SUPPORTING INFORMATION

Gold(I)-Catalyzed Enantioselective [2 + 2 + 2] Cycloadditions. An Expedient Entry to Enantioenriched Tetrahydropyran Scaffolds

Iván Varela,[†] Hélio Faustino,[†] Elena Díez,[∫] Javier Iglesias-Sigüenza,[∫] Francisca Grande-Carmona,[∫] Rosario Fernández,[∫] José M. Lassaletta,[§] José L. Mascareñas,*[†] Fernando López*[‡,†]

[†]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica. Universidad de Santiago de Compostela, 15782, Santiago de Compostela, Spain
[‡]Instituto de Química Orgánica General CSIC, Juan de la Cierva 3, 28006, Madrid, Spain
[§]Instituto Investigaciones Químicas (CSIC-USe), Avda. Américo Vespucio, 49, 41092 Sevilla, Spain
[∫]Departamento de Química Orgánica, C/ Prof. García González, 1, 41012 Sevilla, Spain

Corresponding Authors

fernando.lopez@csic.es, joseluis.mascarenas@usc.es.

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General Procedures

Dry CH_2Cl_2 was directly purchased from Aldrich. Chiral gold complexes **Au1**[1], (*S,S,S*)-**Au2**[1], (*S,R,R*)- and (*R,S,S*)-**Au2**[2], **Au9**[1], **Au10**[3], **Au11**[4], **Au12**[3] and **Au13**[5] are known compounds and were synthesized from the corresponding phosphoramidite ligands following reported procedures. **Au14**[6], **Au15**[7], **Au16**[8] and **Au17**[9] are known compounds and were prepared according well-established procedures. **Au5** is a known complex that was prepared from the corresponding azolium salt according to the previously reported method.[10] AgBArF was synthesized from NaBARF following a reported procedure.[11]

4-Methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1a**)[12] and 3-(Propa-1,2-dien-1-yl)oxazolidin-2-one (**1b**)[13] are known compounds and were synthesized following reported procedures. 3-methyl-1H-indene (**2e**)[14] was synthesized according to a reported procedure, from 2,3-dihydro-1H-inden-1-one and MeMgBr (65% yield). But-1-en-2-ylbenzene (**2b**)[15] and (3-methylbut-1-en-2-yl)benzene (**2c**)[16] were synthesized from their corresponding ketones following previously reported procedures.[17]

(*E*)-(Prop-1-en-2-yl-1-d)benzene (*E*-d-**2a**) was prepared following a reported procedure,[18] using CH_2Cl_2 as solvent instead of 1,2-dichloroethane.

Tetrahydropyran cycloadducts **4baa**, **4baa'**, **4bae**, **4bae'**, **4baf**, **4baf'**, **4bda** **4bea** and **4bfa** had been previously synthesized in racemic manner.[19] Their corresponding $[\alpha]_D$ values are included in the Characterization data section, together with the chiral HPLC analysis.

1,3-Dichloroisoquinoline,[20] 2-(phenylethynyl)benzaldehyde (**6**),[21] 2-(*tert*-butyl)-1-chloronaphthalene (**8a**),[22] 2-(2-(*tert*-butyl)naphthalen-1-yl)-4,4,5,5-tetramethyl-1,3-dioxolane (**9a**)[23] and 3-chloro-1-(2-*tert*-butylnaphthalen-1-yl)-isoquinoline (**10a**) were prepared according to literature procedures. 1,1'-Bis(diphenylphosphino)ferrocene (dppf), $Pd_2(dba)_3$, $Pd(PPh_3)_4$ and $NiCl_2(PMe_3)_2$ were purchased from commercial suppliers.

All other alkenes, aldehydes and silver salts used were bought from Aldrich, Alfa Aesar, TCI or Acros and used without further purification. Reactions were conducted in dry solvents under Argon atmosphere unless otherwise stated. The abbreviation "rt" refers to reactions carried out approximately at 23 ºC. Reaction mixtures were stirred using Teflon-coated magnetic stirring bars. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, and/or by treating the plates with *p*-anisaldehyde or cerium nitrate solutions, followed by heating. Flash chromatography was carried out on silica gel unless otherwise stated. Dryings were performed with anhydrous Na_2SO_4 or $MgSO_4$. Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator followed by residual solvent removal under high vacuum. NMR spectra were recorded in $CDCl_3$, at 300 MHz, 400 MHz or 500 MHz. Carbon types and structure assignments were determined from DEPT-NMR and two-dimensional experiments (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestreNova© NMR data processing software (www.mestrelab.com). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; dd, double doublet; td, triple doublet; m, multiplet; br, broad. Electrospray ionization (ESI) mass spectra were recorded at the CACTUS facility of the University of Santiago de Compostela. CI, EI, LSIMS and high–resolution mass spectra (AUTOSPEC-Q mass spectrometer) were recorded at the CITIUS facility of the Univesity of Seville. The reactions were monitored by TLC or GC-MS using the Agilent Technologies 6890N, Network GC System, equipped with the Agilent 190915-433 column and the Agilent 5973 Inert Mass Selective Detector in Electron Impact or Chemical Ionization Mode (with Methane). Enantioselectivities were determined in an Agilent HPLC 1100 Series with Chiralpak IA, IB, IA-3, IE-3, IF-3 and Chiralcel OZ-H analytical columns. X-Ray diffraction experiments of **4baa** and **4baa'** were carried out at the University of Pais Vasco (UPV/EHU), in a an Agilent

Technologies Super-Nova diffractometer, which was equipped with monochromated Cu ka radiation (l = 1.54184 Å) and Atlas CCD detector. Measurement was carried out at 150.00(10) K with the help of an Oxford Cryostream 700 PLUS temperature device. Analysis of the absolute structure using likelihood methods (Hooft, Straver & Spek, 2008) was performed using PLATON (Spek, 2010). The results indicated that the absolute structures had been correctly assigned. The method calculated that the probability that the structures are inverted are smaller than 10^{-35}. The absolute structure parameters *y* (Hooft, Straver & Spek, 2008) were calculated using PLATON (Spek, 2010). The resulting values [*y*=0.00(8), and y= 0.07(6)], together with Flack parameter values, indicate that the absolute structures have been determined correctly.

Additional information related to footnote 26

Boat-like transition states such as **TS1'** - **TS4'** **(**Figure S1**)**, although less likely, could also be operative in some cases.

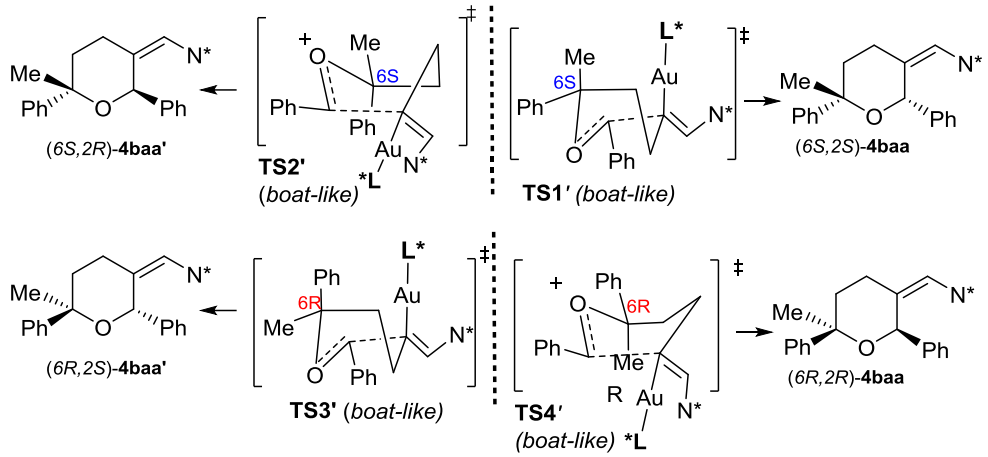


Figure S1. Additional information related to footnote 26

Optimization of the catalyst and reaction conditions

Table S1. Screening of different chiral gold catalysts in the model [2+2+2] cycloaddition reaction.[a]

1b **2a** **3a** **4baa** (2,6-*cis*) **4baa'** (2,6-*trans*)

Entry	[**Au**] (X%)	AgX	Solv.	T (ºC)	t (h)	**4baa** : **4baa'**	Yield[b]	ee (**4baa**)	ee (**4baa'**)
1	(*R,S,S*)-**Au1** (5)	$AgNTf_2$	CH_2Cl_2	-78	3	2 : 1	85%	9%	18%
2	(*R,R,R*)-**Au1** (5)	$AgNTf_2$	CH_2Cl_2	-78	1	2 : 1	83%	2%	20%
3	(*R,S,S*)-**Au2** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.5	2 : 1	97%	70%	81%
4[c]	(*R,S,S*)-**Au2** (5)	$AgNTf_2$	TFT[d]	-25	0.2	2 : 1	77%	56%	80%
5[c]	(*R,S,S*)-**Au2** (5)	$AgNTf_2$	Toluene	-78	1	6 : 1	59%	22%	31%
6[c]	(*R,S,S*)-**Au2** (5)	$AgNTf_2$	Et_2O	-78	0.5	4 : 1	72%	30%	36%
7	(*R,S,S*)-**Au2** (5)	$AgNTf_2$	$CHCl_3$	-60	0.2	4 : 1	90%	41%	51%
8	(*R,S,S*)-**Au2** (5)	$AgNTf_2$	CH_2Cl_2	-94	0.5	2 : 1	93%	74%	88%
9	(*R,S,S*)-**Au2** (5)	$AgSbF_6$	CH_2Cl_2	-78	0.1	2 : 1	97%	68%	81%
10	(*R,S,S*)-**Au2** (5)	$AgBF_4$	CH_2Cl_2	-94	0.5	4 : 1	91%	74%	90%
11	(*R,R,R*)-**Au2** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.2	2 : 1	95%	68%	54%
12	(*R,S,S*)-**Au3** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.2	1 : 1	91%	10%	66%
13	(*R,S,S*)-**Au4** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.1	3 : 1	97%	50%	26%
14[e]	(*R*)-**Au8** (5)	$AgNTf_2$	CH_2Cl_2	-78	3	2 : 1	77%	54%	40%
15	(*R,R,R*)-**Au9** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.1	2 : 1	98%	50%	38%
16	(*S,R,R*)-**Au10** (5)	$AgNTf_2$	CH_2Cl_2	-78	3	2 : 1	79%	15%	28%
17	(*R,R,R*)-**Au10** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.1	2 : 1	95%	29%	23%
18	(*S,R,R*)-**Au11** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.2	3 : 1	97%	46%	18%
19	(*S,S,S*)-**Au11** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.1	3 : 1	97%	52%	32%
20	(*R,R,R*)-**Au12** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.1	6 : 1	92%	40%	30%
21	(*R,R,R*)-**Au13** (5)	$AgNTf_2$	CH_2Cl_2	-78	0.1	6 : 1	98%	46%	7%
22	(*S*)-**Au14** (5)	$AgNTf_2$	CH_2Cl_2	-78	1.5	3 : 1	70%	4%	14%
23	(*R*)-**Au15** (5)	$AgNTf_2$	CH_2Cl_2	-78 -> -15	5	2 : 1	67%	29%	14%
24	(*S*)-**Au16** (5)	$AgNTf_2$	CH_2Cl_2	-78	2	3 : 1	74%	13%	49%
25	(*R*)-**Au17** (5)	$AgNTf_2$	CH_2Cl_2	-78	2	9 : 1	92%	58%	6%
26	(*R*)-**Au5** (5)	$AgNTf_2$	CH_2Cl_2	-70 -> -30	4	5 : 1	79%	78%	19%
27[f]	(*R*)-**Au5** (5)	$AgSbF_6$	CH_2Cl_2	-78 -> -70	26	8 : 1	30%	82%	18%
28	(*R*)-**Au6** (5)	$AgNTf_2$	CH_2Cl_2	-70 -> -30	20	5 : 1	37%	77%	4%
29	(*R*)-**Au7** (5)	$AgNTf_2$	CH_2Cl_2	-70 -> -30	8	6 : 1	95%	77%	21%
30	(*R*)-**Au5** (10)	$AgNTf_2$	CH_2Cl_2	-70	24	9 : 1	80%	87%	22%
31	(*R*)-**Au5** (10)	AgBArF	CH_2Cl_2	-70	24	7 : 1	65%	82%	40%

32	**Au18** (5)	**AgPh-1**	CH_2Cl_2	-78 -> -45	16	2 : 1	80%	0%	0%
33	(*S,R,R*)-**Au2** (5)	**AgPh-1**	CH_2Cl_2	-78 -> -30	16	2 : 1	60%	52%	58%
34[g]	(*S*)-**Au5** (10)	**AgPh-1**	CH_2Cl_2	-70 -> -30	24	5 : 1	50%	75%	11%
35[h]	(*R*)-**Au5** (10)	**AgPh-1**	CH_2Cl_2	-70 -> -30	19	5 : 1	39%	59%	2%

[a] **1b** (1 equiv) added to a solution of **2a** (2 equiv), **3a** (10 equiv), [**Au**] (X %), AgX (X %) and 4Å MS, in CH_2Cl_2 at the indicated temperature. Conversions (>99%), and *dr* determined by ^{1}H-NMR of the crude mixture with internal standard. [b] Isolated combined yield of **4baa** + **4baa'** (both isomers can be separated by chromatography). [c] The solution needed to be sonicated for 10-15 seconds at rt and quickly cooled again, repeatedly until complete solubilization of the allenamide. [d] α,α,α-Trifluorotoluene. [e] 80% conversion. [f] 65% conversion. [g] 50% conversion. [h] 39% conversion.

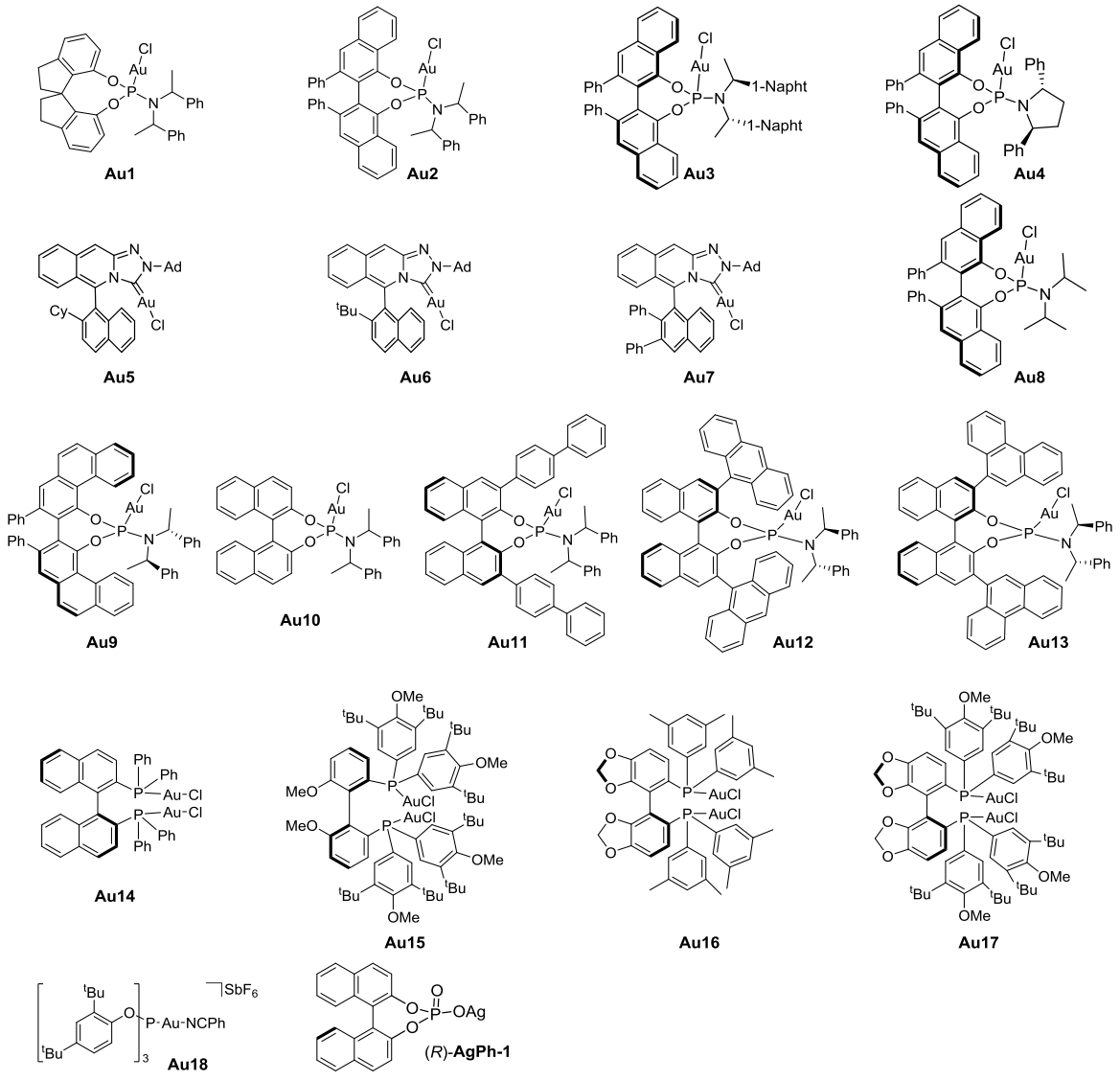
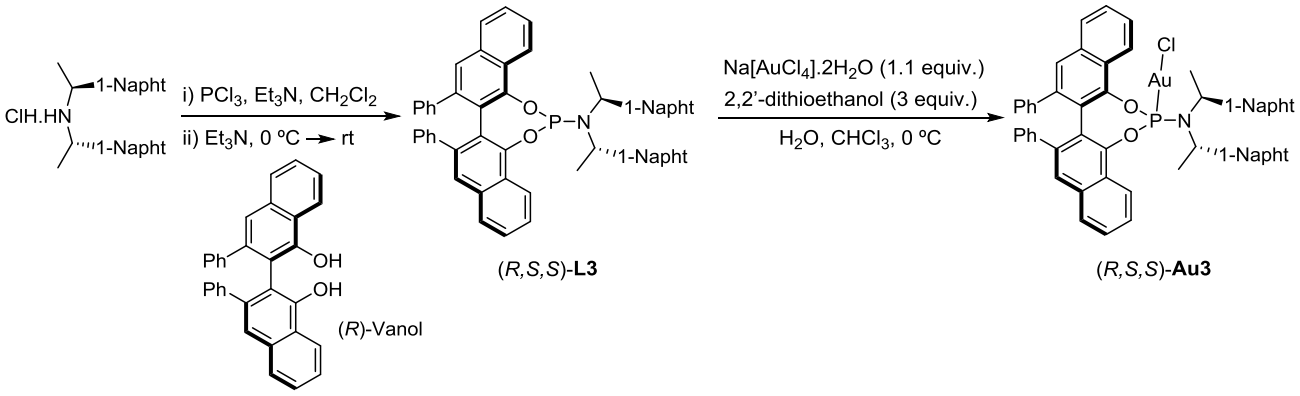


Figure S2. Catalysts employed in the screening of Table S1

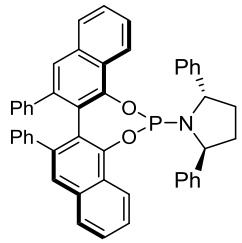
Procedures for the synthesis and characterization data of new gold catalysts

Chiral phosphoramidite ligands and their corresponding gold catalysts were prepared according to previously reported literature procedures.[1,3] **Au1**[1], (*S,S,S*)-**Au2**[1], (*R,S,S*)-**Au2**[2], **Au9**[1], **Au10**[3], **Au11**[4], **Au12**[3] and **Au13**[5] had been previously reported. The chiral NHC-gold complex **Au5**, as well as its axially chiral triazoloisoquinolin-3-ylidene precursor had also been previously reported.[10] Their ^{1}H and ^{31}P-NMR data was in complete agreement with the reported values.

General Procedures for the synthesis of phosphoramidite ligands and their corresponding gold(I) complexes (exemplified for the synthesis of (*R,S,S*)-**Au3** and its phosphoramidite precursor (*R,S,S*)-**L3**.

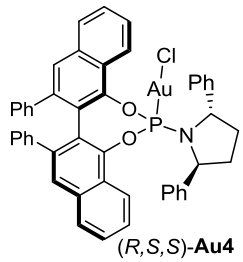


PCl_3 (11 µL, 0.125 mmol), CH_2Cl_2 (0.245 mL) and Et_3N (0.079 mL, 0.57 mmol) were added to a Schlenk tube containing 3A MS, and the mixture was cooled at 0 ºC. Then, a solution of Bis[(*S*)-(-)-(1-naphtyl)ethyl]amine hydrochloride (0.045 g, 0.125 mmol) and Et_3N (0.024 mL, 0.171 mmol) in CH_2Cl_2 was added over 30 min and the resulting mixture was warmed at rt and stirred for 90 min. Then, the mixture was cooled again down to 0 ºC and a solution of (*R*)-Vanol (0.05 g, 0.114 mmol) and Et_3N (0.04 mL, 0.285 mmol) was added over 30 min. The reaction was stirred at rt overnight, concentrated and purified by flash chromatography (Hexane:DCM:EtOAc 18:2:0 – 15:3:2) to give (*R,S,S*)-**L3** (40 mg, 0.051 mmol, 44% yield) as a white powder. (*R,S,S*)-**L3** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.75 – 7.69 (m, 2H), 7.66 – 7.51 (m, 5H), 7.46 (d, *J* = 11.3 Hz, 2H), 7.40 – 7.31 (m, 7H), 7.22 – 7.05 (m, 4H), 6.94 (q, *J* = 8.0 Hz, 4H), 6.83 – 6.66 (m, 2H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.49 (d, 2H), 5.98 – 5.40 (m, 2H), 2.00 – 1.27 (m, 6H). **^{31}P NMR** (202 MHz, D_2O) δ 145.8. The transformation of (*R,S,S*)-**L3** into (*R,S,S*)-**Au3** was carried out using a standard procedure previously reported for related phosphoramidite gold complexes,[1-3,6] (*R,S,S*)-**Au3** (85% yield) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.78 (m, 5H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.61 – 7.51 (m, 6H), 7.48 (s, 1H), 7.34 (ddt, *J* = 10.7, 6.9, 3.4 Hz, 5H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.13 (dt, *J* = 12.2, 7.4 Hz, 2H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 2H), 6.69 (t, *J* = 7.5 Hz, 2H), 6.61 (d, *J* = 7.2 Hz, 2H), 6.42 (d, *J* = 7.2 Hz, 2H), 5.93 – 5.83 (m, 2H), 1.88 (s, 6H). **^{31}P NMR** (202 MHz, D_2O) δ 127.78. **MS** (m/z, ESI): 988.2618 (M^+ –Cl), 481.0896, 314.0126.



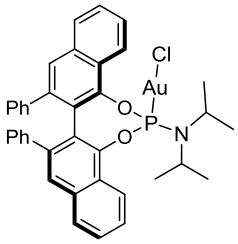
(*R,S,S*)-**L4**

White powder. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.41 (m, 2H), 7.39 – 7.17 (m, 13H), 7.06 – 6.99 (m, 2H), 6.84 (q, *J* = 7.6, 7.1 Hz, 4H), 6.36 (d, *J* = 8.3 Hz, 1H), 6.26 (d, *J* = 6.8 Hz, 1H), 4.70 (s, 2H), 2.25 – 2.14 (m, 2H), 1.87 – 1.77 (m, 2H). **^{31}P NMR** (202 MHz, D_2O) δ 151.39. **MS** (m/z, ESI): 710.2705, 708.2648, 485.1297.



(*R,S,S*)-**Au4**

White powder. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.29 – 7.23 (m, 5H), 7.20 – 7.14 (m, 6H), 7.01 – 6.96 (m, 2H), 6.81 – 6.76 (m, 4H), 6.22 (d, *J* = 7.1 Hz, 2H), 6.09 (d, *J* = 7.3 Hz, 2H), 4.87 (m, 2H), 2.45 – 2.34 (m, 2H), 1.81 – 1.71 (m, 2H). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 130.32. **MS** (m/z, ESI): 944.3 $(M+Na)^+$, 927.2 (M(NCMe) –Cl).

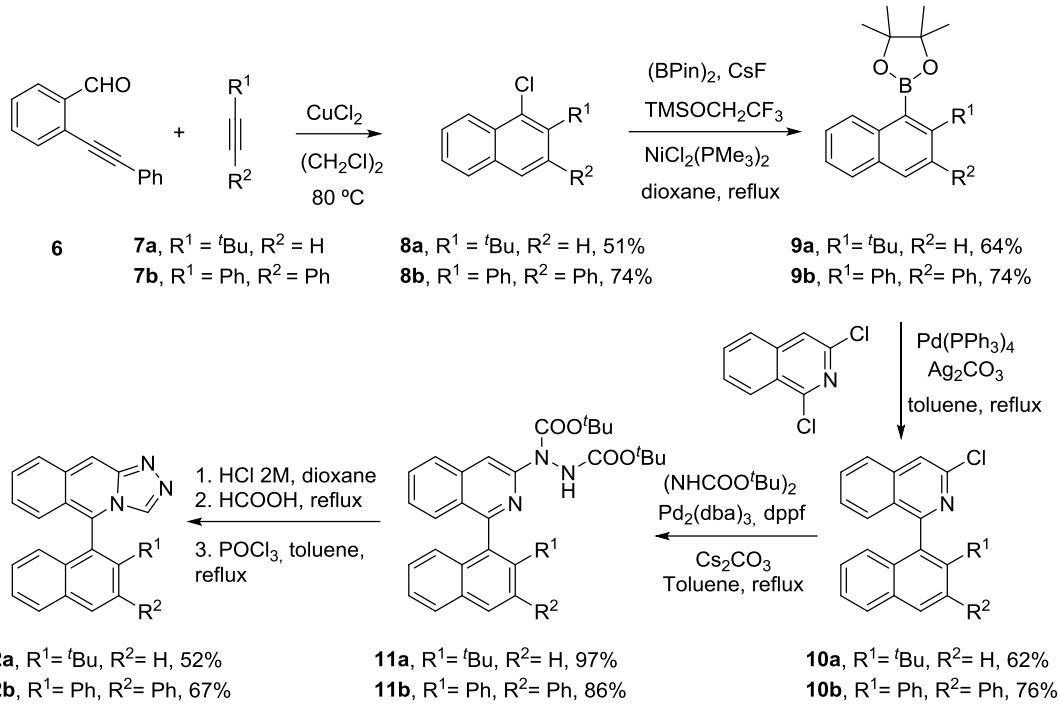


(*R*)-**Au8**

White powder. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (t, *J* = 8.0 Hz, 2H), 7.77 (t, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.50 (m, 3H), 7.44 (s, 1H), 7.39 (s, 1H), 7.08 – 6.98 (m, 2H), 6.88 (t, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 7.7 Hz, 2H), 6.45 (d, *J* = 7.1 Hz, 2H), 6.32 (d, *J* = 7.1 Hz, 2H), 3.62 – 3.53 (m, 2H), 1.25 (d, *J* = 6.7 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 130.89. **MS** (m/z, ESI): 823.2 $(M+Na)^+$, 805.3 (M(NCMe) –Cl).

Procedure for the synthesis of triazoloisoquinolin-3-ylidene-gold-chloride complexes Au6 and Au7.

Flash chromatography was carried out on silica-gel (40-63 μm or 70-200 μm). Melting points were recorded in a metal block and are uncorrected. CI, EI and LSIMS mass spectra and high–resolution mass spectra were recorded in an AUTOSPEC-Q mass spectrometer (three sectors high-resolution mass spectrometer with added quadrupole). Racemic mixtures were resolved by HPLC on chiral stationary phases (semipreparative Chiralpak IA column) using CH_2Cl_2 or CH_2Cl_2/hexane mixtures as eluents.



6

7a, R^1 = ^{t}Bu, R^2 = H
7b, R^1 = Ph, R^2 = Ph

8a, R^1 = ^{t}Bu, R^2 = H, 51%
8b, R^1 = Ph, R^2 = Ph, 74%

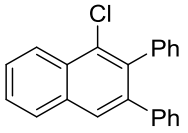
9a, R^1= ^{t}Bu, R^2= H, 64%
9b, R^1= Ph, R^2= Ph, 74%

10a, R^1= ^{t}Bu, R^2= H, 62%
10b, R^1= Ph, R^2= Ph, 76%

11a, R^1= ^{t}Bu, R^2= H, 97%
11b, R^1= Ph, R^2= Ph, 86%

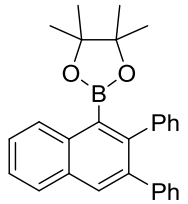
12a, R^1= ^{t}Bu, R^2= H, 52%
12b, R^1= Ph, R^2= Ph, 67%

1-Chloro-2,3-diphenylnaphthalene (8b)



To a suspension of $CuCl_2$ (8.23 g, 60 mmol) in dry 1,2-dichloroetane (72 mL) were successively added 2-(phenylethynyl)benzaldehyde **6** (6.19 g, 30 mmol) and diphenylacetylene **7b** (10.7 g, 60 mmol) at rt under an Ar atmosphere. The mixture was stirred at reflux for 24 h, cooled to rt, and filtered through a celite pad and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (pentane) to yield **8b** (6.97 g, 74%) as a white solid. **M.p.** 108–111 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.44 – 8.37 (m, 1H), 7.93 – 7.87 (m, 2H), 7.84 (s, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.2, 6.9, 1.6 Hz, 1H), 7.31 – 7.21 (m, 4H), 7.21 – 7.10 (m, 5H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.0, 140.6, 138.9, 137.8, 133.4, 131.1, 130.8, 130.4, 130.0, 129.8, 129.4, 128.1, 127.9, 127.6, 127.3, 127.0, 126.9, 126.6, 126.3, 125.1. **LRMS** (*m/z*, CI): 317 (18, M^++1, ^{37}Cl), 316 (38, M+, ^{37}Cl), 315 (56, M^++1, ^{35}Cl), 314 (100, M^+, ^{35}Cl), 280 (66), 279 (51), 278 (61). **HRMS** Calculated for $C_{22}H_{15}Cl$: 314.0862, found 314.0851.

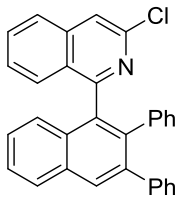
2-(2,3-Diphenylnaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3-dioxolane (9b)



To a suspension of $NiCl_2(PMe_3)_2$ (171 mg, 5 mol%, 0.58 mmol), bis(pinacolato)diboron (4.47 g, 17.6 mmol) and CsF (3.55 g, 23.4 mmol) in dry toluene (94 mL) under an Ar atmosphere, were added *via* syringe a solution of 1-choro-2,3-diphenylnaphthalene **8b** (3.67 g, 11.7 mmol) in dry toluene (94 mL) and $TMSOCH_2CF_3$ (4.5 mL, 24.6 mmol). The resulting mixture was heated under reflux overnight. EtOAc was added and the mixture was filtered through a celite pad. The organic layer was washed with saturated NH_4Cl (2 x 20 mL), dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (1:3→1:1 CH_2Cl_2–cyclohexane) to yield **9b** (3.52 g, 74%) as a white solid. **M.p.** 174–176 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 1H), 7.90 – 7.84 (m, 2H), 7.54 – 7.47 (m, 2H), 7.25 – 7.11 (m, 10H), 1.18 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.0, 142.2, 141.7, 139.2, 135.1, 132.4, 130.9, 130.2, 130.0, 128.3, 127.6, 127.5, 127.3,

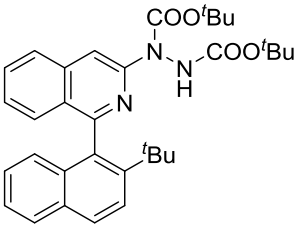
126.6, 126.3, 126.2, 125.8, 84.0, 24.9. **LRMS** (*m/z*, EI): 407 (32, M^++1), 406 (100, M^+), 307 (30), 290 (48). **HRMS** Calculated for $C_{28}H_{27}BO_2$: 406.2104, found 406.2104.

3-Chloro-1-(2,3-diphenylnaphthalen-1-yl)isoquinoline (10b)



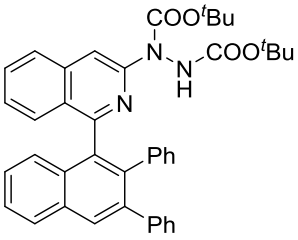
A round-bottom flask was charged with 1,3-dichloroisoquinoline (2 g, 10 mmol), boronic ester **9b** (4.87 g, 12 mmol), $Pd(PPh_3)_4$ (2.31 g, 20 mmol%), and Ag_2CO_3 (3.58 g, 13 mmol) under an argon atmosphere, and the mixture was dissolved in dry toluene (80 mL). The mixture was heated under reflux overnight. EtOAc was added, and the mixture was filtered through a celite pad. The organic layer was washed with brine (2 × 10 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (1:3 CH_2Cl_2−cyclohexane) to yield **10b** (3.36 g, 76%) as a white solid. **M.p.** 164–166 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.99 – 7.96 (m, 1H), 7.66 – 7.63 (m, 1H), 7.62 (d, *J* = 1.0 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.47 – 7.44 (m, 1H), 7.33 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.24 – 7.14 (m, 7H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.80 – 6.74 (m, 1H), 6.68 – 6.60 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.0, 144.3, 141.4, 139.7, 139.0, 138.9, 137.9, 134.6, 132.8, 131.8, 131.5, 130.8, 130.2, 130.0, 128.1, 127.6, 127.3, 127.0, 126.8, 126.7, 126.7, 126.4, 126.3, 126.0, 125.9, 125.8, 118.9. **LRMS** (*m/z*, EI): 444 (23, M^++1, ^{37}Cl), 443 (46, M^+, ^{37}Cl), 442 (77, M^++1, ^{35}Cl), 441 (100, M^+, ^{35}Cl), 407 (16, M^+– Cl), 406 (20). **HRMS** Calculated for $C_{31}H_{20}NCl$: 441.1284, found 441.1278.

Di-*tert*-butyl-1-(1-(2-*tert*-butylnaphthalen-1-yl)isoquinolin-3-yl)hydrazine-1,2-dicarboxylate (11a)



3-Chloro-1-(2-*tert*-butylnaphthalen-1-yl)-isoquinoline **10a** (973 mg, 2.82 mmol), di(*tert*-butyl)-1,2-hydrazodicarboxylate (2.02 g, 8.46 mmol), dppf (320 mg, 20 mol%), $Pd_2(dba)_3$ (387 mg, 15 mol%) and Cs_2CO_3 (2.32 g, 7.05 mmol) were solved in dry toluene (14 mL) under an argon atmosphere. The mixture was heated under reflux overnight. The reaction mixture was filtered through a celite pad, washed with brine (2 × 10 mL), dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (100:1:2 CH_2Cl_2–EtOAc–Et_2O) to yield **11a** (1.48 g, 97%) as a light brown foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (br s, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.62 – 7.57 (m, 1H), 7.38 – 7.26 (m, 4H), 7.14 – 7.08 (m, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 1.54 (s, 9H), 1.40 (s, 9H), 1.08 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.0, 161.3, 154.7, 153.9, 147.4, 146.0, 137.3, 133.6, 132.5, 131.7, 130.3, 128.8, 128.7, 128.5, 127.6, 127.4, 126.9, 126.8, 126.3, 126.1, 125.2, 82.3, 81.0, 37.3, 32.5, 28.2, 28.2. **LRMS** (*m/z*, EI): 541 (1, M^+), 441 (9), 385 (12), 367 (17), 342 (24), 341 (100), 340 (18). **HRMS** Calculated for $C_{33}H_{39}N_3O_4$: 541.2941, found 541.2927.

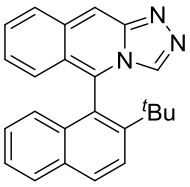
Di-*tert*-butyl-1-(1-(2,3-diphenylnaphthalen-1-yl)isoquinolin-3-yl)hydrazine-1,2-dicarboxylate (11b)



3-Chloro-1-(2,3-diphenylnaphthalen-1-yl)isoquinoline **10b** (1.24 g, 2.82 mmol), di(*tert*-butyl)-1,2-hydrazodicarboxylate (2.02 g, 8.46 mmol), dppf (320 mg, 20 mol%), $Pd_2(dba)_3$ (387 mg, 15 mol%) and Cs_2CO_3 (2.32 g, 7.05 mmol) were solved in dry toluene (14 mL) under an argon atmosphere. The mixture was heated under reflux overnight. The reaction mixture was filtered through a celite pad, washed with brine (2 × 10 mL), dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (100:1:2 CH_2Cl_2–EtOAc–Et_2O) to yield **11b** (1.55

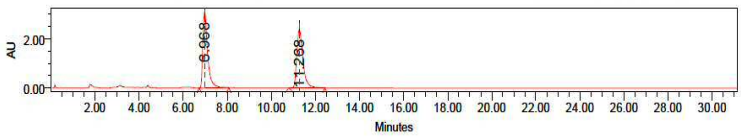
g, 86%) as a light yellow solid. **M.p.** 102–104 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.41 – 7.33 (m, 1H), 7.32 – 7.28 (m, 1H), 7.25 – 7.14 (m, 8H), 7.13 – 7.02 (m, 2H), 6.84 (br s, 1H), 6.76 – 6.71 (m, 1H), 6.68 – 6.64 (m, 2H), 1.54 (s, 9H), 1.43 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.0, 159.0, 154.9, 153.8, 147.1, 141.5, 139.7, 139.0, 138.9, 137.5, 135.5, 132.8, 131.9, 131.5, 130.9, 130.3, 130.1, 129.9, 128.0, 127.6, 127.2, 127.1, 126.6, 126.4, 126.4, 126.3, 125.9, 114.7, 82.2, 81.1, 28.2, 26.1. **LRMS** (*m/z*, CI): 638 (4, M^++1), 637 (1, M^+), 538 (18), 480 (26), 438 (62), 437 (100), 422 (32), 408 (10). **HRMS** Calculated for $C_{41}H_{40}N_3O_4$: 638.3019, found 638.3022.

5-(2-*tert*-Butylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinoline (12a)



To a solution of compound **11a** (1.08 g, 2 mmol) in 1,4-dioxane (7 mL) was added 4M HCl in 1,4-dioxane (7 mL) under an argon atmosphere and the mixture was stirred at rt overnight. The mixture was concentrated and the residue was solved in HCOOH (10 mL) and refluxed under argon for 24h. The mixture was concentrated and the resulting residue was solved in dry toluene (10 mL). $POCl_3$ (559 µL, 6 mmol) was added and the mixture was heated under reflux for 24h. The solvent was removed in vacuo and the residue was solved in EtOAc, washed with 2M NaOH (2 × 10 mL), and brine (2 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (2:1 EtOAc–cyclohexane) to yield **12a** (365 mg, 52%) as a yellow solid. **M.p.** 248–250 °C (dec). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.29 (d, *J* = 0.9 Hz, 1H), 8.10 (dd, *J* = 9.0, 0.9 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.83 – 7.77 (m, 1H), 7.45 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.15 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.47 (dd, *J* = 8.4, 1.1 Hz, 1H,), 1.01 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.7, 148.1, 133.4, 133.1, 132.8, 132.3, 132.1, 130.9, 128.2, 128.1, 127.9, 127.8, 127.1, 126.5, 126.4, 125.3, 124.2, 123.4, 123.2, 110.6, 37.7, 31.7. **LRMS** (*m/z*, EI): 352 (87, M^++1), 351 (100, M^+), 308 (15), 267 (19), 265 (17). **HRMS** Calculated for $C_{24}H_{21}N_3$: 351.1735, found 351.1735.

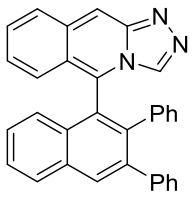
The racemic mixture was resolved by semipreparative HPLC on a Chiralpak IA column. Analytical Chiralpak IA, 100% CH_2Cl_2, 1 mL/min, 30 °C, λ = 245.0 nm: first enantiomer, compound **(*R*)-12a**, t_R = 6.9 min, $[\alpha]_D^{24}$ = –135.4 (*c* 0.05, $CHCl_3$); second enantiomer, compound **(*S*)-12a**, t_R = 11.3 min, $[\alpha]_D^{23}$= +126.6 (*c* 0.50, $CHCl_3$).



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.0 nm	6.968	46142711	50.10	3098568
2	PDA 245.0 nm	11.268	45967445	49.90	2389616

Figure S3. HPLC trace report of **11a**

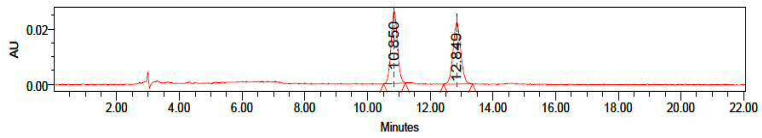
5-(2,3-Diphenylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinoline (12b)



To a solution of compound **11b** (1.27 g, 2 mmol) in 1,4-dioxane (7 mL) was added 4M HCl in 1,4-dioxane (7 mL) under an argon atmosphere and the mixture was stirred at rt overnight. The mixture was concentrated and the residue was solved in HCOOH (10 mL) and refluxed under argon for 24h. The mixture was concentrated and the resulting residue was solved in dry toluene (10 mL). $POCl_3$ (559 µL, 6 mmol) was added and the mixture was heated under reflux for 24h. The solvent was removed in vacuo and the residue was solved in EtOAc, washed with 2M NaOH (2 × 10 mL), and brine (2 × 10 mL). The combined organic layers

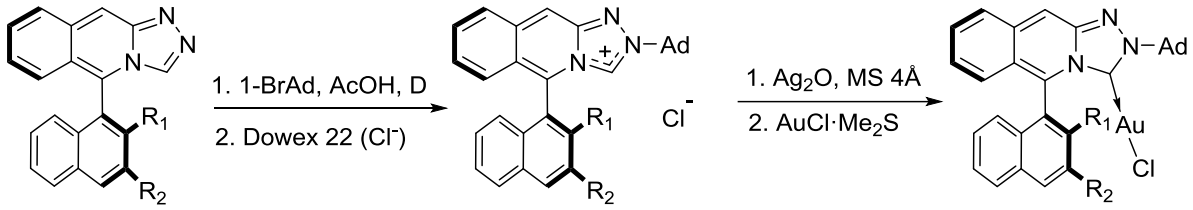
were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (2:1 EtOAc–cyclohexane) to yield **12b** (599 mg, 67%) as a yellow solid. **M.p.** 140–142 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.26 (s, 1H), 8.20 (s, 1H), 8.11 – 8.06 (m, 1H), 7.69 – 7.63 (m, 1H), 7.60 (ddd, *J* = 8.2, 6.8, 1.1 Hz, 1H), 7.35 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.25 – 7.15 (m, 8H), 7.08 – 7.06 (m, 1H), 6.93 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.71 – 6.65 (m, 2H), 6.64 – 6.59 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.9, 141.3, 140.4, 140.4, 137.6, 133.3, 133.0, 132.5, 132.3, 131.1, 130.7, 129.9, 129.2, 128.8, 128.4, 128.2, 127.9, 127.8, 127.8, 127.5, 127.4, 127.2, 127.2, 127.1, 126.9, 126.4, 125.1, 124.6, 122.5, 110.5. **LRMS** (*m/z*, EI): 448 (33, M^++1), 447 (100, M^+), 378 (30). **HRMS** Calculated for $C_{32}H_{21}N_3$: 447.1735, found 447.1730.

The racemic mixture was resolved by semipreparative HPLC on a Chiralpak IA column. Analytical Chiralpak IA, CH_2Cl_2–hexane–DEA 90:10:0.1, 1 mL/min, 30 °C, λ = 394.7 nm: first enantiomer, compound (+)-**12b**, t_R = 10.9 min, $[\alpha]_D^{24}$ = +284.3 (*c* 0.53, $CHCl_3$); second enantiomer, compound (–)-**12b**, t_R = 12.9 min, $[\alpha]_D^{23}$ = –266.1 (*c* 0.51, $CHCl_3$).



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 394.7 nm	10.850	372481	49.36	26155
2	PDA 394.7 nm	12.849	382081	50.64	22219

Figure S4. HPLC trace report of **11b**

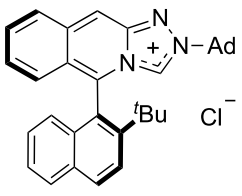


(*R*)-**12a**: R^1 = ^{t}Bu, R^2 = H
(*R*)-**12b**: R^1 = Ph, R^2 = Ph

(*R*)-**13a**: R^1 = ^{t}Bu, R^2 = H, 98%
(*R*)-**13b**: R^1 = Ph, R^2 = Ph, 98%

(*R*)-**Au-6**: R^1 = ^{t}Bu, R^2 = H, 87%
(*R*)-**Au-7**: R^1 = Ph, R^2 = Ph, 81%

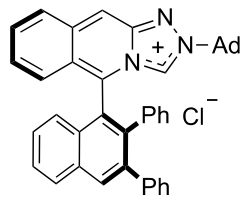
2-(Adamantan-1-yl)-5-(2-*tert*-butylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinolin-2-ium chloride (13a)



(*R*)-**12a** (211 mg, 0.6 mmol) and 1-bromoadamantane (761 mg, 3 mmol) were solved in acetic acid (6 mL) under an argon atmosphere and the mixture was stirred at reflux for 2 days. The mixture was concentrated and the residue was purified by flash chromatography (CH_2Cl_2 → CH_2Cl_2-MeOH 4%) to yield (*R*)-**13a(Br$^-$)** (336 mg, 98%) as a yellow solid. This salt was eluted through a Dowex 22 anion exchange resin column using methanol as eluant. The solvent was removed in vacuo and the residue was solved in CH_2Cl_2, dried ($MgSO_4$) and concentrated to yield (*R*)-**13a(Cl$^-$)** (313 mg, quantitative) as a yellow solid. **M.p.** 190 °C (dec.). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.60 (s, 1H), 8.20 (d, *J* = 9.1 Hz, 1H), 8.02 (t, *J* = 9.2 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.58 – 7.50 (m, 1H), 7.44 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.20 – 7.13 (m, 2H), 6.38 – 6.34 (m, 1H), 2.55 – 2.45 (m, 6H), 2.30 (br s, 3H), 1.89 – 1.67 (m, 6H), 1.08 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.4, 144.9, 137.8, 136.0, 132.4, 131.9, 131.3, 131.2, 128.9,

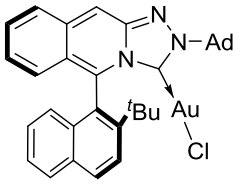
128.8, 128.0, 127.6, 127.6, 126.4, 125.9, 125.7, 123.1, 120.5, 110.9, 67.5, 42.2, 37.7, 35.3, 31.7, 29.7. **LRMS** (*m/z,* CI): 486 (82, M^+), 485 (78, M^+–1), 428 (60), 135 (100, Ad^+). **HRMS** Calculated for $C_{34}H_{36}N_3$: 486.2906, found 486.2894. $[\alpha]_D^{24}$ = –108.5 (*c* 0.5, $CHCl_3$).

2-(Adamantan-1-yl)-5-(2,3-diphenylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinolin-2-ium chloride (13b)



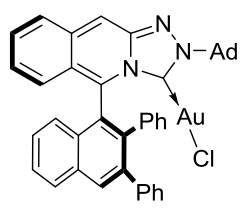
(+)-**12b** (268 mg, 0.6 mmol) and 1-bromoadamantane (761 mg, 3 mmol) were solved in acetic acid (6 mL) under an argon atmosphere and the mixture was stirred at reflux for 2 days. The mixture was concentrated and the residue was purified by flash chromatography (CH_2Cl_2 → CH_2Cl_2-MeOH 4%) to yield (+)-**13b(Br$^-$)** (388 mg, 98%) as a yellow solid. This salt was eluted through a Dowex 22 anion exchange resin column using methanol as eluant. The solvent was removed in vacuo and the residue was solved in CH_2Cl_2, dried with $MgSO_4$ and concentrated to yield (+)-**13b(Cl$^-$)** (370 mg, quantitative) as a yellow solid. **M.p.** 214–216 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.54 (s, 1H), 8.33 (s, 1H), 8.21 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.58 (t, *J* = 7.5 Hz), 7.55 – 7.49 (m, 2H), 7.47 – 7.45 (m, 1H), 7.43 – 7.39 (m, 3H), 7.39 – 7.32 (m, 1H), 7.23 – 7.12 (m, 4H), 6.79 – 6.72 (m, 2H), 6.60 – 6.59 (m, 1H), 6.52 – 6.48 (m, 1H), 2.42 – 2.35 (m, 6H), 2.28 (br s, 3H), 1.84 – 1.64 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.5, 139.9, 139.7, 139.5, 137.0, 134.6, 134.4, 133.0, 132.4, 131.3, 129.97, 129.9, 129.6, 129.5, 128.2, 127.9, 127.2, 127.1, 126.7, 126.6, 126.5, 126.2, 126.1, 125.8, 125.6, 124.9, 124.9, 123.7, 123.3, 109.4, 65.6, 41.0, 34.4, 28.5. **LRMS** (*m/z,* EI): 581 (40, M^+−1), 447 (81, M^+−Ad), 378 (23), 135 (100, Ad^+). **HRMS** Calculated for $C_{42}H_{35}N_3$: 581.2831, found 581.2841. $[\alpha]_D^{24}$ = +141.0 (*c* 0.60, $CHCl_3$).

Au (I) complex (*R*)-Au6



(*R*)-**13a(Cl$^-$)** (156 mg, 0.30 mmol), Ag_2O (42 mg, 0.18 mmol) and 4Å molecular sieves were suspended in dry $CHCl_3$ (5 mL) under an argon atmosphere and in the dark. The mixture was stirred at rt for 12 h and then filtered using a HPLC syringe filter. The solvent was evaporated and the residue was solved in dry toluene (6 mL) and AuCl•Me_2S (106 mg, 0.36 mmol) was added. The mixture was stirred at rt in the dark for 12 h. The reaction was filtered using a HPLC syringe filter and the solvent was evaporated. The residue was purified by flash chromatography (45:45:10 EtOAc–cyclohexane–CH_2Cl_2) to yield (*R*)-**Au6** (164 mg, 76%) as a yellow solid. **M.p.** 165–166 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 1H), 8.21 (s, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.41 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.14 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.02 – 6.93 (m, 2H), 6.41 – 6.35 (m, 1H), 2.77 – 2.68 (m, 6H), 2.28 – 2.23 (br s, 3H), 1.80 – 1.70 (m, 6H), 1.07 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 148.7, 144.7, 139.6, 134.9, 132.7, 132.3, 131.1, 129.6, 128.5, 127.3, 127.1, 126.9, 126.6, 126.5, 125.9, 124.4, 124.4, 124.0, 110.1, 65.2, 43.9, 37.8, 35.8, 31.8, 30.1. **LRMS** (*m/z,* FAB): 682 (25, M^+–Cl), 486 (52, M^+–AuCl), 459 (30), 237 (100), 135 (78, Ad^+). **HRMS** Calculated for $C_{34}H_{35}N_3Au$: 682.2497, found 682.2510. $[\alpha]_D^{27}$ = –181.6 (*c* 0.53, $CHCl_3$).

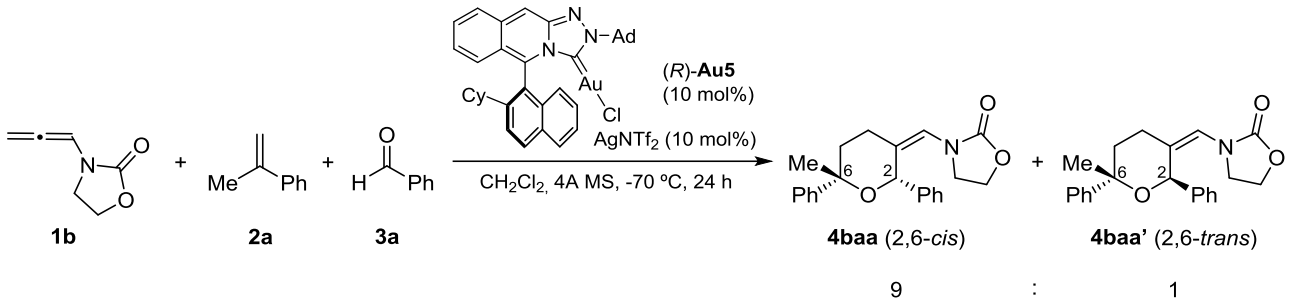
Au (I) complex (+)-Au7



(+)-**13b(Cl$^-$)** (185 mg, 0.30 mmol), Ag_2O (42 mg, 0.18 mmol) and 4Å molecular sieves were suspended in dry $CHCl_3$ (5 mL) under an argon atmosphere and in the dark. The mixture was stirred at rt for 12 h and then filtered using a HPLC syringe filter. The solvent was evaporated and the residue was solved in dry toluene (6 mL) and AuCl•Me_2S (106 mg, 0.36 mmol) was added. The mixture was stirred at rt in the dark for 12 h. The reaction was filtered using a HPLC syringe filter and the solvent was evaporated. The residue was purified by flash chromatography (45:45:10 EtOAc–cyclohexane–CH_2Cl_2) to yield (+)-**Au7** (198 mg, 81%) as a yellow solid. **M.p.** 175–177 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.96 (s, 1H), 7.63 – 7.54 (m, 2H), 7.38 – 7.28 (m, 5H), 7.23 – 7.20 (m, 1H), 7.19 – 7.09 (m, 4H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.76 – 6.71 (m, 1H), 6.66 – 6.60 (m, 3H), 2.65– 2.61 (m, 6H), 2.23 (br s, 3H), 1.78 – 1.69 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.8, 144.5, 141.0, 140.9, 140.3, 138.3, 137.2, 134.4, 133.4, 132.8, 131.5, 130.3, 130.3, 129.2, 129.1, 128.9, 128.9, 128.2, 127.8, 127.6, 127.5, 127.0, 126.9, 126.7, 126.7, 126.5, 126.4, 126.4, 125.3, 124.4, 124.4, 110.1, 64.8, 43.8, 35.8, 30.0. **LRMS** (*m/z,* FAB): 778 (58, M^+–Cl), 582 (30, M^+–AuCl), 555 (52), 442 (32), 237 (51), 135 (100, Ad^+). **HRMS** Calculated for $C_{42}H_{35}N_3Au$: 778.2497, found 778.2475. $[\alpha]_D^{27}$ = +159.7 (*c* 0.25, $CHCl_3$).

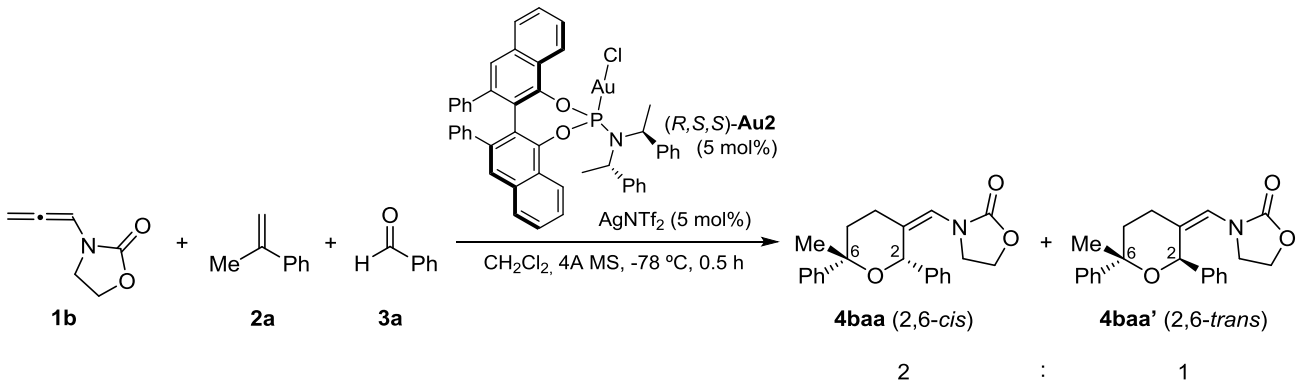
Representative general procedures for the [2 + 2 + 2] cycloadditions

General Procedure A: Reactions catalyzed by (*S*)-**Au5** or (*R*)-**Au5**. (Exemplified for the reaction between allenamide **1b**, α-methylstyrene (**2a**) and benzaldehyde (**3a**), catalyzed by *(R)*-**Au5**, Table 1 main manuscript, entry 10).



Benzaldehyde (**3a**) (162 µL, 1.6 mmol) and α-methylstyrene (**2a**) (42 µL, 0.32 mmol) were added to a Schlenk tube containing 200 mg of 4Å MS and a solution of *(R)*-**Au5** (11.9 mg, 0.016 mmol) and $AgNTf_2$ (6.2 mg, 0.016 mmol) in CH_2Cl_2 (1.5 mL), at -70 ºC. Then, 3-(propa-1,2-dienyl)oxazolidin-2-one (**1b**) (20 mg, 0.16 mmol) was added at once. The mixture was stirred at -70 ºC for 24 h (the progress of the reaction was easily monitored by tlc; 40% EtOAc in hexane) and filtered through a short pad of florisil eluting with EtOAc. After rotary evaporation, the crude mixture was purified by column chromatography (10-50% EtOAc in hexanes) to give 44.7 mg of 3-((*Z*)-((6*S*)-6-methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one as a 9 : 1 mixture of (*6S*,*2S*)-**4baa** and (*6S*,*2R*)-**4baa'** (*dr* = 9:1, 80% combined yield). Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IE-3 (Hexane : iPrOH = 90:10, at rt) or a Chiralcel OZ-H (Hexane : iPrOH = 80:20, 0.5mL/min, at rt) column. As expected, the reactions catalyzed by (*R*)-**Au5** and (*S*)-**Au5** provide equal results but opposite enantiomers of the corresponding THP products of type **4** and **4'**.This could be easily confirmed in several examples by analyzing the chiral HPLC traces of the products as well as by measuring their corresponding $[\alpha]_D$ values.

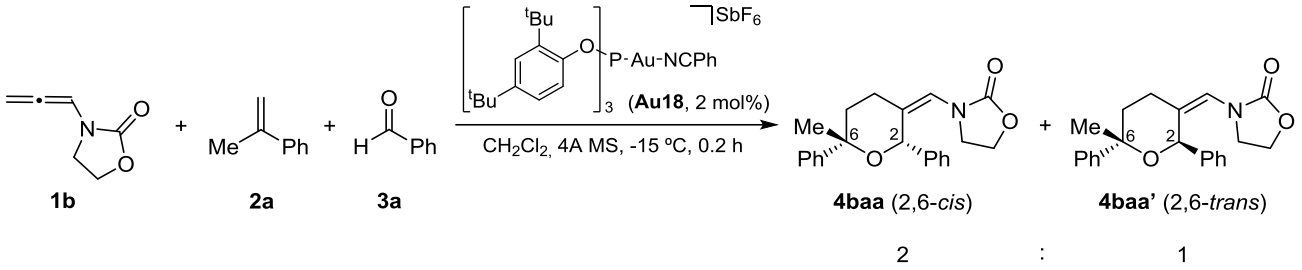
General Procedure B: Reactions catalyzed by (*R,S,S*)-**Au2** or its enantiomer (*S,R,R*)-**Au2** (exemplified for the reaction between allenamide **1b**, α-methylstyrene (**2a**) and benzaldehyde (**3a**) catalyzed by (*R,S,S*)-**Au2** (table 1 main manuscript, entry 2).



Benzaldehyde (**3a**) (162 µL, 1.6 mmol) and α-methylstyrene (**2a**) (42 µL, 0.32 mmol) were added to a Schlenk tube containing 200 mg of 4Å MS and a solution of *(R,S,S)*-**Au2** (7.4 mg, 0.008 mmol) and $AgNTf_2$ (3.1 mg, 0.008 mmol) in CH_2Cl_2 (1.5 mL), at -78 ºC. Then, 3-(propa-1,2-dienyl)oxazolidin-2-one (**1b**) (20 mg, 0.16

mmol) was added at once. The mixture was stirred at -78 ºC for 0.5 h (the progress of the reaction was easily monitored by tlc; 40% EtOAc in hexane) and filtered through a short pad of florisil eluting with EtOAc. After rotary evaporation, the crude mixture was purified by column chromatography (10-50% EtOAc in hexanes) to give 54.1 mg of 3-((*Z*)-((6*S*)-6-methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one as a 2 : 1 mixture of (6*S*, 2*S*)-**4baa** and (6*S*, 2*R*)-**4baa'** (*dr* = 2:1, 97% combined yield). Enantioselectivity was determined by chiral HPLC analysis using a Chiralpak IE-3 (Hexane : iPrOH = 90:10, at rt) or a Chiralcel OZ-H (Hexane : iPrOH = 80:20, 0.5mL/min) column. As expected, the reactions catalyzed by (*R,S,S*)-**Au2** and its enantiomeric partner (*S,R,R*)-**Au2** provide equal results but opposite enantiomers of the corresponding THP products of type **4** and **4'**.This could be easily confirmed in several examples by analyzing the chiral HPLC traces of the products as well as by measuring their corresponding [□]D values.

General Procedure C: Reactions catalyzed by the phosphite achiral catalyst **Au18**, following the previously reported general procedure.[19]



1b **2a** **3a** **4baa** (2,6-*cis*) : **4baa'** (2,6-*trans*)

2 : 1

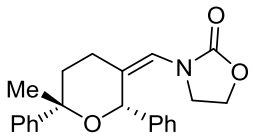
Benzaldehyde (**3a**) (162 µL, 1.6 mmol) and α-methylstyrene (**2a**) (42 µL, 0.32 mmol) were added to a Schlenk tube containing 200 mg of 4Å MS and a solution of the phosphite gold complex **Au18** (3.9 mg, 0.0032 mmol) in CH_2Cl_2 (1.5 mL), at -15 ºC. Then, 3-(propa-1,2-dienyl)oxazolidin-2-one (**1b**) (20 mg, 0.16 mmol) was added at once. The mixture was stirred at -15 ºC for 0.2 h (the progress of the reaction was easily monitored by tlc; 40% EtOAc in hexane) and filtered through a short pad of florisil eluting with EtOAc. After rotary evaporation, the crude mixture was purified by column chromatography (10-50% EtOAc in hexanes) to give 54.7 mg of 3-((*Z*)-(6-Methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one as a 2 : 1 mixture of **4baa** and **4baa'** (*dr* = 2:1, 98% combined yield).When the same reaction is carried out at -78ºC, a 98% yield and a dr = 3.5:1 is obtained.[19] Enantiomeric composition was analyzed by chiral HPLC analysis using a Chiralpak IE-3 (Hexane : iPrOH = 90:10, at rt) or a Chiralcel OZ-H (Hexane : iPrOH = 80:20, 0.5mL/min) column.

Characterization data (NMR, HPLC and X-ray)

3-((*Z*)-((2*S*,6*S*)-6-Methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4baa**) and **3-((*Z*)-((2*R*,6*S*)-6-Methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4baa'**)

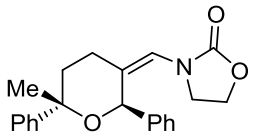
General Procedure	Catalyst	Manuscript result	React. time (h)	**4baa** : **4baa'** [a]	Yield[b]	ee **4baa**	ee **4baa'**
A	(*R*)-**Au5**	Table 1, entry 10	24	9 : 1	80%	87%	22%
B	(*R,S,S*)-**Au2**	Table 1, entry 2	0.5	2 : 1	97%	70%	81%
B[c]	(*R,S,S*)-**Au2**	Table 1, entry 4	0.5	4 : 1	91%	74%	90%
C[19]	**Au18**[d]	-	0.5	2 : 1	98%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers. [c] Carried out with $AgBF_4$ at -94 ºC. [d] Carried out at -15 ºC (see reference 19).



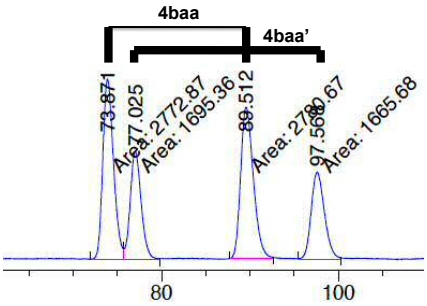
4baa

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 4H), 7.37 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 5.78 – 5.75 (m, 1H), 5.60 (s, 1H), 3.96 (td, *J* = 8.8, 5.3 Hz, 1H), 3.59 (q, *J* = 8.7 Hz, 1H), 3.31 (q, *J* = 8.6 Hz, 1H), 2.78 (td, *J* = 8.8, 5.3 Hz, 1H), 2.58 – 2.49 (m, 1H), 2.38 (dt, *J* = 14.3, 4.7 Hz, 1H), 2.25 (dt, *J* = 13.3, 5.0 Hz, 1H), 2.05 (ddd, *J* = 13.3, 11.5, 4.1 Hz, 1H), 1.67 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.7 (C), 148.7 (C), 141.2 (C), 139.0 (C), 128.2 (CH), 128.0 (CH), 127.9 (CH), 126.3 (CH), 124.7 (CH), 116.7 (CH), 75.7 (C), 73.0 (CH), 61.7 (CH_2), 45.3 (CH_2), 37.1 (CH_2), 27.1 (CH_3), 25.9 (CH_2). **LRMS** (*m/z, ESI*): 372.16 $(M+Na)^+$, 332.16, 263.14, 245.13, 143.11, 117.11. **HRMS** Calculated for $C_{22}H_{23}NNaO_3$: 372.1570, found 372.1560. Mp = 153 – 155 °C. $[\alpha]_D^{23}$ = -71 (*c* 0.5, $CHCl_3$), measured from a pure sample of **4baa** obtained from the reaction catalyzed by (*R*)-**Au5**. Enantioselectivities could be determined by chiral HPLC analysis using the Chiralpak IE-3 column at rt (Hexane : iPrOH = 90:10) as well as the Chiralcel OZ-H column, at rt (Hexane:iPrOH = 80:20, 0.5mL/min).



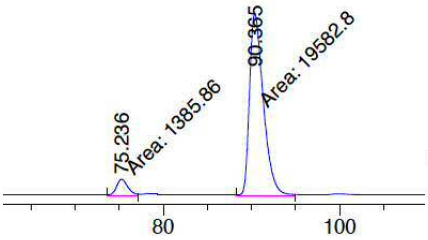
4baa'

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 4H), 7.38 – 7.27 (m, 5H), 7.22 – 7.15 (m, 1H), 5.81 (q, *J* = 1.8 Hz, 1H), 5.15 (t, *J* = 1.6 Hz, 1H), 3.79 (ddd, *J* = 9.2, 8.4, 5.9 Hz, 1H), 3.55 – 3.46 (m, 1H), 3.20 (ddd, *J* = 9.2, 8.3, 7.6 Hz, 1H), 2.86 – 2.72 (m, 1H), 2.72 – 2.60 (m, 1H), 2.47 – 2.41 (m, 1H), 2.31 – 2.27 (m, 2H), 1.43 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.8 (C), 146.7 (C), 140.7 (C), 137.0 (C), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 126.7 (CH), 125.3 (CH), 116.9 (CH), 76.7 (C), 73.9 (CH), 61.7 (CH_2), 45.3 (CH_2), 34.6 (CH_2), 32.7 (CH_3), 26.3 (CH_2). **LRMS** (*m/z, ESI*): 372.16 $(M+Na)^+$, 332.16, 263.14, 245.13, 143.11, 117.11. **HRMS** Calculated for $C_{22}H_{23}NNaO_3$: 372.1570, found 372.1560. Mp = 154 – 158 °C. $[\alpha]_D^{23}$ = +16 (*c* 0.5, $CHCl_3$), measured from a 10:1 mixture of **4baa'** and **4baa,** obtained from the reaction catalyzed by (*R,S,S*)-**Au2.** Enantioselectivities were determined by chiral HPLC analysis using the Chiralpak IE-3 column at rt (Hexane:iPrOH = 90:10) as well as the Chiralcel OZ-H column, at rt (Hexane : iPrOH = 80:20, 0.5mL/min).



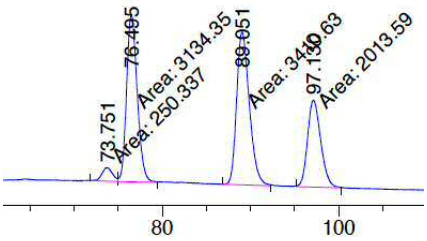
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	73.871	MF	1.4044	2772.87402	32.90699	31.1049
2	77.025	FM	1.4343	1695.35669	19.70020	19.0178
3	89.512	MM	1.6742	2780.67065	27.68176	31.1924
4	97.568	MM	1.7450	1665.67615	15.90895	18.6849

Figure S5. HPLC trace report of a racemic sample of **4baa** : **4baa'** (1.7:1 ratio) (Hexane:iPrOH = 90:10), Chiralpak IE-3.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	75.236	MM	1.4716	1385.85754	15.69571	6.6092
2	90.365	MM	1.8157	1.95828e4	179.75328	93.3908

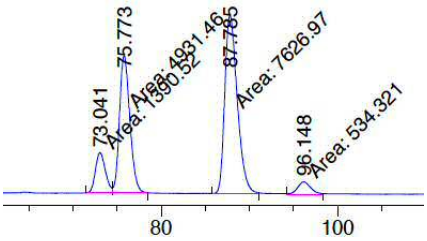
Figure S6. HPLC report of a sample from the reaction catalyzed by (*R*)-**Au5** (**4baa** : **4baa'** ratio = 1:0) (Hexane:iPrOH = 90:10), Table 1 main manuscript, entry 10, 87% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	73.751	MF	1.3798	250.33696	3.02375	2.8419
2	76.495	FM	1.4041	3134.35352	37.20457	35.5816
3	89.051	MM	1.6682	3410.62939	34.07509	38.7179
4	97.130	MM	1.7309	2013.59351	19.38833	22.8586

4baa (Peak 1 and 3): 87% ee
4baa' (Peak 2 and 4): 22% ee

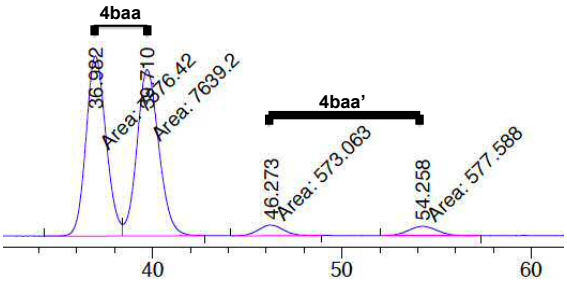
Figure S7. HPLC trace report of a sample from the reaction catalyzed by (*R*)-**Au5** (**4baa** : **4baa'** ratio = 1 : 1.5) (Hexane : iPrOH = 90:10), Table 1 main manuscript, entry 10.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	73.041	MF	1.3123	1390.51990	17.65993	9.6009
2	75.773	FM	1.3693	4931.46289	60.02578	34.0494
3	87.785	MM	1.6288	7626.96729	78.04227	52.6605
4	96.148	MM	1.6768	534.32074	5.31096	3.6892

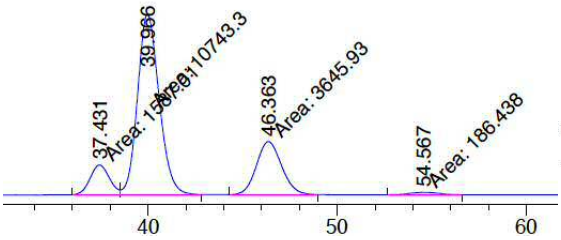
4baa (Peak 1 and 3): 70% ee
4baa' (Peak 2 and 4): 81% ee

Figure S8. HPLC trace report of a sample from the reaction catalyzed by (*R,S,S*)-**Au2** (**4baa** : **4baa'** ratio = 1.8:1) (Hexane : iPrOH = 90:10), Table 1 main manuscript, entry 2.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.982	MF	1.2256	7576.41602	103.03393	46.2929
2	39.710	FM	1.3383	7639.19971	95.13256	46.6765
3	46.273	MM	1.5604	573.06256	6.12079	3.5015
4	54.258	MM	1.7946	577.58765	5.36421	3.5291

Figure S9. HPLC trace report of a racemic sample of **4baa** : **4baa'** (13 : 1 ratio, obtained after column chromatography) (Hexane:iPrOH = 80:20), Chiralcel OZ-H.

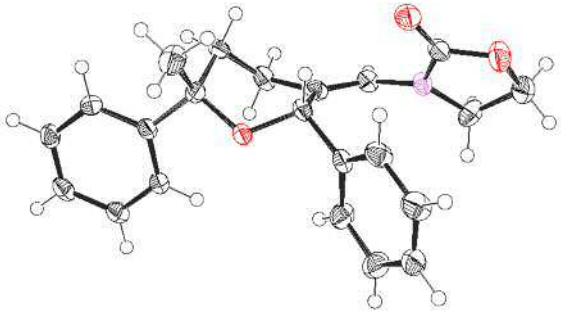


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.431	MF	1.1849	1587.00757	22.32209	9.8190
2	39.966	FM	1.3259	1.07433e4	135.04855	66.4697
3	46.363	MM	1.5351	3645.93115	39.58395	22.5578
4	54.567	MM	1.7211	186.43848	1.80539	1.1535

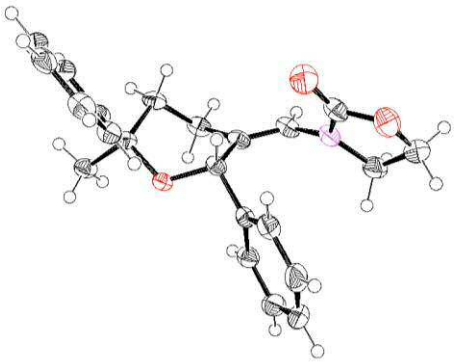
4baa (Peak 1 and 2): 74% ee
4baa' (Peak 3 and 4): 90% ee

Figure S10. HPLC trace report of a sample from the reaction catalyzed by (*R,S,S*)-**Au2** / $AgBF_4$ at -94 ºC (Hexane:iPrOH = 80:20), Table 1 main manuscript, entry 4.

Absolute configuration of samples of 4aaa (obtained from the reaction catalyzed by (*R*)-**Au5**) **and 4aaa'** (obtained from the reaction catalyzed by (*S,R,R*)-**Au2**).



CCDC 1520019



CCDC 1520020

Figure S11. CCDC 1520019 [left, (6S, 2S)-**4aaa,** obtained from the reaction catalyzed by (*R*)-**Au5**] and CCDC 1520020 [right, (6*R*, 2*S*)-**4aaa'**, obtained from the reaction catalyzed by (*S,R,R*)-**Au2**]

CCDC 1520019 (Figure S2 left) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif. Analysis of the absolute structure using likelihood methods (Hooft, Straver & Spek, 2008) was performed using PLATON (Spek, 2010). The results indicated that the absolute structure had been correctly assigned. The method calculated that the probability that the structure is inverted is smaller than 10^{-35}. The absolute structure parameter *y* (Hooft,

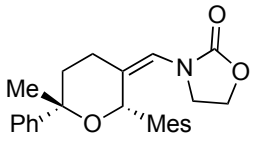
Straver & Spek, 2008) was calculated using PLATON (Spek, 2010). The resulting value was *y*=0.00(8), which together with Flack parameter value, indicate that the absolute structure has probably been determined correctly.

CCDC 1520020 (Figure S2 right) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif. (b) Analysis of the absolute structure using likelihood methods (Hooft, Straver & Spek, 2008) was performed using PLATON (Spek, 2010). The results indicated that the absolute structure had been correctly assigned. The method calculated that the probability that the structure is inverted is smaller than 10^{-44}. The absolute structure parameter *y* (Hooft, Straver & Spek, 2008) was calculated using PLATON (Spek, 2010). The resulting value was *y*=0.07(6), which together with Flack parameter value, indicate that the absolute structure has probably been determined correctly

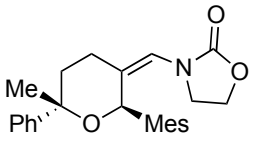
3-((*Z*)-((2*S*,6*S*)-2-Mesityl-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4bab**) and **3-((*Z*)-((2*R*,6*S*)-2-Mesityl-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4bab'**)

General Procedure	Catalyst	Manuscript result	React. time (h)	**4bab** : **4bab'** [a]	Yield[b]	ee **4baa**	ee **4baa'**
A	(*R*)-**Au5**	Table 2, entry 2	23	4 : 1	93%	91%	13%
B	(*R,S,S*)-**Au2**	Table 3, entry 2	0.3	1 : 4	98%	49%	81%[c]
C	**Au18**	-	1.5	1 : 1.7	92%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers. [c] For this particular case, (*R,S,S*)-**Au2** and (*R*)-**Au5** provide the 2,6-*trans* isomer with opposite absolute configurations (see HPLC traces).



4bab



4bab'

Characterization data of 4bab and **4bab'** (deduced from a 1:1.7 mixture of **4bab** : **4bab'**, obtained in the racemic reaction). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.1 Hz, 0.74H), 7.44 (dd, *J* = 8.3, 1.4 Hz, 1.26H), 7.40 – 7.32 (m, 2H), 7.28 (t, *J* = 7.3 Hz, 0.63H), 7.24 (t, *J* = 7.3 Hz, 0.37H), 6.90 (s, 0.74H), 6.87 (s, 1.26H), 5.97 (s, 0.37H), 5.60 (s, 0.63H), 5.57 (s, 0.37H), 5.43 (s, 0.63H), 3.94 – 3.88 (m, 0.37H), 3.83 – 3.77 (m, 0.63H), 3.42 – 3.32 (m, 1H), 3.22 (q, *J* = 9.2 Hz, 0.37H), 3.06 (q, *J* = 9.0 Hz, 0.63H), 2.73 – 2.65 (m, 0.63H), 2.64 – 2.59 (m, 0.37H), 2.57 – 2.44 (m, 4.63H), 2.41 (s, 1.11H), 2.39 – 2.27 (m, 6.89H), 2.14 – 2.05 (m, 0.37H), 1.69 (s, 1.11H), 1.48 (s, 1.89H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.58 (C), 157.11 (C), 156.54 (C), 148.55 (C), 146.73 (C), 145.24 (C), 144.27 (C), 139.72 (C), 137.83 (C), 137.13 (C), 137.09 (C), 135.83 (C), 134.04 (C), 133.95 (C), 129.75 (CH), 128.69 (CH), 128.49 (CH), 128.03 (CH), 126.95 (CH), 126.43 (CH), 125.54 (CH), 124.99 (CH), 115.85 (CH), 115.00 (CH), 76.68 (C), 76.35 (C), 69.89 (CH), 68.23 (CH), 62.27 (CH_2), 62.22 (CH_2), 46.18 (CH_2), 45.66 (CH_2), 37.04 (CH_2), 33.73 (CH_2), 32.53 (CH_3), 26.92 (CH_3), 26.71 (CH_2), 25.65 (CH_2), 21.24 (CH_3), 20.95 (CH_3), 20.83 (CH_3), 20.27 (CH_3). **LRMS** (*m/z, ESI*): 414.2038 $(M+Na)^+$, 305.1900, 185.1306, 159.1171. **HRMS** Calculated for $C_{25}H_{29}NNaO_3$: 414.2040, found 414.2038. Mp = 90 – 115 °C. $[\alpha]_D^{23}$ = +44 (*c* 1, $CHCl_3$), measured from a 1:4 mixture of **4bab** : **4bab'**, obtained from the reaction catalyzed by (*R,S,S*)-**Au2**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane:iPrOH = 90:10; 0.5 mL/min).

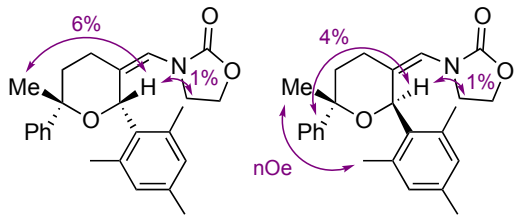
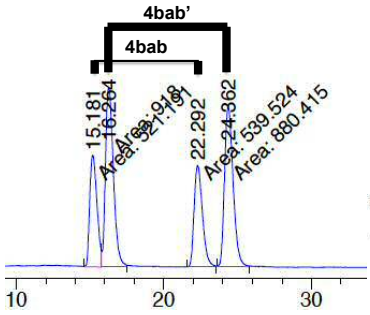
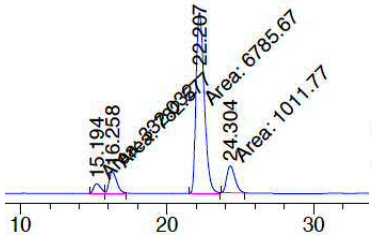


Figure S12. Significant nOe's observed for **4bab** and **4bab'**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.181	MF	0.5708	521.19061	15.21928	18.2290
2	16.264	FM	0.6248	917.99969	24.48866	32.1077
3	22.292	MM	0.6515	539.52448	13.80315	18.8702
4	24.362	MM	0.6742	880.41547	21.76289	30.7931

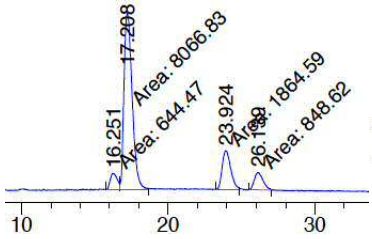
Figure S13. HPLC trace report of a racemic sample of **4bab** and **4bab'** (1 : 1.7 ratio) (Hexane : iPrOH = 90:10), Chiralpak IA-3.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.194	MF	0.5751	332.03198	9.62249	3.1445
2	16.258	FM	0.6192	782.57739	21.06416	7.4114
3	22.207	MM	0.6499	6785.67188	174.01309	64.2640
4	24.304	MM	0.6560	1011.77026	25.70470	9.5820

4bab (Peak 1 and 3): 91% ee
4bab' (Peak 2 and 4): 13% ee

Figure S14. HPLC trace report of a sample from the reaction catalyzed by (*R*)-**Au5** (**4bab** : **4bab'** ratio = 4 : 1), (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 2.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.251	MF	0.5611	644.47009	19.14383	5.6411
2	17.208	FM	0.6456	8066.82764	208.23814	70.6099
3	23.924	MM	0.6749	1864.58777	46.04598	16.3209
4	26.139	MM	0.6942	848.62006	20.37385	7.4281

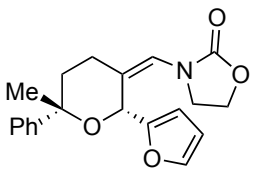
4bab (Peak 1 and 3): 49% ee
4bab' (Peak 2 and 4): 81% ee

Figure S15. HPLC trace report of a sample from the reaction catalyzed by (*R,S,S*)-**Au2** (**4bab** : **4bab'** ratio = 1 : 4) (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 2.

3-((*Z*)-((2*R*,6*S*)-2-(Furan-2-yl)-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (*Z*-**4bac**) and **3-((*Z*)-((2*S*,6*S*)-2-(Furan-2-yl)-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (*Z*-**4bac'**)

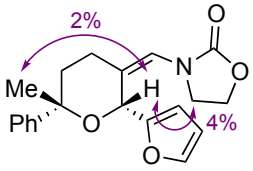
General Procedure	Catalyst	Manuscript result	React. time (h)	*Z*-(**4bac** : **4bac'**)[a]	Yield[b]	ee *Z*-**4bac**	ee *Z*-**4bac'**
A	(*R*)-**Au5**	Table 2, entry 3	15	4 : 1	76%	88%	27%
B	(*R,S,S*)-**Au2**	Table 3, entry 3	0.3	1 : 3[c]	81%[c]	65%	86%
C	**Au18**	-	3	[d]	66%[e]	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of *Z*-**4bac** and Z-**4bac'**. [c] Traces of the *E*-isomers (*E*-**4bac** and *E*-**4bac'**) were detected in the crude mixture. [d] A 1 : 12 : 2 : 10 mixture of *Z*-**4bac,** *Z*-**4bac',** *E*-**4bac** and *E*-**4bac'** was observed in the crude mixture. [e] Overall yield for both *Z* and *E* isomers (*Z*-**4bac**+*Z*-**4bac'**+*E*-**4bac**+*E*-**4bac'**).



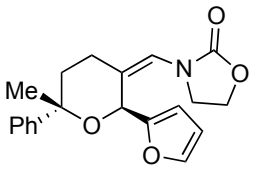
Z-**4bac**

Characterization data of *Z*-4bac (deduced from a 3:1 mixture of *Z*-**4bac** : *Z*-**4bac'** obtained after column chromatography). Colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.15 – 7.07 (m, 1H), 6.17 (s, 1H), 6.13 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.07 (d, *J* = 3.3 Hz, 1H), 5.79 (s, 1H), 4.25 – 4.14 (m, 2H), 3.56 – 3.43 (m, 2H), 2.76 – 2.57 (m, 1H), 2.54 – 2.34 (m, 2H), 2.13 – 2.00 (m, 1H), 1.58 – 1.51 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.80 (C), 153.39 (C), 147.19 (C), 142.06 (CH), 127.90 (CH), 127.25 (C), 126.23 (CH), 124.98 (CH), 118.48 (CH), 110.33 (CH), 109.09 (CH), 75.62 (C), 66.73 (CH), 62.20 (CH_2), 45.55 (CH_2), 35.58 (CH_2), 31.08 (CH_3), 25.84 (CH_2). **LRMS** (*m/z, ESI*): 362.1363 $(M+Na)^+$, 253.1216, 235.1110, 135.0459. **HRMS** Calculated for $C_{20}H_{21}NNaO_4$: 362.1363, found 362.1363. $[\alpha]_D^{23}$ = -7 (*c* 1, $CHCl_3$), measured from a 4:1 mixture of **4bac** : **4bac'**, obtained from the reaction catalyzed by (*R*)-**Au5**.



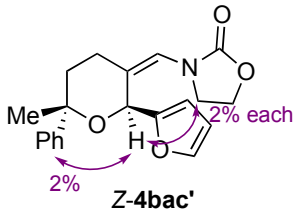
Z-**4bac**

Figure S16. Significant nOe's observed for *Z*-**4bac**.



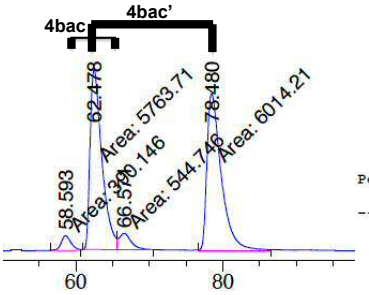
Z-**4bac'**

Characterization data of *Z*-4bac' (deduced from a 1:16 mixture of *Z*-**4bac** : *Z*-**4bac'** obtained after column chromatography). Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 3H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.27 (m, 1H), 6.42 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.39 (d, *J* = 3.1 Hz, 1H), 5.98 (s, 1H), 5.38 (s, 1H), 4.12 – 4.07 (m, 1H), 4.01 (q, *J* = 8.2 Hz, 1H), 3.39 (q, *J* = 8.4 Hz, 1H), 3.24 (td, *J* = 8.8, 6.0 Hz, 1H), 2.74 – 2.65 (m, 1H), 2.41 (dt, *J* = 14.3, 5.8 Hz, 1H), 2.33 – 2.23 (m, 2H), 1.45 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.47 (C), 153.32 (C), 146.72 (C), 142.64 (CH), 130.67 (C), 128.70 (CH), 127.02 (CH), 125.54 (CH), 118.08 (CH), 110.73 (CH), 108.79 (CH), 77.35 (C), 67.04 (CH), 62.07 (CH_2), 45.51 (CH_2), 34.93 (CH_2), 32.00 (CH_3), 25.97 (CH_2). **LRMS** (*m/z, ESI*): 362.1362 $(M+Na)^+$, 253.1217, 235.1110, 135.0478. **HRMS** Calculated for $C_{20}H_{21}NNaO_4$: 362.1363, found 362.1364. $[\alpha]_D^{23}$ = +21 (*c* 0.5, $CHCl_3$), measured from a 1 : 3 mixture of *Z*-**4bac** : *Z*-**4bac'**, obtained from the reaction catalyzed by (*R,S,S*)-**Au2**. Enantioselectivities were determined by chiral HPLC analysis using the Chiralpak IB column, at rt (Hexane : iPrOH = 92:8; 0.5 mL/min).



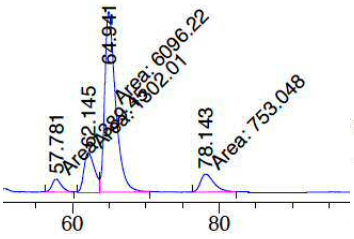
Z-**4bac'**

Figure S17. Significant nOe's observed for *Z*-**4bac'**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	58.593	MM	1.5499	390.14609	4.19538	3.0689
2	62.478	MF	1.8666	5763.71240	51.46380	45.3378
3	66.571	FM	1.9446	544.74640	4.66893	4.2850
4	78.480	MM	2.2357	6014.21484	44.83492	47.3083

Figure S18. HPLC trace report of a racemic sample of **4bac** : **4bac'** (1 : 12 ratio) (Hexane : iPrOH = 92:8), Chiralpak IB.

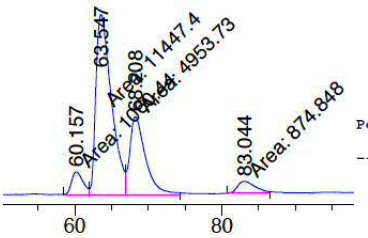


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	57.781	MM	1.5298	389.45023	4.24294	4.5599
2	62.145	MF	1.6819	1302.01184	12.90196	15.2447
3	64.941	FM	1.7339	6096.21631	58.59935	71.3782
4	78.143	MM	2.1210	753.04816	5.91730	8.8171

4bac (Peak 1 and 3): 88% ee

4bac' (Peak 2 and 4): 27% ee

Figure S19. HPLC trace report of a sample from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 92:8), Table 2 main manuscript, entry 3.



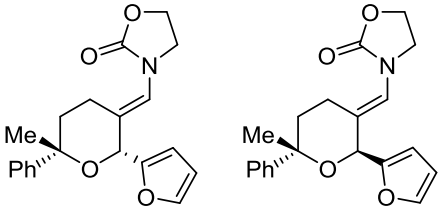
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	60.157	MM	1.7978	1060.44031	9.83064	5.7832
2	63.547	MF	2.4526	1.14474e4	77.79216	62.4299
3	68.208	FM	2.4574	4953.73291	33.59793	27.0158
4	83.044	MM	2.8108	874.84802	5.18735	4.7711

4bac (Peak 1 and 3): 65% ee

4bac' (Peak 2 and 4): 86% ee

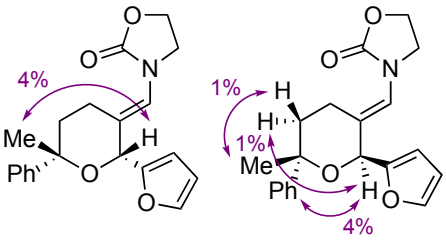
Figure S20. HPLC trace report of a sample from the reaction catalyzed by (*R,S,S*)-**Au2** (Hexane : iPrOH = 92:8), Table 3 main manuscript, entry 3.

3-((*E*)-((2*R,6*S**)-2-(Furan-2-yl)-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (*E*-**4bac**) and **3-((*E*)-((2*S**,6*S**)-2-(Furan-2-yl)-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (*E*-**4bac'**)



E-**4bac** *E*-**4bac'**

Characterization data for *E*-4bac and *E*-4bac (deduced from a 1:4 mixture of *E*-**4bac** : *E*-**4bac'** obtained after column chromatography. These *E*-isomers could only be detected in significant amounts by ^{1}H-NMR in the crude mixture from the reaction catalyzed by the achiral catalyst **Au18**). Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.40 (m, 2.4H), 7.36 (t, *J* = 7.8 Hz, 0.4H), 7.29 (t, *J* = 7.2 Hz, 1.2H), 6.43 (dd, *J* = 3.4, 1.9 Hz, 0.2H), 6.42 (dd, *J* = 3.4, 1.9 Hz, 0.8H), 6.30 (d, *J* = 3.4 Hz, 0.2H), 6.28 (d, *J* = 3.3 Hz, 0.8H), 6.24 (s, 0.2H), 6.17 (s, 0.2H), 6.12 (s, 0.8H), 5.84 (s, 0.8H), 4.54 – 4.48 (m, 0.8H), 4.48 – 4.42 (m, 1.2H), 3.91 (q, *J* = 9.2 Hz, 0.8H), 3.83 (q, *J* = 9.1 Hz, 0.2H), 3.73 – 3.65 (m, 1H), 3.16 (dt, *J* = 16.0, 5.2 Hz, 0.8H), 2.82 (t, *J* = 5.7 Hz, 0.4H), 2.54 (t, *J* = 13.5Hz, 0.8H), 2.46 – 2.40 (m, 0.8H), 2.14 – 2.03 (m, 0.4H), 2.02 – 1.95 (m, 0.8H), 1.69 (s, 0.6H), 1.46 (s, 2.4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.94 (C), 158.85 (C), 152.14 (C), 147.80 (C), 144.16 (C), 142.18 (CH), 142.02 (CH), 133.07 (CH), 132.96 (CH), 129.04 (CH), 128.35 (CH), 127.28 (CH), 126.96 (CH), 125.62 (CH), 124.70 (CH), 113.22 (CH), 112.71 (CH), 111.52 (CH), 111.42 (CH), 110.47 (CH), 110.32 (CH), 78.74 (CH), 78.46 (CH), 77.36 (C), 76.91 (C), 62.79 (CH_2), 39.96 (CH_2), 39.73 (CH_2), 39.72 (CH_2), 34.98 (CH_2), 33.31 (CH_2), 32.96 (CH_3), 26.37 (CH_3), 23.70 (CH_2), 23.48 (CH_2). **LRMS** (*m/z, ESI*): 362.1371 $(M+Na)^+$, 253.1222, 235.1116. **HRMS** Calculated for $C_{20}H_{21}NNaO_4$: 362.1363, found 362.1364.



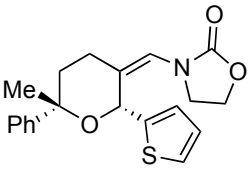
E-**4bac** *E*-**4bac'**

Figure S21. Significant nOe's observed for *E*-**4bac** and *E*-**4bac'**.

3-((*Z*)-((2*R*,6*S*)-6-Methyl-6-phenyl-2-(thiophen-2-yl)dihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4bad**) and **3-((*Z*)-((2*S*,6*S*)-6-Methyl-6-phenyl-2-(thiophen-2-yl)dihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4bad'**)

General Procedure	Catalyst	Manuscript result	React. time (h)	**4bad** : **4bad'** [a]	Yield[b]	ee **4bad**	ee **4bad'**
A	(*R*)-**Au5**	Table 2, entry 4	16	4 : 1	92%	81%	41%
B	(*R,S,S*)-**Au2**	Table 3, entry 4	0.3	1 : 1	95%	60%	75%
C	**Au18**	-	1	1.7 : 1	96%	-	-

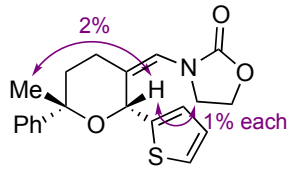
[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers.



4bad

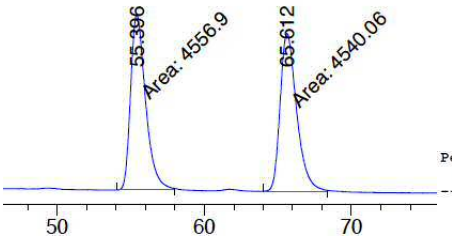
Characterization data of 4bad (deduced from a 8:1 mixture of **4bad** : **4bad'**, obtained after column chromatography). Orange oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.1 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.21 – 7.14 (m, 1H), 7.05 (d, *J* = 3.5 Hz, 1H), 6.89 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.98 (s, 1H), 5.95 (s, 1H), 4.11 (td, *J* = 8.9, 5.6 Hz, 1H), 3.95 (q, *J* = 8.4 Hz, 1H), 3.51 (q, *J* = 8.5 Hz, 1H), 3.24 (td, *J* = 8.8, 5.6 Hz, 1H), 2.66 – 2.51 (m, 1H), 2.41 – 2.24 (m, 2H), 2.09 – 1.95 (m, 1H), 1.64 (s, 3H). **^{13}C NMR** (75

MHz, $CDCl_3$) δ 156.05 (C), 148.47 (C), 144.58 (C), 133.90 (C), 127.93 (CH), 126.35 (CH), 126.13 (CH), 125.88 (CH), 125.53 (CH), 124.77 (CH), 117.85 (CH), 75.92 (C), 68.50 (CH), 62.11 (CH_2), 45.45 (CH_2), 37.07 (CH_2), 28.44 (CH_3), 25.63 (CH_2). **LRMS** (*m/z, ESI*): 378.1133 $(M+Na)^+$, 269.0991, 151.0221, 123.0275. **HRMS** Calculated for $C_{20}H_{21}NNaO_3S$: 378.1134, found 378.1133. Enantioselectivities were determined by chiral HPLC analysis using the Chiralpak IF3 column, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).



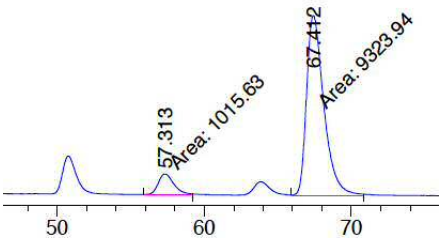
4bad

Figure S22. Significant nOe's observed for **4bad**.



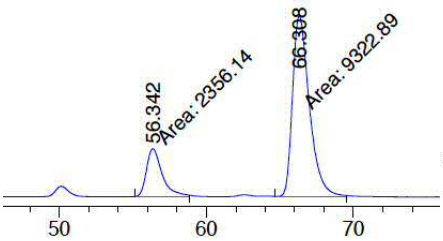
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.396	MM	1.1847	4556.89990	64.10583	50.0926
2	65.612	MM	1.3096	4540.05664	57.77736	49.9074

Figure S23. HPLC trace report of a racemic sample of **4bad** (Hexane : iPrOH = 90:10), Chiralpak IF3.



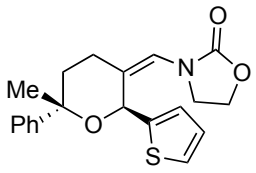
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	57.313	MM	1.2617	1015.62708	13.41624	9.8227
2	67.412	MM	1.3589	9323.93750	114.35721	90.1773

Figure S24. HPLC trace report of a sample from the reaction catalyzed by (*R*)-**Au5** (**4bad** : **4bad'** ratio = 4:1) (Hexane:iPrOH = 90:10), Table 2 main manuscript, entry 4, 81% ee (*the minor peaks of the HPLC trace corresponds to the **4bad'** isomer, obtained with 41% ee, which was further confirmed when a pure sample of **4bad'** was analyzed (see below)*.



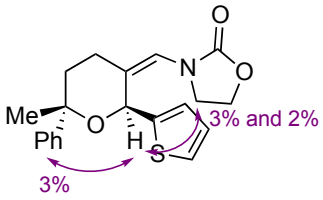
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	56.342	MM	1.2690	2356.13989	30.94366	20.1741
2	66.308	MM	1.3400	9322.89258	115.96020	79.8259

Figure S25. HPLC trace report of a sample of **4bad** from the reaction catalyzed by (*R,S,S*)-**Au2** (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 4, 60% ee.



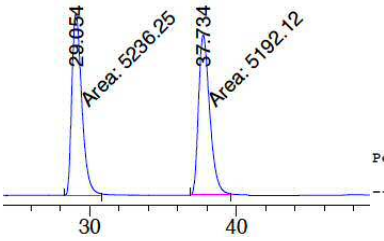
4bad'

Orange oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.07 (d, *J* = 3.5 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.98 (s, 1H), 5.55 (s, 1H), 4.00 (td, *J* = 8.4, 7 Hz, 1H), 3.86 (td, *J* = 8.8, 7.2 Hz, 1H), 3.38 (td, *J* = 8.4, 7.5 Hz, 1H), 3.12 (td, *J* = 8.4, 7 Hz, 1H), 2.76 – 2.62 (m, 1H), 2.41 – 2.17 (m, 3H), 1.44 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.21 (C), 146.85 (C), 144.55 (C), 132.21 (C), 128.53 (CH), 126.89 (CH), 126.53 (CH), 125.95 (CH), 125.83 (CH), 125.39 (CH), 118.19 (CH), 76.94 (C), 69.12 (CH), 62.12 (CH_2), 45.32 (CH_2), 34.94 (CH_2), 32.56 (CH_3), 25.95 (CH_2). **LRMS** (*m/z, ESI*): 378.1134 $(M+Na)^+$, 269.0994, 151.0227, 123.0277. **HRMS** Calculated for $C_{20}H_{21}NNaO_3S$: 378.1134, found 378.1134. Enantioselectivity was determined by chiral HPLC analysis using the Chiralpak IA-3 column, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).



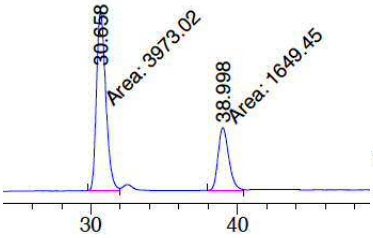
4bad'

Figure S26. Significant nOe's observed for **4bad'**.



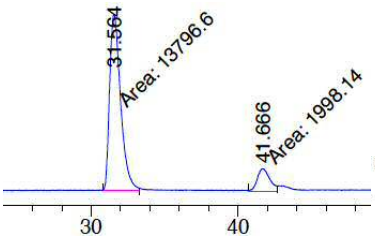
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.054	MM	0.7855	5236.24854	111.09913	50.2116
2	37.734	MM	0.8852	5192.11719	97.76010	49.7884

Figure S27. HPLC trace report of a racemic sample of **4bad'** (Hexane : iPrOH = 90:10), Chiralpak IA3.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.658	MM	0.7357	3973.02148	90.00208	70.6632
2	38.998	MM	0.8592	1649.45459	31.99488	29.3368

Figure S28. HPLC trace report of a sample of **4bad'** from the reaction catalyzed by (*R*)-**Au5** (Hexane:iPrOH = 90:10), Table 2 main manuscript, entry 4, 41% ee.



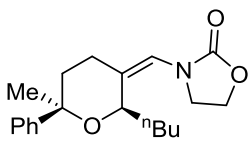
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.564	MM	0.8641	1.37966e4	266.09784	87.3493
2	41.666	MM	0.9888	1998.13867	33.67972	12.6507

Figure S29. HPLC trace report of a sample of **4bad'** from the reaction catalyzed by (*R,S,S*)-**Au2** (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 4, 75% ee.

3-((*Z*)-((2*S*,6*S*)-2-Butyl-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4bae**) and **3-((*Z*)-((2*R*,6*S*)-2-Butyl-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4bae'**)

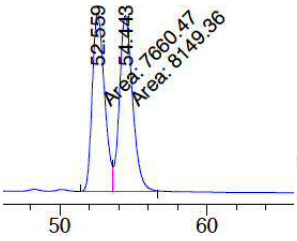
General Procedure	Catalyst	Manuscript result	React. time (h)	**4bae** : **4bae'** [a]	Yield[b]	ee **4bae**	ee **4bae'**
A[c]	(S)-**Au5**	Table 2, entry 5	7	5 : 1	51%	66%	54%
B	(*S,R,R*)-**Au2**	Table 3, entry 5	17	2 : 1	42%	33%	56%
C[19]	**Au18**	-	2	3 : 1	97%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers. [c] Carried out from -70 to -50 ºC. In addition to **4bae** and **4bae'**, an acyclic hydrofunctionalization product was also detected in the crude reaction mixture by ^{1}H-NMR (5% yield based on internal standard).[19]



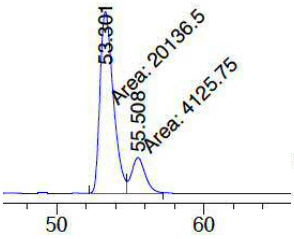
4bae

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.01 (s, 1H), 4.72 (d, *J* = 7.6 Hz, 1H), 4.39 (t, *J* = 8.0 Hz, 2H), 3.87 (q, *J* = 8.2 Hz, 1H), 3.70 (q, *J* = 8.3 Hz, 1H), 2.47 (td, *J* = 12.7, 5.9 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.14 (dt, *J* = 13.4, 4.3 Hz, 1H), 1.90 (td, *J* = 12.5, 5.4 Hz, 1H), 1.70 – 1.58 (m, 1H), 1.52 (s, 3H), 1.57 – 1.46 (m, 2H), 1.47 – 1.36 (m, 1H), 1.38 – 1.18 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.8 (C), 149.6 (C), 133.7 (C), 128.0 (CH), 126.3 (CH), 124.7 (CH), 115.8 (CH), 74.3 (C), 70.7 (CH), 62.1 (CH_2), 45.9 (CH_2), 37.9 (CH_2), 34.3 (CH_2), 30.2 (CH_3), 28.0 (CH_2), 25.9 (CH_2), 22.6 (CH_2), 14.0 (CH_3). **LRMS** (*m/z, ESI*): 352.19 $(M+Na)^+$, 312.20, 243.17, 225.16, 194.11, 169.10, 155.09, 123.12. **HRMS** Calculated for $C_{20}H_{27}NNaO_3$: 352.1883, found 352.1891. Mp = 112 – 115 °C. $[\alpha]_D^{23}$ = +59 (*c* 0.5, $CHCl_3$) measured from a pure sample of **4bae**, obtained from the reaction catalyzed by (*S*)-**Au5**. Enantioselectivities were determined by chiral HPLC analysis using the Chiralpak IF-3 column, at rt (Hexane : iPrOH = 95:5; 0.5 mL/min).



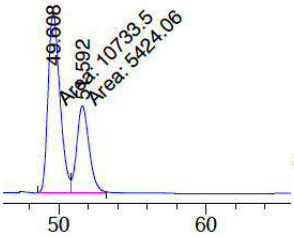
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.559	MF	0.9646	7660.47070	132.35405	48.4539
2	54.443	FM	1.0396	8149.35596	130.64726	51.5461

Figure S30. HPLC trace report of a racemic sample of **4bae** (Hexane : iPrOH = 95 : 5), Chiralpak IF-3.



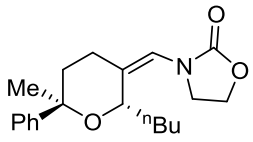
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	53.301	MF	1.0536	2.01365e4	318.53091	82.9952
2	55.508	FM	1.0927	4125.74951	62.92761	17.0048

Figure S31. HPLC trace report of a sample of **4bae** from the reaction catalyzed by (*S*)-**Au5** (Hexane : iPrOH = 95:5), Table 2 main manuscript, entry 5, 66% ee.



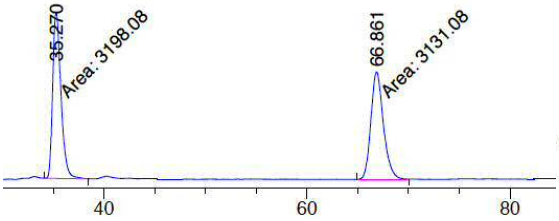
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.608	MF	0.9345	1.07335e4	191.42714	66.4302
2	51.592	FM	0.9748	5424.05957	92.74001	33.5698

Figure S32. HPLC trace report of a sample of **4bae** from the reaction catalyzed by (*S,R,R*)-**Au2** (Hexane : iPrOH = 95:5), Table 3 main manuscript, entry 5, 33% ee.



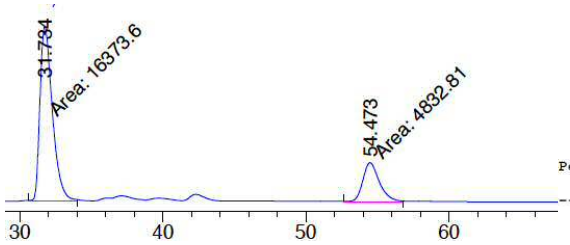
4bae'

Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 1H), 5.89 (t, *J* = 1.7 Hz, 1H), 4.26 – 4.17 (m, 3H), 3.50 – 3.41 (m, 1H), 3.05 – 2.96 (m, 1H), 2.59 – 2.48 (m, 1H), 2.28 – 2.21 (m, 2H), 2.19 – 2.11 (m, 1H), 1.75 – 1.66 (m, 1H), 1.67 – 1.51 (m, 2H), 1.43 (s, 3H), 1.44 – 1.22 (m, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.1 (C), 147.1 (C), 133.6 (C), 128.1 (CH), 126.5 (CH), 125.7 (CH), 116.3 (CH), 75.4 (C), 70.8 (CH), 62.1 (CH_2), 45.3 (CH_2), 35.1 (CH_2), 34.0 (CH_2), 33.8 (CH_3), 27.6 (CH_2), 25.6 (CH_2), 22.8 (CH_2), 14.1 (CH_3). **LRMS** (*m/z, ESI*): 352.19 $(M+Na)^+$, 298.05, 243.17, 225.16. **HRMS** Calculated for $C_{20}H_{27}NNaO_3$: 352.1883, found 352.1892. $[\alpha]_D^{23}$ = -26 (*c* 0.5, $CHCl_3$), measured from a pure sample of **4bae'**, obtained from the reaction catalyzed by (*S*)-**Au5**. Enantioselectivities were determined by chiral HPLC analysis using the Chiralpak IB column, at rt (Hexane:iPrOH = 95:5; 0.5 mL/min).



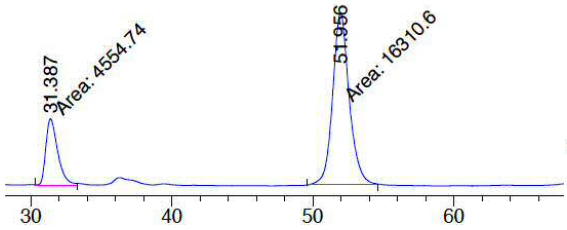
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.270	MM	0.9405	3198.08472	56.67187	50.5293
2	66.861	MM	1.4263	3131.08276	36.58852	49.4707

Figure S33. HPLC trace report of a racemic sample of **4bae'** (Hexane : iPrOH = 95 : 5), Chiralpak IB.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.734	MM	1.0020	1.63736e4	272.33640	77.2107
2	54.473	MM	1.3284	4832.80518	60.63256	22.7893

Figure S34. HPLC trace report of a sample of **4bae'** from the reaction catalyzed by (*S*)-**Au5** (Hexane : iPrOH = 95:5), Table 2 main manuscript, entry 5, 54% ee.



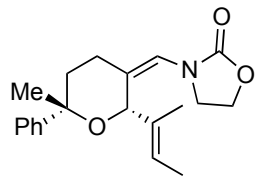
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.387	MM	0.9846	4554.73633	77.10294	21.8292
2	51.956	MM	1.3653	1.63106e4	199.11090	78.1708

Figure S35. HPLC trace report of a sample of **4bae'** from the reaction catalyzed by (*S,R,R*)-**Au2** (Hexane : iPrOH = 95:5), Table 3 main manuscript, entry 5, 56% ee.

3-((*Z*)-((2*S*,6*S*)-2-((*E*)-But-2-en-2-yl)-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4baf**) and **3-((*Z*)-((2*R*,6*S*)-2-((*E*)-But-2-en-2-yl)-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4baf'**)

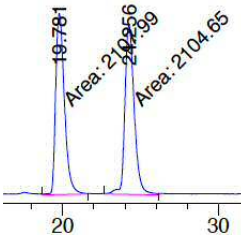
General Procedure	Catalyst	Manuscript result	React. time (h)	**4baf** : **4baf'** [a]	Yield[b]	ee **4baf**	ee **4baf'**
A	*(R)*-**Au5**	Table 2, entry 6	24	5 : 1	85%	83%	43%
B	*(R,S,S)*-**Au2**	Table 3, entry 6	0.3	2 : 1	91%	72%	77%
C[19]	**Au18**	-	1	3 : 1	94%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers.



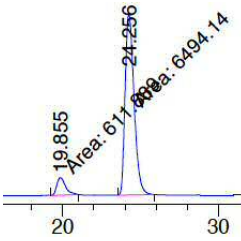
4baf

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.36 – 7.31 (m, 2H), 7.25 – 7.20 (m, 1H), 5.95 (t, *J* = 1.6 Hz, 1H), 5.67 – 5.61 (m, 1H), 5.02 (s, 1H), 4.34 – 4.24 (m, 2H), 3.76 (td, *J* = 8.8, 7.2 Hz, 1H), 3.56 (td, *J* = 8.8, 6.7 Hz, 1H), 2.47 – 2.34 (m, 1H), 2.27 – 2.19 (m, 2H), 1.96 – 1.87 (m, 1H), 1.76 (t, *J* = 1.1 Hz, 3H), 1.64 (dd, *J* = 6.8, 1.2 Hz, 3H), 1.61 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.16 (C), 149.31 (C), 134.88 (C), 134.23 (C), 127.91 (CH), 126.29 (CH), 124.64 (CH), 123.45 (CH), 116.60 (CH), 76.10 (CH), 74.90 (C), 62.03 (CH_2), 45.81 (CH_2), 37.55 (CH_2), 27.90 (CH_3), 26.21 (CH_2), 13.42 (CH_3), 12.75 (CH_3). **LRMS** (*m/z, ESI*): 350.1729 $(M+Na)^+$, 223.1472, 162.0913, 131.0862, 105.0691. **HRMS** Calculated for $C_{20}H_{25}NNaO_3$ 350.1727, found 350.1729). Mp = 105 – 108 ºC. $[\alpha]_D^{23}$ = -48 (*c* 0.5, $CHCl_3$), measured from a pure sample of **4baf**, obtained from the reaction catalyzed by (*R,S,S*)-**Au2**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane:iPrOH = 90:10; 0.5 mL/min).



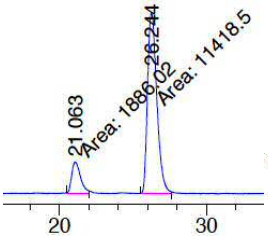
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.781	MM	0.6503	2107.98999	54.02301	50.0396
2	24.256	MM	0.6933	2104.65308	50.59189	49.9604

Figure S36. HPLC trace report of a racemic sample of **4baf** (Hexane:iPrOH = 90:10), Chiralpak IA-3.



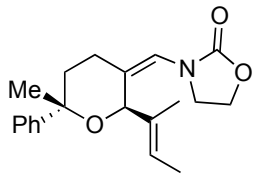
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.855	MM	0.6477	611.88922	15.74624	8.6108
2	24.256	MM	0.6655	6494.14160	162.63956	91.3892

Figure S37. HPLC trace report of a sample of **4baf**, from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 6, 83% ee.



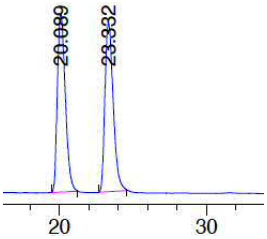
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.063	MM	0.6886	1886.01843	45.64644	14.1757
2	26.244	MM	0.7281	1.14185e4	261.36386	85.8243

Figure S38. HPLC trace report of a sample of **4baf,** from the reaction catalyzed by (*R,S,S*)-**Au2** (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 6, 72% ee.



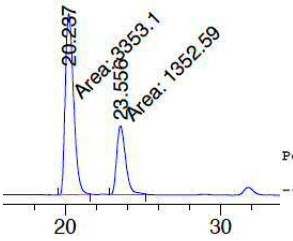
4baf'

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.36 (dd, *J* = 8.6, 6.9 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.00 (t, *J* = 1.9 Hz, 1H), 5.63 (qt, *J* = 6.7, 1.2 Hz, 1H), 4.60 (s, 1H), 4.25 – 4.13 (m, 2H), 3.61 (td, *J* = 8.6, 6.5 Hz, 1H), 3.30 (td, *J* = 8.7, 7.6 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.31 – 2.20 (m, 2H), 2.19 – 2.09 (m, 1H), 1.76 (t, *J* = 1.2 Hz, 3H), 1.70 (d, *J* = 6.8 Hz, 3H), 1.47 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.69 (C), 147.25 (C), 134.68 (C), 132.66 (C), 128.29 (CH), 126.56 (CH), 125.34 (CH), 123.24 (CH), 117.08 (CH), 76.74 (CH), 75.90 (C), 62.11 (CH_2), 45.73 (CH_2), 35.17 (CH_2), 32.57 (CH_3), 26.30 (CH_2), 13.57 (CH_3), 12.69 (CH_3). **LRMS** (*m/z, ESI*): 350.1735 $(M+Na)^+$, 282.0801, 223.1478, 193.1015, 131.0841. **HRMS** Calculated for $C_{20}H_{25}NNaO_3$ 350.1727, found 350.1735. Mp = 105 – 108 ºC. $[\alpha]_D^{23}$ = +19 (*c* 0.5, $CHCl_3$), measured from a 1 : 14 mixture of **4baf** : **4baf'**, obtained after column chromatography from the reaction catalyzed by (*R,S,S*)-**Au2**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).



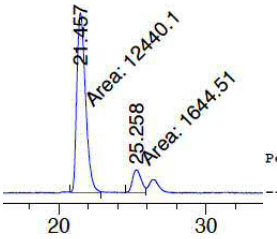
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.089	BB	0.5872	2967.22949	79.17326	49.5861
2	23.332	BB	0.6139	2937.81494	74.85155	49.0946

Figure S39. HPLC trace report of a racemic sample of **4baf'** (Hexane : iPrOH = 90:10), Chiralpak IA-3.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.237	MM	0.6183	3353.10352	90.39112	71.2563
2	23.556	MM	0.6592	1352.59058	34.19812	28.7437

Figure S40. HPLC trace report of a sample of **4baf'** from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 6, 43% ee.



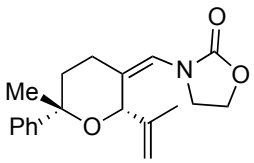
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.457	MM	0.6839	1.24401e4	303.14728	88.3241
2	25.258	MM	0.6986	1644.50793	39.23587	11.6759

Figure S41. HPLC trace report of a sample of **4baf'** from the reaction catalyzed by (*R,S,S*)-**Au2** (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 6, 77% ee.

3-((*Z*)-((2*S*,6*S*)-6-Methyl-6-phenyl-2-(prop-1-en-2-yl)dihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4bag**) and **3-((*Z*)-((2*R*,6*S*)-6-Methyl-6-phenyl-2-(prop-1-en-2-yl)dihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4bag'**)

General Procedure	Catalyst	Manuscript result	React. time (h)	**4bag** : **4bag'** [a]	Yield[b]	ee **4bag**	ee **4bag'**
A	(*R*)-**Au5**	Table 2, entry 7	17	5 : 1	60%	74%	27%
C	**Au18**	-	2	2 : 1	76%	-	-

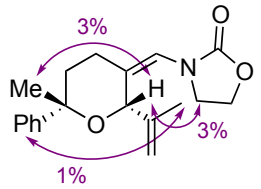
[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers.



4bag

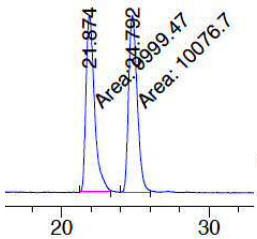
Characterization data of 4bag (deduced from a 16 : 1 mixture of **4bag** : **4bag'**, obtained after column chromatography). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.05 (s, 1H), 5.12 (s, 1H), 5.08 (s, 1H), 4.97 (s, 1H), 4.32 (t, *J* = 8.0 Hz, 2H), 3.80 (q, *J* = 8.2 Hz, 1H), 3.63 (q, *J* = 8.0 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.30 – 2.20 (m, 2H), 1.98 – 1.90 (m, 1H), 1.89 (s, 3H), 1.61 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.42 (C), 149.60 (C), 143.85 (C), 132.93 (C), 128.07 (CH), 126.46 (CH), 124.69 (CH), 117.22 (CH), 114.15 (CH_2), 75.16 (C), 74.41 (CH), 62.16

(CH_2), 45.73 (CH_2), 37.81 (CH_2), 28.42 (CH_3), 26.21 (CH_2), 18.99 (CH_3). **LRMS** (*m/z, ESI*): 336.1570 $(M+Na)^+$, 209.1331, 179.0872, 105.0720. **HRMS** Calculated for $C_{19}H_{23}NNaO_3$: 336.1570, found 336.1570. Mp = 124 – 128 ºC. $[\alpha]_D^{23}$ = -52 (*c* 0.5, $CHCl_3$), measured from a pure sample of **4bag** obtained from the reaction catalyzed by (*R*)-**Au5**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).



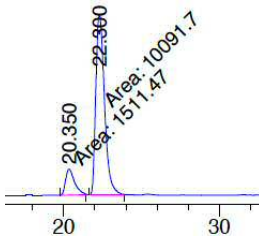
4bag

Figure S42. Significant nOe's observed for **4bag**.



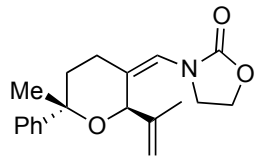
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.874	MM	0.6723	9999.47070	247.90593	49.8076
2	24.792	MM	0.6750	1.00767e4	248.82431	50.1924

Figure S43. HPLC trace report of a racemic sample of **4bag** (Hexane : iPrOH = 90:10), Chiralpak IA-3.



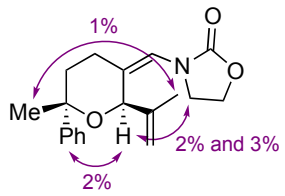
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.350	MM	0.6716	1511.47241	37.51031	13.0263
2	22.300	MM	0.6458	1.00917e4	260.43591	86.9737

Figure S44. HPLC trace report of a sample of **4bag** from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 7, 74% ee.



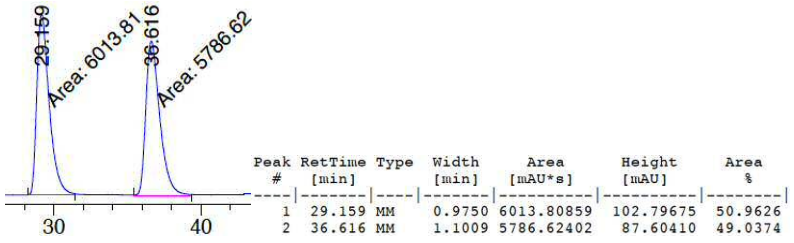
4bag'

Characterization data of 4bag' (deduced from a 1:4 mixture of **4bag** : **4bag'** obtained after column chromatography). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.22 (m, 1H), 6.07 (s, 1H), 5.09 (s, 1H), 5.02 (s, 1H), 4.70 (s, 1H), 4.21 (t, *J* = 7.8 Hz, 2H), 3.63 (q, *J* = 8.2, 7.8 Hz, 1H), 3.29 (q, *J* = 8.6 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.30 – 2.16 (m, 3H), 1.89 (s, 3H), 1.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.92 (C), 147.33 (C), 144.33 (C), 130.35 (C), 128.40 (CH), 126.75 (CH), 125.46 (CH), 117.89 (CH), 113.91 (CH_2), 76.21 (C), 75.00 (CH), 62.16 (CH_2), 45.57 (CH_2), 35.36 (CH_2), 32.45 (CH_3), 26.04 (CH_2), 19.05 (CH_3). **LRMS** (*m/z, ESI*): 336.1569 $(M+Na)^+$, 209.1333, 179.0874, 105.0714. **HRMS** Calculated for $C_{19}H_{23}NNaO_3$: 336.1570, found 336.1569. Mp = 124 – 128 ºC. $[\alpha]_D^{23}$ = +21 (*c* 0.5, $CHCl_3$) measured from a pure sample of **4bag'** obtained from the reaction catalyzed by (*R*)-**Au5**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IB column, at rt (Hexane :iPrOH = 90:10; 0.5 mL/min).



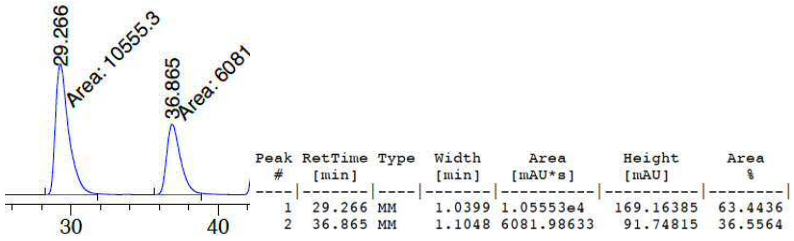
4bag'

Figure S45. Significant nOe's observed for **4bag'**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.159	MM	0.9750	6013.80859	102.79675	50.9626
2	36.616	MM	1.1009	5786.62402	87.60410	49.0374

Figure S46. HPLC trace report of a racemic sample of **4bag'** (Hexane : iPrOH = 90:10), Chiralpak IB.



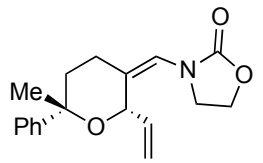
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.266	MM	1.0399	1.05553e4	169.16385	63.4436
2	36.865	MM	1.1048	6081.98633	91.74815	36.5564

Figure S7. HPLC trace report of a sample of **4bag'** from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 7, 27% ee.

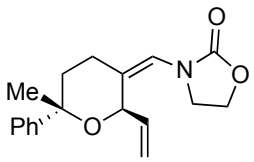
3-((*Z*)-((2*S*,6*S*)-6-Methyl-6-phenyl-2-vinyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4bah**) and **3-((*Z*)-((2*R*,6*S*)-6-Methyl-6-phenyl-2-vinyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4bah'**)

General Procedure	Catalyst	Manuscript result	React. time (h)	**4bah** : **4bah'** [a]	Yield[b]	ee **4bah**	ee **4bah'**
A	(*R*)-**Au5**	Table 2, entry 8	15	6 : 1	85%	83%	48%
C	**Au18**	-	3	2 : 1	95%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers.



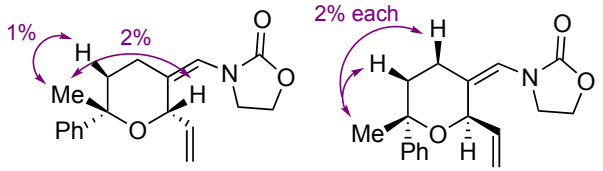
4bah



4bah'

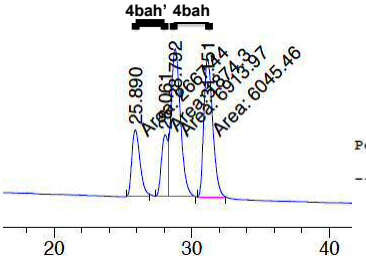
Characterization data of 4bah : 4bah' (deduced from the 2:1 mixture of **4bah** : **4bah'** obtained in the racemic reaction). Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 1.34H), 7.42 (d, *J* = 7.3 Hz, 0.66H), 7.38 – 7.30 (m, 2H), 7.27 – 7.21 (m, 1H), 6.19 (s, 0.67H), 6.11 – 6.04 (m, 0.33H), 5.96 (s, 0.33H), 5.83 (m, 0.67H), 5.38 (d, *J* = 17.3 Hz, 0.33H), 5.26 (d, *J* = 10.3 Hz, 0.33H), 5.23 (d, *J* = 5.5 Hz, 0.67H), 5.17 (d, *J* = 17.2 Hz, 0.67H), 5.01 (d, *J* = 10.3 Hz, 0.67H), 4.78 (d, *J* = 6.0 Hz, 0.33H), 4.39 – 4.30 (m, 1.34H), 4.25 (t, *J* = 8.0 Hz, 0.66H), 3.82 – 3.72 (m, 1.34H), 3.59 (q, *J* = 8.3 Hz, 0.33H), 3.37 (q, *J* = 8.5 Hz, 0.33H), 2.54 – 2.45 (m, 1H), 2.40 – 2.22 (m, 2H), 2.20 – 2.15 (m, 0.33H),

2.03 – 1.94 (m, 0.67H), 1.53 (s, 2.01H), 1.49 (s, 0.99H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.16 (C), 157.04 (C), 148.62 (C), 146.71 (C), 137.50 (CH), 137.14 (CH), 131.78 (C), 128.52 (CH), 128.45 (C), 128.09 (CH), 126.87 (CH), 126.72 (CH), 125.56 (CH), 125.43 (CH), 117.94 (CH), 117.89 (CH), 116.72 (CH_2), 116.12 (CH_2), 76.40 (C), 75.09 (C), 72.54 (CH), 72.38 (CH), 62.17 (CH_2), 62.02 (CH_2), 45.96 (CH_2), 45.69 (CH_2), 36.13 (CH_2), 34.96 (CH_2), 32.55 (CH_3), 30.77 (CH_3), 25.51 (CH_2), 25.42 (CH_2). **LRMS** (*m/z, ESI*): 322.14 $(M+Na)^+$, 282.08, 195.12, 167.08. **HRMS** Calculated for $C_{18}H_{21}NNaO_3$: 322.1414, found 322.1413. $[\alpha]_D^{23}$ = -25 (*c* 0.5, $CHCl_3$), measured from a 6 : 1 mixture of **4bah** : **4bah'**, obtained from the reaction catalyzed by (*R*)-**Au5**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IF-3 column, at rt (Hexane : iPrOH = 79:21; 0.5 mL/min).



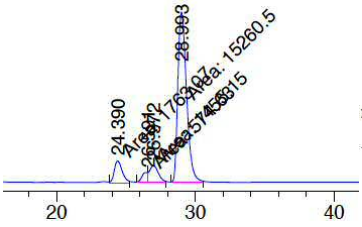
4bah **4bah'**

Figure S48. Significant nOe's observed for **4bah** and **4bah'**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.890	MM	0.6888	2667.43872	64.54742	15.2415
2	28.061	MF	0.5223	1874.29980	59.80369	10.7096
3	28.792	FM	0.8062	6913.96533	142.93965	39.5057
4	31.151	MM	0.7548	6045.45850	133.49290	34.5432

Figure S49. HPLC trace report of a racemic sample of **4bah** : **4bah'** (2:1 ratio) (Hexane : iPrOH = 79 : 21), Chiralpak IF-3.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.390	MM	0.6607	1763.06738	44.47628	9.2533
2	26.591	MF	0.4828	574.62988	19.83627	3.0159
3	26.972	FM	0.7171	1455.15051	33.81920	7.6372
4	28.993	MM	0.7248	1.52605e4	350.93591	80.0935

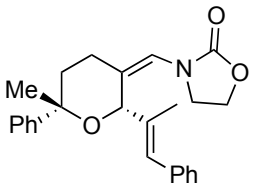
4bah (Peak 3 and 4): 83% ee; **4bah'** (Peak 1 and 2): 51% ee.

Figure S50. HPLC trace report of a sample from the reaction catalyzed by (*R*)-**Au5** (**4bah** : **4bah'** ratio = 6 : 1), (Hexane : iPrOH = 79:21), Table 2 main manuscript, entry 8.

3-((*Z*)-((2*S*,6*S*)-6-Methyl-6-phenyl-2-((*E*)-1-phenylprop-1-en-2-yl)dihydro-2*H*-pyran-3(4*H*)-ylidene)methyl) oxazolidin-2-one (**4bai**) and **3-((*Z*)-((2*R*,6*S*)-6-Methyl-6-phenyl-2-((*E*)-1-phenylprop-1-en-2-yl)dihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4bai'**)

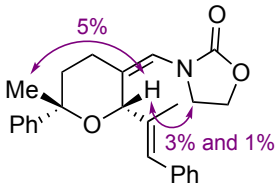
General Procedure	Catalyst	Manuscript result	React. time (h)	**4bai** : **4bai'** [a]	Yield[b]	ee **4bai**	ee **4bai'**
A	(*R*)-**Au5**	Table 2, entry 9	20	4 : 1	80%	78%	39%
B	(*S,R,R*)-**Au2**	Table 3, entry 7	1	1 : 1	98%	65%	77%
C	**Au18**	-	1	2 : 1	80%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers.



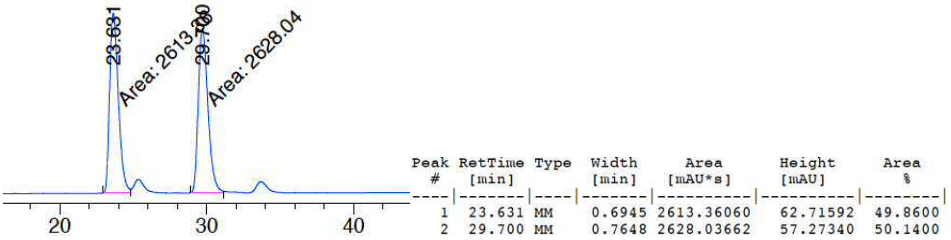
4bai

Characterization data of 4bai (deduced from a 6 :1 mixture of **4bai** : **4bai'** obtained after column chromatography). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.63 (s, 1H), 5.96 (s, 1H), 5.20 (s, 1H), 4.20 (td, *J* = 8.9, 6.2 Hz, 1H), 4.10 (td, *J* = 8.9, 7.3 Hz, 1H), 3.73 (td, *J* = 8.8, 7.4 Hz, 1H), 3.51 (td, *J* = 8.8, 6.2 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.34 – 2.25 (m, 2H), 2.02 (d, *J* = 1.3 Hz, 3H), 2.01 – 1.94 (m, 1H), 1.66 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.23 (C), 149.26 (C), 137.38 (C), 136.27 (C), 135.81 (C), 129.07 (CH), 128.48 (CH), 128.26 (CH), 128.11 (CH), 126.76 (CH), 126.52 (CH), 124.83 (CH), 117.05 (CH), 76.96 (CH), 75.28 (C), 62.12 (CH_2), 46.07 (CH_2), 37.38 (CH_2), 27.98 (CH_3), 26.21 (CH_2), 14.95 (CH_3). **LRMS** (*m/z, ESI*): 412.1886 $(M+Na)^+$, 372.1958, 285.1645, 254.1180. **HRMS** Calculated for $C_{25}H_{27}NNaO_3$: 412.1883, found 412.1886. Mp = 135 – 150 °C. $[\alpha]_D^{23}$ = +65 (*c* 0.5, $CHCl_3$), measured from a pure sample of **4bai** obtained from the reaction catalyzed by (*S,R,R*)-**Au2**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).



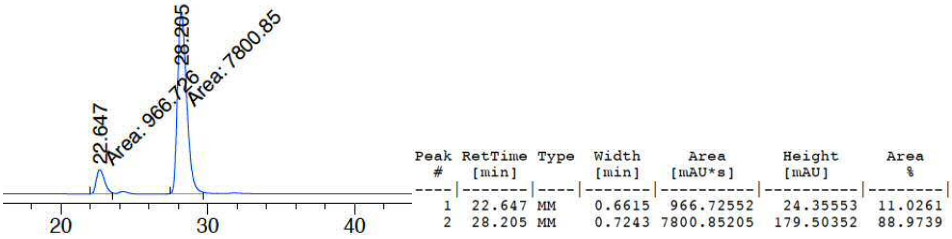
4bai

Figure S51. Significant nOe's observed for **4bai**.



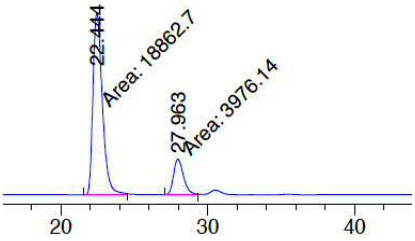
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.631	MM	0.6945	2613.36060	62.71592	49.8600
2	29.700	MM	0.7648	2628.03662	57.27340	50.1400

Figure S52. HPLC trace report of a racemic sample of **4bai** (Hexane : iPrOH = 90:10), Chiralpak IA-3 (the minor peaks observed in the HPLC trace correspond to the 2,6-*trans* isomers **4bai'**).



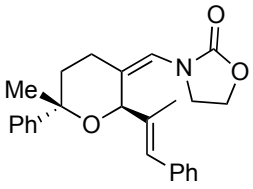
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.647	MM	0.6615	966.72552	24.35553	11.0261
2	28.205	MM	0.7243	7800.85205	179.50352	88.9739

Figure S53. HPLC trace report of a sample of **4bai** from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 9, 78% ee.



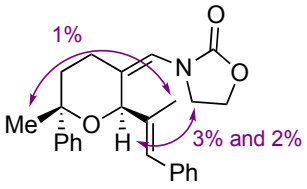
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.444	MM	0.7470	1.88627e4	420.85883	82.5905
2	27.963	MM	0.7970	3976.13940	83.15231	17.4095

Figure S54. HPLC trace report of a sample of **4bai** from the reaction catalyzed by (*S,R,R*)-**Au2** (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 7, 65% ee.



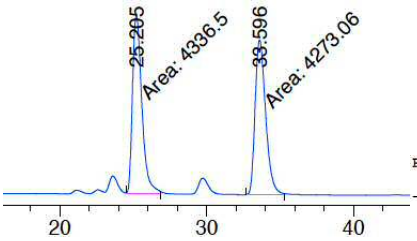
4bai'

Characterization data of 4bai' (deduced from a > 1 : 20 mixture of **4bai** : **4bai'**, obtained after column chromatography). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.32 (m, 6H), 7.29 – 7.24 (m, 2H), 6.60 (s, 1H), 6.00 (s, 1H), 4.76 (s, 1H), 4.07 (dt, *J* = 8.8, 6.7 Hz, 2H), 3.63 (td, *J* = 8.6, 6.5 Hz, 1H), 3.33 (td, *J* = 8.7, 7.4 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.36 – 2.25 (m, 2H), 2.23 – 2.16 (m, 1H), 2.02 (d, *J* = 1.3 Hz, 3H), 1.50 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.69 (C), 147.18 (C), 137.32 (C), 136.70 (C), 134.02 (C), 128.98 (CH), 128.38 (CH), 128.22 (CH), 127.89 (CH), 126.71 (CH), 126.66 (CH), 125.29 (CH), 117.43 (CH), 77.47 (CH), 76.17 (C), 62.09 (CH_2), 46.05 (CH_2), 34.95 (CH_2), 32.37 (CH_3), 26.19 (CH_2), 14.73 (CH_3). **LRMS** (*m/z, ESI*): 412.1881 $(M+Na)^+$, 372.1954, 285.1634, 254.1174. **HRMS** Calculated for $C_{25}H_{27}NNaO_3$: 412.1883, found 412.1881. Mp = 135 – 150 °C. $[\alpha]_D^{23}$ = -1 (*c* 0.5, $CHCl_3$), measured in a pure sample of **4bai'** obtained from the reaction catalyzed by (*S,R,R*)-**Au2**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane : iPrOH = 90 : 10; 0.5 mL/min).



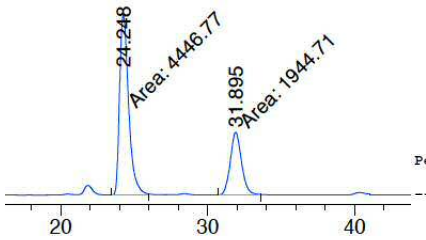
4bai'

Figure S55. Significant nOe's observed for **4bai'**.



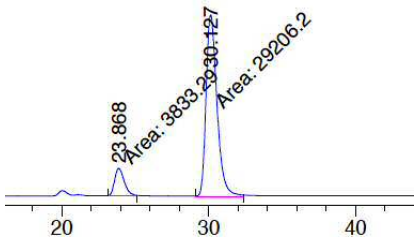
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.205	MM	0.7329	4336.50439	98.61423	50.3684
2	33.596	MM	0.8321	4273.06299	85.58444	49.6316

Figure S56. HPLC trace report of a racemic sample of **4bai'** (Hexane : iPrOH = 90:10), Chiralpak IA-3 (the minor peaks observed in the HPLC trace correspond to the 2,6-*cis* enantiomers **4bai** (**4bai** : **4bai'** = 1:14).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.248	MM	0.7146	4446.77197	103.70921	69.5734
2	31.895	MM	0.8959	1944.71497	36.17617	30.4266

Figure S57. HPLC trace report of a sample of **4bai'** from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 9, 39% ee.



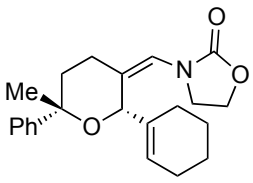
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.868	MM	0.7538	3833.28809	84.75872	11.6021
2	30.127	MM	0.8605	2.92062e4	565.70258	88.3979

Figure S58. HPLC trace report of a sample of **4bai'** from the reaction catalyzed by (*S,R,R*)-**Au2** (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 7, 77% ee.

3-((*Z*)-((2*S*,6*S*)-2-(Cyclohex-1-en-1-yl)-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl) oxazolidin-2-one (**4baj**) and **3-((*Z*)-((2*R*,6*S*)-2-(Cyclohex-1-en-1-yl)-6-methyl-6-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4baj'**)

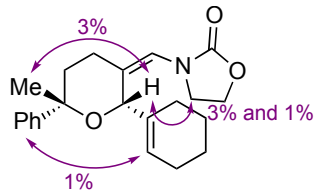
General Procedure	Catalyst	Manuscript result	React. time (h)	**4baj** : **4baj'** [a]	Yield[b]	ee **4baj**	ee **4baj'**
A	*(R)*-**Au5**	Table 2, entry 10	16	7 : 1	77%	81%	25%
B	*(R,S,S)*-**Au2**	Table 3, entry 8	0.3	2 : 1	80%	62%	75%
C	**Au18**	-	1	2 : 1	97%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers.



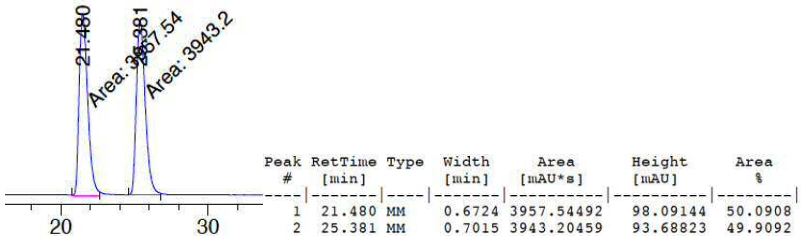
4baj

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.24 – 7.15 (m, 1H), 5.97 (s, 1H), 5.76 (s, 1H), 4.99 (s, 1H), 4.30 (t, *J* = 8.0 Hz, 2H), 3.76 (q, *J* = 8.2 Hz, 1H), 3.59 (q, *J* = 8.1 Hz, 1H), 2.46 – 2.32 (m, 1H), 2.30 – 1.82 (m, 7H), 1.75 – 1.44 (m, 4H), 1.58 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.53 (C), 149.61 (C), 136.63 (C), 134.12 (C), 128.17 (CH), 126.54 (CH), 126.15 (CH), 124.92 (CH), 116.75 (CH), 75.27 (C), 74.97 (CH), 62.19 (CH_2), 45.85 (CH_2), 37.43 (CH_2), 28.37 (CH_3), 26.30 (CH_2), 25.41 (CH_2), 24.84 (CH_2), 22.77 (CH_2), 22.40 (CH_2). **LRMS** (*m/z, ESI*): 376.1883 $(M+Na)^+$, 336.1959, 267.1739, 249.1632. **HRMS** Calculated for $C_{22}H_{27}NNaO_3$: 376.1883, found 376.1883. Enantioselectivities was determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).



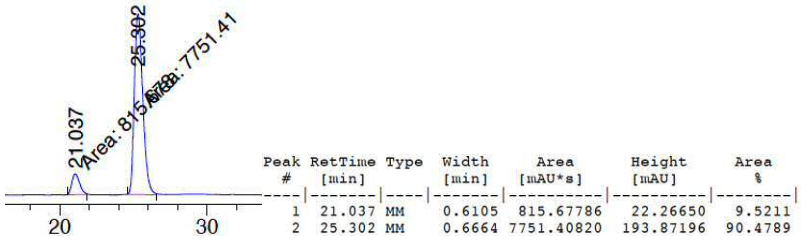
4baj

Figure S59. Significant nOe's observed for **4baj**.



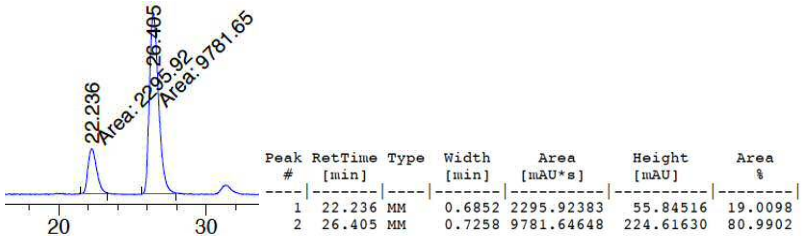
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.480	MM	0.6724	3957.54492	98.09144	50.0908
2	25.381	MM	0.7015	3943.20459	93.68823	49.9092

Figure S60. HPLC trace report of a racemic sample of **4baj** (Hexane : iPrOH = 90:10), Chiralpak IA-3.



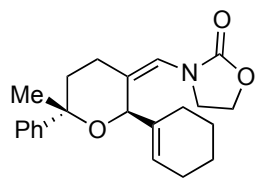
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.037	MM	0.6105	815.67786	22.26650	9.5211
2	25.302	MM	0.6664	7751.40820	193.87196	90.4789

Figure S61. HPLC trace report of a sample of **4baj** from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 10, 81% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.236	MM	0.6852	2295.92383	55.84516	19.0098
2	26.405	MM	0.7258	9781.64648	224.61630	80.9902

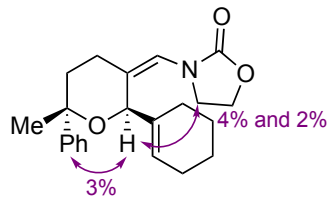
Figure S62. HPLC trace report of a sample of **4baj** from the reaction catalyzed by (*R,S,S*)-**Au2** (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 8, 62% ee.



4baj'

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 4H), 7.27 – 7.19 (m, 1H), 6.01 (s, 1H), 5.78 (s, 1H), 4.57 (s, 1H), 4.29 – 4.10 (m, 2H), 3.60 (td, *J* = 8.5, 6.5 Hz, 1H), 3.27 (q, *J* = 8.5 Hz, 1H), 2.59 – 2.44 (m, 1H), 2.29 – 1.97 (m, 7H), 1.73 – 1.53 (m, 4H), 1.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.88 (C), 147.56 (C), 136.80 (C), 131.59 (C), 128.36 (CH), 126.65 (CH), 125.50 (CH), 117.25 (CH), 75.95 (C), 75.67 (CH), 62.27 (CH_2), 45.69 (CH_2), 35.39 (CH_2), 32.56 (CH_3), 26.30 (CH_2), 25.55 (CH_2), 24.93 (CH_2),

22.89 (CH_2), 22.51 (CH_2). **LRMS** (*m/z, ESI*): 376.1883 $(M+Na)^+$, 336.1964, 267.1742, 249.1633. **HRMS** Calculated for $C_{22}H_{27}NNaO_3$: 376.1883, found 376.1883. Enantioselectivities were determined by chiral HPLC analysis on a Chiralpak IA-3, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).



4baj'

Figure S63. Significant nOe's observed for **4baj'**.

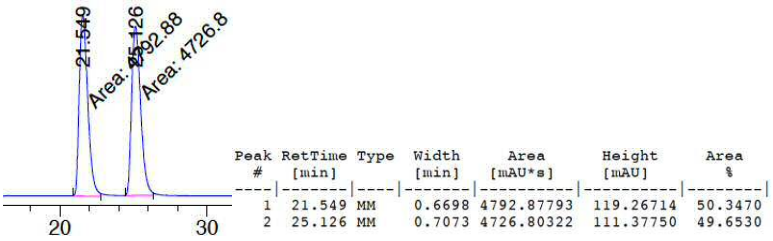


Figure S64. HPLC trace report of a racemic sample of **4baj'** (Hexane : iPrOH = 90:10), Chiralpak IA-3.

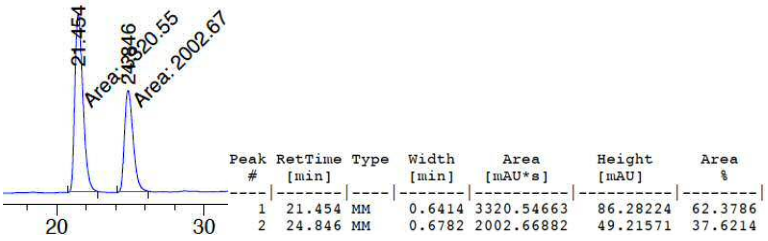


Figure S65. HPLC trace report of a sample of **4baj'** from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 10, 25% ee.

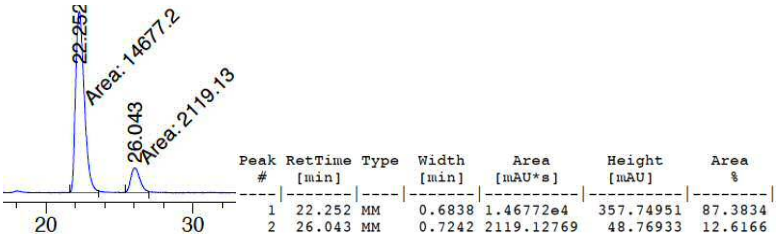
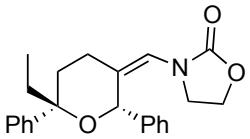


Figure S66. Sample of **4baj'** from the reaction catalyzed by **4baj'** with (*R,S,S*)-**Au2** (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 8, 75% ee.

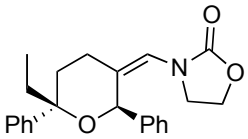
3-((*Z*)-((2*S*,6*S*)-6-Ethyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4bba**) and **3-((*Z*)-((2*R*,6*S*)-6-Ethyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4bba'**)

General Procedure	Catalyst	Manuscript result	React. time (h)	**4bba** : **4bba'** [a]	Yield[b]	ee **4bba**	ee **4bba'**
A	(*R*)-**Au5**	Table 2, entry 10	21	3 : 1	76%	88%	5%
C	**Au18**[c]	-	1.5	1 : 1	85%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers. [c] A small fraction (≈10%) of the [2+2] cycloadduct was also obtained.

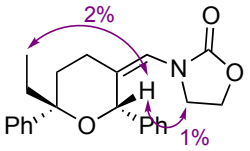


4bba

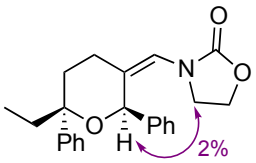


4bba'

Characterization data of 4bba : 4bba' (deduced from the 1:1 mixture of **4bba** : **4bba'** obtained in the racemic reaction). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 – 7.22 (m, 9.5H), 7.22 – 7.14 (m, 0.5H), 5.79 – 5.74 (m, 1H), 5.49 (s, 0.5H), 5.13 (s, 0.5H), 4.00 – 3.90 (m, 0.5H), 3.82 – 3.72 (m, 0.5H), 3.61 (q, *J* = 8.3 Hz, 0.5H), 3.51 (q, *J* = 8.3 Hz, 0.5H), 3.31 (q, *J* = 8.2 Hz, 0.5H), 3.17 (q, *J* = 8.3 Hz, 0.5H), 2.84 – 2.69 (m, 1H), 2.68 – 2.19 (m, 4H), 2.07 – 1.94 (m, 0.5H), 1.93 – 1.63 (m, 1.5H), 0.70 (t, *J* = 7.4 Hz, 1.5H), 0.62 (t, *J* = 7.3 Hz, 1.5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.05 (C), 155.82 (C), 146.74 (C), 144.73 (C), 141.40 (C), 141.02 (C), 139.24 (C), 137.61 (C), 128.31 (CH), 128.24 (CH), 128.12 (CH), 127.99 (CH), 127.85 (CH), 126.76 (CH), 126.43 (CH), 126.18 (CH), 125.59 (CH), 116.84 (CH), 116.55 (CH), 79.25 (C), 78.43 (C), 73.79 (CH), 72.66 (CH), 61.85 (CH_2), 61.81 (CH_2), 45.47 (CH_2), 45.42 (CH_2), 37.88 (CH_2), 37.56 (CH_2), 32.69 (CH_2), 31.81 (CH_2), 26.68 (CH_2), 25.80 (CH_2), 8.19 (CH_3), 8.18 (CH_3). **LRMS** (*m/z, ESI*): 386.1727 $(M+Na)^+$, 277.159, 259.1479, 117.0714. **HRMS** Calculated for $C_{23}H_{25}NNaO_3$: 386.1727, found 386.1727. Mp = 125 – 148 ºC. $[\alpha]_D^{23}$ = -62 (*c* 0.5, $CHCl_3$), measured from a mixture 3 : 1 of **4bba** : **4bba'**, obtained from the reaction catalyzed by (*R*)-**Au5**. Enantioselectivities was determined by chiral HPLC analysis using a Chiralpak IA-3, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).

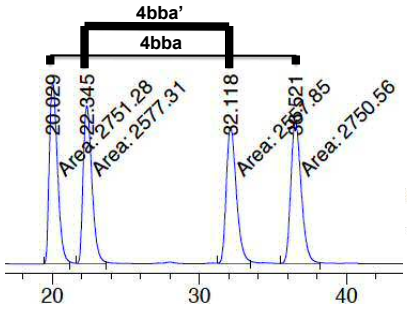


4bba



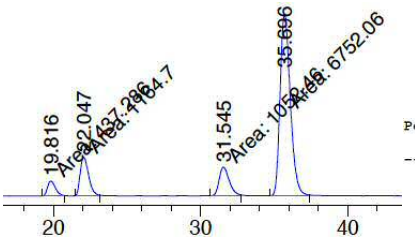
4bba'

Figure S67. Significant nOe's observed for **4bba** and **4bba'**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.029	MM	0.6418	2751.27759	71.45097	25.8652
2	22.345	MM	0.6891	2577.31348	62.33203	24.2297
3	32.118	MM	0.7923	2557.84961	53.80664	24.0467
4	36.521	MM	0.8190	2750.55640	55.97258	25.8584

Figure S68. HPLC trace report of a racemic sample of **4bba** : **4bba'** (1.1:1 ratio) (Hexane : iPrOH = 90:10), Chiralpak IA-3.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.816	MM	0.6332	437.28610	11.51040	4.6488
2	22.047	MM	0.6586	1164.70435	29.47217	12.3819
3	31.545	MM	0.7948	1052.46497	22.06869	11.1887
4	35.696	MM	0.8069	6752.06055	139.47307	71.7807

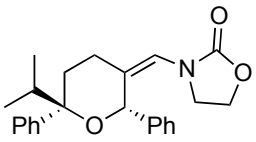
4bba (Peak 1 and 4): 88% ee; **4bba'** (Peak 2 and 3): 5% ee

Figure S69. HPLC trace report of a sample from the reaction catalyzed by (*R*)-**Au5**, (**4bba** : **4bba'** ratio = 3 : 1) (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 11.

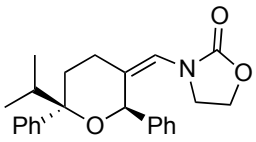
3-((*Z*)-((2*S*,6*R*)-6-Isopropyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (**4bca**) and **3-((*Z*)-((2*R*,6*R*)-6-Isopropyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one** (**4bca'**)

General Procedure	Catalyst	Manuscript result	React. time (h)	**4bca** : **4bca'** [a]	Yield[b]	ee **4bca**	ee **4bca'**
A[c]	(*R*)-**Au5**	Table 2, entry 12	27	1 : 2	52%	76%	10%
B	(*R,S,S*)-**Au2**	Table 3, entry 9	0.3	1 : 1.1	96%	61%	45%
C	**Au18**		1.5	1 : 2	98%	-	-

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Overall yield of both isomers. [c] Carried out from -70 to -50 ºC.

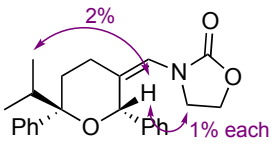


4bca

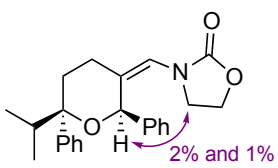


4bca'

Characterization data of 4bca : 4bca' (deduced from a 1.1:1 mixture of **4bca** : **4bca'** obtained in the reaction with **Au2** after column chromatography). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.22 (m, 19.48H), 7.22 – 7.17 (m, 0.52H), 5.77 (s, 0.48H), 5.74 (s, 0.52H), 5.57 (s, 0.52H), 5.09 (s, 0.48H), 3.95 (td, *J* = 8.8, 5.3 Hz, 0.52H), 3.79 (td, *J* = 8.7, 6.0 Hz, 0.48H), 3.58 (q, *J* = 8.3 Hz, 0.52H), 3.55 – 3.51 (q, J = 8.3 Hz, 0.48H), 3.29 (q, *J* = 8.7 Hz, 0.52H), 3.17 (q, *J* = 8.4 Hz, 0.48H), 2.78 – 2.68 (m, 1H), 2.60 – 2.53 (m, 0.48H), 2.49 (dt, *J* = 13.3, 4.3 Hz, 0.52H), 2.45 – 2.24 (m, 3H), 2.21 – 2.13 (m, 0.52H), 1.95 (hept, *J* = 6.9 Hz, 0.48H), 0.92 (d, *J* = 6.8 Hz, 1.44H), 0.87 (d, *J* = 6.9 Hz, 1.56H), 0.72 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.24 (C), 155.84 (C), 143.20 (C), 142.98 (C), 141.67 (C), 141.21 (C), 139.73 (C), 137.29 (C), 128.26 (CH), 128.22 (CH), 127.94 (CH), 127.87 (CH), 127.81 (CH), 127.59 (CH), 127.28 (CH), 127.05 (CH), 126.83 (CH), 126.34 (CH), 116.81 (CH), 116.29 (CH), 81.28 (C), 80.82 (C), 73.58 (CH), 73.14 (CH), 61.86 (CH_2), 61.85 (CH_2), 45.58 (CH_2), 45.47 (CH_2), 40.20 (CH), 35.49 (CH), 33.19 (CH_2), 29.59 (CH_2), 27.37 (CH_2), 26.13 (CH_2), 17.75 (CH_3), 17.54 (CH_3), 17.19 (CH_3), 17.09 (CH_3). **LRMS** (*m/z, ESI*): 400.1882 $(M+Na)^+$, 291.1746, 273.1637, 105.0688. **HRMS** Calculated for $C_{24}H_{27}NNaO_3$: 400.1883, found 400.1882. $[\alpha]_D^{23}$ = -9 (*c* 0.5, $CHCl_3$), measured from a sample consisting on a 1 : 4 mixture of **4bca** : **4bca'**, obtained from the reaction catalyzed by (*R*)-**Au5** after column chromatography. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).

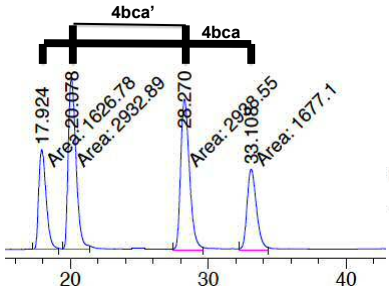


4bca



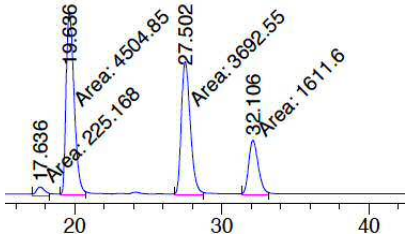
4bca'

Figure S70. Significant nOe's observed for **4bca** and **4bca'**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.924	MM	0.6187	1626.77917	43.82201	17.7300
2	20.078	MM	0.6526	2932.88843	74.90697	31.9650
3	28.270	MM	0.7390	2938.55103	66.27594	32.0267
4	33.108	MM	0.7889	1677.09717	35.42916	18.2784

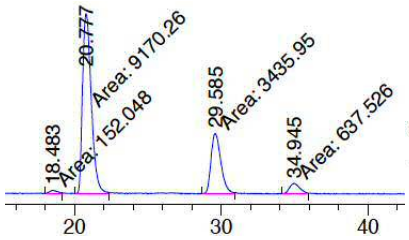
Figure S71. HPLC trace report of a racemic sample of **4bca** : **4bca'** (1 : 1.8 ratio) (Hexane : iPrOH = 90:10), Chiralpak IA-3.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.636	MM	0.6782	225.16817	5.53314	2.2440
2	19.636	MM	0.6344	4504.84619	118.35294	44.8951
3	27.502	MM	0.7123	3692.54956	86.39387	36.7998
4	32.106	MM	0.7609	1611.59766	35.30209	16.0611

4bca (Peak 1 and 4): 76% ee; **4bca'** (Peak 2 and 3): 10% ee

Figure S72. HPLC trace report of a sample from the reaction catalyzed by (*R*)-**Au5** (sample from column chromatography, **4bca** : **4bca'** ratio = 1 : 4). (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 12.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.483	MM	0.6237	152.04834	4.06291	1.1350
2	20.777	MM	0.6909	9170.26367	221.21883	68.4563
3	29.585	MM	0.7751	3435.95190	73.88642	25.6495
4	34.945	MM	0.8243	637.52582	12.88964	4.7592

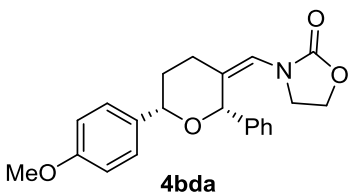
4bca (Peak 1 and 4): 61% ee; **4bca'** (Peak 2 and 3): 45% ee

Figure S73. HPLC trace report of a sample from the reaction catalyzed by (*R,S,S*)-**Au2** (sample from column chromatography, **4bca : 4bca'** ratio = 1 : 15). (Hexane : iPrOH = 90:10), Table 3 main manuscript, entry 8.

3-((*Z*)-((2*S*,6*S*)-6-(4-methoxyphenyl)-2-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one

General Procedure	Catalyst	Manuscript results	React. time (h)	**4bda** : **4bda'**	Yield	ee **4bda**
A[a]	(*R*)-**Au5**	Table 2, entry 13	17	1 : 0	57%	60%
C[19]	**Au18**	-	0.5	1 : 0	65%	-

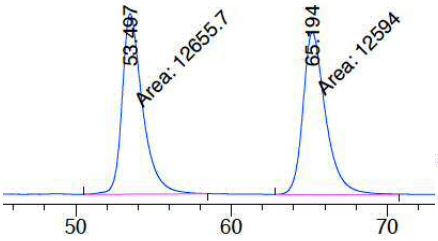
[a] Small amounts of the [2+2] and [2C+2C+2C] cycloadducts were also isolated.



4bda

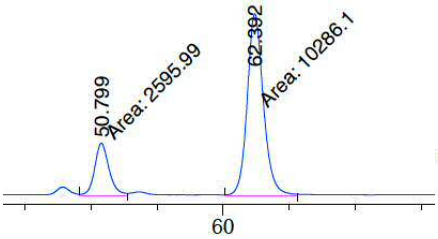
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.36 – 7.27 (m, 5H), 6.88 – 6.80 (m, 2H), 5.96 (d, *J* = 1.3 Hz, 1H), 5.48 (s, 1H), 4.64 (dd, *J* = 10.3, 4.5 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.77 (s, 3H), 3.70 (q, *J* = 8.5 Hz, 1H), 3.35 (q, *J* = 8.6 Hz, 1H), 3.09 (td, *J* = 8.8, 5.5 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.58 – 2.50 (m, 1H), 2.15 – 2.06 (m, 1H), 2.02 – 1.94 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.8 (C), 156.2 (C), 140.5 (C), 135.1 (C), 133.8 (C), 128.1 (CH), 127.8

(CH), 127.4 (CH), 127.0 (CH), 118.5 (CH), 113.6 (CH), 78.9 (CH), 76.6 (CH), 61.8 (CH_2), 55.2 (CH_3), 45.7 (CH_2), 33.2 (CH_2), 28.5 (CH_2). **LRMS** (*m/z, ESI*): 388.15 (M+Na)+, 348.16, 278.14, 261.13, 214.09, 145.07, 117.07. **HRMS** Calculated for $C_{22}H_{23}NNaO_4$: 388.1519, found 388.1521. Mp = 157 – 162 ºC. Enantioselectivities were determined by chiral HPLC analysis on Chiralpak IA at rt, (Hexane : iPrOH = 90:10, 0.5 mL/min). $[\alpha]_D^{23}$ = -1 (*c* 0.5, $CHCl_3$), measured from a pure sample of **4bad** obtained from the reaction catalyzed by (*R*)-**Au5**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	53.497	MM	1.5214	1.26557e4	138.64243	50.1223
2	65.194	MM	1.6839	1.25940e4	124.65340	49.8777

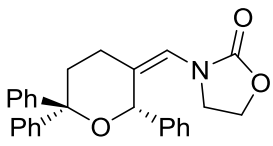
Figure S74. HPLC trace report of a racemic sample of **4bda** (Hexane : iPrOH = 90:10), Chiralpak IA.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.799	MM	1.2489	2595.99097	34.64269	20.1520
2	62.392	MM	1.4190	1.02861e4	120.81602	79.8480

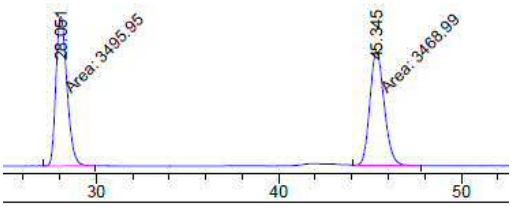
Figure S75. HPLC trace report of a sample of **4bda** obtained from the reaction catalyzed by (*R*)-**Au5** (Hexane : iPrOH = 90:10), Table 2 main manuscript, entry 13, 60% ee.

(S,Z)-3-((2,6,6-triphenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4bda)



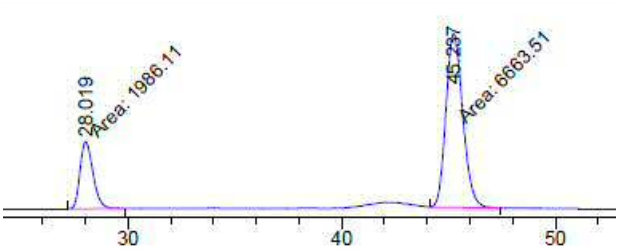
4bda

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.45 (m, 4H), 7.47 – 7.29 (m, 7H), 7.33 – 7.16 (m, 3H), 7.20 – 7.07 (m, 1H), 5.78 (d, *J* = 1.5 Hz, 1H), 5.24 (s, 1H), 3.88 – 3.69 (m, 1H), 3.48 (q, *J* = 8.2 Hz, 1H), 3.19 (q, *J* = 8.0 Hz, 1H), 2.88 – 2.65 (m, 2H), 2.69 – 2.42 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0 (C), 148.1 (C), 144.1 (C), 140.6 (C), 136.9 (C), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.8 (CH), 127.1 (CH), 127.0 (CH), 126.3 (CH), 125.2 (CH), 117.2 (CH), 80.0 (C), 73.8 (CH), 61.7 (CH_2), 45.4 (CH_2), 35.5 (CH_2), 26.5 (CH_2). **LRMS** (*m/z, ESI*): 434.17 $(M+Na)^+$, 394.18, 325.26, 241.09, 193.10, 145.07, 117.07. **HRMS** Calculated for $C_{27}H_{25}NNaO_3$: 434.1727, found 434.1721. Enantioselectivities were determined by chiral HPLC analysis on Chiralpak IA-3 at rt, (Hexane : iPrOH = 90:10, 0.5 mL/min).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.051	MM	0.7010	3495.94629	83.11995	50.1935
2	45.345	MM	0.9124	3468.98828	63.37048	49.8065

Figure S76. HPLC trace report of a racemic sample of **4bda** (Chiralpak IA-3, (Hexane : iPrOH = 90:10, 0.5 mL/min)



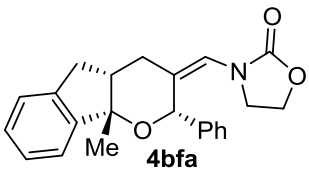
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.019	MM	0.7034	1986.10950	47.05887	22.9618
2	45.237	MM	0.9102	6663.51221	122.01191	77.0382

Figure S77. HPLC trace report of a sample of **4bda** obtained from the reaction catalyzed by (*R, S, S*)-**Au2**

3-((*Z*)-((2*S*,4a*R*,9b*S*)-9b-methyl-2-phenyl-4,4a,5,9b-tetrahydroindeno[1,2-*b*]pyran-3(2*H*)-ylidene)methyl) oxazolidin-2-one (**4bfa**)

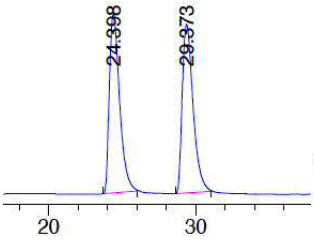
General Procedure	Catalyst	Manuscript result	React. time (h)	Yield	ee **4bfa**
B[a]	(*R,S,S*)-**Au2**	Table 3, entry 11	2	50%	82%
C	**Au18**	-	5	69%	-

[a] Carried out from -78 to -50 ºC. Conversion was not complete (80%).



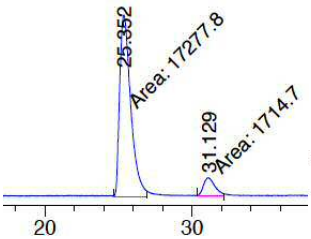
4bfa

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.19 (m, 9H), 5.96 (t, *J* = 1.9 Hz, 1H), 5.69 (s, 1H), 4.08 – 4.00 (m, 1H), 3.85 (q, *J* = 9.2, 8.4 Hz, 1H), 3.41 – 3.31 (m, 2H), 2.92 – 2.85 (m, 1H), 2.79 (dd, *J* = 17.2, 2.1 Hz, 1H), 2.59 – 2.44 (m, 3H), 1.70 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.85 (C), 146.75 (C), 140.86 (C), 140.56 (C), 136.69 (C), 128.34 (CH), 128.33 (CH), 128.02 (CH), 127.96 (CH), 126.96 (CH), 124.75 (CH), 124.38 (CH), 117.01 (CH), 85.04 (C), 73.21 (CH), 61.87 (CH_2), 45.23 (CH_2), 45.11 (CH), 37.92 (CH_2), 34.29 (CH_2), 25.24 (CH_3). **LRMS** (*m/z, ESI*): 384.16 (M+Na)+, 294.08, 257.13, 143.09, 129.07. **HRMS** Calculated for $C_{23}H_{23}NNaO_3$: 384.1570, found 384.1568. Mp = 171-175 ºC. $[\alpha]_D^{23}$ = +66 (*c* 0.5, $CHCl_3$), measured from a pure sample of **4bfa,** obtained from the reaction catalyzed by (*R,S,S*)-**Au2**. Enantioselectivities were determined by chiral HPLC analysis using a Chiralpak IA-3 column, at rt (Hexane : iPrOH = 90:10; 0.5 mL/min).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
3	24.398	BB	0.7467	5497.27051	113.56830	49.8053
4	29.373	BB	0.7907	5468.49609	106.91963	49.5446

Figure S78. HPLC trace report of a racemic sample of **4bfa** (Hexane : iPrOH = 90:10), Chiralpak IA-3.



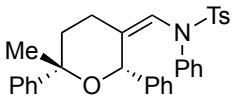
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.352	MM	0.8710	1.72778e4	330.61380	90.9717
2	31.129	MM	0.8841	1714.69702	32.32427	9.0283

Figure S79. HPLC trace report of a sample of **4bfa** obtained with (*R,S,S*)-**Au2** (Hex. : iPrOH = 90:10), Table 3 main manuscript, entry 11, 82% ee

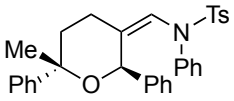
4-Methyl-*N*-((*Z*)-((2*S*,6*S*)-6-methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)-*N*-phenyl benzenesulfonamide (*Z*-**4aaa**), **4-Methyl-*N*-((*E*)-((2*S*,6*S*)-6-methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)-*N*-phenylbenzenesulfonamide** (*E*-**4aaa**), **4-Methyl-*N*-((*Z*)-((2*R*,6*S*)-6-methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)-*N*-phenylbenzenesulfonamide** (*Z*-**4aaa'**) and **4-Methyl-*N*-((*E*)-((2*R*,6*S*)-6-methyl-2,6-diphenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)-*N*-phenylbenzenesulfonamide** (*E*-**4aaa'**)

General procedure	Catalyst	Manuscript result	React. time (h)	*Z*-**4aaa** : *E*-**4aaa** : *Z*-**4aaa'** : *E*-**4aaa'** [a]	Yield[b]	ee *Z*-**4aaa**	ee *Z*-**4aaa'**	ee *E*-**4aaa**	ee *E*-**4aaa'**
A	(*R*)-**Au5**	reference 21	23	14 : 1 : 3 : 0	15%	81%	30%		
B	(*S,R,R*)-**Au2**	Table 3, entry 12	1	5 : 5 : 1 : 1	92%	89%	74%	94%	25%
C[c]	**Au18**	-	0.5	4 : 5 : 1 : 1	85%	-		-	

[a] Ratios obtained by ^{1}H-NMR of the crude reaction mixtures. [b] Combined yield of isomers. [c] The reaction was carried out at -70 ºC.

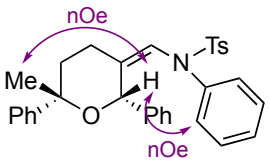


Z-**4aaa**

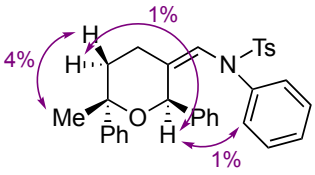


Z-**4aaa'**

Characterization data of *Z*-4aaa : *Z*-4aaa (deduced from a *Z*-**4aaa** : *Z*-**4aaa'** mixture obtained in the reaction catalyzed by **Au5**). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.03 (m, 16.42H), 6.97 (t, *J* = 7.7 Hz, 0.58H), 6.64 (d, *J* = 6.6 Hz, 1.42H), 6.45 (d, *J* = 8.0 Hz, 0.58H), 6.14 – 6.11 (m, 1H), 5.54 (s, 0.71H), 4.98 (s, 0.29H), 2.72 – 2.65 (m, 0.29H), 2.64 – 2.56 (m, 0.71H), 2.42 (s, 2.13H), 2.38 (s, 0.87H), 2.38 – 2.26 (m, 2H), 2.14 – 2.07 (m, 0.29H), 2.02 – 1.94 (m, 0.71H), 1.52 (s, 2.13H), 1.38 (s, 0.87H). **^{13}C NMR** (126 MHz, CDCl3) δ 149.30 (C), 147.37 (C), 143.85 (C), 143.72 (C), 142.37 (C), 140.33 (C), 140.09 (C), 140.03 (C), 139.76 (C), 139.71 (C), 134.48 (C), 134.36 (C), 129.48 (CH), 129.37 (CH), 128.56 (CH), 128.53 (CH), 128.46 (CH), 128.39 (CH), 128.38 (CH), 128.33 (CH), 128.21 (CH), 128.01 (CH), 127.98 (CH), 127.88 (CH), 127.72 (CH), 127.63 (CH), 127.04 (CH), 127.03 (CH), 126.96 (CH), 126.80 (CH), 126.58 (CH), 126.32 (CH), 125.21 (CH), 124.80 (CH), 120.81 (CH), 120.50 (CH), 76.45 (C), 75.36 (C), 73.74 (CH), 73.05 (CH), 37.96 (CH_2), 35.17 (CH_2), 32.88 (CH_3), 28.37 (CH_3), 26.24 (CH_2), 26.23 (CH_2), 21.71 (CH_3), 21.67 (CH_3).

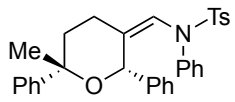


Z-**4aaa**

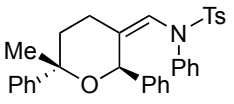


Z-**4aaa'**

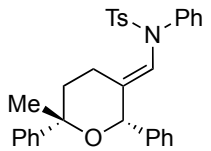
Figure S80. Significant nOe's observed for *Z*-**4aaa** and *Z*-**4aaa'**.



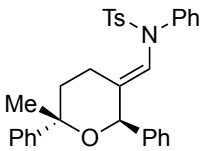
Z-**4aaa**



Z-**4aaa'**



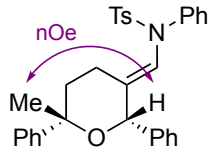
E-**4aaa**



E-**4aaa'**

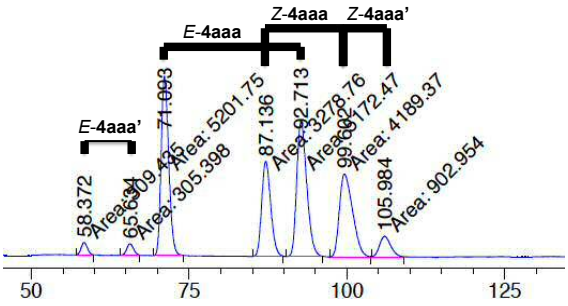
Characterization data of *Z*-4aaa : *E*-4aaa : *Z*-4aaa' : *E*-4aaa' (deduced from a 6:5:1:1 mixture of *Z*-**4aaa** : *E*-**4aaa** : *Z*-**4aaa'** : *E*-**4aaa'** obtained in the reaction with (*R,S,S*)-**Au1** (Scheme 2 main manuscript) after column chromatography) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 – 6.92 (m, 17.86H), 6.64 (d, *J* = 6.8 Hz, 1H), 6.45 (d, *J* = 8.7 Hz, 0.14H), 6.13 (s, 0.57H), 5.54 (s, 0.5H), 5.41 (s, 0.36H), 5.40 (s, 0.36H), 5.28 (s, 0.07H), 4.98 (s, 0.07H), 4.92 (s, 0.07H), 2.74 – 2.65 (m, 0.14H), 2.65 – 2.51 (m, 0.86H), 2.42 (s, 1.5H), 2.37 (s, 1.08H), 2.36 – 2.21 (m, 1.92H), 2.12 (s, 0.07H), 2.03 – 1.92 (m, 0.93H), 1.84 (td, *J* = 13.2, 4.0 Hz, 0.07H), 1.75 – 1.67 (m, 0.43H), 1.64 (s, 1.08H), 1.52 (s, 1.5H), 1.42 (s, 0.21H), 1.38 (s, 0.21H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.44 (C), 148.84 (C), 144.48 (C), 143.98 (C), 143.90 (C), 143.84 (C), 142.48 (C), 141.62 (C), 141.40 (C),

140.50 (C), 140.45 (C), 140.21 (C), 140.15 (C), 139.88 (C), 139.83 (C), 139.35 (C), 139.33 (C), 134.59 (C), 134.47 (C), 134.16 (C), 134.11 (C), 129.57 (CH), 129.46 (CH), 129.44 (CH), 129.42 (CH), 129.08 (CH), 128.91 (CH), 128.65 (CH), 128.62 (CH), 128.55 (CH), 128.48 (CH), 128.45 (CH), 128.42 (CH), 128.30 (CH), 128.22 (CH), 128.18 (CH), 128.10 (CH), 128.07 (CH), 127.97 (CH), 127.93 (CH), 127.81 (CH), 127.72 (CH), 127.18 (CH), 127.12 (CH), 127.05 (CH), 127.00 (CH), 126.96 (CH), 126.89 (CH), 126.67 (CH), 126.65 (CH), 126.41 (CH), 126.10 (CH), 125.30 (CH), 124.88 (CH), 124.61 (CH), 124.53 (CH), 123.89 (CH), 120.89 (CH), 120.58 (CH), 77.36 (CH), 76.44 (C), 75.94 (C), 75.57 (CH), 75.35 (C), 74.62 (CH), 73.73 (CH), 73.04 (CH), 53.52 (CH_2), 37.88 (CH_2), 36.26 (CH_2), 35.09 (CH_2), 33.80 (CH_2), 33.71 (CH_3), 32.79 (CH_3), 28.28 (CH_3), 26.12 (CH_2), 23.70 (CH_3), 23.30 (CH_2), 22.75 (CH_2), 21.59 (CH_3), 21.54 (CH_3). **LRMS** (*m/z, ESI*): 532.1921 $(M+Na)^+$, 374.1225, 263.1419, 218.0968. **HRMS** Calculated for $C_{32}H_{32}NO_3S$: 510.2097, found 510.2095. Mp = 90 – 125 ºC. $[\alpha]_D^{23}$ = +51 (*c* 0.5, $CHCl_3$), measured in a sample consisting of a 7 : 5 : 1 : 1 mixture of ***Z*-4aaa**, ***E*-4aaa**, ***Z*-4aaa'** and ***E*-4aaa' ,** obtained from the reaction catalyzed by (*R,S,S*)-**Au1**. Enantioselectivities were determined by chiral HPLC analysis using Chiralpak IE-3 (for ***Z*-4aaa, *E*-4aaa** and ***E*-4aaa'**) and IA-3 (for ***Z*-4aaa**') columns, at rt (Hexane : iPrOH = 97:3; 0.5 mL/min).



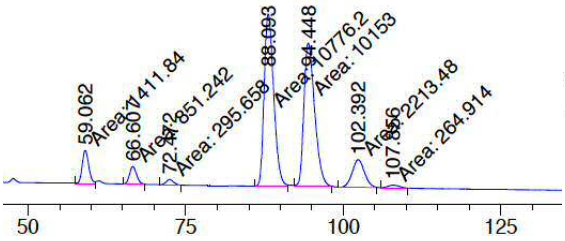
***E*-4aaa**

Figure S81. Significant nOe's observed for ***E*-4aaa**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	58.372	MM	1.1674	309.43460	4.41766	1.5983
2	65.634	MM	1.2673	305.39755	4.01643	1.5775
3	71.093	MM	1.3923	5201.75049	62.26762	26.8684
4	87.136	MM	1.6539	3278.76147	33.04006	16.9356
5	92.713	MM	1.8495	5172.47119	46.61037	26.7171
6	99.602	MM	2.4212	4189.36572	28.83774	21.6391
7	105.984	MM	2.0748	902.95386	7.25346	4.6640

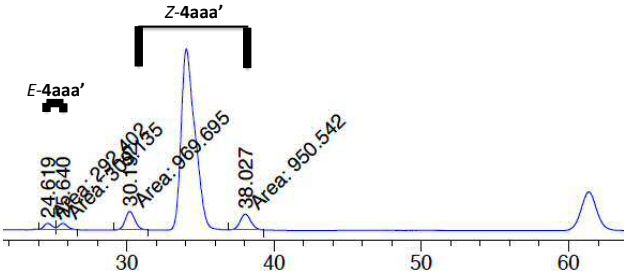
Figure S82. HPLC trace report of a racemic sample of ***Z*-4aaa** : ***E*-4aaa** : ***Z*-4aaa'** : ***E*-4aaa'** (9 : 15 : 2 : 1 ratio, obtained from the column chromatography of the reaction catalyzed by **Au18**), (Hexane : iPrOH = 97:3), Chiralpak IE-3.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	59.062	MM	1.1973	1411.84229	19.65306	5.4372
2	66.607	MM	1.3259	851.24188	10.69986	3.2783
3	72.472	MM	1.4678	295.65781	3.35705	1.1386
4	88.093	MM	1.7529	1.07762e4	102.46114	41.5005
5	94.448	MM	1.9817	1.01530e4	85.38801	39.1008
6	102.392	MM	2.2436	2213.48413	16.44268	8.5244
7	107.856	MM	2.3244	264.91376	1.89949	1.0202

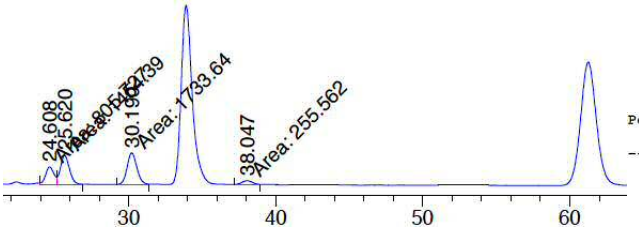
***Z*-4aaa** (Peak 4 and 6): 89% ee (calculated using the ee of (*Z*)-**4aaa'** obtained in Chiralpak IA-3, see below)
***E*-4aaa** (Peak 3 and 5): 94% ee
***E*-4aaa'** (Peak 1 and 2): 25% ee

Figure S83. HPLC trace report of a sample obtained from the reaction catalyzed by (*S,R,R*)-**Au2** (***Z*-4aaa** : ***E*-4aaa** : ***Z*-4aaa'** : ***E*-4aaa'** ratio = 5 : 5 : 1 : 1), (Hexane : iPrOH = 97:3), Table 3 main manuscript, entry 12.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.619	MF	0.6592	292.40219	7.39307	11.5951
2	25.640	FM	0.6995	309.13483	7.36520	12.2586
3	30.192	MM	0.7598	969.69489	21.27077	38.4529
4	38.027	MM	0.8633	950.54156	18.35089	37.6934

Figure S84. HPLC trace report of a racemic sample of *Z*-**4aaa** : *E*-**4aaa** : *Z*-**4aaa'** : *E*-**4aaa'** (9 : 15 : 2 : 1; Hexane : iPrOH = 97:3), Chiralpak IA-3.



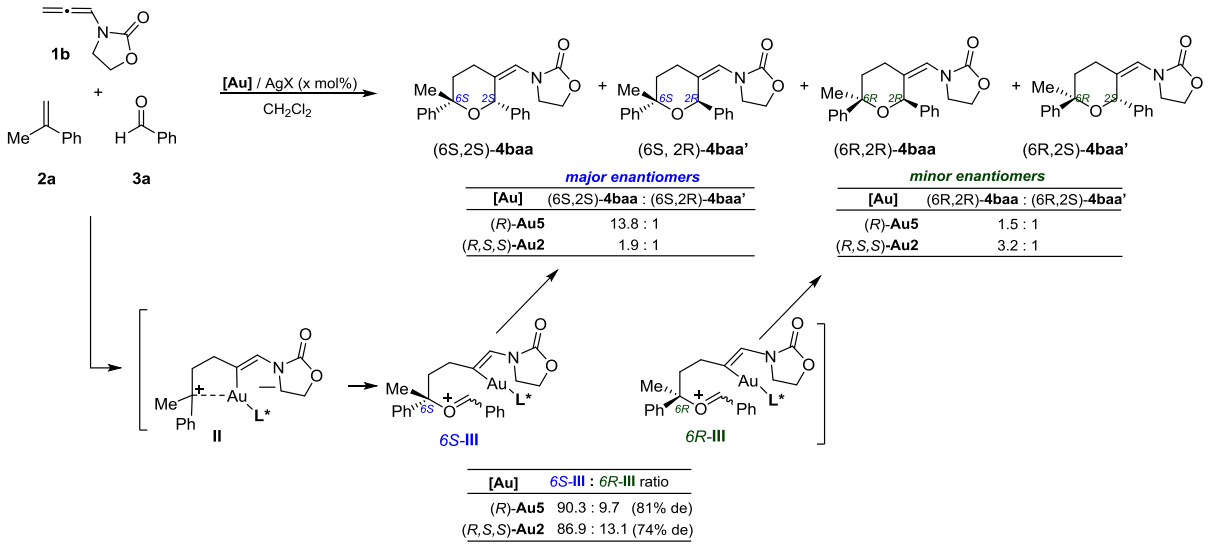
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.608	MF	0.6587	805.72717	20.38813	18.9613
2	25.620	FM	0.7137	1454.39209	33.96206	34.2265
3	30.190	MM	0.7738	1733.64050	37.33979	40.7981
4	38.047	MM	0.8713	255.56165	4.88847	6.0142

Z-**4aaa'** (Peak 3 and 5): 74% ee

Figure S85. HPLC trace report of a *Z*-**4aaa** : *E*-**4aaa** : *Z*-**4aaa'** : *E*-**4aaa'** (9 : 1 5:2:1) with (*S,R,R*)-**Au2** (Hexane : iPrOH = 97:3), Table 3 main manuscript, entry 12.

Analysis of the diastereomeric excess of the putative formal intermediate of type III

(exemplified for the model reaction of **1b**, **2a** and **3a**)



major enantiomers	
[Au]	(6S,2S)-**4baa** : (6S,2R)-**4baa'**
(*R*)-**Au5**	13.8 : 1
(*R,S,S*)-**Au2**	1.9 : 1

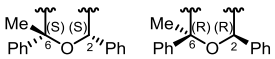
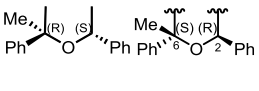
minor enantiomers	
[Au]	(6R,2R)-**4baa** : (6R,2S)-**4baa'**
(*R*)-**Au5**	1.5 : 1
(*R,S,S*)-**Au2**	3.2 : 1

[Au]	*6S*-**III** : *6R*-**III** ratio
(*R*)-**Au5**	90.3 : 9.7 (81% de)
(*R,S,S*)-**Au2**	86.9 : 13.1 (74% de)

Case 1: Table 1 main manuscript, entry 10, reaction carried out by (*R*)-**Au5**/AgNTf$_2$ at –70 ºC

(R)-**Au5** / AgNTf2
Experimental results
(table 1, entry 10, -70ºC):
Global dr = 9:1
2,6-cis: 87% ee
2,6-trans: 22% ee

- 90 (2,6-*cis*) — 87% ee (er =93.5 : 6.5) → 84.2 (6S,2S) & 5.8 (6R,2R)
- 10 (2,6- — 22% ee (er = 61 :39) →
  - 6.1 (6R,2S) & 3.9 (6S,2R) **Option 1**
  - or
  - 6.1 (6S,2R) & 3.9 (6R,2S) **Option 2**

Option 1:
- 84.2 (6S,2S) + 3.9 (6S,2R) } *dr* = 22 : 1
- 5.8 (6R,2R) + 6.1 (6R,2S) } *dr* = 1 : 1

Major enantiomers of both 2,6-cis and 2,6-trans isomers are of opposite configuration at C6 => X **Does NOT fit with X-Ray data**

de int. **III** = 88.1 (6S) - 11.9 (6R) = 76.2% de

Option 2
- 84.2 (6S,2S) + 6.1 (6S,2R) } *dr* = 13.8 : 1
- 5.8 (6R,2R) + 3.9 (6R,2S) } *dr* = 1.5 : 1

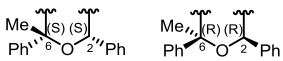
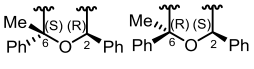
Major enantiomers of both isomers (i.e 6R,2R and 6R,2S) with the same configuration at C6 => **Fits with X-Ray data.**

de int. **III** = 90.3 (6S) - 9.7 (6R) = 80.6% de de

Case 2: Table 1 main manuscript, entry 2, reaction carried out by (*R,S,S*)-**Au2**/AgNTf$_2$ at –78 ºC

(*R,S,S*)-**Au2** / AgNTf$_2$
Experimental results
(table 1, entry 2, -78ºC):
Global *dr* = 2:1
2,6-cis: 70% ee
2,6-trans: 81% ee

- 67 (2,6-*cis*) — 70% ee (er =85:15) → 57.0 (6S,2S) & 10.0 (6R,2R)
- 33 (2,6- — 81% ee (er = 90.5: 9.5) →
  - 29.9 (6R,2S) & 3.1 (6S,2R) **Option 1**
  - or
  - 29.9 (6S,2R) & 3.1 (6R,2S) **Option 2**

Option 1:
- 57.0 (6S,2S) + 3.1 (6S,2R) } *dr* = 18 : 1
- 10.0 (6R,2R) + 29.9 (6R,2S) } *dr* = 1 : 3

Major enantiomers of both 2,6-cis and 2,6-trans isomers are of opposite configuration at C6 => X **Does NOT fit with X-Ray data**

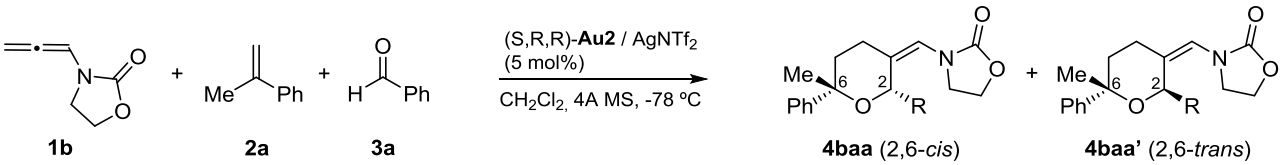
de int. **III** = 60.1 (6S) / 39.9 (6R) = 20.2% de

Option 2
- 57.0 (6S,2S) + 29.9 (6S,2R) } *dr* = 1.9 : 1
- 10.0 (6R,2R) + 3.1 (6R,2S) } *dr* = 3.2 : 1

Major enantiomers of both isomers (i.e 6R,2R and 6S,2R) with the same configuration at C6 => **Fits with X-Ray data.**

de int. **III** = 86.9 (6S) / 13.1 (6R) =73.8%

Effect of the number of equivalents of aldehyde on the selectivity of the process



1b **2a** **3a** **4baa** (2,6-*cis*) **4baa'** (2,6-*trans*)

equiv. **2a**	equiv. **3a**	Catalyst (X mol%)	Conv.	yield	**4baa** : **4baa'**	ee, **4baa**	ee **4baa'**
2	10	(*S,R,R*)-**Au2** (5)	100%	97%	2 : 1	70%	81%
2	5	(*S,R,R*)-**Au2** (5)	100%	90%	1.7 : 1	66%	79%
1.2	2	(*S,R,R*)-**Au2** (5)	100%	87%	1.5 : 1	59%	75%
2	10	(*S*)-**Au5** (10)	100%	80%	9 : 1	87%	22%
2	5	(*S*)-**Au5** (10)	100%	79%	7 : 1	83%	21%
1.2	2	(*S*)-**Au5** (10)	100%	78%	7 : 1	82%	11%

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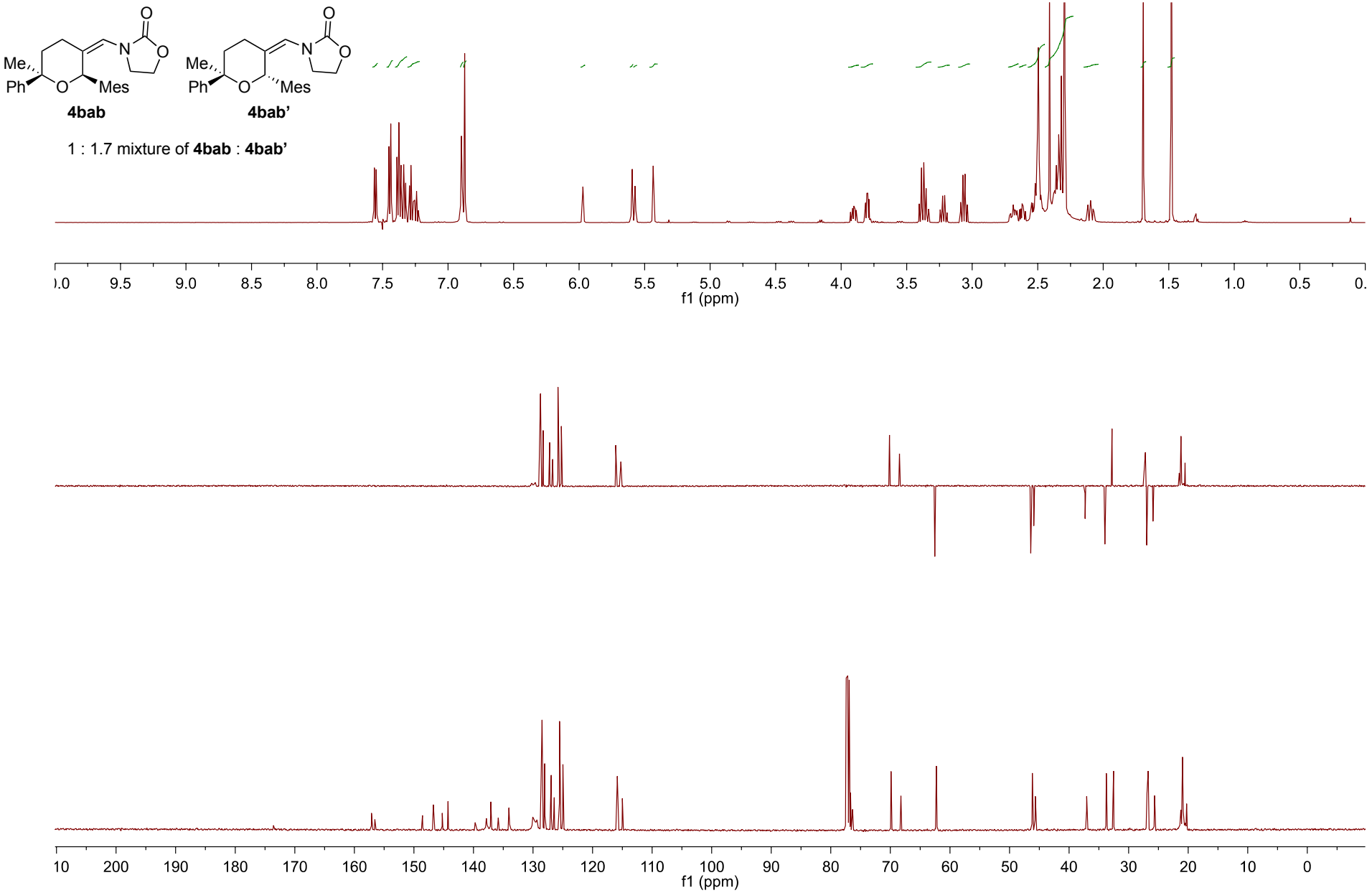
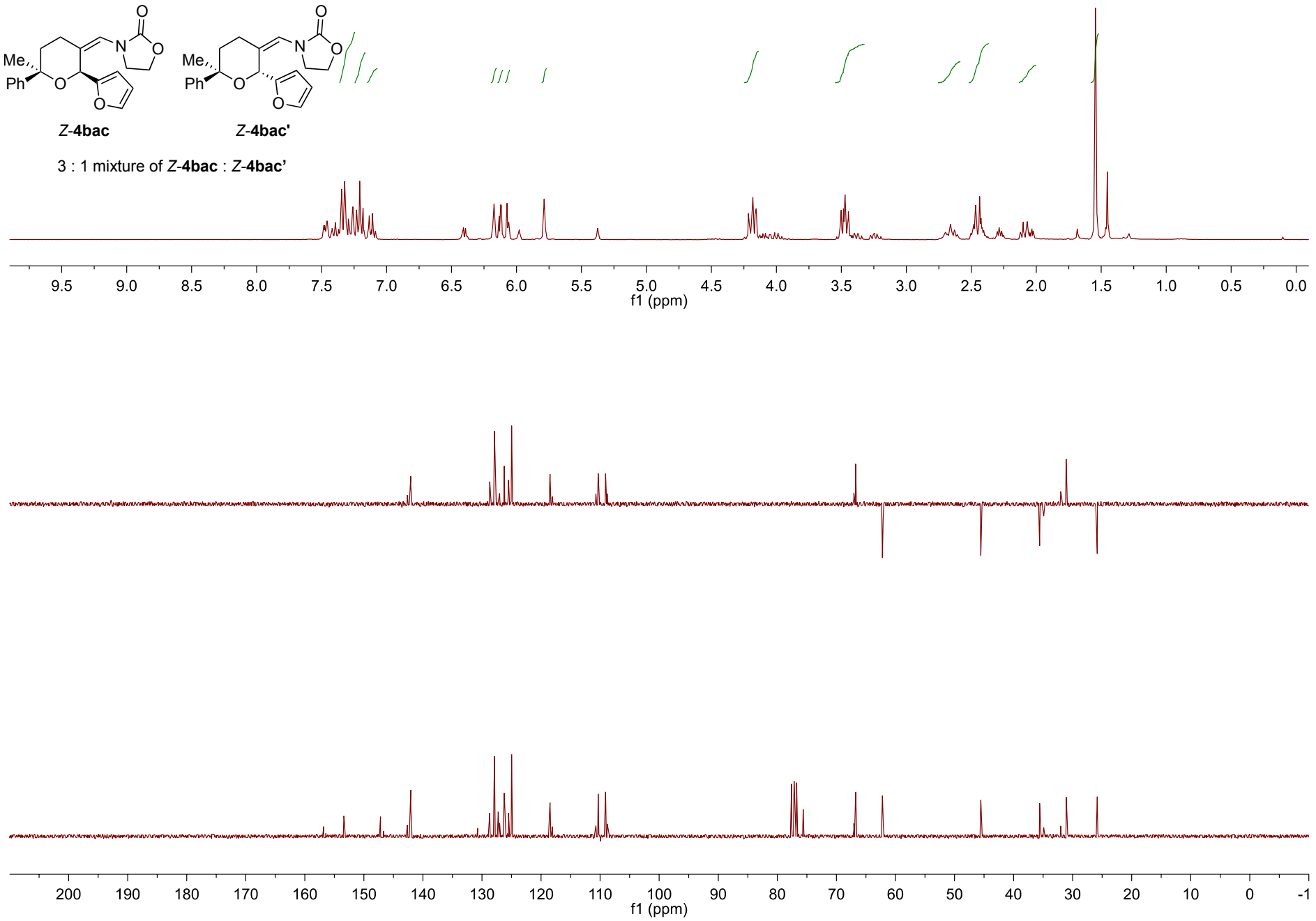
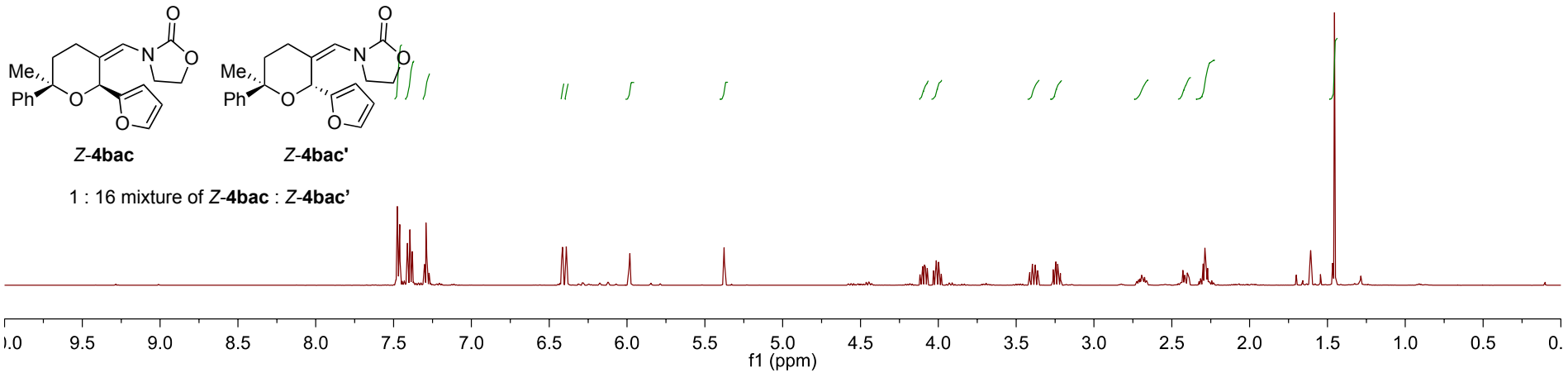
NMR Spectra

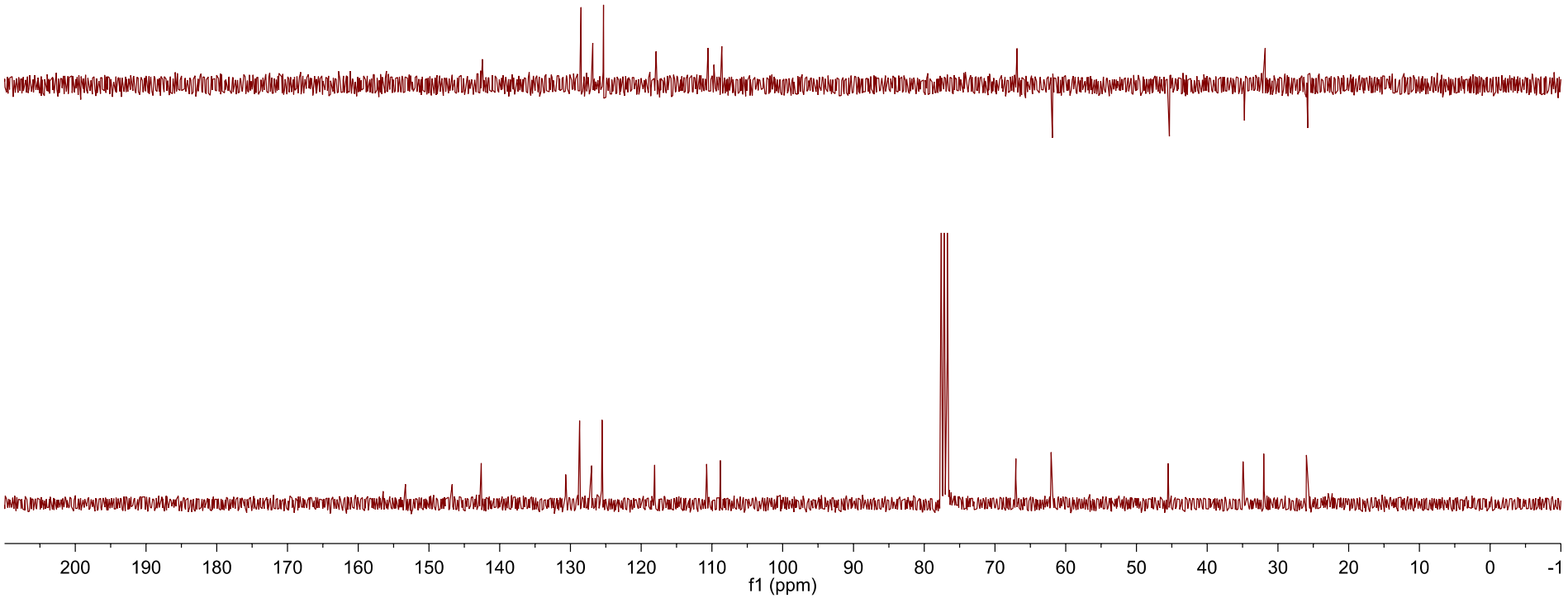


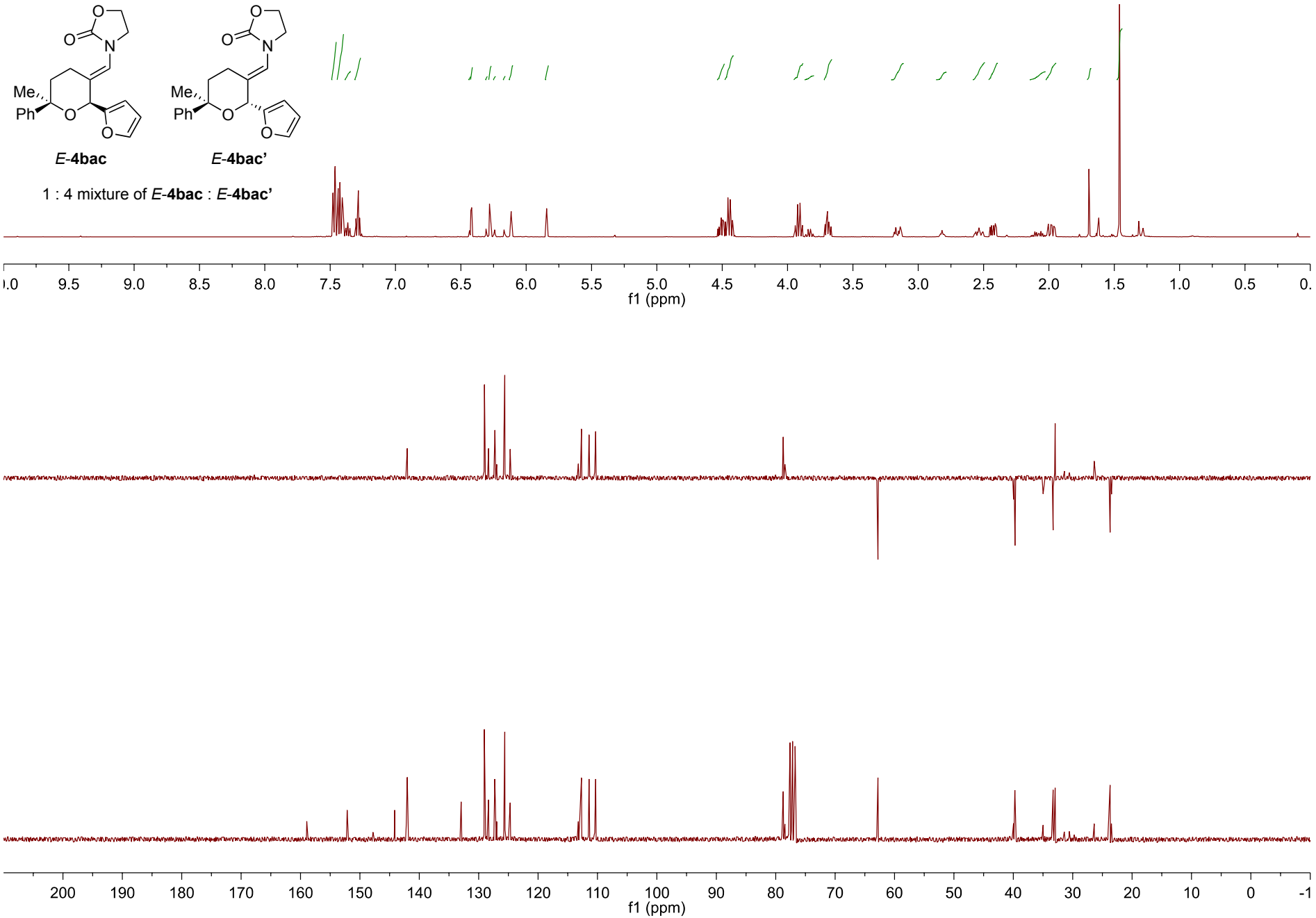

Me
Ph
O
N
O
O
O
Me
Ph
O
N
O
O
O
Z-4bac
Z-4bac'
3 : 1 mixture of Z-4bac : Z-4bac'
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

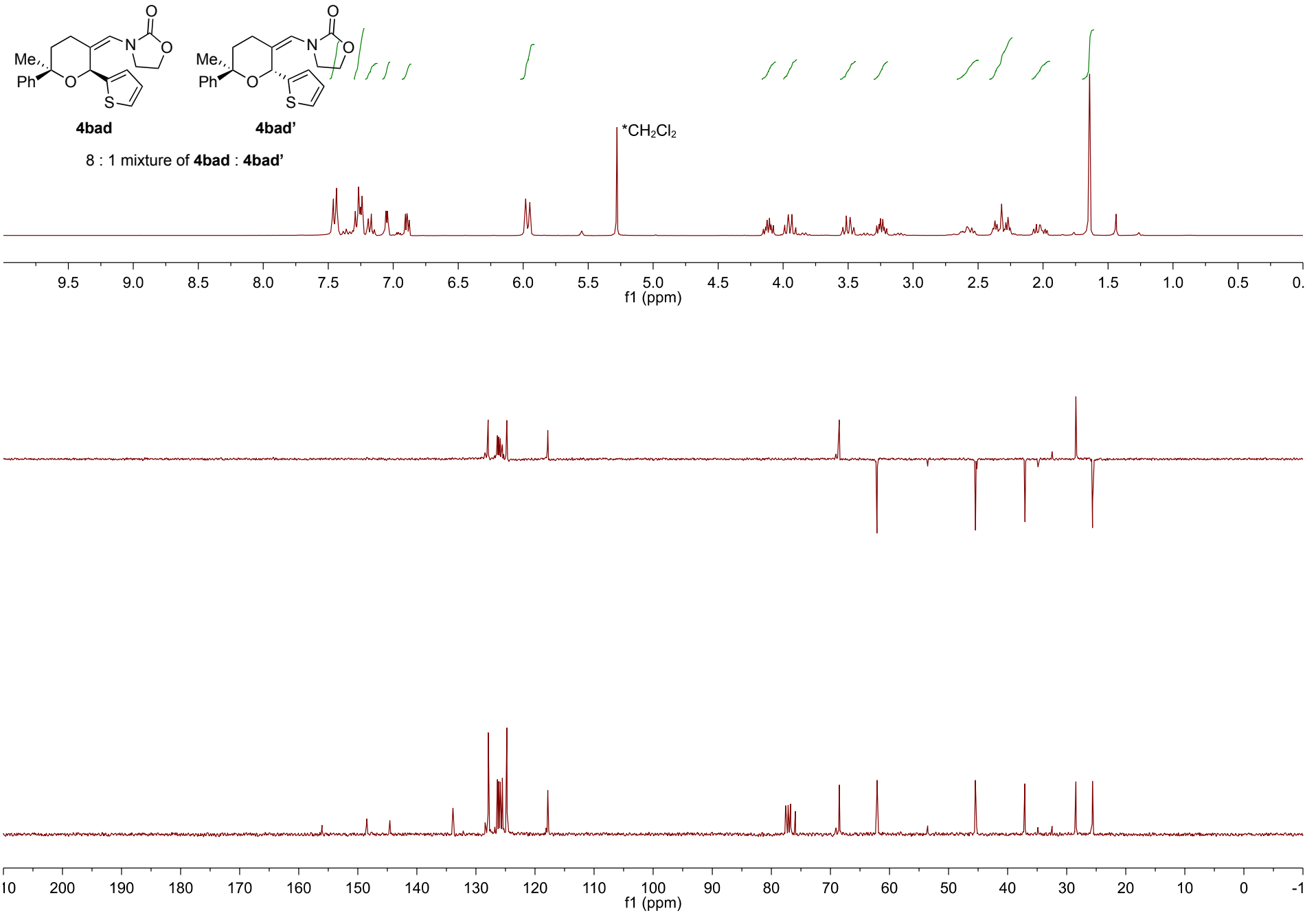


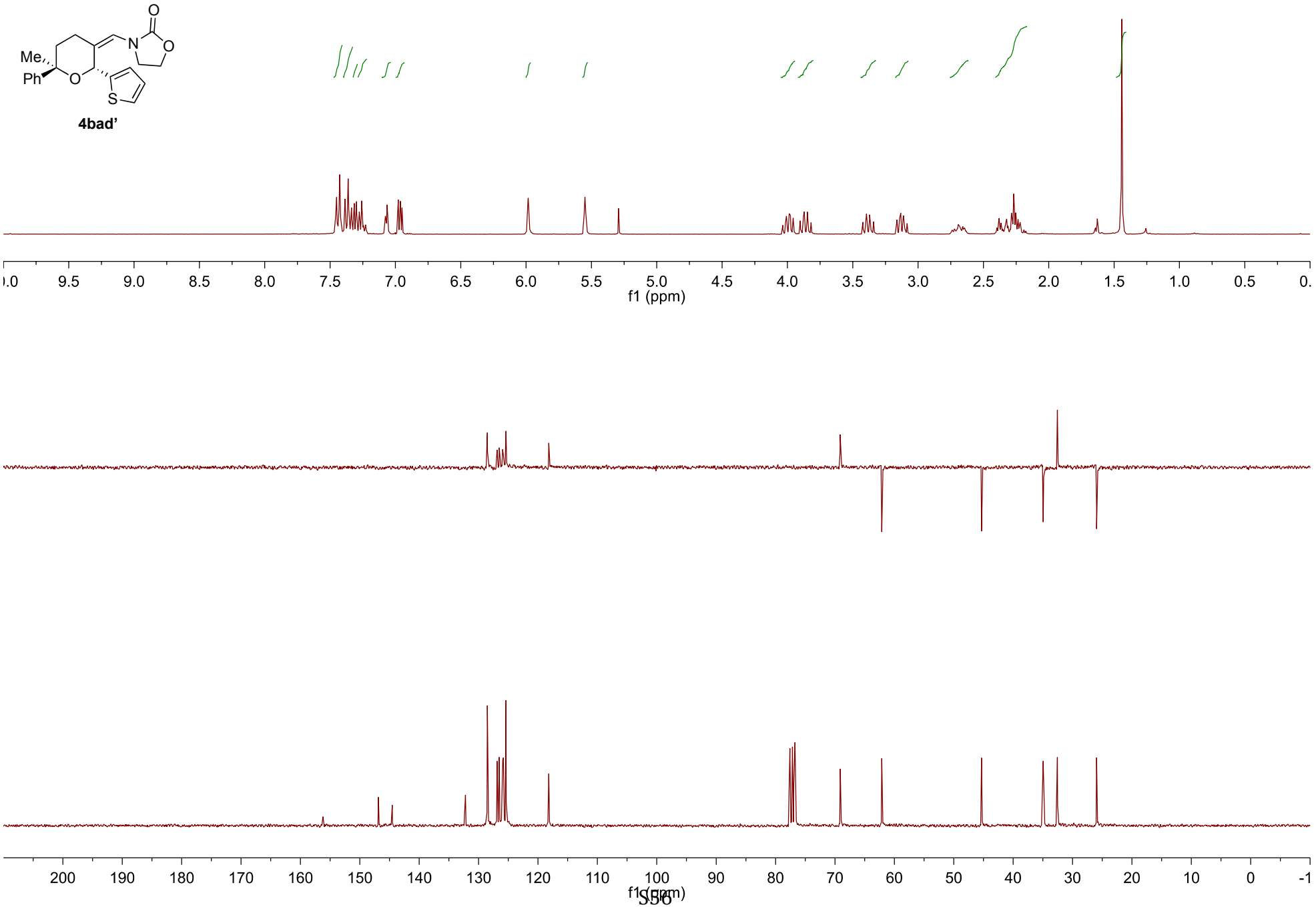
Z-**4bac** *Z*-**4bac'**

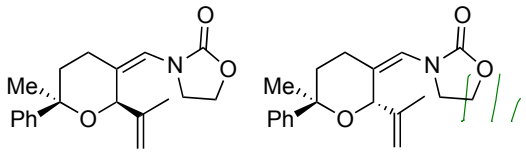
1 : 16 mixture of *Z*-**4bac** : *Z*-**4bac'**




Me
Ph
O
N
O
O
E-4bac
E-4bac'
1 : 4 mixture of E-4bac : E-4bac'
f1 (ppm)
f1 (ppm)


Me
Ph
O
N
O
S
4bad
4bad'
8 : 1 mixture of 4bad : 4bad'
*CH2Cl2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

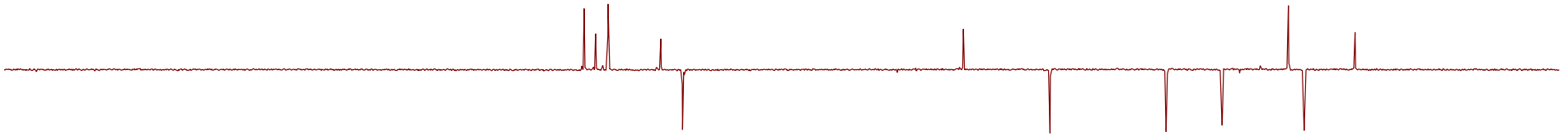

Me
Ph
O
N
O
O
S
4bad'
f1 (ppm)
f1 (ppm)

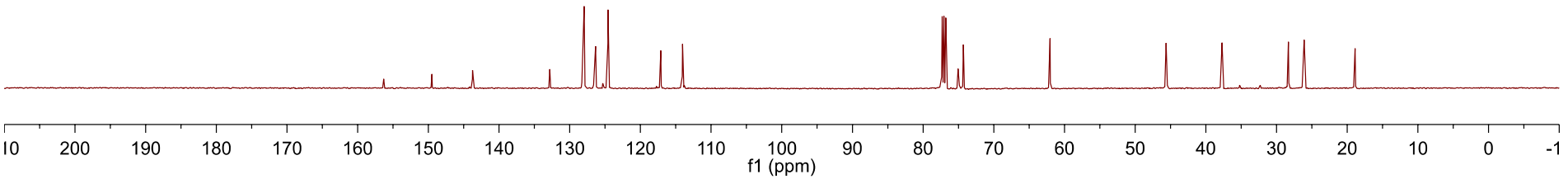


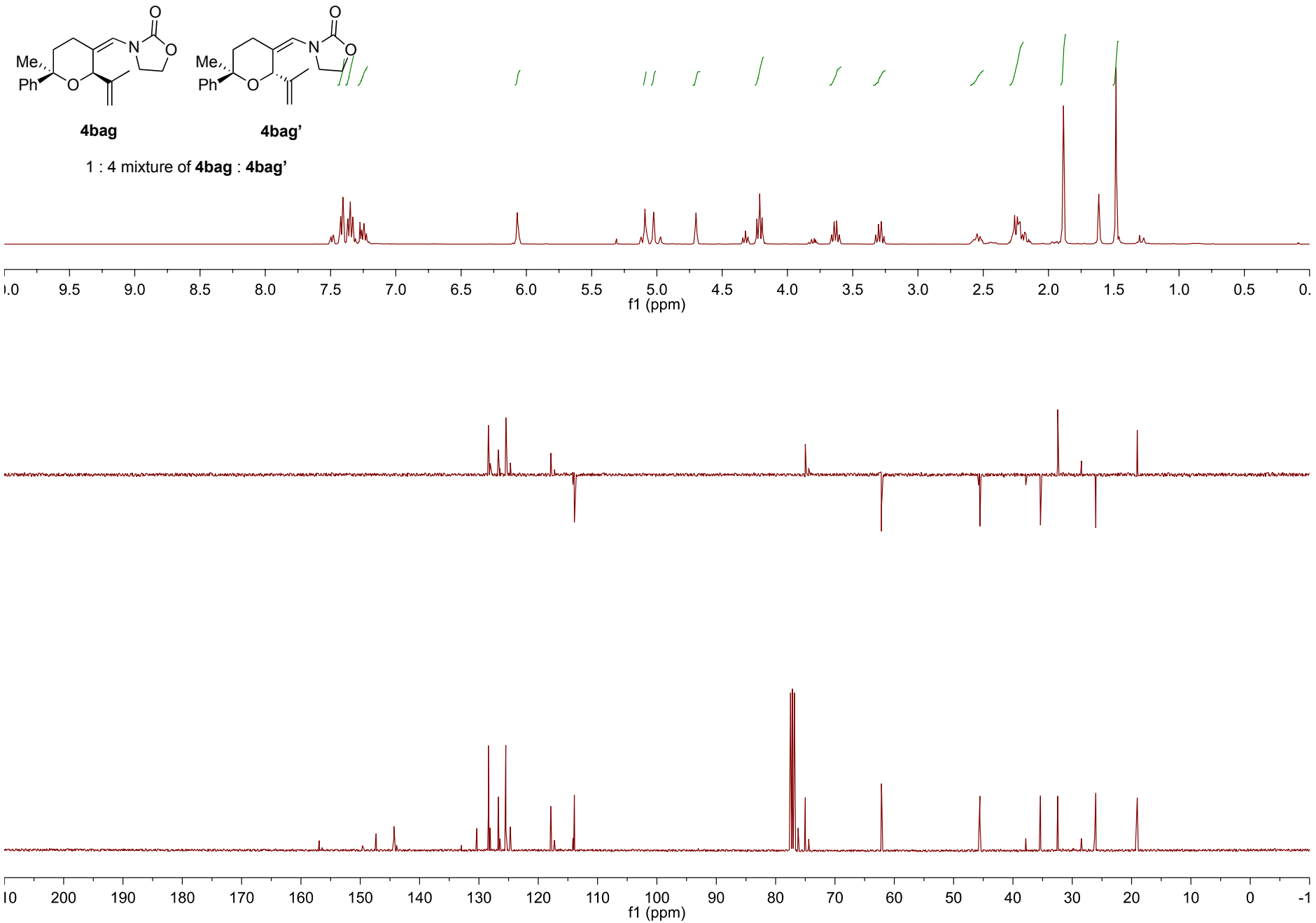
4bag

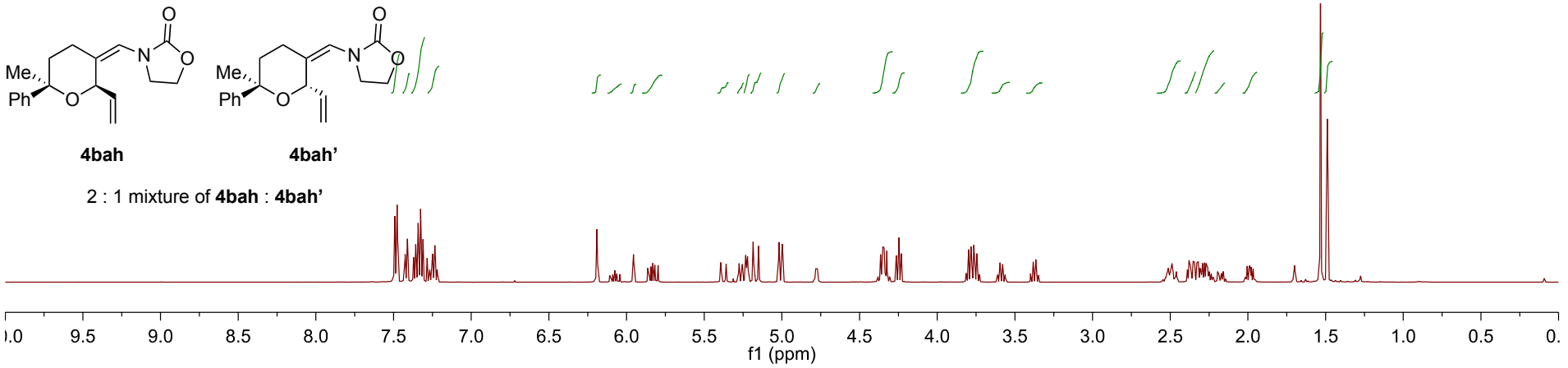
4bag'

16 : 1 mixture of **4bag** : **4bag'**



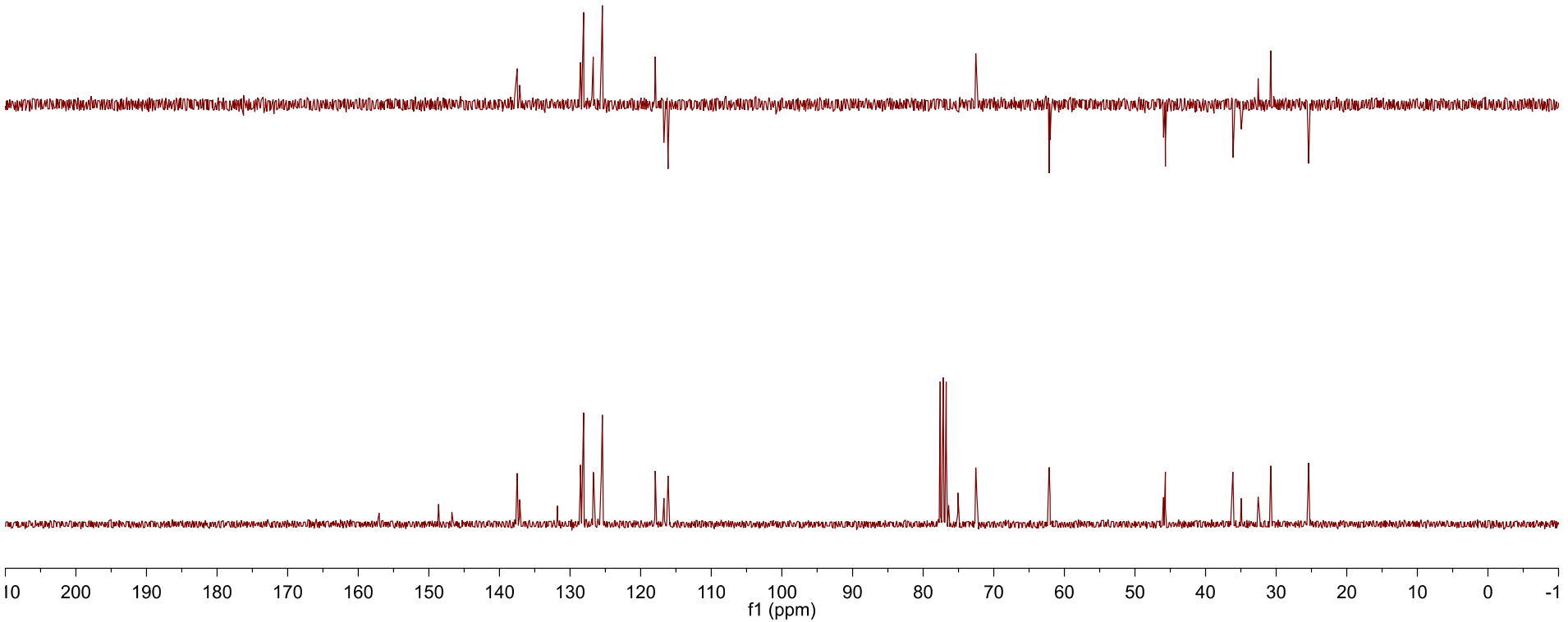


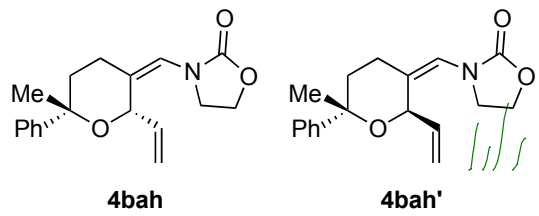

Me
Ph
O
N
O
O
Me
Ph
O
N
O
O
4bag
4bag'
1 : 4 mixture of 4bag : 4bag'
f1 (ppm)
f1 (ppm)



4bah **4bah'**

2 : 1 mixture of **4bah** : **4bah'**

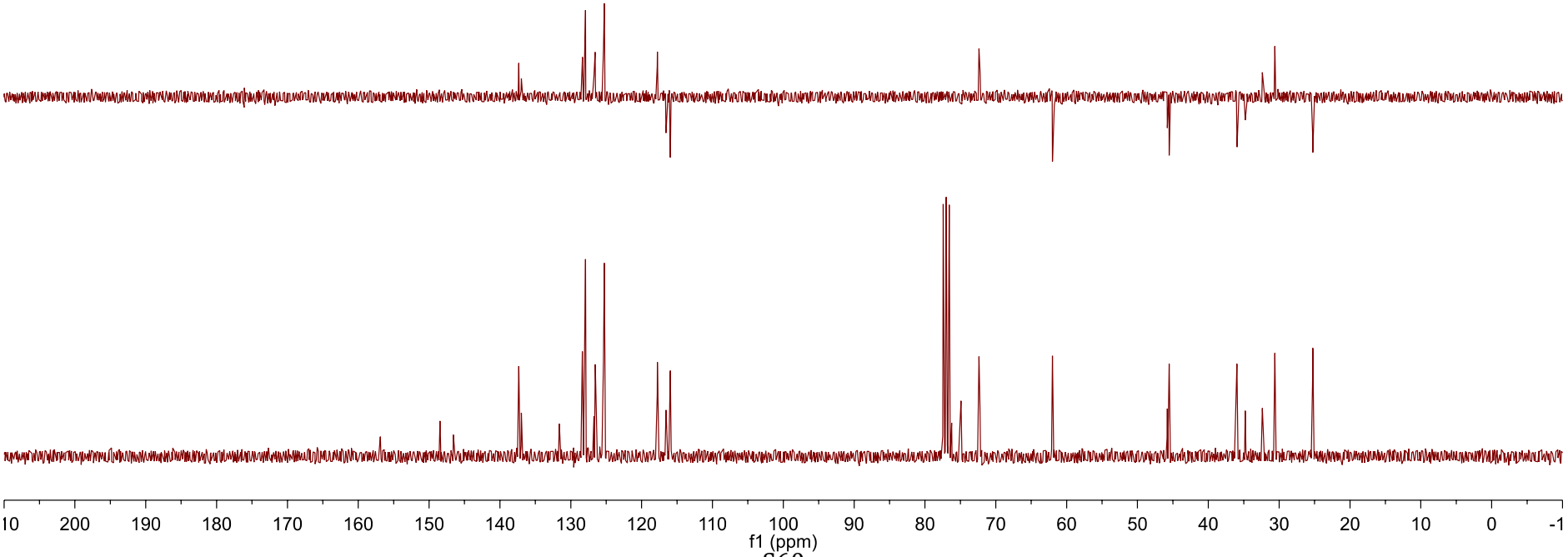


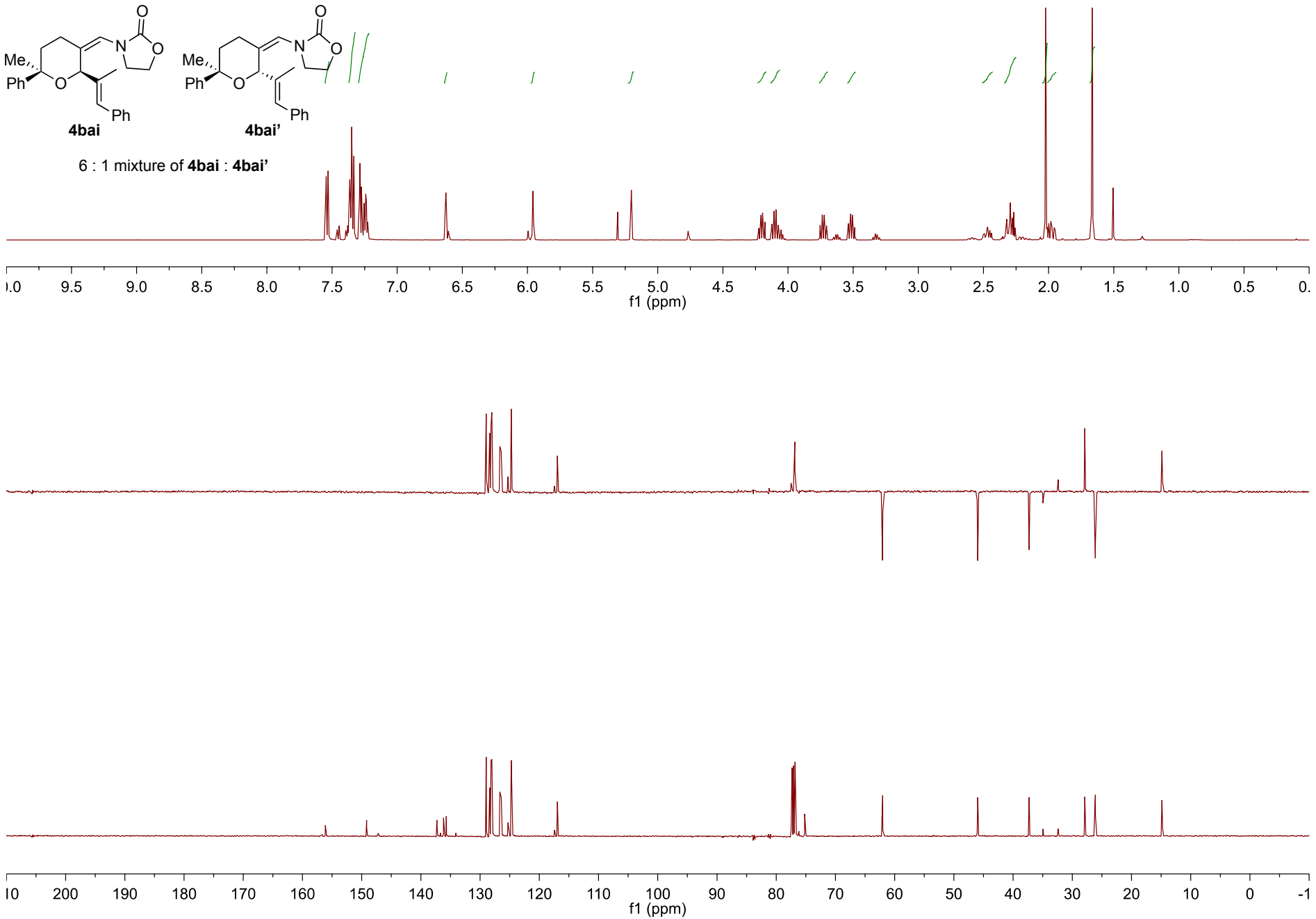


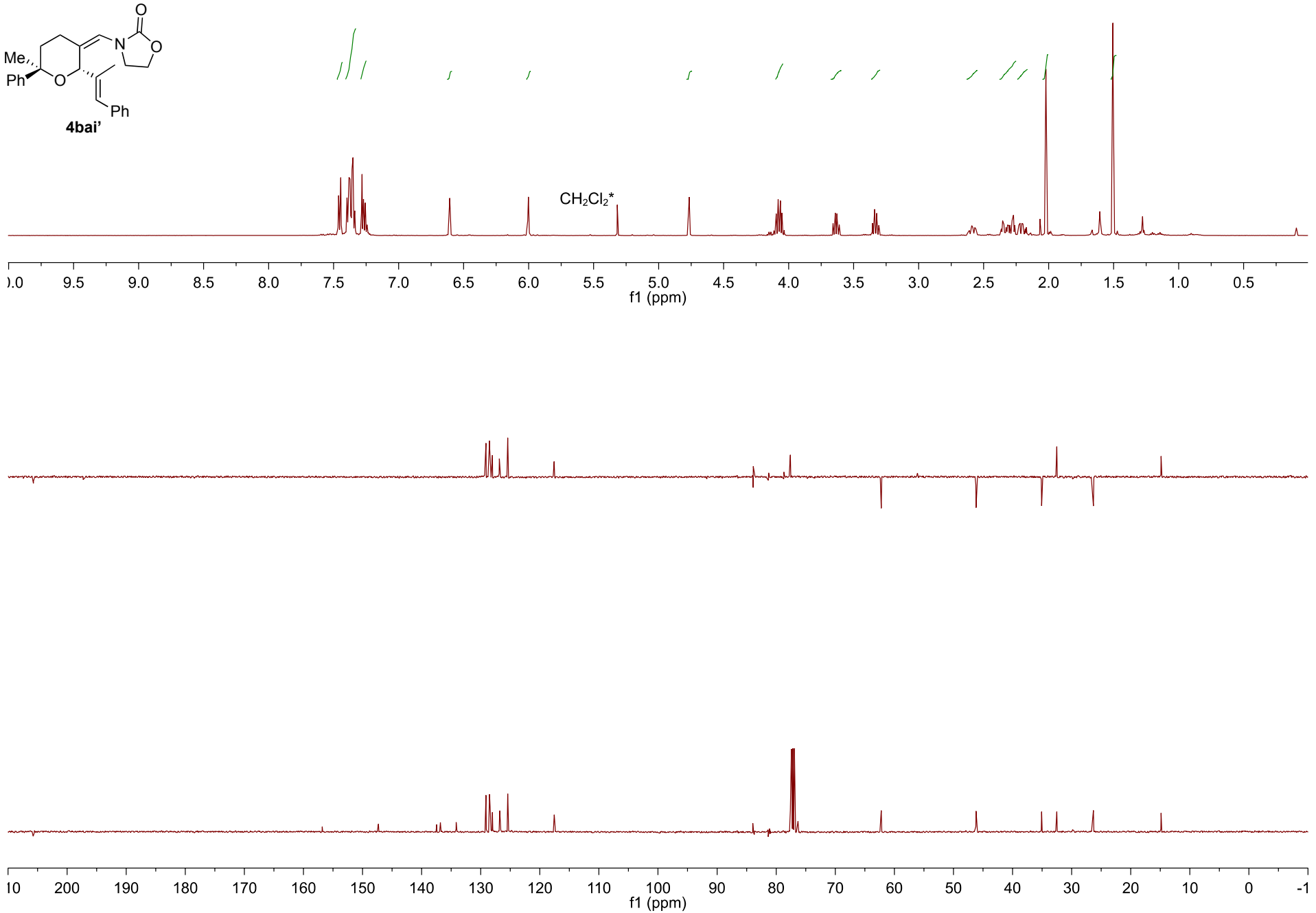
4bah

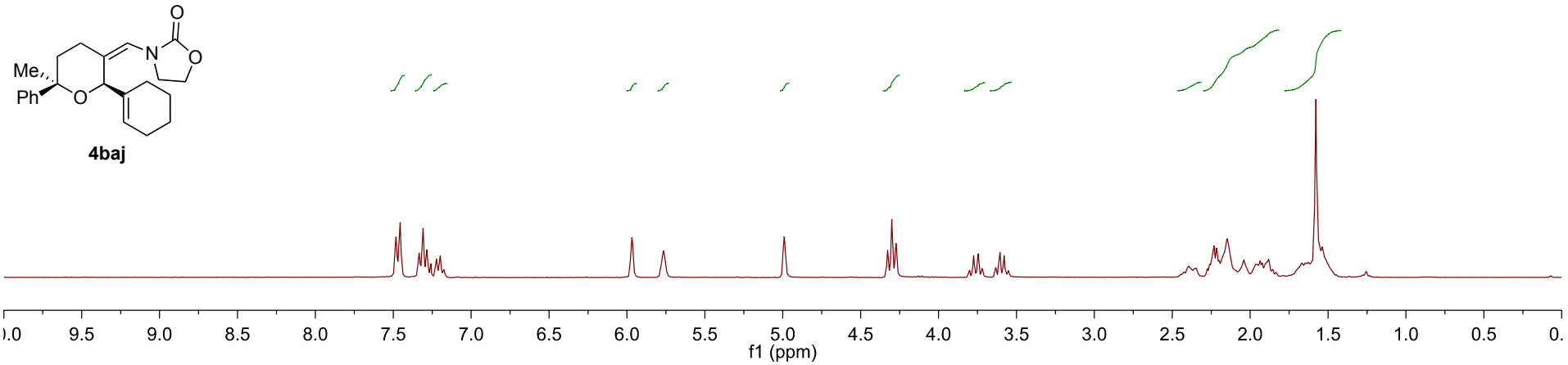
4bah'

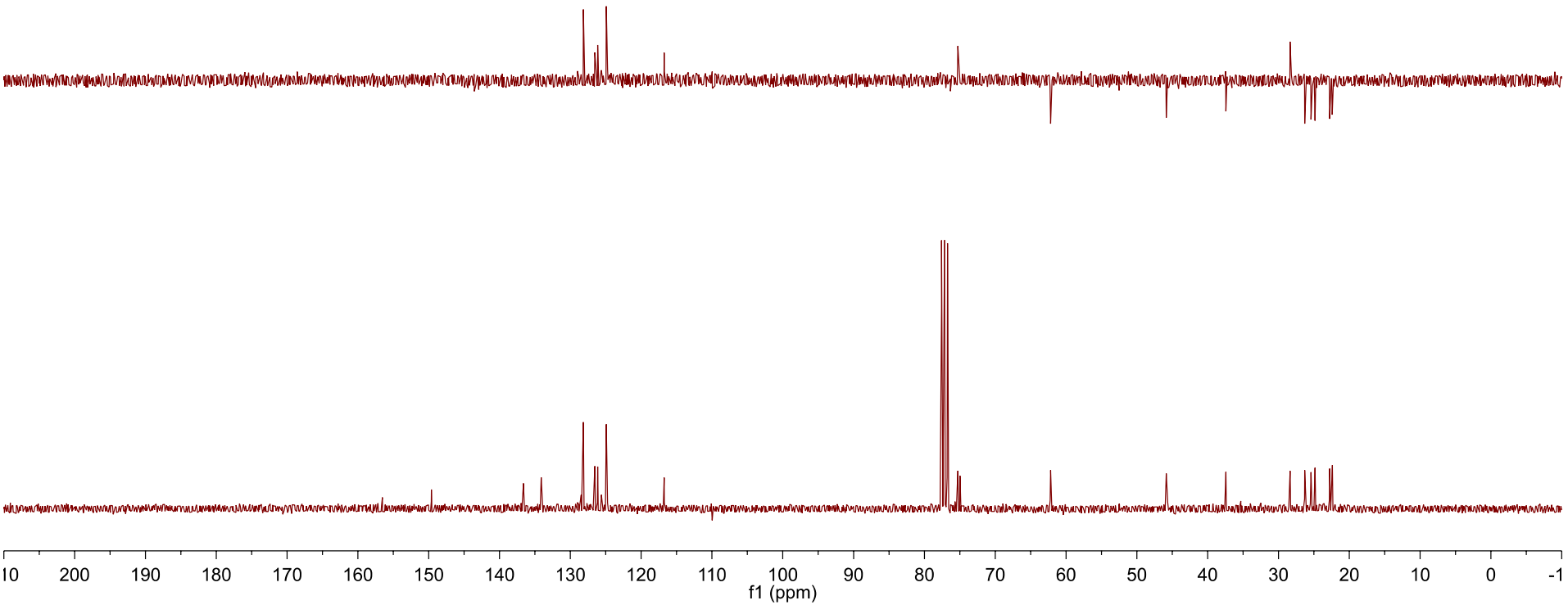
4:1 mixture of **4bah**:**4bah'**

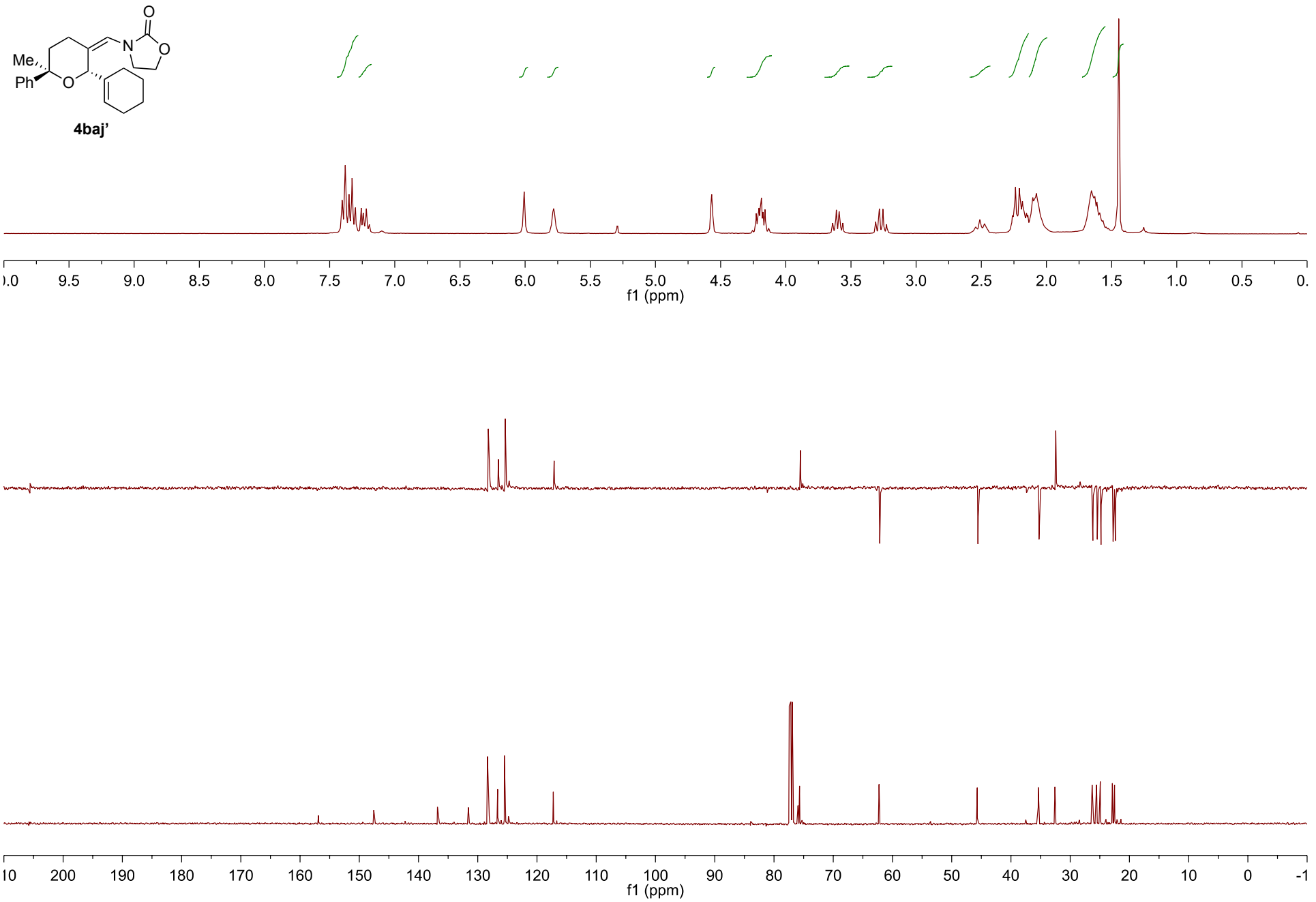


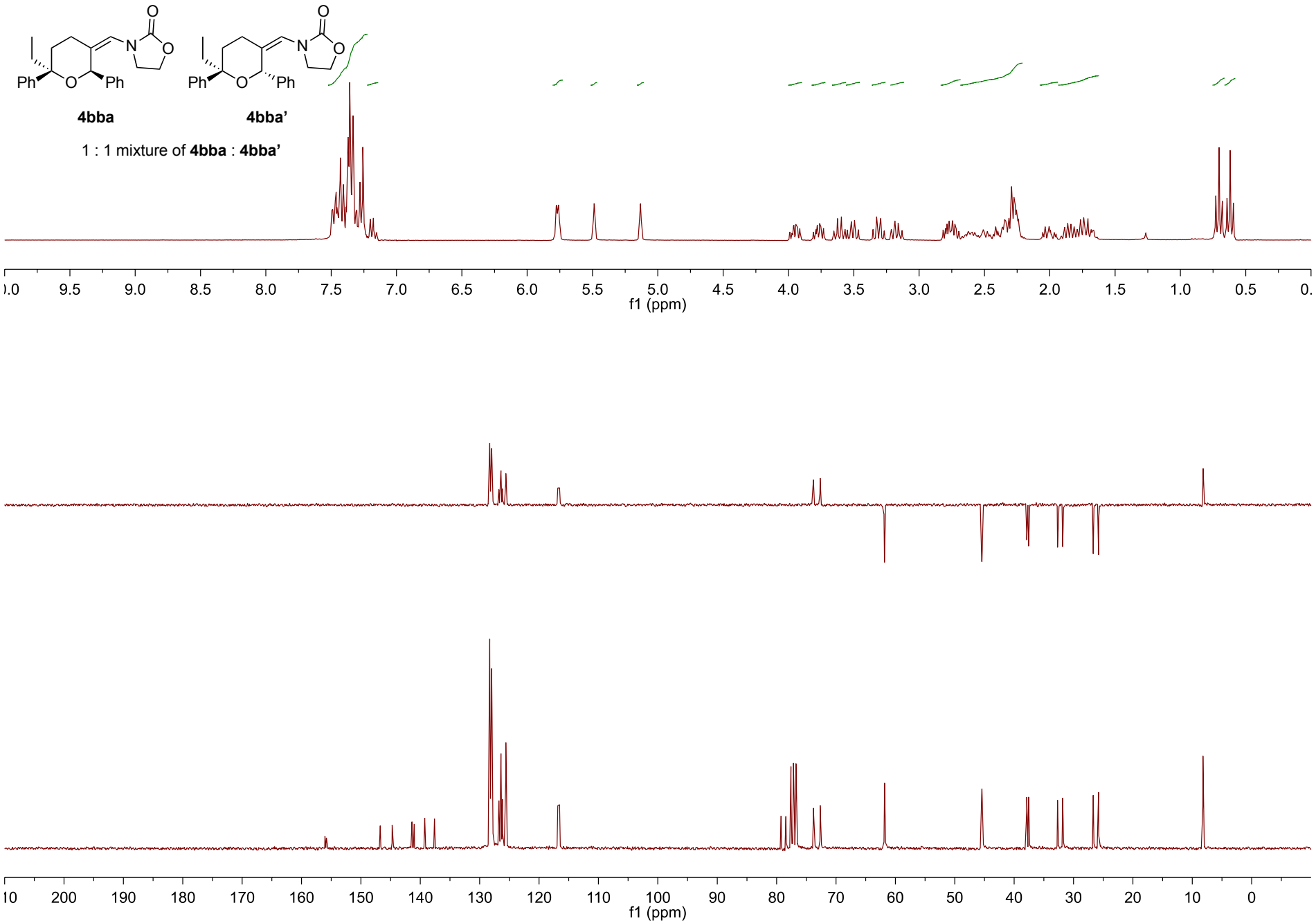

Me
Ph
O
N
O
Ph
4bai
Me
Ph
O
N
O
Ph
4bai'
6 : 1 mixture of 4bai : 4bai'
f1 (ppm)
f1 (ppm)

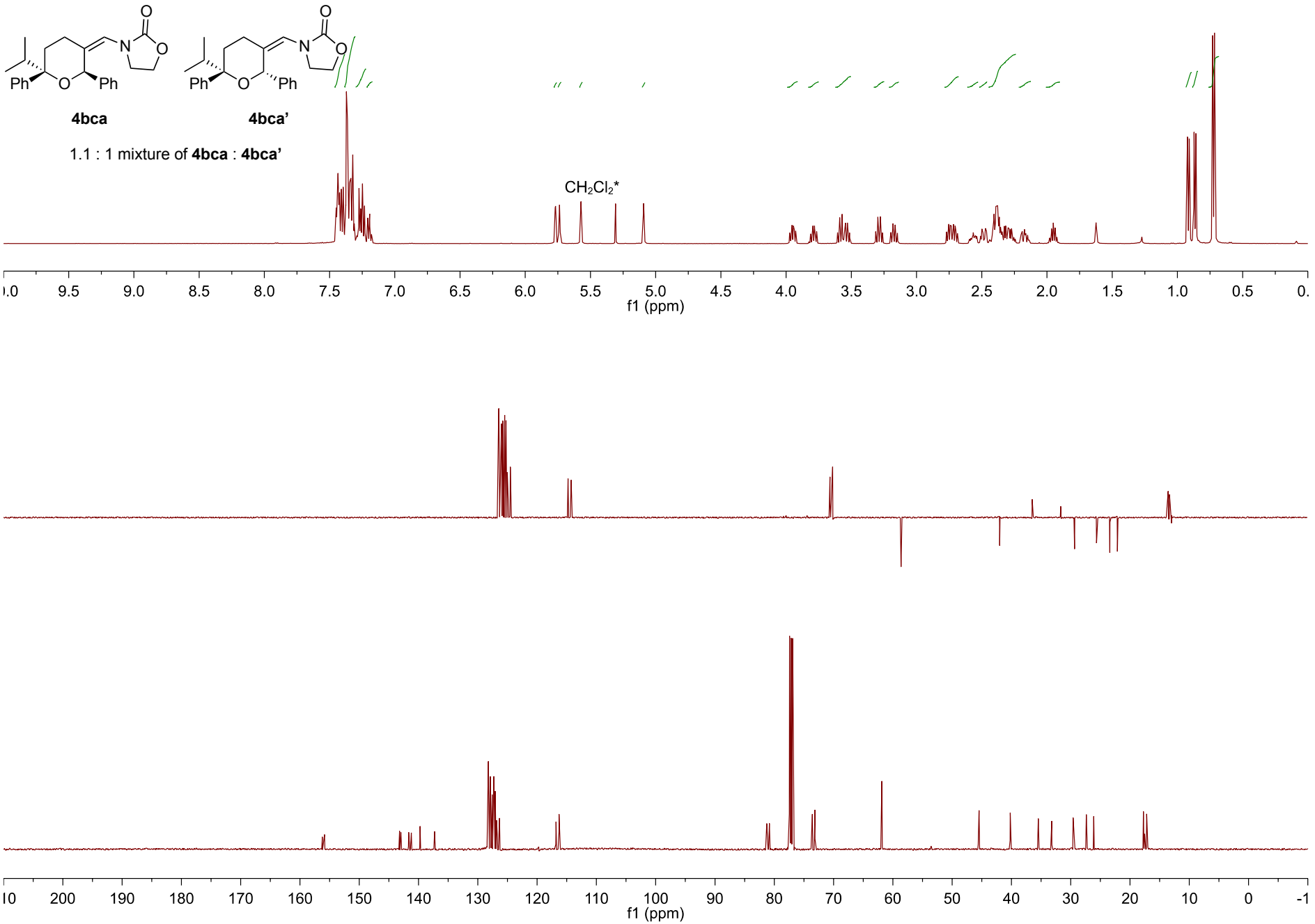

Me
Ph
O
N
O
O
Ph
4bai'
CH2Cl2*
f1 (ppm)
f1 (ppm)

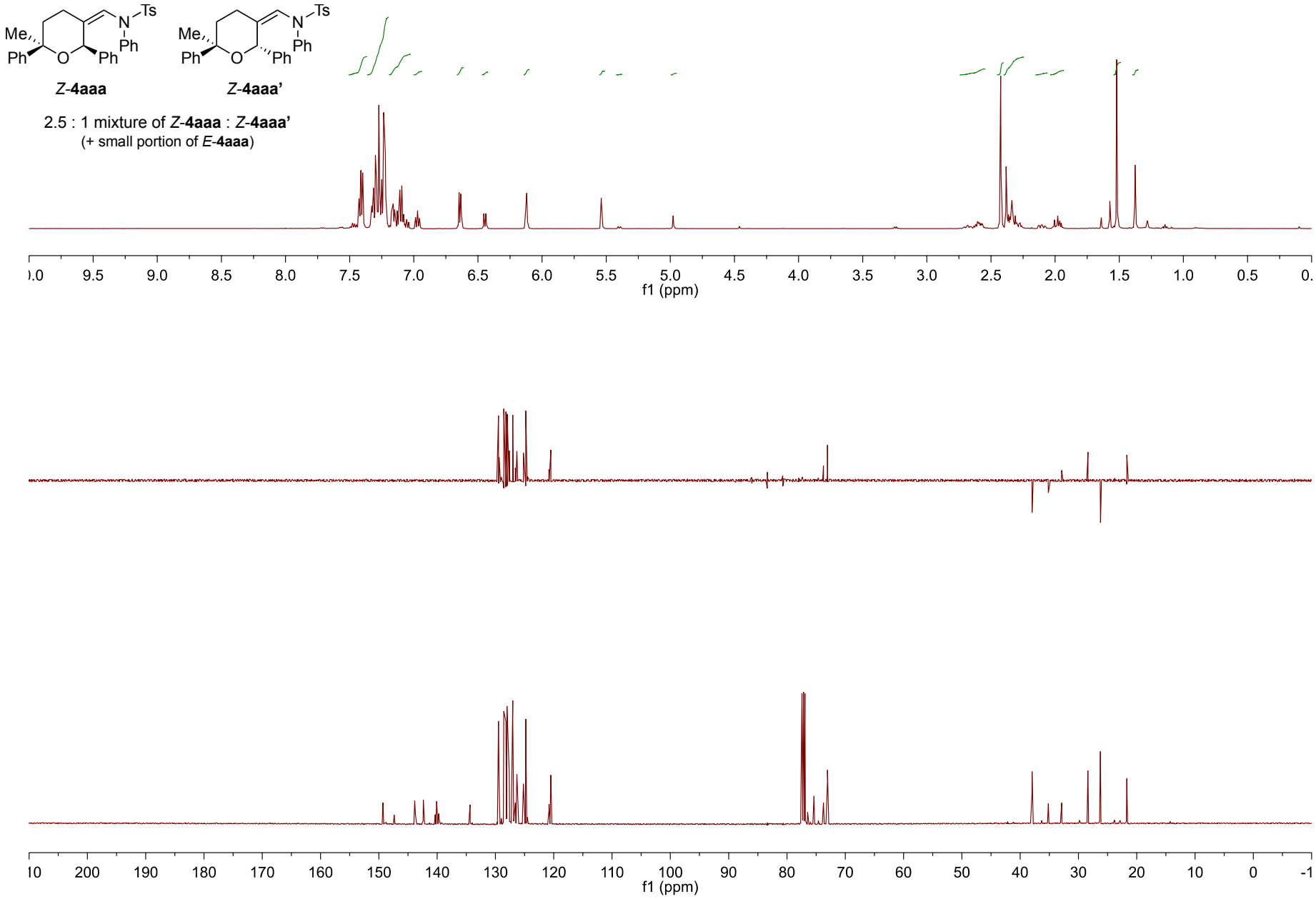

Me
Ph
O
N
O
O
4baj
f1 (ppm)

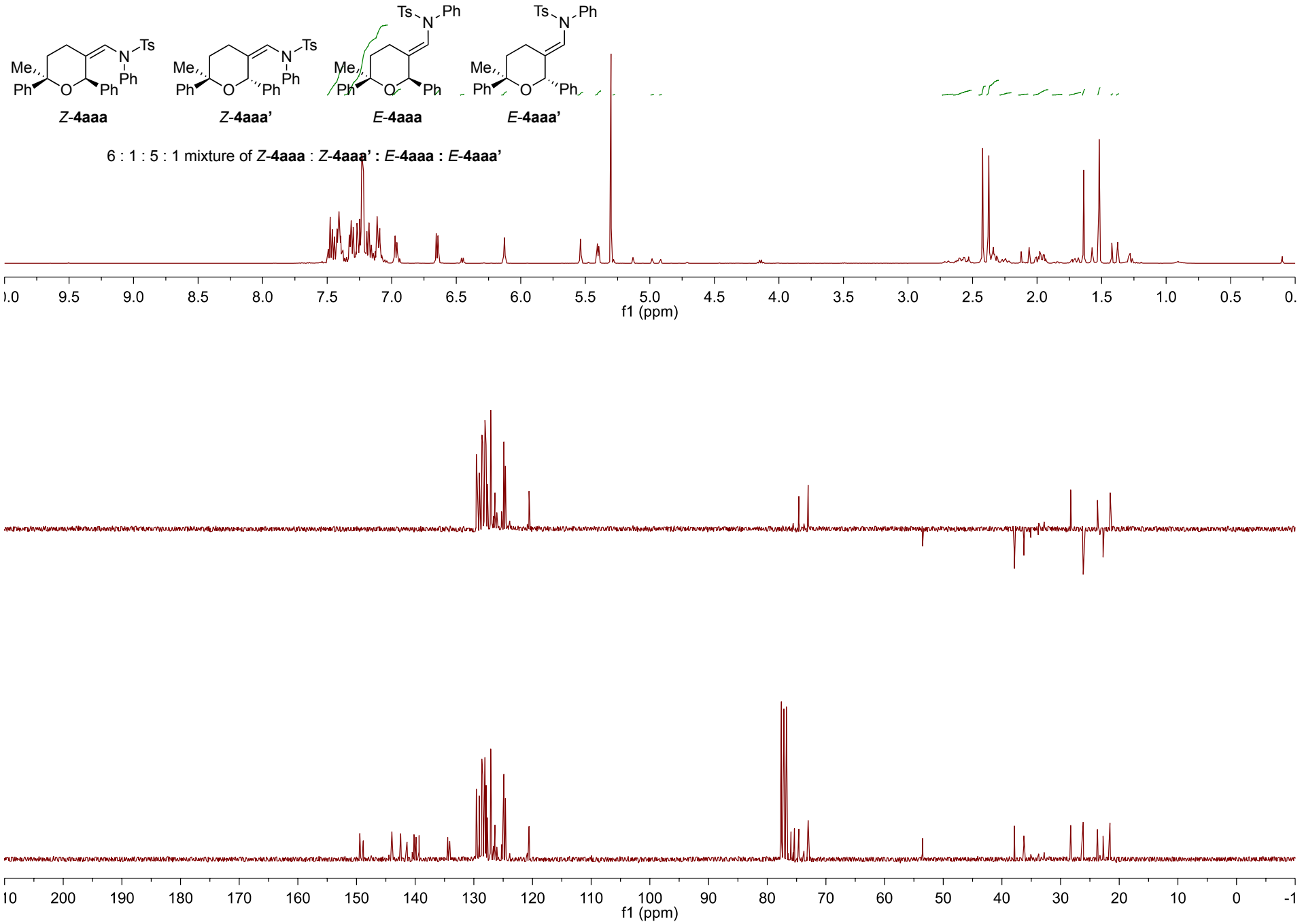

f1 (ppm)

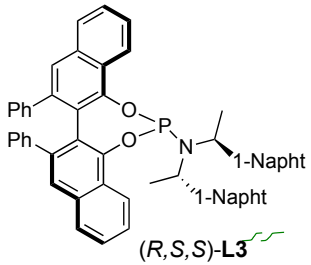

Me
Ph
O
N
O
O
4baj'
f1 (ppm)
f1 (ppm)


Ph
O
Ph
N
O
O
4bba
4bba'
1 : 1 mixture of 4bba : 4bba'
f1 (ppm)
f1 (ppm)

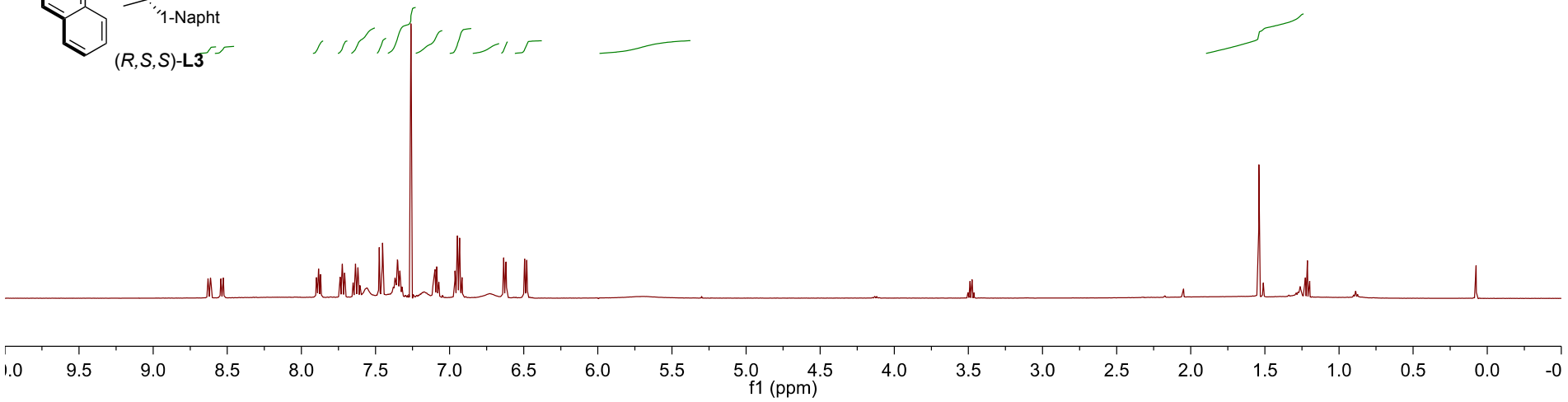

Ph
O
Ph
N
O
O
4bca
4bca'
1.1 : 1 mixture of 4bca : 4bca'
CH2Cl2*
f1 (ppm)
f1 (ppm)

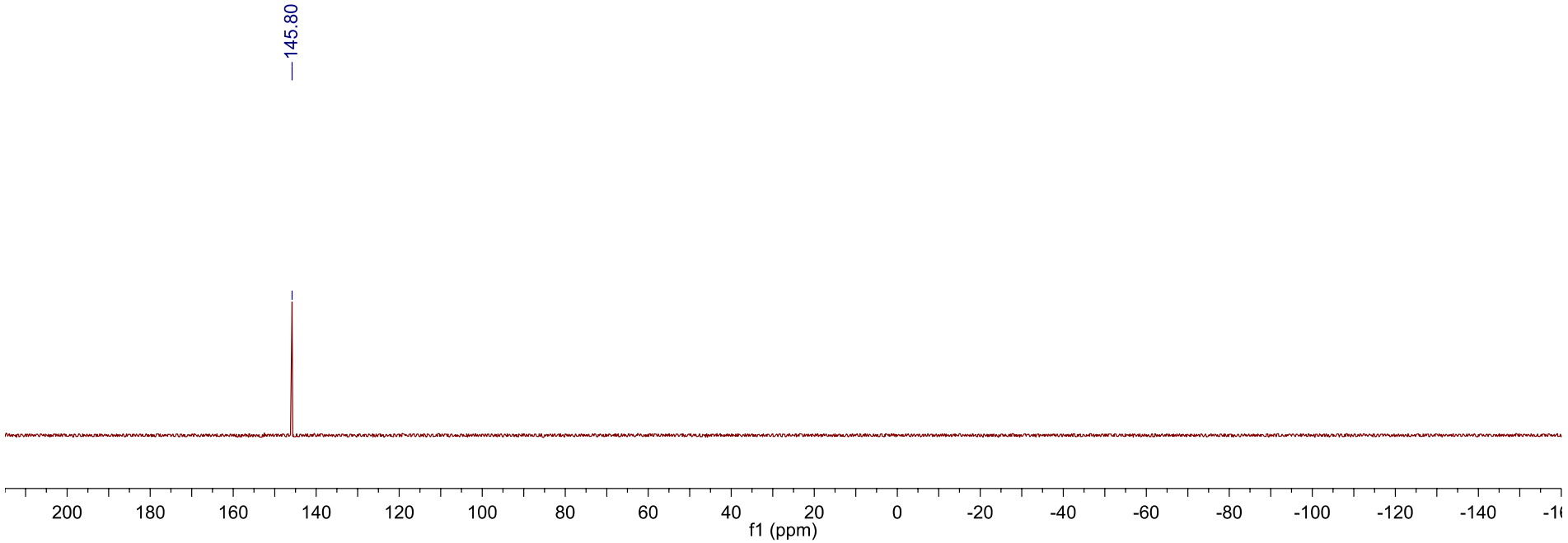

Me
Ph
O
Ph
N
Ts
Ph
Z-4aaa
Z-4aaa'
2.5 : 1 mixture of Z-4aaa : Z-4aaa'
(+ small portion of E-4aaa)
f1 (ppm)
f1 (ppm)

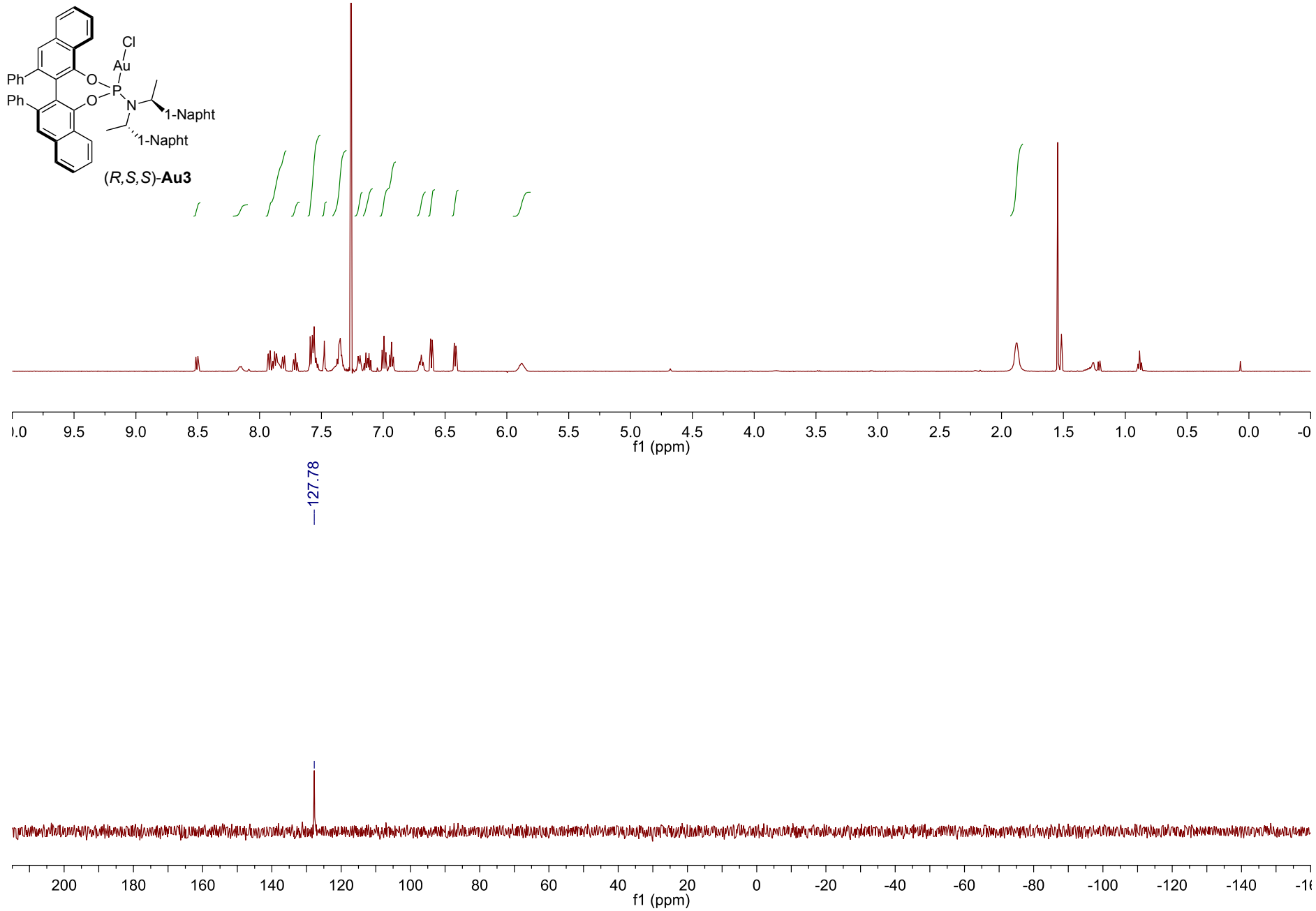

Me
Ph
O
Ph
N
Ts
Ph
Z-4aaa
Z-4aaa'
E-4aaa
E-4aaa'
6 : 1 : 5 : 1 mixture of Z-4aaa : Z-4aaa' : E-4aaa : E-4aaa'
f1 (ppm)
f1 (ppm)

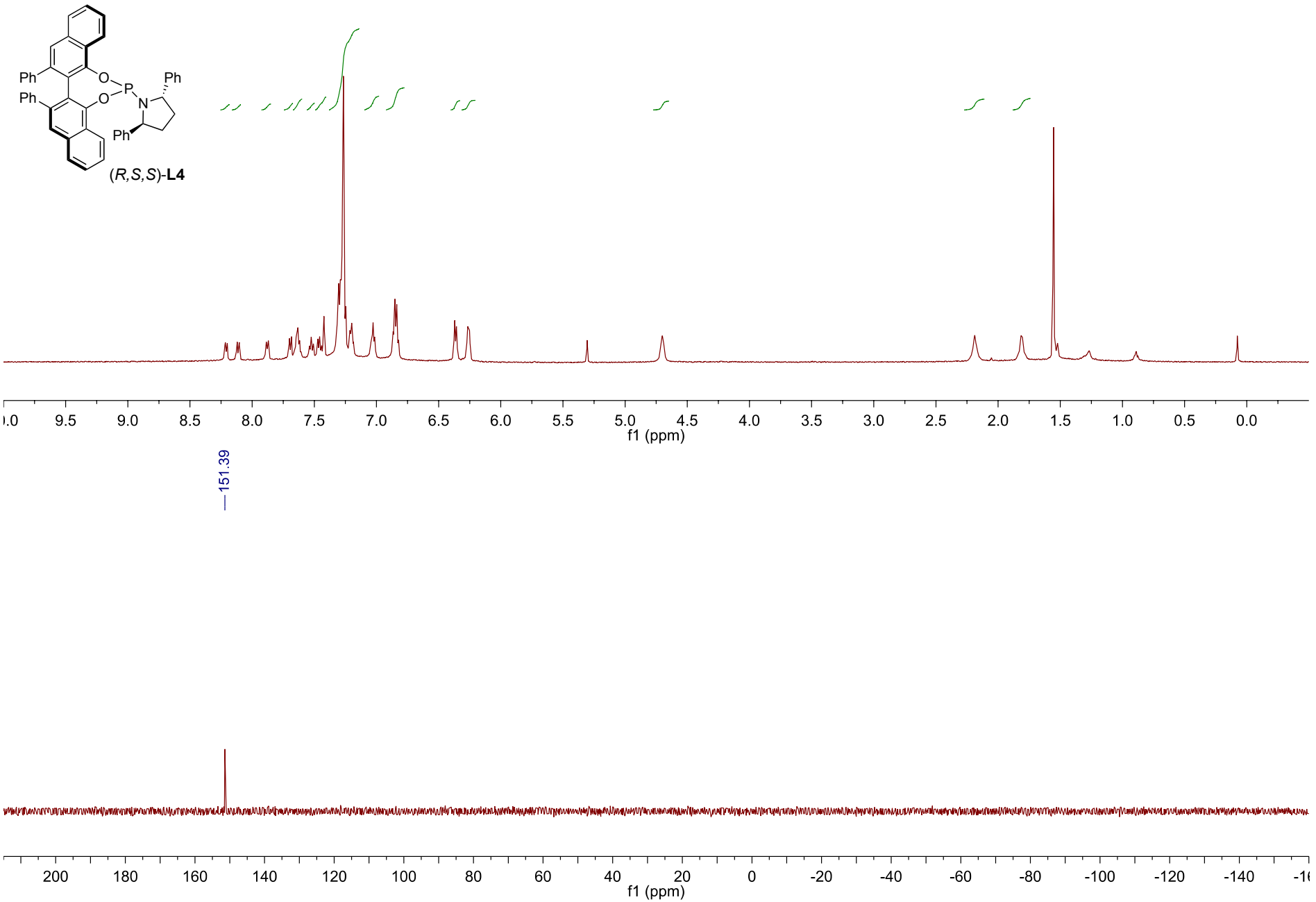

Ph
Ph
O
O
P
N
1-Napht
1-Napht

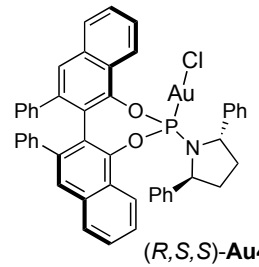
(*R*,*S*,*S*)-**L3**


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.80
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
f1 (ppm)

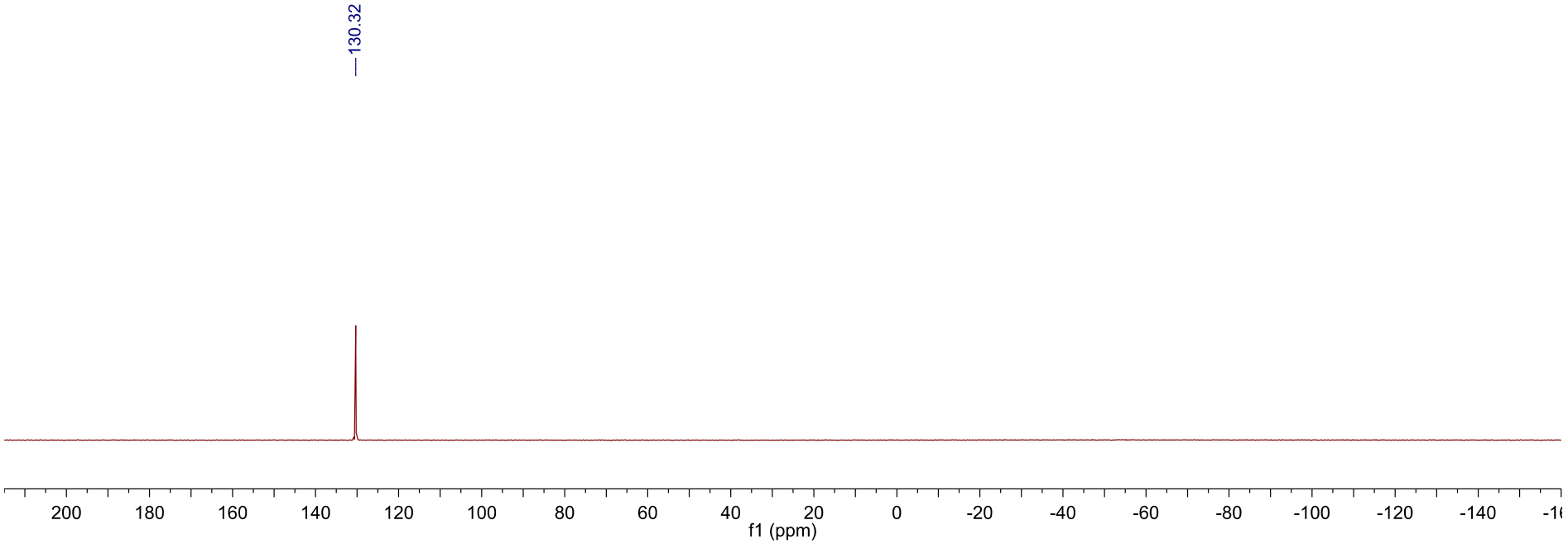

Cl
Au
Ph
Ph
O
O
P
N
1-Napht
1-Napht
(R,S,S)-Au3
f1 (ppm)
127.78
f1 (ppm)

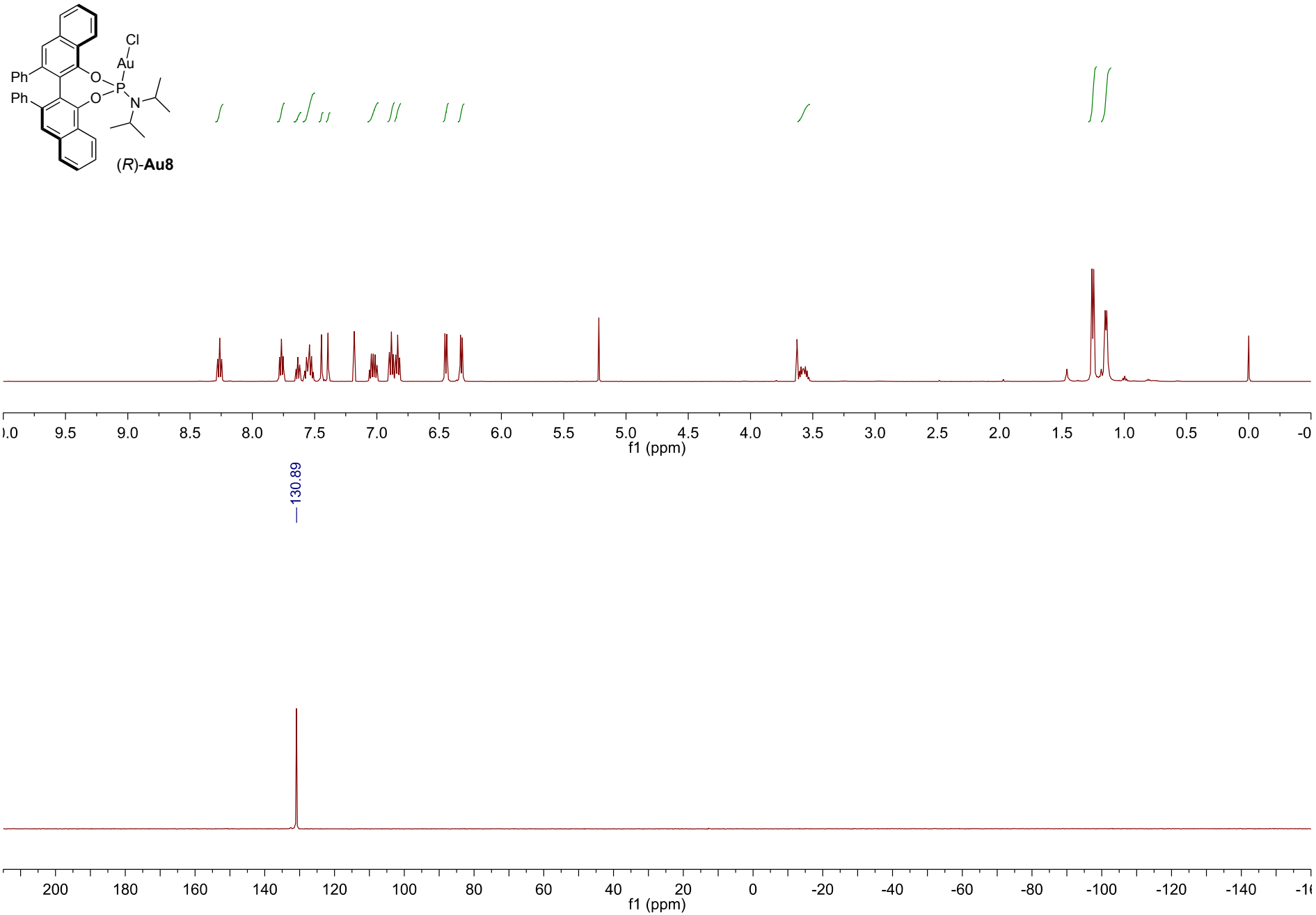

Ph
Ph
O
O
P
N
Ph
Ph
(R,S,S)-L4
151.39
f1 (ppm)
f1 (ppm)


Cl
Au
Ph
Ph
O
O
P
N
Ph
Ph

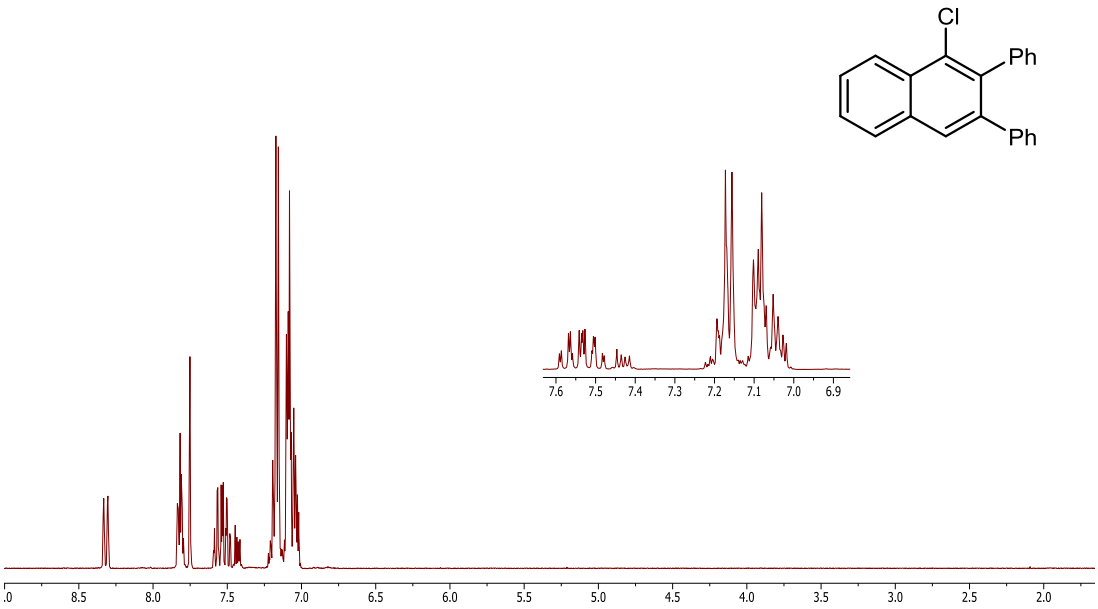
(*R*,*S*,*S*)-**Au4**

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

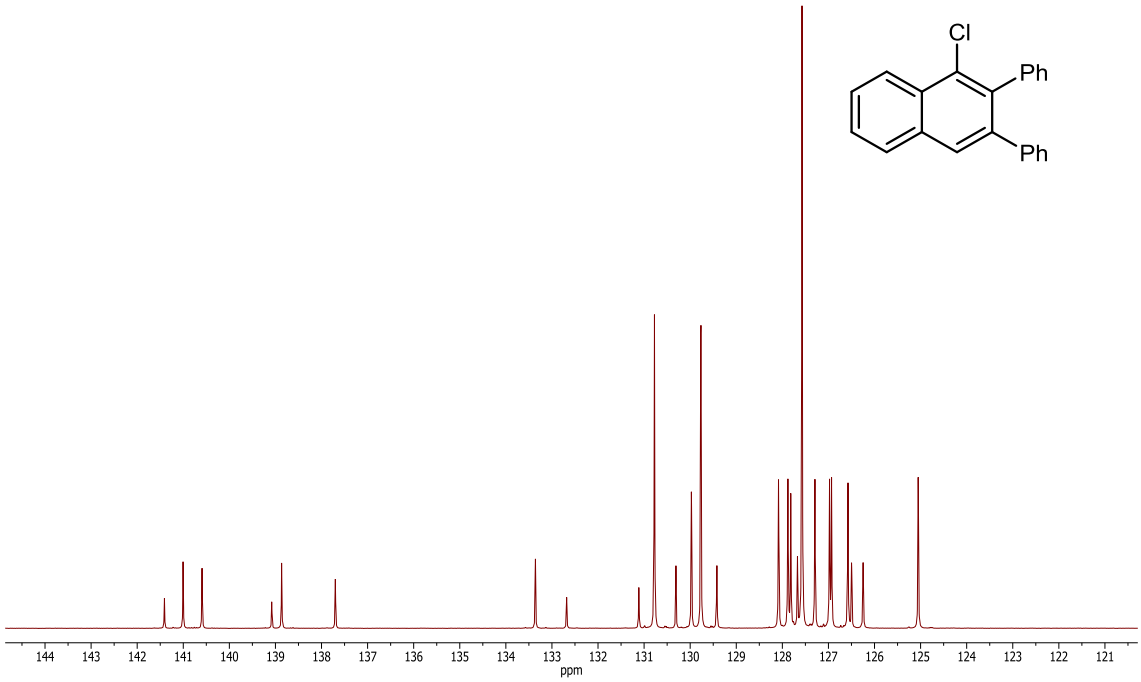

130.32
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
f1 (ppm)


Cl
Au
Ph
Ph
O
O
P
N
(R)-Au8
f1 (ppm)
130.89
f1 (ppm)

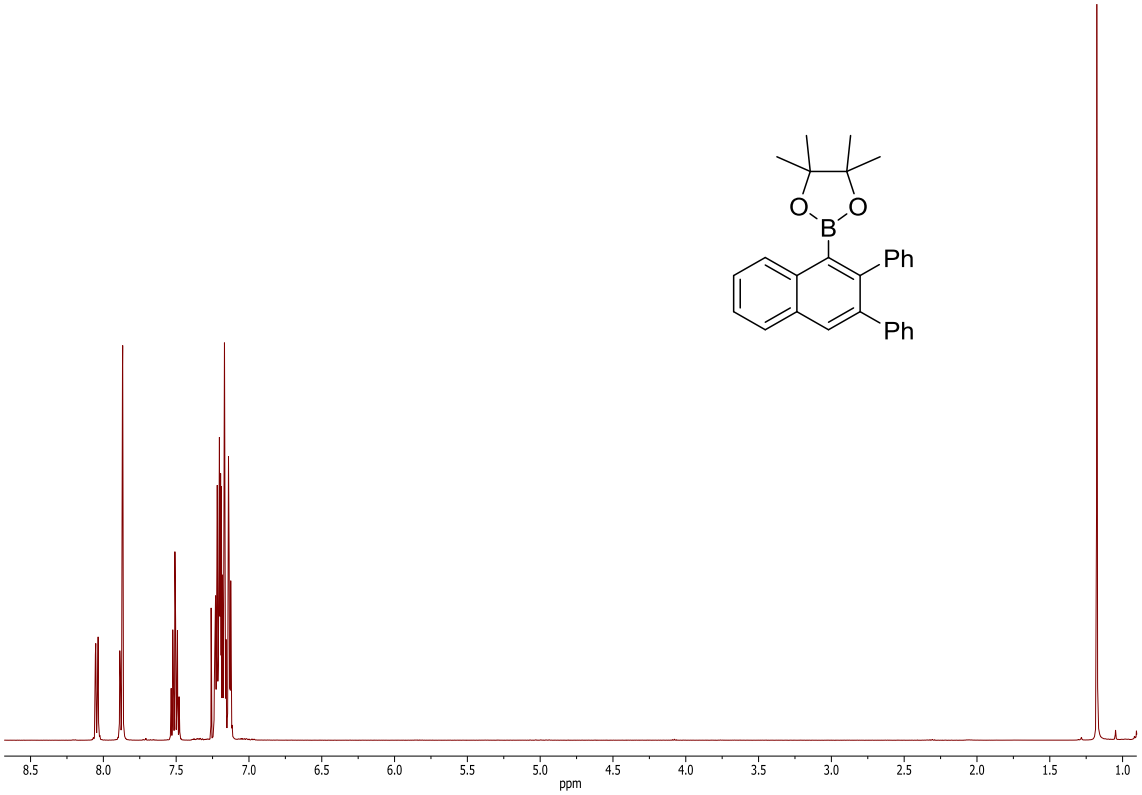
^{1}H NMR (300 MHz, $CDCl_3$) of **8b**:



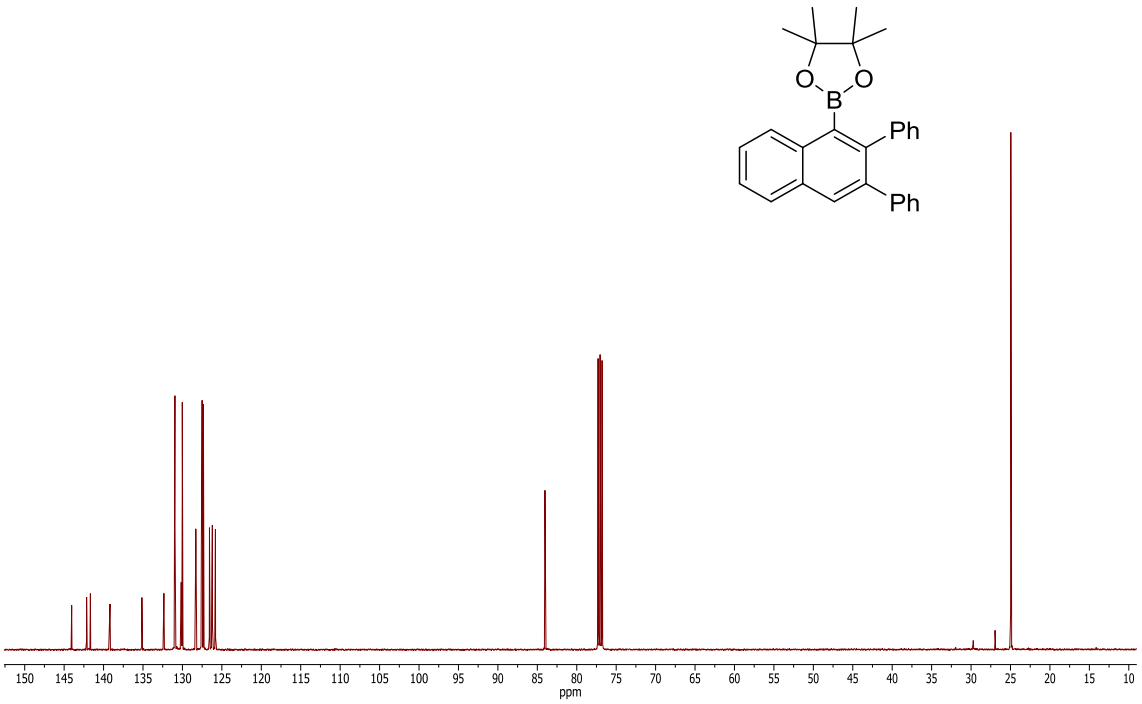
^{13}C NMR (125 MHz, $CDCl_3$) of **8b**:



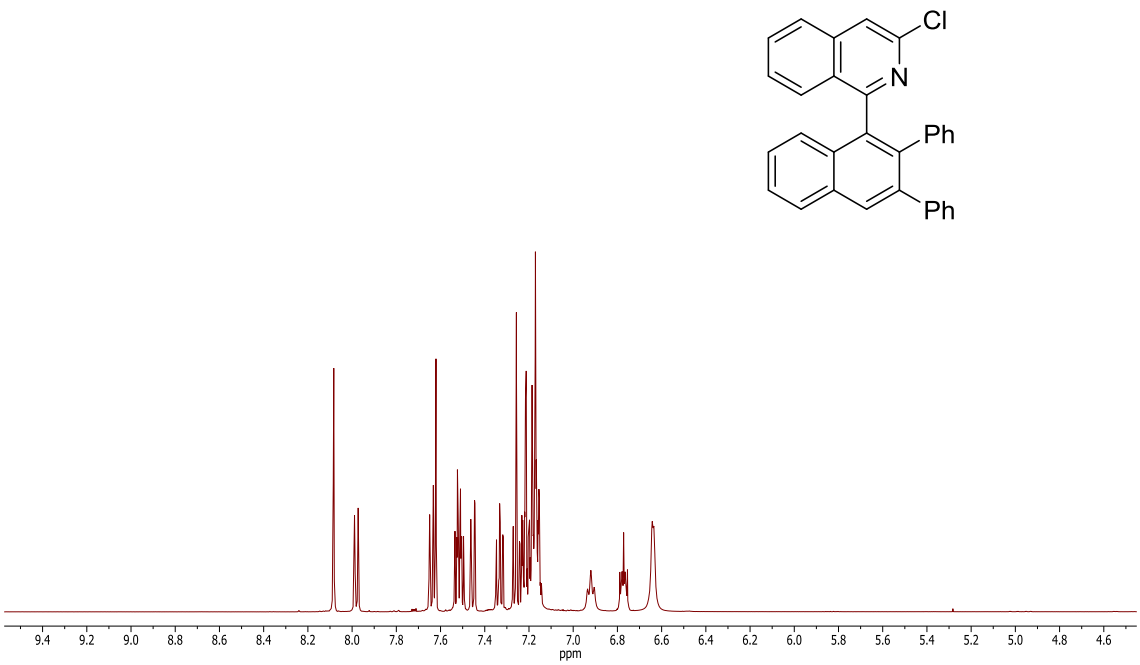
^{1}H NMR (500 MHz, $CDCl_3$) of **9b**:



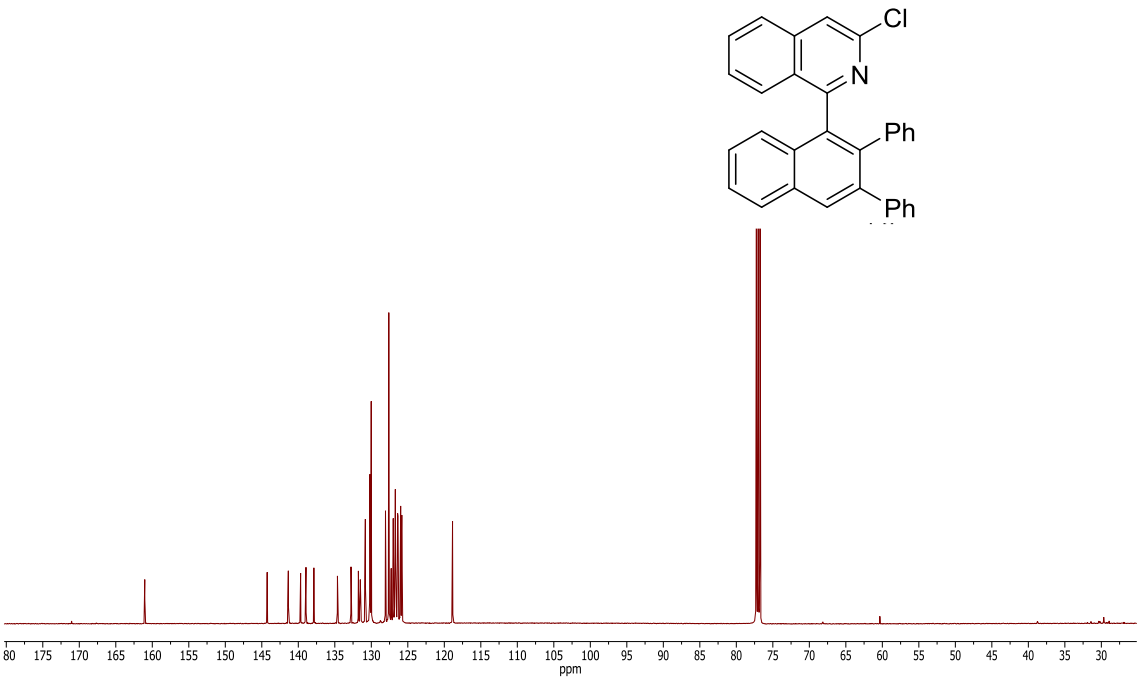
^{13}C NMR (125 MHz, $CDCl_3$) of **9b**:



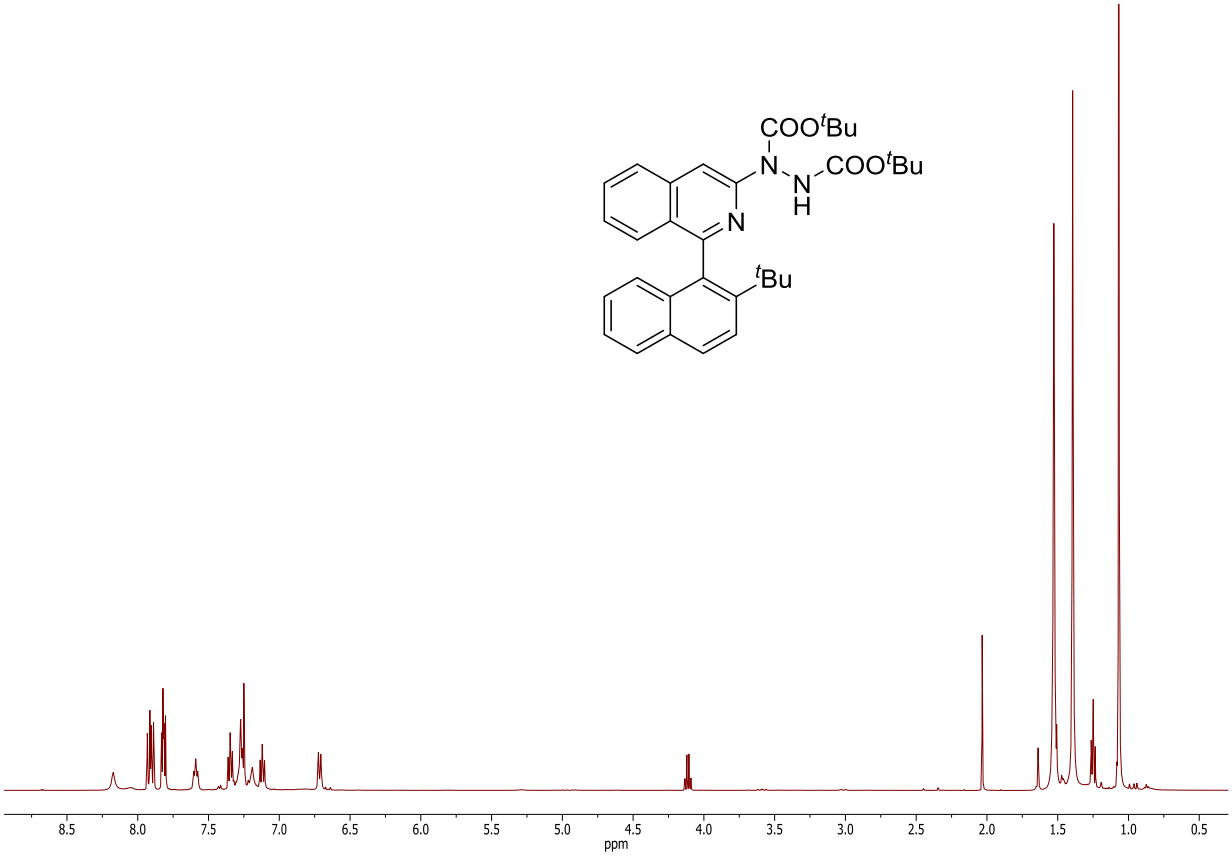
^{1}H NMR (500 MHz, $CDCl_3$) of **10b**:



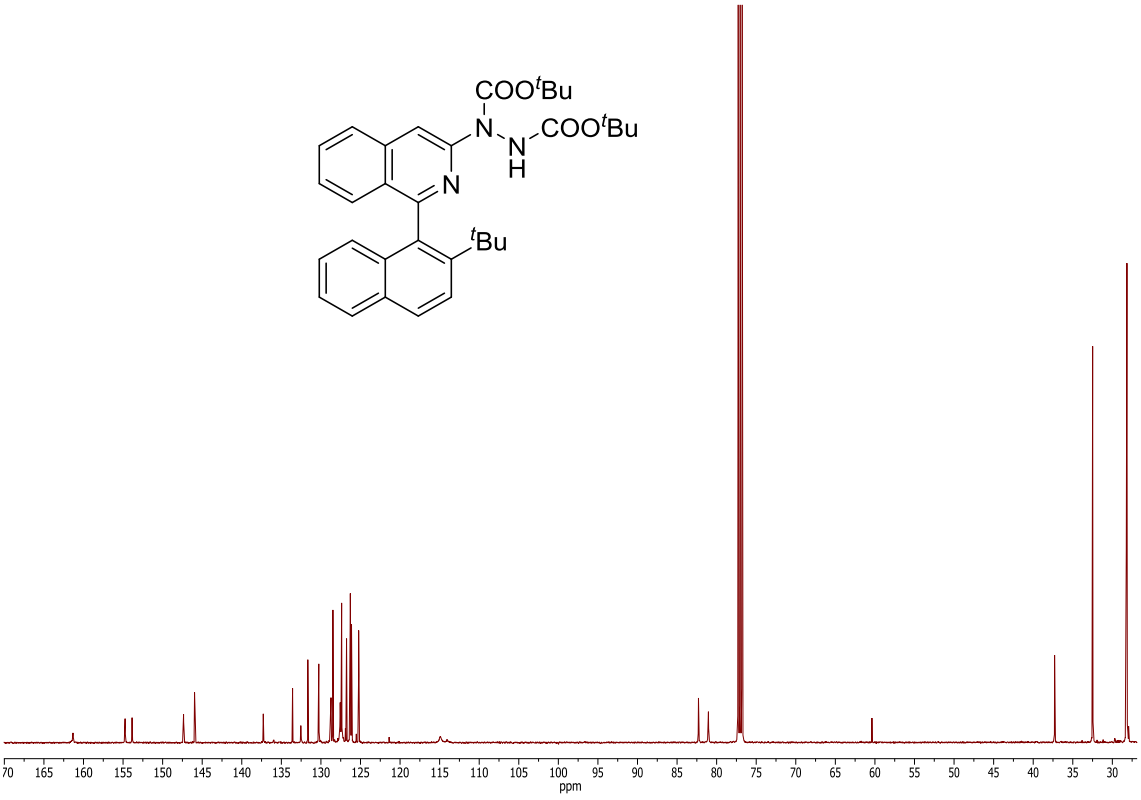
^{13}C NMR (125 MHz, $CDCl_3$) of **10b**:



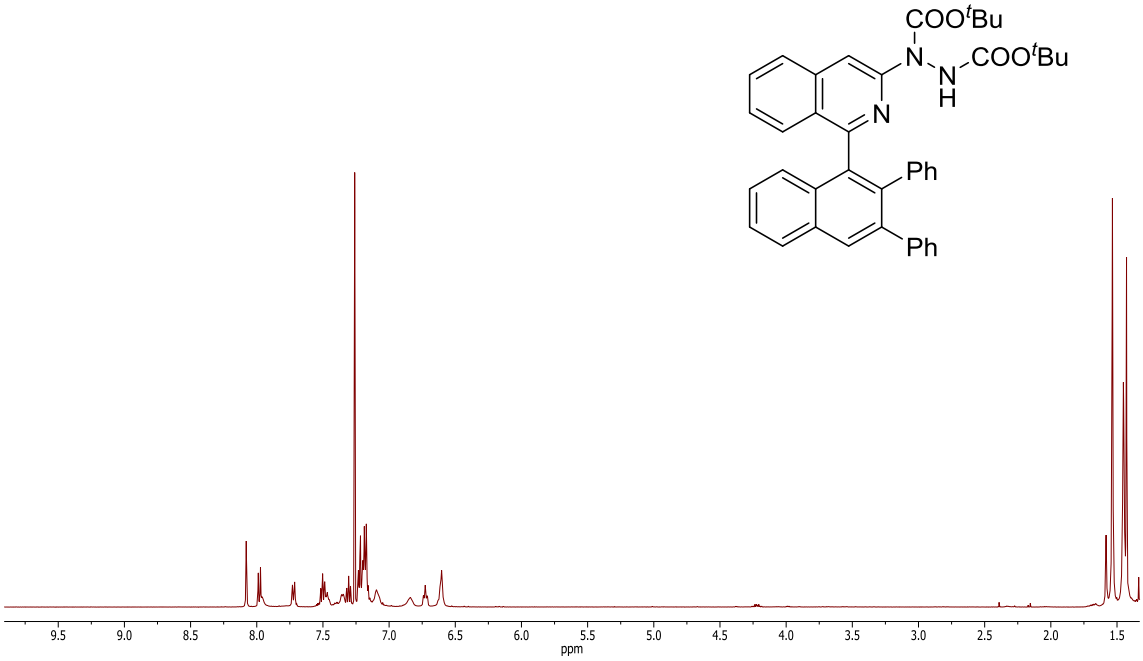
^{1}H NMR (500 MHz, $CDCl_3$) of **11a**:



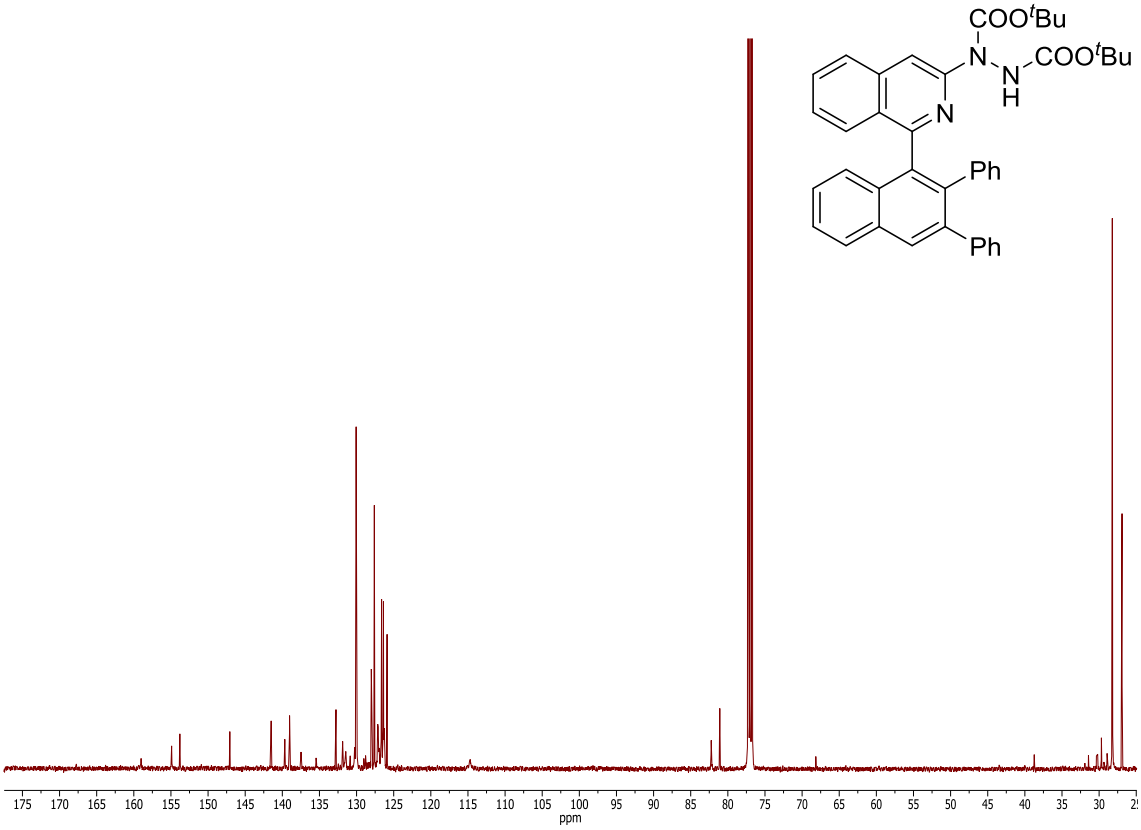
^{13}C NMR (125 MHz, $CDCl_3$) of **11a**:



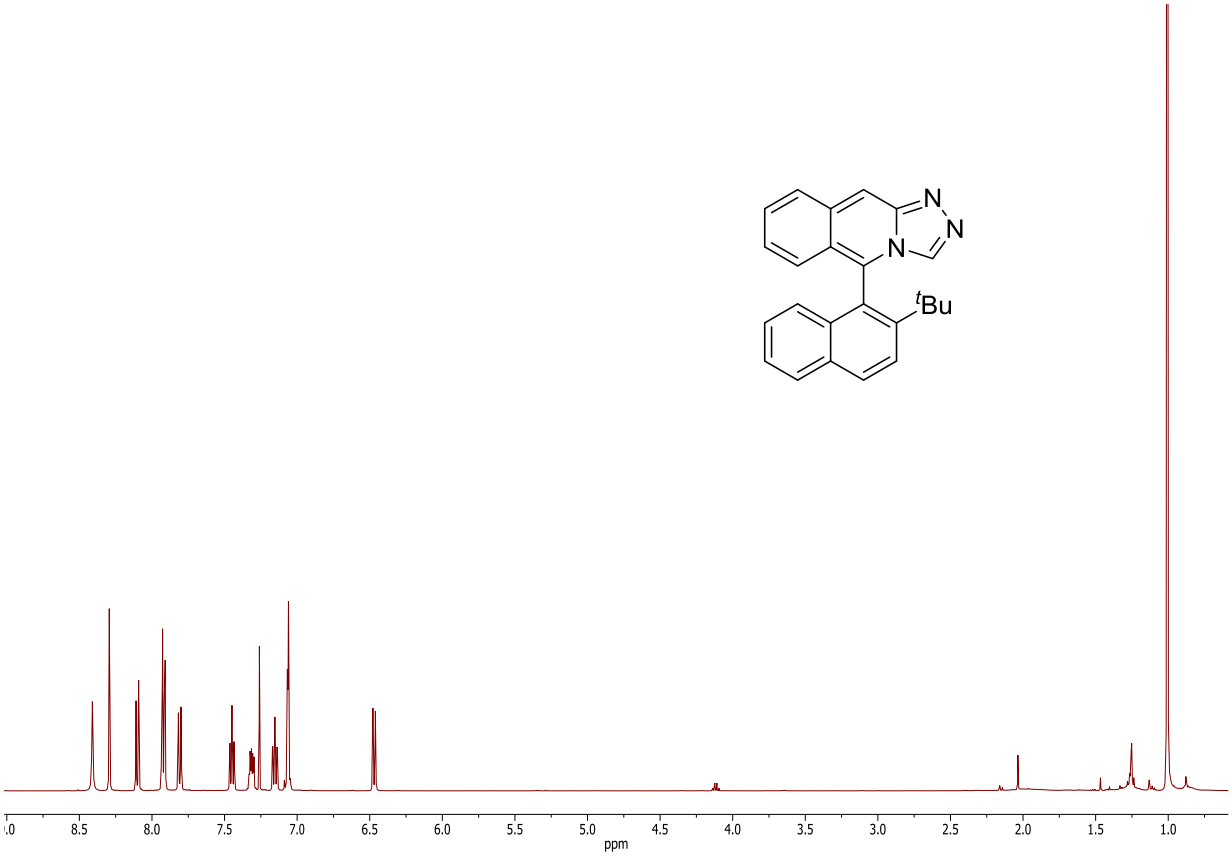
^{1}H NMR (500 MHz, $CDCl_3$) of **11b**:



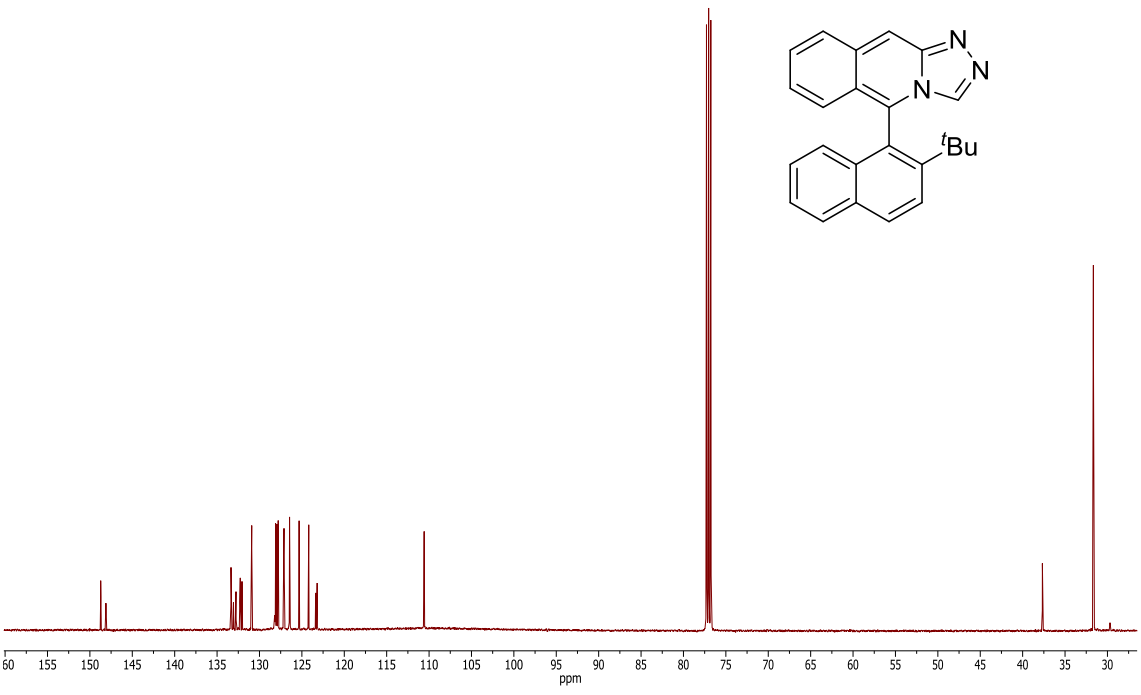
^{13}C NMR (125 MHz, $CDCl_3$) of **11b**:



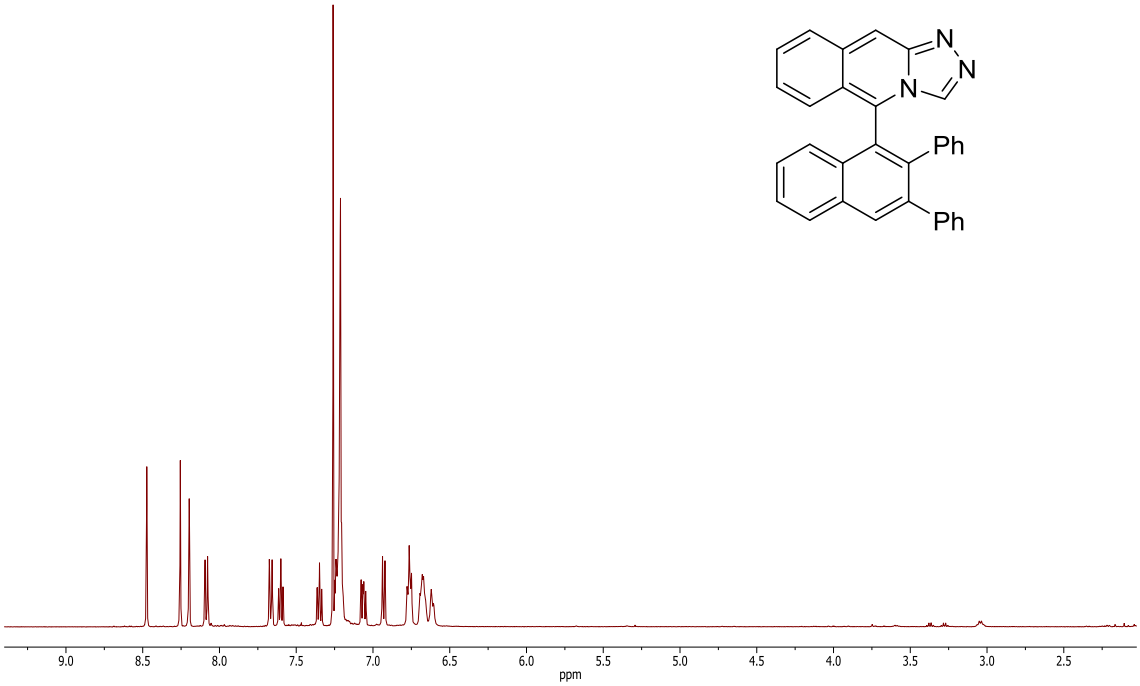
^{1}H NMR (500 MHz, $CDCl_3$) of **12a**:



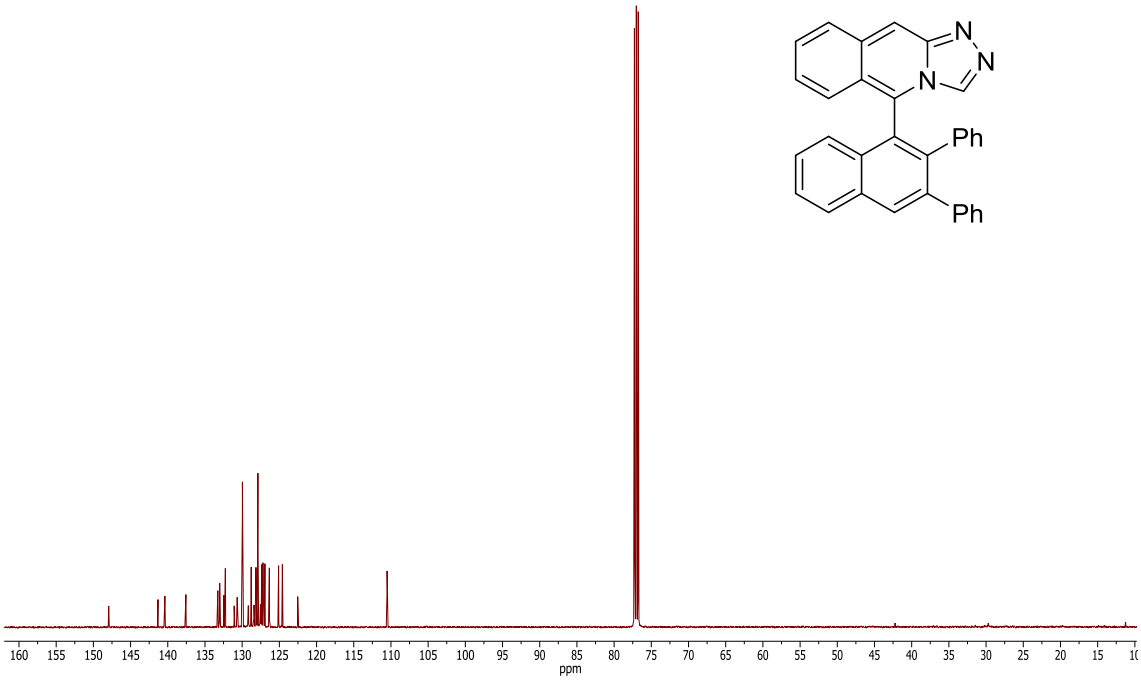
^{13}C NMR (125 MHz, $CDCl_3$) of **12a**:



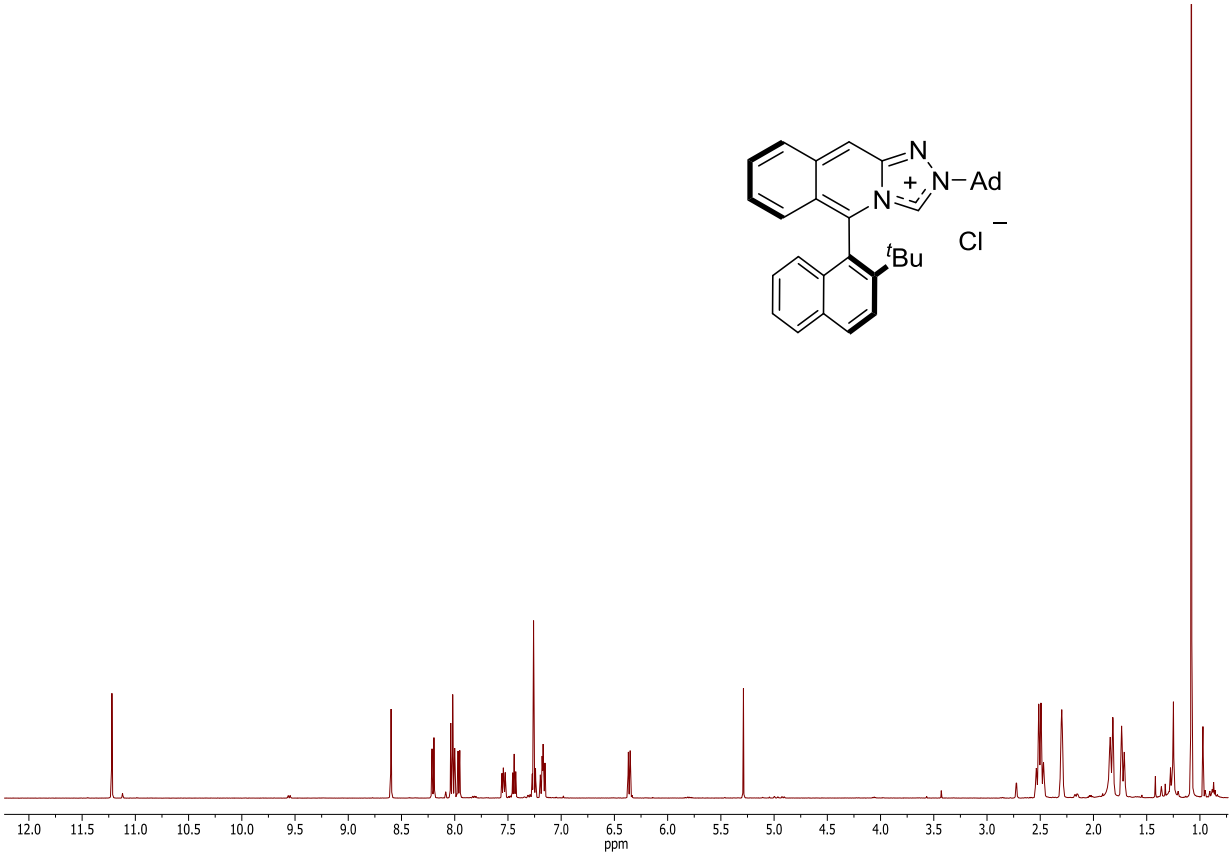
^{1}H NMR (500 MHz, $CDCl_3$) of **12b**:



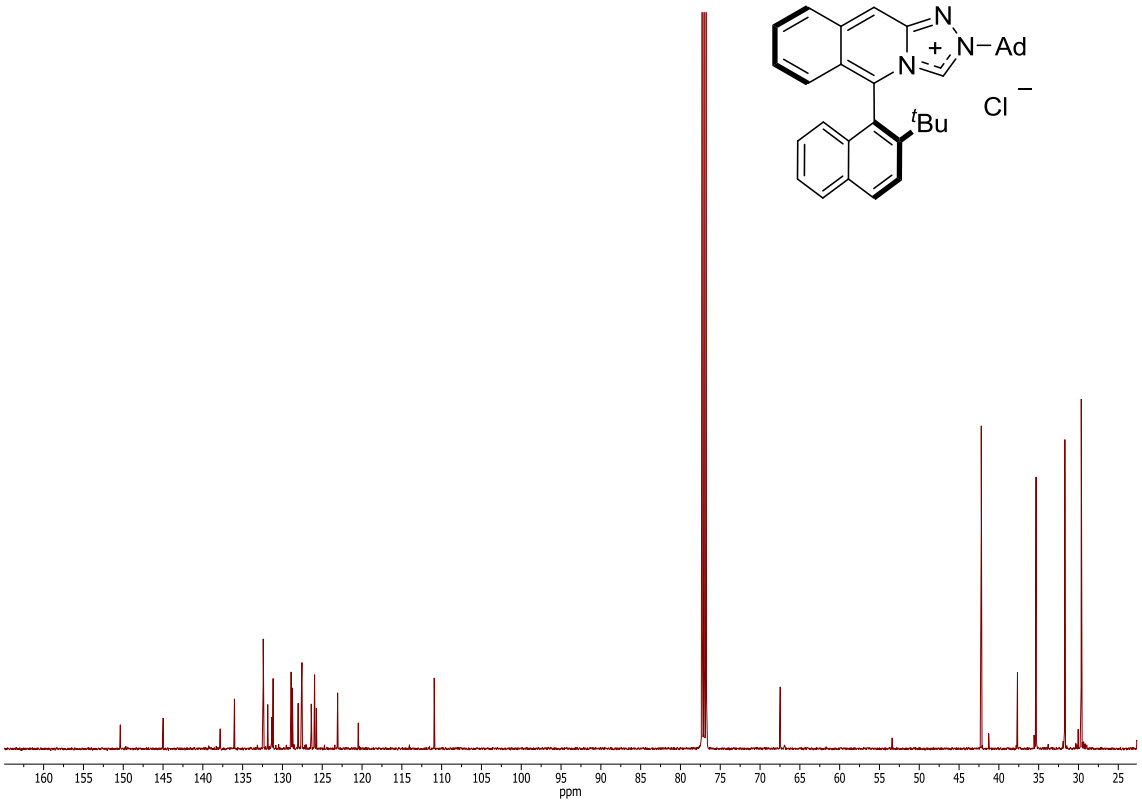
^{13}C NMR (125 MHz, $CDCl_3$) of **12b**:



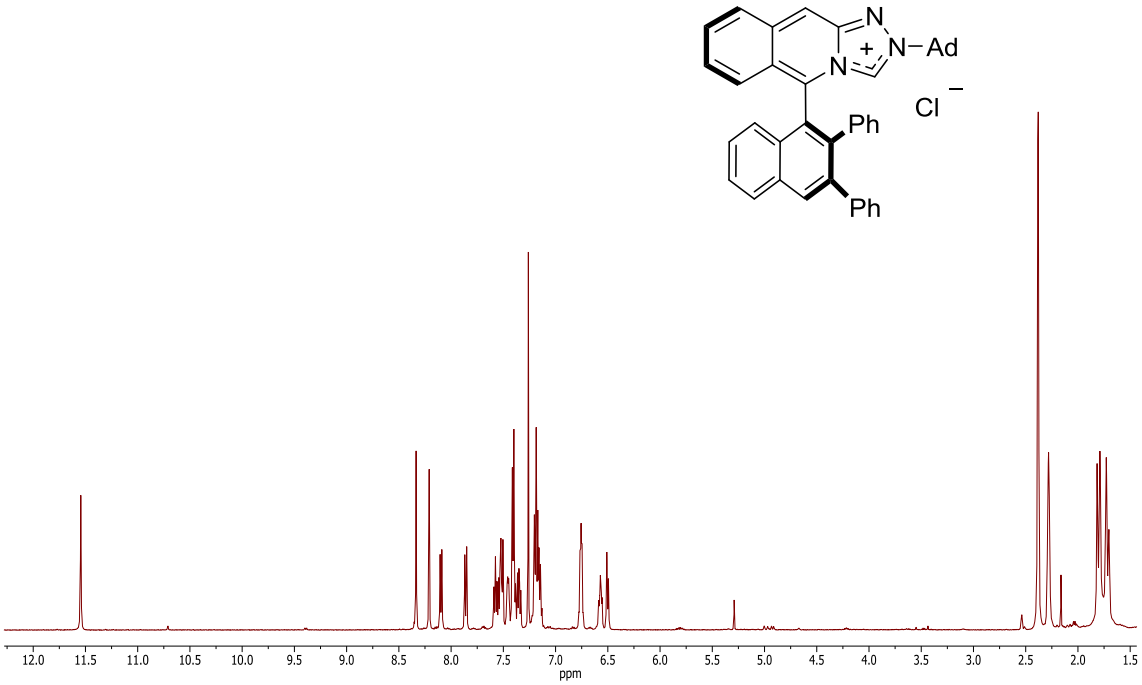
^{1}H NMR (500 MHz, $CDCl_3$) of **(*R*)-13a**:



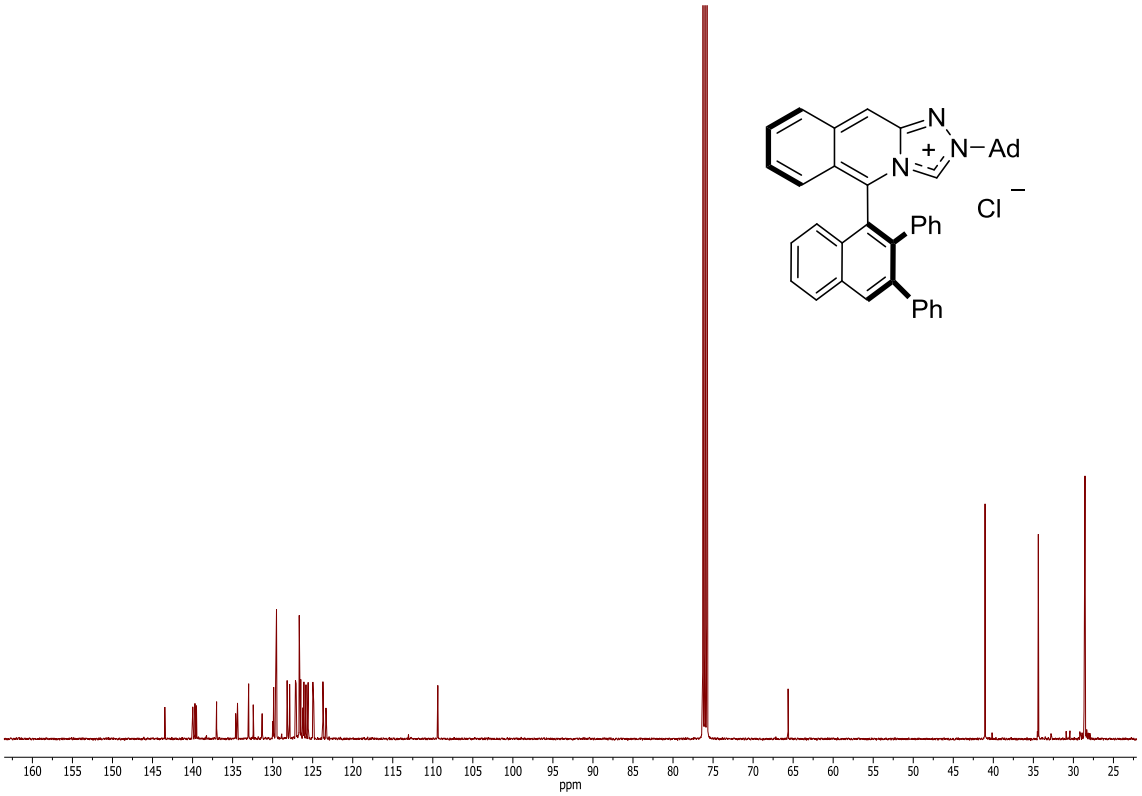
^{13}C NMR (125 MHz, $CDCl_3$) of **(*R*)-13a**:



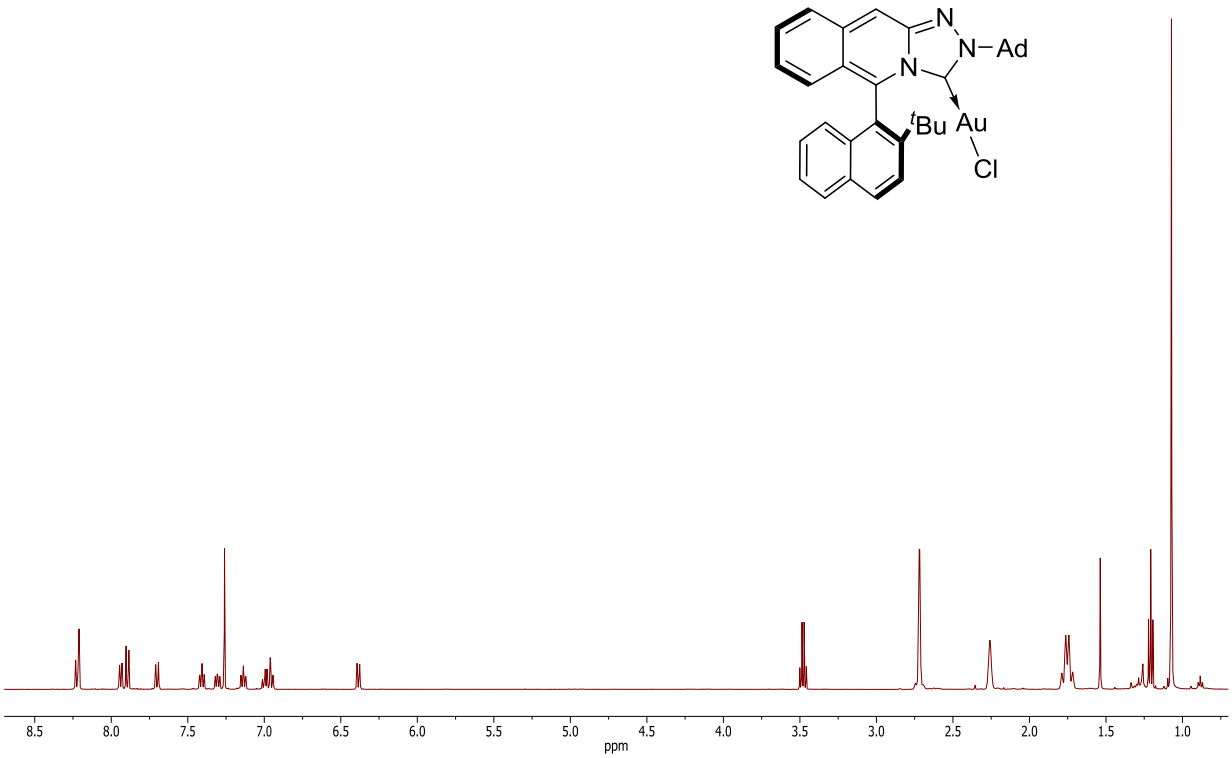
^{1}H NMR (500 MHz, $CDCl_3$) of **(+)-13b**:



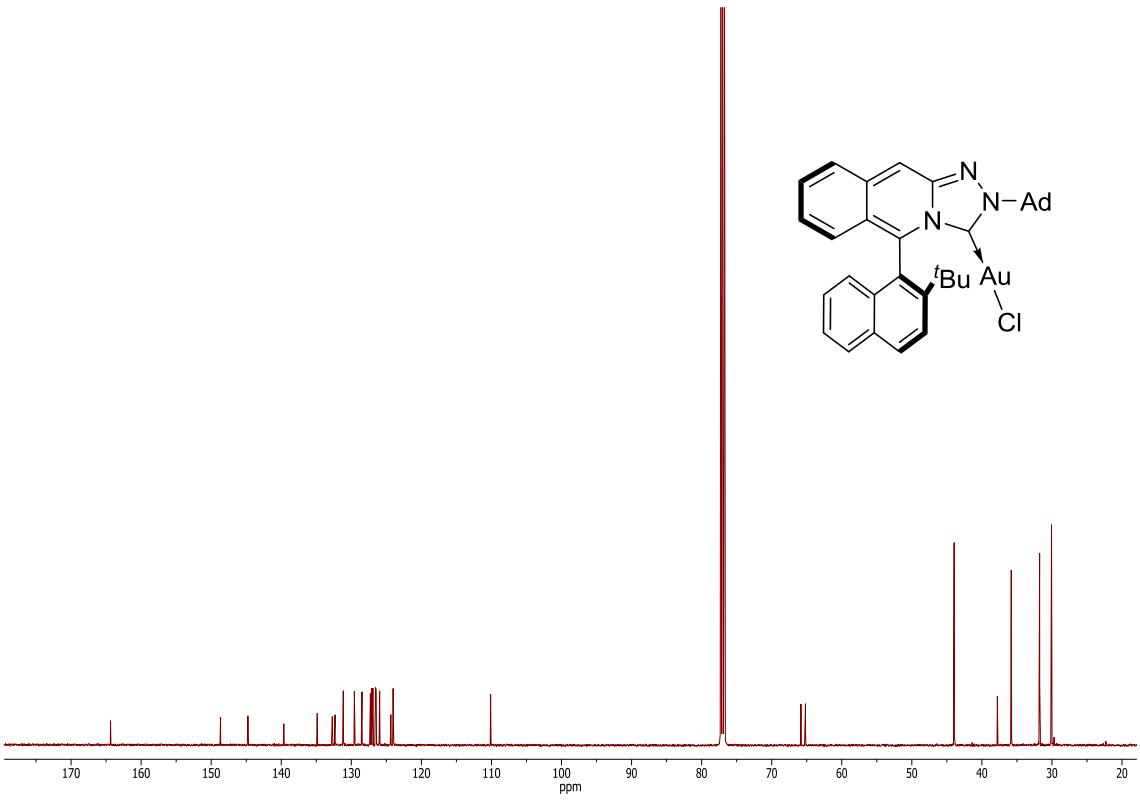
^{13}C NMR (125 MHz, $CDCl_3$) of **(+)-13b**:



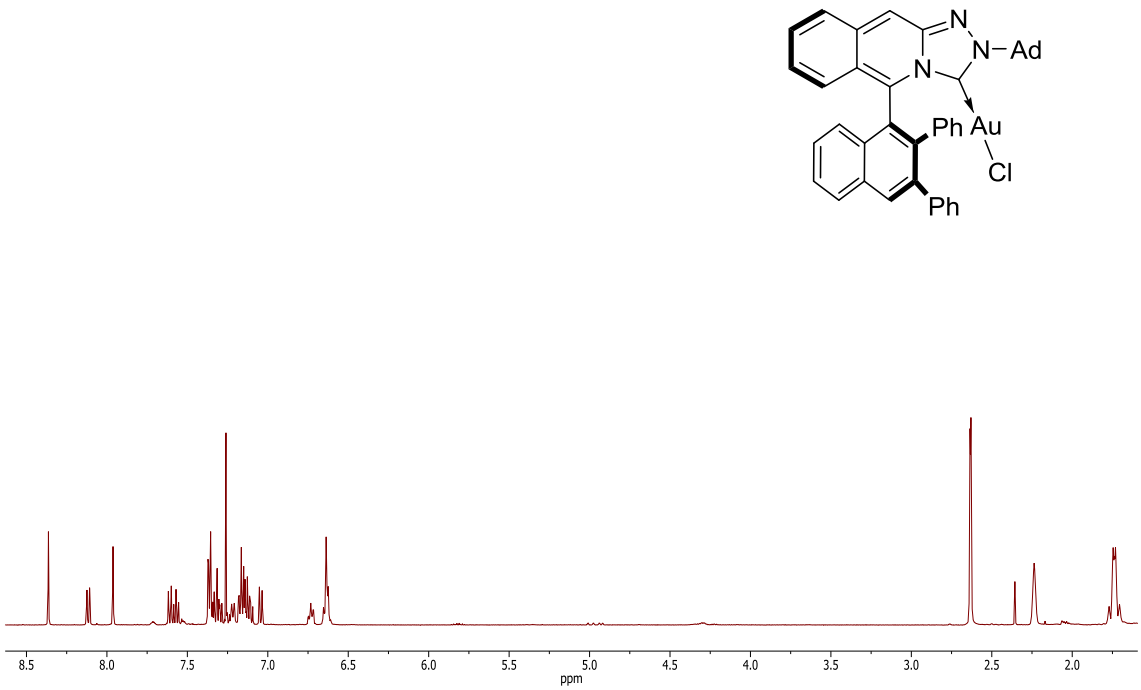
^{1}H NMR (500 MHz, $CDCl_3$) of **(*R*)-Au6**:



^{13}C NMR (125 MHz, $CDCl_3$) of **(*R*)-Au6**:



^{1}H NMR (500 MHz, $CDCl_3$) of **(+)-Au7**:



^{13}C NMR (125 MHz, $CDCl_3$) of **(+)-Au7**: