic displacement of the halogen with a thioacetate group.



Scheme S1: Synthesis of **1[T3]1**.

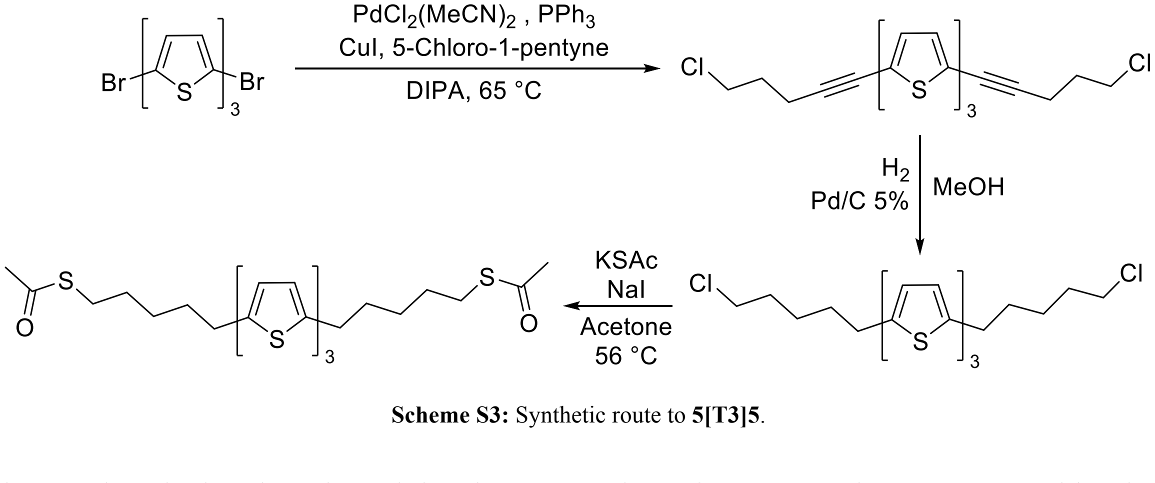
2,2’:5’,2”-terthiophene was synthesised via Kumada coupling as reported in many literature sources[2,3] using [$NiCl_2$(dppe)] as catalyst in THF. Double Vilsmeier-Haack formylation of 2,2’:5’,2”-terthiophene using $POCl_3$ in DMF afforded the dicarbaldehyde[4,5] that was subsequently reduced with $NaBH_4$ in MeOH to [2,2’:5’,2”-terthiophene]5,5”-dimethanol as in the procedure developed by Lin *et al.*[6]



Scheme S2: Synthesis of [2,2’:5’,2”-terthiophene]5,5”-dimethanol.

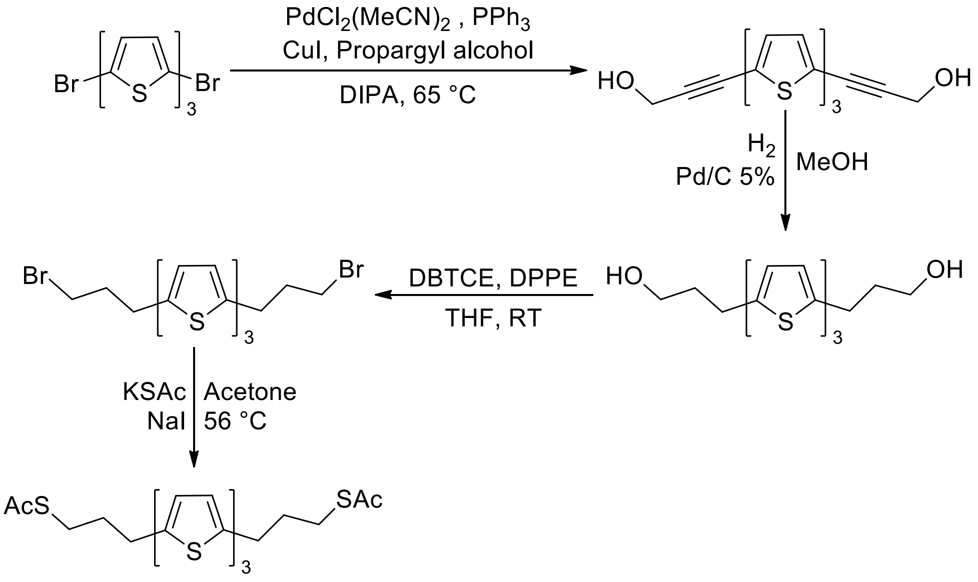
5[T3]5 was synthesised adapting the procedure developed by Leary *et al.* for the synthesis of α,ω-dithiaalkane molecular wires[7]. Dichlorobis(acetonitrile)palladium(II) [$PdCl_2(MeCN)_2$] was synthesised according to the procedure reported by Ito and Ozawa.[8] Bromination of 2,2’:5’,2”-terthiophene (prepared as discussed earlier) were performed using NBS in DMF according to the procedure developed by Bäuerle *et al.*[9]

The synthetic steps were Sonogashira cross-coupling of 5,5’’-dibromo-2,2’:5’,2’’-terthiophene with 5-chloro-1-pentyne, H_2/Pd reduction of the alkynyl function and treatment with KSAc to afford the corresponding thioacetic acid esters.



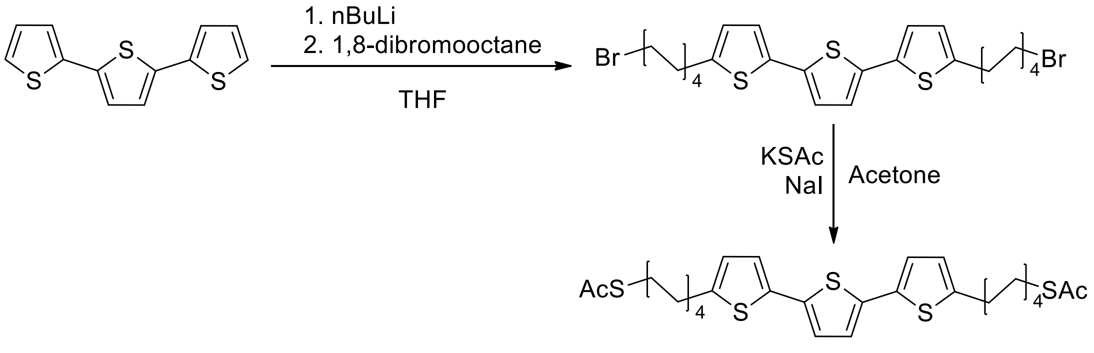
Scheme S3: Synthetic route to **5[T3]5**.

A modified procedure had to be adopted for the preparation of **3[T3]3** and **4[T3]4** as 4-chlorobutyne is not commercially available and propargyl chloride is known to react with the Pd pre-catalyst to form a π-allenyl complex with loss of the halogen moiety. The Sonogashira coupling therefore employed terminal alkynes with alcohol moieties on the opposite terminus: H_2/Pd reduction to alkane, modified Appel procedure (using DPPE and 1,2-dibromotetrachloroethane) to substitute the alcoholic function with a bromide and final treatment with KSAc afforded the desired compound as thioacetic acid ester.



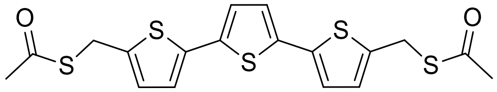
Scheme S4: Synthetic example: route to **3[T3]3**.

8[T3]8 was prepared with a different route due to the absence of commercially available starting materials for Pd-catalysed C-C cross-coupling. 5,5''-bis(8-bromooctyl)-2,2':5',2''-terthiophene was prepared in low yield by adding 5,5''-dilithio-2,2':5',2''-terthiophene (freshly prepared by lithiation of 2,2':5',2''-terthiophene with n-BuLi) in THF to a concentrated solution of 1,8-dibromooctane in THF kept at -78 °C. Nucleophilic displacement of the halogen with KSAc afforded 8[T3]8.



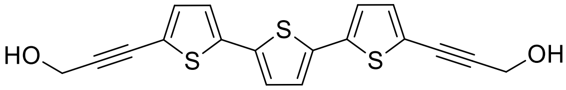
Scheme S5: Synthesis of **8[T3]8**.

1[T3]1



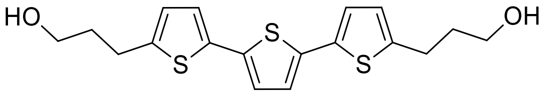
$SOCl_2$ (0.24 mL, 3.31 mmol) was added to a solution of [2,2':5',2"-terthiophene]5,5"-dimethanol (103 mg, 0.34 mmol) in dry THF at 0 °C and stirred at RT under Ar for 1 h. Ar was then flushed through the reaction flask until all the solvent and remaining $SOCl_2$ had been stripped away. KSAc (150 mg, 1.31 mmol) in dry degassed acetone (40 mL) was added *via* syringe and the resulting suspension was refluxed for 16 h under Ar. The solvent was then removed *in vacuo,* CH_2Cl_2 was added, the resulting suspension filtered and the crude product was purified by flash chromatography on silica (CH_2Cl_2 as eluant) to give the title compound as a yellow solid (119 mg, 83 %). Found: C = 49.79, H = 3.71, S = 37.75 %. $C_{18}H_{16}O_2S_5$ requires C = 50.91, H = 3.80, S = 37.76 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (s, 2H, Th), 6.94 (d, 2H, J = 3.6, Th), 6.86 (d, 2H, J = 3.6, Th) 4.28 (s, 4H, CH_2), 2.38 (s, 6H, CH_3), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 194.8, 139.5, 136.9, 136.0, 127.5, 124.2, 123.3, 30.4, 28.3 ppm. *m/z* (HRMS, CI, CH_4) 424.9748 $[M+H]^+$. $C_{18}H_{17}O_2S_5$ calc. 424.9832. No impurities were detected in the proton or ^{13}C NMR, thus the low C figure in the elemental analysis was attributed to incomplete combustion.

3,3'-([2,2':5',2"-terthiophene]-5,5"-diyl)bis(prop-2-yn-1-ol)



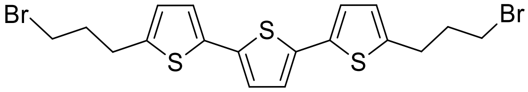
Diisopropylamine (DIPA; 40 ml) was degassed by bubbling Ar for 20 minutes prior to the addition of 5,5''–dibromo–2,2':5',2''–terthiophene (570 mg, 1.4 mmol), $[PdCl_2(MeCN)_2]$ (15 mg, 0.06 mmol), PPh_3 (48 mg, 0.18 mmol) and CuI (7 mg, 0.03 mmol). After flushing with Ar for an additional 10 minutes, propargyl alcohol (0.2 mL, 3.5 mmol) was added and the reaction was heated to 60°C under Ar and stirred for 16 hours. The resulting suspension was then allowed to cool down to room temperature, the orange solids were filtered, washed with hexanes and water and dried *in vacuo* (279 mg, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03 (d, 2H. J = 3.6, Th), 7.01 (d, 2H, J = 3.6, Th), 6.98 (s, 2H, Th), 4.50 (s, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 135.6, 134.9, 126.8, 126.3, 123.2, 90.1, 88.7, 45.2. *m/z* (HRMS, CI, CH_4) 357.0072 $[M+H]^+$, $C_{18}H_{13}O_2S_3$ calc. 357.0078

3,3'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(propan-1-ol)



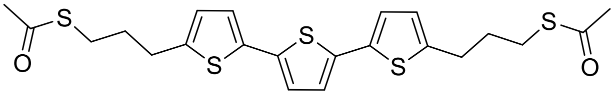
3,3'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(prop-2-yn-1-ol) (250 mg, 0.70 mmol) was subjected to catalytic hydrogenation (50 mL MeOH, 20 mg Pd/C 10%, H_2 atmosphere, 24 h, room temperature). The resulting suspension was filtered through a bed of Celite and the solvent was removed *in vacuo* to give the title compound as an orange solid (249 mg, 98 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (s, 2H, Th), 6.96 (d, 2H, J = 3.4, Th), 6.67 (d, 2H, J = 3.4, Th) 3.68 (t, J = 6.4, 4H, CH_2) 2.68 (t, J = 7.7, 4H, CH_2), 1.93-1.84 (m, 4H, CH_2). *m/z* (HRMS, CI, CH_4) 365.0699 $[M+H]^+$, $C_{18}H_{21}O_2S_3$ calc. 365.0703.

5,5''–bis(3-bromopropyl)–2,2':5',2''–terthiophene



To a solution of DPPE (220 mg, 0.55 mmol) in THF (20 mL) under Ar was added 1,2-dibromotetrachloroethane (360 mg, 1.11 mmol). To the resulting white suspension was added dropwise 3,3'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(propan-1-ol) (200 mg, 0.55 mmol) in THF (10 mL) while cooling on an ice bath. After a short time, the solid dissolved and the solution was allowed to stir overnight (16 h), after which time a greyish solid had precipitated. The suspension was filtered, the solvent was removed *in vacuo* and the crude product was purified by flash chromatography on silica (0 - 20 % CH_2Cl_2 in hexanes as eluant) to give the title compound as a yellow solid (198 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (s, 2H, Th), 6.96 (d, 2H, J = 3.4 Th), 6.67 (d, 2H, J = 3.4, Th) 3.42 (t, 4H, J = 6.8, CH_2) 2.61 (t, 4H, J = 7.3, CH_2), 1.94-1.86 (m, 4H, CH_2). *m/z* (HRMS, CI, NH_3) 488.9023 $[M+H]^+$, $C_{18}H_{19}Br_2S_3$ calc. 488.9016.

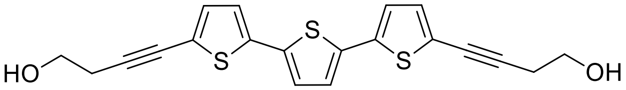
3[T3]3



A solution of 5,5''–bis(3-bromopropyl)–2,2':5',2''–terthiophene (120 mg, 0.25 mmol), sodium iodide (20 mg, 0,13 mmol) and potassium thioacetate (100 mg, 0.87 mmol) in acetone (25 mL) was refluxed under Ar atmosphere for 24 hours. The solvent was then removed *in vacuo* and the crude product was purified by flash chromatography on silica (CH_2Cl_2 as eluant) to give the title compound as a yellow solid (54 mg, 46 %). Found: C = 54.90, H = 5.09, S = 33.29 %. $C_{22}H_{24}O_2S_5$ requires C = 54.96, H = 5.03, S = 33.35 %. ^{1}H NMR (400 MHz,

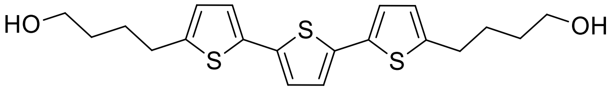
$CDCl_3$) δ: 6.97 (s, 2H, Th), 6.95 (d, 2H, J = 3.4, Th), 6.67 (d, 2H, J = 3.4, Th), 2.94 (t, 4H, J = 7.1 Hz, CH_2), 2.88 (m, 4H, CH_2), 2.35 (s, 6H, CH_3), 1.98-1.89 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ: 200.6, 145.4, 136.5, 135.1, 125.9, 124.1, 123.6, 31.7, 31.0, 29.8, 28.6. MS (CI+ (NH_3)) *m/z* 498.1 ($[M+NH_4]^+$, 28 %) 481.0 ($[M+H]^+$, 100 %). *m/z* (HRMS, CI, CH_4) 481.0448 $[M+H]^+$, $C_{22}H_{25}O_2S_5$ calc. 481.0458.

4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(but-3-yn-1-ol)



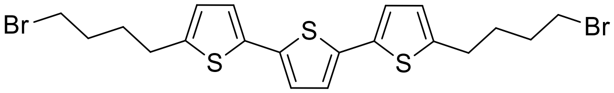
DIPA (40 mL) was degassed by bubbling Ar through for 20 minutes prior to the addition of 5,5''–dibromo–2,2':5',2''–terthiophene (550 mg, 1.37 mmol), $[PdCl_2(MeCN)_2]$ (15 mg, 0.06 mmol), PPh_3 (48 mg, 0.18 mmol) and CuI (7 mg, 0.03 mmol). After flushing with Ar for an additional 10 minutes, 3-butyn-1-ol (240 mg, 3.4 mmol) was added and the reaction was heated to 60 °C under Ar and stirred for 16 hours. The resulting suspension was then allowed to cool down to room temperature, the orange solids were filtered, washed with water and hexanes and recrystallised from boiling THF to afford a bright orange powder (336 mg, 64 % yield). ^1H NMR (400 MHz, THF-d8) δ: 7.09 (m, 6H. J = 3.9, Th), 4.02 (s, 2H, OH), 3.65 (4H, dd, J = 6.0, 6.3 Hz, CH_2) 2.61 (t, 4H, J = 6.2 Hz, CH_2). ^{13}C NMR (100 MHz, THF-d8): δ: 136.2, 132.5, 129.2, 125.1, 123.9, 123.5, 100.21, 93.7, 73.9, 60.7. *m/z* (HRMS, CI, CH_4) 385.0389 $[M+H]^+$, $C_{20}H_{17}O_2S_3$ calc. 385.0391.

4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(butan-1-ol)



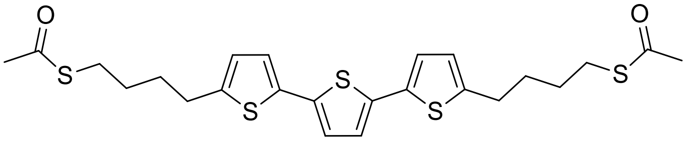
4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(but-3-yn-1-ol) (325 mg, 0.85 mmol) was subjected to catalytic hydrogenation (50 mL MeOH, 30 mg Pd/C 10%, H_2 atmosphere, 24 h, room temperature). The resulting suspension was filtered through a bed of celite and the solvent removed *in vacuo* to give the title compound as an orange solid (323 mg, 97 %). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.97 (m, 2H, Th), 6.96 (s, 2H, Th), 6.69 (d, 2H, J = 3.4, Th), 3.69 (t, 4H, J = 5.9 Hz, CH_2), 2.84 (t, 4H, J = 7.4 Hz, CH_2) 1.80-1.63 (m, 8H, CH_2), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.1, 136.3, 135.2, 125.5, 123.9, 123.6, 62.8, 32.5, 30.3, 28.2. *m/z* (HRMS, CI, CH_4) 393.1020 $[M+H]^+$, $C_{20}H_{25}O_2S_3$ calc. 393.1017.

5,5''-bis(4-bromobutyl)-2,2':5',2''-terthiophene



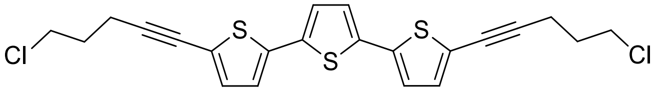
To a solution of DPPE (318 mg, 0.8 mmol) in THF (20 mL) under Ar was added 1,2-dibromotetrachloroethane (521 mg, 1.6 mmol). To the resulting white suspension was added dropwise 4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(butan-1-ol) (300 mg, 0.77 mmol) in THF (10 mL) while cooling on an ice bath. After a short time the solid dissolved and the solution was allowed to stir overnight (16 h), after which time a grey solid had precipitated. The suspension was filtered, the solvent was removed *in vacuo* and the crude product was purified by flash chromatography on silica (0 - 20 % CH_2Cl_2 in hexanes as eluant) to give the title compound as a yellow solid (307 mg, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (m, 4H, Th), 6.69 (d, 2H, J = 3.6, Th), 3.44 (t, 4H, J = 6.4, CH_2), 2.83 (t, 4H, J = 8.6, CH_2) 1.98-1.90 (m, 4H, CH_2) 1.89-1.81 (m, 4H, CH_2). *m/z* (HRMS, CI, NH_3) 516.9322 $[M+H]^+$, $C_{20}H_{23}Br_2S_3$ calc. 516.9328.

4[T3]4



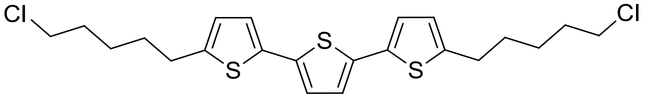
A solution of 5,5''-bis(4-bromobutyl)-2,2':5',2''-terthiophene (300 mg, 0.58 mmol), sodium iodide (43 mg, 0.29 mmol) and potassium thioacetate (231 mg, 2 mmol) in acetone (35 mL) was refluxed under Ar atmosphere for 24 hours. The solvent was then removed *in vacuo* and the crude product was purified by flash chromatography on silica (CH_2Cl_2 as eluant) to give the title compound as a yellow solid (154 mg, 52 %). Found: C = 56.55, H = 5.54, S = 31.43 %. $C_{24}H_{28}O_2S_5$ requires C = 56.65, H = 5.55, S = 31.51 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96 (s, 2H, Th), 6.95 (d, 2H, Th), 6.65 (d, 2H, J = 3.4, Th) 2.89 (t, 4H, J = 6.9, CH_2), 2.58 (t, 4H, J = 7.3, CH_2), 2.32 (s, 6H, CH_3), 1.74-1.58 (m, 8H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ: 195.9, 144.4, 136.5, 135.9, 125.9, 123.3, 122.9, 33.6, 31.4, 30.5, 29.8, 28.8. *m/z* (HRMS, CI, CH_4) 509.0738 $[M+H]^+$, $C_{24}H_{29}O_2S_5$ calc. 509.0771.

5,5''-bis(5-chloropent-1-yn-1-yl)-2,2':5',2''-terthiophene



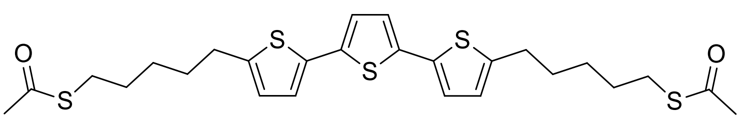
DIPA:THF (1:1, 40 mL) was degassed by bubbling Ar for 30 minutes prior to the addition of 5,5’’–dibromo–2,2’:5’,2’’–terthiophene (0.5 g, 1.23 mmol), $[PdCl_2(MeCN)_2]$ (16 mg, 0.06 mmol), PPh_3 (48 mg, 0.18 mmol) and CuI (7 mg, 0.04 mmol). After flushing with Ar for an additional 10 minutes, 5-chloro-1-pentyne (378 mg, 3.69 mmol) was added and the reaction was heated to 60 °C under Ar and stirred for 16 hours. The resulting suspension was then allowed to cool down to room temperature and filtered. The residue was washed with 3x20 mL CH_2Cl_2 and the combined filtrates were then concentrated *in vacuo*. The crude product was purified by flash chromatography on silica (20 % CH_2Cl_2 in hexanes as eluant) to give the title compound as a bright yellow powder (0.449 g, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (s, 2H, Th), 7.01 (2 overlapping d, 4H, J = 4.05, Th), 3.71, (t, 4H, J = 6.8, CH_2), 2.65 (t, 4H, J = 7.4, CH_2), 2.07 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 137.3, 135.9, 132.2, 124.7, 123.4, 122.6, 93.7, 74.5, 43.7, 31.2, 17.3. *m/z* (HRMS, CI, CH_4) 449.0018 $[M+H]^+$, $C_{22}H_{19}Cl_2S_3$ calc. 449.0025.

5,5''-bis(5-chloropentyl)-2,2':5',2''-terthiophene



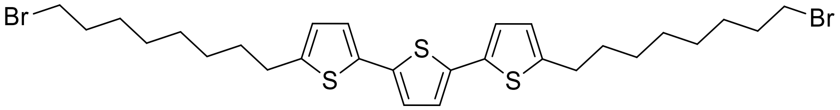
5,5''-bis(5-chloropent-1-yn-1-yl)-2,2':5',2''-terthiophene (0.431 g, 0.96 mmol) was subjected to catalytic hydrogenation (50 mL EtOAc, 50 mg Pd/C 10 %, H_2 atmosphere, 36 h, room temperature). The resulting solution was filtered through a bed of Celite and the solvent was removed *in vacuo* to give a yellow solid. The crude product was purified by flash chromatography on silica (10 % CH_2Cl_2 in hexanes as eluant) to obtain the title compound as a yellow powder (0.424 g, 95 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97 (s, 2H, Th), 6.95 (d, 2H, J = 3.6, Th), 6.68 (d, 2H, J = 3.6, Th) 3.54 (t, 4H, J = 7.3, CH_2), 2.80 (t, 4H, J = 7.5, CH_2), 1.81 (m, 4H, CH_2), 1.71 (m, 4H, CH_2), 1.52 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 144.6, 136.1, 134.8, 125.0, 123.6, 123.2, 44.9, 32.3, 30.9, 30.0, 26.3. *m/z* (HRMS, CI, CH_4) 457.0662 $[M+H]^+$, $C_{22}H_{27}Cl_2S_3$ calc. 457.0652.

5[T3]5



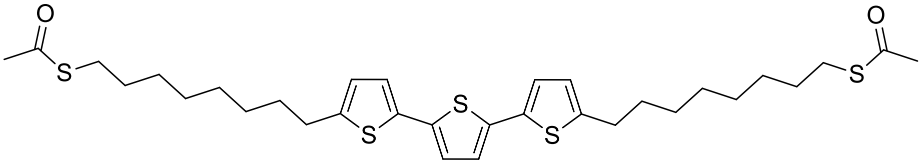
A solution of 5,5''-bis(5-chloropentyl)-2,2':5',2''-terthiophene (0.397 g, 0.87 mmol), sodium iodide (70 mg, 0.4 mmol) and KSAc (0.375 g, 3.2 mmol) in acetone (30mL) was refluxed under Ar atmosphere for 16 hours. The resulting brown suspension was filtered, the residue was washed with cold acetone and the combined filtrates were concentrated *in vacuo*. The obtained crude product was purified by flash chromatography on silica (CH_2Cl_2 as eluant) to give the title compound as a yellow powder (0.279 g, 60 %). Found: C = 58.11, H = 6.00, S = 29.65 %. $C_{26}H_{32}O_2S_5$ requires C = 58.17, H = 6.01, S = 29.86 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.89 (s, 2H, Th), 6.88 (d, 2H, J = 3.4, Th), 6.59 (d, 2H, J = 3.4, Th), 2.79 (t, 4H, J = 7.0, CH_2), 2.71 (t, 4H, J = 7.4, CH_2), 2.25 (s, 6H, CH_3), 1.62 (m, 4H, CH_2), 1.54 (m, 4H, CH_2) 1.37 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ: 196.0, 144.8, 136.1, 134.8, 125.0, 123.5, 123.2, 31.0, 30.7, 30.0, 29.3, 29.0, 28.2. *m/z* (HRMS, CI, CH_4) 537.1090 $[M+H]^+$, $C_{26}H_{33}O_2S_5$ calc. 537.1084.

5,5''-bis(8-bromooctyl)-2,2':5',2''-terthiophene



To an argon-purged flask was added 2,2':5',2''-terthiophene (0.5 g, 2.01 mmol) and 15 mL of dry THF. The solution was cooled to -78 °C and n-BuLi (caution! 1.58 M in hexane, 2.6 mL, 4.10 mmol) was added dropwise. The resulting yellow suspension was allowed to stir at -78 °C for one hour, then warmed to room temperature before transfer dropwise via wide bore needle syringe to a separate argon-purged flask containing 1,8-dibromooctane (2.2 g, 8.05 mmol) in 15 mL of THF at -78 °C. The reaction was allowed to warm to room temperature overnight and was then poured into ice water, extracted with CH_2Cl_2 (4 x 35 mL), the combined organics washed with water and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica (10 % CH_2Cl_2 in hexanes as eluant) to give the title compound as a yellow solid (74 mg, 5 %). Found: C = 53.47, H = 5.95, S = 15.73 %. $C_{24}H_{22}Cl_2S_3$ requires C = 53.33, H = 6.07, S = 15.25 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.97 (s, 2H, Th), 6.96 (d, 2H, J = 3.7, Th), 6.67 (d, 2H J = 3.6, Th), 3.40 (t, 4H, J = 6.9, CH_2), 2.78 (t, 4H, J = 7.8, CH_2), 1.85 (m, 4H, CH_2), 1.68 (m, 4H, J = 7.5, CH_2), 1.24-1.48 (m, 16H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.3, 136.1, 133.8, 124.9, 123.5, 123.2, 34.1, 32.7, 31.5, 30.1, 29.2, 28.9, 28.6, 28.1.

8[T3]8

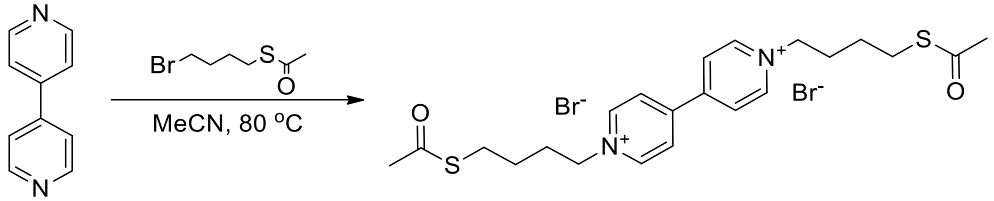


A solution of 5,5''-bis(8-bromooctyl)-2,2':5',2''-terthiophene (60 mg, 0.095 mmol), KSAc (40 mg, 0.33 mmol) and NaI (7 mg, 0.05 mmol) in acetone (15 mL) was refluxed under Ar atmosphere for 16 hours. The resulting brown suspension was filtered, the residue was washed with cold acetone and the combined filtrates were concentrated *in vacuo*. The obtained crude product was purified by flash column chromatography on silica (CH_2Cl_2 as eluant) to give the title compound as a yellow solid (34 mg, 55 %). Found: C = 61.78, H = 7.15, S =

25.75 %. $C_{32}H_{44}O_2S_5$ requires C = 61.89, H = 7.14, S = 25.82 %. ^1H NMR (400 MHz, $CDCl_3$) δ = 6.97 (s, 2H, Th), 6.95 (d, 2H, J = 3.4, Th), 6.67 (d, 2H, J = 3.4, Th), 2.86 (t, 4H, J = 7.5 Hz, CH_2), 2.78 (t, 4H, J = 7.9, CH_2), 2.32 (s, 6H, CH_3), 1.67 (m, 4H, CH_2), 1.56 (m, 4H, CH_2), 1.45 – 1.28 (m, 16H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.1, 145.3, 136.1, 134.7, 124.8, 123.5, 123.2, 31.5, 30.6, 30.1, 29.5, 29.2, 29.1, 29.0, 28.9, 28.8. *m/z* (HRMS, CI, CH_4) 621.2019 $[M+H]^+$, $C_{32}H_{45}O_2S_5$ calc. 621.2023.

X[V]X

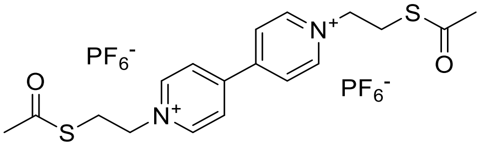
The viologen–containing molecules were prepared by quaternisation of 4,4’-bipyridyl, using the corresponding 1-acetylthio-ω-bromoalkane in acetonitrile or DMF, as bromide salt.



Scheme S6: Synthetic example: preparation of **4[V]4** as dibromide salt

The 4[V]4 dibromide salt was found to be particularly hygroscopic, to the point of deliquescence; it was therefore dissolved in H_2O and then treated with excess NH_4PF_6 to precipitate the hexafluorophosphate salt. 1-Acetylthio-4-bromobutane was prepared according to literature procedure.[10]

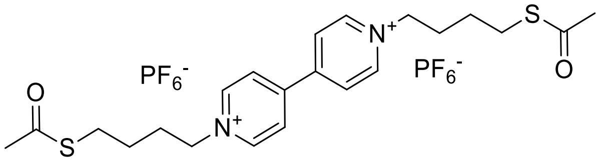
2[V]2



A solution of 1-acetylthio-2-bromoethane (5.83 mmol, 1.07 g) and 4,4'-bipyridyl (1.61 mmol, 0.252 g) in DMF (3 mL) was heated at 110 °C for two days. The mixture was cooled to RT, filtered and the precipitate was washed with EtOH (20 mL) to afford the crude product as a dibromide salt in 70 % yield (1.12 mmol, 0.588 g). The crude solid (0.39 mmol, 0.205 g) was dissolved in H_2O and an excess of $NaPF_6$ (0.300 g) was added to precipitate the corresponding hexafluorophosphate salt which was sonicated, filtered off and dried, to afford the product in 87% yield (0.34 mmol, 0.224 g). ^1H NMR (400 MHz, Acetone-d_6) δ = 9.49 (4H, d, J = 6.9, Ar), 8.89 (4H, d, J = 6.9, Ar), 5.16 (4H, t, J = 6.3, CH_2), 3.71 (4H, t, J = 6.3, CH_2), 2.32 ppm (6H, s, CH_3). ^{13}C NMR (100

MHz, Acetone-d$_6$) δ = 194.2, 150.4, 146.6, 127.2, 31.3, 31.4, 27.3. *m/z* (HRMS, ES+, MeOH) 675.0301 [M+Na]$^+$, $C_{18}H_{22}F_{12}N_2O_2NaP_2S_2$ calc. 675.0304.

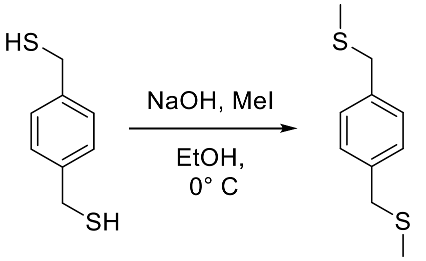
4[V]4



A solution of 1-acetylthio-4-bromobutane (2.42 g, 11.45 mmol) and 4,4'-bipyridyl (0.447 g, 2.86 mmol) in MeCN (10 mL) was refluxed for 36 hours. The mixture was allowed to cool down to RT, sonicated, filtered and the precipitate was washed with cold EtOH (20 mL) and diethyl ether (20 mL), to afford the crude product as >90 % pure (NMR) deliquescent dibromide salt (*ca.* 1.4 g, 85 %). A portion of the crude solid was transferred to a Schlenk flask and dried overnight *in vacuo* before weighing (0.44 g, 0.76 mmol). It was then dissolved in H_2O (25 mL) and excess NH_4PF_6 (0.51 g, 3 mmol) was added to precipitate the corresponding hexafluorophosphate salt. The resulting white suspension was stirred for 10 minutes, sonicated, filtered off, washed with cold water (25 mL) and dried overnight *in vacuo* to afford the product as a white solid (0.491 g, 91 %). The hexafluorophosphate salt showed no sign of hygroscopicity. Found: C = 37.26, H = 4.15, N = 3.94 %. $C_{22}H_{30}F_{12}N_2O_2P_2S_2$ requires C = 37.19, H = 4.17, N = 3.95 %. ^{1}H NMR (400 MHz, acetone-d$_6$) δ = 9.47 (d, 4H, J = 7, Py), 8.86 (d, 4H, J = 7, Py), 5.02 (t, 4H, J = 7.3, CH$_2$), 2.96 (t, 4H, J = 7.2, CH$_2$), 2.31 (s, 6H, CH$_3$), 2.28 (*obs* m, 4H, CH$_2$), 1.75 (m, 4H, CH$_2$). ^{13}C NMR (100 MHz, acetone-d$_6$) δ = 195.0, 150.2, 146.1, 127.3, 61.7, 30.2, 29.7, 27.6, 26.2. MS: *m/z* 563 [M-PF$_6$]$^+$, 731 [M+Na]$^+$. *m/z* (HRMS, ES+, MeOH) 731.0928 [M+Na]$^+$. $C_{22}H_{30}F_{12}N_2O_2NaP_2S_2$ calc. 731.0930.

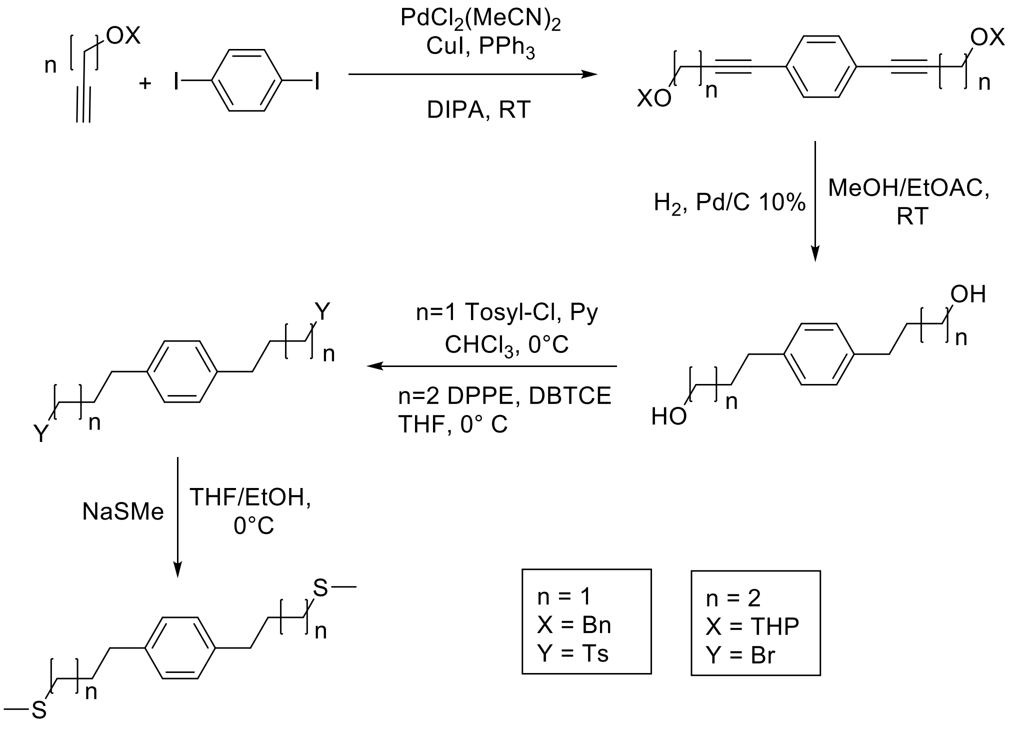
X[Ph]X-SMe

1[Ph]1-SMe was prepared by methylation of the corresponding thiol using iodomethane in basic conditions.



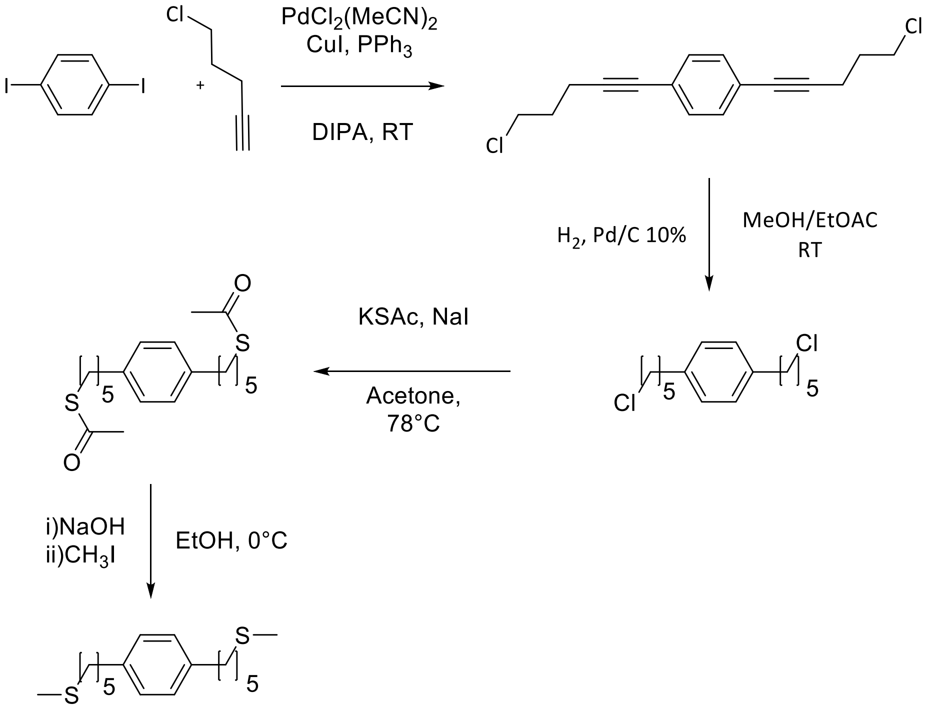
Scheme S7: Synthesis of **1[Ph]1-SMe**

The preparation of **3[Ph]3-SMe** and **4[Ph]4-SMe** proved more challenging, as the products of Sonogashira coupling between 1,4-diiodobenzene and propargyl alcohol or 3-butyn-1-ol were impossible to purify by usual means (chromatography / recrystallization). The alcoholic function had to be protected (as benzyl or THP ether), and then deprotected in the subsequent catalytic hydrogenation. Substitution of the hydroxyl function with a more reactive bromide or tosyl group and nucleophilic displacement with sodium thiomethoxide afforded the target compounds.



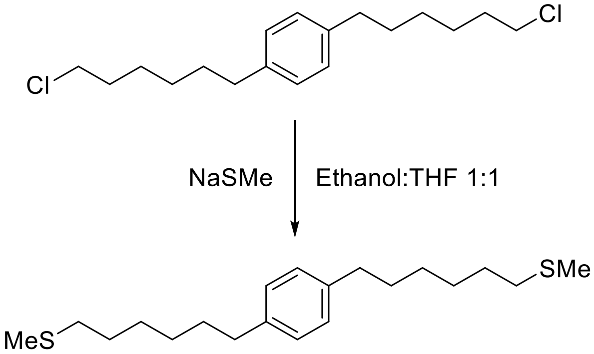
Scheme S8: Synthesis of **3[Ph]3-SMe** and **4[Ph]4-SMe**

5[Ph]5-SMe was prepared by Sonogashira cross-coupling of 1,4-diiodobenzene with 5-chloro-1-pentyne, H_2/Pd reduction of the alkynyl function, treatment with KSAc to afford the corresponding thioacetic acid esters and methylation with iodomethane in basic conditions.



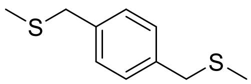
Scheme S9: Synthesis of **5[Ph]5-SMe**

6[Ph]6-SMe was prepared by treating 1,4-bis(5-chlorohexyl)benzene[7] with sodium thiomethoxide in a mixture of THF and ethanol.



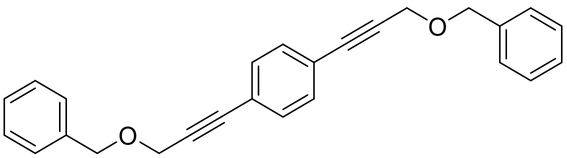
Scheme S10: Synthesis of **6[Ph]6-SMe**

1[Ph]1-SMe



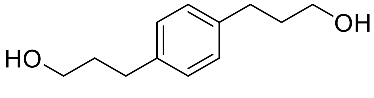
To a solution of sodium hydroxide (282 mg, 7.1 mmol) in ethanol (20 mL) was added 1,4-benzenedimethanethiol (200 mg, 1.17 mmol) while cooling in an ice bath. The resulting suspension was stirred for 10 minutes at 0 ˚C and then iodomethane (0.147 mL, 2.35 mmol) was added. After stirring overnight, the resulting suspension was quenched with NH_4Cl (aq. sat., 15 mL). The mixture was concentrated under vacuum and then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$, filtered and the solvent was removed under vacuum. Purification by column chromatography on silica (2 % EtOAc in hexanes) afforded the title compound as white crystals (190 mg, 82 %). Found C = 60.18, H = 7.14, S = 32.22 %. $C_{10}H_{14}S_2$ requires C = 60.55, H = 7.11, S = 32.33 %. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25 (s, 4H, Ph), 3.66 (s, 4H, CH_2), 1.97 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 129.0, 38.1, 15.0. *m/z* (HRMS, CI, NH_3) 216.0884 $[M+NH_4]^+$. $C_{10}H_{18}NS_2$ calc. 216.0881.

1,4-bis(3-(benzyloxy)prop-1-yn-1-yl)benzene



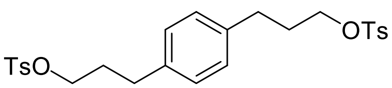
1,4 diiodobenzene (2 g, 6.06 mmol), $[PdCl_2(MeCN)_2]$ (80 mg, 0.30 mmol), triphenylphosphine (240 mg, 0.92 mmol) and CuI (116 mg, 0.60 mmol) were mixed in DIPA (80 mL) and the resulting suspension was degassed by bubbling Ar through for 50 minutes. Benzyl 2-propynyl ether (2.22 g, 15.15 mmol) was added, and the resulting suspension was stirred for 24 hours under Ar atmosphere at room temperature. The solvent was then removed *in vacuo*, the solid was extracted into CH_2Cl_2 and the suspension was filtered. After removal of the solvent, the crude product was purified by flash chromatography on silica (15 % EtOAc in hexanes) and recrystallized from hexanes:CH_2Cl_2 (95:5) to give the title compound as pale yellow solid (2.01 g, 89 %) .^1H NMR (400 MHz, $CDCl_3$,) δ: 7.38 (s, 4H, Ph), 7.37 (m, 10H, Ph), 4.67 (s, 4H, CH_2) 4.40 (s, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 131.7, 128.5, 128.2, 127.9, 122.8, 87.0, 86.0, 71.8, 57.9. *m/z* 389.2 $[M+Na]^+$.

3,3'-(1,4-phenylene)bis(propan-1-ol)



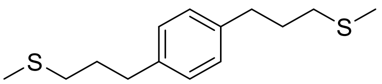
1,4-bis(3-(benzyloxy)prop-1-yn-1-yl)benzene (2 g, 5.46 mmol) was subjected to catalytic hydrogenation (25 mL EtOAc, 25 mL MeOH, 300 mg Pd/C 10 %, H_2 atmosphere, 52 h, room temperature). The resulting solution was filtered through a bed of Celite and the solvent was removed *in vacuo* to give the title compound as white solid (1 g, 94 %). Found C = 73.69, H = 9.31 %. $C_{12}H_{18}O_2$ requires C = 74.19, H = 9.34 %. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.12 (s, 4H, Ph), 3.68 (t, 4H, J = 6.4, CH_2), 2.68 (t, 4H, J = 8, CH_2) 1.88 (m, J = 6.4, 4H, CH_2) ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.38, 128.56, 62.37, 34.22, 31.65. *m/z* (HRMS, CI, CH_4) 177.1281. $C_{12}H_{17}O$ calc. 177.1279.

1,4-phenylenebis(propane-3,1-diyl) bis(4-methylbenzenesulfonate)



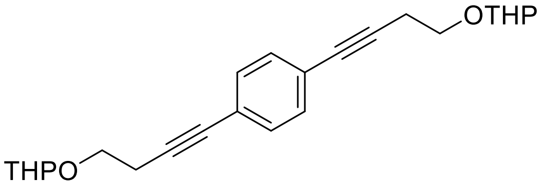
To a solution of 3,3'-(1,4-phenylene)bis(propan-1-ol) (0.3 g, 1.54 mmol) in chloroform (15 mL) pyridine (0.5 mL, 6.2 mmol) was added followed by *p*-toluenesulfonyl chloride (0.9 g, 4.63 mmol) while cooling in an ice bath. After stirring overnight, diethyl ether (40 mL) and water (15 mL) were added to the mixture and the layers were separated. The combined organics were washed successively with HCl (2N, 20 mL), $NaHCO_3$ (5%, 20 mL), and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica (25% EtOAc in hexanes) to give the title compound as white solid (600 mg, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, 4H, J = 8 Hz, Ph), 7.49 (d, 4H, J = 8 Hz, Ph), 6.99 (s, 4H Ph) 4.03 (t, 4H, J = 5.6 Hz, CH_2), 2.59 (t, 4H, J = 8 Hz, CH_2), 2.47 (s, 6H, CH_3), 1.91 (m, 4H). *m/z* 525.1 $[M+Na]^+$.

3[Ph]3-SMe



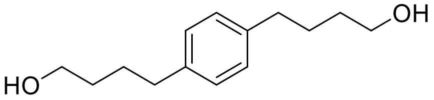
To a solution of sodium thiomethoxide (0.22 g, 3.1 mmol) in dry ethanol (15 mL) under Ar, 1,4-phenylenebis(propane-3,1-diyl) bis(4-methylbenzenesulfonate) (0.26 g, 0.52 mmol) dissolved in dry THF (15 mL) was added. After stirring for three hours the resulting suspension was quenched with water (25 mL) and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic portions were washed successively with brine (2 × 25 mL) and water (2 × 25 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by flash column chromatography on silica (4 % EtOAc in hexanes as eluant) followed by recrystallization from hexanes (RT to -78 °C) to give the title compound as white solid that melted on standing to a colorless oil (120 mg, 90 %). Found C = 67.12, H = 8.86, S = 24.37 %. $C_{14}H_{22}S_2$ requires C = 66.08, H = 8.71, S = 25.20 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.11 (s, 4H, Ph), 2.69 (t, 4H, J = 7.6 Hz, CH_2), 2.51 (t, 4H, J = 7.6 Hz, CH_2) 2.10 (s, 6H, CH_3), 1.90 (m, 4H, CH_2) ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.2, 128.6, 34.4, 33.6, 30.8, 15.4. *m/z* 255.1245 $[M+H]^+$, $C_{14}H_{23}S_2$ calc. 255.1241. The low S and somewhat high C and H figures are attributable to residual solvents, identified in the ^{1}H NMR spectrum (*vide infra*), that was not completely removed on pumping in vacuo.

1,4-bis(4-((tetrahydro-2H-pyran-2-yl)oxy)but-1-yn-1-yl)benzene



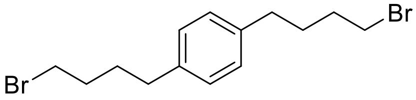
1,4 diiodobenzene (1.6 g, 4.85 mmol), [$PdCl_2(MeCN)_2$] (63 mg, 0.24 mmol), triphenylphosphine (190 mg, 0.73 mmol) and CuI (92 mg, 0.48 mmol) were mixed in DIPA (80 mL) and the resulting suspension was degassed by bubbling argon for 50 minutes. After this time, 2-(but-3-yn-1-yloxy)tetrahydro-2H-pyran (1.9 mL, 12.12 mmol), was added, and the resulting suspension was stirred for 24 hours under argon atmosphere at room temperature. The solvent was then removed *in vacuo*, the solid was extracted into CH_2Cl_2 and the suspension was filtered. After removal of the solvent, the crude product was purified by flash chromatography on silica (10% EtOAc in hexanes) and recrystallized from hexanes:CH_2Cl_2 (95:5) to give the title compound as pale yellow solid (1.2 g, 65 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30 (s, 4H, Ph) 4.69, (t, 2H, J = 3.2, CH), 3.91 (m, 4H, CH_2), 3.58 (m, 4H, CH_2), 2.71 (m, 4H, CH_2), 1.85 (m, 4H, CH_2) 1.74 (m, 4H, CH_2), 1.61 (m, 4H, CH_2).^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.65, 123.00, 98.77, 88.71, 81.21, 65.53, 62.12, 30.36, 25.34, 21.12, 19.11. *m/z* 405.2 $[M+Na]^+$.

4,4'-(1,4-phenylene)bis(butan-1-ol)



1,4-bis(4-((tetrahydro-2H-pyran-2-yl)oxy)but-1-yn-1-yl)benzene (1 g, 3.14 mmol) was subjected to catalytic hydrogenation (25 mL EtOAc, 25 mL MeOH, 100 mg Pd/C 10 %, H_2 atmosphere, 48 h, room temperature). The resulting solution was filtered through a bed of Celite and the solvent was removed *in vacuo* to give the title compound as white solid (0.55 g, 94 %). ^1H NMR (400 MHz, CD_3OD) δ: 7.08 (s, 4H, Ph), 3.55 (t, 4H, J = 6.4, CH_2), 2.59 (t, 4H, J = 8, CH_2) 1.65 (m, 4H, CH_2) 1.56 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.60, 127.93, 61.42, 34.89, 31.81, 27.62. *m/z* 240.0 $[M+NH_4]^+$, 223.3 $[M+H]^+$.

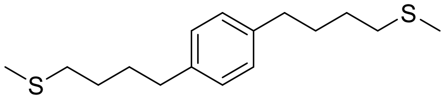
1,4-bis(4-bromobutyl)benzene



To a solution of DPPE (690 mg, 1.73 mmol) in THF (20 mL) was added 1,2-dibromotetrachloroethane (1.28 g, 3.94 mmol), while cooling in an ice bath and the mixture was left stirring for 15 minutes. 4,4'-(1,4-

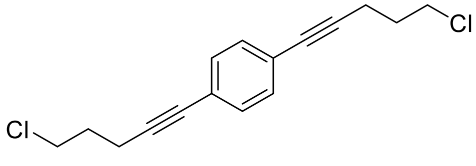
Phenylene)bis(butan-1-ol) (350 mg, 1.57 mmol) was added and the mixture was allowed to slowly warm to room temperature overnight, whilst stirring. The solvent was evaporated, hexanes (50 mL) and EtOAc (5 mL) were added, the mixture was filtrated and the solvent was then removed *in vacuo*. The crude product was purified by flash chromatography on silica (hexanes) to give the title compound as white crystals (140 mg, 25 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10 (s, 4H, Ph), 3.42 (t, 4H, J = 6.8, CH_2), 2.61 (t, 4H, J = 7.6, CH_2) 1.89 (m, 4H, CH_2) 1.76 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 130.6, 36.7, 35.8, 34.4, 32.1. *m/z* 366.0 $[M+NH_4]^+$.

4[Ph]4-SMe



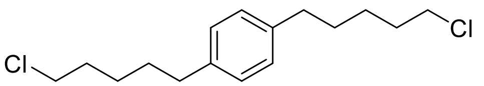
To a solution of sodium thiomethoxide (0.12 g, 1.7 mmol) in dry ethanol (8 mL) under Ar, 1,4-bis(4-bromobutyl)benzene (0.103 g, 0.287 mmol) dissolved in dry THF (7 mL) was added. After stirring for three hours the resulting suspension was quenched with water (15 mL), and the product was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed successively with brine (2 × 15 mL) and water (2 × 20mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography on silica (4% EtOAc in hexanes) and recrystallised from boiling hexanes to give the title compound as white solid that liquefied overnight. (68 mg, 83 %). Found C = 68.69, H = 9.60, S = 20.02 %. $C_{16}H_{26}S_2$ requires C = 68.02, H = 9.28, S = 22.70 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (s, 4H, Ph.), 2.60 (t, 4H, J = 7.2 Hz, CH_2), 2.51 (t, 4H, J = 7.2, CH_2), 2.08 (s, 6H, CH_3), 1.68 (m, 8H, CH_2) ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6, 128.3, 35.1, 34.1, 30.5, 28.7, 15.5. *m/z* (HRMS, CI, CH_4) 283.1553 $[M+H]^+$. $C_{16}H_{27}S_2$ calc. 283.1554. The low S and somewhat high C and H figures are attributable to residual solvents, identified in the ^{1}H NMR spectrum (*vide infra*), that were not completely removed on pumping in vacuo.

1,4-bis(5-chloropent-1-yn-1-yl)benzene



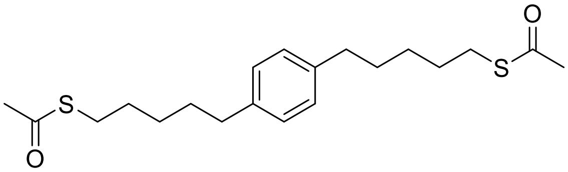
1,4 diiodobenzene (1.5 g, 4.55 mmol), $[PdCl_2(MeCN)_2]$ (59 mg, 0.23 mmol), triphenylphosphine (179 mg, 0.66 mmol) and CuI (87 mg, 0.45 mmol) were mixed in DIPA (60 mL) and the resulting suspension was degassed by bubbling argon through for 50 minutes. 5-Chloro-1-pentyne (1.2 mL, 11.38 mmol) was added and the resulting suspension was stirred for 24 hours under argon atmosphere at room temperature. The solvent was then removed *in vacuo*, the solid was extracted into CH_2Cl_2 and the suspension was filtered. After further removal of the solvent, the crude product was purified by flash chromatography on silica (0.5 % EtOAc in hexanes) and recrystallised from hexanes to give the title compound as pale yellow solid (830 mg, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (s, 4H, Ph.), 3.71 (t, 4H, J = 6.4, CH_2), 2.62 (t, 4H, J = 6.8, CH_2), 2.06 (q, 4H, J = 6.4, 6.8, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.45, 123.02, 89.75, 81.24, 43.73, 31.41, 16.70. *m/z* 304.2 $[M+NH_4]^+$.

1,4-bis(5-chloropentyl)benzene



1,4-bis(5-chloropent-1-yn-1-yl)benzene (0.8 g, 2.86 mmol) was subjected to catalytic hydrogenation (25 mL EtOAc, 25 mL MeOH, 130 mg Pd/C 10 %, H_2 atmosphere, 24 h, room temperature). The resulting solution was filtered through a bed of Celite® and the solvent was removed *in vacuo.* The crude product was purified by flash chromatography on silica (10 % EtOAc in hexanes) to give the title compound as white solid (0.722 g, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (s, 4H, Ph.), 3.53 (t, 4H, J=6.8, CH_2), 2.59 (t, 4H, J = 8, CH_2), 1.80 (m, 4H, CH_2), 1.63 (m, 4H, CH_2), 1.47 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.78, 128.13, 45.06, 35.09, 32.28, 30.76, 26.65. *m/z* 304.2 $[M+NH_4]^+$.

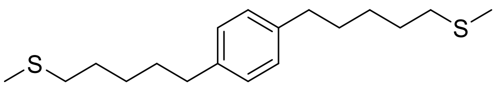
S,S'-(1,4-phenylenebis(pentane-5,1-diyl)) diethanethioate



Potassium thioacetate (1 g, 8.8 mmol), sodium iodide (188 mg, 1.26 mmol) and 1,4-bis(5-chloropentyl)benzene (700 mg, 2.48 mmol) were mixed in acetone (70 mL) and the resulting suspension gently refluxed overnight. The resulting mixture was evaporated and water was added (10 mL), the product was extracted with CH_2Cl_2 (3 × 40 mL), the combined organic portions were washed with brine (20 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography on silica (20 % EtOAc in hexanes) and recrystallised from hexanes to give the title compound as orange crystals (478 mg, 54 %). Found C = 65.37, H = 8.13, S = 17.82 %. $C_{20}H_{30}O_2S_2$ requires C = 65.53, H = 8.25, S = 17.49 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.07 (s, 4H, Ph.), 2.86 (t, 4H, J = 7.2, CH_2), 2.56 (t, 4H, J = 7.6, CH_2), 2.32 (s, 6H,

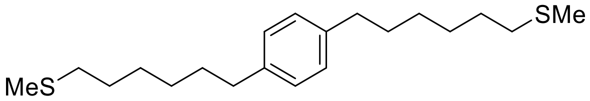
CH_3), 1.60 (m, 8H, CH_2), 1.40 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.13, 139.70, 128.21, 35.32, 31.02, 30.65, 29.42, 29.05, 28.48. *m/z* (HRMS, CI, NH_3) 367.1775 $[M+H]^+$. $C_{20}H_{31}O_2S_2$ calc. 367.1765.

5[Ph]5-SMe



To a solution of *S,S'*-(1,4-phenylenebis(pentane-5,1-diyl))diethanethioate (180 mg, 0.51 mmol) in ethanol (5 mL) was added a solution of sodium hydroxide (100 mg, 255 mmol) in ethanol (6 mL) while cooling in an ice bath. The suspension was stirred for 15 minutes at 0° C before iodomethane (0.063 mL, 1.02 mmol) in ethanol (0.6 mL) was added. After stirring overnight, the resulting suspension was quenched with NH_4Cl (aq. sat., 15 mL), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$, filtered, and the solvent removed under vacuum. Purification by column chromatography on silica (30 % CH_2Cl_2 in hexanes) afforded the title compound as clear oil (130 mg, 86 %). Found C = 70.87, H = 9.98, S = 20.25 %. $C_{18}H_{30}S_2$ requires C = 69.62, H = 9.74, S = 20.65 %. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.08 (s, 4H, Ph.), 2.58 (t, 4H, J = 7.6, CH_2), 2.49 (t, 4H, J = 7.6, CH_2), 2.09 (s, 6H, CH_3), 1.62 (m, 8H, CH_2), 1.43 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.8, 128.3, 35.4, 34.2, 31.2, 29.1, 28.5, 15.6. *m/z* (HRMS, CI, CH_4) 311.1873 $[M+H]^+$. $C_{18}H_{31}S_2$ calc. 311.1867.

6[Ph]6-SMe



To a solution of sodium thiomethoxide (1.32 g, 18.8 mmol) in ethanol (25 mL) was added dropwise a solution of 1,4-bis(chlorohexyl)benzene[7] (0.987 g, 3.14 mmol) in THF (20 mL). The resulting solution was stirred at room temperature for 16 hours, during which time a white precipitate appeared. The suspension was filtered, the filtrate concentrated *in vacuo* to a thick oil, which was extracted in CH_2Cl_2 (30 mL) and washed with water (3 x 25 mL) and brine (25 mL). The organic phase was then dried over $MgSO_4$, filtered, and concentrated *in vacuo* to a yellow oil. Column chromatography on silica (20 % CH_2Cl_2 in hexanes) afforded the title compound as clear oil (0.574 g, 54 %). Found C = 71.42, H = 10.21, S = 18.37 %. $C_{20}H_{34}S_2$ requires C = 70.94, H = 10.12, S = 18.94 %. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.08 (s, 4H, Ph.), 2.57 (t, 4H, J = 7.6, CH_2), 2.48 (t, 4H, J = 7.2, CH_2), 2.08 (s, 6H, CH_3), 1.59 (m, 8H, CH_2), 1.48-1.32 (m, 8H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.9, 128.3, 35.5, 34.3, 31.4, 29.1, 28.9, 28.7, 15.6. *m/z* (HRMS, CI, CH_4) 339.2183 $[M+H]^+$. $C_{20}H_{35}S_2$ calc. 339.2180.

2. Single-molecule conductance data

Single-molecule conductance data obtained using the STM *I(z)* technique are presented as 1-dimensional linear histogram (left) and 2d "density" plots (right). The y-axis in the histograms is arbitrary counts (not shown for clarity), and the colour scale in the 2d plots goes from blue (low density) to red (high density). Linear histograms show a distribution of the conductance values measured during the *I(z)* experiments, and the same values are plotted as a function of electrode separation (tip-substrate distance) in the 2d plots. Peaks in the histogram correspond to high-density areas in the 2d plots, giving information about junction geometry and break-off length.

1[T3]1

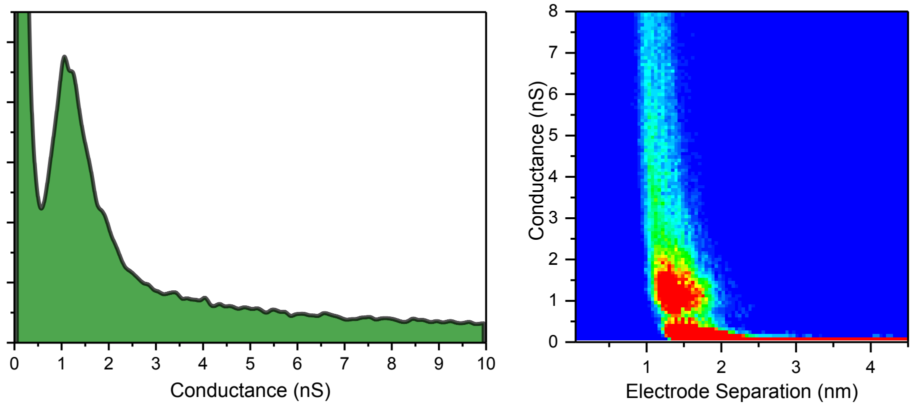


Figure S1: SMC data for **1[T3]1**. 20 nA setpoint, 0.3 V bias.

3[T3]3

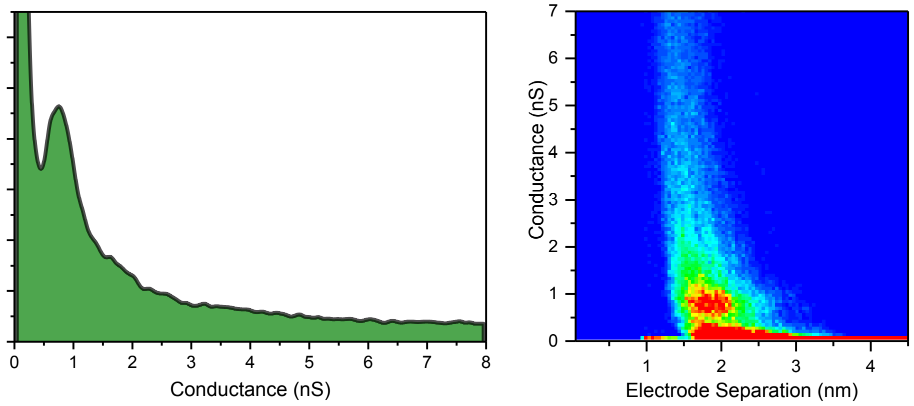


Figure S2: SMC data for **3[T3]3**. 7 nA setpoint, 0.3 V bias.

4[T3]4

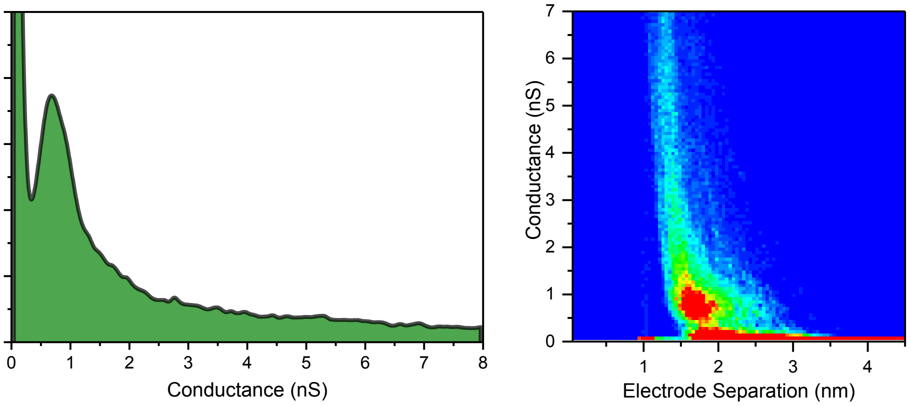


Figure S3: SMC data for **4[T3]4**. 7 nA setpoint, 0.3 V bias.

5[T3]5

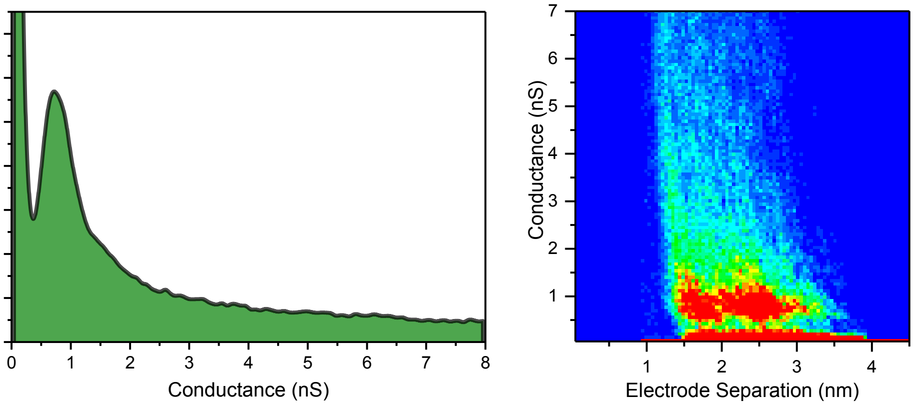


Figure S4: SMC data for **5[T3]5**. 7 nA setpoint, 0.3 V bias.

6[T3]6

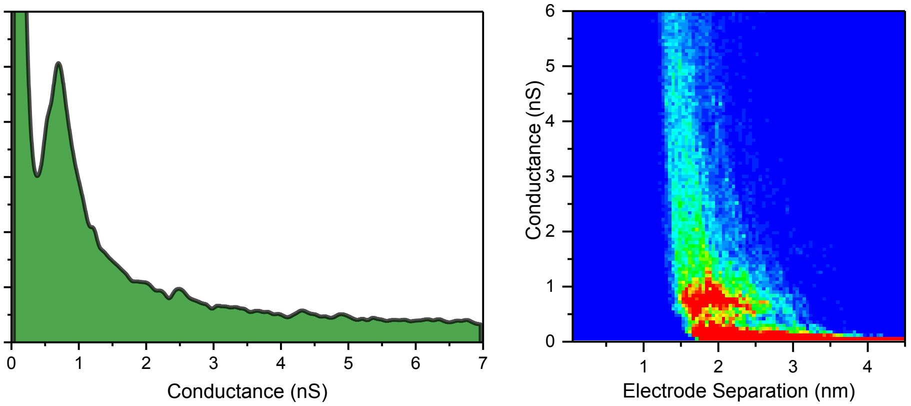


Figure S5: SMC data for **6[T3]6**. 7 nA setpoint, 0.3 V bias.

8[T3]8

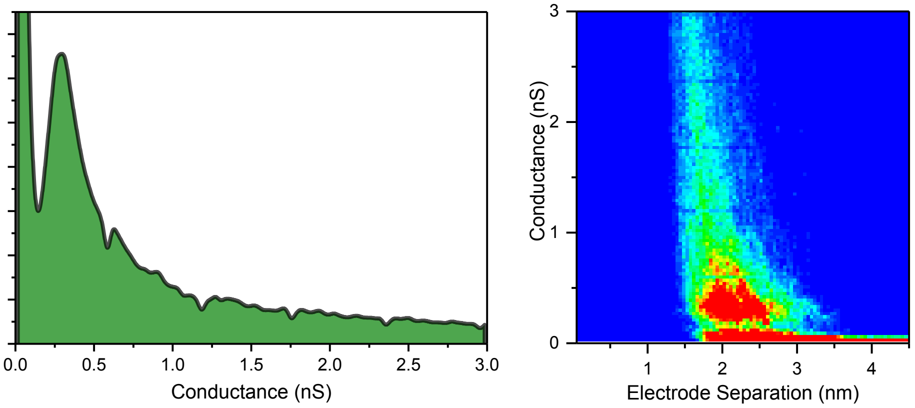


Figure S6: SMC data for **8[T3]8**. 7 nA setpoint, 0.3 V bias.

2[V]2

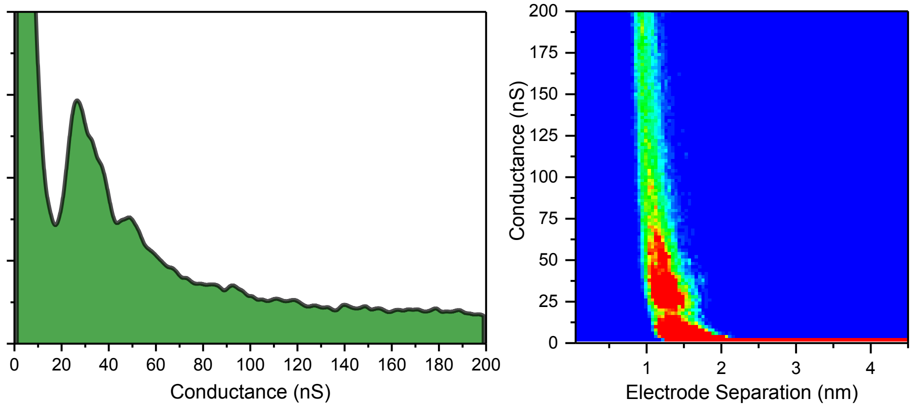


Figure S7: SMC data for **2[V]2**. 60 nA setpoint, 0.3 V bias.

4[V]4

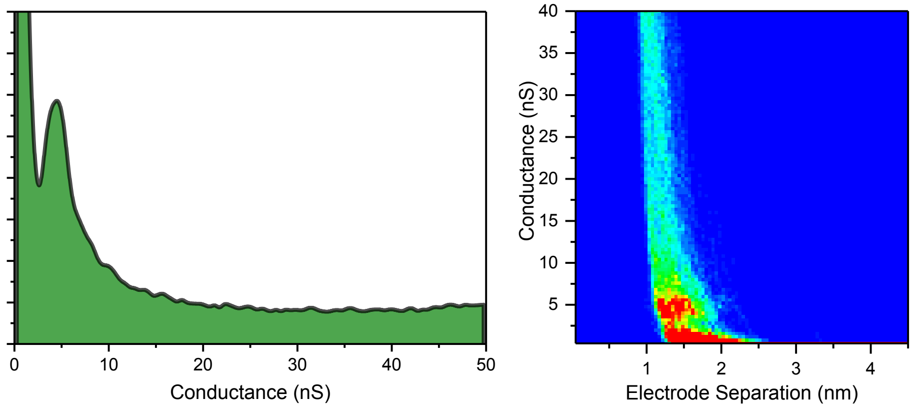


Figure S8: SMC data for **4[V]4**. 20 nA setpoint, 0.3 V bias.

6[V]6

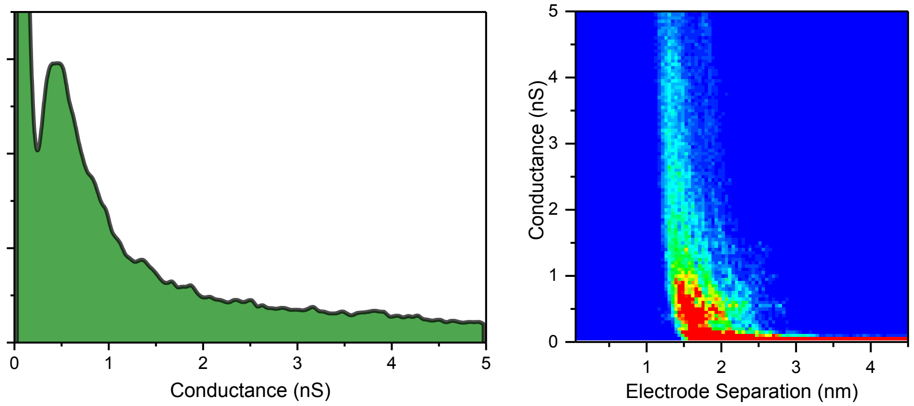


Figure S9: SMC data for **6[V]6**. 8 nA setpoint, 0.3 V bias.

9[V]9

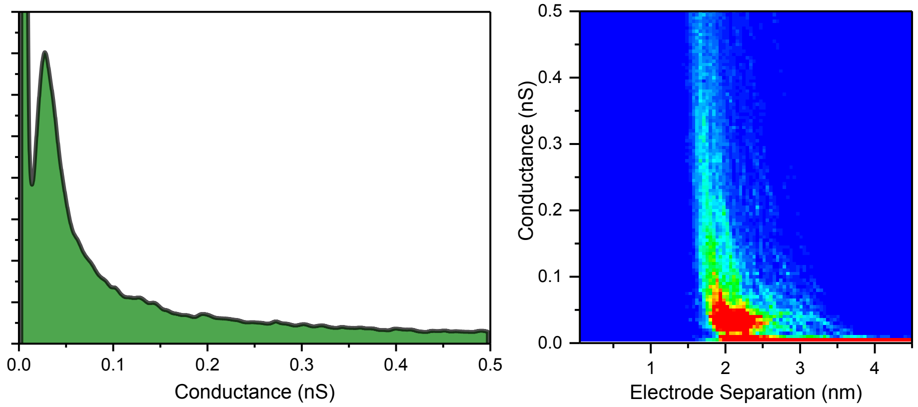


Figure S10: SMC data for **9[V]9**. 5 nA setpoint, 0.3 V bias.

1[Ph]1-SMe

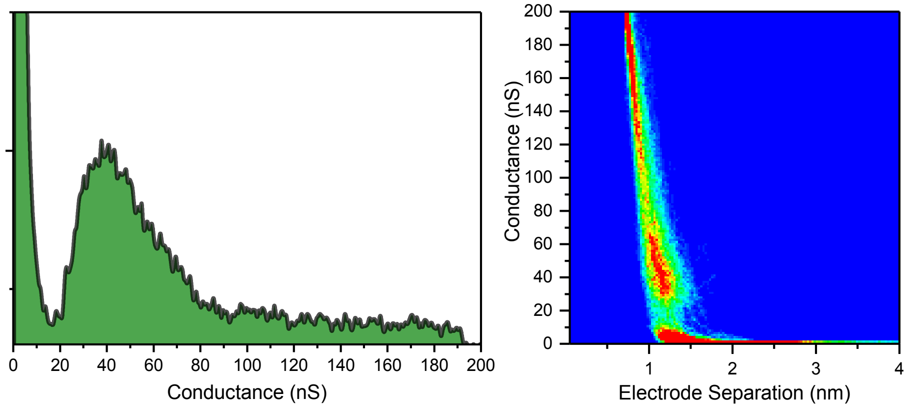


Figure S11: SMC data for **1[Ph]1-SMe**. 60 nA setpoint, 0.3 V bias.

3[Ph]3-SMe

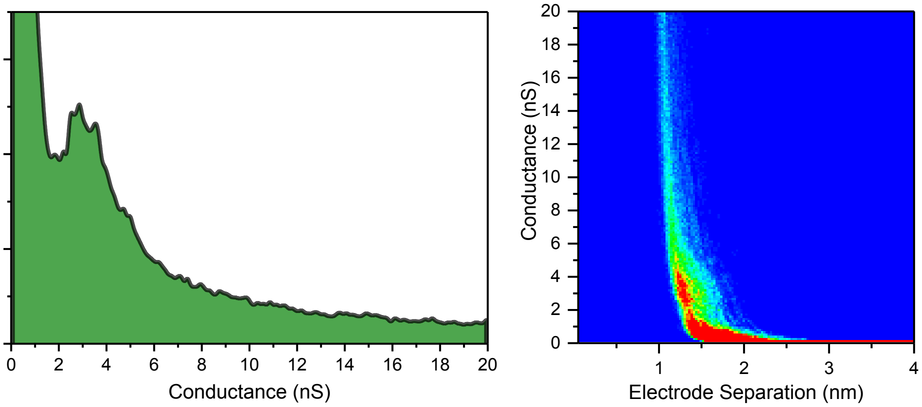


Figure S12: SMC data for **3[Ph]3-SMe**. 60 nA setpoint, 0.3 V bias.

4[Ph]4-SMe

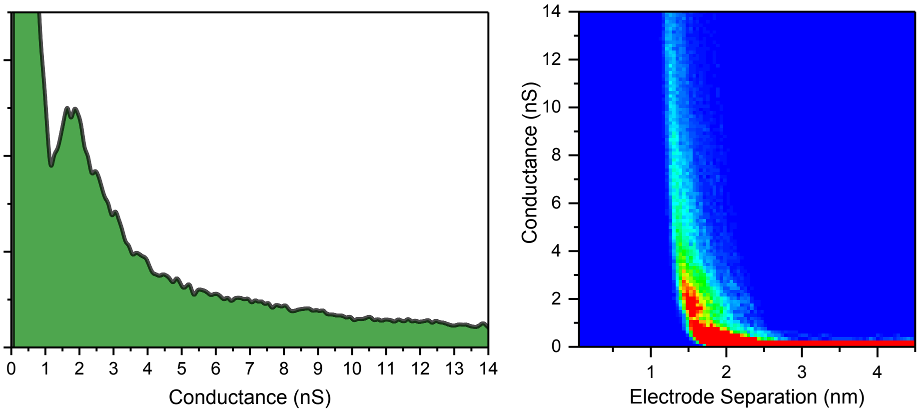


Figure S13: SMC data for **4[Ph]4-SMe**. 60 nA setpoint, 0.3 V bias.

5[Ph]5-SMe

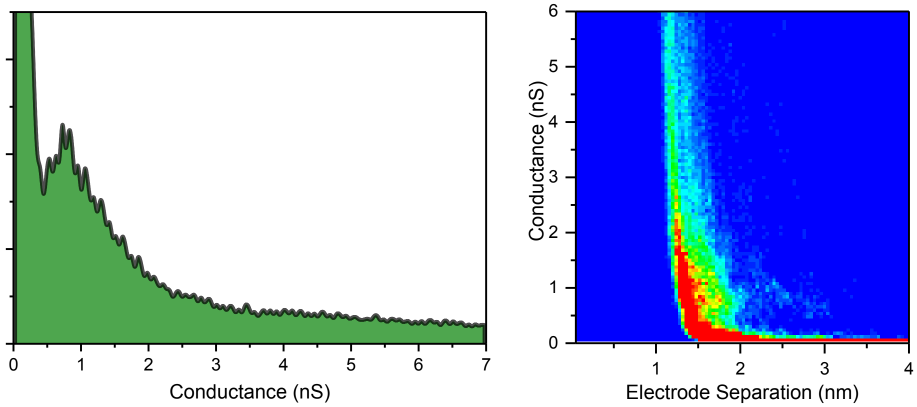


Figure S14: SMC data for **5[Ph]5-SMe**. 60 nA setpoint, 0.3 V bias.

6[Ph]6-SMe

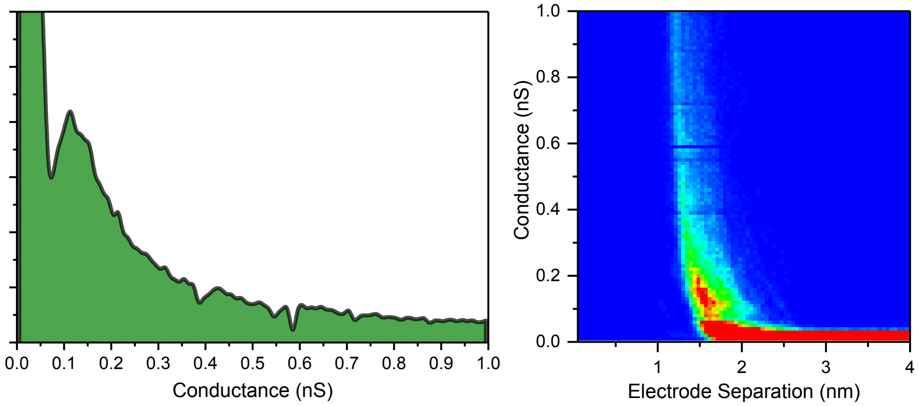


Figure S15: SMC data for **6[Ph]6-SMe**. 20 nA setpoint, 0.3 V bias.

Comparison between *I(z)* and *STM-BJ* results

In order to understand whether the results obtained with the *I(z)* technique and the more widely used *STM-BJ* technique[11] are comparable, we performed measurement on the most conductive molecular wire **1[Ph]1-SMe** with both techniques and found the same main conductance value.

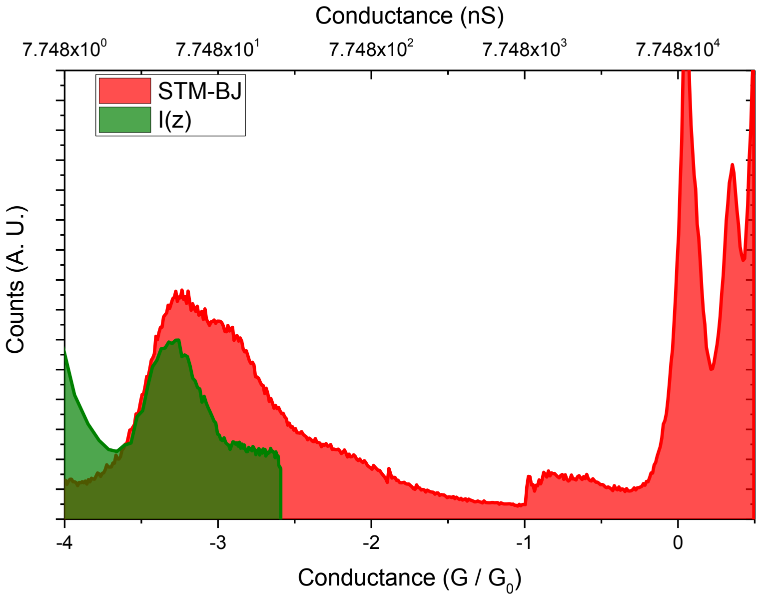


Figure S16: Comparison between conductance histogram compiled with unselected STM-BJ (red) and *I(z)* (green) data. Both techniques gave the same conductance value, 44 nS (5.6×10^{-4} G_0)

As can be seen in the histogram, the main conductance values is comparable in both technique. The *STM-BJ* technique, however, display a marked shoulder at higher conductance, consistent with multiple molecule bridging the gap. The obtained conductance is also consistent with the literature value of 3.5×10^{-4} G_0.[12]

3. Effect of the anchoring group on the transmission curves

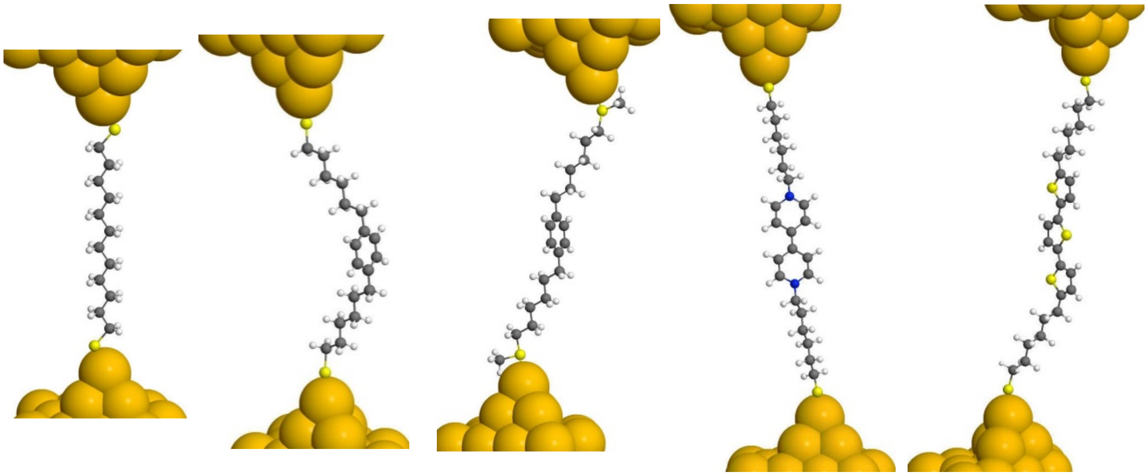


Figure S17: Structures of molecules connected to the electrodes

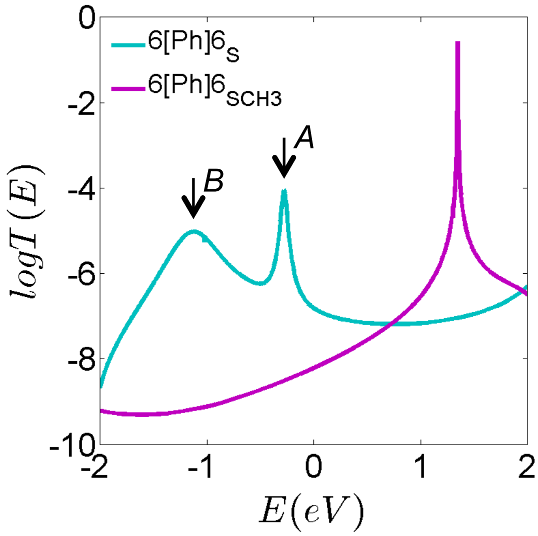
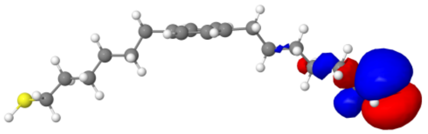
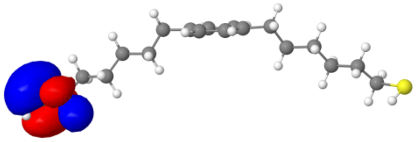
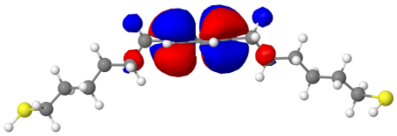
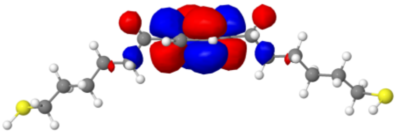
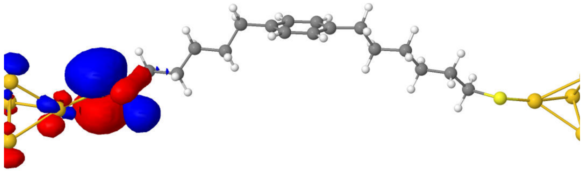
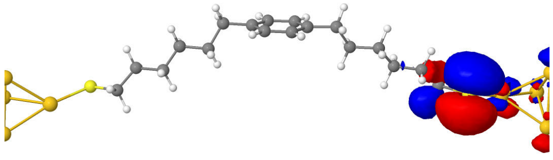
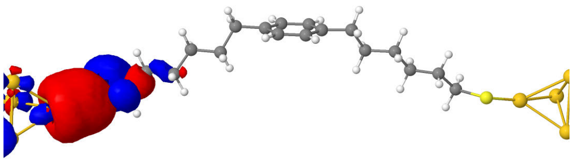
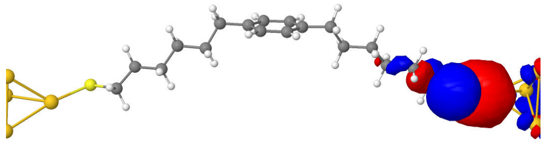


Figure S18: Transmission coefficient for **6[Ph]6** (thiol contacts, green curve) and **6[Ph]6-SMe** (thiomethyl contacts, purple curve). The wavefunctions at energies A and B are shown in the figure S19.

The resonances close to $E = 0$ in **ADT** and **6[Ph]6** arise from the part-filled sulfur orbitals (HFSO) which create resonances close to the Fermi energy, and its magnitude is much larger in **X[Ph]X** than **ADT**. To demonstrate that this is due to the much larger effect of the sulfur atoms in **X[Ph]X,** we calculated the molecular orbitals for HOMO and LUMO for isolated molecule (Table S1, 1 and b), for the molecule in presence of gold tip (Table S1, c and d) and the local density of state in Au/**6[Ph]6**/Au and Au/**6[Ph]6-SMe**/Au junctions (Figure S19). As shown in table S1 (a and b), HOMO is localised on the sulfur atoms whereas the LUMO is localised on the phenyl. This clearly demonstrates that the HOMO resonance (shown by A in Figure S18) is due to the sulfur atoms. In addition, the wave function in the presence of gold tips at points A and B (shown in Figure S18) are localised mostly on the sulfur atoms. This demonstrates that not only the HOMO resonance is due to the sulfur atom but the resonance in B is also due to the sulfur atoms. Furthermore, local density calculation in the presence of Au electrodes confirms this as shown in Figure S19. It is clear that in the case of the molecule bearing thiolate (-SH) anchors **X[Ph]X** a larger density of electrons is localised on the sulfur atoms and partly on the alkyl chain, indicating much larger contribution of the HFSO to the transport.

Table S1: Molecular orbitals of **6[Ph]6**. (a,b) HOMO and LUMO iso-surfaces for isolated molecule, (c,d) molecular orbitals in the first and second peak shown by A, B respectively in figure S18.

	
a) HOMO (Degenerate) for isolated molecule	
	
b) LUMO (Degenerate) for isolated molecule	
	
c) Wavefunction (Degenerate) in the first peak shown by A in figure S18 for the MMM junction	
	
d) Wavefunction (Degenerate) at the second peak shown by B in figure S18 for the MMM junction	

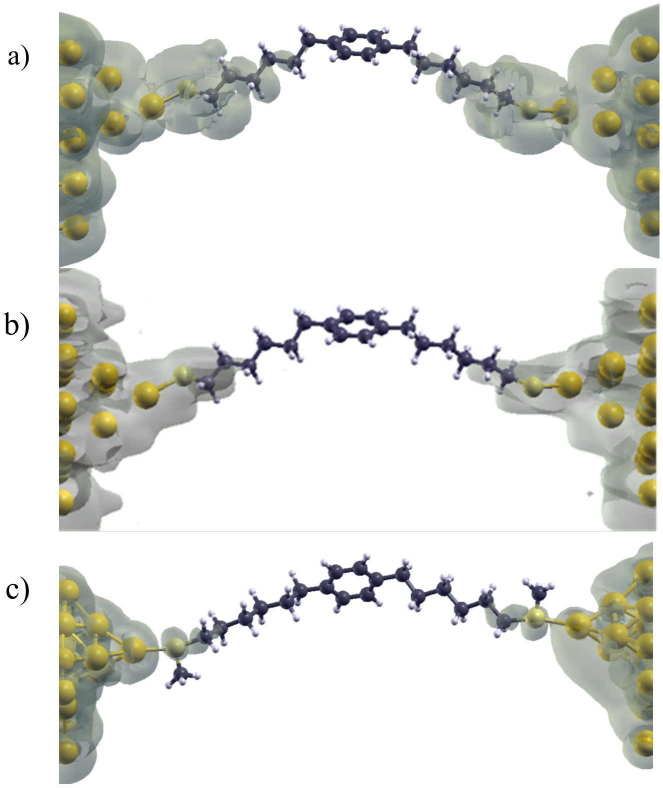


Figure S19: LDOS a) E= -0.15 eV, b) E= -1.11 ev for **6[Ph]6** and c) E= -0.15 ev **6[Ph]6-SMe** sandwiched between two Au electrodes.

Gateway states are not only limited to thiol contacts, but also appear when there is a strong coupling of the molecular backbone to the metallic leads, and have been observed, among others, in junctions with C-Au bonds.[13,14]

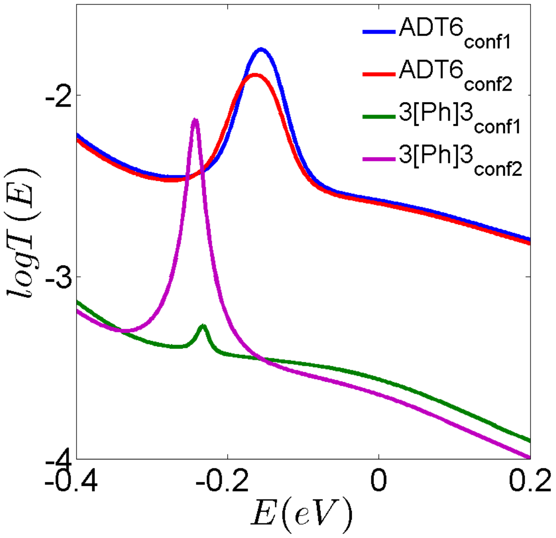


Figure S20: Transmission coefficient vs energy for ADT and 3[Ph]3 with two different confirmations. Conf2's are in ground state energy, whereas conf1's total energy are higher.

We also noted that the height of the resonances is more pronounced in **3[Ph]3** than 1,6-hexanedithiol (**ADT6**). We explain this with different conformations of the molecules. To demonstrate that the height of the resonances with different molecules depends on the conformation of the molecules, we have chosen two configurations for each **ADT6** and **3[Ph]3** molecules. As shown in Figure S20, the resonances due to the sulfur are sensitive to the junction confirmation. The junctions of the curves shown in Figure S20, are similar where red and purple are in ground state energy whereas the blue and green configurations total energy are higher by 0.006 eV and 0.036 eV respectively in which at the room temperature. This shows that by slightly changing the conformation of the molecules, the conductance could be altered significantly in the phenyl case but not for the pure alkane. This difference arises, because in the phenyl case the tunnelling barrier (*e.g.* α in model C below) formed by the backbone between the thiols is correlated with the thiol-gold coupling (*e.g.* γ_L,, γ_R in model C), such that their product is approximately constant, whereas the correlation is much weaker in the case of the pure alkyl chain. This correlation arises from conformation changes in both S-Au bond and the phenyl-methylene bonds in **3[Ph]3**.

4. Two level Breit-Wigner formula:

For two levels systems, the Hamiltonian H is given by:

$$H=\begin{pmatrix} \varepsilon_1 & V_d \\ V_d & \varepsilon_2 \end{pmatrix}$$

where ε_1 and ε_2 are the levels energy coupled to each-other by V_d . If ε_1 (ε_2) is coupled to the left (right) lead, the transmission coefficient *T(E)* could be written as:[15]

$$T= 4\Gamma_L\Gamma_R\, V_d^{\,2} / \left[(E - \varepsilon_1 - \sigma_L + i\Gamma_L)(E - \varepsilon_2 - \sigma_R + i\Gamma_R) - |V_d|^2\right]^2 \qquad \text{(eq. S1)}$$

Where $\sigma_{L,R}$ ($\Gamma_{L,R}$) is the real (imaginary) part of the self-energy due to the left *L* and the right *R* leads.

5. A hierarchy of models for transport through gateway orbitals.

To understand why equation (3) of the main text can be used to describe the role of gateway orbitals, consider the following series of tight binding models.

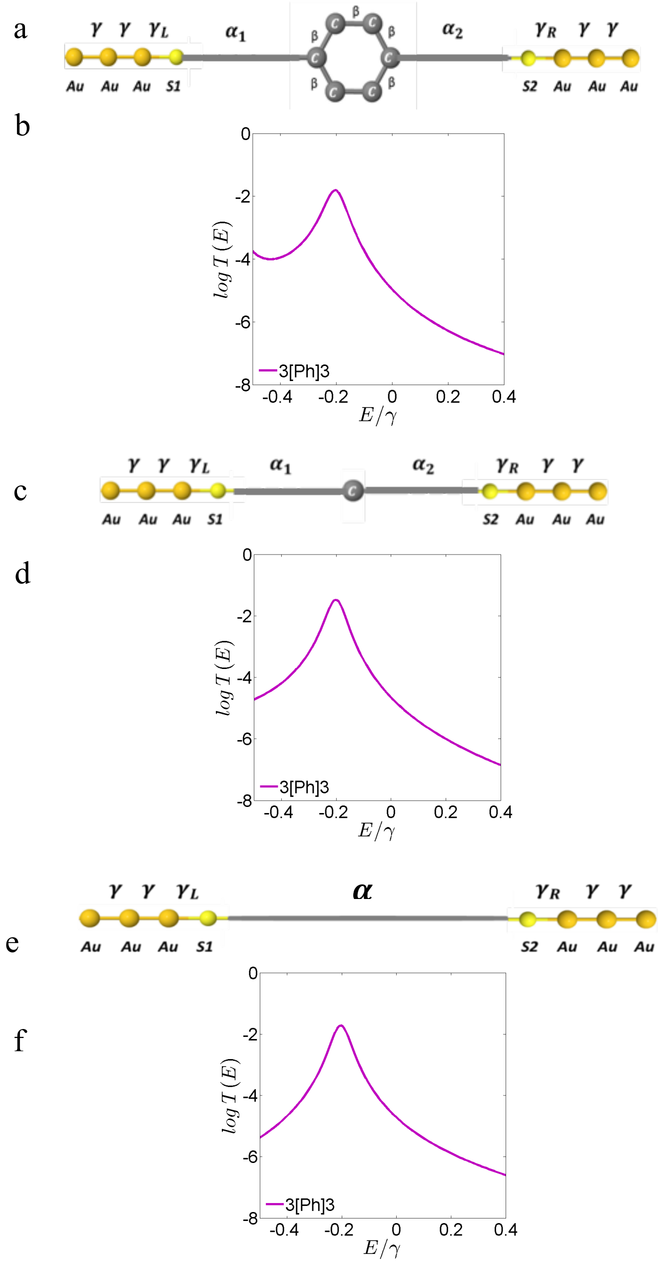


Figure S21: a,b) Tight binding model for X[Ph]X, with complete ring and transmission curve corresponding models shown in figure SI.5.a, c,d) simplified model of the ring with one atom at middle and transmission curve corresponding models respectively, e,f) model with future simplifying by α for X[Ph]X, and transmission curve corresponding model respectively.

In the tunnelling regime, model (a) can be mapped onto (b) and then onto (c) using decimation. Alternatively, an appropriate choice of parameters can be made in each case to yield transmission curves which are almost identical for the three models. This shows that the minimal model (c) described by equation (3), captures the main features of the more complex models (b) and (a).

Fitting equation (3) to DFT results.

The following tables show the result of fitting a simple bridge model of equation (3) to DFT results. The fitted formula is: $T = T_0 + T_1$, where T_1 is given by equation (3) of the main text and T_0 describes parallel conductance channels not contained in equation (1). These fitted curves are plotted in figure SI.22 below.

Table S2: Parameters extracted from DFT results for phenyl used in bridge model.

n(CH$_2$)	ε_F	Γ	α	T_0	T_1	$\Gamma\times\alpha$	a $=\alpha/\Gamma$	*Au_S_C Angle left lead*	*Au_S_C Angle right lead*	*phenyl _left chain Angle*	*Phenyl_right chain Angle*
2	-0.124	0.058	3.3×10^{-03}	8.0×10^{-04}	1.53×10^{-04}	1.91×10^{-04}	0.0569	102.2	101.6	113.9	113.3
6	-0.189	0.039	7.8×10^{-04}	1.1×10^{-04}	2.69×10^{-05}	3.04×10^{-05}	0.02	110	109.3	115.1	117.6
8	-0.234	0.048	5.0×10^{-04}	1.1×10^{-05}	7.8×10^{-05}	2.40×10^{-05}	0.0104	110.7	109	110.8	113.5
12	-0.277	0.025	2.0×10^{-04}	4.1×10^{-08}	1.57×10^{-04}	5.0×10^{-06}	0.0080	111.3	108.8	114.7	114.8

Table S3: Parameters extracted from DFT results for alkane used in bridge model.

n(CH$_2$)	ε_F	Γ	α	T_0	T_1	$\Gamma\times\alpha$	a $= \alpha/\Gamma$	*Au_S_C Angle left lead*	*Au_S_C Angle right lead*
6	-0.109	0.027	1.82×10^{-03}	2.70×10^{-03}	2.2×10^{-05}	4.91×10^{-05}	0.0674	118.2	116.4
8	-0.123	0.029	4.15×10^{-04}	3.30×10^{-04}	1.95×10^{-06}	1.20×10^{-05}	0.0143	116.5	115
10	-0.142	0.026	5.15×10^{-05}	4.86×10^{-05}	4×10^{-08}	1.34×10^{-06}	0.0020	115.6	113
12	-0.151	0.028	2.70×10^{-05}	7.40×10^{-06}	2×10^{-08}	7.56×10^{-07}	0.000964	115.2	113.2

Figure S22 shows a comparison between the transmission coefficients form the above ‘inert bridge model’ and the DFT results of figure 7a and 7c. This shows that the different beta’ value arises from a systematic variation in the self energy of the phenyls, which is not present for the alkanes.

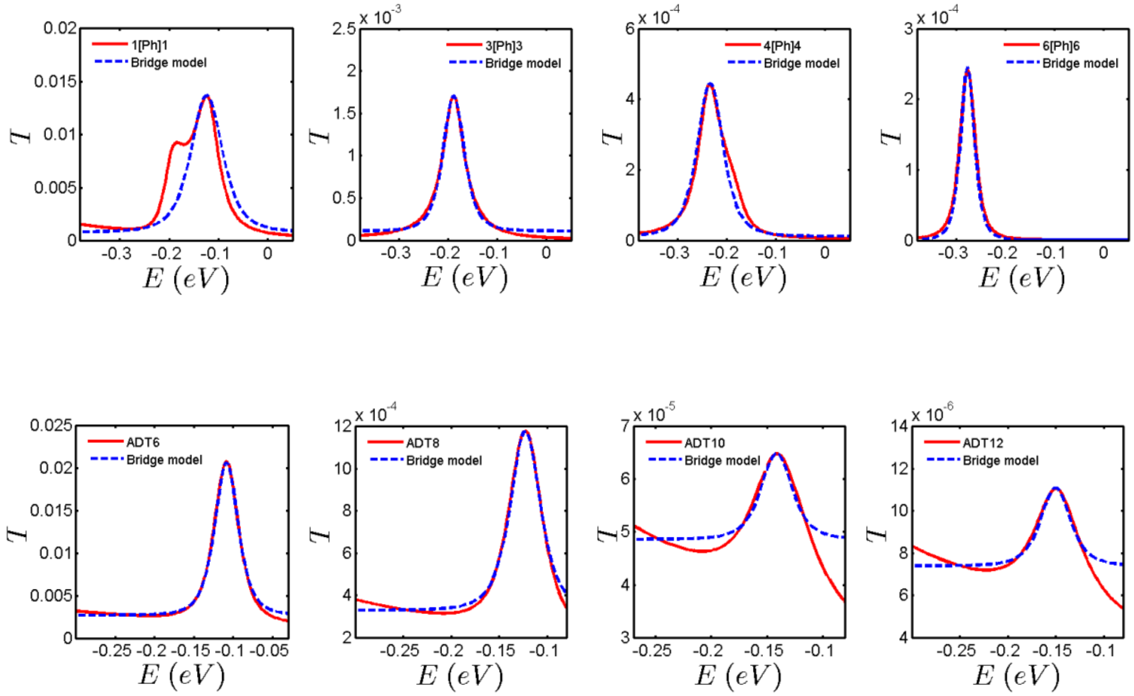


Figure S22: Transmission coefficients form the above 'inert bridge model' and the DFT results of figure 4a) phenyl and 4c) alkane.

Role of geometry and fluctuations – sensitivity to geometry

The right-most columns of Tables S2 and S3 show systematic variations in selected bond angles of the molecules with length. These angles are defined as follows:

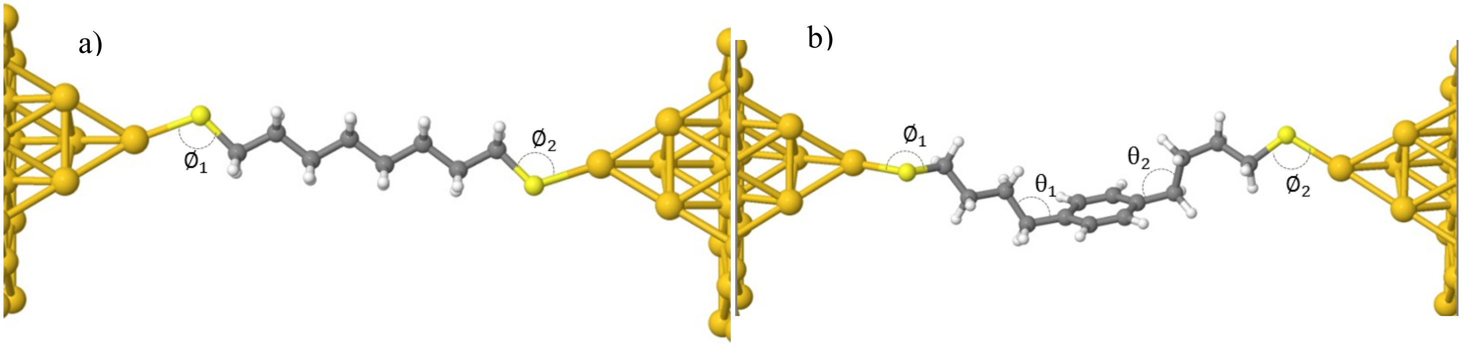


Figure S23: Relaxed structure of a) **ADT8** and b) **4[Ph]4** where, $\emptyset_1$ is an angle of Au-S-C to the left lead and $\emptyset_2$ is an angle of Au-S-C to the right lead. θ_1 is an angle of phenyl to the right chain and θ_2 is an angle of phenyl to the left chain.

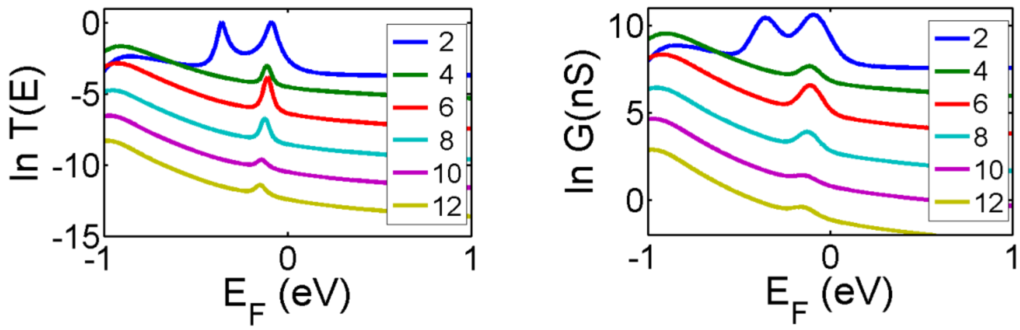
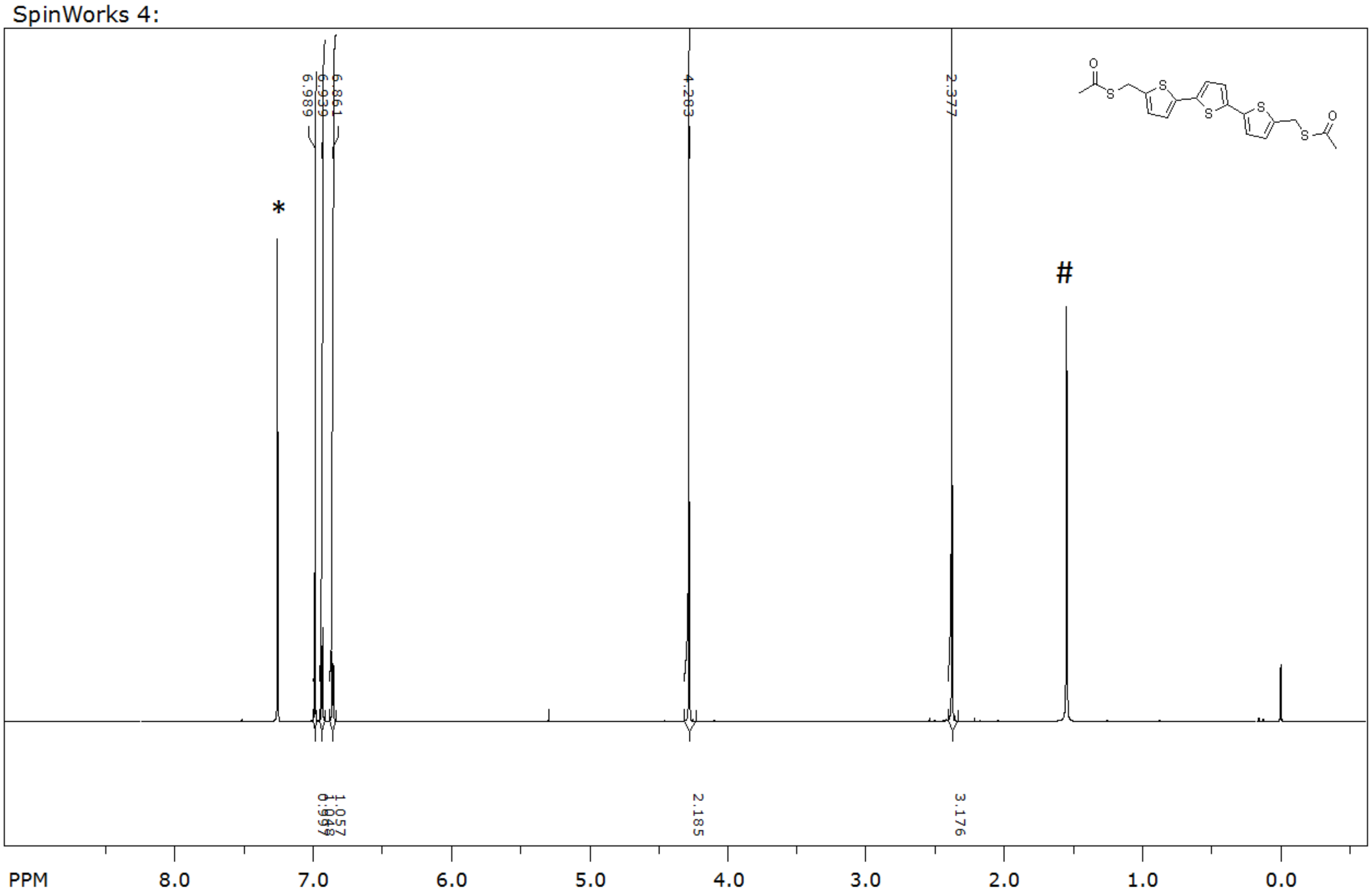


Figure S24: a) Transmission coefficients of **ADT**, b) The room-temperature conductances of **ADT**, vs. Fermi energy for alkyl chains with different numbers of CH_2 groups. $E_F = 0$ corresponds to the DFT-predicted Fermi energy.

6. NMR spectra

1[T3]1



file: ...phene-dimethylthioac. CDCl3 1H\fid expt: <zg30>
transmitter freq.: 400.132801 MHz
time domain size: 65536 points
width: 6377.55 Hz = 15.9386 ppm = 0.097314 Hz/pt
number of scans: 96

freq. of 0 ppm: 400.130010 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

Figure S25: ^{1}H NMR of **1[T3]1**. 400 MHz, $CDCl_3$. Solvent peak starred, H_2O peak hashed.

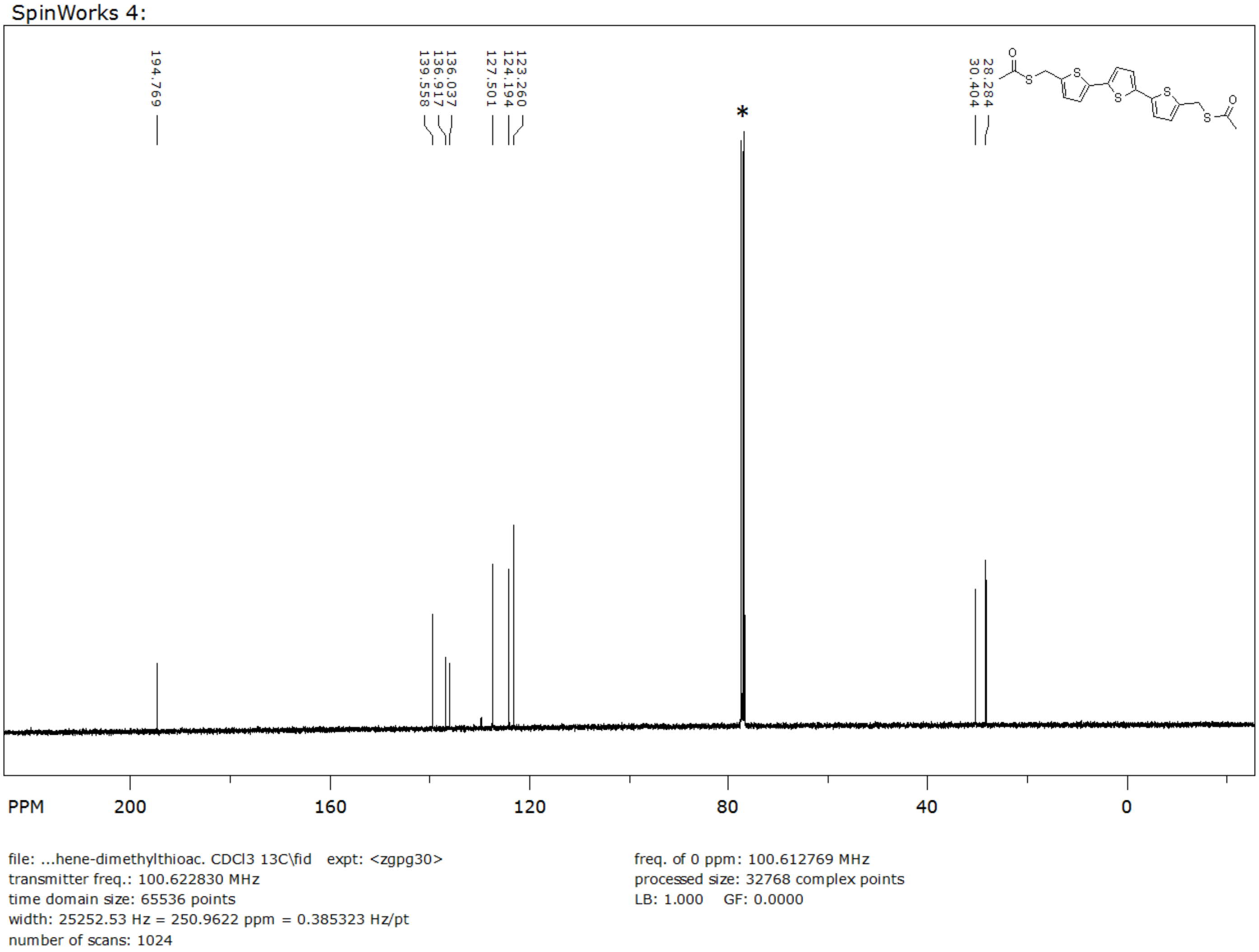


Figure S26: ^{13}C NMR of **1[T3]1**. 100 MHz, $CDCl_3$. Solvent peak starred.

3[T3]3

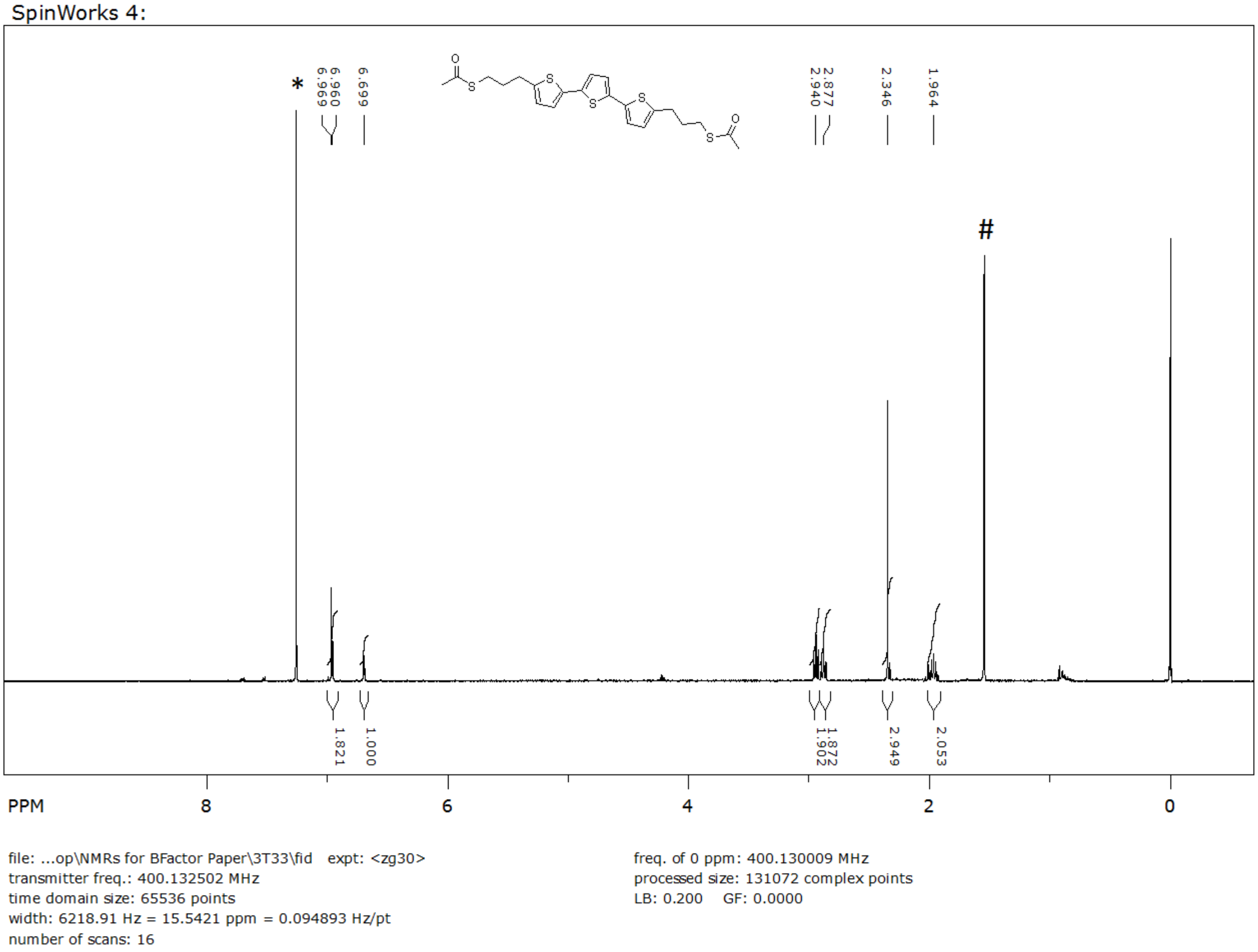
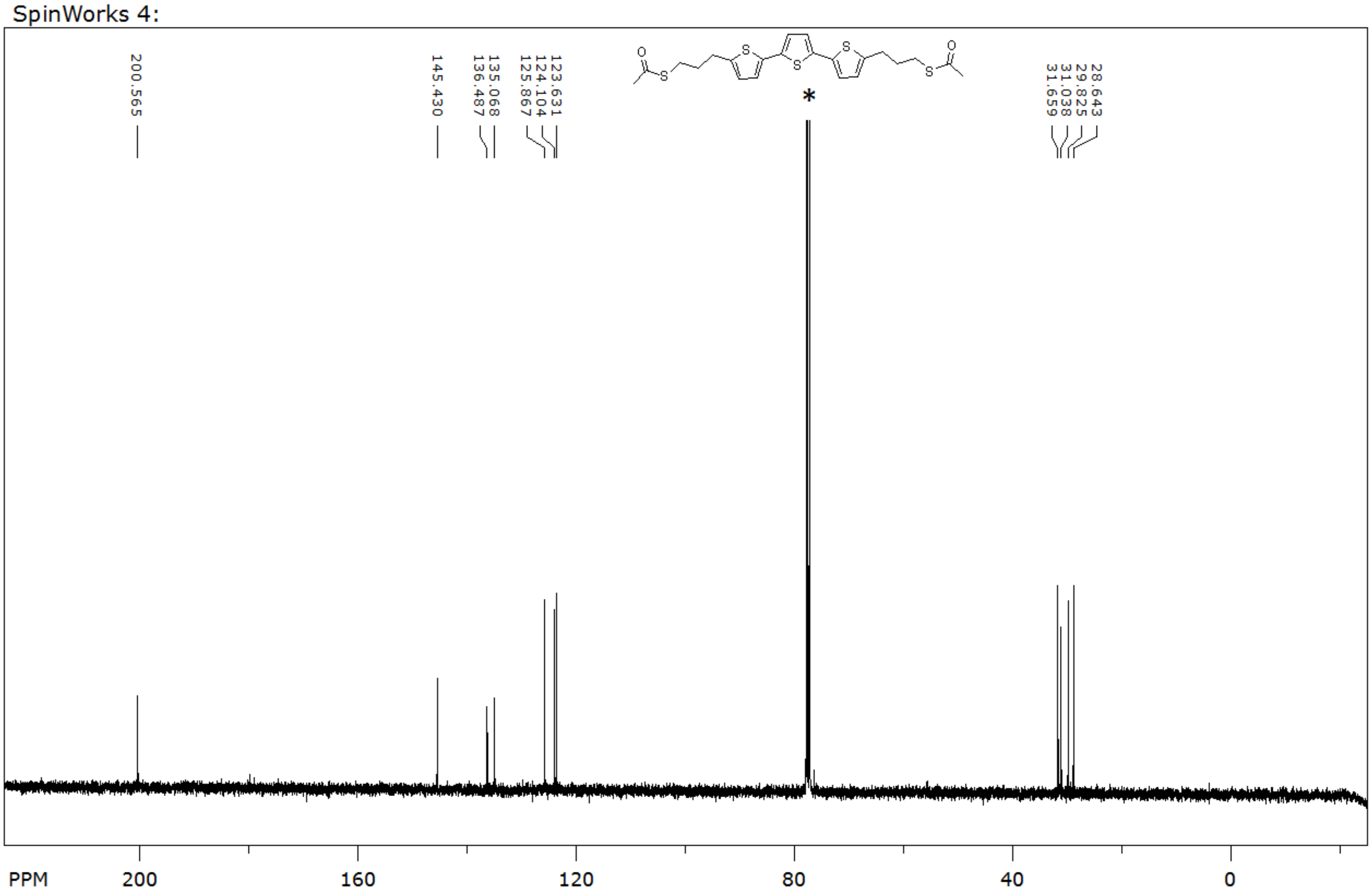


Figure S27: ^{1}H NMR of **3[T3]3**. 400 MHz, $CDCl_3$. Solvent peak starred, H_2O peak hashed.

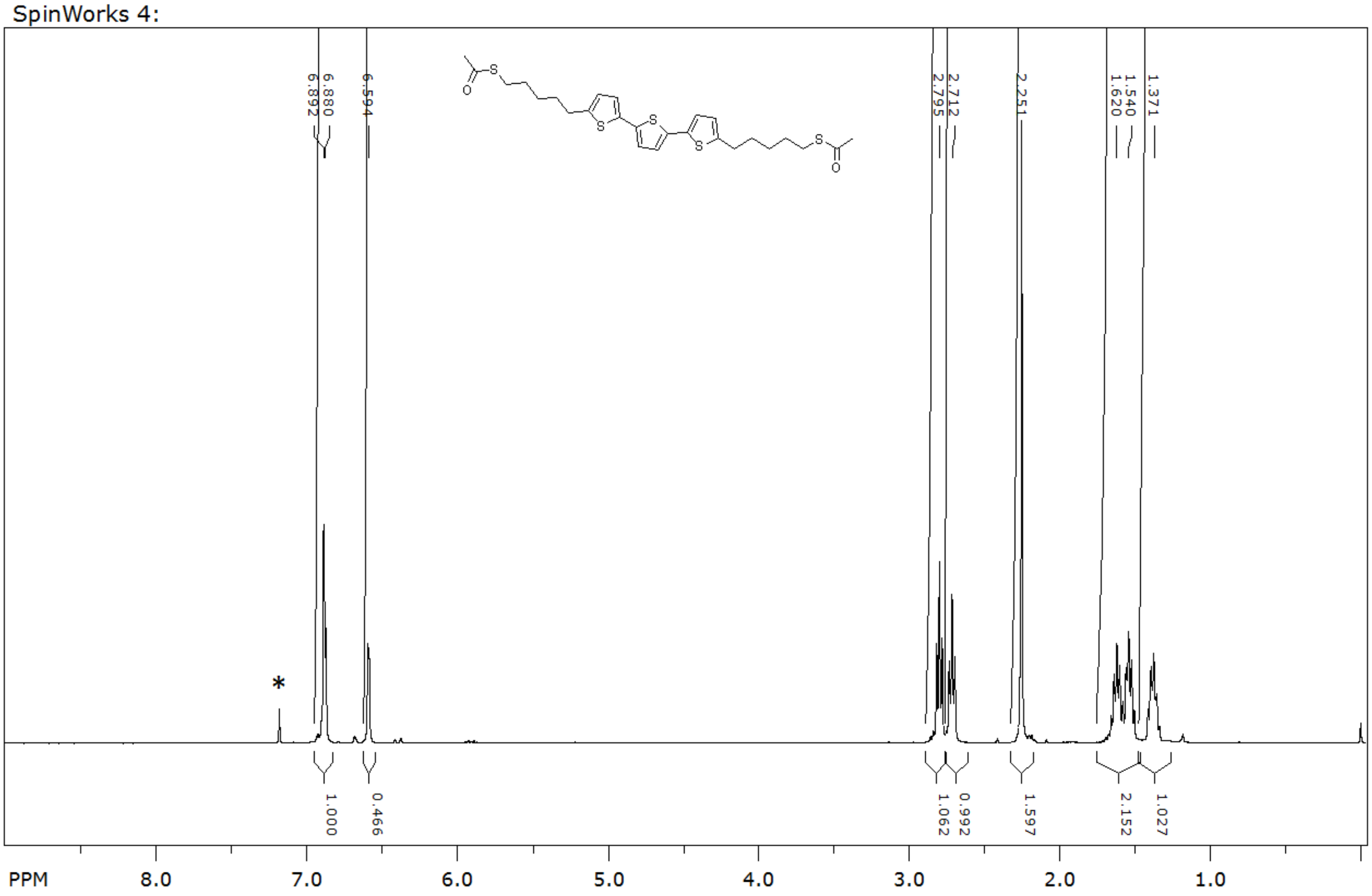


```
file: C:\Users\vezzo\Desktop\542\fid   expt: <zgpg30>
transmitter freq.: 100.622790 MHz
time domain size: 32768 points
width: 25125.63 Hz = 249.7012 ppm = 0.766773 Hz/pt
number of scans: 1024
```

```
freq. of 0 ppm: 100.612729 MHz
processed size: 65536 complex points
LB: 1.000    GF: 0.0000
```

Figure S28: ^{13}C NMR of **3[T3]3**. 100 MHz, $CDCl_3$. Solvent peak starred.

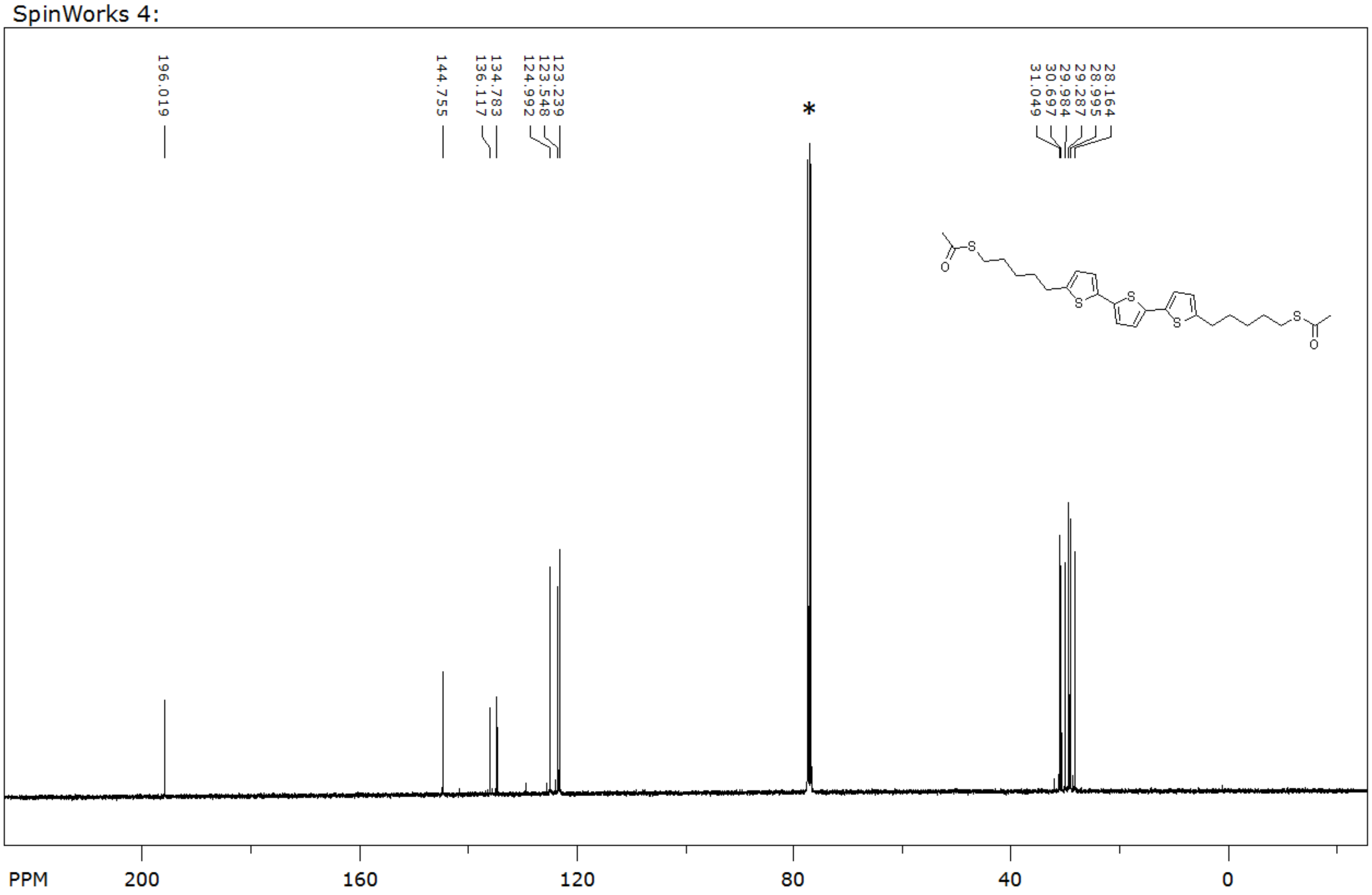
5[T3]5



```
file: ...ioacetate (dicoupled) CDCl3 1H\fid   expt: <zg30>
transmitter freq.: 400.132801 MHz
time domain size: 65536 points
width: 6393.86 Hz = 15.9793 ppm = 0.097563 Hz/pt
number of scans: 64

freq. of 0 ppm: 400.130038 MHz
processed size: 65536 complex points
LB: 0.300     GF: 0.0000
```

Figure S29: ^{1}H NMR of **5[T3]5**. 400 MHz, $CDCl_3$. Solvent peak starred.



```
file: ...ioacetate (dicoupled) CDCl3 13\fid   expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 25252.53 Hz = 250.9622 ppm = 0.385323 Hz/pt
number of scans: 1024

freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000     GF: 0.0000
```

Figure S30: ^{13}C NMR of **5[T3]5**. 100 MHz, CDCl$_3$. Solvent peak starred.

8[T3]8

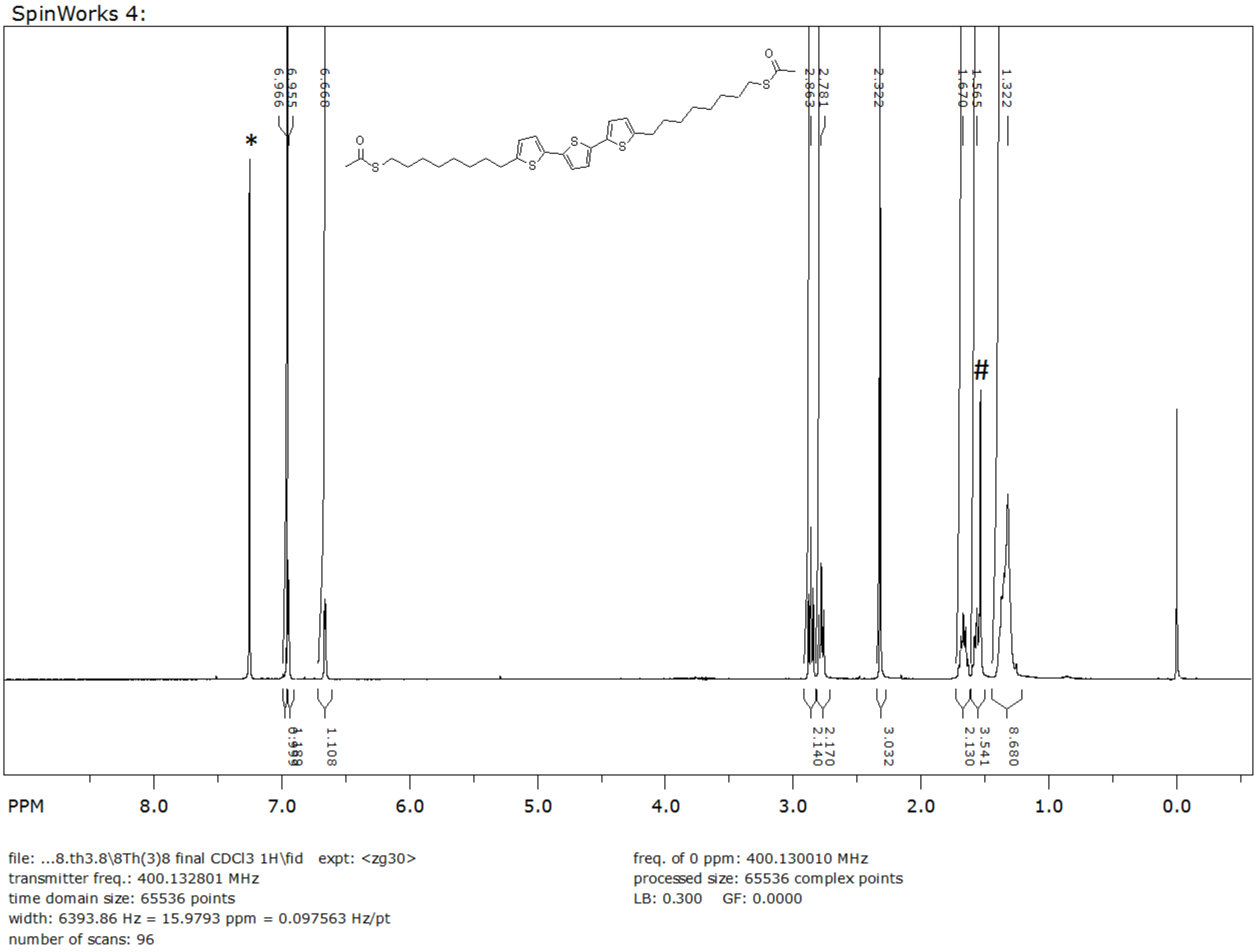
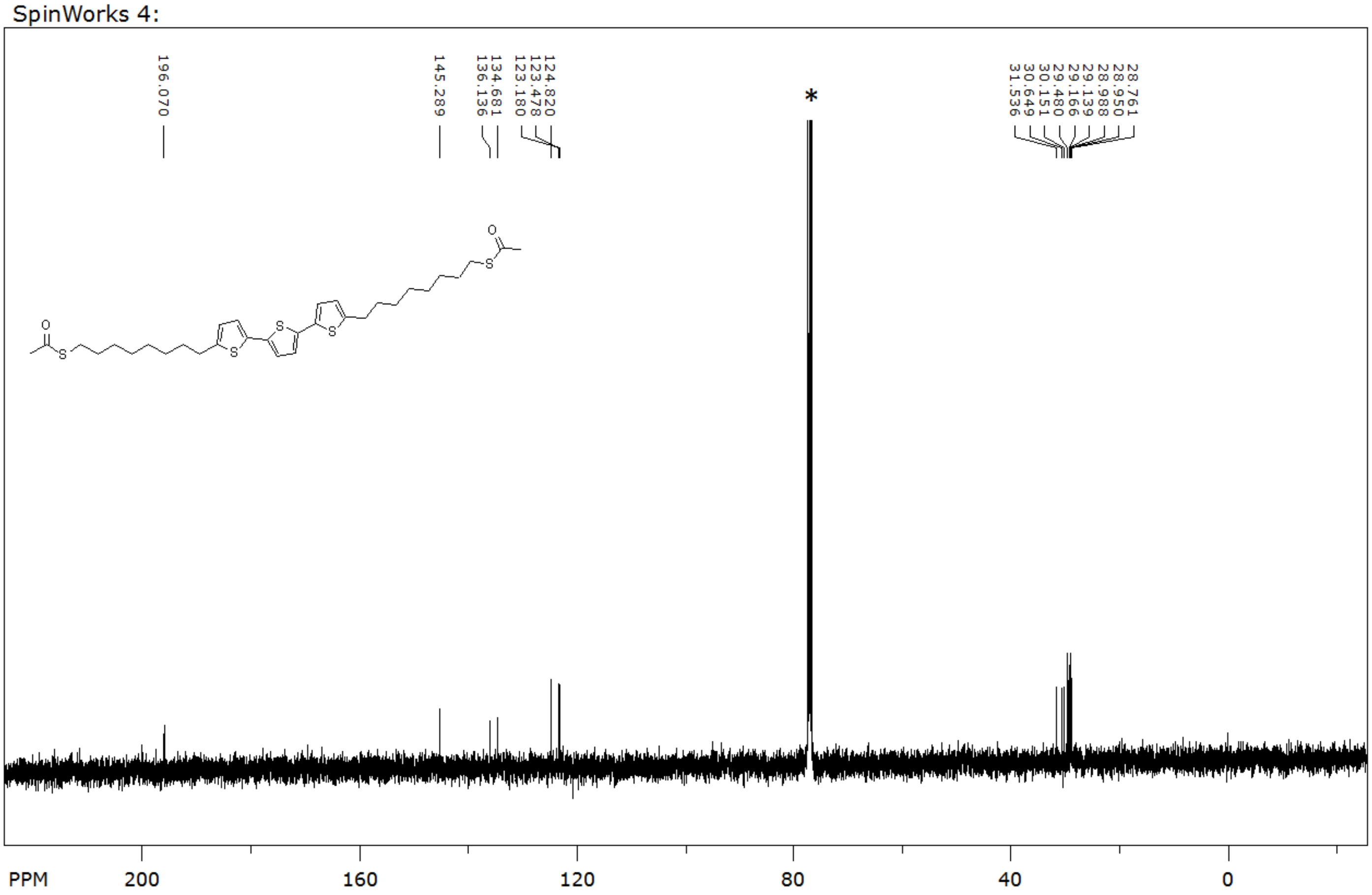


Figure S31: ^{1}H NMR of **8[T3]8**. 400 MHz, $CDCl_3$. Solvent peak starred, H_2O peak hashed.

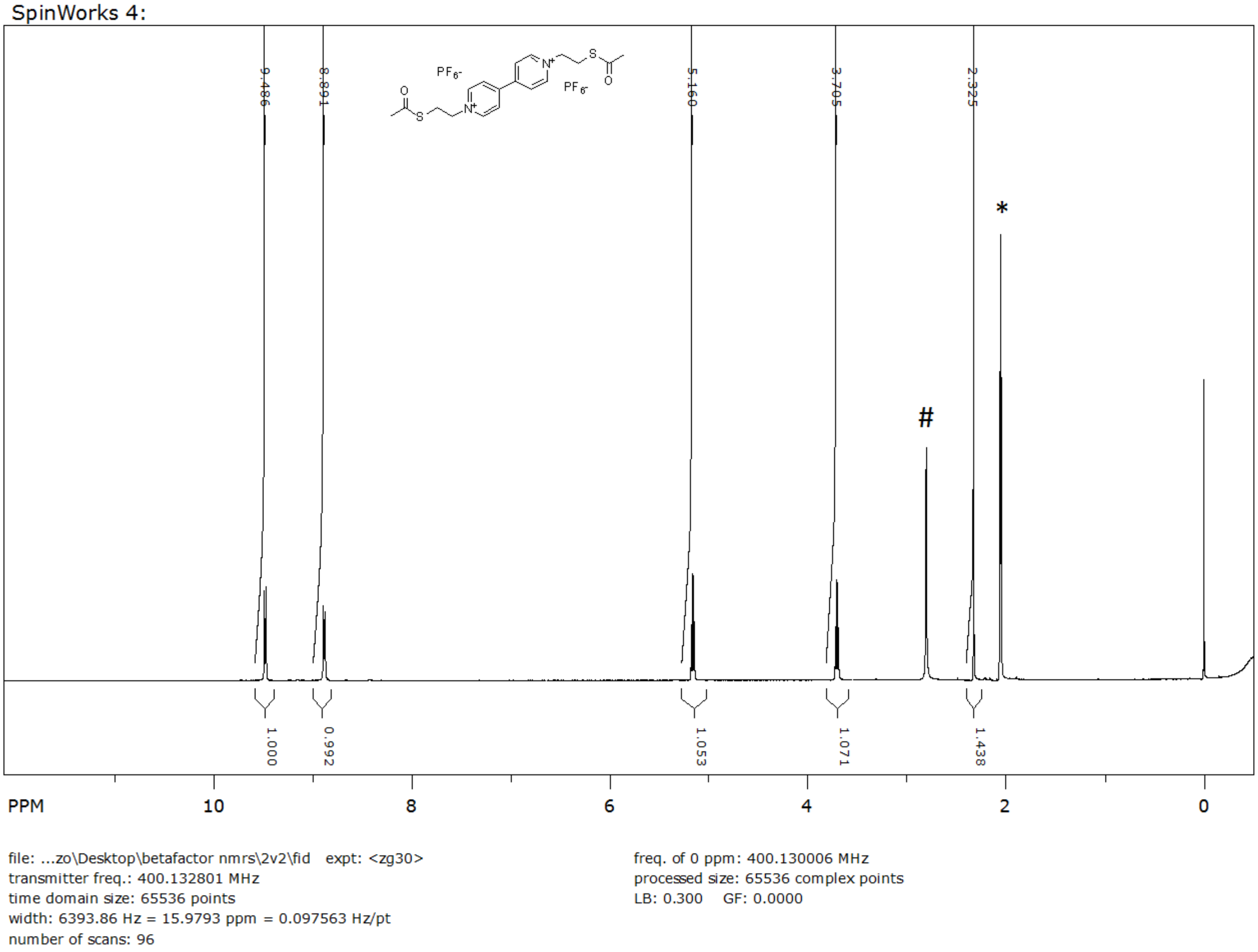


file: ....th3.8\8Th(3)8 final CDCl3 13C\fid   expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 25252.53 Hz = 250.9622 ppm = 0.385323 Hz/pt
number of scans: 1024

freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000   GF: 0.0000

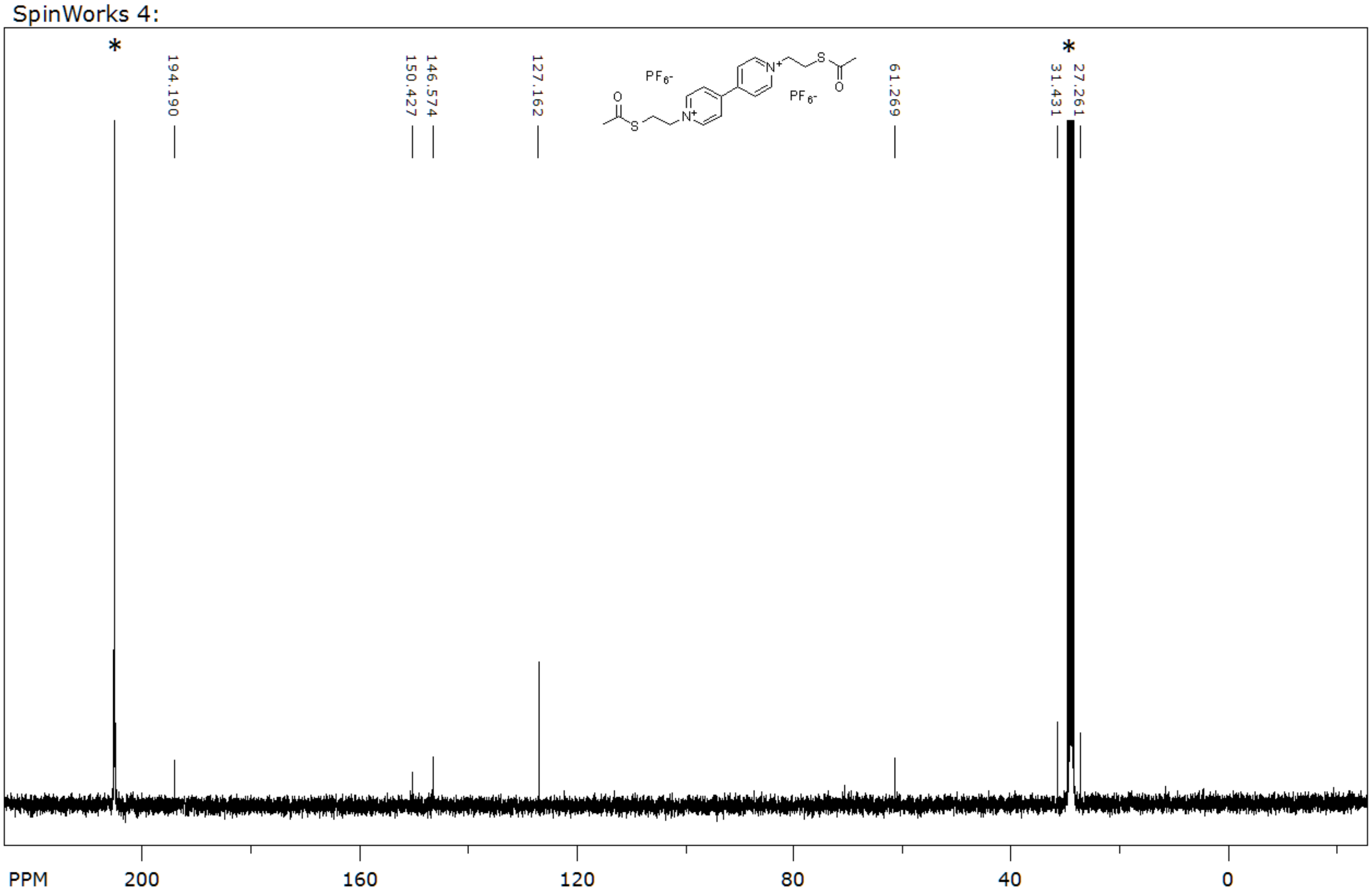
Figure S32: ^{13}C NMR of **8[T3]8**. 100 MHz, $CDCl_3$. Solvent peak starred.

2[V]2



```
file: ...zo\Desktop\betafactor nmrs\2v2\fid   expt: <zg30>
transmitter freq.: 400.132801 MHz
time domain size: 65536 points
width: 6393.86 Hz = 15.9793 ppm = 0.097563 Hz/pt
number of scans: 96
freq. of 0 ppm: 400.130006 MHz
processed size: 65536 complex points
LB: 0.300    GF: 0.0000
```

Figure S33: ^{1}H NMR of **2[V]2**. 400 MHz, $(CD_3)_2CO$. Solvent peak starred, H_2O peak hashed.



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transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 25252.53 Hz = 250.9622 ppm = 0.385323 Hz/pt
number of scans: 1024
```

```
freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000    GF: 0.0000
```

Figure S34: ^{13}C NMR of **2[V]2**. 100 MHz, $(CD_3)_2CO$. Solvent peaks starred.

4[V]4

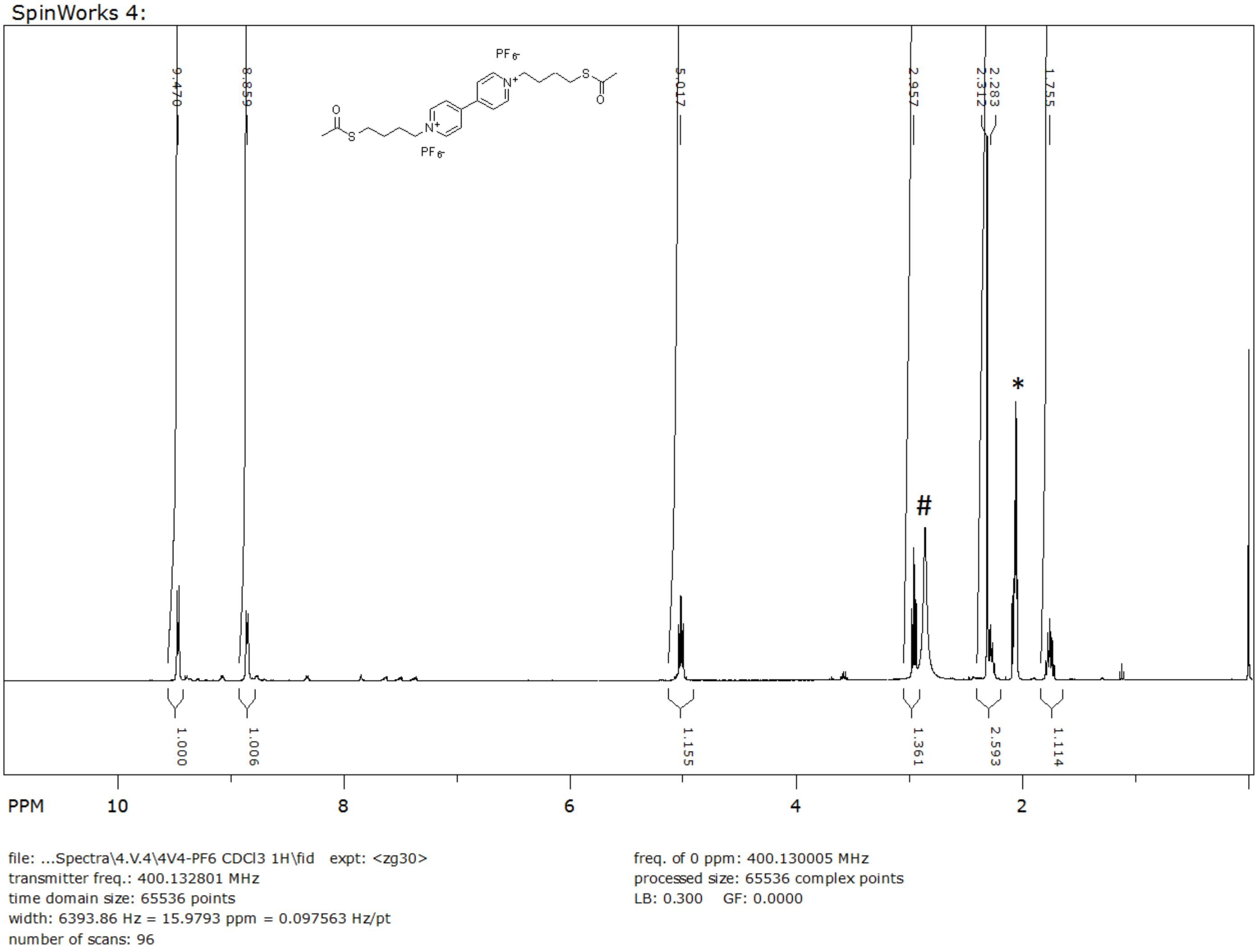


Figure S35: ^{1}H NMR of **4[V]4**. 400 MHz, $(CD_3)_2CO$. Solvent peak starred, H_2O peak hashed.

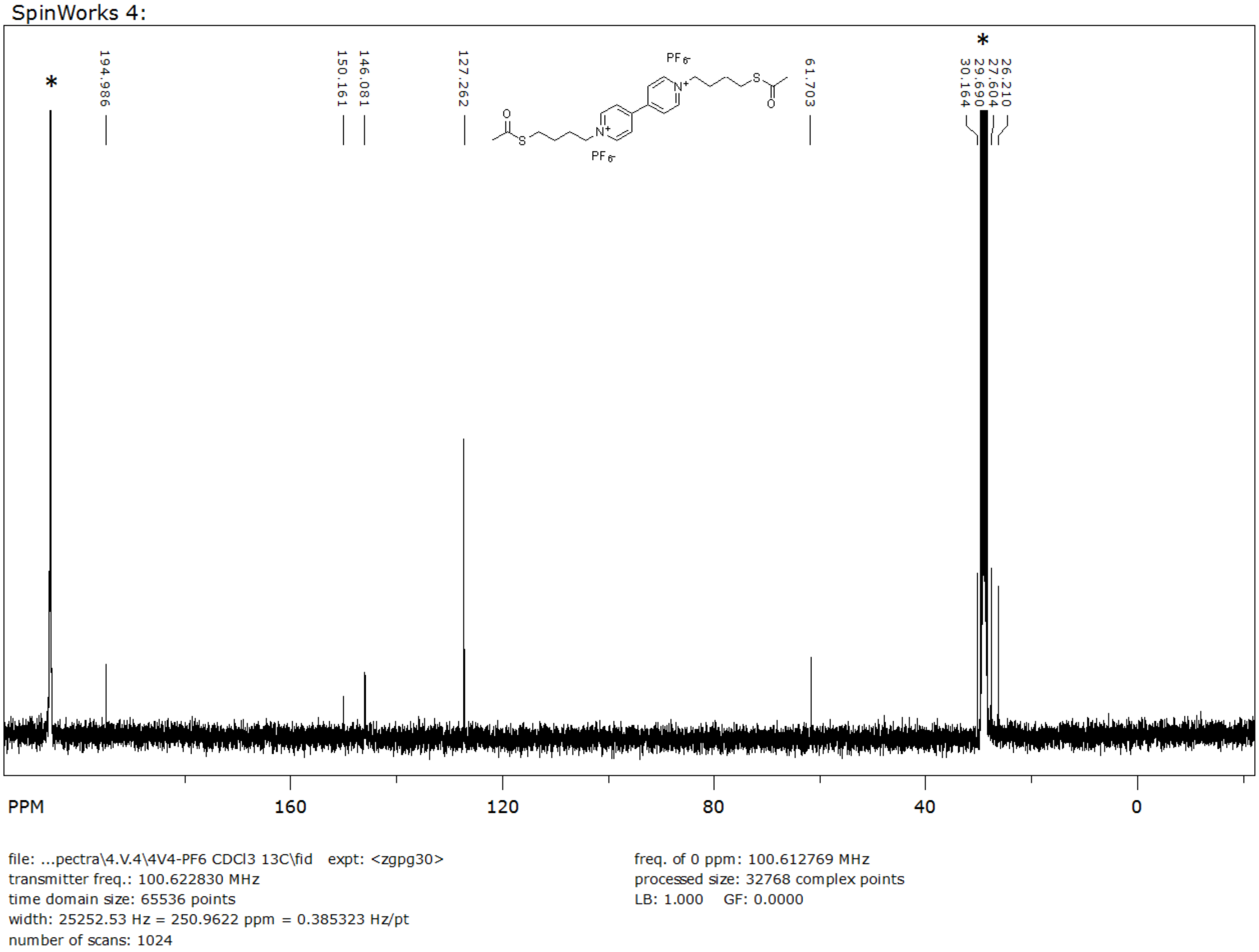
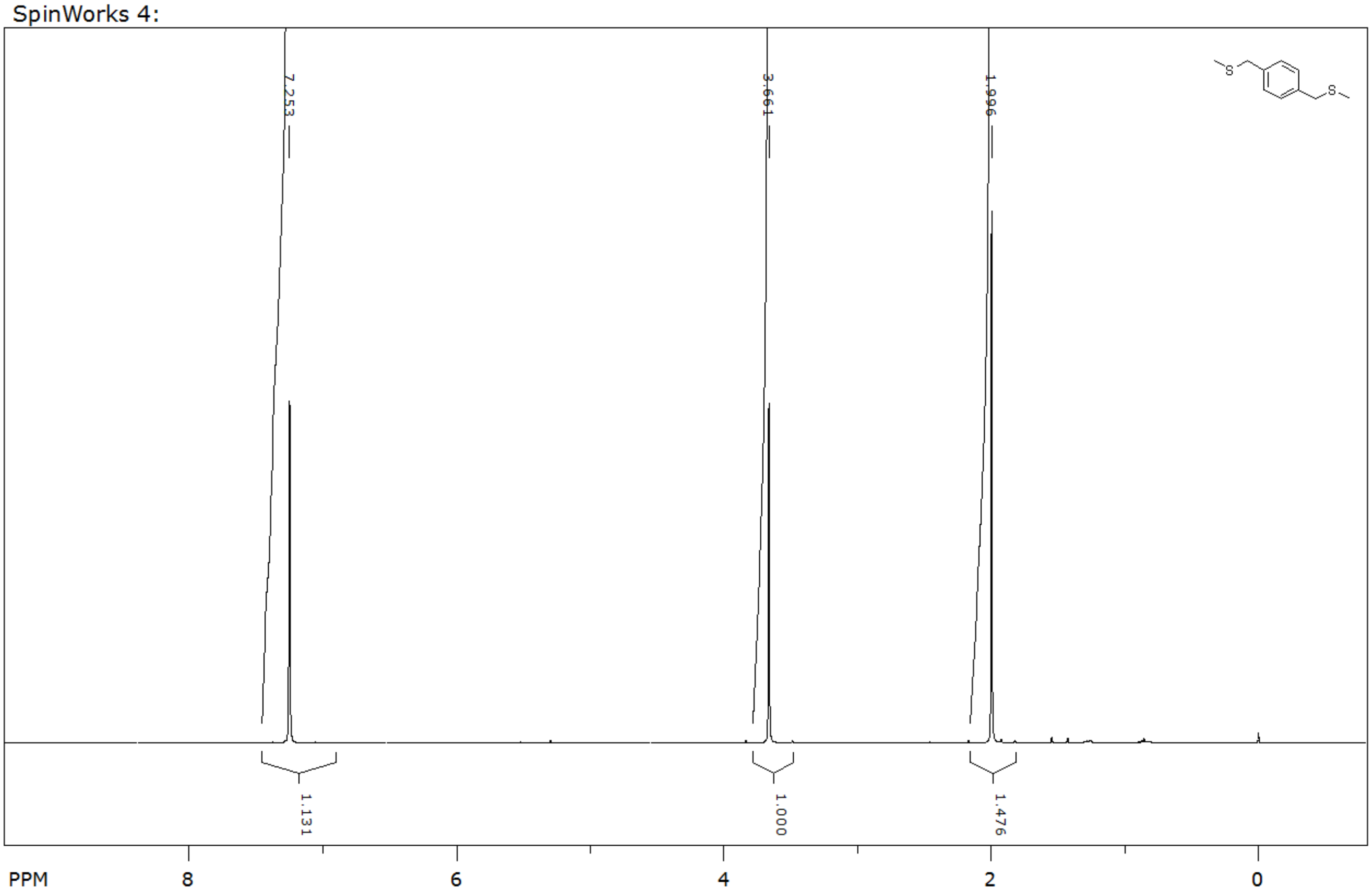


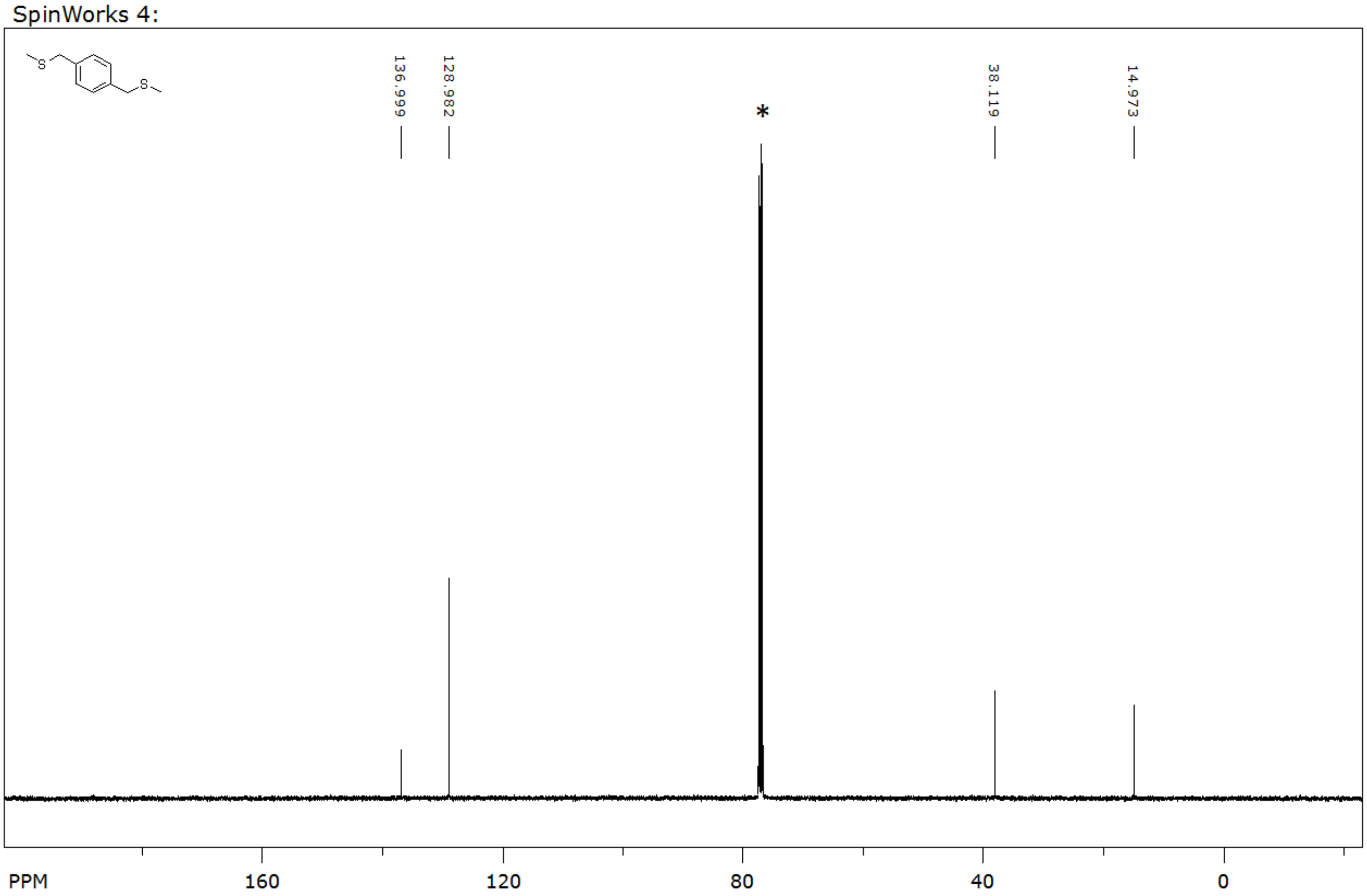
Figure S36: ^{13}C NMR of **4[V]4**. 100 MHz, $(CD_3)_2CO$. Solvent peaks starred.

1[Ph]1-SMe



```
file: ...p\betafactor nmrs\1ph1sme\100H\fid   expt: <zg30>          freq. of 0 ppm: 400.130010 MHz
transmitter freq.: 400.132801 MHz                                   processed size: 65536 complex points
time domain size: 65536 points                                      LB: 0.300     GF: 0.0000
width: 6393.86 Hz = 15.9793 ppm = 0.097563 Hz/pt
number of scans: 64
```

Figure S37: ^{1}H NMR of **1[Ph]1-SMe**. 400 MHz, $CDCl_3$. Solvent peak obscured by resonance at 7.25 ppm.

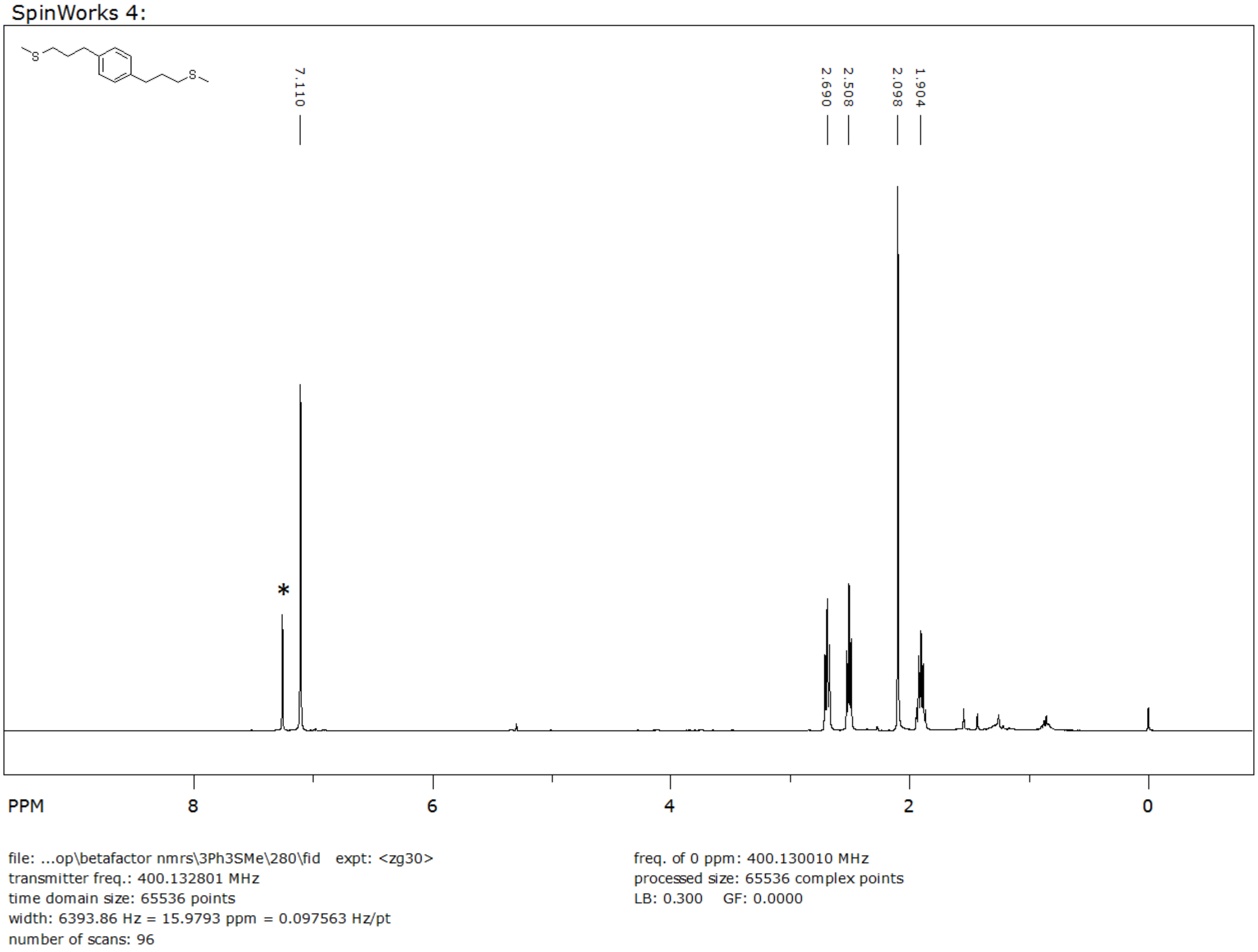


```
file: ...p\betafactor nmrs\1ph1sme\101C\fid   expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 25252.53 Hz = 250.9622 ppm = 0.385323 Hz/pt
number of scans: 1024

freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000    GF: 0.0000
```

Figure S38: ^{13}C NMR of **1[Ph]1-SMe**. 100 MHz, $CDCl_3$. Solvent peak starred.

3[Ph]3-SMe



```
file: ...op\betafactor nmrs\3Ph3SMe\280\fid   expt: <zg30>
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time domain size: 65536 points
width: 6393.86 Hz = 15.9793 ppm = 0.097563 Hz/pt
number of scans: 96

freq. of 0 ppm: 400.130010 MHz
processed size: 65536 complex points
LB: 0.300    GF: 0.0000
```

Figure S39: ^{1}H NMR of **3[Ph]3-SMe**. 400 MHz, $CDCl_3$. Residual solvent peak starred.

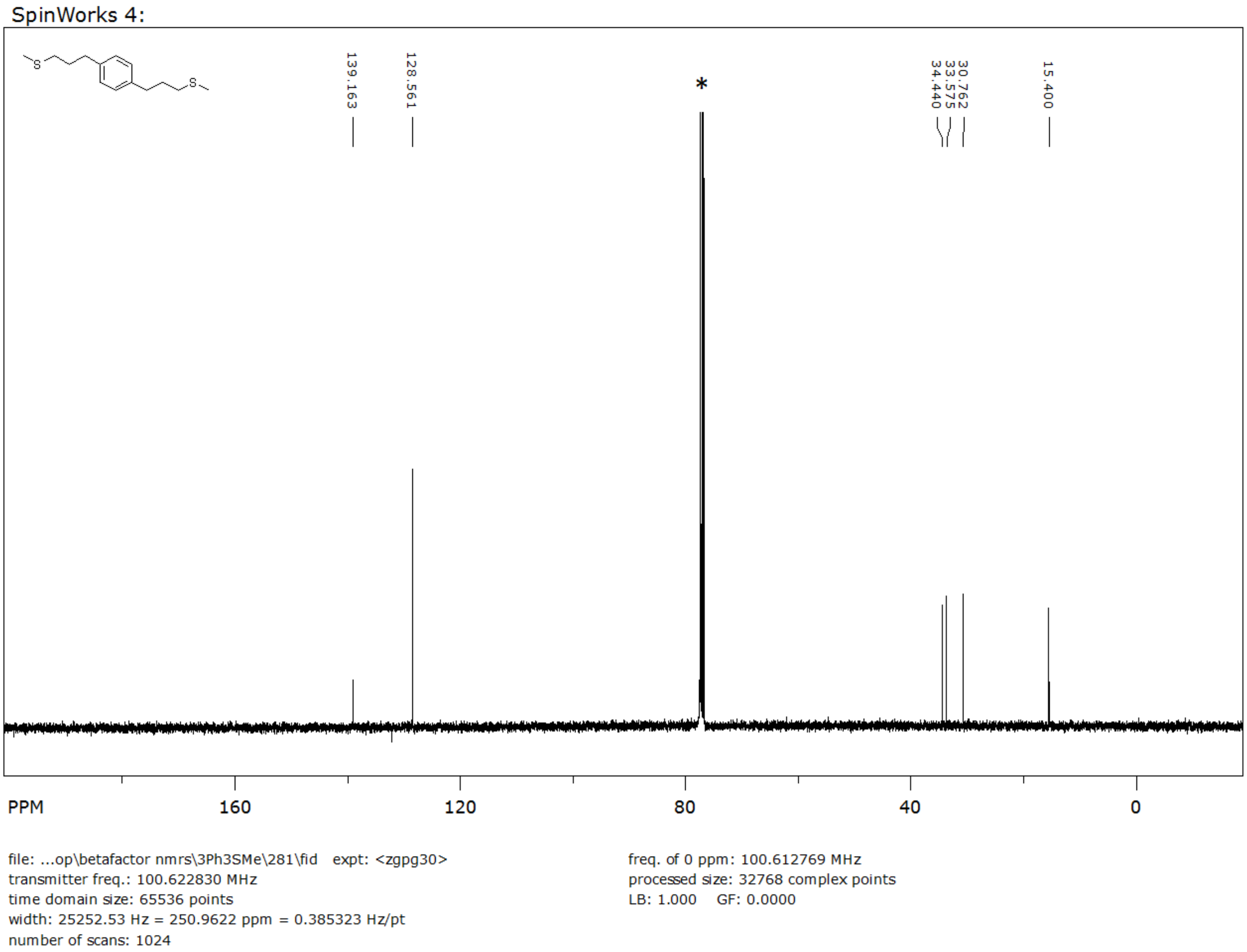
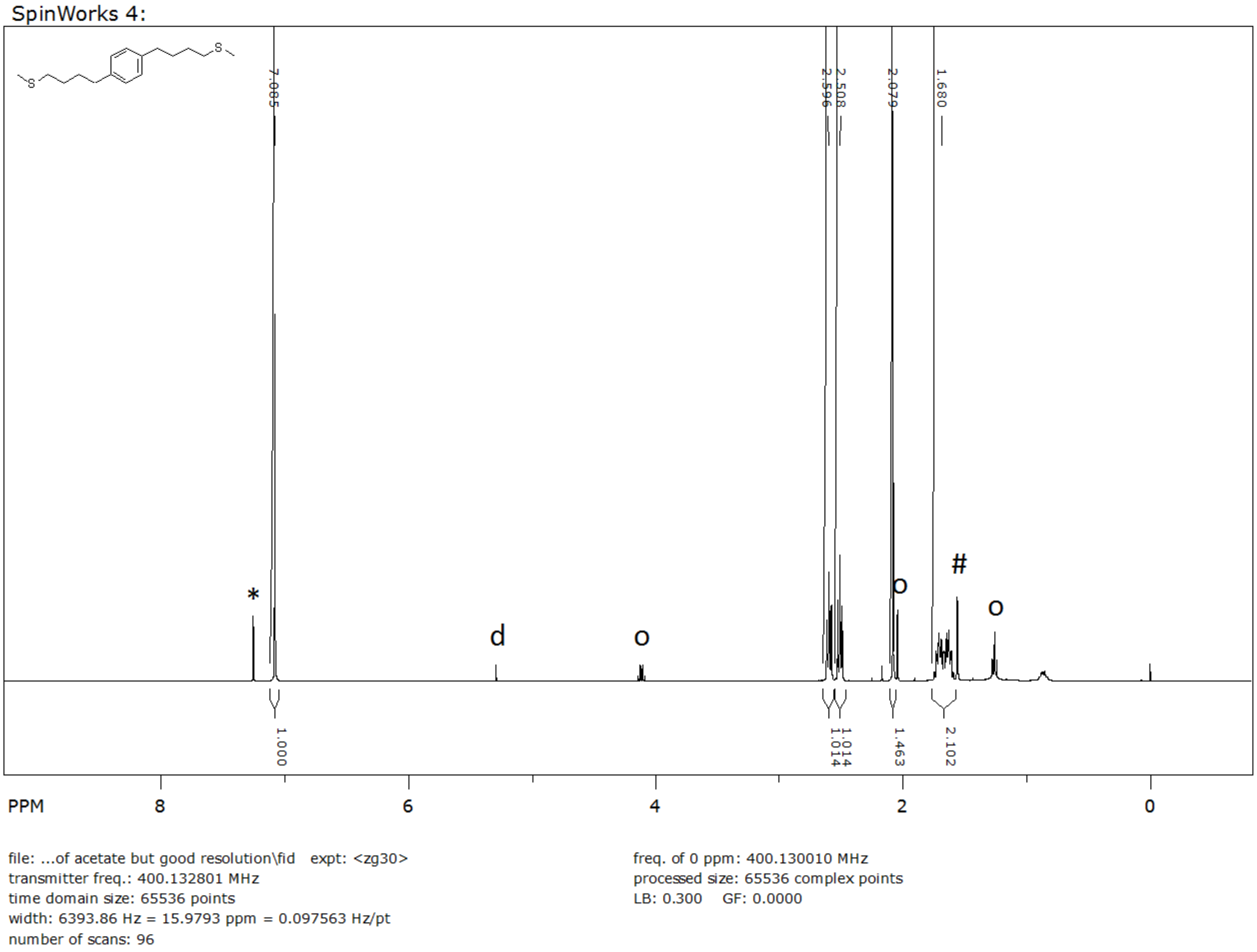


Figure S40: ^{13}C NMR of **3[Ph]3-SMe**. 100 MHz, $CDCl_3$. Solvent peak starred.

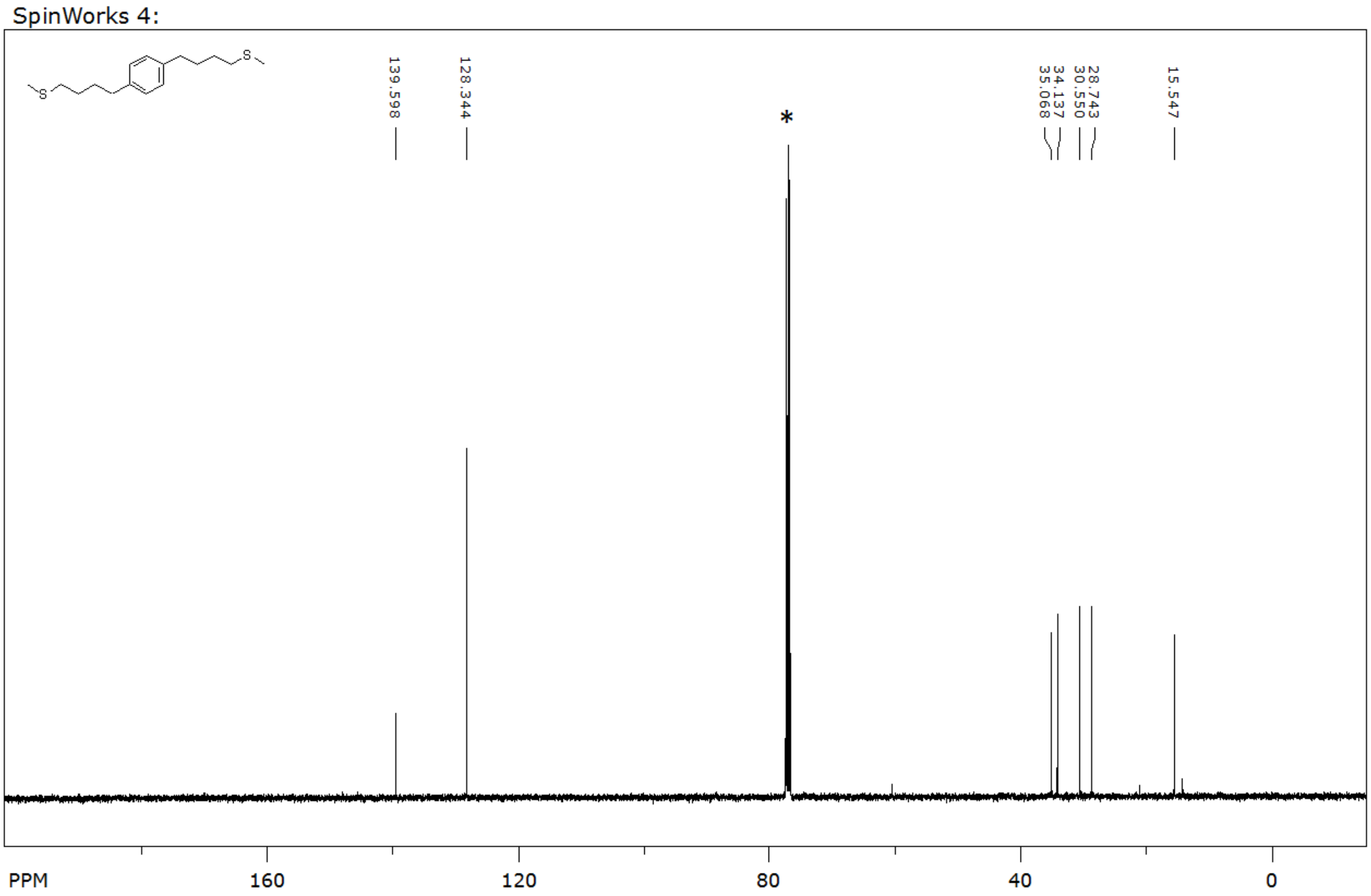
4[Ph]4-SMe



```
file: ...of acetate but good resolution\fid   expt: <zg30>
transmitter freq.: 400.132801 MHz
time domain size: 65536 points
width: 6393.86 Hz = 15.9793 ppm = 0.097563 Hz/pt
number of scans: 96
```

```
freq. of 0 ppm: 400.130010 MHz
processed size: 65536 complex points
LB: 0.300     GF: 0.0000
```

Figure S 41: ^{1}H NMR of **4[Ph]4-SMe**. 400 MHz, $CDCl_3$. Residual solvent peak starred, water peak hashed. O is residual ethyl acetate and d is residual dichloromethane that couldn't be removed on pumping in vacuo.

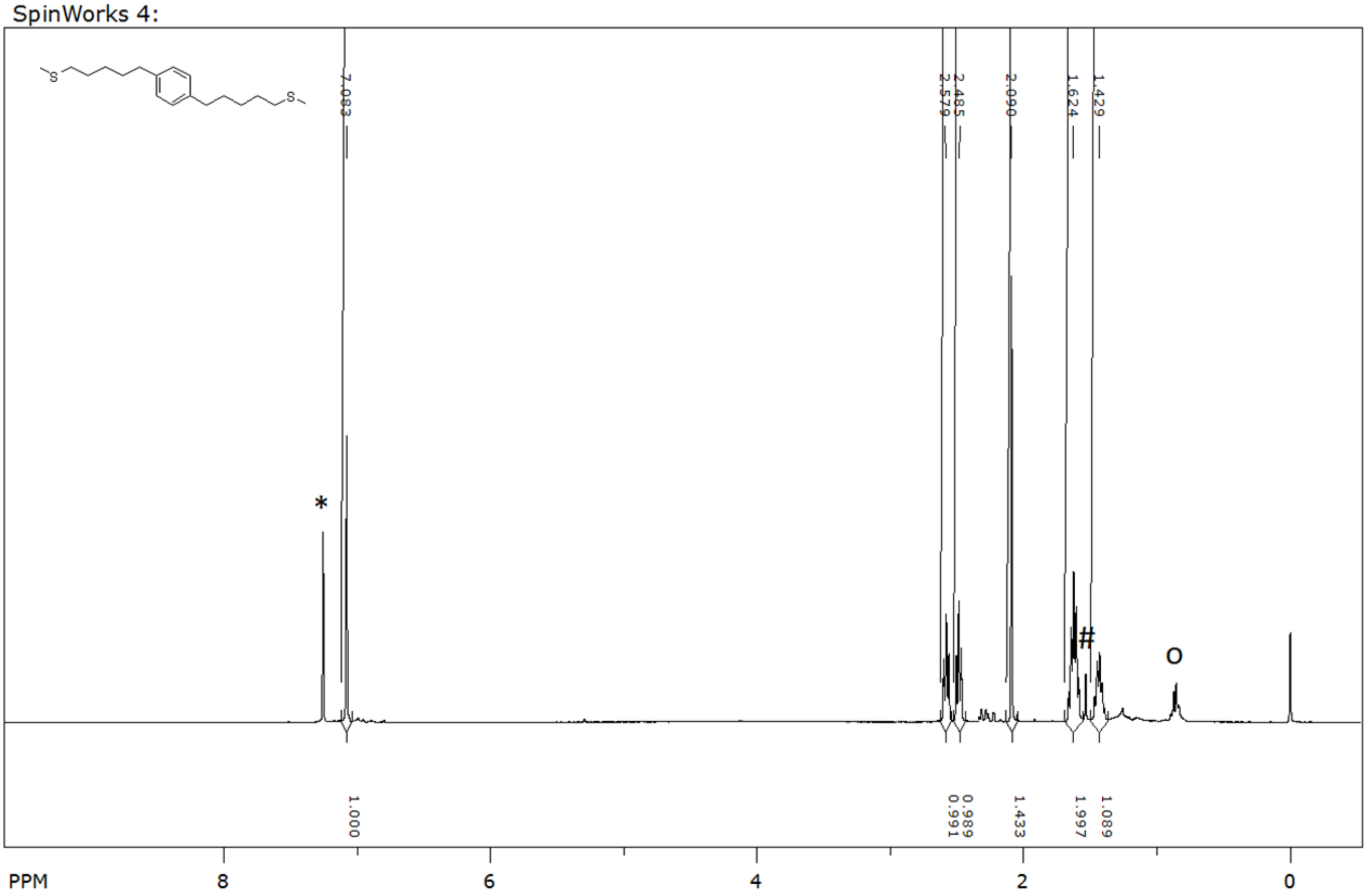


```
file: ...or nmrs\4Ph4SMe\231carbon conc\fid   expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 25252.53 Hz = 250.9622 ppm = 0.385323 Hz/pt
number of scans: 1024
```

```
freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000     GF: 0.0000
```

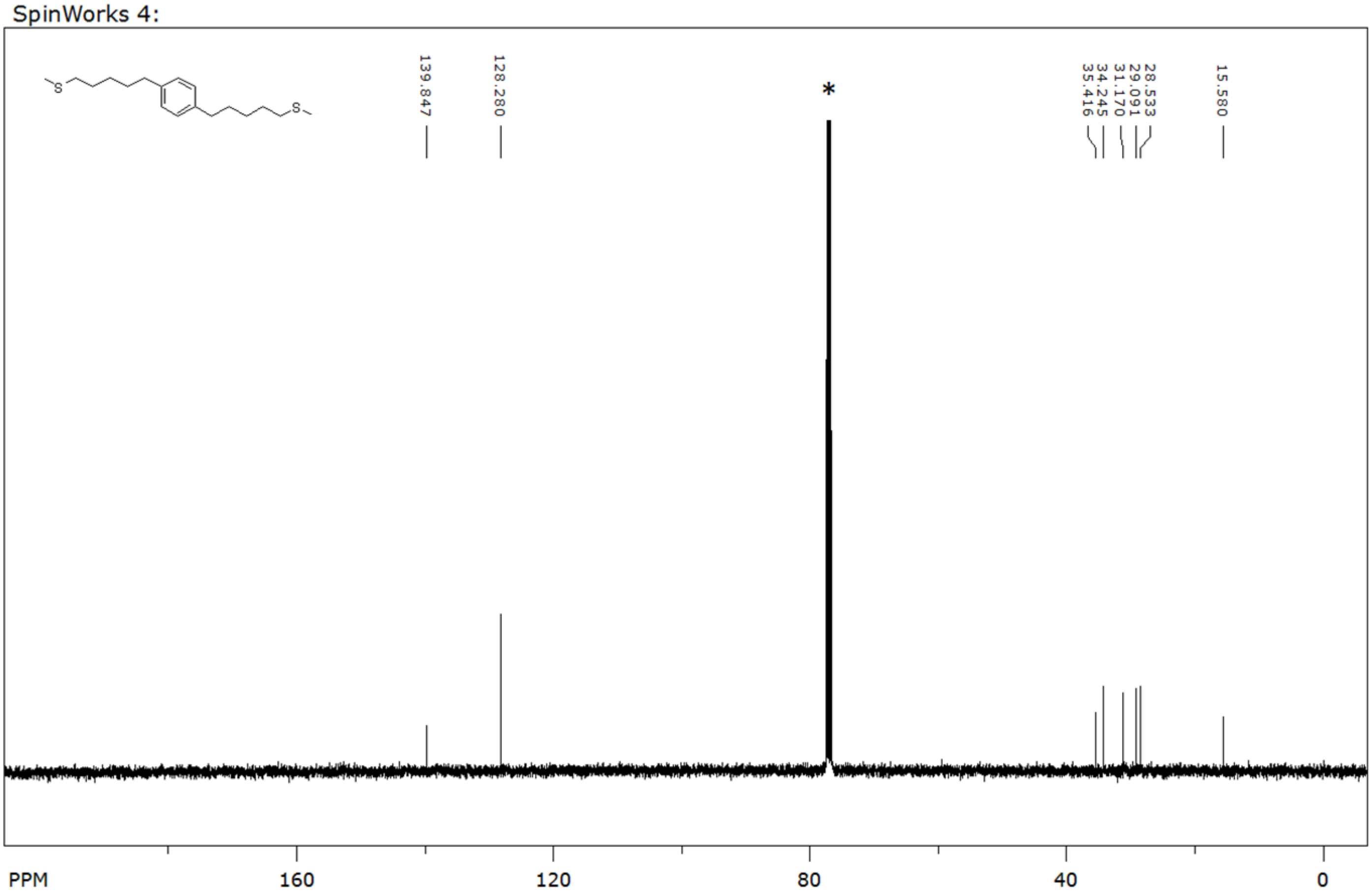
Figure S42: ^{13}C NMR of **4[Ph]4-SMe**. 100 MHz, $CDCl_3$. Solvent peak starred.

5[Ph]5-SMe



```
file: ...op\betafactor nmrs\5PH5SME\290\fid   expt: <zg30>     freq. of 0 ppm: 400.130010 MHz
transmitter freq.: 400.132801 MHz                           processed size: 65536 complex points
time domain size: 65536 points                              LB: 0.300    GF: 0.0000
width: 6393.86 Hz = 15.9793 ppm = 0.097563 Hz/pt
number of scans: 256
```

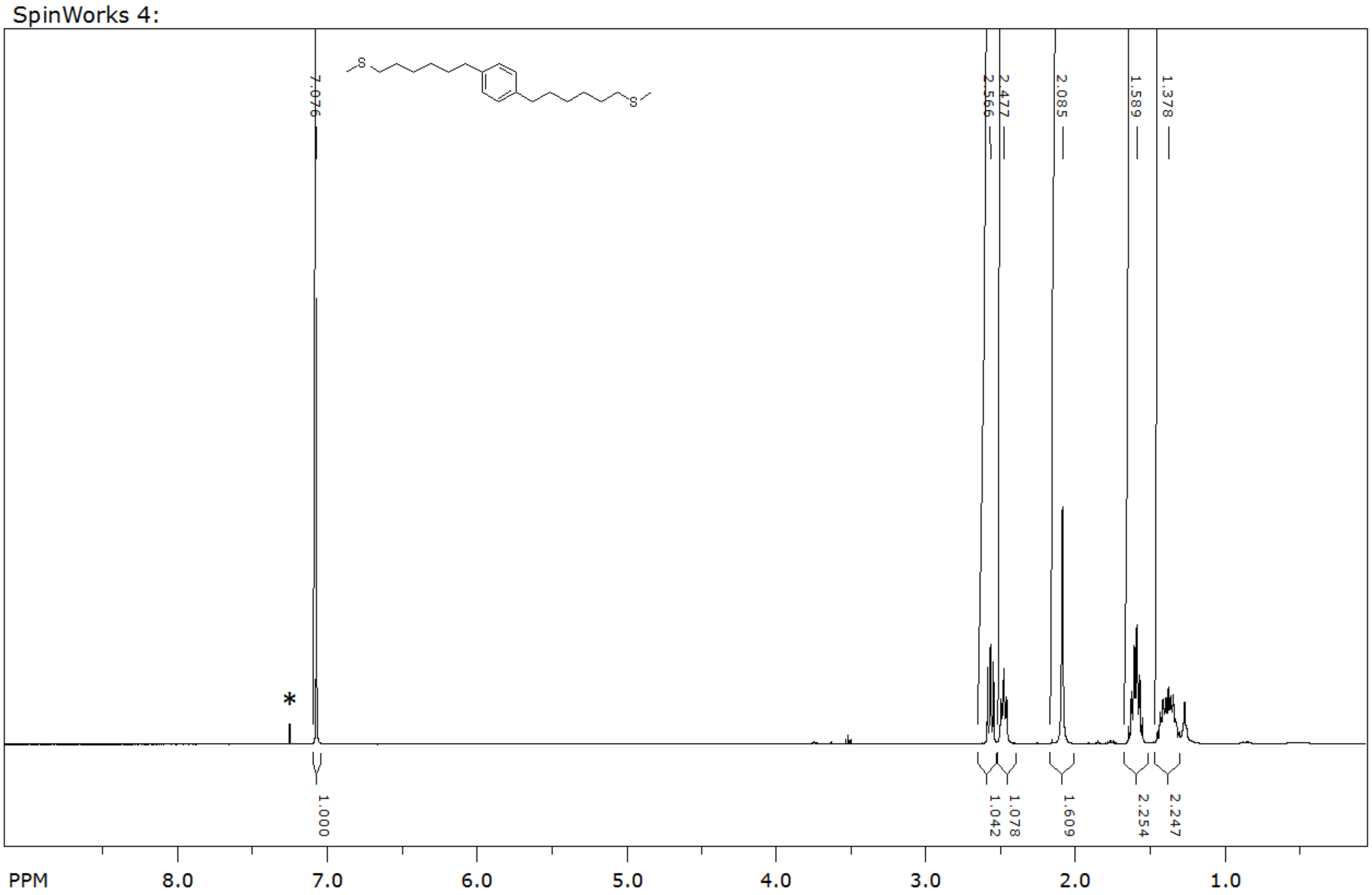
Figure S43: ^{1}H NMR of **5[Ph]5-SMe**. 400 MHz, $CDCl_3$. Residual solvent peak starred, water peak hashed. O is residual hexane that couldn't be removed on pumping in vacuo.



```
file: ...op\betafactor nmrs\5PH5SME\291\fid   expt: <zgpg30>          freq. of 0 ppm: 100.612769 MHz
transmitter freq.: 100.622830 MHz                                      processed size: 32768 complex points
time domain size: 65536 points                                         LB: 1.000    GF: 0.0000
width: 25252.53 Hz = 250.9622 ppm = 0.385323 Hz/pt
number of scans: 1024
```

Figure S44: 13C NMR of **5[Ph]5-SMe**. 100 MHz, $CDCl_3$. Solvent peak starred.

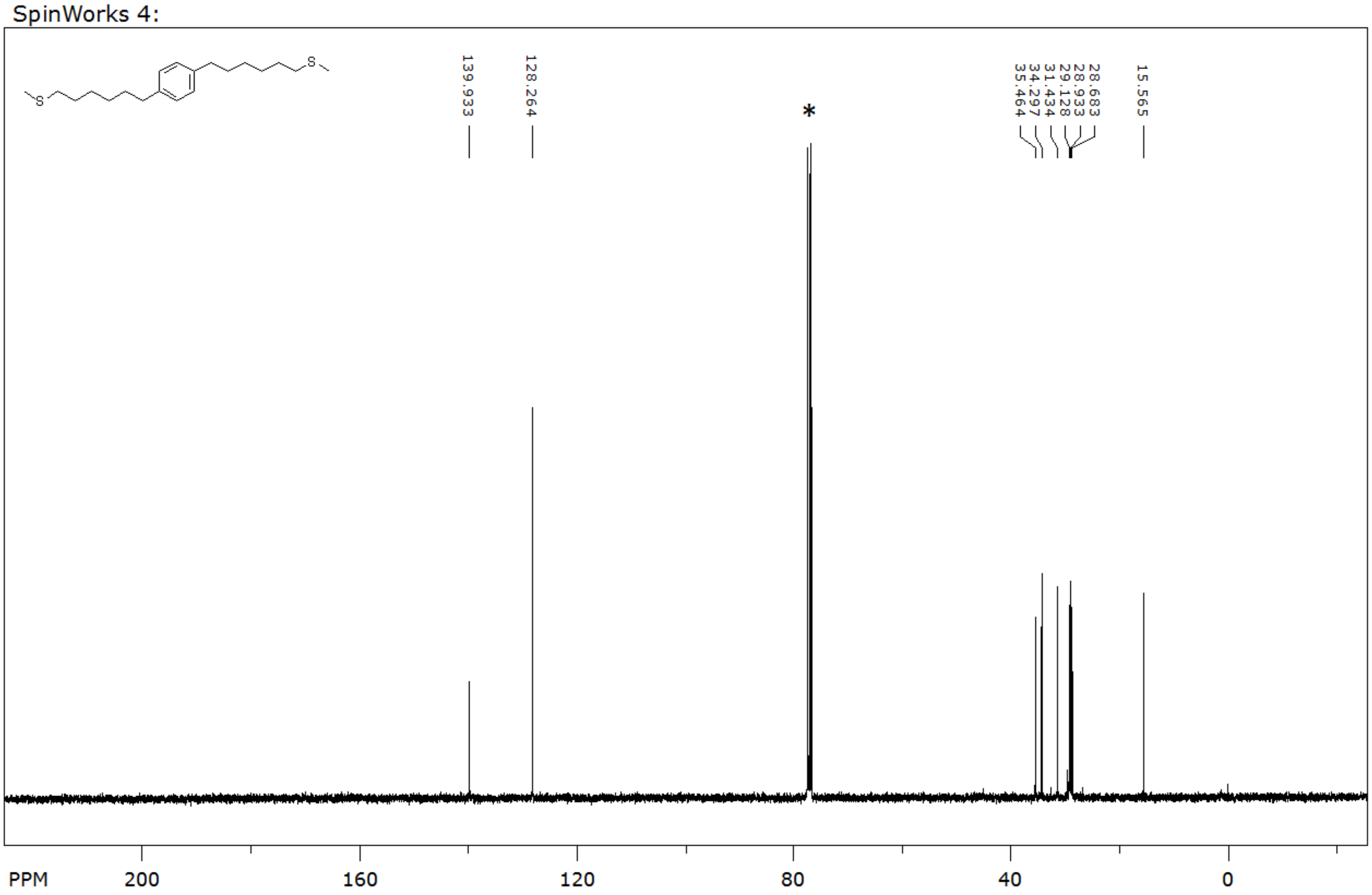
6[Ph]6-SMe



```
file: ...esktop\betafactor nmrs\6ph6sme\fid   expt: <zg30>
transmitter freq.: 400.132801 MHz
time domain size: 65536 points
width: 6393.86 Hz = 15.9793 ppm = 0.097563 Hz/pt
number of scans: 96
```

```
freq. of 0 ppm: 400.130012 MHz
processed size: 65536 complex points
LB: 0.300    GF: 0.0000
```

Figure S45: ^{1}H NMR of **6[Ph]6-SMe**. 400 MHz, $CDCl_3$. Residual solvent peak starred, water peak obscured by the resonance at 1.59 ppm, increasing its integration.



file: ...NMR\Phenyls\6Ph6-SMe CDCl3 13C\fid   expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 25252.53 Hz = 250.9622 ppm = 0.385323 Hz/pt
number of scans: 1024

freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000   GF: 0.0000

Figure S46: 13C NMR of **6[Ph]6-SMe**. 100 MHz, $CDCl_3$. Solvent peak starred.

7. Further analytical discussion

To illustrate the difference in the calculated parameters for the **ADT** and **X[Ph]X** systems, results for ε_F, Γ, α and $a = |\alpha|/\Gamma$, obtained from fits of equation (3) of the main text to density-functional calculations of $T(E_F)$ are presented in Table S4. For comparison, these parameters are plotted versus n(CH_2) in Figure S47, along with the resulting logarithmic transmission coefficient $\ln T(E_F)$, whose slope defines the attenuation coefficient β (β'). As shown in the bottom-right panel of Figure S47, the β' value for **X[Ph]X** is predicted to be significantly lower than β for **ADT**.

Table S4. Parameters extracted from DFT results for **X[Ph]X** (left) and **ADT** (right) as a function of the number n(CH_2) of alkyl units.

X[Ph]X				
n(CH_2)	ε_F	Γ	α	a $=\alpha/\Gamma_L$
2	-0.124	0.058	3.3×10^{-03}	0.0569
6	-0.189	0.039	7.8×10^{-04}	0.02
8	-0.234	0.048	5.0×10^{-04}	0.0104
12	-0.277	0.025	2.0×10^{-04}	0.0080

ADT				
n(CH_2)	ε_F	Γ	α	a $= \alpha/\Gamma_L$
6	-0.109	0.027	1.82×10^{-03}	0.0674
8	-0.123	0.029	4.15×10^{-04}	0.0143
10	-0.142	0.026	5.15×10^{-05}	0.0020
12	-0.151	0.028	2.70×10^{-05}	0.000964

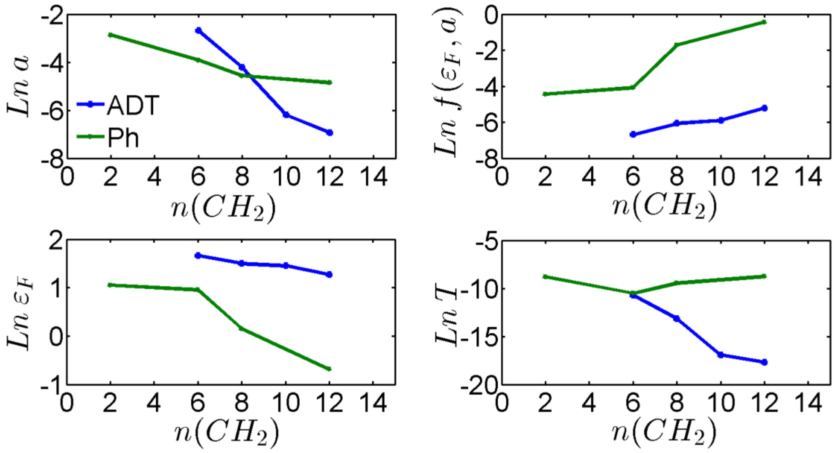


Figure S47: Plots of the dimensionless parameters ε_F, Γ, a, $f(\varepsilon_F, a)$ and $T(E_F)$ appearing in equation (3), versus the number of alkyl units n(CH_2). The negative slopes of the green and blue ln T plots define, respectively, β' for **X[Ph]X** and β for **ADT**.

As expected, the dimensionless coupling parameter a decreases exponentially with the number of alkyl units n(CH_2). However this is not the only contribution to β. Equation (3) in the main text reveals that $\ln T = 2\ln a +$

$\ln f(\varepsilon_F, a) + \text{constant}$, so β = -[the slope of $2 \ln a$ + slope of $\ln f(\varepsilon_F, a)$]. Figure S47 shows that in the case of **X[Ph]X**, the resonance position ε_F changes with length, whereas it is insensitive to n(CH_2) for **ADT**, reflecting the fact that the position of the **X[Ph]X** resonances (relative to the Fermi energy) are sensitive to n(CH_2), whereas they are relatively insensitive for **ADT**. As discussed in the main text, when combined with the variation in a, this leads to a steeper slope for $\ln f(\varepsilon_F, a)$, which cancels the trend in $\ln a$, leading to a decrease in the value of β', in agreement with experimental results and DFT calculations.

8. References

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