Electronic Supplementary Information

Asymmetric dual catalysis via fragmentation of a single rhodium precursor complex

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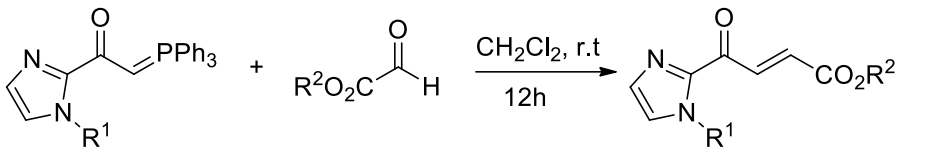
Contents

1. General Information

All reactions were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Solvents were distilled under argon from calcium hydride (CH_3CN, CH_2Cl_2) or sodium/benzophenone (THF, toluene). Rhodium complex *rac*-**Rh2** and Δ-**Rh2**,[1] Wittig reagents **S1a-c**,[2] glyoxylates **S2a** and **S2c-d**,[3,4] α,α-disubstituted aldehydes **3b-j**[5] and α, β-unsaturated acyl imidazole **2b-c**[6,7] were prepared according to published procedures. All other reagents were purchased from Acros, Aldrich, Alfa and J&K, and used without further purification. Column chromatography was performed with silica gel (300-400 mesh, Yantai Jiangyou Silica Gel Development Co., Ltd). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM (400 MHz) or a Bruker AM (500 MHz) spectrometer at ambient temperature. NMR standards were used as follows: $CDCl_3$ = 7.26 ppm (^1H NMR), 77.0 ppm (^{13}C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0T FT-MS instrument using ESI technique. Optical rotations were measured on an Anton Paar MCP 500 polarimeter at concentrations of 1.0 g/100 mL. Enantioselectivities were determined by chiral HPLC and diastereoselectivities were determined by ^1H NMR.

2. Synthesis of the Substrates and Racemic Products

2.1 Synthesis of α,β-Unsaturated Acyl Imidazoles



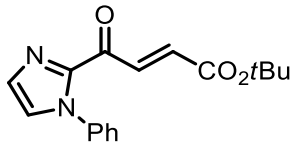
S1a (R^1 = Ph)
S1b (R^1 = Me)
S1c (R^1 = *i*Pr)

S2a (R^2 = *t*Bu)
S2b (R^2 = Et)
S2c (R^2 = Me)
S2d (R^2 = *i*Pr)

2a (R^1 = Ph, R^2 = *t*Bu)
2b (R^1 = Me, R^2 = Et)
2c (R^1 = *i*Pr, R^2 = Et)
2d (R^1 = Ph, R^2 = Et)
2e (R^1 = Ph, R^2 = Me)
2f (R^1 = Ph, R^2 = *i*Pr)

General Procedure. The α,β-unsaturated acyl imidazole substrates **2a-f** were synthesized following published methods.[6,7] Accordingly, to a solution of **S1a-c** (5.0 mmol) in CH_2Cl_2 (25 mL) was added corresponding glyoxylate **S2a-d** (6.0 mmol). The reaction was stirred for 12 hours at room temperature. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 5:1 to 3:1) to afford **2a-f**.

(*E*)-*tert*-butyl 4-oxo-4-(1-phenyl-1*H*-imidazol-2-yl)but-2-enoate (2a)



Following the general procedure, reaction of Wittig reagent **S1a** (2.23 g, 5.0 mmol) and *tert*-butyl glyoxylate **S2a** (0.781 g, 6.0 mmol) afforded **2a** as a pale yellow solid (1.07 g, 3.59 mmol, yield: 72%).

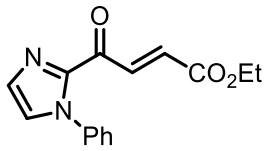
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 15.9 Hz, 1H), 7.48 (t, J = 3.2 Hz, 3H), 7.37 (d, J = 0.5 Hz, 1H), 7.34-7.28 (m, 2H), 7.25 (d, J = 0.6 Hz, 1H), 6.78 (d, J = 15.8 Hz, 1H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 164.6, 143.2, 138.0, 136.0, 134.0, 130.5, 129.1, 129.0, 128.0, 125.8, 81.7, 28.0.

IR (film) ν_{max}: 2918, 2850, 1716, 1673, 1631, 1492, 1446, 1404, 1369, 1306, 1149, 1042, 974, 858, 764, 737, 692, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{17}H_{18}N_2O_3Na$ $(M+Na)^+$: 321.1210, found: 321.1211.

(*E*)-ethyl 4-oxo-4-(1-phenyl-1*H*-imidazol-2-yl)but-2-enoate (2d)



Following the general procedure, reaction of Wittig reagent **S1a** (2.23 g, 5.0 mmol) and ethyl glyoxylate **S2b** (0.613 g, 6.0 mmol) afforded **2d** as a pale yellow solid (1.06 g, 3.92 mmol, yield: 78%).

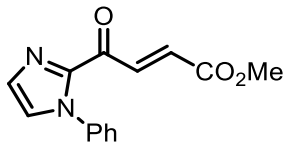
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 15.9 Hz, 1H), 7.49 (t, J = 3.1 Hz, 3H), 7.38 (s, 1H), 7.31 (q, J = 2.8 Hz, 2H), 7.27 (s, 1H), 6.85 (d, J = 15.8 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H) 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.1, 165.4, 143.2, 138.0, 136.9, 131.8, 130.6, 129.1, 129.0, 128.1, 125.8, 61.2, 14.1.

IR (film) ν_{max}: 2917, 2849, 2283, 1720, 1673, 1492, 1445, 1402, 1299, 1040, 762, 691, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{15}H_{14}N_2O_3Na$ $(M+Na)^+$: 293.0897, found: 293.0899.

(*E*)-methyl 4-oxo-4-(1-phenyl-1*H*-imidazol-2-yl)but-2-enoate (2e)



Following the general procedure, reaction of Wittig reagent **S1a** (2.23 g, 5.0 mmol) and methyl glyoxylate **S2c** (0.528 g, 6.0 mmol) afforded **2e** as a pale yellow solid (0.961 g, 3.75 mmol, yield: 75%).

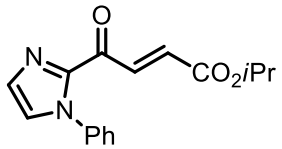
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 15.9 Hz, 1H), 7.49 (s, 3H), 7.38 (s, 1H), 7.31 (d, J = 3.1 Hz, 2H), 7.27 (s, 1H), 6.85 (d, J = 15.9 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 165.8, 143.1, 137.9, 137.2, 131.2, 130.6, 129.1, 129.0, 128.2, 125.8, 52.2.

IR (film) ν_{max}: 2918, 2849, 1725, 1699, 1668, 1631, 1557, 1538, 1493, 1444, 1401, 1301, 1213, 1169, 1155, 1088, 1043, 974, 914, 804, 756, 701, 689, 678, 557, 523 cm^{-1}.

HRMS (ESI) calcd for $C_{14}H_{12}N_2O_3Na$ $(M+Na)^+$: 279.0740, found: 279.0744.

(*E*)-isopropyl 4-oxo-4-(1-phenyl-1*H*-imidazol-2-yl)but-2-enoate (2f)



Following the general procedure, reaction of Wittig reagent **S1a** (2.23 g, 5.0 mmol) and isopropyl glyoxylate **S2d** (0.697 g, 6.0 mmol) afforded **2f** as a pale yellow solid (0.995 g, 3.50 mmol, yield: 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 15.9 Hz, 1H), 7.49 (t, J = 3.1 Hz, 3H), 7.38 (s, 1H), 7.31

(q, *J* = 2.7 Hz, 2H), 7.27 (s, 1H), 6.83 (d, *J* = 15.9 Hz, 1H), 5.22-5.06 (m, 1H), 1.30 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 164.9, 143.2, 138.0, 136.6, 132.5, 130.5, 129.1, 129.0, 128.1, 125.8, 68.8, 21.7.

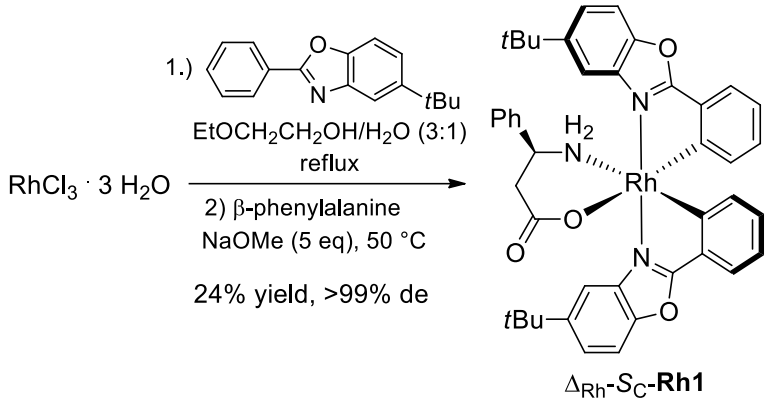
IR (film) ν_{max}: 2917, 2849, 1716, 1673, 1492, 1445, 1402, 1295, 1042, 762, 691, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{16}H_{16}N_2O_3Na$ $(M+Na)^+$: 307.1053, found: 307.1050.

2.2 Synthesis of the Racemic Products as HPLC References

General Procedure. To a solution of **2a-f** (0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) was added the racemic rhodium complex *rac*-**Rh2** (1.66 mg, 0.0020 mmol) in a glass vial. After being stirred at room temperature for 30 min, **3a-p** (0.30 mmol) and *N*-methylbenzylamine (0.020 mmol) were added. The reaction mixture was stirred at 20 °C for 12 h. After evaporation of the volatile organic solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 5:1 to 3:1) to afford the racemic products *rac*-**4a-u** as HPLC reference for the determination of enantiomeric excess in the asymmetric reaction.

3. Synthesis of Rhodium Catalyst Δ_{Rh}-S_C-Rh1



Δ_{Rh}-S_C-**Rh1**

Compound Δ_{Rh}-S_C-Rh1.[1] 5-*tert*-butyl-2-phenylbenzo[*d*]oxazole (1.030 g, 4.1 mmol) was added to $RhCl_3 \cdot 3H_2O$ (418.5 mg, 2.0 mmol) in a mixture of 2-ethoxyethanol and water (3:1, 92.0 mL). The reaction mixture was heated at 120 °C for 24 h under an atmosphere of argon. The resulting precipitate was collected by centrifugation, washed with methanol and dried to obtain the rhodium dimer (779.62 mg, 0.61 mmol, yield: 61%) as a pale yellow solid.

Subsequently, to a solution of NaOMe (40.5 mg, 0.75 mmol) in MeOH (16.0 mL), (*S*)-3-amino-3-phenylpropanoic acid (49.6 mg, 0.30 mmol) was added in one portion. The mixture was stirred for 30 min, to which rhodium dimer (201.3 mg, 0.150 mmol) was added. The mixture was stirred and heated at 50 °C for 12 h to give a clear, yellow solution. The solvent was removed in *vacuo* and the mixture of two diastereoisomers was washed with CH_2Cl_2/Et_2O (1:20, v/v) until the filtrate was almost colorless. The residual insoluble solid was dissolved in CH_2Cl_2. After filtering, the filtrate was dried and collected as Δ_{Rh}-S_C-**Rh1** (92.1 mg, 0.117 mmol, yield: 39%). The total yield in two steps is 24%. The absolute configuration of the rhodium (III) complex was assigned as Δ_{Rh}-S_C by its X-ray crystal structure.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 1.4 Hz, 1H), 7.78 (d, J = 6.8 Hz, 1H), 7.72 (d, J = 6.8 Hz,

1H), 7.67 (q, *J* = 5.2 Hz, 2H), 7.60 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.54 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.27 (s, 1H), 7.17 (q, *J* = 12.2 Hz, 3H), 7.05-6.95 (m, 2H), 6.93-6.84 (m, 2H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.36 (d, *J* = 7.7 Hz, 1H), 4.82 (t, *J* = 12.2 Hz, 1H), 3.63 (d, *J* = 10.9 Hz, 1H), 2.88 (d, *J* = 16.9 Hz, 1H), 2.55 (t, *J* = 12.5 Hz, 1H), 2.42 (q, *J* = 11.3 Hz, 1H), 1.40 (s, 9H), 1.18 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3, 172.4, 171.2, 166.4, 166.2, 164.2, 163.9, 151.5, 150.0, 148.3, 143.8, 138.3, 137.7, 135.0, 133.5, 131.3, 130.6, 129.0, 128.0, 125.8, 125.7, 125.1, 123.8, 123.5, 123.1, 123.0, 115.0, 111.7, 110.7, 110.6, 56.2, 47.3, 35.5, 35.0, 31.7, 31.4.

IR (film) ν_{max}: 2923, 2852, 1736, 1659, 1589, 1524, 1449, 1428, 1383, 1261, 1088, 1037, 1015, 932, 805, 738, 557 cm^{-1}.

HRMS (ESI) calcd for $C_{43}H_{42}N_3O_4RhNa$ $(M+Na)^+$: 790.2123, found: 790.2130.

CD (MeOH): λ, nm (Δε, $M^{-1}cm^{-1}$) 391 (+46), 338 (-65), 297 (+73), 253 (-37), 230 (+10), 214 (-77), 202 (+7).

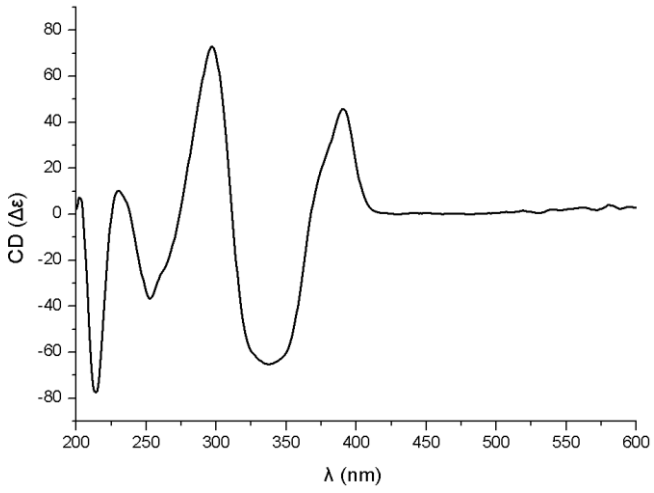


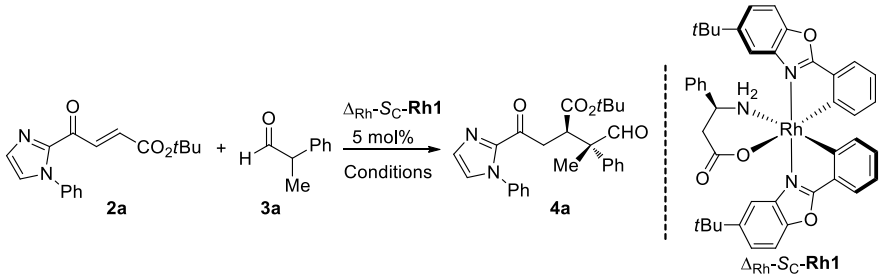
Figure S1. CD spectrum of complex Δ_{Rh}-S_C-**Rh1** recorded in CH_3OH (0.20 mM)

4. Asymmetric Michael Addition Catalyzed by Δ_{Rh}-S_C-Rh1

4.1 Optimization of the Asymmetric Michael Addition Catalyzed by Δ_{Rh}-S_C-Rh1

General Procedure. To a solution of **2a** (29.8 mg, 0.10 mmol) in the indicated solvent (0.10 mL) were added the catalyst Δ_{Rh}-S_C-**Rh1** (3.84 mg, 0.0050 mmol), the indicated additive and **3a** (0.041 mL, 0.30 mmol) stepwise. The reaction mixture was stirred for the indicated time at the indicated temperature. After evaporation of the solvent, the crude product was used directly for determination of the conversion and diastereomeric ratio by ^{1}H NMR as well as ee values by chiral HPLC.

Table S1. Conditions optimization of the asymmetric Michael-Stork addition.



Entry	Solvent	Additive	*T* (°C)	*t* (h)	Conv. (%)[a]	d.r.[a]	ee (%)[b]
1	DCE	10 mol% NH_4PF_6	50	3	>95	2.5:1	98.7/94
2	DCE	20 mol% NH_4PF_6	50	3	>95	2.7:1	99.1/94
3	DCE	40 mol% NH_4PF_6	50	3	>95	2.5:1	98.6/92
4	DCE	5 mol% TFA	50	2	>95	2.2:1	97/98
5	DCE	10 mol% TFA	50	2	>95	3.7:1	97.7/98
6	DCE	20 mol% TFA	50	2	>95	3.4:1	99.0/95
7	DCE	40 mol% TFA	50	2	>95	3.6:1	98.4/89
8	DCE	80 mol% TFA	50	2	>95	2.7:1	96/57
9	THF	40 mol% TFA	50	2	>95	2.9:1	97/97.5
10	Toluene	40 mol% TFA	50	2	>95	3.5:1	97.8/96
11	CH_3CN	40 mol% TFA	50	2	>95	2.9:1	97/85
12	MTBE	40 mol% TFA	50	2	>95	3:1	97.5/97
13	IPA	40 mol% TFA	50	2	>95	2.8:1	97.5/96
14	DCE	40 mol% TFA	20	4	>95	4.7:1	98.8/86
15	DCE	40 mol% TFA	0	14	>95	5.8:1	98.9/90
16	DCE	40 mol% TFA	-20	49.5	85	5.6:1	98.6/74

[a]Determined by ^{1}H NMR spectroscopy. [b]Determined by HPLC analysis on a chiral stationary phase. DCE = 1,2-dichloroethane, MTBE = *tert*-butyl methyl ether, IPA = isopropanol, TFA = trifluoroacetic acid.

4.2 Control Experiments

General Procedure for Table 1. To a solution of **2a** (29.8 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the indicated catalyst (0.0050 mmol) and **3a** (0.041 mL, 0.30 mmol) stepwise. The reaction mixture was stirred for the indicated time at 0 or 50 °C. After evaporation of the volatile organic solvent, the crude product was used directly for determination of the conversion and diastereomeric ratio by ^{1}H NMR as well as enantiomeric excess by chiral HPLC.

General Procedure for Table S2. To a solution of **2c** (23.6 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst Δ_{Rh}-*S*$_C$-**Rh1** with different ee values (25, 50, 75, 90 or 95% ee, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and **3a** (0.041 mL, 0.30 mmol) stepwise. The reaction mixture was stirred for the indicated time for 14 h at 0 °C. After evaporation of the volatile organic solvent, the crude product was used directly for determination of the conversion and diastereomeric ratio by ^{1}H NMR as well as enantiomeric excess by chiral HPLC.

Table S2. The relationship between ee values of Δ_{Rh}-*S*$_C$-**Rh1** and ee values of the major diastereomer of **4c**.

Entry	ee values of Δ_{Rh}-*S*$_C$-**Rh1** (%)	Conv. (%)	ee values of the major diastereomer of **4c** (%)
1	25	>95	-11
2	50	>95	-16
3	75	>95	-8
4	90	>95	48
5	95	>95	74
6	>99	>95	95

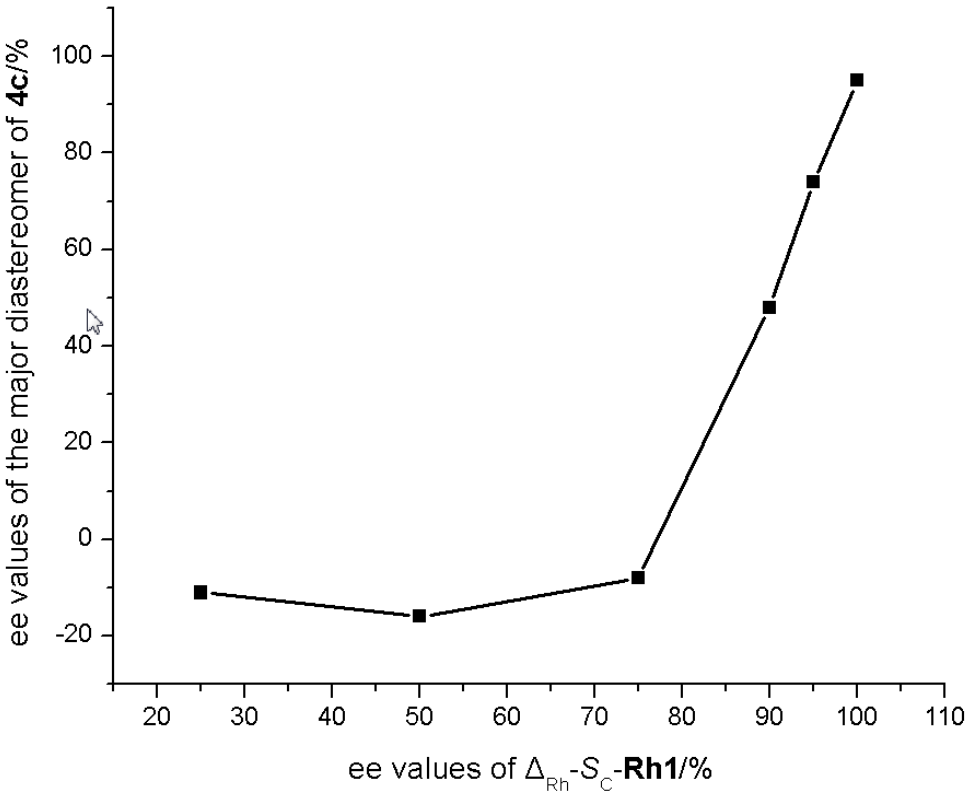
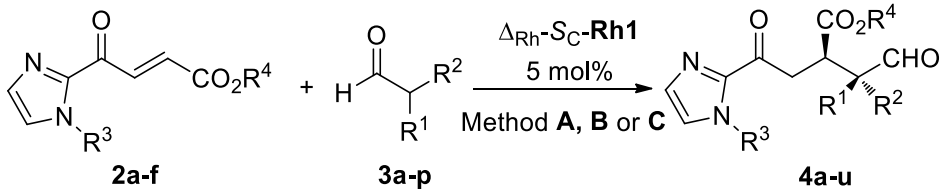


Figure S2. The relationship between ee values of Δ_{Rh}-S_C-**Rh1** and ee values of the major diastereomer of **4c**.

4.3 Substrate Scope with Δ_{Rh}-S_C-Rh1



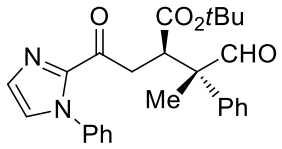
Method A. To a solution of **2a-f** (0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst Δ_{Rh}-S_C-**Rh1** (3.84 mg, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and **3a-e** or **3g-i** (0.30 mmol). The reaction mixture was stirred for 14 h at 0 °C. After evaporation of the

solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 5:1 to 3:1) to afford the product **4a-j** or **4l-n**.

Method B. To a solution of **2a** (0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst Δ_{Rh}-S_C-**Rh1** (3.84 mg, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and **3f** or **3j** (0.30 mmol). The reaction mixture was stirred for 48 h or 36 h at 20 °C. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 5:1 to 3:1) to afford the product **4k** or **4o**.

Method C. To a solution of **2a** (0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst Δ_{Rh}-S_C-**Rh1** (3.84 mg, 0.0050 mmol), NH_4PF_6 (0.010 mmol) and **3k-p** (0.30 mmol). The reaction mixture was stirred for 10 h at 20 °C. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 3:1 to 1:1) to afford the product **4p-u**.

Compound 4a



Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3a** (0.041 mL, 0.30 mmol) afforded **4a** (37.6 mg, 0.0869 mmol, yield: 87%). The diastereomeric ratio was determined as 5.8:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.9%/90% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 92:8, flow rate: 0.4 mL/min, 25 °C,

t_r(major) = 25.3 min, t_r(major) = 29.3 min, t_r(minor) = 31.6 min, t_r(minor) = 73.2 min). $[\alpha]_D^{20}$ = -127.9˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

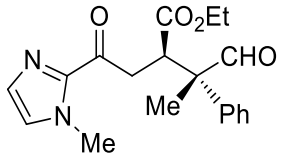
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.50-7.46 (m, 3H), 7.40-7.36 (m, 3H), 7.30-7.27 (m, 5H), 7.19 (s, 1H), 4.14 (dd, *J* = 11.4, 1.6 Hz, 1H), 3.87 (q, *J* = 11.2 Hz, 1H), 2.45 (dd, *J* = 17.8, 2.0 Hz, 1H), 1.55 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 189.0, 171.2, 142.5, 138.2, 137.2, 129.4, 129.2, 128.9, 128.8, 127.6, 127.0, 126.8, 125.8, 82.5, 55.2, 46.3, 35.5, 27.8, 13.7.

IR (film) ν_{max}: 2925, 2853, 2720, 1726, 1689, 1597, 1527, 1494, 1447, 1410, 1368, 1344, 1304, 1235, 1154, 1075, 1035, 1002, 968, 931, 914, 884, 844, 764, 697, 554, 523 cm^{-1}.

HRMS (ESI) calcd for $C_{26}H_{28}N_2O_4Na$ $(M+Na)^+$: 455.1941, found: 455.1942.

Compound 4b



Following **Method A**, reaction of **2b** (20.8 mg, 0.10 mmol) and **3a** (0.041 mL, 0.30 mmol) afforded **4b** (23.9 mg, 0.0698 mmol, yield: 70%). The diastereomeric ratio was determined as 3.9:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96%/78% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.8 mL/min, 25 °C,

t_r(major) = 24.2 min, t_r(major) = 27.6 min, t_r(minor) = 33.9 min, t_r(minor) = 49.4 min). $[\alpha]_D^{20}$ = -86.7° (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

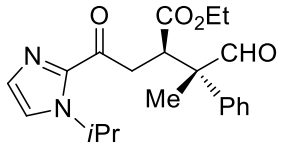
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.37 (d, *J* = 2.8 Hz, 4H), 7.26 (t, *J* = 3.6 Hz, 1H), 7.10 (s, 1H), 6.99 (s, 1H), 4.25-4.19 (m, 1H), 4.18-4.10 (m, 2H), 3.94 (s, 3H), 3.85-3.75 (m, 1H), 2.62 (dd, *J* = 18.2, 2.1 Hz, 1H), 1.54 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 190.0, 172.2, 142.2, 136.9, 129.2, 128.8, 128.7, 127.7, 127.1, 61.4, 55.1, 45.3, 36.1, 35.7, 14.0, 13.9.

IR (film) ν_{max}: 2956, 2921, 2850, 1728, 1678, 1646, 1494, 1467, 1446, 1414, 1371, 1351, 1326, 1289, 1258, 1218, 1180, 1157, 1135, 1080, 1030, 995, 915, 930, 915, 867, 767, 701, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{22}N_2O_4Na$ $(M+Na)^+$: 365.1472, found: 365.1471.

Compound 4c



<u>Reaction with 3 equivalents of 3a:</u> Following **Method A**, reaction of **2c** (23.6 mg, 0.10 mmol) and **3a** (0.041 mL, 0.30 mmol) afforded **4c** (24.4 mg, 0.0659 mmol, yield: 66%). The diastereomeric ratio was determined as 4.0:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 95%/61% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol =

93:7, flow rate: 0.4 mL/min, 25 °C, t_r(minor) = 43.0 min, t_r(major) = 51.8 min, t_r(minor) = 80.7 min, t_r(major) = 84.6 min). $[\alpha]_D^{20}$ = -94.9° (*c* 1.0, $CHCl_3$).

Reaction with 1.2 equivalents of 3a: To a solution of **2c** (23.6 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst Δ_{Rh}-S_C-**Rh1** (3.84 mg, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and **3a** (0.016 mL, 0.12 mmol). The reaction mixture was stirred for 33 h at 0 °C (Conv. > 95%). After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 5:1 to 3:1) to afford the product **4c** (21.2 mg, 0.0539 mmol, yield: 54%). The diastereomeric ratio was determined as 4.2:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 94%/44%.

Analytic data of the major diastereomer:

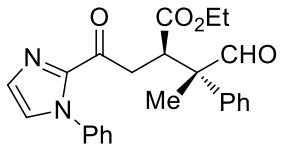
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.40-7.37 (m, 4H), 7.30-7.28 (m, 1H), 7.22 (s, 1H), 7.12 (s, 1H), 5.51-5.47 (m, 1H), 4.25-4.22 (m, 1H), 4.19-4.14 (m, 2H), 3.85-3.80 (m, 1H), 2.64 (dd, *J* = 18.0, 2.2 Hz, 1H), 1.54 (s, 3H), 1.41 (q, *J* = 6.3 Hz, 6H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 190.2, 172.3, 141.6, 136.9, 129.4, 129.2, 127.7, 127.2, 121.1, 61.3, 55.2, 49.2, 45.4, 36.2, 23.5, 23.5, 14.1, 13.9.

IR (film) ν_{max}: 2957, 2922, 2850, 1728, 1676, 1494, 1466, 1397, 1371, 1351, 1255, 1180, 1133, 1087, 1027, 986, 929, 916, 764, 700 cm^{-1}.

HRMS (ESI) calcd for $C_{21}H_{26}N_2O_4Na$ $(M+Na)^+$: 393.1785, found: 393.1785.

Compound 4d



Following **Method A**, reaction of **2d** (27.0 mg, 0.10 mmol) and **3a** (0.041 mL, 0.30 mmol) afforded **4d** (31.8 mg, 0.0786 mmol, yield: 79%). The diastereomeric ratio was determined as 3.5:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 98.0%/97% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.8 mL/min, 25 °C, t_r(major) = 19.7 min, t_r(minor) = 21.6 min, t_r(major) = 33.8 min, t_r(minor) = 39.2 min). $[\alpha]_D^{20}$ = -111.7˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

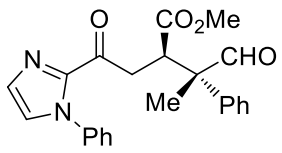
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.50-7.45 (m, 3H), 7.40-7.35 (m, 3H), 7.30-7.26 (m, 5H), 7.14 (s, 1H), 4.20-4.10 (m, 3H), 3.87 (q, *J* = 6.7 Hz, 1H), 2.55 (dd, *J* = 18.0, 1.6 Hz, 1H), 1.52 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 188.6, 172.1, 142.2, 138.0, 136.8, 129.4, 129.3, 128.9, 128.7, 127.7, 127.6, 127.1, 125.8, 61.4, 55.1, 45.2, 35.6, 14.0, 13.9.

IR (film) ν_{max}: 2955, 2919, 2850, 2934, 1730, 1687, 1493, 1467, 1409, 1377, 1304, 1039, 967 cm^{-1}.

HRMS (ESI) calcd for $C_{24}H_{24}N_2O_4Na$ $(M+Na)^+$: 427.1628, found: 427.1628.

Compound 4e



Following **Method A**, reaction of **2e** (25.6 mg, 0.10 mmol) and **3a** (0.041 mL, 0.30 mmol) afforded **4e** (37.3 mg, 0.0955 mmol, yield: 96%). The diastereomeric ratio was determined as 3.8:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 98.0%/95% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 60:40, flow rate: 0.8 mL/min, 25 °C, t_r(minor) = 17.5 min, t_r(major) = 21.1 min, t_r(major) = 26.3 min, t_r(minor) = 41.2 min). $[\alpha]_D^{20}$ = -133.5˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

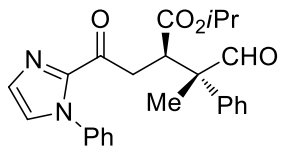
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.50-7.47 (m, 3H), 7.40-7.37 (m, 3H), 7.30-7.26 (m, 5H), 7.16 (s, 1H), 4.20 (dd, *J* = 11.2, 1.7 Hz, 1H), 3.87 (q, *J* = 11.3 Hz, 1H), 3.65 (s, 3H), 2.63 (dd, *J* = 18.2, 2.0 Hz, 1H), 1.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 188.5, 172.6, 142.2, 138.0, 136.8, 129.4, 129.3, 129.0, 128.9, 127.8, 127.4, 127.1, 125.8, 55.2, 52.0, 45.2, 35.9, 14.1.

IR (film) ν_{max}: 2955, 2918, 2850, 1732, 1687, 1494, 1467, 1410, 1377, 1040 cm^{-1}.

HRMS (ESI) calcd for $C_{23}H_{22}N_2O_4Na$ $(M+Na)^+$: 413.1472, found: 413.1474.

Compound 4f



Following **Method A**, reaction of **2f** (28.4 mg, 0.10 mmol) and **3a** (0.041 mL, 0.30 mmol) afforded **4f** (35.2 mg, 0.0841 mmol, yield: 84%). The diastereomeric ratio was determined as 3.9:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 98.1%/93% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate: 1 mL/min, 25 °C, t_r(major) = 18.9 min, t_r(minor) = 22.8 min, t_r(major) = 35.4 min, t_r(minor) = 64.1 min). $[\alpha]_D^{20}$ = -129.3˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

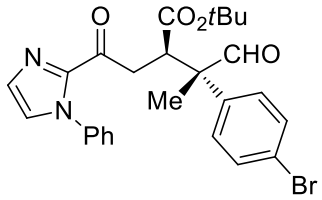
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.50-7.46 (m, 3H), 7.40-7.36 (m, 3H), 7.30-7.27 (m, 5H), 7.16 (d, *J* = 1.0 Hz, 1H), 5.02-4.98 (m, 1H), 4.17 (dd, *J* = 11.3, 2.2 Hz, 1H), 3.90 (q, *J* = 11.3 Hz, 1H), 2.54 (dd, *J* = 18.0, 2.3 Hz, 1H), 1.55 (s, 3H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 188.8, 171.6, 142.4, 138.1, 137.1, 129.4, 129.3, 128.9, 128.8, 128.7, 127.7, 127.1, 125.8, 69.4, 55.2, 45.5, 35.7, 21.6, 21.4, 14.0.

IR (film) ν_{max}: 2956, 2924, 2852, 1727, 1689, 1597, 1494, 1447, 1410, 1375, 1341, 1304, 1261, 1224, 1180, 1147, 1107, 1075, 1036, 1002, 968, 931, 914, 871, 767, 698, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{25}H_{26}N_2O_4Na$ $(M+Na)^+$: 441.1785, found: 441.1787.

Compound 4g



Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3b** (64.0 mg, 0.30 mmol) afforded **4g** (50.6 mg, 0.0990 mmol, yield: 99%). The diastereomeric ratio was determined as 5.4:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.7%/93% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 92:8, flow rate: 0.4 mL/min, 25 °C, t_r(major) = 21.5 min, t_r(major) = 25.8 min, t_r(minor) = 35.5 min, t_r(minor) = 51.9 min). $[\alpha]_D^{20}$ = -136.5˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

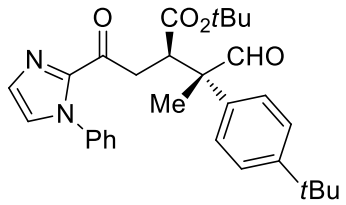
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.50-7.46 (m, 5H), 7.30-7.24 (m, 5H), 7.16-7.15 (m, 1H), 4.07 (dd, *J* = 11.1, 2.2 Hz, 1H), 3.84 (q, *J* = 11.1 Hz, 1H), 2.42 (dd, *J* = 17.8, 2.3 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.2, 188.7, 170.9, 142.3, 138.1, 136.3, 132.3, 129.7, 129.5, 128.9, 128.8, 127.0, 125.8, 122.0, 82.7, 54.9, 46.1, 35.4, 27.8, 13.8.

IR (film) ν_{max}: 2922, 2851, 1726, 1688, 1597, 1493, 1448, 1410, 1368, 1344, 1304, 1235, 1153, 1038, 1008, 968, 914, 766, 693, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{26}H_{27}BrN_2O_4Na$ $(M+Na)^+$: 533.1046, found: 533.1049.

Compound 4h



Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3c** (57.1 mg, 0.30 mmol) afforded **4h** (45.7 mg, 0.0935 mmol, yield: 94%). The diastereomeric ratio was determined as 2.5:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97%/95% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.5 mL/min, 25 °C, t_r(major) = 11.2 min, t_r(major) = 12.2 min, t_r(minor) = 16.5 min, t_r(minor) = 22.5 min). $[\alpha]_D^{20}$ = -115.6˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

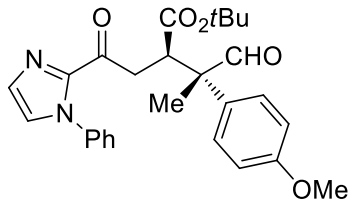
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.46-7.41 (m, 3H), 7.37-7.34 (m, 2H), 7.27-7.20 (m, 5H), 7.14 (s, 1H), 4.12 (d, *J* = 11.5 Hz, 1H), 3.85 (q, *J* = 11.7 Hz, 1H), 2.46 (dd, *J* = 17.7, 1.7 Hz, 1H), 1.50 (s, 3H), 1.38 (s, 9H), 1.27 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 189.3, 171.4, 150.5, 142.5, 138.2, 133.8, 129.4, 128.9, 128.7, 127.7, 126.7, 126.2, 125.7, 82.4, 54.8, 46.2, 34.4, 31.2, 27.8, 22.6, 13.6.

IR (film) ν_{max}: 2962, 2927, 2869, 1726, 1689, 1597, 1505, 1494, 1447, 1410, 1367, 1345, 1304, 1270, 1234, 1155, 1116, 1074, 1036, 1021, 1002, 968, 914, 885, 844, 766, 6932, 579 cm^{-1}.

HRMS (ESI) calcd for $C_{30}H_{36}N_2O_4Na$ $(M+Na)^+$: 511.2567, found: 511.2569.

Compound 4i



Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3d** (49.3 mg, 0.30 mmol) afforded **4i** (41.5 mg, 0.0897 mmol, yield: 90%). The diastereomeric ratio was determined as 4.7:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.6%/95% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 93:7, flow rate: 0.6 mL/min, 25 °C, t_r(major) = 23.6 min, t_r(major) = 28.3 min, t_r(minor) = 30.5 min, t_r(minor) = 47.2 min). $[\alpha]_D^{20}$ = -166.1˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

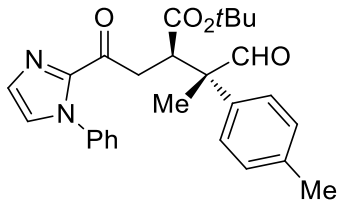
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.45-7.42 (m, 3H), 7.28-7.23 (m, 5H), 7.14 (s, 1H), 6.89-6.84 (m, 2H), 4.08-4.05 (m, 1H), 3.87-3.80 (m, 1H), 3.76 (s, 3H), 2.46 (dd, *J* = 17.9, 1.9 Hz, 1H), 1.49 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5, 189.1, 171.3, 158.9, 142.4, 138.1, 129.4, 129.2, 128.9, 128.8, 128.2, 126.8, 125.7, 114.6, 82.4, 55.2, 54.5, 46.2, 35.4, 27.8, 13.8.

IR (film) ν_{max}: 2956, 2922, 2850, 1724, 1688, 1608, 1513, 1494, 1447, 1410, 1368, 1344, 1303, 1255, 1186, 1154, 1075, 1033, 1002, 968, 914, 884, 844, 830, 768, 731, 695, 549 cm^{-1}.

HRMS (ESI) calcd for $C_{27}H_{30}N_2O_5Na$ $(M+Na)^+$: 485.2047, found: 485.2051.

Compound 4j



Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3e** (44.5 mg, 0.30 mmol) afforded **4j** (39.8 mg, 0.0891 mmol, yield: 89%). The diastereomeric ratio was determined as 5.5:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.8%/94% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 93:7, flow rate: 0.6 mL/min, 25 °C, t_r(major) = 14.0 min, t_r(major) = 16.7 min, t_r(minor) = 20.9 min, t_r(minor) = 30.4 min). $[\alpha]_D^{20}$ = -142.9˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

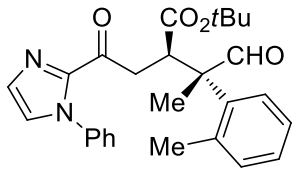
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.45-7.41 (m, 3H), 7.28-7.20 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 4H), 4.14-4.08 (m, 1H), 3.83 (q, *J* = 11.5 Hz, 1H), 2.44 (d, *J* = 17.8 Hz, 1H), 2.29 (s, 3H), 1.49 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 189.1, 171.3, 142.4, 138.1, 137.4, 134.0, 130.0, 129.3, 128.9, 128.8, 126.9, 126.8, 125.8, 82.4, 54.8, 46.2, 35.5, 27.8, 20.9, 13.7.

IR (film) ν_{max}: 2924, 2852, 1725, 1689, 1597, 1494, 1448, 1410, 1368, 1344, 1304, 1235, 1154, 1038, 1002, 968, 914, 845, 813, 767, 722, 694, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{27}H_{30}N_2O_4Na$ $(M+Na)^+$: 469.2098, found: 469.2101.

Compound 4k



Following **Method B**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3f** (44.5 mg, 0.30 mmol) afforded **4k** (31.5 mg, 0.0705 mmol, yield: 71%). The diastereomeric ratio was determined as 2.3:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IB column, ee = 89%/86% (HPLC: IB, 254 nm, *n*-hexane/isopropanol = 92:8, flow rate: 0.4 mL/min, 25 °C, t_r(major) = 19.8 min, t_r(major) = 21.3 min, t_r(minor) = 23.8 min, t_r(minor) = 26.6 min). $[\alpha]_D^{20}$ = -89.5˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

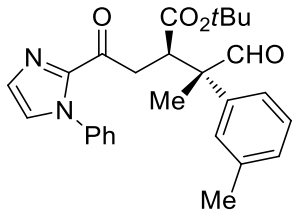
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.43-7.40 (m, 5H), 7.33-7.23 (m, 3H), 7.18-7.09 (m, 3H), 4.18 (dd, *J* = 11.2, 2.1 Hz, 1H), 3.82-3.75 (m, 1H), 2.48 (dd, *J* = 17.5, 2.2 Hz, 1H), 2.38 (s, 3H), 1.57 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.3, 189.1, 171.8,, 142.6, 138.2, 137.4, 136.4, 132.8, 129.6, 128.8, 128.7, 128.2, 127.8, 126.8, 126.5, 125.7, 82.0, 55.8, 44.9, 36.7, 27.8, 23.1, 17.5.

IR (film) ν_{max}: 2925, 2853, 1722, 1689, 1597, 1493, 1447, 1409, 1368, 1345, 1304, 1256, 1233, 1152, 1037, 1002, 967, 914, 845, 762, 727, 693, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{27}H_{30}N_2O_4Na$ $(M+Na)^+$: 469.2098, found: 469.2098.

Compound 4l



Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3g** (44.5 mg, 0.30 mmol) afforded **4l** (38.9 mg, 0.0871 mmol, yield: 87%). The diastereomeric ratio was determined as 3.4:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97.8%/97.6% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 92:8, flow rate: 0.5 mL/min, 25 °C, t_r(major) = 16.0 min, t_r(major) = 18.0 min, t_r(minor) = 20.4 min, t_r(minor) = 44.7 min). $[\alpha]_D^{20}$ = -141.4° (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

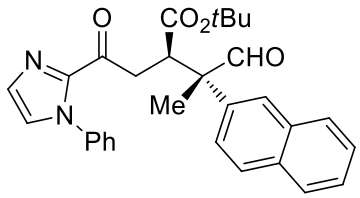
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.45-7.41 (m, 3H), 7.27-7.20 (m, 4H), 7.13 (s, 2H), 7.10-7.04 (m, 2H), 4.11 (d, *J* = 11.1 Hz, 1H), 3.85 (q, *J* = 11.4 Hz, 1H), 2.44 (d, *J* = 17.8 Hz, 1H), 2.31 (s, 3H), 1.50 (s, 3H), 1.38 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 189.2, 171.3, 142.6, 138.9, 138.2, 137.0, 129.5, 129.0, 128.9, 128.7, 128.3, 127.7, 126.8, 125.7, 124.0, 82.4, 55.0, 46.3, 35.4, 27.8, 21.6, 13.6.

IR (film) ν_{max}: 2925, 2853, 1727, 1689, 1598, 1493, 1448, 1410, 1368, 1344, 1304, 1233, 1154, 1075, 1036, 1022, 1002, 968, 930, 914, 844, 765, 694 cm^{-1}.

HRMS (ESI) calcd for $C_{27}H_{30}N_2O_4Na$ $(M+Na)^+$: 469.2098, found: 469.2097.

Compound 4m



Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3h** (56.0 mg, 0.30 mmol) afforded **4m** (47.8 mg, 0.0991 mmol, yield: 99%). The diastereomeric ratio was determined as 3.8:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.3%/95% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 92:8, flow rate: 0.7 mL/min, 25 °C, t_r(major) = 16.4 min, t_r(major) = 20.8 min, t_r(minor) = 24.7 min, t_r(minor) = 28.9 min). $[\alpha]_D^{20}$ = -169.8˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

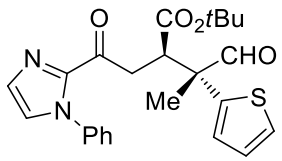
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.84-7.76 (m, 4H), 7.50-7.46 (m, 3H), 7.44-7.40 (m, 3H), 7.20-7.18 (m, 3H), 7.09 (d, *J* = 0.9 Hz, 1H), 4.26 (dd, *J* = 11.2, 2.3 Hz, 1H), 3.91-3.84 (m, 1H), 2.46 (dd, *J* = 17.9, 2.4 Hz, 1H), 1.65 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 188.9, 171.2, 142.3, 138.1, 134.6, 133.4, 132.3, 129.3, 129.0, 128.9, 128.8, 128.1, 127.4, 126.8, 126.7, 126.5, 126.5, 125.7, 124.1, 82.5, 55.2, 46.3, 35.6, 27.8, 13.9.

IR (film) ν_{max}: 2924, 2852, 1725, 1689, 1597, 1494, 1448, 1410, 1368, 1344, 1304, 1235, 1154, 1037, 1002, 968, 914, 894, 843, 817, 758, 694, 522, 478 cm^{-1}.

HRMS (ESI) calcd for $C_{30}H_{30}N_2O_4Na$ $(M+Na)^+$: 505.2098, found: 505.2100.

Compound 4n



Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3i** (43.0 mg, 0.30 mmol) afforded **4n** (32.3 mg, 0.0737 mmol, yield: 74%). The diastereomeric ratio was determined as 3.7:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.9%/98.5% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 92:8, flow rate: 0.5 mL/min, 25 °C, t_r(major) = 25.3 min, t_r(major) = 26.7 min, t_r(minor) = 29.3 min, t_r(minor) = 42.8 min). $[\alpha]_D^{20}$ = -132.8˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

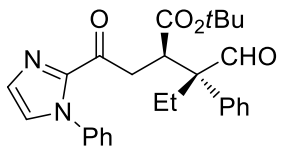
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.45-7.43 (m, 3H), 7.29-7.25 (m, 4H), 7.16 (s, 1H), 7.02-6.97 (m, 1H), 6.93 (d, *J* = 3.0 Hz, 1H), 3.98-3.90 (m, 2H), 2.67 (d, *J* = 15.3 Hz, 1H), 1.56 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.7, 188.9, 170.4, 142.5, 141.6, 138.1, 129.5, 128.9, 128.8, 127.7, 126.9, 126.3, 125.8, 125.7, 82.7, 54.4, 47.1, 35.5, 27.8, 15.0.

IR (film) ν_{max}: 2923, 2851, 1728, 1689, 1597, 1494, 1448, 1410, 1368, 1344, 1304, 1236, 1153, 1076, 1036, 1002, 968, 914, 884, 844, 767, 695, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{24}H_{26}N_2O_4SNa$ $(M+Na)^+$: 461.1505, found: 461.1507.

Compound 4o



Following **Method B**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3j** (44.5 mg, 0.30 mmol) afforded **4o** (40.8 mg, 0.0915 mmol, yield: 92%). The diastereomeric ratio was determined as 2.0:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IA column, ee = 96%/85% (HPLC: IA, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.4 mL/min, 25 °C, t_r(major) = 38.7 min, t_r(major) = 39.6 min, t_r(minor) = 51.7 min, t_r(minor) = 55.7 min). $[\alpha]_D^{20}$ = -57.0˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

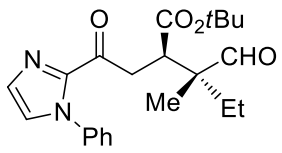
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.44-7.38 (m, 4H), 7.29-7.22 (m, 7H), 7.14 (s, 1H), 3.87-3.73 (m, 2H), 3.00 (dd, *J* = 17.7, 2.0 Hz, 1H), 2.11-1.94 (m, 2H), 1.29 (s, 9H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 188.9, 171.7, 142.4, 138.1, 137.0, 129.4, 128.9, 128.7, 128.6, 128.1, 127.5, 126.8, 125.8, 81.6, 58.5, 44.7, 37.4, 27.7, 24.6, 9.0.

IR (film) ν_{max}: 2964, 2925, 2852, 1723, 1689, 1597, 1494, 1447, 1409, 1368, 1304, 1256, 1231, 1153, 1038, 1002, 966, 914, 886, 846, 762, 701, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{27}H_{30}N_2O_4Na$ $(M+Na)^+$: 469.2098, found: 469.2099.

Compound 4p



Following **Method C**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3k** (0.033 mL, 0.30 mmol) afforded **4p** (35.9 mg, 0.0935 mmol, yield: 94%). The diastereomeric ratio was determined as 2.1:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.4%/97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.4 mL/min, 25 °C, t_r(major) = 28.4 min, t_r(minor) = 29.6 min, t_r(minor) = 33.7 min, t_r(major) = 36.2 min). $[\alpha]_D^{20}$ = -59.0˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

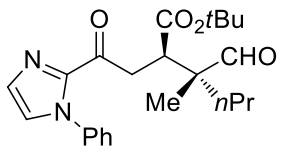
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.44-7.41 (m, 3H), 7.28-7.25 (m, 3H), 7.20 (s, 1H), 3.81 (q, *J* = 11.1 Hz, 1H), 3.41 (dd, *J* = 11.2, 3.0 Hz, 1H), 3.00 (dd, *J* = 17.7, 3.1 Hz, 1H), 1.63-1.54 (m, 2H), 1.33 (s, 9H), 1.03 (s, 3H), 0.81 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.0, 189.3, 171.7, 142.7, 138.2, 129.6, 128.9, 128.7, 126.9, 125.7, 82.0, 50.6, 45.5, 35.1, 27.8, 27.7, 14.1, 8.2.

IR (film) ν_{max}: 2955, 2918, 2850, 1726, 1691, 1494, 1467, 1410, 1367, 1153, 1041, 967, 764, 556 cm^{-1}.

HRMS (ESI) calcd for $C_{22}H_{28}N_2O_4Na$ $(M+Na)^+$: 407.1941, found: 407.1943.

Compound 4q



Following **Method C**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3l** (0.037 mL, 0.30 mmol) afforded **4q** (38.3 mg, 0.0961 mmol, yield: 96%). The diastereomeric ratio was determined as 1.8:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.3%/98.8% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 94:6, flow rate: 0.5 mL/min, 25 °C, t_r(major) = 18.0 min, t_r(minor) = 19.9 min, t_r(minor) = 21.0 min, t_r(major) = 22.7 min). $[\alpha]_D^{20}$ = -55.1˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

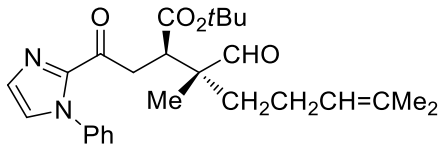
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.44-7.43 (m, 3H), 7.29-7.26 (m, 3H), 7.20 (s, 1H), 3.83 (q, *J* = 11.2 Hz, 1H), 3.40 (dd, *J* = 11.2, 2.6 Hz, 1H), 3.00 (dd, *J* = 17.7, 2.7 Hz, 1H), 1.50-1.46 (m, 2H), 1.33 (s, 9H), 1.04 (s, 3H), 0.90-0.84 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.1, 189.3, 171.6, 142.7, 138.2, 129.6, 128.9, 128.7, 126.9, 125.7, 82.0, 50.5, 45.6, 37.5, 35.2, 27.7, 17.0, 14.6, 14.6.

IR (film) ν_{max}: 2960, 2924, 2851, 1724, 1689, 1597, 1494, 1447, 1410, 1367, 1304, 1250, 1229, 1149, 1039, 967, 914, 846, 765, 692, 522 cm^{-1}.

HRMS (ESI) calcd for $C_{23}H_{30}N_2O_4Na$ $(M+Na)^+$: 421.2098, found: 421.2099.

Compound 4r



Following **Method C**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3m** (0.0480 mL, 0.30 mmol) afforded (41.6 mg, 0.0949 mmol, yield: 95%). The diastereomeric ratio was determined as 1.8:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.4%/99.3% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 88:12, flow rate: 0.2 mL/min, 25 °C, t_r(major) = 28.8 min, t_r(minor) = 31.8 min, t_r(minor) = 32.7 min, t_r(major) = 34.9 min). $[\alpha]_D^{20}$ = -39.8˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

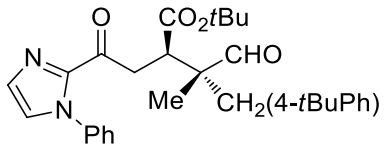
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.44-7.43 (m, 3H), 7.29-7.25 (m, 3H), 7.19 (s, 1H), 5.04-4.95 (m, 1H), 3.82 (q, *J* = 11.1 Hz, 1H), 3.41 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.01 (dd, *J* = 17.7, 2.9 Hz, 1H), 2.01-1.87 (m, 3H), 1.81-1.73 (m, 1H), 1.64 (s, 3H), 1.53 (s, 3H), 1.33 (s, 9H), 1.06 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 189.2, 171.5, 142.7, 138.2, 132.5, 129.6, 128.9, 128.7, 126.9, 125.7, 123.2, 82.0, 50.4, 45.7, 35.2, 35.2, 27.7, 25.6, 22.4, 17.6, 14.4.

IR (film) ν_{max}: 2922, 2851, 1722, 1689, 1645, 1598, 1494, 1447, 1409, 1367, 1344, 1304, 1244, 1150, 1074, 1038, 1021, 1001, 966, 914, 845, 764, 692 cm^{-1}.

HRMS (ESI) calcd for $C_{26}H_{34}N_2O_4Na$ $(M+Na)^+$: 461.2411, found: 461.2412.

Compound 4s



Following **Method C**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3n** (0.0650 mL, 0.30 mmol) afforded **4s** (48.9 mg, 0.0973 mmol, yield: 97%). The diastereomeric ratio was determined as 2.7:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 99.2%/23% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate: 1 mL/min, 25 °C, t_r(major) = 31.2 min, t_r(major) = 40.4 min, t_r(minor) = 49.2 min, t_r(minor) = 85.7 min). $[\alpha]_D^{20}$ = -61.3˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

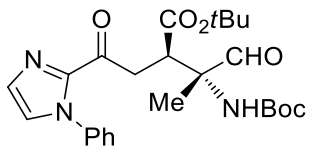
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.44-7.43 (m, 3H), 7.30-7.25 (m, 5H), 7.20 (s, 1H), 6.97 (d *J* = 8.0 Hz, 2H), 3.91 (q, *J* = 11.0 Hz, 1H), 3.46 (dd, *J* = 11.0, 2.6 Hz, 1H), 3.28-3.22 (m, 1H), 2.94 (d, *J* = 13.8 Hz, 1H), 2.74 (d, *J* = 13.7 Hz, 1H), 1.33 (s, 9H), 1.27 (s, 9H), 1.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.0, 189.0, 171.6, 149.6, 142.7, 138.1, 132.2, 130.2, 130.0, 129.7, 128.9, 126.9, 125.7, 125.2, 82.1, 51.4, 45.6, 40.7, 35.6, 34.3, 31.2, 27.7, 15.1.

IR (film) ν_{max}: 2962, 2927, 2869, 2720, 1725, 1690, 1598, 1494, 1448, 1410, 1367, 1345, 1305, 1246, 1152, 1110, 1074, 1036, 1021, 1002, 967, 914, 874, 844, 803, 766, 693, 571, 524 cm^{-1}.

HRMS (ESI) calcd for $C_{31}H_{38}N_2O_4Na$ $(M+Na)^+$: 525.2724, found: 525.2720.

Compound 4t



Following **Method C**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3o** (52.0 mg, 0.30 mmol) afforded **4t** (46.7 mg, 0.0990 mmol, yield: 99%). The diastereomeric ratio was determined as 4.2:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 98.2%/97% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 93:7, flow rate: 0.8 mL/min, 25 °C, t_r(minor) = 22.7 min, t_r(major) = 27.0 min, t_r(major) = 31.6 min, t_r(minor) = 58.0 min). $[\alpha]_D^{20}$ = -38.3˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

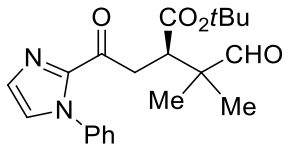
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.44-7.40 (m, 3H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.25-7.23 (m, 2H), 7.17 (d, *J* = 0.7 Hz, 1H), 5.94 (s, 1H), 3.73-3.67 (m, 1H), 3.35-3.31 (m, 1H), 3.26-3.19 (m, 1H), 1.43 (s, 3H), 1.43 (s, 9H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 188.2, 170.7, 154.7, 142.3, 138.1, 129.7, 128.9, 128.7, 127.0, 125.8, 82.5, 61.9, 44.9, 36.7, 28.2, 27.8, 22.6, 14.1.

IR (film) ν_{max}: 3390, 2976, 2927, 2854, 1716, 1695, 1598, 1494, 1449, 1411, 1393, 1368, 1305, 1259, 1157, 1057, 1036, 967, 914, 845, 802, 761, 693, 521 cm^{-1}.

HRMS (ESI) calcd for $C_{25}H_{33}N_3O_6Na$ $(M+Na)^+$: 494.2262, found: 494.2260.

Compound 4u



Following **Method C**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3p** (52.0 mg, 0.30 mmol) afforded **4u** (30.3 mg, 0.0820 mmol, yield: 82%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.2% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.7 mL/min, 25 °C, t_r(minor) = 11.8 min, t_r(major) = 13.9 min). $[\alpha]_D^{20}$ = -49.5˚ (*c* 1.0, $CHCl_3$).

Analytic data of the major diastereomer:

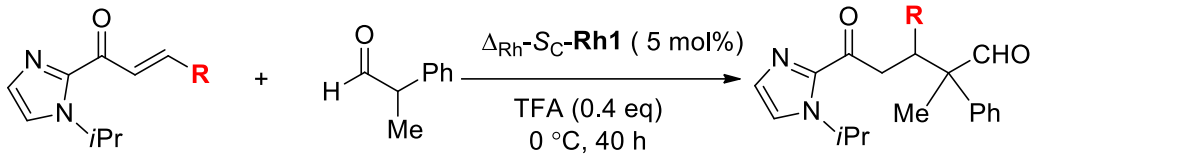
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.40-7.32 (m, 3H), 7.24-7.16 (m, 3H), 7.12 (s, 1H), 3.73 (q, *J* = 11.1 Hz, 1H), 3.22 (d, *J* =8.8 Hz, 1H), 2.95 (d, *J* = 16.0 Hz, 1H), 1.27 (s, 9H), 1.00 (d, *J* = 3.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 189.1, 171.5, 142.6, 138.1, 129.6, 128.9, 128.7, 126.9, 125.7, 81.8, 47.3, 45.9, 35.6, 27.7, 20.5, 17.7.

IR (film) ν_{max}: 2974, 2923, 1725, 1689, 1641, 1597, 1547, 1493, 1447, 1410, 1368, 1305, 1260, 1146, 1086, 1038, 966, 914, 846, 801, 768, 693, 523 cm^{-1}.

HRMS (ESI) calcd for $C_{21}H_{26}N_2O_4Na$ $(M+Na)^+$: 393.1785, found: 393.1780.

Additional Substrates with Different β-Substituents on α,β-Unsaturated Acyl Imidazoles

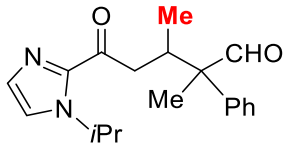


2g (R = Me);
2h (R = Ph).

3a

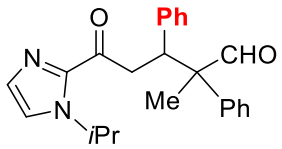
4w (R = Me), <5% Conv.
4v (R = Ph), 11% Yield, 8.3:1 d.r., 7%/66% ee

Compound 4v



To a solution of **2g** (17.8 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst Δ$_{Rh}$-*S*$_C$-**Rh1** (3.84 mg, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and **3a** (0.041 mL, 0.30 mmol). The reaction mixture was stirred for 40 h at 0 °C. After evaporation of the volatile organic solvent, the crude product was used directly for determination of the conversion by ^{1}H NMR (Conv. < 5%).

Compound 4w



To a solution of **2h** (24.0 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst Δ$_{Rh}$-*S*$_C$-**Rh1** (3.84 mg, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and **3a** (0.041 mL, 0.30 mmol). The reaction mixture was stirred for 40 h at 0 °C (Conv. < 20%). After

evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 5:1 to 3:1) to afford the product **4w** (4.1 mg, 0.011 mmol, yield: 11%). The diastereomeric ratio was determined as 8.3:1 by ^{1}H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 7%/60% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 94:6, flow rate: 0.7 mL/min, 25 °C, t_r(major) = 13.7 min, t_r(minor) = 15.1 min, t_r(minor) = 17.4 min, t_r(major) = 26.5 min).

Analytic data of the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.22-7.20 (m, 1H), 7.19-7.18 (m, 1H), 7.15-7.13 (m, 1H), 7.12-7.09 (m, 1H), 7.08-7.06 (m, 3H), 6.97-6.94 (m, 3H), 6.85-6.82 (m, 2H), 5.30-5.23 (m, 1H), 4.24-4.21 (m, 1H), 4.04-3.98 (m, 1H), 3.35-3.30 (m, 1H), 1.45 (s, 3H), 1.41 (d, J = 6.6 Hz, 6H).

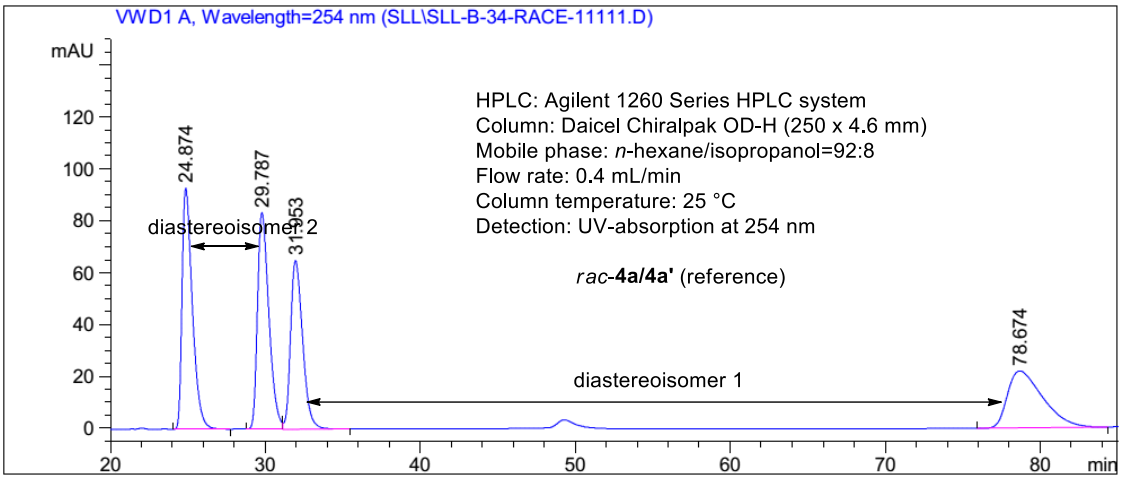
^{13}C NMR (126 MHz, $CDCl_3$) δ 202.3, 190.5, 142.4, 139.4, 139.0, 129.5, 129.3, 128.5, 127.6, 127.5, 127.2, 126.4, 121.0, 57.6, 49.0, 46.0, 40.4, 29.7, 23.3, 16.1.

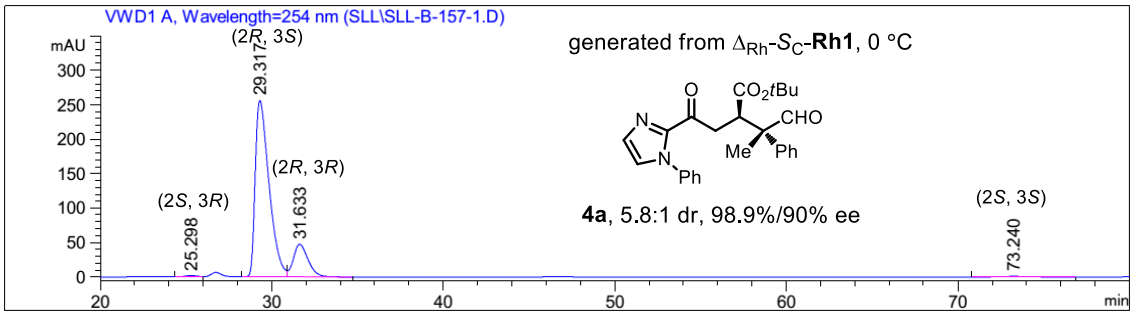
5. Stereochemical Assignment of the Products

The absolute and relative configuration of product **4a** (the major diastereomer) was assigned as 2*R*,3*S* based on single crystal X-ray diffraction of its ester derivative **6a**. Absolute and relative configuration of product **4a'** (the minor diastereomer) were assigned as 2*R*,3*R* based on single crystal X-ray diffraction of its ester derivative **6a'**. See section 6.2 for synthesis of compounds **6a** and **6a'**, and section 8 for crystallographic data of **6a** and **6a'**.

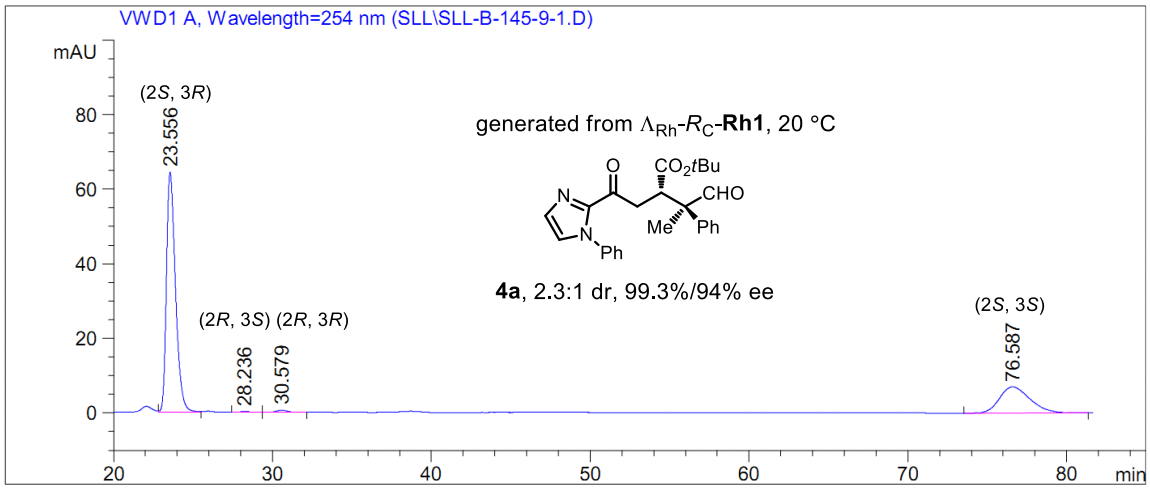
HPLC peaks were assigned according to comparison of HPLC traces of the products generated from *rac*-Rh2, Δ_{Rh}-*S*$_C$-Rh1, and Λ_{Rh}-*R*$_C$-Rh1.

Enantiomeric excess of the compound **4a** was determined with a Daicel Chiralpak OD-H column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using *n*-hexane/isopropanol as mobile phase, the temperature was 25 °C and UV-absorption was measured at 254 nm.





#	[min]		[min]	[mAU*s]	[mAU]	%
1	25.298	BV	0.7155	82.37826	1.82887	0.4758
2	29.317	BV	0.8495	1.42716e4	255.57661	82.4309
3	31.633	VB	0.9098	2809.95361	47.11834	16.2299
4	73.240	BB	1.5857	149.48834	1.10683	0.8634

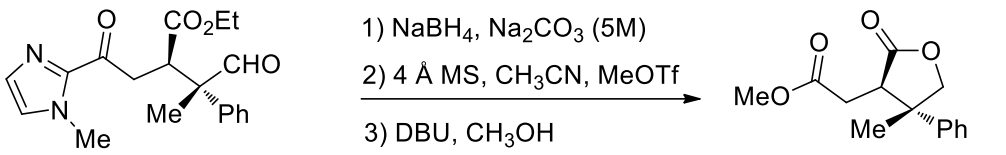


#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.556	VV	0.6067	2551.89722	64.34626	72.3667
2	28.236	BB	0.6686	9.02234	1.97649e-1	0.2559
3	30.579	BB	0.7618	28.54434	5.76318e-1	0.8095
4	76.587	BB	2.0414	936.87592	7.00013	26.5679

Figure S3. HPLC traces of *rac*-**4a**/**4a'**, (*2R*,*3S*)-**4a** generated from Δ_{Rh}-S_C-**Rh1**, and (*2S*,*3R*)-**4a** generated from Λ_{Rh}-R_C-**Rh1.**

6. Transformation of the Michael Addition Product

6.1 Transformation to a Chiral γ-Lactone



4b
single diastereomer (major)
96% ee

5b
single diastereomer
95% ee

Compound 5b.[1,8] A solution of sodium borohydride (19.0 mg, 0.502 mmol) and Na_2CO_3 (88.6 g, 0.836 mmol) in deionized water (0.167 mL) at room temperature was treated with **4b** (143 mg, 0.418 mmol, the major diastereomer of **4b** after flash chromatography, >99% de, 96% ee) in one portion. The resulting mixture was stirred for 1 h, worked up with saturated NH_4Cl solution, and extracted with ether. The extracts were dried (Na_2SO_4) and the solvent was evaporated in *vacuo*. The residue was used for the next reaction without further purification.

Subsequently, to a solution of the residue in CH_3CN (4.2 mL) was added 4 Å MS (210 mg) under argon atmosphere. The suspension was stirred vigorously under a positive pressure of argon for 2 h at room temperature, then MeOTf (0.143 mL, 1.26 mmol) was added and stirred at room temperature for 26 h. After that, methanol (1.04 mL) and DBU (0.094 mL, 0.629 mmol) were added successively at room temperature. After stirring at room temperature for 1 h, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 6:1 to 3:1) to afford **5b** (39.9 mg, 0.161 mmol, yield: 39%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 95% (HPLC: OJ, 220 nm, *n*-hexane/isopropanol = 80:20, flow rate: 1 mL/min, 25 °C, t_r(major) = 21.7 min, t_r(minor) =

24.7 min). $[\alpha]_D^{20}$ = +14.1˚ (*c* 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.44-7.40 (m, 3H), 4.24 (d, *J* = 8.9 Hz, 1H), 4.16 (d, *J* = 8.9 Hz, 1H), 3.58 (q, *J* = 3.4 Hz, 1H), 3.52 (s, 3H), 2.64 (q, *J* = 7.8 Hz, 1H), 2.38 (dd, *J* = 11.1, 5.1 Hz, 1H), 1.38 (s, 3H).

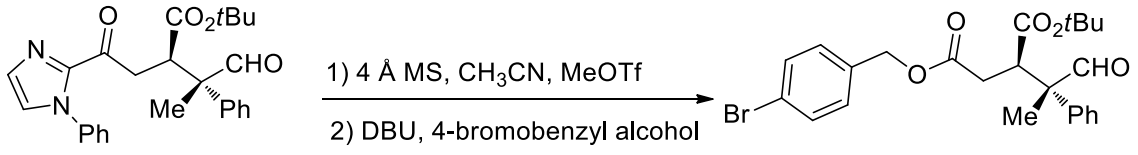
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 171.5, 141.0, 129.0, 127.6, 125.6, 78.2, 52.1, 46.5, 46.3, 29.9, 20.6.

IR (film) ν_{max}: 2959, 2923, 2852, 1769, 1731, 1462, 1377, 1260, 1095, 1017, 800 cm^{-1}.

HRMS (ESI) calcd for $C_{14}H_{16}O_4Na$ $(M+Na)^+$: 271.0941, found: 271.0944.

6.2 Transformation to Ester Derivatives 6a and 6a' for Crystallography Study

General Method. A diastereomeric mixture of **4a** and **4a'** (dr = 5.8:1, ee = 98.9%/90%) afforded in the catalytic asymmetric Michael addition was first separated by a silica gel flash chromatography. The isolated single diastereomer **4a** or **4a'** was converted to their corresponding ester derivatives through *N*-methylation of the imidazole moiety with MeOTf followed by alcoholysis.



4a
single diastereomer (major)
98.9% ee

6a
single diastereomer
82% ee

Compound 6a. To a solution of **4a** (565.5 mg, 1.306 mmol, the major diastereomer, 98.9% ee) in CH_3CN (13.1 mL) was added 4 Å MS (653 mg) under argon atmosphere. The suspension was

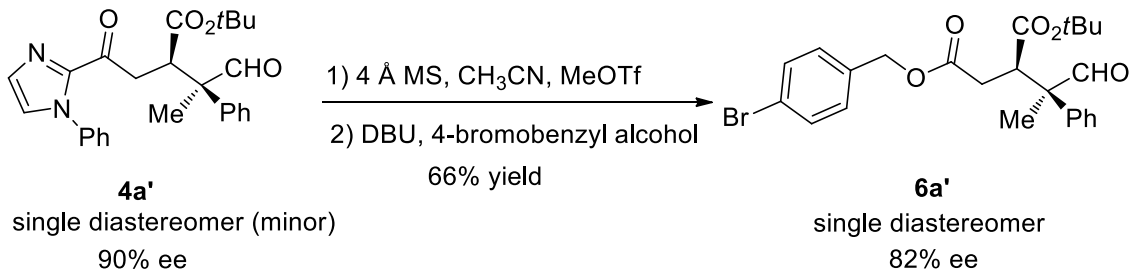
stirred vigorously under a positive pressure of argon for 2 h at room temperature, then MeOTf (0.22 mL, 1.961 mmol) was added and stirred at room temperature for 26 h. Afterwards, 4-bromobenzyl alcohol (1.466 g, 7.84 mmol) and DBU (0.29 mL, 1.961 mmol) were added in turn at room temperature. The mixture was stirred at room temperature for additional 1 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 6:1 to 3:1) to afford **6a** (389.5 mg, 0.821 mmol, yield: 63%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IB column, ee = 82% (HPLC: IB, 220 nm, *n*-hexane/isopropanol = 92:8, flow rate: 0.5 mL/min, 25 °C, t_r(major) = 15.5 min, t_r(minor) = 16.2 min). $[\alpha]_D^{20}$ = -106.7° (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.55-7.46 (m, 2H), 7.43-7.39 (m, 2H), 7.37-7.28 (m, 3H), 7.25-7.17 (m, 2H), 5.03 (s, 2H), 3.94 (d, *J* = 10.7 Hz, 1H), 2.69 (q, *J* = 5.3 Hz, 1H), 2.03 (d, *J* = 16.9 Hz, 1H), 1.46 (s, 3H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 171.9, 170.9, 136.9, 134.7, 131.6, 129.8, 129.3, 127.8, 127.0, 122.2, 82.7, 65.7, 55.1, 47.1, 31.1, 27.8, 13.7.

IR (film) ν_{max}: 2977, 1730, 1597, 1490, 1446, 1369, 1337, 1260, 1148, 1071, 1014, 886, 843, 802, 763, 700 cm^{-1}.

HRMS (ESI) calcd for $C_{24}H_{27}BrO_5Na$ $(M+Na)^+$: 497.0934, found: 497.0939.



4a'
single diastereomer (minor)
90% ee

6a'
single diastereomer
82% ee

Compound 6a'. To a solution of **4a'** (377.5 mg, 0.948 mmol, the minor diastereomer, 90% ee) in CH_3CN (9.5 mL) was added 4 Å MS (474.1 mg) under argon atmosphere. The suspension was stirred vigorously under a positive pressure of argon for 2 h at room temperature, then MeOTf (0.161 mL, 1.422 mmol) was added and stirred at room temperature for 26 h. Afterwards, 4-bromobenzyl alcohol (1.06 g, 5.69 mmol) and DBU (0.213 mL, 1.422 mmol) were added in turn at room temperature. The mixture was stirred at room temperature for additional 1 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (300-400 mesh, *n*-hexane/ethyl acetate = 6:1 to 3:1) to afford **6a'** (296.8 mg, 0.626 mmol, yield: 66%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IB column, ee = 82% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.7 mL/min, 25 °C, t_r(minor) = 15.6 min, t_r(major) = 17.2 min). $[\alpha]_D^{20}$ = -77.2° (*c* 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.52-7.48 (m, 2H), 7.43-7.38 (m, 2H), 7.37-7.32 (m, 1H), 7.31-7.28 (m, 2H), 7.25-7.23 (m, 2H), 5.08 (s, 2H), 3.64 (q, *J* = 2.8 Hz, 1H), 2.83 (q, *J* = 11.5 Hz, 1H), 2.56 (q, *J* = 2.9 Hz, 1H), 1.60 (s, 3H), 1.06 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 171.6, 171.5, 136.7, 134.7, 131.7, 129.9, 128.7, 128.0, 127.9, 122.2, 80.9, 65.7, 54.8, 46.7, 33.4, 27.3, 14.6.

IR (film) ν_{max}: 2975, 2925, 2851, 1721, 1598, 1490, 1446, 1408, 1368, 1349, 1260, 1149, 1071,

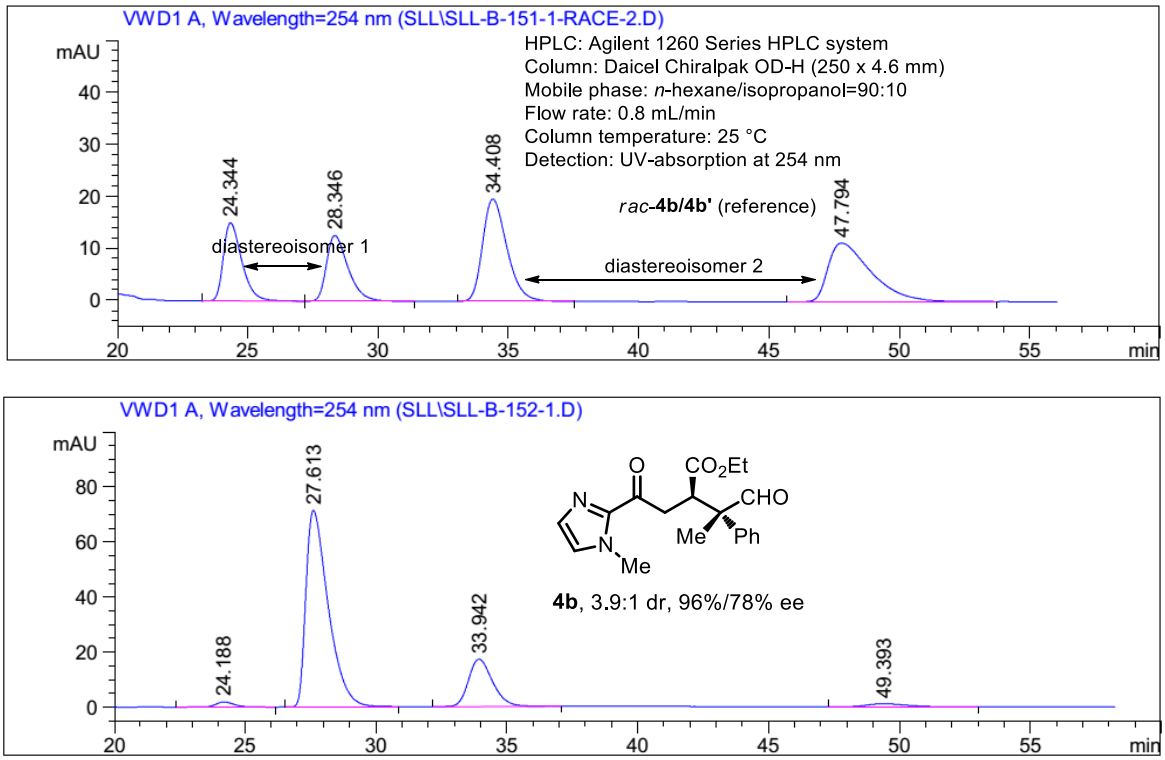
1013, 844, 802, 759, 740, 699, 546 cm^{-1}.

HRMS (ESI) calcd for $C_{24}H_{27}BrO_5Na$ $(M+Na)^+$: 497.0934, found: 497.0929.

7. Chiral HPLC Traces

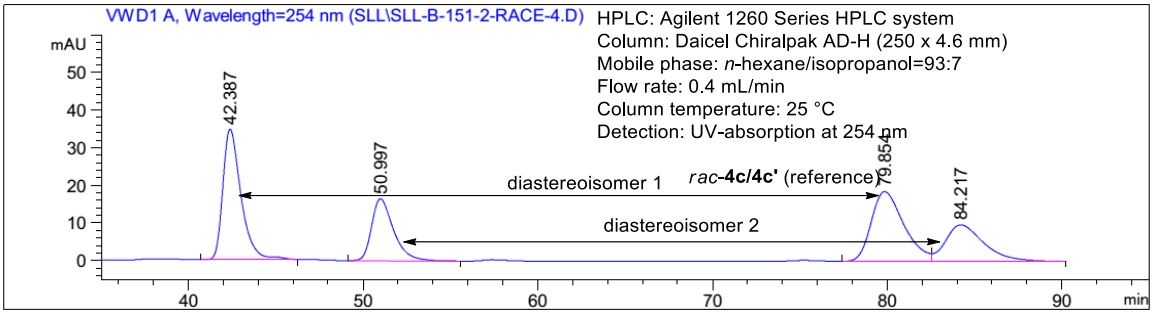
7.1 Chiral HPLC Traces of the Michael Addition Products

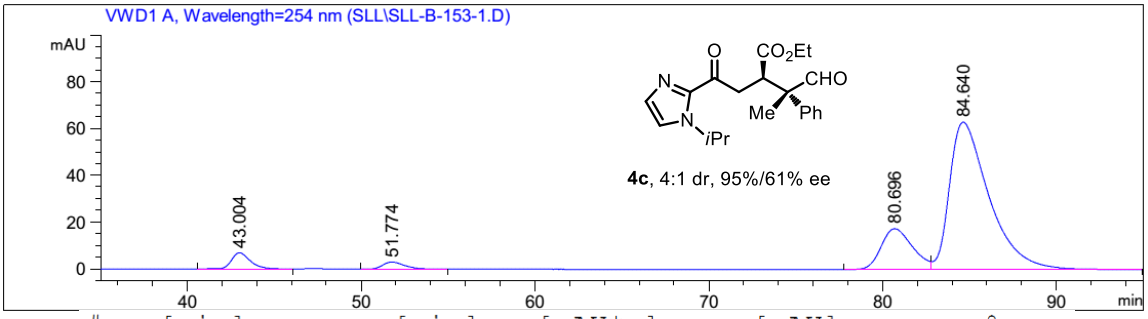
Enantiomeric excess of the compounds **4b-u** and **4w** were determined with a Daicel Chiralpak AD-H, IA, IB, IC or OD-H column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using *n*-hexane/isopropanol as mobile phase, the temperature was 25 °C and UV-absorption was measured at 254 nm.



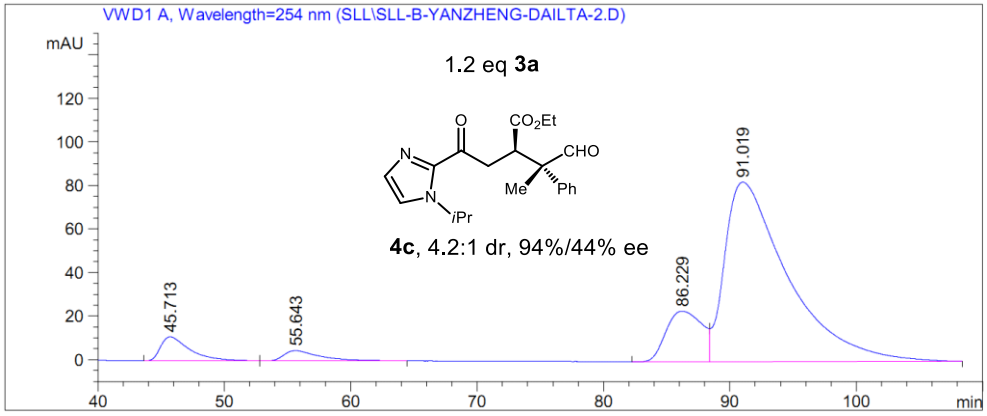
#	[min]		[min]	[mAU*s]	[mAU]	%
1	24.188	BB	0.7704	96.63501	1.93582	1.7347
2	27.613	BB	0.8966	4233.79736	71.31780	76.0018
3	33.942	BB	0.9833	1106.34583	17.17960	19.8603
4	49.393	BB	1.5792	133.87372	1.20966	2.4032

Figure S4. HPLC traces of *rac*-**4b/4b'** and (*2R,3S*)-**4b.**



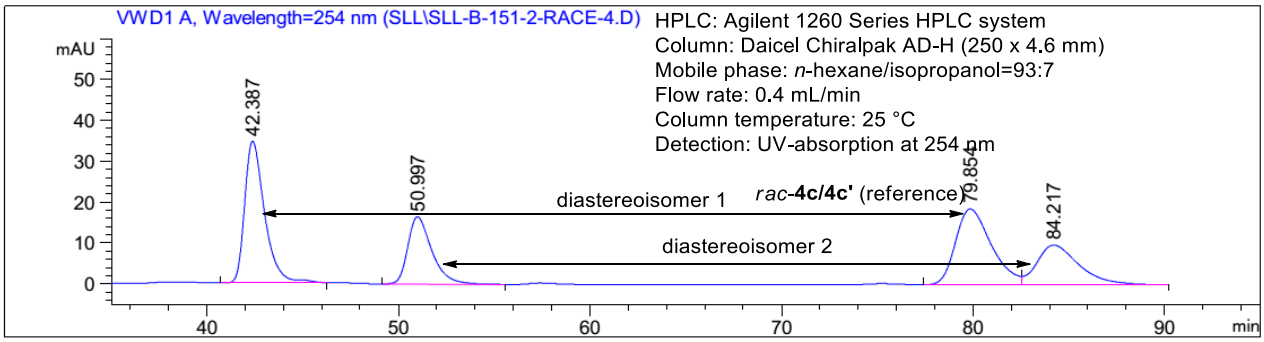


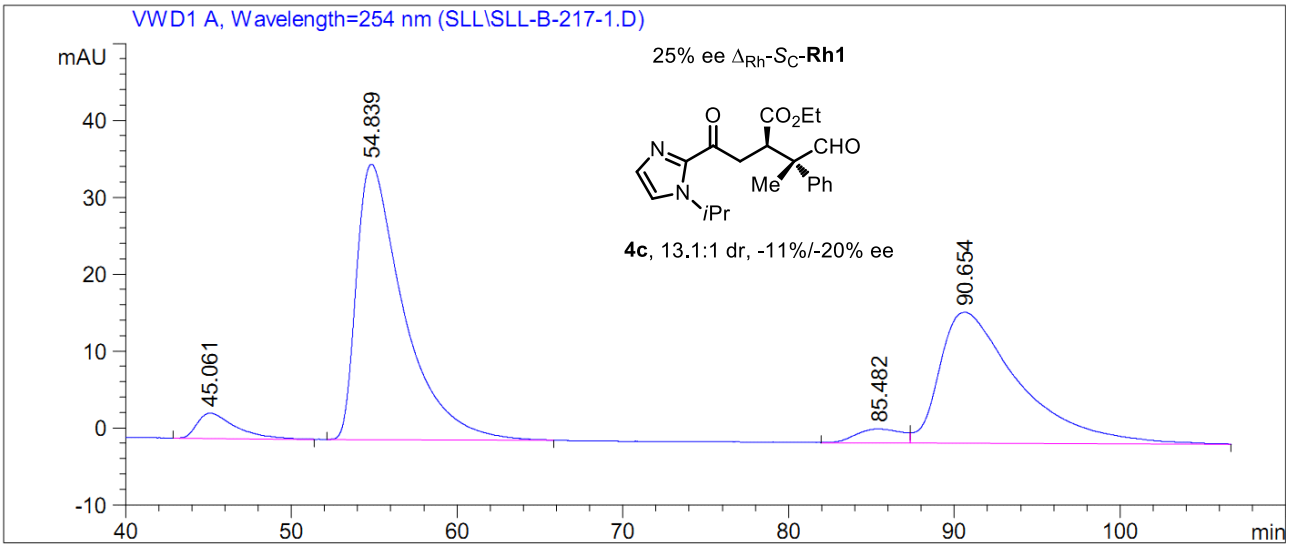
#	[min]		[min]	[mAU*s]	[mAU]	%
1	43.004	BB	1.1646	530.29926	6.93134	4.1018
2	51.774	BB	1.3480	267.85925	3.03990	2.0718
3	80.696	BV	1.9263	2184.65820	17.42970	16.8980
4	84.640	VBA	2.3625	9945.70313	62.97588	76.9284



#	[min]		[min]	[mAU*s]	[mAU]	%
1	45.713	BV	2.2333	1790.96680	11.03615	4.9674
2	55.643	VV	2.5298	970.15643	4.73610	2.6908
3	86.229	BV	2.7278	4597.01074	23.27937	12.7501
4	91.019	VBA	4.7813	2.86965e4	82.51560	79.5917

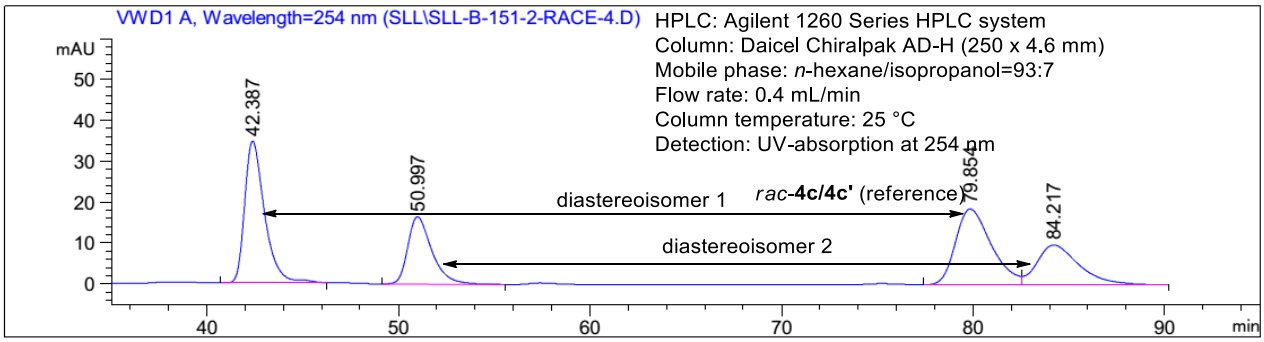
Figure S5. HPLC traces of *rac*-**4c/4c'** and (*2R,3S*)-**4c.**

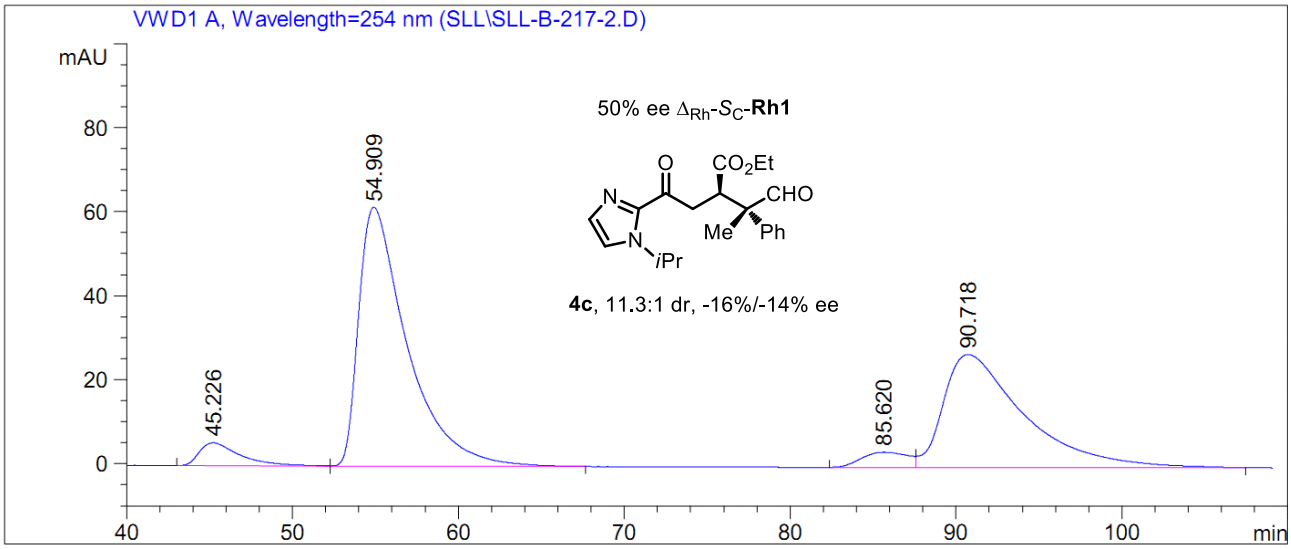




#	[min]		[min]	[mAU*s]	[mAU]	%
1	45.061	BB	1.9661	526.45111	3.29847	3.8680
2	54.839	BB	2.8111	7086.49561	35.83607	52.0662
3	85.482	BV	2.2384	344.85666	1.81685	2.5337
4	90.654	VBA	3.9444	5652.75439	17.03047	41.5321

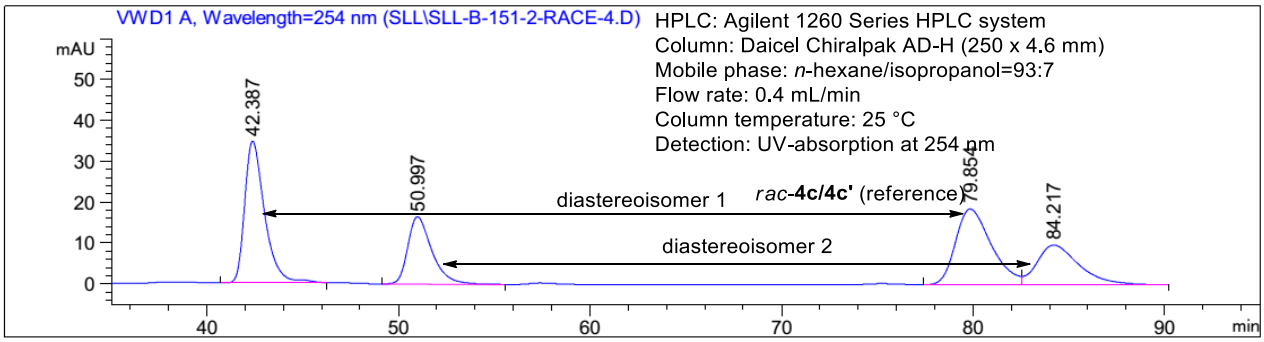
Figure S6. HPLC traces of *rac*-**4c/4c'** and *nonrac*-**4c.**

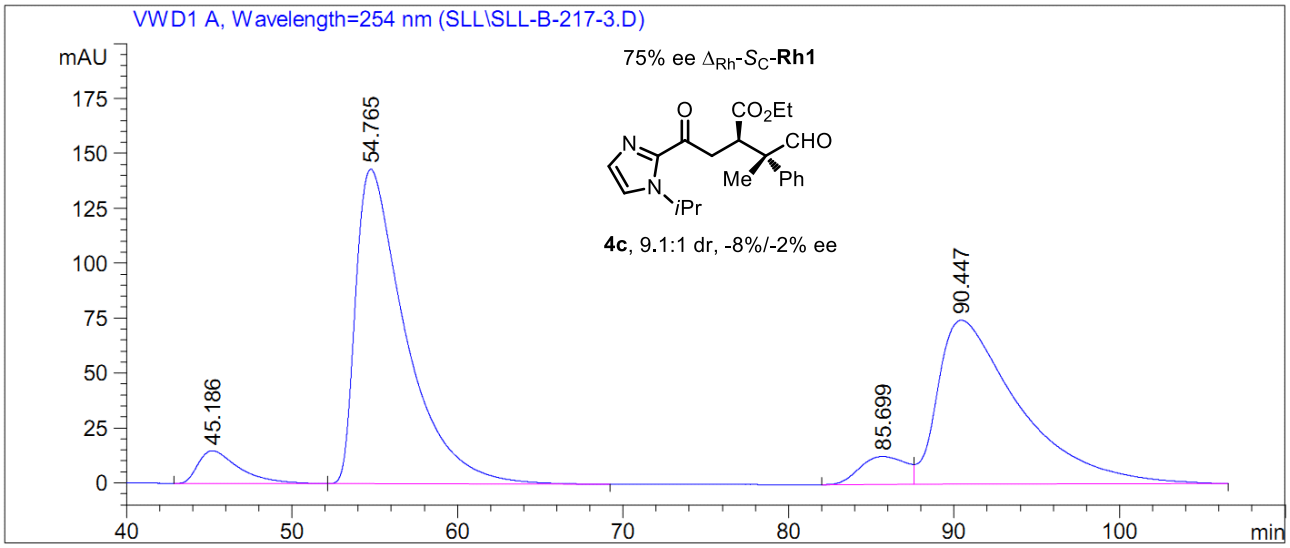




#	[min]		[min]	[mAU*s]	[mAU]	%
1	45.226	BB	2.0834	924.46692	5.44896	3.9994
2	54.909	BB	2.9040	1.24597e4	61.59382	53.9023
3	85.620	BV	2.2886	697.74603	3.59465	3.0185
4	90.718	VB	4.3655	9033.40723	26.90232	39.0798

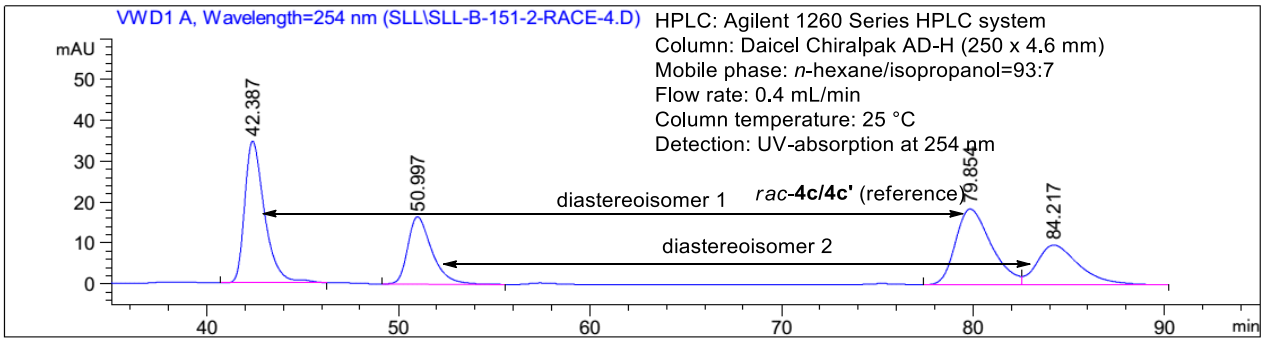
Figure S7. HPLC traces of *rac*-**4c/4c'** and *nonrac*-**4c.**

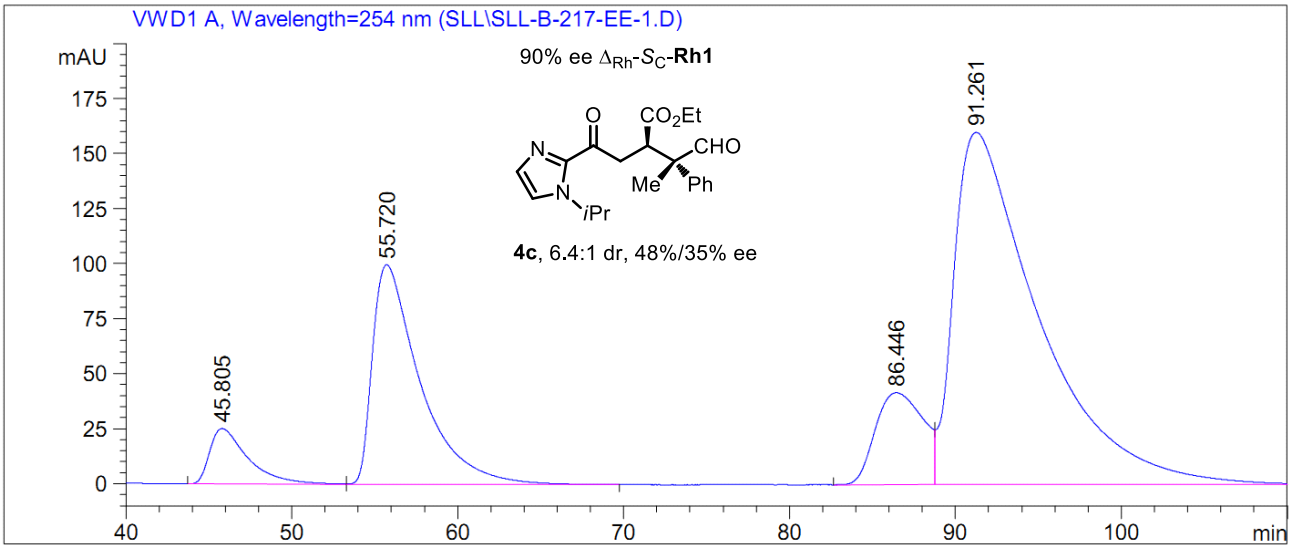




#	[min]		[min]	[mAU*s]	[mAU]	%
1	45.186	BV	2.4440	2576.10254	14.87844	4.2368
2	54.765	VB	3.0384	3.01349e4	143.24397	49.5617
3	85.699	BV	2.3308	2459.62012	12.70397	4.0452
4	90.447	VBA	4.7805	2.56321e4	74.67561	42.1562

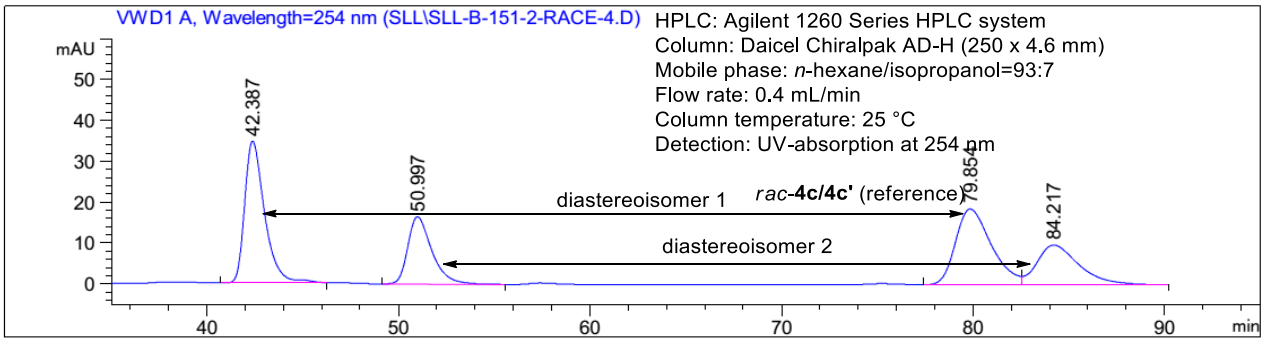
Figure S8. HPLC traces of *rac*-**4c/4c'** and *nonrac*-**4c.**

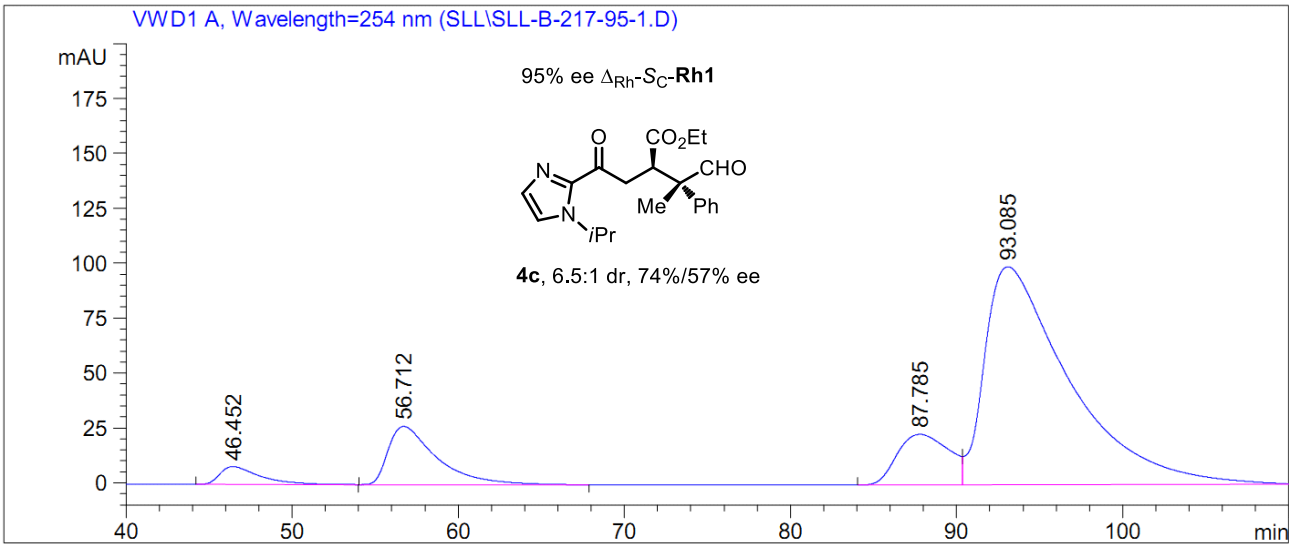




#	[min]		[min]	[mAU*s]	[mAU]	%
1	45.805	BV	2.3037	4043.39209	25.20390	4.5344
2	55.720	VB	2.8836	1.99208e4	99.67765	22.3397
3	86.446	BV	3.0280	8382.80859	41.79522	9.4007
4	91.261	VBA	4.8854	5.68254e4	159.92836	63.7253

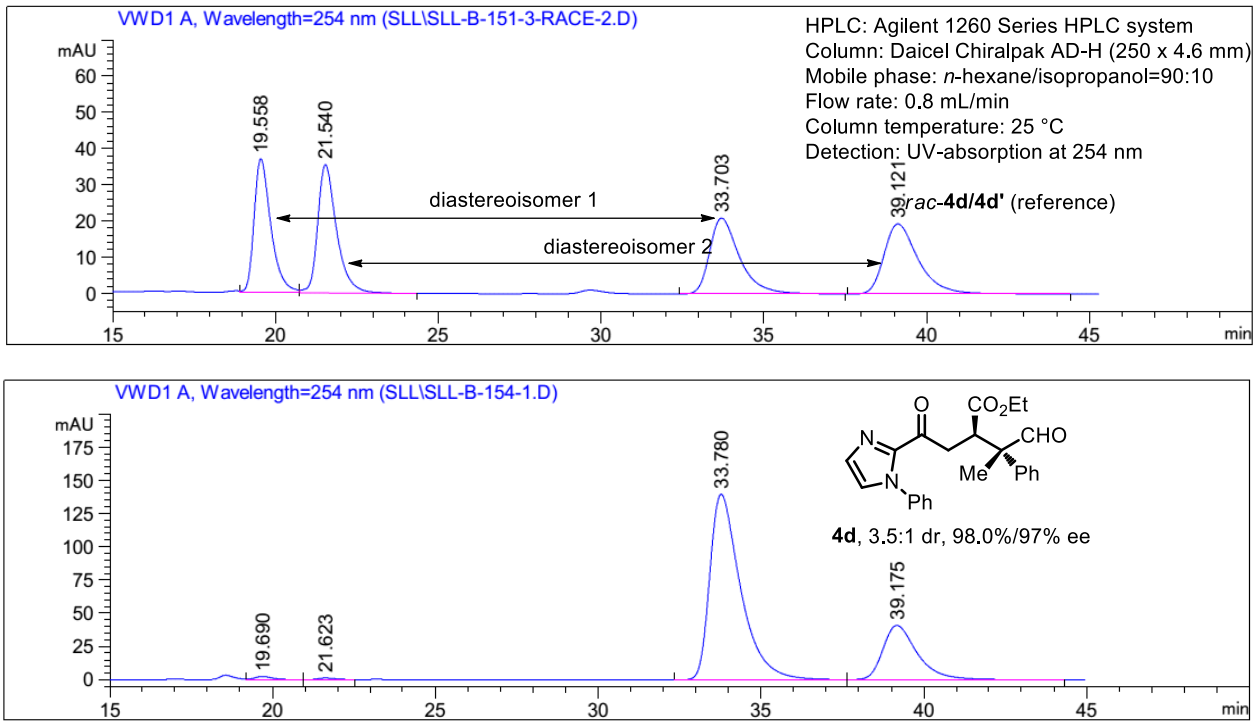
Figure S9. HPLC traces of *rac*-**4c/4c'** and *nonrac*-**4c.**





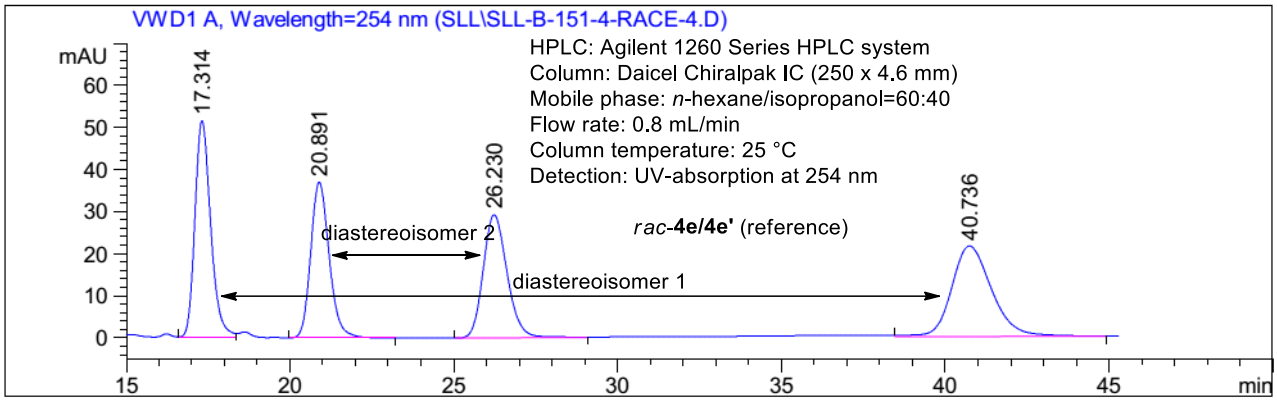
#	[min]		[min]	[mAU*s]	[mAU]	%
1	46.452	BB	2.2480	1363.05542	8.16351	2.8959
2	56.712	BB	2.7696	5372.50342	26.49571	11.4143
3	87.785	BV	2.8588	4995.60596	23.02883	10.6135
4	93.085	VB	4.8916	3.53372e4	99.30236	75.0763

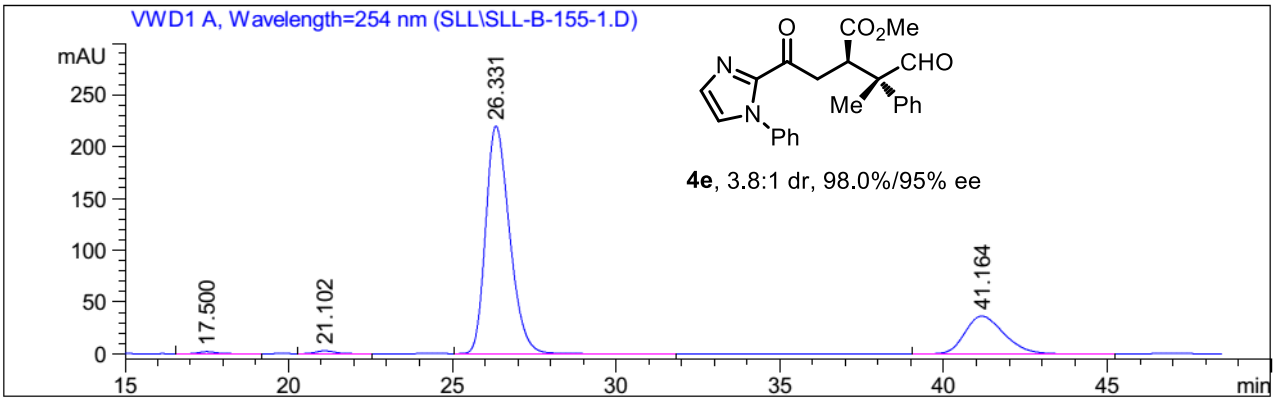
Figure S10. HPLC traces of *rac*-**4c**/**4c'** and *nonrac*-**4c.**



#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.690	VB	0.5705	92.24740	2.43205	0.7458
2	21.623	BV	0.6111	47.69607	1.19122	0.3856
3	33.780	BV	0.9863	9205.88379	139.42200	74.4242
4	39.175	VB	1.1114	3023.65308	40.85518	24.4445

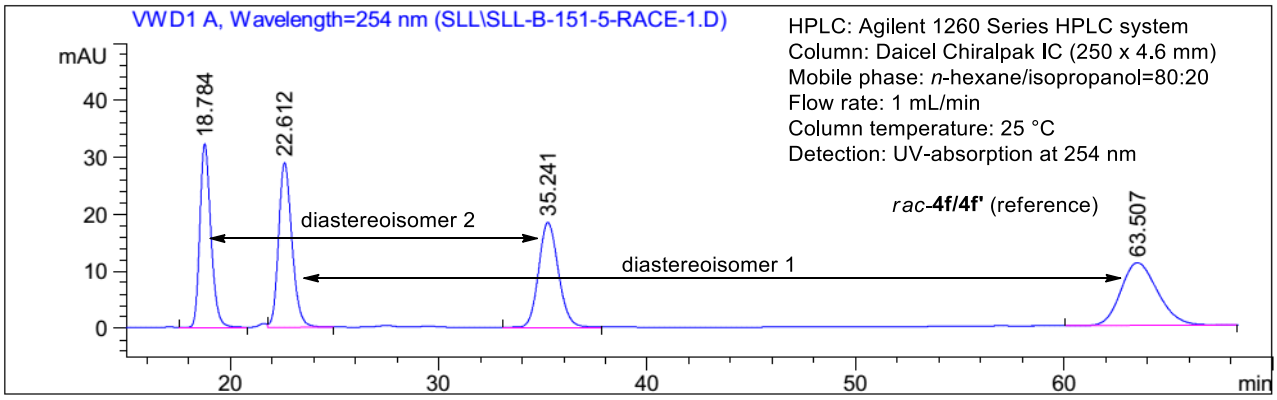
Figure S11. HPLC traces of *rac*-**4d/4d'** and (*2R,3S*)-**4d.**

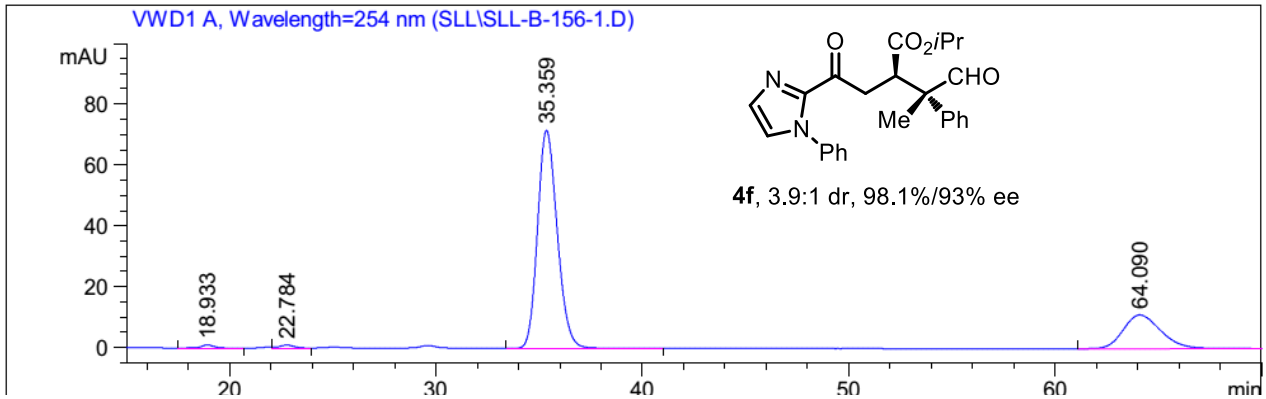




#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.500	BV	0.5800	80.62440	2.09974	0.5567
2	21.102	VB	0.6322	119.36416	2.92454	0.8242
3	26.331	VB	0.7858	1.11988e4	220.01375	77.3250
4	41.164	BB	1.3068	3083.98315	36.75906	21.2942

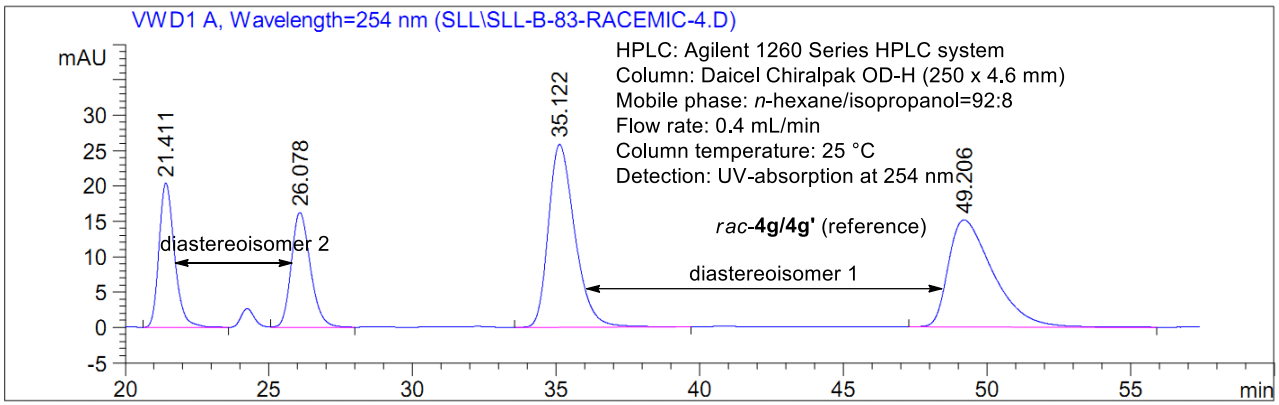
Figure S12. HPLC traces of *rac*-**4e/4e'** and (*2R,3S*)-**4e.**

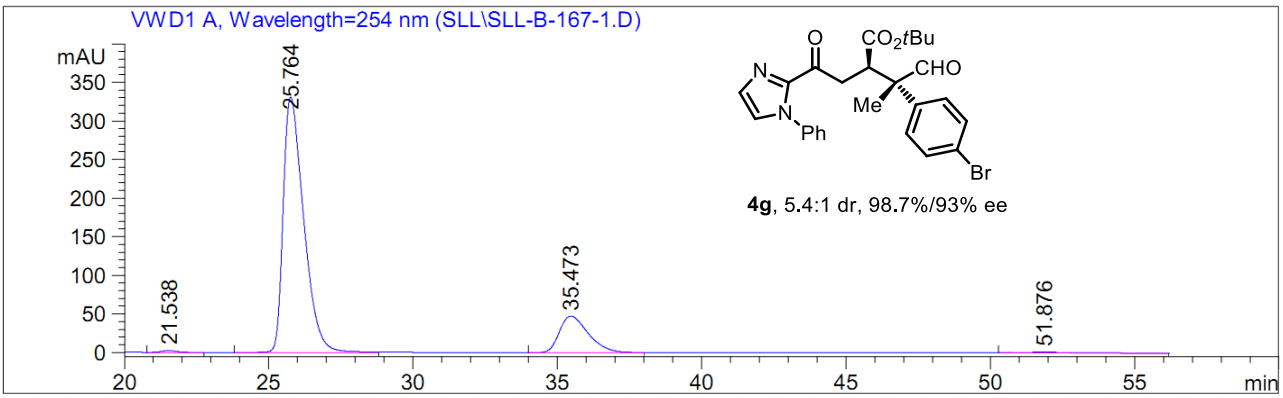




#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.933	BB	0.6619	45.88395	1.06660	0.7313
2	22.784	VV	0.7949	54.46227	1.05392	0.8680
3	35.359	BB	1.0261	4758.69238	71.72264	75.8463
4	64.090	BB	1.9611	1415.08960	11.11648	22.5544

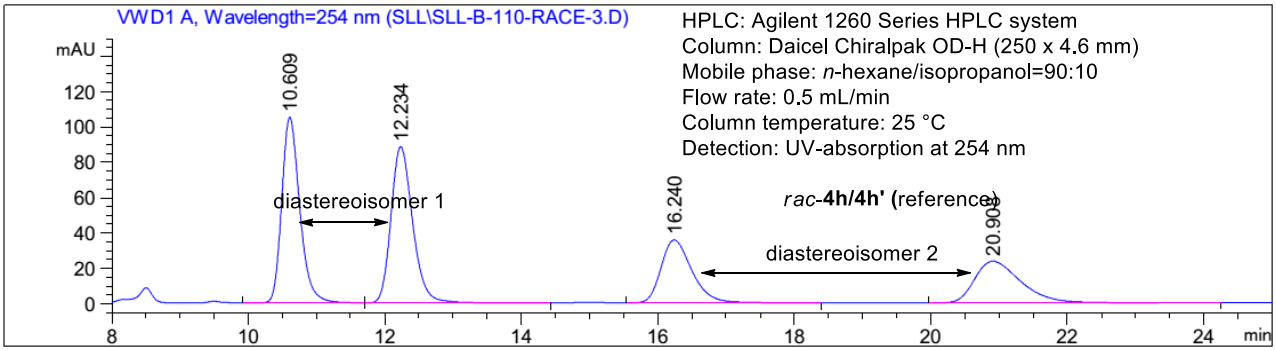
Figure S13. HPLC traces of *rac*-**4f/4f'** and (*2R,3S*)-**4f.**

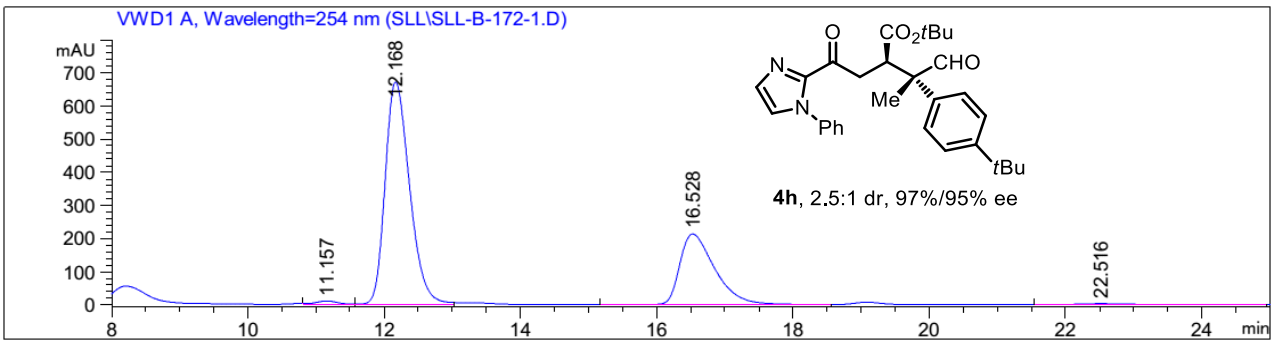




#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.538	VV	0.6456	103.35990	2.42338	0.5186
2	25.764	BV	0.7529	1.63677e4	330.97818	82.1229
3	35.473	BV	1.0772	3342.13232	47.48074	16.7687
4	51.876	VBA	1.5692	117.55809	1.03186	0.5898

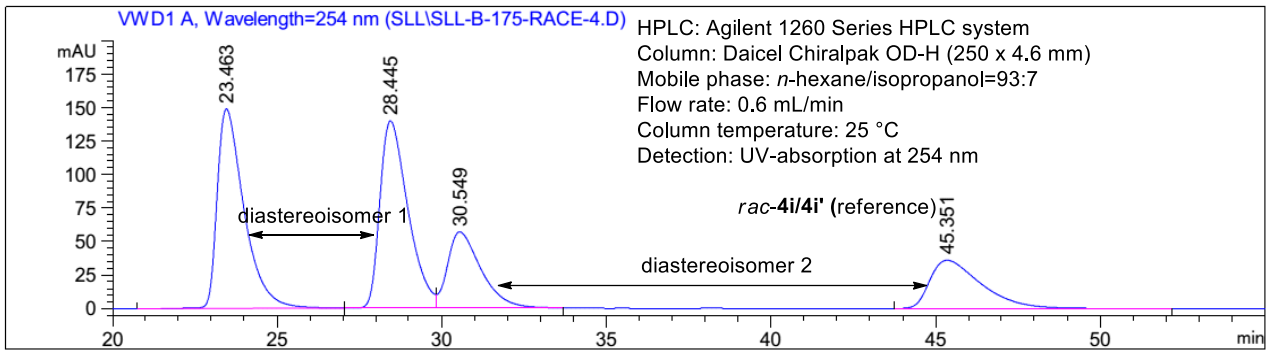
Figure S14. HPLC traces of *rac*-**4g/4g'** and (*2R,3S*)-**4g.**

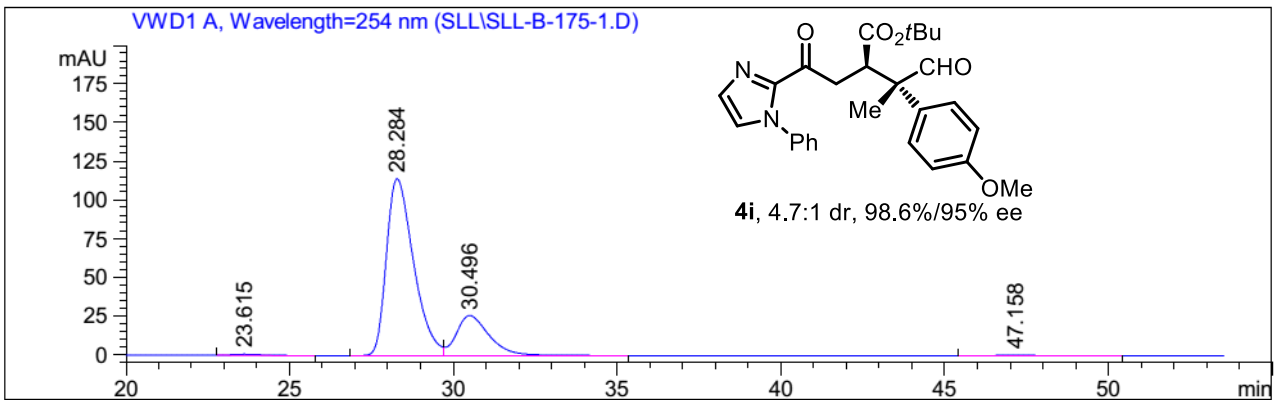




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.157	VV	0.3501	249.94885	10.79427	1.0062
2	12.168	MF R	0.4156	1.67582e4	672.08405	67.4640
3	16.528	BV	0.5459	7633.56104	213.12372	30.7308
4	22.516	BB	0.8671	198.47200	3.47116	0.7990

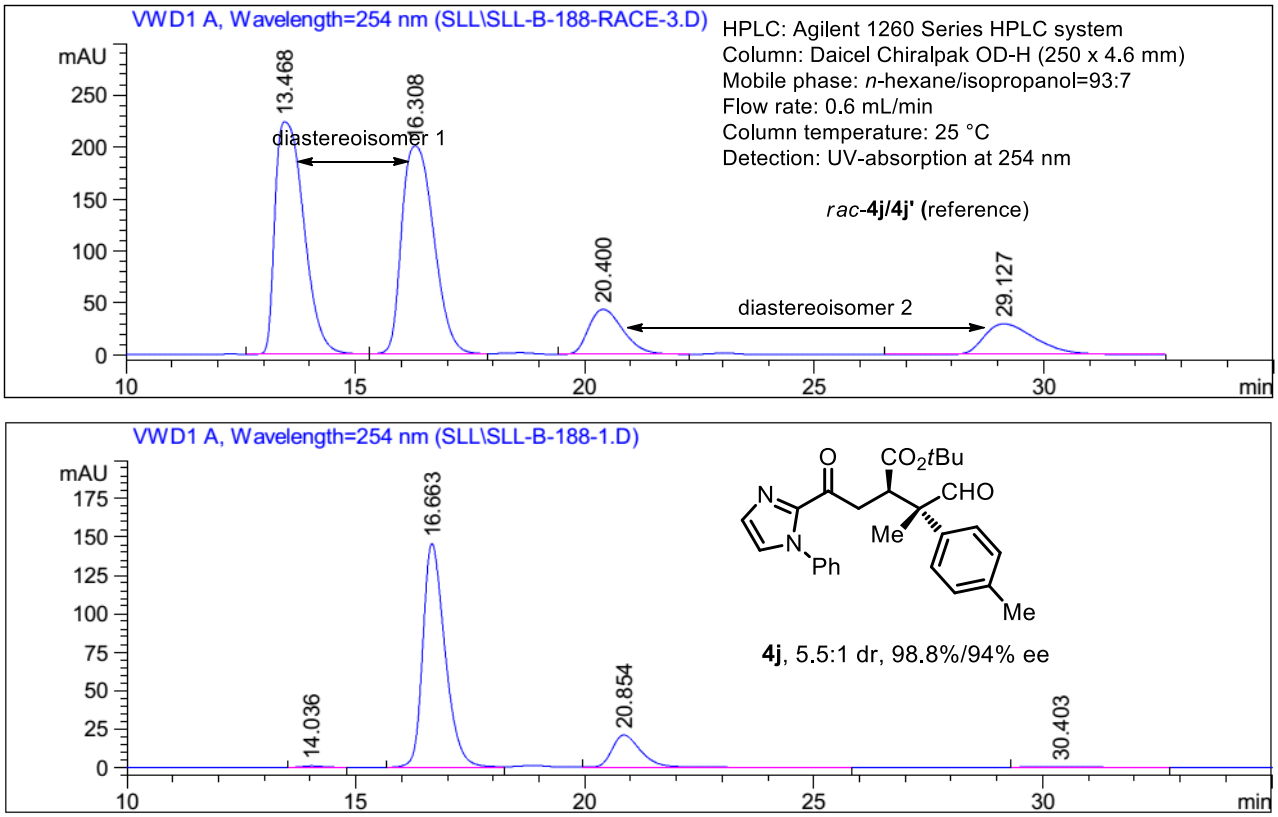
Figure S15. HPLC traces of *rac*-**4h/4h'** and (*2R,3S*)-**4h.**





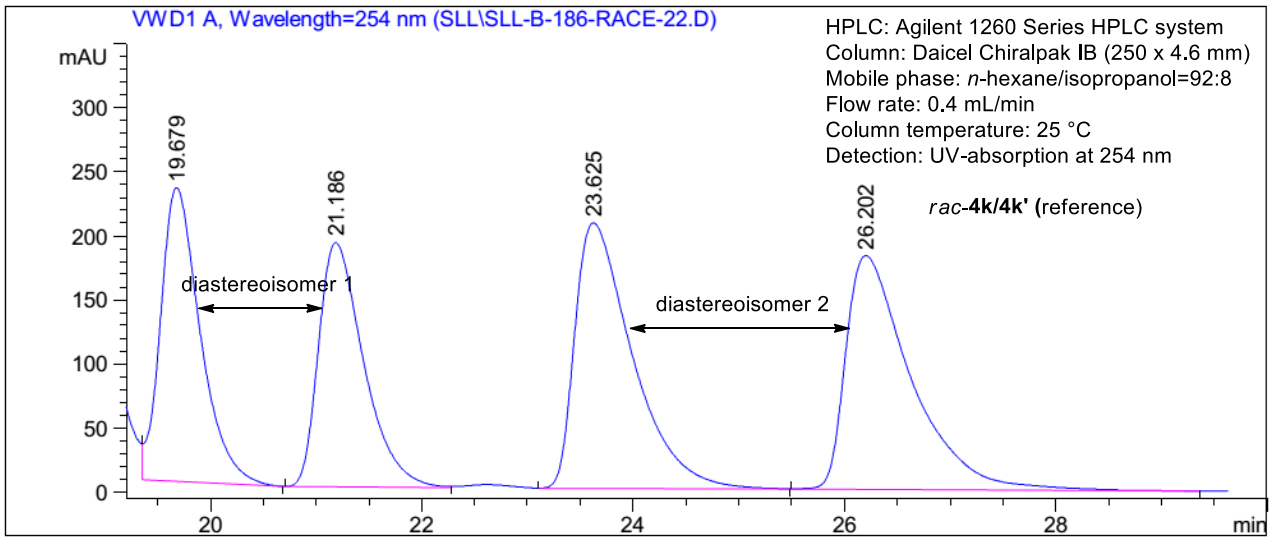
#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.615	BB	0.8607	47.85446	8.15441e-1	0.5579
2	28.284	BV	0.8821	6618.24463	114.54440	77.1562
3	30.496	MF R	1.1891	1858.90955	26.05553	21.6714
4	47.158	BB	1.3723	52.71111	4.94232e-1	0.6145

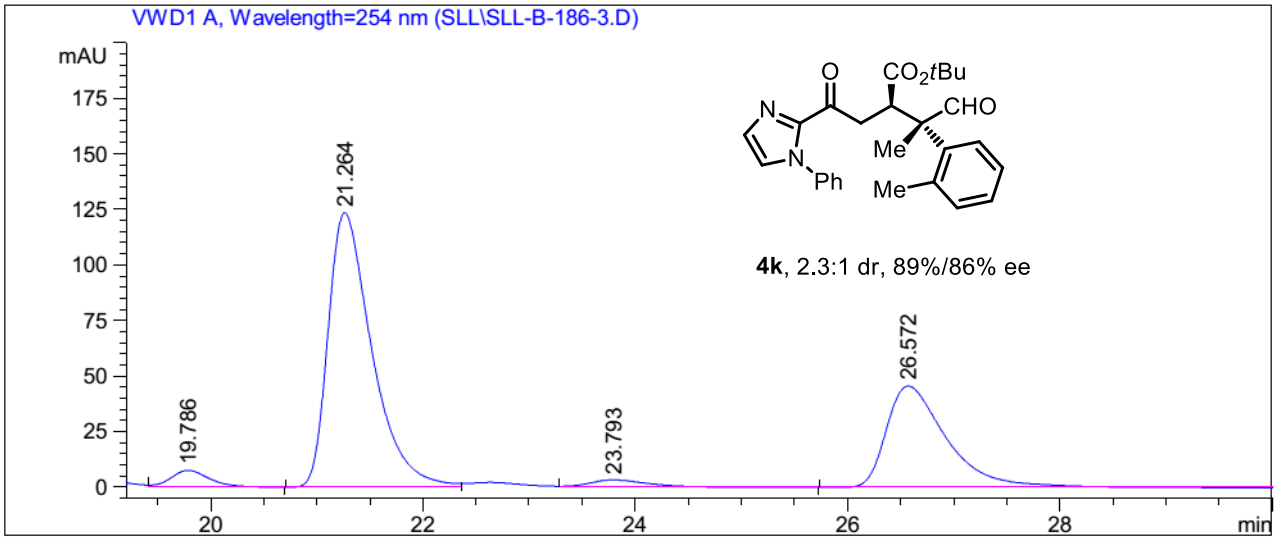
Figure S16. HPLC traces of *rac*-**4i/4i'** and (*2R,3S*)-**4i.**



#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.036	VB	0.4645	29.71147	9.94677e-1	0.5031
2	16.663	BV	0.5175	4914.44824	145.70193	83.2232
3	20.854	VB	0.6773	932.24817	21.02324	15.7871
4	30.403	FM R	1.2406	28.73661	3.86056e-1	0.4866

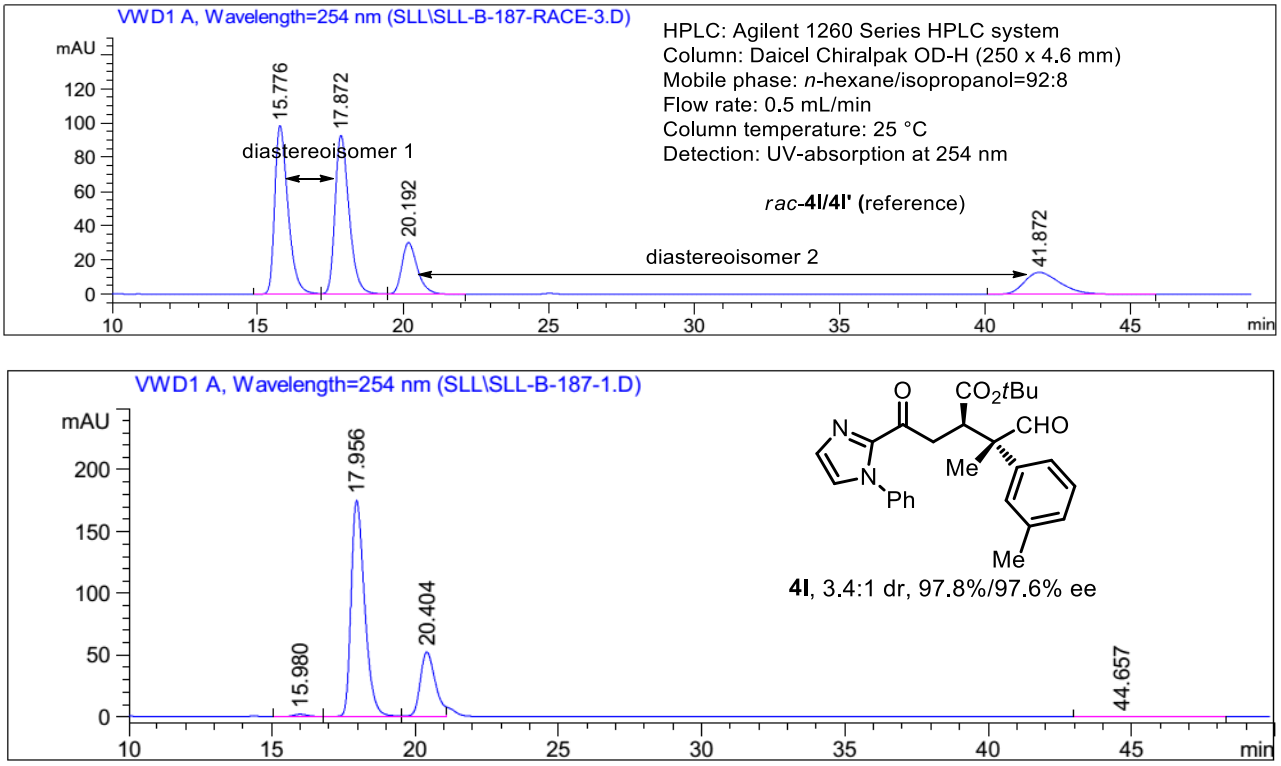
Figure S17. HPLC traces of *rac*-**4j/4j'** and (*2R,3S*)-**4j.**





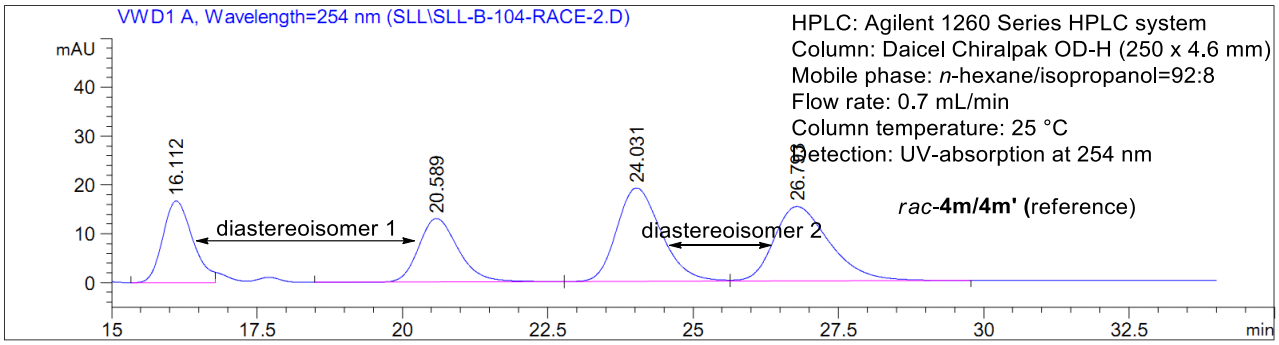
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.786	VB	0.3903	198.24091	7.65114	3.4719
2	21.264	BV	0.4349	3546.69165	123.55233	62.1154
3	23.793	VB	0.6318	140.51363	3.33341	2.4609
4	26.572	BB	0.6018	1824.39404	45.69287	31.9518

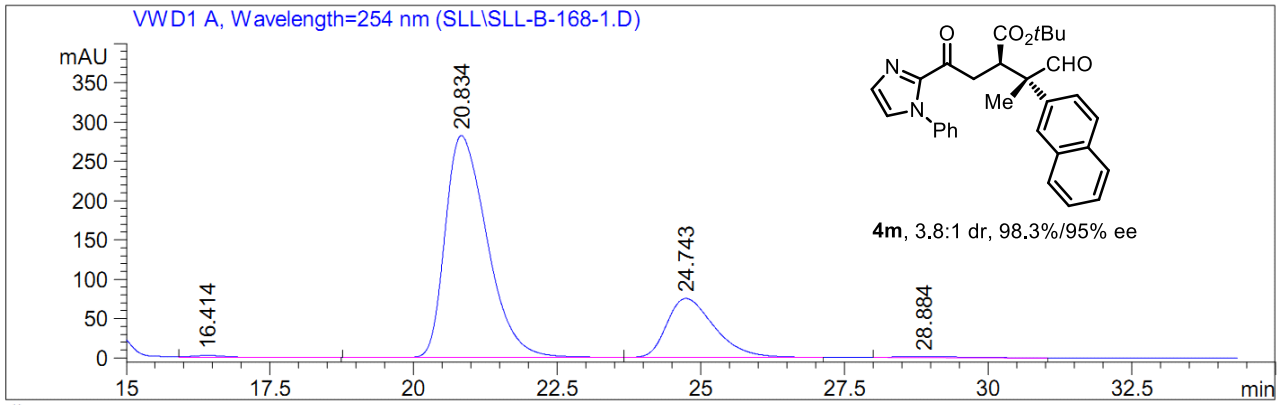
Figure S18. HPLC traces of *rac*-**4k/4k'** and (*2R,3S*)-**4k.**



#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.980	BV	0.4876	64.14021	1.99231	0.8232
2	17.956	VV	0.5085	5770.70557	175.09467	74.0623
3	20.404	MF R	0.6150	1932.87842	52.38326	24.8069
4	44.657	BB	1.2829	23.97040	2.25005e-1	0.3076

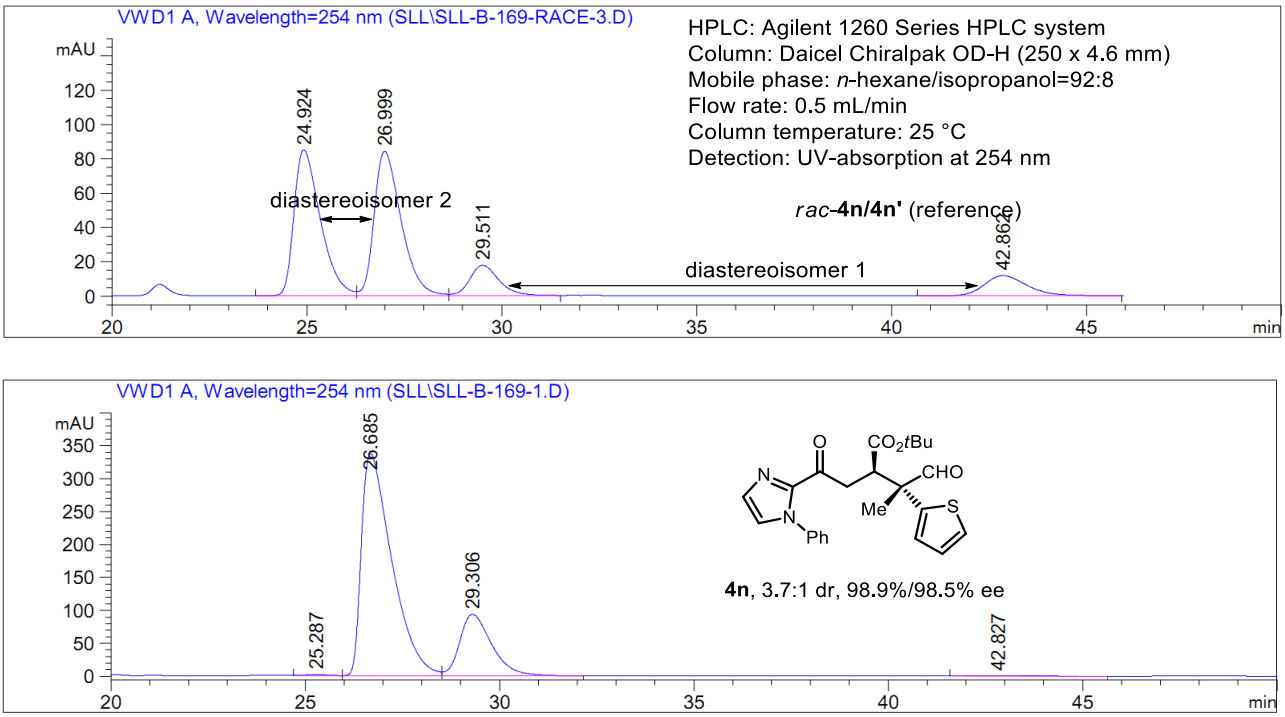
Figure S19. HPLC traces of *rac*-**4l/4l'** and (*2R*,*3S*)-**4l.**





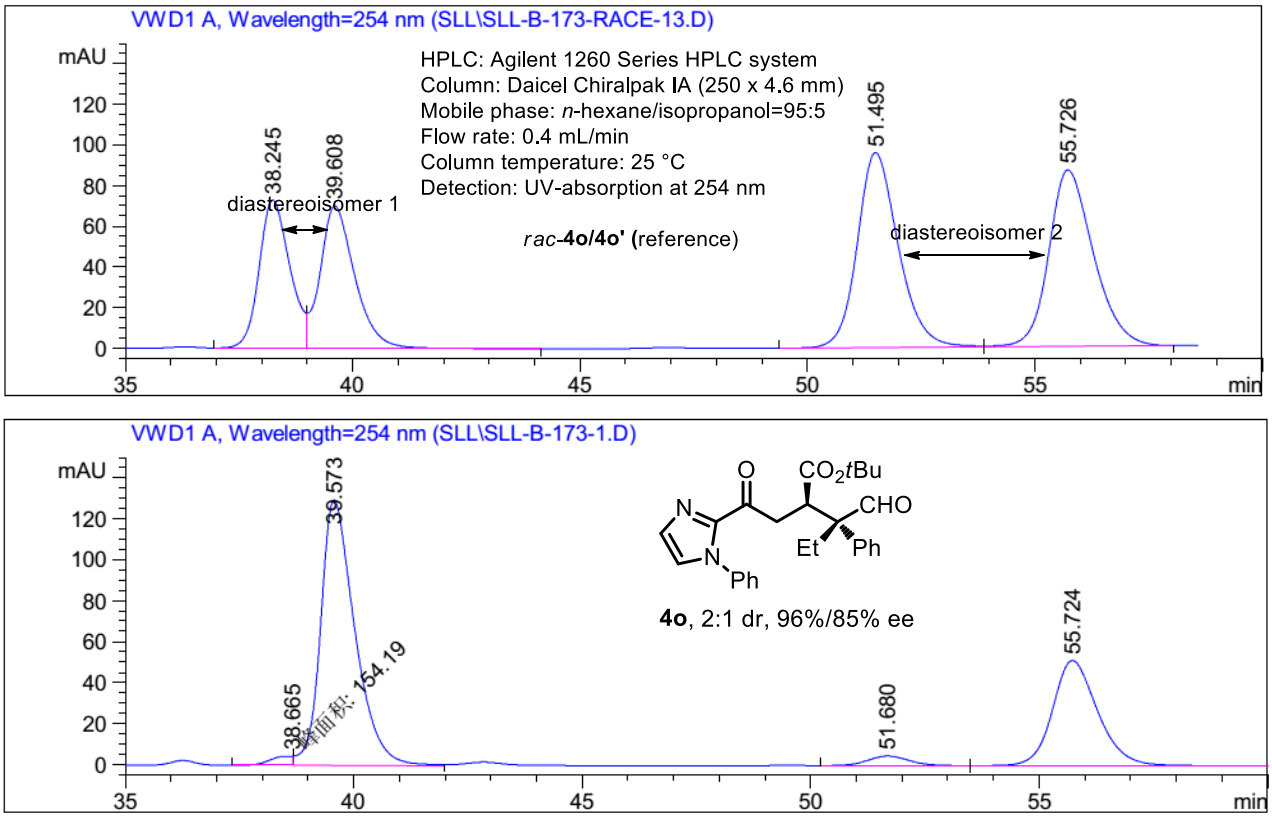
#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.414	VB	0.6752	125.71252	2.76120	0.6669
2	20.834	BB	0.8026	1.42902e4	282.30334	75.8097
3	24.743	BV	0.8873	4315.95654	75.00455	22.8963
4	28.884	VB	1.1141	118.20686	1.55633	0.6271

Figure S20. HPLC traces of *rac*-**4m/4m'** and (*2R,3S*)-**4m.**



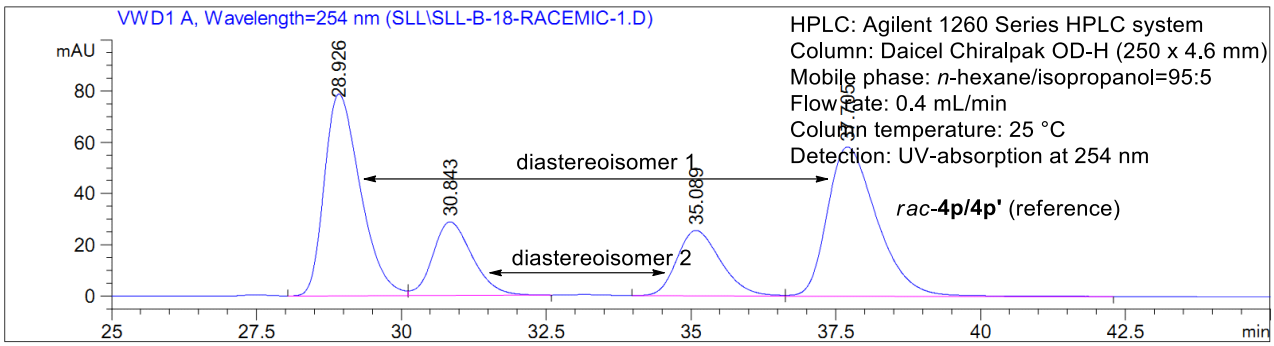
#	[min]		[min]	[mAU*s]	[mAU]	%
1	25.287	FM R	0.8358	98.13863	1.95701	0.4107
2	26.685	VV	0.8151	1.83762e4	337.59070	76.9093
3	29.306	VB	0.8743	5371.39453	93.49200	22.4807
4	42.827	VB	1.0537	47.60646	5.75130e-1	0.1992

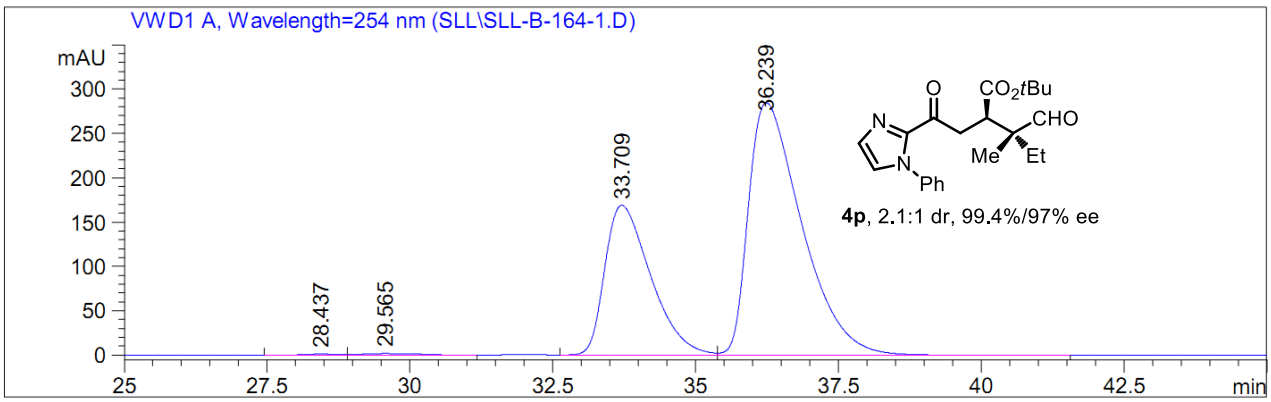
Figure S21. HPLC traces of *rac*-**4n/4n'** and (*2R,3R*)-**4n.**



#	[min]		[min]	[mAU*s]	[mAU]	%
1	38.665	MF	0.5680	154.19012	4.52475	1.4348
2	39.573	FM R	0.8681	6753.11230	129.65034	62.8386
3	51.680	VV	0.9763	301.70148	4.72884	2.8074
4	55.724	VBA	1.0431	3537.75732	51.39439	32.9193

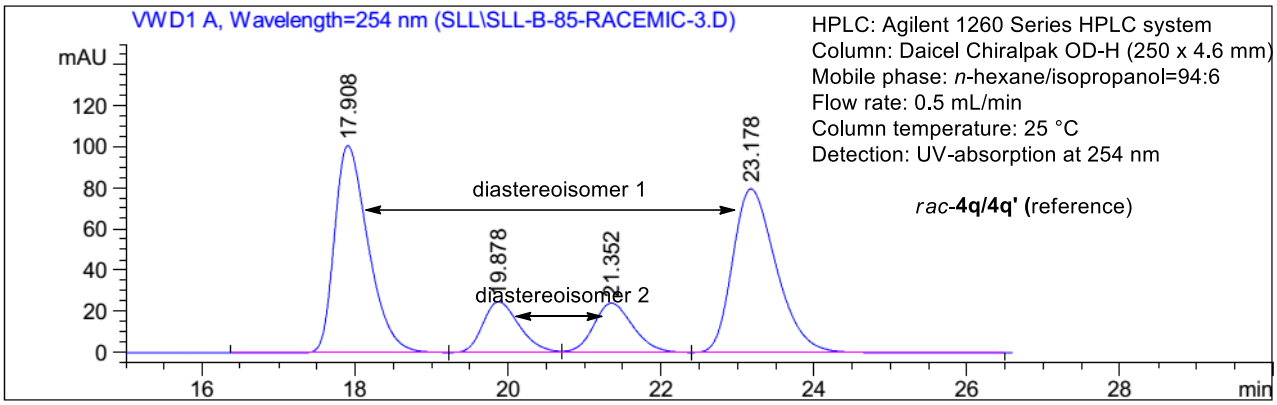
Figure S22. HPLC traces of *rac*-**4o**/**4o'** and (*2R,3S*)-**4o.**

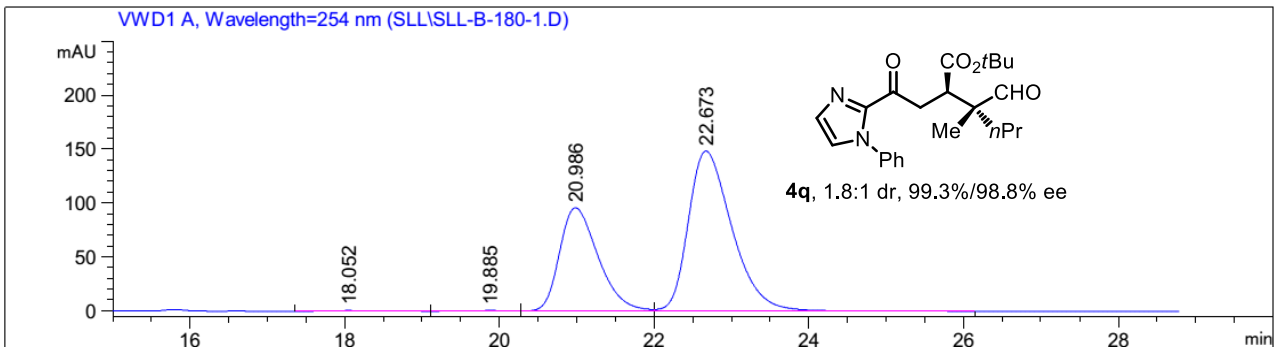




#	[min]		[min]	[mAU*s]	[mAU]	%
1	28.437	BV	0.6971	58.44868	1.31878	0.2076
2	29.565	VB	1.1274	136.74725	1.93750	0.4858
3	33.709	BV	0.8595	9435.02246	168.94382	33.5151
4	36.239	VB	0.9907	1.85214e4	284.80167	65.7916

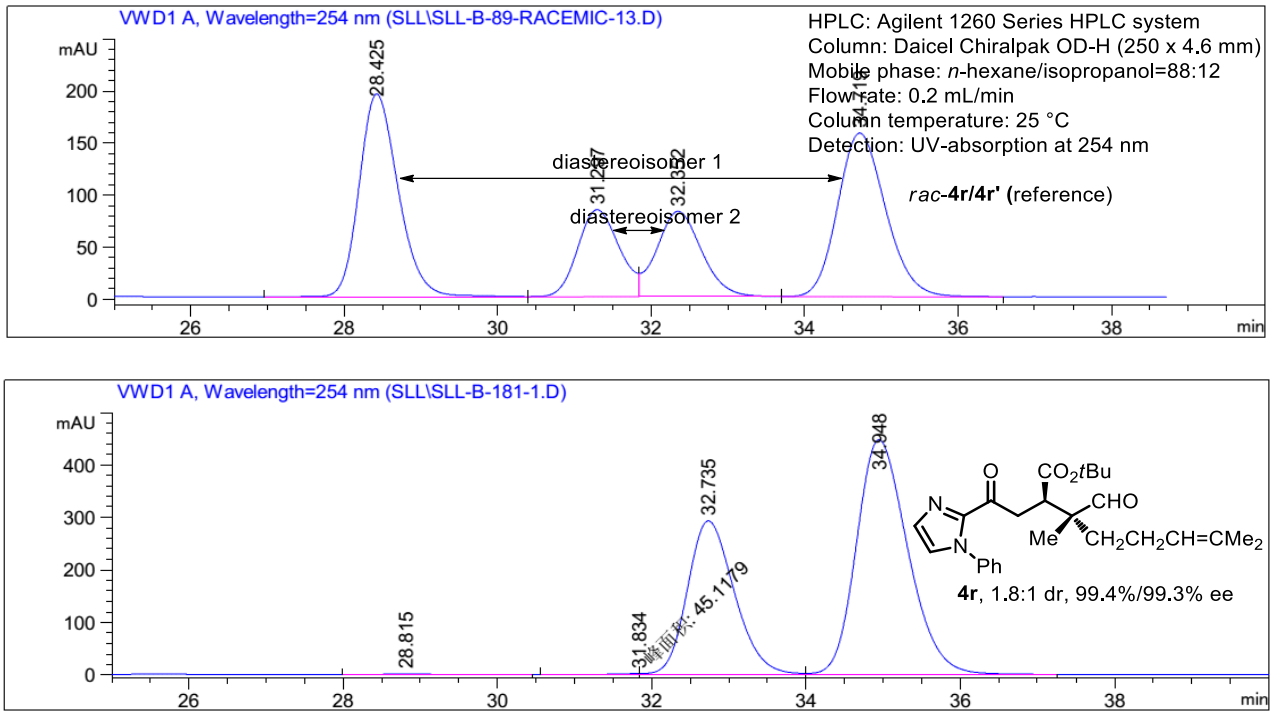
Figure S23. HPLC traces of *rac*-**4p**/**4p'** and (*2R*,*3R*)-**4p.**





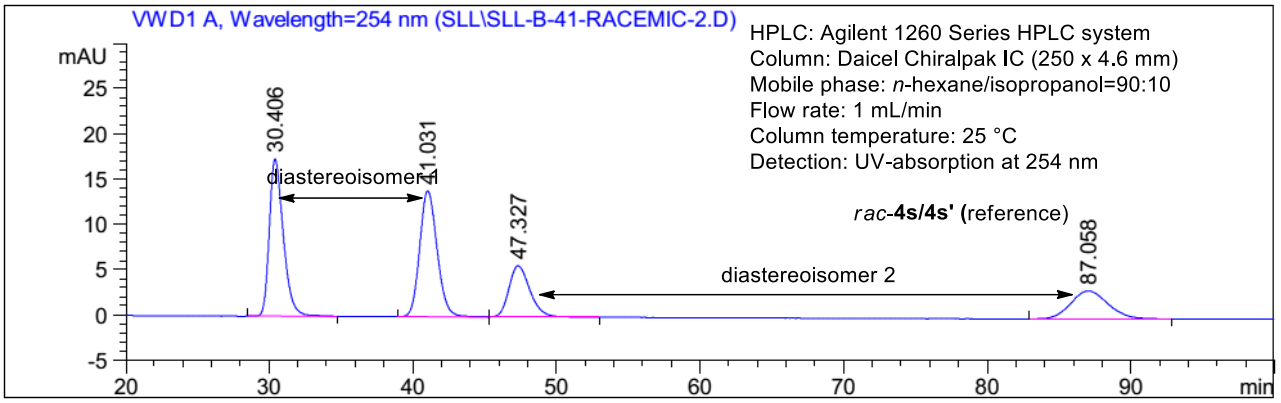
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.052	BB	0.5031	20.09775	6.05772e-1	0.2190
2	19.885	BV	0.5099	19.93505	6.02760e-1	0.2172
3	20.986	VV	0.5368	3321.02222	95.70311	36.1801
4	22.673	VB	0.6023	5818.07666	148.10440	63.3837

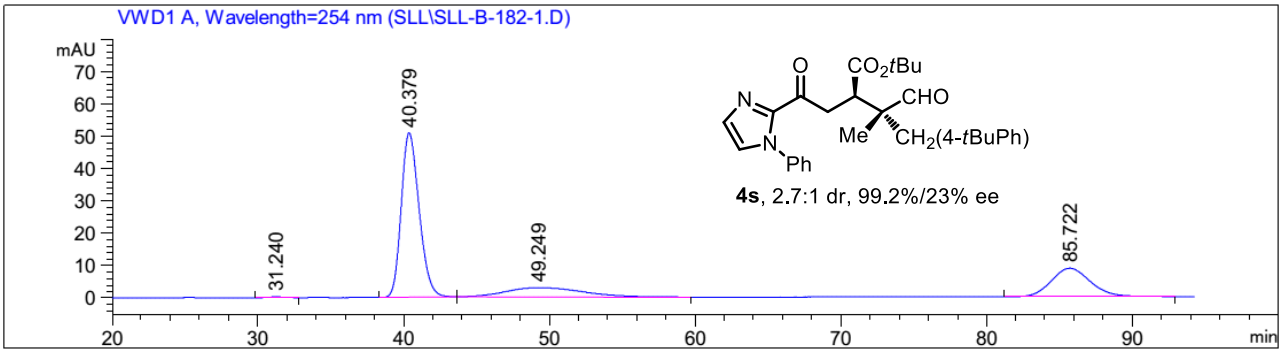
Figure S24. HPLC traces of *rac*-**4q**/**4q'** and (*2R,3R*)-**4q.**



#	[min]		[min]	[mAU*s]	[mAU]	%
1	28.815	BB	0.5947	70.45504	1.82391	0.2126
2	31.834	MF	0.3735	45.11794	2.01316	0.1361
3	32.735	FM R	0.7048	1.23815e4	292.78854	37.3589
4	34.948	VB	0.7147	2.06450e4	447.08990	62.2924

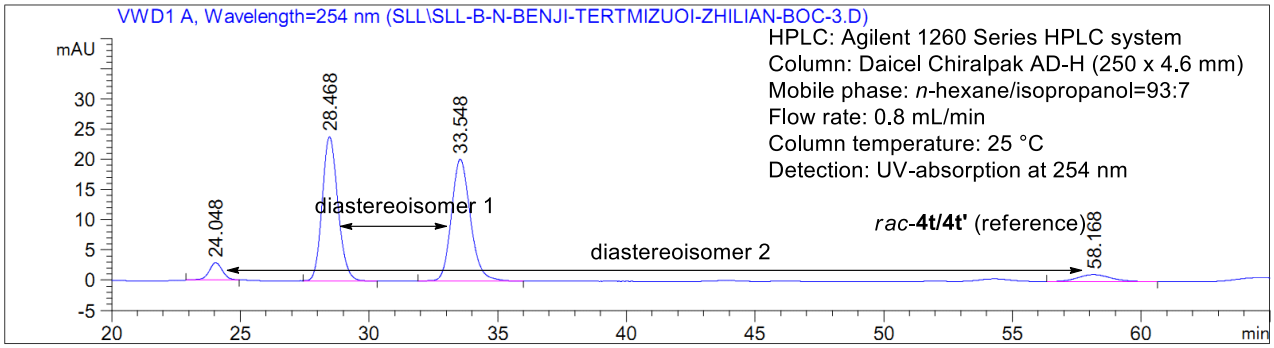
Figure S25. HPLC traces of *rac*-**4r/4r'** and (*2R*,*3R*)-**4r.**

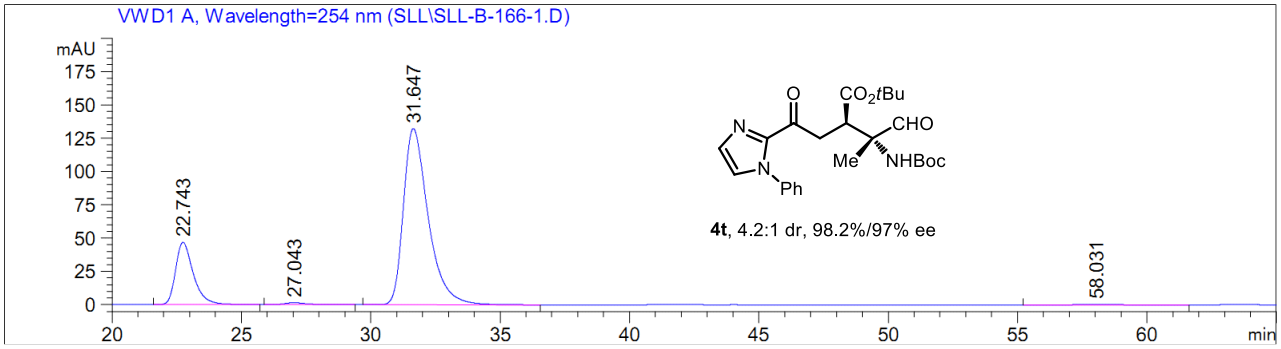




#	[min]		[min]	[mAU*s]	[mAU]	%
1	31.240	BB	0.8654	18.69509	2.58003e-1	0.2658
2	40.379	BB	1.3182	4324.98975	50.75278	61.5025
3	49.249	BB	4.2992	1041.45581	2.83936	14.8098
4	85.722	BB	2.6802	1647.07312	8.76554	23.4218

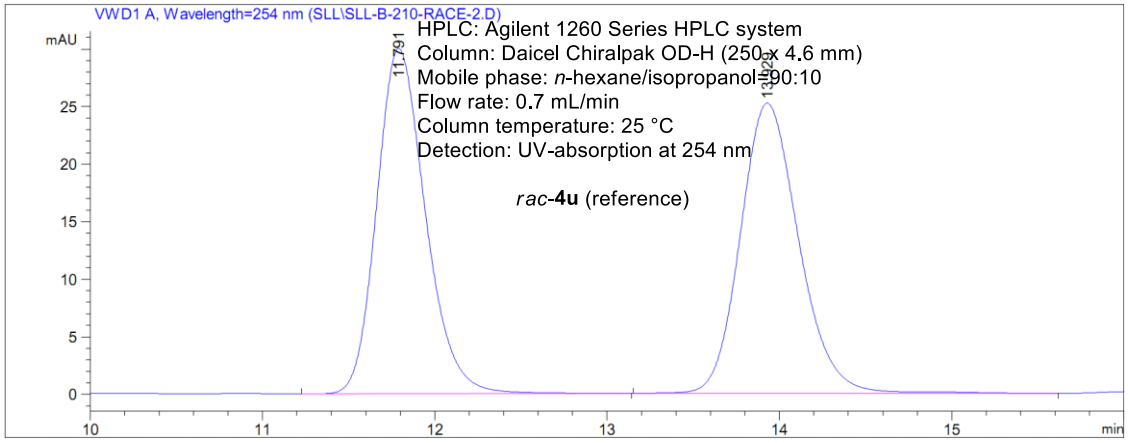
Figure S26 HPLC traces of *rac*-**4s**/**4s'** and (*2R*,*3R*)-**4s.**

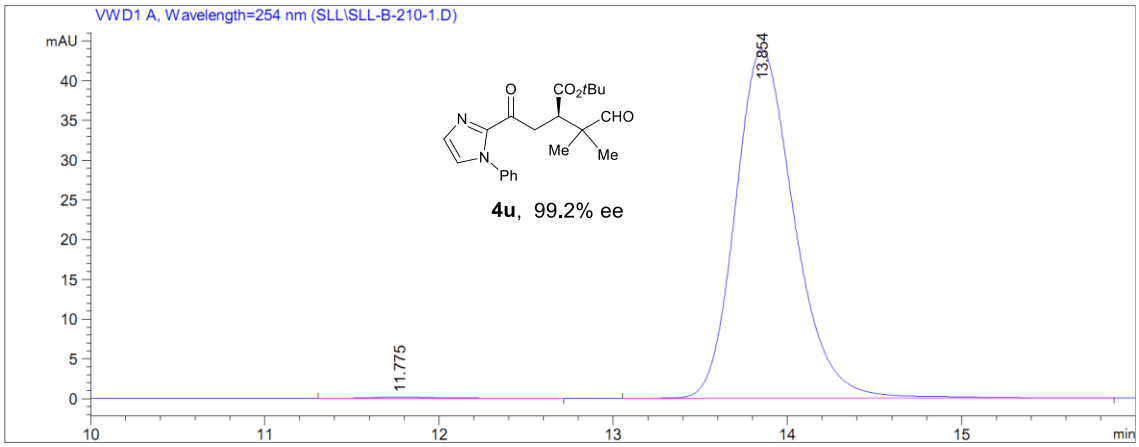




#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.743	BB	0.7228	2230.52734	46.73566	19.9764
2	27.043	BB	0.8064	80.18365	1.43395	0.7181
3	31.647	BB	1.0122	8823.47949	132.27562	79.0222
4	58.031	MM R	1.8306	31.64014	2.88062e-1	0.2834

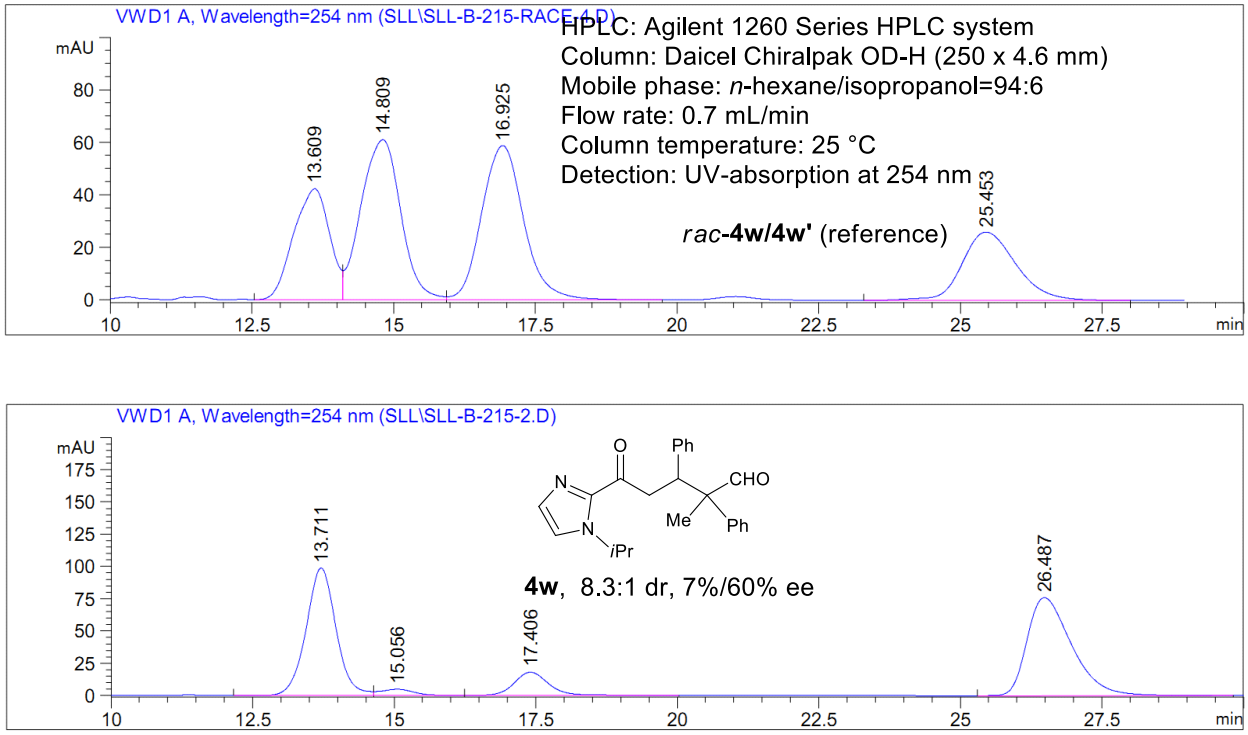
Figure S27. HPLC traces of *rac*-**4t/4t'** and (*2R,3R*)-**4t.**





#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.775	BB	0.3282	4.07099	1.85404e-1	0.3935
2	13.854	BV	0.3624	1030.59558	43.81099	99.6065

Figure S28. HPLC traces of *rac*-**4u** and (*R*)-**4u.**

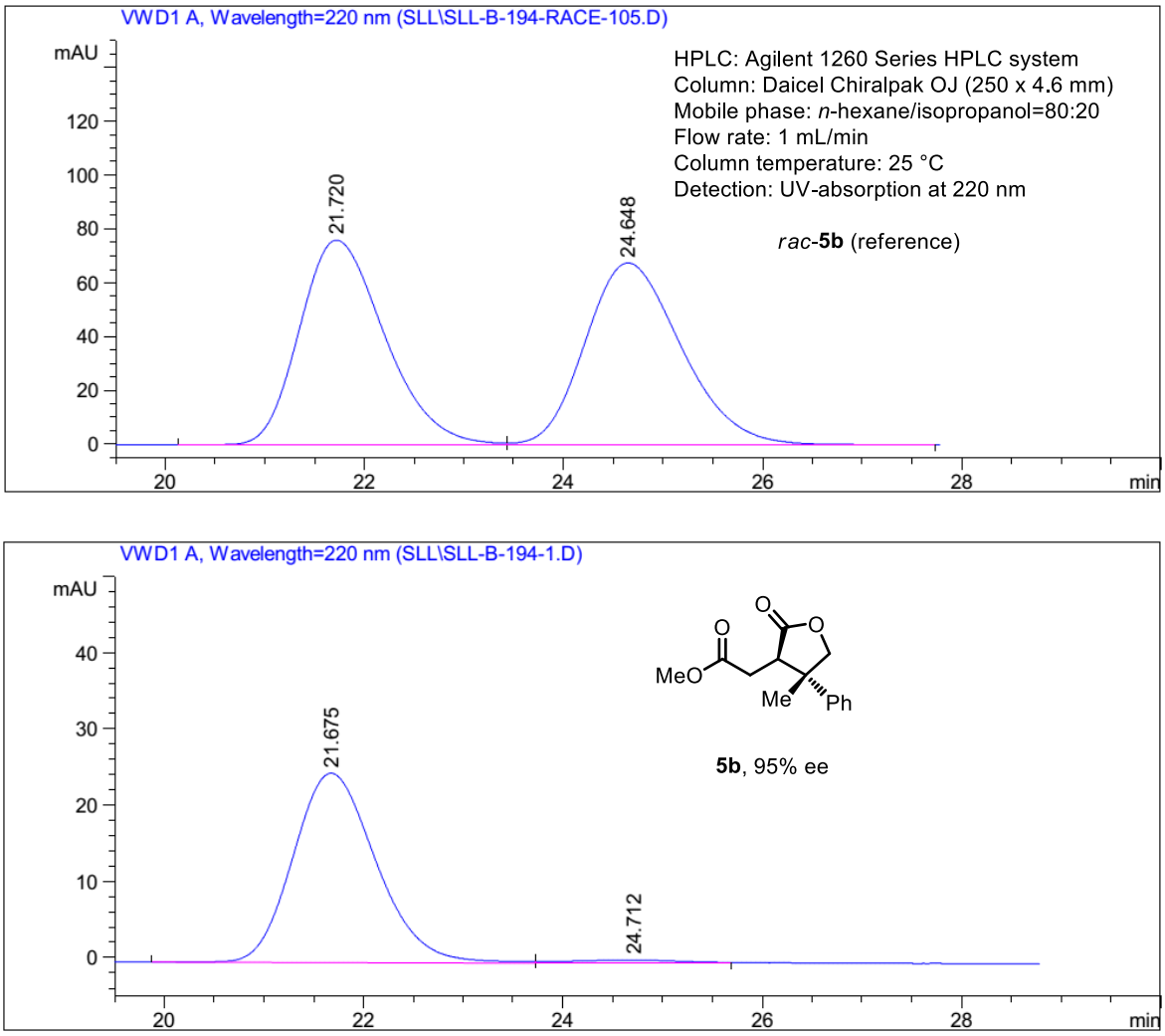


#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.711	BV	0.5596	3635.56543	98.73522	41.5244
2	15.056	VB	0.5997	197.13937	4.91720	2.2517
3	17.406	BB	0.6523	778.00952	18.14328	8.8862
4	26.487	BB	0.8388	4144.54395	75.92959	47.3378

Figure S29. HPLC traces of *rac*-**4w/4w'** and *nonrac*-**4w.**

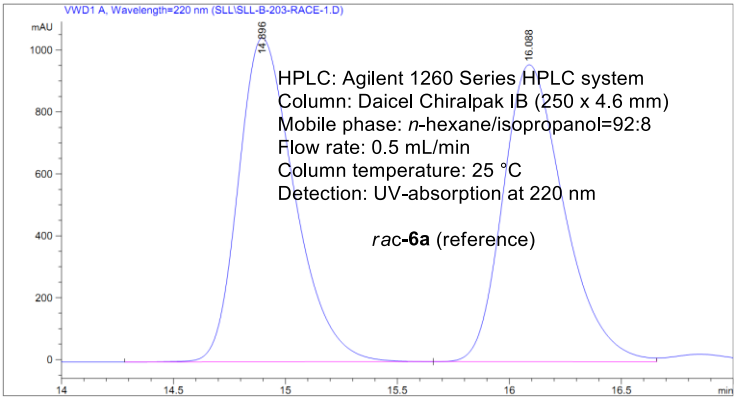
7.2 Chiral HPLC Traces of the Transformation Products

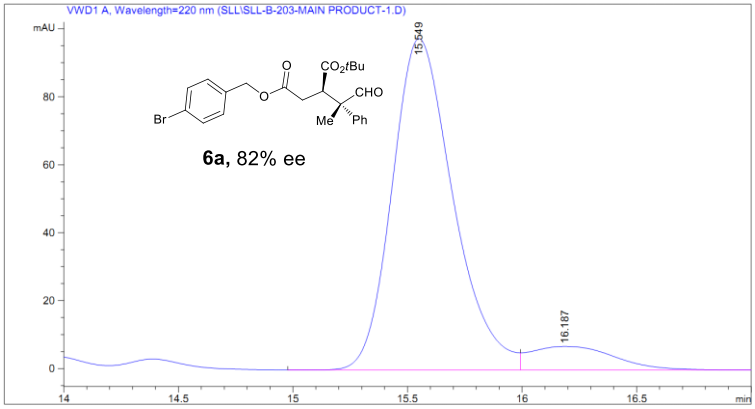
Enantiomeric excess of **5b**, **6a** and **6a'** were determined with a Daicel Chiralpak OJ, IB or OD-H column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using *n*-hexane/isopropanol as mobile phase, the temperature was 25 °C and UV-absorption was measured at 220 nm.



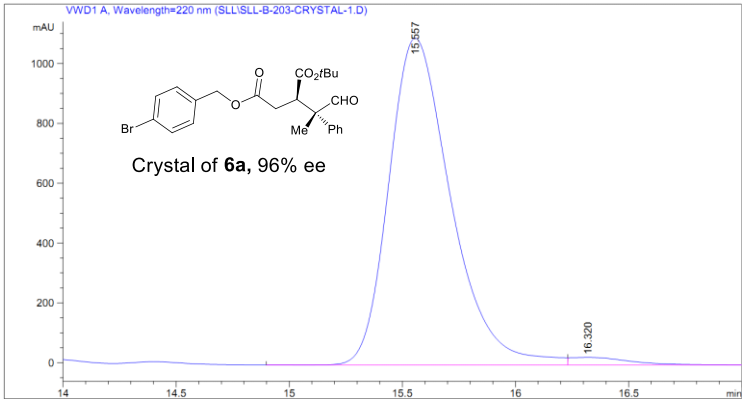
#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.675	BV	0.8995	1437.69116	24.83216	97.6992
2	24.712	MF R	1.2974	33.85800	4.34960e-1	2.3008

Figure S30. HPLC traces of *rac*-**5b** and (*3R,4S*)-**5b.**



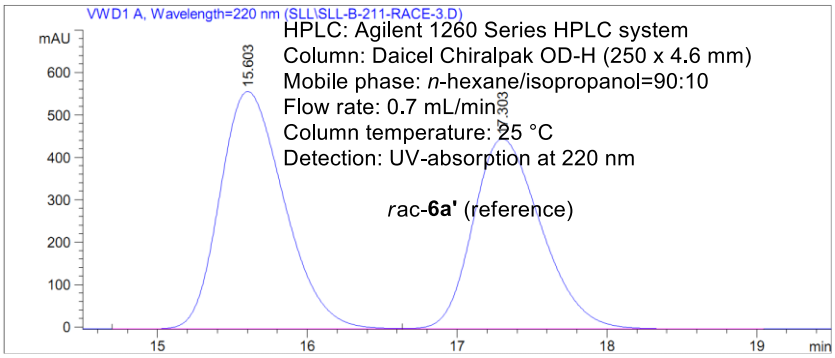


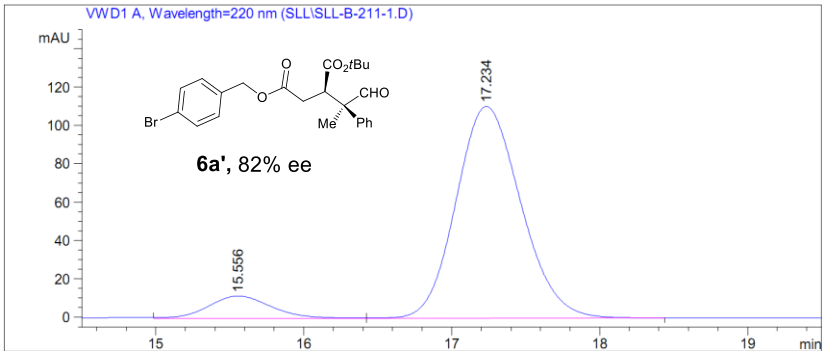
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.549	MF R	0.3088	1806.85425	97.52367	91.0972
2	16.187	FM R	0.4243	176.58191	6.93652	8.9028



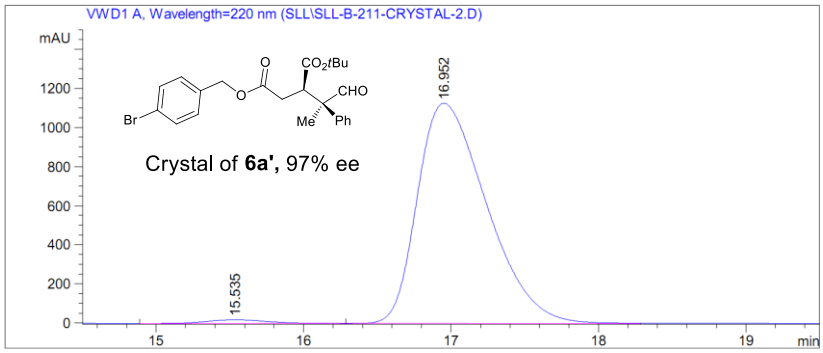
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.557	MF R	0.3179	2.08326e4	1092.12524	97.8612
2	16.320	FM R	0.3016	455.30652	25.16312	2.1388

Figure S31. HPLC traces of *rac*-**6a**, (*2R*,*3S*)-**6a** (synthesized from product **4a** with 98.9% ee) and (*2R*,*3S*)-**6a** (crystal).





#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.556	FM R	0.4843	336.03784	11.56466	9.0914
2	17.234	VV	0.4714	3360.16895	110.29673	90.9086



#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.535	BB	0.4414	528.33820	18.71237	1.4148
2	16.952	BV	0.5094	3.68145e4	1126.13953	98.5852

Figure S32. HPLC traces of *rac*-**6a'**, (*2R,3R*)-**6a'** (synthesized from product **4a'** with 90% ee) and (*2R,3R*)-**6a'** (crystal).

8. Single Crystal X-Ray Diffraction

8.1 Single Crystal X-Ray Diffraction of Rhodium Catalyst Δ_{Rh}-*S*C-Rh1

Crystals of Δ_{Rh}-*S*C-**Rh1** was obtained by slow diffusion from a solution of the compound in CH_2Cl_2 layered with Et_2O at room temperature for several days. Data were collected on an Oxford Xcalibur, Sapphire3, Gemini ultra detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on F^2 data of one twin domain using SHELXL-97. The absolute configuration was determined. The structure is shown in Figure S33. The detailed information is listed in the Table S3. Crystallographic data for Δ_{Rh}-*S*C-**Rh1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1465210.

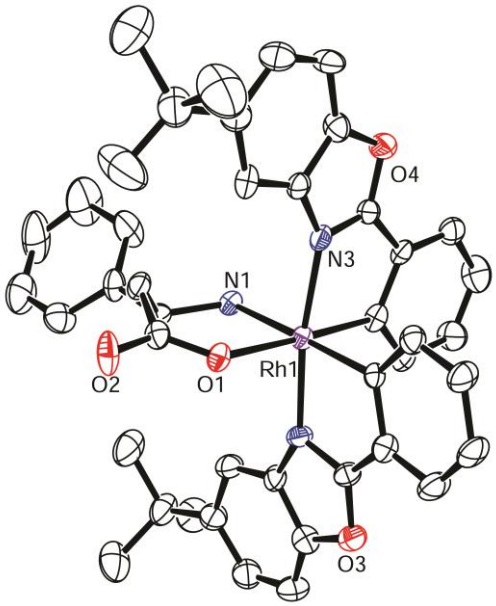


Figure S33. Ortep drawing of rhodium catalyst Δ_{Rh}-*S*C-**Rh1** with 50% probability thermal ellipsoids, the absolute configuration was identified as Δ_{Rh}-*S*C.

8.2 Single Crystal X-Ray Diffraction of the Converted Product 6a

Crystals of compound **6a** were obtained by recrystallization from a solution of the compound in *n*-hexane. Diffraction data were collected on a Bruker Apex CCD area detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 203 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on F^2 data of one twin domain using SHELXL-97. The absolute configuration was determined. The structure is shown in Figure S34. The detailed information is listed in the Table S3. Crystallographic data for **6a** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1460793.

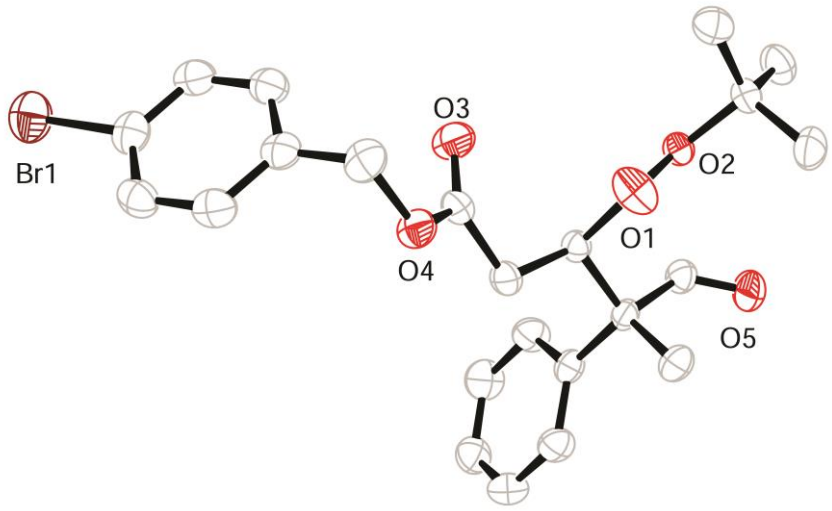


Figure S34. Ortep drawing of **6a** with 50% probability thermal ellipsoids, the absolute configuration was identified as 2*R*,3*S*.

8.3 Single Crystal X-Ray Diffraction of the Converted Product 6a'

Crystals of compound **6a'** were obtained by recrystallization from a solution of the compound in *n*-hexane. Diffraction data were collected on a Bruker Apex CCD area detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on F^2 data of one twin domain using SHELXL-97. The absolute configuration was determined. The structure is shown in Figure S35. The detailed information is listed in the Table S3. Crystallographic data for **6a'** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1472577 .

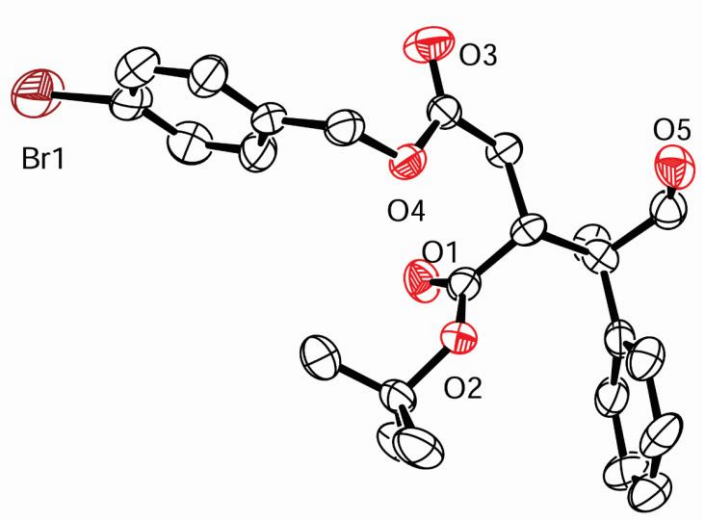


Figure S35. Ortep drawing of **6a'** with 50% probability thermal ellipsoids, the absolute configuration was identified as 2*R*,3*R*.

Table S3. Data collection and refinement statistics for the compounds Δ_{Rh}-S_C-**Rh1**, **6a** and **6a'**.

	Δ_{Rh}-S_C-**Rh1**	**6a**	**6a'**
Empirical formula	C_{43} H_{44} Br N_3 O_5 Rh	C_{24} H_{27} Br O_5	C_{24} H_{27} Br O_5
Formula weight	785.72	475.37	475.37
Temperature (K)	173(2)	203(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	P2(1)2(1)2(1)	P2(1)	P2(1)2(1)2(1)
Cell dimensions			
a, b, c (Å)	12.6831, 13.3648, 25.5629	11.882, 6.1817, 15.840	6.202, 12.159, 30.276
α, β, γ (°)	90, 90, 90	90, 108.485, 90	90, 90, 90
Volume ($Å^3$)	4333.1 (3)	1103.4(5)	2283.1
Z	4	2	4
Density (calculated, mg/m^3)	1.204	1.431	1.383
Absorption coefficient (mm^{-1})	0.437	1.895	1.832
F(000)	1632	492	984
Crystal size (mm^3)	0.19 x 0.17 x 0.16	0.30 x 0.22 x 0.16	0.20 x 0.15 x 0.10
Theta range for data collection	3.05 to 25.99°	1.36 to 26.00°	1.35 to 25.00°
Index ranges	-13<=h<=15, -16<=k<=9, -31<=l<=27	-14<=h<=14, -7<=k<=7, -19<=l<=19	-7<=h<=7, -14<=k<=14, -36<=l<=36
Reflections collected	13357	8155	16429
Independent reflections	8035[R(int) = 0.0445]	4165 [R(int) = 0.0198]	4033 [R(int) =0.0973]

Completeness	99.1 %	98.1 %	100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8035 / 12 / 478	4165 / 1 / 271	4033 / 0 / 271
Goodness-of-fit on F^2	1.001	1.013	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0792, wR2 = 0.2105	R1 = 0.0331, wR2 = 0.0860	R1 = 0.0601, wR2 = 0.1068
R indices (all data)	R1 = 0.0888, wR2 = 0.2191	R1 = 0.0367, wR2 = 0.0871	R1 = 0.0922, wR2 = 0.1140
Absolute structure parameter	0.03(7)	0.031(8)	0.021(13)
Largest diff. peak and hole (e.$Å^{-3}$)	1.933 and -0.975	0.438 and -0.209	0.612 and -0.349

9. References

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10. ^{1}H NMR and ^{13}C NMR Spectra

10.1 ^{1}H NMR and ^{13}C NMR Spectra of Rhodium Catalyst Δ_{Rh}-S_C-Rh1

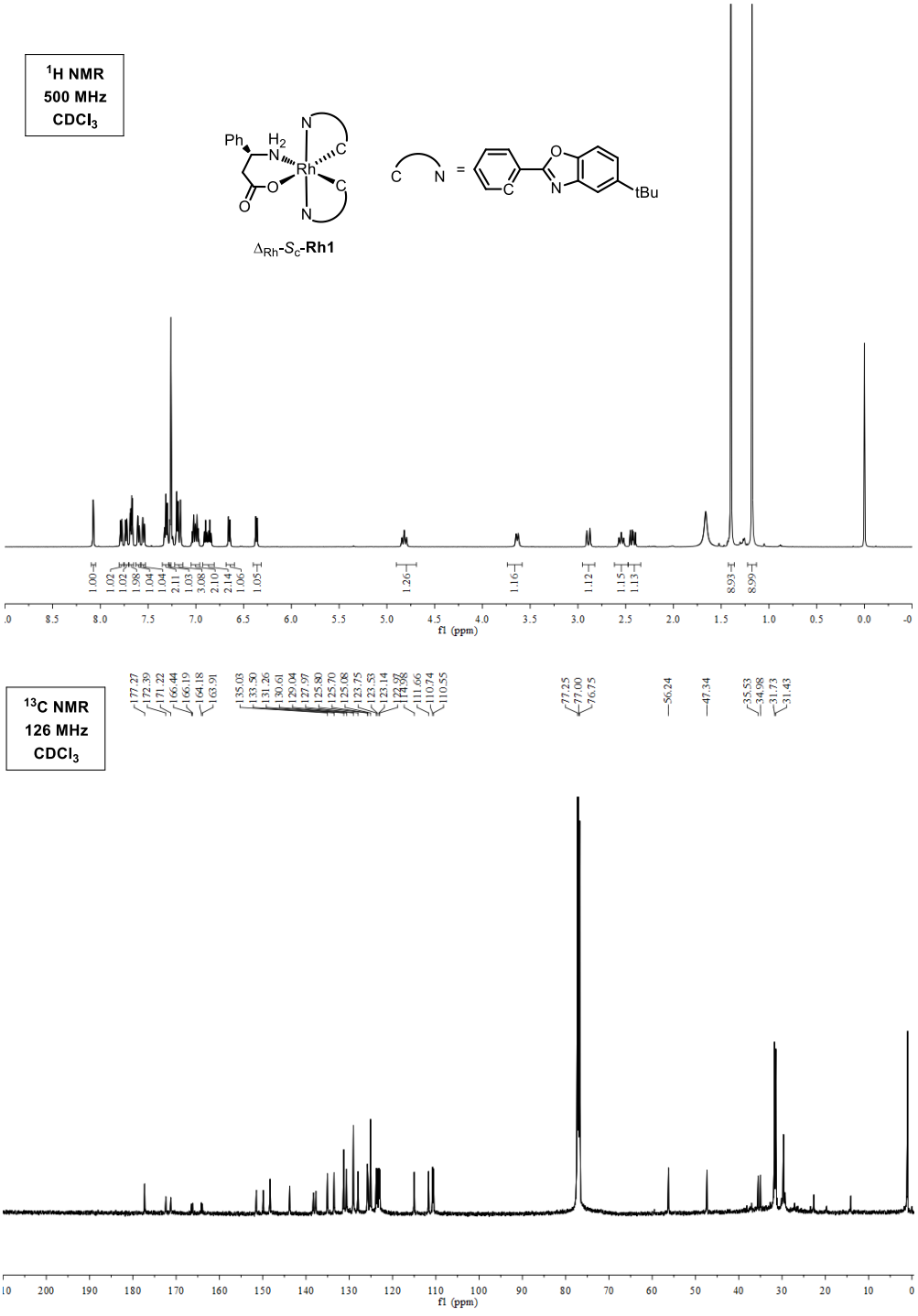

Figure S36. ^{1}H and ^{13}C NMR spectrum for Δ_{Rh}-S_C-**Rh1.**

10.2 ^{1}H NMR and ^{13}C NMR Spectra of Substrates and Products

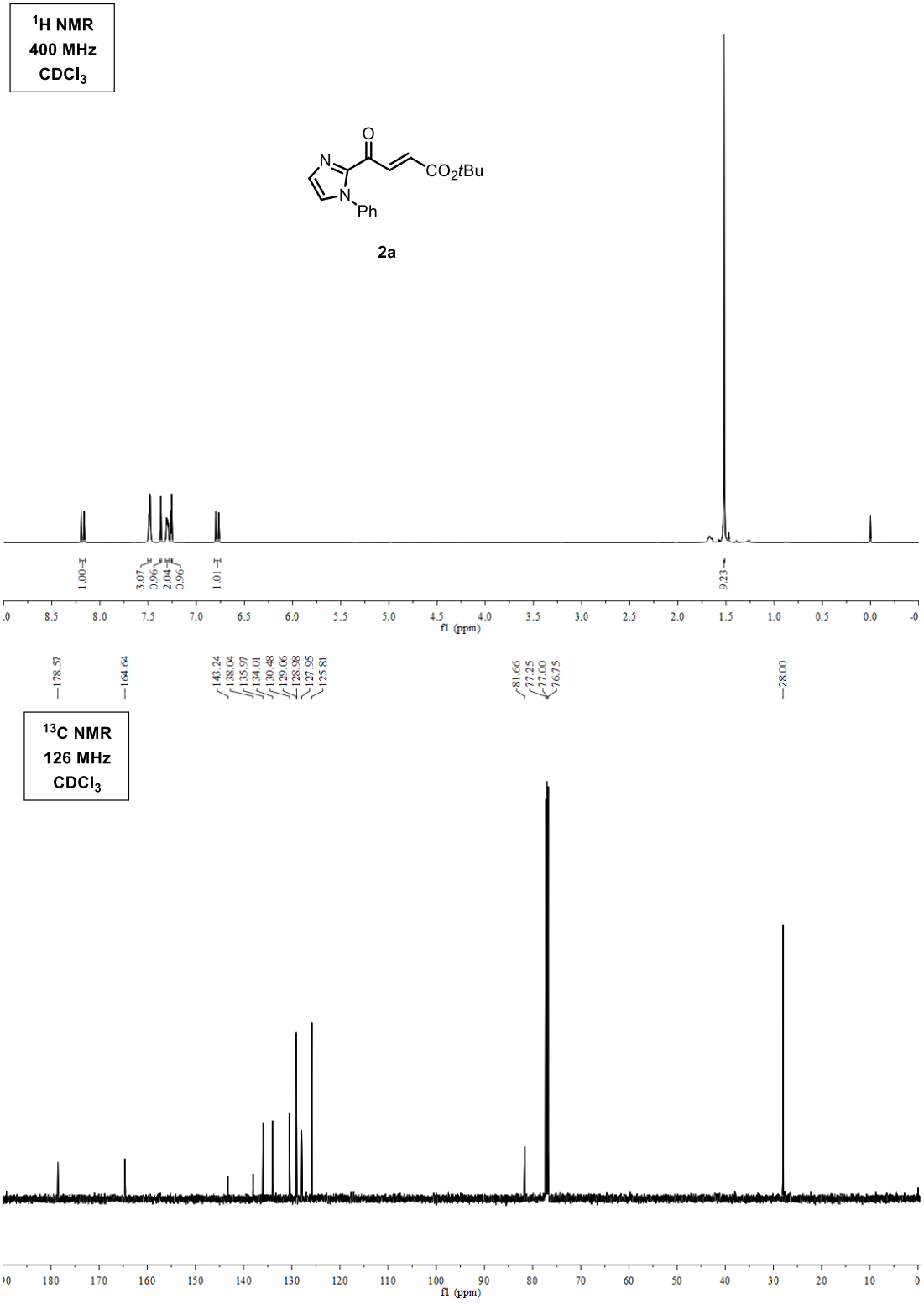

Figure S37. ^{1}H and ^{13}C NMR spectrum for **2a.**

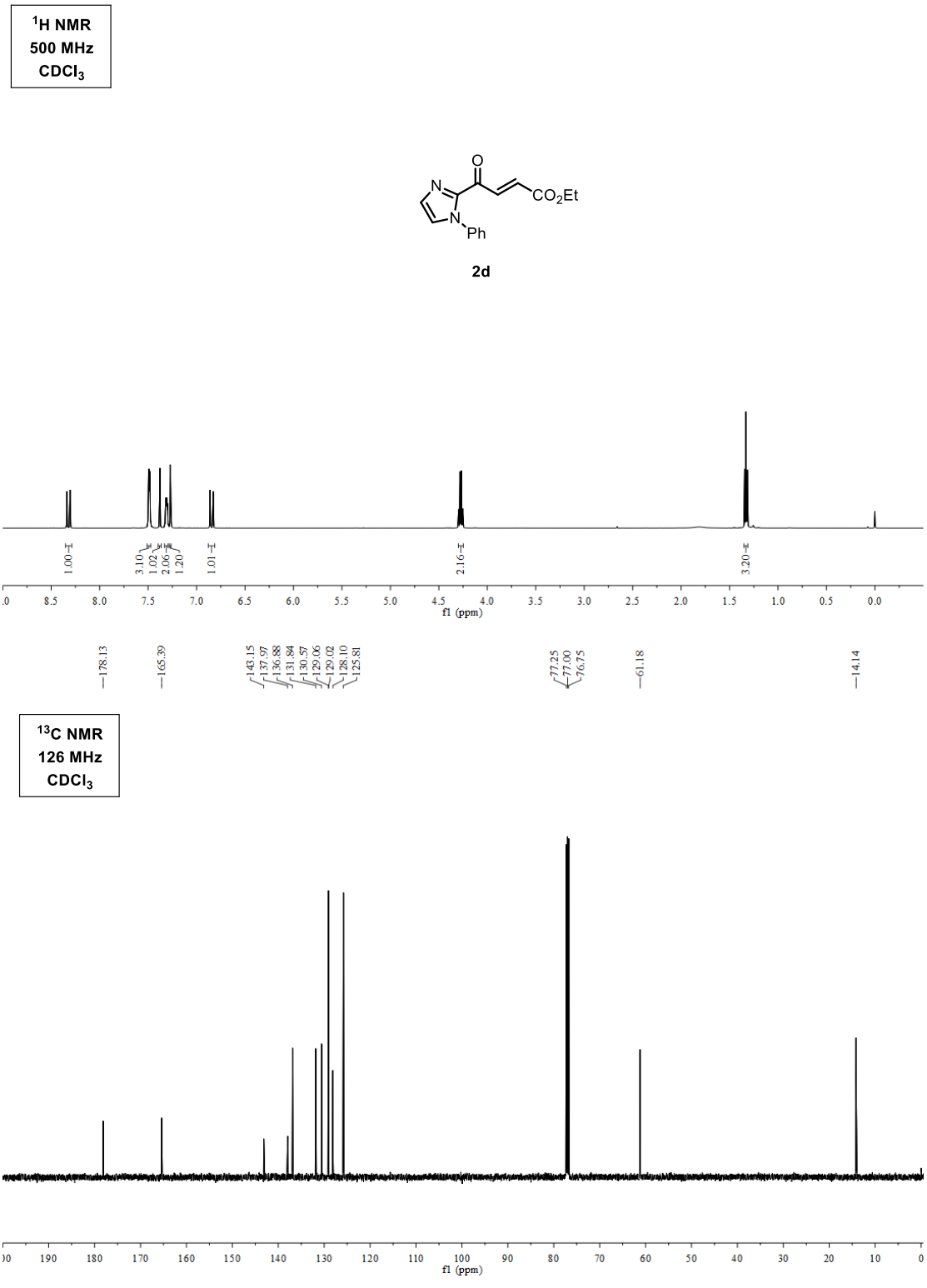

Figure S38. ^{1}H and ^{13}C NMR spectrum for **2d.**

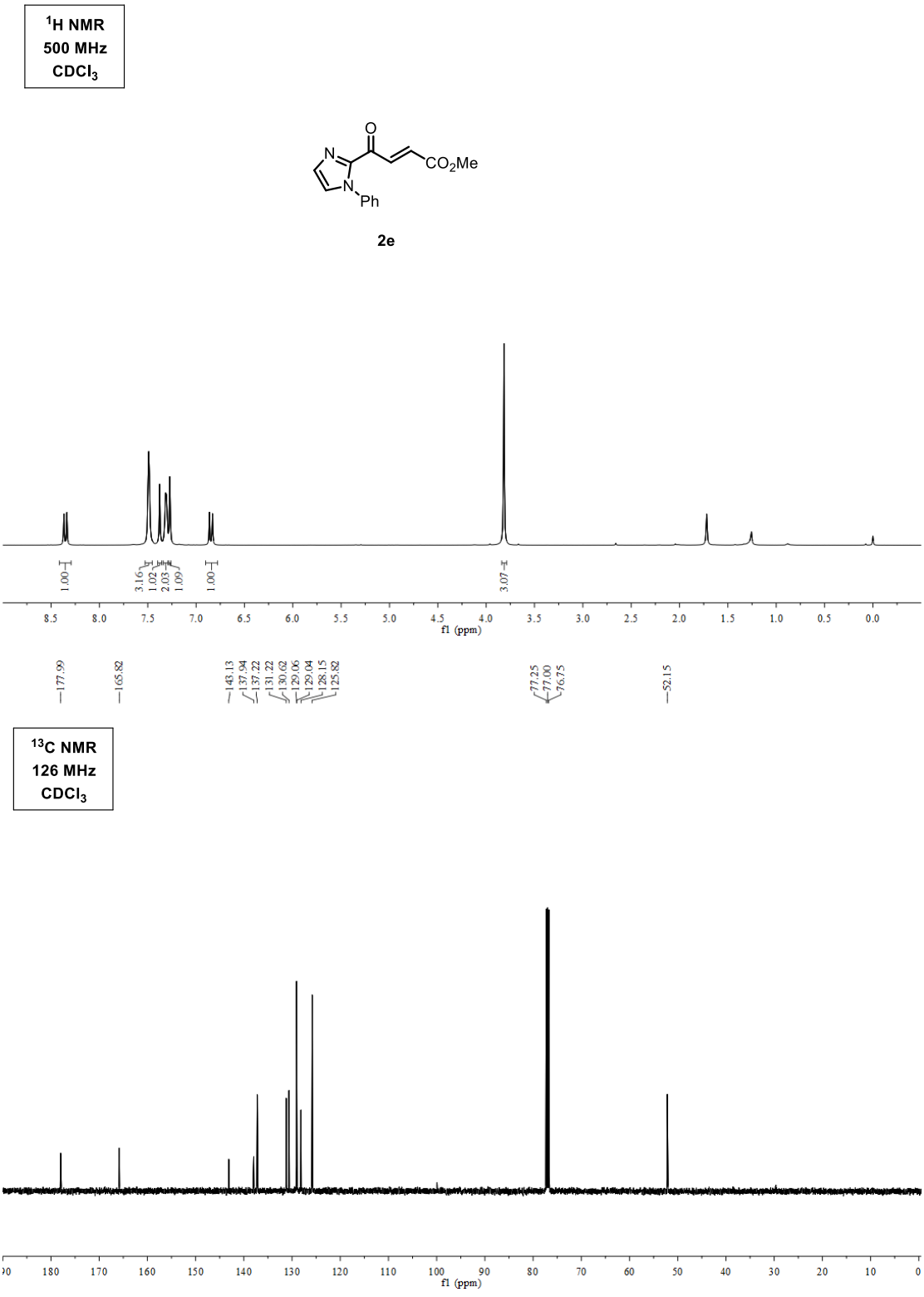

Figure S39. ^{1}H and ^{13}C NMR spectrum for **2e.**

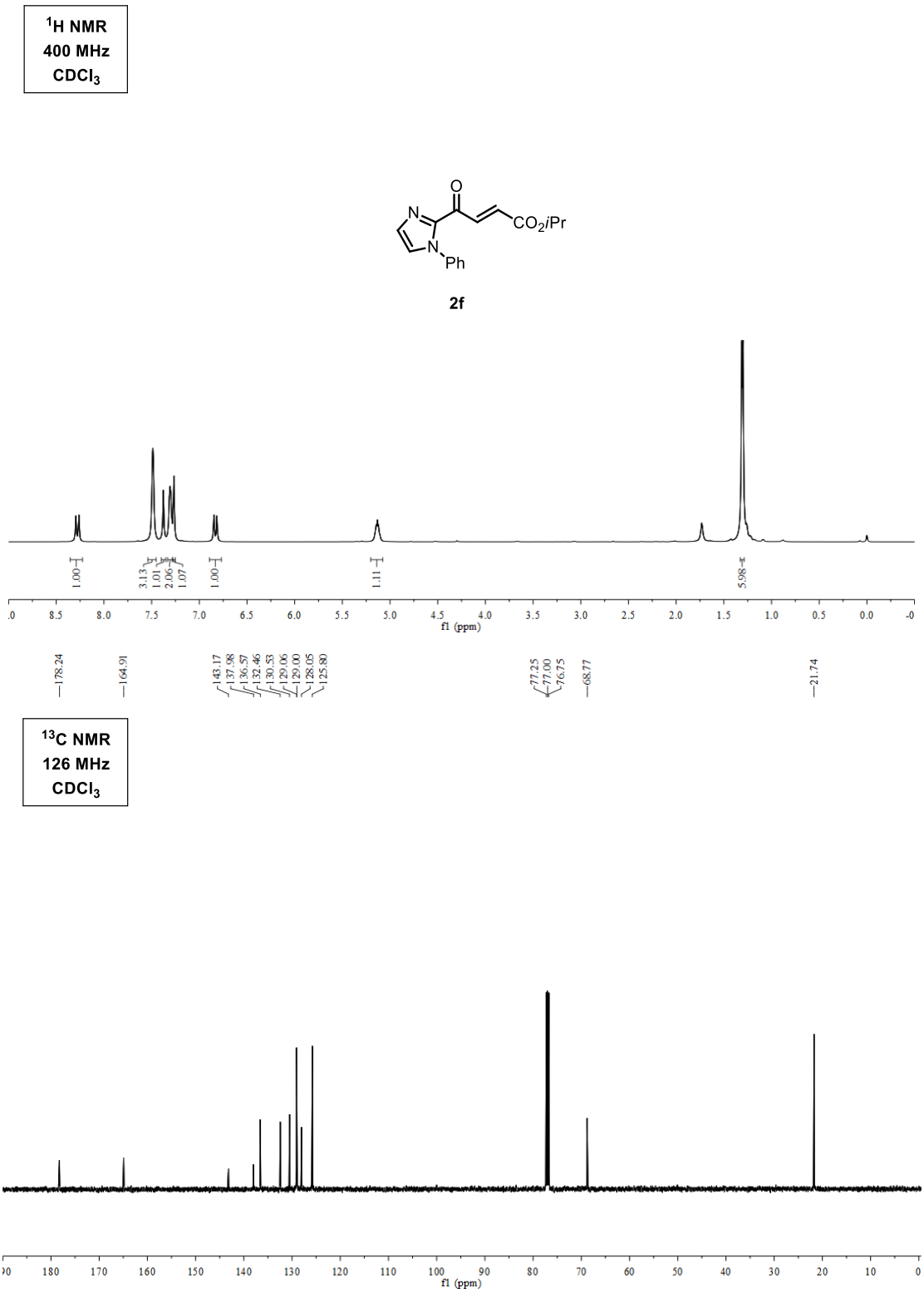

Figure S40. ^{1}H and ^{13}C NMR spectrum for **2f.**

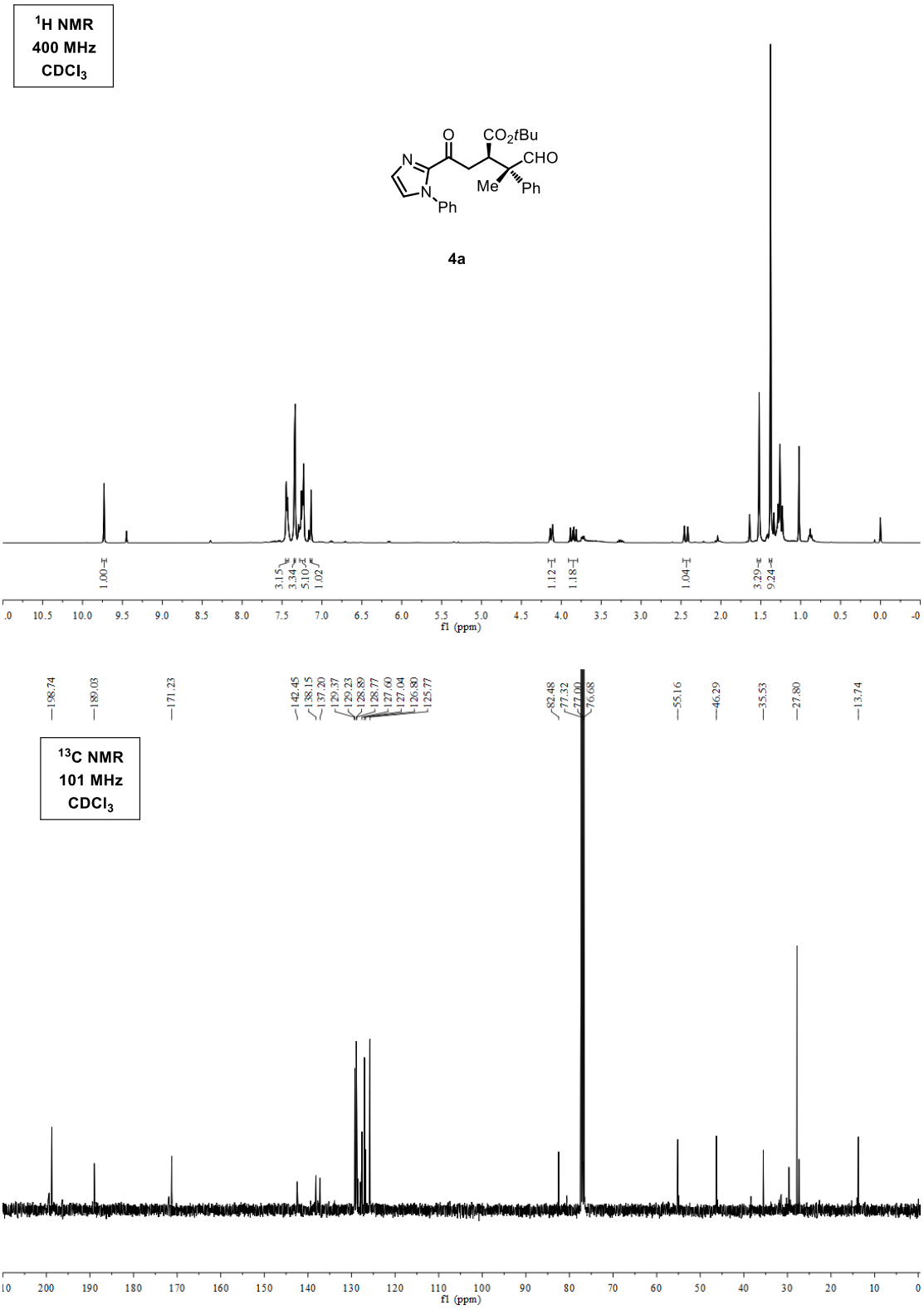

Figure S41. ^{1}H and ^{13}C NMR spectrum for **4a.**

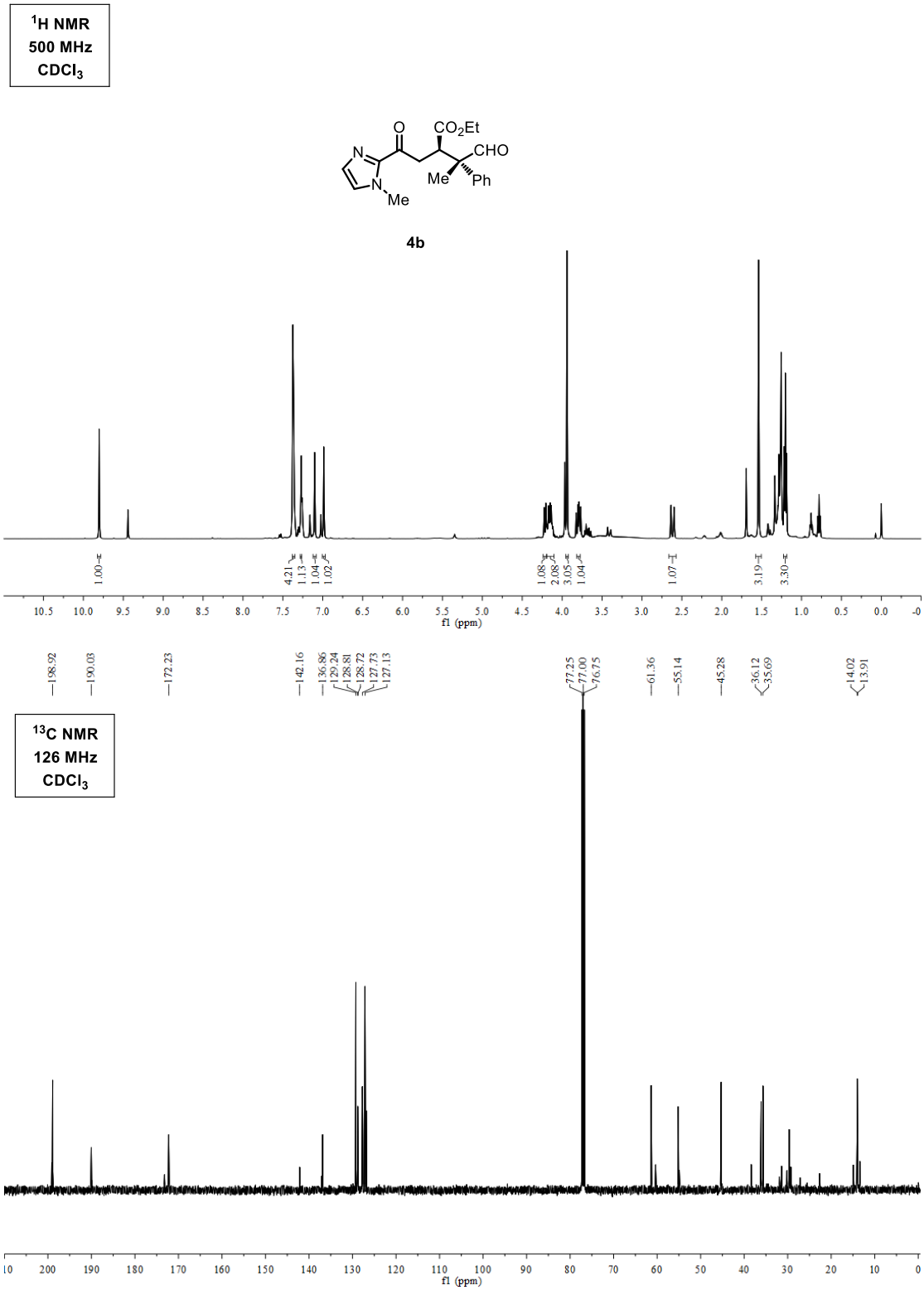

Figure S42. ^{1}H and ^{13}C NMR spectrum for **4b.**

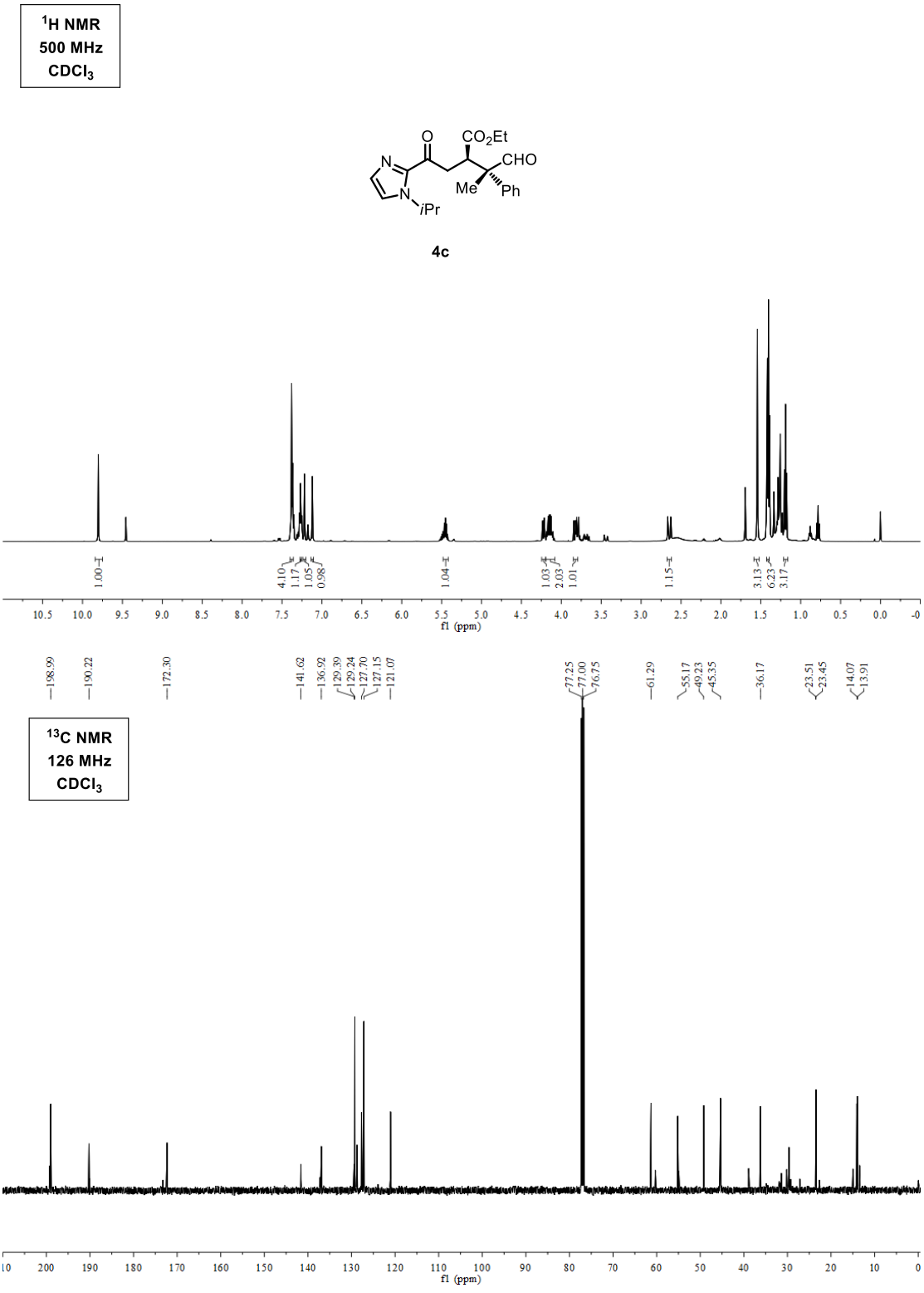

Figure S43. ^{1}H and ^{13}C NMR spectrum for **4c.**

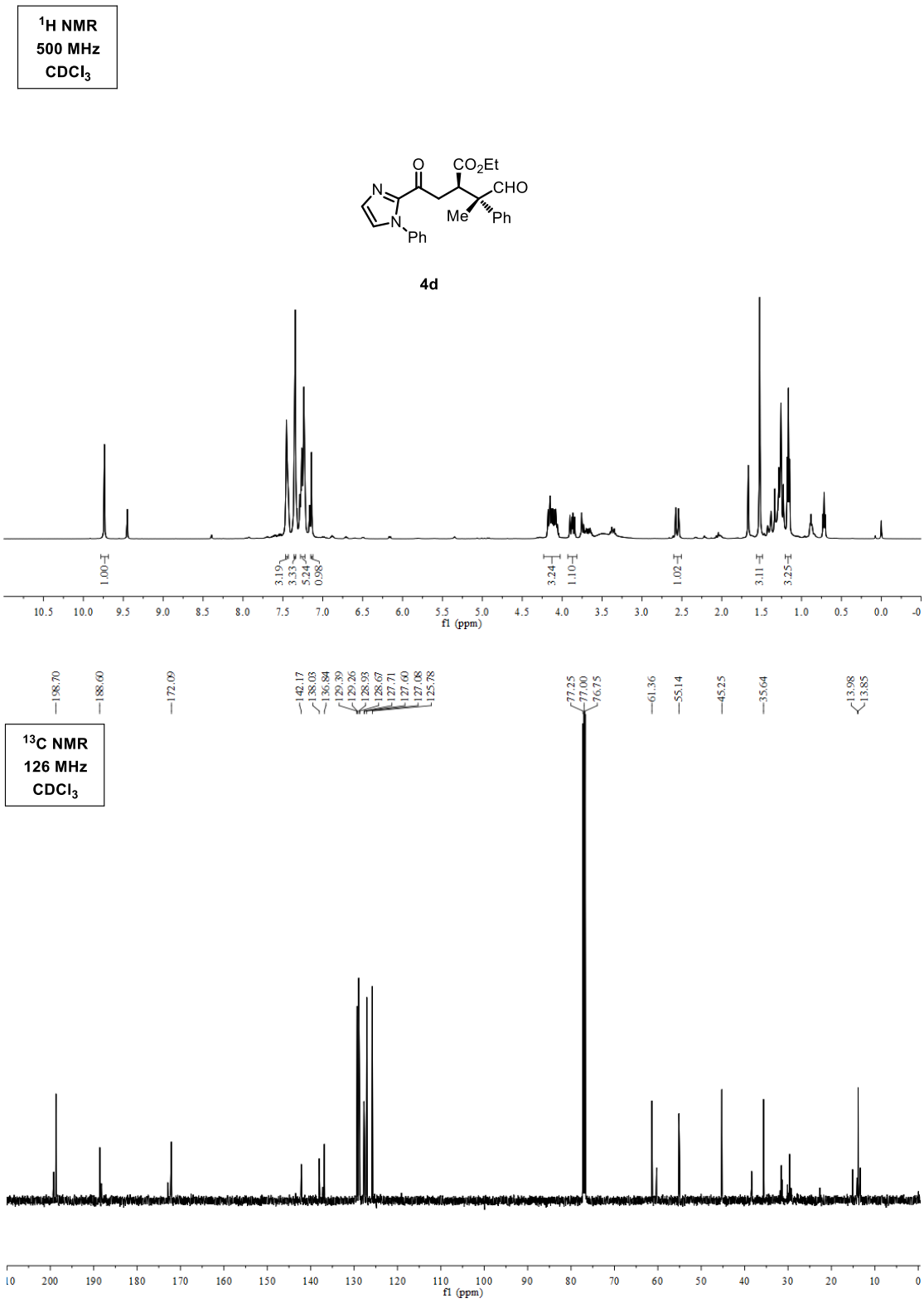

Figure S44. ^{1}H and ^{13}C NMR spectrum for **4d.**

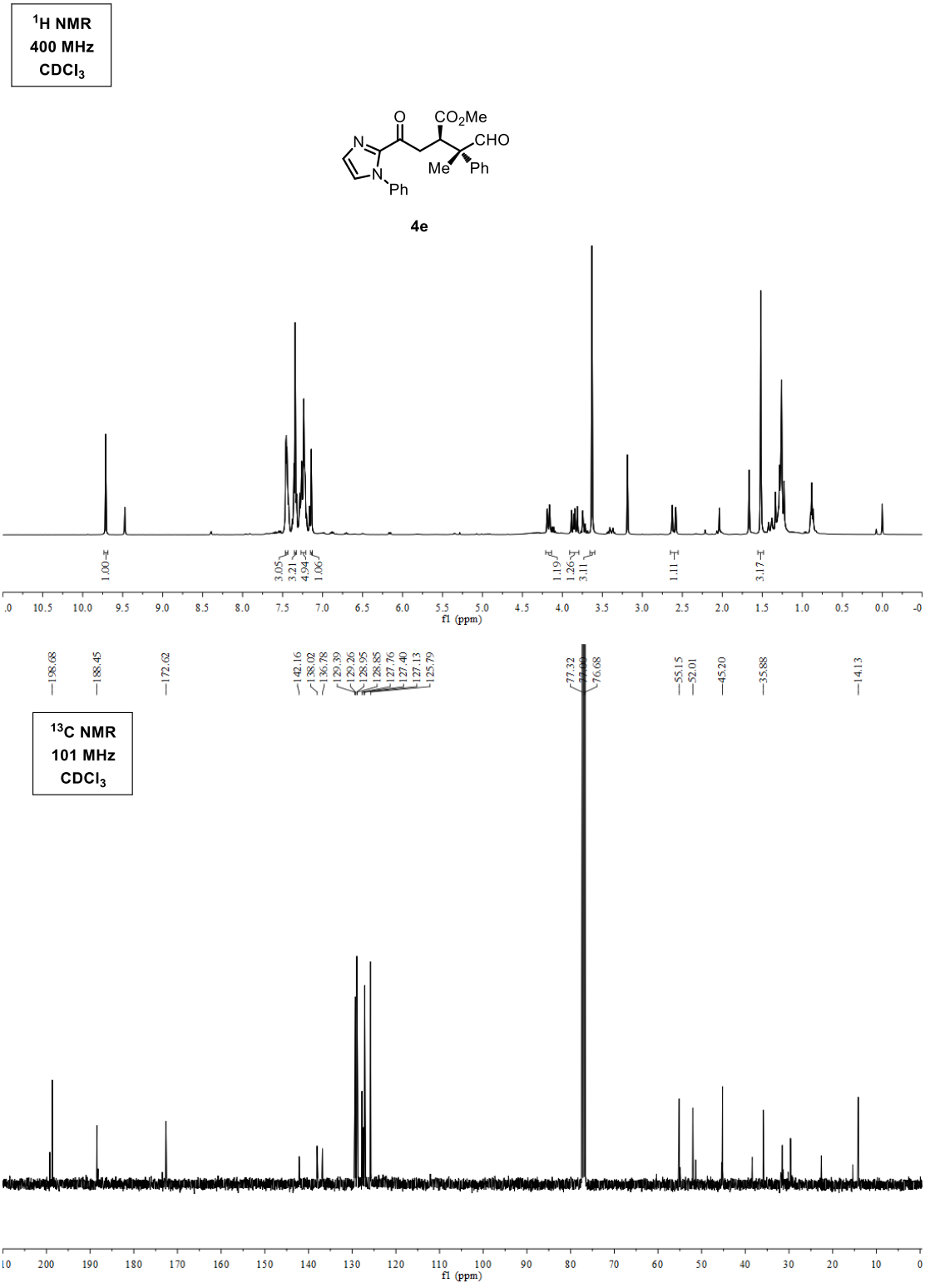

Figure S45. ^{1}H and ^{13}C NMR spectrum for **4e.**

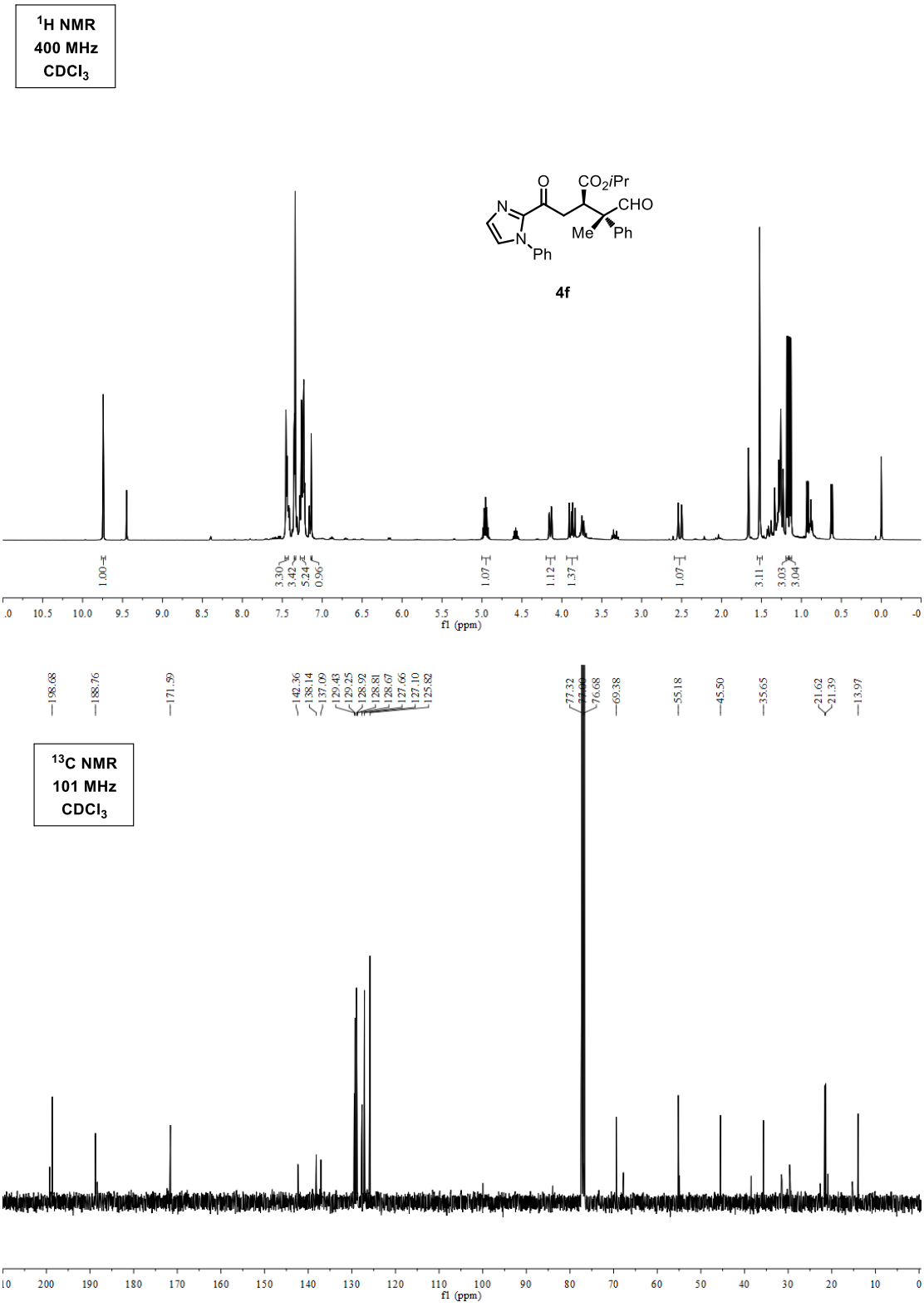

Figure S46. ^{1}H and ^{13}C NMR spectrum for **4f.**

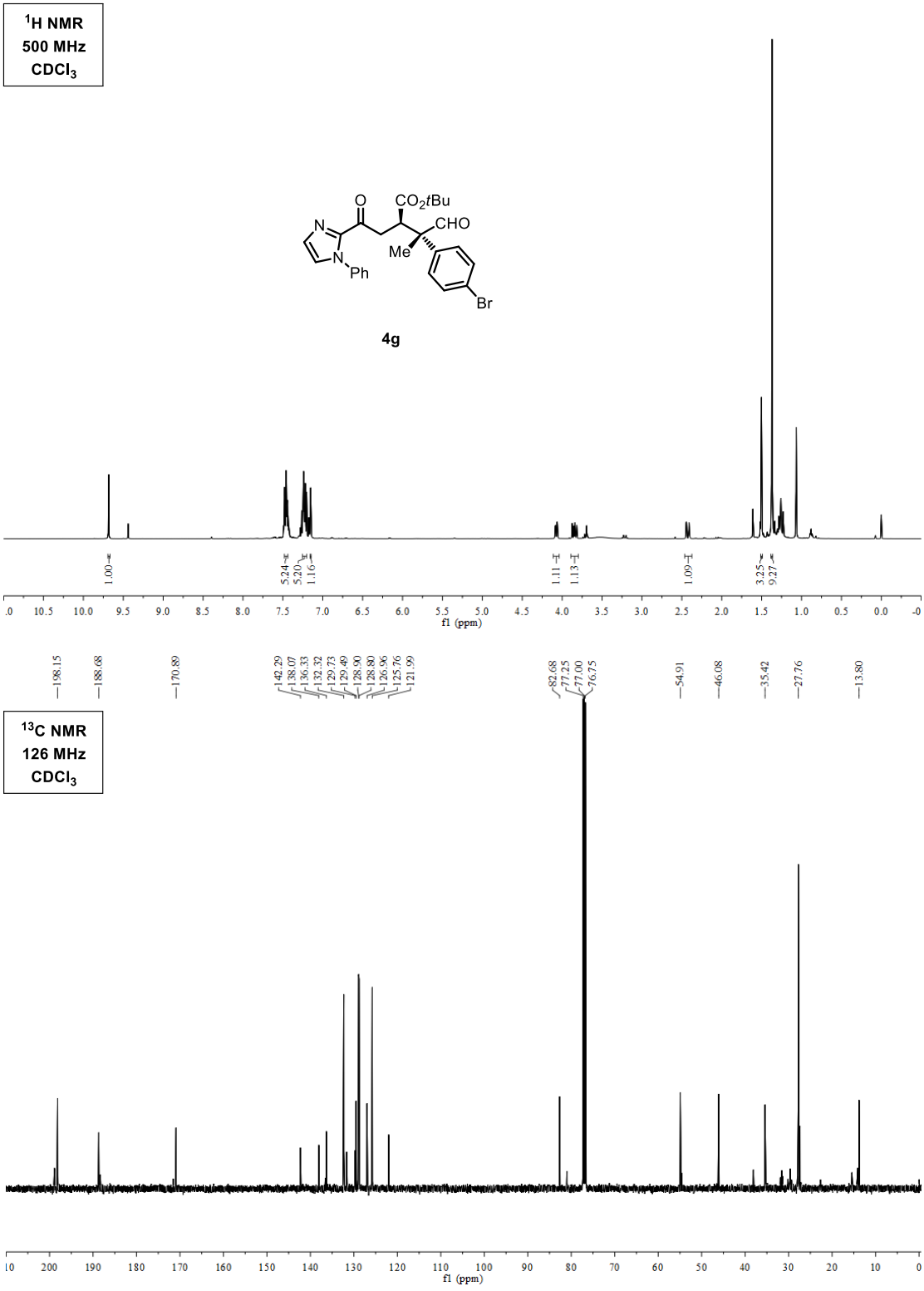

Figure S47. ^{1}H and ^{13}C NMR spectrum for **4g.**

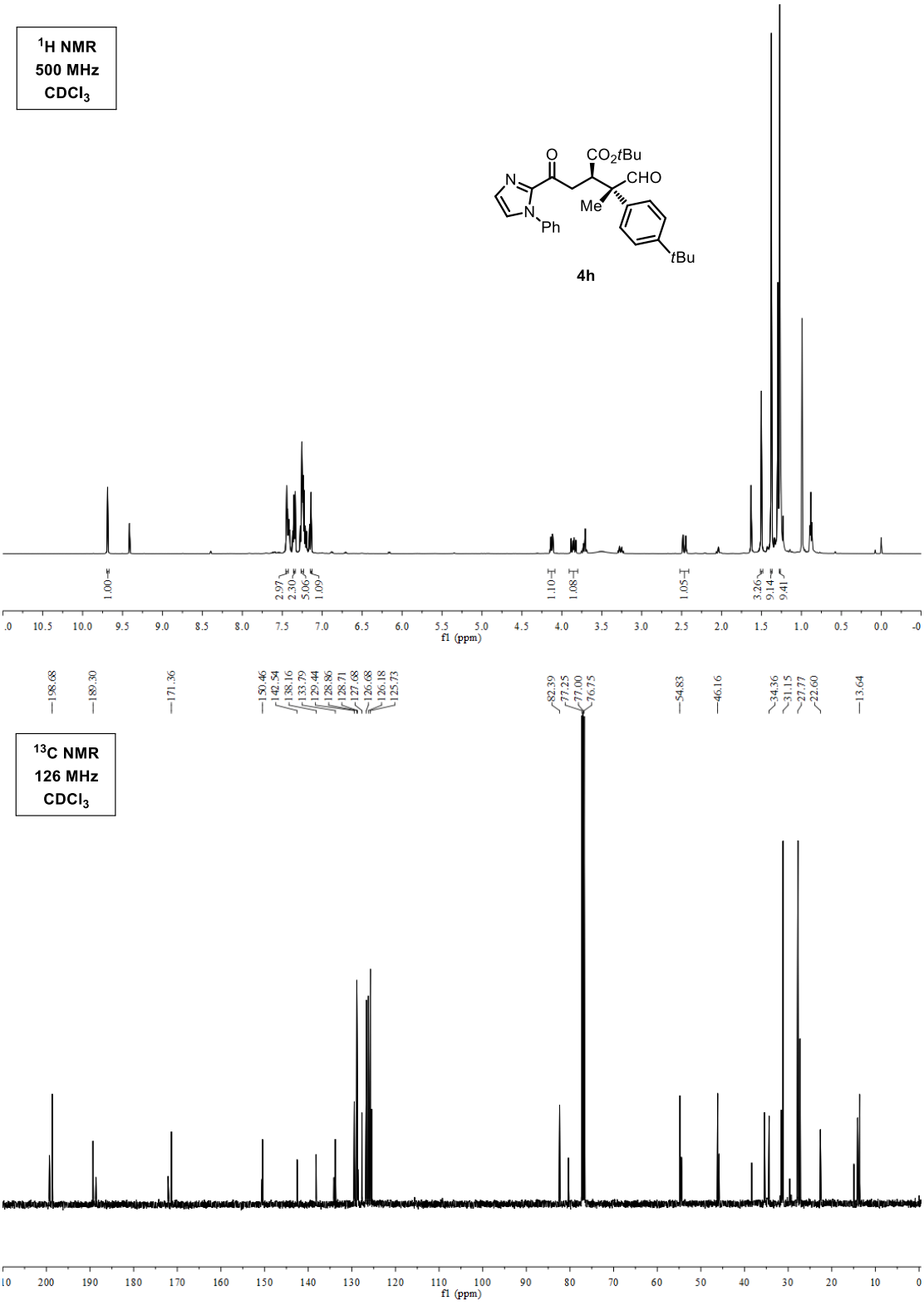

Figure S48. ^{1}H and ^{13}C NMR spectrum for **4h.**

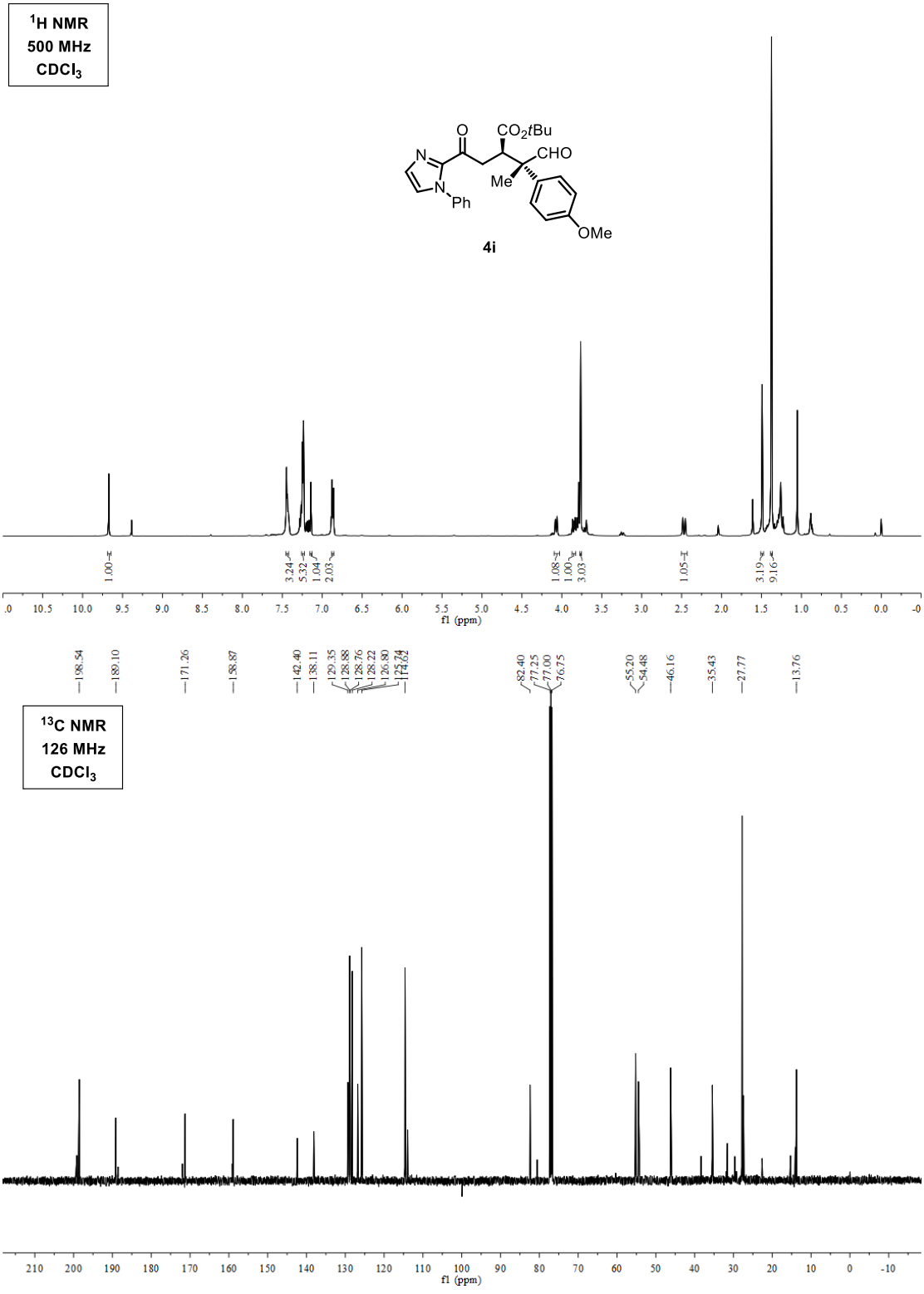

Figure S49. ^{1}H and ^{13}C NMR spectrum for **4i.**

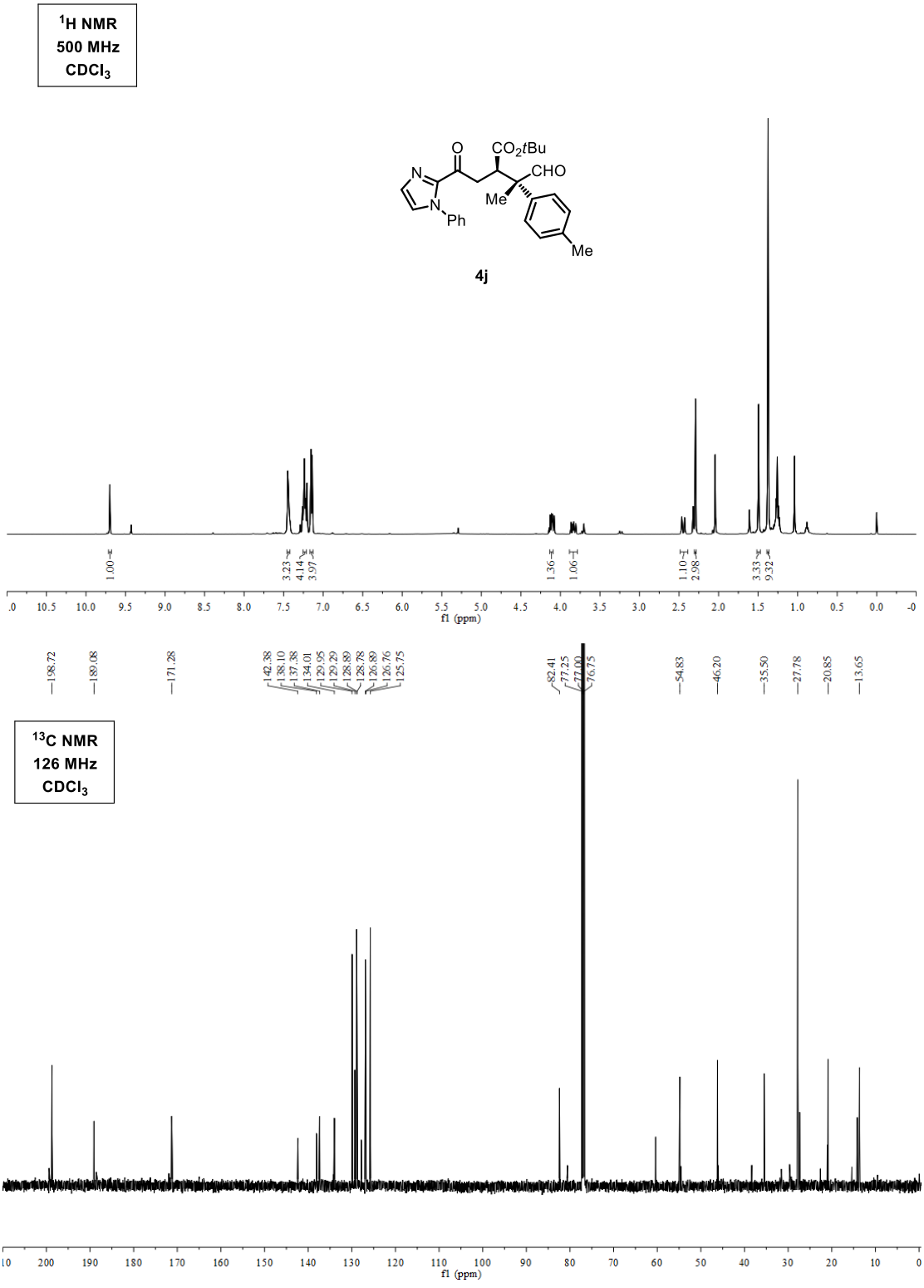

Figure S50. ^{1}H and ^{13}C NMR spectrum for **4j.**

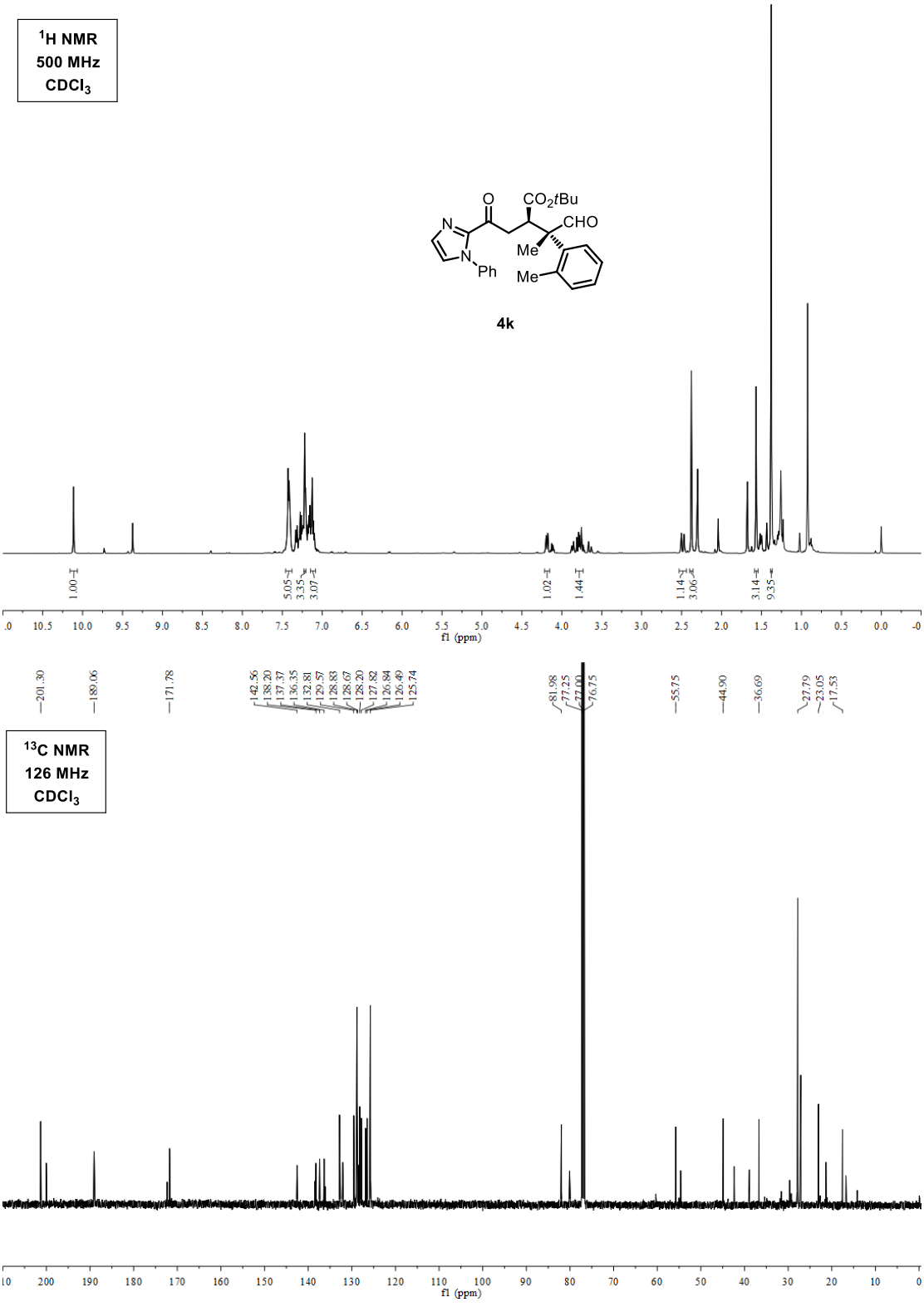

Figure S51. ^{1}H and ^{13}C NMR spectrum for **4k.**

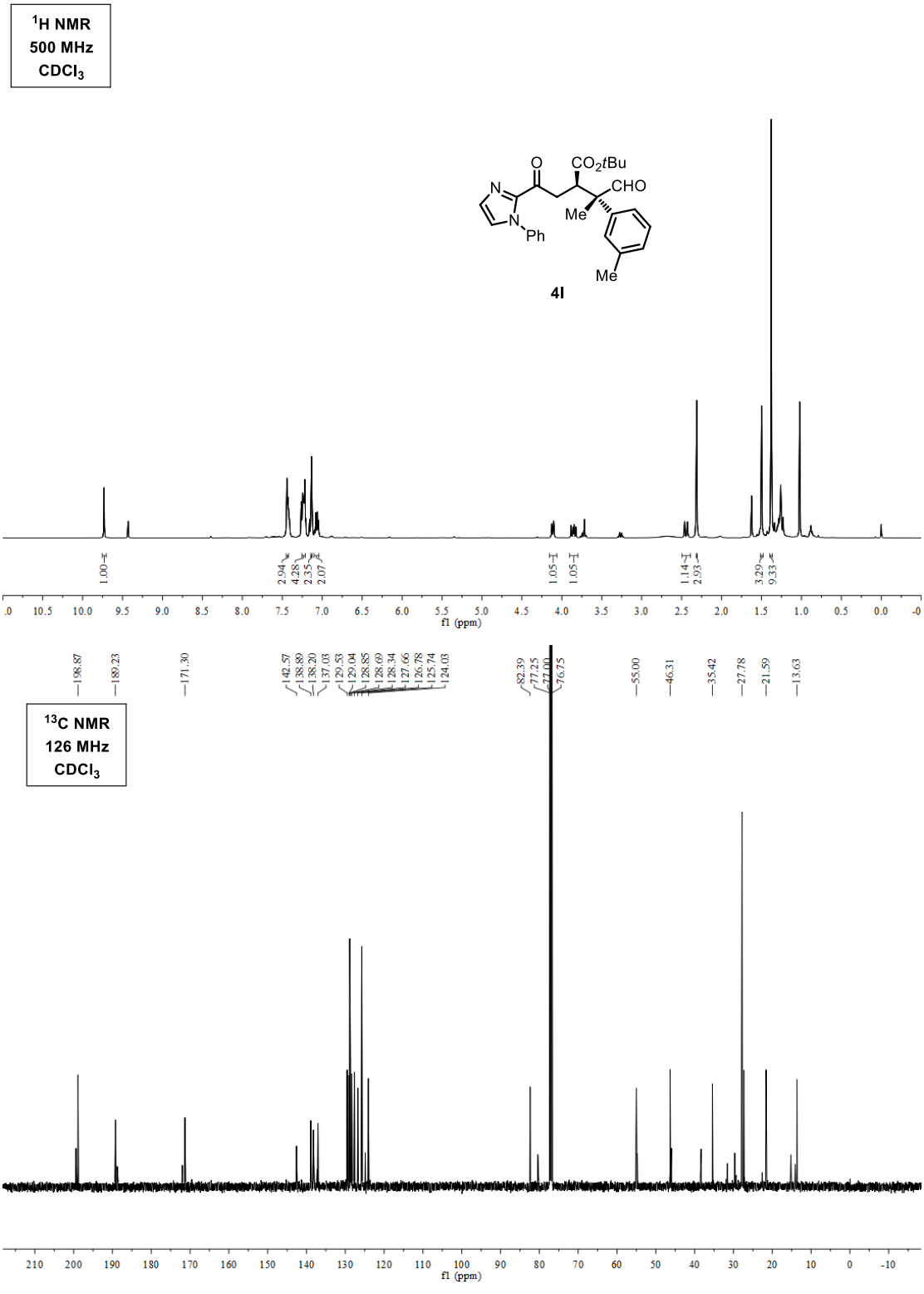

Figure S52. ^{1}H and ^{13}C NMR spectrum for **4l.**

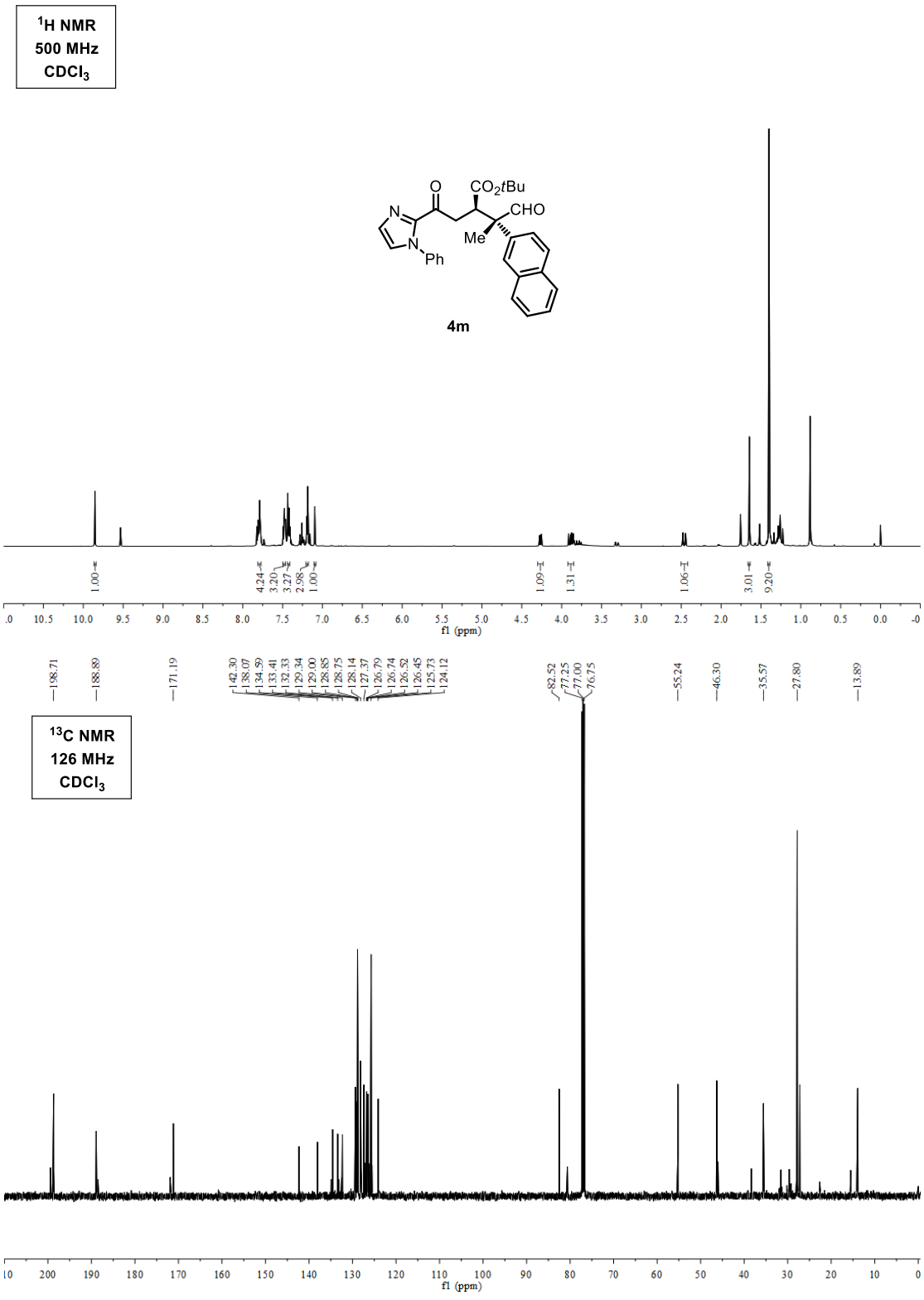

Figure S53. ^{1}H and ^{13}C NMR spectrum for **4m.**

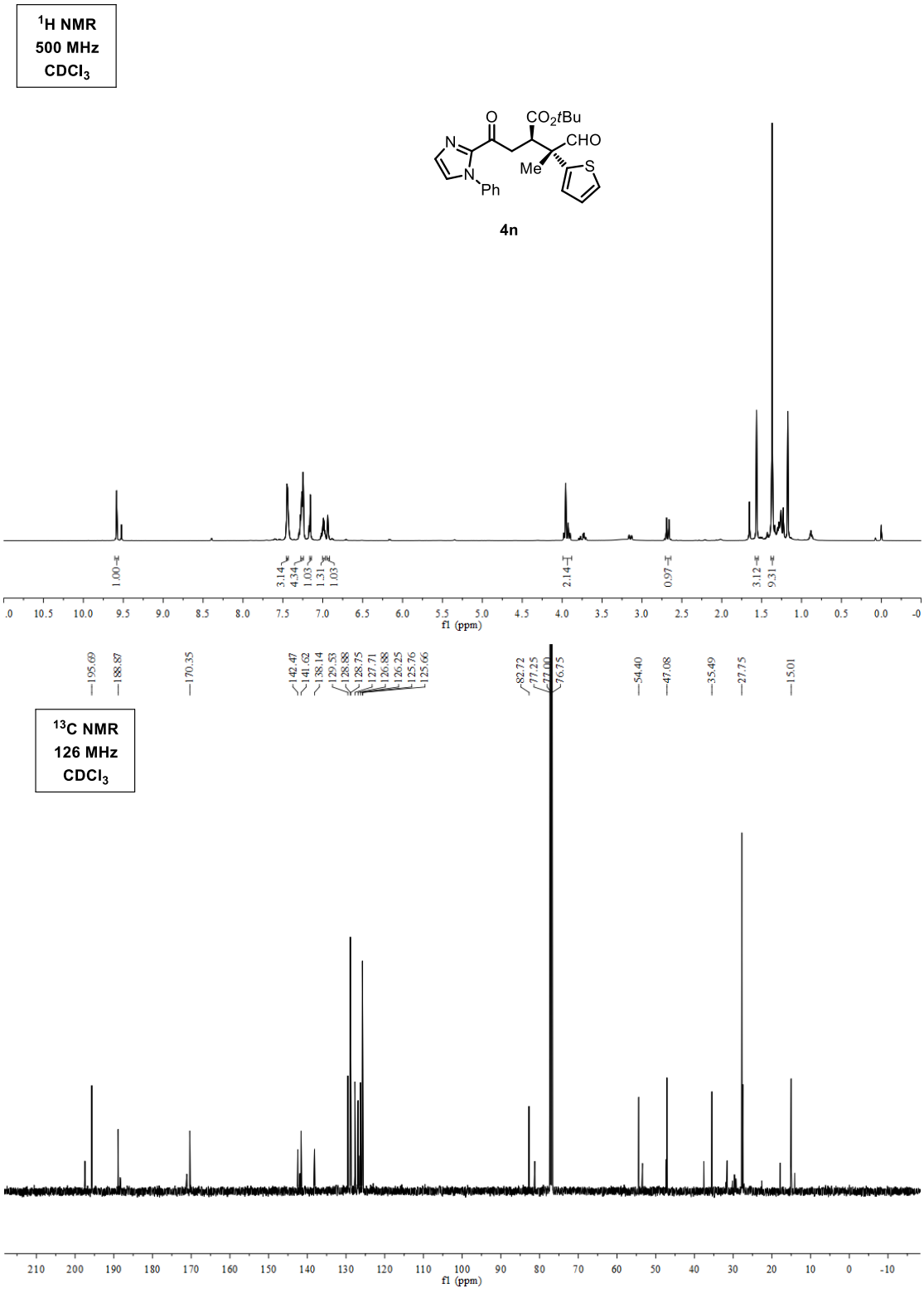

Figure S54. ^{1}H and ^{13}C NMR spectrum for **4n.**

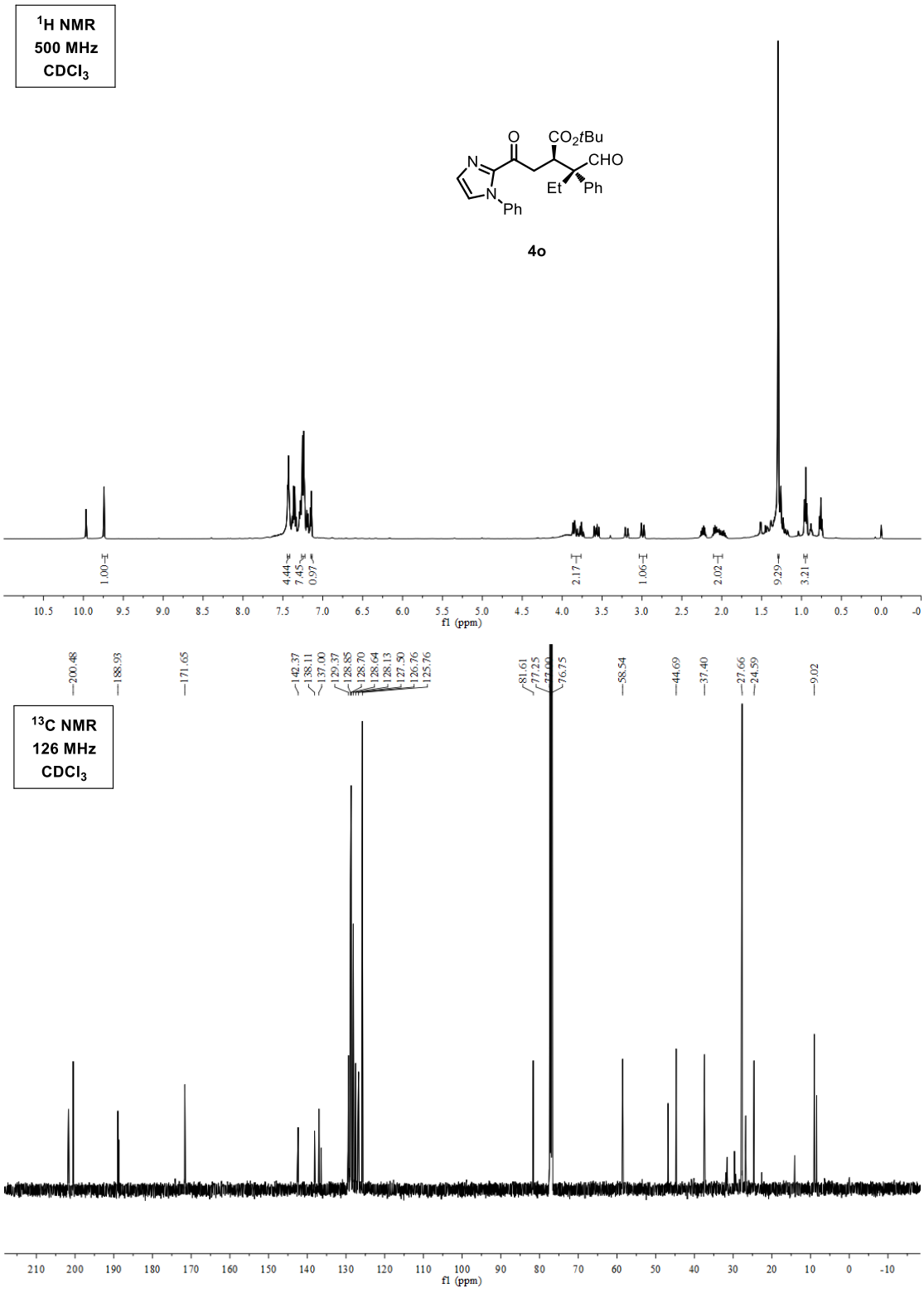

Figure S55. ^{1}H and ^{13}C NMR spectrum for **4o.**

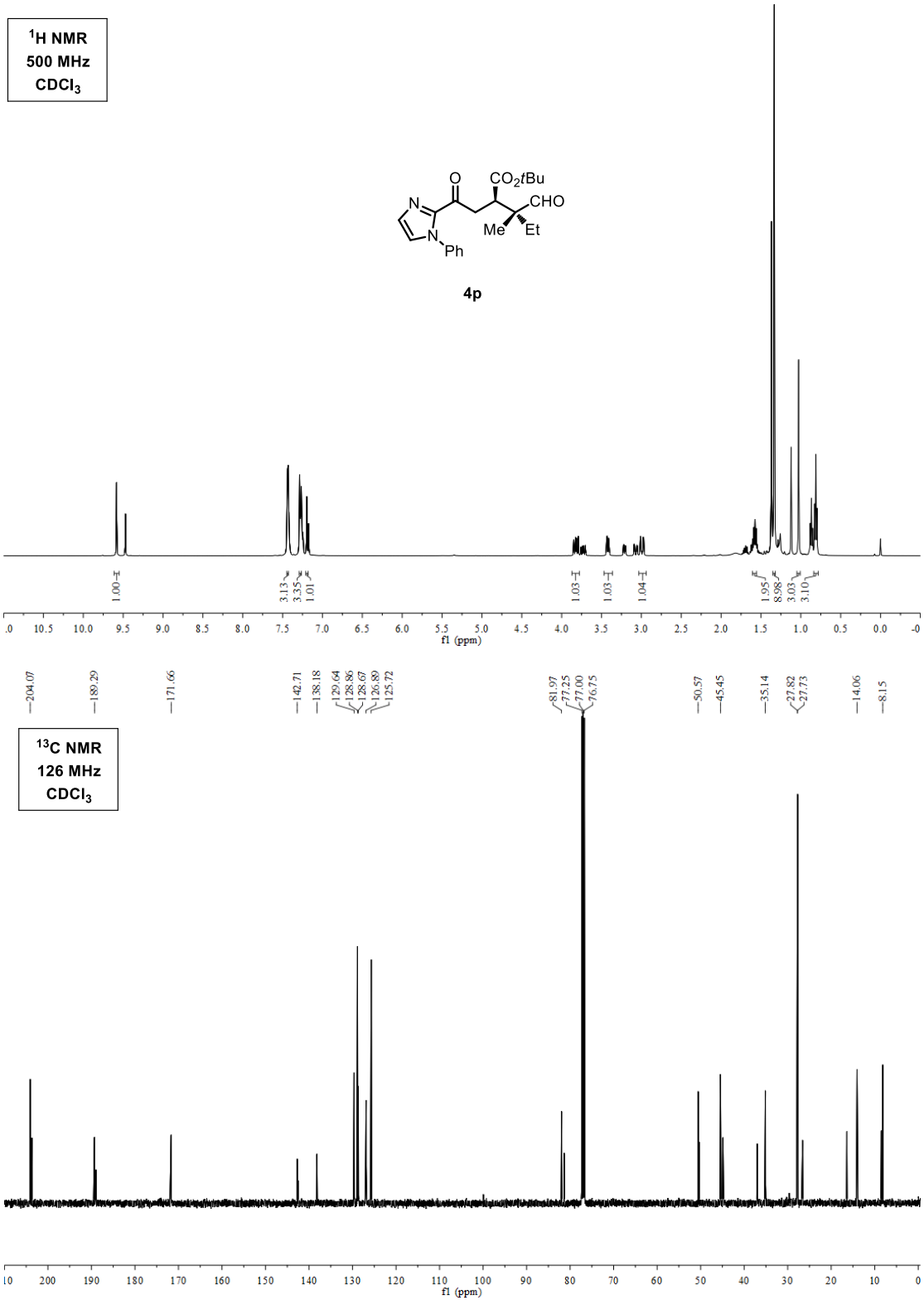

Figure S56. ^{1}H and ^{13}C NMR spectrum for **4p.**

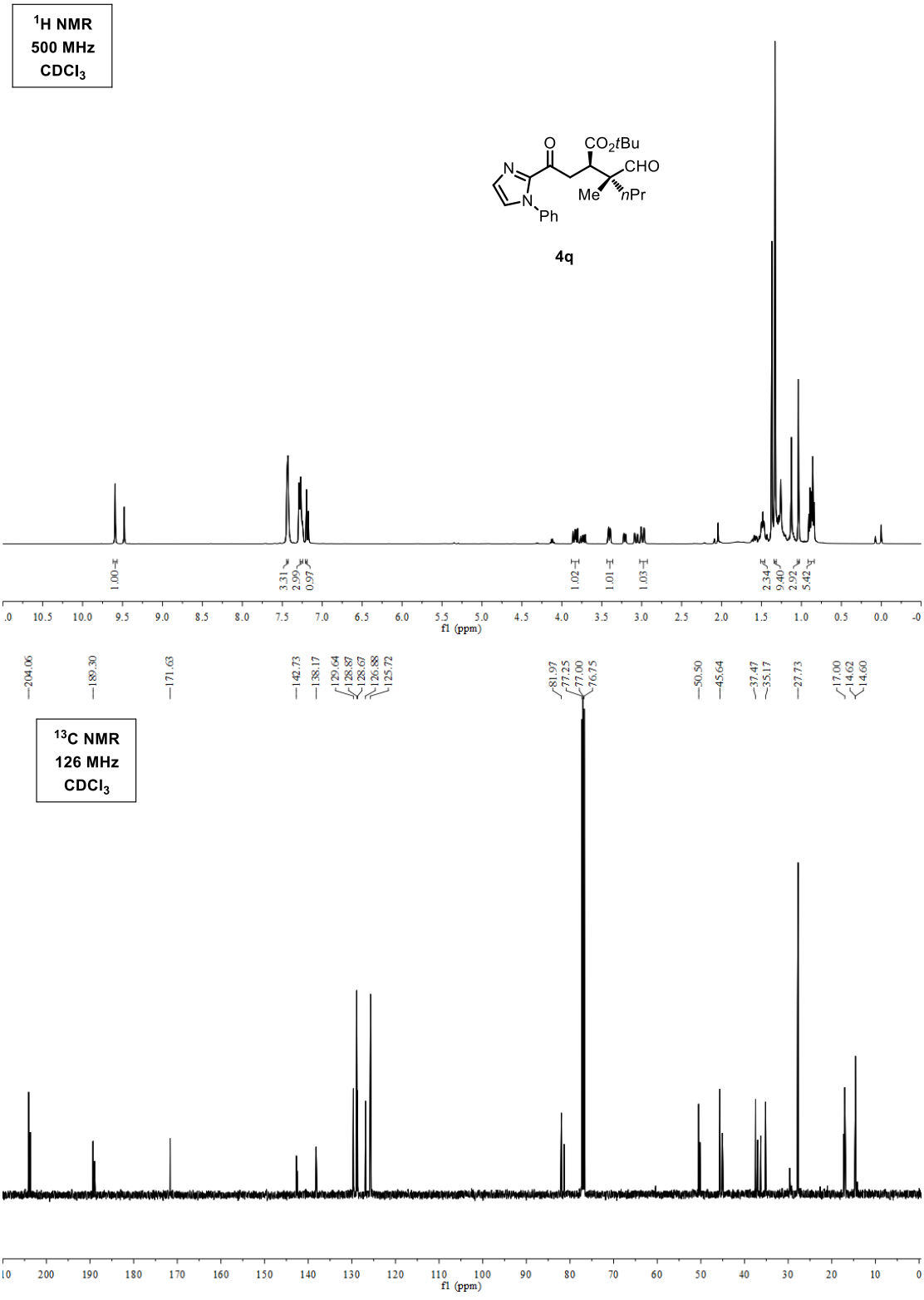

Figure S57. ^{1}H and ^{13}C NMR spectrum for **4q.**

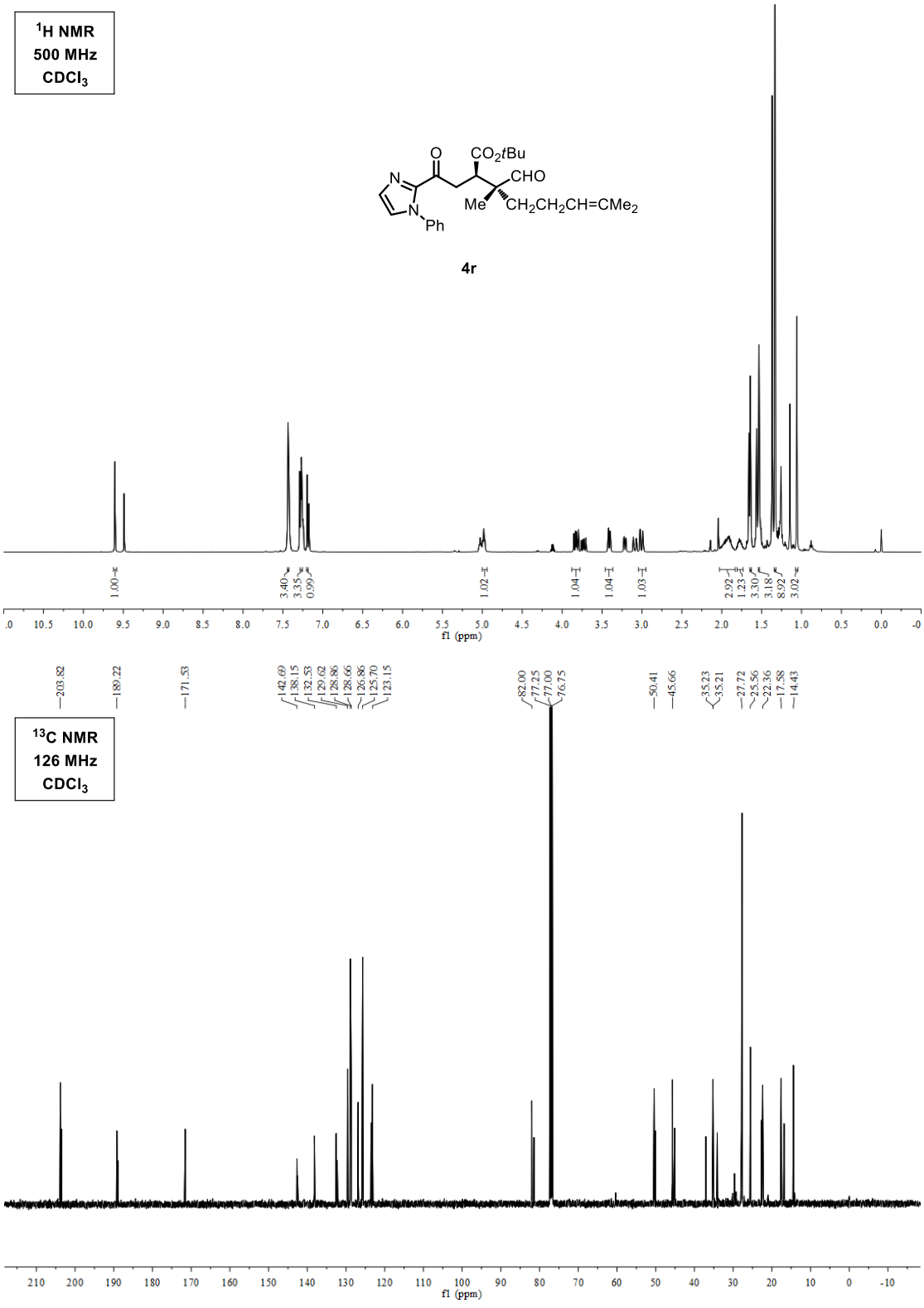

Figure S58. ^{1}H and ^{13}C NMR spectrum for **4r.**

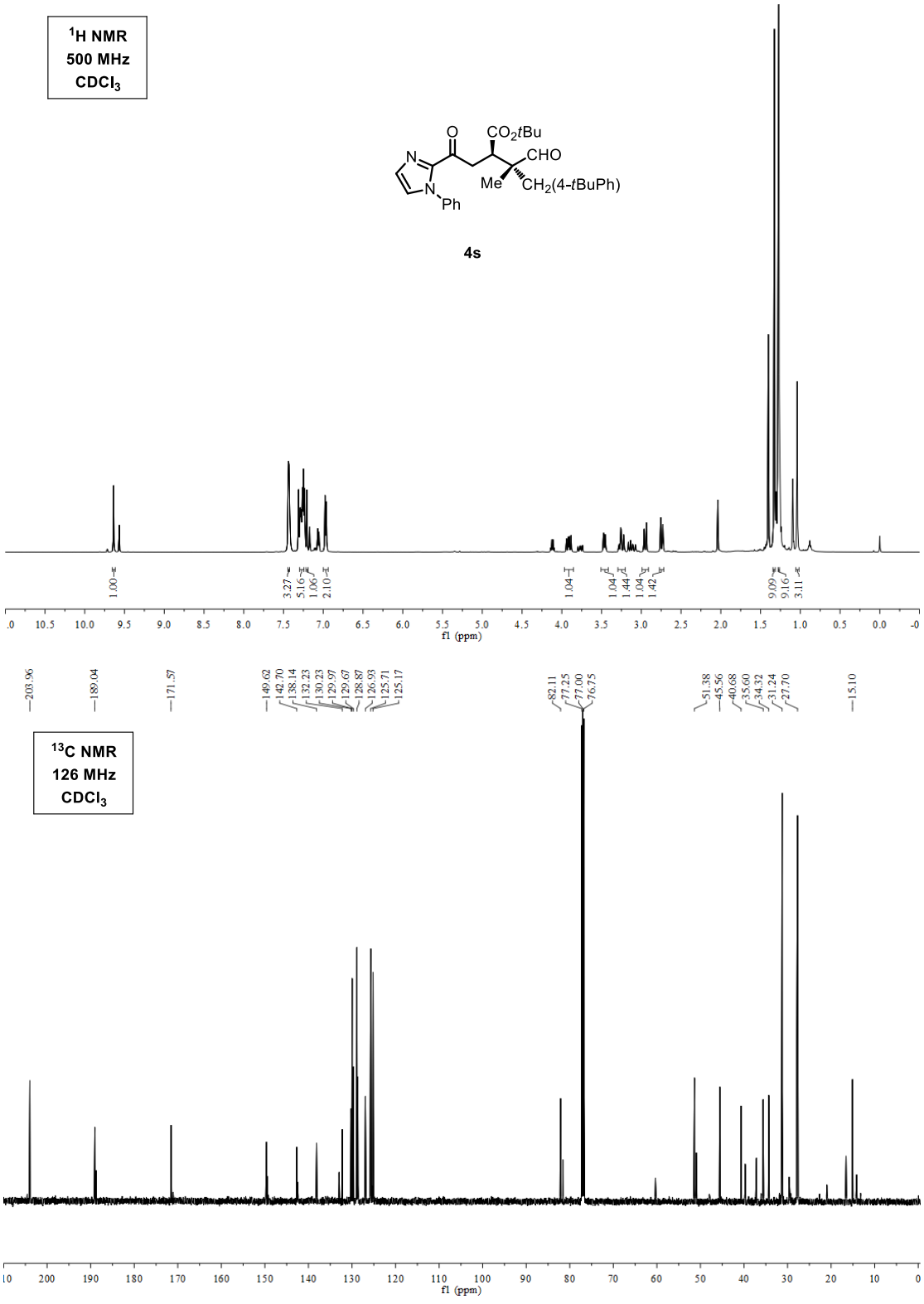

Figure S59. ^{1}H and ^{13}C NMR spectrum for **4s.**

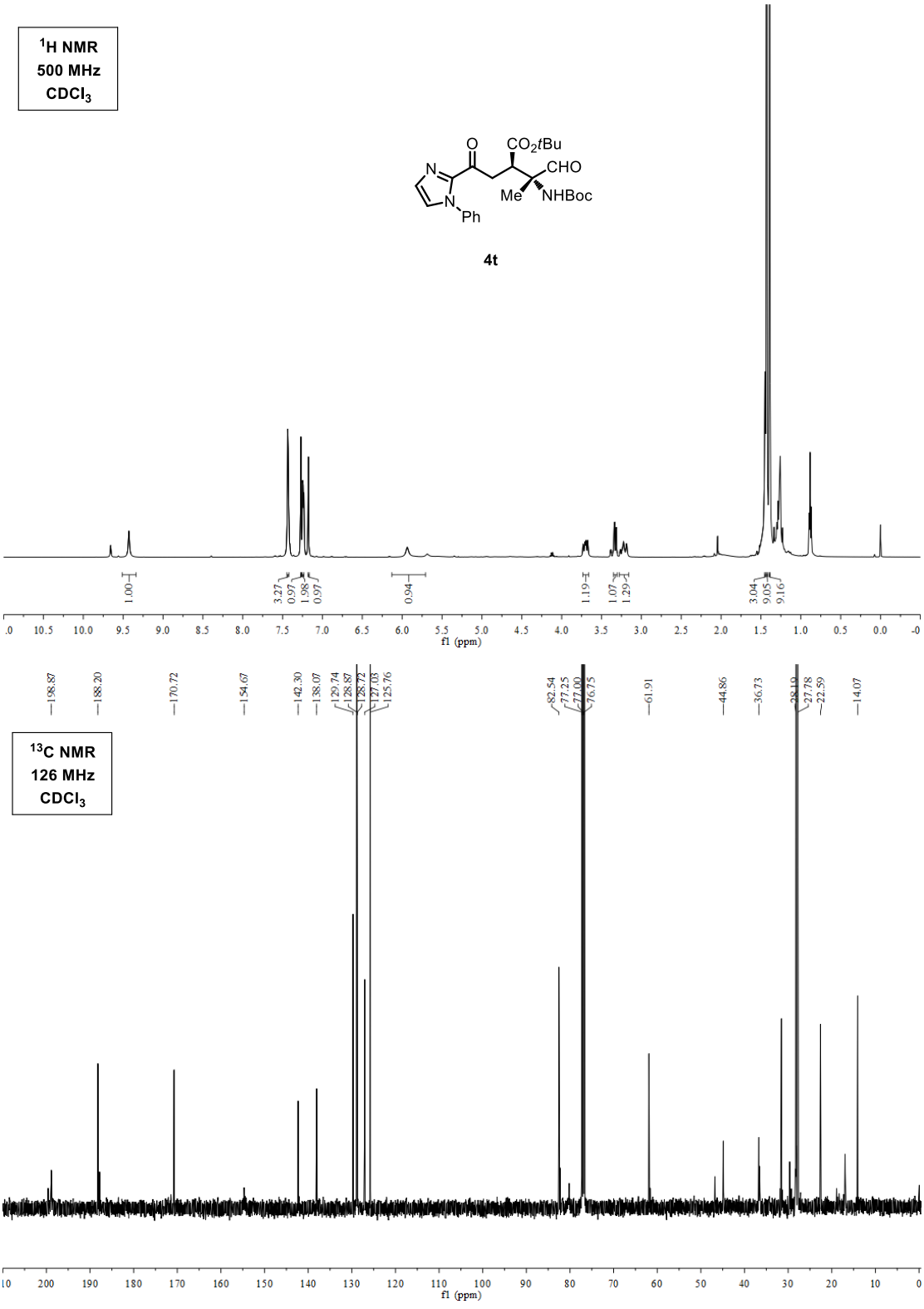

Figure S60. ^{1}H and ^{13}C NMR spectrum for **4t.**

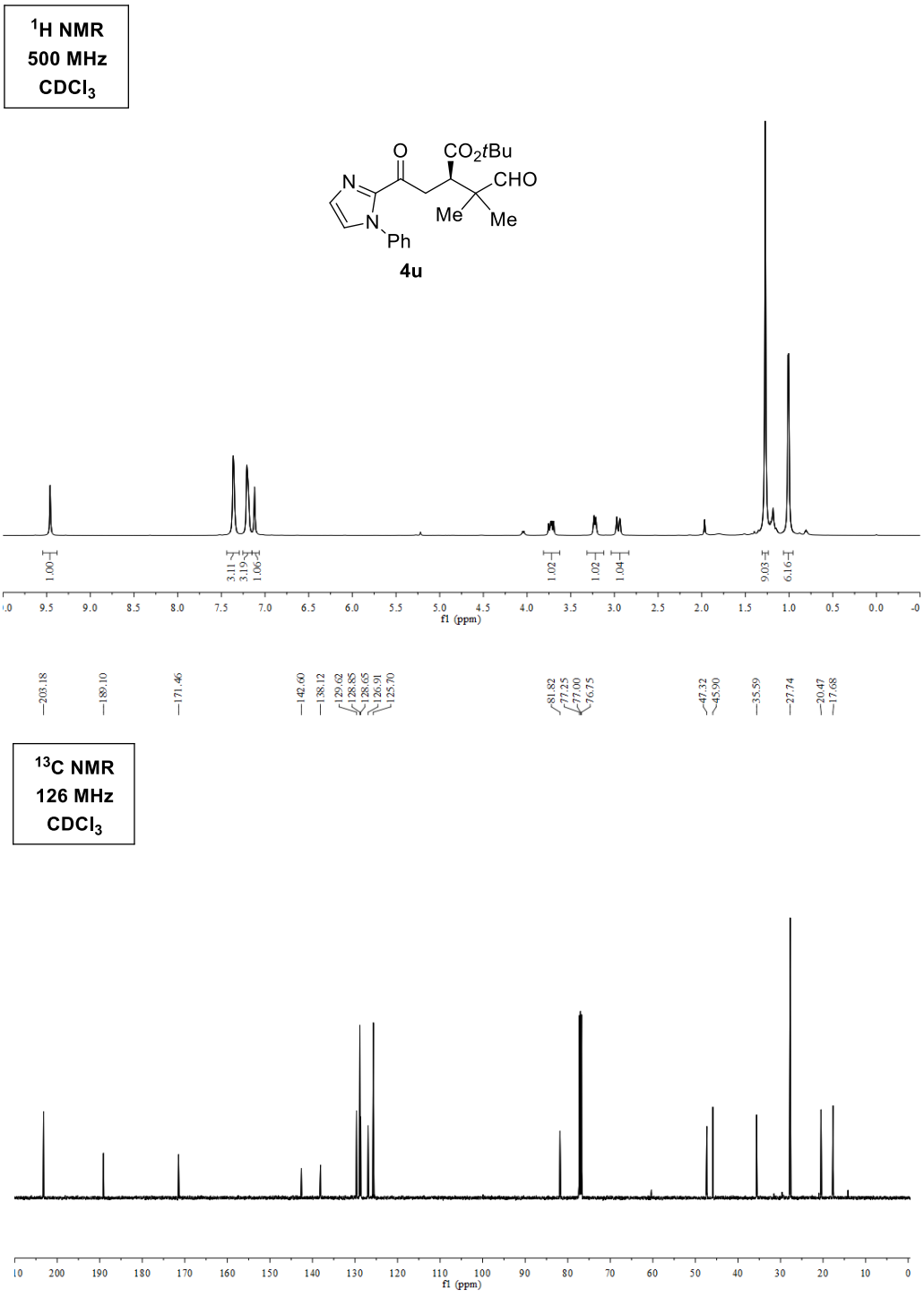

Figure S61. ^{1}H and ^{13}C NMR spectrum for **4u.**

9.3 ^{1}H NMR and ^{13}C NMR Spectra of the Transformation Product

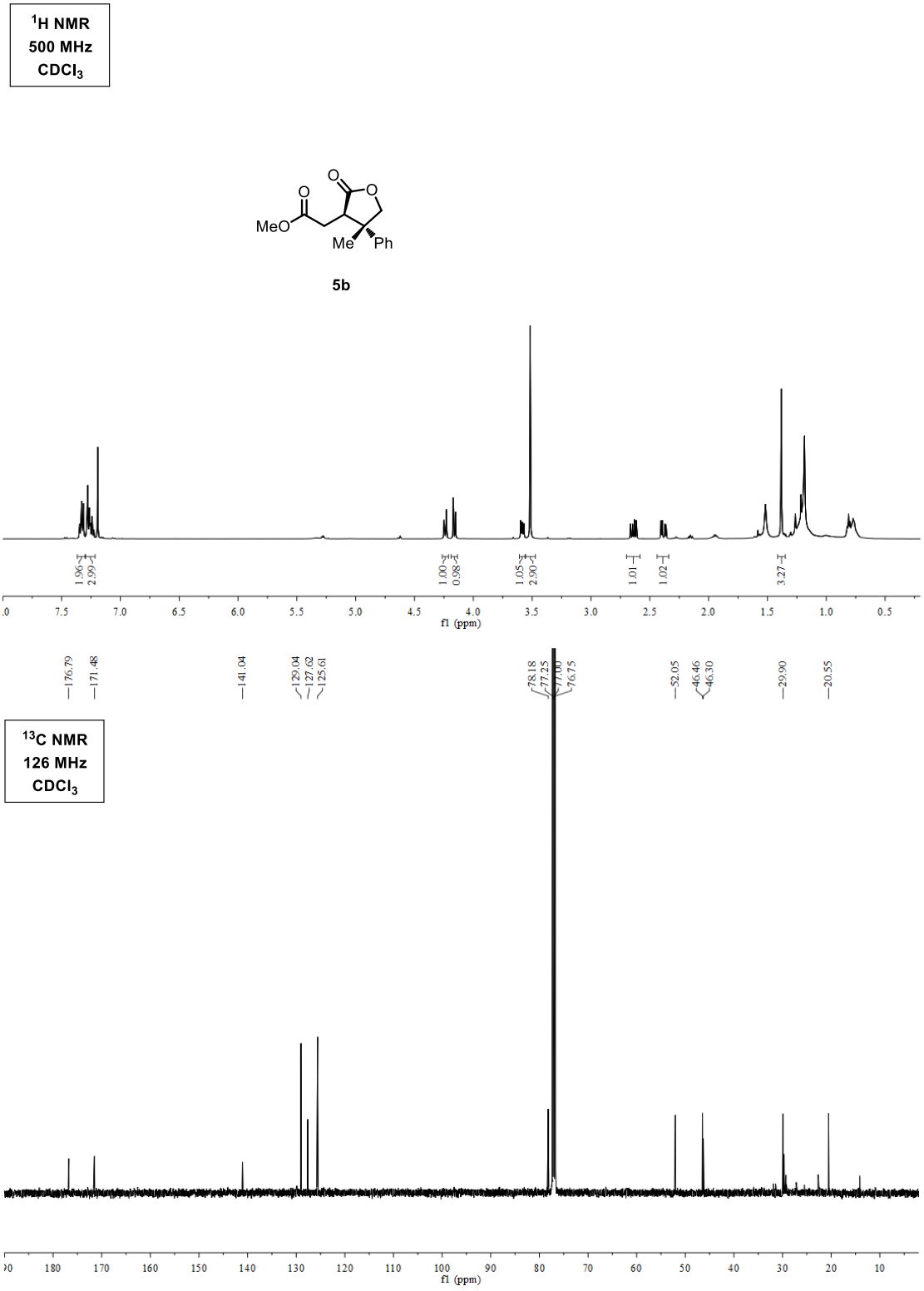

Figure S62. ^{1}H and ^{13}C NMR spectrum for **5b.**

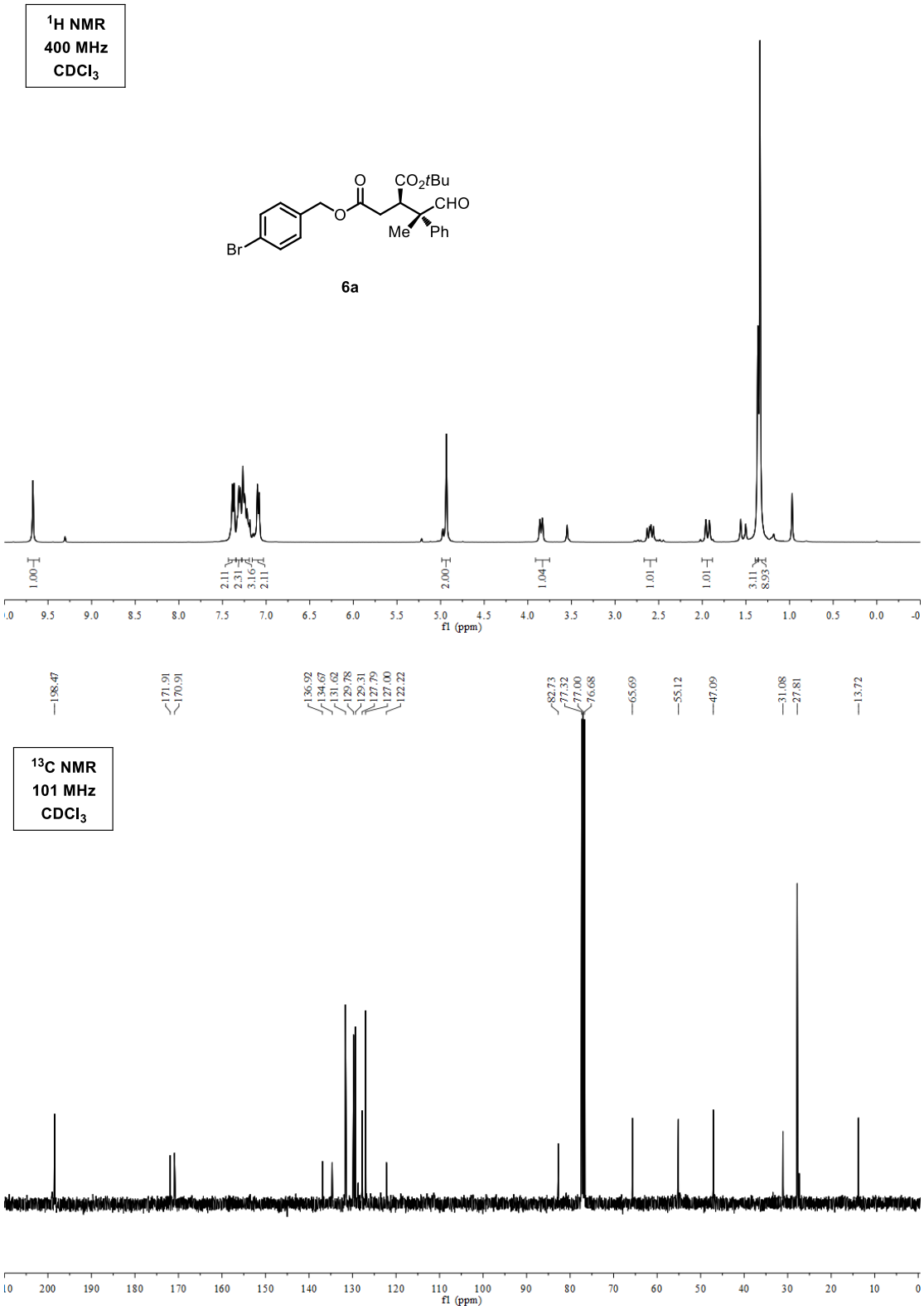

Figure S63. ^{1}H and ^{13}C NMR spectrum for **6a.**

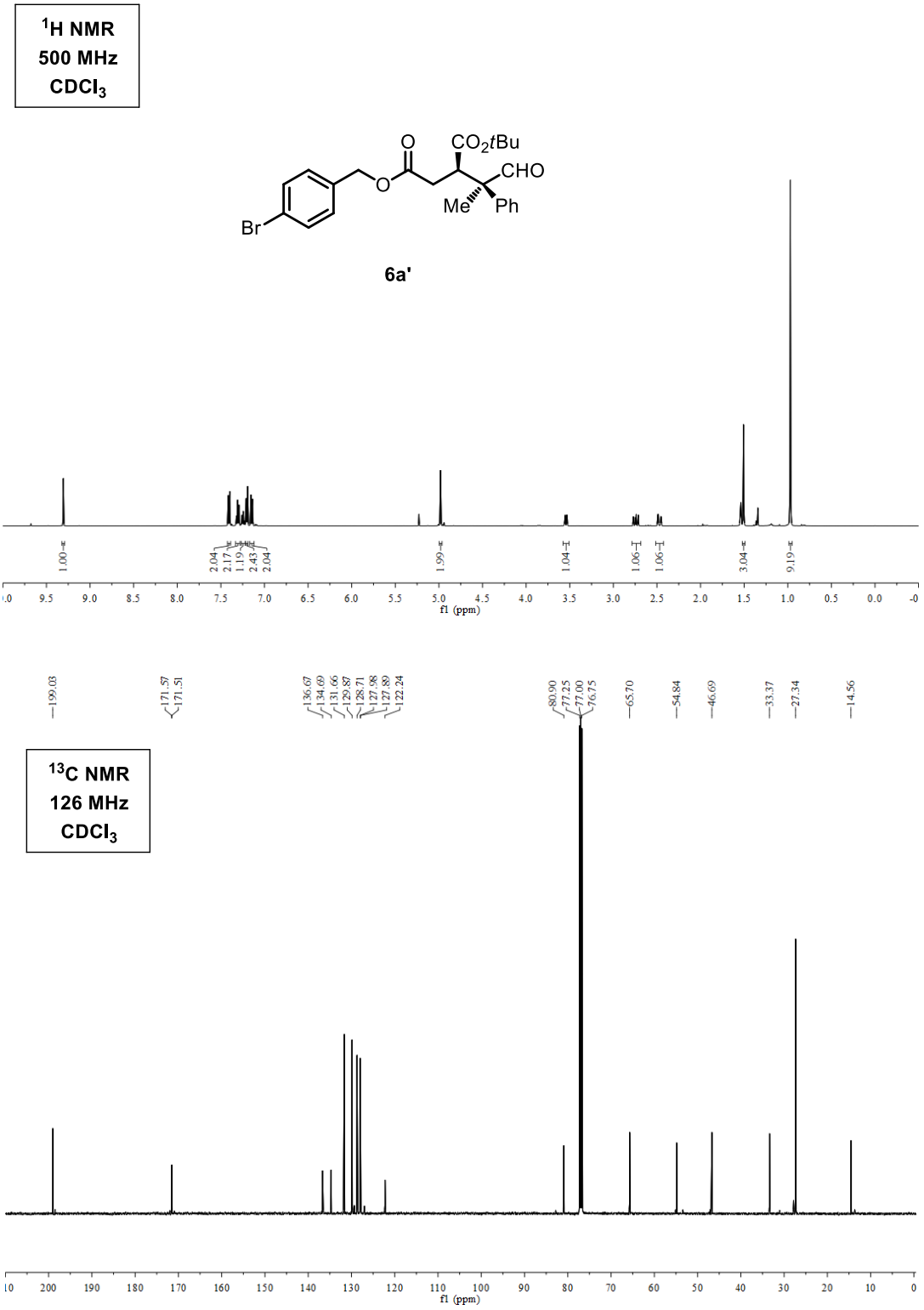

Figure S64. ^{1}H and ^{13}C NMR spectrum for **6a'.**

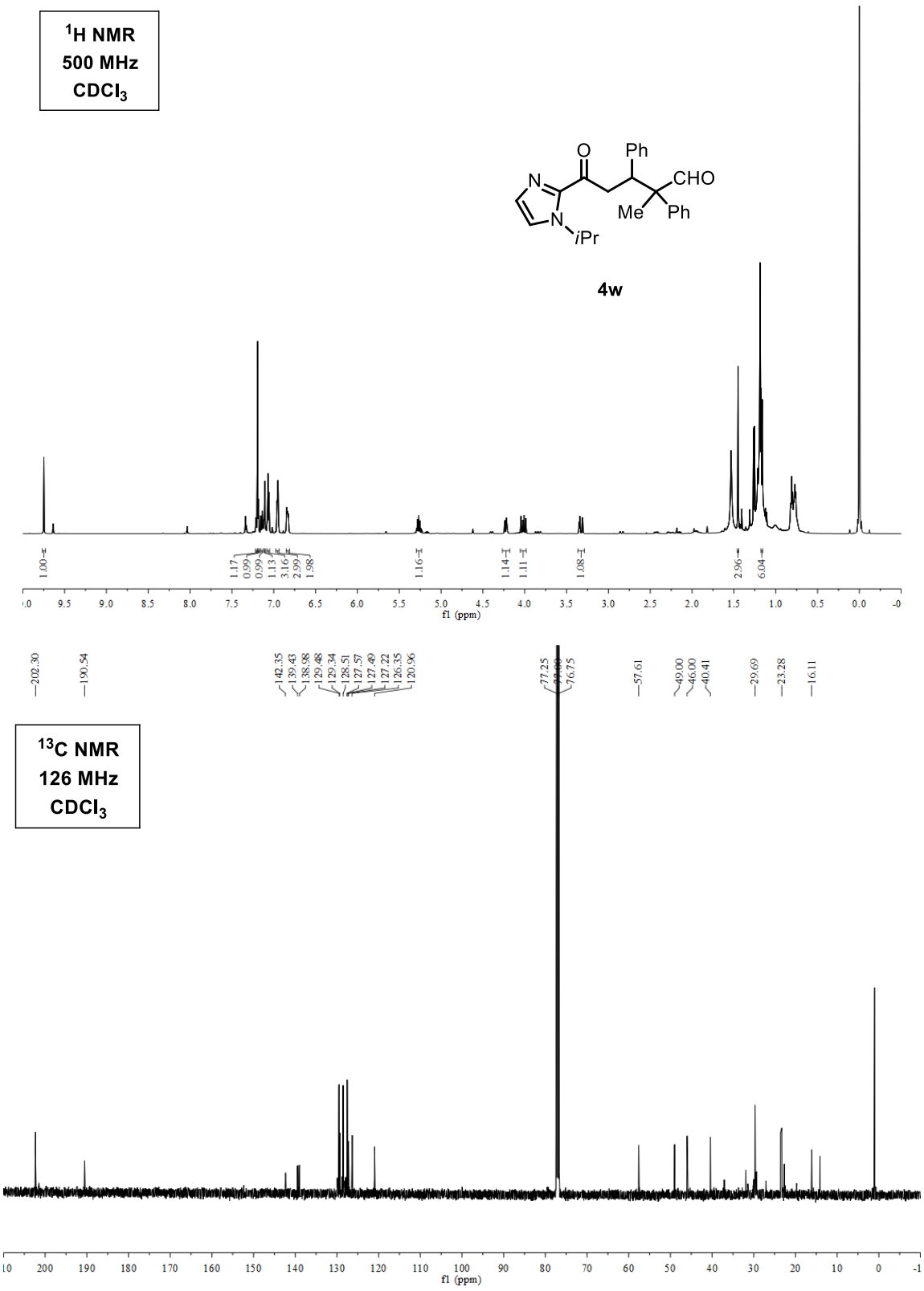

Figure S65. ^{1}H and ^{13}C NMR spectrum for **4w.**