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Synthesis and applications to catalysis of novel cyclopentadienone iron tricarbonyl complexes†

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A series of cyclopentadienone iron tricarbonyl complexes with diverse structures were prepared, in each case using the intramolecular cyclisation of a diyne as a key step. The complexes were generated as enantiomerically enriched through (i) asymmetric synthesis of a *C*2-symmetric diol following a reported protocol, (ii) resolution of enantiomerically-enriched diastereoisomers formed from a chiral alcohol and (iii) kinetic resolution of a racemic ketone-containing iron tricarbonyl complex. The approaches underline the diversity of the synthetic routes which can be employed in the synthesis of homochiral cyclopentadienone iron tricarbonyl complexes. Although the complexes proved to be effective as catalysts for the reduction of ketones, the alcohol products were formed in low ees (not exceeding *ca.* 35%), highlighting the challenging nature of asymmetric catalysis using complexes of this type.

Introduction

Cyclopentadienone iron tricarbonyl complexes **1** have recently found a significant number of applications in the catalysis of a number of organic transformations,[1–3] notably hydrogenation[4] and transfer hydrogenation,[5] and formation of C–N bonds *via* reductive amination[6] and 'hydrogen borrowing' reactions.[7] The hydrogen transfer is believed to proceed *via* formation of the hydride **2** and 16-electron species **3**, with the hydride transfer itself through the transition state also illustrated in Fig. 1.[8]

A number of derivatives of this class of catalyst have been reported, for example **4–11**, and some of these have been applied in enantioselective catalysis of ketone and imine reduction reactions.[9] In other examples, non-chiral cyclopentadienone iron tricarbonyl complexes have been used in conjunction with an asymmetric reagent, such as a phosphonic acid, in the catalysis of asymmetric reduction reactions (Fig. 2).[10]

In a recent study, we described an efficient route to the synthesis of catalysts such as **12**, through the reaction of iron pentacarbonyl with the derivatives of a *C*2-symmetric diol **13** (Scheme 1).[11]

Herein we describe the synthesis and applications of a series of cyclopentadienone iron tricarbonyl complexes with diverse structures, and efficient routes to their formation. Whilst the complexes are competent pre-catalysts for asymmetric reactions, the induced enantioselectivities remain low, reflecting the challenge of achieving high enantioselectivities with this class of complex.

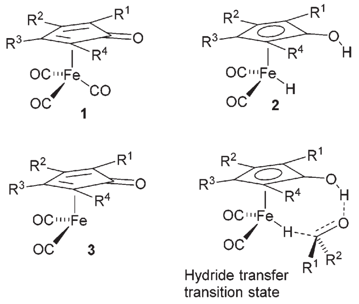

Fig. 1 Iron tricarbonyl cyclopentadienone structures.

Results and discussion

In the first extension of our studies, we sought to determine what effect an electron-donating group on the side chains of the catalyst might have. Towards this end we prepared the pyridine-containing complex **14**, from diol **15**[12] and *via* the dialkyne precursor **16**, following the route illustrated in Scheme 2a. Treatment of **14** with slightly more than 1 equivalent of trimethylamine *N*-oxide (TMAO)[13] resulted in formation of a new species which appears to match the structure **17** in which one CO group was replaced by the pyridine in an

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† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra, GC examples. X-ray data. Chiral HPLC of the ligands prior to complexation. CCDC 1567218–1567222. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt03250a

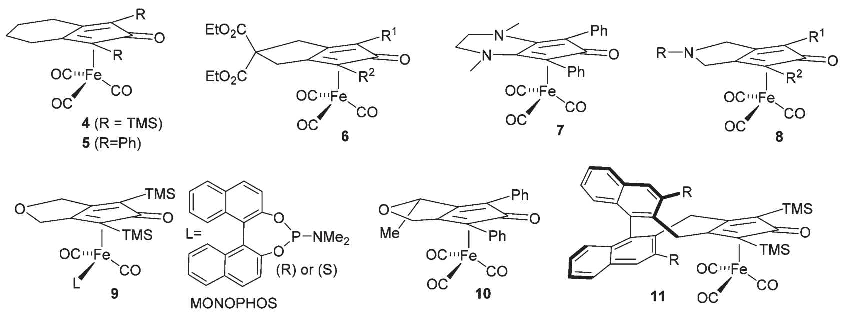
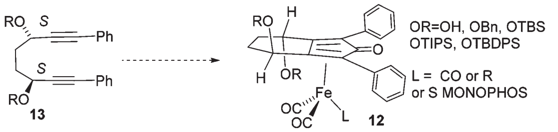
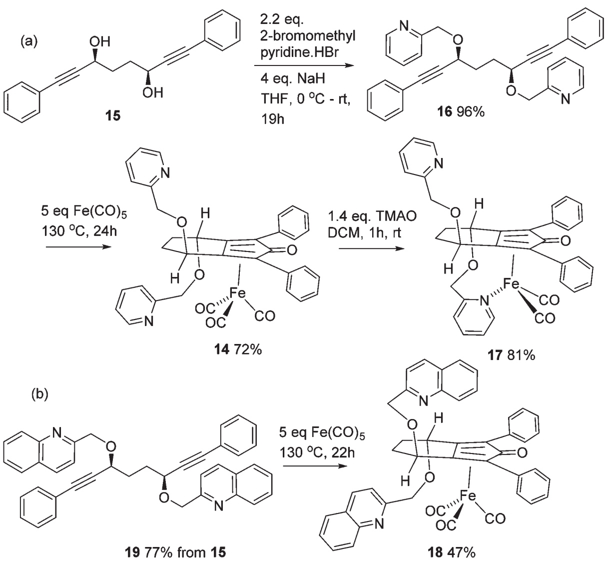


Fig. 2 Reported asymmetric and non-asymmetric catalysts based on iron tricarbonyl cyclopentadienone structures.

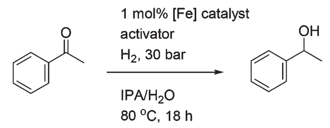


Scheme 1 Previously-reported asymmetric iron complexes derived from *C*2-symmetric diols.



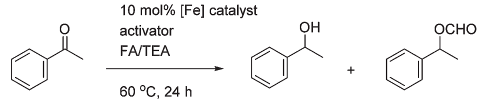
Scheme 2 Synthesis of pyridine-containing complexes.

Table 1 Hydrogenation of acetophenone using complexes **14**, **17** and **18**



Entry	Catalyst	Activator/%	Solvent	Conv./%
1	**14**	K_2CO_3 (3%)	IPA/H_2O	17.3
2	**14**	K_2CO_3 (2%)	IPA/H_2O	18.6
3	**14**	TMAO (1%)	IPA/H_2O	37.1
4	**17**	K_2CO_3 (5%)	IPA/H_2O	15.4
5	**17**	TMAO (1%)	IPA/H_2O	36.3
6	**17**	TMAO (2%)	IPA/H_2O	30.3
7	**18**	—	IPA/H_2O	70.9
8	**18**	K_2CO_3 (5%)	IPA/H_2O	51.2
9	**18**	TMAO (1%)	IPA/H_2O	99.8
10	**18**	TMAO (2%)	IPA/H_2O	99.7
11	**18**	TMAO (3%)	IPA/H_2O	99.8

Table 2 Asymmetric transfer hydrogenation of acetophenone using complexes **14**, **17** and **18**



Entry	Catalyst	Activator/%	Conv./%	Alcohol/% (ee/%)	Formate/% (ee/%)
1	**14**	—	73.7	63.1 (2.4 *R*)	10.6 (2.6 *R*)
2	**14**	TMAO (10%)	99.7	90.8 (2 *R*)	8.9 (2.8 *R*)
3	**17**	—	99.9	85.5 (4.2 *R*)	14.4 (3 *R*)
4	**17**	TMAO (10%)	99.9	87.8 (3.4 *R*)	11.8 (3 *R*)
5[a]	**18**	TMAO (10%)	58.1	45.4 (3.4 *R*)	12.7 (5.2 *R*)

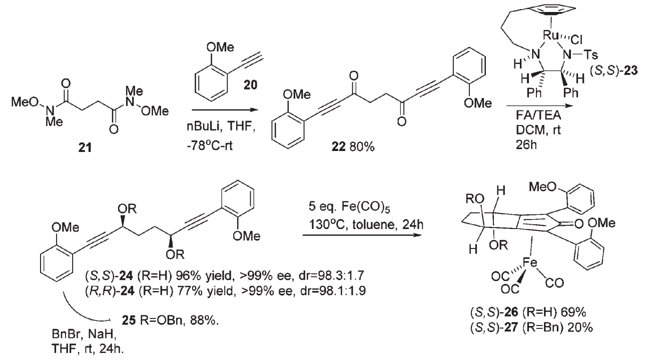
[a] Hetereogenous reaction (catalyst is not soluble).

intramolecular reaction. The addition of triphenylphosphine to the cyclic complex **17** led to formation of a new product with a peak at δ 57.57 in the ^{31}P NMR which is indicative of the formation of an iron triphenylphosphine complex. In addition, a further complex, **18**, containing a quinoline, was prepared from the dialkyne **19** (Scheme 2b). Complexes **14**, **17** and **18** proved to be effective catalysts for the reduction of ketones, with selected results shown in Table 1 for hydrogenation and Table 2 for transfer hydrogenation (full results are in the ESI†).

In the hydrogenation reactions, catalysts **14** and **17** gave products in low conversions, although the addition of K_2CO_3 or TMAO as an activating agent resulted in the highest conversions. In common with previous results, the addition of triphenylphosphine served to inhibit the reaction (see ESI†). The similarity between the results obtained with **14** and **17** suggest that they are reacting through a common intermediate, *i.e.* the formation (possibly reversible) of **17** from **14** upon treatment with TMAO. The quinoline-derived complex **18** gave improved conversions compared to the pyridine-containing complexes, although the addition of TMAO was again essential for optimal activation, and an excess of TMAO did not reduce the conversions. In all cases the ees were low however and no higher than *ca.* 7–8% (full results for these and other tests are given in the ESI†).

In the attempted asymmetric transfer hydrogenations (ATH), using a formic acid/triethylamine 5 : 2 azeotrope (FA/TEA) mixture as both reducing agent and solvent, the pyridine-containing complex **14** required the addition of TMAO to give optimal results however the cyclic complex **17** proved to be just as active with or without the addition of TMAO. This suggests that **17** may represent an 'activated' version of **14**, with reversible coordination of the pyridine acting to free a coordination site for hydride delivery and subsequent hydrogen transfer. The quinoline complex **18** gave poor conversion even with the addition of TMAO, however it appeared to not be soluble in the reaction mixture. Again the ees were low in all cases (between 2–4% only).

Previously reported catalysts **12**, and those illustrated in Scheme 2, contain unsubstituted phenyl rings adjacent to the central C═O of the cyclopentadienone, therefore we sought to see if an improvement could be made by the introduction of an *ortho*-substituent to these rings, since the extra steric hindrance has the potential to further influence the asymmetry of the reduction reactions. The synthesis of a series of compounds containing *ortho*-methoxy groups on the aromatic rings was completed (Scheme 3) following a route based on the method previously reported, using the reaction of the lithium salt of alkyne **20** with bis-Weinreb reagent **21**, to give diketone **22**, followed by ATH catalysed by tethered Ru(II) complex **23**, to the corresponding diol **24** in high ee. Both enantiomers, and the racemic standard (for HPLC analysis) were prepared for comparison, although the (*S*,*S*)-configuration products **24** were converted to catalysts for evaluation. Conversion of diol **24** to the dibenzyl derivative **25** was achieved efficiently. Both the diol and its two derivatives were treated at 130 °C for 24 h with three equivalents of $Fe(CO)_5$ to form the required complexes **26** and **27** respectively. In each case, a stable complex was formed and fully characterised, including by X-ray crystallography (Fig. 3).



Scheme 3 Synthesis of *ortho*-methoxy substituted complexes.

The X-ray crystallographic analysis of **26** and **27** (Fig. 3) confirmed the expected structures of the complexes, however there was no obvious transfer of chirality to the *o*-OMe aromatic rings. This flexibility may be responsible for the lack of selectivity in the subsequent reductions in which the catalysts were tested.

In the hydrogenation tests (Table 3; further results are listed in the ESI†), we focussed initially on the diol complex **26**. Again it was found that activation was required for best results, with full conversions being generated using TMAO. Previously, and in initial tests, a combination of IPA and water was used as solvent, as this had been found to give good results. A series of alternative solvents were tested however these gave, with the exception of THF, inferior results in terms of conversion, and no significant change to the ee. Reactions at slightly lower temperatures (60 °C and 40 °C) resulted in lower conversions, and the reduction of a series of acetophenone derivatives were also tested. In these tests, *ortho*-chloroacetophenone gave a product in lower conversion than the less hindered or electron-rich ketones. The dibenzyloxy-substituted catalyst **27** was also effective although slightly more active in THF than isopropanol/water (IPA/H_2O), and gave a product in up to 21% ee, which was higher than the average for the diol. This indicates that the extra steric hindrance created by the combined ring and *ortho*-aromatic substrates had a small positive effect on the selectivity (Table 4).

In the case of the ATH reactions, again the conversions were improved by the use of an activator at 80 °C, the ees of acetophenone reduction, however, were improved to 25–30%.

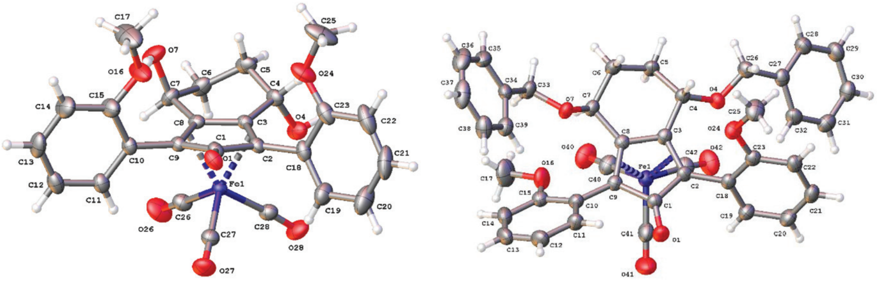
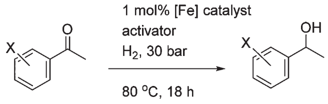


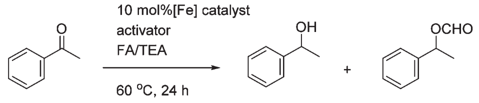
Fig. 3 X-ray crystallographic structures of complexes **26** and **27**.

Table 3 Hydrogenation of ketones using complexes **26** and **27**



Entry	Catalyst	Substrate	Activator/%	Solvent/other changes	Conv./%	ee/%
1	**26**	PhCOMe	—	IPA/H_2O	54.4	10 (*R*)
2	**26**	PhCOMe	K_2CO_3 (5%)	IPA/H_2O	19.5	9.2 (*R*)
3	**26**	PhCOMe	TMAO (1%)	IPA/H_2O	99.8	9.4 (*R*)
4	**26**	PhCOMe	TMAO (1%)	IPA	89.3	3.6 (*R*)
5	**26**	PhCOMe	TMAO (1%)	H_2O	57.2	7.4 (*R*)
6	**26**	PhCOMe	TMAO (1%)	Toluene	98.1	2.2 (*R*)
7	**26**	PhCOMe	TMAO (1%)	Chlorobenzene	85.9	0.2 (*R*)
8	**26**	PhCOMe	TMAO (1%)	THF	98.6	9.4 (*R*)
9	**26** 60 °C	PhCOMe	TMAO (1%)	IPA/H_2O	87.5	9.0 (*R*)
10	**26** 40 °C	PhCOMe	TMAO (1%)	IPA/H_2O	21.8	12.0 (*R*)
11	**26**	2-(OMe)C_6H_4COMe	TMAO (1%)	IPA/H_2O	>99	8.6 (*S*)
12	**26**	4-(OMe)C_6H_4COMe	TMAO (1%)	IPA/H_2O	91.6	6.0 (*R*)
13	**26**	2-ClC_6H_4COMe	TMAO (1%)	IPA/H_2O	56.8	3.6 (*R*)
14	**26**	4-ClC_6H_4COMe	TMAO (1%)	IPA/H_2O	96.6	10.2 (*S*)
15	**27**	PhCOMe	TMAO (1%)	IPA/H_2O	77.8	21.0 (*R*)
16	**27**	PhCOMe	TMAO (1%)	THF	100	16.0 (*R*)

Table 4 Asymmetric transfer hydrogenation of acetophenone using complexes **26** and **27**



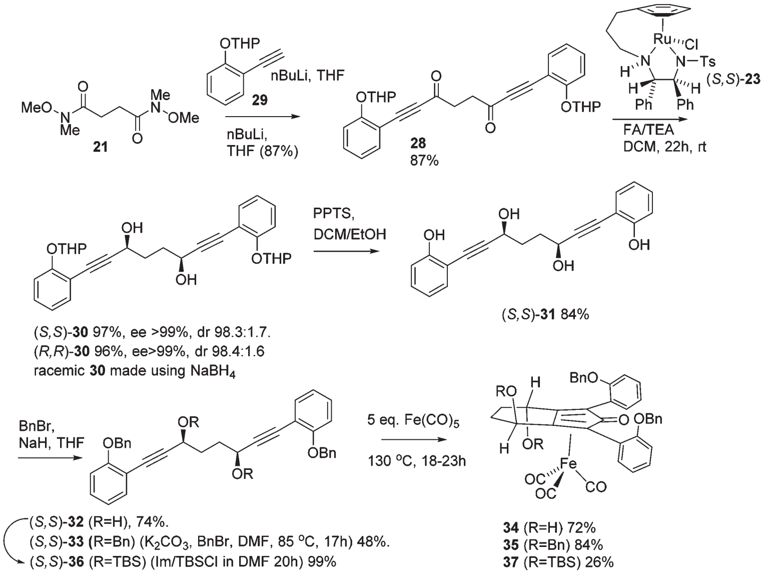
Entry	Catalyst	Activator/%	Conv./%	Alcohol/% (ee/%)	Formate/% (ee/%)
1	**26**	—	54.9	46.8 (28.4 *R*)	8.2 (25 *R*)
2	**26**	TMAO (10%)	99.6	87.2 (30.2 *R*)	12.3 (28 *R*)
3[a]	**26** 30 °C 24 h	TMAO (10%)	25.7	25.2 (35.2 *R*)	0.5 (n/a)
4[a]	**26** 30 °C 48 h	TMAO (10%)	51.5	49.9 (34.4 *R*)	1.6 (n/a)
5[a]	**26** 30 °C 72 h	TMAO (10%)	87.8	81.9 (34.6 *R*)	5.9 (n/a)
6	**27**	TMAO (10%)	93.3	89.4 (28.0 *R*)	10.6 (29.3 *R*)

[a] Followed over time and at lower temp. of 30 °C.

A reaction was followed over time at a lower temperature of *ca.* 30 °C, and in this case the ee improved to *ca.* 35%, although the reaction required 3 days to reach *ca.* 82%. In this case, as was the case for all reductions using FA/TEA, some formate was also formed, presumably through formylation of the initial alcohol product, although the ee of the formate was similar to that of the alcohol. In previous work, we have established that the alcohol and formate products in these reactions are of the same configuration.[11] The result with the dibenzyl-substituted complex **27** was comparable to that for the diol catalyst **26**, indicating that the increase of steric bulk had little effect on the reaction enantioselectivity.

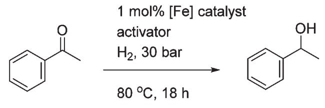
In order to improve the enantioselectivity, we sought to place a larger group on the *ortho* position of the aromatic rings adjacent to the C═O of the cyclopentadienone and towards this end we prepared the acetylene reagent precursor *o*(OBn) C_6H_4CCH (OBn = OCH_2Ph), however the subsequent reaction was very problematic with deprotonation at the benzylic CH_2 resulting in the formation of side products. In an alternative, successful, approach, we prepared the tetrahedropyran (THP)-protected diketone **28** using alkyne **29**, and subsequently the diol **30** through the sequence shown in Scheme 4. Unfortunately the cyclisation of this diol failed to give a clean product. However the hydrolysis of the THP groups gave the tetrol **31** which was either di- or tetrabenzylated to give **32** and **33** respectively. Both dialkynes were cyclised with $Fe(CO)_5$ in good yield to form complexes **34** and **35**. Reaction of the dibenzyl intermediate **32** with *t*-butyldimethylsilyl chloride (TBSCl) resulted in formation of **36** which was cyclised successfully but in low isolated yield to **37**. Peaks corresponding to the product in the ^1H NMR spectrum of **37** were very broad, however the mass spectrum indicated formation of the desired complex.

The application of complexes **34**, **35** and **37** to the reduction of acetophenone was tested, through both hydrogenation with hydrogen gas and ATH. Further results are given in the ESI.† In the pressure hydrogenation of acetophenone (Table 5) the tetrabenzyl complex **35** required activation but gave a product of *ca.* 23% ee consistently. The dibenzyl **34** (*i.e.* containing



Scheme 4 Synthesis of benzyloxy-substituted complexes *via* OTHP intermediate **30**.

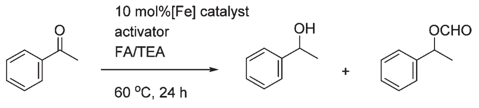
Table 5 Hydrogenation of acetophenone using complexes **34**, **35** and **37**



Entry	Catalyst	Activator/%	Solvent	Conv./%	ee/%
1	**35**	—	IPA/H_2O	4.8	25.2 (*R*)
2	**35**	K_2CO_3 (5%)	IPA/H_2O	>99	23.2 (*R*)
3	**35**	TMAO (1%)	IPA/H_2O	>99	23 (*R*)
4	**34**	—	IPA/H_2O	>99	3.4 (*R*)
5	**34**	K_2CO_3 (5%)	IPA/H_2O	12	5.2 (*R*)
6	**34**	TMAO (1%)	IPA/H_2O	>99	3.2 (*R*)
7	**35**	1% TMAO	EtOAc	>99	24.5 (*R*)
8	**35**	1% TMAO	Toluene	54.2	16.2 (*R*)
9	**35**	1% TMAO	THF	91.6	25.2 (*R*)
10	**35**	1% TMAO	IPA	>99	19.2 (*R*)
11	**35**	1% TMAO	Neat	87.6	18.8 (*R*)
12	**35**	1% TMAO	*t*BuOH	98.8	19.6 (*R*)
13	**37**	TMAO 1%	IPA/H_2O	85.2%	12 (*R*)

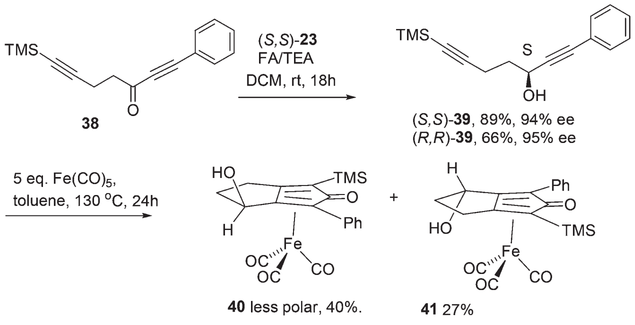
hydroxyl groups in the ring fused to the cyclopentadienone) worked without activation and indeed were less active in the presence of K_2CO_3; a trend we have noticed before.[11] Further solvents were tested (Table 5 and ESI†) and of these, EtOAc, THF, IPA and *t*BuOH gave good but not improved results. A reaction at 60 °C gave a lower conversion with no improvement to the ee. A similar result was obtained using complex **37**. In ATH reactions (Table 6) the ee (26%) generated by the dibenzyloxy complex **34** was not as high as the 36% ee achieved using the tetra OBn complex **35** however in both cases the reactions in FA/TEA gave a higher ee than the hydrogenation reaction with the same substrate. Although not fully purified, the bis-OTBS-substituted complex **37** gave a product of *ca.* 34% ee in a preliminary ATH test. Once again, the formate side-product was of similar ee to the alcohol in each case.

Table 6 Asymmetric transfer hydrogenation of acetophenone using complexes **34**, **35** and **37**



Entry	Catalyst	Activator/%	Conv./%	Alcohol/% (ee/%)	Formate/% (ee/%)
1	**35**	TMAO (10%)	55.7	47.9 (35.6 *R*)	7.8 (35.8 *R*)
2	**34**	TMAO (10%)	96.2	88.3 (25.8 *R*)	7.9 (26.4 *R*)
3	**37**	TMAO (10%)	98.6	91.1 (34.2 *R*)	8.5 (32.6 *R*)

Further extension of the range of complexes for investigation was achieved through the asymmetric synthesis of complexes containing a single chiral centre and non-identical groups flanking the central C=O of the cyclone. This concept of planar chirality has been applied before in similar reductions[9c,14] however the opportunity was taken to explore new routes to the synthesis of Fe cyclone catalysts (Scheme 5).



Scheme 5 Synthesis of diastereoisomeric complexes **40** and **41**.

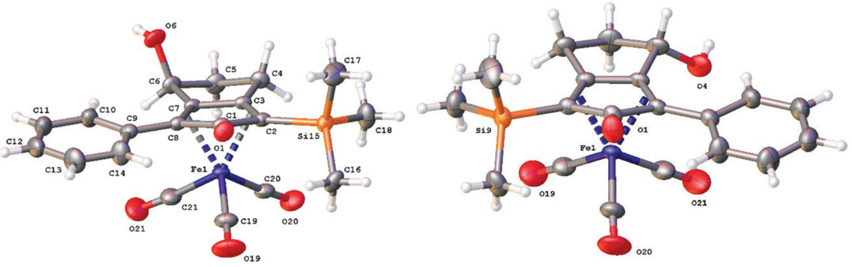
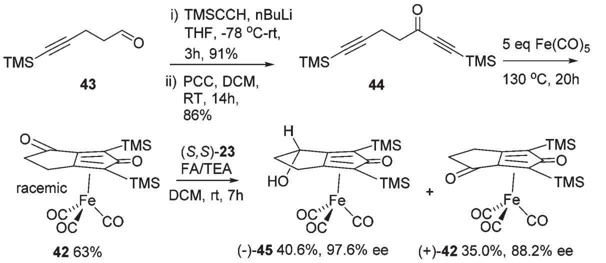


Fig. 4 X-ray crystallographic structures of complexes **40** and **41** respectively.



Scheme 6 Synthesis of enantiomerically-enriched complexes *via* a dynamic kinetic resolution.

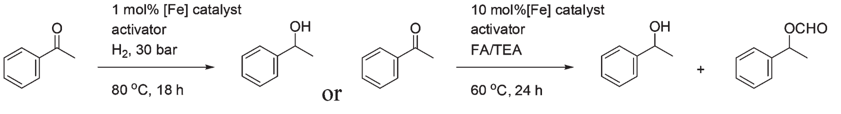
Addition of phenylacetylide anion to $TMSCCCH_2CH_2CHO$ followed by oxidation gave ketone **38** which was subsequently reduced to **39** in 94–95% ee using ATH with both enantiomers of tethered catalyst **23**. Cyclisation of **39** gave a mixture of two diastereomeric complexes **40** and **41** which were readily resolved by flash chromatography on silica gel and characterised by X-ray crystallography to confirm the relative stereochemistry in each isomer (Fig. 4). These create compounds with planar chirality about the centre C=O of the cyclone group.

In the reduction tests on acetophenone, both hydrogenation and transfer hydrogenation (Table 7), the diastereoisomeric complexes **40** and **41** gave alcohols of opposite configuration, indicating that the planar symmetry of the molecule created the primary directing effect. However the enantioselectivity was very low in all cases. Once again, for the hydrogenation reaction, activation was required, with TMAO giving the best results.

A kinetic resolution approach was also used to prepare a final class of asymmetric catalyst (Scheme 6); we prepared the bistrimethylsilyl (bisTMS) complex **42** (previously prepared by Pearson *et al.*), in racemic form[2c] from aldehyde **43** *via* ketone **44**. Asymmetric reduction, following a precedent set by previous work in our group,[15] with tethered catalyst **23**, led to preferential reduction of one enantiomer of racemic **42** to leave enriched ketone **42** and alcohol **45**, both in high ee, which could be separated by chromatography on silica gel (Scheme 6). The X-ray crystallographic structure of alcohol **45** was also obtained (Fig. 5), in order to confirm the *endo* relationship of the alcohol to the iron centre, as would be anticipated from the expected addition of hydride to the face of the ketone away from the $Fe(CO)_3$ unit due to steric hindrance.[15]

Although TMS groups flank both sides of the central ketone in this case, the asymmetric complexes provide the opportunity to gauge the effect of distant chiral centres on any asymmetric induction. Both new catalysts were also tested in asymmetric reductions of acetophenone (Table 8) but gave only moderate results, although it was reassuring to see the oppo-

Table 7 Asymmetric hydrogenation (entries 1–6) and ATH (entries 7 and 8) of acetophenone using complexes **40** and **41**



Entry	Catalyst	Activator/%	Solvent	Conv./%	ee/%
1	**40**	—	IPA/H_2O	4	5 (*R*)
2	**40**	K_2CO_3 (5%)	IPA/H_2O	68	7.4 (*R*)
3	**40**	TMAO (1%)	IPA/H_2O	99.7	6.2 (*R*)
4	**41**	—	IPA/H_2O	11.9	11.4 (*S*)
5	**41**	K_2CO_3 (5%)	IPA/H_2O	82.3	11.6 (*S*)
6	**41**	TMAO (1%)	IPA/H_2O	99.8	12.2 (*S*)

Entry	Catalyst	Activator/%	Solvent	Alcohol/% (ee/%)	Formate/% (ee/%)
7	**40**	TMAO (10%)	FA/TEA	91.1 (3.8 *R*)	8.1 (4 *R*)
8	**41**	TMAO (10%)	FA/TEA	88.4 (5.8 *S*)	9.9 (5.6 *S*)

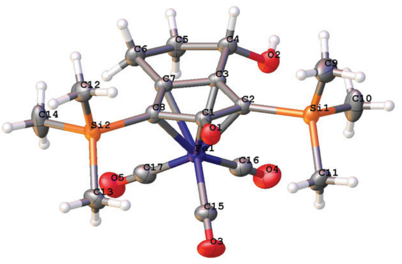


Fig. 5 Solid state structure of (−)-**45** with atom labels and thermal ellipsoids at 50% probability level.

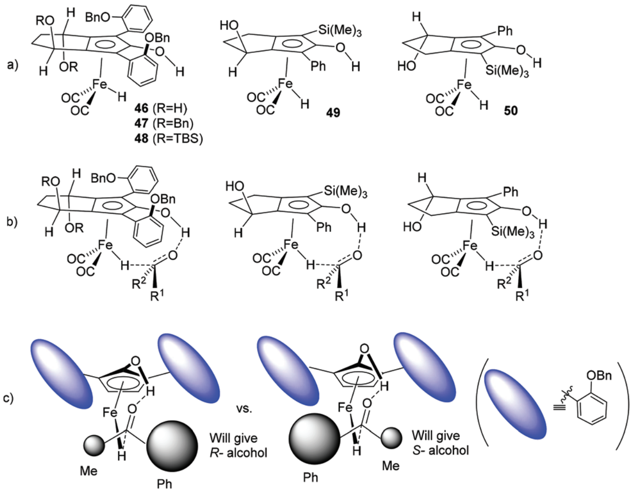


Fig. 6 (a) Hydrides formed from complexes **34**, **35**, **37**, **40** and **41** respectively. (b) Likely modes of hydride transfer from complexes **46–50** based on literature precedents. (c) Transition state control model for asymmetric hydride transfer from **46–48** to each face of the ketone substrate (the ovals representing positions of the tilted aromatic rings) indicating their diastereomeric nature and potential for enantiodifferentiation.

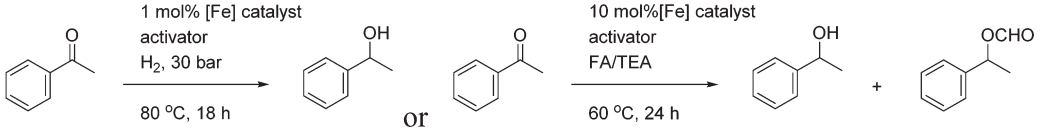
site sense of induction between **42** and **45** in the asymmetric hydrogenation reactions, as would be predicted on the basis of planar chirality control. Although in reality they are too low to indicate any significant directing effect.

Although the measured enantiomeric excesses are low, some trends emerge from the data which suggest that the steric bulk and substitution on the groups flanking the central C═O bond influence the process of asymmetric induction. Hydrides **46–50** (Fig. 6a), formed through activation of **34**, **35**, **37**, **40** and **41** respectively, are representative of those that would be formed from the iron tricarbonyl precursors. Assuming that the proposed concerted mechanism for hydride transfer (illustrated in Fig. 6b for each complex) is operating, then our working model for **46–48** is that the tilt of the aromatic rings is influenced by the alkoxy groups on the 4-carbon backbone and this creates a chiral environment in the region where hydride transfer takes place (Fig. 6c). In turn this is likely to create a difference in the steric hindrance of one face of the ketone to the complex relative to the other face, and has in turn the potential to differentiate between addition of the hydride to the *Re* or *Si* face of the ketone substrate. The ees of the reduction products are generally higher using catalysts with larger alkoxy groups on the 4-C backbone, which may suggest that the ‘tilt’ of the aromatic rings is slightly better-defined and this leads in turn to improved differentiation of the faces of the ketone in the reduction step.

In the case of **49** and **50**, the complexes have a pseudo-planar chirality and in this case a similar differentiation of the faces of the ketone substrate can operate (not illustrated) due to the difference in the steric bulk of the substituents either side of the central C═O bond. This would be likely to disfavour approach from one face over the other sufficiently to generate an enantioselectivity, and would account for the reversal in enantioselectivity from **49** to **50.**

However the limited enantioselectivity may be the result of the significant distance from the groups flanking the central C═O of the cyclopentadienone ring from the ketone substituents in the proposed reduction model. Until this distance can

Table 8 Asymmetric hydrogenation (entries 1–6) and ATH (entry 7) of acetophenone using catalysts **42** and **45**



Entry	Catalyst	Activator/%	Solvent	Conv./%	ee/%
1	**45**	—	IPA/H_2O	13.7	6.8 (*S*)
2	**45**	K_2CO_3 (5%)	IPA/H_2O	99.4	9.4 (*S*)
3	**45**	TMAO (10%)	IPA/H_2O	99.6	4.2 (*S*)
4	**42**	—	IPA/H_2O	>99	3.8 (*R*)
5	**42**	K_2CO_3 (5%)	IPA/H_2O	9.6	2.6 (*R*)
6	**42**	TMAO (1%)	IPA/H_2O	>99	0.4 (*R*)

Entry	Catalyst	Activator (%)	Solvent	Alcohol/% (ee/%)	Formate/% (ee/%)
7	**42**	TMAO (10%)	FA/TEA	3.9 (3.8 ee *R*)	24.2 (4 ee *R*)

be closed, or the mechanism better understood, progress towards high enantioselectivities with this class of catalyst will remain challenging. The improved ees obtained using the ATH process also cannot be directly explained with the model in Fig. 6c, and suggest the operation of an additional directing effect by the solvent.

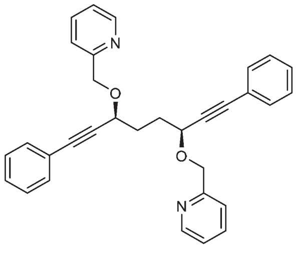
In conclusion, we have completed the synthesis of a range of enantiomerically-enriched cyclopentadienone iron tricarbonyl complexes through a range of diverse approaches, thus opening up routes to a range of valuable derivatives for testing as reduction and oxidation catalysts. Larger functional groups flanking the central C═O bond in the catalyst appear to give improved enantioselectivities in reductions, however even the best enantiomeric excesses were relatively modest. Whilst the synthesis of the iron-based catalysts was successful, the results indicate that significant work remains to be carried out in order to translate our understanding of the mechanism to the synthesis of a highly enantioselective catalyst for the target applications. This remains the subject of ongoing studies in our group.

Experimental section

General experimental methods

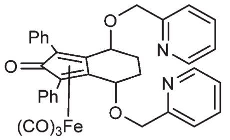
All solvents and reagents were degassed before use and all reactions were carried out under a nitrogen atmosphere. Reactions were monitored by TLC using aluminium backed silica gel plates, visualized using UV 254 nm and phosphomolybdic acid or potassium permanganate. Flash column chromatography was carried out routinely on silica gel. Reagents and solvents were used as received from commercial sources unless otherwise stated. The synthesis of iron complexes was carried out in ACE 15 Ml 150 psi pressure tested pressure tubes and heated in aluminium heating blocks. Pressure hydrogenation reactions were carried out in a Parr pressure vessel. ^{1}H NMR spectra were recorded on a Bruker DPX (400 or 500 MHz) spectrometer. Chemical shifts are reported in δ units, parts per million relative to 7.26 ppm for chloroform and 0.00 ppm for TMS. Mass spectra for analysis of synthetic products were recorded on a Bruker Esquire 2000 or a Bruker MicroTOF mass spectrometer. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR Golden Gate instrument. Melting points were recorded on a Stuart Scientific SMP 1 instrument and are uncorrected.

2,2′-((((3*S*,6*S*)-1,8-Diphenylocta-1,7-diyne-3,6-diyl)bis(oxy))bis(methylene))dipyridine 16.



This compound is novel. In an round bottom flask under a nitrogen atmosphere (3*S*,6*S*)-1,8-diphenylocta-1,7-diyne-3,6-diol **15** (812 mg, 2.80 mmol) and 2-(bromomethyl)pyridine hydrobromide (1.56 g, 6.17 mmol) was dissolved/suspended in anhydrous THF (80 cm^3). The mixture was cooled at 0 °C and NaH (60% in mineral oil, 447 mg, 11.2 mmol) was added in small portions. After 19 hours, H_2O (100 cm^3) was added dropwise and the mixture was stirred 10 minutes. Then THF was removed and the product was extracted with DCM (3 × 100 cm^3). The reunited organic layers were washed with brine (50 cm^3) and dried over $MgSO_4$. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 1 : 1 to petroleum ether/EtOAc = 1 : 4) to give 2,2′-((((3*S*,6*S*)-1,8-diphenylocta-1,7-diyne-3,6-diyl)bis(oxy))bis(methylene))dipyridine **16** (1.27 g, 2.69 mmol, yield: 96%) as colourless solid. M.p. 64.2–66.4 °C. $[\alpha]_D^{25}$ −88.6 (c 0.50, $CHCl_3$). IR$_{(neat)}$ 3058, 2966, 2931, 2893, 2868, 2836, 2220, 1591, 1571, 1489, 1476, 1457, 1441, 1388, 1343, 1329, 1299, 1242. δ_H (500 MHz, $CDCl_3$), 8.56 (2H, d, J = 4.9 Hz, Py*H*), 7.68 (2H, td, J = 7.7, 1.7 Hz, Py*H*), 7.51 (2H, d, J = 7.8 Hz, Py*H*), 7.40–7.46 (4H, m, Ar*H*), 7.23–7.34 (6H, m, Ar*H*), 7.18 (2H, dd, J = 6.9, 5.3 Hz, Py*H*), 5.02 (2H, d, J = 13.3 Hz, PyC*H*H), 4.74 (2H, d, J = 13.3 Hz, PyCH*H*), 4.49–4.61 (2H, m, C*H*OR), 2.11–2.32 (4H, m, C*H*$_2$). δ_C (125 MHz, $CDCl_3$), 158.4 (C), 148.9 (CH), 136.6 (CH), 131.8 (CH), 128.4 (CH), 128.2 (CH), 122.5 (C), 122.3 (CH), 121.5 (CH), 87.4 (C), 86.5 (C), 71.5 (CH_2), 69.8 (CH), 31.6 (CH_2). m/z (ESI) $[M + H]^+$, 473.2; $[M + Na]^+$, 495.2. HRMS (ESI-Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{32}H_{28}N_2O_2Na$ 495.2043; found 495.204.

Tricarbonyl-((4*S*,7*S*)-1,3-diphenyl-4,7-bis(pyridin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron 14.

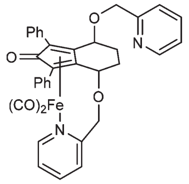


This compound is novel. In an ACE pressure tube under a nitrogen atmosphere 2,2′-((((3*S*,6*S*)-1,8-diphenylocta-1,7-diyne-3,6-diyl)bis(oxy))bis(methylene))dipyridine **16** (500 mg, 1.06 mmol) was dissolved in anhydrous toluene (5 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (0.79 cm^3, 5.86 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C. After 24 hours the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: EtOAc to EtOAc/MeOH = 9/1) to give tricarbonyl-((4*S*,7*S*)-1,3-diphenyl-4,7-bis(pyridin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron **14** (485 mg, 0.76 mmol, yield: 72%) as an orange solid.

M.p. 55.6 °C dec. $[\alpha]_D^{25}$ +82.3 (c 0.52, $CHCl_3$). IR$_{(neat)}$ 3056, 3013, 2931, 2864, 2062, 1983, 1633, 1590, 1571, 1499, 1475, 1435, 1388, 1362, 1329 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 8.53 (1 H, dq, J = 4.9, 0.8 Hz, Py*H*), 8.47 (1 H, dq, J = 4.9, 0.6 Hz, Py*H*), 7.78–7.83 (2 H, m, Ar*H*), 7.71–7.77 (2 H, m, Ar*H*), 7.58 (1 H, td,

J = 7.7, 1.7 Hz, Py*H*), 7.51 (1 H, td, J = 7.7, 1.7 Hz, Py*H*), 7.27–7.42 (6 H, m, Ar*H*), 7.18 (1 H, ddd, J = 7.3, 5.0, 0.8 Hz, Py*H*), 7.14 (1 H, ddd, J = 7.3, 5.0, 0.8 Hz, Py*H*), 7.03 (1 H, d, J = 7.8 Hz, Py*H*), 6.71 (1 H, d, J = 7.8 Hz, Py*H*), 4.82 (1 H, t, J = 3.2 Hz, C*H*OR), 4.73 (1 H, d, J = 12.1 Hz, PyCH*H*), 4.60 (1 H, d, J = 12.1 Hz, PyCH*H*), 4.57 (1 H, d, J = 12.1 Hz, PyCH*H*), 4.52 (1 H, t, J = 3.3 Hz, C*H*OR), 4.28 (1 H, d, J = 12.1 Hz, PyCH*H*), 2.14–2.35 (3 H, m, CH_2), 2.03–2.12 (1 H, m, CH_2). δ_C (125 MHz, $CDCl_3$), 208.16 (C), 170.08 (C), 157.18 (C), 156.91 (C), 148.93 (CH), 148.80 (CH), 136.60 (CH), 136.50 (CH), 131.23 (C), 131.06 (C), 130.08 (CH), 129.71 (CH), 128.38 (CH), 128.34 (CH), 128.02 (CH), 122.62 (CH), 122.52 (CH), 122.25 (CH), 121.69 (CH), 100.15 (C), 100.08 (C), 83.28 (C), 81.69 (C), 72.82 (CH_2), 72.62 (CH_2), 70.80 (CH), 68.74 (CH), 22.09 (CH_2), 21.98 (CH_2). *m*/*z* (ESI) $[M + H]^+$, 641.1; $[M + Na]^+$, 663.1. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{36}H_{28}FeN_2O_6Na$ 663.1190; found 663.1191.

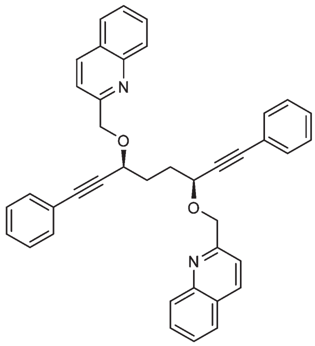
Dicarbonyl-((4*S*,7*S*)-1,3-diphenyl-4,7-bis(pyridin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron 17.



This compound is novel. In an round bottom flask under a nitrogen atmosphere, tricarbonyl-((4*S*,7*S*)-1,3-diphenyl-4,7-bis(pyridin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one) Iron **14** (500 mg, 0.78 mmol) was dissolved in anhydrous DCM (20 cm^3). Then trimethylamine *N*-oxide (77 mg, 1.10 mmol) was added and the reaction mixture was stirred for 1 hour and the volatiles were removed. The product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 3 : 7 to 1 : 4) to give dicarbonyl-((4*S*,7*S*)-1,3-diphenyl-4,7-bis(pyridin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron **17** (386 mg, 0.63 mmol, yield: 81%) as orange solid. M.p. 150 °C dec. $[\alpha]_D^{25}$ +985.3 (c 6.8 × 10^{-3}, $CHCl_3$). $IR_{(neat)}$ 3095, 3077, 3052, 2988, 2952, 2910, 1992, 1934, 1617, 1597, 1571, 1497, 1477, 1447, 1437, 1393, 1367, 1314, 1242 cm^{-1}.

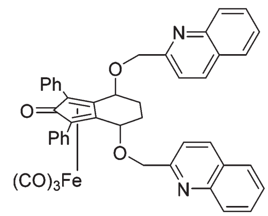
δ_H (500 MHz, $CDCl_3$), 8.62 (1H, d, J = 5.0 Hz, Py*H*), 8.40 (1H, d, J = 4.3 Hz, Py*H*), 7.82–7.88 (2H, m, Ar*H*), 7.48–7.58 (3H, m, 2× Ar*H* and 1× Py*H*), 7.45 (1H, dd, J = 7.7, 1.7 Hz, Py*H*), 7.20–7.32 (3H, m, Ar*H*), 7.18 (1H, d, J = 6.9 Hz, Py*H*), 7.07 (1H, dd, J = 6.7, 5.2 Hz, Py*H*), 6.95–7.02 (3H, m, Ar*H*), 6.76 (1H, ddd, J = 7.3, 6.0, 1.4 Hz, Py*H*), 6.55 (1H, d, J = 7.8 Hz, Py*H*), 5.65 (1H, d, J = 13.0 Hz, PyC*H*H), 5.32 (1H, d, J = 4.4 Hz, C*H*OR), 4.71–4.79 (2H, m, 1× PyC*H*H and 1× C*H*OR), 4.42 (1H, d, J = 12.0 Hz, PyC*H*H), 3.93 (1H, d, J = 12.0 Hz, PyCH*H*), 2.65 (1H, tt, J = 14.4, 3.0 Hz CH*H*), 2.54 (1H, tdd, J = 14.4, 5.6, 3.5 Hz CH*H*), 2.43 (1H, dq, J = 14.4, 3.0 Hz, CH*H*), 2.22–2.31 (1H, m, CH*H*). δ_C (125 MHz, $CDCl_3$), 217.0 (C), 211.6 (C), 168.7 (C), 162.3 (C), 159.7 (CH), 157.5 (C), 148.5 (CH), 138.1 (CH), 136.4 (CH), 133.5 (C), 132.0 (C), 129.4 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 127.2 (CH), 126.0 (CH), 125.5 (CH), 124.6 (CH), 122.3 (CH), 121.8 (CH), 99.4 (C), 82.7 (C), 81.7 (C), 73.1 (CH_2), 71.5 (C), 70.7, 69.3 (CH_2), 69.1 (CH), 27.5 (CH_2), 23.9 (CH_2). *m*/*z* (ESI) $[M + H]^+$, 613.1; $[M + Na]^+$, 635.1. HRMS (ESI-Q-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{35}H_{29}FeN_2O_5$ 613.1421; found 613.1427.

2,2′-((((3*S*,6*S*)-1,8-Diphenylocta-1,7-diyne-3,6-diyl)bis(oxy))bis(methylene))diquinoline 19.



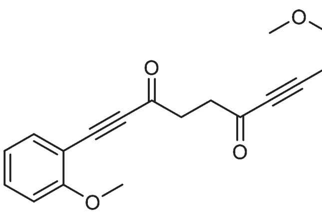
This compound is novel. In an round bottom flask under a nitrogen atmosphere (3*S*,6*S*)-1,8-diphenylocta-1,7-diyne-3,6-diol **15** (1.00 g, 3.44 mmol) was dissolved in anhydrous DMF (40 cm^3). The mixture was cooled at 0 °C and NaH (60% in mineral oil, 826 mg, 20.65 mmol) was added in small portions. Then and 2-(chloromethyl)quinoline hydrochloride (1.56 g, 7.94 mmol) was added in small portions and the reaction mixture was warmed at room temperature. After 24 hours, NH_4Cl aqueous (30 cm^3) and H_2O (50 cm^3) were added. The product was extracted with 3 × 150 cm^3 and the reunited organic layers were washed with 3 × 100 cm^3 of H_2O. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: pentane/EtOAc = 9 : 1 to 3 : 7) to give 2,2′-((((3*S*,6*S*)-1,8-diphenylocta-1,7-diyne-3,6-diyl)bis(oxy))bis(methylene))diquinoline **19** (1.52 g, 2.65 mmol, yield: 77%) as brown solid which was enough pure by NMR to be used without further purification. A sample for full characterisation was purified by double crystallisation from hot hexane giving a white solid. M.p. 98.4–99.6 °C. $[\alpha]_D^{25}$ −148.0 (c 0.66, $CHCl_3$). $IR_{(neat)}$ 3056, 2961, 2937, 2868, 2228, 1735, 1709, 1616, 1596, 1561, 1503, 1490, 1444, 1425, 1384, 1335, 1313, 1254, 1228, 1206. δ_H (500 MHz, $CDCl_3$), 8.13 (2H, d, J = 8.5 Hz, Ar*H*), 8.05 (2H, d, J = 8.5 Hz, Ar*H*), 7.78 (2H, d, J = 8.1 Hz, Ar*H*), 7.64–7.73 (4H, m, Ar*H*), 7.48–7.54 (2H, m, Ar*H*), 7.38–7.44 (4H, m, Ar*H*), 7.24–7.33 (6H, m, Ar*H*), 5.17 (2H, d, J = 13.3 Hz, ArCH*H*), 4.92 (2H, d, J = 13.3 Hz, ArC*H*H), 4.57–4.68 (2H, m, C*H*OR), 2.18–2.36 (4H, m, CH_2). δ_C (125 MHz, $CDCl_3$), 159.1 (C), 147.4 (C), 136.6 (CH), 131.8 (CH), 129.5 (CH), 128.9 (CH), 128.4 (CH), 128.2 (CH), 127.6 (CH), 127.5 (C), 126.2 (CH), 122.5 (C), 119.6 (CH), 87.5 (C), 86.7 (C), 72.2 (CH_2), 70.0 (CH), 31.7 (CH_2). *m*/*z* (ESI) $[M + H]^+$, 573.2; $[M + Na]^+$, 595.2. HRMS (ESI-Q-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{40}H_{33}N_2O_2N$ 573.2537; found 573.2537.

Tricarbonyl-(4*S*,7*S*)-1,3-diphenyl-4,7-bis(quinolin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 18.



This compound is novel. In an ACE pressure tube under a nitrogen atmosphere 2,2′-((((3*S*,6*S*)-1,8-diphenylocta-1,7-diyne-3,6-diyl)bis(oxy))bis(methylene))diquinoline **19** (400 mg, 0.70 mmol) was dissolved in anhydrous toluene (5 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (0.47 cm^3, 3.49 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C. After 22 hours the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: pentane/EtOAc = 1 : 1 to 3 : 7) to give tricarbonyl-(4*S*,7*S*)-1,3-diphenyl-4,7-bis(quinolin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron **18** (244 mg, 0.33 mmol, 47%) as yellow/orange solid. M.p. 74.7 °C dec. $[\alpha]_D^{25}$ +23.0 (*c* 0.10, $CHCl_3$). $IR_{(neat)}$ 3056, 2930, 2862, 2064, 2011, 1988, 1733, 1633, 1599, 1565, 1501, 1442, 1427, 1364, 1311, 1218, 1070 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.91–8.07 (4H, m, Ar*H*), 7.75–7.82 (6H, m, Ar*H*), 7.63–7.75 (2H, m, Ar*H*), 7.49–7.58 (2H, m, Ar*H*), 7.27–7.39 (6H, m, Ar*H*), 7.08 (1H, d, *J* = 8.4 Hz, Ar*H*), 6.75 (1H, d, *J* = 8.4 Hz, Ar*H*), 4.85–4.95 (2H, m, 1× C*H*OR and 1× ArCH*H*), 4.76 (2H, dd, *J* = 15.2, 12.1 Hz, ArC*H*H), 4.60–4.65 (1H, m, C*H*OR), 4.47 (1H, d, *J* = 12.1 Hz, ArCH*H*), 2.18–2.40 (3H, m, C*H*$_2$), 2.08–2.15 (1H, m, C*H*$_2$); δ_C (125 MHz, $CDCl_3$), 208.2 (C), 170.1 (C), 157.7 (C), 157.4 (C), 147.3 (C), 147.2 (C), 136.6 (CH), 136.5 (CH), 131.2 (C), 131.1 (C), 130.2 (CH), 129.64 (CH), 129.57 (CH), 129.0 (CH), 128.9 (CH), 128.44 (CH), 128.40 (CH), 128.1 (CH), 127.6 (CH), 127.53 (C), 127.50 (C), 126.5 (CH), 126.4 (CH), 120.1 (CH), 119.5 (CH), 100.2 (C), 100.0 (C), 83.5 (C), 81.6 (C), 73.4 (CH_2), 73.3 (CH_2), 71.0 (CH), 69.0 (CH), 22.2 (CH_2), 22.1 (CH_2). *m*/*z* (ESI) $[M + H]^+$, 741.2; $[M + Na]^+$, 763.2. HRMS (ESI-Q-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{44}H_{33}FeN_2O_6$ 741.1683; found 741.1670.

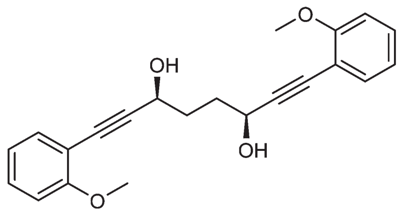
1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-dione 22.



This compound is novel. In a round bottom flask under a nitrogen atmosphere 1-ethynyl-2-methoxybenzene **20** (0.5 cm^3, 3.86 mmol) was dissolved in anhydrous THF (10 cm^3). The mixture was cooled at −78 °C and *n*-butyllithium (2.5 M in hexanes, 1.55 cm^3, 3.88 mmol) was added dropwise. The mixture was warmed to room temperature and stirred at this temperature for 1 hour. Then the mixture was cooled to 0 °C and transferred *via* cannula dropwise to a flask containing N^1,N^4-dimethoxy-N^1,N^4-dimethylsuccinamide **21** (359 mg, 1.76 mmol) dissolved/suspended in THF (15 cm^3) at −78 °C. After 5 minutes the mixture was warmed at room temperature and stirred at this temperature for 90 minutes. Then the mixture was cooled to −40 °C and saturated $NaHCO_3$ aqueous solution (10 cm^3) was added. The mixture was warmed to room temperature and H_2O (30 cm^3) was added. The product was extracted with DCM (3 × 50 cm^3) and the reunited organic layers were washed with brine (50 cm^3) and dried over Na_2SO_4. The volatiles were removed and the product was purified by filtration through a silica plug washing with DCM to give 1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-dione **22** (458 mg, 1.32 mmol, yield: 80%) as colourless solid.

M.p. 128.8–130.1 °C. $IR_{(neat)}$ 2983, 2948, 2919, 2840, 2183, 1656, 1593, 1569, 1488, 1460, 1427, 1402, 1314, 1282, 1252, 1216 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.52 (2H, dd, *J* = 7.5, 1.2 Hz, Ar*H*), 7.39–7.46 (2H, m, Ar*H*), 6.85–6.99 (4H, m, Ar*H*), 3.90 (6H, s, C*H*$_3$), 3.15 (4H, s, C*H*$_2$). δ_C (125 MHz, $CDCl_3$), 185.4 (C), 161.6 (C), 135.0 (CH), 132.6 (CH), 120.6 (CH), 110.8 (CH), 109.0 (C), 91.5 (C), 89.1 (C), 55.8 (CH_3), 39.2 (CH_2). *m*/*z* (ESI) $[M + Na]^+$ 369.0. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{22}H_{18}O_4Na$ 369.1097; found 369.1094.

(3*S*,6*S*)-1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24.

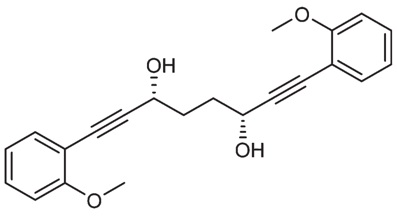


This compound is novel. In an round bottom flask under a nitrogen atmosphere 1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-dione **22** (450 mg, 1.30 mmol) was dissolved in anhydrous DCM (1.5 cm^3). [(*S*,*S*)-Teth-TsDpen-RuCl] **23** (8 mg, 0.013 mmol) and an azeotropic mixture of formic acid/triethylamine (5 : 2 mixture, 1.5 cm^3) were added. After 26 hours, saturated $NaHCO_3$ aqueous solution (5 cm^3) and H_2O (5 cm^3) were added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 20 cm^3). The reunited organic layers were washed with brine (15 cm^3) and dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 7 : 3 to 3 : 7) to give (3*S*,6*S*)-1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol **24** (438 mg, 1.25 mmol, yield: 96%, dr = 98.3 : 1.7, >99% ee) as colourless solid. The enantiomeric and diastereomeric excess were determined by HPLC analysis with a ChiralPak IB column: 0.46 cm × 25 cm, mobile phase EtOAc : hexane 3 : 2, flow rate 1 mL min^{-1}, temperature 30 °C, UV detection at λ = 254 nm; t_R = 6.4 min (*R*,*R*), t_R = 11.8 min

(*R*,*S*), t_R = 22.9 min (*S*,*S*). M.p. 113.3–114.8 °C. $[\alpha]_D^{25}$ −16.8 (*c* 0.62, $CHCl_3$). $IR_{(neat)}$ 3489, 3070, 3021, 2968, 2948, 2892, 2867, 2838, 2226, 1596, 1574, 1488, 1428, 1406, 1346, 1316, 1257, 1232, 1205 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.40 (2H, dd, *J* = 7.6, 1.6 Hz, Ar*H*), 7.29 (2H, ddd, *J* = 8.4, 7.5, 1.7 Hz, Ar*H*), 6.90 (2H, dd, *J* = 7.5, 0.8 Hz, Ar*H*), 6.87 (2H, d, *J* = 8.4 Hz, Ar*H*), 4.83 (2H, q, *J* = 4.7 Hz, C*H*OH), 3.88 (6H, s, C*H*$_3$), 2.64 (2H, d, *J* = 5.6 Hz, O*H*), 2.06–2.24 (4H, m, C*H*$_2$).

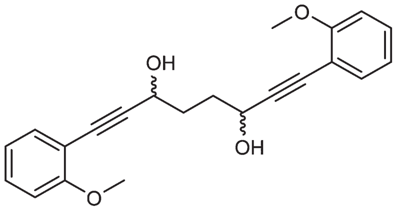
δ_C (125 MHz, $CDCl_3$), 160.0 (C), 133.6 (CH), 129.9 (CH), 120.4 (CH), 111.7 (C), 110.6 (CH), 94.0 (C), 81.5 (C), 62.6 (CH), 55.7 (CH_3), 33.4 (CH_2). *m*/*z* (ESI) $[M + Na]^+$ 373.1. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{22}H_{22}O_4Na$ 373.1410; found 373.1403.

(3*R*,6*R*)-1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24.



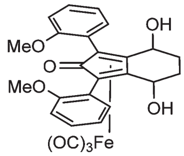
This compound is novel. In an round bottom flask under a nitrogen atmosphere 1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-dione **22** (100 mg, 0.29 mmol) was dissolved in anhydrous DCM (1.0 cm^3). [(*R*,*R*)-Teth-TsDpen-RuCl] **23** (1.8 mg, 0.0029 mmol) and an azeotropic mixture of formic acid/triethylamine (5 : 2 mixture, 0.5 cm^3) were added. After 26 hours saturated $NaHCO_3$ aqueous solution (5 cm^3) and H_2O (5 cm^3) were added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 20 cm^3). The reunited organic layers were washed with brine (15 cm^3) and dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 7 : 3 to 3 : 7) to give (3*R*,6*R*)-1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol **24** (78 mg, 0.22 mmol, yield: 77%, dr = 98.1 : 1.9, >99% ee) as colourless solid. The enantiomeric and diastereomeric excess were determined by HPLC analysis with a ChiralPak IB column: 0.46 cm × 25 cm, mobile phase EtOAc : hexane 3 : 2, flow rate 1 mL min^{-1}, temperature 30 °C, UV detection at λ = 254 nm; t_R = 6.4 min (*R*,*R*), t_R = 11.8 min (*R*,*S*), t_R = 22.9 min (*S*,*S*). $[\alpha]_D^{25}$ +16.6 (*c* 0.46, $CHCl_3$).

1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24.



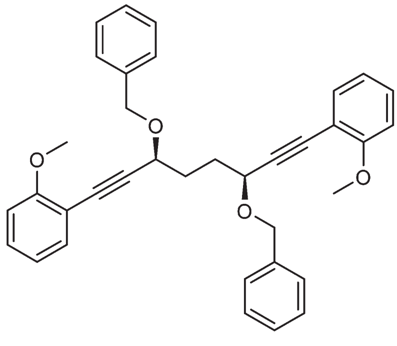
This compound is novel. In an round bottom flask under a nitrogen atmosphere 1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-dione **22** (50 mg, 0.14 mmol) was dissolved in DCM/MeOH 1 : 1 (2 cm^3). $NaBH_4$ (14 mg, 0.37 mmol) was added and the reaction was stirred for 2 hours. Then H_2O (10 cm^3) was added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 10 cm^3). The reunited organic layers were washed with brine (10 cm^3) and dried over Mg_2SO_4. The volatiles were removed and the product was purified by filtration through a silica plug washing with EtOAc to give 1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol **24** (46 mg, 0.13 mmol, yield: 90.9%) as light brown solid. δ_H (500 MHz, $CDCl_3$), 7.37–7.42 (4H, m, Ar*H*), 7.26–7.32 (4H, m, Ar*H*), 6.84–6.92 (8H, m, Ar*H*), 4.82 (1.7H, br. s., C*H*OH), 4.76 (2.3H, br. s., C*H*OH), 3.88 (12H, d, *J* = 5.2 Hz, C*H*$_3$), 3.03 (2H, d, *J* = 5.5 Hz, O*H*), 2.69 (2H, d, *J* = 2.7 Hz, O*H*), 2.06–2.25 (8H, m, C*H*$_2$). δ_C (125 MHz, $CDCl_3$), 160.05 (C), 160.03 (C), 133.6 (CH), 133.5 (CH), 129.9 (CH), 120.45 (CH), 120.42 (CH), 111.7 (C), 110.6 (CH), 94.1 (C), 94.0 (C), 81.6 (C), 81.4 (C), 62.8 (CH), 62.6 (CH), 55.72 (CH_3), 55.69 (CH_3), 33.9 (CH_2), 33.3 (CH_2).

Tricarbonyl-(4*S*,7*S*)-4,7-dihydroxy-1,3-bis(2-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 26.



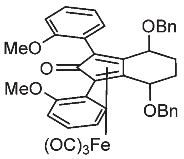
This compound is novel. In an ACE pressure tube under a nitrogen atmosphere (3*S*,6*S*)-1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol **24** (190 mg, 0.54 mmol) was dissolved/suspended in anhydrous toluene (5 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (0.37 cm^3, 2.74 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C for 24 hours. After the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: pentane/EtOAc = 7 : 3 to 1 : 4) to give tricarbonyl-(4*S*,7*S*)-4,7-dihydroxy-1,3-bis(2-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron **26** (193 mg, 0.37 mmol, yield: 69%) as yellow solid. M.p. 183.0–184.0 °C. $[\alpha]_D^{25}$ −88.8 (*c* 0.49, $CHCl_3$). $IR_{(neat)}$ 3367 (broad), 3077, 3008, 2936, 2856, 2837, 2071, 2027, 1979, 1737, 1625, 1600, 1497, 1466, 1435, 1388, 1310, 1278, 1244 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.69 (1H, dd, *J* = 7.6, 1.0 Hz, Ar*H*), 7.43 (1H, dd, *J* = 7.5, 1.2 Hz, Ar*H*), 7.33–7.41 (2H, m, Ar*H*), 6.95–7.10 (4H, m, Ar*H*), 4.91–5.00 (1H, m, C*H*OH), 4.76–4.83 (1H, m, C*H*OH), 3.904 (3H, s, C*H*$_3$), 3.895 (3H, s, C*H*$_3$), 2.80 (1H, d, *J* = 1.4 Hz, O*H*), 2.42 (1H, d, *J* = 3.2 Hz, O*H*), 2.22–2.35 (2H, m, C*H*$_2$), 1.75–1.88 (1H, m, CH*H*), 1.56–1.71 (1H, m, C*H*H). δ_C (125 MHz, $CDCl_3$), 208.5 (C), 169.1 (C), 157.0 (C), 156.5 (C), 134.4 (CH), 133.1 (CH), 130.3 (CH), 130.2 (CH), 121.7 (CH), 121.2 (CH), 119.98 (C), 118.96 (C), 111.8 (CH), 111.6 (CH), 105.1 (C), 104.5 (C), 80.1 (C), 79.1 (C), 63.7 (CH), 63.5 (CH), 55.7 (CH_3), 55.5 (CH_3), 28.5 (CH_2), 28.3 (CH_2). *m*/*z* (ESI) $[M + H]^+$ 519.0; $[M + Na]^+$ 540.9. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{26}H_{22}FeO_8Na$ 541.0556; found 541.0558.

2,2′-((3*S*,6*S*)-3,6-Bis(benzyloxy)octa-1,7-diyne-1,8-diyl)bis (methoxybenzene) 25.



This compound is novel. In an round bottom flask under a nitrogen atmosphere (3*S*,6*S*)-1,8-bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol **24** (383 mg, 1.09 mmol) was dissolved in anhydrous THF (10 cm^3) and NaH (60% in mineral oil, 109 mg, 2.72 mmol) was added in small portions. After 30 minutes, benzyl bromide (0.29 cm^3, 2.44 mmol) and tetrabutylammonium iodide (158 mg, 0.43 mmol) were added. After 24 hours, saturated aqueous NH_4Cl solution (50 cm^3) was added and the product was extracted with DCM (3 × 50 cm^3). The reunited organic layers were washed with brine (50 cm^3) and dried over $MgSO_4$. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 9 : 1) to give 2,2′-((3*S*,6*S*)-3,6-bis(benzyloxy)octa-1,7-diyne-1,8-diyl)bis(methoxybenzene) **25** (511 mg, 0.96 mmol, 88%) as yellow oil. $[\alpha]_D^{30}$ −133.4 (*c* 0.515, $CHCl_3$). $IR_{(neat)}$ 3062, 3029, 3004, 2961, 2934, 2836, 2224, 1596, 1575, 1547, 1492, 1454, 1434, 1333, 1291, 1261 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.41 (6H, d, *J* = 7.5 Hz, Ar*H*), 7.33 (4H, t, *J* = 7.4 Hz, Ar*H*), 7.24–7.30 (4H, m, Ar*H*), 6.83–6.92 (4H, m, Ar*H*), 4.89 (2H, d, *J* = 11.7 Hz, PhC*H*H), 4.62 (2H, d, *J* = 11.7 Hz, PhCH*H*), 4.40–4.48 (2H, m, C*H*OR), 3.85 (6H, s, C*H*$_3$), 2.06–2.24 (4H, m, C*H*$_2$). δ_C (125 MHz, $CDCl_3$), 160.2 (C), 138.2 (C), 133.5 (CH), 129.7 (CH), 128.3 (CH), 128.1 (CH), 127.5 (CH), 120.3 (CH), 112.0 (C), 110.6 (CH), 92.2 (C), 82.5 (C), 70.3 (CH_2), 69.0 (CH), 55.6 (CH_3), 31.7 (CH_2). *m*/*z* (ESI) $[M + Na]^+$, 553.1. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{36}H_{34}O_4Na$ 553.2349; found 553.2344.

Tricarbonyl-(4*S*,7*S*)-4,7-bis(benzyloxy)-1,3-bis(2-methoxyphenyl)-4,5,6,7-tetrahydro-2-2*H*-inden-2-one iron 27.

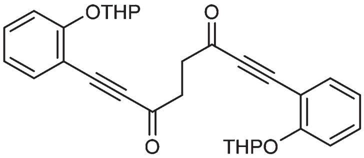


This compound is novel. In an ACE pressure tube under a nitrogen atmosphere 2,2′-((3*S*,6*S*)-3,6-bis(benzyloxy)octa-1,7-diyne-1,8-diyl)bis(methoxybenzene) **25** (323 mg, 0.61 mmol) was dissolved in anhydrous toluene (5 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (0.40 cm^3, 3.04 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C for 18 hours. After the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane to hexane/EtOAc = 1 : 1) to give tricarbonyl-(4*S*,7*S*)-4,7-bis(benzyloxy)-1,3-bis(2-methoxyphenyl)-4,5,6,7-tetrahydro-2-2*H*-inden-2-one iron **27** (85 mg, 0.12 mmol, yield: 20%) as yellow solid. M.p. 148.0–149.0 °C. $[\alpha]_D^{25}$ −123.4 (*c* 0.23, $CHCl_3$). $IR_{(neat)}$ 3059, 3029, 2996, 2930, 2900, 2834, 2061, 2008, 1987, 1632, 1586, 1562, 1484, 1456, 1421, 1344, 1312, 1239 cm^{-1}.

δ_H (500 MHz, $CDCl_3$), 7.93 (1H, d, *J* = 5.2 Hz, Ar*H*), 7.27–7.39 (3H, m, Ar*H*), 7.09–7.22 (6H, m, Ar*H*), 6.95–7.07 (2H, m, Ar*H*), 6.84–6.94 (2H, m, Ar*H*), 6.69 (4H, d, *J* = 7.2 Hz, Ar*H*), 4.70–4.77 (1H, m, C*H*OR), 4.62–4.69 (1H, m, C*H*OR), 4.43 (1H, d, *J* = 11.0 Hz, CH*H*), 4.34 (1H, d, *J* = 10.5 Hz, CH*H*), 4.22 (1H, d, *J* = 11.0 Hz, C*H*H), 4.07 (1H, d, *J* = 10.5 Hz, C*H*H), 3.84 (3H, s, C*H*$_3$), 3.79 (3H, br. s., C*H*$_3$), 2.27–2.45 (2H, m, C*H*$_2$), 1.83–1.95 (1H, m, CH*H*), 1.65–1.77 (1H, m, C*H*H). δ_C (125 MHz, $CDCl_3$), 209.0 (C), 157.4 (C), 156.5 (C), 137.3 (C), 133.1 (CH), 129.4 (CH), 129.3 (CH), 128.2 (CH), 127.9 (CH), 127.68 (CH), 127.67 (CH), 127.63 (CH), 127.3 (CH), 120.5 (CH), 119.88 (C), 119.83 (C), 110.9 (CH), 71.8 (CH_2), 71.38 (CH_2), 71.36 (CH), 70.3 (br., CH), 55.2 (CH_3), 54.5 (CH_3), 25.5 (CH_2), 24.7 (CH_2). *m*/*z* (ESI) $[M + H]^+$ 699.0; $[M + Na]^+$ 721.0.

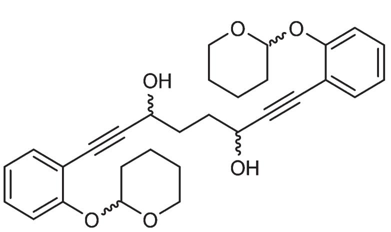
HRMS (ESI-Q-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{40}H_{35}FeO_8$ 699.1676; found 699.1685.

1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-dione 28.



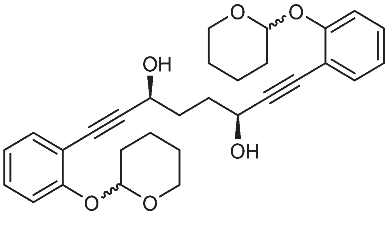
This compound is novel. In an round bottom flask under a nitrogen atmosphere 2-(2-ethynylphenoxy)tetrahydro-2*H*-pyran **29** (6.76 g, 33.42 mmol) was dissolved in anhydrous THF (100 cm^3). The mixture was cooled at −78 °C and *n*-butyllithium (2.5 M in hexanes, 14 cm^3, 35.00 mmol) was added dropwise over a period of 15 minutes. The mixture was warmed to −40 °C and stirred at this temperature for 30 minutes. Then the mixture was transferred *via* cannula dropwise to a flask containing N^1,N^4-dimethoxy-N^1,N^4-dimethylsuccinamide **21** (3.1 g, 15.18 mmol) dissolved/suspended in THF (80 cm^3) at −78 °C. After 5 minutes the mixture was warmed at 0 °C and stirred at this temperature for 30 minutes. Then the mixture was cooled to −40 °C and saturated $NaHCO_3$ aqueous solution (100 cm^3) was added. The mixture was warmed to room temperature and H_2O (200 cm^3) was added. The product was extracted with DCM (3 × 500 cm^3) and the reunited organic layers were dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane/DCM = 1 : 1 to DCM/EtOAc = 4 : 1) to give 1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl) oxy)phenyl)octa-1,7-diyne-3,6-dione **28** (6.46 g, 13.27 mmol, yield: 87%) as a white solid. M.p. 127.6–129.4 °C. IR$_{(neat)}$ 2965, 2940, 2874, 2859, 2193, 1662, 1595, 1572, 1486, 1447, 1405, 1388, 1355, 1316, 1283, 1251, 1203 cm^{-1}. δ_H (500 MHz, CDCl$_3$), 7.52 (2H, dd, *J* = 7.6, 1.5 Hz), 7.35–7.43 (2H, m), 7.17 (2H, d, *J* = 8.4 Hz), 6.98 (2H, td, *J* = 7.6, 0.6 Hz), 5.56 (2H, t, *J* = 2.7 Hz), 3.90 (2H, td, *J* = 11.1, 2.7 Hz), 3.56–3.66 (1H, m), 3.13 (4H, s), 2.03–2.15 (2H, m), 1.95–2.03 (2H, m), 1.84–1.93 (2H, m), 1.59–1.76 (6H, m). δ_C (125 MHz, CDCl$_3$), 185.1 (C), 159.1 (C), 134.7 (CH), 132.5 (CH), 121.5 (CH), 115.1 (CH), 110.1 (C), 96.4 (CH), 91.4 (C), 89.1 (C), 61.8 (CH$_2$), 39.2 (CH$_2$), 30.1 (CH$_2$), 25.1 (CH$_2$), 18.2 (CH$_2$). *m*/*z* (ESI) [M + Na]$^+$ 509.2. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{30}H_{30}O_6Na$ 509.1935; found 509.1928.

1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30.



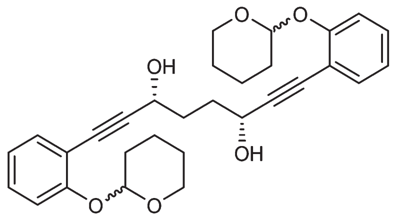
This compound is novel. In an round bottom flask under a nitrogen atmosphere 1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy) phenyl)octa-1,7-diyne-3,6-dione **28** (110 mg, 0.23 mmol) was dissolved/suspended in DCM/MeOH (1 : 1, 3 cm^3). NaBH$_4$ (26 mg, 0.69 mg) was added. After 4 hours H$_2$O (10 cm^3) was added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 15 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 1 : 4 to 3 : 2) to give 1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol **30** (83 mg, 0.17 mmol, yield: 74.8%) as sticky colourless solid. δ_H (500 MHz, CDCl$_3$), 7.37 (4H, d, *J* = 7.6 Hz, Ar*H*), 7.20–7.28 (4H, m, Ar*H*), 7.10 (4H, d, *J* = 8.2 Hz, Ar*H*), 6.92 (4H, t, *J* = 7.6 Hz, Ar*H*), 5.49 (4H, br. s., C*H*), 4.62–4.83 (4H, 2 overlapping br. s. at 4.78 and 4.74, C*H*OH), 3.82–4.04 (4H, m, CH*H*), 3.47–3.68 (4H, m, C*H*H), 2.62–2.85 (4H, m, O*H*), 1.52–2.24 (32H, m, C*H*$_2$). δ_C (125 MHz, CDCl$_3$), 157.6 (C), 133.24 (CH), 133.21 (CH), 129.7 (CH), 121.48 (CH), 121.45 (CH), 115.6 (CH), 115.52 (CH), 115.51 (CH), 113.10 (C), 113.07 (C), 96.72 (CH), 96.68 (CH), 96.66 (CH), 93.56 (C), 93.46 (C), 81.6 (C), 62.70 (CH$_2$), 62.68 (CH$_2$), 62.55 (CH$_2$), 62.54 (CH$_2$), 62.96 (CH$_2$), 61.94 (CH$_2$), 33.80 (CH$_2$), 33.77 (CH$_2$), 33.74 (CH$_2$), 33.4 (CH$_2$), 30.2 (CH$_2$), 25.1 (CH$_2$), 18.5 (CH$_2$).

(3*S*,6*S*)-1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30.



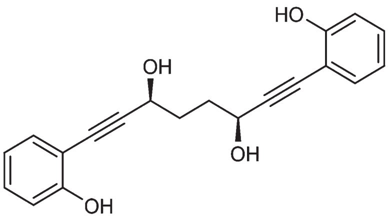
This compound is novel. In an round bottom flask under a nitrogen atmosphere 1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy) phenyl)octa-1,7-diyne-3,6-dione **28** (2.0 g, 4.11 mmol) was dissolved/suspended in anhydrous DCM (7 cm^3). [(*S*,*S*)-Teth-TsDpen-RuCl] **23** (26 mg, 0.042 mmol) and an azeotropic mixture of formic acid/triethylamine (5 : 2 mixture, 5.0 cm^3) were added. After 22 hours saturated NaHCO$_3$ aqueous solution (50 cm^3) and H$_2$O (50 cm^3) were added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 150 cm^3). The reunited organic layers were washed with brine (100 cm^3) and dried over MgSO$_4$. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 7 : 3 to 1 : 1) to give (3*S*,6*S*)-1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy) phenyl)octa-1,7-diyne-3,6-diol **30** (1.95 g, 3.99 mmol, yield: 96.7%, dr = 98.3 : 1.7, >99% ee) as a sticky colourless solid. The enantiomeric and diastereomeric excess were determined by HPLC analysis with a ChiralPak IB column: 0.46 cm × 25 cm, mobile phase EtOAc : hexane 7 : 3, flow rate 1 mL min^{-1}, temperature 30 °C, UV detection at λ = 254 nm; t_R = 13.4 and 13.9 min (*R*,*R*), t_R = 16.2, 16.6 and 17.2 min (*R*,*S*), t_R = 26.2, 28.3 and 30.2 min (*S*,*S*). $[\alpha]_D^{25}$ −0.58 (*c* 1.3, CHCl$_3$). IR$_{(neat)}$ 3400 (br), 2942, 2869, 2853, 2228, 1596, 1574, 1488 1445, 1389, 1356, 1326, 1285, 1254, 1229, 1200, 1182 cm^{-1}. δ_H (500 MHz, CDCl$_3$), 7.37 (2H, d, *J* = 7.6 Hz, Ar*H*), 7.24 (2H, t, *J* = 8.3 Hz, Ar*H*), 7.10 (2H, d, *J* = 8.4 Hz, Ar*H*), 6.92 (2H, t, *J* = 7.5 Hz, Ar*H*), 5.50 (2H, br. s., C*H*), 4.78 (2H, br. s., C*H*OH), 3.85–4.02 (2H, m, CH*H*), 3.50–3.65 (2H, m, C*H*H), 2.74 (2H, br. d, O*H*), 1.99–2.23 (6H, m, C*H*$_2$), 1.90–1.99 (2H, m, C*H*$_2$), 1.81–1.90 (2H, m, C*H*$_2$), 1.50–1.73 (6H, m, C*H*$_2$) δ_C (125 MHz, CDCl$_3$), 157.5 (C), 133.25 (CH), 133.23 (CH), 129.7 (CH), 121.4 (CH), 115.54 (CH), 115.50 (CH), 113.07 (C), 113.05 (C), 96.7 (CH), 93.5 (C), 81.61 (C), 81.59 (C), 62.54 (CH$_2$), 62.52 (CH), 61.9 (CH$_2$), 33.3 (CH$_2$), 30.2 (CH$_2$), 25.1 (CH$_2$), 18.5 (CH$_2$). *m*/*z* (ESI) [M + Na]$^+$ 513.1. HRMS (ESI-Q-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{30}H_{34}O_6Na$ 513.2248; found 513.2254.

(3*R*,6*R*)-1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30.



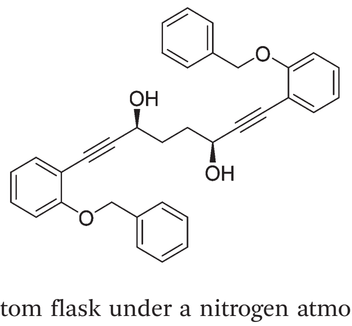
This compound is novel. In an round bottom flask under a nitrogen atmosphere 1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy) phenyl)octa-1,7-diyne-3,6-dione **28** (150 mg, 0.31 mmol) was dissolved/suspended in anhydrous DCM (1.0 cm^3). [(*R*,*R*)-Teth-TsDpen-RuCl] **23** (1.9 mg, 0.003 mmol) and an azeotropic mixture of formic acid/triethylamine (5 : 2 mixture, 0.5 cm^3) were added. After 23 hours saturated NaHCO$_3$ aqueous solution (5 cm^3) and H$_2$O (10 cm^3) were added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 20 cm^3). The reunited organic layers were washed with brine (20 cm^3) and dried over $MgSO_4$. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 7 : 3 to 1 : 1) to give (3*R*,6*R*)-1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol **31** (146 mg, 0.30 mmol, yield: 96%, dr = 98.4 : 1.6, >99% ee) as a sticky colourless solid. The enantiomeric and diastereomeric excess were determined by HPLC analysis with a ChiralPak IB column: 0.46 cm × 25 cm, mobile phase EtOAc : hexane 7 : 3, flow rate 1 mL min^{-1}, temperature 30 °C, UV detection at λ = 254 nm; t_R = 13.4 and 13.9 min (*R*,*R*), t_R = 16.2, 16.6 and 17.2 min (*R*,*S*), t_R = 26.2, 28.3 and 30.2 min (*S*,*S*). ^1H and ^{13}C NMR were identical to the reported data for (3*S*,6*S*)-1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol. $[\alpha]_D^{27}$ +0.58 (*c* 1.8, $CHCl_3$).

(3*S*,6*S*)-1,8-Bis(2-hydroxyphenyl)octa-1,7-diyne-3,6-diol 31.



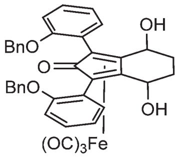
This compound is novel. In an round bottom flask (3*S*,6*S*)-1,8-bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol **30** (1.55 g, 3.17 mmol) was dissolved in a mixture of DCM/EtOH (1 : 3, 25 cm^3) and pyridinium *p*-toluenesulfonate (107 mg, 0.43 mmol) was added. The mixture was stirred for 19 hours and the volatiles were removed. The product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 3 : 2 to EtOAc) to give (3*S*,6*S*)-1,8-bis(2-hydroxyphenyl)octa-1,7-diyne-3,6-diol **31** (859 g, 2.66 mmol, yield: 84%) as colourless solid. $[\alpha]_D^{27}$ +15.2 (*c* 0.9, CH_3OH). M.p. 144.0–145.6 °C. $IR_{(neat)}$ 3419 (br.), 3145 (br.), 2225, 1604, 1585, 1502, 1450, 1391, 1365, 1324, 1288, 1258 cm^{-1}. δ_H (500 MHz, DMSO-d_6), 9.79 (2H, s, O*H*), 7.24 (2H, dd, *J* = 7.6, 1.5 Hz, Ar*H*), 7.12–7.18 (2H, m, Ar*H*), 6.86 (2H, d, *J* = 8.2 Hz, Ar*H*), 6.75 (2H, t, *J* = 7.5 Hz, Ar*H*), 5.41 (2H, d, *J* = 5.5 Hz, O*H*), 4.50 (2H, d, *J* = 5.3 Hz, C*H*OH), 1.73–1.92 (4H, m, C*H*$_2$). δ_C (125 MHz, DMSO-d_6), 158.2 (C), 132.9 (CH), 129.6 (CH), 119.0 (CH), 115.4 (CH), 109.9 (C), 95.4 (C), 80.1 (C), 60.8 (CH), 33.8 (CH_2). *m*/*z* (ESI) $[M + Na]^+$ 345.1. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{20}H_{18}O_4Na$ 345.1097; found 345.1101.

(3*S*,6*S*)-1,8-Bis(2-(benzyloxy)phenyl)octa-1,7-diyne-3,6-diol 32.



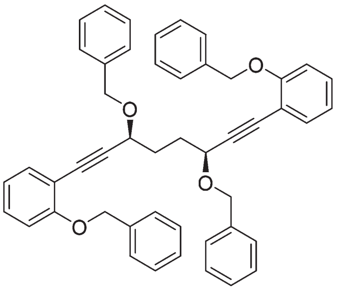
In a round bottom flask under a nitrogen atmosphere (3*S*,6*S*)-1,8-bis(2-hydroxyphenyl)octa-1,7-diyne-3,6-diol **31** (200 mg, 0.62 mmol) was dissolved in anhydrous DMF (2 cm^3). Benzyl bromide (0.17 cm^3, 1.43 mmol) and anhydrous potassium carbonate (214 mg, 1.55 mmol) were added and the mixture was heated to 85 °C. After 17 hours, the mixture was cooled to room temperature and H_2O (15 cm^3) was added. The product was extracted with DCM (20 cm^3) and the organic layer was washed with H_2O (15 cm^3) and brine (15 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 3 : 7 to 1 : 4) to give (3*S*,6*S*)-1,8-bis(2-(benzyloxy)phenyl)octa-1,7-diyne-3,6-diol **32** (231 mg, 0.46 mmol, yield: 74%) as colourless solid. M.p. 122.3–123.5 °C. $[\alpha]_D^{27}$ −15.5 (*c* 0.10, CH_3CN). $IR_{(neat)}$ 3257 (broad), 3078, 3033, 2951, 2900, 2859, 1599, 1575, 1494, 1444, 1414, 1377, 1312, 1290, 1281, 1264, 1241 cm^{-1}. δ_H (500 MHz, CD_3CN), 7.48 (4H, d, *J* = 7.6 Hz, Ar*H*), 7.36 (6H, ddd, *J* = 7.6, 4.7, 3.1 Hz, Ar*H*), 7.23–7.32 (4H, m, Ar*H*), 7.01 (2H, d, *J* = 8.2 Hz, Ar*H*), 6.91 (2H, td, *J* = 7.5, 0.9 Hz, Ar*H*), 5.13 (4H, s, PhC*H*$_2$), 4.56–4.64 (2H, m, C*H*OR), 3.49 (2H, d, *J* = 5.5 Hz, O*H*), 1.91–1.95 (4H, m, C*H*$_2$). δ_C (125 MHz, CD_3CN), 160.1 (C), 138.2 (C), 134.4 (CH), 130.9 (CH), 129.5 (CH), 128.8 (CH), 128.3 (CH), 121.9 (CH), 114.0 (CH), 113.6 (C), 96.0 (C), 81.3 (C), 71.0 (CH_2), 62.7 (CH), 34.6 (CH_2). *m*/*z* (ESI) $[M + Na]^+$ 525.2; $[M + K]^+$ 541.2. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{34}H_{30}O_4Na$ 525.2036; found 525.2045.

Tricarbonyl-(4*S*,7*S*)-1,3-bis(2-(benzyloxy)phenyl)-4,7-dihydroxy-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 34.



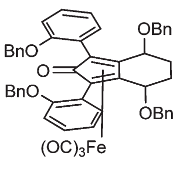
This compound is novel. In an ACE pressure tube under a nitrogen atmosphere (3*S*,6*S*)-1,8-bis(2-(benzyloxy)phenyl)-octa-1,7-diyne-3,6-diol **32** (200 mg, 0.40 mmol) was dissolved/suspended in anhydrous toluene (3 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (0.27 cm^3, 2.00 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C for 22 hours. After the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 1 : 4 to 1 : 1) to give tricarbonyl-(4*S*,7*S*)-1,3-bis(2-(benzyloxy)-phenyl)-4,7-dihydroxy-4,5,6,7-tetrahydro-2*H*-inden-2-one iron **34** (193 mg, 0.29 mmol, yield: 72%) as yellow solid. M.p. 155 °C dec. $[\alpha]_D^{26}$ −82.5 (*c* 0.19, $CHCl_3$). $IR_{(neat)}$ 3370 (broad), 3062, 3034, 2958, 2924, 2856, 2063, 2011, 1988, 1737, 1717, 1616, 1597, 1579, 1494, 1450, 1373, 1297, 1278, 1226 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.16–7.40 (14H, m, Ar*H*), 7.07 (2H, t, *J* = 7.5 Hz, Ar*H*), 6.99 (1H, d, *J* = 8.1 Hz, Ar*H*), 6.90 (1H, d, *J* = 8.2 Hz, Ar*H*), 5.00–5.15 (4H, m, C*H*$_2$), 4.76–4.83 (1H, m, C*H*OH), 4.59–4.65 (1H, m, C*H*OH), 3.34 (1H, s, O*H*), 2.18–2.27 (1H, m, CH*H*), 2.09–2.18 (2H, m, CH*H* and O*H*), 1.66–1.79 (1H, m, C*H*H), 1.50–1.63 (1H, m, C*H*H). δ_C (125 MHz, $CDCl_3$), 208.2 (C), 170.8 (C), 156.51 (C), 156.47 (C), 136.6 (C), 136.2 (C), 135.0 (CH), 134.4 (CH), 130.4 (CH), 130.2 (CH), 128.59 (CH), 128.52 (CH), 127.89 (CH), 127.80 (CH), 127.2 (CH), 126.9 (CH), 122.5 (CH), 121.8 (CH), 120.1 (C), 119.9 (C), 114.8 (CH), 113.3 (CH), 106.5 (C), 105.1 (C), 81.1 (C), 80.8 (C), 71.9 (CH_2), 70.6 (CH_2), 62.6 (CH), 62.4 (CH), 27.8 (CH_2), 27.4 (CH_2). *m*/*z* (ESI) $[M + H]^+$ 671.1; $[M + Na]^+$ 693.1.

2,2′-((3*S*,6*S*)-3,6-Bis(benzyloxy)octa-1,7-diyne-1,8-diyl)bis((benzyloxy)benzene) 33.



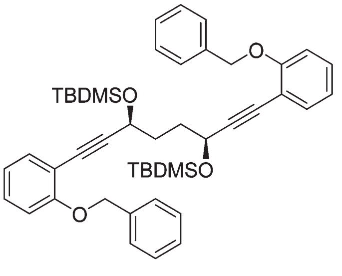
This compound is novel. In an round bottom flask under a nitrogen atmosphere (3*S*,6*S*)-1,8-bis(2-hydroxyphenyl)octa-1,7-diyne-3,6-diol **31** (250 mg, 0.78 mmol) was dissolved in anhydrous THF (2 cm^3). NaH (60% in mineral oil, 155 mg, 3.88 mmol) and benzyl bromide (0.46 cm^3, 3.87 mmol) were added and the mixture was heated at 50 °C. After 18 hours, the mixture was cooled to room temperature and saturated NH_4Cl aqueous solution (5 cm^3) and H_2O (10 cm^3) were added. The product was extracted with DCM (3 × 20 cm^3) and the reunited organic layers were dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane to hexane/EtOAc = 5 : 1) to give 2,2′-((3*S*,6*S*)-3,6-bis(benzyloxy)octa-1,7-diyne-1,8-diyl)bis((benzyloxy)benzene) **33** (256 mg, 0.37 mmol, yield: 48%) as yellow oil. $[\alpha]_D^{28}$ −127.3 (*c* 0.41, $CHCl_3$). $IR_{(neat)}$ 3086, 3063, 3030, 2928, 2860, 1595, 1574, 1489, 1444, 1380, 1332, 1289, 1261, 1227 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.45 (4H, d, *J* = 7.6 Hz), 7.40 (2H, d, *J* = 7.5 Hz), 7.21–7.33 (16H, m), 7.16–7.21 (2H, m), 6.85–6.94 (4H, M), 5.12 (4H, s), 4.80 (2H, d, *J* = 11.9 Hz), 4.53 (2H, d, *J* = 11.9 Hz), 4.37 (2H, t, *J* = 5.5 Hz), 2.02–2.20 (4H, m). δ_C (125 MHz, $CDCl_3$), 159.4 (C), 138.1 (C), 136.8 (C), 133.6 (CH), 129.6 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.8 (CH), 127.5 (CH), 127.1 (CH), 120.7 (CH), 112.8 (C), 112.4 (CH), 92.3 (C), 82.5 (C), 70.34 (CH_2), 70.30 (CH_2), 68.8 (CH), 31.7 (CH_2). *m*/*z* (ESI) $[M + Na]^+$ 705.3; $[M + K]^+$ 721.3. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{48}H_{42}O_4Na$ 705.2975; found 705.2976.

Tricarbonyl-(4*S*,7*S*)-4,7-bis(benzyloxy)-1,3-bis(2-(benzyloxy)phenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 35.



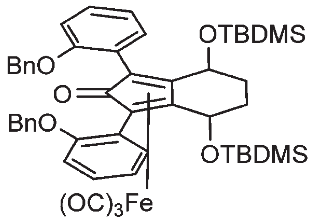
This compound is novel. In an ACE pressure tube under a nitrogen atmosphere (3*S*,6*S*)-1,8-bis(2-(benzyloxy)phenyl)-octa-1,7-diyne-3,6-diol **33** (1.00 g, 1.46 mmol) was dissolved/suspended in anhydrous toluene (7 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (1.0 cm^3, 7.42 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C for 23 hours. After the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 9 : 1 to 7 : 3) to give tricarbonyl-(4*S*,7*S*)-4,7-bis(benzyloxy)-1,3-bis(2-(benzyloxy)phenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron **35** (1.04 g, 1.22 mmol, yield: 84%) as yellow solid. M.p. 65.4–67.0 °C. $[\alpha]_D^{21}$ −90.1 (*c* 0.25, $CHCl_3$). $IR_{(neat)}$ 3060, 3030, 2926, 2860, 2060, 1981, 1644, 1599, 1579, 1495, 1450, 1364, 1338, 1277, 1224 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.59 (1H, br. s., Ar*H*), 6.84–7.42 (25H, m, Ar*H*), 6.77 (1H, d, *J* = 8.2 Hz, Ar*H*), 6.70 (2H, d, *J* = 7.2 Hz, Ar*H*), 4.66–5.33 (4H, m, C*H*$_2$ and C*H*OR), 4.17–4.64 (4H, m, C*H*$_2$ and C*H*OR), 3.90–4.12 (2H, m, C*H*$_2$), 2.14 (1H, br. s., C*H*H), 1.97 (1H, br. s., C*H*H), 1.83 (1H, br. s., CH*H*), 1.59 (2H, br. s., CH*H*). δ_C (125 MHz, $CDCl_3$), 208.8 (C), 156.8 (C), 137.8 (C), 137.4 (C), 137.2 (C), 136.9 (C), 133.0 (CH), 129.6 (CH), 129.5 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 127.95 (CH), 127.92 (CH), 127.87 (CH), 127.6 (CH), 127.34 (CH), 127.29 (CH), 127.23 (CH), 126.68 (CH), 126.56 (CH), 121.7 (br., CH), 120.4 (CH), 119.9 (C), 113.2 (CH), 112.8 (CH), 71.7 (CH_2), 71.4 (CH_2), 70.5 (CH_2), 70.4 (CH), 69.6 (br., CH_2), 68.7 (CH), 24.0 (CH_2), 23.5 (CH_2). *m*/*z* (ESI) $[M + H]^+$ 851.2; $[M + Na]^+$ 873.1. HRMS (ESI-Q-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{52}H_{43}FeO_8$ 851.2303; found 851.2302.

(5*S*,8*S*)-5,8-Bis((2-(benzyloxy)phenyl)ethynyl)-2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodecane 36.



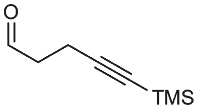
This compound is novel. In an round bottom flask under a nitrogen atmosphere (3*S*,6*S*)-1,8-bis(2-benzyloxyphenyl)octa-1,7-diyne-3,6-diol **32** (500 mg, 0.99 mmol) was dissolved in anhydrous DMF (10 cm^3). Imidazole (339 mg, 4.98 mmol) and *tert*-butylchlorodimethylsilane (375 mg, 2.49 mmol) were added. After 20 hours, H_2O (50 cm^3) was added and the product was extracted with EtOAc (200 cm^3). The organic layer was washed with brine (3 × 50 cm^3) and dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane to hexane/EtOAc = 19 : 1) to give (5*S*,8*S*)-5,8-bis((2-(benzyloxy)phenyl) ethynyl)-2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodecane: **36** (718 mg, 0.98 mmol, yield: 99%) as colourless oil. $[\alpha]_D^{27}$ −23.2 (*c* 1.6, $CHCl_3$). $IR_{(neat)}$ 3067, 3033, 2953, 2928, 2884, 2855, 1596, 1574, 1490, 1471, 1444, 1407, 1380, 1360, 1338, 1289, 1257, 1229 cm^{-1}. δ_H (500 MHz, CD_3Cl), 7.43 (4H, d, *J* = 7.5 Hz, Ar*H*), 7.30–7.40 (6H, m, Ar*H*), 7.15–7.26 (4H, m, Ar*H*), 6.82–6.90 (4H, m, Ar*H*), 5.11 (4H, s, CH_2OR), 4.59–4.72 (2H, m, C*H*OR), 1.90–2.14 (4H, m, CH_2), 0.90 (18H, d, *J* = 2.6 Hz, CH_3), 0.13 (12H, dd, *J* = 8.9, 2.5 Hz, CH_3). δ_C (125 MHz, $CDCl_3$), 159.2 (C), 136.9 (C), 133.6 (CH), 129.3 (CH), 128.4 (CH), 127.6 (CH), 127.0 (CH), 120.6 (CH), 113.2 (C), 112.6 (CH), 95.1 (C), 80.6 (C), 70.2 (CH_2), 63.4 (CH), 34.5 (CH_2), 25.8 (CH_3), 18.3 (C), −4.4 (CH_3), −5.0 (CH_3). *m*/*z* (ESI) $[M + Na]^+$ 753.4; $[M + K]^+$ 769.3. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{46}H_{58}O_4Si_2Na$ 753.3766; found 753.3759.

Tricarbonyl-(4*S*,7*S*)-1,3-bis(2-(benzyloxy)phenyl)-4,7-bis((*tert*-butyldimethylsilyl)oxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 37.



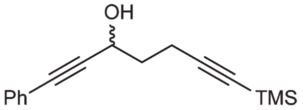
This compound is novel. In an ACE pressure tube under a nitrogen atmosphere (5*S*,8*S*)-5,8-bis((2-(benzyloxy)phenyl)ethynyl)-2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodecane **36** (500 mg, 0.68 mmol) was dissolved/suspended in anhydrous toluene (5 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (0.46 cm^3, 3.41 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C for 19 hours. After the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane to hexane/EtOAc = 1 : 1) to give tricarbonyl-(4*S*,7*S*)-1,3-bis(2-(benzyloxy)phenyl)-4,7-bis((*tert*-butyldimethylsilyl)oxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron **37** (162 mg, 0.18 mmol, yield: 26%) as yellow solid. M.p. 92 °C dec. $[\alpha]_D^{21}$ −192.3 (*c* 0.1, $CHCl_3$). $IR_{(neat)}$ 2950, 2927, 2882, 2854, 2061, 2008, 1980, 1648, 1599, 1579, 1497, 1450, 1363, 1277, 1248 cm^{-1}. δ_H (500 MHz, $CDCl_3$, −50 °C), 7.75 (0.5H, dd, *J* = 23.0, 7.5 Hz, Ar*H*), 7.14–7.50 (10H, m, Ar*H*), 6.72–7.13 (7H, m, Ar*H*), 6.64 (1H, d, *J* = 8.6 Hz, Ar*H*), 4.40–5.50 (6H, m, CH_2OR and C*H*OR), 1.32–2.37 (4H, m, CH_2), 0.48–0.78 (18H, m, CH_3), −0.35–0.05 (6H, m, CH_3), −0.98–−0.60 (6H, m, CH_3). *m*/*z* (ESI) $[M + H]^+$ 899.2; $[M + Na]^+$ 921.2. HRMS (ESI-Q-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{50}H_{59}FeO_8Si_2$ 899.3094; found 899.3102.

5-(Trimethylsilyl)pent-4-ynal.



In a round bottom flask, under nitrogen, oxalyl chloride (2 M in DCM, 14.2 cm^3, 28.40 mmol) was diluted with DCM (15 cm^3). The solution was cooled to −78 °C and anhydrous DMSO (4 cm^3, 56.31 mmol) was added dropwise. Then the mixture was stirred for 30 minutes and a solution of 5-(trimethylsilyl)pent-4-yn-1-ol (3.7 g, 23.7 mmol) in DCM (25 cm^3) was added dropwise. After 30 minutes Et_3N (16.5 cm^3, 118.4 mmol) was added dropwise. The mixture was continued to stir at −78 °C for 1 hour then warmed to room temperature. After 16 hours a saturated aqueous solution of $NaHCO_3$ (100 cm^3) was added and the product was extracted with DCM (3 × 100 cm^3). The reunited organic layers were washed with brine (50 cm^3) and dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether to petroleum ether/EtOAc = 9/1) to give 5-(trimethylsilyl)pent-4-ynal (2.69 g, 17.43 mmol, 74%) as yellow oil. ^1H NMR and ^{13}C NMR were identical to the reported data;[16] δ_H (500 MHz, $CDCl_3$), 9.79 (1H, s, O═C*H*), 2.64–2.70 (2H, m, CH_2), 2.52–2.58 (2H, m, CH_2), 0.14 (9H, s, CH_3). δ_C (125 MHz, $CDCl_3$), 200.4 (CH), 104.7 (C), 85.8 (CH), 42.5 (CH_2), 13.1 (CH_2), 0.0 (CH_3).

1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 30.

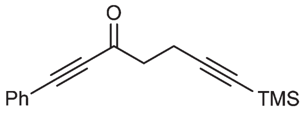


In a Schlenk tube under a nitrogen atmosphere phenylacetylene (0.85 cm^3, 7.74 mmol) was dissolved in anhydrous THF (20 cm^3). The mixture was cooled at −78 °C and *n*-butyllithium (2.5 M in hexanes, 3.1 cm^3, 7.75 mmol) was added dropwise. The mixture was warmed to room temperature and stirred at this temperature for 1 hour. Then the mixture was cooled to −78 °C and transferred *via* cannula dropwise to a flask containing 5-(trimethylsilyl)pent-4-ynal (1.0 g, 6.48 mmol) dissolved in anhydrous THF (20 cm^3) at −78 °C. After 5 minutes the mixture was warmed at room temperature and stirred at this temperature for 3 hours. Then H_2O (50 cm^3) was added dropwise and the product was extracted with DCM (3 × 50 cm^3). The reunited organic layers were washed with brine (50 cm^3) and dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether to petroleum ether/EtOAc = 13/1) to give racemic 1-phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol **39** (1.54 g, 6.00 mmol, 93%) as yellow oil.

^1H NMR and ^{13}CNMR were identical to the reported data.[17] δ_H (500 MHz, $CDCl_3$), 7.40–7.47 (2H, m, Ar*H*), 7.28–7.34 (3H, m, Ar*H*), 4.76 (1H, q, *J* = 5.8 Hz, C*H*OH), 2.41–2.59 (2H, m, CH_2), 2.15 (1H, d, *J* = 5.3 Hz, CHO*H*), 2.02 (2H, q, *J* = 6.9 Hz, CH_2), 0.16 (9H, s, CH_3). δ_C (125 MHz, $CDCl_3$), 131.7 (CH), 128.5

(CH), 128.3 (CH), 122.4 (C), 106.1 (C), 89.2 (C), 85.6 (C), 85.3 (C), 62.0 (CH), 36.4 (CH_2), 16.0 (CH_2), 0.1 (CH_3).

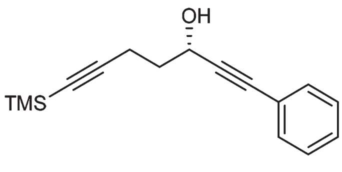
1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-one 38.



This compound is novel. In an round bottom flask under a nitrogen atmosphere, racemic 1-phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol **39** (820 mg, 3.20 mmol) was dissolved in DCM (20 cm^3). Then PCC (1.38 g, 6.40 mmol) was added. After 24 hours the mixture was filtered through a Celite plug washing through with DCM (30 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether to petroleum ether/EtOAc = 49/1) to give 1-phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-one **38** (504 mg, 1.98 mmol, yield: 62%) as pale yellow oil. $IR_{(neat)}$ 2972, 2959, 2935, 2925, 2896, 2201, 2177, 1671, 1489, 1443, 1407, 1358, 1334, 1278, 1249, 1190 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.56–7.61 (2H, m, Ar*H*), 7.44–7.49 (1H, m, Ar*H*), 7.36–7.42 (2H, m, Ar*H*), 2.89–2.96 (2H, m, C*H*$_2$), 2.59–2.67 (2H, m, C*H*$_2$), 0.14 (9H, s, C*H*$_3$). δ_C (125 MHz, $CDCl_3$), 185.4 (C), 133.1 (CH), 130.9 (CH), 128.6 (CH), 119.8 (C), 104.7 (C), 91.6 (C), 87.3 (C), 85.6 (C), 44.2 (CH_2), 14.7 (CH_2), 0.0 (CH_3). *m*/*z* (ESI) $[M + H]^+$ 255.1; $[M + Na]^+$ 277.1.

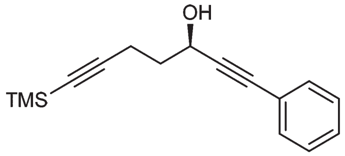
HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{16}H_{18}OSiNa$ 277.1019; found 277.1024.

(*S*)-1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 39.



In an round bottom flask under a nitrogen atmosphere 1-phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-one **38** (476 mg, 1.87 mmol) was dissolved in anhydrous DCM (1.3 cm^3). [(*S*,*S*)-Teth-TsDpen-RuCl] **23** (11.6 mg, 0.019 mmol) and an azeotropic mixture of formic acid/triethylamine (5 : 2 mixture, 1.3 cm^3) were added. After 18 hours saturated $NaHCO_3$ aqueous solution (10 cm^3) and H_2O (10 cm^3) were added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 20 cm^3). The reunited organic layers were dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether to petroleum ether/EtOAc = 9 : 1) to give (*S*)-1-phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol **39** (426 mg, 1.66 mmol, yield: 89%, 94% ee) as white solid. The enantiomeric excess was determined by HPLC analysis with a ChiralPak OD column: 0.46 cm × 25 cm, mobile phase iso-propanol : hexane 9 : 1, flow rate 1 mL min^{-1}, temperature 30 °C, UV detection at λ = 254 nm; t_R = 6.5 min (*R*), t_R = 13.8 min (*S*). ^1H NMR and ^{13}CNMR were identical to the reported data.[17] M.p. 34.8–36.4 °C. $[\alpha]_D^{25}$ +47.6 (*c* 0.45, $CHCl_3$). $IR_{(neat)}$ 3288 (broad), 2957, 2897, 2865, 2228, 2169, 1598, 1489, 1440, 1353, 1335, 1327, 1312, 1279, 1247. δ_H (500 MHz, $CDCl_3$), 7.40–7.47 (2H, m, Ar*H*), 7.28–7.34 (3H, m, Ar*H*), 4.76 (1H, q, *J* = 5.8 Hz, C*H*OH), 2.41–2.59 (2H, m, C*H*$_2$), 2.15 (1H, d, *J* = 5.3 Hz, CHO*H*), 2.02 (2H, q, *J* = 6.9 Hz, C*H*$_2$), 0.16 (9H, s, C*H*$_3$). δ_C (125 MHz, $CDCl_3$), 131.7 (CH), 128.5 (CH), 128.3 (CH), 122.4 (C), 106.1 (C), 89.2 (C), 85.6 (C), 85.3 (C), 62.0 (CH), 36.4 (CH_2), 16.0 (CH_2), 0.1 (CH_3).

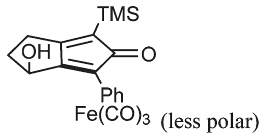
(*R*)-1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 30.

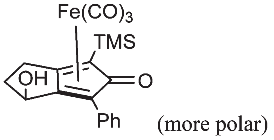


In an round bottom flask under a nitrogen atmosphere 1-phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-one **38** (100 mg, 0.39 mmol) was dissolved in anhydrous DCM (0.3 cm^3). [(*R*,*R*)-Teth-TsDpen-RuCl] **23** (2.4 mg, 0.039 mmol) and an azeotropic mixture of formic acid/triethylamine (5 : 2 mixture, 0.3 cm^3) were added. After 7 hours saturated $NaHCO_3$ aqueous solution (5 cm^3) and H_2O (5 cm^3) were added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 20 cm^3). The reunited organic layers were dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane to hexane/EtOAc = 9 : 1) to give (*R*)-1-phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol **39** (66 mg, 0.26 mmol, yield: 66%, 95% ee) as white solid. The enantiomeric excess was determined by HPLC analysis with a ChiralPak OD column: 0.46 cm × 25 cm, mobile phase iso-propanol : hexane 9 : 1, flow rate 1 mL min^{-1}, temperature 30 °C, UV detection at λ = 254 nm; t_R = 6.5 min (*R*), t_R = 13.8 min (*S*).

^1H NMR and ^{13}C NMR were identical to the reported data.[17] M.p. 34.6–36.0 °C. $[\alpha]_D^{25}$ −47.3 (*c* 0.45, $CHCl_3$) (lit $[\alpha]_D^{22}$ −36.3 (*c* 0.88, $CHCl_3$), 90% ee *R*).

Compounds 40 and 41



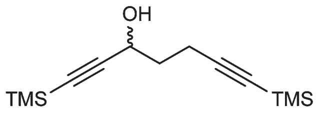


These compound are novel. In an ACE pressure tube under a nitrogen atmosphere (*S*)-1-phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol **39** (300 mg, 1.16 mmol) was dissolved in anhydrous toluene (6 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (0.79 cm^3, 5.86 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C for 24 hours. After the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the products were purified by flash chromatography on silica gel (eluent: hexane to hexane/EtOAc = 13/1) to give first the less polar **40** (198 mg, yield: 40%) as a yellow solid and then more polar **41** (136 mg, yield: 27%) as an orange solid.

Data for 40; m.p. 193 °C dec. $[\alpha]_D^{30}$ −204.6 (*c* 0.14, $CHCl_3$). $IR_{(neat)}$ 3336 (broad), 3060, 2954, 2900, 2059, 1981, 1632, 1586, 1505, 1447, 1413, 1379, 1304, 1247 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 8.04 (2H, d, *J* = 7.9 Hz, Ar*H*), 7.23–7.40 (3H, m, Ar*H*), 5.33–5.44 (1H, m, C*H*OH), 3.02 (1H, ddd, *J* = 16.4, 9.3, 7.5 Hz, C*H*H), 2.85 (1H, br. S, O*H*), 2.51–2.62 (1H, m, CH*H*), 2.35–2.43 (1H, m, C*H*H), 2.23–2.35 (1H, m, CH*H*), 0.34 (9H, s, CH_3). δ_C (125 MHz, $CDCl_3$), 208.1 (C), 177.0 (C), 131.7 (C), 128.7 (CH), 128.2 (CH), 127.93 (CH), 127.90 (CH), 115.5 (C), 105.3 (C), 80.1 (C), 71.9 (CH), 69.9 (C), 36.5 (CH_2), 25.4 (CH_2), −0.7 (CH_3). *m/z* (ESI) $[M + H]^+$ 425.0; $[M + Na]^+$ 446.9. HRMS (ESI-Q-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{20}FeO_5SiNa$ 447.0322; found 447.0324.

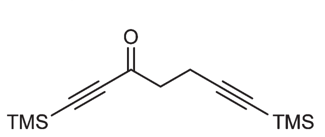
Data for 41; m.p. 196 °C dec. $[\alpha]_D^{29}$ +155.6 (*c* 0.16, $CHCl_3$). $IR_{(neat)}$ 3369 (broad), 3076, 2959, 2923, 2898, 2853, 2071, 2025, 1978, 1590, 1505, 1453, 1414, 1376, 1309, 1248 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 7.93 (2H, d, *J* = 7.5 Hz, Ar*H*), 7.30–738 (2H, m, Ar*H*), 7.28 (1H, d, *J* = 7.2 Hz, Ar*H*), 5.51 (1H, td, *J* = 7.8, 4.4 Hz, C*H*OH), 2.52–2.78 (4H, m, CH_2 and O*H*), 1.83–1.95 (1H, m, CH*H*), 0.32 (9H, s, CH_3). δ_C (125 MHz, $CDCl_3$), 208.1 (C), 175.8 (C), 131.2 (C), 129.0, 128.4, 128.0, 115.4 (C), 109.9 (C), 80.6 (C), 71.4 (CH), 67.5 (C), 35.7 (CH_2), 24.7 (CH_2), −0.7 (CH_3). *m/z* (ESI) $[M + H]^+$ 425.0; $[M + Na]^+$ 446.9. HRMS (ESI-Q-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{20}FeO_5SiNa$ 447.0322; found 447.0325.

1,7-Bis(trimethylsilyl)hepta-1,6-diyn-3-ol.



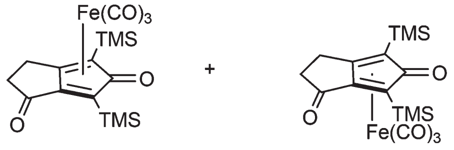
This compound is novel. In a Schlenk tube under a nitrogen atmosphere phenylacetylene (0.67 cm^3, 4.74 mmol) was dissolved in anhydrous THF (10 cm^3). The mixture was cooled at −78 °C and *n*-butyllithium (2.5 M in hexanes, 1.9 cm^3, 4.76 mmol) was added dropwise. The cooling bath was removed and stirred for 10 minutes. Then the mixture was cooled to −78 °C and transferred *via* cannula dropwise to a flask containing 5-(trimethylsilyl)pent-4-ynal **43** (580 mg, 3.76 mmol) dissolved in anhydrous THF (20 cm^3) at −78 °C. After 5 minutes the mixture was warmed at room temperature and stirred at this temperature for 3 hours. Then H_2O (20 cm^3) was added dropwise and the product was extracted with DCM (3 × 25 cm^3). The reunited organic layers were washed with brine (25 cm^3) and dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane to hexane/Et_2O = 9/1) to give 1,7-bis(trimethylsilyl)hepta-1,6-diyn-3-ol (877 mg, 3.47 mmol, 91%) as colourless oil. $IR_{(neat)}$ 3346 (broad), 2956, 2900, 2857, 2175, 1444, 1408, 1331, 1249 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 4.51 (1H, q, *J* = 6.1 Hz, C*H*OH), 2.46 (1H, dt, *J* = 17.1, 7.5 Hz, CH*H*), 2.38 (1H, dt, *J* = 17.1 Hz, *J* = 6.9 Hz, C*H*H), 2.08 (1H, d, *J* = 5.6 Hz, O*H*), 1.91 (2H, q, *J* = 6.9 Hz, CH_2), 0.18 (9H, s, CH_3), 0.15 (9H, s, CH_3). δ_C (125 MHz, $CDCl_3$), 106.1 (C), 105.7 (C), 90.0 (C), 85.5 (C), 61.8 (CH), 36.2 (CH_2), 15.9 (CH_2), 0.1 (CH_3), −0.2 (CH_3). *m/z* (ESI) $[M + Na]^+$ 274.8. HRMS (ESI-Q-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{18}OSiNa$ 275.1258; found 275.1258.

1,7-Bis(trimethylsilyl)hepta-1,6-diyn-3-one 44.



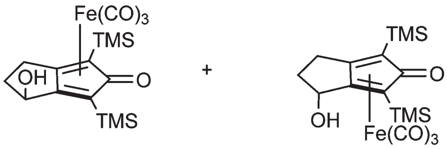
This compound is novel. In an round bottom flask 1,7-bis(trimethylsilyl)hepta-1,6-diyn-3-ol (877 mg, 3.47 mmol) was dissolved DCM (20 cm^3). Then PCC (1.12 g, 6.40 mmol) and molecular sieves were added. After 14 hours the mixture was filtered through a Celite plug washing through with DCM (50 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 97/3) to give 1,7-bis(trimethylsilyl)hepta-1,6-diyn-3-one **44** (771 mg, 3.08 mmol, 86%) as a colourless oil. $IR_{(neat)}$ 2960, 2901, 2178, 2149, 1680, 1409, 1355, 1333, 1250, 1224 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 2.77–2.83 (2H, m, CH_2), 2.50–2.56 (2H, m, CH_2), 0.23 (9H, s, CH_3), 0.12 (9H, s, CH_3). δ_C (125 MHz, $CDCl_3$), 185.4 (C), 133.1 (CH), 130.9 (CH), 128.6 (CH), 119.8 (C), 104.7 (C), 91.6 (C), 87.3 (C), 85.6 (C), 44.2 (CH_2), 14.7 (CH_2), 0.0 (CH_3). ^{13}C NMR (126 MHz, chloroform-d) δ = 185.1 (C), 104.6 (C), 101.4 (C), 98.7 (C), 85.5 (C), 44.0 (CH_2), 14.5 (CH_2), 0.0 (CH_3), −0.8 (CH_3). *m/z* (ESI) $[M + Na]^+$ 272.8. HRMS (ESI-Q-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{22}OSi_2Na$ 273.1101; found 273.1111.

Tricarbonyl-4,6-bis(trimethylsilyl)-2,3-dihydropentalene-1,5-dione iron 42.



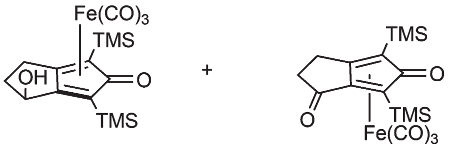
In an ACE pressure tube under a nitrogen 1,7-bis(trimethylsilyl)hepta-1,6-diyn-3-one **44** (745 mg, 2.97 mmol) was dissolved/suspended in anhydrous toluene (5 cm^3) previously degassed by freeze–pump–thaw cycles. $Fe(CO)_5$ (2.0 cm^3, 14.83 mmol) was added, the pressure tube was sealed and the mixture was heated at 130 °C for 20 hours. After the mixture was cooled to room temperature and the pressure tube was carefully opened into the fumehood to release CO pressure. Then the mixture was diluted with EtOAc (15 cm^3) and filtered through a Celite plug washing through with EtOAc (100 cm^3). The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: petroleum ether to petroleum ether /EtOAc = 9 : 1) to give tricarbonyl-4,6-bis(trimethylsilyl)-2,3-dihydropentalene-1,5-dione iron **42** (789 mg, 1.89 mmol, yield: 63%) as yellow solid. ^1H NMR and $^{13}CNMR$ were identical to the reported data.[2c] M.p. 105.5 °C dec. $IR_{(neat)}$ 2958, 2900, 2071, 2016, 1994, 1717, 1626, 1446, 1426, 1404, 1347, 1263, 1244, 1226, 1203 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 3.15 (1H, dt, *J* = 17.2, 6.9 Hz, C*H*H), 3.02 (1H, dt, *J* = 17.4, 5.0 Hz, CH*H*), 2.78 (2H, dd, *J* = 6.9, 5.0 Hz, CH_2), 0.34 (9H, s, CH_3), 0.32 (9H, s, CH_3). δ_C (125 MHz, $CDCl_3$), 206.8 (C), 204.5 (C), 183.4 (C), 129.8 (C), 98.0 (C), 78.9 (C), 77.3 (C), 76.8 (C), 67.4 (C), 36.9 (CH_2), 23.5 (CH_2), −0.4 (CH_3), −0.8 (CH_3).

Tricarbonyl-4-hydroxy-1,3-bis(trimethylsilyl)-5,6-dihydropentalen-2(4*H*)-one iron 45.



In an round bottom flask tricarbonyl-4,6-bis(trimethylsilyl)-2,3-dihydropentalene-1,5-dione iron **42** (100 mg, 0.24 mmol) was dissolved in EtOH (12 cm^3) $NaBH_4$ (11.5 mg, 0.30 mmol) was added and the reaction was stirred for 1 hours. Then H_2O (1 cm^3) was added and the mixture was stirred 30 minutes. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: pentane/EtOAc = 19 : 1 to 9 : 1) to give tricarbonyl-4-hydroxy-1,3-bis(trimethylsilyl)-5,6-dihydropentalen-2(4*H*)-one iron **45** (75 mg, 0.18 mmol, 75%) as a yellow solid. ^1H NMR and ^{13}C NMR were identical to the reported data.[2c] M.p. 172.9–173.7 °C. $[\alpha]_D^{25}$ −88.8 (*c* 0.49, $CHCl_3$). $IR_{(neat)}$ 3289 (broad), 2961, 2934, 2900, 2064, 2013, 1975, 1583, 1453, 1406, 1380, 1356, 1312, 1247 cm^{-1}. δ_H (500 MHz, $CDCl_3$), 5.21 (1H, td, *J* = 7.6, 5.0 Hz, C*H*OH), 2.60–2.69 (2H, m, CH_2), 2.51–2.60 (1H, m, C*H*H), 2.24–2.34 (1H, m, CHO*H*), 1.72–1.83 (1H, m, CH*H*), 0.31 (9H, s, CH_3), 0.26 (9H, s, CH_3). δ_C (125 MHz, $CDCl_3$), 208.4 (C), 183.1 (C), 118.9 (C), 117.7 (C), 71.3 (CH), 70.5 (C), 68.2 (C), 35.4 (CH_2), 24.9 (CH_2), −0.1 (CH_3), −0.7 (CH_3). *m*/*z* (ESI) $[M + H]^+$, 421.1; $[M + Na]^+$, 443.0. HRMS (ESI-Q-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{17}H_{24}FeO_5Si_2Na$ 443.0404; found 443.0406.

Enantiomerically enriched (−)-45 and (+)-42.



In an round bottom flask under a nitrogen atmosphere, racemic tricarbonyl-4-hydroxy-1,3-bis(trimethylsilyl)-5,6-dihydropentalen-2(4*H*)-one iron **42** (500 mg, 1.19 mmol) was dissolved in anhydrous DCM (2 cm^3). [(*S*,*S*)-Teth-TsDpen-RuCl] **23** (26 mg, 0.12 mmol) and an azeotropic mixture of formic acid/triethylamine (5 : 2 mixture, 0.8 cm^3) were added. After 7 hours saturated $NaHCO_3$ aqueous solution (10 cm^3) and H_2O (15 cm^3) were added and the mixture was stirred 30 minutes. The product was extracted with DCM (3 × 30 cm^3). The reunited organic layers were washed with brine (100 cm^3) and dried over Na_2SO_4. The volatiles were removed and the product was purified by flash chromatography on silica gel (eluent: pentane to pentane/EtOAc = 9 : 1) to give alcohol (−)-**45** (204 mg, 0.49 mmol, yield: 40.6%, 97.6% ee) as yellow solid and ketone (+)-**42** (175 mg, 0.42 mmol, yield: 35.0%, 88.2% ee) as yellow solid. The enantiomeric excesses ere determined by HPLC analysis with a ChiralPak IA column: 0.46 cm × 25 cm, mobile phase iso-propanol : hexane 3 : 97, flow rate 1 mL min^{-1}, temperature 30 °C, UV detection at λ = 254 nm; t_R = 6.1 min (ketone), t_R = 7.0 min (ketone), t_R = 11.4 min (alcohol), t_R = 14.3 min (alcohol). Alcohol (−)-**45**; $[\alpha]_D^{24}$ −37.1 (*c* 0.48, $CHCl_3$). Ketone (+)-**42**; $[\alpha]_D^{24}$ +98.2 (*c* 0.11, $CHCl_3$).

The alcohols formed by reductions have been reported and our procedures and characterisation followed the protocols reported.[11,18]

Conflicts of interest

There are no conflicts to declare.

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