Electronic Supplementary Material (ESI) for Chemical Communications.

Iron-Catalysed Enantioconvergent Suzuki-Miyaura Cross-Coupling to Afford Enantioenriched 1,1-Diarylalkanes

Chet C. Tyrol, Nang S. Yone, Connor F. Gallin, Jeffery A. Byers*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States

General Considerations. Unless stated otherwise, all reactions were carried out in oven-dried glassware in a nitrogen-filled glovebox or using standard Schlenk-line techniques.[1] Solvents including dichloromethane, pentane, toluene, diethyl ether, and tetrahydrofuran were purified by passage through two activated alumina columns under a blanket of argon and then degassed by brief exposure to vacuum.[2] Phenylboronic acid, 2-naphthaleneboronic acid, 4-methoxyphenylboronic acid, *p*-*t*Bu-phenylboronic acid, *p*-tolylboronic acid and 4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane were bought from Oakwood

Chemicals and dried over P_2O_5 followed by passage through an alumina plug in the glovebox before use. All prepared boronic pinacol esters were used after passage through alumina under a nitrogen atmosphere. Methylethyl amine was purchased from TCI America. Lithium dimethylamide and 2,3-dimethyl-2,3-butanediol were purchased from Alfa and used without further purification. Anhydrous iron (II) chloride was purchased from Sigma Aldrich and used without further purification. Bis(oxazoline) ligand (4*S*)-(+)-Phenyl-α-[(4*S*)-phenyloxazolidin-2-ylidene]-2-oxazoline-2-acetonitrile was purchased from Sigma-Aldrich and dried over P_2O_5 before use in the glovebox. All alkyl halides were purchased from Sigma-Aldrich, Oakwood Chemicals and Fisher Scientific. Liquid alkyl halides were dried over calcium hydride for at least 24 hours before being vacuum-distilled, while all solids were dried over P_2O_5 before use in the glovebox. ^1H, ^{11}B and $\{^1H\}^{13}C$, nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on Varian VNMRS operating at 400 MHz, 500 MHz, or 600 MHz for ^1H NMR, at 160 MHz for ^{11}B NMR and 125 MHz for $\{^1H\}^{13}C$. All $\{^1H\}^{13}C$ NMR was collected while broad-band decoupling was applied to the ^1H region. The residual protio solvent impurity was used as an internal reference for ^1H NMR spectra and $\{^1H\}^{13}C$ NMR spectra. Boron trifluoride diethyl etherate was used as an external standard ($BF_3{\cdot}O(C_2H_5)_2$: 0.0 ppm) for ^{11}B NMR. The line listing for NMR spectra of diamagnetic compounds are reported as follows: chemical shift (multiplicity, coupling constant, integration) while paramagnetic compounds are reported as chemical shift (peak width at half height, number of protons). Solvent suppressed spectra were collected for paramagnetic compounds in protio THF using the PRESAT macro on the VNMR software. Infrared (IR) spectra were recorded on a Bruker Alpha attenuated total reflectance infrared spectrometer. High-resolution mass spectra were obtained at the Boston College Mass Spectrometry Facility on a JEOL AccuTOF DART instrument. Enantiomeric ratios were determined by HPLC analysis (high-performance liquid chromatography) with an Agilent 1200 series instrument with Chiral Technologies Chiralcel OD-H (4.6 x 250 mm), Chiral Technologies Chiralcel OJ-H (4.6 x 250 mm) or Chiral Technologies Chiralcel IC (4.6 x 250 mm) columns

eluting with HPLC grade hexanes and isopropyl alcohol. Racemic samples were prepared using a 1:1 mixture of the (*R*),(*R*)-CN-BOX^{Ph}FeCl and (*S*),(*S*)-CN-BOX^{Ph}FeCl complexes which led to some discrepancies in obtaining purely racemic HPLC traces. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Synthetic Procedures:

Synthesis of cyano-bis(oxazoline) ligands.

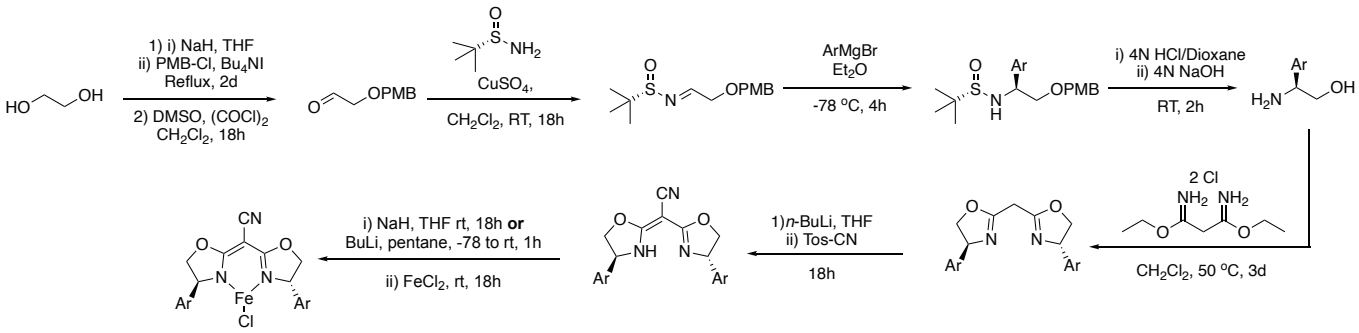


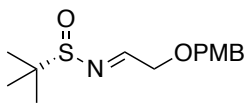
Figure S1. Synthesis of cyano-bis(oxazoline) ligands and cyano-bisoxazoline iron chloride complexes.

Synthesis of 2-(4-methoxybenzyloxy)ethanol. To an oven-dried 500 mL, two-neck flask with reflux condenser and stir bar under a N_2 atmosphere was added anhydrous tetrahydrofuran (100 mL). Sodium hydride (3.92 g, 98.0 mmol, 60% in mineral oil.) was added followed by dropwise addition of ethylene glycol (9.01 mL, 161.1 mmol) at which point the reaction effervesced. After 30 minutes, 4-methoxybenzyl chloride (7.24 mL, 53.6 mmol) and tetrabutylammonium iodide (1.96 g, 53.6 mmol) were added. The reaction was brought to reflux and allowed to stir for 18 hours. The reaction was quenched with saturated NH_4Cl (aq) (65 mL). The collected aqueous layers were extracted with ethyl acetate (50 mL x 3) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture

was purified by silica gel column chromatography (1:1 EtOAc/Hex) to yield a yellow oil (6.94 g, 71%) (R_f = 0.3, 1:1 EtOAc/Hex); ^{1}H NMR (500MHz, $CDCl_3$) δ 3.56-3.59 (m, 2H), 3,73-3.76 (m, 2H), 3.81 (s, 3H), 4.50 (s, 2H), 6.87-6.89 (d, *J* = 8.7 Hz, 2H), 7.25-7.29 (d, *J* = 8.4 Hz, 2H) ppm. Spectral data are in accordance with the literature.[3]

Synthesis of 2-4(4-methoxybenzyloxy)acetaldehyde. To an oven-dried 1 L , three-neck flask with stir bar under a N_2 atmosphere was added anhydrous dichloromethane (350 mL) and oxalyl chloride (5.95 mL, 68.4 mmol). The flask was brought to -78°C in a dry ice acetone bath and DMSO (9.39 mL, 132.0 mmol) was added dropwise. The reaction was allowed to stir for 30 minutes before dropwise addition of PMB-protected alcohol solution in CH_2Cl_2 (9.82 g, 53.9 mmol). After three hours at -78°C was added triethylamine (36.1 mL, 259 mmol). The reaction was allowed to slowly warm to room temperature and was stirred overnight. The reaction was quenched with deionized H_2O (240 mL). The collected aqueous layers were extracted with dichloromethane (3 x 400 mL) and washed with 400 mL 1M HCl and 400 mL saturated $NaHCO_3$ (aq). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* The crude mixture was purified by silica gel column chromatography (1:3 EtOAc/Hex) to yield a clear oil (12.78 g, 85%) R_f = 0.40 (1:1 EtOAc/Hex); ^{1}H NMR (500MHz, $CDCl_3$) δ 3.81 (s, 3H), 4.07 (s, 2H), 6.88-6.91 (d, *J* = 8.6 Hz, 2H), 7.27-7.31 (d, *J* = 8.6 Hz, 2H), 9.70 (t, *J* = 0.9 Hz, 1H) ppm. Spectral data are in accordance with the literature.[3]

Synthesis of (S,E)-N-(2-(4-methoxylbenzyloxy)ethylidene)-2-methylpropane-2-sulfinamide, To an oven-dried 100 mL two-neck flask



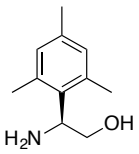
with stir bar under a N_2 atmosphere was added anhydrous dichloromethane (55 mL), (*S*)-2-methylpropane-2-sulfinamide (3.26 g, 26.9 mmol), aldehyde (4.4 g, 24.4 mmol) and anhydrous copper sulfate (5.25 g, 32.9 mmol). The reaction immediately turned light green and was allowed to stir overnight. The reaction was filtered though a plug of celite and washed with excess dichloromethane. The solvent was removed *in vacuo* and crude mixture purified by silica gel

column chromatography (35% EtOAc/Hex) to yield a light-yellow oil (5.83 g, 84%). R_f = 0.45 (35% EtOAc/Hex);[1]H NMR (500MHz, $CDCl_3$) δ 8.12 (t, J = 3.18 Hz, 1 H), 7.27-7.30 (d, *J* = 8.6 Hz, 2H), 6.88-6.91 (d, *J* = 8.6 Hz, 2H), 4.57 (s, 2H), 4.37 (dd, J = 3.51, 1.49 Hz, 2H), 3.81 (s, 3H, 1.22 (s, 9H) ppm. Spectral data are in accordance with the literature.[4]

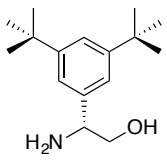
Synthesis of (*S)-N-(S)-mesityl-2(4-methoxybenzyloxy)ethyl)-2-methylpropane-2-sulfinamine.* To an oven-dried 50 mL, two-neck flask with reflux condenser and stir bar under a N_2 atmosphere was added anhydrous diethyl ether (36 mL), magnesium (1.22 g, 50.2 mmol) and mesityl bromide (5.67 mL, 37.6 mmol). The flask was brought to reflux at 90 ºC and allowed to stir for 3 hours at which point a brown-orange solution formed. To a new oven-dried 250 mL, two-neck flask with reflux condenser and stir bar under a N_2 atmosphere was added anhydrous toluene (21 mL) and (*S*,E)-N-(2-(4-methoxylbenzyloxy)ethylidene)-2-methylpropane-2-sulfinamide (3.18 g, 12.5 mmol). The flask was brought to -78 ºC in a dry ice acetone bath before dropwise addition of the Grignard solution. After complete addition, the solution was allowed to stir at -78 ºC for 2 hours. The reaction was quenched with saturated NH_4Cl (aq) and the collected aqueous layers were extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* The viscous oil was filtered through a plug of celite, eluting with hexanes to remove the protodemetalated Grignard reagents and then filtered with 40% EtOAc:Hex to collect sulfonamine as a yellow oil. R_f = 0.1 (40:60 EtOAc/Hex); [1]H NMR (500MHz, $CDCl_3$) δ 1.19 (s, 9H), 2.23 (s, 6H), 2.28 (s, 3H), 3.51 (dd, J = 10.0, 5.0 Hz, 1H), 3.81 (s, 3H), 3.95 (t, *J* = 10.3 Hz, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.56 (AB_q, *J* = 11.6 Hz, 2H), 5.12 (ddd, *J* = 10.5, 4.1, 1.2 Hz, 1H), 6.81 (s, 2H), 6.87 (d, 2H, J = 8.4 Hz), 7.26 (d, 2H, J = 8.8 Hz) ppm. Spectral data are in accordance with the literature.[5]

General procedure for synthesis of amino alcohols: To an oven-dried 250 mL, two-neck flask with stir bar under a N_2 atmosphere was added anhydrous methanol (50 mL) and sulfonamine (9.26 mmol, 1 equiv.). 4M HCl in dioxane (43.52 mL, 174 mmol) was added dropwise and the reaction was allowed to stir for 1 hour with tracking by TLC analysis (10% MeOH:CH_2Cl_2). The reaction mixture was concentrated *in vacuo.* The crude oil was passed through a silica gel plug, eluting with 50% EtOAc/Hex to eliminate sulfur impurities, followed by 10% MeOH: CH_2Cl_2 to elute product. The product was concentrated *in vacuo*. The crude amine (9.26 mmol, 1 equiv.) was dissolved in anhydrous methanol (19.31 mL) and 10% Pd/C (2.26 g, 2.1 mmol) and 4M HCl in dioxane (20 mL, 80 mmol) were added. The N_2 atmosphere was replaced with a H_2 balloon and the reaction was allowed to stir for 24 hours. Upon completion, the reaction was filtered through a plug of celite with EtOAc and solvent was removed *in vacuo*. The concentrate was dissolved in 80 mL of EtOAc and added to 80 mL of 4M NaOH and allowed to stir for 20 minutes. The collected aqueous layers were extracted with (3 x 30 mL) ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield a white or yellow solid which could be further purified if necessary by silica gel column chromatography (10% MeOH:CH_2Cl_2).

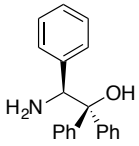
(*S*)-2-amino-2-mesitylethanol was synthesized according to the general procedure using (*S*)-N-(*S*)-mesityl-2(4-methoxybenzyloxy)ethyl)-2-methylpropane-2-sulfinamine (3.46 g, 9.26 mmol) which afforded a white, crystalline solid (1.2 g, 75%). R_f = 0.1 (10% MeOH/CH_2Cl_2); ^{1}H NMR (500MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.40 (s, 6H), 3.62 (dd, *J* = 10.7, 5.2 Hz, 1H), 3.82 (t, *J* = 12 Hz, 1H), 4.47 (dd, *J* = 10.0, 5.2 Hz, 1H), 6.83 (s, 2H) ppm. Spectral data are in accordance with the literature.[5]



(*S*)-2-amino-2-3,5-di-tert-butylphenylethanol was synthesized according to the general procedure using (*S*)-N-(*S*)-3,5-di-*t*ert-butylphenyl-2(4-methoxybenzyloxy)ethyl)-2-methylpropane-2-sulfinamine (2.83 g, 5.97 mmol) which afforded a white, crystalline solid (1.21 g, 81%). R_f = 0.1 (10% MeOH/CH_2Cl_2); ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 2.0 Hz 1H), 7.16 (d, J = 1.9 Hz, 2H), 4.03 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.75 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.56 (dd, *J* = 10.7, 8.4 Hz, 1H), 1.58 (s, 2H), 1.33 (s, 18H) ppm. Spectral data are in accordance with the literature.[6]



(*S*)-2-amino-2-1,1,2-triphenylethanol. To an oven-dried 250 mL, two-neck flask with reflux condenser and stir bar under a N_2 atmosphere was added bromo(phenyl)magnesium (3 M, 16.53 mL) in diethyl ether (90 mL). The flask was cooled to 0 ºC before batchwise addition of (*S*)-2-phenylglycine methyl ester hydrochloride (2 g, 9.92 mmol) over 10 minutes. The reaction was brought to reflux and allowed to stir for 24 hours.The reaction was cooled to room temperature and quenched with deionized H_2O (30 mL). The collected aqueous layers were extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield a pure yellow-white solid which was recrystallized from hot methanol (1.52 g, 5.25 mmol, 52.96% yield). R_f = 0.1 (10% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59 (bs , 2H), 4.65 (s, 1H), 5.00 (s, 1H), 6.95 – 7.06 (m, 3H), 7.07 – 7.16 (m, 7H), 7.27 (t, *J* = 7.5 Hz 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 2H) ppm. Spectral data are in accordance with the literature.[7]



General procedure for synthesis of bisoxazolines: To an oven-dried 50 mL, two-neck flask with stir bar under a N_2 atmosphere was added anhydrous CH_2Cl_2 (4 mL) and diethyl malonimidate dihydrochloride (1.19 mmol) and the flask was cooled to 0 ºC. Amino alcohol (2.38 mmol) was added and the reaction was allowed to stir at room temperature for 3 days. After this time the reaction was quenched with ice water (30 mL). The collected aqueous layers were

extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield a crude yellow oil which was further purified by silica gel column chromatography (1-10% MeOH/CH_2Cl_2). Product was collected as a yellow/orange oil.

2,2-Methylene-[(4S)-mesityl-2-oxazoline] was synthesized according to the general procedure using malonimidate dihydrochloride (275 mg, 1.19 mmol) and (*R*)-2-amino-2-(mesitylphenyl)ethanol (427 mg, 2.38 mmol) to afford a yellow/orange oil (200 mg, 43%). R_f = 0.5 (10% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.29 (s, 6H), 3.49 (s, 2H), 4.17 (dd, J = 9.4, 1.39 Hz, 2H), 4.63 (dd, J = 9.89, 3.18Hz, 2H), 5.66 (t, J = 10.9, 2H), 6.82 (s, 4H) ppm. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{25}H_{30}N_2O_2$ 390.57; found 390.24.

2,2-methylene-[(4R)-3,5-t-Butylphenyl-2-oxazoline] was synthesized according to the general procedure using malonimidate dihydrochloride (557 mg, 2.41 mmol) and (*R*)-2-amino-2-(3,5-di-tertbutylphenyl)ethanol (1.21 g, 4.85 mmol) to afford a yellow/orange oil (840 mg, 82%). R_f = 0.5 (10% MeOH/CH_2Cl_2) ^{1}H NMR (500MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.11 (d, J = 3.6 Hz, 4H), 5.21 (t, J = 8.9 Hz, 2H), 4.67 (dd, J = 9.8, 3.8 Hz, 2H), 4.25 (dd, J = 8.0, 4.6 Hz, 2H), 3.61 (s, 2H), 1.29 (s, 36H) ppm. Spectral data are in accordance with the literature.[6]

2,2-Methylene-[(4S)-benzyl-2-oxazoline] was synthesized according to the general procedure using malonimidate dihydrochloride (8.44 g, 36.5 mmol) and (*R*)-2-amino-2-(benzyl)ethanol (11.03 g, 73.0 mmol) to afford an off-white solid (10.0 g, 81%). R_f =0.4 (10% MeOH/CH_2Cl_2); ^{1H} NMR (500MHz, $CDCl_3$) δ 2.68 (dd, *J* = 13.9, 8.6 Hz, 2H), 3.12 (dd, *J* = 13.8,

5.4 Hz, 2H), 3.32 (t, *J* = 1.1 Hz, 2H), 4.02 (dd, *J* = 8.5, 7.2 Hz, 2H), 4.24 (dd, *J* = 9.4, 8.5 Hz, 2H), 4.40 – 4.49 (m, 2H), 7.20 – 7.24 (m, 6H), 7.30 (tt, *J* = 7.1, 1.0 Hz, 4H) ppm. Spectral data are in accordance with the literature.[8]

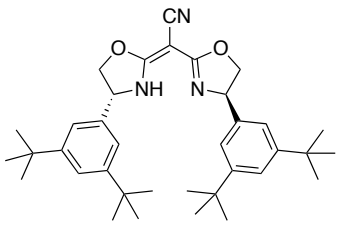
2,2-Methylene-[(4S)-isopropyl-2-oxazoline] was synthesized according to the general procedure using malonimidate dihydrochloride (1.25 g, 5.4 mmol) and (*R*)-2-amino-2-(isopropyl)ethanol (1.12 g, 10.8 mmol) to afford an off-white solid (865 mg, 83%). R_f =0.35 (10% MeOH/CH_2Cl_2); ^{1}H NMR (500MHz, $CDCl_3$) δ 0.87 (d, *J* = 6.8 Hz, 6H), 0.94 (d, *J* = 6.8 Hz, 6H), 1.75 (dp, *J* = 14.1, 7.4, 7.0 Hz, 2H), 3.33 (d, *J* = 2.3 Hz, 2H), 3.33 (s, 2H), 3.89 – 4.02 (m, 2H), 4.26 (dd, *J* = 9.6, 8.3 Hz, 2H) ppm. Spectral data are in accordance with the literature.[9]

***2,2'-Methylenebis*[*(4S)-4,5,5-triphenyl-2- oxazoline*]** was synthesized according to the general procedure using malonimidate dihydrochloride (599 mg, 2.59 mmol) and (*R*)-2-amino-2-(isopropyl)ethanol (1.5 g, 5.18 mmol) to afford a yellow solid (891 mg, 59%). R_f =0.25 (10% MeOH/CH_2Cl_2); ^{1}H NMR (500MHz, $CDCl_3$) δ 3.91 (s, 2H), 6.05 (s, 2H), 7.04−6.88 (m, 16H), 7.12−7.10 (m, 4H), 7.34 (t, *J* = 6.95 Hz, 2H), 7.40 (dd, *J* = 7.25, 6.95 Hz, 4H), 7.68 (d, *J* = 7.25 Hz, 4H). Spectral data are in accordance with the literature.[10]

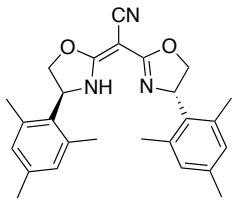
General procedure for synthesis of cyanobis(oxazolines): To an oven-dried 25 mL, two-neck flask with stir bar under a N_2 atmosphere was added anhydrous tetrahydrofuran (4 mL) and bisoxazoline (0.46 mmol). The flask was cooled to -78 ºC and *n*BuLi in Hexanes (2.6 M, 0.18 mL, 0.46 mmol) was added dropwise to the flask followed by TMEDA (0.067 mL, 0.46 mmol). The reaction was allowed to stir at -78 ºC down for 1 hour before dropwise addition of a tosyl cyanide (80 mg, 0.46 mmol) solution in THF (1 mL). After stirring at room temperature

overnight the reaction was quenched with saturated NH_4Cl (aq) (20 mL) and the reaction was stirred for an additional 5 minutes before separating the layers. The collected aqueous layers were extracted with Et_2O (3 x 30 mL) and CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield a crude yellow solid which was purified by neutral alumina column chromatography (20% EtOAc/Hex) to yield a white solid.

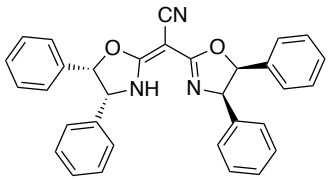
Bis-[(4R)-(3,5-tert-butylphenyl)-4,5-dihydro-oxazol-2-yl]-acetonitrile **(4a)** was synthesized according to the general procedure using 2,2-methylene-[(4*S*)- 3,5-di-tertbutylphenyl -2-oxazoline] (535 mg, 1.01 mmol) and tosyl cyanide (192 mg, 1.01 mmol) to afford a white solid (230 mg, 41%). R_f = 0.2 (1:4 EtOAc:Hexanes) , $[\alpha_D^{24}]$ = -31.2° (c = 1.20 , $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, 2H), 7.06 (s, 4H), 5.13 (s, 2H), 4.84 (s, 2H), 4.35 (s, 2H), 1.28 (s, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) 31.6, 35.1, 65.6, 76.4, 121.1, 123, 129.9, 139.3, 151.8, 167.9; HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_{36}H_{49}N_3O_2$ 555.3898; found 555.3898. Spectral data are in accordance with the literature.[11]



Bis-[(4S)-(mesityl)-4,5-dihydro-oxazol-2-yl]-acetonitrile **(5a)** was synthesized according to the general procedure using 2,2-methylene-[(4*S*)-mesityl-2-oxazoline] (1.5 g, 4.90 mmol) and tosyl cyanide (887 mg, 4.90 mmol) to afford a white solid (1.62 g, 49%). R_f = 0.24 (20% EtOAc/Hex), $[\alpha_D^{24}]$ = 227.9° (c = 5.0, $CHCl_3$), ^{1}H NMR (500MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.27 (s, 6H), 4.34 (t, *J* = 8.6Hz, 2H), 4.80 (t, *J* = 10Hz, 2H), 5.62 (t, J = 9.68 Hz, 2H), 6.84 (s, 4H);^{13}C NMR (125MHz, $CDCl_3$) δ 20.3, 20.7, 60, 73.2, 130.6, 131.7, 136.8, 137.8, 167.1; IR (neat) 2921, 2206, 1643, 1587, 1458, 1053; HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_{26}H_{29}N_3O_2$ 415.1806; found 415.1816.

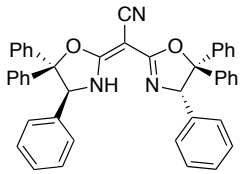


2,2-Methylene-[(4R,5S)-diphenyl-2-oxazoline]Bis-[(4R,5S)-(diphenyl)-4,5-dihydro-oxazol-2-yl]-acetonitrile. **(6a)** was



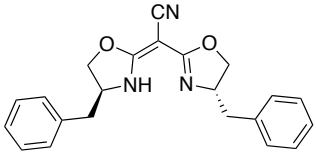
synthesized according to the general procedure using 2,2-methylene-[(4*R,5S*)-(diphenyl-2-oxazoline] (1.0 g, 2.2 mmol) and tosyl cyanide (399 mg, 2.2 mmol) to afford a white solid (600 mg, 57%). R_f =0.40 (10% MeOH/CH_2Cl_2) , $[\alpha_D^{24}]$ = -80.43° (c = 2.2, $CHCl_3$), ^{1}H NMR (500MHz, $CDCl_3$) δ 5.49 (d, *J* = 9 Hz, 2H), 6.08 (d, *J* = 9 Hz, 2H), 6.89-6.86 (m, 4H), 7.00-6.95 (m, 4H), (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) 50.5, 69.1, 88.6, 126.5, 127.5, 128.0, 128.1, 128.2, 128.22, 134.5, 136.7, 168.3; HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_{32}H_{25}N_3O_2$ 483.2016; found 483.2020. Spectral data are in accordance with the literature.[11]

Bis-[(4S)-4,5,5-triphenyl)-4,5-dihydro-oxazol-2-yl]-acetonitrile **(7a)**



was synthesized according to the general procedure using 2,2-Methylene-[(4S)-4,4,5-triphenyl-2-oxazoline] (891 mg, 1.46 mmol) and tosyl cyanide (264 mg, 1.46 mmol) to afford a white solid (603 mg, 65%). R_f = 0.20 (20% EtOAc/Hex) , $[\alpha]_D^{24}$= -111.1º (c = 0.70 , $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$-*d*) δ 5.86 (s, 2H), 6.95 (dd, *J* = 6.6, 2.8 Hz, 4H), 6.99 (s, 10H), 7.07 (dd, *J* = 5.1, 2.0 Hz, 6H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.74 (d, *J* = 7.7 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.46, 82.96, 97.98, 110.01, 128.90, 129.13, 129.77, 130.09, 130.59, 130.65, 130.74, 131.08, 131.33, 140.19, 141.52, 145.68, 168.84.; IR (neat) 3207, 2207, 1642, 1575, 1347, 1069, 693; HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_{44}H_{34}N_3O_2$ molecular weight**:** 635.2628; found 635.2646.

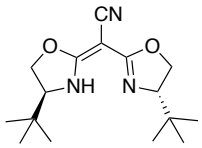
Bis-[(4S)-benzyl-4,5-dihydro-oxazol-2-yl]-acetonitrile **(8a)** was



synthesized according to the general procedure using 2,2-methylene-[(4*S*)- benzyl -2-oxazoline] (1.0 g, 3.0 mmol) and tosyl cyanide (542

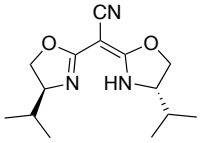
mg, 3.0 mmol) to afford a white solid (350 mg, 32%). R_f =0.35 (10% MeOH/CH_2Cl_2), [α_D^{24}] = 21.99º (c = 0.30, $CHCl_3$), ^{1}H NMR (500MHz, $CDCl_3$) δ 2.75 (dd, *J* = 13.7, 7.5 Hz, 2H), 2.96 (dd, *J* = 13.7, 6.4 Hz, 2H), 4.20 (dd, *J* = 8.5, 6.3 Hz, 2H), 4.36 (p, *J* = 6.9 Hz, 2H), 4.42 – 4.48 (m, 2H), 7.16 (d, *J* = 7.4 Hz, 4H), 7.22 – 7.33 (m, 6H). ^{13}C NMR (124 MHz, $CDCl_3$) 41.8, 46.7, 62.3, 73.3, 127.2, 129, 129.2, 137, 167.2; HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_{22}H_{21}N_3O_2$ 359.1716; found 359.1707. Spectral data are in accordance with the literature.[11]

Bis-[(4S)-(tert-butyl)-4,5-dihydro-oxazol-2-yl]-acetonitrile **(9a)** was



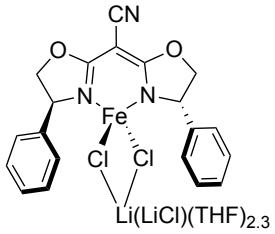
synthesized according to the general procedure using 2,2-methylene-[(4*S*)-tertbutyl -2-oxazoline] (400 mg, 1.5 mmol) and tosyl cyanide (272 mg, 1.5 mmol) to afford a white solid (350 mg, 80%). α_D^{24} = 62.5° (c 0.6, $CHCl_3$), R_f =0.30 (10% MeOH/CH_2Cl_2); ^{1}H NMR (500MHz, $CDCl_3$) δ 0.89 (s, 18H), 3.87 (dd, *J* = 9.3, 6.8 Hz, 2H), 4.27 (dd, *J* = 8.9, 6.8 Hz, 2H), 4.41 (t, *J* = 9.1 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) 25.3, 33.7, 53.5, 70.0, 70.2, 167.1. Spectral data are in accordance with the literature.[11]

Bis-[(4S)-(isopropyl)-4,5-dihydro-oxazol-2-yl]-acetonitrile **(10a)** was



synthesized according to the general procedure using 2,2-methylene-[(4*S*)-isopropyl -2-oxazoline] (500 mg, 2.1 mmol) and tosyl cyanide (380 mg, 2.1 mmol) to afford a white solid (400 mg, 72%). R_f =0.35 (10% MeOH/CH_2Cl_2), [α_D^{24}] = 15.07° (c = 2.60, $CHCl_3$), IR 2951, 2867, 2208, 1637, 1579, 1469, 1377, 1265, 1070 (neat). ^{1}H NMR (500MHz, $CDCl_3$) δ 0.90 (d, *J* = 6.7 Hz, 6H), 0.97 (d, *J* = 6.7 Hz, 6H), 1.73 (dq, *J* = 13.4, 6.7 Hz, 1H), 3.87 (dt, *J* = 8.9, 7.1 Hz, 2H), 4.16 (dd, *J* = 8.7, 7.1 Hz, 2H), 4.48 (t, *J* = 8.8 3Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 18.5, 18.7, 33.0, 67.1, 72.1, 117.2, 167.2; HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_{14}H_{21}N_3O_2$ 263.1707; found 263.1707.

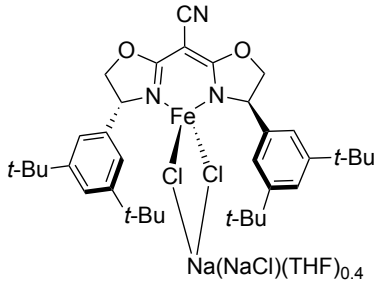
Synthesis of (2,2-bis((S)-4-phenyl-4,5-dihydrooxazol-2-yl)acetonitrile) Iron Chloride (1). To an oven-dried 25 mL, two-neck flask with stir bar under a N_2 atmosphere was added 2,2-bis((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)acetonitrile (0.81 g, 2.5 mmol). Tetrahydrofuran (5 mL) was added followed by dropwise addition of *n*-butyl-lithium (2.1 M, 1.19 mL, 2.5 mmol) at -78 ºC. This mixture was stirred for 1 hour before being pumped down to a white/yellow solid. The solid was brought into the glovebox and washed thoroughly with pentane. To a 20 mL scintillation vial equipped with a stir-bar was added iron dichloride (0.31 g, 2.5 mmol) and THF (5 mL). After stirring for one hour, the lithium salt was added as a THF solution and allowed to stir for 24 hours. The solvent was removed *in vacuo* and pentane was added to precipitate the complex as a white solid. This yielded an off-white solid (0.95 g, 81%). $[\alpha_D^{24}]$ -322° (c = 0.50, THF), ^{1}H NMR (500 MHz, THF) δ -26.95 ($w_{1/2}$ = 307 Hz, 4H), -3.87 ($w_{1/2}$ = 110 Hz, 3H), -3.51 ($w_{1/2}$ = 83 Hz, 3H), -0.60 ($w_{1/2}$ = 59 Hz, 2H), 11.12 ($w_{1/2}$ = 76 Hz, 2H), 57.58 ($w_{1/2}$ = 512 Hz, 1H). IR: 2203, 1606, 1533, 1440, 1067, 694 cm^{-1}. Elemental analysis for $C_{20}H_{16}ClFeN_3O_2$•$(LiCl)_2(THF)_{2.3}$ calc'd: C, 52.21%; H, 5.17%; N 6.23%. Found: C, 52.21%, H, 5.13%, N 6.62%.



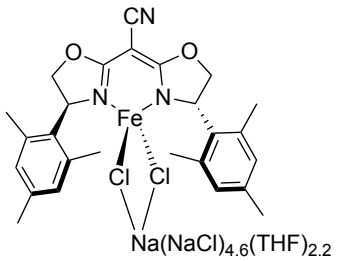
General procedure for synthesis of cyanobis(oxazoline) iron chloride complexes: To a 20 mL scintillation vial with stir bar under a N_2 atmosphere was added cyanobis(oxazoline) (0.81 g, 2.5 mmol) and sodium hydride (60 mg, 2.5 mmol). The reaction was allowed to stir overnight. In the glovebox, to a new 20 mL scintillation vial equipped with a stir-bar was added iron dichloride (0.31 g, 2.5 mmol) and THF (5 mL). After stirring for one hour, the sodium salt was added as a THF solution and allowed to stir for 24 hours. The solvent was removed *in vacuo* and pentane was added to precipitate the complex as a white solid. This yielded an off-white solid (0.95 g, 81%). ^{1}H-NMR spectrums were taken in a 10 mM LiCl THF solution to help solubilize the complexes. Elemental analysis of the following iron complexes revealed samples with C, H, and N ratios that match what would be expected for the desired complexes containing variable amounts of NaCl and THF. This difficulty has been observed previously in the

purification of similar complexes.[12] The elemental analysis of complex **11** could not be accurately determined.

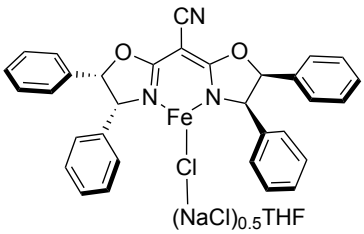
(2,2-bis((R)-4-(3,5-tertbutylphenyl)-4,5-dihydrooxazol-2-yl)acetonitrile) Iron Chloride (**4**) was synthesized according to the general procedure using 2,2-bis((S)-4-(3,5-tertbutylphenyl)-4,5-dihydrooxazol-2-yl)acetonitrile (166 mg, 0.3 mmol), sodium hydride (7.2 mg, 0.3 mmol) and $FeCl_2$ (100 mg, 0.3 mmol) to afford an off-white solid (632 mg, 98%).[α_D^{24}] = -26° (c = 0.50, THF), IR: 2959, 2205, 1607, 1429, 1362, 1248, 2075, 873, 712 cm^{-1}. ^1H NMR (600 MHz, THF) δ -27.46 ($w_{1/2}$ = 382 Hz, 2H), -12.93 ($w_{1/2}$ = 300 Hz, 3H), -5.31 ($w_{1/2}$ = 44 Hz, 1H), -0.70 ($w_{1/2}$ = 41 Hz, 36 H), 7.40 ($w_{1/2}$ = 76 Hz, 3H), 12.02 ($w_{1/2}$ = 100 Hz, 1H), 35.81 ($w_{1/2}$ = 524 Hz, 1H). (Compound contained minor species). Elemental analysis for $C_{36}H_{48}ClFeN_3O_2$•$(NaCl)_2(THF)_{0.4}$ calc'd: C, 57.03%; H, 6.51%; N, 5.31%. Found C, 57.20%; H, 6.48%; N, 5.31%.



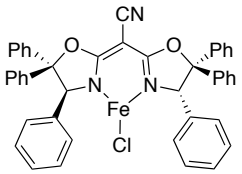
(2,2-bis((S)-4-(mesityl)-4,5-dihydrooxazol-2-yl)acetonitrile) Iron Chloride **(5)** was synthesized according to the general procedure using 2,2-bis((S)-4-(isopropyl)-4,5-dihydrooxazol-2-yl)acetonitrile (566 mg, 1.36 mmol), sodium hydride (36 mg, 1.5 mmol) and $FeCl_2$ (38.0 mg, 0.68 mmol) to afford an off-white solid (200 mg, 29%).[α_D^{24}] = 66° (c = 0.50, THF), IR: 2361, 2202, 1616, 1539, 1427. ^1H NMR (600 MHz, THF) δ -20.80 ($w_{1/2}$ = 262 Hz, 6H), -16.12 ($w_{1/2}$ = 102 Hz, 1H), -12.44 ($w_{1/2}$ = 100 Hz, 2H), -10.02 ($w_{1/2}$ = 73 Hz, 2H),), -8.06 ($w_{1/2}$ = 100 Hz, 6H), -5.79 ($w_{1/2}$ = 48 Hz, 7H), -3.81 ($w_{1/2}$ = 48 Hz, 2H), 11.57 ($w_{1/2}$ = 86 Hz, 2H), 62.14 ($w_{1/2}$ = 531 Hz, 1H). Elemental analysis for $C_{26}H_{28}ClFeN_3O_2$•$(NaCl)_{5.6}(THF)_{2.2}$ calc'd: C, 42.23%; H, 4.64%; N, 4.25%. Found C, 42.23%; H, 4.81%; N, 4.31%.



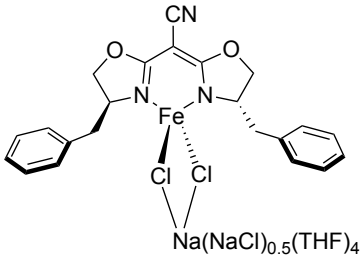
(2,2-bis((R)-4-(-[(4R,5S)-diphenyl)-4,5-dihydrooxazol-2-yl)acetonitrile) Iron Chloride (**6**) was synthesized according to the general procedure using 2,2-bis((*S*)-4-((4*R*,5*S*)- diphenyl)-4,5-dihydrooxazol-2-yl)acetonitrile (250 mg, 0.52 mmol), sodium hydride (13.7 mg, 0.57 mmol) and iron dichloride (65.5 mg, 0.52 mmol) to afford an off-white solid (252 mg, 85%). $[\alpha_D^{24}]$ = -80° (c = 0.50, THF), IR: 2205, 1622, 1545, 1429, 1054, 758, 695, 604, 528 cm^{-1}. ^1H NMR (600 MHz, THF) δ -25.14 ($w_{1/2}$ = 451 Hz, 4H), -8.42 ($w_{1/2}$ = 139 Hz, 2H), -2.69 ($w_{1/2}$ = 112 Hz, 4H), -0.14 ($w_{1/2}$ = 85 Hz, 1H),), 6.18 ($w_{1/2}$ = 85 Hz, 3H), 8.11 ($w_{1/2}$ = 122 Hz, 4H), 8.39 ($w_{1/2}$ = 81 Hz, 5H), 53.99 ($w_{1/2}$ = 663 Hz, 1H). Elemental analysis for $C_{32}H_{24}ClFeN_3O_2$•$(NaCl)_{0.5}$THF calc'd: C, 64.04%; H, 4.78%; N, 6.22%. Found: C, 63.49%, H, 4.28%, N, 6.50%.



(2,2-bis((S)-4-(-[(4S,5S,5R)-diphenyl)-4,5-dihydrooxazol-2-yl)acetonitrile) Iron Chloride **(7)** was synthesized according to the general procedure using 2,2-bis((S)-4-((4*R*,5*S*,5*R*)-triphenyl)-4,5-dihydrooxazol-2-yl)acetonitrile (530 mg, 0.84 mmol), sodium hydride (20 mg, 0.84 mmol) and iron dichloride (47 mg, 0.84 mmol) to afford an off-white solid (400 mg, 65%). $[\alpha_D^{24}]$ = -112° (c = 0.50, THF). IR: 2196, 1612, 1529, 1428. ^1H NMR (600 MHz, THF) δ -23.75 ($w_{1/2}$ = 840 Hz, 4H), -3.79 ($w_{1/2}$ = 208 Hz, 6H), -1.21 ($w_{1/2}$ = 127 Hz, 2H), 5.03 ($w_{1/2}$ = 141 Hz, 4H), 8.17 ($w_{1/2}$ = 130 Hz, 4H), 9.19 ($w_{1/2}$ = 173 Hz, 6H), 9.65 ($w_{1/2}$ = 230 Hz, 6H), 51.63 ($w_{1/2}$ = 742 Hz, 1H). Elemental analysis for $C_{44}H_{32}ClFeN_3O_2$ calc'd: C, 72.79%; H, 4.44; N, 5.79%. Found: C, 73.68%, H, 4.96%, N, 4.86%.

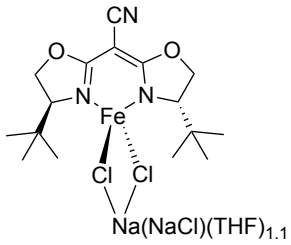


(2,2-bis((S)-4-(benzyl)-4,5-dihydrooxazol-2-yl)acetonitrile)Iron Chloride (**8**) was synthesized according to the general procedure using 2,2-bis((S)-4-(benzyl)- 4,5-dihydrooxazol-2-yl)acetonitrile (350 mg, 0.97 mmol), sodium hydride (25.7 mg, 1.07 mmol) and iron dichloride (123 mg, 0.97 mmol) to afford an off-white solid (350 mg, 79%).

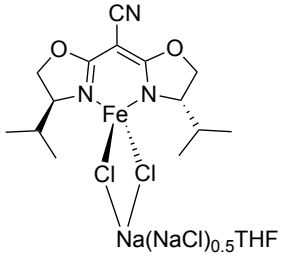


$[\alpha_D^{24}]$ = 6° (c = 0.50, THF), IR: 2361, 2207, 1623, 1538, 1433, 1030, 701, 505 cm^{-1}. ^1H NMR (600 MHz, THF) δ -62.82 ($w_{1/2}$ = 656 Hz, 2H), -42.45 ($w_{1/2}$ = 484 Hz, 2H), -5.04 ($w_{1/2}$ = 163 Hz, 5H), -4.77 ($w_{1/2}$ = 112 Hz, 3H), 37.21 ($w_{1/2}$ = 560 Hz, 2H). (One peak was unable to be integrated due to overlapping with THF resonances) Elemental analysis for $C_{22}H_{20}ClFeN_3O_2$•$(NaCl)_{1.5}(THF)_4$ calc'd: C, 55.27%; H, 6.35%; N, 5.09%. Found: C, 55.54%; H, 6.85%; N, 4.02%.

(2,2-bis((S)-4-(tertbutyl)-4,5-dihydrooxazol-2-yl)acetonitrile) Iron Chloride (**9**) was synthesized according to the general procedure using 2,2-bis((S)-4-(tertbutyl)-4,5-dihydrooxazol-2-yl)acetonitrile (200 mg, 0.69 mmol), sodium hydride (18.2 mg, 0.76 mmol) and iron dichloride (0.1 g, 0.3 mmol) to afford an off-white solid (260 mg, 99%). IR: 2200, 1602, 1536, 1440, 1068, 744 cm^{-1}. Elemental analysis for $C_{16}H_{24}ClFeN_3O_2$•$(NaCl)_2(THF)_{1.1}$ calc'd: C, 42.43%; H, 5.73%; N, 7.26%. Found: C, 42.38%; H, 5.40%; N, 8.04%. ^1H-NMR spectroscopy could not be used on this complex due to its insolubility in THF and other organic solvents.



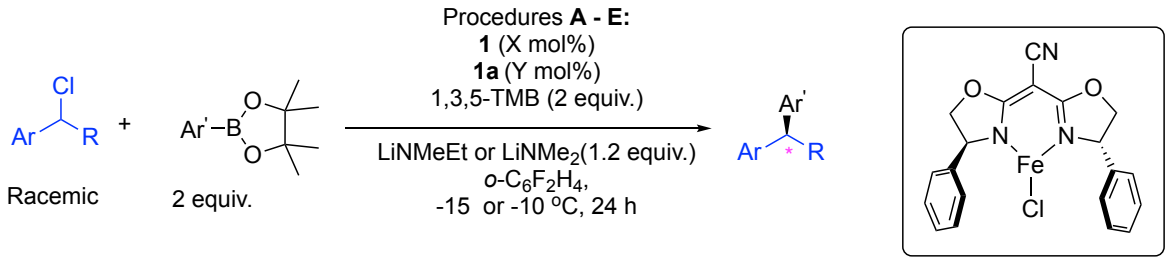
(2,2-bis((S)-4-(isopropyl)-4,5-dihydrooxazol-2-yl)acetonitrile) Iron Chloride (**10**) was synthesized according to the general procedure using 2,2-bis((*S*)-4-(isopropyl) -4,5-dihydrooxazol-2-yl)acetonitrile (134 mg, 0.54 mmol), sodium hydride (12.5 mg, 0.54 mmol) and $FeCl_2$ (30.2 mg, 0.54 mmol to afford an off-white solid (110 mg, 57%). $[\alpha_D^{24}]$ = 66° (c = 0.50 ,THF), IR:



2201, 1619. ^{1}H NMR (600 MHz, THF) δ -68.44 ($w_{1/2}$ = 728 Hz, 1H), -23.41 ($w_{1/2}$ = 241 Hz, 6H), -18.15 ($w_{1/2}$ = 114 Hz, 6H), -7.90 ($w_{1/2}$ = 88 Hz, 2H), -3.21 ($w_{1/2}$ = 24 Hz, 1H), 4.54 ($w_{1/2}$ = 29 Hz, 1H), 37.41 ($w_{1/2}$ = 560 Hz, 1H). Elemental analysis for $C_{14}H_{20}ClFeN_3O_2$•$(NaCl)_{1.5}$THF calc'd: C, 42.11; H, 5.50; N, 8.18. Found: C, 41.31%, H, 5.03%, N, 8.78%.

2,2'-methylene-[(4S)-phenyl-2-oxazoline] Iron Chloride (**11**). To an oven-dried 25 mL, two-neck flask with stir bar under a N_2 atmosphere was added 2,2'-methylene-[(4*S*)-phenyl-2-oxazoline](224 mg, 0.73 mmol). Tetrahydrofuran (3 mL) was added followed by dropwise addition of *n*-butyl-lithium (2.1 M, 0.35 mL, 0.731 mmol) at -78˚C. This mixture was stirred for 1 hour before being pumped down to a white/yellow solid. The solid was brought into the glovebox and washed thoroughly with pentane. To a 20 mL scintillation vial equipped with a stir-bar was added iron dichloride (40.8 mg, 0.731 mmol) and THF (5 mL). After stirring for one hour, the lithium salt was added as a THF solution and allowed to stir for 24 hours. The solvent was removed *in vacuo* and pentane was added to precipitate the complex as a yellow solid (290 mg, 99%). $[\alpha_D^{24}]$ = 250˚ (c = 0.50, THF). IR: 2960, 1596, 1452, 1266, 1027, 758, 698. ^{1}H NMR (600 MHz, THF) -15.76 ($w_{1/2}$ = 442 Hz, 4H), -0.79 ($w_{1/2}$ = 139 Hz, 3H),), 25.02 ($w_{1/2}$ = 276 Hz, 2H), 28.39 ($w_{1/2}$ = 185 Hz, 2H), 30.94 ($w_{1/2}$ = 345 Hz, 2H), 40.14 ($w_{1/2}$ = 360Hz, 2H), 115.54 – 117.92 ($w_{1/2}$ = 560 Hz,1H). Elemental analysis for $C_{19}H_{17}ClFeN_2O_2$ calc'd: C, 57.53%; H, 4.32%; N, 7.06%. Found: C, 56.60%, H, 6.47%, N, 8.26%.

General procedure for enantioselective iron-complex-catalyzed Suzuki-Miyaura cross-coupling between benzylic chlorides and arylboronic pinacol esters



Standard Reaction Conditions (Conditions A)*:* To a 10 mL one-neck flask with stir bar under a N_2 atmosphere was added **1** (10.54 mg, 25.0 μmol), **1a** (3.91 mg, 12.5 μmol), 1,3,5-trimethoxybenzene (42.0 mg, 0.25 mmol) and lithium methylethylamide (19.0 mg, 0.30 mmol). A vacuum adapter fitted with a teflon stopcock was assembled to the flask and the flask brought outside of the glovebox, secured to the Schlenk line, and cooled to -15 ºC. To the flask was added a 1,2-difluorobenzene solution (3 mL) of arylboronic acid pinacol ester (0.50 mmol) and alkyl halide (0.25 mmol). The reaction was allowed to stir vigorously for 24 hours at -15 ºC. Typically, the reaction turns a pale brown color and stays heterogenous throughout the course of the reaction with solid depositing on the sides of the flask. After 24 hours, the reaction was quenched with saturated NH_4Cl (aq) (10 mL) and the collected aqueous layers were extracted with dichloromethane (3 x 40 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* An NMR yield was determined from the crude reaction mixture using the added 1,3,5-trimethoxybenzene reagent as the internal standard. The benzylic proton resonances were used as diagnostic peaks for determining the NMR yield. The crude mixture was purified by silica gel column chromatography (Hexanes).

Reaction with lithium dimethylamide and no added exogenous ligand (Conditions B)*:* To a 10 mL one-neck flask with stir bar under a N_2 atmosphere was added **1** (15.8 mg, 37.5 μmol), 1,3,5-trimethoxybenzene (84.1 mg, 0.50 mmol) and lithium-dimethyl amide (15.4 mg, 0.30 mmol). A vacuum adapter fitted with a teflon stopcock was assembled to the flask and the flask brought outside of the glovebox, secured to the Schlenk line, and cooled to -15 ºC. To the flask was added a 1,2-difluorobenzene solution (3 mL) of arylboronic acid pinacol ester (0.50

mmol) and alkyl halide (0.25 mmol). The reaction was allowed to stir vigorously for 24 hours at -15 ºC. Typically, the reaction turns a pale brown color and stays heterogenous throughout the course of the reaction with solid depositing on the sides of the flask. After 24 hours, the reaction was quenched with saturated NH_4Cl (aq) (10 mL) and the collected aqueous layers were extracted with dichloromethane (3 x 40 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* An NMR yield was determined from the crude reaction mixture using the added 1,3,5-trimethoxybenzene reagent as the internal standard. The benzylic proton resonances were used as diagnostic peaks for determining the NMR yield. The crude mixture was purified by silica gel column chromatography (Hexanes).

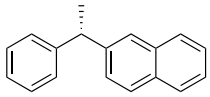
Reaction run at -10° C with lithium dimethylamide (Conditions C)*:* To a 10 mL one-neck flask with stir bar under a N_2 atmosphere was added **1** (15.8 mg, 37.5 μmol), **1a** (6.21 mg, 18.75 μmol), 1,3,5-trimethoxybenzene (84.1 mg, 0.50 mmol) and lithium-dimethyl amide (15.4 mg, 0.30 mmol). A vacuum adapter fitted with a teflon stopcock was assembled to the flask and the flask brought outside of the glovebox, secured to the Schlenk line, and cooled to -10 ºC. To the flask was added a 1,2-difluorobenzene solution (3 mL) of arylboronic acid pinacol ester (0.50 mmol) and alkyl halide (0.25 mmol). The reaction was allowed to stir vigorously for 24 hours at -10 ºC. Typically, the reaction turns a pale brown color and stays heterogenous throughout the course of the reaction with solid depositing on the sides of the flask. After 24 hours, the reaction was quenched with saturated NH_4Cl (aq) (10 mL) and the collected aqueous layers were extracted with dichloromethane (3 x 40 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* An NMR yield was determined from the crude reaction mixture using the added 1,3,5-trimethoxybenzene reagent as the internal standard. The benzylic proton resonances were used as diagnostic peaks for determining the NMR yield. The crude mixture was purified by silica gel column chromatography (Hexanes).

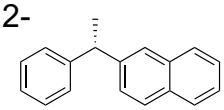
Reaction run at -10° C with lithium methylethylamide (Conditions D)*:* To a 10 mL one-neck flask with stir bar under a N_2 atmosphere was added **1** (15.8 mg, 37.5 μmol), **1a** (6.21 mg, 18.75

μmol), 1,3,5-trimethoxybenzene (84.1 mg, 0.50 mmol) and lithium-dimethyl amide (15.4 mg, 0.30 mmol). A vacuum adapter fitted with a teflon stopcock was assembled to the flask and the flask brought outside of the glovebox, secured to the Schlenk line, and cooled to -10 ºC. To the flask was added a 1,2-difluorobenzene solution (3 mL) of arylboronic acid pinacol ester (0.50 mmol) and alkyl halide (0.25 mmol). The reaction was allowed to stir vigorously for 24 hours at -10 ºC. Typically, the reaction turns a pale brown color and stays heterogenous throughout the course of the reaction with solid depositing on the sides of the flask. After 24 hours, the reaction was quenched with saturated NH_4Cl (aq) (10 mL) and the collected aqueous layers were extracted with dichloromethane (3 x 40 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* An NMR yield was determined from the crude reaction mixture using the added 1,3,5-trimethoxybenzene reagent as the internal standard. The benzylic proton resonances were used as diagnostic peaks for determining the NMR yield. The crude mixture was purified by silica gel column chromatography (Hexanes).

Reaction run at -10° C, 40% catalyst loading, lithium dimethylethylamide and no added exogenous ligand (Conditions E): To a 10 mL one-neck flask with stir bar under a N_2 atmosphere was added **1** (42.57 mg, 0.10 mmol), 1,3,5-trimethoxybenzene (84.1 mg, 0.50 mmol) and lithium methylethylamide (19.0 mg, 0.30 mmol). A vacuum adapter fitted with a teflon stopcock was assembled to the flask and the flask brought outside of the glovebox, secured to the Schlenk line, and cooled to -10 ºC. To the flask was added a 1,2-difluorobenzene solution (3 mL) of arylboronic acid pinacol ester (0.50 mmol) and alkyl halide (0.25 mmol). The reaction was allowed to stir vigorously for 24 hours at -10 ºC. Typically, the reaction turns a pale brown color and stays heterogenous throughout the course of the reaction with solid depositing on the sides of the flask. After 24 hours, the reaction was quenched with saturated NH_4Cl (aq) (10 mL) and the collected aqueous layers were extracted with dichloromethane (3 x 40 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* An NMR

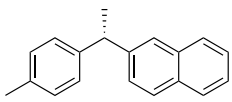
yield was determined from the crude reaction mixture using the added 1,3,5-trimethoxybenzene reagent as the internal standard. The benzylic proton resonances were used as diagnostic peaks for determining the NMR yield. The crude mixture was purified by silica gel column chromatography (Hexanes).

(S)-1-(1-Phenylethyl)naphthalene **(2)** was synthesized from 1-chloroethylbenzene and 2-naphthylboronic pinacol ester according to General Procedure A. Product  was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (91% spectroscopic yield, 80% isolated yield), R_f = 0.60 (5% Et_2O in Hexanes, (85:15 er)) $[\alpha_D^{24}]$ = 20.2° (c = 1.00 , $CHCl_3$), Chiral Column HPLC (OD-H) 1 mL/ min, 100% Hexanes (85:15 er)) ^1H NMR (400 MHz, $CDCl_3$) δ 1.77 (d, *J* = 7.2 Hz, 3H), 4.35 (q, *J* = 7.2 Hz, 1H), 7.22 (td, *J* = 6.8, 1.9 Hz, 1H), 7.26 – 7.36 (m, 5H), 7.42 – 7.52 (m, 2H), 7.73 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 7.9, 5.9 Hz, 2H) ppm; ^{13}C NMR (125MHz, $CDCl_3$) δ 21.0, 40.1, 125.6, 126.1, 126.3, 127.1, 127.8, 128.0, 128.2, 128.6, 132.3, 133.7, 144.0, 146.4 ppm; HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{18}H_{16}$ molecular Weight: 232.13; found 231.12. Spectral data are in accordance with the literature.[13] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[13]

(S)-1-(1-Phenylethyl)naphthalene **(2)** was synthesized from 2-chloronapthylbenzene and phenylboronic pinacol ester according to General  Procedure A. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (90% spectroscopic yield, 85% isolated yield), R_f = 0.60 (5% Et_2O in Hexanes, (85:15 er)) $[\alpha_D^{24}]$ = 20.2° (c = 1.00 , $CHCl_3$), Chiral Column HPLC (OD-H) 1 mL/ min, 100% Hexanes (73:27 er)) ^1H NMR (400 MHz, $CDCl_3$) δ 1.77 (d, *J* = 7.2 Hz, 3H), 4.35 (q, *J* = 7.2 Hz, 1H), 7.22 (td, *J* = 6.8, 1.9 Hz, 1H), 7.26 – 7.36 (m, 5H),

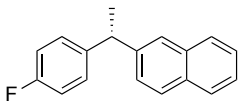
7.42 – 7.52 (m, 2H), 7.73 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 7.9, 5.9 Hz, 2H) ppm; ^{13}C NMR (125MHz, $CDCl_3$) δ 21.0, 40.1, 125.6, 126.1, 126.3, 127.1, 127.8, 128.0, 128.2, 128.6, 132.3, 133.7, 144.0, 146.4 ppm; HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{18}H_{16}$ molecular weight: 232.1169; found 232.1168. Spectral data are in accordance with the literature.[13] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[13]

(S)-2-(1-(p-tolyl)ethyl)naphthalene **(13)** was synthesized from 1-(1-chloroethyl)-4-methyl-benzene and 2-naphthylboronic pinacol ester



according to General Procedure A. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (78% spectroscopic yield, 63 % isolated yield). R_f = 0.60 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = 13.2° (c = 3.4, $CHCl_3$), Chiral Column HPLC (OD-H) 1 mL/ min, 100% Hexanes (82:18 er)) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (d, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 4.32 (q, *J* = 7.2 Hz, 1H), 7.11–7.22 (m, 4H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.43–7.52 (m, 2H), 7.72–7.76 (m, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.80–7.85 (m, 2H) ppm; ^{13}C NMR (125MHz, $CDCl_3$) δ 21.0, 21.8, 44.4, 125.3, 125.3, 125.9, 126.8, 127.5, 127.6, 127.7, 127.9, 129.1, 132.1, 133.5, 135.6, 143.3, 144.0 ppm; HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{18}H_{15}F$ molecular weight: 246.1239; found 246.1325. Spectral data are in accordance with the literature.[13] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[13]

(S)-2-(1-(4-fluorophenyl)ethyl)naphthalene **(14)** was synthesized from 1-(1-chloroethyl)-4-fluoro-benzene and 2-naphthylboronic pinacol ester



according to General Procedure A. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a white solid (54% spectroscopic yield, 42% isolated yield). R_f = 0.60 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ **=** 12.8° (c = 2.8 ,

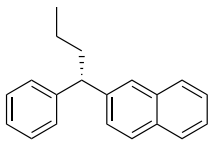
$CHCl_3$),Chiral Column HPLC (OD-H) 1 mL/ min, 100% Hexanes (77:23 er))^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (d, *J* = 7.2 Hz, 3H), 4.30 (q, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 8.7 Hz, 2H), 7.21 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.26 (s, 1H), 7.39 – 7.50 (m, 2H), 7.67 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 2H) ppm.^{13}C NMR (125MHz, $CDCl_3$) δ 21.90, 44.10, 125.27, 125.45, 126.01, 126.62, 127.56, 127.69, 128.03, 129.09 (d, *J* = 8.0 Hz), 132.10, 133.48, 141.87 (d, *J* = 3.2 Hz), 143.53, 161.28 (d, *J* = 244.0 Hz). ppm; HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{18}H_{15}F$ molecular weight: 250.1067; found 250.1074. Spectral data are in accordance with the literature.[13] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[13]

(+)-2-(1-(4*-tert-butyldimethylsilyloxy)*)ethyl)naphthalene **(15)** was synthesized from 1-(4-tert-Butyldiemethylsilyloxy)phenylchloride and 2-naphthylboronic pinacol ester according to General Procedure A.. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (45% spectroscopic yield, 40% isolated yield). R_f = 0.35 (Hexanes) $[\alpha_D^{24}]$ = 10.8° (c = 3.2, $CHCl_3$),Chiral Column HPLC (OD-H) 1 mL/ min, 100% Hexanes (82:18 er)), ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 6H), 0.99 (s, 10H), 1.71 (d, *J* = 7.2 Hz, 3H), 4.27 (q, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.40 – 7.49 (m, 2H), 7.67 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.74, 20.84, 24.64, 28.36, 46.74, 122.45, 127.91, 127.94, 128.54, 129.50, 130.20, 130.35, 130.51, 131.26, 134.70, 136.18, 141.48, 146.95, 156.47 ppm. IR (neat); 2955, 2923, 2872, 2859, 1458, 1378. HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_{24}H_{30}OSi$ molecular weight: 362.2129; found 362.2139.

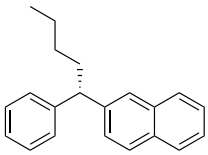
(S)-2-(1-phenylpropyl)naphthalene **(16)** was synthesized from 1-chloropropylbenzene and 2-naphthylboronic pinacol ester according to General Procedure A. Product was purified by silica gel flash column chromatography, eluting

with hexanes to afford purified product as a colorless oil (84% spectroscopic yield, 68% isolated yield). R_f = 0.60 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = 6.7° (c = 3.56 , $CHCl_3$),Chiral Column HPLC (OD-H) 1 mL/ min, 100% Hexanes (81:19 er)) ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.3 Hz, 3H), 2.14 – 2.28 (m, 2H), 3.99 (t, *J* = 7.7 Hz, 1H), 7.20 (qq, *J* = 5.0, 2.3 Hz, 1H), 7.28 – 7.34 (m, 4H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.46 (dddd, *J* = 21.2, 8.0, 6.8, 1.4 Hz, 2H), 7.73 – 7.78 (m, 2H), 7.81 (ddd, *J* = 13.8, 8.1, 1.3 Hz, 2H) ppm. ^{13}C NMR (125MHz, $CDCl_3$) δ 12.8, 28.5, 53.3, 125.3, 125.9, 125.9, 126.1, 126.8, 127.5, 127.7, 128.0, 128.2, 128.4, 132.1, 142.6, 145.0 ppm. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{19}H_{18}$ molecular weight: 246.1329; found 246.1325. Spectral data are in accordance with the literature.[13] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[13]

(S)-2-(1-phenylbutyl)naphthalene **(17)** was synthesized from 1-chlorobutyllbenzene and 2-naphthylboronic pinacol ester according to General Procedure A. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (77% spectroscopic yield, 73% isolated yield). R_f = 0.60 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = 5.2° (c = 3.41, $CHCl_3$), Chiral Column HPLC (OD-H)1 mL/ min, 100% Hexanes (79:21 er)), ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.35 (h, *J* = 7.5 Hz, 2H), 2.09 – 2.22 (m, 2H), 4.10 (t, *J* = 7.8 Hz, 1H), 7.16 – 7.22 (m, 1H), 7.26 – 7.34 (m, 4H), 7.36 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.44 (dddd, *J* = 21.7, 8.1, 6.8, 1.4 Hz, 2H), 7.72 – 7.77 (m, 2H), 7.80 (ddd, *J* = 14.2, 8.4, 1.4 Hz, 2H) ppm.^{13}C NMR (125 MHz, $CDCl_3$) 16.78, 23.86, 40.35, 53.75, 127.96, 128.52, 128.54, 128.73, 129.49, 130.21, 130.35, 130.66, 131.04, 134.78, 136.20, 145.41, 147.84. IR (neat); 3055, 3024, 2954, 2925, 2869, 1451, 722 ppm. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{20}H_{20}$ molecular weight: 260.1481; found 260.1574. Absolute configuration assigned by analogy to sign of optical rotation for **16**.[13]

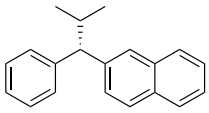


(S)-2-(1-phenylpentyl)naphthalene **(18)** was synthesized from 1-chloropentylbenzene and 2-naphthylboronic pinacol ester according to



General Procedure A. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (91% spectroscopic yield, 69% isolated yield). R_f = 0.60 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = 7.4° (c = 4.6, $CHCl_3$),Chiral Column HPLC (OD-H) 1 mL/ min, 100% Hexanes (78:22 er)), ^1H NMR (600 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.35 – 1.46 (m, 2H), 2.12 – 2.25 (m, 2H), 4.09 (t, *J* = 7.8 Hz, 1H), 7.21 (tt, *J* = 6.4, 2.1 Hz, 1H), 7.28 – 7.35 (m, 4H), 7.38 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.42 – 7.50 (m, 2H), 7.73 – 7.79 (m, 2H), 7.82 (dd, *J* = 15.1, 8.0 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.72, 25.44, 32.97, 37.92, 42.44, 54.08, 127.98, 128.55, 128.56, 128.74, 129.50, 130.24, 130.39, 130.67, 131.07, 134.81, 136.23, 145.47, 147.91 ppm. IR (neat);3055, 3024, 2954, 2927, 2857, 1506, 698. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{21}H_{22}$ molecular weight: 274.1642; found 274.1639. Absolute configuration assigned by analogy to sign of optical rotation for **16**.[13]

(-)-2-(2-methyl-1-phenylpropyl)naphthalene **(19)** was synthesized from 1-chloroisobutylbenzene and 2-naphthylboronic pinacol ester according to



General Procedure A. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (39% spectroscopic yield, 37% isolated yield). R_f = 0.60 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = -2.9° (c = 1.3, $CHCl_3$), Chiral Column HPLC (1B) 0.8 mL/ min, 100% Hexanes (73:273 er)). ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (ddd, *J* = 10.1, 6.5, 1.2 Hz, 6H), 2.62 (tt, *J* = 12.8, 6.6 Hz, 1H), 3.59 (d, *J* = 10.8 Hz, 1H), 7.10 – 7.17 (m, 1H), 7.23 – 7.29 (m, 1H), 7.33 – 7.36 (m, 2H), 7.39 (ddt, *J* = 8.1, 6.9, 1.4 Hz, 1H), 7.41 – 7.46 (m, 2H), 7.72 – 7.81 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.87, 24.50, 24.57, 34.28, 63.56, 127.84, 128.45, 128.63, 128.92, 129.20, 130.14, 130.27, 130.66, 130.74, 131.03, 136.22,

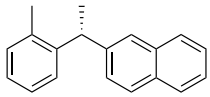
145.06, 147.34 ppm. IR (neat); 3055, 3023, 2953, 2923, 2853, 1494, 699. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{20}H_{20}$ molecular weight: 260.1557; found 260.1603.

***(-)-1-(1-(naphthalen-2-yl)ethyl)naphthalene* (20)** was synthesized from 1-(1-chloroethyl)naphthalene and 2-naphthylboronic pinacol ester according to General Procedure B. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (64 % spectroscopic yield, 64% isolated yield). R_f = 0.55 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = -20.63° (c = 1.25 , $CHCl_3$),Chiral Column HPLC (1C 0.8 mL/ min, 100% Hexanes (77:23 er)) ^1H NMR (400 MHz, $CDCl_3$) δ 1.86 (d, *J* = 7.1 Hz, 3H), 5.09 (q, *J* = 7.1 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.38 – 7.49 (m, 6H), 7.68 – 7.82 (m, 5H), 7.87 (dd, *J* = 6.4, 3.4 Hz, 1H), 8.08 – 8.13 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.40, 40.68, 123.93, 124.59, 125.30, 125.33, 125.45, 125.50, 125.87, 125.91, 126.80, 127.05, 127.54, 127.70, 128.01, 128.78, 131.74, 132.07, 133.56, 134.00, 141.47, 144.13 ppm. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{22}H_{18}$ molecular weight: 282.1391; found 282.1403. Spectral data are in accordance with the literature.[14]

***(-)-2-(1-(o-*chloro*)ethyl)naphthalene* (21)** was synthesized from 1-chloro-2-(1-chloroethyl) benzene and 2-naphthylboronic pinacol ester according to General Procedure B. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (54% spectroscopic yield, 45% isolated yield). R_f = 0.60 (5% Et_2O in Hexanes) $[\alpha_D^{24}]$ = -51.4° (c = 2.5, $CHCl_3$),Chiral Column HPLC (OD-H) 1 mL/ min, 100% Hexanes (93:7 er)),^1H NMR (400 MHz, $CDCl_3$) δ 1.71 (d, *J* = 7.2 Hz, 3H), 4.82 (q, *J* = 7.2 Hz, 1H), 7.09 – 7.27 (m, 3H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.37 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.44 (tt, *J* = 8.5, 6.0 Hz, 2H), 7.69 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.82 (m, 2H) ppm.^{13}C NMR (125 MHz, $CDCl_3$) δ 21.9, 41.1, 125.3, 125.4, 126.1, 126.1, 126.7, 126.9, 127.5, 127.7 127.9, 130.4, 132.0, 133.5, 136.1, 143.7, 143.8 ppm. HRMS (ESI) *m/z* $[M]^+$ calcd.

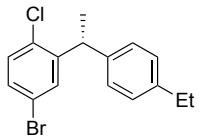
for $C_{18}H_{15}Cl$ molecular weight: 266.0849; found 266.0857. Spectral data are in accordance with the literature.[16] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[16]

***(-)-2-(1-(o-tolyl)ethyl)naphthalene* (22)** was synthesized from 1-chloro-2-(1-methylethyl)benzene and 2-naphthylboronic pinacol ester according to



General Procedure B. Product was purified by silica gel flash column chromatography, eluting with hexanes to afford purified product as a colorless oil (70 % spectroscopic yield, 67% isolated yield). R_f = 0.60 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = -11. 6° (c = 1.93 , $CHCl_3$),Chiral Column HPLC (OD-H)1 mL/ min, 100% Hexanes (95:5 er)) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (d, *J* = 7.2 Hz, 3H), 2.30 (s, 3H), 4.50 (q, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 4.5 Hz, 2H), 7.23 (dt, *J* = 8.0, 4.3 Hz, 1H), 7.26 – 7.34 (m, 2H), 7.40 – 7.49 (m, 2H), 7.62 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 9.1 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.93, 22.08, 41.25, 125.42, 125.57, 126.01, 126.21, 126.31, 127.03, 127.06, 127.68, 127.82, 128.04, 130.59, 132.14, 133.65, 136.30, 143.83, 143.95 ppm. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{19}H_{18}$ molecular weight: 246.1399; found 246.1403. Spectral data are in accordance with the literature.[14]

***(+)-4-bromo-1-chloro-2-(1-(4-ethylphenyl)ethyl)benzene* (23)** was synthesized from 4-bromo-1-chloro-2-(1-chloroethyl)benzene and 2-naphthylboronic pinacol ester according to General Procedure E. Product was purified by silica gel flash



column chromatography, eluting with hexanes to afford purified product as a colorless oil (45% spectroscopic yield, 35% isolated yield). A minor impurity seen in alkyl region of ^{13}C was inseparable by silica gel column chromatography. R_f = 0.50 (Hexanes) $[\alpha_D^{24}]$ = 29.3° (c = 1.8, $CHCl_3$),Chiral Column HPLC (OD-H) 0.8 mL/ min, 100% Hexanes (99:1 er)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.6 Hz, 3H), 1.59 (d, *J* = 7.2 Hz, 3H), 2.63 (q, *J* = 7.6 Hz, 2H), 4.57 (q, *J* =

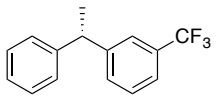
7.2 Hz, 1H), 7.14 (s, 4H), 7.21-7.27 (m, 1H), 7.25 (d, *J* = 2.3 Hz, 1H), 7.35 (d, *J* = 2.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) 15.4, 21.1, 28.4, 40.6, 120.6, 127.5, 127.9, 130.3, 130.9, 131.5, 141.2 ,142.3, 146.1, 152.4 ppm. IR (neat); 2955, 2922, 2872, 2859, 1457, 1378. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{16}H_{16}BrCl$ molecular weight: 322.0042; found 322.0040.

(S)-1-methyl-4-(1-phenylethyl)benzene **(24)** was synthesized from 1-chloroethylbenzene and *p*-tolylboronic pinacol ester according to General Procedure D. Product was purified by silica gel flash column chromatography, eluting with 10% Et_2O in hexanes to afford purified product as a colorless oil (67% spectroscopic yield, 58% isolated yield). R_f = 0.4 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = -1.3° (c = 0.15, $CHCl_3$), Chiral Column HPLC (OD-H 1 mL/ min, 100% Hexanes (74:26 er)) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (d, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 4.12 (q, *J* = 7.2 Hz, 1H), 7.07 – 7.13 (m, 4H), 7.17 (t, *J* = 7.1 Hz, 1H), 7.20 – 7.23 (m, 2H), 7.26-7.29 (m, 2H) ppm. ^{13}C NMR (125MHz, $CDCl_3$) δ 20.98, 21.95, 44.40, 125.94, 127.49, 127.58, 128.34, 129.06, 135.48, 143.42, 146.62 ppm. Spectral data are in accordance with the literature.[15] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[15]

(S)-1-methoxy-4-(1-phenylethyl)benzene **(25)** was synthesized from 1-chloroethylbenzene and *p*-methoxyphenylboronic pinacol ester according to General Procedure C. Product was purified by silica gel flash column chromatography, eluting with 10% Et_2O in hexanes to afford purified product as a colorless oil (67% spectroscopic yield, 59% isolated yield). R_f = 0.43 (10% Et_2O in Hexanes), $[\alpha_D^{24}]$ = 4.49° (c = 0.8, $CHCl_3$), Chiral Column HPLC (OJ-H) 1 mL/ min, 99:1 Hexanes:IPA (81:19 er)) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (d, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 4.12 (q, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 7.15 (*J* = 8.7 Hz, 2H), 7.18 – 7.24 (m, 3H), 7.25 – 7.30 (m, 3H) ppm; ^{13}C NMR (125MHz, $CDCl_3$) δ 22.27, 44.15, 55.46, 113.93, 126.13, 127.74, 128.53, 128.72, 138.77, 146.98, 158.04 ppm.

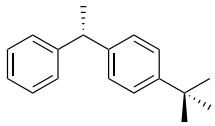
HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{15}H_{16}O$ molecular weight: 212.1271; found 212.1274. Spectral data are in accordance with the literature.[16] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[16]

(*R*)-1-(1-phenylethyl)-3-(trifluoromethyl)benzene. (26) was synthesized from 1-chloroethylbenzene and *m*-trifluoromethylphenylboronic pinacol ester



according to General Procedure C. Product was purified by silica gel flash column chromatography, eluting with 5% Et_2O in hexanes to afford purified product as a colorless oil (44% spectroscopic yield, 39% isolated yield). The dimer of the alkyl halide was a minor impurity which was inseparable by silica gel column chromatography. R_f = 0.43 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = 0.52° (c = 0.77, $CHCl_3$), Chiral Column HPLC (OJ-H 1 mL/ min, 100% Hexanes (80:20 er)) ^1H NMR (500 MHz, $CDCl_3$) δ 1.69 (dd, *J* = 7.2, 2.3 Hz, 3H), 4.23 (q, *J* = 7.2 Hz, 1H), 7.24 (ddt, *J* = 7.7, 5.9, 2.6 Hz, 3H), 7.33 (td, *J* = 7.9, 2.3 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.50 – 7.45 (m, 1H) 7.52 (s, 1H) ppm. ^{13}C NMR (125MHz, $CDCl_3$) δ 21.7, 44.6, 123.0 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 3.8 Hz), 124.7, 126.4, 127.5, 128.6, 128.8, 130.5 (q, *J* = 32 Hz), 131.1, 145.3, 147.3 ppm. HRMS (ESI) *m/z* $[M]^+$ calcd. for $C_{15}H_{13}F_3$ molecular weight: 250.0890; found 250.0886. Spectral data are in accordance with the literature.[17] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[18]

***(S)-1-tertbutyl-4-(1-phenylethyl)benzene* (27)** was synthesized from 1-chloroethylbenzene and *p*-tert-butylphenylboronic pinacol ester according to

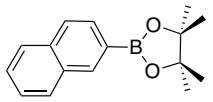


General Procedure C. Product was purified by silica gel flash column chromatography, eluting with 10% Et_2O in hexanes to afford purified product as a colorless oil (47% spectroscopic yield, 43% isolated yield). R_f = 0.5 (5% Et_2O in Hexanes), $[\alpha_D^{24}]$ = 1.28° (c = 0.312, $CHCl_3$), Chiral Column HPLC (OJ-H, 1 mL/ min, 100% Hexanes (79:21 er)) ^1H NMR (500 MHz, $CDCl_3$) δ 1.30 (s, 9H), 1.64 (d, *J* = 7.2 Hz, 3H), 4.13 (q, *J* = 7.3 Hz, 1H), 7.15 – 7.20 (m, 3H), 7.23 – 7.36 (m,

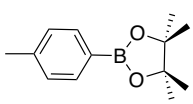
6H), 7.44 – 7.57 (AB_q, J = 31 Hz) ppm. ^{13}C NMR (125MHz, $CDCl_3$) δ 22.06, 31.55, 34.50, 44.50, 125.36, 126.10, 127.32, 127.78, 128.47, 143.39, 146.77 ppm. HRMS (ESI) *m/z* $[M]^{+3}$ calcd. for $C_{15}H_{22}$ molecular weight: 238.1644; found 238.1638. Spectral data are in accordance with the literature.[15] Absolute configuration assigned by reference to literature retention times of chiral column HPLC and sign of optical rotation.[15]

General procedure for the preparation of arylboronic pinacol esters. All boronic esters were prepared according to a procedure adapted from previous syntheses.[19] To an oven-dried 250 mL two-neck flask containing a stir bar under a nitrogen atmosphere was added arylboronic acid (30 mmol) and anhydrous pentane (110 mL). The flask was brought to 0 ºC and pinacol (31 mmol) was added to the reaction. The reaction was stirred at room temperature for 24 hours. Na_2SO_4 was added to the solution and then filtered, washed with diethyl ether, and concentrated *in vacuo to* yield a crude white solid. The white solid was dissolved in dichloromethane and passed through a plug of silica gel eluting with excess dichloromethane to afford product that was analytically pure by ^1H NMR spectroscopy.

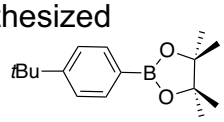
4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane was synthesized according to the general procedure using naphthalen-2-ylboronic acid(10 g, 58.14 mmol) and pinacol (6.87 g, 58.14 mmol) to afford a crystalline white solid (12 g, 81%). ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 12 H), 7.48 (m, 2 H), 7.81–7.84 (m, 3H), 7.85–7.89 (m, 1H), 8.37 (s, 1H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.30 ppm. Spectral data are in accordance with the literature.[20]



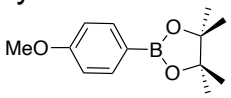
4,4,5,5-tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane was synthesized according to the general procedure using *p*-tolylboronic acid (1.00 g, 7.36 mmol)



and pinacol (912 mg, 7.36 mmol) to afford a crystalline white solid (1.55 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 12H), 2.36 (s, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.44 ppm. Spectral data are in accordance with the literature.[20]

2-(4-(*tert*-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was synthesized according to the general procedure using (4-(*tert*-butyl)phenyl)boronic acid 

(2.00 g, 11.23 mmol) and pinacol (1.33 g, 11.23 mmol) to afford a crystalline white solid (2.80 g, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.32 (s, 9H), 1.33 (s, 12H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 25.60 ppm. Spectral data are in accordance with the literature.[21]

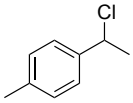
2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was synthesized according to the general procedure using (4-methoxyphenyl)boronic acid 

(3.25 g, 21.39 mmol) and pinacol (6.87 g, 58.14 mmol) to afford a crystalline white solid (4.50 g, 89%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 1.33 (s, 12H), 3.83 (s, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.68 ppm. Spectral data are in accordance with the literature.[21]

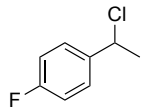
General procedure for the preparation of benzylic chlorides: All benzylic chlorides were prepared according to a procedure adapted from previous syntheses.[22] To an oven-dried 100 mL two-neck flask containing a stir bar under a nitrogen atmosphere was added benzylic alcohol (10 mmol) and anhydrous CH_2Cl_2 (20 mL). The flask was equipped with an outlet connected to a beaker of $NaHCO_3$ (aq) to quench HCl gases. The flask was brought to 0 ºC and thionyl chloride (10 mmol) was added dropwise. The reaction was allowed to stir at room temperature for 1-18 hours and monitored by TLC. The reaction was concentrated *in vacuo to* yield a crude

oil which was either purified by Kugelrohr distillation or passed through a plug of silica gel eluting with hexanes. Product was afforded that was analytically pure by ^{1}H NMR spectroscopy.

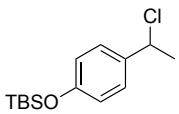
1-(1-chloroethyl)-4-methyl-benzene **(13a)** was synthesized according to the general procedure using 1-(*p*-tolyl)ethanol (1.5 mL, 10.9 mL) to afford purified product as a colorless oil (1.0 g, 59%). R_f = 0.9 (20% EtOAc/Hex). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 1.49 (d, *J* = 6.4 Hz, 4H), 2.35 (s, 3H), 4.87 (qd, *J* = 6.6, 2.3 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H) ppm. Spectral data are in accordance with the literature.[23]



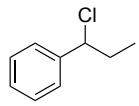
1-(1-chloroethyl)-4-fluoro-benzene **(14a)** was synthesized according to the general procedure using 1-(*p*-fluoro)ethanol (1.5 mL, 11.9 mmol) to afford purified product as a colorless oil (1.5 g, 77%).R_f = 0.9 (20% EtOAc/Hex). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.47 (d, *J* = 6.4 Hz, 3H), 4.88 (qd, *J* = 6.4, 3.2 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 7.29 – 7.38 (m, 2H) ppm. Spectral data are in accordance with the literature.[23]



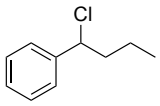
***tert*-butyl(4-(1-chloroethyl)phenoxy)dimethylsilane (15a)** was synthesized according to the general procedure using 1-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)ethan-1-ol (1.15 mL, 17.6 mmol) to afford purified product as a colorless oil (4.0 g, 84%). (R_f = 0.9, Hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.20 (s, 6H), 0.95 – 1.01 (m, 9H), 1.83 (d, *J* = 6.8 Hz, 3H), 5.08 (q, *J* = 6.8 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ -4.31, 18.28, 25.77, 26.57, 58.87, 120.12, 127.83, 135.72, 155.71 ppm.; IR (neat): 2956, 2929, 2858, 1607, 1512, 1268. HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_{14}H_{23}OSiCl$ molecular weight: 270.1276; found 270.1280.



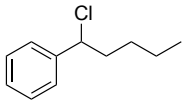
1-chloroethylbenzene (16a) was synthesized according to the general procedure using 1-phenylpropan-1-ol (1.15 mL, 17.6 mmol) to afford purified product as a colorless oil (4.0 g, 84%). R_f = 0.9 (20% EtOAc/Hex). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7.3 Hz, 3H), 2.03 – 2.20 (m, 2H), 4.79 (dd, *J* = 8.0, 6.4 Hz, 1H), 7.28 – 7.32 (m, 1H), 7.33 – 7.41 (m, 4H) ppm. Spectral data are in accordance with the literature.[23]



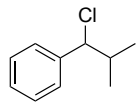
1-chlorobutylbenzene **(17a)** was synthesized according to the general procedure using 1-phenylbutan-1-ol (1.50 mL, 9.79 mmol) to afford purified product as a colorless oil (1.33 g, 80%). R_f = 0.9 (20% EtOAc/Hex). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H), 1.26 – 1.35 (m, 1H), 1.43 (ddd, *J* = 13.1, 10.3, 5.6 Hz, 1H), 1.68 (ddt, *J* = 13.5, 9.9, 5.8 Hz, 1H), 1.74 – 1.84 (m, 2H), 4.68 (ddd, *J* = 8.5, 6.0, 3.0 Hz, 1H), 7.24 – 7.30 (m, 1H), 7.32 – 7.36 (m, 3H) ppm. Spectral data are in accordance with the literature.[24]



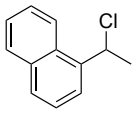
1-chloropentylbenzene **(18a)** was synthesized according to the general procedure using 1-phenylpentan-1-ol (1.50 mL, 8.77 mmol) to afford purified product as a colorless oil (1.34 g, 83%). R_f = 0.9 (20% EtOAc/Hex) ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.20 – 1.53 (m, 4H), 1.96 – 2.21 (m, 2H), 4.84 (dd, *J* = 8.1, 6.5 Hz, 1H), 7.24 – 7.46 (m, 5H) ppm. Spectral data are in accordance with the literature.[24]



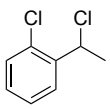
(1-chloro-2-methylpropyl)benzene (19a) was synthesized according to the general procedure using 2-methyl-1-phenylpropan-1-ol (1.50 mL, 10.0 mmol) to afford purified product as a colorless oil (1.31 g, 77%).R_f = 0.9 (20% EtOAc/Hex). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.79 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H), 4.36 (dd, *J* = 6.9, 3.0 Hz, 1H), 7.24 – 7.36 (m, 5H) ppm. Spectral data are in accordance with the literature.[25]



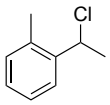
1-(1-chloroethyl)naphthalene (20a) was synthesized according to the general procedure using 1 -phenylpentan-1-ol (1.50 mL, 8.77 mmol) to afford purified product as a colorless oil (1.34 g, 83%).R_f = 0.9 (20% EtOAc/Hex). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.06 (dd, *J* = 6.9, 0.9 Hz, 3H), 5.90 (q, *J* = 6.8 Hz, 1H), 7.45 – 7.54 (m, 2H), 7.55 – 7.61 (m, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H) ppm. Spectral data are in accordance with the literature.[24]



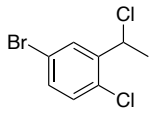
1-chloro-2-(1-chloroethyl)benzene (21a) was synthesized according to the general procedure using 1-(2-chlorophenyl)ethan-1-ol (1.50 g, 9.58 mmol) to afford purified product as a colorless oil (1.34 g, 79%).R_f = 0.9 (20% EtOAc/Hex). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (d, *J* = 6.8 Hz, 3H), 5.58 (q, *J* = 6.8 Hz, 1H), 7.18 – 7.27 (m, 1H), 7.28 – 7.38 (m, 2H), 7.64 (dd, *J* = 7.8, 1.7 Hz, 1H) ppm.Spectral data are in accordance with the literature.[24]



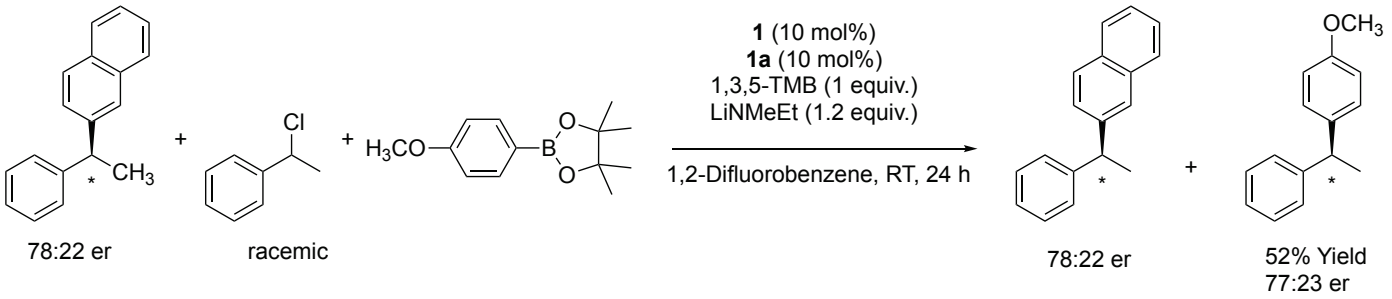
1-(1-chloroethyl)-2-methylbenzene (22a). To a 100 mL 1-(*o*-tolyl)ethan-1-ol (2.00 mL, 14.69 mmol) to afford purified product as a colorless oil (2.00 g, 88%). R_f = 0.9 (20% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.87 (d, *J* = 6.9 Hz, 3H), 2.42 (s, 3H), 5.35 (q, *J* = 6.8 Hz, 1H), 7.13 – 7.28 (m, 4H), 7.53 (dd, *J* = 7.6, 1.5 Hz, 1H) ppm.Spectral data are in accordance with the literature.[23]

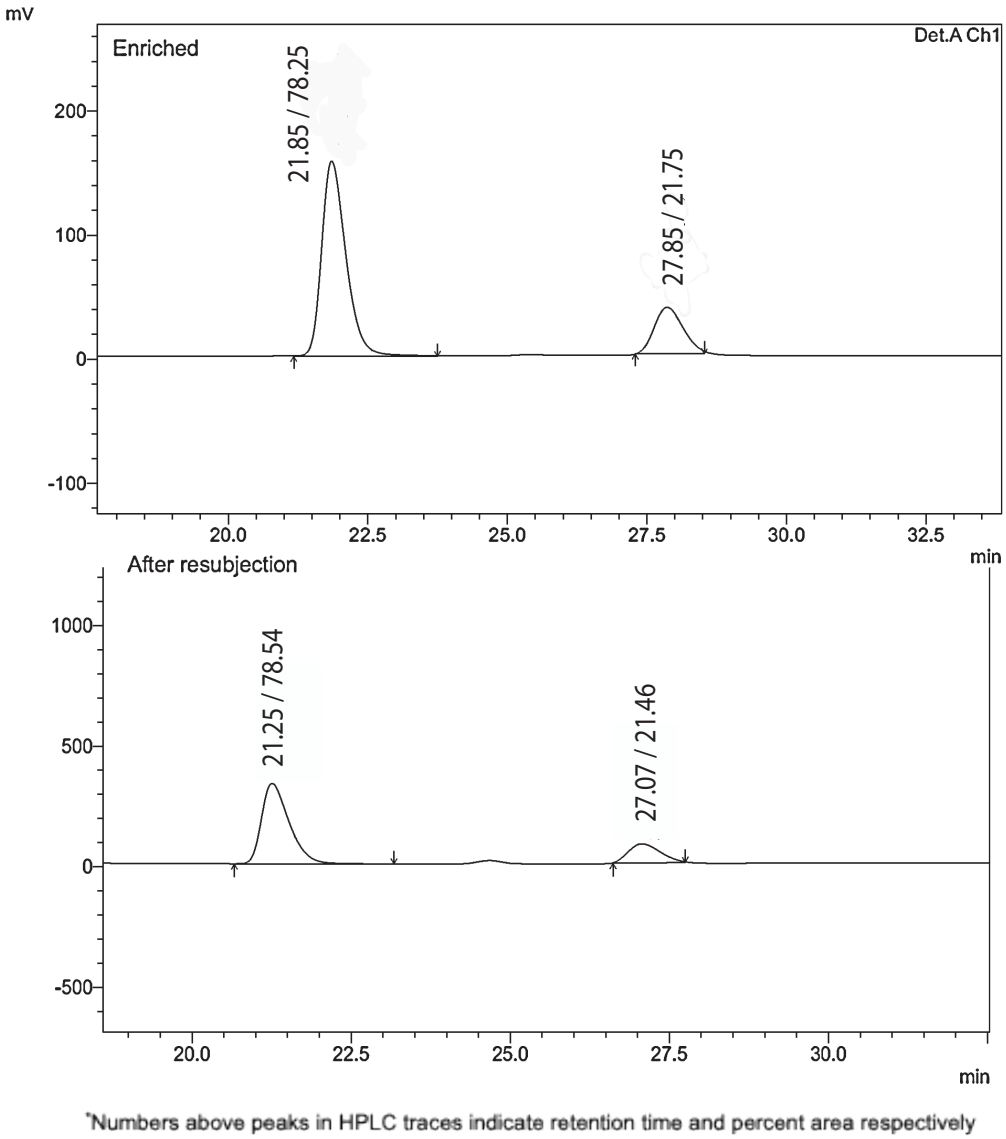


4-bromo-1-chloro-2-(1-chloroethyl)benzene (23a) To a two-neck flask with stir bar under a N_2 atmosphere was added 1-(5-bromo-2-chlorophenyl)ethan-1-ol(1.55 g, 6.58 mmol) and anhydrous CH_2Cl_2 (25 mL). PCl_5 (1.37 g, 6.58 mmol) was added to the flask at 0° C. The reaction was slowly warmed to room temperature and allowed to stir for 2 hours. The reaction was quenched with deionized H_2O (10 mL) and the collected aqueous layers were extracted with dichloromethane (3 x 40 mL). The combined organic layers were washed with $NaHCO_3$ (aq) (20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo.* The concentrate



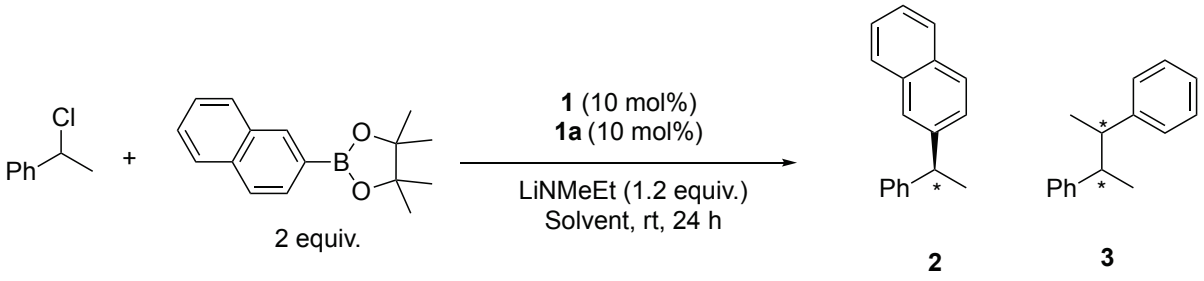
was passed through a plug of silica gel and washed with excess hexanes to afford purified product as a colorless oil (2.00 g, 88%). (R_f = 0.9, Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (d, *J* = 7.0, 3H), 5.42 – 5.51 (q, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 8.6, 1H), 7.76 (s, 1H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ 25.51, 53.69, 121.00, 130.96, 130.99, 132.26, 141.97, 223.78 ppm; IR (neat):2926, 2852, 1465, 1389, 1263, 1070. HRMS (ESI) *m/z* $[M]^+$ calcd. For $C_8H_6Cl_2Br$ molecular weight: 251.9113; found 251.9103.





*Numbers above peaks in HPLC traces indicate retention time and percent area respectively

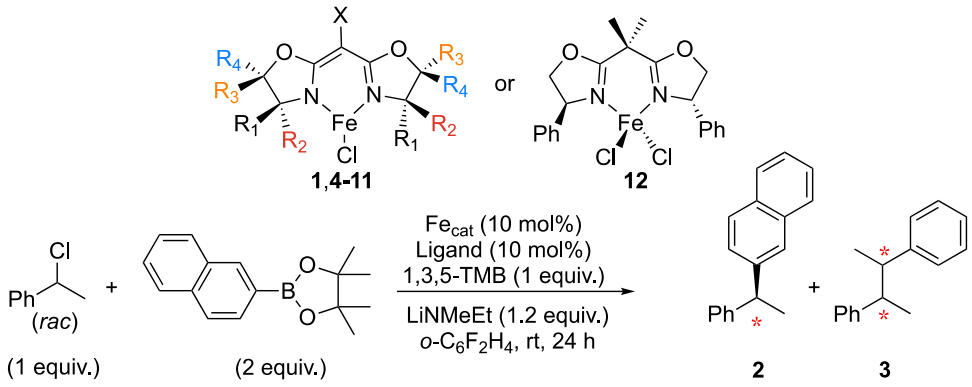
Figure S2. Subjection of enantiomerically enriched diarylalkane product to a cross-coupling reaction between 1-chloroethylbenzene and 4-methoxyphenyl boronic pinacol ester



Entry	Solvent	Additive	Yield **2** (%)[a]	er of **2**[b]	Yield **3** (%)[a]
1	Benzene	None	64	74:26	10
2	MTBE	None	13	N/A	10
3	Trifluorotoluene	None	55	76:24	12
4	Fluorobenzene	None	49	81:19	8
5	Anisole	None	61	74:26	9
6	1,2-difluorobenzene	None	66	76:24	11
7[c]	1,2-difluorobenzene	1,3,5-TMB	73	79:21	9
8[d]	1,2-difluorobenzene	1,3,5-TMB	75	81:19	8
9[c]	1,4-difluorobenzene	1,3,5-TMB	75	77:23	18
9[e]	Benzene	1,2,4-TMB	Trace	N/A	90
10[f]	Benzene	DME	0	N/A	N/A
11[g]	1,2-difluorobenzene	NaI	45	76:24	20
11[h]	1,2-difluorobenzene	TEMPO	14	79:21	21

[a] Yields were determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] enantiomeric ratios were determined by chiral column HPLC. [c] 1,3,5-trimethoxybenzene (1 equiv.) added. [d] 1,3,5-trimethoxybenzene (5 equiv.) added. [e] 1,2,4-trimethoxybenzene (5 equiv.) added. [f] dimethoxyethane (1 equiv.) added. [g] Sodium iodide (0.5 equiv.) added. [h] TEMPO (0.1 equiv.) added.

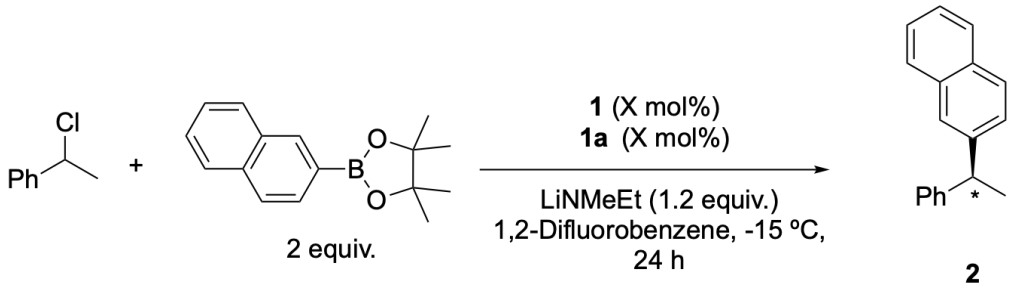
Table S1. Solvent and additive screen for the cross-coupling reaction between 1-chloroethylbenzene and 2-naphthylboronic pinacol ester



Entry	Fe_{cat}	R_1	R_2	R_3	R_4	X	**2** (%)[a]	er of **2**[b]	**3** (%)[a]
1[c,e]	**1**	Ph	H	H	H	CN	64	74:26	9
2[c,e]	$FeCl_2$	Ph	H	H	H	CN	19	74:26	19
3	**1**	Ph	H	H	H	CN	73	79:21	9
4	**4**	H	3,5-*t*BuPh	H	H	CN	36	32:68	9
5	**5**	Mes	H	H	H	CN	15	65:35	27
6	**6**	H	Ph	H	Ph	CN	71	26:74	5
7	**7**	Ph	H	Ph	Ph	CN	64	65:35	13
8	**8**	Bn	H	H	H	CN	8	61:39	33
9	**9**	*t*Bu	H	H	H	CN	0	N/A	0
10	**10**	*i*Pr	H	H	H	CN	16	73:27	20
11	**11**	Ph	H	H	H	H	57	76:24	18
12	**12**	Ph	N/A	N/A	N/A	N/A	0	N/A	45
13[d]	**1**	Ph	H	H	H	CN	85	77:23	5
14[d,e]	**1**	Ph	H	H	H	CN	68	75:25	9
15[f]	**1**	Ph	H	H	H	CN	90	85:15	0

[a] Yields determined by ^{1}H-NMR spectroscopy relative to an internal or external standard. [b] enantiomeric ratios determined by chiral column HPLC. [c] Benzene was used as the solvent. [d]]No extra ligand [e] No 1,3,5-TMB additive. [f] 5% ligand at -15 °C for 24 hours.

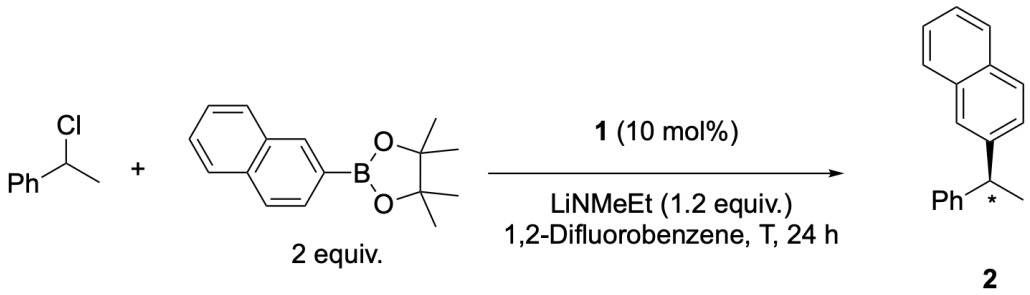
Table S2. Optimization of the Suzuki-Miyaura cross-coupling reaction between 1-chloroethylbenzene and 2-napthylboronic pinacol ester catalyzed by bis(oxazoline) iron complexes.



Entry	Fe-Loading (mol%)	[R-Cl]	Yield of **2**[a]	er of **2**[b]
1	5	83 mM	59	83:17
2	10	83 mM	90	84:16
3	15	83 mM	81	82:18
4	10	42 mM	72	83:17
5	10	63 mM	90	83:17
6	10	125 mM	73	84:16

[a] Yields were determined by $_1$H-NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] enantiomeric ratios were determined by chiral column HPLC.

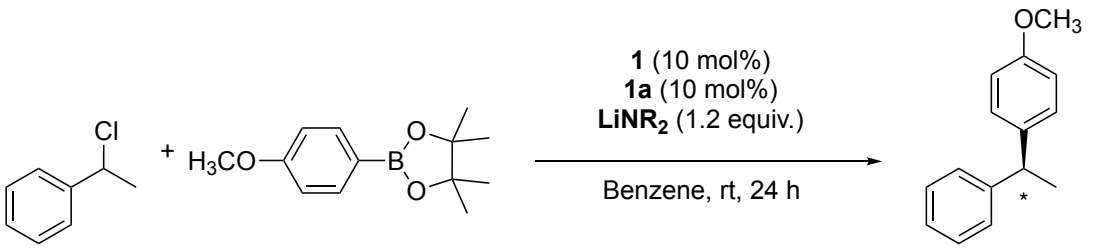
Table S3. Effect of catalyst loading and alkyl halide concentration on the cross-coupling reaction between 1-chloroethylbenzene and 2-naphthylboronic pinacol ester



Entry	Temperature (°C)	Yield of **2**[a]	er of **2**[b]
1	rt	90	77:23
2	-15	90	80:20
3[c]	-15	90	85:15
4	-25	57	78:22
5	-50	13	79:21

[a] Yields were determined by $_1$H-NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] enantiomeric ratios were determined by chiral column HPLC. [c] 5% ligand

Table S4. Effect of temperature on the cross-coupling reaction between 1-chloroethylbenzene and 2-naphthylboronic pinacol ester

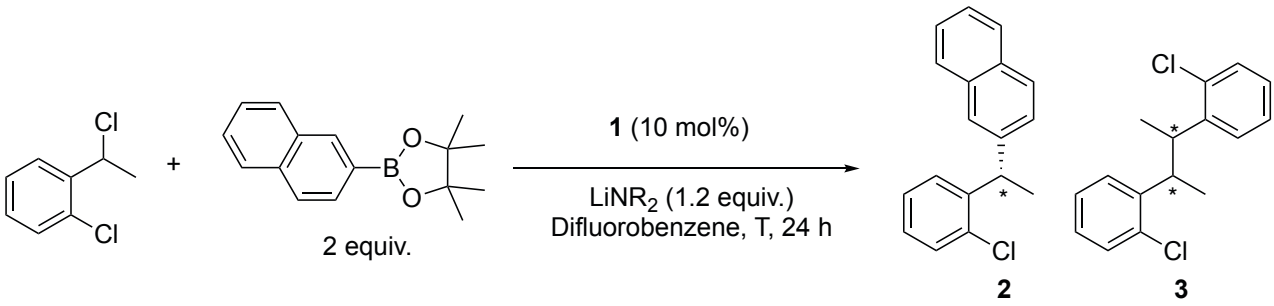


racemic

Entry	Base	Yield **2** (%)[a]	er of **2**[b]
1	$LiNMe_2$	0	N/A
2	LiNMeEt	25	76:24
3[c]	LiNMeEt	42	76:24
4	$LiNEt_2$	0	N/A
5	LiMeBu	0	N/A

[a] Yields were determined by $_1$H-NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] enantiomeric ratios were determined by chiral column HPLC. [c] 1,3,5-trimethoxybenzene (1 equiv.) added.

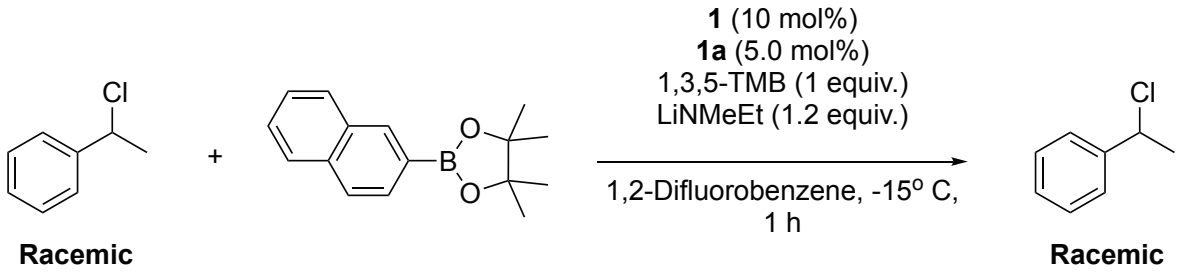
Table S5. Effect of amide base on the cross-coupling reaction between1-chloroethylbenzene and 4-methoxyphenyl boronic pinacol ester



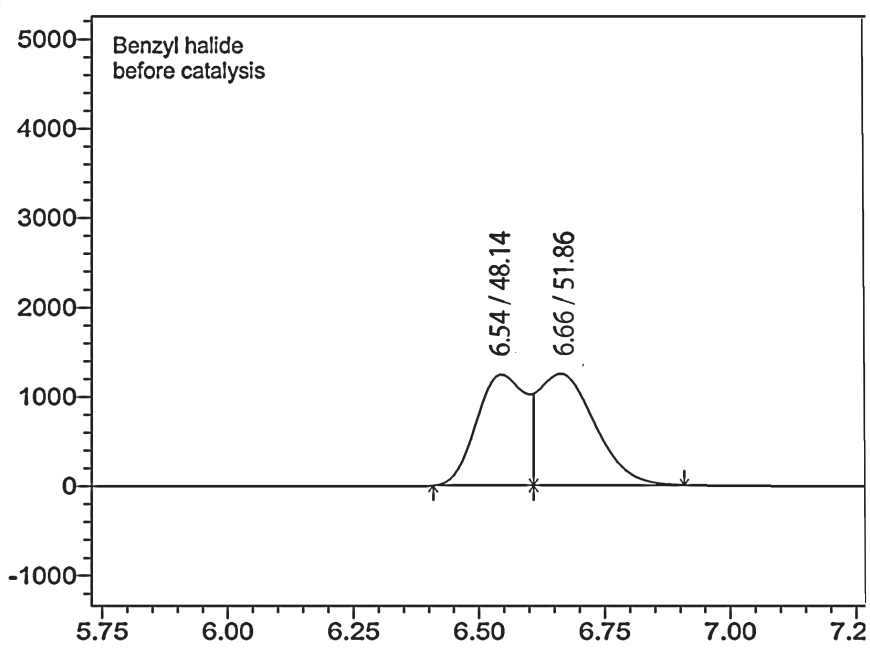
Entry	[Fe] (mol%)	T (ºC)	$LiNR_2$	1,3,5-TMB (equiv.)	Yield **2** (%)[a]	er of **2**[b]	Yield **3** (%)[a]
1	10	-15	LiNMeEt	1	24	92:8	32
2	10	-10	LiNMeEt	3	45	92:8	32
3	20	-15	LiNMeEt	3	48	92:8	38
4	15	-15	$LiNMe_2$	2	54	92:8	12

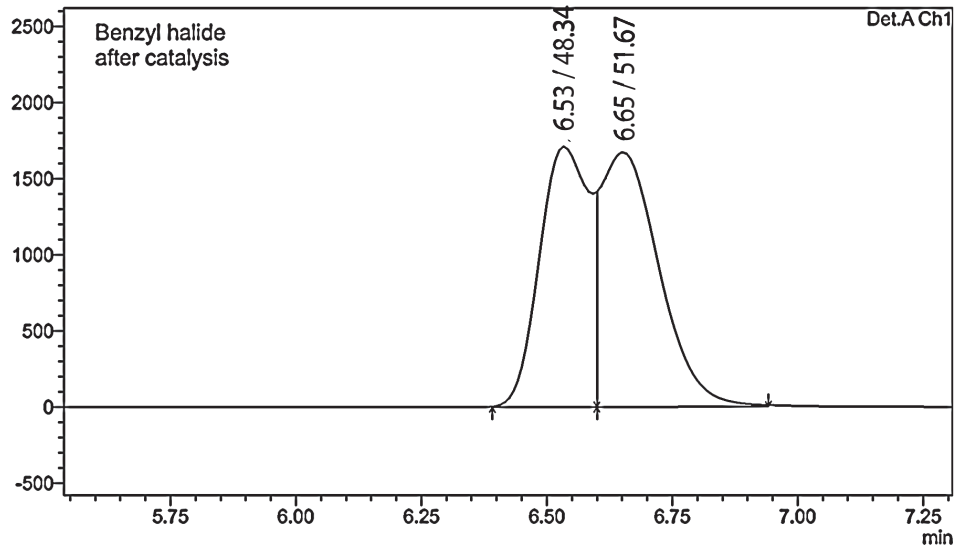
[a] Yields were determined by $_1$H-NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] enantiomeric ratios were determined by chiral column HPLC.

Table S6. Optimization of conditions for coupling ortho-substituted alkyl halides specifically for 1-chloro-2-(1-chloroethyl)benzene and 2-naphthylboronic pinacol ester



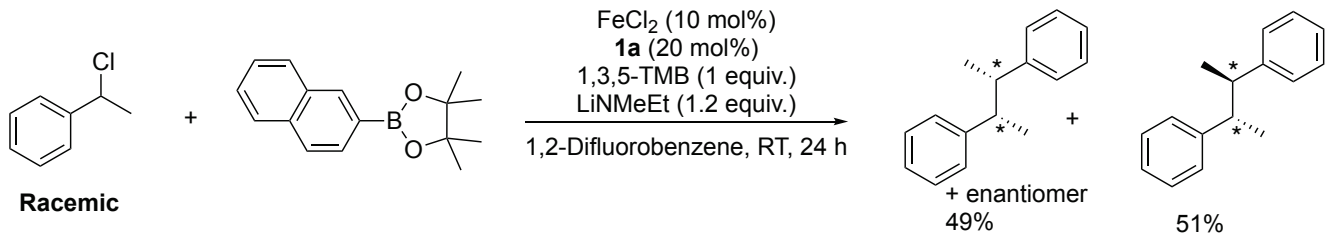
Racemic **Racemic**

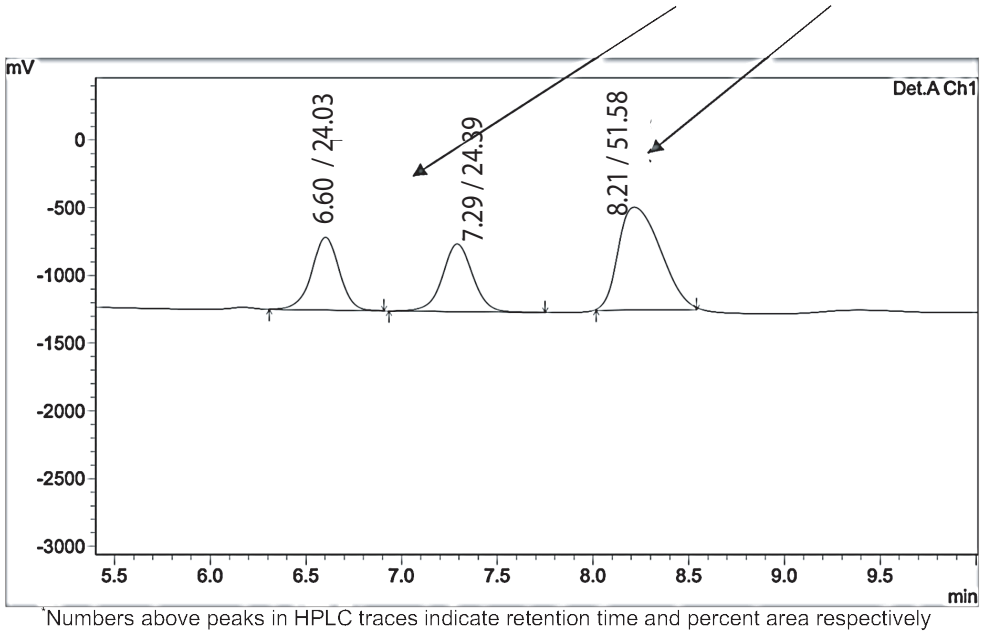




*Numbers above peaks in HPLC traces indicate retention time and percent area respectively

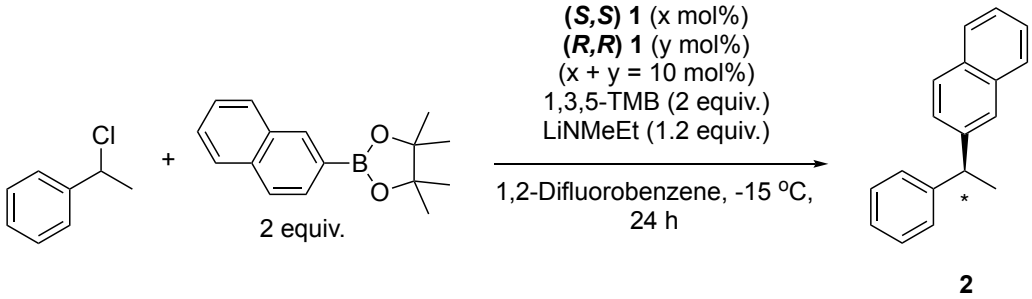
Figure S3. Enantiopurity of benzylic chloride starting material before and after catalysis at partial conversion





Numbers above peaks in HPLC traces indicate retention time and percent area respectively

Figure S4. Analysis of the enantiopurity of the dimer product after catalysis



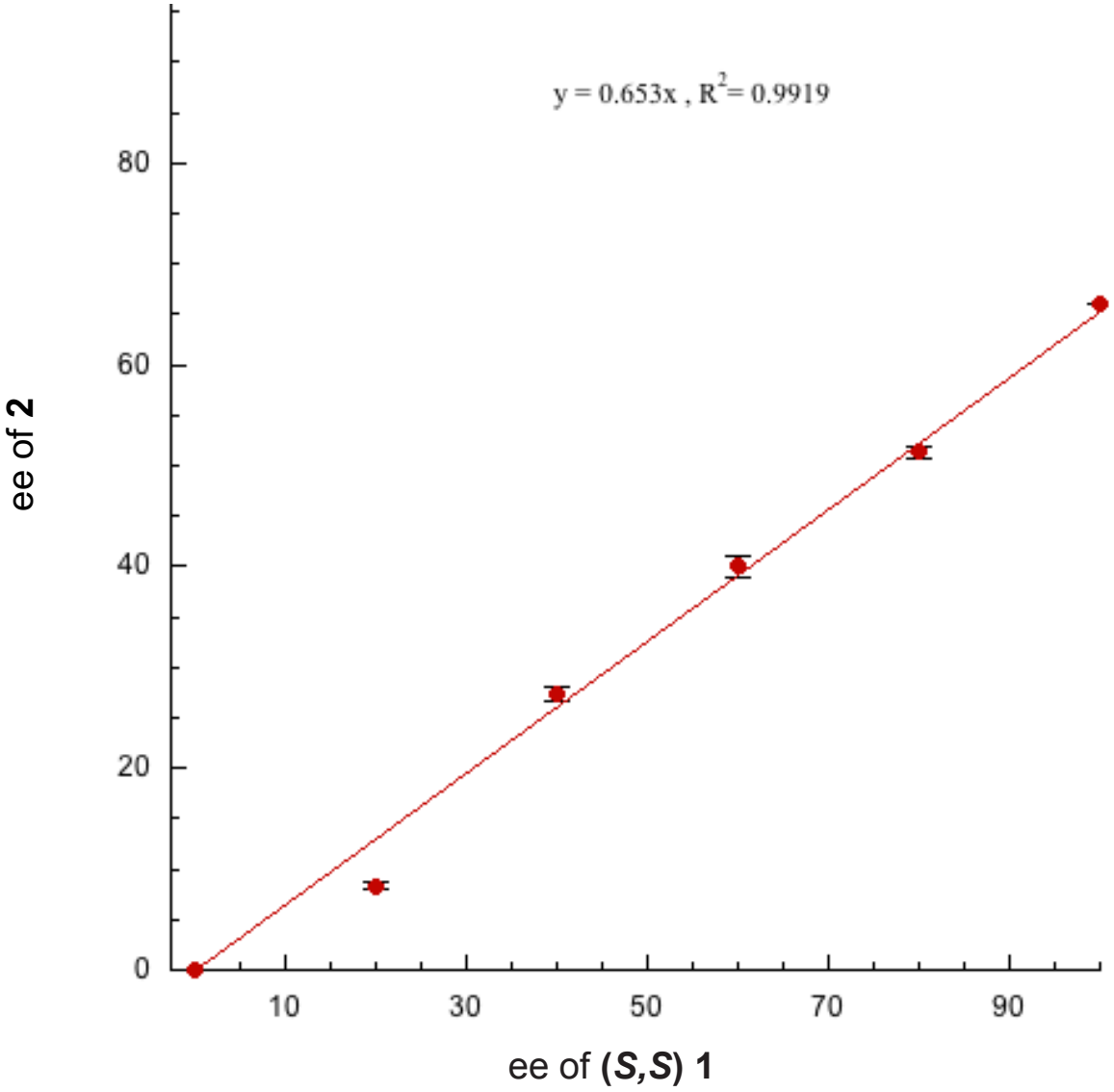


Figure S5. Non-linear effect experiment between diarylalkane product **2** and iron complex **1**

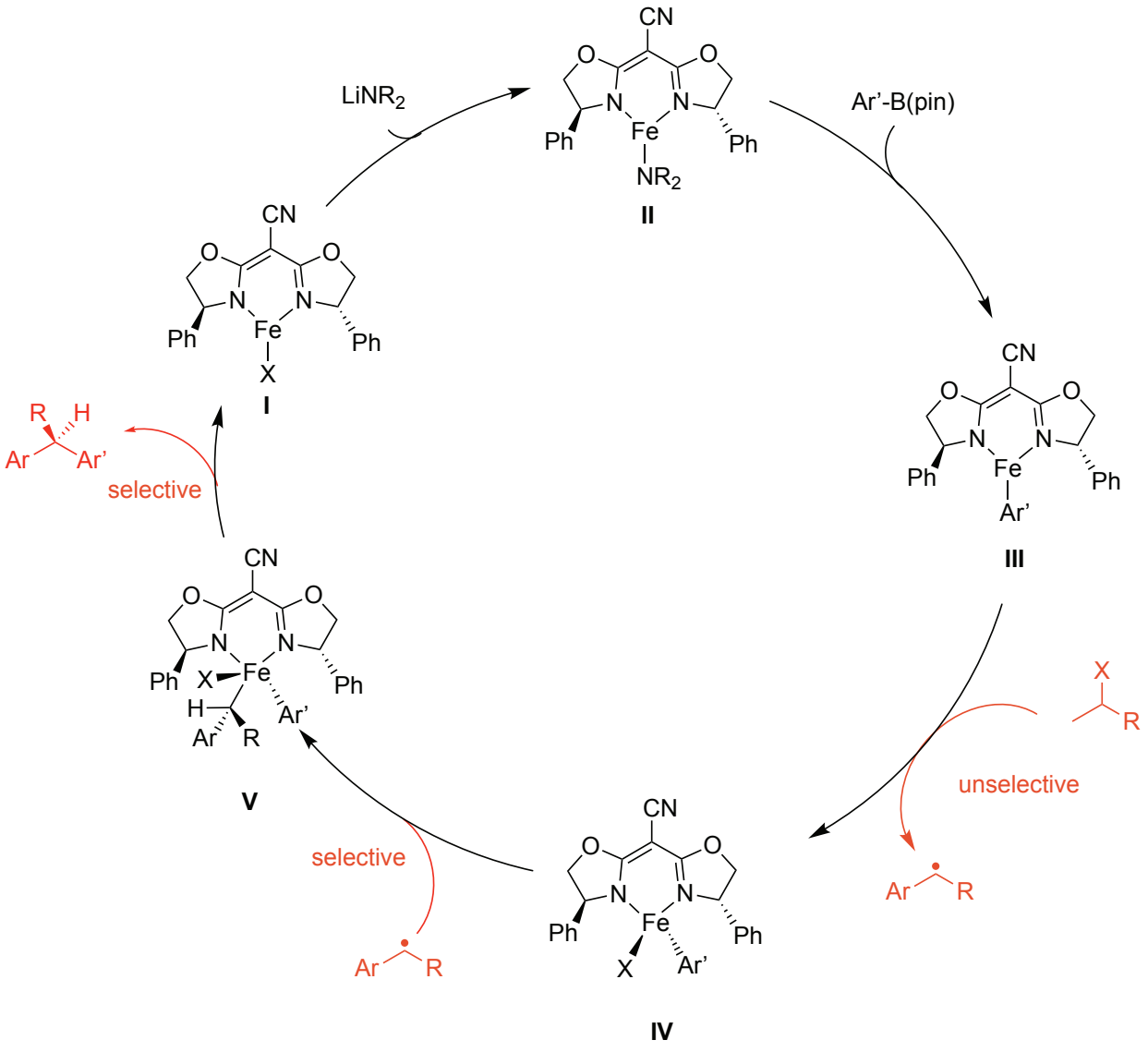


Figure S6. Mechanistic cycle for the Suzuki-Miyaura cross-coupling between benzylic halides and arylboronic pinacol esters catalysed by iron-cyanobis(oxazoline) complexes involving an iron(IV) intermediate.

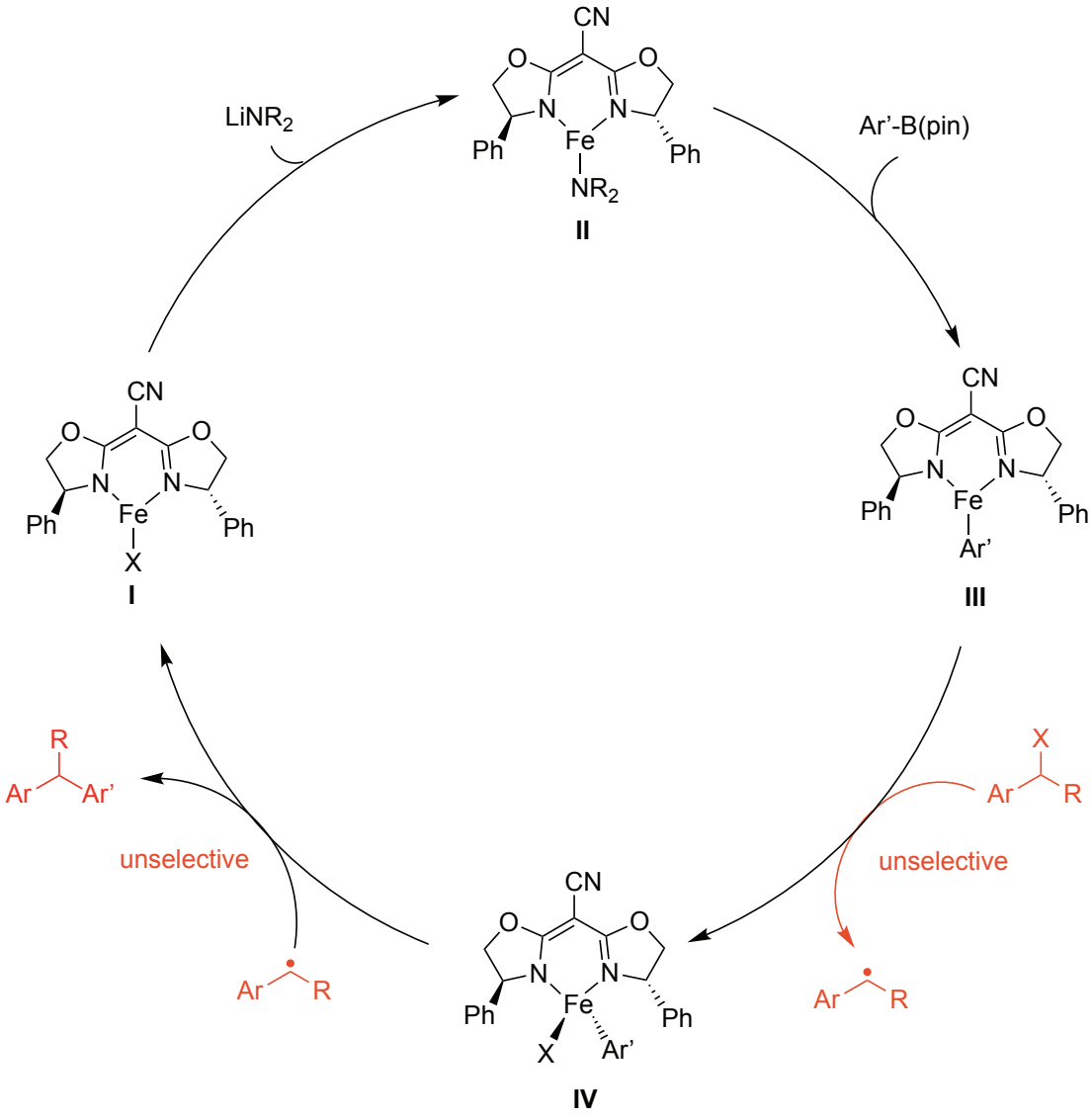
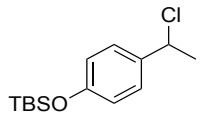


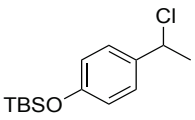
Figure S7. Mechanistic cycle for the Suzuki-Miyaura cross-coupling between benzylic halides and arylboronic pinacol esters catalysed by iron-cyanobis(oxazoline) complexes with an unselective radical rebound

NMR Spectra and HPLC Traces:

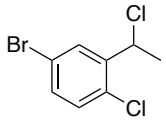
^{1}H, 600 MHz, $CDCl_3$

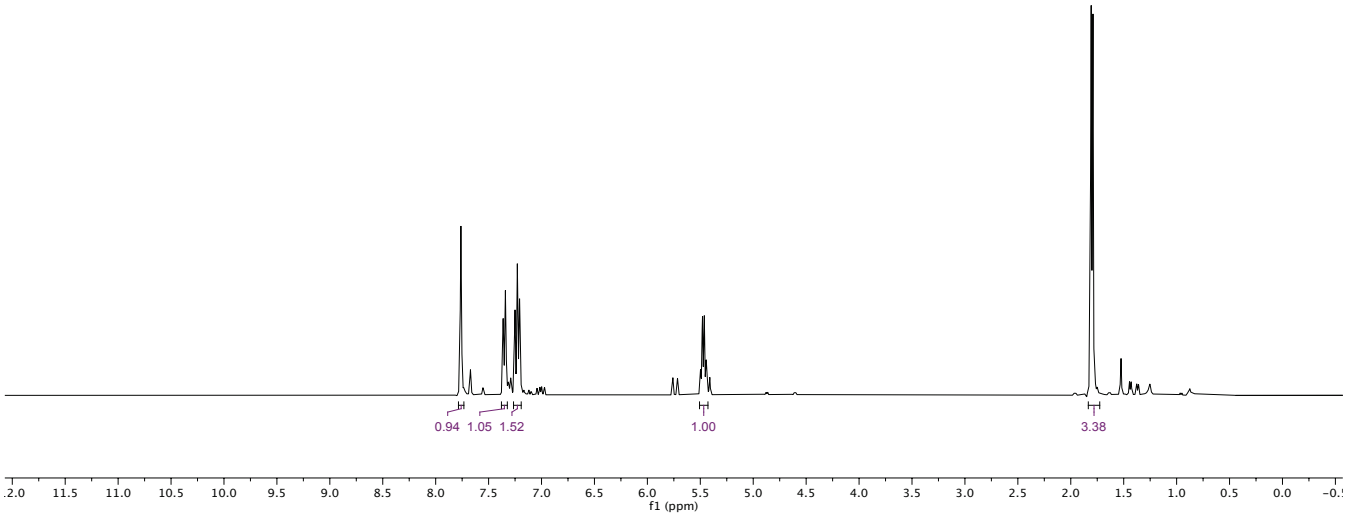


^{1}H, 125 MHz, $CDCl_3$

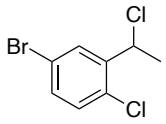


^{1}H, 400 MHz, $CDCl_3$

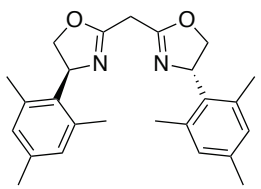




^{13}C, 125 MHz, $CDCl_3$

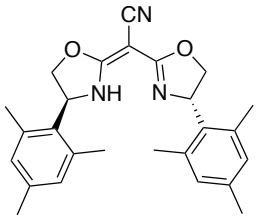


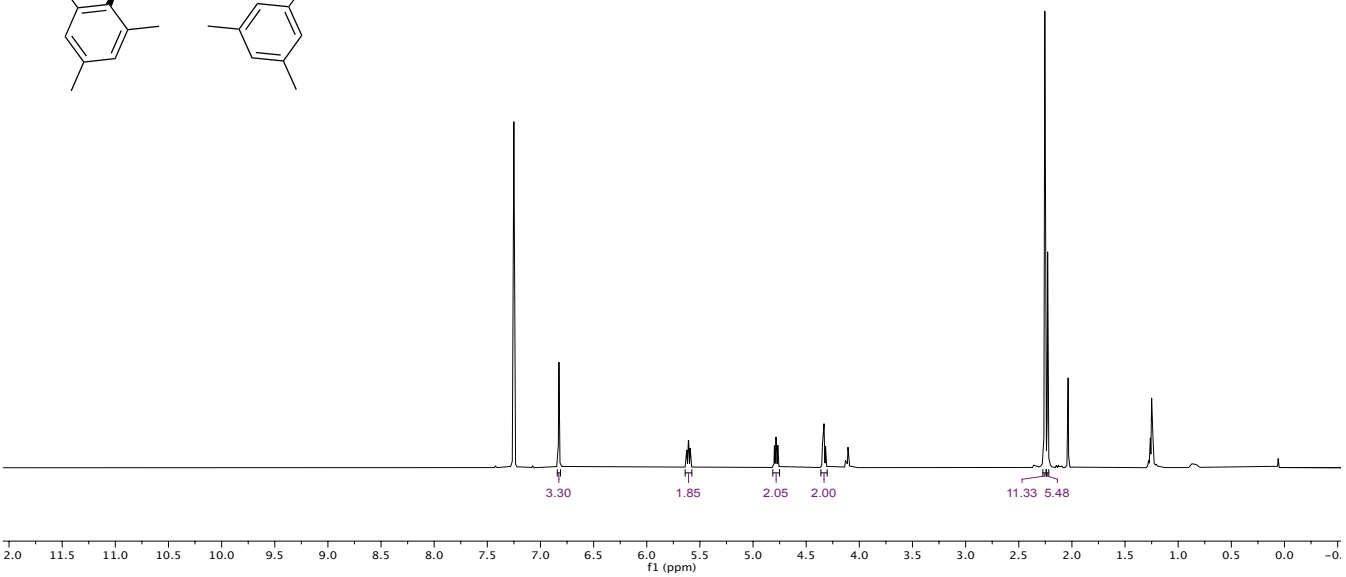
^{1}H, 500 MHz, $CDCl_3$



^{1}H, 500 MHz, $CDCl_3$

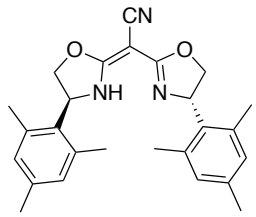
5a

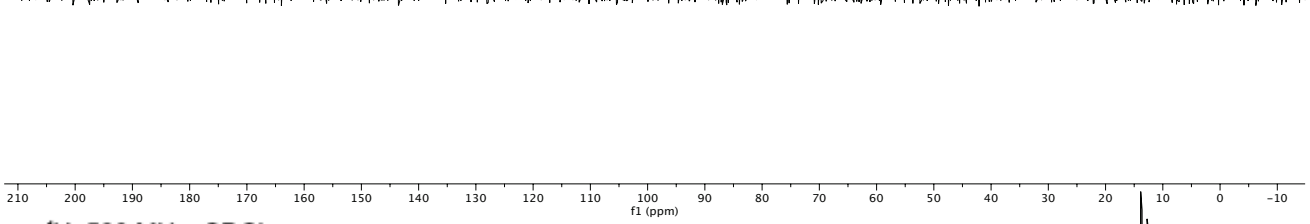




^{13}C, 125 MHz, $CDCl_3$

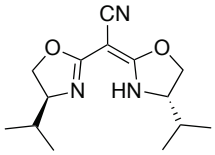
5a





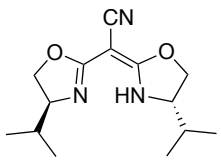
^{1}H, 500 MHz, $CDCl_3$

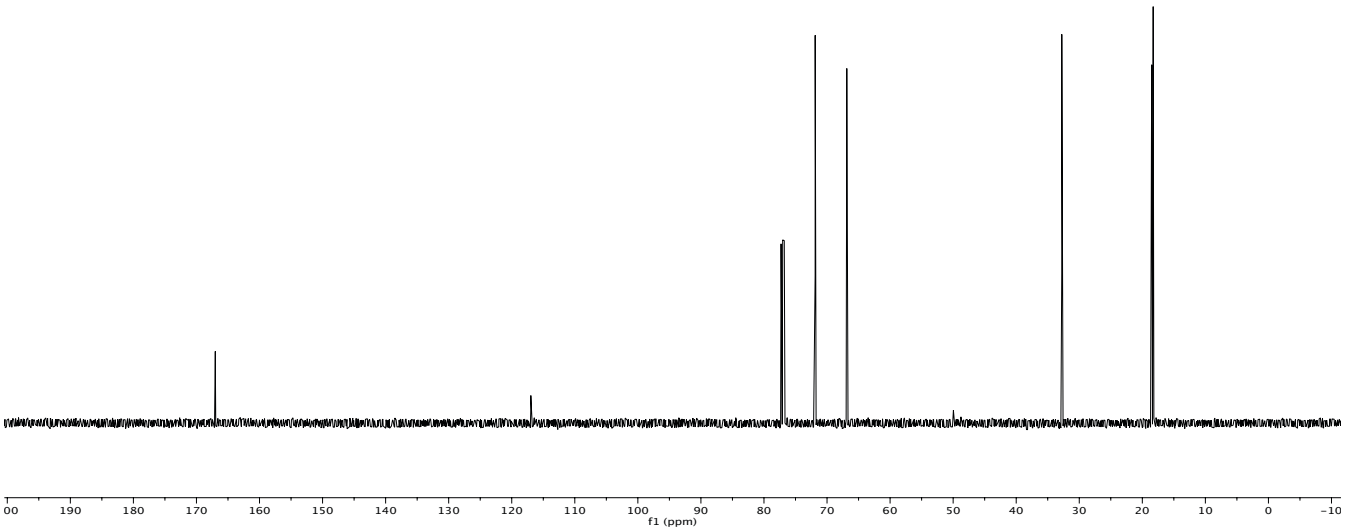
10a



^{13}C, 125 MHz, $CDCl_3$

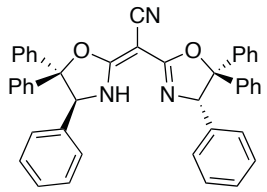
10a

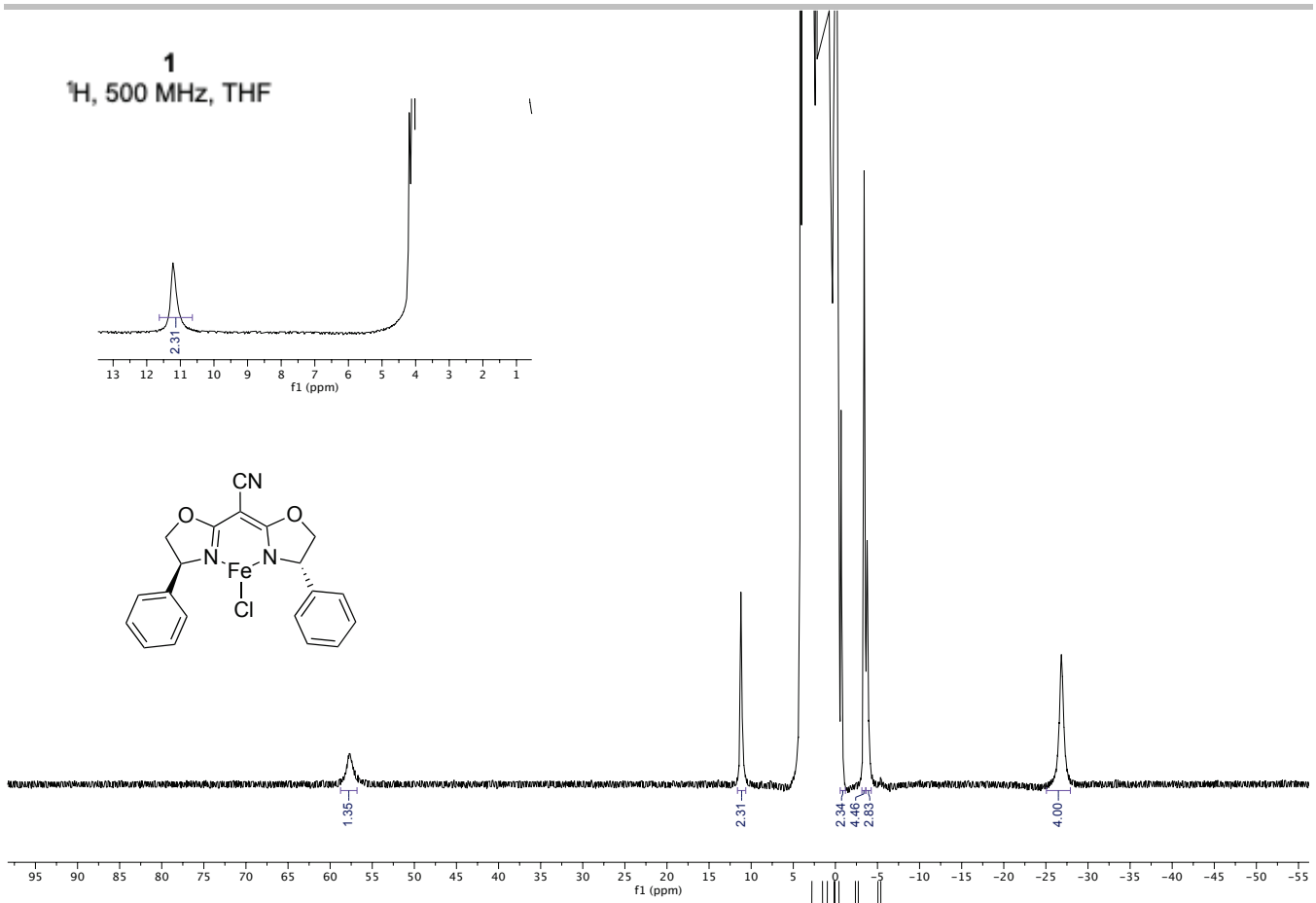


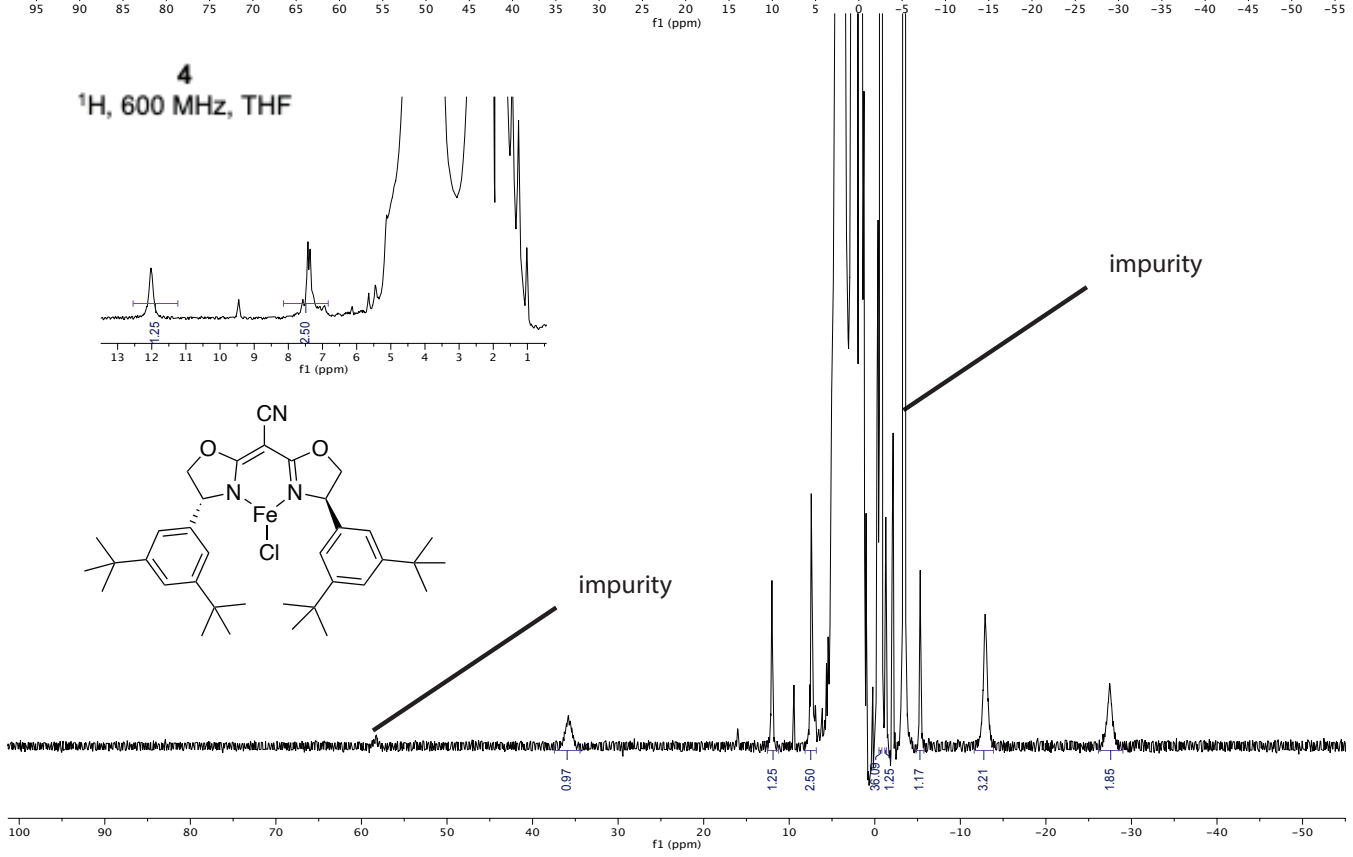


^{1}H, 600 MHz, $CDCl_3$

7a

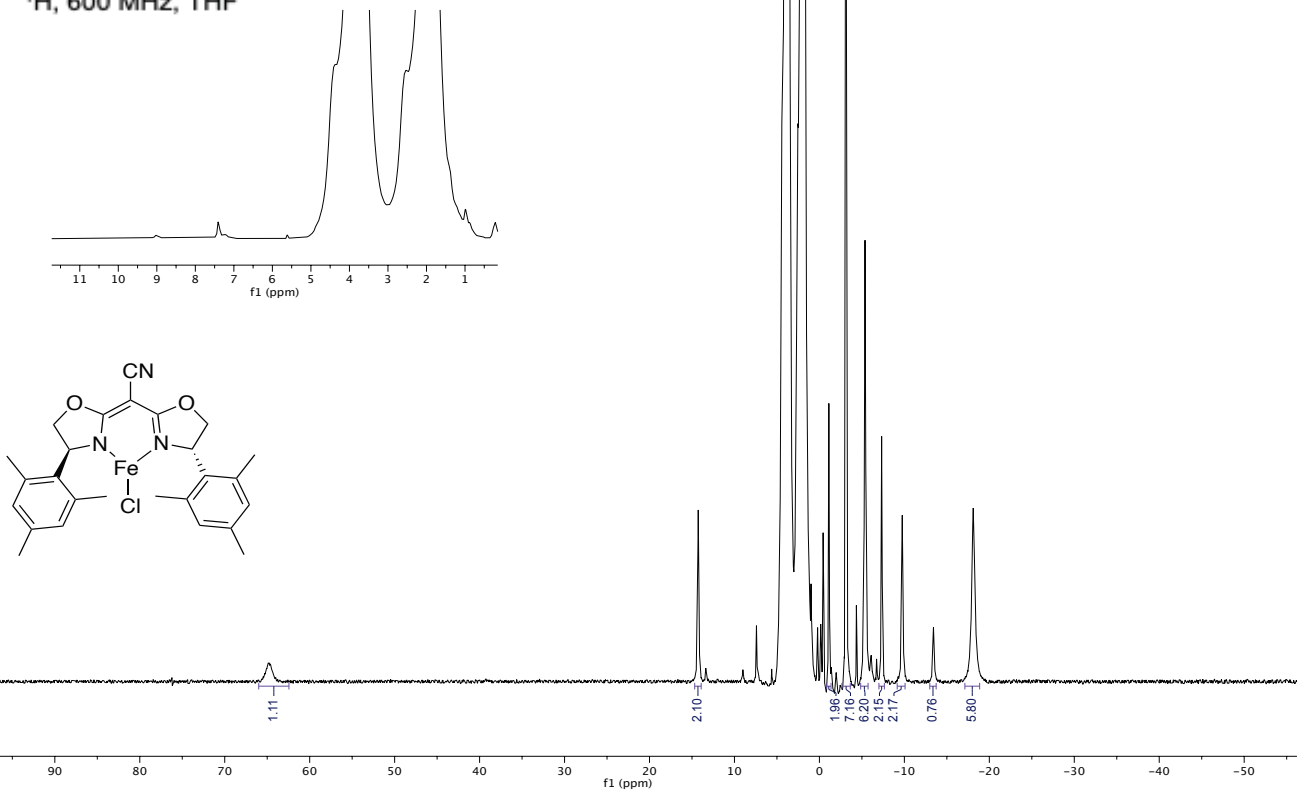



1
1H, 500 MHz, THF
CN
O
O
N
Fe
N
Cl
f1 (ppm)


4
1H, 600 MHz, THF
CN
O
O
N
Fe
N
Cl
impurity
impurity
f1 (ppm)

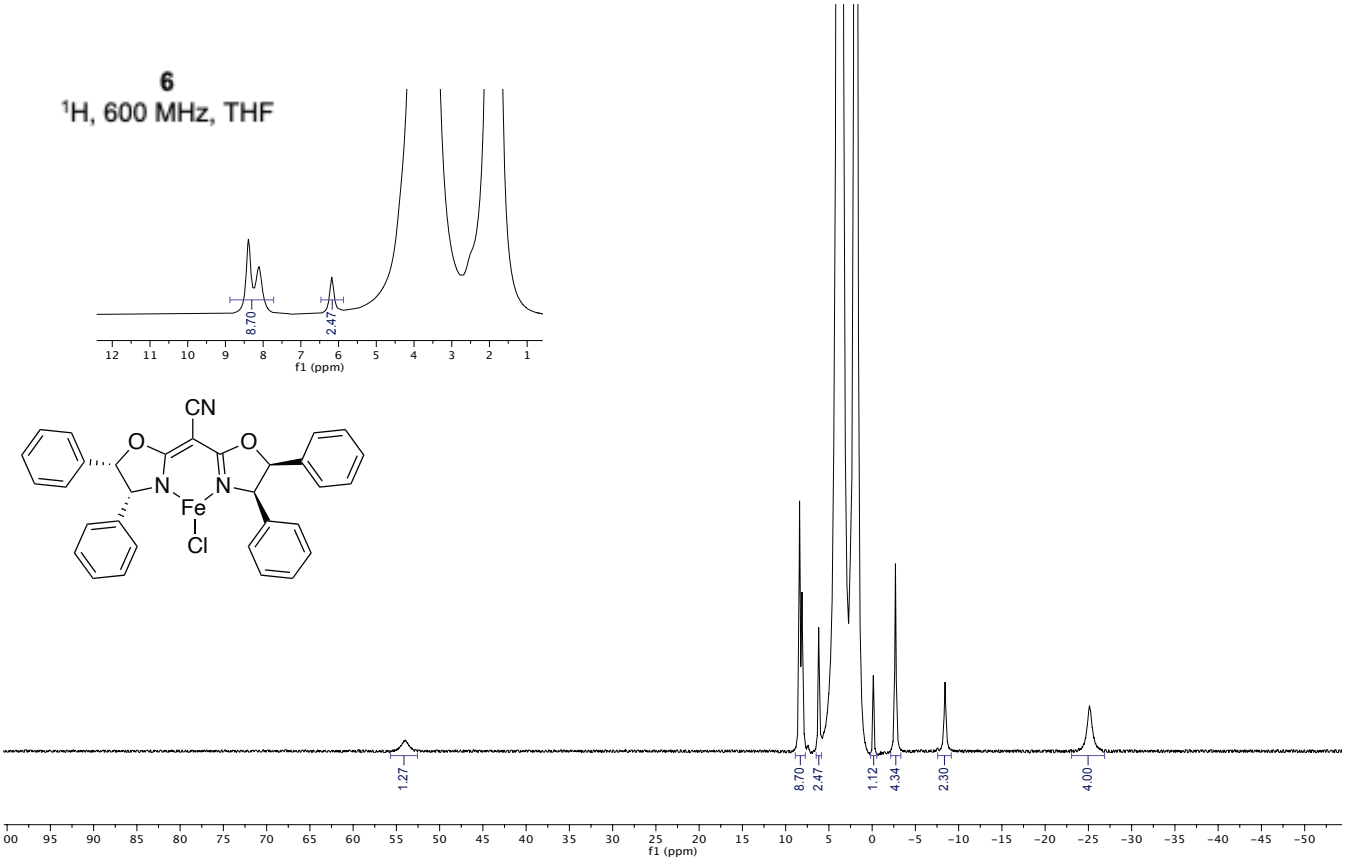
5

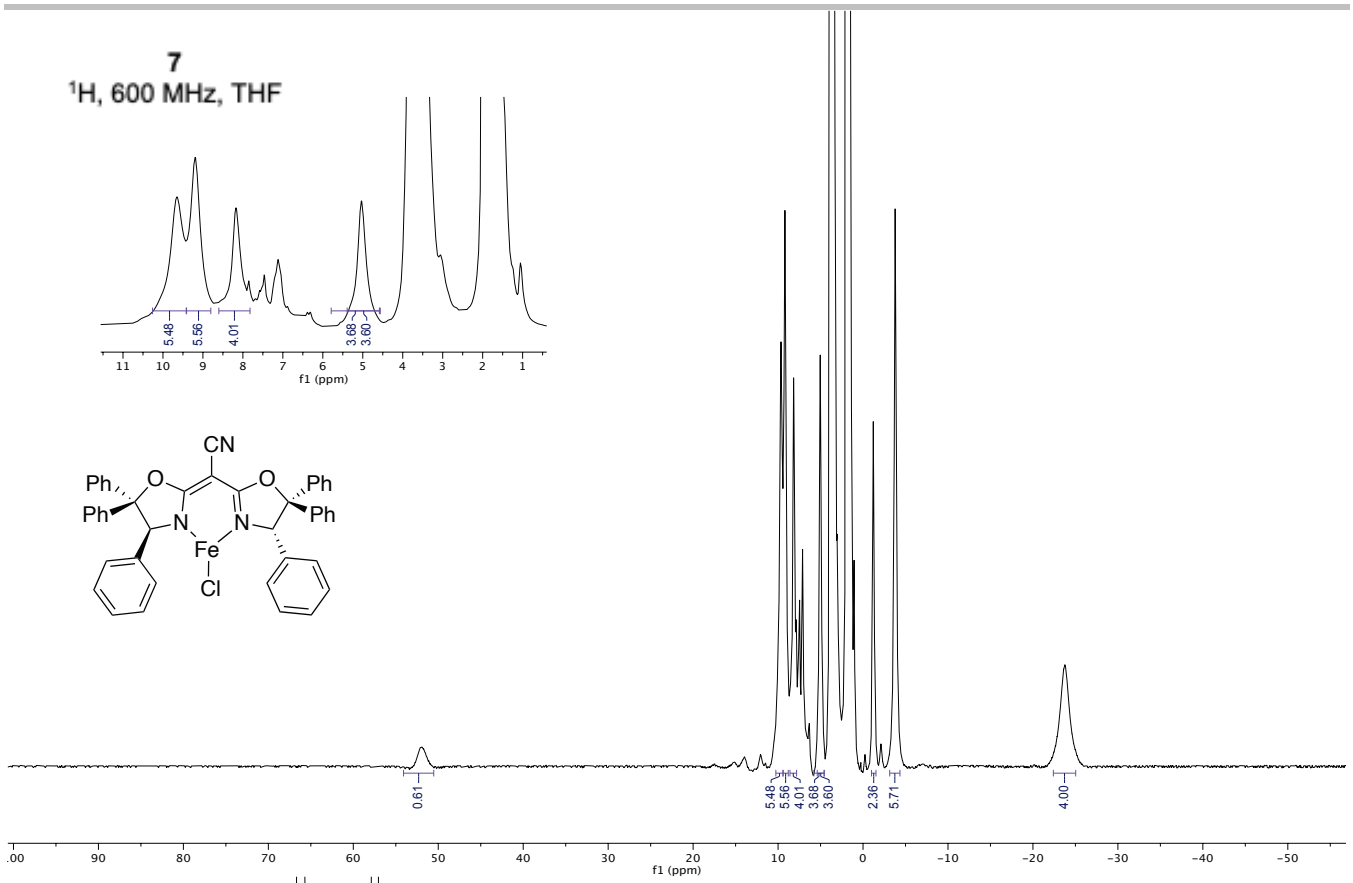
^{1}H, 600 MHz, THF

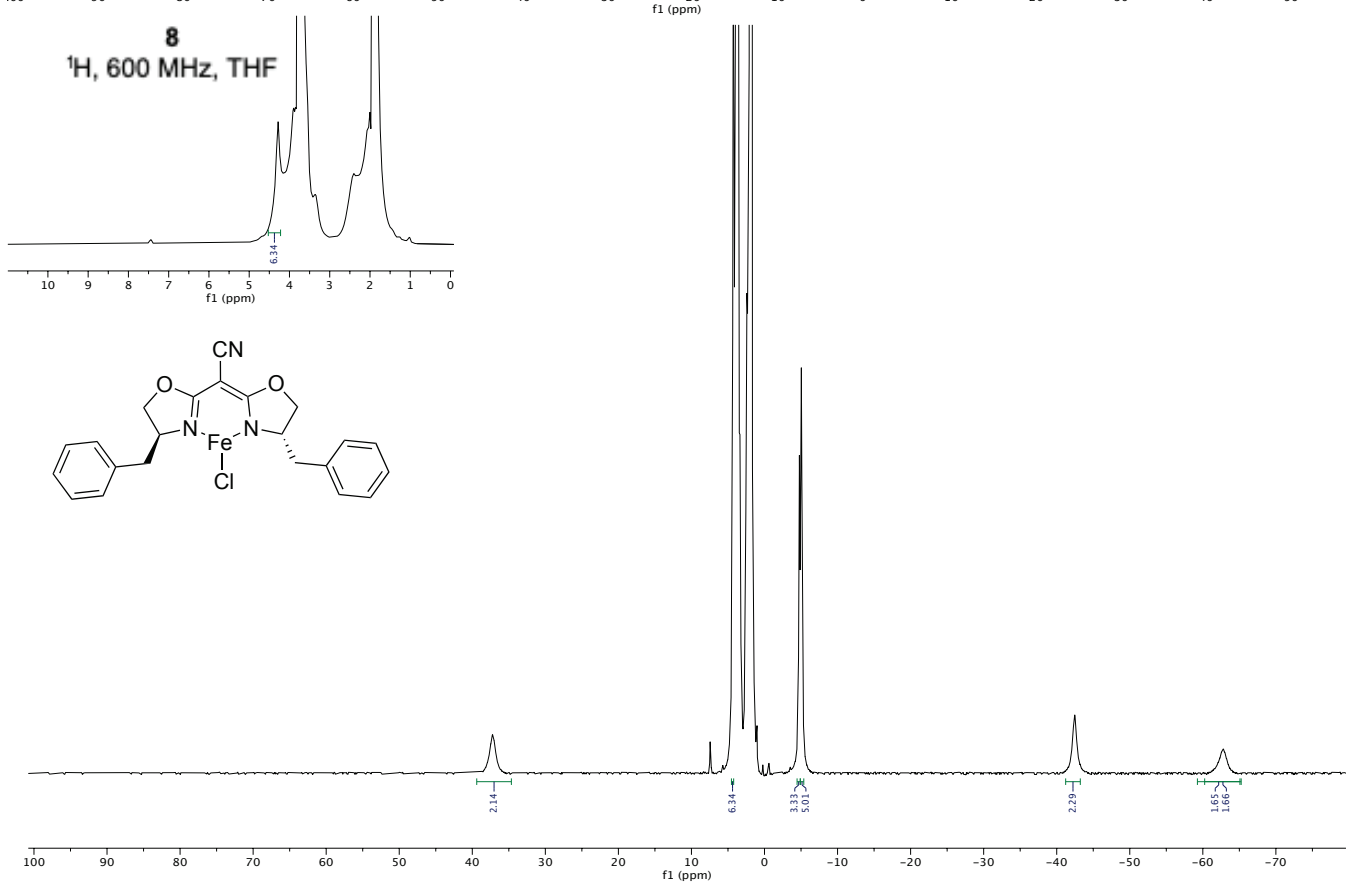


6

^{1}H, 600 MHz, THF

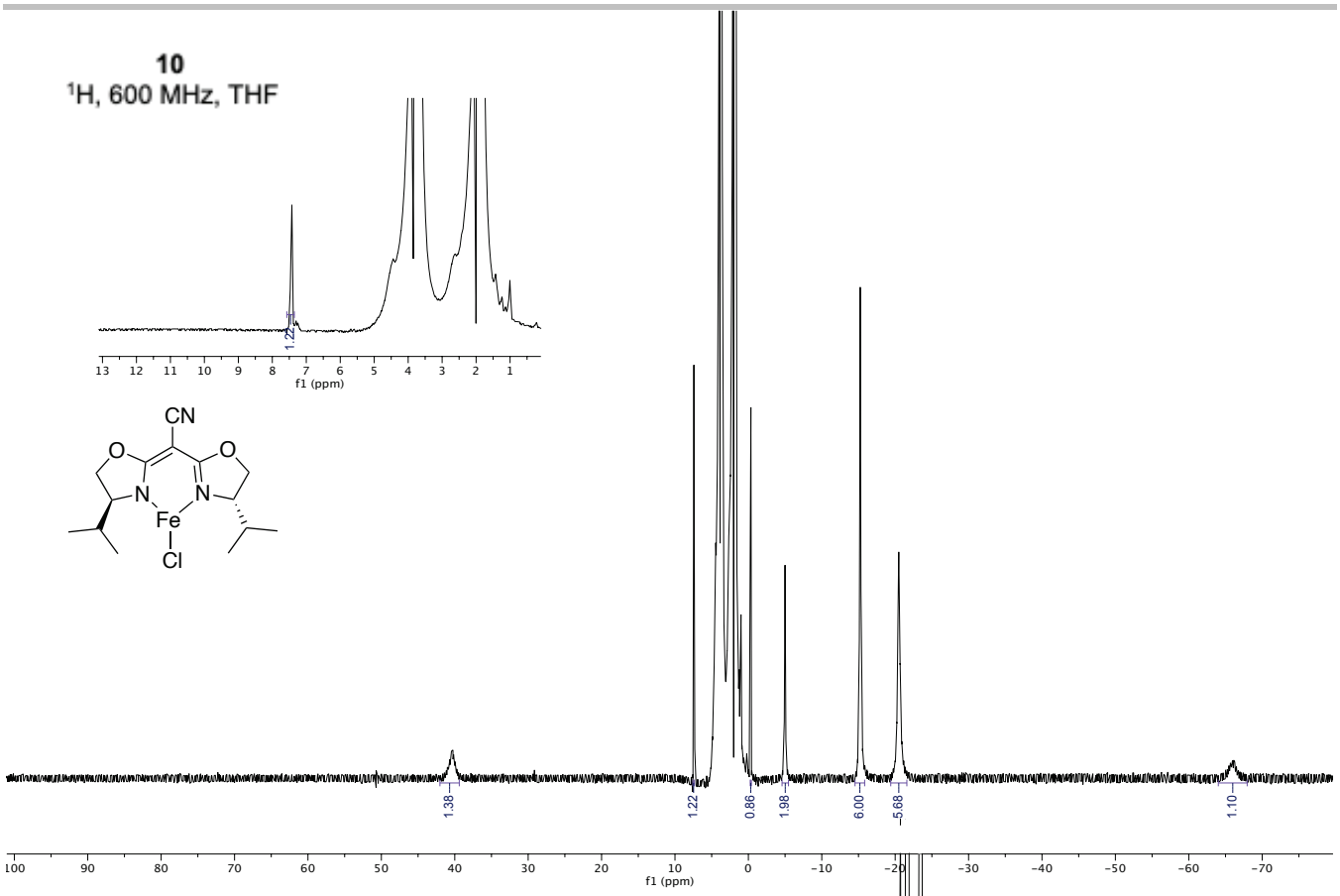



7
1H, 600 MHz, THF
CN
Ph
Ph
Ph
Ph
O
O
N
N
Fe
Cl
f1 (ppm)


8
1H, 600 MHz, THF
CN
O
O
N
N
Fe
Cl
f1 (ppm)

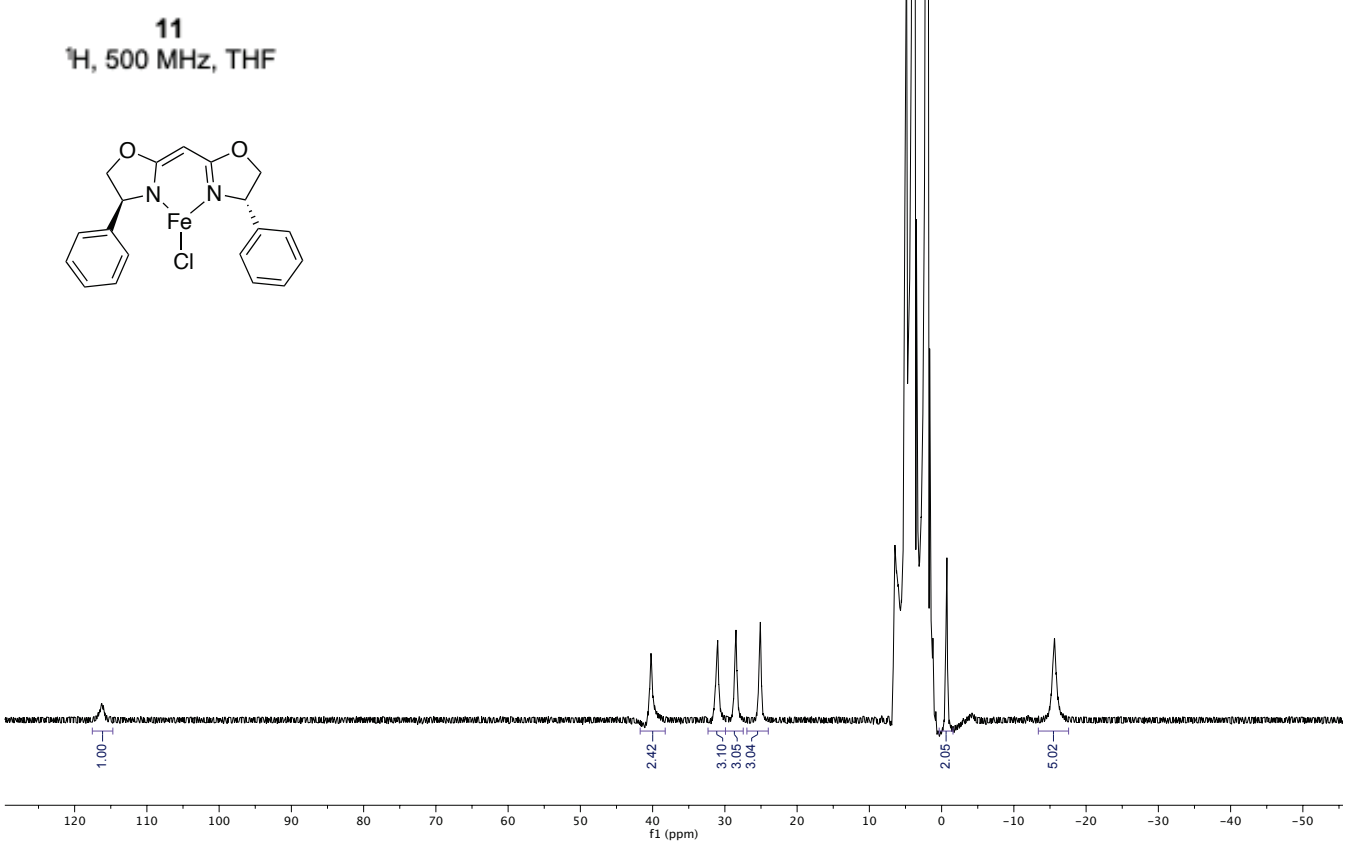
10

^{1}H, 600 MHz, THF



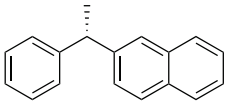
11

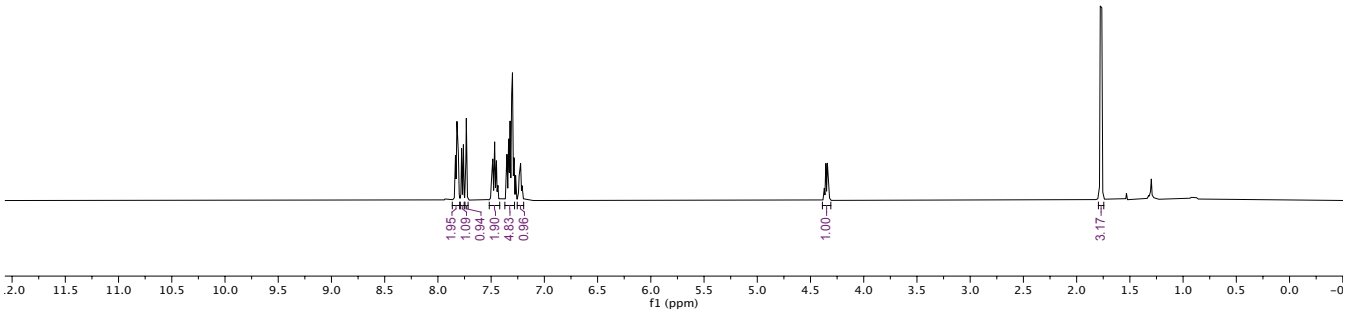
^{1}H, 500 MHz, THF



2

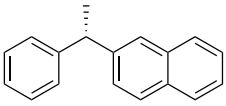
^{1}H, 400 MHz, $CDCl_3$

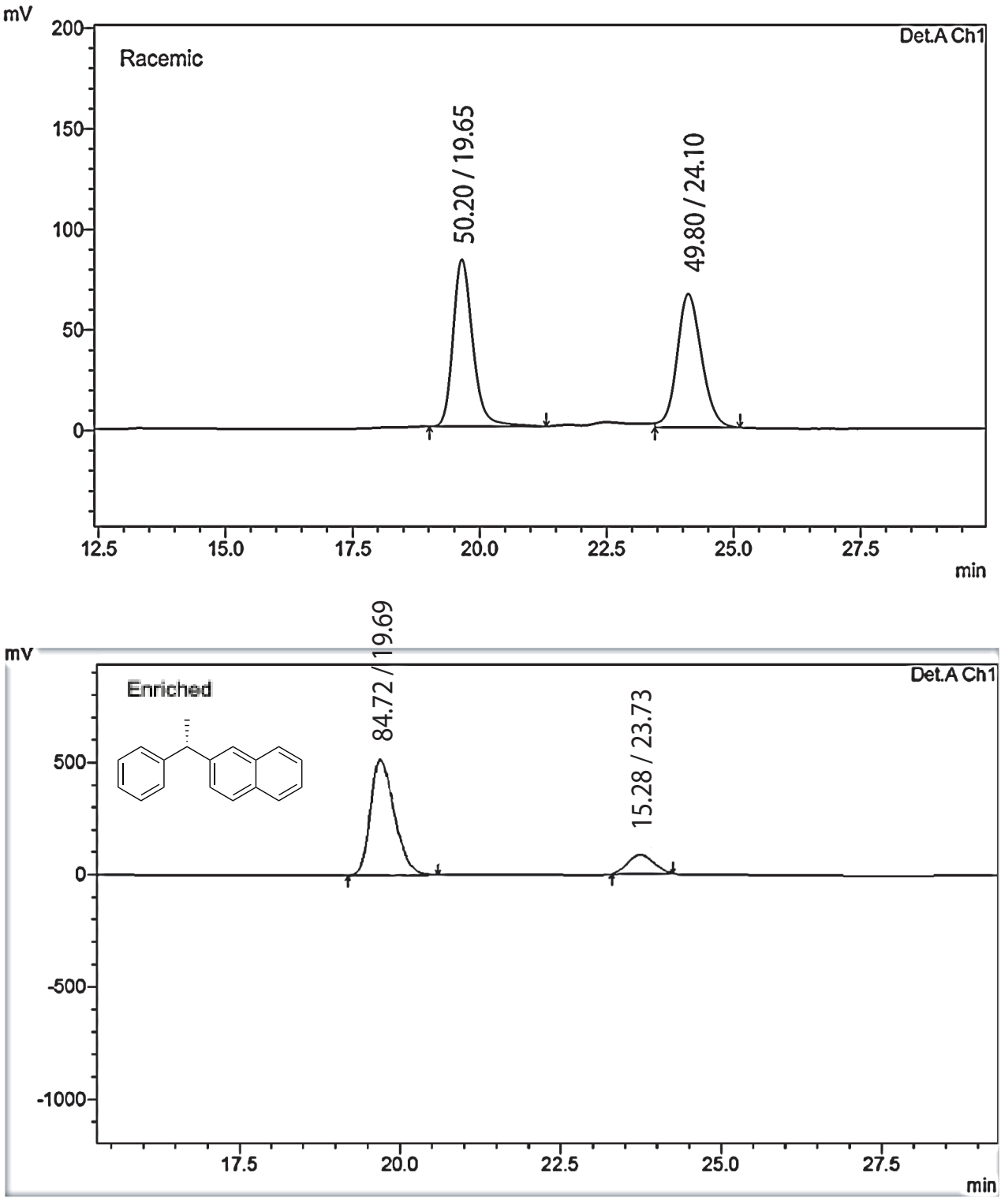




2

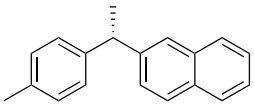
^{13}C, 125 MHz, $CDCl_3$



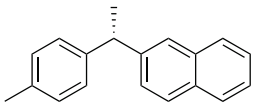


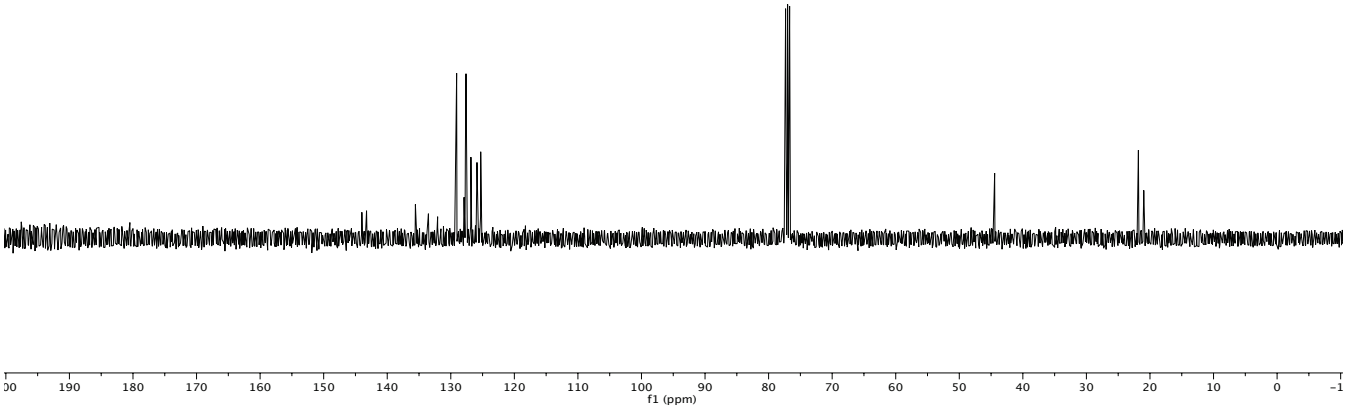
*Numbers above peaks in HPLC trace indicate retention time and percent area respectively

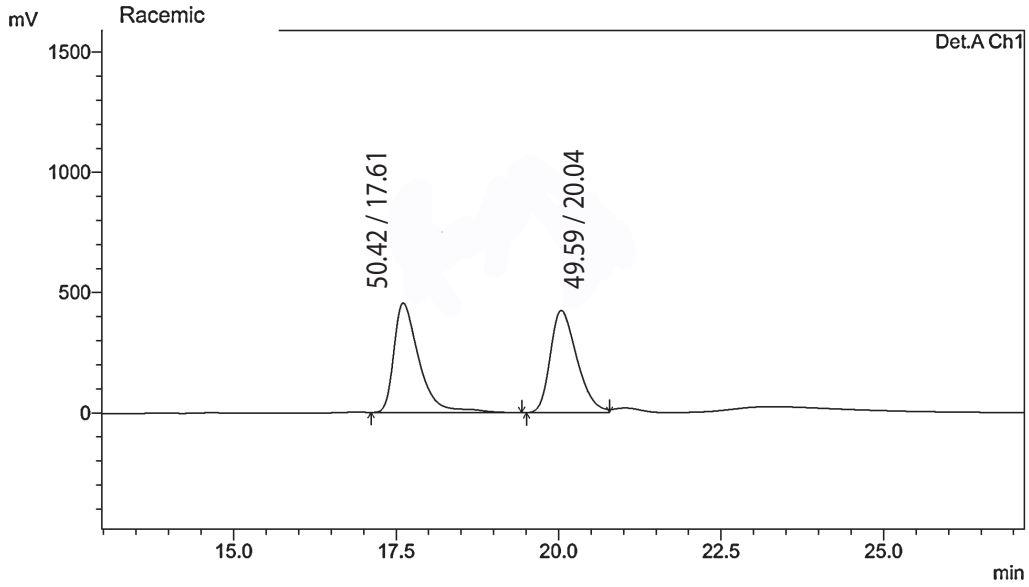
13
^{1}H, 400 MHz, $CDCl_3$



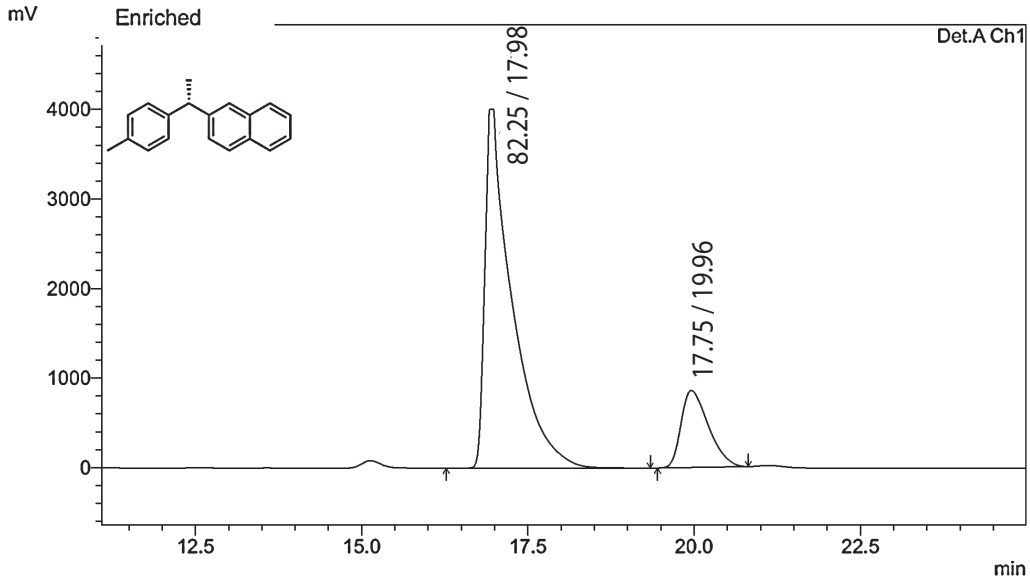
13
^{13}C, 125 MHz, $CDCl_3$







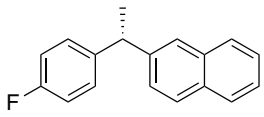
*Numbers above peaks in HPLC traces indicate percent area and retention time respectively



*Numbers above peaks in HPLC traces indicate percent area and retention time respectively

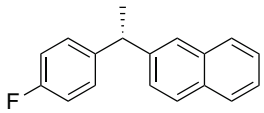
14

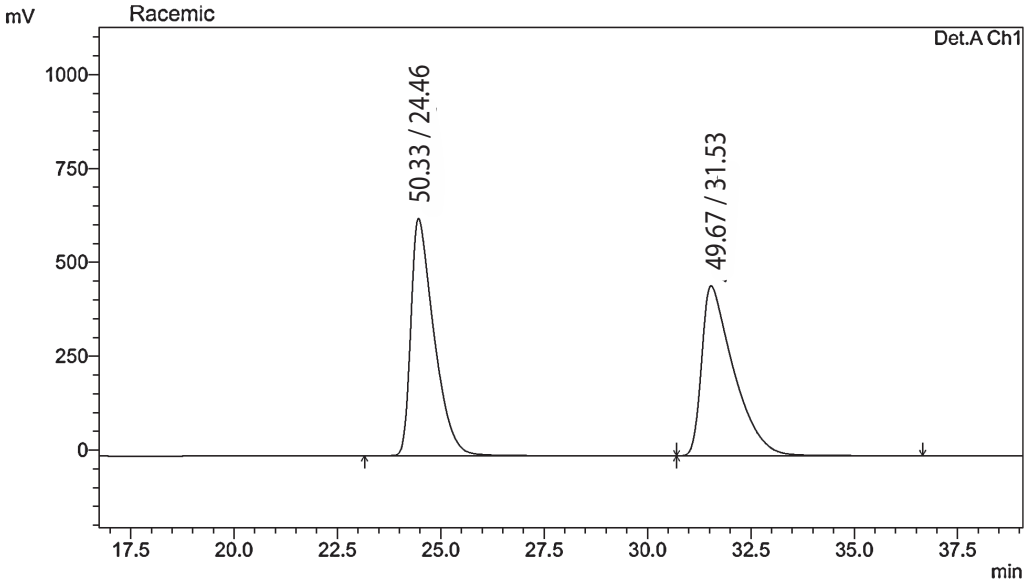
^{1}H, 400 MHz, $CDCl_3$

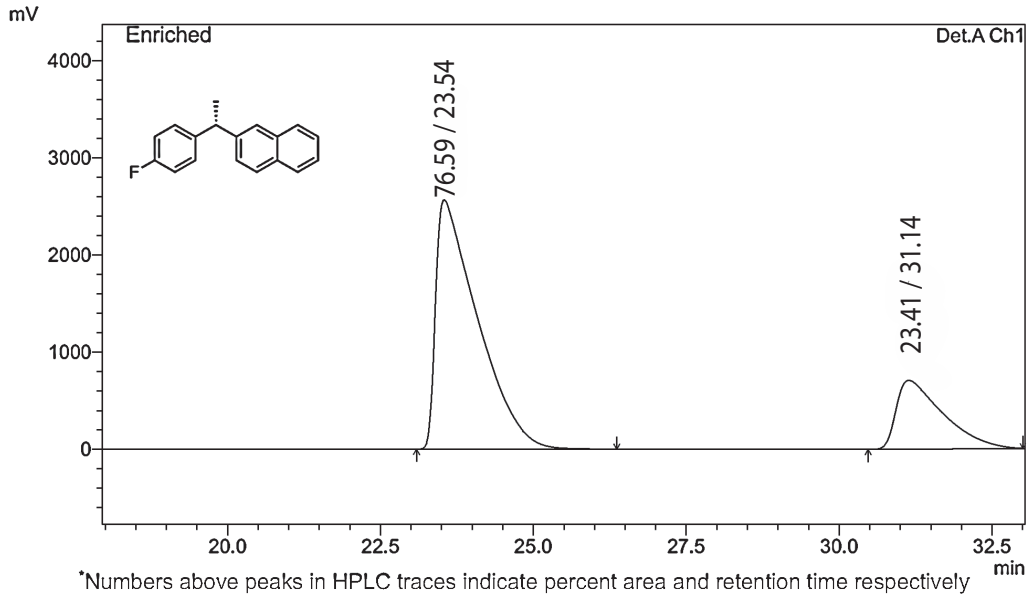


14

^{13}C, 125 MHz, $CDCl_3$



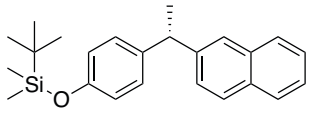




*Numbers above peaks in HPLC traces indicate percent area and retention time respectively

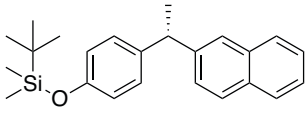
15

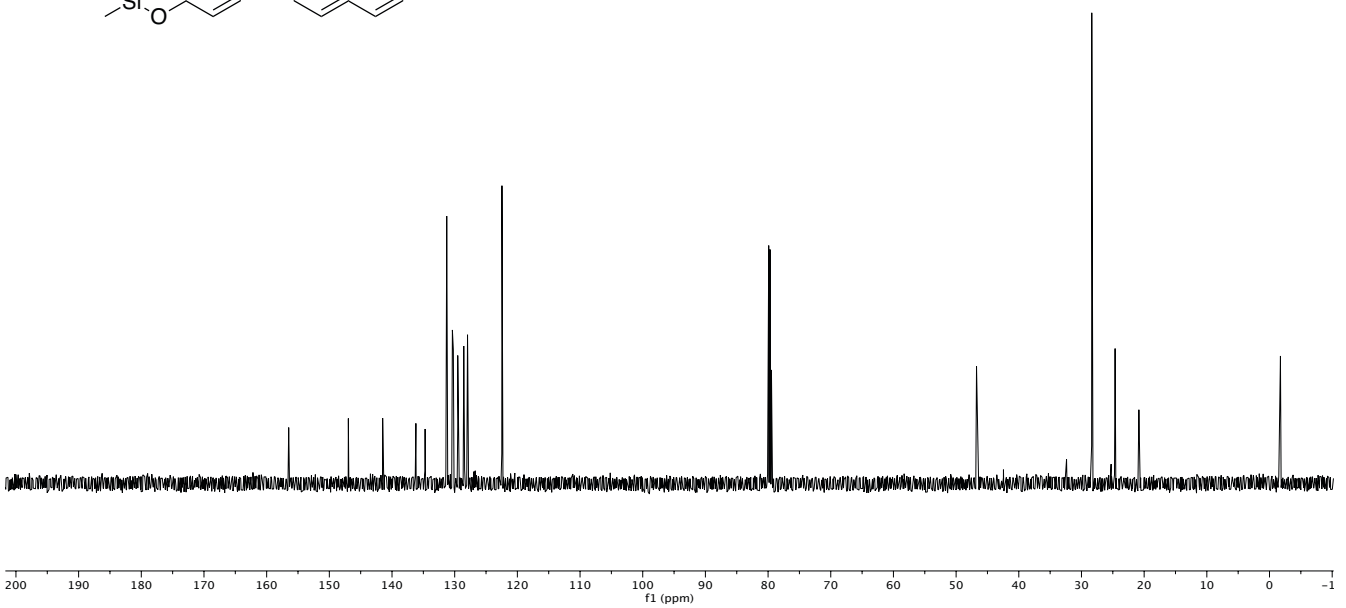
^{1}H, 400 MHz, $CDCl_3$

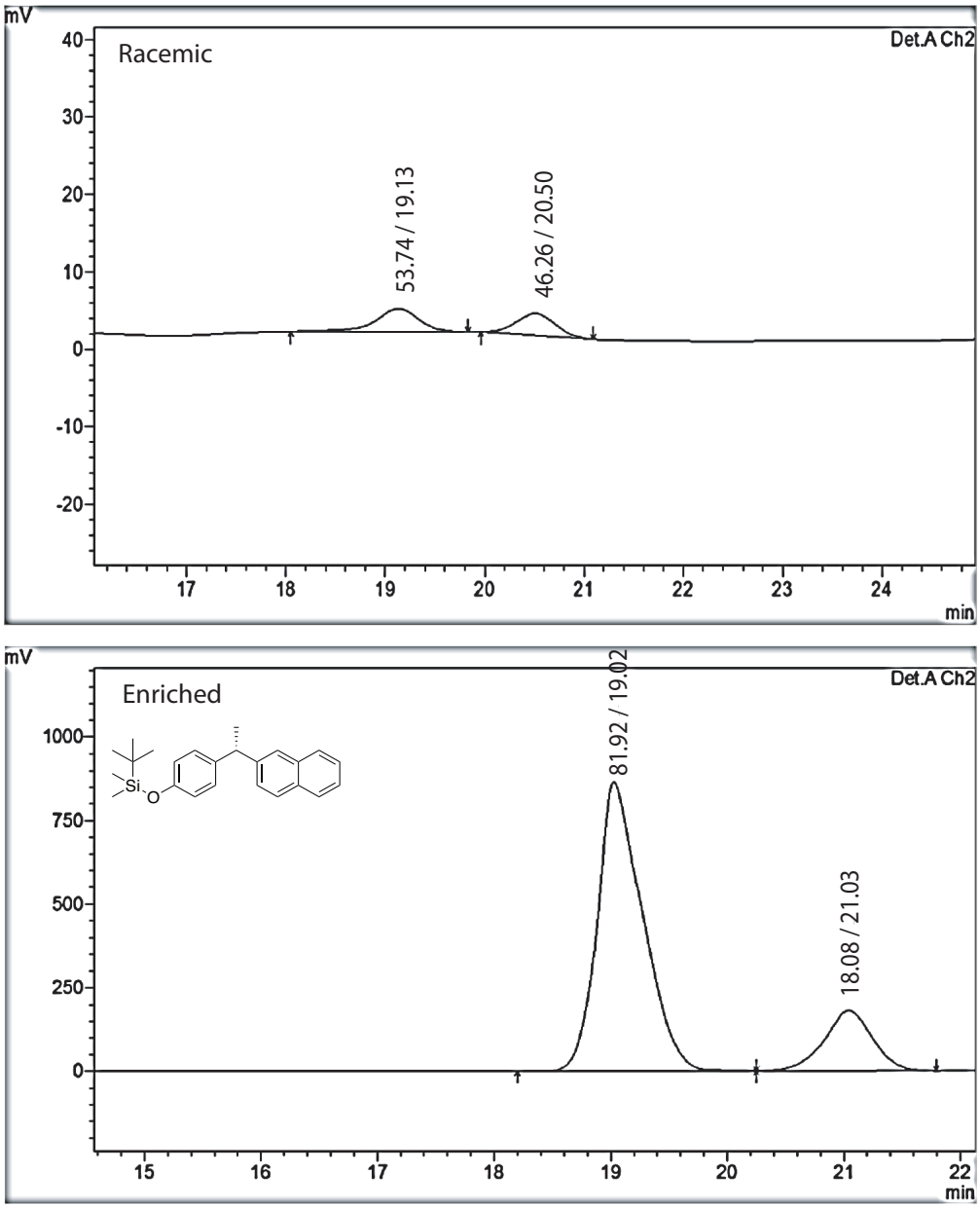


15

^{13}C, 125 MHz, $CDCl_3$



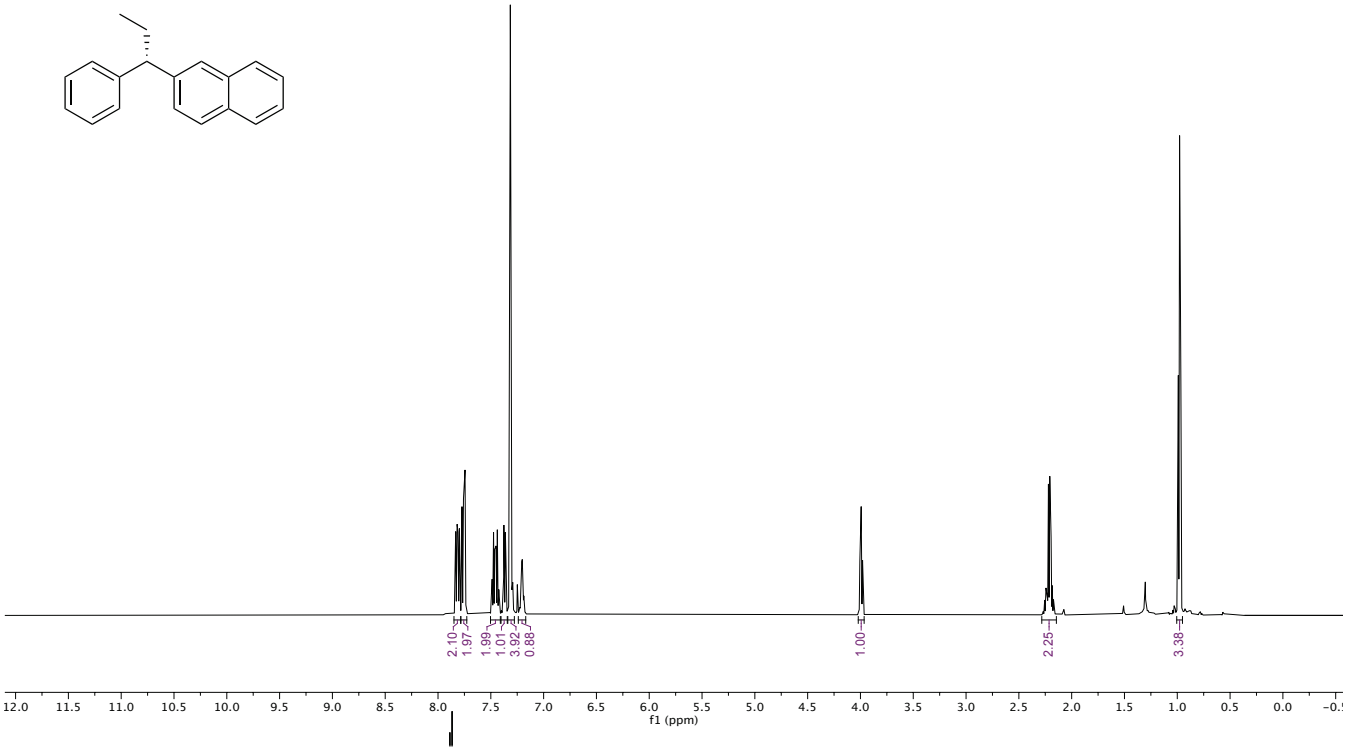




*Numbers above peaks in HPLC trace indicate retention time and percent area respectively

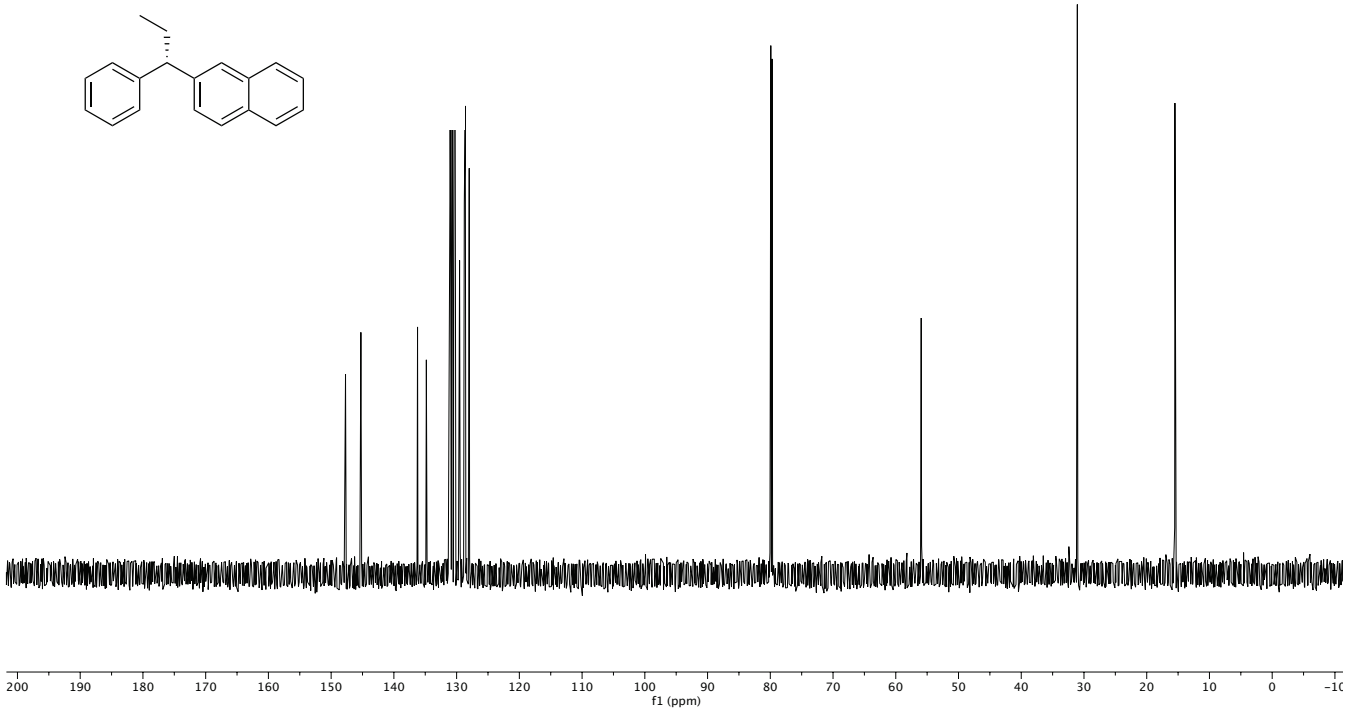
16

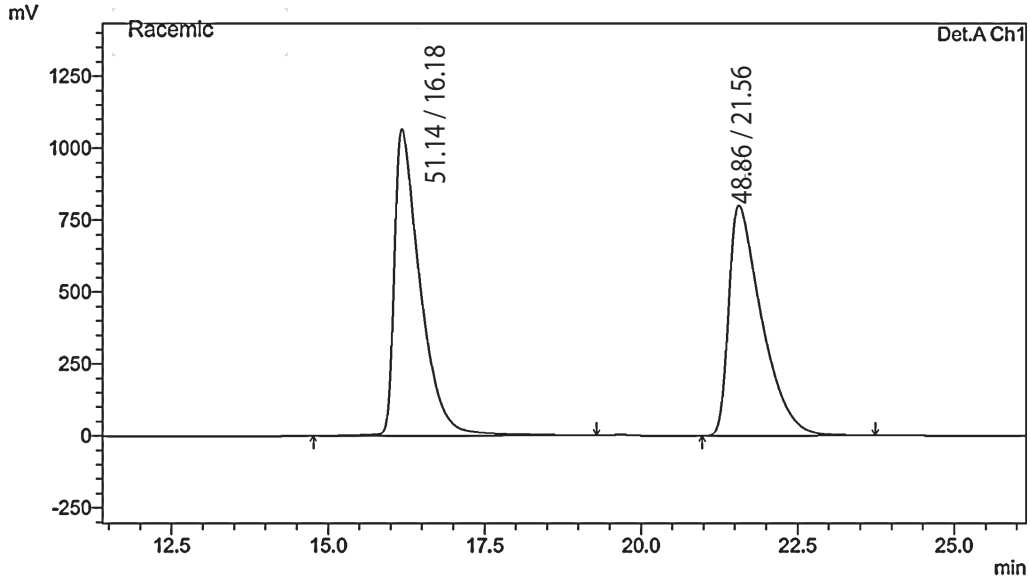
^{1}H, 400 MHz, $CDCl_3$

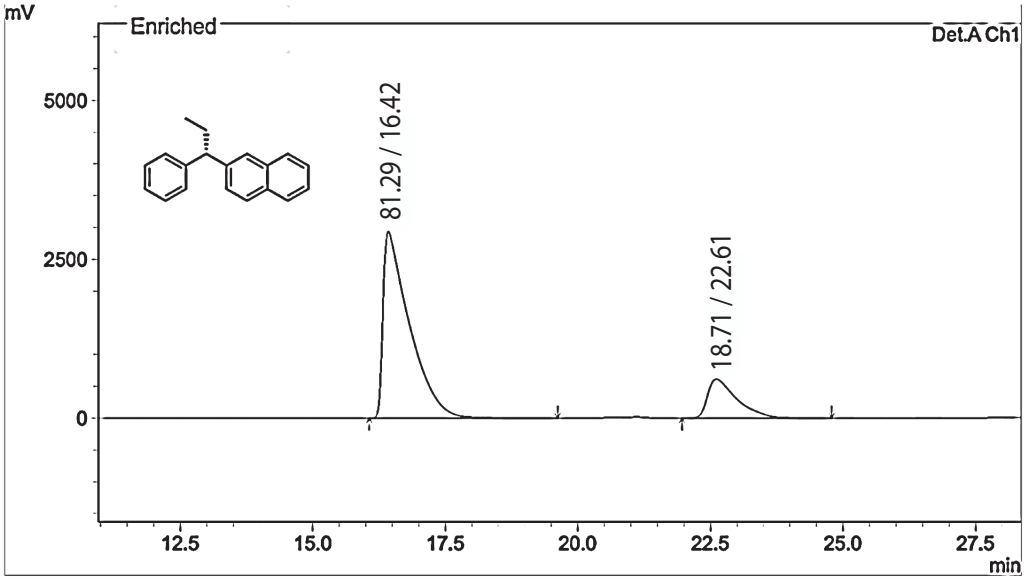


16

^{13}C, 125 MHz, $CDCl_3$



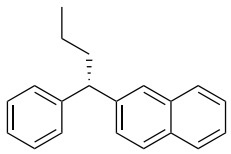




*Numbers above peaks in HPLC traces indicate percent area and retention time respectively

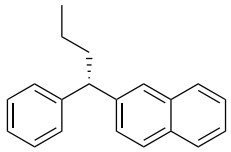
17

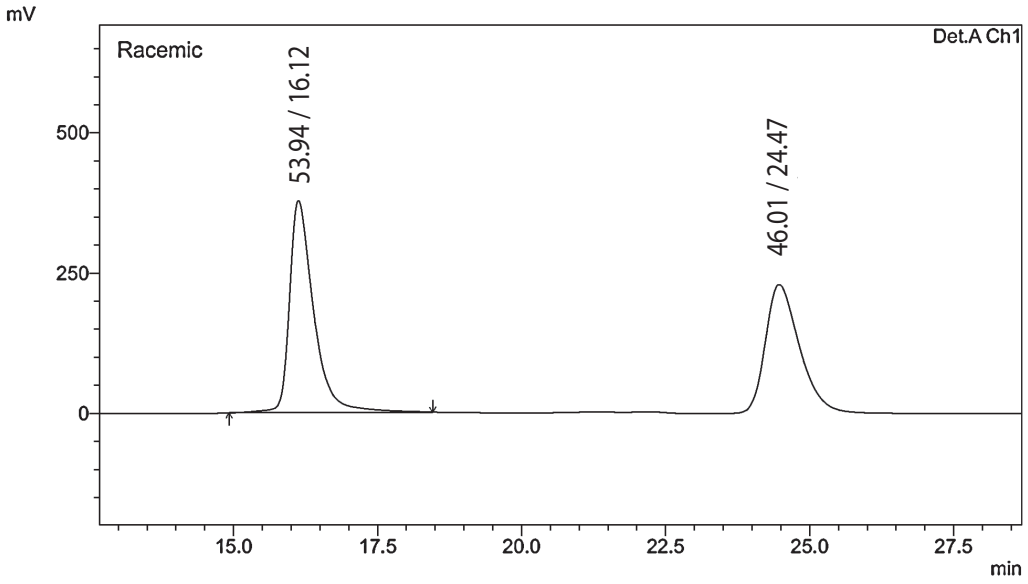
^{1}H, 400 MHz, $CDCl_3$

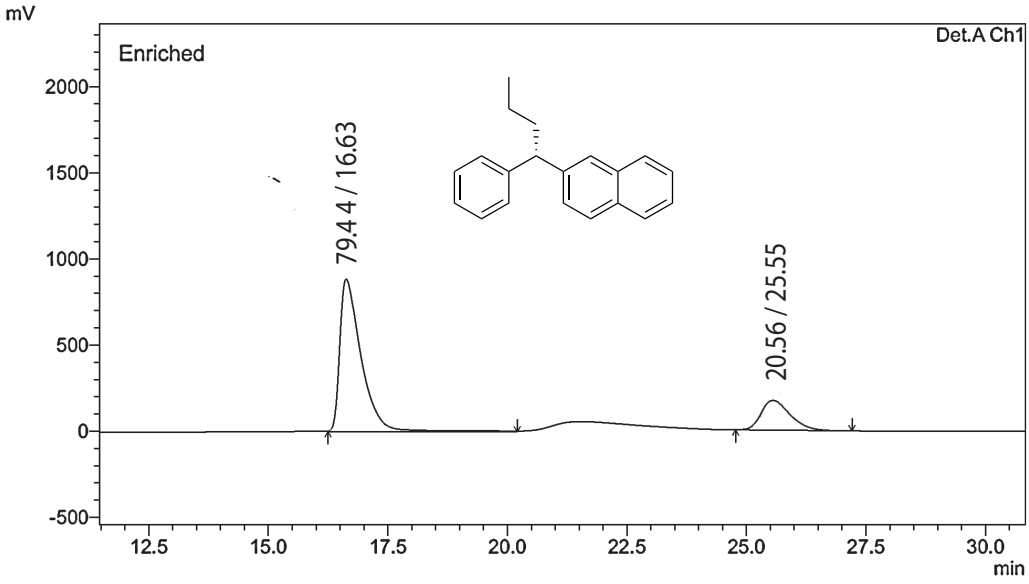


17

^{13}C, 125 MHz, $CDCl_3$



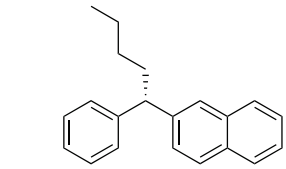




*Numbers above peaks in HPLC traces indicate percent area and retention time respectively

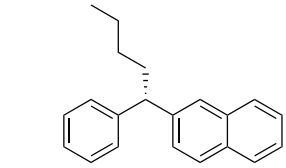
18

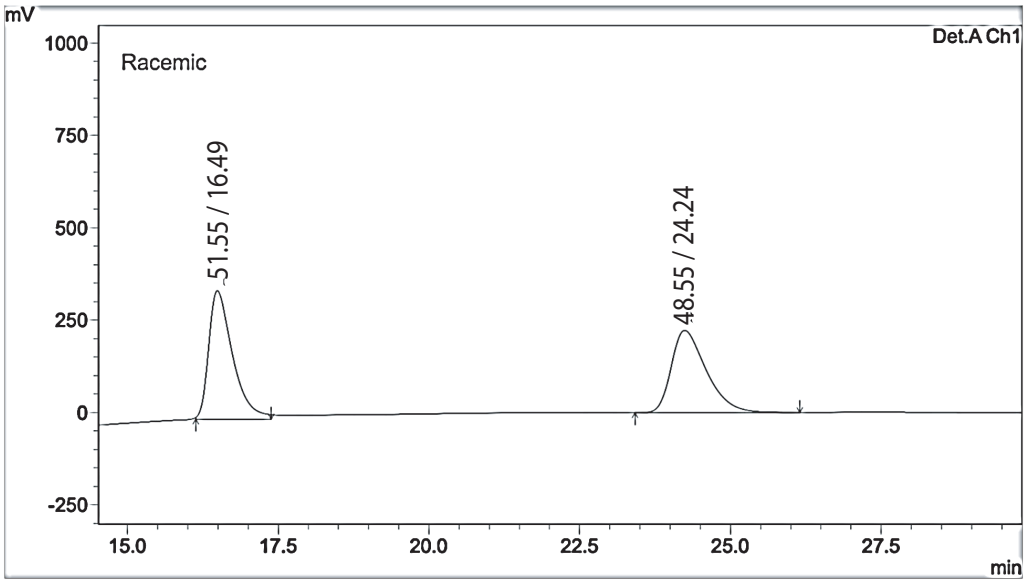
^{1}H, 400 MHz, $CDCl_3$

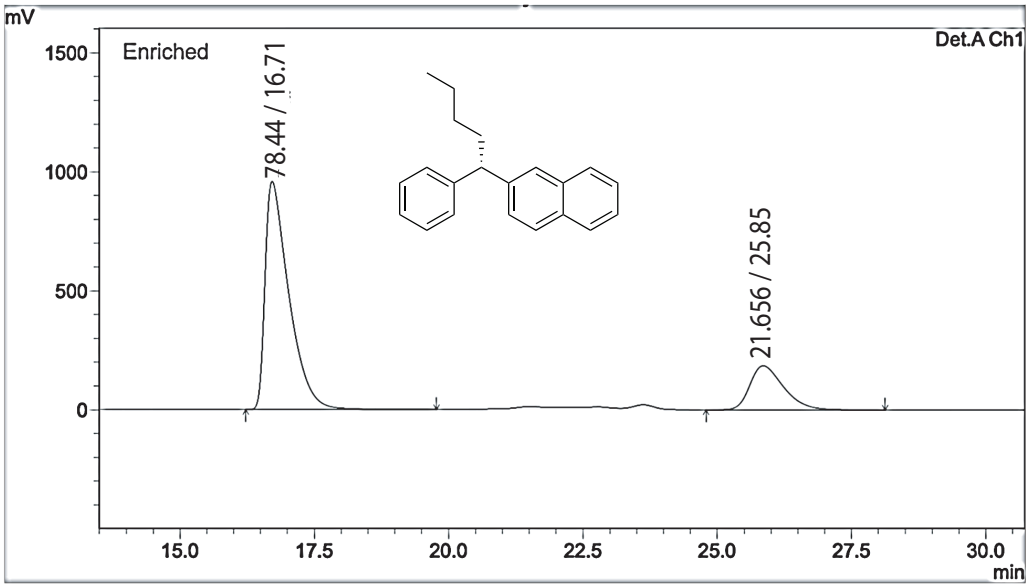


18

^{13}C, 125 MHz, $CDCl_3$



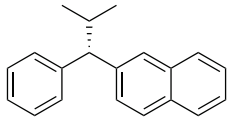




Numbers above peaks in HPLC traces indicate percent area and retention time respectively

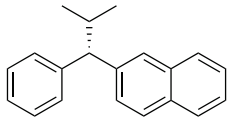
19

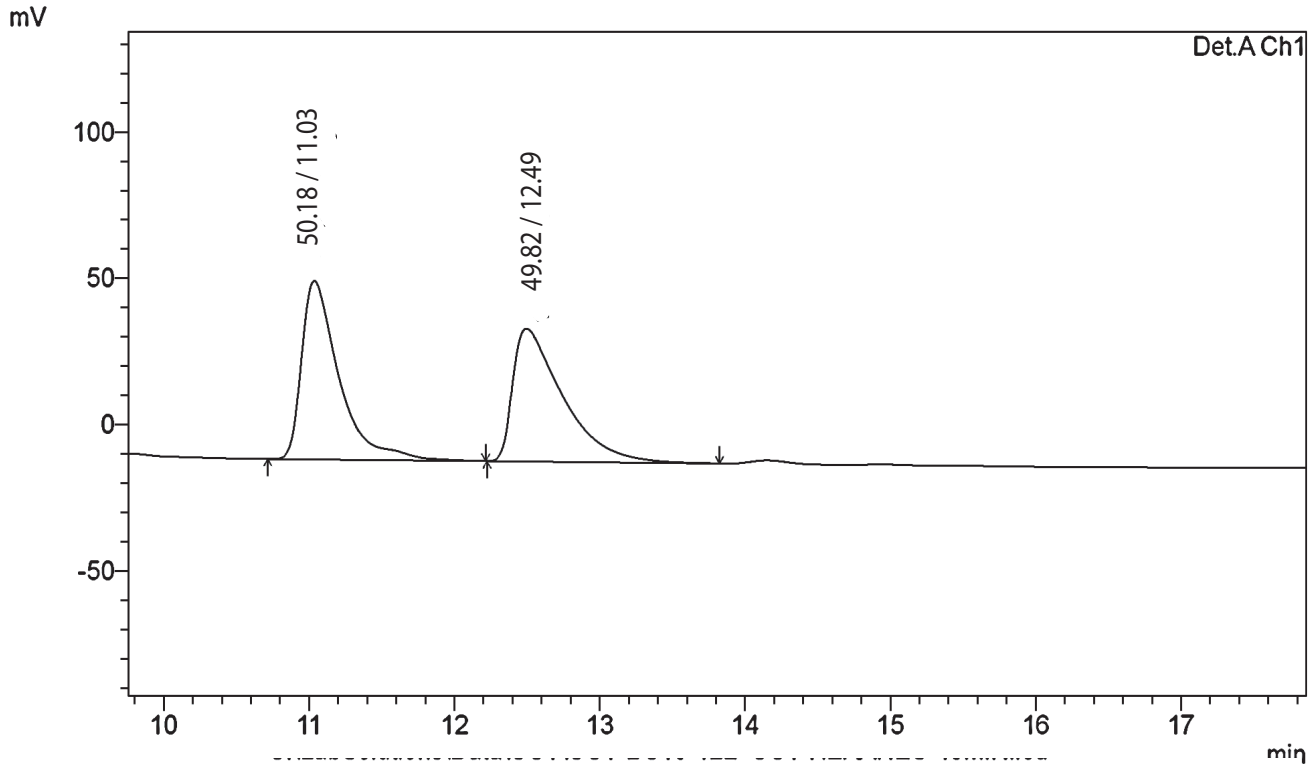
^{1}H, 400 MHz, $CDCl_3$

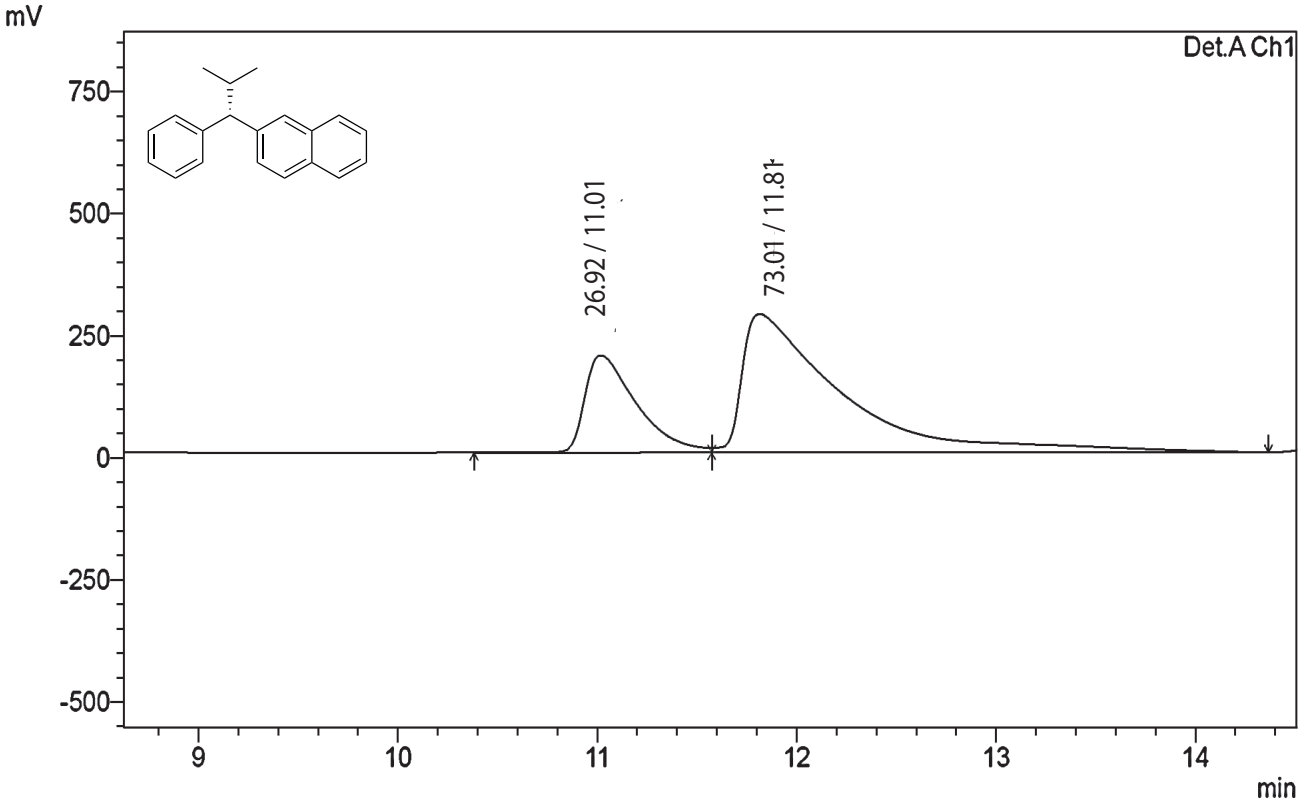


19

^{13}C 125 MHz, $CDCl_3$



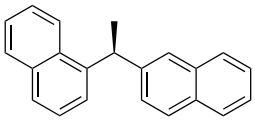




*Numbers above peaks in HPLC traces indicate percent area and retention time respectively

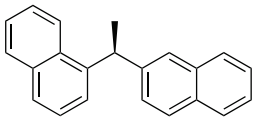
20

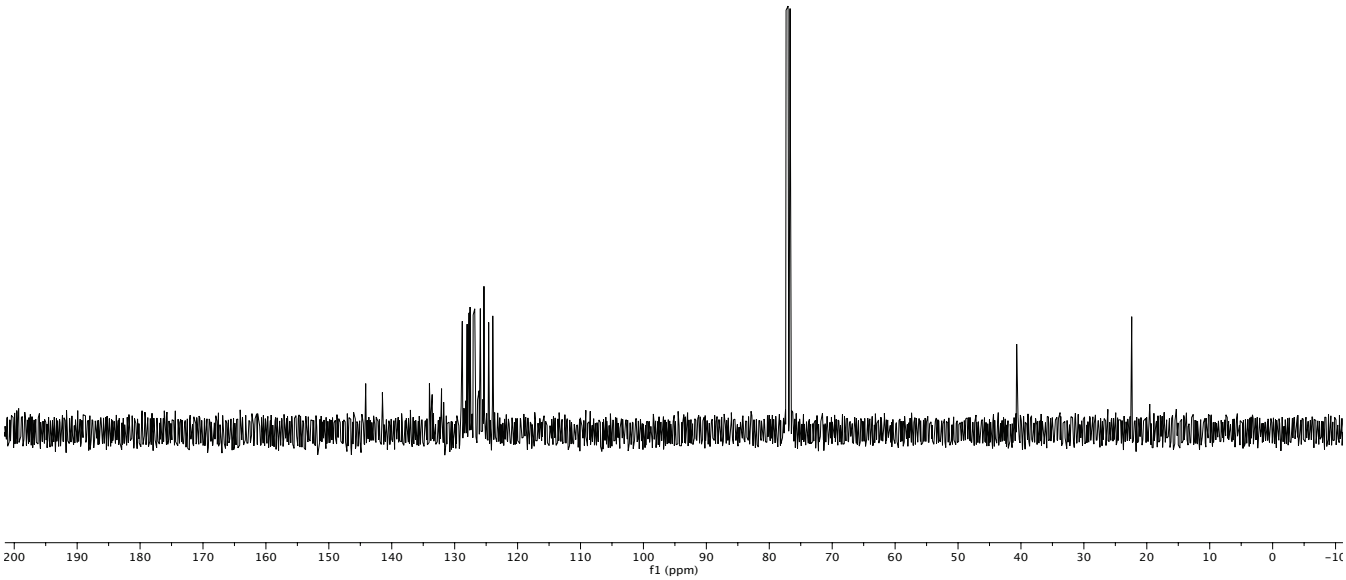
^{1}H, 400 MHz, $CDCl_3$

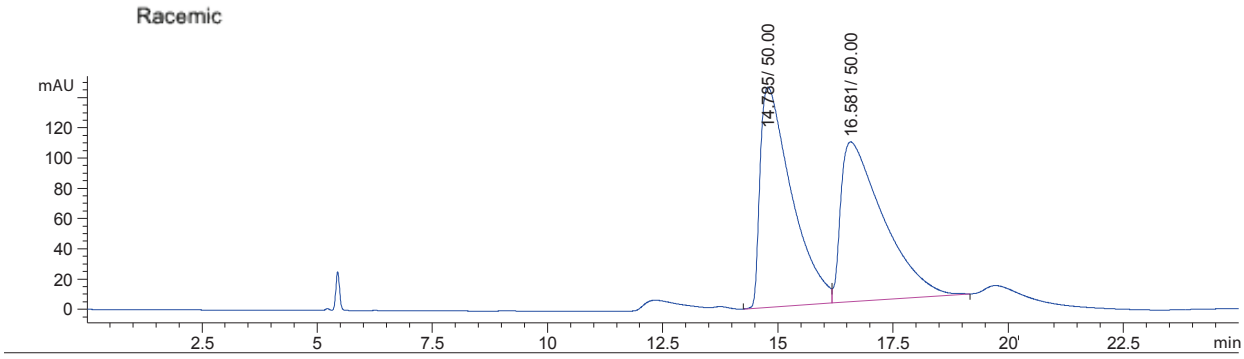


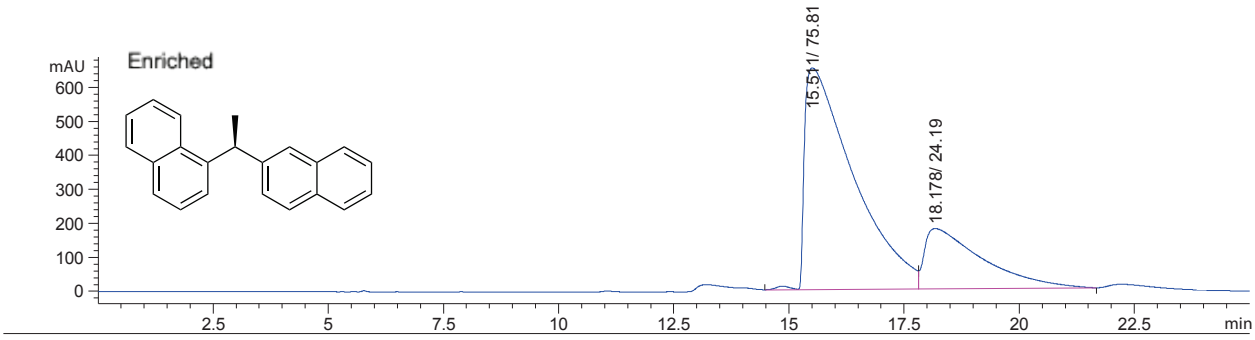
20

^{13}C, 125 MHz, $CDCl_3$





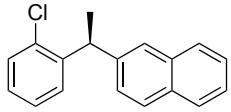


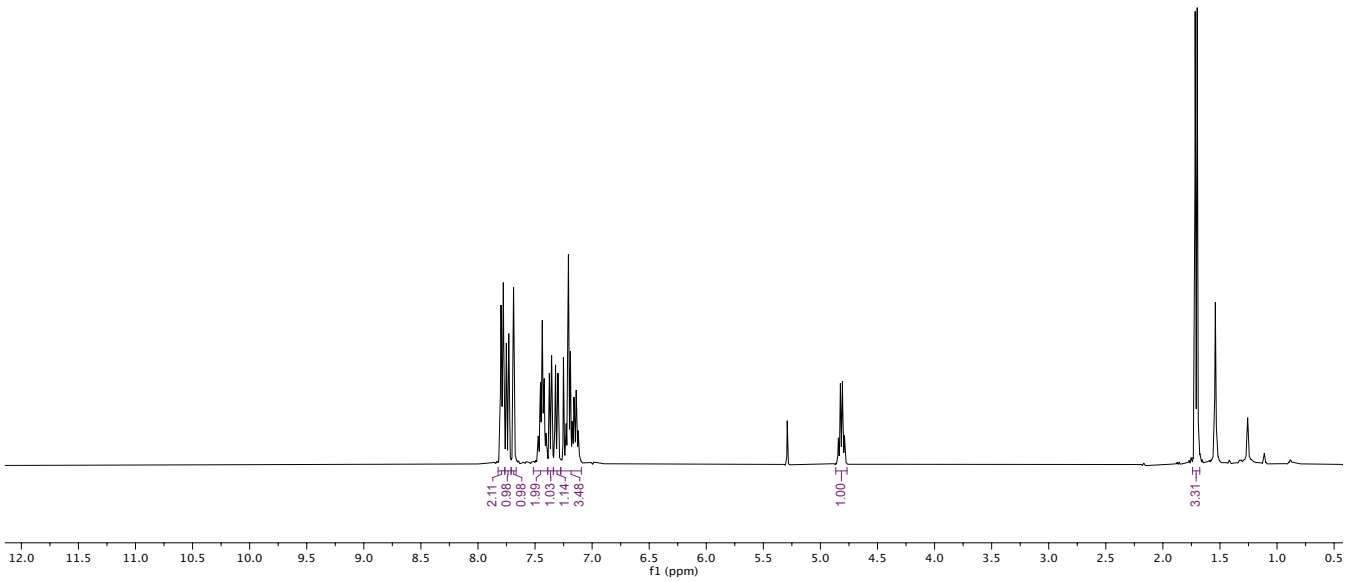


Numbers above peaks in HPLC trace indicate retention time and percent area respectively

21

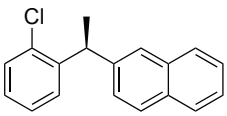
^{1}H, 400 MHz, $CDCl_3$

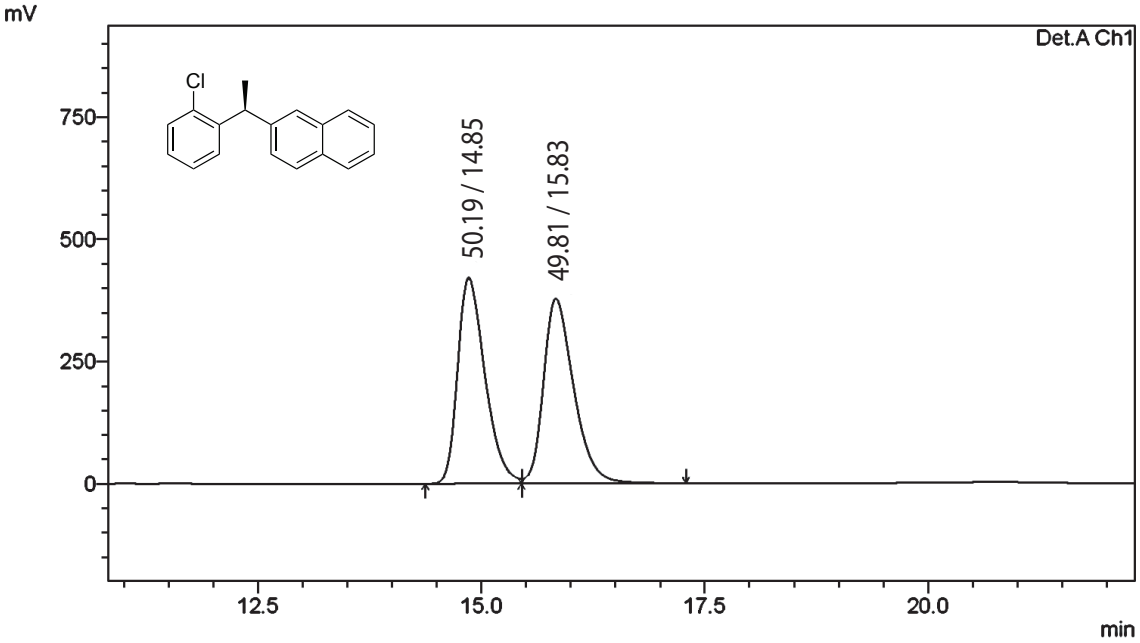


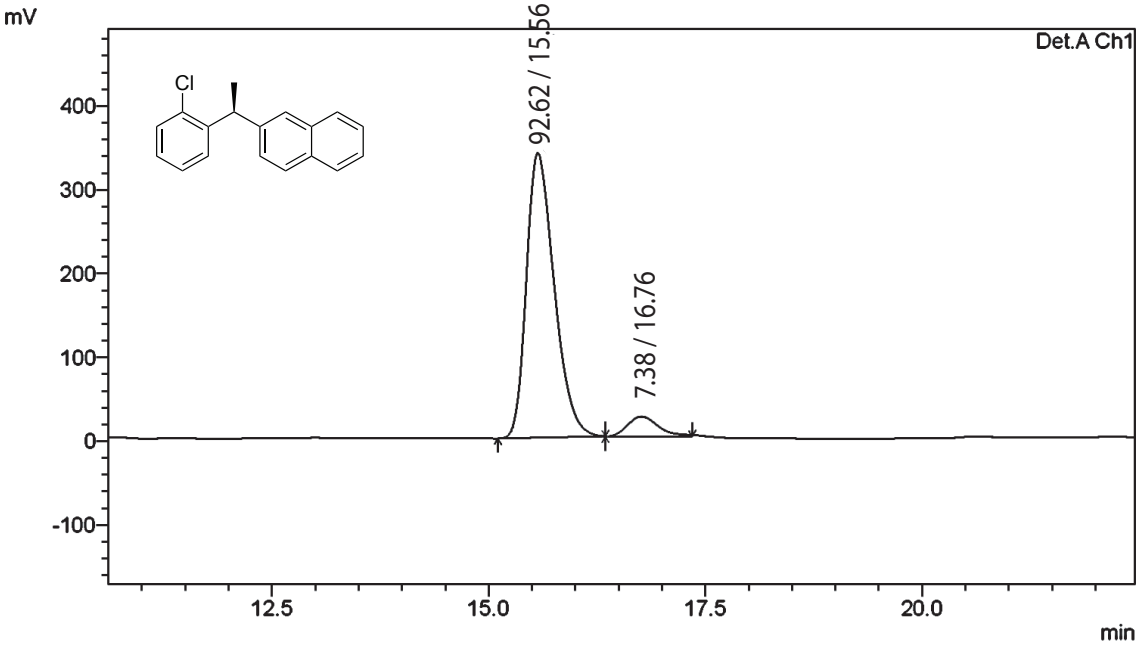


21

^{13}C, 125 MHz, $CDCl_3$



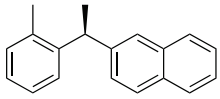




*Numbers above peaks in HPLC trace indicate percent area and retention time respectively

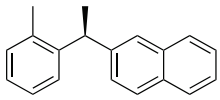
22

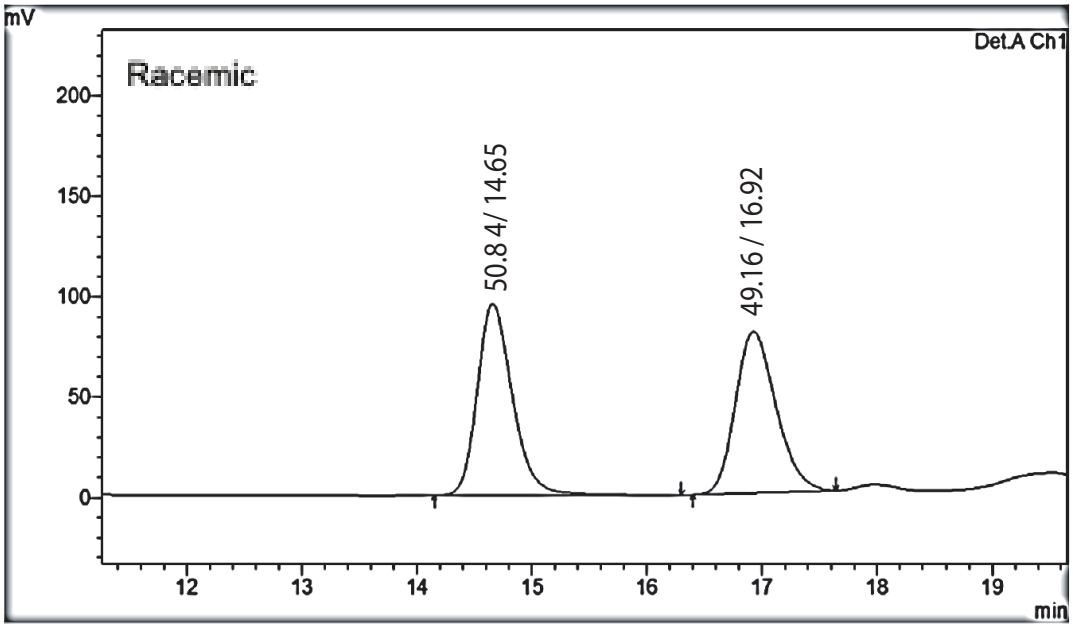
^{1}H, 400 MHz, $CDCl_3$

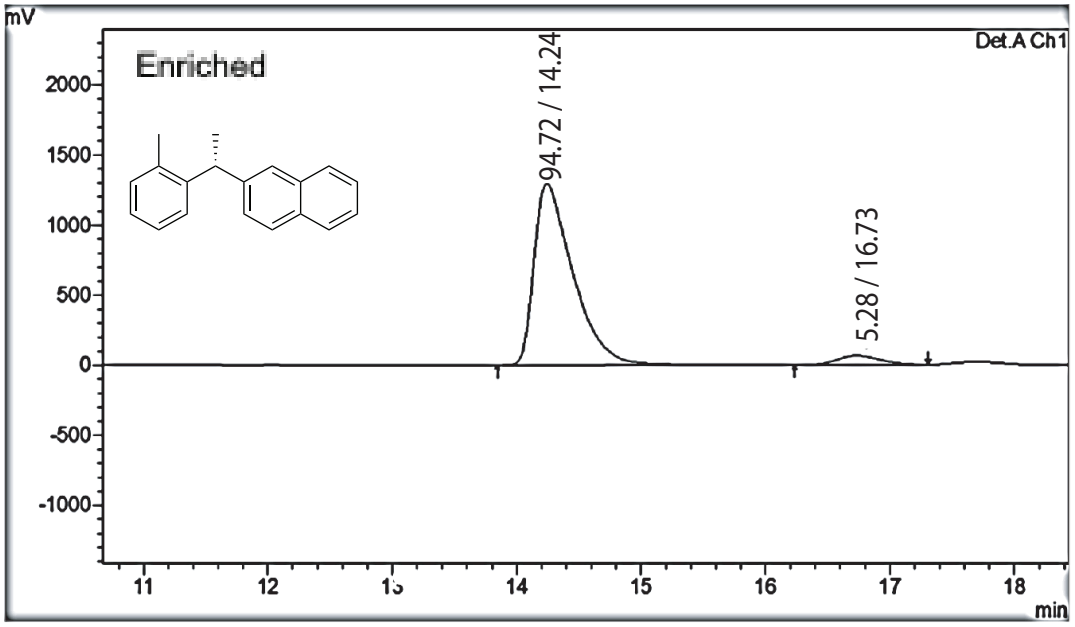


22

^{13}C, 125 MHz, $CDCl_3$



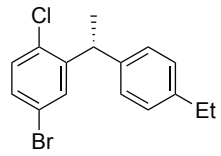




*Numbers above peaks in HPLC trace indicate retention time and percent area respectively

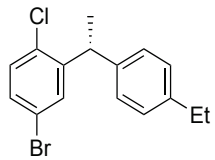
23

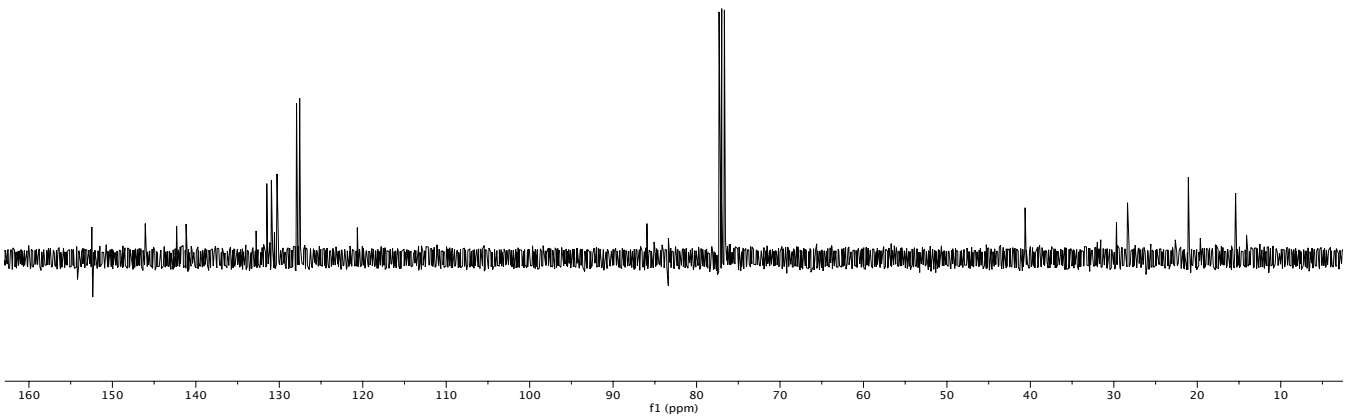
^{1}H, 500 MHz, $CDCl_3$

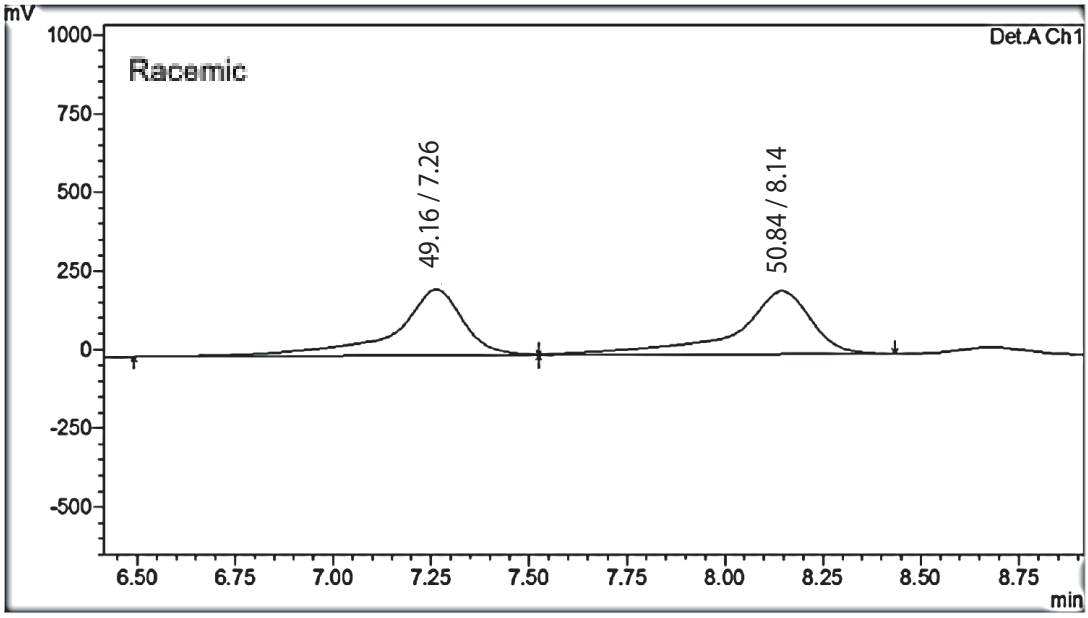


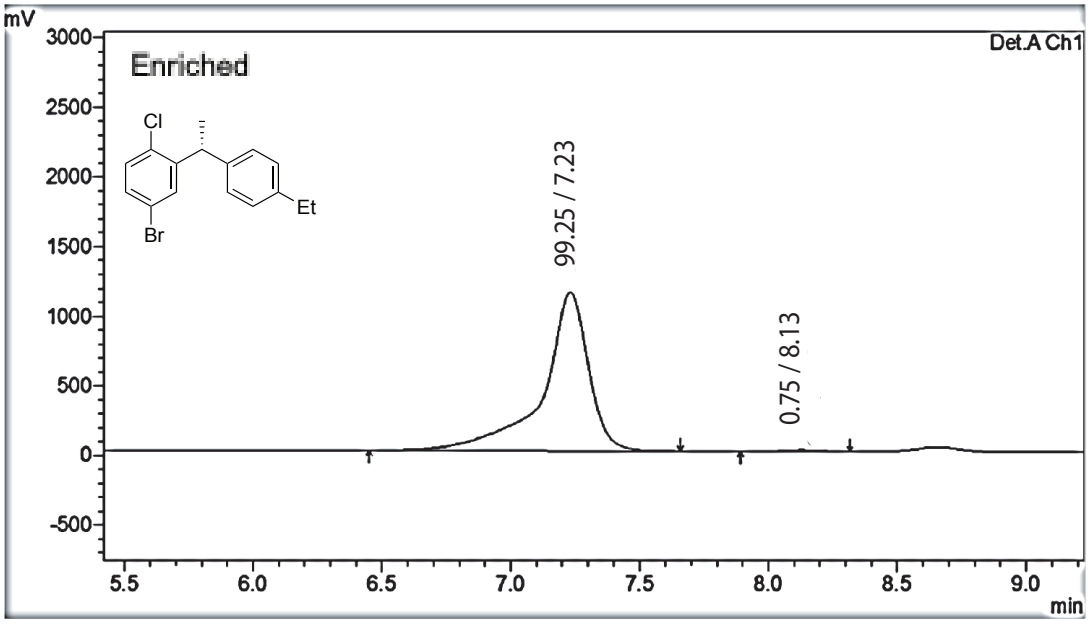
23

^{13}C, 125 MHz, $CDCl_3$



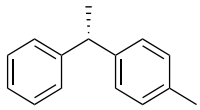




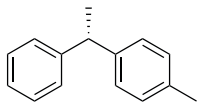


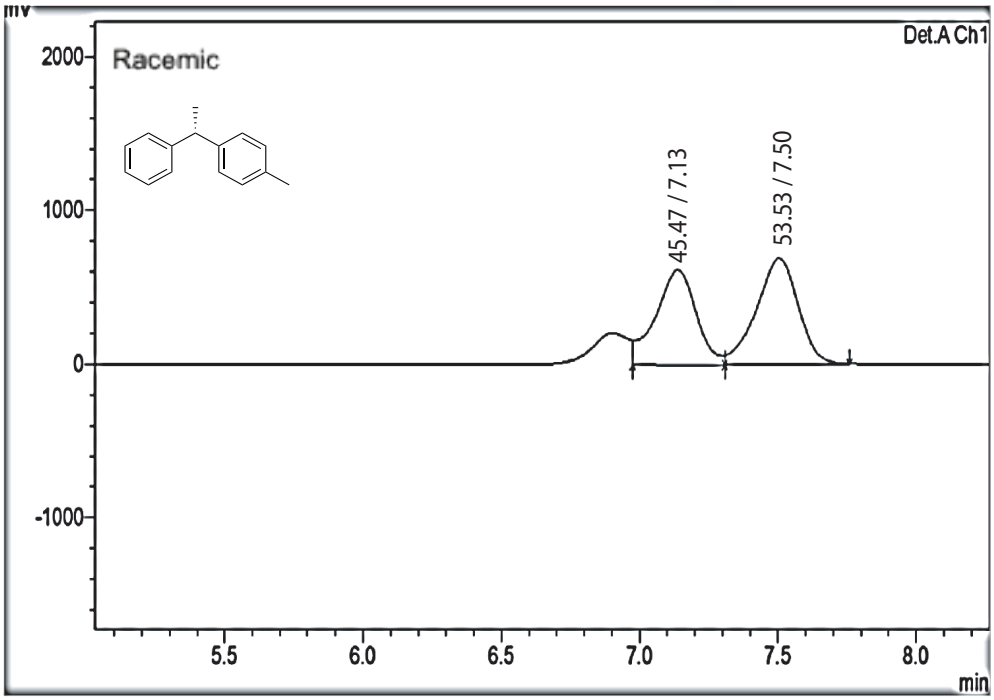
*Numbers above peaks indicate percent area and retention time respectively

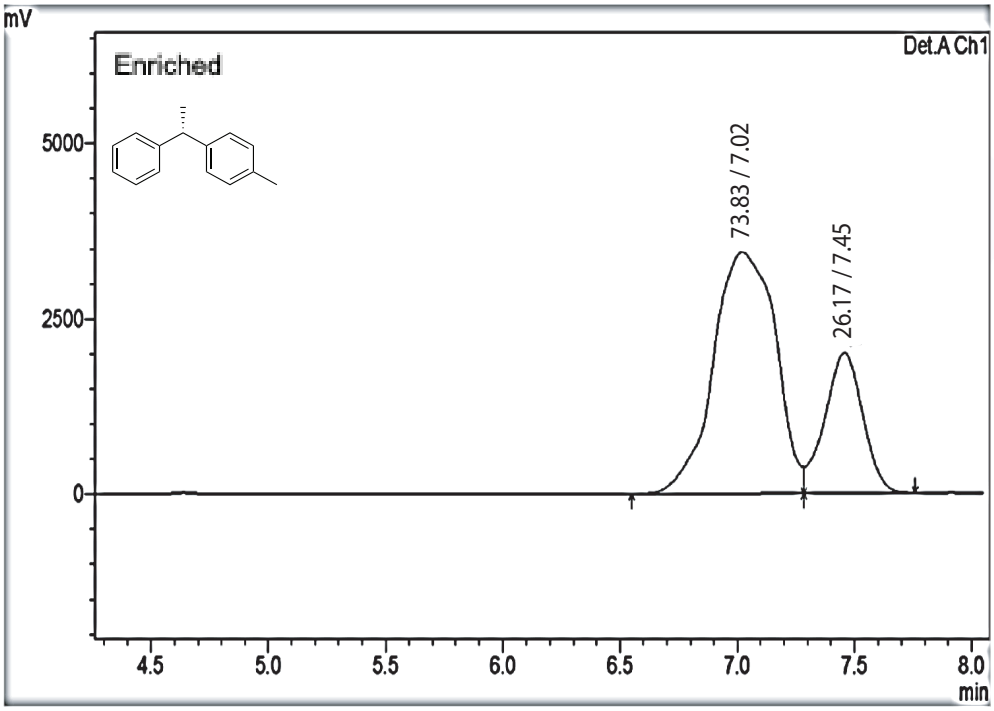
24
^{1}H, 500 MHz, $CDCl_3$



24
^{13}C, 125 MHz, $CDCl_3$



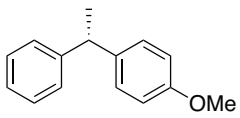




*Numbers above peaks in HPLC trace indicate retention time and percent area respectively

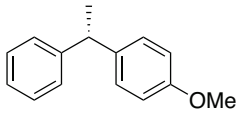
25

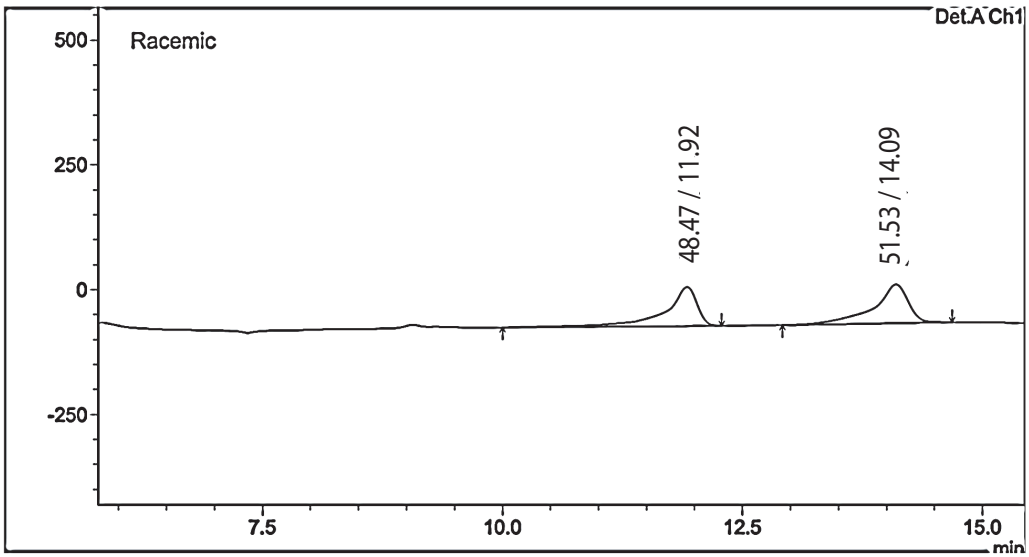
^{1}H, 400 MHz, $CDCl_3$

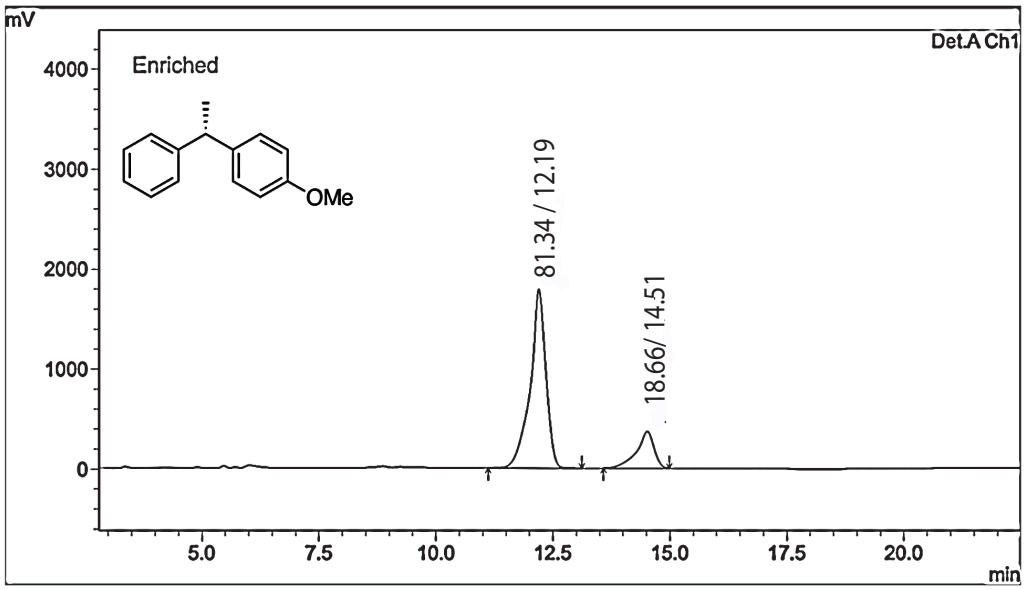


25

^{13}C, 125 MHz, $CDCl_3$



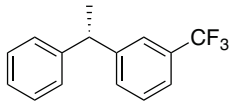


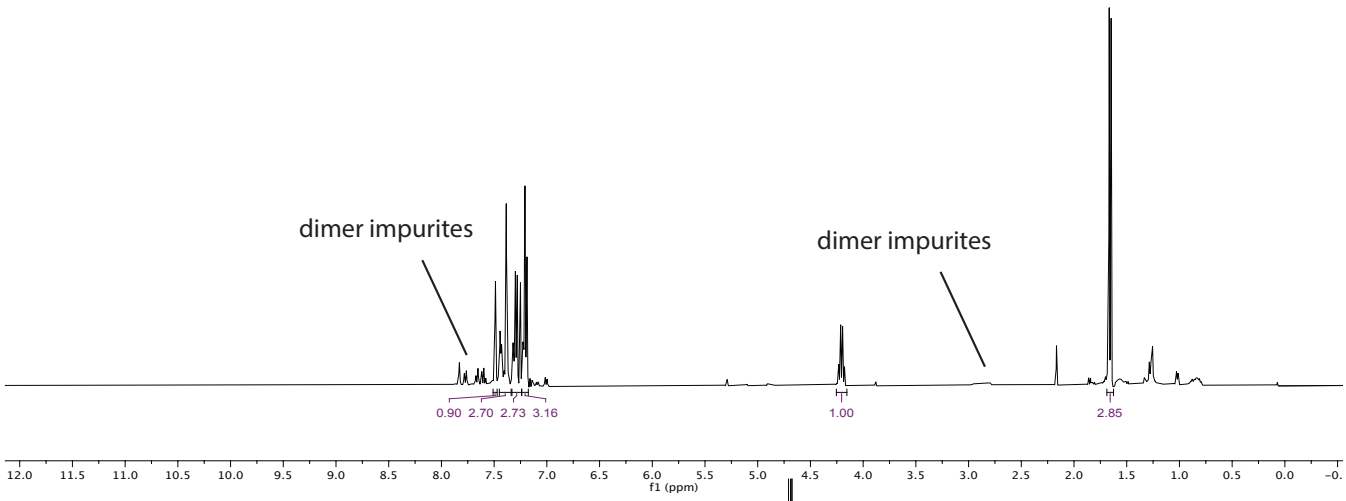


*Numbers above peaks in HPLC traces indicate percent area and retention time respectively

26

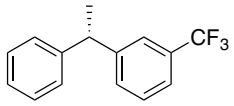
^{1}H, 500 MHz, $CDCl_3$

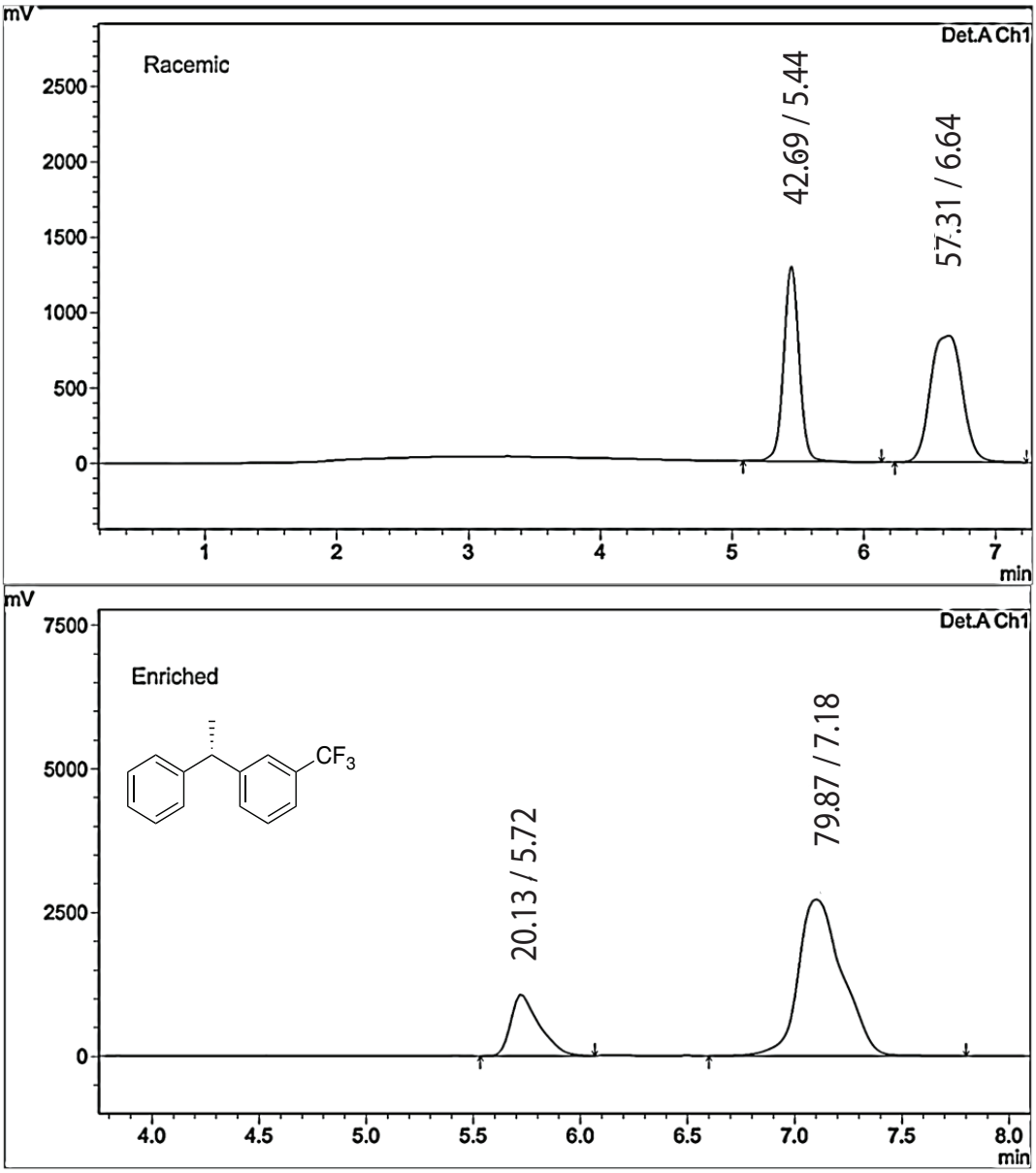




26

^{13}C, 125 MHz, $CDCl_3$

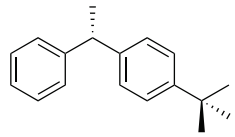




*Numbers above peaks in HPLC traces indicate percent area and retention time respectively

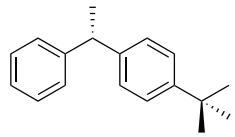
27

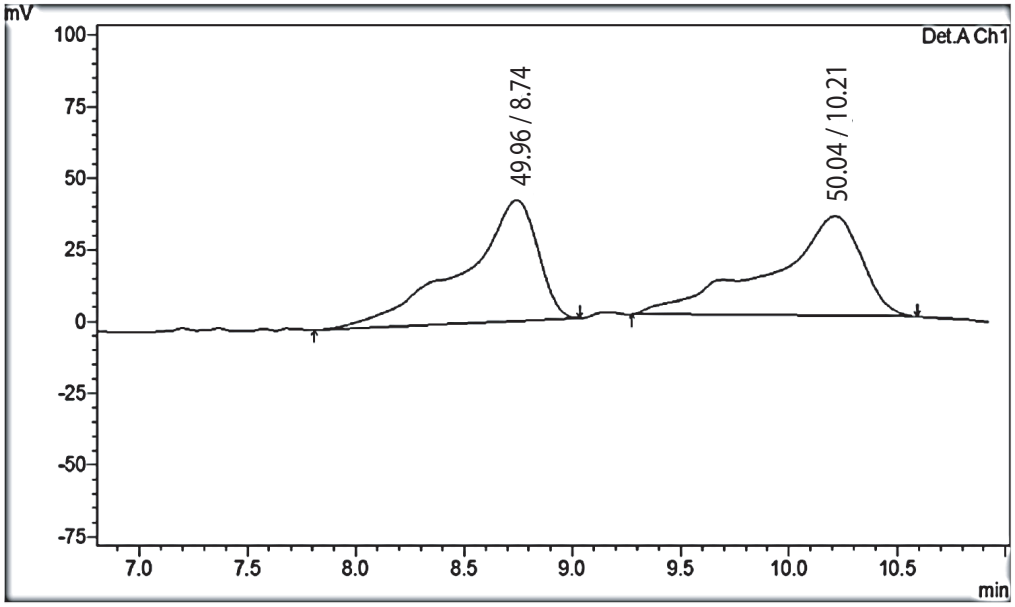
^{1}H, 500 MHz, $CDCl_3$

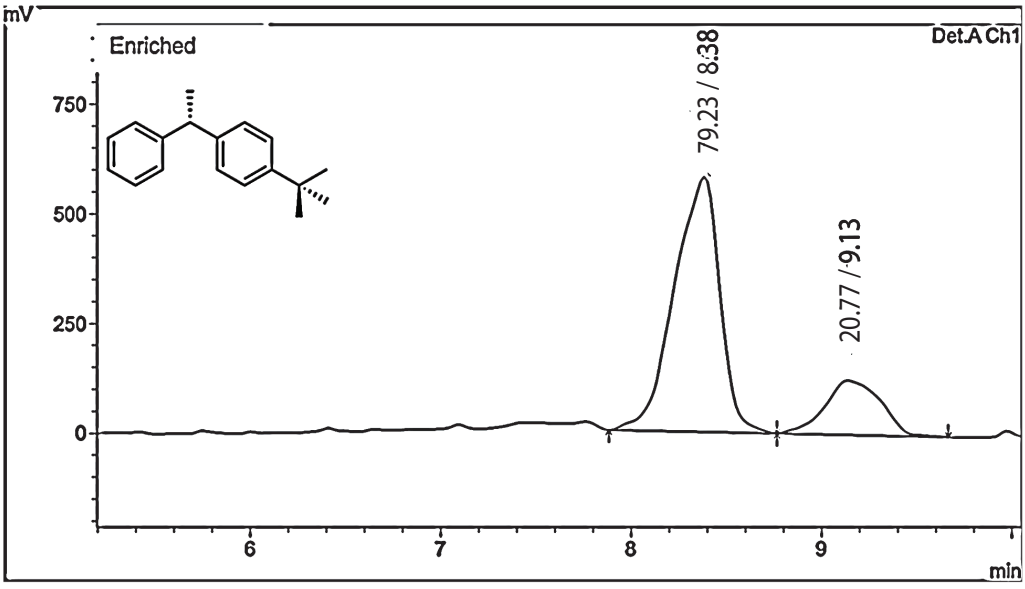


27

^{13}C, 125 MHz, $CDCl_3$







*Numbers above peaks in HPLC traces indicate percent area and retention time respectively

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