Supplementary information for:

"Rapid Sonogashira cross-coupling of iodoferrocenes and the unexpected cyclo-oligomerization of 4-ethynylphenylthioacetate"

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CONTENTS

EXPERIMENTAL

Conditions and materials

All preparations were carried out using standard Schlenk line and air-sensitive chemistry techniques under an atmosphere of nitrogen. No special precautions were taken to exclude air or moisture during workup, unless otherwise stated. Solvents used in reactions were sparged with nitrogen and dried with alumina beads, Q5 Copper catalyst on molecular sieves, or 3A molecular sieves,[1] where appropriate. 1,1'-Diiodoferrocene,[2] $PdCl_2(PPh_3)_2$[3] and 4-ethynylphenylthioacetate[4] were prepared via literature methods from commercially available starting materials. $PdCl_2(MeCN)_2$ was synthesized by refluxing $PdCl_2$ in acetonitrile for 1 hr. The resulting solution was filtered through Celite and concentrated to crystallize the product, which was washed with acetonitrile and diethyl ether before drying in air.[5] All other materials were

purchased from commercial suppliers and used without further purification. The purity of all phosphine ligands was assessed using $^{1}H/^{31}P\{^{1}H\}$ NMR spectroscopy to be >95%.

Instrumentation

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra were recorded at ambient temperature on a Bruker 400 MHz spectrometer and internally referenced to the residual solvent peaks of $CDCl_3$ at δ 7.26 (^{1}H) and 77.16 ppm ($^{13}C\{^{1}H\}$); CD_2Cl_2 at δ 5.32 (^{1}H) and 53.84 ($^{13}C\{^{1}H\}$) ppm;[6] or externally to 85% phosphoric acid (0.00 ppm). $^{13}C\{^{1}H\}$ spectra were fully assigned where possible using 2D correlation spectroscopy. UV-vis and IR spectra were recorded on a PerkinElmer LAMBDA 25 UV/vis spectrophotometer or a PerkinElmer Spectrum 100 FT-IR spectrometer, respectively. Mass spectrometry analyses were conducted by the Mass Spectrometry Service, Imperial College London. Microanalyses were carried out by Stephen Boyer of the Science Centre, London Metropolitan University, or Alan Dickerson of the Department of Chemistry, University of Cambridge.

Sonogashira cross-coupling reactions with phenylacetylene

Typical procedure using $PdCl_2(PPh_3)_2$ catalyst. THF and the relevant amine were added to a flask containing 1,1'-diiodoferrocene (0.51 g, 1.16 mmol), $PdCl_2(PPh_3)_2$ (0.050 g, 0.071 mmol) and copper iodide (0.014 g, 0.073 mmol). The mixture was sparged with nitrogen, whereby phenylacetylene (0.51 mL, 4.64 mmol) was added and the resulting black suspension stirred at the appropriate temperature for 20 h. The mixture was subsequently opened to air and reagent grade CH_2Cl_2 (5 mL) was added (NOTE: large solvent volumes were evaporated to dryness first). An aliquot (~1 mL) was taken, eluted through a silica plug using CH_2Cl_2, dried, and analyzed by ^{1}H NMR spectroscopy *(vida infra)*.

Typical procedure using $PdCl_2(MeCN)_2$ catalyst. THF (0.75 mL) was added to a flask containing 1,1'-diiodoferrocene (0.25 g, 0.57 mmol), $PdCl_2(MeCN)_2$ (0.009 g, 0.035 mmol) and copper iodide (0.007 g, 0.037 mmol). The mixture was sparged with nitrogen, whereby phosphine ligand (0.070 mmol), freshly distilled and deoxygenated DIPA (0.25 mL), and phenylacetylene (0.25 mL, 2.27 mmol) were added (in that order). The resulting black suspension was stirred at the

appropriate temperature for 20 h, after which time the mixture was opened to air and reagent grade CH_2Cl_2 (5 mL) was added. An aliquot (~1 mL) was taken, eluted through a silica plug using CH_2Cl_2, dried, and analyzed by ^{1}H NMR spectroscopy *(vida infra)*.

Partial isolation of reaction products by column chromatography. Column chromatography (silica; CH_2Cl_2/*n*-hexane [1:4]) of the dried residue from a catalysis run yielded several bands of co-eluting ferrocene-containing components. These were identified by high resolution mass spectrometry and characteristic cyclopentadienyl ^{1}H NMR resonances *(Fig.* **S-1***)*.[7] Band 1: Unreacted 1,1'-diiodoferrocene (**A**) and iodoferrocene (**B**). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.15 (pseudo-t, $J_{\alpha\beta}$ = ~1.8 Hz, 2H, **B**), 4.18 (pseudo-t, $J_{\alpha\beta}$ = 1.8 Hz, 4H, **A**), 4.19 (s, 5H, **B**), 4.37 (pseudo-t, $J_{\alpha\beta}$ = ~1.8 Hz, 4H, **A**), 4.41 (pseudo-t, $J_{\alpha\beta}$ = 1.7 Hz, 2H, **B**). HR-MS ES+: *m/z* 311.9113 ($[M]^+$ Calc.: 311.9098, **B**), 437.8072 ($[M]^+$ Calc.: 437.8065, **A**). Band 2: (phenylethynyl)ferrocene (**C**) and 1-iodo-1'-(phenylethynyl)ferrocene (**D**). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.23 (pseudo-t, $J_{\alpha\beta}$ = ~1.8 Hz, 2H, **D**), 4.25 (s, 5H, **C**), 4.26 (pseudo-t, $J_{\alpha\beta}$ = 1.9 Hz, 2H, **D**), 4.45 (pseudo-t, $J_{\alpha\beta}$ = ~1.8 Hz, 2H, **D**), 4.47 (pseudo-t, $J_{\alpha\beta}$ = 1.8 Hz, 2H, **D**), 4.50 (pseudo-t, $J_{\alpha\beta}$ = 1.9 Hz, 2H, **C**) (NOTE: a pseudo-t, 2H for **C** is obscured by overlapping resonances for **D**). HR-MS ES+: *m/z* 286.0446 ($[M]^+$ Calc.: 286.0445, **C**), 412.9482 ($[M+H]^+$ Calc.: 412.9490, **D**). Band 3: 1,1'-bis(phenylethynyl)ferrocene (**E**). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.32 (pseudo-t, $J_{\alpha\beta}$ = 1.8 Hz, 4H, **E**), 4.55 (pseudo-t, $J_{\alpha\beta}$ = 1.9 Hz, 4H, **E**). HR-MS ES+: *m/z* 387.0821 ($[M+H]^+$ Calc.: 387.0836, **E**).

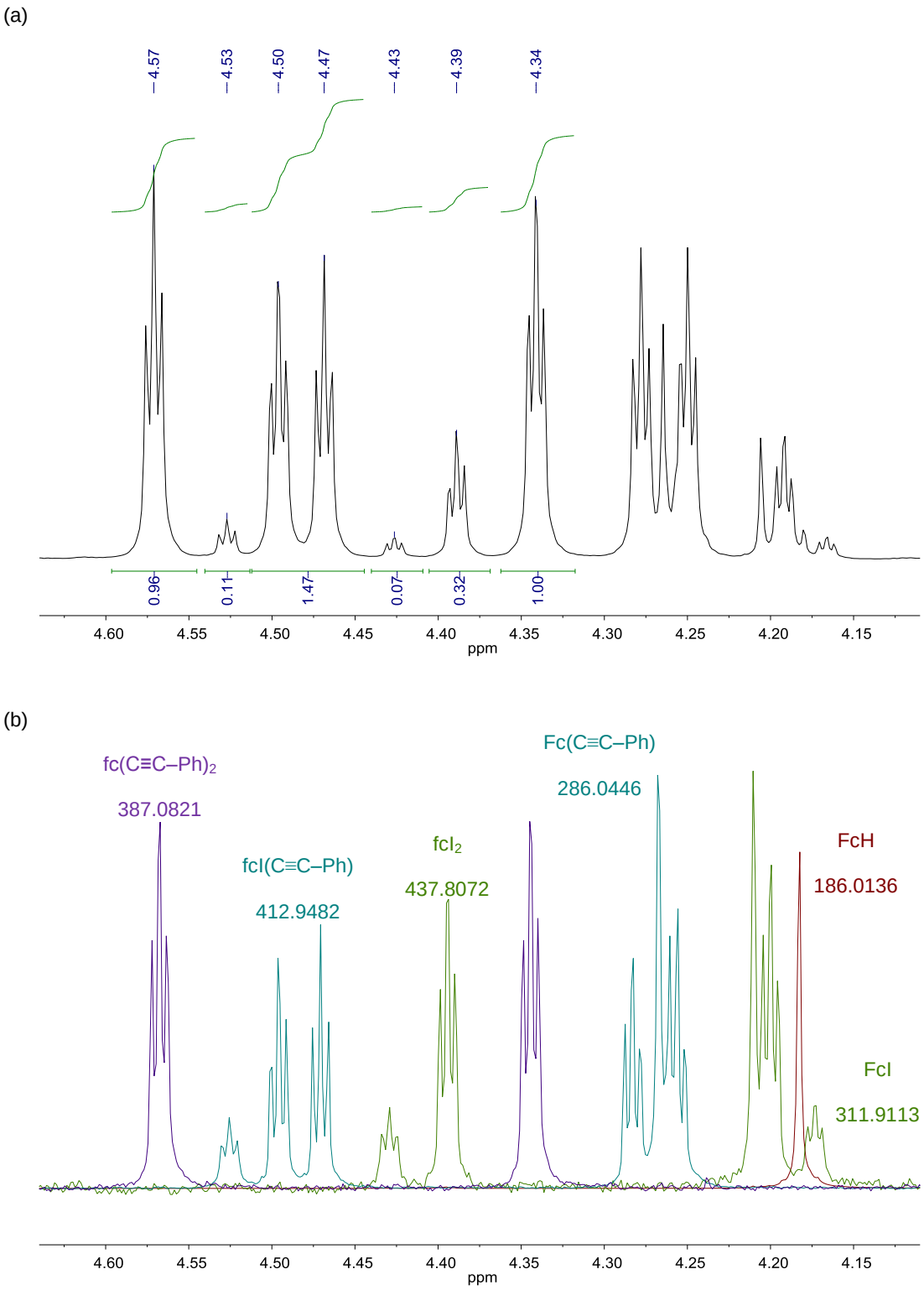


Fig. S-1 A comparison of the ^{1}H NMR spectra of (a) the crude mixture resulting from a typical catalysis run, and (b) the superposition of isolated and partially isolated components from the mixture. Accurate mass spectroscopic analyses support ^{1}H NMR resonance assignments.

Method of analyzing product composition

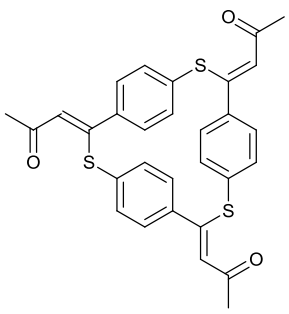
The % composition of individual species in the mixture was obtained from the ratio of the integral value representing a single proton intensity for that component (representative of the number of moles of that component) and an integral value representing the sum of all the single proton intensities (representative of the total number of moles) for all species (eqn (S.1)). A worked example for the spectrum in Fig. S-1(a) is given in Table S-1 (sum of single proton intensities = 0.778).

$$\%\,\text{component} = 100 \times \frac{\text{single proton intensity of component}}{\text{sum of single proton intensities for all components}} \qquad \text{(S.1)}$$

Table S-1 A worked example showing % composition of components calculated from the ^{1}H NMR spectrum in Fig. **S-1**(a).

component	integrated resonance /ppm (intensity)	division factor	single proton intensity	% composition
FcI	4.43 (0.07)	2	0.035	4
fcI_2	4.39 (0.32)	4	0.080	10
Fc(C≡C–Ph)	4.53 (0.11)	2	0.055	7
fcI(C≡C–Ph)	4.47, 4.50 (1.47)	4	0.368	47
$fc(C{\equiv}C{-}Ph)_2$	4.57 (0.96)	4	0.240	31

Cyclization product of 4-ethynylphenylthioacetate (4)

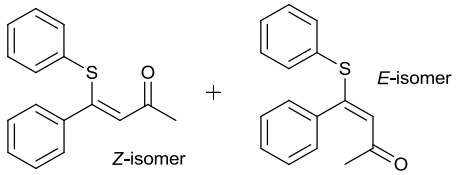


4

A solution of 4-ethynylphenylthioacetate (0.21 g, 1.19 mmol) in THF (0.4 mL) and DIPEA (0.2 mL) was degassed (freeze-pump-thaw). $PdCl_2(PPh_3)_2$ (0.022 g, 0.031 mmol) and copper iodide (0.007 g, 0.037 mmol) were added against nitrogen and the mixture stirred at 55°C for 24 h. After cooling and solvent removal, the crude material was purified by column chromatography (silica; CH_2Cl_2/diethyl ether [19:1]) and dried *in vacuo* to provide **4** as a bright yellow solid (0.05 g, 24%). Crystals suitable for X-ray diffraction were grown by diffusion of diethyl ether into a CH_2Cl_2 solution. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 2.28 (s, 9H, C*H*$_3$), 6.42 (s, 3H, C=C*H*), 7.03 (s,

12H, Ar–*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2): δ (ppm) 30.84 (*C*H_3), 125.87 (C=*C*H), 129.59 (Ar, *C*–H), 133.81 (Ar, *C*–H), 134.27 (Ar, *C*–R), 138.76 (Ar, *C*–R), 155.83 (*C*=CH), 196.03 (*C*=O). IR (ATR): ν (cm^{-1}) 1659 (C=O). UV-vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) 303sh (31554), 325 (47443), 363sh (11759). HR-MS ES+: *m/z* 529.0955, ($[M+H]^+$ Calc.: 529.0966). (Found: C, 68.11; H, 4.56. Calc. for $C_{30}H_{24}O_3S_3$: C, 68.15; H, 4.58%).

Mixture of isomers (5-*Z* and 5-*E*)



5

A mixture of THF (1 mL), DIPEA (0.5 mL), $PdCl_2(PPh_3)_2$ (0.070 g, 0.100 mmol) and CuI (0.019 g, 0.100 mmol) was sparged with nitrogen. S-phenylthioacetate (0.44 mL, 3.25 mmol) and phenylacetylene (0.40 mL, 3.64 mmol) were added after 5 and 10 minutes, respectively. Upon addition of the latter, the suspension immediately changed colour from yellow to dark red. After stirring at 55°C for 24 h, the mixture was cooled, solvent removed, and the residue purified by column chromatography (silica; ethyl acetate/petroleum benzene [1:9]) to provide **5** (a mixture of *Z/E* isomers [81/19]) as a soft yellow solid (0.66 g, 80%). Spectroscopic data was consistent with that reported previously.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.72 (s, 3H, C*H*$_3$, *E*), 2.35 (s, 3H, C*H*$_3$, *Z*), 5.71 (s, 1H, C=C*H*, *E*), 6.49 (s, 1H, C=C*H*, *Z*), 6.95-7.60 (m, 10H, Ph–*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 30.25 (*C*H_3, *E*), 30.86 (*C*H_3, *Z*), 123.12 (C=*C*H, *E*), 123.54 (C=*C*H, *Z*), 127.85 (Ph), 127.96 (Ph), 128.46 (Ph), 128.62 (Ph), 128.92 (Ph), 129.01 (Ph), 129.68 (Ph), 129.97 (Ph), 130.10 (Ph), 132.63 (Ph), 134.31 (Ph), 135.52 (Ph), 138.40 (Ph), 159.34 (*C*=CH), 196.40 (*C*=O). IR (ATR): ν (cm^{-1}) 1646 (C=O), 1659 (C=O). HR-MS ES+: *m/z* 255.0844, ($[M+H]^+$ Calc.: 255.0844). (Found: C, 75.63; H, 5.58. Calc. for $C_{16}H_{14}OS$: C, 75.55; H, 5.55%).

CATALYSIS DATA

Table S-2 Effects of changing concentration on reaction yield, using $PdCl_2(PPh_3)_2$.[a]

				% conversion[b]		
#	amine/solvent	T /°C	[fcI_2] /mM	fcI(C≡CPh)	fc(C≡CPh)$_2$	side products
1	DIPA	90	580	1	85	15
2	DIPA/THF (1:3 v/v)	80	580	0	88	12
3	DIPA/THF (1:3 v/v)	80	114	9	82	8
4	DIPA/THF (1:3 v/v)	80	28	24	63	9
5	DIPA/THF (1:3 v/v)	80	4	42	29	8
6	DIPA/THF (1:3 v/v)	rt	580	46	10	7

[a] All reactions were run for 20 h and performed with 6 mol% $Pd(PPh_3)_2Cl_2$, 6 mol% CuI and 400 mol% phenylacetylene (2 equivalents per iodo functionality), relative to fcI_2. [b] Conversion obtained via ^{1}H NMR spectroscopy, given here as the average of two runs.

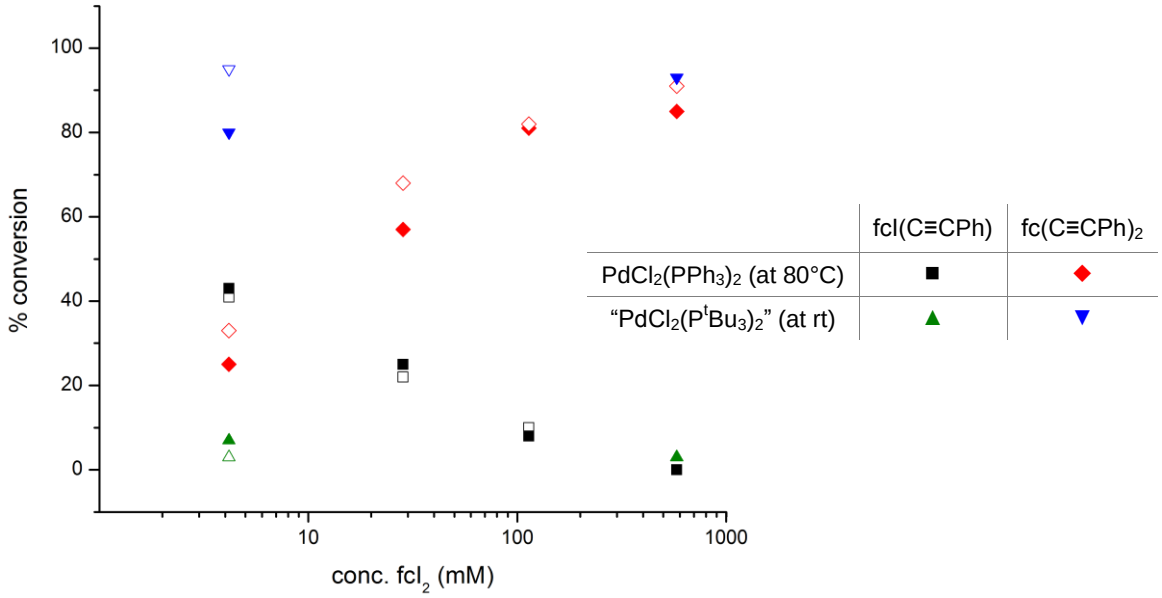


Fig. S-2 Effects of changing concentration on the conversion of fcI_2 to fcI(C≡CPh) and fc(C≡CPh)$_2$ (entries 2-5, Table S-2; entries 25, 31-32, Table S-7). Solid symbols = run 1, open symbols = run 2.

Table S-3 Effects of changing amine and solvent on reaction yield.[a]

		% conversion[b]		
#	amine/solvent (1:3 v/v)	fcI(C≡CPh)	fc(C≡CPh)$_2$	side products
6	DIPA/THF	46	10	7
7	TEA/THF	27	2	13
8[c]	DIPEA/THF	30	4	12
9	DEA/THF	18	1	29
10[c]	DIPA/toluene	28	2	8
11	DIPA/CH_2Cl_2	36	3	4

[a] All reactions were run for 20 h at room temperature and performed with 6 mol% $PdCl_2(PPh_3)_2$ catalyst, 6 mol% CuI and 400 mol% phenylacetylene (2 equivalents per iodo functionality), relative to fcI_2 (concentration = 580 mM). [b] Conversion obtained via ^{1}H NMR spectroscopy, given here as the average of two runs (unless otherwise stated). [c] Conversion given as the average of three runs.

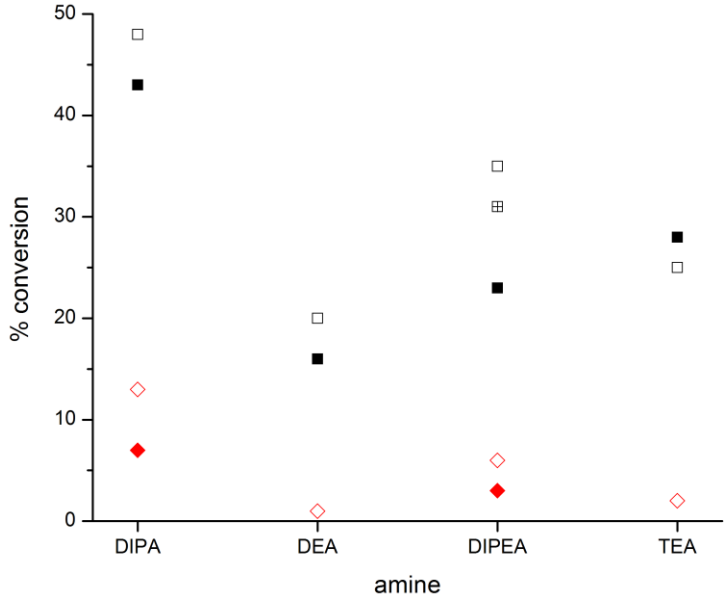


Fig. S-3 Effects of changing amine on the conversion of fcI_2 to fcI(C≡CPh) (black squares) and fc(C≡CPh)$_2$ (red diamonds), entries 6-9, Table S-3. Solid symbols = run 1, open symbols = run 2, crossed symbols = run 3 (DIPEA only).

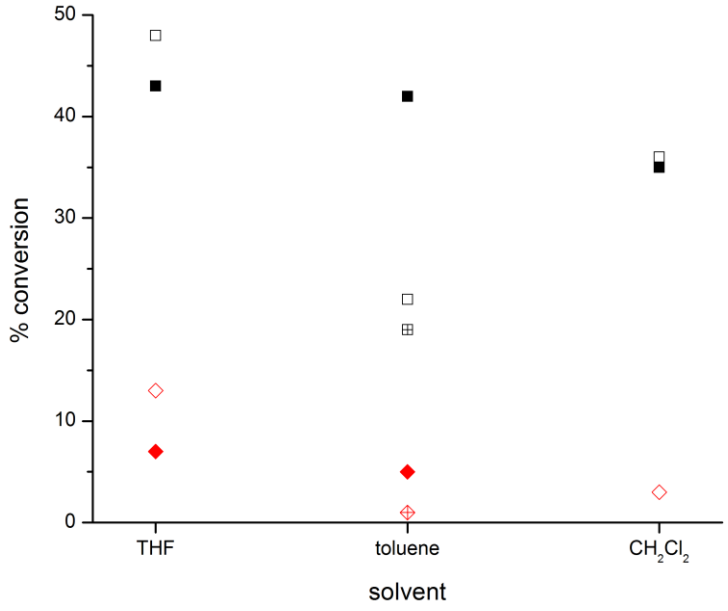


Fig. S-4 Effects of changing solvent on the conversion of fcI_2 to fcI(C≡CPh) (black squares) and $fc(C{\equiv}CPh)_2$ (red diamonds), entries 6,10-11, Table S-3. Solid symbols = run 1, open symbols = run 2, crossed symbols = run 3 (toluene only).

Table S-4 Effects of changing phosphine on reaction yield.[a]

		% conversion[b]			phosphine[9]	
#	catalytic system	fcI(C≡CPh)	fc(C≡CPh)$_2$	side products	θ (°)	ν_{el} (cm^{-1})
12	$Pd(PPh_3)_2Cl_2$	39	5	10	145	2068.9
13	$Pd(MeCN)_2Cl_2/PPh_3$	35	4	11	145	2068.9
14	$Pd(MeCN)_2Cl_2$ /P(C$_6$H$_4$-*p*-Cl)$_3$	18	1	10	145	2072.8
15	$Pd(MeCN)_2Cl_2/P(C_6H_4$-*p*-OMe$)_3$	22	1	8	145	2066.1
16	$Pd(MeCN)_2Cl_2/P($*p*-tolyl$)_3$	29	3	10	145	2066.7
17	$Pd(MeCN)_2Cl_2/P($*o*-tolyl$)_3$	2	0	2	194	2066.6
18	$Pd(MeCN)_2Cl_2/PPh_2($*o*-tolyl)	21	2	9	161	2068.1
19	$Pd(MeCN)_2Cl_2/PPh_2Me$	1	0	5	136	2067.0
20	$Pd(MeCN)_2Cl_2/PPh_2(C_6F_5)$	6	0	0	158	2074.8
21	$Pd(MeCN)_2Cl_2/P(C_6F_5)_3$	2	0	2	184	2090.9
22	$Pd(MeCN)_2Cl_2/PBz_3$	0	0	0	165	2066.4
23	$Pd(MeCN)_2Cl_2/PCy_3$	0	0	2	170	2056.4
24	$Pd(MeCN)_2Cl_2/P(^nBu)_3$	0	0	0	132	2060.3
25	$Pd(MeCN)_2Cl_2/P(^tBu)_3$	3	93	4	182	2056.1
26	$Pd(MeCN)_2Cl_2/P(O\text{-}^iPr)_3$	1	0	4	130	2075.9

[a] All reactions were run for 20 h at room temperature in DIPA/THF (1:3 v/v) and performed with 6 mol% Pd catalyst, 6 mol% CuI, 12 mol% phosphine (where applicable) and 400 mol% phenylacetylene (2 equivalents per iodo functionality), relative to fcI_2 (concentration = 580 mM). [b] Conversion obtained via ^{1}H NMR spectroscopy, given as the average of two runs (difference of ≤5% between runs).

Table S-5 Effects of longer reaction times and moderate heating on reaction yield.[a]

				% conversion[b]		
#	amine/solvent (1:3 v/v)	T /°C	time /h	fcI(C≡CPh)	fc(C≡CPh)$_2$	side products
6	DIPA/THF	rt	20	46	10	7
27	DIPA/THF	rt	60	46	29	15
8	DIPEA/THF	rt	20	30	4	12
28	DIPEA/THF	55	20	44	32	12

[a] All reactions were performed with 6 mol% $Pd(PPh_3)_2Cl_2$, 6 mol% CuI and 400 mol% phenylacetylene (2 equivalents per iodo functionality), relative to fcI_2 (concentration = 580 mM). [b] Conversion obtained via ^{1}H NMR spectroscopy, given as the average of two runs.

Table S-6 Effects of changing fcI_2/phenylacetylene ratio on reaction yield.[a]

		% conversion[b]		
#	mol% phenylacetylene	fcI(C≡CPh)	$fc(C{\equiv}CPh)_2$	side products
6	400	46	10	7
29[c]	300	41	7	9
30[c]	220	41	9	11

[a] All reactions were run for 20 h in DIPA/THF (1:3 v/v) and performed with 6 mol% $Pd(PPh_3)_2Cl_2$ and 6 mol% CuI, relative to fcI_2 (concentration = 580 mM). [b] Conversion obtained via ^{1}H NMR spectroscopy, given as the average of two runs (unless otherwise stated). [c] Conversion given as the average of three runs.

Table S-7 Effects of changing concentration on reaction yield, using $Pd(MeCN)_2Cl_2$/$P(^tBu)_3$.[a]

		% conversion[b]		
#	[fcI_2] /mM	fcI(C≡CPh)	$fc(C{\equiv}CPh)_2$	side products
25[c]	580	3	93	4
31	4	7	80	13
32	4	3	95	2

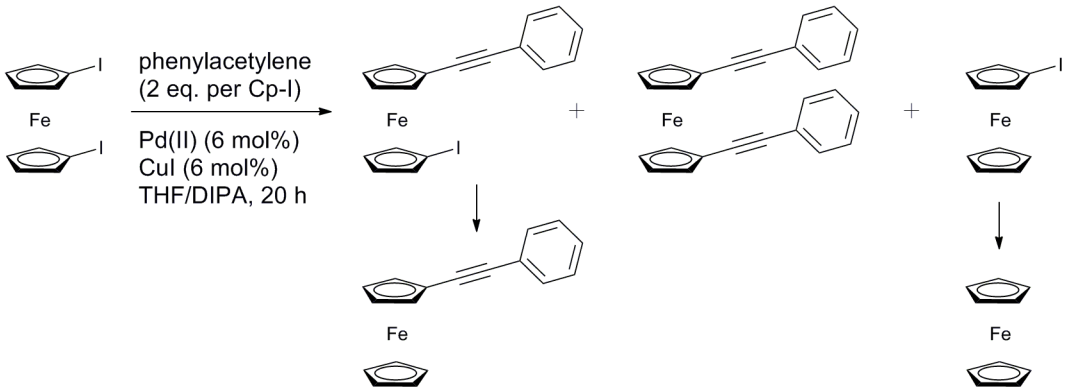
[a] All reactions were run in DIPA/THF (1:3 v/v) at room temperature for 20 h and performed with 6 mol% $Pd(MeCN)_2Cl_2$, 12 mol% $P(^tBu)_3$, 6 mol% CuI and 400 mol% phenylacetylene (2 equivalents per iodo functionality), relative to fcI_2. [b] Conversion obtained via ^{1}H NMR spectroscopy. [c] Conversion given as the average of two runs (difference of ≤5% between runs).

In addition to the results discussed in the paper manuscript, it was observed that: (i) DIPA/THF proved a superior medium cf. other amine/solvent combinations (diethylamine, triethylamine, diisopropylethylamine, CH_2Cl_2 or toluene); (ii) only modest improvements in yield could be achieved with extended reaction times (60 h); (iii) no significant differences in yield were provided by decreasing the ratio of phenylacetylene to fcI_2 (4:1 → 2.2:1).

COMMENTS ON SIDE PRODUCT FORMATION

By full or partial isolation, ^{1}H NMR and accurate mass spectrometric analyses, crude mixtures from typical runs were shown to contain iodoferrocene, (phenylethynyl)ferrocene, and even

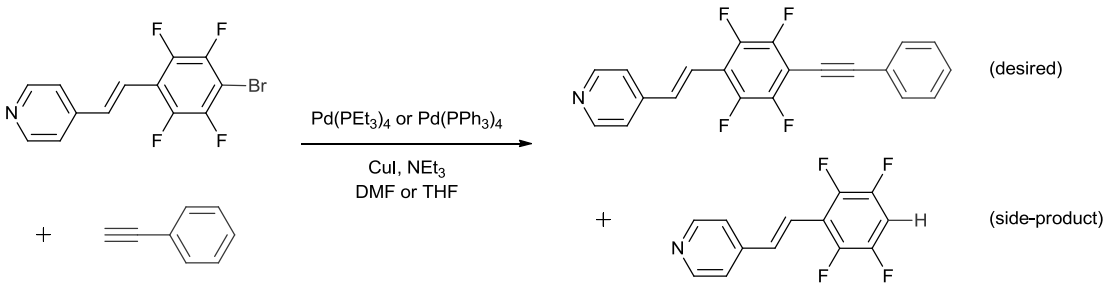
ferrocene, in addition to the expected two cross-coupled products and unreacted starting material (Scheme 1). These limit the full conversion of 1,1'-diiodoferrocene to the desired cross-coupled compounds (Table S-2-Table S-6), and are likely formed via conversion of the Fc–I bond to Fc–H under Sonogashira conditions (Scheme S-1). It should be reiterated here with confidence that no iodoferrocene/ferrocene impurities were present in the 1,1'-diiodoferrocene starting material used.[2]



Scheme S-1 The apparent conversion of Cp–I to Cp–H under Sonogashira conditions is hypothesised to generate side products as shown.

Such hydrodehalogenation side reactions have been noted in Sonogashira cross-couplings of fluorinated aryl halides,[10] very recently investigated in detail by Orbach *et al.*[11] Studying the reaction shown in Scheme S-2, labelling studies with THF-d_8 (containing trace water isotopomers) and THF-d_8/D_2O (6:1 v/v) were used to implicate (adventitious) water as the hydrogen source. No hydrodehalogenation took place in rigorously dried THF-d_8, though it was observed in anhydrous DMF (50 ppm water). The phosphine appeared to play an important role. Whereas full conversion of the fluorinated aryl bromide to the aryl hydride was ultimately achieved by reaction of the former with $Pd(PEt_3)_4$ (1 eq.) or PEt_3 (3 eq.) in THF/H_2O (6:1 v/v) after 5 min, no reaction was observed with $Pd(PPh_3)_4$ (1 eq.) under these conditions, and extended reaction times and elevated temperatures (43 h, 100°C) were required to achieve 43% conversion with PPh_3 (3 eq.). Hydrodehalogenation was not observed under any of the above conditions with non-fluorinated arylbromides. It was postulated that this reaction proceeds via

formation of a phosphonium salt ([aryl–PR_3]Br), followed by hydrolysis with water (forming $R_3P{=}O$ and HBr).



Scheme S-2 The reaction used by Orbach *et al.* to study hydrodehalogenation of fluorinated aryl halides under Sonogashira conditions.

In experiments performed by these authors with iodoferrocenes, room temperature runs using either phenylacetylene-d_1/THF or phenylacetylene/THF-d_8 showed no observable labelled products by ^{1}H NMR spectroscopy – though in the former case the acetylenic proton of unreacted phenylacetylene is clearly observed in the crude product spectrum (indicating proton/deuterium exchange under the reaction conditions). Reactions in toluene or CH_2Cl_2 (Table S-3) resulted in comparable quantities of hydrodehalogenated products, suggesting that the solvent is an unlikely source of hydrogen. Broader variations with amine (Table S-3, DEA providing significantly more side products than the others) were observed, suggesting this component plays some role. In agreement with the findings of Orbach *et al.* the extent of hydrodehalogenation appears dependant on the nature of the Pd/phosphine combination – with side product formation linked to the rate of cross-coupling in most cases (Table S-4).

Though reasonable efforts were made to dry the amine and solvent used in all reactions (over 3A molecular sieves and drying columns, respectively), (adventitious) water cannot yet be ruled out as a plausible hydrogen source here. Hydrodehalogenation was never observed in any ‘standard’ Sonogashira cross-couplings of aryl-iodides or bromides using the very same lab solvents (unpublished synthetic work); implicating iodoferrocenes as a special case in addition to the aforementioned fluorinated aryl halides.

$^{1}H/^{13}C\{^{1}H\}$ NMR SPECTRA

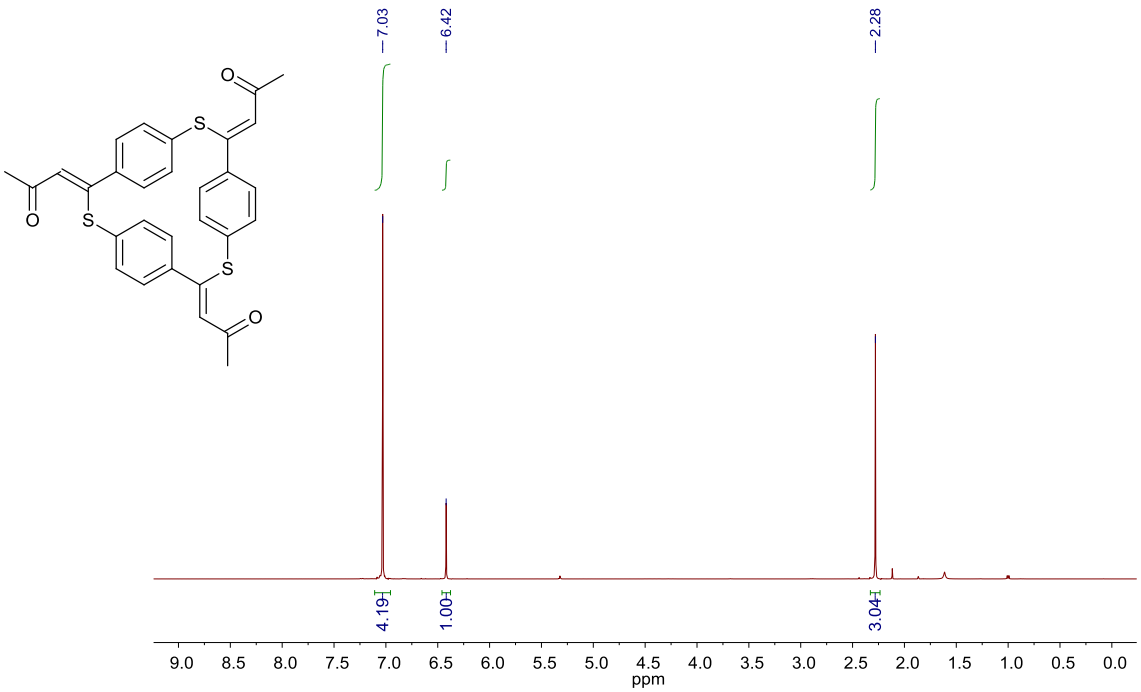


Fig. S-5 ^{1}H NMR spectrum for **4** in CD_2Cl_2

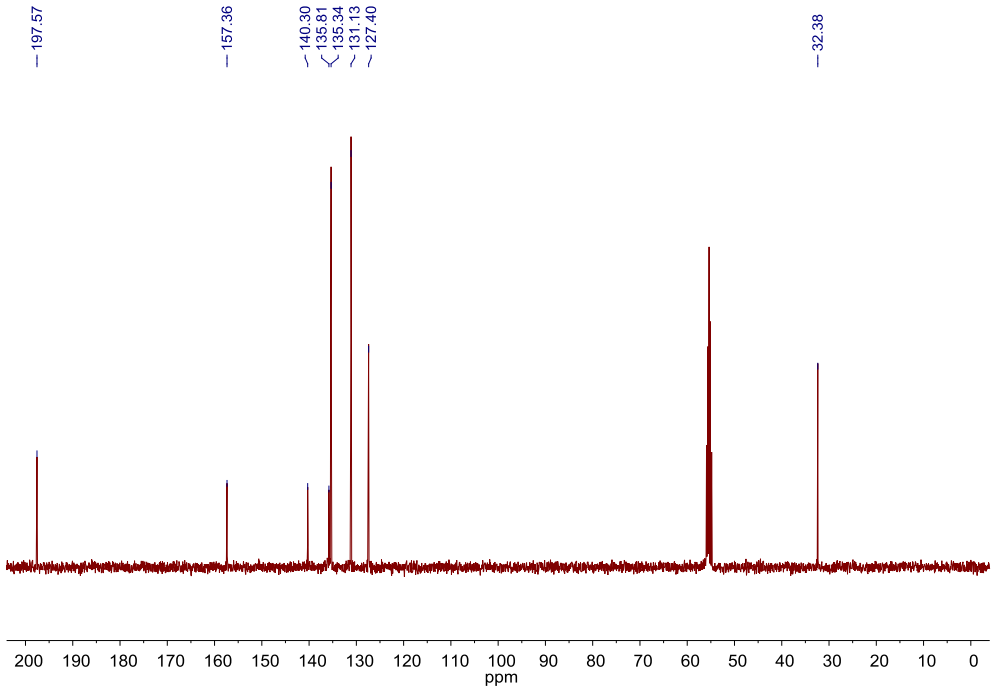


Fig. S-6 $^{13}C\{^{1}H\}$ NMR spectrum for **4** in CD_2Cl_2

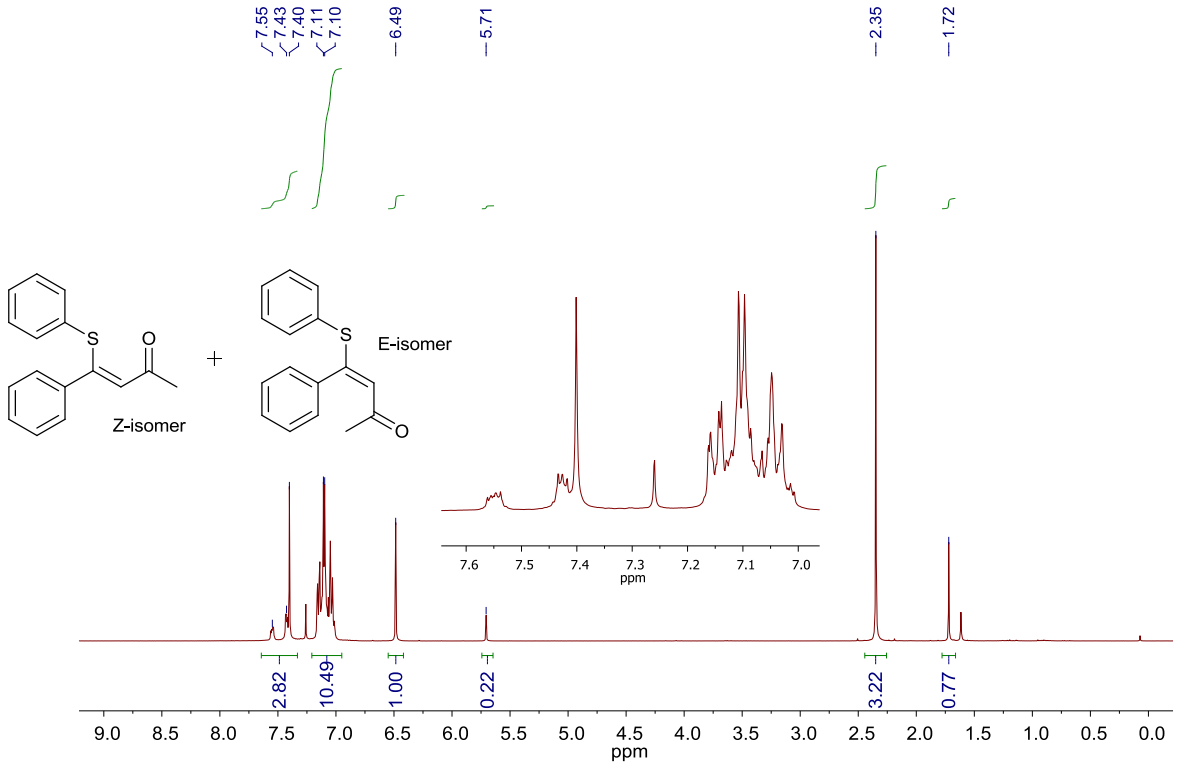


Fig. S-7 ^{1}H NMR spectrum for **5** in $CDCl_3$

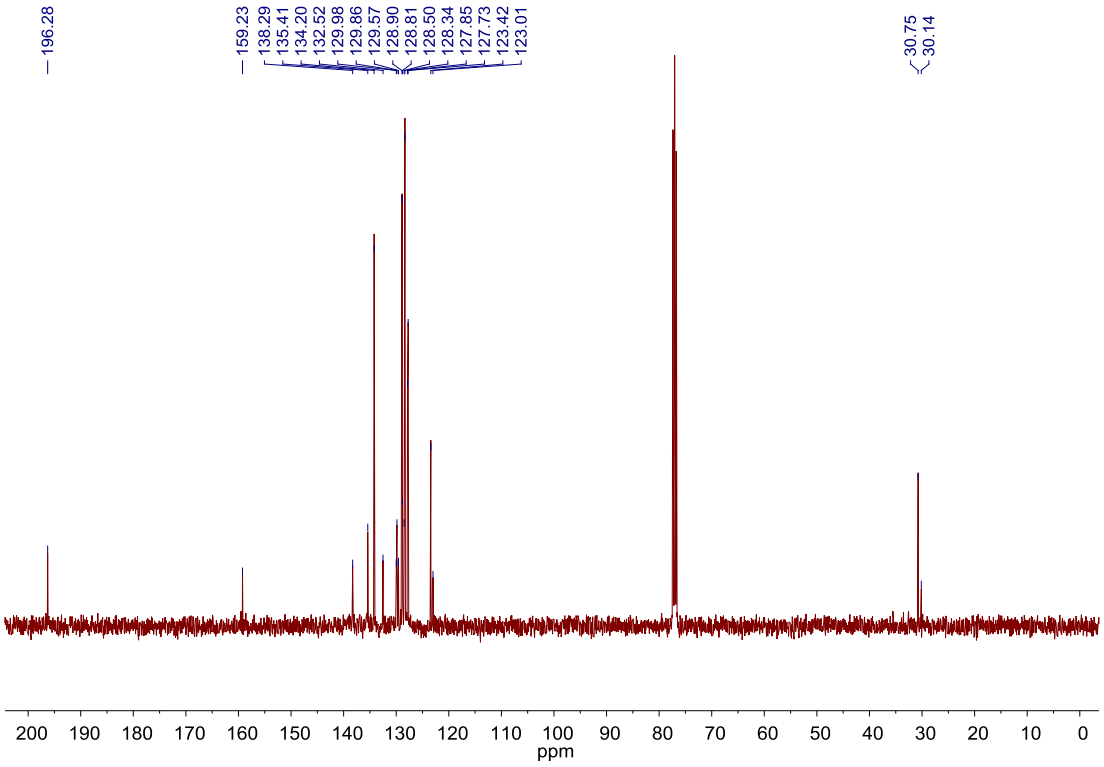


Fig. S-8 $^{13}C\{^{1}H\}$ NMR spectrum for **5** in $CDCl_3$

CRYSTALLOGRAPHIC INFORMATION

The X-ray crystal structure of 4

The crystal structure of **4** was found to contain three independent molecules, named **4-A**, **4-B** and **4-C** respectively, and three unique dichloromethane solvent molecules. All three solvent molecules were found to be disordered, and in each case three partial occupancy orientations were identified, of ca. 37, 36 and 27% occupancy for the C(40)-based molecule, ca. 36, 34 and 30% occupancy for the C(50)-based molecule, and ca. 39, 32 and 29% occupancy for the C(60)-based molecule. The geometries of all nine orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically. The absolute structure of **4** was determined by a combination of R-factor tests [$R_1^+ = 0.0489$, $R_1^- = 0.0498$] and by use of the Flack parameter [$x^+ = 0.00(4)$, $x^- = 1.01(4)$].

Figures

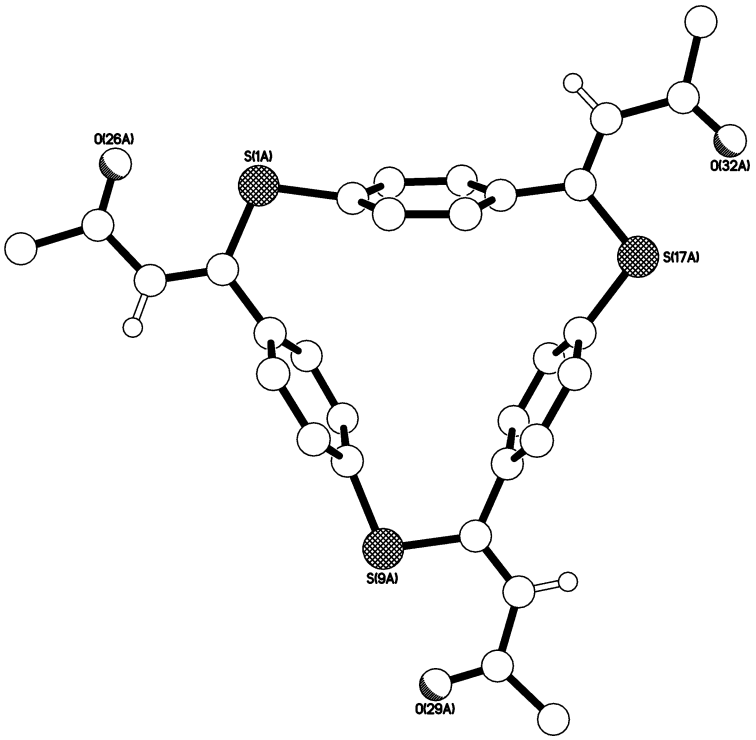


Fig. S-9 The crystal structure of one (**4-A**) of the three independent molecules present in the crystals of **4**.

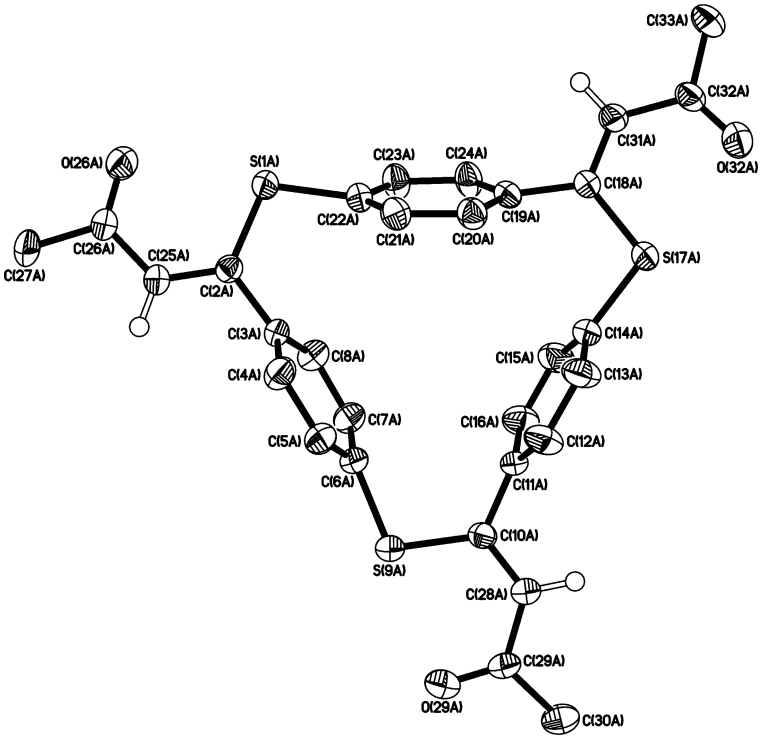


Fig. S-10 The crystal structure of one (**4-A**) of the three independent molecules present in the crystals of **4** (50% probability ellipsoids).

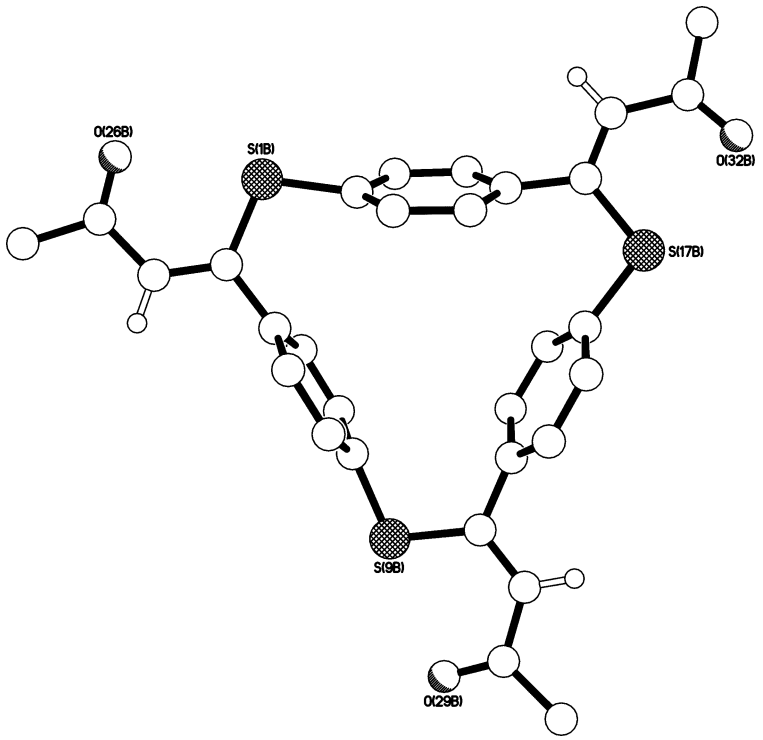


Fig. S-11 The crystal structure of one (**4-B**) of the three independent molecules present in the crystals of **4**.

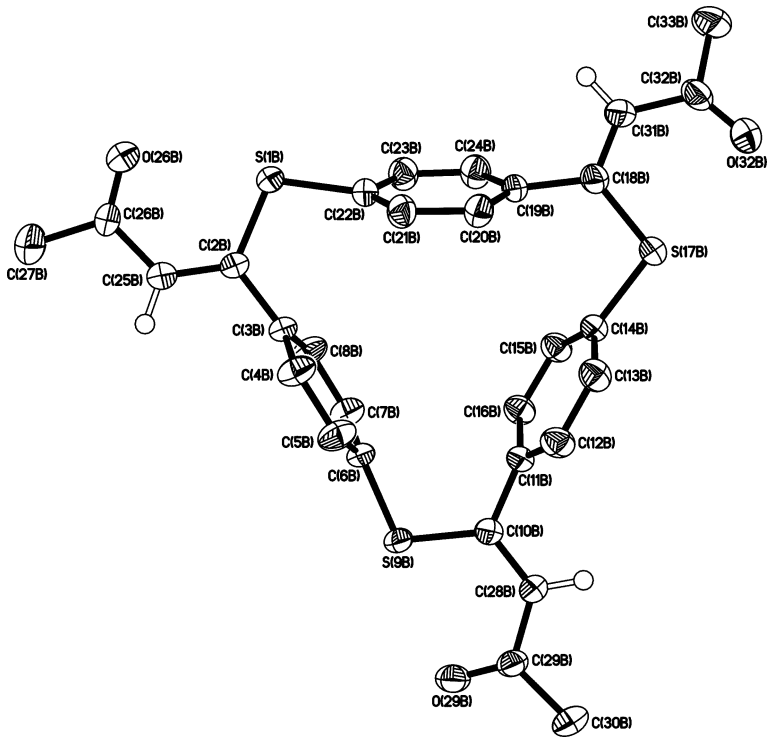


Fig. S-12 The crystal structure of one (**4-B**) of the three independent molecules present in the crystals of **4** (50% probability ellipsoids).

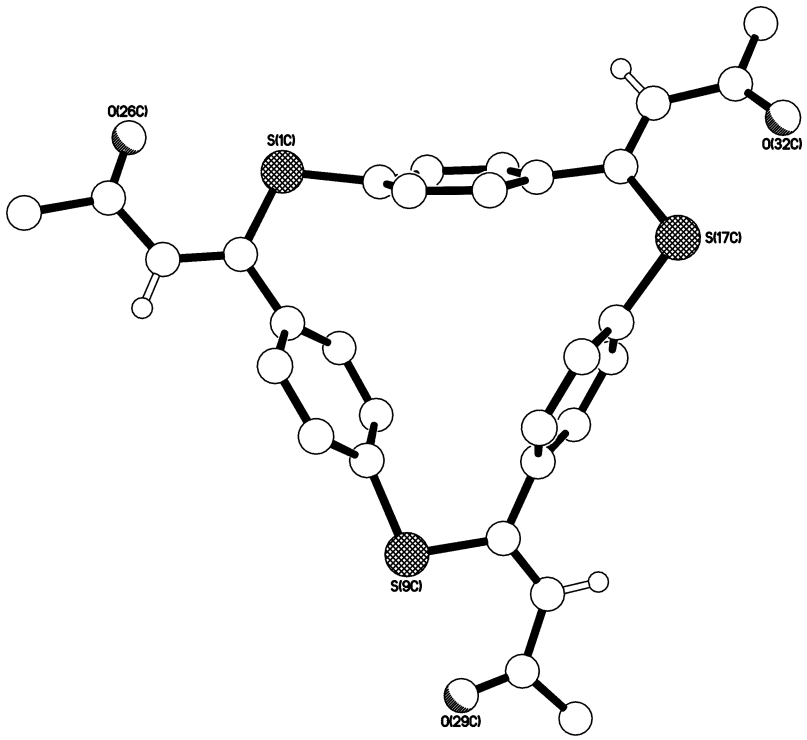


Fig. S-13 The crystal structure of one (**4-C**) of the three independent molecules present in the crystals of **4**.

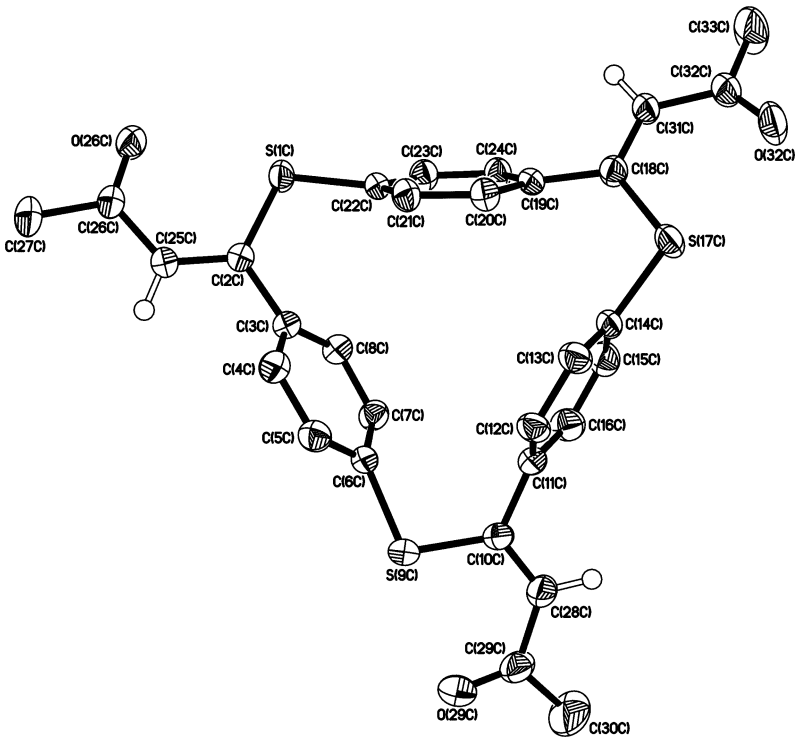


Fig. S-14 The crystal structure of one (**4-C**) of the three independent molecules present in the crystals of **4** (50% probability ellipsoids).

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