Supporting Information

Consecutive Chirality Transfer: Efficient Synthesis of Chiral C,O-Chelated BINOL/Gold(III) Complexes for Asymmetric Catalysis and Chiral Resolution of Disubstituted BINOLs

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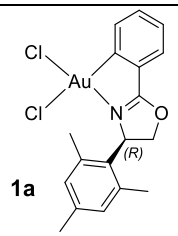
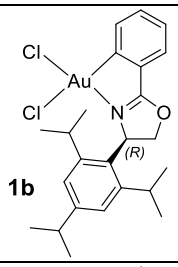
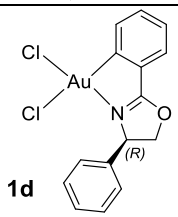
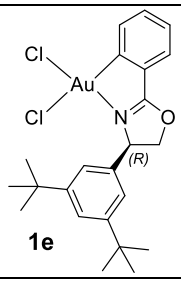
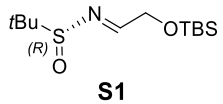
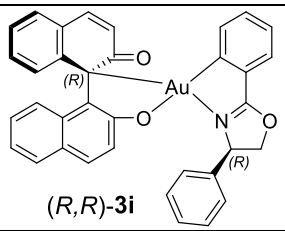
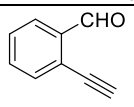
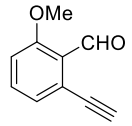
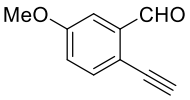
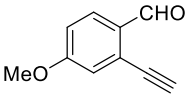
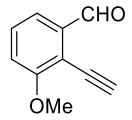
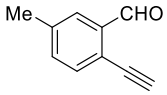
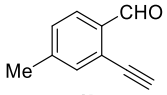
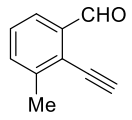
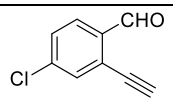
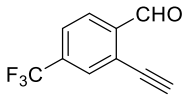
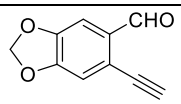
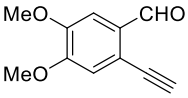
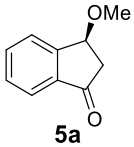
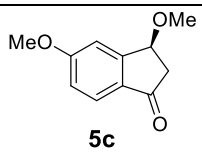
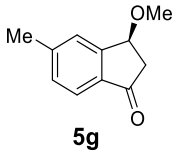
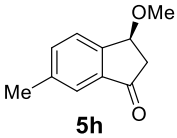
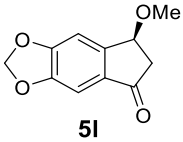
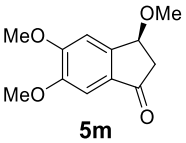
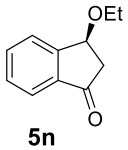
General Procedures

Chemicals are purchased from commercial resources and used without further purification. Thin layer chromatography was performed on precoated silica gel 60 F254 plates. Flash column chromatography was performed using silica gel 60 (230-400 mesh ASTM). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-400 or DPX-600 and internally referenced to TMS. Data for ^{1}H NMR were reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet; brs = broad singlet; d = doublet; dd = double doublet; t = triplet; td = triple doublet; tt = triple triplet; q = quartet; qd = quadruple doublet, m = multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are recorded in terms of chemical shift (δ, ppm). High resolution mass spectra (HR-MS) were measured on Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS system equipped with an ion spray source in the positive ion mode. X-ray crystal structures were determined by Bruker D8 Venture single crystal X-Ray diffractometer for small molecule. Compounds described in the literature were characterized by comparison of their ^{1}H and/or ^{13}C NMR spectra to the previously reported data.

Literature References

 **1a**	J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.
 **1b**	J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.
 **1d**	J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.
 **1e**	J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.
 **S1**	J. C. Barrow, P. L. Ngo, J. M. Pellicore, H. G Selnick, P. G. Nantermet, *Tetrahedron Lett.*, 2001, **42**, 2051 – 2054.
 (*R*,*R*)-**3i**	J.-F. Cui, H.-M. Ko, K.-P. Shing, J.-R. Deng, N. C.-H. Lai, M.-K. Wong, *Angew. Chem. Int. Ed.*, 2017, **56**, 3074 – 3079.
 **4a**	M. D. Acqua, D. Facoetti, G. Abbiati, E. Rossi, *Synthesis*, 2010, **14**, 2367 – 2378.

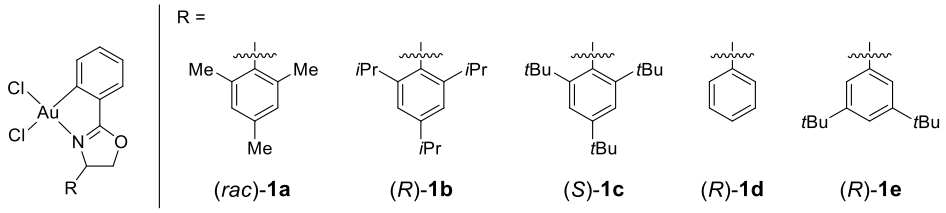
 **4b**	H. Luo, C. He, H. Jiang, S. Zhu, *Chin. J. Chem.*, 2020, **38**, 1052 – 1056.
 **4c**	Y. Ohta, Y. Kubota, T. Watabe, H. Chiba, S. Oishi, N. Fujii, H. Ohno, *J. Org. Chem.*, 2009, **16**, 6299 – 6302.
 **4d**	J. Kong, F. Zhang, C. Zhang, W. Chang, L. Liu, J. Li, *Molecular Catalysis*, 2022, **530**, 112633.
 **4e**	W. Debrouwer, R. A. J. Seigneur, T. S. A. Heugebaerta, C. V. Stevens, *Chem. Commun.,* 2015, **51**, 729 – 732.
 **4g**	W. Debrouwer, R. A. J. Seigneur, T. S. A. Heugebaerta, C. V. Stevens, *Chem. Commun.,* 2015, **51**, 729 – 732.
 **4h**	Y. Ohta, Y. Kubota, T. Watabe, H. Chiba, S. Oishi, N. Fujii, H. Ohno, *J. Org. Chem.*, 2009, **74**, 6299 – 6302.
 **4i**	G. He, C.Wu, J. Zhou, Q. Yang, C. Zhang, Y. Zhou, H. Zhang, H. Liu, *J. Org. Chem.*, 2018, **83**, 13356 − 13362.
 **4j**	J. Nejedlý, M. Šámal, J. Rybáček, I. G. Sánchez, V. Houska, T. Warzecha, J.Vacek, L. Sieger, M. Buděšínský, L. Bednárová, P. Fiedler, I. Císařová, I. Starý*, I. G. Stará* *J. Org. Chem.*, 2020, **85**, 248 – 276.
 **4k**	J.-R. Deng, N. C.-H. Lai, K. K.-Y. Kung, B. Yang, S.-F. Chung, A. S.-L. Leung, M.-C. Choi, Y.-C. Leung, M.-K Wong, *Commun. Chem.*, 2020, **3**, 67.
 **4l**	Z. Cao, H. Zhang, X. Zhang, L. Zhang, X. Meng, G. Chen, X.-E. Zhao, X. Suna, J. You, *RSC Adv.*, 2015, **5**, 103155 – 103158.
 **4m**	Z. Cao, H. Zhang, X. Zhang, L. Zhang, X. Meng, G. Chen, X.-E. Zhao, X. Suna, J. You, *RSC Adv.*, 2015, **5**, 103155 – 103158.
 **5a**	J.-J. Jiang, J.-F. Cui, B. Yang,Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.
 **5c**	J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.

 **5g**	J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.
 **5h**	J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.
 **5l**	Z. Cao, H. Zhang, X. Zhang, L. Zhang, X. Meng, G. Chen, X.-E. Zhao, X. Suna, J. You, *RSC Adv.*, 2015, **5**, 103155 – 103158.
 **5m**	Z. Cao, H. Zhang, X. Zhang, L. Zhang, X. Meng, G. Chen, X.-E. Zhao, X. Suna, J. You, *RSC Adv.*, 2015, **5**, 103155 – 103158.
 **5n**	J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai, M.-K. Wong, *Org. Lett.*, 2019, **21**, 6289 – 6294.

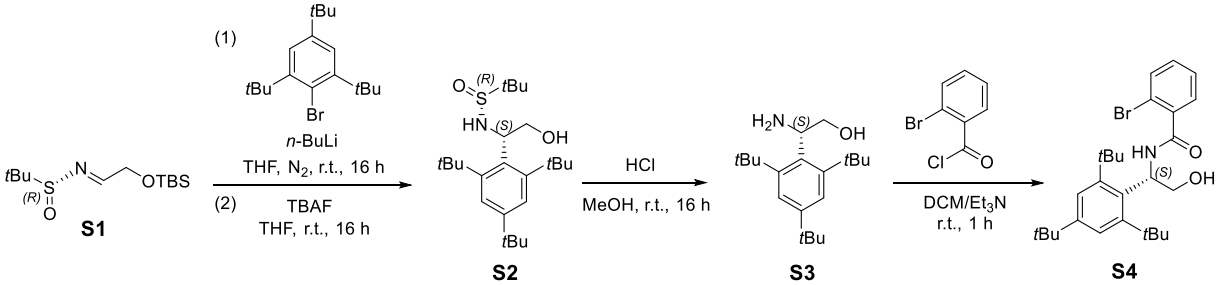
Experimental Procedures

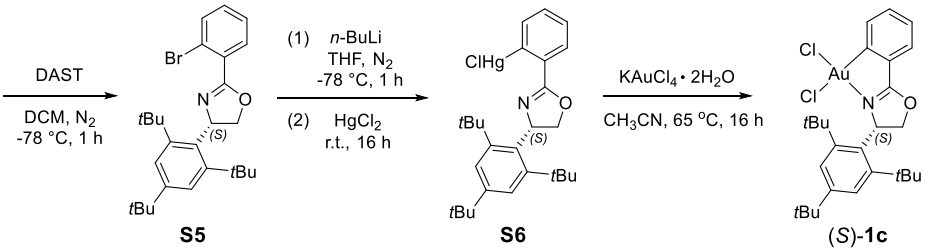
Synthesis of C,O-Chelated BINOL/Gold(III) Complexes 3a, 3g-3j

(1) Preparation of Gold(III) Dichloride Complexes 1a-1e



Compounds (*rac*)-**1a**, (*R*)-**1b**, (*R*)-**1d** and (*R*)-**1e** were synthesized and identified with reference to the characterization data of our previously reported paper.[1]





Compound **S1** was synthesized and identified with reference to the characterization data of literature.[2]

Compound **S2**: A solution of 2-Bromo-1,3,5-tri-tert-butylbenzene (5.47 g, 16.8 mmol) in anhydrous THF (90 mL) was cooled to 0 °C under N_2, followed by the dropwise addition of *n*-butyllithium (*n*-BuLi, 1.6 M solution in hexane, 12.25 mL). The solution was warmed to room temperature and stirred for 2 h. Compound **S1** (3.89 g, 14 mmol) was dissolved in anhydrous THF (10 mL) and dropwise added to the solution. The reaction mixture was stirred for further 16 h. When the reaction completed, saturated NH_4Cl aqueous solution (30 mL) was added. The aqueous phase was extracted by EA (50 mL × 3). The organic phase was combined, dried with anhydrous $MgSO_4$, concentrated under reduced pressure, and subjected to flash column chromatography (hexane/EA), affording product as a pale-yellow oil (2.32 g, 4.43 mmol, 32% yield). The product was then treated with tetra-n-butylammonium fluoride (TBAF, 1.0 M solution in THF, 5.27 mL) in THF (22 mL). The reaction mixture was stirred at room temperature for 16 h. When the reaction completed, water (30 mL) was added. The reaction mixture was extracted with EA (20 mL × 3) and washed with brine (30 mL). The organic phase was combined, dried with anhydrous $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (hexane/DCM/EA), affording compound **S2** as a white solid (922 mg, 2.25 mmol, 51% yield).

Compound **S3**: Compound **S2** (865 mg, 2.11 mmol) was suspended in the solution of HCl aqueous solution (12 M, 6 mL) and MeOH (6 mL). After stirring for 2 h at room temperature, the reaction mixture became a clear pale-yellow solution. The solution was cooled to 0 °C and adjusted to pH 12. The solution was diluted with water and then extracted with DCM (20 mL × 5) and washed with brine (30 mL). The organic phase was combined, dried with anhydrous $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (DCM/MeOH), affording compound **S3** as a white solid (638 mg, 2.08 mmol, 99% yield).

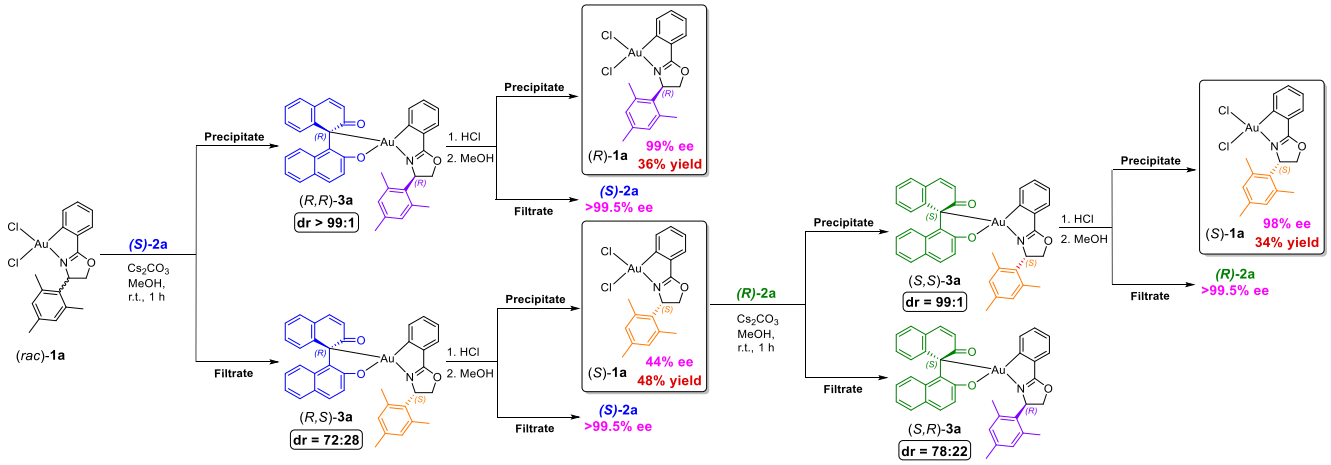
Compound **S4**: 2-bromobenzoyl chloride (483 mg, 2.2 mmol, 287 µL) was added dropwise to a solution of compound **S3** (611 mg, 2 mmol) and triethylamine (Et_3N, 1 mL) in DCM (2 mL) at 0 °C. The solution was then allowed to warm to room temperature and stirred for 1 h. When the reaction was completed, the water (10 mL) was added. The reaction mixture was extracted with EA (10 mL × 3) and washed with brine (30 mL). The organic phase was combined, dried with anhydrous $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (hexane/acetone), affording compound **S4** as a white solid (713 mg, 1.46 mmol, 73% yield).

Compound **S5**: A solution of compound **S4** (691 g, 1.42 mmol) in dry DCM (10 mL) was cooled to -78 °C under N_2, followed by the dropwise addition of diethylaminosulfur trifluoride (DAST, 251 mg, 1.56 mmol, 204 µL) and stirred for 1 h. Potassium carbonate (K_2CO_3, 179 mg, 2.13 mmol) was added. The reaction mixture was warmed to room temperature and stirred for further 1 h. When the reaction completed, saturated $NaHCO_3$ was slowly added to the mixture until no bubble coming out. The reaction mixture was extracted with DCM (30 mL × 3) and washed with brine (30 mL). The organic phase was combined, dried with anhydrous $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (hexane/EA), affording compound **S5** as a white solid (563 mg, 1.20 mmol, 84% yield).

Compound **S6**: A solution of compound **S5** (471 g, 1 mmol) in anhydrous THF (5 mL) was cooled to -78 °C under N_2, followed by the dropwise addition of *n*-butyllithium (*n*-BuLi, 1.6 M solution in hexane, 938 µL) and stirred for 1 h. $HgCl_2$ (326 mg, 1.2 mmol) was added and the mixture was warmed to room temperature and stirred for further 16 h. The reaction was quenched by water and filtered through celite. The filtrate was extracted by DCM (10 mL × 3) and washed with brine (30 mL). The organic phase was combined, dried with anhydrous $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (hexane/DCM), affording compound **S6** as a white solid (333 mg, 0.532 mmol, 53% yield).

Compound (*S*)-**1c**: A mixture of compound **S6** (265 mg, 0.423 mmol) and $KAuCl_4{\cdot}2H_2O$ (193 mg, 0.465 mmol) in CH_3CN (2 mL) was heated to 65 °C and stirred for 16 h. When the reaction completed, the solution was dried under reduced pressure and suspended by DCM. The suspension was filter through celite and the filtrate was subjected to flash column chromatography (hexane/acetone). The resulting solid was washed by isopropanol, affording compound (*S*)-**1c** as a white solid (145 mg, 0.220 mmol, 52% yield).

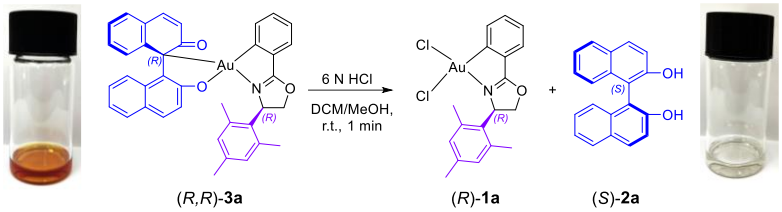
(2) Column-Free Chiral Resolution Method for Preparation of Gold(III) Dichloride Complexes (*R*)-1a and (*S*)-1a



Diastereomeric resolution: A mixture of racemic cyclometalated gold(III) complex (C^N)$AuCl_2$ (*rac*)-**1a** (1.0 g, 1.878 mmol, 1.0 equiv.), BINOL (*S*)-**2a** (590 mg, 2.066 mmol, 1.1 equiv.) and Cs_2CO_3 (1.34 g, 4.132 mmol, 2.2 equiv.) in MeOH was stirred for 1 h at room temperature. Orange red precipitate mixed with a red solution was observed. The precipitate was collected by filtration, washed with MeOH and dried under reduced pressure to give the corresponding C,O-chelated cyclometalated BINOL/gold(III) complex (*R,R*)-**3a** with dr > 99:1 as orange red solid. The filtrate was diluted with EA and washed with water. The resulting solution was concentrated

under reduced pressure and diluted by hexane to precipitate the crude BINOL/gold(III) complex (*R,S*)-**3a** with dr = 72:28 as orange red solid.

Acid treatment: The obtained (*R,R*)-**3a** was dissolved in DCM/MeOH (1:1, 20 mL) resulting in a red solution. After addition of 6 N hydrochloric acid (0.94 mL, 5.634 mmol, 3 equiv.) at room temperature, the color of the solution immediately changed from red to colorless within 1 min. The solvent was removed under reduced pressure to give a crude mixture of (*R*)-**1a** and (*S*)-**2a**. MeOH was added into the crude mixture and the resulting suspension was collected by filtration affording (*R*)-**1a** (99% ee) as white solid (360 mg, 0.676 mmol, 36% yield). Using the same method for (*R,S*)-**3a**, (*S*)-**1a** (44% ee) was obtained as white solid (480 mg, 0.902 mmol, 48% yield). Two filtrates were combined and purified flash column chromatography over silica gel to recover the BINOL (*S*)-**2a** (560 mg, 1.962 mmol, 95% yield).



Scheme S1. Acid treatment of (*R,R*)-**3a** to give (*R*)-**1a** and (*S*)-**2a**.

Repeat the diastereomeric resolution method with (*S*)-**1a** (44% ee) by changing the resolving agent to (*R*)-**2a** (284 mg, 0.992 mmol, 1.1 equiv) to give (*S,S*)-**3a** (dr = 99:1) and crude (*S,R*)-**3a** (dr = 78:22). After acid treatment for (*S,S*)-**3a**, (*S*)-**1a** (98% ee) was obtained (280 mg, 0.638 mmol, 34% yield) and BINOL (*R*)-**2a** was recovered (272 mg, 0.952 mmol, 96% yield).

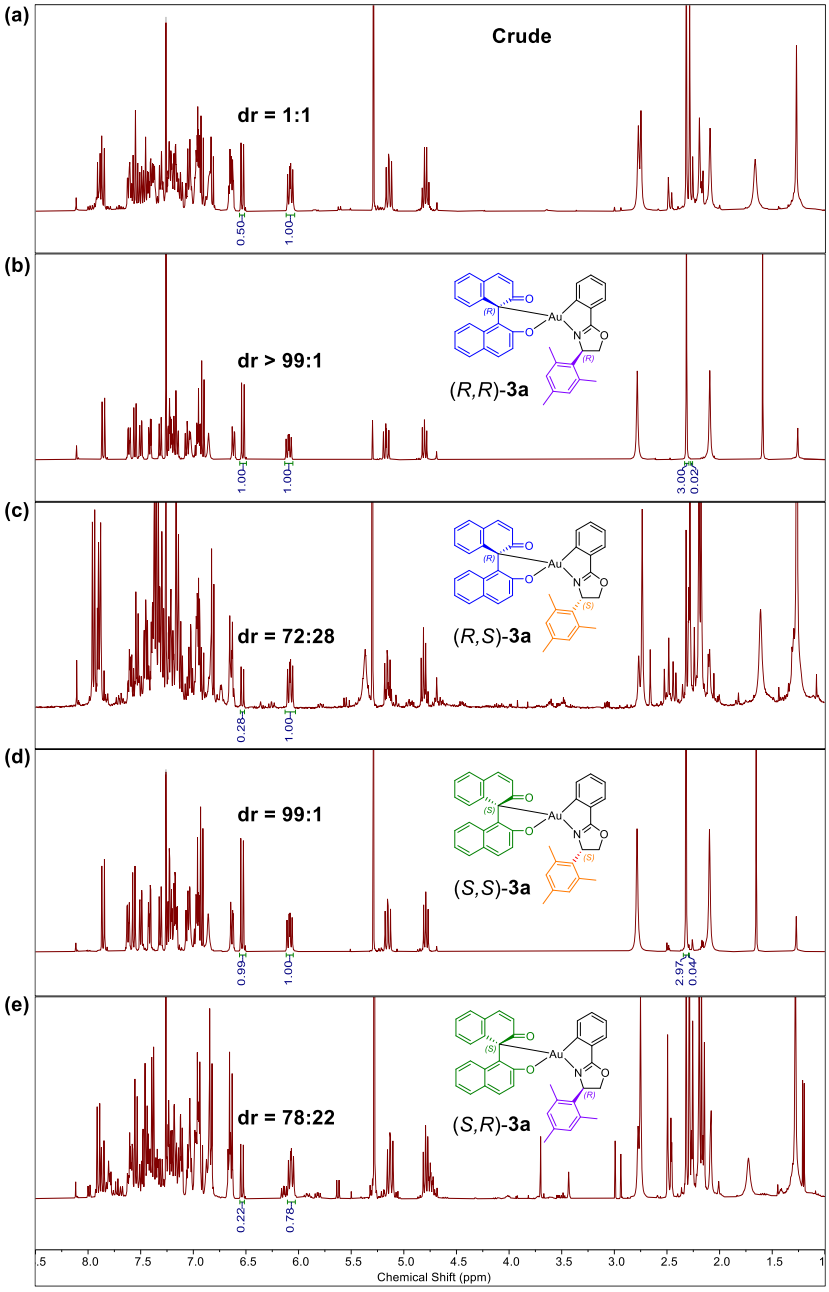
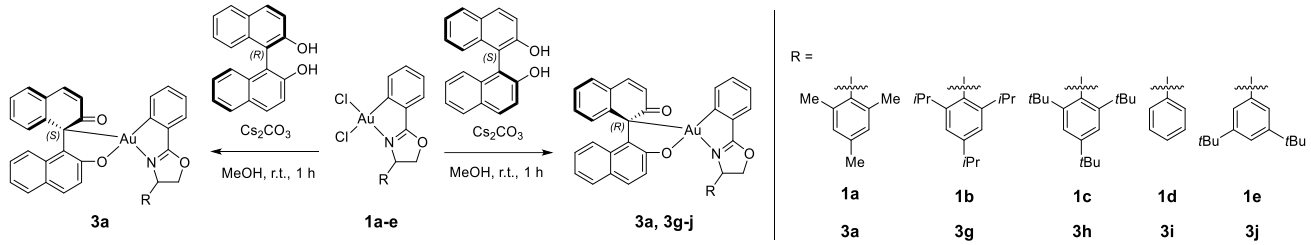


Figure S1. Determination of dr of **(a)** crude mixture of **3a**; **(b)** (*R,R*)-**3a**; **(c)** (*R,S*)-**3a**; **(d)** (*S,S*)-**3a**; **(e)** (*S,R*)-**3a** by ^{1}H NMR analysis.

(3) Preparation of BINOL/Gold(III) Complexes



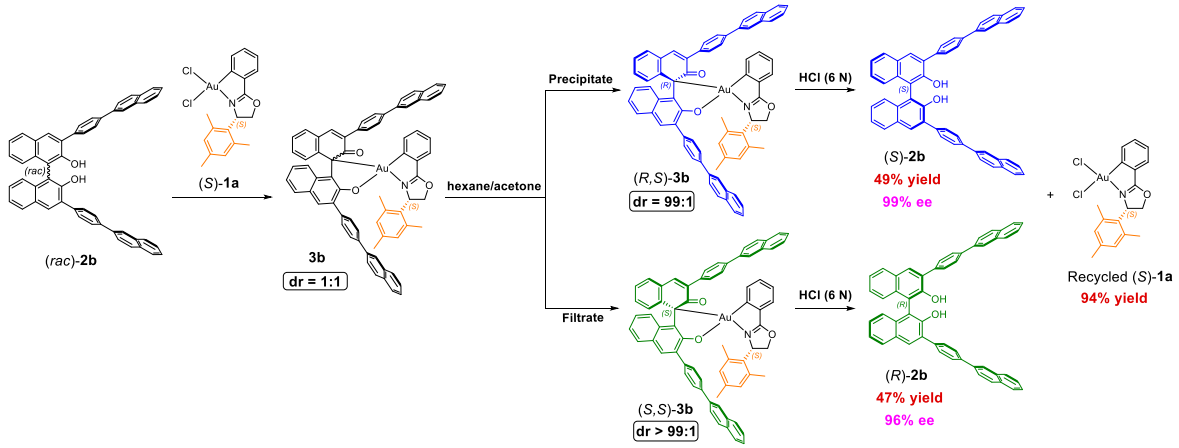
(*R,R*)-**3a** (602 mg, 0.808 mmol, 43% yield) and (*S,S*)-**3a** (504 mg, 0.676 mmol, 36% yield) can be prepared by the above diastereomeric resolution method using (*rac*)-**1a**.

(*R,S*)-**3a**: A mixture of enantiopure cyclometalated gold(III) complex (*S*)-**1a** (22.0 mg, 0.0413 mmol, 1.1 equiv.), BINOL (*S*)-**2a** (10.8 mg, 0.0376 mmol, 1.0 equiv.) and Cs_2CO_3 (26.9 mg, 0.0826 mmol, 2.2 equiv.) in MeOH was stirred for 1 h at room temperature, giving an orange red solution. The resulting solution was filtered through celite. The filtrate was diluted with EA and washed with water. The resulting solution was concentrated under reduced pressure and diluted by hexane to precipitate BINOL/gold(III) complex as orange red solid (23.8 mg, 0.0320 mmol, 85% yield).

(*S,R*)-**3a**: A mixture of enantiopure cyclometalated gold(III) complex (*R*)-**1a** (22.0 mg, 0.0413 mmol, 1.1 equiv.), BINOL (*R*)-**2a** (10.8 mg, 0.0376 mmol,1.0 equiv.) and Cs_2CO_3 (26.9 mg, 0.0826 mmol, 2.2 equiv.) in MeOH was stirred for 1 h at room temperature, giving an orange red solution. The resulting solution was filtered through celite. The filtrate was diluted with EA and washed with water. The resulting solution was concentrated under reduced pressure and diluted by hexane to precipitate BINOL/gold(III) complex as orange red solid(25.2 mg, 0.0338 mmol, 90% yield).

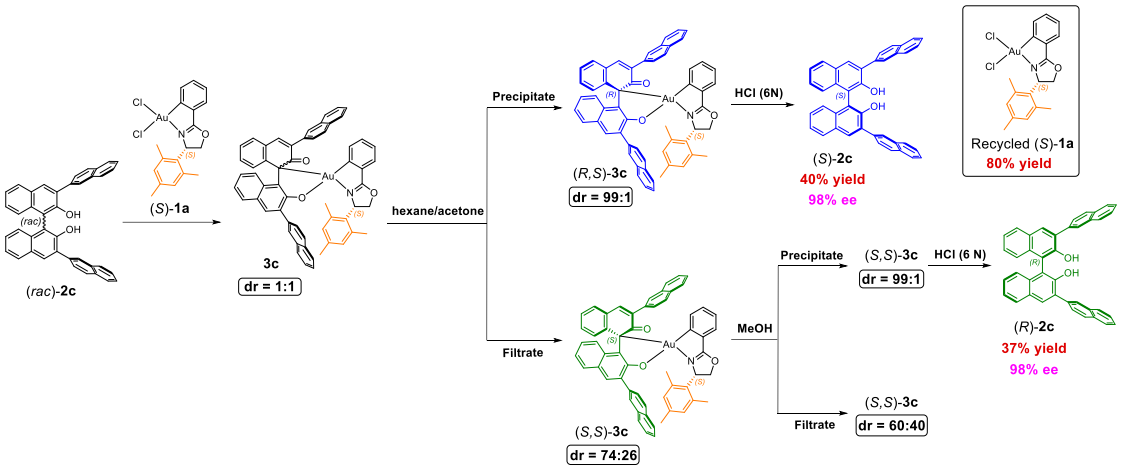
(*R,R*)-**3g**, (*R,S*)-**3h**, (*R,R*)-**3i** and (*R,R*)-**3j**: A mixture of enantiopure cyclometalated gold(III) complex (C^N)$AuCl_2$ **1** (1.0 equiv.), BINOL (*S*)-**2a** (1.1 equiv.) and Cs_2CO_3 (2.2 equiv.) in MeOH was stirred for 1 h at room temperature. Orange red precipitate was formed in a suspension. The precipitate was collected by filtration, washed with MeOH and dried under reduced pressure to give the corresponding C,O-chelated cyclometalated BINOL/gold(III) complexes (*R,R*)-**3g** (orange red solid, 78 mg, 0.0935 mmol, 85% yield), (*R,S*)-**3h** (salmon orange solid, 20 mg, 0.0229 mmol, 78% yield), (*R,R*)-**3i** (orange solid, 237 mg, 0.337 mmol, 82% yield) and (*R,R*)-**3j** (orange solid, 114 mg, 0.140 mmol, 82% yield).

Synthesis of C,O-Chelated BINOL/Gold(III) Complexes 3b-3f and Resolution of BINOLs 2b-2f



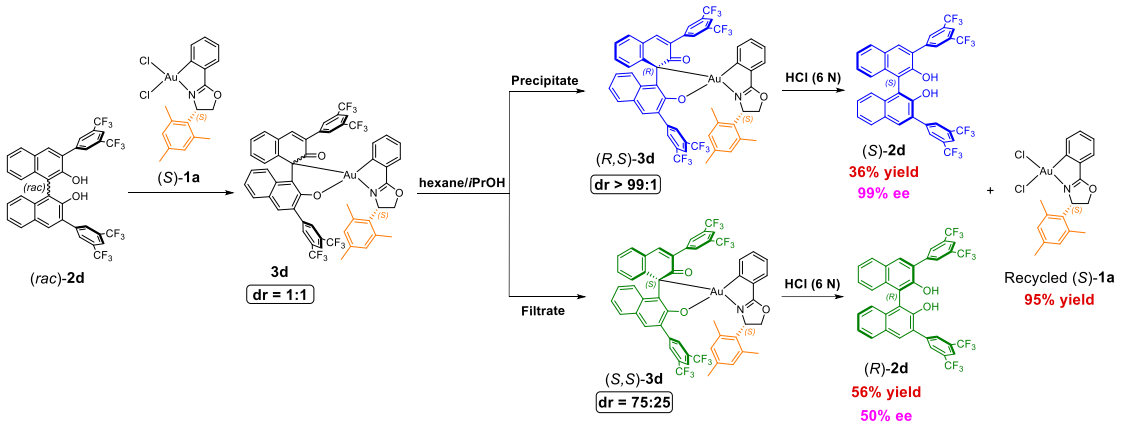
A mixture of gold(III) complex (*S*)-**1a** (22 mg, 0.0413 mmol, 1.1 equiv.), racemic BINOL (*rac*)-**2b** (25.9 mg, 0.0375 mmol, 1.0 equiv.) and Cs_2CO_3 (26.9 mg, 0.0827 mmol, 2.2 equiv.) in MeOH (2 mL) was stirred for 1 h at room temperature. Orange red precipitate was formed in a suspension. The precipitate was collected by filtration affording the diastereomeric mixtures of **3b** with dr = 1:1. After addition of hexane/acetone (1:1, 4 mL), orange red precipitate mixed with a red solution was observed. The precipitate was collected to give BINOL/gold(III) complex (*R,S*)-**3b** with dr = 99:1 as orange red solid (21.6 mg, 0.0187 mmol, 50% yield). The filtrate was concentrated under reduced pressure and diluted by hexane to precipitate the BINOL/gold(III) complex (*S,S*)-**3b** with dr > 99:1 as orange red solid (21.1 mg, 0.0184 mmol, 49% yield).

The obtained (*R,S*)-**3b** and (*S,S*)-**3b** was separately dissolved in DCM/MeOH (1:1, 2 mL). After addition of 6 N hydrochloric acid (19 µL, 0.0188 mmol, 3 equiv.) at room temperature, the color of the solution immediately changed from red to colorless within 1 min. The solvent was removed under reduced pressure and subjected to flash column chromatography (hexane/DCM), affording BINOL (*S*)-**2b** (white solid, 12.7 mg, 0.0184 mmol, 49% yield, 99% ee), BINOL (*R*)-**2b** (white solid, 12.2 mg, 0.0176 mmol, 47% yield, 96% ee) and recovered (*S*)-**1a** (20.7 mg, 0.0388 mmol, 94% yield).



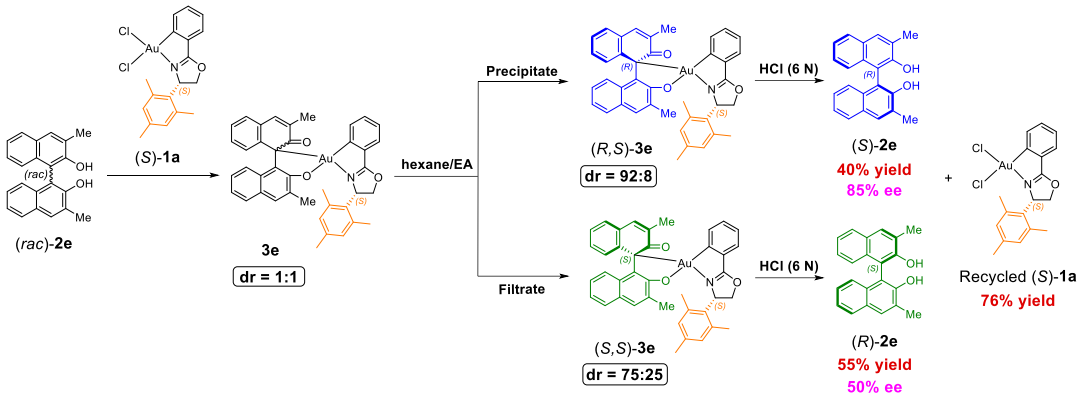
A mixture of gold(III) complex (*S*)-**1a** (22 mg, 0.0413 mmol, 1.1 equiv.), racemic BINOL (*rac*)-**2c** (20.2 mg, 0.0375 mmol, 1.0 equiv.) and Cs_2CO_3 (26.9 mg, 0.0827 mmol, 2.2 equiv.) in MeOH (2 mL) was stirred for 1 h at room temperature. The reaction mixture was diluted with DCM and washed with water. The resulting solution was concentrated under reduced pressure affording the diastereomeric mixture **3c** with dr = 1:1. After addition of hexane/acetone (5:1, 12 mL), orange red precipitate mixed with a red solution was observed. The precipitate was collected to give BINOL/gold(III) complex (*R,S*)-**3c** with dr = 99:1 as orange red solid (15.7 mg, 0.0157 mmol, 42% yield). The filtrate was concentrated under reduced pressure and diluted by hexane to precipitate the crude BINOL/gold(III) complex (*S,S*)-**3c** with dr = 74:26 as orange red solid. MeOH (5 mL) was subsequently added to the obtained crude (*S,S*)-**3c**. Orange red precipitate mixed with pale yellow solution was observed. The precipitate was collected by filtration to give BINOL/gold(III) complex (*S,S*)-**3c** with dr = 99:1 as orange red solid (14.6 mg, 0.0146 mmol, 39% yield).

The obtained (*R,S*)-**3c** and (*S,S*)-**3c** was separately added in DCM/MeOH (1:1, 2 mL). After addition of 6 N hydrochloric acid (19 μL, 0.0188 mmol, 3 equiv.) at room temperature, the color of the solution immediately changed from red to colorless within 1 min. The solvent was removed under reduced pressure and subjected to flash column chromatography (hexane/DCM), affording BINOL (*S*)-**2c** (white solid, 8.1 mg, 0.0150 mmol, 40% yield, 98% ee), BINOL (*R*)-**2c** (white solid, 7.5 mg, 0.0139 mmol, 37% yield, 98% ee) and recovered (*S*)-**1a** (17.6 mg, 0.0330 mmol, 80% yield).



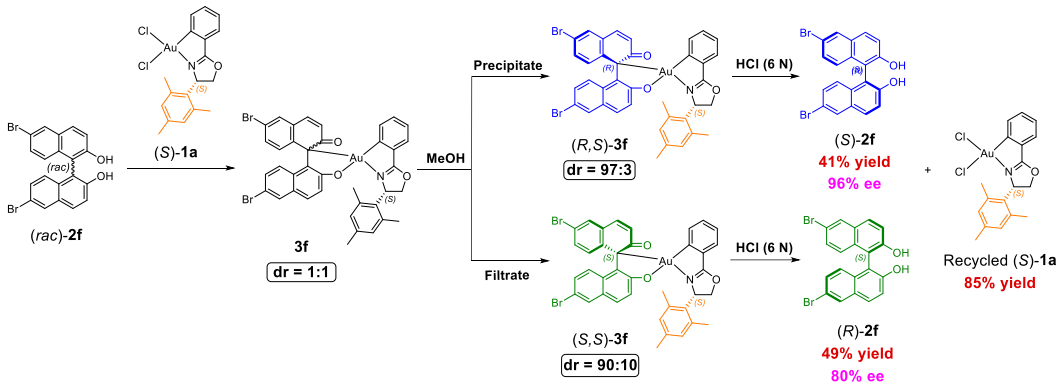
A mixture of gold(III) complex (*S*)-**1a** (22 mg, 0.0413 mmol, 1.1 equiv.), racemic BINOL (*rac*)-**2d** (27.9 mg, 0.0375 mmol, 1.0 equiv.) and Cs_2CO_3 (26.9 mg, 0.0827 mmol, 2.2 equiv.) in MeOH (2 mL) was stirred for 1 h at room temperature. The reaction mixture was diluted with EA and washed with water. The resulting solution was concentrated under reduced pressure affording the diastereomeric mixtures of **3d** with dr = 1:1. After addition of hexane/*i*PrOH (9:1, 20 mL), yellow precipitate mixed with a red solution was observed. The precipitate was collected to give BINOL/gold(III) complex (*R,S*)-**3d** with dr > 99:1 as orange red solid (17.5 mg, 0.0150 mmol, 40% yield). The filtrate was concentrated under reduced pressure and diluted by hexane to precipitate the crude BINOL/gold(III) complex (*S,S*)-**3d** with dr = 75:25 as yellow solid.

The obtained (*R,S*)-**3d** and crude (*S,S*)-**3d** was separately dissolved in EA/MeOH (1:1, 2 mL). After addition of 6 N hydrochloric acid (19 μL, 0.0188 mmol, 3 equiv.) at room temperature, the color of the solution immediately changed from red to colorless within 1 min. The solvent was removed under reduced pressure and subjected to flash column chromatography (hexane/DCM), affording BINOL (*S*)-**2d** (white solid, 10.0 mg, 0.0135 mmol, 36% yield, 99% ee), BINOL (*R*)-**2d** (white solid, 15.6 mg, 0.0210 mmol, 56% yield, 50% ee) and recovered (*S*)-**1a** (20.9 mg, 0.0392 mmol, 95% yield).



A mixture of gold(III) complex (*S*)-**1a** (22 mg, 0.0413 mmol, 1.1 equiv.), racemic BINOL (*rac*)-**2e** (11.8 mg, 0.0375 mmol, 1.0 equiv.) and Cs_2CO_3 (26.9 mg, 0.0827 mmol, 2.2 equiv.) in MeOH (2 mL) was stirred for 1 h at room temperature. The reaction mixture was diluted with DCM and washed with water. The resulting solution was concentrated under reduced pressure affording the diastereomeric mixtures of **3e** with dr = 1:1. After addition of hexane/EA (2:1, 12 mL), orange red precipitate mixed with red solution was observed. The precipitate was collected to give BINOL/gold(III) complex (*R,S*)-**3e** with dr = 92:8 as orange red solid (12.2 mg, 0.0157 mmol, 42% yield). The filtrate was concentrated under reduced pressure and diluted by hexane to precipitate the crude BINOL/gold(III) complex (*S,S*)-**3e** with dr = 75:25 as orange red solid.

The obtained (*R,S*)-**3e** and crude (*S,S*)-**3e** was separately added in DCM/MeOH (1:1, 2 mL). After addition of 6 N hydrochloric acid (19 μL, 0.0188 mmol, 3 equiv.) at room temperature, the color of the solution immediately changed from red to colorless within 1 min. The solvent was removed under reduced pressure and subjected to flash column chromatography (hexane/DCM), affording BINOL (*S*)-**2e** (white solid, 4.7 mg, 0.0150 mmol, 40% yield, 85% ee), BINOL (*R*)-**2e** (white solid, 6.5 mg, 0.0206 mmol, 55% yield, 50% ee) and recovered (*S*)-**1a** (16.7 mg, 0.0314 mmol, 76% yield).



A mixture of gold(III) complex (*S*)-**1a** (28 mg, 0.0525 mmol, 1.4 equiv.), racemic BINOL (*rac*)-**2f** (16.7 mg, 0.0375 mmol, 1.0 equiv.) and Cs_2CO_3 (34.2 mg, 0.105 mmol, 2.8 equiv.) in MeOH (1 mL) was stirred for 1 h at room temperature. Orange red precipitate was formed in a suspension. The precipitate was collected by filtration affording the diastereomeric mixtures of **3f** with dr = 1:1. After addition of MeOH (10 mL), orange red precipitate mixed with red solution was observed. The precipitate was collected to give BINOL/gold(III) complex (*R,S*)-**3f** with dr = 97:3 as orange red solid (14.2 mg, 0.0157 mmol, 43% yield). The filtrate was concentrated under reduced pressure and diluted by hexane to precipitate the BINOL/gold(III) complex (*S,S*)-**3f** with dr = 90:10 as orange red solid (17.9 mg, 0.0199 mmol, 53% yield).

The obtained (*R,S*)-**3f** and (*S,S*)-**3f** was separately added in DCM/MeOH (1:1, 2 mL). After addition of 6 N hydrochloric acid (19 μL, 0.0188 mmol, 3 equiv.) at room temperature, the color of the solution immediately changed from red to colorless within 1 min. The solvent was removed under reduced pressure and subjected to flash column chromatography (hexane/DCM), affording compound BINOL (*S*)-**2f** (white solid, 6.8 mg, 0.0154 mmol, 41% yield, 96% ee), BINOL (*R*)-**2f** (white solid, 8.2 mg, 0.0184 mmol, 49% yield, 80% ee) and recovered (*S*)-**1a** (23.8 mg, 0.0446 mmol, 85% yield).

(1) ^{1}H NMR Analysis for Determination of Diastereomeric Ratio of 3b-3f

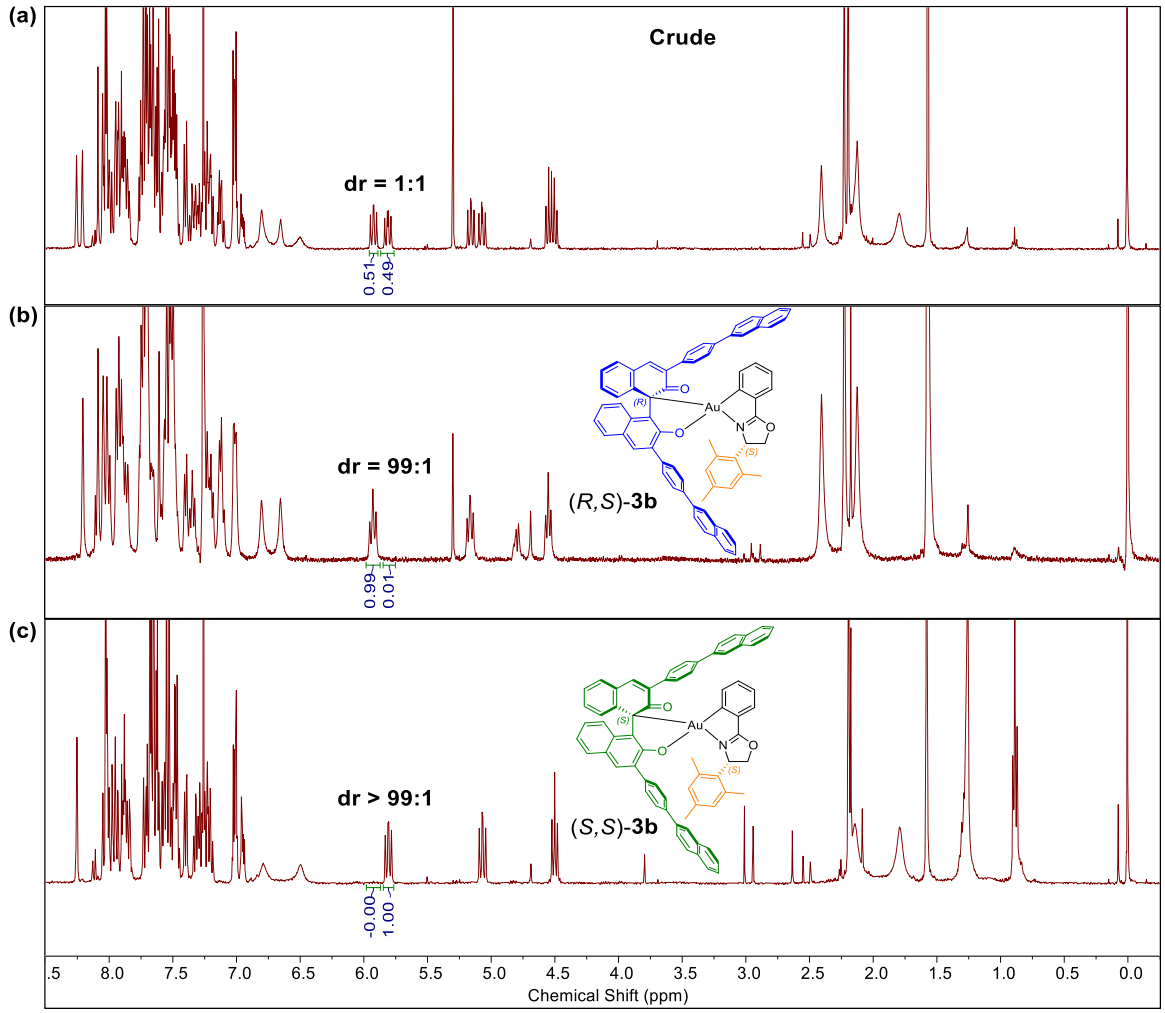


Figure S2. Determination of dr of **(a)** crude mixture of **3b**; **(b)** (*R*,*S*)-**3b**; **(c)** (*S*,*S*)-**3b** by ^{1}H NMR analysis.

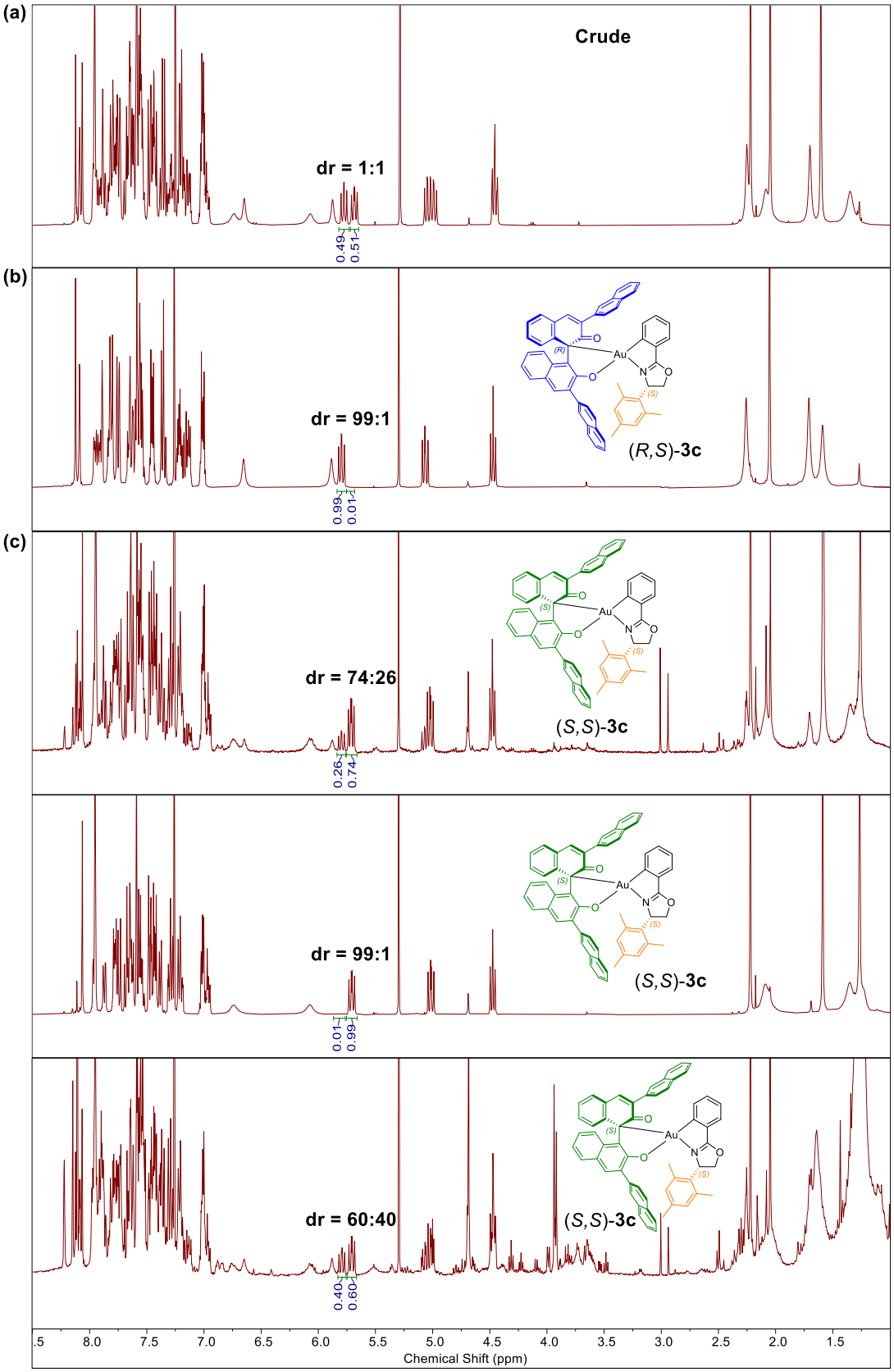


Figure S3. Determination of dr of **(a)** crude mixture of **3c**; **(b)** (*R*,*S*)-**3c**; **(c)** (*S*,*S*)-**3c** by ^{1}H NMR analysis.

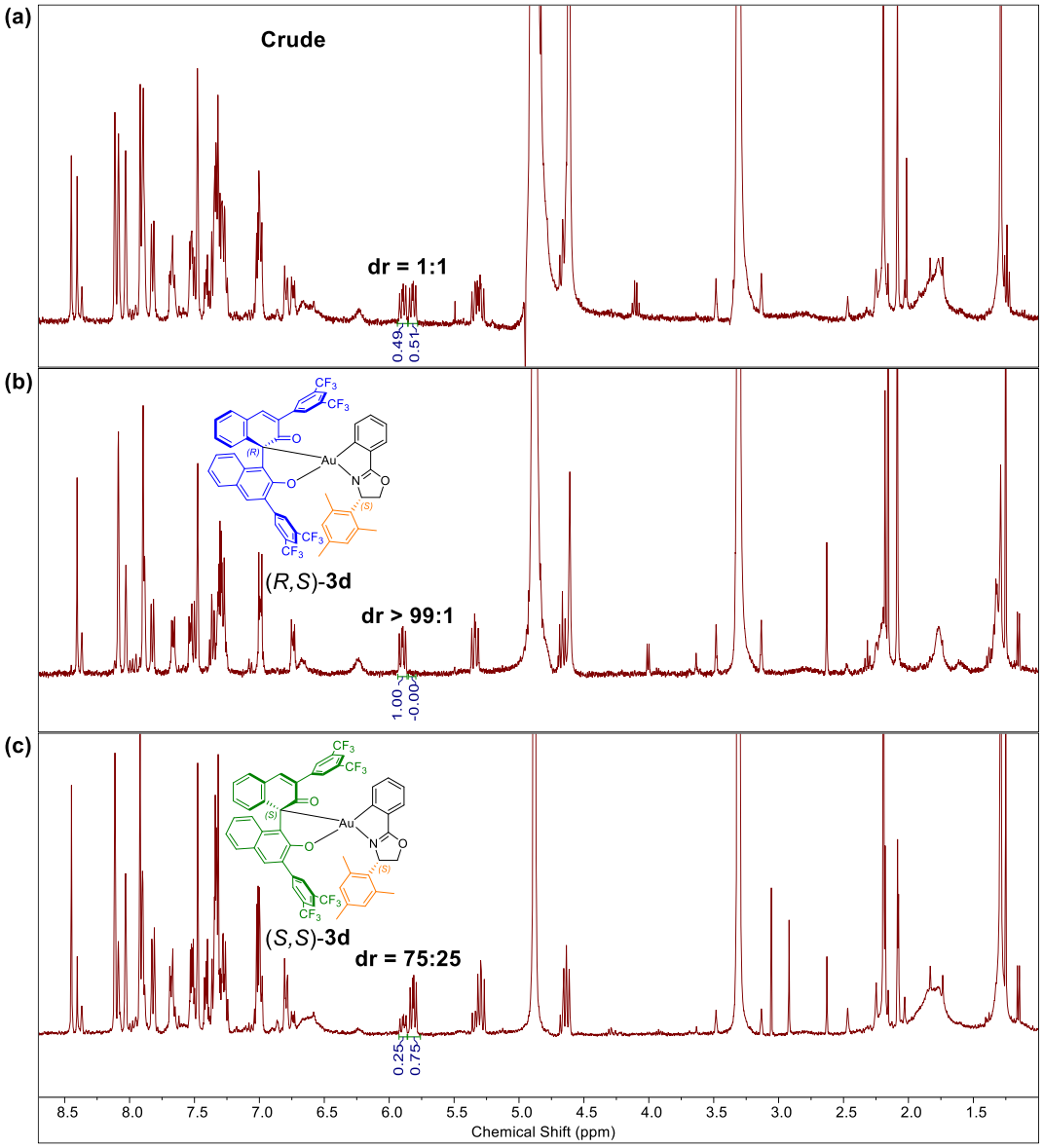


Figure S4. Determination of dr of **(a)** crude mixture of **3d**; **(b)** (*R,S*)-**3d**; **(c)** (*S,S*)-**3d** by ^{1}H NMR analysis.

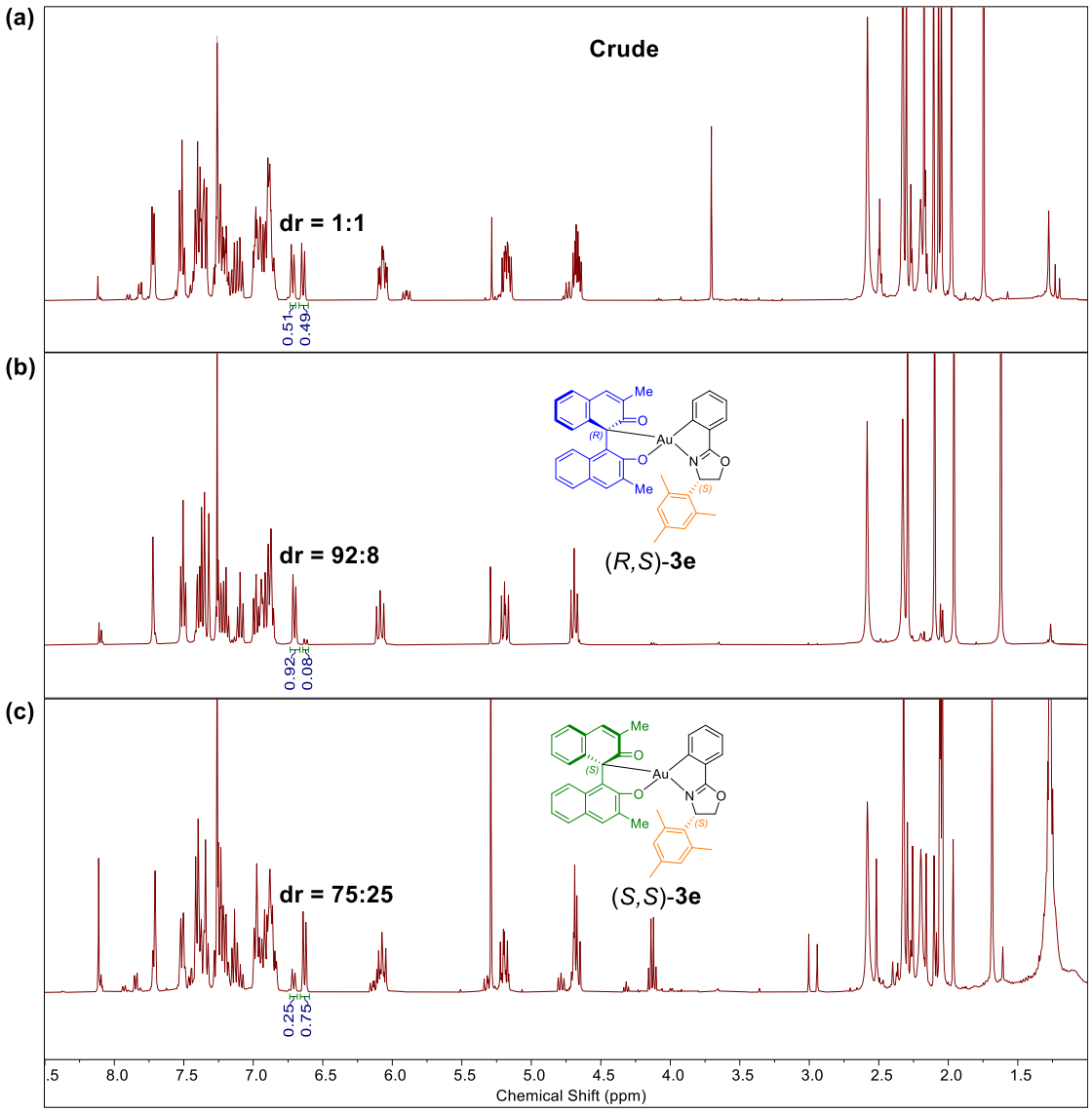


Figure S5. Determination of dr of **(a)** crude mixture of **3e**; **(b)** (*R*,*S*)-**3e**; **(c)** (*S*,*S*)-**3e** by ^{1}H NMR analysis.

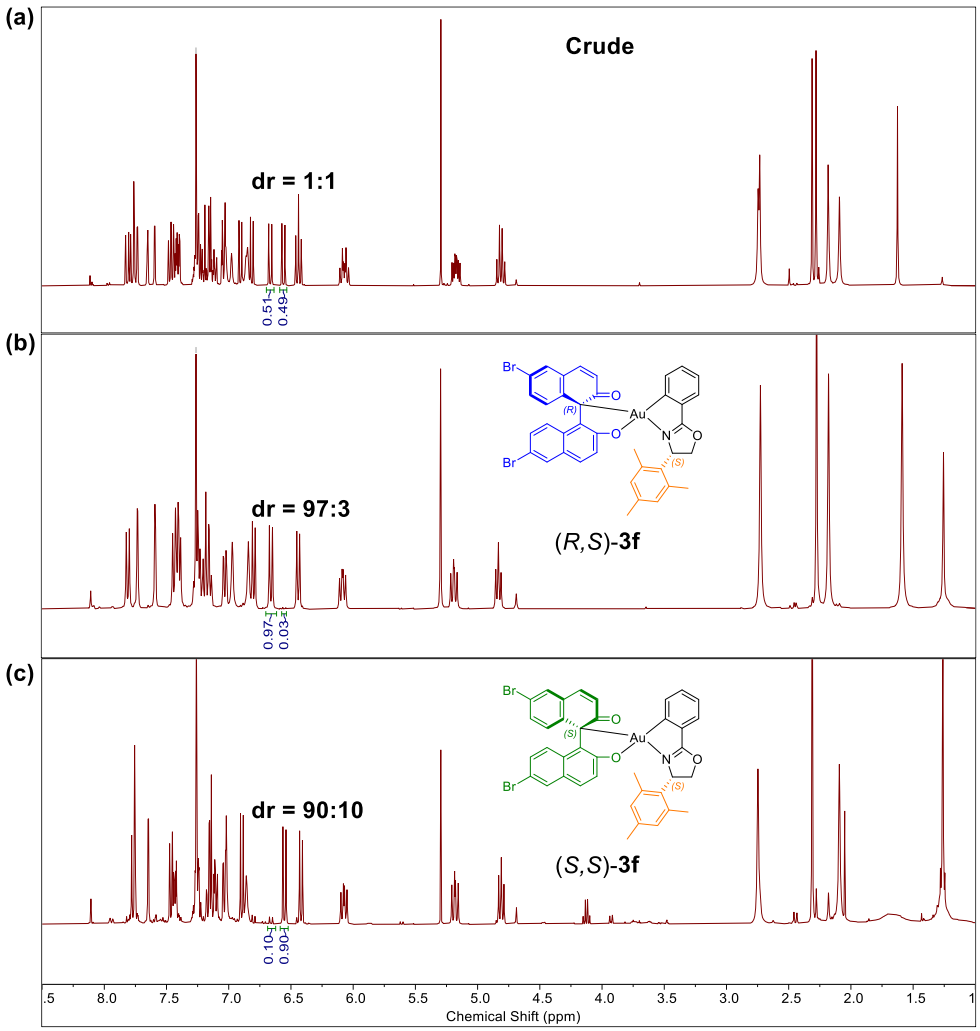
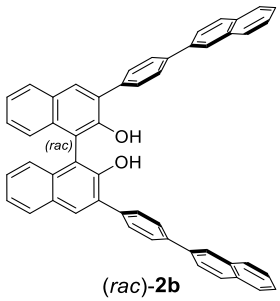


Figure S6. Determination of dr of **(a)** crude mixture of **3f**; **(b)** (*R*,*S*)-**3f**; **(c)** (*S*,*S*)-**3f** by ^{1}H NMR analysis.

(2) HPLC Analysis of Resolved BINOLs 2b-2f



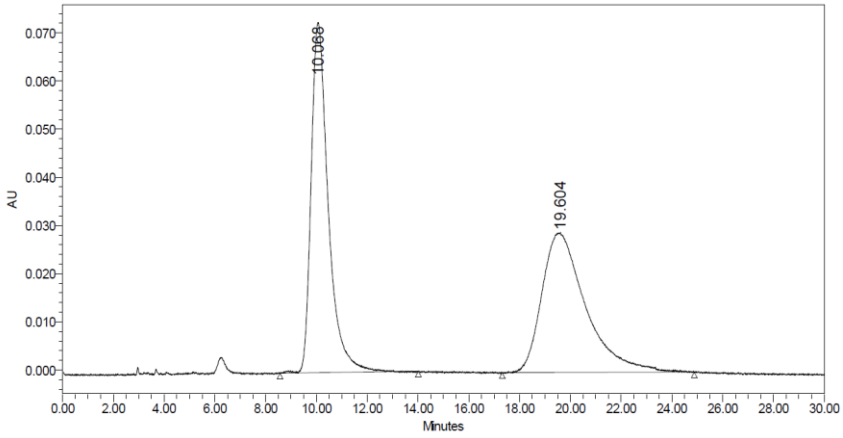
(*rac*)-**2b**

Chiralpak IC column,

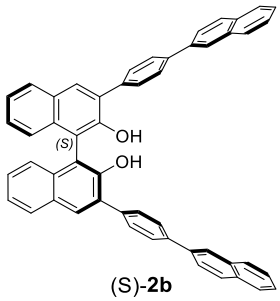
55:45 hexane/isopropanol, 1 mL/min,

t_R = 10.1 min, 19.6 min,

ee = 0%.



	RT	Area	% Area	Height
1	10.068	3407855	49.57	72703
2	19.604	3467350	50.43	29070



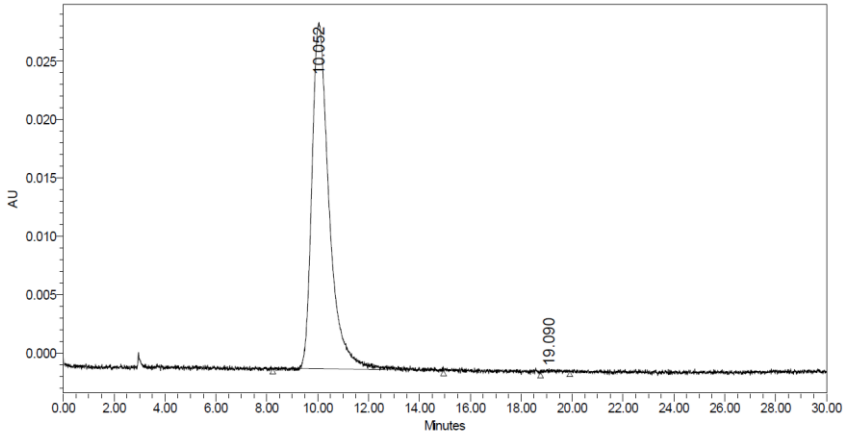
(S)-**2b**

Chiralpak IC column,

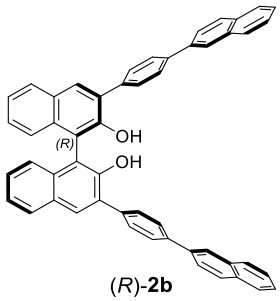
55:45 hexane/isopropanol, 1 mL/min,

t_R = 10.1 min (major), 19.1 min (minor),

ee = 99%.



	RT	Area	% Area	Height
1	10.052	1402756	99.62	29687
2	19.090	5306	0.38	261



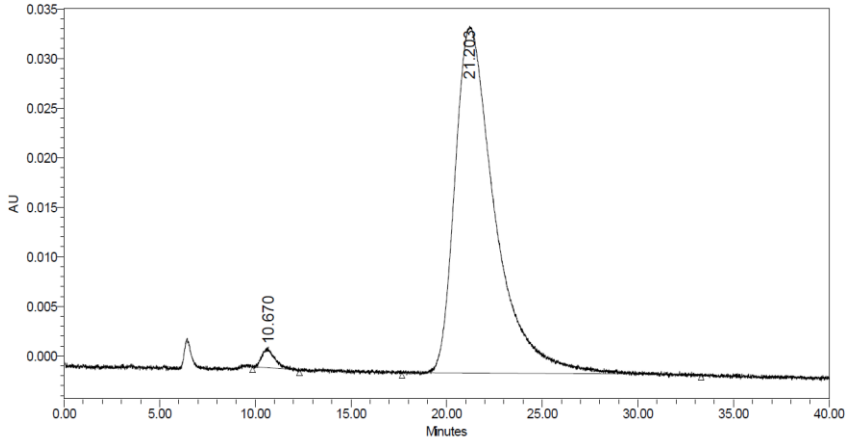
(*R*)-**2b**

Chiralpak IC column,

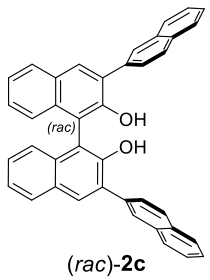
55:45 hexane/isopropanol, 1 mL/min,

t_R = 10.7 min (minor), 21.2 min (major),

ee = 96%.



	RT	Area	% Area	Height
1	10.670	91573	1.77	2086
2	21.203	5088501	98.23	34982



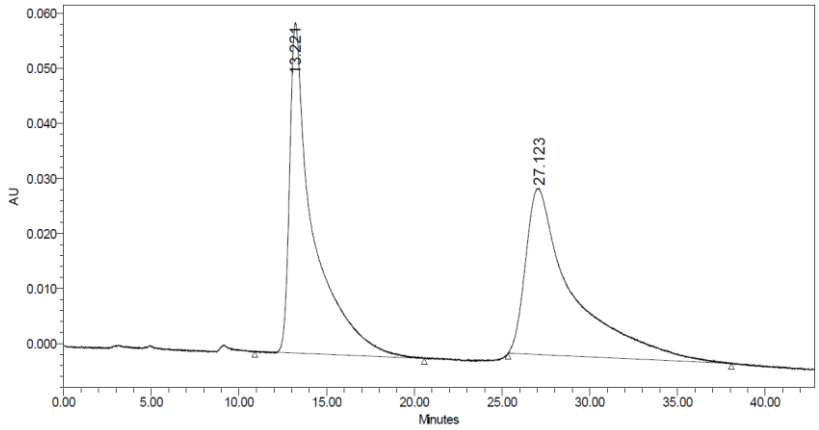
(*rac*)-**2c**

Chiralpak AD-H column,

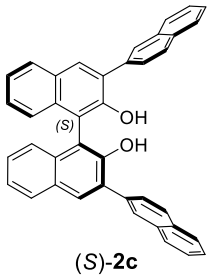
55:45 hexane/isopropanol, 1 mL/min,

t_R = 13.2 min, 27.1 min,

ee = 0%.



	RT	Area	% Area	Height
1	13.221	5547564	49.86	60060
2	27.123	5578178	50.14	30224



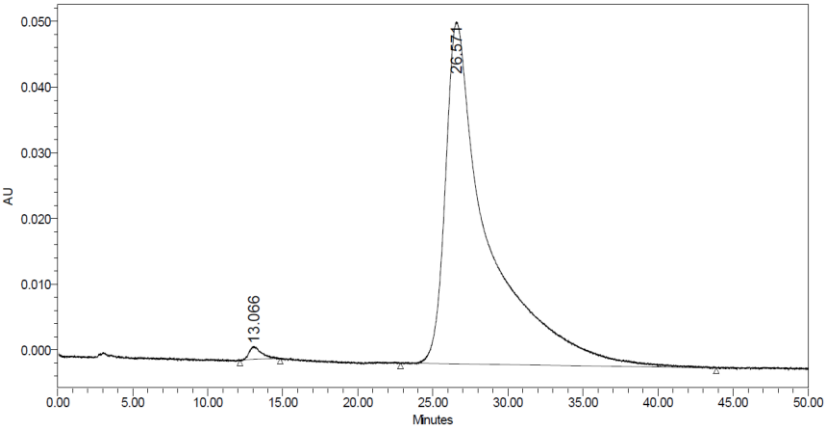
(*S*)-**2c**

Chiralpak AD-H column,

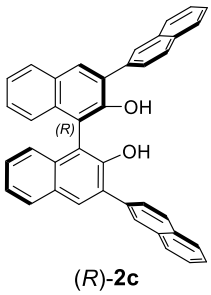
55:45 hexane/isopropanol, 1 mL/min,

t_R = 13.1 min (minor), 26.6 min (major),

ee = 98%.



	RT	Area	% Area	Height
1	13.066	111180	1.07	2013
2	26.571	10291249	98.93	52032



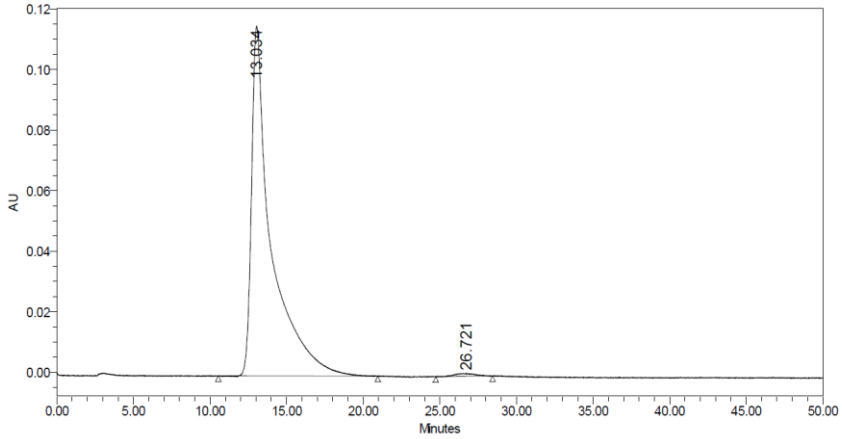
(*R*)-**2c**

Chiralpak AD-H column,

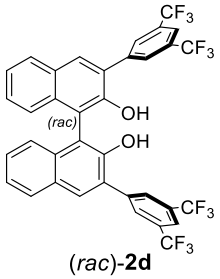
55:45 hexane/isopropanol, 1 mL/min,

t_R = 13.0 min (major), 26.7 min (minor),

ee = 98%.



	RT	Area	% Area	Height
1	13.034	10292059	99.14	115506
2	26.721	89427	0.86	1036



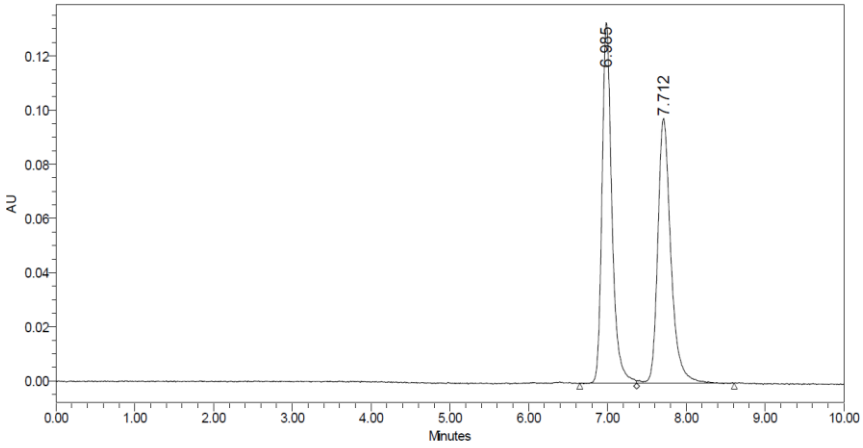
(*rac*)-**2d**

Chiralpak AD-H column,

99:1 hexane/isopropanol, 0.5 mL/min,

t_R = 7.0 min, 7.7 min,

ee = 0%.



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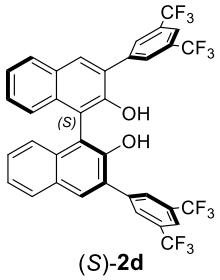
1	6.985	1155465	50.60	133081
2	7.712	1127890	49.40	97675



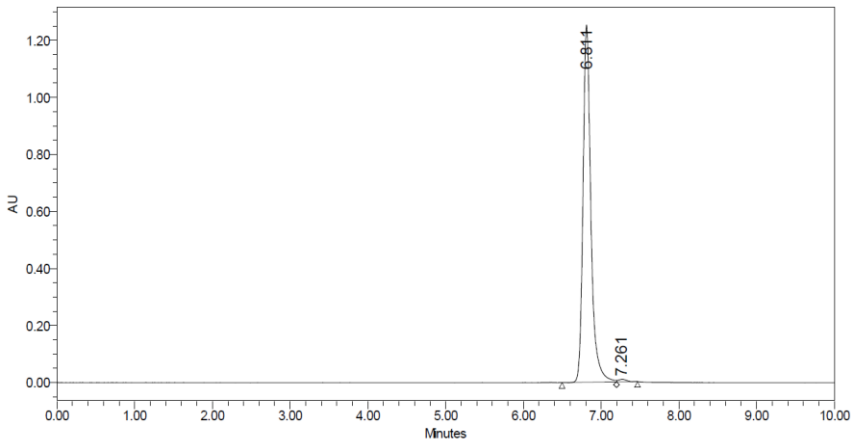
(*S*)-**2d**

Chiralpak AD-H column,

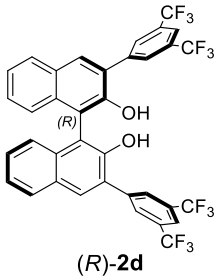
99:1 hexane/isopropanol, 0.5 mL/min,

t_R = 6.8 min (major), 7.3 min (minor),

ee = 99%.



	RT	Area	% Area	Height
1	6.811	8838431	99.31	1252022
2	7.261	61777	0.69	8458



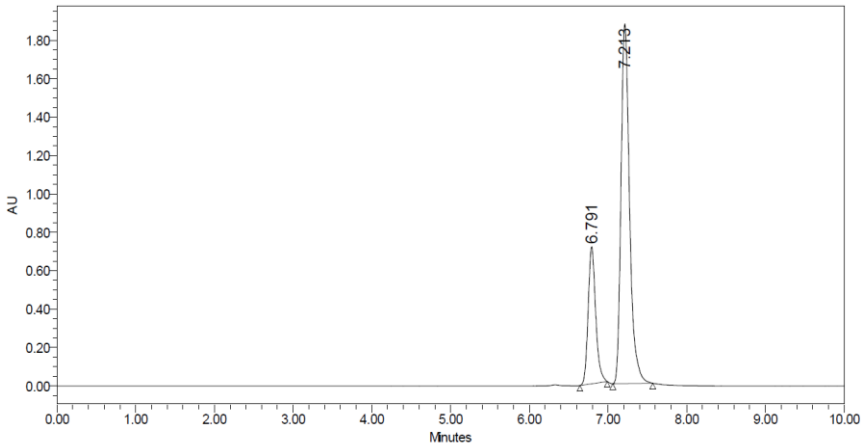
(*R*)-**2d**

Chiralpak AD-H column,

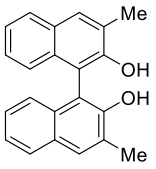
99:1 hexane/isopropanol, 0.5 mL/min,

t_R = 6.8 min (minor), 7.2 min (major),

ee = 50%.



	RT	Area	% Area	Height
1	6.791	4722529	25.08	712671
2	7.213	14106097	74.92	1872273



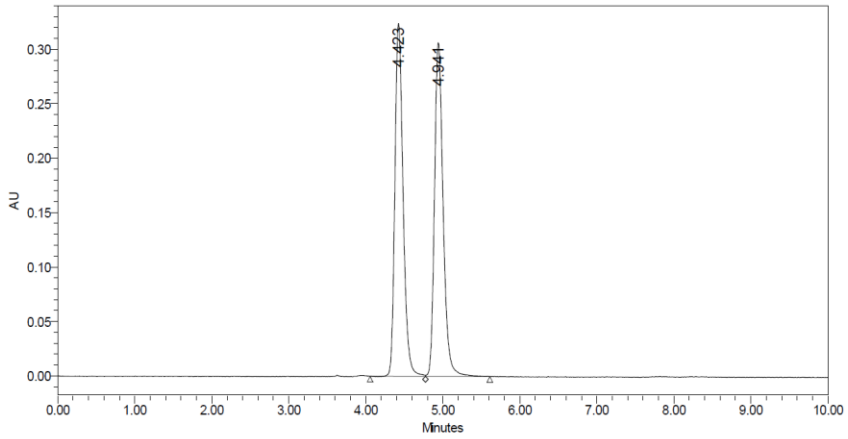
(*rac*)-**2e**

Chiralpak IC column,

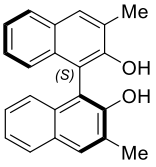
98:2 hexane/isopropanol, 1 mL/min,

t_R = 4.4 min, 4.9 min,

ee = 0%.



	RT	Area	% Area	Height
1	4.423	2396054	50.06	324145
2	4.941	2390388	49.94	306579



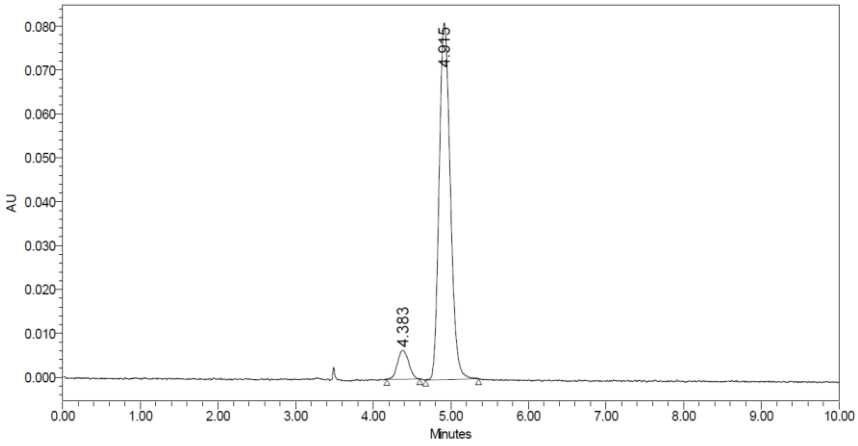
(*S*)-**2e**

Chiralpak IC column,

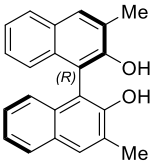
98:2 hexane/isopropanol, 1 mL/min,

t_R = 4.4 min (minor), 4.9 min (major),

ee = 85%.



	RT	Area	% Area	Height
1	4.383	65677	7.49	6544
2	4.915	811170	92.51	81283



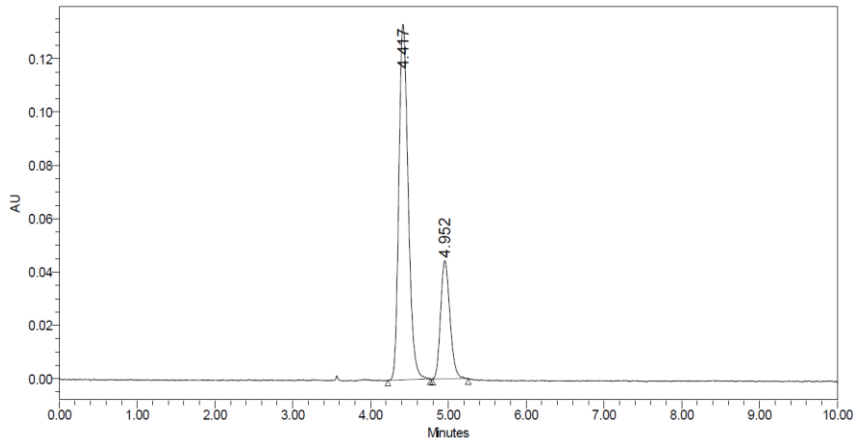
(*R*)-**2e**

Chiralpak IC column,

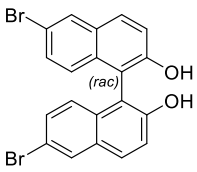
98:2 hexane/isopropanol, 1 mL/min,

t_R = 4.4 min (major), 5.0 min (minor),

ee = 50%.



	RT	Area	% Area	Height
1	4.417	1108486	75.02	133269
2	4.952	369118	24.98	44338



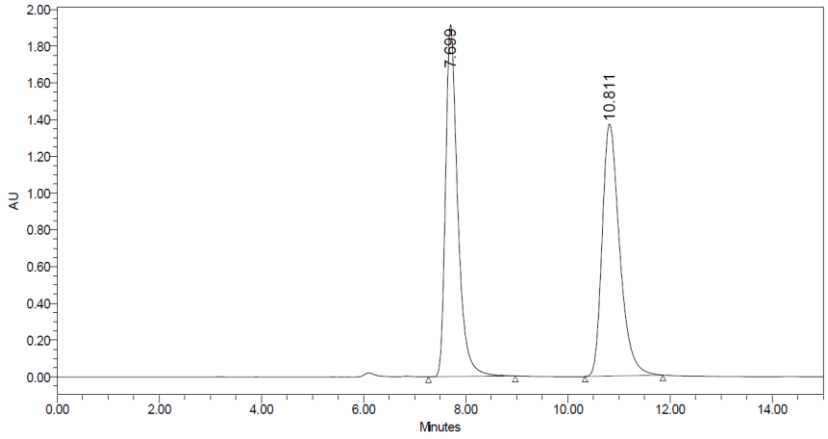
(*rac*)-**2f**

Chiralpak IC column,

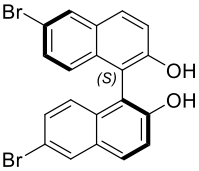
95:5 hexane/isopropanol, 1 mL/min,

t_R = 7.7 min, 10.8 min,

ee = 0%.



	RT	Area	% Area	Height
1	7.699	31596231	49.23	1914315
2	10.811	32588649	50.77	1370909



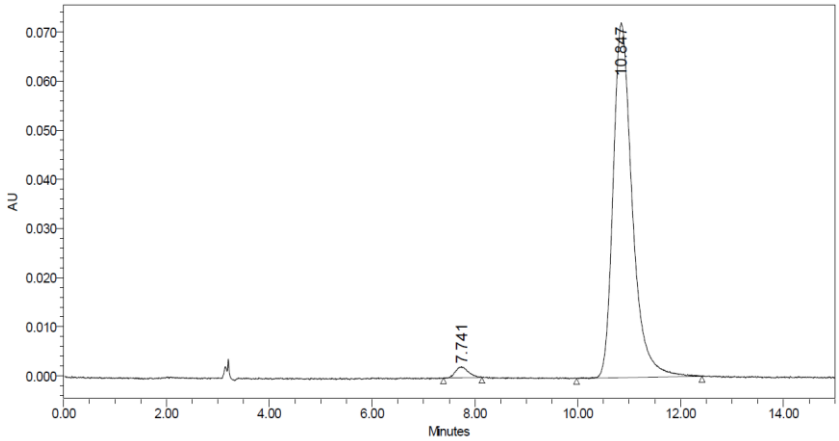
(*S*)-**2f**

Chiralpak IC column,

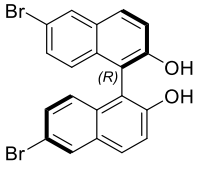
95:5 hexane/isopropanol, 1 mL/min,

t_R = 7.7 min (minor), 10.8 min (major),

ee = 96%.



	RT	Area	% Area	Height
1	7.741	38545	2.03	2266
2	10.847	1863208	97.97	72205



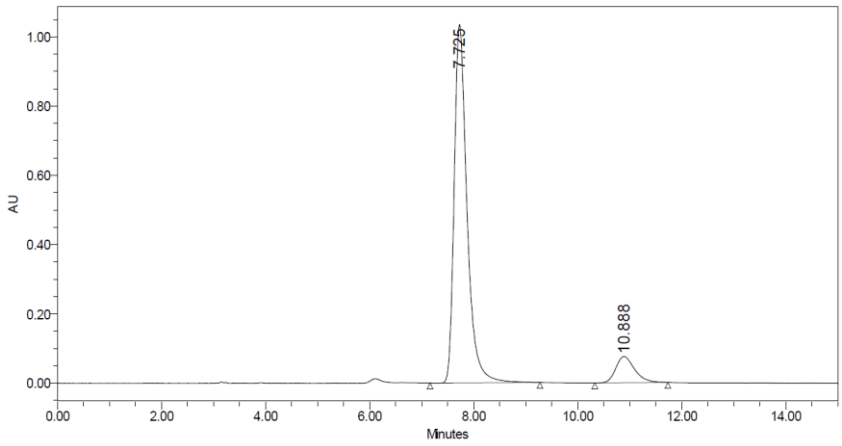
(*R*)-**2f**

Chiralpak IC column,

95:5 hexane/isopropanol, 1 mL/min,

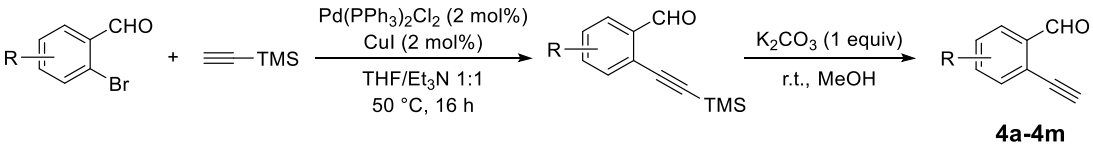
t_R = 7.7 min (major), 10.9 min (minor),

ee = 80%.



	RT	Area	% Area	Height
1	7.725	17699961	90.28	1035064
2	10.888	1904821	9.72	75778

Synthesis of Substrates 4a-m

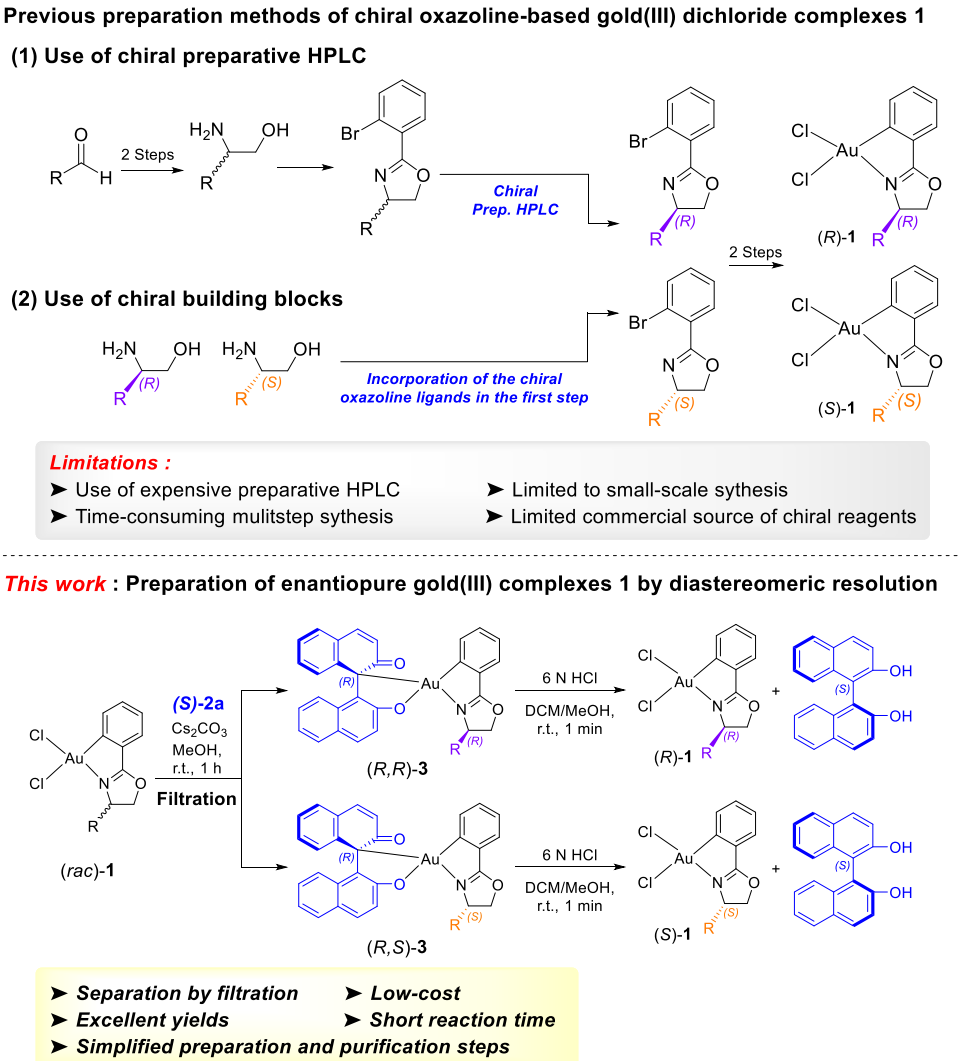


4a-4m

Substrates **4a-4e, 4g-4m** were synthesized and identified with reference to the characterization data of literatures.[5-13] For synthesis of **4f**, a mixture of 2-bromo-6-methylbenzaldehyde (3 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.06 mmol, 0.02 equiv.) and CuI (0.06 mmol, 0.02 equiv.) in THF/Et_3N (1:1, 10 mL) was degassed by three freeze-pump-thaw cycles. Then, trimethylsilylacetylene (4.5 mmol, 1.5 equiv.) was added to the mixture by syringe. The reaction mixture was heated to 50 °C for 16 h. When the reaction is completed, the resulting mixture was filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography over silica gel with hexane/EA as the eluent to give the corresponding reaction intermediate (86% yield). The reaction intermediate was then treated with K_2CO_3 (0.56 g, 2.58 mmol) in MeOH (10 mL) at room temperature. When the reaction was completed, as monitored by TLC, water was added. The residue was extracted with CH_2Cl_2 and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure and purified by flash column chromatography over silica gel with n-hexane/EA to give **4f** (pale yellow solid, 0.19 g, 1.34 mmol, 52% yield).

General Procedure for Gold(III) Catalyzed Asymmetric Carboalkoxylation of *ortho*-Alkynylbenzaldehydes

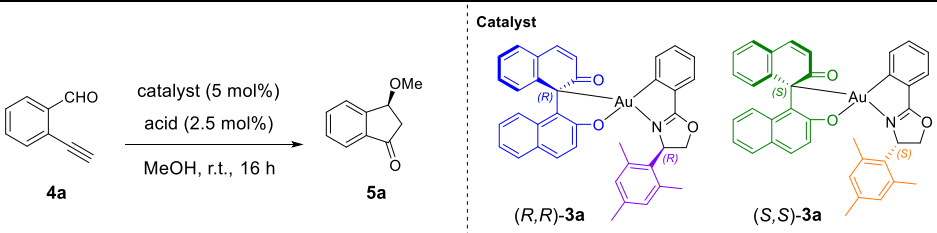
The asymmetric carboalkoxylation affording **5a** is representative. Substrate **4a** (0.20 mmol) was added to a mixture of gold(III) catalyst (*R,R*)-**3a** (0.010 mmol, 5 mol %) and D-camphorsulfonic acid (0.005 mmol, 2.5 mol %) in MeOH (2 mL). The reaction mixture was stirred at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography over silica gel with hexane/EA to afford **5a** as pale yellow oil. This general procedure was applied to **5b-5m**. For **5n-5o**, MeOH was replaced by EtOH. Racemic samples were obtained with $KAuCl_4 \cdot 2H_2O$ as catalyst and no addition of acid. Products **5a, 5c, 5g-5h, 5l-5m** were identified with reference to the characterization data in literatures.[1,3]



Scheme S2. Comparison of previous methods for the preparation of chiral oxazoline-based gold(III) complexes with this work.

Study of Carboalkoxylation of *ortho*-Alkynylbenzaldehydes

Table S1. Study of the effect of the chirality of CSA on the reaction enantioselectivity.[a]

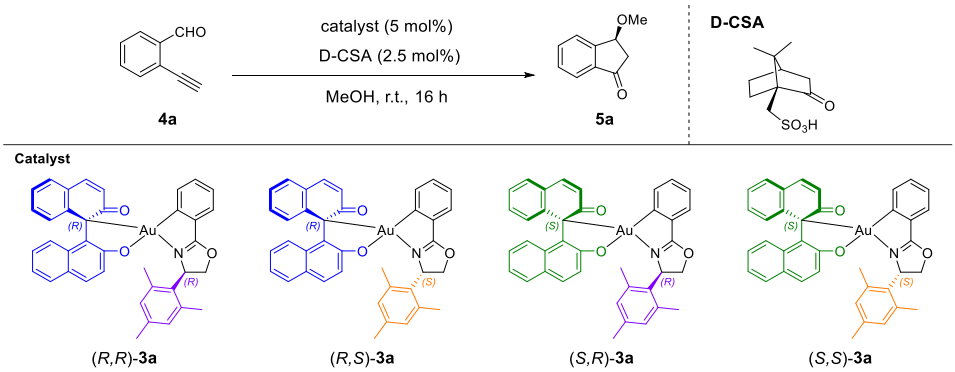


Entry	Catalyst	Acid	Yield (%) [b]	ee (%) [c]
1	(*R*,*R*)-**3a**	L-CSA	38	80
2	(*R*,*R*)-**3a**	D-CSA	47	89
3	(*S*,*S*)-**3a**	L-CSA	38	-85
4	(*S*,*S*)-**3a**	D-CSA	41	-89

[a] Reaction conditions: 0.2 mmol of substrate **4a**, 2 mL of MeOH. [b] Isolated yield. [c] Determined by chiral HPLC.

In entries 1 and 2, the use of (*R*,*R*)-**3a** with L-CSA afforded the product with 80% ee which was slightly lower than that with D-CSA (89% ee). In entries 3 and 4, the use of (*S*,*S*)-**3a** with L-CSA or D-CSA afforded products with similar ee (-85% and -89% respectively). These results indicated that the chirality of CSA only has limited effect on the reaction enantioselectivity.

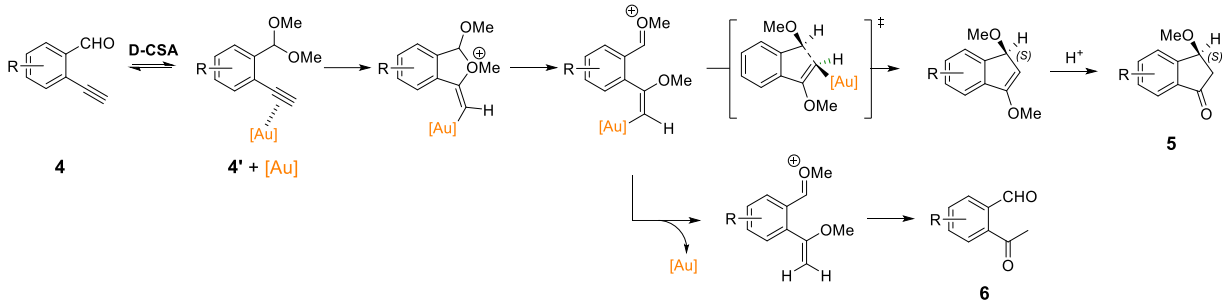
Table S2. ^{1}H NMR yield of carboalkoxylation of 2-ethynylbenzaldehyde **4a** using **3a** as catalysts.[a]



Entry	Catalyst	^{1}H NMR Yield (%) [b]
1	(*R*,*R*)-**3a**	50
2	(*R*,*S*)-**3a**	35
3	(*S*,*R*)-**3a**	38
4	(*S*,*S*)-**3a**	49

[a] Reaction conditions: 5 mol% of different catalysts, 2.5 mol% of D-CSA, 0.2 mmol of substrate **4a**, 2 mL of MeOH. [b] Yields were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

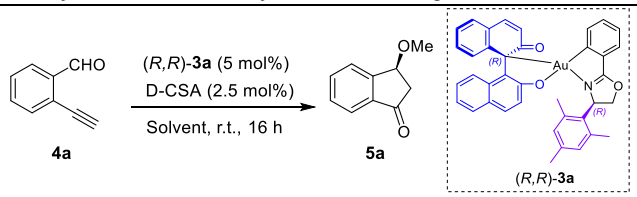
The enantiomer pair (*R*,*R*)-**3a** and (*S*,*S*)-**3a** afforded product **5a** with 50% yield and 49% yield respectively, while the other enantiomer pair (*R*,*S*)-**3a** and (*S*,*R*)-**3a** gave 35% yield and 38% yield respectively. The NMR yield determination suggested that enantiomeric catalysts showed similar yield. The product yield afforded by (*R*,*R*)-**3a** and (*S*,*S*)-**3a** enantiomer pair was slightly higher than the (*R*,*S*)-**3a** and (*S*,*R*)-**3a** enantiomer pair.



Scheme S3. Reaction mechanism of carboalkoxylation of *ortho*-alkynylbenzaldehydes.

The aldehyde group of **4** was first rapidly converted into dimethyl acetal group in the presence of D-CSA and MeOH, affording alkyne **4'**. The mechanism of carboalkoxylation reaction of alkynes has been previously studied in literatures.[2-4] According to the proposed mechanism, the alkyne group of **4'** was then activated by gold(III) catalyst followed by intramolecular nucleophilic addition resulting in the cyclic acetal. The cyclic acetal intermediates then underwent Petasis-Ferrier rearrangement to generate oxonium ion [-CH=(OMe)+]. This oxonium ion could either undergo 5-exo-trig cyclization to afford the desired chiral product **5**, or protodeauration to generate the hydration product **6**.

Table S3. Comparison of product yields of carboalkoxylation of **4a** using methanol with different water content.[a]

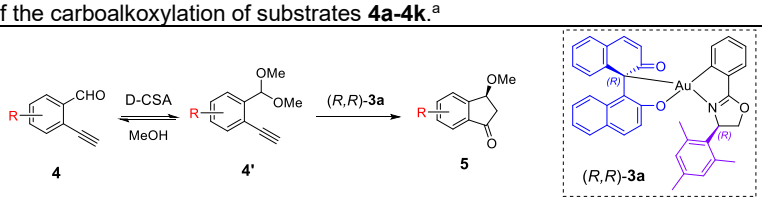


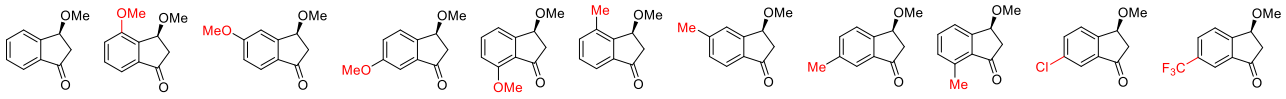
Entry	Solvent	Air/N_2	Yield (%) [b]
1	Methanol	Air	47
2	Anhydrous methanol	N_2	44

[a] Reaction conditions: 5 mol% of (*R,R*)-**3a**, 2.5 mol% of D-CSA, 0.2 mmol of substrate **4a**, 2 mL of solvent. [b] Isolated yield.

Similar yields of product **5** were obtained using methanol with different water content. Moreover, the hydration product **6** was still observed in TLC even though anhydrous methanol was used as solvent for the reaction. This result indicated that the presence of water in the solvent did not significantly contribute to the hydration product formation. The formation of the hydration product **6** was possibly attributed to the competing reaction of the protodeauration (Scheme S3).

Table S4. ^{1}H NMR study of the carboalkoxylation of substrates **4a-4k**.[a]





Entry	Substrate	Conversion of acetal **4'** (%)	^{1}H NMR Yield (%) [b]
1	**4a**	100	50
2	**4b**	100	83
3	**4c**	95	42
4	**4d**	100	73
5	**4e**	97	31
6	**4f**	94	77
7	**4g**	100	60
8	**4h**	100	70
9	**4i**	95	59
10	**4j**	86	37
11	**4k**	41	n.d.

[a] Reaction conditions: 5 mol% of different catalysts, 2.5 mol% of D-CSA, 0.2 mmol of substrate **4**, 2 mL of MeOH. [b] Yields were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

The acetal forms of the substrates **4a** – **4i** without substituent or bearing an electron donating group were almost consumed after 16 h but gave moderate yields, which possibly revealed that the presence of competing reaction (i.e., the formation of hydration product **6**) limited the formation of product. The acetal forms of the substrates **4j** and **4k** bearing electron withdrawing group showed incomplete conversion, which was possibly due to the withdrawing properties of -Cl and -CF_3 lowering the rate of the intramolecular nucleophilic cyclization step as well as the 5-exo-trig cyclization step, affording **5j** with low yield while **5k** was not determined.

X-Ray Crystal Structure of (*R,R*)-3a

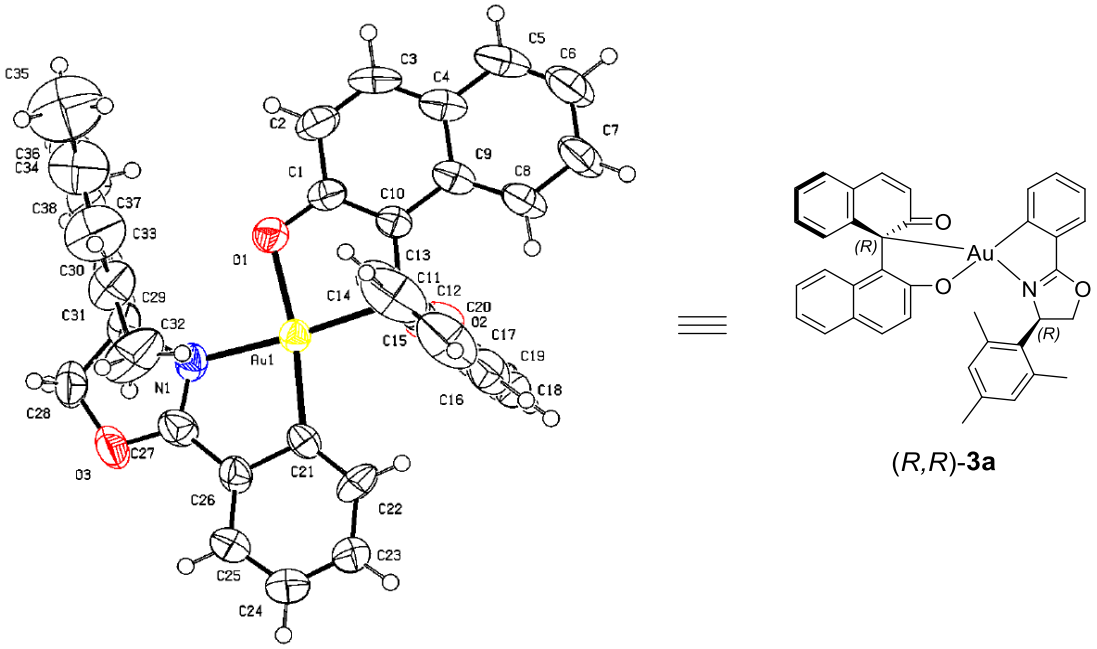


Figure S7. X-ray crystal structure of (*R,R*)-**3a**.

Table S5. Crystal data and structure refinement for (*R,R*)-**3a**.

Empirical formula	$C_{38}H_{30}AuNO_3$
Formula weight	745.60
Temperature/K	216(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	10.4093(9)
b/Å	13.2093(12)
c/Å	23.861(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3280.9(5)
Z	4
ρcalcg/cm^3	1.510
μ/mm-1	4.520
F(000)	1472.0
Crystal size/mm3	0.06 × 0.04 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.27 to 55.944
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -31 ≤ l ≤ 31
Reflections collected	54762
Independent reflections	7895 [R_{int} = 0.1107, R_{sigma} = 0.0553]
Data/restraints/parameters	7895/0/391
Goodness-of-fit on F^2	1.143
Final R indexes [I>=2σ (I)]	R_1 = 0.0533, wR_2 = 0.1123
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1177
Largest diff. peak/hole / e Å^{-3}	1.86/-4.17
Flack parameter	0.011(5)

Table S6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (*R,R*)-**3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Au1	6833.2(5)	4622.0(3)	5296.9(2)	38.84(12)
C1	6196(13)	3996(11)	6381(5)	46(3)
C2	6113(16)	3371(13)	6859(7)	66(4)
C3	5352(19)	3660(14)	7295(6)	71(5)
C4	4629(16)	4537(13)	7275(5)	61(4)
C5	3810(20)	4812(16)	7718(7)	84(6)
C6	3050(30)	5649(14)	7687(7)	91(7)
C7	3110(20)	6278(12)	7220(6)	82(5)
C8	3921(17)	6048(12)	6790(6)	64(4)
C9	4710(14)	5189(10)	6798(5)	49(3)
C10	5504(13)	4887(9)	6344(5)	41(3)
C11	5661(11)	5546(8)	5816(5)	37(3)
C12	6419(14)	6490(9)	5942(6)	48(3)
C13	7521(18)	6465(14)	6229(7)	73(5)
C14	8260(30)	7299(18)	6346(8)	105(8)
C15	7830(30)	8218(18)	6165(10)	107(9)
C16	6660(30)	8302(12)	5887(8)	84(6)
C17	5960(19)	7416(11)	5760(6)	63(4)
C18	4770(20)	7482(14)	5484(7)	74(5)
C19	4020(16)	6680(15)	5348(8)	71(5)
C20	4390(13)	5649(10)	5520(5)	46(3)
C21	6902(13)	5411(10)	4560(4)	43(2)
C22	6451(15)	6303(10)	4400(7)	58(4)
C23	6628(18)	6702(12)	3865(6)	66(4)
C24	7279(18)	6156(14)	3471(7)	78(5)
C25	7810(15)	5250(14)	3616(6)	67(4)
C26	7643(13)	4852(9)	4140(6)	48(3)
C27	8204(19)	3932(10)	4337(6)	58(3)
C28	9321(19)	2515(13)	4393(7)	71(5)
C29	8677(15)	2704(11)	4960(7)	57(4)
C30	9516(15)	2745(11)	5468(7)	59(4)
C31	10418(16)	3547(13)	5548(8)	76(5)
C32	10570(20)	4436(14)	5151(10)	108(8)
C33	11200(20)	3524(19)	6020(11)	103(8)
C34	11110(20)	2800(20)	6423(11)	109(8)
C35	11930(30)	2830(20)	6965(12)	161(13)
C36	10270(19)	2010(17)	6336(8)	82(5)
C37	9546(17)	1982(13)	5878(7)	62(4)
C38	8570(20)	1124(13)	5825(7)	84(6)
N1	7957(10)	3647(8)	4845(4)	46(3)
O1	6923(10)	3686(7)	5960(4)	50(2)
O2	3756(10)	4890(9)	5428(4)	74(4)
O3	8957(13)	3354(9)	4038(5)	80(4)

Table S7. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (*R*,*R*)-**3a**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	35.28(19)	37.42(19)	43.8(2)	0.6(2)	3.1(2)	-0.7(2)
C1	45(7)	51(8)	44(7)	10(6)	-5(6)	-3(6)
C2	62(10)	71(11)	66(10)	28(8)	-5(8)	6(8)
C3	89(13)	80(12)	43(8)	29(8)	0(8)	-17(10)
C4	77(10)	64(9)	41(7)	7(7)	3(7)	-17(10)
C5	116(16)	95(15)	41(8)	11(9)	17(9)	-21(13)
C6	130(19)	82(13)	60(10)	-5(8)	45(12)	-1(14)
C7	118(15)	65(10)	62(9)	-12(8)	45(11)	-4(12)
C8	88(12)	60(9)	43(8)	-5(7)	22(8)	-13(9)
C9	58(8)	52(9)	38(6)	-5(6)	4(6)	-19(7)
C10	45(7)	42(7)	37(6)	-2(5)	0(5)	-6(5)
C11	43(6)	26(6)	42(6)	2(5)	15(5)	-1(5)
C12	64(9)	32(6)	48(8)	1(6)	15(7)	-11(6)
C13	74(12)	74(11)	70(11)	-21(9)	12(9)	-37(9)
C14	110(17)	112(17)	93(14)	-30(13)	23(14)	-74(16)
C15	130(20)	79(14)	108(17)	-34(12)	48(16)	-60(16)
C16	124(19)	41(8)	88(13)	-4(8)	46(14)	-1(11)
C17	92(13)	42(8)	54(9)	-4(6)	25(9)	3(8)
C18	92(14)	66(11)	65(11)	20(8)	28(10)	31(10)
C19	51(9)	102(13)	59(9)	14(11)	-1(8)	34(9)
C20	45(7)	55(8)	37(6)	-1(5)	15(5)	10(6)
C21	37(5)	47(6)	44(6)	-5(5)	8(5)	-6(7)
C22	64(10)	34(7)	76(10)	19(7)	-10(7)	0(6)
C23	70(12)	63(9)	64(9)	19(7)	15(8)	15(9)
C24	97(15)	75(11)	62(10)	26(9)	19(9)	15(10)
C25	69(11)	78(11)	54(8)	14(8)	19(7)	9(9)
C26	41(7)	42(8)	61(8)	4(6)	16(6)	-2(5)
C27	70(9)	47(7)	57(8)	1(6)	18(9)	-7(9)
C28	72(13)	57(10)	86(13)	-4(9)	16(10)	23(10)
C29	47(8)	43(8)	83(10)	3(7)	4(7)	8(6)
C30	41(8)	50(8)	88(12)	-6(7)	11(8)	9(7)
C31	41(8)	72(11)	115(15)	18(10)	-4(9)	-15(8)
C32	76(13)	71(12)	180(20)	59(14)	-12(14)	-32(10)
C33	66(13)	111(18)	130(20)	10(15)	-26(13)	-39(12)
C34	79(15)	130(20)	113(19)	2(17)	-17(13)	-28(15)
C35	130(30)	200(30)	160(30)	0(20)	-70(20)	-30(30)
C36	75(13)	100(15)	72(12)	4(11)	13(10)	-4(11)
C37	58(9)	64(10)	62(10)	-10(8)	12(8)	-4(8)
C38	140(20)	59(9)	57(9)	0(8)	9(10)	-7(11)
N1	37(6)	41(5)	60(7)	1(4)	6(5)	1(4)
O1	46(5)	53(5)	51(5)	5(4)	1(5)	3(5)
O2	66(7)	95(8)	61(7)	7(5)	-24(5)	-52(6)
O3	103(10)	58(7)	79(8)	2(6)	47(7)	25(6)

Table S8. Bond Lengths for (*R*,*R*)-**3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	C11	2.125(11)	C18	C19	1.35(3)
Au1	C21	2.045(11)	C19	C20	1.47(2)
Au1	N1	2.047(10)	C20	O2	1.220(16)
Au1	O1	2.009(8)	C21	C22	1.325(18)
C1	C2	1.410(19)	C21	C26	1.464(17)
C1	C10	1.383(18)	C22	C23	1.39(2)
C1	O1	1.324(16)	C23	C24	1.37(2)
C2	C3	1.36(2)	C24	C25	1.36(2)
C3	C4	1.38(2)	C25	C26	1.368(19)
C4	C5	1.41(2)	C26	C27	1.43(2)
C4	C9	1.431(19)	C27	N1	1.296(16)
C5	C6	1.36(3)	C27	O3	1.306(18)
C6	C7	1.39(2)	C28	C29	1.53(2)
C7	C8	1.36(2)	C28	O3	1.45(2)
C8	C9	1.40(2)	C29	C30	1.49(2)
C9	C10	1.419(18)	C29	N1	1.480(17)
C10	C11	1.540(15)	C30	C31	1.43(2)
C11	C12	1.505(17)	C30	C37	1.40(2)
C11	C20	1.505(19)	C31	C32	1.52(2)
C12	C13	1.34(2)	C31	C33	1.39(3)
C12	C17	1.38(2)	C33	C34	1.36(3)
C13	C14	1.37(2)	C34	C35	1.55(3)
C14	C15	1.36(4)	C34	C36	1.38(3)
C15	C16	1.39(3)	C36	C37	1.33(3)
C16	C17	1.41(3)	C37	C38	1.53(2)
C17	C18	1.41(3)			

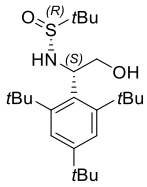
Table S9. Bond Angles for (*R*,*R*)-**3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	Au1	C11	103.2(5)	C18	C19	C20	120.4(15)
C21	Au1	N1	81.2(5)	C19	C20	C11	116.3(13)
N1	Au1	C11	175.5(4)	O2	C20	C11	119.1(12)
O1	Au1	C11	85.5(4)	O2	C20	C19	124.6(15)
O1	Au1	C21	171.3(4)	C22	C21	Au1	133.5(10)
O1	Au1	N1	90.1(4)	C22	C21	C26	116.0(12)
C10	C1	C2	121.2(14)	C26	C21	Au1	110.4(9)
O1	C1	C2	117.9(13)	C21	C22	C23	123.6(15)
O1	C1	C10	120.8(11)	C24	C23	C22	119.8(15)
C3	C2	C1	119.3(15)	C25	C24	C23	119.4(15)
C2	C3	C4	121.7(14)	C24	C25	C26	121.2(15)
C3	C4	C5	121.5(15)	C25	C26	C21	119.9(13)
C3	C4	C9	120.0(14)	C25	C26	C27	125.1(13)
C5	C4	C9	118.6(17)	C27	C26	C21	114.9(12)
C6	C5	C4	121.6(16)	N1	C27	C26	118.2(14)
C5	C6	C7	120.1(17)	N1	C27	O3	117.5(14)
C8	C7	C6	119.8(19)	O3	C27	C26	124.3(13)
C7	C8	C9	122.4(15)	O3	C28	C29	106.2(12)
C8	C9	C4	117.6(13)	C30	C29	C28	117.9(13)
C8	C9	C10	124.0(12)	N1	C29	C28	101.2(12)
C10	C9	C4	118.2(14)	N1	C29	C30	114.6(13)
C1	C10	C9	119.6(12)	C31	C30	C29	121.3(15)
C1	C10	C11	118.6(11)	C37	C30	C29	123.4(15)
C9	C10	C11	121.8(11)	C37	C30	C31	115.1(16)
C10	C11	Au1	102.3(7)	C30	C31	C32	123.8(17)
C12	C11	Au1	106.9(8)	C33	C31	C30	118.5(17)
C12	C11	C10	111.2(10)	C33	C31	C32	117.7(17)
C20	C11	Au1	106.4(8)	C34	C33	C31	123.3(19)
C20	C11	C10	109.9(10)	C33	C34	C35	122(2)
C20	C11	C12	118.7(11)	C33	C34	C36	118(2)
C13	C12	C11	122.1(14)	C36	C34	C35	119(2)
C13	C12	C17	118.6(15)	C37	C36	C34	120(2)
C17	C12	C11	119.3(14)	C30	C37	C38	117.4(16)
C12	C13	C14	124(2)	C36	C37	C30	124.4(17)
C15	C14	C13	118(3)	C36	C37	C38	117.8(17)
C14	C15	C16	120.4(19)	C27	N1	Au1	115.1(10)
C15	C16	C17	119.4(18)	C27	N1	C29	108.5(12)
C12	C17	C16	119.1(19)	C29	N1	Au1	136.2(9)
C12	C17	C18	120.4(16)	C1	O1	Au1	112.4(8)
C18	C17	C16	120.4(18)	C27	O3	C28	106.5(12)
C19	C18	C17	124.8(16)				

Table S10. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (*R*,*R*)-**3a**.

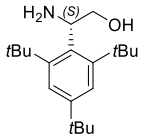
Atom	x	y	z	U(eq)
H2	6577.05	2760.94	6875.74	79
H3	5318.79	3252.92	7618.04	85
H5	3785.17	4409.47	8042.42	101
H6	2480.93	5802.04	7982.19	109
H7	2587.68	6859.2	7200.11	98
H8	3953.53	6480.94	6478.23	76
H13	7809.1	5833.36	6360.45	87
H14	9034.9	7237.99	6544.91	126
H15	8334.16	8799.27	6228.98	129
H16	6342.89	8941.22	5785.51	101
H18	4470.43	8130.61	5386.32	89
H19	3260.45	6781.64	5143.02	85
H22	5986.48	6688.79	4661.78	70
H23	6299.16	7345.03	3775.59	79
H24	7361.27	6402.21	3103.42	93
H25	8300.09	4891.74	3351.31	80
H28A	10256.81	2486.03	4435.19	86
H28B	9024.52	1873.43	4231.76	86
H29	8040.58	2157.62	5020.03	69
H32A	10136.43	5023.93	5306.81	162
H32B	10182.67	4268.08	4791.84	162
H32C	11470.08	4584.54	5099.37	162
H33	11818.9	4034.74	6062.92	124
H35A	11662.02	2286.08	7213.36	242
H35B	11821.06	3473.24	7150.45	242
H35C	12830.54	2734.83	6868.23	242
H36	10209.56	1487.52	6602.56	99
H38A	8867.27	541.4	6035.34	127
H38B	8474.75	940.12	5433.15	127
H38C	7747.64	1345.27	5971.45	127

Characterization Data of Compounds



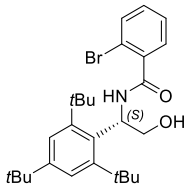
S2

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.46 (s, 1H), 5.66 (dt, *J* = 7.2, 3.4 Hz, 1H), 4.49 (td, *J* = 7.6, 3.8 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.60 (d, *J* = 3.3 Hz, 1H), 1.60 (s, 9H), 1.53 (s, 9H), 1.31 (s, 9H), 1.28 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 150.75, 149.92, 148.86, 133.59, 126.28, 123.01, 67.62, 58.80, 56.33, 38.69, 37.92, 35.26, 34.99, 33.69, 31.35, 22.92.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{24}H_{44}NO_2S]^+$ 410.3087, found 410.3094.



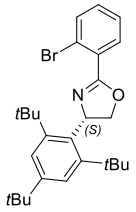
S3

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (s, 2H), 4.91 (dd, *J* = 10.7, 5.7 Hz, 1H), 4.08 (t, *J* = 10.6 Hz, 1H), 3.52 (dd, *J* = 10.6, 5.7 Hz, 1H), 1.52 (s, 18H), 1.31 (d, *J* = 1.3 Hz, 9H), 1.19 (d, *J* = 1.3 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 149.60, 147.99, 137.12, 65.23, 52.70, 35.00, 31.45, 21.65.
HRMS (ESI): $[M + Na]^+$ Calcd. for $[C_{20}H_{35}NNaO]^+$ 328.2611, found 328.2620.



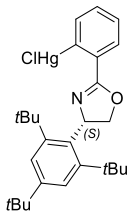
S4

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.48 (s, 1H), 7.42 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.26 (m, 1H), 6.46 (s, 1H), 6.20 (td, *J* = 4.9, 2.2 Hz, 1H), 5.14 (d, *J* = 9.5 Hz, 1H), 4.71 (dd, *J* = 11.6, 7.6 Hz, 1H), 4.00 – 3.90 (m, 1H), 1.60 (s, 9H), 1.53 (s, 9H), 1.31 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.21, 149.55, 137.49, 133.73, 131.96, 131.59, 128.83, 127.68, 119.44, 68.86, 58.04, 35.26, 35.10, 33.40, 31.37.
HRMS (ESI): $[M + Na]^+$ Calcd. for $[C_{27}H_{38}BrNNaO_2]^+$ 510.1978, found 510.1985.



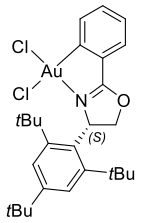
S5

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.48 (s, 2H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.30 (td, *J* = 7.7, 1.7 Hz, 1H), 6.50 (t, *J* = 12.7 Hz, 1H), 4.64 (dd, *J* = 12.3, 8.3 Hz, 1H), 4.22 (dd, *J* = 13.2, 8.3 Hz, 1H), 1.52 (s, 18H), 1.33 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 161.96, 150.98, 148.35, 134.15, 133.86, 131.68, 131.65, 130.35, 127.29, 123.68, 121.94, 74.89, 67.64, 38.19, 35.02, 34.00, 31.48.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{27}H_{37}BrNO]^+$ 470.2053, found 470.2059.



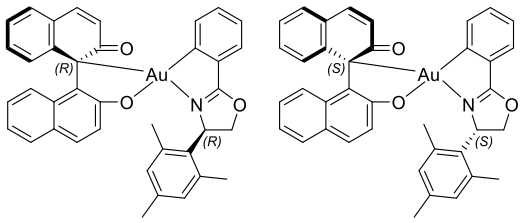
S6

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.57 (td, *J* = 7.4, 1.3 Hz, 1H), 7.48 – 7.39 (m, 4H), 6.45 (t, *J* = 12.5 Hz, 1H), 4.65 (dd, *J* = 12.2, 8.3 Hz, 1H), 4.22 (dd, *J* = 12.9, 8.3 Hz, 1H), 1.53 – 1.36 (m, 18H), 1.32 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 167.11, 150.97, 148.46, 137.35, 133.34, 132.64, 132.50, 128.85, 128.76, 66.80, 53.57, 35.03, 33.97, 33.20, 31.47, 30.65, 28.10, 13.67.
HRMS (ESI): $[M + Na]^+$ Calcd. for $[C_{27}H_{37}ClHgNO]^+$ 628.2264, found 628.2266.



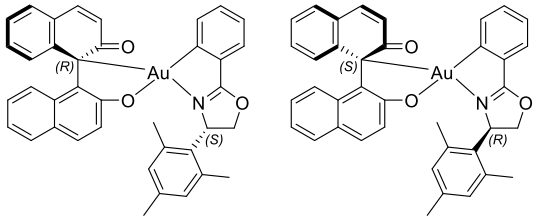
(*S*)-**1c**

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.39 (m, 2H), 6.55 (t, *J* = 12.0 Hz, 1H), 5.45 – 5.38 (m, 1H), 5.17 – 5.10 (m, 1H), 1.55 (s, 9H), 1.47 (s, 9H), 1.31 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 180.96, 151.25, 150.61, 150.26, 148.90, 135.29, 131.04, 128.65, 128.56, 128.09, 127.90, 127.14, 123.29, 65.12, 39.31, 37.60, 35.24, 35.01, 34.56, 31.31.
HRMS (ESI): $[M - Cl]^+$ Calcd. for $[C_{27}H_{36}AuClNO]^+$ 622.2145, found 622.2153.



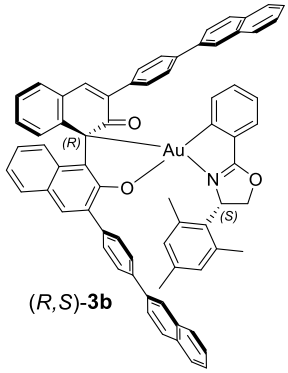
(*R,R*)-**3a** (*S,S*)-**3a**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 10.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.14 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.04 – 7.01 (m, 1H), 6.98 – 6.91 (m, 2H), 6.90 (d, *J* = 8.9 Hz, 1H), 6.85 (s, 1H), 6.61 (d, *J* = 9.0 Hz, 1H), 6.52 (d, *J* = 10.0 Hz, 1H), 6.10 (dd, *J* = 11.9, 8.0 Hz, 1H), 5.18 (dd, *J* = 11.8, 8.6 Hz, 1H), 4.81 (t, *J* = 8.3 Hz, 1H), 2.78 (s, 3H), 2.31 (s, 3H), 2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.84, 179.13, 170.85, 146.75, 144.84, 140.42, 138.42, 133.52, 132.75, 130.72, 130.66, 130.29, 130.11, 129.56, 129.52, 128.89, 128.83, 128.58, 128.51, 128.10, 127.61, 126.76, 126.49, 125.92, 124.94, 121.65, 120.60, 120.54, 77.53, 70.10, 61.77, 20.98.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{38}H_{31}AuNO_3]^+$ 746.1964, found 746.1967.



(*R,S*)-**3a** (*S,R*)-**3a**

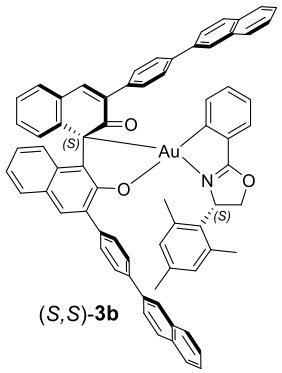
^{1}H NMR (400 MHz, $CDCl_3$)δ 7.89 (d, J = 9.8 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.40 – 7.35 (m, 2H), 7.25 – 7.17 (m, 2H), 7.12 (td, J = 7.5, 1.4 Hz, 1H), 7.04 (td, J = 7.6, 1.5 Hz, 1H), 6.99 – 6.91 (m, 3H), 6.85 – 6.78 (m, 2H), 6.68 – 6.57 (m, 2H), 6.10 (dd, J = 11.6, 7.8 Hz, 1H), 5.17 (dd, J = 11.4, 8.9 Hz, 1H), 4.83 (dd, J = 8.9, 8.0 Hz, 1H), 2.75 (s, 3H), 2.28 (s, 3H), 2.17 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 200.84, 179.18, 170.94, 147.38, 145.11, 141.57, 138.64, 134.10, 132.76, 132.19, 130.53, 130.47, 130.38, 130.35, 129.73, 129.22, 129.15, 128.97, 128.86, 128.61, 128.24, 127.74, 126.77, 126.48, 126.04, 125.10, 121.67, 120.72, 120.62, 77.59, 70.12, 61.96, 21.01.



(*R,S*)-**3b**

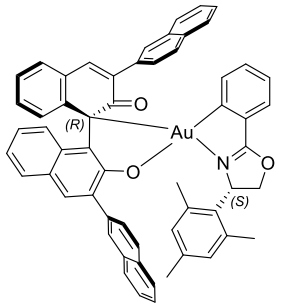
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 – 8.19 (m, 1H), 8.09 (s, 1H), 8.06 – 7.99 (m, 3H), 7.95 – 7.89 (m, 4H), 7.86 (dd, *J* = 8.8, 1.1 Hz, 1H), 7.78 – 7.72 (m, 4H), 7.72 – 7.68 (m, 4H), 7.68 – 7.64 (m, 1H), 7.61 (s, 1H), 7.59 – 7.52 (m, 4H), 7.52 – 7.46 (m, 4H), 7.40 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.35 (td, *J* = 7.7, 1.7 Hz, 1H), 7.21 (dtd, *J* = 18.7, 7.4, 1.1 Hz, 2H), 7.15 – 7.09 (m, 2H), 7.03 – 6.99 (m, 2H), 6.80 (s, 1H), 6.65 (s, 1H), 5.93 (dd, *J* = 11.0, 8.7 Hz, 1H), 5.17 (dd, *J* = 11.0, 8.6 Hz, 1H), 4.55 (t, *J* = 8.6 Hz, 1H), 2.41 (s, 3H), 2.22 (s, 3H), 2.13 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 199.26, 179.42, 168.09, 146.96, 143.17, 141.64, 140.95, 139.33, 138.98, 138.81, 138.54, 138.32, 137.54, 135.80, 134.10, 134.02, 133.79, 133.58, 132.78, 132.73, 132.46, 131.33, 131.08, 130.68, 130.55, 130.29, 130.07, 129.63, 129.52,

129.49, 129.27, 129.08, 128.69, 128.58, 128.54, 128.38, 127.87, 127.78, 127.28, 127.10, 126.92, 126.87, 126.85, 126.48, 126.43, 126.16, 126.10, 125.98, 125.89, 125.65, 125.62, 125.43, 121.20, 120.51, 78.25, 70.08, 63.55, 20.94.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{70}H_{51}AuNO_3]^+$ 1150.3529, found 1150.3527.



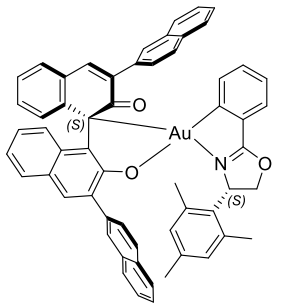
(*S,S*)-**3b**

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 – 8.24 (m, 1H), 8.05 – 7.99 (m, 4H), 7.98 – 7.93 (m, 2H), 7.88 (dd, *J* = 8.9, 5.8 Hz, 2H), 7.86 – 7.84 (m, 1H), 7.72 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.67 – 7.64 (m, 4H), 7.64 – 7.61 (m, 2H), 7.57 (ddd, *J* = 8.2, 4.5, 1.1 Hz, 2H), 7.55 – 7.52 (m, 3H), 7.51 – 7.45 (m, 3H), 7.40 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.22 (dtd, *J* = 17.7, 7.4, 1.2 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.97 – 6.92 (m, 1H), 6.79 (s, 1H), 6.49 (s, 1H), 5.82 (dd, *J* = 11.4, 8.3 Hz, 1H), 5.09 (dd, *J* = 11.4, 8.8 Hz, 1H), 4.52 (d, *J* = 8.5 Hz, 1H), 2.19 (s, 3H), 2.16 (d, *J* = 16.5 Hz, 3H), 1.79 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 198.92, 179.54, 168.46, 146.53, 142.79, 140.71, 140.67, 139.72, 138.80, 138.52, 138.30, 138.13, 137.35, 135.59, 134.06, 133.92, 133.77, 133.53, 132.76, 132.74, 132.48, 131.45, 130.99, 130.63, 130.32, 129.96, 129.87, 129.57, 129.40, 129.03, 128.71, 128.53, 128.49, 128.37, 128.34, 127.87, 127.76, 127.72, 127.07, 127.04, 126.99, 126.87, 126.68, 126.47, 126.40, 126.16, 126.05, 125.96, 125.80, 125.63, 125.54, 125.30, 121.14, 120.49, 78.10, 70.48, 62.74, 31.73, 22.80, 20.92, 14.28.



(*R,S*)-**3c**

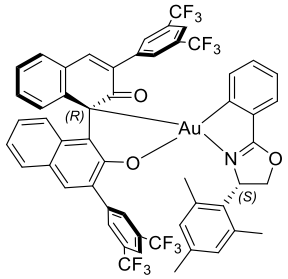
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.09 (s, 1H), 7.98 – 7.94 (m, 1H), 7.94 – 7.90 (m, 1H), 7.89 (s, 1H), 7.85 – 7.79 (m, 3H), 7.75 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.68 – 7.65 (m, 1H), 7.64 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.60 – 7.52 (m, 5H), 7.46 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.21 (tdd, *J* = 7.6, 4.8, 1.1 Hz, 2H), 7.18 – 7.11 (m, 2H), 7.04 – 6.99 (m, 2H), 6.66 (s, 1H), 5.89 (s, 1H), 5.80 (dd, *J* = 11.1, 8.9 Hz, 1H), 5.06 (dd, *J* = 11.2, 8.7 Hz, 1H), 4.47 (t, *J* = 8.8 Hz, 1H), 2.26 (s, 3H), 2.05 (s, 3H), 1.71 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 199.41, 179.28, 168.35, 147.01, 143.51, 141.59, 139.13, 138.36, 137.22, 134.37, 134.19, 133.99, 133.88, 133.39, 133.19, 132.55, 131.42, 130.63, 130.50, 130.47, 130.24, 129.47, 129.41, 129.26, 129.10, 128.66, 128.52, 128.47, 128.42, 128.18, 127.76, 127.65, 127.54, 127.52, 127.39, 127.09, 126.98, 126.89, 126.87, 126.83, 126.23, 126.14, 126.09, 125.44, 121.12, 120.48, 77.91, 70.13, 63.06, 20.98, 20.79.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{58}H_{43}AuNO_3]^+$ 998.2903, found 998.2902.



(*S,S*)-**3c**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.98 – 7.93 (m, 3H), 7.89 – 7.85 (m, 1H), 7.81 – 7.76 (m, 2H), 7.74 (d, J = 8.5 Hz, 1H), 7.70 – 7.61 (m, 4H), 7.60 – 7.51 (m, 4H), 7.47 (dt, J = 8.4, 1.5 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.38 (dd, J = 7.3, 1.7 Hz, 1H), 7.29 (tt, J = 7.4, 1.6 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.04 – 6.98 (m, 2H), 6.98 – 6.94 (m, 1H), 6.74 (s, 1H), 6.07 (s, 1H), 5.71 (dd, J = 11.4, 8.3 Hz, 1H), 5.01 (dd, J = 11.4, 8.8 Hz, 1H), 4.47 (t, J = 8.5 Hz, 1H), 2.22 (s, 3H), 2.09 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 198.98, 179.44, 168.60, 146.58, 143.21, 140.68, 138.86, 138.65, 137.32, 134.68, 134.04, 133.88, 133.47, 133.32, 133.09, 132.58, 132.52, 131.49, 131.02, 130.67, 130.29, 129.95, 129.86, 129.69, 129.33, 129.01, 128.81, 128.66, 128.55, 128.44, 128.38, 128.13, 127.84, 127.64, 127.62, 127.59, 127.54, 127.41, 127.36, 127.19, 127.06, 127.01, 126.48, 126.15, 125.99, 125.49, 125.46, 121.11, 120.55, 77.91, 70.67, 62.49, 29.84, 20.96, 20.08.

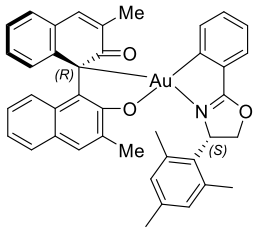


(*R,S*)-**3d**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.03 – 7.98 (m, 2H), 7.94 – 7.89 (m, 3H), 7.80 (s, 1H), 7.67 – 7.60 (m, 2H), 7.57 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.34 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.26 – 7.22 (m, 1H), 7.04 – 6.97 (m, 2H), 6.87 – 6.79 (m, 1H), 6.66 (s, 1H), 6.25 (s, 1H), 5.82 (dd, *J* = 11.1, 8.4 Hz, 1H), 5.14 (dd, *J* = 11.1, 8.9 Hz, 1H), 4.60 (t, *J* = 8.6 Hz, 1H), 2.29 – 2.00 (s, 6H), 1.78 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 198.04, 179.25, 167.66, 146.64, 144.09, 142.94, 140.10, 138.41, 138.05, 135.92, 135.83, 133.79, 132.91, 131.84, 131.55, 131.41, 131.33, 131.23, 131.01, 130.68, 130.23, 129.89, 129.67, 129.58, 129.51, 129.27, 129.12, 129.04, 128.83, 128.64, 128.21, 127.39, 127.28, 127.02, 126.58, 124.87, 124.36, 123.06, 122.55, 121.64, 120.17, 77.96, 70.14, 62.28, 20.55.

HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{54}H_{35}AuF_{12}NO_3]^+$ 1170.2085, found 1170.2084.

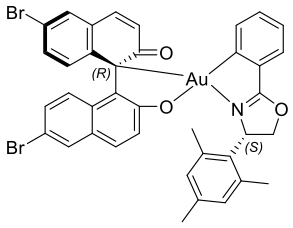


(*R,S*)-**3e**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 1.5 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 2H), 7.39 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.32 (t, *J* = 1.0 Hz, 1H), 7.24 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.19 (td, *J* = 7.4, 1.2 Hz, 1H), 7.09 (td, *J* = 7.4, 1.3 Hz, 1H), 6.98 (td, *J* = 7.5, 1.4 Hz, 1H), 6.95 – 6.84 (m, 4H), 6.73 – 6.67 (m, 1H), 6.09 (dd, *J* = 11.2, 9.5 Hz, 1H), 5.20 (dd, *J* = 11.2, 8.8 Hz, 1H), 4.70 (t, *J* = 9.2 Hz, 1H), 2.58 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H), 2.10 (d, *J* = 1.3 Hz, 3H), 1.95 (d, *J* = 1.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 200.80, 179.37, 169.79, 146.83, 142.07, 141.65, 138.26, 136.84, 136.73, 134.20, 132.31, 131.70, 130.78, 130.67, 130.52, 130.48, 129.66, 129.42, 129.16, 129.14, 127.92, 127.68, 127.36, 126.61, 126.41, 124.84, 124.68, 120.46, 120.23, 77.42, 69.44, 62.81, 29.84, 20.96, 16.65, 16.36.

HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{40}H_{35}AuNO_3]^+$ 774.2277, found 774.2276.

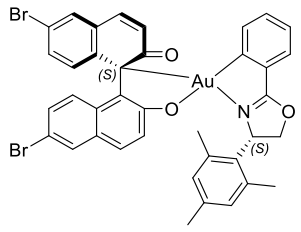


(*R,S*)-**3f**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.9 Hz, 1H), 7.73 (d, *J* = 2.3 Hz, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.29 – 7.22 (m, 2H), 7.22 – 7.12 (m, 2H), 7.03 (dd, *J* = 9.0, 2.1 Hz, 1H), 6.97 (s, 1H), 6.84 (s, 1H), 6.80 (d, *J* = 8.9 Hz, 1H), 6.66 (d, *J* = 9.9 Hz, 1H), 6.44 (d, *J* = 9.0 Hz, 1H), 6.08 (dd, *J* = 11.5, 8.0 Hz, 1H), 5.19 (dd, *J* = 11.5, 9.0 Hz, 1H), 4.83 (t, *J* = 8.5 Hz, 1H), 2.73 (s, 3H), 2.28 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 200.01, 179.25, 171.43, 146.04, 143.58, 140.96, 138.75, 134.39, 133.25, 132.21, 131.91, 131.24, 131.16, 130.25, 130.22, 130.19, 130.08, 129.73, 129.23, 129.07, 128.04, 127.09, 124.76, 122.89, 122.10, 120.06, 114.20, 77.64, 67.97, 61.50, 20.54.

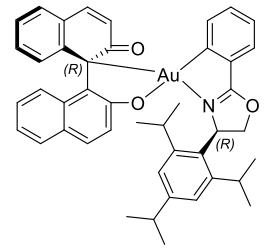
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{38}H_{29}AuBr_2NO_3]^+$ 902.0174, found 902.0171.



(*S,S*)-**3f**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.43 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.18 – 7.08 (m, 3H), 7.05 – 7.00 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.85 (d, *J* = 10.6 Hz, 1H), 6.55 (d, *J* = 9.9 Hz, 1H), 6.42 (d, *J* = 9.0 Hz, 1H), 6.08 (dd, *J* = 11.6, 8.0 Hz, 1H), 5.19 (dd, *J* = 11.6, 8.9 Hz, 1H), 4.81 (t, *J* = 8.5 Hz, 1H), 2.75 (s, 3H), 2.31 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 200.13, 179.34, 171.45, 145.52, 143.43, 139.81, 138.67, 133.88, 133.34, 132.17, 131.79, 131.27, 131.09, 130.64, 130.49, 130.24, 130.21, 130.00, 129.70, 129.62, 129.49, 129.46, 129.25, 128.04, 127.20, 124.74, 122.98, 122.15, 120.25, 114.24, 77.72, 69.14, 61.86, 21.10.

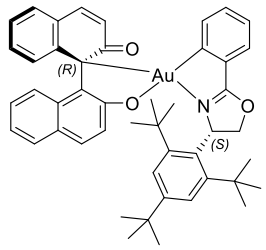


(*R,R*)-**3g**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 10.0 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.24 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.20 – 7.18 (m, 1H), 7.18 – 7.16 (m, 1H), 7.11 (td, *J* = 7.4, 1.2 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.95 – 6.89 (m, 2H), 6.76 (d, *J* = 9.0 Hz, 1H), 6.69 – 6.64 (m, 1H), 6.54 (d, *J* = 9.8 Hz, 1H), 6.22 – 6.15 (m, 1H), 5.18 (dd, *J* = 11.7, 8.7 Hz, 1H), 4.68 (dd, *J* = 9.9, 8.6 Hz, 1H), 3.71 (p, *J* = 6.8 Hz, 1H), 2.93 (p, *J* = 6.9 Hz, 1H), 2.70 (p, *J* = 6.7 Hz, 1H), 2.13 (s, 1H), 2.03 (s, 2H), 1.63 (d, *J* = 6.7 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 6H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.00, 179.11, 171.11, 149.35, 148.70, 148.29, 147.14, 145.02, 141.10, 133.70, 132.81, 130.65, 130.22, 130.11, 129.87, 129.63, 129.02, 128.85, 128.72, 128.19, 127.94, 127.64, 126.73, 126.60, 125.99, 125.04, 123.31, 121.88, 121.25, 120.59, 79.16, 70.07, 61.32, 34.30, 29.93, 29.84, 28.69, 26.24, 25.85, 24.18, 23.97, 23.89, 23.78.

HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{44}H_{43}AuNO_3]^+$ 830.2903, found 830.2904.

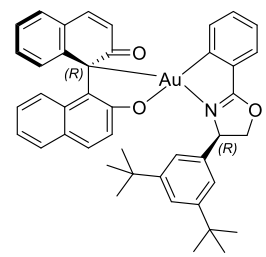


(*R,S*)-**3h**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.9 Hz, 1H), 7.69 (s, 1H), 7.63 (s, 1H), 7.56 – 7.51 (m, 1H), 7.47 – 7.37 (m, 4H), 7.28 (s, 1H), 7.25 – 7.21 (m, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.90 (m, 2H), 6.70 (t, *J* = 12.5 Hz, 1H), 6.67 – 6.62 (m, 1H), 6.60 (d, *J* = 9.8 Hz, 1H), 6.28 (d, *J* = 8.9 Hz, 1H), 5.22 (dd, *J* = 12.2, 8.8 Hz, 1H), 4.99 (dd, *J* = 12.6, 8.7 Hz, 1H), 1.68 (s, 9H), 1.52 (s, 9H), 1.41 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 200.70, 178.57, 171.12, 151.64, 151.29, 149.45, 147.47, 144.89, 141.93, 133.89, 132.67, 130.55, 130.48, 130.35, 129.98, 129.96, 129.18, 128.82, 128.79, 128.71, 128.22, 127.88, 127.72, 126.67, 126.48, 125.90, 124.66, 122.29, 121.68, 120.40, 120.37, 78.56, 70.41, 63.74, 39.54, 37.75, 35.32, 35.16, 34.34, 31.50.

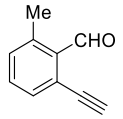
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{47}H_{49}AuNO_3]^+$ 872.3372, found 872.3370.



(*R,R*)-**3j**

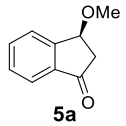
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 10.0 Hz, 1H), 7.63 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.45 (s, 3H), 7.41 (dt, *J* = 7.0, 0.9 Hz, 1H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.22 – 7.18 (m, 1H), 7.16 (td, *J* = 7.4,

1.2 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.99 – 6.94 (m, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.58 (d, *J* = 9.8 Hz, 1H), 5.73 (dd, *J* = 9.8, 5.8 Hz, 1H), 5.18 (t, *J* = 9.4 Hz, 1H), 5.09 (dd, *J* = 9.0, 5.8 Hz, 1H), 1.36 (s, 18H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 200.84, 178.83, 170.68, 151.61, 147.13, 145.02, 140.98, 137.33, 133.80, 132.89, 130.53, 130.39, 130.32, 129.74, 129.51, 129.06, 128.96, 128.83, 128.81, 128.25, 127.93, 126.82, 126.62, 126.08, 125.27, 122.75, 121.87, 121.64, 120.81, 120.68, 78.82, 70.07, 66.08, 35.18, 31.64.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{43}H_{41}AuNO_3]^+$ 816.2746, found 816.2749.



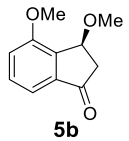
4f

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 7.51 – 7.46 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 3.45 (s, 1H), 2.61 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.96, 140.86, 134.72, 132.75, 132.65, 132.12, 127.35, 84.62, 80.13, 21.47.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{10}H_9O_3]^+$ 145.0648, found 145.0648.



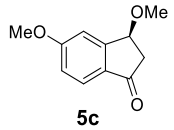
5a

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.51 – 7.47 (m, 1H), 5.03 (dd, *J* = 6.5, 2.8 Hz, 1H), 3.50 (s, 3H), 3.00 (dd, *J* = 18.5, 6.5 Hz, 1H), 2.66 (dd, *J* = 18.5, 2.8 Hz, 1H).
HPLC (Chiralpak IC column, 98:2 hexane/isopropanol, 1 mL/min), t_R = 32.0 min (minor), 34.9 min (major); ee = 99%.



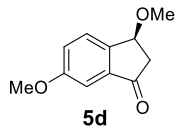
5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 5.15 (dd, *J* = 6.4, 1.6 Hz, 1H), 3.93 (s, 3H), 3.45 (s, 3H), 2.90 (dd, *J* = 18.8, 6.3 Hz, 1H), 2.68 (dd, *J* = 18.8, 1.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 203.98, 157.85, 140.71, 138.88, 131.62, 116.27, 115.10, 74.71, 57.25, 55.92, 43.32.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{11}H_{13}O_3]^+$ 193.0859, found 193.0862.
HPLC (Chiralpak IC column, 50:50 hexane/isopropanol, 1 mL/min), t_R = 10.6 min (minor), 12.7 min (major); ee = 72%.



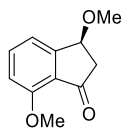
5c

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.3 Hz, 1H), 4.99 – 4.95 (m, 1H), 3.91 (s, 3H), 3.49 (s, 3H), 2.97 (dd, *J* = 18.4, 6.4 Hz, 1H), 2.64 (dd, *J* = 18.4, 3.0 Hz, 1H).
HPLC (Chiralpak IC column, 50:50 hexane/isopropanol, 1 mL/min), t_R = 8.4 min (major), 9.5 min (minor); ee = 97%.



5d

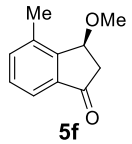
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 4.95 (dd, *J* = 6.2, 2.5 Hz, 1H), 3.82 (s, 3H), 3.45 (s, 3H), 2.98 (dd, *J* = 18.7, 6.2 Hz, 1H), 2.64 (dd, *J* = 18.6, 2.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 202.98, 161.02, 146.07, 138.30, 127.38, 124.09, 104.47, 76.29, 56.96, 55.65, 43.99.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{11}H_{13}O_3]^+$ 193.0859, found 193.0862.
HPLC (Chiralpak IC column, 50:50 hexane/isopropanol, 1 mL/min), t_R = 7.6 min (minor), 8.3 min (major); ee = 82%.



5e

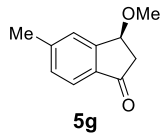
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 4.94 (dd, *J* = 6.5, 3.0 Hz, 1H), 3.94 (s, 4H), 3.46 (s, 3H), 2.95 (dd, *J* = 18.3, 6.5 Hz, 1H), 2.64 (dd, *J* = 18.3, 3.0 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.76, 157.63, 155.76, 136.95, 124.87, 118.19, 111.12, 76.21, 57.07, 56.01, 43.92.

HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{11}H_{13}O_3]^+$ 193.0859, found 193.0861.
HPLC (Chiralpak IC column, 50:50 hexane/isopropanol, 1 mL/min), t_R = 16.6 min (minor), 32.0 min (major); ee = 40%.



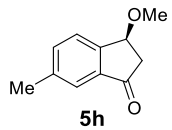
5f

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.45 (dt, *J* = 7.3, 1.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 5.09 (dd, *J* = 6.4, 2.0 Hz, 1H), 3.43 (s, 3H), 2.95 (dd, *J* = 18.8, 6.4 Hz, 1H), 2.69 (dd, *J* = 18.8, 2.0 Hz, 1H), 2.48 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 204.00, 151.15, 137.77, 137.18, 136.45, 129.99, 120.82, 76.29, 56.74, 42.78, 29.84, 17.80.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{11}H_{13}O_2]^+$ 177.0910, found 177.0911.
HPLC (Chiralpak IC column, 80:20 hexane/isopropanol, 1 mL/min), t_R = 11.1 min (minor), 13.0 min (major); ee = 46%.



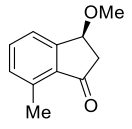
5g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.9 Hz, 1H), 7.49 (s, 1H), 7.29 (d, J = 8.1 Hz, 1H), 4.98 (dd, J = 6.5, 2.9 Hz, 1H), 3.49 (s, 3H), 2.98 (dd, J = 18.5, 6.4 Hz, 1H), 2.64 (dd, J = 18.6, 2.8 Hz, 2H), 2.47 (s, 3H).
HPLC (Chiralpak IC column, 80:20 hexane/isopropanol, 1 mL/min), t_R = 11.1 min (major), 12.8 min (minor); ee = 99%.



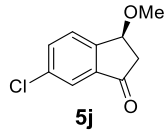
5h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 7.46 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.97 (dd, *J* = 6.4, 2.8 Hz, 1H), 3.45 (s, 3H), 2.95 (dd, *J* = 18.6, 6.4 Hz, 1H), 2.62 (dd, *J* = 18.8, 2.6 Hz, 1H), 2.40 (s, 3H).
HPLC (Chiralpak IC column, 90:10 hexane/isopropanol, 1 mL/min), t_R = 15.6 min (minor), 18.8 min (major); ee = 92%.



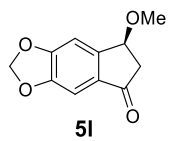
5i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.24 – 7.20 (m, 1H), 4.96 (dd, *J* = 6.5, 2.9 Hz, 1H), 3.48 (s, 3H), 2.95 (dd, *J* = 18.4, 6.5 Hz, 1H), 2.68 – 2.60 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 204.04, 153.98, 138.60, 134.41, 134.32, 131.45, 123.90, 76.35, 57.11, 44.00, 18.51.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{11}H_{13}O_2]^+$ 177.0910, found 177.0913.
HPLC (Chiralpak IC column, 98:2 hexane/isopropanol, 1 mL/min), t_R = 21.9 min (minor), 24.2 min (major); ee = 11%.



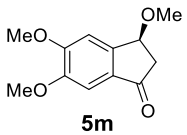
5j

^{1}H NMR (60 MHz, $CDCl_3$) δ 7.72 (t, *J* = 1.3 Hz, 1H), 7.65 – 7.62 (m, 2H), 4.99 (dd, *J* = 6.4, 2.8 Hz, 1H), 3.49 (s, 3H), 3.03 (dd, *J* = 18.6, 6.4 Hz, 1H), 2.69 (dd, *J* = 18.6, 2.8 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.66, 150.19, 140.35, 136.26, 135.18, 127.91, 123.33, 75.86, 57.43, 43.40.
HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{10}H_{10}O_2]^+$ 197.0364, found 197.0366.
HPLC (Chiralpak IC column, 90:10 hexane/isopropanol, 1 mL/min), t_R = 10.8 min (minor), 11.6 min (major); ee = 92%.



5l

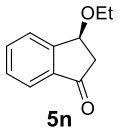
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 7.03 (s, 1H), 6.11 – 6.08 (m, 2H), 4.90 (dd, *J* = 6.2, 2.7 Hz, 1H), 3.46 (s, 3H), 2.96 (dd, *J* = 18.5, 6.2 Hz, 1H), 2.63 (dd, *J* = 18.4, 2.5 Hz, 1H).
HPLC (Chiralpak IC column, 80:20 hexane/isopropanol, 1 mL/min), t_R = 22.5 min (minor), 25.4 min (major); ee = 57%.



5m

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.09 (s, 1H), 4.96 (dd, *J* = 6.2, 2.6 Hz, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 3.48 (s, 3H), 2.96 (dd, *J* = 18.3, 6.2 Hz, 1H), 2.63 (dd, *J* = 18.3, 2.6 Hz, 1H).

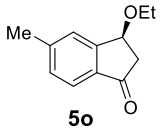
HPLC (Chiralpak IC column, 70:30 hexane/isopropanol, 1 mL/min), t_R = 19.2 min (major), 20.9 min (minor); ee = 55%.



5n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 5.11 (dd, *J* = 6.5, 2.9 Hz, 1H), 3.70 (qd, *J* = 7.0, 3.1 Hz, 2H), 3.02 (dd, *J* = 18.6, 6.4 Hz, 1H), 2.67 (dd, *J* = 18.6, 2.9 Hz, 1H), 1.29 (t, *J* = 7.0 Hz, 3H).

HPLC (Chiralpak IC column, 95:5 hexane/isopropanol, 1 mL/min), t_R = 15.6 min (minor), 17.8 min (major); ee = 67%.



5o

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.65 (d, J = 7.8 Hz, 1H), 7.49 (s, 1H), 7.28 (d, J = 7.9 Hz, 1H), 5.06 (dd, J = 6.4, 2.8 Hz, 1H), 3.69 (qd, J = 7.0, 1.9 Hz, 2H), 2.99 (dd, J = 18.4, 6.4 Hz, 1H), 2.65 (dd, J = 18.4, 2.8 Hz, 1H), 2.47 (s, 3H), 1.30 (t, J = 7.0 Hz, 4H).

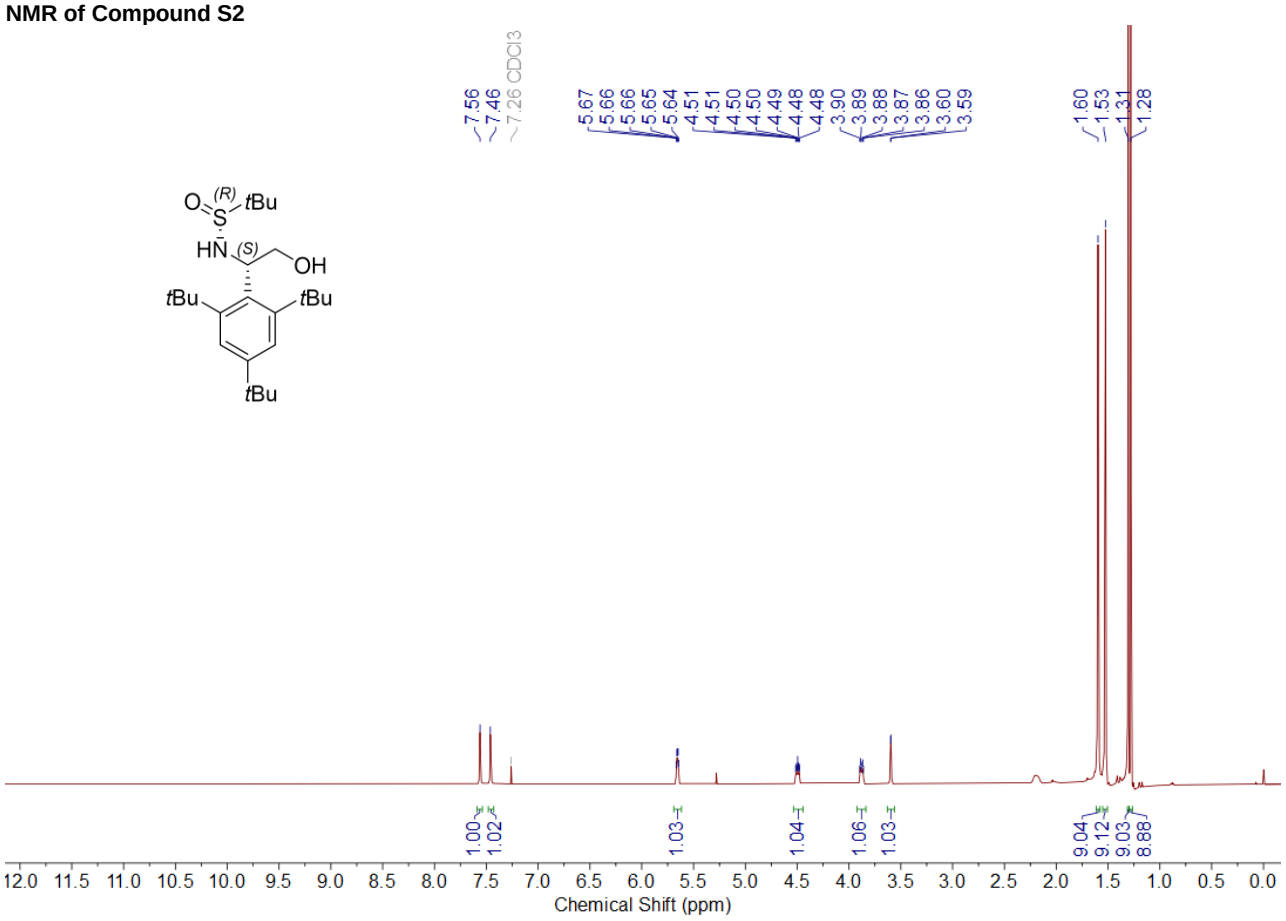
^{13}C NMR (100 MHz, $CDCl_3$) δ 202.94, 154.17, 146.50, 134.65, 130.83, 126.85, 123.24, 75.27, 65.49, 44.48, 29.84, 22.28, 15.64.

HRMS (ESI): $[M + H]^+$ Calcd. for $[C_{12}H_{15}O_2]^+$ 191.1067, found 191.1068.

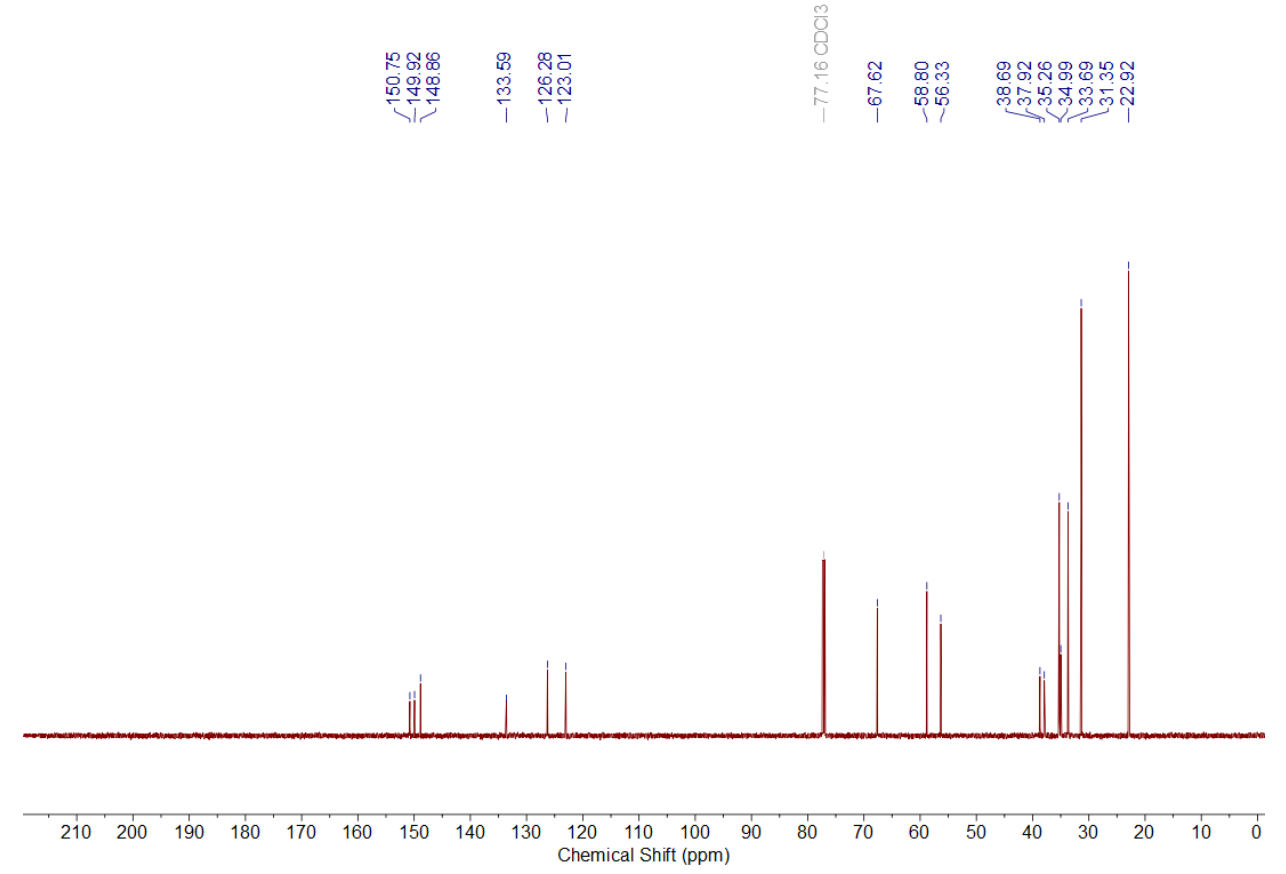
HPLC (Chiralpak IC column, 80:20 hexane/isopropanol, 1 mL/min), t_R = 9.9 min (major), 10.6 min (minor); ee = 63%.

NMR Spectra

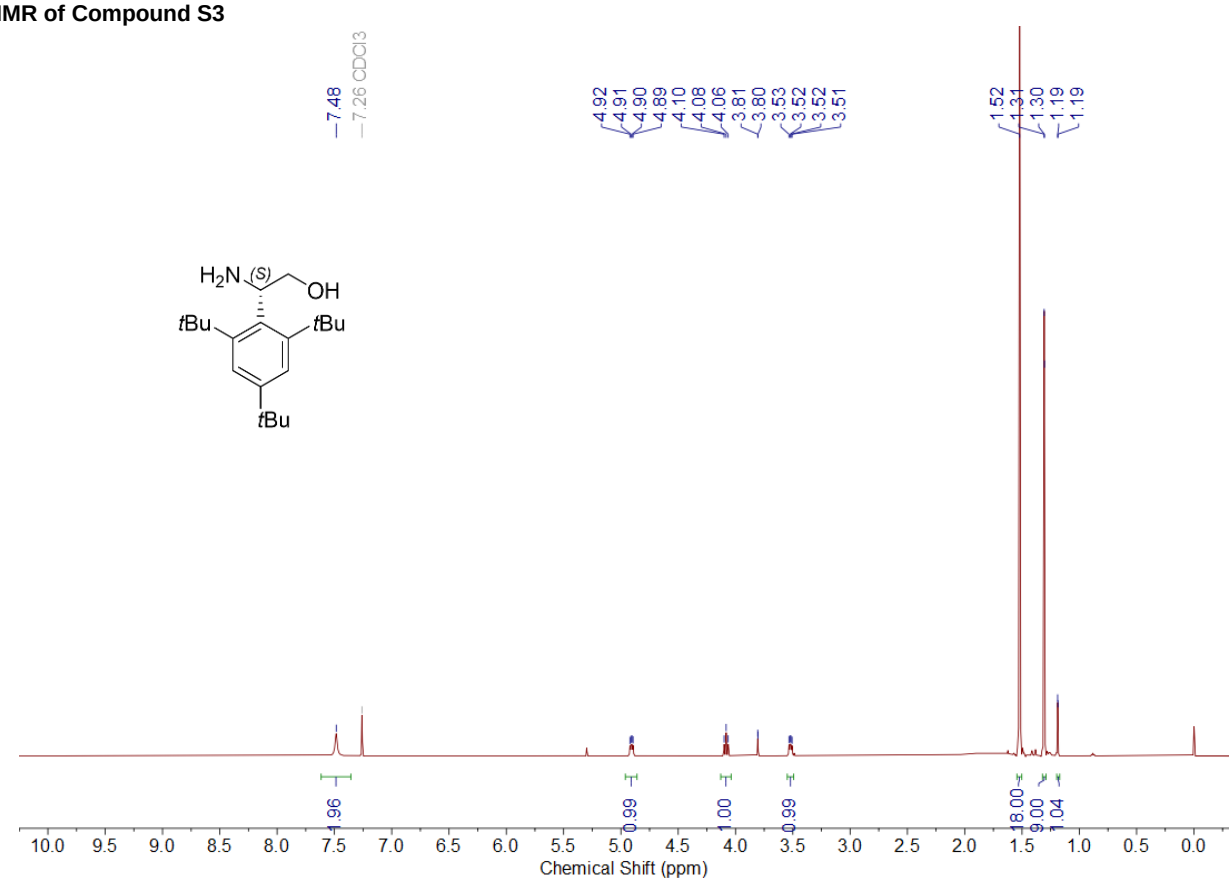
^{1}H NMR of Compound S2



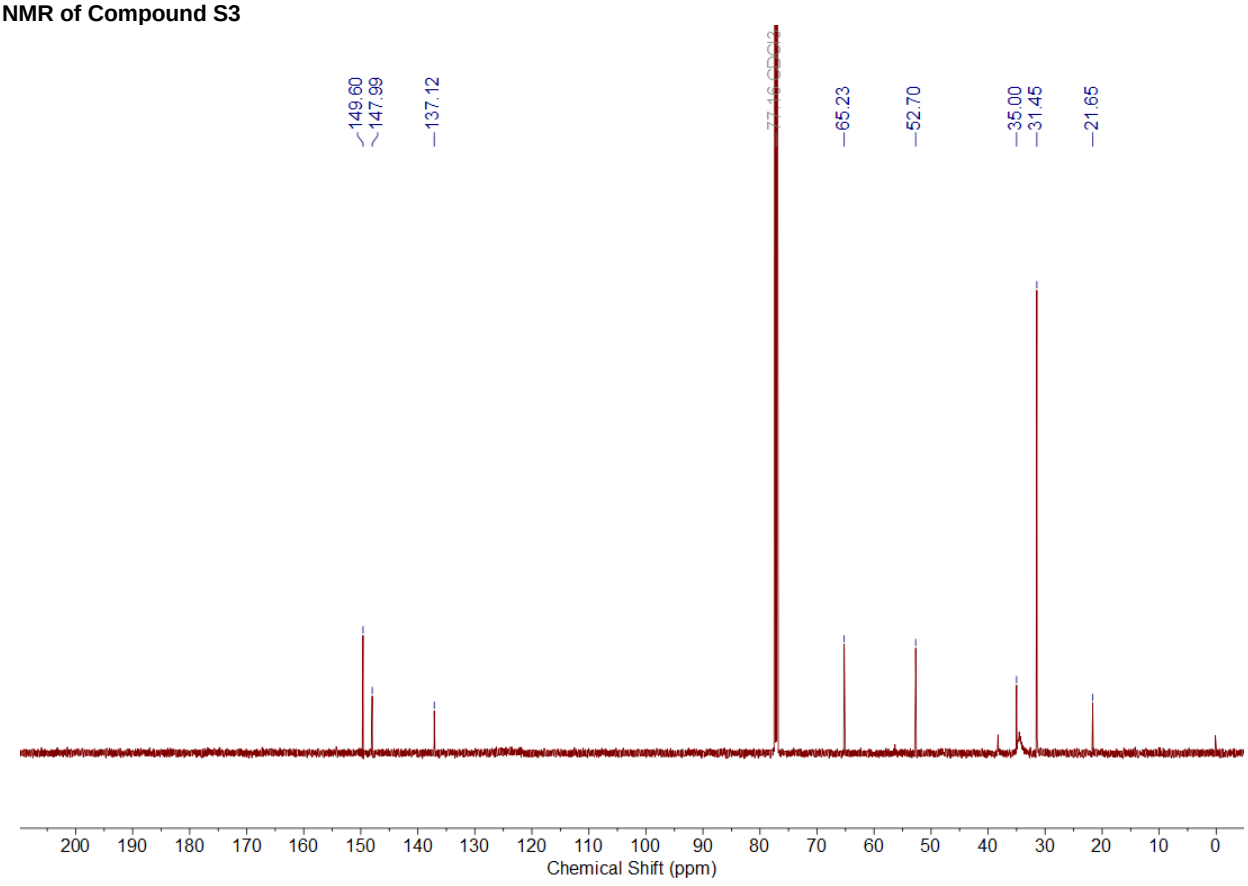
^{13}C NMR of Compound S2



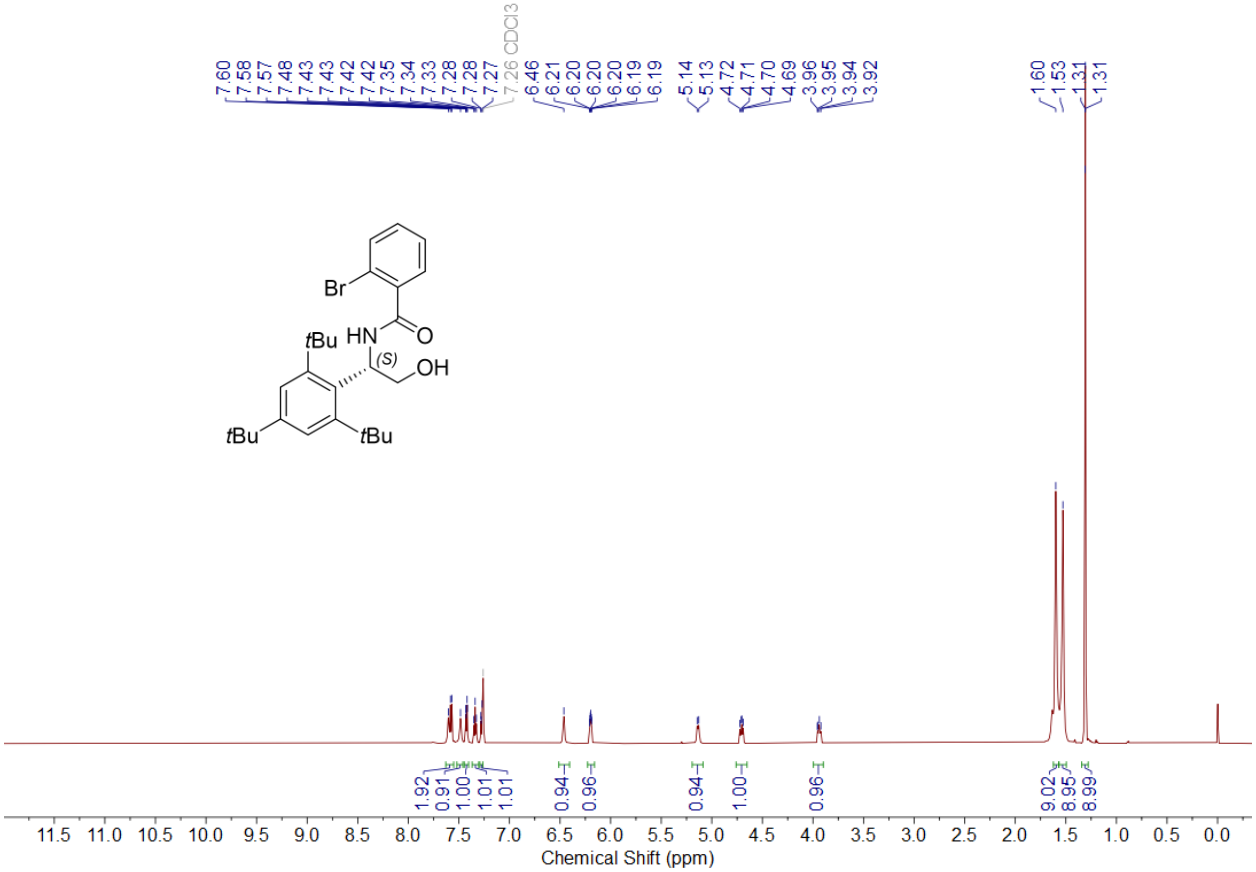
^{1}H NMR of Compound S3



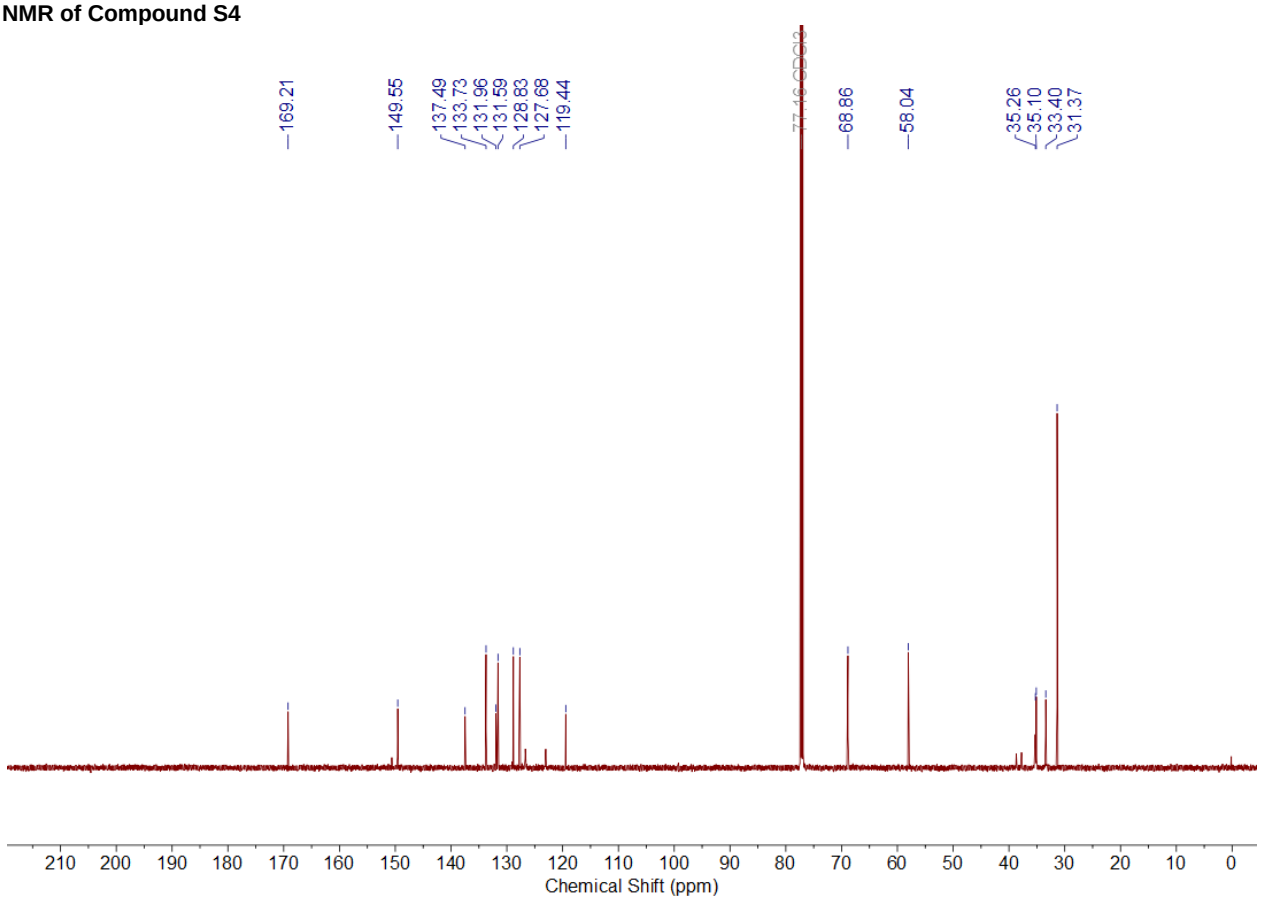
^{13}C NMR of Compound S3



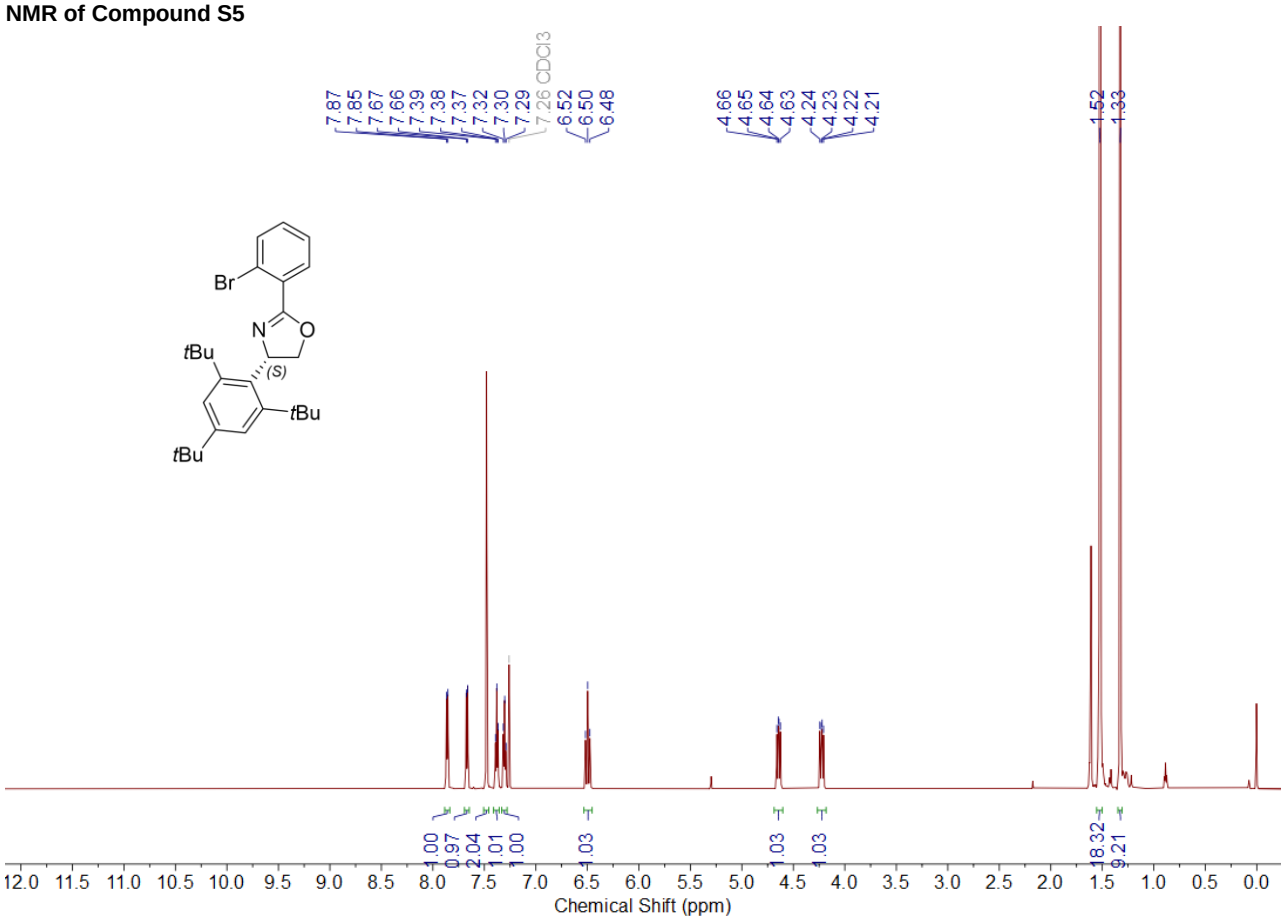
^{1}H NMR of Compound S4



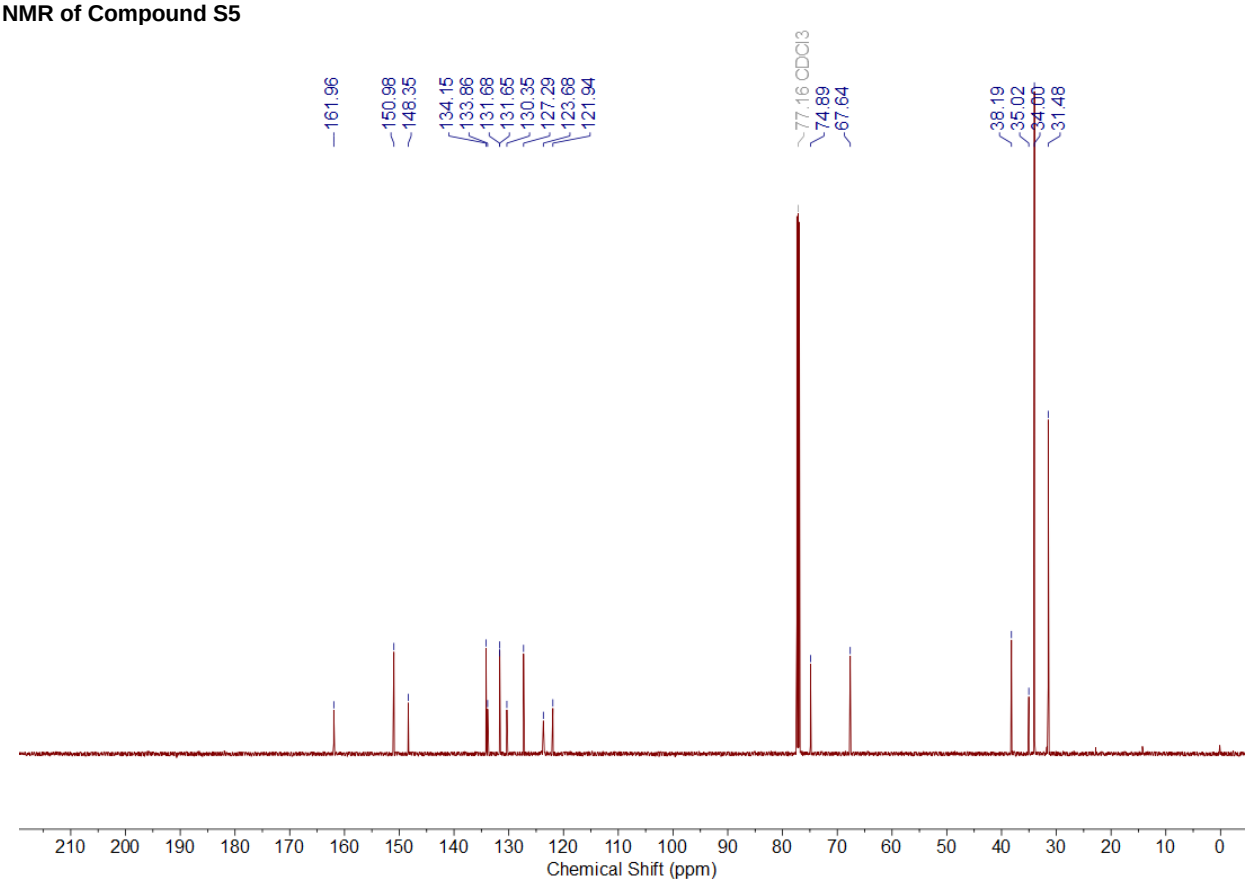
^{13}C NMR of Compound S4



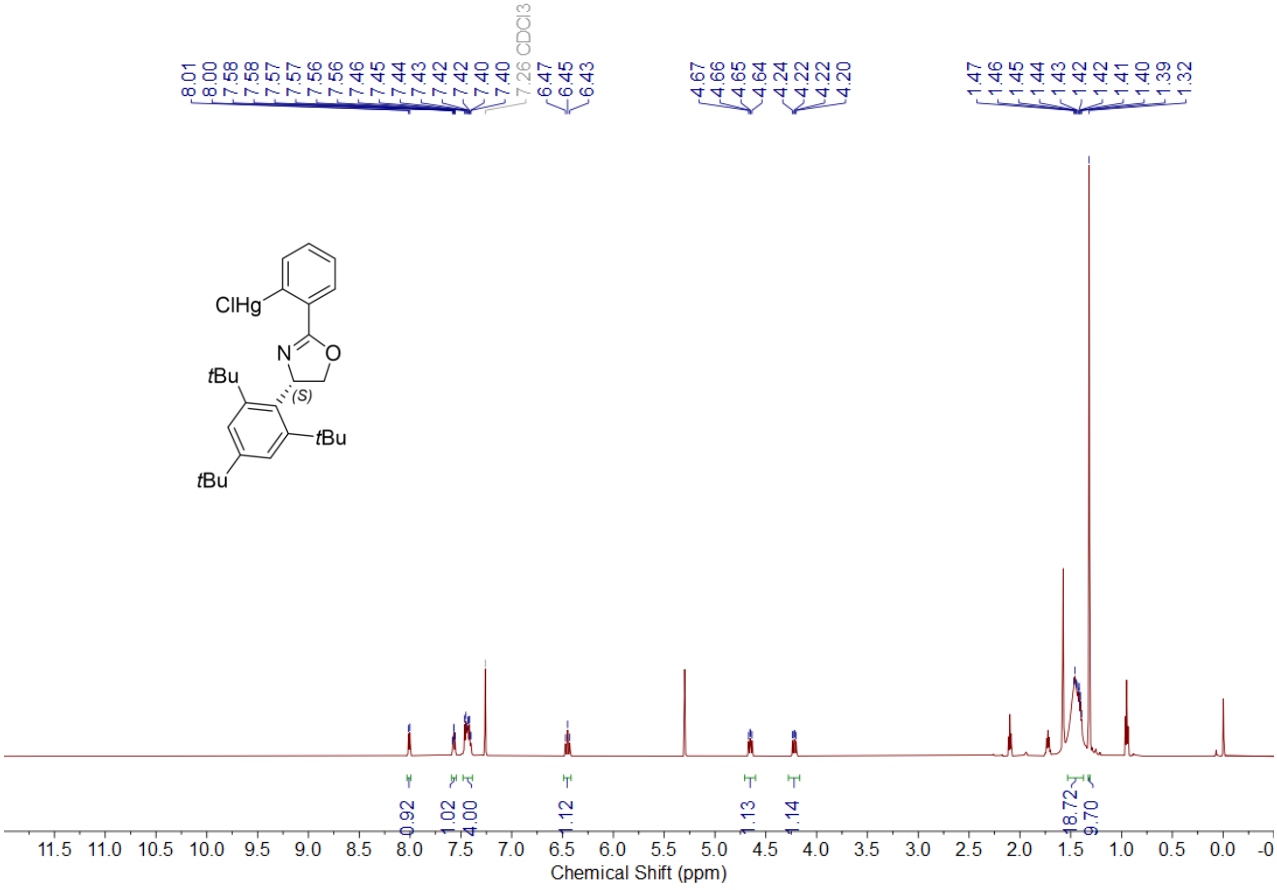
^{1}H NMR of Compound S5



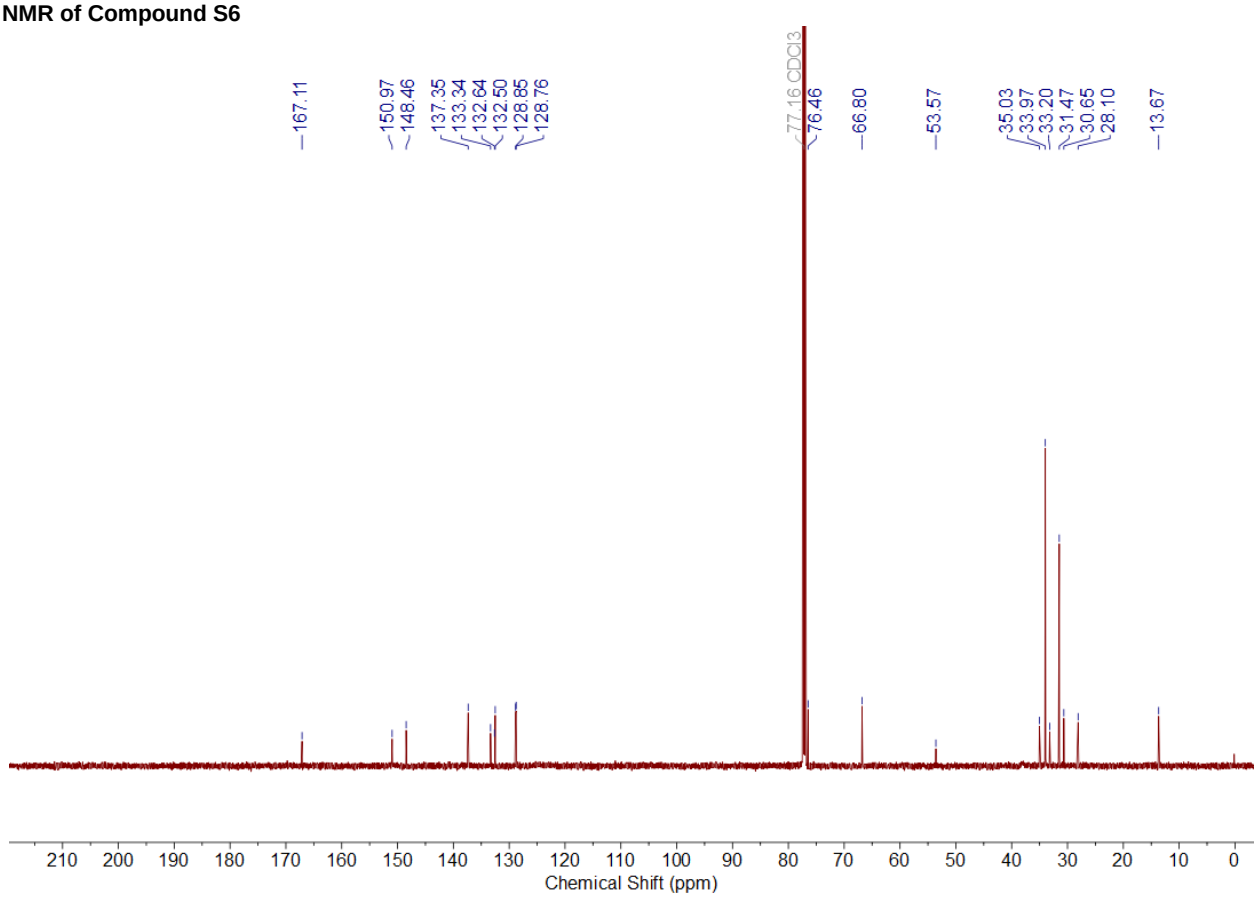
^{13}C NMR of Compound S5



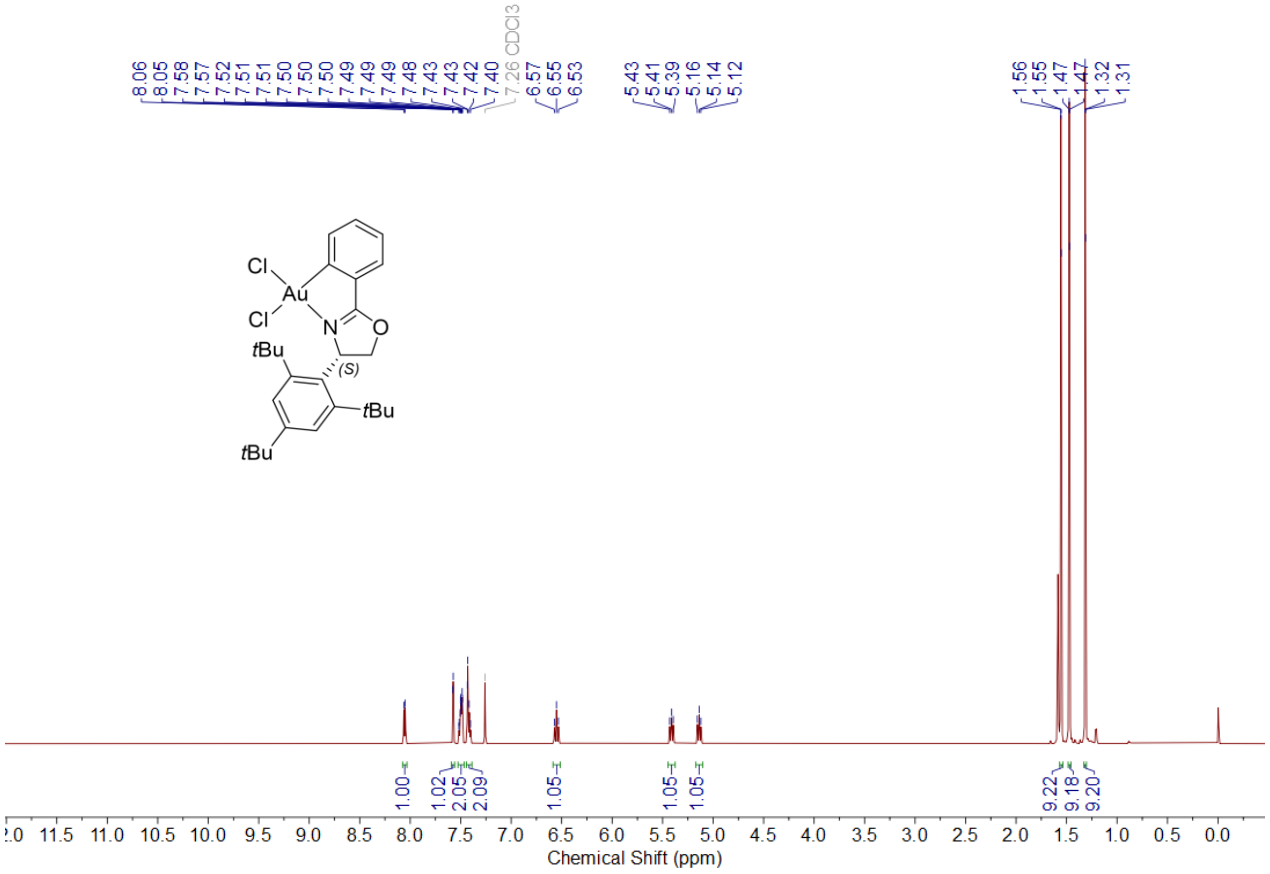
^{1}H NMR of Compound S6



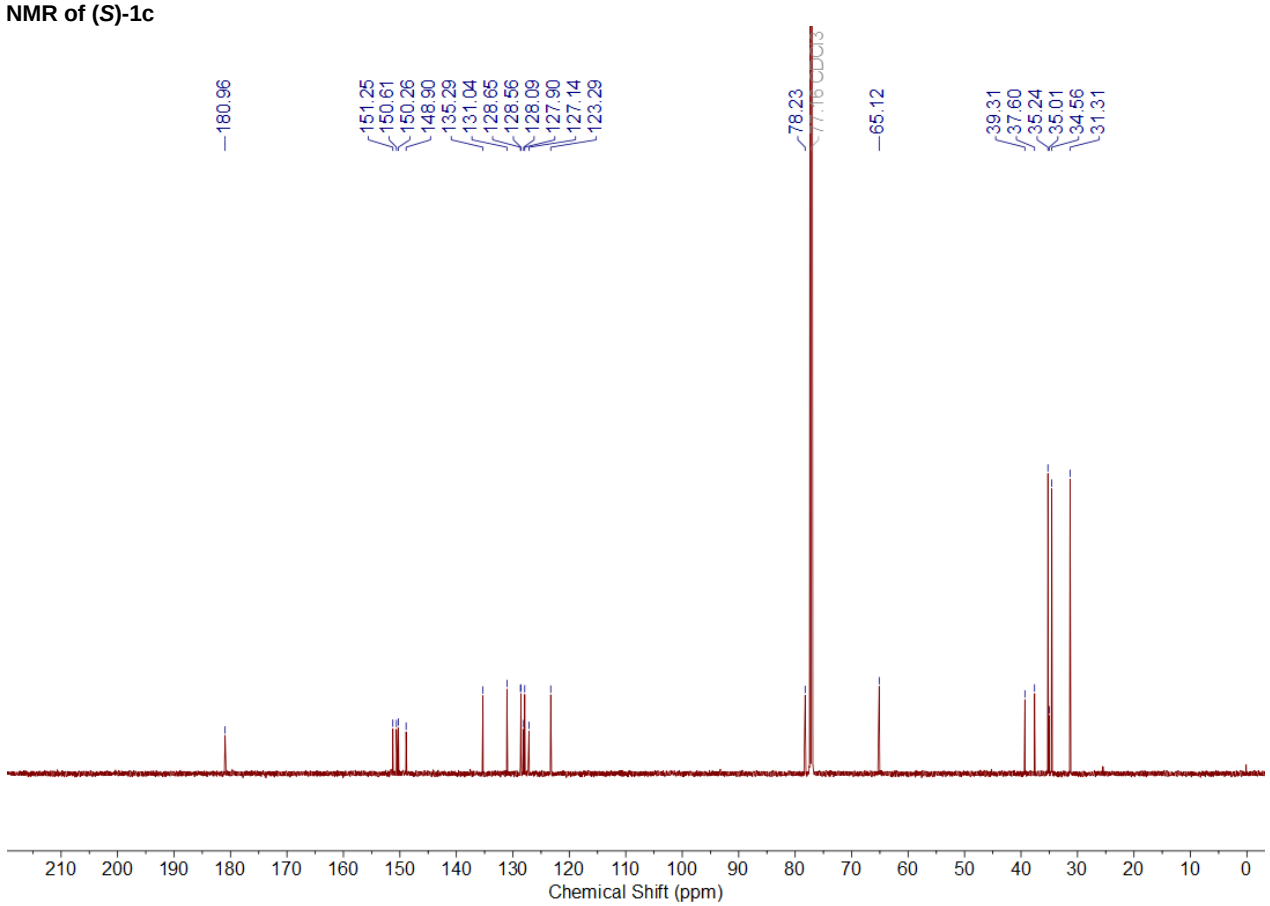
^{13}C NMR of Compound S6



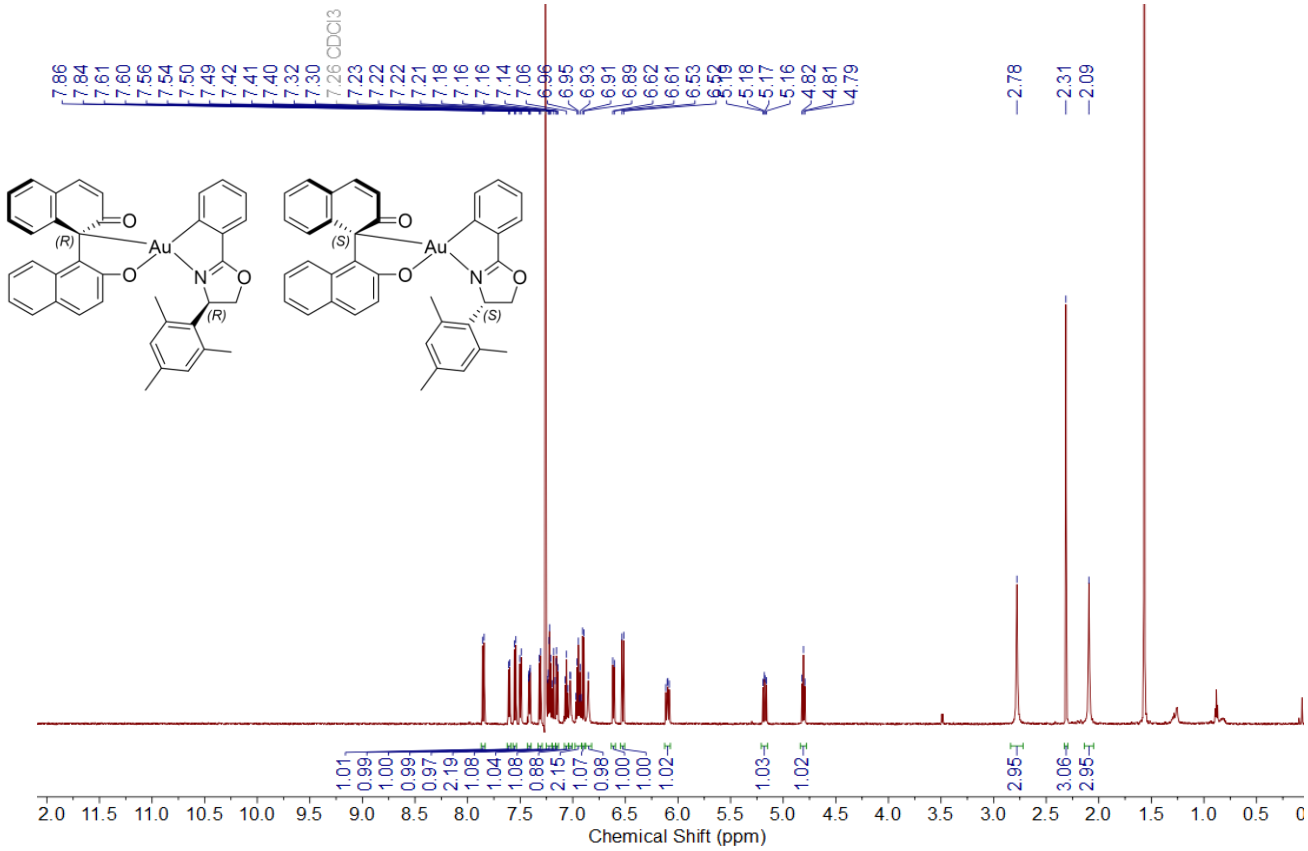
^{1}H NMR of (*S*)-1c



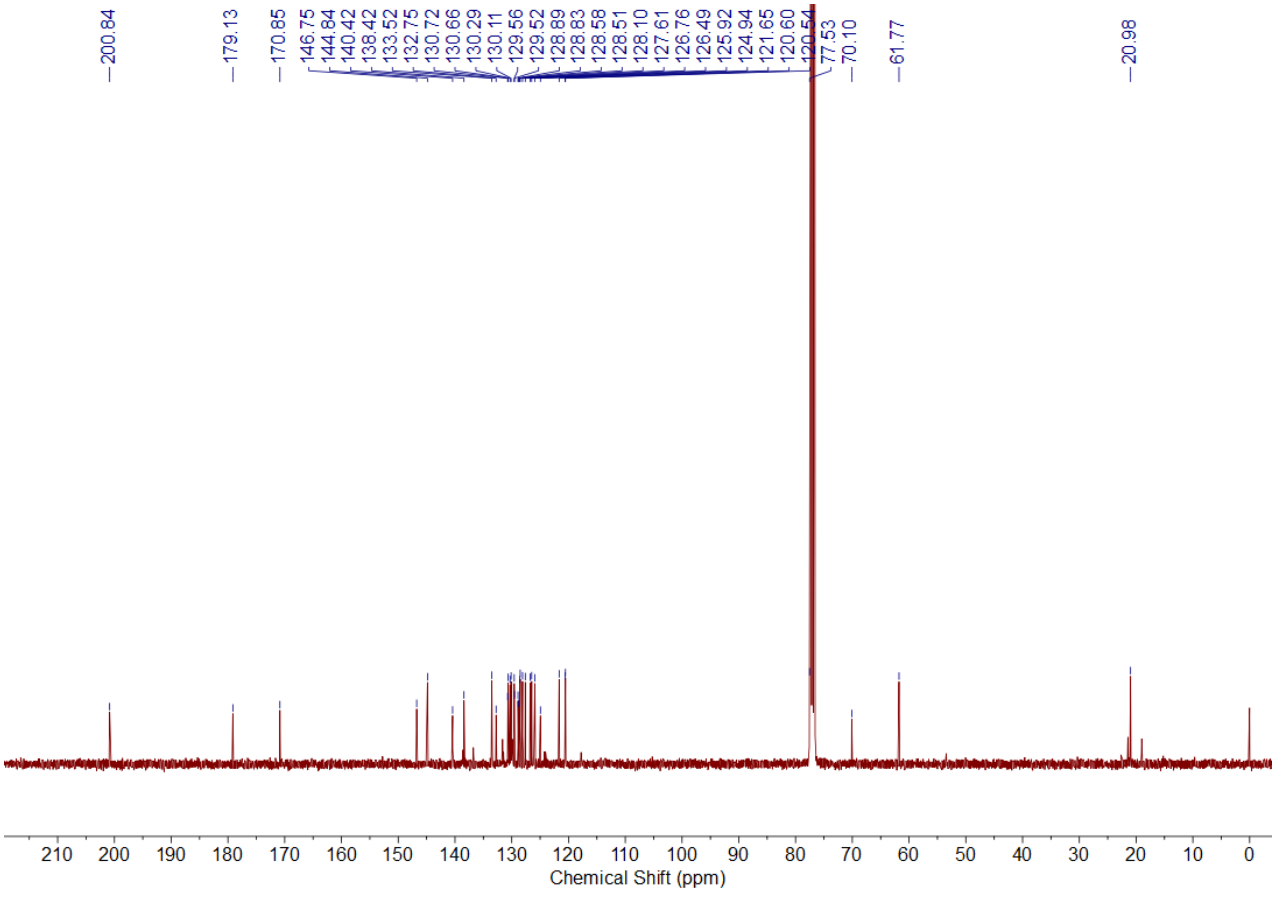
^{13}C NMR of (*S*)-1c



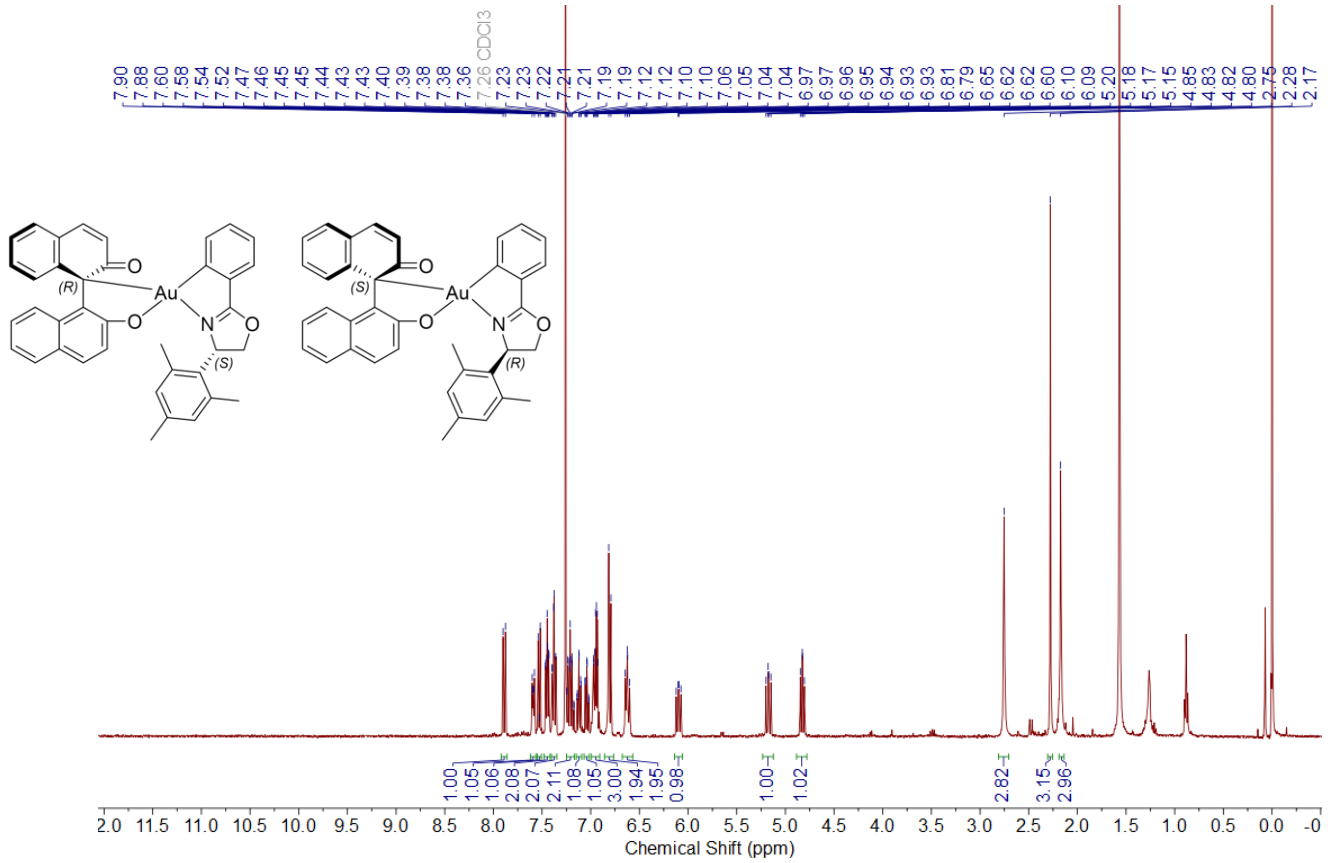
^{1}H NMR of (*R*,*R*)-3a and (*S*,*S*)-3a



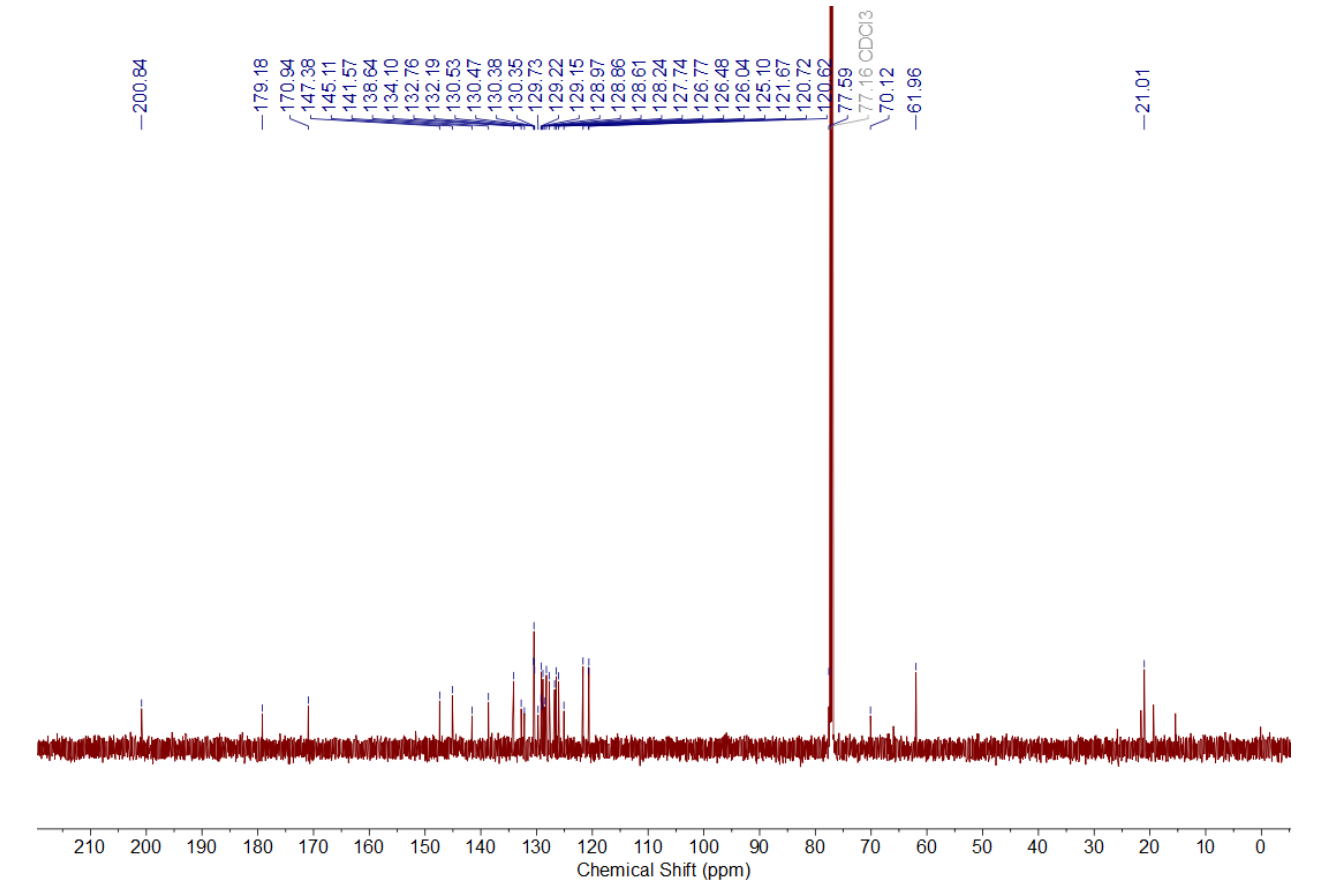
^{13}C NMR of (*R*,*R*)-3a and (*S*,*S*)-3a



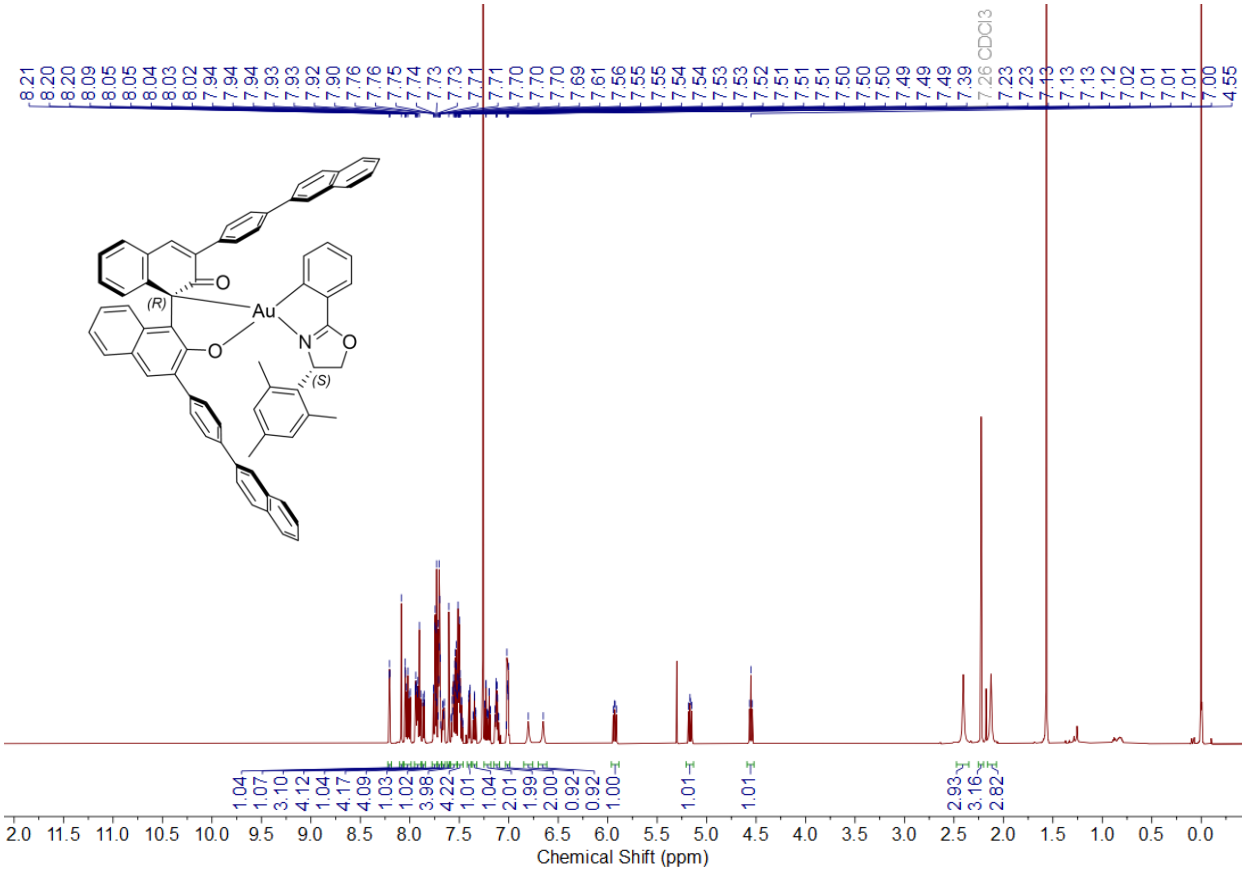
^{1}H NMR of (*R*,*S*)-3a and (*S*,*R*)-3a



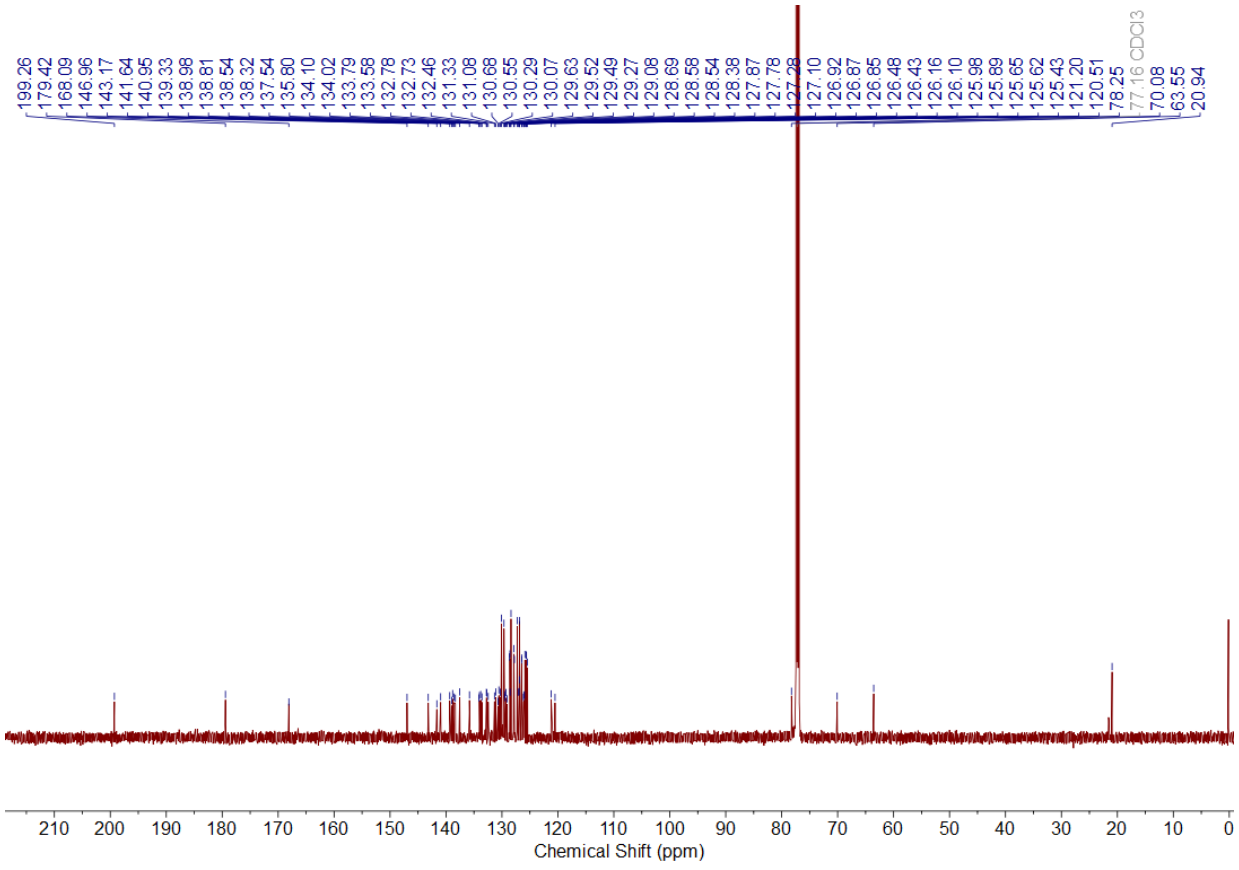
^{13}C NMR of (*R*,*S*)-3a and (*S*,*R*)-3a



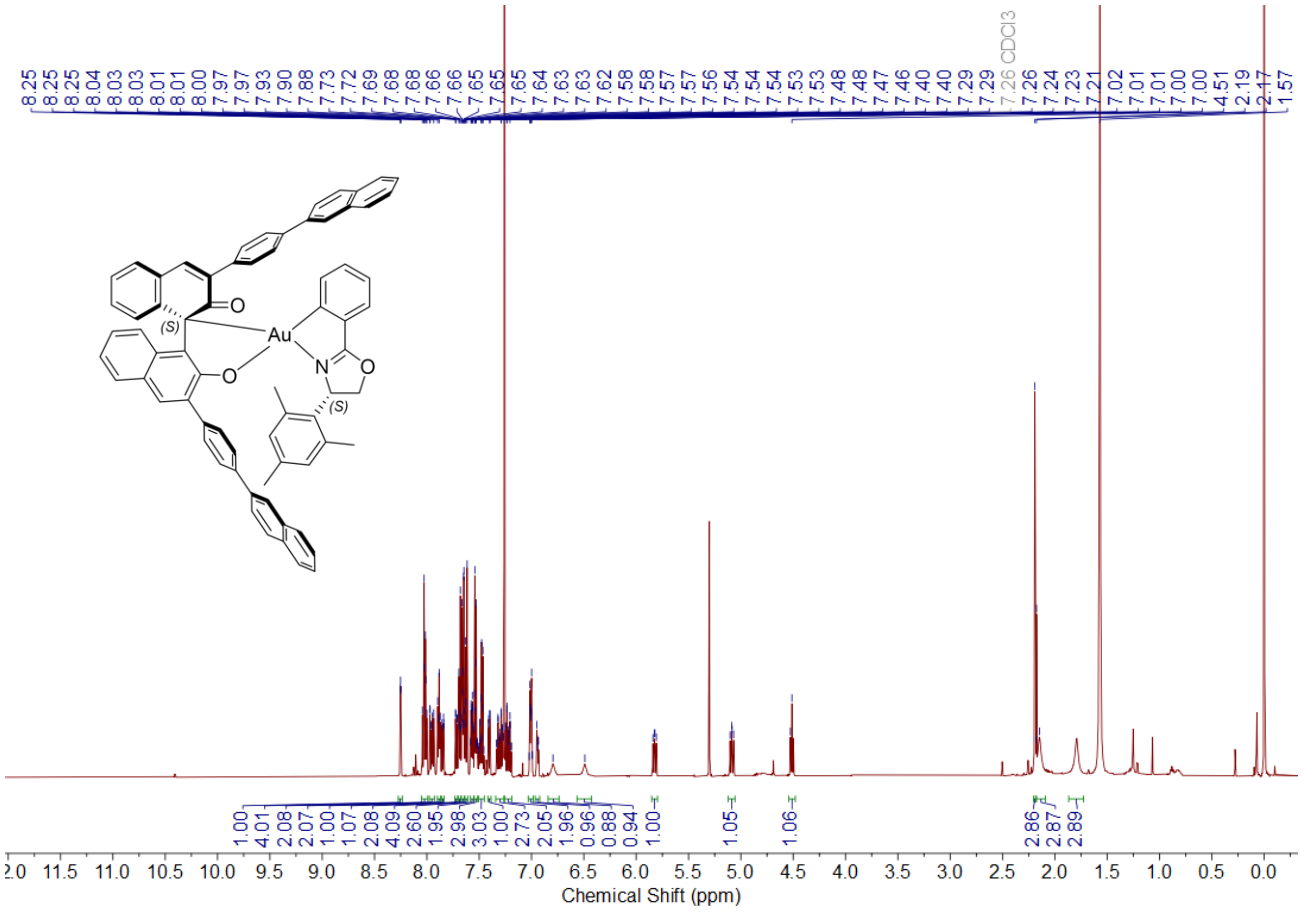
^{1}H NMR of (*R,S*)-3b



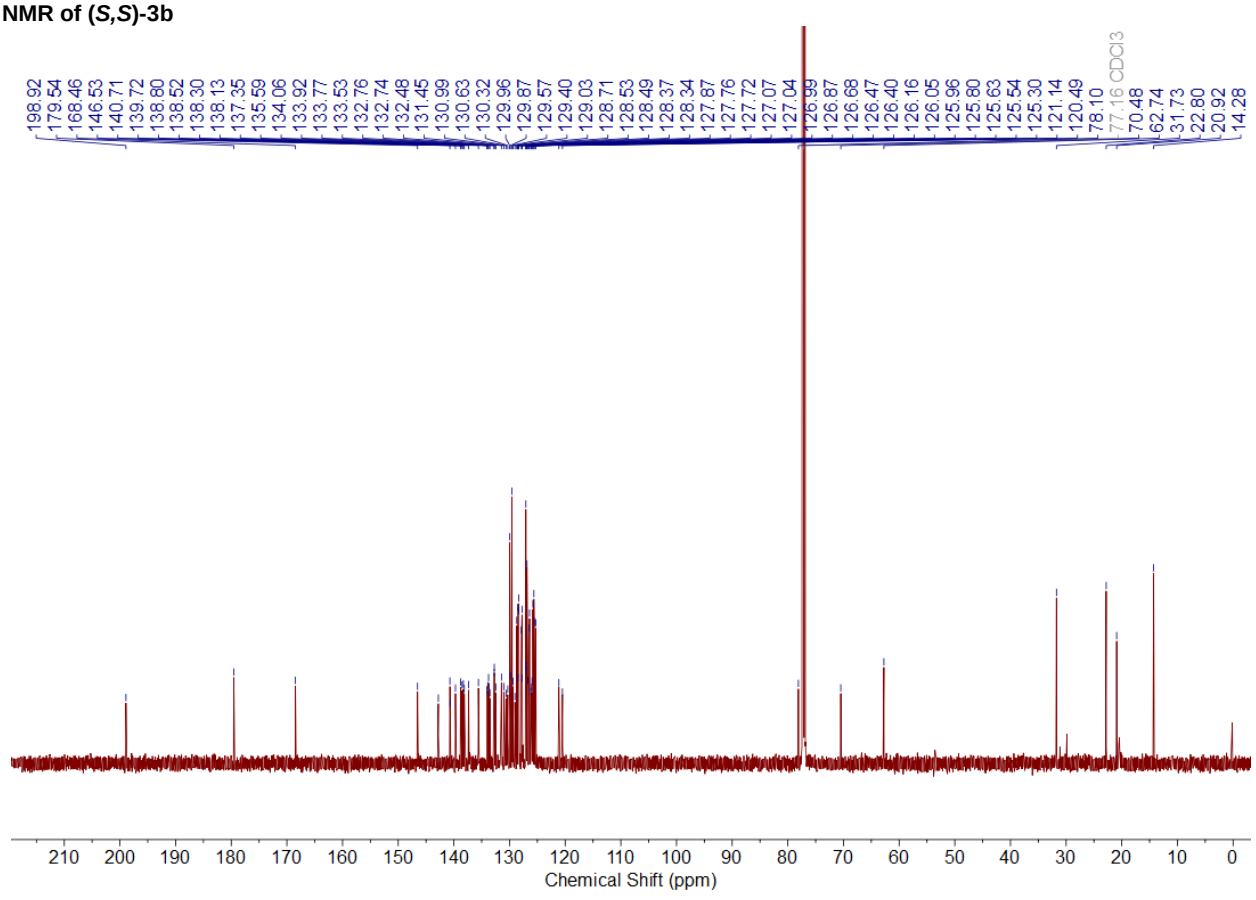
^{13}C NMR of (*R,S*)-3b



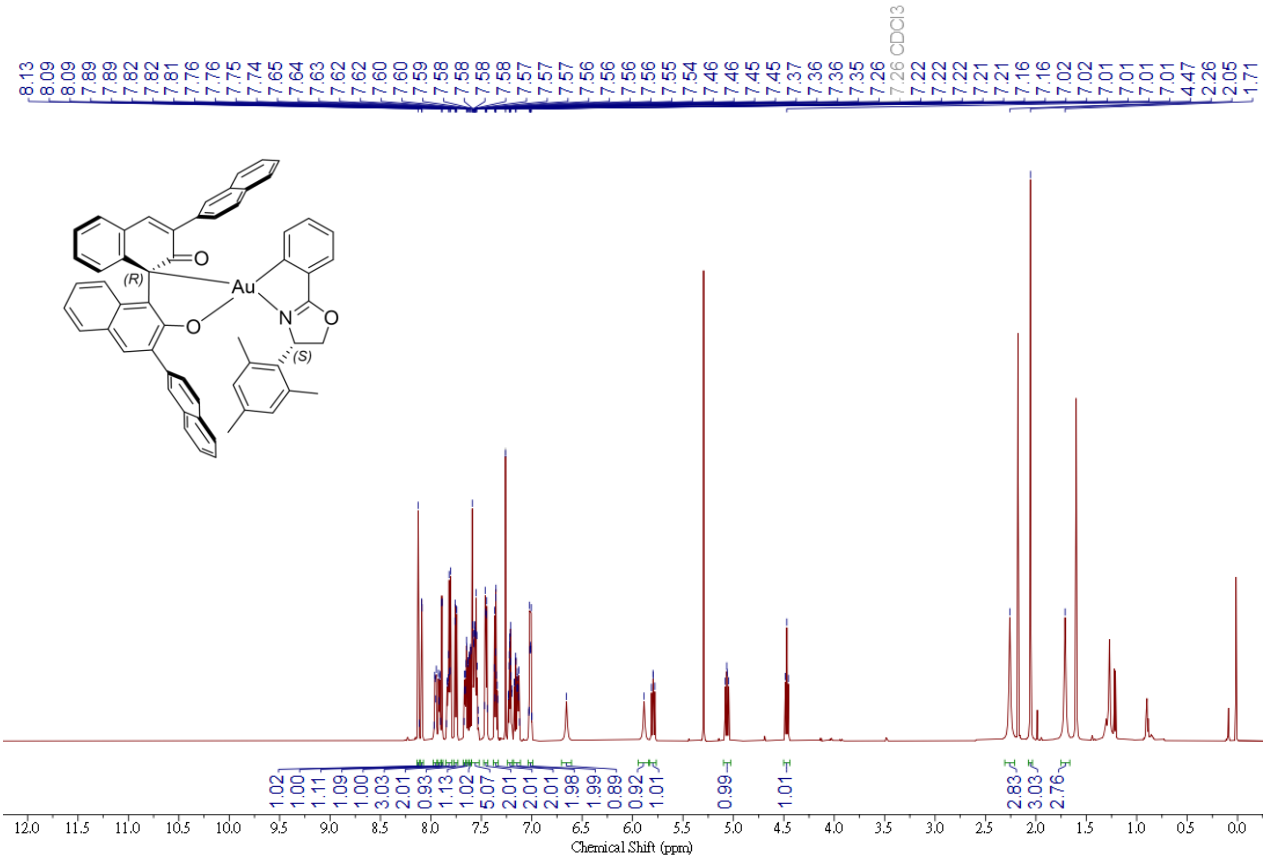
^{1}H NMR of (*S*,*S*)-3b



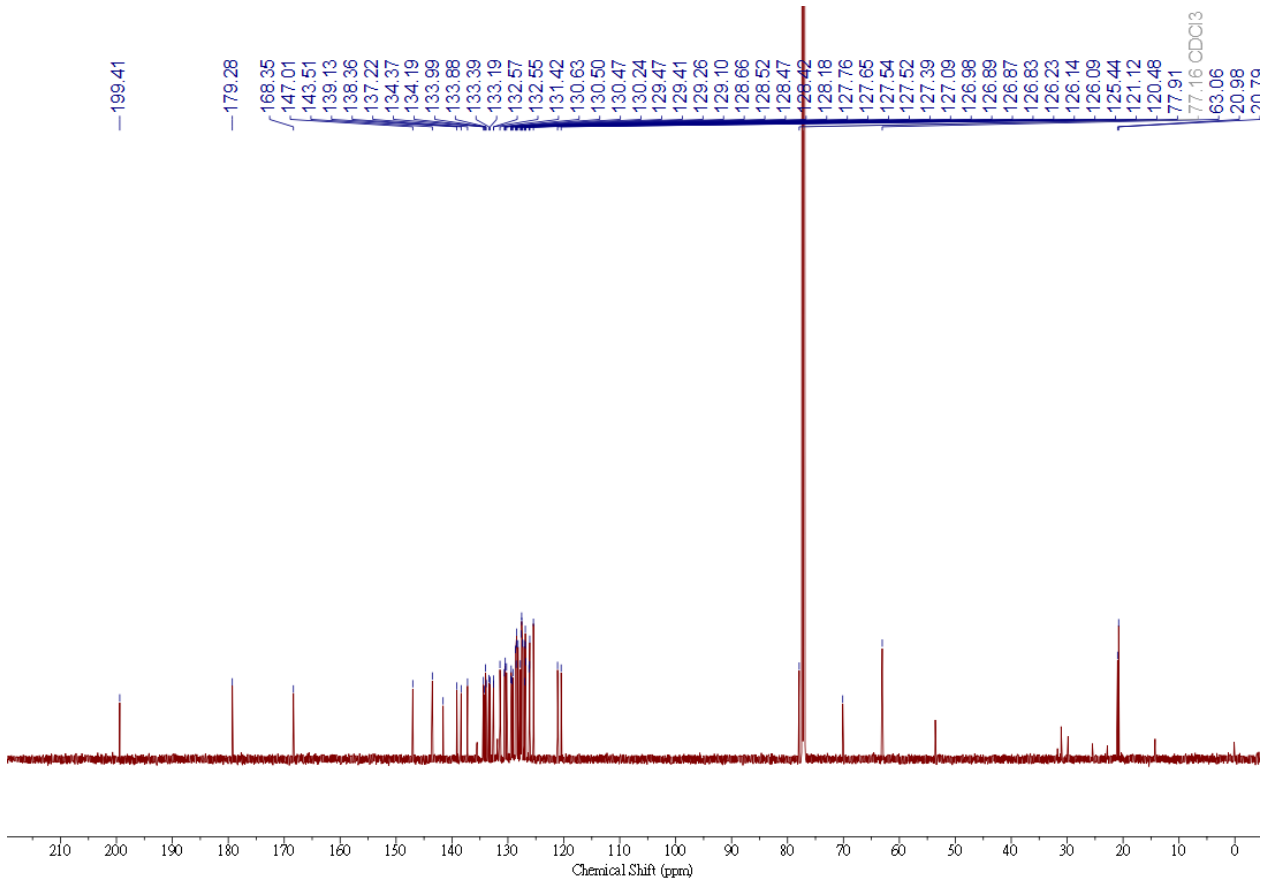
^{13}C NMR of (*S*,*S*)-3b



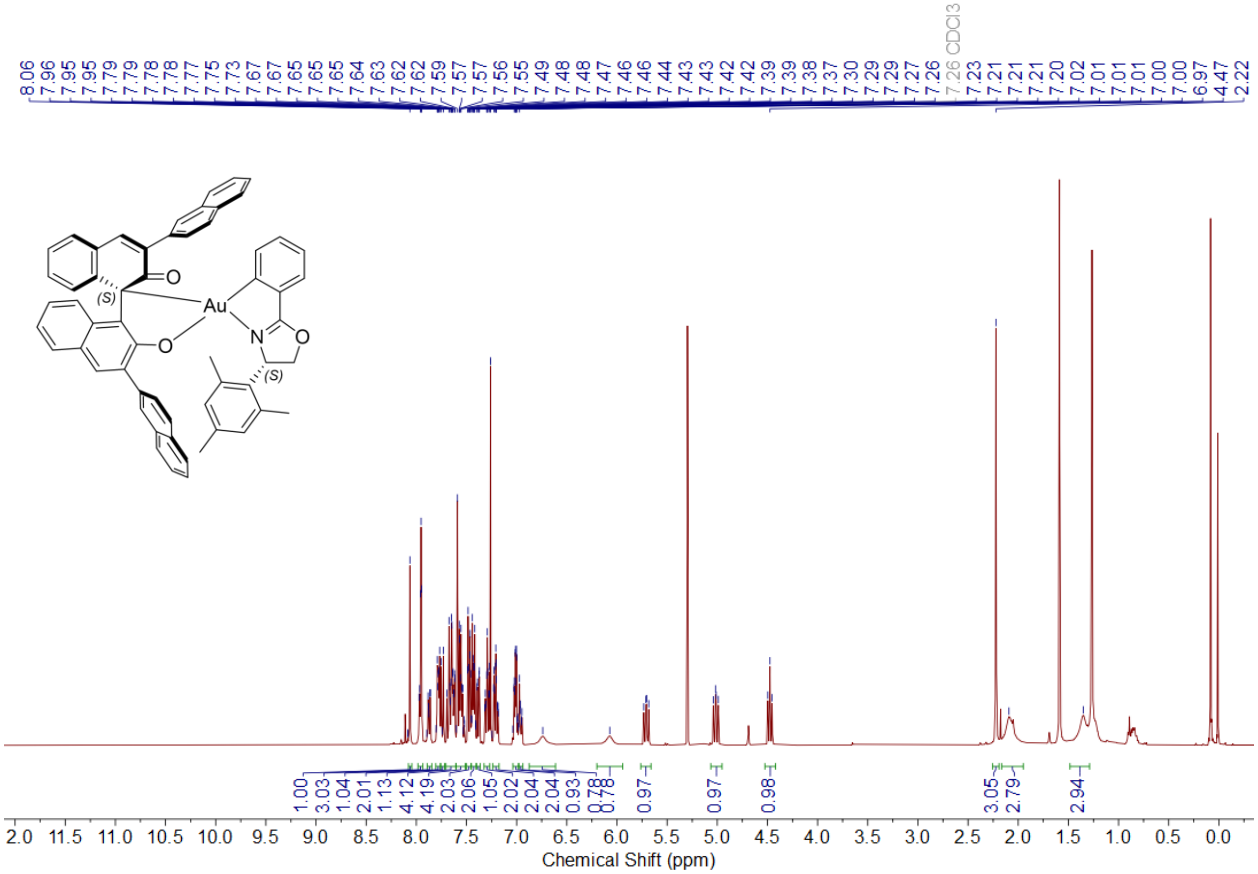
^{1}H NMR of (*R*,*S*)-3c



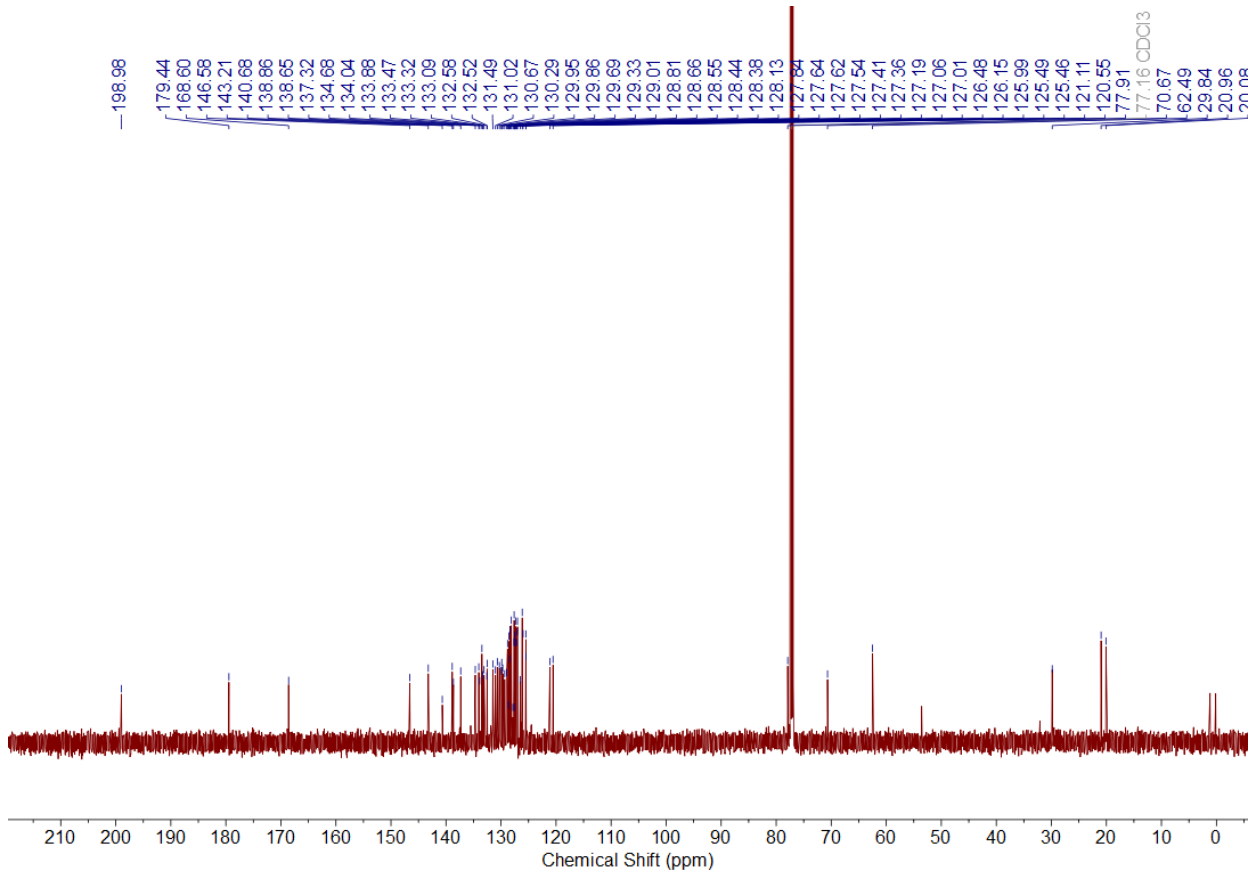
^{13}C NMR of (*R*,*S*)-3c



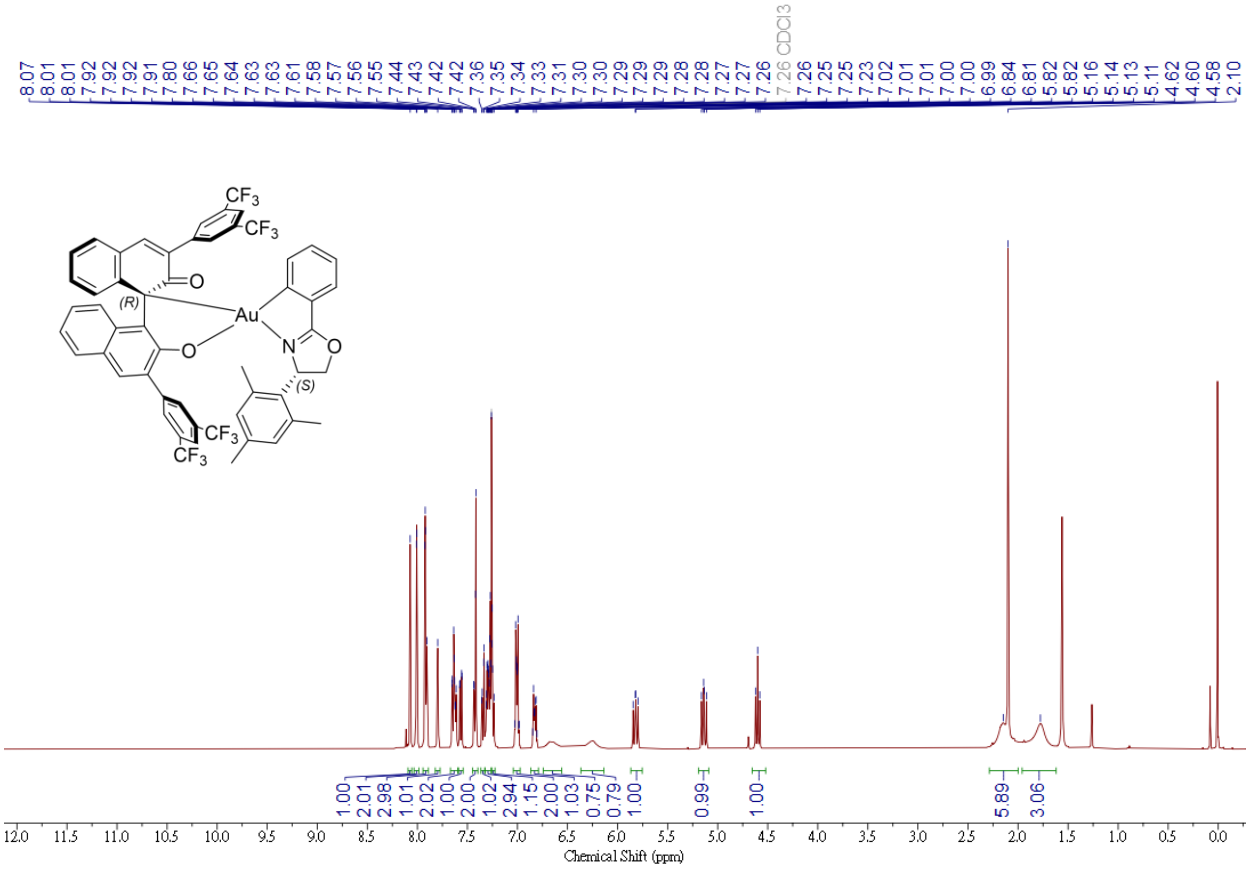
^{1}H NMR of (*S*,*S*)-3c



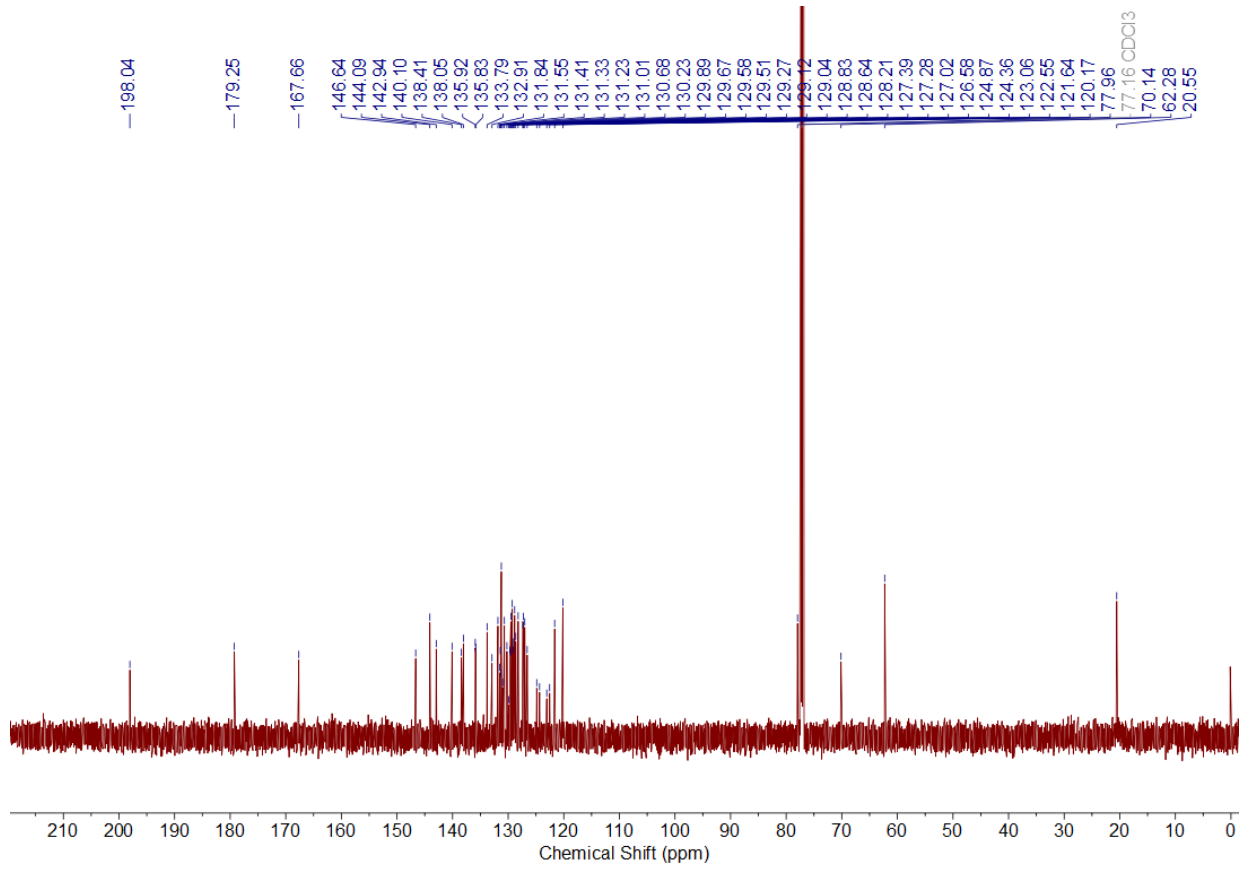
^{13}C NMR of (*S*,*S*)-3c



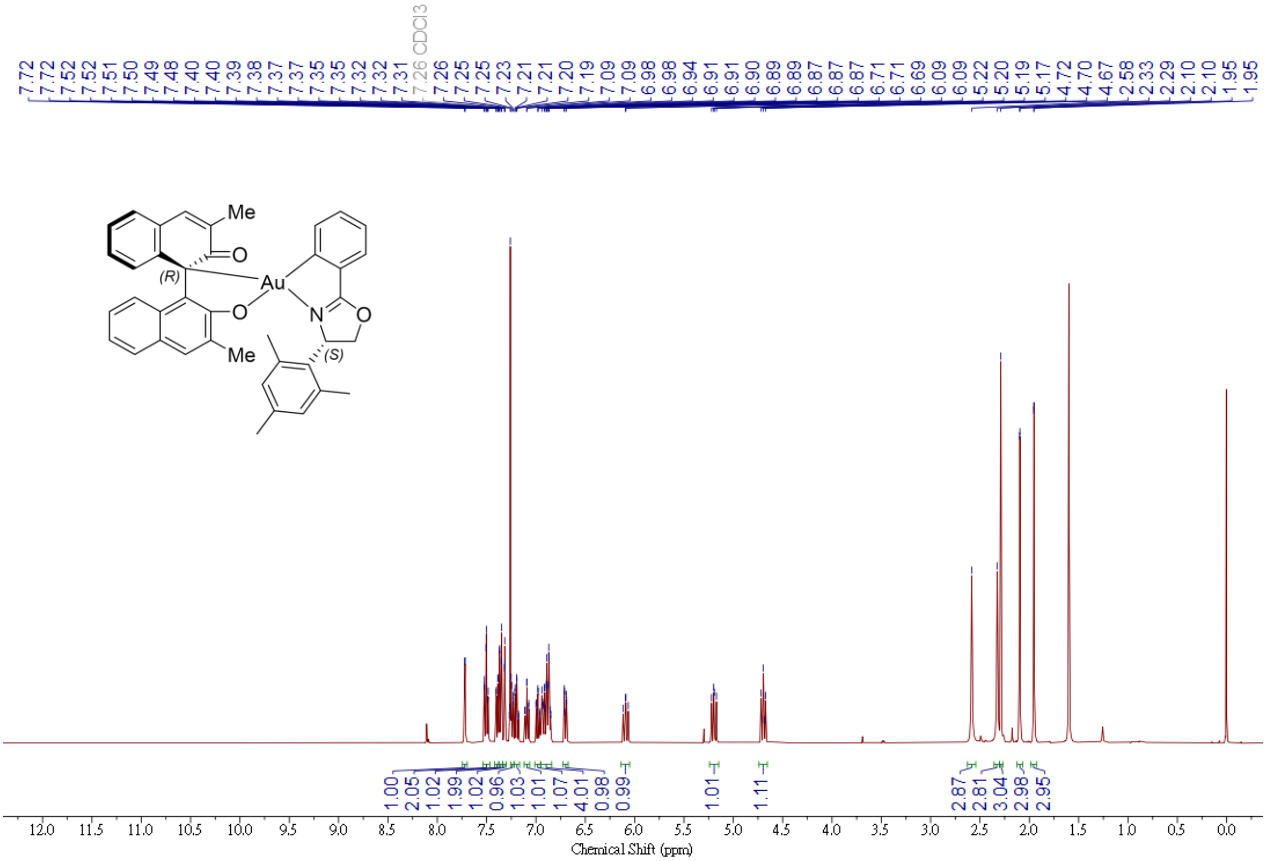
^{1}H NMR of (*R*,*S*)-3d



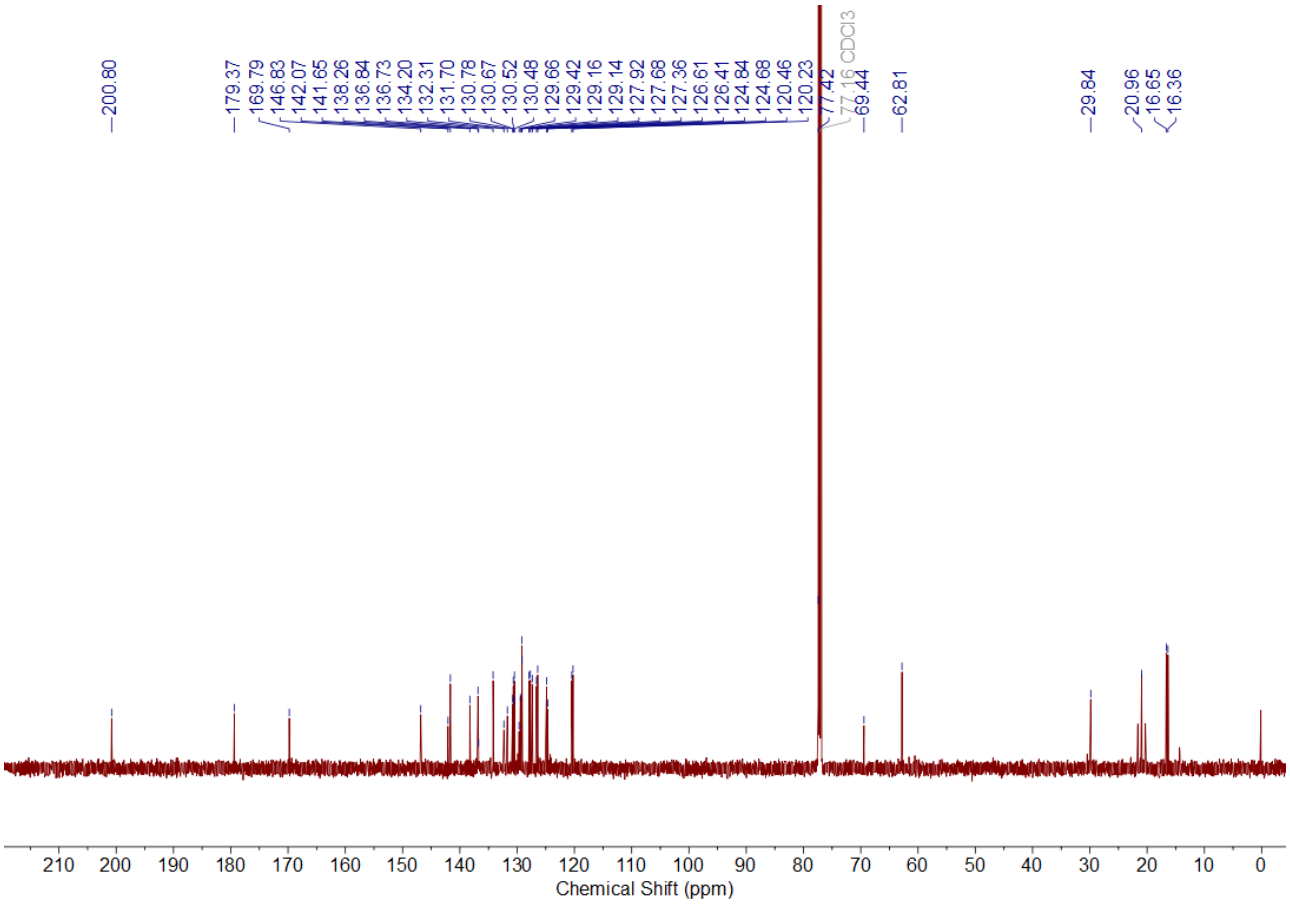
^{13}C NMR of (*R*,*S*)-3d



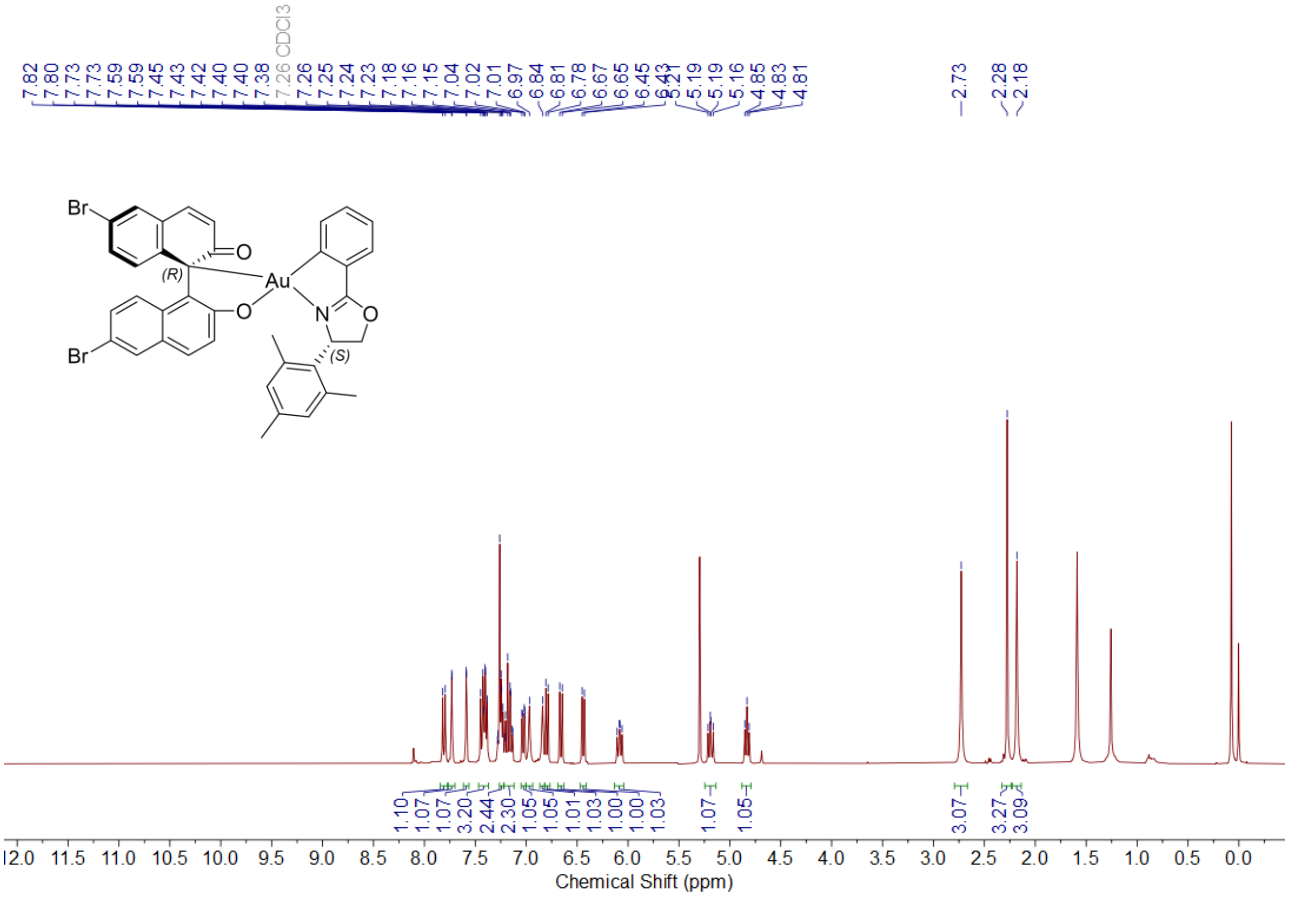
^{1}H NMR of (*R*,*S*)-3e



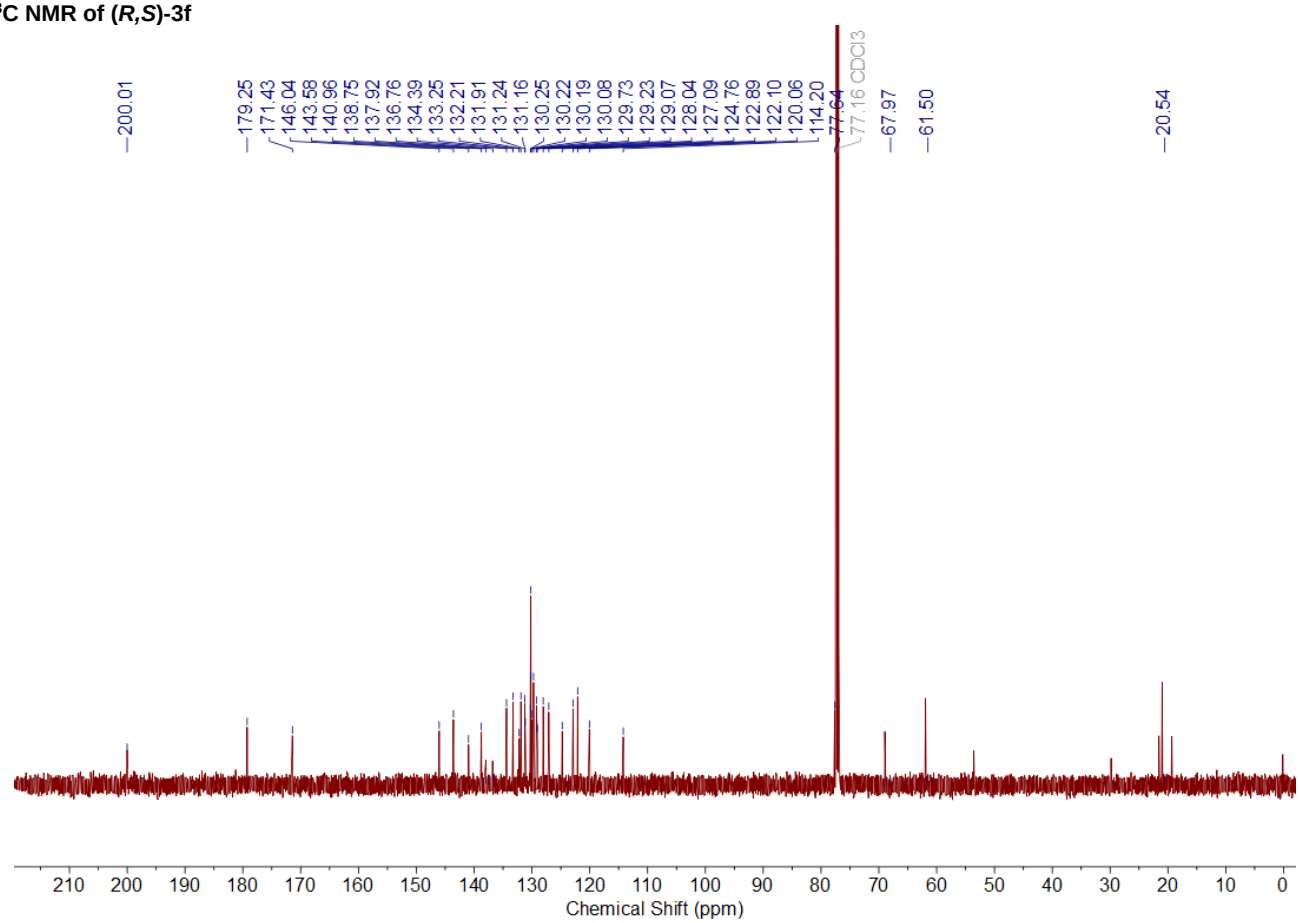
^{13}C NMR of (*R*,*S*)-3e



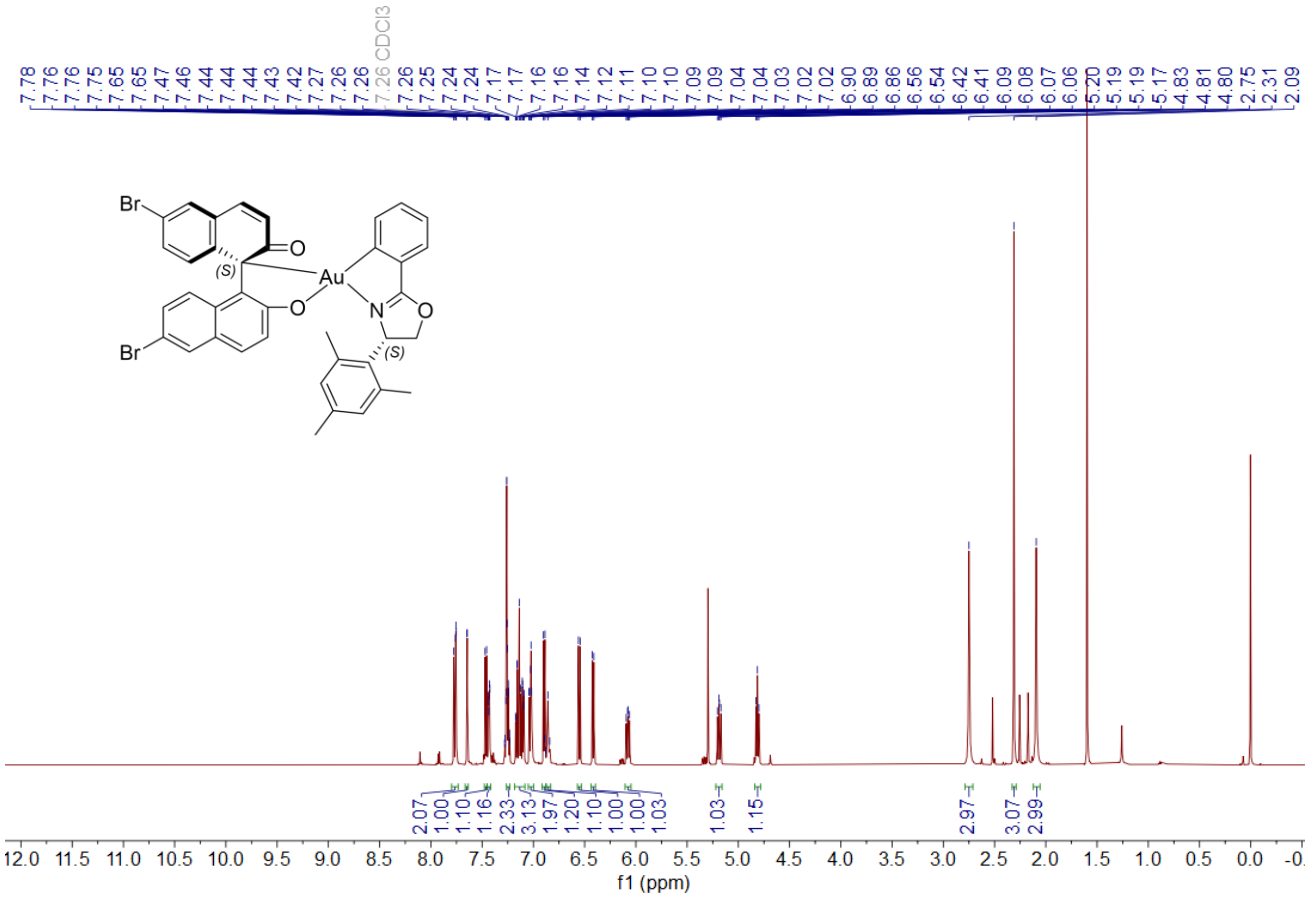
^{1}H NMR of (*R*,*S*)-3f



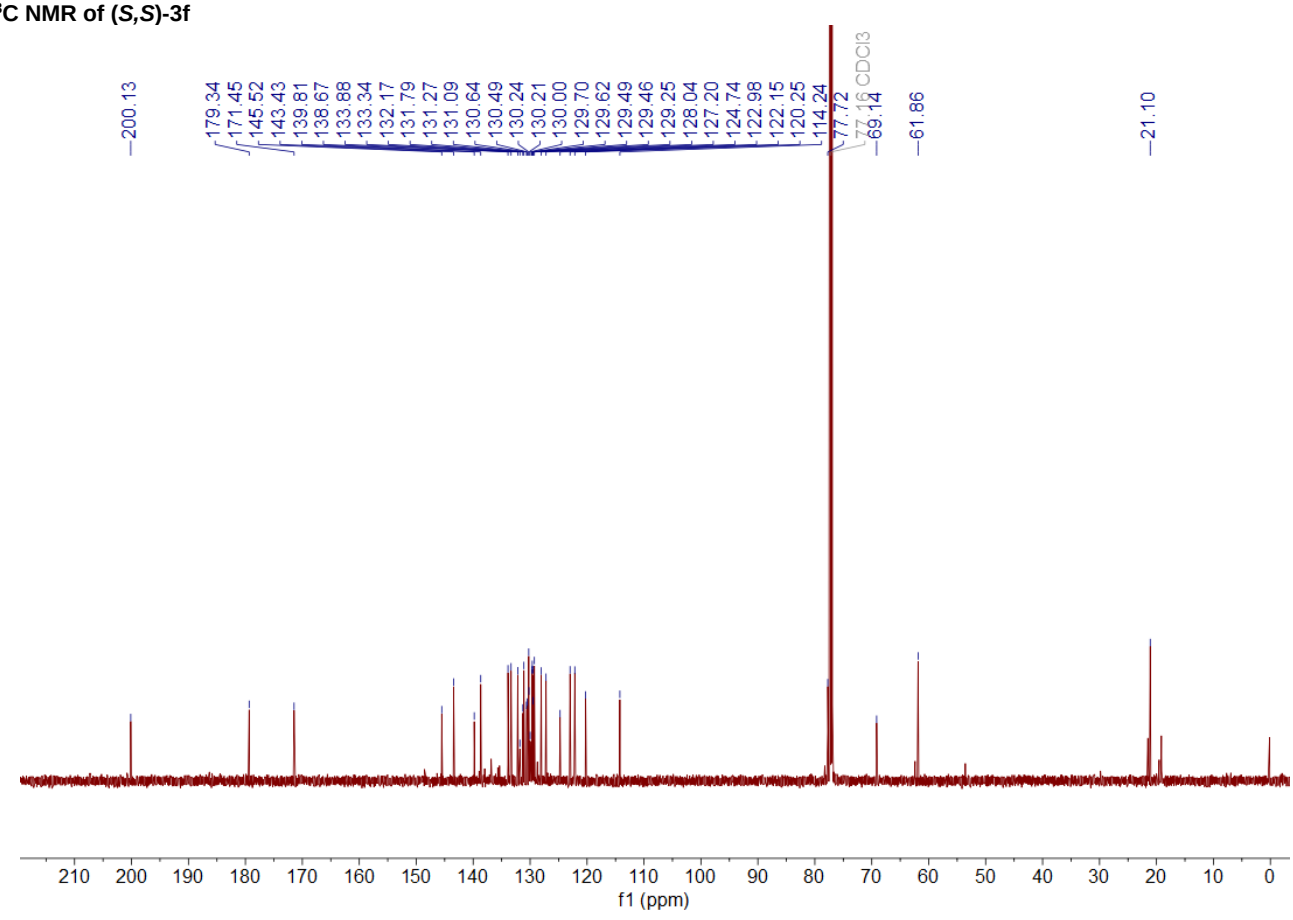
^{13}C NMR of (*R*,*S*)-3f



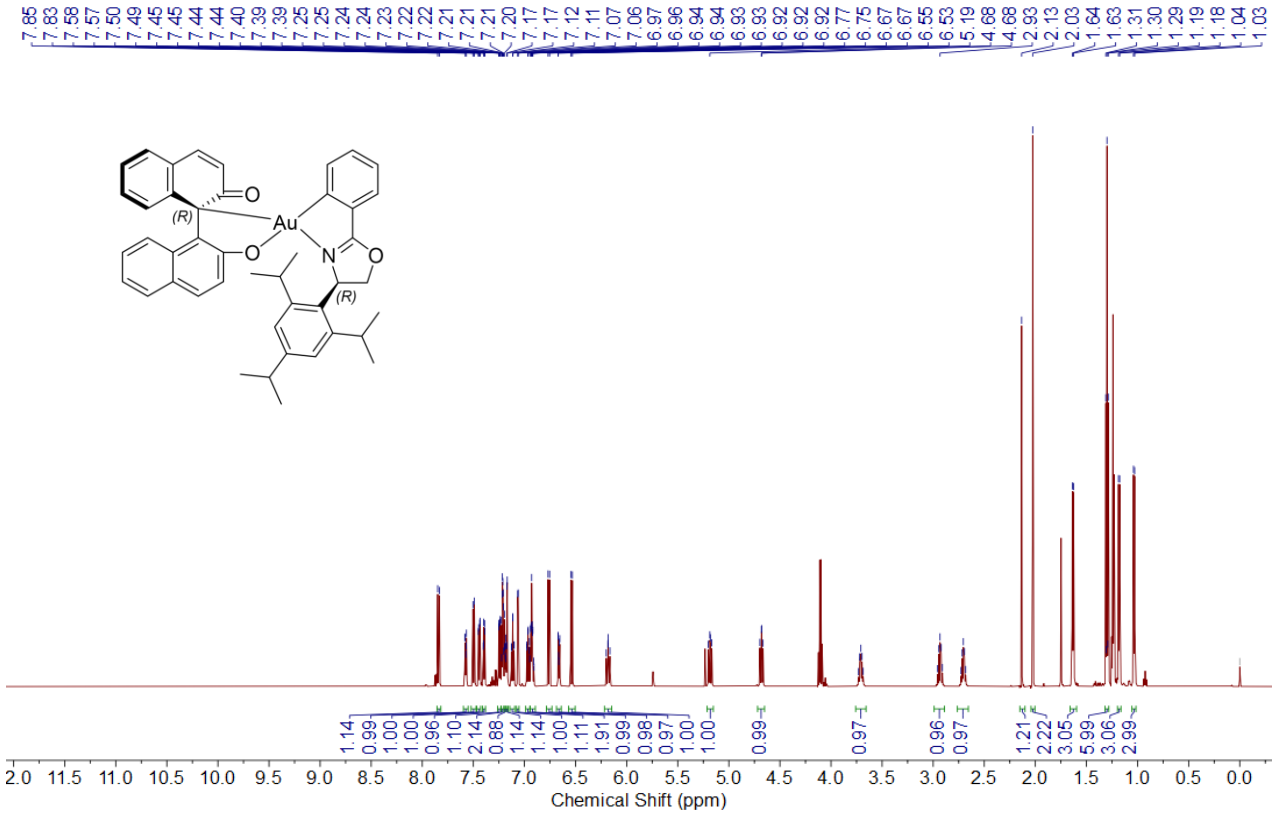
^{1}H NMR of (*S,S*)-3f



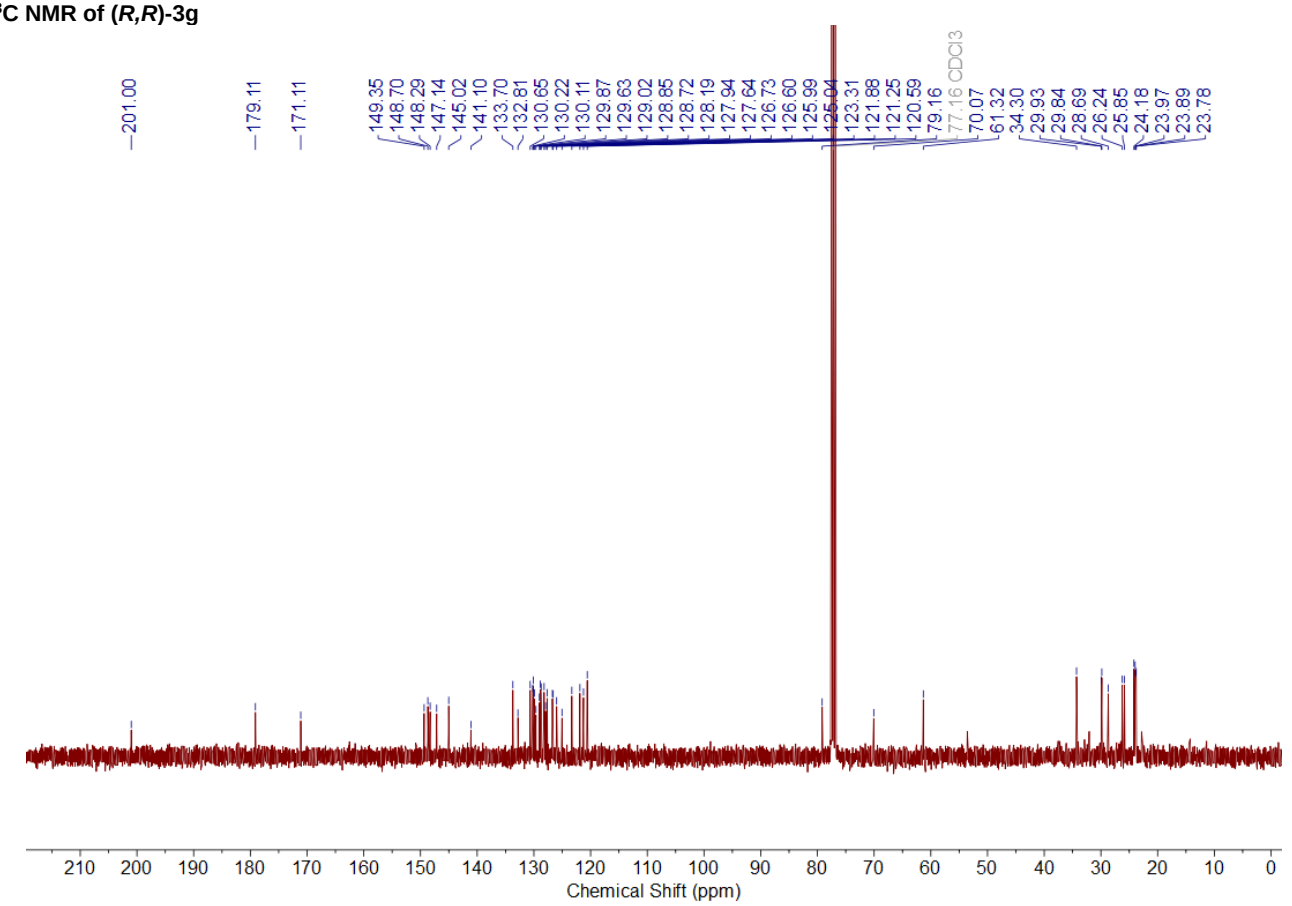
^{13}C NMR of (*S,S*)-3f



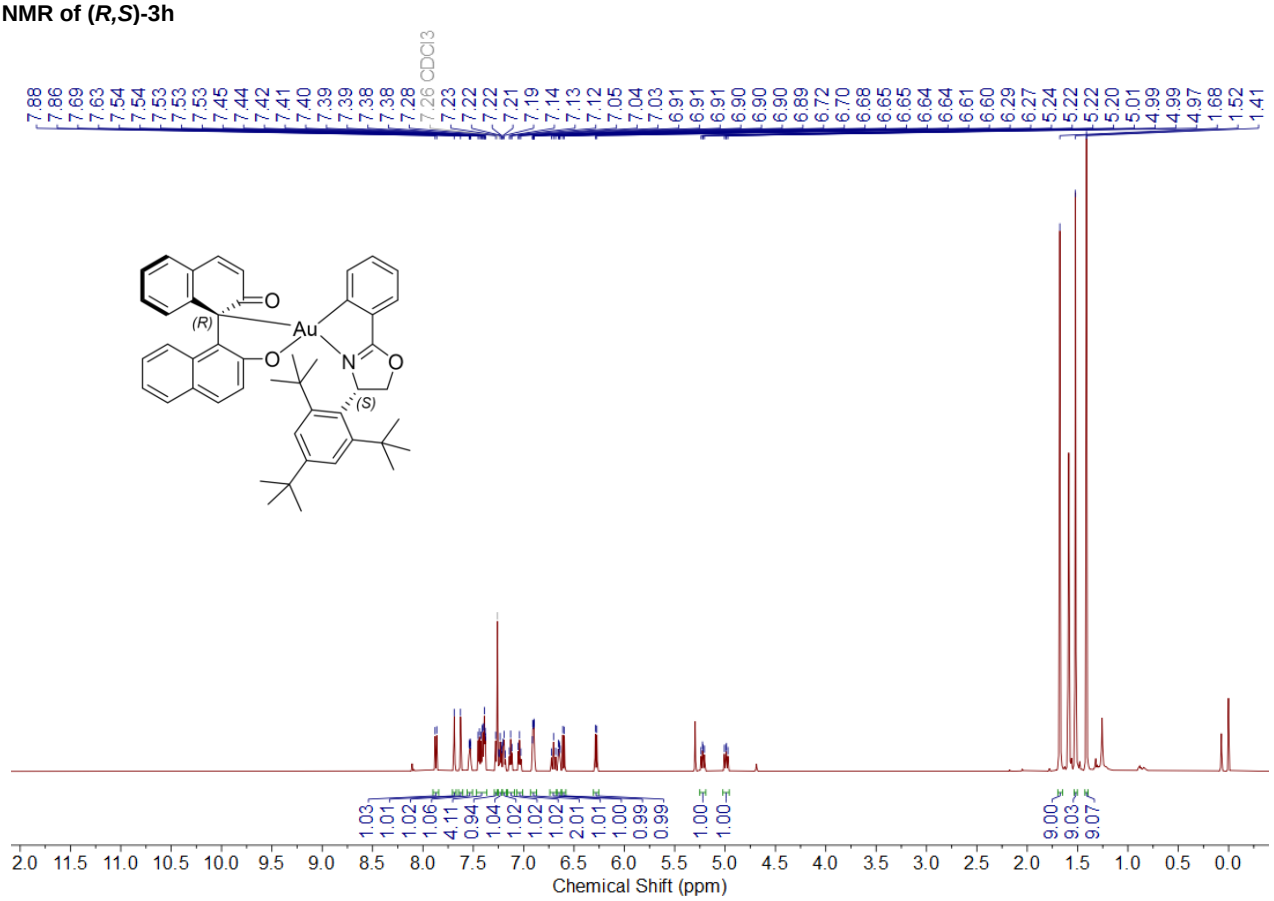
^{1}H NMR of (*R*,*R*)-3g



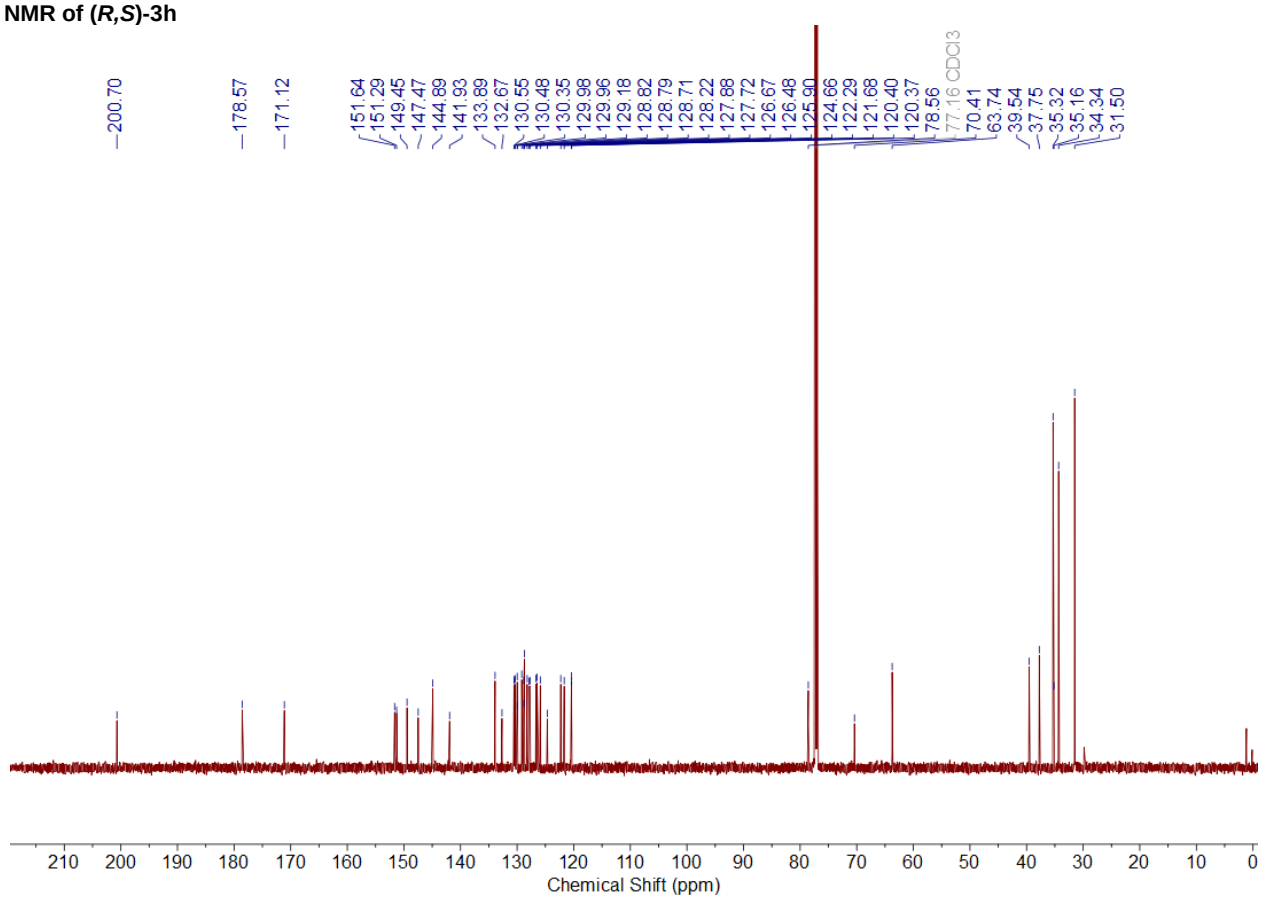
^{13}C NMR of (*R*,*R*)-3g



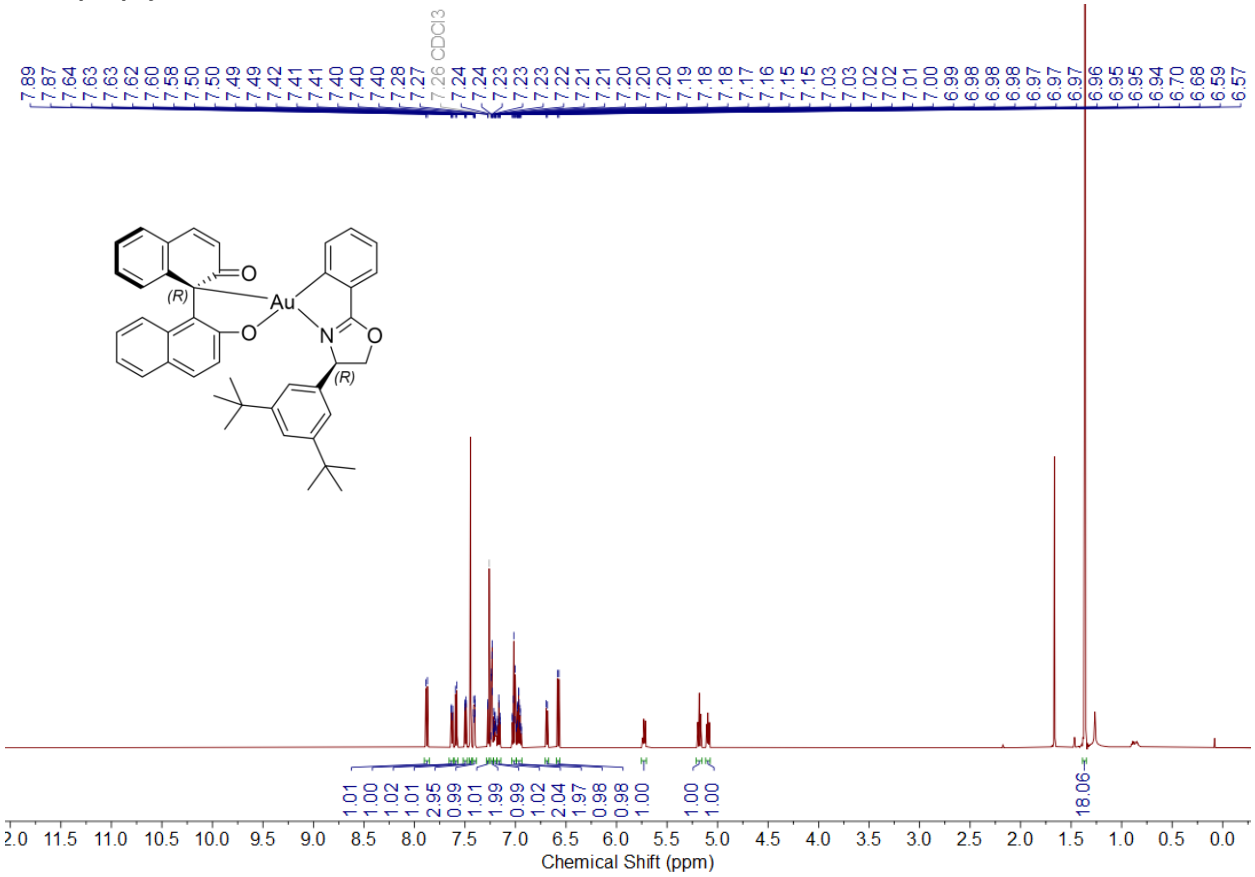
^{1}H NMR of (*R*,*S*)-3h



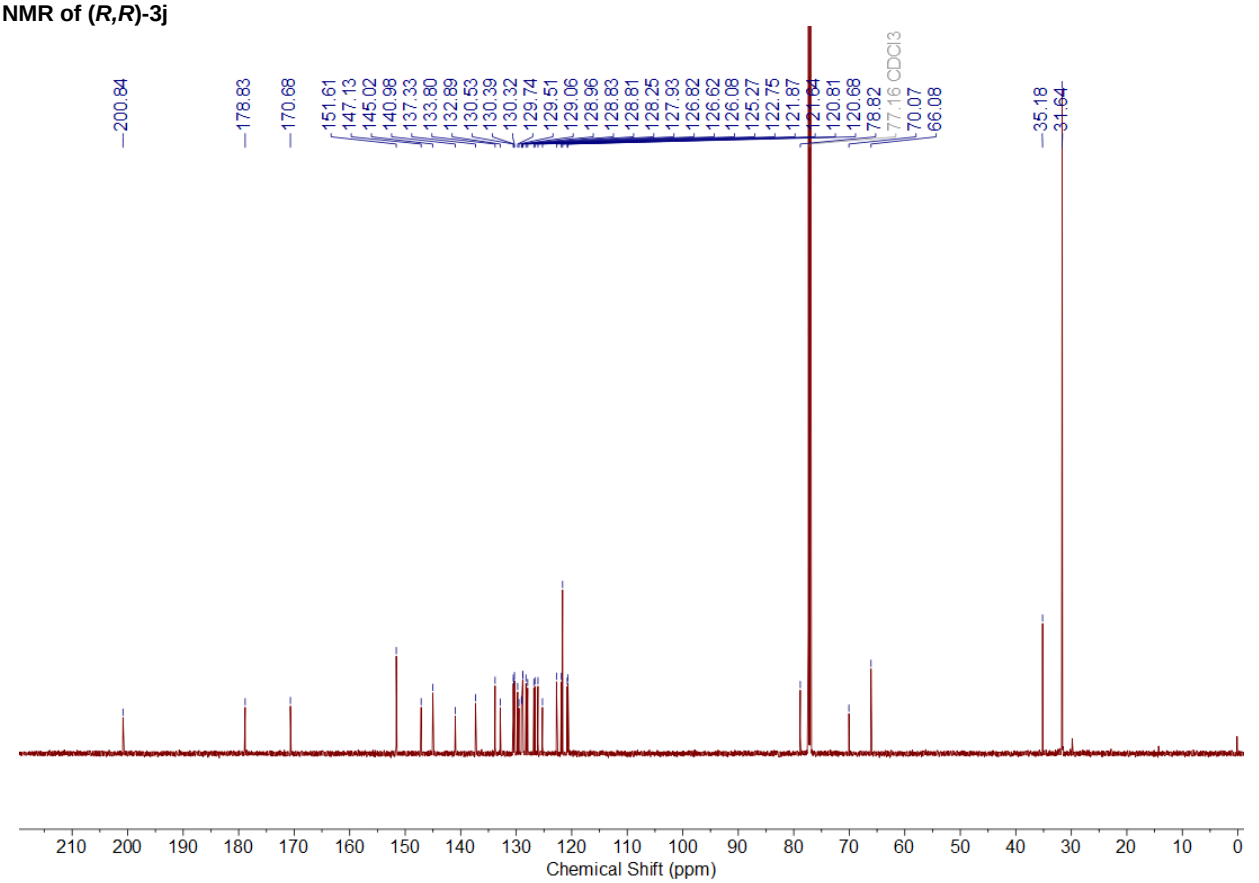
^{13}C NMR of (*R*,*S*)-3h



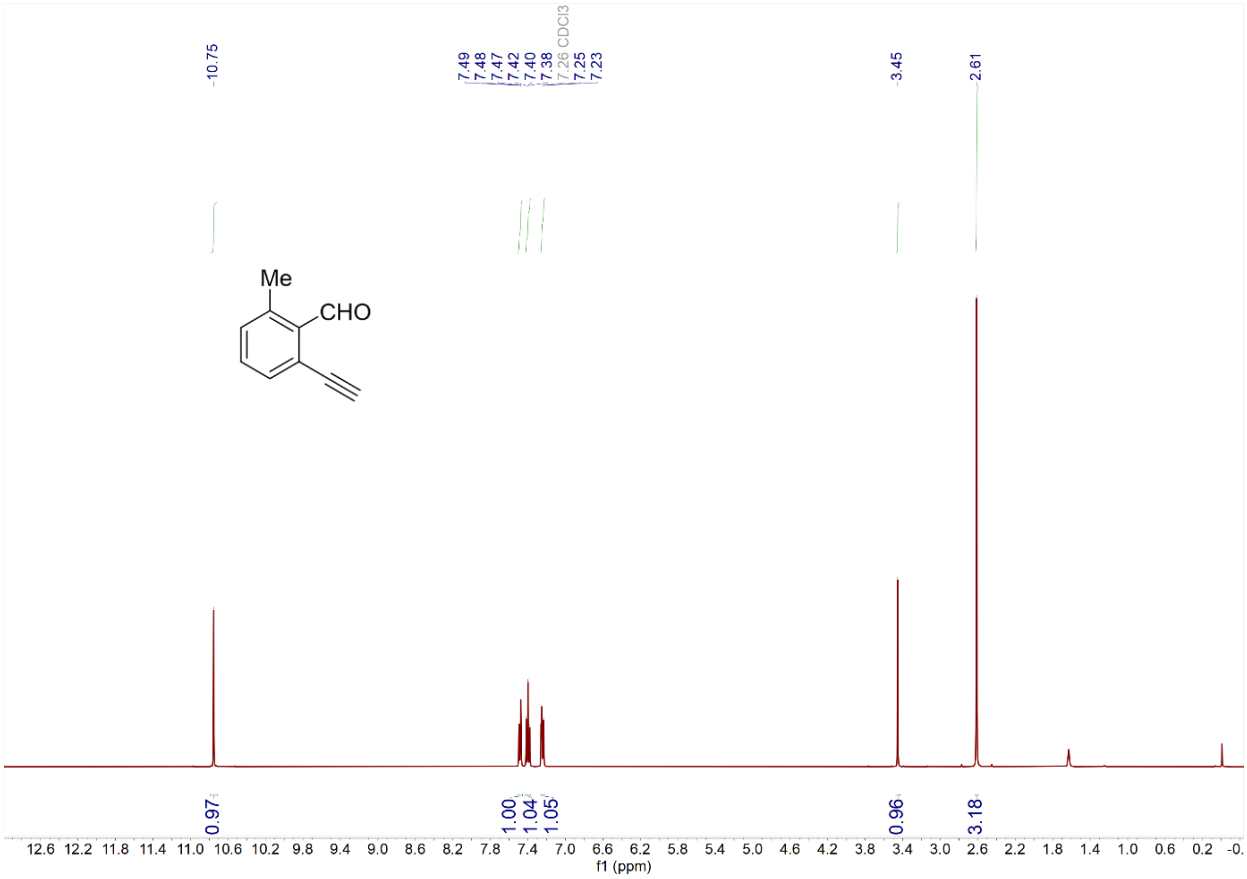
^{1}H NMR of (*R*,*R*)-3j



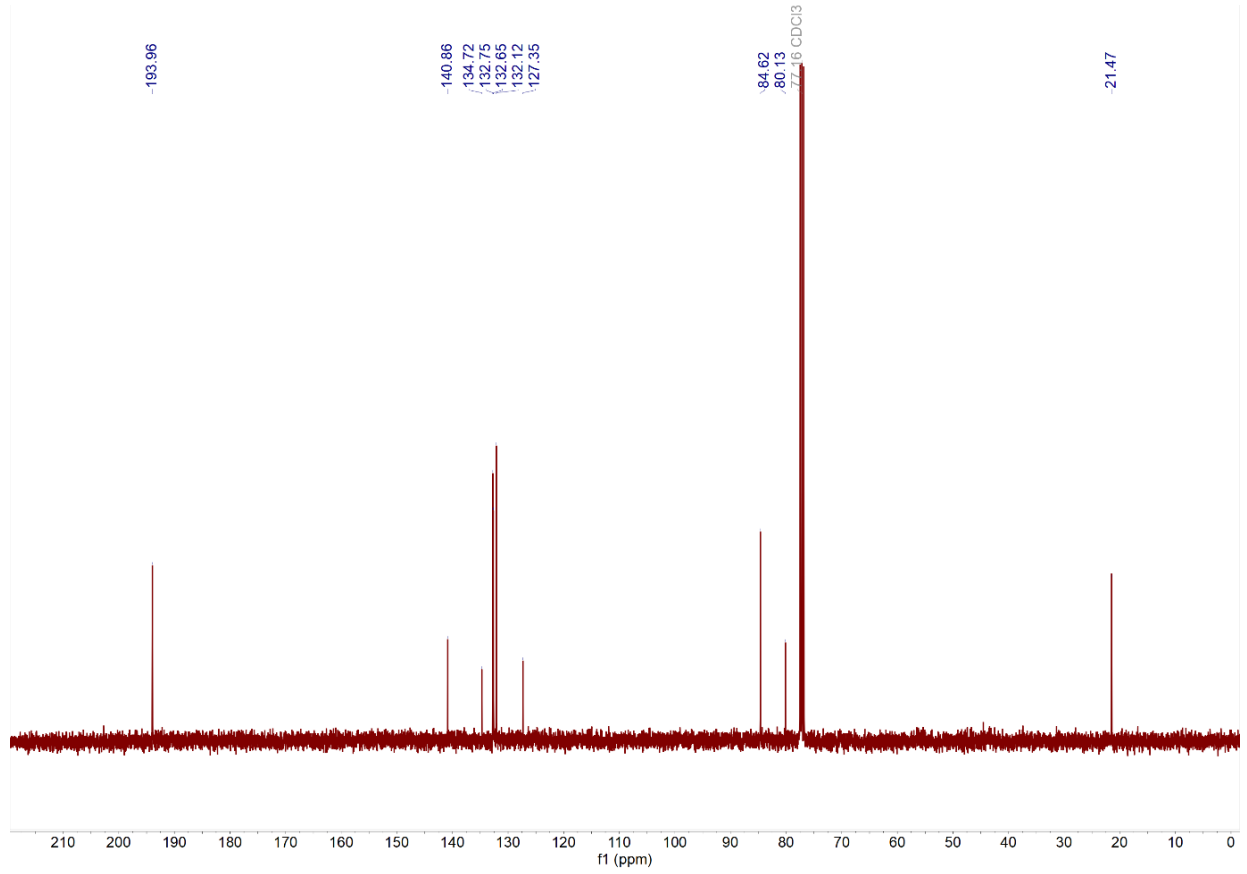
^{13}C NMR of (*R*,*R*)-3j



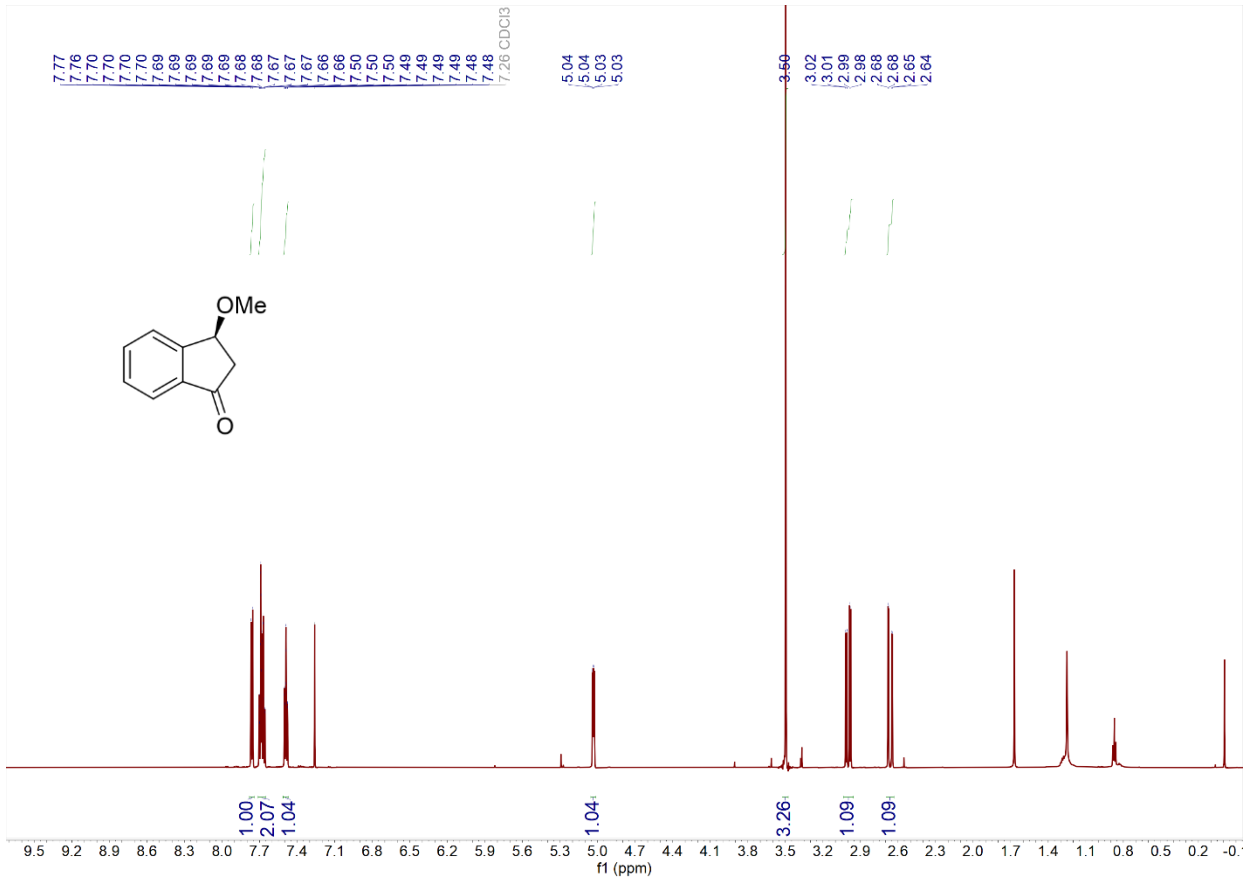
^{1}H NMR of 4f



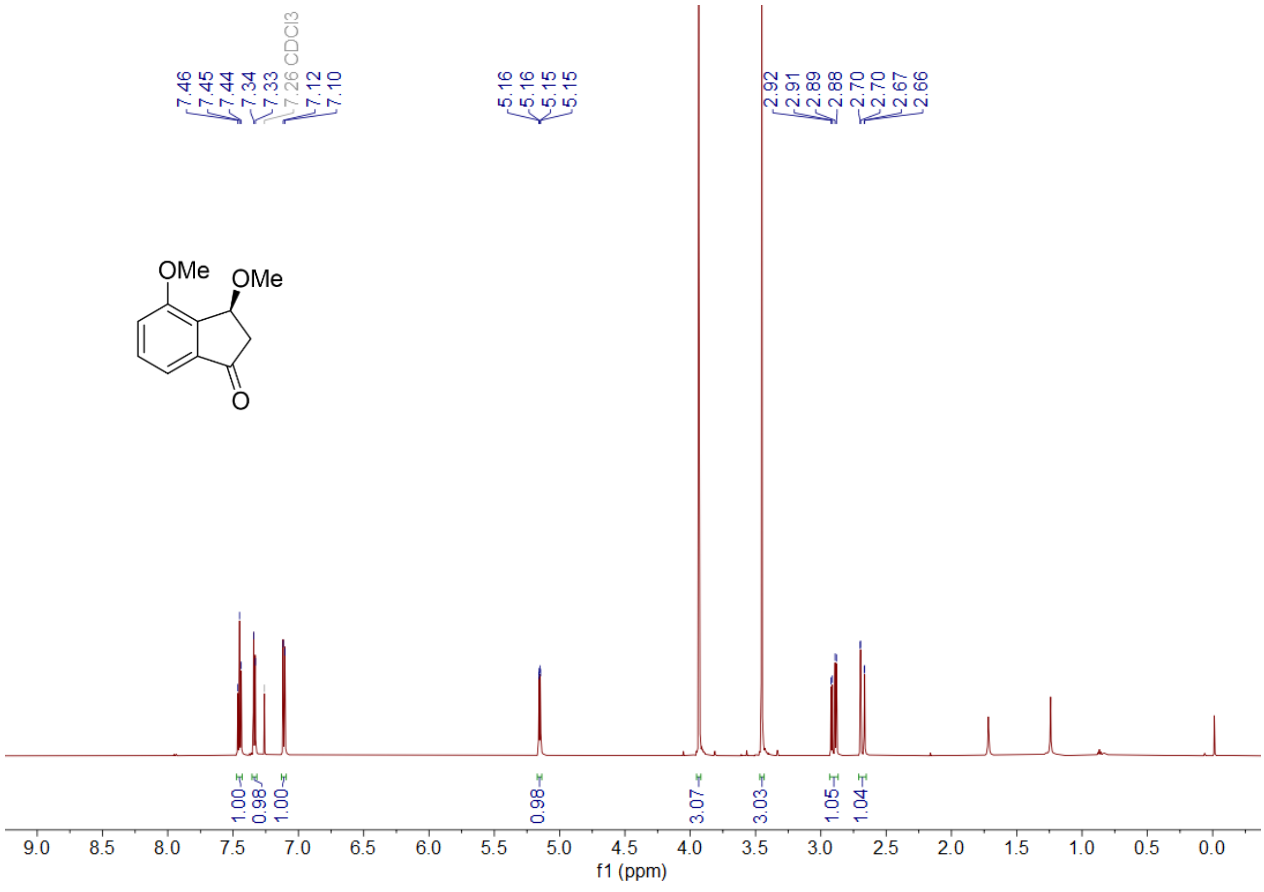
^{13}C NMR of 4f



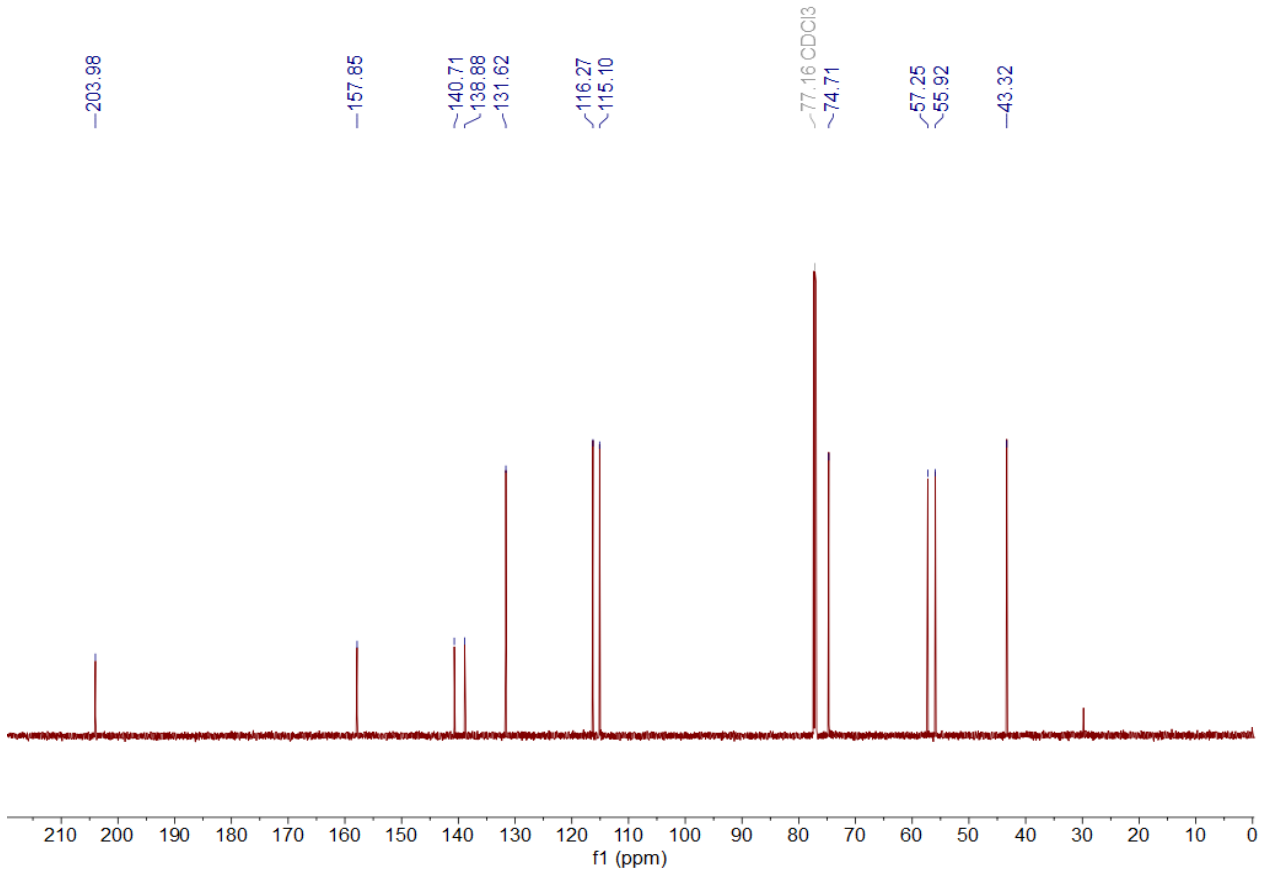
^{1}H NMR of 5a



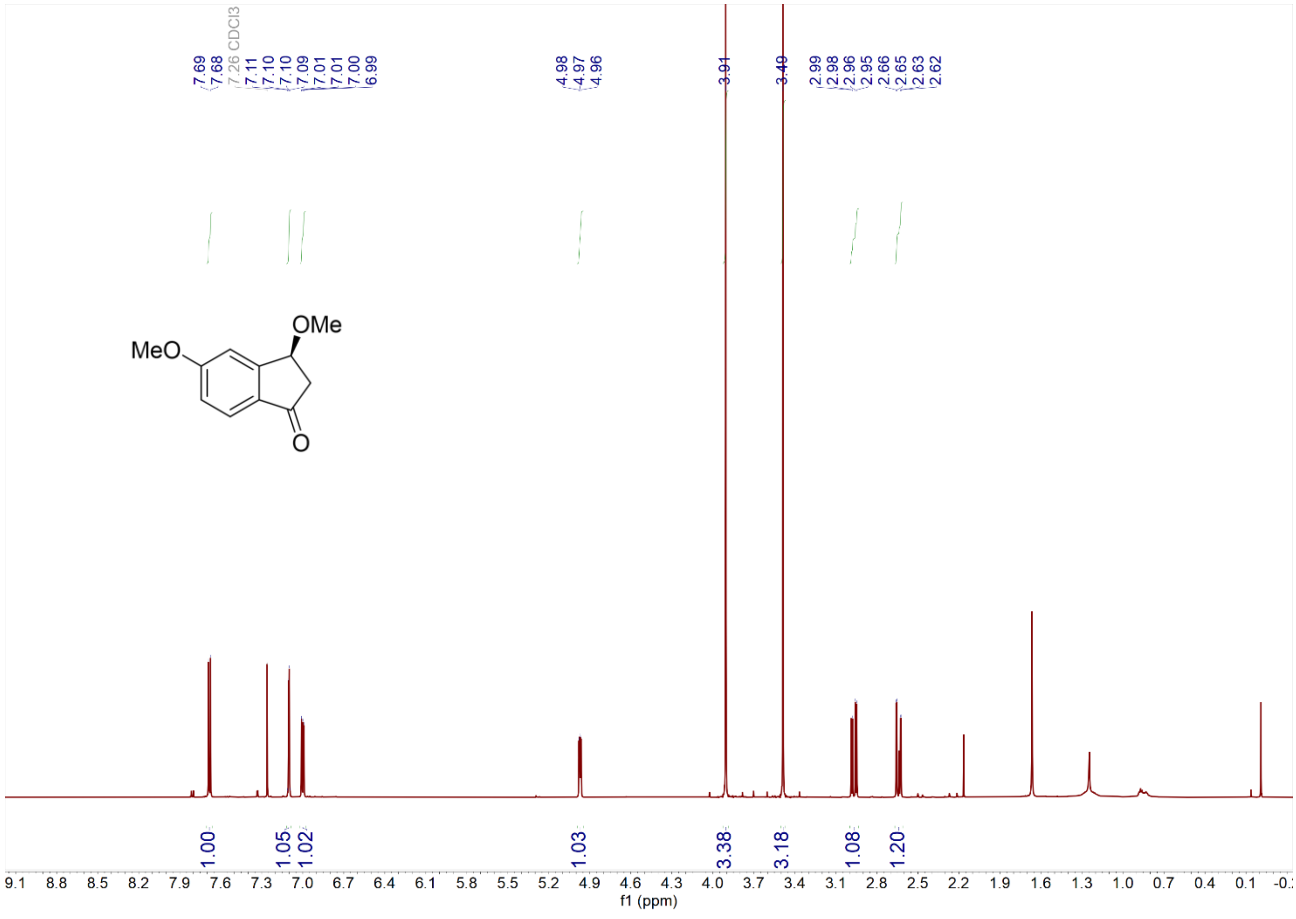
^{1}H NMR of 5b



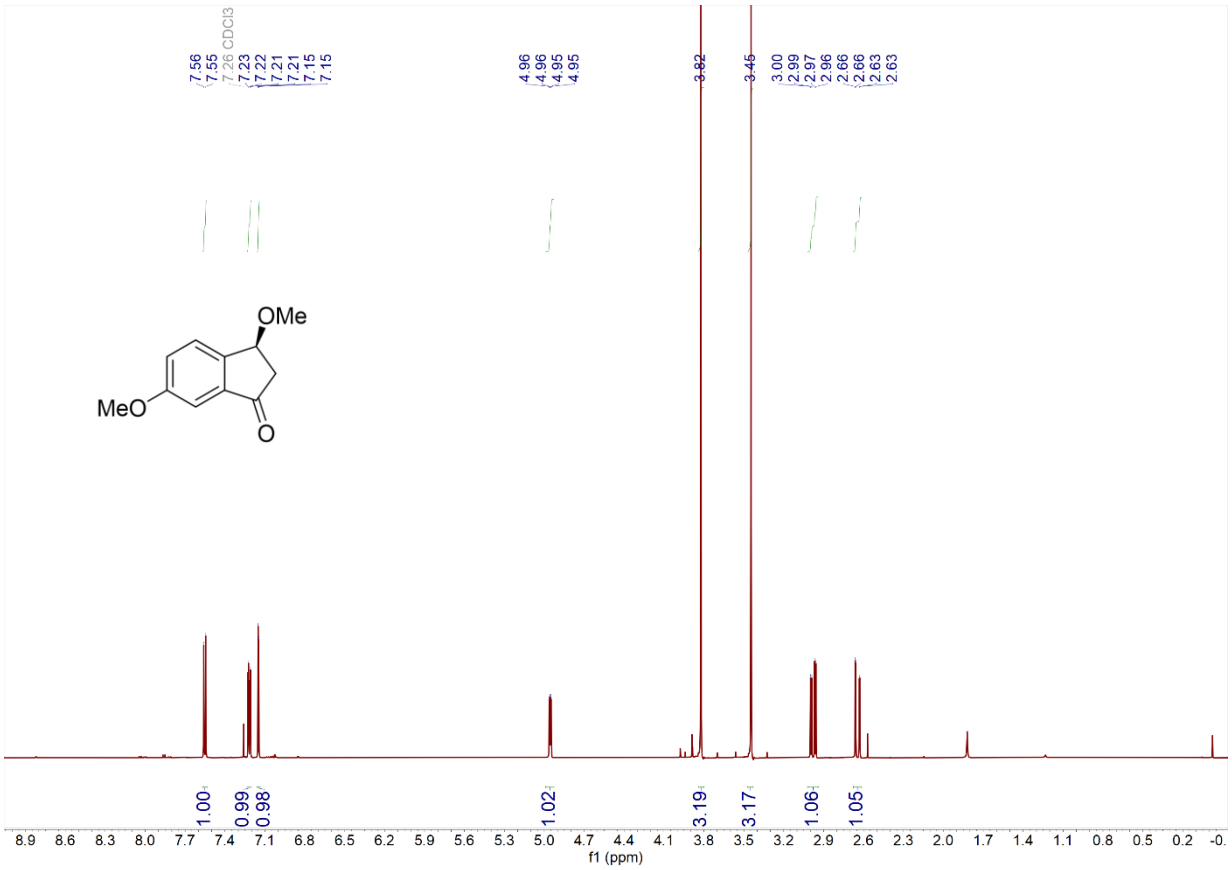
^{13}C NMR of 5b



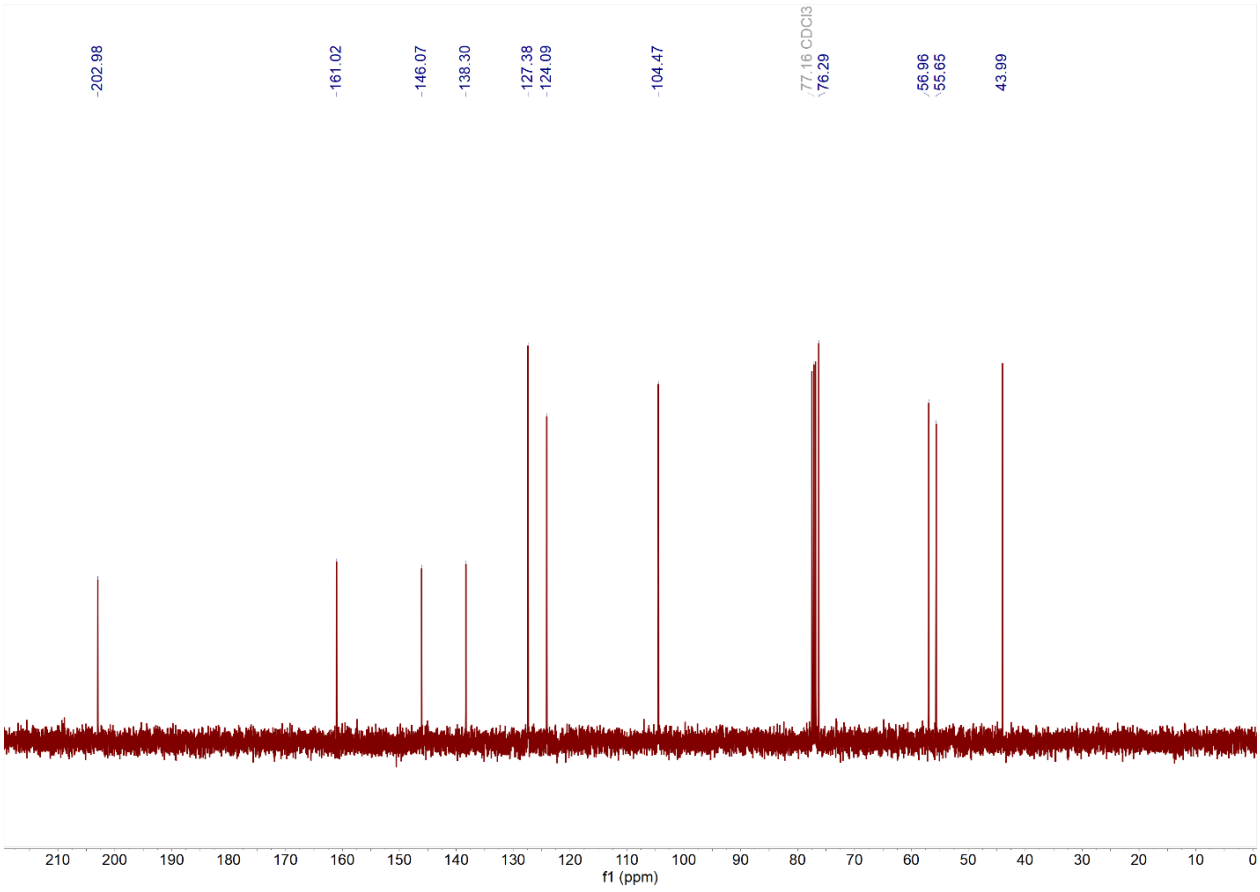
^{1}H NMR of 5c



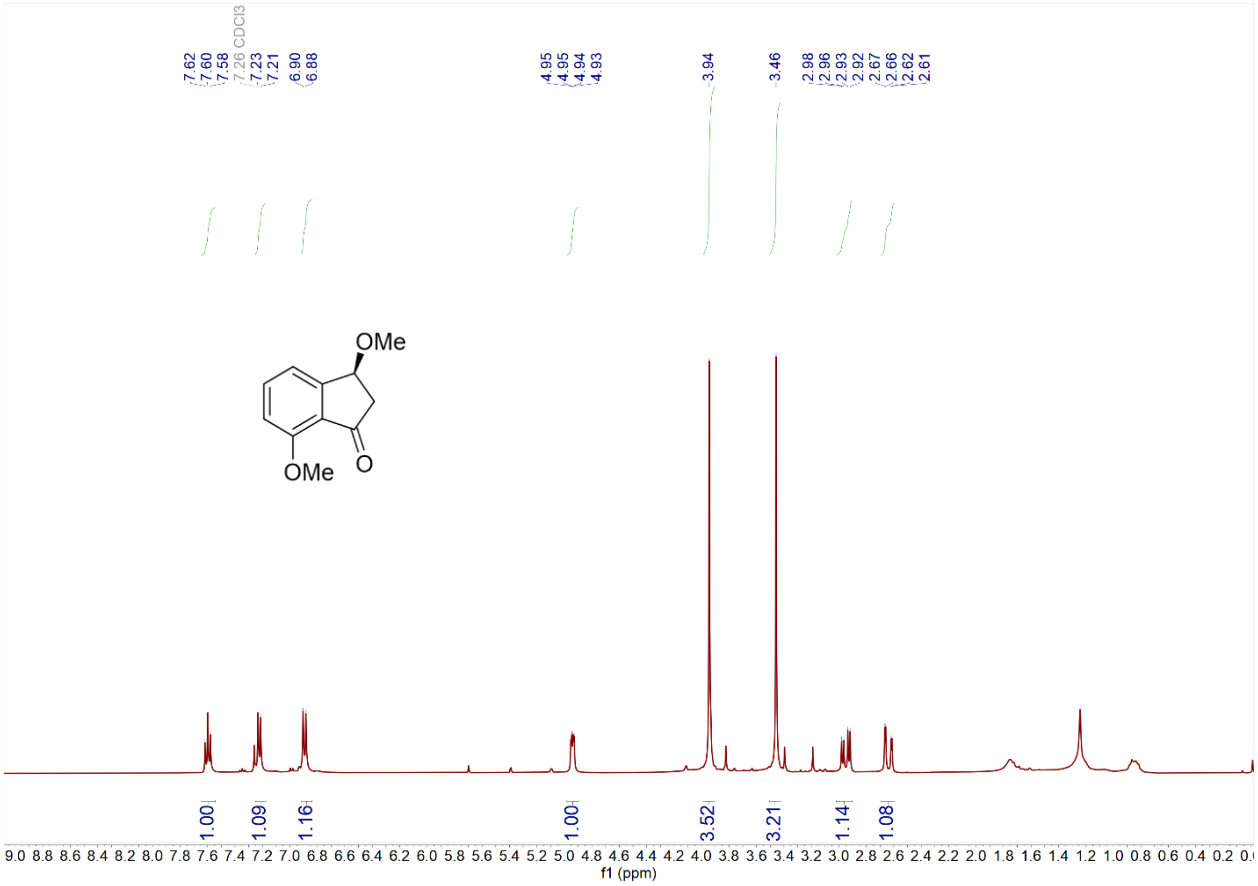
^{1}H NMR of 5d



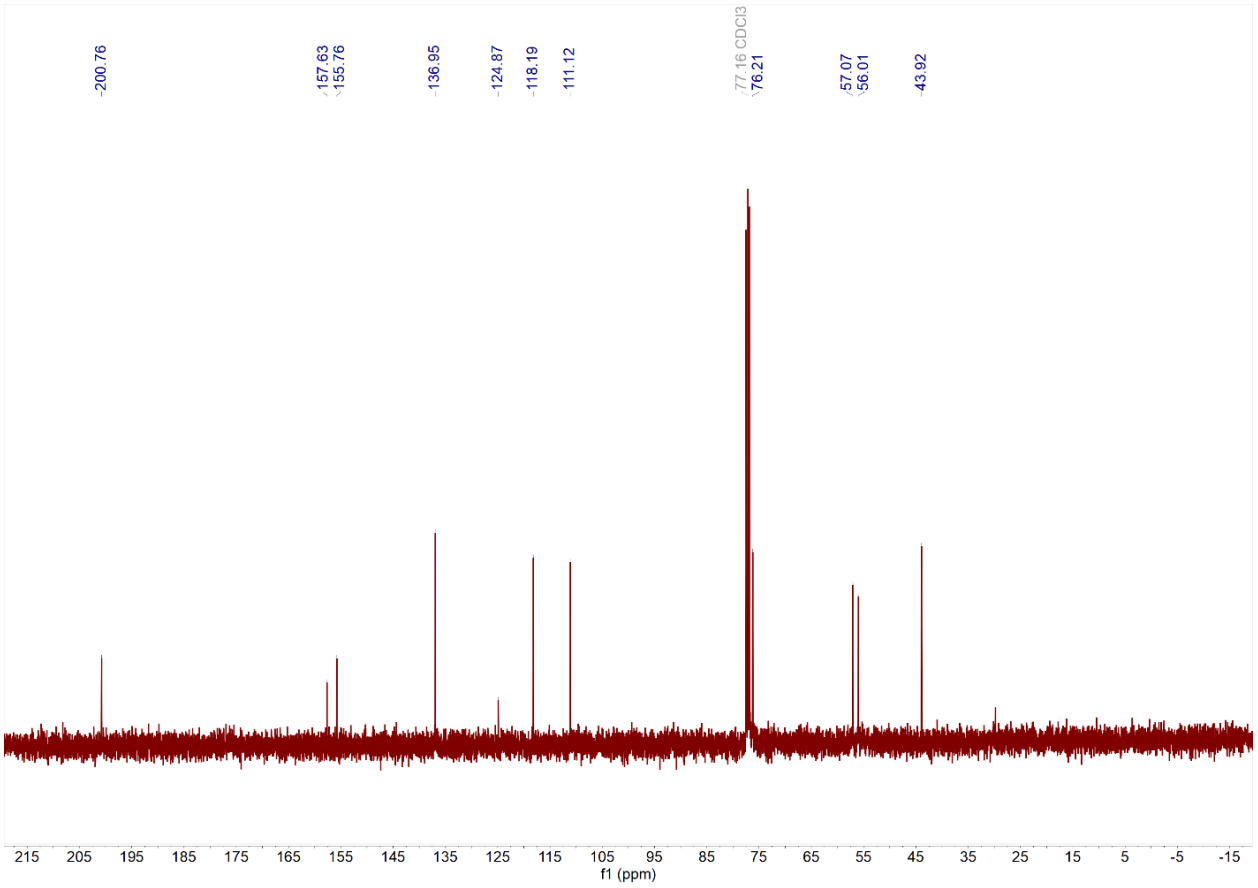
^{13}C NMR of 5d



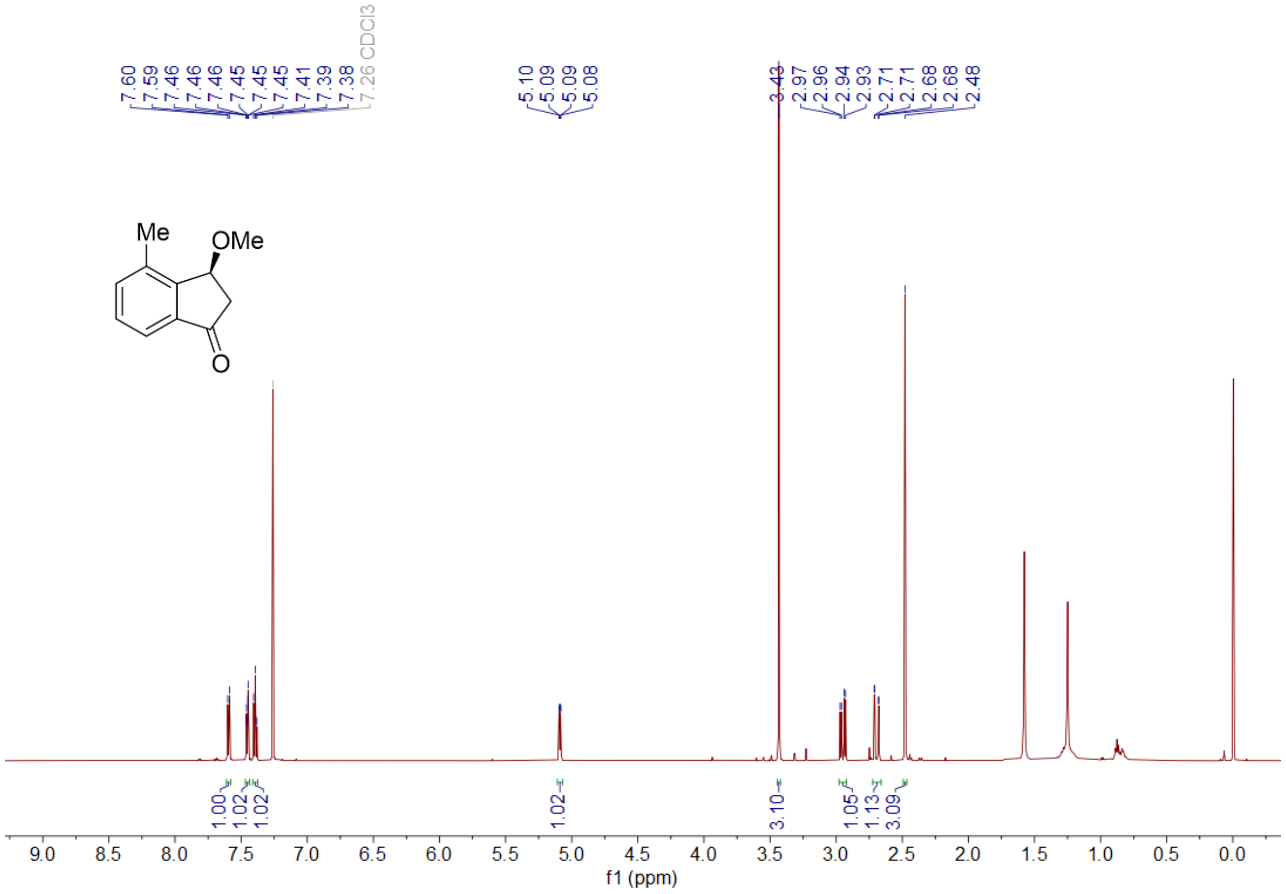
^{1}H NMR of 5e



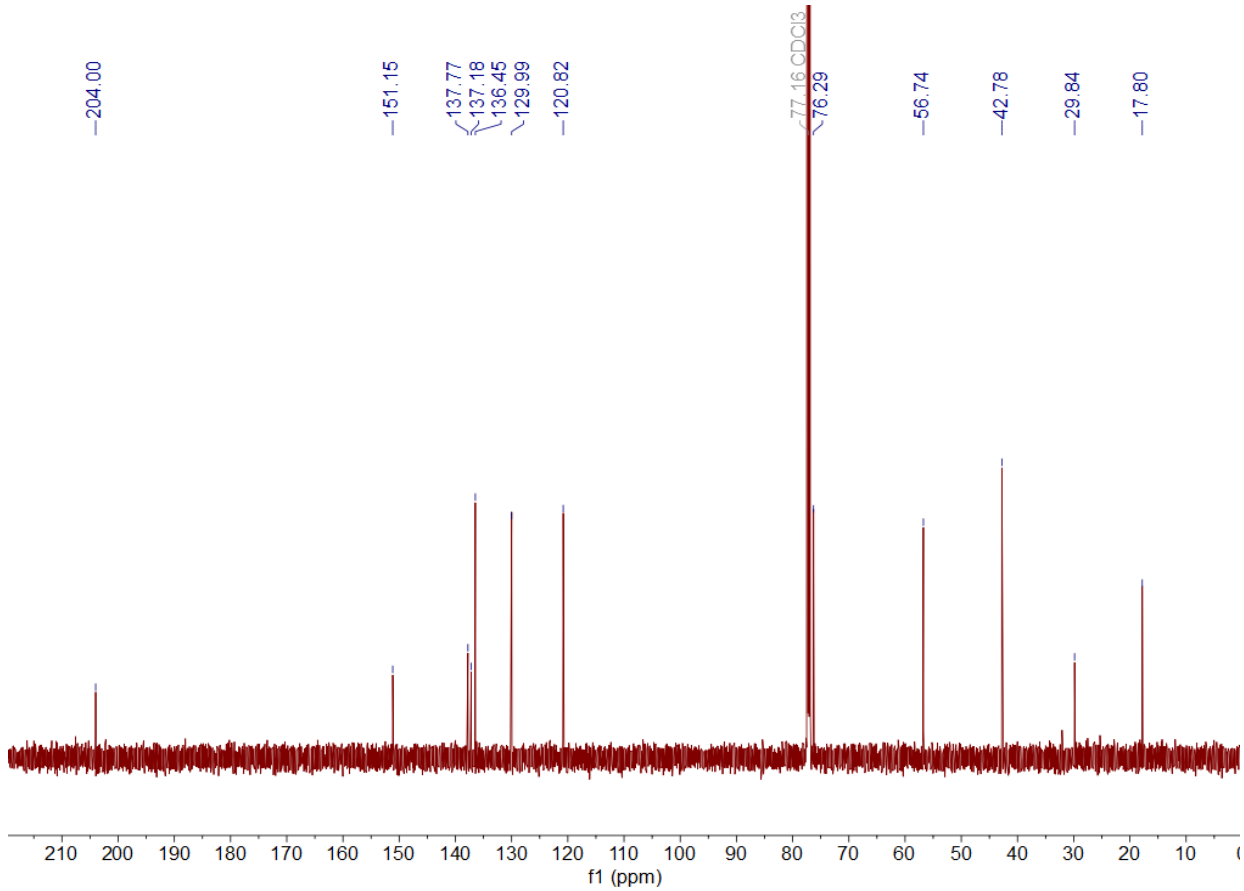
^{13}C NMR of 5e



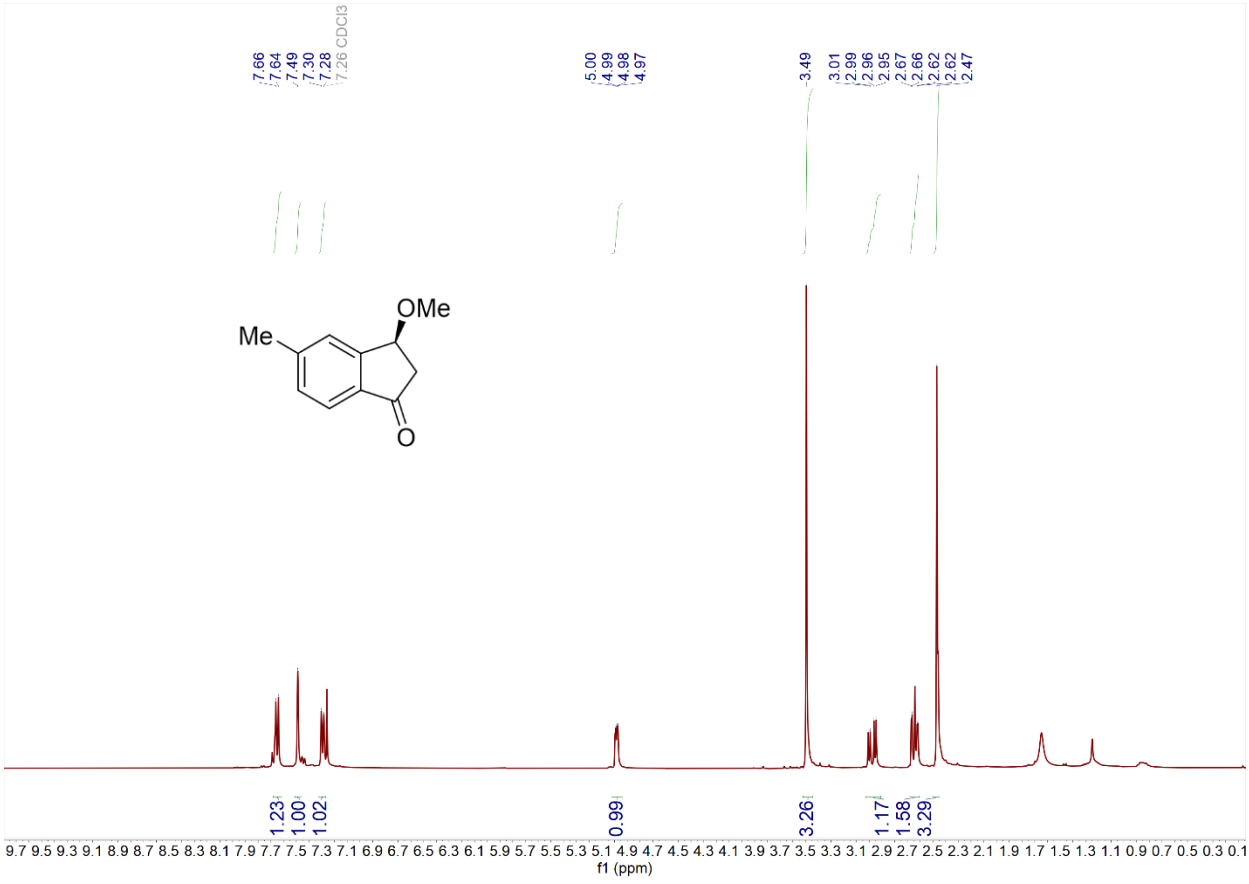
^{1}H NMR of 5f



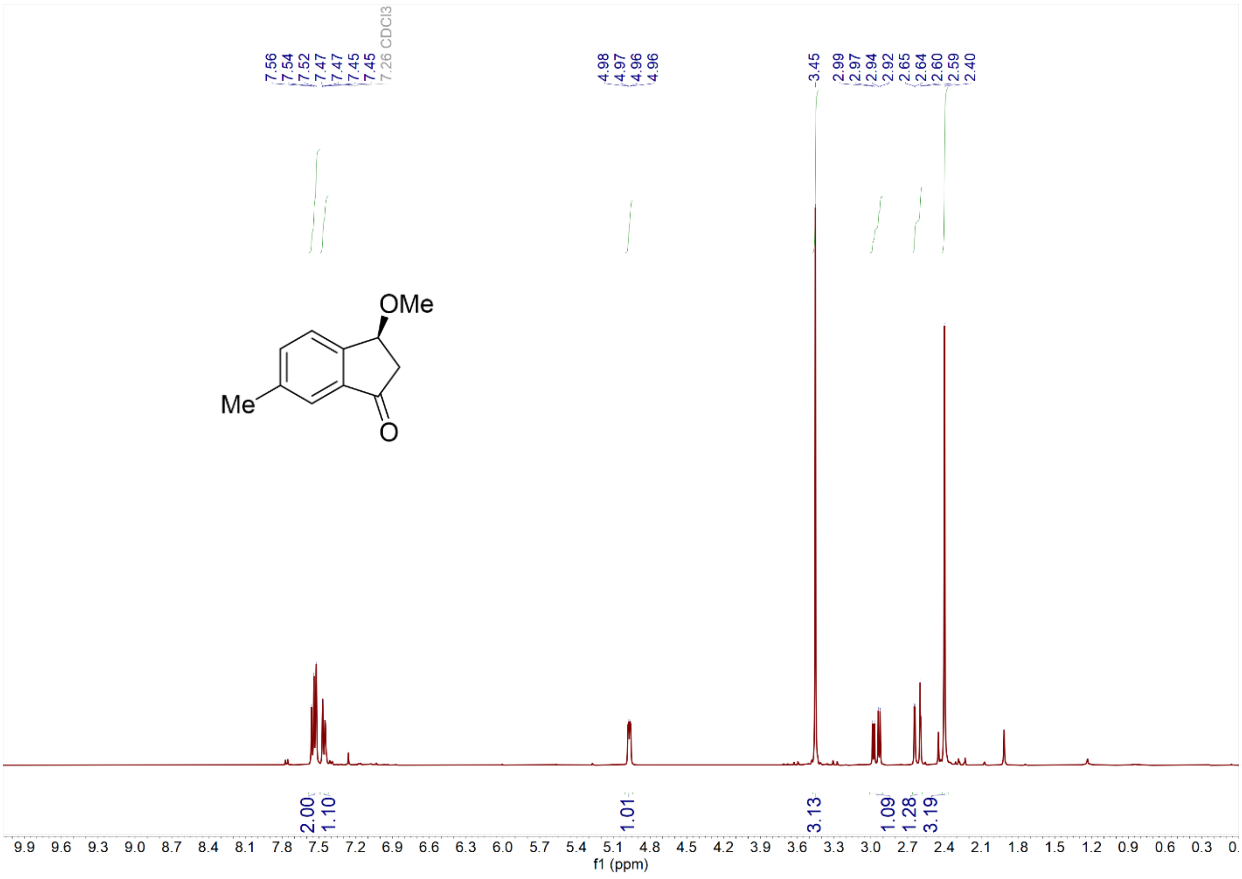
^{13}C NMR of 5f



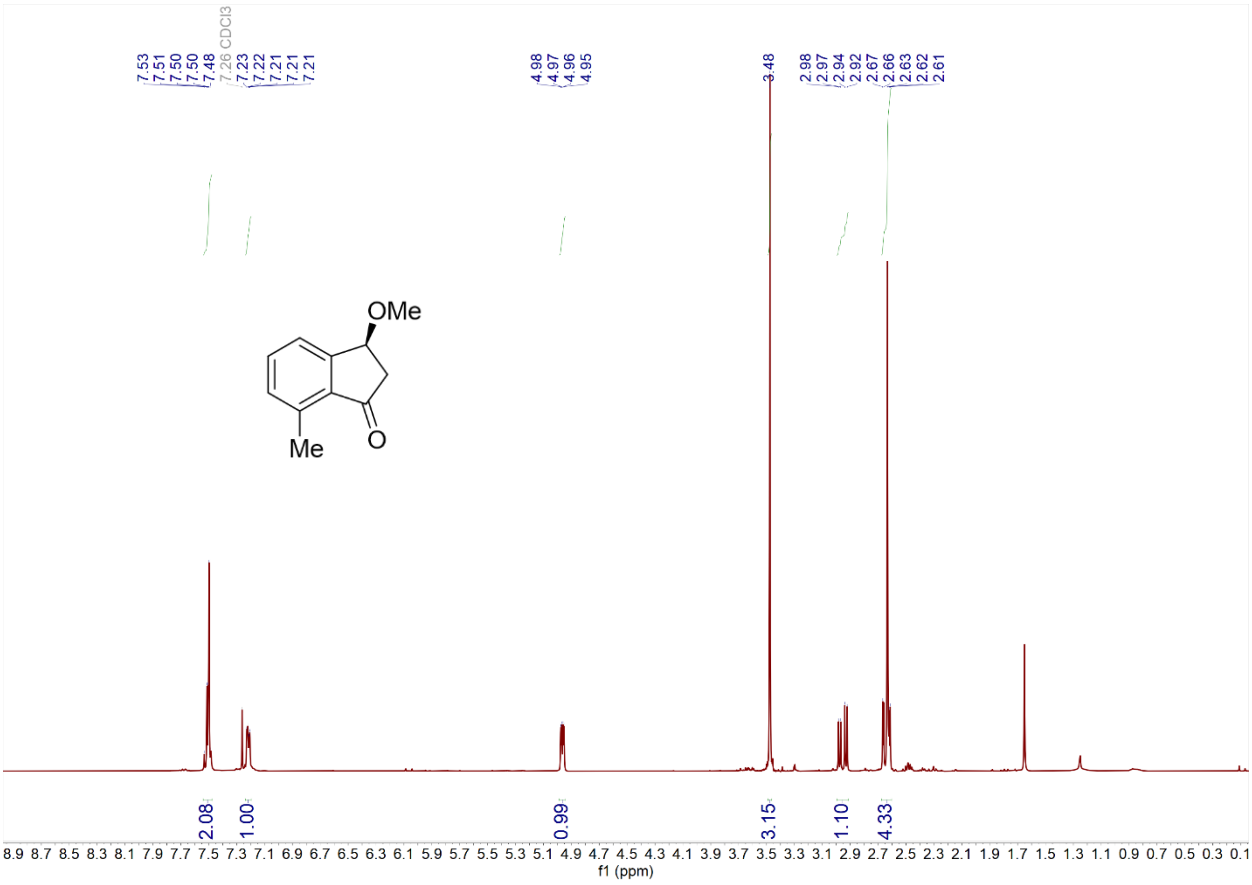
^{1}H NMR of 5g



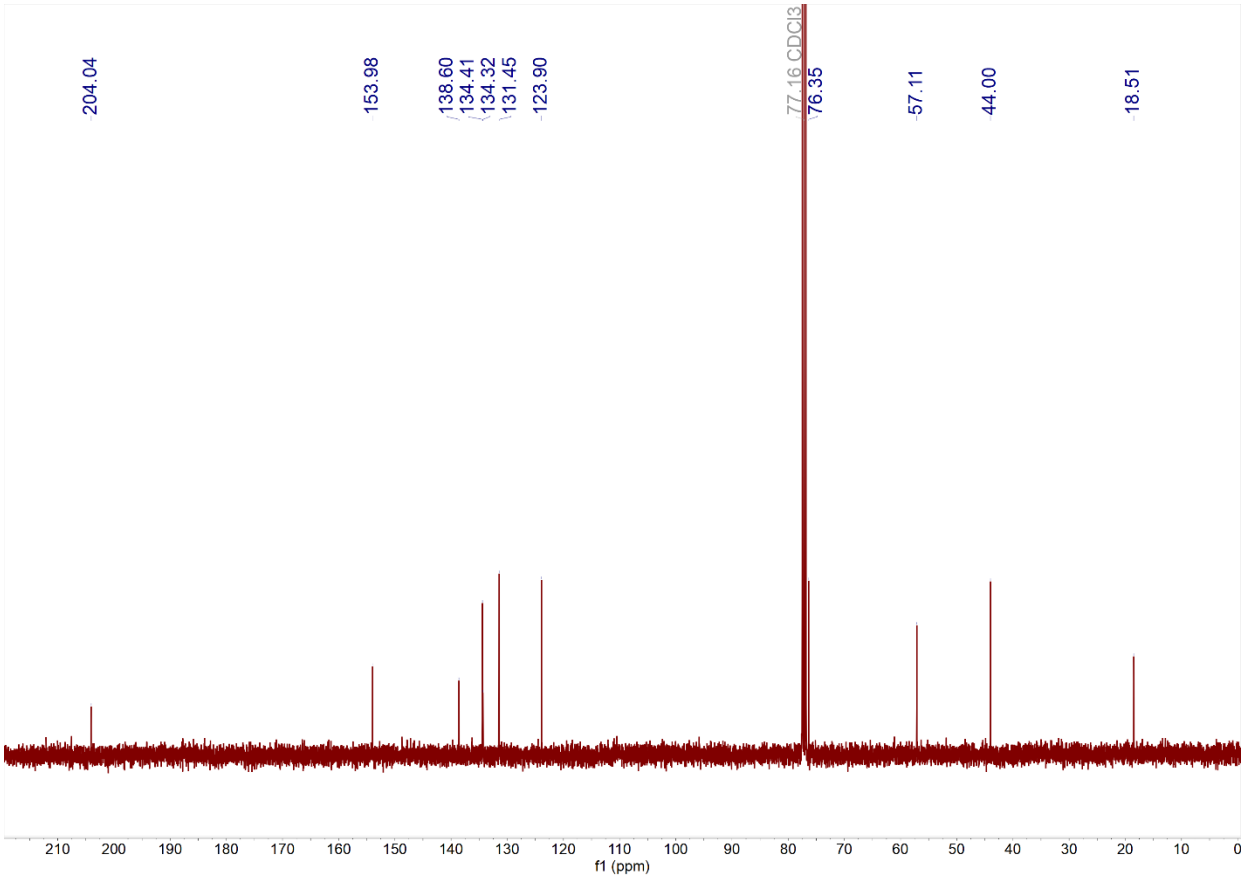
^{1}H NMR of 5h



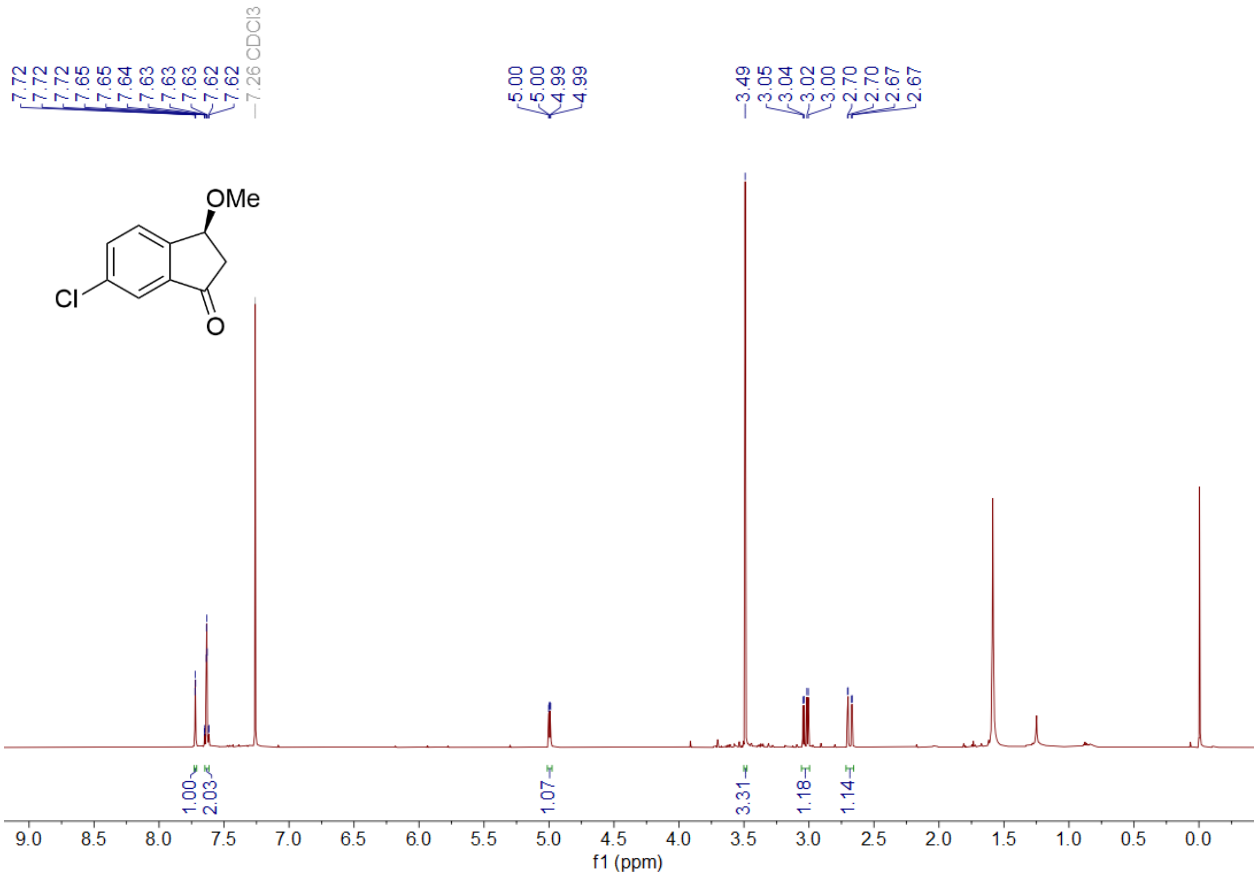
^{1}H NMR of 5i



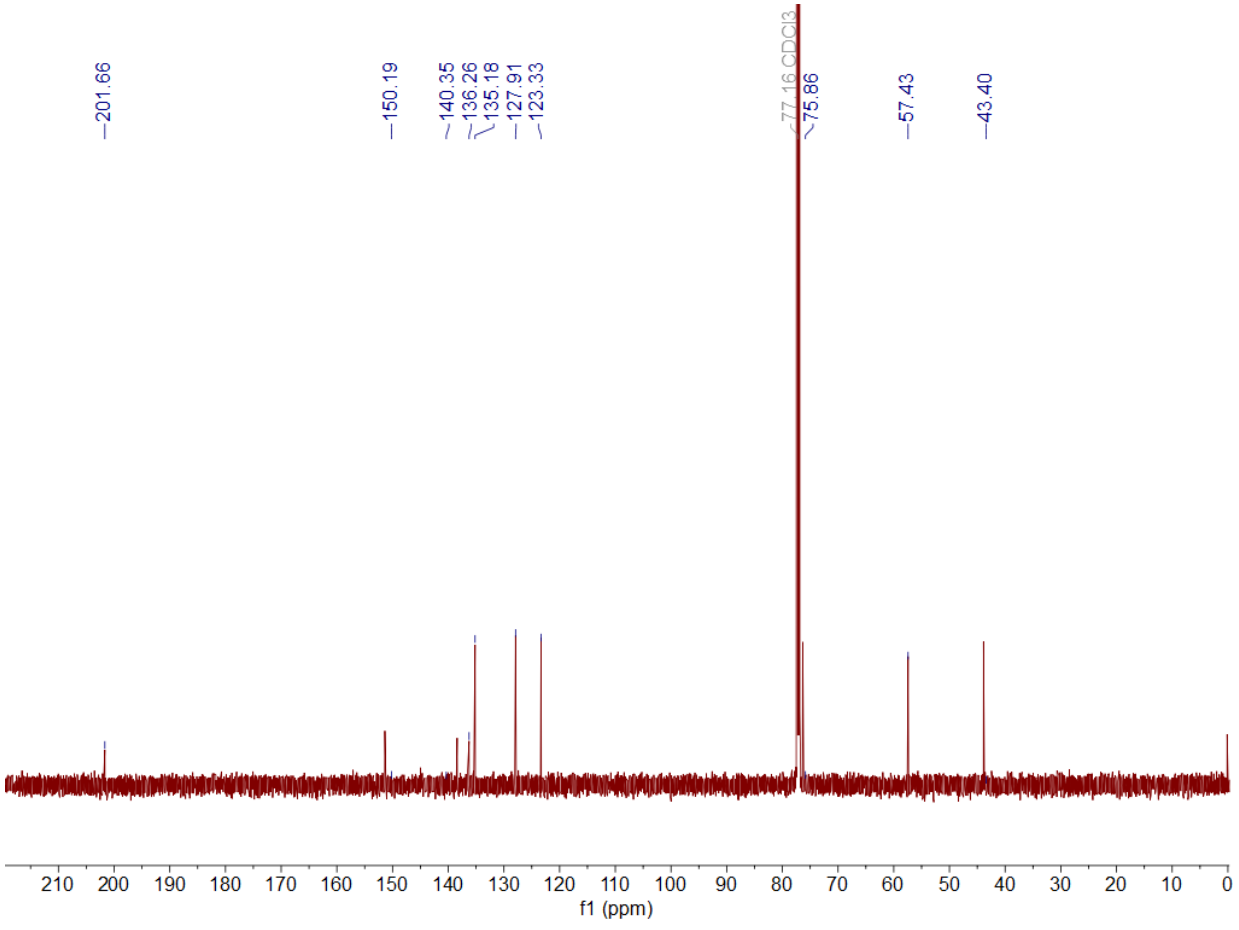
^{13}C NMR of 5i



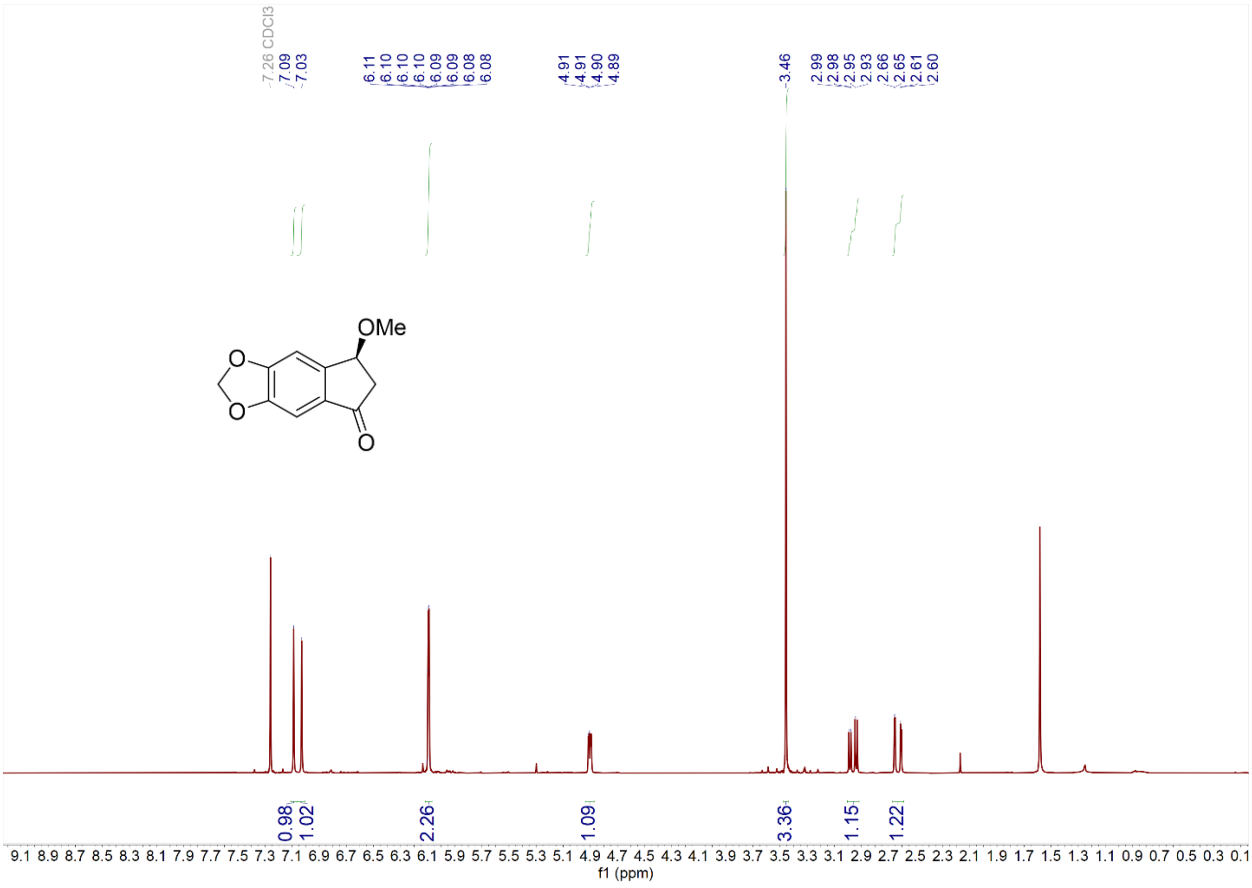
^{1}H NMR of 5j



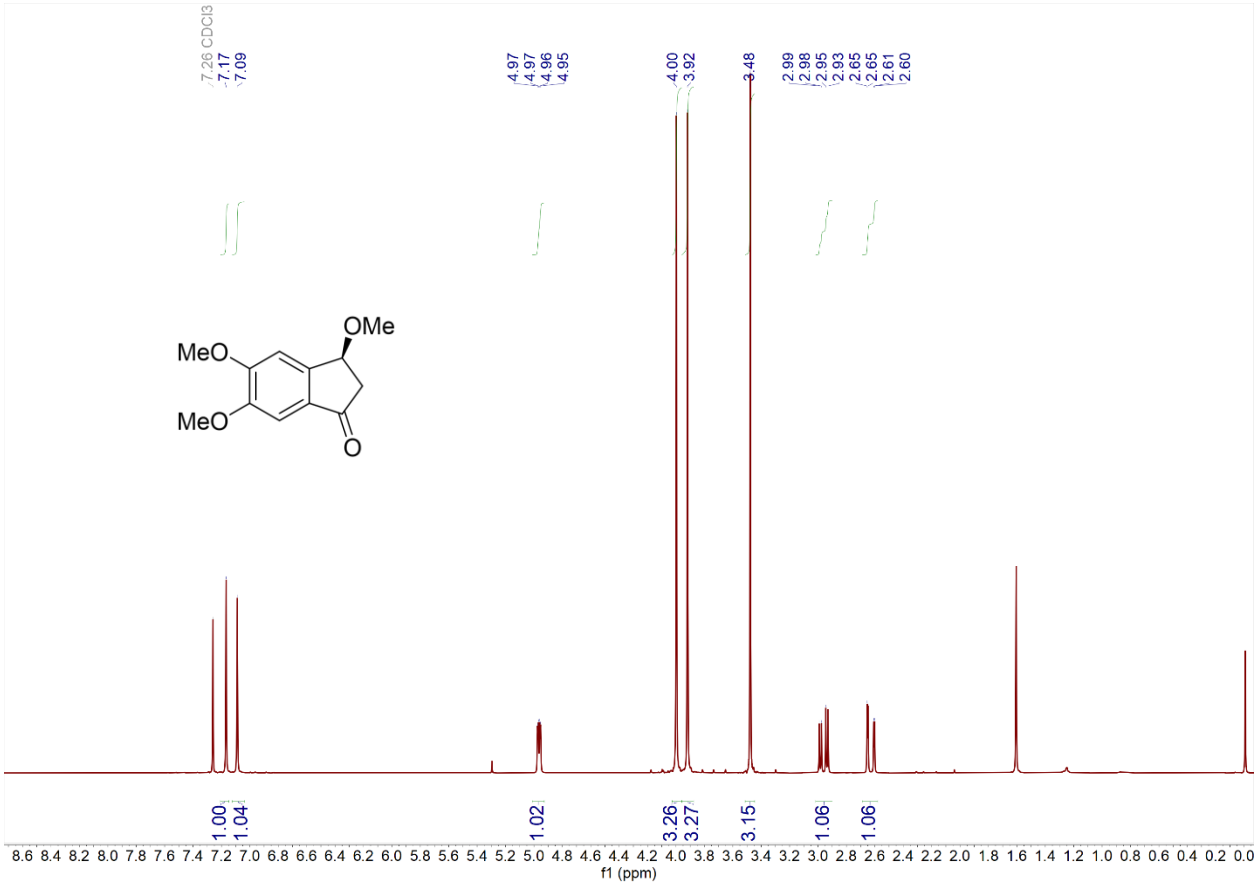
^{13}C NMR of 5j



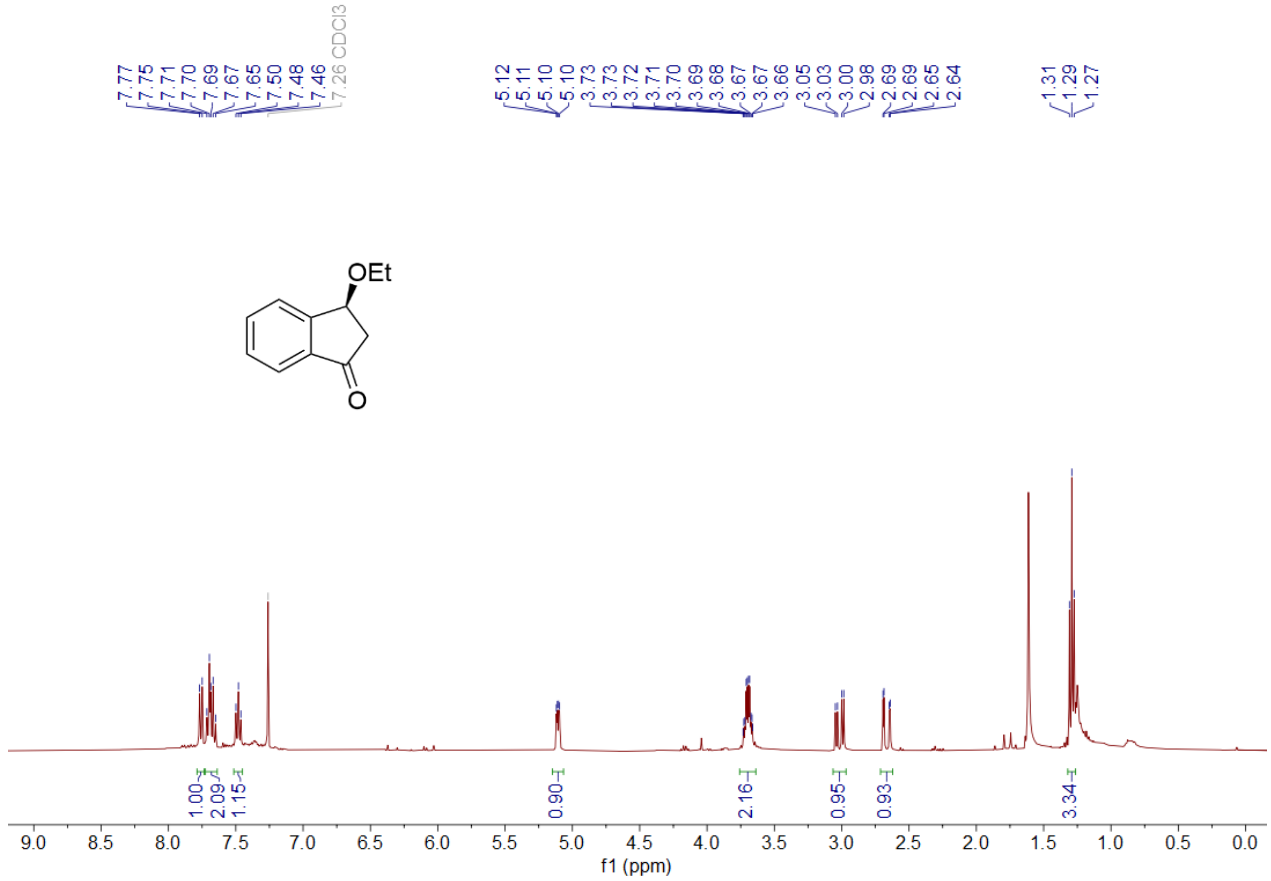
^{1}H NMR of 5l



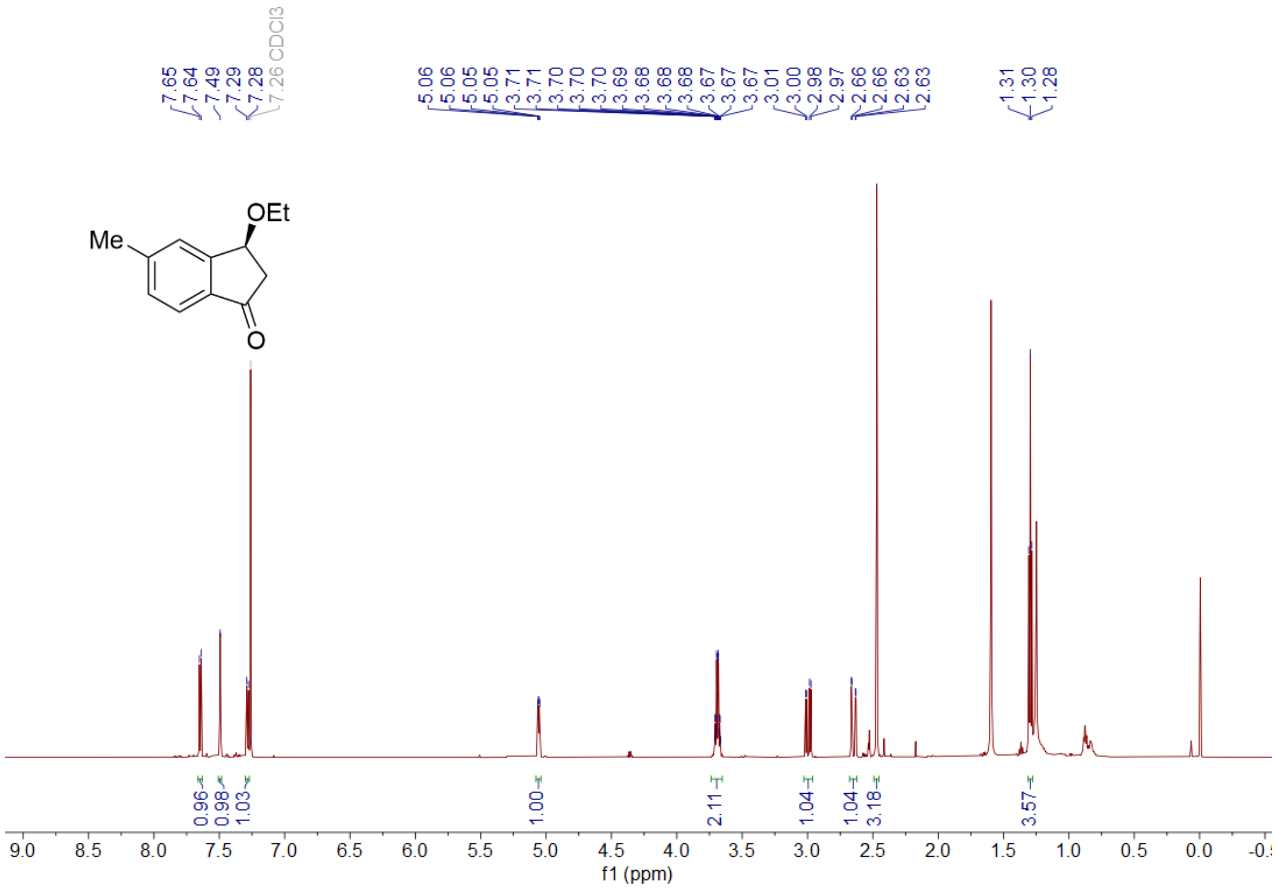
^{1}H NMR of 5m



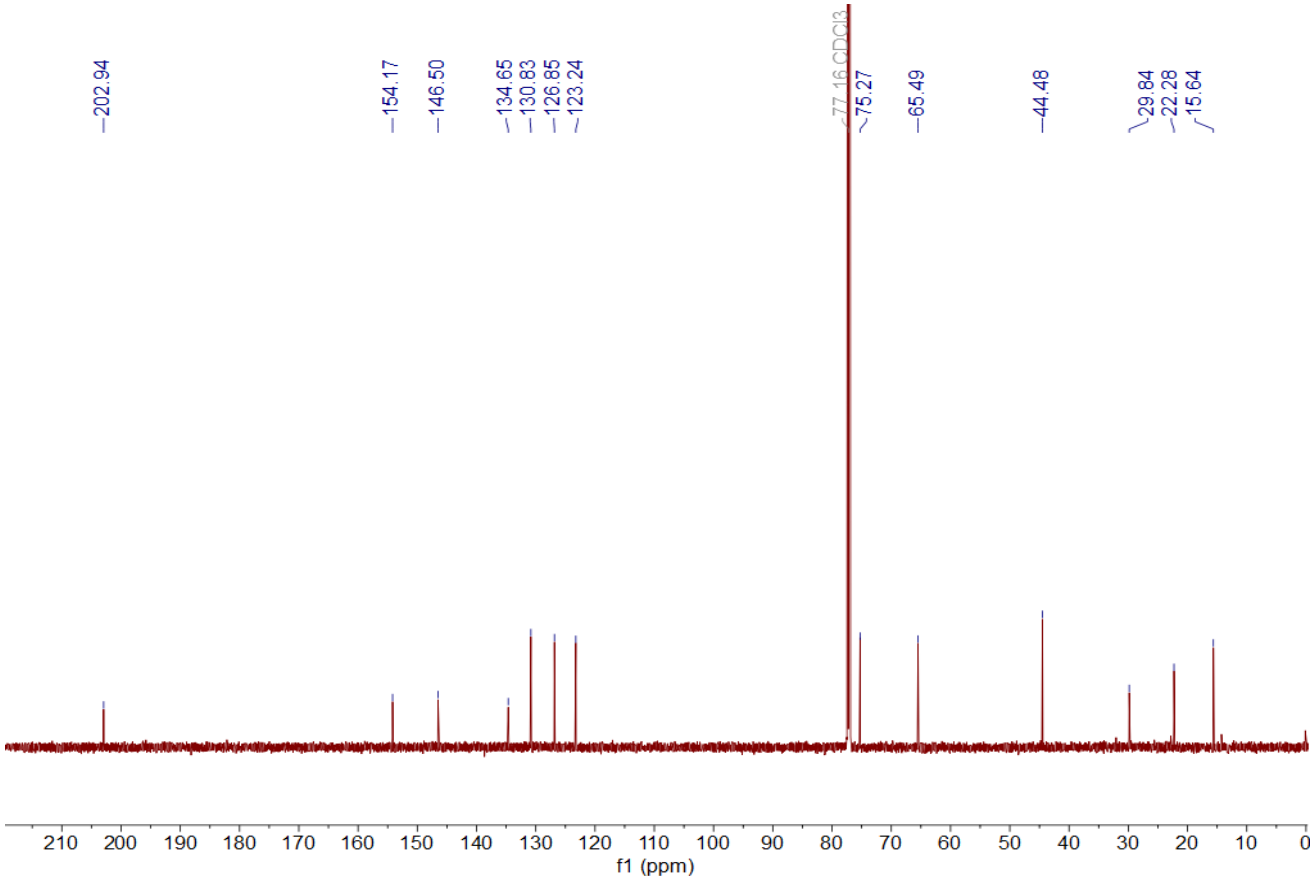
^{1}H NMR of 5n



^{1}H NMR of 5o

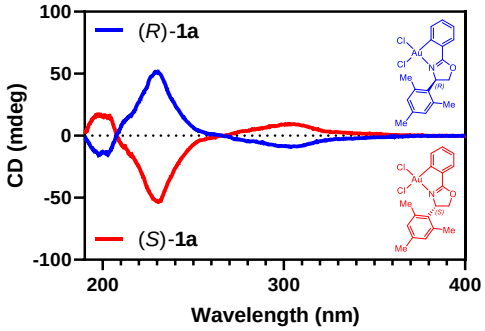


^{13}C NMR of 5o

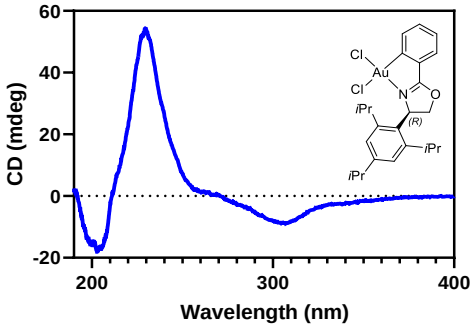

202.94
154.17
146.50
134.65
130.83
126.85
123.24
77.16 CDCl3
75.27
65.49
44.48
29.84
22.28
15.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Circular Dichroism Spectra

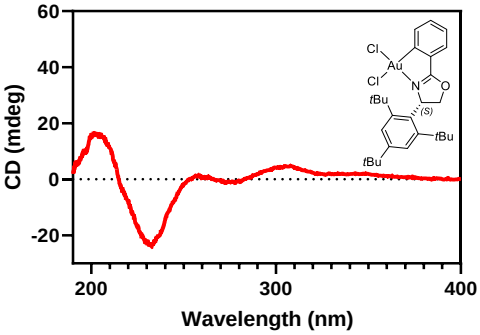
CD spectra of (*R*)-1a & (*S*)-1a in CH_3CN (25 μM)



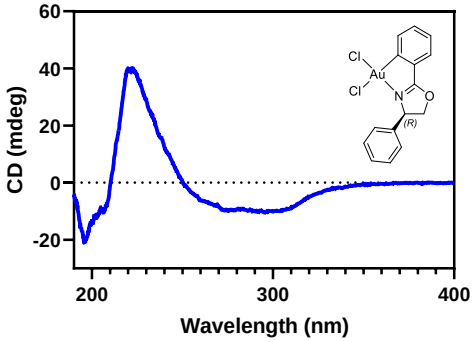
CD spectrum of (*R*)-1b in CH_3CN (25 μM)



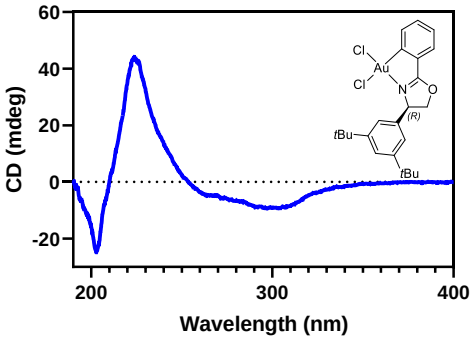
CD spectrum of (*S*)-1c in CH_3CN (25 μM)



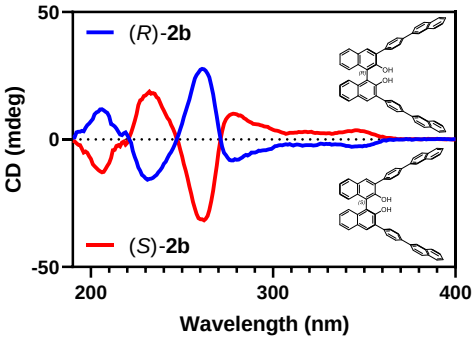
CD spectrum of (*R*)-1d in CH_3CN (25 μM)



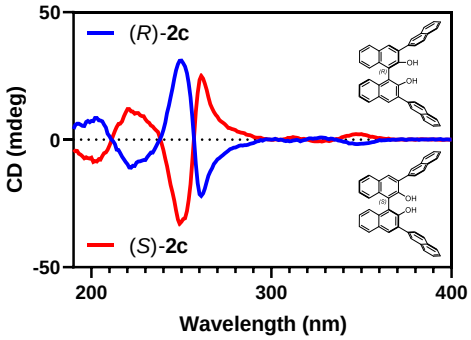
CD spectrum of (*R*)-1e in CH_3CN (25 μM)



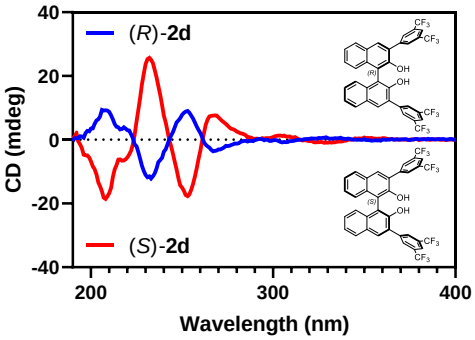
CD spectra of (*R*)-2b & (*S*)-2b in CH_3CN (10 μM)



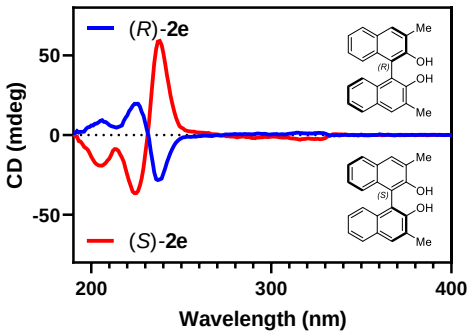
CD spectra of (*R*)-2c & (*S*)-2c in CH_3CN (10 μM)



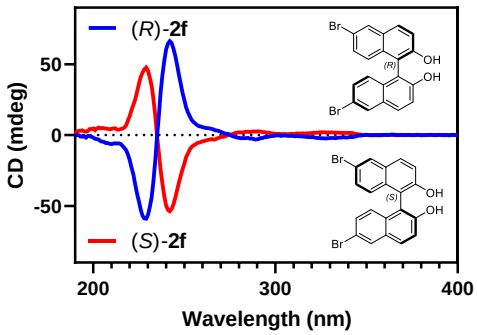
CD spectra of (*R*)-2d & (*S*)-2d in CH_3CN (10 μM)



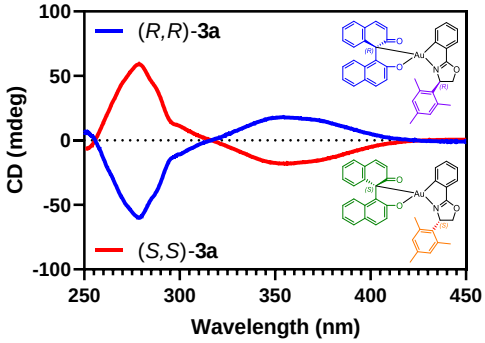
CD spectra of (*R*)-2e & (*S*)-2e in CH_3CN (10 μM)



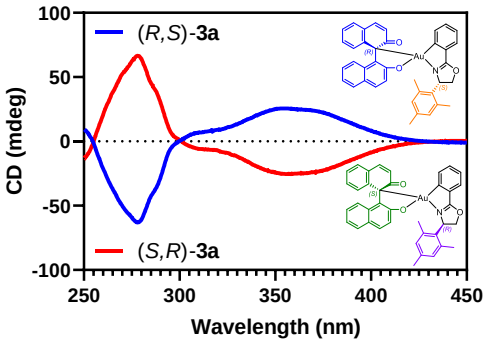
CD spectra of (*R*)-2f & (*S*)-2f in CH_3CN (10 μM)



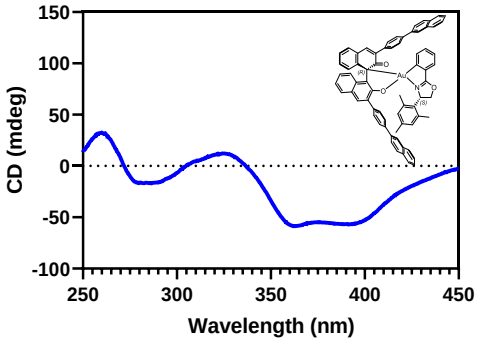
CD spectra of (*R,R*)-3a & (*S,S*)-3a in CH_3CN (25 μM)



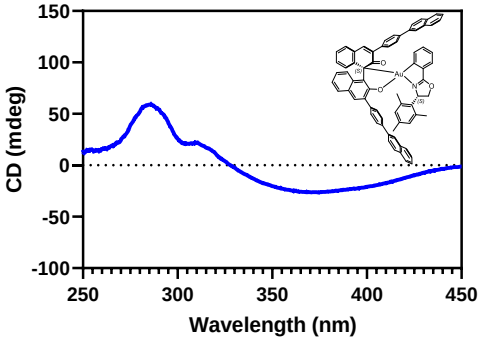
CD spectra of (*R,S*)-3a & (*S,R*)-3a in CH_3CN (25 μM)



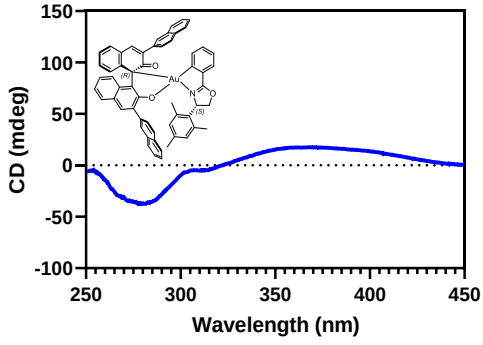
CD spectrum of (*R,S*)-3b in CH_3CN (25 μM)



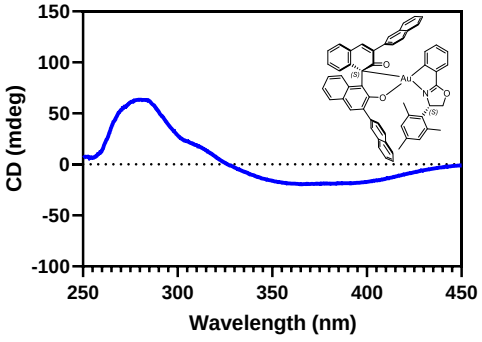
CD spectrum of (*S,S*)-3b in CH_3CN (25 μM)



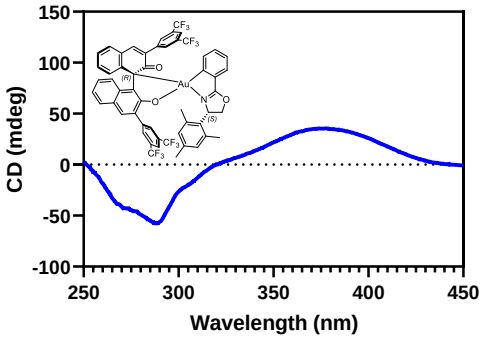
CD spectra of (*R,S*)-3c in CH_3CN (25 μM)



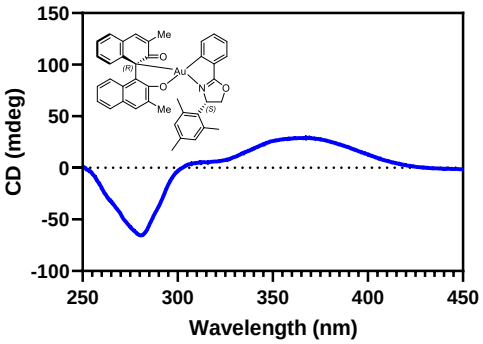
CD spectrum of (*S,S*)-3c in CH_3CN (25 μM)



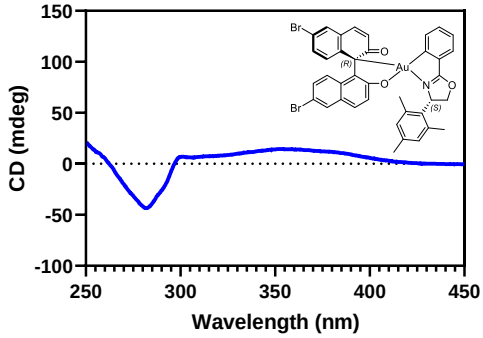
CD spectrum of (*R*,*S*)-3d in CH_3CN (25 μM)



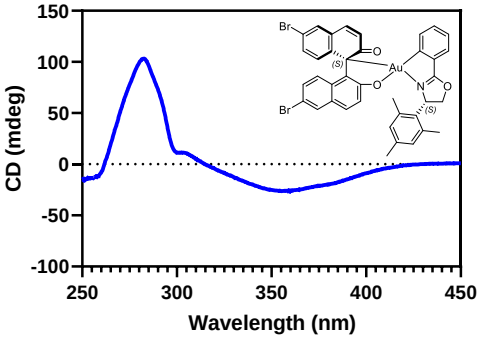
CD spectrum of (*R*,*S*)-3e in CH_3CN (25 μM)



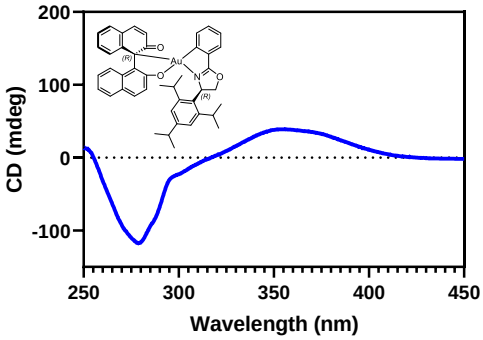
CD spectrum of (*R*,*S*)-3f in CH_3CN (25 μM)



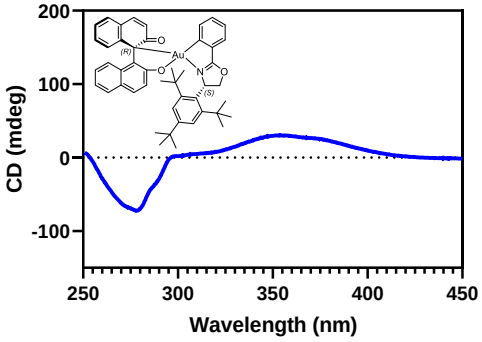
CD spectrum of (*S*,*S*)-3f in CH_3CN (25 μM)



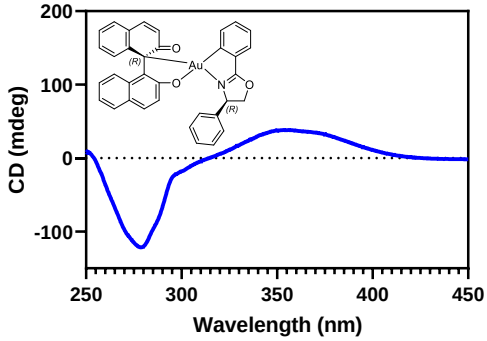
CD spectrum of (*R*,*R*)-3g in CH_3CN (25 μM)



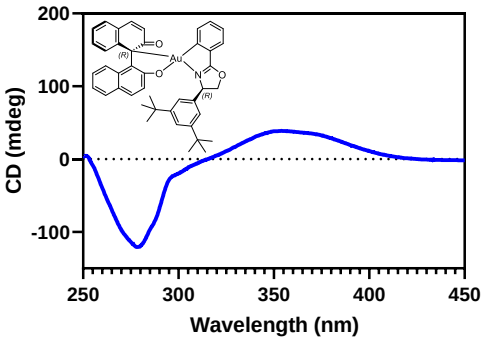
CD spectrum of (*R*,*S*)-3h in CH_3CN (25 μM)

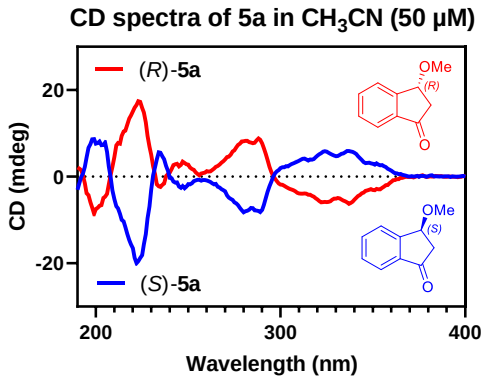


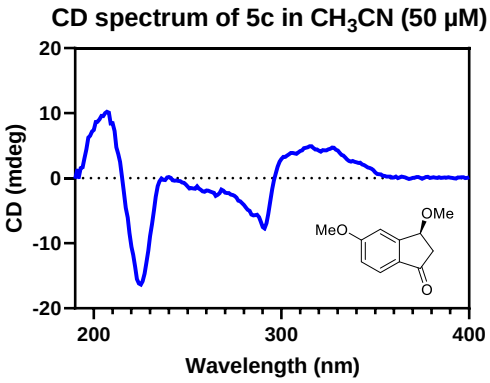
CD spectrum of (*R*,*R*)-3i in CH_3CN (25 μM)

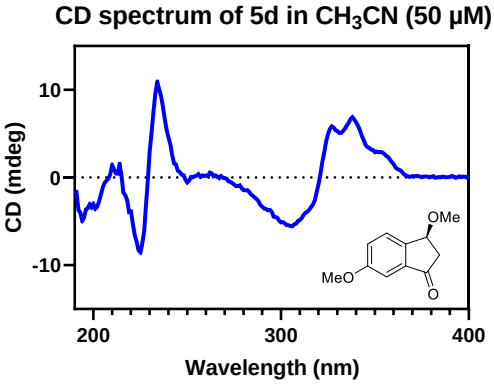


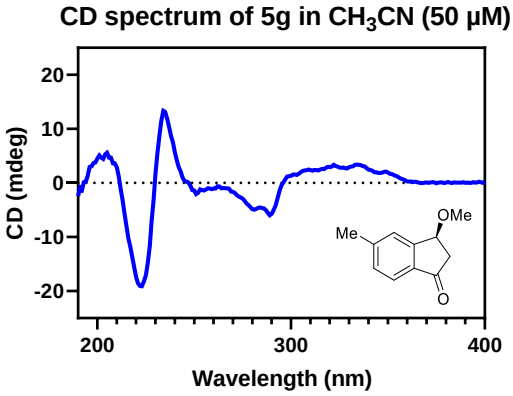
CD spectrum of (*R*,*R*)-3j in CH_3CN (25 μM)

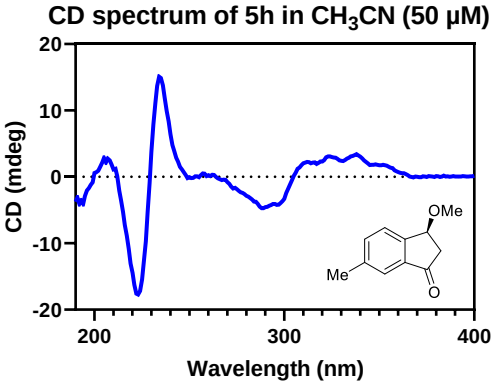


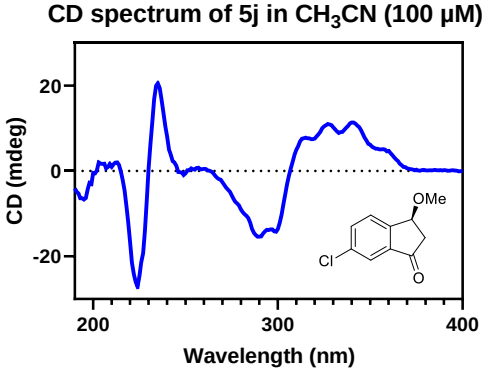

CD spectra of 5a in CH3CN (50 μM)
(R)-5a
(S)-5a
OMe
(R)
OMe
(S)
O
O
CD (mdeg)
20
0
-20
200
300
400
Wavelength (nm)


CD spectrum of 5c in CH3CN (50 μM)
CD (mdeg)
20
10
0
-10
-20
MeO
OMe
O
200
300
400
Wavelength (nm)

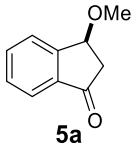

CD spectrum of 5d in CH3CN (50 μM)
CD (mdeg)
10
0
-10
MeO
OMe
O
200
300
400
Wavelength (nm)


CD spectrum of 5g in CH3CN (50 μM)
CD (mdeg)
20
10
0
-10
-20
Me
OMe
O
200
300
400
Wavelength (nm)

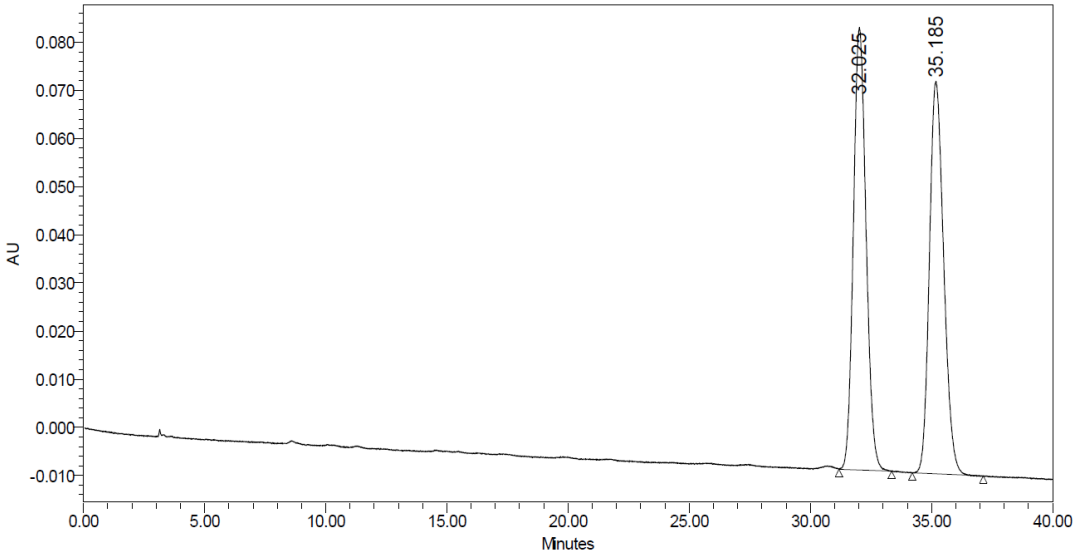

CD spectrum of 5h in CH3CN (50 μM)
CD (mdeg)
20
10
0
-10
-20
Me
OMe
O
200
300
400
Wavelength (nm)


CD spectrum of 5j in CH3CN (100 μM)
CD (mdeg)
20
0
-20
Cl
OMe
O
200
300
400
Wavelength (nm)

Chiral HPLC Spectra



5a



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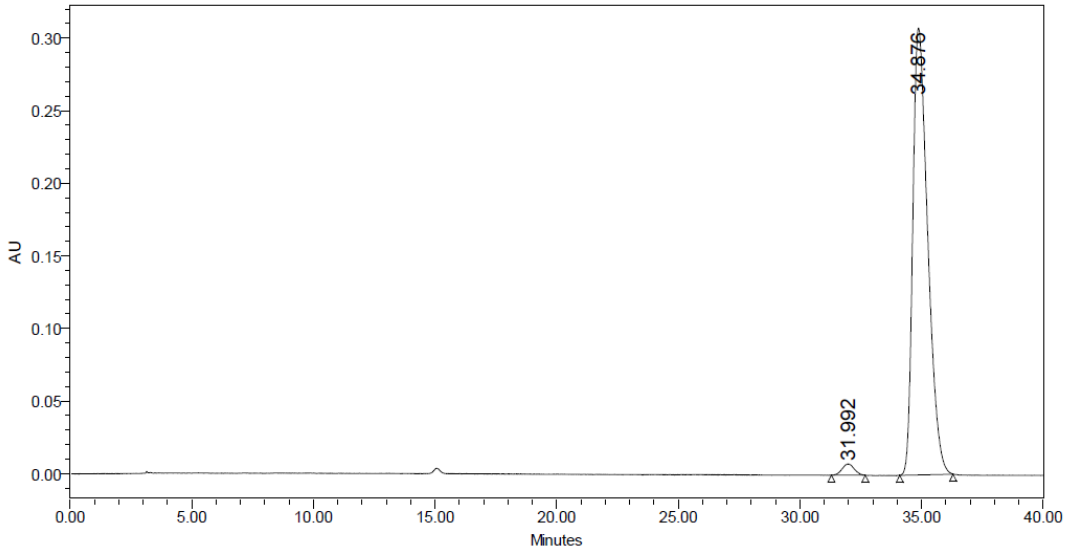
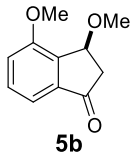
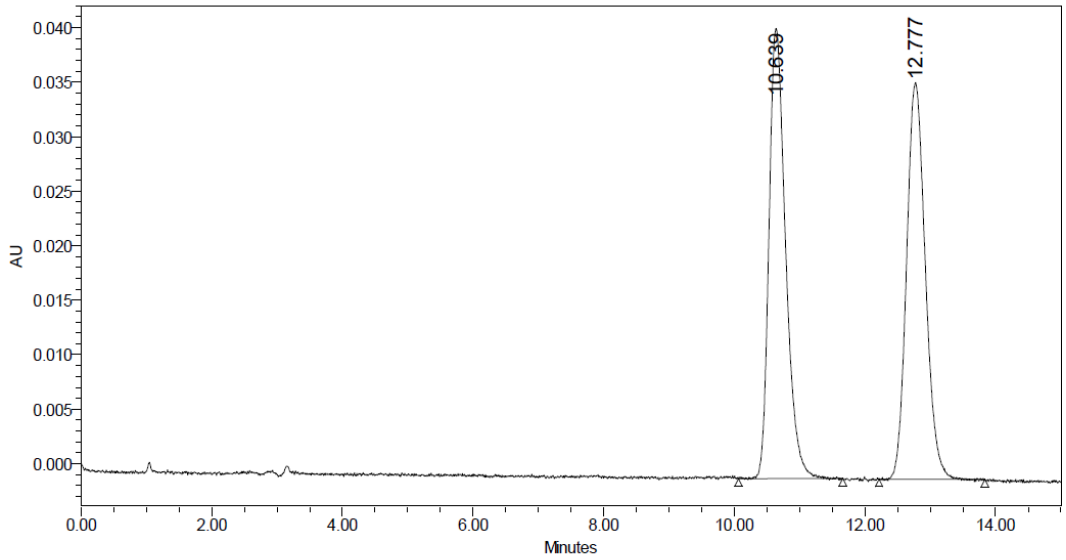
1	32.025	3335751	49.97	91905
2	35.185	3339876	50.03	81532



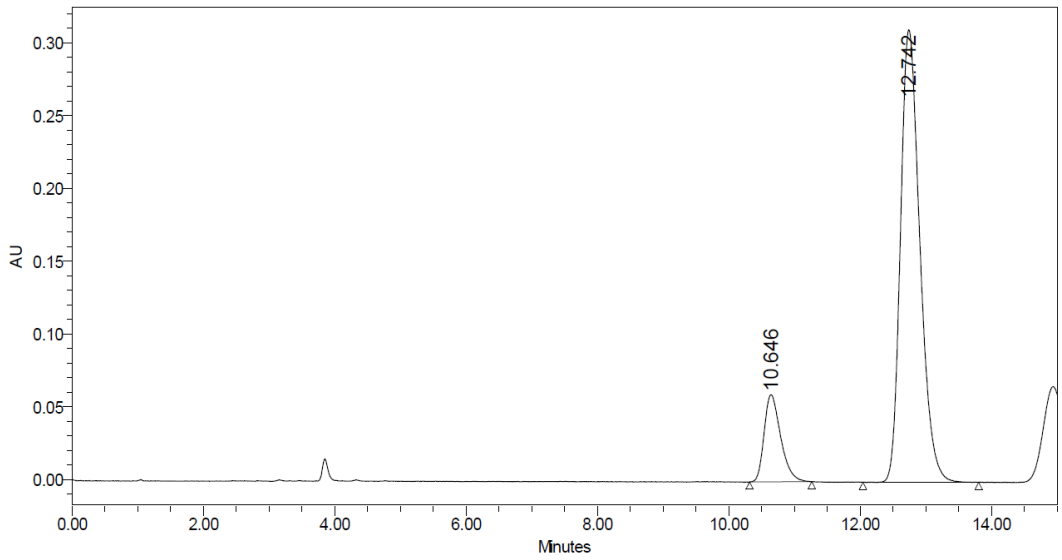
	RT	Area	% Area	Height
1	31.992	266726	2.00	7820
2	34.876	13090260	98.00	307810



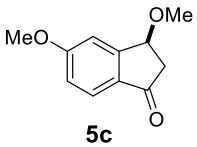
5b



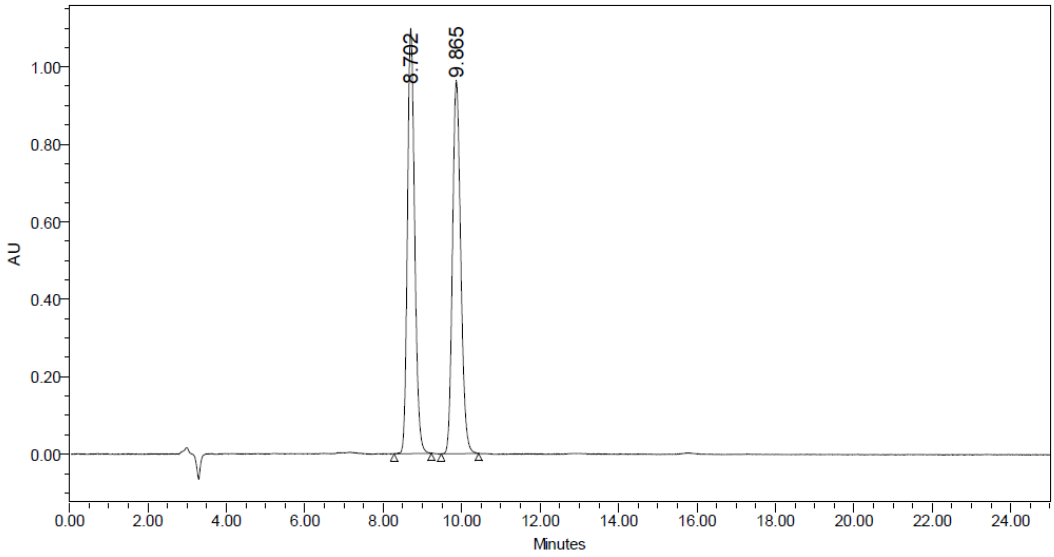
	RT	Area	% Area	Height
1	10.639	728809	50.10	41286
2	12.777	725877	49.90	36392



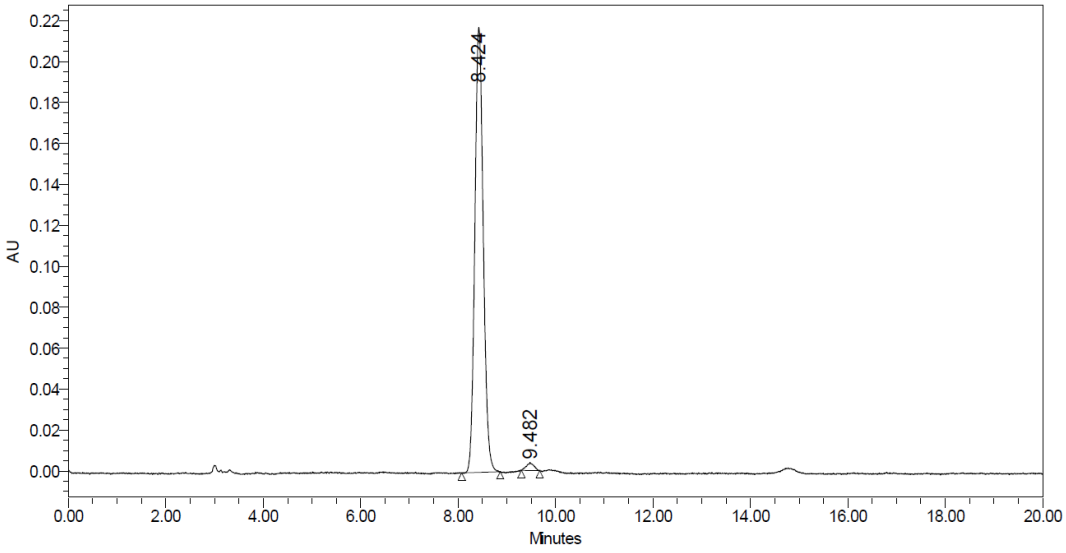
	RT	Area	% Area	Height
1	10.646	1045041	14.12	59786
2	12.742	6353486	85.88	310405



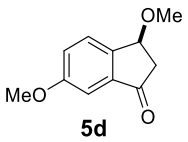
5c



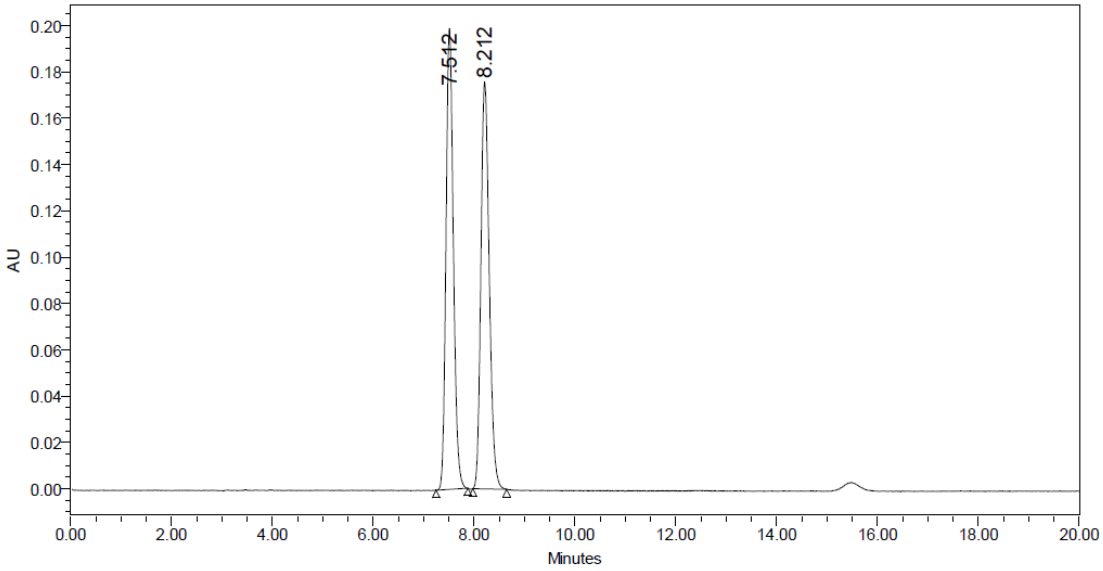
	RT	Area	% Area	Height
1	8.702	14067188	49.96	1097850
2	9.865	14090697	50.04	962786



	RT	Area	% Area	Height
1	8.424	2606862	98.45	217243
2	9.482	41037	1.55	3822



5d



	RT	Area	% Area	Height
1	7.512	2017376	49.97	199046
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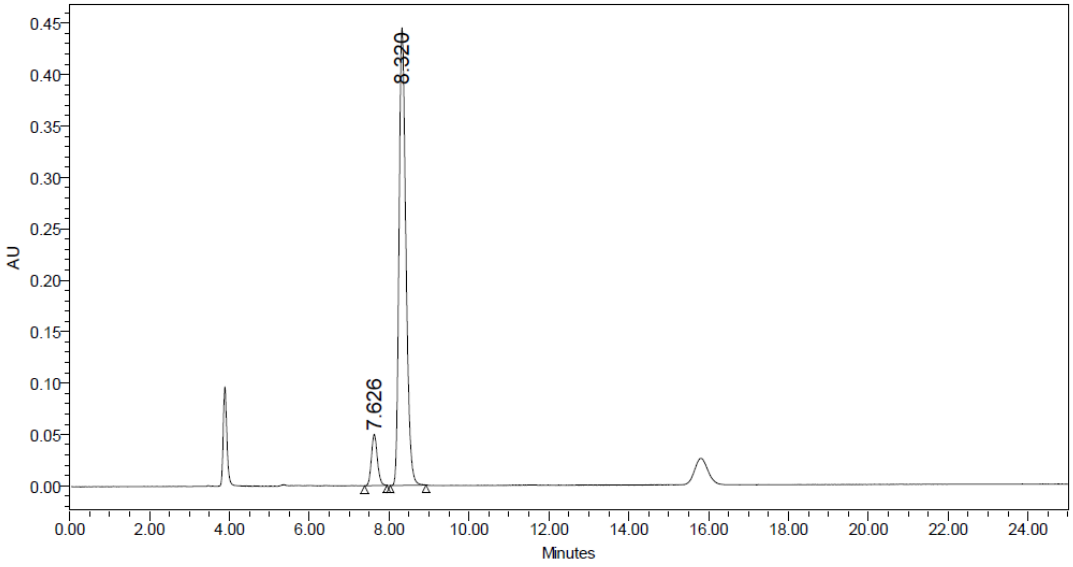
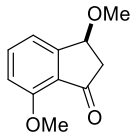
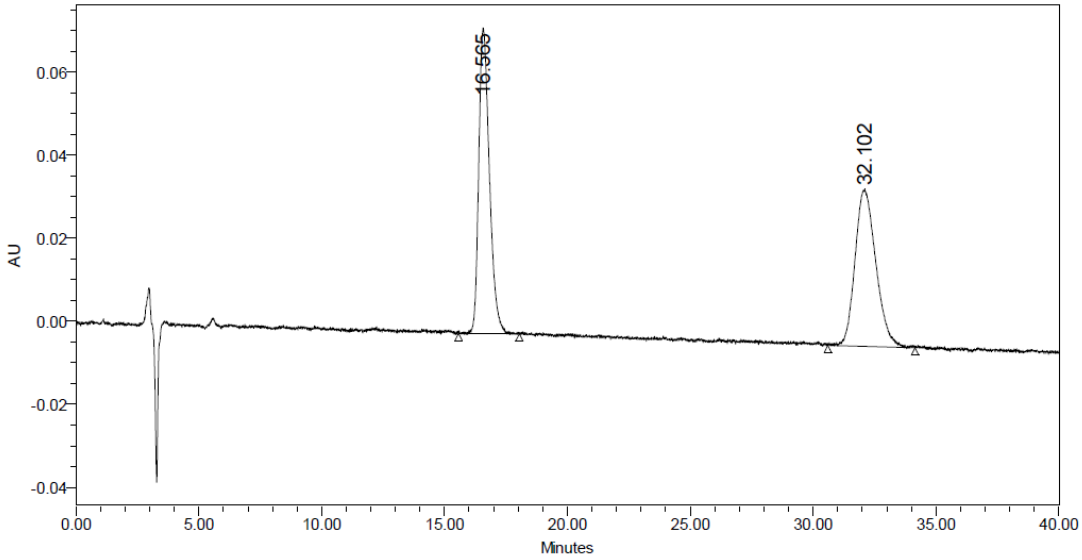


	RT	Area	% Area	Height
1	7.626	513803	8.80	49879
2	8.320	5322388	91.20	444969



5e



	RT	Area	% Area	Height
1	16.565	2215504	49.82	73561
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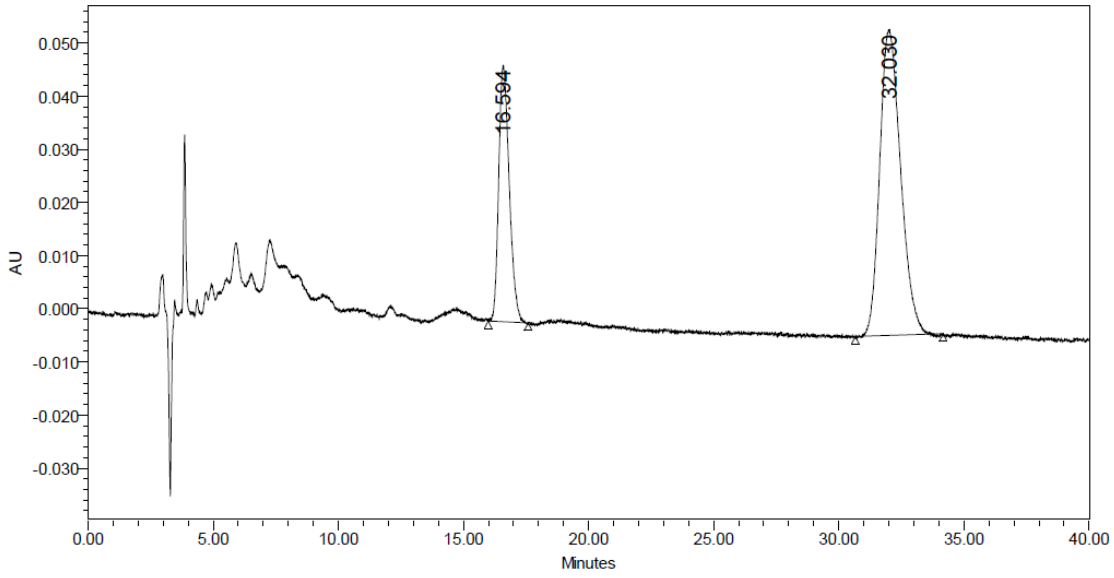
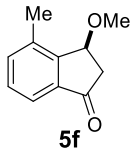
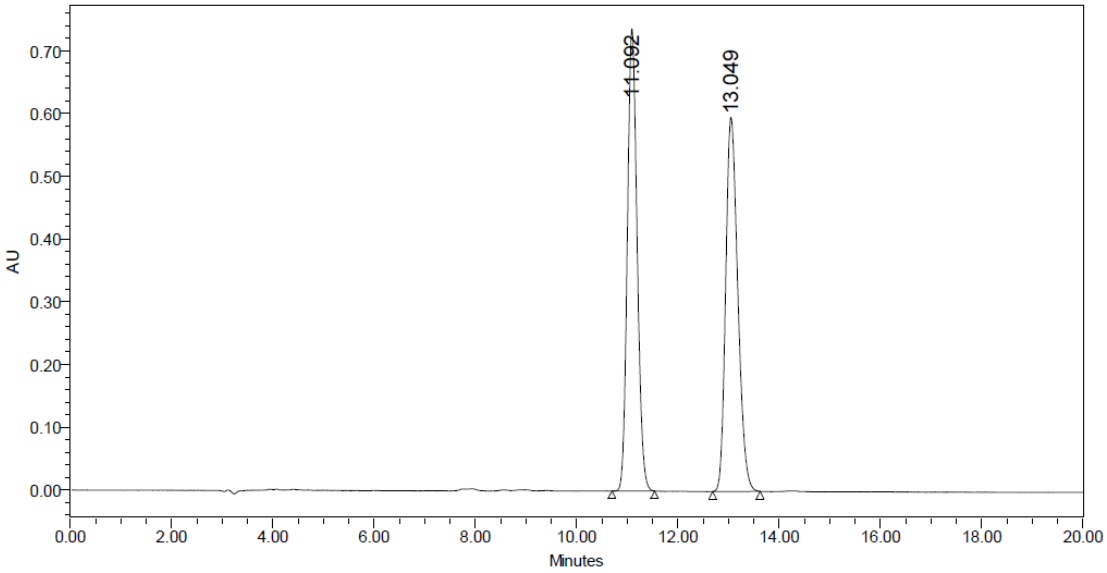


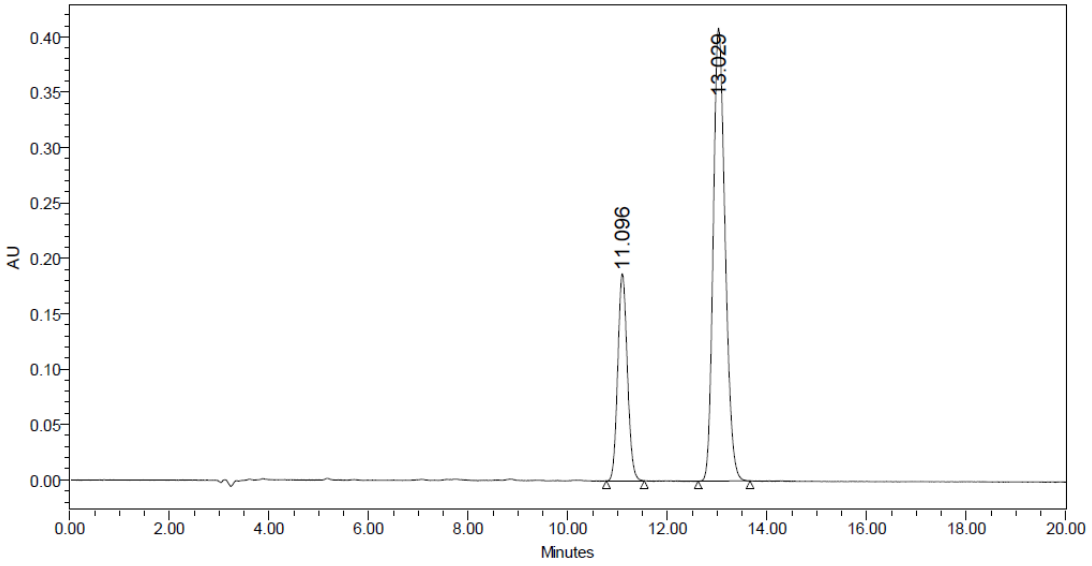
	RT	Area	% Area	Height
1	16.594	1413867	29.67	48268
2	32.030	3351940	70.33	57559



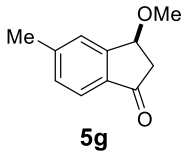
5f



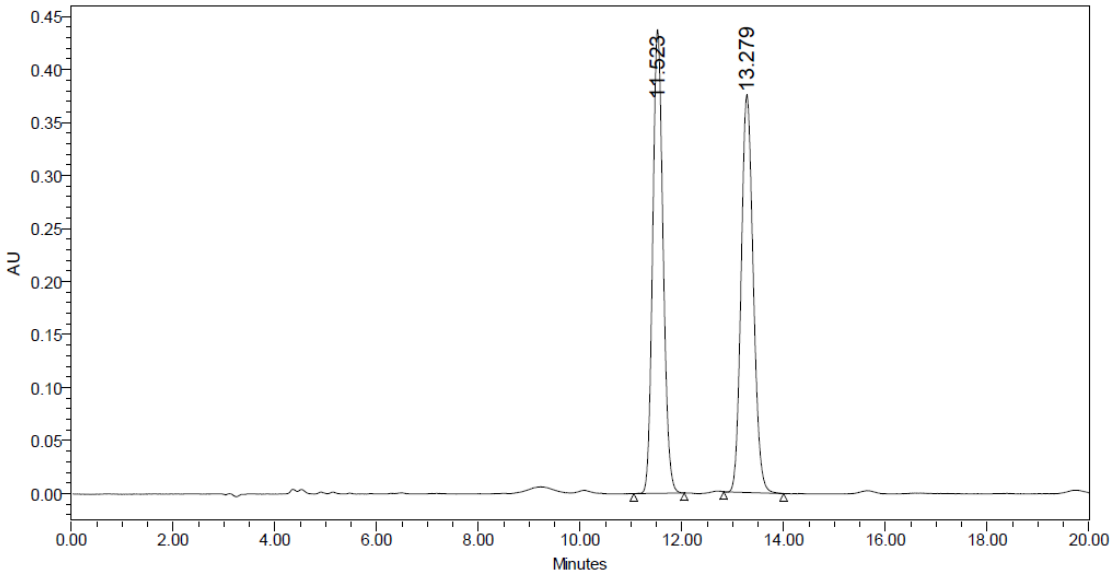
	RT	Area	% Area	Height
1	11.092	9868393	49.92	736806
2	13.049	9899020	50.08	595959



	RT	Area	% Area	Height
1	11.096	2497917	26.95	186921
2	13.029	6771027	73.05	409026



5g



	RT	Area	% Area	Height
1	11.523	6209010	50.02	437394
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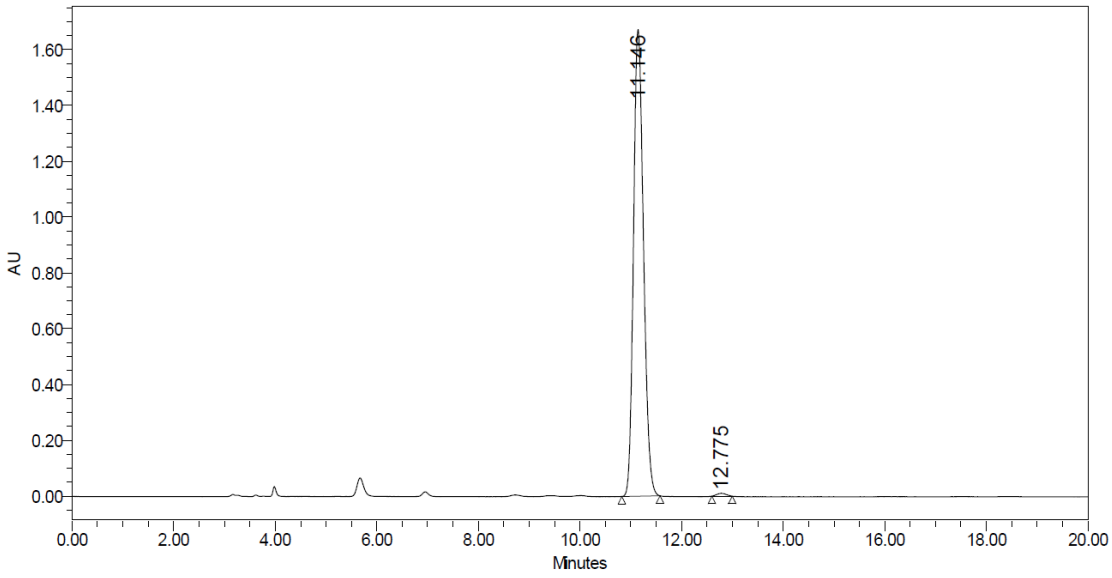

	RT	Area	% Area	Height
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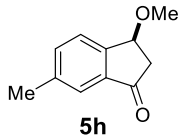
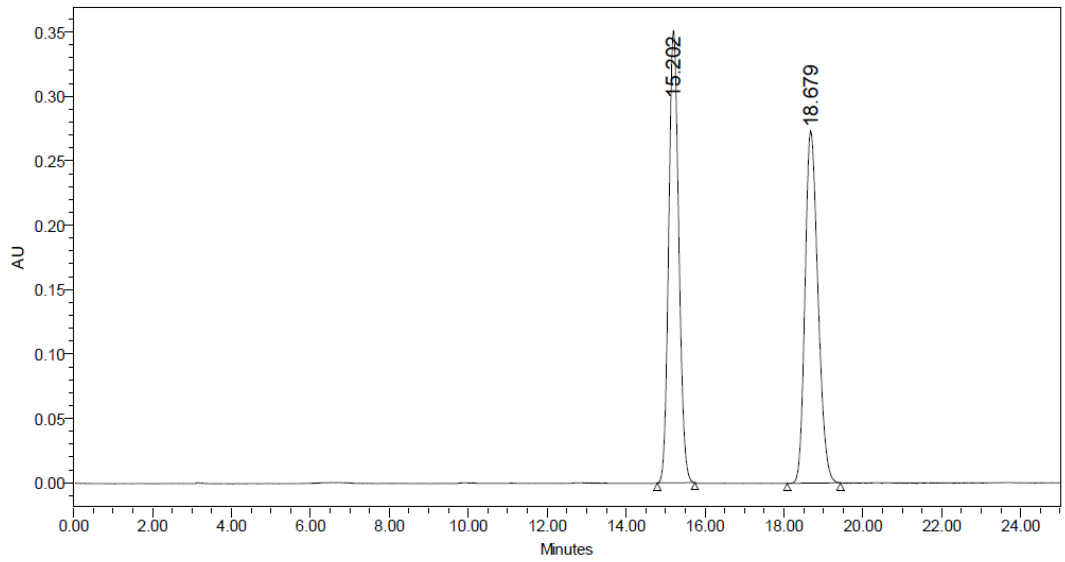
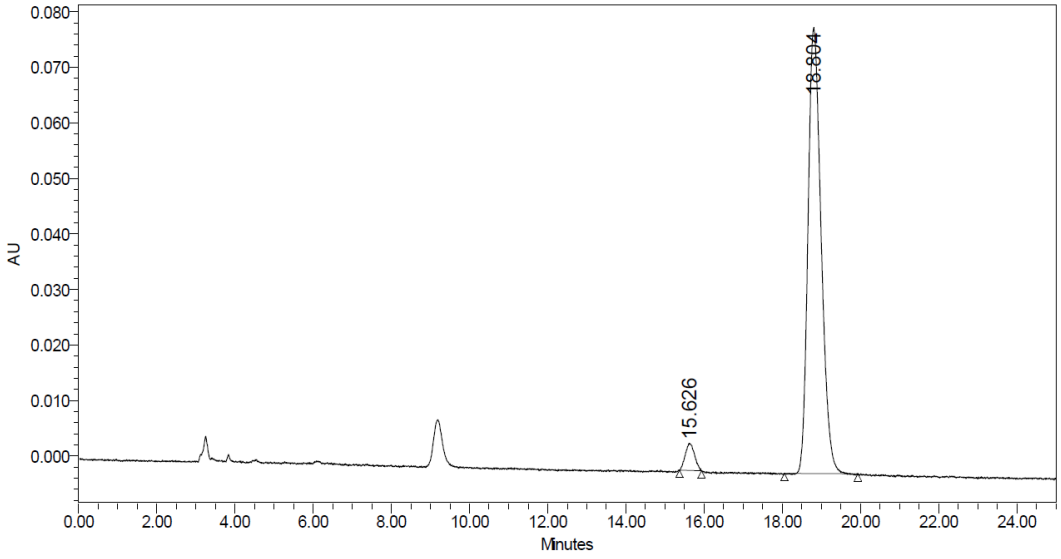


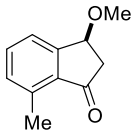
5h



	RT	Area	% Area	Height
1	15.202	6216918	49.95	351253
2	18.679	6229821	50.05	273614



	RT	Area	% Area	Height
1	15.626	80493	4.12	4869
2	18.804	1870862	95.88	80325



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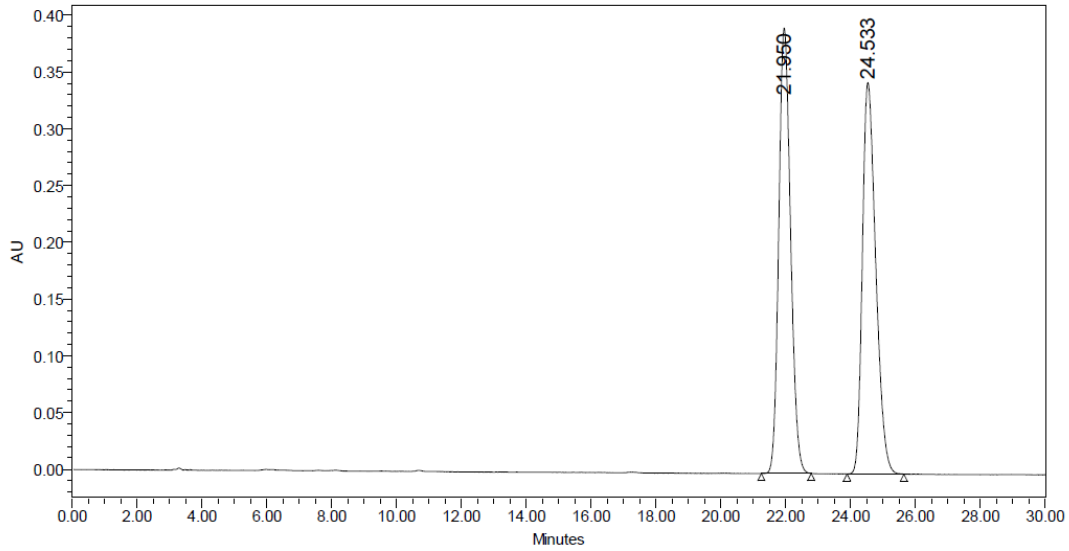
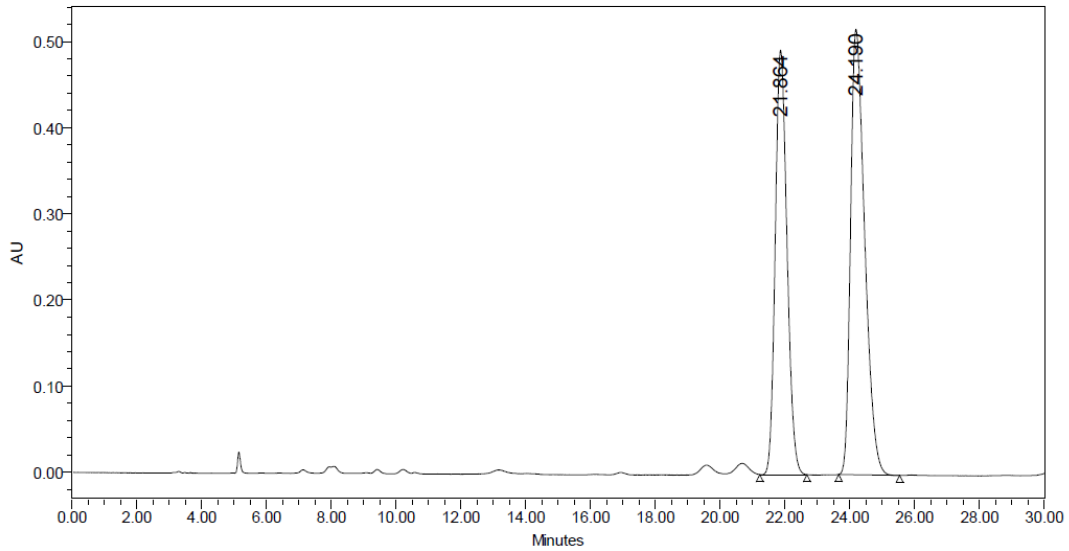
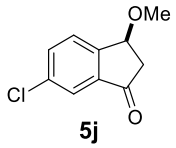


	RT	Area	% Area	Height
1	21.950	9882286	49.98	392346
2	24.533	9890811	50.02	344861



	RT	Area	% Area	Height
1	21.864	12420463	44.23	492907
2	24.190	15657952	55.77	517294



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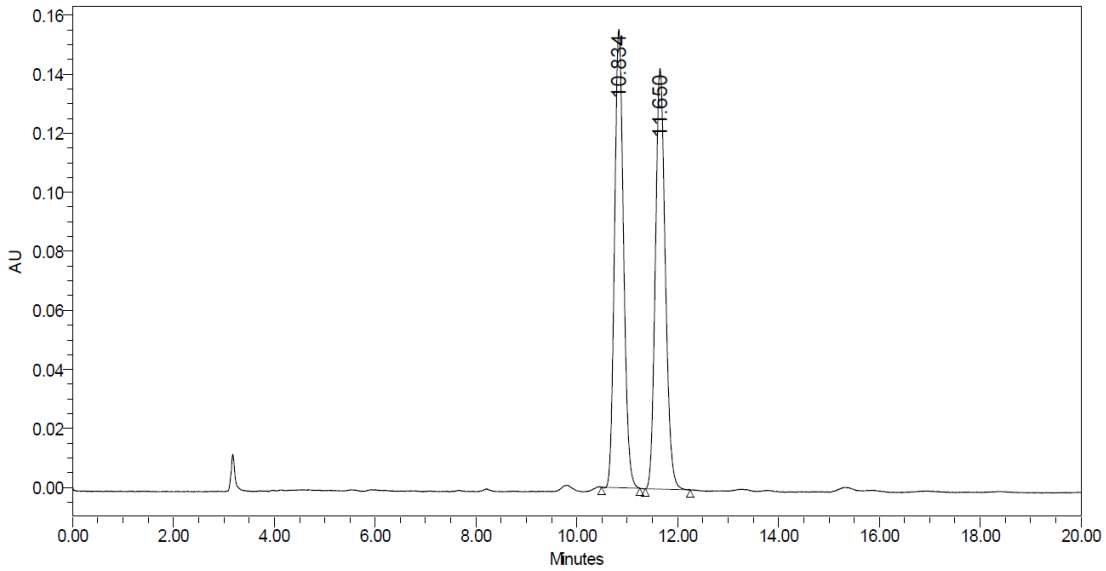
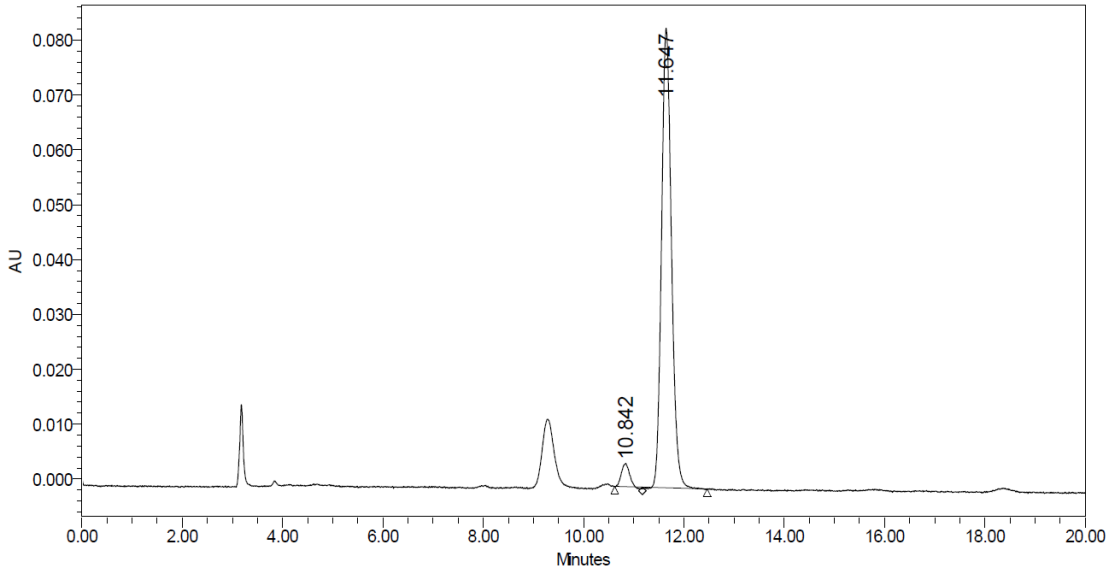
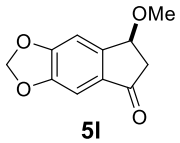


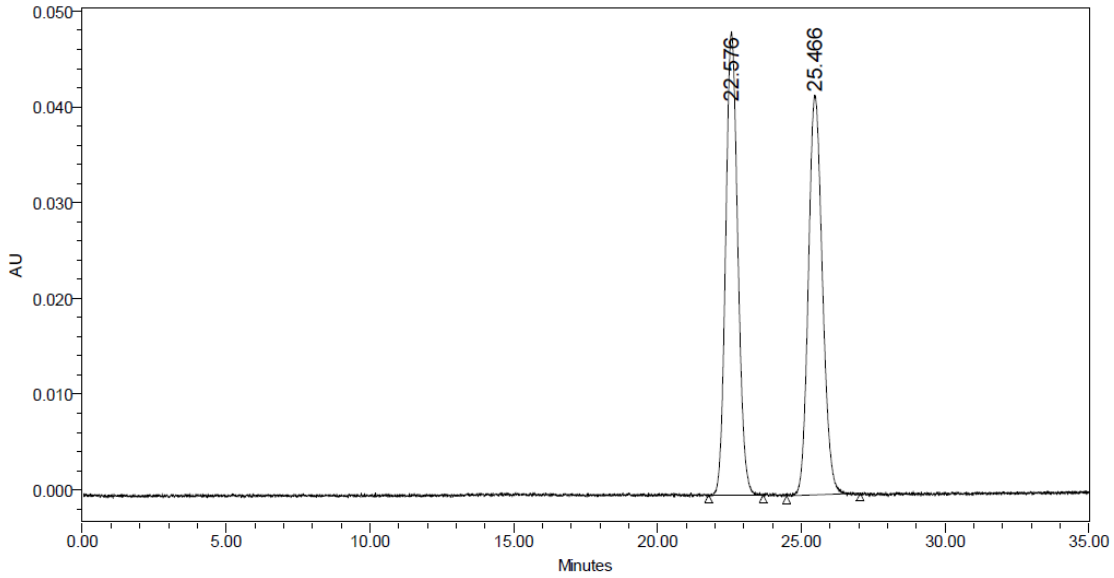
	RT	Area	% Area	Height
1	10.834	1926271	49.80	155179
2	11.650	1941972	50.20	142341



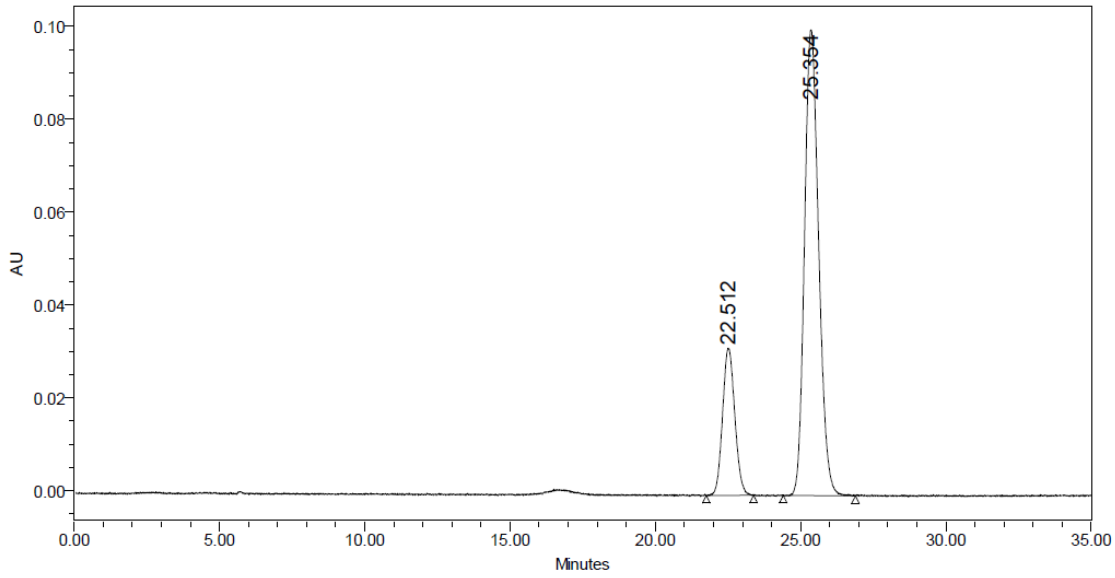
	RT	Area	% Area	Height
1	10.842	48848	4.08	4222
2	11.647	1148199	95.92	83746



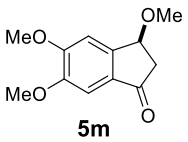
5l



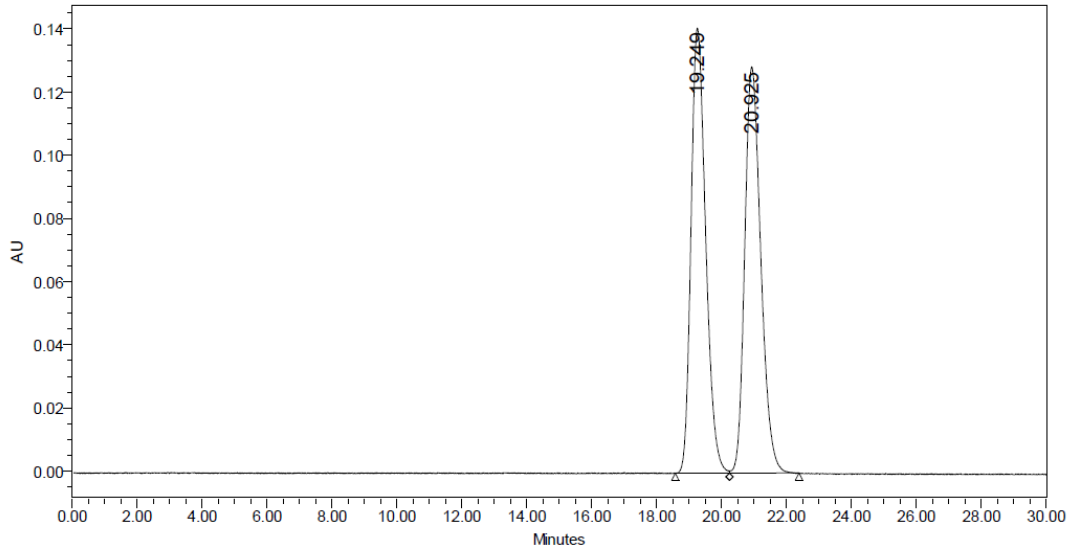
	RT	Area	% Area	Height
1	22.576	1414220	49.92	48379
2	25.466	1418849	50.08	41742



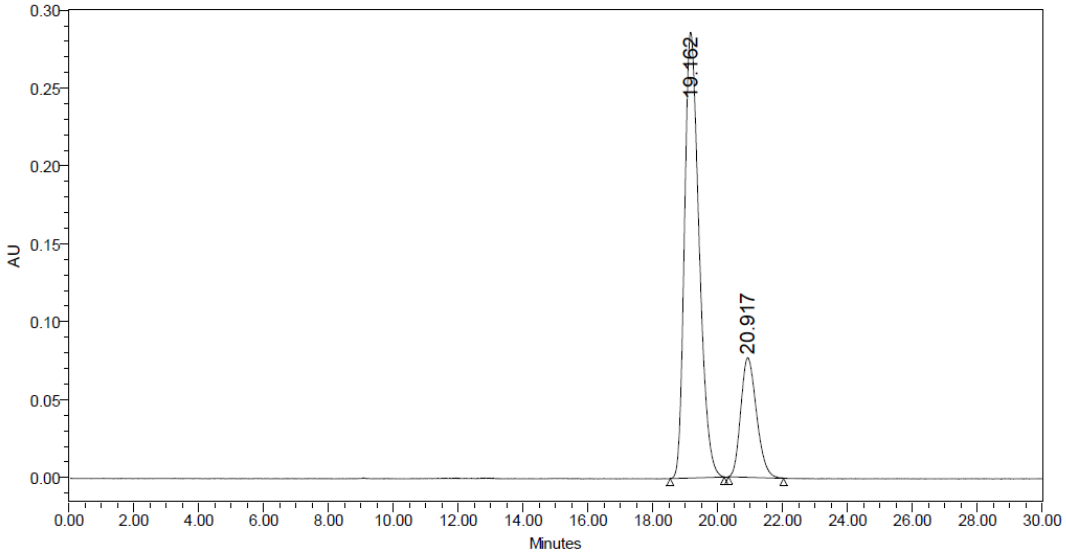
	RT	Area	% Area	Height
1	22.512	926649	21.42	31678
2	25.354	3398684	78.58	100307



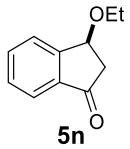
5m



	RT	Area	% Area	Height
1	19.249	4413641	49.98	140948
2	20.925	4416559	50.02	128657



	RT	Area	% Area	Height
1	19.162	8949849	77.51	286188
2	20.917	2596948	22.49	76762



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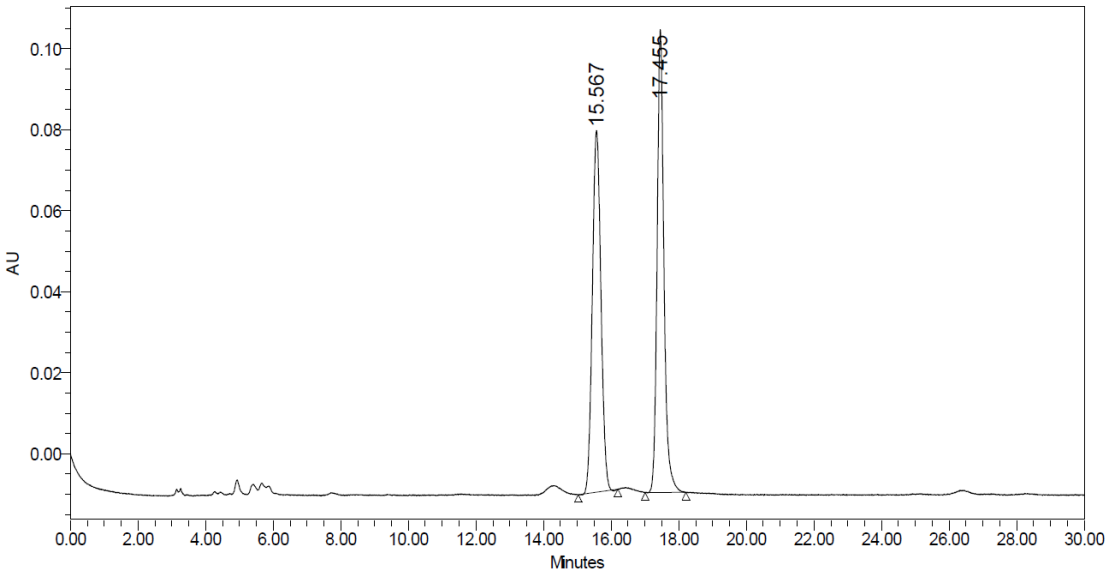
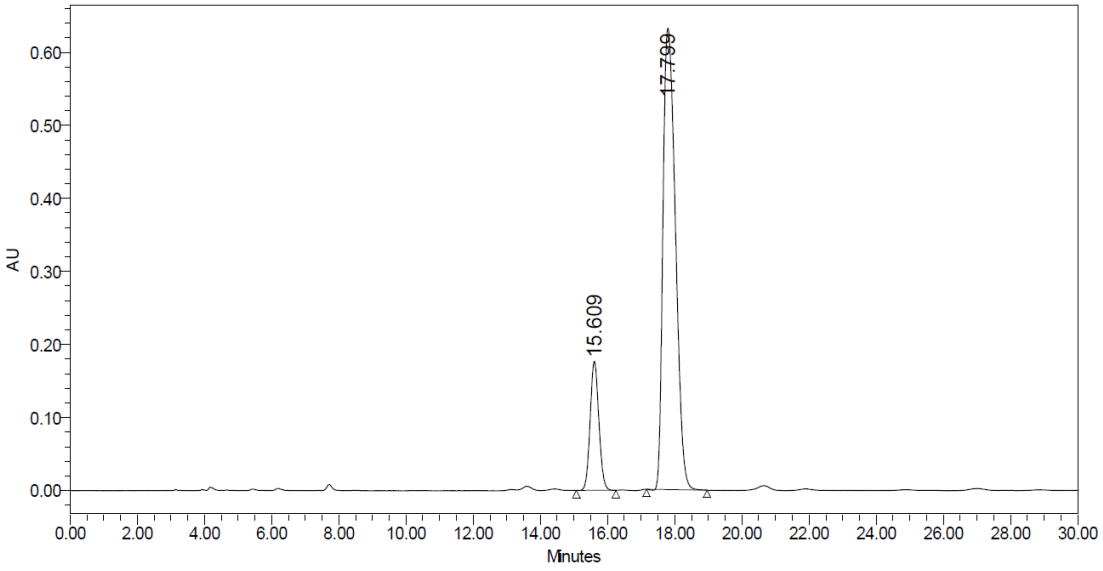
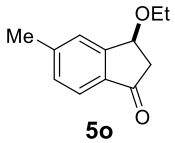


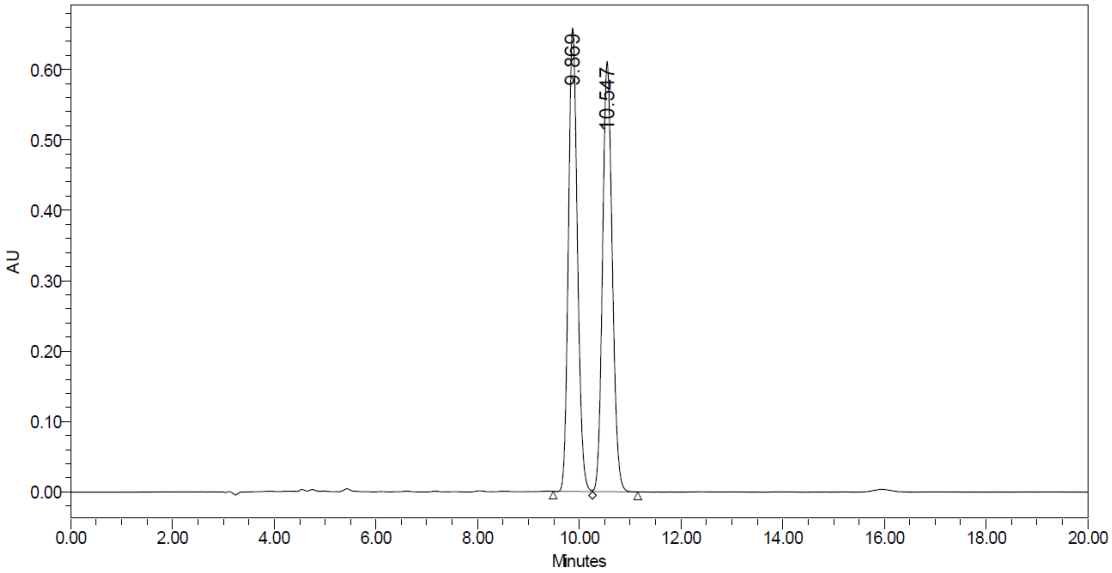
	RT	Area	% Area	Height
1	15.567	1575045	49.68	89313
2	17.455	1595096	50.32	114268



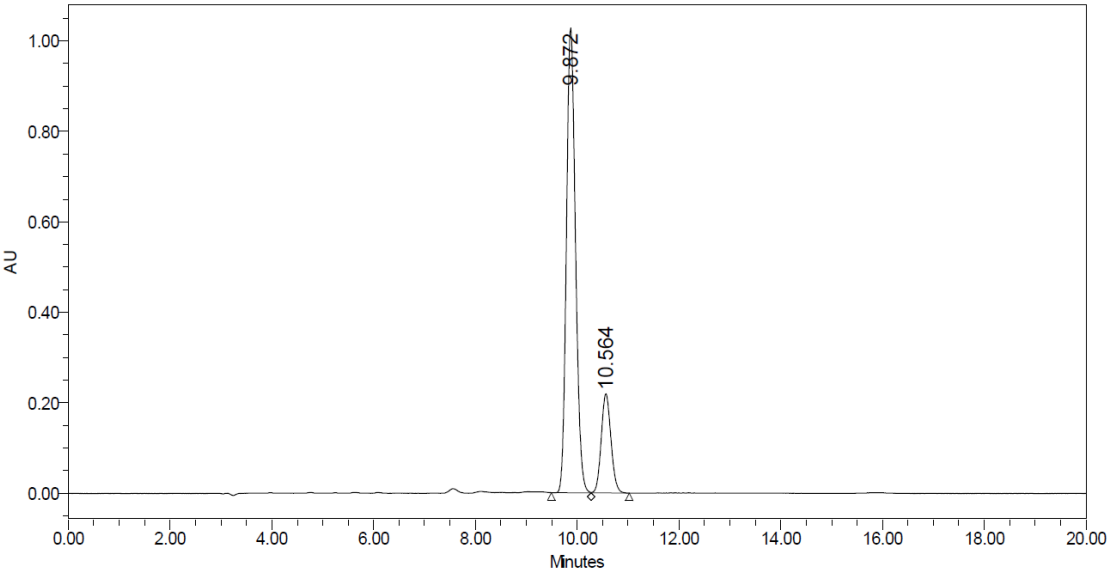
	RT	Area	% Area	Height
1	15.609	3183785	16.37	176664
2	17.799	16259591	83.63	631625



5o



	RT	Area	% Area	Height
1	9.869	8106296	49.97	657677
2	10.547	8114833	50.03	610820



	RT	Area	% Area	Height
1	9.872	12719001	81.38	1027080
2	10.564	2909641	18.62	219077

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