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Asymmetric carbonyl-ene and Friedel–Crafts reactions catalysed by Lewis acid platinum group metal complexes of the enantiopure atropisomeric biaryl-like diphosphine (*S*)-Me$_2$-CATPHOS: a comparison with BINAP

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ABSTRACT

Lewis acid platinum and palladium complexes of (*S*)-Me$_2$-CATPHOS catalyse the carbonyl-ene reaction between allylbenzene derivatives and ethyl trifluoropyruvate to give the expected α-hydroxy esters with ee's up to 97%, while the corresponding reaction involving 2-allylfuran and thiophene was exclusively selective for Friedel–Crafts-type reactivity and gave the corresponding 2-hydroxy-trifluoromethyl ethyl esters in good yield and moderate to good enantioselectivity.

1. Introduction

The asymmetric carbonyl-ene reaction between electron deficient enophiles, such as alkyl or aryl glyoxylates or the less reactive α-ketoesters and 1,1-disubtituted or trisubstituted alkenes, is a powerful atom economical C–C bond forming reaction that provides access to non-racemic synthetically versatile γ,δ-unsaturated-α-hydroxy esters[1]; for example, an asymmetric carbonyl-ene reaction involving silyl enol ethers has recently been used to prepare optically active β-hydroxy silyl enol ethers with a quaternary carbon stereocentre,[2] while the carbonyl-ene reaction between racemic silyloxyallenes and 2-bromobenzaldehyde has been coupled to an intramolecular palladium-catalysed Heck reaction in order to construct substituted indanones with the efficient transfer of stereochemistry from the initial enantioenriched carbinol to the C3 position.[3] Since the first report of a catalytic enantioselective variant of this reaction, which used a chiral aluminium complex of enantiopure BINOL,[4] a host of highly efficient Lewis acid complexes have been developed including combinations of Ti-BINOL,[5] Cu-Box,[6] Cu-sulfoximine,[7] Co-Salen,[8] Cr-terdentate Schiff bases,[9] In-pybox[10] and Sc-PyBox,[11] Ni(II)-*N*,*N*′-dioxides[12] as well as a chiral Brønsted acid *N*,*N*-triflylphosphoramide based organocatalyst.[13] Recently, cationic 'coordinately unsaturated' square planar platinum group metal complexes of the type [M(diphosphine)]$^{2+}$ (M = Pt, Pd, Ni) have emerged as an alternative class of Lewis acid catalyst[14] with a number of potentially advantageous properties unique to and characteristic of the late transition metals including functional group tolerance, well-defined coordination geometries, which allow control of the stereochemical environment, high carbophilicity, slow rates of ligand exchange and tunable electronic properties (Lewis acidity).[15] Indeed, this class of Lewis acid complexes have proven to be highly efficient catalysts for a host of important enantioselective transformations including Diels–Alder[16] and hetero Diels–Alder reactions,[17] 1,3-dipolar cycloadditions,[18] asymmetric Prins cyclisations,[19] the Conia-ene reaction,[20] conjugate additions of amines to α,β-unsaturated *N*-alkenylimides,[21] asymmetric reactions via palladium enolates,[22] the alkenylation and alkynylation of electrophiles,[23] ene-type reactions between aldehydes and 1,3-dienes,[24] as well as cycloisomerisations and cyclisations.[25]

As part of an ongoing programme to develop new, efficient and modular approaches to the synthesis of biaryl and biaryl-like phosphines[26] we have recently prepared an entirely new and architecturally distinct class of diphosphine R$_2$-CATPHOS (R = H, Me) via a double [4+2] cycloaddition between 1,4-bis(diphenylphosphino)buta-1,3-diyne and anthracene (Chart 1).[27] Preliminary studies have shown that rhodium complexes of enantiopure (*S*)-Me$_2$-CATPHOS are highly efficient catalysts for the asymmetric hydrogenation of (*E*)-β-aryl-β-(enamido)phosphonates, giving ee's in excess of 99%, the highest values reported for this class of substrate.[28] Since platinum group metal Lewis acid complexes based on BINAP,[29] BIPHEP,[30] MeO-BIPHEP[31] and NUPHOS[32] (Chart 1) are efficient catalysts for the carbonyl-ene reaction and, with a specific interest in exploring the use of Me$_2$-CATPHOS as a possible surrogate for more conventional biaryl diphosphines, we have undertaken a systematic and thorough comparison of [M{(*S*)-Me$_2$-CATPHOS}]$^{2+}$ (M = Pt, Pd) as Lewis acid catalysts for the carbonyl-ene reaction. The data presented herein provide evidence that the performance of platinum group metal Lewis acid complexes is highly substrate specific and depends critically on the metal-phosphine combination and that catalysts based on Me$_2$-CATPHOS can rival their BINAP counterparts for selected substrates.

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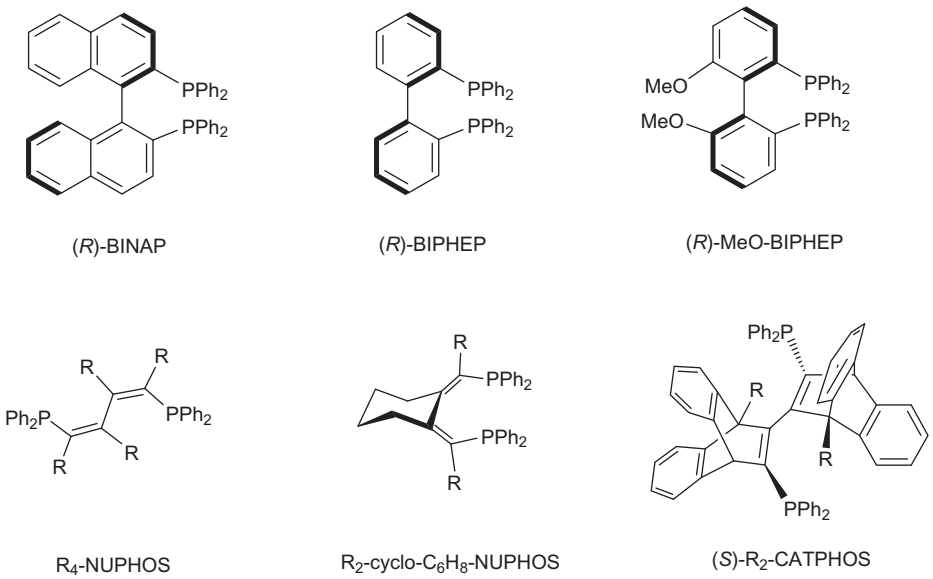
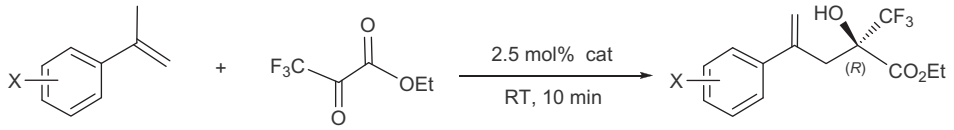


Chart 1.

Table 1
Asymmetric carbonyl-ene reaction between α-methylstyrene derivatives **3a-c** and ethyl trifluoropyruvate catalysed by (*S*)-**1a–b** and (*S*)-**2a–b** in CH_2Cl_2[a]



3a-c **4a-c**

Entry[a]	X	**3**	Catalyst	Yield[d,b] (%)	% ee[c,d]
1	H	**3a**	(*S*)-**1a**	93	65
2	H	**3a**	(*S*)-**1b**	97	55
3	H	**3a**	(*S*)-**2a**	98	79
4	H	**3a**	(*S*)-**2b**	93	36
5	4-Cl	**3b**	(*S*)-**1a**	98	43
6	4-Cl	**3b**	(*S*)-**1b**	97	38
7	4-Cl	**3b**	(*S*)-**2a**	91	88
8	4-Cl	**3b**	(*S*)-**2b**	94	58
9	2-Me	**3c**	(*S*)-**1a**	94	50
10	2-Me	**3c**	(*S*)-**1b**	90	20
11	2-Me	**3c**	(*S*)-**2a**	97	81
12	2-Me	**3c**	(*S*)-**2b**	96	31

[a] Reaction conditions: 2.5 mol % catalyst, styrene (0.5 mmol) and ethyl trifluoropyruvate (0.75 mmol) in 2.0 mL of CH_2Cl_2, room temperature.
[b] Isolated yield.
[c] Enantiomeric excess determined by chiral GC using a Supelco Beta DEX column.
[d] Average of three runs.

2. Results and discussion

Since the carbonyl-ene reaction has been catalysed by a host of Lewis acids, including those based on palladium and platinum, it was considered an ideal transformation to evaluate the performance of platinum group metal complexes of enantiopure (*S*)-Me_2-CATPHOS against their BINAP counterparts. The catalysts required herein were prepared in situ by the reaction of [MCl_2(cycloocta-1,5-diene)] (M = Pd, Pt) with either (*S*)-Me_2-CATPHOS or (*S*)-BINAP in dichloromethane to generate [MCl_2(diphosphine)], which was subsequently converted into the corresponding Lewis acid [M(diphosphine)][OTf]$_2$ by activation with two equivalents of silver trifluoromethanesulfonate (Eqs. (1) and (2)). After stirring for 30 min at ambient temperature, the dienophile and alkene were added and the progress of the reaction monitored by GC.

Our study began with a comparison of the performance of Lewis acids **1a–b** and **2a–b** as catalysts for the carbonyl-ene reaction of α-methylstyrene and its derivatives with ethyl trifluoropyruvate, full details of which are summarised in Table 1. Although the reaction proceeded in THF, chloroform, 1,2-dichloroethane and toluene, the ee's were consistently lower than those obtained in

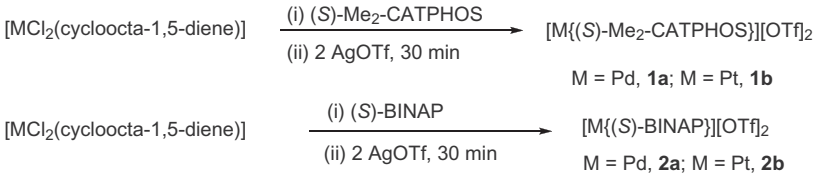
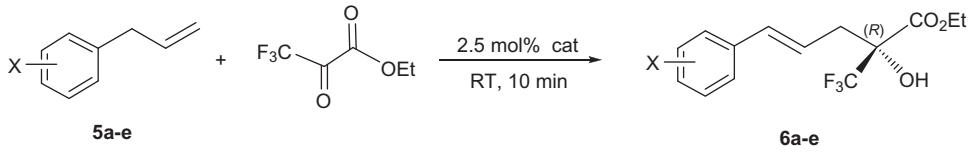


Table 2
Asymmetric carbonyl-ene reaction between allylbenzene derivatives **5a–e** and ethyl trifluoropyruvate catalysed by (*S*)-**1a–b** and (*S*)-**2a–b** in CH_2Cl_2[a]



Entry	X	5	Catalyst	Yield[b,d] (%)	% ee[c,d]
1	H	**5a**	(*S*)-**1a**	98	72
2	H	**5a**	(*S*)-**1b**	97	93
3	H	**5a**	(*S*)-**2a**	98	99
4	H	**5a**	(*S*)-**2b**	95	99
5	4-Me	**5b**	(*S*)-**1a**	92	68
6	4-Me	**5b**	(*S*)-**1b**	90	55
7	4-Me	**5b**	(*S*)-**2a**	93	97
8	4-Me	**5b**	(*S*)-**2b**	91	93
9	2-Me	**5c**	(*S*)-**1a**	95	60
10	2-Me	**5c**	(*S*)-**1b**	89	67
11	2-Me	**5c**	(*S*)-**2a**	94	90
12	2-Me	**5c**	(*S*)-**2b**	93	96
13	3,5-Me_2	**5d**	(*S*)-**1a**	92	78
14	3,5-Me_2	**5d**	(*S*)-**1b**	96	94
15	3,5-Me_2	**5d**	(*S*)-**2a**	90	99
16	3,5-Me_2	**5d**	(*S*)-**2b**	94	99
17	4-Cl	**5e**	(*S*)-**1a**	95	72
18	4-Cl	**5e**	(*S*)-**1b**	97	>99
19	4-Cl	**5e**	(*S*)-**2a**	94	93
20	4-Cl	**5e**	(*S*)-**2b**	98	99

[a] Reaction conditions: 2.5 mol % catalyst, allylbenzene (0.5 mmol) and ethyl trifluoropyruvate (0.75 mmol) in 2.0 mL of CH_2Cl_2, room temperature.
[b] Isolated yield.
[c] Enantiomeric excess determined by chiral GC.
[d] Average of three runs.

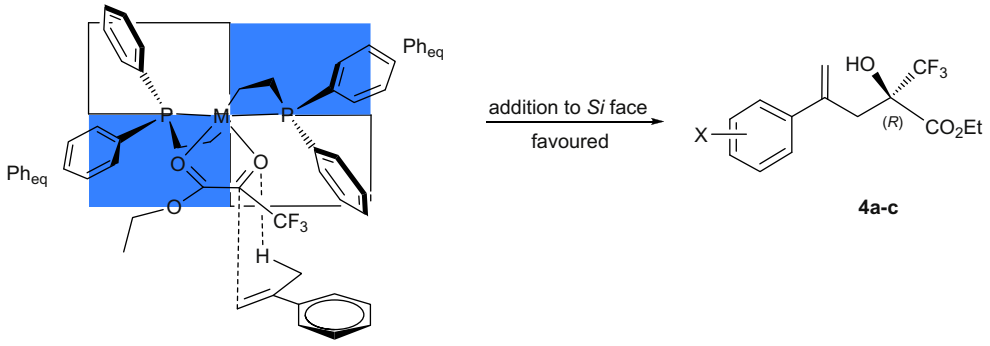
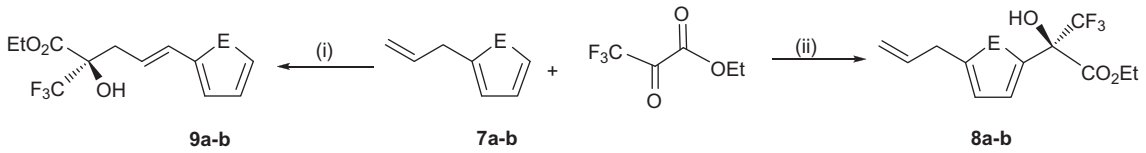


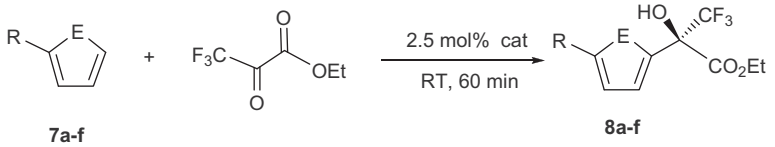
Figure 1. Stereochemical model to rationalise the preferential *Si*-face approach of allylbenzene to afford α-hydroxyesters with an (*R*)-configuration.

dichloromethane, which was used as the solvent of choice. Preliminary tests revealed that while good conversions were obtained for each catalyst examined, the enantioselectivities varied from moderate to good and showed a marked dependence on the metal-phosphine combination, as well as the substrate. For each substrate tested, Lewis acids based on palladium were markedly more efficient than their platinum counterparts and those formed from (*S*)-BINAP gave consistently higher enantioselectivities than the



Scheme 1. Showing (i) the carbonyl-ene and (ii) the Friedel–Crafts products resulting from the reaction of 2-allylfuran (E = O) and thiophene (E = S) with ethyl trifluoropyruvate.

Table 3
Asymmetric Friedel–Crafts reaction between heteroaromatics and ethyl trifluoropyruvate catalysed by (*S*)-**1a**–**b** and (*S*)-**2a**–**b** in CH_2Cl_2[a]



Entry	E	R	7	Catalyst	Yield[b,d] (%)	% ee[c,d]
1	O	Allyl	**7a**	(*S*)-**1a**	87	50
2	O	Allyl	**7a**	(*S*)-**1b**	98	67
3	O	Allyl	**7a**	(*S*)-**2a**	97	43
4	O	Allyl	**7a**	(*S*)-**2b**	95	12
5	S	Allyl	**7b**	(*S*)-**1a**	99	31
6	S	Allyl	**7b**	(*S*)-**1b**	92	43
7	S	Allyl	**7b**	(*S*)-**2a**	93	60
8	S	Allyl	**7b**	(*S*)-**2b**	95	63
9	O	H	**7c**	(*S*)-**1a**	96	65
10	O	H	**7c**	(*S*)-**1b**	93	57
11	O	H	**7c**	(*S*)-**2a**	98	52
12	O	H	**7c**	(*S*)-**2b**	92	45
13	S	H	**7d**	(*S*)-**1a**	90	30
14	S	H	**7d**	(*S*)-**1b**	97	80
15	S	H	**7d**	(*S*)-**2a**	98	32
16	S	H	**7d**	(*S*)-**2b**	90	83
17	O	Me	**7e**	(*S*)-**1a**	98	80
18	O	Me	**7e**	(*S*)-**1b**	90	17
19	O	Me	**7e**	(*S*)-**2a**	96	62
20	O	Me	**7e**	(*S*)-**2b**	94	40
21	S	Me	**7f**	(*S*)-**1a**	95	76
22	S	Me	**7f**	(*S*)-**1b**	99	60
23	S	Me	**7f**	(*S*)-**2a**	95	57
24	S	Me	**7f**	(*S*)-**2b**	90	84

[a] Reaction conditions: 2.5 mol % catalyst, heterocycle (0.5 mmol) and ethyl trifluoropyruvate (0.75 mmol) in 2.0 mL of CH_2Cl_2, room temperature.
[b] Isolated yield.
[c] Enantiomeric excess determined by chiral GC.
[d] Average of three runs.

corresponding M/(*S*)-Me_2-CATPHOS-based systems. The disparate performance of catalysts based on (*S*)-BINAP and (*S*)-Me_2-CATPHOS manifests itself most evidently in reactions involving substituted styrenes. For example, Pd/(*S*)-BINAP catalysed the carbonyl-ene reaction between 4-chlorostyrene and ethyl trifluoropyruvate to give α-hydroxyester **4b** in good yield and with excellent enantioselectivity (88%) compared with an ee of only 43% with Pd/(*S*)-Me_2-CATPHOS (entry 7 vs entry 5). As expected, the stereochemistry of α-hydroxy esters **4a**–**c** obtained with catalysts based on (*S*)-Me_2-CATPHOS are the same as those obtained with catalysts generated with (*S*)-BINAP; the absolute configuration was assigned as (*R*) by analogy with the corresponding product obtained from the reaction between methylenecyclohexane and ethyl trifluoropyruvate. The sense of asymmetric induction for the carbonyl-ene reaction catalysed by (*S*)-**1a**–**b** and (*S*)-**2a**–**b** is consistent with a transition state model, which involves coordination of the pyruvate through both carbonyl oxygen atoms in a bidentate manner to form a square planar adduct, similar to that used by Oi et al.[14,17b] and Ghosh and Matusda[16] for the [M{(*S*)-BINAP](X) (M = Pd, Pt)-catalysed Diels–Alder reaction between *N*-acryloyloxazolidinones and dienes and the [Cu{(*S*,*S*)-*t*-Bu-Box)][SbF_6]$_2$ catalysed Diels–Alder and aldol reactions of α-dicarbonyl substrates (Fig. 1).[33] According to this model, palladium and platinum complexes of (*S*)-Me_2-CATPHOS have the same spatial arrangement of axial and equatorial P-Ph rings as their BINAP counterparts with the two equatorial phenyl rings occupying the upper right and lower left quadrants such that the *Re*-face of the pyruvate is effectively shielded, thus rendering approach of the styrene to the *Si*-face to afford α-hydroxy esters with an (*R*)-configuration more favourable.

The substrate specific, disparate and marked metal-phosphine dependent performance of catalyst **1a**–**b** and **2a**–**b** prompted us to extend our comparative catalyst evaluation to include the addition of allylbenzene and its derivatives to ethyl trifluoropyruvate, the full details of which are provided in Table 2. Under the same conditions, both platinum-based Lewis acid catalysts are more efficient than their palladium counterparts for the majority of substrates examined, and the difference in performance between the

systems based on (*S*)-Me_2-CATPHOS and (*S*)-BINAP is not as pronounced as for α-methylstyrene and its derivatives. In general, each catalyst gave α-hydroxy esters **6a–e** in good yield, complete *E*-selectivity and with moderate to excellent enantioselectivity. The Pt/(*S*)-BINAP combination was consistently the most efficient catalyst across the range of substrates examined, giving enantioselectivities ranging from 93% to 99%, although encouragingly Pt/(*S*)-Me_2-CATPHOS also gave ee's as high as 99% for selected substrates. This is most apparent for the reaction between 1-allyl-4-chlorobenzene as both catalysts gave α-hydoxy ester **6e** in excellent yield and 99% ee. Mikami has recently resolved a platinum(II) complex of 1,1′-bis(diphenylphosphino)biphenyl and shown that the derived enantiopure Lewis acid catalyses the carbonyl-ene reaction between allylbenzene and ethyl trifluoropyruvate to give ester **6a** with high enantioselectivity and *E*-selectivity.[34] The absolute configuration of α-hydroxy ester **6a** was determined to be (*R*) by comparison of the GC retention times and the specific rotations with those reported in the literature; the absolute configurations for **6b–e** were assigned by analogy. The sense of asymmetric induction is also entirely consistent with the stereochemical model described above which was used to rationalise the stereochemical outcome obtained from the carbonyl-ene reaction between α-methylstyrene and its derivatives.

Encouraged by the efficacy of Lewis acids **1a–b** and **2a–b** as catalysts for the enantioselective reaction between allylbenzene derivatives and ethyl trifluoropyruvate, substrate testing was further extended to include 2-allylfuran and thiophene, **7a** and **7b**, respectively, with the aim of accessing the corresponding heteroaromatic esters **9a** and **9b**. However, under the same conditions as those described above, each of the catalysts gave the corresponding hydroxy trifluoromethyl ester, **8a** and **8b**, as the sole product, with no evidence for the desired carbonyl-ene adducts **9a** and **9b** (Scheme 1). The identity of **8a–b** as the product of a Friedel–Crafts type alkylation at the 4-position of the heterocycle was unequivocally established by a combination of ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis, after purification by column chromatography.

A cursory analysis of the data in Table 3 shows that the catalyst performance is highly variable as well as substrate specific. This is clearly evident in the case of 2-allylfuran as both (*S*)-Me_2-CATPHOS-based catalysts outperformed their BINAP counterparts, giving hydroxy trifluoromethyl ester **8a** in excellent yield and with moderate to poor enantioselectivity; 50% and 67% for **1a** and **1b**, respectively, compared with 43% and 12% for **2a** and **2b**, respectively. In contrast, both BINAP-based systems proved to be markedly more efficient than their Me_2-CATPHOS counterparts for the corresponding reaction of 2-allylthiophene; ee values of 60% and 63% were obtained for **8b** with the BINAP systems, which were higher than those obtained with the CATPHOS systems, which were modest (31% and 43%). Having established that **1a–b** and **2a–b** selectively catalyse the Friedel–Crafts reaction, the range of substrates was expanded to include furan, thiophene and their 2-methyl-substituted derivatives; the varied and disparate enantioselectivities obtained further emphasise the substrate-specific and metal-ligand dependent performance of these catalysts (Table 3). For example, both palladium systems catalysed the reaction with furan and gave **8c** with higher ee's than their platinum counterparts, albeit only marginally, whereas the platinum-based combinations were markedly more efficient than their palladium counterparts for the reaction involving thiophene, as evidenced by the ee's of 80% and 83%, compared with 30% and 32%, respectively. High ee's were also obtained for the reaction of 2-methylfuran and thiophene with ethyl trifluoropyruvate. The Pd/(*S*)-Me_2-CATPHOS system proved to be the most efficient catalyst for the reaction of 2-methylfuran giving ester **8e** in 80% ee, which is a marked improvement on that obtained with its platinum counterpart (62%). Similarly, Pd/(*S*)-Me_2-CATPHOS also gave the 2-methylthiophene derived product **8f** with good enantioselectivity (76%), although in this case Pt/(*S*)-BINAP was slightly more efficient and gave adduct **8f** in 84% ee. The absolute configurations of **8c–f** have been determined by comparison of the sign of the specific rotations with those reported by Jørgensen for the bis(oxazoline)-copper(II) catalysed Friedel–Crafts reaction of furan, thiophene and their 2-Me-substituted derivatives with ethyl trifluoropyruvate, which gave the corresponding hydroxy trifluoromethyl esters in low isolated yield but good enantioselectivity.[35] The sense of asymmetric induction for these Friedel–Crafts reactions is consistent with the two point binding model described above in which the alternating edge-face arrangement of the P-Ph rings controls access of the heteroaromatic to favour attack at the *Si*-face of the pyruvate.

3. Conclusions

Herein we have shown that platinum group metal Lewis acids catalyse the carbonyl-ene reaction between allylbenzene and its derivatives to give the corresponding homoallylic α-hydroxy esters in excellent yield and with good to excellent enantioselectivity and that, for selected substrates, catalysts based on (*S*)-Me_2-CATPHOS can rival their BINAP counterparts with palladium outperforming platinum for the majority of substrates tested. In contrast, platinum-based Lewis acids were more efficient than their palladium counterparts for reactions involving α-methyl styrene and its derivatives; in this case, yields were excellent but the ee's were significantly lower than those obtained with allylbenzene. Extending the study to 2-allylfuran and thiophene revealed that these Lewis acids selectively catalyse Friedel–Crafts reactivity with no evidence for the carbonyl-ene reaction; each catalyst gave the corresponding hydroxy trifluoromethyl ester in excellent yield and moderate to good enantioselectivity. Even though the efficiency of these platinum group metal Lewis acids is clearly substrate specific and markedly dependent on the metal-phosphine combination, the performance of (*S*)-Me_2-CATPHOS is encouraging. To this end, studies are currently underway to further explore the applications of this diphosphine in a wide range of asymmetric transformations including rhodium-, palladium- and gold-catalysed cyclisations and cycloisomerisations, palladium-catalysed conjugate additions and the ruthenium-catalysed hydrogenation of ketones and to prepare a library of related diphosphines in order to develop a structure-performance relationship and identify an optimum architecture.

4. Experimental

4.1. General procedures

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Dichloromethane was distilled from calcium hydride, diethyl ether from Na/K alloy, dioxane from sodium and THF from sodium/benzophenone. Ethyl trifluoropyruvate, allylmagnesium bromide, aryl bromides, allylbenzene, indole and styrene derivatives were purchased from commercial suppliers and used without further purification. (*S*)-Me_2-CATPHOS,[27b] [M(cycloocta-1,5-diene)Cl_2],[36] allylbenzene derivatives,[32a] 2-allylfuran,[37] and 2-allylthiophene[38] were prepared as previously described. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL ECS-400 instrument. Optical rotations were measured on an Optical Activity PolAAr 2001 digital polarimeter with a sodium lamp and are reported as follows: $[\alpha]_D^{20}$ (*c* g/100 mL, solvent). Thin-layer chromatography (TLC) was carried out on aluminium sheets pre-coated with silica gel 60F 254 and

column chromatography was performed using Merck Kieselgel 60. Gas chromatography was performed on a Shimadzu 2010 series gas chromatograph equipped with a split-mode capillary injection system and flame ionisation detection using a SUPELCO BETA DEX column (injection temp. 170 °C; column conditions 140 °C for 45 min ramp to 180 °C at 3 °C/min, hold for 40 min) and enantiomeric excesses were calculated from the GC profile.

4.2. General procedure for carbonyl-ene reaction between styrene derivatives and ethyl trifluoropyruvate

A flame-dried Schlenk flask was charged with (*S*)-Me$_2$-CATPHOS (0.010 g, 0.013 mmol), [MCl$_2$(cycloocta-1,5-diene)] (0.013 mmol) and CH_2Cl_2 (2 mL) and the mixture was stirred at room temperature for 2 h. After this time, AgOTf (0.090 g, 0.025 mmol) was added and stirring was continued for a further 30 min before adding ethyl trifluoropyruvate (0.099 mL, 0.75 mmol) and styrene (0.057 mL, 0.5 mmol). The resulting mixture was stirred for a further 10 min at room temperature after which time the solution was filtered through a short plug of silica eluting with CH_2Cl_2, the solvent removed, and the resulting residue purified by column chromatography, eluting with hexane/CH_2Cl_2. The products were analysed by ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, and the enantiomeric excess determined by chiral GC.

4.2.1. Ethyl 2-hydroxy-4-phenyl-2-trifluoromethylpent-4-enoate 4a

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = +26.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.26–7.17 (m, 5H, C_6H_5), 5.30 (s, 1H, =C*H*$_a$H$_b$), 5.20 (s, 1H, =CH$_a$*H*$_b$), 3.99–3.89 (m, 1H, OC*H*$_a$H$_b$), 3.73 (d, *J* = 0.7 Hz, 1H, O*H*), 3.59–3.49 (m, 1H, OCH$_a$*H*$_b$), 3.21 (d, *J* = 14.0 Hz, 1H, =CC*H*$_a$H$_b$), 2.95 (d, *J* = 14.0 Hz, 1H, =CCH$_a$*H*$_b$), 1.02 (t, *J* = 7.2 Hz, 3H, OCH$_2$*CH*$_3$); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 169.0 (*C*=O), 141.5 (C_6H_5), 141.3 (*C*=CH$_2$), 128.2 (C_6H_5), 127.7 (C_6H_5), 126.8 (C_6H_5), 123.5 (q, $J_{C\text{-}F}$ = 286.1 Hz, *C*F$_3$), 119.0 (C=*C*H$_2$), 77.5 (q, $J_{C\text{-}F}$ = 29.1 Hz, *C*CF$_3$), 63.4 (OCH$_2$CH$_3$), 37.2 (=*C*CH$_2$), 13.5 (OCH$_2$*C*H$_3$); LRMS (EI) *m*/*z* 288 [M]$^+$; HRMS (EI) exact mass calcd for $C_{14}H_{15}F_3O_3$ [M]$^+$ requires *m*/*z* 288.0973, found *m*/*z* 288.0978; Retention times: major (2*R*)-enantiomer t_r = 63.6 min, minor (2*S*)-enantiomer t_r = 63.0 min; 65% ee. Absolute stereochemistry assigned by analogy.

4.2.2. Ethyl 4-(4-chlorophenyl)-2-hydroxy-2-trifluoromethylpent-4-enoate 4b

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = +14.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.25–7.1 (m, 4H, Ar-*H*), 5.38 (s, 1H, =C*H*$_a$H$_b$), 5.28 (s, 1H, =CH$_a$*H*$_b$), 4.17–4.06 (m, 1H, OC*H*$_a$H$_b$), 3.83–3.73 (m, 1H, OCH$_a$*H*$_b$), 3.79 (s, 1H, O*H*), 3.22 (d, *J* = 14.1 Hz, 1H, =CC*H*$_a$H$_b$), 3.03 (d, *J* = 14.1 Hz, 1H, =CCH$_a$*H*$_b$), 1.17 (t, *J* = 7.2 Hz, 3H, CH$_2$*CH*$_3$); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 169.0 (*C*=O), 140.6 (C_6H_4), 139.8 (*C*=CH$_2$), 133.8 (C_6H_4), 128.4 (C_6H_4), 128.1 (C_6H_4), 123.5 (q, $J_{C\text{-}F}$ = 286.2 Hz, *C*F$_3$), 119.3 (C=*C*H$_2$), 77.6 (q, $J_{C\text{-}F}$ = 29.1 Hz, *C*CF$_3$), 63.5 (OCH$_2$CH$_3$), 37.0 (=*C*CH$_2$), 13.6 (OCH$_2$*C*H$_3$); LRMS (EI) *m*/*z* 322 [M]$^+$; HRMS (EI) exact mass calcd for $C_{14}H_{14}ClF_3O_3$ [M]$^+$ requires *m*/*z* 322.0583, found *m*/*z* 322.0577. Retention times: major (2*R*)-enantiomer t_r = 63.6 min, minor (2*S*)-enantiomer t_r = 63.9 min; 38% ee. Absolute stereochemistry assigned by analogy.

4.2.3. Ethyl 4-(*o*-tolyl)-2-hydroxy-2-trifluoromethylpent-4-enoate 4c

A sample was isolated as a colourless oil after purification by column chromatography. $[\alpha]_D$ = +43.0 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.15–6.95 (m, 4H, Ar-*H*), 5.35 (s, 1H, =C*H*$_a$H$_b$), 5.05 (s, 1H, =CH$_a$*H*$_b$), 3.95–3.82 (m, 1H, OC*H*$_a$H$_b$), 3.75 (s, 1H, O*H*), 3.5–3.38 (m, 1H, OCH$_a$*H*$_b$), 3.2–3.1 (d, *J* = 14.6 Hz, 1H, =CC*H*$_a$H$_b$), 2.95–2.85 (d, *J* = 13.7 Hz, 1H, =CCH$_a$*H*$_b$), 2.25 (s, 3H, *CH*$_3$), 1.10–0.95 (t, *J* = 7.15 Hz, 3H, CH$_2$*CH*$_3$); ^{13}C{^{1}H} NMR 75.5 MHz, $CDCl_3$, δ): 169.5 (*C*=O), 141 (C_6H_4), 140.7 (C_6H_4), 135.2 (*C*=CH$_2$), 130.4 (C_6H_4), 129.2 (C_6H_4), 127.7 (C_6H_4), 125.67 (C_6H_4), 122.1 (q, $J_{C\text{-}F}$ = 286.2 Hz, *C*F$_3$), 121.7 (C=*C*H$_2$), 78.1 (q, $J_{C\text{-}F}$ = 29.1 Hz, *C*CF$_3$), 63.8 (OCH$_2$), 38.9 (=CCH$_2$), 20.2 (Ar-*C*H$_3$), 13.72 (CH$_2$*C*H$_3$); LRMS (EI) *m*/*z* 302 [M]$^+$, HRMS (EI) exact mass calculated for $C_{15}H_{17}F_3O_3$ [M]$^+$ requires *m*/*z* 302.1489, found *m*/*z* 302.1474; Retention times: major (2*R*)-enantiomer t_r = 51.4 min, minor (2*S*)-enantiomer t_r = 51.8 min; 82% ee. Absolute stereochemistry assigned by analogy.

4.3. General procedure for the carbonyl-ene reaction of allylbenzene and its derivatives with ethyl trifluoropyruvate

A flame-dried Schlenk flask was charged with (*S*)-Me$_2$-CATPHOS (0.010 g, 0.013 mmol), [MCl$_2$(cycloocta-1,5-diene)] (0.013 mmol) and CH_2Cl_2 (2 mL), and then stirred at room temperature for 1 h. After this time AgOTf (0.090 g, 0.025 mmol) was added and stirring was continued for a further 30 min before adding the ethyl trifluoropyruvate (0.099 mL, 0.75 mmol) and allylbenzene (0.066 mL, 0.5 mmol). The resulting mixture was stirred for a further 10 min at room temperature after which time the solution was flushed through a short plug of silica with dichloromethane, the solvent removed, and the resulting residue purified by column chromatography, eluting with hexane/CH_2Cl_2. The products were analysed by ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, and the enantiomeric excess determined by chiral GC.

4.3.1. Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-*p*-tolylpent-4-enoate 6b

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = +34.2 (*c* 1.22, CH_2Cl_2); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.23 (d, *J* = 8.0 Hz, 2H, C_6H_4), 7.12 (d, *J* = 8.0 Hz, 2H, C_6H_4), 6.51 (d, *J* = 15.8 Hz, 1H, C_6H_4CH=), 6.10–6.00 (m, 1H, =*CH*CH$_2$), 4.29–4.27 (m, 2H, OC*H*$_2$CH$_3$), 3.94 (s, 1H, O*H*), 2.92–2.78 (m, 2H, =CHC*H*$_2$), 2.34 (s, 3H, C*H*$_3$C$_6$H$_4$), 1.33 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 169.3 (*C*=O), 137.6 (C_6H_4), 135.5 (C_6H_4CH=), 134.2 (C_6H_4), 129.2 (C_6H_4), 126.2 (C_6H_4), 123.5 (q, $J_{C\text{-}F}$ = 286.2 Hz, *C*F$_3$), 119.6 (=*C*HCH$_2$), 77.9 (q, $J_{C\text{-}F}$ = 29.2 Hz, *C*CF$_3$), 63.7 (OCH$_2$CH$_3$), 35.8 (=CH*C*H$_2$), 21.0 (*C*H$_3$C$_6$H$_4$), 14.0 (OCH$_2$*C*H$_3$); LRMS (EI) *m*/*z* 302 [M]$^+$; HRMS (EI) exact mass calcd for $C_{15}H_{17}F_3O_3$ [M]$^+$ requires *m*/*z* 302.1129, found *m*/*z* 302.1134. Retention times: major (*R*)-enantiomer t_r = 50.9 min, minor (*S*)-enantiomer t_r = 52.1 min; 70% ee. Absolute stereochemistry assigned by analogy.

4.3.2. Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(2-methylphenyl)pent-4-enoate 6c

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = +21.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.28–7.26 (m, 1H, C_6H_4), 7.09–7.05 (m, 3H, C_6H_4), 6.66 (d, *J* = 15.7 Hz, 1H, C_6H_4CH=), 5.93–5.83 (m, 1H, =*CH*CH$_2$), 4.32–4.21 (m, 2H, OC*H*$_2$CH$_3$), 3.86 (s, 1H, O*H*), 2.87–2.72 (m, 2H, =CHC*H*$_2$), 2.23 (s, 3H, C*H*$_3$C$_6$H$_4$), 1.35 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 169.3 (*C*=O), 137.6 (C_6H_4), 135.5 (C_6H_4CH=), 134.2 (C_6H_4), 129.2 (C_6H_4), 126.2 (C_6H_4), 123.5 (q, $J_{C\text{-}F}$ = 286.2 Hz, *C*F$_3$), 119.6 (=*C*HCH$_2$), 77.9 (q, $J_{C\text{-}F}$ = 29.1 Hz, *C*CF$_3$), 63.7 (OCH$_2$CH$_3$), 35.8 (=CH*C*H$_2$), 21.0 (*C*H$_3$C$_6$H$_4$), 14.0 (OCH$_2$*C*H$_3$); LRMS (EI) *m*/*z* 302 [M]$^+$; HRMS (EI) exact mass calcd for $C_{15}H_{17}F_3O_3$ [M]$^+$ requires *m*/*z* 302.112979, found *m*/*z* 302.112846. Retention times: t_R of major (*R*)-enantiomer (*R*)-enantiomer 49.8 min, t_R of minor (*S*)-enantiomer 50.2 min, 67% ee. Absolute stereochemistry assigned by analogy.

4.3.3. Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(3,5-dimethylphenyl)pent-4-enoate 6d

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = +43.0 (*c* 0.81, CH_2Cl_2); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 6.96 (s, 2H, C_6H_3), 6.91 (s, 1H, C_6H_3), 6.48 (d, *J* = 15.8 Hz, 1H, C_6H_3CH=), 6.13–6.03 (m, 1H, =$CH$$CH_2$), 4.40–4.33 (m, 2H, OCH_2CH_3), 3.96 (s, 1H, O*H*), 2.93–2.79 (m, 2H, =$CHCH_2$), 2.31 (s, 6H, $(CH_3)_2C_6H_4$), 1.34 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 169.3 (*C*=O), 138.1 (C_6H_3), 136.9 (C_6H_3), 135.9 (C_6H_3CH=), 129.5 (C_6H_3), 124.3 (C_6H_3), 123.5 (q, $J_{C\text{-}F}$ = 286.2 Hz, CF_3), 120.2 (=$CHCH_2$), 77.9 (q, $J_{C\text{-}F}$ = 29.1 Hz, CCF_3), 63.7 (OCH_2CH_3), 35.8 (=$CHCH_2$), 21.1 ($C_6H_3(CH_3)_2$), 14.0 (OCH_2CH_3); LRMS (EI) *m*/*z* 316 $[M]^+$; HRMS (EI) exact mass calcd for $C_{16}H_{19}O_3F_3$ $[M]^+$ requires *m*/*z* 316.1286, found *m*/*z* 316.1283; Retention times: t_R of major (*R*)-enantiomer 56.8 min, t_R of minor (*S*)-enantiomer 57.4 min; 94% ee. Absolute stereochemistry assigned by analogy.

4.3.4. Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(4-chlorophenyl)pent-4-enoate 6e

A sample was isolated as a crystalline solid after purification by column chromatography. $[\alpha]_D$ = +33.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.23–7.16 (m, 4H, C_6H_4), 6.43 (d, *J* = 15.9 Hz, 1H, C_6H_4CH=), 6.08–5.97 (m, 1H, =$CH$$CH_2$), 4.34–4.24 (m, 2H, OCH_2CH_3), 3.95 (s, 1H, O*H*), 2.86–2.73 (m, 2H, =$CHCH_2$), 1.25 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 169.2 (*C*=O), 135.4 (C_6H_4), 134.3 (C_6H_4CH=), 133.6 (C_6H_4), 128.8 (C_6H_4), 127.5 (C_6H_4), 123.4 (q, $J_{C\text{-}F}$ = 286.2 Hz, CF_3), 121.6 (=$CHCH_2$), 77.8 (q, $J_{C\text{-}F}$ = 29.2 Hz, CCF_3), 63.7 (OCH_2CH_3), 35.7 (=$CHCH_2$), 13.9 (OCH_2CH_3); LRMS (EI) *m*/*z* 322 $[M]^+$; HRMS (EI) exact mass calcd for $C_{14}H_{14}ClF_3O_3$ $[M]^+$ requires *m*/*z* 322.0583, found *m*/*z* 322.0581. Retention times: t_R of major (*R*)-enantiomer 59.6 min, t_R of minor (*S*)-enantiomer 60.2 min; 99% ee. Absolute stereochemistry assigned by analogy.

4.4. General procedure for the Friedel–Crafts reaction between heteroaromatics and ethyl trifluoropyruvate

A flame-dried Schlenk flask was charged with (*S*)-Me_2-CATPHOS (0.010 g, 0.013 mmol), [MCl_2(cycloocta-1,5-diene)] (0.013 mmol) and CH_2Cl_2 (2 mL) and was stirred at room temperature for 1 h. After this time, AgOTf (0.090 g, 0.025 mmol) was added and stirring was continued for a further 30 min before adding ethyl trifluoropyruvate (0.099 mL, 0.75 mmol) and 2-allyl furan (0.054 g, 0.5 mmol). The resulting mixture was stirred for a further 60 min at room temperature after which time the solution was flushed through a short plug of silica with dichloromethane, the solvent removed, and the resulting residue purified by column chromatography, eluting with hexane/CH_2Cl_2. The products were analysed by ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, and the enantiomeric excess determined by chiral GC.

4.4.1. Ethyl 2-(5-allylfuran-2-yl)-3,3,3-trifluoro-2-hydroxypropanoate 8a

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = −16.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 6.48–6.45 (d, *J* = 3.3 Hz, 1H, C_4H_2O), 6.00 (d, *J* = 3.3 Hz, 1H, C_4H_2O), 5.92–5.78 (m, 1H, =$CH$$CH_2$), 5.13–5.05 (m, 2H, =$CHCH_2$), 4.40 (q, *J* = 7.1 Hz, 2H, OCH_2), 4.30 (br s, 1H, O*H*), 3.50–3.40 (m, 2H, CH_2CH=), 1.32 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 167.0 (*C*=O), 152.6 (OCC=), 143.1 ($OCCH_2$), 134.0 (CH=CH_2), 120.0 (q, $J_{C\text{-}F}$ = 288.3 Hz, CF_3), 116.8 (CH_2=CH), 110.1 (C=CHC), 115.8 (C=CHC), 76.9 (q, $J_{C\text{-}F}$ = 29.2 Hz, CCF_3), 63.9 (OCH_2CH_3), 32.5 (=$CHCH_2$), 14.0 (OCH_2CH_3); LRMS (ESI) $[M]^+$ *m*/*z* 278; HRMS (ESI) exact mass calculated for $C_{12}H_{13}F_3O_4$ $[M]^+$ requires *m*/*z*: 278.0760, found *m*/*z*: 278.0747. Retention times: t_R of major (*R*)-enantiomer = 22.2 min; t_R of minor (*S*)-enantiomer = 22.8 min; 67% ee. Absolute stereochemistry assigned by analogy.

4.4.2. Ethyl 2-(5-allylthiophen-2-yl)-3,3,3-trifluoro-2-hydroxypropanoate 8b

A sample was isolated as light brown oil after purification by column chromatography. $[\alpha]_D$ = −16.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.14–7.10 (d, *J* = 3.6 Hz, 1H, C_4H_3S), 6.70 (d, *J* = 3.6 Hz, 1H, C_4H_3S), 5.96–5.81 (m, 1H, C_4H_3S), 5.11–4.99 (m, 2H, =CH), 4.49 (s, 1H, O*H*), 4.42 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.49 (d, *J* = 6.7 Hz, 2H, CH_2), 1.35 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 168.2 (*C*=O), 145.0 (C_4H_3S), 135.9 (C_4H_3S), 133.5 (*C*=CH_2), 127.6 (C_4H_3S), 125.0 (C_4H_3S), 121.1 (q, $J_{C\text{-}F}$ = 283.2 Hz, CF_3), 116.9 (C=CH_2), 77.0 (q, $J_{C\text{-}F}$ = 27.1 Hz, CCF_3), 65.1 (OCH_2), 34.2 (=CCH_2), 14.0 (OCH_2CH_3); LRMS $[M]^+$ *m*/*z* 294; HRMS (ESI): exact mass calculated for $C_{12}H_{13}F_3O_3S$ $[M]^+$, requires *m*/*z* 294.0534, found *m*/*z* 294.0547. Retention times: t_R of major (*R*)-enantiomer = 25.5 min; t_R of minor (*S*)-enantiomer = 25.1 min; 63% ee. Absolute stereochemistry assigned by analogy.

4.4.3. Ethyl 3,3,3-trifluoro-2-(furan-2-yl)-2-hydroxypropanoate 8c

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = −15.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.40 (s, 1H, C_4H_3O), 6.56 (s, 1H, C_4H_3O), 6.36 (s, 1H, C_4H_3O), 4.56 (br s, 1H, O*H*), 4.45–4.30 (m, 2H, OCH_2CH_3), 1.28 (t, *J* = 7.6 Hz, 3H, OCH_2CH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, δ): 167.0 (*C*=O), 152.6 (OCC=), 143.1 ($OCCH_3$), 120.0 (q, $J_{C\text{-}F}$ = 283.5 Hz, CF_3), 115.8 (C=CHC), 110.1 (C=CHC), 76.9 (q, $J_{C\text{-}F}$ = 27.4 Hz, CCF_3), 63.9 (OCH_2CH_3), 14.0 (OCH_2CH_3); LRMS (EI) *m*/*z* 236 $[M-H]^+$. Retention times: t_R of major (*R*)-enantiomer = 10.3 min; t_R of minor (*S*)-enantiomer = 10.9 min; 67% ee. Absolute stereochemistry assigned by analogy.

4.4.4. Ethyl 3,3,3-trifluoro-2-hydroxy-2-(thiophen-2-yl) propanoate 8d

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = −13.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.35–7.29 (d, *J* = 5.1 Hz, 2H, C_4H_3S), 6.99 (dd, *J* = 3.9 Hz, 1.2 Hz, 1H, C_4H_3S), 4.58 (br s, 1H, O*H*), 4.46–4.32 (m, 2H, OCH_2CH_3), 1.35 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C{^{1}H} NMR 75.5 MHz, $CDCl_3$, δ): 167 (*C*=O), 137.2 (C_4H_3S), 135.6 (C_4H_3S), 127.1 (C_4H_3S), 127.0 (C_4H_3S), 119.8 (q, $J_{C\text{-}F}$ = 282.9 Hz, CF_3), 76.8 (q, $J_{C\text{-}F}$ = 27.8 Hz, CCF_3), 64.2 (OCH_2), 12.5 (OCH_2CH_3); LRMS (EI) *m*/*z* 253 $[M-H]^+$. Retention times: t_R of major (*R*)-enantiomer = 16.5 min; t_R of minor (*S*)-enantiomer = 16.8 min; 79% ee. Absolute stereochemistry assigned by analogy.

4.4.5. Ethyl 3,3,3-trifluoro-2-hydroxy-2-(5-methylfuran-2-yl)propanoate 8e

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = −11.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 6.41 (d, *J* = 3.3 Hz, 1H, C_4H_2O), 5.92 (d, *J* = 3.3 Hz, 1H, C_4H_2O), 4.43–4.32 (m, 2H, OCH_2), 2.22 (s, 3H, CH_3), 1.32 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C{^{1}H} (NMR 75.5 MHz, $CDCl_3$, δ): 167.0 (*C*=O), 152.6 (OCC=), 143.1 ($OCCH_3$), 120.0 (q, $J_{C\text{-}F}$ = 283.0 Hz, CF_3), 115.8 (C=CHC), 110.1 (C=CHC), 76.9 (q, $J_{C\text{-}F}$ = 26.8 Hz, CCF_3), 63.9 (OCH_2), 14.0 (OCH_2CH_3), 13.7 (CH_3); LRMS (EI) *m*/*z* 251 $[M-H]^+$. Retention times: t_R of major (*R*)-enantiomer = 15.5 min; t_R of minor (*S*)-enantiomer = 15.9 min; 80% ee. Absolute stereochemistry assigned by analogy.

4.4.6. Ethyl 3,3,3-trifluoro-2-hydroxy-2-(5-methylthiophen-2-yl)propanoate 8f

A sample was isolated as colourless oil after purification by column chromatography. $[\alpha]_D$ = −6.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300.78 MHz, $CDCl_3$, δ): 7.08 (d, *J* = 3.7 Hz, 1H, C_4H_2S), 6.62 (d, *J* = 3.7 Hz, 1H, C_4H_2S), 4.55 (br s, 1H, O*H*) 4.39–4.25 (m, 2H, OCH_2), 2.36 (s, 3H, CH_3), 1.32 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C{^{1}H}

NMR (75.5 MHz, $CDCl_3$, δ): 167.1 (*C*=O), 140.8 (q, C_4H_2S), 132.2 (C_4H_2S), 126.4 (C_4H_2S), 124.5 (C_4H_2S), 120.0 (q, $J_{C\text{-}F}$ = 283.0 Hz, CF_3), 76.9 (q, $J_{C\text{-}F}$ = 26.8 Hz, CCF_3), 63.9 (OCH_2), 14.9 (OCH_2CH_3), 13.8 (CH_3); LRMS (EI) *m*/*z* 268 $[M-H]^+$. Retention times: t_R of major (*R*)-enantiomer = 43.1 min; t_R of minor (*S*)-enantiomer = 43.7 min; 67% ee. Absolute stereochemistry assigned by analogy.

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