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Supporting Information

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Iridium-Catalyzed Regio- and Enantioselective *N*-Allylation of Indoles

Levi M. Stanley and John F. Hartwig

Department of Chemistry, University of Illinois, 600 South Mathews Avenue, Urbana, Illinois 61801

Supporting Information

Table of Contents

General Experimental Details

All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. THF and CH_2Cl_2 were degassed by purging with argon for 45 minutes and dried with a solvent purification system containing a one-meter column of activated alumina. Potassium phosphate and cesium carbonate were dried by heating at 110 °C in a vacuum oven for 24 h. Ethyl indole-2-carboxylate **4a**, methyl indole-3-carboxylate **4g**, indole-3-carboxaldehyde **4h**, 3-acetylindole **4i**, 3-cyanoindole **4j**, 2-phenylindole-3-carboxaldehyde **4m**, and carbazole **4p** were purchased from Sigma-Aldrich and

used without further purification. Ethyl 5-methoxyindole-2-carboxylate **4b**, ethyl 5-fluoroindole-2-carboxylate **4c**, ethyl 5-chloroindole-2-carboxylate **4d**, and 7-azaindole **7** were purchased from Alfa Aesar and used without further purification. Ethyl 5-nitroindole-2-carboxylate **4e** was purchased from Acros and used without further purification. Indole-2-carboxaldehyde **4f**,[1] 3-phenylindole **4k**,[2] 3-methylindole-2-carboxaldehyde **4l**,[2] and 2,3-diphenylindole **4n**[3] were synthesized according to published procedures. 3-Methyl-2-phenylindole **4o** was prepared according to a literature procedure from phenylhydrazine and propiophenone.[3]

$[Ir(COD)Cl]_2$ was synthesized from $IrCl_3 \cdot xH_2O$ and 1,5-cyclooctadiene according to a literature procedure[4] or was obtained from Johnson-Mathey and used without further purification. Phosphoramidite ligands **L1** and **L2** were synthesized according to literature procedures.[5] [Ir(COD)(κ^2-**L1**)(ethylene)] (**1**)[6] and [Ir(COD)(κ^2-**L2**)(ethylene)] (**2**)[7] were prepared according to literature procedures.

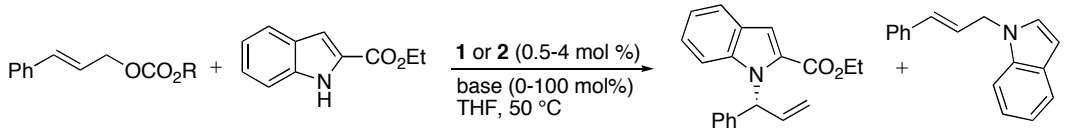
Methyl cinnamyl carbonate was synthesized from the reaction of cinnamyl alcohol with methyl chloroformate using pyridine as the base. Allylic Boc carbonates were synthesized from reactions of the corresponding allylic alcohols with Boc_2O using 30% aq. NaOH as the base and a catalytic quantity of Bu_4HSO_4 as a phase transfer catalyst.[8] Cinnamyl alcohol, trans, trans-2,4-hexadiene-1-ol, and *trans*-2-hexen-1-ol were purchased from Aldrich. (*E*)-4-Methoxycinnamyl alcohol, (*E*)-2-methoxycinnamyl alcohol, and (*E*)-3-(2-furanyl)-2-propen-1-ol were synthesized by reduction of corresponding commercially available aldehydes with $NaBH_4$. (*E*)-3-(4-bromophenyl)prop-2-en-1-ol, (*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol, (*E*)-3-methoxycinnamyl alcohol, (*E*)-3-cyclohexylprop-2-en-1-ol, and (*E*)-4-(benzyloxy)but-2-en-1-ol were synthesized by reduction of the corresponding α,β-unsaturated ethyl esters with DIBAL-H. The α,β-unsaturated ethyl esters were synthesized from the appropriate aldehyde and triethyl phosphonoacetate by the Roush-Masamune modification of the Horner-Wadsworth-Emmons reaction.[9]

Elemental analyses were performed by the University of Illinois at Urbana-Champaign Microanalysis Laboratory and by Roberston Microlit Laboratories, Inc. (Madison, NJ). HRMS (ESI) analyses were performed by the University of Illinois Mass Spectrometry Center. GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an FID detector. Optical rotations were measured on a Rudolph Instruments (Denville, NJ) Autopol IV polarimeter. NMR spectra were acquired on 500 MHz Varian Unity or Inova instruments at the University of Illinois VOICE NMR facility. Chemical shifts are reported in ppm relative to a residual solvent peak ($CDCl_3$ = 7.26 ppm for ^1H and 77.23 ppm for ^{13}C) or to an external standard (85% H_3PO_4 = 0 ppm for ^{31}P). Coupling constants are reported in hertz. HPLC analyses were carried out on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector).

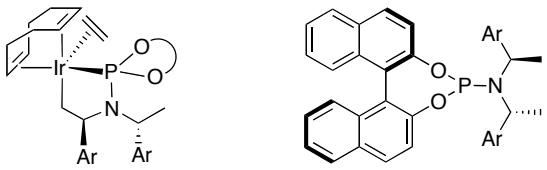
Flash column chromatography was performed on Silicycle Siala-P silica gel using hexanes/ethyl acetate, hexanes/acetone, hexanes/isopropanol, or chloroform/MeOH mixtures. Products were visualized on TLC by UV or by staining with $KMnO_4$ or ceric ammonium molybdate.

Development of Reaction Conditions for the Iridium-Catalyzed *N*-Allylation of 4a

Table S1. Study of reaction conditions for the *N*-allylation of **4a** with alkyl cinnamyl carbonates.



R = Me, Et, *i*Pr or *t*Bu **4a** **5a** **6a**



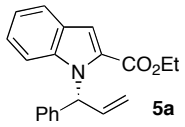
[Ir(COD)(κ²-**L1**)(ethylene)] (**1**) **L1**: Ar = Ph
[Ir(COD)(κ²-**L2**)(ethylene)] (**2**) **L2**: Ar = 2-MeO-C_6H_4

Entry	Catalyst (mol%)	R	Base (mol %)	Conversion [%]	**5a**:**6a**	Yield **5a** [%]	Ee [%]
1	**1** (4)	Me	K_3PO_4 (100)	69	98:2	48	96
2	**1** (2)	Me	K_3PO_4 (100)	64	94:6	52	96
3	**1** (2)	Me	Cs_2CO_3 (100)	96	97:3	86	97
4	**2** (2)	Me	Cs_2CO_3 (100)	99	98:2	90	99
5	**2** (1)	Me	Cs_2CO_3 (100)	81	98:2	77	99
6	**2** (0.5)	Me	Cs_2CO_3 (100)	68	98:2	62	99
7	**2** (2)	Me	Cs_2CO_3 (50)	99	98:2	89	99
8	**2** (2)	Me	Cs_2CO_3 (20)	99	97:3	83	99
9	**2** (2)	Me	Cs_2CO_3 (10)	99	97:3	87	99
10	**2** (2)	Me	--	96	98:2	78	99
11	**2** (2)	Et	Cs_2CO_3 (10)	99	97:3	82	99
12	**2** (2)	*i*Pr	Cs_2CO_3 (10)	99	96:4	85	99
13	**2** (2)	*t*Bu	Cs_2CO_3 (10)	99	97:3	89	99

In a nitrogen-filled dry-box, the catalyst precursor **1** or **2** (0.5-4 mol %), base (0-100 mol %), ethyl indole-2-carboxylate **4a** (0.104 g, 0.550 mmol), and THF (1 mL) were added to a 1-dram vial. Then, the alkyl cinnamyl carbonate (0.500 mmol) and dodecane (20 μL) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and heated at 50 °C in an oil bath. Reaction progress was monitored by GC. When the reaction to be complete, the vial was removed from the oil bath, cooled to room temperature, then filtered through a 0.5 inch plug of silica gel (eluting with EtOAc). The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (23 μL) was added as an internal standard. The branched-to-linear ratio was then determined by ^1H NMR spectroscopy. After this analysis, the crude reaction mixture was purified by flash column column chromatography (97:3 hexanes:EtOAc) to yield **5a**. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.8 min (*S*); t_R 6.0 min (*R*) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min].

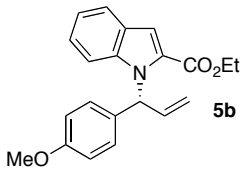
General Procedure for *N*-Allylation of Indoles

In a nitrogen-filled dry-box, the catalyst precursor **2** (0.010 mmol, 0.020 equiv), Cs_2CO_3 (0.050 mmol, 0.100 equiv), indole nucleophile **4** or azaindole **7** (0.550 mmol, 1.10 equiv), and THF (1 mL) were added to a 1-dram vial. Then, the allylic carbonate **3** (0.500 mmol, 1.00 equiv) and dodecane (20 μL) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and heated at 50 °C in an oil bath. Reaction progress was monitored by GC. When the reaction was judged to be complete, the vial was removed from the oil bath, cooled to room temperature, then filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove solid Cs_2CO_3. The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (23 μL) was added as an internal standard. The branched-to-linear ratio was then determined by ^{1}H NMR spectroscopy. After this analysis, the crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, hexanes:acetone, or chloroform:MeOH mixtures) to yield product **5** or **8**.



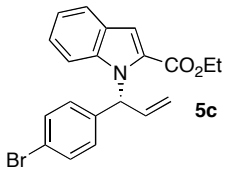
5a

(*R*)-Ethyl 1-(1-phenylallyl)-1*H*-indole-2-carboxylate (**5a**): Prepared according to the general procedure from **3a** (0.0961 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 97:3 branched:linear ratio. The mixture was purified by flash column chromatography (97:3 hexanes:EtOAc) to give **5a** as a white amorphous solid in 89% yield (0.136 g, 0.445 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.8 min (minor); t_R 6.0 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +45.5° (c 1.27, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.44 (t, *J* = 7.0 Hz, 3H), 4.40 (q, *J* = 7.0 Hz, 2H), 5.27 (d, *J* = 17.5 Hz, 1H), 5.43 (d, *J* = 10.5 Hz, 1H), 6.64 (ddd, *J* = 17.5, 10.5, 6.5 Hz, 1H), 7.09-7.14 (m, 3H), 7.25-7.35 (m, 5H), 7.47 (s, 1H), 7.62 (d, *J* = 6.5 Hz, 1H), 7.70-7.72 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5, 60.7, 60.9, 112.0, 114.1, 119.4, 120.7, 122.8, 124.7, 126.9, 127.0, 127.4, 128.1, 128.7, 135.2, 138.5, 139.8, 162.5. Anal. Calcd. for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27, N, 4.59; found: C, 78.74; H, 6.45; N, 4.56.

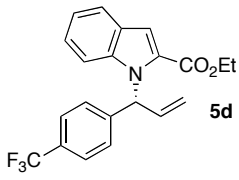


5b

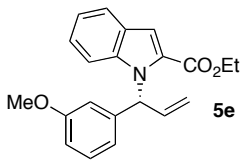
(*R*)-Ethyl 1-(1-(4-methoxyphenyl)allyl)-1*H*-indole-2-carboxylate (**5b**): Prepared according to the general procedure from **3b** (0.111 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 99:1 branched:linear ratio. The mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **5b** as a colorless oil in 88% yield (0.147 g, 0.438 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.8 min (minor); t_R 11.6 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +40.2° (c 1.23, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 3.79 (s, 3H), 4.40 (q, 7.0 Hz, 2H), 5.22 (d, *J* = 17.0 Hz, 1H), 5.40 (d, *J* = 10.5 Hz, 1H), 6.01 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.08-7.14 (m, 3H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.45 (s, 1H), 7.54 (d, *J* = 6.5 Hz, 1H), 7.67-7.71 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.6, 55.5, 60.4, 60.9, 112.0, 114.1, 114.3, 119.1, 120.8, 122.9, 124.7, 127.0, 128.2, 128.3, 132.0, 135.6, 138.6, 158.9, 162.6. Anal. Calcd. for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31, N, 4.18; found: C, 75.44; H, 6.54; N, 3.99.



(*R*)-Ethyl 1-(1-(4-bromophenyl)allyl)-1*H*-indole-2-carboxylate (5c): Prepared according to the general procedure from **3c** (0.160 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 5 h). ^{1}H NMR spectroscopy showed a 97:3 branched:linear ratio. The mixture was purified by flash column chromatography (98:2 hexanes:EtOAc) to give **5c** as a colorless oil in 87% yield (0.168 g, 0.437 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.2 min (minor); t_R 8.0 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +14.8° (c 1.42, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 4.39 (q, *J* = 7.0 Hz, 2H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.43 (d, *J* = 10.5 Hz, 1H), 6.57 (ddd, *J* = 17.0, 10.5, 7.0 Hz, 1H), 7.06-7.17 (m, 5H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.46 (s, 1H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5, 60.3, 60.9, 112.2, 113.8, 119.9, 120.9, 121.4, 123.0, 124.9, 126.9, 127.9, 128.7, 131.8, 134.7, 138.3, 138.9, 162.5. Anal. Calcd. for $C_{20}H_{18}NO_2Br$: C, 62.51; H, 4.72, N, 3.65; found: C, 62.78; H, 4.87; N, 3.61.

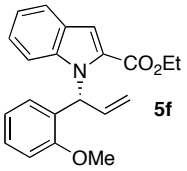


(*R*)-Ethyl 1-(1-(4-(trifluoromethyl)phenyl)allyl)-1*H*-indole-2-carboxylate (5d): Prepared according to a modified version of the general procedure from **3d** (0.151 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) using 4 mol % **2** (0.0185 g, 0.0200 mmol) as the catalyst precursor (reaction time = 24 h). ^{1}H NMR spectroscopy showed a 91:9 branched:linear ratio. The mixture was purified by flash column chromatography (96:4 hexanes:EtOAc) to give **5d** as a colorless oil in 85% yield (0.159 g, 0.426 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.4 min (major); t_R 7.0 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +7.1° (c 1.21, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.42 (t, *J* = 7.0 Hz, 3H), 3.39 (q, *J* = 7.0 Hz, 2H), 5.32 (d, *J* = 17.0 Hz, 1H), 5.47 (d, *J* = 10.5 Hz, 1H), 6.60 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.12-7.18 (m, 2 H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.48 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 6.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5, 60.5, 61.0, 112.3, 113.7, 120.3, 121.0, 123.1, 124.3 (q, J = 271 Hz), 125.1, 125.7 (q, J_{CF} = 3.6 Hz), 127.0, 127.3, 127.9, 129.7 (q, J_{CF} = 33 Hz), 134.5, 138.4, 144.0, 152.5. Anal. Calcd. for $C_{21}H_{18}NO_2F_3$: C, 67.55; H, 4.86, N, 3.75; found: C, 67.70; H, 5.00; N, 3.76.



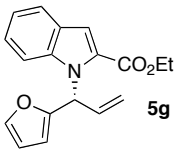
(*R*)-Ethyl 1-(1-(3-methoxyphenyl)allyl)-1*H*-indole-2-carboxylate (5e): Prepared according to the general procedure from **3e** (0.132 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 8 h). ^{1}H NMR spectroscopy showed a 98:2 branched:linear ratio. The mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **5f** as a colorless oil in 95% yield (0.159 g, 0.474 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.6 min (minor); t_R 8.9 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 99%. $[\alpha]_D^{26}$ = +48.1° (c 1.36, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 3.74 (s, 3H), 4.40 (q, *J* = 7.0 Hz, 2H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 6.61 (ddd, *J* = 17.0, 10.5, 7.0 Hz, 1H), 6.80-6.84 (m, 3H), 7.09-7.14 (m, 3H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.46 (s, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.68-7.71 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.8, 55.3, 60.6, 60.8, 112.0, 112.3, 113.1, 114.1, 119.3, 119.4, 120.7, 122.8, 124.7, 126.8, 128.0, 129.7,

135.0, 138.5, 141.5, 159.9, 162.5. Anal. Calcd. for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31, N, 4.18; found: C, 75.24; H, 6.49; N, 3.94.



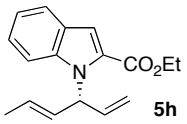
5f

(*R*)-Ethyl 1-(1-(2-methoxyphenyl)allyl)-1*H*-indole-2-carboxylate (5f): Prepared according to a modified version of the general procedure (reaction temperature = room temperature) from **3f** (0.132 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 20 h). ^{1}H NMR spectroscopy showed a 95:5 branched:linear ratio. The mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **5f** as a colorless oil in 72% yield (0.121 g, 0.361 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.2 min (major); t_R 8.0 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 96%. $[\alpha]_D^{26}$ = +132.3° (c 0.60, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.44 (t, *J* = 7.0 Hz, 3H), 3.62 (s, 3H), 4.42 (q, *J* = 7.0 Hz, 2H), 5.08 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.42 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.58 (ddd, *J* = 17.0, 10.5, 4.5 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.0 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.5, 1H), 7.37 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.71-7.72 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.6, 55.5, 56.6, 60.7, 110.7, 111.1, 114.1, 117.4, 120.1, 120.2, 122.5, 124.1, 126.7, 127.7, 128.9, 129.1, 129.3, 135.4, 138.9, 157.9, 162.5. Anal. Calcd. for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31, N, 4.18; found: C, 74.92; H, 6.59; N, 4.03.



5g

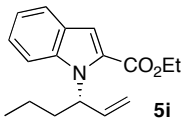
(*R*)-Ethyl 1-(1-(furan-2-yl)allyl)-1*H*-indole-2-carboxylate (5g): Prepared according to a modified version of the general procedure (reaction temperature = room temperature) from **3g** (0.112 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 91:9 branched:linear ratio. The mixture was purified by flash column chromatography (98:2 hexanes:EtOAc) to give **5g** as a colorless oil in 85% yield (0.125 g, 0.423 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.1 min (minor); t_R 11.5 min (major) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 99%. $[\alpha]_D^{24}$ = +24.7° (c 0.70, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.45 (t, *J* = 7.0 Hz, 3H), 4.43 (q, *J* = 7.0 Hz, 2H), 5.13 (ddd, *J* = 17.0, 2.0, 1.0 Hz, 1H), 5.39 (ddd, *J* = 10.5, 2.0, 1.0 Hz, 1H), 6.37 (app d, *J* = 1.0 Hz, 2H), 6.50 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1H), 7.14 (ddd, *J* = 8.0, 8.0, 1.0 Hz, 1H), 7.21 (ddd, *J* = 8.5, 8.0, 1.0 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.34 (dd, *J* = 1.0, 1.0 Hz, 1H), 7.45 (d, *J* = 1.0, 1H), 7.70 (ddd, *J* = 8.0, 1.0, 1.0 Hz, 1H), 7.72 (ddd, *J* = 5.5, 2.0, 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5, 55.1, 60.9, 108.3, 110.4, 112.0, 113.7, 118.4, 120.8, 122.8, 124.9, 126.7, 127.6, 133.4, 138.7, 142.6, 152.4, 162.5. Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80, N, 4.74; found: C, 73.18; H, 5.93; N, 4.66.



5h

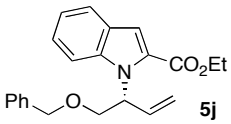
(*R*,*E*)-Ethyl 1-(hexa-1,4-dien-3-yl)-1*H*-indole-2-carboxylate (5h): Prepared according to a modified version of the general procedure (reaction temperature = room temperature) from **3h** (0.0991 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 23 h). ^{1}H NMR spectroscopy showed a 99:1 branched:linear ratio. The mixture was purified by flash column chromatography (98:2 hexanes:EtOAc) to give **5h** as a colorless oil in 86% yield (0.116 g, 0.429 mmol). The enantiomeric excess after reduction of the ester with lithium aluminum hydride was determined by HPLC analysis (254 nm, 25 °C) t_R 12.2 min (major); t_R 13.9 min (minor) [Chiracel AD-H

(0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = -18.6° (c 1.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 1.74 (d, *J* = 6.5 Hz, 3H), 4.39 (q, *J* = 7.0 Hz, 2H), 5.20 (d, *J* = 17.0 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.69-5.76 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.97 (ddd, *J* = 15.5, 6.0, 1.5 Hz, 1H), 6.28 (ddd, *J* = 17.0, 10.5, 4.5 Hz, 1H), 6.91 (br s, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.37 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.5, 18.0, 58.9, 60.8, 111.5, 114.1, 116.7, 120.6, 122.8, 124.5, 126.7, 127.4, 128.7, 129.2, 137.3, 138.5, 162.5. Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11, N, 5.20; found: C, 75.83; H, 7.25; N, 5.15.



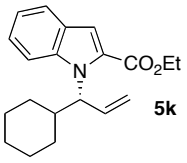
5i

(*S*)-Ethyl 1-(hex-1-en-3-yl)-1*H*-indole-2-carboxylate (5i): Prepared according to a modified version of the general procedure (reaction temperature = room temperature) from **3i** (0.100 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 4 h). ^{1}H NMR spectroscopy showed a 94:6 branched:linear ratio. The mixture was purified by flash column chromatography (97:3 hexanes:EtOAc) to give **5i** as a colorless oil in 92% yield (0.125 g, 0.460 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.4 min (major); t_R 6.1 min (minor) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +61.5° (c 1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, *J* = 7.0 Hz, 3H), 0.93-1.02 (m, 1H), 1.23-1.30 (m, 1H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.96-2.06 (m, 1H), 2.21-2.29 (m, 1H), 4.39 (q, *J* = 7.0 Hz, 2H), 5.16 (dd, *J* = 16.5, 1.5 Hz, 1H), 5.24 (dd, *J* = 10.0, 1.5 Hz, 1H), 6.25-6.32 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.5 Hz, 1H), 7.37 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 14.5, 19.7, 35.0, 57.5, 60.8, 111.3, 113.9, 115.9, 120.5, 122.9, 124.4, 126.7, 128.4, 138.0, 138.2, 162.6. Anal. Calcd. for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80, N, 5.16; found: C, 75.33; H, 7.81; N, 5.12.

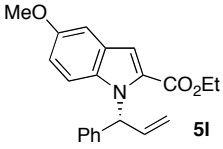


5j

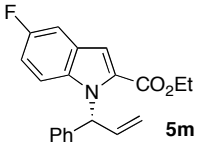
(*R*)-Ethyl 1-(1-(benzyloxy)but-3-en-2-yl)-1*H*-indole-2-carboxylate (5j): Prepared according to a modified version of the general procedure (reaction temperature = room temperature) from **3j** (0.139 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 77:23 branched:linear ratio. The mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **5j** as a colorless oil in 70% yield (0.122 g, 0.349 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 10.0 min (minor); t_R 16.5 min (major) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = +25.8° (c 0.86, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 4.06-4.12 (m, 2H), 4.39 (q, *J* = 7.0 Hz, 2H), 4.41 (d, *J* = 12.5 Hz, 1H), 4.48 (d, *J* = 12.5 Hz, 1H), 5.21 (ddd, *J* = 17.5, 1.0, 1.0 Hz, 1H), 5.33 (ddd, *J* = 11.0, 1.0, 1.0 Hz, 1H), 6.32 (ddd, *J* = 17.5, 11.0, 4.5 Hz, 1H), 6.58 (br s, 1H), 7.12-7.28 (m, 7H), 7.42 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5, 57.2, 60.8, 70.6, 72.9, 111.7, 113.7, 117.4, 120.7, 122.9, 124.5, 126.9, 127.5, 127.6, 128.4, 128.6, 134.7, 138.2, 138.6, 162.5. Anal. Calcd. for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63, N, 4.01; found: C, 75.47; H, 6.57; N, 3.87.



(*R*)-Ethyl 1-(1-cyclohexylallyl)-1*H*-indole-2-carboxylate (5k): Prepared according to a modified version of the general procedure from **3k** (0.120 g, 0.500 mmol) and **4a** (0.104 g, 0.550 mmol) using 4 mol % **2** (0.0185 g, 0.0200 mmol) as the catalyst precursor (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 87:13 branched:linear ratio. The mixture was purified by flash column chromatography (98:2 hexanes:EtOAc) to give **5k** as a colorless oil in 54% yield (0.0841 g, 0.270 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 3.8 min (major); t_R 5.0 min (minor) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +92.6° (c 0.48, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.84-1.33 (series of m, 6H), 1.43 (t, *J* = 7.5 Hz, 3H), 1.44-2.31 (series of m, 5H), 4.34-4.40 (m, 2H), 5.14 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 5.83 (br s, 1H), 6.44 (ddd, *J* = 17.0, 10.5, 7.0 Hz, 1H), 7.13 (dd, *J* = 8.5, 8.0 Hz, 1H), 7.27 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.34 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.6, 26.0, 26.2, 26.5, 29.6, 31.5, 40.0, 60.8, 64.0, 111.4, 113.8, 118.5, 120.5, 123.0, 123.2, 124.5, 126.7, 128.5, 135.6, 139.3, 162.7. Anal. Calcd. for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09, N, 4.50; found: C, 76.86; H, 8.24; N, 4.34.

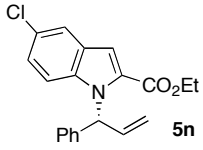


(*R*)-Ethyl 5-methoxy-1-(1-phenylallyl)-1*H*-indole-2-carboxylate (5l): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4b** (0.121 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 97:3 branched:linear ratio. The mixture was purified by flash column chromatography (96:4 hexanes:EtOAc) to give **5l** as a white amorphous solid in 88% yield (0.147 g, 0.438 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.2 min (minor); t_R 9.2 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +52.1° (c 1.12, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 3.83 (s, 3H), 4.39 (q, 7.0 Hz, 2H), 5.25 (d, *J* = 17.5 Hz, 1H), 5.42 (d, *J* = 10.0 Hz, 1H), 6.60 (ddd, *J* = 17.5, 10.0, 7.0 Hz, 1H), 6.81 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.99 (d, *J* = 9.5 Hz, 1H), 7.09 (d, *J* = 2.5 Hz, 1H), 7.23-7.34 (m, 5H), 7.38 (s, 1H), 7.60 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5, 55.7, 60.6, 60.8, 102.6, 111.3, 115.0 116.2, 119.2, 127.0, 127.2, 127.4, 128.3, 128.6, 133.9, 135.3, 139.9, 154.6, 162.4. Anal. Calcd. for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31, N, 4.18; found: C, 75.24; H, 6.58; N, 4.09.



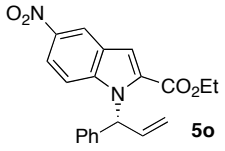
(*R*)-Ethyl 5-fluoro-1-(1-phenylallyl)-1*H*-indole-2-carboxylate (5m): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4c** (0.114 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 94:6 branched:linear ratio. The mixture was purified by flash column chromatography (97:3 hexanes:EtOAc) to give **5m** as a white amorphous solid in 84% yield (0.136 g, 0.421 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.6 min (minor); t_R 5.8 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{26}$ = +62.4° (c 1.10, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 4.40 (q, *J* = 7.0 Hz, 2H), 5.24 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.43 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.58 (ddd, *J* = 17.0, 10.5, 7.0 Hz, 1H), 6.88 (dt, *J* = 2.5, 9.0 Hz, 1H), 7.01 (dd, *J* = 9.0, 4.0 Hz, 1H), 7.22-7.34 (m, 6H), 7.40 (s, 1H), 7.61 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5, 60.7, 61.0, 106.8 (d, J_{CF} = 22.9 Hz), 111.5, (d, J_{CF} = 4.5 Hz), 113.8 (d, J_{CF} = 26.6 Hz), 115.1 (d, J_{CF} = 9.1 Hz), 119.5, 127.0,

127.1, 127.5, 128.8, 129.5, 134.96, 135.04, 139.6, 158.1 (d, J_{CF} = 237.5 Hz), 162.3. Anal. Calcd. for $C_{20}H_{18}FNO_2$: C, 74.29; H, 5.61, N, 4.33; found: C, 74.05; H, 5.79; N, 4.23.



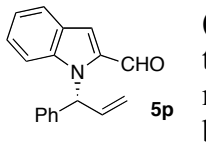
5n

(*R*)-Ethyl 5-chloro-1-(1-phenylallyl)-1*H*-indole-2-carboxylate (**5n**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4d** (0.123 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 95:5 branched:linear ratio. The mixture was purified by flash column chromatography (97:3 hexanes:EtOAc) to give **5n** as a white amorphous solid in 91% yield (0.154 g, 0.454 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.9 min (minor); t_R 5.8 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{26}$ = +46.9° (c 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 4.39 (q, *J* = 7.0 Hz, 2H), 5.22 (d, *J* = 17.0 Hz, 1H), 5.43 (d, *J* = 10.5 Hz, 1H), 6.57 (ddd, *J* = 17.0, 10.0, 7.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 7.05 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 2H), 7.27-7.34 (m, 3H), 7.37 (s, 1H), 7.60 (d, *J* = 7.0 Hz, 1H), 7.65 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.6, 60.8, 61.2, 111.2, 115.3, 119.6, 122.0, 125.2, 126.6, 127.0, 127.7, 127.8, 128.9, 129.4, 134.9, 136.8, 139.5, 162.3. Anal. Calcd. for $C_{20}H_{18}ClNO_2$: C, 70.69; H, 5.34, N, 4.12; found: C, 70.84; H, 5.49; N, 4.00.



5o

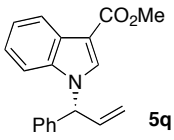
(*R*)-Ethyl 5-nitro-1-(1-phenylallyl)-1*H*-indole-2-carboxylate (**5o**): Prepared according to a modified version of the general procedure from methyl cinnamyl carbonate (0.0961 g, 0.500 mmol) and **4e** (0.129 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 94:6 branched:linear ratio. The mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **5o** as a pale yellow amorphous solid in 90% yield (0.158 g, 0.451 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.8 min (minor); t_R 10.3 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +36.6° (c 1.46, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43 (t, *J* = 7.0 Hz, 3H), 4.41 (q, *J* = 7.0 Hz, 2H), 5.21 (d, *J* = 17.0 Hz, 1H), 5.46 (d, *J* = 10.0 Hz, 1H), 6.56 (ddd, *J* = 17.0, 10.0, 6.5 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.26-7.34 (m, 3H), 7.57 (s, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.95 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.63 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.4, 61.1, 61.5, 113.6, 114.2, 119.5, 119.9, 120.0, 125.9, 126.9, 127.9, 128.9, 131.4, 134.3, 138.8, 140.8, 142.4, 161.7. Anal. Calcd. for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18, N, 8.00; found: C, 68.63; H, 5.25; N, 7.97.



5p

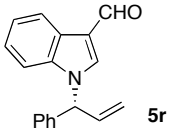
(*R*)-1-(1-Phenylallyl)-1*H*-indole-2-carbaldehyde (**5p**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4f** (0.0798 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 98:2 branched:linear ratio. The mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **5p** as a yellow oil in 89% yield (0.117 g, 0.447 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.3 min (minor); t_R 6.9 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +27.8° (c 1.32, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.10 (d, *J* = 17.0 Hz, 1H), 5.52 (d, *J* = 10.5 Hz, 1H), 6.18 (d, *J* = 5.5 Hz, 1H), 6.38 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1H), 7.23-7.42 (m, 8H), 7.74 (s, 1H), 8.36 (dd, *J* = 8.5, 1.5 Hz, 1H), 10.0 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 60.9, 114.2, 119.6, 119.8, 121.2, 123.7, 126.7, 127.1,

127.4, 127.6, 128.7, 135.0, 135.7, 139.3, 139.9, 183.0. Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79, N, 5.36; found: C, 82.57; H, 5.74; N, 5.22.



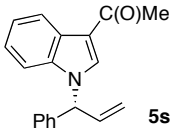
5q

(*R*)-Methyl 1-(1-phenylallyl)-1*H*-indole-3-carboxylate (**5q**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4g** (0.0963 g, 0.550 mmol) (reaction time = 3 h). ^{1}H NMR spectroscopy showed a 96:4 branched:linear ratio. The mixture was purified by flash column chromatography (90:10 hexanes:EtOAc) to give **5q** as a colorless oil in 84% yield (0.123 g, 0.422 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.2 min (minor); t_R 11.1 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 97%. $[\alpha]_D^{25}$ = -25.7° (c 1.23, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.92 (s, 3H), 5.07 (d, *J* = 17.0 Hz, 1H), 5.47 (d, *J* = 10.5 Hz, 1H), 6.15 (d, *J* = 5.5 Hz, 1H), 6.36 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1H), 7.20-7.38 (m, 8H), 7.88 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 51.1, 62.6, 110.9, 120.1, 121.9, 122.3, 123.0, 127.0, 127.7, 128.5, 129.1, 133.0, 135.3, 136.8, 137.8, 165.7. Anal. Calcd. for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88, N, 4.81; found: C, 78.19; H, 6.16; N, 4.73.



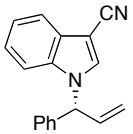
5r

(*R*)-1-(1-Phenylallyl)-1*H*-indole-3-carbaldehyde (**5r**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4h** (0.0798 g, 0.550 mmol) (reaction time = 3 h). ^{1}H NMR spectroscopy showed a 94:6 branched:linear ratio. The mixture was purified by flash column chromatography (80:20 hexanes:EtOAc) to give **5r** as a tan amorphous solid in 87% yield (0.114 g, 0.436 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 15.2 min (minor); t_R 21.7 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 96%. $[\alpha]_D^{25}$ = +1.3° (c 1.21, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.08 (d, *J* = 17.0 Hz, 1H), 5.50 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 6.0 Hz, 1H), 6.37 (ddd, *J* = 17.0, 10.0, 6.0 Hz, 1H), 7.22-7.41 (m, 8H), 7.73 (s, 1H), 8.36 (d, *J* = 7.5 Hz, 1H), 9.99 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 62.7, 111.0, 118.4, 120.3, 122.2, 123.2, 124.1, 125.7, 127.8, 128.8, 129.2, 134.9, 137.2, 137.3, 137.5, 184.8. Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79, N, 5.36; found: C, 82.76; H, 5.84; N, 5.30.



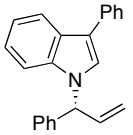
5s

(*R*)-1-(1-(1-Phenylallyl)-1*H*-indol-3-yl)ethanone (**5s**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4i** (0.0875 g, 0.550 mmol) (reaction time = 5 h). ^{1}H NMR spectroscopy showed a 98:2 branched:linear ratio. The mixture was purified by flash column chromatography (75:25 hexanes:EtOAc) to give **5s** as a colorless oil in 88% yield (0.122 g, 0.442 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 15.0 min (minor); t_R 20.0 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 96%. $[\alpha]_D^{25}$ = -19.9° (c 0.73, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.52 (s, 3H), 5.10 (d, *J* = 17.0 Hz, 1H), 5.51 (d, *J* = 10.0 Hz, 1H), 6.16 (d, *J* = 5.5 Hz, 1H), 6.39 (ddd, *J* = 17.0, 10.0, 5.5 Hz, 1H), 7.20-7.40 (m, 8H), 7.77 (s, 1H), 8.43 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.8, 62.6, 110.8, 117.5, 120.3, 122.7, 122.9, 123.4, 126.7, 127.6, 128.6, 129.1, 133.4, 135.1, 137.1, 137.7, 193.3. Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22, N, 5.09; found: C, 82.94; H, 6.05; N, 4.96.



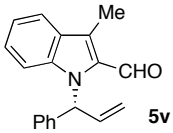
5t

(*R*)-1-(1-Phenylallyl)-1*H*-indole-3-carbonitrile (**5t**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4j** (0.0782 g, 0.550 mmol) (reaction time = 3 h). ^{1}H NMR spectroscopy showed a 96:4 branched:linear ratio. The mixture was purified by flash column chromatography (85:15 hexanes:EtOAc) to give **5t** as a white amorphous solid in 93% yield (0.120 g, 0.465 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 14.9 min (minor); t_R 15.9 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 96%. $[\alpha]_D^{25}$ = -5.6° (c 1.07, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.06 (d, *J* = 17.0 Hz, 1H), 5.50 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 6.0 Hz, 1H), 6.33 (ddd, *J* = 17.0, 10.0, 6.0 Hz, 1H), 7.20-7.41 (m, 8H), 7.60 (s, 1H), 7.77-7.79 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 62.8, 86.2, 111.5, 116.1, 120.0, 120.4, 122.5, 124.0, 127.7, 128.2, 128.9, 129.2, 133.7, 134.8, 135.6, 137.2. Anal. Calcd. for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46, N, 10.84; found: C, 83.59; H, 5.64; N, 10.79.



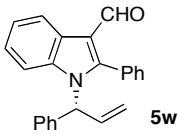
5u

(*R*)-3-Phenyl-1-(1-phenylallyl)-1*H*-indole (**5u**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4k** (0.106 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 99:1 branched:linear ratio. The mixture was purified by flash column chromatography (97:3 hexanes:EtOAc) to give **5u** as a pale yellow oil in 21% yield (0.0332 g, 0.107 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.7 min (minor); t_R 6.1 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 97%. $[\alpha]_D^{25}$ = -41.0° (c 0.42, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.12 (d, *J* = 17.0 Hz, 1H), 5.45 (d, *J* = 10.5 Hz, 1H), 6.18 (d, *J* = 6.0 Hz, 1H), 6.42 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 7.18-7.36 (m, 10H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.98 (dd, *J* = 7.5, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 62.2, 110.6, 117.4, 119.4, 120.2, 120.5, 122.2, 124.2, 126.0, 126.8, 127.6, 127.8, 128.2, 128.9, 129.0, 135.8, 136.2, 137.1, 139.0. Anal. Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19, N, 4.53; found: C, 89.78; H, 6.13; N, 4.41.



5v

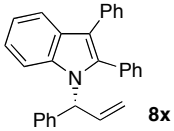
(*R*)-3-Methyl-1-(1-phenylallyl)-1*H*-indole-2-carbaldehyde (**5v**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4l** (0.0875 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 98:2 branched:linear ratio. The mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **5v** as a pale yellow oil in 82% yield (0.113 g, 0.410 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.9 min (minor); t_R 5.5 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{26}$ = +42.4° (c 1.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.70 (s, 3H), 5.25 (d, *J* = 17.0 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 6.58 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.24-7.34 (m, 5H), 7.59 (d, *J* = 6.5 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 10.22 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 8.8, 60.6, 113.9, 119.3, 120.4, 121.5, 127.0, 127.2, 127.4, 128.0, 128.4, 128.7, 130.9, 135.2, 138.8, 139.7, 181.7. Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22, N, 5.09; found: C, 82.83; H, 6.31; N, 5.05.



5w

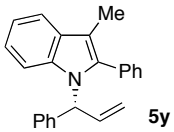
(*R*)-2-Phenyl-1-(1-phenylallyl)-1*H*-indole-3-carbaldehyde (**5w**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4m** (0.122 g, 0.550 mmol) (reaction time = 3 h). ^{1}H NMR spectroscopy showed a

96:4 branched:linear ratio. The mixture was purified by flash column chromatography (80:20 hexanes:EtOAc) to give **5w** as an amorphous white solid in 93% yield (0.156 g, 0.463 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.7 min (major); t_R 10.0 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 97%. $[\alpha]_D^{26}$ = +194.1° (c 1.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.15 (d, *J* = 17.0 Hz, 1H), 5.48 (d, *J* = 10.5 Hz, 1H), 6.07 (d, *J* = 6.5 Hz, 1H), 6.57 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.27-7.34 (m, 4H), 7.50-7.60 (m, 5H), 8.49 (d, *J* = 8.0 Hz, 1H), 9.78 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 61.6, 113.7, 116.4, 120.3, 122.4, 123.2, 123.8, 126.1, 126.8, 128.1, 128.8, 129.0, 129.1 130.3, 130.9, 133.9, 135.4, 138.0, 152.1, 187.1. HRMS (ESI) calcd. for $C_{24}H_{20}NO^+$ $[M+H]^+$ 338.1545, found 338.1534.



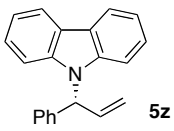
8x

(*R*)-2,3-Diphenyl-1-(1-phenylallyl)-1*H*-indole (**5x**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4n** (0.148 g, 0.550 mmol) (reaction time = 2 h). ^{1}H NMR spectroscopy showed a 98:2 branched:linear ratio. The mixture was purified by flash column chromatography (97:3 hexanes:EtOAc) to give **5x** as an amorphous white solid in 95% yield (0.184 g, 0.477 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 42.8 min (major); t_R 48.9 min (minor) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.9:0.1, 0.3 mL/min] to be 99%. $[\alpha]_D^{24}$ = +180.5° (c 0.84, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.16 (dt, *J* = 17.0, 1.5 Hz 1H), 5.46 (dt, *J* = 10.5, 1.5 Hz, 1H), 6.11 (d, *J* = 6.5 Hz, 1H), 6.62 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 7.08-7.18 (m, 3H), 7.24 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.30-7.45 (m, 14H), 7.87 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 61.3, 113.4, 116.0, 119.4, 119.9, 120.3, 121.9, 125.8, 127.0, 127.6, 128.3, 128.5 (2C), 128.7, 128.8, 130.1, 131.4, 132.4, 135.0, 135.3, 135.4, 138.5, 139.6. Anal. Calcd. for $C_{29}H_{23}N$: C, 90.35; H, 6.01, N, 3.63; found: C, 90.04; H, 6.04; N, 3.43.



5y

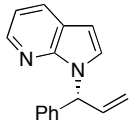
(*R*)-3-Methyl-2-phenyl-1-(1-phenylallyl)-1*H*-indole (**5y**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4o** (0.114 g, 0.550 mmol) (reaction time = 4 h). ^{1}H NMR spectroscopy showed a 98:2 branched:linear ratio. The mixture was purified by flash column chromatography (98:2 hexanes:EtOAc) to give **5y** as an amorphous white solid in 89% yield (0.143 g, 0.443 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 3.6 min (major); t_R 4.2 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 99%. $[\alpha]_D^{26}$ = +157.5° (c 1.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.34 (s, 3H), 5.10 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.39 (dt, 10.5, 1.5 Hz, 1H), 6.01 (d, *J* = 6.5 Hz, 1H), 6.54 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 7.00 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.05 (dt, *J* = 1.0, 8.0 Hz, 1H), 7.14 (dt, *J* = 1.0, 8.0 Hz, 1H), 7.23-7.35 (m, 5H), 7.43-7.49 (m, 5H), 7.65 (dt, *J* = 8.0, 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.7, 61.3, 109.6, 113.1, 119.0, 119.1, 119.4, 121.5, 127.0, 127.4, 128.3, 128.6, 128.7, 129.8, 130.8, 132.6, 135.2, 135.4, 138.5, 139.9. Anal. Calcd. for $C_{24}H_{21}N$: C, 89.12; H, 6.54, N, 4.33; found: C, 88.89; H, 6.42; N, 4.25.



5z

(*R*)-9-(1-Phenylallyl)-9*H*-carbazole (**5z**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **4p** (0.0920 g, 0.550 mmol) (reaction time = 5 h). ^{1}H NMR spectroscopy showed a 98:2 branched:linear ratio. The mixture was purified by flash column chromatography (98:2

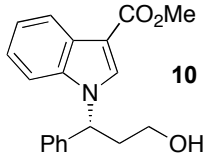
hexanes:EtOAc) to give **5z** as an amorphous white solid in 88% yield (0.125 g, 0.441 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.0 min (minor); t_R 6.9 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = +55.7° (c 1.10, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.33 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.50 (dt, *J* = 10.5, 1.5 Hz, 1H), 6.55 (d, *J* = 6.5 Hz, 1H), 6.68 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 7.33 (dt, *J* = 1.0, 8.0 Hz, 2H), 7.36-7.41 (m, 7H), 7.44 (dt, *J* = 1.5, 8.0 Hz, 2H), 8.22 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 60.4, 110.6, 119.3, 119.4, 120.5, 123.6, 125.7, 127.3, 127.8, 128.9, 134.4, 138.7, 140.2. Anal. Calcd. for $C_{21}H_{17}N$: C, 89.01; H, 6.05, N, 4.94; found: C, 89.09; H, 6.06; N, 4.91.



8

(*R*)-1-(1-Phenylallyl)-1*H*-pyrrolo[2,3-*b*]pyridine (**8**): Prepared according to the general procedure from **3a** (0.117 g, 0.500 mmol) and **7** (0.0650 g, 0.550 mmol) (reaction time = 6 h). ^{1}H NMR spectroscopy showed a 91:9 branched:linear ratio. The mixture was purified by flash column chromatography (90:10 hexanes:EtOAc) to give **8** as a colorless oil in 79% yield (0.0921 g, 0.393 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.3 min (major); t_R 6.3 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +201.4° (c 1.15, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.06 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.42 (dt, *J* = 10.5, 1.5 Hz, 1H), 6.44 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 6.89 (d, *J* = 5.0 Hz, 1H), 7.11 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.23 (d, *J* = 6.0 Hz, 1H), 7.30-7.38 (m, 5H), 7.95 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.40 (dd, *J* = 5.0, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 58.9, 100.1, 116.2, 118.3, 120.7, 126.4, 127.91, 127.92, 128.7, 128.9, 136.6, 139.5, 143.0, 147.6. Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02, N, 11.96; found: C, 82.14; H, 6.27; N, 11.67.

Synthesis of (*R*)-Methyl 1-(3-hydroxy-1-phenylpropyl)-1*H*-indole-3-carboxylate (10)

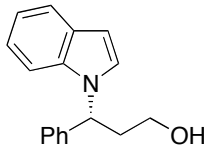


10

N-Allyl indole **5q** (0.797 g, 2.74 mmol, 97% ee) was dissolved in dry, degassed THF (11 mL) and cooled to -78 °C. Then 9-BBN (11 mL as a 0.5 M solution in THF, 5.5 mmol) was added to the reaction vessel. The reaction mixture was stirred for 1 h at -78 °C, then allowed to warm slowly to room temperature and stirred overnight. The resulting solution was cooled to 0 °C, at which time EtOH (4.4 mL), 3 M NaOH (2.2 mL), and 30% H_2O_2 (2.3 mL) were added in the specified order. The reaction was allowed to warm to room temperature and was stirred for an additional 6 h. The reaction was diluted with ether, then washed with 1 M NaOH and saturated aqueous NH_4Cl. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column silica gel chromatography (40:60 hexanes:EtOAc) to give (*R*)-methyl 1-(3-hydroxy-1-phenylpropyl)-1*H*-indole-3-carboxylate **10** as an amorphous white solid in 97% yield (0.820 g, 2.65 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 13.9 min (minor); t_R 15.4 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 97%. $[\alpha]_D^{25}$ = +1.9° (c 0.96, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.94 (br s, 1H), 2.49-2.60 (m, 2H), 3.54 (ddd, *J* = 11.0, 7.0, 5.0, 1H), 3.66 (ddd, *J* = 11.0, 5.0, 5.0 Hz, 1H), 3.92 (s, 3H), 5.84 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.19-7.32 (m, 7H), 7.39 (d, *J* = 8.0 Hz, 1H), 8.05 (s, 1H), 8.18 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.4, 51.3, 56.8, 58.8, 107.8, 110.9, 121.8, 122.3, 123.1, 126.7,

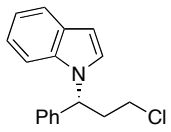
126.8, 128.3, 129.1, 132.0, 137.1, 139.9, 165.9. Anal. Calcd. for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19, N, 4.53; found: C, 73.49; H, 6.13; N, 4.34.

Synthesis of (*R*)-3-(1*H*-Indol-1-yl)-3-phenylpropan-1-ol[10]



(*R*)-Methyl 1-(3-hydroxy-1-phenylpropyl)-1*H*-indole-3-carboxylate **10** (0.400 g, 1.29 mmol) and solid KOH (0.290 g, 5.17 mmol) were combined in a reaction vessel. To this mixture was added MeOH (12 mL) and H_2O (8 mL). The reaction was heated at reflux for 4 h, then cooled to room temperature. The solution was transferred to a separatory funnel, acidified with 3 M HCl, and extracted three times with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and concentrated. (*R*)-1-(3-Hydroxy-1-phenylpropyl)-1*H*-indole-3-carboxylic acid was isolated as an amorphous white solid in 96% yield (0.367 g, 1.24 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 26.6 min (minor); t_R 34.1 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 97%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.52-2.65 (m, 2H), 3.60 (ddd, *J* = 11.0, 7.0, 5.0 Hz, 1H), 3.71 (ddd, *J* = 11.0, 5.0, 5.0, 1H), 5.87 (app t, *J* = 7.5 Hz, 1H), 7.22-7.35 (m, 7H), 7.41 (d, *J* = 8.0 Hz, 1H), 8.16 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.4, 56.7, 58.9, 107.3, 111.0, 122.0, 122.6, 123.3, 126.7, 127.1, 128.4, 129.2, 133.3, 137.3, 139.7, 170.6. HRMS (ESI) calcd. for $C_{18}H_{18}NO_3^+$ $[M+H]^+$ 296.1287, found 296.1296. (*R*)-1-(3-Hydroxy-1-phenylpropyl)-1*H*-indole-3-carboxylic acid (0.200 g, 0.677 mmol) was dissolved in bromobenzene (5 mL). The reaction was heated at reflux for 20 h, and then was allowed to cool to room temperature. Bromobenzene was removed *in vacuo*, and the crude reaction mixture was purified by flash column silica gel chromatography (75:25 hexanes:EtOAc) to give (*R*)-3-(1*H*-indol-1-yl)-3-phenylpropan-1-ol as a green oil in 71% yield (0.120 g, 0.479 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.3 min (major); t_R 10.0 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 97%. $[\alpha]_D^{26}$ = +112.5° (c 0.48, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.82 (br s, 1H), 2.52-2.57 (m, 2H), 3.50 (ddd, *J* = 11.0, 6.5, 5.5, 1H), 3.64 (ddd, *J* =11.0, 5.5, 5.5 Hz, 1H), 5.82 (dd, *J* = 7.5, 7.5 Hz, 1H) 6.63 (d, *J* = 3.5 Hz, 1H), 7.14 (ddd, *J* = 8.0, 8.0, 1.0 Hz, 1H), 7.20 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.24-7.33 (m, 6H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.6, 55.8, 59.3, 102.2, 110.1, 119.8, 121.1, 121.8, 125.2, 126.6, 127.7, 128.7, 128.9, 136.6, 141.3. HRMS (ESI) calcd. for $C_{17}H_{18}NO^+$ $[M+H]^+$ 252.1388, found 252.1394.

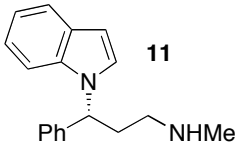
Synthesis of (*R*)-1-(3-Chloro-1-phenylpropyl)-1*H*-indole[11]



(*R*)-3-(1*H*-Indol-1-yl)-3-phenylpropan-1-ol (0.0641 g, 0.255 mmol) and PPh_3 (0.0803 g, 0.306 mmol) were combined in a 1-dram vial. To this mixture was added CH_2Cl_2 (1.9 mL) and CCl_4 (0.1 mL). Then the vial was sealed, and the reaction heated at 50 °C. After 18 h, the reaction was cooled to room temperature and filtered through a plug of silica gel (eluting with 75:25 hexanes to EtOAc). The crude reaction mixture was concentrated under reduced pressure and purified by flash column silica gel chromatography (95:5 hexanes:EtOAc) to give (*R*)-1-(3-chloro-1-phenylpropyl)-1*H*-indole as a colorless oil in 91% yield (0.0624 g, 0.231 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.5 min (major); t_R 6.0 min (minor) [Chiracel AD-H (0.46 cm

x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 97%. $[\alpha]_D^{25}$ = +106.0° (c 0.65, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.74 (m, 1H), 2.85 (m, 1H), 3.41 (ddd, *J* = 11.5, 8.0, 4.5, 1H), 3.56 (ddd, *J* = 11.5, 5.5, 5.5 Hz, 1H), 5.87 (dd, *J* = 9.0, 5.5 Hz, 1H), 6.63 (dd, *J* = 3.0, 0.5 Hz, 1H), 7.14 (ddd, *J* = 8.0, 8.0, 1.0 Hz, 1H), 7.21 (ddd, *J* = 8.0, 8.0, 1.0 Hz, 1H), 7.24-7.36 (m, 6H), 7.39 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.67 (dd, *J* = 8.0, 0.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.7, 41.7, 56.4, 102.6, 110.2, 120.0, 121.2, 122.0, 125.1, 126.6, 128.1, 128.9, 129.1, 136.5, 140.3. HRMS (ESI) calcd. for $C_{17}H_{17}NCl^+$ $[M+H]^+$ 270.1050, found 270.1047.

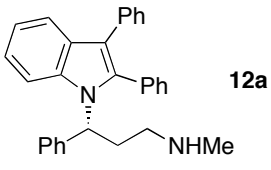
Synthesis of (*R*)-3-(1*H*-Indol-1-yl)-*N*-methyl-3-phenylpropan-1-amine (11)[11]



To (*R*)-1-(3-chloro-1-phenylpropyl)-1*H*-indole (0.0613 g, 0.227 mmol) in a 10 mL medium-walled pressure vessel equipped with a vacuum valve was added methylamine (33% in EtOH, 2.5 mL). The pressure vessel was sealed and heated at 90 °C for 4 h. The reaction mixture was concentrated under reduced pressure and purified by flash column silica gel chromatography (90:10 $CHCl_3$:MeOH) to give (*R*)-3-(1*H*-indol-1-yl)-*N*-methyl-3-phenylpropan-1-amine **11** as a white amorphous solid in 95% yield (0.0573 g, 0.217 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.5 min (minor); t_R 13.4 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 97%. $[\alpha]_D^{24}$ = +76.6° (c 0.49, MeOH). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.48 (s, 3H), 2.57-2.61 (m, 1H), 2.69-2.84 (m, 3H), 3.40 (br s, 1H), 5.92 (dd, *J* = 9.0, 6.0 Hz, 1H), 6.56 (d, *J* = 3.5 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 1H), 7.24-7.37 (m, 5H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 3.5 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 31.1, 32.7, 46.0, 56.1, 101.8, 110.4, 119.4, 120.5, 121.2, 125.4, 126.4, 127.7, 128.2, 128.6, 135.9, 141.1. HRMS (ESI) calcd. for $C_{18}H_{21}N_2^+$ $[M+H]^+$ 265.1705, found 265.1703.

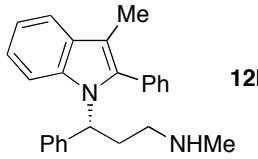
General Procedure for the Synthesis of 3-(1*H*-indol-1-yl)-*N*-methyl-3-arylpropan-1-amines 12a-12c

N-allyl indole **5x**, **5y**, or **5z** (0.400 mmol) and Cp_2ZrHCl (0.103 g, 0.400 mmol) were added to a 1-dram vial. Then, dry, degassed THF (2 mL) was added, and the vial was sealed with a cap containing a PTFE/silicone liner. The heterogeneous solution was stirred at room temperature until the mixture became homogeneous (5-15 h). Then, the septum cap was removed from the vial, *N*-methyl hydroxylamine-*O*-sulfonic acid (0.0763 g, 0.600 mmol) was added to the reaction mixture, and the vial was resealed. The vial was removed from the dry-box, and the reaction was heated in an oil bath at 60 °C for 5 h. The reaction was cooled to room temperature, diluted with CH_2Cl_2, and transferred to separatory funnel. The organic layer was washed with 1 M NaOH, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column silica gel chromatography (90:10 $CHCl_3$:MeOH) to give **12a**, **12b**, or **12c**.



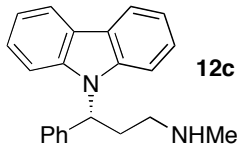
(*R*)-3-(2,3-Diphenyl-1*H*-indol-1-yl)-*N*-methyl-3-phenylpropan-1-amine (12a): Prepared according to the general procedure from **5x** (0.154 g, 0.400 mmol) to give **12a** as an amorphous white solid in 63% yield (0.105 g, 0.253 mmol). The enantiomeric excess after acylation with trifluoroacetic anhydride was determined by HPLC analysis (254 nm, 25

°C) t_R 23.3 min (minor); t_R 30.0 min (major) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 0.5 mL/min] to be 99%. $[\alpha]_D^{26}$ = +162.7° (c 0.59, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.17-2.23 (m, 1H), 2.25 (s, 3H), 2.29-2.35 (m, 1H), 2.49 (br s, 1H), 2.54-2.61 (m, 1H), 2.71-2.79 (m, 1H), 5.63 (dd, *J* = 11.0, 4.5 Hz, 1H), 7.10-7.23 (m, 4H), 7.27-7.41 (m, 14H), 7.84 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.2, 36.0, 48.5, 56.3, 113.2, 115.9, 120.1, 120.5, 122.1, 125.8, 126.5, 127.4, 128.3, 128.46, 128.51, 128.8, 128.9, 130.2, 131.1, 131.2, 132.2, 135.2, 139.0, 140.8. Anal. Calcd. for $C_{30}H_{29}N_2$: C, 86.50; H, 6.78, N, 6.72; found: C, 86.90; H, 6.69; N, 6.45.



12b

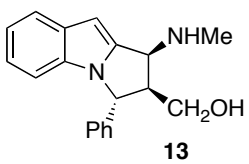
(*R*)-*N*-Methyl-3-(3-methyl-2-phenyl-1*H*-indol-1-yl)-3-phenylpropan-1-amine (**12b**): Prepared according to the general procedure from **5y** (0.129 g, 0.400 mmol) to give **12b** as an amorphous white solid in 69% yield (0.0981 g, 0.276 mmol). The enantiomeric excess after acylation with trifluoroacetic anhydride was determined by HPLC analysis (254 nm, 25 °C) t_R 6.9 min (minor); t_R 9.6 min (major) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{24}$ = +173.3° (c 0.48, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09-2.22 (m, NH + CH_2, 2H), 2.23-2.29 (m, CH_3 + CH_2, 4H), 2.32 (s, 3H), 2.46-2.53 (m, 1H), 2.63-2.71 (m, 1H), 5.53 (dd, *J* = 11.5, 5.0 Hz, 1H), 7.05-7.16 (m, 3H), 7.28-7.47 (m, 10H), 7.66 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.7, 32.4, 36.1, 48.5, 56.4, 109.2, 112.9, 119.2, 119.4, 121.7, 126.5, 127.2, 128.3, 128.7, 128.8, 129.8, 130.7, 132.5, 135.1, 139.0, 141.2. Anal. Calcd. for $C_{25}H_{26}N_2$: C, 84.70; H, 7.13, N, 7.40; found: C, 84.36; H, 7.13; N, 7.40.



12c

(*R*)-3-(9*H*-Carbazol-9-yl)-*N*-methyl-3-phenylpropan-1-amine (**12c**): Prepared according to the general procedure from **5z** (0.113 g, 0.400 mmol) to give **12c** as an amorphous white solid in 73% yield (0.0913 g, 0.290 mmol). The enantiomeric excess after acylation with trifluoroacetic anhydride was determined by HPLC analysis (254 nm, 25 °C) t_R 8.2 min (major); t_R 9.0 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = +95.7° (c 0.51, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12 (br s, 1H), 2.29 (s, 3H), 2.35-2.66 (m, 2H), 2.70-2.76 (m, 1H), 2.80-2.87 (m, 1H), 6.14 (dd, *J* = 11.0, 4.5 Hz, 1H), 7.24-7.39 (m, 11H), 8.15 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 31.6, 36.4, 48.8, 55.0, 110.5, 119.2, 120.4, 123.4, 125.7, 126.8, 127.5, 128.8, 140.26, 140.33. Anal. Calcd. for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05, N, 8.91; found: C, 83.71; H, 6.95; N, 8.80.

Synthesis of ((1*S*,2*R*,3*R*)-1-(methylamino)-3-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)methanol (13)

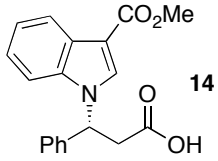


13

N-Allyl indole **5p** (0.100 g, 0.383 mmol, 99% ee), *N*-methylhydroxylamine hydrochloride (0.0959 g, 1.15 mmol), and sodium acetate (0.0973 g, 1.19 mmol) were combined in a 10 mL round bottom flask. THF (3.0 mL) was added to this mixture. The reaction mixture was heated at reflux. After 5 h the reaction mixture was cooled to room temperature and concentrated. The resulting residue was dissolved in $CHCl_3$ and washed with water. The water layer was extracted with two additional portions of $CHCl_3$. The combined organic layer was washed with brine, and then dried over $MgSO_4$, filtered, and concentrated. Analysis of the crude reaction

mixture by ^{1}H NMR spectroscopy showed a 90:10 regioisomeric ratio and the presence of the major regioisomer as a single diasteromer. The regioisomeric mixture was purified by flash column silica gel chromatography (60:40 hexanes:EtOAc) to give the major cycloadduct as a single isomer as an amorphous white solid in 83% yield (0.0924 g, 0.318 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 12.9 min (minor); t_R 17.0 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +193.6° (c 0.59, $CHCl_3$). Anal. Calcd. for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25, N, 9.65; found: C, 78.46; H, 6.34; N, 9.55. The purified cycloadduct (0.0400 g, 0.138 mmol) and zinc powder (0.132 g, 2.07 mmol) were combined in a 5 mL round bottom flask. AcOH (1.5 mL) and H_2O (0.5 mL) were added to the flask, and the reaction mixture was heated at 60 °C for 7 h. At this time, the reaction was cooled to room temperature and made basic by addition of concentrated NH_4OH (2.6 mL). The resulting mixture was extracted with $CHCl_3$ (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The product was purified by flash column silica gel chromatography (70:30 $CHCl_3$:*i*PrOH) to give ((1*S*,2*R*,3*R*)-1-(methylamino)-3-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)methanol **13** as an amorphous tan solid in 87% yield (0.0351 g, 0.120 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 10.8 min (minor); t_R 28.4 min (major) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 80:20, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = +120.0° (c 0.46, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.67 (s, 3H), 2.94 (dddd, *J* = 8.0, 7.0, 6.5, 4.0, 1H), 3.12 (br s, 2H), 3.90 (dd, *J* = 12.5, 6.0 Hz, 1H), 4.09 (dd, *J* = 12.5, 4.0 Hz, 1H), 4.41 (d, *J* = 7.0 Hz, 1H), 5.41 (d, *J* = 8.0 Hz, 1H), 6.45 (s, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.97 (app t, *J* = 7.5, 1H), 7.07 (app t, *J* = 7.5, 1H), 7.20-7.22 (m, 2H), 7.35-7.39 (m, 3H), 7.64 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 35.9, 58.3, 60.2, 60.7, 61.7, 93.7, 111.1, 119.9, 121.2, 121.3, 127.0, 128.4, 129.1, 132.5, 132.9, 139.6, 145.1. HRMS (ESI) calcd. for $C_{19}H_{21}N_2O^+$ $[M+H]^+$ 293.1654, found 293.1660.

Synthesis of (*R*)-3-(3-(methoxycarbonyl)-1*H*-indol-1-yl)-3-phenylpropanoic acid (14)



14

(*R*)-Methyl 1-(3-hydroxy-1-phenylpropyl)-1*H*-indole-3-carboxylate **10** (0.150 g, 0.485 mmol), iodobenzene diacetate (0.344g, 1.07 mmol), TEMPO (0.0152 g, 0.0970 mmol), and sodium bicarbonate (0.0815 g, 0.970 mmol) were combined in a 1-dram vial. Acetonitrile (1 mL) and H_2O (1 mL) were added to the vial. The vial was sealed with a PTFE/silicone-lined septum cap, and the reaction was stirred at room temperature for 1 h. The reaction mixture was poured into 1 M HCl (10 mL) and extracted with CH_2Cl_3 (2 x 20 mL). The combined organic layers were concentrated. The crude product was purified by flash column silica gel chromatography (40:60 hexanes:EtOAc) to give (*R*)-3-(3-(methoxycarbonyl)-1*H*-indol-1-yl)-3-phenylpropanoic acid **14** as a pale yellow solid in 81% yield (0.126 g, 0.391 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 15.7 min (minor); t_R 21.9 min (major) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 97%. $[\alpha]_D^{26}$ = +4.6° (c 0.56, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.34 (dd, *J* = 17.0, 7.0 Hz, 1H), 3.41 (dd, *J* = 17.0, 8.0 Hz, 1H), 3.91 (s, 3H), 6.08 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.20-7.34 (m, 7H), 7.38 (d, *J* = 7.5 Hz, 1H), 8.03 (s, 1H), 8.17 (dd, *J* = 8.0, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 39.9, 51.3, 56.5, 108.2, 110.7, 121.9, 122.4, 123.2, 126.4, 126.8, 128.7, 129.3, 131.9, 136.7, 138.4, 165.9, 174.4. HRMS (ESI) calcd. for $C_{19}H_{18}NO_4^+$ $[M+H]^+$ 324.1236, found 324.1241.

References

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LS-II-110-1H-VXR500-1

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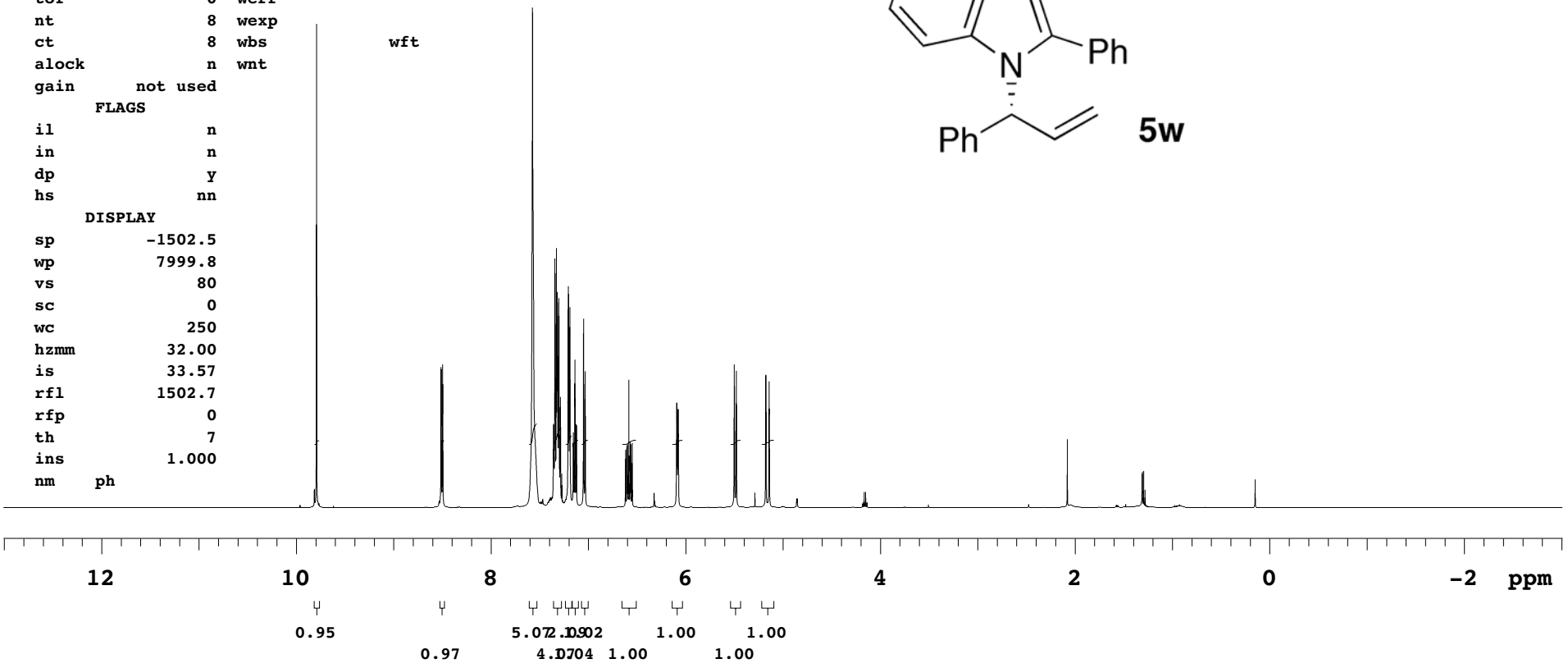

5w

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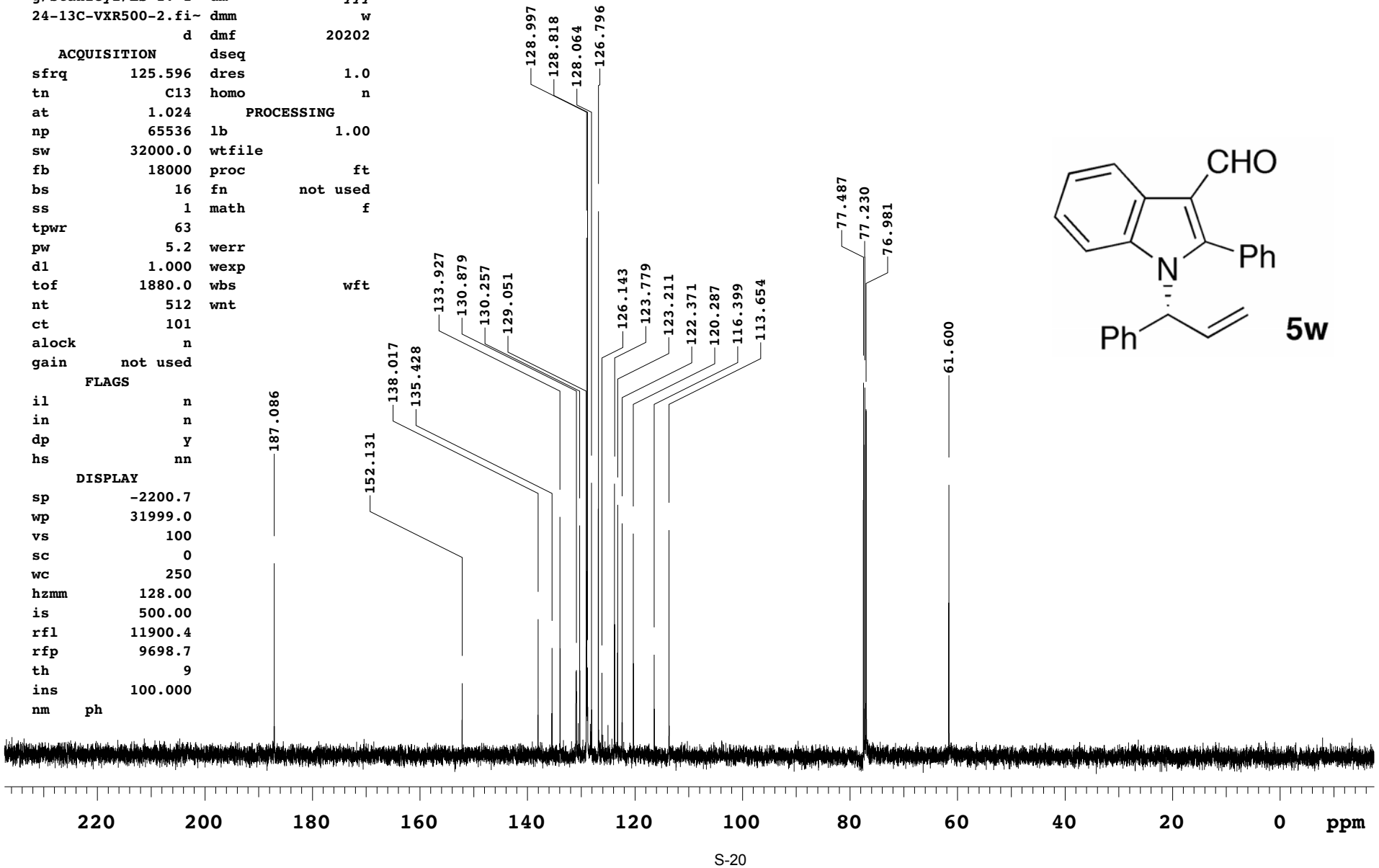

5w

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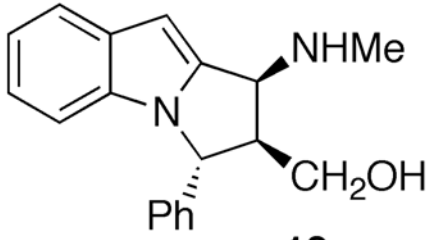

13

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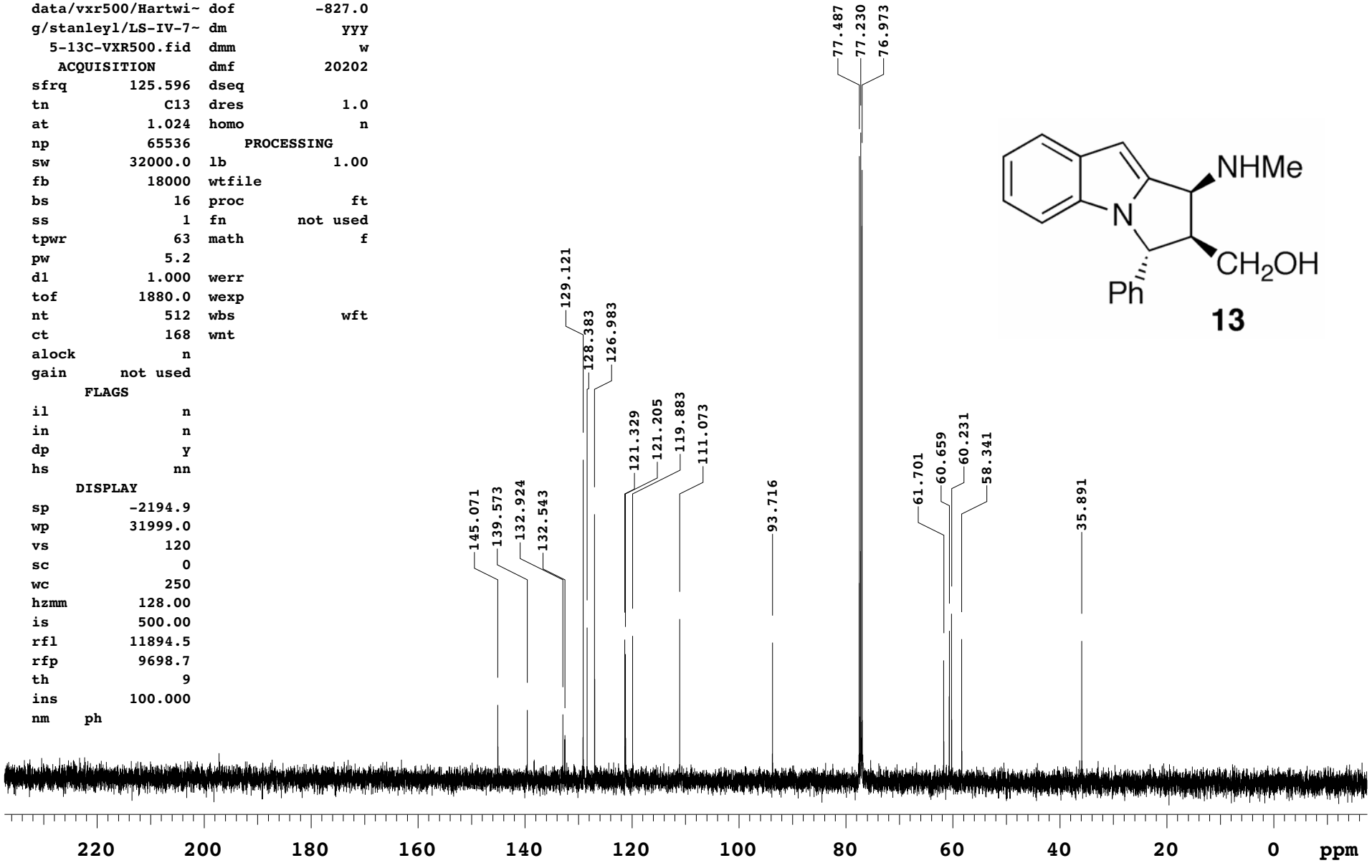

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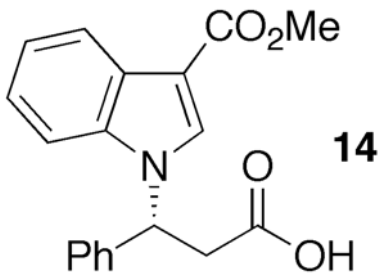

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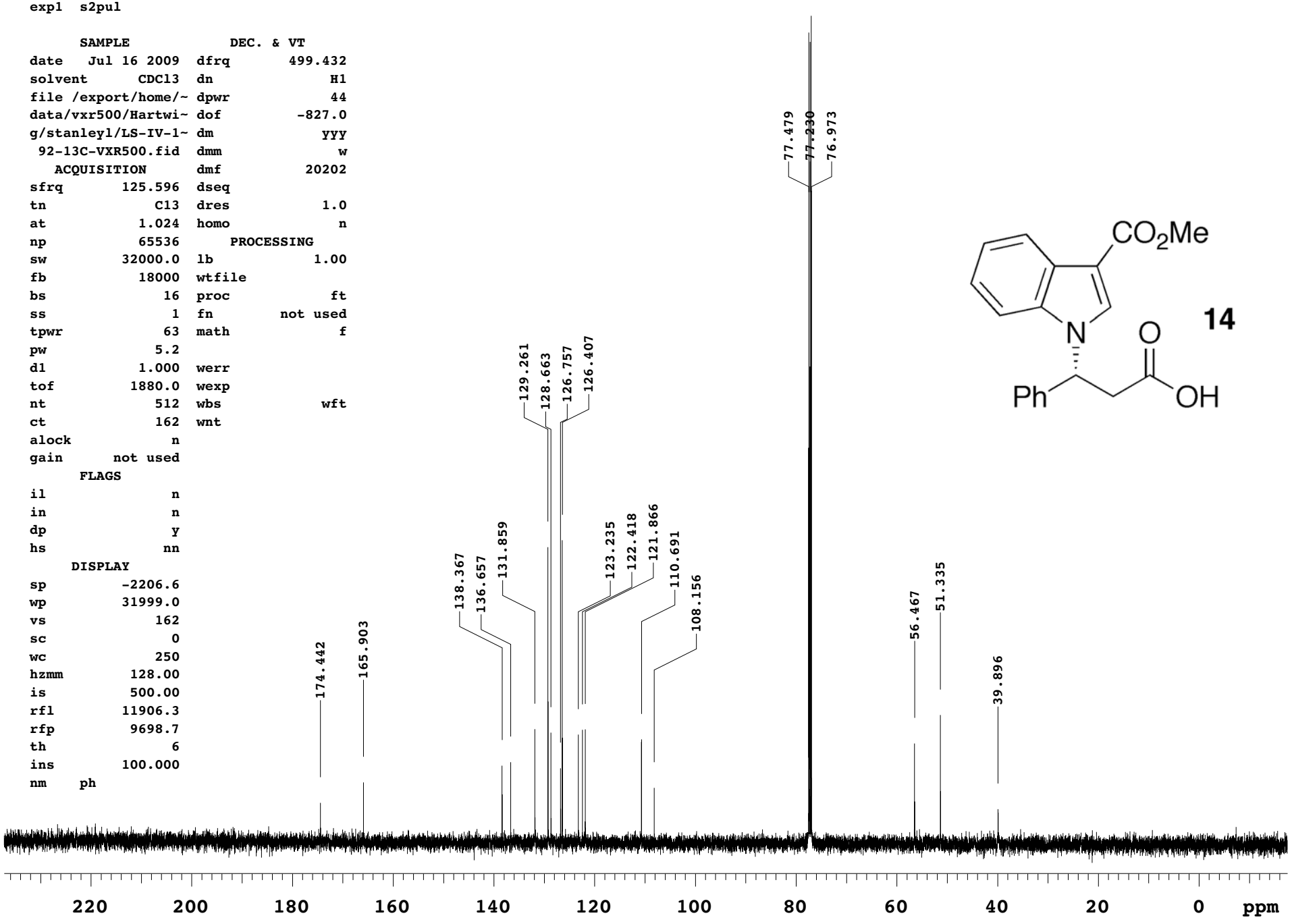

14