Supporting Information

Asymmetric Suzuki-Miyaura Cross-Coupling of 1-Bromo-2-naphthoates using the Helically Chiral Polymer Ligand PQXphos

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1. General

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. $^1$H and $^{13}$C NMR spectra were recorded on a Varian 400-MR spectrometer at ambient temperature. $^1$H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane ($\delta$ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br = broad), coupling constant (Hz), and integration. $^{13}$C NMR chemical shifts are reported in ppm downfield from tetramethylsilane ($\delta$ scale). $^{31}$P NMR chemical shifts are reported in ppm downfield from H$_3$PO$_4$ (85%). All $^{13}$C NMR and $^{31}$P NMR spectra were obtained with complete proton decoupling.

Toluene and THF were dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.), [PdCl($\eta^3$-C$_3$H$_5$)]$_2$ (TCI), distilled water (Nacalai tesque), 1-bromo-2-naphthoic acid (TCI), methanol (Nacalai tesque), ethanol (Nacalai tesque), 2-propanol (Nacalai tesque), 3-pentanol (TCI), 2,4-dimethyl-3-pentanol (TCI), dicyclohexylmethanol (Aldrich), cyclohexanol (Wako), t-butyl alcohol (Wako), phenol (TCI), 2,6-dimethylphenol (TCI), oxalyl chloride (Wako), 1-naphthaleneboronic acid (Wako), 2-methylphenylboronic acid (Wako), 4-methyl-1-naphthaleneboronic acid (Alfa Aesar), 4-methoxy-1-naphthaleneboronic acid (Aldrich), 4-fluoro-1-naphthaleneboronic acid (Aldrich), 1-pyreneboronic acid (Wako), 2,3-dimethylphenylboronic acid (Wako), 2,5-dimethylphenylboronic acid (Wako), 5-fluoro-2-methylphenylboronic acid (Wako), 4-fluoro-2-methylphenylboronic acid (Alfa Aesar), lithium alminium hydride (Wako), and potassium hydroxide (Nacalai tesque) were used as received from the commercial sources. 1,1,2-trichloroethane (Wako), dimethylformamide (Nacalai tesque), and pyridine (Wako) were purchased from the commercial sources and distilled before use. Potassium phosphate (Nacalai tesque) was purchased and dried prior to use. PQXphos L1-L6 were synthesized by the method reported previously.$^{51}$

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2. Experimental Procedures and Spectral Data for New Compounds

2.1 Preparation of Aryl Bromide

**General procedure:** To a solution of 1-bromo-2-naphthoic acid (1.11 g, 4.40 mmol) in CH₂Cl₂ (20 mL) was added oxalyl chloride (416 μL, 4.84 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. After evaporation of the solvent, to the mixture was added pyridine (1.0 mL, 13.3 mmol), alcohol (13.3 mmol), and CH₂Cl₂ (20 mL). The mixture was stirred at room temperature for 18 h. The resulting mixture was quenched by water and extracted with CH₂Cl₂. After drying with anhydrous MgSO₄, the concentrated mixture was purified by column chromatography (hexane:CH₂Cl₂ = 2:1) to give a desired product.

**Methyl 1-bromo-2-naphthoate (1A):** 95% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.58-7.70 (m, 3H), 4.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 135.2, 132.2, 131.2, 128.6, 128.2, 128.1, 128.1, 127.8, 125.7, 122.6, 52.7; IR (ATR) μ 2925, 1717, 1456, 1429, 1265, 1242, 1126, 1126, 1003, 866, 827, 760 cm⁻¹; HRMS (ESI) m/z calcld for C₁₂H₉BrO₂⁺H⁺ (M⁺H⁺): 264.9859, found: 264.9851.

**Isopropyl 1-bromo-2-naphthoate (1B):** 82% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.44 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.56-7.67 (m, 3H), 5.36 (sep, J = 6.0 Hz, 1H), 1.44 (d, J = 6.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 135.0, 132.2, 132.2, 128.4, 128.2, 128.0, 127.9, 127.8, 125.6, 122.0, 69.7, 21.8 (2C); IR (ATR) μ 2986, 1722, 1460, 1373, 1271, 1242, 1172, 1099, 978, 926, 823, 788, 762 cm⁻¹; HRMS (ESI) m/z calcld for C₁₄H₁₃BrO₂⁺H⁺ (M⁺H⁺): 293.0172, found: 293.0162.
Pentan-3-yl 1-bromo-2-naphthoate (1C): 87% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$ = 8.0 Hz, 1H), 7.85 (dd, $J$ = 8.0 Hz, 1.2 Hz, 1H), 7.84 (d, $J$ = 8.4 Hz, 1H), 7.56-7.67 (m, 3H), 5.12 (quin, $J$ = 6.0 Hz, 1H), 1.77 (dq, $J$ = 7.6 Hz, 6.0 Hz, 4H), 1.03 (t, $J$ = 7.6 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.5, 134.9, 132.4, 132.3, 128.4, 128.2, 128.0, 127.9, 127.8, 125.5, 121.9, 78.8, 26.5 (2C), 9.8 (2C); IR (ATR) $\nu$ 2966, 1728, 1558, 1456, 1265, 1234, 1150, 1136, 1109, 1045, 974, 930, 822, 758 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{16}$H$_{17}$BrO$_2$+H$^+$ (M+H$^+$): 321.0485, found: 321.0475.

2,4-Dimethylpentan-3-yl 1-bromo-2-naphthoate (1D): 80% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46 (d, $J$ = 8.4 Hz, 1H), 7.84 (dd, $J$ = 7.2 Hz, 0.8 Hz, 1H), 7.84 (d, $J$ = 8.4 Hz, 1H), 7.56-7.70 (m, 3H), 4.97 (t, $J$ = 6.0 Hz, 1H), 2.07 (dsep, $J$ = 6.4 Hz, 6.0 Hz, 2H), 1.03 (t, $J$ = 6.4 Hz, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.5, 135.0, 132.4, 132.3, 128.5, 128.1, 128.0, 127.9, 127.8, 125.7, 122.1, 84.7, 26.6 (2C), 19.7 (2C), 17.5 (2C); IR (ATR) $\nu$ 2963, 1717, 1558, 1325, 1276, 1240, 1171, 1117, 972, 935, 893, 810, 754 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{18}$H$_{21}$BrO$_2$+H$^+$ (M+H$^+$): 349.0798, found: 349.0787.

Dicyclohexylmethyl 1-bromo-2-naphthoate (1E): 80% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J$ = 8.4 Hz, 1H), 7.84 (d, $J$ = 8.0 Hz, 2H), 7.56-7.72 (m, 3H), 5.00-5.04 (m, 1H), 1.56-1.78 (m, 12H), 1.15-1.34 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 135.0, 132.4, 132.1, 128.6, 128.1, 128.0, 127.9, 127.8, 125.8, 122.3, 83.3, 38.6 (2C), 30.0 (2C), 27.7 (2C), 26.4 (2C), 26.3 (2C), 26.1 (2C); IR (ATR) $\nu$ 2929, 2851, 1728, 1683, 1653, 1558, 1265, 1238, 1167, 1124, 975, 754 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{32}$H$_{59}$BrO$_2$+H$^+$ (M+H$^+$): 429.1424, found: 429.1411.
Cyclohexyl 1-bromo-2-naphthoate (1F): 92% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$ = 8.4 Hz, 1H), 7.84 (dd, $J$ = 8.0 Hz, 1.2 Hz, 1H), 7.83 (d, $J$ = 8.4 Hz, 1H), 7.56-7.67 (m, 3H), 5.13 (sep, $J$ = 4.0 Hz, 1H), 2.02-2.07 (m, 2H), 1.80-1.85 (m, 2H), 1.51-1.70 (m, 3H), 1.41-1.51 (m, 2H), 1.29-1.39 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1, 135.0, 132.3 (2C), 128.4, 128.2, 128.0, 127.9, 127.8, 125.7, 122.0, 74.5, 31.6 (2C), 125.4, 23.7 (2C); IR (ATR) $\nu$ 2933, 1717, 1558, 1506, 1456, 1285, 1248, 1170, 1128, 1011, 980, 824, 756 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{17}$H$_{17}$BrO$_2$+H$^+$ (M+H$^+$): 333.0485, found: 333.0473.

Cyclooctyl 1-bromo-2-naphthoate (1G): 93% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$ = 8.4 Hz, 1H), 7.84 (dd, $J$ = 8.4 Hz, 1H), 7.83 (d, $J$ = 8.4 Hz, 1H), 7.56-7.66 (m, 3H), 5.30 (sep, $J$ = 4.0 Hz, 1H), 1.90-2.07 (m, 4H), 1.74-1.83 (m, 2H), 1.55-1.66 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.0, 135.0, 132.4, 132.2, 128.4, 128.0, 127.9, 127.8, 125.6, 122.0, 77.2, 31.4 (2C), 27.1 (2C), 25.4, 23.0 (2C); IR (ATR) $\nu$ 2920, 1717, 1558, 1506, 1456, 1285, 1248, 1170, 1128, 1011, 980, 824, 756 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{19}$H$_{21}$BrO$_2$+H$^+$ (M+H$^+$): 361.0798, found: 361.0784.

tert-Butyl 1-bromo-2-naphthoate (1H): 63% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.42 (d, $J$ = 8.0 Hz, 1H), 7.83 (d, $J$ = 8.0 Hz, 1H), 7.82 (d, $J$ = 8.4 Hz, 1H), 7.55-7.65 (m, 3H), 1.67 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.9, 134.8, 133.4, 132.2, 128.3, 128.1, 127.9, 127.8, 127.7, 125.5, 121.3, 82.9, 28.2 (3C); IR (ATR) $\nu$ 1724, 1684, 1558, 1506, 1456, 1367, 1294, 1248, 1126, 822, 754, 654 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{15}$H$_{15}$BrO$_2$+H$^+$ (M+H$^+$): 307.0328, found: 307.0317.
Phenyl 1-bromo-2-naphthoate (1I): 79% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.51 (dd, $J = 8.4$ Hz, 0.8 Hz, 1H), 7.87-7.93 (m, 3H), 7.69 (ddd, $J = 8.4$ Hz, 7.2 Hz, 1.2 Hz, 1H), 7.64 (ddd, $J = 8.0$ Hz, 6.8 Hz, 1.2 Hz, 1H), 7.45-7.50 (m, 2H), 7.29-7.35 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.8, 150.8, 135.4, 132.4, 130.5, 129.6 (2C), 128.7, 128.4, 128.3, 128.0, 126.2, 125.9, 123.4, 121.6 (2C); IR (ATR) $\nu$ 1734, 1718, 1684, 1558, 1489, 1456, 1229, 1190, 968, 822, 758, 745, 691 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{17}$H$_{11}$BrO$_2$+H$^+$ (M+H$^+$): 307.0015, found: 307.0003.

2,6-Dimethylphenyl 1-bromo-2-naphthoate (1J): 78% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.54 (d, $J = 8.4$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.8$ Hz, 1H), 7.90 (d, $J = 8.8$ Hz, 1H), 7.70 (ddd, $J = 8.4$ Hz, 6.8 Hz, 1.2 Hz, 1H), 7.65 (ddd, $J = 8.0$ Hz, 6.8 Hz, 1.2 Hz, 1H), 7.12-7.19 (m, 3H), 2.36 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.9, 148.2, 135.4, 132.4, 130.3, 130.2 (2C), 128.8 (2C), 128.4, 128.3, 128.2, 128.0, 126.1, 125.8 (2C), 123.5, 16.7 (2C); IR (ATR) $\nu$ 2358, 1684, 1653, 1647, 1558, 1506, 754 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{19}$H$_{15}$BrO$_2$+H$^+$ (M+H$^+$): 355.0328, found: 355.0316.

2.2 Preparation of Aryl Chloride 1D’

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 1H), 7.66 (dd, $J = 6.8$ Hz, 6.4 Hz, 1H), 7.61 (dd, $J = 6.8$ Hz, 6.4 Hz, 1H), 7.56 (dd, $J = 6.8$ Hz, 6.4 Hz, 1H).

2,4-Dimethylpentan-3-yl 1-chloro-2-naphthoate: To a solution of 1D (349 mg, 1.0 mmol) in DMF (1.0 mL) was added CuCl (109 mg, 1.1 mmol). The mixture was stirred at 140 °C for 18 h. After filtration of the reaction mixture with Et$_2$O, the filtrate was extracted by Et$_2$O and washed by water, dried over MgSO$_4$. After evaporation of the solvent, the residue was purified by column chromatography (hexane:CH$_2$Cl$_2$ = 2:1) to give a desired product (254 mg, 84%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 1H), 7.66 (dd, $J = 6.8$ Hz, 6.4 Hz, 1H), 7.61 (dd, $J = 6.8$ Hz, 6.4 Hz, 1H), 7.56 (dd, $J = 6.8$ Hz, 6.4 Hz, 1H)
Hz, 1H), 4.97 (t, J = 6.0 Hz, 1H), 2.06 (dsep, J = 6.4 Hz, 6.0 Hz, 2H), 1.01 (t, J = 6.4 Hz, 12H);
13C NMR (100 MHz, CDCl3) δ 166.7, 135.1, 131.5, 131.2, 128.9, 128.1 (2C), 127.7, 126.9, 125.8, 125.7, 84.5, 29.6 (2C), 19.7 (2C), 17.4 (2C); IR (ATR) ν 2963, 1717, 1464, 1331, 1272, 1242, 1120, 989, 893, 812, 754 cm⁻¹; HRMS (ESI) m/z calcd for C13H12ClO2Na⁺ (M+Na⁺): 327.1122, found: 327.1118.

2.3 General Procedure for Asymmetric Suzuki-Miyaura Cross-coupling (Tables 1–3 and Eq 1)

To a solution of (P)-(R)-PQXphos (27 mg, 4.0 μmol phosphorous atom) in THF (300 μL) was added [PdCl(η3-C3H5)]2 (0.01 M in THF, 100 μL, 1 μmol), K3PO4 (43 mg, 0.2 mmol), 1 (0.10 mmol), 2 (0.15 mmol), H2O (40 μL) in this order. The reaction was stirred at 40 °C for 24–48 h. After the reaction, subsequent addition of MeCN (10 mL) resulted in precipitation of the polymer complex. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was subjected to PTLC (hexane/Et2O = 4/1) to give a desired product. Further purification was performed by GPC if necessary. The enantiomeric excesses of the products were determined by HPLC or SFC with a chiral stationary phase.

2.4 Gram-Scale Reaction (Table 3, entry 6)

To a solution of (P)-(R)-PQXphos (595 mg, 96 μmol phosphorous atom) in THF (16 mL) was added [PdCl(η3-C3H5)]2 (14.6 mg, 40 μmol), K3PO4 (1.70 g, 8.0 mmol), 1 (1.40 g, 4.0 mmol), 2 (900 mg, 6.0 mmol), H2O (1.6 mL) in this order. The reaction was stirred at 40 °C for 72 h. After the reaction, subsequent addition of MeCN (30 mL) resulted in precipitation of the PQXphos. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was isolated by column chromatography (hexane/Et2O = 4/1) to give a desired product 3Dg (1.31 g, 87% yield). The enantiomeric excess of this compound was determined by SFC analysis.

2.5 Reuse of Catalyst (Scheme 1)

[Initial Run] To a solution of (P)-(R)-PQXphos (27 mg, 4.0 μmol phosphorous atom) in THF (300 μL) was added [PdCl(η3-C3H5)]2 (0.01 M in THF, 100 μL, 1 μmol), K3PO4 (43 mg, 0.2 mmol), 1D (0.12 mmol, 42 mg), 2g (0.10 mmol, 15 mg), H2O (40 μL) in this order. The reaction was stirred at 40 °C for 40 hours. After the reaction, acetonitrile was added to the mixture to precipitate polymer complex. The insoluble materials were washed by acetonitrile to extract the product. After evaporation of the extract, the residue was purified by by PTLC (hexane/Et2O = 4/1) to give a desired product (20 mg, 53%). The enantiomeric excesses of the
products were determined by SFC with a chiral stationary phase. The polymer catalyst remaining in the reaction vessel was dried under vacuum and used for the next run.

[2nd and 3rd Runs] To a mixture of polymer catalyst and THF (400 µL) was added K₃PO₄ (43 mg, 0.2 mmol), 1D (0.12 mmol, 42 mg), 2g (0.10 mmol, 15 mg), H₂O (40 µL) in this order. The reaction was stirred at 40 °C. After the reaction, acetonitrile was added to the mixture to precipitate polymer complex. The insoluble materials were washed by acetonitrile to extract the product. After evaporation of the extract, the residue was purified by PTLC (hexane/Et₂O = 4/1) to give a desired product (2nd run, 25 mg, 66%; 3rd run, 26 mg 69%). The enantiomeric excesses of the products were determined by SFC with a chiral stationary phase.

2.6 Asymmetric Suzuki-Miyaura Coupling Using Helically Inversed PQXphos (Scheme 2)

(R)-L₆ (27 mg, 4.0 µmol phosphorus atom) in 1,1,2-trichloroethane (0.6 mL) and THF (0.2 mL) was stirred at 60 °C for 24 h. To the mixture was added [PdCl(η²-C₅H₅)]₂ [0.01 M in THF/1,1,2-TCE (5/2), 100 µL, 1 µmol], and the solution was stirred at 60 °C for 10 min. To the mixture was added K₃PO₄ (43 mg, 0.2 mmol), 1D (35 mg, 0.1 mmol), 2f (37 mg, 0.15 mmol), and H₂O (40 µL). The mixture was stirred at 40 °C for 48 h. After the reaction, subsequent addition of MeCN (10 mL) resulted in precipitation of the PQXphos. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was subjected to PTLC (hexane/Et₂O = 4/1), Further purification was performed by GPC to give a desired product (44 mg, 93% yield). The enantiomeric excess of this compound was determined by SFC analysis.

2.7 Reduction and Hydrolysis of (S)-3Dg (Scheme 3)

[Reduction] To a solution of (S)-3Dg (35 mg, 0.094 mmol) in Et₂O (7.0 mL) was added lithium aluminum hydride (7 mg, 0.20 mmol) at 0 °C. The mixture was stirred at 80 °C for 1 h. After the reaction, the mixture was quenched by water and extracted with Et₂O. After drying with anhydrous MgSO₄, the concentrated mixture was purified by column chromatography (hexane/Et₂O = 3/1) to give a desired product (S)-4 (21 mg, 84% yield). The enantiomeric excess of this compound was determined by SFC analysis.

[Hydrolysis] To a solution of (S)-3Dg (131 mg, 0.35 mmol) in EtOH (30.0 mL) was added KOH (11 g, 200 mmol). The mixture was stirred at 80 °C for 12 hours. After the reaction, the mixture was extracted with Et₂O and the extracts were washed with water. After drying with anhydrous MgSO₄, the concentrated mixture was purified by column chromatography (hexane:Et₂O = 1:1) to give a desired product (S)-5 (94 mg, 98% yield). The enantiomeric excess of this compound was determined by SFC analysis.
excess of this compound was determined by SFC analysis.

2.8 Determination of Absolute Configuration

![Chemical structure](image)

To a solution of 3Da (26 mg, 0.066 mmol, 84% ee) in EtOH (7.0 mL) was added KOH (3.0 g, 53 mmol). The mixture was stirred at 80 °C for 12 hours. After the reaction, the mixture was extracted with Et₂O and the extracts were washed with water. After drying with anhydrous MgSO₄, the concentrated mixture was purified by column chromatography (hexane:Et₂O = 1:1) to give a desired product 6 (16 mg, 83% yield). The enantiomeric excess of this compound was determined by SFC analysis. The absolute configuration was determined by comparing its optical rotation with reported data.⁵²a (S1): ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.92-7.95 (m, 3H), 7.52-7.57 (m, 2H), 7.45 (ddd, J = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.33 (dd, J = 6.8 Hz, 0.8 Hz, 1H), 7.21-7.30 (m, 3H), 7.15 (d, J = 8.0 Hz, 1H); [α]D²³ = -20.1 [c 0.810, CH₂Cl₂, 84% ee (S)].

![Chemical structure](image)

To a solution of 3Db (42 mg, 0.12 mmol, 82% ee) in Et₂O (7.0 mL) was added lithium aluminum hydride (9 mg, 0.24 mmol) at 0 °C. The mixture was stirred at 80 °C for 1 h. After the reaction, the mixture was quenched by water and extracted with Et₂O. After drying with anhydrous MgSO₄, the concentrated mixture was purified by column chromatography (hexane/Et₂O = 3/1) to give a desired product 7 (23 mg, 80% yield). The enantiomeric excess of this compound was determined by SFC analysis. The absolute configuration was determined by comparing its optical rotation with reported data.⁵²b (S2): ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 9.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.36 (ddd, J = 7.6 Hz, 6.8 Hz, 0.8 Hz, 1H), 7.15-7.28 (m, 5H), 7.05 (d, J = 7.2 Hz, 1H), 4.39 (d, J = 5.6 Hz, 2H), 1.82 (s, 3H); [α]D²³ = -33.7 [c 1.070, CH₂Cl₂, 81% ee (S)].

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2.9 Spectral Data for New Compounds

Methyl 1-(1-naphthyl)-2-naphthoate (3Aa): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J$ = 8.4 Hz, 1H), 8.01 (d, $J$ = 8.4 Hz, 1H), 7.94-7.98 (m, 3H), 7.59 (dd, $J$ = 8.4 Hz, 6.8 Hz, 1H), 7.55 (ddd, $J$ = 8.0 Hz, 5.2 Hz, 2.4 Hz, 1H), 7.46 (ddd, $J$ = 8.4 Hz, 6.8 Hz, 1.6 Hz, 1H), 7.37 (ddd, $J$ = 6.8 Hz, 1.2 Hz, 1H), 7.29-7.32 (m, 2H), 7.25-7.28 (m, 1H), 7.22 (d, $J$ = 8.4 Hz, 1H), 3.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.0, 140.2, 136.9, 134.8, 133.2, 133.1, 132.9, 128.7, 128.2, 128.1, 128.0, 127.8, 127.8, 127.6, 126.9, 126.7, 126.0, 126.0, 125.7, 125.7, 125.2, 51.8; IR (ATR) $\nu$ 3057, 2947, 2841, 1724, 1712, 1504, 1431, 1280, 1240, 1122, 831, 798, 763, 731 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{22}$H$_{16}$O$_2$+H$^+$ (M+H$^+$): 313.1223, found: 313.1215; [$\alpha$]$^{27}_{D}$ -20.1 [c 1.240, CH$_2$Cl$_2$, 70% ee (S)].

Isopropyl 1-(1-naphthyl)-2-naphthoate (3Ba): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J$ = 8.8 Hz, 1H), 8.00 (d, $J$ = 8.8 Hz, 1H), 7.92-7.99 (m, 3H), 7.56 (dd, $J$ = 8.0 Hz, 6.8 Hz, 1H), 7.53 (ddd, $J$ = 8.4 Hz, 6.4 Hz, 2.0 Hz, 1H), 7.45 (ddd, $J$ = 8.4 Hz, 5.2 Hz, 3.2 Hz, 1H), 7.25-7.35 (m, 5H), 4.74 (sep, $J$ = 6.4 Hz, 1H), 0.57 (d, $J$ = 6.4 Hz, 3H), 0.54 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.7, 139.3, 137.3, 134.7, 133.3, 133.1, 129.8, 128.0, 128.0, 127.9, 127.9, 127.6, 127.4, 127.1, 126.6, 126.4, 125.9, 125.8, 125.7, 125.1, 67.9, 20.8, 20.8; IR (ATR) $\nu$ 3057, 2977, 2931, 1699, 1371, 1278, 1103, 822, 766 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{22}$H$_{20}$O$_2$+H$^+$ (M+H$^+$): 341.1536, found: 341.1530; [$\alpha$]$^{28}_{D}$ -7.3 [c 1.050, CH$_2$Cl$_2$, 79% ee (S)].

3-pentyl 1-(1-naphthyl)-2-naphthoate (3Ca): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (d, $J$ = 8.4 Hz, 1H), 8.01 (d, $J$ = 8.4 Hz, 1H), 7.94-7.98 (m, 3H), 7.59 (dd, $J$ = 8.4 Hz, 6.8 Hz, 1H), 7.55 (ddd, $J$ = 8.0 Hz, 5.2 Hz, 2.4 Hz, 1H), 7.46 (ddd, $J$ = 8.4 Hz, 6.8 Hz, 1.6 Hz, 1H), 7.37 (ddd, $J$ = 6.8 Hz, 1.2 Hz, 1H), 7.29-7.32 (m, 2H), 7.25-7.28 (m, 1H), 7.22 (d, $J$ = 8.4 Hz, 1H), 3.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.0, 140.2, 136.9, 134.8, 133.2, 133.1, 132.9, 128.7, 128.2, 128.1, 128.0, 127.8, 127.8, 127.6, 126.9, 126.7, 126.0, 126.0, 125.7, 125.7, 125.2, 51.8; IR (ATR) $\nu$ 3057, 2947, 2841, 1724, 1712, 1504, 1431, 1280, 1240, 1122, 831, 798, 763, 731 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{22}$H$_{16}$O$_2$+H$^+$ (M+H$^+$): 313.1223, found: 313.1215; [$\alpha$]$^{27}_{D}$ -20.1 [c 1.240, CH$_2$Cl$_2$, 70% ee (S)].
Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.94 (m, 3H), 7.56 (dd, J = 8.4 Hz, 7.2 Hz, 1H), 7.54 (ddd, J = 8.4 Hz, 5.2 Hz, 4.8 Hz, 1H), 7.45 (ddd, J = 8.0 Hz, 4.4 Hz, 3.2 Hz, 1H), 7.36 (ddd, J = 6.8 Hz, 1.2 Hz, 1H), 7.28-7.30 (m, 2H), 7.24-7.27 (m, 2H), 4.58 (sept, J = 2.4 Hz, 1H), 0.74-1.09 (m, 4H), 0.54 (t, J = 7.2 Hz, 3H), 0.43 (t, J = 7.6 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 167.9, 139.5, 137.4, 134.8, 133.3, 133.3, 133.2, 129.5, 128.1, 128.0 (2C), 127.8, 127.6, 127.5, 127.0, 126.6, 126.4, 126.1, 125.9, 125.7, 125.1, 77.4, 25.9, 25.7, 9.5, 9.2; IR (ATR) \(\nu\) 3057, 2966, 2933, 1699, 1327, 1269, 1136, 833, 766 cm\textsuperscript{-1}; HRMS (ESI) \textit{m}/\textit{z} calcld for C\textsubscript{26}H\textsubscript{32}O\textsubscript{2}+H\textsuperscript{+} (M+H\textsuperscript{+}): 369.1849, found: 369.1841; [\(\alpha\)]\textsubscript{D}\textsuperscript{20} -6.4 [c 1.105, CH\textsubscript{2}Cl\textsubscript{2}, 82% ee (S)].

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\textbf{2,4-Dimethylpentan-3-yl 1-(1-naphthyl)-2-naphthoate (3Da): \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.13 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 2.4 Hz, 1H), 7.93 (d, J = 2.0 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.56 (dd, J = 8.0 Hz, 6.8 Hz, 1H), 7.52 (ddd, J = 8.0 Hz, 6.4 Hz, 1.6 Hz, 1H), 7.43 (ddd, J = 8.0 Hz, 5.2 Hz, 2.8 Hz, 1H), 7.38 (ddd, J = 6.8 Hz, 1.2 Hz, 1H), 7.20-7.29 (m, 4H), 4.55 (t, J = 6.0 Hz, 1H), 1.46 (sep, J = 6.4 Hz, 1H), 1.39 (sep, J = 6.4 Hz, 1H), 0.66 (d, J = 6.8 Hz, 3H), 0.63 (d, J = 6.8 Hz, 3H) 0.50 (d, J = 6.4 Hz, 3H), 0.30 (d, J = 6.4 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 168.1, 139.4, 137.1, 134.7, 133.4, 133.3, 133.1, 129.6, 128.1, 128.0, 127.8, 127.4, 127.3, 126.6, 126.4, 126.2, 126.0, 125.7, 125.2, 83.7, 29.1, 19.2, 19.2, 17.4 (2C), 16.5 (2C); IR (ATR) \(\nu\) 2963, 2359, 1726, 1699, 1558, 1506, 1456, 1232, 1117, 800, 770 cm\textsuperscript{-1}; HRMS (ESI) \textit{m}/\textit{z} calcld for C\textsubscript{26}H\textsubscript{32}O\textsubscript{2}+H\textsuperscript{+} (M+H\textsuperscript{+}): 397.2162, found: 397.2155; [\(\alpha\)]\textsubscript{D}\textsuperscript{20} -6.7 [c 1.030, CH\textsubscript{2}Cl\textsubscript{2}, 87% ee (S)].

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\end{center}

\textbf{Dicyclohexymethyl 1-(1-naphthyl)-2-naphthoate (3Ea): \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.16 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 1.6 Hz, 1H), 7.94 (s, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.56 (dd, J = 8.0 Hz, 6.8 Hz, 1H), 7.52 (ddd, J = 8.0 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.44 (ddd, J = 8.0 Hz, 6.0 Hz, 2.4 Hz, 1H), 7.38 (dd, J = 6.8 Hz, 1.2 Hz, 1H), 7.19-7.28 (m, 4H), 4.59 (t, J = 6.0 Hz, 1H), 0.03-1.57 (m, 22H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 168.2, 139.3, 137.2,
134.7, 133.4, 133.3, 133.2, 129.4, 128.1 (2C), 128.0, 127.8, 127.6, 127.4, 127.2, 126.5 (2C), 126.5, 126.0, 125.6, 125.1, 82.3, 37.9 (2C), 29.5, 29.2, 27.7, 26.2, 26.2, 26.1, 26.1, 26.0, 25.9, 25.8; IR (ATR) ν 2924, 2849, 1726, 1699.1446, 1271, 1121, 907, 766, 729 cm⁻¹; HRMS (ESI) m/z caked for C₃₀H₁₁₇O₂⁺H⁺ (M+H⁺): 477.2788, found: 477.2777; [α]D²⁹ = -1.2 [c 1.735, CH₂Cl₂, 82% ee (S)].

Cyclohexyl 1-(1-naphthyl)-2-naphthoate (3Fa):¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 4.0 Hz, 1H), 7.94 (d, J = 4.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.0 Hz, 6.8 Hz, 1H), 7.53 (ddd, J = 8.0 Hz, 4.8 Hz, 2.8 Hz, 1H), 7.45 (ddd, J = 8.0 Hz, 3.6 Hz, 3.6 Hz, 1H), 7.35 (dd, J = 6.8 Hz, 1.2 Hz, 1H), 2.75-2.79 (m, 4H), 4.53 (tt, J = 9.6 Hz, 4.0 Hz, 1H), 1.25-1.34 (m, 5H), 0.99-1.12 (m, 2H), 0.87-0.97 (m, 1H) 0.52-0.65 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.7, 139.2, 137.3, 134.7, 133.3, 133.2, 133.1, 129.9, 128.0 (2C), 127.9, 127.7, 127.4, 127.1, 126.6, 126.4, 125.9 (2C), 125.7, 125.2, 73.1, 30.7 (2C), 25.1 (2C), 23.4, 23.4; IR (ATR) ν 2930, 1699, 1327, 1279, 1111, 912, 764 cm⁻¹; HRMS (ESI) m/z caked for C₂₇H₂₆O₂⁺H⁺ (M+H⁺): 381.1849, found: 381.1840; [α]D²⁹ = -5.2 [c 1.030, CH₂Cl₂, 80% ee (S)].

Cyclooctyl 1-(1-naphthyl)-2-naphthoate (3Ga):¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.95 (dd, J = 6.0 Hz, 0.8 Hz, 1H), 7.92-7.94 (m, 2H), 7.56 (dd, J = 8.0 Hz, 6.8 Hz, 1H), 7.52 (dd, J = 8.0 Hz, 4.0 Hz, 4.0 Hz, 1H), 7.46 (ddd, J = 8.0 Hz, 4.8 Hz, 2.8 Hz, 1H), 7.34 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.25-7.29 (m, 4H), 4.72 (sep, J = 4.0 Hz, 1H), 1.10-1.31 (m, 12H), 0.80-1.02 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.7, 139.0, 137.3, 134.7, 133.4, 133.3, 133.1, 130.0, 128.0, 128.0, 127.9, 127.9, 127.7, 127.3, 127.1, 126.5, 126.4, 126.0, 125.9, 125.7, 75.7, 30.0, 30.0, 27.1, 27.1, 25.0, 22.4, 22.3; IR (ATR) ν 2922, 1705, 1335, 1269, 1134, 945, 762 cm⁻¹; HRMS (ESI) m/z caked for C₂₉H₂₉O₂⁺H⁺ (M+H⁺): 409.2162, found: 409.2152; [α]D³⁰ = -10.5 [c 1.240, CH₂Cl₂, 80% ee (S)].
tert-Butyl 1-(1-naphthyl)-2-naphthoate (3Ha): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92-7.99 (m, 5H), 7.56 (dd, $J = 8.4$ Hz, 6.8 Hz, 1H), 7.51 (ddd, $J = 8.4$ Hz, 6.0 Hz, 2.4 Hz, 1H), 7.46 (ddd, $J = 8.0$ Hz, 5.6 Hz, 2.4 Hz, 1H), 7.35 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H), 7.24-7.31 (m, 4H), 0.81 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.0, 138.2, 137.4, 134.5, 133.4, 133.3, 133.0, 131.4, 128.0, 127.9, 127.9, 127.8, 127.6, 127.3, 127.2, 126.6, 126.5, 126.0, 125.8, 125.7, 125.2, 80.9, 27.1 (3C); IR (ATR) ν 2976, 1699, 1367, 1334, 1286, 1124, 853, 766 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{25}$H$_{22}$O$_2$+Na$^+$ (M+Na$^+$): 377.1512, found: 377.1502; [α]$_{D}^{27}$ $-$21.5 [c 0.810, CH$_2$Cl$_2$, 68% ee (S)].

Phenyl 1-(1-naphthyl)-2-naphthoate (3Ia): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.8$ Hz, 1H), 7.56-7.61 (m, 2H), 7.44-7.48 (m, 2H), 7.39 (d, $J = 8.0$ Hz, 1H), 7.27-7.36 (m, 3H), 7.13-7.19 (m, 2H), 7.06 (ddddd, $J = 8.8$ Hz, 6.8Hz, 1.2 Hz, 1.2 Hz, 1H), 6.46-6.49 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.4, 150.4, 140.3, 136.6, 135.0, 133.5, 130.0, 132.9, 129.0 (2C), 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 128.3, 126.2, 126.0, 125.8, 125.8, 125.4, 125.1, 121.0 (2C); IR (ATR) ν 2962, 1728, 1591, 1265, 1188, 1099, 1068, 798, 762 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{27}$H$_{18}$O$_2$+H$^+$ (M+H$^+$): 375.1380, found: 375.1370; [α]$_{D}^{10}$ +29.7 [c 0.640, CH$_2$Cl$_2$, 78% ee (S)].

2,6-Dimethylphenyl 1-(1-naphthyl)-2-naphthoate (3Ja): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.32
2,4-Dimethylpentan-3-yl 1-(2-methylphenyl)-2-naphthoate (3Db): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 8.8$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.54 (dddd, $J = 8.0$ Hz, 6.4 Hz, 0.8 Hz, 1H), 7.40 (dddd, $J = 8.4$ Hz, 6.4 Hz, 1.2 Hz, 1H), 7.29-7.36 (m, 3H), 7.25 (dddd, $J = 7.2$ Hz, 1.6 Hz, 0.8 Hz, 1H), 7.12 (dd, $J = 6.8$ Hz, 1.2 Hz, 1H), 4.71 (t, $J = 6.4$ Hz, 1H), 1.97 (s, 3H), 1.79 (sep, $J = 6.8$ Hz, 1H), 1.71 (sep, $J = 6.8$ Hz, 1H), 0.81 (d, $J = 6.8$ Hz, 3H), 0.80 (d, $J = 6.8$ Hz, 3H), 0.74 (d, $J = 6.8$ Hz, 3H), 0.74 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.1, 140.7, 138.7, 136.7, 134.6, 132.4, 129.6, 129.5, 128.4, 127.9, 127.6, 127.5, 127.4, 127.3, 126.6, 125.9, 125.4, 83.6, 29.4, 29.4, 20.0, 19.4, 19.4, 17.5, 17.2; IR (ATR) v 2922, 1695, 1558, 1261, 1118, 937, 770, 760, 731 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{25}$H$_{28}$O$_2$+H$^+$ (M+H$^+$): 361.2162, found: 361.2151; $[\alpha]_D^{25}$ $^{25}$ = -40.5 [c 1.020, CH$_2$Cl$_2$, 88% ee (S)].

2,4-Dimethylpentan-3-yl 1-(4-methyl-1-naphthyl)-2-naphthoate (3Dc): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J = 8.4$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.8$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.50 (dd, $J = 8.0$ Hz, 4.0 Hz, 1H), 7.45 (ddd, $J = 8.4$ Hz, 4.8 Hz, 2.8 Hz, 1H), 7.38 (dd, $J = 7.2$ Hz, 0.8 Hz, 1H), 7.21-7.26 (m, 5H), 4.53 (t, $J = 6.4$ Hz, 1H), 2.78 (d, $J = 0.4$ Hz, 3H), 1.49 (sep, $J = 6.8$ Hz, 1H), 1.42 (sep, $J = 6.8$ Hz, 1H), 0.65 (d, $J = 6.8$ Hz, 3H), 0.61 (d,
$J = 6.8 \text{ Hz, 3H}$, 0.47 (d, $J = 6.8 \text{ Hz, 3H}$), 0.36 (d, $J = 6.8 \text{ Hz, 3H}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.1, 139.7, 135.3, 134.6, 134.0, 133.5, 133.2, 132.5, 129.7, 128.1, 127.8, 127.7, 127.3, 127.0, 126.9, 126.5, 126.1, 125.9, 125.6, 125.5, 124.2, 83.5, 29.1, 29.1, 19.5, 19.2, 19.2, 17.2, 16.6; IR (ATR) ν 2962, 1699, 1456, 1271, 1236, 1124, 947, 827, 750 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{29}$H$_{30}$O$_2$+H$^+$ (M+H$^+$): 411.2319, found: 411.2308; [$\alpha$]$^D_{\text{D}}$ = -5.6 [c 0.815, CH$_2$Cl$_2$, 92% ee (S)].

![Structure](image)

2,4-Dimethylpentan-3-yl 1-(4-methoxy-1-naphthyl)-2-napthoate (3Dd): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.34 (d, $J = 8.4 \text{ Hz, 1H}$), 8.07 (d, $J = 8.8 \text{ Hz, 1H}$), 7.98 (d, $J = 8.4 \text{ Hz, 1H}$), 7.93 (d, $J = 8.0 \text{ Hz, 1H}$), 7.51 (ddd, $J = 8.0 \text{ Hz, 6.0 Hz, 1.6 Hz, 1H}$), 7.42 (ddd, $J = 8.0 \text{ Hz, 6.8 Hz, 1.2 Hz, 1H}$), 7.23-7.32 (m, 4H), 7.17 (d, $J = 8.4 \text{ Hz, 1H}$), 6.91 (d, $J = 8.0 \text{ Hz, 1H}$), 4.55 (t, $J = 6.0 \text{ Hz, 1H}$), 4.08 (s, 3H), 1.53 (sep, $J = 6.8 \text{ Hz, 1H}$), 1.44 (sep, $J = 6.8 \text{ Hz, 1H}$), 0.69 (d, $J = 6.8 \text{ Hz, 3H}$), 0.62 (d, $J = 6.8 \text{ Hz, 3H}$), 0.48 (d, $J = 6.8 \text{ Hz, 3H}$), 0.41 (d, $J = 6.8 \text{ Hz, 3H}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.4, 155.2, 139.3, 134.6, 134.0, 133.7, 130.2, 129.1, 128.1, 127.8, 127.3, 127.2, 126.5, 126.5, 126.3, 126.0, 125.4, 125.0, 122.0, 103.3, 83.5, 55.6, 29.2, 29.2, 19.3, 19.2, 17.2, 16.6; IR (ATR) ν 2924, 1718, 1683, 1558, 1506, 1456, 1236, 1088, 762 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{29}$H$_{30}$O$_2$+H$^+$ (M+H$^+$): 427.2268, found: 427.2260; [$\alpha$]$^D_{\text{D}}$ +1.7 [c 1.870, CH$_2$Cl$_2$, 88% ee (S)].

![Structure](image)

2,4-Dimethylpentan-3-yl 1-(4-fluoro-1-naphthyl)-2-napthoate (3De): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J = 8.4 \text{ Hz, 1H}$), 8.11 (d, $J = 8.8 \text{ Hz, 1H}$), 8.01 (d, $J = 8.4 \text{ Hz, 1H}$), 7.95 (d, $J = 8.0 \text{ Hz, 1H}$), 7.53 (ddd, $J = 8.4 \text{ Hz, 6.8 Hz, 1.2 Hz, 1H}$), 7.50 (ddd, $J = 8.4 \text{ Hz, 6.8 Hz, 1.2 Hz, 1H}$), 7.20-7.32 (m, 6H), 4.56 (t, $J = 6.4 \text{ Hz, 1H}$), 1.53 (sep, $J = 6.8 \text{ Hz, 1H}$), 1.48 (sep, $J = 6.8 \text{ Hz, 1H}$), 0.68 (d, $J = 6.8 \text{ Hz, 3H}$), 0.65 (d, $J = 7.2 \text{ Hz, 3H}$), 0.54 (d, $J = 6.8 \text{ Hz, 3H}$), 0.37 (d, $J =
6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.0, 158.5 ($J_{CF} = 250.1$ Hz), 138.5, 134.7, 134.4 ($J_{CF} = 4.7$ Hz), 133.4, 133.0 ($J_{CF} = 4.6$ Hz), 129.9, 128.2, 127.9, 127.8, 127.5, 127.0, 126.8 ($J_{CF} = 8.5$ Hz), 126.7, 126.4 ($J_{CF} = 2.3$ Hz), 126.1, 126.0 ($J_{CF} = 1.5$ Hz), 123.6 ($J_{CF} = 16.3$ Hz), 120.6 ($J_{CF} = 5.4$ Hz), 108.8 ($J_{CF} = 20.1$ Hz), 83.7, 29.2 (2C), 19.3, 19.2, 17.3, 16.5; IR (ATR) $\nu$ 2966, 1718, 1684, 1558, 1506, 1456, 1246, 1126, 953, 841, 759 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{38}$H$_{30}$O$_2$F+H$^+$ (M+H$^+$): 415.2068, found: 415.2057; $[\alpha]^{30}_D$ = -7.1 [c 1.955, CH$_2$Cl$_2$, 90% ee (S)].

2,4-Dimethylpentan-3-yl 1-(1-pyrenyl)-2-naphthoate (3Df): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (d, $J = 7.6$ Hz, 1H), 8.06-8.23 (m, 6H), 8.01 (d, $J = 7.6$ Hz, 1H), 7.99 (d, $J = 7.6$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 9.2$ Hz, 1H), 7.53 (ddd, $J = 8.4$ Hz, 6.8 Hz, 1.2 Hz, 1H), 7.48 (d, $J = 9.2$ Hz, 1H), 7.23 (ddd, $J = 8.4$ Hz, 6.4 Hz, 1.2 Hz, 1H), 7.12 (dd, $J = 8.4$ Hz, 0.8 Hz, 1H), 4.48 (t, $J = 6.8$ Hz, 1H), 1.41 (sep, $J = 6.8$ Hz, 1H), 1.38 (sep, $J = 6.4$ Hz, 1H), 0.59 (d, $J = 6.8$ Hz, 3H), 0.56 (d, $J = 6.8$ Hz, 3H), 0.45 (d, $J = 6.8$ Hz, 3H), 0.27 (d, $J = 6.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9, 139.8, 134.6, 134.4, 133.5, 131.3, 130.9, 130.8, 129.9, 129.7, 128.1, 128.0, 127.8, 127.4, 127.4 (2C), 127.2, 126.6, 126.0, 125.8, 125.5, 125.0, 124.9, 124.7, 124.6, 83.5, 29.0, 29.0, 19.1, 19.1, 17.0, 16.5; IR (ATR) $\nu$ 2964, 1716, 1699, 1456, 1276, 1186, 847, 750, 721, 667 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{45}$H$_{32}$O$_2$F+H$^+$ (M+H$^+$): 471.2319, found: 471.2307; $[\alpha]^{30}_D$ = -67.1 [c 2.165, CH$_2$Cl$_2$, 95% ee (S)].
2,4-Dimethylpentan-3-yl 1-(2,5-dimethylphenyl)-2-naphthoate (3Dh): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 8.8$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 2H), 7.53 (ddd, $J = 8.4$ Hz, 6.0 Hz, 2.4 Hz, 1H), 7.34-7.41 (m, 2H), 7.19 (d, $J = 7.6$ Hz, 1H), 7.13 (ddd, $J = 8.0$ Hz, 1.6 Hz, 1H), 6.94 (d, $J = 1.2$ Hz, 1H), 4.71 (t, $J = 6.0$ Hz, 1H), 2.31 (s, 3H), 1.93 (s, 3H), 1.78 (sep, $J = 6.8$ Hz, 1H), 1.69 (sep, $J = 6.8$ Hz, 1H), 0.81 (d, $J = 6.8$ Hz, 6H), 0.74 (d, $J = 6.8$ Hz, 3H), 0.73 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 140.8, 138.5, 134.6, 134.6, 133.6, 132.4, 130.3, 129.4, 128.5, 128.3, 127.9, 127.5, 127.4, 127.3, 126.6, 126.0, 83.6, 29.4 (2C), 20.9, 19.5, 19.4, 19.4, 17.4, 17.1; IR (ATR) ν 2962, 1699, 1558, 1464, 1329, 1261, 1234, 1121, 1106, 943, 899, 810, 768 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{26}$H$_{30}$O$_2$+H$^+$ (M+H$^+$): 375.2319, found: 375.2309; [α]$^{29}_{D}$ = −44.6 [c 1.460, CH$_2$Cl$_2$, 96% ee (S)].

2,4-Dimethylpentan-3-yl 1-(2,5-dimethylphenyl)-2-naphthoate (3Di): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 6.4$ Hz, 1H), 7.56 (ddd, $J = 8.4$ Hz, 6.8 Hz, 1.2 Hz, 1H), 7.41 (ddd, $J = 8.4$ Hz, 6.8 Hz, 1.2 Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.26 (dd, $J = 8.4$ Hz, 6.4 Hz, 1H), 7.04 (ddd, $J = 8.4$ Hz, 8.4 Hz, 2.8 Hz, 1H), 6.87 (dd, $J = 9.2$ Hz, 2.8 Hz, 1H), 4.73 (t, $J = 6.4$ Hz, 1H), 1.91 (s, 3H), 1.80 (sep, $J = 6.8$ Hz, 1H), 1.75 (sep, $J = 6.8$ Hz, 1H), 0.84 (d, $J = 6.8$ Hz, 3H), 0.83 (d, $J = 6.8$ Hz, 3H), 0.81 (d, $J = 7.2$ Hz, 3H), 0.75 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.7, 160.9 ($J$$_{CF}$ = 243.1 Hz), 140.5 ($J$$_{CF}$ = 7.8 Hz), 139.5, 134.7, 132.4 ($J$$_{CF}$ = 3.1 Hz), 132.0, 130.8 ($J$$_{CF}$ = 8.5 Hz), 128.2, 128.0, 127.9, 127.6, 127.1, 126.9, 126.0, 116.5 ($J$$_{CF}$ = 20.9 Hz), 114.2 ($J$$_{CF}$ = 20.9 Hz), 83.8, 29.4, 29.4, 19.4 (2C), 19.1, 17.4, 17.2; IR (ATR) ν 2924, 1717, 1558, 1488, 1254, 1130, 951.
889, 804, 760 cm\(^{-1}\); HRMS (ESI) \(m/z\) calcd for \(\text{C}_{28}\text{H}_{33}\text{FO}_{2}\text{H}^+\) (M+H\(^+\)): 379.2068, found: 379.2059; \([\alpha]_D^{28} = -37.5\) [c 1.705, \(\text{CH}_2\text{Cl}_2\), 93% ee (S)].

\[
\begin{align*}
\text{(2,4-Dimethylpentan-3-yl 1-(4-fluoro-2-methylphenyl)-2-naphthoate (3Dj):} & \quad \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \ \delta 8.01 \ (d, J = 8.8 \text{ Hz, 1H}), 7.92 \ (d, J = 8.4 \text{ Hz, 1H}), 7.91 \ (d, J = 8.4 \text{ Hz, 1H}), 7.55 \ (\text{ddd, } J = 8.0 \text{ Hz, 6.8 Hz, 1.2 Hz, 1H}), 7.42 \ (\text{ddd, } J = 8.4 \text{ Hz, 6.8 Hz, 1.2 Hz, 1H}), 7.31 \ (\text{dd, } J = 8.0 \text{ Hz, 0.4 Hz, 1H}), 7.08 \ (\text{dd, } J = 8.4 \text{ Hz, 6.0 Hz, 1H}), 7.04 \ (\text{dd, } J = 9.6 \text{ Hz, 2.4 Hz, 1H}), 6.96 \ (\text{ddd, } J = 8.8 \text{ Hz, 8.8 Hz, 2.4 Hz, 1H}), 4.72 \ (t, J = 6.4 \text{ Hz, 1H}), 1.96 \ (s, 3H), 1.83 \ (\text{sep, } J = 6.8 \text{ Hz, 1H}), 1.77 \ (\text{sep, } J = 6.8 \text{ Hz, 1H}), 0.83 \ (d, J = 6.8 \text{ Hz, 6H}), 0.77 \ (d, J = 6.8 \text{ Hz, 3H}), 0.77 \ (d, J = 6.8 \text{ Hz, 3H}); \quad \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \ \delta 167.9, 162.3 \ (J_{\text{CF}} = 243.9 \text{ Hz}), 139.6, 139.2 \ (J_{\text{CF}} = 7.7 \text{ Hz}), 134.7, 134.5 \ (J_{\text{CF}} = 3.1 \text{ Hz}), 132.5, 130.9 \ (J_{\text{CF}} = 7.7 \text{ Hz}), 128.8, 128.0, 127.8, 127.4, 127.1, 126.8, 125.9, 116.3 \ (J_{\text{CF}} = 20.9 \text{ Hz}), 112.2 \ (J_{\text{CF}} = 20.9 \text{ Hz}), 83.7, 29.4 \ (2\text{C}), 20.1, 19.4, 19.4, 17.4, 17.2; \quad \text{IR (ATR) } \nu = 2923, 1684, 1558, 1506, 1456, 1329, 1238, 1110, 895, 770 \text{ cm}^{-1}; \quad \text{HRMS (ESI)} \ \text{m/z calcd for } \text{C}_{28}\text{H}_{33}\text{FO}_{2}\text{H}^+ \ (\text{M}+\text{H}^+) \ : 379.2068, \text{ found: 379.2060; } \ [\alpha]_D^{28} \ = \ -34.1 \ [c \ 1.730, \text{CH}_2\text{Cl}_2, 87\% \text{ ee (S)}].
\end{align*}
\]

\[
2,4\text{-Dimethylpentan-3-yl 1-(3-methoxy-2-methylphenyl)-2-naphthoate (3Dk):} \quad \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \ \delta 8.01 \ (d, J = 8.8 \text{ Hz, 1H}), 7.90 \ (d, J = 10.8 \text{ Hz, 1H}), 7.90 \ (d, J = 6.0 \text{ Hz, 1H}), 7.53 \ (\text{ddd, } J = 8.0 \text{ Hz, 5.2 Hz, 3.2 Hz, 1H}), 7.36\text{-}7.38 \ (m, 2H), 7.21 \ (\text{dd, } J = 8.4 \text{ Hz, 8.0 Hz, 1H}), 6.92 \ (d, J = 8.0 \text{ Hz, 1H}), 6.76 \ (\text{dd, } J = 7.6 \text{ Hz, 0.8 Hz, 1H}), 4.71 \ (t, J = 6.0 \text{ Hz, 1H}), 3.90 \ (s, 3H), 1.83 \ (s, 3H), 1.79 \ (\text{sep, } J = 6.8 \text{ Hz, 1H}), 1.71 \ (\text{sep, } J = 6.8 \text{ Hz, 1H}), 0.82 \ (d, J = 6.8 \text{ Hz, 3H}), 0.79 \ (d, J = 6.8 \text{ Hz, 3H}), 0.74 \ (d, J = 6.8 \text{ Hz, 3H}), 0.73 \ (d, J = 6.8 \text{ Hz, 3H}); \quad \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \ \delta 168.1, 157.5, 140.6, 139.9, 134.6, 132.5, 128.3, 127.8, 127.6, 127.4, 127.3, 126.6, 125.9, 125.8, 125.5, 122.2, 109.2, 83.5, 55.4, 29.4, 29.3, 19.4, 19.4, 17.4, 17.1, 13.0; \quad \text{IR (ATR) } \nu = 2960, 1730, 1684, 1653, 1558, 1456, 1242, 1126, 1088, 945, 835, 775 \text{ cm}^{-1}; \quad \text{HRMS}
\]

S18
(ESI) m/z calcd for C_{26}H_{30}O_3+H^+ (M+H^+): 391.2268, found: 391.2257; [α]^{29}_D −33.7 [c 1.725, CH_{2}Cl_{2}, 91% ee (S)].

[1-(2,3-dimethylphenyl)naphthalen-2-yl]methanol (4): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8.8$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.46 (ddd, $J = 8.0$ Hz, 6.8 Hz, 1.6 Hz, 1H), 7.35 (ddd, $J = 8.4$ Hz, 6.8 Hz, 1.2 Hz, 1H), 7.26-7.30 (m, 2H), 7.21 (ddd, $J = 7.6$ Hz, 7.2 Hz, 1H), 7.00 (d, $J = 7.2$ Hz, 1H), 4.50 (s, 2H), 2.39 (s, 3H), 1.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.8, 137.6, 137.2, 135.5, 135.4, 132.9, 132.5, 129.3, 127.9, 127.8, 127.7, 126.3, 126.1, 125.7, 125.7, 125.6, 63.5, 20.5, 16.4; IR (ATR) ν 3192, 2923, 2362, 1446, 1068, 1014, 827, 815, 744, 723 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{19}$H$_{18}$O$^+$ (M+Na$^+$): 285.1250, found: 285.1243; [α]^{24}_D −49.6 [c 1.040, CH$_2$Cl$_2$, 96% ee (S)].

1-(2,3-dimethylphenyl)-2-naphthoic acid (5): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, $J = 8.8$ Hz, 1H), 7.91 (d, $J = 8.8$ Hz, 2H), 7.56 (ddd, $J = 10.0$ Hz, 8.0 Hz, 1.6 Hz, 1H), 7.34-7.41 (m, 2H), 7.25 (d, $J = 8.8$ Hz, 1H), 7.17 (dd, $J = 8.0$ Hz, 7.2 Hz, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 2.38 (s, 3H), 1.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.5, 143.1, 138.1, 136.5, 135.3, 135.2, 132.6, 129.3, 127.9, 127.9, 127.5, 127.1, 126.7, 126.2, 126.1, 125.1, 20.4, 16.5; IR (ATR) ν 2924, 2359, 1695, 1666, 1558, 1288, 939, 773 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{19}$H$_{18}$O$_2$−H$^-$ (M−H$^-$): 275.1078, found: 275.1082; [α]^{25}_D −48.0 [c 0.695, CH$_2$Cl$_2$, 97% ee (S)].
3. Determination of the Enantiomeric Excesses of the Products by HPLC or SFC with a Chiral Stationary Phase

**Table S1.** SFC separation conditions and retention times of products

<table>
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<tr>
<th>entry</th>
<th>Compound</th>
<th>column</th>
<th>Eluent</th>
<th>Flow rate (mL/min)</th>
<th>$t_R$ of (R)-isomer (min)</th>
<th>$t_R$ of (S)-isomer (min)</th>
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<td><img src="image" alt="3Aa" /></td>
<td>AD-H</td>
<td>i-PrOH/CO$_2$ 1/20</td>
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<td>11.5</td>
<td>13.7</td>
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<tr>
<td>2</td>
<td><img src="image" alt="3Ba" /></td>
<td>AD-H</td>
<td>i-PrOH/CO$_2$ 1/10</td>
<td>3.3</td>
<td>5.3</td>
<td>6.7</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="3Ca" /></td>
<td>AD-H</td>
<td>i-PrOH/CO$_2$ 1/10</td>
<td>3.3</td>
<td>6.3</td>
<td>7.1</td>
</tr>
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<td><img src="image" alt="3Ha" /></td>
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<td>5.6</td>
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<td>Solvent</td>
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<td>$t_{1/4}$</td>
<td>$t_{1/10}$</td>
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<td>tR (min)</td>
<td>k'</td>
<td>RSD (%)</td>
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<sup>a</sup> Determined by chiral HPLC.
SFC trace for 3Aa
SFC trace for 3Ba

S24
SFC trace for **3Ca**
SFC trace for 3Da
SFC trace for 3Ea
SFC trace for 3Fa
SFC trace for 3Ga
SFC trace for 3Ha
SFC trace for 31a
SFC trace for 3Ja
SFC trace for 3Db
SFC trace for 3De
SFC trace for 3Dd
SFC trace for 3De
SFC trace for (S)-3Df
SFC trace for 3Dg
SFC trace for 3Dh
SFC trace for 3Di
SFC trace for 3Dj
SFC trace for 3Dj (after single recrystallization)
SFC trace for 3Dk
クロマトグラム情報
ユーザー名: JASCO
更新日時: 2014/10/07 18:22:05
システム: JASCO SFC
測定日: 2014/10/07 18:01:54
流量: 1.00 (μL)
サンプル/分: 25
プロンプト名: Akai
分析時間: 14.6 (min)
測定ソース: PDA
溶媒: MeOH, 15min, 220nm

ピーク情報

<table>
<thead>
<tr>
<th>ピーク</th>
<th>流速 (μL/分)</th>
<th>頻度 (μL/分)</th>
<th>質量 %</th>
<th>定義値</th>
<th>反応時間</th>
<th>位置</th>
<th>HTR</th>
<th>分離度</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st peak</td>
<td>0.01</td>
<td>150444</td>
<td>120186</td>
<td>98.13%</td>
<td>58.27%</td>
<td>N/A</td>
<td>16.80</td>
<td>3.22</td>
</tr>
<tr>
<td>2nd peak</td>
<td>3.01</td>
<td>22124</td>
<td>2196</td>
<td>1.86%</td>
<td>1.72%</td>
<td>N/A</td>
<td>56.46</td>
<td>N/A</td>
</tr>
</tbody>
</table>

SFC trace for 4Dg

S45
SFC trace for 5Dg
SFC trace for S1
SFC trace for S2
4. References


     Capacci, A. G.; Wei, X.; Zhang, Y.; Gao, J. J.; Li, W.; Rodriguez, S.; Lu, B. Z.; Yee, N. K.;
5. NMR Spectra and GPC Chart of New Compounds

$^1$H NMR of compound 1A
$^{13}$C NMR of compound 1A
$^1$H NMR of compound 1B
$^{13}$C NMR of compound 1B
$^{1}$H NMR of compound 1C
$^{13}$C NMR of compound 1C
$^1$H NMR of compound 1D
$^{13}$C NMR of compound 1D
S

1H NMR of compound IE
$^{13}$C NMR of compound 1E
$^1$H NMR of compound 1F
$^{13}$C NMR of compound 1F
$^1$H NMR of compound 1G
$^{13}$C NMR of compound 1G
¹H NMR of compound 1H
$^{13}$C NMR of compound 1H
$^1$H NMR of compound 11

S66
$^1$C NMR of compound 11
S68

H NMR of compound 1J

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

400-MHz-nova

Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (x2q1)

Solvent: deuterium

Data collected on: Mar 6 2014

Operator: wwl

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions

1H NMR of compound 1J

ppm

8 9 1 2 3 4 5 6

1.97 2.84 0.92 1.33 0.94

7.15 7.23 7.57 7.64 7.77 7.83 7.94 8.14 8.20

0.59 1.70 1.72 1.73 1.73 1.74 1.74 1.75 1.75

6.00
$^{13}$C NMR of compound 1J
$^1$H NMR of compound 3Aa
$^{13}$C NMR of compound 3Aa

**STANDARD CARBON PARAMETERS**

Sample Name:
Data Collected on: 4/04/2010
Archive directory:
Sample directory:
File: CARM
Pulse Sequence: CARBON (x2pul)
Solvent: d6-dil
Data collected on: Sep 15 2014

Operator: vml

Relax. delay 0.715 sec
Pulse 45.0 degrees
Amp. time 1.285 sec
Width 25510.3 Hz
64 repetitions

OBSERVE C13, 100.607944 MHz
DECOUPLE X, 399.8855244 MHz
Power 42 dB
continuously on
WALKE-1d modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min

[Graph showing carbon NMR spectrum]
$^1$H NMR of compound 3Ba
$^{13}$C NMR of compound 3Ba
\[ HNMR \text{ of compound 3Ca} \]
$^{13}$C NMR of compound 3Ca
$^1$H NMR of compound 3Da
$^{13}$C NMR of compound 3Da
$^1$H NMR of compound 3Ea
$^{13}$C NMR of compound 3Ea
$^1$H NMR of compound 3Fα
$^{13}$C NMR of compound 3Fa
$^1$H NMR of compound 3Ga
$^{13}$C NMR of compound 3Ga

Sample Name:
Data Collected on: 400 MHz
Archive directory:
Sample directory:
Filename: CARBON
Pulse Sequence: CARBON (2pz1l)
Solvent: CDCl3
Data collected on: Sep 18 2014
Operator: vornl

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.395 sec
Width 288510.2 Hz
26 repetitions

RESENSE: 0.1, 100.550795 Hz
DECOUPL: 2.1, 399.855346 Hz
Power 63 dB
continuously on
WALTZ-16 modulated

Data Processing
Line broadening: 1.0 Hz
FT size 49550
Total time 17 min
$^1$H NMR of compound 3Ha
$^{13}$C NMR of compound 3Ha
$^1$H NMR of compound 31a
$^{13}$C NMR of compound 31a
S88

\(^1\text{H NMR of compound 3Ja}\)
$^{13}$C NMR of compound 3Ja
$^1$H NMR of compound 3Db
$^{13}$C NMR of compound 3Db
$^1$H NMR of compound 3Dc
$^{13}$C NMR of compound 3Dc
H NMR of compound 3Dd
**STANDARD CARBON PARAMETERS**

- **Sample Name:**
- **Data Collected on:** 450-MD-2011-09-15
- **Archive directory:**
- **Sample directory:**
- **File:** C2H12

**Pulse Sequence:** C2H12 [1p1]

**Solvent:** 1:1:1

**Data collected on:** Sep 15 2014

**Operator:** venki

- **Relax. delay 0.715 sec**
- **Pulse 45.0 degrees**
- **Ang. time 1.285 sec**
- **Width 25.0 Hz**
- **128 repetitions**
- **OBSERVE 115.1, 100.5007943 MHz**
- **DECOUPLE 115.1, 399.8855346 MHz**
- **Power 4.5 dB**

**continuously on**

**WALTHER modulated**

**DATA PROCESSING**

- **Line Broadening 1.0 Hz**
- **FT size 60526**
- **Total time 17 min**

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**13C NMR of compound 3Dd**

![13C NMR spectrum of compound 3Dd](image)
$^1$H NMR of compound 3De

S96
$^{13}$C NMR of compound 3De
$^1$H NMR of compound 3Df
$^{13}$C NMR of compound 3DF

STANDARD CARBON PARAMETERS

Sample Name: L935

Data Collected on: 400-MHz-vona400

Archive directory: 

Sample directory: 

File: CANNON

Pulse Sequence: CARNON (x2qul)

Solvent: caimj

Data collected on: Jul 30 2014

File: CANNON

Pulse Sequence: CARNON (x2qul)

Solvent: caimj

Data collected on: Jul 30 2014
$^1$H NMR of compound 3Dg
$^{13}$C NMR of compound 3Dh
$^1$H NMR of compound 3Di
$^{13}$C NMR of compound 3Di
$^1$H NMR of compound 3Dj
$^{13}$C NMR of compound 3Dj
$^1$H NMR of compound 3Dk
$\text{C NMR of compound 3Dk}$
$^1$H NMR of compound 4Dg
$^{13}$C NMR of compound 4Dg
$^1$H NMR of compound 5Dg
C NMR of compound SDG

STANDARD CARBON PARAMETERS

Sample Name:
Data Collected on:
ECD-MS-micro400
Archive directory:

FidFile: CARBON
Pulse Sequence: CARBON (x2pi1)
Solvent: ch13
Data collected on: Oct 3 2014

Operator: vxt1
Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25310.2 Hz
320 repetitions

OBSERVE C13, 100.550874 MHz
DECOUPLING H1, 395.885555 MHz
Power 45 dB
continuously on

MULTI-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 10 hr

220 200 180 160 140 120 -100 80 60 40 20 0 ppm