# Supporting Information

# Axially Chiral Triazoloisoquinolin-3-ylidene Ligands in Gold(I)-Catalyzed Asymmetric Intermolecular (4+2) Cycloadditions of Allenamides and Dienes

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

[†]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica. Unidad Asociada al CSIC, 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

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## Experimental Section

### General experimental methods.

Solvents were purified and dried by standard procedures. Melting points were recorded in a metal block and are uncorrected. The abbreviation "*rt*" refers to reactions carried out at a temperature between 21-25 ºC. Reaction mixtures were stirred using Teflon-coated magnetic stir bars. High reaction temperatures were maintained using Thermowatch-controlled silicone oil baths. 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 (40-63 μm or 70-200 μm). 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 high vacuum. $^1$H NMR spectra were recorded at 250, 300, 400 and 500 MHz; $^{13}$C NMR spectra were recorded at 62, 75, 100 and 125 MHz, with the solvent peak used as the internal reference. 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; dd, double doublet; dt, double triplet; m, multiplet; br, broad. 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), as well as at the CACTUS facility of the University of Santiago de Compostela.

3-(Propa-1,2-dien-1-yl)oxazolidin-2-one (**1a**),[1] 1-(propa-1,2-dien-1-yl)pyrrolidin-2-one (**1b**),[1] 3-(buta-1,2-dien-1-yl)oxazolidin-2-one (**1c**), [2] (E)-5-(buta-1,3-dien-1-yl)-1,2,3-trimethoxybenzene (**2b**), [3] (E)-1-bromo-4-(buta-1,3-dien-1-yl)benzene (**2c**),[3] (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (**2d**),[4] (1*E*,3*E*)-penta-1,3-dienylbenzene (**2f**), [5] are known compounds and were synthesized according to those previously reported procedures. tert-Butyl((2*E*,4*E*)-hexa-2,4-dien-1-yloxy)dimethylsilane (**2j**) was prepared from (2*E*,4*E*)-hexa-2,4-dien-1-ol by standard TBS silylation using TBSCl and imidazole (98 % yield). Spectral properties are in accordance to literature.[6] (*E*)-3-(Buta-1,3-dien-1-yl)oxazolidin-2-one (**2k**) was prepared from oxazolidin-2-one, and pyridinium *p*-toluenesulfonate following a known procedure.[7] Spectral properties of cycloadducts **3a**, **3d**, **3f**, **3g**, **3h**, **3i**, **3j**, **3db**, and **3dc** are in accordance to those previously reported.[2] 1,3-Dichloroisoquinoline **4**,[8] 2-methylnaphthalen-1-ylboronic acid **5a**[9] and 1-bromo-2-cyclohexylnaphthalene[10] were prepared according to literature procedures. 1,1'-Bis(diphenylphosphino)ferrocene (dppf), $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ were purchased from commercial suppliers or kindly supplied by Johnson-Matthey PLC. 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.

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[3] McNulty, J.; Das, P. *Tetrahedron Lett.* **2009**, *50*, 5737-5740.

[4] Y. Nakao, H. Idei, K. S. Kanyiva and T. Hiyama, *J. Am. Chem. Soc.* **2009**, *131*, 5070-5071.

[5] Antonioletti, R.; Bonadies, F.; Ciammaichella, A.; Viglianti, A. *Tetrahedron* **2008**, *64*, 4644-4648.

[6] Sodeoka, M.; Yamada, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1990**, *112*, 4906-4911.

[7] (a) Mcalonan, H.; Murphy, J. P.; Nieuwenhuyzen, M.; Reynolds, K.; Sarma, P. K. S.; Stevenson, P. J.; Thompson, N.*J. Chem. Soc., Perkin Trans. 1*, **2002**, 69 (b) (*E*)-3-(buta-1,3-dien-1-yl)oxazolidin-2-one (0,588 g, 4,23 mmol, 12 % yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, *J* = 14.2 Hz, 1H), 6.25 (dt, *J* = 16.9, 10.4 Hz, 1H), 5.46 (dd, *J* = 14.2, 10.6 Hz, 1H), 5.10 – 4.96 (m, 1H), 4.96 – 4.84 (m, 1H), 4.38 (t, *J* = 7.7 Hz, 2H), 3.68 (t, *J* = 7.7 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 155.0 (*C*), 133.9 (*C*H), 126.6 (*C*H), 114.3 ($CH_2$), 111.9 (*C*H), 62.1 ($CH_2$), 42.2 ($CH_2$).

[8] Lee, C.H.; Bayburt, E.K.; DiDomenico, S.Jr.; Drizin, I.; Gomtsyan, A.R.; Koenig, J.R.; Perner, R.j.; Schmidt, R.G.Jr.; Turner, S.C.; White, T.K.; Zheng, G.Z. US 2004/0157849 A1.

[9] (a) Clews, J.; Curtis, A.D.M.; Malkin, H. *Tetrahedron* **2000**, *56*, 8735. (b) Lim, C.; Tissot, O.; Mattison, A.; Hooper, M.; Brown, J.; Cowley, A.; Hulmes, D.; Blacker, A. *Organic Process Research & Development* **2003**, *7*, 379.

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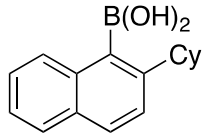
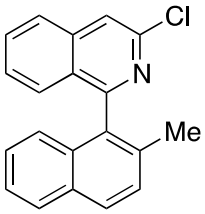
## Synthesis of gold(I) complexes Au7 and Au8

### 2-Cyclohexylnaphthalen-1-ylboronic acid (5b).



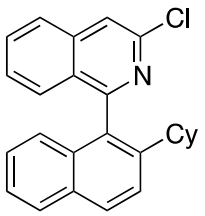

Freshly activated Mg turnings (340 mg, 14 mmol) and a catalytic amount of $I_2$ were placed in a 2-necked flask equipped with a condenser under an argon atmosphere. A solution of 1-bromo-2-cyclohexylnaphthalene (3.40 g, 11.7 mmol) in anhydrous THF (14 mL) was added slowly under a constant reflux. The reaction mixture was stirred for 2 h at rt, then cooled to −78 °C and trimethyl borate (2.2 ml, 20 mmol) was added slowly. The mixture was allowed to warm to rt and stirred overnight. 2N HCl (5 ml) was added and most of the THF was removed under reduced pressure. The mixture was extracted with $CH_2Cl_2$ (3 × 10 mL) and the combined organic layer was dried ($MgSO_4$), filtered and concentrated. Addition of cyclohexane afforded a precipitated that was washed with cold $Et_2O$, yielding 2.39 g (80%) of **5b** as a white solid. M.p. 156–158 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.83–7.77 (m, 3H), 7.50–7.38 (m, 3H), 4.97 (br s, 2H), 2.73 (tt, *J* = 11.8, 3.2 Hz, 1H), 1.96–1.74 (m, 5H), 1.73–1.46 (m, 3H), 1.44–1.21 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.1, 134.9, 131.6, 129.1, 128.2, 127.7, 126.2, 125.1, 124.2, 46.3, 34.8, 26.9, 26.1. *m/z* (EI) 254 (100, $M^+$), 253 (25, $M^+$–1), 167 (61), 142 (28). HRMS *m/z* calcd for $C_{16}H_{19}BO_2$ 254.1478, found 254.1482.

### 3-Chloro-1-(2-methylnaphthalen-1-yl)isoquinoline (6a).[11]




A schlenk tube was charged with 1,3-dichloroisoquinoline **4** (2 g, 10 mmol) and $Pd(PPh_3)_4$ (463 mg, 4 mmol%) under an argon atmosphere and the mixture was solved in DME (15 mL) with the help of a gentle heating. 2-Methylnaphthalen-1-yl boronic acid **5a** (2.23 g, 12 mmol) and CsF (3.36 g, 22 mmol) were added in one portion and the mixture was heated under reflux overnight. $Et_2O$ 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 (1:4 $CH_2Cl_2$–cyclohexane) to yield **6a** (2.50 g, 82%) as a white solid. M.p. 124–127 °C. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.86–7.78 (m, 4H), 7.63 (ddd, *J* = 8.2, 3.8, 2.1 Hz, 1H), 7.42–7.39 (d, *J* = 8.4 Hz, 1H), 7.36–7.30 (m, 3H), 7.24–7.16 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 2.06 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 161.5, 145.2, 138.4, 134.5, 133.4, 132.7, 132.0, 131.3, 128.8, 128.6, 128.0, 127.7, 127.5, 127.3, 126.4, 126.3, 125.4, 125.1, 119.2, 20.2. *m/z* (CI) 304 (40, $M^+$+1), 303 (53, $M^+$), 302 (100), 301 (53), 268 (5). HRMS *m/z* calcd for $C_{20}H_{14}NCl$ 303.0815, found 303.0811.

### 3-Chloro-1-(2-cyclohexylnaphthalen-1-yl)isoquinoline (6b).

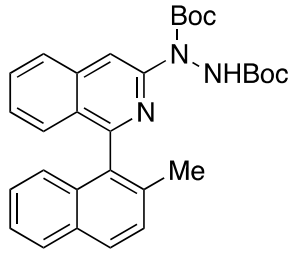



A schlenk tube was charged with 1,3-dichloroisoquinoline **4** (2 g, 10 mmol) and $Pd(PPh_3)_4$ (463 mg, 4 mmol %) under an argon atmosphere and the mixture was solved in DME (15 mL) with the help of a gentle heating. 2-Cyclohexylnaphthalen-1-ylboronic acid **5b** (3.05 g, 12 mmol) and CsF (3.36 g, 22 mmol) were added in one portion and the mixture was heated under reflux overnight. $Et_2O$ 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 (1:5 $CH_2Cl_2$-cyclohexane) to yield **6b** (2.23 g, 60%) as a light yellow foam. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.7 Hz, 1H), 7.88–7.85 (m, 3H), 7.72–7.66 (m, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.41–7.37 (m, 1H), 7.36–7.32 (m, 1H), 7.25–7.20 (m, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 2.13–2.07 (m, 1H), 2.00–1.97 (m, 1H), 1.73 (br d, *J* = 13.1 Hz, 1H), 1.67–1.55 (m, 4H), 1.53–1.43 (m, 1H), 1.26–1.14 (m, 1H), 1.10–1.01 (m, 1H), 0.90–0.79 (m, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 161.5, 145.1, 143.9, 138.1, 132.6, 132.3, 132.0, 131.2, 129.1, 127.8, 127.6, 127.4, 126.2,

[11] Ford, A.; Sinn, E.; Woodward, S. *J. Chem. Soc., Perkin Trans 1*, **1997**, 927.

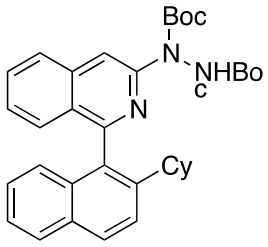
126.1, 125.9, 125.1, 124.5, 119.1, 41.9, 34.0, 33.3, 26.5, 26.5, 26.0. *m/z* (EI) 373 (35, $M^+$, $^{37}Cl$), 372 (38, $M^+$+1), 371 (100, $M^+$, $^{35}Cl$), 336 (18), 302 (25). HRMS *m/z* calcd for $C_{25}H_{22}NCl$ 371.1441, found 371.1443.

**Di-*tert*-butyl-1-(1-(2-methylnaphthalen-1-yl)isoquinolin-3-yl)hydrazine-1,2-dicarboxylate (7a).**



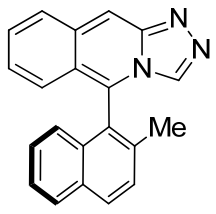

3-Chloro-1-(2-methylnaphthalen-1-yl)isoquinoline **6a** (1 g, 3.3 mmol), di(*tert*-butyl)-1,2-hydrazodicarboxylate (2.37 g, 9.9 mmol), dppf (366 mg, 0.66 mmol, 20 mol%), $Pd_2(dba)_3$ (453 mg, 0.50 mmol, 15 mol%) and $CsCO_3$ (2.70 g, 8.25 mmol) were solved in dry toluene (16 mL) under an argon atmosphere. 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 (1:10 → 1:5 EtOAc-cyclohexane) to yield **7a** (1.43 g, 87%) as a light yellow solid. M.p. 104–106 °C. $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.20 (br s, 1H, NH), 8.10 (s, 1H), 7.96–7.88 (m, 3H), 7.66–7.63 (m, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33–7.29 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 2.12 (s, 3H), 1.55 (s, 9H), 1.43 (s, 9H). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 165.3, 159.3, 155.0, 153.9, 148.1, 138.0, 134.5, 134.2, 132.8, 132.0, 130.5, 129.7, 128.6, 128.5, 127.9, 127.5, 127.0, 126.9, 126.3, 125.6, 125.0, 82.3, 81.2, 28.1, 20.1. *m/z* (CI) 500 (15, $M^+$+1), 400 (19), 344 (48), 343 (21), 300 (56), 299 (100), HRMS *m/z* calcd for $C_{30}H_{34}N_3O_4$ 500.2549, found 500.2540.

**Di-*tert*-butyl-1-(1-(2-cyclohexylnaphthalen-1-yl)isoquinolin-3-yl)hydrazine-1,2-dicarboxylate (7b).**




3-Chloro-1-(2-cyclohexylnaphthalen-1-yl)isoquinoline **6b** (1 g, 2.82 mmol), di(*tert*-butyl)-1,2-hydrazodicarboxylate (1.96 g, 8.46 mmol), dppf (313 mg, 0.56 mmol, 20 mol%), $Pd_2(dba)_3$ (387 mg, 0.42 mmol, 15 mol%) and $CsCO_3$ (2.30 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 (1:10 EtOAc-cyclohexane) to yield **7b** (1.56 g, 95%) as a light yellow solid. M.p. 142–144 °C. $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.10 (br s, 1H, NH), 7.83 (t, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.54–7.45 (m, 2H), 7.28–7.19 (m, 2H), 7.17–7.03 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 1H), 2.01–1.99 (m, 1H), 1.84 (br d, *J* = 11.4 Hz, 1H), 1.61–1.53 (m, 1H), 1.51–1.39 (m, 3H), 1.44 (s, 9H), 1.26–1.38 (m, 2H), 1.31 (s, 9H), 1.12–0.99 (m, 1H), 0.99–0.84 (m, 1H), 0.81–0.64 (m, 1H). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 159.4, 154.7, 153.8, 147.7, 143.8, 137.6, 133.0, 132.6, 131.9, 130.3, 128.7, 127.7, 127.4, 127.0, 126.7, 126.0, 124.9, 124.4, 114.6, 82.1, 80.9, 41.7, 34.3, 33.0, 28.1, 26.8, 26.5, 26.4, 25.9. *m/z* (CI) 568 (8, $M^+$+1), 367 (100), 246 (60), 129 (42). HRMS *m/z* calcd for $C_{35}H_{42}N_3O_4$ 568.3175, found 568.3161.

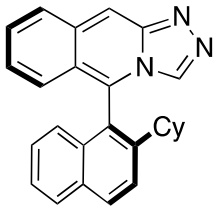
**5-(2-Methylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinoline (8a).**




To a solution of **7a** (1.43 g, 2.87 mmol) in dioxane (7.9 mL) was added 4M HCl in dioxane (7.9 mL) under an argon atmosphere and the mixture was stirred at rt overnight. The mixture was concentrated and the residue was solved in HCOOH (11 mL) and refluxed for 24 h. The mixture was concentrated and the resulting residue was solved in dry toluene (16 mL). $POCl_3$ (802 µL, 8.61 mmol) was added and the mixture was heated under reflux for 24 h, concentrated and the residue was solved in EtOAc, washed with NaOH 2M (2 × 5 mL), and brine (1 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (100:1 → 50:1 $CH_2Cl_2$-MeOH) to yield **8a** (620 mg, 70%) as a yellow solid. M. p. 79–81 °C. $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.30 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 9.0, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.50 (td, *J* = 8.2, 5.9 Hz, 1H), 7.35–7.31 (m, 1H), 7.30–7.28 (m, 1H), 7.09–7.06 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 2.05 (s, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 148.3, 136.6, 133.0, 132.4, 131.6, 131.1, 131.0, 128.8, 128.6, 128.2, 128.1, 127.9,

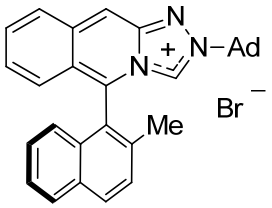
126.7, 126.2, 125.8, 124.7, 124.0, 121.9, 110.7, 110.6, 19.7. *m/z* (CI) 310 (72, $M^+$+1), 309 (100, $M^+$), 280 (10), 254 (9). HRMS *m/z* calcd for $C_{21}H_{15}N_3$ 309.1266, found 309.1263. The racemic mixture was resolved by semipreparative HPLC on a Chiralpak IA column. Analytical Chiralpak IA, 90:10 $CH_2Cl_2$/Hexane, 1 mL/min, 30 °C, λ = 229.7 nm: first enantiomer, compound (*R*)-**8a**, $t_R$ = 15.3 min, $[\alpha]^{26}_D$ = –323.1 (*c* 0.34, $CHCl_3$); second enantiomer, compound (*S*)-**8a**, $t_R$ = 20.3 min, $[\alpha]^{23}_D$ = +314.9 (*c* 0.4, $CHCl_3$).

**5-(2-Cyclohexylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinoline (8b).**



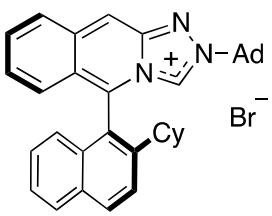
To a solution of compound **7b** (1.03 g, 1.82 mmol) in dioxane (5 mL) was added 4M HCl in dioxane (5 mL) under an argon atmosphere and the mixture was stirred at rt overnight. The mixture was concentrated and the residue was solved in HCOOH (7 mL) and refluxed under argon for 24h. The mixture was concentrated and the resulting residue was solved in dry toluene (10 mL). $POCl_3$ (509 µL, 5.46 mmol) was added and the mixture was heated under reflux for 24 h. The solvent was removed in vacuo and the residue was solved in EtOAc, washed with 2M NaOH (2 × 5 mL), and brine (15 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (100:1 → 50:1 $CH_2Cl_2$-MeOH) to yield **8b** (370 mg, 54%) as a yellow solid. M.p. 115–117 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.29 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.33 (ddd, *J* = 8.9, 5.7, 1.6 Hz, 1H), 7.24–7.20 (m, 1H), 7.12–7.02 (m, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 1.94–1.88 (m, 1H), 1.74–1.48 (m, 5H), 1.30–1.23 (m, 1H), 1.20–1.10 (m, 2H), 0.84–0.87 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 148.2, 146.3, 133.1, 133.0, 132.6, 131.5, 131.4, 131.3, 128.5, 128.4, 128.0, 127.8, 126.6, 126.3, 125.0, 124.8, 124.4, 124.3, 122.6, 110.6, 42.6, 34.1, 34.0, 26.3, 26.2, 25.6. *m/z* (EI) 378 (30, $M^+$+1), 377 (100, $M^+$), 265 (16). HRMS *m/z* calcd for $C_{26}H_{23}N_3$ 377.1892, found 377.1898. 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 = 232.0 nm: first enantiomer, compound (*R*)-**8b**, $t_R$ = 6.0 min, $[\alpha]^{24}_D$ = –139.8 (*c* 0.95, $CHCl_3$); second enantiomer, compound (*S*)-**8b**, $t_R$ = 9.2 min, $[\alpha]^{23}_D$ = +139.6 (*c* 0.85, $CHCl_3$).

**2-(Adamantan-1-yl)-5-(2-methylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinolin-2-ium bromide [9a(Br$^-$)].**



(*S*)-**8a** (715 mg, 2.31 mmol) and 1-bromoadamantane (1.49 g, 6.93 mmol) were solved in acetic acid (10 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 ($CH_2Cl_2$ → 99:1 $CH_2Cl_2$-MeOH) to yield (*S*)-**9a(Br$^-$)** (1.0 g, 76%) as a yellow solid. M.p. 252 °C (dec). $[\alpha]^{25}_D$ = +254.7 (*c* 0.74, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.49 (s, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 9.4 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.52 (dd, *J* = 9.1, 6.0 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 1H), 7.28–7.24 (m, 2H), 7.21 (dd, *J* = 9.1, 1.0 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 2.51–2.45 (m, 6H), 2.39 (s, 3H), 2.26 (br s, 3H), 1.83–1.77 (m, 3H), 1.73–1.68 (m, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 145.4, 139.8, 136.2, 135.3, 132.4, 132.1, 131.0, 131.0, 130.1, 129.7, 129.3, 129.0, 127.9, 127.6, 125.9, 125.1, 124.5, 122.5, 122.4, 110.8, 66.9, 41.7, 35.3, 29.5, 21.5. *m/z* (CI) 444 (11, $M^+$), 310 (29), 309 (26), 136 (12), 135 (100). HRMS *m/z* calcd for $C_{31}H_{30}N_3$ 444.2434, found 444.2440.

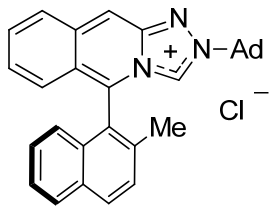
**2-(Adamantan-1-yl)-5-(2-cyclohexylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinolin-2-ium bromide [9b(Br$^-$)].**



(*R*)-**8b** (110 mg, 0.29 mmol) and 1-bromoadamantane (221 mg, 0.87 mmol) were solved in acetic acid (10 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 ($CH_2Cl_2$ → 99:1 $CH_2Cl_2$-MeOH) to yield (*R*)-**9b(Br$^-$)** (158 mg, 92%) as a yellow solid. M.p. 168–170 °C. $[\alpha]^{24}_D$ = –24.7 (*c* 0.95, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.71

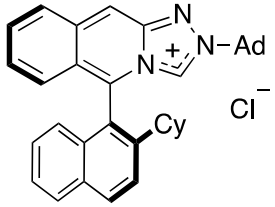
(s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.55 (dd, *J* = 9.0, 6.3 Hz, 1H), 7.50 (br t, *J* = 6.9 Hz, 1H), 7.35 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.26–7.23 (m, 1H), 7.15 (dd, *J* = 9.2, 0.8 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 2.48–2.41 (m, 6H), 2.32– 2.27 (m, 3H), 1.87–1.40 (m, 14H), 1.28–1.09 (m, 1H), 0.90–0.68 (m, 2H).[13]C NMR (125 MHz, $CDCl_3$) δ 146.4, 145.5, 136.3, 134.9, 133.1, 132.8, 131.4, 131.1, 129.1, 128.9, 128.8, 128.5, 128.0, 126.8, 125.3, 125.2, 125.1, 124.7, 121.9, 111.6, 66.9, 43.3, 42.2, 35.4, 34.3, 34.1, 29.5, 26.3, 25.6. HRMS *m/z* calcd for $C_{36}H_{38}N_3$ 512.3060, found 512.3071.

**2-(Adamantan-1-yl)-5-(2-methylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinolin-2-ium chloride [9a(Cl⁻)].**



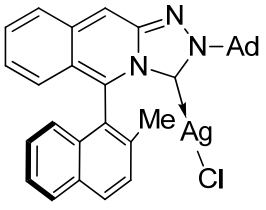

(*S*)-**9a(Br⁻)** (189 mg, 0.36 mmol) was eluted through a Dowex 22 anion exchange resin column using methanol as eluant.[12] The solvent was removed in vacuo and the residue was solved in $CH_2Cl_2$, dried with $MgSO_4$ and concentrated to yield (*S*)-**9a(Cl⁻)** as a yellow solid in quantitative yield (173 mg). M.p. 180 °C (dec). $[\alpha]^{25}_D$ = +230.3 (*c* 0.71, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.48 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.51 (dd, *J* = 8.9, 6.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.26–7.18 (m, 3H), 6.52 (d, *J* = 8.4 Hz, 1H), 2.49–2.44 (m, 6H), 2.38 (s, 3H), 2.25 (br s, 3H), 1.80–1.78 (m, 3H), 1.71–1.68 (m, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 145.3, 139.8, 136.2, 135.4, 132.4, 132.1, 131.0, 131.0, 130.2, 130.0, 129.3, 129.0, 127.8, 127.5, 125.8, 125.1, 124.5, 122.5, 122.4, 110.7, 66.8, 41.7, 35.3, 29.5, 21.5. HRMS *m/z* calcd for $C_{31}H_{30}N_3$ 444.2434, found 444.2438.

**2-(Adamantan-1-yl)-5-(2-cyclohexylnaphthalen-1-yl)-[1,2,4]triazolo[4,3-*b*]isoquinolin-2-ium chloride [9b(Cl⁻)].**




(*R*)-**9b(Br⁻)** (158 mg, 0.267 mmol) was eluted through a Dowex 22 anion exchange resin column using methanol as eluant.[12] The solvent was removed in vacuo and the residue was solved in $CH_2Cl_2$, dried with $MgSO_4$ and concentrated to yield (*R*)-**9b(Cl⁻)** (146 mg, quantitative) as a yellow solid. M.p. 200 °C (dec). $[\alpha]^{25}_D$ = –27.3 (*c* 1, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.74 (s, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33–7.14 (m, 2H), 7.09 (d, *J* = 9.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 2.33–2.24 (m, 10H), 1.79–1.38 (m, 12H), 1.15–1.03 (m, 2H), 0.81–0.64 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 146.6, 145.5, 136.3, 134.9, 133.0, 132.7, 131.3, 129.3, 129.0, 128.9, 128.4, 128.1, 126.7, 125.3, 125.2, 124.8, 124.1, 124.0, 121.8, 111.8, 66.9, 43.2, 42.2, 35.3, 34.2, 34.0, 29.5, 26.2, 25.5. *m/z* (EI) 512 (26, $M^+$), 511 (64), 377 (39), 135 (100, $Ad^+$). HRMS *m/z* calcd for $C_{36}H_{37}N_3$ 511.2987, found 511.2973.

**NHC-Ag complex (*S*)-10a**

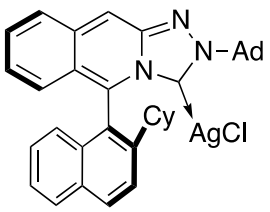



(*S*)-**9a(Cl⁻)** (180 mg, 0.37 mmol), $Ag_2O$ (51 mg, 0.22 mmol) and 4Å molecular sieves were suspended in dry $CHCl_3$ (6 mL) under an argon atmosphere and in the darkness. The mixture was stirred at rt for 12 h and then filtered through a HPLC syringe filter. The solvent was evaporated and to yield (*S*)-**10a** (177 mg, 82%) as a yellow foam. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.26–7.23 (m, 1H), 7.00 (dd, *J* = 9.1, 6.4 Hz, 1H), 6.91 (d, *J* = 9.1 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 2.50–2.49 (m, 6H), 2.24 (br s, 3H), 2.07 (s, 3H), 1.74 (s, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.2 (2 d, $J_{C,Ag}$ = 266.3 and 230.9 Hz), 145.7,

[12] The resin was washed thoroughly with methanol prior to use.

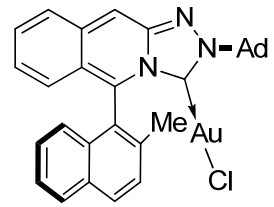
137.7, 136.4, 135.2, 132.8, 132.0, 131.6, 129.5, 129.3, 129.0, 127.6, 127.1, 126.7, 126.0, 126.0, 125.5, 123.4, 122.7, 109.9, 63.8, 44.3, 35.7, 29.8, 20.2.

**NHC-Ag complex (*R*)-10b**



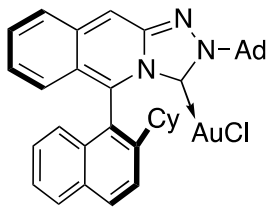

(*R*)-**9b(Cl$^-$)** (165 mg, 0.30 mmol), $Ag_2O$ (42 mg, 0.18 mmol) and 4Å molecular sieves were suspended in dry $CHCl_3$ (5 mL) under an argon atmosphere and in the darkness. The mixture was stirred at rt for 12 h and then filtered using a HPLC syringe filter. The solvent was evaporated to yield (*R*)-**10b** (196 mg, quantitative) as a yellow foam. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 1H), 8.23 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.73 (br d, *J* = 8.9 Hz, 1H), 7.46 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.34–7.29 (m, 1H), 7.22 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.02–6.91 (m, 2H), 6.63 (br d, *J* = 8.3 Hz, 1H), 2.50–2.49 (m, 5H), 2.25 (br s, 3H), 1.98–1.46 (m, 15H), 1.25–1.07 (m, 1H), 0.90–0.65 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.7 (2 d, $J_{C,Ag}$ = 262.5 and 225.0 Hz), 145.9, 145.7, 145.6, 138.0, 135.2, 133.0, 132.4, 131.3, 129.6, 129.3, 127.6, 127.1, 126.4, 126.2, 125.9, 125.3, 124.7, 124.0, 123.3, 109.9, 63.8, 44.3, 43.2, 35.8, 34.6, 33.8, 29.9, 26.4, 26.4, 25.7.

**Au (I) complex (*S*)-Au7**




A solution of (*S*)-**10a** (147 mg, 0.25 mmol) and AuCl•$Me_2S$ (89 mg, 0.30 mmol) in dry toluene (7.5 mL) was stirred at rt in the darkness 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 (*S*)-**Au7** (120 mg, 71%) as a yellow solid. M.p. 140 °C (dec). $[\alpha]^{26}_D$ = +155.5 (*c* 0.70, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.24–8.21 (m, 2H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.32 (dd, *J* = 9.0, 6.2 Hz, 1H), 7.26–7.23 (m, 1H), 7.00 (dd, *J* = 9.2, 6.2 Hz, 1H), 6.94 (br d, *J* = 9.2 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 2.75–2.68 (m, 6H), 2.25 (br s, 3H), 2.04 (s, 3H), 1.78–1.71 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.3, 163.4, 145.0, 137.6, 137.0, 135.2, 132.6, 131.5, 129.6, 129.0, 128.7, 127.3, 127.1, 127.0, 126.9, 125.8, 125.7, 123.7, 123.2, 110.3, 65.2, 44.0, 35.8, 30.1, 20.4. HRMS *m/z* calcd for $C_{31}H_{29}N_3ClAu$ 675.1710, found 675.1702.

**Au (I) complex (*R*)-Au8**



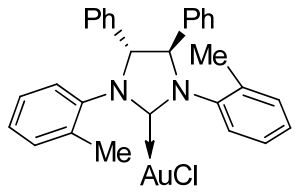

A solution of (*R*)-**10b** (50 mg, 0.076 mmol) and AuCl•$Me_2S$ (27 mg, 0.092 mmol) in dry toluene (2 mL) was stirred at rt in the darkness for 12 h. The reaction was filtered using a HPLC syringe filter and the solvent was evaporated. The residue was purified by flash chromatography (45:45:10 EtOAc-cyclohexane-$CH_2Cl_2$) to yield (*R*)-**Au8** (56 mg, quantitative) as a yellow solid. M.p. 140 °C (dec). $[\alpha]^{27}_D$ = –51.8 (*c* 0.65, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 1H), 8.22 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.43 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.35–7.28 (m, 1H), 7.22 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 6.98–6.97 (m, 2H), 6.65 (br d, *J* = 8.3 Hz, 1H), 2.70–2.69 (m, 5H), 2.25 (br s, 3H), 1.79–1.50 (m, 15H), 1.23–1.07 (m, 1H), 0.95–0.69 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.8, 146.0, 145.0, 137.7, 135.0, 132.8, 132.3, 131.8, 129.7, 128.9, 127.2, 127.0, 126.5, 126.2, 125.8, 125.8, 125.0, 124.2, 123.7, 110.2, 65.1, 43.9, 43.4, 35.8, 33.8, 30.0, 26.5, 26.4, 25.9. *m/z* (EI) 745 (19, $M^+$, $^{37}$Cl), 743 (46, $M^+$, $^{35}$Cl), 708 (28, $M^+$–Cl), 707 (68), 705 (40), 543 (26), 511 (28, $M^+$–AuCl), 376 (26), 135 (100, $Ad^+$). HRMS *m/z* calcd for $C_{36}H_{37}N_3ClAu$ 743.2342, found 743.2323.

Data for (*S*)-**Au8** $[\alpha]^{25}_D$ = +57.4 (*c* 0.5, $CHCl_3$).

Good quality crystals of enantiomerically pure (*R*)-**Au8** suitable for X-ray diffractometry were obtained by slow evaporation of a solution of the complex in a 6:2:1 cyclohexane/EtOAc/$CH_2Cl_2$ mixture.

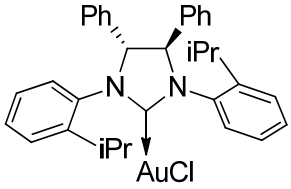
## Other Gold(I) complexes from Table 1. [13]

**((4*R*,5*R*)-4,5-diphenyl-1,3-di-o-tolylimidazolidin-2-ylidene)gold(I) chloride** (**Au1**).



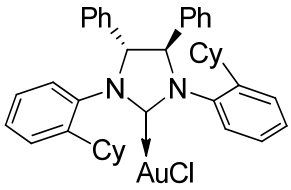

Prepared from the corresponding dihydroimidazolium salt ((4*R*,5*R*)-4,5-diphenyl-1,3-di-o-tolyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate)[14] by formation of the silver carbene,[15] and subsequent transmetallation with $AuCl{\cdot}SMe_2$.[16]. **$^1$H-NMR**: (300 MHz, $cdcl_3$) δ 7.56 – 7.23 (m, 10H), 7.20 – 6.95 (m, 8H), 5.30 (s, 2H), 2.38 (br s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 193.59, 137.38, 135.00, 131.51, 129.45, 129.28, 128.89, 127.68, 126.86, 76.47, 18.87.; **LRMS** (ESI-MS) 657.13 [M + Na ($C_{29}H_{26}AuClN_2Na)^+$], 1233.3 [2M – Cl ($C_{58}H_{52}Au_2ClN_4)^+$], 627.18 [2M – Cl + Na ($C_{58}H_{52}Au_2ClN_4Na)^{2+}$]. Experimental and theoretical isotopic patterns are in agreement. **HRMS** (ESI-MS) calculated for $C_{29}H_{26}AuClN_2Na$ 657.1342, found 657.1355.

**((4R,5R)-1,3-bis(2-isopropylphenyl)-4,5-diphenylimidazolidin-2-ylidene)gold(I) chloride** (**Au2**).




Prepared from the corresponding dihydroimidazolium salt (4R,5R)-1,3-bis(2-isopropylphenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate)[17] by formation of the silver carbene,[15] and subsequent transmetallation with $AuCl{\cdot}SMe_2$.[16] $^1$H NMR (300 MHz, $cdcl_3$) δ 7.51 – 7.26 (m, 16H), 6.99 – 6.76 (m, 2H), 5.40-5.16 (m, 2H), 3.36 (br s, 1.2H), 3.04 (br s, 0.8H), 1.70 – 1.15 (m, 12H), 0.51-0.26 (m, 2H). **$^{13}$C NMR** (75 MHz, $cdcl_3$) δ = 129.52, 129.41, 128.29, 127.82, 127.59, 126.86, 126.55, 79.08, 28.39, 25.09, 23.99. **LRMS** (ESI-MS) 713.2 [M + Na ($C_{33}H_{34}AuClN_2Na)^+$], 1345.4 [2M – Cl ($C_{66}H_{68}Au_2ClN_4)^+$], 683.2 [2M – Cl + Na ($C_{66}H_{68}Au_2ClN_4Na)^{2+}$]. Experimental and theoretical isotopic patterns are in agreement. **HRMS** (ESI-MS) calculated for $C_{33}H_{34}AuClN_2Na$ 713.1968, found 713.1954.

**((4R,5R)-1,3-bis(2-yclohexylphenyl)-4,5-diphenylimidazolidin-2-ylidene)gold(I) chloride** (**Au3**).




Prepared from the corresponding dihydroimidazolium salt (4R,5R)-1,3-bis(2-cyclohexylphenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate)[18] by formation of the silver carbene,[15] and subsequent transmetallation with $AuCl{\cdot}SMe_2$.[16] $^1$H NMR (300 MHz, $CDCl_3$) δ 7.60 – 6.80 (m, 18H), 5.50-5.06 (m, 2H), 3.35-0.86 (m, 22H). **$^{13}$C NMR** (75 MHz, $cdcl_3$) δ = 146.2, 144.8, 137.6, 135.7, 130.9, 130.3, 129.4, 128.5, 128.2, 128.0, 127.6, 126.9, 126.6, 79.4, 78.6, 39.0, 38.6, 37.8, 34.4, 27.6, 27.3, 27.0, 26.5, 26.1. **LRMS** (ESI-MS) 793.26 [M + Na ($C_{39}H_{42}AuClN_2Na)^+$], 1505.6 [2M – Cl ($C_{68}H_{84}Au_2ClN_4)^+$], 763.3 [2M – Cl + Na ($C_{68}H_{84}Au_2ClN_4Na)^{2+}$]. Experimental and theoretical isotopic patterns are in agreement. **HRMS** (ESI-MS) calculated for $C_{39}H_{42}AuClN_2Na$ 793.2594, found 793.2582.

---

[13] Gold complex (4*S*,5*S*)-1,3-Dibenzhydryl-4,5-diphenylimidazolidin-2- ylidenegold(I) chloride **Au5** is a known compound, see: (a) Yamada, K.-i.; Matsumoto, Y.; Selim, K. B.; Yamamoto, Y.; Tomioka, K. *Tetrahedron* **2012**, *68*, 4159. (b) Selim, K.; Matsumoto, Y.; Yamada, K.; Tomioka, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 8733

[14] (4*R*,5*R*)-4,5-diphenyl-1,3-di-o-tolyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate is a known compound that was prepared following the procedure described in: Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett*. **2001**, *3*, 3225.

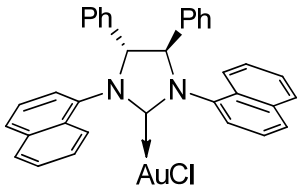
[15] Lee, K.; Hoveyda, A. H. *J. Org. Chem*. **2009**, *74*, 4455

[16] For instance, see: Matsumoto, Y.; Yamada, K.; Tomioka, K. *J. Org. Chem.* **2008**, *73*, 4578.

[17] (4*R*,5*R*)-1,3-bis(2-isopropylphenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate) is a known compound that was prepared following the procedure described in: Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett*. **2001**, *3*, 3225.

[18] (4*R*,5*R*)-1,3-bis(2-cyclohexylphenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate is a known compound that was prepared following the procedure described in: Chaulagain, M. R.; Sormunen, G. J. Montgomery, J. *J. Am. Chem. Soc*. **2007**, *129*, 9568.

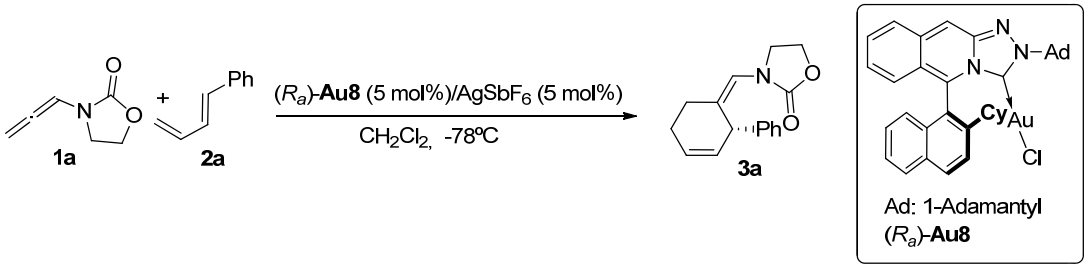
**((4R,5R)-1,3-di(naphthalen-1-yl)-4,5-diphenylimidazolidin-2-ylidene)gold(III) chloride** (**Au4**).



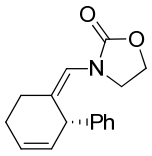
Prepared from the corresponding dihydroimidazolium salt ((4R,5R)-1,3-di(naphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium[19] by formation of the silver carbene,[15] and subsequent transmetallation with AuCl·$SMe_2$.[16] **$^1$H NMR** (300 MHz, $CDCl_3$) δ 8.36 – 8.01 (m, 2H), 8.00 – 7.75 (m, 4H), 7.74 – 7.07 (m, 17H), 5.75 – 5.57 (m, 2H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 137.36, 134.61, 134.37, 129.67, 129.53, 129.25, 128.77, 127.40, 126.55, 125.42, 121.51, 77.38. **LRMS** (ESI-MS) 729.13 [M + Na $(C_{35}H_{26}AuClN_2Na)^+$], 1377.3 [2M – Cl $(C_{70}H_{52}Au_2ClN_4)^+$], 699.2 [2M – Cl + Na $(C_{70}H_{52}Au_2ClN_4Na)^{2+}$]. Experimental and theoretical isotopic patterns are in agreement. **HRMS** (ESI-MS) calculated for $C_{35}H_{26}AuClN_2Na$ 729.1342, found 729.1337.

**General procedure for the (4+2) cycloaddition of allenamides and acyclic dienes catalyzed by** (*R*)-**Au8**

(Exemplified for the preparation of (S)-**3a**, according to the conditions of table 2, entry 5)

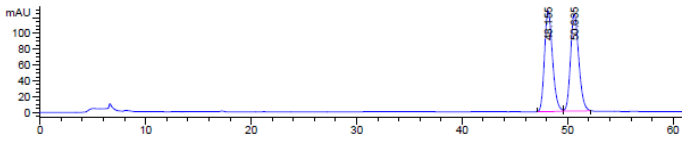



(*E*)-Buta-1,3-dienylbenzene (**2a**, 46,8 mg, 0,360 mmol) was added to solution of (*R*)-**Au8** (4.46 mg, 5,99 µmol) and $AgNTf_2$ (2,36 mg, 5,99 µmol) in $CH_2Cl_2$ (1.2 ml), in a dried Schlenk tube containing 200 mg of 4 Å MS. The resulting mixture was cooled to -78 °C and allenamide**1a** (15 mg, 0,120 mmol) was then added. The mixture was stirred at that temperature for 3h (the progress of the reaction was easily monitored by *tlc*) and filtered through a short pad of florisil®, eluting with $Et_2O$. The filtrate was concentrated and purified by flash chromatography (95:5 -> 90:10 hexanes/ethyl acetate) to give 3-{(*Z*)-[(2*S*)-2-phenylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (**3a**,[2] 45 mg, 88% yield, Mp = 92-94 ºC; 99% ee, [α]$D^{20}$ = - 161.9 (*c* = 1.6); 99%ee).



**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.21 (d, *J* = 7.1 Hz, 2H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.03 (s, 1H), 5.87 – 5.81 (m, 1H), 5.77 – 5.69 (m, 1H), 4.33 (s, 1H), 4.22 – 4.09 (m, 2H), 3.58 (dd, *J* = 16.3, 8.8 Hz, 1H), 3.47 (td, *J* = 8.9, 6.2 Hz, 1H), 2.37 – 2.26 (m, 2H), 2.22 – 2.15 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 157.1 (C), 143.3 (C), 133.0 (C), 128.6 (CH), 128.5 (CH), 127.5 (CH), 127.3 (CH), 126.3 (CH), 118.2 (CH), 62.1 ($CH_2$), 46.1 ($CH_2$), 41.8 (CH), 28.2 ($CH_2$), 26.8 ($CH_2$). **LRMS** (*m/z, CI*): 256 [$M^+$+1, 39], 178 (14), 169 (100), 101 (77), 88 (65), 77 (10). **HRMS** Calculated for $C_{16}H_{18}NO_2$: 256.1338, found 256.1338. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA, rt, (Hexane - iPrOH = 98:2, 0.5 ml/min). (*R*,*Z*)-**3a**, $t_R$ = 72.4 min, (*S*,*Z*)-**3a**, $t_R$ = 77.3 min, or Chiralpak IA-3, rt, (Hexane - iPrOH = 95:5, 0.5 ml/min). (*R*,*Z*)-**3a**, $t_R$ = 48.1 min, (*S*,*Z*)-**3a**, $t_R$ = 50.6 min.

Racemic sample, Chiralpak IA-3

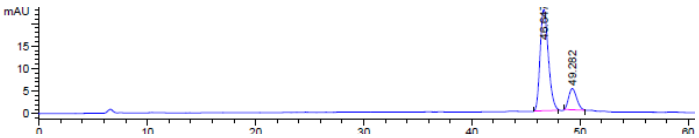



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 48.155 | BB | 0.8199 | 6721.79248 | 126.90887 | 50.0955 |
| 2 | 50.635 | BB | 0.8387 | 6696.16211 | 122.68955 | 49.9045 |

[19] (4*R*,5*R*)-1,3-di(naphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate is a known compound (e.g. see: Martin, D.; Kehrli, S.; d'Augustin, M.; Clavier, H.; Mauduit, M.; Alexakis, A. *J. Am. Chem. Soc*. **2006**, *128*, 8416), which was prepared following the procedure described in:. Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett*. **2001**, *3*, 3225

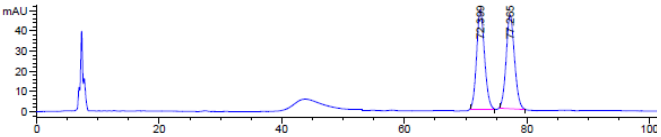
[2] Faustino, H.; López, F.; Castedo, L.; Mascareñas, J. L. *Chem. Sci.* **2011**, *2*, 633

Entry 1, 63% ee, (Catalyst: (*S*)-**Au7**/$AgSbF_6$), Chiralpak IA-3



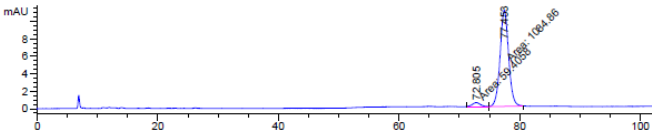
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 46.647 | BB | 0.8273 | 2.72099e4 | 506.06177 | 81.3291 |
| 2 | 49.281 | BB | 0.8616 | 6246.63477 | 112.18047 | 18.6709 |

Racemic sample, Chiralpak IA



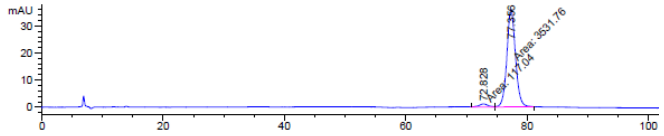
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 72.399 | BB | 1.2891 | 4456.78369 | 49.18649 | 50.2412 |
| 2 | 77.265 | BB | 1.3907 | 4413.98438 | 46.44863 | 49.7588 |

Entry 2, 90% ee, (Catalyst: (*R*)-**Au8**/$AgSbF_6$), Chiralpak IA



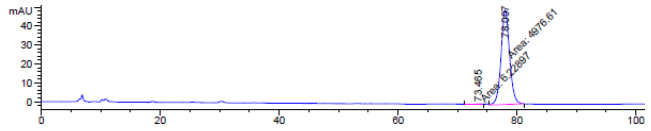
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 72.805 | MM | 1.8367 | 59.40580 | 5.39063e-1 | 5.1916 |
| 2 | 77.453 | MM | 1.6429 | 1084.85583 | 11.00561 | 94.8084 |

Entry 3, 94% ee (Catalyst: (*R*)-**Au8**/$AgNTf_2$), Chiralpak IA



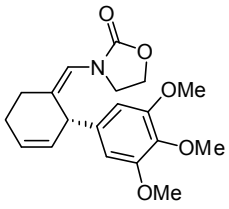
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 72.821 | MF | 1.7061 | 97.41557 | 9.51619e-1 | 3.0684 |
| 2 | 77.359 | FM | 1.6442 | 3077.33911 | 31.19383 | 96.9316 |

Entry 4, 99% ee (Catalyst: (*R*)-**Au8**/$AgNTf_2$) Chiralpak IA



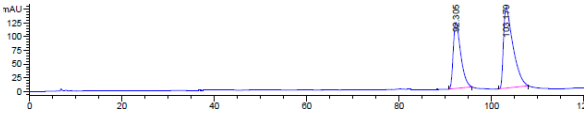
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 73.465 | MM | 1.8377 | 6.22897 | 5.64928e-2 | 0.1250 |
| 2 | 78.007 | MM | 1.6592 | 4976.61230 | 49.98865 | 99.8750 |

**3-{(*Z*)-[(2*S*)-2-(3,4,5-trimethoxyphenyl)cyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3b)**

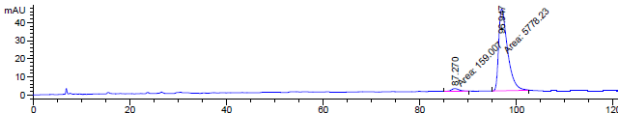


58% yield, white solid, 94% ee, $[\alpha]_D^{20}$ = - 103.4 (*c* = 0.8); **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.48 (s, 2H), 6.02 (s, 1H), 5.92-5.74 (m, 2H), 4.34-4.20 (m, 3H), 3.82 (s, 6H), 3.64 (s, 3H), 3.62-3.50 (m, 2H), 2.32-2.20 (m, 4H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.2 (C), 153.1 (C), 138.8 (C), 136.5 (C), 135.2 (C), 128.4 (CH), 127.8 (CH), 118.2 (C), 104.5 (CH), 62.2 ($CH_2$), 60.8 (CH), 56.1 ($CH_3$), 46.4 ($CH_2$), 41.9 ($CH_3$), 28.1 ($CH_2$), 26.9 ($CH_2$). **LMRS** (*m/z, CI*): 345 [$M^+$, 95], 258 (80), 177 (90), 87 (80). **HRMS** [$M^+$+1], Calculated for $C_{19}H_{23}NO_5$: 346.1654, found 346.1646. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA-3, rt, (Hexane - iPrOH = 90:10, 0.5 ml/min). (*R*,*Z*)-**3b**, $t_R$ = 92.3 min, (*S*,*Z*)-**3b**, $t_R$ = 103.2 min.

Racemic sample

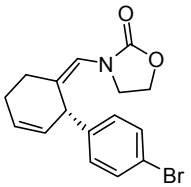


Entry 5, 94% ee (Catalyst: (*R*)-**Au8**/$AgNTf_2$)



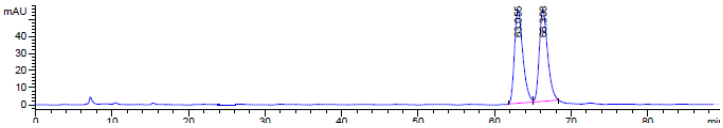
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 87.270 | MM | 1.7970 | 159.00691 | 1.47477 | 2.6781 |
| 2 | 96.947 | MM | 2.1370 | 5778.23486 | 45.06569 | 97.3219 |

**(3-{(*Z*)-[(2*S*)-2-(4-bromophenyl)cyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3c)**



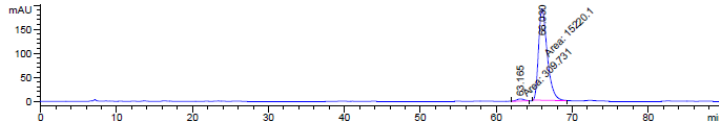
55% yield, white solid, 96% ee, $[\alpha]_D^{20}$ = - 14.1 (*c* = 0.3); **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.18-7.16 (m, 2H), 6.08 (s, 1H), 5.95-5.91 (m, 1H), 5.77-5.74 (m, 1H), 4.31-4.22 (m, 3H), 3.67-3.54 (m, 2H), 2.34-2.19 (m, 4H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.0 (C), 142.4 (C), 133.1 (C), 131.5 (CH), 129.2 (CH), 128.0 (CH), 120.2 (C), 118.5 (CH), 62.1 ($CH_2$), 46.2 ($CH_2$), 41.4 (CH), 27.9 ($CH_2$), 26.8 ($CH_2$). **LMRS** (*m/z, CI*): 334 [$M^+$, 20], 247 (20), 178 (30), 115 (100), 87 (80). **HRMS** [$M^+$+1], Calculated for $C_{16}H_{16}BrNO_2$: 336.0422, found 336.0421. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA-3, rt, (Hexane - iPrOH = 90:10, 0.5 ml/min). (*R*,*Z*)-**3c**, $t_R$ = 63.1 min, (*S*,*Z*)-**3c**, $t_R$ = 66.3 min.

Racemic sample



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 63.055 | BB | 1.1239 | 4138.36914 | 54.49714 | 50.6250 |
| 2 | 66.308 | BB | 1.1442 | 4036.19287 | 53.37809 | 49.3750 |

Entry 6, 96% ee (Catalyst: (*R*)-**Au8**/$AgNTf_2$)



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 63.165 | MM | 1.1650 | 309.73148 | 4.43102 | 1.9944 |
| 2 | 66.030 | MM | 1.3314 | 1.52201e4 | 190.52400 | 98.0056 |

The absolute configuration of (*S*)-**3c** was determined by X-Ray analysis.

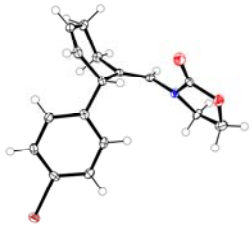
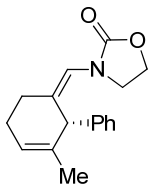


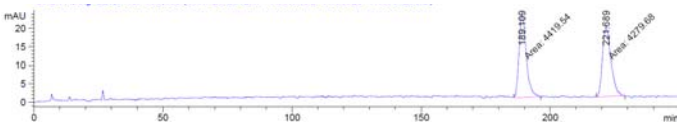
**Figure S1**: X-Ray structure of **(*S*,*Z*)-3c**

**3-{(*Z*)-[(2*S*)-3-methyl-2-phenylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3d)**.[2]



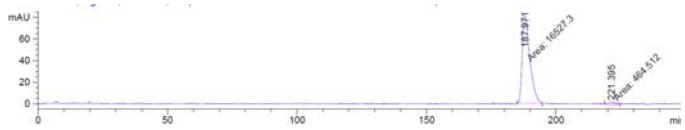
88% yield, white solid, Mp = 106 -108 ºC, 95% ee, $[\alpha]_D^{20}$ = - 166.5 (*c* = 1.0); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 7.16 (d, J = 7.3 Hz, 2H), 7.11 (td, J = 7.2, 1.3 Hz, 1H), 5.66 (s, 1H), 5.62 (s, 1H), 4.27 – 4.20 (m, 1H), 4.18 – 4.13 (m, 1H), 4.10 (s, 1H), 3.67 (dt, *J* = 16.7, 8.3 Hz, 1H), 3.39 – 3.34 (m, 1H), 2.27 – 2.17 (m, 2H), 2.16 – 2.10 (m, 1H), 2.10 – 2.02 (m, 1H), 1.50 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 156.9 (C), 142.5 (C), 138.2 (C), 133.7 (C), 128.2 (CH), 128.0 (CH), 126.3 (CH), 123.5 (CH), 116.1 (CH), 62.0 ($CH_2$), 46.9 (CH), 46.5 ($CH_2$), 26.8 ($CH_2$), 26.6 ($CH_2$), 22.2 ($CH_3$). **LRMS** (*m/z, CI*): 270 [$M^+$+1, 62], 254 (1), 192 (6), 183 (100), 167 (84), 105 (20), 101 (76), 88 (77), 77 (12). **HRMS** Calculated for $C_{17}H_{20}NO_2$: 270.1494, found 270.1496. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA-3, rt, (Hexane - iPrOH = 99:1, 0.5 ml/min). (*S*,*Z*)-**3d**, $t_R$ = 189.1 min, (*R*,*Z*)-**3d**, $t_R$ = 221.7 min.

Racemic sample



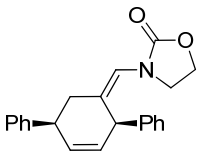
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 189.109 | MM | 3.2790 | 4419.54004 | 22.46386 | 50.8039 |
| 2 | 221.689 | MM | 3.7687 | 4279.67920 | 18.92657 | 49.1961 |

Entry 7, 95% ee (Catalyst: (*R*)-**Au8**/$AgNTf_2$)



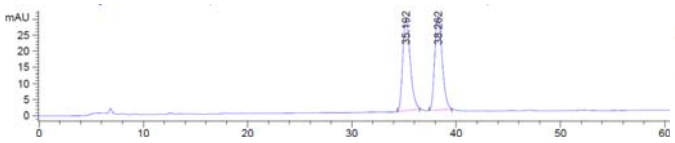
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 187.971 | MM | 3.4156 | 1.65273e4 | 80.64577 | 97.2663 |
| 2 | 221.395 | MM | 4.3571 | 464.51172 | 1.77682 | 2.7337 |

**3-{(*Z*)-[(2*R*,5*S*)-2,5-diphenylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3e)**



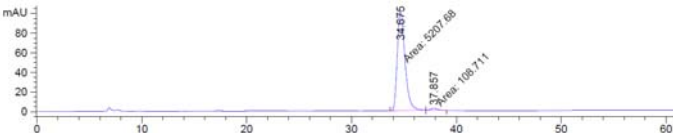
48% yield, 96% ee, $[\alpha]_D^{20}$ = + 65,7 (*c* = 0.5); Carried out with catalyst: (*S*)-**Au8**. **$^1$H NMR** (400 MHz, cdcl$_3$) δ 7.31 – 7.20 (m, 6H), 7.19 – 7.10 (m, 4H), 6.14 (s, 1H), 5.94 – 5.83 (m, 2H), 4.42 (s, 1H), 4.28 – 4.17 (m, 2H), 3.62 – 3.55 (m, 2H), 3.53 – 3.46 (m, 1H), 2.46 (dd, *J* = 13.2, 5.4 Hz, 1H), 2.26 (t, *J* = 11.5 Hz, 1H); **$^{13}$C NMR** (101 MHz, cdcl$_3$) δ 157.24 (C=O), 144.80 (C), 142.88 (C), 131.71 (CH), 130.73 (C), 129.17 (CH), 128.68 (CH), 128.56 (CH), 127.27 (CH), 127.23 (CH), 126.50 (CH), 118.93 (CH), 62.20 ($CH_2$), 46.09 ($CH_2$), 44.63 (CH), 41.35 (CH), 38.20 ($CH_2$). **LRMS** (*m/z, CI*): 332 [$M^+$+1, 61], 254 (13), 245 (93), 88 (100). **HRMS** Calculated for $C_{22}H_{22}NO_2$ : 268.1701 found 332.1664. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA-3, rt, (Hexane - iPrOH = 92:8, 0.5 ml/min). (*R*,*S*)-**3e**, $t_R$ = 35.1 min, (*S*,*R*)-**3e**, $t_R$ = 38.2 min.

Racemic sample



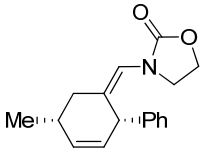
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 35.192 | BB | 0.7625 | 1426.12708 | 28.46803 | 49.5749 |
| 2 | 38.262 | BB | 0.7665 | 1450.58362 | 29.25558 | 50.4251 |

Entry 8, 96% ee (Catalyst: (*S*)-**Au8**/$AgNTf_2$)



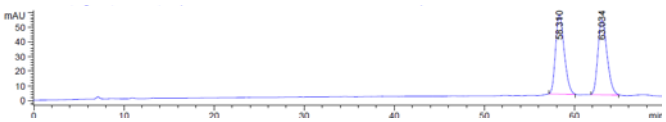
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 34.675 | MM | 0.8535 | 5207.68066 | 101.69589 | 97.9552 |
| 2 | 37.857 | MM | 0.8663 | 108.71086 | 2.09159 | 2.0448 |

**3-{(*Z*)-[(2*S*,5*R*)-5-methyl-2-phenylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3f).**[2]



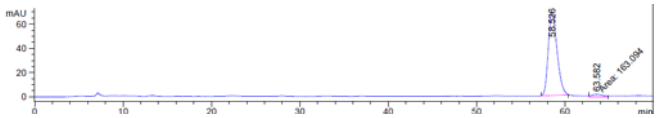
85% yield, white solid, 94% ee, $[\alpha]_D^{20}$ = - 148.7 (*c* = 1); **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 4H), 7.23 – 7.18 (m, 1H), 6.12 (s, 1H), 5.77 – 5.68 (m, 2H), 4.38 (s, 1H), 4.30 – 4.19 (m, 2H), 3.69 – 3.56 (m, 2H), 2.44 – 2.30 (m, 2H), 2.01 – 1.92 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 157.2 (C), 143.1 (C), 134.0 (CH), 132.0 (C), 128.5 (CH), 127.5 (CH), 127.2 (CH), 126.3 (CH), 118.3 (CH), 62.1 ($CH_2$), 46.1 ($CH_2$), 41.5 (CH), 37.0 ($CH_2$), 32.8 (CH), 21.2 ($CH_3$). **LRMS** (*m/z, CI*): 270.9 [$M^+$ +1, 30], 269.9 (100), 254 (46), 183 (82), 167 (39). Enantioselectivity determined by chiral HPLC analysis, Chiralpak IB, rt, (Hexane - iPrOH = 95:5, 0.5 ml/min). (*S*,*R*)-**3f**, $t_R$ = 58.5 min, (*R*,*S*)-**3f**, $t_R$ = 63.6 min.

Racemic sample



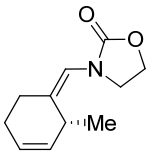
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 58.310 | BB | 1.0241 | 3629.47510 | 54.00108 | 50.0798 |
| 2 | 63.034 | BB | 1.0796 | 3617.91357 | 50.88175 | 49.9202 |

Entry 9, 94% ee (Catalyst: (*R*)-**Au8**/$AgNTf_2$)



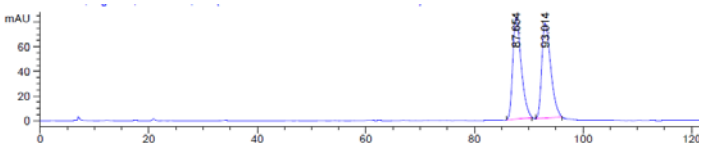
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 58.537 | MM | 1.1981 | 243.36792 | 3.38554 | 96.9305 |
| 2 | 63.579 | MM | 1.3782 | 7.70687 | 9.32021e-2 | 3.0695 |

**3-{(*Z*)-[(2*R*)-2-methylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3g)**.[2]



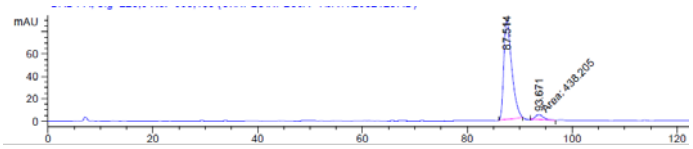
71% yield, colourless oil, 91% ee, $[\alpha]_D^{20}$ = - 54.9 (*c* = 0.9); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.95 (s, 1H), 5.70 – 5.59 (m, 1H), 5.56 – 5.45 (m, 1H), 4.34 (t, *J* = 8.0 Hz, 2H), 3.86 (dd, *J* = 16.1, 8.3 Hz, 1H), 3.78 (dd, *J* = 16.1, 8.6 Hz, 1H), 3.14 – 3.03 (m, 1H), 2.33 – 2.22 (m, 1H), 2.20 – 2.10 (m, 2H), 2.10 – 1.97 (m, 1H), 1.14 (d, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 157.4 (C), 134.4 (C), 131.0 (CH), 126.1 (CH), 116.3 (CH), 62.0 ($CH_2$), 46.4 ($CH_2$), 31.4 (CH), 27.3 ($CH_2$), 26.7 ($CH_2$), 21.5 ($CH_3$). **LRMS** (*m/z, CI*): 194 [$M^+$ +1, 78], 135 (23), 126 (43), 107 (100); 88 (91). **HRMS** Calculated for $C_{11}H_{16}NO_2$: 194.1181, found 194.1178. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA, rt, (Hexane - iPrOH = 98:2, 0.5 ml/min). (*R*)-**3g**, $t_R$ = 87.5 min, (*S*)-**3g**, $t_R$ = 93.6 min.

Racemic sample



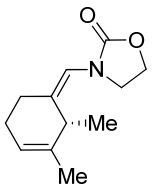
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 87.654 | BB | 1.6091 | 8937.78809 | 82.29618 | 50.4699 |
| 2 | 93.014 | BB | 1.7152 | 8771.36621 | 76.64111 | 49.5301 |

Entry 10, 91% ee (Catalyst: (*R*)-**Au8**/$AgNTf_2$)



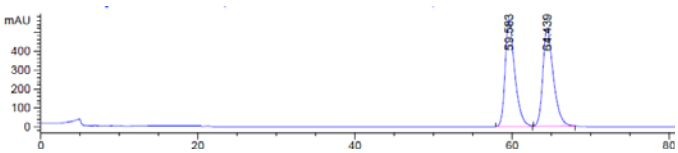
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 87.514 | BB | 1.5477 | 9303.65332 | 88.12592 | 95.5018 |
| 2 | 93.671 | MM | 1.6839 | 438.20462 | 4.33708 | 4.4982 |

**3-{(*Z*)-[(2*R*)-2,3-dimethylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3h).**[2]



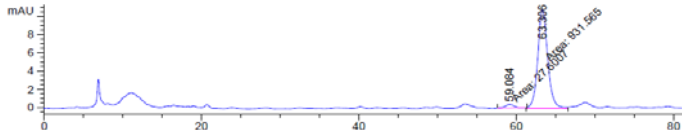
56% yield, white solid, Mp = 98-99 ºC, 94% ee, $[\alpha]_D^{20}$ = 27.0 (*c* = 0.9); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.90 (d, *J* = 1.8 Hz, 1H), 5.38 (brs, 1H), 4.37 (t, *J* = 8.0 Hz, 2H), 3.88 (dd, *J* = 16.1, 8.2 Hz, 1H), 3.77 (dt, *J* = 16.1, 8.1 Hz, 1H), 2.88 (q, *J* = 6.9 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.18 – 1.99 (m, 3H), 1.68 (s, 3H), 1.20 (d, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 157.5 (C), 136.3 (C), 136.2 (C), 121.4 (CH), 115.5 (CH), 62.0 ($CH_2$), 46.7 ($CH_2$), 35.7 (CH), 27.2 ($CH_2$), 26.2 ($CH_2$), 21.7 ($CH_3$), 19.9 ($CH_3$). **LRMS** (*m/z, CI*): 208 [$M^+$ +1, 100], 121 (96), 100 (33), 88 (38). **HRMS** Calculated for $C_{12}H_{18}NO_2$: 208.1338, found 208.1339. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA, rt, (Hexane - iPrOH = 98:2, 0.5 ml/min). (*S*)-**3h**, $t_R$ = 59.6 min, (*R*)-**3h**, $t_R$ = 64.4 min.

Racemic sample



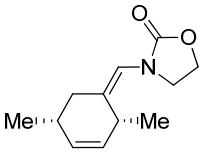
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 59.583 | BB | 1.2696 | 4.65223e4 | 544.09015 | 49.7626 |
| 2 | 64.438 | BB | 1.4188 | 4.69661e4 | 495.07809 | 50.2374 |

Entry 11, 94% ee (Catalyst: (*R*)-**Au8**/AgNTf$_2$)



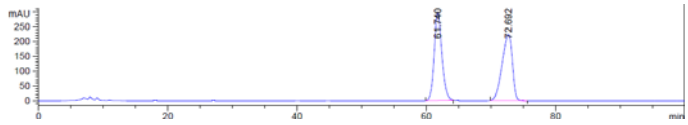
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 59.084 | MM | 1.2602 | 27.60068 | 3.65018e-1 | 2.8776 |
| 2 | 63.306 | MM | 1.4408 | 931.56482 | 10.77608 | 97.1224 |

**3-{(*Z*)-[(2*R*,5*R*)-2,5-dimethylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3i).**[2]



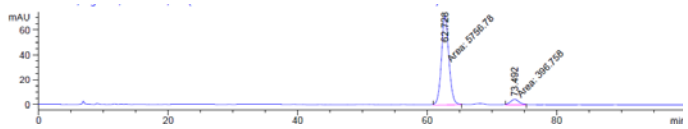
56% yield, white solid, Mp = 89-90 ºC, 87% ee, $[\alpha]_D^{20}$ = -7 (*c* = 0.6); **$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.92 (s, 1H), 5.44 (s, 2H), 4.34 – 4.24 (m, 2H), 3.91 – 3.69 (m, 2H), 3.09 – 2.98 (m, 1H), 2.27 – 2.16 (m, 1H), 2.13 (dd, *J* = 13.1, 4.3 Hz, 1H), 1.94 – 1.79 (m, 1H), 1.13 – 1.03 (m, 3H), 0.95 (dd, *J* = 6.8, 3.2 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.3 (C), 133.9 (C), 132.6 (CH), 130.1 (CH), 116.3 (CH), 62.0 ($CH_2$), 46.3 ($CH_2$), 35.8 ($CH_2$), 33.2 (CH), 31.1 (CH), 21.6 ($CH_3$), 21.3 ($CH_3$). **LRMS** (*m/z, CI*): 208 [$M^+$+1, 97], 192 (93), 121 (89), 105 (91), 88 (90). **HRMS** Calculated for $C_{12}H_{18}NO_2$: 208.1338, found 208.1337. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA, rt, (Hexane - iPrOH = 98:2, 0.5 ml/min). (*R,R*)-**3i**, $t_R$ = 62.7 min, (*S,S*)-**3i**, $t_R$ = 73.5 min.

Racemic sample



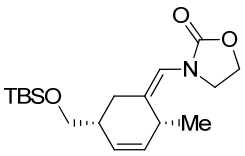
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 61.740 | BB | 1.2556 | 2.46248e4 | 297.51160 | 49.9621 |
| 2 | 72.692 | BB | 1.6980 | 2.46621e4 | 224.09070 | 50.0379 |

Entry 12, 87% ee (Catalyst: (*R*)-**Au8**/AgNTf$_2$)



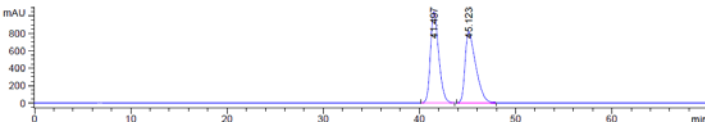
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 62.728 | MM | 1.3414 | 5756.78418 | 71.52571 | 93.5524 |
| 2 | 73.492 | MM | 1.4848 | 396.75793 | 4.45356 | 6.4476 |

**3-{(*Z*)-[(2*R*,5*R*)-5-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)-2-methylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3j).**[2]



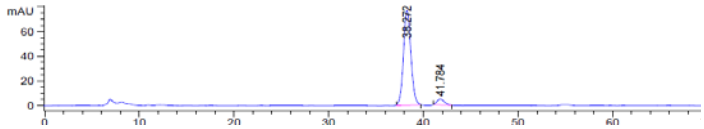
50% yield, white solid, Mp = 68-70 ºC, 89% ee, $[\alpha]_D^{20}$ = -14 (*c* = 2.1); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.98 (d, *J* = 1.5 Hz, 1H), 5.53-5.58 (m, 2H), 4.34 (t, *J* = 8.0 Hz, 2H), 3.86 (dd, *J* = 16.1, 8.3 Hz, 1H), 3.79 (dt, *J* = 16.0, 7.9 Hz, 1H), 3.53 – 3.41 (m, 2H), 3.14 – 3.05 (m, 1H), 2.38 – 2.27 (m, 1H), 2.21 (dd, *J* = 13.0, 5.2 Hz, 1H), 2.03 – 1.94 (m, 1H), 1.13 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 9H), 0.01 (s, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 157.4 (C), 133.6 (C), 131.7 (CH), 127.9 (CH), 116.6 (CH), 67.0 ($CH_2$), 62.00 ($CH_2$), 46.4 ($CH_2$), 41.3 (CH), 31.7 (CH), 30.6 ($CH_2$), 25.8 ($CH_3$), 21.6 ($CH_3$), 18.2 (C), -5.5 ($CH_3$). **LRMS** (*m/z, CI*): 338 [$M^+$+1, 65], 322 (33), 280 (37), 205 (100). **HRMS** Calculated for $C_{18}H_{32}NO_3Si$: 338.2151, found 338.2158. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA, rt, (Hexane - iPrOH = 98:2, 0.5 ml/min). (*R,R*)-**3j**, $t_R$ = 41.5 min, (*S,S*)-**3j**, $t_R$ = 45.1 min.

Racemic sample



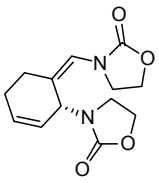
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 41.497 | BB | 0.9178 | 6.27639e4 | 1046.38867 | 50.0194 |
| 2 | 45.123 | BB | 1.1556 | 6.27152e4 | 811.51758 | 49.9806 |

Entry 13, 89% ee (Catalyst: (*R*)-**Au8**/AgNTf$_2$)



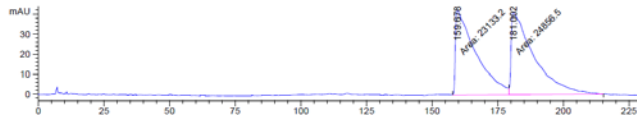
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 38.272 | BB | 0.8360 | 4162.65479 | 76.83870 | 94.3367 |
| 2 | 41.784 | BB | 0.7054 | 249.89476 | 4.60306 | 5.6633 |

**(3-{(*Z*)-[(2*R*)-2-(2-oxo-1,3-oxazolidin-3-yl)cyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3k)**



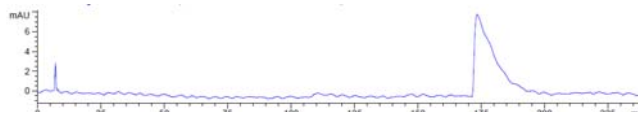
69% yield, white solid, 99% ee, $[\alpha]_D^{20}$ = -77.4 (*c* = 0.9); **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.46 (s, 1H), 6.13-6.08 (m, 1H), 5.50-5.47 (m, 1H), 5.19 (s, 1H), 4.40-4.24 (m, 4H), 4.17-4.11 (m, 1H), 3.93-3.87 (m, 1H), 3.55-3.43 (m, 2H), 2.35-2.02 (m, 4H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.4 (C), 157.4 (C), 133.1 (CH), 123.8 (CH), 122.7 (CH), 120.1 (C), 62.6 ($CH_2$), 62.1 ($CH_2$), 46.5 (CH), 45.1 ($CH_2$), 41.4 ($CH_2$), 29.1 ($CH_2$), 25.9 ($CH_2$). **LMRS** (*m/z, CI*): 265 [$M^+$+1, 50], 180 (90), 134 (50), 87 (100). **HRMS** [$M^+$+1], Calculated for $C_{13}H_{16}N_2O_4$: 265.1188, found 265.1178. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA-3, rt, (Hexane - iPrOH = 90:10, 0.5 ml/min).

Racemic sample



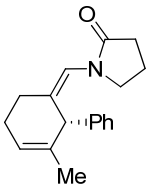
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 159.678 | MF | 9.1063 | 2.31332e4 | 42.33924 | 48.2044 |
| 2 | 181.002 | FM | 10.0561 | 2.48565e4 | 41.19649 | 51.7956 |

Entry 14, >99% ee (Catalyst: (*R*)-**Au8**/AgNTf$_2$)



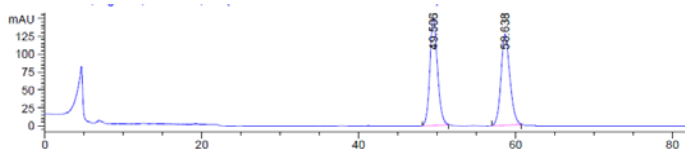
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 173.384 | MM | 9.4849 | 4765.00098 | 8.37300 | 100.0000 |

**1-{(*Z*)-[(2*S*)-3-methyl-2-phenylcyclohex-3-en-1-ylidene]methyl}pyrrolidin-2-one (3db).**[2]



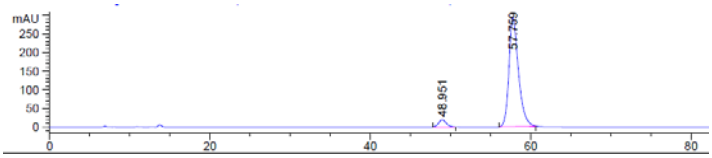
50% yield, white solid, 90% ee, $[\alpha]_D^{20}$ = -152.8 (*c* = 0.6); **$^1$H NMR** (500 MHz, cdcl$_3$) δ 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 5.81 (s, 1H), 5.71 (s, 1H), 4.18 (s, 1H), 3.65 – 3.53 (m, 1H), 3.34 – 3.24 (m, 1H), 2.45 – 2.36 (m, 2H), 2.35 – 2.28 (m, 2H), 2.27 – 2.15 (m, 2H), 2.07 – 2.00 (m, 1H), 1.98 – 1.90 (m, 1H), 1.60 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 174.2 (C), 142.7 (C), 137.2 (C), 134.0 (C), 128.0 (CH), 128.0 (CH), 126.1 (CH), 123.4 (CH), 116.7 (CH), 49.2 ($CH_2$), 47.3 (CH), 30.6 ($CH_2$), 27.1 ($CH_2$), 26.7 ($CH_2$), 22.2 ($CH_3$), 18.4 ($CH_2$). **LRMS** (*m/z, CI*): 268 [$M^+$+1, 41], 252 (19), 183 (88), 86 (100). **HRMS** Calculated for $C_{18}H_{22}NO$ 268.1701, found 268.1703. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IA, rt, (Hexane - iPrOH = 98:2, 0.5 ml/min). (*R*)-**3db**, $t_R$ = 49.5 min, (*S*)-**3db**, $t_R$ = 58.6 min.

Racemic sample



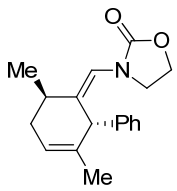
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 49.506 | BB | 1.0243 | 1.01263e4 | 149.86145 | 50.2310 |
| 2 | 58.638 | BB | 1.1952 | 1.00331e4 | 126.78928 | 49.7690 |

Entry 15, 90% ee (Catalyst: (*R*)-**Au8**/AgNTf$_2$)



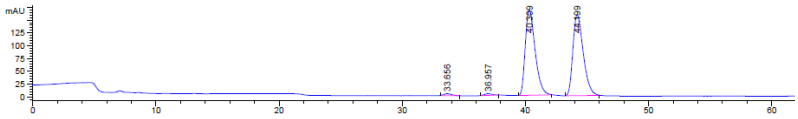
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 48.951 | BB | 0.9890 | 1270.24207 | 19.32253 | 4.9821 |
| 2 | 57.759 | BB | 1.2219 | 2.42257e4 | 293.21762 | 95.0179 |

**3-{(*Z*)-[(2*S*,6*R*)-3,6-dimethyl-2-phenylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3dc).**[2]



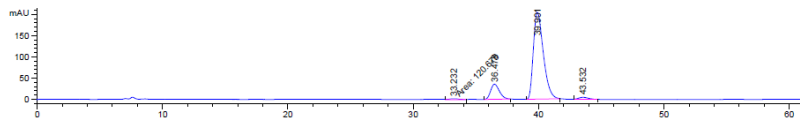

64% yield, white solid, Mp = 85-87 ºC, 93% ee, $[\alpha]_D^{20}$ = -129.5 (*c* = 0.8); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 2H), 7.17 – 7.14 (m, 2H), 7.14 – 7.10 (m, 1H), 5.61 – 5.58 (m, 1H), 5.57 (s, 1H), 4.34 – 4.22 (m, 2H), 4.21 (s, 1H), 3.73 (td, *J* = 8.9, 7.4 Hz, 1H), 3.45 (td, *J* = 8.8, 6.2 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.32 – 2.22 (m, 1H), 1.83 – 1.74 (m, 1H), 1.54 (d, *J* = 1.5 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 157.3 (C), 143.7 (C), 142.5 (C), 133.5 (C), 128.2 (CH), 128.1 (CH), 126.3 (CH), 123.4 (CH), 114.8 (CH), 62.0 ($CH_2$), 47.5 (CH), 47.1 ($CH_2$), 36.0 ($CH_2$), 29.3 (CH), 22.1 ($CH_3$), 17.6 ($CH_3$). **LRMS** (*m/z, CI*): 284 [$M^+$+1, 66], 268 (12), 206 (8), 197 (100), 181 (99), 88 (89). **HRMS** Calculated for $C_{18}H_{22}NO_2$: 284.1651, found 284.1652. Enantioselectivity determined by chiral HPLC analysis, Chiralpak IB, rt, (Hexane - iPrOH = 95:5, 0.5 ml/min). (*R*,*R*)-**3dc** $t_R$ = 33.6 min, (*S*,*S*)-**3dc'** $t_R$ = 36.9 min, (S,*R*)-**3dc**, $t_R$ = 40.3 min, (*R*,*S*)-**3dc**, $t_R$ = 44.2 min.

Racemic Sample




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 33.656 | BB | 0.5527 | 152.44183 | 3.59511 | 0.8140 |
| 2 | 36.957 | BB | 0.5520 | 135.25322 | 3.13108 | 0.7222 |
| 3 | 40.309 | BB | 0.8518 | 9240.87598 | 166.41714 | 49.3414 |
| 4 | 44.199 | BB | 0.9074 | 9199.87891 | 157.52042 | 49.1225 |

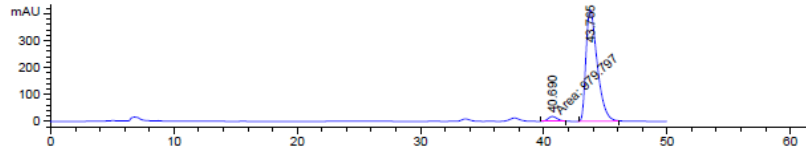
Entry 16, 97% ee, (Catalyst: (*R*)-**Au8**/$AgNTf_2$)




| Peak # | RetTime [min] | Area % |
|---|---|---|
| 1 | 33.232 | 0.9031 |
| 2 | 36.478 | 12.7769 |
| 3 | 39.901 | 84.5089 |
| 4 | 43.532 | 1.8111 |

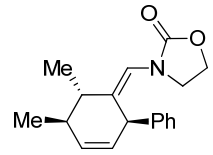
| Peak # | RetTime [min] | Area % |
|---|---|---|
| 1 | 39.901 | 97.9019 |
| 2 | 43.532 | 2.0981 |

Entry 17, 93% ee, (Catalyst: (*S*)-**Au7**/$AgSbF_6$) (1*R*,3*S*)-**3dc**



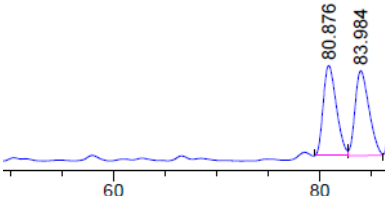

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 40.690 | MM | 0.9012 | 979.79700 | 18.12050 | 3.5816 |
| 2 | 43.765 | BB | 0.9735 | 2.63766e4 | 413.90356 | 96.4184 |

**3-{(*Z*)-[(2*R*,5*R*,6*S*)-5,6-dimethyl-2-phenylcyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one (3fc)**



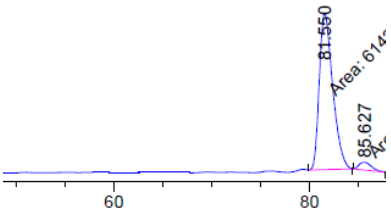

51% yield, 91%ee, $[\alpha]_D^{20}$ = + 86.5 (*c* = 0.3);.. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 4H), 7.17 – 7.02 (m, 1H), 5.89 (s, 1H), 5.62 – 5.53 (m, 2H), 4.27 (s, 1H), 3.91 (ddd, *J* = 9.2, 8.4, 5.6 Hz, 1H), 3.71 – 3.56 (m, 1H), 3.45 – 3.31 (m, 1H), 3.07 – 2.95 (m, 1H), 2.67 – 2.50 (m, 1H), 2.49 – 2.31 (m, 1H), 0.95 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 156.20 (C), 144.07 (C), 138.81(C), 131.11 (CH), 128.29 (CH), 128.25 (CH), 127.56 (CH), 126.02 (CH), 118.90 (CH), 61.80 ($CH_2$), 45.44 ($CH_2$), 43.33 (CH), 38.79 (CH), 34.96 (CH), 16.84 ($CH_3$), 15.42 ($CH_3$). ). **LRMS** (*m/z, ESI*): 306.14 $(M+Na)^+$, 197.13, 140.07, 100.04. **HRMS** Calculated for $C_{18}H_{21}NO_2Na$: 306.1465, found 306.1468. The relative stereochemistry is 3fc was confirmed by $^2$D-NMR experiments ( HMBC, HMQC, NOESY) as well as by analogy with **3dc**.Enantioselectivity determined by chiral HPLC analysis, Chiralpak IB, rt, (Hexane - iPrOH = 98:2, 0.5 ml/min). (*R*,*R*,*S*)-**3fc** $t_R$ = 80.9 min, (*S*,*S*;*R*)-**3fc** $t_R$ = 84.0 min.

Racemic simple



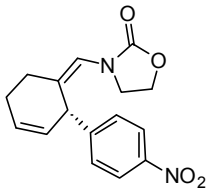

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 80.876 | BV | 1.3088 | 3290.13916 | 37.23976 | 50.0681 |
| 2 | 83.984 | VV | 1.3516 | 3281.19092 | 34.93907 | 49.9319 |

Entry 18, 91% ee, (Catalyst: (*S*)-**Au8**/$AgSbF_6$)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 81.550 | MM | 1.5930 | 6142.18604 | 64.26116 | 95.6311 |
| 2 | 85.627 | MM | 1.4425 | 280.60748 | 3.24205 | 4.3689 |

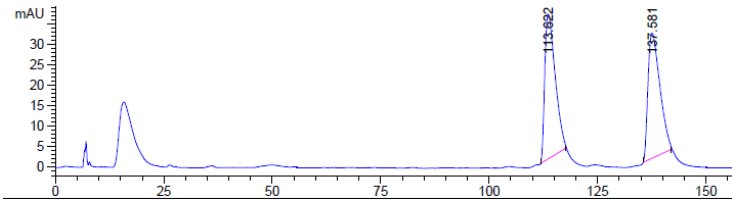
**Additional example of reference 26 (main manuscript)**



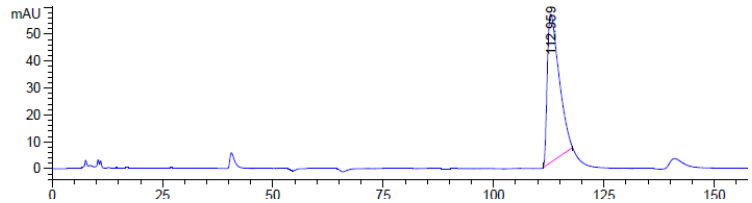
**(3-{(*Z*)-[(2*S*)-2-(4-nitrophenyl)cyclohex-3-en-1-ylidene]methyl}-1,3-oxazolidin-2-one**

11% yield, 92%ee. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 6.05 (s, 1H), 6.04 – 5.91 (m, 1H), 5.81 – 5.69 (m, 1H), 4.54 – 4.46 (m, 1H), 4.38 – 4.14 (m, 2H), 3.67 (td, *J* = 8.9, 7.3 Hz, 1H), 3.53 (td, *J* = 8.8, 6.4 Hz, 1H), 2.39 – 2.20 (m, 4H). $^{13}$C NMR (75 MHz, cdcl$_3$) δ 156.91 (C), 150.93 (C), 146.52 (C), 132.87 (C), 129.08 (CH), 128.35 (CH), 127.07 (CH), 123.69 (CH), 119.04 (CH), 62.11 ($CH_2$), 46.22 ($CH_2$), 41.83 (CH), 27.79 ($CH_2$), 26.80 ($CH_2$).

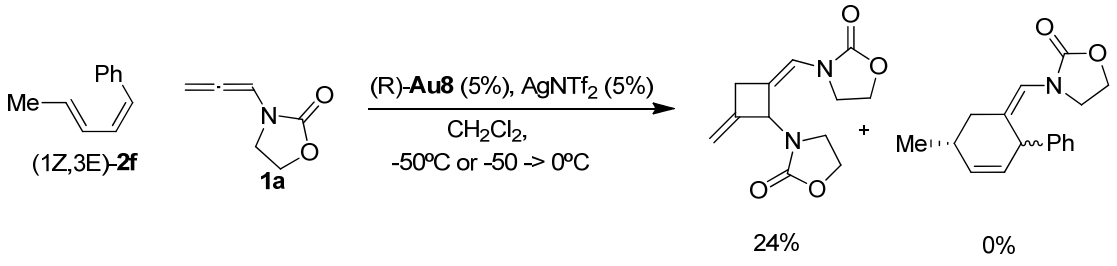
Racemic simple




92% ee, (Catalyst: (*S*)-**Au8**/$AgNTf_2$)




**Additional information regarding reaction of (1*Z*,3*E*)-2f with 1a (reference 28 main manuscript)**



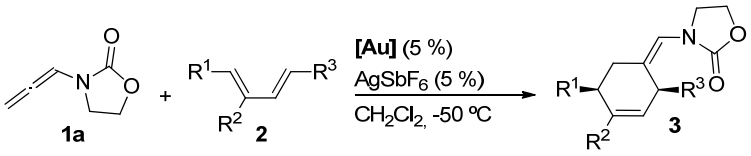
The reaction of (1*Z*,3*E*)-**2f** with 1a under standard conditions at -50ºC or even at higher temperatures (allowing the reaction temperature to reach 0ºC) did not provide any (4+2) cycloadduct. Only the **bis-1a,** the allenamide 2+2 cycloaddition adduct, could be isolated in a modest 24% yield. This result suggests that a concerted cycloaddition between the diene (in a *s*-cis conformation) and the gold-allyl cation derived from **1a** could be taking place. Both, concerted (4+2) or (4+3) cycloadditions, this later followed by a 1,2-ring contraction, could be equally feasible. references 5a,b and 7a of the main manuscript for related mechanistic information.

**Complementary screening to Table 1, employing other chiral gold complexes.**

We also tested phosphoramidite-based chiral gold complexes, previously developed by us in the context of intramolecular allene-diene asymmetric (4+2) and (4+3) cycloadditions.[20] As shown in Scheme S1, catalyst (*R*,*R*,*R*)-**Au9**/$AgSbF_6$ (5 mol %) promoted the cycloaddition of allenamide **1a** with 1-phenyl-1,3-butadiene (**2a**), affording the desired adduct in 86% yield and a 60% ee. However, all attempts to improve this result varying the phosphoramidite and/or the reaction conditions were unsuccessful. Additionally, this catalyst proved to be less effective with dienes incorporating a methyl group at the prochiral center (**2d**), and completely ineffective with a 1,4-di-substituted diene such as **2i**, for which a low yield and poor enantioselectivity were obtained (Scheme S1).

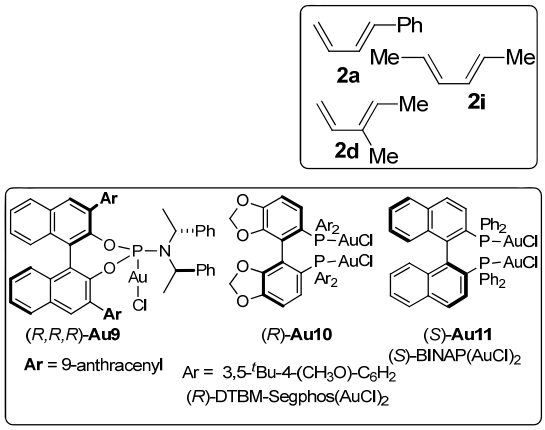
Other frequently used chiral gold complexes such as DTBM-Segphos$(AuCl)_2$/$AgSbF_6$ did also catalyze the cycloaddition of **1a** and **2a** with good yield (80%) and 77%ee, but again, its performance with dienes such as **2b** or **2c** was really poor (low yields, low selectivity and ee´s).

**Scheme S1.** Performance of other chiral Au catalysts.



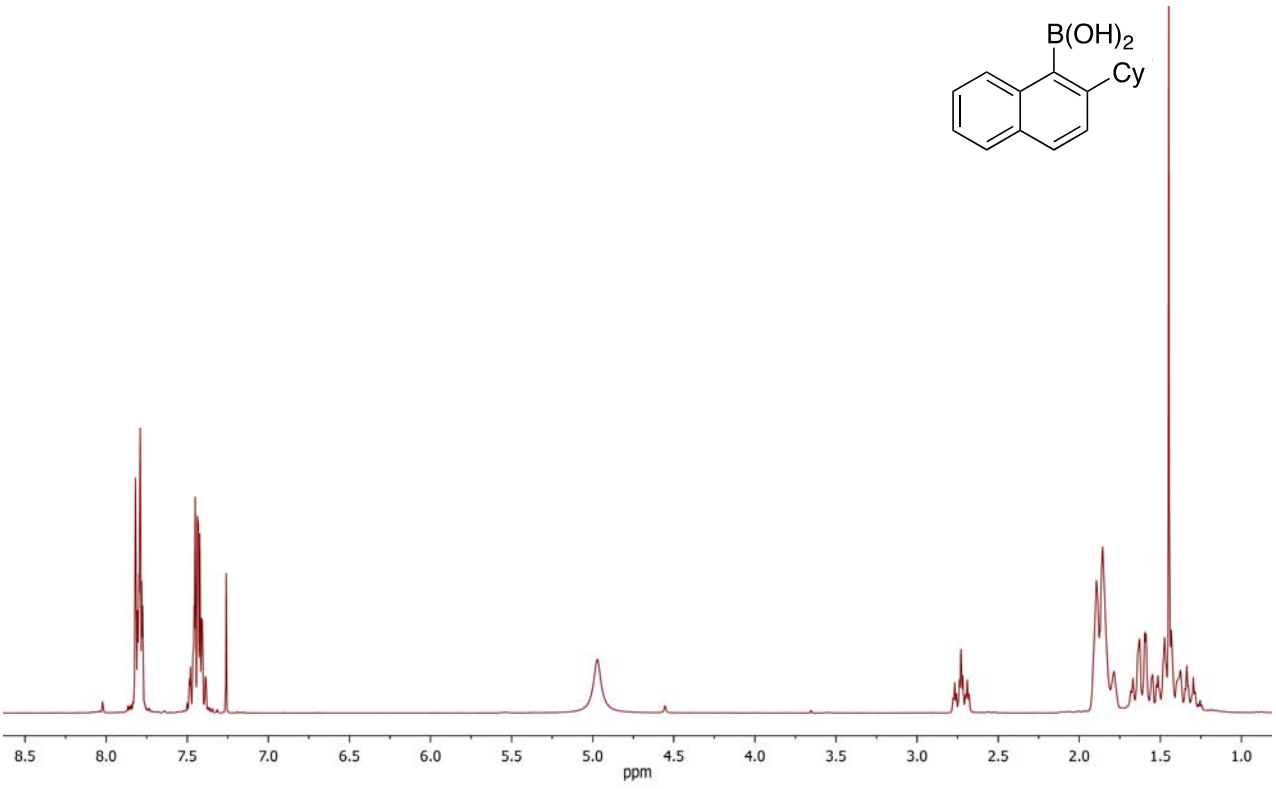

| entry | Au | 2 | $R^1$ | $R^2$ | $R^3$ | 3, yield (%) | ee (%) |
|---|---|---|---|---|---|---|---|
| 1 | **Au9** | **2a** | Ph | H | H | 86 | 60 |
| 2 | **Au9** | **2d** | Me | Me | H | 52 | 40 |
| 3 | **Au9** | **2i** | Me | H | Me | 16 | 9 |
| 4 | **Au10** | **2a** | Ph | H | H | 80 | 77 |
| 5 | **Au10** | **2d** | Me | Me | H | 16[a] | <5 |
| 6 | **Au10** | **2i** | Me | H | Me | 5[b] | <5 |
| 7 | **Au11** | **2a** | Ph | H | H | 60 | 4 |

[a] the 2+2 adduct was isolated in 17% yield
[b] the 2+2 adduct was isolated in 8% yield

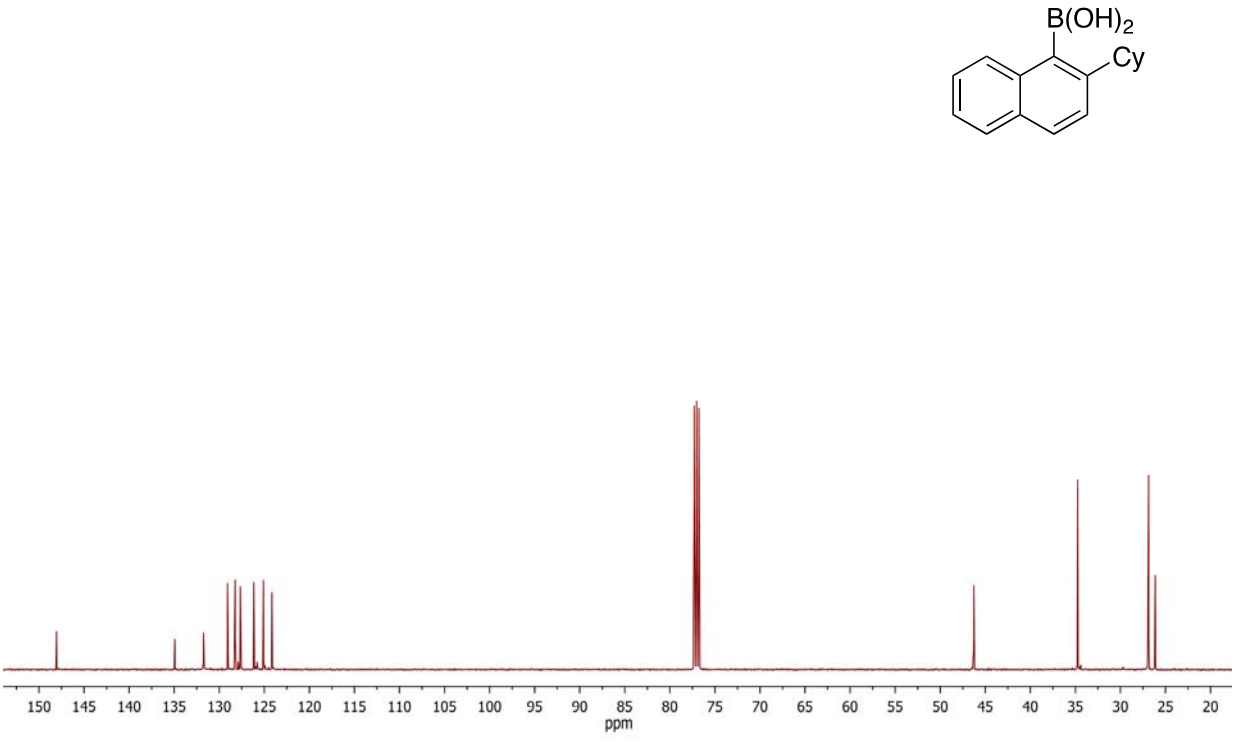



[20] (a) Alonso, I.; Trillo, B.; López, F.; Montserrat, S.; Ujaque, G.; Castedo, L.; Lledós, A.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2009**, *131*, 13020. (b) González, A. Z.; Toste, F. D. *Org. Lett.* **2010**, *12*, 200. (b) Alonso, I.; Faustino, H.; López, F.; Mascareñas, J. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 11496.

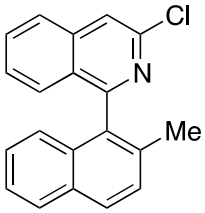
$^{1}$H NMR (300 MHz, $CDCl_3$) of **5b**:

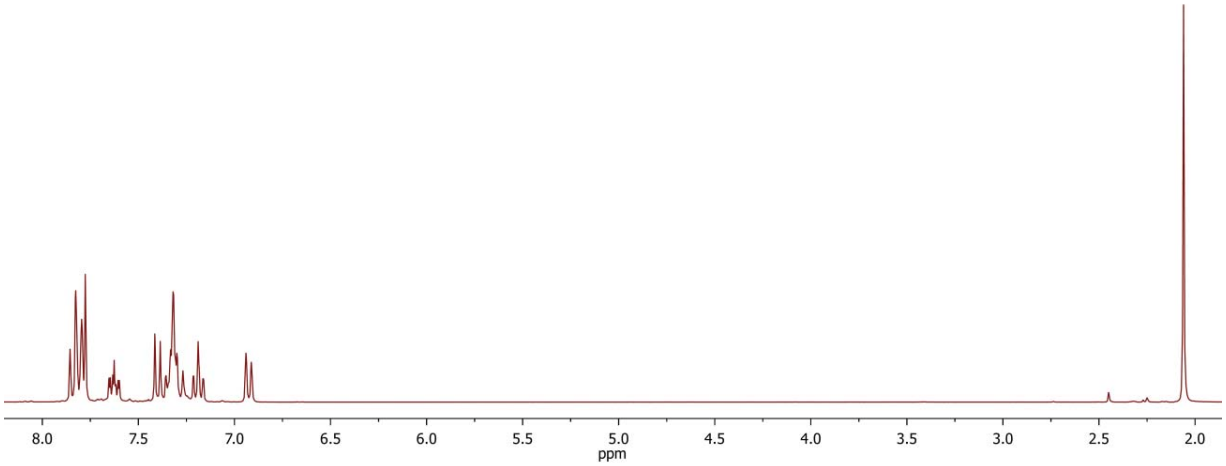



$^{13}$C NMR (125 MHz, $CDCl_3$) of **5b**:

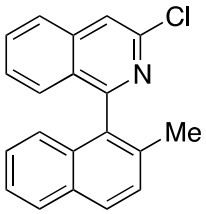


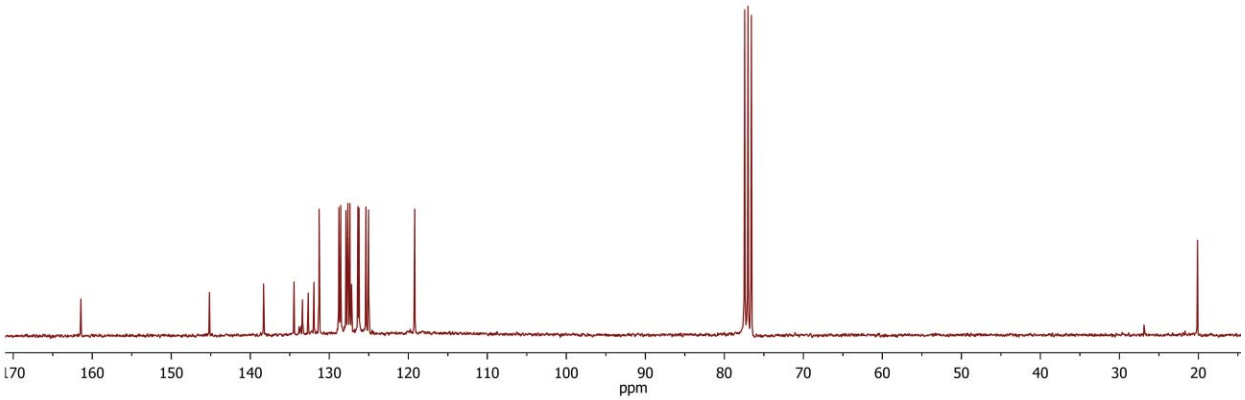
$^{1}$H NMR (300 MHz, $CDCl_3$) of **6a**:



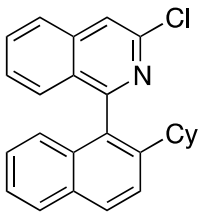



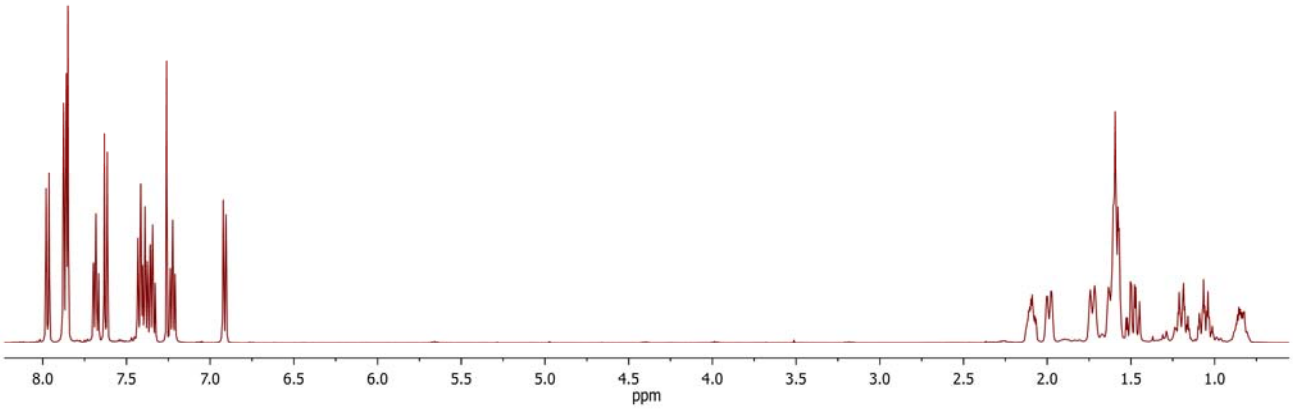

$^{13}$C NMR (75 MHz, $CDCl_3$) of **6a**:



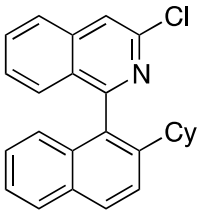



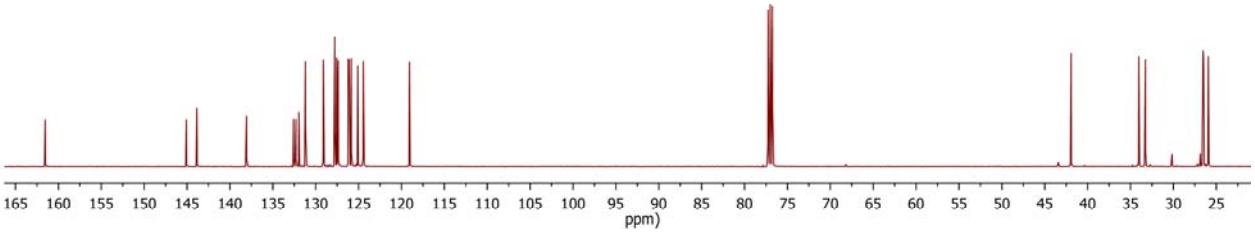
$^{1}$H NMR (500 MHz, $CDCl_3$) of **6b**:



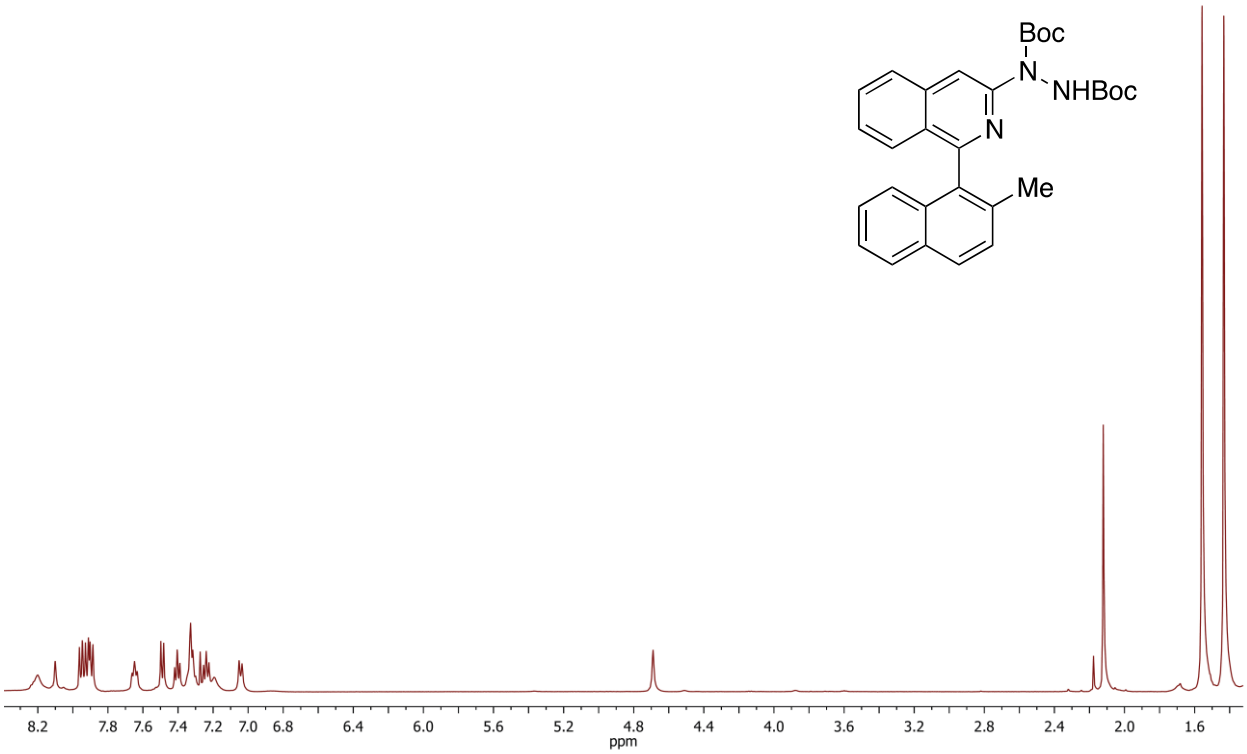




$^{13}$C NMR (125 MHz, $CDCl_3$) of **6b**:

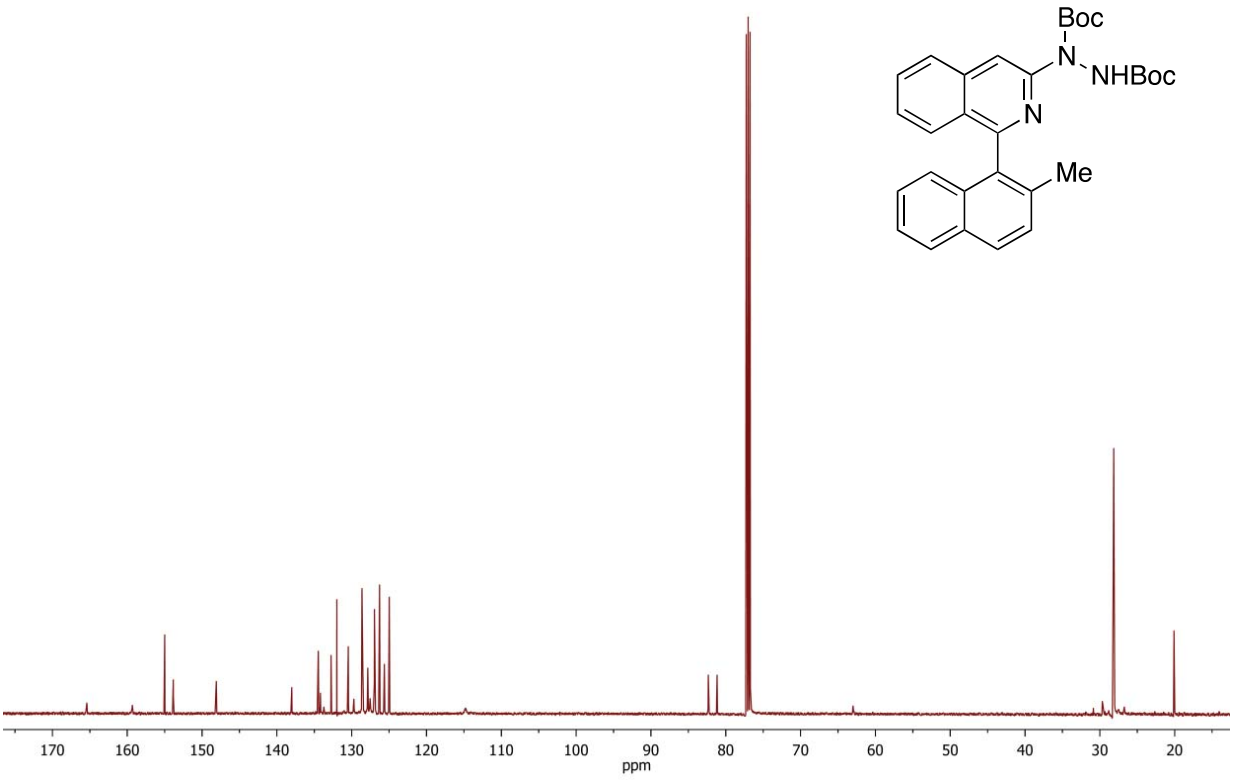


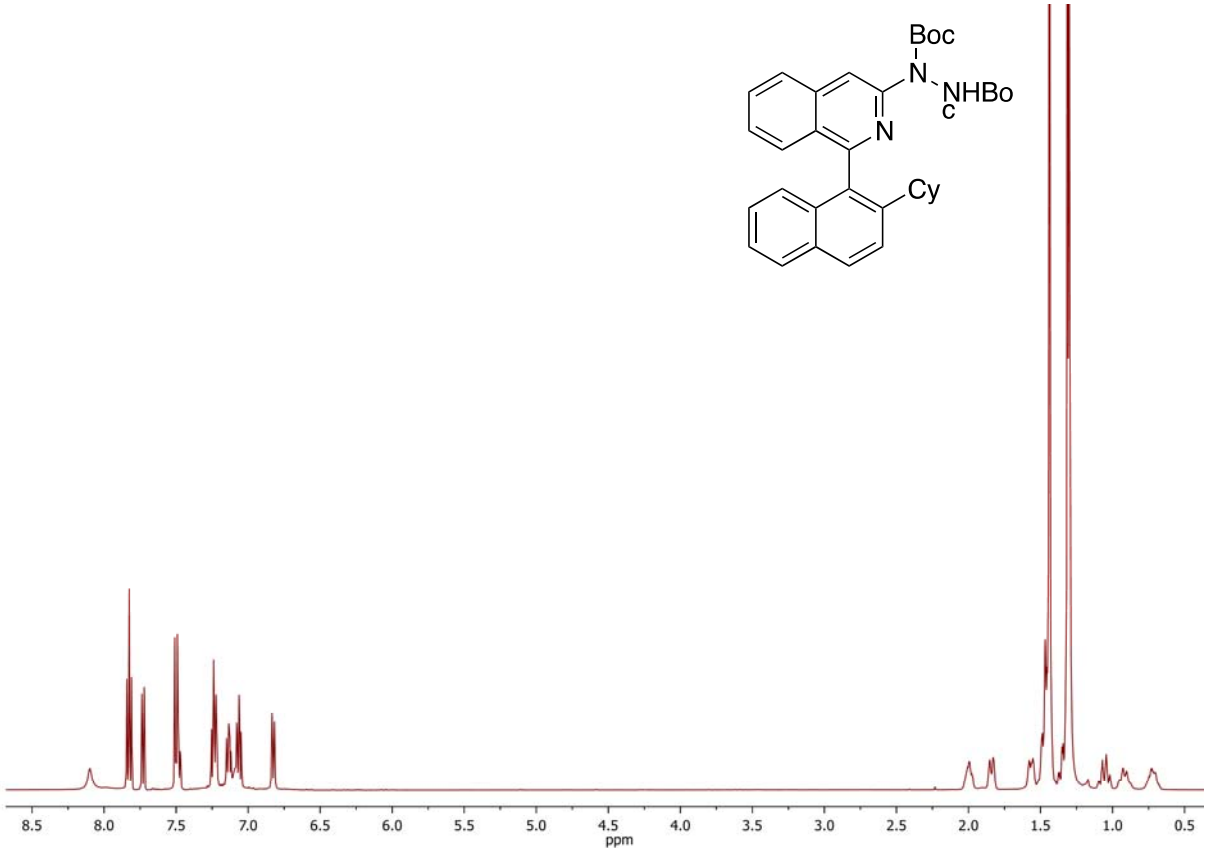
$^{1}$H NMR (500 MHz, $CDCl_3$) of **7a**:



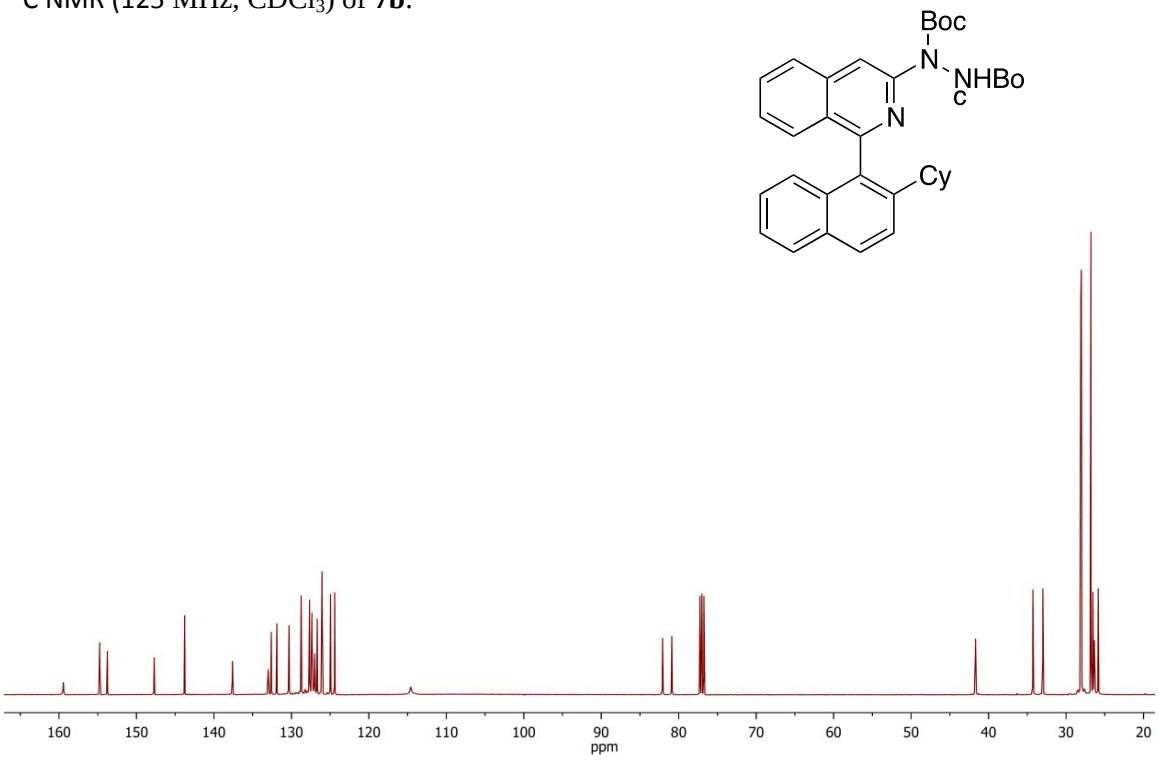

$^{13}$C NMR (125 MHz, $CDCl_3$) of **7a**:



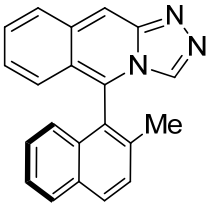
$^{1}$H NMR (500 MHz, $CDCl_3$) of **7b**:

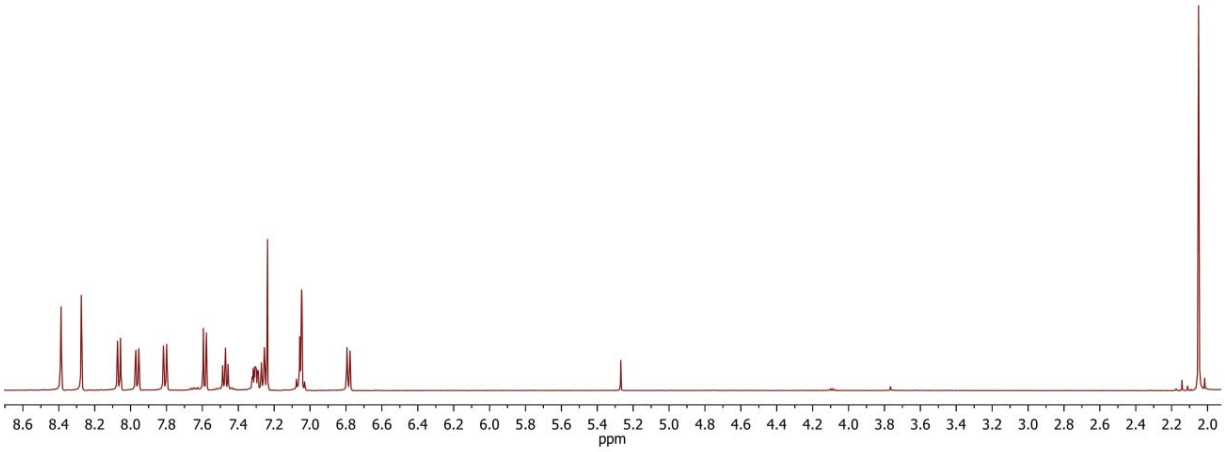



$^{13}$C NMR (125 MHz, $CDCl_3$) of **7b**:

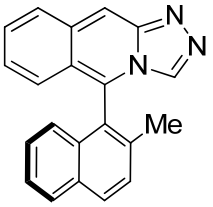


$^{1}$H NMR (500 MHz, $CDCl_3$) of (*S*)-**8a**:

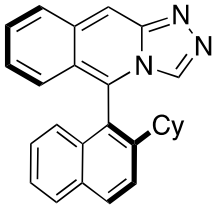


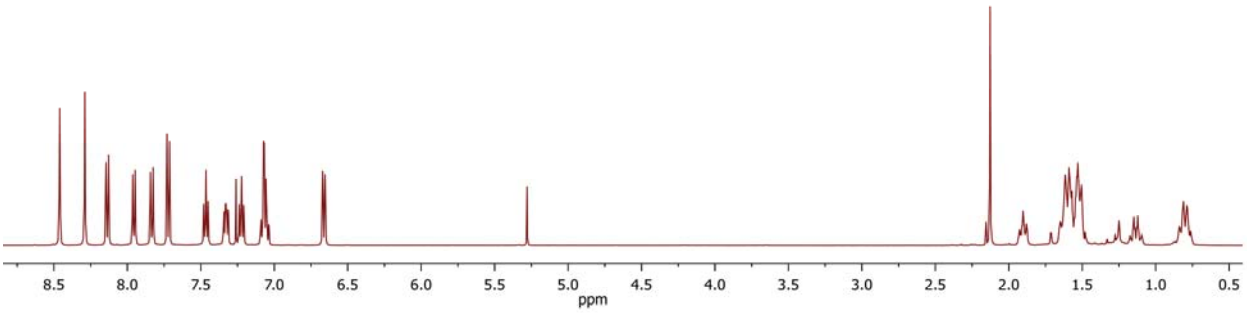




$^{13}$C NMR (125 MHz, $CDCl_3$) of (*S*)-**8a**:

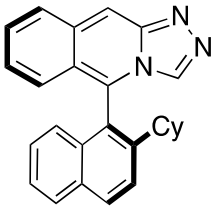


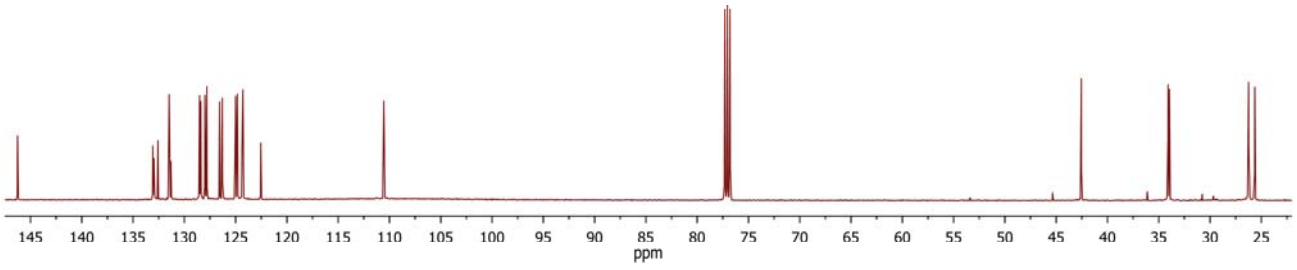
$^{1}$H NMR (500 MHz, $CDCl_3$) of (*R*)-**8b**:



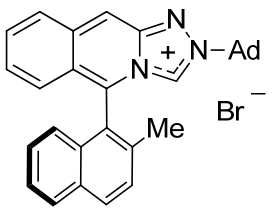



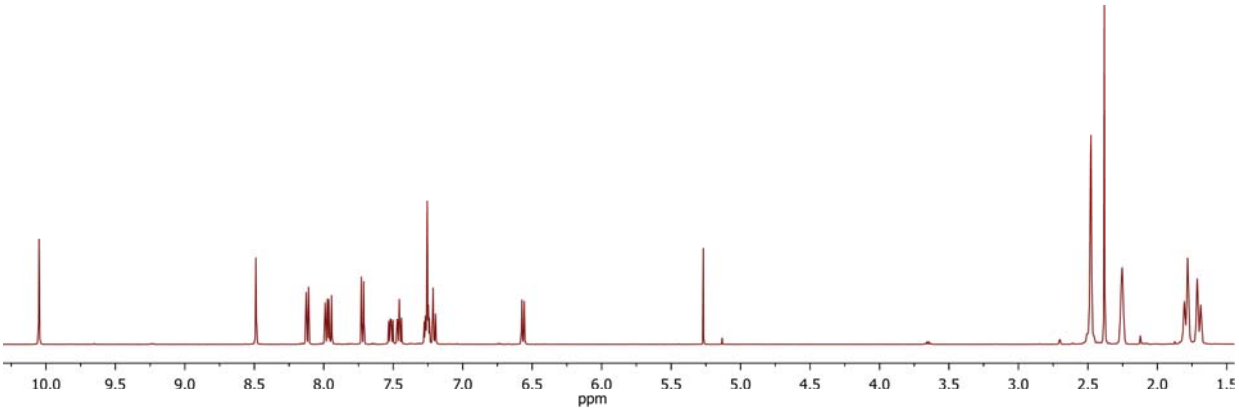

$^{13}$C NMR (125 MHz, $CDCl_3$) of (*R*)-**8b**:



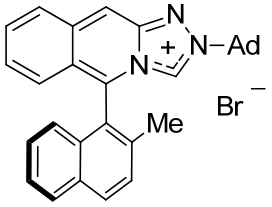



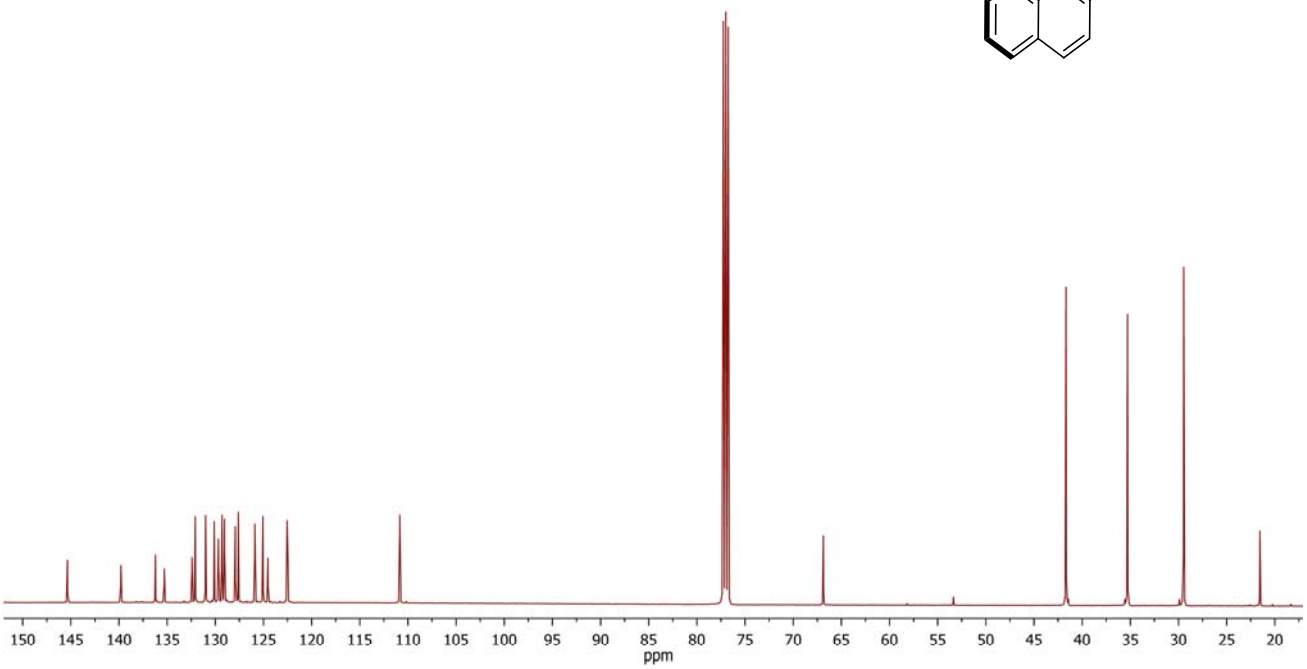
$^{1}$H NMR (500 MHz, $CDCl_3$) of (*S*)-**9a(Br$^-$)**:



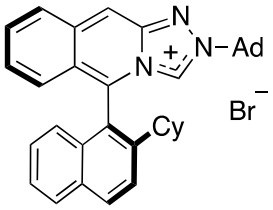



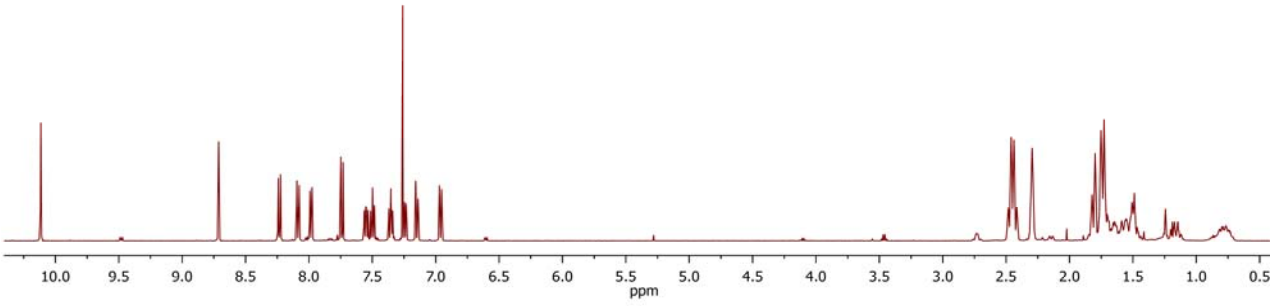

$^{13}$C NMR (125 MHz, $CDCl_3$) of (*S*)-**9a(Br$^-$)**:



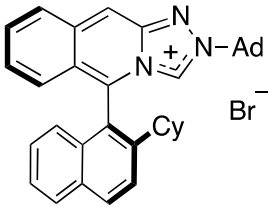



$^{1}$H NMR (500 MHz, $CDCl_3$) of (*R*)-**9b(Br$^-$)**:

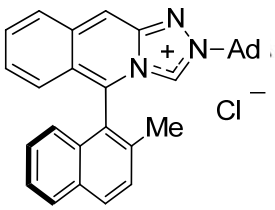


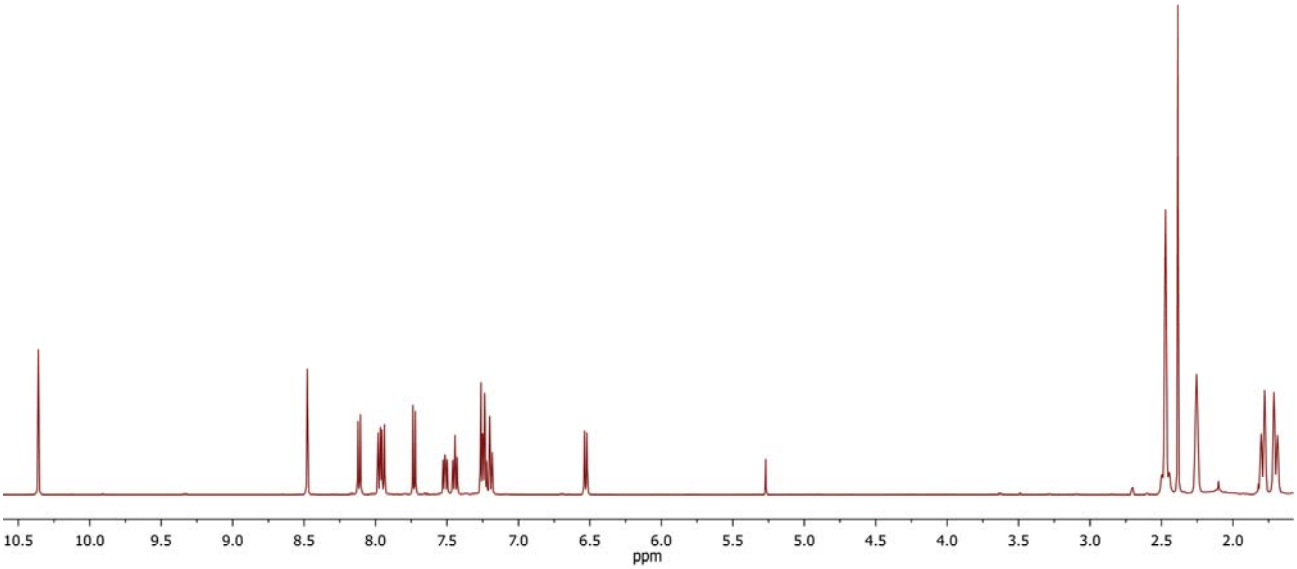




$^{13}$C NMR (125 MHz, $CDCl_3$) of (*R*)-**9b(Br$^-$)**:

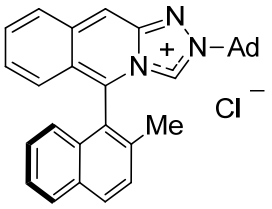


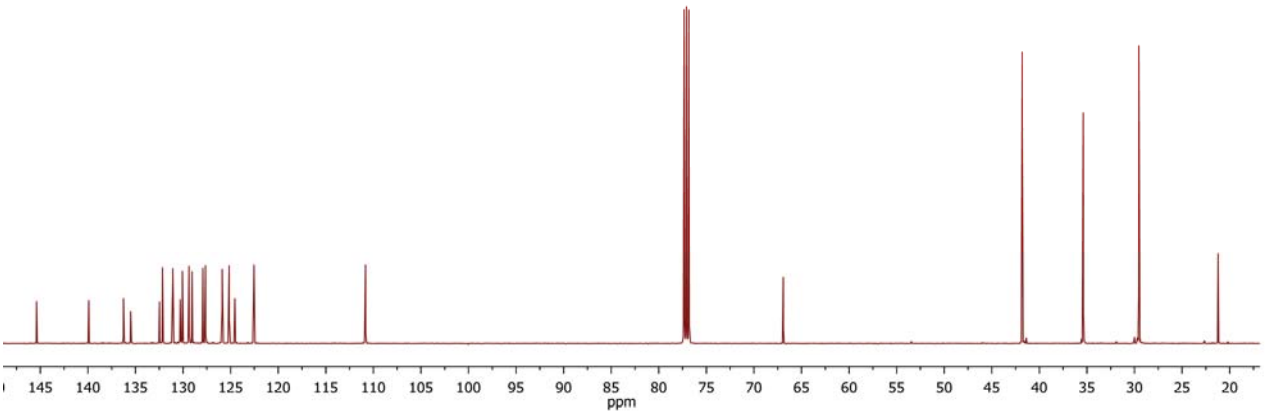
$^{1}$H NMR (500 MHz, $CDCl_3$) of (*S*)-**9a(Cl$^-$)**:



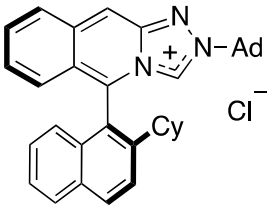



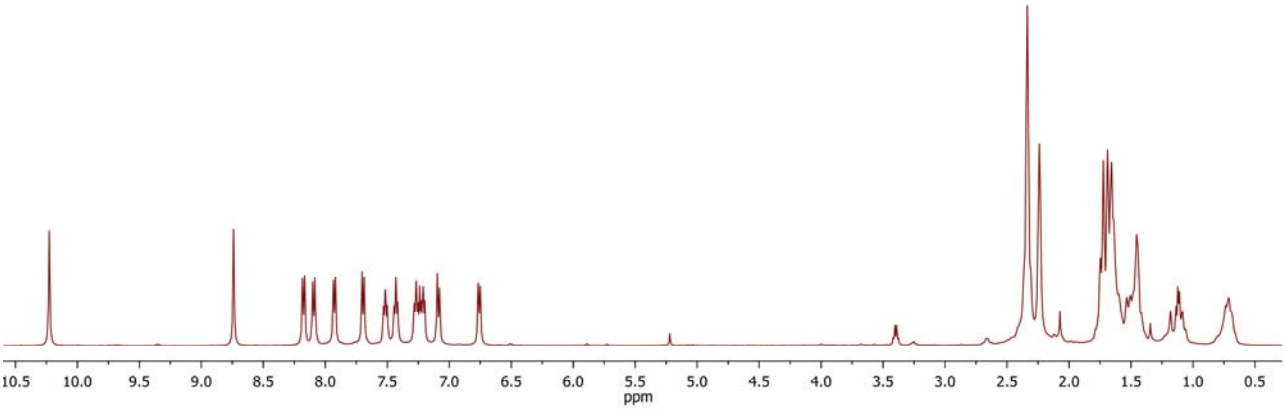

$^{13}$C NMR (125 MHz, $CDCl_3$) of (*S*)-**9a(Cl$^-$)**:



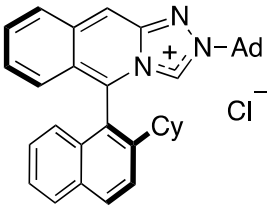



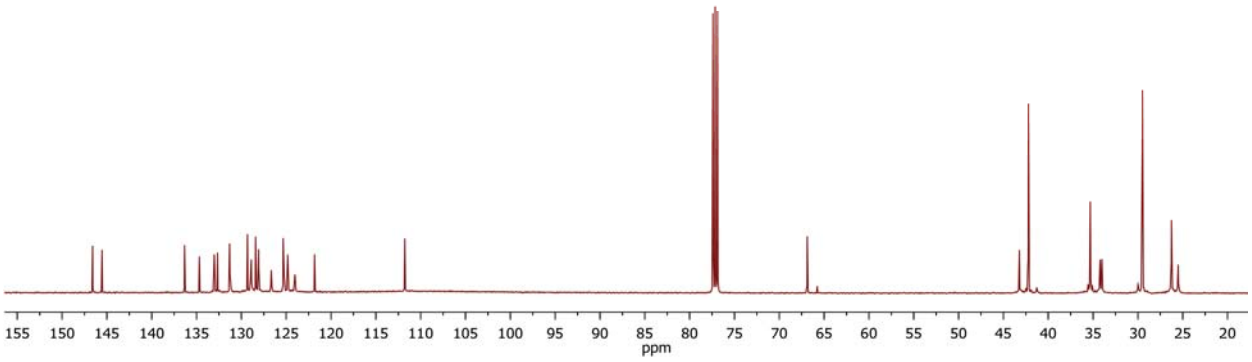
$^{1}$H NMR (500 MHz, $CDCl_3$) of (*R*)-**9b(Cl$^-$)**:



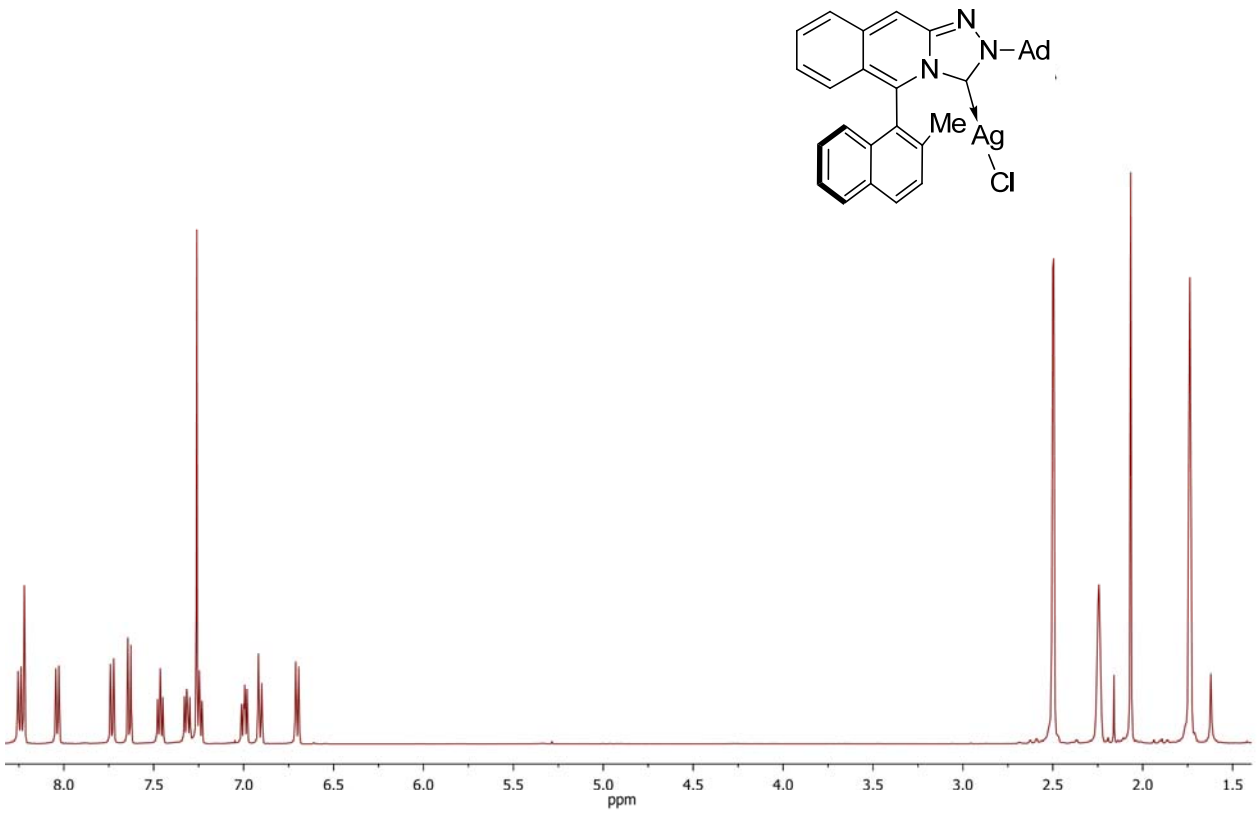




$^{13}$C NMR (125 MHz, $CDCl_3$) of (*R*)-**9b(Cl$^-$)**:

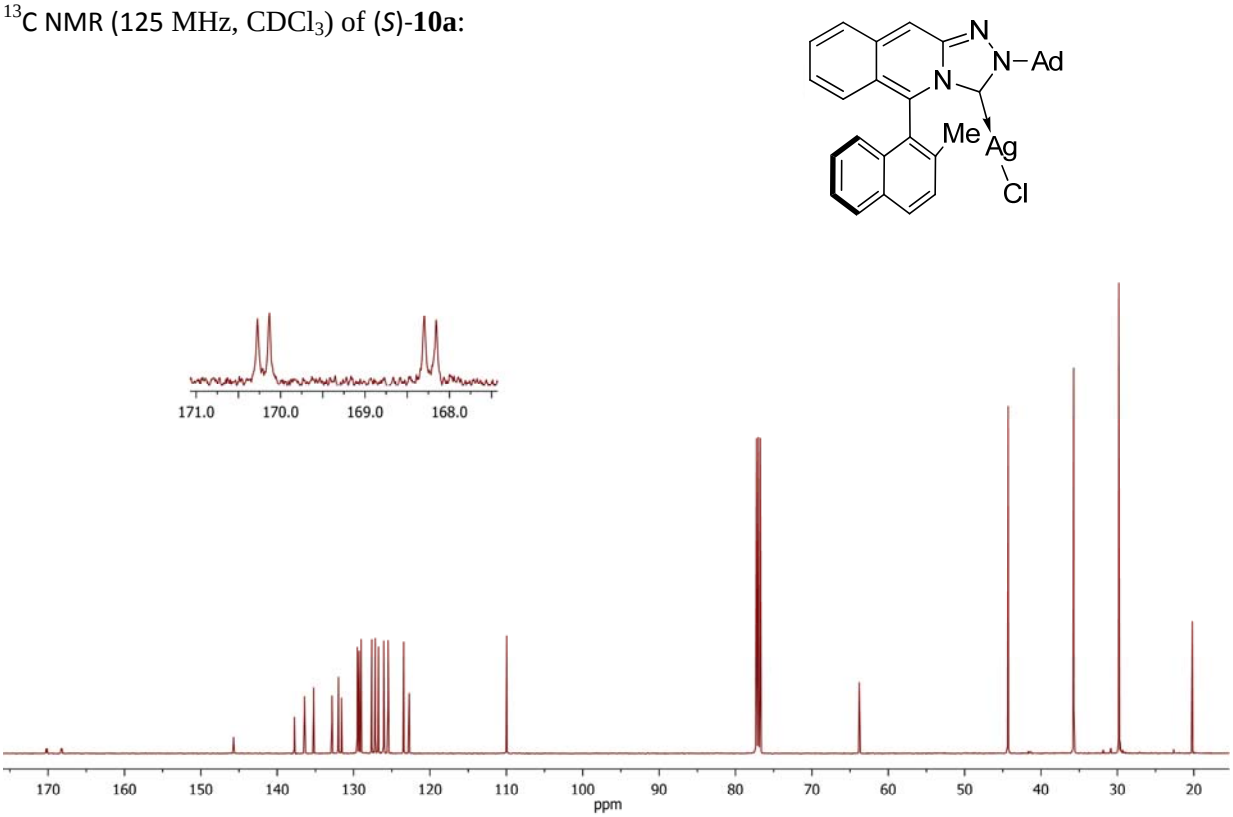


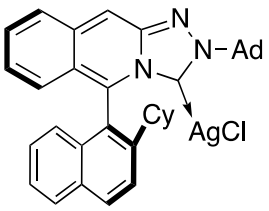
$^{1}$H NMR (500 MHz, $CDCl_3$) of (*S*)-**10a**:

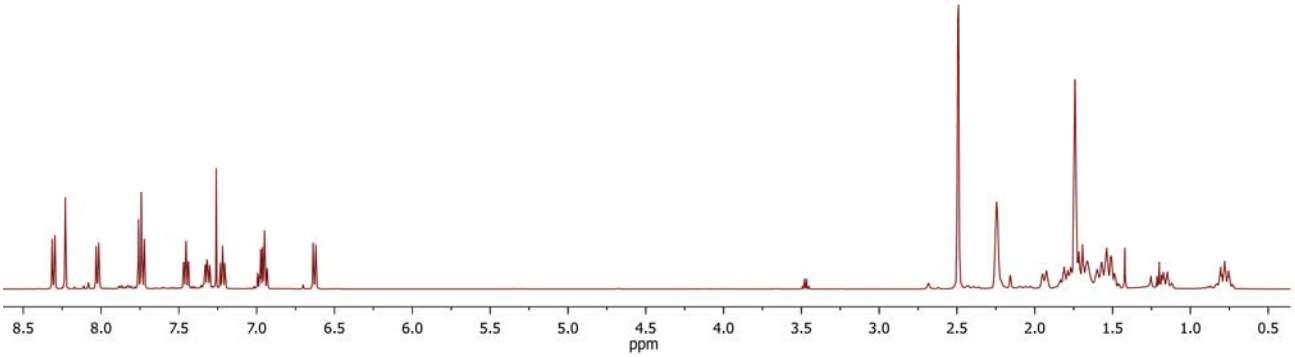



$^{13}$C NMR (125 MHz, $CDCl_3$) of (*S*)-**10a**:

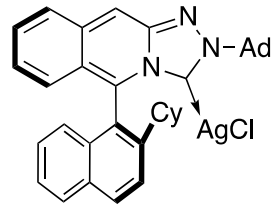


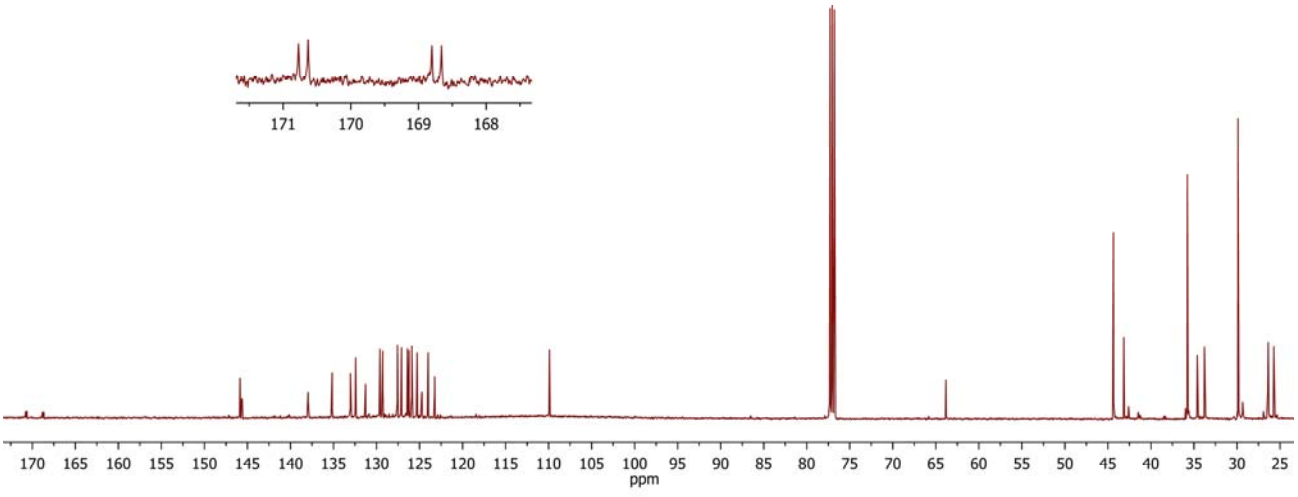
$^{1}$H NMR (500 MHz, $CDCl_3$) of (*R*)-**10b**:



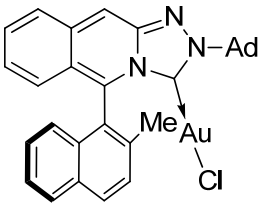



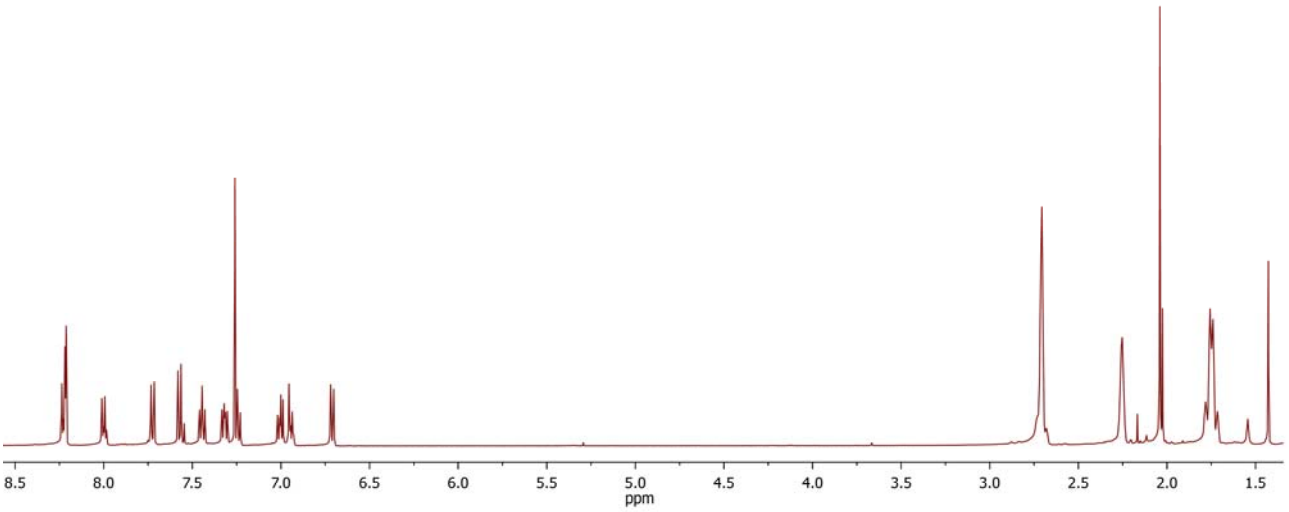

$^{13}$C NMR (125 MHz, $CDCl_3$) of (*R*)-**10b**:



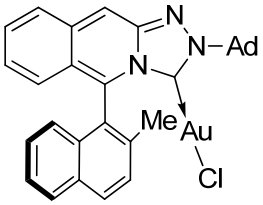



$^{1}$H NMR (500 MHz, $CDCl_3$) of (*S*)-**Au7**:

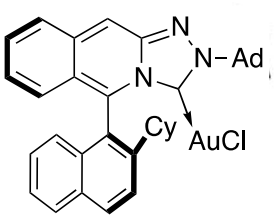


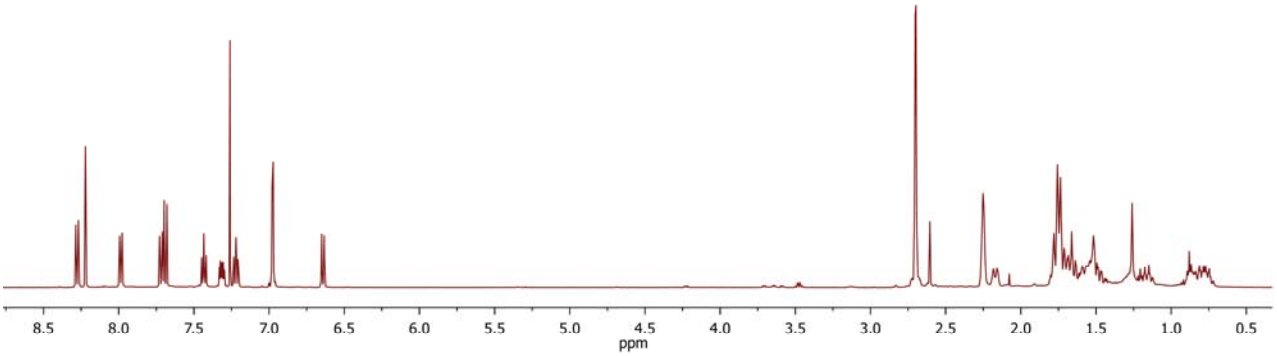




$^{13}$C NMR (125 MHz, $CDCl_3$) of (*S*)-**Au7**:

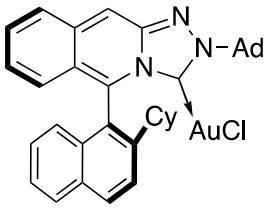


$^{1}$H NMR (500 MHz, $CDCl_3$) of (*R*)-**Au8**:

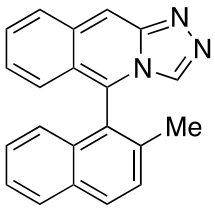


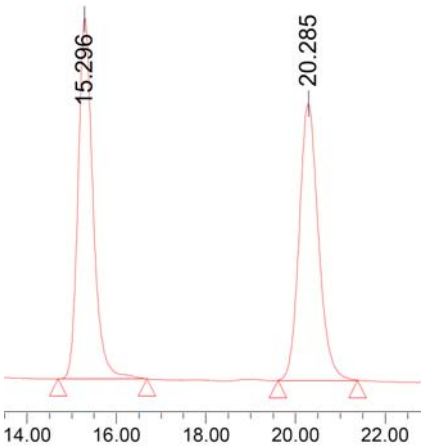




$^{13}$C NMR (125 MHz, $CDCl_3$) of (*R*)-**Au8**:



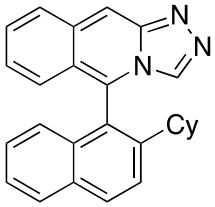
HPLC resolution of compound **8a**: Analytical IA column ($CH_2Cl_2$-Hexane 90:10): first enantiomer, compound (*R*)-**8a**, $t_R$ = 15.3 min; second enantiomer, compound (*S*)-**8a**, $t_R$ = 20.3 min.

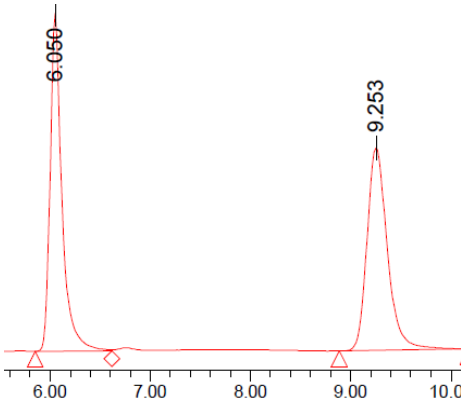


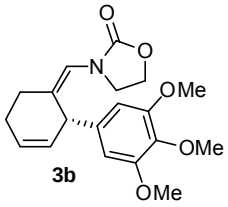

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 272.3 nm | 15.296 | 1632868 | 50.04 | 71018 |
| 2 | PDA 272.3 nm | 20.285 | 1630335 | 49.96 | 54665 |

HPLC resolution of compound **8b**: Analytical IA column (100% $CH_2Cl_2$): first enantiomer, (*R*)-**8b**, $t_R$ = 6.05 min; second enantiomer, (*S*)-**8b**, $t_R$ = 9.25 min.



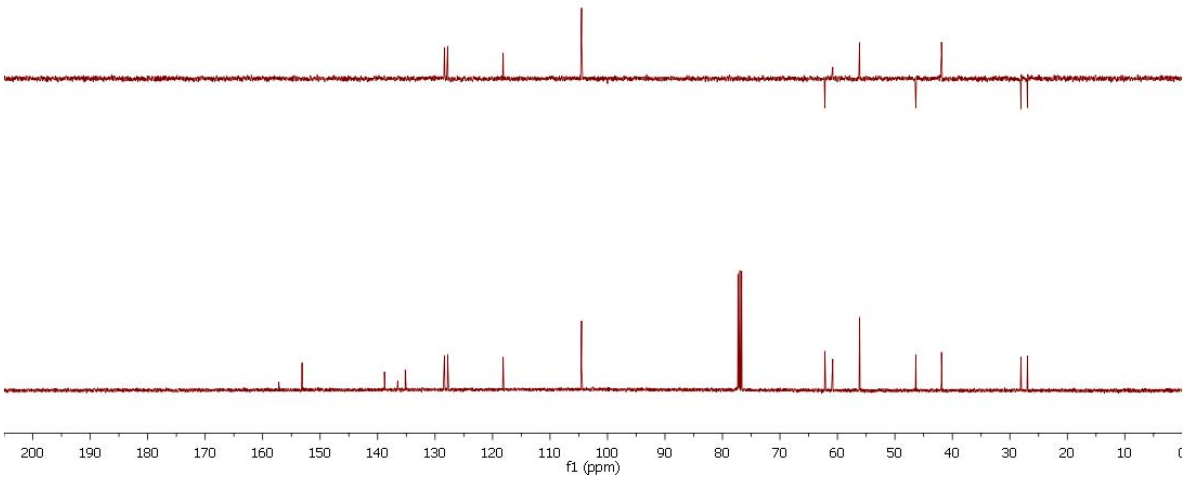



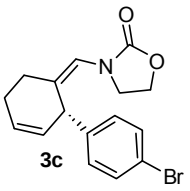

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 232.0 nm | 6.050 | 13674311 | 49.38 | 1650686 |
| 2 | PDA 232.0 nm | 9.253 | 14018502 | 50.62 | 995268 |


O
O
N
OMe
OMe
OMe

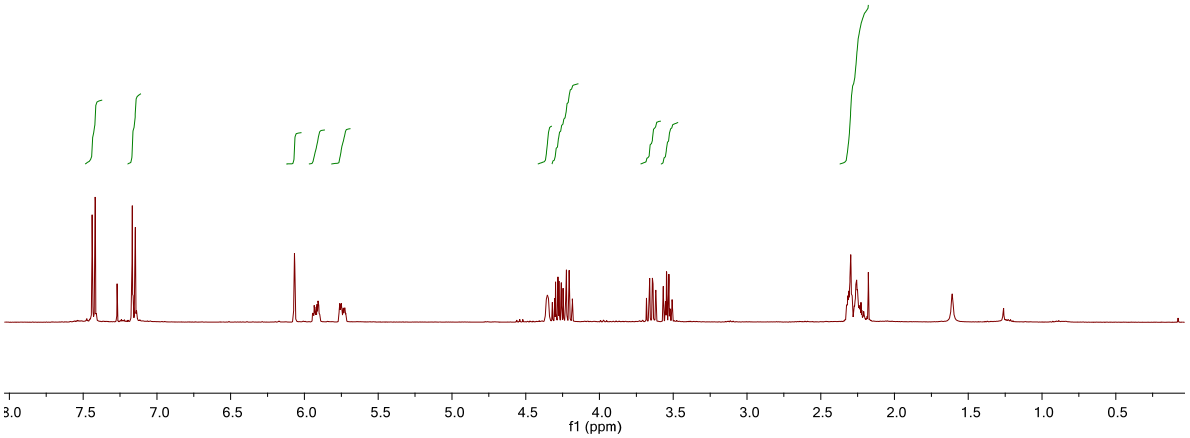
**3b**

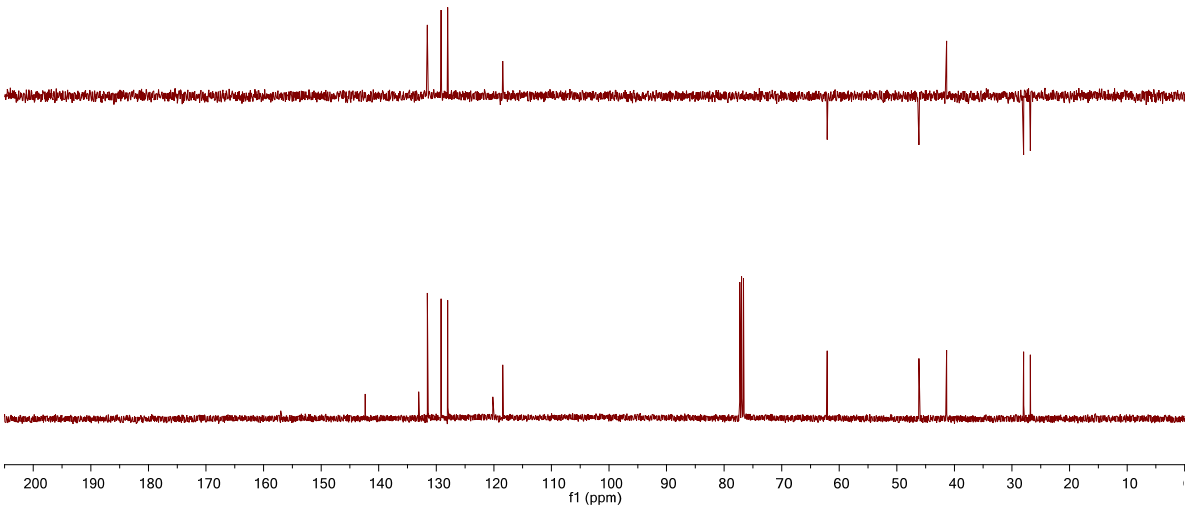

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

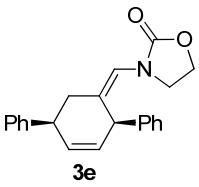

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
N
O
Br

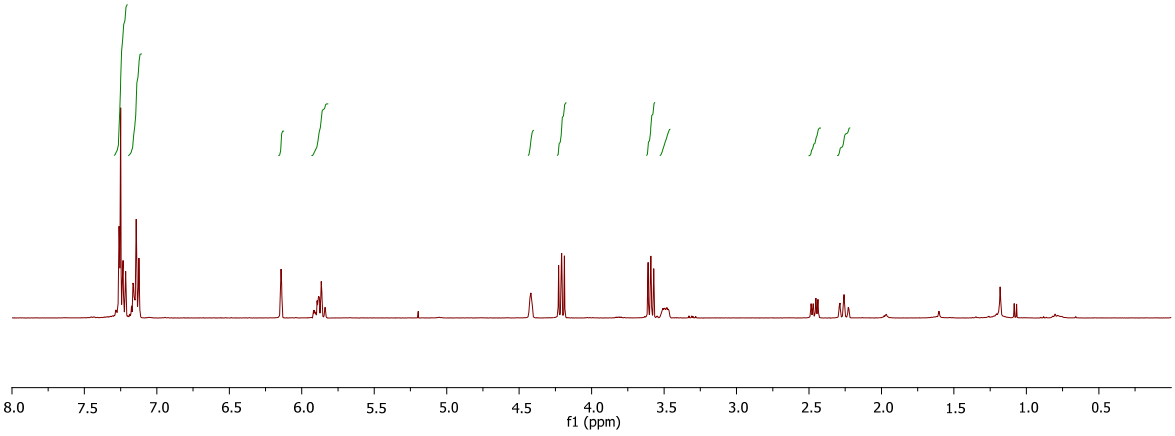
**3c**

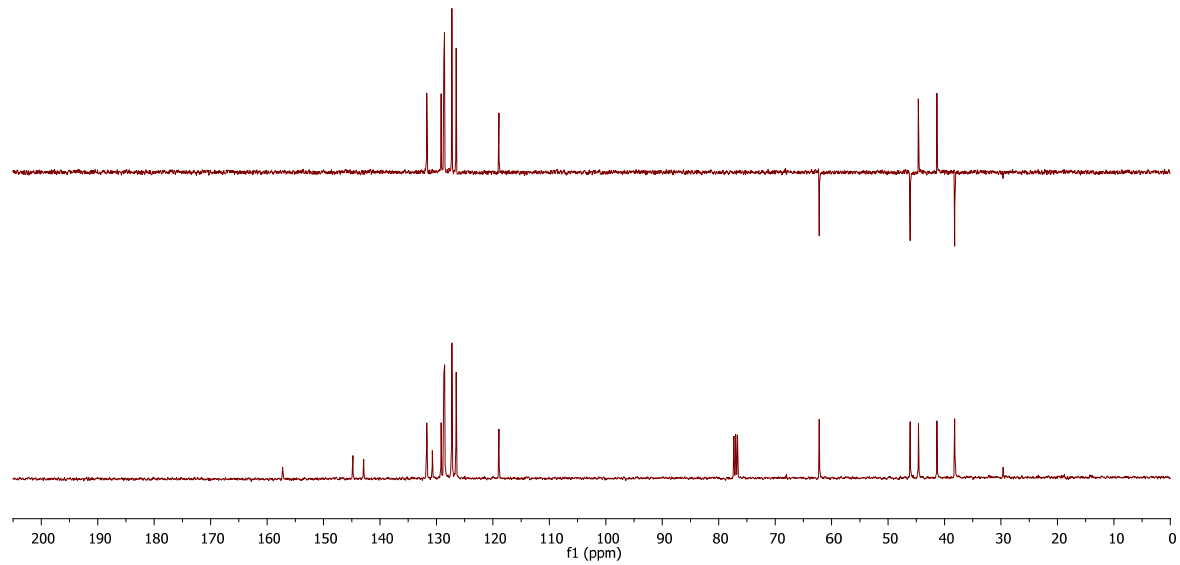

3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

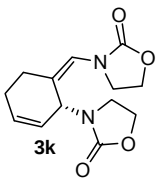

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

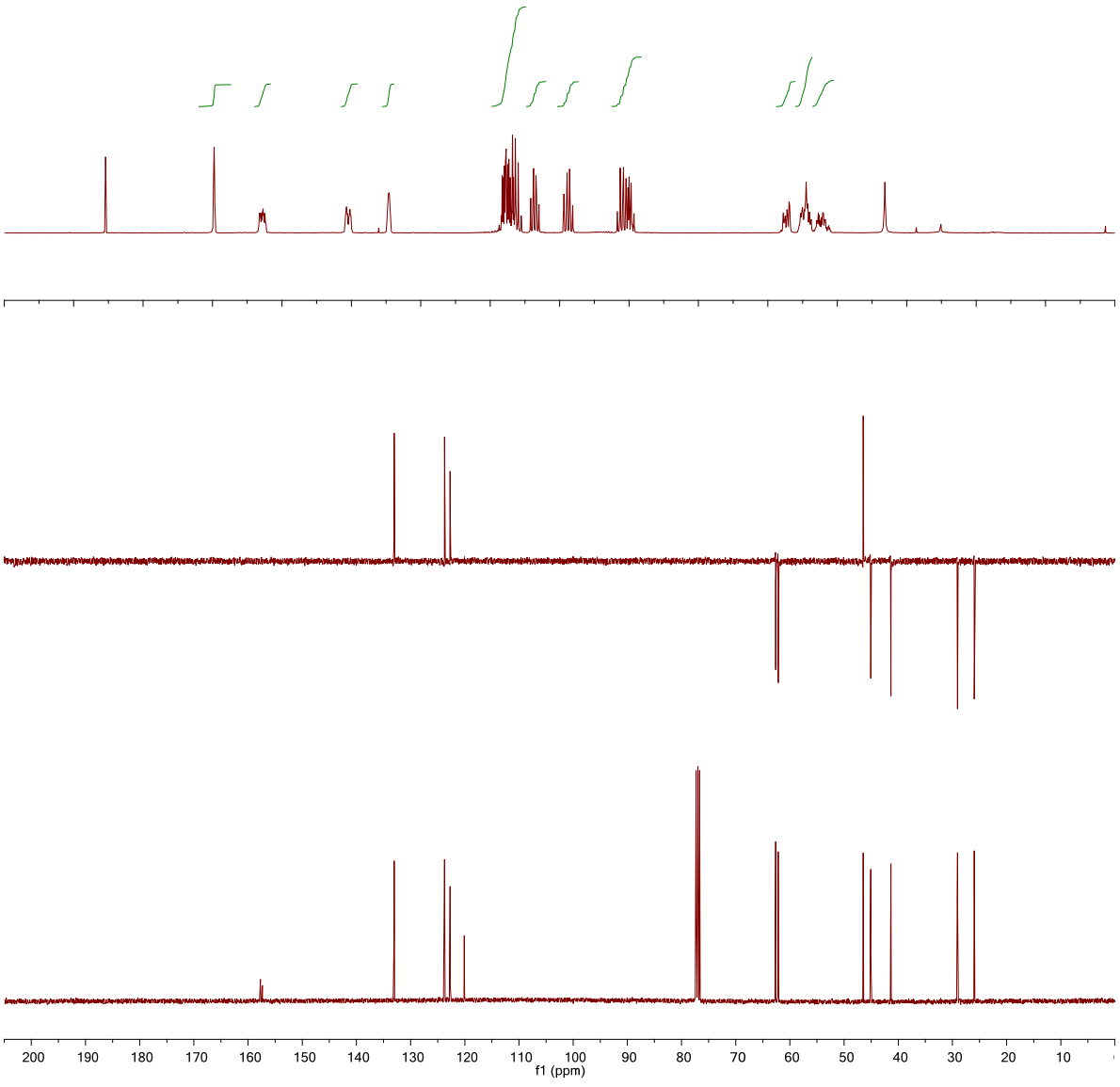

O
O
N
Ph
Ph

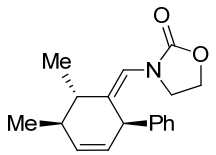
**3e**


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
f1 (ppm)

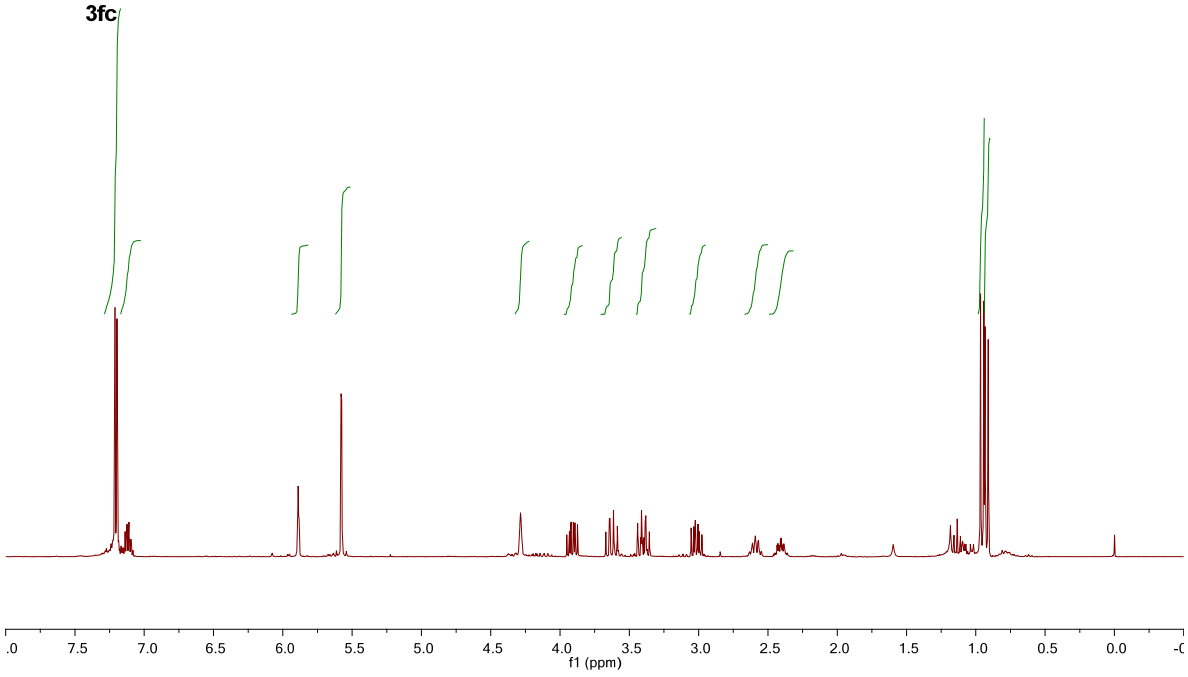

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

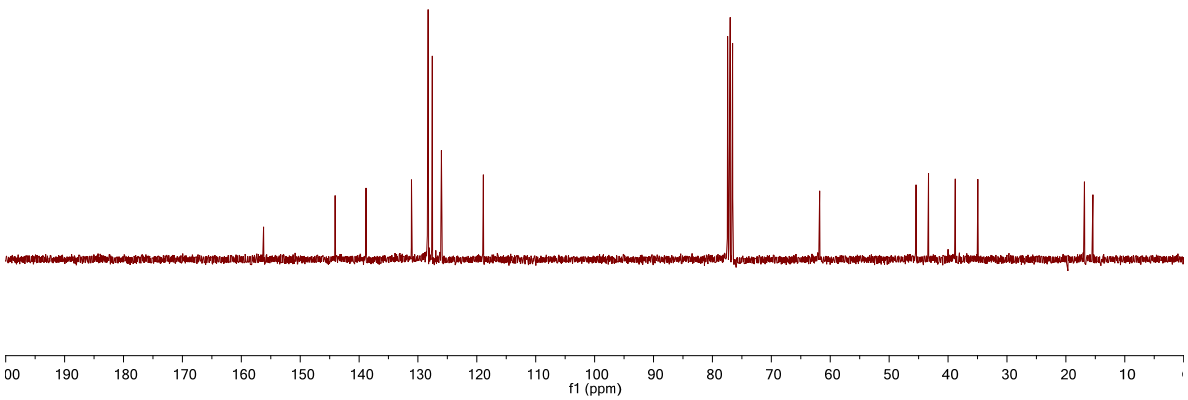

O
N
O
N
O
O
3k


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
Me
N
O
Me
Ph

**3fc**


.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)


00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)