nature catalysis

SUPPLEMENTARY INFORMATION

https://doi.org/10.1038/s41929-018-0106-5

In the format provided by the authors and unedited.

Pentamethylcyclopentadienyl rhodium(III)–chiral disulfonate hybrid catalysis for enantioselective C–H bond functionalization

Shun Satake[1], Takumaru Kurihara[1], Keisuke Nishikawa[2], Takuya Mochizuki[2], Manabu Hatano[2], Kazuaki Ishihara[2], Tatsuhiko Yoshino[1]* and Shigeki Matsunaga[1]*

[1]Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo, Japan. [2]Graduate School of Engineering, Nagoya University, Nagoya, Japan.
*e-mail: tyoshino@pharm.hokudai.ac.jp; smatsuna@pharm.hokudai.ac.jp

Supplementary Information

Pentamethylcyclopentadienyl rhodium(III)/chiral disulfonate hybrid catalysis for enantioselective C-H bond functionalization

Shun Satake,[1] Takumaru Kurihara,[1] Keisuke Nishikawa,[2] Takuya Mochizuki,[2] Manabu Hatano,[2] Kazuaki Ishihara,[2] Tatsuhiko Yoshino,*[,1] and Shigeki Matsunaga*[,1]

[1]Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan.

[2]Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.

Phone: +81-11-706-3236 / Fax: +81-11-706-4981

Email: tyoshino@pharm.hokudai.ac.jp (T. Y.); smatsuna@pharm.hokudai.ac.jp (S. M.)

Table of Contents

1. Supplementary Methods

General Information

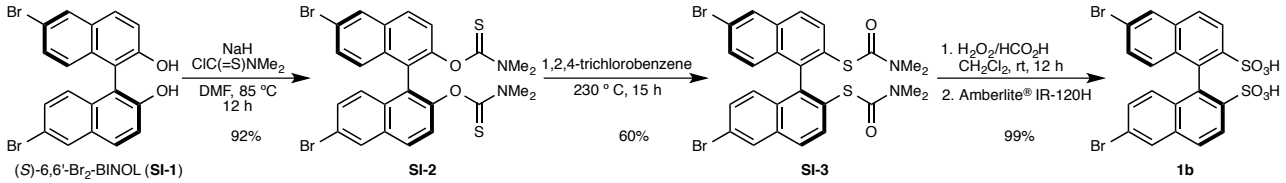
General: Reported melting points were uncorrected. Optical rotations were measured on a JASCO P-1030 digital polarimeter with a sodium lamp (589 nm). Infrared (IR) spectra were recorded on a JASCO FT/IR-5300 spectrophotometer and absorbance bands are reported in wave numbers (cm^{-1}). NMR spectra were recorded on JEOL JNM-ECP400 spectrometers operating at 399.78 MHz for ^{1}H NMR and 100.53 MHz for ^{13}C NMR, JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for ^{1}H NMR and 98.52 MHz for ^{13}C NMR, JOEL JNM-ECX400 spectrometers, operating at 395.88 MHz for ^{1}H NMR and 99.55 MHz for ^{13}C NMR, and JNM-ECA500 spectrometers, operating at 500.16 MHz for ^{1}H NMR and 125.77 MHz for ^{13}C NMR and 470.54 MHz for ^{19}F NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^{1}H NMR), $CHCl_3$ (7.26 ppm for ^{1}H NMR), CH_3OH (3.34 ppm for ^{1}H NMR), $CDCl_3$ (77.0 ppm for ^{13}C NMR), C_6F_6 (–164.9 ppm for ^{19}F NMR), $C_6H_5CF_3$ (–63.72 ppm for ^{19}F NMR) as an internal reference, respectively. ESI mass spectra were measured on JEOL JMS-T100LCP spectrometer. Column chromatography was performed with silica gel Kanto Silica gel 60 N (40-50 mesh) or Yamazen YFLC AI-580 using Universal Column SiOH. TLC analysis was carried out on Merck Kieselgel 60 F_{254} plates with visualization by UV light, anisaldehyde stain solution or phosphomolybdic acid stain solution. Gel permeation chromatography (GPC) was performed with YMC LC-forte/R using CHCl3 as an eluent. Chiral HPLC analysis was performed on a JASCO PU-2080 intelligent HPLC pump with JASCO MD-4017 intelligent UV/VIS detector using DAICEL Chiralpak IA, IB, ID, IE and AD-H columns (0.46 cm x 25 cm).

Materials: 1,2-dichloroethane (CaH_2) was distilled from CaH_2, purged with argon for over 30 min, and stored over activated molecular sieves 4A under argon atmosphere before use. Commercially available toluene, THF, CH_2Cl_2, MeOH (Wako Ltd., deoxidized grade) and Et_2O, acetone (KANTO Chemical Co., Inc., dehydrated grade) were used without further manipulation unless otherwise stated. All other reagents were commercially available and used as received.

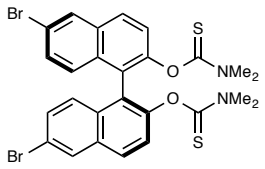
A. Preparation of Cp*Rh-BINSate Catalysts

A-1. Preparation of (*S*)-6,6'-Br_2-BINSA 1b

(*S*)-6,6'-Br_2-BINSA (**1b**) was synthesized as shown in Scheme **SI-1** according to procedures reported in the literatures.[1,2,3]



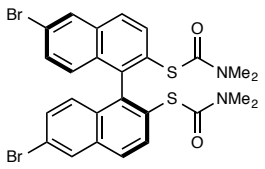
(*S*)-*O*,*O*'-[6,6'-dibromo-(1,1'-binaphthalene)-2,2'-diyl] bis(dimethylcarbamothioate) (SI-2)



To a solution of 6,6'-dibromo BINOL (**SI-1**, 2.66 g, 6.0 mmol) in DMF (12 mL) was added NaH (960 mg, 24.0 mmol, 60% oil dispersion) at 0 ºC. The reaction mixture was immediately warmed to room temperature, and stirred for 30 min. To the resulting solution was added *N*,*N*-dimethylthiocarbamoyl chloride (3.3 g, 24 mmol), and the solution was stirred at 85 ºC for 12 h. The reaction mixture was cooled to room temperature, and poured into 1% aqueous KOH (50 mL). The colorless precipitates were filtered, washed with water, and dissolved in CH_2Cl_2. The solution was washed brine, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (hexane/AcOEt = 9:1 to 3:1) to give **SI-2** (3.42 g, 92%).

Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.64 (s, 6H), 3.12 (s, 6H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.36 (dd, *J* = 8.8, 1.9 Hz, 2H), 7.61 (d, *J* = 9.2 Hz, 2H), 7.87 (d, *J* = 9.2 Hz, 2H), 8.07 (d, *J* = 1.9 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 38.2, 42.9, 120.0, 123.7, 124.8, 127.6, 128.5, 129.80, 129.84, 131.7, 132.5, 149.7, 185.9. **$[\alpha]_D^{19}$**= –76.1 (c 0.97, $CHCl_3$). **HRMS** (ESI): *m/z* Calcd for $C_{26}H_{22}O_2N_2Br_2S_2Na^+$ [M+Na^+]: 638.9382, found: 638.9391.

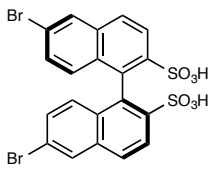
(*S*)-*S*,*S*'-[6,6'-dibromo-(1,1'-binaphthalene)-2,2'-diyl] bis(dimethylcarbamothioate) (SI-3)



A solution of **SI-2** (1.23 g, 2.0 mmol) in 1,2,4-trichlorobenzene (10 mL) was refluxed at 230 ºC for 15 h with stirring. The reaction mixture was cooled to room temperature, and directly purified by silica gel column chromatography (hexane/AcOEt = 7:1 to 1:1) to give **SI-3** (756 mg, 60%).

Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.74 (brs, 6H), 2.85 (brs, 6H), 6.93 (d, *J* = 9.2 Hz, 2H), 7.30 (dd, *J* = 9.2, 2.0 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 8.07 (d, *J* = 2.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 36.8, 121.1, 127.3, 128.5, 129.1, 129.87, 129.91, 131.5, 134.3, 140.4, 165.6. **$[\alpha]_D^{17}$**= –10.7 (c 0.99, $CHCl_3$). **HRMS** (ESI): *m/z* Calcd for $C_{26}H_{22}O_2N_2Br_2S_2Na^+$ [M+Na^+]: 638.9382, found: 638.9393.

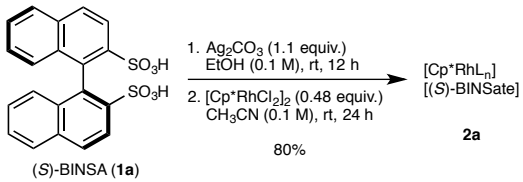
(*S*)-6,6'-dibromo-(1,1'-binaphthalene)-2,2'-disulfonic acid (1b)



A performic acid solution was prepared by mixing and stirring 30% H_2O_2 (3.5 mL, 36 mmol) and formic acid (35 mL) at room temperature for 30 min. To this solution was added **SI-3** (618 mg, 1.0 mmol) in CH_2Cl_2 (35 mL) dropwise. After stirring at room temperature for 10 h, MnO_2 (17.4 mg, 0.2 mmol) was added, and the mixture was stirred at room temperature for further 6 h until the peroxides were completely decomposed (checked by KI starch paper). The reaction mixture was filtered through a plug of Celite, and washed with CH_2Cl_2. The filtrate was concentrated in *vacuo* to furnish the crude product, which was subjected to silica gel column chromatography (CH_2Cl_2/MeOH = 4:1). The obtained salts of **1b** was dissolved in water and passed through a cation exchange column (200 cm^3, Amberlite IR120H ion-exchange resin from Aldrich). The eluent was concentrated in *vacuo*. The residue was dissolved in H_2O, and passed again through a cation exchange column. The filtrate was concentrated in *vacuo* to afford **1b** (570 mg, 99%).

Red solid. **^{1}H NMR** (500 MHz, CD_3OD): δ 6.93 (d, *J* = 9.2 Hz, 2H), 7.35 (d, *J* = 9.2 Hz, 2H), 8.02 (d, *J* = 9.2 Hz, 2H), 8.16 (s, 2H), 8.19 (d, *J* = 9.2 Hz, 2H). **^{13}C NMR** (125 MHz, CD_3OD): δ 122.5, 127.0, 128.7, 130.8, 130.9, 131.0, 133.2, 134.9, 136.5, 141.4. **$[\alpha]_D^{17}$** = 13.3 (c 1.11, CH_3OH). **HRMS** (ESI): *m/z* Calcd for $C_{20}H_{11}O_6S_2Br_2^-$ [M–H$^-$]: 568.8369, found: 568.8369.

A-2. Synthesis of [Cp*RhL$_N$][(*S*)-6,6'-BINSate] 2a[4]

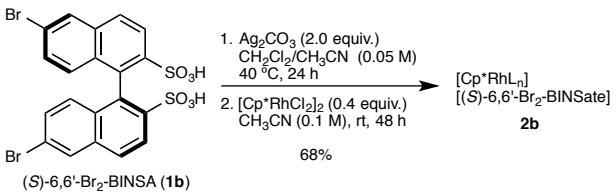


To a stirred solution of (*S*)-BINSA **1a** (107 mg, 0.25 mmol) in EtOH (2.5 mL) was added Ag_2CO_3 (75.8 mg, 0.275 mmol) at room temperature. After stirring for 12 h in dark, the reaction mixture was filtered through a Celite pad, and washed with MeOH/CH_3CN (1:1). The filtrate was evaporated in *vacuo* to furnish Ag_2-(*S*)-BINSate (152 mg, 96%) as a colorless solid, which was directly used for the next step without purification. To a flame-dried Schlenk flask were added $[Cp^*RhCl_2]_2$ (71.7 mg, 0.116 mmol), Ag_2-(*S*)-BINSate (152 mg, 0.24 mmol), CH_3CN (2.5 mL) in a glovebox. The flask was taken out of the glovebox, and the mixture was stirred at room temperature under argon atmosphere. After 24 h, the resulting precipitates were removed by filtration through a Celite pad, and washed with CH_3CN. The filtrate was concentrated in *vacuo*, and the residue was dissolved in CH_3CN (1 mL). To this solution was added Et_2O dropwise, and the resulting orange precipitates were collected by filtration, washed with Et_2O, and dried in *vacuo* to afford [Cp*RhL$_N$][(*S*)-BINSate] **2a** (138 mg, 80% as dihydrate).

Orange-solid. **IR** (KBr): ν 3399, 3234, 3060, 1626, 1590, 1563, 1504, 1454, 1376, 1307, 1257, 1132, 1063, 1015, 943, 872, 818, 776, 752, 701, 686, 660, 603 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.56 (s, 15H), 6.97

(d, J = 8.1 Hz, 2H), 7.22 (dd, J = 8.1, 8.1 Hz, 2H), 7.46 (dd, J = 8.1, 8.1 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 8.7, 92.9 (d, $^1J_{CRh}$ = 11.4 Hz), 123.6, 127.1, 127.5, 127.6, 127.8, 128.4, 133.0, 133.5, 133.9, 139.6. **Anal.** Calcd for $C_{30}H_{31}O_8RhS_2$ (dihydrate): C, 52.48; H, 4.55. Found: C, 51.88; H, 4.03, N, <0.30.

A-3 Synthesis of [Cp*RhL$_N$][(*S*)-6,6'-Br$_2$-BINSate] 2b[4]

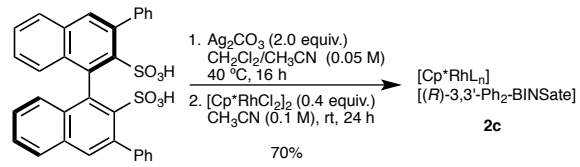


(*S*)-6,6'-Br$_2$-BINSA (**1b**)

To a stirred solution of (*S*)-6,6'-Br$_2$-BINSA **1b** (114 mg, 0.20 mmol) in CH_2Cl_2/CH_3CN (1:1, 4 mL) was added Ag_2CO_3 (110 mg, 0.40 mmol) at 40 ºC. After stirring for 24 h in dark, the reaction mixture was filtered through a Celite pad, and washed with CH_2Cl_2/CH_3CN (1:1). The filtrate was evaporated in *vacuo* to furnish Ag$_2$-(*S*)-6,6'-Br$_2$-BINSate (142 mg, 90%) as an orange solid, which was directly used for the next step without purification. To a flame-dried Schlenk flask were added $[Cp^*RhCl_2]_2$ (50 mg, 0.081 mmol), Ag$_2$-(*S*)-6,6'-Br$_2$-BINSate (142 mg, 0.18 mmol), CH_3CN (1.8 mL) in a glovebox. The flask was taken out of the glovebox, and the mixture was stirred at room temperature and under argon atmosphere. After 48 h, the resulting precipitates were removed by filtration through a Celite pad and washed with CH_3CN. The filtrate was concentrated in *vacuo* and the residue was dissolved in CH_3CN (1 mL). To this solution was added Et_2O dropwise, and the resulting orange precipitates were collected by filtration, washed with Et_2O, and dried in *vacuo* to afford [Cp*RhL$_N$][(*S*)-6,6'-Br$_2$-BINSate] **2b** (115 mg, 68% as dihydrate).

Orange solid. **IR** (KBr): ν 3067, 1608, 1558, 1487, 1450, 1247, 1169, 1140, 1078, 1060, 1020, 876, 806, 718, 697, 680, 668, 623, 608 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.54 (s, 15H), 6.80 (d, J = 9.2 Hz, 2H), 7.29 (dd, J = 9.2, 1.7 Hz, 2 H), 7.91 (d, J = 8.6 Hz, 2H), 8.05 (d, J = 1.7 Hz, 2H), 8.15 (d, J = 8.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 8.7, 93.1 (d, $^1J_{CRh}$ = 10.5 Hz), 122.3, 124.9, 127.7, 129.4, 129.9, 130.7, 131.4, 133.1, 135.1, 140.1. **Anal.** Calcd for $C_{30}H_{29}Br_2O_8RhS_2$ (dihydrate): C, 42.67; H, 3.46. Found: C, 42.48; H, 3.04; N, <0.30.

Synthesis of [Cp*RhL$_N$][(*R*)-3,3'-Ph$_2$-BINSate] 2c



(*R*)-3,3'-Ph$_2$-BINSA (**1c**)

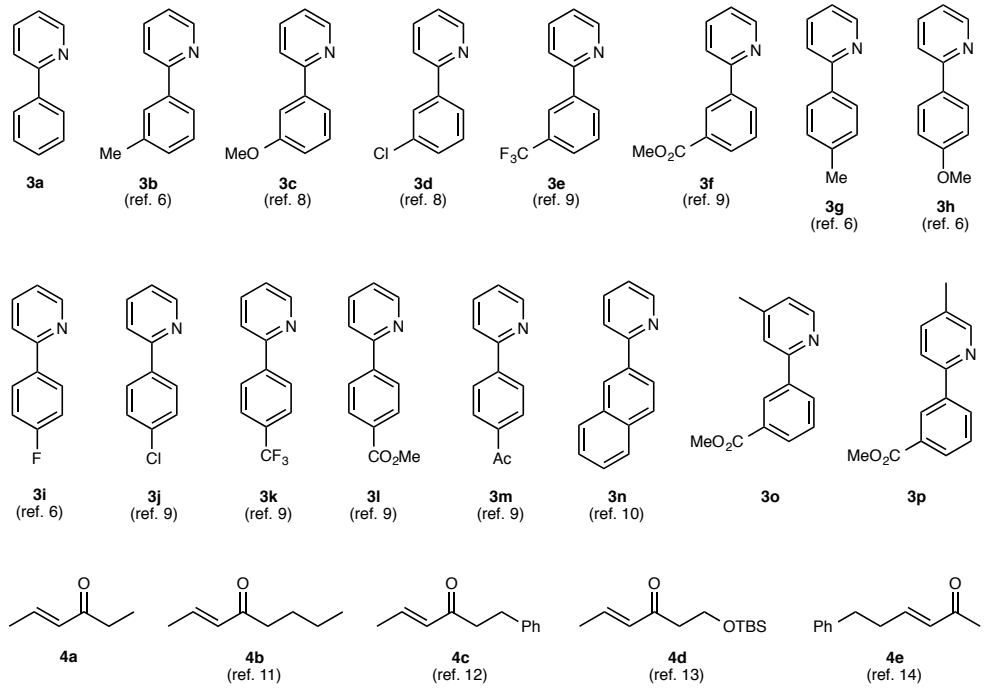
Following the procedure **A-3.**, (*R*)-3,3'-Ph$_2$-BINSA **1c**[5] (32.4 mg, 57 μmol), Ag_2CO_3 (30.3 mg, 110 μmol), and CH_2Cl_2/CH_3CN (1:1) were stirred at 40 ºC for 16 h in dark. The reaction mixture was filtered and

evaporated in *vacuo* to furnish Ag_2-3,3'-Ph_2-BINSate (38.6 mg, 87%) as an colorless solid, which was directly used for the next step without purification. Ag_2-3,3'-Ph_2-BINSate (38.6 mg, 50 μmol), $[Cp^*RhCl_2]_2$ (13.6 mg, 22 μmol) and CH_3CN (1 mL) were stirred at room temperature for 24 h. The reaction mixture was filtered and concentrated in *vacuo*. The filterate was further dried in *vacuo* at 40 ºC to afford [Cp*RhL_N][(*R*)-3,3'-Ph_2-BINSate] **2c** (33.5 mg, 70% as dihydrate) without recrystallization.

Orange solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.47 (s, 15H), 7.01 (d, *J* = 8.1 Hz, 2H), 7.22-7.26 (m, 2H), 7.37-7.48 (m, 8H), 7.70 (d, *J* = 6.7 Hz, 4H), 7.79 (d, *J* = 6.7 Hz, 4H). **Anal.** Calcd for $C_{42}H_{39}O_8RhS_2$ (dihydrate): C, 60.14; H, 4.69. Found: C, 59.84; H, 4.33; N, <0.30. No assignable ^{13}C NMR spectrum was obtained because **1c** was scarcely soluble in non-polar solvents and coordinatively unstable in polar solvents.

B. Preparation of Substrates

B-1. Structures of substrates



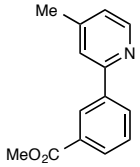
2-Phenylpyridine **3a** and (*E*)-4-hexen-3-one **4a** are commercially available. Other 2-phenylpyridine derivatives **3b-p** were synthesized using general procedure (**B-2.)** as described in the literature.[6] **4b-e** were synthesized according to a procedure reported in the literature.[7] The ^{1}H NMR spectra of known compounds were matched those reported in the literatures.[6, 8-14]

B-2. Preparation of 2-phenylpyridine derivatives[6]

2-Phenylpyridine derivatives **3b-p** were synthesized according to the following procedure.[6] A mixture of 2-chloropyridine (1 mmol), the corresponding arylboronic acid (2 mmol), $Pd(OAc)_2$ (11.2 mg, 5 mol %), and K_3PO_4 (650 mg, 3 mmol) in *i*PrOH/H_2O (1:1, 4 mL) was stirred at 80 ºC overnight. The mixture was poured

into brine and extracted with AcOEt. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography.

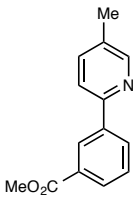
Methyl 3-(4-methylpyridin-2-yl)benzoate (3o)



3o

Colorless oil (264 mg, 58% yield). **TLC**: R_f = 0.41 (hexane/AcOEt = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.40 (s, 3H), 3.94 (s, 3H), 7.07 (d, *J* = 4.6 Hz, 1H), 7.53 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.59 (s, 1H), 8.07 (ddd, *J* = 8.0, 1.7, 1.7 Hz, 1H), 8.22 (ddd, *J* = 8.0, 1.7, 1.7 Hz, 1H), 8.55 (d, *J* = 4.6 Hz, 1H), 8.62 (dd, *J* = 1.7, 1.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.0, 52.0, 121.4, 123.4, 127.8, 128.7, 129.7, 130.4, 131.2, 139.6, 147.8, 149.4, 156.0, 166.8. **HRMS** (ESI): *m/z* calcd for $C_{14}H_{14}O_2N^+$ [M+H$^+$]: 228.1019, found: 228.1020.

Methyl 3-(5-methylpyridin-2-yl)benzoate (3p)



3p

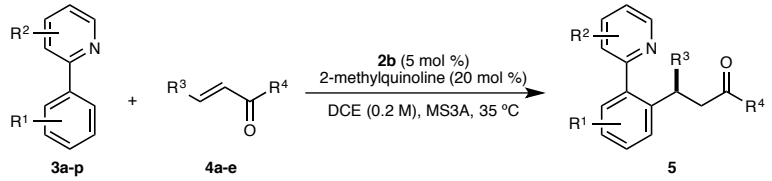
Colorless solid (195 mg, 43% yield). **TLC**: R_f = 0.47 (hexane/AcOEt 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.36 (s, 3H), 3.94 (s, 3H), 7.53 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 8.06 (ddd, *J* = 7.4, 1.7, 1.7 Hz, 1H), 8.20 (ddd, *J* = 7.4, 1.7, 1.7 Hz, 1H), 8.53 (s, 1H), 8.62 (dd, *J* = 1.7, 1.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 18.1, 52.0, 119.9, 127.6, 128.7, 129.5, 130.5, 131.0, 132.0, 137.3, 139.6, 150.1, 153.5, 166.9. **HRMS** (ESI): *m/z* calcd for $C_{14}H_{14}O_2N^+$ [M+H$^+$]: 228.1019, found: 228.1020.

C. Asymmetric Conjugate Addition of 2-Phenylpyridines

C-1. Optimization of reaction conditions (Table 1)

To a dried screw-capped vial were added **2a** or **2b** (2.5 μmol, 5 mol %), MS3A (0 or 2 mg), solvent (0.25 mL) under argon atmosphere in a glovebox. To the resulting mixture were successively added 2-phenylpyridine (**3a**) (8.6 μL, 0.060 mmol), an additive (0 or 0.01 mmol), and enone **4a** (5.5 μL, 0.050 mmol). The vial was capped, taken out of the glovebox, and the mixture was heated at 35 ºC with stirring under argon atmosphere for 16-18 h. The resulting mixture was filtered through a short silica gel pad, and washed with AcOEt. The filtrate was concentrated to afford the crude mixture. Dibenzyl ether (internal standard, ca. 10 mg, precisely weighted in each reaction) and $CDCl_3$ were added to the crude mixture, and the yield of **5aa** was determined by ^{1}H NMR analysis. An aliquot of the crude mixture was purified by preparative TLC, and the enantiomeric ratio of **5aa** was determined by HPLC analysis (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm). The results are summarized in Table 1.

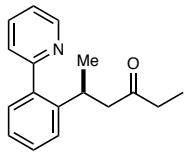
C-2. General procedure of asymmetric conjugate addition via C–H activation (Table 2)



To a dried screw-capped vial were added **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), and DCE (0.5 mL) under argon atmosphere in a glovebox. To the resulting mixture were successively added 2-phenylpyridine derivative **3** (0.10 mmol), 2-methylquinoline (2.7 μL, 0.02 mmol, 20 mol %), and enone **4** (0.11 or 0.13 mmol). The vial was capped, taken out of the glovebox, and the mixture was heated at 35 ºC with stirring under argon atmosphere. Upon completion, as judged by TLC analysis of the reaction mixture, the reaction mixture was directly purified by silica gel column chromatography to afford the desired product **5**.

C-3. Characterization of products 5

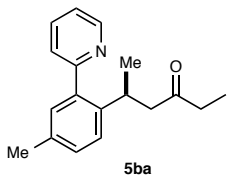
(*S*)-5-[2-(pyridin-2-yl)phenyl]hexan-3-one (5aa)



5aa

Following the general procedure (**C-2.**), 2-phenylpyridine **3a** (14.4 μL, 0.10 mmol), enone **4a** (12.6 μL, 0.11 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 48 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 6:1 to 3:1) to afford **5aa** (22.8 mg, 93%w/w purity, 84% yield, 91:9 er), which was further purified by GPC. Colorless oil. **TLC**: R_f = 0.38 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.20 (d, *J* = 6.8 Hz, 3H), 2.27 (q, *J* = 7.5 Hz, 2H), 2.54 (dd, *J* = 15.9, 9.1 Hz, 1H), 2.83 (dd, *J* = 15.9, 5.4 Hz, 1H), 3.52-3.63 (m, 1H), 7.23-7.29 (m, 2H), 7.32 (dd, *J* = 6.8, 0.9 Hz, 1H), 7.33-7.41 (m, 2H), 7.43 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.76 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 8.65-8.69 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.7, 21.7, 30.7, 36.0, 50.8, 121.8, 124.3, 125.9, 126.0, 128.6, 129.9, 136.2, 140.0, 144.1, 149.1, 160.0, 210.4. **HRMS** (ESI): *m/z* calcd for $C_{17}H_{20}ON^+$ [M+H$^+$]: 254.1539, found: 254.1543. **$[\alpha]_D^{17}$** = 18.9 (c = 0.72, $CHCl_3$). **HPLC**: 91:9 er. (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 6.6 min, t_R (minor) = 7.4 min).

(*S*)-5-[4-methyl-2-(pyridin-2-yl)phenyl]hexan-3-one (5ba)

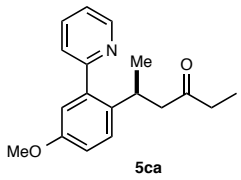


5ba

Following the general procedure (**C-2.**), **3b** (15.6 μL, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 36 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 4:1 to 3:2) to afford **5ba** (23.7 mg, 89% yield, 90:10 er): Pale yellow oil. **TLC**: R_f = 0.31 (hexane/AcOEt = 3:1). **^{1}H**

NMR (500 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.4 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 2.26 (q, *J* = 7.4 Hz, 2H), 2.35 (s, 3H), 2.53 (dd, *J* = 16.0, 8.6 Hz, 1H), 2.80 (dd, *J* = 16.0, 5.7 Hz, 1H), 3.47-3.56 (m, 1H), 7.14 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.22-7.29 (m, 3H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.77 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 8.68 (d, *J* = 4.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 20.8, 21.8, 30.4, 36.0, 50.8, 121.7, 124.2, 125.8, 129.3, 130.5, 135.4, 136.1, 139.8, 141.0, 149.0, 160.0, 210.5. **HRMS** (ESI): *m/z* calcd for $C_{18}H_{22}ON^+$ [M+H$^+$]: 268.1696, found: 268.1696. **$[\alpha]_D^{22}$** = 19.0 (c = 0.99, $CHCl_3$). **HPLC**: 90:10 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 6.5 min, t_R (minor) = 7.7 min).

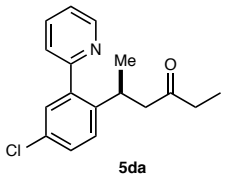
(*S*)-5-[4-methoxy-2-(pyridin-2-yl)phenyl]hexan-3-one (5ca)



5ca

Following the general procedure (**C-2.**), **3c** (15.8 μL, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 48 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 3:1 to 1:1) to afford **5ca** (26.6 mg, 89% yield, 90:10 er). Colorless oil. **TLC**: R_f = 0.38 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.3 Hz, 3H), 1.17 (d, *J* = 7.0 Hz, 3H), 2.26 (q, *J* = 7.3 Hz, 2H), 2.52 (dd, *J* = 16.1, 8.4 Hz, 1H), 2.79 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.41-3.51 (m, 1H), 3.81 (s, 3H), 6.86 (d, *J* = 2.9 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.9 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 7.7, 5.1 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.80 (ddd, *J* = 7.7, 7.7, 1.5 Hz, 1H), 8.69 (d, *J* = 5.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.7, 22.0, 30.2, 36.1, 50.9, 55.3, 114.6, 114.9, 121.9, 124.3, 127.0, 136.2, 136.4, 140.8, 149.0, 157.4, 159.6, 210.6. **HRMS** (ESI): *m/z* calcd for $C_{18}H_{22}O_2N^+$ [M+H$^+$]: 284.1645, found: 284.1646. **$[\alpha]_D^{22}$** = 19.0 (c = 0.87, $CHCl_3$). **HPLC**: 90:10 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 9.7 min, t_R (minor) = 14.4 min).

(*S*)-5-[4-chloro-2-(pyridine-2-yl)phenyl]hexan-3-one (5da)

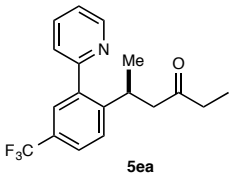


5da

Following the general procedure (**C-2.**), **3d** (15.0 μL, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 60 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 4:1 to 3:2) to afford **5da** (25.5 mg, 89% yield, 92:8 er). Colorless oil. **TLC**: R_f = 0.30 (hexane/AcOEt = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 2.27 (q, *J* = 7.3 Hz, 2H), 2.53 (dd, *J* = 16.0, 8.6 Hz, 1H), 2.79 (dd, *J* = 16.0, 5.7 Hz, 1H), 3.49-3.58 (m, 1H), 7.28-7.32 (m, 3H), 7.34 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.78 (ddd, *J* = 7.4, 7.4, 1.7, 1H), 8.67 (d, *J* = 4.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.7, 21.8, 30.3, 36.1 50.5, 122.3, 124.3, 127.5, 128.6, 129.8, 131.5, 136.5, 141.6, 142.7, 149.3, 158.5, 210.0. **HRMS** (ESI): *m/z* calcd for $C_{17}H_{19}ONCl^+$ [M+H$^+$]: 288.1150, found: 288.1151. **$[\alpha]_D^{21}$** = 15.8 (c = 0.73, $CHCl_3$), **HPLC**: 92:8 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) =

6.5 min, t_R (minor) = 8.7 min).

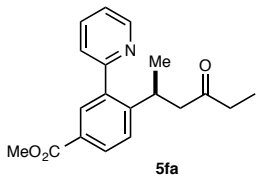
(*S*)-5-[2-(pyridin-2-yl)-4-(trifluoromethyl)phenyl]hexan-3-one (5ea)



5ea

Following the general procedure (**C-2.**), **3e** (17.4 μL, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 84 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 9:1 to 7:3) to afford the mixture of **5ea** (21.0 mg, 95%w/w purity, 62% yield, 93:7 er), which was further purified by GPC. Colorless oil. **TLC**: R_f = 0.36 (hexane/AcOEt = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 2.30 (q, *J* = 7.2 Hz, 2H), 2.58 (dd, *J* = 16.5, 8.6 Hz, 1H), 2.85 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.58-3.67 (m, 1H), 7.32 (dd, *J* = 7.4, 5.4, 1.5 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.81 (ddd, *J* = 7.4, 7.4, 1.5 Hz, 1H), 8.69 (d, *J* = 5.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.6, 21.6, 30.7, 36.1, 50.2, 122.4, 124.1 (q, $^1J_{CF}$ = 272.3 Hz), 124.3, 125.2 (q, $^3J_{CF}$ = 4.9 Hz), 126.5, 126.8 (q, $^3J_{CF}$ = 3.6 Hz), 128.3 (q, $^2J_{CF}$ = 32.4 Hz), 136.5, 140.6, 148.4, 149.3, 158.6, 209.7. **^{19}F NMR** (470 MHz, $CDCl_3$): δ –63.4. **HRMS** (ESI): *m/z* calcd for $C_{18}H_{19}ONF_3^+$ [M+H$^+$]: 322.1413, found: 322.1419. **$[\alpha]_D^{24}$** = 9.1 (c = 0.61, $CHCl_3$). **HPLC**: 93:7 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 4.8 min, t_R (minor) = 5.3 min).

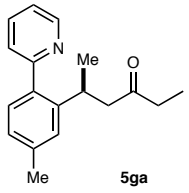
Methyl (*S*)-4-(4-oxohexan-2-yl)-3-(pyridin-2-yl)benzoate (5fa)



5fa

Following the general procedure (**C-2.**), **3f** (21.3 mg, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 4:1 to 3:2) to afford **5fa** (22.1 mg, 71% yield, 93:7 er). Pale yellow oil. **TLC**: R_f = 0.21 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 3H), 2.28 (q, *J* = 7.3 Hz, 2H), 2.57 (dd, *J* = 16.2, 8.2 Hz, 1H), 2.85 (dd, *J* = 16.2, 5.9 Hz, 1H), 3.58-3.68 (m, 1H), 3.90 (s, 3H), 7.31 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.81 (ddd, *J* = 7.7, 7.7, 1.5 Hz, 1H), 8.00 (d, *J* = 1.8 Hz, 1H), 8.04 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.68 (d, *J* = 4.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.6, 21.6, 30.9, 36.1, 50.3, 52.0, 122.2, 124.4, 126.2, 127.9, 129.7, 131.2, 136.6, 140.1, 149.0, 149.7, 158.9, 166.7, 209.8. **HRMS** (ESI): *m/z* calcd for $C_{19}H_{22}O_3N^+$ [M+H$^+$]: 312.1594, found: 312.1597. **$[\alpha]_D^{22}$** = 18.2 (c = 0.82, $CHCl_3$). **HPLC**: 93:7 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 17.2 min, t_R (minor) = 24.2 min).

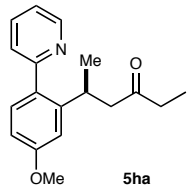
(*S*)-5-[5-methyl-2-(pyridin-2-yl)phenyl]hexan-3-one (5ga)



5ga

Following the general procedure (**C-2.**), **3g** (15.6 μL, 0.10 mmol), enone **4a** (12.6 μL, 0.11 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 5:1 to 3:2) to afford the mixture of **5ga** (23.9 mg, 93% w/w purity, 83% yield, 90:10 er), which was further purified by GPC. Colorless oil. **TLC**: R_f = 0.31 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.4 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 2.27 (q, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 2.54 (dd, *J* = 15.9, 8.6 Hz, 1H), 2.81 (dd, *J* = 15.9, 5.4 Hz, 1H), 3.52-3.63 (1H, m), 7.08 (d, *J* = 7.7 Hz, 1H), 7.15 (s, 1H), 7.20-7.27 (m, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.74 (dd, *J* = 7.7, 7.7 Hz, 1H), 8.66 (d, *J* = 4.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.7, 21.4, 21.6, 30.6, 36.0, 50.9, 121.6, 124.3, 126.6, 126.8, 129.9, 136.1, 137.2, 138.2, 144.0, 149.1, 160.1, 210.6. **HRMS** (ESI): *m/z* calcd for $C_{18}H_{22}ON$ [M+H$^+$]: 268.1696, found: 268.1700. **$[\alpha]_D^{20}$** = 26.7 (c = 0.71, $CHCl_3$), **HPLC**: 90:10 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 6.7 min, t_R (minor) = 7.5 min).

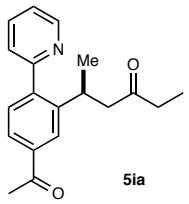
(*S*)-5-[5-methoxy-2-(pyridin-2-yl)phenyl]hexan-3-one (5ha)



5ha

Following the general procedure (**C-2.**), **3h** (18.5 mg, 0.10 mmol), enone **4a** (12.6 μL, 0.11 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 5:1 to 3:2) to afford **5ha** (18.8 mg, 66% yield, 91:9 er). Colorless oil. **TLC**: R_f = 0.19 (hexane/AcOEt = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.4Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 2.28 (q, *J* = 7.4 Hz, 2H), 2.53 (dd, *J* = 15.8, 9.2 Hz, 1H), 2.82 (dd, *J* = 15.8, 5.4 Hz, 1H), 3.58-3.66 (m, 1H), 6.81 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.88 (d, *J* = 2.3 Hz, 1H), 7.24 (ddd, *J* = 7.4, 5.2, 1.1 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.75 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 8.66 (d, *J* = 5.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 21.6, 30.8, 36.0, 50.8, 55.2, 110.7, 112.1, 121.5, 124.4, 131.3, 132.7, 136.3, 145.9, 149.0, 159.7, 159.8, 210.3. **HRMS** (ESI): *m/z* calcd for $C_{18}H_{22}O_2N^+$ [M+H$^+$]: 284.1645, found: 284.1649. **$[\alpha]_D^{19}$** = 21.7 (c = 0.94, $CHCl_3$), **HPLC**: 91:9 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 10.5 min, t_R (minor) = 12.4 min).

(*S*)-5-[5-acetyl-2-(pyridin-2-yl)phenyl]hexan-3-one (5ia)

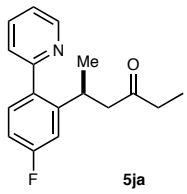


5ia

Following the general procedure (**C-2.**), **3i** (21.3 mg, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 2:1 to 1:1) to afford **5ia** (20.3 mg, 65% yield, 92:8 er). Colorless oil. **TLC**: R_f = 0.40 (hexane/AcOEt = X:X). **^{1}H NMR** (400 MHz,

$CDCl_3$): δ 0.96 (t, *J* = 7.3 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 3H), 2.30 (q, *J* = 7.3 Hz, 2H), 2.63 (dd, *J* = 16.5, 8.4 Hz, 1H), 2.65 (s, 3H), 2.88 (dd, *J* = 16.5, 5.9 Hz, 1H), 3.56-3.67 (m, 1H), 7.31 (ddd, *J* = 7.7, 5.1, 1.1 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.79 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.98 (d, *J* = 1.8 Hz, 1H), 8.70 (ddd, *J* = 5.1, 1.8, 1.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 21.8, 26.7, 30.5, 36.2, 50.3, 122.3, 124.2, 125.7, 126.2, 130.3, 136.4, 137.0, 144.6, 145.0, 149.3, 158.9, 198.0, 209.9. **HRMS** (ESI): *m/z* calcd for $C_{19}H_{21}O_2NNa^+$ [M+Na^+]: 318.1465, found: 318.1469. **$[\alpha]_D^{26}$** = 24.6 (c = 0.93, $CHCl_3$), **HPLC**: 92:8 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 17.5 min, t_R (minor) = 29.4 min).

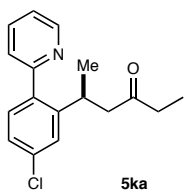
(*S*)-5-[5-fluoro-2-(pyridin-2-yl)phenyl]hexan-3-one (5ja)



5ja

Following the general procedure (**C-2.**), **3j** (17.3 mg, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 120 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 4:1 to 3:2) to afford the mixture of **5ja** (21.0 mg, 97% w/w purity, 75% yield, 92:8 er), which was further purified by GPC. Colorless oil. **TLC**: R_f = 0.30 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 2.29 (q, *J* = 7.2 Hz, 2H), 2.53 (dd, *J* = 16.3, 8.6 Hz, 1H), 2.80 (dd, *J* = 16.3, 5.4 Hz, 1H), 3.53-3.63 (m, 1H), 6.96 (ddd, *J* = 8.6, 7.7, 2.7 Hz, 1H), 7.03 (dd, *J* = 10.9, 2.7 Hz, 1H), 7.25-7.32 (m, 2H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.77 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 8.66 (d, *J* = 4.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.6, 21.5, 30.7, 36.1, 50.4, 112.7 (d, $^2J_{CF}$ = 21.6 Hz), 112.9 (d, $^2J_{CF}$ = 20.3 Hz), 121.8, 124.3, 131.6 (d, $^3J_{CF}$ = 8.4 Hz), 136.1 (d, $^4J_{CF}$ = 2.4 Hz), 136.3, 146.9 (d, $^3J_{CF}$ = 7.2 Hz), 149.1, 159.0, 162.9 (d, $^1J_{CF}$ = 247.1 Hz), 209.8. **^{19}F NMR** (470 MHz, $CDCl_3$): δ –116.4. **HRMS** (ESI): *m/z* calcd for $C_{17}H_{19}ONF^+$ [M+H^+]: 272.1445, found: 272.1449. **$[\alpha]_D^{17}$** = 11.9 (c = 0.99, $CHCl_3$). **HPLC**: 92:8 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 6.3 min, t_R (minor) = 7.3 min).

(*S*)-5-[5-chloro-2-(pyridin-2-yl)phenyl]hexan-3-one (5ka)

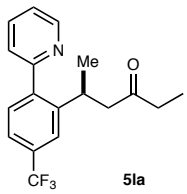


5ka

Following the general procedure (**C-2.**), **3k** (18.9 mg, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.68 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 96 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 4:1 to 3:2) to afford the mixture of **5ka** (24.1 mg, 92% w/w purity,77% yield, 92:8 er), which was further purified by GPC. Colorless oil. **TLC**: R_f = 0.29 (hexane/AcOEt = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.97 (t, *J* = 7.2 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 2.29 (q, *J* = 7.2 Hz, 2H), 2.55 (dd, *J* = 16.0, 8.6 Hz, 1H), 2.81 (dd, *J* = 16.0, 5.7 Hz, 1H), 3.53-3.61 (m, 1H), 7.23-7.29 (m, 3H), 7.31 (d, *J* = 1.7 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.77 (ddd, *J* = 8.0, 8.0, 1.7 Hz, 1H), 8.67 (d, *J* = 4.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.7, 21.6, 30.6, 36.2, 50.4, 122.1,

124.3, 126.2, 126.2, 131.3, 134.5, 136.4, 138.4, 146.4, 149.2, 158.8, 209.8. **HRMS** (ESI): *m/z* calcd for $C_{17}H_{19}ONCl^+$ [M+H$^+$]: 288.1190, found: 288.1155. $[\alpha]_D^{19}$ = 23.8 (c = 0.50, $CHCl_3$). **HPLC**: 92:8 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 6.5 min, t_R (minor) = 7.2 min).

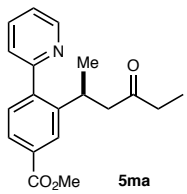
(*S*)-5-[2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl]hexan-3-one (5la)



5la

Following the general procedure (**C-2.**), **3l** (22.3 mg, 0.1 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 4:1 to 3:2) to afford the mixture of **5la** (22.0 mg, 96% w/w purity, 66% yield, , 92:8 er), which was further purified by GPC. Colorless oil. **TLC**: R_f = 0.31 (hexane/AcOEt = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 2.30 (q, *J* = 7.3 Hz, 2H), 2.59 (dd, *J* = 16.4, 8.3 Hz, 1H), 2.84 (dd, *J* = 16.4, 5.2 Hz, 1H), 3.59-3.66 (m, 1H), 7.32 (ddd, *J* = 8.0, 4.9, 1.1 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.81 (ddd, *J* = 8.0, 8.0, 1.7 Hz, 1H), 8.69 (d, *J* = 4.9 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 21.6, 30.5, 36.2, 50.2, 122.4, 122.7-122.9 (m, 2C), 124.1 (q, $^1J_{CF}$ = 272.3 Hz), 124.2, 130.4, 130.6 (q, $^2J_{CF}$ = 32.4 Hz), 136.5, 143.4, 145.4, 149.3, 158.6, 209.7. **^{19}F NMR** (470 MHz, $CDCl_3$): δ –63.5. **HRMS** (ESI): *m/z* calcd for $C_{18}H_{19}ONF_3$ [M+H$^+$]: 322.1413, found: 322.1419. $[\alpha]_D^{17}$ = 7.5 (c = 0.68, $CHCl_3$). **HPLC**: 92:8 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 4.7 min, t_R (minor) = 5.2 min).

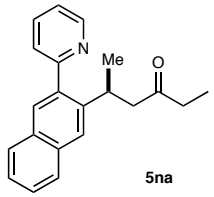
Methyl (*S*)-3-(4-oxohexan-2-yl)-4-(pyridin-2-yl)benzoate (5ma)



5ma

Following the general procedure (**C-2.**), **3m** (21.3 mg, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.68 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 4:1 to 3:2) to afford **5ma** (25.1 mg, 81% yield, 92:8 er). Colorless solid. **TLC**: R_f = 0.21 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.3 Hz, 3H), 1.22 (d, *J* = 6.6 Hz, 3H), 2.30 (q, *J* = 7.3 Hz, 2H), 2.62 (dd, *J* = 16.5, 8.4 Hz, 1H), 2.87 (dd, *J* = 16.5, 5.9 Hz, 1H), 3.55-3.65 (m, 1H), 3.95 (s, 3H), 7.31 (dd, *J* = 7.7, 4.4 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.81 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 7.93 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.04 (d, *J* = 1.5 Hz, 1H), 8.70 (d, *J* = 4.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.6, 21.8, 30.5, 36.2, 50.3, 52.1, 122.3, 124.2, 127.1, 127.3, 130.1, 130.1, 136.4, 144.3, 144.7, 149.2, 158.9, 166.9, 209.9. **HRMS** (ESI): *m/z* calcd for $C_{19}H_{22}O_3N^+$ [M+H$^+$]: 312.1594, found: 312.1595. $[\alpha]_D^{23}$ = 26.6 (c = 0.69, $CHCl_3$), **HPLC**: 92:8 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 13.0 min, t_R (minor) = 18.3 min).

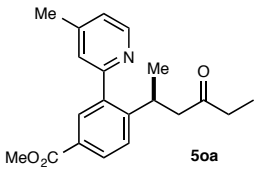
(*S*)-5-[3-(pyridin-2-yl)naphthalen-2-yl]hexan-3-one (5na)



5na

Following the general procedure (**C-2.**), **5n** (20.5 mg, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 96 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 9:1 to 7:3) to afford the mixture of **5na** (30.5 mg, 91% w/w purity, 91% yield, 91:9 er), which was further purified by GPC. Colorless oil. **TLC**: R_f = 0.24 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.28 (d, *J* = 6.8 Hz, 3H), 2.28 (q, *J* = 7.3 Hz, 2H), 2.60 (dd, *J* = 16.2, 8.8 Hz, 1H), 2.95 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.68-3.79 (m, 1H), 7.32 (ddd, *J* = 7.7, 4.6, 0.9 Hz, 1H), 7.43-7.51 (m, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.78-7.85 (m, 5H), 8.72 (d, *J* = 4.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 21.7, 30.7, 36.0, 51.0, 121.9, 124.5, 124.7, 125.7, 126.3, 127.3, 127.8, 129.3, 131.7, 133.3, 136.3, 139.0, 142.5, 149.1, 160.0, 210.4. **HRMS** (ESI): *m/z* calcd for $C_{21}H_{22}ON^+$ [M+H$^+$]: 304.1696, found: 304.1696. **$[\alpha]_D^{23}$** = 31.7 (c = 0.71, $CHCl_3$). **HPLC**: 91:9 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 9.9 min, t_R (minor) = 15.1 min).

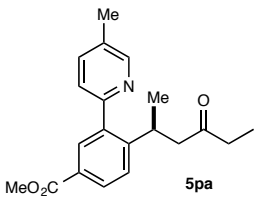
Methyl (*S*)-3-(4-methylpyridin-2-yl)-4-(4-oxohexan-2-yl)benzoate (5oa)



5oa

Following the general procedure (**C-2.**), **3o** (22.7 mg, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 3:1 to 1:1) to afford **5oa** (22.9 mg, 70% yield, 93:7 er). Colorless oil. **TLC**: R_f = 0.19 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.3 Hz, 3H), 1.21 (d, *J* = 6.6 Hz, 3H), 2.29 (q, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 2.57 (dd, *J* = 16.1, 8.8 Hz, 1H), 2.86 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.58-3.68 (m, 1H), 3.90 (s, 3H), 7.12 (dd, *J* = 5.1, 0.7 Hz, 1H), 7.28 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 1.8 Hz, 1H), 8.03 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.52 (d, *J* = 5.1 Hz, 1H). **^{13}C NMR** (125 Mhz, $CDCl_3$): δ 7.7, 21.3, 21.4, 30.9, 36.1, 50.4, 52.0, 123.2, 125.2, 126.2, 127.8, 129.5, 131.2, 140.2, 147.7, 148.8, 149.8, 158.8, 166.8, 209.9. **HRMS** (ESI): *m/z* calcd for $C_{18}H_{24}O_3N^+$ [M+H$^+$]: 326.1751, ound: 326.1756. **$[\alpha]_D^{20}$** = 16.9 (c = 1.14, $CHCl_3$). **HPLC**: 93:7 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 20.5 min, t_R (minor) = 26.8 min).

Methyl (*S*)-3-(5-methylpyridin-2-yl)-4-(4-oxohexan-2-yl)benzoate (5pa)

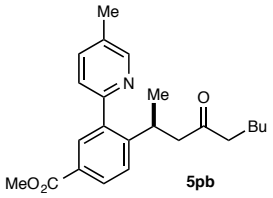


5pa

Following the general procedure (**C-2.**), **3p** (22.7 mg, 0.10 mmol), enone **4a** (14.9 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 4:1 to 3:2) to afford **5pa** (30.2 mg, 93% yield, 95:5 er). Colorless oil. **TLC**: R_f = 0.23 (hexane/AcOEt = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.3 Hz, 3H), 1.21 (d, *J* = 6.2 Hz, 3H), 2.29 (q, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 2.58 (dd, *J* = 16.5, 8.4 Hz, 1H), 2.85 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.58-3.68 (m, 1H), 3.89 (s, 3H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.1, 1.8 Hz, 1H), 7.99 (d, *J* = 1.8 Hz, 1H), 8.02 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.51 (dd, *J* = 1.8, 0.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 18.2, 21.5, 30.8, 36.1, 50.3, 52.0, 123.7, 126.1, 127.8, 129.4, 131.3, 131.6, 137.0, 140.2, 149.6, 149.7, 156.2, 166.8, 209.9. **HRMS** (ESI): *m/z* calcd for $C_{20}H_{24}O_2N^+$ [M+H$^+$]: 326.1751, found: 326.1756. **$[\alpha]_D^{18}$** = 19.5 (c = 1.24, $CHCl_3$). **HPLC**: 95:5 er. (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 16.5 min, t_R (minor) = 20.0 min).

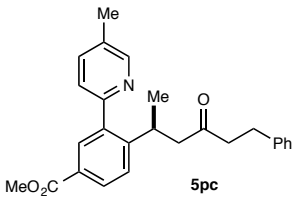
Methyl (*S*)-3-(5-methylpyridin-2-yl)-4-(4-oxooctan-2-yl)benzoate (5pb)



5pb

Following the general procedure (**C-2.**), **3p** (22.7 mg, 0.10 mmol), enone **4b** (18.2 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 3:1 to 2:1) to afford the mixture of **5pb** (36.2 mg, 93% w/w purity, 95% yield, 95:5 er), which was further purified by GPC. Colorless oil. **TLC**: R_f = 0.38 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 mHz, $CDCl_3$): δ 0.86 (t, *J* = 7.3 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.18-1.27 (m, 2H), 1.41-1.51 (m, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 2.57 (dd, *J* = 16.4, 8.6 Hz, 1H), 2.85 (dd, *J* = 16.4, 5.5 Hz, 1H), 3.61-3.72 (m, 1H), 3.91 (s, 3H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 1.8 Hz, 1H), 8.03 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.51 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.9, 18.4, 21.6, 22.4, 26.0, 30.9, 42.9, 50.8, 52.1, 123.9, 126.3, 127.9, 129.6, 131.4, 131.7, 137.2, 140.3, 149.7, 149.9, 156.3, 166.9, 209.8. **HRMS** (ESI): *m/z* calcd for $C_{22}H_{28}O_3N^+$ [M+H$^+$]: 354.2064, found: 354.2062. **$[\alpha]_D^{18}$** = 8.1 (c = 1.47, $CHCl_3$). **HPLC**: 95:5 er (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 14.4 min, t_R (minor) = 20.0 min).

Methyl (*S*)-3-(5-methylpyridin-2-yl)-4-(4-oxo-6-phenylhexan-2-yl)benzoate (5pc)

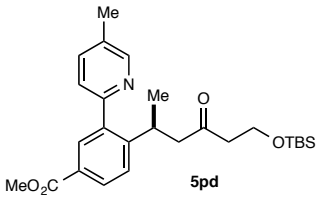


5pc

Following the general procedure (**C-2.**), **3p** (22.7 mg, 0.10 mmol), enone **4c** (22.4 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 8:1 to 3:2) to afford **5pc** (35.3 mg, 88% yield, 95:5 er). Colorless oil. **TLC**: R_f = 0.26 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.19 (d, *J* = 6.6 Hz, 3H), 2.38 (s, 3H), 2.50-2.62 (m, 3H), 2.79 (t, *J* = 7.7 Hz, 2H), 2.85 (dd, *J* = 15.9, 6.0 Hz, 1H), 3.58-3.69 (m, 1H), 3.89 (s, 3H), 7.09 (d, *J* = 7.3 Hz, 2H), 7.15-7.20 (m, 1H), 7.22-7.28 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.58 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.98 (d, *J* = 2.1 Hz, 1H), 8.01 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.45 (s, 1H).**^{13}C NMR** (100

MHz, $CDCl_3$): δ 18.4, 21.6, 29.7, 31.0 44.5, 51.2, 52.2, 123.9, 126.2, 126.3, 128.0, 128.4, 128.6, 129.6, 131.4, 131.8, 137.2, 140.2, 141.1, 149.7, 149.8, 156.3, 166.9, 208.6. **HRMS** (ESI): *m/z* calcd for $C_{26}H_{28}O_3N^+$ [M+H$^+$]: 402.2064, found: 402.2062. $[\alpha]_D^{18}$ = –4.8 (c = 0.68, $CHCl_3$). **HPLC**: 95:5 er. (Chiralpak IB, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 8.6 min, t_R (minor) = 11.3 min).

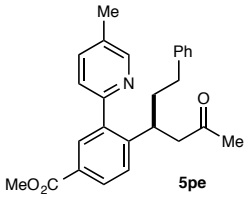
Methyl (*S*)-4-(6-((*tert*-butyldimethylsilyl)oxy)-4-oxohexan-2-yl)-3-(5-methylpyridin-2-yl)benzoate (5pd)



5pd

Following the general procedure (**C-2.**), **3p** (22.7 mg, 0.10 mmol), enone **4d** (32.3 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 50 ºC for 84 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 6:1 to 2:1) to afford **5pc** (34.6 mg, 76% yield, 93:7 er). Colorless oil. **TLC**: R_f = 0.30 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.00 (s, 6H), 0.84 (s, 9H), 1.19 (d, *J* = 6.8 Hz, 3H), 2.38 (s, 3H), 2.47 (t, *J* = 6.3 Hz, 2H), 2.62 (dd, *J* = 16.4, 8.8 Hz, 1H), 2.88 (dd, *J* = 16.4, 5.4 Hz, 1H), 3.59-3.70 (m, 1H), 3.79 (t, *J* = 6.3 Hz, 2H), 3.88 (s, 3H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.98 (d, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.50 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ –5.5, 18.2, 21.5, 25.8, 30.5, 45.7, 51.7, 52.0, 52.0, 58.6, 123.8, 126.2, 127.8, 129.5, 131.3, 131.6, 137.0, 140.1, 149.6, 149.8, 156.1, 166.8, 208.2. **HRMS** (ESI): *m/z* calcd for $C_{26}H_{38}O_4NSi^+$ [M+H$^+$]: 456.2565, found: 456.2566. $[\alpha]_D^{18}$ = 9.5 (c = 1.14, $CHCl_3$). **HPLC**: 93:7 er. (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 8.7 min, t_R (minor) = 10.4 min).

Methyl (*S*)-3-(5-methylpyridin-2-yl)-4-(5-oxo-1-phenylhexan-3-yl)benzoate (5pe)

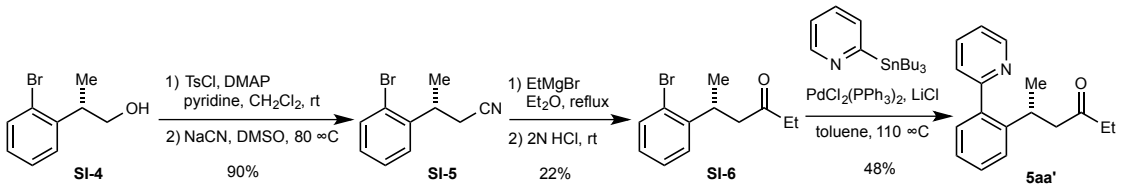


5pe

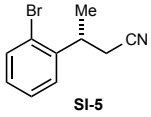
Following the general procedure (**C-2**)**.**, **3p** (22.7 mg, 0.10 mmol), enone **4e** (21.6 μL, 0.13 mmol), **2b** (4.3 mg, 5 μmol, 5 mol %), MS3A (4 mg), 2-methylquinoline (2.7 μL, 0.02 mmol), and DCE (0.5 mL) were stirred at 35 ºC for 72 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 6:1 to 3:2) to afford **5pc** (34.9 mg, 87% yield, 88:12 er). Colorless oil. **TLC**: R_f = 0.21 (hexane/AcOEt = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.87-1.93 (m, 2H), 2.00 (s, 3H), 2.35 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.70 (dd, *J* = 16.3, 7.7 Hz, 1H), 2.92 (dd, *J* = 16.3, 6.0 Hz, 1H), 3.55-3.62 (m, 1H), 3.91 (s, 3H), 6.97 (d, *J* = 7.4 Hz, 2H), 7.11 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.17 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.02 (d, *J* = 1.7 Hz, 1H), 8.06 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.46 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 18.2, 30.1, 33.4, 35.7, 37.5, 50.5, 52.0, 123.8, 125.6, 126.4, 128.0, 128.1 (2C), 129.5, 131.3, 131.5, 136.9, 141.1, 141.7, 147.8, 149.4, 156.0, 166.7, 207.3. **HRMS** (ESI): *m/z* calcd for $C_{26}H_{28}O_3N^+$ [M+H$^+$]: 402.2064, found: 402.2063. $[\alpha]_D^{21}$ = 63.8 (c = 0.65, $CHCl_3$). **HPLC**: 88:12 er. (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (minor) = 22.4 min, t_R (major) = 27.4 min).

D. Determination of Absolute Configuration of 5aa

An authentic sample of **5aa'** with (*R*)-configuration was synthesized from **SI-4**[15] as follows.



(*R*)-3-(2-bromophenyl)butanenitrile (SI-5) (not optimized)

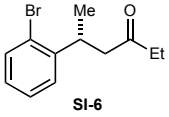


To a solution of **SI-4** (394.5 mg, 1.83 mmol) and pyridine (0.44 mL, 5.5 mmol) in CH_2Cl_2 (10 mL) was added TsCl (385 mg, 2.0 mmol) at 0 °C. The mixture was warmed to room temperature, and stirred at for 30 min. To the mixture was added DMAP (22 mg, 0.18 mmol), and the mixture was further stirred at room temperature for 15 h. After the addition of pyridine (2 mL, 25 mmol) and TsCl (210 mg, 1.1 mmol), the mixture was stirred for further 3 h. The reaction was quenched by 2 N aqueous HCl (30 mL), and the mixture was extracted with Et_2O (50 mL and 25 mL x 2). The combined organic layers were successively washed with 1 N aqueous HCl, saturated aqueous $NaHCO_3$, and brine, and dried over Na_2SO_4. Filtration and evaporation afforded a crude mixture, which contained small amount of unreacted **SI-4** and TsCl. To this mixture were added CH_2Cl_2 (5 mL), pyridine (2 mL, 25 mml), and DMAP (26 mg, 0.21 mmol), and the mixture was stirred at room temperature for 3 h. After the same aqueous work-up as above, the crude mixture was used for the next step without further purification.

The obtained crude mixture was dissolved in DMSO (5 mL), and NaCN (451 mg, 9.2 mmol) was added. The mixture was heated at 80 °C for 12 h with stirring. After cooling to room temperature, saturated aqueous $NaHCO_3$ and water were added. The mixture was extracted with AcOEt/hexane = 2:1 three times. The combined organic layers were washed with water (x 3) and brine, and dried over Na_2SO_4. Filtration and evaporation afforded a crude mixture, which was purified by silica gel column chromatography (hexane/AcOEt = 100:0 to 81:19, gradient) to afford **SI-5** (368 mg, 90%).

Colorless oil. **TLC**: R_f = 0.38 (hexane/AcOEt = 8:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.48 (d, *J* = 4.2 Hz, 3H), 2.59 (dd, *J* = 16.8, 7.5 Hz, 1H), 2.69 (dd, *J* = 16.8, 5.4 Hz, 1H), 3.63-3.73 (m, 1H), 7.10-7.17 (m, 1H), 7.30-7.37 (m, 2H), 7.56-7.60 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.1, 24.7, 34.6, 118.0, 124.1, 126.9, 127.9, 128.7, 133.1, 141.4. **$[\alpha]_D^{16}$** = 42.5 (c = 1.03, $CHCl_3$). **HRMS (ESI):** *m/z* calcd for $C_{10}H_{10}NBrNa^+$ [M+Na^+]: 245.9889, found: 245.9895.

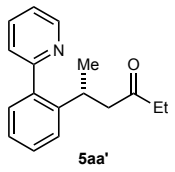
(*R*)-5-(2-bromophenyl)hexan-3-one (SI-6) (not optimized)



To a solution of **SI-5** (149 mg, 0.665 mmol) in Et_2O (2 mL) was added EtMgBr (0.33 mL, 3 M in Et_2O, 1 mmol) at room temperature, and the mixture was refluxed for 1 h. After cooling to 0 °C, 2 N aqueous HCl (2 mL) was carefully added. After stirring at room

temperature for 20 min, the mixture was extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4. Filtration and evaporation afforded a crude mixture, which was purified by silica gel column chromatography (hexane/Et_2O = 93:7 to 85:15, gradient) to afford **SI-6** (37.3 mg, 22%).
Colorless oil. **TLC**: R_f = 0.23 (hexane/Et_2O = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.03 (t, *J* = 7.3 Hz, 3H), 1.25 (t, *J* = 6.9 Hz, 3H), 2.34-2.48 (m, 2H), 2.58 (dd, *J* = 16.2, 8.9 Hz, 1H), 2.78 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.75-3.84 (m, 1H), 7.03-7.08 (m, 1H), 7.21-7.30 (m, 2H), 7.54 (dd, *J* = 7.7, 1.1 Hz 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 20.4, 34.1, 36.0, 49.5, 124.2, 127.1, 127.7, 127.7, 133.0, 144.8, 209.8. **$[\alpha]_D^{15}$** = –2.3 (c = 1.34, $CHCl_3$). **HRMS (ESI):** *m/z* calcd for $C_{12}H_{15}OBrNa$ [M+Na^+]: 277.0199, found: 277.0205.

5aa' (not optimized)



5aa'

To a Schlenk tube were added **SI-6** (22.3 mg, 0.0874 mmol), LiCl (15 mg, 0.35 mmol), and $PdCl_2(PPh_3)_2$ (6.1 mg, 0.0087 mmol). The mixture was charged with toluene (1 mL) and tributyl(2-pyridyl)tin (56 μL, 0.18 mmol) under Ar, and heated at 110 °C for 16 h. The mixture was cooled to room temperature, and water and an excess amount of KF were added. After stirring at room temperature for further 30 min, the mixture was extracted with AcOEt three times. The combined organic layers were dried over Na_2SO_4. Filtration and evaporation afforded a crude mixture, which was purified by silica gel column chromatography (hexane/AcOEt = 82:18 to 61:39, gradient) followed by GPC to afford **5aa'** (10.5 mg, 48%). The ^{1}H NMR spectrum of **5aa'** was matched with that of **5aa** obtained in the reaction catalyzed by **2b** described above.

Comparison of chiral HPLC analysis of **5aa** and **5aa'** (Supplementary Figure 1, Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm) indicated that the absolute configuration of **5aa**, a major isomer obtained in the reaction catalyzed by **2b**, was opposite to **5aa'**, and thus determined to be (*S*). It was also supported by the opposite optical rotation of **5aa**: **$[\alpha]_D^{17}$** = 18.9 (c = 0.72, $CHCl_3$) and **5aa'**: **$[\alpha]_D^{14}$** = –21.8 (c = 0.47, $CHCl_3$).

E. Evaluation of Other Chiral Organic Anions (Table 3)

Preparation of Ag salts

Ag-BINSate **6** was prepared as described above, and used without further purification.

7 and **9**: To a stirred solution of the corresponding chiral acid (0.10 mmol) in CH_2Cl_2/CH_3CN (1:1, 2 mL) was added Ag_2CO_3 (28 mg, 0.10 mmol), and the mixture was stirred at 40 °C for 12 h in dark. The reaction mixture was filtered through a Celite pad, and washed with CH_2Cl_2/CH_3CN (1:1). The filtrate was evaporated in *vacuo*, and the obtained Ag salts were used without further purification.

Ag-TRIP **8** was prepared according to the literature.[16]

General procedure of evaluation of other chiral organic anions

To dried screw-capped vial were added $[Cp^*RhCl_2]_2$ (0.77 mg, 1.25 μmol), Ag salt **6-9** (2.5 or 5.0 μmol), MS3A (2 mg), and DCE (0.25 mL) under argon atmosphere in glovebox. To the mixture were successively added 2-phenylpyridine **3a** (7.2 μL, 50 μmol), 2-methylquinoline (0 or 10 μmol), and enone **4a** (7.5 μL, 65 μmol). The vial was capped, taken out of the glovebox, and the mixture was heated at 35 ºC with stirring under argon atmosphere for 48 h. The reaction mixture was filtered through a short silica gel pad, and washed with AcOEt. The filtrate was concentrated to afford the crude mixture. Dibenzyl ether (internal standard, ca. 10 mg, precisely weighted in each reaction) and $CDCl_3$ were added to the crude mixture, and the yield of **5aa** was determined by ^1H NMR analysis. An aliquot of the crude mixture was purified by preparative TLC, and the enantiomeric ratio of **5aa** was determined by HPLC analysis (Chiralpak ID, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm).

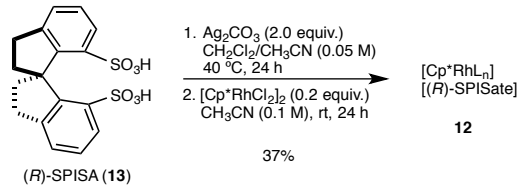
F. Asymmetric Conjugate Addition of 6-Arylpurines

6-Arylpurines **10** were prepared from commercially available 6-chloropurine according to the literature.[17]

F-1. Optimization of reaction conditions

To a dried screw-capped vial were added model substrate **10a** (34.4 mg, 0.12 mmol), **2b** (5 μmol, 5 mol %), MS3A (0 or 4 mg), solvent (0.5 mL) under argon atmosphere in a glovebox. To the resulting mixture were successively added an additive (0 or 0.02 mmol), and enone **4a** (11.5 μL, 0.10 mmol). The vial was capped, taken out of the glovebox, and the mixture was heated at 35 ºC with stirring under argon atmosphere for 48 h. The reaction mixture was directly purified by silica gel column chromatography to afford the desired product **11a**, and the enantiomeric ratio of **11a** was determined by HPLC analysis (Chiralpak AD-H, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm). The results are summarized in Supplementary Figure 2 and 3.

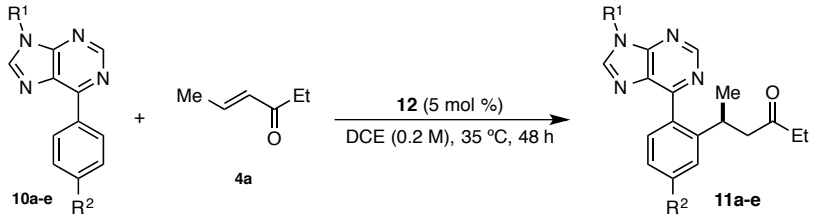
F-2. Synthesis of [Cp*RhL$_N$][(*R*)-SPISate] 12



To a stirred solution of (*R*)-SPISA[18] **13** (152 mg, 0.40 mmol) in CH_2Cl_2/CH_3CN (1:1, 8 mL) was added Ag_2CO_3 (221 mg, 0.80 mmol) at 40 ºC. After stirring for 24 h in dark, the reaction mixture was filtered through a Celite pad, and washed with CH_2Cl_2/CH_3CN (1:1). The filtrate was evaporated in *vacuo* to furnish Ag_2-(*R*)-SPISate (105 mg, 44%) as an orange solid, which was directly used for the next step without purification. To a flame-dried Schlenk flask were added $[Cp^*RhCl_2]_2$ (49 mg, 0.080 mmol), Ag_2-(*R*)-SPISate (105 mg, 0.17 mmol), CH_3CN (0.8 mL) in a glovebox. The flask was taken out of the glovebox, and the mixture was stirred at room temperature and under argon atmosphere. After 24 h, the resulting precipitates were removed by filtration through a Celite pad and washed with CH_3CN. The filtrate was concentrated in *vacuo* to afford [Cp*RhL$_N$][(*R*)-SPISate] **12** (97 mg, 37% as $Cp^*Rh(CH_3CN)_{0.2}(H_2O)_{1.8}$).

Orange solid. **IR** (KBr): ν 3273, 3060, 2934, 2843, 2361, 2332, 2241, 1633, 1455, 1254, 1200, 1152, 1124, 1018, 744, 734, 626, 600, 577 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.60 (s, 15H), 2.04-2.15 (m, 2H), 2.44-2.55 (m, 2H), 2.84-2.95 (m, 2H), 2.93-3.05 (m, 2H), 7.20 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.70 (d, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 9.0, 30.3, 38.3, 63.9, 93.1 (d, $^1J_{CRh}$ = 10.5 Hz), 126.0, 126.2, 127.2, 140.2, 145.4, 146.4. **Anal.** Calcd for $C_{24.7}H_{33.2}N_{0.2}O_{7.8}RhS_2$ ($Cp^*Rh(CH_3CN)_{0.2}(H_2O)_{1.8}$): C, 50.08; H, 5.09; N, 0.43. Found: C, 50.02; H, 4.68; N, 0.79.

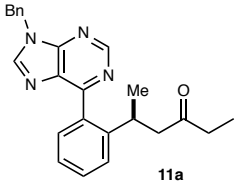
F-3. General procedure of asymmetric conjugate addition of 6-arylpurines (Table 4)



To a dried screw-capped vial were added purine derivative **10** (0.12 mmol), **12** (3.3 mg, 5 μmol, 5 mol %) and DCE (0.5 mL) under argon atmosphere in a glovebox. To the resulting mixture was added enone **4a** (11.5 μL, 0.10 mmol). The vial was capped, taken out of the glovebox, and the mixture was heated at 35 ºC with stirring under argon atmosphere. After 48 h, the reaction mixture was directly purified by silica gel column chromatography to afford the desired product **11**.

F-4. Characterization of products 11

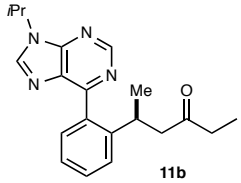
(*S*)-5-(2-(9-benzyl-9*H*-purin-6-yl)phenyl)hexan-3-one (11a)



11a

Following the general procedure (**F-3.**), **10a** (34.4 mg, 0.12 mmol), enone **4a**, catalyst **12** and DCE (0.5 mL) were stirred at 35 ºC for 48 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 3:2 to 2:3) to afford **11a** (25.2 mg, 94% w/w purity, 62% yield, 87:13 er) with a small amount of byproduct resulted from the second C-H bond addition, which was further purified by GPC to give a pure analytical sample. Yellow oil. **TLC**: R_f = 0.35 (hexane/AcOEt = 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 2.26 (q, *J* = 7.3 Hz, 2H), 2.58 (dd, *J* = 16.0, 9.2 Hz, 1H), 2.93 (dd, *J* = 16.0, 4.6 Hz, 1H), 3.58-3.67 (m, 1H), 5.48 (d, *J* = 15.5 Hz, 1H), 5.52 (d, *J* = 15.5 Hz, 1H), 7.32-7.42 (m, 6H), 7.43-7.49 (m, 2H), 7.60 (d, *J* = 7.4 Hz, 1H), 8.03 (s, 1H), 9.07 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 21.4, 31.0, 36.0, 47.4, 51.1, 126.0, 126.6, 127.9, 128.6, 129.2, 129.9, 130.8, 132.4, 134.0, 135.0, 144.4, 145.4, 151.9, 152.3, 158.8, 210.4. **HRMS** (ESI): *m/z* calcd for $C_{24}H_{25}ON_4^+$ [M+H$^+$]: 385.2023, found: 385.2027. **$[\alpha]_D^{22}$** = 13.6 (c = 0.90, $CHCl_3$). **HPLC**: 87:13 er. (Chiralpak AD-H, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 12.2 min, t_R (minor) = 13.8 min).

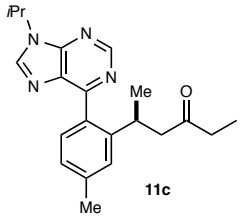
(*S*)-5-(2-(9-isopropyl-9*H*-purin-6-yl)phenyl)hexan-3-one (11b)



11b

Following the general procedure (**F-3.**), **10b** (28.6 mg, 0.12 mmol), enone **4a**, catalyst **12** and DCE (0.5 mL) were stirred at 35 ºC for 48 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 1:1 to 1:2) to afford **11b** (28.4 mg, 85% yield, 89:11 er). Colorless oil. **TLC**: R_f = 0.22 (hexane/AcOEt = 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.4 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.70 (d, *J* = 6.9 Hz, 6H), 2.28 (q, *J* = 7.4 Hz, 2H), 2.59 (dd, *J* = 16.0, 9.7 Hz, 1H), 2.93 (dd, *J* = 16.0, 4.0 Hz, 1H), 3.57-3.65 (m, 1H), 4.99 (sept, *J* = 6.9 Hz, 1H), 7.35 (ddd, *J* = 7.4, 6.3, 2.3 Hz, 1H), 7.44-7.48 (m, 2H), 7.59 (d, *J* =7.4 Hz, 1H), 8.12 (s, 1H), 9.02 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 21.4, 22.5, 22.5, 31.0, 36.0, 47.4, 51.1, 126.0, 126.5, 129.9, 130.7, 132.9, 134.1, 142.4, 145.4, 151.5, 151.6, 158.6, 210.5. **HRMS** (ESI): *m/z* calcd for $C_{20}H_{25}ON_4^+$ [M+H$^+$]: 337.2023, found: 337.2025. **$[\alpha]_D^{22}$** = 21.3 (c = 0.85, $CHCl_3$). **HPLC**: 89:11 er. (Chiralpak AD-H, hexane/*i*-PrOH = 19:1, 1.0 mL/min, 254 nm, t_R (major) = 11.8 min, t_R (minor) = 16.0 min).

(*S*)-5-(2-(9-isopropyl-9*H*-purin-6-yl)-5-methylphenyl)hexan-3-one (11c)

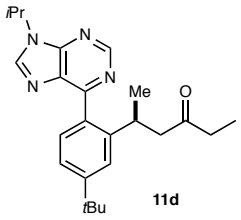


11c

Following the general procedure (**F-3.**), **10c** (30.3 mg, 0.12 mmol), enone **4a**, catalyst **12** and DCE (0.5 mL) were stirred at 35 ºC for 48 h, and the mixture was purified by silica gel column chromatography (toluene/AcOEt = 4:1 to 2:1) to afford **11c** (21.6 mg, 62% yield, 90:10 er). Colorless oil. **TLC**: R_f = 0.28 (hexane/AcOEt =

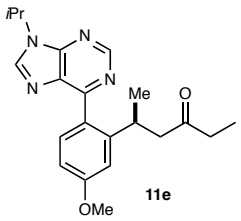
1:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.70 (d, *J* = 7.0 Hz, 6 H), 2.26-2.31 (m, 1H), 2.42 (s, 3H), 2.58 (dd, *J* = 15.9, 9.7 Hz, 1H), 2.93 (dd, *J* = 15.9, 4.3 Hz, 1H), 3.60-3.68 (m, 1H), 4.99 (sept, *J* = 7.0 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.25 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 8.11 (s, 1H), 9.02 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.9, 21.6, 21.7, 22.7, 22.7, 31.0, 36.2, 47.6, 51.3, 127.0, 127.4, 131.0, 133.0, 140.0, 142.4, 145.5, 151.6, 151.6, 158.7, 210.8. (One of the aromatic peaks was missing probably due to overlapping.) **HRMS** (ESI): *m/z* calcd for $C_{21}H_{27}ON_4^+$ [M+H$^+$]: 351.2179, found: 351.2181. **$[\alpha]_D^{18}$** = 24.8 (c = 1.08, $CHCl_3$). **HPLC**: 90:10 er (Chiralpak IA, hexane/*i*-PrOH = 19:1, 1.0 mL/min, 254 nm, t_R (major) = 10.8 min, t_R (minor) = 15.1 min).

(*S*)-5-(5-(*tert*-butyl)-2-(9-isopropyl-9*H*-purin-6-yl)phenyl)hexan-3-one (11d)



Following the general procedure (**F-3**)., **10d** (35.3 mg, 0.12 mmol), enone **4a**, catalyst **12** and DCE (0.5 mL) were stirred at 35 ºC for 48 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 7:3 to 2:3) to afford **11d** (28.7 mg, 73% yield, 91:9 er). Colorless oil. **TLC**: R_f = 0.38 (hexane/AcOEt = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.37 (s, 9H), 1.70 (d, *J* = 6.7 Hz, 6H), 2.29 (q, *J* = 7.3 Hz, 2H), 2.58 (dd, *J* = 15.7, 9.9 Hz, 1H), 2.95 (dd, *J* = 15.7, 4.5 Hz, 1H), 3.63-3.72 (m, 1H), 5.00 (sept, *J* = 6.7 Hz, 1H), 7.38 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 8.12 (s, 1H), 9.02 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.7, 21.4, 22.5, 22.5, 31.2 (4C), 34.9, 35.9, 47.4, 51.3, 123.2, 123.4, 130.6, 131.0, 132.8, 142.2, 144.9, 151.4, 151.5, 152.8, 158.7, 210.7. **HRMS** (ESI): *m/z* calcd for $C_{24}H_{33}ON_4^+$ [M+H$^+$]: 393.2649, found: 393.2649. **$[\alpha]_D^{22}$** = 22.0 (c = 1.27, $CHCl_3$). **HPLC**: 91:9 er (Chiralpak IA, hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 5.1 min, t_R (minor) = 5.8 min).

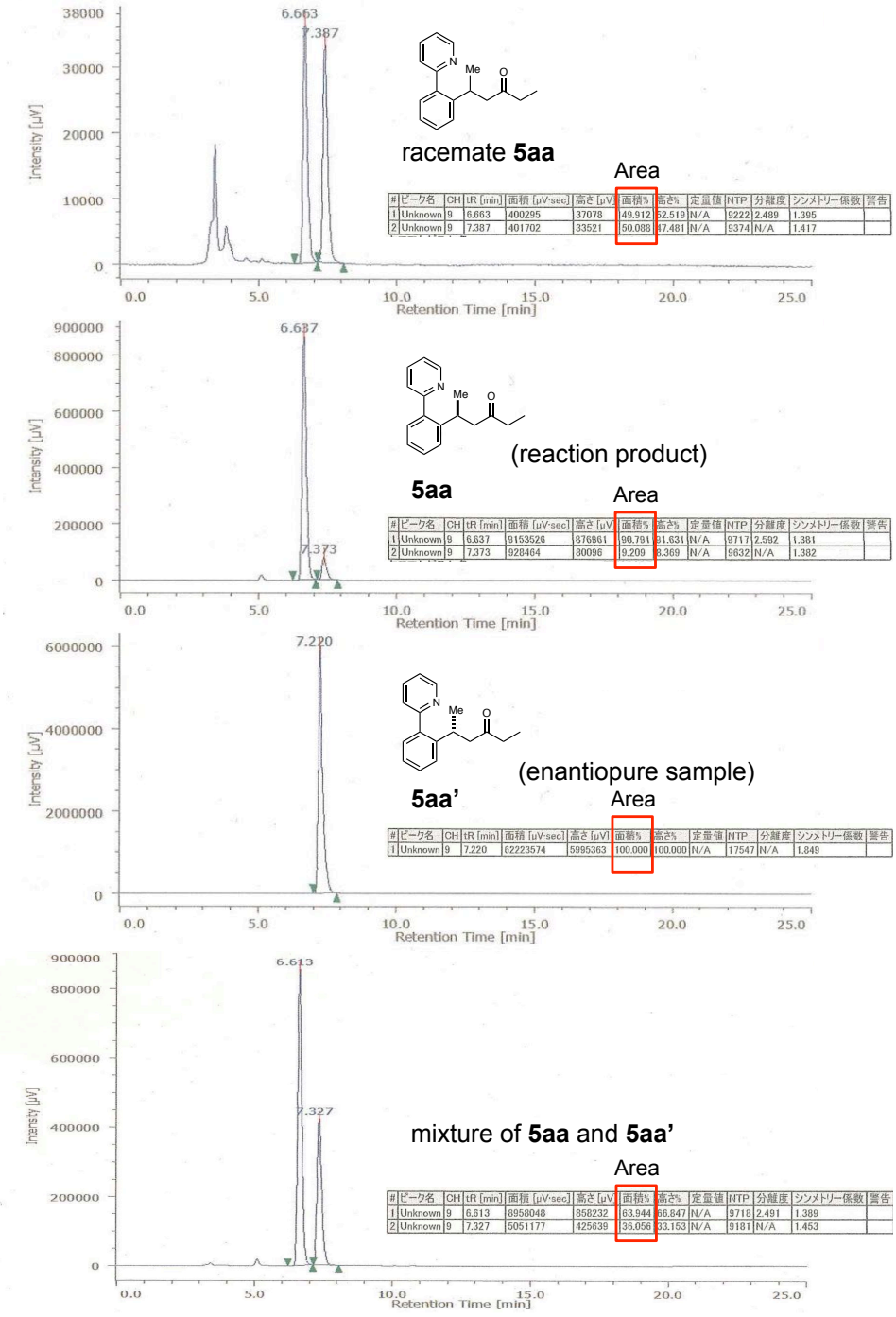
(*S*)-5-(2-(9-isopropyl-9*H*-purin-6-yl)-5-methoxyphenyl)hexan-3-one (11e)



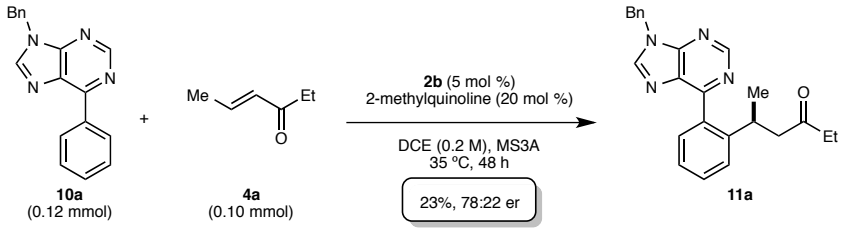
Following the general procedure (**F-3.**), **10e** (31.2 mg, 0.12 mmol), enone **4a**, catalyst **12** and DCE (0.5 mL) were stirred at 35 ºC for 48 h, and the mixture was purified by silica gel column chromatography (hexane/AcOEt = 1:1 to 3:8) to afford **11e** (16.0 mg, 43% yield, 91:9 er). Colorless oil. **TLC**: R_f = 0.16 (hexane/AcOEt = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.70 (d, *J* = 6.7 Hz, 6H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.57 (dd, *J* = 16.0, 9.4 Hz, 1H), 2.95 (dd, *J* = 16.0, 4.5 Hz, 1H), 3.72-3.81 (m, 1H), 4.99 (sept, *J* = 6.7 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 8.12 (s, 1H), 9.00 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 7.8, 21.4, 22.5, 22.6, 31.0, 36.0, 47.4, 51.2, 55.3, 110.8, 113.1, 132.8, 142.1, 147.7, 151.4, 151.6, 158.3, 160.9, 210.5. (Two aromatic peaks were missing probably due to overlapping.) **HRMS** (ESI): *m/z* calcd for $C_{21}H_{27}O_2N_4^+$ [M+H$^+$]: 367.2129, found: 367.2128. **$[\alpha]_D^{22}$** = 23.4 (c = 0.49, $CHCl_3$). **HPLC**: 91:9 er (Chiralpak ID,

hexane/*i*-PrOH = 9:1, 1.0 mL/min, 254 nm, t_R (major) = 23.4 min, t_R (minor) = 29.3 min).

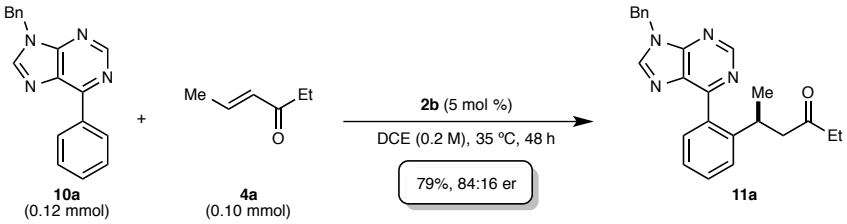
2. Supplementary Figures



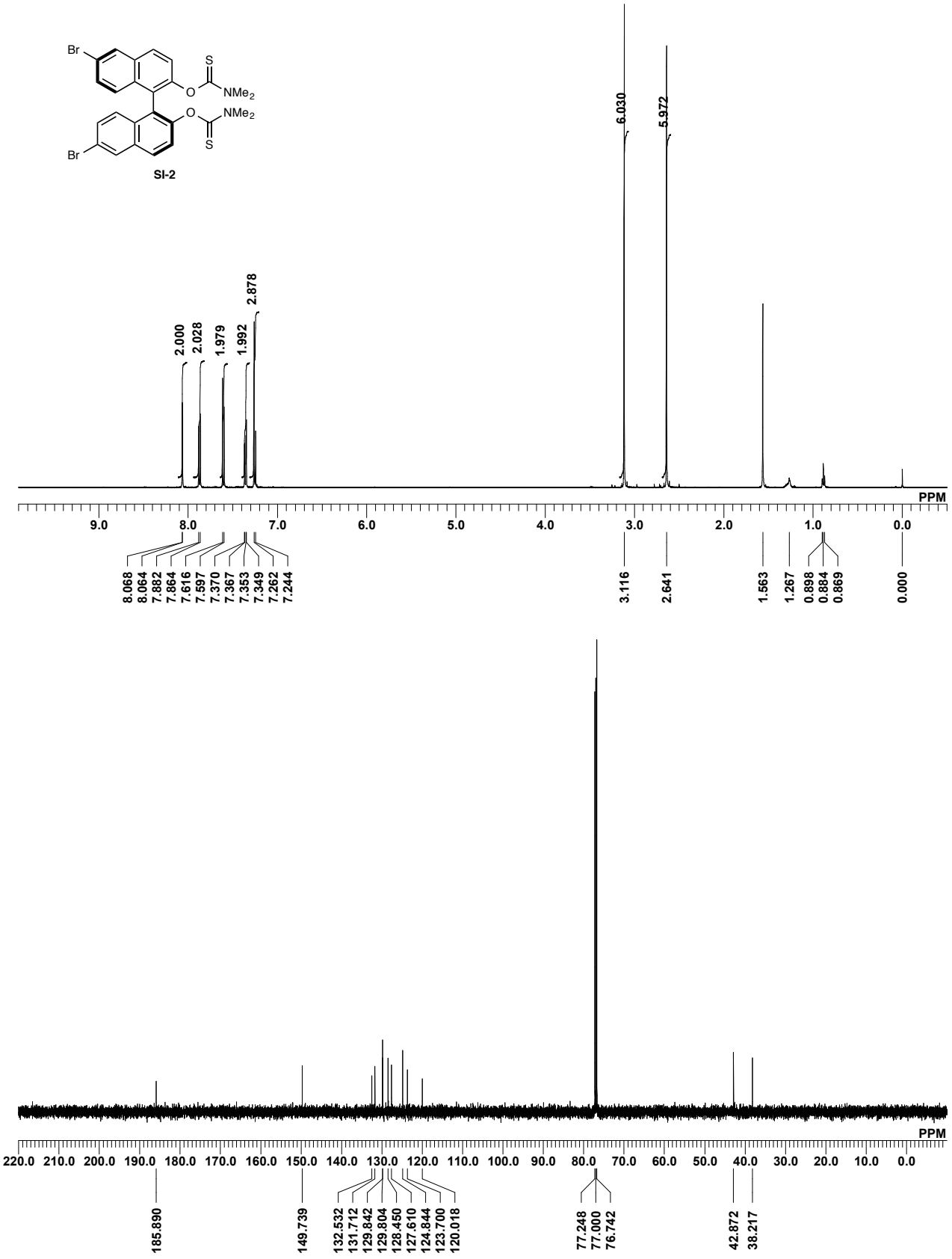
Supplementary Figure 1. Comparison of chiral HPLC analysis of **5aa** and **5aa'.**



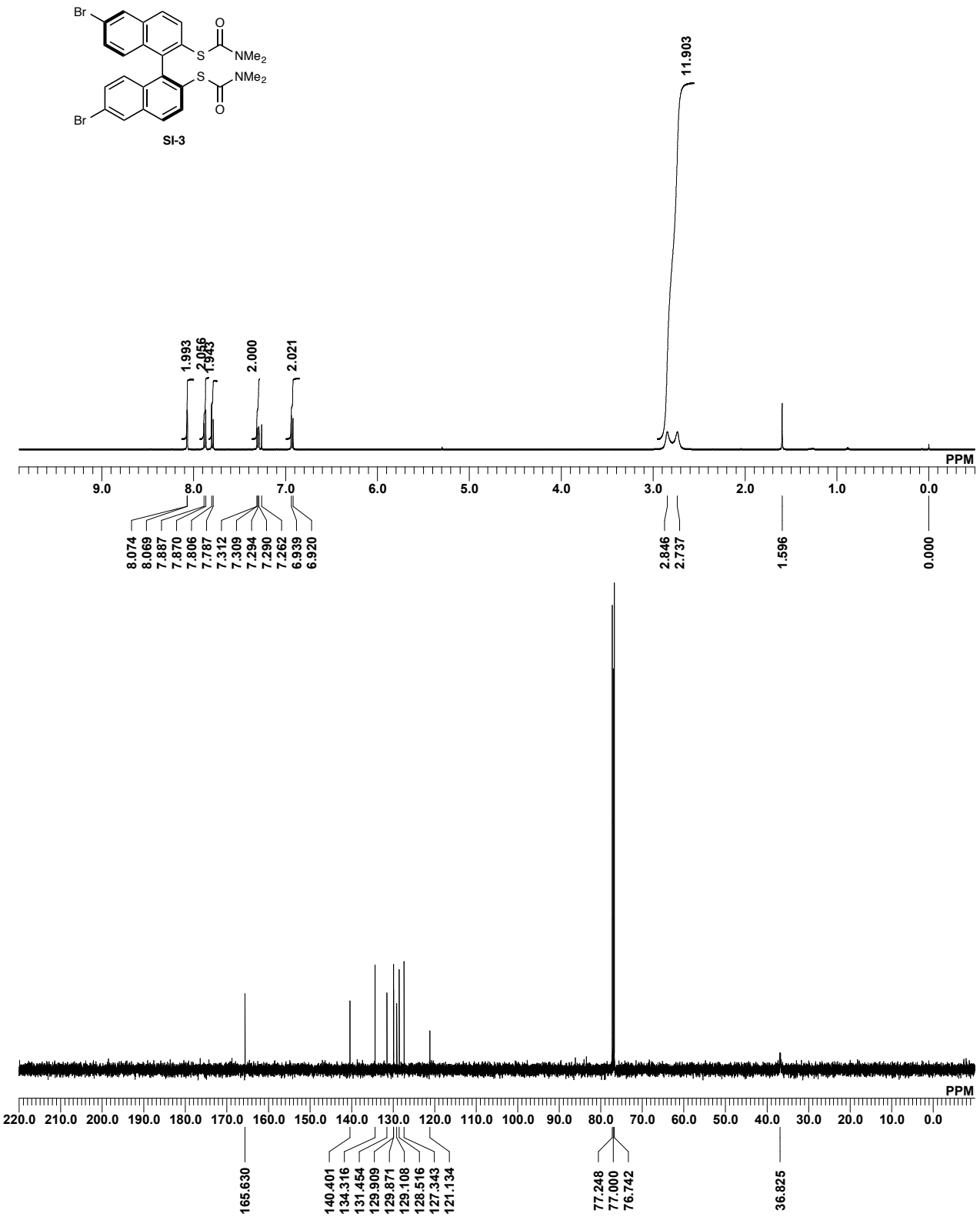
Supplementary Figure 2. Conjugate addition of **10a** under the optimized conditions for 2-phenylpyridines.



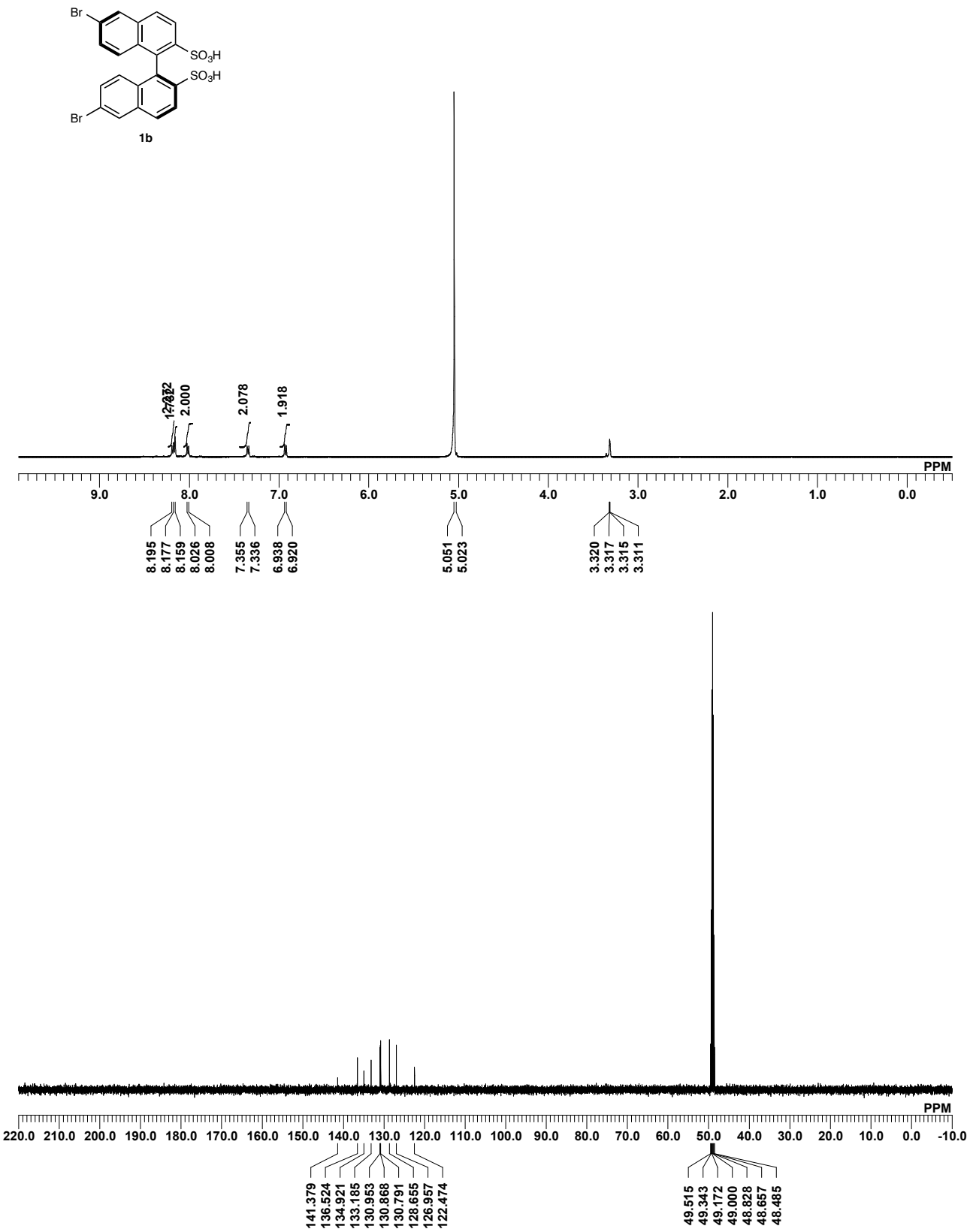
Supplementary Figure 3. Conjugate addition of **10a** without any additives.



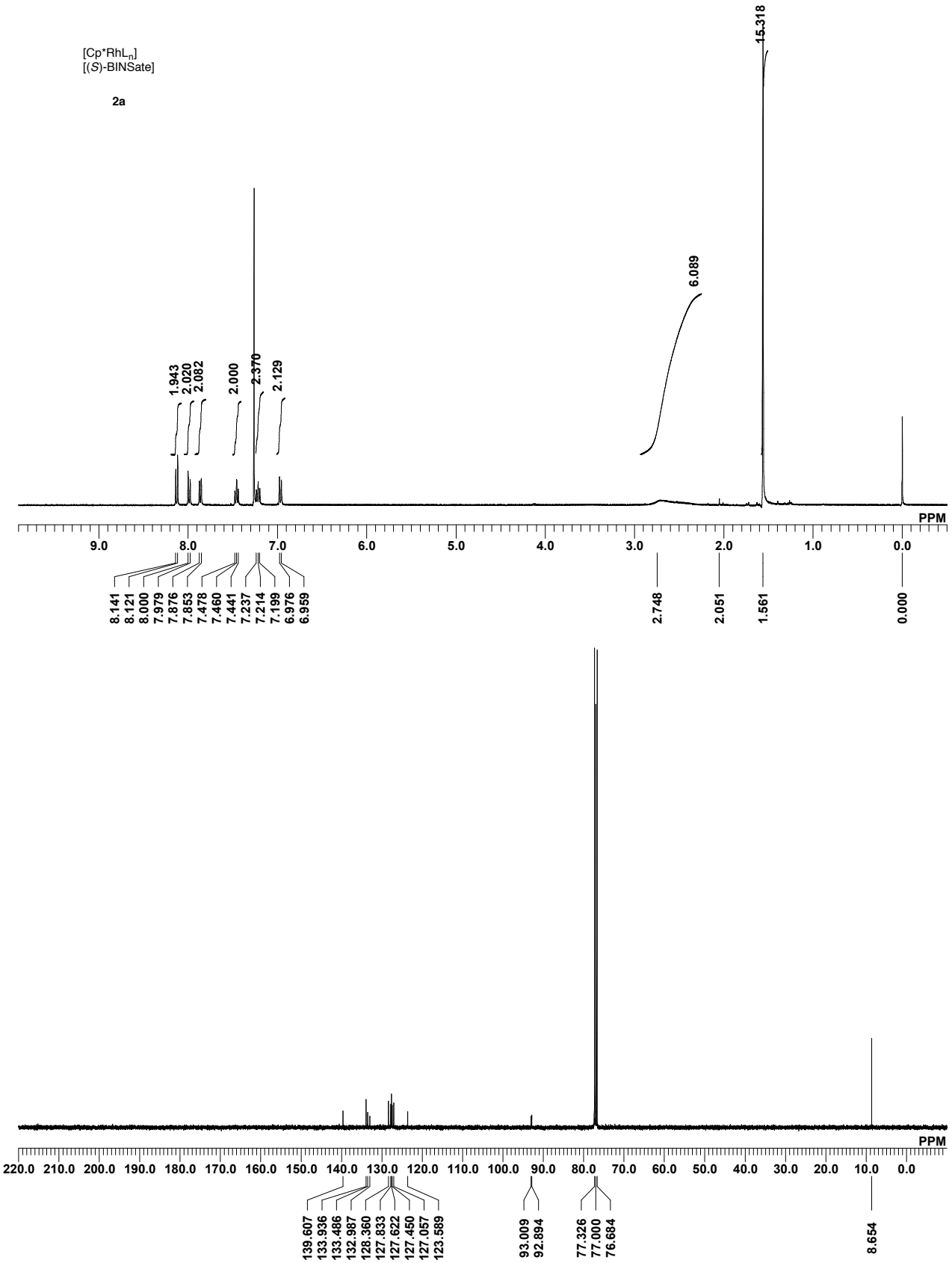
Supplementary Figure 4. NMR spectra of **SI-2.**



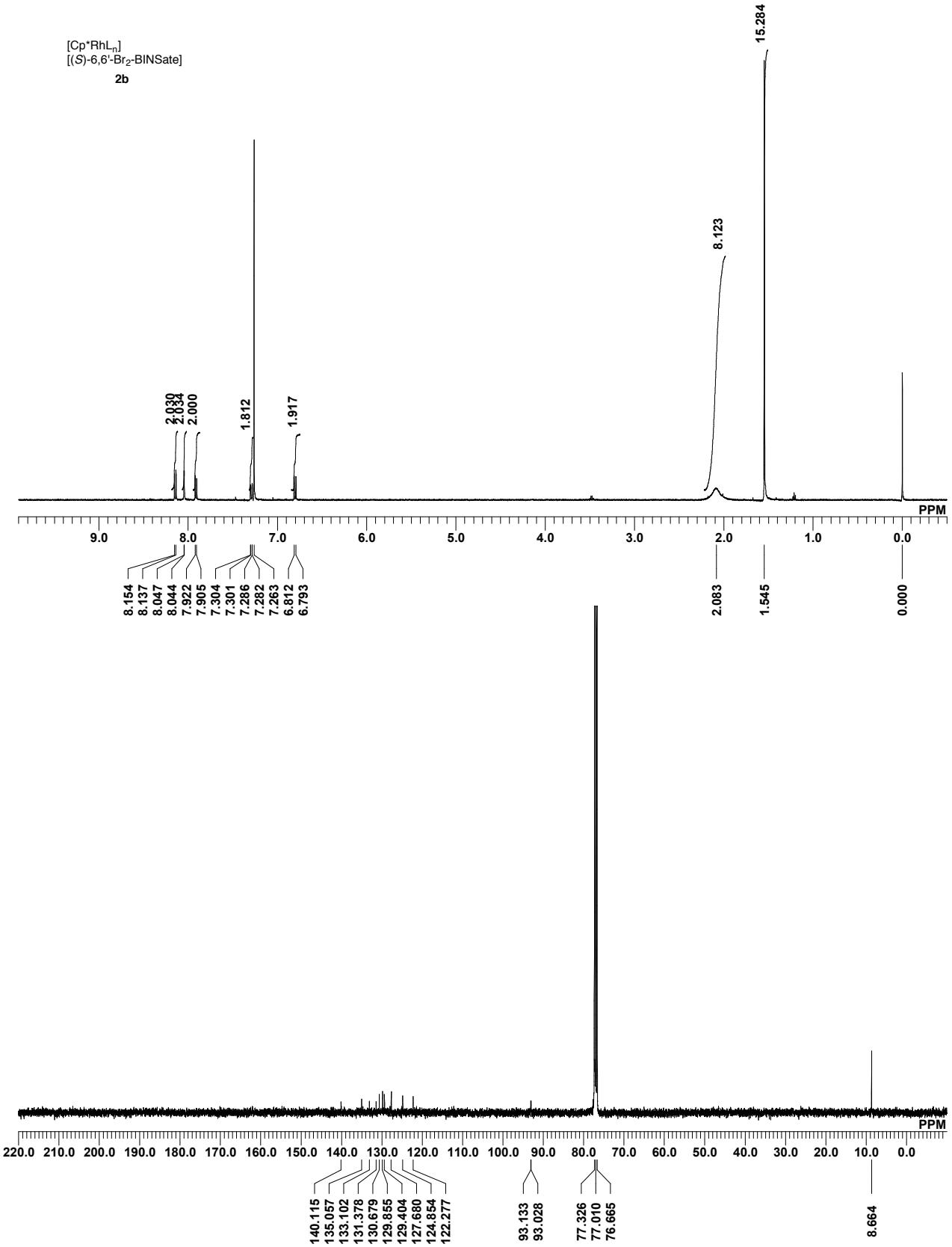
Supplementary Figure 5. NMR spectra of **SI-3.**



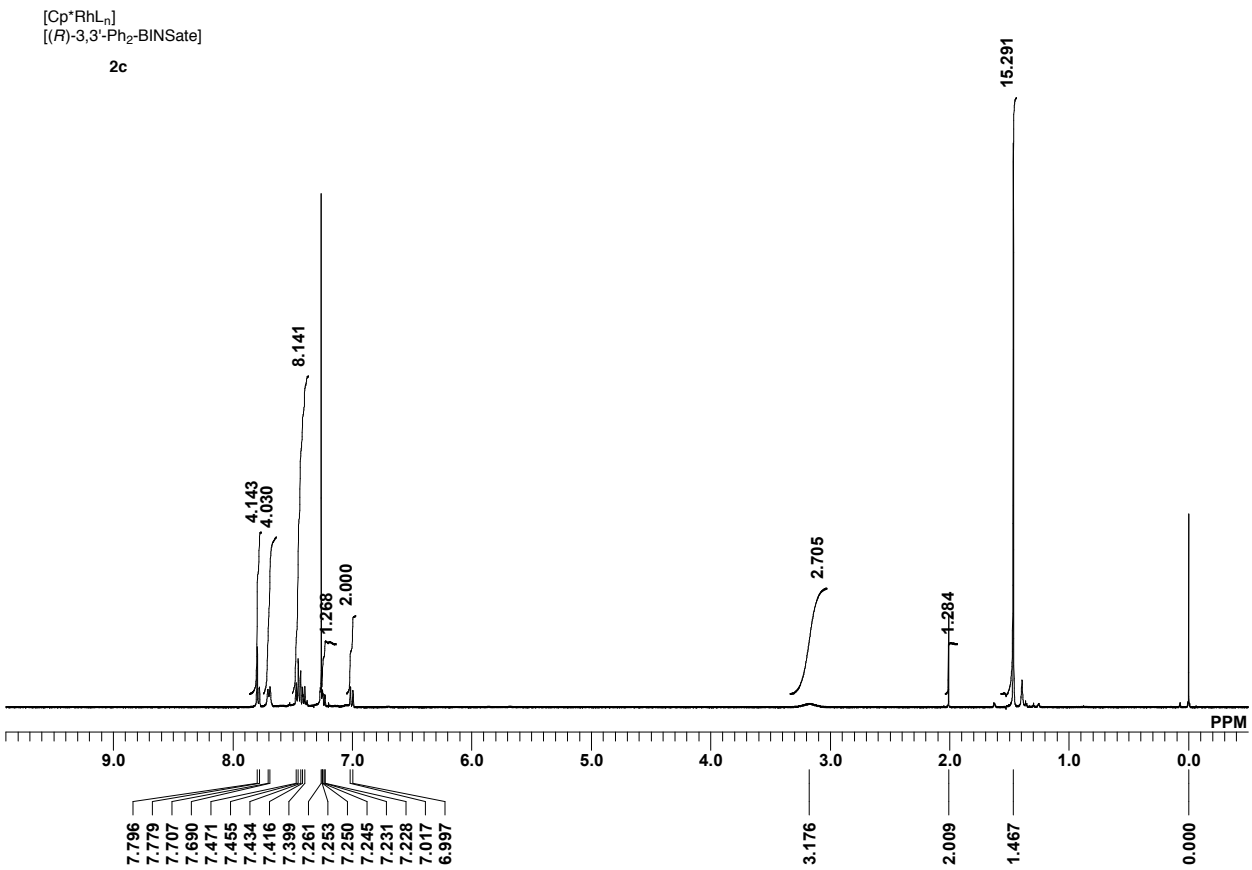
Supplementary Figure 6. NMR spectra of **1b.**



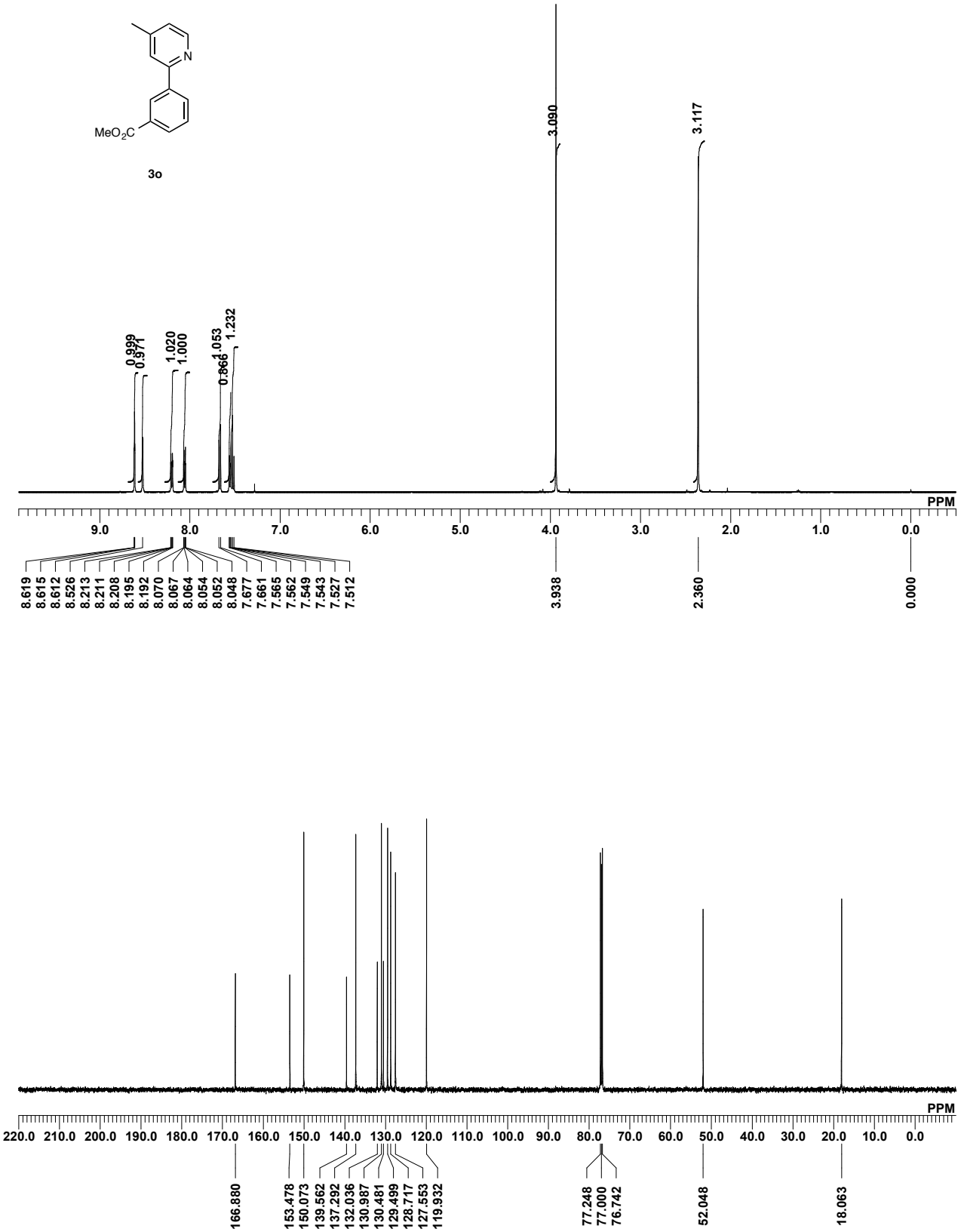
Supplementary Figure 7. NMR spectra of **[Cp*RhL$_N$][(*S*)-BINSate] 2a**.



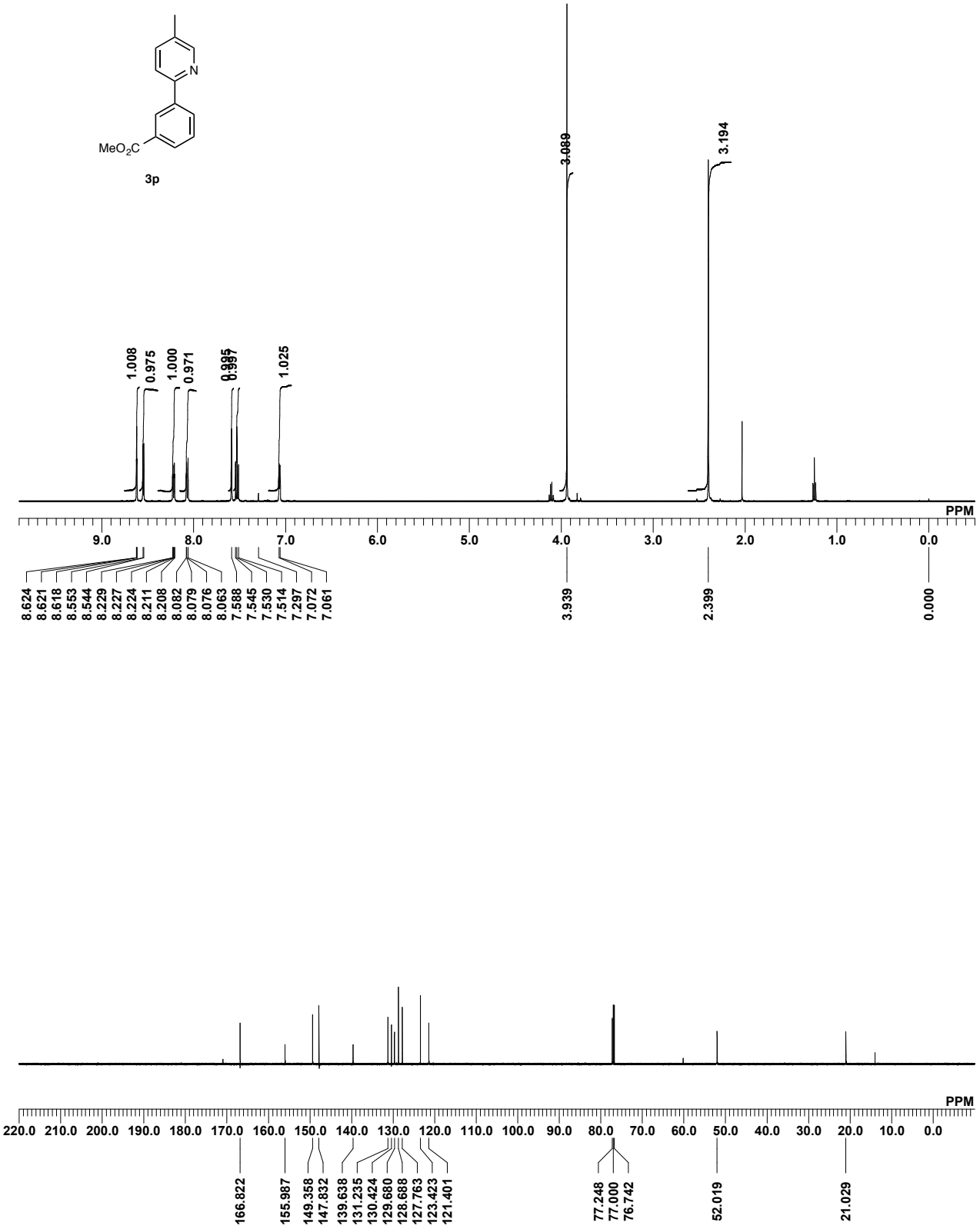
Supplementary Figure 8. NMR spectra of **[Cp*RhL$_N$][(*S*)-6,6'-Br$_2$-BINSate] 2b**.



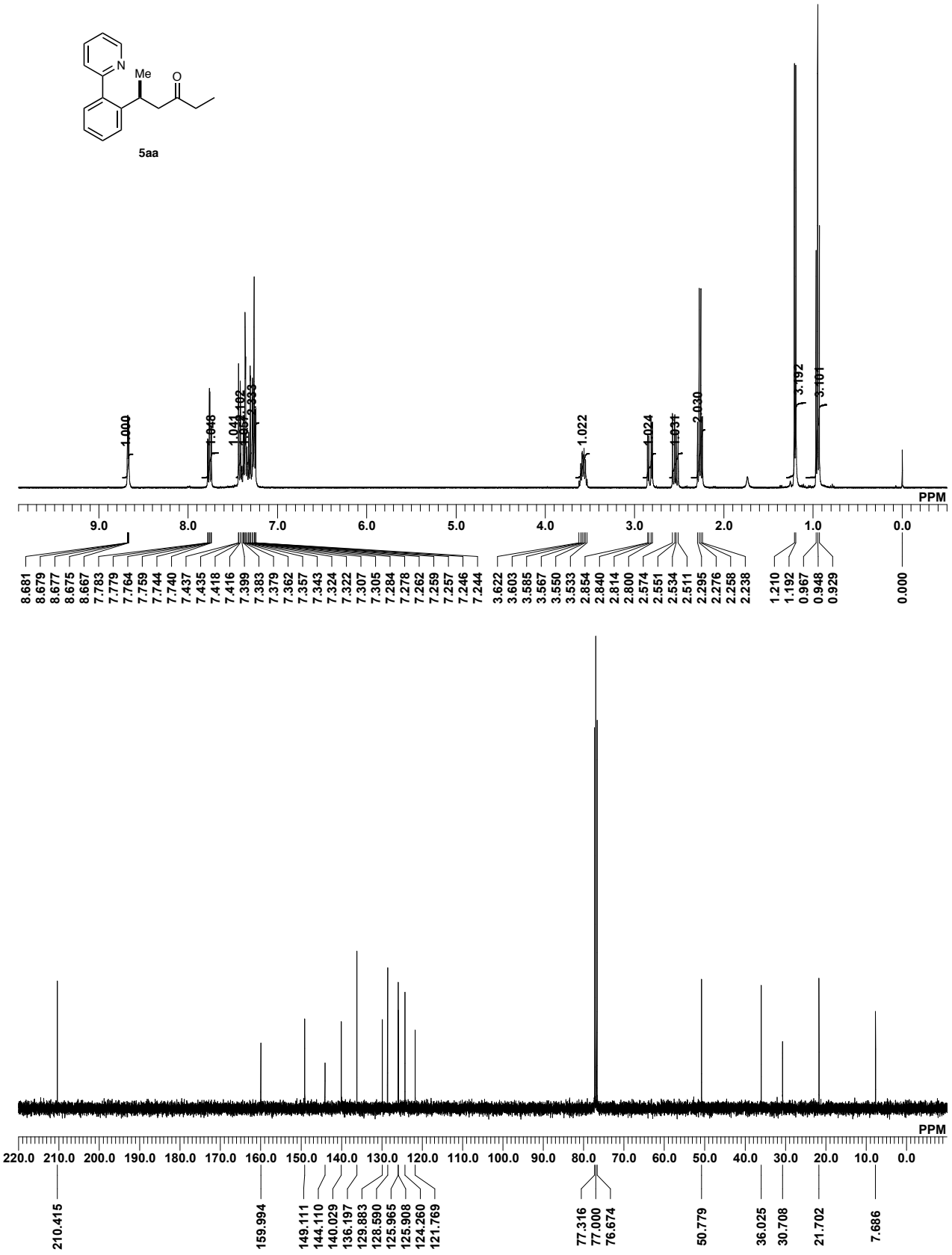
Supplementary Figure 9. 1H NMR spectrum of **[Cp*RhL$_N$][(*R*)-3,3'-Ph$_2$-BINSate] 2c**.



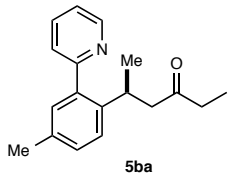
Supplementary Figure 10. NMR spectra of **3o**.



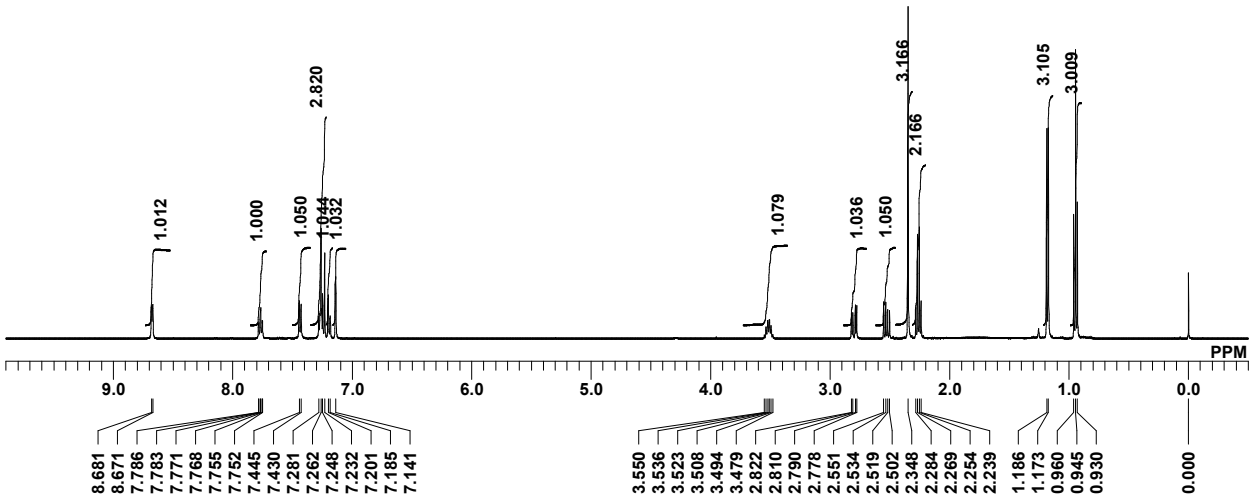
Supplementary Figure 11. NMR spectra of **3p**.

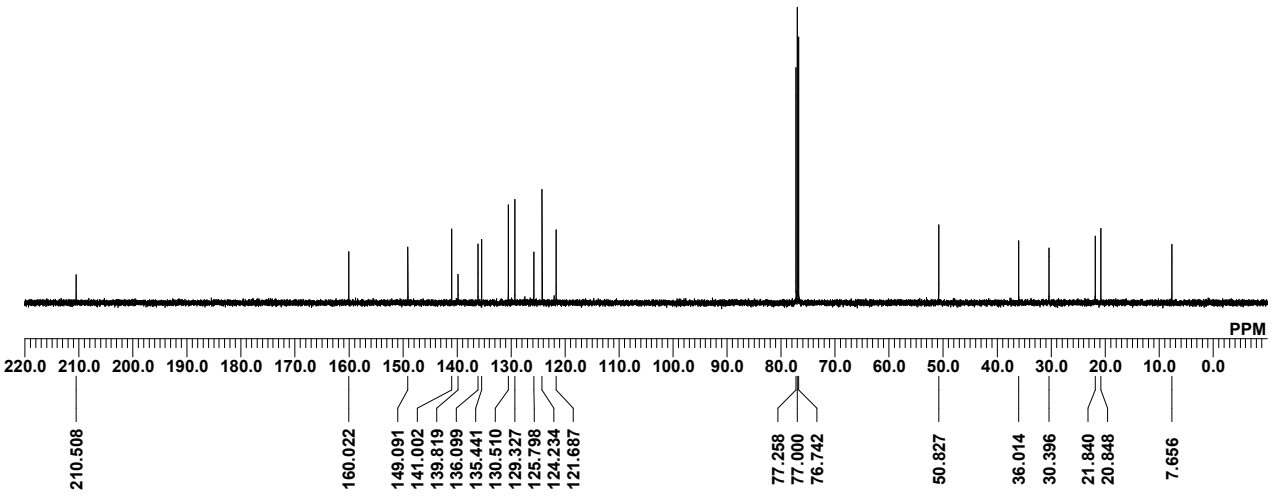


Supplementary Figure 12. NMR spectra of **5aa**.

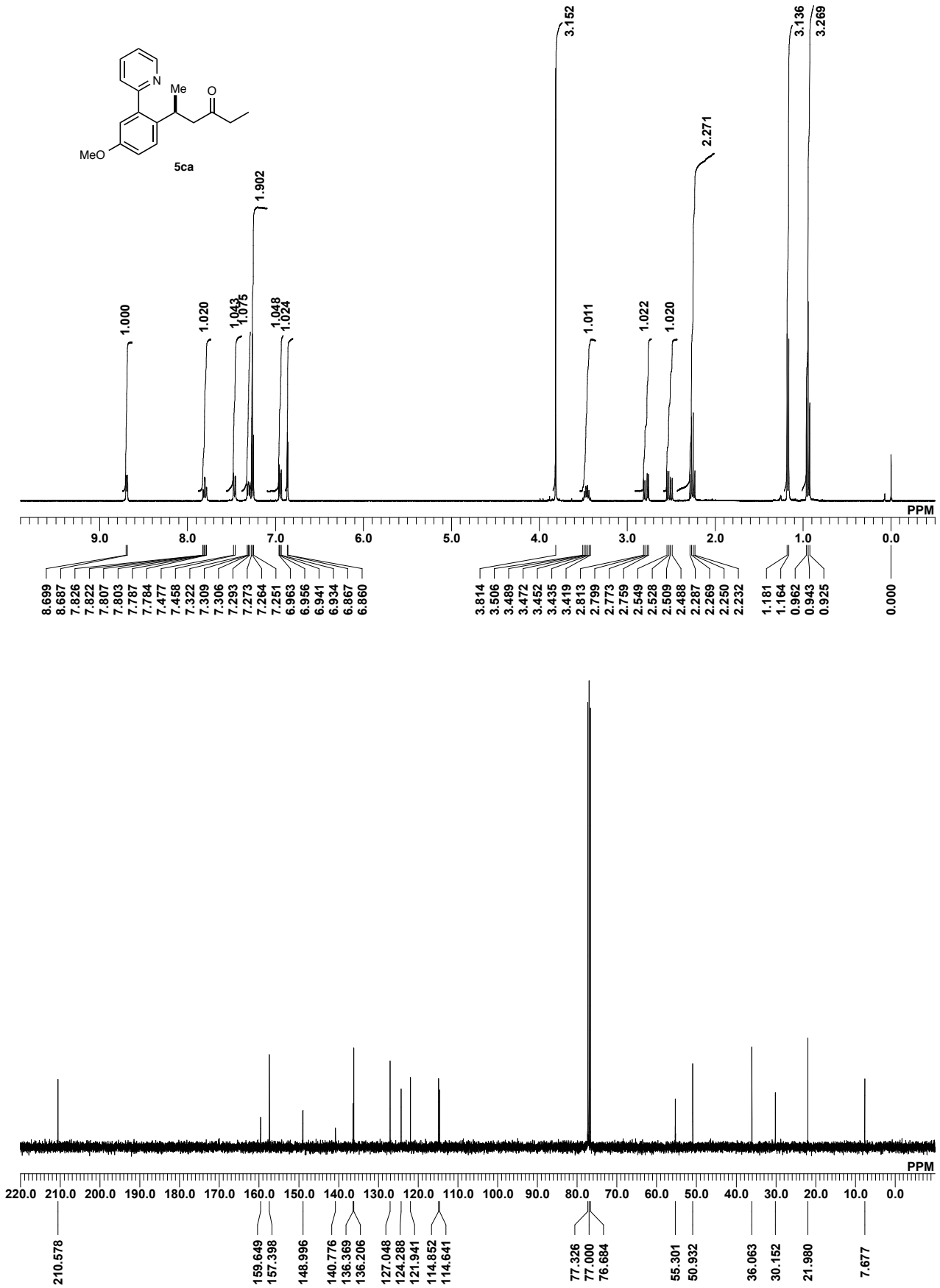


5ba

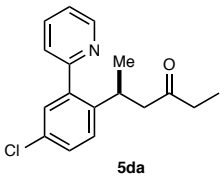




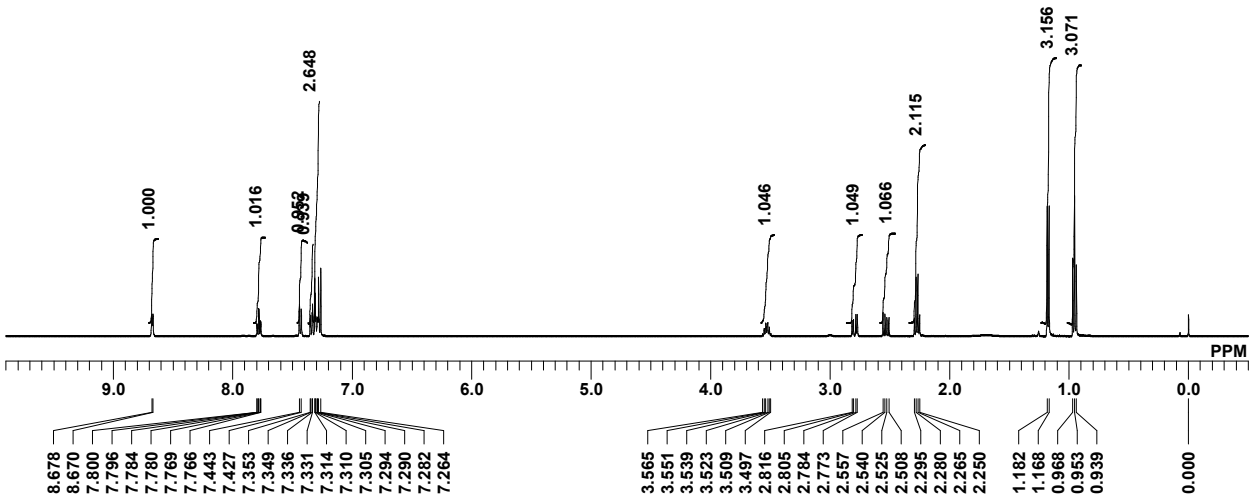
Supplementary Figure 13. NMR spectra of **5ba**.

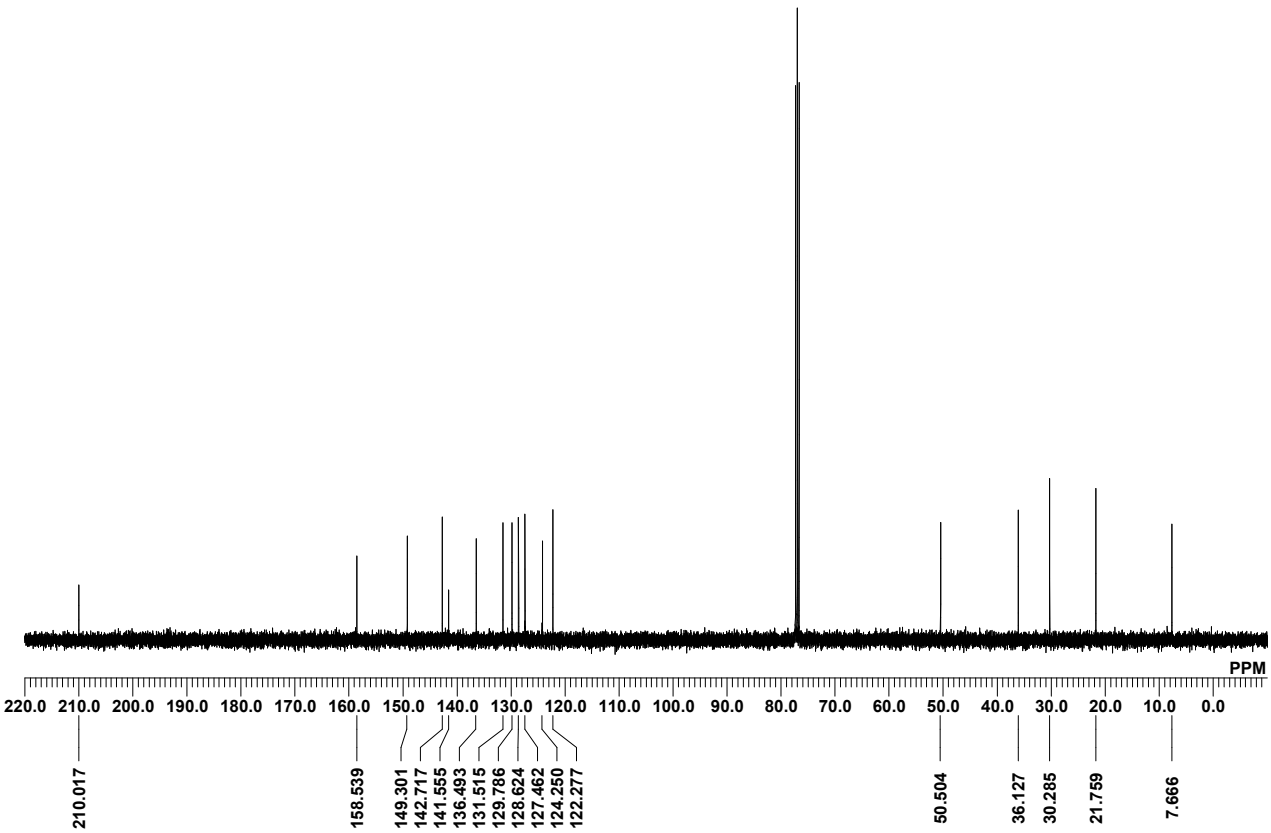


Supplementary Figure 14. NMR spectra of **5ca**.

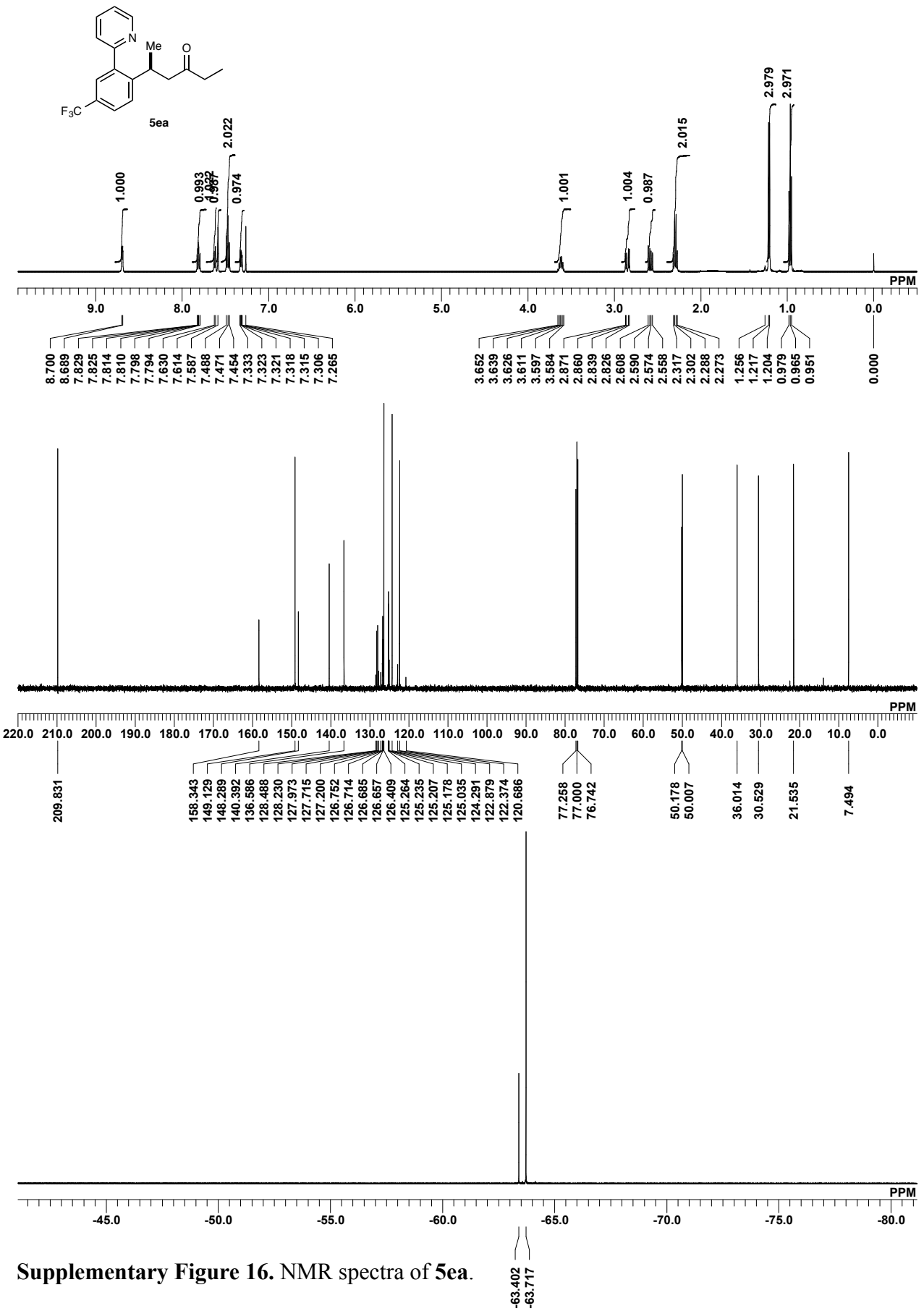


5da

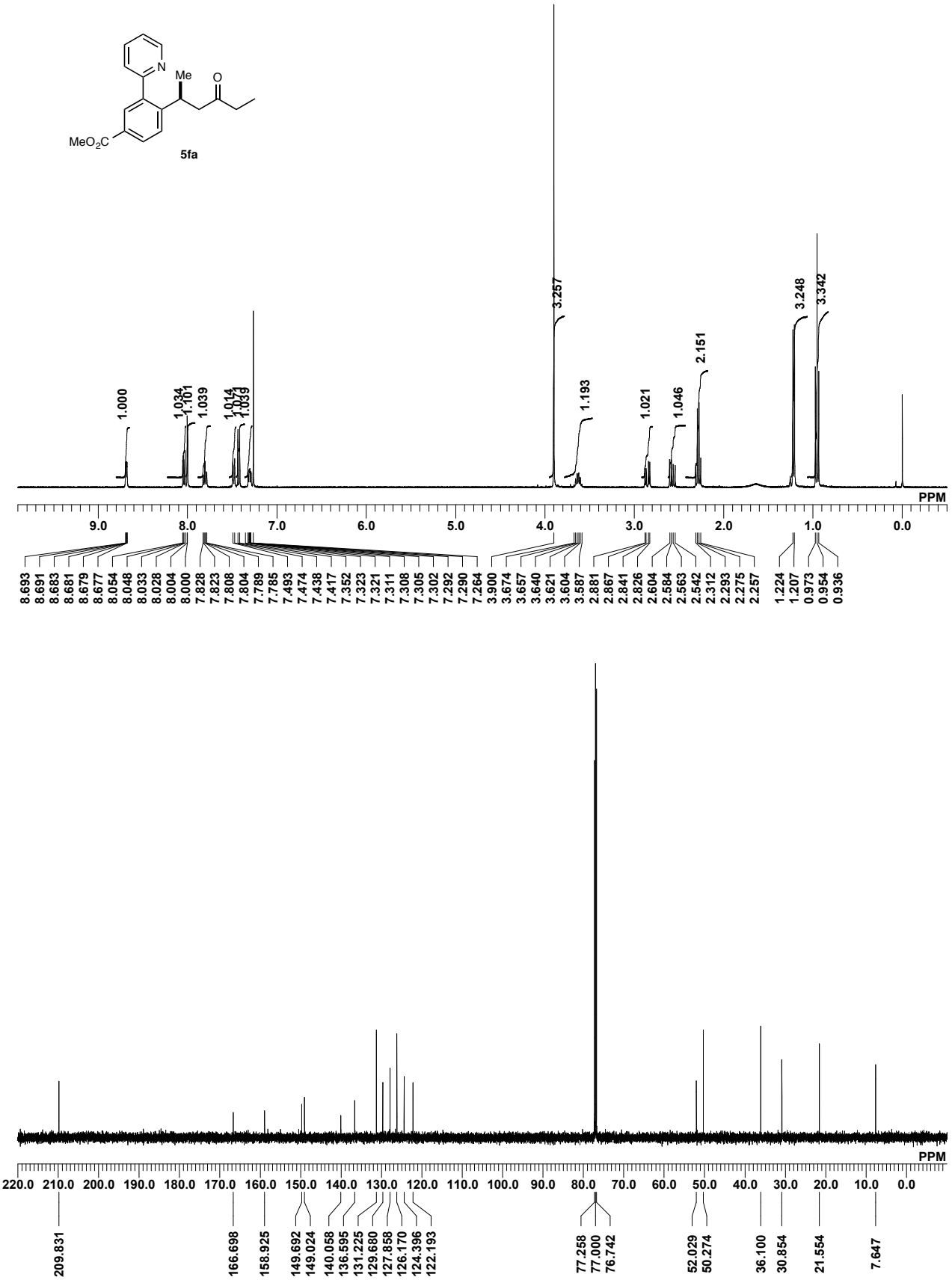




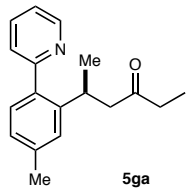
Supplementary Figure 15. NMR spectra of **5da**.

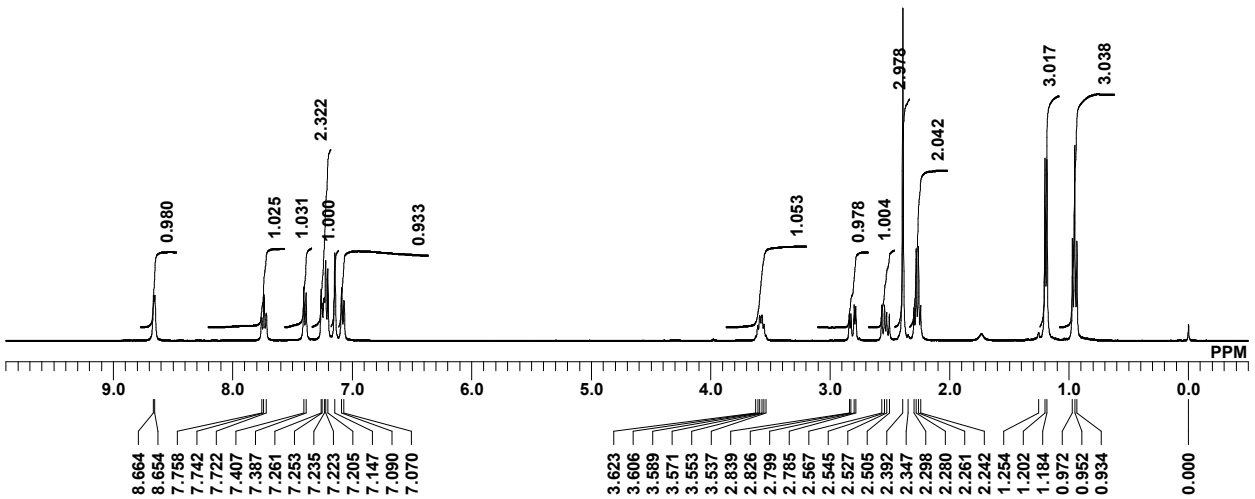


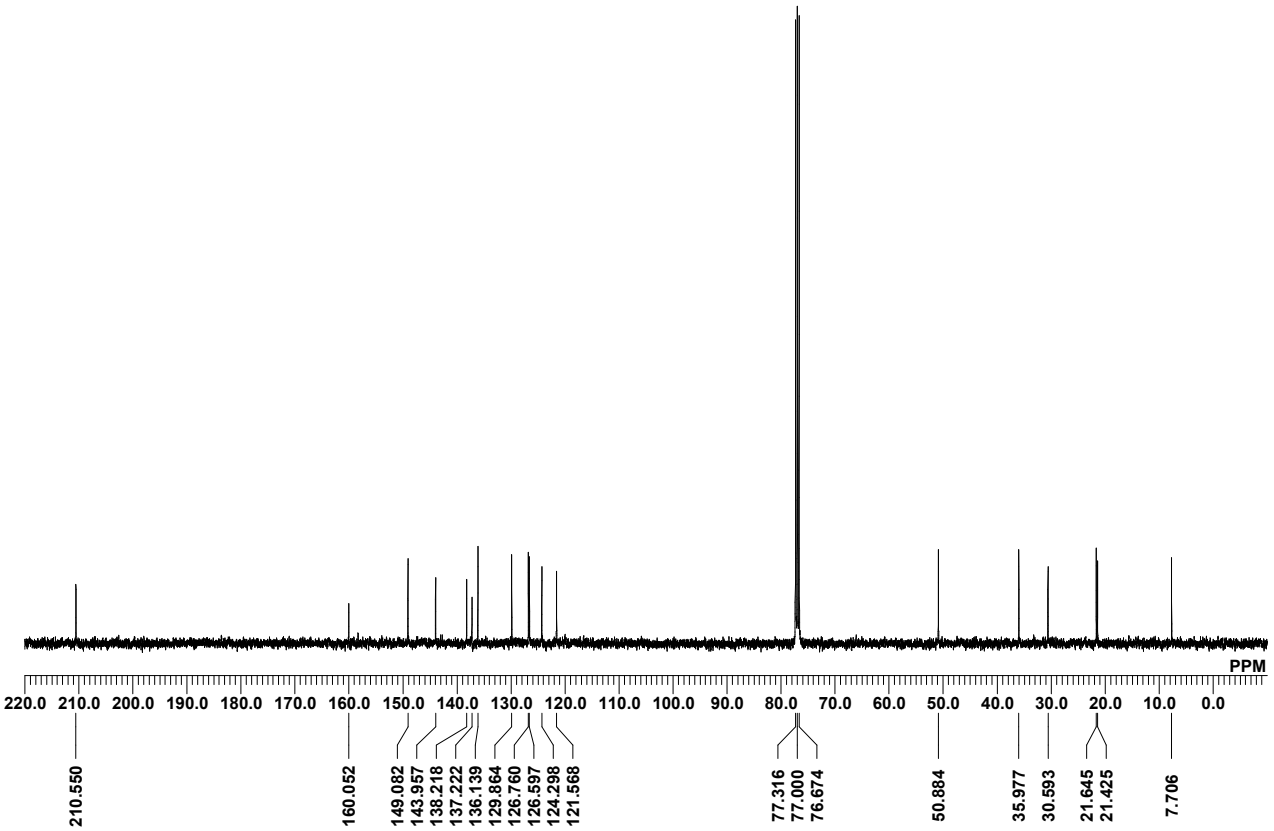
Supplementary Figure 16. NMR spectra of **5ea**.



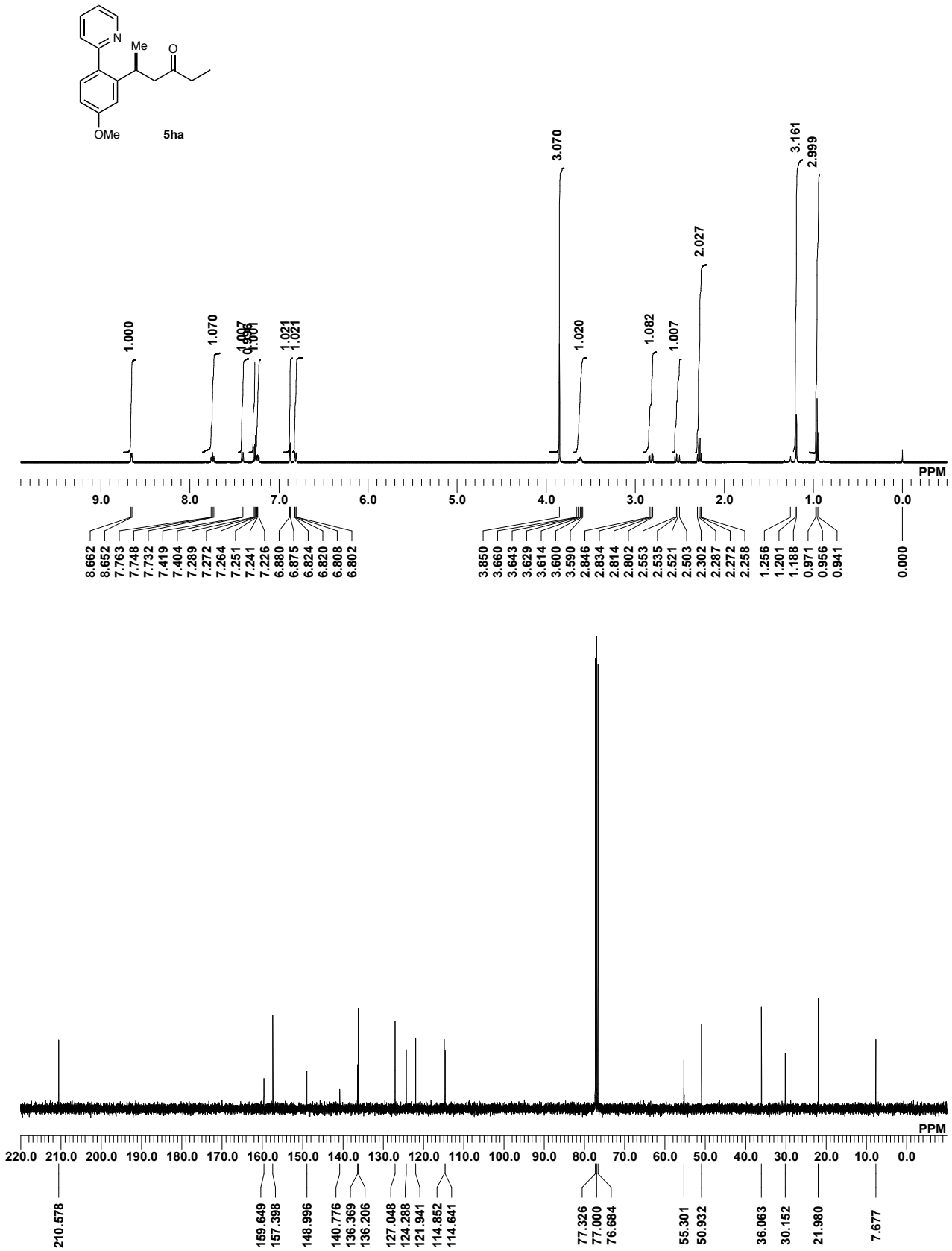
Supplementary Figure 17. NMR spectra of **5fa**.



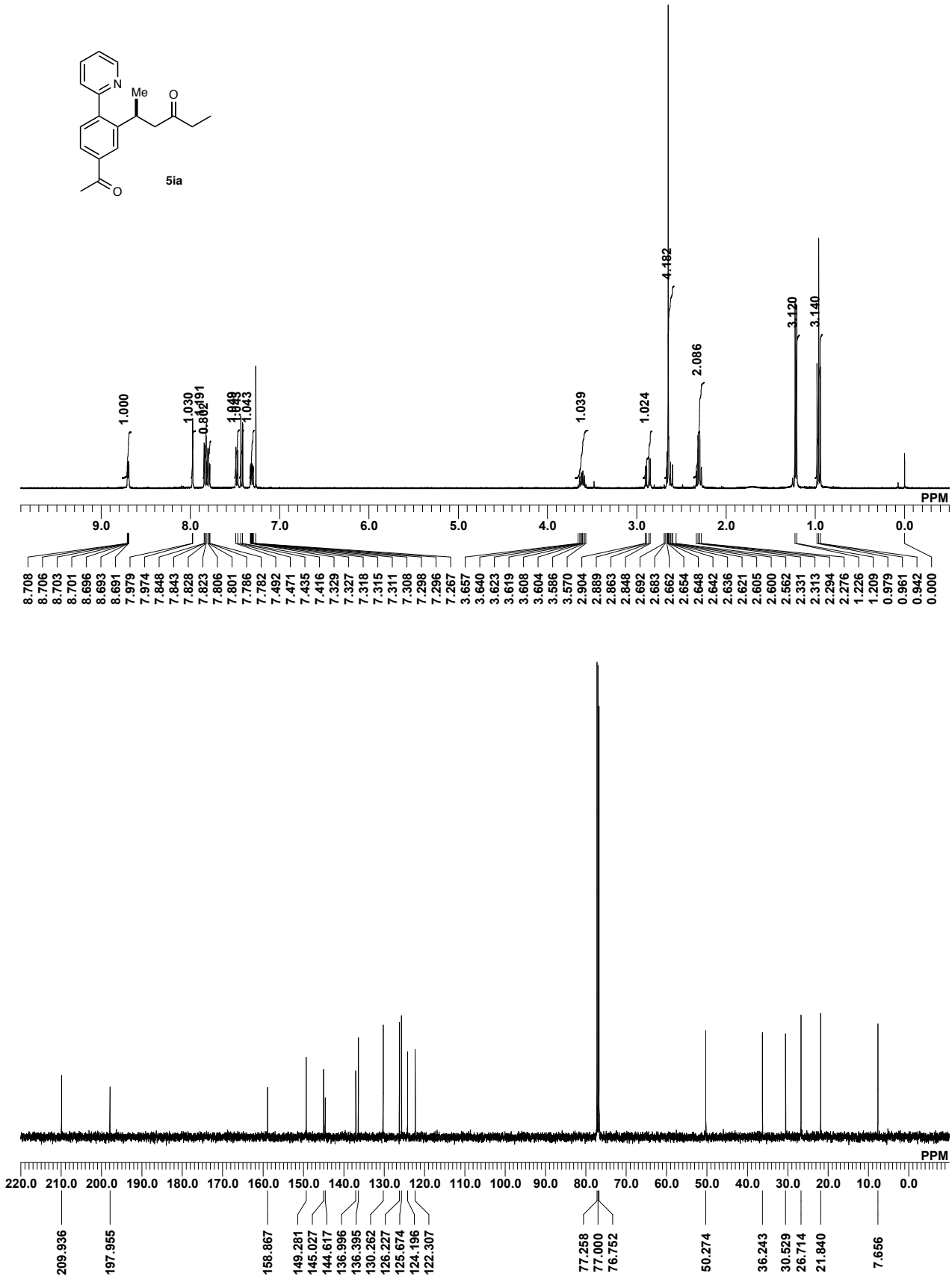




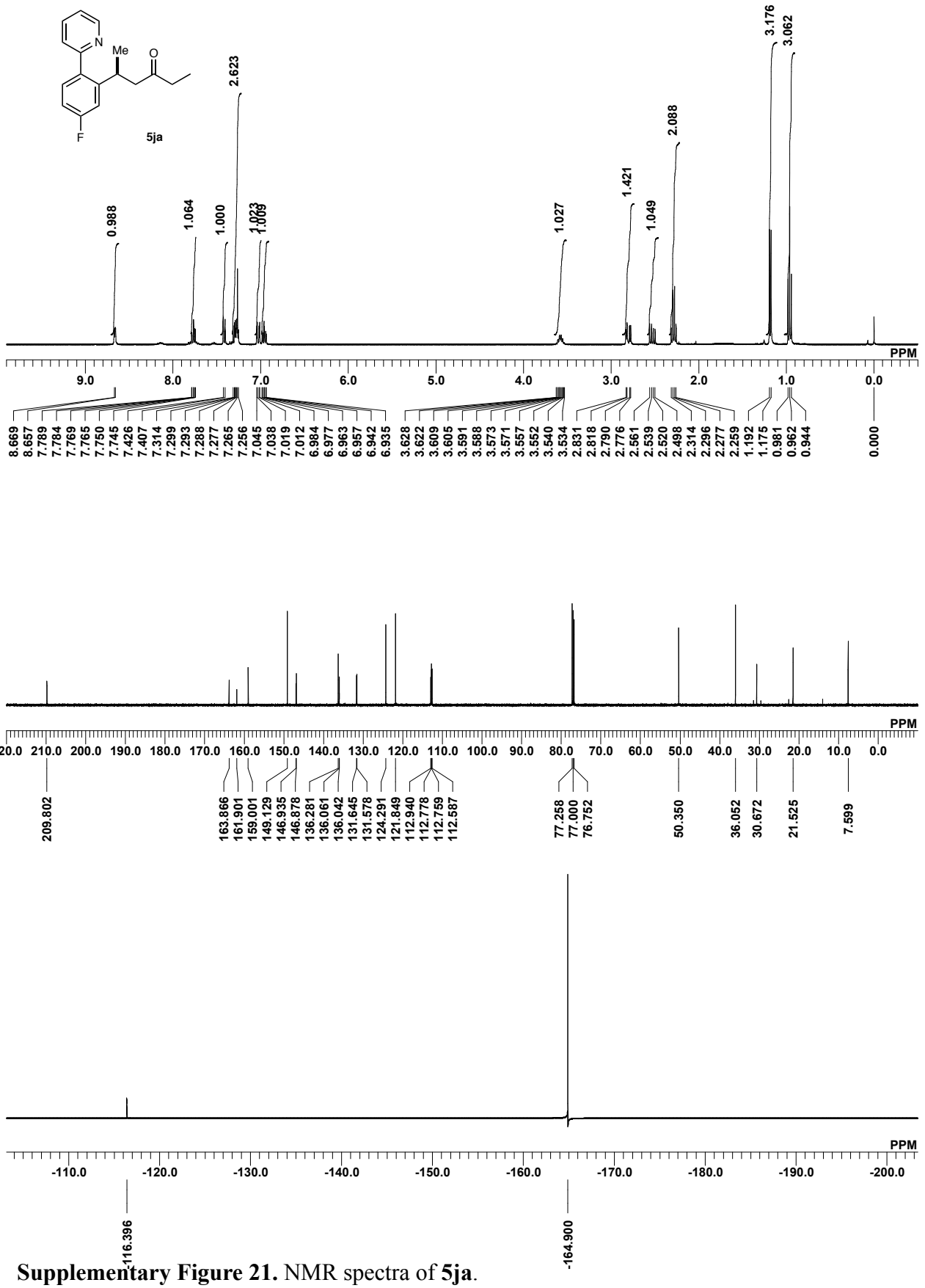
Supplementary Figure 18. NMR spectra of **5ga**.



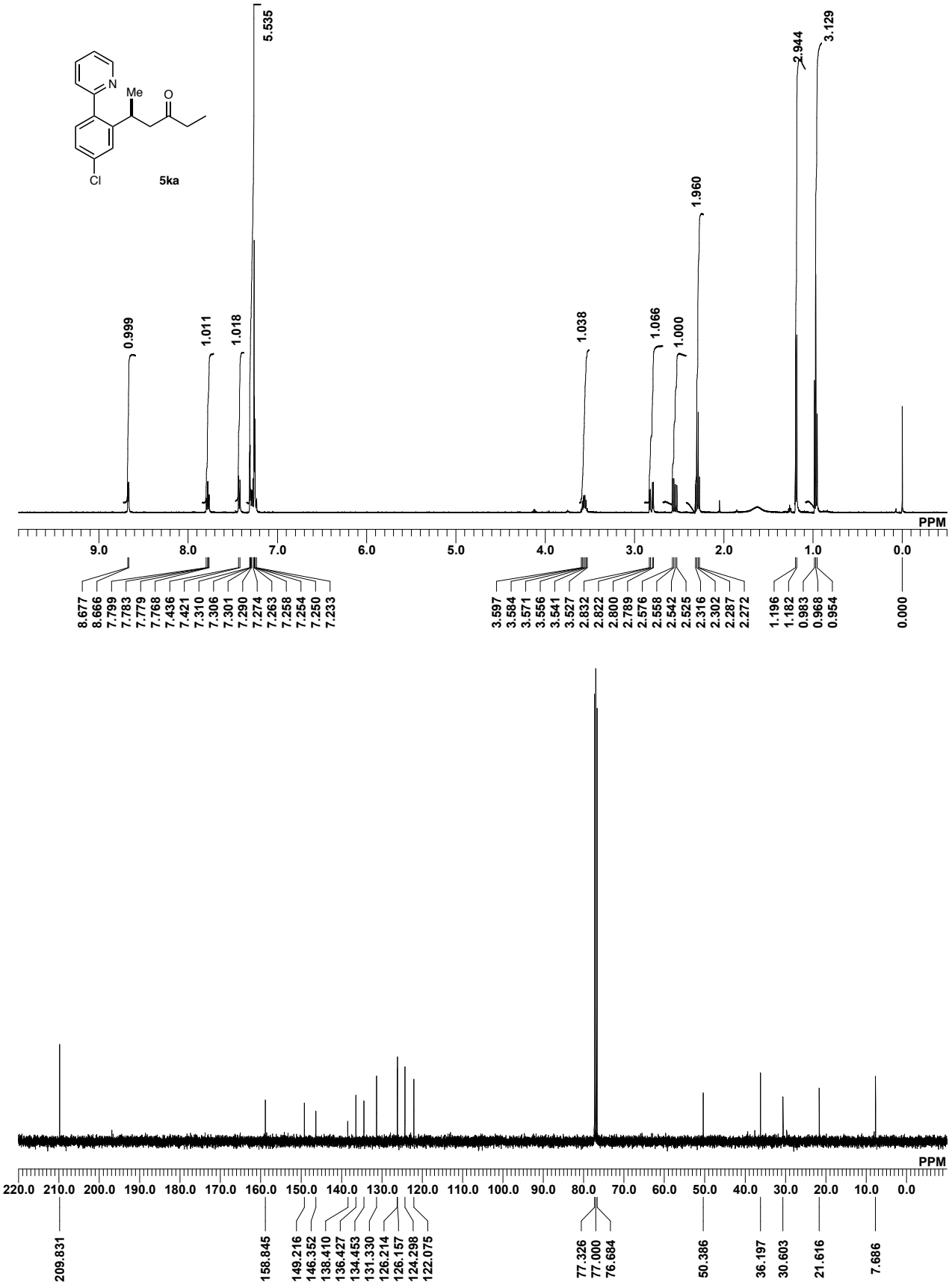
Supplementary Figure 19. NMR spectra of **5ha**.



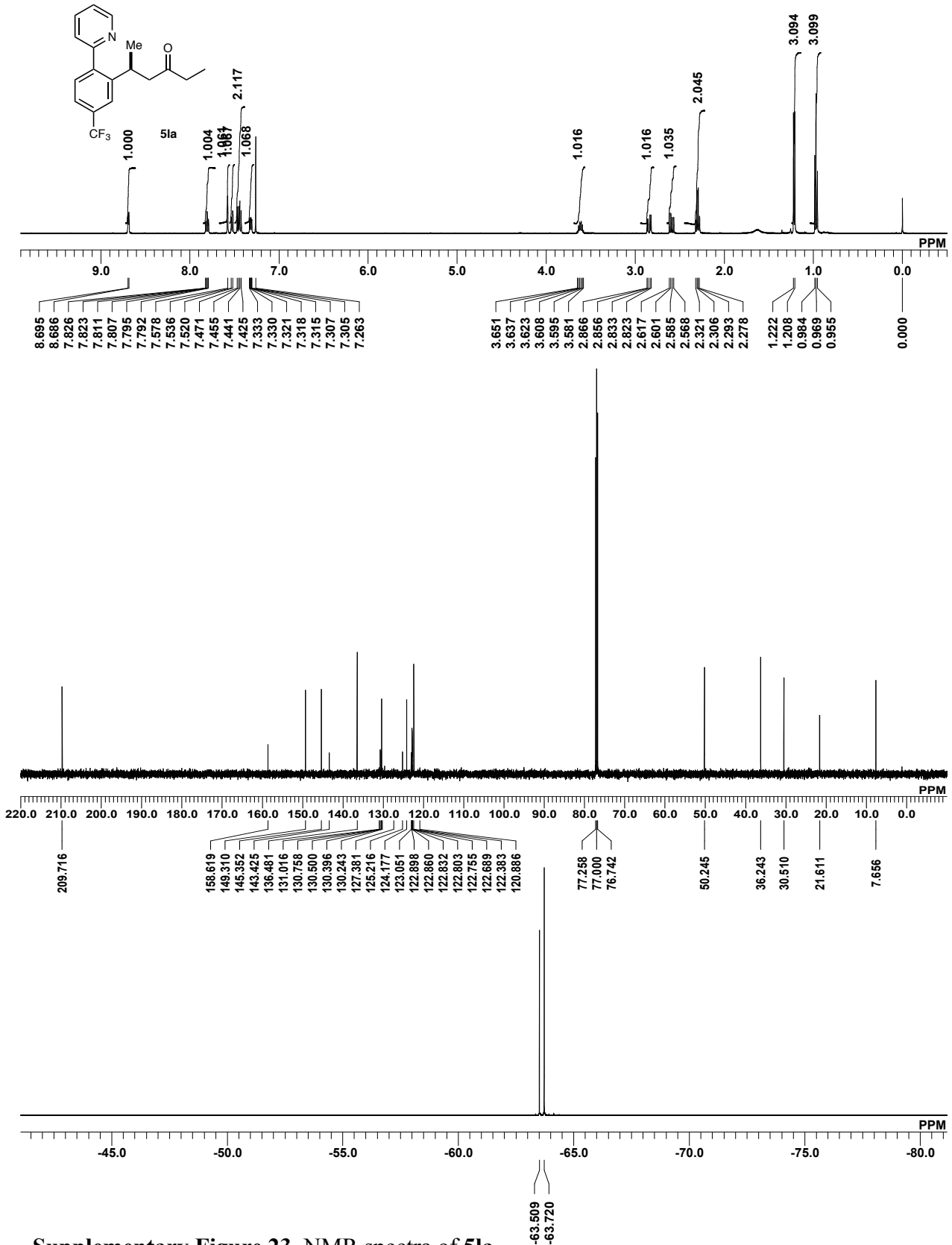
Supplementary Figure 20. NMR spectra of **5ia**.



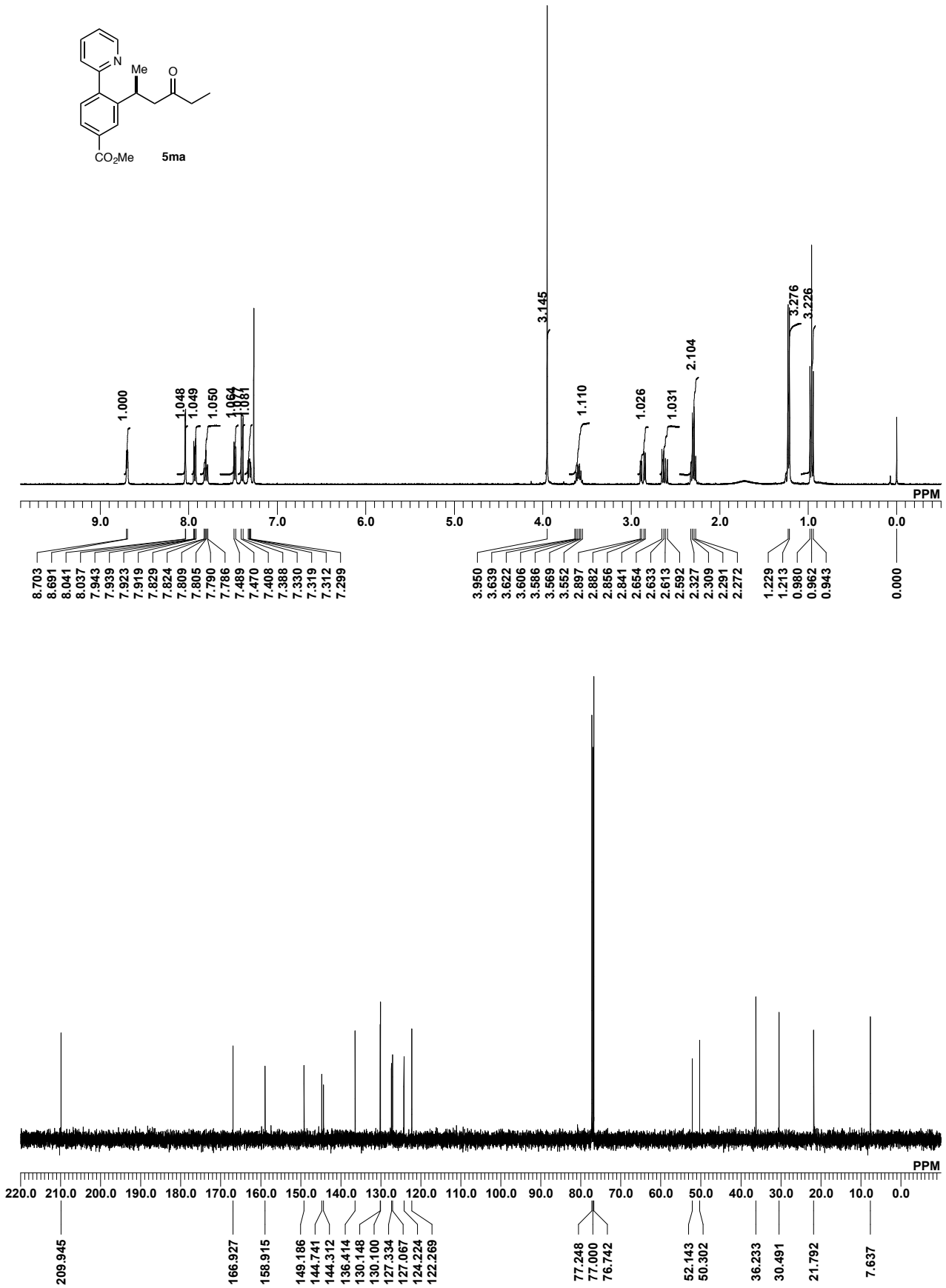
Supplementary Figure 21. NMR spectra of **5ja**.



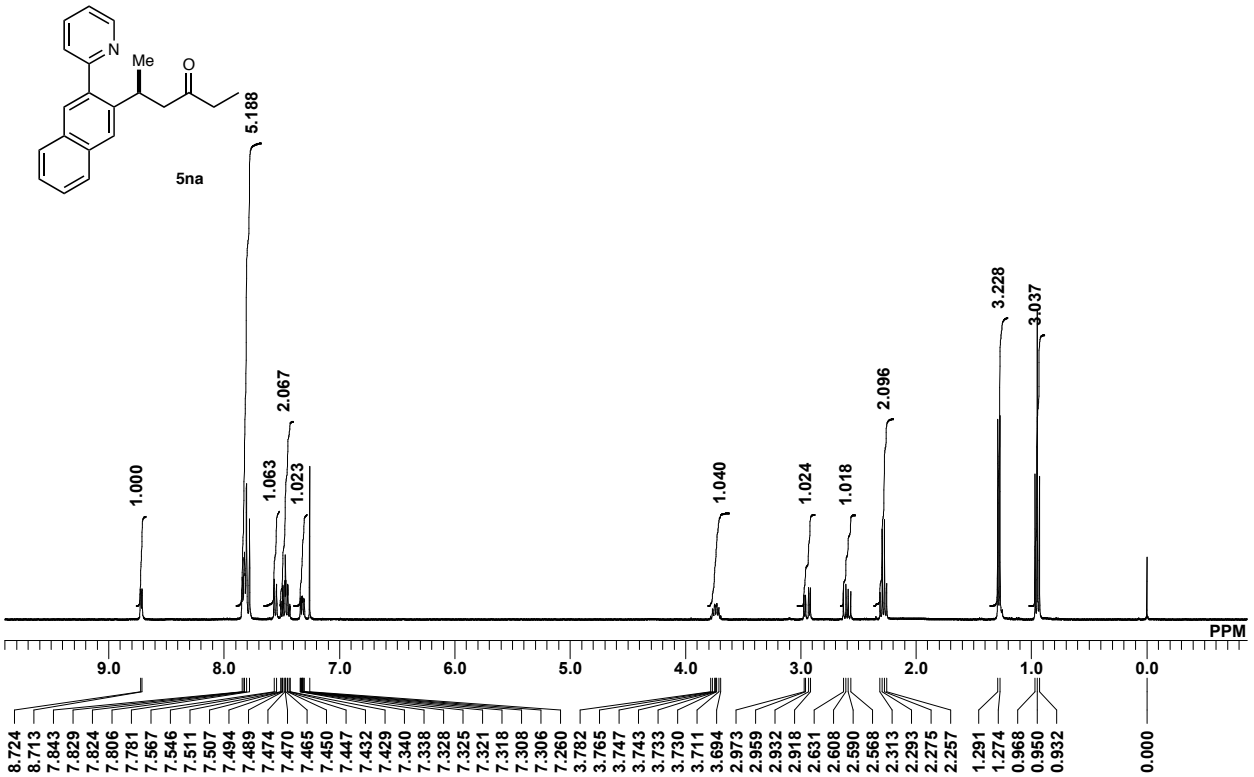
Supplementary Figure 22. NMR spectra of **5ka**.

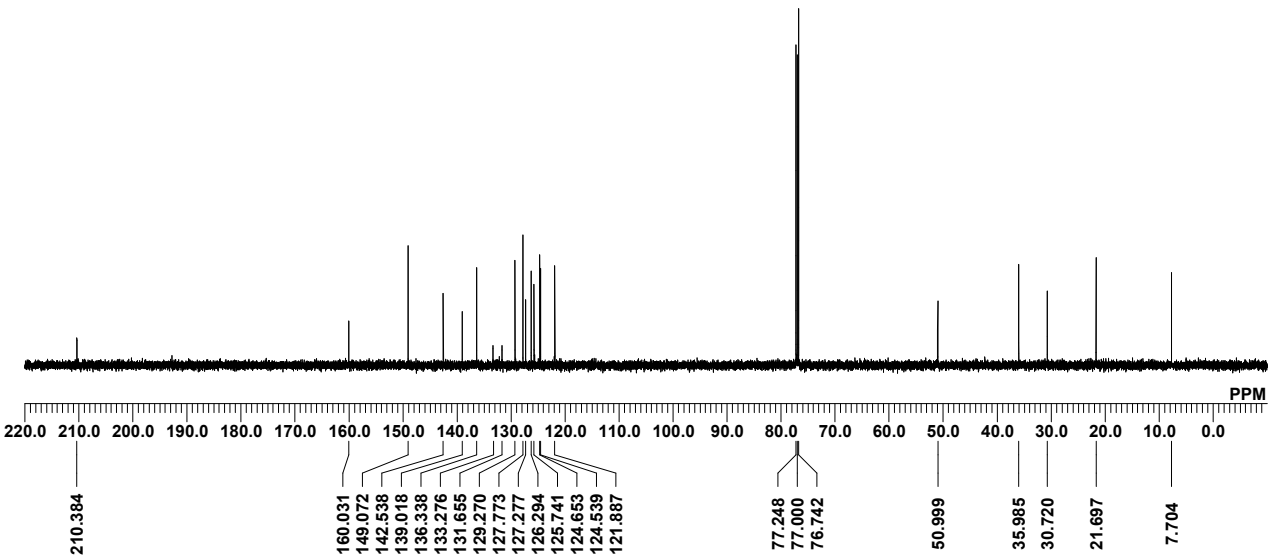


Supplementary Figure 23. NMR spectra of **5la**.

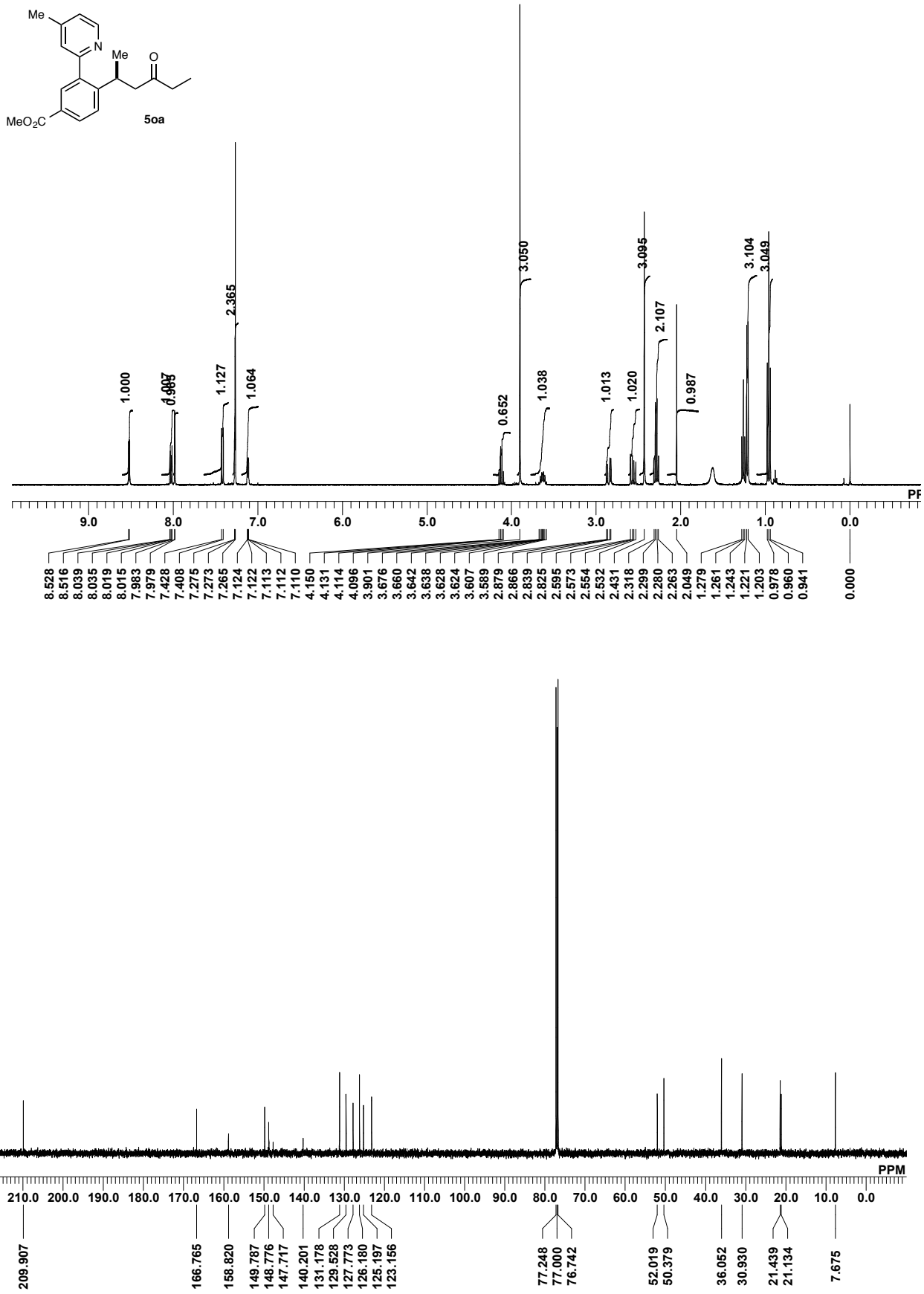


Supplementary Figure 24. NMR spectra of **5ma**.

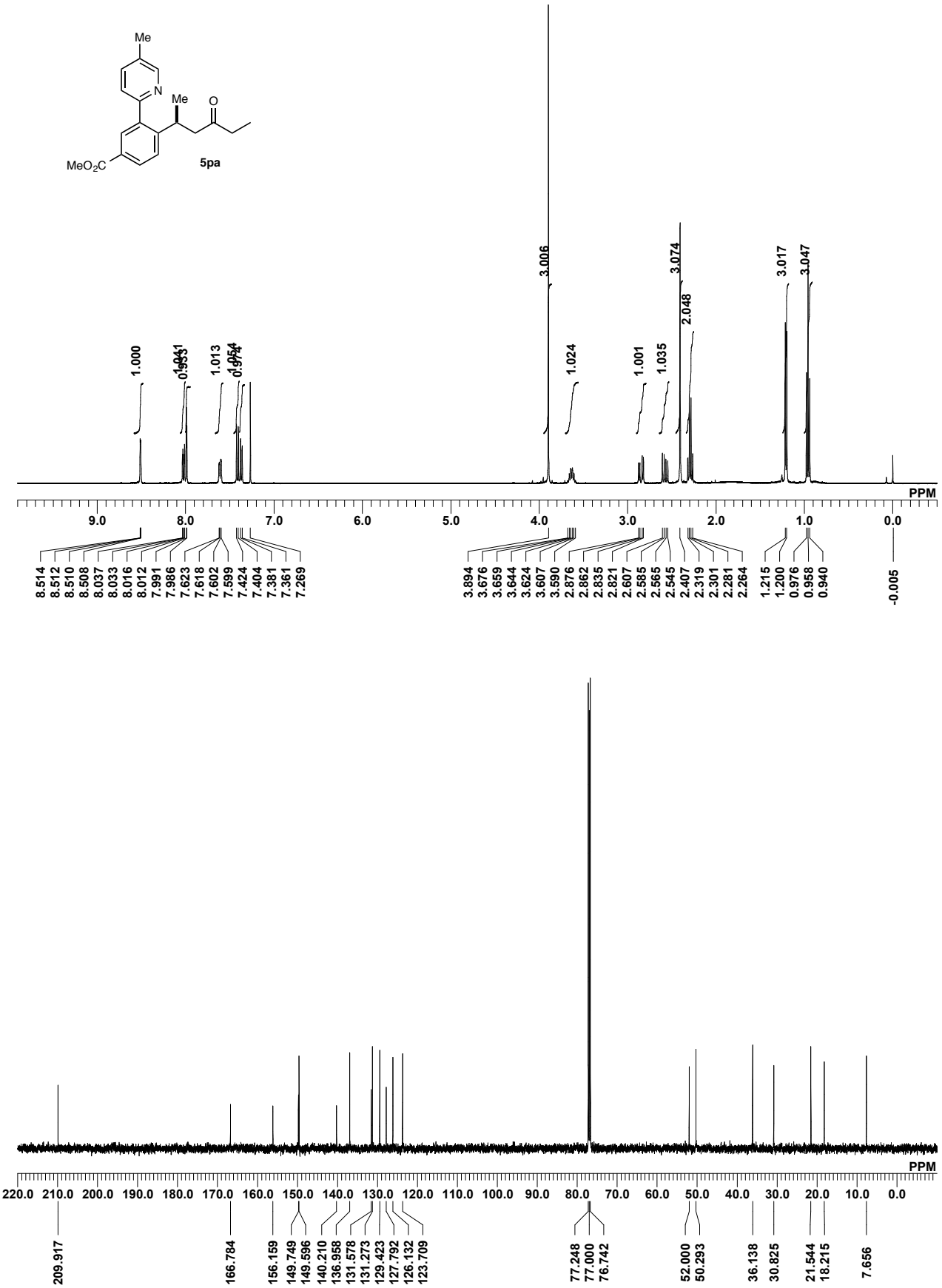




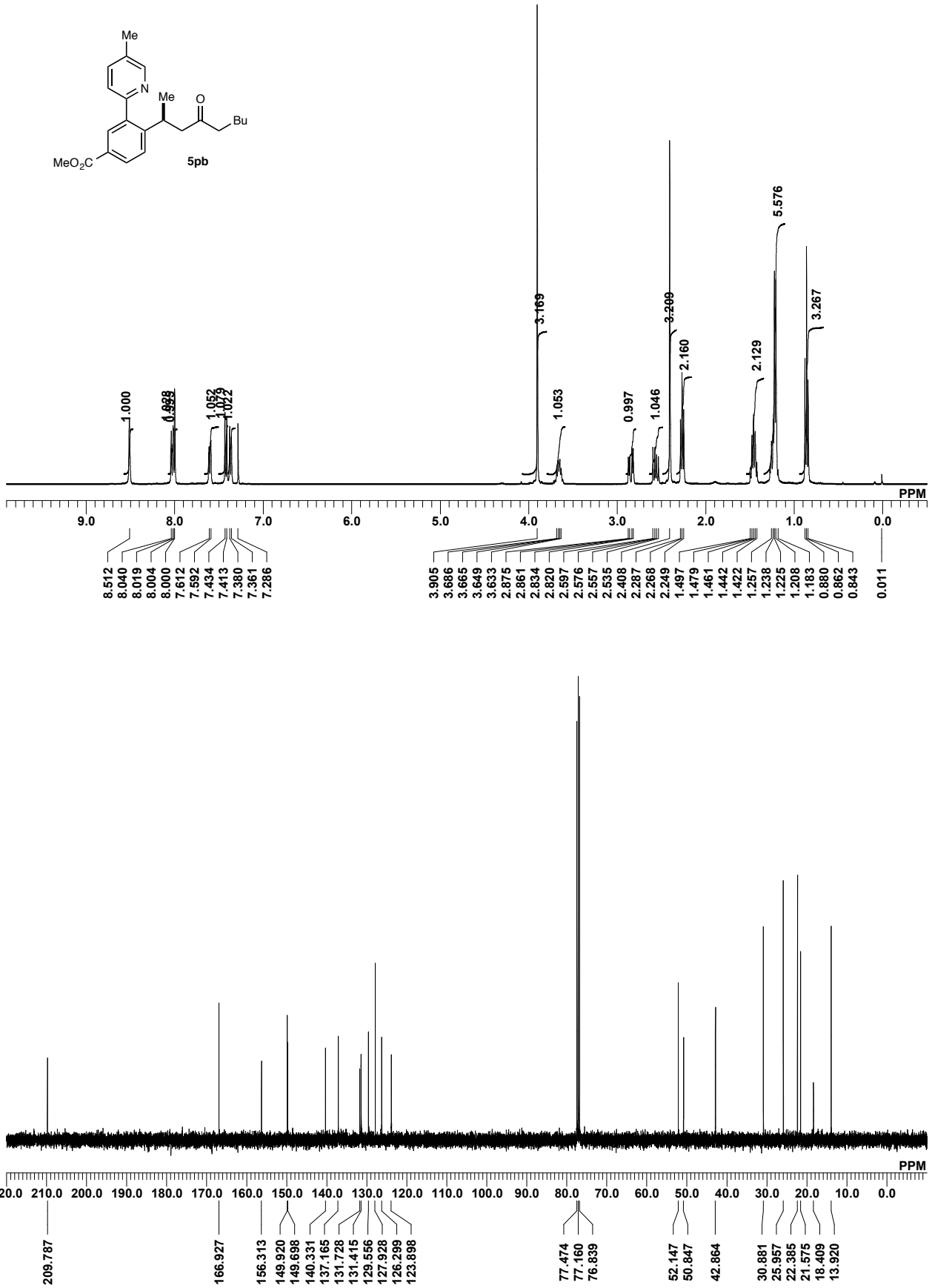
Supplementary Figure 25. NMR spectra of **5na**.



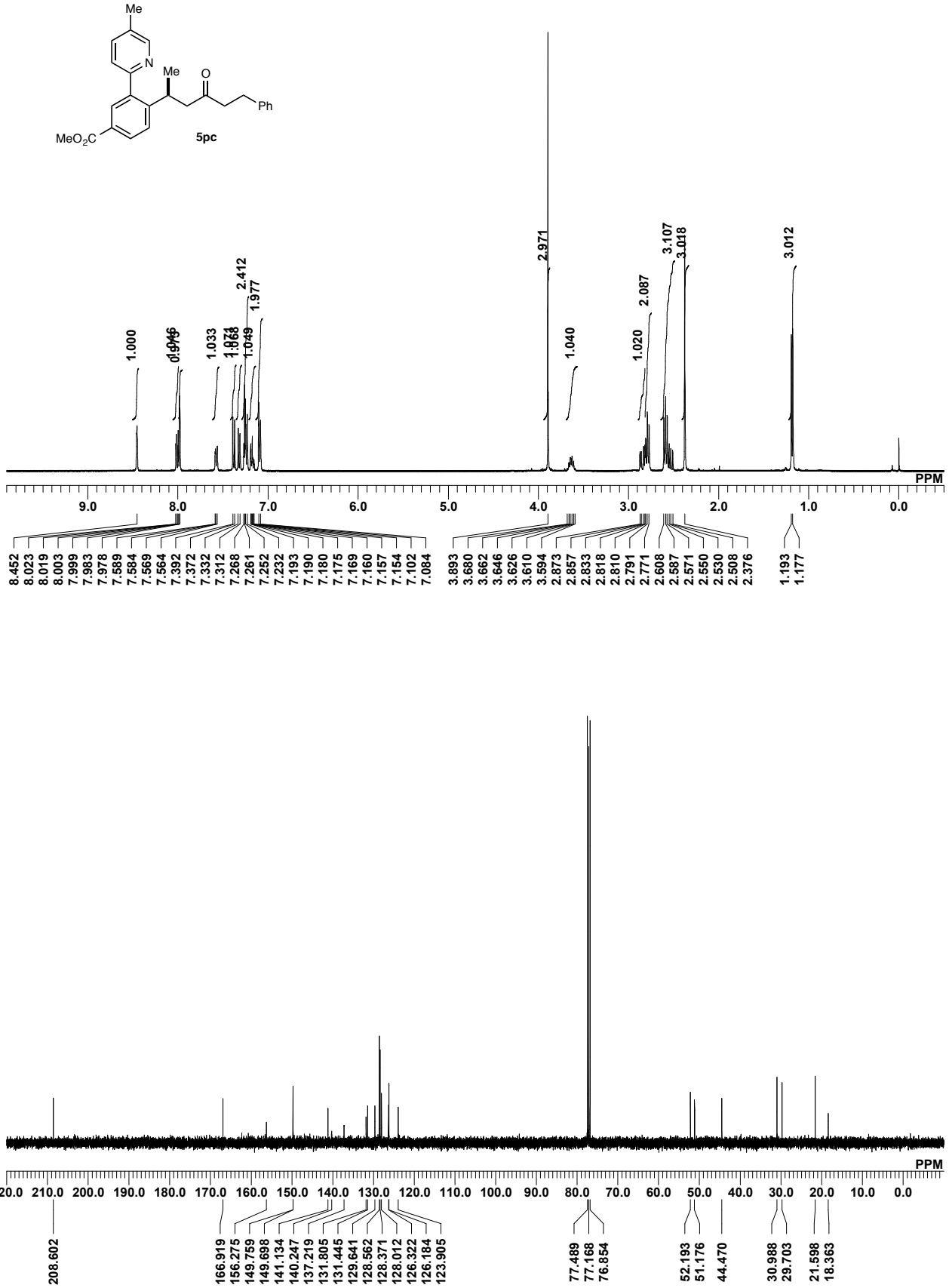
Supplementary Figure 26. NMR spectra of **5oa**.



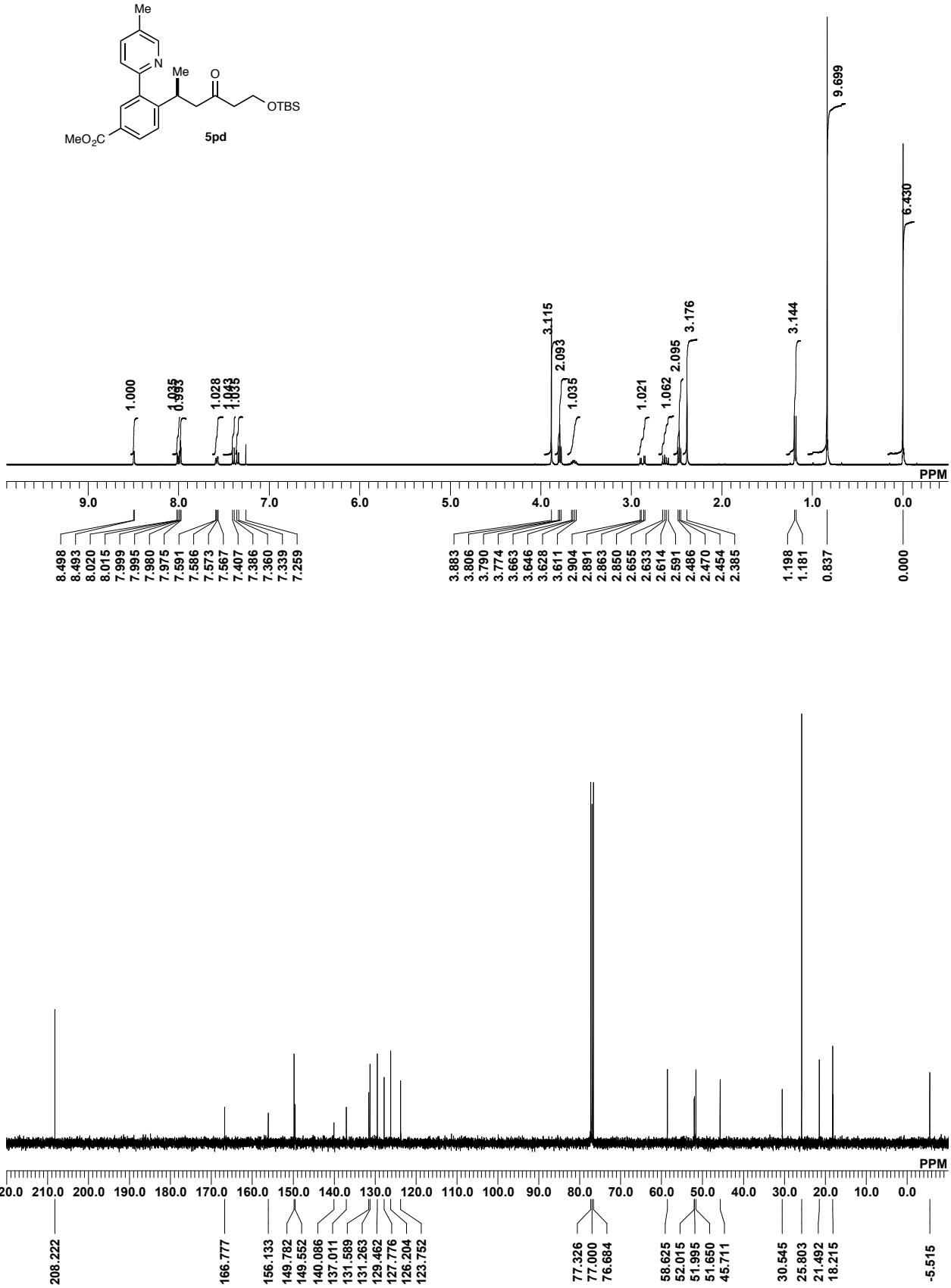
Supplementary Figure 27. NMR spectra of **5pa**.



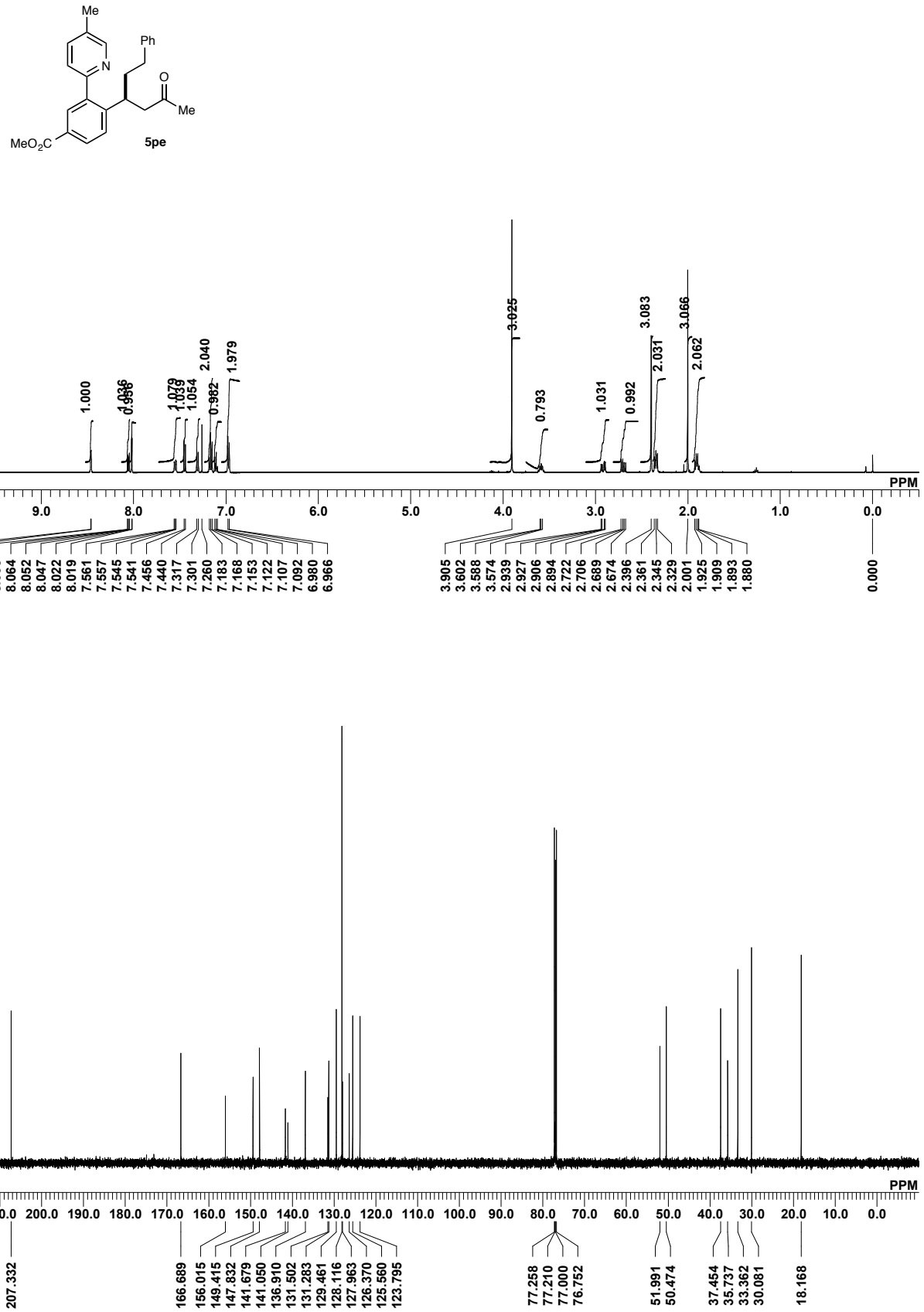
Supplementary Figure 28. NMR spectra of **5pb**.



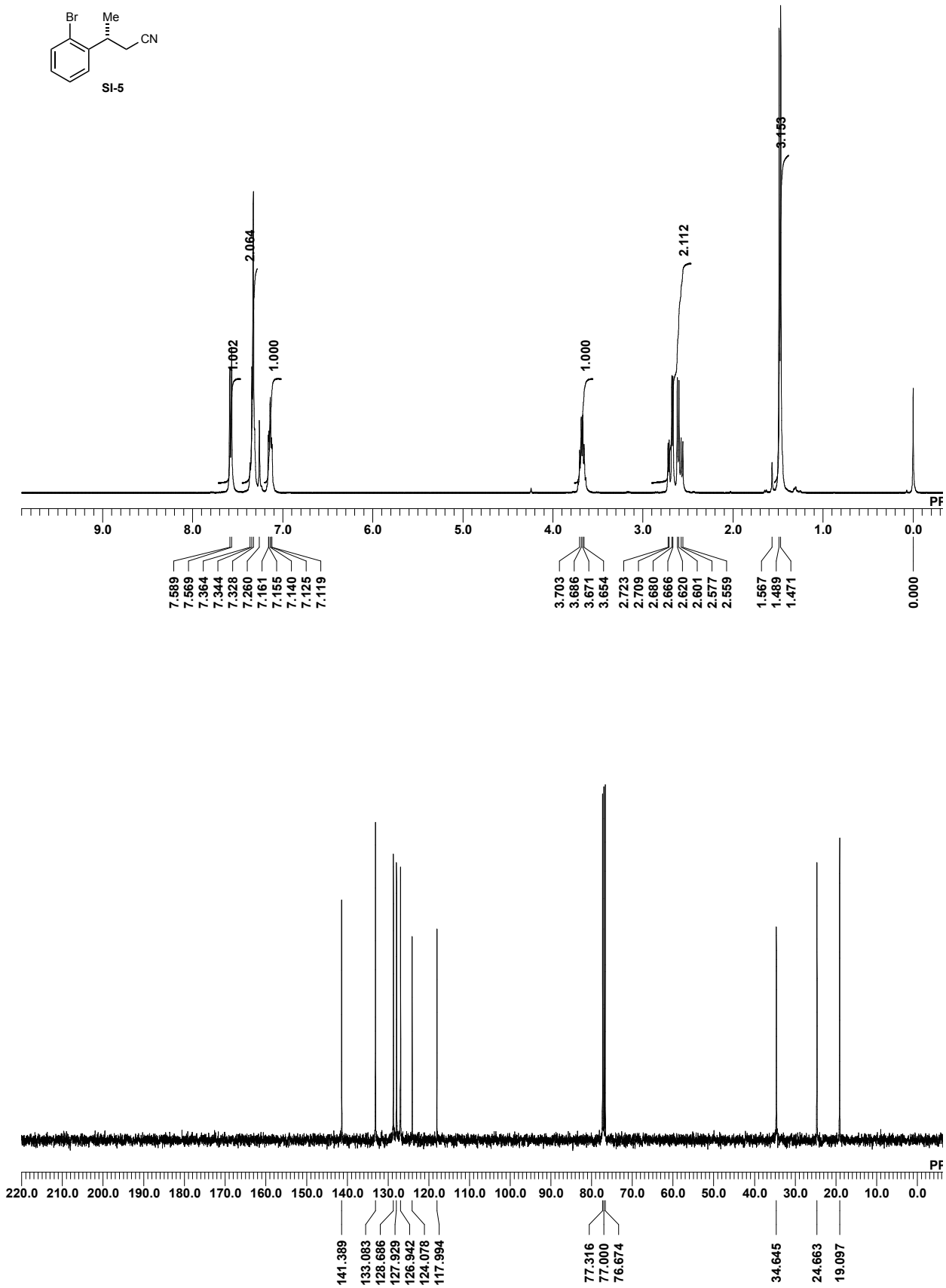
Supplementary Figure 29. NMR spectra of **5pc**.



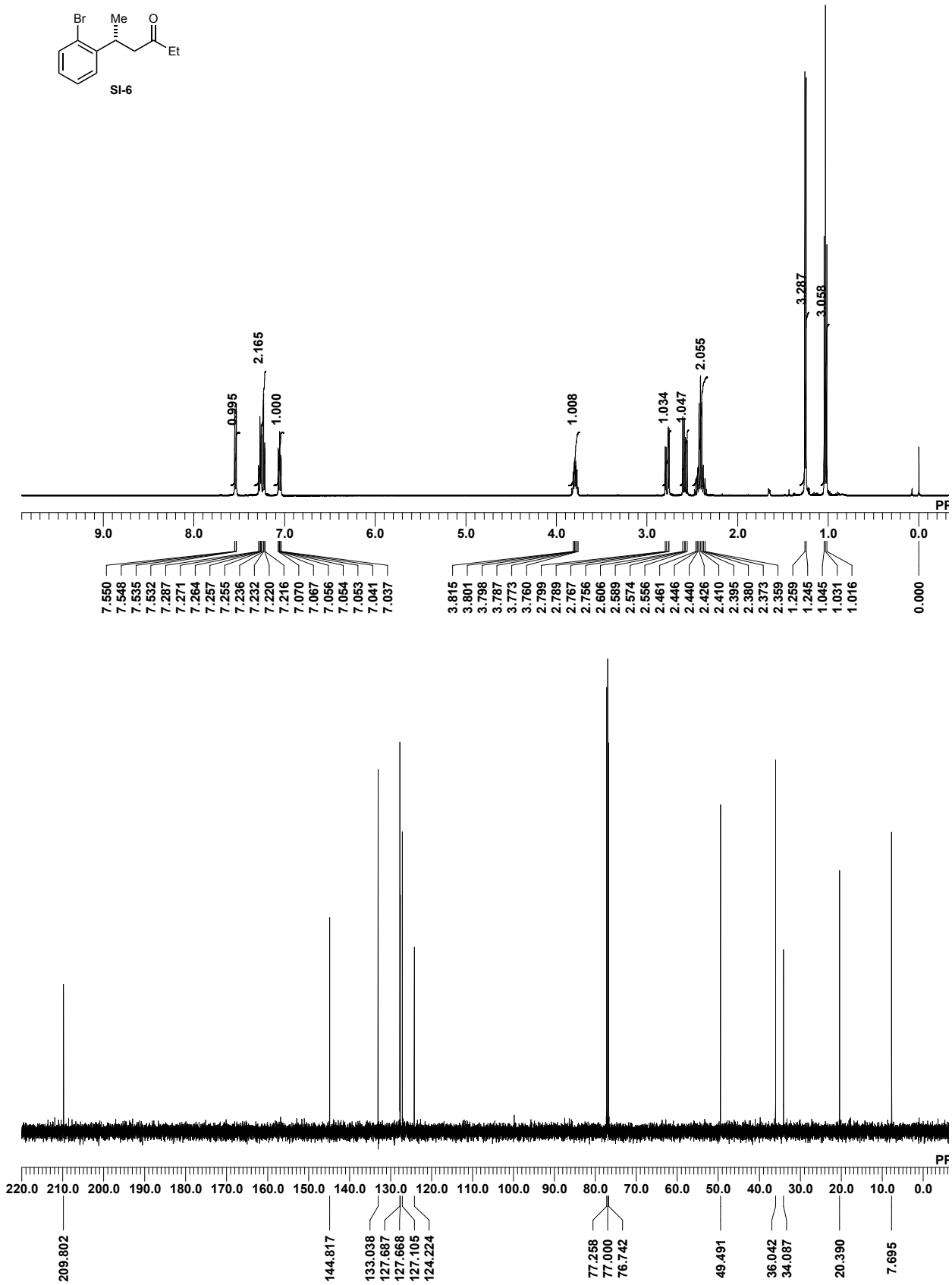
Supplementary Figure 30. NMR spectra of **5pd**.



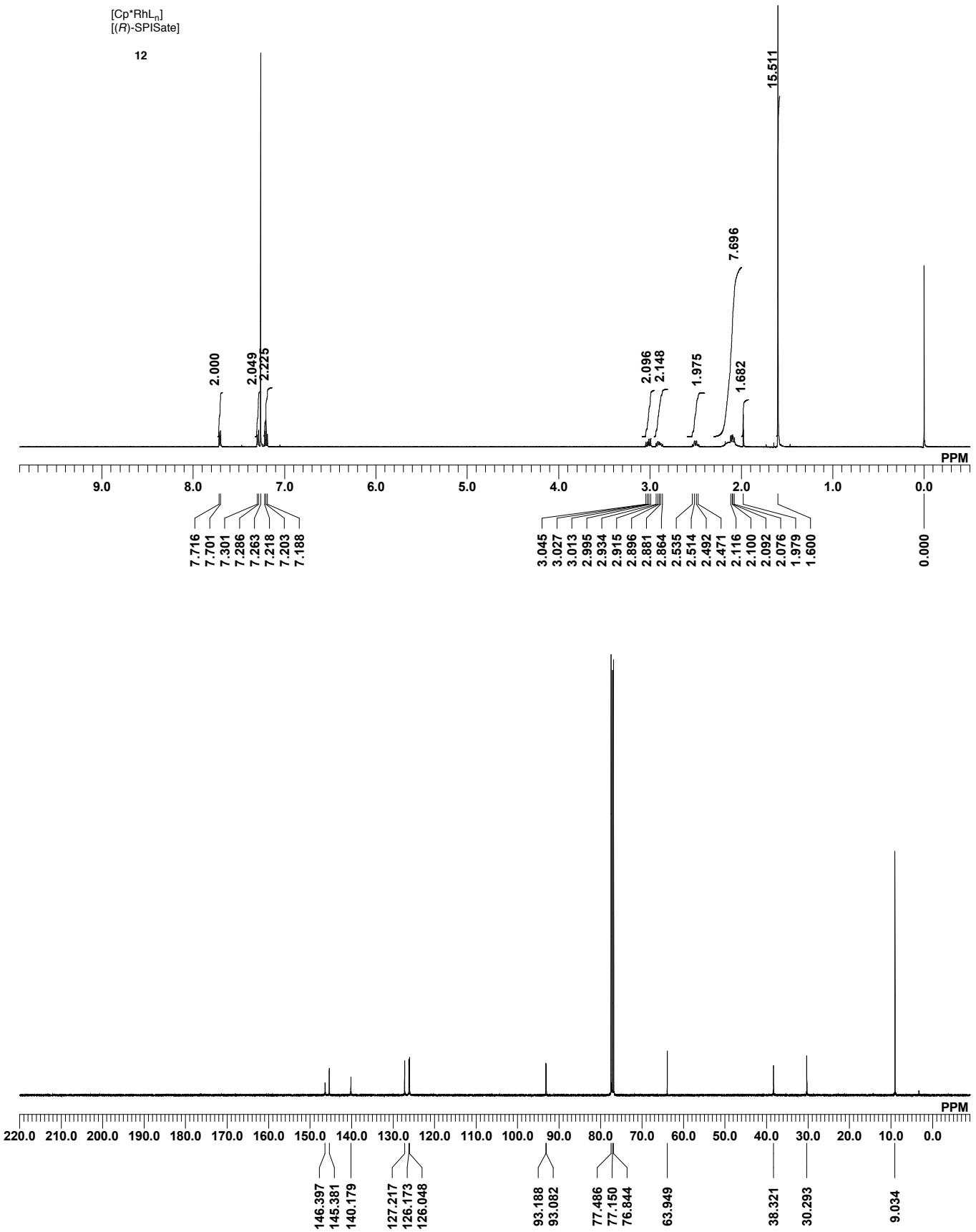
Supplementary Figure 31. NMR spectra of **5pe**.



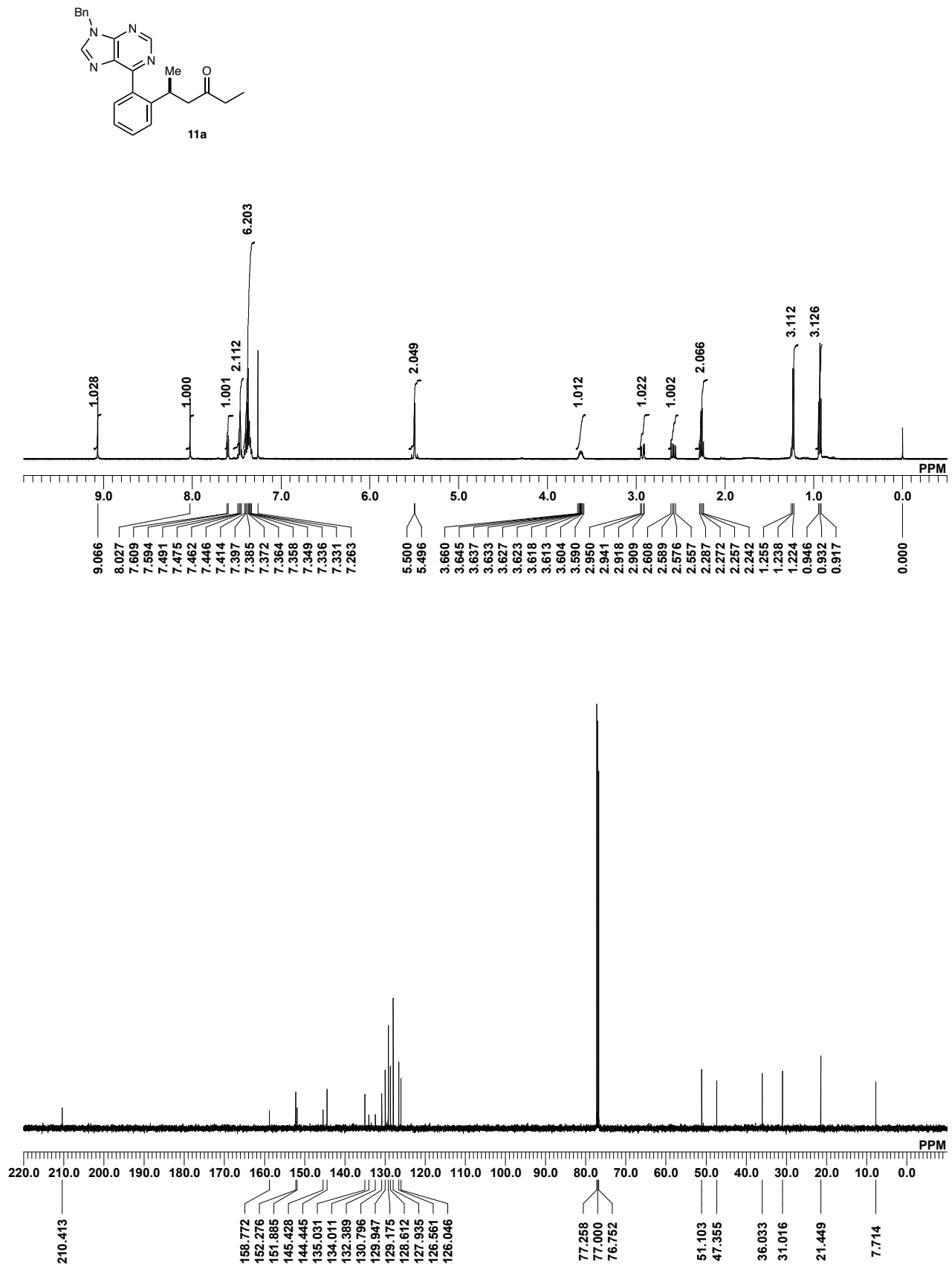
Supplementary Figure 32. NMR spectra of **SI-5**.



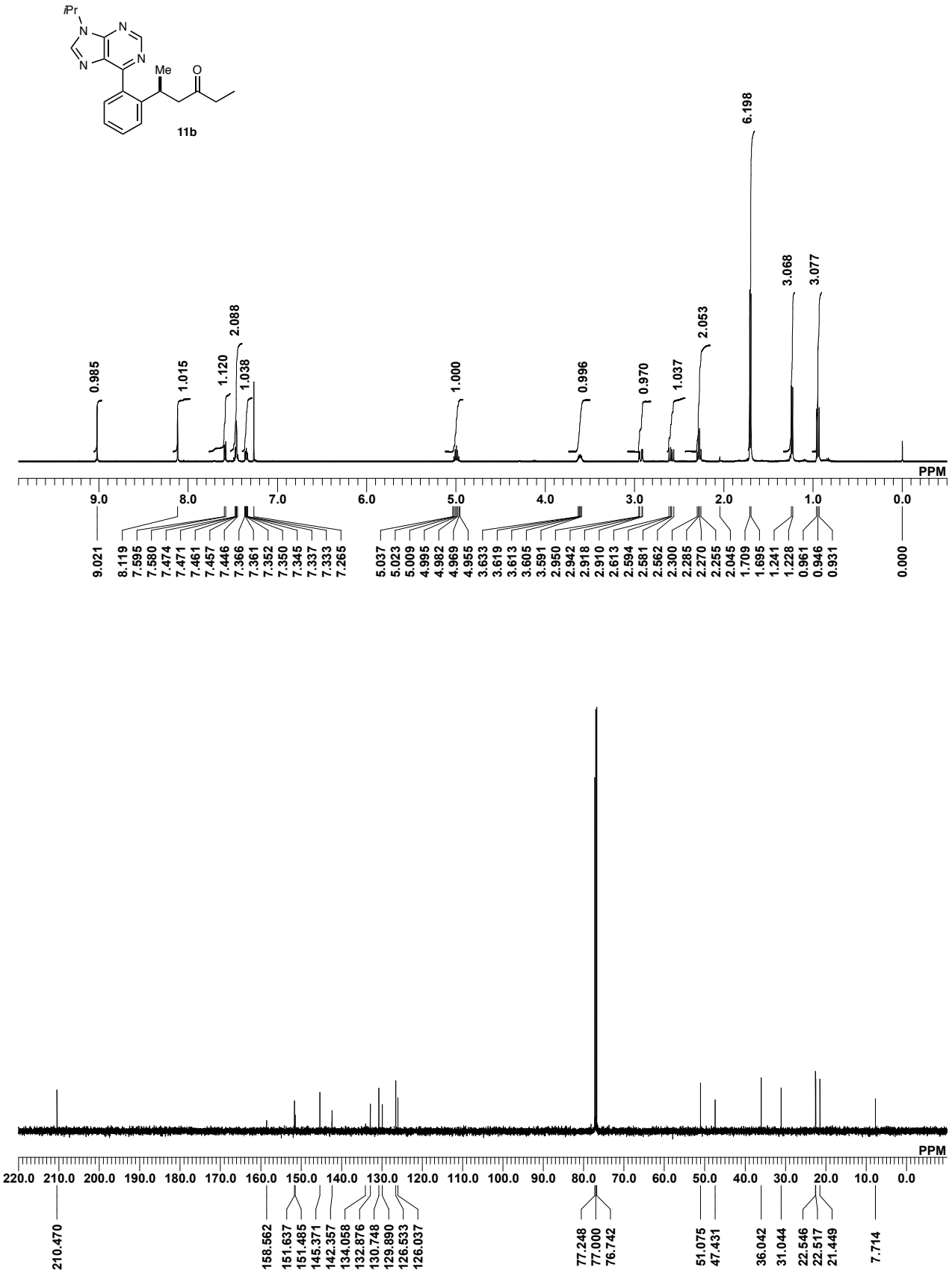
Supplementary Figure 33. NMR spectra of **SI-6**.



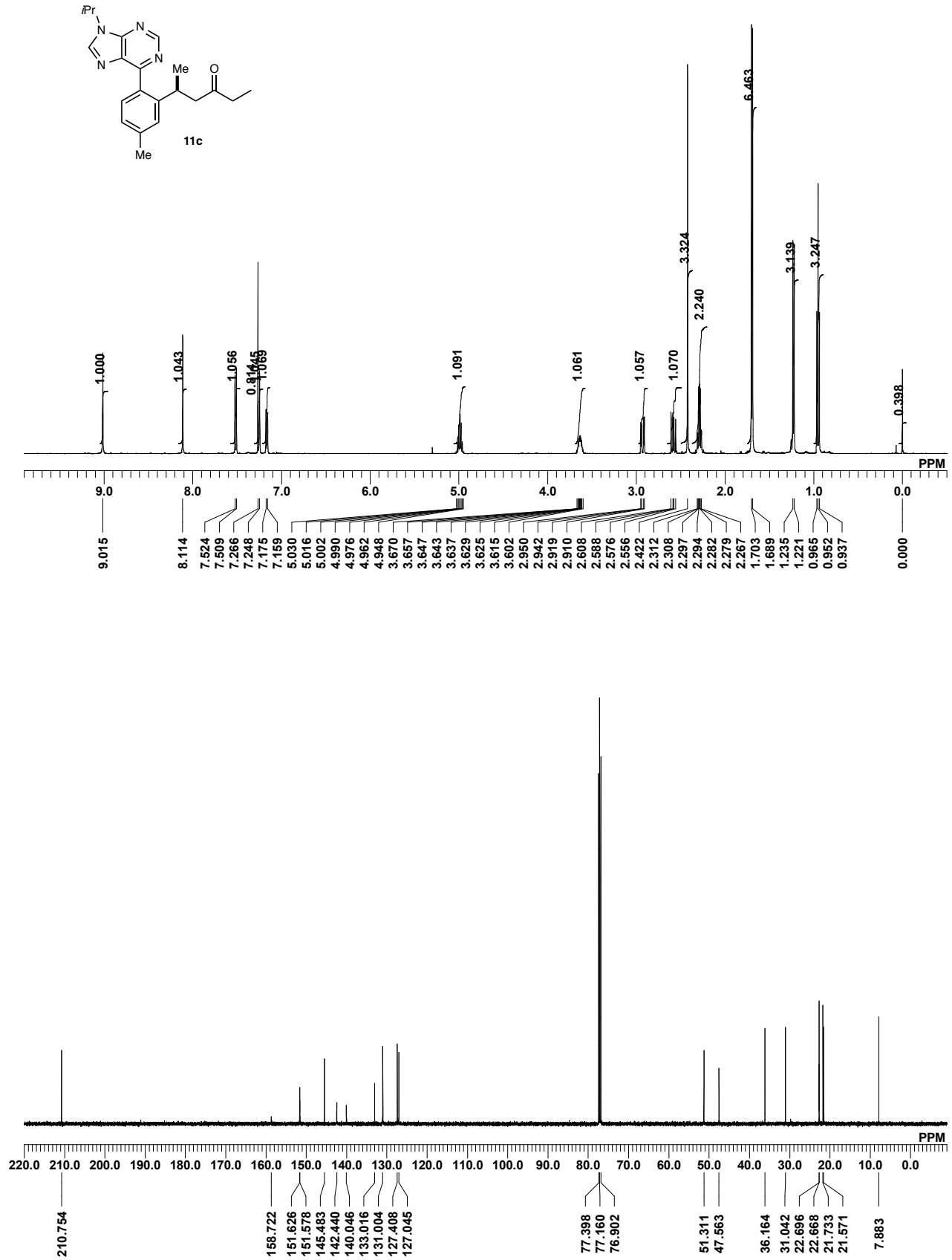
Supplementary Figure 34. NMR spectra of **12**.



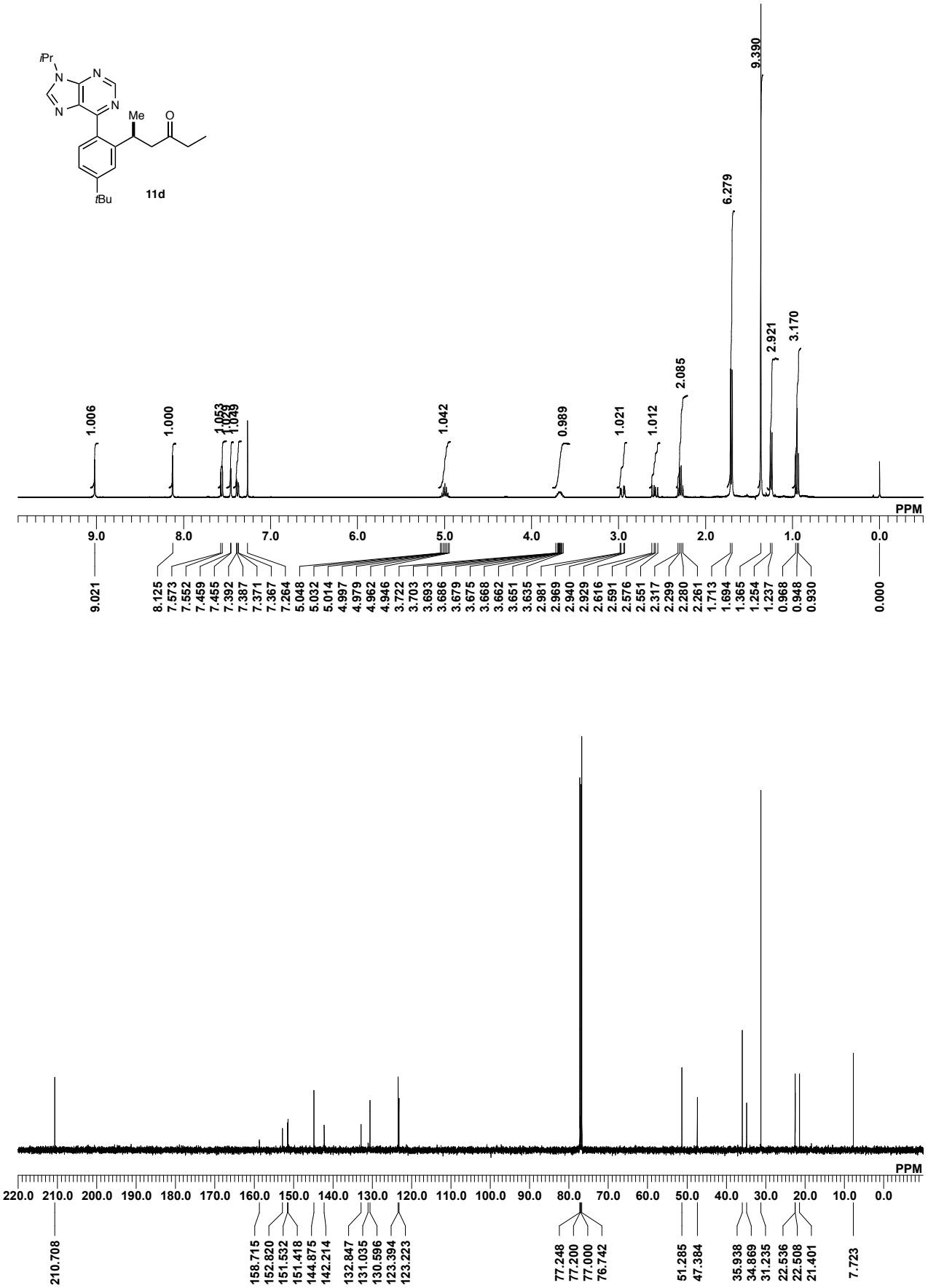
Supplementary Figure 35. NMR spectra of **11a**.



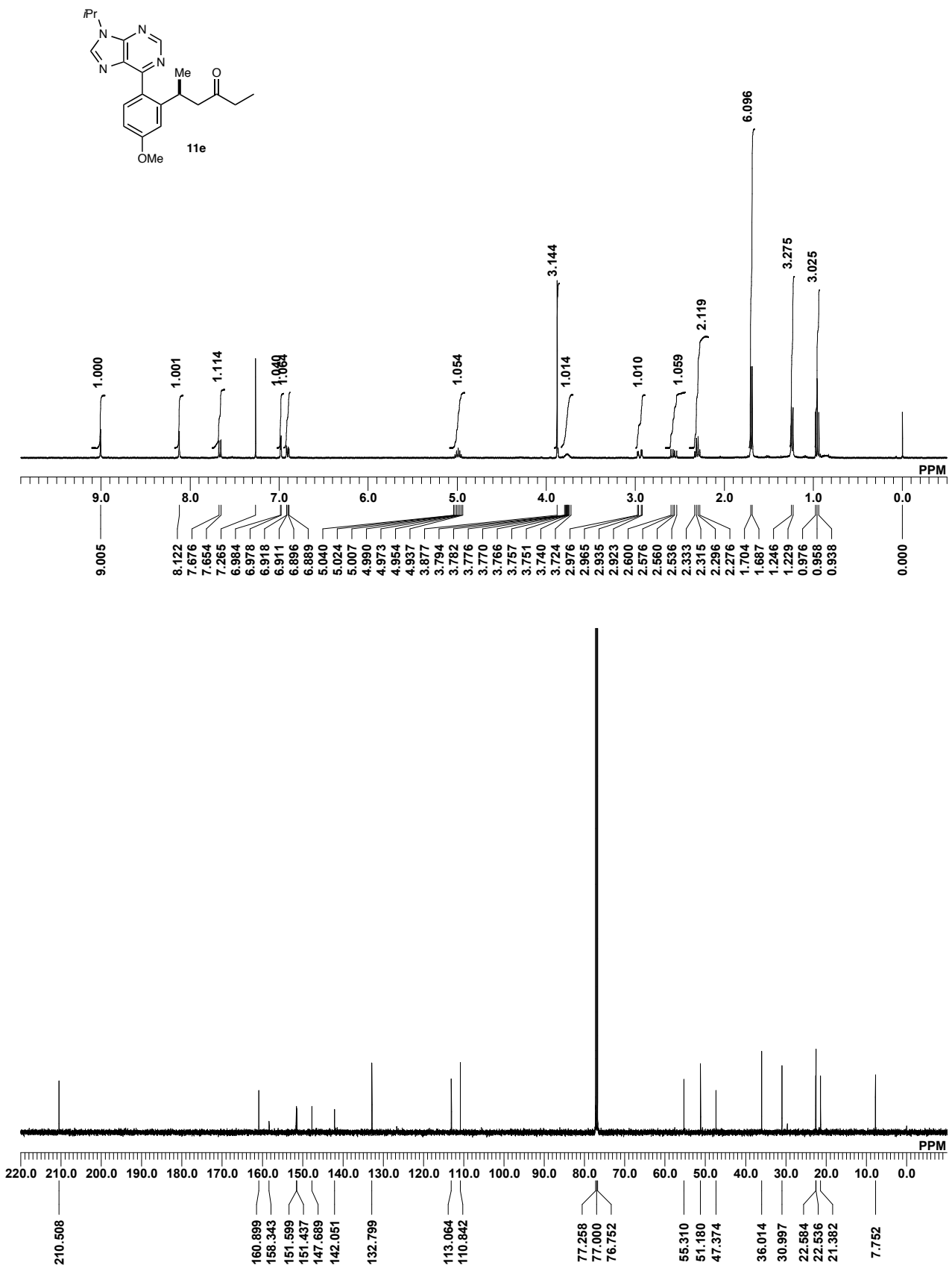
Supplementary Figure 36. NMR spectra of **11b**.



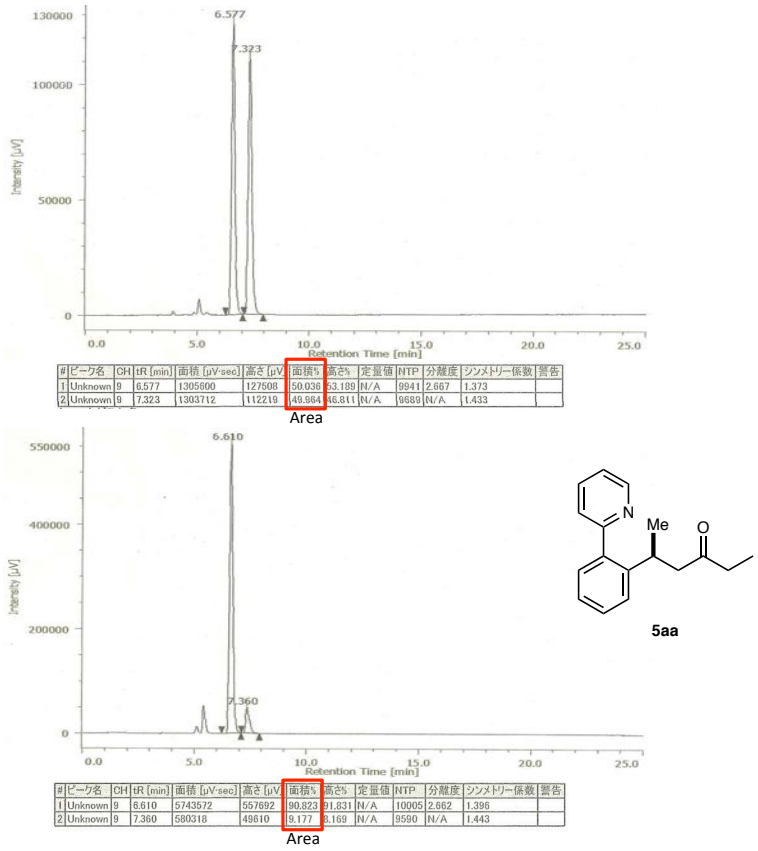
Supplementary Figure 37. NMR spectra of **11c**.



Supplementary Figure 38. NMR spectra of **11d**.



Supplementary Figure 39. NMR spectra of **11e**.



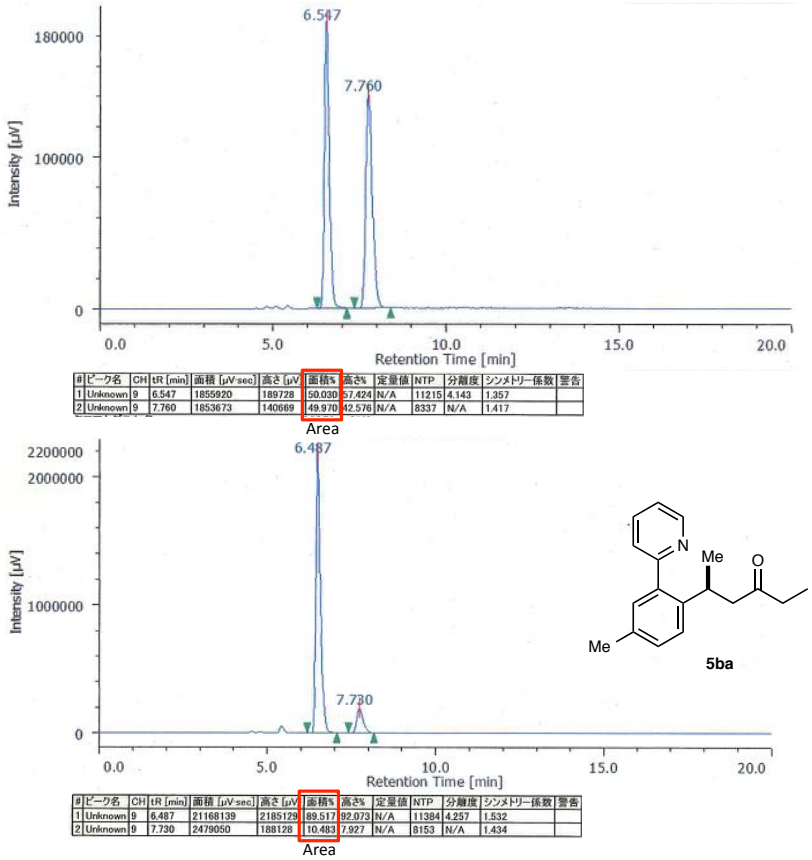
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.577	1305600	127508	50.036	53.189	N/A	9941	2.667	1.373	
2	Unknown	9	7.323	1303712	112219	49.964	46.811	N/A	9689	N/A	1.433	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.610	5743572	557692	90.823	91.831	N/A	10005	2.662	1.396	
2	Unknown	9	7.360	580318	49610	9.177	8.169	N/A	9590	N/A	1.443	

Area

Supplementary Figure 40. Chiral HPLC analysis of product **5aa**.



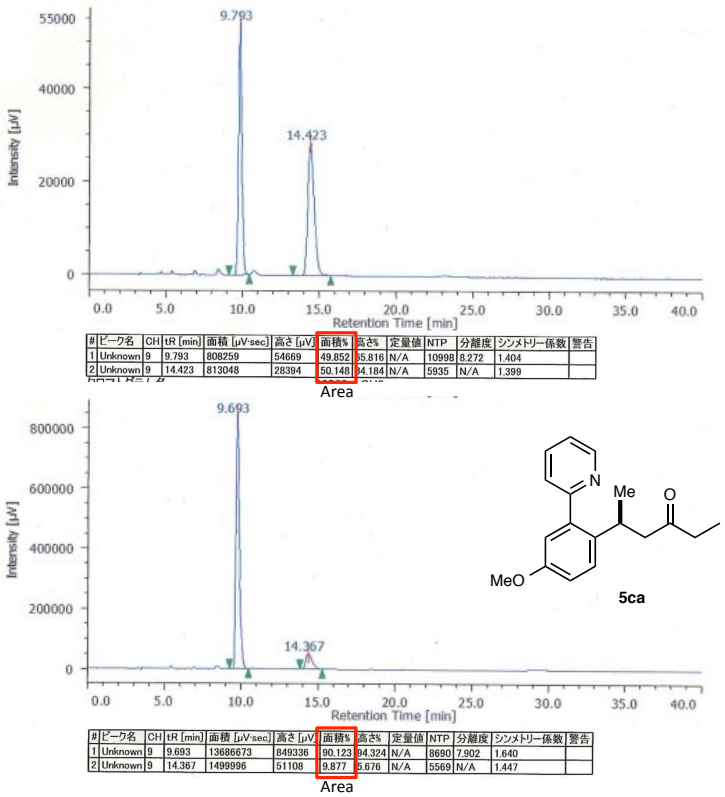
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.547	1855920	189728	50.030	57.424	N/A	11215	4.143	1.357	
2	Unknown	9	7.760	1853673	140669	49.970	42.576	N/A	8337	N/A	1.417	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.487	21168139	2185129	89.517	92.073	N/A	11384	4.257	1.532	
2	Unknown	9	7.730	2479050	188128	10.483	7.927	N/A	8153	N/A	1.434	

Area

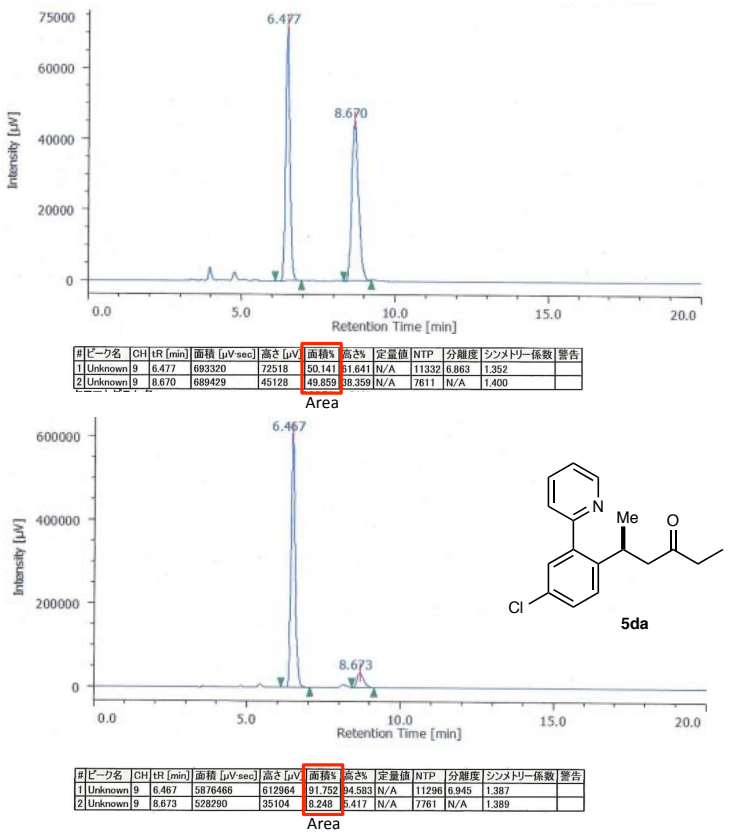
Supplementary Figure 41. Chiral HPLC analysis of product **5ba**.



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	9.793	808259	54669	49.852	65.816	N/A	10998	8.272	1.404	
2	Unknown	9	14.423	813048	28394	50.148	34.184	N/A	5935	N/A	1.399	

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	9.693	13686673	849336	90.123	94.324	N/A	8690	7.902	1.640	
2	Unknown	9	14.367	1499996	51108	9.877	5.676	N/A	5569	N/A	1.447	

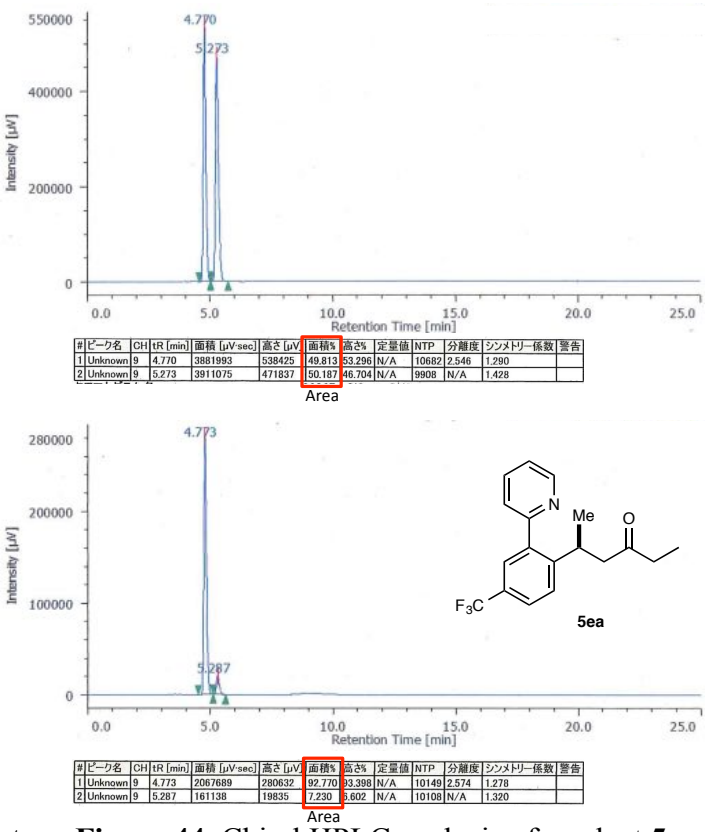
Supplementary Figure 42. Chiral HPLC analysis of product **5ca**.



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.477	693320	72518	50.141	61.641	N/A	11332	6.863	1.352	
2	Unknown	9	8.670	689429	45128	49.859	38.359	N/A	7611	N/A	1.400	

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.467	5876466	612964	91.752	94.583	N/A	11296	6.945	1.387	
2	Unknown	9	8.673	528290	35104	8.248	5.417	N/A	7761	N/A	1.389	

Supplementary Figure 43. Chiral HPLC analysis of product **5da**.



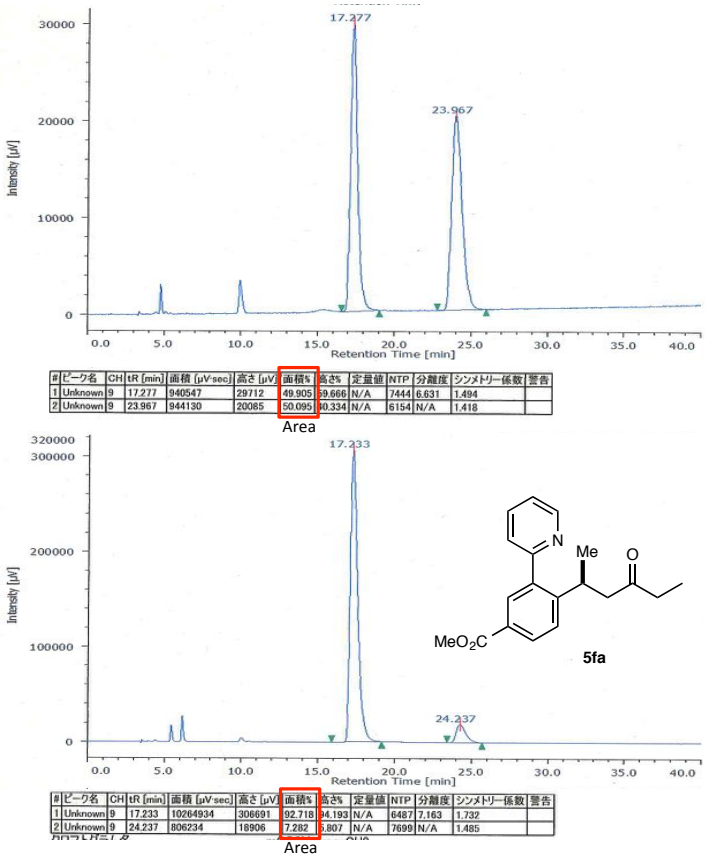
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	4.770	3881993	538425	49.813	53.296	N/A	10682	2.546	1.290	
2	Unknown	9	5.273	3911075	471837	50.187	46.704	N/A	9908	N/A	1.428	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	4.773	2067689	280632	92.770	93.398	N/A	10149	2.574	1.278	
2	Unknown	9	5.287	161138	19835	7.230	6.602	N/A	10108	N/A	1.320	

Area

Supplementary Figure 44. Chiral HPLC analysis of product **5ea**.



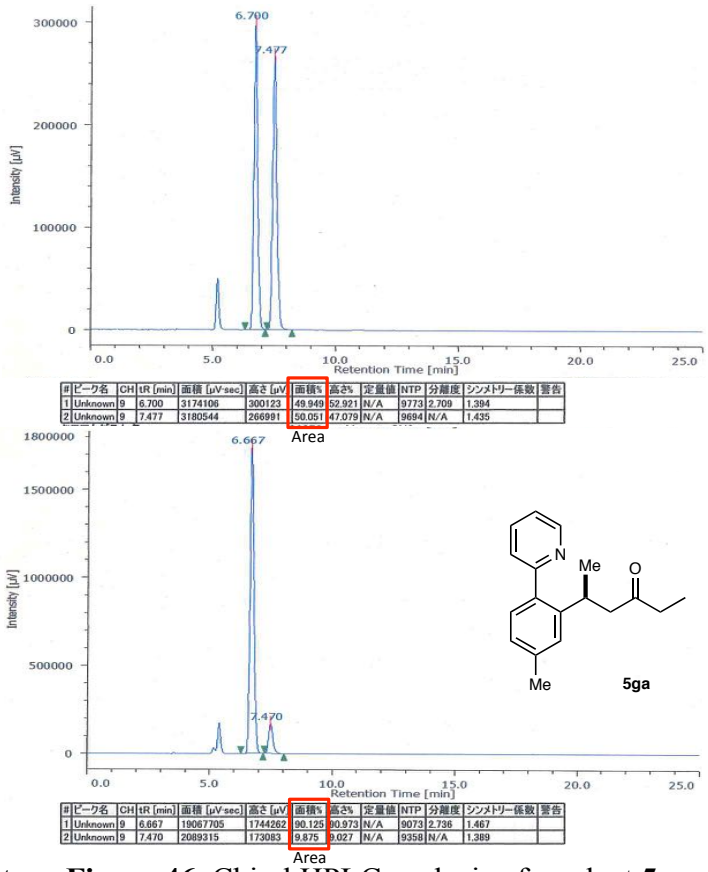
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	17.277	940547	29712	49.905	59.666	N/A	7444	6.631	1.494	
2	Unknown	9	23.967	944130	20085	50.095	40.334	N/A	6154	N/A	1.418	

Area

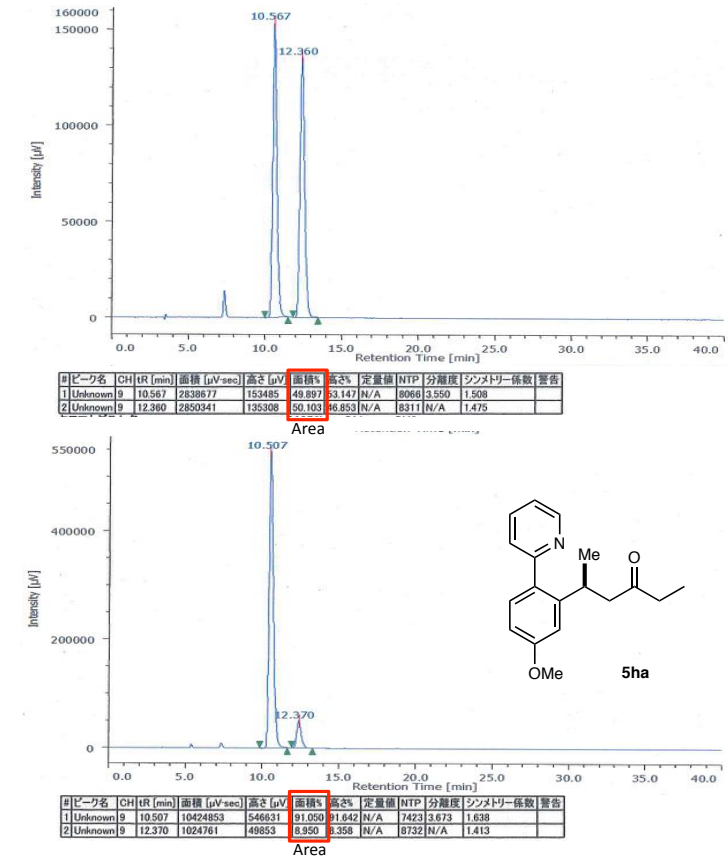
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	17.233	10264934	306691	92.718	94.193	N/A	6487	7.163	1.732	
2	Unknown	9	24.237	806234	18906	7.282	5.807	N/A	7699	N/A	1.485	

Area

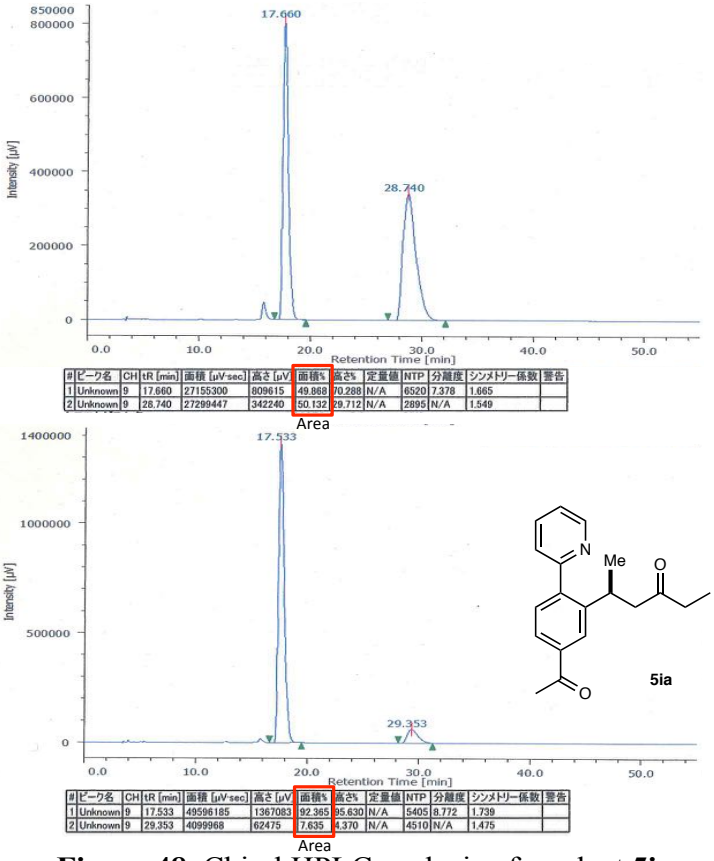
Supplementary Figure 45. Chiral HPLC analysis of product **5fa**.



Supplementary Figure 46. Chiral HPLC analysis of product **5ga**.



Supplementary Figure 47. Chiral HPLC analysis of product **5ha**.



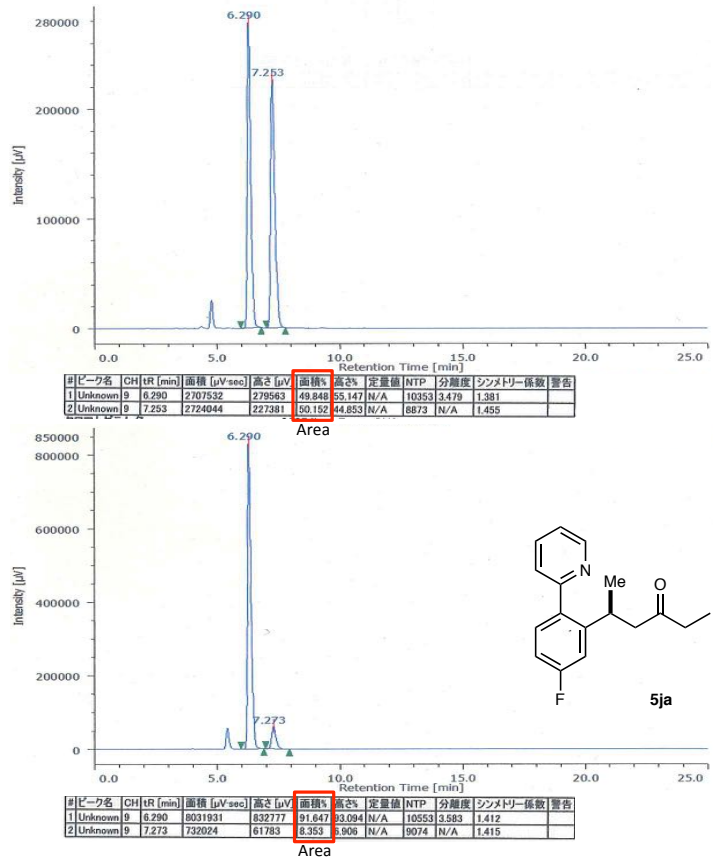
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	17.660	27155300	809615	49.868	70.288	N/A	6520	7.378	1.665	
2	Unknown	9	28.740	27299447	342240	50.132	29.712	N/A	2895	N/A	1.549	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	17.533	49596185	1367083	92.365	95.630	N/A	5405	8.772	1.739	
2	Unknown	9	29.353	4099968	62475	7.635	4.370	N/A	4510	N/A	1.475	

Area

Supplementary Figure 48. Chiral HPLC analysis of product **5ia**.



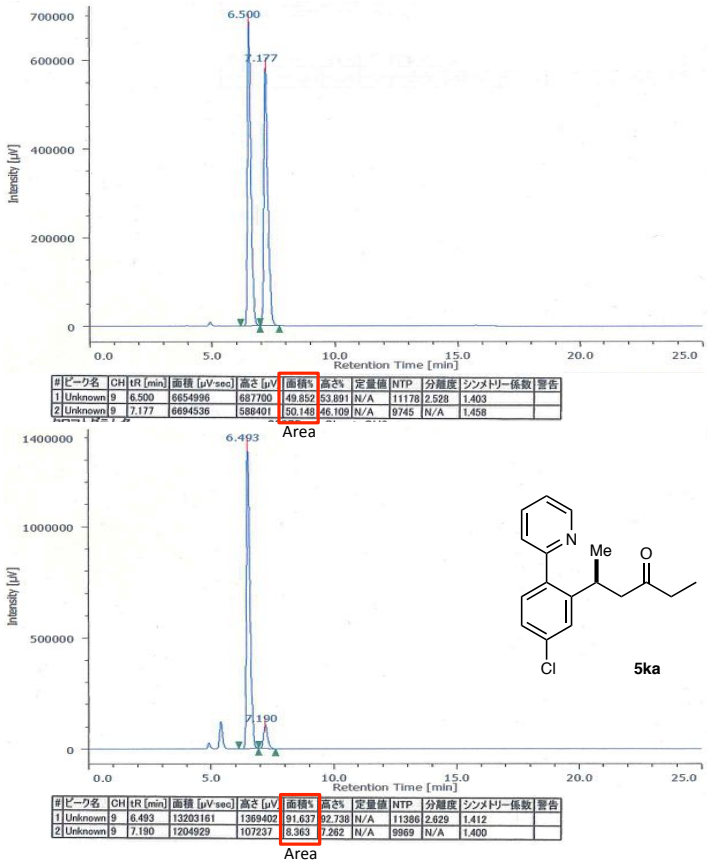
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.290	2707532	279563	49.848	55.147	N/A	10353	3.479	1.381	
2	Unknown	9	7.253	2724044	227381	50.152	44.853	N/A	8873	N/A	1.455	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.290	8031931	832777	91.647	93.094	N/A	10553	3.583	1.412	
2	Unknown	9	7.273	732024	61783	8.353	6.906	N/A	9074	N/A	1.415	

Area

Supplementary Figure 49. Chiral HPLC analysis of product **5ja**.



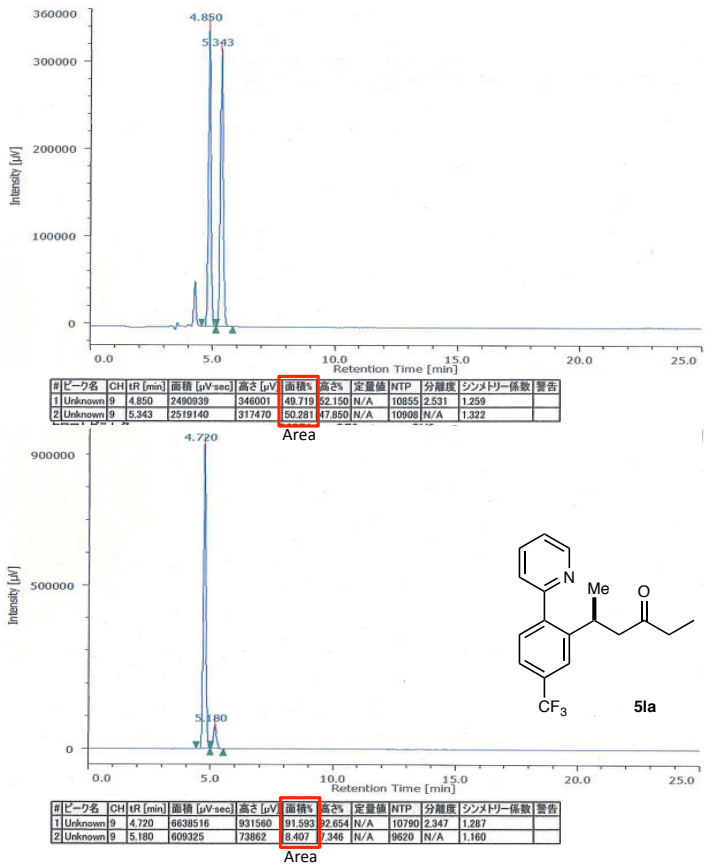
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.500	6654996	687700	49.852	53.891	N/A	11178	2.528	1.403	
2	Unknown	9	7.177	6694536	588401	50.148	46.109	N/A	9745	N/A	1.458	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	6.493	13203161	1369402	91.637	92.738	N/A	11386	2.629	1.412	
2	Unknown	9	7.190	1204929	107237	8.363	7.262	N/A	9969	N/A	1.400	

Area

Supplementary Figure 50. Chiral HPLC analysis of product **5ka**.



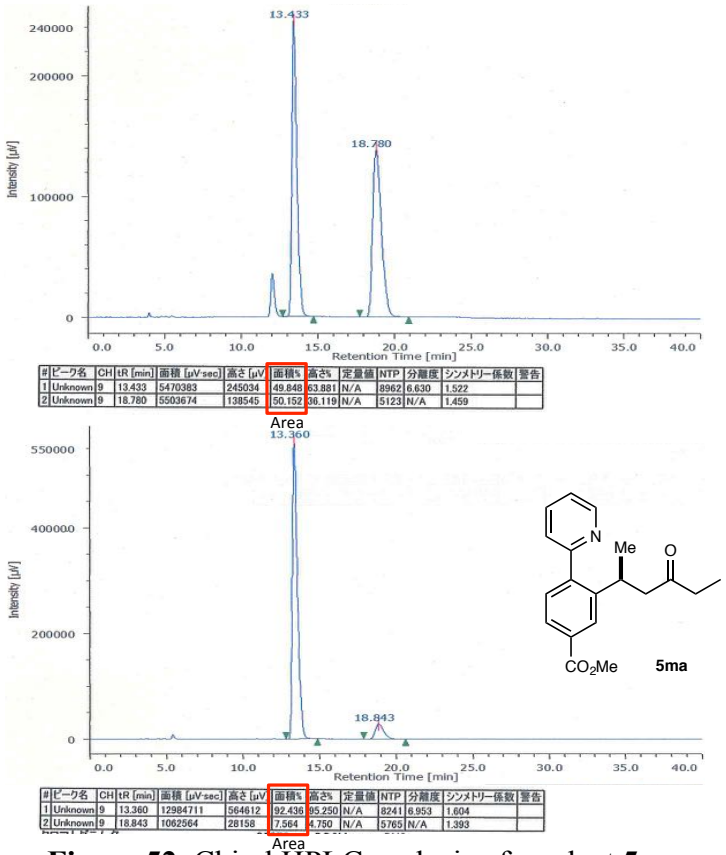
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	4.850	2490939	346001	49.719	52.150	N/A	10855	2.531	1.259	
2	Unknown	9	5.343	2519140	317470	50.281	47.850	N/A	10908	N/A	1.322	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	4.720	6638516	931560	91.593	92.654	N/A	10790	2.347	1.287	
2	Unknown	9	5.180	609325	73862	8.407	7.346	N/A	9620	N/A	1.160	

Area

Supplementary Figure 51. Chiral HPLC analysis of product **5la**.



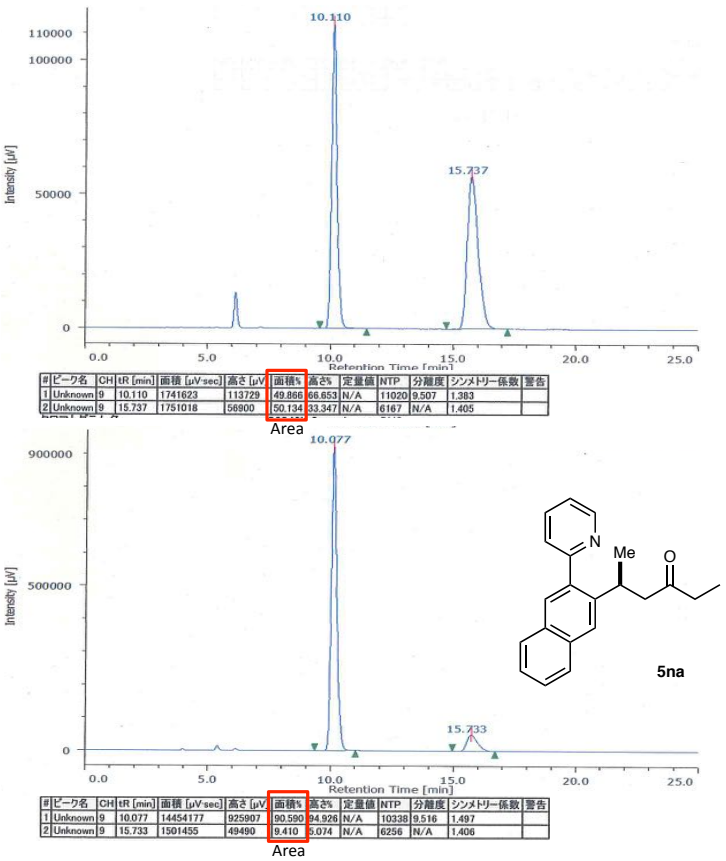
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	13.433	5470383	245034	49.848	63.881	N/A	8962	6.630	1.522	
2	Unknown	9	18.780	5503674	138545	50.152	36.119	N/A	5123	N/A	1.459	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	13.360	12984711	564612	92.436	95.250	N/A	8241	6.953	1.604	
2	Unknown	9	18.843	1062564	28158	7.564	4.750	N/A	5765	N/A	1.393	

Area

Supplementary Figure 52. Chiral HPLC analysis of product **5ma**.



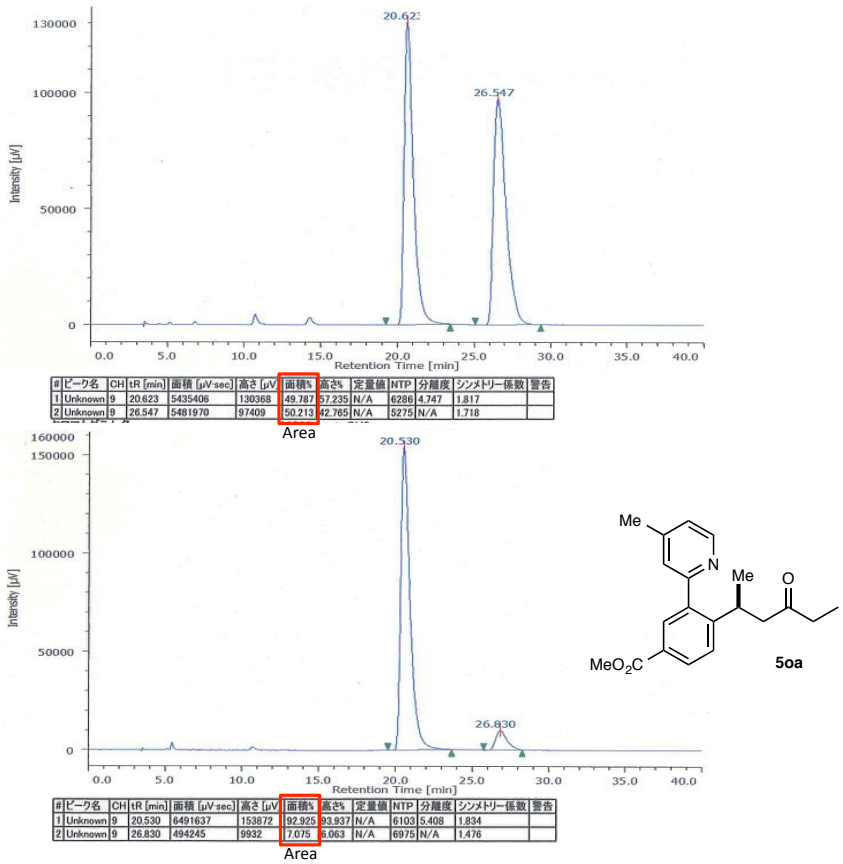
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	10.110	1741623	113729	49.866	66.653	N/A	11020	9.507	1.383	
2	Unknown	9	15.737	1751018	56900	50.134	33.347	N/A	6167	N/A	1.405	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	10.077	14454177	925907	90.590	94.926	N/A	10338	9.516	1.497	
2	Unknown	9	15.733	1501455	49490	9.410	5.074	N/A	6256	N/A	1.406	

Area

Supplementary Figure 53. Chiral HPLC analysis of product **5na**.



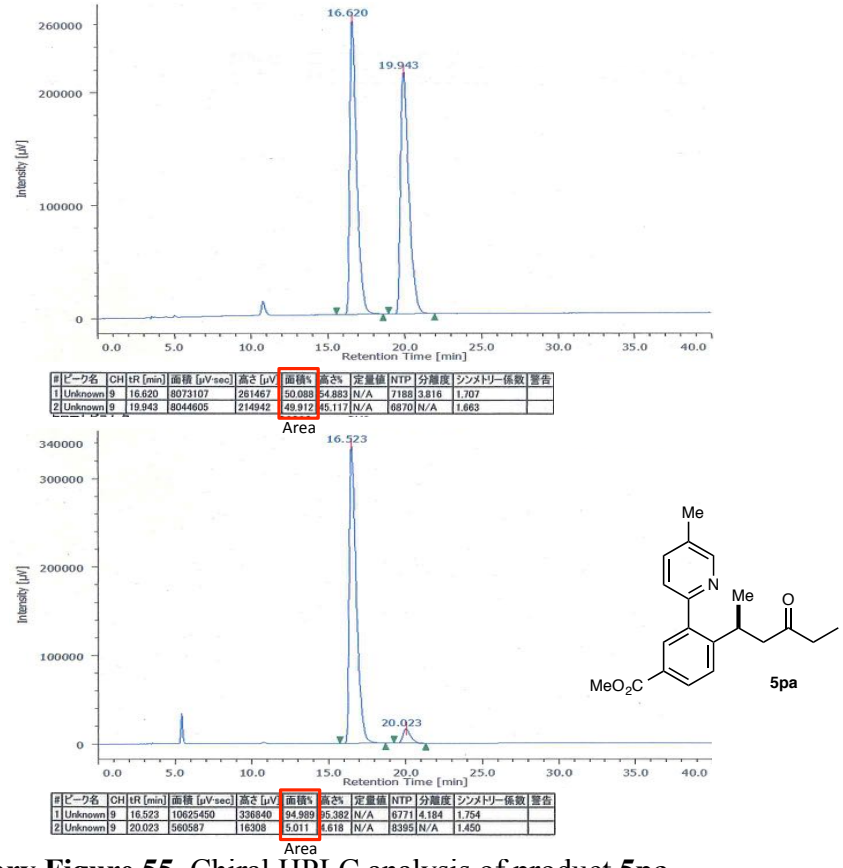
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	20.623	5435406	130368	49.787	57.235	N/A	6286	4.747	1.817	
2	Unknown	9	26.547	5481970	97409	50.213	42.765	N/A	5275	N/A	1.718	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	20.530	6491637	153872	92.925	93.937	N/A	6103	5.408	1.834	
2	Unknown	9	26.830	494245	9932	7.075	6.063	N/A	6975	N/A	1.476	

Area

Supplementary Figure 54. Chiral HPLC analysis of product **5oa**.



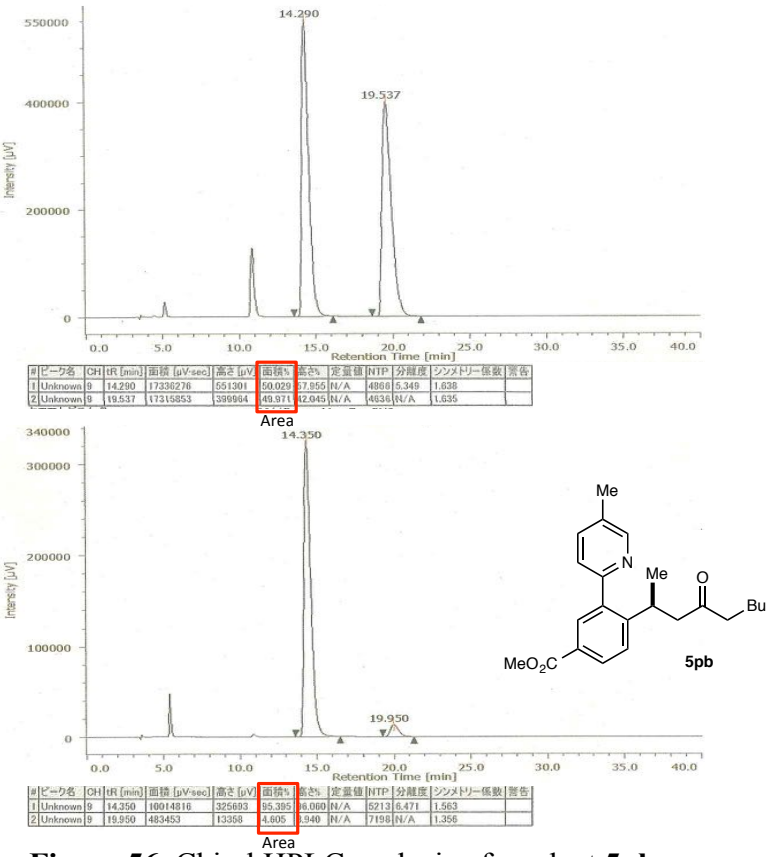
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	16.620	8073107	261467	50.088	54.883	N/A	7188	3.816	1.707	
2	Unknown	9	19.943	8044605	214942	49.912	45.117	N/A	6870	N/A	1.663	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	16.523	10625450	336840	94.989	95.382	N/A	6771	4.184	1.754	
2	Unknown	9	20.023	560587	16308	5.011	4.618	N/A	8395	N/A	1.450	

Area

Supplementary Figure 55. Chiral HPLC analysis of product **5pa**.



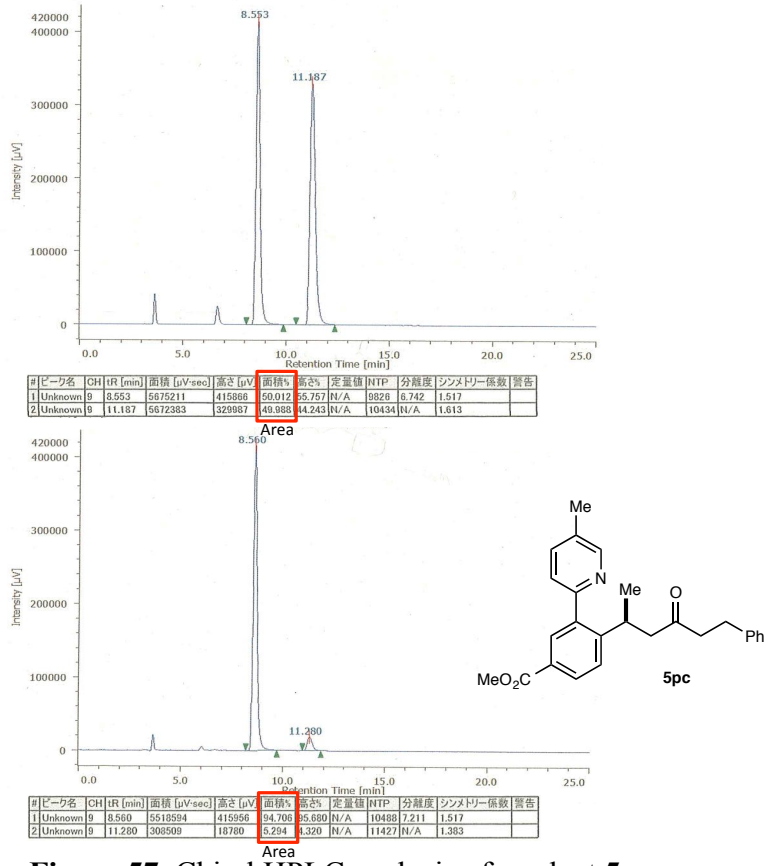
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	14.290	17336276	551301	50.029	57.955	N/A	4866	5.349	1.638	
2	Unknown	9	19.537	17315853	399964	49.971	42.045	N/A	4636	N/A	1.635	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	14.350	10014816	325693	95.395	96.060	N/A	5213	6.471	1.563	
2	Unknown	9	19.950	483453	13358	4.605	3.940	N/A	7198	N/A	1.356	

Area

Supplementary Figure 56. Chiral HPLC analysis of product **5pb**.



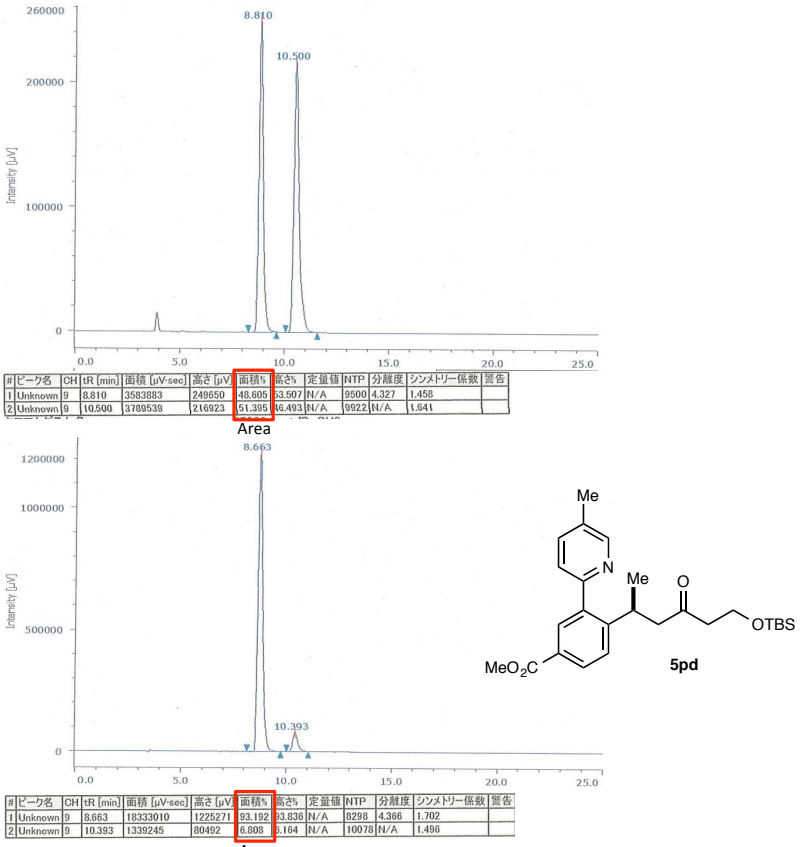
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	8.553	5675211	415866	50.012	55.757	N/A	9826	6.742	1.517	
2	Unknown	9	11.187	5672383	329987	49.988	44.243	N/A	10434	N/A	1.613	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	8.560	5518594	415956	94.706	95.680	N/A	10488	7.211	1.517	
2	Unknown	9	11.280	308509	18780	5.294	4.320	N/A	11427	N/A	1.383	

Area

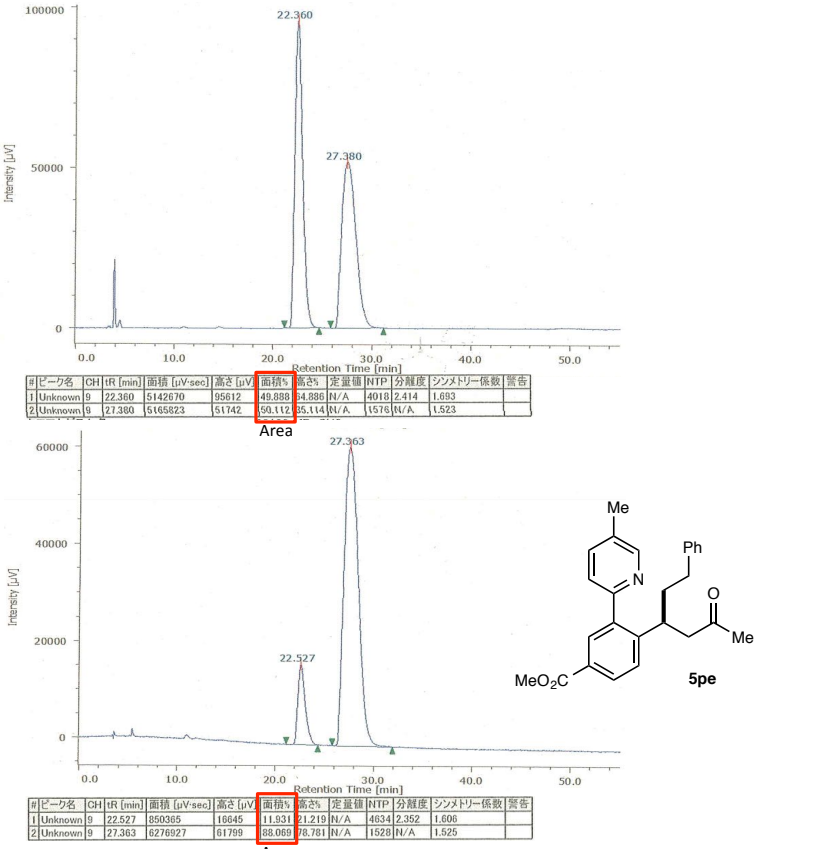
Supplementary Figure 57. Chiral HPLC analysis of product **5pc**.



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	8.810	3583883	249650	48.605	53.507	N/A	9500	4.327	1.458	
2	Unknown	9	10.500	3789538	216923	51.395	46.493	N/A	9922	N/A	1.641	

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	8.663	18333010	1225271	93.192	93.836	N/A	8298	4.366	1.702	
2	Unknown	9	10.393	1339245	80492	6.808	6.164	N/A	10078	N/A	1.496	

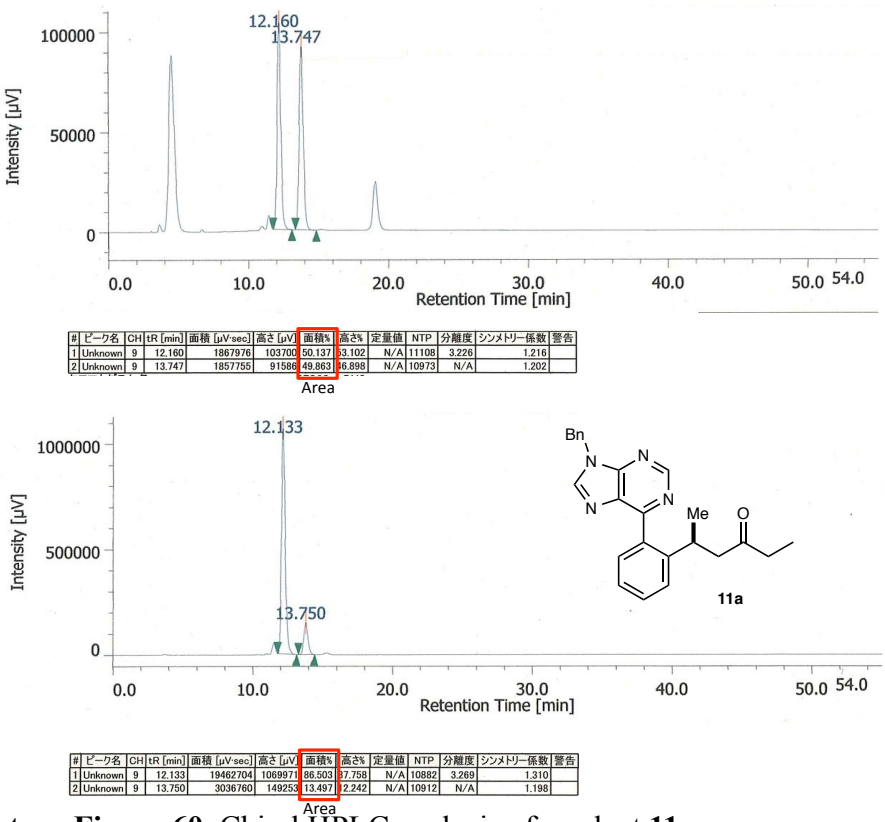
Supplementary Figure 58. Chiral HPLC analysis of product **5pd**.



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	22.360	5142670	95612	49.888	64.886	N/A	4018	2.414	1.693	
2	Unknown	9	27.380	5165823	51742	50.112	35.114	N/A	1576	N/A	1.523	

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	22.527	850365	16645	11.931	21.219	N/A	4634	2.352	1.606	
2	Unknown	9	27.363	6276927	61799	88.069	78.781	N/A	1528	N/A	1.525	

Supplementary Figure 59. Chiral HPLC analysis of product **5pe**.



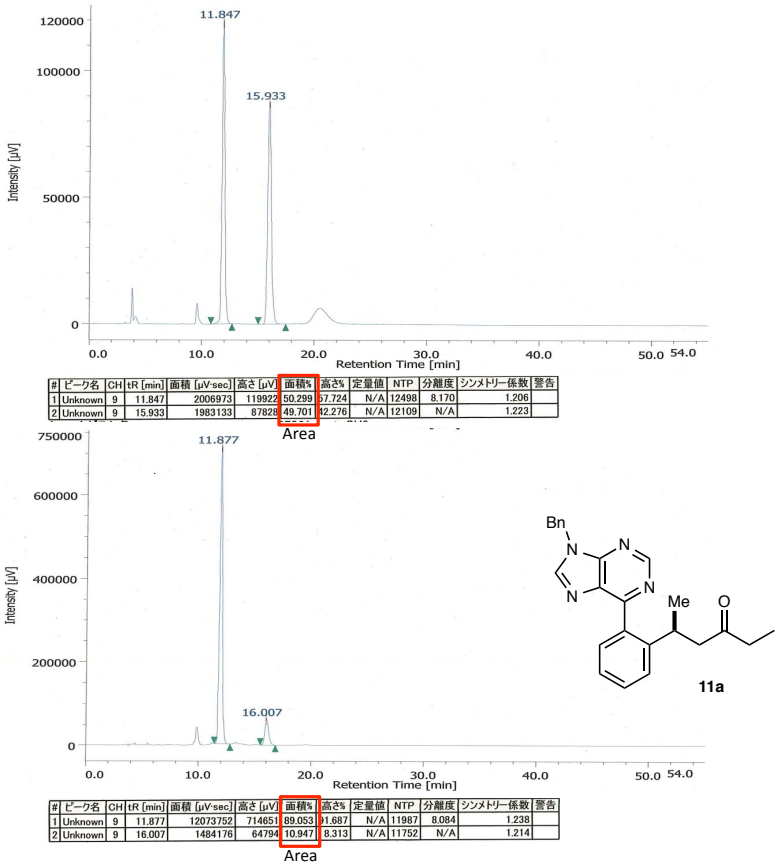
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	12.160	1867976	103700	50.137	53.102	N/A	11108	3.226	1.216	
2	Unknown	9	13.747	1857755	91586	49.863	46.898	N/A	10973	N/A	1.202	

Area

#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	12.133	19462704	1069971	86.503	87.758	N/A	10882	3.269	1.310	
2	Unknown	9	13.750	3036760	149253	13.497	12.242	N/A	10912	N/A	1.198	

Area

Supplementary Figure 60. Chiral HPLC analysis of product **11a**.



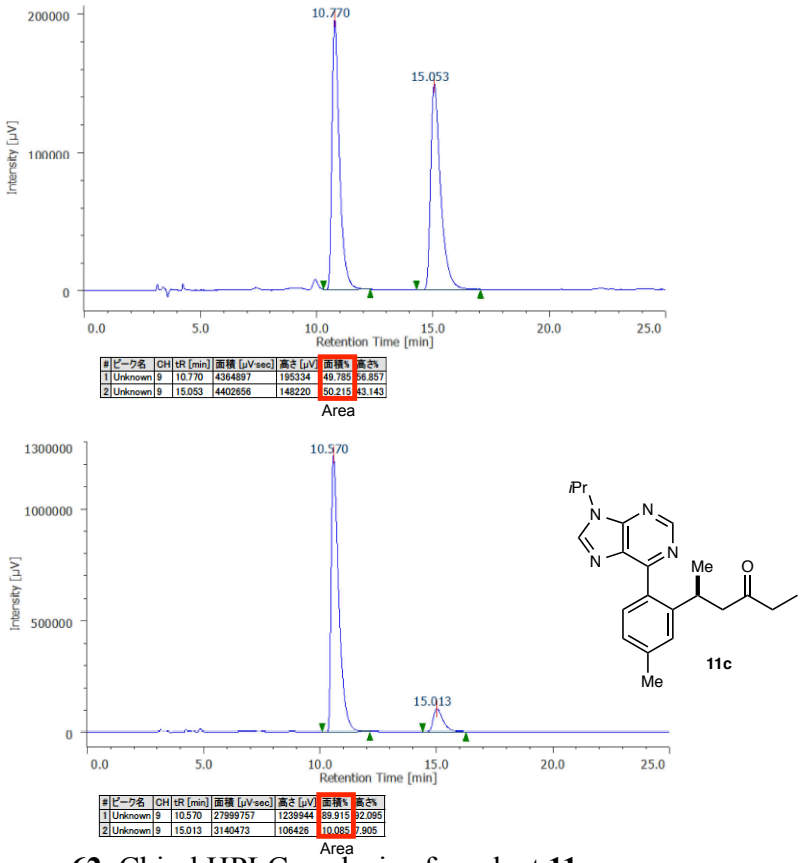
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	11.847	2006973	119922	50.299	57.724	N/A	12498	8.170	1.206	
2	Unknown	9	15.933	1983133	87828	49.701	42.276	N/A	12109	N/A	1.223	

Area

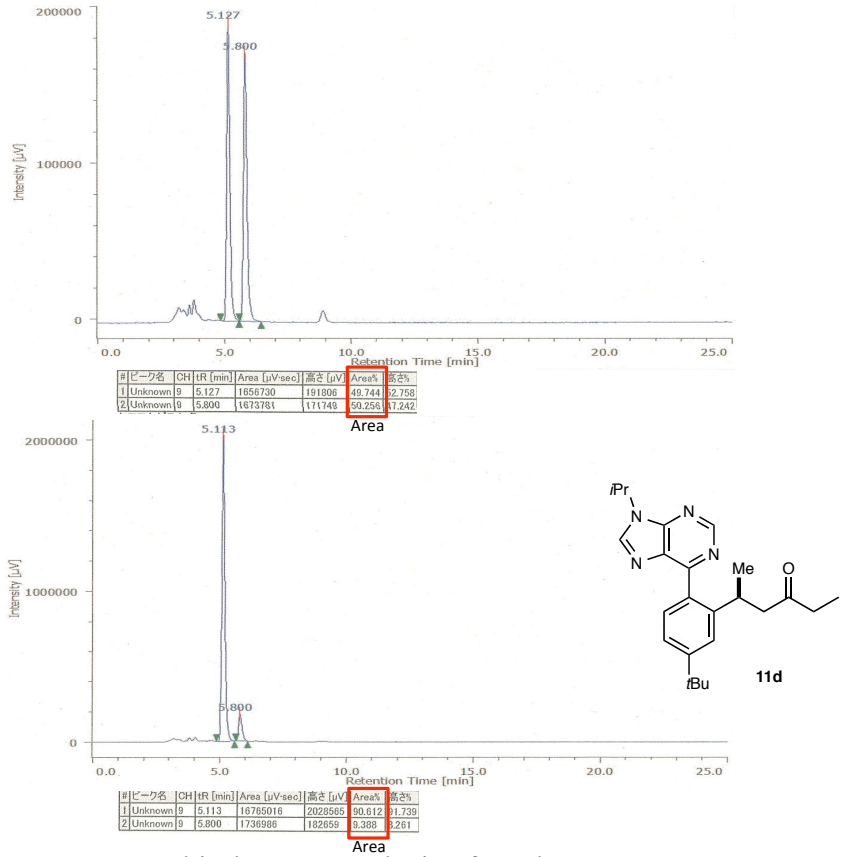
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	11.877	12073752	714651	89.053	91.687	N/A	11987	8.084	1.238	
2	Unknown	9	16.007	1484176	64794	10.947	8.313	N/A	11752	N/A	1.214	

Area

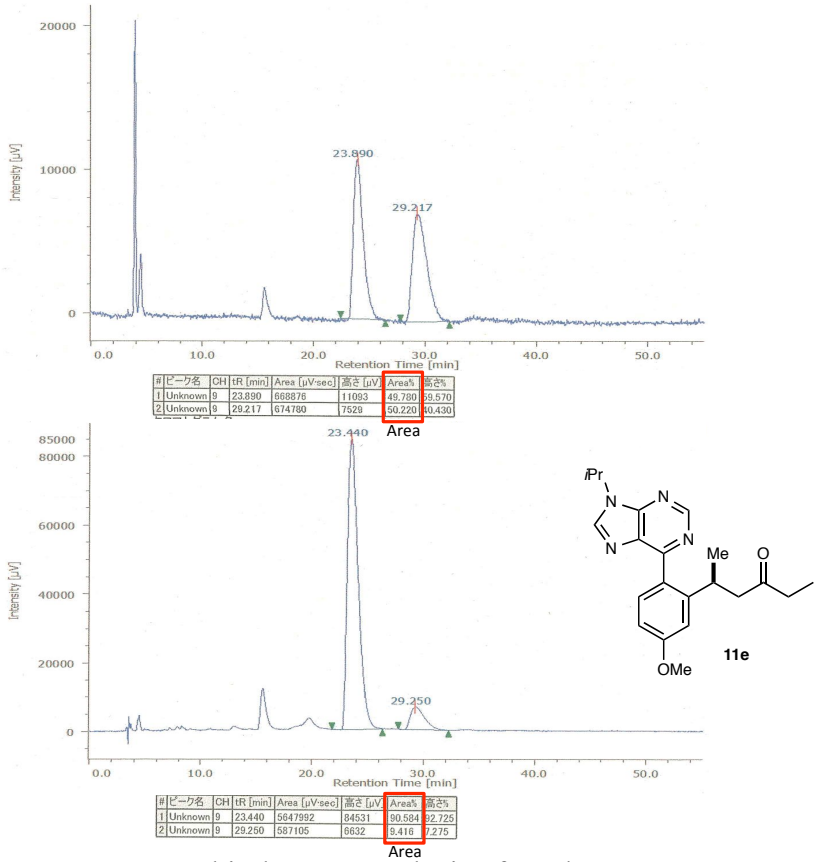
Supplementary Figure 61. Chiral HPLC analysis of product **11b**.



Supplementary Figure 62. Chiral HPLC analysis of product **11a**.



Supplementary Figure 63. Chiral HPLC analysis of product **11b**.



#	ピーク名	CH	tR [min]	Area [μV·sec]	高さ [μV]	Area%	高さ%
1	Unknown	9	23.890	668876	11093	49.780	59.570
2	Unknown	9	29.217	674780	7529	50.220	40.430

#	ピーク名	CH	tR [min]	Area [μV·sec]	高さ [μV]	Area%	高さ%
1	Unknown	9	23.440	5647992	84531	90.584	92.725
2	Unknown	9	29.250	587105	6632	9.416	7.275

Supplementary Figure 64. Chiral HPLC analysis of product **11e**.

3. Supplementary References

1. Hatano, M., Maki, T., Arinobe, M. & Ishihara, K. Pyridinium 1,1'-binaphthyl-2,2'-disulfonates as highly effective chiral Brøensted acid-base combined salt catalysts for enantioselective Mannich-type reaction. *J. Am. Chem. Soc.* **131**, 16858-16860 (2008).
2. García-García, P., Lay, F., García-García, P., Rabalakos, C. & List, B. A powerful chiral counteranion motif for asymmetric catalysis. *Angew. Chem. Int. Ed.* **48**, 4363-4366 (2009).
3. LaLonde, R. L., Wang, Z. J., Mba, M., Lackner, A. D. & Toste, F. D. Gold(I)-catalyzed enantioselective synthesis of pyrazolidines, isoxazolidines, and tetrahydrooxazines. *Angew. Chem. Int. Ed.* **49***,* 598-601 (2010).
4. White, C., Thompson, S. J. & Maitlis, P. M. Pentamethylcyclopentadienyl-rhodium and -iridium complexes. Part XII. *J. C. S. Dalton* 1654-1661 (1977).
5. Hatano, M., Ozaki, T., Nishikawa, K. & Ishihara, K. Synthesis of optically pure 3,3'-diaryl binaphthyl disulfonic acids *via* stepwise N–S bond cleavage. *J. Org. Chem.* **78**, 10405-10413 (2013).
6. Liu, C. & Yang, W. A fast and oxygen-promoted protocol for the ligand-free Suzuki reaction of 2-halogenated pyridines in aqueous media. *Chem. Commun.* 6267-6269 (2009).
7. Chinthapally, K., Massaro, N. P. & Sharma, I. Rhodium carbenoid initiated O–H insertion/aldol/oxy-Cope cascade for the stereoselective synthesis of functionalized oxacycles. *Org. Lett.* **18**, 6340-6343 (2016).
8. Terashima, M., Seki, K., Yoshida, C., Ohkura, K. & Kanaoka, Y. Photo-arylation. IV. Synthesis of 2-arylpyridines by photo-reaction of 2-iodopyridine with substituted benzenes. *Chem. Pharm. Bull.* **33**, 1009-1015 (1985).
9. Gosmini, C., Bassene-Ernst, C. & Durandetti, M. Synthesis of functionalized 2-arylpyridines from 2-halopyridines and various aryl halides via a nickel catalysis. *Tetrahedron* **65**, 6141-6146 (2009).
10. Núñez, A., Sánchez, A., Burgos, C. & Alvarez-Builla, J. Synthesis of carbo- and heterobiaryls by intermolecular radical addition of aryl bromides onto aromatic solvents. *Tetrahedron* **60**, 6217-6224 (2004).
11. Yu, M., Li, G., Wang, S. & Zhang, L. Gold-catalyzed efficient formation of α,β-unsaturated ketones from propargylic acetates. *Adv. Synth. Catal.* **349**, 871-875 (2007).
12. Trost, B. M., Ball, Z. T. & Jöge, T. A chemoselective reduction of alkynes to (*E*)-alkenes. *J. Am. Chem. Soc.* **124**, 7922-7923 (2002).
13. Tan, H., Chen, X., Zheng, C., Liu, Z. & Wang, D. Z. Total synthesis of angelone enabled by a remarkable biomimetic sequence. *Tetrahedron* **68**, 3952-3955 (2012).
14. Hon, Y.-S. & Lee, C.-F. The reaction of triphenylphosphonium or triphenylarsonium salts with aldehyde: effect of the counteranion on their reactivity. *Tetrahedron* **56**, 7893-7902 (2000).

15. Dong, Z., Karpowicz, Jr, R. J., Bai, S., Yap, G. P. A. & Fox, J. M. Control of absolute helicity in single-stranded abiotic metallofoldamers. *J. Am. Chem. Soc.* **128**, 14242-14243 (2006).
16. Hamilton G. L., Kang E. J., Mba M. & Toste F. D. A powerful chiral counterion strategy for asymmetric transition metal catalysis. *Science* **317**, 496-499 (2007).
17. Havelková, M., Dvořák, D. & Hocek, M. The Suzuki–Miyaura cross-coupling reaction of 2-, 6- or 8-halopurines with boronic acid leading to 2-, 6- or 8-aryl- and -alkenylpurine derivatives. *Synthesis* 1704-1710 (2001).
18. Kurihara, T., Satake, S., Hatano, M., Ishihara, K., Yoshino, T. & Matsunaga, S. Synthesis of 1,1'-spirobiindane-7,7'-disulfonic acid and disulfonimide: application for catalytic asymmetric aminalization. *Chem. Asian. J.* DOI: 10.11002/asia.201800341.