Supporting Information

Enantioselective, Catalytic Trichloromethylation through Visible-Light-Activated Photoredox Catalysis with a Chiral Iridium Complex

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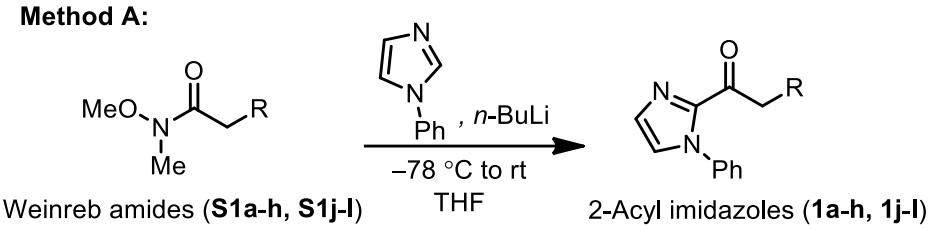
1. General Information

All reactions were carried out under an atmosphere of argon with magnetic stirring. Catalysis reactions were performed in a Schlenk tube (10 mL). As light sources served a 20 W energy saving household white light lamp. The photocatalysts Λ-**IrO**[1] and Λ-**IrS**[2] were synthesized according to our published procedures. Solvents were distilled under nitrogen from calcium hydride (CH_3CN, CH_2Cl_2), sodium/benzophenone (THF), or magnesium turnings/iodine (MeOH). Reagents that were purchased from commercial suppliers were used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irregular shaped, 230–400 mesh, pH 6.8, pore volume: 0.81 mL × g^{-1}, mean pore size: 66 Å, specific surface: 492 m^2 × g^{-1}, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^{1}H NMR and proton decoupled ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), δ = 5.32 ppm (CD_2Cl_2). $^{13}C\{^1H\}$ NMR spectroscopy: δ = 77.0 ppm ($CDCl_3$), δ = 53.8 ppm (CD_2Cl_2). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI or APCI technique. Chiral HPLC chromatography was performed with an Agilent 1200 or Agilent 1260 HPLC system. UV/Vis measurements were taken on a Spectra Max M5 microplate reader in a 10.0 mm quartz cuvette. Optical rotations were measured on a Krüss P8000-T polarimeter with $[\alpha]_D^{22}$ values reported in degrees with concentrations reported in g/100 mL.

2. Synthesis of Substrates

2.1 Synthesis of 2-Acyl Imidazoles

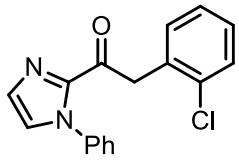
2-Acyl imidazoles **1a-h**, **1j-l** and the corresponding Weinreb amides were synthesized according to our recently published procedures (method A).[3] 2-Acyl imidazole **2i** was synthesized according to a reported procedure with some modifications (method B).[4]



General procedure for method A. To a solution of *N*-phenylimidazole (1.1 eq) in THF at –78 °C was added *n*-BuLi (1.1 eq) dropwise. The reaction was stirred at –78 °C for 30 min, then stirred at room temperature for 30 min. The corresponding Weinreb amide (1.0 eq in THF) was added dropwise to the flask after the reaction was cooled back down to –78 °C. The overall concentration of Weinreib amide was 0.4 M. The reaction was allowed to warm to room temperature slowly (over a period of 3-4 h) and stirred overnight. The reaction was quenched with AcOH (6.0 eq) at room temperature and extracted with EtOAc. The organic layer was washed with aqueous saturated $NaHCO_3$ and brine. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:3) to produce **1a-h**, **1j-l**.

The experimental data of **1f** and **1l** are shown below. The other 2-acyl imidazoles (**1a-e**, **1g-h**, **1j-k**) have been reported previously.[3]

2-(2-Chlorophenyl)-1-(1-phenyl-*1H*-imidazol-2-yl)ethanone (1f)



Following the general procedure, Weinreb amide **S1f** (852 mg, 4.0 mmol) was converted to 2-acyl imidazole **1f** (890 mg, 3.0 mmol, yield: 75%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-6.99 (m, 12H), 4.69 (s, 2H).

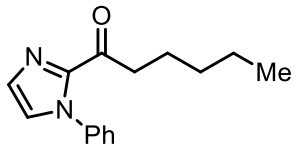
^{13}C NMR (75 MHz, $CDCl_3$) δ 187.1, 142.7, 138.2, 134.8, 133.0, 132.2, 129.7, 129.4, 128.9, 128.7,

128.4, 127.3, 126.7, 125.9, 43.8.

IR (film): ν (cm^{-1}) 3136, 3069, 3014, 2914, 1727, 1677, 1590, 1484, 1442, 1393, 1306, 1141, 1032, 957, 909, 744, 685, 538, 503, 442.

HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{14}ClN_2O$ $[M+H]^+$: 297.0789, found: 297.0789.

1-(1-Phenyl-1H-imidazol-2-yl)hexan-1-one (1l)



Following the general procedure, Weinreb amide **S1l** (636 mg, 4.0 mmol) was converted to 2-acyl imidazole **1l** (808 mg, 3.4 mmol, yield: 84%) as a colorless oil.

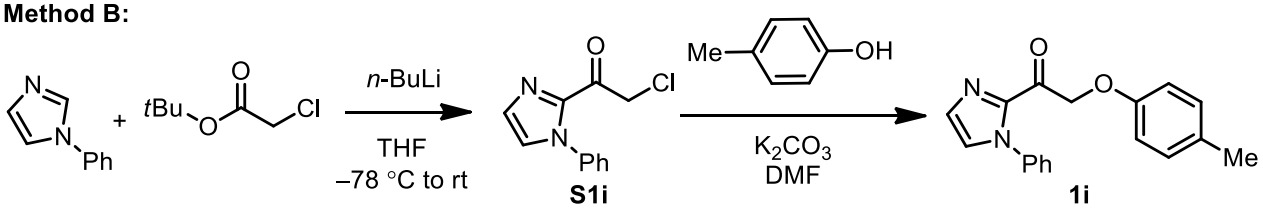
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.40 (m, 3H), 7.37-7.23 (m, 3H), 7.19 (d, J = 0.9 Hz, 1H), 3.16 (t, J = 7.5 Hz, 2H), 1.88-1.47 (m, 2H), 1.58-1.11 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 143.2, 138.5, 129.4, 128.9, 128.6, 126.9, 125.9, 39.2, 31.4, 23.7, 22.4, 13.9.

IR (film): ν (cm^{-1}) 3109, 3062, 2954, 2928, 2863, 1683, 1596, 1496, 1446, 1404, 1306, 1040, 957, 910, 761, 691, 554, 515.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{19}N_2O$ $[M+H]^+$: 243.1492, found: 243.1493.

Method B:

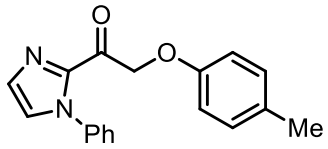


Procedure for the preparation of 1i. To a solution of *N*-phenylimidazole (864 mg, 6.0 mmol) in THF (15 mL) at −78 °C was added *n*-BuLi (2.4 mL, 2.5 M in hexane, 6.0 mmol) dropwise. The reaction was stirred at −78 °C for 1 h, then stirred at room temperature for 30 min. The *tert*-butyl chloroacetate (1.3 mL, 7.5 mmol) was added at one portion to the flask after the reaction was cooled back down to −78 °C. The reaction was allowed to warm to room temperature slowly (over a period of 3-4 h) and stirred overnight. The reaction was quenched with water at room temperature and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered,

and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:3) to produce **S1i** (960 mg, 4.4 mmol, yield: 73%) as a white solid.

To a mixture of **S1i** (880 mg, 4.0 mmol) and K_2CO_3 (552 mg, 4.0 mmol) in DMF (8.0 mL) at 0 °C were added *p*-cresol (648 mg, 6.0 mmol). The reaction mixture was stirred at room temperature for overnight. The reaction was quenched with water (8 mL) at room temperature and extracted with DCM (4 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:3) to afford **1i** (595 mg, 2.0 mmol, yield: 50%) as a white solid.

1-(1-Phenyl-*1H*-imidazol-2-yl)-2-(*p*-tolyloxy)ethanone (1i)



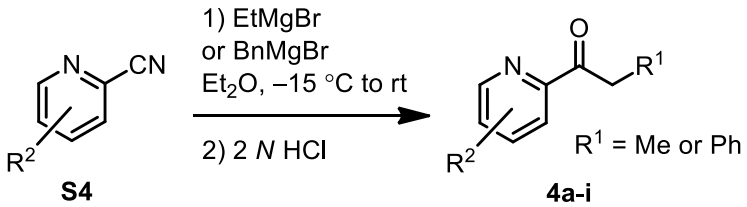
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.39 (m, 3H), 7.39-7.30 (m, 3H), 7.28 (d, *J* = 1.0 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.50 (s, 2H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 184.8, 156.0, 140.8, 137.6, 130.5, 130.0, 129.9, 129.0, 128.9, 127.3, 125.9, 114.5, 70.1, 20.4.

All spectroscopic data were in agreement with the literature.[4]

2.2 Synthesis of 2-Acyl Pyridines

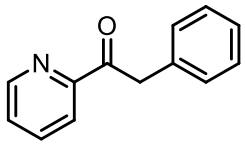
All 2-acyl pyridines (**4a-i**) were synthesized according to reported procedures with some modifications.[5]



General procedure for the synthesis of 2-acyl pyridines. To a solution of the corresponding 2-pyridinecarbonitrile **S4** (1.0 eq) in Et_2O (0.5 M) at −15 °C were added ethylmagnesium bromide or benzylmagnesium bromide (1.2 eq, 1.0 M in THF). The reaction mixture was stirred at −15 °C for 30 min, then allowed to warm to room temperature and stirred for a further 2.5 h. The mixture was added 2 *N* HCl (2.4 eq) and stirred at room temperature for 15 min. The reaction was

neutralized with 2 *N* NaOH to pH 8 and diluted with EtOAc. The organic layer was washed with aqueous saturated $NaHCO_3$ and brine (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:10) to obtain the pure compounds **4a-i**.

2-Phenyl-1-(pyridin-2-yl)ethanone (4a)



Following the general procedure, 2-pyridinecarbonitrile (1.5 mL, 16.0 mmol) was converted to 2-acyl pyridine **4a** (2.648 g, 13.4 mmol, yield: 84%) as a white solid.

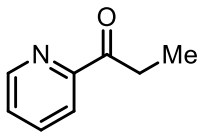
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (ddd, J = 4.7, 1.7, 0.9 Hz, 1H), 8.06-7.88 (m, 1H), 7.74 (td, J = 7.7, 1.7 Hz, 1H), 7.39 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 7.32-7.07 (m, 5H), 4.48 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 153.1, 148.9, 136.9, 134.8, 129.9, 128.4, 127.1, 126.6, 122.3, 43.9.

IR (film): ν (cm^{-1}) 3058, 3032, 2890, 1698, 1578, 1494, 1435, 1396, 1333, 1219, 991, 769, 737, 697, 562.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{12}NO$ $[M+H]^+$: 198.0913, found: 198.0917.

1-(Pyridin-2-yl)propan-1-one (4b)



Following the general procedure, 2-pyridinecarbonitrile (1.5 mL, 16.0 mmol) was converted to 2-acyl pyridine **4b** (1.837 g, 13.6 mmol, yield: 85%) as a colorless oil.

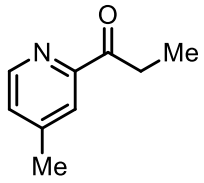
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (ddd, J = 4.7, 1.6, 0.8 Hz, 1H), 8.03-7.86 (m, 1H), 7.75 (td, J = 7.7, 1.7 Hz, 1H), 7.38 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 3.17 (q, J = 7.3 Hz, 2H), 1.14 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 153.5, 148.9, 136.8, 126.9, 121.7, 31.0, 7.9.

IR (film): ν (cm^{-1}) 3057, 2977, 2938, 2881, 1696, 1580, 1459, 1353, 1222, 1093, 996, 954, 756, 667, 617, 568.

HRMS (ESI, *m*/*z*) calcd for $C_8H_{10}NO$ $[M+H]^+$: 136.0757, found: 136.0758.

1-(4-Methylpyridin-2-yl)propan-1-one (4c)



Following the general procedure, 4-methyl-2-pyridinecarbonitrile (733 mg, 6.2 mmol) was converted to 2-acyl pyridine **4c** (711 mg, 4.8 mmol, yield: 77%) as a colorless oil.

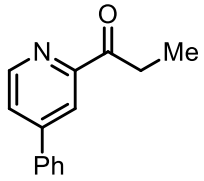
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, J = 4.9 Hz, 1H), 8.16-7.57 (m, 1H), 7.46-7.00 (m, 1H), 3.23 (q, J = 7.3 Hz, 2H), 2.43 (s, 3H), 1.22 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.8, 153.4, 148.7, 148.1, 127.7, 122.5, 31.1, 21.0, 8.0.

IR (film): ν (cm^{-1}) 3052, 2976, 2936, 2879, 1696, 1599, 1457, 1408, 1345, 1266, 1165, 1032, 996, 972, 841, 801, 672, 577, 526, 481.

HRMS (ESI, *m*/*z*) calcd for $C_9H_{11}NONa$ $[M+Na]^+$: 172.0733, found: 172.0733.

1-(4-Phenylpyridin-2-yl)propan-1-one (4d)



Following the general procedure, 4-phenyl-2-pyridinecarbonitrile (900 mg, 5.0 mmol) was converted to 2-acyl pyridine **4d** (847 mg, 4.0 mmol, yield: 80%) as a colorless oil.

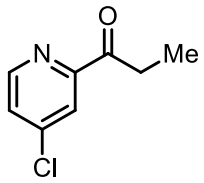
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (d, J = 5.1 Hz, 1H), 8.38-8.20 (m, 1H), 7.81-7.59 (m, 3H), 7.58-7.39 (m, 3H), 3.28 (q, J = 7.3 Hz, 2H), 1.25 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 154.0, 149.4, 137.5, 129.4, 129.2, 127.0, 124.6, 119.6, 31.3, 8.0.

IR (film): ν (cm^{-1}) 2975, 2933, 2898, 1696, 1589, 1543, 1501, 1454, 1402, 1342, 1282, 1196, 964, 760, 683, 609, 449.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{13}NONa$ $[M+Na]^+$: 234.0889, found: 234.0890.

1-(4-Chloropyridin-2-yl)propan-1-one (4e)



Following the general procedure, 4-chloro-2-pyridinecarbonitrile (889 mg, 6.4 mmol) was converted to 2-acyl pyridine **4e** (898 mg, 5.3 mmol, yield: 83%) as a pale yellow oil.

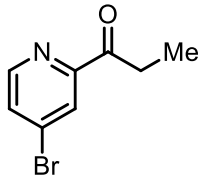
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (dd, J = 5.2, 0.4 Hz, 1H), 7.95 (dd, J = 2.1, 0.5 Hz, 1H), 7.38 (dd, J = 5.2, 2.1 Hz, 1H), 3.14 (q, J = 7.3 Hz, 2H), 1.14 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 154.7, 149.8, 145.4, 127.0, 122.2, 31.2, 7.8.

IR (film): ν (cm^{-1}) 3056, 2978, 2939, 2907, 2880, 1700, 1562, 1458, 1399, 1346, 1279, 1221, 1095, 1022, 971, 899, 841, 793, 706, 487.

HRMS (ESI, *m*/*z*) calcd for $C_8H_8NOClNa$ $[M+Na]^+$: 192.0187, found: 192.0188.

1-(4-Bromopyridin-2-yl)propan-1-one (4f)



Following the general procedure, 4-bromo-2-pyridinecarbonitrile (819 mg, 4.5 mmol) was converted to 2-acyl pyridine **4f** (776 mg, 3.4 mmol, yield: 76%) as a white solid.

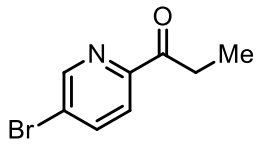
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59-8.38 (m, 1H), 8.32-8.02 (m, 1H), 7.71-7.53 (m, 1H), 3.42-2.92 (m, 2H), 1.38-1.11 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 154.3, 149.7, 134.0, 130.0, 125.2, 31.2, 7.8.

IR (film): ν (cm^{-1}) 3051, 2976, 2937, 2907, 2879, 1699, 1554, 1455, 1392, 1344, 1215, 1082, 1020, 967, 899, 837, 801, 777, 684, 576, 478.

HRMS (ESI, *m*/*z*) calcd for $C_8H_8NOBrNa$ $[M+Na]^+$: 235.9681 and 237.9661, found: 235.9684 and 237.9664.

1-(5-Bromopyridin-2-yl)propan-1-one (4g)



Following the general procedure, 5-bromo-2-pyridinecarbonitrile (819 mg, 4.5 mmol) was converted to 2-acyl pyridine **4g** (796 mg, 3.5 mmol, yield: 78%) as a white solid.

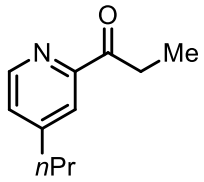
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (dd, J = 2.1, 0.9 Hz, 1H), 7.94 (dd, J = 8.4, 2.1 Hz, 1H), 7.90 (dd, J = 8.4, 0.9 Hz, 1H), 3.17 (q, J = 7.3 Hz, 2H), 1.18 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 151.7, 150.0, 139.5, 125.0, 122.9, 31.0, 7.8.

IR (film): ν (cm^{-1}) 3113, 2912, 2867, 1693, 1556, 1454, 1369, 1342, 1253, 1208, 1122, 1079, 997, 949, 862, 800, 728, 620, 559, 497.

HRMS (ESI, m/z) calcd for $C_8H_8NOBrNa$ $[M+Na]^+$: 235.9681 and 237.9661, found: 235.9686 and 237.9666.

1-(4-Propylpyridin-2-yl)propan-1-one (4h)



Following the general procedure, 4-*n*-propyl-2-pyridinecarbonitrile (819 mg, 4.0 mmol) was converted to 2-acyl pyridine **4h** (572 mg, 3.2 mmol, yield: 80%) as a colorless oil.

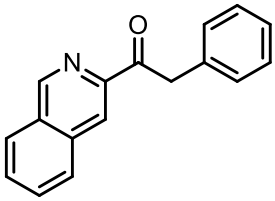
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, J = 4.9 Hz, 1H), 7.67 (d, J = 1.0 Hz, 1H), 7.07 (dd, J = 4.9, 1.7 Hz, 1H), 3.03 (q, J = 7.3 Hz, 2H), 2.64-2.19 (m, 2H), 1.80-1.25 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H), 0.75 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.9, 153.4, 152.6, 148.7, 127.1, 121.8, 37.3, 31.2, 23.3, 13.6, 8.0.

IR (film): ν (cm^{-1}) 3051, 2965, 2934, 2872, 1697, 1598, 1460, 1412, 1347, 1254, 1164, 1023, 993, 862, 833, 801, 492.

HRMS (ESI, m/z) calcd for $C_{11}H_{15}NONa$ $[M+Na]^+$: 200.1046, found: 200.1046.

1-(Isoquinolin-3-yl)-2-phenylethanone (4i)



Following the general procedure, isoquinoline-3-carbonitrile (363 mg, 2.4 mmol) was converted to 2-acyl pyridine **4i** (248 mg, 1.0 mmol, yield: 42%) as a white solid.

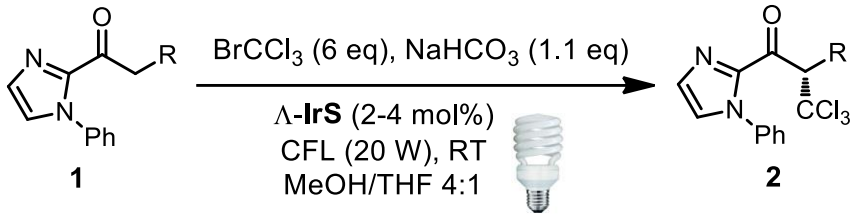
^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.33 (s, 1H), 8.49 (s, 1H), 8.17-7.92 (m, 2H), 7.85- 7.67 (m, 2H), 7.49-7.17 (m, 5H), 4.69 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 151.8, 147.4, 135.6, 135.1, 130.9, 130.2, 130.0, 129.4, 128.6, 128.4, 127.5, 126.6, 121.0, 44.7.

IR (film): ν (cm^{-1}) 3083, 3027, 2924, 1683, 1618, 1584, 1489, 1448, 1381, 1264, 1222, 1115, 1030, 945, 902, 834, 755, 719, 686, 557, 481.

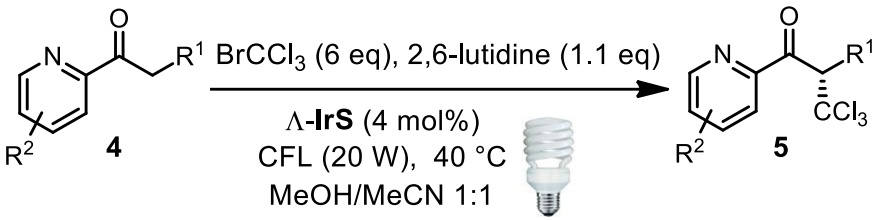
HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{14}NO$ $[M+H]^+$: 248.1070, found: 248.1070.

3. Iridium-Catalyzed Photoredox Reactions



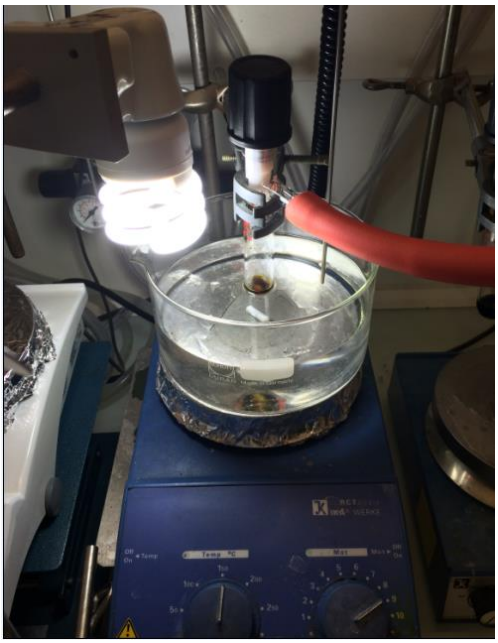
General procedure A: α-trichloromethylation of 2-acyl imidazoles. A dried 10 mL Schlenk tube was charged with the catalyst Λ-**IrS** (2 or 4 mol%), $NaHCO_3$ (18.5 mg, 0.22 mmol, 1.1 eq) and the corresponding 2-acyl imidazole **1a-l** (0.2 mmol, 1.0 eq). The tube was purged with argon and MeOH/THF (4:1, 0.5 mL) was added via syringe, followed by bromotrichloromethane (118.0 μL, 1.2 mmol, 6.0 eq). The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 20 W white light energy saving lamp. The reaction was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was diluted with CH_2Cl_2 (8 mL), the inorganic salt was removed by centrifugation. The combined organic layers were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:15 to 1:10) to afford the products **2a-l**. Racemic samples were obtained by carrying out the reactions with *rac*-**IrS**. The enantiomeric excess was determined by chiral HPLC analysis.

Exemplary reaction setup:

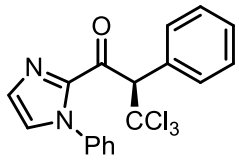


General procedure B: α-trichloromethylation of 2-acyl pyridines. A dried 10 mL Schlenk tube was charged with the catalyst Λ-**IrS** (4 mol%) and the corresponding 2-acyl pyridine **4a-i** (0.2 mmol, 1.0 eq). The tube was purged with nitrogen and MeOH/MeCN (1:1, 0.5 mL) was added via syringe, followed by 2,6-lutidine (25.0 μL, 0.22 mmol, 1.1 eq) and bromotrichloromethane (118.0 μL, 1.2 mmol, 6.0 eq). The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 20 W white light energy saving lamp. The reaction was stirred at 40 °C (silicone oil bath) for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:30 to 1:15) to afford the products **5a-i**. Racemic samples were obtained by carrying out the reactions with *rac*-**IrS**. The enantiomeric excess was determined by chiral HPLC analysis.

Exemplary reaction setup:



(*R*)-3,3,3-Trichloro-2-phenyl-1-(1-phenyl-*1H*-imidazol-2-yl)propan-1-one (2a)



Starting from 2-acyl imidazole **1a** (52.4 mg, 0.20 mmol) according to the general procedure A to give **2a** as a white solid (58.3 mg, 0.154 mmol, yield: 77%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 99.7% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 12.3 min, t_r (major) = 13.0 min). $[\alpha]_D^{22}$ = –206.4° (*c* 0.7, CH_2Cl_2).

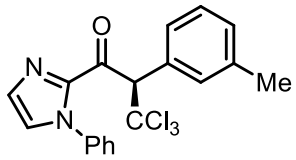
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.76-7.63 (m, 2H), 7.58-7.46 (m, 3H), 7.45-7.36 (m, 3H), 7.31-7.19 (m, 4H), 6.58 (s, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 183.5, 142.8, 138.5, 132.5, 132.1, 130.5, 129.6, 129.5, 129.4, 128.9, 128.8, 126.1, 98.9, 67.7.

IR (film): *v* (cm^{-1}) 1686, 1592, 1494, 1448, 1392, 1304, 1153, 1062, 1032, 958, 914, 871, 760, 740, 691, 634, 547.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{13}Cl_3N_2ONa$ $[M+Na]^+$: 400.9997 and 402.9969, found: 401.0000 and 402.9971.

(*R*)-3,3,3-Trichloro-1-(1-phenyl-*1H*-imidazol-2-yl)-2-(*m*-tolyl)propan-1-one (2b)



Starting from 2-acyl imidazole **1b** (55.2 mg, 0.20 mmol) according to the general procedure A to give **2b** as a white solid (71.0 mg, 0.181 mmol, yield: 91%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 99.0% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 12.6 min, t_r (major) = 11.2 min). $[\alpha]_D^{22}$ = –229.4° (*c* 0.7, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.66-7.46 (m, 5H), 7.40-7.06 (m, 6H), 6.54 (s, 1H), 2.38 (s, 3H).

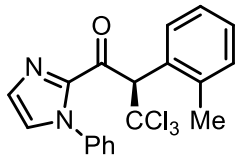
^{13}C NMR (75 MHz, CD_2Cl_2) δ 183.5, 142.8, 138.7, 138.5, 132.6, 132.3, 130.5, 130.4, 129.5, 129.3, 129.1, 128.9, 128.6, 126.1, 98.9, 67.8, 21.6.

IR (film): *v* (cm^{-1}) 3125, 3064, 2966, 2919, 2856, 1685, 1594, 1492, 1447, 1393, 1306, 1145, 1050,

968, 877, 823, 761, 716, 638, 556, 517.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{16}Cl_3N_2O$ $[M+H]^+$: 393.0323 and 395.0295, found: 393.0326 and 395.0295.

(*R*)-3,3,3-Trichloro-1-(1-phenyl-*1H*-imidazol-2-yl)-2-(*o*-tolyl)propan-1-one (2c)



Starting from 2-acyl imidazole **1c** (55.2 mg, 0.20 mmol) according to the general procedure A to give **2c** as a white solid (64.3 mg, 0.164 mmol, yield: 82%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee > 99.9% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 8.7 min, t_r (major) = 9.9 min). $[\alpha]_D^{22}$ = –270.8° (*c* 0.7, CH_2Cl_2).

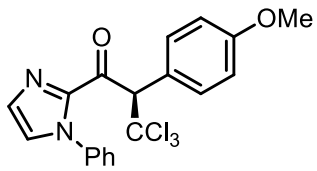
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.60-7.39 (m, 3H), 7.29 (dd, *J* = 5.2, 1.1 Hz, 2H), 7.27-7.12 (m, 5H), 6.89 (s, 1H), 2.84 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 183.8, 143.0, 140.6, 138.5, 131.7, 131.2, 130.5, 130.4, 129.6, 129.5, 129.3, 128.9, 126.1, 126.0, 99.6, 63.0, 20.9.

IR (film): *v* (cm^{-1}) 3118, 3061, 2978, 1691, 1596, 1494, 1449, 1393, 1307, 1057, 960, 916, 872, 725, 693, 635, 543.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{16}Cl_3N_2O$ $[M+H]^+$: 393.0323 and 395.0295, found: 393.0326 and 395.0296.

(*R*)-3,3,3-Trichloro-2-(4-methoxyphenyl)-1-(1-phenyl-*1H*-imidazol-2-yl)propan-1-one (2d)



Starting from 2-acyl imidazole **1d** (58.4 mg, 0.20 mmol) according to the general procedure A to give **2d** as a white solid (73.1 mg, 0.179 mmol, yield: 90%). Enantiomeric excess established by HPLC analysis using a Chiralpak IC column, ee = 99.4% (HPLC: IC, 254 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 11.2 min, t_r (major) = 8.1 min). $[\alpha]_D^{22}$ = –236.4°

(*c* 0.7, CH_2Cl_2).

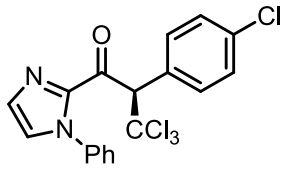
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 8.9 Hz, 2H), 7.55-7.46 (m, 3H), 7.35-7.16 (m, 4H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.51 (s, 1H), 3.80 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 183.8, 160.9, 142.8, 138.6, 133.3, 130.5, 129.5, 129.4, 128.8, 126.2, 124.4, 114.2, 99.4, 67.1, 55.7.

IR (film): *v* (cm^{-1}) 3135, 2967, 2927, 2842, 1687, 1602, 1505, 1451, 1392, 1308, 1254, 1179, 1072, 1024, 952, 767, 723, 627, 535.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{15}Cl_3N_2O_2$ $[M+Na]^+$: 431.0091 and 433.0064, found: 431.0094 and 433.0065.

(*R*)-3,3,3-Trichloro-2-(4-chlorophenyl)-1-(1-phenyl-*1H*-imidazol-2-yl)propan-1-one (2e)



Starting from 2-acyl imidazole **1e** (59.2 mg, 0.20 mmol) according to the general procedure A to give **2e** as a white solid (56.2 mg, 0.136 mmol, yield: 68%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 99.4% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 11.5 min, t_r (major) = 10.5 min). $[\alpha]_D^{22}$ = –222.8° (*c* 0.5, CH_2Cl_2).

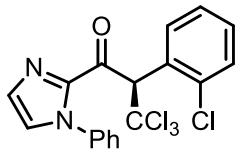
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.57-7.46 (m, 3H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.32-7.20 (m, 4H), 6.58 (s, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 183.2, 142.7, 138.5, 135.9, 133.4, 131.2, 130.7, 129.6, 129.5, 129.1, 129.0, 126.2, 98.5, 66.9.

IR (film): *v* (cm^{-1}) 2965, 2927, 2880, 1691, 1594, 1492, 1448, 1394, 1307, 1092, 1062, 957, 764, 717, 691, 645, 543, 438.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{12}Cl_4N_2ONa$ $[M+Na]^+$: 434.9596, 436.9568 and 438.9541, found: 434.9597, 436.9567 and 438.9539.

(*R*)-3,3,3-Trichloro-2-(2-chlorophenyl)-1-(1-phenyl-*1H*-imidazol-2-yl)propan-1-one (2f)



Starting from 2-acyl imidazole **1f** (59.2 mg, 0.20 mmol) according to the general procedure A to give **2f** as a white solid (68.0 mg, 0.165 mmol, yield: 83%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 99.6% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 12.5 min, t_r (major) = 13.6 min). $[\alpha]_D^{22}$ = –269.6° (*c* 0.7, CH_2Cl_2).

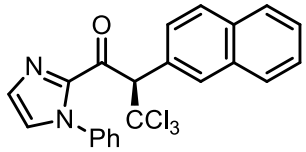
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.92 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.62-7.43 (m, 4H), 7.43-7.15 (m, 7H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 183.1, 142.9, 138.5, 137.5, 132.2, 130.9, 130.83, 130.78, 130.5, 129.6, 129.4, 129.2, 126.9, 126.2, 98.8, 62.2.

IR (film): *v* (cm^{-1}) 3132, 3090, 3037, 2852, 1686, 1591, 1486, 1443, 1395, 1301, 1147, 1051, 961, 863, 759, 716, 687, 630, 540.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{12}Cl_4N_2ONa$ $[M+Na]^+$: 434.9596, 436.9568 and 438.9541, found: 434.9595, 436.9566 and 438.9537.

(*R*)-3,3,3-Trichloro-2-(naphthalen-2-yl)-1-(1-phenyl-*1H*-imidazol-2-yl)propan-1-one (2g)



Starting from 2-acyl imidazole **1g** (62.4 mg, 0.20 mmol) according to the general procedure A to give **2g** as a white solid (61.2 mg, 0.143 mmol, yield: 71%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 99.2% (HPLC: OD-H, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 10.5 min, t_r (major) = 13.6 min). $[\alpha]_D^{22}$ = –279.2° (*c* 0.5, CH_2Cl_2).

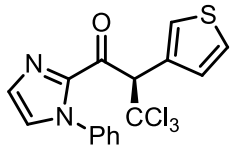
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.19 (d, *J* = 1.1 Hz, 1H), 7.99-7.77 (m, 4H), 7.63-7.46 (m, 5H), 7.33-7.22 (m, 3H), 7.21 (d, *J* = 0.9 Hz, 1H), 6.76 (s, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 183.4, 142.8, 138.5, 133.8, 133.4, 131.8, 130.5, 129.9, 129.5, 129.4, 129.2, 128.9, 128.7, 128.3, 128.0, 127.4, 126.8, 126.2, 99.0, 67.8.

IR (film): ν (cm^{-1}) 2969, 2927, 2884, 1686, 1596, 1498, 1449, 1392, 1306, 1152, 1056, 950, 817, 761, 724, 690, 477.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{15}Cl_3N_2ONa$ $[M+Na]^+$: 451.0142 and 453.0116, found: 451.0143 and 453.0114.

(*R*)-3,3,3-Trichloro-1-(1-phenyl-*1H*-imidazol-2-yl)-2-(thiophen-3-yl)propan-1-one (2h)



Starting from 2-acyl imidazole **1h** (53.6 mg, 0.20 mmol) according to the general procedure A to give **2h** as a white solid (48.0 mg, 0.125 mmol, yield: 62%). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column, ee = 96% (HPLC: AD-H, 254 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 8.6 min, t_r (major) = 11.2 min). $[\alpha]_D^{22}$ = –158.8° (*c* 0.3, CH_2Cl_2).

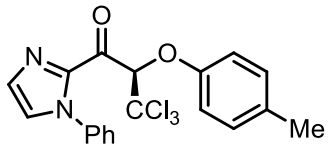
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.62 (dd, *J* = 2.8, 1.4 Hz, 1H), 7.57-7.45 (m, 3H), 7.35 (qd, *J* = 5.0, 2.1 Hz, 2H), 7.30-7.22 (m, 4H), 6.74 (s, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 183.4, 142.8, 138.6, 132.7, 130.6, 130.2, 129.6, 129.4, 129.1, 128.4, 126.2, 125.6, 98.7, 63.3.

IR (film): ν (cm^{-1}) 3144, 3107, 3067, 2847, 1686, 1491, 1444, 1394, 1302, 1148, 1062, 966, 761, 713, 671, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{11}Cl_3N_2OSNa$ $[M+Na]^+$: 406.9550 and 408.9521, found: 406.9552 and 408.9523.

(*R*)-3,3,3-Trichloro-1-(1-phenyl-*1H*-imidazol-2-yl)-2-(*p*-tolyloxy)propan-1-one (2i)



Starting from 2-acyl imidazole **1i** (58.4 mg, 0.20 mmol) according to the general procedure A to give **2i** as a colorless oil (52.1 mg, 0.128 mmol, yield: 64%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 92% (HPLC: OD-H, 254 nm, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 8.4 min, t_r (major) = 9.7 min).

$[\alpha]_D^{22}$ = –92.8° (*c* 1.0, CH_2Cl_2).

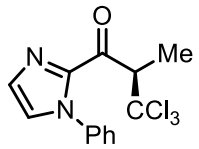
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.54-7.45 (m, 3H), 7.41 (d, *J* = 0.9 Hz, 1H), 7.35 (d, *J* = 0.9 Hz, 1H), 7.32-7.25 (m, 2H), 7.10 (br s, 4H), 6.93 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 181.6, 155.6, 143.3, 137.9, 133.0, 131.2, 130.55, 129.60, 129.5, 129.0, 126.0, 116.7, 96.5, 83.4, 20.7.

IR (film): *v* (cm^{-1}) 3121, 3036, 2924, 2862, 1698, 1598, 1503, 1447, 1398, 1303, 1218, 1060, 946, 901, 809, 766, 727, 689, 580, 521.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{15}Cl_3N_2O_2Na$ $[M+Na]^+$: 431.0091 and 433.0064, found: 431.0092 and 433.0062.

(*R*)-3,3,3-Trichloro-2-methyl-1-(1-phenyl-*1H*-imidazol-2-yl)propan-1-one (2j)



Starting from 2-acyl imidazole **1j** (40.0 mg, 0.20 mmol) according to the general procedure A to give **2j** as a white solid (46.0 mg, 0.146 mmol, yield: 73%). Enantiomeric excess established by HPLC analysis using a Chiralpak IC column, ee = 98.8% (HPLC: IC, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 9.4 min, t_r (major) = 8.2 min). $[\alpha]_D^{22}$ = +25.2° (*c* 0.5, CH_2Cl_2).

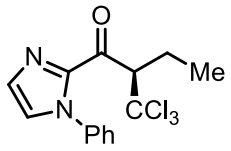
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.49-7.33 (m, 3H), 7.28-7.12 (m, 4H), 5.30 (q, *J* = 6.8 Hz, 1H), 1.50 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 186.6, 142.9, 138.6, 130.5, 129.5, 129.3, 128.9, 126.2, 100.5, 58.3, 16.0.

IR (film): *v* (cm^{-1}) 3154, 3122, 3065, 2961, 2930, 1688, 1591, 1492, 1449, 1399, 1299, 1151, 1078, 1012, 953,905, 831, 767, 687, 601, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{11}Cl_3N_2ONa$ $[M+Na]^+$: 338.9829 and 340.9801, found: 338.9830 and 340.9800.

(*R*)-1-(1-Phenyl-*1H*-imidazol-2-yl)-2-(trichloromethyl)butan-1-one (2k)



Starting from 2-acyl imidazole **1k** (42.8 mg, 0.20 mmol) according to the general procedure A to give **2k** as a white solid (63.3 mg, 0.192 mmol, yield: 96%). Enantiomeric excess established by HPLC analysis using a Chiralpak IC column, ee = 99.4% (HPLC: IC, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 7.3 min, t_r (major) = 6.3 min). $[\alpha]_D^{22}$ = –1.6° (*c* 0.6, CH_2Cl_2).

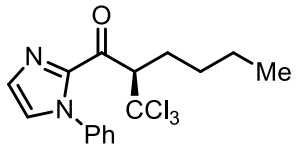
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.35 (m, 3H), 7.27 (d, *J* = 0.9 Hz, 1H), 7.26-7.15 (m, 3H), 5.23 (dd, *J* = 8.7, 5.2 Hz, 1H), 2.25-1.92 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 186.6, 144.0, 138.1, 130.3, 129.2, 128.9, 128.1, 125.6, 99.2, 63.9, 24.3, 11.6.

IR (film): *v* (cm^{-1}) 3120, 3059, 2971, 2878, 1735, 1686, 1495, 1448, 1399, 1308, 1201, 1148, 1113, 1073, 1031, 961, 762, 684.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{13}Cl_3N_2ONa$ $[M+Na]^+$: 352.9986 and 354.9957, found: 352.9986 and 354.9958.

(*R*)-1-(1-Phenyl-*1H*-imidazol-2-yl)-2-(trichloromethyl)hexan-1-one (2l)



Starting from 2-acyl imidazole **1l** (48.4 mg, 0.20 mmol) according to the general procedure A to give **2l** as a colorless oil (54.4 mg, 0.152 mmol, yield: 76%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 98.8% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 6.3 min, t_r (major) = 6.8 min). $[\alpha]_D^{22}$ = –28.0° (*c* 0.5, CH_2Cl_2).

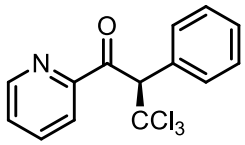
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58-7.44 (m, 3H), 7.40-7.20 (m, 4H), 5.36 (dd, *J* = 10.3, 3.4 Hz, 1H), 2.22-1.96 (m, 2H), 1.51-1.17 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 186.9, 144.3, 138.7, 130.6, 129.5, 129.3, 128.9, 126.2, 100.0, 62.6, 31.2, 29.5, 23.0, 13.9.

IR (film): ν (cm^{-1}) 3113, 3064, 2957, 2930, 2865, 1688, 1596, 1497, 1448, 1399, 1310, 1039, 905, 854, 761, 685, 547.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{17}Cl_3N_2ONa$ $[M+Na]^+$: 381.0299 and 383.0271, found: 381.0298 and 383.0269.

(*R*)-3,3,3-Trichloro-2-phenyl-1-(pyridin-2-yl)propan-1-one (5a)



Starting from 2-acyl pyridine **4a** (39.4 mg, 0.20 mmol) according to the general procedure B to give **5a** as a white solid (52.0 mg, 0.166 mmol, yield: 83%). Enantiomeric excess established by HPLC analysis using a Chiralpak IC column, ee = 99.6% (HPLC: IC, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 9.6 min, t_r (major) = 7.6 min). $[\alpha]_D^{22}$ = –85.0° (*c* 0.3, CH_2Cl_2).

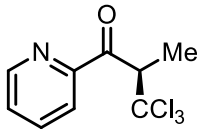
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.64 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.10 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.84 (td, *J* = 7.7, 1.7 Hz, 1H), 7.78-7.66 (m, 2H), 7.46 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.40-7.33 (m, 3H), 6.89 (s, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 194.3, 152.6, 149.4, 137.7, 132.4, 129.5, 128.7, 128.2, 123.2, 99.3, 65.8.

IR (film): ν (cm^{-1}) 3057, 2949, 1704, 1580, 1436, 1324, 1248, 1213, 1067, 992, 893, 871, 809, 742, 699, 616, 560.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{10}Cl_3N_2ONa$ $[M+Na]^+$: 335.9720 and 337.9692, found: 335.9722 and 337.9692.

(*R*)-3,3,3-Trichloro-2-methyl-1-(pyridin-2-yl)propan-1-one (5b)



Starting from 2-acyl pyridine **4b** (27.0 mg, 0.20 mmol) according to the general procedure B to give **5b** as a colorless oil (33.6 mg, 0.134 mmol, yield: 67%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 254 nm, hexane/isopropanol =

99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 7.8 min, t_r (major) = 6.7 min). $[\alpha]_D^{22}$ = +40.3° (*c* 0.4, CH_2Cl_2).

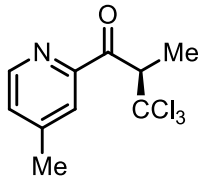
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.05 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.82 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 5.60 (q, *J* = 6.9 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 152.3, 149.0, 137.3, 127.7, 122.7, 100.0, 55.5, 15.7.

IR (film): *v* (cm^{-1}) 3288, 3170, 3130, 3061, 2957, 2924, 1701, 1578, 1443, 1333, 1213, 968, 923, 810, 768, 741, 665, 582, 408.

HRMS (ESI, *m*/*z*) calcd for $C_9H_8Cl_3NONa$ $[M+Na]^+$: 273.9564 and 275.9535, found: 273.9565 and 275.9535.

(*R*)-3,3,3-Trichloro-2-methyl-1-(4-methylpyridin-2-yl)propan-1-one (5c)



Starting from 2-acyl pyridine **4c** (29.8 mg, 0.20 mmol) according to the general procedure B to give **5c** as a colorless oil (34.2 mg, 0.129 mmol, yield: 65%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 93% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 11.1 min, t_r (major) = 7.5 min). $[\alpha]_D^{22}$ = +43.1° (*c* 0.4, CH_2Cl_2).

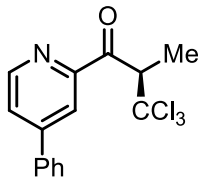
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58-8.32 (m, 1H), 7.98-7.68 (m, 1H), 7.26 (ddd, *J* = 4.9, 1.7, 0.7 Hz, 1H), 5.59 (q, *J* = 6.9 Hz, 1H), 2.38 (s, 3H), 1.54 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 152.2, 148.8, 128.6, 123.5, 100.0, 55.5, 21.1, 15.7.

IR (film): *v* (cm^{-1}) 3112, 3055, 2989, 2952, 2878, 1702, 1598, 1497, 1451, 1400, 1317, 1158, 1019, 981, 934, 842, 817, 771, 727, 671, 584, 514, 427.

HRMS (ESI, *m*/*z*) calcd for $C_{10}H_{10}Cl_3NONa$ $[M+Na]^+$: 287.9720 and 289.9691, found: 287.9722 and 289.9693.

(*R*)-3,3,3-Trichloro-2-methyl-1-(4-phenylpyridin-2-yl)propan-1-one (5d)



Starting from 2-acyl pyridine **4d** (42.2 mg, 0.20 mmol) according to the general procedure B to give **5d** as a white solid (46.5 mg, 0.142 mmol, yield: 71%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 94% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 14.4 min, t_r (major) = 10.0 min). $[\alpha]_D^{22}$ = +48.7° (*c* 0.4, CH_2Cl_2).

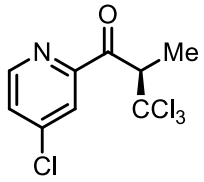
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 5.1, 0.6 Hz, 1H), 8.27 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.66 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.61 (dt, *J* = 8.5, 2.3 Hz, 2H), 7.53-7.31 (m, 3H), 1.58 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 152.9, 149.9, 149.5, 137.2, 129.6, 129.3, 127.1, 125.4, 120.5, 100.0, 55.6, 15.7.

IR (film): *v* (cm^{-1}) 3062, 3034, 2962, 2927, 1699, 1591, 1455, 1401, 1324, 1262, 1188, 1087, 1027, 984, 930, 825, 768, 707, 667, 578, 507, 428.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{12}Cl_3NONa$ $[M+Na]^+$: 349.9877 and 351.9849, found: 349.9879 and 351.9849.

(*R*)-3,3,3-Trichloro-1-(4-chloropyridin-2-yl)-2-methylpropan-1-one (5e)



Starting from 2-acyl pyridine **4e** (33.8 mg, 0.20 mmol) according to the general procedure B to give **5e** as a colorless oil (46.0 mg, 0.161 mmol, yield: 81%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 9.9 min, t_r (major) = 6.7 min). $[\alpha]_D^{22}$ = +44.4° (*c* 0.5, CH_2Cl_2).

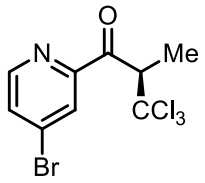
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.2 Hz, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.46 (dd, *J* = 5.2, 2.0 Hz, 1H), 5.52 (q, *J* = 6.8 Hz, 1H), 1.54 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, CDCl3) δ 196.0, 153.5, 149.9, 145.9, 127.8, 123.1, 99.6, 55.7, 15.6.

IR (film): ν (cm^{-1}) 3083, 3057, 2992, 2952, 2879, 1709, 1562, 1454, 1395, 1322, 1214, 1094, 993, 930, 829, 777, 700, 666, 583, 517, 425.

HRMS (ESI, *m*/*z*) calcd for $C_9H_8Cl_4NO$ $[M+H]^+$: 285.9355, 287.9325 and 289.9297, found: 285.9356, 287.9327 and 289.9297.

(*R*)-1-(4-Bromopyridin-2-yl)-3,3,3-trichloro-2-methylpropan-1-one (5f)



Starting from 2-acyl pyridine **4f** (42.6 mg, 0.20 mmol) according to the general procedure B to give **5f** as a colorless oil (44.8 mg, 0.136 mmol, yield: 68%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 92% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 10.5 min, t_r (major) = 6.8 min). $[\alpha]_D^{22}$ = +36.9° (*c* 0.3, CH_2Cl_2).

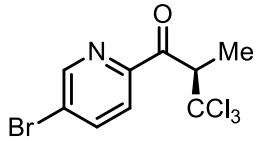
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.2 Hz, 1H), 8.25 (dd, *J* = 1.9, 0.4 Hz, 1H), 7.69 (dd, *J* = 5.2, 1.9 Hz, 1H), 5.58 (q, *J* = 6.9 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9, 153.2, 149.7, 134.4, 130.8, 126.2, 99.6, 55.7, 15.6.

IR (film): ν (cm^{-1}) 3091, 3055, 2991, 2961, 2879, 1707, 1555, 1453, 1386, 1326, 1205, 1086, 989, 931, 829, 778, 674, 581, 509, 425.

HRMS (ESI, *m*/*z*) calcd for $C_9H_8BrCl_3NO$ $[M+H]^+$: 329.8849, 331.8825, 333.8798 and 335.8771, found: 329.8852, 331.8827, 333.8800 and 335.8773.

(*R*)-1-(5-Bromopyridin-2-yl)-3,3,3-trichloro-2-methylpropan-1-one (5g)



Starting from 2-acyl pyridine **4g** (42.6 mg, 0.20 mmol) according to the general procedure B to give **5g** as a colorless oil (60.1 mg, 0.182 mmol, yield: 91%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, hexane/isopropanol =

99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 10.5 min, t_r (major) = 8.5 min). $[\alpha]_D^{22}$ = +24.8° (*c* 0.6, CH_2Cl_2).

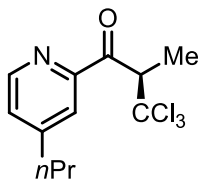
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 1.9, 0.9 Hz, 1H), 8.04-7.91 (m, 2H), 5.49 (q, *J* = 6.8 Hz, 1H), 1.54 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 150.5, 150.2, 140.1, 126.1, 123.9, 99.7, 55.4, 15.6.

IR (film): *v* (cm^{-1}) 3053, 2983, 2942, 2879, 1703, 1560, 1453, 1370, 1329, 1208, 1086, 1006, 967, 826, 777, 676, 625, 583.

HRMS (ESI, *m*/*z*) calcd for $C_9H_8BrCl_3NO$ $[M+H]^+$: 329.8849, 331.8825, 333.8798 and 335.8771, found: 329.8853, 331.8828, 333.8803 and 335.8774.

(*R*)-3,3,3-Trichloro-2-methyl-1-(4-propylpyridin-2-yl)propan-1-one (5h)



Starting from 2-acyl pyridine **4h** (35.4 mg, 0.20 mmol) according to the general procedure B to give **5h** as a colorless oil (39.3 mg, 0.134 mmol, yield: 67%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 94% (HPLC: OD-H, 254 nm, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 7.8 min, t_r (major) = 6.0 min). $[\alpha]_D^{22}$ = +44.3° (*c* 0.4, CH_2Cl_2).

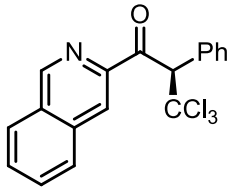
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.9 Hz, 1H), 7.93 (s, 1H), 7.33 (dd, *J* = 4.9, 1.6 Hz, 1H), 5.66 (q, *J* = 6.9 Hz, 1H), 2.87-2.50 (m, 2H), 1.70 (dq, *J* = 14.8, 7.5 Hz, 2H), 1.61 (d, *J* = 6.9 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 153.2, 152.3, 148.8, 127.9, 122.8, 100.1, 55.6, 37.3, 23.3, 15.7, 13.6.

IR (film): *v* (cm^{-1}) 2961, 2934, 2871, 1706, 1597, 1414, 1324, 1159, 1003, 934, 825, 779, 731, 669, 580, 428.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{14}Cl_3NONa$ $[M+Na]^+$: 316.0033, 318.0005 and 319.9977, found: 316.0034, 318.0005 and 319.9977.

(*R*)-3,3,3-Trichloro-1-(isoquinolin-3-yl)-2-phenylpropan-1-one (5i)



Starting from 2-acyl pyridine **4i** (49.4 mg, 0.20 mmol) according to the general procedure B to give **5i** as a white solid (52.3 mg, 0.144 mmol, yield: 72%). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, ee = 90% (HPLC: OD-H, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 11.1 min, t_r (major) = 7.5 min). $[\alpha]_D^{22}$ = –102.0° (*c* 0.4, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.22 (s, 1H), 8.56 (s, 1H), 8.10-7.90 (m, 2H), 7.86-7.64 (m, 4H), 7.47-7.25 (m, 3H), 7.01 (s, 1H).

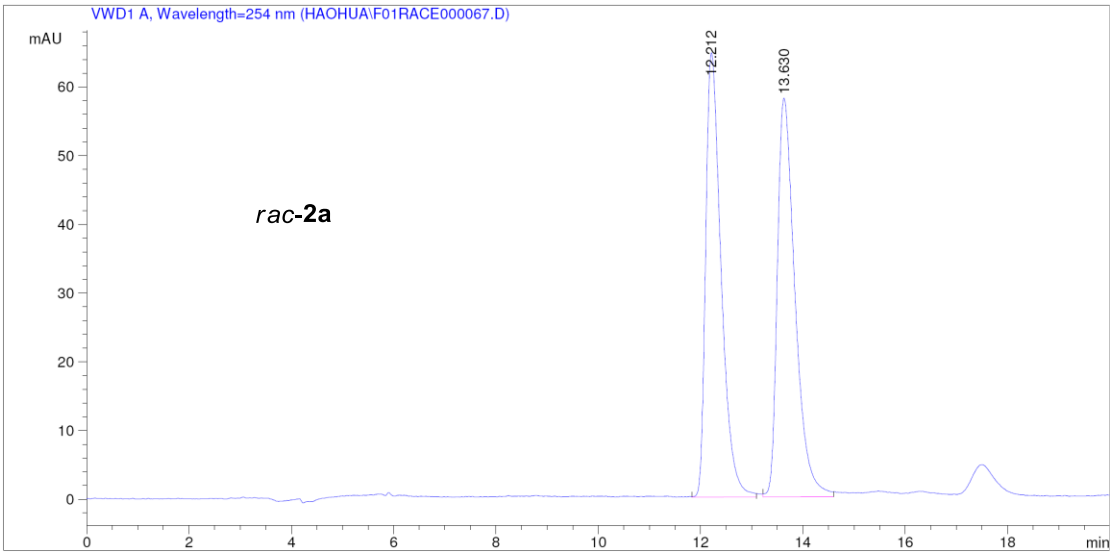
^{13}C NMR (75 MHz, CD_2Cl_2) δ 194.5, 152.3, 146.8, 136.0, 132.6, 132.5, 131.7, 130.9, 130.5, 129.5, 129.1, 128.7, 128.0, 122.3, 99.5, 66.5.

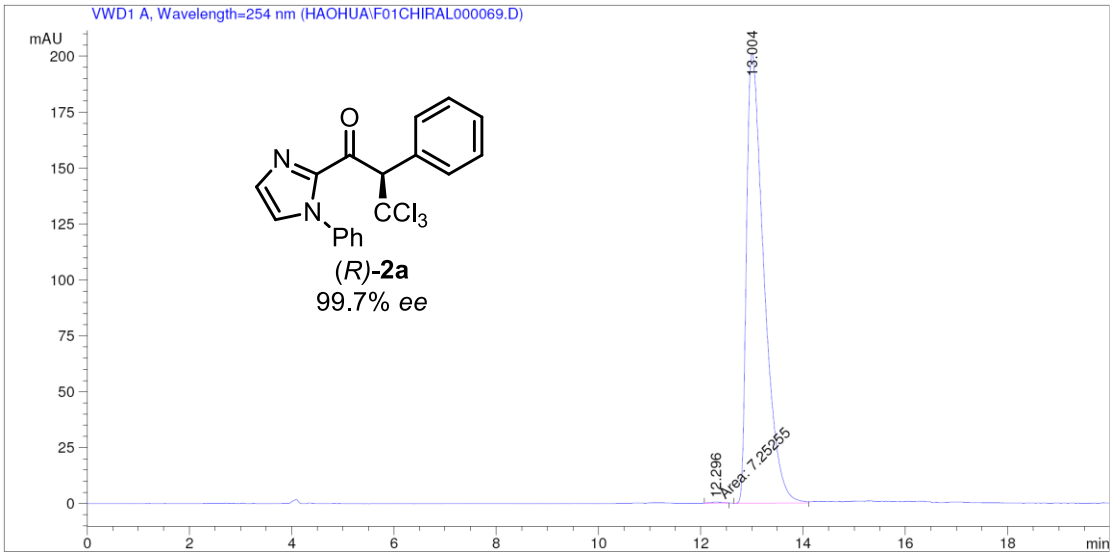
IR (film): ν (cm^{-1}) 3058, 2947, 2855, 1963, 1694, 1490, 1444, 1384, 1309, 1245, 1161, 1124, 1060, 939, 908, 864, 737, 697, 622, 562, 485.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{12}Cl_3NONa$ $[M+Na]^+$: 385.9877, 387.9849 and 389.9823, found: 385.9878, 387.9849 and 389.9820.

4. Enantioselectivities as Determined by Chiral HPLC

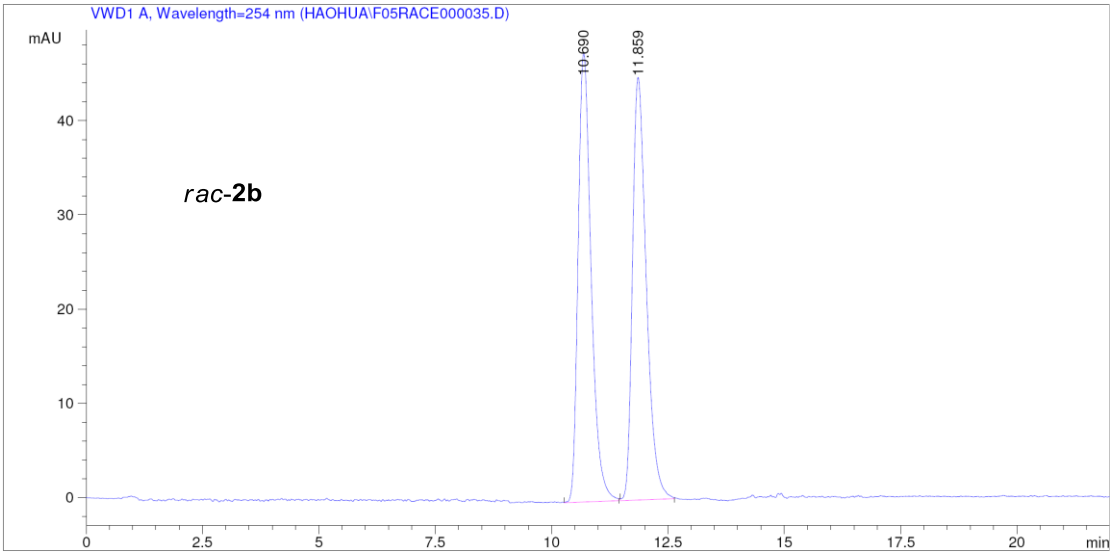
Enantiomeric purities of the reaction products were determined with a Daicel Chiralpak AD-H, OD-H or IC (250 × 4.6 mm) HPLC column on an Agilent 1200 or 1260 Series HPLC System using hexane/isopropanol as a mobile phase. The column temperature was 25 °C and UV-absorption was measured at 254 nm.

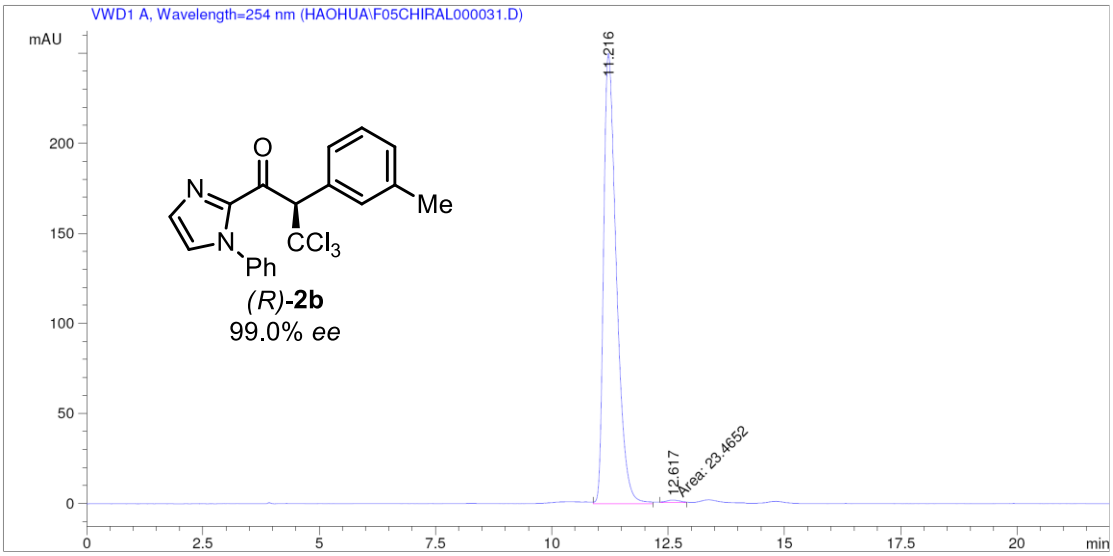




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.296	MM	0.2512	7.25255	4.81241e-1	0.1520
2	13.004	VB	0.3575	4764.04932	201.40443	99.8480

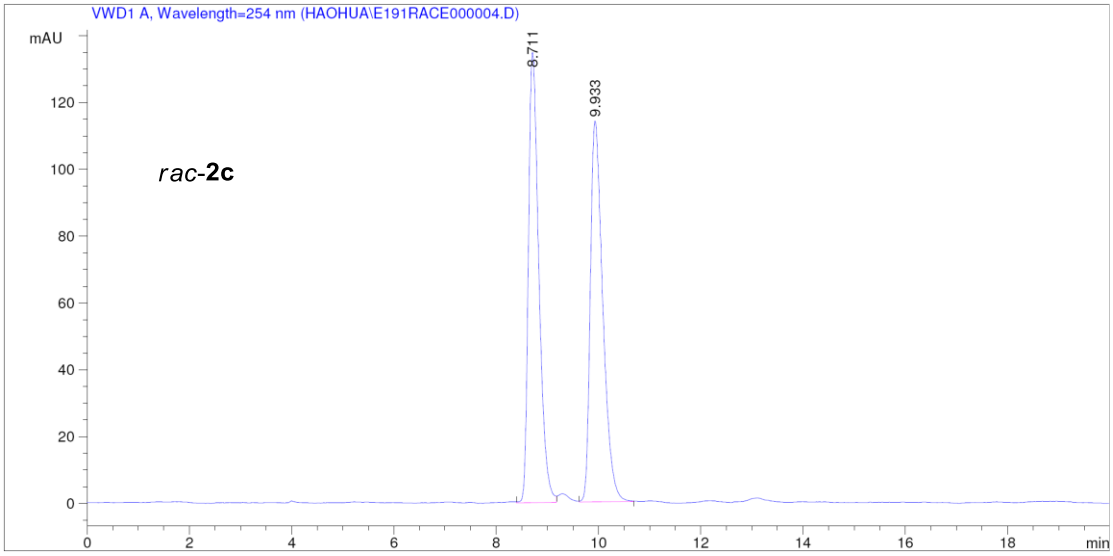
Figure S1. HPLC traces of *rac*-**2a** (reference) and (*R*)-**2a**.

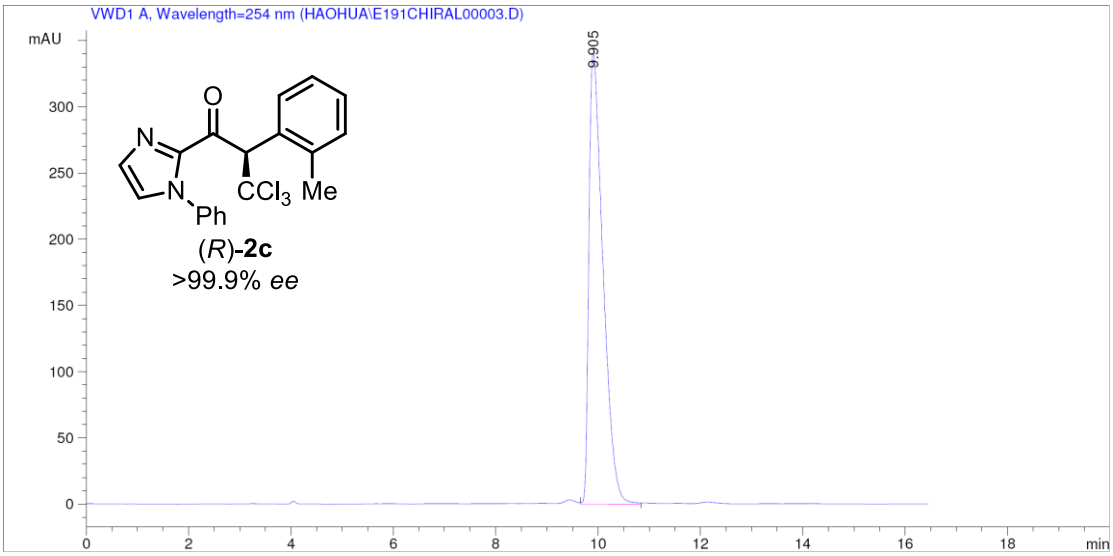




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.216	BB	0.2920	4793.23633	250.08548	99.5128
2	12.617	MM	0.3165	23.46524	1.23577	0.4872

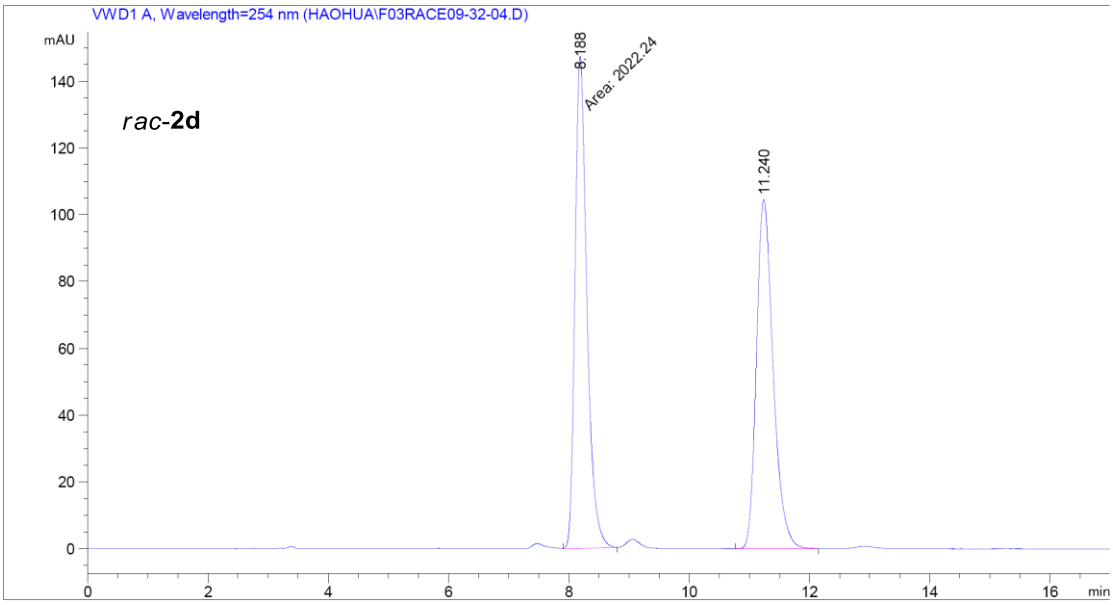
Figure S2. HPLC traces of *rac*-**2b** (reference) and (*R*)-**2b**.

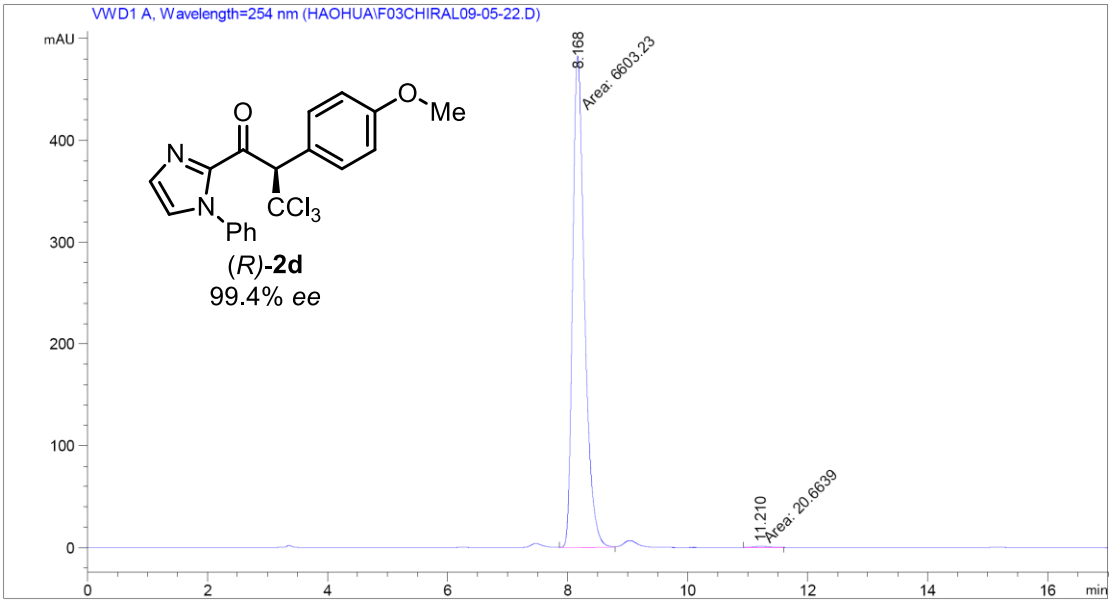




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.905	VV	0.2894	6497.80615	340.78189	100.0000

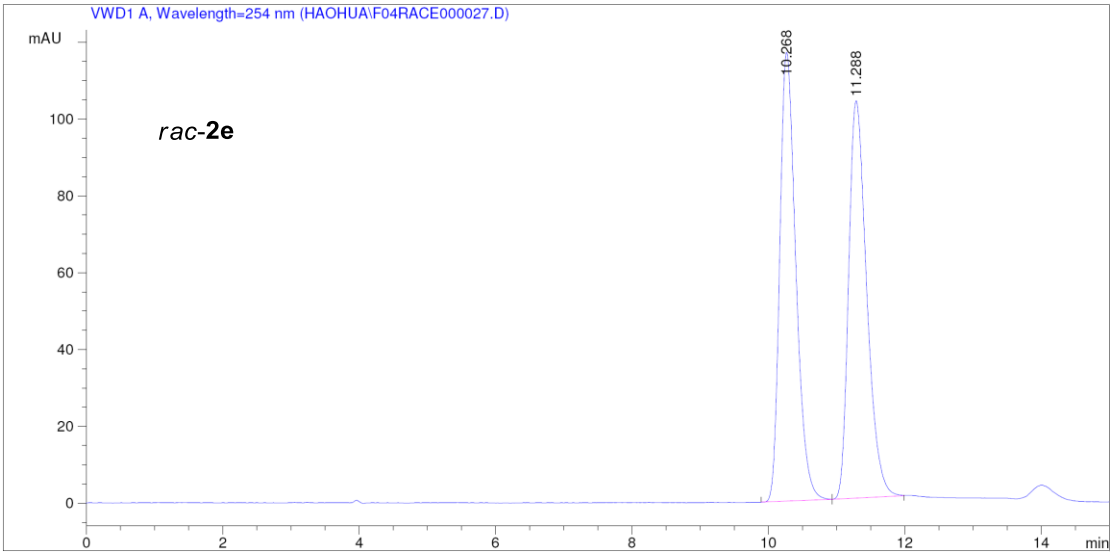
Figure S3. HPLC traces of *rac*-**2c** (reference) and (*R*)-**2c**.

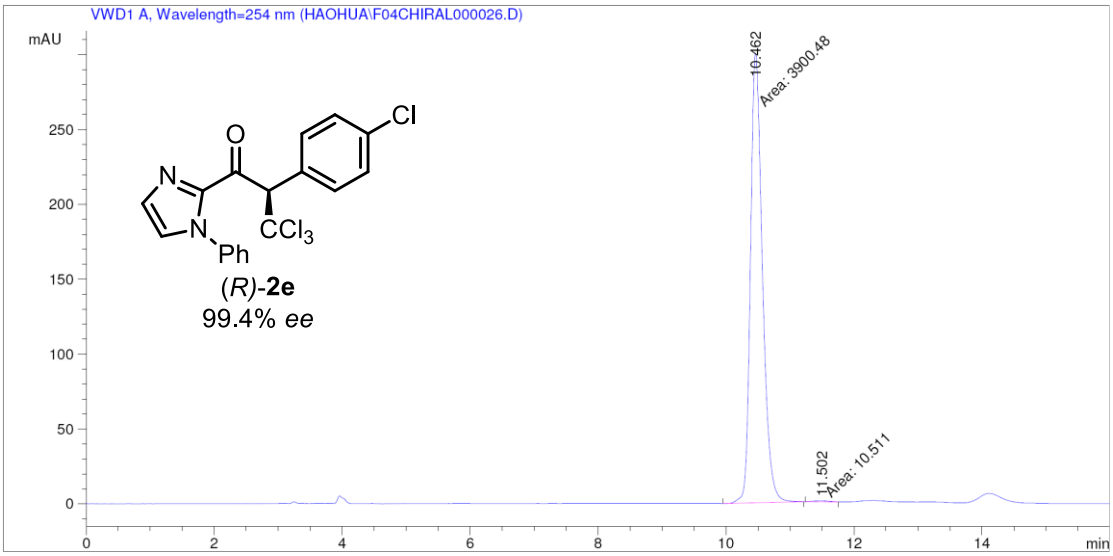




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.168	MF	0.2278	6603.23242	483.07080	99.6880
2	11.210	MM	0.2973	20.66391	1.15835	0.3120

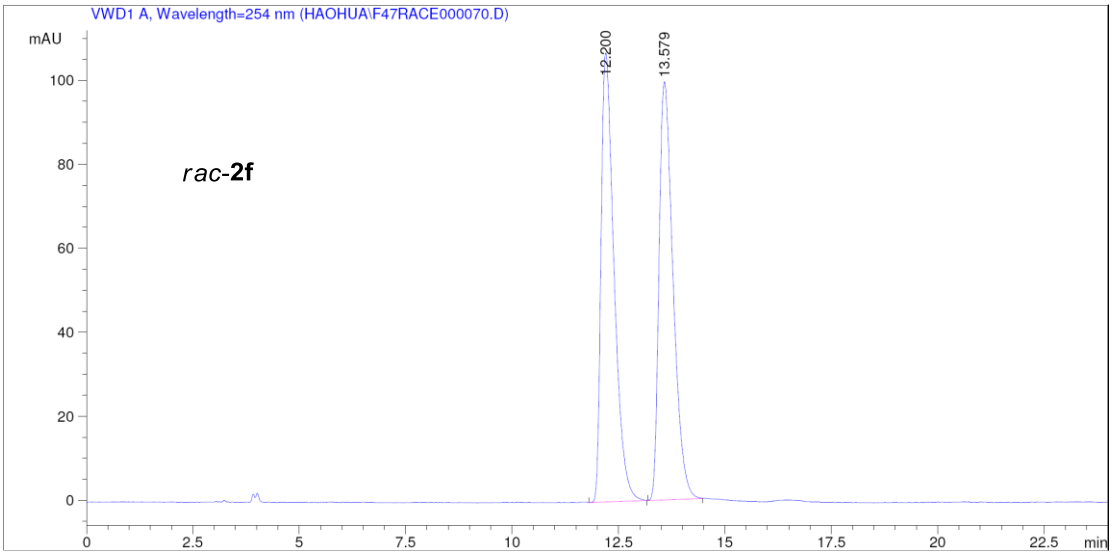
Figure S4. HPLC traces of *rac*-**2d** (reference) and (*R*)-**2d**.

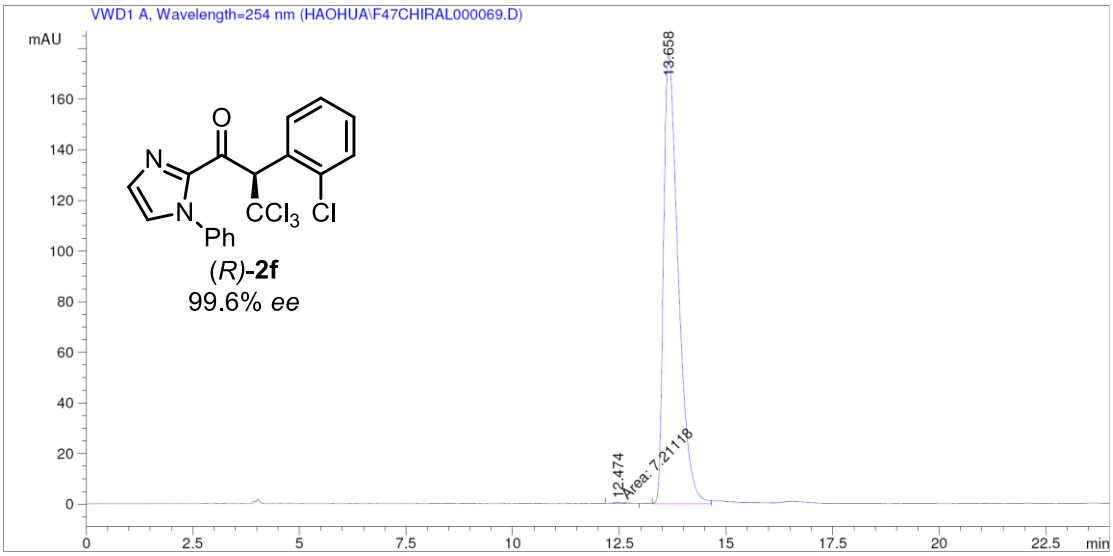




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.462	MM	0.2165	3900.48364	300.29077	99.7312
2	11.502	MM	0.2736	10.51101	6.40245e-1	0.2688

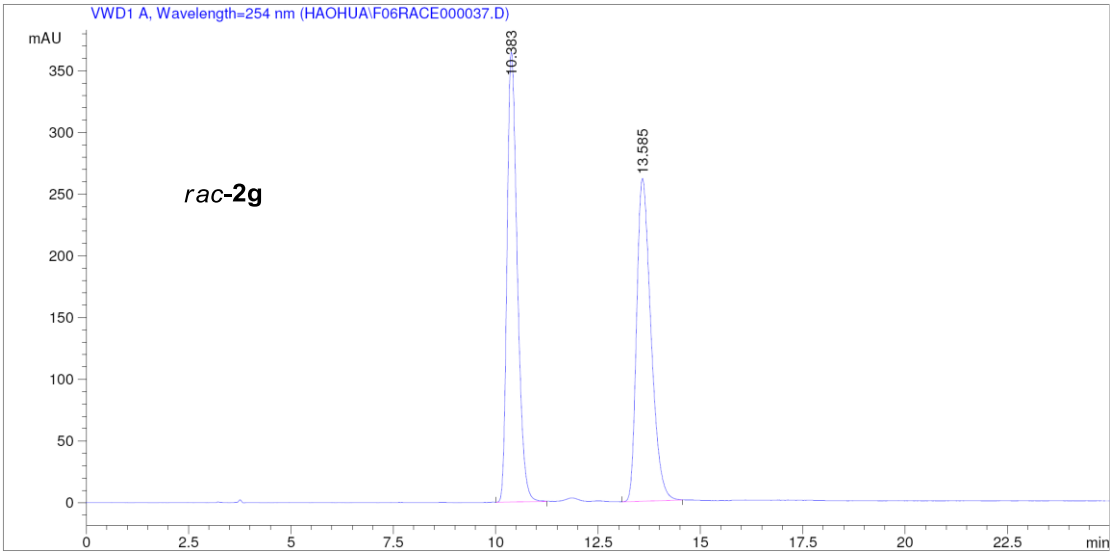
Figure S5. HPLC traces of *rac*-**2e** (reference) and (*R*)-**2e**.

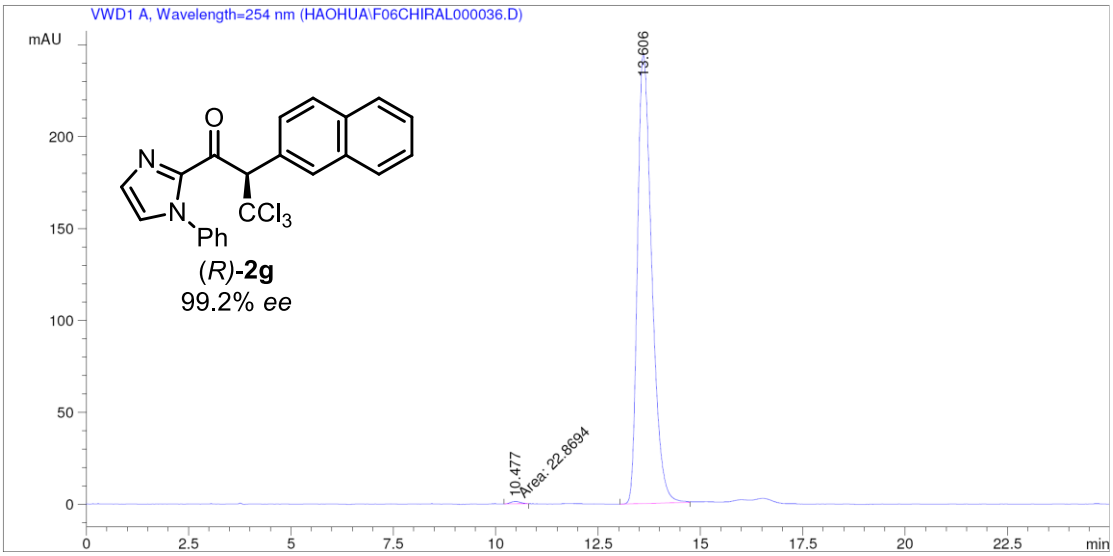




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.474	MM	0.3260	7.21118	3.68660e-1	0.1695
2	13.658	BB	0.3646	4246.32178	177.78749	99.8305

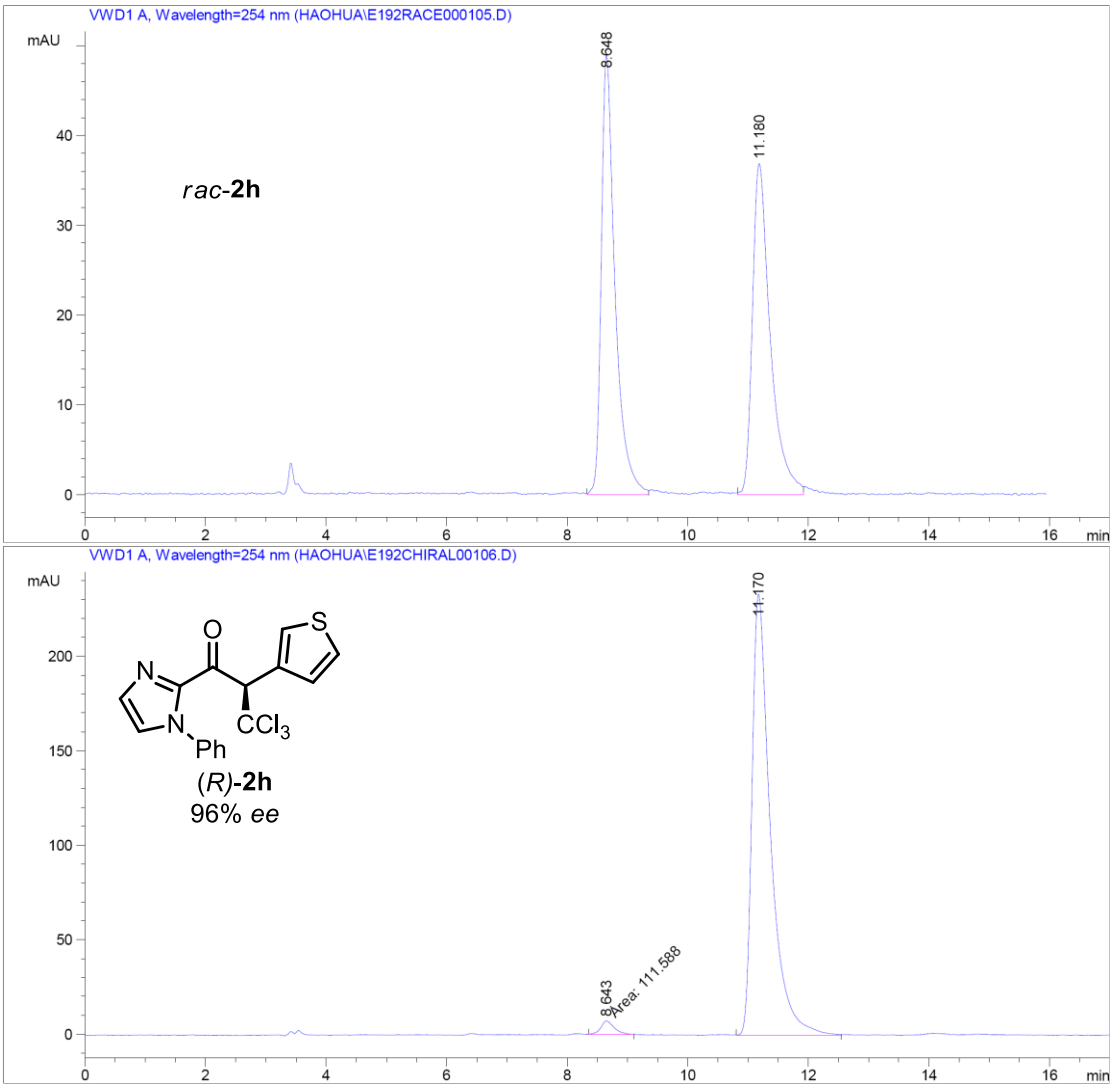
Figure S6. HPLC traces of *rac*-**2f** (reference) and (*R*)-**2f**.





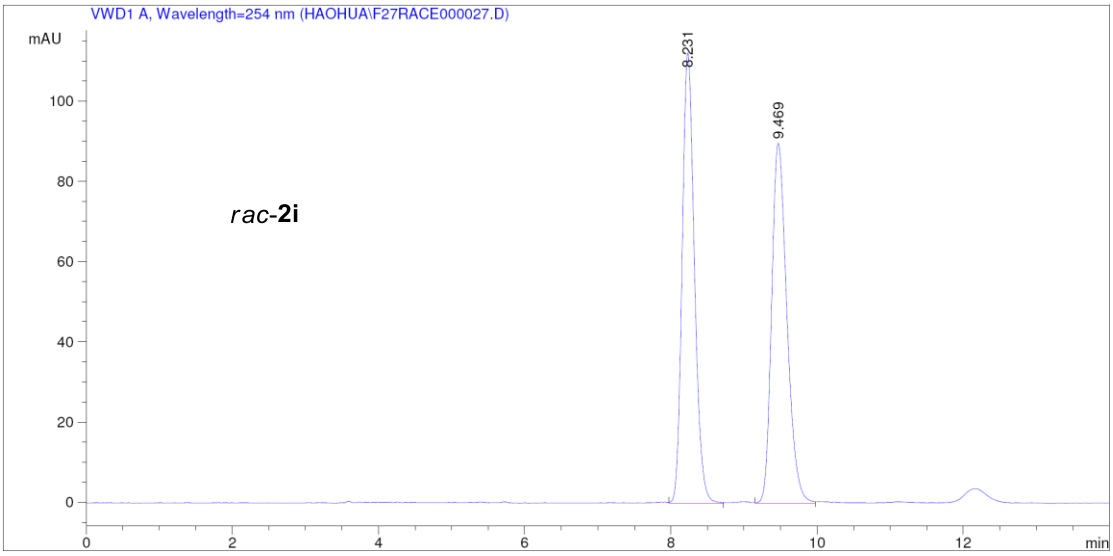
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.477	MM	0.2738	22.86938	1.39204	0.3836
2	13.606	VB	0.3717	5938.30176	244.87686	99.6164

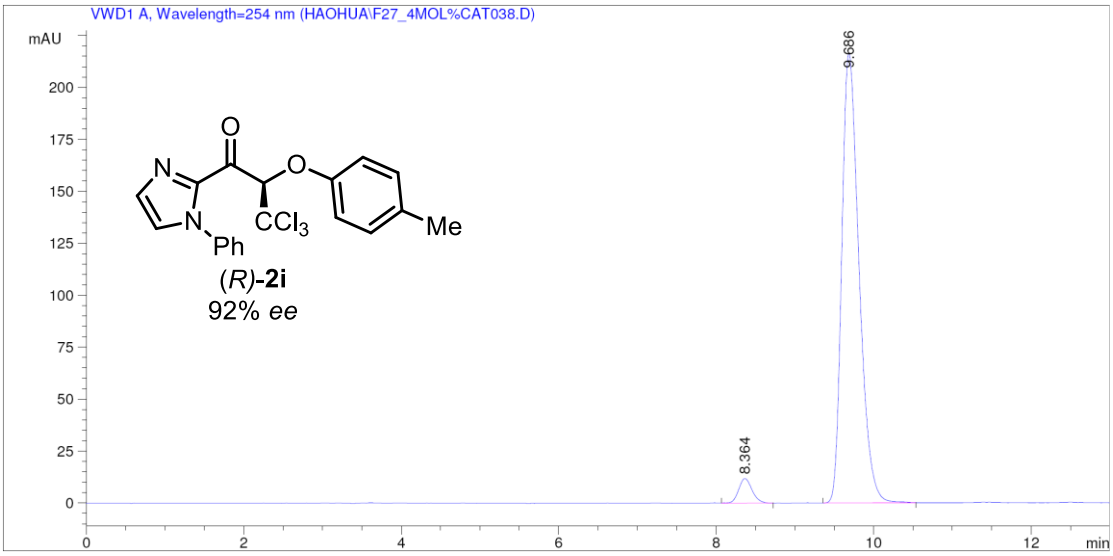
Figure S7. HPLC traces of *rac*-**2g** (reference) and (*R*)-**2g**.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.643	MM	0.2606	111.58772	7.13766	2.1984
2	11.170	VV	0.3120	4964.29834	233.56781	97.8016

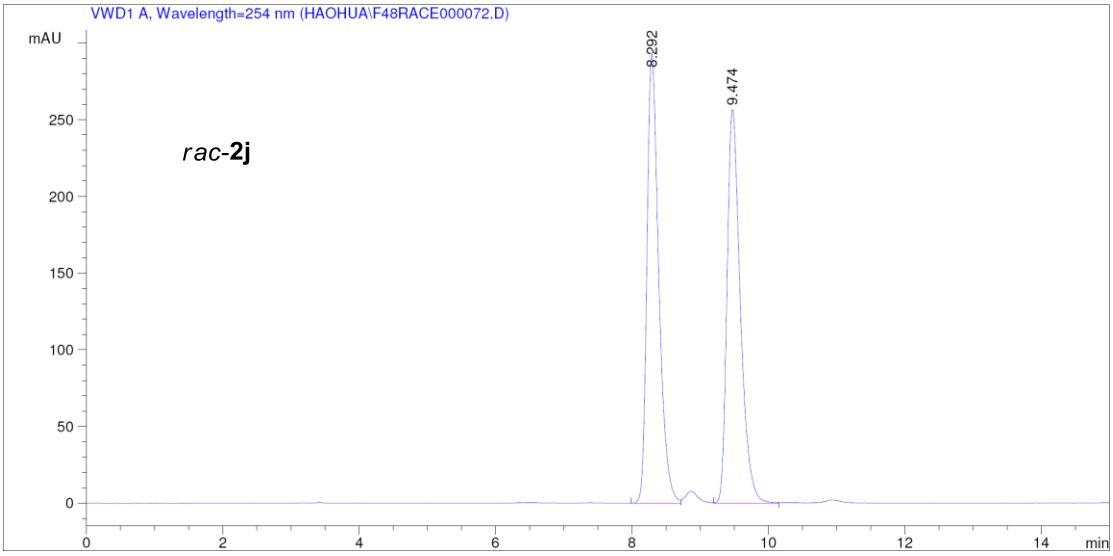
Figure S8. HPLC traces of *rac*-**2h** (reference) and (*R*)-**2h**.

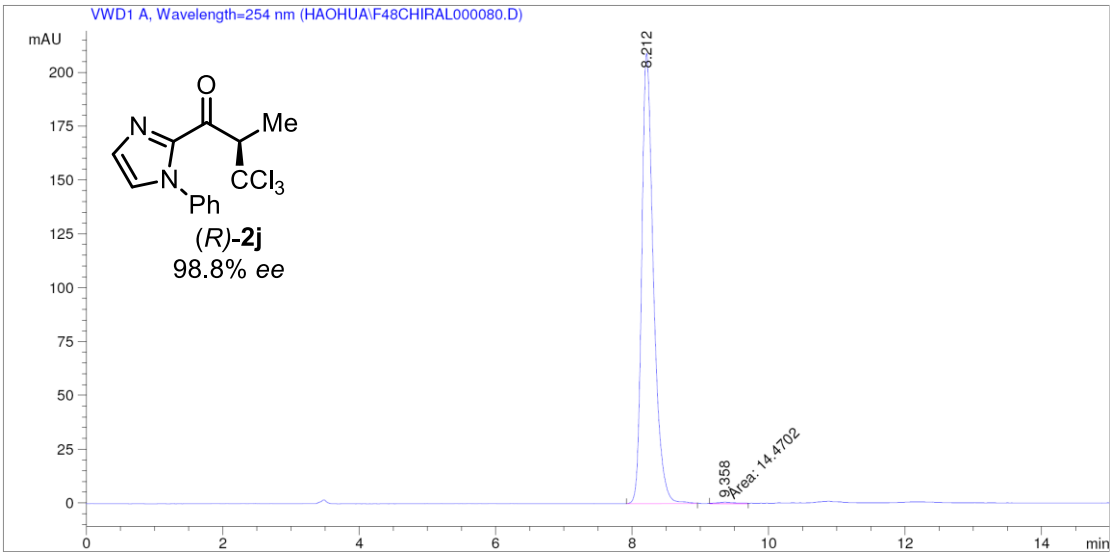




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.364	VB	0.1847	141.92641	11.86826	4.1291
2	9.686	VB	0.2343	3295.32300	216.61507	95.8709

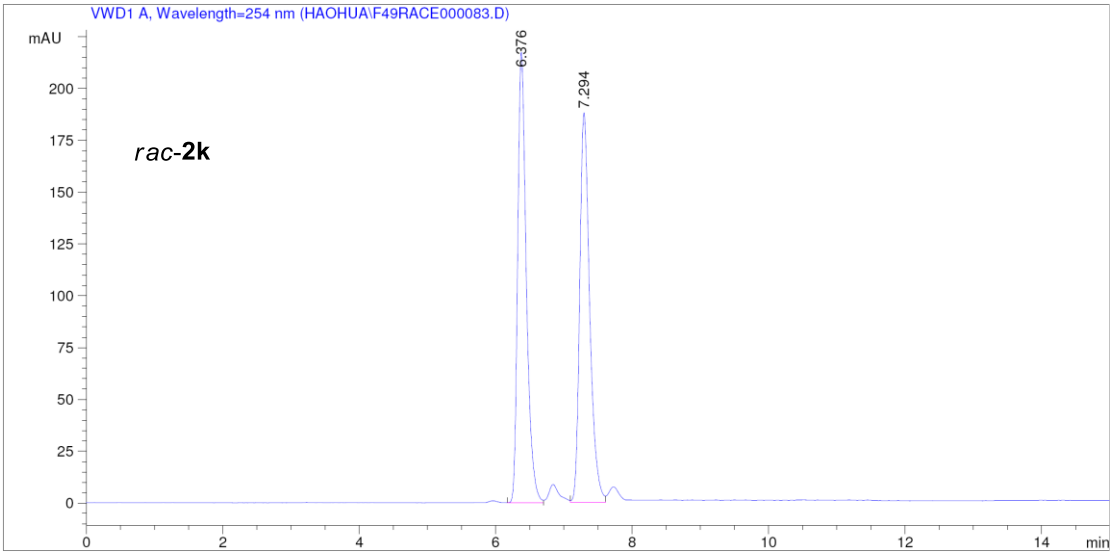
Figure S9. HPLC traces of *rac*-**2i** (reference) and (*R*)-**2i**.

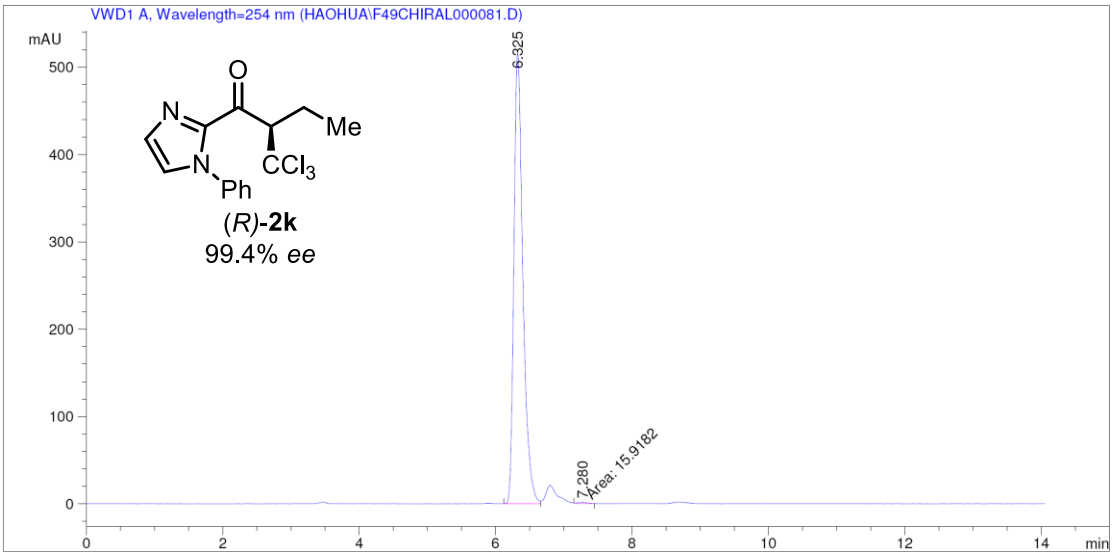




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.212	BB	0.1818	2500.74487	209.02557	99.4247
2	9.358	MM	0.3440	14.47021	7.01170e-1	0.5753

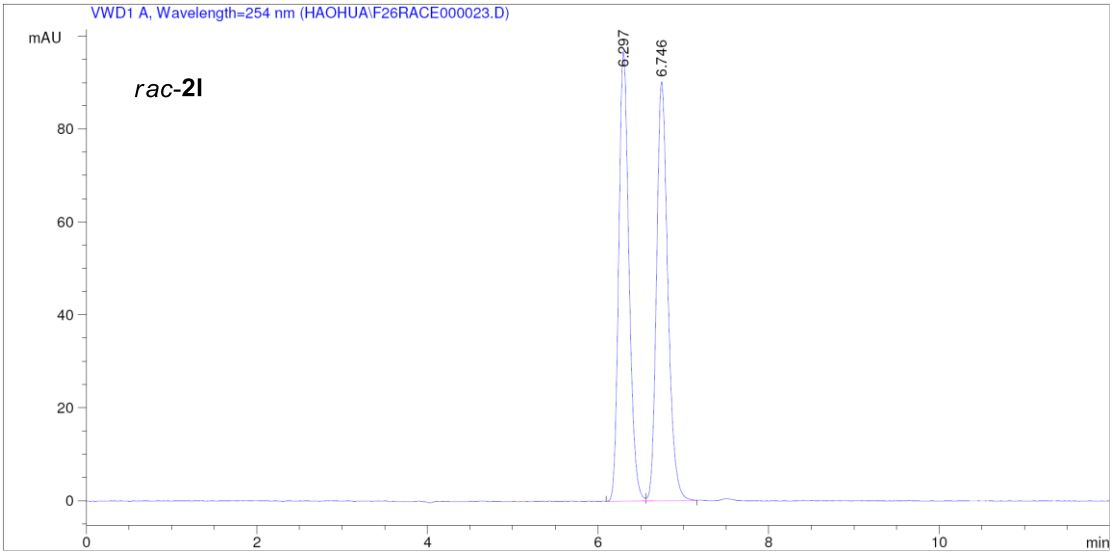
Figure S10. HPLC traces of *rac*-**2j** (reference) and (*R*)-**2j**.

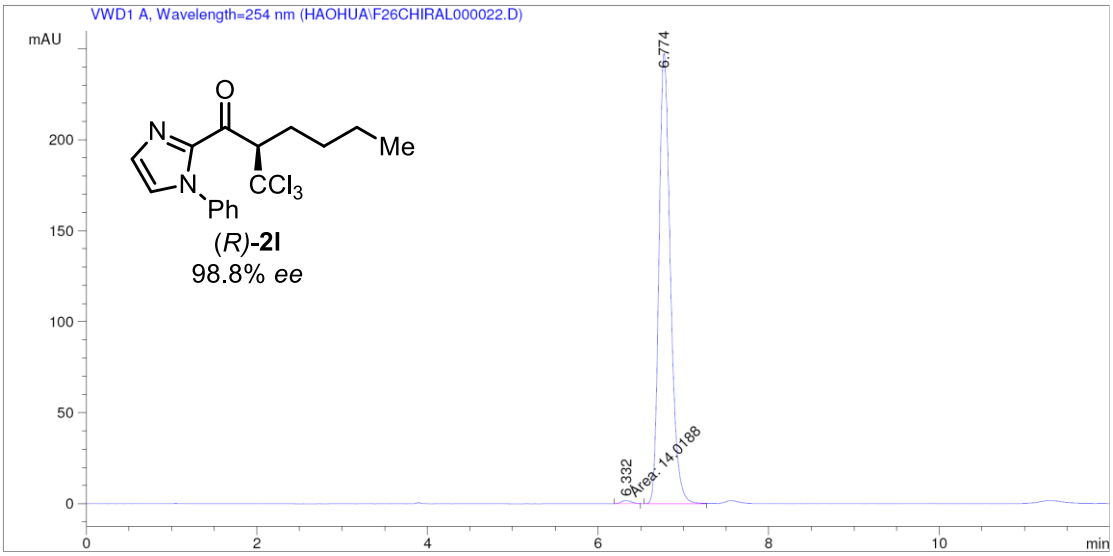




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.325	VV	0.1392	4737.03857	515.78339	99.6651
2	7.280	MM	0.1897	15.91819	1.39826	0.3349

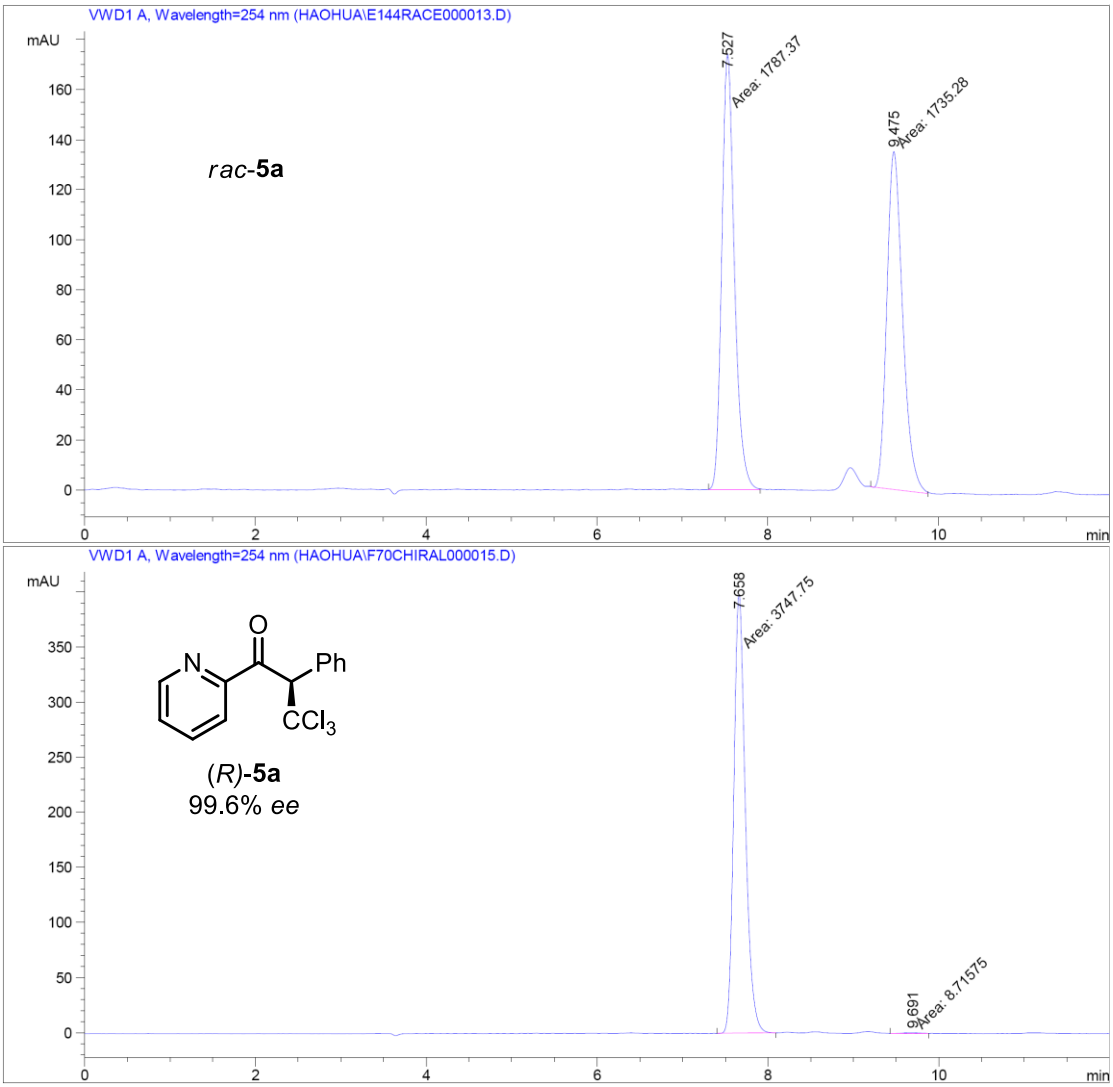
Figure S11. HPLC traces of *rac*-**2k** (reference) and (*R*)-**2k**.





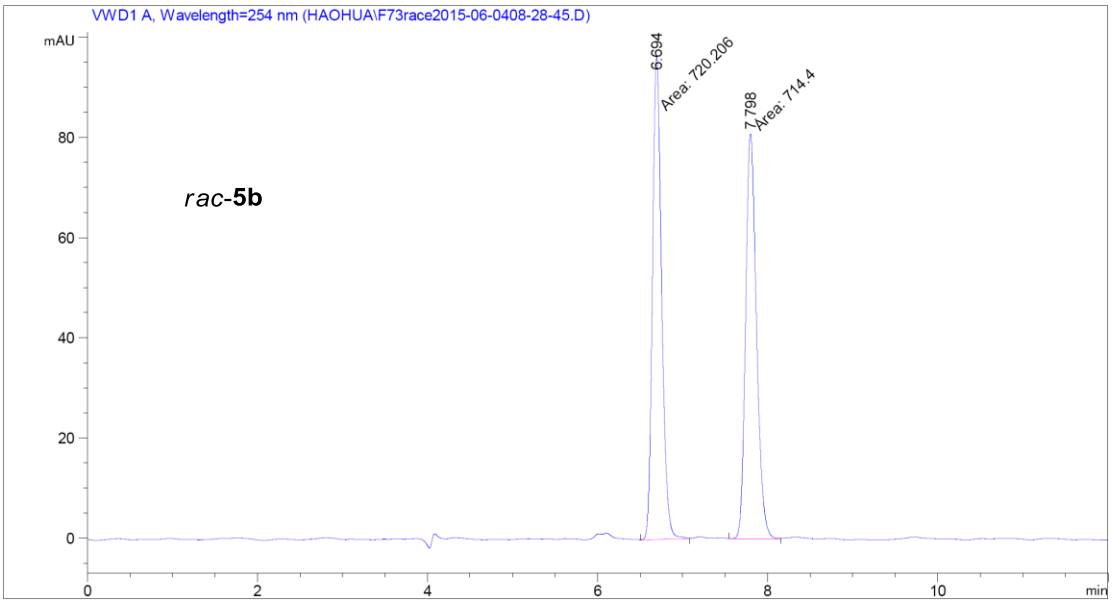
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.332	MM	0.1343	14.01876	1.73929	0.6009
2	6.774	VB	0.1442	2319.01855	247.60158	99.3991

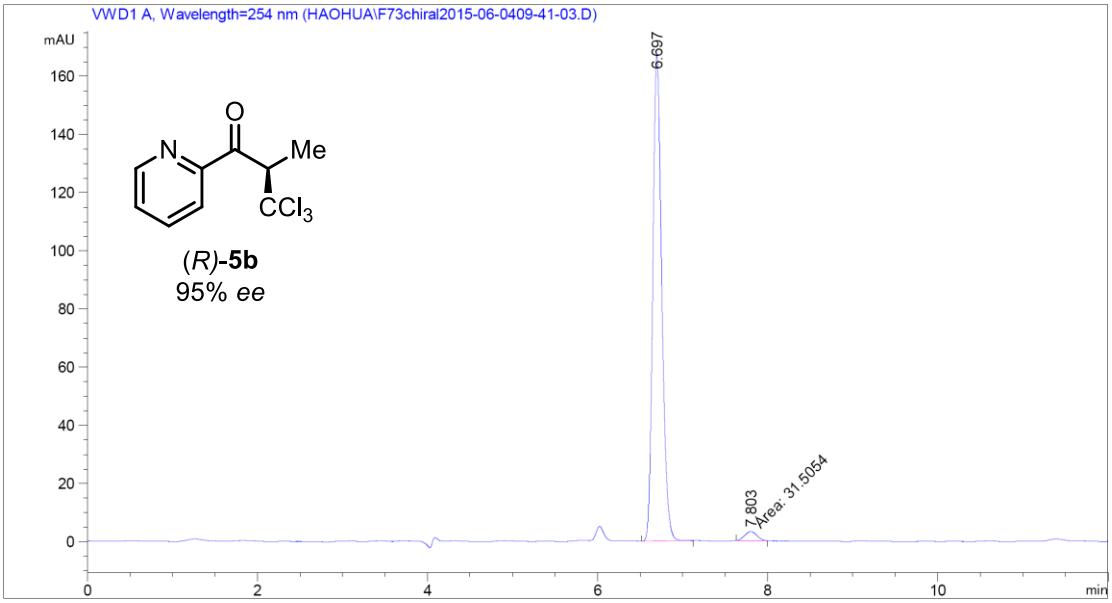
Figure S12. HPLC traces of *rac*-**2l** (reference) and (*R*)-**2l**.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.658	MM	0.1567	3747.74731	398.54758	99.7680
2	9.691	MM	0.2226	8.71575	6.52687e-1	0.2320

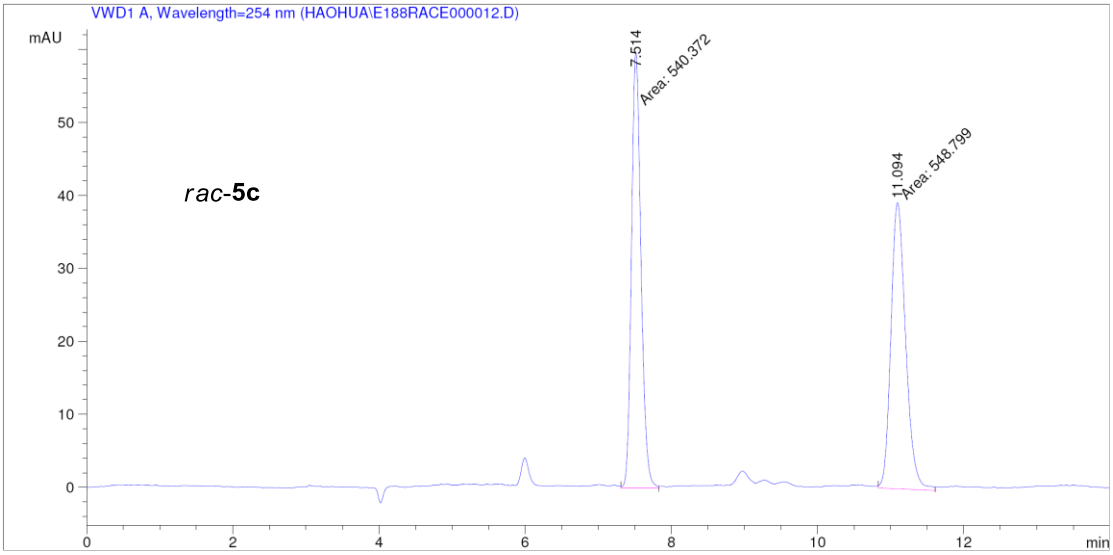
Figure S13. HPLC traces of *rac*-**5a** (reference) and (*R*)-**5a**.

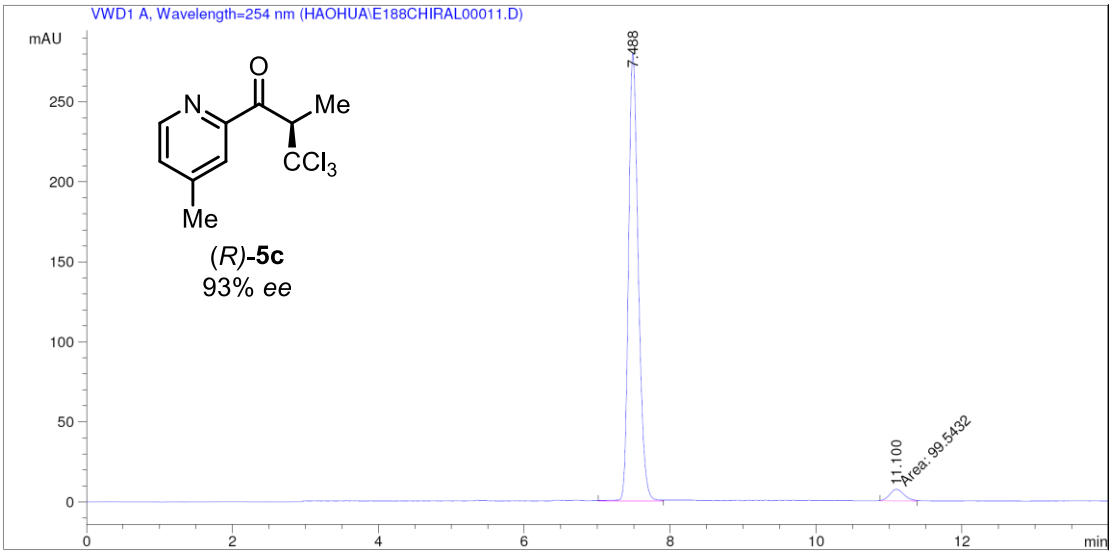




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.697	BB	0.1129	1221.17432	166.82132	97.4850
2	7.803	MM	0.1663	31.50538	3.15839	2.5150

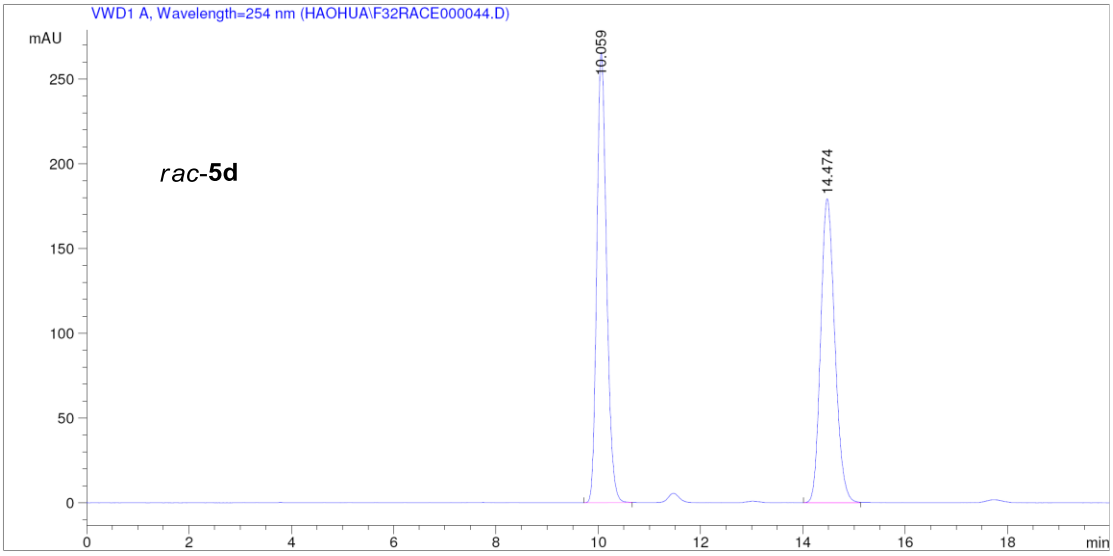
Figure S14. HPLC traces of *rac*-**5b** (reference) and (*R*)-**5b**.

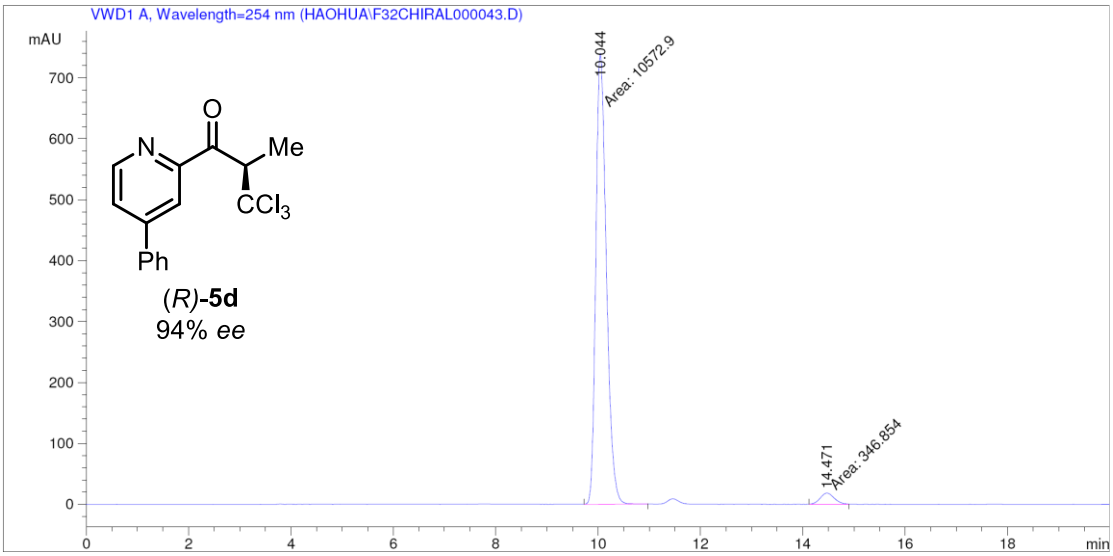




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.488	VB	0.1419	2603.13940	280.15851	96.3169
2	11.100	FM	0.2301	99.54321	7.21026	3.6831

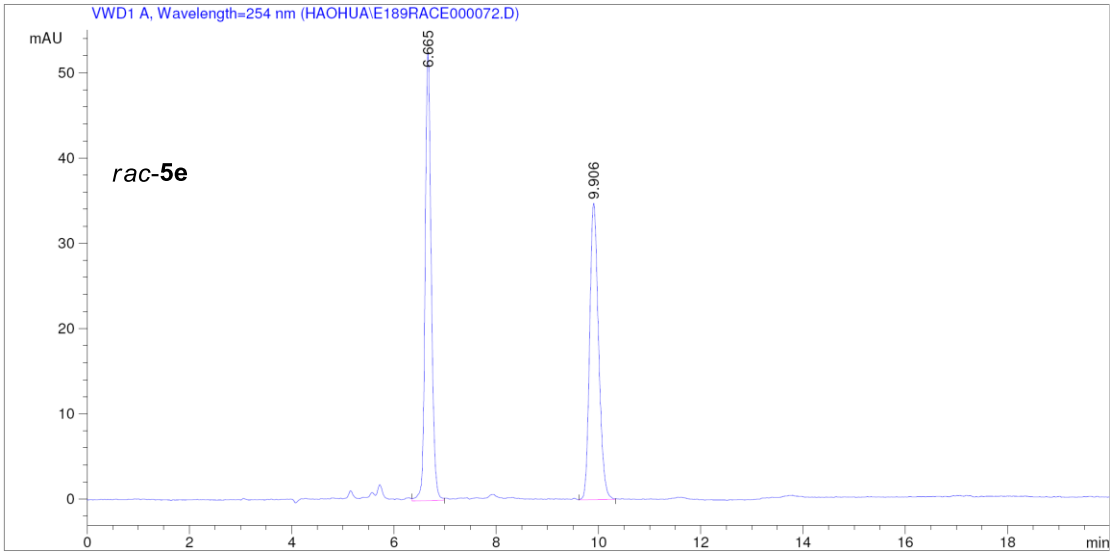
Figure S15. HPLC traces of *rac*-**5c** (reference) and (*R*)-**5c**.

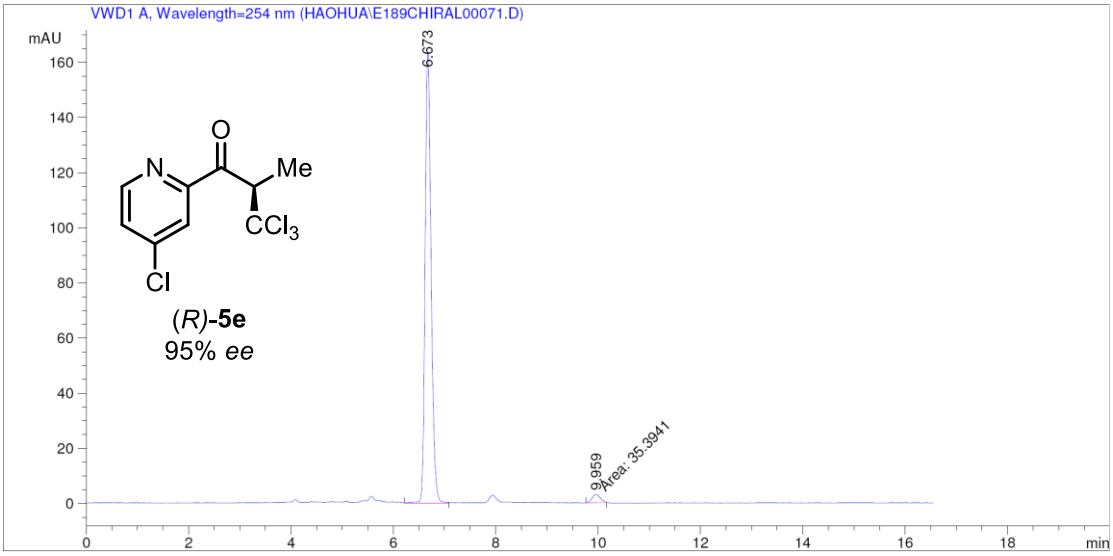




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.044	MM	0.2380	1.05729e4	740.45496	96.8236
2	14.471	MM	0.3171	346.85449	18.23022	3.1764

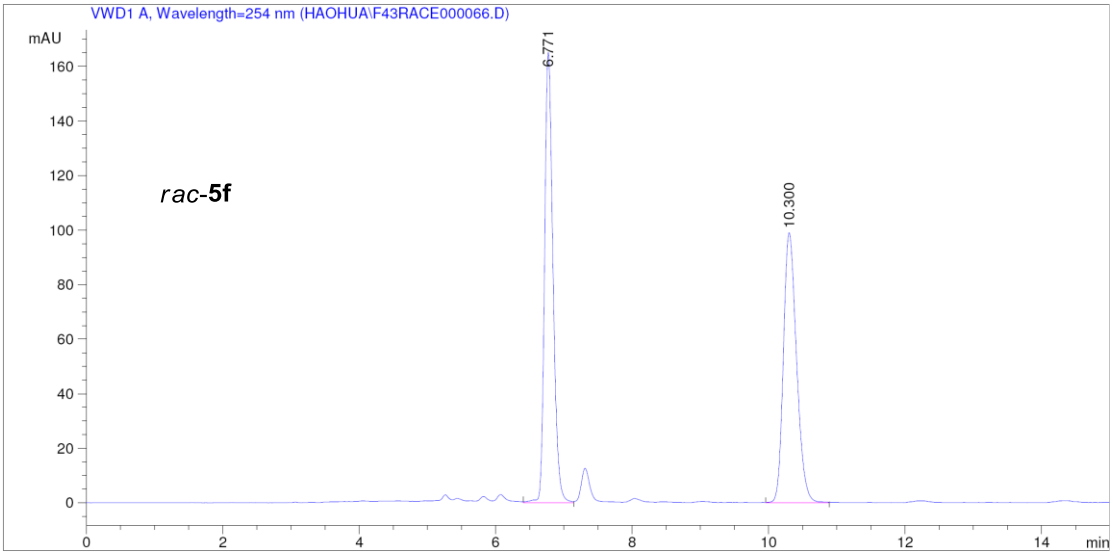
Figure S16. HPLC traces of *rac*-**5d** (reference) and (*R*)-**5d**.

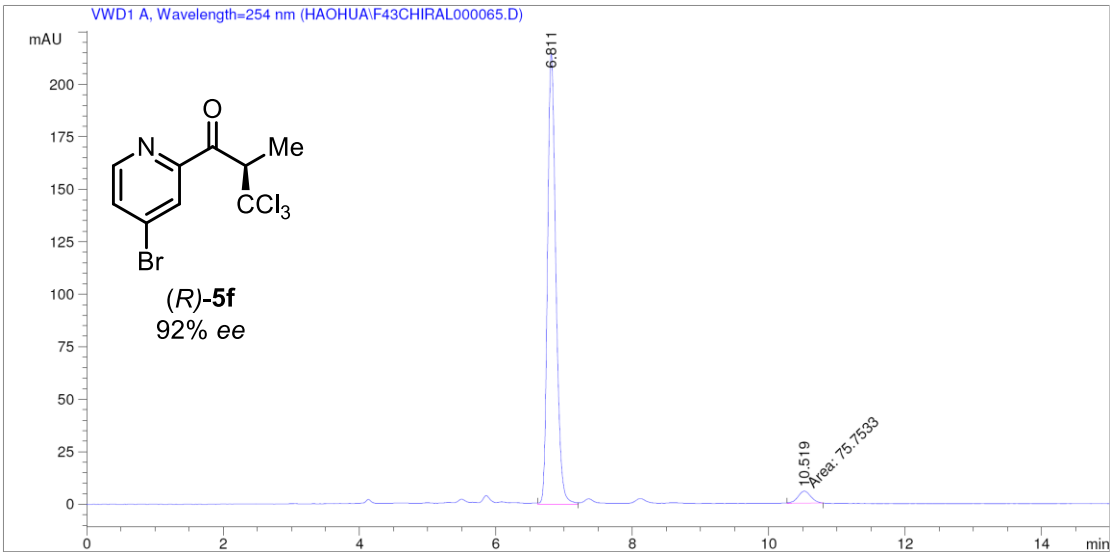




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.673	VB	0.1258	1334.12207	163.49278	97.4156
2	9.959	MM	0.1914	35.39411	3.08165	2.5844

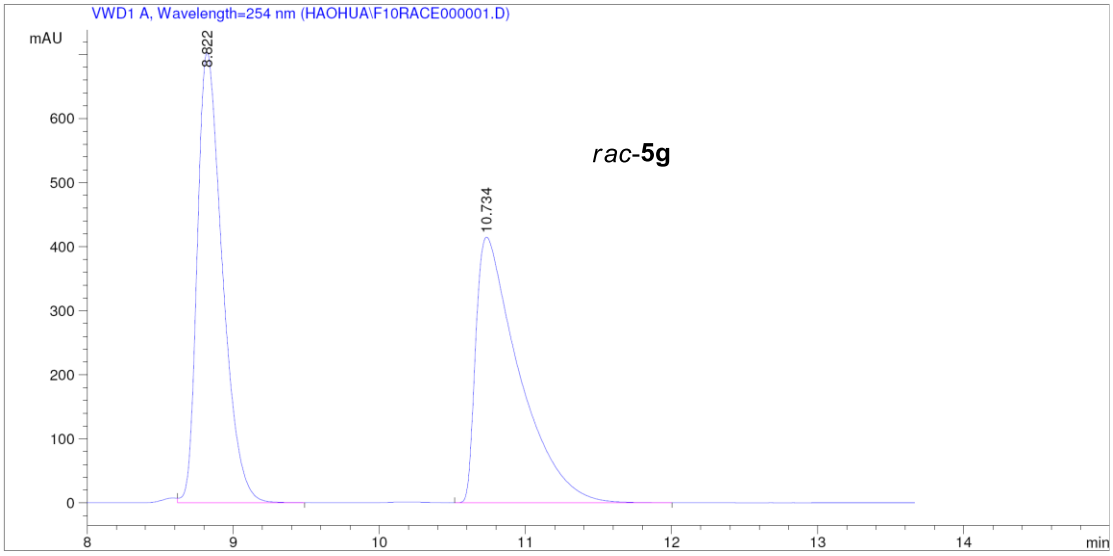
Figure S17. HPLC traces of *rac*-**5e** (reference) and (*R*)-**5e**.

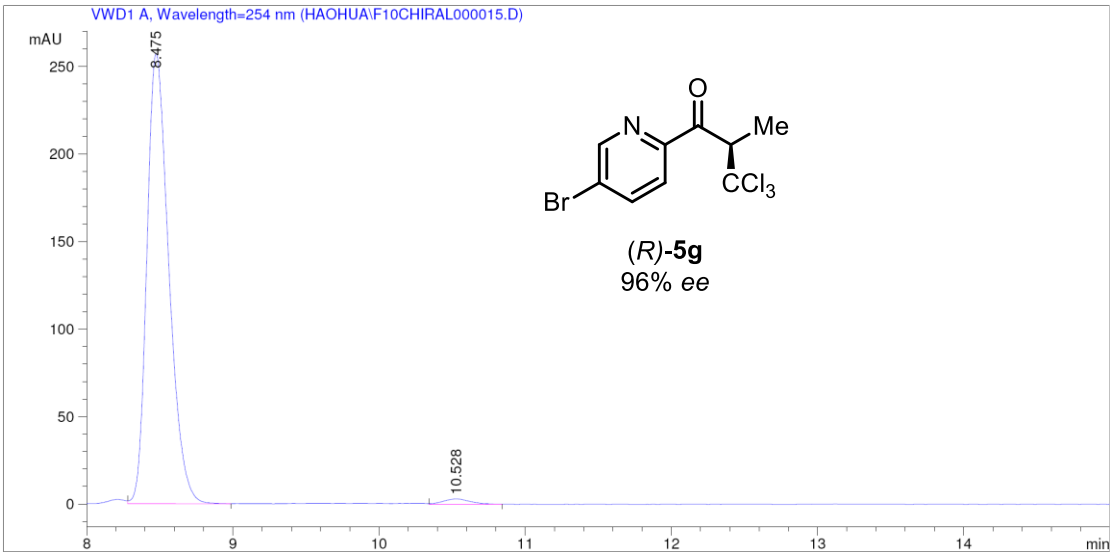




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.811	VV	0.1311	1825.24316	214.89055	96.0151
2	10.519	MM	0.2199	75.75334	5.74265	3.9849

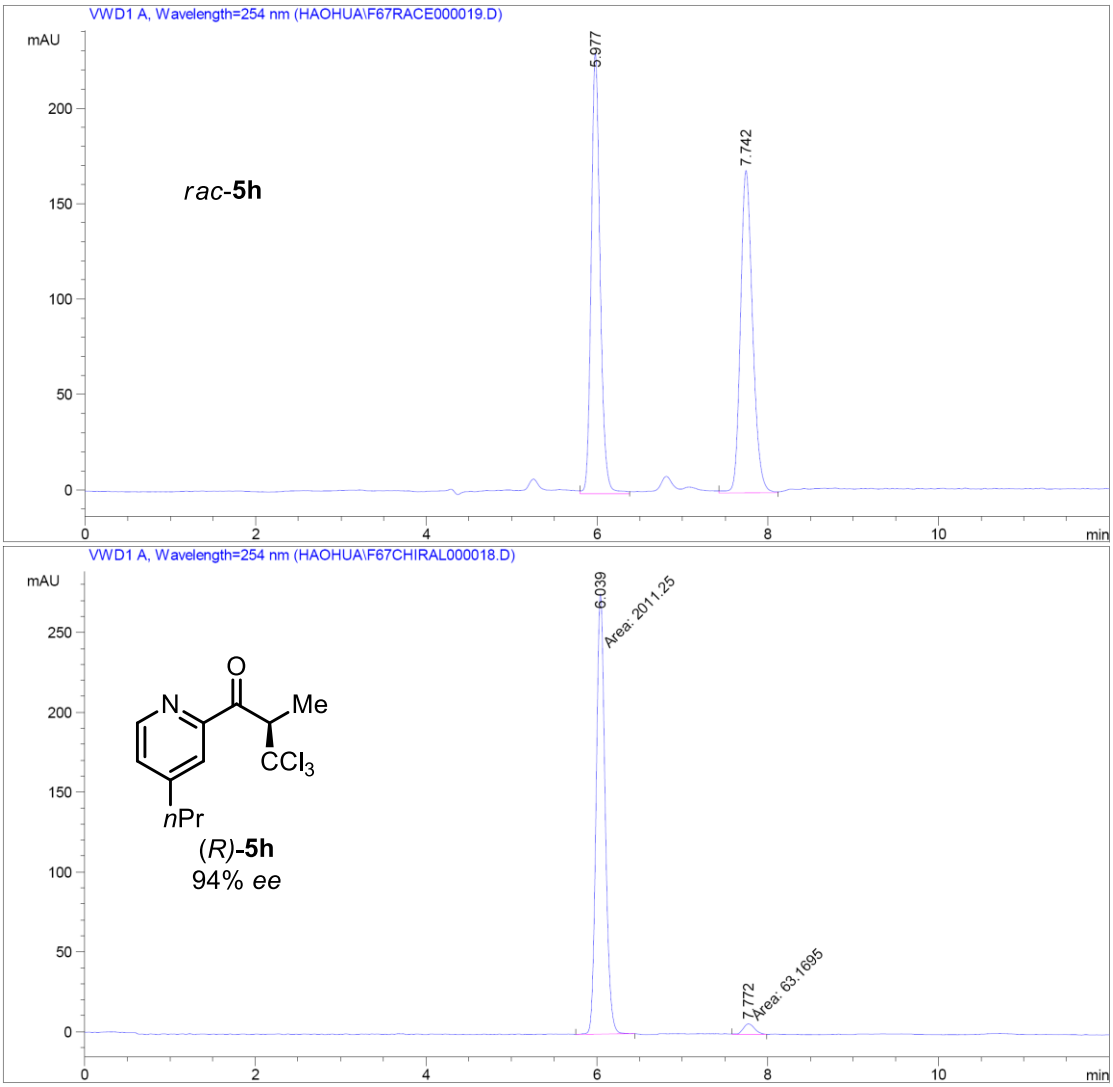
Figure S18. HPLC traces of *rac*-**5f** (reference) and (*R*)-**5f**.





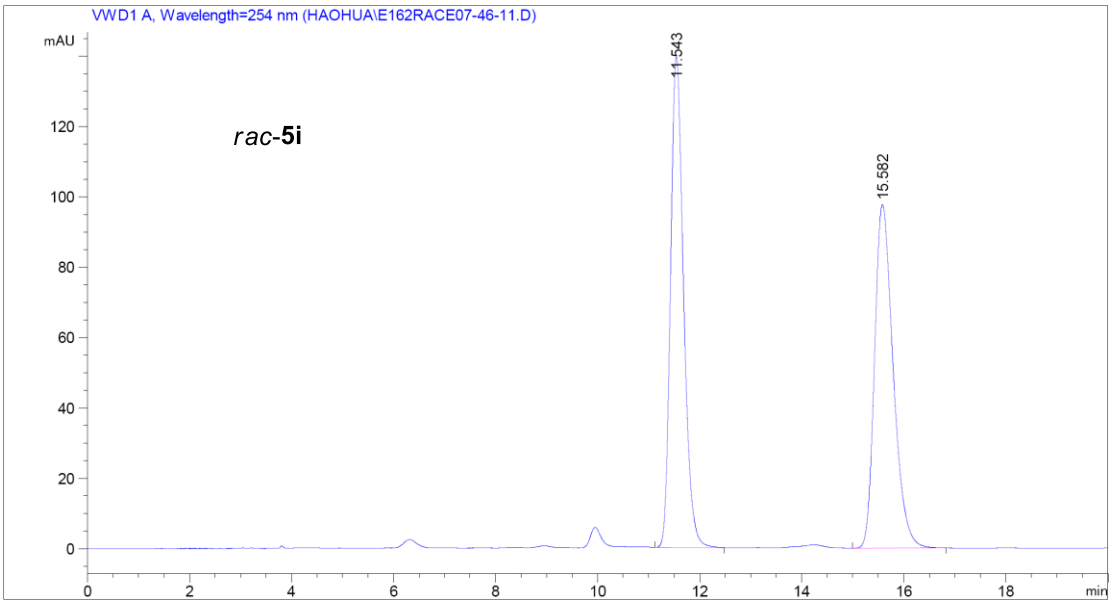
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.475	VB	0.1595	2682.81641	257.37753	98.5830
2	10.528	VV	0.1949	38.56234	3.00438	1.4170

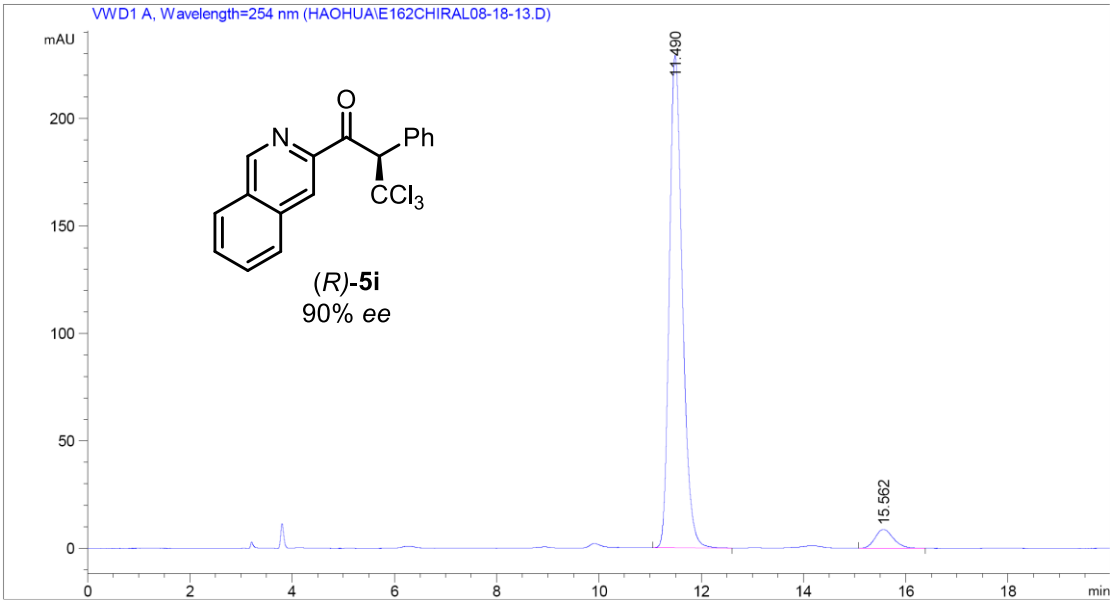
Figure S19. HPLC traces of *rac*-**5g** (reference) and (*R*)-**5g**.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.039	MM	0.1213	2011.25476	276.23572	96.9548
2	7.772	MM	0.1592	63.16945	6.61336	3.0452

Figure S20. HPLC traces of *rac*-**5h** (reference) and (*R*)-**5h**.





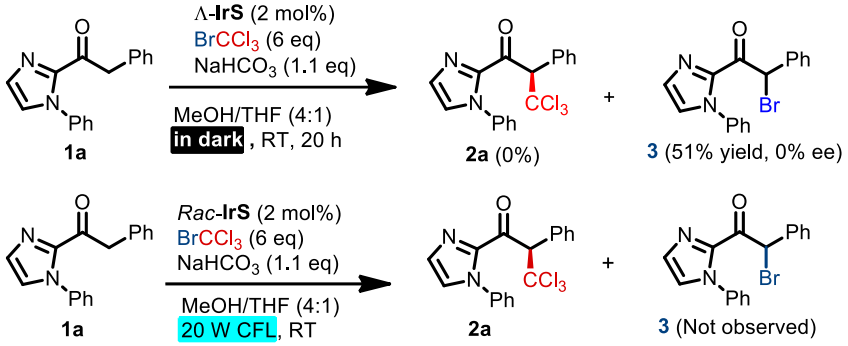
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.490	BB	0.2691	4045.28320	228.98859	94.8699
2	15.562	BB	0.2932	218.74881	8.80795	5.1301

Figure S21. HPLC traces of *rac*-**5i** (reference) and (*R*)-**5i**.

5. Mechanistic Experiments

5.1 Control Experiments for Table 1

a) Formation of the brominated product:



The control experiments were performed according the general catalysis procedure with 0.2 mmol 2-acylimidazole **1a**. No trichloromethylated product **2a** was observed in the dark. The conversion of the photochemical process was determined by ^{1}H-NMR analysis of aliquots from the reaction mixture taken out of the reaction system via syringe at different times. The NMR spectra shown below demonstrate that no detectable brominated product **3** was formed in this photoredox reaction.

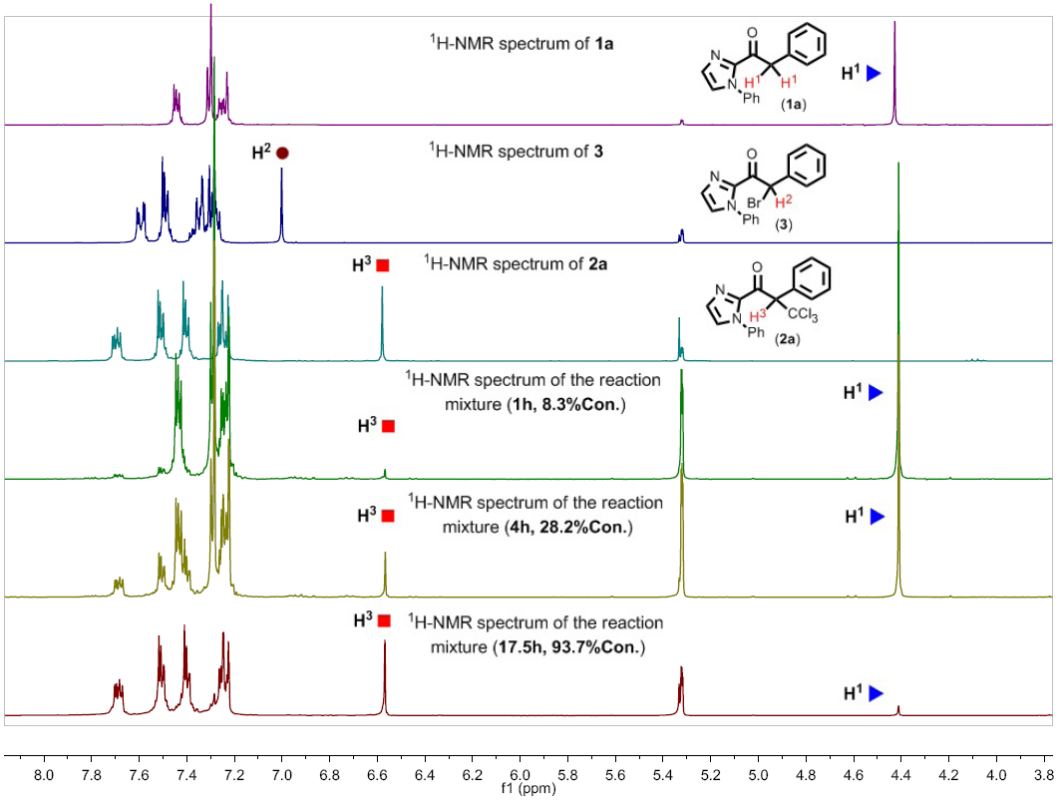
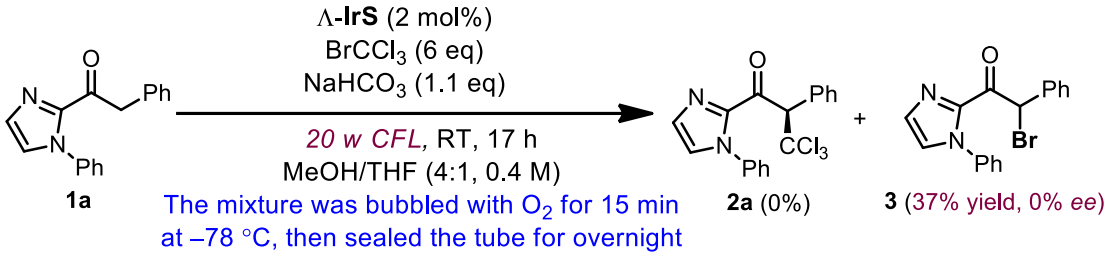
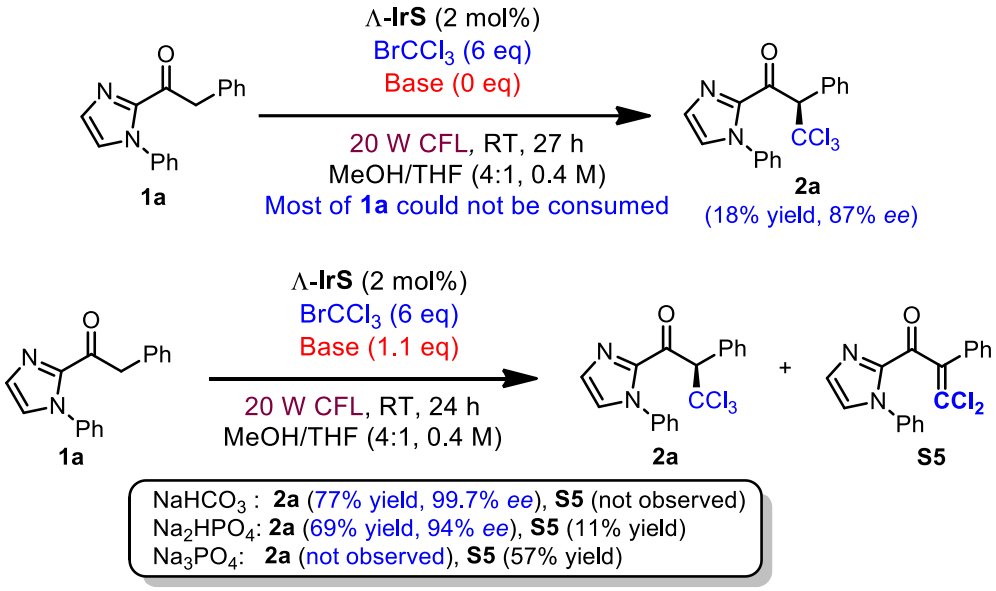


Figure S22. ^{1}H NMR (300 MHz, in CD_2Cl_2) spectra of **1a**, **2a**, **3** (as references) and the crude product from the photolysis. Conversion was inferred by integration ratio (signals H^1 and H^3).

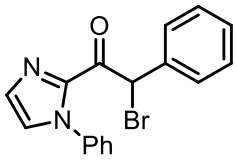
b) Effect of aerobic conditions:



c) Effect of different Brønsted bases:



2-Bromo-2-phenyl-1-(1-phenyl-*1H*-imidazol-2-yl)ethanone (3)



White solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.55-7.45 (m, 2H), 7.44-7.34 (m, 3H), 7.31-7.13 (m, 7H), 6.90 (s, 1H).

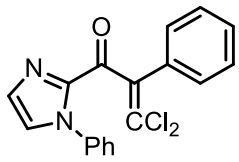
^{13}C NMR (75 MHz, CD_2Cl_2) δ 182.3, 141.1, 138.4, 136.3, 130.6, 130.0, 129.5, 129.4, 129.1, 129.0, 126.2, 50.2.

IR (film): ν (cm^{-1}) 1686, 1591, 1492, 1446, 1394, 1304, 1148, 1064, 1028, 955, 914, 867, 741, 690, 633, 547.

HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{14}BrN_2O$ $[M+H]^+$: 341.0284 and 343.0265, found: 341.0297 and

343.0277.

3,3-Dichloro-2-phenyl-1-(1-phenyl-*1H*-imidazol-2-yl)prop-2-en-1-one (S5)



White solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.47-7.36 (m, 5H), 7.34-7.24 (m, 4H), 7.24-7.15 (m, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 181.6, 142.1, 140.5, 138.2, 134.4, 131.6, 130.0, 129.6, 129.4, 129.3, 129.2, 129.0, 128.4, 126.1, 122.7.

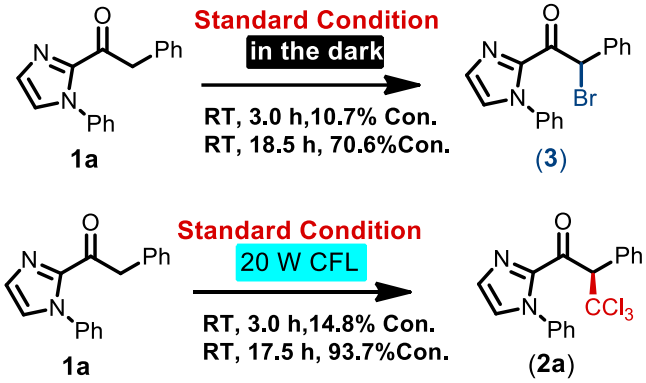
IR (film): ν (cm^{-1}) 1669, 1597, 1494, 1446, 1389, 1301, 1252, 1203, 1150, 1073, 1029, 996, 937, 913, 839, 802, 756, 692, 643, 576, 536.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{13}Cl_2N_2O$ $[M+H]^+$: 343.0399 and 345.0373, found: 343.0414 and 345.0388.

5.2 Discussion of Competition between Bromination and Trichloromethylation

As shown in Table 1, the bromination product is the only observed product in the dark, whereas upon photolysis with visible light only the trichlormethylation product is observed. The following control experiments were performed to gain insight into the reason for not observing any brominated product in the presence of light.

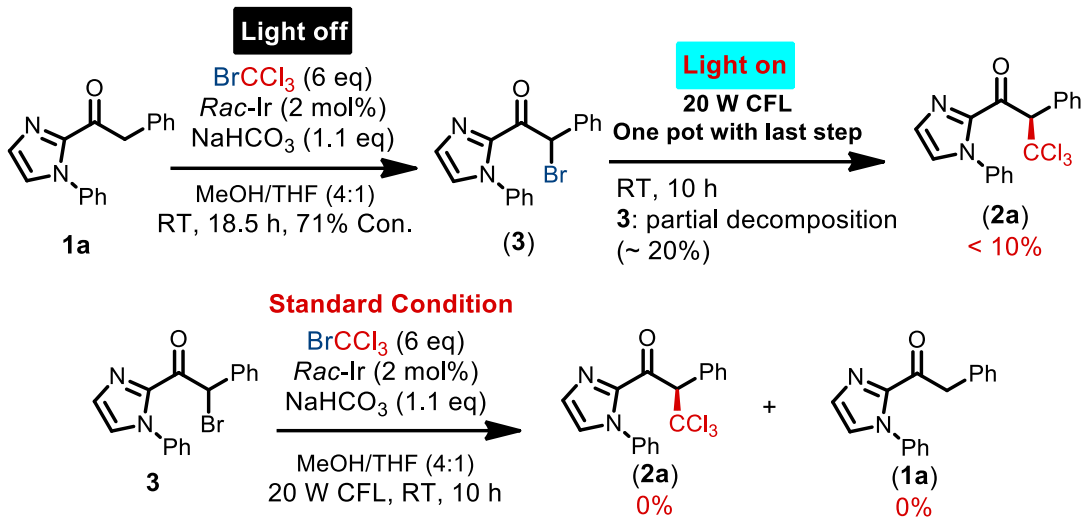
Comparison of initial rates for the dark reaction and photoreaction:



The comparision experiments were performed according the general catalysis procedure with 0.2 mmol 2-acylimidazole **1a**. The conversion was determined by ^{1}H-NMR analysis of aliquots from the reaction mixture. Outcome: The overall rate of the photoreaction is slightly faster compared to

the bromination reaction in the dark.

Considering a possible transformation of the bromination product:



The reactions were performed with 0.2 mmol 2-acylimidazole **1a**. In a first experiment, the reaction mixture was run in the dark until the brominated product **3** was formed with 71% conversion as monitored by ^{1}H NMR. Then, the reaction was run for a further 10 hours under 20 W CFL. As a result, the trichloromethylation was not observed in significant amounts by ^{1}H-NMR (<10%) and product **3** was partially decomposed under irradiation. In a second experiment, the isolated bromination compound **3** was photolyzed under the standard reaction conditions. As a result, no trichloromethylation product or starting compound could be detected.

Proposed mechanism for the competition between bromination and trichloromethylation:

Based on the above control experiments, the following plausible mechanism is proposed which can explain why the bromination reaction is not able to compete with the trichloromethylation in the presence of light. Accordingly, both catalytic cycles run through the intermediate iridium enolate complex **II**. The bromination product is formed through the reaction of **II** with the electrophile $BrCCl_3$, whereas the CCl_3-product is formed through the reaction of **II** with a reductively formed trichloromethyl radical. Since the radical addition must be a very fast process that is almost diffusion controlled, the bromination reaction with the weak electrophile $BrCCl_3$ will not be able to compete so that all enolate intermediate **II** only reacts with the trichloromethyl radical. Note that although the enolate reaction steps of the two catalytic cycles differ strongly, this is not the case for the overall reaction cycle which is in large parts dominated by slow ligand exchange processes.

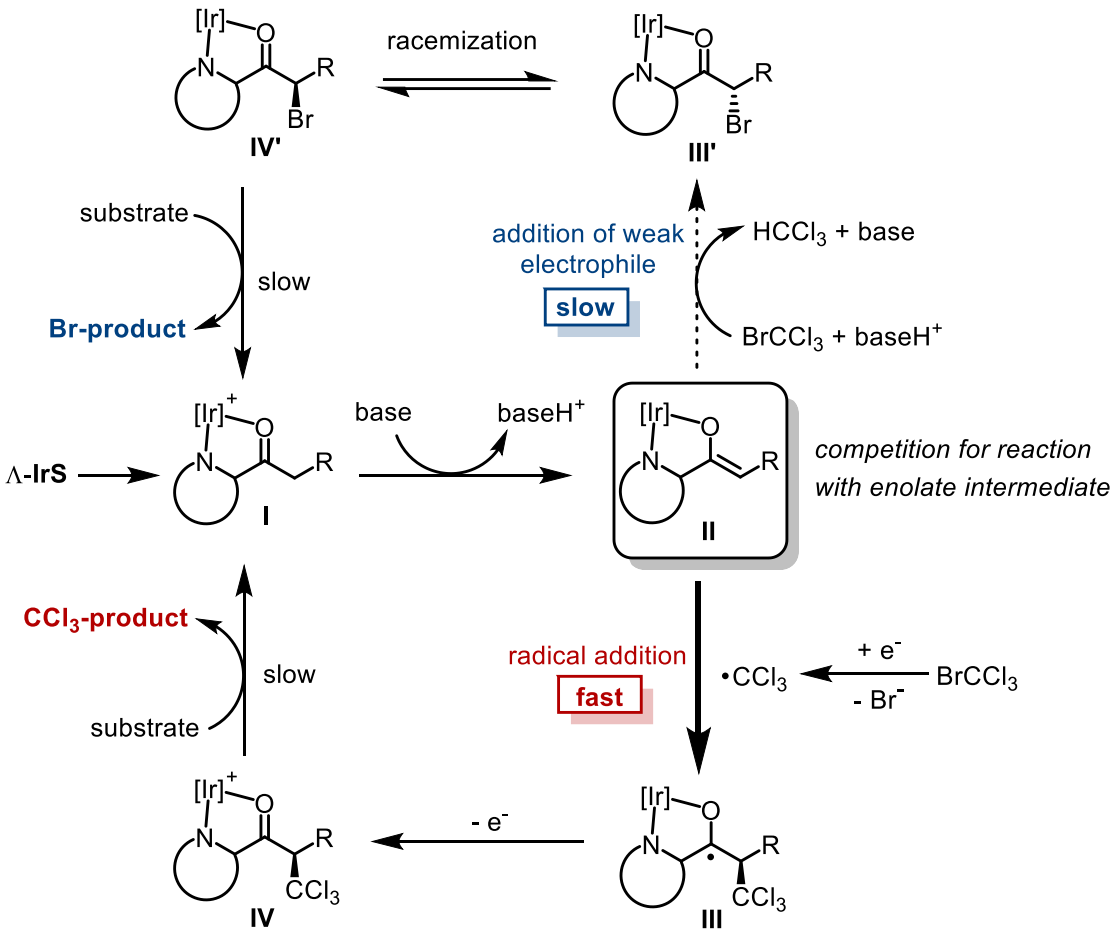
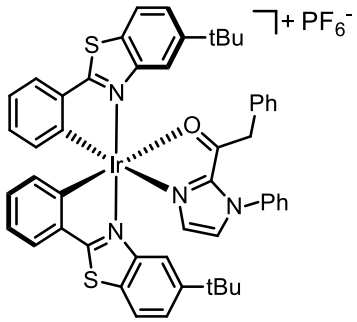


Figure S23. Plausible mechanism for explaining the suppressed bromination and exclusive formation of the trichloromethylated product in the presence of visible light.

5.3 Synthesis of the Proposed Intermediate Complexes I and II

Intermediate **I**



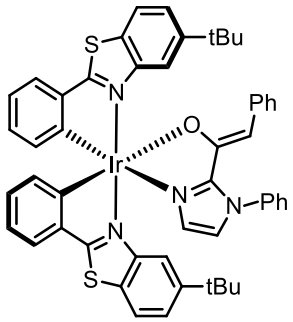
The racemic complex **I** was obtained by reacting substrate **1a** (31.4 mg, 0.12 mmol) with racemic Δ/Λ-**IrS** (95.2 mg, 0.10 mmol) at room temperature overnight in CH_2Cl_2 (2.0 mL). Afterwards, the mixture was concentrated under vacuum. The residue black solid was washed by Et_2O (4 × 1 mL), the yellow solid was obtained (110.0 mg, yield: 97%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.98 (dd, J = 8.6, 1.4 Hz, 2H), 7.83 (ddd, J = 11.8, 7.7, 1.0 Hz, 2H), 7.75 (tt, J = 7.5, 1.1 Hz, 1H), 7.70-7.58 (m, 4H), 7.54 (dd, J = 8.6, 1.8 Hz, 1H), 7.50 (d, J = 1.5 Hz, 1H), 7.16 (d, J = 1.2 Hz, 1H), 7.08 (dddd, J = 9.3, 8.2, 4.7, 3.6 Hz, 4H), 6.94 (t, J = 7.4 Hz, 1H), 6.84 (dtd, J = 8.8, 7.5, 1.4 Hz, 2H), 6.72-6.56 (m, 3H), 6.50 (d, J = 7.4 Hz, 1H), 6.41 (d, J = 7.3 Hz, 1H), 5.92 (d, J = 7.5 Hz, 2H), 4.02 (d, J = 14.0 Hz, 1H), 3.76 (d, J = 14.0 Hz, 1H), 1.38 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 196.4, 183.2, 179.9, 152.9, 152.6, 149.8, 149.1, 147.3, 146.8, 141.9, 140.0, 137.4, 134.8, 134.1, 133.2, 132.7, 131.93, 131.88, 131.86, 129.9, 129.22, 129.18, 128.9, 128.5, 128.4, 126.9, 126.6, 125.2, 124.8, 124.1, 123.8, 123.6, 123.5, 115.4, 114.9, 45.8, 35.5, 35.2, 31.8, 31.5.

IR (film): ν (cm^{-1}) 3214, 3060, 2962, 2868, 1578, 1503, 1444, 1404, 1360, 1289, 1245, 1161, 1113, 1025, 994, 838, 760, 731, 694, 554, 455.

Intermediate **II**



To a mixture of catalyst Δ/Λ-**IrS** (95.2 mg, 0.10 mmol) and $NaHCO_3$ (16.8 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) was added substrate **1a** (52.4 mg, 0.20 mmol). The reaction mixture was concentrated after around 12 hours. The residue was purified by flash chromatography on activated basic aluminum oxide (EtOAc / hexane= 1:10) to afford the enolate complex **II** as a red solid (89.8 mg, 0.091 mmol, yield: 91%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.84 (d, J = 1.7 Hz, 1H), 7.86-7.68 (m, 4H), 7.59-7.38 (m, 6H), 7.29 (d, J = 7.3 Hz, 2H), 7.16 (d, J = 6.9 Hz, 2H), 7.05-6.88 (m, 4H), 6.86 (d, J = 1.4 Hz, 1H), 6.71 (td, J = 8.5, 1.2 Hz, 3H), 6.64-6.53 (m, 2H), 6.45 (d, J = 7.5 Hz, 1H), 4.59 (s, 1H), 1.21 (s, 9H), 1.07 (s, 9H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 181.4, 179.8, 155.8, 154.6, 154.3, 152.4, 151.4, 151.3, 149.6, 142.4, 142.1, 139.9, 138.3, 135.2, 134.5, 130.6, 130.4, 129.7, 129.1, 128.9, 127.5, 127.4, 127.3, 126.1,

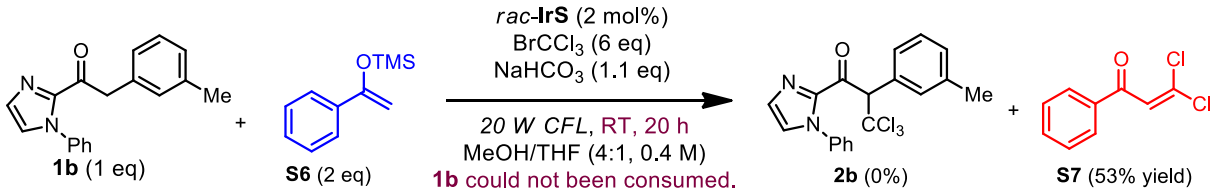
126.0, 125.3, 124.8, 123.7, 123.3, 123.1, 122.4, 121.7, 121.4, 120.9, 119.0, 117.1, 104.6, 35.3, 35.2, 31.8, 31.4.

IR (film): ν (cm^{-1}) 3112, 3049, 2956, 2903, 2864, 1584, 1492, 1462, 1421, 1378, 1285, 1243, 1196, 1156, 1096, 1018, 991, 926, 909, 868, 810, 781, 760, 733, 692, 666, 502, 466.

5.4 Luminescence Quenching Experiments (Figure 5)

Emission intensities were recorded on a Spectra Max M5 microplate reader in a 10.0 mm quartz cuvette. The methyl imidazole derivatives were used due to higher stability of the enolate complex.[2a] Catalyst Δ/Λ-**IrS** solutions were excited at λ_{max} = 420 nm and the emission was measured at 550 nm (emission maximum). The complex **I** (*N* = Me) solutions were excited at λ_{max} = 420 nm and the emission measured at 550 nm (emission maximum). The enolate complex **II** (*N* = Me) solutions were excited at λ_{max} = 440 nm and the emission measured at 550 nm (emission maximum). The concentration of iridium complex (**IrS** and intermediate complex **I** and **II**) was 0.2 mM in MeOH/THF (4:1). The concentration of the quencher ($BrCCl_3$) stock solution was 200 mM in MeOH/THF (4:1). For each quenching experiment, 5 µL of this stock solution were titrated to a solution (1 mL) of iridium complex in a screw-top 10.0 mm quartz cuvette. The addition of 5 µL stock solution refers to an increase of the quencher concentration of 1 mM. After degassing with an argon stream for 5 minutes, the emission intensity was collected. See Figure 5 for the obtained Stern-Volmer plots.

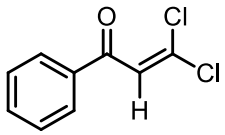
5.5 Trapping Experiments with Electron Rich Alkenes



Adding two equivalents of the 1-phenyl-1-(trimethylsilyloxy)ethene (**S6**) into the reaction mixture caused a complete inhibition of the formation of **2b**. Instead, the compound **S7** was isolated in a yield of 53%. Apparently, reductively generated trichloromethyl radicals are trapped effectively by the enolether **S6**, which seems reasonable considering that the steady-state concentration of the enolate intermediate complex **II** cannot exceed the amount of added iridium catalyst (2 mol%

catalyst loading) and is therefore much lower compared to **S6**. The product **S7** can be rationalized as being the HCl elimination product of the initial CCl_3 product which is not stable under the basic conditions.

3,3-Dichloro-1-phenylprop-2-en-1-one (S7)



Colorless oil.

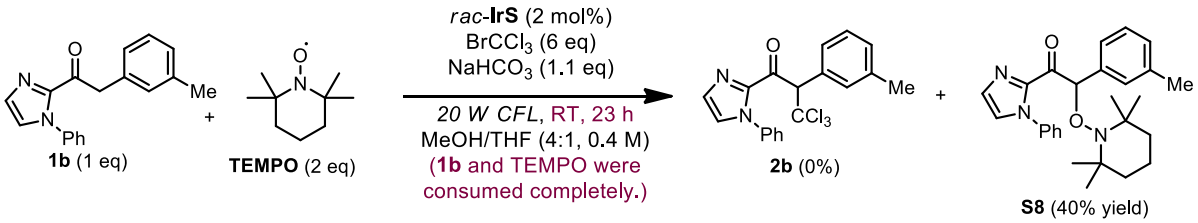
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.78 (m, 2H), 7.58-7.49 (m, 1H), 7.48-7.35 (m, 2H), 7.19 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 186.6, 137.0, 135.4, 133.7, 128.8, 128.5, 124.1.

IR (film): ν (cm^{-1}) 1668, 1595, 1563, 1447, 1318, 1293, 1265, 1216, 1181, 1011, 935, 843, 794, 769, 690, 624, 491.

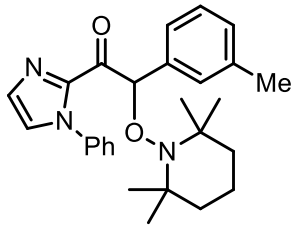
HRMS (ESI, *m*/*z*) calcd for $C_9H_6Cl_2ONa$ $[M+Na]^+$: 222.9688 and 224.9659, found: 222.9688 and 224.9659.

5.6 Trapping Experiment with TEMPO



When two equivalents of TEMPO was added to the reaction after irradiation for 23 h, the trichloromethylation product **2b** could not be detected. The corresponding alkoxyamine adduct of the 2-acyl imidazole **1b** was formed in 40% yield. It was confirmed that the generation of the oxyaminated product did not occur under dark conditions.

1-(1-Phenyl-*1H*-imidazol-2-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(*m*-tolyl)ethanone (S8)



^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.47-7.35 (m, 3H), 7.34-7.24 (m, 3H), 7.23-7.13 (m, 2H), 7.11-6.97 (m, 3H), 6.58 (s, 1H), 2.32 (s, 3H), 1.45 (s, 6H), 1.17 (s, 3H), 1.05 (s, 6H), 0.78 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 189.3, 142.9, 138.6, 138.37, 138.35, 130.2, 129.3, 129.0, 128.9, 128.7, 128.4, 127.6, 125.9, 125.8, 90.0, 60.2, 60.0, 40.6, 34.1, 33.6, 21.6, 20.3, 17.6.

IR (film): ν (cm^{-1}) 3139, 2969, 2926, 1688, 1496, 1493, 1448, 1398, 1303, 1252, 1140, 1062, 1012, 959, 916, 862, 762, 693, 632, 546, 442.

HRMS (APCI, *m*/*z*) calcd for $C_{27}H_{33}N_3O_2Na$ $[M+Na]^+$: 454.2465, found:454.2468.

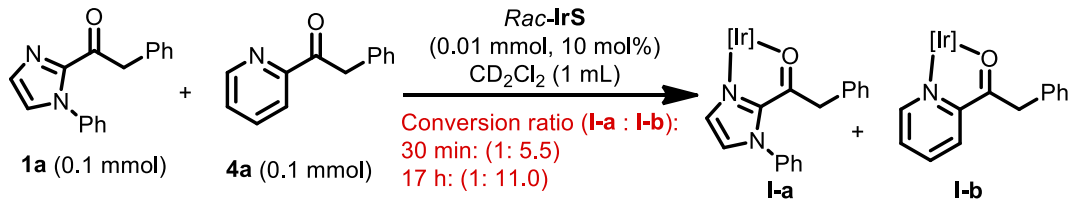
5.7 Coordination Strength Comparison of 2-Acylimidazoles and 2-Acylpyridines

In order to evaluate the differences in coordinative strength between 2-acylimidazole **1a** and the 2-acylpyridine **4a**, a competition experiment was deviced and analyzed by ^{1}H-NMR. The result demonstrates that the binding constant of the pyridine substrate exceeds the binding constant of the imidazole substrate by around one order of magnitude.

Reaction 1 (serves as a reference): **1a** (0.2 mmol) plus *Rac*-**IrS** (0.01 mmol, 5 mol%)

Reaction 2 (serves as a reference): **4a** (0.2 mmol) plus *Rac*-**IrS** (0.01 mmol, 5 mol%)

Reaction 3 (competition reaction): **1a** (0.1 mmol), **4a** (0.1 mmol) plus *Rac*-**IrS** (0.01 mmol, 10 mol%)



● Signals of *t*Bu in complex **I-a**.
■ Signals of *t*Bu in complex **I-b**.
♥ Signals of released CH_3CN.

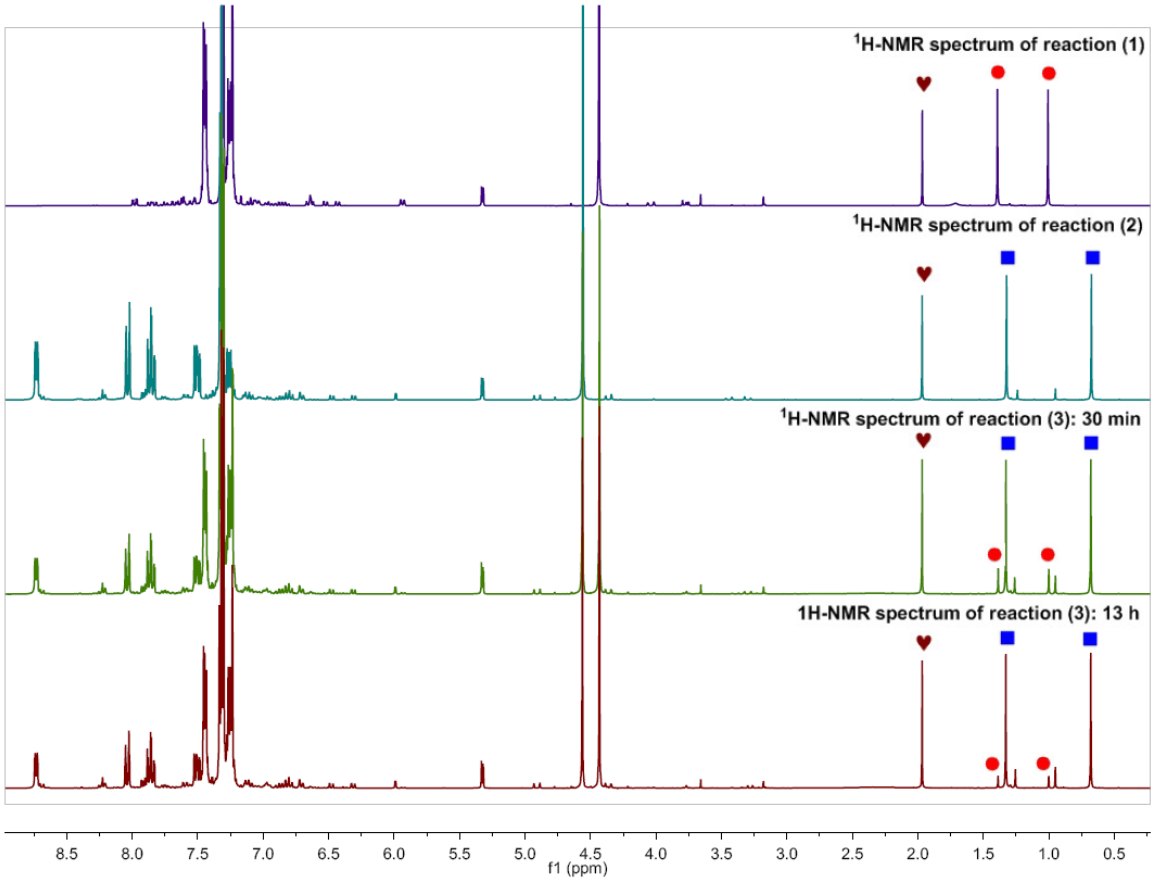


Figure S24. ^{1}H NMR (300 MHz, in CD_2Cl_2) spectra of reactions 1-3. Conversion was inferred by area integration ratio (signals '●' and '■').

5.8 Quantum Yield Measurement

The quantum yield was measured by standard ferrioxalate actinometry. A 6 W blue LED lamp (420 nm) was used as the light source. The measured method was designed according to a published procedures with slight modifications.[6]

The solutions were prepared and stored in the dark:

Potassium ferrioxalate solution (0.15 M): 736.9 mg of potassium ferrioxalate hydrate was dissolved in 10 mL of 0.05 M H_2SO_4.

Buffered solution of phenanthroline: 50 mg of 1,10-phenanthroline and 11.25 g of sodium acetate were dissolved in 50 mL of 0.5 M H_2SO_4.

a) Measurement of light intensity at 420 nm

1 mL of the ferrioxalate solution was added to a quartz cuvette (l = 10 mm). The actinometry

solution was irradiated with 6 W blue LED lamp (420 nm ± 10 nm) for 90.0 seconds. After irradiation, 175 μL of the phenanthroline solution was added to the cuvette. The solution was kept in dark for 30 min to make sure the complete coordination. The absorbance of the actinometry solution was monitored at 510 nm. The absorbance of a non-irradiated (in dark) sample was also measured at 510 nm.

The moles of Fe^{2+} formed was determined using Beer's Law:

$$\text{moles } Fe^{2+} = \frac{V_1 \times V_3 \times \Delta A(510nm)}{10^3 \times V_2 \times l \times \varepsilon(510nm)}$$

Where V_1 (1 mL) is the irradiated volume, V_2 (1 mL) is the aliquot of the irradiated solution taken for the determination of the ferrous ions. V_3 (1.175 mL) is the final volume after complexation with phenanthroline (all in mL), l is the path length (1 cm), and ΔA(510nm) is the optical difference in absorbance between the irradiated and non-irradiated solutions, ε(510 nm) is the molar absorptivity of $Fe(phen)_3^{2+}$ (11100 L mol^{-1} cm^{-1}).

The photon flux can be calculated as:

$$\text{photon flux (einstein } s^{-1}) = \frac{moles\ Fe^{2+}}{\Phi \cdot t \cdot f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.05 for a 0.15 solution at 412 nm; 1.04 for a 0.15 solution at 422 nm; 1.03 for a 0.15 solution at 433 nm),[7] t is the irradiated time (90.0 s), and f is the fraction of light absorbed at λ = 420 nm ($f = 1–10^{-A}$, A is the absorbance of above ferrioxalate solution at 420 nm is > 3, indicating f is > 0.999).

The calculations were done as follows:

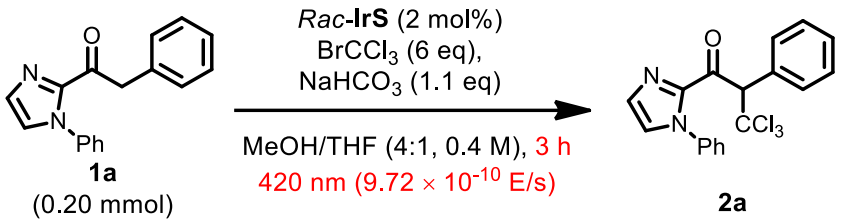
ΔA(510nm) was calculated (average of three cycles) to be 0.860.

$$\text{moles } Fe^{2+} = \frac{1mL \times 1.175mL \times 0.860}{10^3 \times 1mL \times 1cm \times 11100\,L \cdot mol^{-1} \cdot cm^{-1}} = 9.103 \times 10^{-8} \text{ mol}$$

$$\text{photon flux} = \frac{9.103 \times 10^{-8}\,mol}{1.04 \times 90s \times 1.0} = 9.72 \times 10^{-10} \text{ einstein/s}$$

b) Measurement of quantum yield:

Model reaction:



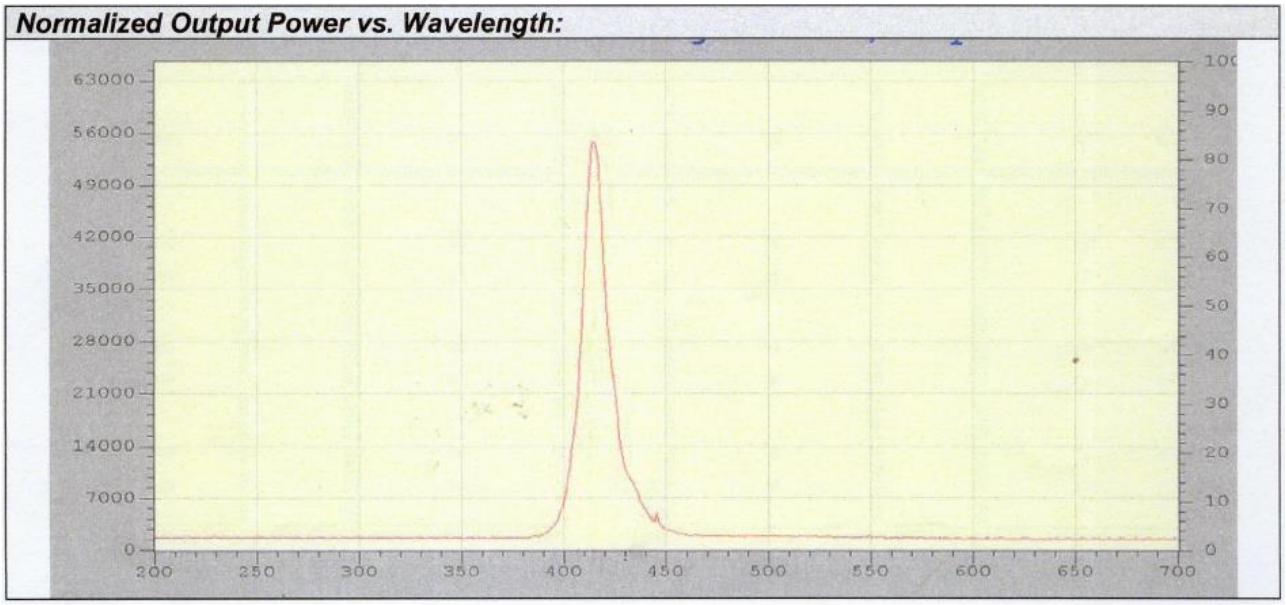
A screw-top cuvette (10.0 mm) was charged with the catalyst *rac*-**IrS** (2 mol%), 2-acyl imidazole **1a** (0.2 mmol, 1.0 eq), $NaHCO_3$ (0.22 mmol, 1.1 eq), 0.5 mL MeOH/THF (4:1, 0.4 M), bromotrichloromethane (1.2 mmol, 6.0 eq) and a small magnetic stir bar. The cuvette was degassed with an argon stream for 10 min. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 8 cm from a 6 W blue lamp. The reaction mixture was stirred and irradiated for 10800 s (3 h). After irradiation, the reaction mixture was passed through a short silica gel column. The yield of product formed was measured by ^{1}H-NMR with trimethyl(phenyl)silane as internal standard.

Experiment 1: *Rac*-**IrS** (3.8 mg, 0.004 mmol), 2-acyl imidazole **1a** (52.4 mg, 0.2 mmol), $NaHCO_3$ (18.5 mg, 0.22 mmol), MeOH/THF (4:1, 0.4 M, 0.5 mL), bromotrichloromethane (118.0 μL, 1.2 mmol). After irradiation for 10800 s, the product **2a** was formed in 26.8% yield. The quantum yield calculation as following:

$$\Phi = \frac{moles\ of\ product\ formed}{einsteinsof\ light\ absorbed} = \frac{0.2\times10^{-3}\times0.268\,mol}{9.72\times10^{-10}einstein\cdot s^{-1}\times10800\,s} = 5.1$$

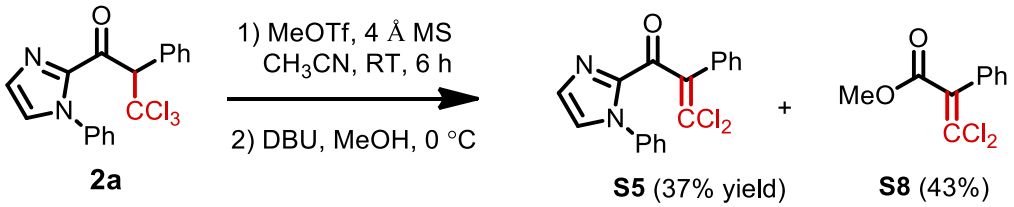
Experiment 2: *Rac*-**IrS** (3.8 mg, 0.004 mmol), 2-acyl imidazole **1a** (52.5 mg, 0.2 mmol), $NaHCO_3$ (18.4 mg, 0.22 mmol), MeOH/THF (4:1, 0.4 M, 0.5 mL), bromotrichloromethane (118.0 μL, 1.2 mmol). After irradiation for 10800 s, the product **2a** was formed in 28.5% yield. The quantum yield calculation as following:

$$\Phi = \frac{moles\ of\ product\ formed}{einsteinsof\ light\ absorbed} = \frac{0.2\times10^{-3}\times0.285\,mol}{9.72\times10^{-10}einstein\cdot s^{-1}\times10800\,s} = 5.4$$



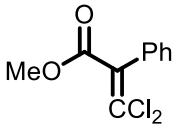
The output wavelength of the used 6 w blue LED (420 nm ± 10 nm).

6. Attempted Transformation of 2-Acyl Imidazole Products



To a solution of *rac*-**2a** (151.2 mg, 0.4 mmol) in CH_3CN (2.0 mL) was added 4 Å MS (200 mg, 50 mg/0.1 mmol of **2a**) under nitrogen atmosphere. The suspension was stirred vigorously under a positive pressure of nitrogen for 2 h at room temperature, then methyl trifluoromethansulfonate (88 μL, 0.8 mmol) was added at room temperature. After being stirred at room temperature for 6 h, MeOH (0.32 mL, 8.0 mmol) and DBU (90 μL, 0.6 mmol) were added to the reaction mixture at 0 °C. After being stirred at 0 °C for 60 min, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:50) to give **S5** (50.2 mg, 0.15 mmol, yield: 37%) as a white solid and **S8** (40.0 mg, 0.17 mmol, yield: 43%) as a colorlss oil.

Methyl 3,3-dichloro-2-phenylacrylate (S8)

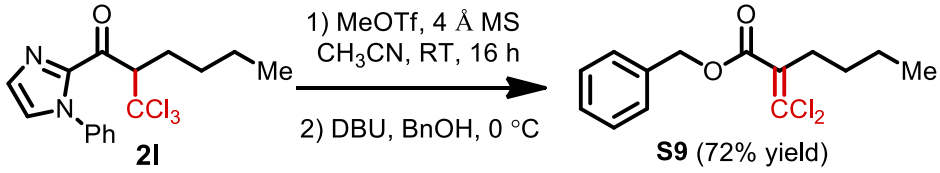


^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.57-7.23 (m, 5H), 3.79 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 165.8, 134.5, 134.3, 129.4, 129.0, 129.0, 127.5, 53.2.

IR (film): ν (cm^{-1}) 3059, 3027, 2952, 2844, 1729, 1599, 1490, 1435, 1272, 1211, 1073, 1034, 954, 881, 839, 706, 589.

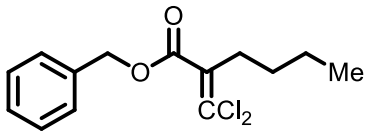
HRMS (ESI, *m*/*z*) calcd for $C_{10}H_8Cl_2O_2Na$ $[M+Na]^+$: 252.9794 and 254.9765, found: 252.9799 and 254.9766.



To a solution of *rac*-**2l** (107.0 mg, 0.3 mmol) in CH_3CN (1.5 mL) was added 4 Å MS (150 mg, 50 mg/0.1 mmol of **2l**) under nitrogen atmosphere. The suspension was stirred vigorously under a

positive pressure of nitrogen for 2 h at room temperature, then methyl trifluoromethansulfonate (98 μL, 0.9 mmol) was added at room temperature. After being stirred at room temperature for 16 h, BnOH (0.31 mL, 3.0 mmol) and DBU (90 μL, 0.6 mmol) were added to the reaction mixture at 0 °C. After being stirred at 0 °C for 60 min, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:50) to give **S9** (62.1 mg, 0.22 mmol, yield: 72%) as a colorlss oil.

Benzyl 2-(dichloromethylene)hexanoate (S9)



^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.52-7.20 (m, 5H), 5.24 (s, 2H), 2.66-2.35 (m, 2H), 1.51-1.20 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 165.9, 135.9, 134.3, 129.0, 128.9, 128.8, 128.6, 67.8, 32.8, 29.8, 22.6, 13.9.

IR (film): ν (cm^{-1}) 3066, 3033, 2958, 2929, 2866, 1725, 1588, 1496, 1455, 1374, 1267, 1203, 1135, 946, 907, 741, 695.

HRMS (ESI, m/z) calcd for $C_{14}H_{16}Cl_2O_2Na$ $[M+Na]^+$: 309.0420 and 311.0391, found: 309.0422 and 311.0395.

7. NMR Spectra

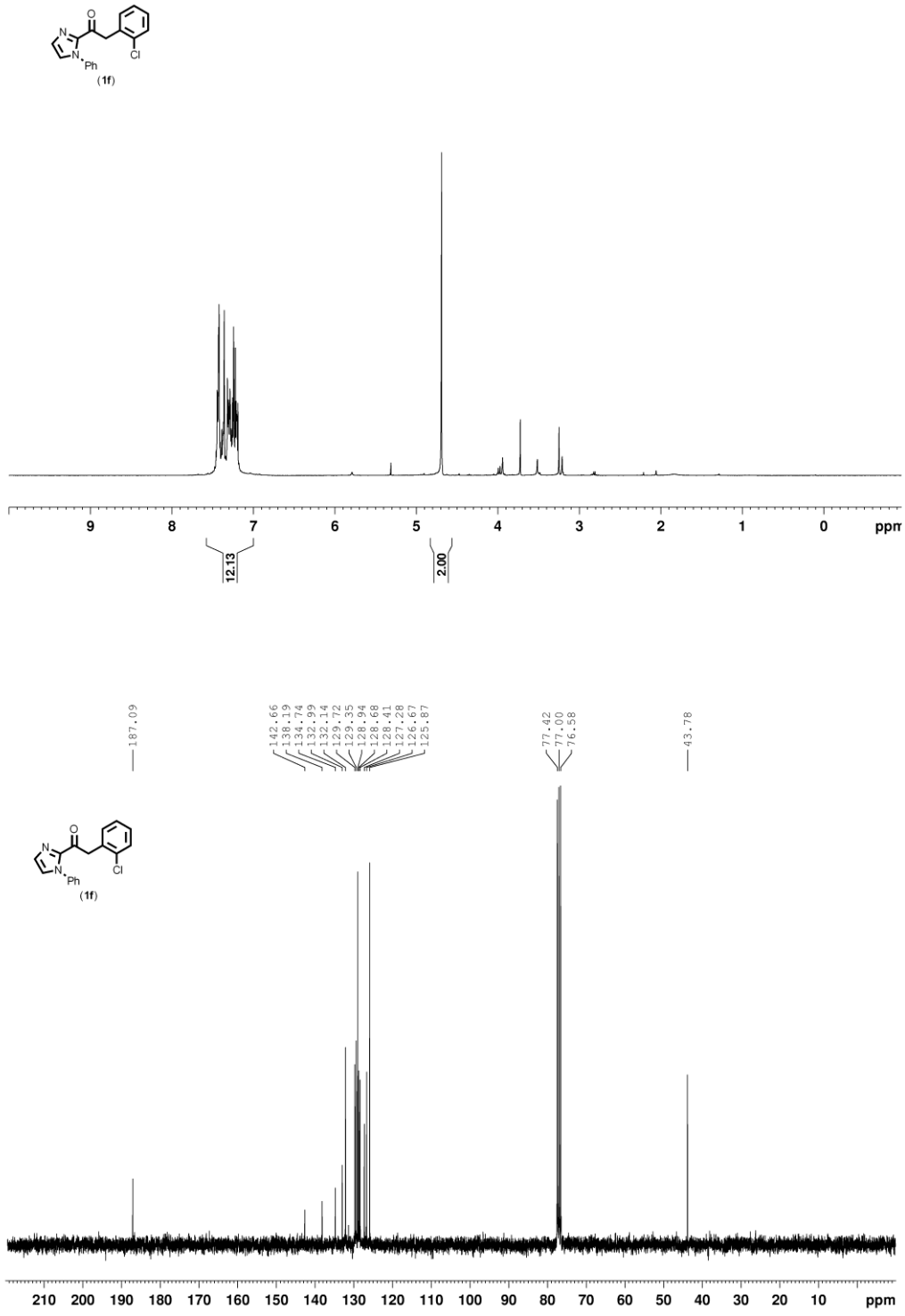


Figure S25. ^{1}H-NMR and ^{13}C-NMR spectrum of **1f**.

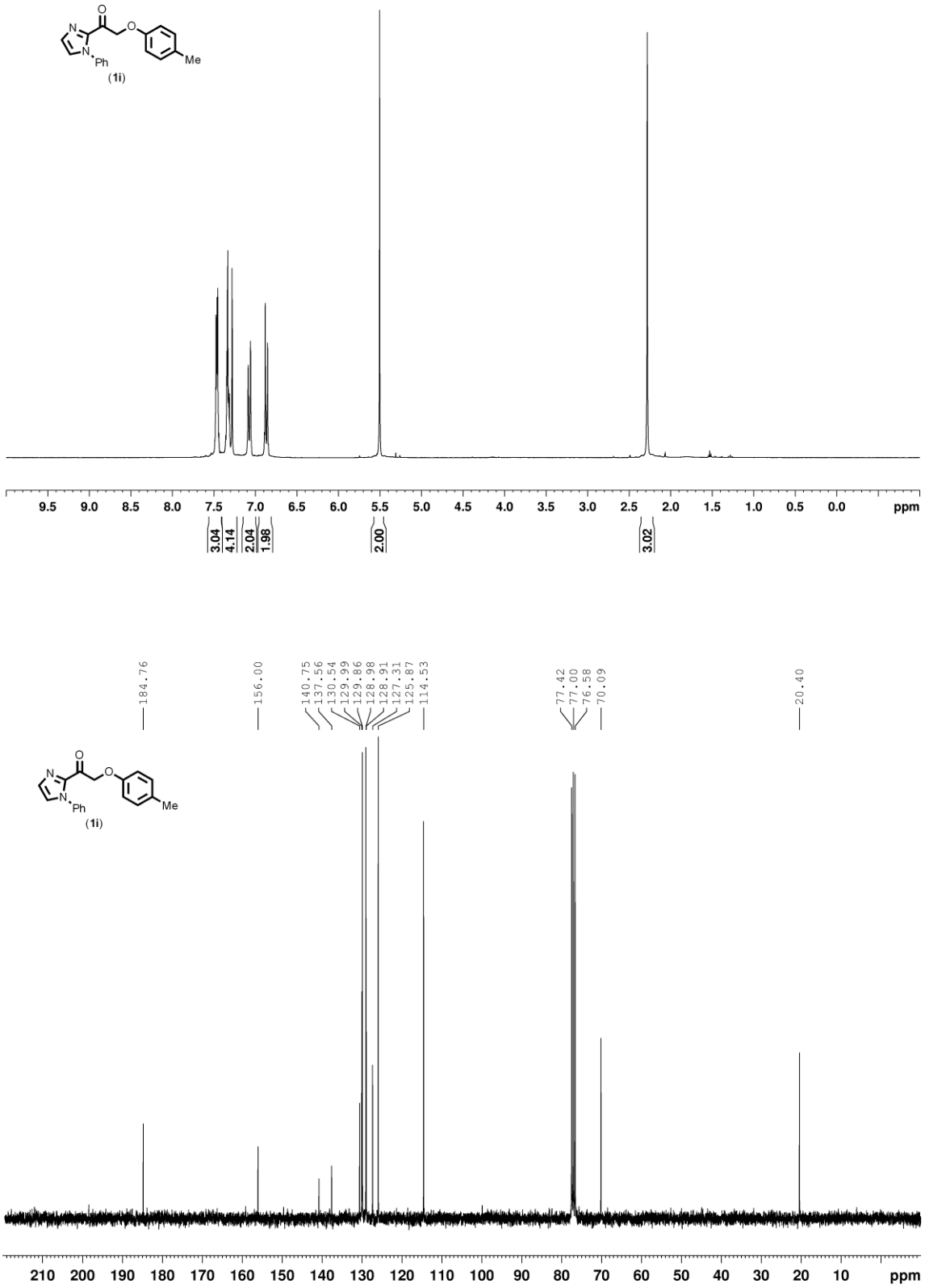


Figure S26. ^{1}H-NMR and ^{13}C-NMR spectrum of **1i**.

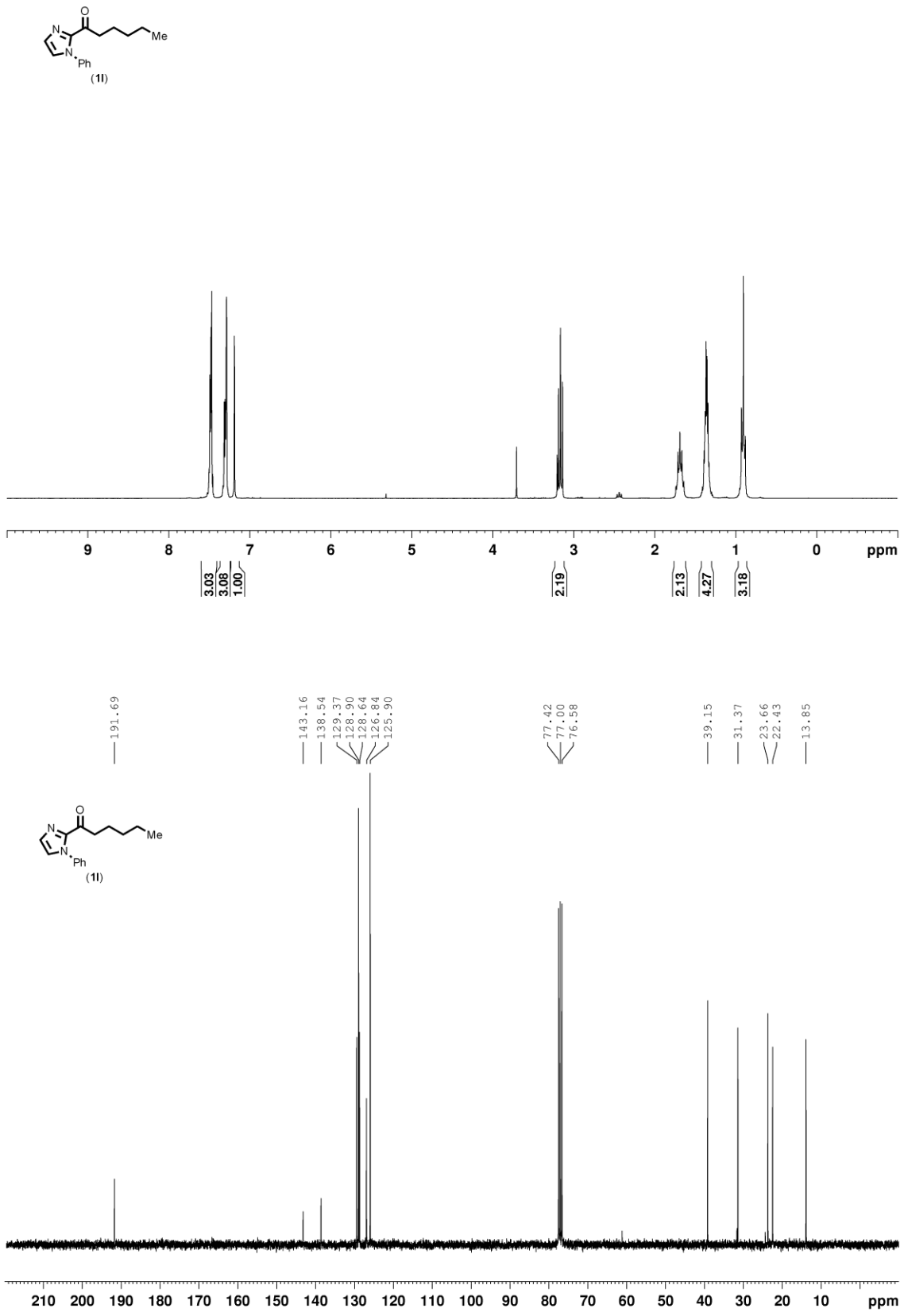


Figure S27. ^{1}H-NMR and ^{13}C-NMR spectrum of **1l**.

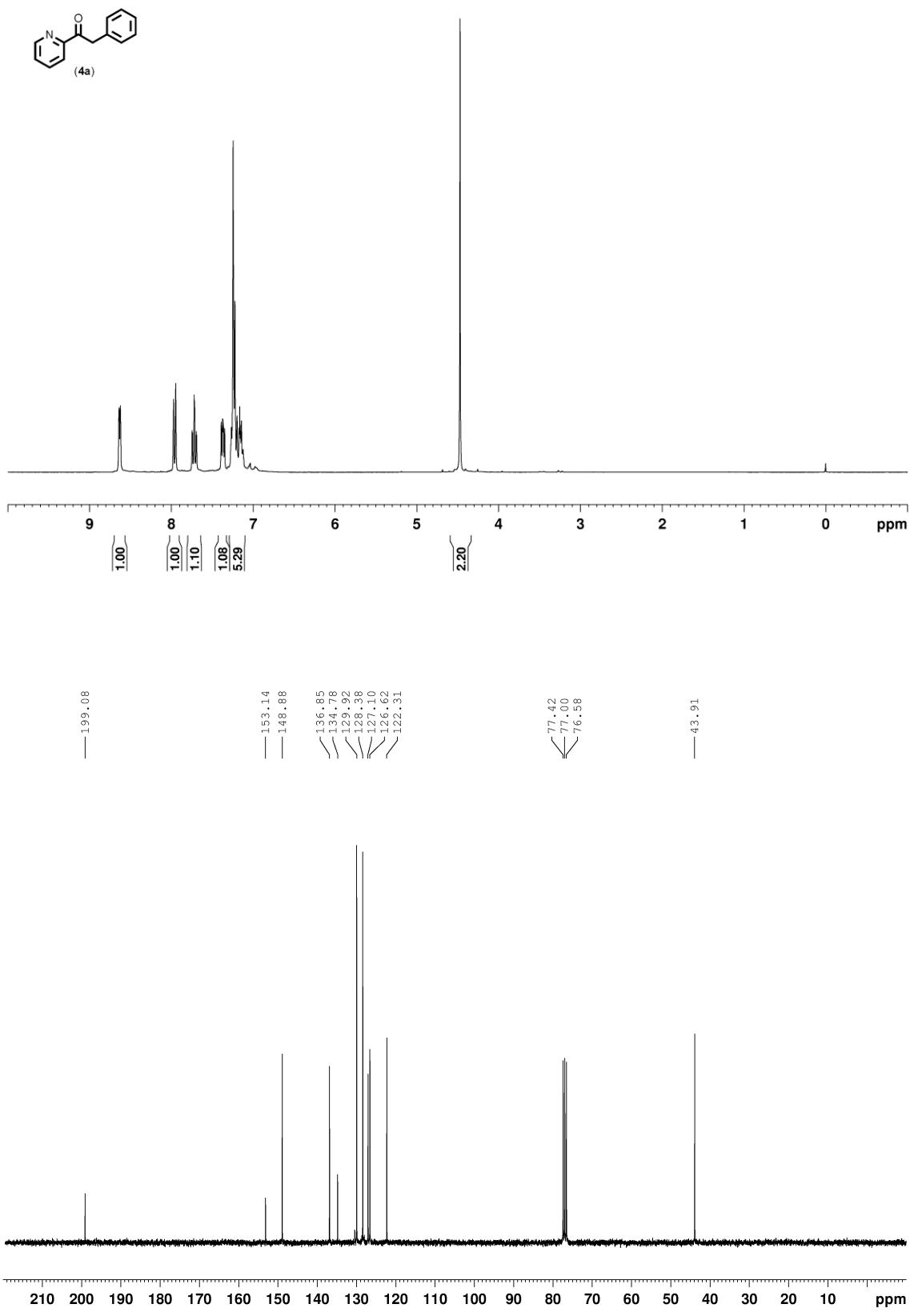


Figure S28. ^{1}H-NMR and ^{13}C-NMR spectrum of **4a**.

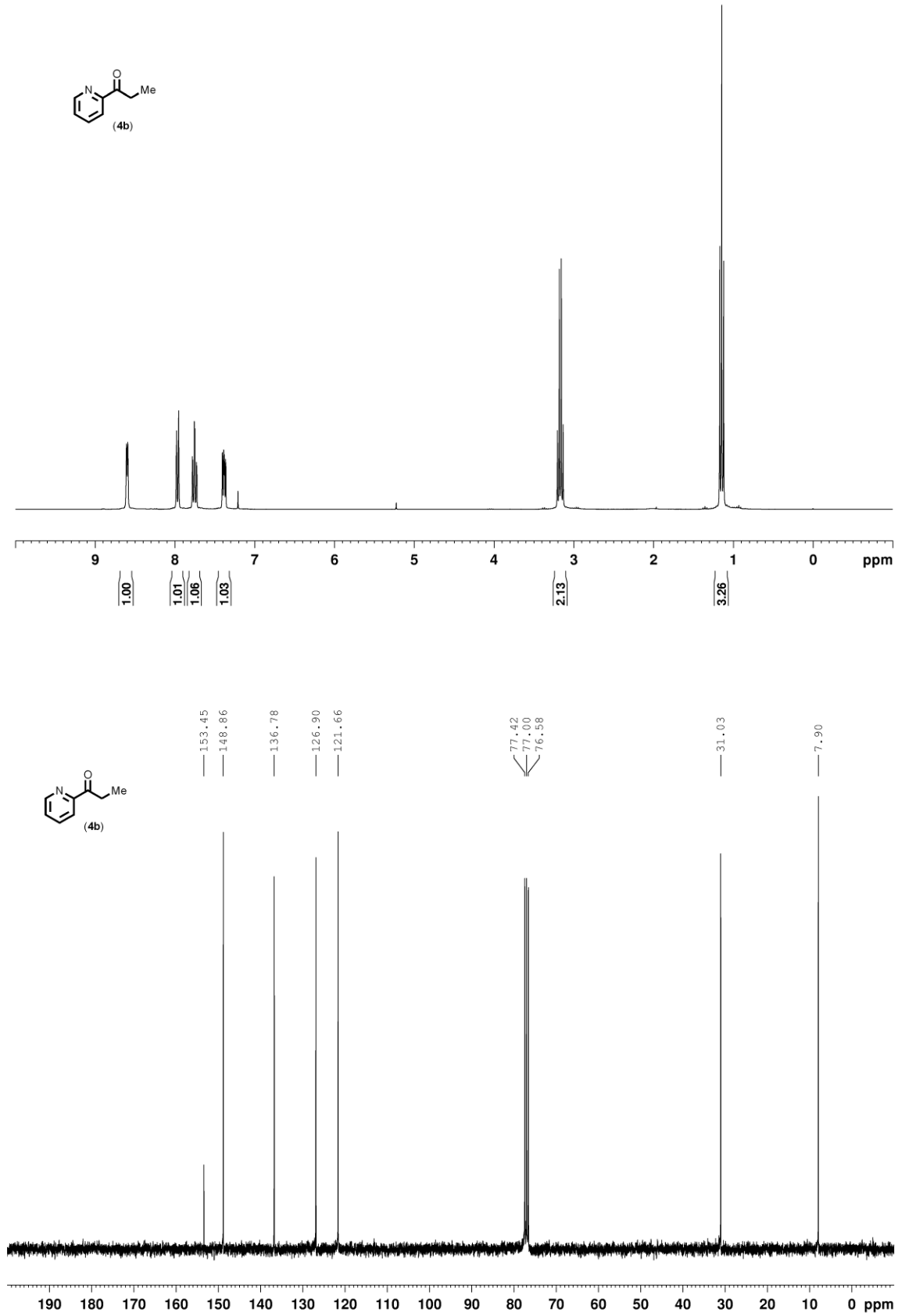


Figure S29. ^{1}H-NMR and ^{13}C-NMR spectrum of **4b**.

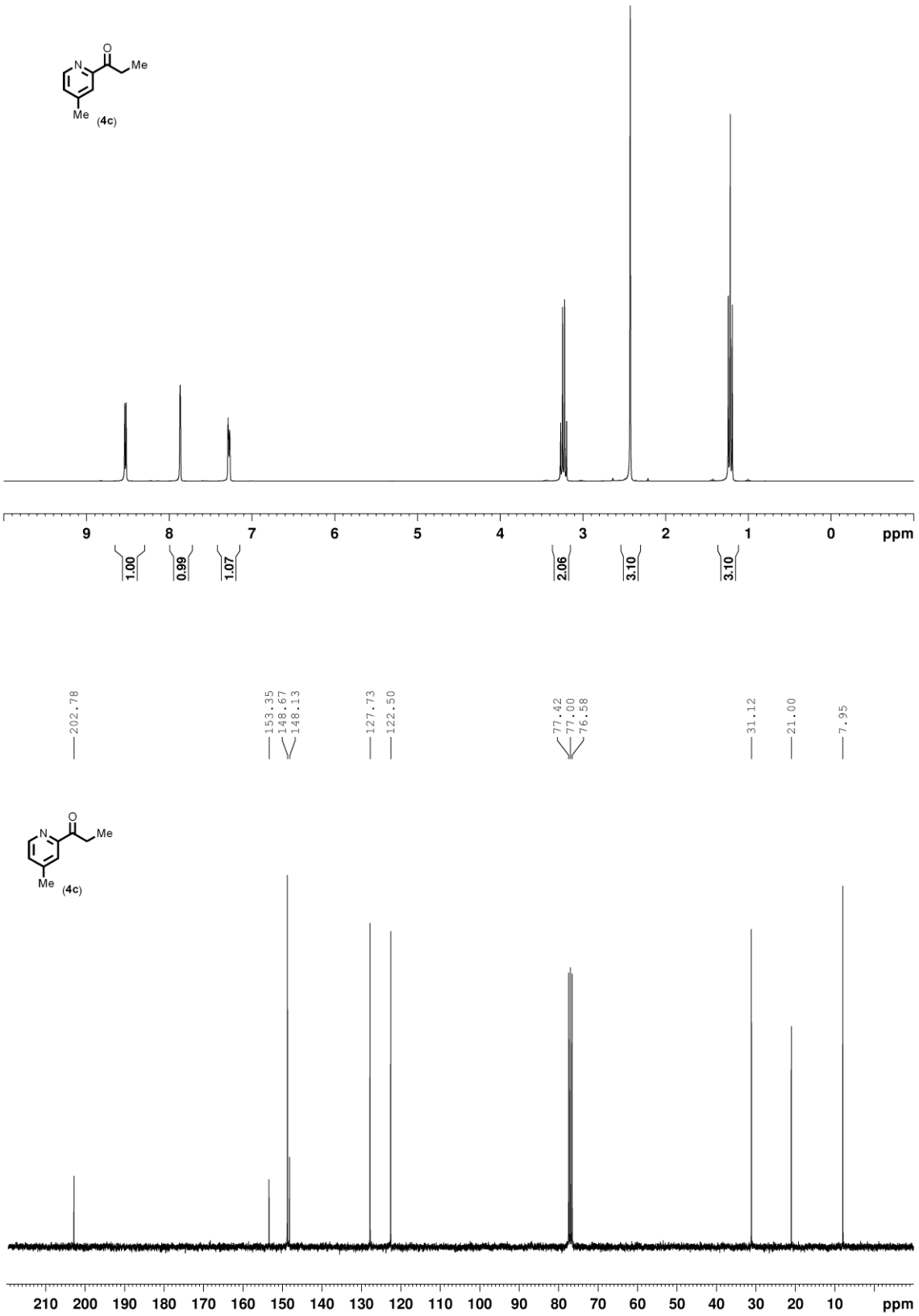


Figure S30. ^{1}H-NMR and ^{13}C-NMR spectrum of **4c**.

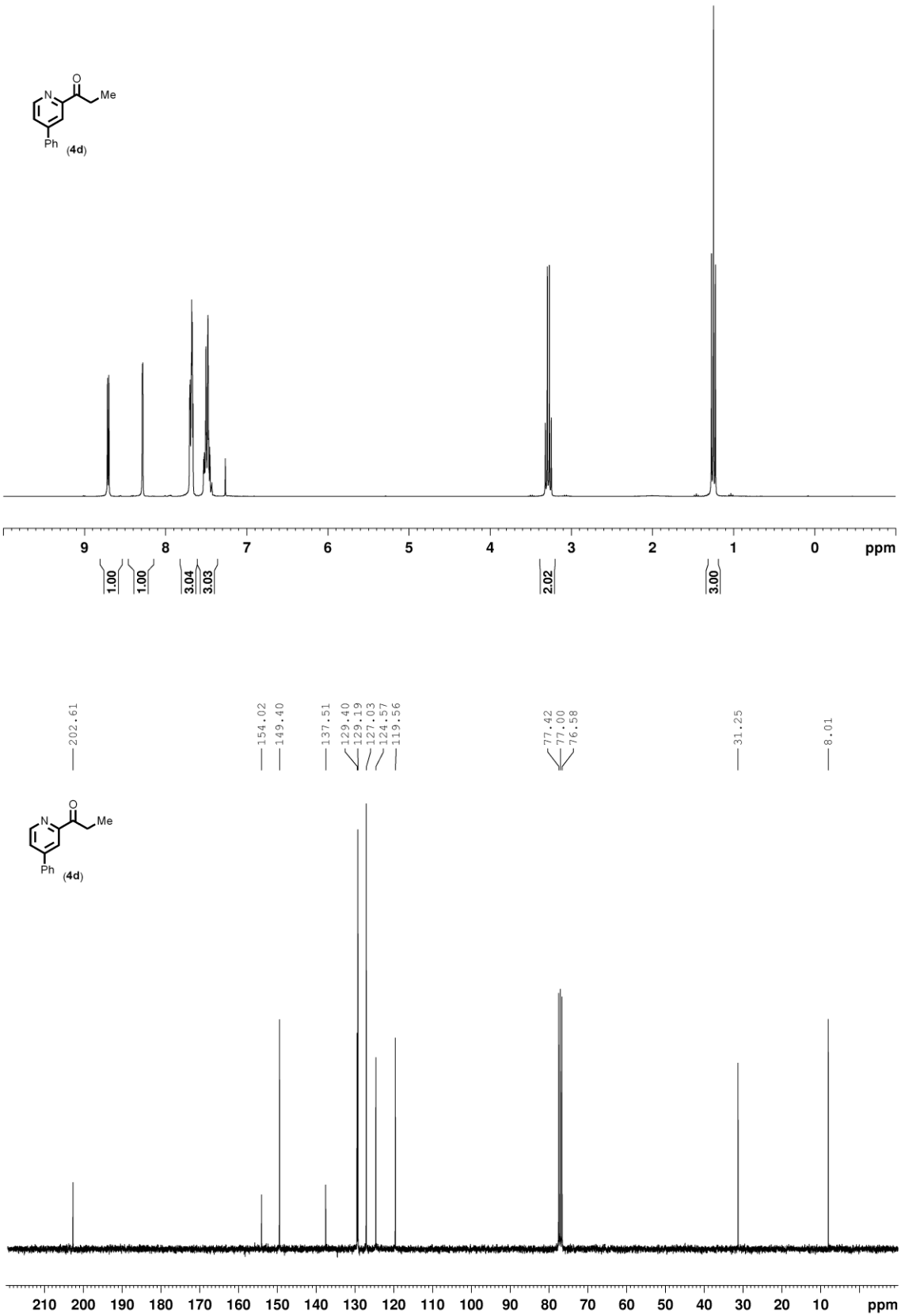


Figure S31. ^{1}H-NMR and ^{13}C-NMR spectrum of **4d**.

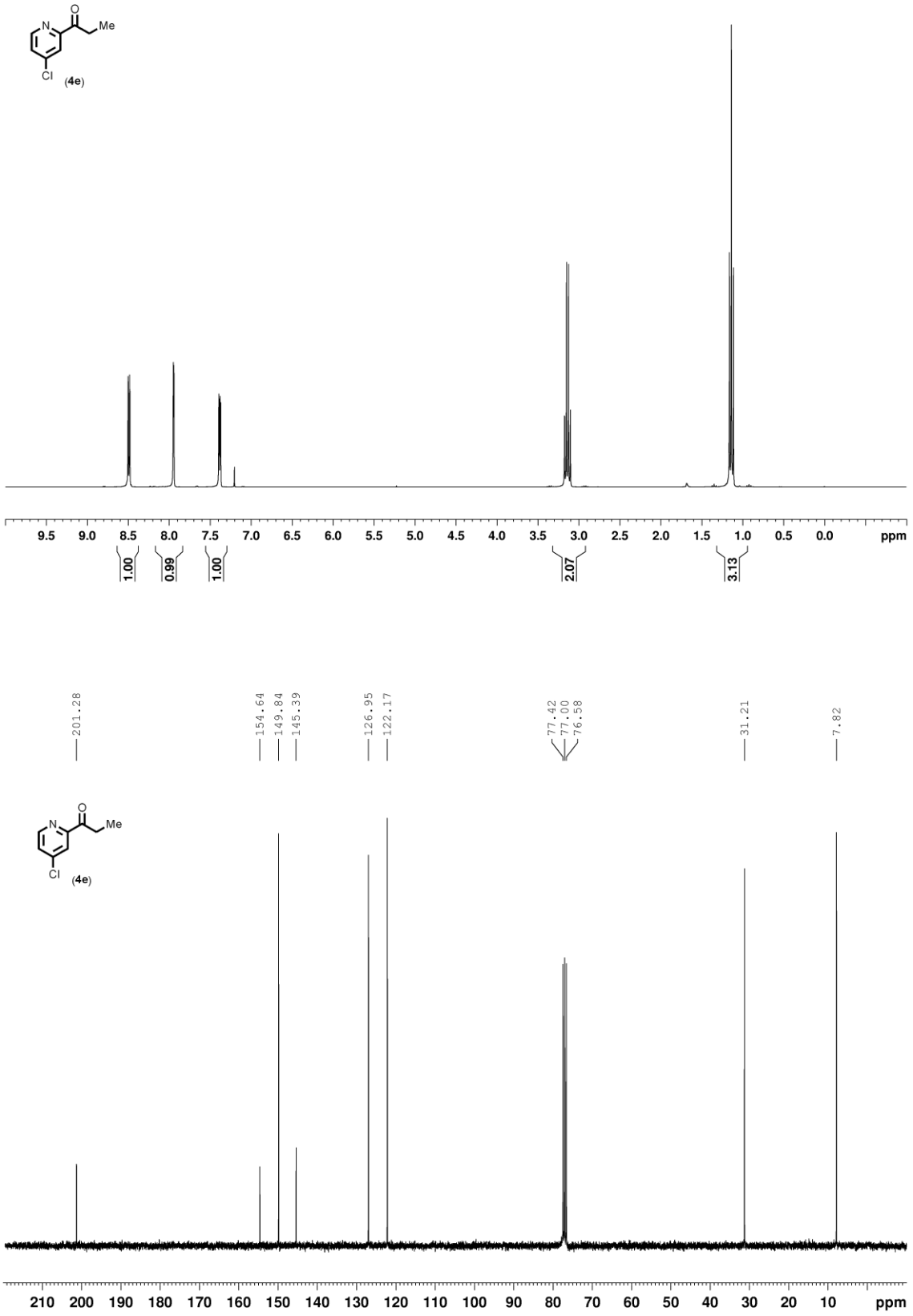


Figure S32. ^{1}H-NMR and ^{13}C-NMR spectrum of **4e**.

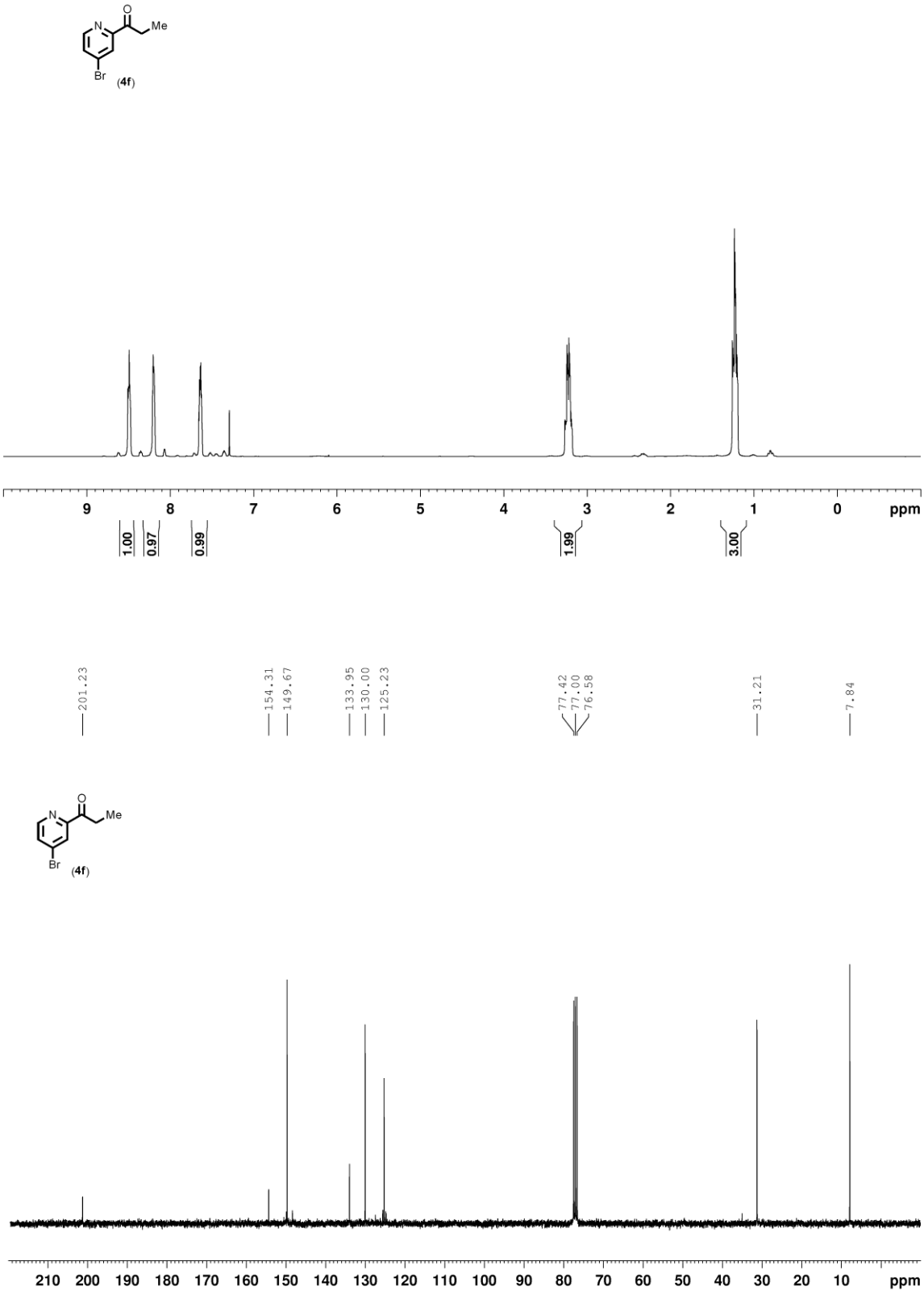


Figure S33. ^{1}H-NMR and ^{13}C-NMR spectrum of **4f**.

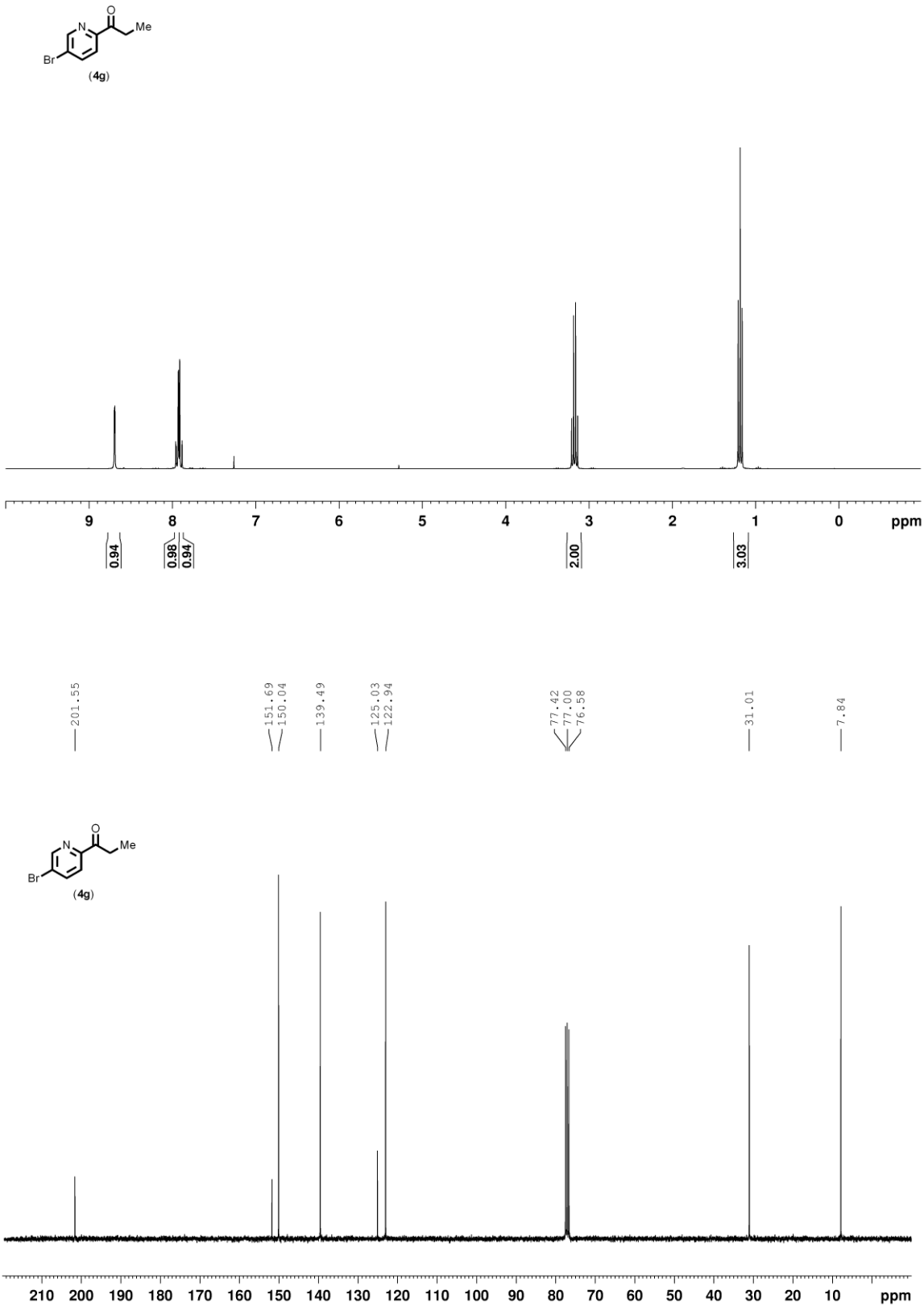


Figure S34. ^{1}H-NMR and ^{13}C-NMR spectrum of **4g**.

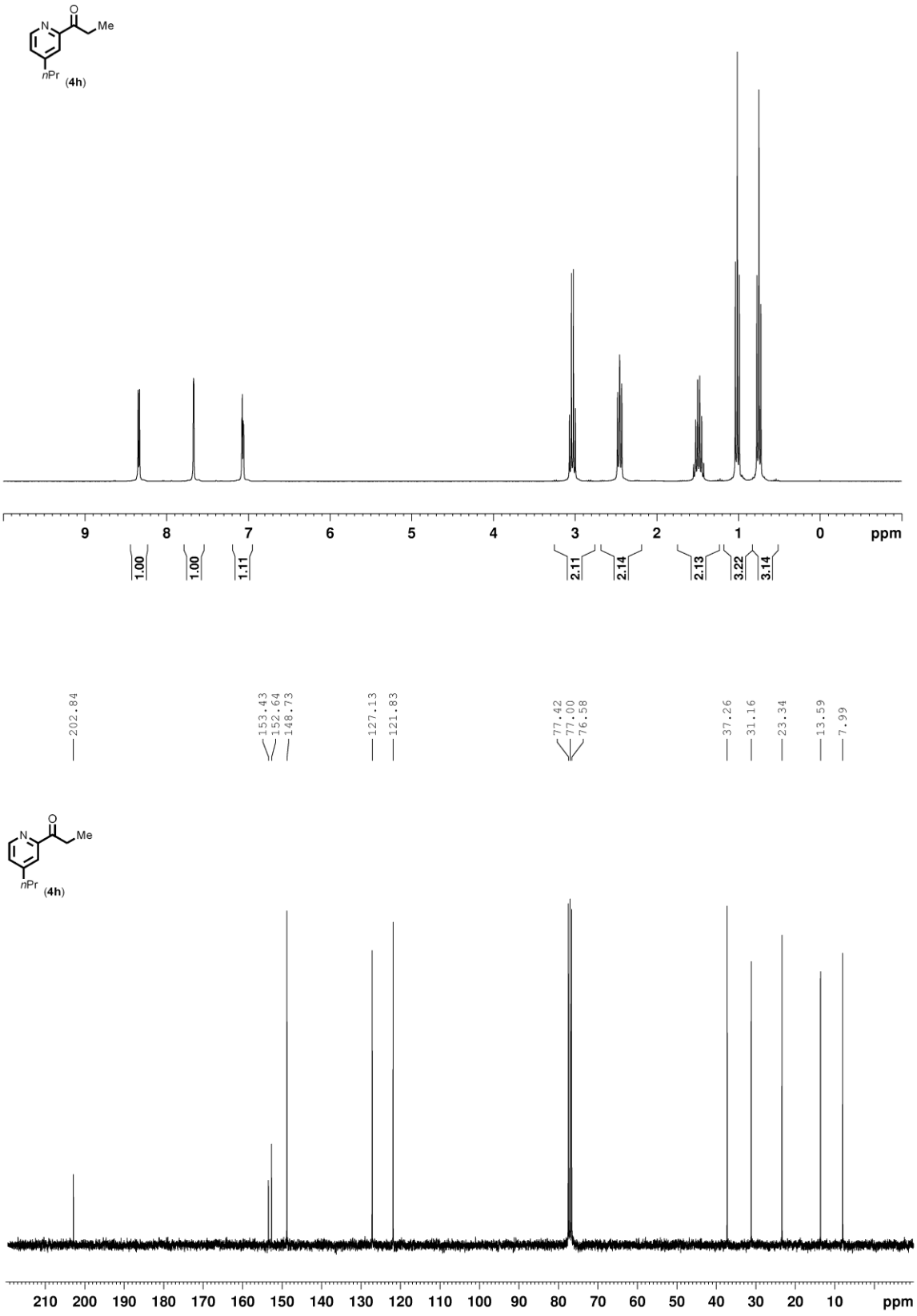


Figure S35. ^{1}H-NMR and ^{13}C-NMR spectrum of **4h**.

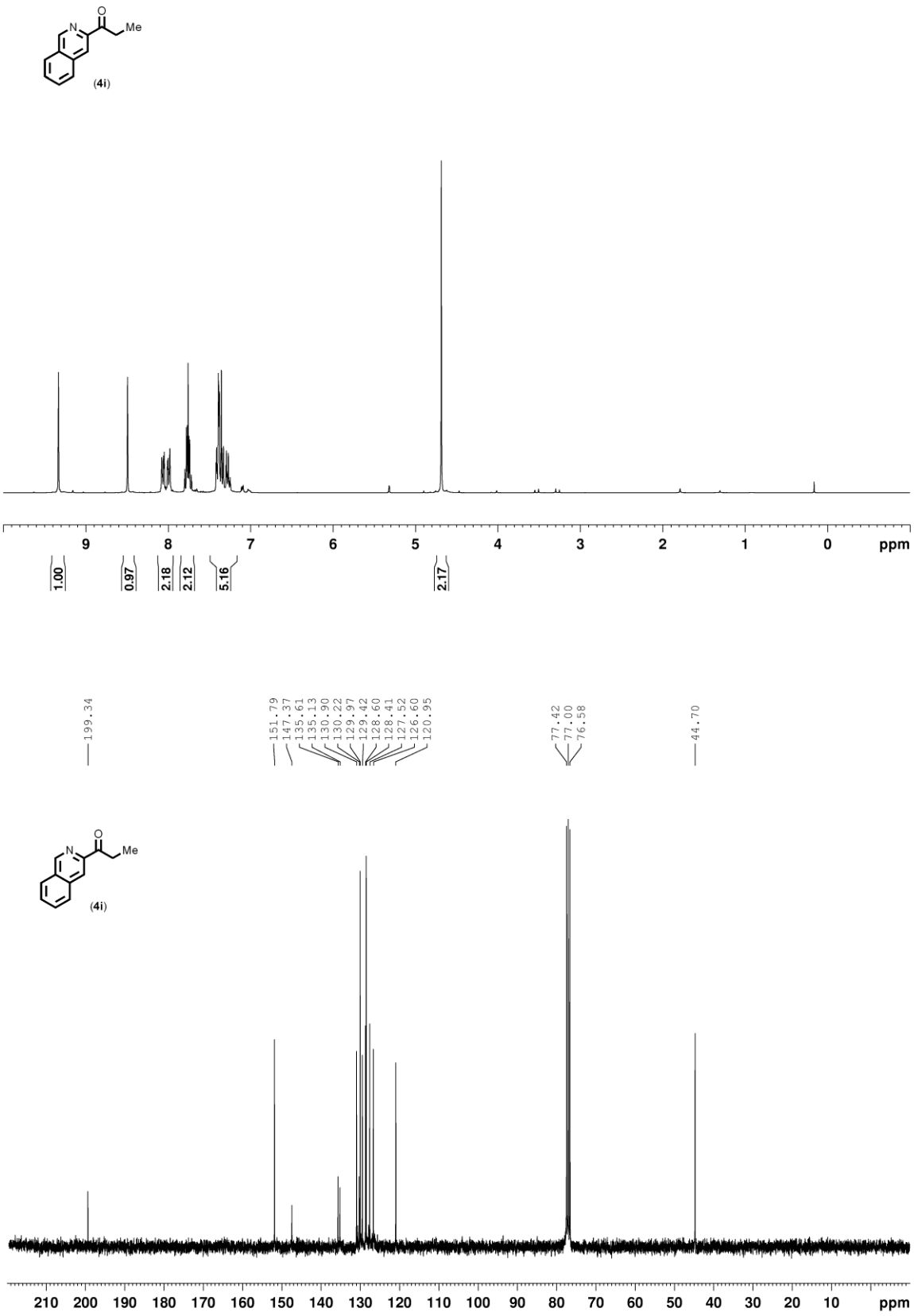


Figure S36. ^{1}H-NMR and ^{13}C-NMR spectrum of **4i**.

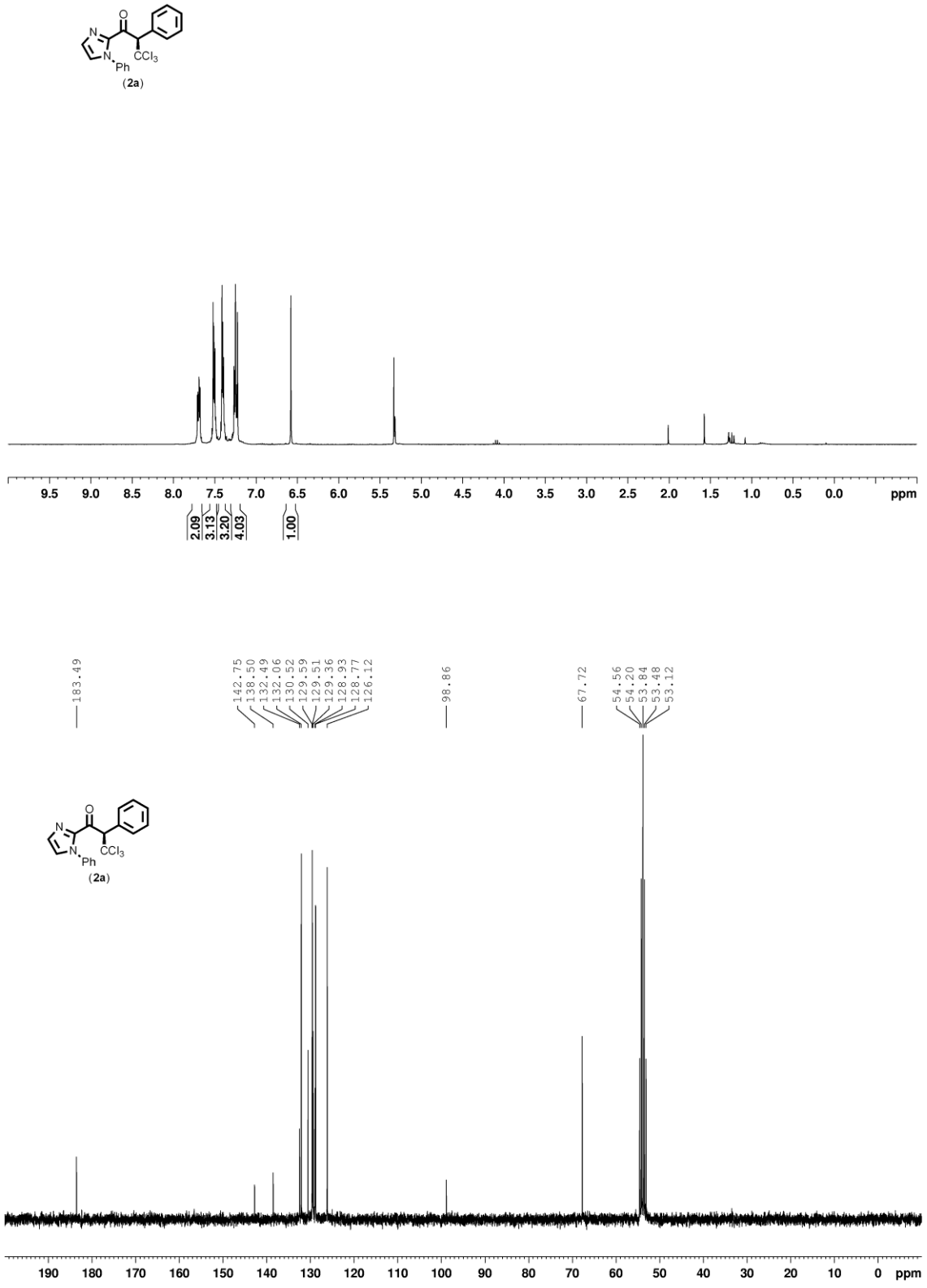


Figure S37. ^{1}H-NMR and ^{13}C-NMR spectrum of **2a**.

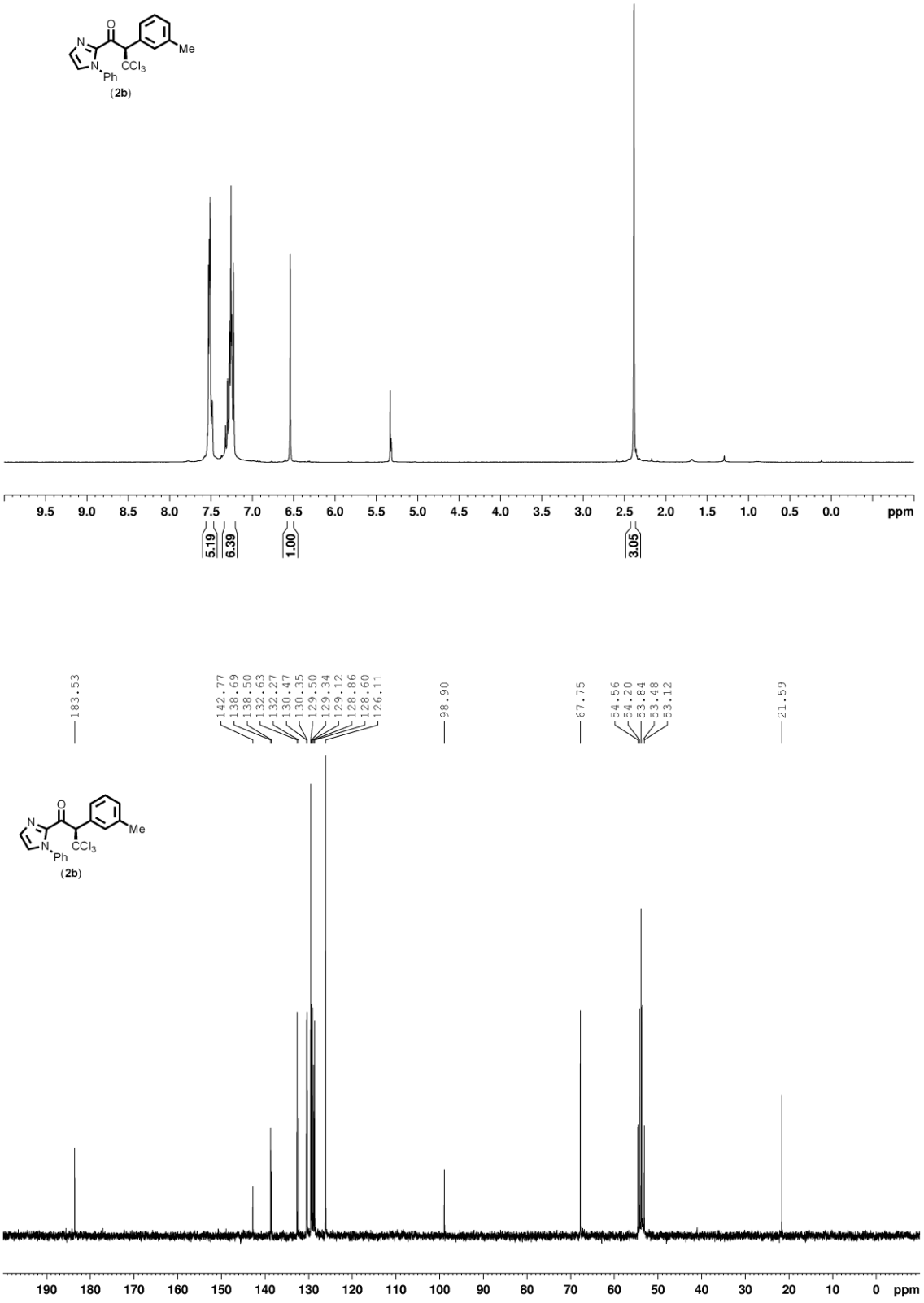


Figure S38. ^{1}H-NMR and ^{13}C-NMR spectrum of **2b**.

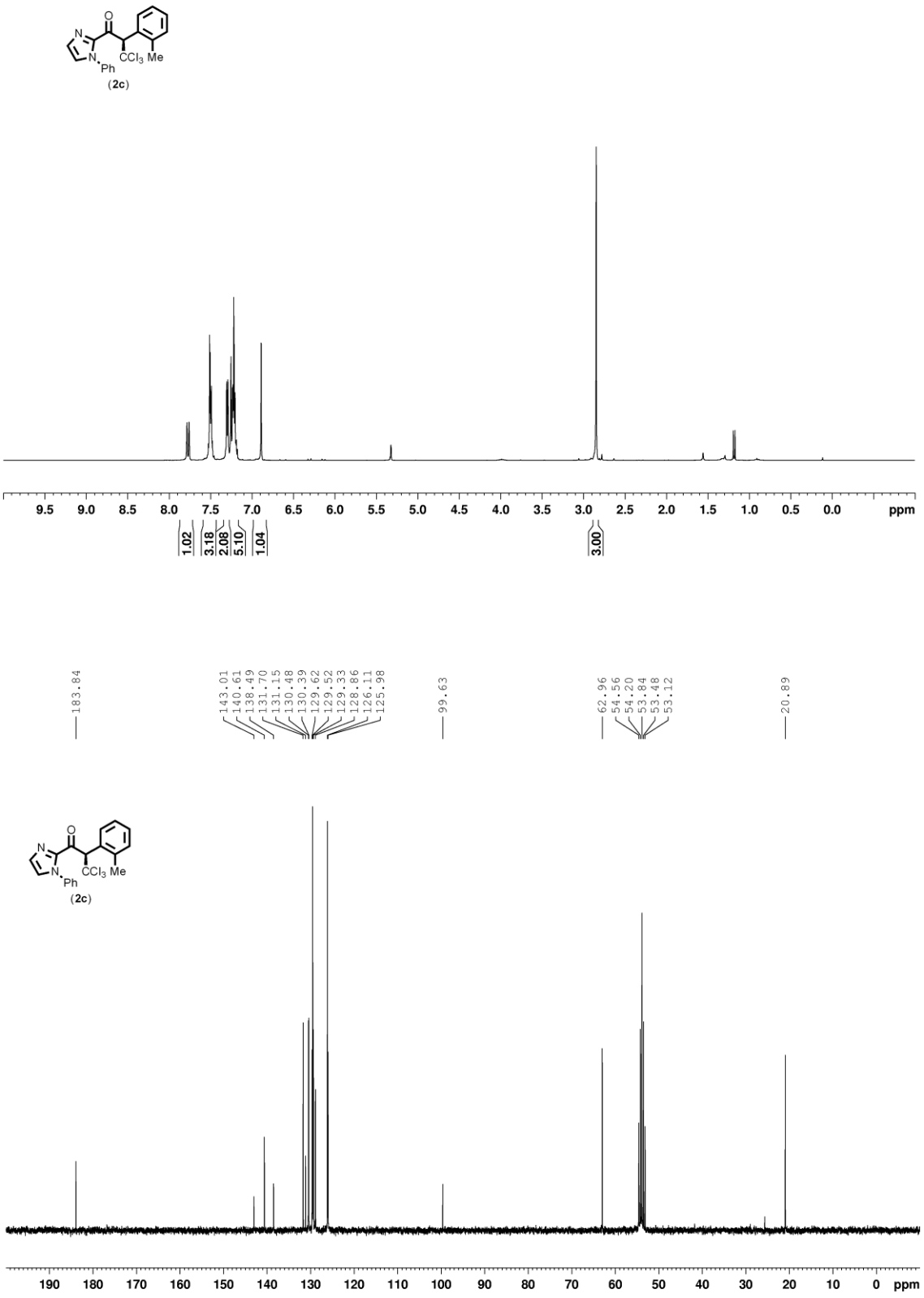


Figure S39. ^{1}H-NMR and ^{13}C-NMR spectrum of **2c**.

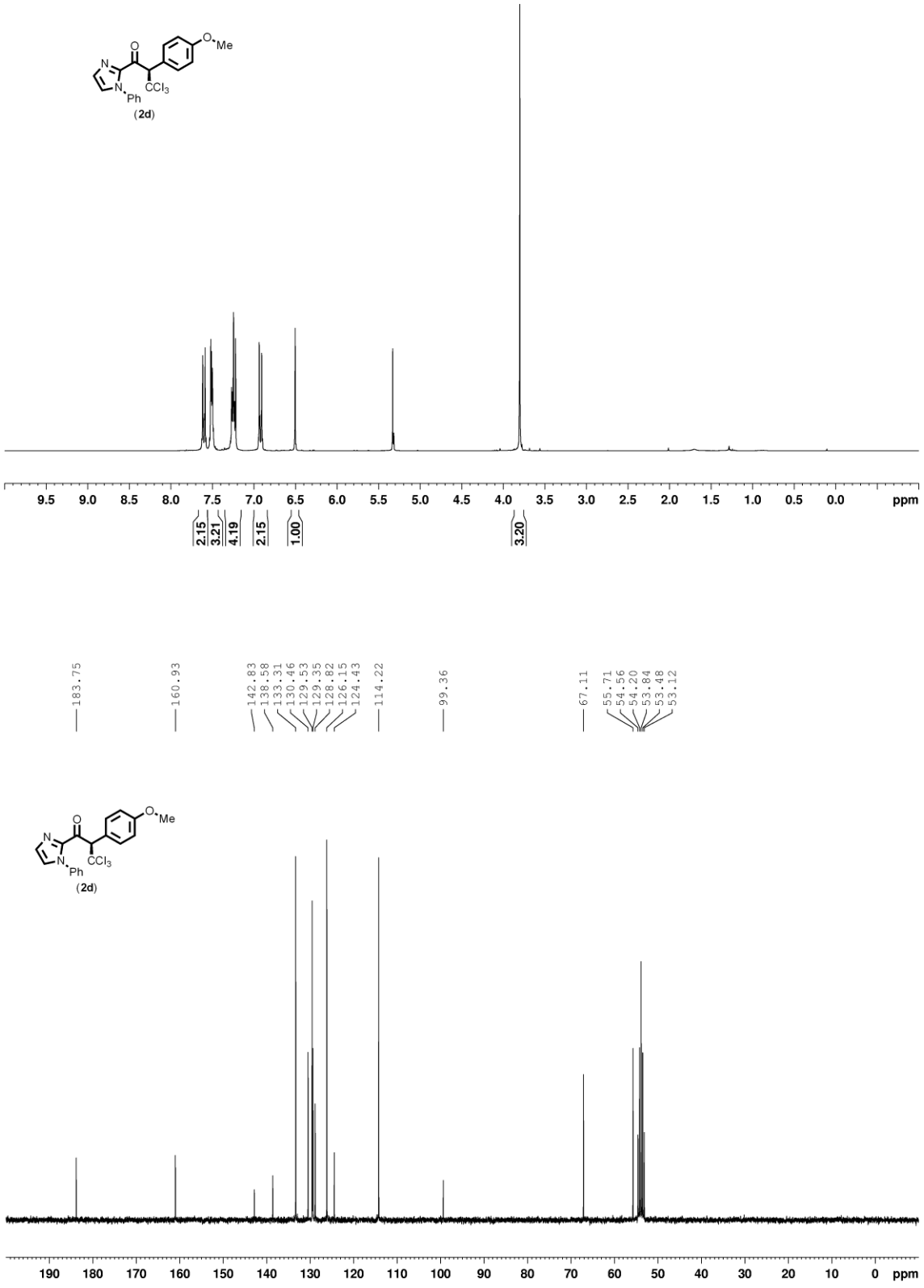


Figure S40. ^{1}H-NMR and ^{13}C-NMR spectrum of **2d**.

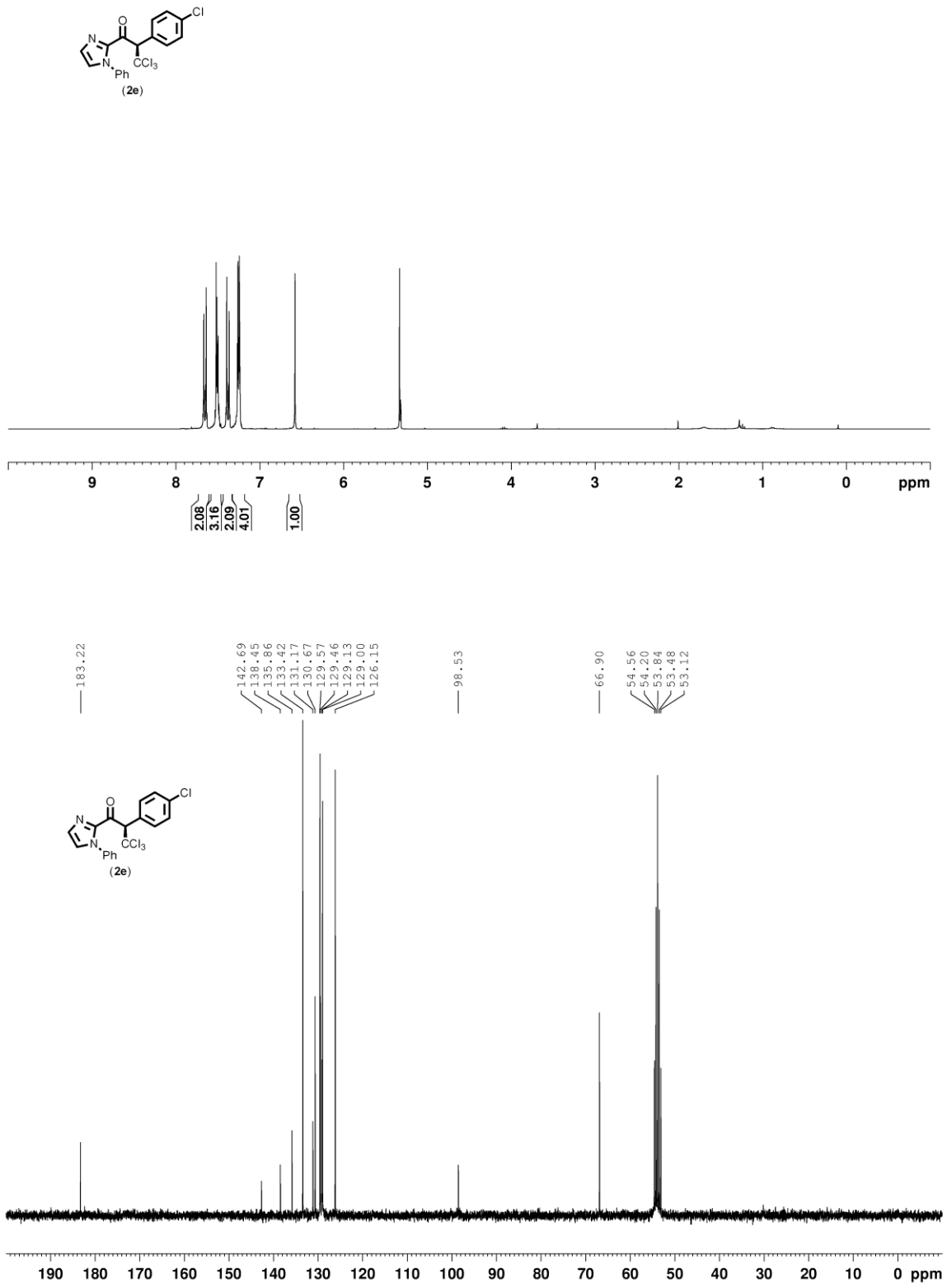


Figure S41. ^{1}H-NMR and ^{13}C-NMR spectrum of **2e**.

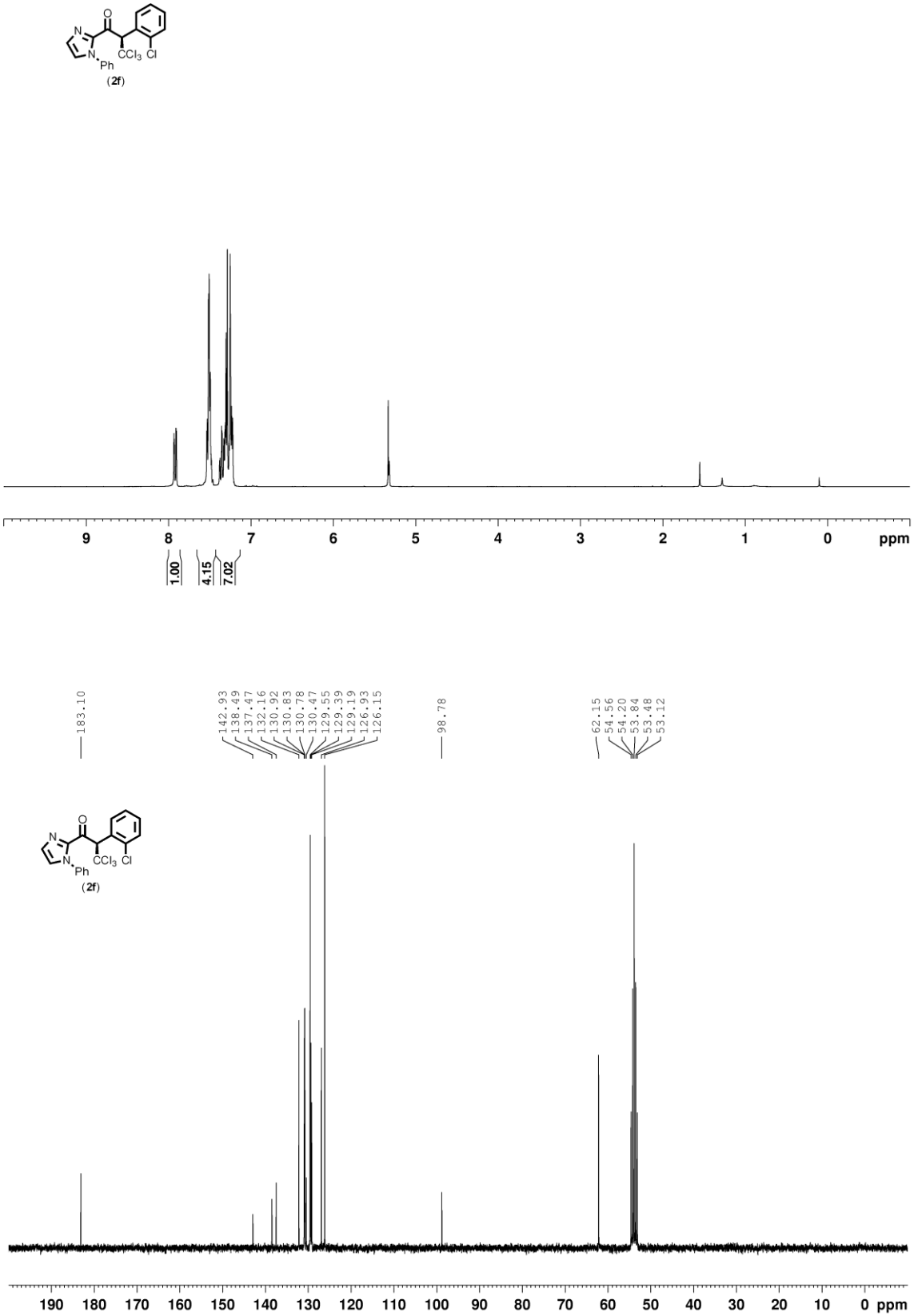


Figure S42. ^{1}H-NMR and ^{13}C-NMR spectrum of **2f**.

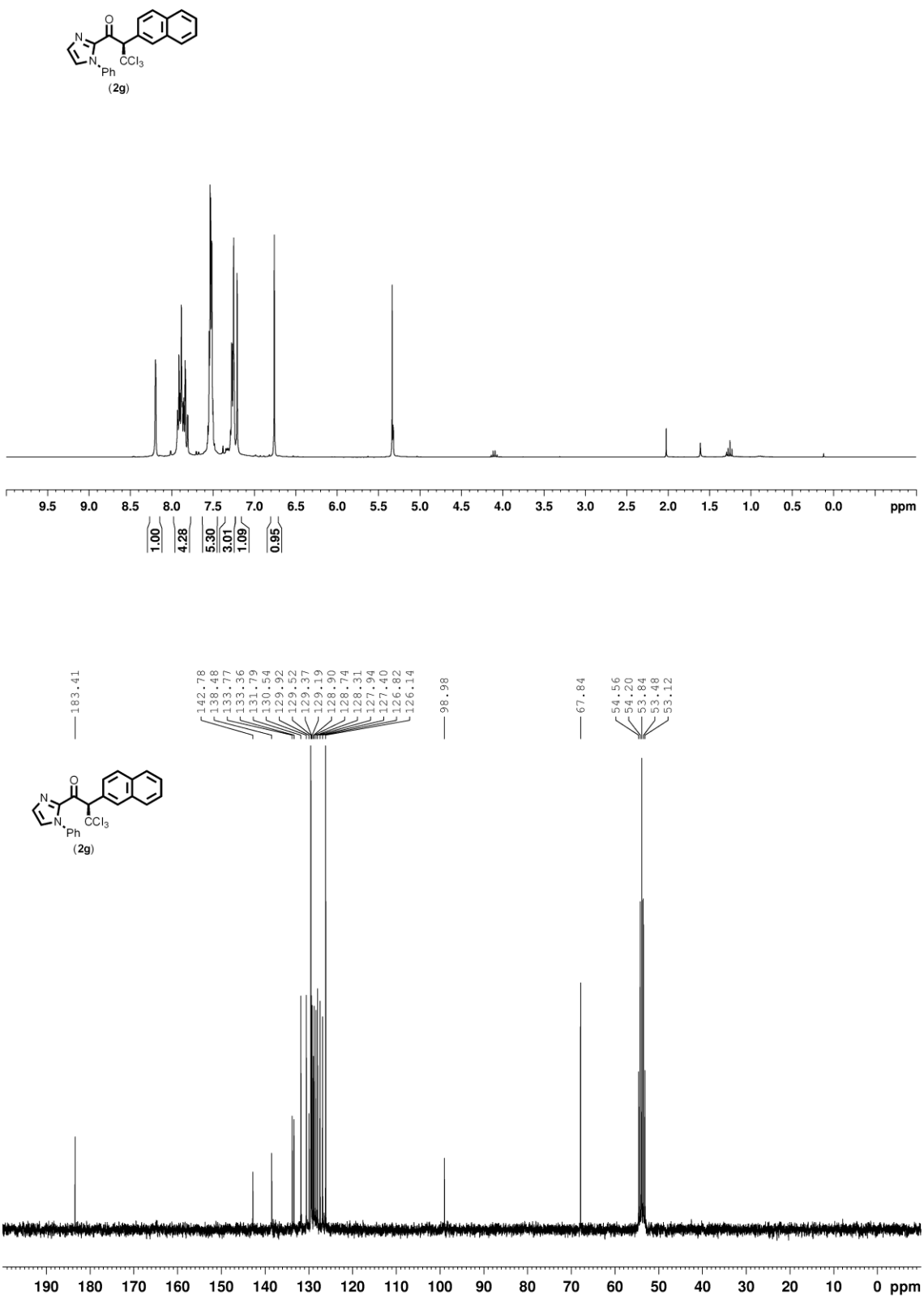


Figure S43. ^{1}H-NMR and ^{13}C-NMR spectrum of **2g**.

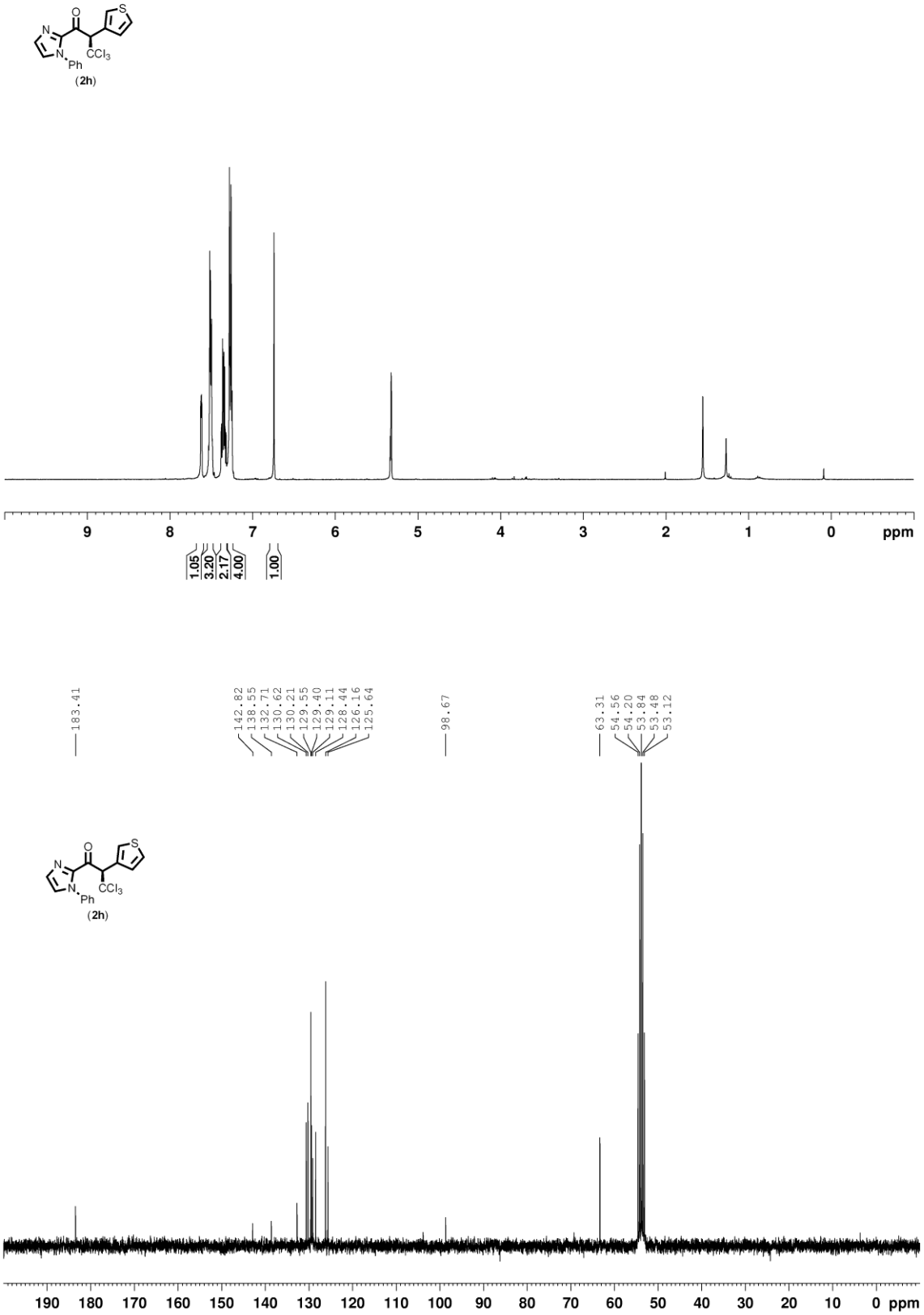


Figure S44. ^{1}H-NMR and ^{13}C-NMR spectrum of **2h**.

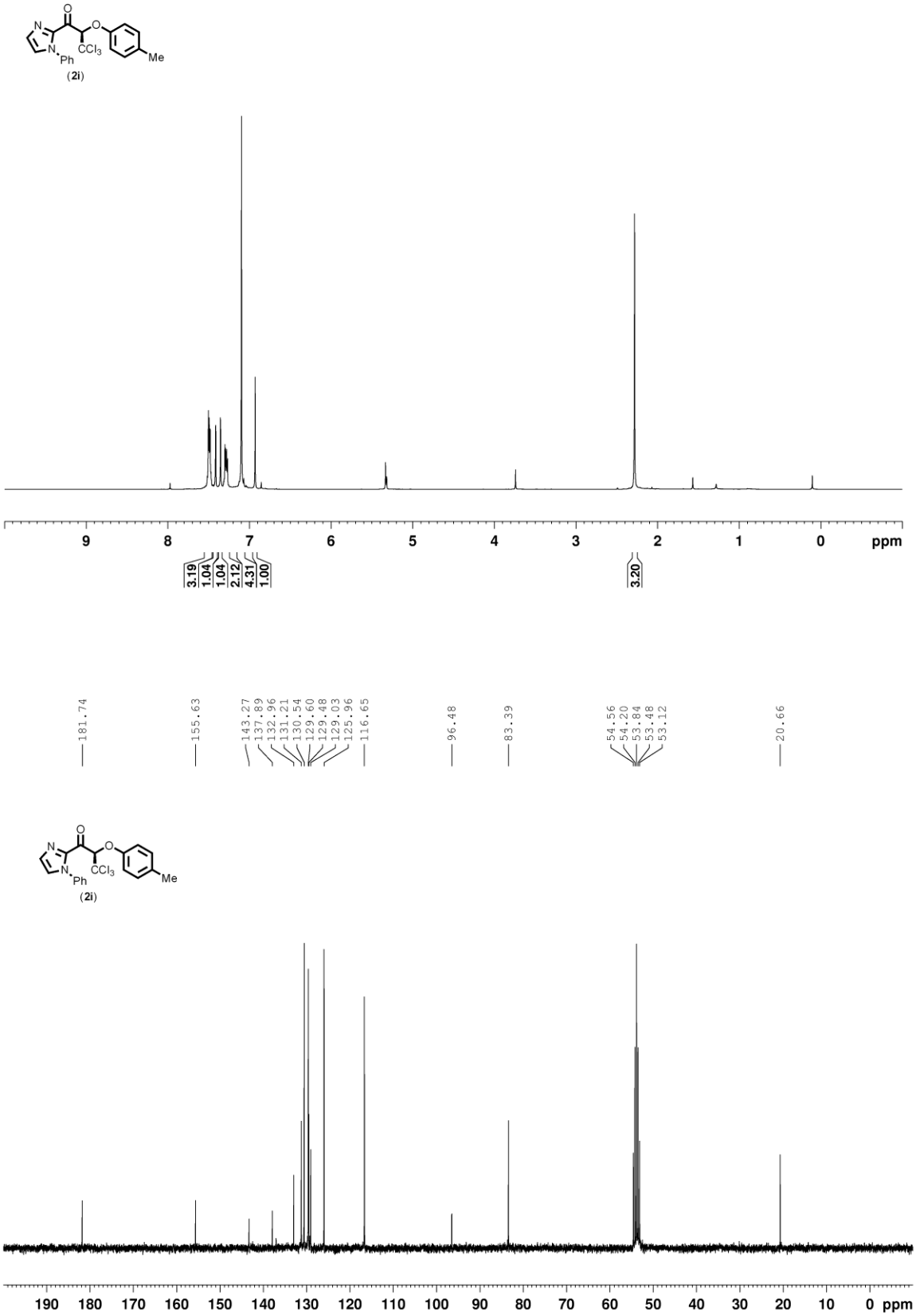


Figure S45. ^{1}H-NMR and ^{13}C-NMR spectrum of **2i**.

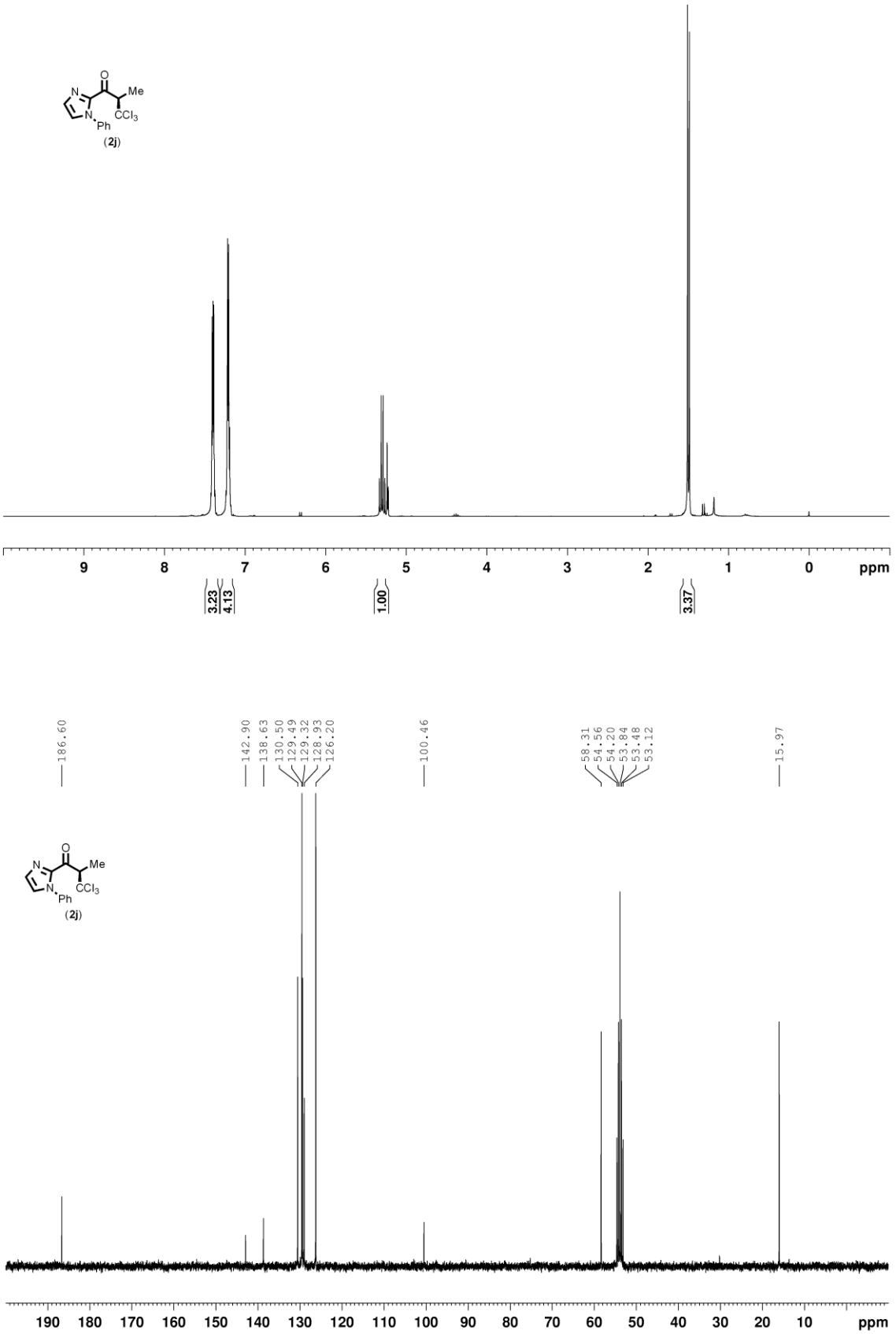


Figure S46. ^{1}H-NMR and ^{13}C-NMR spectrum of **2j**.

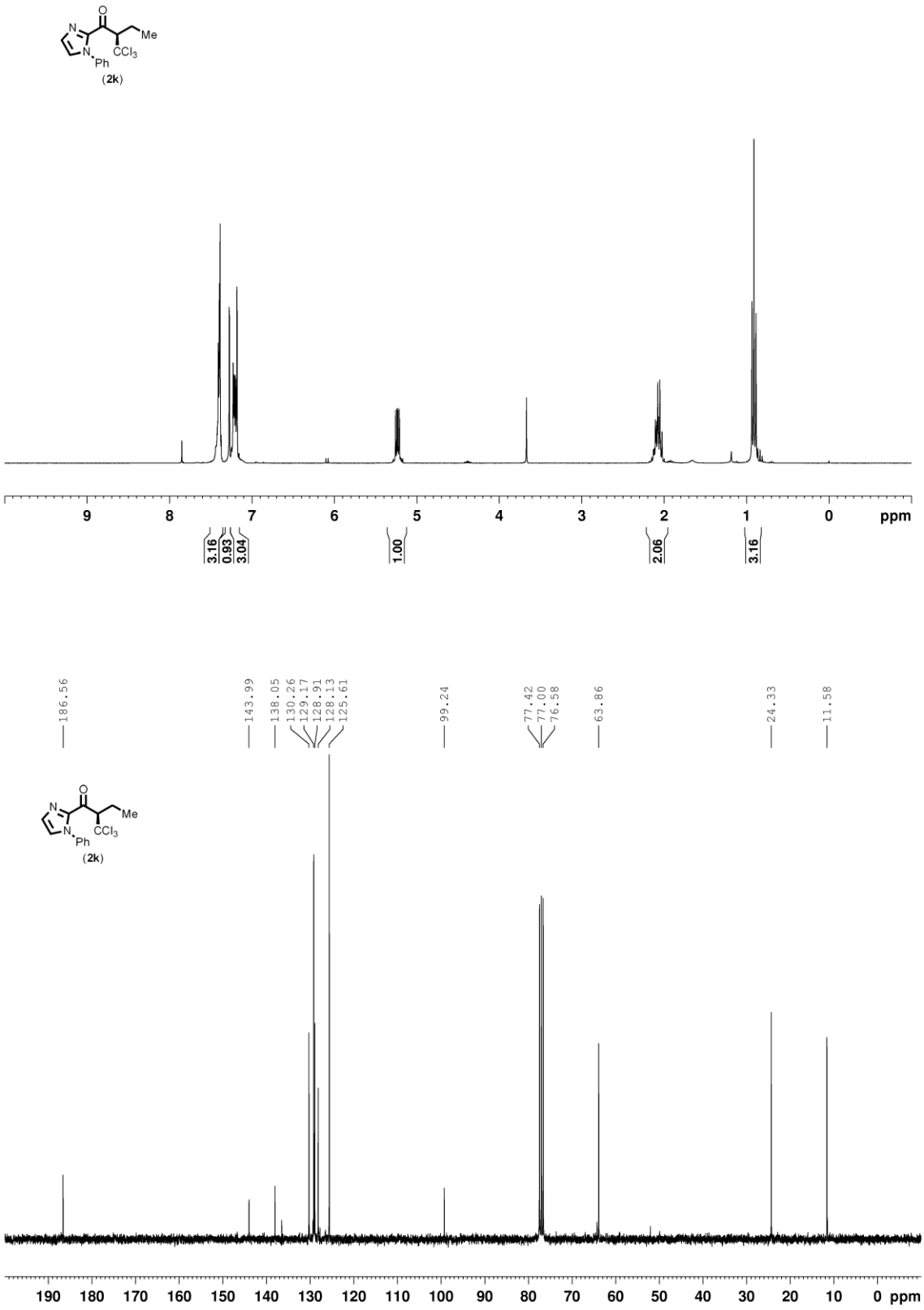


Figure S47. ^{1}H-NMR and ^{13}C-NMR spectrum of **2k**.

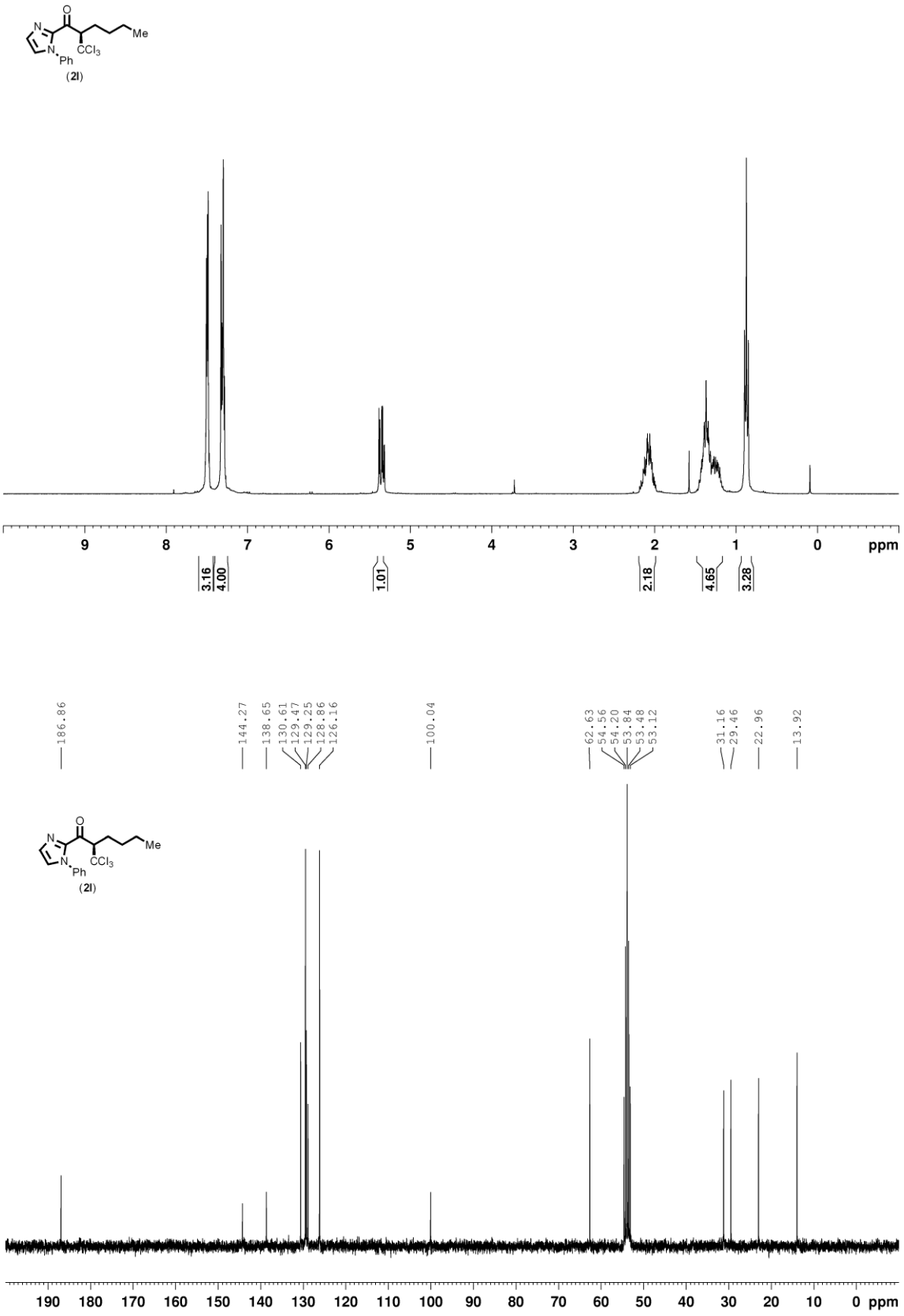


Figure S48. ^{1}H-NMR and ^{13}C-NMR spectrum of **2l**.

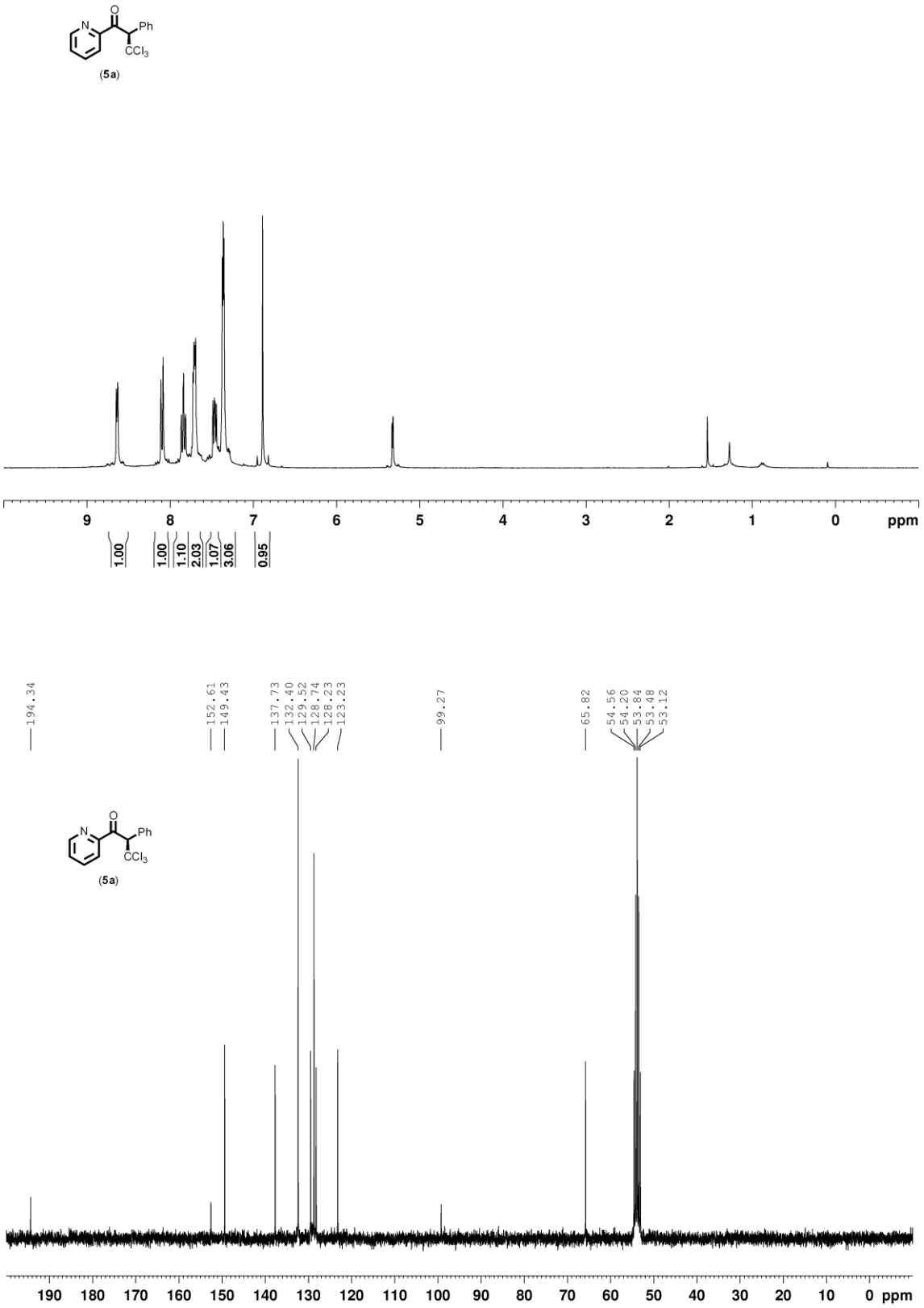


Figure S49. ^{1}H-NMR and ^{13}C-NMR spectrum of **5a**.

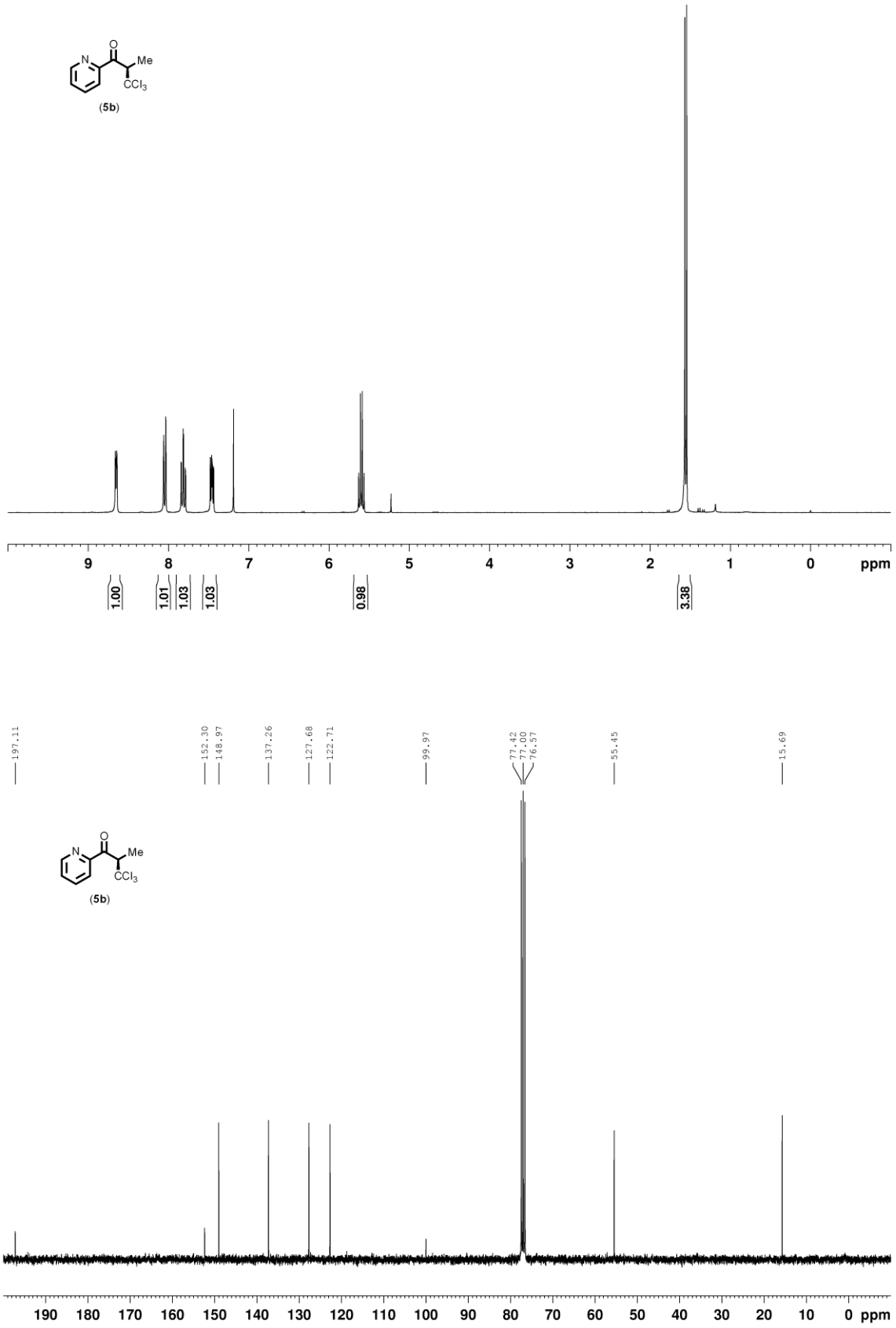


Figure S50. ^{1}H-NMR and ^{13}C-NMR spectrum of **5b**.

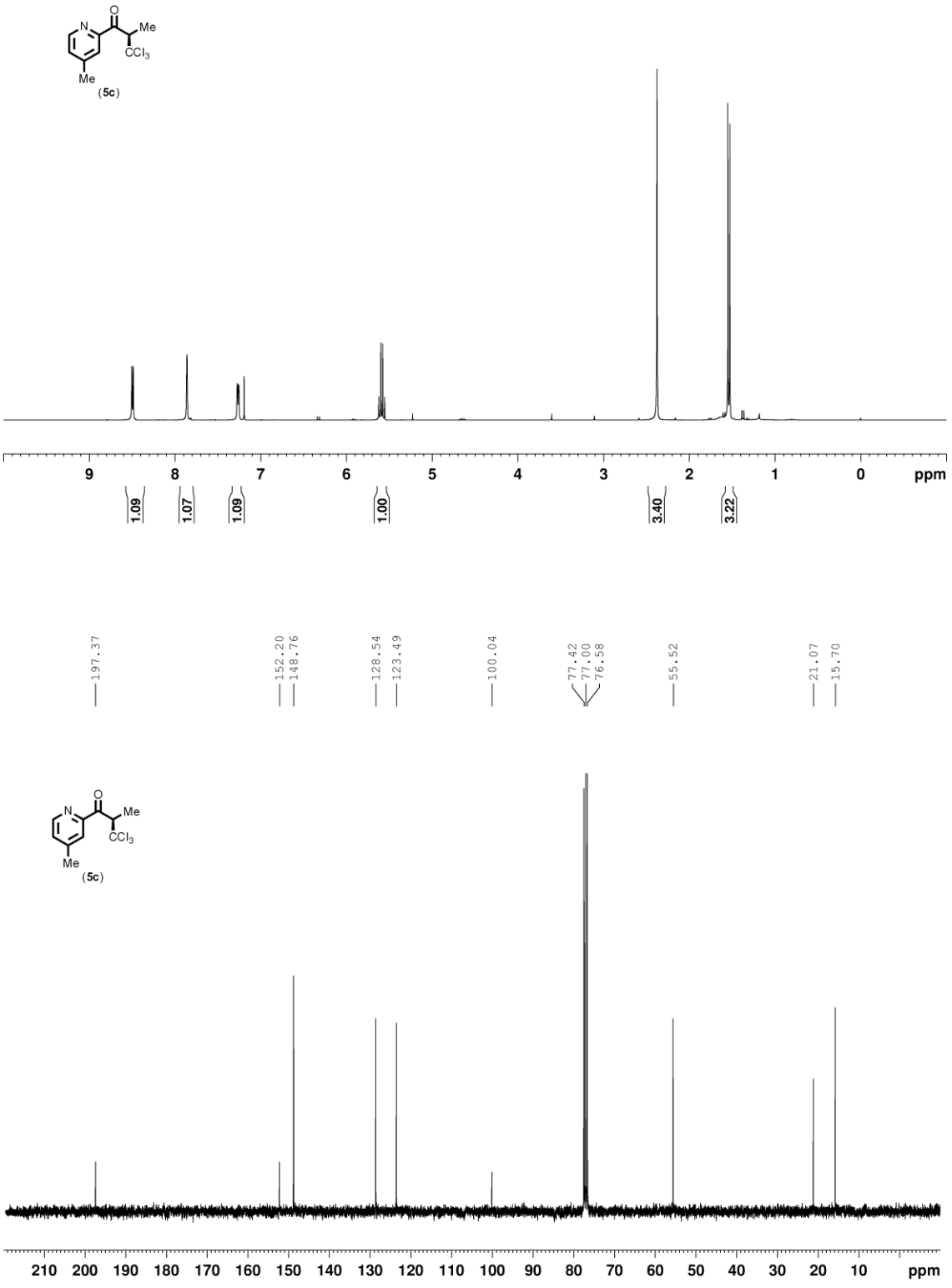


Figure S51. ^{1}H-NMR and ^{13}C-NMR spectrum of **5c**.

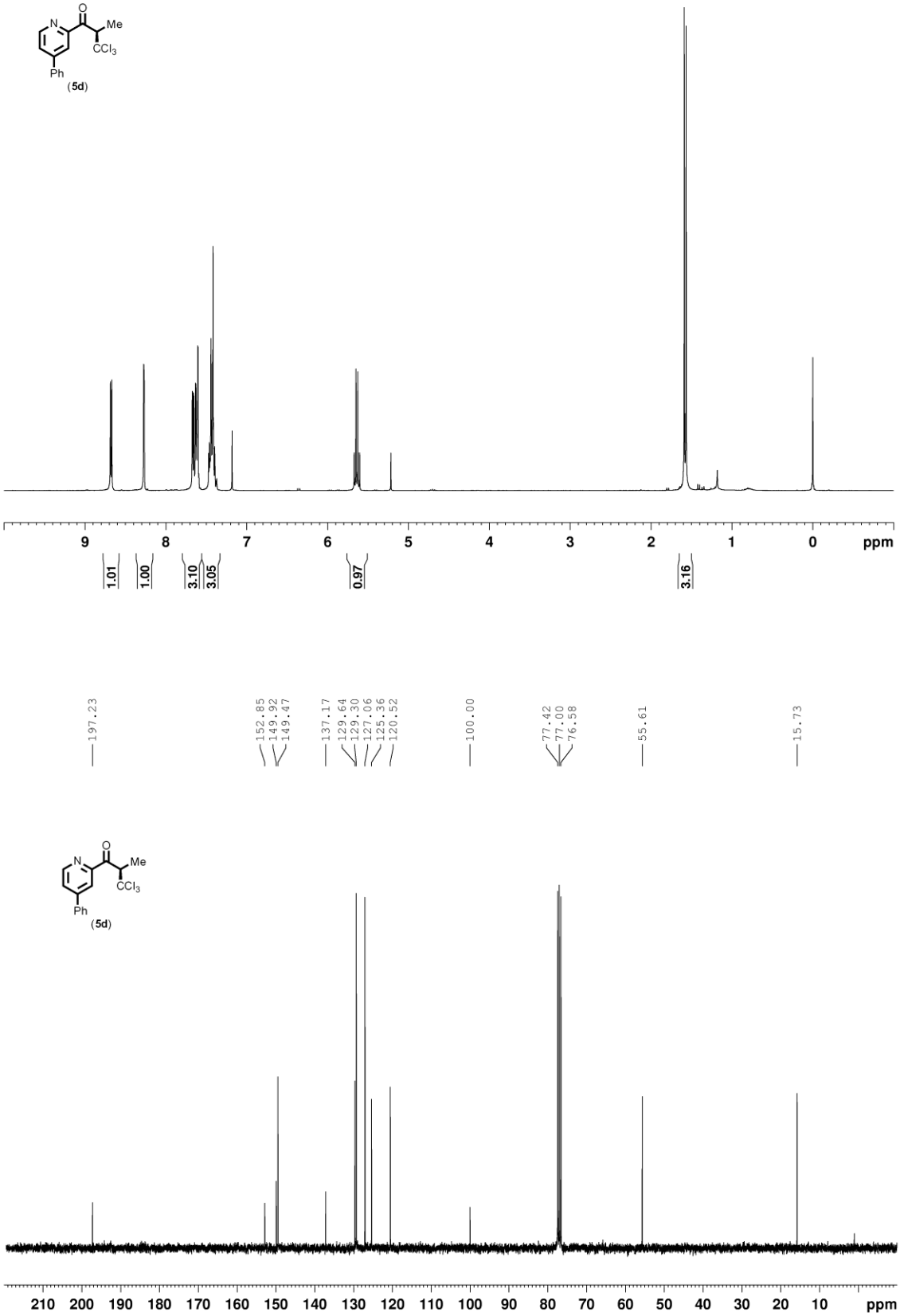


Figure S52. ^{1}H-NMR and ^{13}C-NMR spectrum of **5d**.

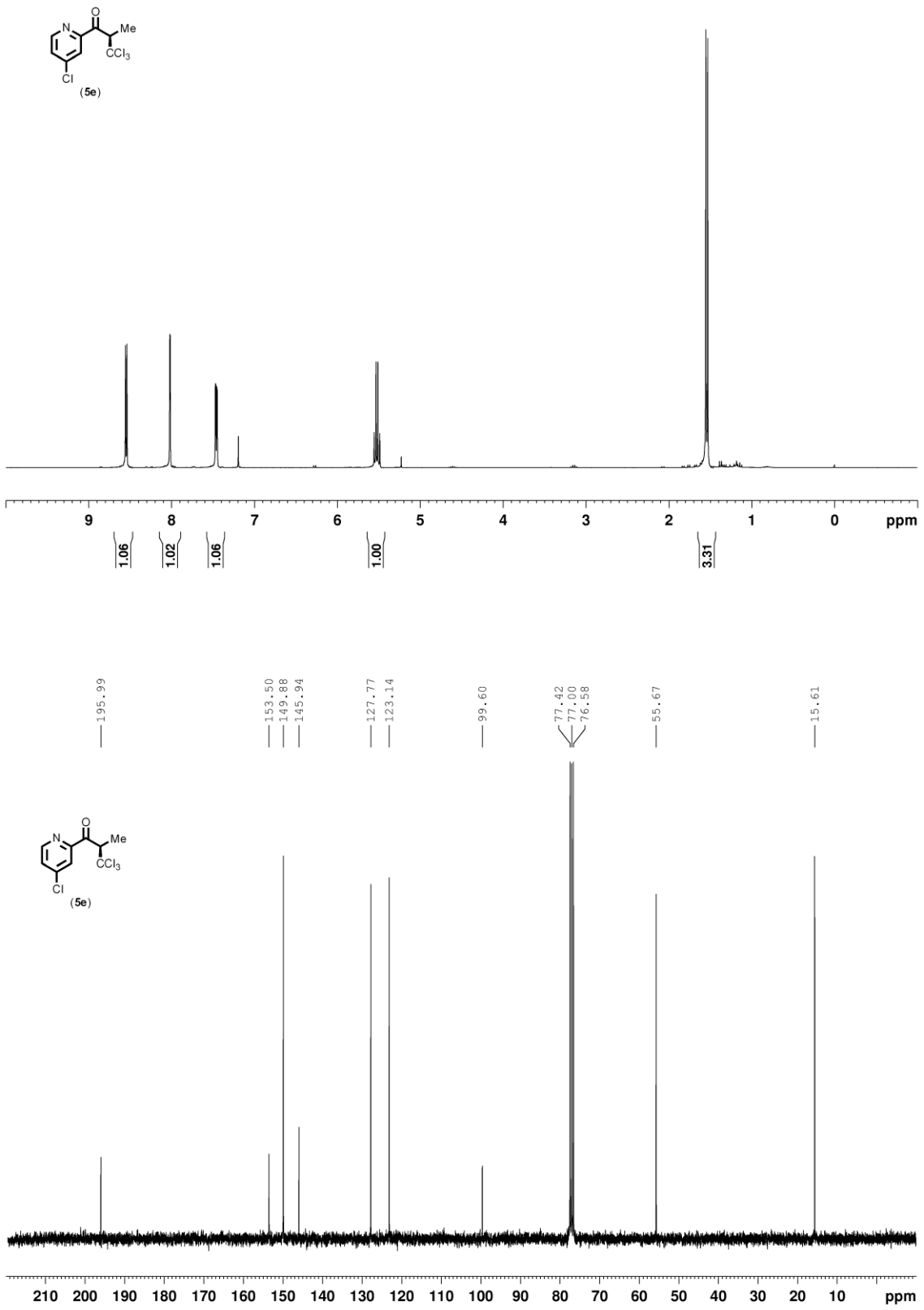


Figure S53. ^{1}H-NMR and ^{13}C-NMR spectrum of **5e**.

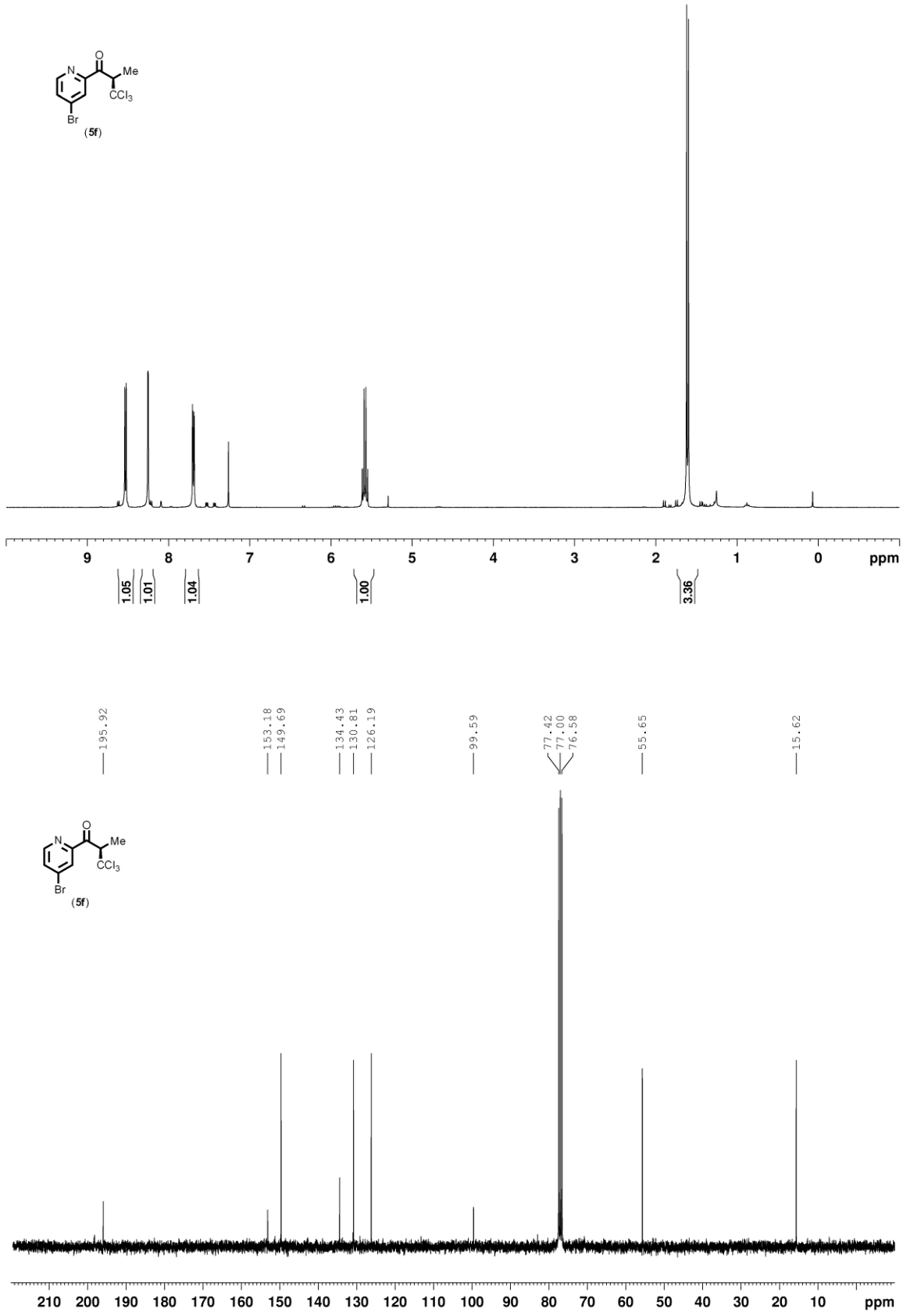


Figure S54. ^{1}H-NMR and ^{13}C-NMR spectrum of **5f**.

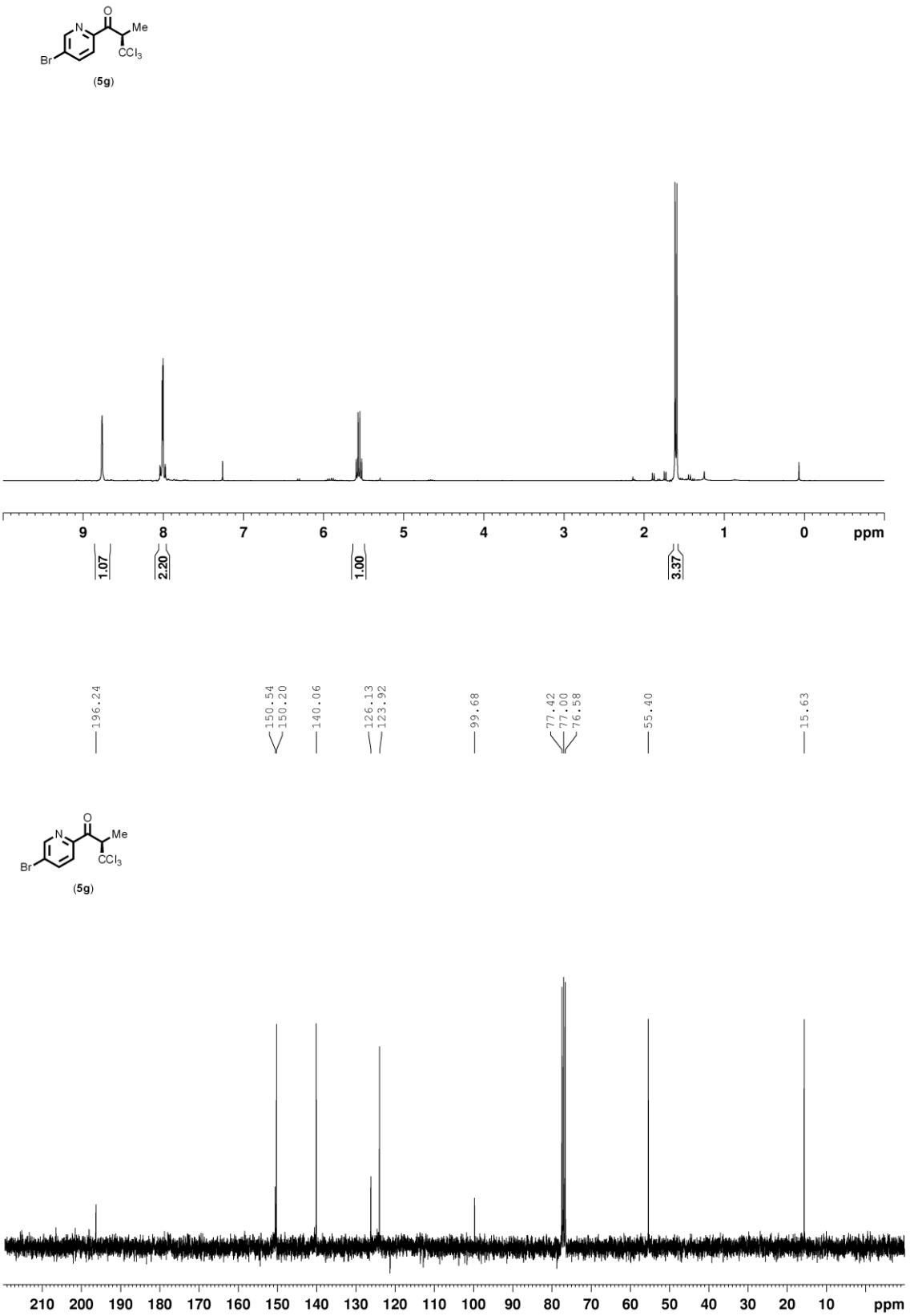


Figure S55. ^{1}H-NMR and ^{13}C-NMR spectrum of **5g**.

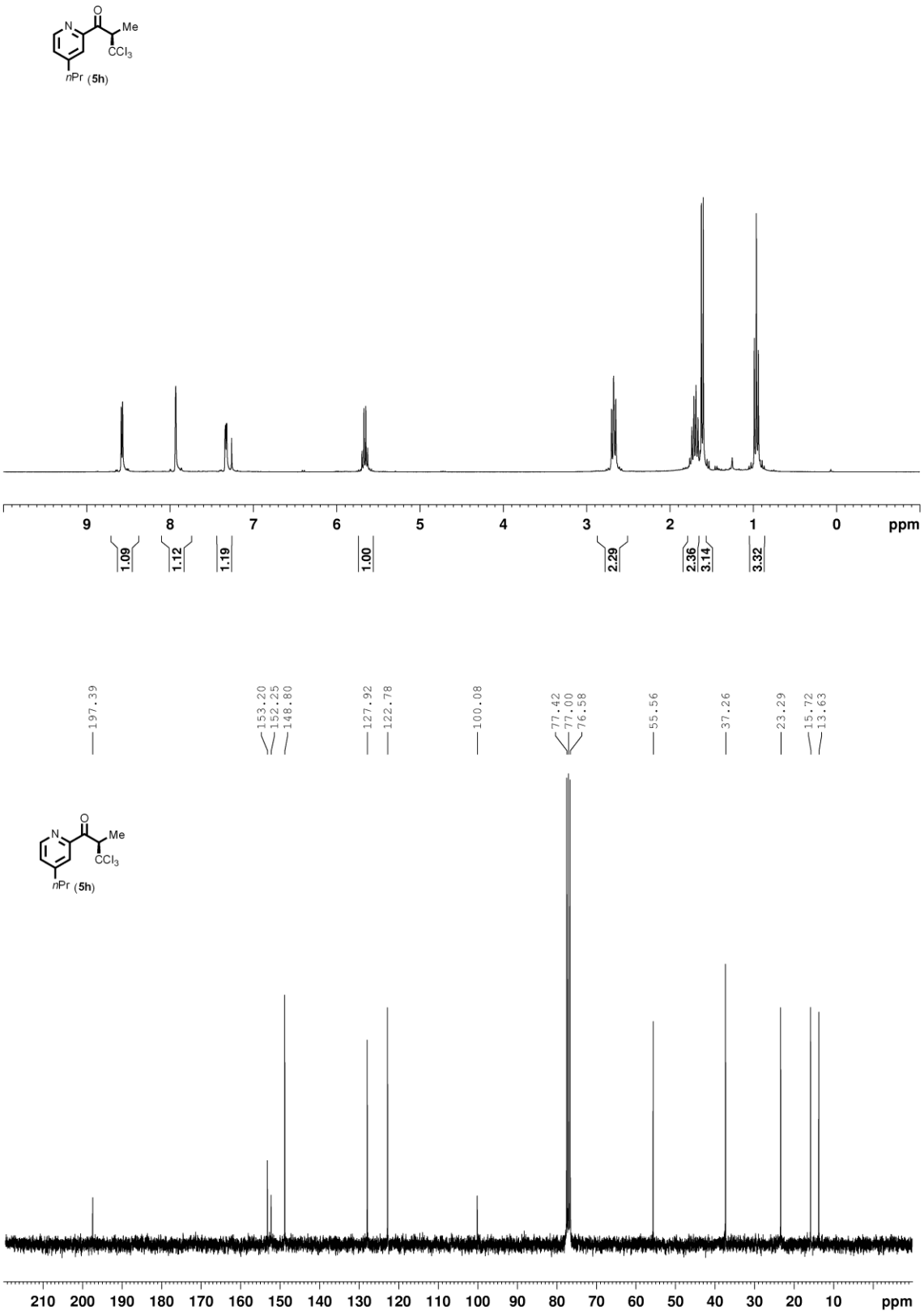


Figure S56. ^{1}H-NMR and ^{13}C-NMR spectrum of **5h**.

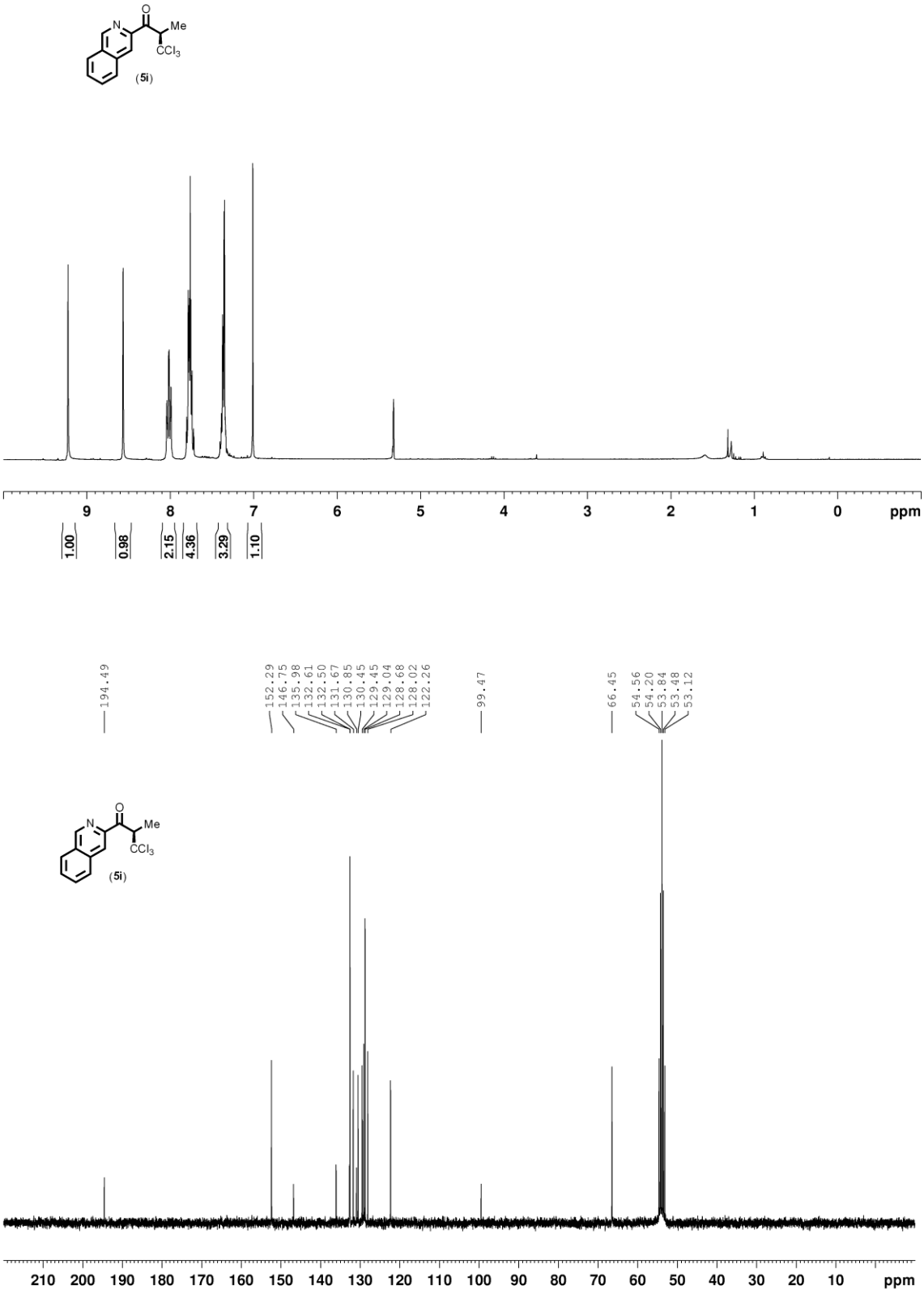


Figure S57. ^{1}H-NMR and ^{13}C-NMR spectrum of **5i**.

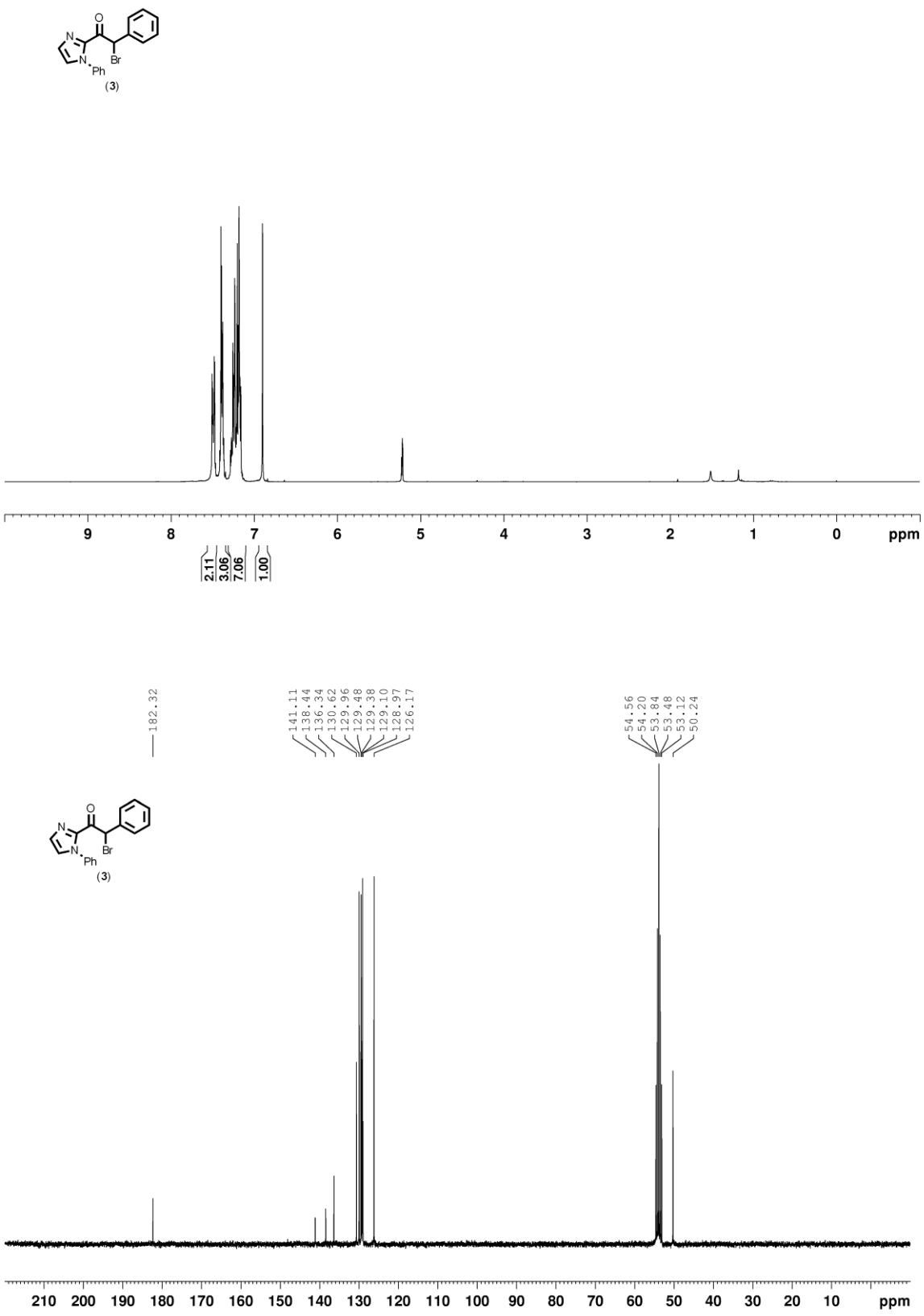


Figure S58. ^{1}H-NMR and ^{13}C-NMR spectrum of **3**.

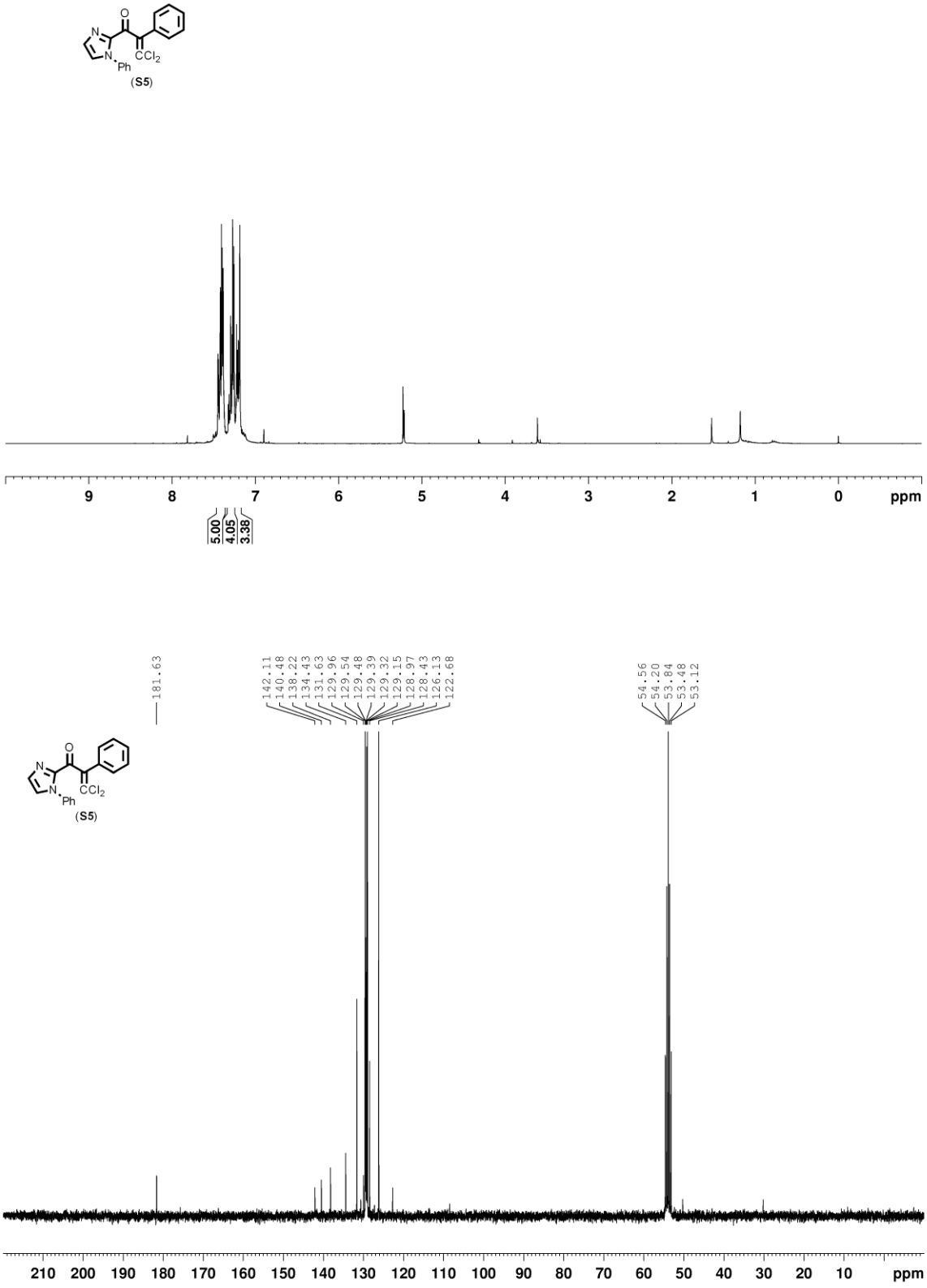


Figure S59. ^{1}H-NMR and ^{13}C-NMR spectrum of **S5**.

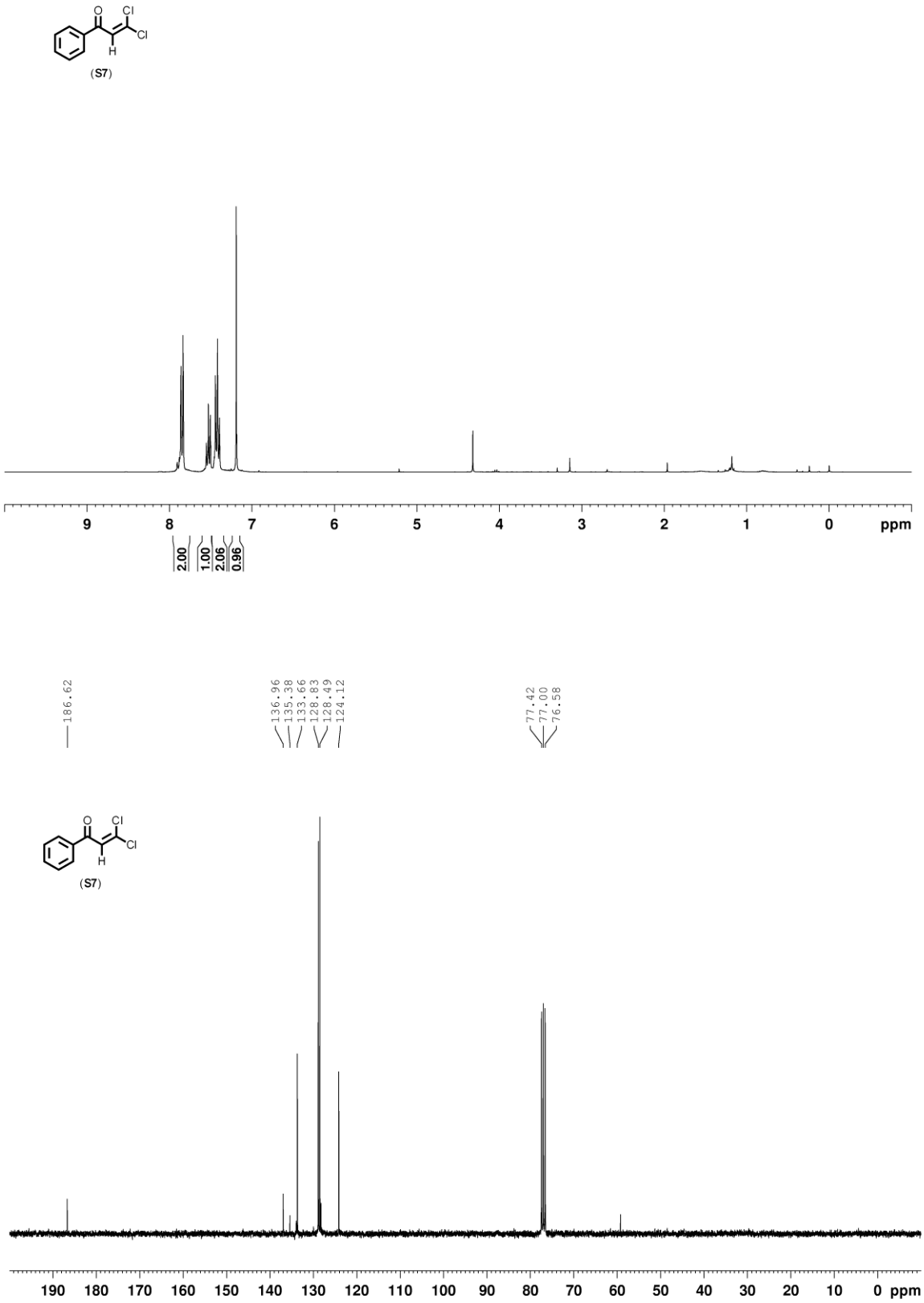


Figure S60. ^{1}H-NMR and ^{13}C-NMR spectrum of **S7**.

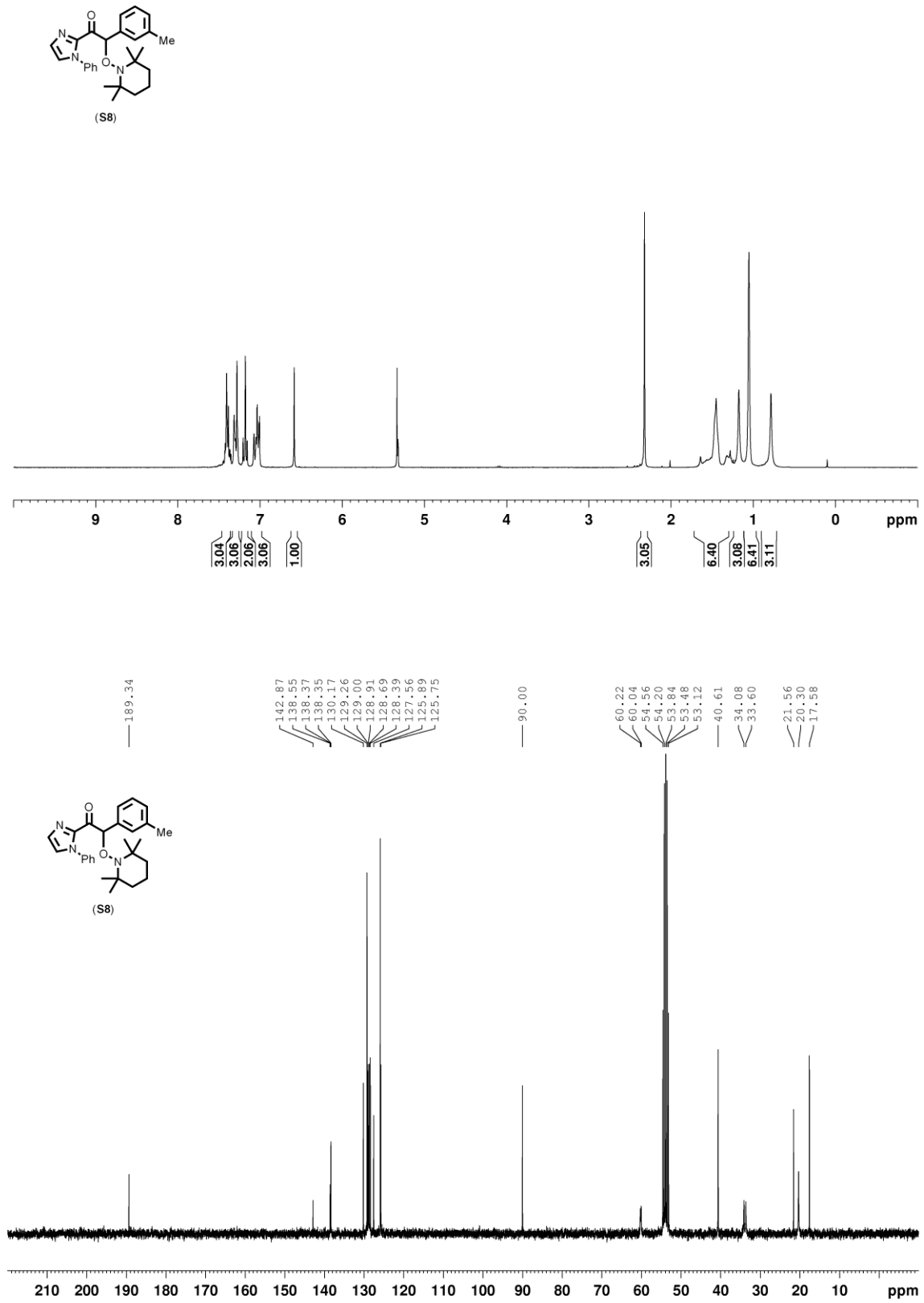


Figure S61. ^{1}H-NMR and ^{13}C-NMR spectrum of **S8**.

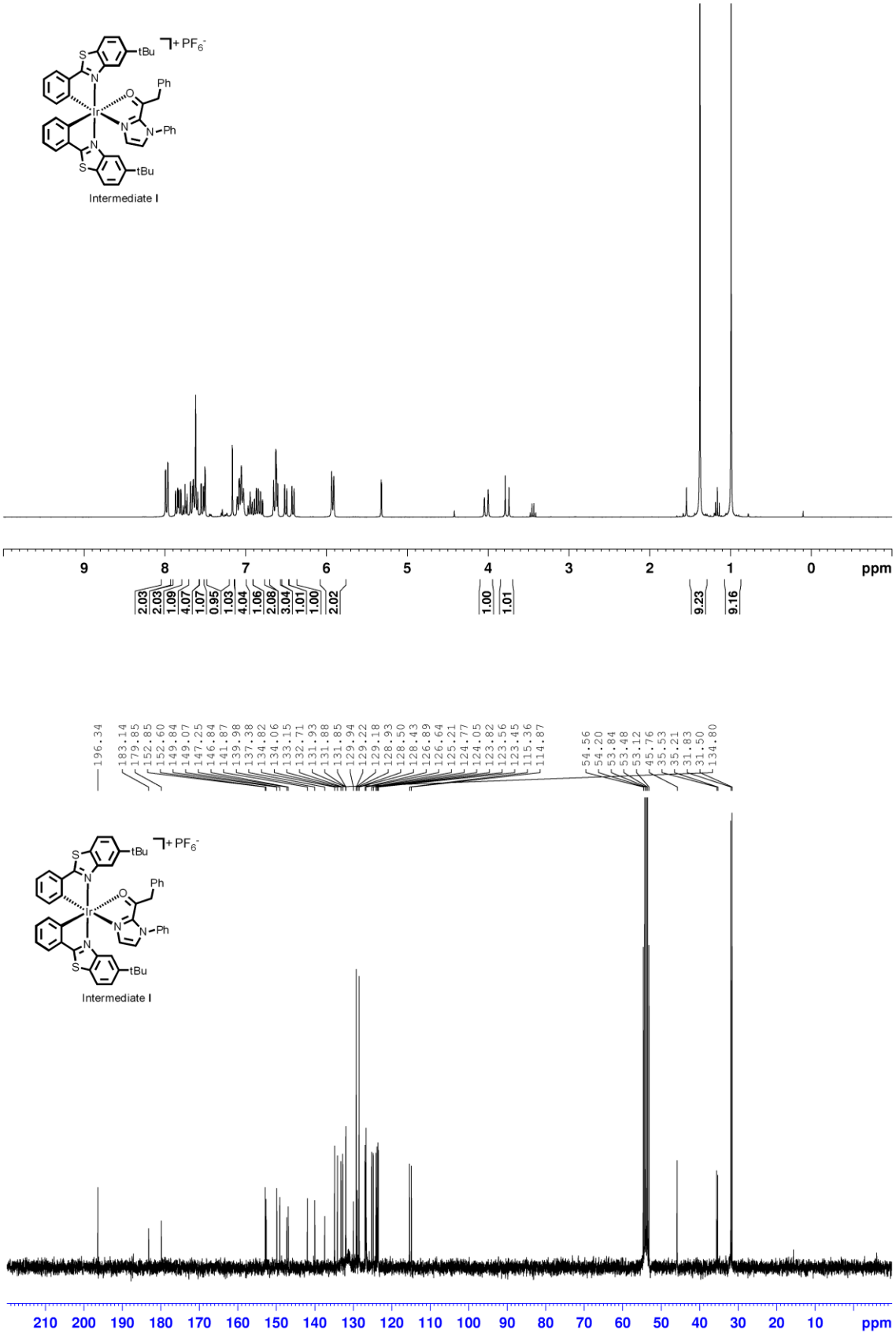


Figure S62. ^{1}H-NMR and ^{13}C-NMR spectrum of **intermediate I**.

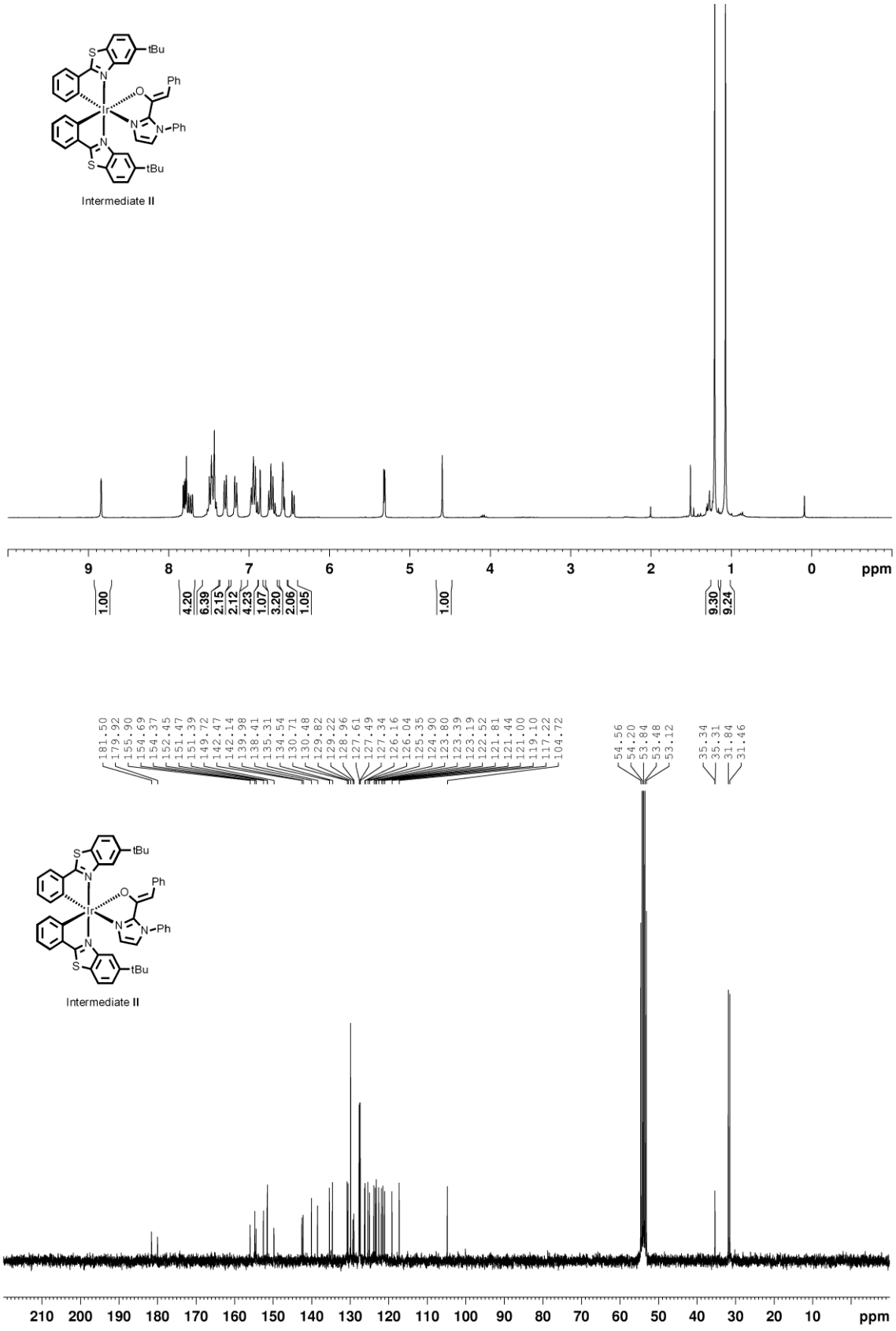


Figure S63. ^{1}H-NMR and ^{13}C-NMR spectrum of **intermediate II**.

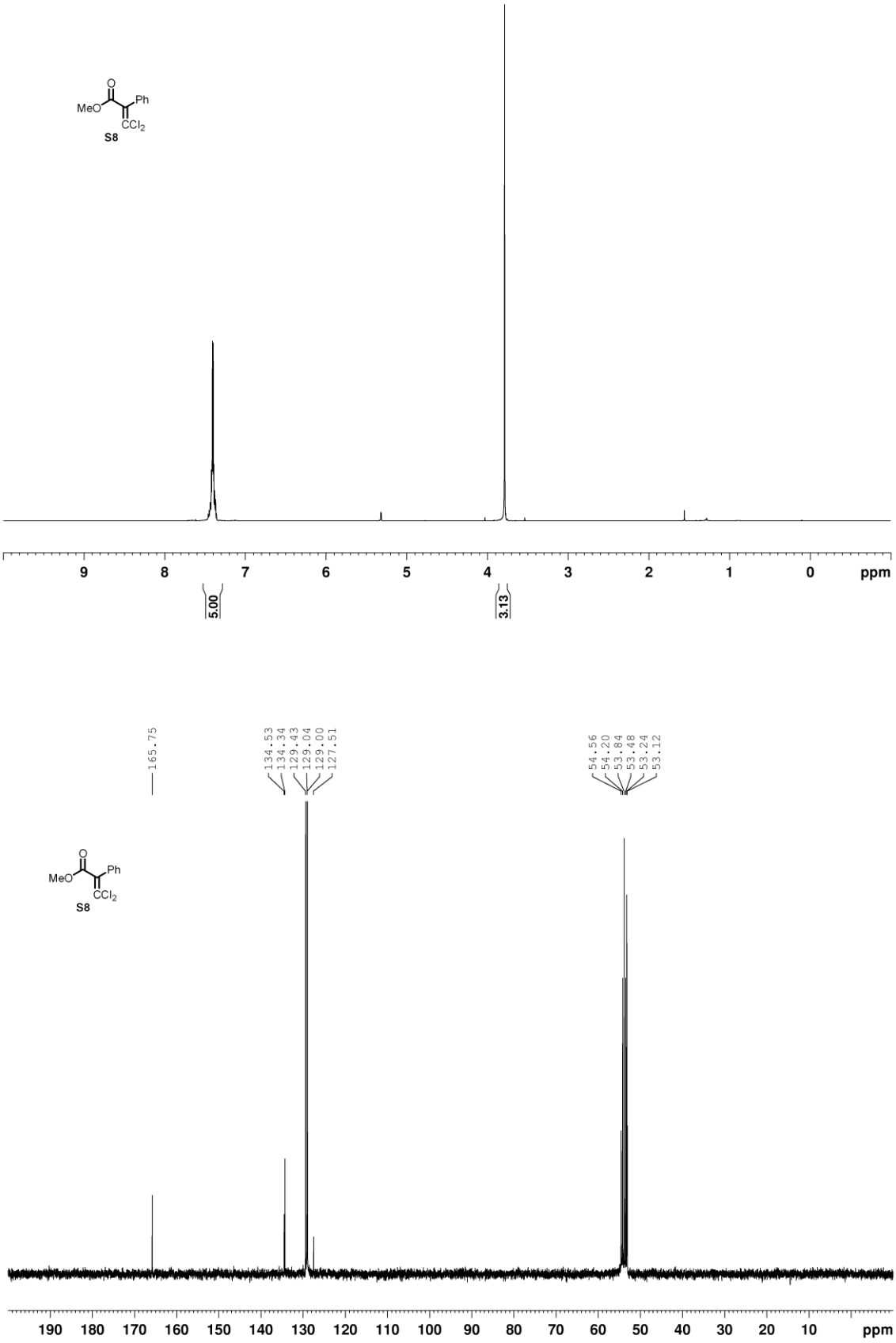


Figure S64. ^{1}H-NMR and ^{13}C-NMR spectrum of **S8**.

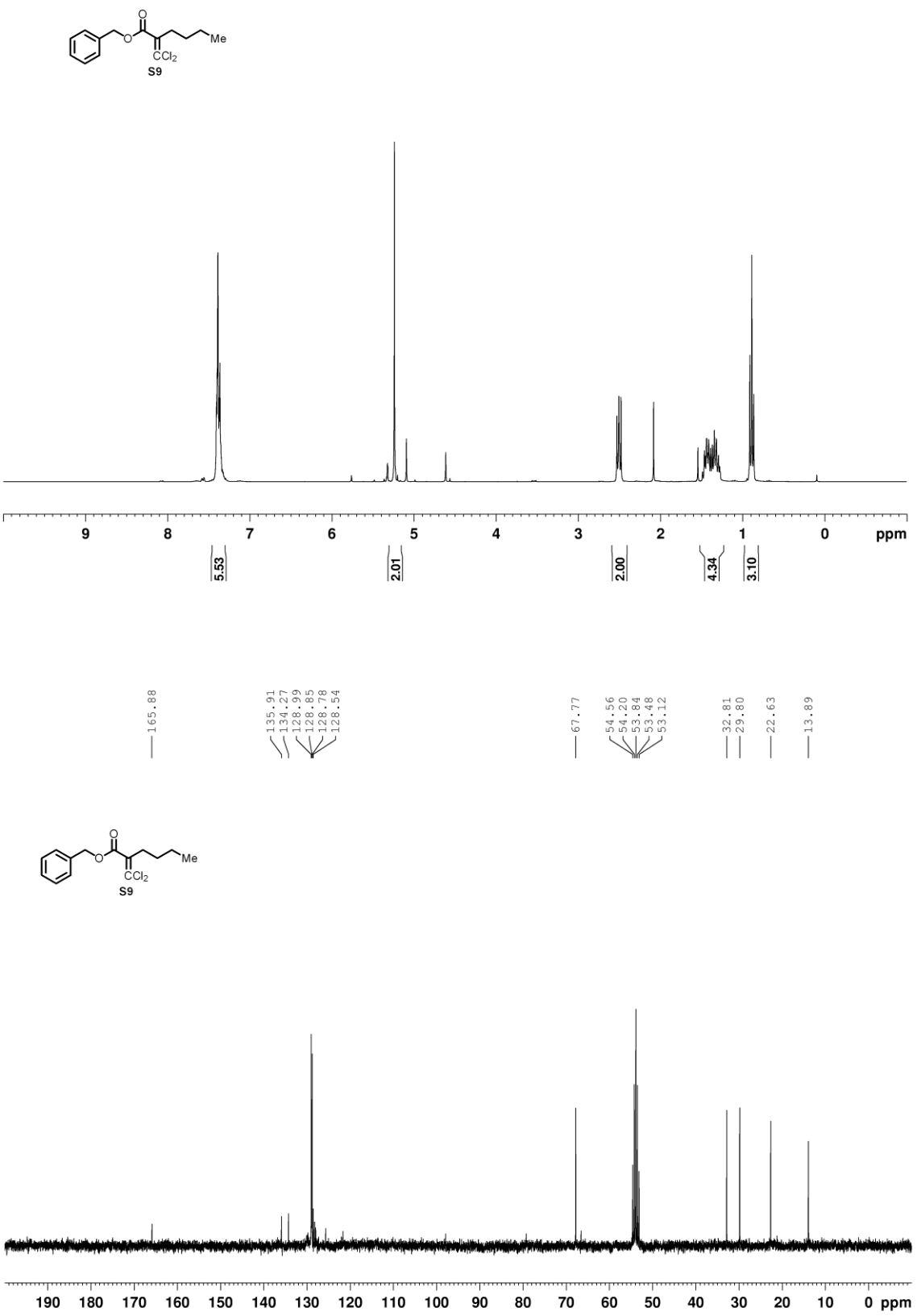


Figure S65. ^{1}H-NMR and ^{13}C-NMR spectrum of **S9**.

8. Single-Crystal X-Ray Diffraction Studies

Single crystals of (*R*)-**2a** (3hnb) suitable for X-ray diffraction were obtained by slow diffusion from a solution of (*R*)-**2a** (30 mg) in CH_2Cl_2 (0.5 mL) layered with *n*-hexane (2.5 mL) at room temperature for several days in a glass tube.

X-ray data were collected with a Bruker 3 circuit D8 Quest diffractometer with MoKa radiation (microfocus tube with multilayer optics) and Photon 100 CMOS detector at 110 K. Scaling and absorption correction was performed by using the SADABS[8] software package of Bruker. Structures were solved using direct methods in SHELXS or SHELXT[9] and refined using the full matrix least squares procedure in SHELXL-2014[10]. The hydrogen atoms were placed in calculated positions and refined as riding on their respective C atom, and Uiso(H) was set at 1.2 Ueq(Csp^2) and 1.5 Ueq(Csp^3). The absolute configurations of compound (*R*)-**2a** (3hnb) has been determined. Crystal data and details of the structure determination are presented in the Supplementary Table S1.

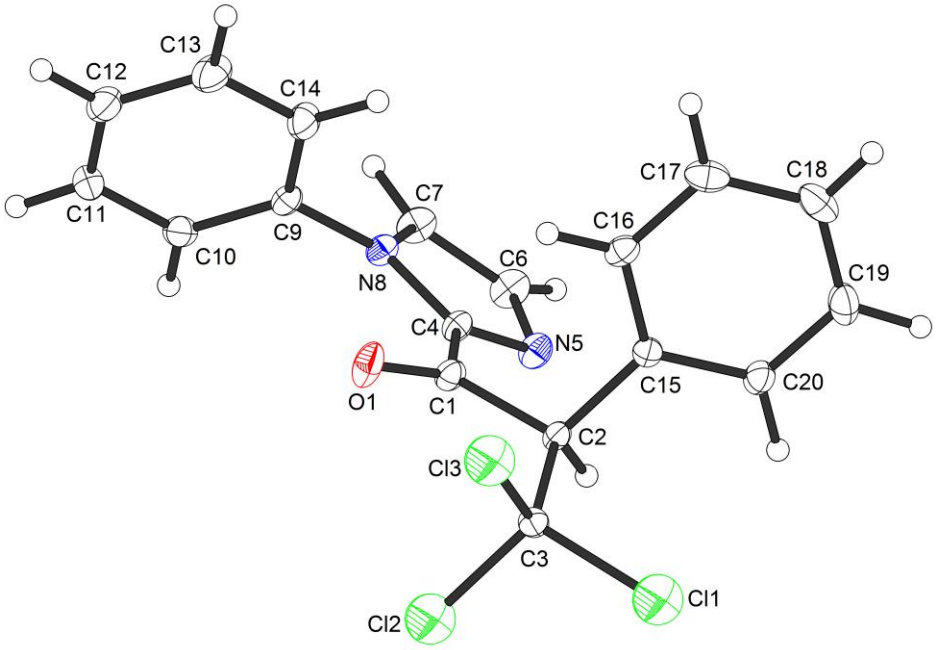


Figure S66. Crystal structure of (*R*)-**2a**. ORTEP drawing with 50% probability thermal ellipsoids. The structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number 1413726.

Table S1. Crystal data and structure refinement for test_0m.

Crystal data

Identification code	test_0m (3hnb)	
Habitus, colour	plate, colourless	
Crystal size	0.35 × 0.23 × 0.05 mm^3	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	Z = 4
Unit cell dimensions	a = 8.5247(3) Å	α= 90°
	b = 9.7490(4) Å	β= 90°
	c = 20.5673(7) Å	γ = 90°
Volume	1709.29(11) $Å^3$	
Cell determination	9868 peaks with Theta 2.3 to 29.6°.	
Empirical formula	C_{18} H_{13} Cl_3 N_2 O	
Moiety formula	C_{18} H_{13} Cl_3 N_2 O	
Formula weight	379.65	
Density (calculated)	1.475 Mg/m^3	
Absorption coefficient	0.543 mm^{-1}	
F(000)	776	

Data collection:

Diffractometer type	Bruker D8 QUEST area detector
Wavelength	0.71073 Å
Temperature	110(2) K
Theta range for data collection	2.312 to 29.602°.
Index ranges	-11<=h<=11, -10<=k<=13, -28<=l<=28
Data collection software	BRUKER APEX2 2014.9-0[11]
Cell refinement software	BRUKER SAINT[12]
Data reduction software	SAINT V8.34A (Bruker AXS Inc., 2013)[12]

Solution and refinement:

Reflections collected	16634
Independent reflections	4796 [R(int) = 0.0228]
Completeness to theta = 25.242°	99.8 %
Observed reflections	4638[I>2sigma(I)]
Reflections used for refinement	4796
Absorption correction	Numerical[8]
Max. and min. transmission	0.97 and 0.79
Flack parameter (absolute struct.)	0.039(11)
Largest diff. peak and hole	0.281 and -0.206 $e.Å^{-3}$
Solution	Direct methods[13]
Refinement	Full-matrix least-squares on F^2 [13]
Treatment of hydrogen atoms	Located, isotropic refinement
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[13,9]
	SHELXL-2014/7 (Sheldrick, 2014)[13,10]
	DIAMOND (Crystal Impact)[14]
Data / restraints / parameters	4796 / 0 / 269
Goodness-of-fit on F^2	1.068
R index (all data)	wR2 = 0.0583
R index conventional [I>2sigma(I)]	R1 = 0.0233

9. References

1. Huo, H.; Fu, C.; Harms, K.; Meggers, E. *J. Am. Chem. Soc.* **2014**, *136*, 2990-2993.

2. (a) Huo, H. H.; Shen, X. D.; Wang, C. Y.; Zhang, L. L.; Rose, P.; Chen, L. A.; Harms, K.; Marsch, M.; Hilt, G.; Meggers, E. *Nature* **2014**, *515*, 100-103. (b) Shen, X.; Huo, H.; Wang, C.; Zhang, B.; Harms, K.; Meggers, E. *Chem. Eur. J.* **2015**, *21*, 9720-9726.

3. Wang, C.; Zheng, Y.; Huo, H.; Rose, P.; Zhang, L.; Harms, K.; Hilt, G.; Meggers, E. *Chem. Eur. J.* **2015**, *21*, 7355-7359.

4. Yang, D.; Li, D.; Wang, L.; Zhao, D.; Wang, R. *J. Org. Chem.* **2015**, *80*, 4336-4348.

5. Easmon, J.; Purstinger, G.; Thies, K. S.; Heinisch, G.; Hofmann, J. *J. Med. Chem.* **2006**, *49*, 6343-6350.

6. Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, DOI: 10.1039/C5SC02185E.

7. Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry* (*Second Edition)*, New York, **1993**.

8. *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, **2014**.

9. Sheldrick, G. M. *SHELXT*, Universität Göttingen, Göttingen, Germany, **2014**.

10. Sheldrick, G. M. *SHELXL*, Universität Göttingen, Göttingen, Germany, **2014**.

11. *APEX2*, Bruker AXS Inc., Madison, Wisconsin, USA, **2014**.

12. *SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA, **2013**.

13. Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112-122.

14. Brandenburg, K. *Diamond - Crystal and Molecular Structure Visualization*, Crystal Impact-Dr. H. Putz & Dr. K. Brandenburg GbR, Bonn, Germany, **2014**.