Kinetic Resolution of Racemic α-Arylalkanoic Acids with Achiral Alcohols via the Asymmetric Esterification Using Carboxylic Anhydrides and Acyl-transfer Catalysts

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Supporting Information

(D) (53 pages) Spectroscopic Data of Carboxylic Acids in **Table 6**

=Appendix=

HPLC Analyses of Compounds

(E) (18 pages) Chiral Compounds in **Table 1**
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General Information. All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with chloroform (in chloroform-*d*) as internal standard. Thin layer chromatography was performed on Wakogel B5F.

All reactions were carried out under argon atmosphere in dried glassware. Dichloromethane was distilled from diphosphorus pentoxide, then calcium hydride, and dried over MS 4Å.

4-Methoxybenzoic anhydride (PMBA), bis(α-naphthyl)methanol (**3**), (*R*)-BTM, and (*S*)-BTM were purchased from Tokyo Kasei Kogyo Co., Ltd (TCI).

(*S*)-2-Amino-3-methyl-1-butanol was prepared from L-valine by reduction using $LiAlH_4$. L-Valine was purchased from TCI.

(*S*)-2-Amino-3,3-dimethyl-1-butanol was purchased from TCI.

(*S*)-2-Amino-3-phenyl-1-propanol was prepared from L-phenylalanine by reduction using $LiAlH_4$. L-Phenylalanine was purchased from TCI.

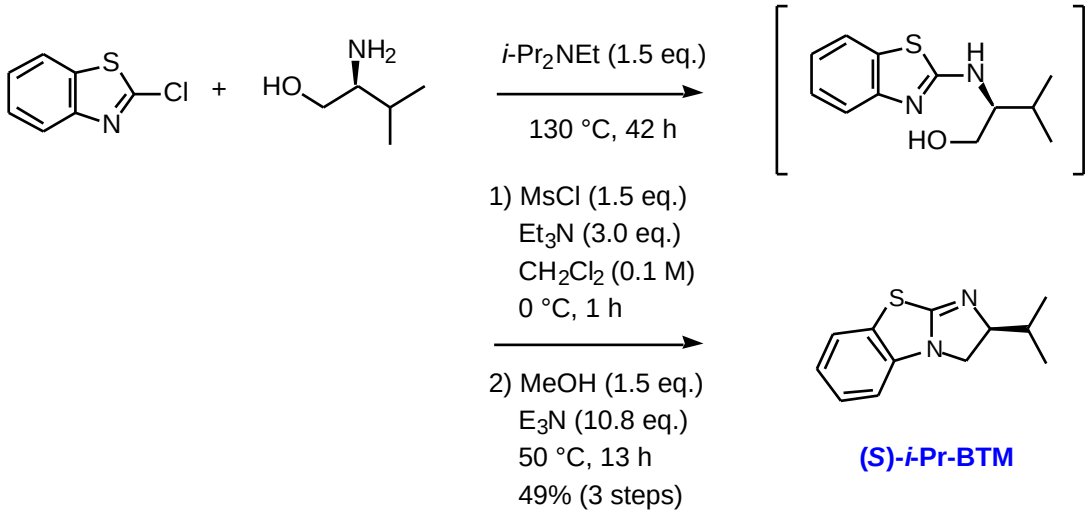
(*R*)-2-Amino-3-(β-naphthyl)-1-propanol was prepared from D-3-(β-naphthyl)alanine by reduction using $LiAlH_4$. D-3-(β-Naphthyl)alanine was purchased from Acros Organics.

(+)-(1*S*,2*R*)-Norephedrine was purchased from TCI.

(–)-(1*R*,2*R*)-*trans*-1-Amino-2-indanol was purchased from Sigma-Aldrich, Inc.

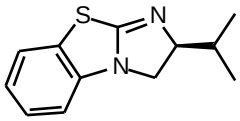
(*S*)-2-Amino-2-(α-naphthyl)-1-ethanol and (*S*)-2-amino-2-(β-naphthyl)-1-ethanol were prepared from L-(α-naphthyl)glycine and L-(β-naphthyl)glycine, respectively, according to the literature method.[1]

(Preparation of (–)-(*S*)-*i*-Pr-BTM)



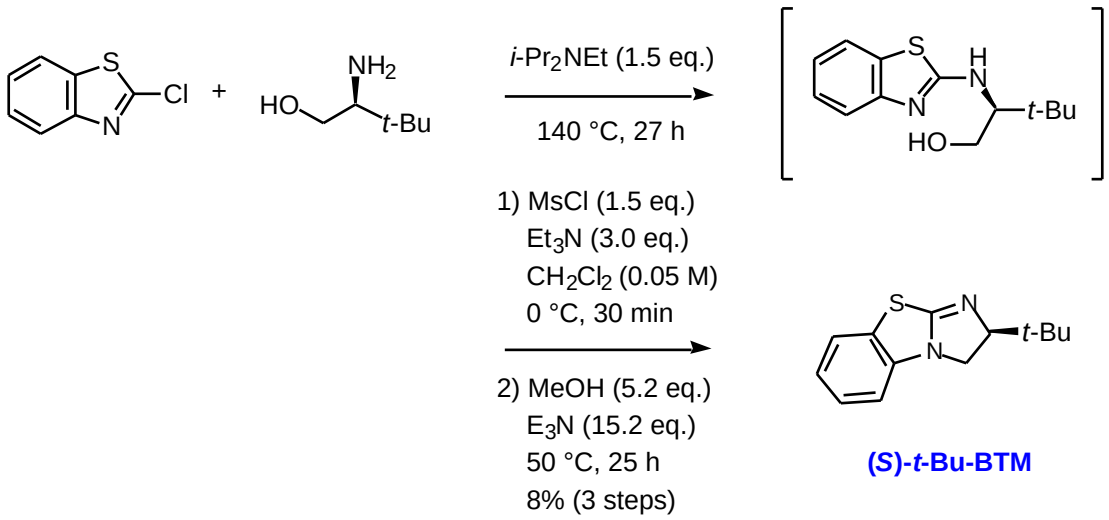
A 50 mL autoclave was charged with 2-chlorobenzothiazole (2.53 mL, 19.4 mmol), (*S*)-2-amino-3-methyl-1-butanol (2.00 g, 19.4 mmol), and diisopropylethylamine (5.07 mL, 29.1 mmol). The vessel was sealed and then the whole mixture was stirred for 42 h at 130 °C. After cooling to room temperature, the reaction mixture was diluted with methanol and dichloromethane and then it was transferred into a 500 mL two-necked flask. The mixture was concentrated in vacuo to afford the crude intermediate, which was used for the next reaction without purification.

To a solution of the above product in dichloromethane (194 mL) at 0 °C were added triethylamine (8.11 mL, 58.2 mmol) and methanesulfonyl chloride (2.25 mL, 29.1 mmol). After stirring for 1 h at 0 °C, methanol (1.21 mL, 29.8 mmol) and triethylamine (29.1 mL, 209 mmol) were successively added at room temperature and the reaction mixture was stirred for 13 h at 50 °C. After cooling to room temperature, it was quenched with aqueous sodium hydroxide (1.0 M) and the organic layer was diluted with dichloromethane and separated, and then the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography on silica (ethyl acetate/hexane = 1/1) to afford (–)-(*S*)-*i*-Pr-BTM (2.07 g, 49% for 3 steps) as a pale yellow oil.



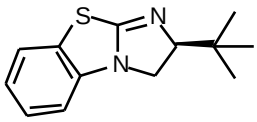
(–)-(*S*)-*i*-Pr-BTM: $[\alpha]_D^{23}$ = –141.6 (c 0.35, benzene); IR (neat): 1599, 1468, 1214, 742 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.25 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.17 (td, *J* = 7.8, 1.2 Hz, 1H), 6.93 (ddd, *J* = 7.8, 7.5, 0.9 Hz, 1H), 6.65 (dd, *J* = 7.8, 0.9 Hz, 1H), 4.38 (ddd, *J* = 9.8, 8.7, 6.6 Hz, 1H), 3.87 (dd, *J* = 9.8, 8.7 Hz, 1H), 3.49 (dd, *J* = 8.7, 8.7 Hz, 1H), 1.91 (dqq, *J* = 6.6, 6.9, 6.6 Hz, 1H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.2, 137.1, 127.0, 126.4, 123.0, 121.1, 108.1, 78.9, 47.2, 33.5, 18.7, 18.3; HR MS: calcd for $C_{12}H_{15}N_2S$ ($M+H^+$) 219.0950, found 219.0943.

(Preparation of (–)-(*S*)-*t*-Bu-BTM)



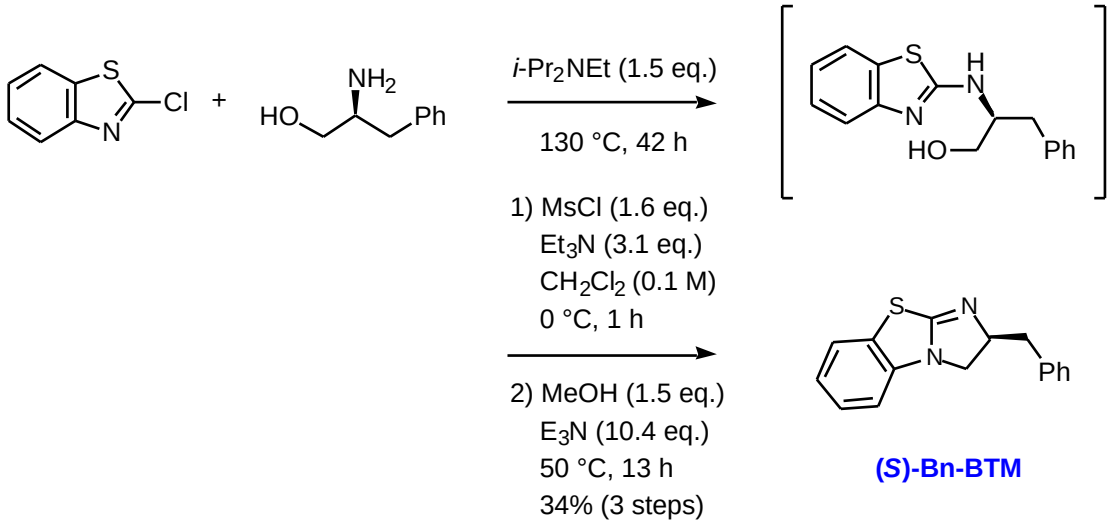
A 10 mL autoclave was charged with 2-chlorobenzothiazole (367 μL, 2.82 mmol), (*S*)-2-amino-3,3-dimethyl-1-butanol (330 mg, 2.82 mmol), and diisopropylethylamine (750 μL, 4.31 mmol). The vessel was sealed and then the whole mixture was stirred for 27 h at 140 °C. After cooling to room temperature, the reaction mixture was diluted with methanol and dichloromethane and then it was transferred into a 300 mL two-necked flask. The mixture was concentrated in vacuo to afford the crude intermediate, which was used for the next reaction without purification.

To a solution of the above product in dichloromethane (56.0 mL) at 0 °C were added triethylamine (1.18 mL, 8.47 mmol) and methanesulfonyl chloride (327 μL, 4.22 mmol). After stirring for 30 min at 0 °C, methanol (600 μL, 14.8 mmol) and triethylamine (6.00 mL, 43.0 mmol) were successively added at room temperature and the reaction mixture was stirred for 25 h at 50 °C. After cooling to room temperature, it was quenched with aqueous sodium hydroxide (1.0 M) and the organic layer was diluted with dichloromethane and separated, and then the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography on silica (ethyl acetate/hexane = 1/9 to 1/1) and by the preparative thin layer chromatography on silica (benzene/diethyl ether/sat. aq. NH_3 = 100/5/10) to afford (–)-(*S*)-*t*-Bu-BTM (50.2 mg, 8% for 3 steps) as a pale yellow oil.



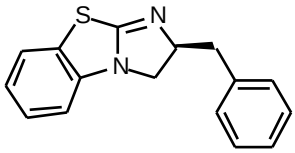
(–)-(*S*)-*t*-Bu-BTM: $[\alpha]_D^{24}$ = –132.0 (c 3.09, benzene); IR (neat): 1602, 1472, 1206, 742 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.17 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H), 6.85 (ddd, *J* = 7.8, 7.5, 0.9 Hz, 1H), 6.58 (dd, *J* = 7.8, 0.9 Hz, 1H), 4.27 (dd, *J* = 9.8, 9.0 Hz, 1H), 3.71 (dd, *J* = 9.8, 9.0 Hz, 1H), 3.49 (dd, *J* = 9.0, 9.0 Hz, 1H), 0.90 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 164.9, 137.1, 127.0, 126.4, 122.9, 121.0, 108.1, 82.5, 45.4, 34.3, 25.8; HR MS: calcd for $C_{13}H_{17}N_2S$ ($M+H^+$) 233.1107, found 233.1111.

(Preparation of (–)-(*S*)-Bn-BTM)



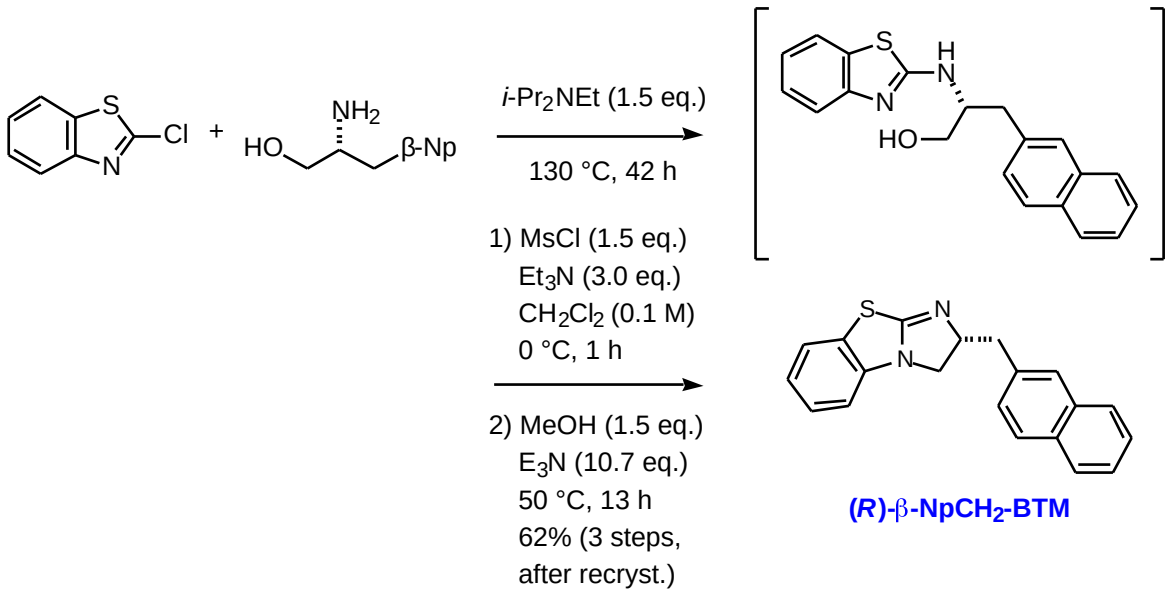
A 50 mL autoclave was charged with 2-chlorobenzothiazole (2.40 mL, 18.4 mmol), (*S*)-2-amino-3-phenyl-1-propanol (3.00 g, 19.8 mmol), and diisopropylethylamine (4.90 mL, 28.1 mmol). The vessel was sealed and then the whole mixture was stirred for 42 h at 130 °C. After cooling to room temperature, the reaction mixture was diluted with methanol and dichloromethane and then it was transferred into a 500 mL two-necked flask. The mixture was concentrated in vacuo to afford the crude intermediate, which was used for the next reaction without purification.

To a solution of the above product in dichloromethane (193 mL) at 0 °C were added triethylamine (8.01 mL, 57.4 mmol) and methanesulfonyl chloride (2.24 mL, 28.9 mmol). After stirring for 1 h at 0 °C, methanol (1.12 mL, 27.6 mmol) and triethylamine (26.7 mL, 192 mmol) were successively added at room temperature and the reaction mixture was stirred for 13 h at 50 °C. After cooling to room temperature, it was quenched with aqueous sodium hydroxide (1.0 M) and the organic layer was diluted with dichloromethane and separated, and then the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography on silica ($CHCl_3$/methanol = 9/1) to afford (–)-(*S*)-Bn-BTM (1.74 g, 34% for 3 steps) as a white solid.



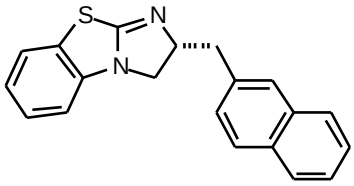
(–)-(*S*)-Bn-BTM: $[\alpha]_D^{22}$ = –97.9 (c 1.00, MeOH); Mp: 88-93 °C; IR (KBr): 1609, 1469, 1212, 746, 704 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.36-7.18 (m, 6H), 7.14 (td, *J* = 7.8, 1.2 Hz, 1H), 6.92 (td, *J* = 7.8, 0.9 Hz, 1H), 6.60 (dd, *J* = 7.8, 0.9 Hz, 1H), 4.87 (dddd, *J* = 9.3, 9.0, 7.5, 5.7 Hz, 1H), 3.77 (dd, *J* = 9.3, 9.0 Hz, 1H), 3.50 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.28 (dd, *J* = 13.8, 5.7 Hz, 1H), 2.82 (dd, *J* = 13.8, 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 165.9, 137.9, 137.1, 129.2, 128.6, 127.1, 126.5, 126.4, 123.0, 121.2, 108.3, 73.8, 49.1, 42.5; HR MS: calcd for $C_{16}H_{15}N_2S$ ($M+H^+$) 267.0950, found 267.0943.

(Preparation of (+)-(*R*)-β-NpCH$_2$-BTM)



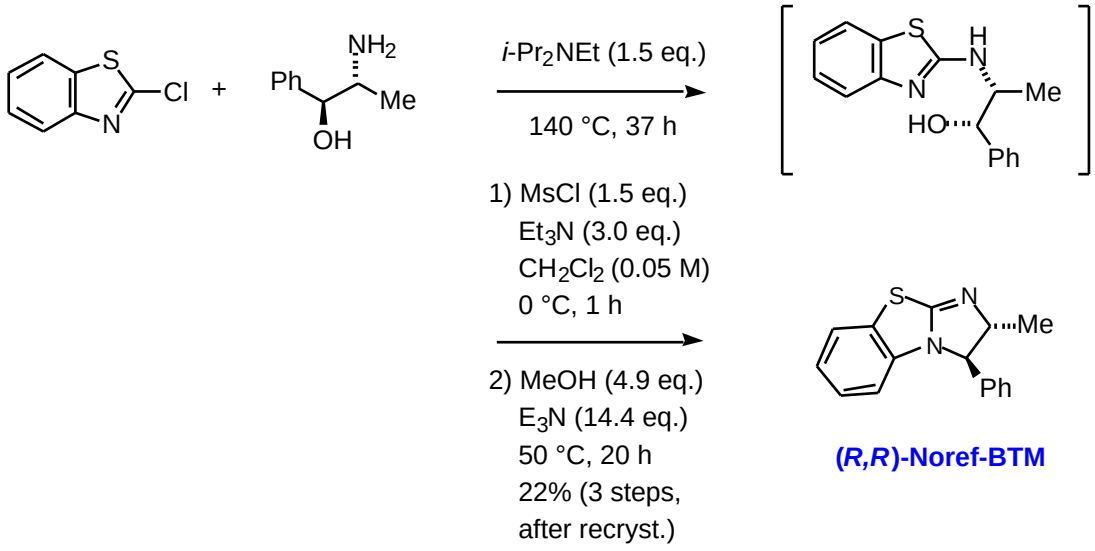
A 10 mL autoclave was charged with 2-chlorobenzothiazole (285 μL, 2.19 mmol), (*R*)-2-amino-3-(β-naphthyl)-1-propanol (395 mg, 1.96 mmol), and diisopropylethylamine (519 μL, 2.98 mmol). The vessel was sealed and then the whole mixture was stirred for 42 h at 130 °C. After cooling to room temperature, the reaction mixture was diluted with methanol and then it was transferred into a 100 mL two-necked flask. The mixture was concentrated in vacuo to afford the crude intermediate, which was used for the next reaction without purification.

To a solution of the above product in dichloromethane (19.6 mL) at 0 °C were added triethylamine (820 μL, 5.88 mmol) and methanesulfonyl chloride (228 μL, 2.95 mmol). After stirring for 1 h at 0 °C, methanol (120 μL, 2.96 mmol) and triethylamine (2.92 mL, 20.9 mmol) were successively added at room temperature and the reaction mixture was stirred for 13 h at 50 °C. After cooling to room temperature, it was quenched with aqueous sodium hydroxide (1.0 M) and the organic layer was diluted with dichloromethane and separated, and then the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography on silica (ethyl acetate/hexane = 1/4 to 1/2), followed by recrystallization from dichloromethane/hexane to afford (+)-(*R*)-β-NpCH$_2$-BTM (387 mg, 62% for 3 steps) as a white solid.



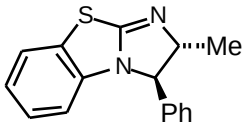
(+)-(*R*)-β-NpCH$_2$-BTM: $[\alpha]_D^{24}$ = +116.9 (c 0.50, MeOH); Mp: 165-166 °C (CH_2Cl_2/hexane); IR (KBr): 1604, 1465, 1213, 740 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.88-7.78 (m, 3H), 7.71 (br s, 1H), 7.52-7.39 (m, 3H), 7.26 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.15 (ddd, *J* = 7.8, 7.5, 1.2 Hz, 1H), 6.93 (ddd, *J* = 7.8, 7.5, 0.9 Hz, 1H), 6.59 (dd, *J* = 7.8, 0.9 Hz, 1H), 4.99 (dddd, *J* = 9.3, 9.0, 7.5, 5.7 Hz, 1H), 3.78 (dd, *J* = 9.3, 9.0 Hz, 1H), 3.56 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.46 (dd, *J* = 13.8, 5.7 Hz, 1H), 2.99 (dd, *J* = 13.8, 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 166.0, 137.1, 135.5, 133.5, 132.3, 128.3, 127.63, 127.59, 127.54, 127.52, 127.1, 126.5, 126.1, 125.5, 123.0, 121.2, 108.3, 73.9, 49.1, 42.7; HR MS: calcd for $C_{20}H_{17}N_2S$ ($M+H^+$) 317.1107, found 317.1110.

(Preparation of (–)-(*R*,*R*)-Noref-BTM)



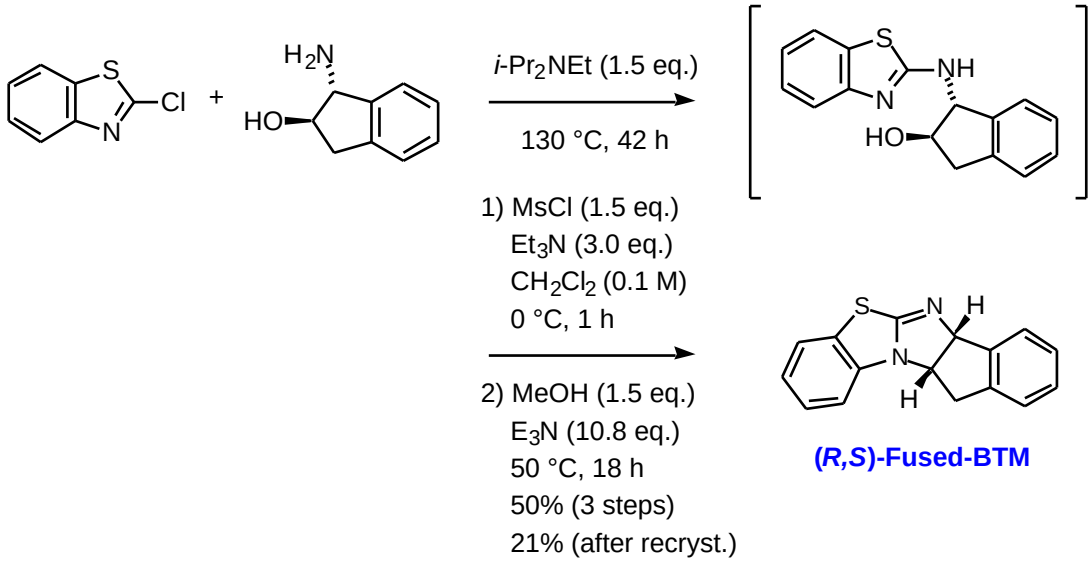
A 50 mL autoclave was charged with 2-chlorobenzothiazole (1.30 mL, 10.0 mmol), (+)-(1*S*,2*R*)-norephedrine (1.52 g, 10.0 mmol), and diisopropylethylamine (2.61 mL, 15.0 mmol). The vessel was sealed and then the whole mixture was stirred for 37 h at 140 °C. After cooling to room temperature, the reaction mixture was diluted with methanol and then it was transferred into a 500 mL two-necked flask. The mixture was concentrated in vacuo to afford the crude intermediate, which was used for the next reaction without purification.

To a solution of the above product in dichloromethane (200 mL) at 0 °C were added triethylamine (4.18 mL, 30.0 mmol) and methanesulfonyl chloride (1.16 mL, 15.0 mmol). After stirring for 1 h at 0 °C, methanol (2.00 mL, 49.3 mmol) and triethylamine (20.0 mL, 144 mmol) were successively added at room temperature and the reaction mixture was stirred for 20 h at 50 °C. After cooling to room temperature, it was quenched with aqueous sodium hydroxide (1.0 M) and the organic layer was diluted with dichloromethane and separated, and then the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography on silica (ethyl acetate/hexane = 4/1 to 1/1) and by the preparative thin layer chromatography on silica (hexane/ethyl acetate/sat. aq. NH_3 = 120/25/10), followed by recrystallization from dichloromethane/hexane to afford (–)-(*R*,*R*)-Noref-BTM (593 mg, 22% for 3 steps) as a white solid.



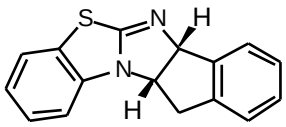
(–)-(*R*,*R*)-Noref-BTM: $[\alpha]_D^{23}$ = –321.2 (c 0.50, benzene); Mp: 109-110 °C (CH_2Cl_2/hexane); IR (KBr): 1599, 1469, 1200, 746, 705 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.44-7.31 (m, 5H), 7.27 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.97 (ddd, *J* = 7.7, 7.5, 1.5 Hz, 1H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 6.23 (dd, *J* = 7.7, 1.2 Hz, 1H), 4.65 (d, *J* = 8.6 Hz, 1H), 4.36 (dq, *J* = 8.6, 6.6 Hz, 1H), 1.49 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 164.9, 139.0, 136.8, 129.1, 128.3, 127.0, 126.4, 126.2, 123.0, 121.3, 108.8, 79.4, 70.2, 21.5; HR MS: calcd for $C_{16}H_{15}N_2S$ ($M+H^+$) 267.0950, found 267.0951.

(Preparation of (+)-(*R*,*S*)-Fused-BTM)



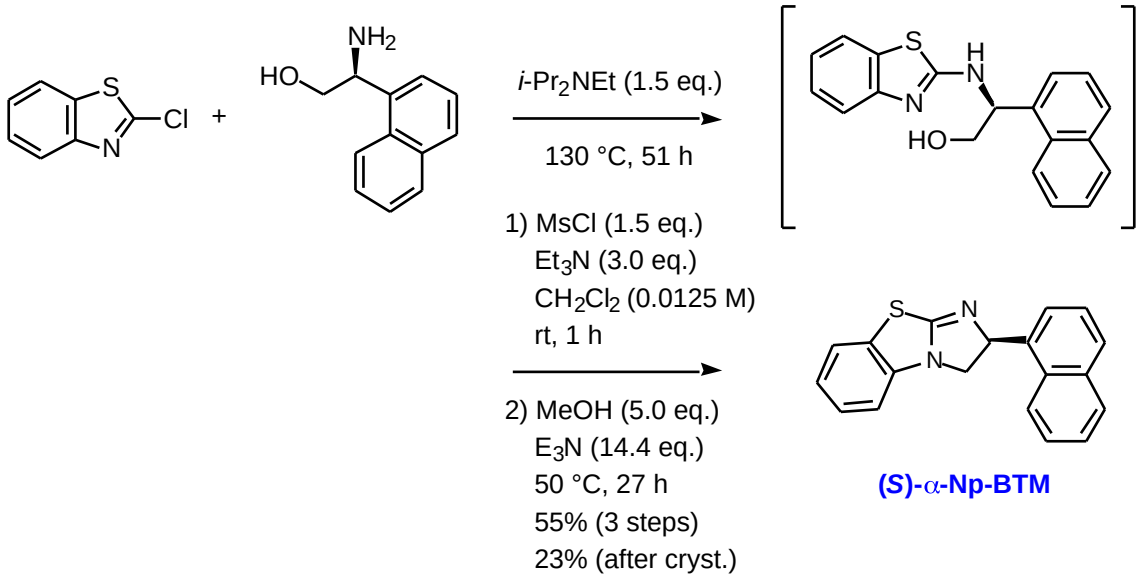
A 10 mL autoclave was charged with 2-chlorobenzothiazole (480 μL, 3.69 mmol), (–)-(1*R*,2*R*)-*trans*-1-amino-2-indanol (500 mg, 3.35 mmol), and diisopropylethylamine (876 μL, 5.03 mmol). The vessel was sealed and then the whole mixture was stirred for 42 h at 130 °C. After cooling to room temperature, the reaction mixture was diluted with methanol and then it was transferred into a 200 mL two-necked flask. The mixture was concentrated in vacuo to afford the crude intermediate, which was used for the next reaction without purification.

To a solution of the above product in dichloromethane (33.5 mL) at 0 °C were added triethylamine (1.40 mL, 10.1 mmol) and methanesulfonyl chloride (390 μL, 5.03 mmol). After stirring for 1 h at 0 °C, methanol (210 μL, 5.18 mmol) and triethylamine (5.03 mL, 36.1 mmol) were successively added at room temperature and the reaction mixture was stirred for 18 h at 50 °C. After cooling to room temperature, it was quenched with aqueous sodium hydroxide (1.0 M) and the organic layer was diluted with dichloromethane and separated, and then the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography on silica (ethyl acetate/hexane = 1/1) to afford (+)-(*R*,*S*)-Fused-BTM (446 mg, 50% for 3 steps) as a pale yellow solid. The product was recrystallized from dichloromethane/hexane to afford the sample for analysis (95 mg, 21%) as a white solid.



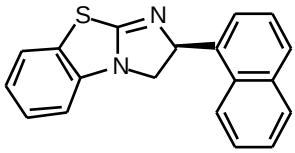
(+)-(*R,S*)-Fused-BTM: $[\alpha]_D^{23}$ = +881.8 (c 1.00, MeOH); Mp: 161-163 °C (CH_2Cl_2/hexane); IR (KBr): 1598, 1477, 1221, 737 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.56-7.48 (m, 1H), 7.34-7.17 (m, 4H), 7.19 (ddd, *J* = 7.7, 7.5, 1.2 Hz, 1H), 6.94 (ddd, *J* = 7.7, 7.5, 0.9 Hz, 1H), 6.80 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.08 (d, *J* = 8.7 Hz, 1H), 4.95 (ddd, *J* = 8.7, 6.8, 2.0 Hz, 1H), 3.52 (dd, *J* = 17.1, 6.8 Hz, 1H), 3.39 (dd, *J* = 17.1, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 165.4, 142.3, 139.4, 136.1, 128.4, 127.7, 127.5, 126.4, 125.4, 125.2, 123.3, 121.2, 107.8, 84.1, 59.8, 37.2; HR MS: calcd for $C_{16}H_{13}N_2S$ ($M+H^+$) 265.0794, found 265.0797.

(Preparation of (+)-(*S*)-α-Np-BTM)



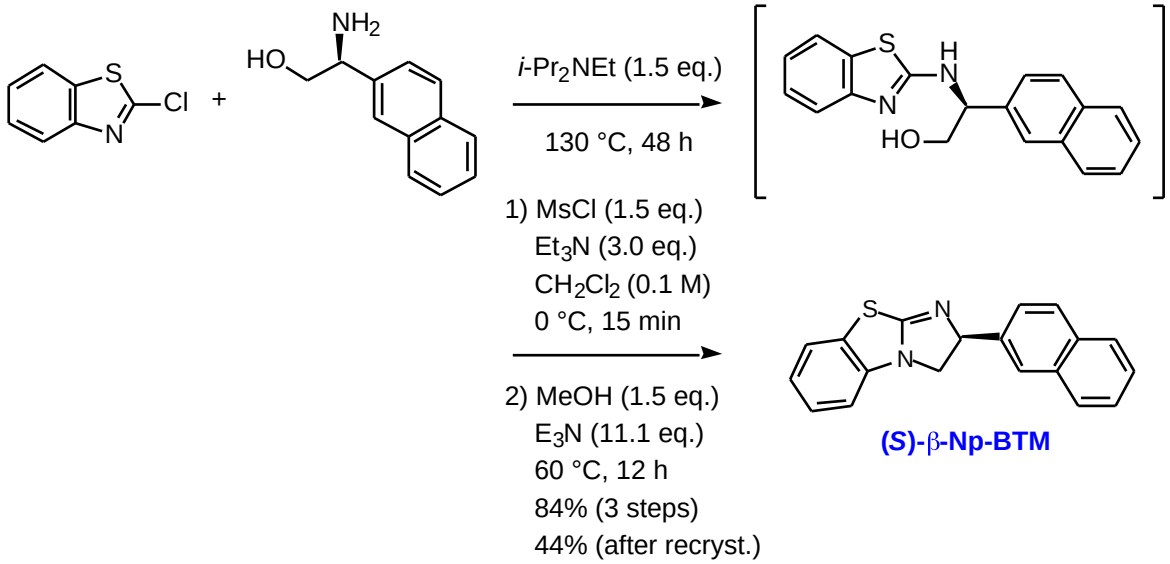
A 10 mL autoclave was charged with 2-chlorobenzothiazole (65.1 μL, 0.500 mmol), (*S*)-2-amino-2-(α-naphthyl)-1-ethanol (93.3 mg, 0.498 mmol, >99% ee), and diisopropylethylamine (131 μL, 0.752 mmol). The vessel was sealed and then the whole mixture was stirred for 51 h at 130 °C. After cooling to room temperature, the reaction mixture was diluted with methanol and dichloromethane and then it was transferred into a 50 mL two-necked flask. The mixture was concentrated in vacuo to afford the crude intermediate, which was used for the next reaction without purification.

To a solution of the above product in dichloromethane (40 mL) at 0 °C were added triethylamine (209 μL, 1.50 mmol) and methanesulfonyl chloride (58.0 μL, 0.749 mmol). After stirring for 1 h at room temperature, methanol (100 μL, 2.47 mmol) and triethylamine (1.00 mL, 7.17 mmol) were successively added at room temperature and the reaction mixture was stirred for 27 h at 50 °C. After cooling to room temperature, it was quenched with aqueous sodium hydroxide (1.0 M) and the organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography on silica (benzene/diethyl ether/sat. aq. NH_3 = 100/10/10) to afford (+)-(*S*)-α-Np-BTM (83.9 mg, 55% for 3 steps) as a pale yellow oil. The product was crystallized from dichloromethane/hexane/diethyl ether to afford the sample for analysis (34.6 mg, 23%, >99.5% ee) as a white solid.



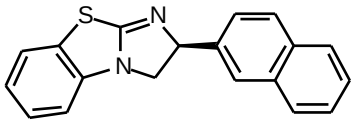
(+)-(*S*)-α-Np-BTM: HPLC (CHIRALCEL OD-H, *i*-PrOH/hexane/Et_2NH = 20/80/0.1, flow rate = 1.0 mL/min): t_R = 47.2 min (>99.5%) [Racemic Authentic Sample: t_R = 17.2 min (51.0%), t_R = 46.1 min (49.0%)]; $[\alpha]_D^{24}$ = +269.5 (c 1.00, MeOH); Mp: 161-162 °C (CH_2Cl_2/hexane); IR (KBr): 1599, 1465, 1216, 798, 775, 741 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.98-7.89 (m, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.62-7.45 (m, 3H), 7.32 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.16 (td, *J* = 7.8, 1.0 Hz, 1H), 6.97 (ddd, *J* = 7.8, 7.5, 0.9 Hz, 1H), 6.62 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.42 (dd, *J* = 10.5, 7.8 Hz, 1H), 4.53 (dd, *J* = 10.5, 8.7 Hz, 1H), 3.71 (dd, *J* = 8.7, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 166.8, 138.6, 137.0, 134.0, 130.3, 129.1, 128.0, 127.3, 126.6, 126.3, 125.8, 125.6, 123.8, 123.2, 122.7, 121.6, 108.5, 71.9, 52.1; HR MS: calcd for $C_{19}H_{15}N_2S$ ($M+H^+$) 303.0950, found 303.0942.

(Preparation of (–)-(*S*)-β-Np-BTM)



A 10 mL autoclave was charged with 2-chlorobenzothiazole (589 μL, 4.52 mmol), (*S*)-2-amino-2-(β-naphthyl)-1-ethanol (847 mg, 4.52 mmol, >99% ee), and diisopropylethylamine (1.18 mL, 6.77 mmol). The vessel was sealed and then the whole mixture was stirred for 48 h at 130 °C. After cooling to room temperature, the reaction mixture was diluted with methanol and dichloromethane and then it was transferred into a 100 mL two-necked flask. The mixture was concentrated in vacuo to afford the crude intermediate, which was used for the next reaction without purification.

To a solution of the above product in dichloromethane (45.3 mL) at 0 °C were added triethylamine (1.89 mL, 13.6 mmol) and methanesulfonyl chloride (525 μL, 6.78 mmol). After stirring for 15 min at 0 °C, methanol (280 μL, 6.90 mmol) and triethylamine (7.00 mL, 50.2 mmol) were successively added at room temperature and the reaction mixture was stirred for 12 h at 60 °C. After cooling to room temperature, it was quenched with aqueous sodium hydroxide (1.0 M), and the organic layer was diluted with diethyl ether and separated, and then the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography on silica (ethyl acetate/hexane = 1/4) to afford (–)-(*S*)-β-Np-BTM (1.15 g, 84% for 3 steps) as a pale yellow solid. The product was recrystallized from ethyl acetate/petroleum ether to afford the sample for analysis (600 mg, 44%, >99.5% ee) as a white solid.

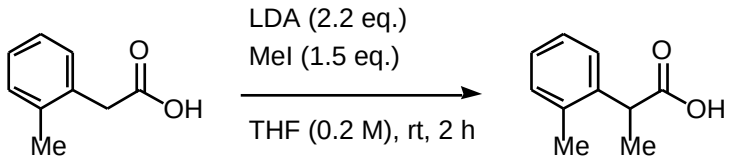


(–)-(*S*)-β-Np-BTM: HPLC (CHIRALCEL OD-H, *i*-PrOH/hexane/Et_2NH = 20/80/0.1, flow rate = 1.0 mL/min): t_R = 27.3 min (>99.5%) [Racemic Authentic Sample: t_R = 24.2 min (49.0%), t_R = 27.4 min (51.0%)]; $[\alpha]_D^{24}$ = –355.3 (c 1.00, MeOH); Mp: 110-112 °C (EtOAc/petroleum ether); IR (KBr): 1610, 1475, 1217, 856, 832, 739 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.90-7.80 (m, 4H), 7.52-7.43 (m, 3H), 7.33 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.19 (ddd, *J* = 7.8, 7.7, 1.3 Hz, 1H), 6.98 (td, *J* = 7.7, 0.9 Hz, 1H), 6.68 (dd, *J* = 7.8, 0.9 Hz, 1H), 5.85 (dd, *J* = 10.3, 8.1 Hz, 1H), 4.35 (dd, *J* = 10.3, 8.9 Hz, 1H), 3.78 (dd, *J* = 8.9, 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 166.9, 140.3, 137.1, 133.4, 132.9, 128.7, 128.0, 127.7, 127.4, 126.6, 126.2, 125.9, 125.2, 124.6, 123.2, 121.5, 108.6, 75.5, 52.4; HR MS: calcd for $C_{19}H_{15}N_2S$ ($M+H^+$) 303.0950, found 303.0942.

(Preparation of Racemic Carboxylic Acids)

Racemic carboxylic acids **4a**, **4b**, **4d**–**4h**, **4r**, and **6** are commercially available.
Racemic 2-(4-methoxyphenyl)propanoic acid (**4c**) was prepared from 2-(4-hydroxyphenyl)propanoic acid according to the literature method.[2]
Racemic carboxylic acids **4i**–**4p**, **4t**–**4v** were prepared by the alkylation at 2-position of the corresponding carboxylic acids according to the literature method.[3]
Racemic carboxylic acids **4q** and **4w** were prepared by the aryl substitution at 2-position of ethyl 2-bromopropanoate according to the literature method.[4]
Racemic 3-methoxy-2-phenylpropanoic acid (**4s**) was prepared from tropic acid as shown below.

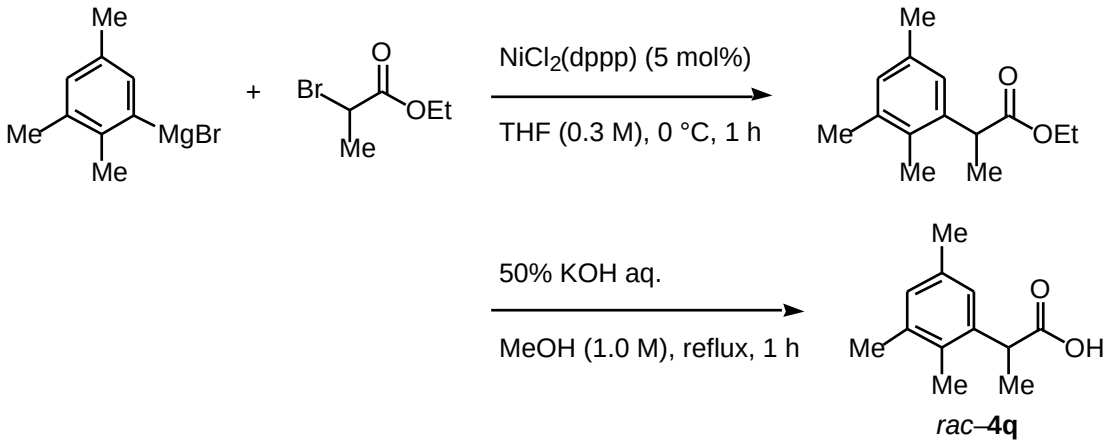
Typical Procedure for the Preparation of Racemic 2-(2-Methylphenyl)propanoic acid (**4i**) by the Methylation at 2-Position of (2-Methylphenyl)acetic Acid[3]



rac–**4i**

To a solution of diisopropylamine (1.55 mL, 11.0 mmol) in THF (20 mL) at 0 °C was added *n*-BuLi in hexane (2.76 M, 3.99 mL, 11.0 mmol) and the mixture was stirred for 30 min. After cooling to –78 °C, 2-methylphenylacetic acid (751 mg, 5.00 mmol) in THF (5 mL) was added to the reaction mixture and then it was stirred for 1 h at 0 °C. After cooling to –78 °C, methyl iodide (467 μL, 7.50 mmol) was added to the reaction mixture and then it was stirred for 2 h at room temperature. After cooling to 0 °C, the reaction mixture was quenched with 1 M hydrochloric acid to adjust to pH = 1. The mixture was extracted with dichloromethane and dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/1) to afford 2-(2-methylphenyl)propanoic acid (**4i**) and it was further purified by recrystallization from petroleum ether to produce a white solid (484 mg, 59%).

Typical Procedure for the Preparation of Racemic 2-(2,3,5-Trimethylphenyl)propanoic Acid (**4q**) via the Aryl Substitution at 2-Position of Ethyl 2-Bromopropanoate[4]

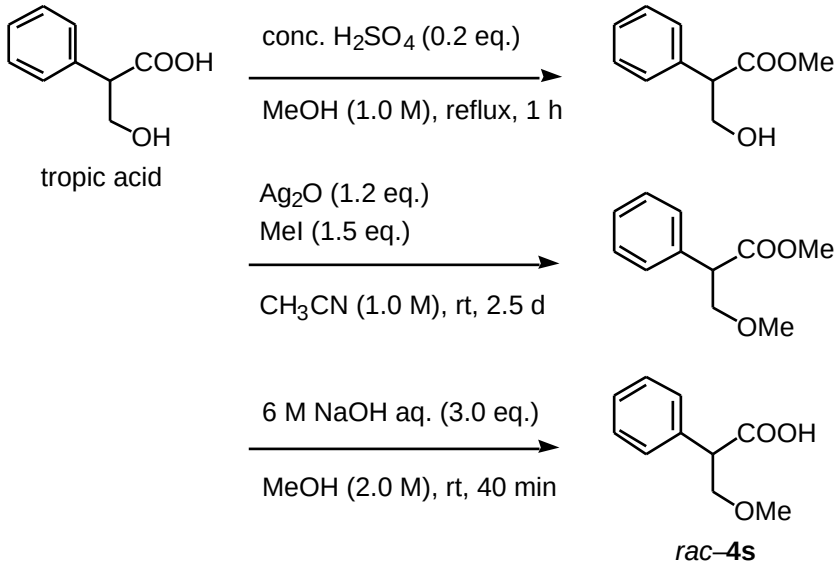


rac–**4q**

To a solution of $NiCl_2$(dppp) (244 mg, 0.45 mmol) in THF (30 mL) at 0 °C were successively added ethyl 2-bromopropanoate (1.40 mL, 10.8 mmol) and 2,3,5-trimethylphenylmagnesium bromide in THF (1.0 M, 9.0 mL, 9.0 mmol) and the whole mixture was stirred for 1 h at the same temperature. The reaction was quenched with saturated aqueous ammonium chloride and the mixture was extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate. After filtration and evaporation of the solvent, the crude product was purified by silica gel column chromatography (hexane to hexane/diethyl ether = 40/1) to afford ethyl 2-(2,3,5-trimethylphenyl)propanoate (887 mg, 45%).

To a solution of ethyl 2-(2,3,5-trimethylphenyl)propanoate (887 mg, 4.03 mmol) in methanol (4 mL) at room temperature was added aqueous 50% KOH (2.0 mL, 17.7 mmol) and the whole mixture was refluxed for 1 h. After cooling to 0 °C, the reaction mixture was quenched with 6 M hydrochloric acid to adjust to pH = 1. The mixture was extracted with dichloromethane and dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/2 to ethyl acetate) to afford 2-(2,3,5-trimethylphenyl)propanoic acid (**4q**) and it was further purified by recrystallization from $CHCl_3$/petroleum ether to produce a white solid (419 mg, 54%).

Preparation of Racemic 3-Methoxy-2-phenylpropanoic Acid (**4s**) from Tropic Acid

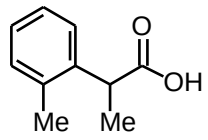


To a solution of tropic acid (2.00 g, 12.0 mmol) in methanol (12 mL) at room temperature was added conc. H_2SO_4 (120 μL, 2.25 mmol) and the mixture was refluxed for 1 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and then it was quenched with saturated aqueous sodium hydrogencarbonate at 0 °C. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with saturated aqueous sodium hydrogencarbonate and water, and dried over magnesium sulfate. The mixture was filtered and concentrated by evaporation of the solvent to afford crude methyl 3-hydroxy-2-phenylpropanoate as a colorless oil.[5] Above prepared methyl 3-hydroxy-2-phenylpropanoate was instantly used in the following reaction without further purification.

To a solution of the above crude methyl 3-hydroxy-2-phenylpropanoate in CH_3CN (12 mL) at room temperature was added Ag_2O (3.35 g, 14.5 mmol). After cooling to 0 °C, methyl iodide (1.12 mL, 18.0 mmol) was added to the reaction mixture. The whole mixture was stirred for 60 h at room temperature under darkness. After filtration of the mixture through a pad of Celite, the crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/20) to afford methyl 3-methoxy-2-phenylpropanoate (1.76 g, 75% for 2 steps) as a colorless oil.[6]

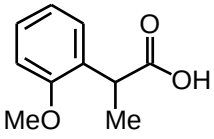
To a solution of methyl 3-methoxy-2-phenylpropanoate (1.76 g, 9.07 mmol) in methanol

(4.5 mL) at room temperature was added aqueous sodium hydroxide (6 M, 4.5 mL, 27.0 mmol) and the whole mixture was stirred at room temperature for 40 min. After cooling to 0 °C, 6 M hydrochloric acid was added to the mixture and it was extracted with dichloromethane and dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by silica gel column chromatography (ethyl acetate/hexane/formic acid = 1/9/0.02) and the product was recrystallized from $CHCl_3$/petroleum ether to produce 3-methoxy-2-phenylpropanoicacid (**4s**) as a white solid (818 mg, 50%).



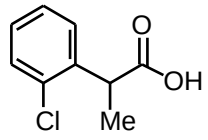
rac–**4i**

2-(2-Methylphenyl)propanoic acid (4i): Mp: 82-83 °C (petroleum ether); IR (KBr): 2990, 1495, 1455, 761, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.5 (br s, 1H, COOH), 7.38-7.14 (m, 4H), 4.01 (q, *J* = 7.2 Hz, 1H), 2.41 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.9, 138.3, 135.9, 130.5, 127.2, 126.53, 126.45, 41.1, 19.6, 17.5; HR MS: calcd for $C_{10}H_{12}O_2Na$ ($M+Na^+$) 187.0730, found 187.0738.



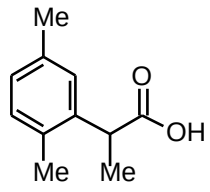
rac–**4j**

2-(2-Methoxyphenyl)propanoic acid (4j): Mp: 90-91 °C ($CHCl_3$/petroleumether); IR (KBr): 2989, 1703, 1495, 1455, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 10.9 (br s, 1H, COOH), 7.09-6.98 (m, 2H), 6.78-6.63 (m, 2H), 3.87 (q, *J* = 7.2 Hz, 1H), 3.61 (s, 3H), 1.27 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.8, 156.6, 128.7, 128.3, 128.0, 120.8, 110.7, 55.5, 39.0, 16.8; HR MS: calcd for $C_{10}H_{12}O_3Na$ ($M+Na^+$) 203.0679, found 203.0677.



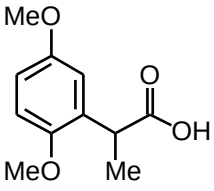
rac–**4k**

2-(2-Chlorophenyl)propanoic acid (4k): Mp: 77-78 °C (petroleum ether); IR (KBr): 2964, 1705, 1477, 755, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 10.7 (br s, 1H, COOH), 7.48-7.36 (m, 2H), 7.35-7.21 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 164.4, 137.6, 133.8, 129.7, 128.5, 128.4, 127.2, 41.9, 17.3; HR MS: calcd for $C_9H_9O_2ClNa$ ($M+Na^+$) 207.0183, found 207.0183.



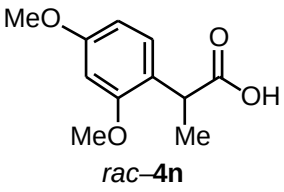
rac–**4l**

2-(2,5-Dimethylphenyl)propanoic acid (4l): Mp: 102-103 °C (CH_2Cl_2/hexane); IR (KBr): 2957, 1705, 1507, 1454, 931, 819 cm^{-1}; ^1H NMR ($CDCl_3$): δ 11.9 (br s, 1H, COOH), 7.11-7.03 (m, 2H), 7.01-6.95 (m, 1H), 3.96 (q, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 1.48 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 181.4, 138.0, 135.9, 132.7, 130.4, 127.9, 127.2, 41.0, 21.0, 19.1, 17.5; HR MS: calcd for $C_{11}H_{14}O_2Na$ ($M+Na^+$) 201.0886, found 201.0890.



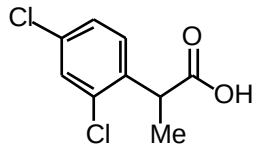
rac–**4m**

2-(2,5-Dimethoxylphenyl)propanoic acid (4m): Mp: 92-93 °C ($CHCl_3$/petroleum ether); IR (KBr): 2992, 1708, 1589, 1506, 1458, 811, 708 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.6 (br s, 1H, COOH), 6.86-6.73 (m, 3H), 4.06 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 1.47 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.5, 153.7, 150.9, 129.8, 114.6, 112.3, 111.8, 56.2, 55.7, 39.1, 16.8; HR MS: calcd for $C_{11}H_{14}O_4Na$ ($M+Na^+$) 233.0784, found 233.0775.



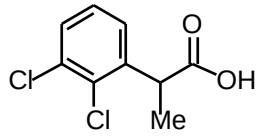
rac–**4n**

2-(2,4-Dimethoxylphenyl)propanoic acid (4n): Mp: 94-96 °C ($CHCl_3$/petroleum ether); IR (KBr): 2972, 1685, 1614, 1586, 841, 779, 660 cm^{-1}; ^1H NMR ($CDCl_3$): δ 11.2 (br s, 1H, COOH), 7.16 (d, *J* = 8.7 Hz, 1H), 6.51-6.46 (m, 2H), 4.01 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 181.3, 159.9, 157.6, 128.3, 121.2, 104.3, 98.7, 55.5, 55.3, 38.4, 17.0; HR MS: calcd for $C_{11}H_{14}O_4Na$ ($M+Na^+$) 233.0784, found 233.0785.



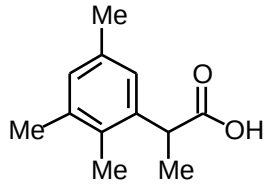
rac–**4o**

2-(2,4-Dichlorophenyl)propanoic acid (4o): Mp: 73-74 °C (petroleum ether); IR (KBr): 2959, 1709, 1592, 1469, 1234, 816, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.6 (br s, 1H, COOH), 7.31 (d, *J* = 1.8 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 1H), 1.42 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 179.5, 136.2, 134.5, 133.7, 129.4, 129.3, 127.5, 41.5, 17.2; HR MS: calcd for $C_9H_8O_2Cl_2Na$ ($M+Na^+$) 240.9794, found 240.9797.



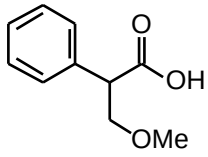
rac–**4p**

2-(2,3-Dichlorophenyl)propanoic acid (4p): Mp: 112-113 °C ($CHCl_3$/petroleum ether); IR (KBr): 2983, 1708, 1458, 1424, 1222, 925, 788, 726 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.4 (br s, 1H, COOH), 7.28 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.09 (dd, *J* = 8.0, 7.5 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 179.9, 139.9, 133.4, 132.3, 129.4, 127.5, 126.6, 42.9, 17.2; HR MS: calcd for $C_9H_8O_2Cl_2Na$ ($M+Na^+$) 240.9794, found 240.9794.



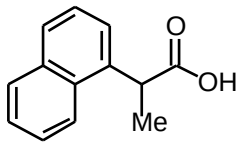
rac–**4q**

2-(2,3,5-Trimethylphenyl)propanoic acid (4q): Mp: 105-106 °C ($CHCl_3$/petroleum ether); IR (KBr): 3094, 1715, 1507, 1451, 942, 677 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 12.0 (br s, 1H, COOH), 7.01 (s, 1H), 6.88 (s, 1H), 3.86 (q, *J* = 7.2 Hz, 1H), 2.26 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 181.6, 135.5, 135.2, 134.3, 132.9, 131.8, 127.6, 40.7, 19.2, 19.1, 18.8, 17.4; HR MS: calcd for $C_{12}H_{16}O_2Na$ ($M+Na^+$) 215.1043, found 215.1039.



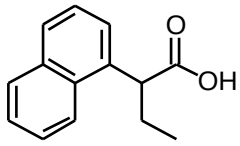
rac–**4s**

3-Methoxy-2-phenylpropanoic acid (4s): Mp: 58-59 °C ($CHCl_3$/petroleumether); IR (KBr): 2954, 1702, 1415, 952, 725, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.67 (br s, 1H, COOH), 7.37-7.27 (m, 5H), 3.98 (dd, *J* = 9.3, 8.4 Hz, 1H), 3.90 (dd, *J* = 9.3, 4.2 Hz, 1H), 3.62 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.38 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 177.7, 135.1, 128.8, 128.2, 127.9, 73.8, 59.1, 51.8; HR MS: calcd for $C_{10}H_{12}O_3Na$ ($M+Na^+$) 203.0679, found 203.0680.



rac–**4t**

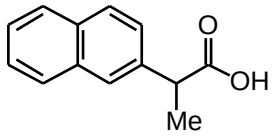
2-(1-Naphthyl)propanoic acid (4t): Mp: 134-135 °C ($CHCl_3$/petroleum ether); IR (KBr): 2984, 1709, 1514, 1454, 795, 778 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.8 (br s, 1H, COOH), 8.09 (d, *J* = 8.4 Hz, 1H), 7.91-7.84 (m, 1H), 7.82-7.76 (m, 1H), 7.58-7.42 (m, 4H), 4.54 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.8, 135.8, 133.8, 131.2, 128.8, 127.9, 126.3, 125.5, 125.4, 124.4, 122.9, 40.9, 17.6; HR MS: calcd for $C_{13}H_{12}O_2Na$ ($M+Na^+$) 223.0730, found 223.0740.



rac–**4u**

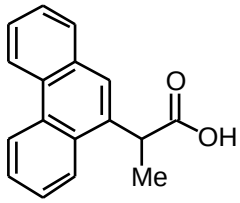
2-(1-Naphthyl)butanoic acid (4u): Mp: 76-77 °C (petroleum ether); IR (KBr): 3020, 1703, 1510, 1458, 799, 779 cm^{-1}; ^1H NMR ($CDCl_3$): δ 11.8 (br s, 1H, COOH), 8.00 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.43-7.23 (m, 4H), 4.17 (dd, *J* = 7.5, 7.2 Hz, 1H), 2.15 (ddq, *J* = 14.3, 7.5, 7.2 Hz, 1H), 1.83 (ddq, *J* = 14.3, 7.2, 7.2 Hz, 1H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.6, 134.6, 134.0, 131.7, 129.0, 127.9, 126.4, 125.6, 125.5, 125.0, 123.1, 48.3,

25.9, 12.4; HR MS: calcd for $C_{14}H_{14}O_2Na$ ($M+Na^+$) 237.0886, found 237.0888.



rac–**4v**

2-(2-Naphthyl)propanoic acid (4v): Mp: 119-120 °C ($CHCl_3$/petroleum ether); IR (KBr): 2986, 1698, 1458, 1419, 804, 747 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.4 (br s, 1H, COOH), 7.86-7.73 (m, 4H), 7.52-7.41 (m, 3H), 3.92 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.7, 137.0, 133.2, 132.5, 128.3, 127.7, 127.5, 126.2, 126.1, 125.8, 125.6, 45.3, 18.0; HR MS: calcd for $C_{13}H_{12}O_2Na$ ($M+Na^+$) 223.0730, found 223.0727.



rac–**4w**

2-(9-Phenanthryl)propanoic acid (4w): Mp: 177-178 °C (benzene/petroleum ether); IR (KBr): 3038, 1707, 1462, 1411, 768, 750, 726 cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.5 (br s, 1H, COOH), 8.91-8.85 (m, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 8.21-8.15 (m, 1H), 7.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.77 (s, 1H), 7.73-7.60 (m, 4H), 4.48 (q, *J* = 7.0 Hz, 1H), 1.61 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (DMSO-d_6): δ 176.0, 136.0, 131.3, 130.44, 130.42, 129.4, 128.6, 127.2, 127.1, 127.0, 126.8, 125.2, 124.3, 123.8, 122.9, 41.5, 17.9; HR MS: calcd for $C_{17}H_{14}O_2Na$ ($M+Na^+$) 273.0886, found 273.0895.

Typical Procedure for Kinetic Resolution of Racemic Carboxylic Acids 4a and 4c Using Pivalic Anhydride with (*S*)-β-Np-BTM [Table 5, Entries 1 and 3]: To a solution of (±)-2-phenylpropanoic acid (**4a**) (30.0 μL, 0.200 mmol), pivalic anhydride (48.7 μL, 0.240 mmol), and bis(α-naphthyl)methanol (**3**) (28.5 mg, 0.100 mmol) in dichloromethane (1.0 mL) at room temperature were successively added diisopropylethylamine (62.7 μL, 0.360 mmol) and (*S*)-β-Np-BTM (3.0 mg, 9.90 μmol). The mixture was stirred for 12 h at room temperature, and then quenched with saturated aqueous ammonium chloride. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by preparative thin layer chromatography on silica (benzene/hexane = 70/30) to afford the corresponding ester (*S*)-**5a** (37.5 mg, 45% yield, 92% ee) as a white solid and a part of the recovered optically active carboxylic acid. The mixed solvent including toluene instead of benzene (toluene/hexane = 70/30) could be also applicable for the eluant in the preparative thin layer chromatography. The aqueous layer was acidified by 1 M hydrochloric acid to adjust to pH = 2 and then the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by preparative thin layer chromatography on silica (formic acid/ethyl acetate/hexane = 2/20/80) to afford the recovered optically active carboxylic acid (*R*)-**4a** (totally 15.3 mg, 51% yield, 59% ee) as a colorless oil. [Table 5, Entry 1]

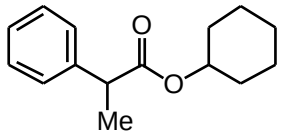
Typical Procedure for Kinetic Resolution of Racemic Carboxylic Acids 4b, and 4d-4h Using Pivalic Anhydride with (*S*)-β-Np-BTM [Table 5, Entries 2, and 4-8]: To a solution of (±)-ibuprofen (**4e**) (41.2 mg, 0.200 mmol), pivalic anhydride (48.7 μL, 0.240 mmol), and bis(α-naphthyl)methanol (**3**) (28.4 mg, 0.100 mmol) in dichloromethane (1.0 mL) at room temperature were successively added diisopropylethylamine (62.7 μL, 0.360 mmol) and (*S*)-β-Np-BTM (3.0 mg, 9.90 μmol). The mixture was stirred for 12 h at room temperature, and then quenched with saturated aqueous ammonium chloride. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by preparative thin layer chromatography on silica (benzene/hexane = 70/30) to afford the corresponding ester (*S*)-**5e** (39.7 mg, 42% yield, 93% ee) as a colorless oil and the recovered optically active ibuprofen ((*R*)-**4e**) (13.3 mg, 32% yield, 67% ee) as a white solid. [Table 5, Entry 5] The mixed solvent including toluene instead of benzene

(toluene/hexane = 70/30) could be also applicable as an eluant in the preparative thin layer chromatography.

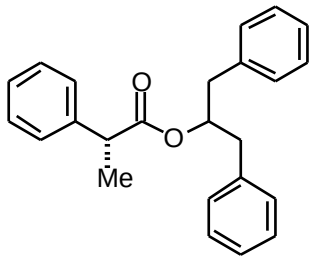
Procedure for Kinetic Resolution of Racemic Naproxen (6) Using PMBA with (*S*)-β-Np-BTM [Scheme 3]: To a solution of PMBA (68.5 mg, 0.239 mmol), (±)-naproxen (**6**) (45.8 mg, 0.199 mmol), and bis(α-naphthyl)methanol (**3**) (28.4 mg, 0.100 mmol) in dichloromethane (2.0 mL) at room temperature were successively added diisopropylethylamine (62.7 μL, 0.360 mmol) and (*S*)-β-Np-BTM (2.9 mg, 9.6 μmol). The mixture was stirred for 12 h at room temperature, and then quenched with saturated aqueous ammonium chloride. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by preparative thin layer chromatography on silica (formic acid/ethyl acetate/hexane = 2/20/80) to afford the corresponding ester (*S*)-**7** (49.1 mg, 49% yield, 93% ee) as a colorless oil and the recovered optically active naproxen ((*R*)-**6**) (23.4 mg, 51% yield, 74% ee) as a white solid. [Scheme 3, Run 4]

Procedure for the Preparation of Optically Active Naproxen ((*S*)-6) from Bis(α-naphthyl)methyl Ester ((*S*)-7) by Deprotection [Scheme 4]: To a solution of (*S*)-naproxen bis(α-naphthyl)methyl ester ((*S*)-**7**) (46.4 mg, 93.4 μmol, 93% ee) in THF (1.9 mL) at room temperature under argon atmosphere was added palladium on carbon (10%, 30.1 mg, 28.3 μmol). The mixture was stirred for 26 h at room temperature under hydrogen atmosphere (1 atm) and then it was replaced by argon atmosphere. After filtration of the mixture through Celite with methanol and evaporation of the solvent, the crude product was purified by thin layer chromatography on silica (formic acid/ethyl acetate/hexane = 2/20/80) to afford (*S*)-naproxen ((*S*)-**6**) (18.2 mg, 85% yield, 93% ee) as a white solid.

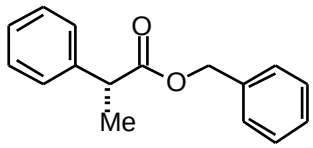
(Carboxylic Esters Derived from 2-Phenylpropanoic Acid (**1**) in **Table 1**)



Cyclohexyl 2-phenylpropanoate [**Table 1**, Entry 3, 0.3% ee]: HPLC (CHIRALCEL OJ-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 17.8 min (50.16%), t_R = 20.6 min (49.84%); IR (neat): 1725, 1496, 1452, 732, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.27-7.12 (m, 5H), 4.75-4.54 (m, 1H), 3.61 (q, *J* = 7.0 Hz, 1H), 1.80-1.13 (m, 10H), 1.41 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.9, 140.8, 128.4, 127.4, 126.9, 72.6, 45.7, 31.4, 31.2, 25.3, 23.5, 23.4, 18.4; HR MS: calcd for $C_{15}H_{20}O_2Na$ ($M+Na^+$) 255.1356, found 255.1352.

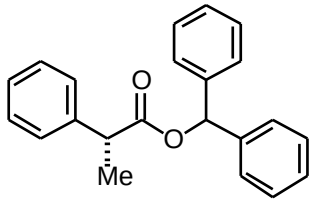


Dibenzylmethyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 4, 2.5% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 31.0 min (48.76%), t_R = 35.0 min (51.24%); IR (neat): 1728, 1603, 1496, 751, 699 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.19-7.07 (m, 6H), 7.06-7.00 (m, 7H), 6.90-6.85 (m, 2H), 5.21 (tt, *J* = 6.5, 6.5 Hz, 1H), 3.49 (q, *J* = 7.0 Hz, 1H), 2.73 (d, *J* = 6.5 Hz, 2H), 2.68 (d, *J* = 6.5 Hz, 2H), 1.24 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.7, 140.3, 137.4, 137.1, 129.4, 129.3, 128.5, 128.3, 128.2, 127.5, 126.9, 126.4, 126.3, 75.4, 45.6, 39.9, 39.7, 18.2; HR MS: calcd for $C_{24}H_{24}O_2Na$ ($M+Na^+$) 367.1669, found 367.1661.

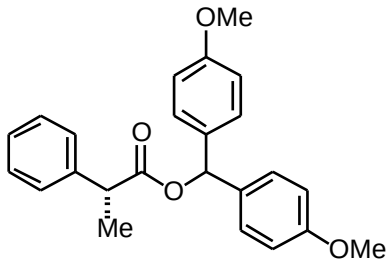


Benzyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 5, 33% ee]: HPLC (CHIRALCEL OJ-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 28.8 min

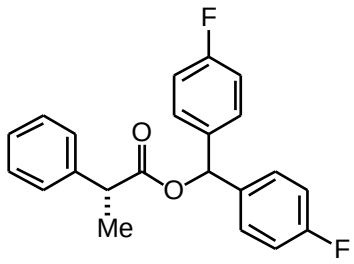
(33.7%), t_R = 32.3 min (66.3%); IR (neat): 1740, 1496, 1454, 734, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.36-7.20 (m, 10H), 5.13 (d, *J* = 12.5 Hz, 1H), 5.07 (d, *J* = 12.5 Hz, 1H), 3.78 (q, *J* = 7.1 Hz, 1H), 1.52 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 174.3, 140.3, 135.9, 128.6, 128.4, 128.0, 127.8, 127.5, 127.1, 66.4, 45.5, 18.4; HR MS: calcd for $C_{16}H_{16}O_2Na$ ($M+Na^+$) 263.1043, found 263.1051.



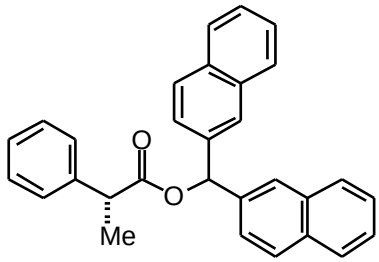
Diphenylmethyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 6, 33% ee]: HPLC (CHIRALCEL OJ-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 26.9 min (66.7%), t_R = 41.3 min (33.3%); IR (neat): 1732, 1496, 1453, 742, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.24-7.14 (m, 10H), 7.13-7.07 (m, 3H), 7.01-6.95 (m, 2H), 6.74 (s, 1H), 3.75 (q, *J* = 7.0 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.2, 140.22, 140.15, 140.0, 128.5, 128.4, 128.2, 127.9, 127.64, 127.57, 127.14, 127.10, 126.6, 77.0, 45.7, 18.1; HR MS: calcd for $C_{22}H_{20}O_2Na$ ($M+Na^+$) 339.1356, found 339.1354.



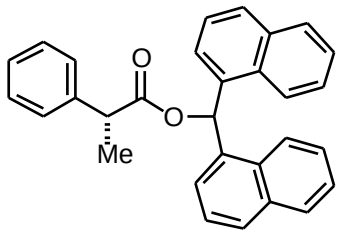
Di(4-methoxyphenyl)methyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 7, 12% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 32.4 min (56.2%), t_R = 37.0 min (43.8%); IR (neat): 1731, 1612, 1513, 828, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.24-7.04 (m, 6H), 6.92-6.83 (m, 2H), 6.77-6.69 (m, 2H), 6.67 (s, 1H), 6.65-6.59 (m, 3H), 3.71 (q, *J* = 7.0 Hz, 1H), 3.66 (s, 3H), 3.64 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.3, 159.1, 158.9, 140.3, 132.6, 132.4, 128.49, 128.46, 127.9, 127.6, 127.0, 113.7, 113.5, 76.4, 55.2, 55.1, 45.7, 18.1; HR MS: calcd for $C_{24}H_{24}O_4Na$ ($M+Na^+$) 399.1567, found 399.1560.



Di(4-fluorophenyl)methyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 8, 27% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 13.0 min (63.3%), t_R = 15.0 min (36.7%); IR (neat): 1735, 1605, 1509, 834, 699 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.35-7.14 (m, 7H), 7.03-6.81 (m, 6H), 6.76 (s, 1H), 3.81 (q, *J* = 7.2 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.1, 162.3 (d, *J* = 247.0 Hz), 162.2 (d, *J* = 245.9 Hz), 140.0, 135.8 (d, *J* = 3.0 Hz), 135.6 (d, *J* = 4.1 Hz), 128.9 (d, *J* = 8.3 Hz), 128.6, 128.3 (d, *J* = 8.2 Hz), 127.6, 127.2, 115.4 (d, *J* = 21.7 Hz), 115.2 (d, *J* = 21.6 Hz), 75.7, 45.6, 17.9; HR MS: calcd for $C_{22}H_{18}O_2F_2Na$ ($M+Na^+$) 375.1167, found 375.1167.



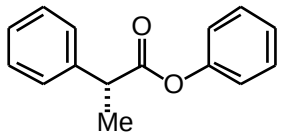
Di(2-naphthyl)methyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 9, 31% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 24.4 min (65.5%), t_R = 28.9 min (34.5%); ^1H NMR ($CDCl_3$): δ 7.83-7.70 (m, 5H), 7.69-7.55 (m, 2H), 7.51-7.29 (m, 11H), 7.23-7.15 (m, 1H), 7.15 (s, 1H), 3.91 (q, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.3, 140.4, 137.3, 137.2, 133.04, 132.98, 132.95, 132.8, 128.67, 128.67, 128.4, 128.10, 128.08, 127.76, 127.76, 127.6, 127.5, 127.2, 126.5, 126.2, 126.1, 126.0, 125.3, 125.2, 124.7, 77.1, 45.8, 18.0; HR MS: calcd for $C_{30}H_{24}O_2Na$ ($M+Na^+$) 439.1669, found 439.1647. Analytical data on racemic compound: Mp: 122-123 °C (CH_2Cl_2/hexane); IR (KBr): 1723, 1508, 1454, 790 cm^{-1}.



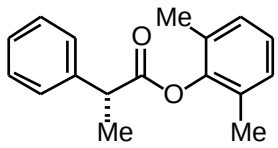
Di(1-naphthyl)methyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 10, 81% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 14.0 min (9.3%), t_R = 18.6 min (90.7%); ^{1}H NMR ($CDCl_3$): δ 8.29 (s, 1H), 7.99-7.94 (m, 1H), 7.84-7.79 (m, 1H), 7.74 (t, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.45-7.38 (m, 2H), 7.35-7.31 (m, 1H), 7.23-7.14 (m, 7H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.5, 140.0, 134.8, 134.6, 133.8, 133.7, 131.2, 130.8, 129.1, 128.9, 128.7, 128.64, 128.57, 127.8, 127.2, 126.7, 126.4, 126.3, 125.9, 125.6, 125.2, 125.0, 123.5, 123.3, 71.1, 45.6, 18.2; HR MS: calcd for $C_{30}H_{24}O_2Na$ ($M+Na^+$) 439.1669, found 439.1662. Analytical data on racemic compound: Mp: 127-128 °C (*i*-PrOH/hexane); IR (KBr): 3067, 1728, 1600, 1509, 776, 699 cm^{-1}.

[**Table 1**, Entry 11, 86% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 28.3 min (6.9%), t_R = 37.4 min (93.1%).

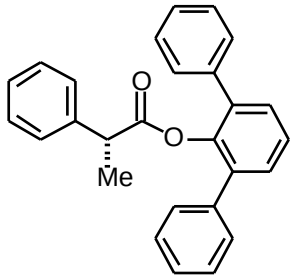
[**Table 1**, Entry 12, 89% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 15.4 min (5.7%), t_R = 20.5 min (94.3%).



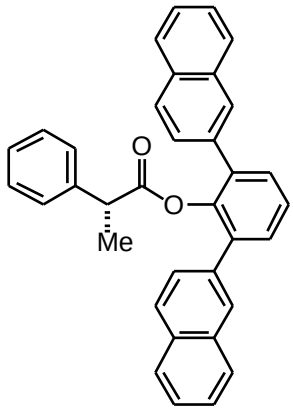
Phenyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 13, 24% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 14.0 min (37.8%), t_R = 15.9 min (62.2%); IR (neat): 1761, 1593, 1493, 749, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.34-7.18 (m, 7H), 7.13-7.07 (m, 1H), 6.94-6.87 (m, 2H), 3.88 (q, *J* = 7.3 Hz, 1H), 1.53 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.0, 150.8, 140.0, 129.3, 128.8, 127.5, 127.3, 125.7, 121.3, 45.6, 18.5; HR MS: calcd for $C_{15}H_{14}O_2Na$ ($M+Na^+$) 249.0886, found 249.0898.



2,6-Dimethylphenyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 14, 44% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 14.0 min (27.8%), t_R = 16.8 min (72.2%); IR (neat): 1748, 1477, 1450, 769, 699 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.52-7.46 (m, 2H), 7.44-7.29 (m, 3H), 7.03 (s, 3H), 4.07 (q, *J* = 7.2 Hz, 1H), 1.97 (s, 6H), 1.72 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 172.0, 148.0, 139.8, 130.1, 128.6, 128.5, 127.7, 127.4, 125.7, 45.5, 18.1, 16.0; HR MS: calcd for $C_{17}H_{18}O_2Na$ ($M+Na^+$) 277.1199, found 277.1206.

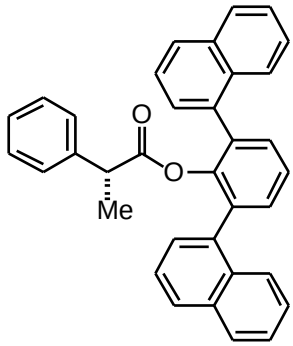


2,6-Diphenylphenyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 15, 58% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 16.1 min (20.9%), t_R = 17.5 min (79.1%); IR (neat): 1757, 1599, 1456, 1422, 757, 699 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.40-7.10 (m, 16H), 6.92-6.85 (m, 2H), 3.43 (q, *J* = 7.3 Hz, 1H), 1.08 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 172.0, 149.2, 145.0, 139.0, 137.49, 137.49, 135.9, 129.89, 129.87, 129.3, 128.94, 128.94, 128.72, 128.67, 128.3, 127.97, 127.97, 127.52, 127.46, 127.2, 126.8, 126.2, 120.6, 45.1, 17.9; HR MS: calcd for $C_{27}H_{22}O_2Na$ ($M+Na^+$) 401.1512, found 401.1531.



2,6-Di(2-naphthyl)phenyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 16, 64% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 21.3 min (18.0%), t_R = 23.9 min (82.0%); ^{1}H NMR ($CDCl_3$): δ 7.93-7.36 (m, 16H), 7.25 (s, 1H), 6.90 (tt, *J* = 7.5, 1.5 Hz, 1H), 6.79-6.70 (m, 2H), 6.67-6.58 (m, 2H), 3.35 (q, *J* = 7.2 Hz, 1H), 0.95 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 172.2, 145.5, 138.8, 136.1, 135.1, 133.1, 132.5, 130.4, 128.3, 128.2, 128.0, 127.6, 127.2, 127.1, 126.7, 126.4, 126.1, 126.0, 45.1, 18.1; HR MS: calcd for $C_{35}H_{26}O_2Na$ ($M+Na^+$) 501.1825, found 501.1812. Analytical data on racemic compound: Mp: 135-136 °C (*i*-PrOH/hexane); IR (KBr): 1754, 1446, 1177, 1126, 820, 797, 749 cm^{-1}.

[**Table 1**, Entry 17, 67% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 21.3 min (16.3%), t_R = 23.9 min (83.7%).

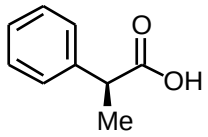


2,6-Di(1-naphthyl)phenyl (*R*)-2-phenylpropanoate [**Table 1**, Entry 18, 77% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 18.8 min (88.4%), t_R = 21.3 min (11.6%). It was observed that there exists equilibrium among three rotamers by ^{1}H NMR. ^{1}H NMR spectra of the major isomer were assigned as follows; ^{1}H NMR ($CDCl_3$): δ 7.92-7.65 (m, 6H), 7.55-7.30 (m, 11H), 7.02-6.69

(m, 3H), 6.28-6.21 (m, 2H), 2.75 (q, *J* = 7.2 Hz, 1H), 0.39 (d, *J* = 7.2 Hz, 3H); HR MS: calcd for $C_{35}H_{26}O_2Na$ ($M+Na^+$) 501.1825, found 501.1842. Analytical data on racemic compound: Mp: 130-131 °C (EtOAc/hexane); IR (KBr): 1756, 1392, 1130, 1118, 798, 777 cm^{-1}.

[**Table 1**, Entry 19, 86% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.3 mL/min): t_R = 29.6 min (93.0%), t_R = 33.6 min (7.0%).

(2-Phenylpropanoic Acid (**1**) in **Table 1**)



(***S***)–**1**

(*S*)-2-Phenylpropanoic acid ((*S*)-1) [**Table 1**, Entry 3, 2.9% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 10/90/0.1, flow rate = 0.5 mL/min): t_R = 12.6 min (48.53%), t_R = 13.9 min (51.47%); ^{1}H NMR ($CDCl_3$): δ 10.95 (br s, 1H, COOH), 7.30-7.16 (m, 5H), 3.67 (q, *J* = 7.2 Hz, 1H), 1.45 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 181.0, 139.7, 128.7, 127.6, 127.4, 45.4, 18.0.

[**Table 1**, Entry 4, 0.0% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 10/90/0.1, flow rate = 0.5 mL/min): t_R = 12.2 min (50.01%), t_R = 13.5 min (49.99%).

[**Table 1**, Entry 5, 23% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 10/90/0.1, flow rate = 1.0 mL/min): t_R = 12.6 min (38.4%), t_R = 14.0 min (61.6%).

[**Table 1**, Entry 6, 19% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 10/90/0.1, flow rate = 0.5 mL/min): t_R = 12.9 min (40.4%), t_R = 14.4 min (59.6%).

[**Table 1**, Entry 7, 0.1% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 36.7 min (50.05%), t_R = 40.6 min (49.95%).

[**Table 1**, Entry 8, 35% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 36.8 min (32.3%), t_R = 40.5 min (67.7%).

[**Table 1**, Entry 9, 41% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 40.1 min (29.7%), t_R = 44.4 min (70.3%).

[**Table 1**, Entry 10, 80% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 37.5 min (9.9%), t_R = 41.6 min (90.1%).

[**Table 1**, Entry 11, 60% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 35.5 min (20.2%), t_R = 38.6 min (79.8%).

[**Table 1**, Entry 12, 27% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 41.3 min (36.6%), t_R = 44.4 min (63.4%).

[**Table 1**, Entry 13, 28% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 37.4 min (36.2%), t_R = 41.2 min (63.8%).

[**Table 1**, Entry 14, 9.0% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 10/90/0.1, flow rate = 0.5 mL/min): t_R = 12.2 min (45.5%), t_R = 13.7 min (54.5%).

[**Table 1**, Entry 15, 7.8% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 35.9 min (46.1%), t_R = 39.5 min (53.9%).

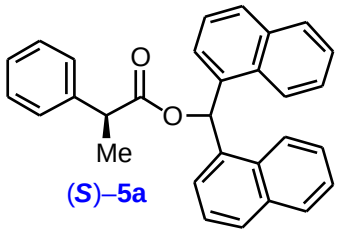
[**Table 1**, Entry 16, 23% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 39.6 min (38.5%), t_R = 43.1 min (61.5%).

[**Table 1**, Entry 17, 11% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 39.6 min (44.5%), t_R = 43.1 min (55.5%).

[**Table 1**, Entry 18, 15% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 39.6 min (42.6%), t_R = 43.3 min (57.4%).

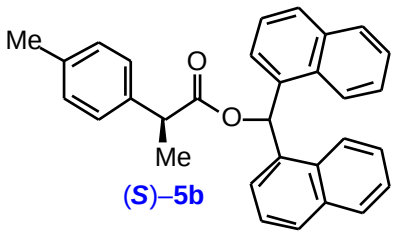
[**Table 1**, Entry 19, 17% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min): t_R = 35.5 min (41.3%), t_R = 39.0 min (58.7%).

(Optically Active Carboxylic Esters in **Table 6**)



(***S***)–**5a**

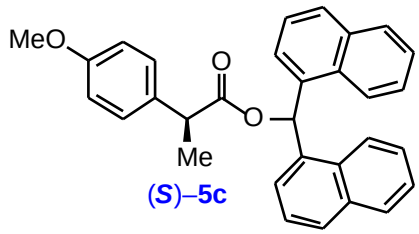
Di(1-naphthyl)methyl (*S*)-2-phenylpropanoate ((*S*)-5a) [**Table 6**, Entry 1, 92% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 14.6 min (96.0%), t_R = 19.6 min (4.0%); ^{1}H NMR ($CDCl_3$): δ 8.29 (s, 1H), 7.99-7.94 (m, 1H), 7.84-7.79 (m, 1H), 7.74 (t, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.45-7.38 (m, 2H), 7.35-7.31 (m, 1H), 7.23-7.14 (m, 7H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.5, 140.0, 134.8, 134.6, 133.8, 133.7, 131.2, 130.8, 129.1, 128.9, 128.7, 128.64, 128.57, 127.8, 127.2, 126.7, 126.4, 126.3, 125.9, 125.6, 125.2, 125.0, 123.5, 123.3, 71.1, 45.6, 18.2; HR MS: calcd for $C_{30}H_{24}O_2Na$ ($M+Na^+$) 439.1669, found 439.1668. Analytical data on racemic compound: Mp: 128 °C (*i*-PrOH/hexane); IR (KBr): 3067, 1728, 1600, 1509, 776, 699 cm^{-1}.



(***S***)–**5b**

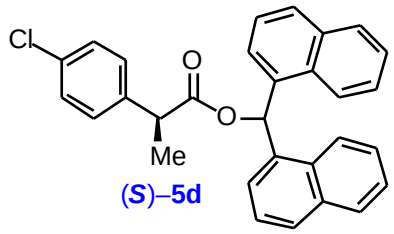
Di(1-naphthyl)methyl (*S*)-2-(4-methylphenyl)propanoate ((*S*)-5b) [**Table 6**, Entry 2, 86% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.75 mL/min): t_R = 9.6 min (93.2%), t_R = 13.8 min (6.8%); IR (neat): 3051, 1733, 1598, 1512, 801, 777, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.27 (s, 1H), 7.98-7.91 (m, 1H), 7.83-7.76 (m, 1H), 7.72 (t, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.44-7.36 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22-7.14 (m, 2H), 7.13-7.01 (m, 4H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 7.5 Hz, 1H), 3.72 (q, *J* = 7.0 Hz, 1H), 2.25 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.7, 137.0, 136.7, 134.9, 134.6, 133.8, 133.7, 131.2, 130.9, 129.2, 129.1, 128.8, 128.7, 128.6, 128.3,

127.6, 126.7, 126.3, 126.2, 125.8, 125.6, 125.3, 125.2, 125.0, 123.5, 123.3, 71.1, 45.2, 21.0, 18.2; HR MS: calcd for $C_{31}H_{26}O_2Na$ ($M+Na^+$) 453.1825, found 453.1816.



(*S*)–**5c**

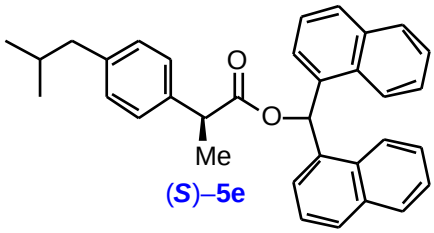
Di(1-naphthyl)methyl (*S*)-2-(4-methoxyphenyl)propanoate ((*S*)-5c) [**Table 6**, Entry 3, 89% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/20, flow rate = 0.75 mL/min): t_R = 20.8 min (94.7%), t_R = 26.6 min (5.3%); IR (neat): 3059, 1733, 1608, 1512, 783, 733 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.26 (s, 1H), 7.97-7.89 (m, 1H), 7.85-7.58 (m, 5H), 7.46-7.04 (m, 9H), 6.93 (d, *J* = 6.9 Hz, 1H), 6.75-6.67 (m, 2H), 3.78-3.68 (m, 4H), 1.42 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.7, 158.7, 134.8, 134.6, 133.8, 133.6, 132.1, 131.2, 130.9, 129.1, 128.83, 128.76, 128.71, 128.6, 128.3, 126.7, 126.3, 126.2, 125.8, 125.6, 125.3, 125.2, 125.0, 123.5, 123.3, 113.9, 71.0, 55.3, 44.8, 18.2; HR MS: calcd for $C_{31}H_{26}O_3Na$ ($M+Na^+$) 469.1774, found 469.1754.



(*S*)–**5d**

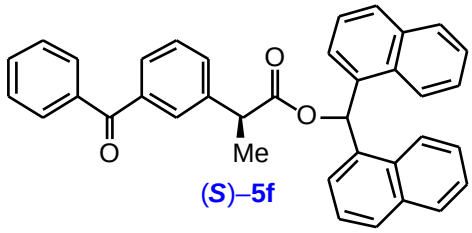
Di(1-naphthyl)methyl (*S*)-2-(4-chlorophenyl)propanoate ((*S*)-5d) [**Table 6**, Entry 4, 82% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 16.4 min (90.8%), t_R = 18.6 min (9.2%); IR (neat): 3052, 1737, 1599, 1510, 837, 777 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.26 (d, *J* = 3.0 Hz, 1H), 7.90 (dd, *J* = 7.5, 3.0 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.75 (t, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 8.5, 3.0 Hz, 1H), 7.45-7.32 (m, 3H), 7.26-7.04 (m, 8H), 6.93 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.73 (qd, *J* = 8.5, 1.5 Hz, 1H), 1.45-1.41 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 173.1, 138.4, 134.5, 134.4, 133.8, 133.7, 133.0, 131.1, 130.8, 129.2, 129.1, 128.9, 128.7, 128.6, 128.3, 126.7, 126.4, 126.1, 125.9, 125.7, 125.3, 125.2, 124.5, 123.3, 123.2, 71.4, 45.0, 18.0; HR MS: calcd for $C_{30}H_{23}O_2ClNa$ ($M+Na^+$)

473.1279, found 473.1284.



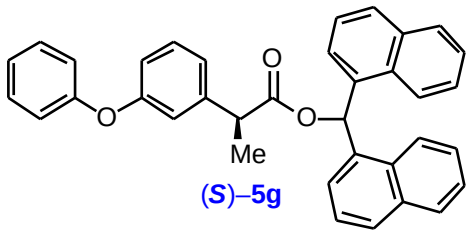
(*S*)–**5e**

(*S*)-Ibuprofen di(1-naphthyl)methyl ester ((*S*)-5e) [**Table 6**, Entry 5, 93% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 12.0 min (96.5%), t_R = 22.1 min (3.5%); IR (neat): 3036, 1735, 1599, 1512, 782, 679 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.29 (s, 1H), 8.02-7.93 (m, 1H), 7.85-7.60 (m, 5H), 7.47-7.26 (m, 3H), 7.24-7.02 (m, 6H), 7.00-6.88 (m, 3H), 3.74 (q, *J* = 7.1 Hz, 1H), 2.38 (d, *J* = 7.1 Hz, 2H), 1.78 (tqq, *J* = 7.1, 6.6, 6.6 Hz, 1H), 1.43 (d, *J* = 7.1 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 173.7, 140.6, 137.2, 134.9, 134.7, 133.8, 133.7, 131.2, 130.9, 129.3, 129.1, 128.8, 128.7, 128.6, 127.5, 126.7, 126.34, 126.25, 125.8, 125.6, 125.2, 125.0, 123.5, 123.4, 70.9, 45.3, 45.0, 30.2, 22.4, 18.1; HR MS: calcd for $C_{34}H_{32}O_2Na$ ($M+Na^+$) 495.2295, found 495.2276.



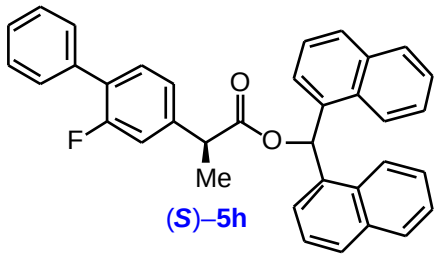
(*S*)–**5f**

(*S*)-Ketoprofen di(1-naphthyl)methyl ester ((*S*)-5f) [**Table 6**, Entry 6, 85% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/4, flow rate = 0.75 mL/min): t_R = 18.8 min (92.4%), t_R = 49.2 min (7.6%); IR (neat): 3035, 1735, 1660, 1599, 1511, 780, 680 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.28 (s, 1H), 7.93-7.85 (m, 1H), 7.82-7.54 (m, 6H), 7.52-7.44 (m, 2H), 7.44-7.06 (m, 13H), 6.95 (d, *J* = 7.1 Hz, 1H), 3.81 (q, *J* = 7.1 Hz, 1H), 1.46 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 196.3, 173.0, 140.1, 137.8, 137.3, 134.5, 134.4, 133.8, 133.7, 132.4, 131.6, 131.1, 130.8, 129.9, 129.5, 129.2, 128.93, 128.91, 128.86, 128.7, 128.6, 128.3, 128.2, 126.7, 126.4, 126.1, 125.9, 125.7, 125.4, 125.2, 125.0, 123.2, 71.4, 45.5, 17.9; HR MS: calcd for $C_{37}H_{28}O_3Na$ ($M+Na^+$) 543.1931, found 543.1910.



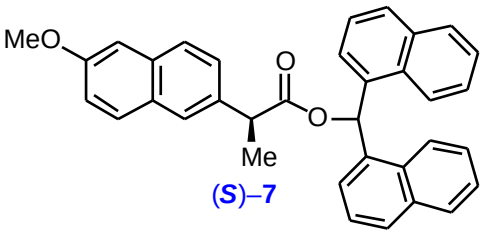
(*S*)–**5g**

(*S*)-Fenoprofen di(1-naphthyl)methyl ester ((*S*)-5g) [**Table 6**, Entry 7, 88% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 21.8 min (94.1%), t_R = 26.1 min (5.9%); IR (neat): 3036, 1735, 1585, 1485, 781, 679 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.28 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.82-7.62 (m, 5H), 7.43-7.30 (m, 3H), 7.27-7.09 (m, 7H), 6.98-6.91 (m, 3H), 6.86-6.83 (m, 1H), 6.82-6.73 (m, 3H), 3.72 (q, *J* = 7.0 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.1, 157.3, 157.0, 141.9, 134.7, 134.6, 133.8, 133.7, 131.2, 130.9, 129.8, 129.7, 129.1, 128.9, 128.8, 128.7, 128.3, 126.7, 126.4, 126.1, 125.9, 125.7, 125.3, 125.2, 125.1, 123.4, 123.3, 123.1, 122.6, 118.7, 118.4, 117.6, 71.2, 45.5, 17.9; HR MS: calcd for $C_{36}H_{28}O_3Na$ ($M+Na^+$) 531.1931, found 531.1948.



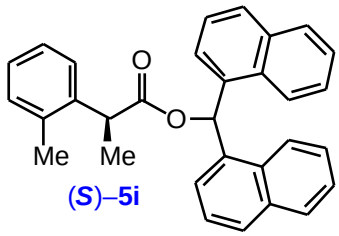
(*S*)–**5h**

(*S*)-Flurbiprofen di(1-naphthyl)methyl ester ((*S*)-5h) [**Table 6**, Entry 8, 87% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.75 mL/min): t_R = 9.6 min (93.5%), t_R = 15.9 min (6.5%); IR (neat): 3035, 1734, 1599, 1513, 783, 679 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.29 (s, 1H), 7.95-7.86 (m, 1H), 7.80-7.72 (m, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.46-7.04 (m, 13H), 7.01-6.90 (m, 3H), 3.74 (q, *J* = 7.0 Hz, 1H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 172.9, 159.6 (d, *J* = 248.2 Hz), 141.3, 141.2, 135.5, 134.6, 134.4, 133.8, 133.7, 131.1, 130.9, 130.7 (d, *J* = 3.7 Hz), 129.2, 128.9 (d, *J* = 3.2 Hz), 128.7, 128.5, 128.3, 127.8 (d, *J* = 13.7 Hz), 127.7, 126.7, 126.4, 126.1, 125.9, 125.7, 125.4, 125.2, 125.0, 123.8 (d, *J* = 3.1 Hz), 123.4, 123.3, 115.4 (d, *J* = 23.6 Hz), 71.5, 45.1, 17.9; HR MS: calcd for $C_{36}H_{27}FO_2Na$ ($M+Na^+$) 533.1887, found 533.1865.



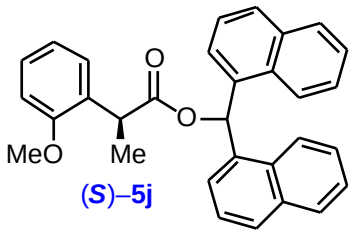
(*S*)–**7**

(*S*)-Naproxen di(1-naphthyl)methyl ester ((*S*)-7) [**Table 6**, Entry 9, 93% ee (Scheme 3, Run 5)]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 1.0 mL/min): t_R = 11.6 min (96.6%), t_R = 14.7 min (3.4%); IR (neat): 3034, 1733, 1604, 1508, 782, 679 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.29 (s, 1H), 8.00-7.90 (m, 1H), 7.82-6.96 (m, 17H), 6.95-6.81 (m, 2H), 3.86 (q, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 1.49 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.6, 157.6, 135.1, 134.7, 134.5, 133.8, 133.7, 133.6, 131.2, 130.8, 129.3, 129.1, 128.9, 128.8, 128.7, 128.6, 128.3, 127.1, 126.7, 126.5, 126.3, 126.2, 125.8, 125.6, 125.3, 125.2, 125.0, 123.4, 123.3, 118.9, 105.5, 71.2, 55.2, 45.5, 18.3; HR MS: calcd for $C_{35}H_{28}O_3Na$ ($M+Na^+$) 519.1931, found 519.1932.



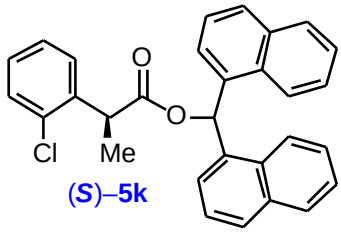
(*S*)–**5i**

Di(1-naphthyl)methyl (*S*)-2-(2-methylphenyl)propanoate ((*S*)-5i) [**Table 6**, Entry 10, 95% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 19.2 min (97.7%), t_R = 27.4 min (2.3%); IR (neat): 3057, 1599, 1510, 752, 730 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.31 (s, 1H), 8.02-7.96 (m, 1H), 7.83-7.78 (m, 1H), 7.73 (t, *J* = 8.0 Hz, 2H), 7.69-7.62 (m, 2H), 7.45-7.39 (m, 2H), 7.34-7.30 (m, 1H), 7.23-7.17 (m, 2H), 7.14-7.00 (m, 6H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.00 (q, *J* = 7.0 Hz, 1H), 2.16 (s, 3H), 1.43 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.7, 138.5, 135.9, 134.9, 134.6, 133.8, 133.7, 131.2, 130.9, 130.5, 129.1, 128.9, 128.7, 128.6, 127.0, 126.9, 126.7, 126.34, 126.30, 126.28, 125.8, 125.6, 125.3, 125.2, 125.0, 123.5, 123.4, 71.0, 41.4, 19.7, 17.6; HR MS: calcd for $C_{31}H_{26}O_2Na$ ($M+Na^+$) 453.1825, found 453.1813.



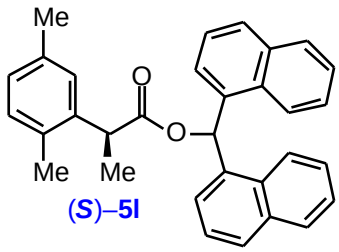
(*S*)–**5j**

Di(1-naphthyl)methyl (*S*)-2-(2-methoxyphenyl)propanoate ((*S*)-5j) [**Table 6**, Entry 11, 98% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 16.6 min (98.9%), t_R = 26.3 min (1.1%); ^{1}H NMR ($CHCl_3$): δ 8.35 (s, 1H), 8.13-7.95 (m, 1H), 7.82-7.53 (m, 5H), 7.46-7.32 (m, 3H), 7.30-7.07 (m, 7H), 6.79 (td, *J* = 7.3, 1.2 Hz, 1H), 6.68 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 1H), 3.39 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CHCl_3$): δ 174.1, 156.8, 135.2, 135.0, 133.8, 133.7, 131.2, 131.0, 128.9, 128.8, 128.74, 128.67, 128.61, 128.3, 128.1, 126.6, 126.4, 126.2, 125.8, 125.7, 125.6, 125.14, 125.06, 123.7, 123.6, 120.5, 110.3, 70.8, 55.0, 39.6, 16.8; HR MS: calcd for $C_{31}H_{26}O_3Na$ ($M+Na^+$) 469.1774, found 469.1770. Analytical data on racemic compound: Mp: 160-161 °C ($CHCl_3$/petroleum ether); IR (KBr): 3060, 1730, 1600, 1494, 778, 758 cm^{-1}.



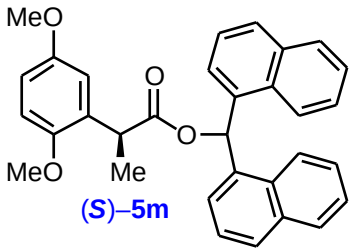
(*S*)–**5k**

Di(1-naphthyl)methyl (*S*)-2-(2-chlorophenyl)propanoate ((*S*)-5k) [**Table 6**, Entry 12, 94% ee]: HPLC (CHIRALPAK IC, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 18.6 min (97.1%), t_R = 23.6 min (2.9%); ^{1}H NMR ($CDCl_3$): δ 8.35 (s, 1H), 8.12-7.96 (m, 1H), 7.83-7.65 (m, 5H), 7.42-7.38 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30-7.21 (m, 3H), 7.19-7.12 (m, 3H), 7.10-6.98 (m, 3H), 4.29 (q, *J* = 7.5 Hz, 1H), 1.43 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.1, 137.8, 134.8, 134.5, 133.83, 133.81, 133.7, 131.2, 130.9, 129.5, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.0, 126.7, 126.4, 126.3, 125.8, 125.7, 125.6, 125.2, 125.0, 123.6, 123.4, 71.4, 42.1, 17.4; HR MS: calcd for $C_{30}H_{23}O_2ClNa$ ($M+Na^+$) 473.1279, found 473.1261. Analytical data on racemic compound: Mp: 143-144 °C (petroleum ether); IR (KBr): 3067, 1718, 1598, 1509, 795, 764 cm^{-1}.



(*S*)–**5l**

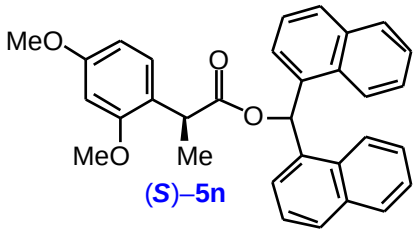
Di(1-naphthyl)methyl (*S*)-2-(2,5-dimethylphenyl)propanoate ((*S*)-5l) [**Table 6**, Entry 13, 98% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 22.2 min (98.8%), t_R = 26.2 min (1.2%); ^{1}H NMR ($CDCl_3$): δ 8.32 (s, 1H), 8.05-7.97 (m, 1H), 7.86-7.62 (m, 5H), 7.49-7.39 (m, 2H), 7.34 (td, *J* = 7.4, 1.0 Hz, 1H), 7.26-7.04 (m, 4H), 6.98-6.84 (m, 4H), 3.97 (q, *J* = 7.1 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 1.41 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.9, 138.3, 135.7, 134.9, 134.6, 133.8, 133.6, 132.6, 131.3, 130.8, 130.4, 129.1, 128.9, 128.64, 128.64, 127.7, 127.4, 126.8, 126.4, 126.3, 125.8, 125.6, 125.3, 125.2, 125.0, 123.5, 123.3, 70.9, 41.3, 20.9, 19.2, 17.7; HR MS: calcd for $C_{32}H_{28}O_2Na$ ($M+Na^+$) 467.1982, found 467.1984. Analytical data on racemic compound: Mp: 156-157 °C (CH_2Cl_2/hexane); IR (KBr): 1719, 1599, 1508, 800, 782 cm^{-1}.



(*S*)–**5m**

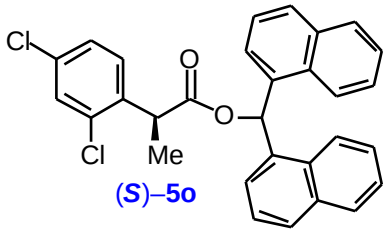
Di(1-naphthyl)methyl (*S*)-2-(2,5-dimethoxyphenyl)propanoate ((*S*)-5m) [**Table 6**, Entry 14, 98% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 1.0 mL/min): t_R = 11.6 min (99.1%), t_R = 17.0 min (0.9%); ^{1}H NMR ($CDCl_3$): δ 8.34 (s, 1H), 8.02-7.94 (m, 1H), 7.85-7.65 (m, 5H), 7.45-7.30 (m, 2H), 7.29-7.09 (m, 6H), 6.67-6.57 (m, 3H), 4.07 (q, *J* = 7.2 Hz, 1H), 3.54 (s, 3H), 3.36 (s, 3H), 1.40 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.9, 153.5, 151.0, 135.1, 134.9, 133.8, 133.7, 131.2, 131.0, 129.8, 129.0, 128.8, 128.7, 128.6, 126.7, 126.4, 126.2, 125.8, 125.7, 125.6, 125.2, 125.1, 123.7, 123.5, 114.2, 112.5, 111.4, 70.8, 55.7, 55.6, 39.5, 16.9; HR MS: calcd for $C_{32}H_{28}O_4Na$ ($M+Na^+$) 499.1880, found 499.1891. Analytical data on racemic compound: Mp: 117-119 °C ($CHCl_3$/petroleum ether); IR

(KBr): 2939, 1733, 1597, 1498, 802, 781 cm^{-1}.



(*S*)–**5n**

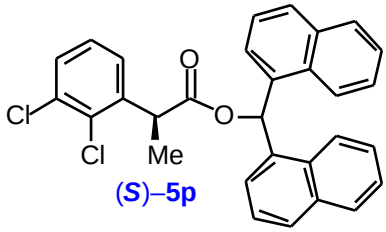
Di(1-naphthyl)methyl (*S*)-2-(2,4-dimethoxyphenyl)propanoate ((*S*)-5n) [**Table 6**, Entry 15, 93% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 1.0 mL/min): t_R = 13.6 min (96.4%), t_R = 19.9 min (3.6%); ^{1}H NMR ($CDCl_3$): δ 8.33 (s, 1H), 8.00-7.88 (m, 1H), 7.83-7.67 (m, 5H), 7.43-7.31 (m, 3H), 7.28-7.18 (m, 3H), 7.14 (d, *J* = 7.0 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.30 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.25 (d, *J* = 2.0 Hz, 1H), 3.99 (q, *J* = 7.3 Hz, 1H), 3.69 (s, 3H), 3.35 (s, 3H), 1.39 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 174.4, 159.8, 157.7, 135.2, 135.0, 133.8, 133.7, 131.2, 131.0, 128.9, 128.8, 128.7, 128.6, 128.4, 126.6, 126.3, 126.2, 125.74, 125.71, 125.6, 125.13, 125.05, 123.8, 123.6, 121.3, 103.9, 98.4, 70.8, 55.3, 55.0, 39.0, 16.9; HR MS: calcd for $C_{32}H_{28}O_4Na$ ($M+Na^+$) 499.1880, found 499.1871. Analytical data on racemic compound: Mp: 94-96 °C ($CHCl_3$/petroleum ether); IR (KBr): 3057, 1732, 1613, 1508, 779 cm^{-1}.



(*S*)–**5o**

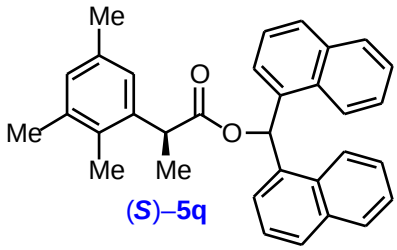
Di(1-naphthyl)methyl (*S*)-2-(2,4-dichlorophenyl)propanoate ((*S*)-5o) [**Table 6**, Entry 16, 91% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 11.6 min (95.7%), t_R = 15.2 min (4.3%); IR (neat): 3060, 1733, 1590, 1510, 1474, 1156, 777 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.35 (s, 1H), 8.01-7.92 (m, 1H), 7.84-7.65 (m, 5H), 7.44-7.32 (m, 2H), 7.29-7.16 (m, 6H), 7.14-7.09 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 1H), 1.42 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 172.7, 136.3, 134.50, 134.45, 134.3, 133.8, 133.7, 133.4, 131.1, 130.9, 129.33, 129.26, 129.18, 129.0, 128.9, 128.7, 127.2, 126.7, 126.4, 126.2, 125.9, 125.74, 125.70, 125.2, 125.0, 123.5,

123.3, 71.7, 41.7, 17.3; HR MS: calcd for $C_{30}H_{22}O_2Cl_2Na$ (M+Na^+) 507.0889, found 507.0896.



(*S*)–**5p**

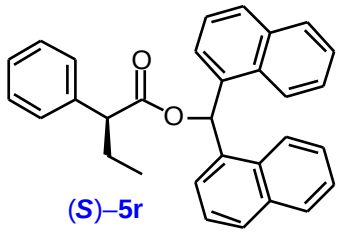
Di(1-naphthyl)methyl (*S*)-2-(2,3-dichlorophenyl)propanoate ((*S*)-5p) [**Table 6**, Entry 17, 93% ee]: HPLC (CHIRALPAK IC, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min): t_R = 15.1 min (96.4%), t_R = 18.2 min (3.6%); ^{1}H NMR ($CDCl_3$): δ 8.32 (s, 1H), 7.98-7.90 (m, 1H), 7.84-7.67 (m, 5H), 7.45-7.32 (m, 3H), 7.31-7.14 (m, 5H), 7.09 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.03 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.94 (dd, *J* = 7.8, 7.5 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 1H), 1.43 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 172.7, 140.1, 134.6, 134.3, 133.8, 133.7, 133.2, 131.1, 130.9, 129.2, 129.0, 128.9, 128.7, 128.3, 127.5, 127.2, 126.7, 126.6, 126.52, 126.45, 126.2, 125.9, 125.8, 125.2, 125.0, 123.5, 123.3, 71.7, 43.1, 17.4; HR MS: calcd for $C_{30}H_{22}O_2Cl_2Na$ (M+Na^+) 507.0889, found 507.0887. Analytical data on racemic compound: Mp: 151-154 °C (petroleum ether); IR (KBr): 3059, 1737, 1598, 1510, 1158, 778 cm^{-1}.



(*S*)–**5q**

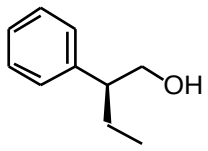
Di(1-naphthyl)methyl (*S*)-2-(2,3,5-trimethylphenyl)propanoate ((*S*)-5q) [**Table 6**, Entry 18, 97% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 11.7 min (98.7%), t_R = 15.2 min (1.3%); ^{1}H NMR ($CDCl_3$): δ 8.41 (s, 1H), 8.14-8.06 (m, 1H), 7.96-7.72 (m, 5H), 7.58-7.49 (m, 2H), 7.47-7.39 (m, 1H), 7.36-7.15 (m, 4H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.92 (s, 2H), 4.04 (q, *J* = 7.0 Hz, 1H), 2.23 (s, 3H), 2.21 (s, 3H), 2.10 (s, 3H), 1.50 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 174.1, 135.8, 135.0, 134.9, 134.6, 134.2, 133.8, 133.6, 132.9, 131.8, 131.3, 130.9, 129.1, 128.8, 128.62, 128.60, 128.0, 126.7, 126.4, 126.3, 125.8,

125.6, 125.3, 125.2, 125.0, 123.6, 123.4, 70.9, 41.0, 19.21, 19.20, 19.0, 17.7; HR MS: calcd for $C_{33}H_{30}O_2Na$ ($M+Na^+$) 481.2138, found 481.2155. Analytical data on racemic compound: Mp: 142-143 °C (CH_2Cl_2/hexane); IR (KBr): 3053, 1730, 1599, 1509, 800, 776 cm^{-1}.

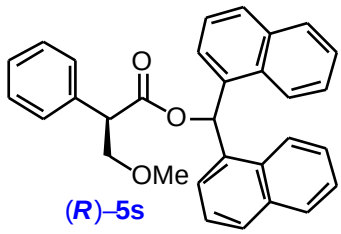


(*S*)–**5r**

Di(1-naphthyl)methyl (*S*)-2-phenylbutanoate ((*S*)-5r) [**Table 6**, Entry 19, 75% ee]: IR (neat): 3034, 1734, 1599, 1510, 779, 679 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.28 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.82-7.76 (m, 1H), 7.71 (dd, *J* = 8.3, 3.5 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.43-7.34 (m, 2H), 7.33-7.26 (m, 1H), 7.20-7.11 (m, 7H), 7.10-7.02 (m, 2H), 6.88 (d, *J* = 6.5 Hz, 1H), 3.50 (dd, *J* = 7.6, 7.4 Hz, 1H), 2.07 (ddq, *J* = 14.0, 7.6, 7.3 Hz, 1H), 1.73 (ddq, *J* = 14.0, 7.4, 7.3 Hz, 1H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.0, 138.5, 134.8, 134.5, 133.8, 133.6, 131.2, 130.8, 129.1, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 127.2, 126.7, 126.3, 126.2, 125.8, 125.6, 125.2, 125.0, 123.5, 123.3, 71.0, 53.5, 26.1, 12.2; HR MS: calcd for $C_{31}H_{26}O_2Na$ ($M+Na^+$) 453.1825, found 453.1834. Enantiomeric excess of **(*S*)-5r** has been determined after converting into (*S*)-2-phenylbutanol.

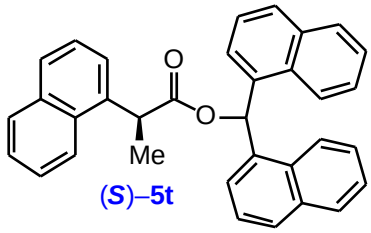


(*S*)-2-Phenylbutanol [75% ee]:[7] HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.75 mL/min): t_R = 24.8 min (12.6%), t_R = 26.5 min (87.4%); IR (neat): 3347, 1603, 1494, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.30-7.22 (m, 2H), 7.20-7.10 (m, 3H), 3.76-3.60 (m, 2H), 2.62 (dddd, *J* = 9.0, 7.5, 5.7, 5.4 Hz, 1H), 1.76-1.61 (m, 1H), 1.59-1.43 (m, 1H), 1.22 (br s, 1H, OH), 0.77 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 142.3, 128.5, 128.0, 126.6, 67.2, 50.4, 24.9, 11.9.



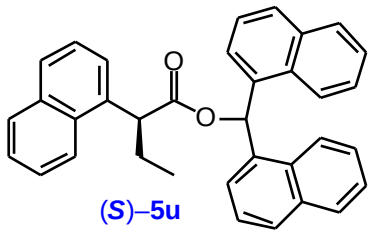
(*R*)–**5s**

Di(1-naphthyl)methyl (*R*)-3-methoxy-2-phenylpropanoate ((*R*)-5s) [**Table 6**, Entry 20, 88% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 20.8 min (5.9%), t_R = 29.5 min (94.1%); IR (neat): 3060, 1737, 1153, 790, 777 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.36 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.90 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.83 (dd, *J* = 8.4, 3.8 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.54-7.38 (m, 3H), 7.35-7.16 (m, 9H), 7.06 (d, *J* = 7.2 Hz, 1H), 4.03 (dd, *J* = 10.5, 10.2 Hz, 1H), 4.02 (dd, *J* = 14.1, 10.2 Hz, 1H), 3.64 (dd, *J* = 14.1, 10.5, 1H), 3.32 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 171.5, 135.2, 134.5, 134.4, 133.8, 133.6, 131.1, 130.9, 129.1, 128.8, 128.65, 128.65, 128.60, 128.26, 128.26, 127.7, 126.6, 126.4, 126.2, 125.8, 125.7, 125.4, 125.2, 125.0, 123.5, 73.8, 71.5, 58.9, 52.1; HR MS: calcd for $C_{31}H_{26}O_3Na$ ($M+Na^+$) 469.1774, found 469.1751.



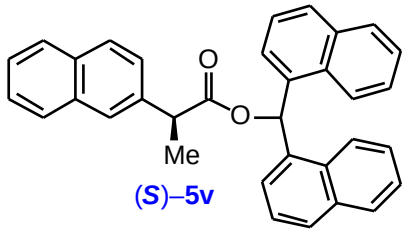
(*S*)–**5t**

Di(1-naphthyl)methyl (*S*)-2-(1-naphthyl)propanoate ((*S*)-5t) [**Table 6**, Entry 21, 96% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 15.6 min (98.1%), t_R = 24.8 min (1.9%); ^1H NMR ($CDCl_3$): δ 8.33 (s, 1H), 7.97-7.83 (m, 2H), 7.83-7.56 (m, 7H), 7.46-6.92 (m, 11H), 6.85 (d, *J* = 7.2 Hz, 1H), 4.54 (q, *J* = 6.9 Hz, 1H), 1.60 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 174.0, 136.0, 134.7, 134.4, 133.9, 133.8, 133.7, 131.4, 131.2, 130.9, 129.0, 128.82, 128.80, 128.7, 128.6, 128.3, 127.8, 126.7, 126.4, 126.22, 126.16, 125.8, 125.7, 125.6, 125.4, 125.1, 124.9, 124.8, 123.5, 123.4, 123.3, 71.3, 41.6, 17.9; HR MS: calcd for $C_{34}H_{26}O_2Na$ ($M+Na^+$) 489.1825, found 489.1809. Analytical data on racemic compound: Mp: 152-153 °C ($CHCl_3$/petroleum ether); IR (KBr): 3055, 1735, 1599, 1509, 778 cm^{-1}.



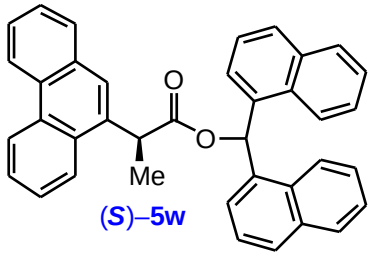
(*S*)–**5u**

Di(1-naphthyl)methyl (*S*)-2-(1-naphthyl)butanoate ((*S*)-5u) [**Table 6**, Entry 22, 95% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 16.7 min (97.7%), t_R = 23.9 min (2.3%); IR (neat): 3055, 1734, 1599, 1510, 960, 761 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.31 (s, 1H), 7.95 (t, *J* = 8.1 Hz, 2H), 7.83-7.73 (m, 2H), 7.73-7.64 (m, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.45-7.21 (m, 8H), 7.10 (t, *J* = 7.2 Hz, 2H), 6.99-6.90 (m, 2H), 6.77 (d, *J* = 7.2 Hz, 1H), 4.34 (t, *J* = 7.2 Hz, 1H), 2.24 (ddq, *J* = 14.2, 7.2, 7.2 Hz, 1H), 1.89 (ddq, *J* = 14.2, 7.2, 7.2 Hz, 1H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.3, 134.8, 134.7, 134.3, 134.0, 133.8, 133.6, 131.7, 131.2, 130.8, 129.0, 128.82, 128.78, 128.62, 128.55, 128.31, 128.31, 127.7, 126.6, 126.24, 126.15, 125.8, 125.6, 125.5, 125.41, 125.39, 125.2, 125.1, 124.9, 123.5, 123.3, 71.1, 48.8, 26.1, 12.6; HR MS: calcd for $C_{35}H_{28}O_2Na$ ($M+Na^+$) 503.1982, found 503.1966.



(*S*)–**5v**

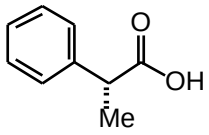
Di(1-naphthyl)methyl (*S*)-2-(2-naphthyl)propanoate ((*S*)-5v) [**Table 6**, Entry 23, 90% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 22.5 min (95.2%), t_R = 46.9 min (4.8%); IR (neat): 3060, 1737, 1599, 1509, 755 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.30 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.86-7.52 (m, 8H), 7.45-7.31 (m, 4H), 7.30-7.11 (m, 4H), 7.10-7.00 (m, 2H), 6.92 (dd, *J* = 7.8, 7.5 Hz, 1H), 6.87 (dd, *J* = 8.1, 6.9 Hz, 1H), 3.92 (q, *J* = 6.9 Hz, 1H), 1.53 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.5, 137.5, 134.7, 134.5, 133.8, 133.6, 133.4, 132.6, 131.2, 130.8, 129.1, 128.8, 128.7, 128.6, 128.3, 128.2, 127.8, 127.5, 126.7, 126.4, 126.3, 126.04, 125.98, 125.84, 125.77, 125.6, 125.3, 125.2, 125.0, 123.4, 123.3, 71.3, 45.8, 18.3; HR MS: calcd for $C_{34}H_{26}O_2Na$ ($M+Na^+$) 489.1825, found 489.1815.



(*S*)–**5w**

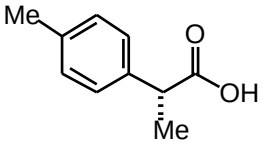
Di(1-naphthyl)methyl (*S*)-2-(9-phenanthryl)propanoate ((*S*)-5w) [**Table 6**, Entry 24, 98% ee]: HPLC (CHIRALPAK IC, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 12.7 min (99.2%), t_R = 19.9 min (0.8%); ^{1}H NMR ($CDCl_3$): δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.38 (s, 1H), 7.99-7.87 (m, 2H), 7.82-7.22 (m, 14H), 7.20-7.05 (m, 2H), 7.01-6.90 (m, 3H), 4.54 (q, *J* = 6.9 Hz, 1H), 1.66 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 174.0, 134.6, 134.4, 134.3, 133.8, 133.7, 131.4, 131.2, 130.9, 130.8, 130.7, 130.4, 129.9, 129.0, 128.83, 128.76, 128.6, 128.3, 126.8, 126.7, 126.6, 126.4, 126.3, 126.2, 125.82, 125.80, 125.72, 125.65, 125.1, 125.0, 123.9, 123.5, 123.3, 123.2, 122.3, 71.4, 42.0, 17.8; HR MS: calcd for $C_{38}H_{28}O_2Na$ ($M+Na^+$) 539.1982, found 539.1968. Analytical data on racemic compound: Mp: 115-117 °C ($CHCl_3$/petroleum ether); IR (KBr): 3058, 1733, 1599, 1509, 779, 747, 726 cm^{-1}.

(Optically Active Carboxylic Acids in **Table 6**)



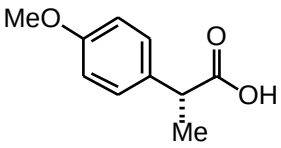
(***R***)–**4a** [= (***R***)–**1**]

(*R*)-2-Phenylpropanoic acid ((*R*)-4a) [**Table 6**, Entry 1, 59% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min); t_R = 39.3 min (79.4%), t_R = 43.2 min (20.6%); ^{1}H NMR ($CDCl_3$): δ 10.95 (br s, 1H, COOH), 7.30-7.16 (m, 5H), 3.67 (q, *J* = 7.2 Hz, 1H), 1.45 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 181.0, 139.7, 128.7, 127.6, 127.4, 45.4, 18.0.



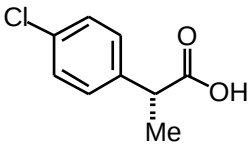
(***R***)–**4b**

(*R*)-2-(4-Methylphenyl)propanoic acid ((*R*)-4b) [**Table 6**, Entry 2, 62% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.5 mL/min); t_R = 40.1 min (81.2%), t_R = 43.9 min (18.8%); ^{1}H NMR ($CDCl_3$): δ 10.63 (br s, 1H, COOH), 7.13 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 3.63 (q, *J* = 7.0 Hz, 1H), 2.26 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 181.3, 137.0, 136.7, 129.3, 127.4, 44.9, 21.0, 18.0.



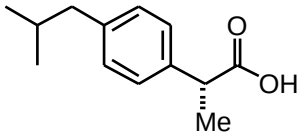
(***R***)–**4c**

(*R*)-2-(4-Methoxyphenyl)propanoic acid ((*R*)-4c) [**Table 6**, Entry 3, 77% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/10/0.01, flow rate = 0.4 mL/min); t_R = 22.0 min (88.4%), t_R = 24.2 min (11.6%); ^{1}H NMR ($CDCl_3$): δ 10.99 (br s, 1H, COOH), 7.17 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 3.72 (s, 3H), 3.61 (q, *J* = 7.2 Hz, 1H), 1.42 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.8, 158.8, 131.8, 128.6, 114.0, 55.2, 44.4, 18.1.



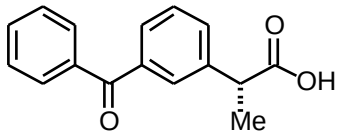
(*R*)–**4d**

(*R*)-2-(4-Chlorophenyl)propanoic acid ((*R*)-4d) [**Table 6**, Entry 4, 68% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.75 mL/min); t_R = 28.9 min (83.9%), t_R = 31.4 min (16.1%); ^{1}H NMR ($CDCl_3$): δ 9.15 (br s, 1H, COOH), 7.39-7.09 (m, 4H), 3.69 (q, *J* = 7.0 Hz, 1H), 1.48 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.6, 138.0, 133.3, 129.0, 128.8, 44.7, 18.0.



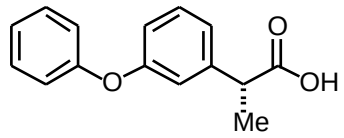
(*R*)–**4e**

(*R*)-Ibuprofen ((*R*)-4e) [**Table 6**, Entry 5, 67% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/100/0.1, flow rate = 1.0 mL/min); t_R = 26.9 min (16.7%), t_R = 28.8 min (83.3%); ^{1}H NMR ($CDCl_3$): δ 10.30 (br s, 1H, COOH), 7.14 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 3.63 (q, *J* = 7.3 Hz, 1H), 2.37 (q, *J* = 7.3 Hz, 2H), 1.77 (tqq, *J* = 7.3, 6.5, 6.5 Hz, 1H), 1.42 (d, *J* = 7.3 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 181.0, 140.8, 136.9, 129.4, 127.3, 45.0, 44.9, 30.2, 22.4, 18.1.



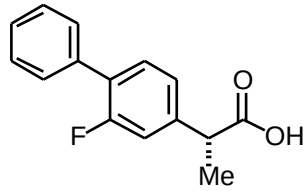
(*R*)–**4f**

(*R*)-Ketoprofen ((*R*)-4f) [**Table 6**, Entry 6, 62% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/10/0.01, flow rate = 1.0 mL/min); t_R = 16.4 min (80.9%), t_R = 19.5 min (19.1%); ^{1}H NMR ($CDCl_3$): δ 10.67 (br s, 1H, COOH), 7.85-7.76 (m, 3H), 7.69 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.63-7.54 (m, 2H), 7.52-7.42 (m, 3H), 3.83 (q, *J* = 7.0 Hz, 1H), 1.56 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 196.5, 180.0, 140.0, 137.9, 137.3, 132.5, 131.6, 130.1, 129.32, 129.26, 128.6, 128.3, 45.2, 18.1.



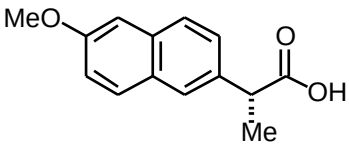
(*R*)–**4g**

(*R*)-Fenoprofen ((*R*)-4g) [**Table 6**, Entry 7, 67% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min): t_R = 34.8 min (83.5%), t_R = 39.6 min (16.5%); ^{1}H NMR ($CDCl_3$): δ 11.8 (br s, 1H, COOH), 7.24-7.10 (m, 3H), 7.00-6.85 (m, 5H), 6.76 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 3.58 (q, *J* = 7.2 Hz, 1H), 1.37 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.8, 157.4, 156.8, 141.6, 129.8, 129.7, 123.3, 122.3, 118.9, 118.2, 117.4, 45.2, 17.9.



(*R*)–**4h**

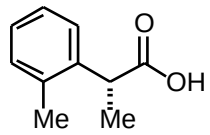
(*R*)-Flurbiprofen ((*R*)-4h) [**Table 6**, Entry 8, 67% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min); t_R = 24.2 min (83.3%), t_R = 32.5 min (16.7%); ^{1}H NMR ($CDCl_3$): δ 9.45 (br s, 1H, COOH), 7.57-7.49 (m, 2H), 7.48-7.33 (m, 4H), 7.22-7.11 (m, 2H), 3.80 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.0, 159.7 (d, *J* = 249.2 Hz), 140.94, 140.87, 135.4, 130.9 (d, *J* = 4.1 Hz), 128.9 (d, *J* = 2.1 Hz), 128.4, 128.2 (d, *J* = 13.4 Hz), 127.7, 123.7 (d, *J* = 3.1 Hz), 115.4 (d, *J* = 23.9 Hz), 44.8, 18.0.



(*R*)–**6**

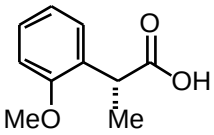
(*R*)-Naproxen ((*R*)-6) [**Table 6**, Entry 9, 69% ee (Scheme 3, Run 5)]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/10/0.01, flow rate = 0.75 mL/min); t_R = 17.7 min (84.6%), t_R = 19.3 min (15.4%); ^{1}H NMR ($CDCl_3$): δ 9.42 (br s, 1H, COOH), 7.68-7.55 (m, 3H), 7.33-7.28 (m, 1H), 7.13-6.99 (m, 2H), 3.83 (s, 3H), 3.79 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.7,

157.7, 134.8, 133.8, 129.3, 128.8, 127.2, 126.2, 126.1, 119.0, 105.5, 55.3, 45.2, 18.1.



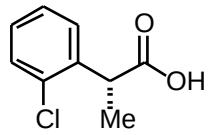
(*R*)–**4i**

(*R*)-2-(2-Methylphenyl)propanoic acid ((*R*)-4i) [**Table 6**, Entry 10, 71% ee]: HPLC (CHIRALCEL OJ-H, *i*-PrOH/hexane/TFA = 1/10/0.01, flow rate = 0.5 mL/min): t_R = 16.0 min (85.3%), t_R = 18.4 min (14.7%).



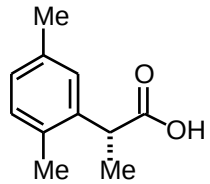
(*R*)–**4j**

(*R*)-2-(2-Methoxyphenyl)propanoic acid ((*R*)-4j) [**Table 6**, Entry 11, 73% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min): t_R = 27.2 min (13.7%), t_R = 32.8 min (86.3%).



(*R*)–**4k**

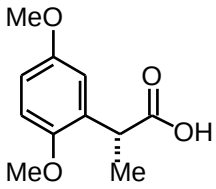
(*R*)-2-(2-Chlorophenyl)propanoic acid ((*R*)-4k) [**Table 6**, Entry 12, 75% ee]: HPLC (CHIRALPAK IC, *i*-PrOH/hexane/TFA = 1/100/0.1, flow rate = 0.5 mL/min): t_R = 36.8 min (12.6%), t_R = 45.2 min (87.4%).



(*R*)–**4l**

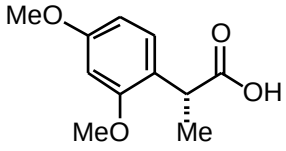
(*R*)-2-(2,5-Dimethylphenyl)propanoic acid ((*R*)-4l) [**Table 6**, Entry 13,

99.5% ee]: HPLC (CHIRALCEL OJ-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min): t_R = 14.8 min (99.76%), t_R = 19.5 min (0.24%).



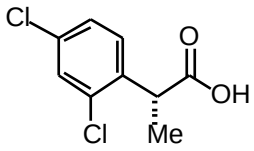
(*R*)–4m

(*R*)-2-(2,5-Dimethoxylphenyl)propanoic acid ((*R*)-4m) [**Table 6**, Entry 14, 73% ee]: HPLC (CHIRALCEL OJ-H, *i*-PrOH/hexane/TFA = 1/10/0.01, flow rate = 0.75 mL/min): t_R = 16.6 min (13.7%), t_R = 18.7 min (86.3%).



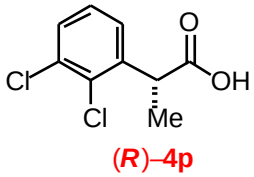
(*R*)–4n

(*R*)-2-(2,4-Dimethoxylphenyl)propanoic acid ((*R*)-4n) [**Table 6**, Entry 15, 68% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/10/0.01, flow rate = 0.5 mL/min): t_R = 21.4 min (16.0%), t_R = 24.5 min (84.0%).



(*R*)–4o

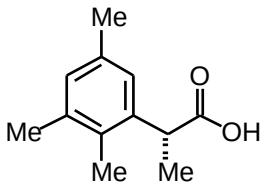
(*R*)-2-(2,4-Dichlorophenyl)propanoic acid ((*R*)-4o) [**Table 6**, Entry 16, 85% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min): t_R = 18.9 min (7.6%), t_R = 21.9 min (92.4%).



(*R*)–4p

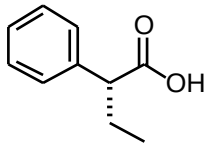
(*R*)-2-(2,3-Dichlorophenyl)propanoic acid ((*R*)-4p) [**Table 6**, Entry 17, 85%

ee]: HPLC (CHIRALCEL OJ-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min): t_R = 25.4 min (7.6%), t_R = 31.1 min (92.4%).



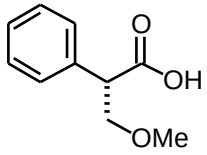
(***R***)–**4q**

(*R*)-2-(2,3,5-Trimethylphenyl)propanoic acid ((*R*)-4q) [**Table 6**, Entry 18, 64% ee]: HPLC (CHIRALCEL OJ-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 0.75 mL/min): t_R = 16.8 min (82.1%), t_R = 21.3 min (17.9%).



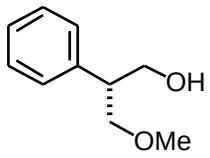
(***R***)–**4r**

(*R*)-2-Phenylbutanoic acid ((*R*)-4r) [**Table 6**, Entry 19, 46% ee]:[8] HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min): t_R = 17.7 min (72.8%), t_R = 20.5 min (27.2%); ^{1}H NMR ($CDCl_3$): δ 11.6 (br s, 1H, COOH), 7.34-7.21 (m, 5H), 3.45 (t, *J* = 7.5 Hz, 1H), 2.10 (ddq, *J* = 14.0, 7.5, 7.2 Hz, 1H), 1.80 (ddq, *J* = 14.0, 7.5, 7.2 Hz, 1H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 180.6, 138.3, 128.6, 128.1, 127.4, 53.3, 26.2, 12.1.

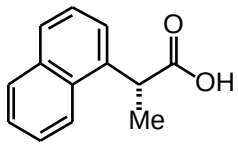


(***S***)–**4s**

(*S*)-3-Methoxy-2-phenylpropanoic acid ((*S*)-4s) [**Table 6**, Entry 20, 39% ee]: Enantiomeric excess of **(*S*)-4s** has been determined after converting into (*R*)-3-methoxy-2-phenylpropanol.

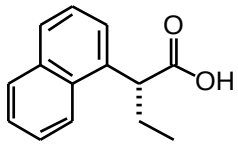


(*R*)-3-Methoxy-2-phenylpropanol [39% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane = 1/50, flow rate = 1.0 mL/min): t_R = 22.4 min (30.5%), t_R = 24.9 min (69.5%); IR (neat): 3416, 1604, 1495, 761, 701 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.22-7.06 (m, 5H), 3.77 (ddd, *J* = 12.0, 7.2, 5.1 Hz, 1H), 3.65 (ddd, *J* = 12.0, 6.0, 5.4 Hz, 1H), 3.59 (dd, *J* = 9.3, 8.0 Hz, 1H), 3.52 (dd, *J* = 9.3, 5.7 Hz, 1H), 3.21 (s, 3H), 2.99 (dddd, *J* = 8.0, 7.2, 5.7, 5.4 Hz, 1H), 2.93 (dd, *J* = 6.0, 5.1 Hz, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 139.7, 128.3, 127.7, 126.7, 75.3, 65.4, 58.7, 47.5; HR MS: calcd for $C_{10}H_{14}O_2Na$ ($M+Na^+$) 189.0886, found 189.0887.



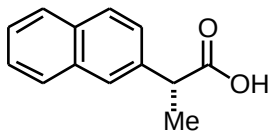
(*R*)–**4t**

(*R*)-2-(1-Naphthyl)propanoic acid ((*R*)-4t) [**Table 6**, Entry 21, 82% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min): t_R = 28.7 min (91.2%), t_R = 33.8 min (8.8%).



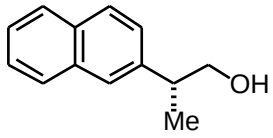
(*R*)–**4u**

(*R*)-2-(1-Naphthyl)butanoic acid ((*R*)-4u) [**Table 6**, Entry 22, 31% ee]: HPLC (CHIRALPAK AD-H, *i*-PrOH/hexane/TFA = 1/50/0.05, flow rate = 1.0 mL/min): t_R = 28.4 min (65.7%), t_R = 40.5 min (34.3%).

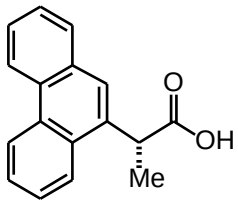


(*R*)–**4v**

(*R*)-2-(2-Naphthyl)propanoic acid ((*R*)-4v) [**Table 6**, Entry 23, 76% ee]: Enantiomeric excess of **(*R*)-4v** has been determined after converting into (*R*)-2-(2-naphthyl)propanol.



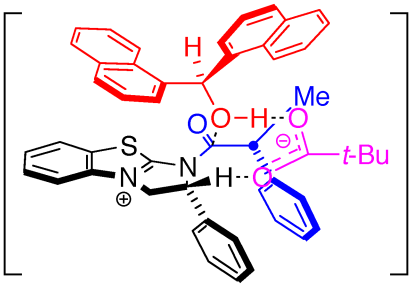
(*R*)-2-(2-Naphthyl)propanol [76% ee]: HPLC (CHIRALPAK AD-H x 2, *i*-PrOH/hexane = 1/9, flow rate = 0.35 mL/min): t_R = 48.4 min (88.2%), t_R = 50.4 min (11.8%); IR (KBr): 3303, 2970, 1600, 1507, 856, 819, 745 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.89-7.78 (m, 3H), 7.69 (s, 1H), 7.53-7.36 (m, 3H), 3.87-3.75 (m, 2H), 3.13 (tq, *J* = 6.9, 6.9 Hz, 1H), 1.60 (br s, 1H, OH), 1.38 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 141.0, 133.5, 132.4, 128.3, 127.57, 127.57, 126.1, 126.0, 125.7, 125.5, 68.5, 42.5, 17.6; HR MS: calcd for $C_{13}H_{14}ONa$ ($M+Na^+$) 209.0937, found 209.0946.

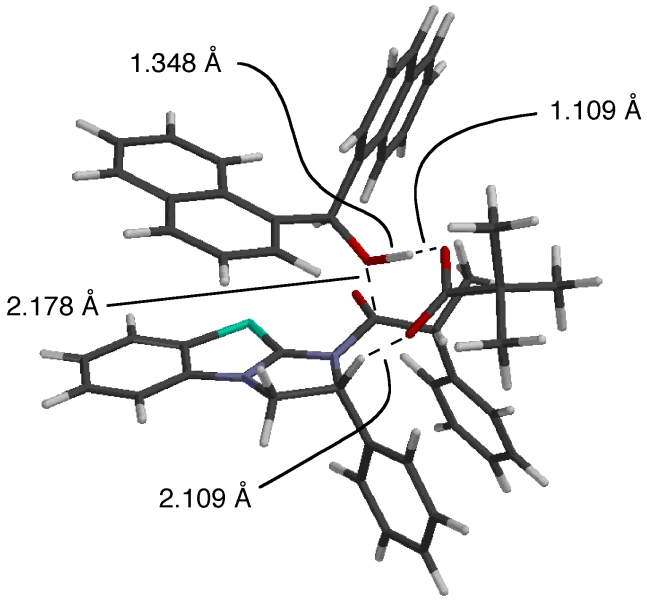


(*R*)–4w

(*R*)-2-(9-Phenanthryl)propanoic acid ((*R*)-4w) [**Table 6**, Entry 24, 86% ee]: HPLC (CHIRALPAK AS-H, *i*-PrOH/hexane/TFA = 1/10/0.01, flow rate = 0.5 mL/min): t_R = 19.1 min (7.1%), t_R = 24.1 min (92.9%).

All calculations were performed with the program package *TITAN* 1.0.5, Schrödinger Inc. and Wavefunction Inc., and the program package *Spartan '08* 1.1.1 of Wavefunction Inc. All structures were optimized and subjected to frequency analysis with the B3LYP/6-31G* method, followed by single point B3LYP/6-31G* calculation.





Transition Structure **ts-1**

E(B3LYP/6-31G*) = -2741.654398 au

ν_{ts} = 170i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
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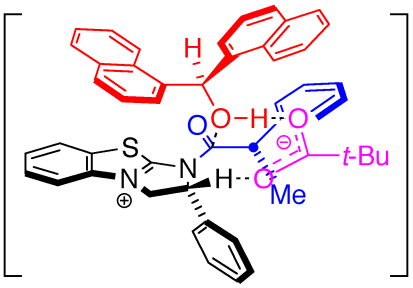
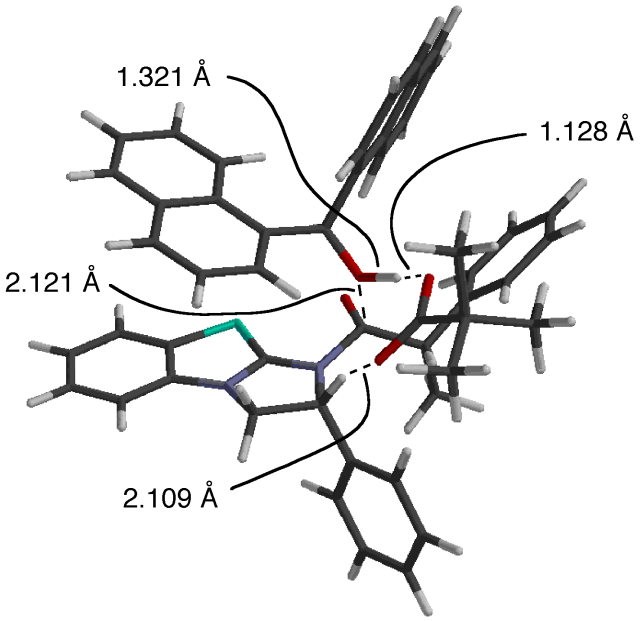
There are 204 alpha and 204 beta electrons

Requested basis set is 6-31G(d)

There are 321 shells and 951 basis functions





Transition Structure **ts-2**

E(B3LYP/6-31G*) = -2741.648526 au

ν_{ts} = 358i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	0.023987223	0.796129228	1.743989059
6	1.168861239	1.782534735	1.964772657
1	1.279432191	2.385377248	1.059154274
8	-0.186593684	-0.180103804	2.458603756
7	-1.193821989	1.349831359	1.112913366
6	-2.309130145	0.627975828	1.156662545
7	-3.228180681	1.001295119	0.254637485
6	-2.686091762	2.014748398	-0.656713737
6	-1.301415421	2.358042557	-0.003563266
6	-1.246647295	3.801581320	0.460176394
6	-0.389755477	4.693343310	-0.194942351
6	-0.367127921	6.041594017	0.171857639
6	-1.196212758	6.507242048	1.192077134
6	-2.059792897	5.622502926	1.844306678
6	-2.088212877	4.278619410	1.476427167
1	-2.761148005	3.595844711	1.991356393
1	-2.709638657	5.980157467	2.638522454
1	-1.173919589	7.555235556	1.478531809
1	0.301829649	6.726745250	-0.341792620
1	0.238777204	4.325818453	-1.001542563
1	-0.497226192	2.151810427	-0.713353245
1	-2.577446327	1.585504675	-1.655741862
1	-3.343897615	2.885834436	-0.693206206

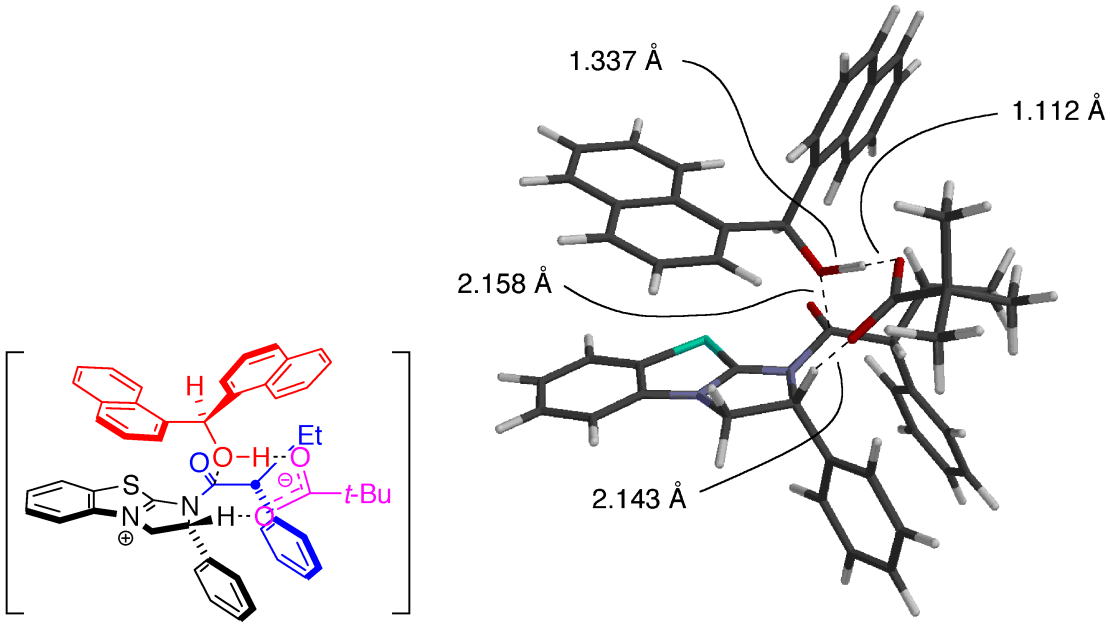
8	0.729302904	0.067114302	-0.118339694
6	0.449409494	-1.301022613	-0.252775893
6	-0.682572183	-1.579297694	-1.258939865
6	-1.432427475	-2.804631750	-1.208288418
6	-2.498473062	-3.015701934	-2.148438987
6	-2.779383709	-2.019920786	-3.122210447
6	-2.038182790	-0.863382915	-3.162216440
6	-0.999503855	-0.642354360	-2.224075949
1	-0.433917202	0.282803672	-2.265589567
1	-2.238544336	-0.110261966	-3.921440334
1	-3.580009566	-2.196210494	-3.837129050
1	0.078326769	-1.642210806	0.722223997
1	1.585263423	0.618250189	-0.960140495
8	2.341192821	1.088026859	-1.652890604
6	1.875200454	2.018692936	-2.439230110
6	2.918752315	2.567050962	-3.434509439
8	0.711252147	2.444607289	-2.416362678
16	-2.801280207	-0.702557875	2.148306376
6	-4.411058549	0.266780669	0.279046462
6	-4.368852926	-0.710874103	1.288908058
6	-5.449573544	-1.563558911	1.491314556
1	-5.419196879	-2.326232246	2.263489634
6	-5.526479473	0.414517256	-0.543363177
1	-5.549114913	1.166648168	-1.325525836
6	-6.605654471	-0.443056407	-0.332570440
1	-7.485490663	-0.351552072	-0.962097762
6	-6.570704182	-1.418422276	0.672071141
1	-7.423509801	-2.074694786	0.815352958
6	1.707297461	-2.121073445	-0.596074710
6	4.015132233	-3.584745753	-1.350590093
6	2.147806568	-2.159615893	-1.905433553
6	2.446347435	-2.837312345	0.406364808
6	3.604466275	-3.592588421	0.007534528
6	3.303349057	-2.875704348	-2.287550201
1	1.584070606	-1.631927839	-2.667836743
1	3.614366224	-2.872328940	-3.329148552
1	4.897640716	-4.154046752	-1.634167951
6	3.427287126	1.393299810	-4.300176864
1	4.206588842	1.738346709	-4.991113695
1	2.614368276	0.966561952	-4.901010092
1	3.841227949	0.598582162	-3.673587269
6	4.097198325	3.161800718	-2.633318475
1	4.865288951	3.544909255	-3.316796291
1	4.552743838	2.404574943	-1.989209310
1	3.768291113	3.997429781	-2.002271727
6	2.285752111	3.646941672	-4.323411227
1	3.024399751	4.027711353	-5.039573978
1	1.921463330	4.488521171	-3.725286750
1	1.433402642	3.248715130	-4.882392058
6	0.787017805	2.720495940	3.139159933
1	1.593340940	3.443365005	3.295988840
1	0.657786432	2.149809397	4.063376560
1	-0.133902736	3.275559115	2.944429676
6	2.499739118	1.100569571	2.253728594

6	5.025246722	-0.000645808	2.836965205
6	3.579550611	1.282396164	1.382680233
6	2.703219581	0.353073139	3.422487914
6	3.953953075	-0.192976723	3.710187002
6	4.831581011	0.737065190	1.669603177
1	3.433879136	1.831865779	0.458379256
1	1.877540263	0.180311030	4.104858745
1	4.088783300	-0.774787149	4.618653839
1	5.652967222	0.885986763	0.973366216
1	5.998772168	-0.428646123	3.061274181
6	-1.169024490	-3.834578787	-0.260003975
1	-0.356619312	-3.716188081	0.447215685
6	-3.248169601	-4.221658798	-2.093675465
1	-4.050752725	-4.365548163	-2.814092799
6	-1.913306067	-4.993937701	-0.236773634
1	-1.684316362	-5.765662608	0.493564129
6	-2.965518491	-5.192642765	-1.160613275
1	-3.543339558	-6.112936655	-1.134285343
6	4.320943516	-4.341149663	0.979664427
1	5.192816123	-4.906343296	0.656801686
6	2.087887221	-2.859258215	1.785713131
1	1.260554119	-2.254695559	2.138385418
6	2.801991633	-3.603187730	2.699555454
1	2.504585798	-3.595839102	3.745220954
6	3.927118933	-4.358104071	2.297140370
1	4.481432581	-4.940304289	3.028966655

There are 204 alpha and 204 beta electrons

Requested basis set is 6-31G(d)

There are 321 shells and 951 basis functions



Transition Structure **ts-1-4r**

E(B3LYP/6-31G*) = -2780.967425 au

ν_{ts} = 176i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	-0.889776782	0.193768213	-1.340463921
6	-2.075246135	-0.764314895	-1.354832029
1	-2.409494331	-0.921989955	-0.324692053
8	-0.119616862	0.338413507	-2.287106804
7	-0.980650337	1.352922864	-0.443527480
6	-0.080563335	2.323379453	-0.568854268
7	0.011214266	3.113854266	0.508629322
6	-0.799240048	2.589842615	1.612936682
6	-1.590862804	1.417316667	0.931437670
6	-3.083242064	1.679603670	0.942594362
6	-3.877166158	0.976737232	1.857323109
6	-5.241303288	1.258327342	1.962209853
6	-5.820214777	2.238277631	1.155400934
6	-5.030957918	2.940071163	0.240248263
6	-3.668625070	2.665246634	0.137473464
1	-3.065004720	3.200604633	-0.591580674
1	-5.478267638	3.696540638	-0.398594003
1	-6.882296511	2.454260536	1.235627713
1	-5.850181224	0.708627959	2.675146636
1	-3.415421443	0.220572774	2.487184923
1	-1.358245538	0.478688910	1.439848018
1	-0.143224507	2.237139689	2.412867305
1	-1.471677062	3.361881272	1.993895226
8	0.207450825	-0.892016735	0.168270454

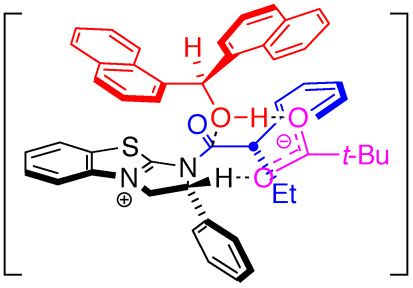
6	1.578803231	-0.932842211	-0.110081199
6	2.388690108	-0.041193889	0.846881112
6	3.673234942	0.479919829	0.471264081
6	4.375101395	1.339773927	1.384007832
6	3.800373421	1.633126266	2.649463295
6	2.581138765	1.101590460	2.997108718
6	1.872888480	0.275928498	2.089692403
1	0.905041157	-0.128544131	2.370800380
1	2.152241600	1.309383133	3.975103486
1	4.347480737	2.273687193	3.337670842
1	1.719992364	-0.512838131	-1.115531363
1	-0.343055183	-1.833383088	0.941877380
8	-0.854887243	-2.621772626	1.536468594
6	-1.379842257	-2.185042425	2.650153130
6	-1.976310939	-3.303464841	3.527565691
8	-1.412272181	-0.995209161	2.994025256
16	0.995962973	2.755304251	-1.851990751
6	0.933797693	4.151341652	0.400763787
6	1.560405863	4.130221881	-0.858338006
6	2.522697515	5.080784007	-1.183876848
1	3.016163217	5.064820272	-2.150745670
6	1.252834855	5.115487858	1.355433703
1	0.770274063	5.119362228	2.327505499
6	2.216329962	6.065893666	1.019821500
1	2.485146639	6.826819235	1.746126564
6	2.842291901	6.052169884	-0.233284717
1	3.589503583	6.803187884	-0.470043746
6	2.115972391	-2.377576809	-0.124686854
6	3.032612420	-5.060428685	-0.028587147
6	2.456089954	-2.987581997	1.067772821
6	2.225537324	-3.130378823	-1.344018297
6	2.702720726	-4.486763087	-1.284033279
6	2.904685256	-4.325680973	1.125163390
1	2.384560516	-2.420925666	1.990687461
1	3.156269072	-4.763537739	2.087697617
1	3.388326363	-6.087885416	0.000983423
6	-1.651085793	-2.134591695	-1.940436654
1	-0.756795607	-2.458029969	-1.405817598
1	-1.370076295	-1.995206473	-2.990247832
6	-3.232921419	-0.161278650	-2.156144969
6	-5.414356444	0.807186328	-3.654430109
6	-3.035935598	0.409490551	-3.422794625
6	-4.539808265	-0.241068223	-1.658198302
6	-5.622113980	0.235880066	-2.398478454
6	-4.116461374	0.891781463	-4.162445585
1	-2.030803469	0.476741116	-3.828480869
1	-4.709840191	-0.670045664	-0.674319826
1	-6.625694827	0.165678916	-1.986895431
1	-3.942042359	1.332342588	-5.141166278
1	-6.254984219	1.181663512	-4.232933919
6	-0.855816319	-4.311880460	3.862149332
1	-1.261532250	-5.147075333	4.446619825
1	-0.065647952	-3.839419540	4.458635636
1	-0.401675665	-4.708413424	2.950079699

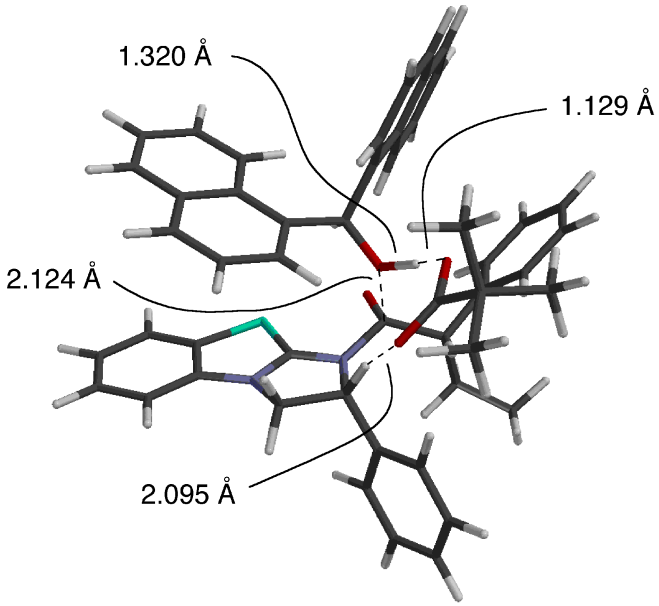
6	-3.084200721	-4.017806376	2.722677896
1	-3.535450587	-4.814863251	3.326377305
1	-2.678987932	-4.461675810	1.809003904
1	-3.883021502	-3.321103951	2.438078462
6	-2.558754049	-2.711030710	4.818787099
1	-2.972536913	-3.509789736	5.446072033
1	-3.358295939	-1.994749794	4.602887381
1	-1.792148664	-2.181344271	5.392855718
6	1.888359922	-2.606710132	-2.626769274
1	1.481251514	-1.605736699	-2.710108937
6	2.837319595	-5.235740209	-2.484107336
1	3.202903483	-6.258079005	-2.415851229
6	2.513823535	-4.690120516	-3.704305094
1	2.621586197	-5.274838505	-4.614230396
6	2.030601059	-3.362816804	-3.770126775
1	1.760297765	-2.935853040	-4.732667564
6	4.293803668	0.186796359	-0.776934655
1	3.802611734	-0.482180208	-1.474440583
6	5.636535959	1.874423569	1.006280708
1	6.155219379	2.523912453	1.708433180
6	6.199344168	1.576459029	-0.213242561
1	7.166909069	1.989878296	-0.485957738
6	5.519263086	0.720633662	-1.110794276
1	5.970164700	0.475333293	-2.068764828
6	-2.738687299	-3.203933209	-1.818653817
1	-2.388129339	-4.147351922	-2.251579183
1	-3.660389488	-2.917391483	-2.336580144
1	-2.982125600	-3.394820582	-0.766553631

There are 208 alpha and 208 beta electrons

Requested basis set is 6-31G(d)

There are 329 shells and 970 basis functions





Transition Structure **ts-2-4r**

E(B3LYP/6-31G*) = -2780.962221 au

ν_{ts} = 324i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	0.129444738	0.841078792	1.647699801
6	1.386065537	1.696752127	1.768267382
1	1.510252266	2.254004084	0.835089302
8	-0.174949991	-0.049055713	2.436891888
7	-1.030540245	1.490170052	1.000657673
6	-2.222137045	0.913931225	1.114297746
7	-3.114525315	1.339288460	0.208576755
6	-2.480811463	2.224342284	-0.774893937
6	-1.046497101	2.434096140	-0.173675151
6	-0.793777671	3.885428199	0.187042638
6	0.119835095	4.620169667	-0.578214880
6	0.323713076	5.978015570	-0.318938047
6	-0.378672394	6.611589561	0.705910159
6	-1.295307766	5.884303086	1.470341314
6	-1.504703740	4.531106638	1.209079485
1	-2.218300829	3.974640456	1.813886091
1	-1.846908323	6.371184133	2.270175204
1	-0.215881091	7.666401885	0.909720087
1	1.034611574	6.538070101	-0.920518685
1	0.653382144	4.124216939	-1.384799851
1	-0.298355972	2.086433572	-0.889632581
1	-2.450166452	1.726490605	-1.747140202
1	-3.029290141	3.165670854	-0.852441757
8	0.680148923	-0.098316059	-0.175365606

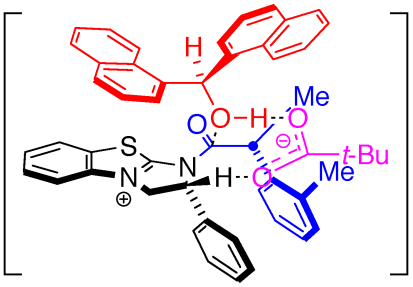
6	0.240952915	-1.430266369	-0.202571549
6	-0.936549414	-1.644960622	-1.174125651
6	-1.818270058	-2.771497173	-1.036880844
6	-2.924567124	-2.911659809	-1.943364326
6	-3.111257330	-1.950947326	-2.973481494
6	-2.244084978	-0.892243487	-3.096625744
6	-1.167516865	-0.735678323	-2.188813711
1	-0.504220113	0.116915837	-2.287880990
1	-2.373711806	-0.167695450	-3.897861265
1	-3.943428697	-2.075951475	-3.662725223
1	-0.145880605	-1.655309842	0.799160089
1	1.567786718	0.288868781	-1.073012732
8	2.341700196	0.615337546	-1.827377829
6	1.948083526	1.523300342	-2.675909391
6	2.982571538	1.829944179	-3.778854385
8	0.846001461	2.090584330	-2.644553908
16	-2.839826412	-0.285451250	2.198195490
6	-4.376432275	0.758150142	0.306710830
6	-4.421308866	-0.156068532	1.374527150
6	-5.590593076	-0.855258354	1.656672896
1	-5.627821948	-1.569492097	2.473574650
6	-5.491590463	0.993173258	-0.495208917
1	-5.448840052	1.696018794	-1.321092021
6	-6.660349306	0.290437738	-0.203539995
1	-7.542567641	0.453741707	-0.815000050
6	-6.712231406	-0.620605821	0.859127273
1	-7.633493691	-1.156856118	1.064593632
6	1.387211417	-2.417701337	-0.497353777
6	3.486274856	-4.200588769	-1.171250949
6	1.816042593	-2.576317433	-1.801655117
6	2.030836755	-3.172767541	0.541682246
6	3.082463221	-4.088395942	0.184227152
6	2.868486797	-3.453189017	-2.144370780
1	1.325032326	-2.016286663	-2.590969762
1	3.173367152	-3.542250458	-3.183981013
1	4.286569871	-4.892847590	-1.423582387
6	3.137873716	0.556412893	-4.640593359
1	3.881304111	0.722876049	-5.429670245
1	2.189739082	0.287995375	-5.122295297
1	3.464221722	-0.289215075	-4.028234709
6	4.337399492	2.175438286	-3.128216447
1	5.086221619	2.379098881	-3.903629348
1	4.695351431	1.349625033	-2.507603165
1	4.258006273	3.069704394	-2.497451804
6	2.496816421	2.998457431	-4.648791633
1	3.209786594	3.187431247	-5.460594449
1	2.399175591	3.918041007	-4.061418075
1	1.518155842	2.783285331	-5.087230389
6	1.159724151	2.719458806	2.923600582
1	1.137118239	2.168442407	3.870417405
1	0.178146485	3.192335025	2.812593323
6	2.650718344	0.884799978	2.013297553
6	5.071470863	-0.467230641	2.510784524
6	3.721752483	0.975729097	1.116683646

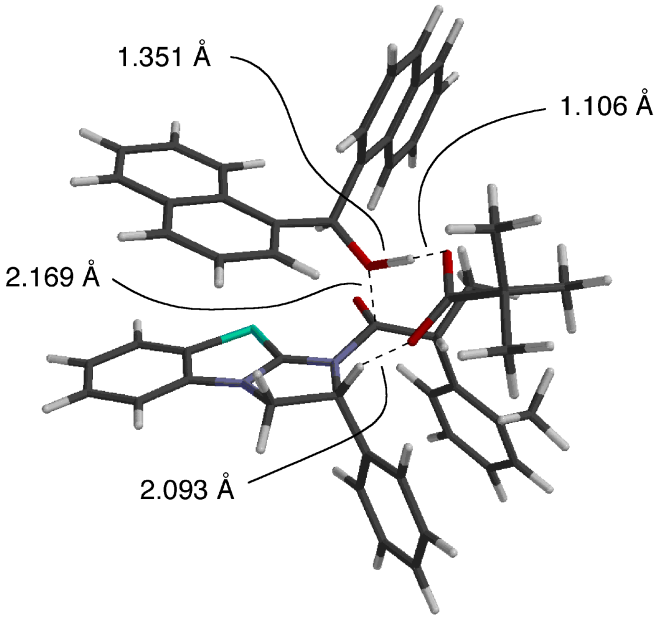
6	2.811506447	0.103391925	3.166487427
6	4.009896715	-0.566998603	3.411025834
6	4.921433255	0.306131752	1.360349810
1	3.608670215	1.553829728	0.205396137
1	1.990439224	0.001565253	3.868404204
1	4.110836751	-1.175124843	4.306254144
1	5.735171324	0.386515061	0.644135993
1	6.003168305	-0.993443085	2.701520235
6	-1.652094721	-3.767579740	-0.032340388
1	-0.810171627	-3.705486005	0.646911739
6	-3.809429597	-4.013877184	-1.797891822
1	-4.641703255	-4.104201718	-2.492822034
6	-2.527597430	-4.825686297	0.079156730
1	-2.371481536	-5.573754823	0.852039953
6	-3.620555478	-4.952196378	-0.809386964
1	-4.302940703	-5.792819654	-0.713476596
6	3.698689997	-4.875812959	1.193742401
1	4.490032818	-5.562986547	0.901301675
6	1.673261008	-3.087525911	1.918905765
1	0.926808906	-2.370437100	2.239485583
6	2.287216555	-3.872836908	2.870213449
1	1.990983694	-3.782125440	3.912344999
6	3.307716831	-4.781903409	2.508769736
1	3.784357932	-5.395590611	3.268995362
6	2.234013946	3.809280369	2.972467009
1	3.233055512	3.380285360	3.098033884
1	2.048629855	4.491171184	3.810121232
1	2.232448641	4.403732093	2.051658017

There are 208 alpha and 208 beta electrons

Requested basis set is 6-31G(d)

There are 329 shells and 970 basis functions





Transition Structure **ts-1-4i**

E(B3LYP/6-31G*) = -2780.969375 au

ν_{ts} = 158i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	0.841287447	0.166786219	1.350809754
6	2.062541918	-0.744300151	1.332184841
1	2.332162362	-0.919503935	0.288925244
8	0.090284687	0.285640484	2.317004881
7	0.842657645	1.317316872	0.445494219
6	-0.099760078	2.244774443	0.590510361
7	-0.250836936	3.027156658	-0.486214548
6	0.548431158	2.524380192	-1.610159243
6	1.450430923	1.437289289	-0.923188383
6	2.906569920	1.862480203	-0.926906751
6	3.735861188	1.367145660	-1.942390799
6	5.050832642	1.824269391	-2.056379811
6	5.548122971	2.768070805	-1.156641695
6	4.725475202	3.258696625	-0.140387695
6	3.408922302	2.813559071	-0.030138429
1	2.779817423	3.192440754	0.770897380
1	5.109536945	3.984967133	0.570648231
1	6.573814314	3.116796701	-1.242509183
1	5.688591629	1.433174726	-2.844704419
1	3.345831651	0.619540905	-2.628519421
1	1.327517288	0.476326241	-1.429997229
1	-0.119172089	2.097519724	-2.362807532
1	1.148517506	3.326840547	-2.043498002
8	-0.225923971	-1.019083510	-0.118207347

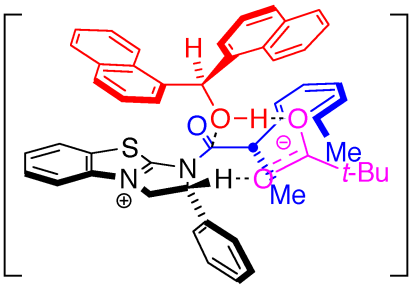
6	-1.604505252	-1.039418353	0.114787646
6	-2.383832633	-0.245903313	-0.949550552
6	-3.682586029	0.300128186	-0.674373591
6	-4.347826342	1.072629184	-1.687548628
6	-3.724823773	1.252276785	-2.951884405
6	-2.491959370	0.697570329	-3.201326959
6	-1.819029744	-0.036518611	-2.193972869
1	-0.834456565	-0.446108700	-2.395345249
1	-2.023574382	0.817760608	-4.175884776
1	-4.245540662	1.823620302	-3.717262204
1	-1.782366510	-0.524936070	1.070569839
1	0.319276879	-1.973113334	-0.903870988
8	0.820679813	-2.763408755	-1.492868484
6	1.553277796	-2.307055030	-2.473558880
6	2.238905605	-3.416215896	-3.295361183
8	1.691246728	-1.107661707	-2.748934336
16	-1.170588155	2.626431818	1.893866644
6	-1.224431015	4.015616483	-0.362765915
6	-1.825271652	3.966270305	0.908224950
6	-2.829016543	4.866786416	1.250841816
1	-3.302264932	4.828103472	2.227163697
6	-1.611629032	4.958969420	-1.312958835
1	-1.149580516	4.985018475	-2.294512953
6	-2.616287548	5.859292646	-0.960307609
1	-2.938514007	6.603037373	-1.682703166
6	-3.216294784	5.817417389	0.304766052
1	-3.996614108	6.529707781	0.554215010
6	-2.140924251	-2.477655821	0.258441421
6	-3.075715950	-5.150757400	0.422879523
6	-2.535994728	-3.179845283	-0.864285109
6	-2.197177406	-3.129285755	1.538664150
6	-2.684834226	-4.480717292	1.611511238
6	-2.995896849	-4.514010781	-0.791438391
1	-2.499715464	-2.692076860	-1.833123368
1	-3.294417078	-5.026513996	-1.702376009
1	-3.438217118	-6.173910175	0.493393945
6	1.721207248	-2.097700438	1.985641440
1	2.616085455	-2.726327524	2.023064573
1	0.945794295	-2.610496394	1.416100777
1	1.368540412	-1.945844525	3.008942544
6	3.252470858	-0.101565206	2.058425080
6	5.438367586	0.969407125	3.471684229
6	3.059526203	0.709358223	3.184890510
6	4.571088394	-0.398527432	1.643146867
6	5.640655655	0.149001585	2.362256341
6	4.138477042	1.247793704	3.886897406
1	2.048439087	0.915398050	3.522050079
1	6.655143950	-0.077247671	2.041336261
1	3.958275763	1.875081019	4.756297751
1	6.290371714	1.378945884	4.008367764
6	1.134497225	-4.272672731	-3.953272395
1	1.583154653	-5.091737283	-4.528668613
1	0.526433164	-3.672822079	-4.641639118
1	0.470730670	-4.701001348	-3.197097142

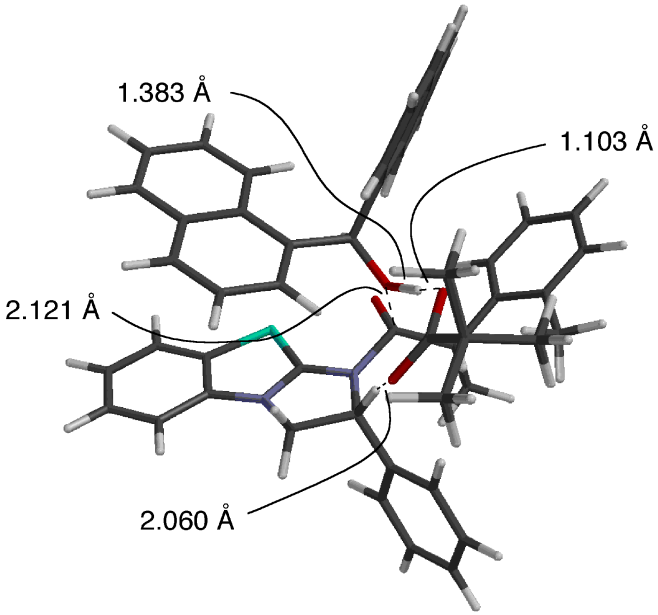
6	3.073981467	-4.298701571	-2.343207451
1	3.545584379	-5.116692847	-2.901663761
1	2.444734821	-4.725737356	-1.558324980
1	3.872094209	-3.718488995	-1.863234704
6	3.141841696	-2.796320866	-4.370900523
1	3.620002435	-3.586001014	-4.963252208
1	3.930139951	-2.184792548	-3.919226258
1	2.571513776	-2.151358933	-5.046250075
6	-1.797536533	-2.504944368	2.755671182
1	-1.380116794	-1.505663931	2.736062158
6	-2.766461630	-5.127868695	2.873884350
1	-3.139814261	-6.149333078	2.907741306
6	-2.382015334	-4.487076201	4.028674825
1	-2.449435182	-4.995370977	4.987170321
6	-1.888673089	-3.163875568	3.962739265
1	-1.568799245	-2.662154176	4.872619111
6	-4.352843364	0.115106899	0.569425779
1	-3.890980747	-0.491074774	1.341001300
6	-5.621924323	1.636373719	-1.408959004
1	-6.111534336	2.218974789	-2.186491947
6	-6.232063341	1.447169129	-0.190420163
1	-7.208625944	1.881578413	0.007079012
6	-5.589544671	0.674751158	0.805451104
1	-6.079808957	0.514103499	1.762175179
6	4.860959331	-1.303206949	0.465575322
1	4.443016606	-0.909518153	-0.467883486
1	4.443609549	-2.307552774	0.607929015
1	5.940517770	-1.411967481	0.322563333

There are 208 alpha and 208 beta electrons

Requested basis set is 6-31G(d)

There are 329 shells and 970 basis functions





Transition Structure **ts-2-4i**

E(B3LYP/6-31G*) = -2780.961268 au

ν_{ts} = 258i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	0.270515494	0.593358338	1.792513479
6	1.641742749	1.210955523	2.059017282
1	1.869444384	1.875083083	1.224092183
8	-0.204737152	-0.343915519	2.430312260
7	-0.754140673	1.532723820	1.276399319
6	-2.028170496	1.154324588	1.310048308
7	-2.820882987	1.856195856	0.486614818
6	-2.030480936	2.758217635	-0.356758486
6	-0.594261485	2.630201622	0.259455801
6	-0.106558520	3.949192599	0.826886900
6	0.917903069	4.628959085	0.157860802
6	1.347160762	5.879664638	0.608271710
6	0.756938855	6.462038003	1.729582215
6	-0.272081011	5.792555172	2.397565835
6	-0.704525620	4.546302908	1.946165207
1	-1.502473153	4.032457171	2.479198637
1	-0.736502886	6.240693741	3.271983942
1	1.092783684	7.433488968	2.082103528
1	2.143300520	6.396775344	0.079442380
1	1.358193097	4.179310350	-0.727752892
1	0.088130778	2.271935458	-0.512739334
1	-2.062652199	2.417030552	-1.394732768
1	-2.412427506	3.779322601	-0.288651924
8	0.688438957	-0.144756633	-0.151178937

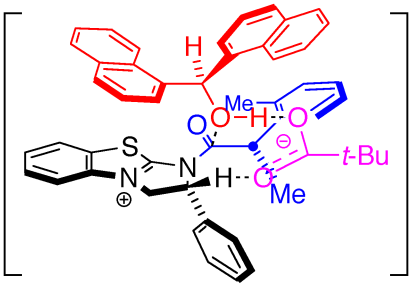
6	0.056913145	-1.385471377	-0.315551261
6	-1.176262838	-1.317267817	-1.240225097
6	-2.202569032	-2.323470948	-1.191681150
6	-3.342996691	-2.206944214	-2.058876680
6	-3.427928012	-1.115208671	-2.963677167
6	-2.430939123	-0.171043342	-2.999516103
6	-1.317923838	-0.268285330	-2.128474092
1	-0.556273879	0.502412286	-2.162852446
1	-2.485054668	0.658617134	-3.701417216
1	-4.289216285	-1.046515093	-3.624648450
1	-0.321850320	-1.679070895	0.671126349
1	1.547739747	0.282313072	-1.146882243
8	2.255173406	0.585256533	-1.937166816
6	1.919565596	1.647532951	-2.626718156
6	2.874296579	1.959183913	-3.796402371
8	0.932911904	2.354575919	-2.389687501
16	-2.858868847	-0.073132156	2.203121175
6	-4.161579058	1.480259096	0.496938214
6	-4.378589783	0.435048477	1.412254242
6	-5.650329910	-0.104207863	1.579119626
1	-5.821664193	-0.919301419	2.275478351
6	-5.203713888	2.009828375	-0.261911976
1	-5.027784391	2.813360471	-0.969826868
6	-6.475510743	1.465503260	-0.086314378
1	-7.303900506	1.856672697	-0.668994771
6	-6.698515721	0.423415896	0.822639090
1	-7.697344928	0.014392344	0.938456885
6	1.027864356	-2.485568129	-0.792316560
6	2.785072151	-4.466816924	-1.808655653
6	1.436245487	-2.488647780	-2.112903270
6	1.515912978	-3.513131436	0.085178394
6	2.389110380	-4.525700036	-0.447790318
6	2.322891287	-3.461518739	-2.623162033
1	1.059974234	-1.721754312	-2.781552647
1	2.621086972	-3.418144270	-3.667642547
1	3.452654019	-5.234585281	-2.193586887
6	2.901260528	0.741730520	-4.745131587
1	3.587116466	0.929397957	-5.580120081
1	1.907429979	0.547047148	-5.166570796
1	3.231713573	-0.156924053	-4.217469198
6	4.290777410	2.204169157	-3.234102436
1	4.986117999	2.427816609	-4.052076302
1	4.658576910	1.326079990	-2.696806644
1	4.302510270	3.057859084	-2.544880827
6	2.383515445	3.205577732	-4.548095177
1	3.051965745	3.427891128	-5.388894405
1	2.356715064	4.080676996	-3.890848929
1	1.371946565	3.059672626	-4.939518038
6	1.536844045	2.063275887	3.353471221
1	2.503829445	2.536008381	3.552621640
1	1.291397095	1.424066002	4.207096429
1	0.783305258	2.851826506	3.276873061
6	2.778574280	0.206730933	2.233422062
6	4.921248837	-1.548062386	2.742861712

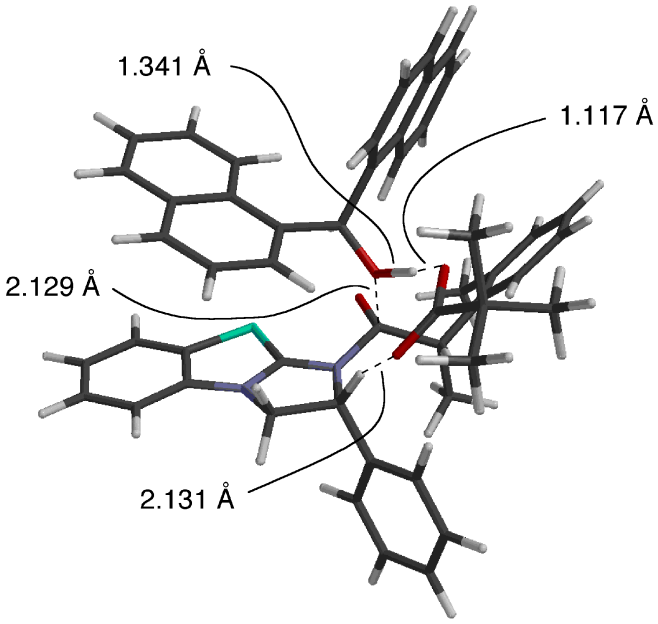
6	4.026826622	0.420647031	1.608476037
6	2.643822744	-0.863100969	3.129199605
6	3.698167223	-1.739695105	3.379603357
6	5.074244967	-0.471231378	1.871948185
1	3.557134832	-2.571166530	4.064779831
1	6.030756737	-0.311769551	1.379036532
1	5.751490190	-2.225964635	2.923712714
6	-2.153127760	-3.441765355	-0.310907522
1	-1.296944616	-3.577282399	0.338700321
6	-4.369162124	-3.187860675	-1.999019564
1	-5.225144922	-3.083045792	-2.662531003
6	-3.166209451	-4.375443825	-0.277767230
1	-3.096843924	-5.219909033	0.403206733
6	-4.288552644	-4.250166304	-1.128378246
1	-5.080142221	-4.994576788	-1.095501802
6	2.837415588	-5.578345962	0.395038198
1	3.494643420	-6.334729817	-0.028997524
6	1.163163484	-3.609695073	1.462929290
1	0.553135383	-2.836360832	1.915297889
6	1.608362423	-4.650137701	2.248798411
1	1.317084722	-4.694676201	3.295335412
6	2.451024036	-5.650745367	1.712708137
1	2.796050404	-6.466740587	2.342600114
1	1.690819841	-1.018117656	3.620742701
6	4.276773747	1.580570946	0.670738462
1	3.652937353	1.508562339	-0.225639379
1	5.321512922	1.588490451	0.344108722
1	4.075848415	2.550021358	1.144531586

There are 208 alpha and 208 beta electrons

Requested basis set is 6-31G(d)

There are 329 shells and 970 basis functions





Transition Structure **ts-2'-4i**

E(B3LYP/6-31G*) = -2780.958623 au

ν_{ts} = 295i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	0.027397398	0.774520497	1.655628830
6	1.150052225	1.791159791	1.865769462
1	1.231642057	2.369226343	0.941334021
8	-0.146643678	-0.221841688	2.353398288
7	-1.222710185	1.310608442	1.064239930
6	-2.326120484	0.573921455	1.157242100
7	-3.280687158	0.918036844	0.280897629
6	-2.781379871	1.912958344	-0.673591943
6	-1.382389979	2.291025942	-0.073258153
6	-1.335797215	3.748256207	0.345830981
6	-0.506958763	4.630737490	-0.356293287
6	-0.492024382	5.989215866	-0.028931747
6	-1.302023075	6.474854034	0.997025561
6	-2.139989512	5.599824939	1.694391998
6	-2.160290859	4.245553574	1.366622939
1	-2.810396022	3.569911757	1.918845809
1	-2.775285974	5.973030299	2.493170709
1	-1.285256260	7.530820017	1.252860891
1	0.155978995	6.666768858	-0.578258908
1	0.105337709	4.248304077	-1.168259724
1	-0.599503724	2.073870963	-0.802126285
1	-2.697086314	1.458649518	-1.663856633
1	-3.451798869	2.774238257	-0.713166869
8	0.676631271	0.059462349	-0.241194326

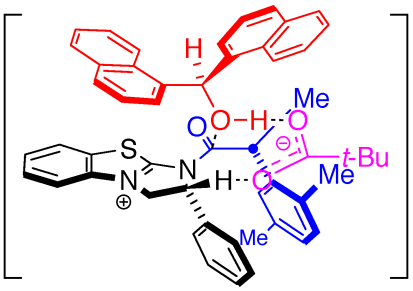
6	0.432104454	-1.317630992	-0.338431869
6	-0.743949518	-1.648899233	-1.274040883
6	-1.469908182	-2.881871324	-1.138511880
6	-2.586808738	-3.140228289	-2.004962328
6	-2.935052184	-2.186435325	-2.998279045
6	-2.212086439	-1.024612034	-3.125571197
6	-1.127436364	-0.753568527	-2.254761389
1	-0.582064061	0.178834785	-2.362101821
1	-2.465403892	-0.304360015	-3.900780365
1	-3.772629147	-2.398170843	-3.659293086
1	0.123918331	-1.651920728	0.660875450
1	1.478069838	0.607698241	-1.166176354
8	2.179696361	1.052475902	-1.912540083
6	1.662269737	1.969965524	-2.685408119
6	2.643200696	2.503828545	-3.748518467
8	0.499740947	2.388447639	-2.600088805
16	-2.769919485	-0.742026118	2.191167860
6	-4.458154243	0.179836623	0.369576423
6	-4.370844166	-0.774344439	1.398586500
6	-5.439198394	-1.624720448	1.665818027
1	-5.373899222	-2.368996045	2.453595678
6	-5.607767516	0.306931180	-0.408135699
1	-5.665292072	1.041229038	-1.205307723
6	-6.674902044	-0.546989309	-0.131600393
1	-7.581332132	-0.470900695	-0.724368858
6	-6.594771628	-1.499377996	0.892495058
1	-7.439370982	-2.153033619	1.087170915
6	1.693765981	-2.108870994	-0.735585452
6	4.000302577	-3.526720225	-1.580124374
6	2.045369331	-2.197549576	-2.069337503
6	2.529399330	-2.745307780	0.244756322
6	3.686361495	-3.477271386	-0.197287557
6	3.198590373	-2.891666761	-2.497249129
1	1.411936524	-1.729150830	-2.815546290
1	3.436204340	-2.930989586	-3.557310518
1	4.882373113	-4.078626171	-1.897600675
6	3.083939255	1.319087022	-4.636109801
1	3.802965753	1.657271078	-5.392520485
1	2.226235097	0.882252996	-5.162352832
1	3.549462718	0.534071623	-4.034223669
6	3.875923545	3.094793416	-3.030183656
1	4.596457827	3.474951474	-3.764755523
1	4.371106267	2.336725932	-2.417307841
1	3.594730423	3.931245931	-2.377691058
6	1.961749046	3.582325774	-4.602705397
1	2.660840970	3.962359687	-5.357605862
1	1.629143204	4.424378146	-3.987037962
1	1.080576100	3.184350538	-5.115525377
6	0.735209154	2.780932558	2.986685942
1	1.585794982	3.429406321	3.218932943
1	0.442375144	2.262789745	3.901291126
1	-0.096297090	3.416073283	2.676180700
6	2.531567686	1.175748319	2.121419580
6	5.198360628	0.289052564	2.399351649

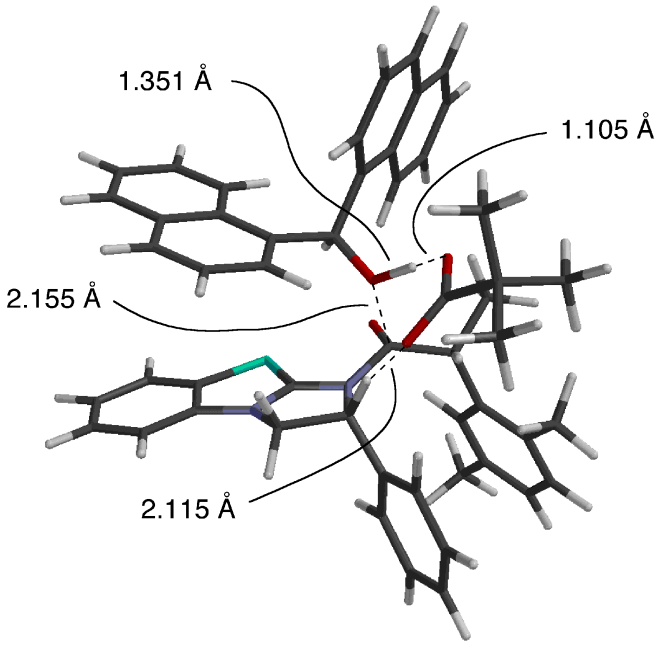
6	3.473080516	1.331854793	1.093187076
6	2.944088569	0.556458456	3.326251996
6	4.275375926	0.123811596	3.428039880
6	4.790633295	0.898849257	1.216946124
1	4.590305404	-0.358692628	4.350873873
1	5.483159032	1.031451805	0.390062029
1	6.219285251	-0.063940563	2.520505717
6	-1.135578705	-3.874348079	-0.172760468
1	-0.281395214	-3.724992475	0.477588540
6	-3.319125199	-4.349183628	-1.857799421
1	-4.162644979	-4.528120703	-2.521560526
6	-1.864574739	-5.038025553	-0.059143309
1	-1.581829276	-5.779459258	0.683677051
6	-2.970622880	-5.280188802	-0.906538040
1	-3.536652189	-6.203084338	-0.809006909
6	4.498638083	-4.144450286	0.758506542
1	5.367247044	-4.695455043	0.403748134
6	2.268446382	-2.705615483	1.644852828
1	1.437586527	-2.119644826	2.019025683
6	3.076483574	-3.367546165	2.543325523
1	2.853333443	-3.312695063	3.605774030
6	4.201067304	-4.100436254	2.100395854
1	4.830299292	-4.618739248	2.819588038
1	3.159263314	1.784860733	0.159299105
6	2.061645175	0.335936906	4.539890658
1	1.973216047	1.246446631	5.147289861
1	2.501858049	-0.432026770	5.185166975
1	1.056794939	0.010539565	4.266046588

There are 208 alpha and 208 beta electrons

Requested basis set is 6-31G(d)

There are 329 shells and 970 basis functions





Transition Structure **ts-1-4l**

E(B3LYP/6-31G*) = -2820.287628 au

ν_{ts} = 154i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	-0.870400754	0.157506518	-1.196939159
6	-1.999085711	-0.864874665	-1.173578587
1	-2.188220239	-1.132268702	-0.132170528
8	-0.189329000	0.401782029	-2.191139549
7	-0.930480865	1.255322252	-0.224715119
6	-0.054467765	2.249728757	-0.344019079
7	0.105464659	2.962934308	0.778142925
6	-0.613935650	2.345169374	1.897450918
6	-1.454334926	1.225343740	1.184204832
6	-2.939570456	1.503153568	1.308704781
6	-3.647283520	0.852247814	2.327949902
6	-4.989078745	1.163285089	2.558369919
6	-5.634635472	2.117704387	1.771899918
6	-4.932994661	2.764810704	0.751964168
6	-3.590481661	2.464789888	0.526052051
1	-3.056052103	2.966179804	-0.276626324
1	-5.432135839	3.501089748	0.128020881
1	-6.680759927	2.353619590	1.947673308
1	-5.530237952	0.651612312	3.349961295
1	-3.140950033	0.100811394	2.929184034
1	-1.205637929	0.251517775	1.612969861
1	0.105748403	1.934646611	2.610050668
1	-1.257620415	3.077354917	2.389262889

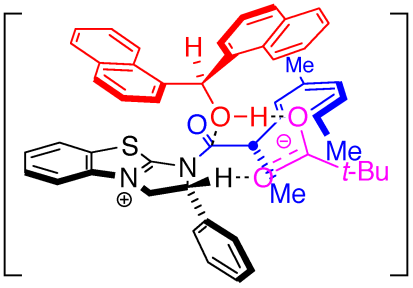
8	0.379828169	-0.980900426	0.138340944
6	1.734141340	-0.901282519	-0.200847966
6	2.544743611	-0.109901596	0.840506646
6	3.792645849	0.513567284	0.501575974
6	4.490798167	1.274982130	1.500608121
6	3.950895914	1.369776993	2.811306577
6	2.766827874	0.743268838	3.119366914
6	2.060896019	0.016589329	2.129239969
1	1.115597034	-0.454955481	2.379374635
1	2.363459319	0.799190834	4.128247310
1	4.495469318	1.935978179	3.563794683
1	1.803124853	-0.332459419	-1.139208859
1	-0.062103842	-2.019998151	0.879241979
8	-0.481916943	-2.880984847	1.430364108
6	-1.104729379	-2.556121023	2.532623236
6	-1.638526359	-3.771370923	3.316634786
8	-1.256882901	-1.396023325	2.938221425
16	0.918248357	2.795237747	-1.666478546
6	1.005833236	4.021054835	0.681172986
6	1.540117376	4.101840266	-0.617248457
6	2.468047607	5.087252085	-0.939217895
1	2.890444574	5.149443823	-1.937426431
6	1.383760971	4.917497183	1.679313046
1	0.973396643	4.843187662	2.681254767
6	2.312129891	5.903471676	1.347429160
1	2.625889835	6.612599495	2.107383901
6	2.846668777	5.990614110	0.055534216
1	3.568471814	6.767268302	-0.177299060
6	2.343050338	-2.295146696	-0.449303817
6	3.400450020	-4.905338919	-0.780607249
6	2.802695332	-3.034867560	0.623991866
6	2.397120956	-2.872805728	-1.764346128
6	2.947112816	-4.193289778	-1.921250760
6	3.324528361	-4.338170820	0.468216656
1	2.769085396	-2.599542430	1.617856969
1	3.673001311	-4.882660562	1.342105375
1	3.808986147	-5.904501984	-0.915130022
6	-1.570312797	-2.135191200	-1.934016149
1	-2.396490706	-2.852634295	-1.953144257
1	-0.708649814	-2.596711650	-1.450759277
1	-1.308911425	-1.890400958	-2.966899961
6	-3.285791229	-0.299090311	-1.789796102
6	-5.625654862	0.620421985	-3.033079736
6	-3.234845136	0.584375506	-2.874718915
6	-4.542642167	-0.746010292	-1.323207300
6	-5.692212629	-0.269293095	-1.962231867
6	-4.388678860	1.062306635	-3.507604817
1	-2.265104735	0.902719446	-3.247473046
1	-6.664449263	-0.610969508	-1.613459191
1	-6.542860740	0.965011305	-3.506167678
6	-0.426888779	-4.614430001	3.773074714
1	-0.771924248	-5.504916568	4.312946434
1	0.220633577	-4.041600820	4.448207197
1	0.168917214	-4.934208646	2.913516585

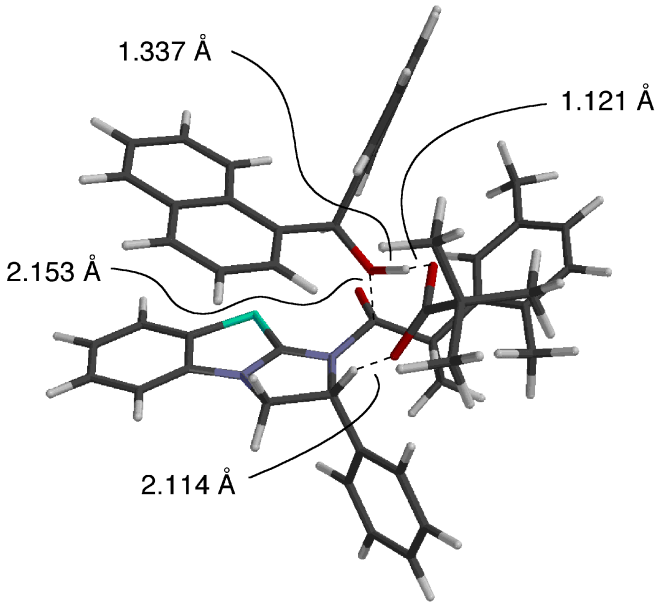
6	-2.529847967	-4.616546286	2.382278229
1	-2.921916846	-5.488201084	2.920508389
1	-1.963632122	-4.965037651	1.514807581
1	-3.385343445	-4.032750917	2.020560243
6	-2.443924174	-3.301326066	4.536761423
1	-2.798117951	-4.167691105	5.108640414
1	-3.315601621	-2.712572785	4.231292359
1	-1.835347817	-2.674411926	5.195430469
6	1.939574043	-2.205258627	-2.938114478
1	1.476291856	-1.228878854	-2.858704590
6	3.027486547	-4.768167509	-3.218169711
1	3.447340606	-5.767290674	-3.314928085
6	2.586232570	-4.086984151	-4.328340616
1	2.654473437	-4.540208006	-5.313975113
6	2.032787566	-2.794397308	-4.180564182
1	1.667846839	-2.261282755	-5.054914237
6	4.379112292	0.418498202	-0.793424339
1	3.892705229	-0.175761484	-1.559018096
6	5.713395425	1.914271444	1.160924166
1	6.228728308	2.487763367	1.928596636
6	6.242693289	1.809572558	-0.104703861
1	7.180896963	2.301078400	-0.349038534
6	5.567502067	1.050023854	-1.088634354
1	5.994625219	0.956661474	-2.083794143
6	-4.682700290	-1.733562738	-0.186169019
1	-4.256952628	-1.348133389	0.747318047
1	-4.179633201	-2.684225038	-0.401042928
1	-5.738051264	-1.954715966	0.001358662
6	-4.291516724	2.038730594	-4.657594652
1	-5.173387495	1.981780935	-5.304810667
1	-3.406313195	1.845965489	-5.274244451
1	-4.216378405	3.075557038	-4.300938932

There are 212 alpha and 212 beta electrons

Requested basis set is 6-31G(d)

There are 337 shells and 989 basis functions





Transition Structure **ts-2-4l**

E(B3LYP/6-31G*) = -2820.279198 au

ν_{ts} = 324i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	0.135358873	0.765146496	1.728647318
6	1.222034002	1.829514910	1.825042730
1	1.066946458	2.523811803	1.000337415
8	0.045348299	-0.220265217	2.454867184
7	-1.163232912	1.264566551	1.232241985
6	-2.252404011	0.525242093	1.405448867
7	-3.274704917	0.883610388	0.615047504
6	-2.853354558	1.900720227	-0.355873332
6	-1.421504468	2.286399929	0.156435463
6	-1.366657018	3.722271235	0.645304522
6	-0.674090269	4.668342236	-0.120667808
6	-0.664121633	6.010797027	0.266295625
6	-1.343245381	6.418444666	1.414495571
6	-2.040191228	5.478784908	2.178854017
6	-2.054960082	4.139037017	1.793325818
1	-2.595904073	3.413001463	2.396958340
1	-2.570322070	5.788839555	3.075386485
1	-1.330307585	7.462548352	1.715337141
1	-0.120953034	6.737143525	-0.332310826
1	-0.153718351	4.344596246	-1.018467971
1	-0.684353763	2.125463127	-0.634148148
1	-2.829958108	1.458896908	-1.354942733
1	-3.534701696	2.754087990	-0.335594211
8	0.641783167	0.044019060	-0.235397297

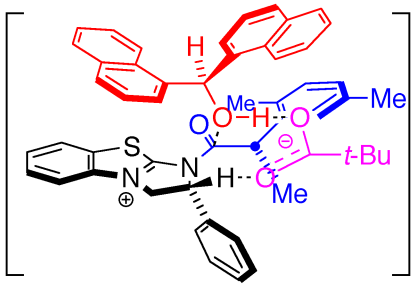
6	0.277084697	-1.303794018	-0.352802729
6	-0.919249771	-1.525247290	-1.302795991
6	-1.713566515	-2.722234869	-1.230322078
6	-2.834012556	-2.878357113	-2.116888132
6	-3.126895886	-1.858022628	-3.061185543
6	-2.346660383	-0.728761027	-3.121648461
6	-1.253154584	-0.562085935	-2.235881306
1	-0.665783778	0.347400573	-2.287851620
1	-2.559467432	0.046474018	-3.854694657
1	-3.969504476	-1.992754267	-3.735740695
1	-0.064385495	-1.625554431	0.639102726
1	1.396635953	0.567239008	-1.207057182
8	2.013924946	0.957701042	-2.057351486
6	1.472442411	1.943283785	-2.717293361
6	2.247262051	2.340813507	-3.991388855
8	0.421642518	2.516505615	-2.392549766
16	-2.613876035	-0.801545301	2.458085004
6	-4.437883113	0.136257309	0.779606046
6	-4.268163772	-0.835602604	1.781676516
6	-5.308530834	-1.697505940	2.113553629
1	-5.180941656	-2.454297896	2.881384746
6	-5.642605248	0.267661907	0.091400721
1	-5.762129240	1.014080195	-0.687288579
6	-6.680984986	-0.598635185	0.431656770
1	-7.629163594	-0.519950270	-0.091327642
6	-6.519255424	-1.567250662	1.430387656
1	-7.342941703	-2.230566305	1.675184778
6	1.462547648	-2.205330648	-0.754838023
6	3.619607140	-3.826751466	-1.632583542
6	1.877818028	-2.214308982	-2.073198485
6	2.149202431	-3.040285857	0.191015381
6	3.228100881	-3.874127677	-0.270043415
6	2.959528790	-3.006400060	-2.515040748
1	1.354418212	-1.597161386	-2.794969930
1	3.253717546	-2.972977611	-3.561002322
1	4.442173468	-4.456047801	-1.964612529
6	2.259528162	1.121159637	-4.939624402
1	2.791968809	1.369591040	-5.866059391
1	1.239769369	0.821003457	-5.210992930
1	2.755246094	0.266431888	-4.470888570
6	3.697136015	2.707955133	-3.610462538
1	4.276225413	2.942543637	-4.512265290
1	4.184500042	1.881631119	-3.086359605
1	3.724605911	3.589508822	-2.958530603
6	1.561061778	3.531410850	-4.676524054
1	2.113437845	3.811379085	-5.581493666
1	1.522361847	4.401410964	-4.013175707
1	0.532415140	3.287234294	-4.959202946
6	0.987682464	2.594807407	3.157457180
1	1.720753426	3.402383104	3.245192452
1	1.121474127	1.917319980	4.005815120
1	-0.012524191	3.035193110	3.211659405
6	2.665986793	1.341016593	1.782441653
6	5.363004367	0.592148005	1.904836430

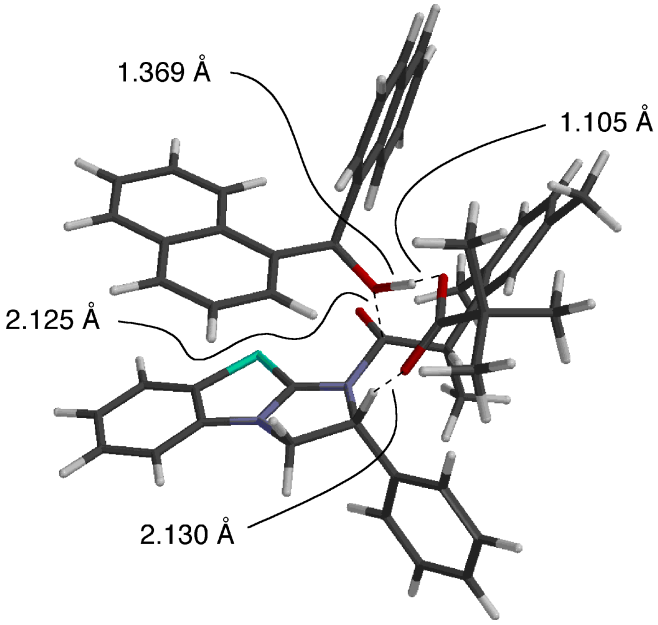
6	3.630230791	2.099046506	1.083663795
6	3.079552642	0.244150679	2.547703563
6	4.420511502	-0.148994282	2.622578404
6	4.967984744	1.694144396	1.151906249
1	5.717449821	2.266937540	0.609797751
1	6.414070912	0.313214151	1.943543505
6	-1.446905334	-3.774984196	-0.308474048
1	-0.596704801	-3.700373732	0.358633995
6	-3.628489217	-4.053839573	-2.038479446
1	-4.471529721	-4.154557196	-2.718885126
6	-2.236092077	-4.903631952	-0.260675501
1	-2.001903261	-5.693306332	0.448598054
6	-3.340074311	-5.048151514	-1.132243990
1	-3.953057231	-5.944645351	-1.087304109
6	3.881381424	-4.746011979	0.643172786
1	4.691431817	-5.369148800	0.270185288
6	1.806784324	-3.115917950	1.573185593
1	1.040734258	-2.463225588	1.974444849
6	2.453593720	-3.981539072	2.428285883
1	2.165386198	-4.015738723	3.476064968
6	3.499492110	-4.812640232	1.962748767
1	4.000924413	-5.491393979	2.647828614
1	2.333191453	-0.318462846	3.098269209
6	3.278184203	3.346495345	0.301905639
1	2.552430966	3.145210490	-0.491755084
1	4.173167399	3.764532051	-0.169457504
1	2.850263370	4.130325546	0.941588819
6	4.838827614	-1.343230723	3.448178504
1	5.834226273	-1.196204185	3.883370282
1	4.875182920	-2.256083908	2.841004572
1	4.135921117	-1.529504360	4.267225912

There are 212 alpha and 212 beta electrons

Requested basis set is 6-31G(d)

There are 337 shells and 989 basis functions





Transition Structure **ts-2'-4l**

E(B3LYP/6-31G*) = -2820.277044 au

ν_{ts} = 240i cm^{-1}

Cartesian Coordinates (Angstroms)

Atomic Number	X	Y	Z
6	-0.068372526	0.765444899	1.663439535
6	1.090492401	1.735875400	1.896261911
1	1.206545097	2.319093119	0.978963162
8	-0.292324519	-0.223790276	2.357439401
7	-1.290518132	1.356005320	1.061582297
6	-2.423780046	0.665212637	1.139874828
7	-3.354767916	1.052187394	0.255645091
6	-2.806247009	2.032130116	-0.687043199
6	-1.396129002	2.344193995	-0.074438323
6	-1.283488227	3.797631226	0.344927094
6	-0.401570623	4.637402263	-0.344571910
6	-0.323885217	5.993955969	-0.018610044
6	-1.124519593	6.520643985	0.994217218
6	-2.015200897	5.689055665	1.679478308
6	-2.097465484	4.336808083	1.352717438
1	-2.788308862	3.694459174	1.895184242
1	-2.643464332	6.094616018	2.467952938
1	-1.059811459	7.574991215	1.249057802
1	0.364904743	6.637687989	-0.558894575
1	0.202703790	4.224864658	-1.147559060
1	-0.620164857	2.090174271	-0.797767401
1	-2.733491310	1.583166665	-1.680629797
1	-3.437709320	2.922474864	-0.723409354
8	0.571482902	0.031661771	-0.224998599

6	0.284237054	-1.337580382	-0.314563076
6	-0.897481440	-1.639223549	-1.254133667
6	-1.653858998	-2.854157795	-1.121582396
6	-2.774291069	-3.084527541	-1.991228862
6	-3.097539950	-2.120855636	-2.983535433
6	-2.347524529	-0.975903514	-3.106301164
6	-1.258169383	-0.732734194	-2.233113287
1	-0.689960023	0.186391856	-2.335724094
1	-2.582607602	-0.247862697	-3.879988206
1	-3.938669702	-2.311352583	-3.646442288
1	-0.039229267	-1.657900587	0.684582791
1	1.409401608	0.563948268	-1.167111409
8	2.116303285	0.979906420	-1.907248313
6	1.610190200	1.888737543	-2.702075448
6	2.594818043	2.386004852	-3.778774374
8	0.456488030	2.327780777	-2.619801389
16	-2.930254030	-0.637251348	2.161723129
6	-4.561915111	0.361828002	0.328613361
6	-4.523151467	-0.600646376	1.353018857
6	-5.626923882	-1.409561843	1.604067675
1	-5.598976722	-2.160468715	2.387809557
6	-5.697537367	0.538074582	-0.459860422
1	-5.718563103	1.278864331	-1.252861261
6	-6.800414150	-0.274645932	-0.199486129
1	-7.696782572	-0.159407957	-0.801224832
6	-6.768623894	-1.234951477	0.819731369
1	-7.640053263	-1.856208927	1.001949553
6	1.522594261	-2.169592573	-0.701427976
6	3.791258135	-3.656446908	-1.530736179
6	1.891092169	-2.253922114	-2.031033026
6	2.318544733	-2.850269562	0.282293545
6	3.455960634	-3.616900241	-0.152563422
6	3.026606843	-2.981316753	-2.451078912
1	1.285918896	-1.753834080	-2.780205257
1	3.279426235	-3.014397089	-3.507849826
1	4.658513726	-4.234371534	-1.842562193
6	3.085116885	1.171208351	-4.595837738
1	3.801310593	1.493557526	-5.361659305
1	2.249522166	0.677274169	-5.107040288
1	3.570829403	0.435281209	-3.949386119
6	3.796769302	3.052765914	-3.073965591
1	4.524768420	3.400548711	-3.816934280
1	4.296663499	2.350216082	-2.402005101
1	3.479683375	3.923663248	-2.486534565
6	1.898112548	3.398633567	-4.699415510
1	2.600183581	3.761199929	-5.460138140
1	1.529240460	4.259118285	-4.132636568
1	1.040295835	2.947910709	-5.208554641
6	0.703347037	2.730892099	3.021635701
1	1.576053733	3.343882269	3.268291663
1	0.381883545	2.216160731	3.928336569
1	-0.099310224	3.401700889	2.709233360
6	2.439854115	1.055419713	2.157452565
6	5.035649337	-0.001204301	2.405552915

6	3.382722273	1.155167091	1.127635070
6	2.816027735	0.410636325	3.361737759
6	4.116447668	-0.103903534	3.446369566
6	4.676979358	0.633128530	1.217071910
1	4.413145041	-0.609556605	4.362793055
1	6.029416596	-0.429672144	2.516458942
6	-1.347239979	-3.854367943	-0.154731302
1	-0.492575573	-3.724838855	0.499006238
6	-3.535538324	-4.275973155	-1.847742518
1	-4.380980340	-4.434022555	-2.514372344
6	-2.104264773	-5.000273643	-0.044248775
1	-1.842338510	-5.748178177	0.699686614
6	-3.212403428	-5.215770181	-0.896084148
1	-3.800577630	-6.124999985	-0.801218164
6	4.226847484	-4.329454375	0.804896791
1	5.080820838	-4.905813167	0.454956010
6	2.035475414	-2.824458160	1.678671313
1	1.222711084	-2.212695839	2.051339294
6	2.801974699	-3.532435336	2.578331375
1	2.562151206	-3.487489423	3.637580478
6	3.906540456	-4.298819313	2.141852586
1	4.502678085	-4.853025486	2.862447671
1	3.088574369	1.634261404	0.199239850
6	1.927340158	0.241142625	4.578981916
1	1.873911644	1.161139118	5.175665285
1	2.337422170	-0.535556176	5.233492583
1	0.909864605	-0.048290259	4.309797196
6	5.630620342	0.747170036	0.051183904
1	6.556447413	0.191847671	0.236760934
1	5.904439118	1.792257251	-0.147753627
1	5.174264236	0.351645419	-0.864100902

There are 212 alpha and 212 beta electrons

Requested basis set is 6-31G(d)

There are 337 shells and 989 basis functions

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