Supporting Information

Chiral-at-Metal Rh(III) Complex-Catalyzed Asymmetric Conjugate Addition of Unactivated Alkenes with *α,β*-Unsaturated 2-Acyl Imidazoles

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I General Information

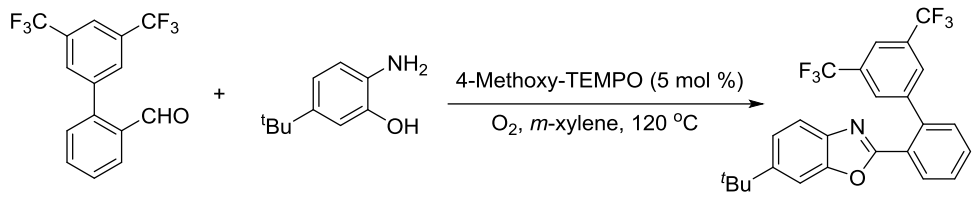
All reactions were performed in Schlenk tubes under an atmosphere of argon using oven-dried glassware. Commercially obtained reagents were used without further purification, unless otherwise noted. Chloroform was distilled over P_2O_5 and stored over 3Å type molecular sieves. THF and toluene were distilled freshly before use over sodium and benzophenone. Acetonitrile (MeCN), Dichloromethane (DCM) and 1,2-dichloroethane (DCE) were distilled from CaH_2. Reactions were checked for completion by TLC analysis and plates were visualized with short-wave UV light (254 nm). The ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ using a Bruker-BioSpin AVANCE III HD NMR spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. Signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in hertz (Hz). HPLC analyses of the compounds were done using chiralcel IA-IF columns using hexane and isopropanol as eluent. The infrared spectra were recorded on a Bruker VERTEX 70 IR spectrometer as KBr pellets, with absorption reported in cm^{-1}. High-resolution mass spectra were recorded on a Bruker Impact II UHR TOF LC/MS Mass Spectrometry. CD spectra were recorded on a MOS-450 circular dichroism spectrometer (600-200 nm, 1 nm bandwidth, 50 nm/min scanning speed, accumulation of 3 scans).

II Experimental Section

Λ-Rh was prepared according to reported procedure.[1] Alkenes **2**[2-3] and *α,β*-unsaturated 2-acyl imidazoles[4] was prepared according to reported procedure.

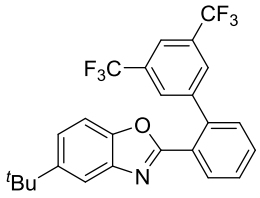
1. Synthesis of chiral catalysts Λ-Rh3.

(i) Synthesis of Ligand L3.



Ligand L3

A solution of 2-amino-4-*tert*-butylphenol (0.825 g, 5.0 mmol) and 3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-carbaldehyde (1.59 g, 5.0 mmol) in *m*-xylene (16.0 mL) was stirred at 120 °C for 30 min. 4-Methoxy-TEMPO (46.5 mg, 5 mol %) was added to the mixture and the reaction was stirred at this temperature for further 8 h under oxygen atmosphere. Then the mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:20) to obtain the product (1.97 g, 85% yield) as a white solid.

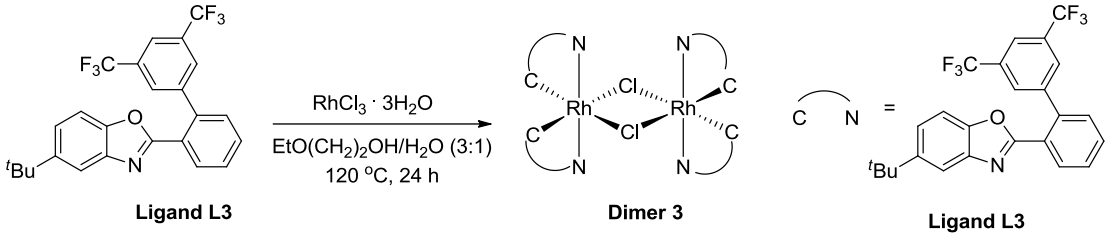


Ligand L3

White solid, mp = 158-160 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30-8.28 (m, 1H), 7.91 (s, 1H), 7.82 (s, 2H), 7.68 (d, *J* = 1.2 Hz, 1H), 7.63-7.57 (m, 2H), 7.45-7.43 (m, 1H), 7.37-7.34 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.2, 148.5, 148.3, 143.1, 141.4, 139.0, 131.3, 131.2, 131.1 (q, *J* = 33.2 Hz), 130.8, 129.6 (q, *J* = 2.7 Hz), 129.0, 126.2, 123.4 (q, *J* = 271.0 Hz), 123.3, 121.1 (q, *J* = 3.9 Hz), 116.7, 109.5, 34.9, 31.7. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = -62.8. IR (KBr): *ν* (cm^{-1}) 3026, 2962, 2870, 1581, 1549, 1481, 1463, 1394, 1380, 1366, 1334,

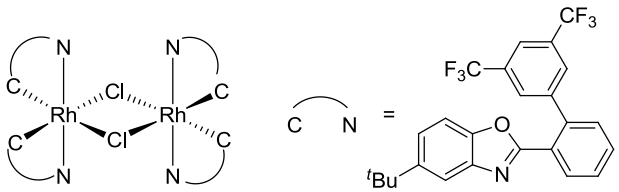
1275, 1179, 1162, 1131, 1115, 1045, 904, 774, 680. HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{20}F_6NO$ $[M+H]^+$: 464.1444, found: 464.1442.

(ii) Synthesis of precursor rhodium complex (Dimer 3):



Ligand L3 Dimer 3 Ligand L3

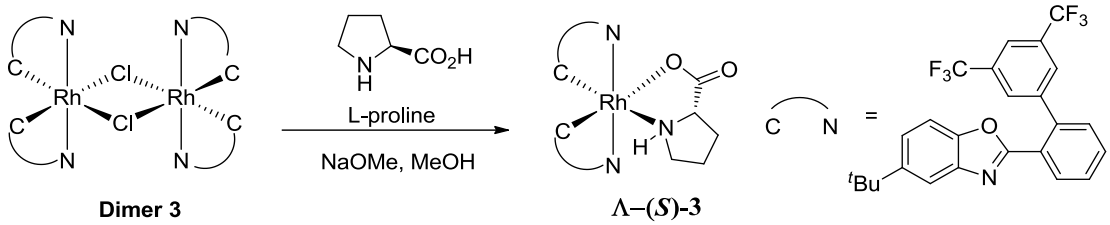
Ligand L3(1.9 g, 4.1 mmol) was added to $RhCl_3$•$3H_2O$ (418.5 mg, 2.0 mmol) in a mixture of 2-ethoxyethanol and water (3:1, 92 mL). The reaction mixture was heated at 120 °C for 24 h under N_2 atmosphere. The resulting precipitate was collected by filtration, washed with methanol and dried to obtain the product **Dimer 3** (1.7 g, 81% yield).



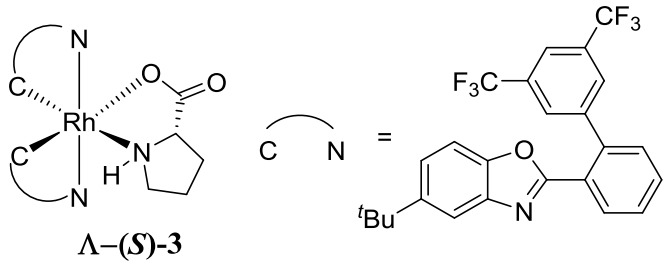
Dimer 3

White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 4H), 7.99 (s, 4H), 7.92 (s, 8H), 7.01 (d, *J* = 8.8 Hz, 4H), 6.91-6.85 (m, 8H), 6.78 (d, *J* = 8.8 Hz, 4H), 6.34 (d, *J* = 7.2 Hz, 4H), 0.88 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 169.0, 167.1, 166.8, 148.5, 147.0, 141.8, 138.3, 137.7, 133.8, 130.3, 127.2, 125.8, 124.2, 123.5 (q, *J* = 271.0 Hz), 121.2 (q, *J* = 4.1 Hz), 121.2 (q, *J* = 3.5 Hz), 115.2, 109.8, 34.7, 31.0. ^{19}F NMR (376.4 MHz, $CDCl_3$) δ = -62.5, -62.7. IR (KBr): *v* (cm^{-1}) 2966, 2908, 2871, 1619, 1606, 1566, 1516, 1483, 1468, 1444, 1414, 1395, 1377, 1355, 1281, 1252, 1178, 1136, 1106, 1057, 933, 900, 846, 806, 710, 682. HRMS (ESI, *m*/z) calcd for $C_{100}H_{72}ClF_{24}N_4O_4Rh_2$: 2090.3042, found: 2090.2991.

(iii) Synthesis of rhodium Auxiliary Complexes Λ-(*S*)-3.



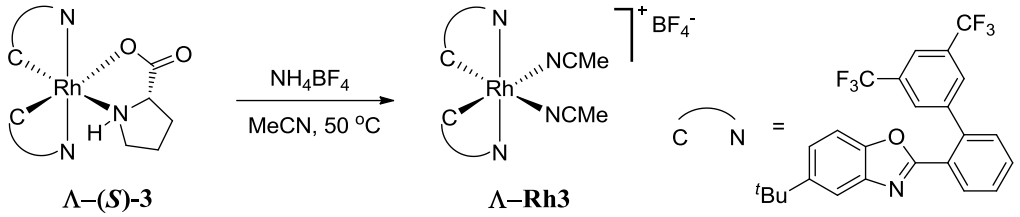
To a solution of NaOMe (230 mg, 2.0 mmol) in methanol (120 mL), L-proline (108 mg, 2.0 mmol) was added in one portion. The mixture was stirred for 10 min, to which a suspension of rhodium dimer (2.08 g, 1.0 mmol) was added. The mixture was stirred and heated at 50 °C for 12 h. After the mixture cooled to room temperature, CH_2Cl_2 (16.0 mL) was added. The reaction mixture was stirred for a further 12 h. The solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (EtOAc/DCM = 1:5) to obtain the product **Λ-(*S*)-3** (752 mg, 33%).



Yellow solid. $[\alpha]_D^{25}$ = + 123.9 (c = 1.0, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 1.2 Hz, 1H), 8.05 (s, 1H), 7.97 (d, *J* = 16.4 Hz, 5H), 7.55-7.52 (m, 2H), 7.33 (t, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 1.2 Hz, 1H), 7.04-6.90 (m, 4H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 4.29-4.24 (m, 1H), 4.07-4.01 (m, 1H), 2.86-2.81 (m, 1H), 2.26-2.21 (m, 2H), 2.09-1.99 (m, 1H), 1.75-1.70 (m, 1H), 1.61-1.49 (m, 1H), 1.40 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.6, 171.5, 171.4,169.9, 169.9, 169.1, 168.8, 168.5, 168.1, 151.5, 150.4, 147.9, 147.9, 142.0, 141.6, 138.7, 138.6, 137.5, 137.1, 135.3, 134.2, 131.3 (q, *J* = 33.1 Hz), 131.0 (q, *J* = 32.5 Hz), 130.5, 130.4, 129.8, 129.8, 127.7, 127.5, 125.9, 125.4, 124.3, 124.2, 123.5 (q, *J* = 271.1 Hz), 123.4 (q, *J* = 271.1 Hz), 121.6 (q, *J* = 3.4 Hz), 121.6 (q, *J* = 4.3 Hz), 121.2 (q, *J* = 4.3 Hz), 121.2 (q, *J* = 3.1 Hz), 115.3, 111.7, 110.6, 110.5, 63.9, 49.4, 35.4, 35.2, 31.7, 31.7, 29.7, 26.9. ^{19}F NMR (376.4 MHz, $CDCl_3$) δ = -62.7. IR (KBr): *v* (cm^{-1}) 1618,

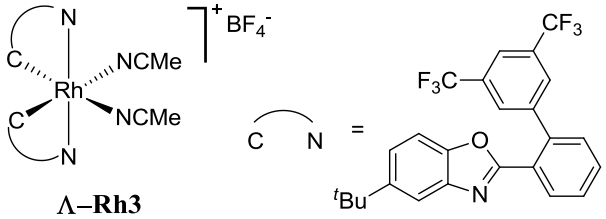
1571, 1560, 1507, 1376, 1363, 1278, 1135, 1057, 709, 682. HRMS (ESI, *m*/*z*) calcd for $C_{55}H_{45}F_{12}N_3O_4Rh$ $[M+H]^+$: 1142.2222, found: 1142.2254.

(iv) Synthesis of Rhodium Catalysts Λ-Rh3.



Λ–(*S*)-3 Λ–Rh3

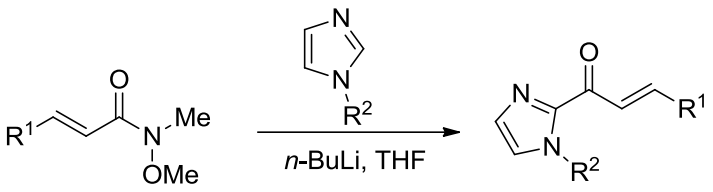
A suspension of the rhodium auxiliary complex **Λ-(*S*)-3** (239.0 mg, 0.28 mmol) and NH_4BF_4 (293.6 mg, 2.80 mmol) in acetonitrile (56.0 mL) was heated at 50 °C for 24 h under nitrogen in the dark. Then removed the solvent under reduced pressure and subjected to flash silica gel chromatography (100% CH_2Cl_2 to CH_2Cl_2/CH_3CN = 10:1) to give the enantiopure catalyst **Λ-Rh3** (127.2 mg, 0.106 mmol, 38%) as a pale yellow solid.



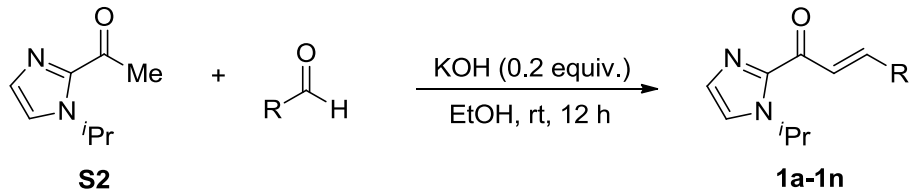
Λ–Rh3

Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-7.90 (m, 8H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.16-6.90 (m, 4H), 6.44 (d, *J* = 7.6 Hz, 2H), 2.40 (d, *J* = 9.6 Hz, 6H), 1.44 (d, *J* = 9.2Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 167.9, 160.8, 160.4, 149.6, 145.8, 139.2, 136.8, 135.0, 131.1, 129.7 (q, *J* = 33.2 Hz), 129.4, 129.4, 128.0, 125.4, 124.9, 123.5, 122.9 (q, *J* = 271.2 Hz), 120.5(q, *J* = 3.4 Hz) , 120.2(q, *J* = 3.6 Hz) , 119.9 (q, *J* = 4.0 Hz), 111.4, 109.4, 33.5, 29.6, 1.4. ^{19}F NMR (376.4 MHz, $CDCl_3$) δ = -62.7, -62.7. IR (KBr): *v* (cm^{-1}) 3056, 2965, 2289, 1620, 1578, 1517, 1378, 1280, 1180, 1135, 1107, 847, 709. HRMS (ESI, *m*/*z*) calcd for $C_{54}H_{42}F_{12}N_4O_2Rh$ $[M]^+$: 1109.2166, found: 1109.2158. CD (MeOH): λ, nm (Δε, M^{-1} cm^{-1}) 402 (- 25), 359 (+ 54), 301 (- 54), 254 (+ 44).

2. Synthesis of substrates

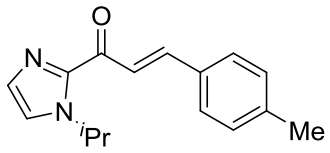


To a solution of *N*-methylimidazole (2.4 mL, 21.4 mmol) or *N*-isopropylimidazole (21.4 mmol) in THF (44.0 mL) at -78 ^{o}C was added *n*-BuLi (8.6 mL, 2.5 M in hexane, 21.4 mmol) drop wise. The reaction was stirred at -78 ^{o}C for 10 min, then stirred at room temperature for 1 h. The Weinreb amide **S1** (2.3 g, 17.8 mmol) was added to the flask after the reaction was cooled back down to -78 ^{o}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 saturated aqueous solution of Na_2CO_3 and extracted with EtOAc (3 × 50 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/Petroleum ether = 1:3) to produce **1**.



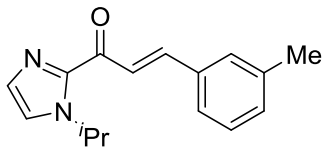
2-Acetyl-1-isopropylimidazole **S2** (10.0 mmol, 1.0 equiv.) and EtOH (20 mL) were added to a 100 mL RBF followed by aromatic aldehyde (10.0 mmol, 1.0 equiv.) and catalytic amount of KOH (0.2 equiv.). The solution was stirred for 12 h then transferred to a separatory funnel. Saturated NaCl (30 mL) and H_2O (10 mL) were added and the mixture was extracted with EtOAc (4 × 75 mL). The combined organic extracts were dried over sodium sulfate, filtered, and concentrated on a rotatory evaporator. The resulting residue was purified by flash column chromatography on silica gel (EtOAc/ Petroleum ether = 1:3).

1a[4a], **1b**[4c], **1c**[4b], **1f**[4c], **1g**[4c], **1i**[4c], **1m**[4c], **1o**[4a], **1p**[4a], **1q**[4c], **1r**[4c], **2**[2-3] were known compounds, and all spectroscopic data were in agreement with literatures.



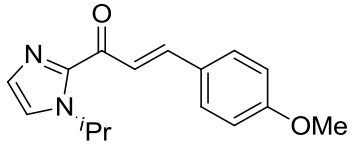
1d

According to the general procedure B, **1d** was obtained as white solid, 1.37 g, 54% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 16.0 Hz, 1H), 7.79 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.31 (s, 1H), 7.25 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.76-5.70 (m, 1H), 2.38 (s, 3H), 1.49 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7, 143.5, 143.3, 140.9, 132.3, 129.7, 129.6, 128.8, 122.5, 121.3, 49.3, 23.7, 21.5. IR (KBr): *v* (cm^{-1}) 3151, 2988, 2960, 1658, 1597, 1567, 1512, 1254, 920, 892, 811, 785, 734. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{18}N_2NaO$ $[M+Na]^+$: 277.1311, found: 277.1310.



1e

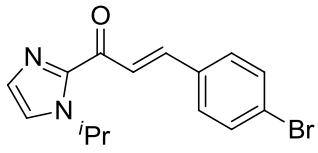
According to the general procedure B, **1e** was obtained as yellow oil, 1.93 g, 76% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 16.0 Hz, 1H), 7.78 (d, *J* = 16.0 Hz, 1H), 7.55(s, 1H), 7.48(d, *J* = 7.6 Hz, 1H), 7.32-7.26 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 1H), 5.77-5.70 (m, 1H), 2.38 (s, 3H), 1.49 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 180.6, 143.4, 138.5, 134.9, 131.3, 129.8, 129.0, 128.7, 126.3, 123.2, 121.4, 49.4, 23.7, 21.3. IR (KBr): *v* (cm^{-1}) 3106, 2981, 2931, 1608, 1464, 1452, 1392, 1016, 919, 864, 848, 837. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{18}N_2NaO$ $[M+Na]^+$: 277.1311, found: 277.1309.



1f

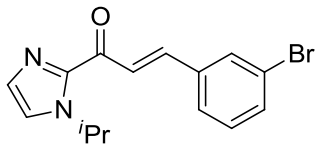
According to the general procedure B, **1f** was obtained as yellow solid, 1.94 g, 72% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 16.0 Hz, 1H), 7.78 (d, *J* = 16.0 Hz,

1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.30 (s, 1H), 7.24 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.77-5.71 (m, 1H), 3.85 (d, *J* = 2.4 Hz, 3H), 1.48 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7, 161.6, 143.5, 143.0, 130.5, 129.6, 127.8, 121.2, 121.2, 114.3, 55.4, 49.3, 23.7. IR (KBr): *v* (cm^{-1}) 3154, 2957, 2833, 1655, 1567, 1511, 1455, 831, 812, 781, 757. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{18}N_2NaO_2$ $[M+Na]^+$: 293.1260, found: 293.1259.



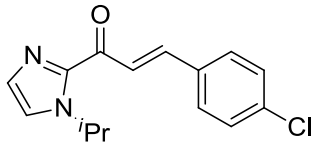
1g

According to the general procedure B, **1g** was obtained as yellow solid, 1.59 g, 50% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 16.0 Hz, 1H), 7.72 (d, *J* = 16.0 Hz, 1H), 7.56-7.51 (m, 4H), 7.33-7.25 (m, 2H), 5.74-5.67 (m, 1H), 1.50-1.48 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.2, 143.3, 141.6, 134.0, 132.1, 130.0, 129.9, 124.6, 124.2, 121.6, 49.4, 23.7. IR (KBr): *v* (cm^{-1}) 3146, 3078, 3034, 2983, 1655, 1586, 1564, 997, 947, 830, 817, 765. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{16}BrN_2O$ $[M+H]^+$: 319.0441, found: 319.0443.



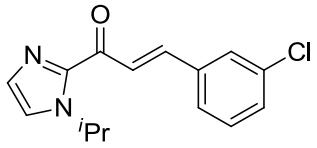
1h

According to the general procedure B, **1h** was obtained as yellow oil, 2.06 g, 65% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13-8.08 (m, 1H), 7.85 (t, *J* = 2.0 Hz, 1H), 7.73-7.67 (m, 1H), 7.57 (d, *J* = 6.4 Hz, 1H), 7.48 (d, *J* = 6.0 Hz, 1H), 7.33-7.23 (m, 3H), 5.74-5.66 (m, 1H), 1.50-1.47 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.0, 143.2, 141.1, 137.1, 133.0, 131.1, 130.3, 129.9, 127.4, 124.8, 123.0, 121.7, 49.4, 23.6. IR (KBr): *v* (cm^{-1}) 2981, 2932, 1605, 1559, 1255, 1198, 1011, 806, 784, 745. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{15}BrN_2NaO$ $[M+Na]^+$: 341.0260, found: 341.0257.



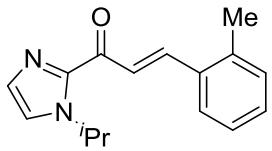
1i

According to the general procedure B, **1i** was obtained as white solid, 1.5 g, 55% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 16.0 Hz, 1H), 7.74 (d, *J* = 16.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.38-7.25 (m, 4H), 5.75-5.68 (m, 1H), 1.49 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.3, 143.3, 141.6, 136.2, 133.5, 129.9, 129.8, 129.1, 124.0, 121.6, 49.4, 23.7. IR (KBr): *v* (cm^{-1}) 3080, 2986, 1655, 1566, 1165, 919, 877, 820, 751, 645. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{15}ClN_2NaO$ $[M+Na]^+$: 297.0765, found: 297.0764.



1j

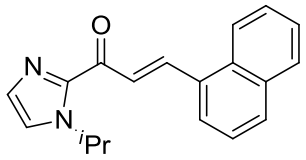
According to the general procedure B, **1j** was obtained as white solid, 1.2 g, 43% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14-8.08 (m, 1H), 7.74-7.67 (m, 2H), 7.55-7.51 (m, 1H), 7.37-7.24 (m, 4H), 5.74-5.67 (m, 1H), 1.50-1.45 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.1, 143.2, 141.3, 141.3, 136.9, 134.9, 130.1, 130.0, 130.0, 128.2, 126.9, 124.9, 121.7, 49.4, 23.7. IR (KBr): *v* (cm^{-1}) 3141, 3070, 2977, 1658, 1600, 1254, 1200, 915, 813, 745. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{16}ClN_2O$ $[M+H]^+$: 275.0946, found: 275.0948.



1k

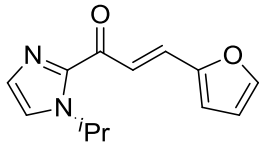
According to the general procedure B, **1k** was obtained as white solid, 1.6 g, 63% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16-8.04 (m, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.32-7.20 (m, 5H), 5.76-5.70 (m, 1H), 2.50 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7, 143.4, 140.6, 138.3, 133.8, 130.8, 130.2, 129.9, 126.8, 126.3, 124.4, 121.4, 49.4, 23.7, 19.8. IR (KBr): *v* (cm^{-1}) 3155, 3098, 2965,

1659, 1596, 1452, 1218, 1074, 921, 856, 774. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{18}N_2NaO$ $[M+Na]^+$: 277.1311, found: 277.1311.



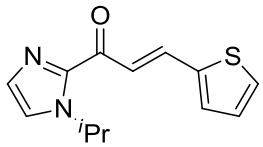
1l

According to the general procedure B, **1l** was obtained as yellow oil, 1.4 g, 49% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 15.6 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 15.6 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.89 (t, *J* = 9.2 Hz, 2H), 7.60-7.49 (m, 3H), 7.33 (s, 1H), 7.27 (s, 1H), 5.80-5.74 (m, 1H), 1.52 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 180.5, 143.4, 139.8, 133.8, 132.2, 131.9, 130.7, 129.9, 128.8, 126.8, 126.1, 125.9, 125.5, 125.5, 123.5, 121.5, 49.5, 23.7. IR (KBr): *v* (cm^{-1}) 3136, 2975, 2931, 1649, 1594, 1572, 1020, 1006, 798, 786, 774. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{18}N_2NaO$ $[M+Na]^+$: 313.1311, found: 313.1310.



1m

According to the general procedure B, **1m** was obtained as brown solid, 1.9 g, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 15.6 Hz, 1H), 7.59-7.51 (m, 2H), 7.31 (s, 1H), 7.23(s, 1H), 6.73(d, *J* = 3.2 Hz, 1H), 6.49-6.48 (m, 1H), 5.74-5.68 (m, 1H), 1.48-1.46 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.4, 152.0, 144.9, 143.3, 129.8, 129.2, 121.6, 121.3, 115.4, 112.5, 49.2, 23.6. IR (KBr): *v* (cm^{-1}) 3102, 2981, 1662, 1552, 1007, 980, 930, 922, 881, 700. HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{14}N_2NaO_2$ $[M+Na]^+$: 253.0947, found: 253.0946.



1n

According to the general procedure B, **1n** was obtained as yellow solid, 1.5 g, 60% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.87 (m, 2H), 7.41-7.25 (m, 4H), 7.07 (s,

1H), 5.74-5.68 (m, 1H), 1.48 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.2, 143.3, 140.7, 135.6, 131.7, 129.8, 129.0, 128.2, 122.5, 121.4, 49.3, 23.7. IR (KBr): ν (cm^{-1}) 3150, 3117, 2980, 1651, 1587, 1515, 966, 919, 837, 770, 743, 716. HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{14}N_2NaOS$ $[M+Na]^+$: 269.0719, found: 269.0719.

3. Substrate Scope

(i) General procedure C for chiral-at-metal rhodium complex catalyzed asymmetric conjugate addition of alkenes with *α,β*-unsaturated 2‐acyl imidazoles.

To an oven-dried 25 mL Schlenk tube equipped with a stir bar, **Λ-Rh3** (1 mol %) was added along with *α,β*-unsaturated 2-acyl imidazole **1** (0.25 mmol), alkene **2** (0.3 mmol) and DCE (0.5 mL). The reaction was stirring at 30℃ until consumption of the 2-acyl imidazole as monitored by thin layer chromatography. The solution directly purified by silica gel column chromatography (EtOAc/Petroleum ether = 1:4) to afford desired adducts **3**.

(**ii**) **According to the general procedure D for hydrogenation reduction of 3k.**

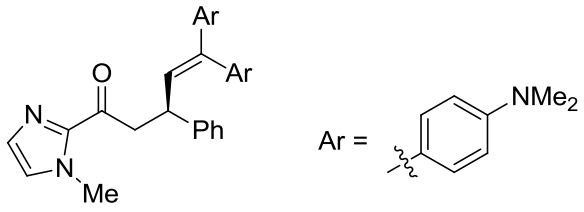
To an oven-dried 25 mL Schlenk tube equipped with a stir bar, **3k** (after recrystallization, ee % > 99%, 0.25 mmol) and 5mol % Pd/C (133 mg) in MeOH (2 ml) at 30 ºC for 23 h under H_2 atmosphere. The solution directly purified by silica gel column chromatography (EtOAc/Petroleum ether = 1:4) to afford desired adduct **4**.

(iii) General procedure for gram-scale experiments with lower catalyst loading.

To an oven-dried 50 mL Schlenk tube equipped with a stir bar, **Λ-Rh3** (1 mol %) was added along with *α,β*-unsaturated 2-acyl imidazole **1k** (3.5 mmol), alkene **2a** (4.2 mmol) and DCE (7 mL). The reaction was stirring at 30℃ for 4 h. The solution directly purified by silica gel column chromatography (EtOAc/Petroleum ether = 1:4) to afford desired adduct **3k**.

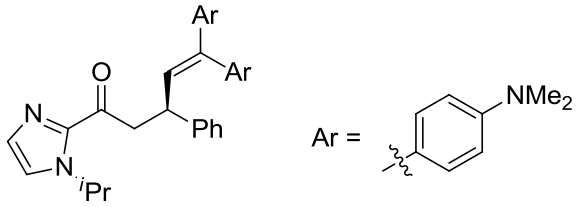
To an oven-dried 50 mL Schlenk tube equipped with a stir bar, **Λ-Rh3** (0.05 mol %) was added along with *α,β*-unsaturated 2-acyl imidazole **1k** (3.93 mmol), alkene **2a**

(4.7 mmol) and DCE (4 mL). The reaction was stirring at 30℃ for 72 h. The solution directly purified by silica gel column chromatography (EtOAc/Petroleum ether = 1:4) to afford desired adduct **3k**.



3a

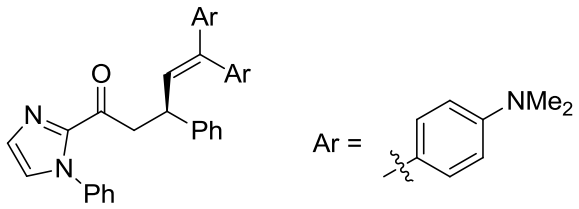
According to the general procedure C, **3a** was obtained as yellow oil, 104 mg, 87% yield, 92% ee, $[\alpha]_D^{25}$ = + 95.8 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, t_{major} = 30.88 min, t_{minor} = 35.18 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H) 7.14 (t, *J* = 7.2 Hz, 1H), 7.08 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.92 (t, *J* = 6.0 Hz, 3H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 6.08 (d, *J* = 10.4 Hz, 1H), 4.28-4.22 (m, 1H), 3.85 (s, 3H), 3.61-3.49 (m, 2H), 2.96 (s, 6H), 2.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 149.7, 149.5, 145.0, 143.4, 141.4, 131.7, 130.6, 128.9, 128.4, 128.4, 128.3, 127.6, 127.3, 126.7, 126.0, 112.1, 112.0, 46.4, 41.7, 40.7, 40.6, 36.1. IR (KBr): *v* (cm^{-1}) 2962, 1674, 1608, 1521, 1407, 1261, 1224, 1192, 1028, 819. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{35}N_4O$ $[M+H]^+$: 479.2805, found: 479.2804.



3b

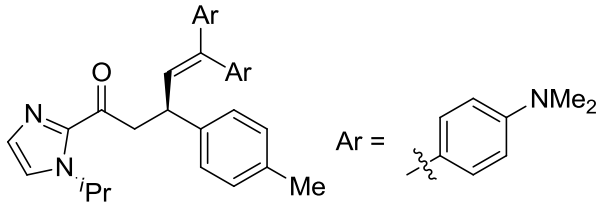
According to the general procedure C, **3b** was obtained as white solid, 118 mg, 93% yield, 95% ee, $[\alpha]_D^{25}$ = + 131.7 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, t_{major} = 30.92 min, t_{minor} = 25.87 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 7.2 Hz, 2H), 7.27-7.23 (m, 2H), 7.19 (d, *J* = 0.4 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8Hz, 2H), 6.09 (d, *J* = 10.4 Hz, 1H), 5.45-5.38 (m, 1H), 4.28-4.22 (m, 1H), 3.57

(d, *J* = 7.6 Hz, 2H), 2.96 (s, 6H), 2.89 (s, 6H), 1.32 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 149.7, 149.5, 145.1, 142.8, 141.4, 131.8, 130.7, 129.4, 128.4, 128.4, 127.6, 127.4, 125.9, 120.9, 112.1, 112.0, 49.0, 47.0, 42.0, 40.7, 40.6, 23.7, 23.5. IR (KBr): *v* (cm^{-1}) 2964, 2800, 1672, 1609, 1522, 1395, 1224, 1192, 947, 819, 701. HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{39}N_4O$ $[M+H]^+$: 507.3118, found: 507.3121.



3c

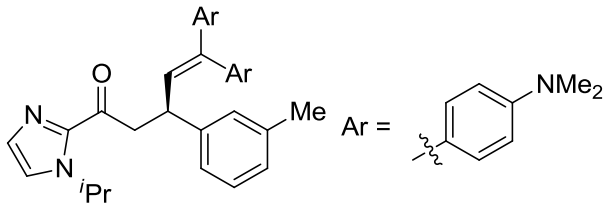
According to the general procedure C, **3c** was obtained as yellow oil, 122 mg, 90% yield, 86% ee, $[\alpha]_D^{25}$ = + 69.2 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, t_{major} = 42.55 min, t_{minor} = 36.63 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.23 (m, 8H), 7.15 (t, *J* = 6.8 Hz, 1H), 7.10 (s, 1H), 7.07-7.01 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.64-6.57 (m, 4H), 6.12 (d, *J* = 10.4 Hz, 1H), 4.28-4.21 (m, 1H), 3.63-3.58 (m, 1H), 3.47-3.42 (m, 1H), 2.94 (s, 6H), 2.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.9, 149.8, 149.5, 145.0, 143.4, 141.6, 138.3, 131.6, 130.6, 129.5, 128.9, 128.5, 128.2, 127.7, 127.1, 126.7, 126.0, 125.7, 112.1, 112.0, 46.9, 42.2, 40.7. IR (KBr): *v* (cm^{-1}) 2963, 2853, 2799, 1683, 1608, 1521, 1193, 1150, 948, 819, 763. HRMS (ESI, *m*/*z*) calcd for $C_{36}H_{37}N_4O$ $[M+H]^+$: 541.2962, found: 541.2962.



3d

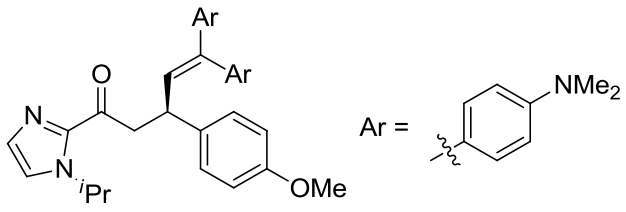
According to the general procedure C, **3d** was obtained as yellow oil, 124 mg, 95% yield, 93% ee, $[\alpha]_D^{25}$ = + 72.0 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 75/25, flow rate 1.0 mL/min,

t_{major} = 9.15 min, t_{minor} = 7.93 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.0 Hz, 3H), 7.14 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 6.07 (d, *J* = 10.4 Hz, 1H), 5.45-5.38 (m, 1H), 4.25-4.18 (m, 1H), 3.60-3.49 (m, 2H), 2.96 (s, 6H), 2.89 (s, 6H), 2.28 (s, 3H), 1.33-1.31 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 149.7, 149.4, 142.8, 142.1, 141.1, 135.3, 131.9, 130.7, 129.4, 129.1, 128.5, 128.4, 127.6, 127.4, 120.8, 112.0, 112.0, 49.0, 47.1, 41.6, 40.7, 40.6, 23.7, 23.5, 21.1. IR (KBr): *v* (cm^{-1}) 2964, 2924, 1673, 1609, 1521, 1397, 1261, 1093, 817. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{41}N_4O$ $[M+H]^+$: 521.3275, found: 521.3277.



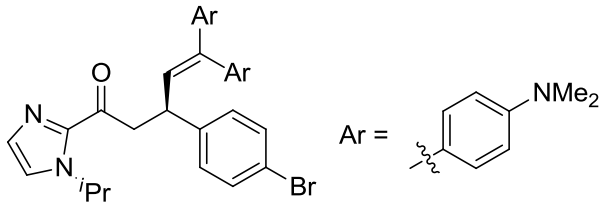
3e

According to the general procedure C, **3e** was obtained as brown solid, 122 mg, 94% yield, 90% ee, $[\alpha]_D^{25}$ = + 138.9 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, t_{major} = 25.62 min, t_{minor} = 20.59 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (s, 1H), 7.16-7.09 (m, 4H), 7.00-6.92 (m, 5H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 6.09 (d, *J* = 10.4 Hz, 1H), 5.45-5.38 (m, 1H), 4.25-4.18 (m, 1H), 3.61-3.49 (m, 2H), 2.96 (s, 6H), 2.88 (s, 6H), 2.29 (s, 3H), 1.32 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 149.7, 149.5, 145.1, 142.8, 141.3, 137.9, 131.9, 130.7, 129.4, 128.5, 128.4, 128.3, 128.3, 127.5, 126.7, 124.7, 120.8, 112.1, 112.0, 49.0, 47.2, 42.0, 40.7, 40.6, 23.7, 23.5, 21.6. IR (KBr): *v* (cm^{-1}) 2884, 2799, 1672, 1608, 1521, 1395, 1351, 947, 820, 706. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{41}N_4O$ $[M+H]^+$: 521.3275, found: 521.3279.



3f

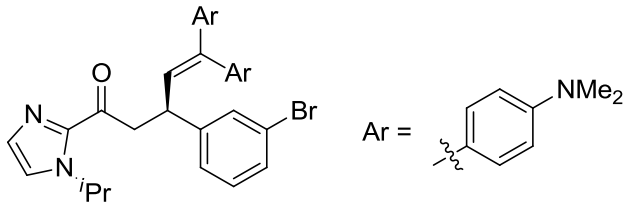
According to the general procedure C, **3f** was obtained as yellow oil, 107 mg, 80% yield, 87% ee, $[\alpha]_D^{25}$ = + 63.6 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, t_{major} = 34.16 min, t_{minor} = 39.30 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.19 (m, 3H), 7.14 (s, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 6.07 (d, *J* = 10.4 Hz, 1H), 5.45-5.38 (m, 1H), 4.24-4.17 (m, 1H), 3.75 (s, 3H), 3.53 (d, *J* = 7.6 Hz, 2H), 2.96 (s, 6H), 2.88 (s, 6H), 1.32 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 157.7, 149.7, 149.4, 142.8, 141.1, 137.3, 131.8, 130.6, 129.4, 128.5, 128.4, 127.6, 120.9, 113.8, 112.1, 112.0, 55.2, 49.0, 47.2, 41.2, 40.7, 40.6, 23.7, 23.5. IR (KBr): *v* (cm^{-1}) 2963, 2800, 1672, 1609, 1396, 1351, 1258, 1091, 1032, 818. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{41}N_4O_2$ $[M+H]^+$: 537.3224, found: 537.3224.



3g

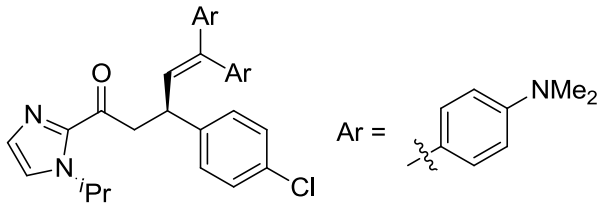
According to the general procedure C, **3g** was obtained as yellow oil, 139 mg, 95% yield, 93% ee, $[\alpha]_D^{25}$ = + 99.5 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, t_{major} = 11.80 min, t_{minor} = 17.33 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.4 Hz, 2H), 7.21 (s, 1H), 7.15 (t, *J* = 5.6 Hz, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 6.03 (d, *J* = 10.0 Hz, 1H), 5.44-5.37 (m, 1H), 4.23-4.17 (m, 1H), 3.58-3.51 (m, 2H), 2.97 (s, 6H), 2.90 (s, 6H), 1.33 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0, 149.8, 149.5,

144.3, 142.6, 142.0, 131.4, 130.5, 129.5, 129.4, 128.4, 128.2, 126.5, 121.0, 119.6, 112.1, 112.0, 49.1, 46.7, 41.3, 40.6, 40.6, 23.7, 23.5. IR (KBr): *v* (cm^{-1}) 2964, 2800, 1672, 1608, 1521, 1394, 1352, 1261, 948, 818. HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{38}BrN_4O$ $[M+H]^+$: 585.2224, found: 585.2227.



3h

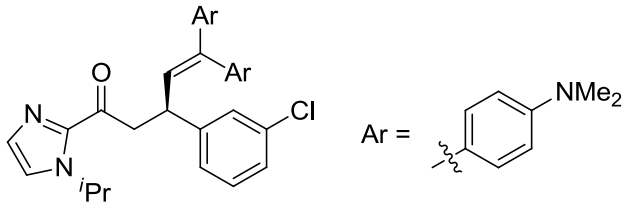
According to the general procedure C, **3h** was obtained as brown oil, 126 mg, 86% yield, 94% ee, $[\alpha]_D^{25}$ = + 91.5 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IE, λ = 254 nm, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, t_{major} = 12.62 min, t_{minor} = 14.50 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (t, *J* = 1.6 Hz, 1H), 7.27-7.25 (m, 1H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.14-7.09 (m, 2H), 7.02-7.00 (m, 2H), 6.91-6.89 (m, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.58 (t, *J* = 4.4 Hz, 2H), 6.04 (d, *J* = 10.4 Hz, 1H), 5.45-5.38 (m, 1H), 4.24-4.17 (m, 1H), 3.55-3.53 (m, 2H), 2.97 (s, 6H), 2.90 (s, 6H), 1.34 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 149.8, 149.5, 147.6, 142.6, 142.3, 131.4, 130.7, 130.5, 129.9, 129.5, 129.0, 128.3, 128.1, 126.3, 126.3, 122.4, 121.0, 112.1, 112.0, 49.1, 46.8, 41.7, 40.6, 40.6, 23.6, 23.5 . IR (KBr): *v* (cm^{-1}) 2964, 2884, 2800, 1673, 1521, 1395, 1353, 1259, 947, 819. HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{38}BrN_4O$ $[M+H]^+$: 585.2224, found: 585.2217.



3i

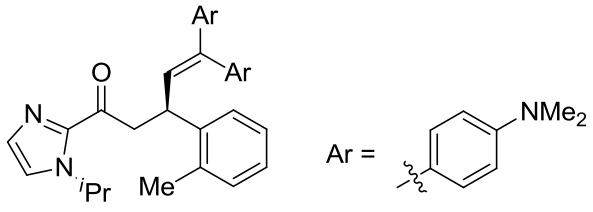
According to the general procedure C, **3i** was obtained as yellow oil, 124 mg, 92% yield, 94% ee, $[\alpha]_D^{25}$ = + 110.1 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, t_{major} = 13.33 min, t_{minor} = 18.81 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* =

4.8 Hz, 5H), 7.14 (s, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 6.04 (d, *J* = 10.4 Hz, 1H), 5.44-5.37 (m, 1H), 4.25-4.19 (m, 1H), 3.60-3.49 (m, 2H), 2.96 (s, 6H), 2.89 (s, 6H), 1.33 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 149.8, 149.5, 143.7, 142.6, 141.9, 131.5, 131.4, 130.5, 129.5, 129.0, 128.5, 128.4, 128.2, 126.6, 121.0, 112.1, 112.0, 49.1, 46.8, 41.3, 40.6, 40.6, 23.7, 23.5. IR (KBr): *v* (cm^{-1}) 2884, 2800, 1673, 1608, 1521, 1396, 1352, 948, 819, 768. HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{38}ClN_4O$ $[M+H]^+$: 541.2729, found: 541.2730.



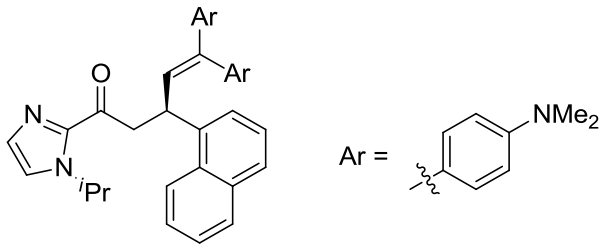
3j

According to the general procedure C, **3j** was obtained as yellow oil, 129 mg, 95% yield, 94% ee, $[\alpha]_D^{25}$ = + 119.3 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IE, λ = 254 nm, hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, t_{major} = 14.22 min, t_{minor} = 16.71 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (s, 1H), 7.21-7.10 (m, 5H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 6.04 (d, *J* = 10.4 Hz, 1H), 5.45-5.38 (m, 1H), 4.25-4.19 (m, 1H), 3.55 (d, *J* = 7.2 Hz, 2H), 2.97 (s, 6H), 2.90 (s, 6H), 1.33 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 149.8, 149.5, 147.3, 142.6, 142.2, 134.1, 131.4, 130.5, 129.7, 129.5, 128.4, 128.1, 127.8, 126.3, 126.1, 125.8, 121.0, 112.1, 112.0, 49.1, 46.8, 41.6, 40.6, 40.6, 23.7, 23.5. IR (KBr): *v* (cm^{-1}) 2964, 2886, 2800, 1673, 1608, 1521, 1396, 1353, 1260, 819, 697. HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{38}ClN_4O$ $[M+H]^+$: 541.2729, found: 541.2727.



3k

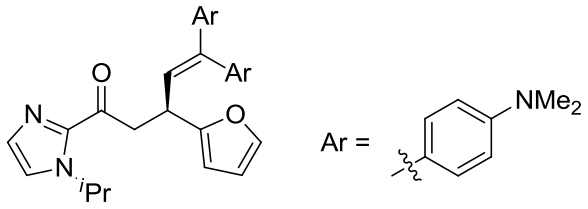
According to the general procedure C, **3k** was obtained as white solid, 124 mg, 95% yield, 93% ee, $[\alpha]_D^{25}$ = + 35.5 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, t_{major} = 27.64 min, t_{minor} = 30.58 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 7.08-7.03 (m, 2H), 7.00-6.96 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 8.4 Hz, 2H), 6.07 (d, *J* = 10.0 Hz, 1H), 5.38-5.28 (m, 1H), 4.37-4.31 (m, 1H), 3.55-3.44 (m, 1H), 3.40-3.35 (m, 1H), 2.87 (s, 6H), 2.82 (s, 6H), 2.04 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 148.6, 148.4, 142.7, 141.8, 140.4, 134.5, 130.7, 129.4, 129.3, 128.4, 127.6, 127.3, 126.4, 125.9, 125.0, 124.6, 119.8, 111.1, 110.9, 47.9, 46.0, 39.6, 39.6, 37.2, 22.6, 22.5, 18.3 . IR (KBr): *v* (cm^{-1}) 2925, 2853, 2798, 1667, 1608, 1521, 1394, 1350, 947, 820, 759. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{41}N_4O$ $[M+H]^+$: 521.3275, found: 521.3276.



3l

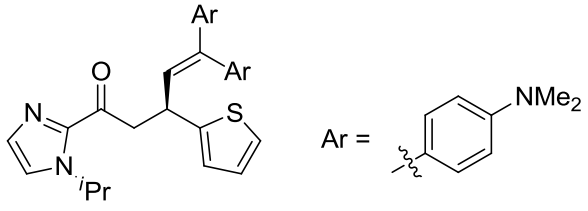
According to the general procedure C, **3l** was obtained as yellow solid, 114 mg, 82% yield, 88% ee, $[\alpha]_D^{25}$ = - 43.6 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, t_{major} = 13.66 min, t_{minor} = 18.18 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 6.0 Hz, 1H), 7.69-7.61 (m, 2H), 7.44-7.38 (m, 3H), 7.19 (d, *J* = 12.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.58-6.55 (m, 4H), 6.28 (s, 1H), 5.41-5.35 (m, 1H), 5.12-5.06 (m, 1H), 3.64 (d, *J* = 7.6 Hz, 2H), 2.93 (s, 6H), 2.90 (s, 6H), 1.30 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 149.7, 149.5, 142.8, 141.8, 141.7, 134.0, 131.8, 131.0, 130.7, 129.5, 128.6, 128.3, 127.1, 126.6, 125.7, 125.6, 125.3, 124.4, 124.2, 120.9, 112.1, 112.0, 49.0, 47.6, 40.7, 40.6, 37.9, 23.6, 23.5. IR (KBr): *v* (cm^{-1}) 2930, 2884, 2800, 1670, 1521, 1395, 1354,

948, 821, 778. HRMS (ESI, *m*/*z*) calcd for $C_{37}H_{41}N_4O$ $[M+H]^+$: 557.3275, found: 557.3269.



3m

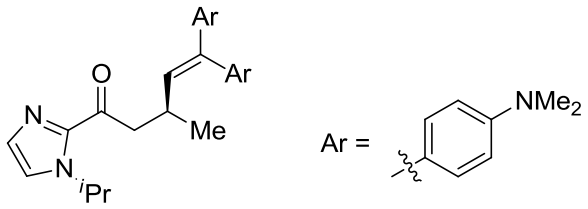
According to the general procedure C, **3m** was obtained as brown oil, 114 mg, 92% yield, 88% ee, $[\alpha]_D^{25}$ = + 90.0 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, t_{major} = 23.65 min, t_{minor} = 15.56 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 1H), 7.20 (s, 1H), 7.12 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 4H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.25-6.24 (m, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 5.94 (d, *J* = 10.4 Hz, 1H), 5.49-5.42 (m, 1H), 4.40-4.34 (m, 1H), 3.68-3.62 (m, 1H), 3.50-3.44 (m, 1H), 2.95 (s, 6H), 2.90 (s, 6H), 1.36-1.34 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 157.6, 149.8, 149.5, 142.7, 142.6, 141.0, 131.6, 130.6, 129.5, 128.5, 128.1, 124.1, 120.9, 112.1, 112.0, 110.1, 104.7, 49.1, 44.3, 40.6, 36.1, 23.6, 23.6. IR (KBr): *v* (cm^{-1}) 2965, 2885, 2799, 1673, 1608, 1521, 1396, 1352, 1165, 819. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{37}N_4O_2$ $[M+H]^+$: 497.2911, found: 497.2914.



3n

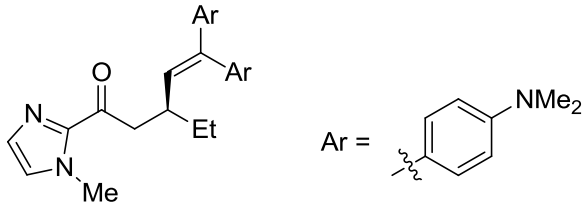
According to the general procedure C, **3n** was obtained as yellow oil, 115 mg, 90% yield, 88% ee, $[\alpha]_D^{25}$ = + 112.4 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 93/7, flow rate 1.0 mL/min, t_{major} = 39.94 min, t_{minor} = 37.48 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (s, 1H), 7.14 (s, 1H), 7.10-7.09 (m, 1H), 7.04-6.99 (m, 4H), 6.89 (t, *J* = 4.0 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.02 (d, *J* = 10.4 Hz, 1H), 5.49-5.43 (m, 1H),

4.58-4.52 (m, 1H), 3.63-3.61 (m, 2H), 2.95 (s, 6H), 2.89 (s, 6H), 1.35 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 149.8, 149.5, 149.2, 142.6, 141.9, 131.4, 130.6, 129.5, 128.5, 128.0, 126.6, 123.2, 123.2, 121.0, 112.1, 112.0, 49.1, 47.4, 40.6, 37.5, 23.7, 23.6. IR (KBr): *v* (cm^{-1}) 2964, 2884, 2799, 1672, 1608, 1521, 1395, 1353, 1256, 1164, 819. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{37}N_4OS$ $[M+H]^+$: 513.2683, found: 513.2684.



3o

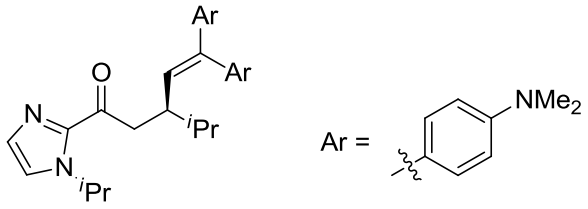
According to the general procedure C, **3o** was obtained as brown oil, 91 mg, 82% yield, 95% ee, $[\alpha]_D^{25}$ = + 69.7 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, t_{major} = 13.75 min, t_{minor} = 21.24 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (s, 1H), 7.13 (s, 1H), 7.03-6.96 (m, 4H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.74 (d, *J* = 8.8 Hz, 1H), 5.52-5.47 (m, 1H), 3.18-3.11 (m, 3H), 2.95 (s, 6H), 2.90 (s, 6H), 1.38 (t, *J* = 6.0 Hz, 6H), 1.12 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 149.6, 149.3, 142.8, 140.3, 132.0, 130.5, 130.4, 129.3, 128.8, 128.2, 120.8, 112.1, 112.1, 49.1, 47.2, 40.7, 31.4, 23.7, 21.8. IR (KBr): *v* (cm^{-1}) 2963, 2869, 2799, 1672, 1609, 1521, 1395, 1350, 1258, 947, 818. HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{37}N_4O$ $[M+H]^+$: 445.2962, found: 445.2962.



3p

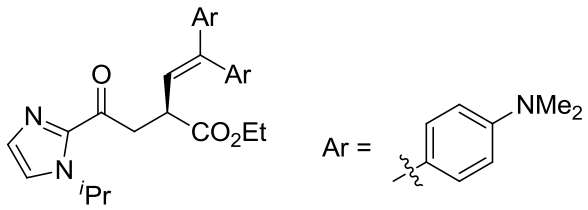
According to the general procedure C, **3p** was obtained as yellow oil, 86 mg, 80% yield, 95% ee, $[\alpha]_D^{25}$ = + 47.4 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min,

t_{major} = 11.19 min, t_{minor} = 18.11 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (t, *J* = 8.4 Hz, 3H), 6.94 (d, *J* = 4.4 Hz, 3H), 6.65 (d, *J* = 7.2 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 2H), 5.69 (d, *J* = 10.4 Hz, 1H), 3.93 (s, 3H), 3.13 (d, *J* = 7.2 Hz, 2H), 2.95 (s, 6H), 2.90 (s, 6H), 1.74 (s, 1H), 1.58-1.52 (m, 1H), 1.46-1.38 (m, 1H), 0.89 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 149.6, 149.2, 143.5, 141.7, 132.1, 130.5, 128.9, 128.8, 128.1, 126.7, 112.1, 112.1, 45.0, 40.7, 37.8, 36.2, 29.1, 11.9. IR (KBr): *v* (cm^{-1}) 2960, 2928, 2799, 1672, 1609, 1520, 1406, 1350, 1224, 1020, 948, 819, 773. HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{35}N_4O$ $[M+H]^+$: 431.2805, found: 431.2808.



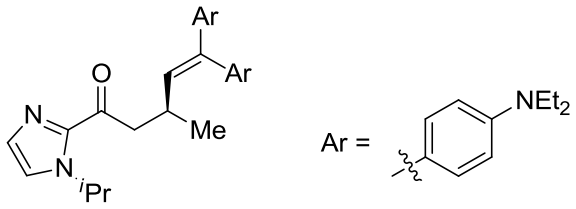
3q

According to the general procedure C, **3q** was obtained as yellow oil, 99 mg, 84% yield, 95% ee, $[\alpha]_D^{25}$ = + 9.2 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, t_{major} = 8.15 min, t_{minor} = 12.24 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (s, 1H), 7.07 (s, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 5.71 (d, *J* = 10.4 Hz, 1H), 5.46-5.39 (m, 1H), 3.23-3.17 (m, 1H), 3.08-3.03 (m, 1H), 2.87 (s, 6H), 2.82 (s, 6H), 1.76-1.64 (m, 2H), 1.30 (t, *J* = 8.0 Hz, 6H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 149.5, 149.1, 142.9, 141.9, 132.4, 130.6, 129.3, 129.0, 128.1, 127.3, 120.8, 112.1, 112.0, 49.1, 43.0, 41.9, 40.7, 40.7, 33.2, 23.7, 23.7, 20.5, 19.5. IR (KBr): *v* (cm^{-1}) 2959, 2872, 2799, 1672, 1609, 1521, 1395, 1256, 1223, 1164, 818. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{41}N_4O$ $[M+H]^+$: 473.3275, found: 473.3277.



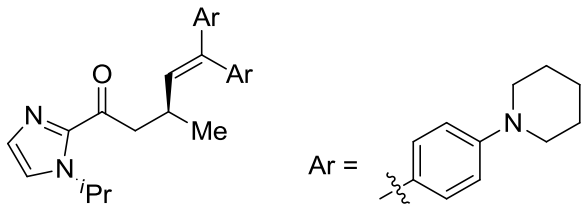
3r

According to the general procedure C, **3r** was obtained as yellow oil, 84 mg, 67% yield, 93% ee, $[\alpha]_D^{25}$ = + 140.4 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, t_{major} = 45.46 min, t_{minor} = 61.38 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (s, 1H), 7.17-7.10 (m, 5H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 5.84 (d, *J* = 10.4 Hz, 1H), 5.49-5.43 (m, 1H), 4.21-4.13 (m, 2H), 3.88-3.82 (m, 1H), 3.78-3.72 (m, 1H), 3.38-3.32 (m, 1H), 2.96 (s, 6H), 2.92 (s, 6H), 1.40-1.35 (m, 6H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 174.3, 149.9, 149.6, 144.5, 142.0, 131.2, 130.8, 129.5, 128.5, 127.7, 120.9, 112.1, 112.0, 60.7, 49.1, 42.8, 41.8, 40.6, 40.6, 23.7, 23.5, 14.2. IR (KBr): *v* (cm^{-1}) 2979, 2934, 2887, 2801, 1729, 1677, 1522, 1397, 1360, 978, 948, 821. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{39}N_4O_3$ $[M+H]^+$: 503.3017, found: 503.3015.



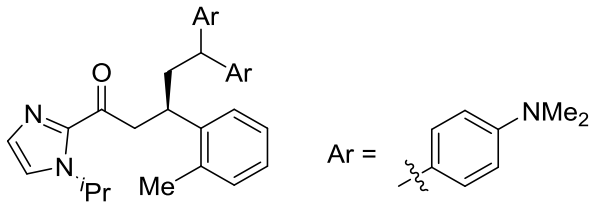
3s

According to the general procedure C, **3s** was obtained as yellow oil, 100 mg, 80% yield, 95% ee, $[\alpha]_D^{25}$ = + 67.3 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 93/7, flow rate 1.0 mL/min, t_{major} = 8.76 min, t_{minor} = 14.65 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (s, 1H), 7.13 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 5.71-5.67 (m, 1H), 5.53-5.46 (m, 1H), 3.37-3.28(m, 8H), 3.14 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 6H), 1.19-1.10 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 146.7, 146.5, 142.8, 140.4, 130.9, 130.7, 129.7, 129.3, 128.4, 127.7, 120.7, 111.2, 49.1, 47.3, 44.3, 44.3, 31.4, 23.7, 21.9, 12.8, 12.6. IR (KBr): *v* (cm^{-1}) 2968, 2928, 2870, 1673, 1608, 1519, 1397, 1263, 1196, 815. HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{45}N_4O$ $[M+H]^+$: 501.3588, found: 501.3592.



3t

According to the general procedure C, **3t** was obtained as yellow oil, 111 mg, 85% yield, 95% ee, $[\alpha]_D^{25}$ = + 50.7 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, t_{major} = 8.55 min, t_{minor} = 13.40 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (s, 1H), 7.13 (s, 1H), 7.02-6.95 (m, 4H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 5.78 (d, *J* = 9.6 Hz, 1H), 5.52-5.45 (m, 1H), 3.18-3.10 (m, 11H), 1.72-1.55 (m, 12H), 1.38 (t, *J* = 8.0 Hz, 6H), 1.11 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.4, 151.1, 150.7, 142.7, 140.1, 134.1, 131.2, 131.1, 130.4, 129.3, 128.0, 120.8, 115.8, 115.8, 50.6, 50.5, 49.1, 47.2, 31.4, 26.0, 25.8, 24.4, 24.3, 23.7, 21.7. IR (KBr): *v* (cm^{-1}) 2928, 2851, 2806, 1672, 1607, 1514, 1260, 1234, 916, 822. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{44}N_4NaO$ $[M+Na]^+$: 547.3407, found: 547.3401.



4

According to the general procedure D, **4** was obtained as yellow oil, 112 mg, 86% yield, > 99% ee, $[\alpha]_D^{25}$ = - 7.7 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, t_{major} = 16.15 min, t_{minor} = 9.47 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 7.6 Hz, 1H), 7.18-7.10 (m, 3H), 7.04-6.97 (m, 6H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 5.44-5.37 (m, 1H), 3.60-3.51 (m, 2H), 3.47-3.46 (m, 2H), 2.89 (s, 6H), 2.85 (s, 6H), 2.48-2.41 (m, 1H), 2.31-2.24 (m, 1H), 1.91 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H). 13C NMR (100 MHz, $CDCl_3$): δ = 192.0, 149.0, 148.9, 142.8, 142.6, 136.6, 134.9, 132.8, 130.1, 129.3, 128.7, 128.1, 126.1, 125.6, 120.8,

113.1, 113.0, 48.9, 46.5, 42.5, 40.9, 23.7, 23.5, 19.5. IR (KBr): ν (cm^{-1}) 2963, 2924, 2799, 1674, 1614, 1518, 1261, 1089, 1021, 947, 806. HRMS (ESI, m/z) calcd for $C_{34}H_{42}N_4NaO$ $[M+Na]^+$: 545.3251, found: 545.3250.

III References

(1) (a) Wang, C.; Chen, L.-A.; Huo, H.; Shen, X.; Harms, K.; Gong, L.; Meggers, E. *Chem. Sci.* **2015**, *6*, 1094. (b) Li, S.-W.; Gong, J.; Kang, Q. *Org. Lett.* **2017**, *19*, 1350.

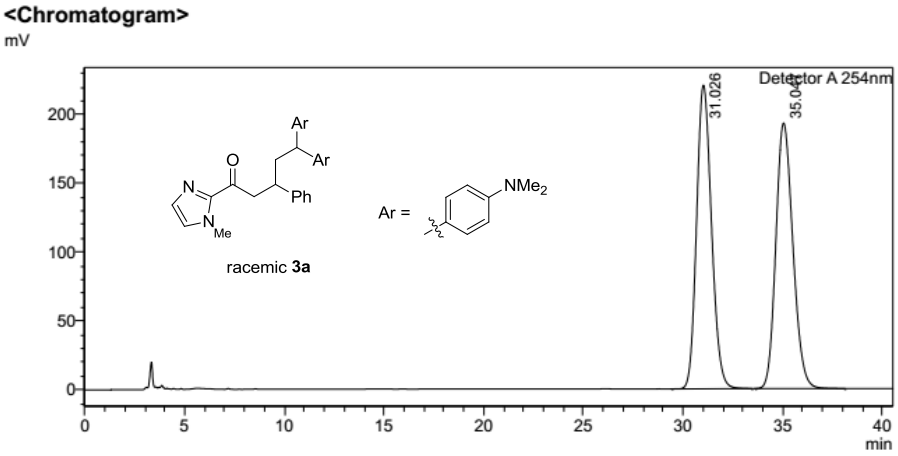
(2) Cui, L.; Zhang, L.; Luo, S.; Cheng, J.-P. *Eur. J. Org. Chem.* **2014**, 3540.

(3) (a) Yoshida, K.; Koujiri, T.; Sakamoto, E.; Kubo, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1748. (b) Liwosz, T. W.; Chemler, S. R. *Chem. – Eur. J.* **2013**, *19*, 12771.

(4) (a) Huo, H.; Fu, C.; Harms, K.; Meggers, E. *J. Am. Chem. Soc*. **2014**, *136*, 2990. (b) Huo, H.; Harms, K.; Meggers, E. *J. Am. Chem. Soc*. **2016**, *138*, 6936. (c) Evans, D. A.; Fandrick, K. R. *Org, Lett*. **2006**, *8*, 2249.

IV chiral HPLC analysis

Racemic **3a**:

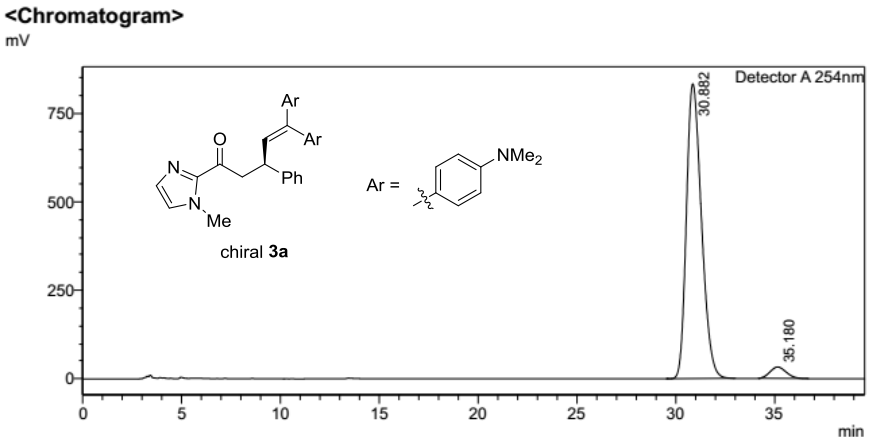


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.026	11471084	220600	50.051		M	
2	35.047	11447712	192917	49.949		M	
Total		22918796	413518				

Chiral **3a**:



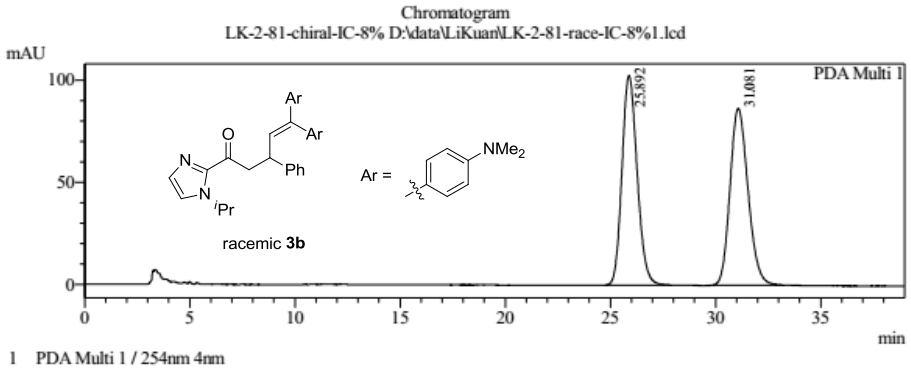
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.882	44136993	833581	96.018		M	
2	35.180	1830412	31969	3.982		M	
Total		45967406	865550				

Figure S1. HPLC traces of racemic **3a** (reference) and chiral **3a**. Area integration = 96.0:4.0 (92% ee)

Racemic **3b**:

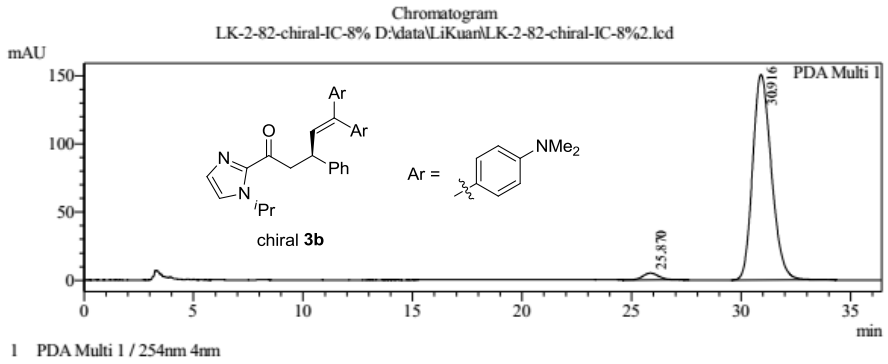


PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1	RT25.892	25.892	5158742	102749	50.025	0.000
2	RT31.081	31.081	5153590	86687	49.975	3.595
Total			10312332	189436	100.000	

Chiral **3b**:



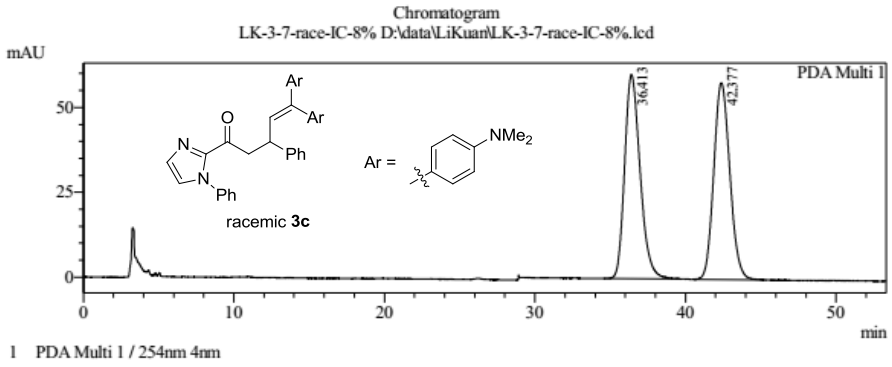
PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1	RT25.870	25.870	252998	5018	2.733	0.000
2	RT30.916	30.916	9005267	150833	97.267	3.506
Total			9258266	155851	100.000	

Figure S2. HPLC traces of racemic **3b** (reference) and chiral **3b**. Area integration = 2.7:97.3 (95% ee)

Racemic **3c**:

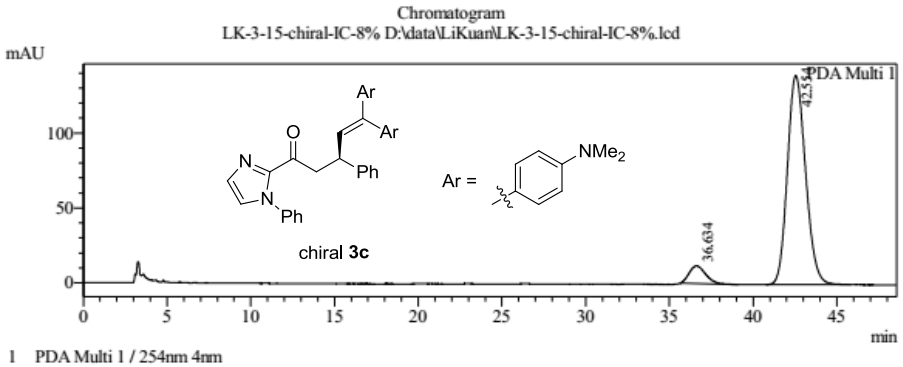


PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1		36.413	4298188	60151	49.984	0.000
2		42.377	4300944	58034	50.016	3.132
Total			8599132	118185	100.000	

Chiral **3c**:



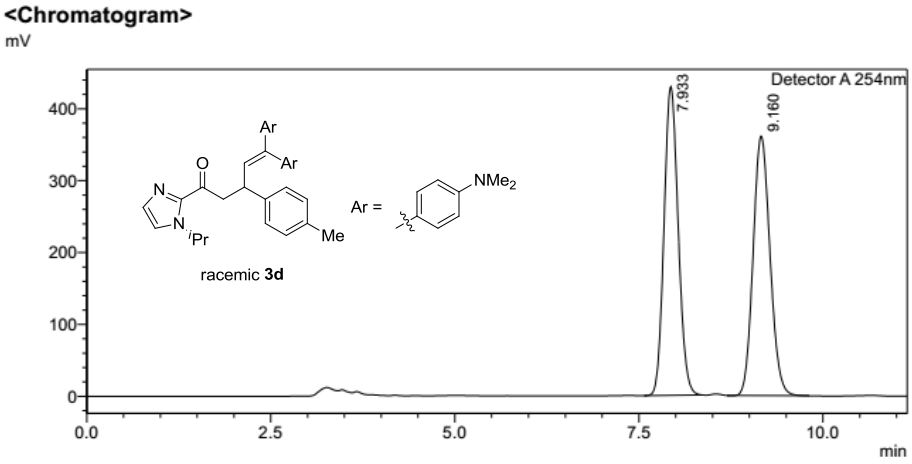
PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1		36.634	812825	11858	7.165	0.000
2		42.554	10531151	139535	92.835	3.094
Total			11343975	151393	100.000	

Figure S3. HPLC traces of racemic **3c** (reference) and chiral **3c**. Area integration = 7.2:92.8 (86% ee)

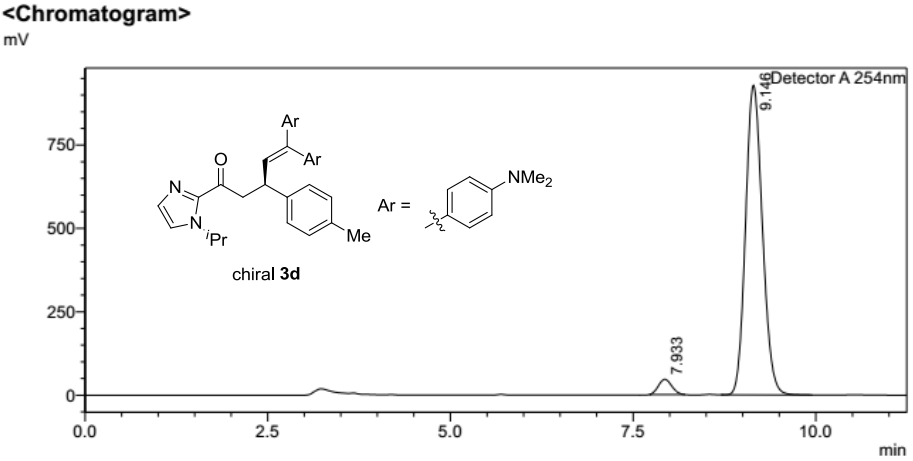
Racemic **3d**



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.933	5742482	429371	49.919		M	
2	9.160	5761158	361255	50.081		M	
Total		11503640	790626				

Chiral **3d**:

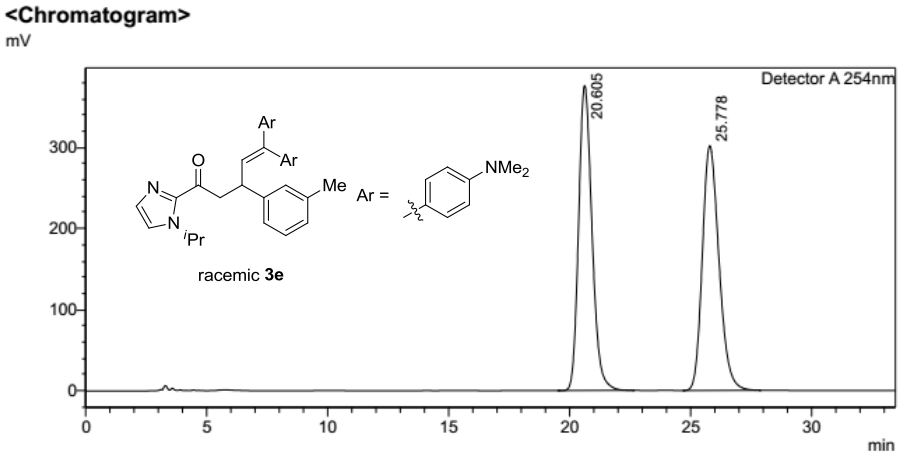


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.933	574234	45319	3.710		M	
2	9.146	14905218	928059	96.290		M	
Total		15479451	973378				

Figure S4. HPLC traces of racemic **3d** (reference) and chiral **3d**. Area integration = 3.7:96.3 (93% ee)

Racemic **3e**

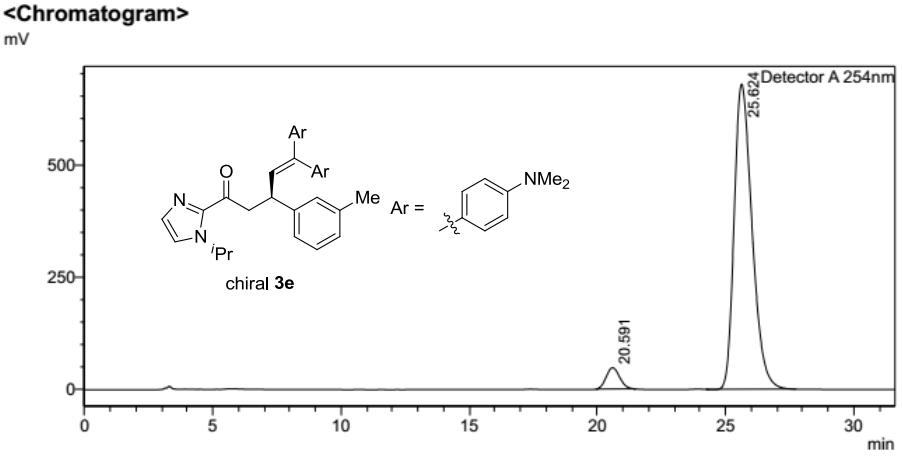


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.605	14436624	375609	50.033		M	
2	25.778	14417387	301333	49.967		M	
Total		28854011	676941				

Chiral **3e**:



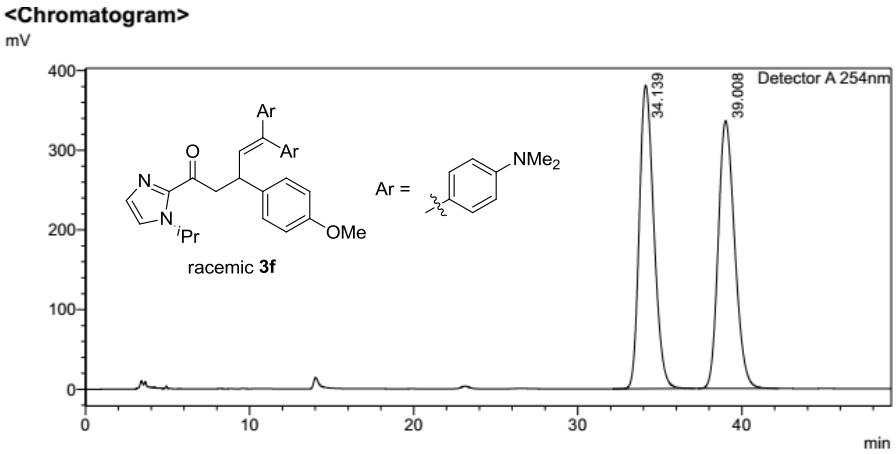
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.591	1724772	47213	4.989		M	
2	25.624	32846353	677319	95.011		M	
Total		34571125	724532				

Figure S8. HPLC traces of racemic **3e** (reference) and chiral **3e**. Area integration = 5.0:95.0 (90% ee)

Racemic **3f**

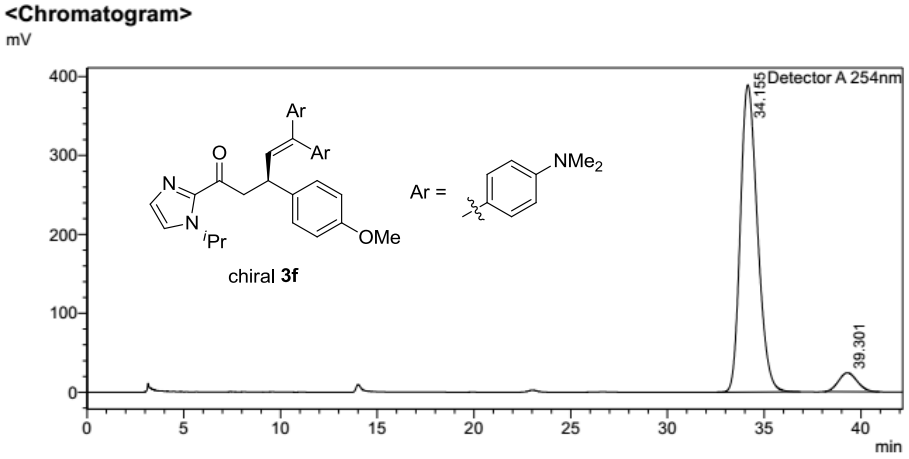


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.139	23388878	380735	50.020		M	
2	39.008	23369871	336021	49.980		M	
Total		46758748	716756				

Chiral **3f**:



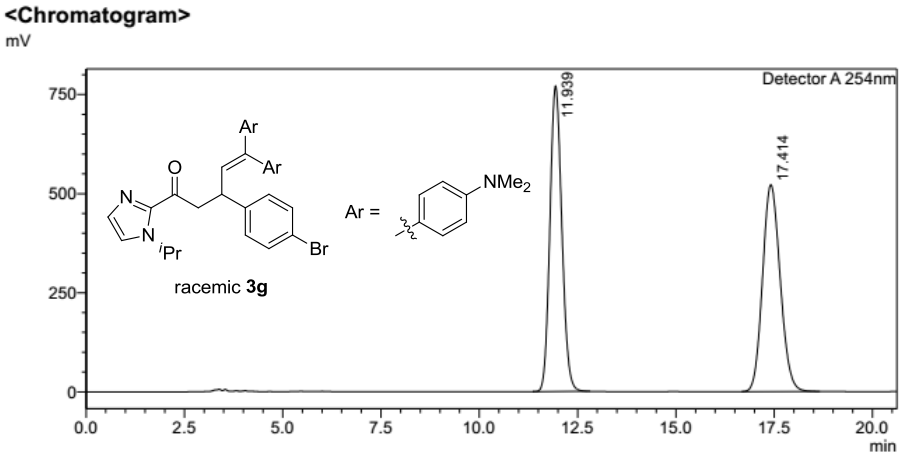
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.155	23859196	389112	93.681		M	
2	39.301	1609456	23921	6.319		M	
Total		25468652	413033				

Figure S10. HPLC traces of racemic **3f** (reference) and chiral **3f**. Area integration = 93.7:6.3 (87% ee)

Racemic **3g**

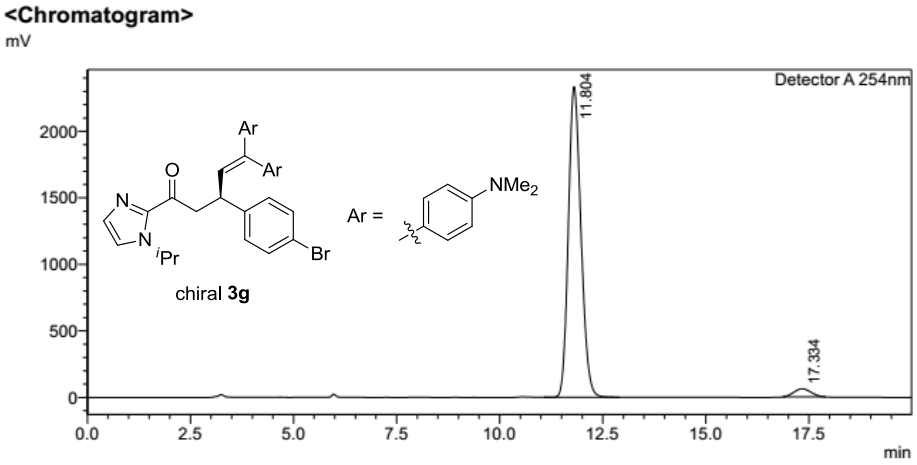


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.939	16238501	770668	49.919		M	
2	17.414	16291424	521471	50.081		M	
Total		32529926	1292138				

Chiral **3g**:



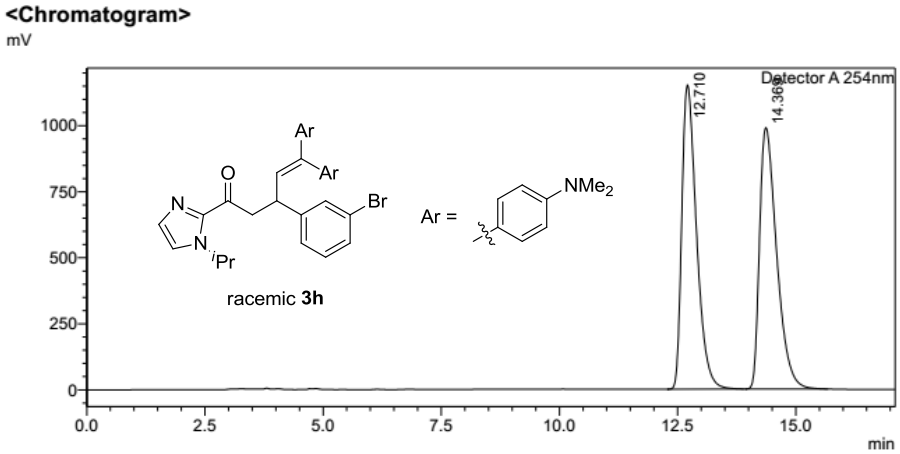
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.804	49567387	2331849	96.581		M	
2	17.334	1754480	60856	3.419		M	
Total		51321867	2392705				

Figure S5. HPLC traces of racemic **3g** (reference) and chiral **3g**. Area integration = 96.6:3.4 (93% ee)

Racemic **3h**

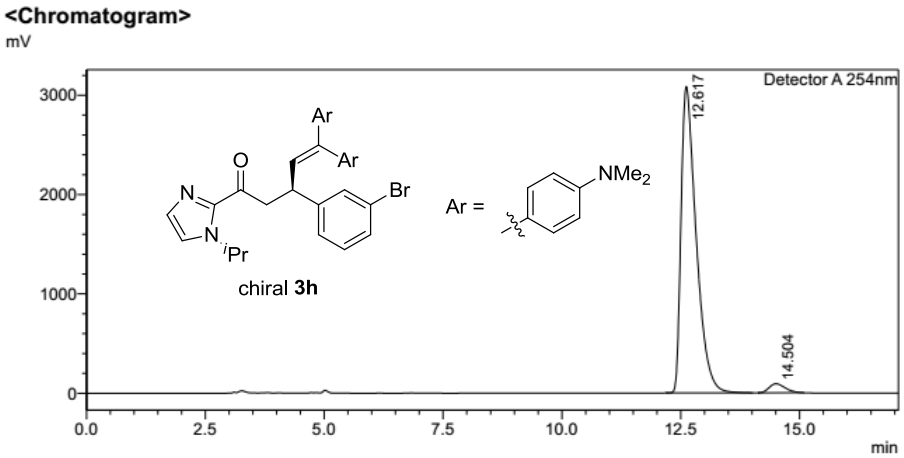


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.710	24907293	1151446	49.969		M	
2	14.369	24938439	989683	50.031		M	
Total		49845732	2141129				

Chiral **3h**:



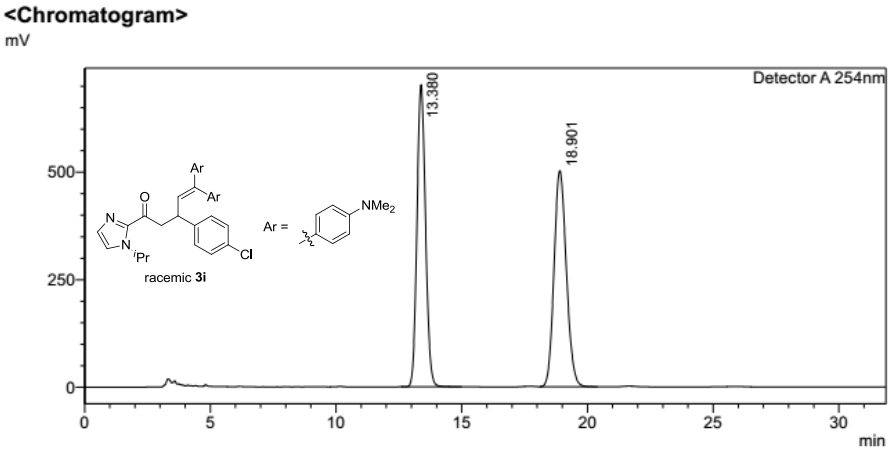
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.617	68004053	3081945	96.992		M	
2	14.504	2109192	90576	3.008		M	
Total		70113245	3172521				

Figure S6. HPLC traces of racemic **3h** (reference) and chiral **3h**. Area integration = 97.0:3.0 (94% ee)

Racemic **3i**

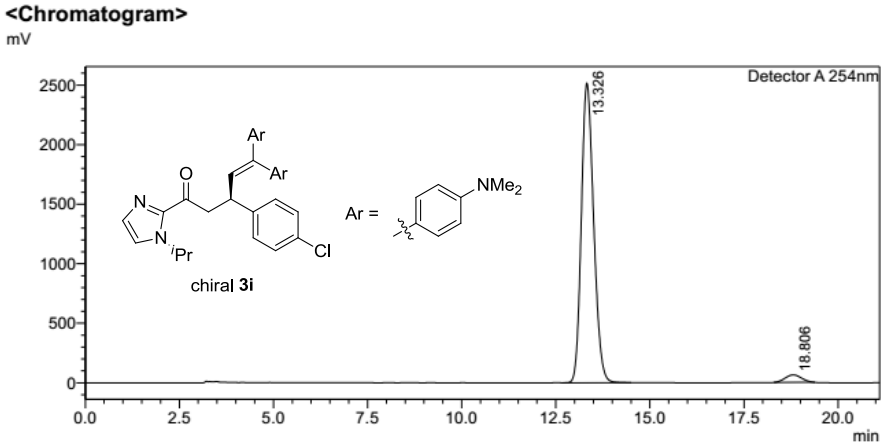


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.380	16610241	702389	49.259		M	
2	18.901	17110307	502716	50.741		M	
Total		33720548	1205105				

Chiral **3i**:



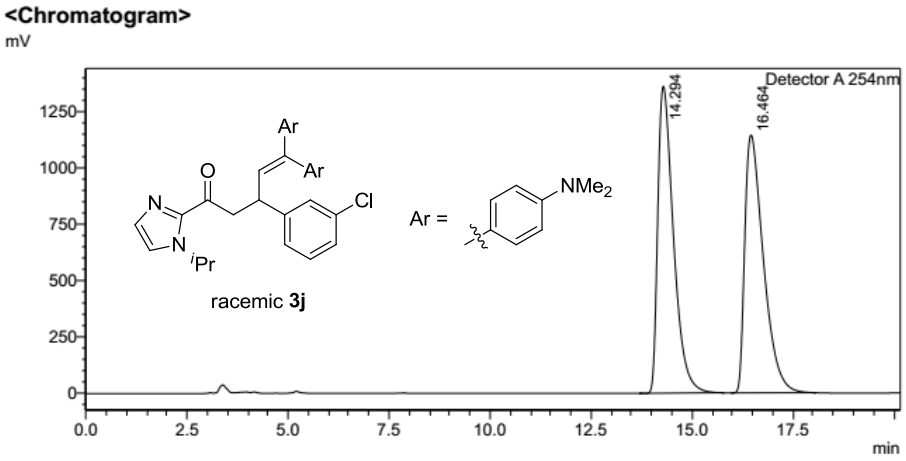
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.326	57214129	2514461	96.839		M	
2	18.806	1867287	62448	3.161		M	
Total		59081417	2576909				

Figure S7. HPLC traces of racemic **3i** (reference) and chiral **3i**. Area integration = 96.8:3.2 (94% ee)

Racemic **3j**

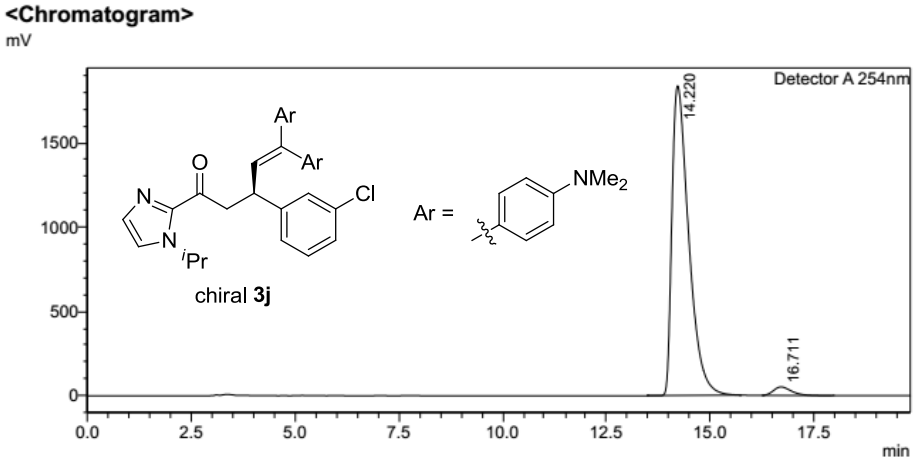


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.294	36600151	1358023	50.001		M	
2	16.464	36598569	1140747	49.999		M	
Total		73198720	2498770				

Chiral **3j**:



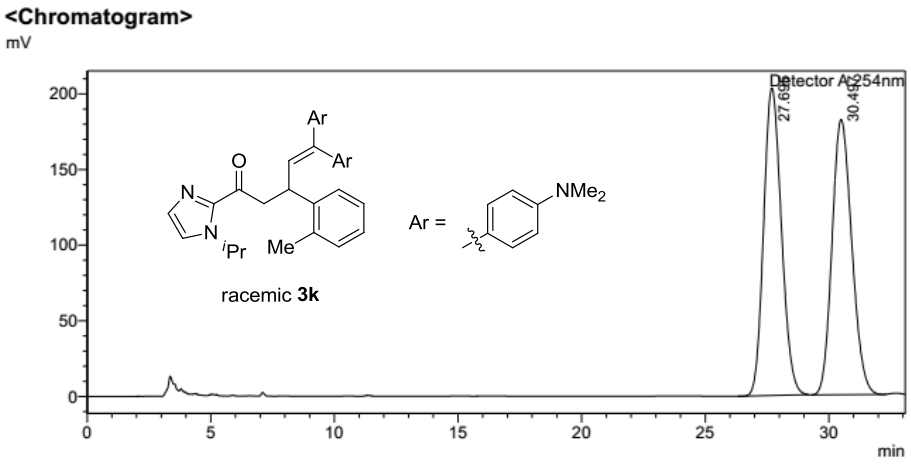
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.220	51656131	1835955	97.185		M	
2	16.711	1495986	49831	2.815		M	
Total		53152117	1885787				

Figure S9. HPLC traces of racemic **3j** (reference) and chiral **3j**. Area integration = 97.2:2.8 (94% ee)

Racemic **3k**

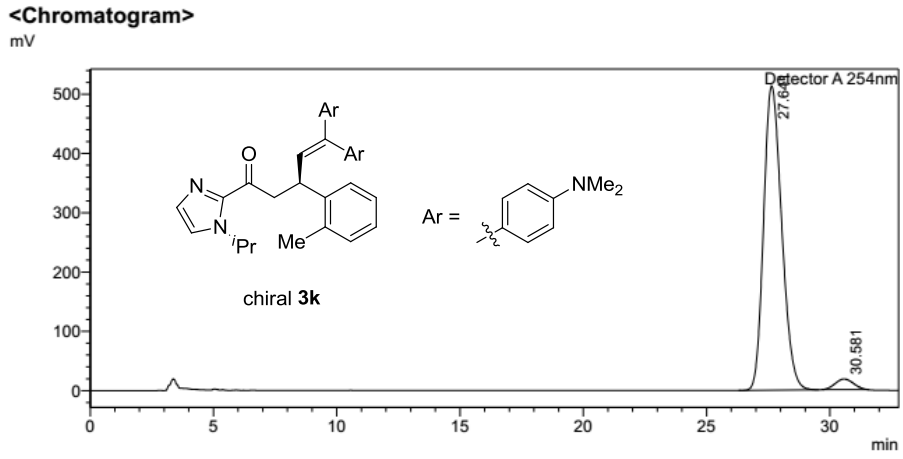


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.695	10165174	203218	50.132		M	
2	30.497	10111628	181874	49.868		M	
Total		20276802	385092				

Chiral **3k**:



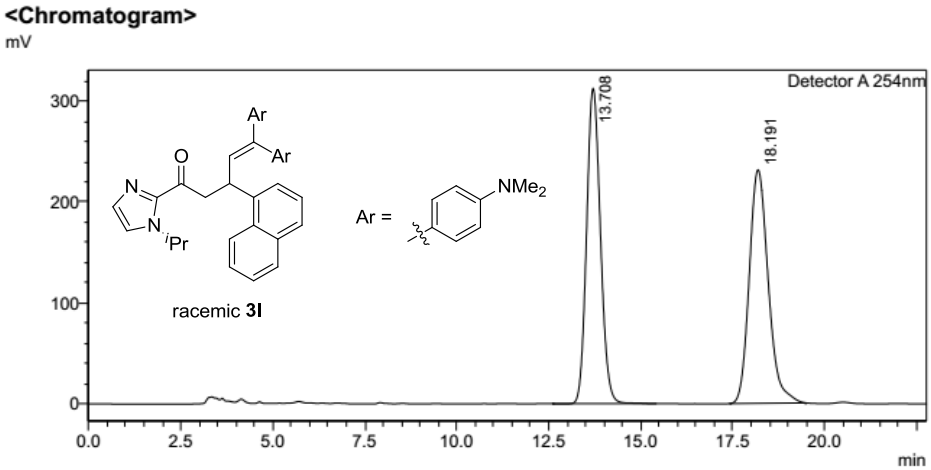
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.641	26134743	512984	96.575		M	
2	30.581	926993	17882	3.425		M	
Total		27061736	530866				

Figure S11. HPLC traces of racemic **3k** (reference) and chiral **3k**. Area integration = 96.6:3.4 (93% ee)

Racemic **3l**

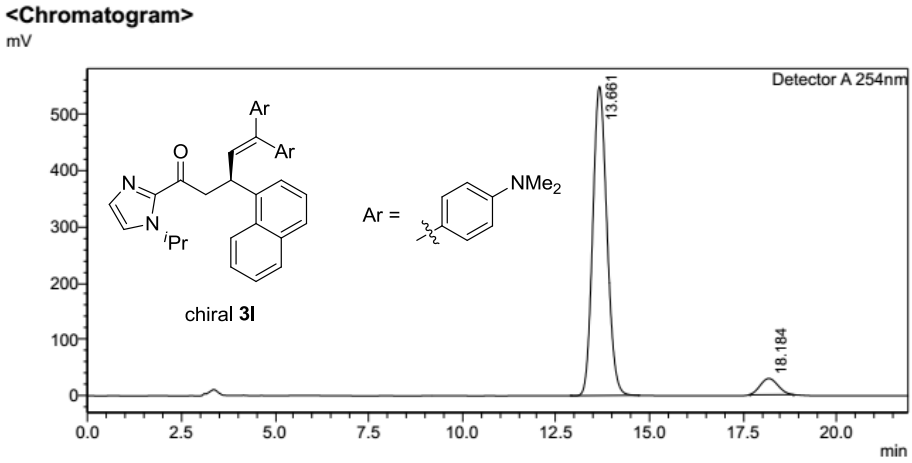


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.708	8161054	312519	49.576		M	
2	18.191	8300508	231416	50.424		M	
Total		16461562	543935				

Chiral **3l**:



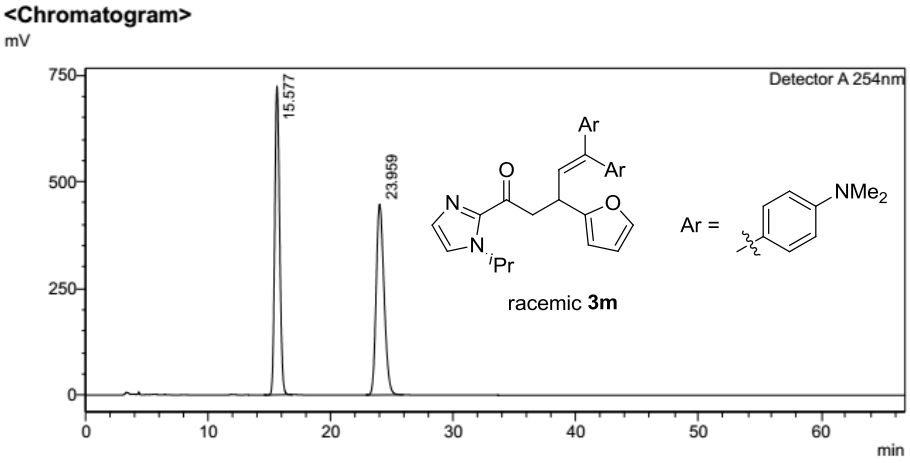
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.661	14436060	549110	93.791		M	
2	18.184	955633	28917	6.209		M	
Total		15391694	578027				

Figure S14. HPLC traces of racemic **3l** (reference) and chiral **3l**. Area integration = 93.8:6.2 (88% ee)

Racemic **3m**

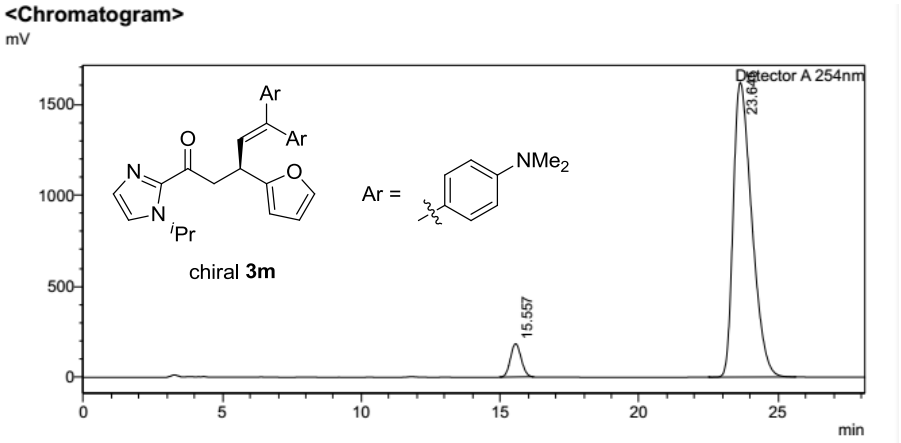


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.577	19976184	723598	49.963		M	
2	23.959	20006016	446828	50.037		M	
Total		39982200	1170426				

Chiral **3m**:



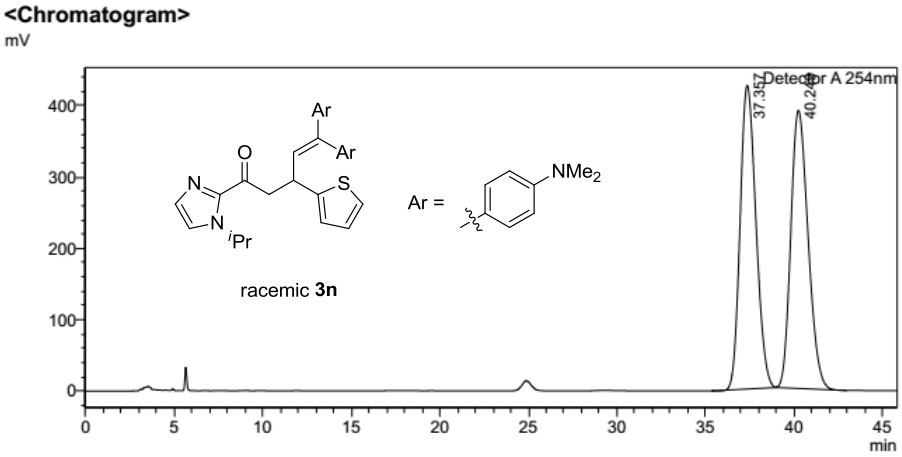
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.557	4892284	182140	6.117		M	
2	23.645	75087902	1618139	93.883		M	
Total		79980185	1800278				

Figure S12. HPLC traces of racemic **3m** (reference) and chiral **3m**. Area integration = 6.1:93.9 (88% ee)

Racemic **3n**

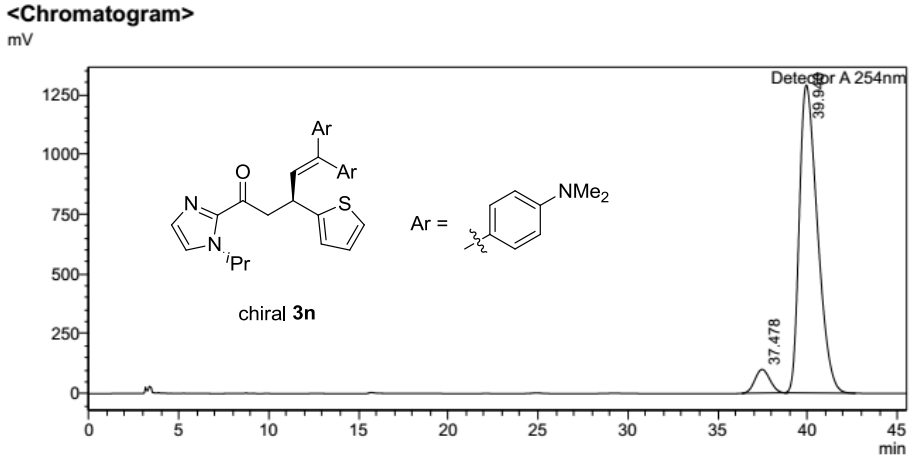


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	37.357	26334923	425916	49.960		M	
2	40.249	26376910	389878	50.040		M	
Total		52711832	815794				

Chiral **3n**:



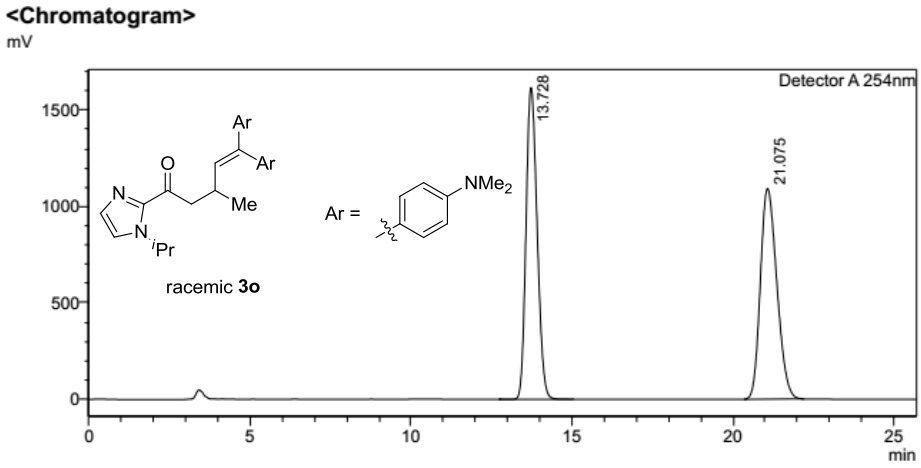
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	37.478	5743408	98810	5.973		M	
2	39.940	90415041	1287675	94.027		M	
Total		96158450	1386485				

Figure S13. HPLC traces of racemic **3n** (reference) and chiral **3n**. Area integration = 6.0:94.0 (88% ee)

Racemic **3o**

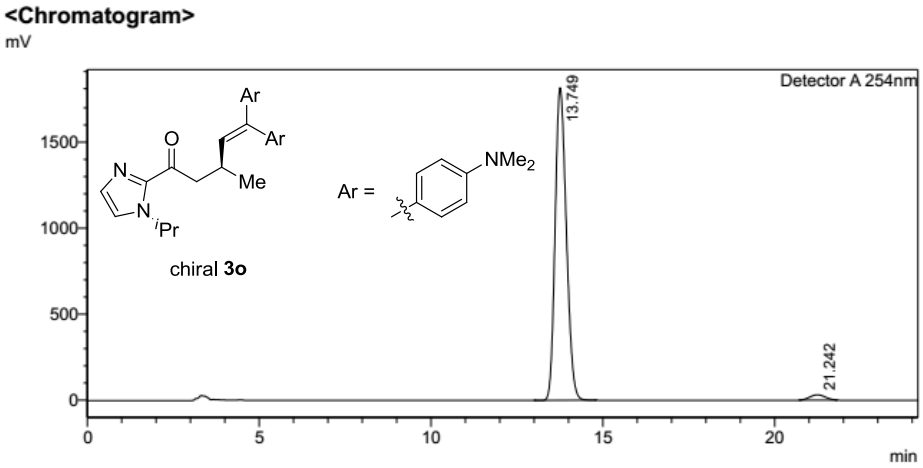


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.728	38732562	1617038	49.919		M	
2	21.075	38857741	1092368	50.081		M	
Total		77590303	2709406				

Chiral **3o**:



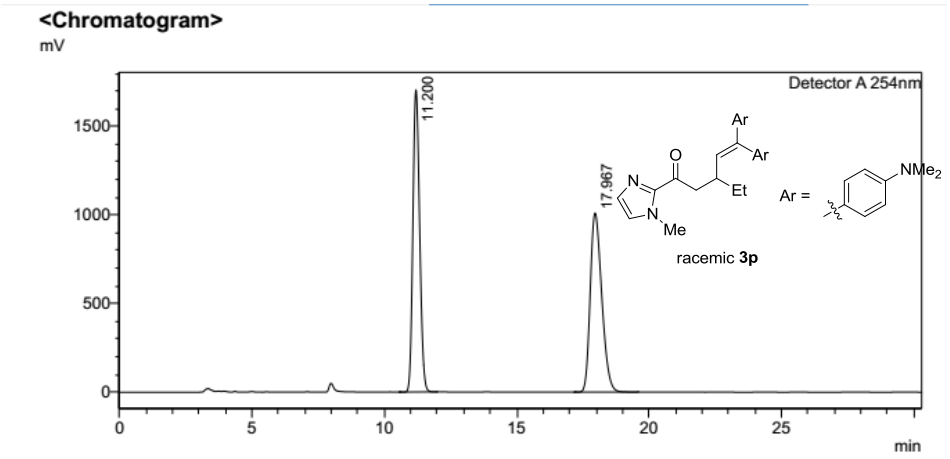
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.749	41014903	1809850	97.688		M	
2	21.242	970784	30925	2.312		M	
Total		41985687	1840774				

Figure S17. HPLC traces of racemic **3o** (reference) and chiral **3o**. Area integration = 97.7:2.3 (95% ee)

Racemic **3p**

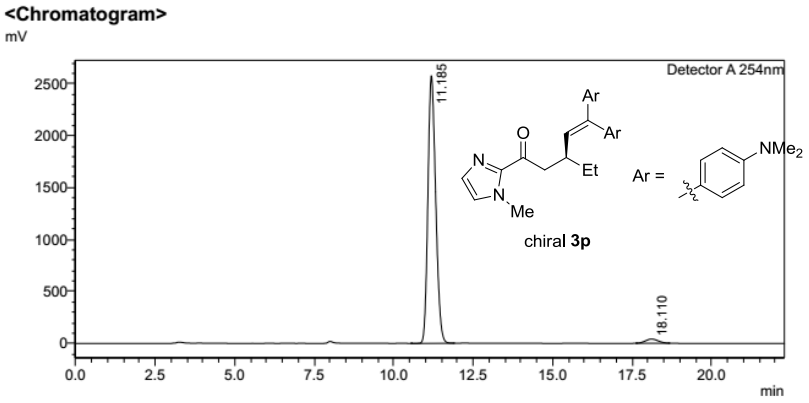


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.200	30118085	1705635	49.714		M	
2	17.967	30464913	1010572	50.286		M	
Total		60582997	2716207				

Chiral **3p**:



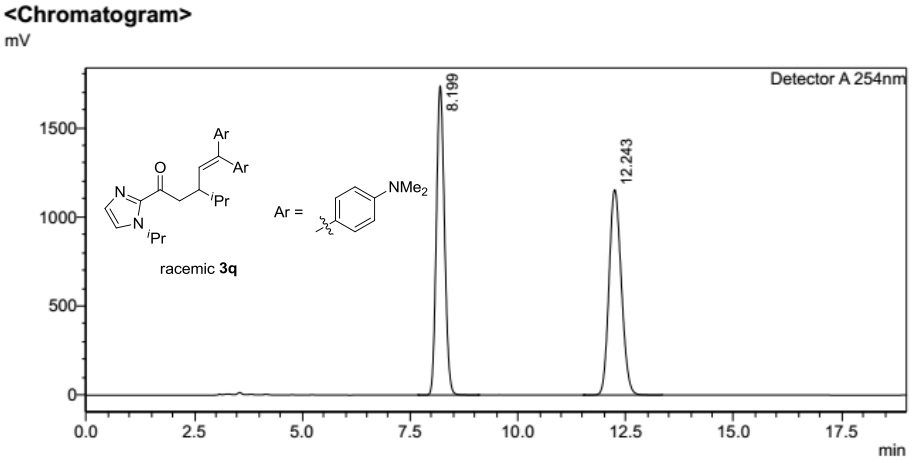
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.185	43840185	2575381	97.509		M	
2	18.110	1119883	40027	2.491		M	
Total		44960068	2615408				

Figure S18. HPLC traces of racemic **3p** (reference) and chiral **3p**. Area integration = 97.5:2.5 (95% ee)

Racemic **3q**

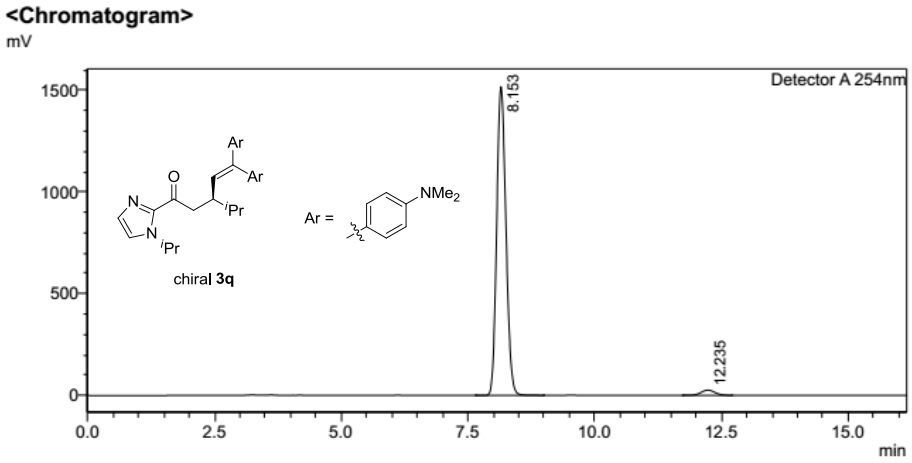


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.199	22636451	1733187	49.821		M	
2	12.243	22799079	1151657	50.179		M	
Total		45435529	2884844				

Chiral **3q**:



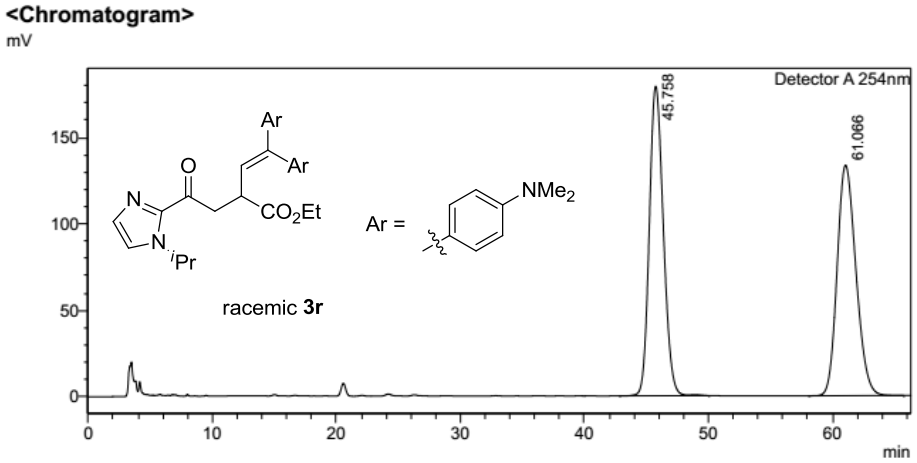
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.153	19246721	1517773	97.525		M	
2	12.235	488460	25737	2.475		M	
Total		19735180	1543510				

Figure S16. HPLC traces of racemic **3q** (reference) and chiral **3q**. Area integration = 97.5:2.5 (95% ee)

Racemic **3r**

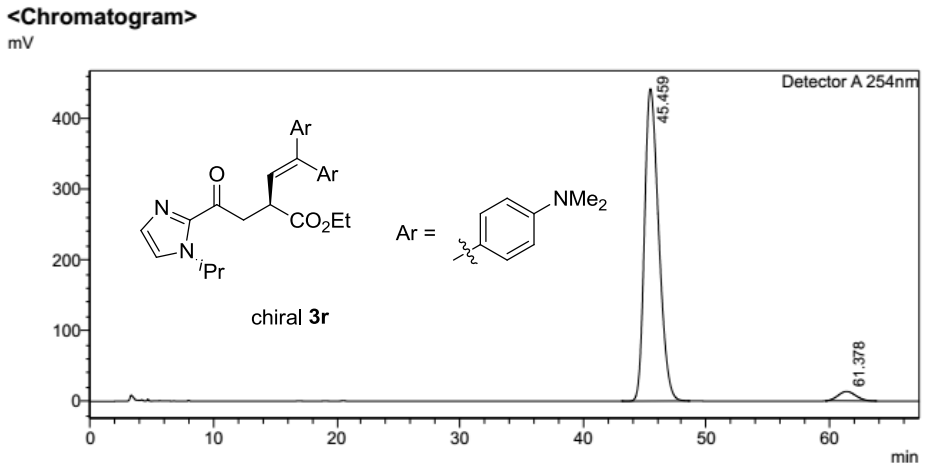


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	45.758	14097815	179211	50.102		M	
2	61.066	14040337	133392	49.898		M	
Total		28138152	312603				

Chiral **3r**:



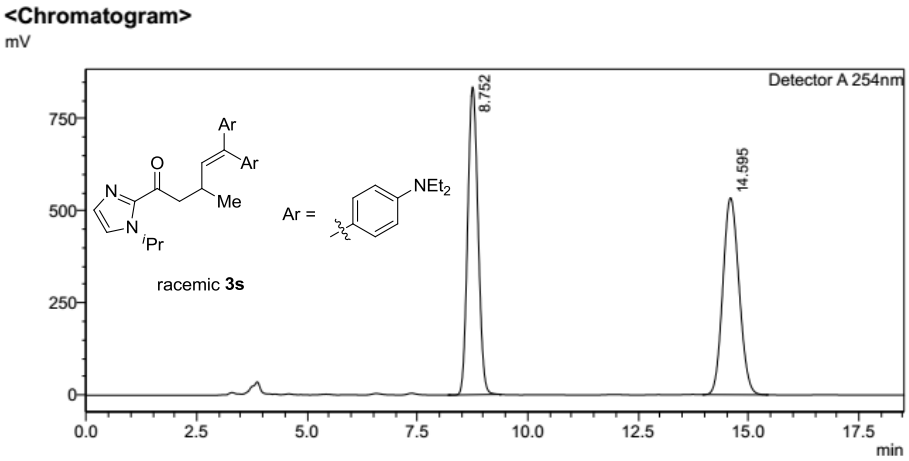
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	45.459	35350204	441447	96.344		M	
2	61.378	1341354	13314	3.656		M	
Total		36691558	454761				

Figure S15. HPLC traces of racemic **3r** (reference) and chiral **3r**. Area integration = 96.3:3.7 (93% ee)

Racemic **3s**

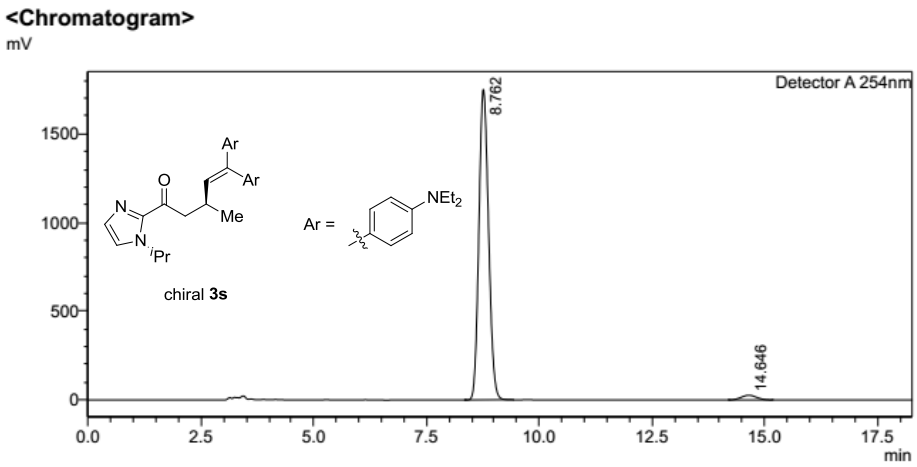


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.752	13594395	835070	49.929		M	
2	14.595	13632973	534271	50.071		M	
Total		27227369	1369342				

Chiral **3s**:



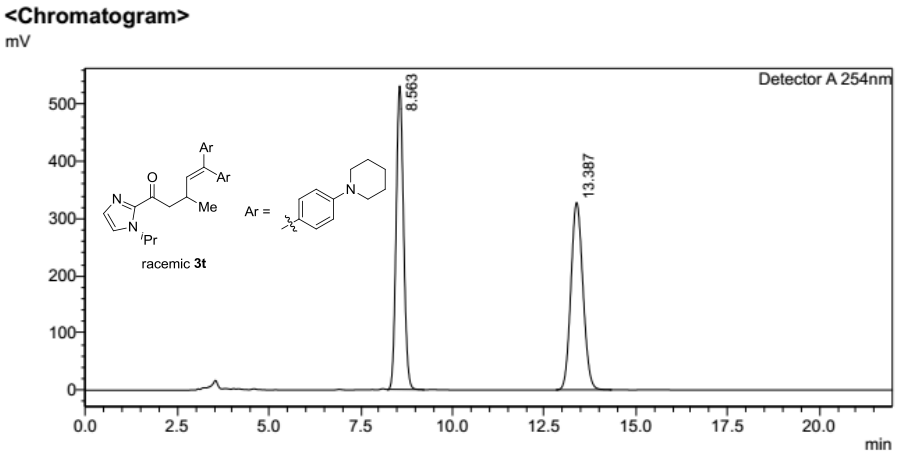
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.762	26022481	1749213	97.673		M	
2	14.646	620075	26204	2.327		M	
Total		26642556	1775417				

Figure S19. HPLC traces of racemic **3s** (reference) and chiral **3s**. Area integration = 97.7:2.3 (95% ee)

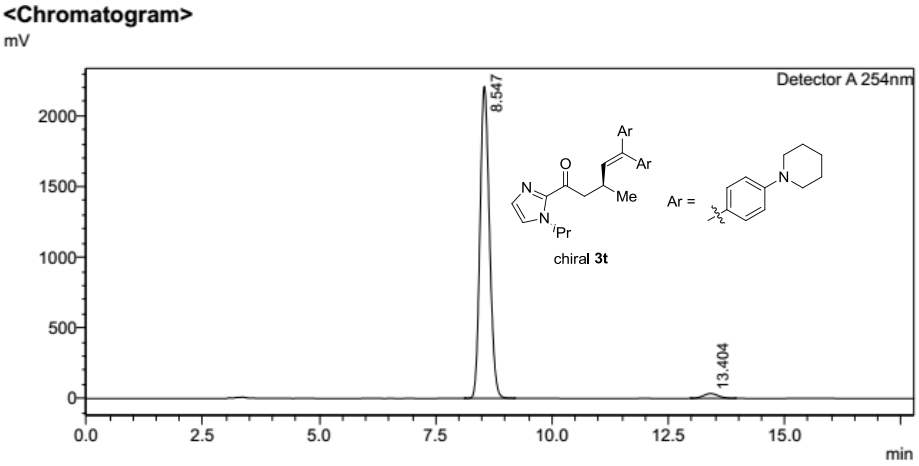
Racemic **3t**



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.563	7451280	531224	49.867		M	
2	13.387	7491054	327797	50.133		M	
Total		14942334	859021				

Chiral **3t**:

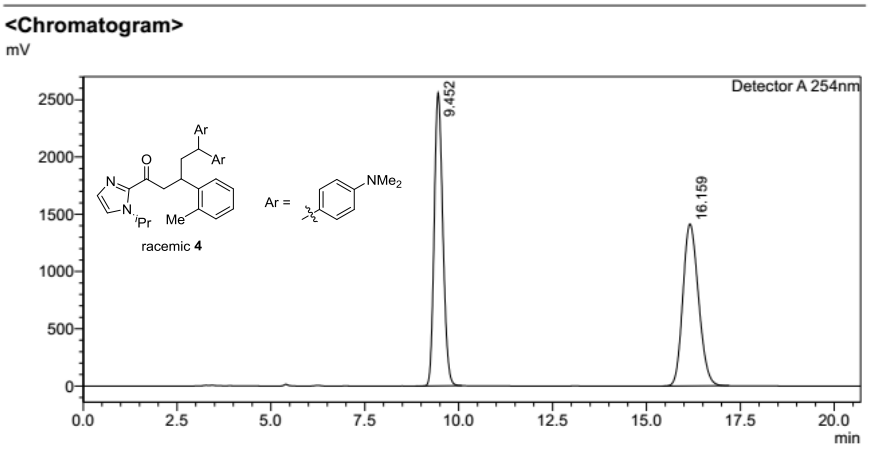


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.547	31123883	2206530	97.607		M	
2	13.404	763164	33979	2.393		M	
Total		31887048	2240509				

Figure S20. HPLC traces of racemic **3t** (reference) and chiral **3t**. Area integration = 97.6:2.4 (95% ee)

Racemic **4**

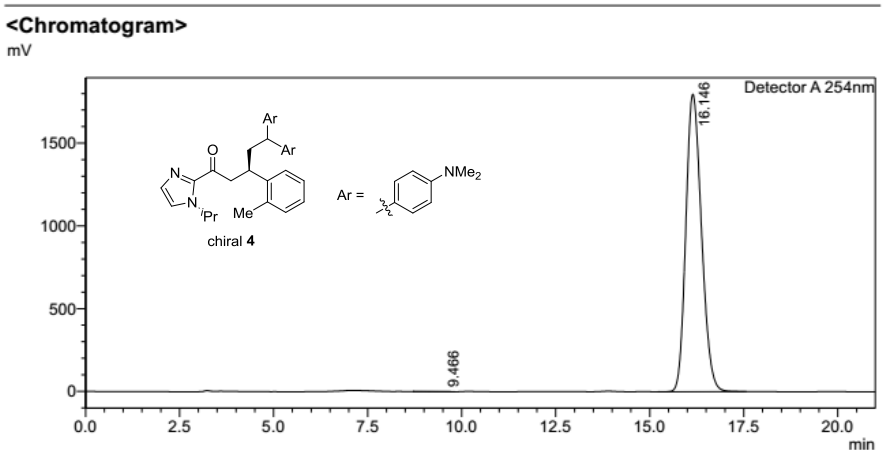


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.452	40781536	2557419	49.872		M	
2	16.159	40991487	1414317	50.128		M	
Total		81773023	3971736				

Chiral **4**



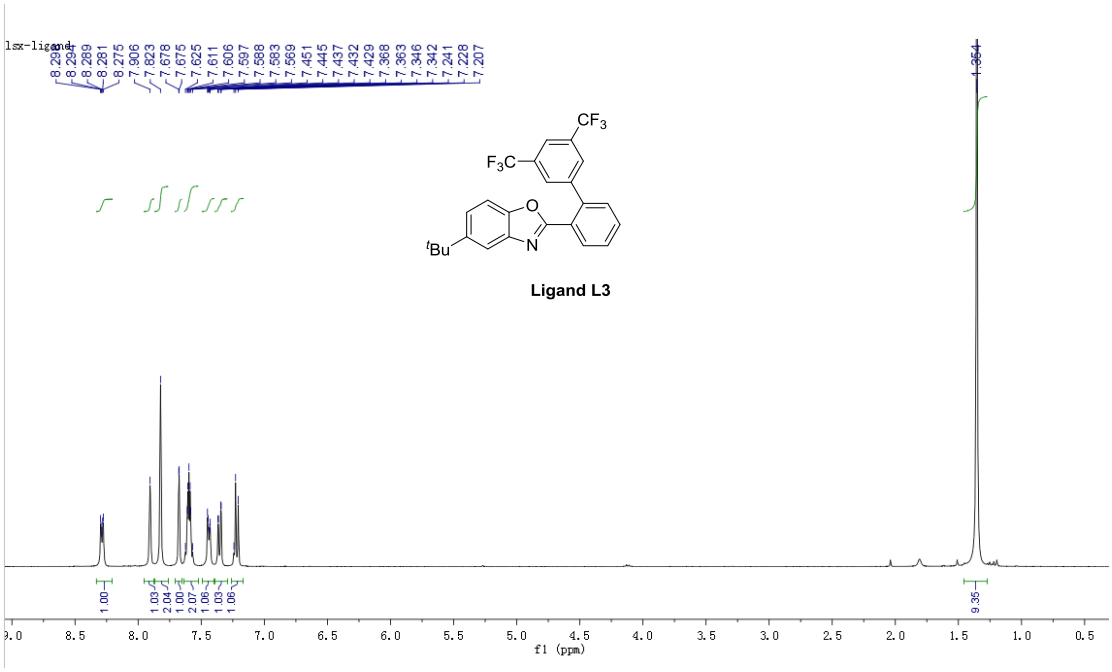
<Peak Table>

Detector A 254nm

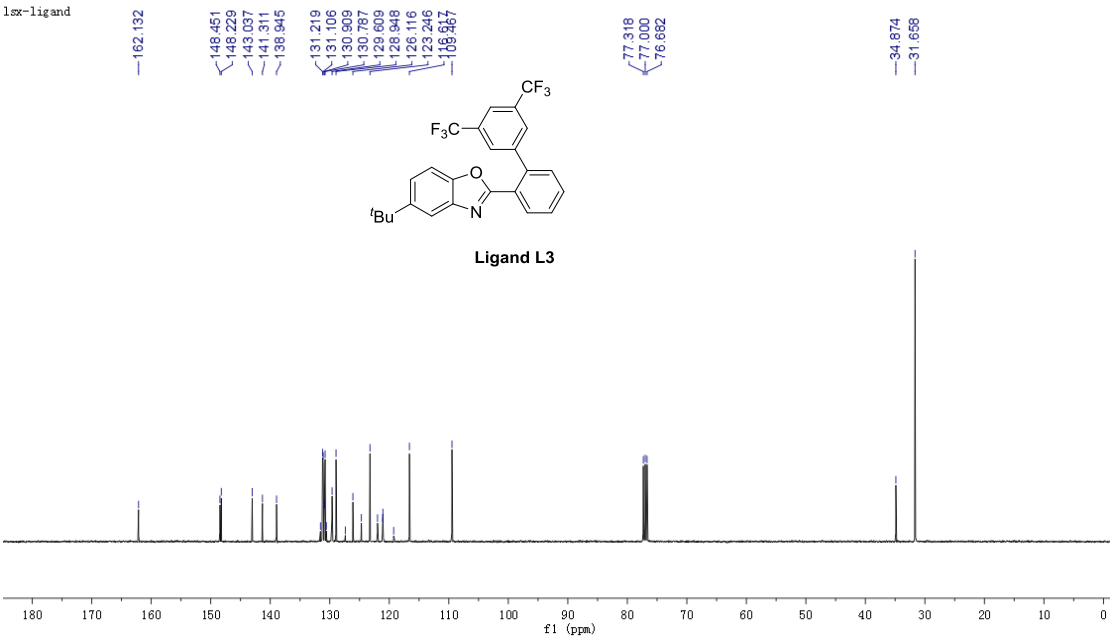
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.466	3453	650	0.007		M	
2	16.146	52001087	1796630	99.993		M	
Total		52004540	1797280				

HPLC traces of racemic **4** (reference) and chiral **4**. Area integration = 0.01:99.99 (> 99% ee)

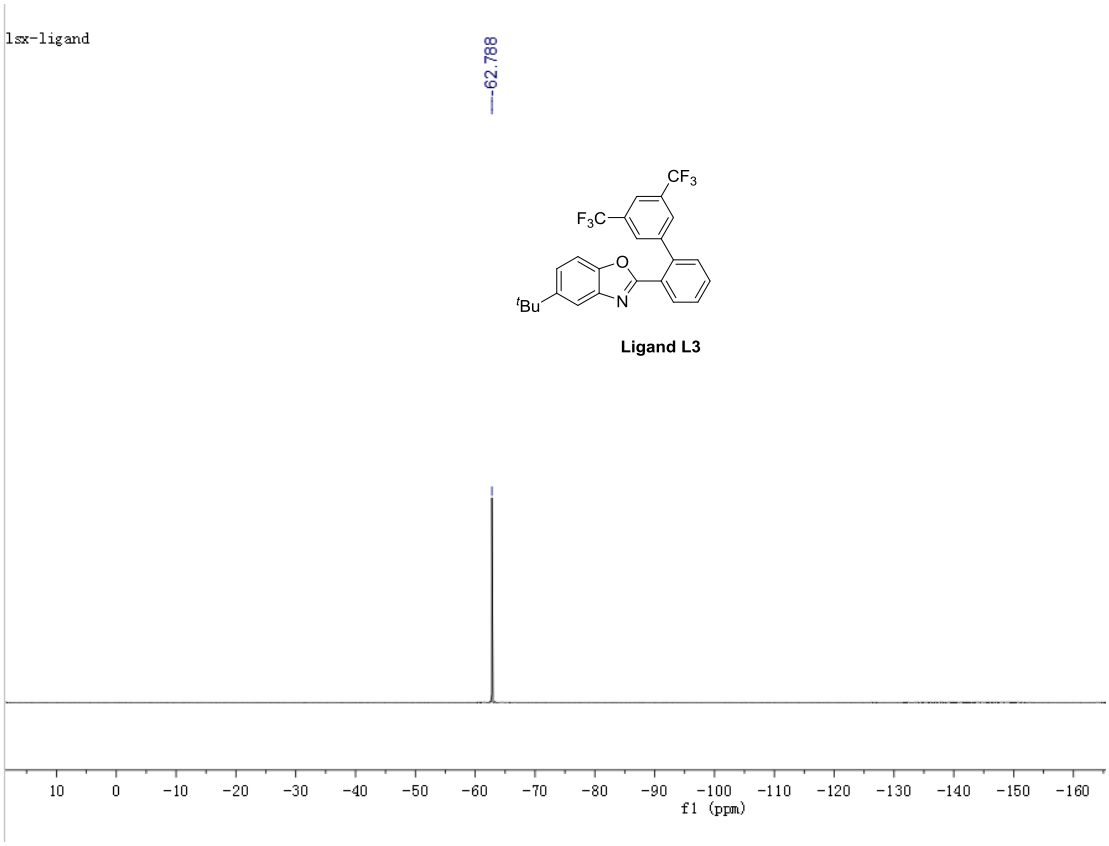
V NMR Spectra of Products



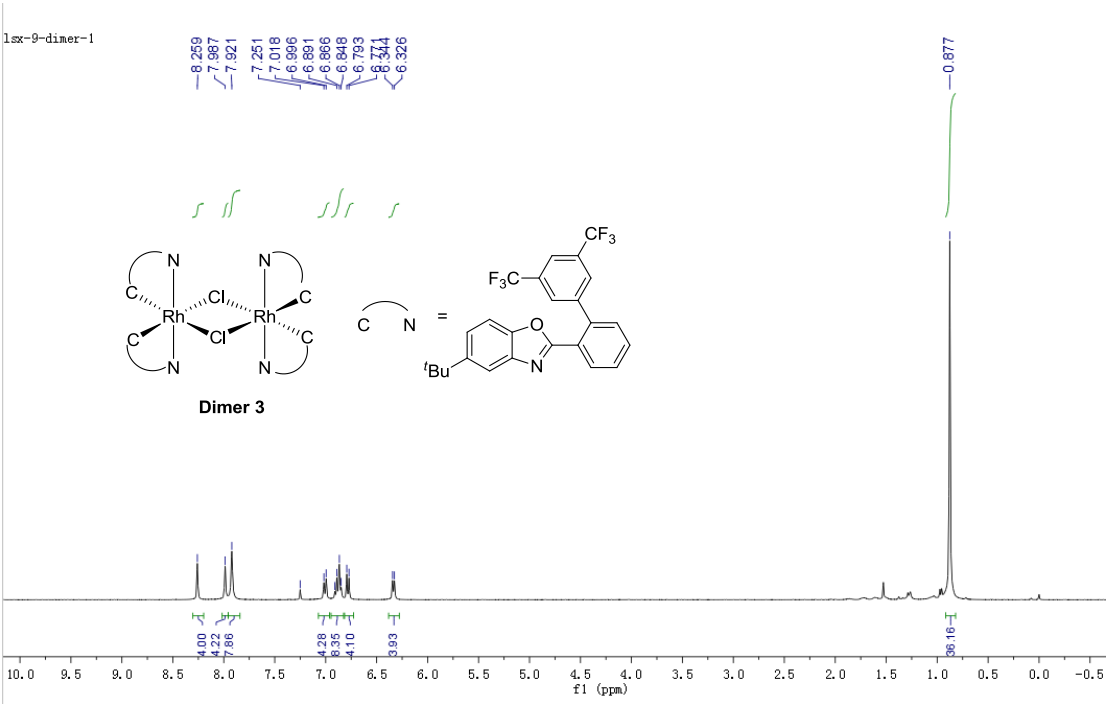
^{1}H NMR (400 MHz) spectra of **Ligand L3**



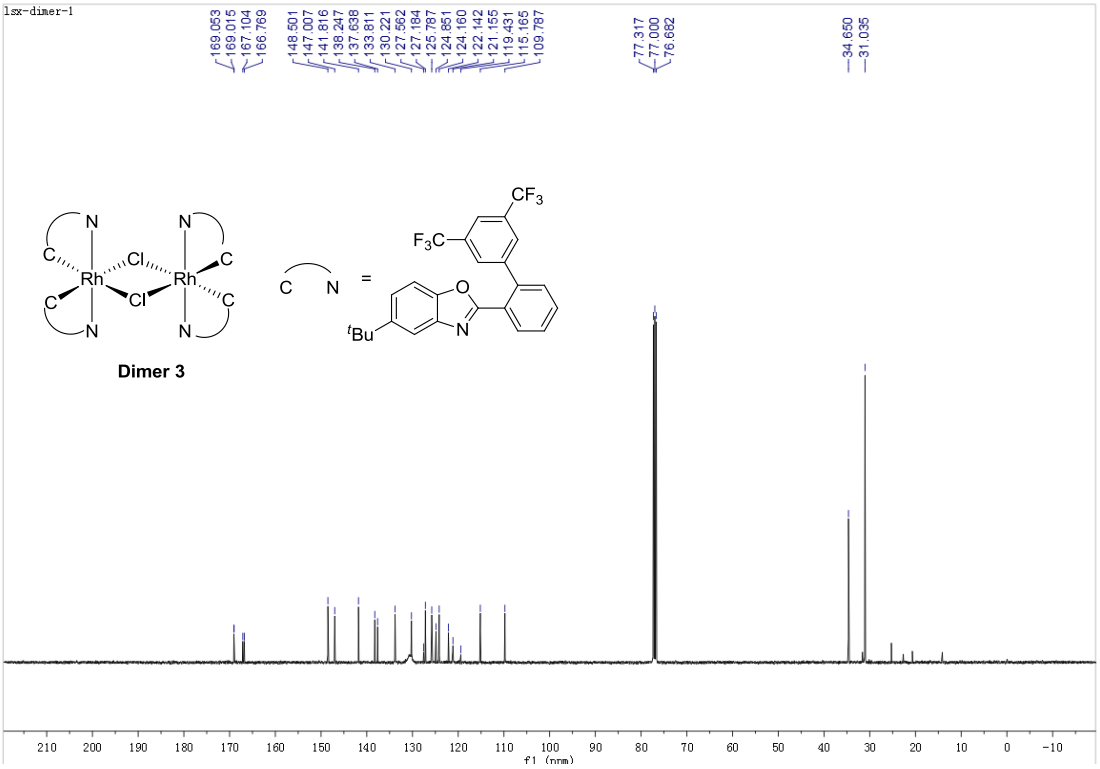
^{13}C NMR (100 MHz) spectra of **Ligand L3**



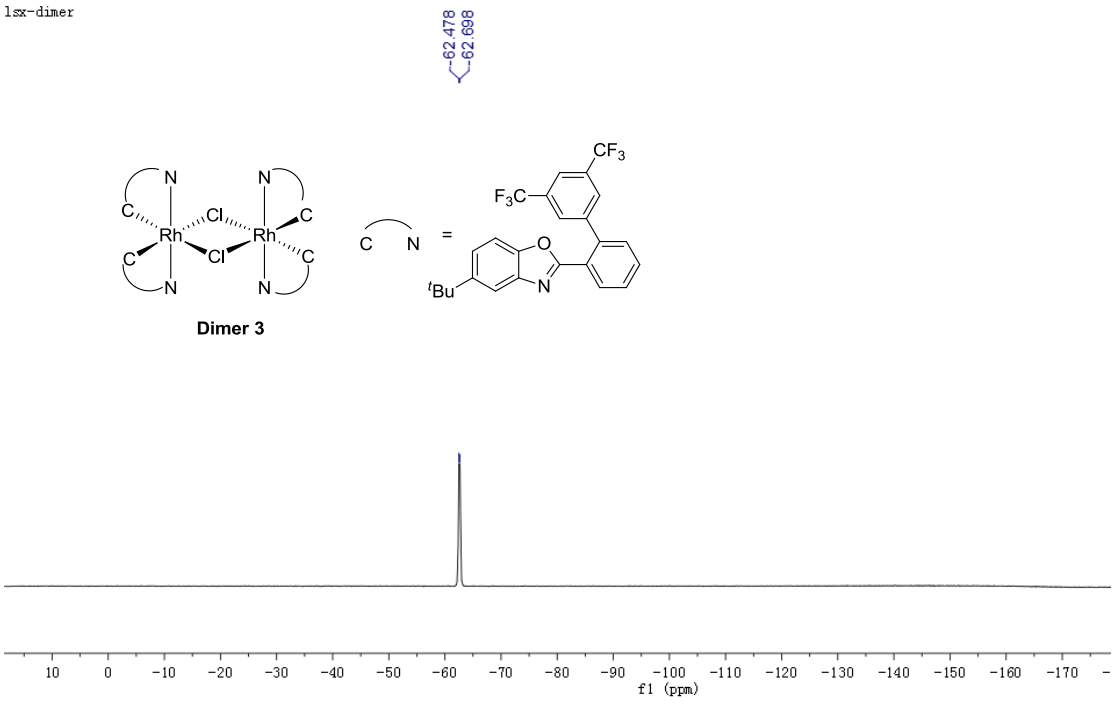
^{19}F NMR (376.4 MHz) spectra of **Ligand L3**



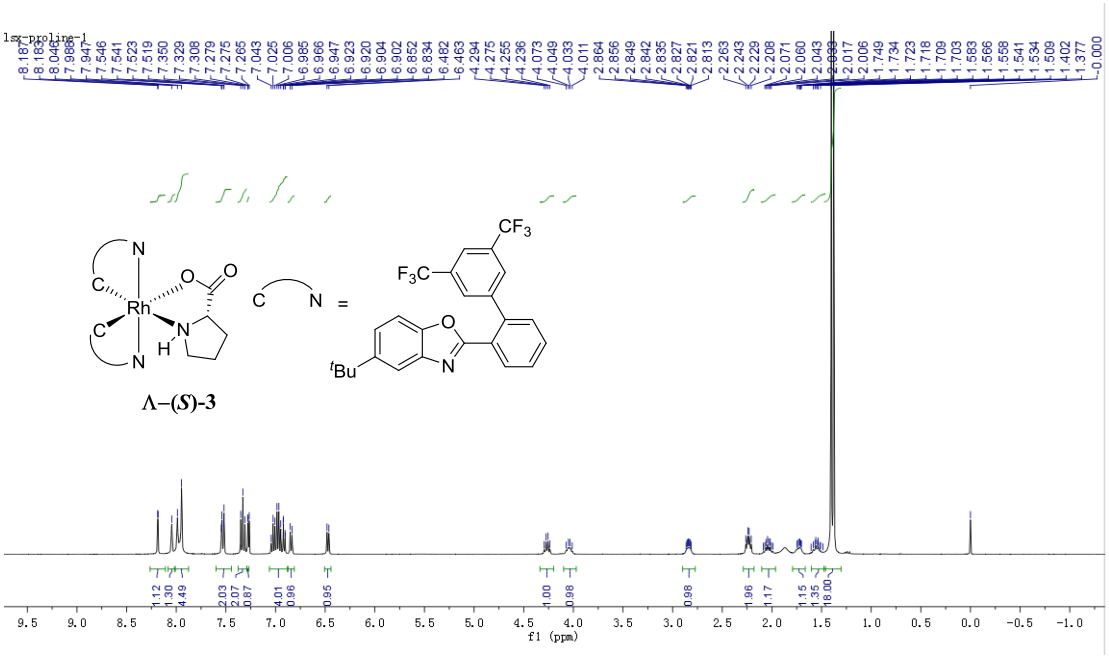
^{1}H NMR (400 MHz) spectra of **Dimer 3**



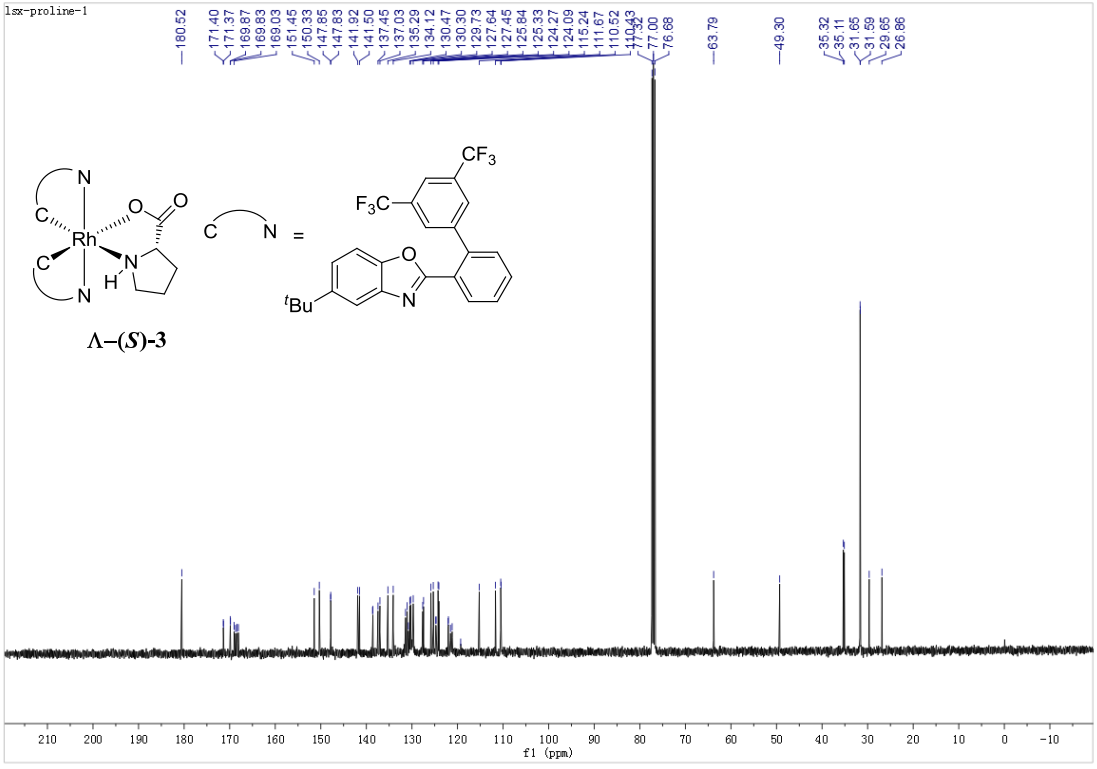
^{13}C NMR (100 MHz) spectra of **Dimer 3**



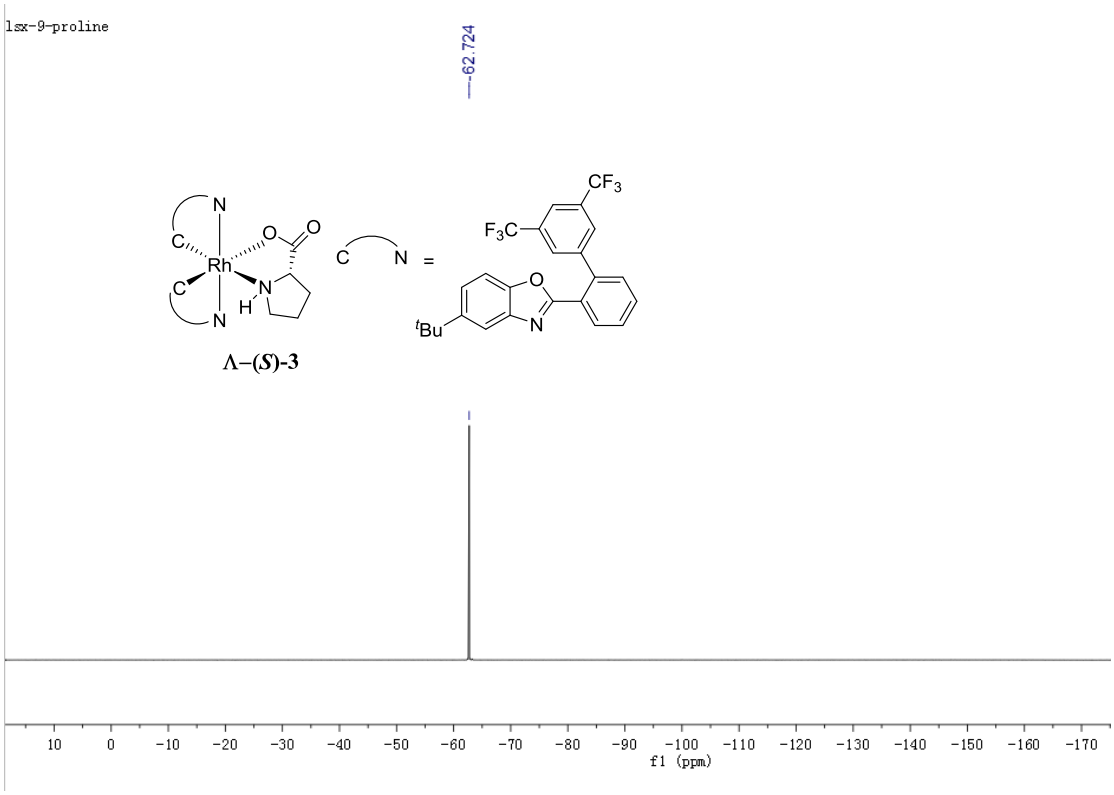
^{19}F NMR (376.4 MHz) spectra of **Dimer 3**



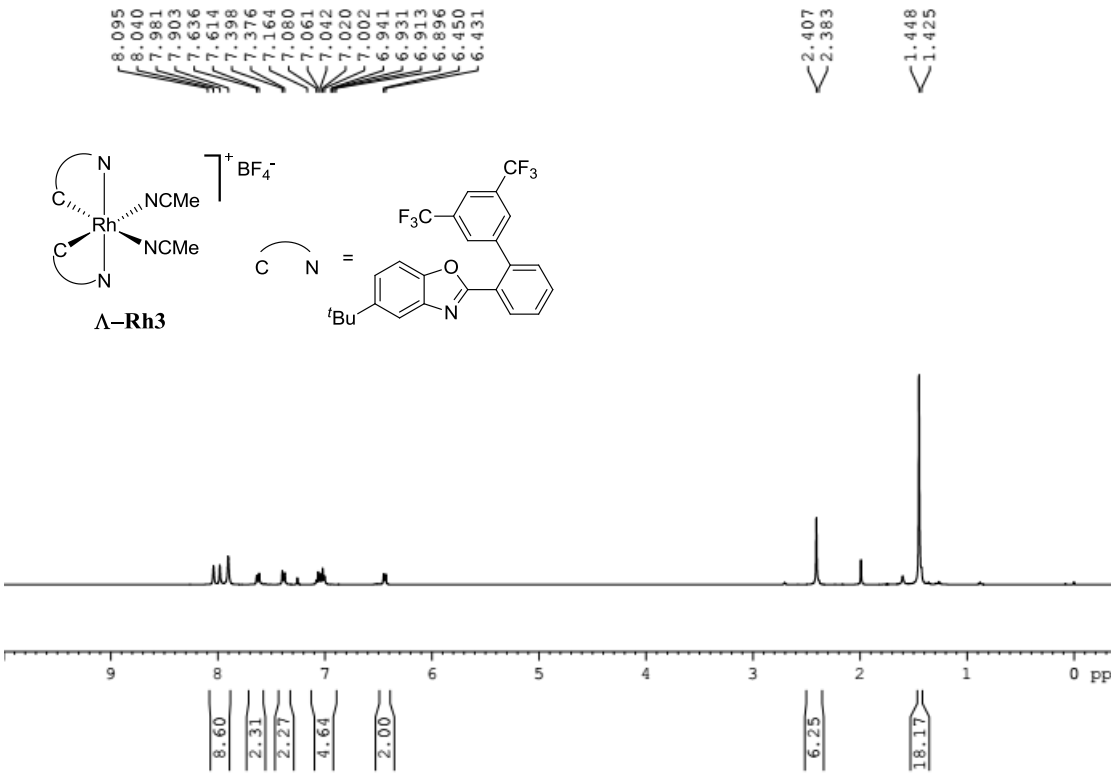
^{1}H NMR (400 MHz) spectra of **Λ-(*S*)-3**



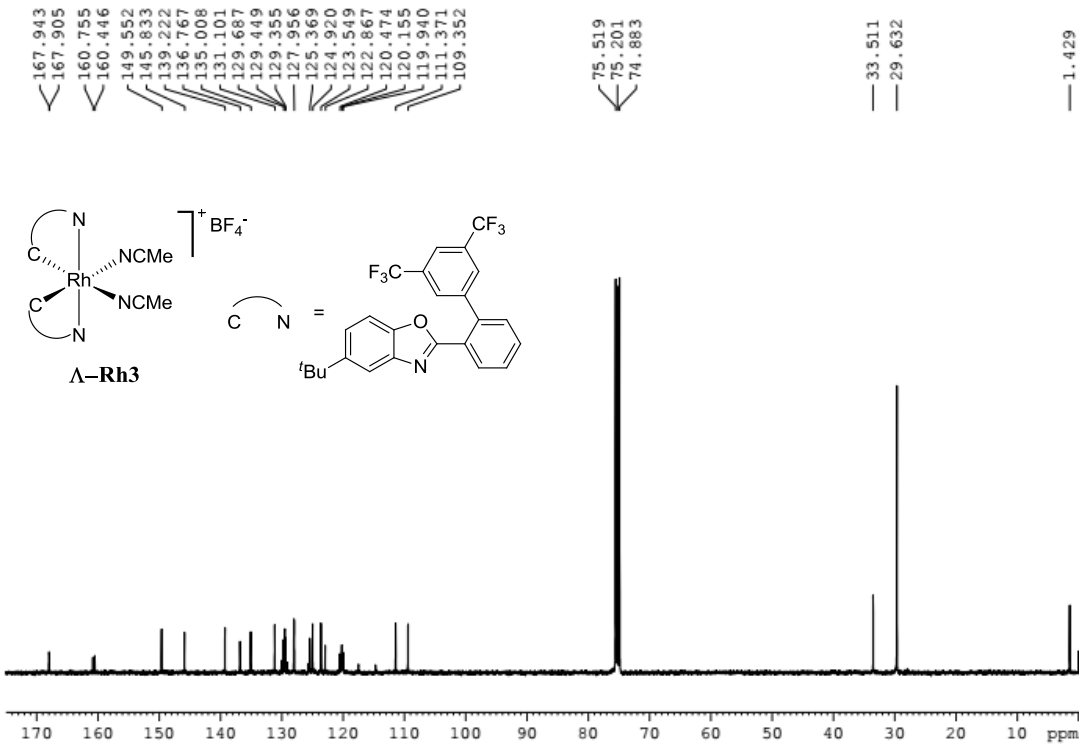
^{13}C NMR (100 MHz) spectra of **Λ-(*S*) -3**



^{19}F NMR (376.4 MHz) spectra of **Λ-(*S*)-3**

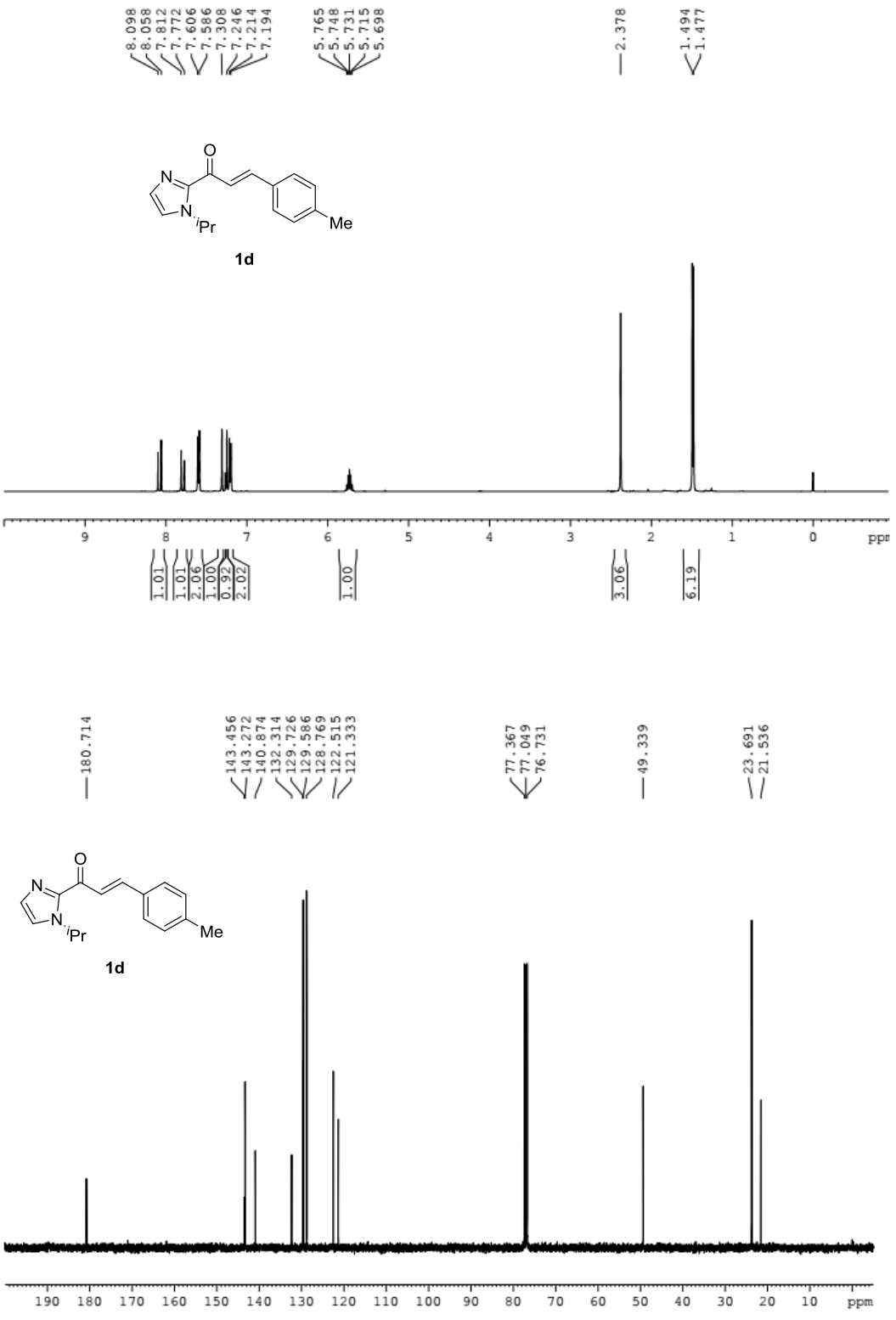


^{1}H NMR (400 MHz) spectra of catalyst **Λ-Rh3**

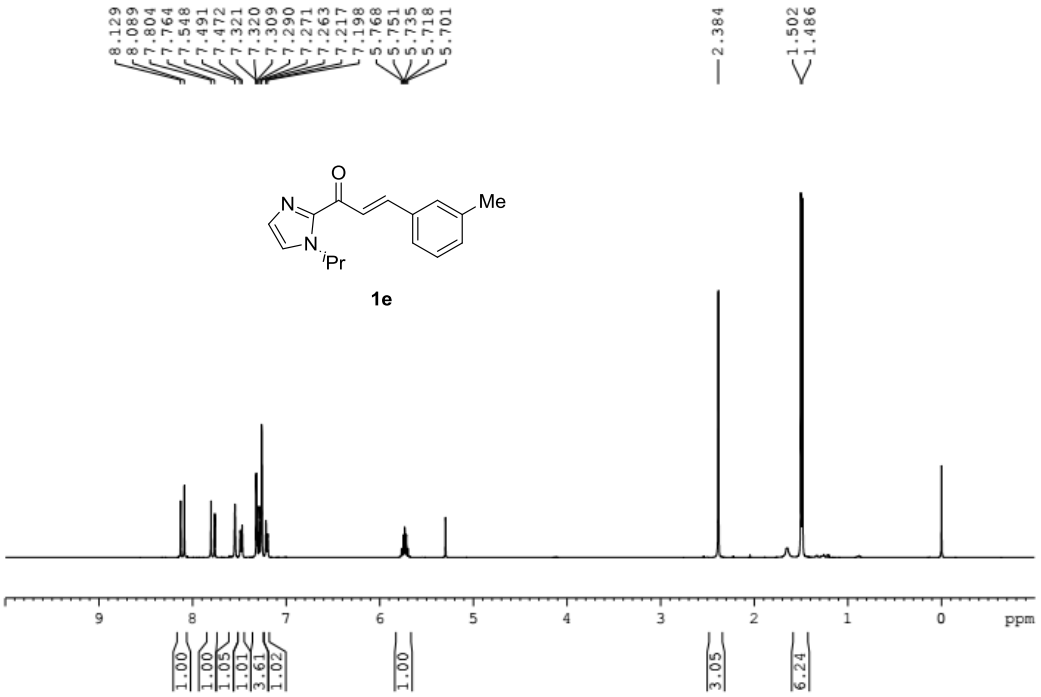


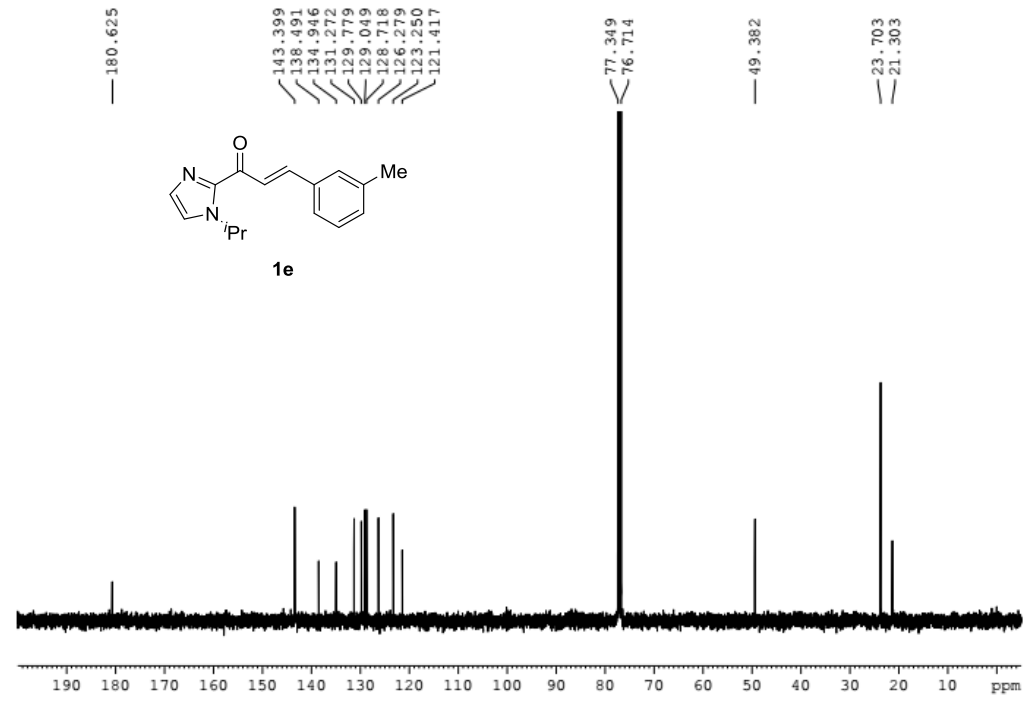
^{13}C NMR (100 MHz) spectra of catalyst **Λ-Rh3**

VI NMR Spectra of Substrates

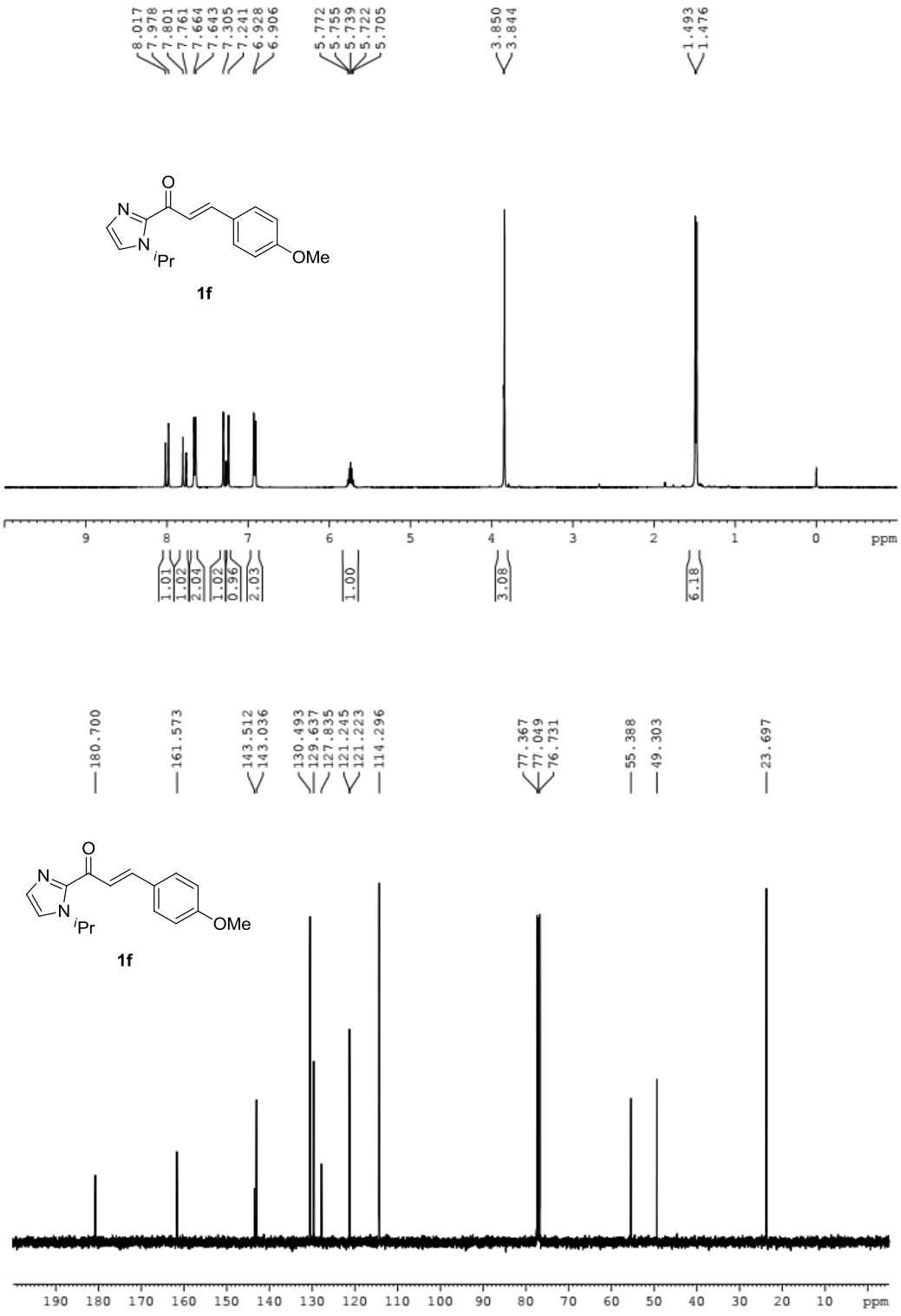


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1d**

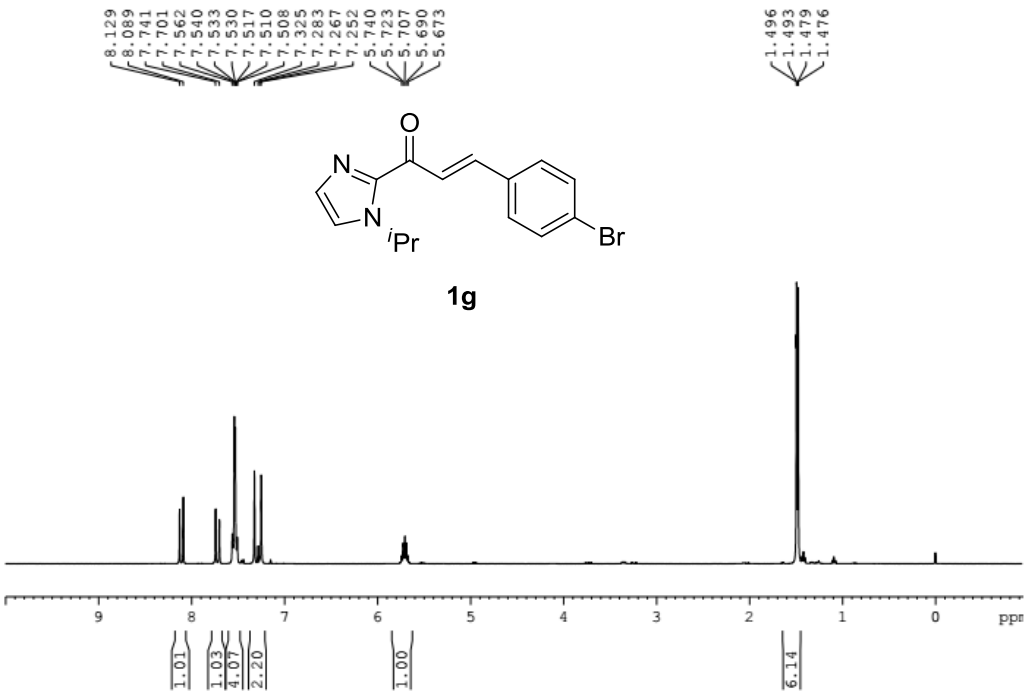


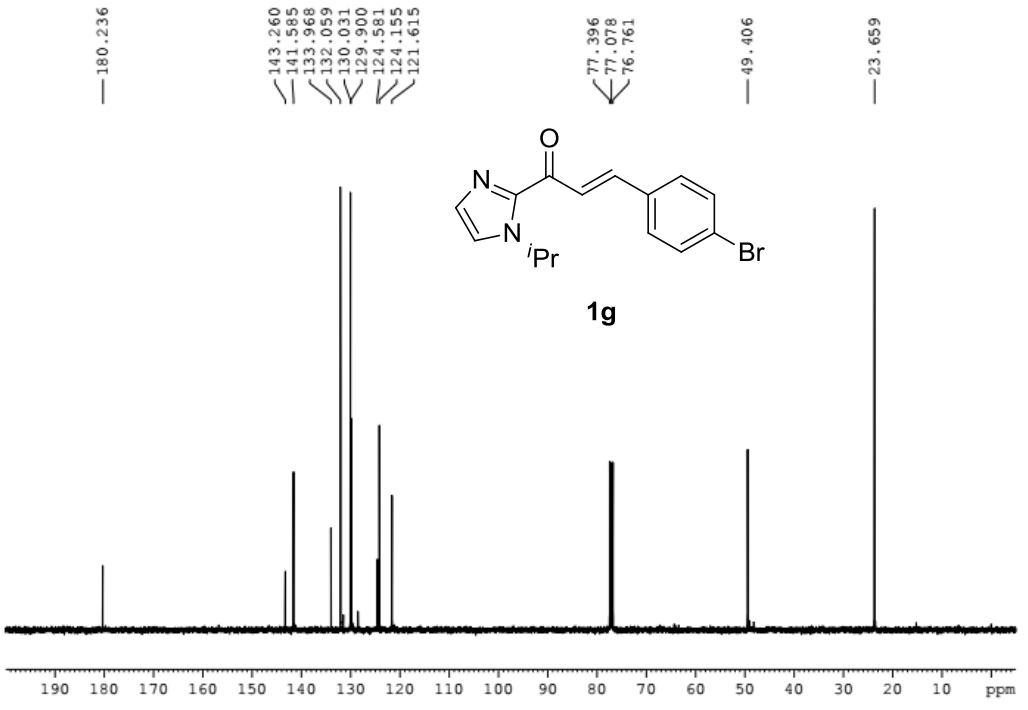


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1e**

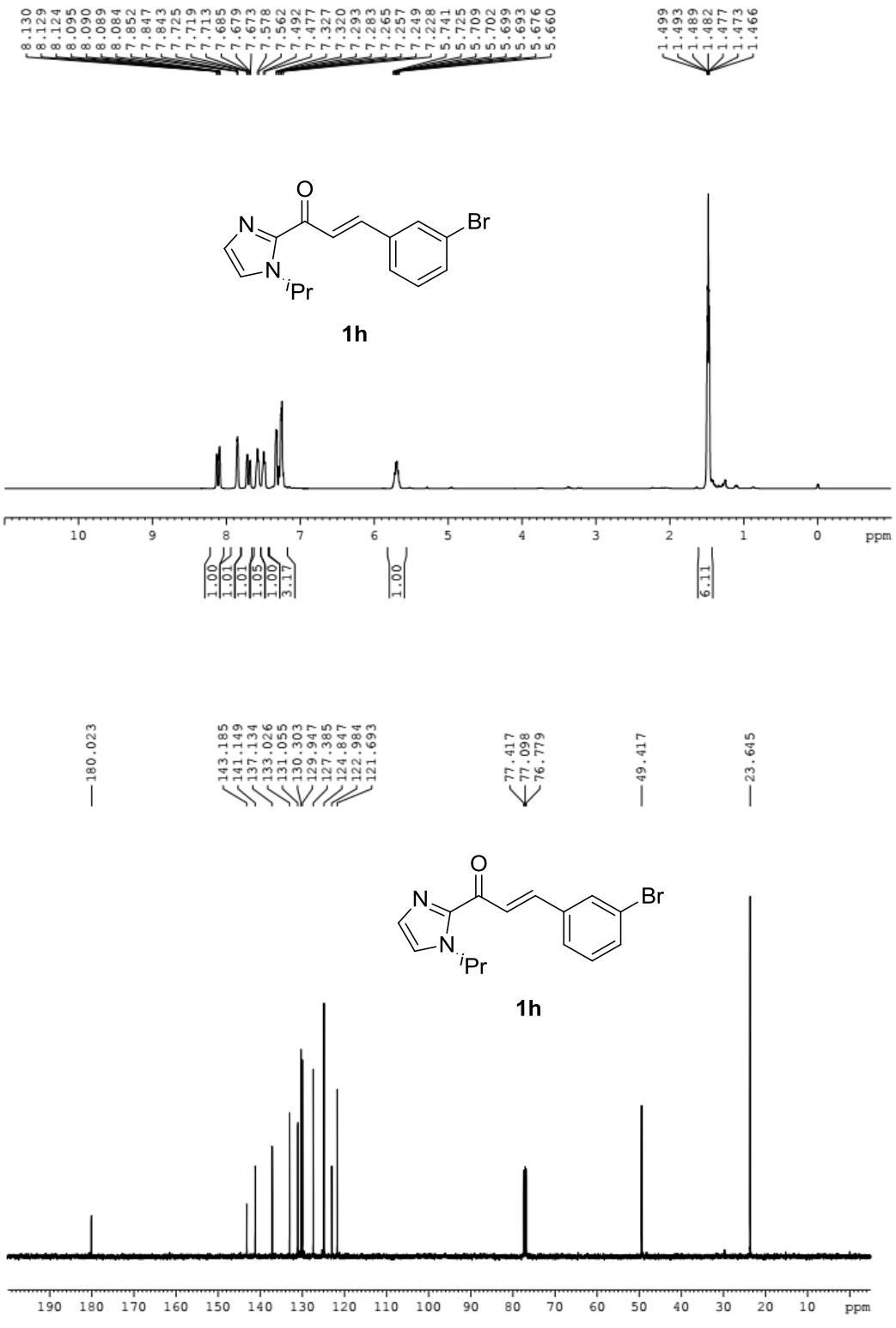


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1f**

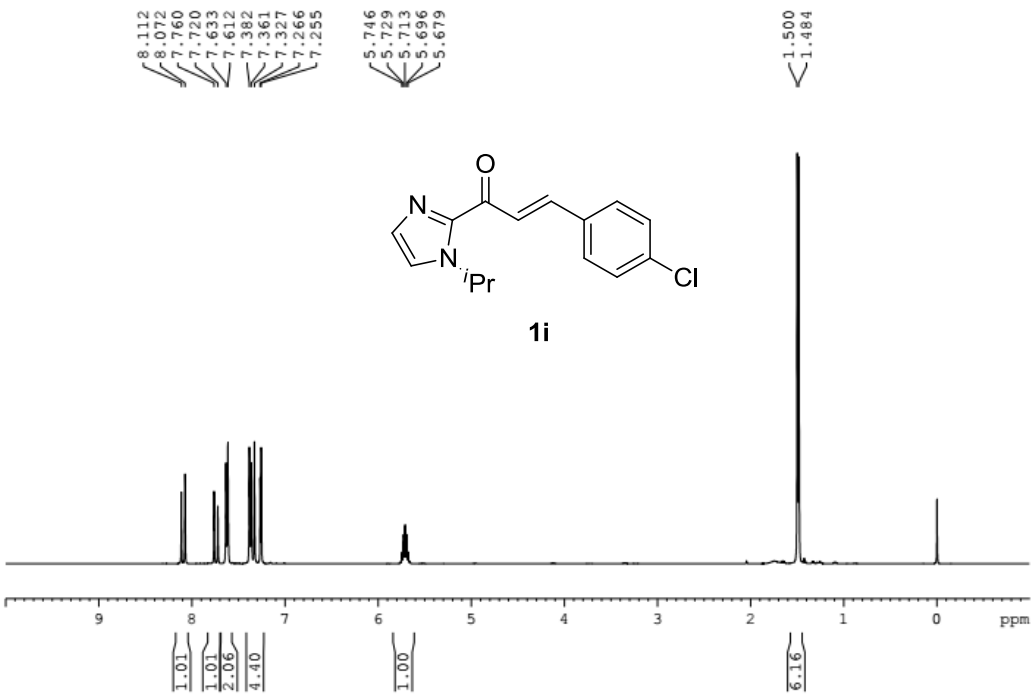


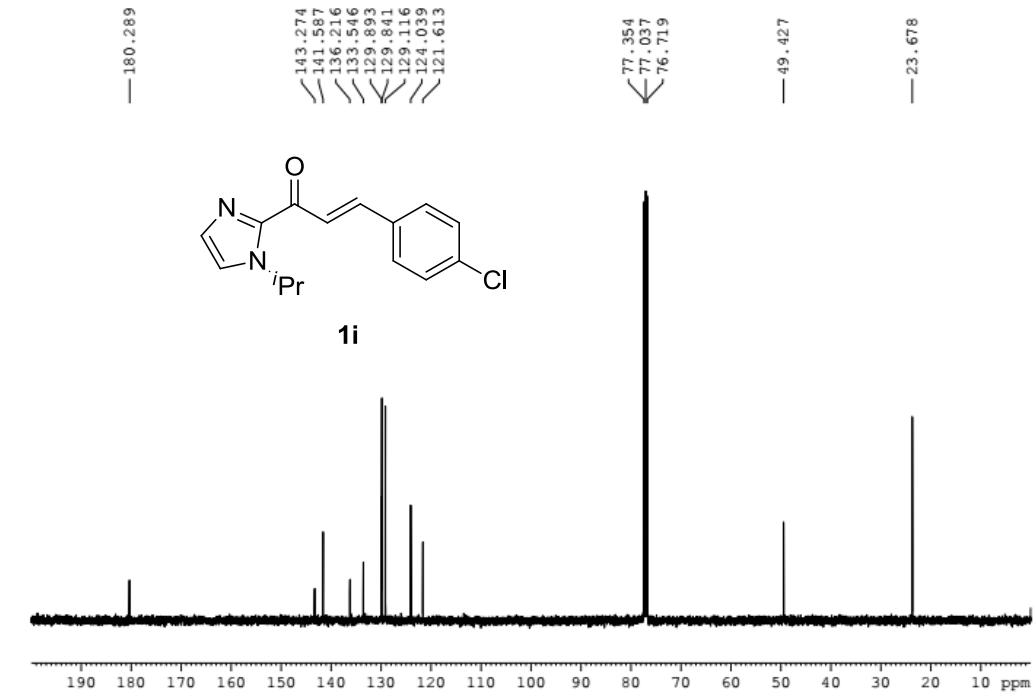


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1g**

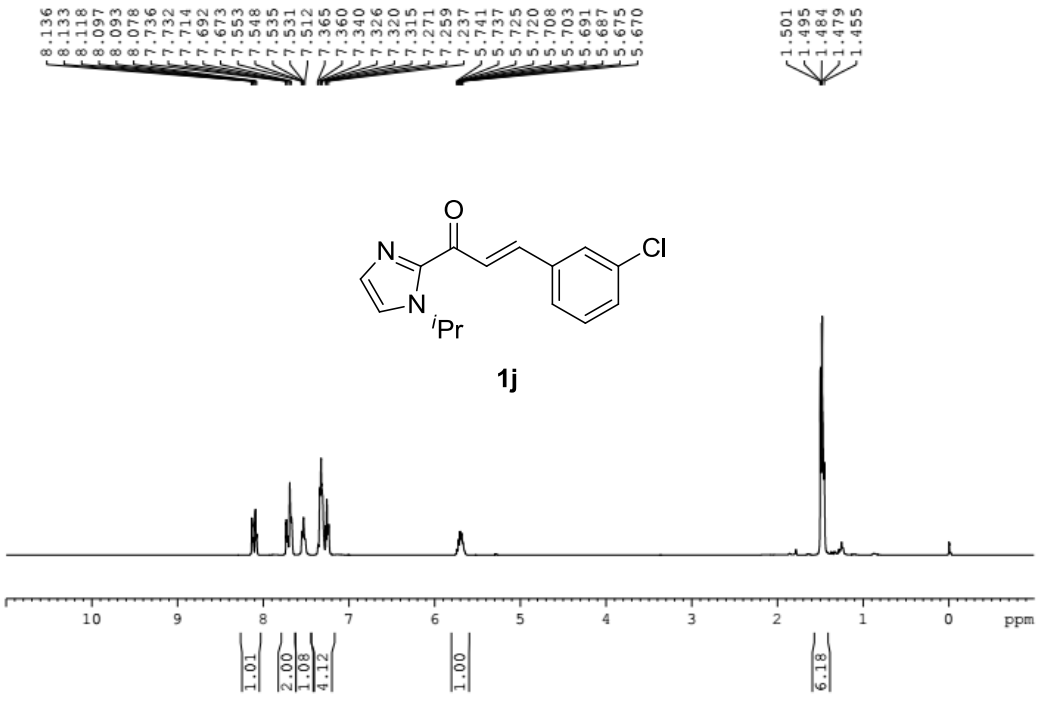


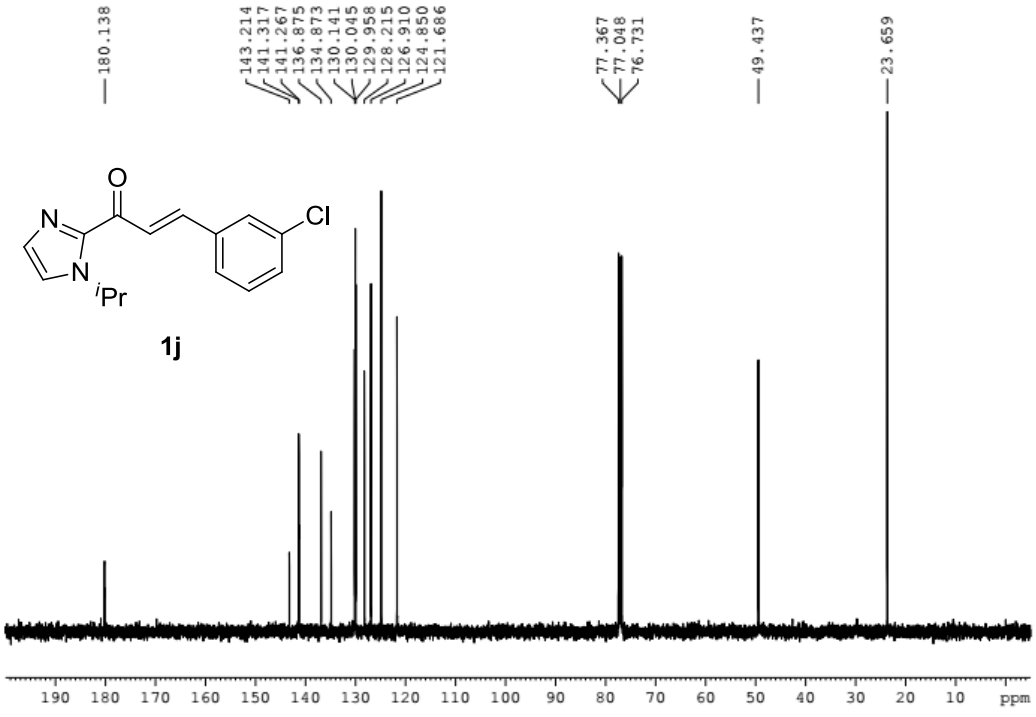
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1h**



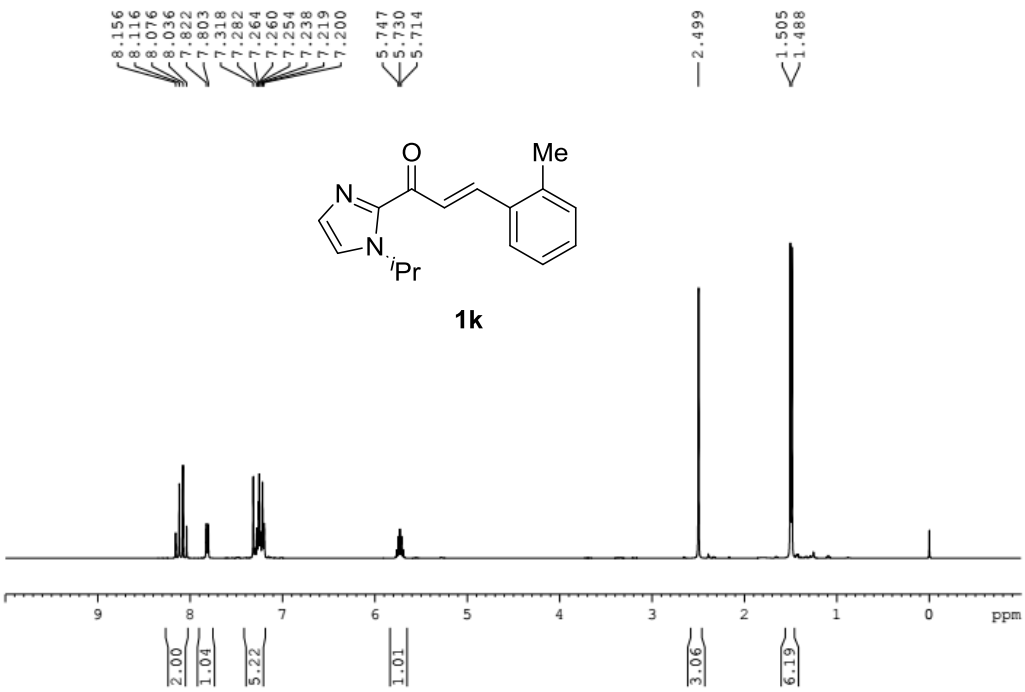


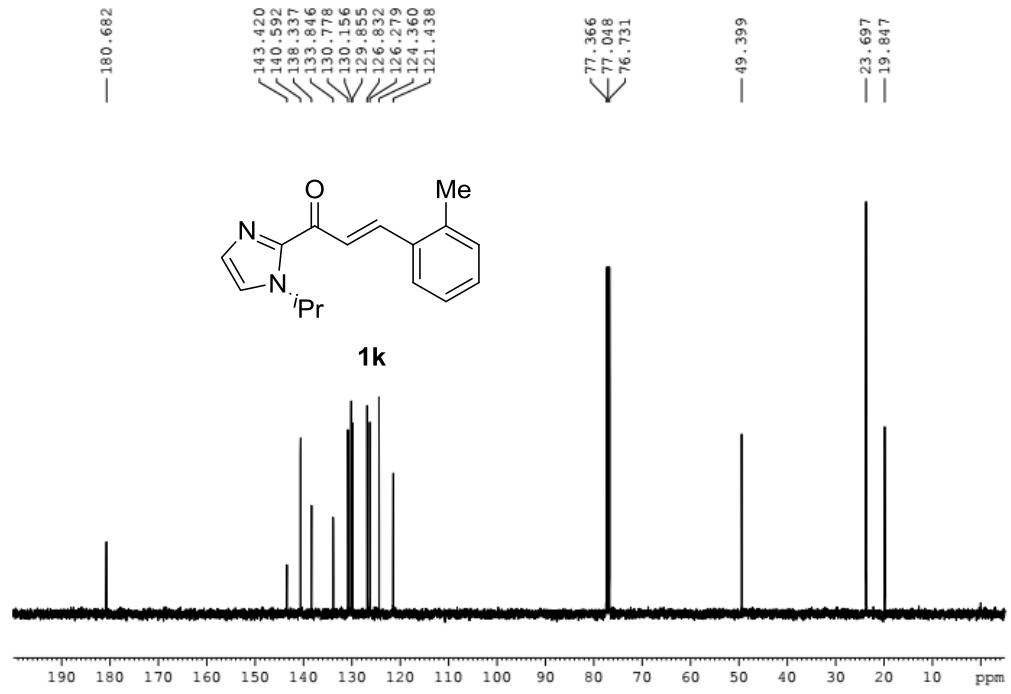
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1i**



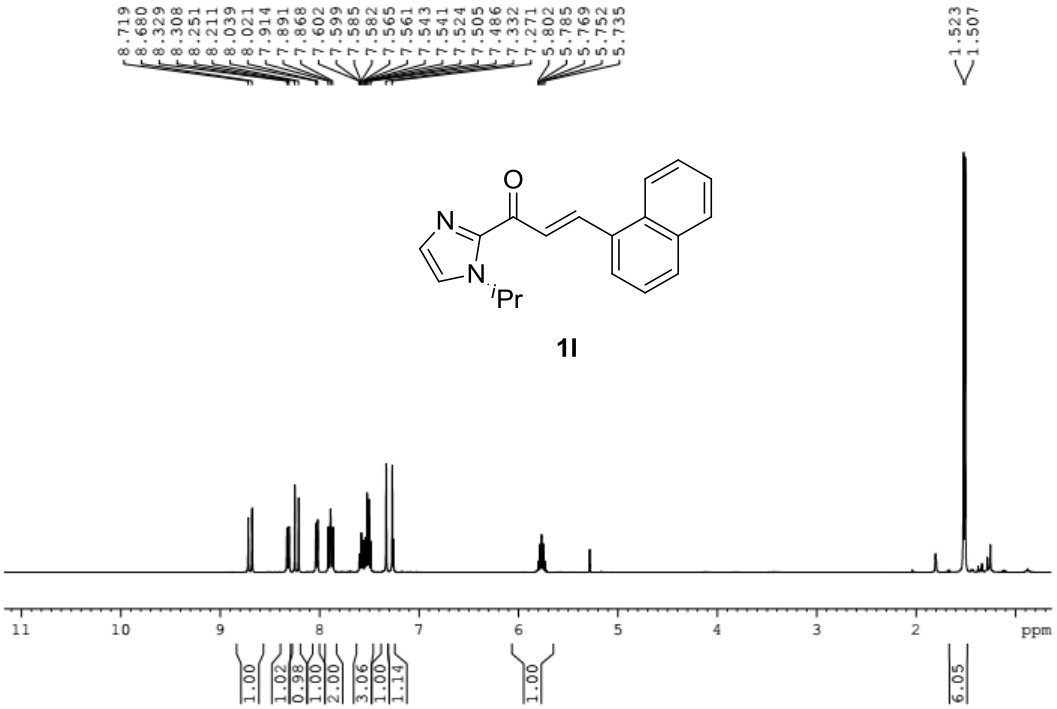


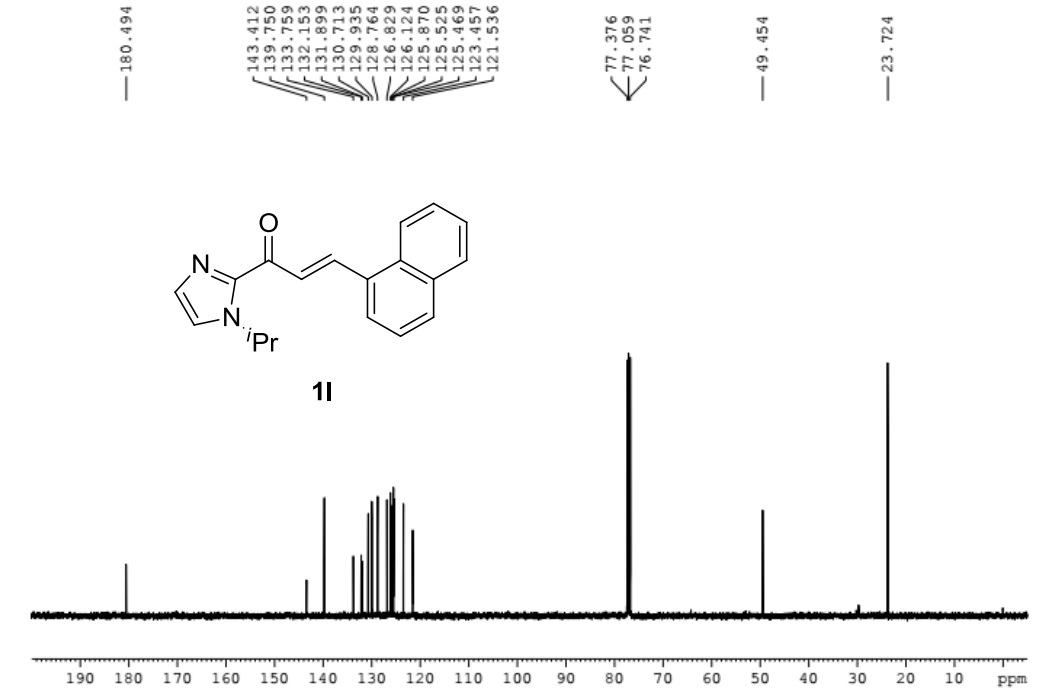
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1j**



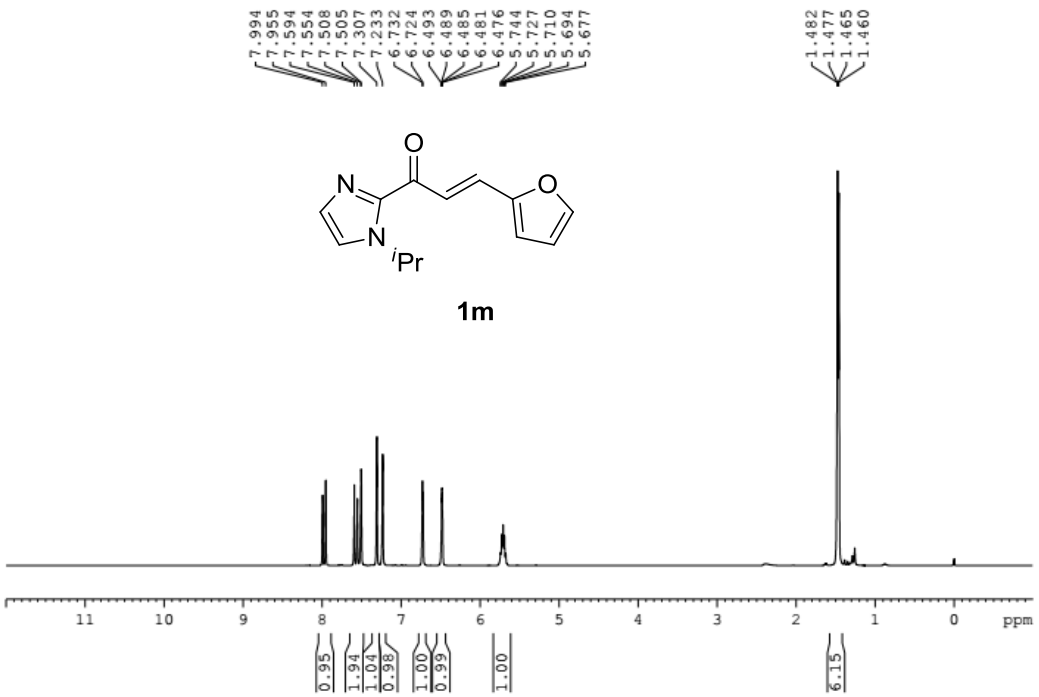


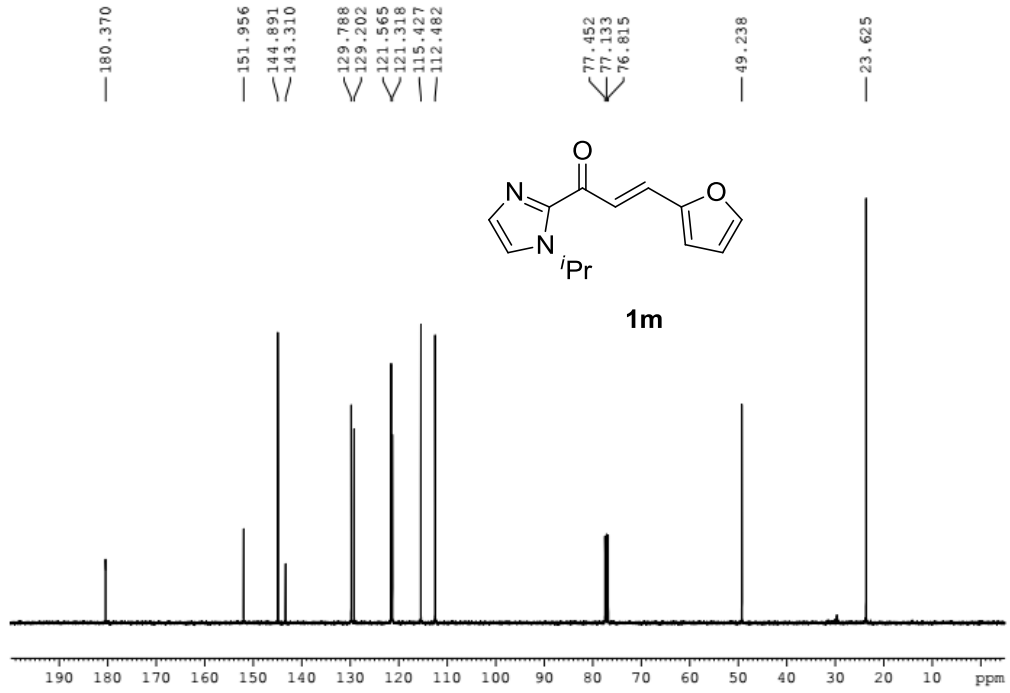
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1k**



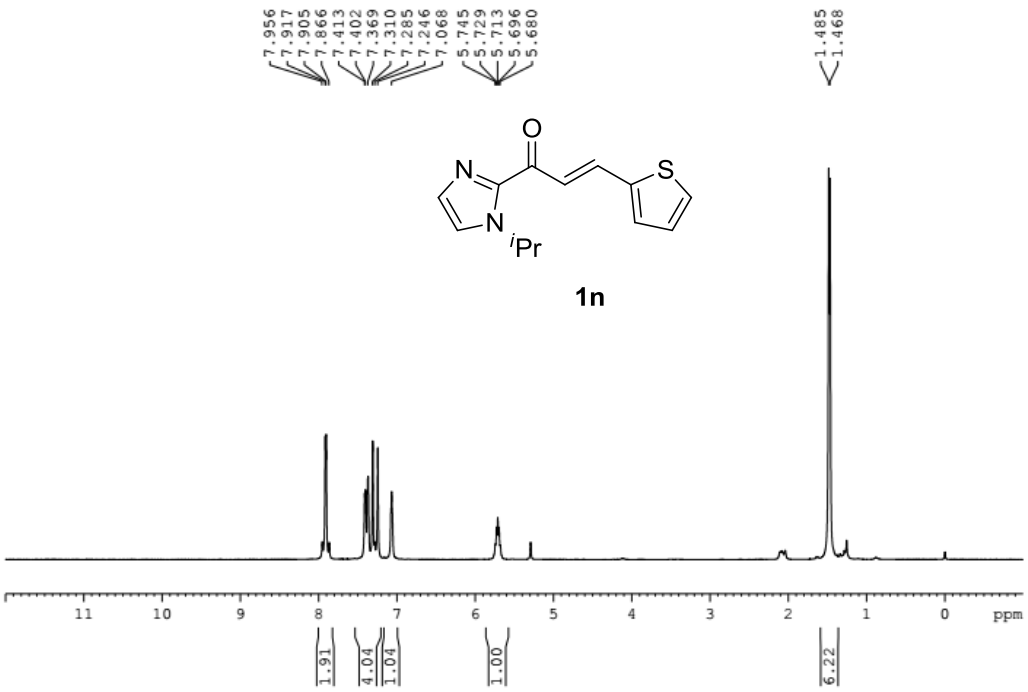


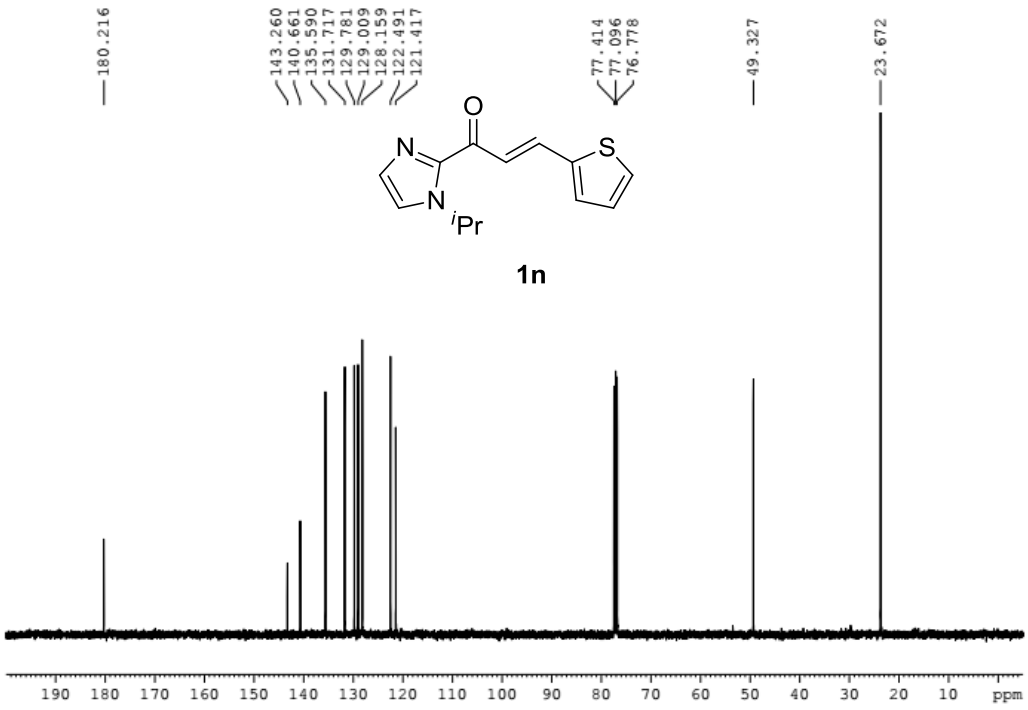
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1l**





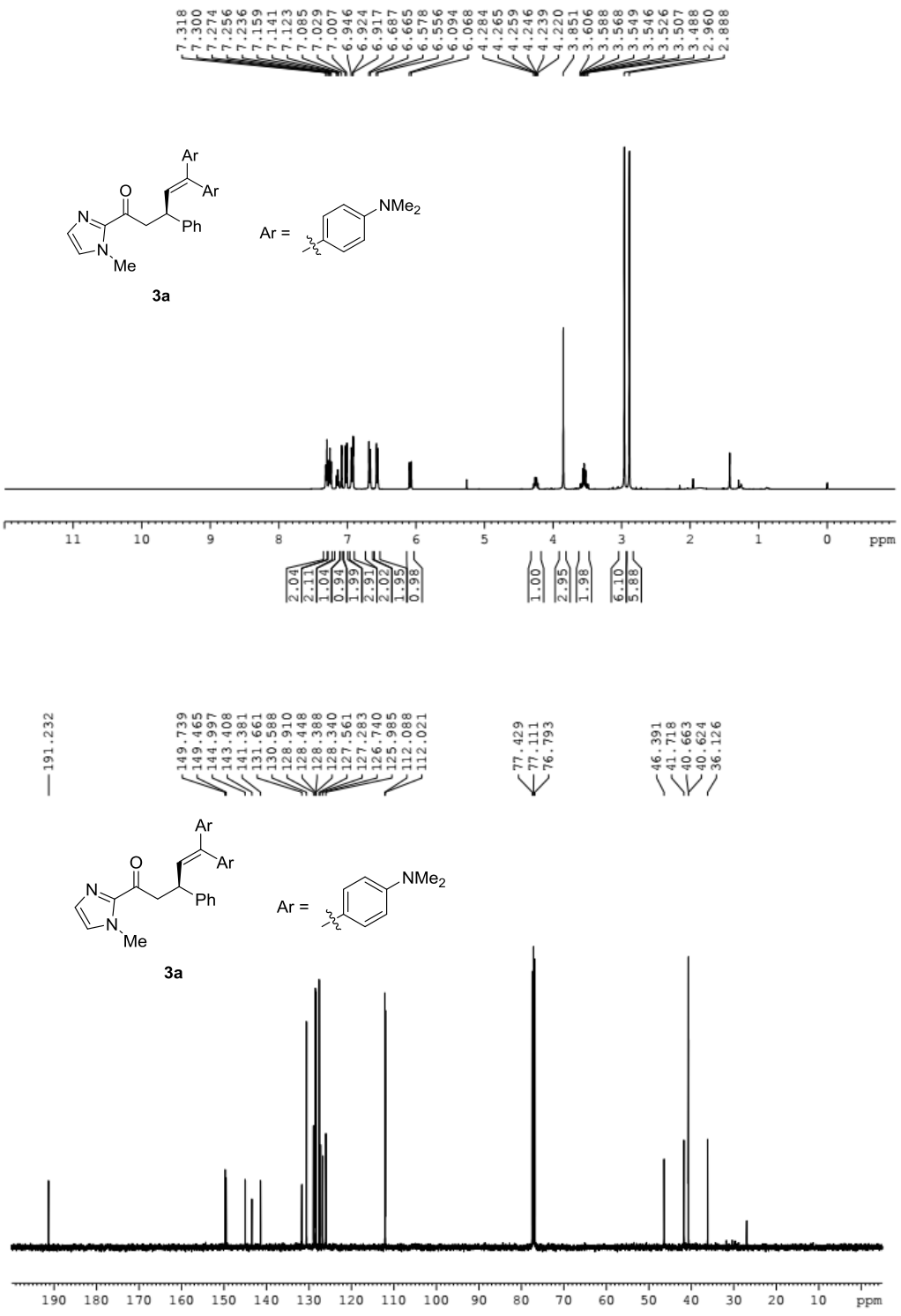
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1m**



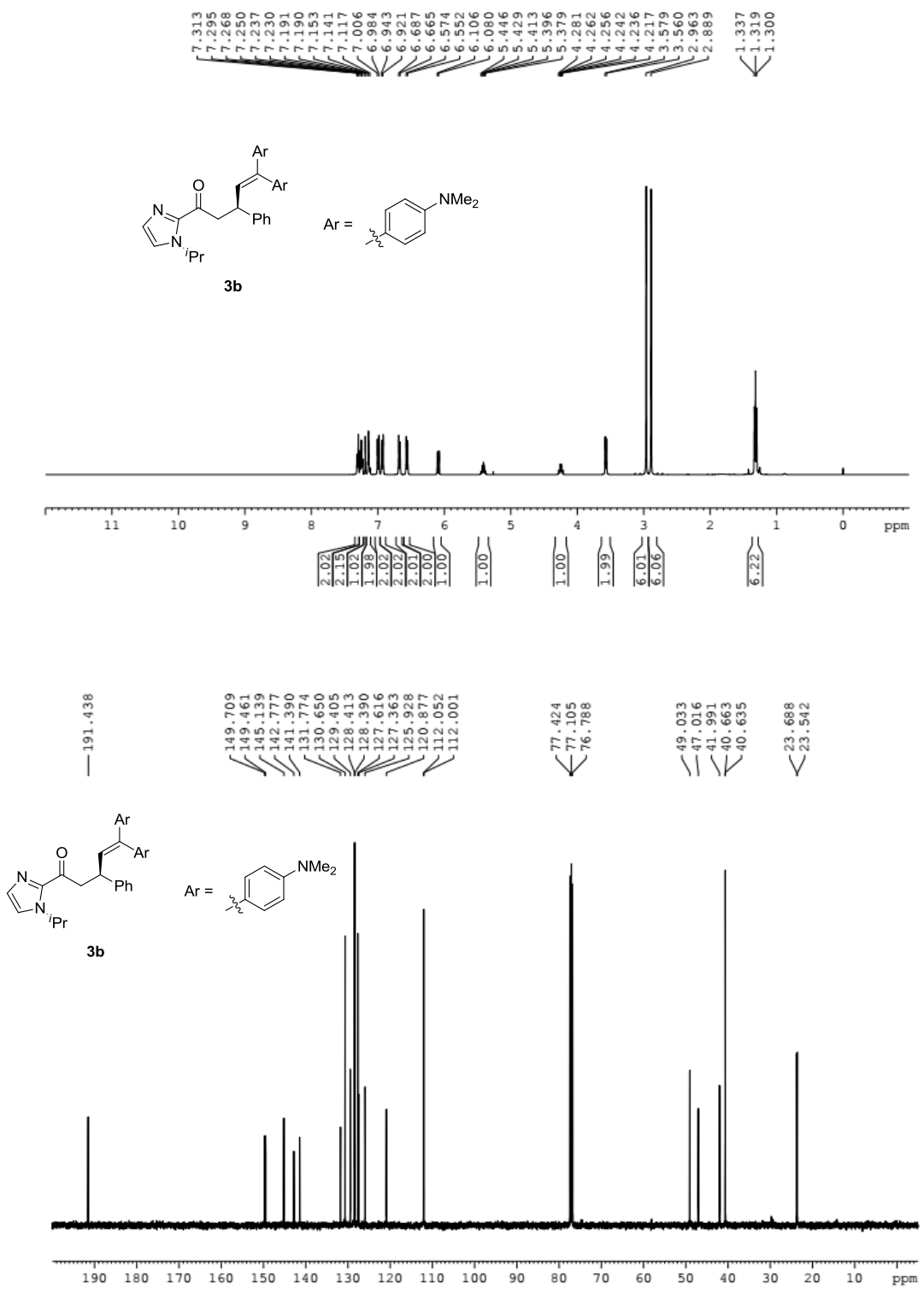


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1n**

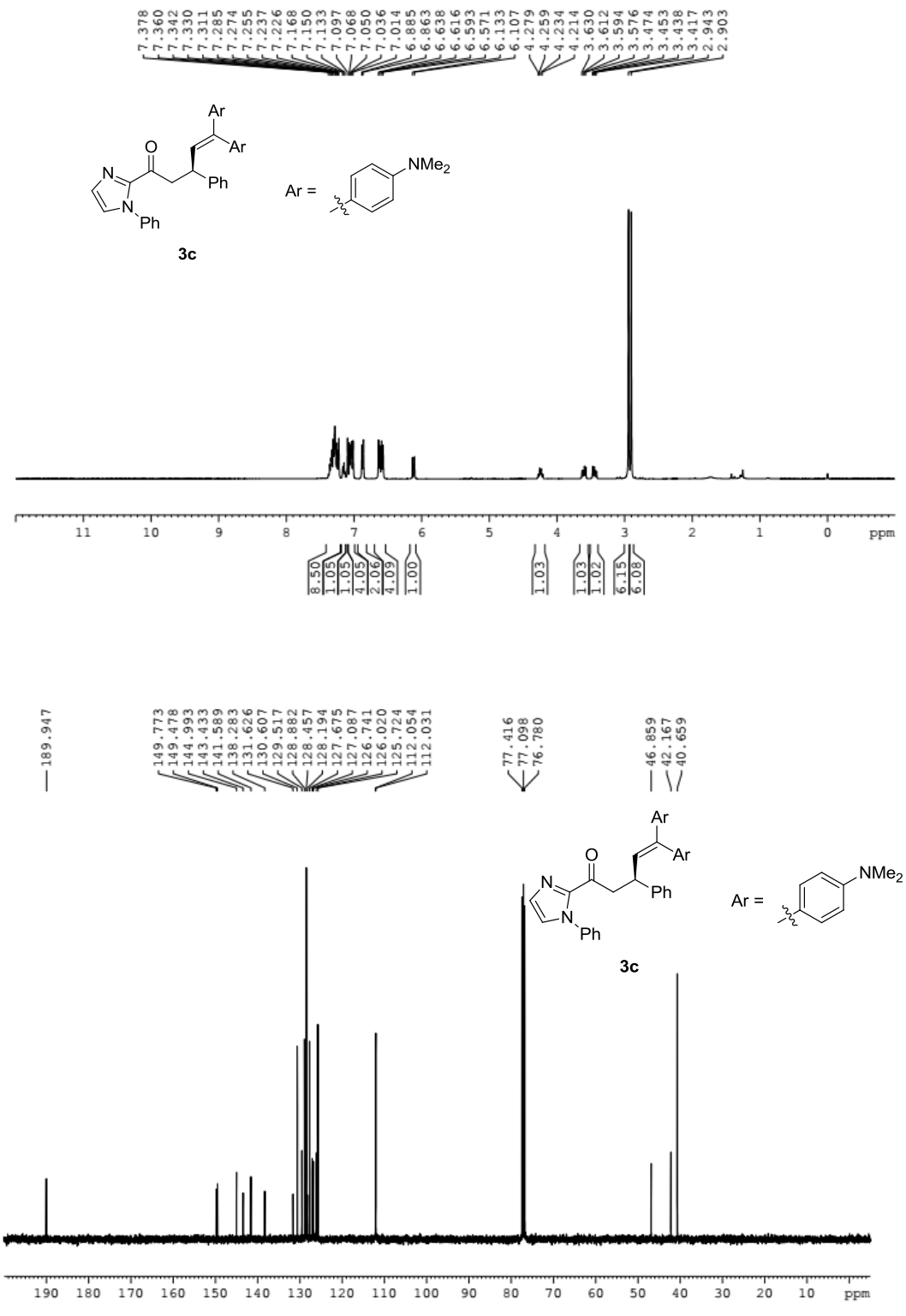
VII NMR Spectra of Products



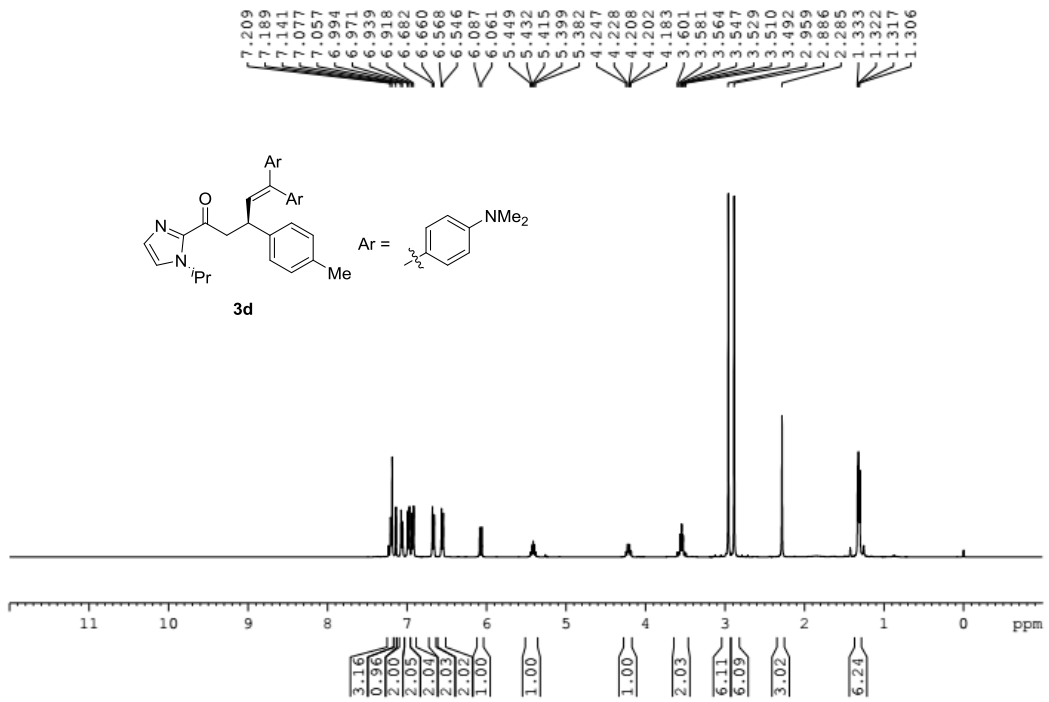
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3a**

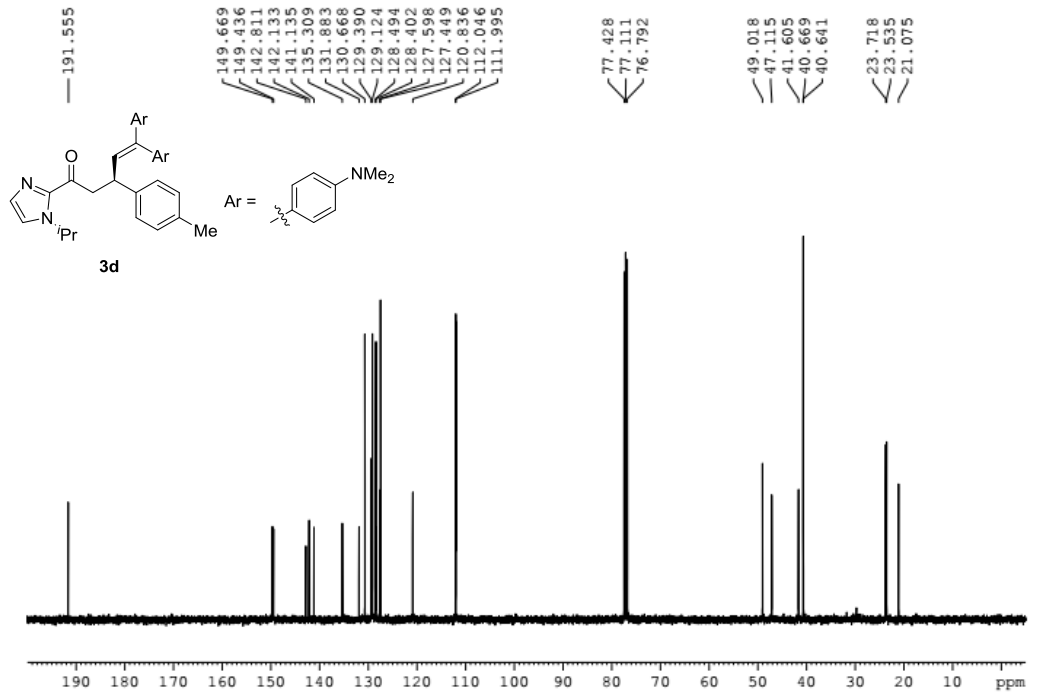


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3b**

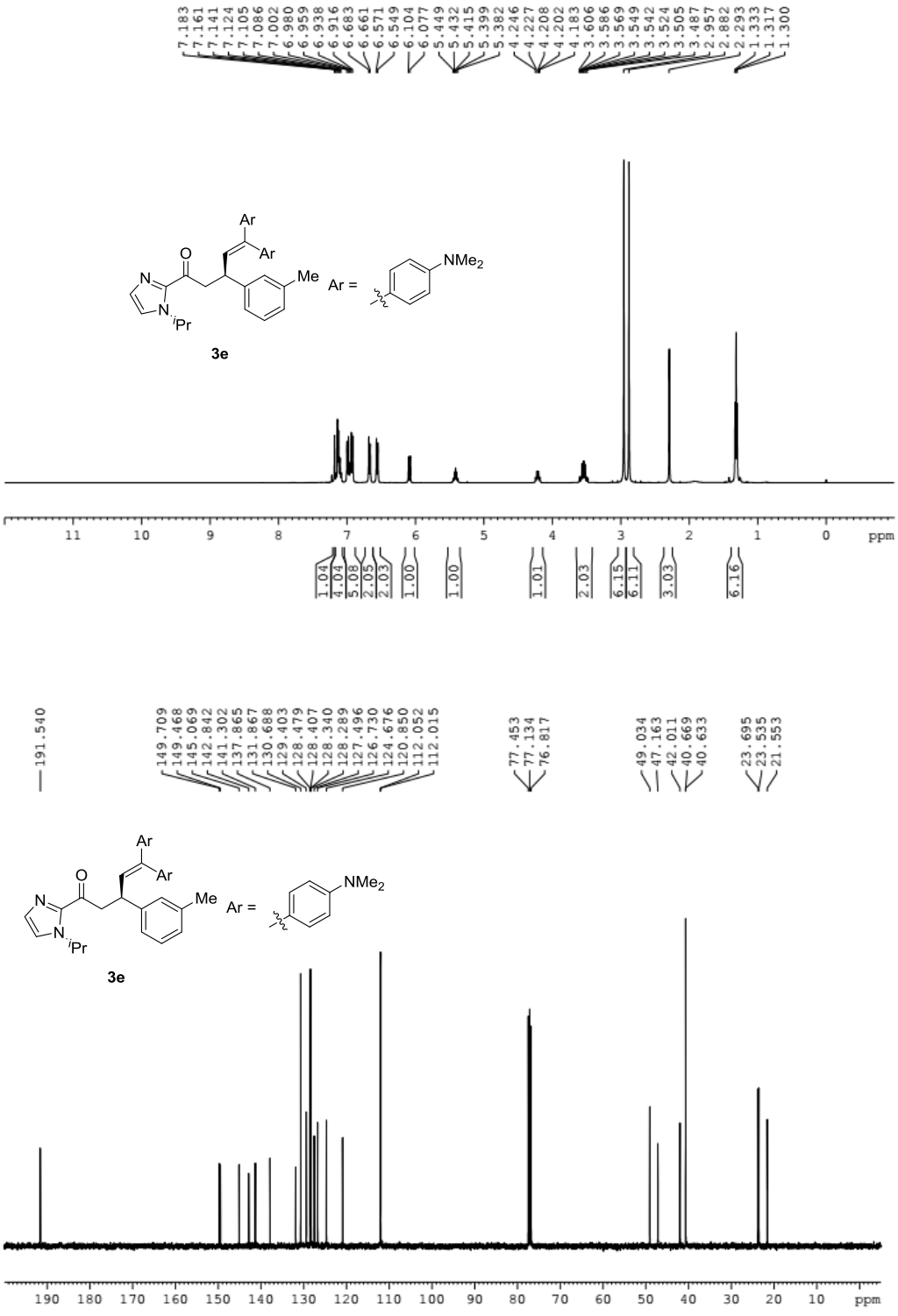


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3c**

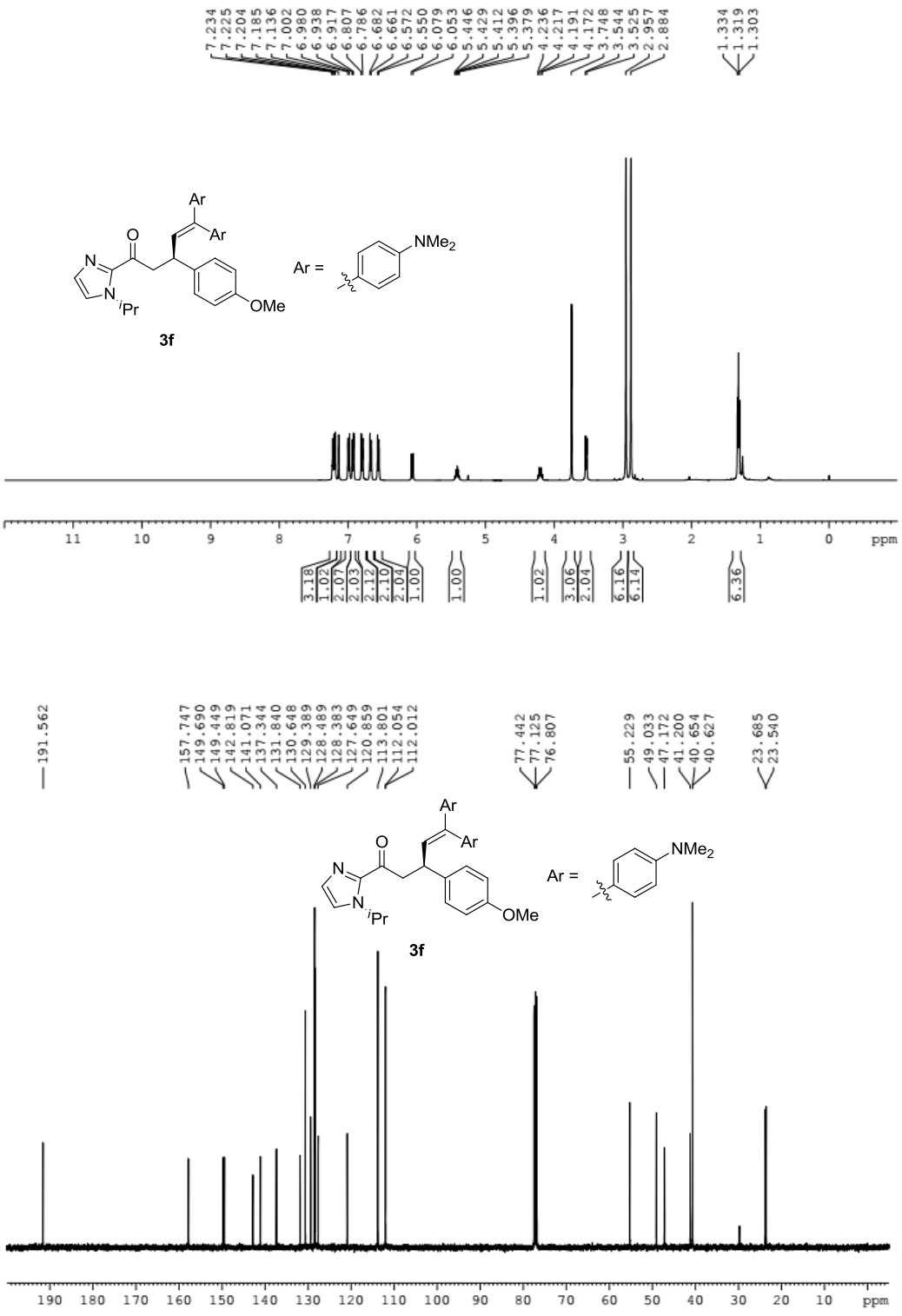




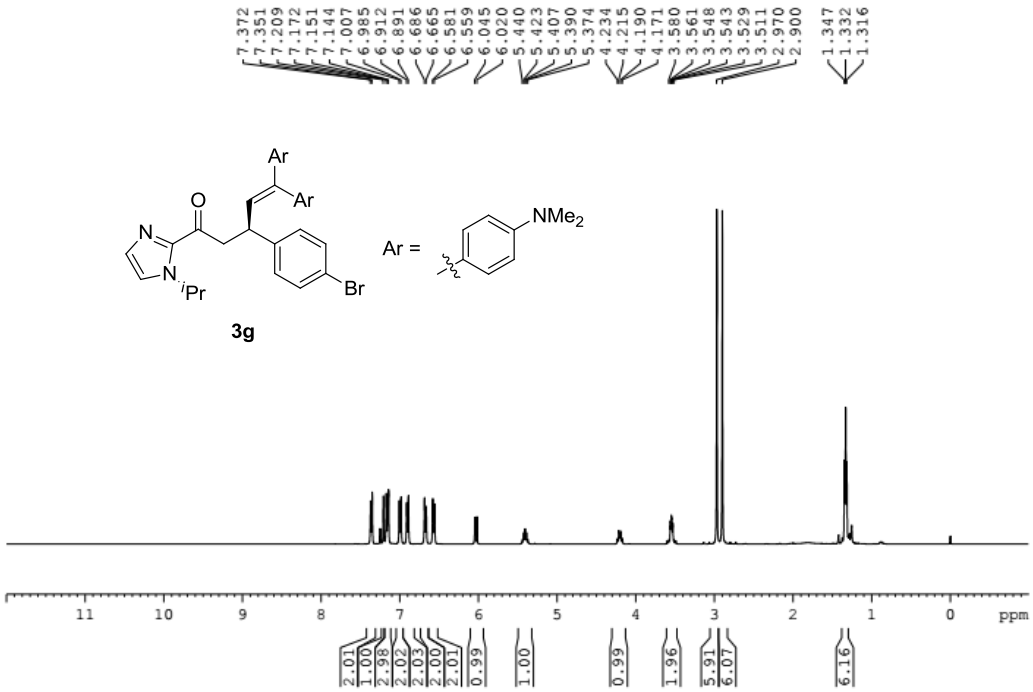
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3d**

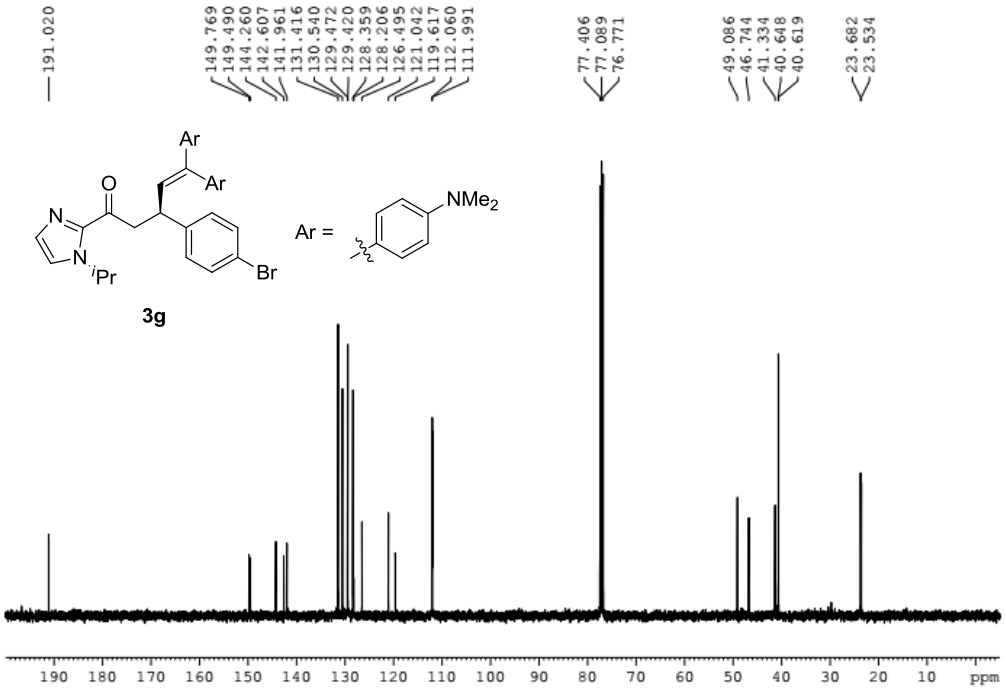


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3e**

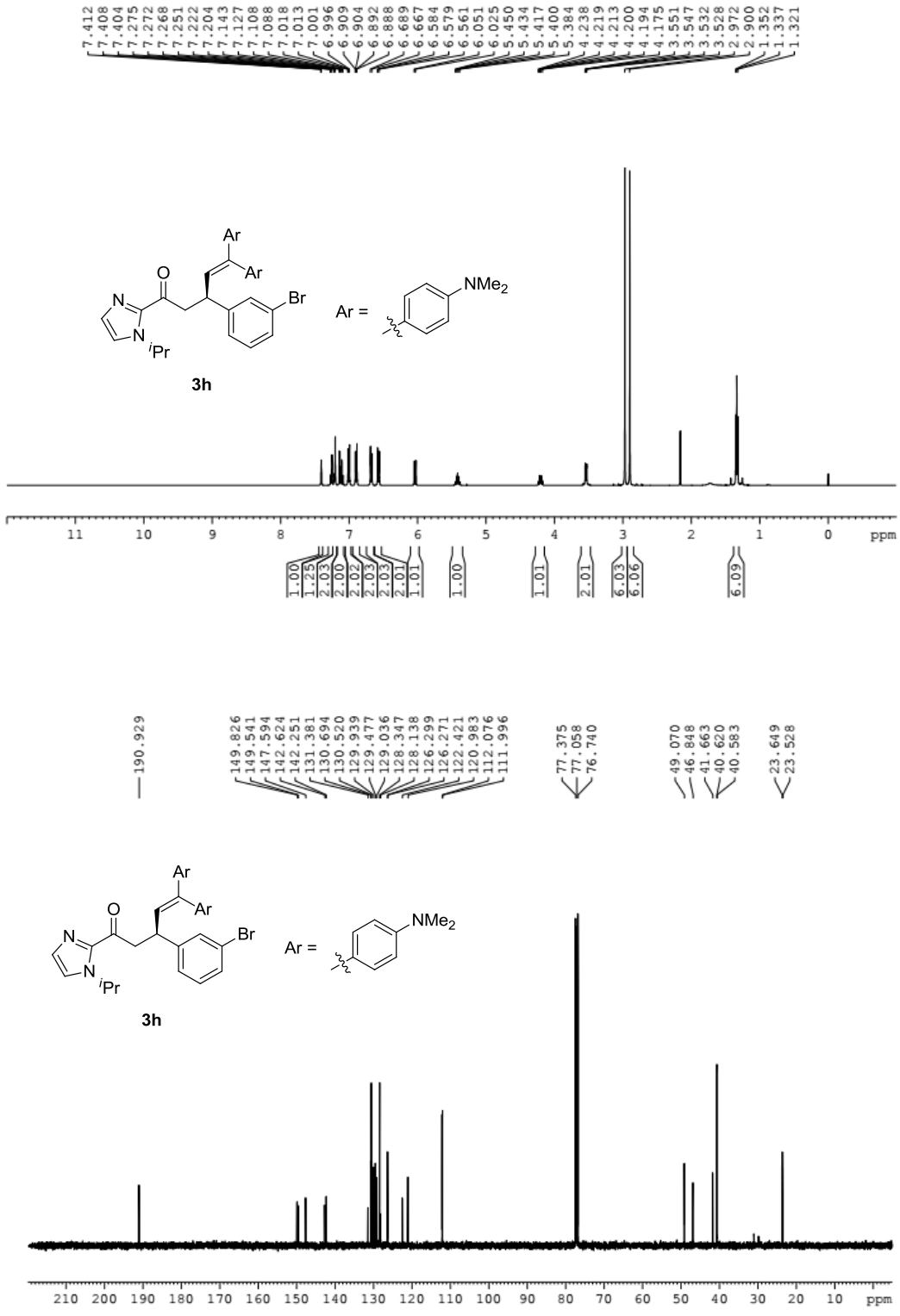


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3f**

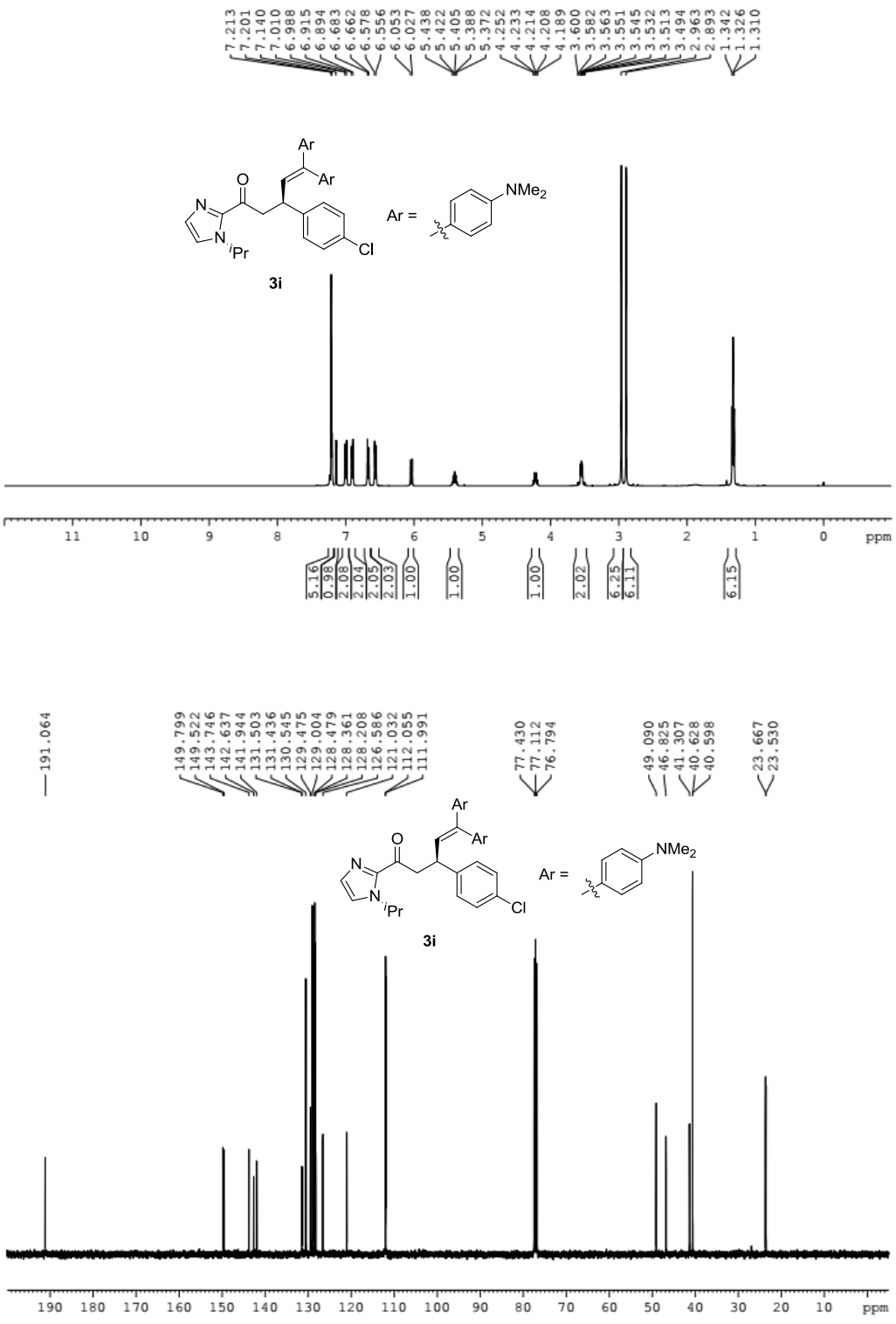




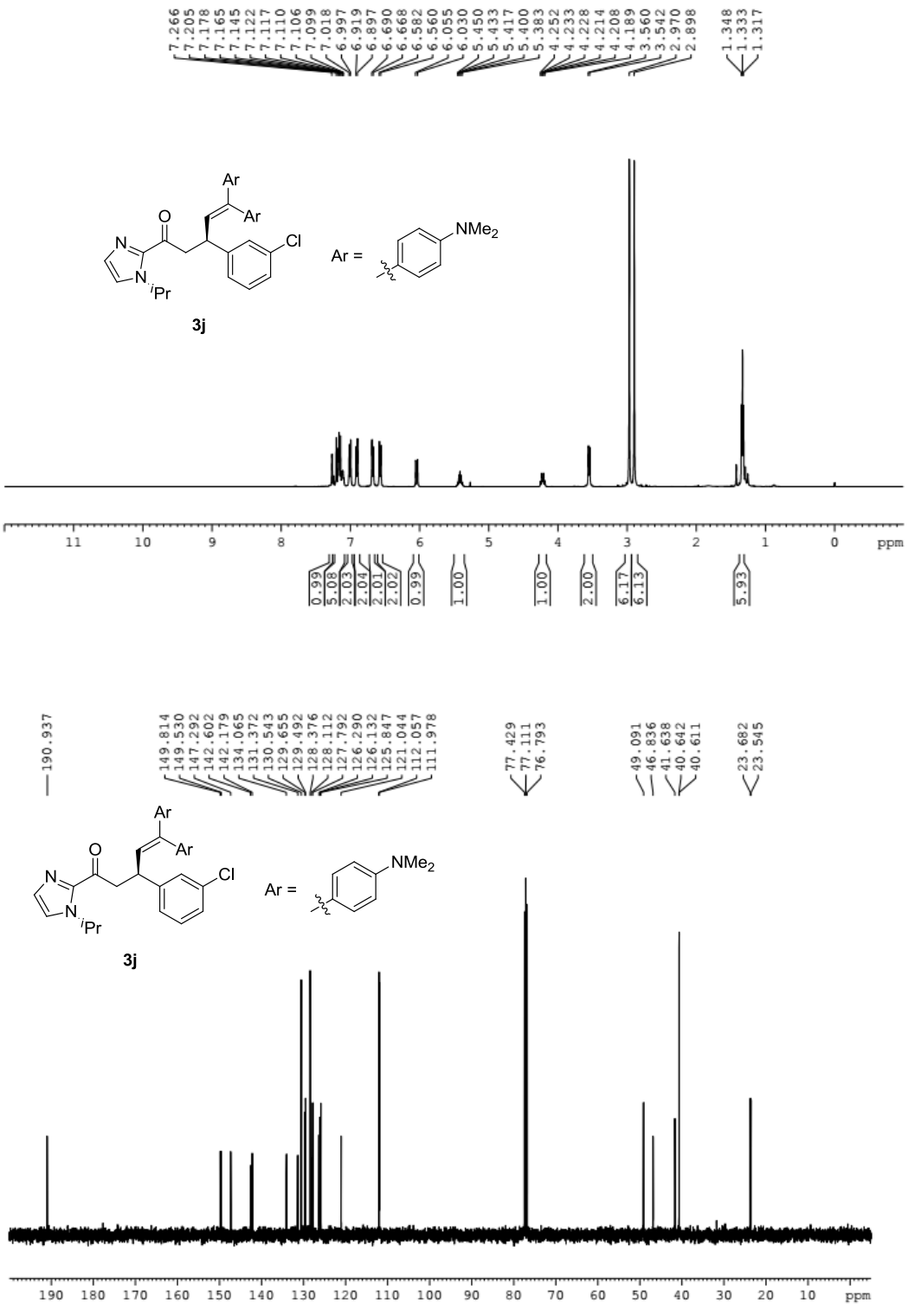
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3g**



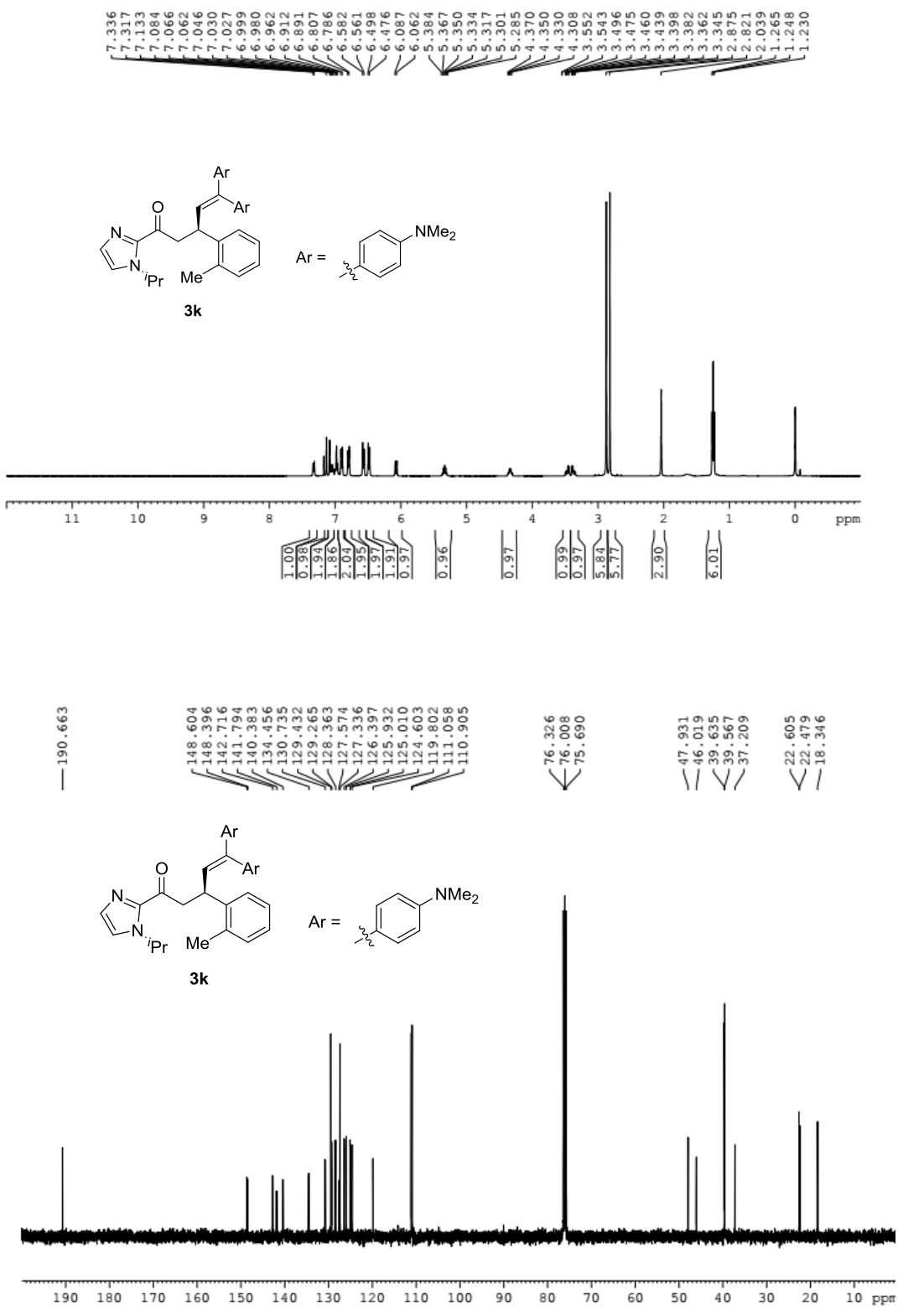
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3h**



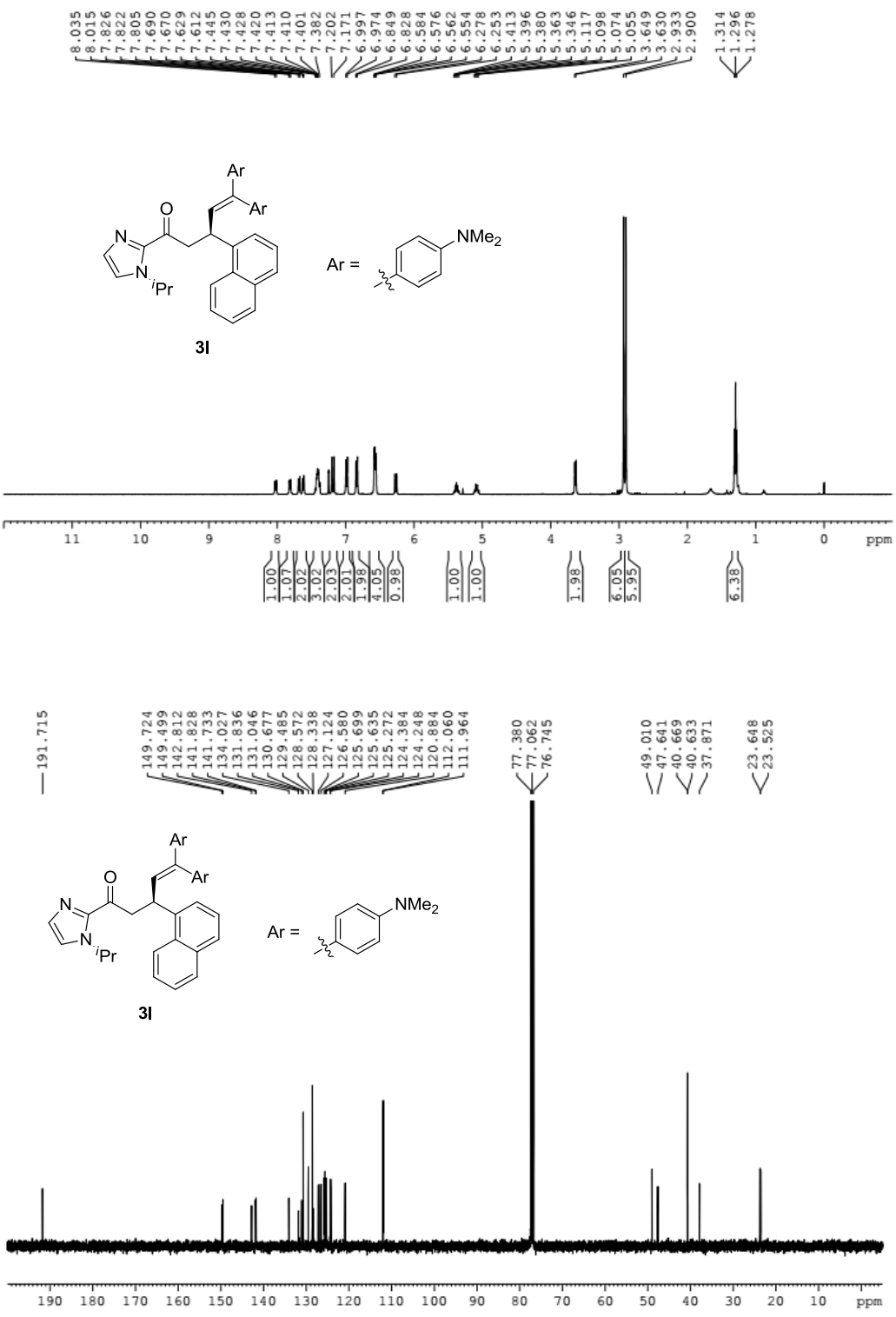
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3i**



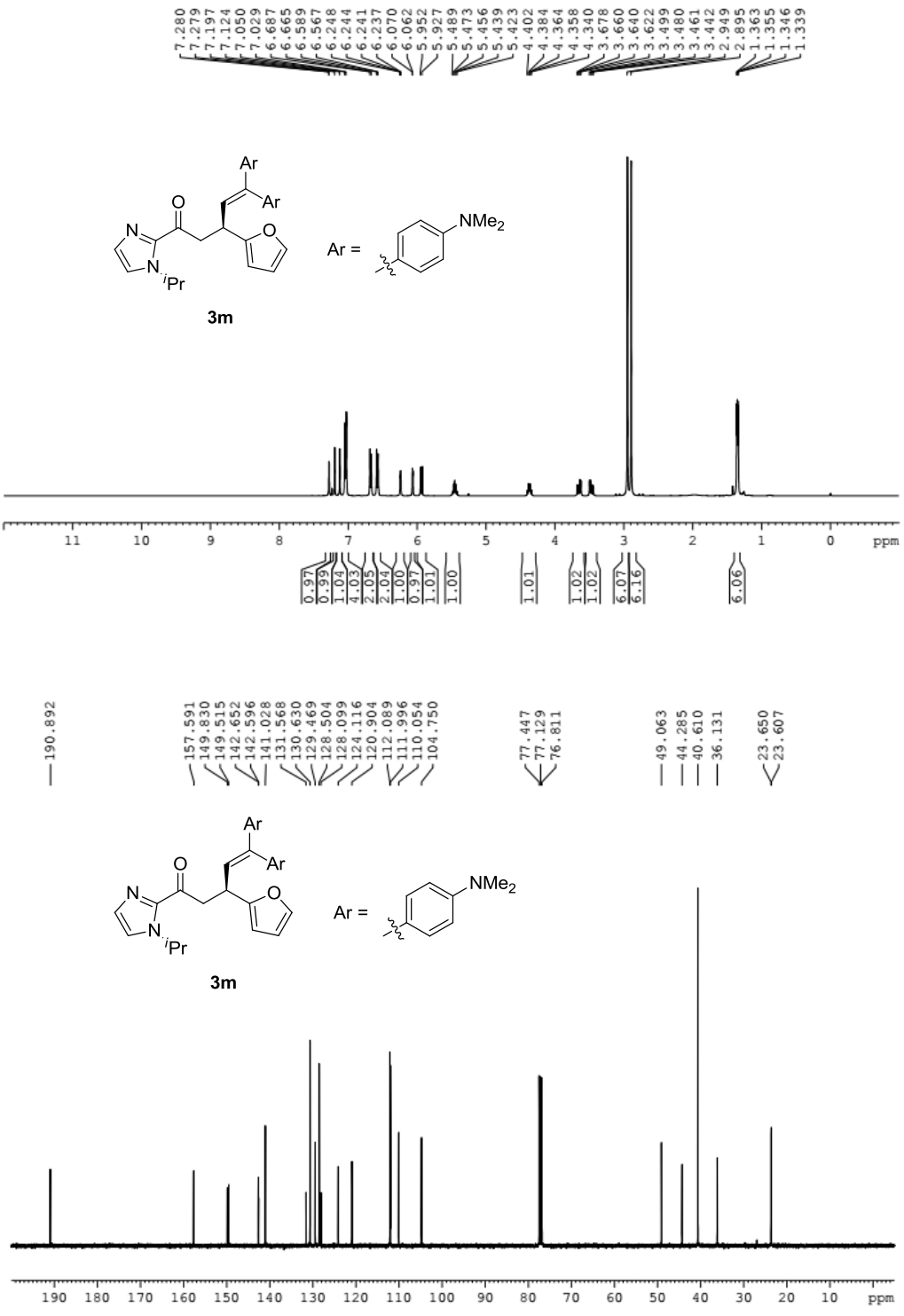
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3j**



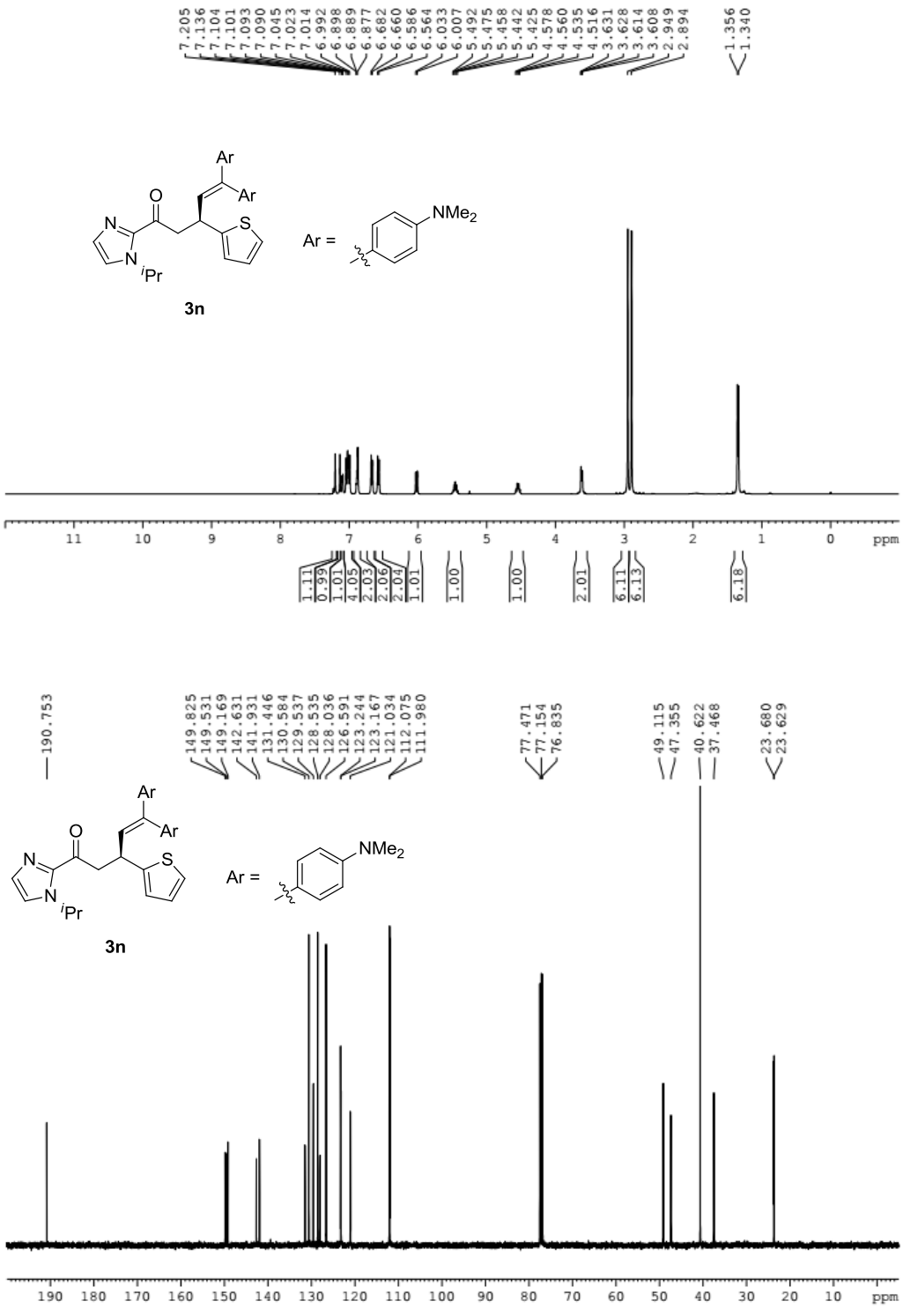
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3k**



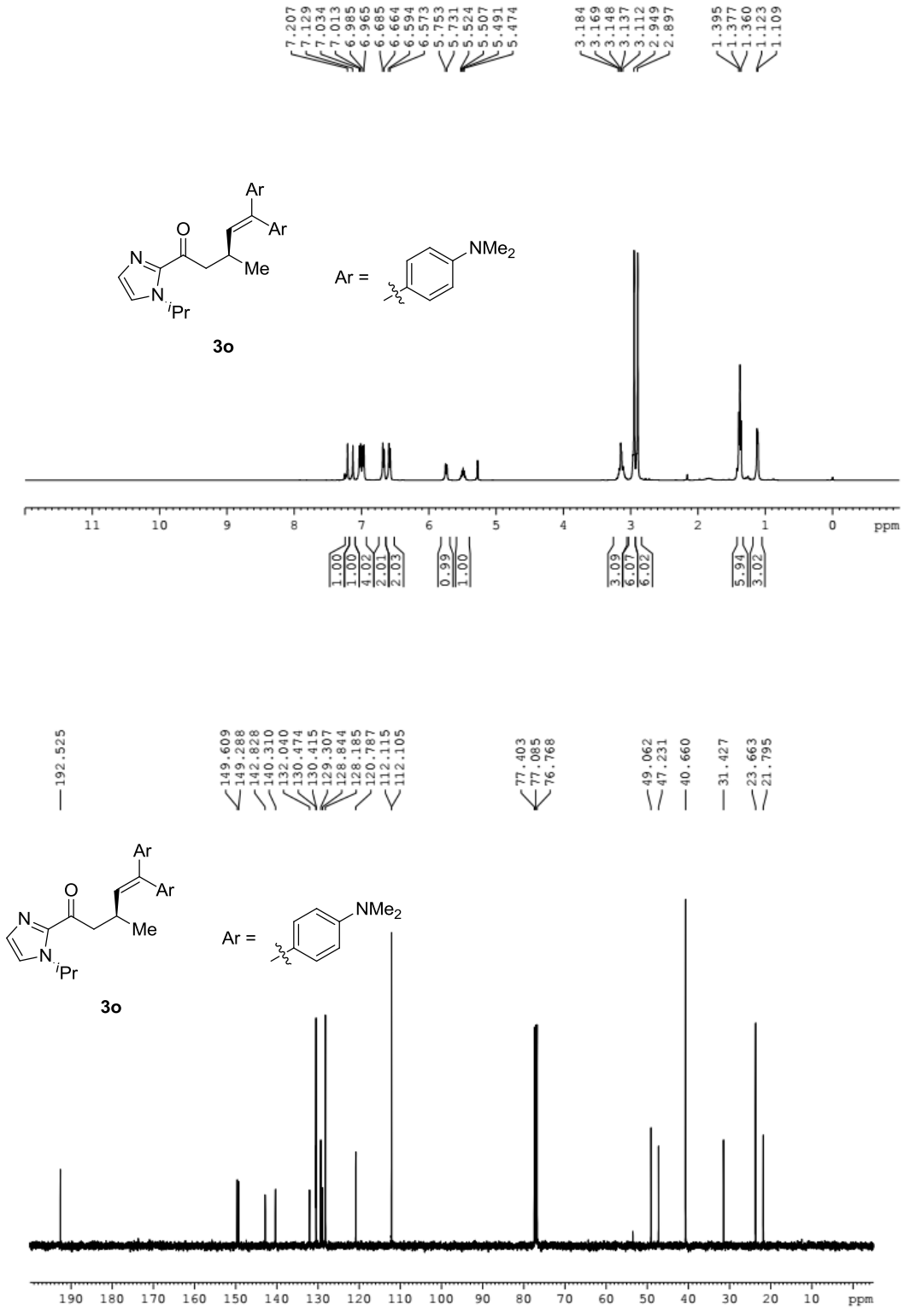
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3l**



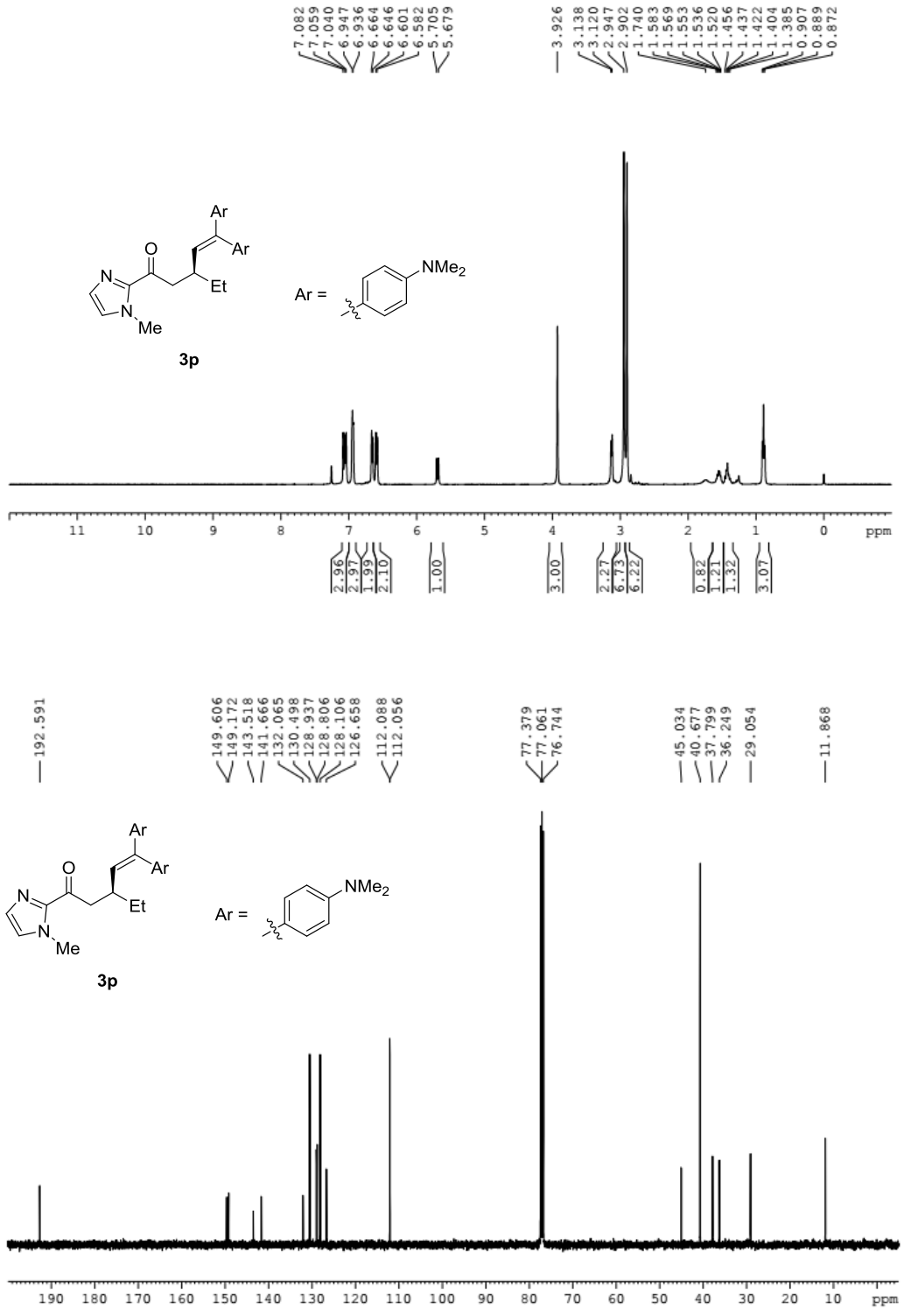
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3m**



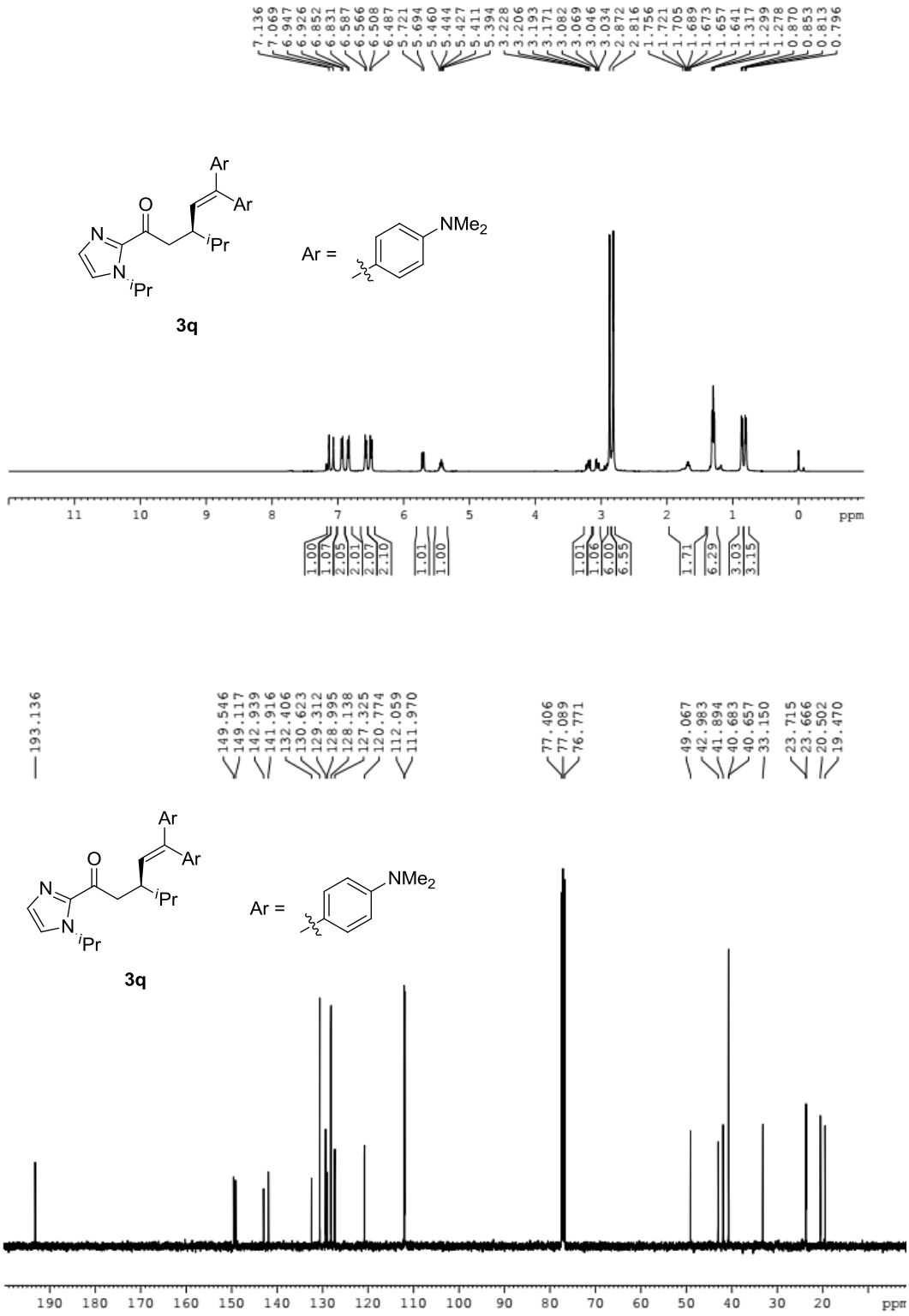
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3n**



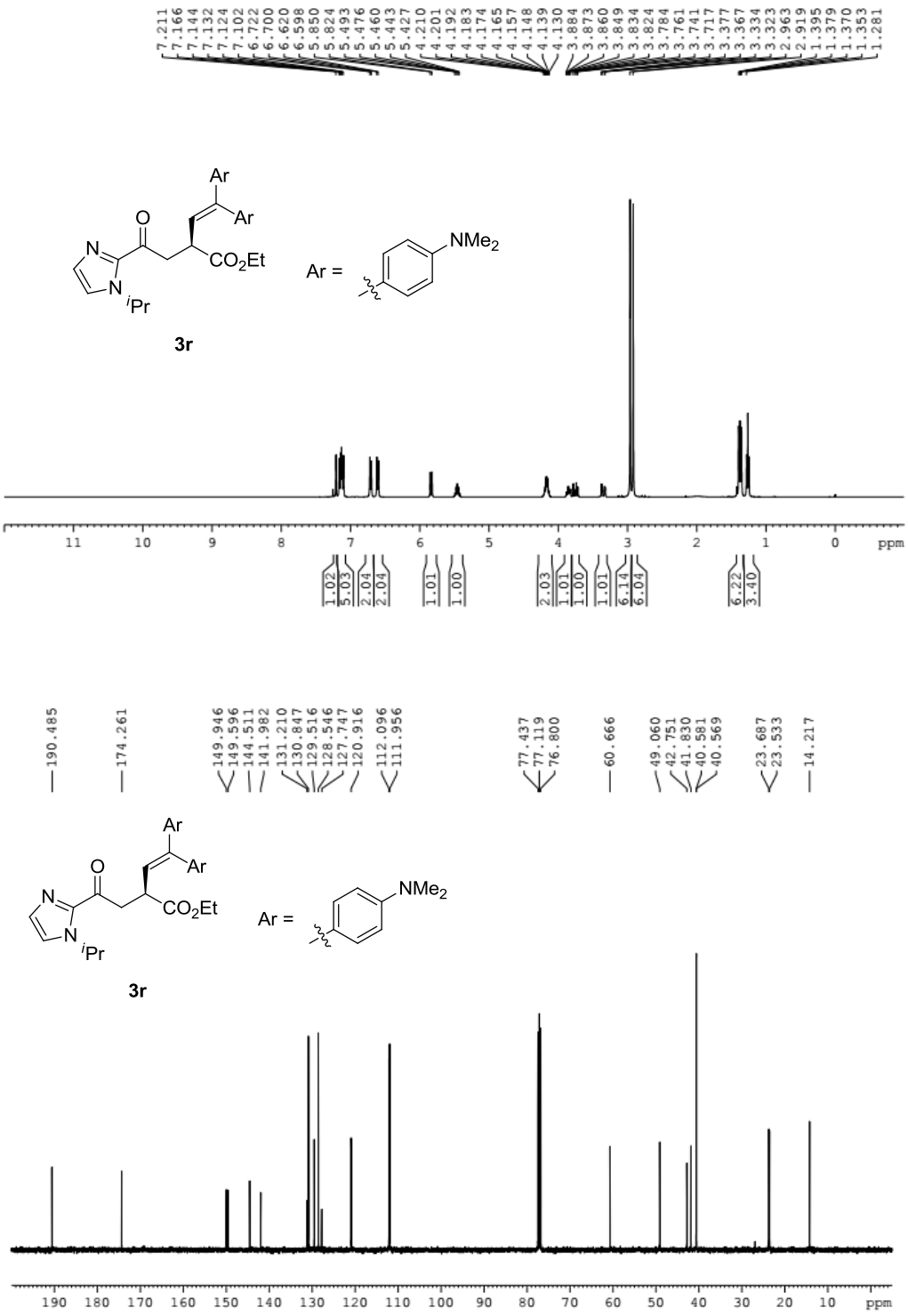
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3o**



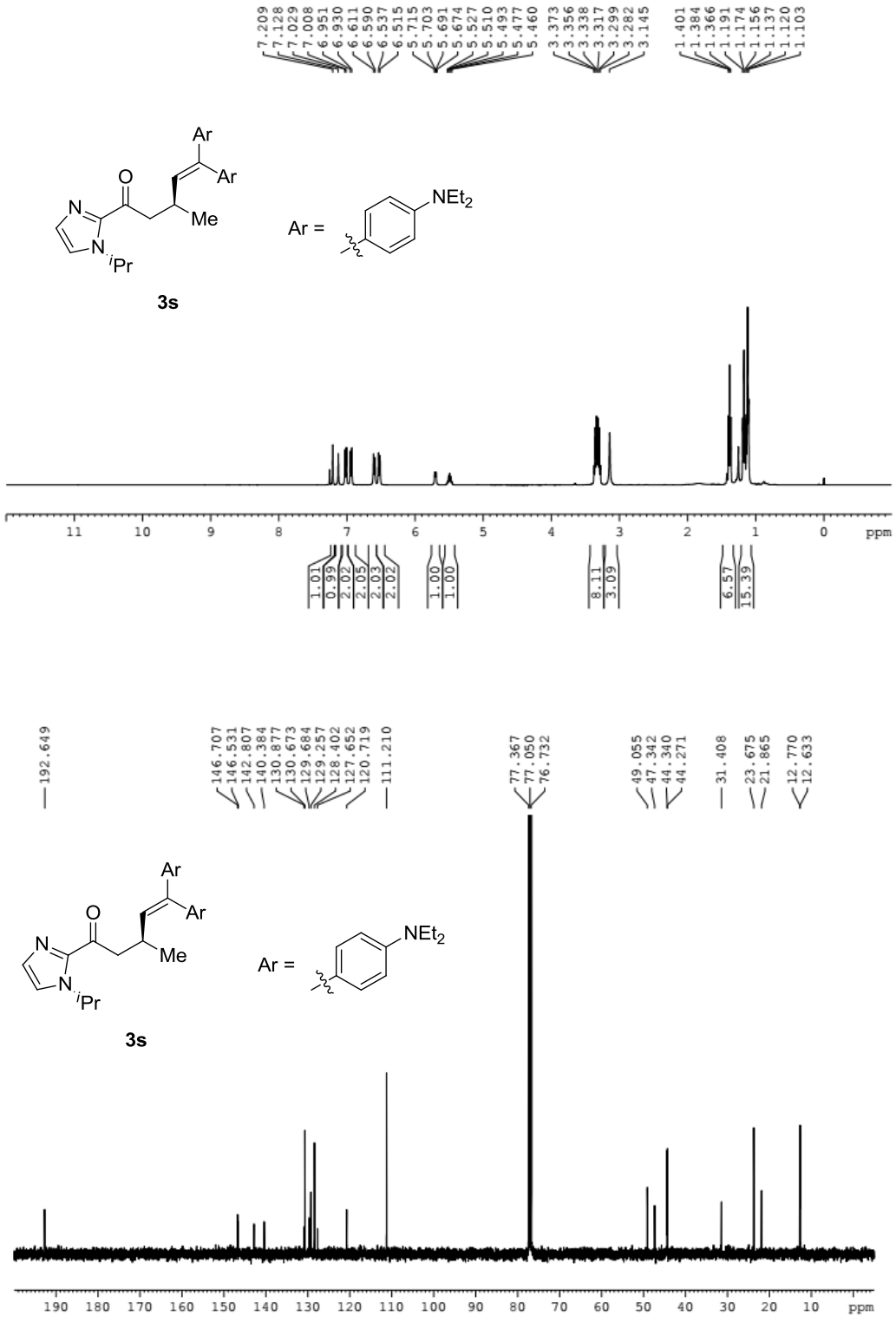
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3p**



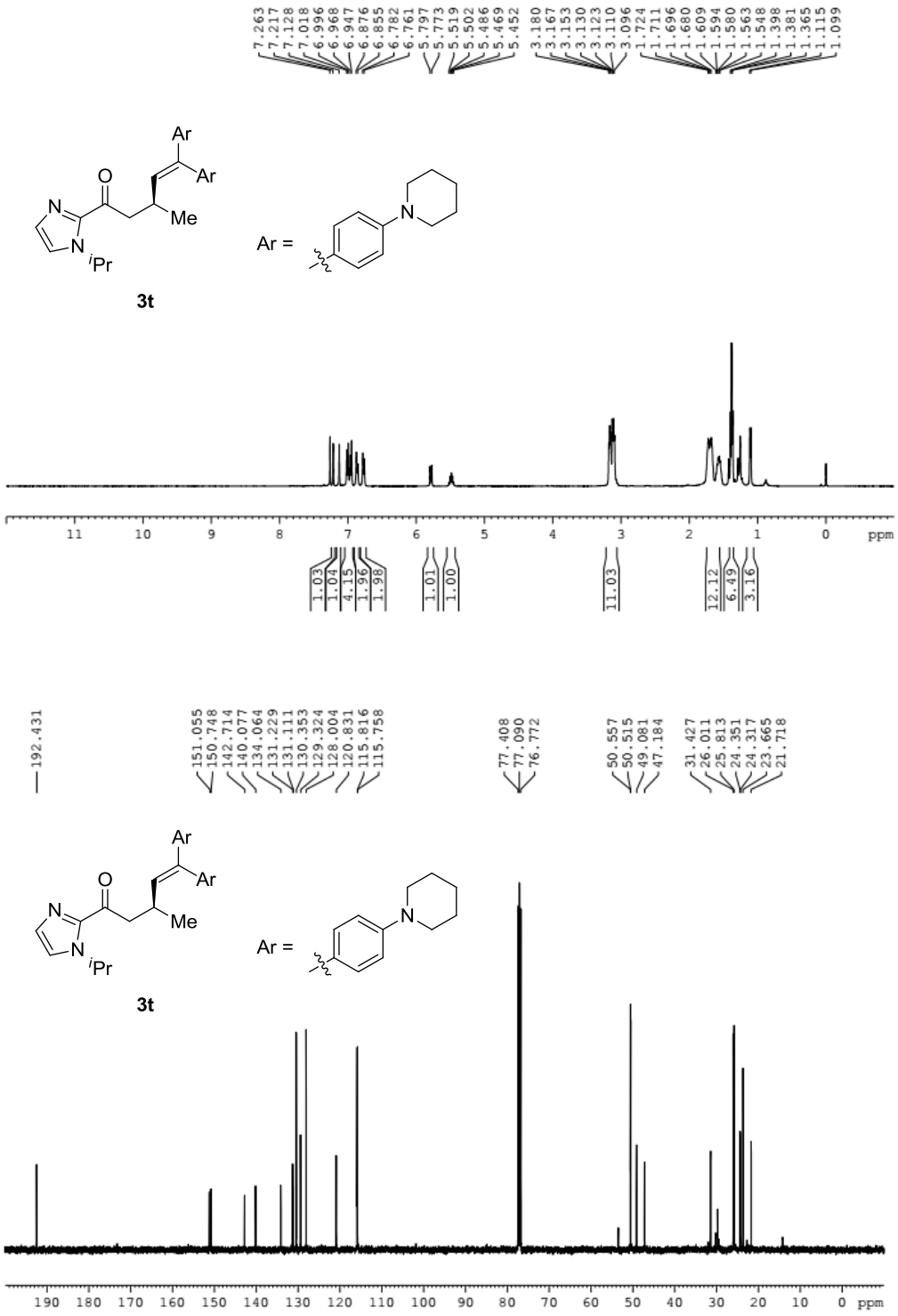
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3q**



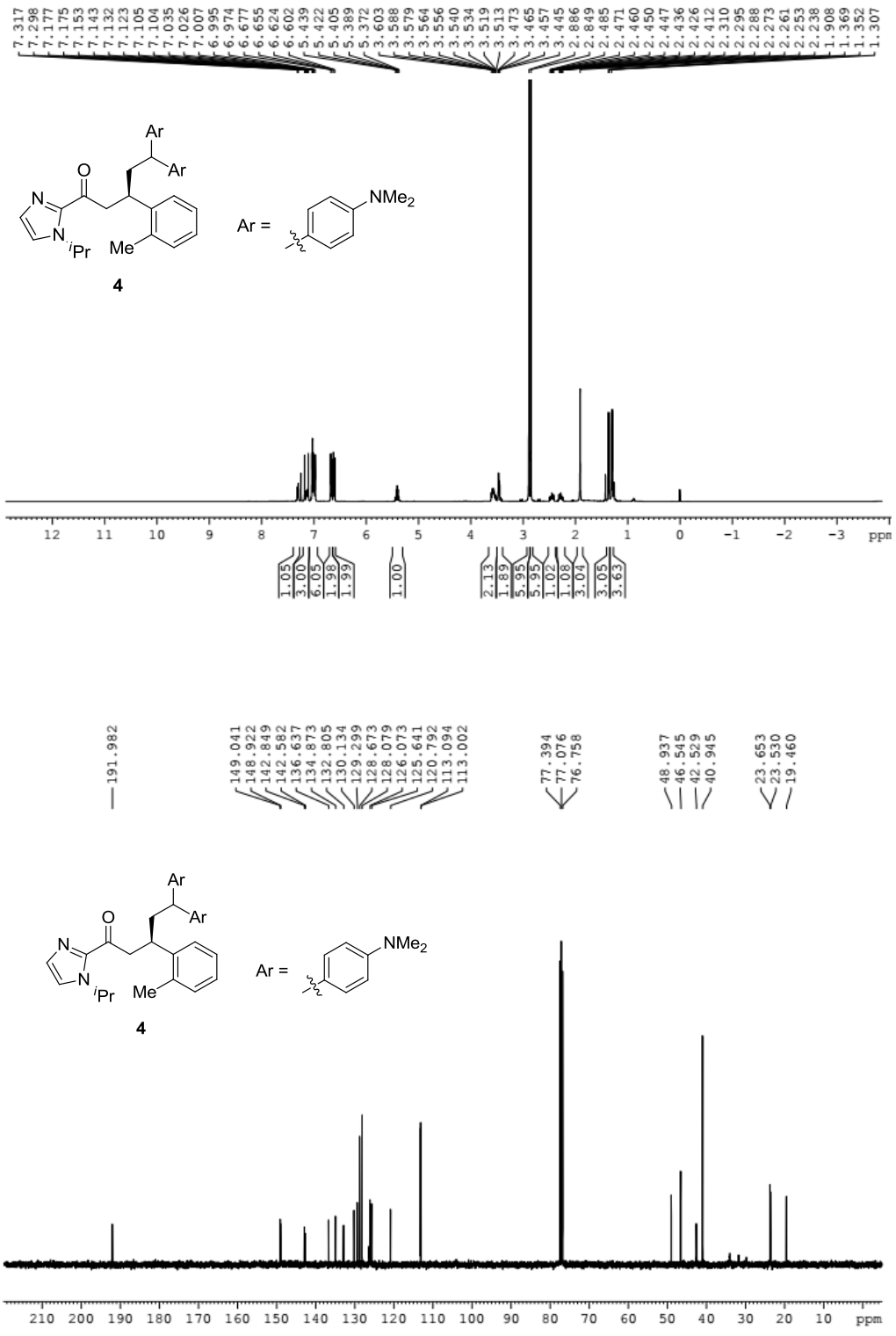
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3r**



^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3s**

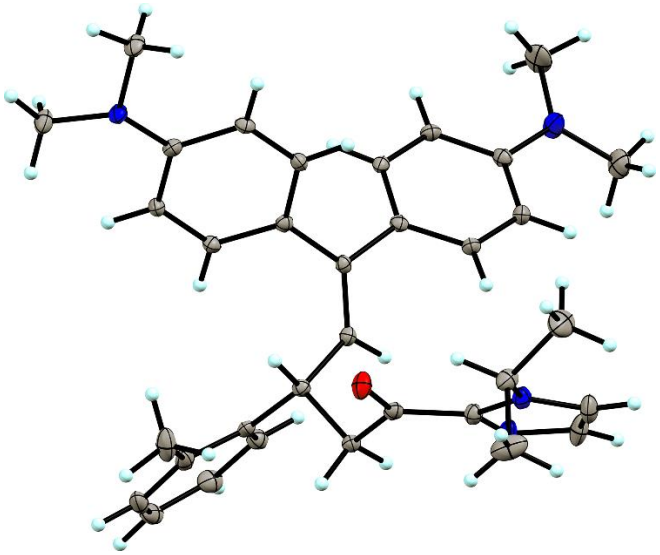


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3t**



^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **4**

VI Single Crystal X-Ray Diffraction of 3k



SFigure 1. X-ray derived ORTEP of **3k** with thermal ellipsoids shown at the 35% probability level

Table 1. Crystal data and structure refinement for data.

Identification code	**3k**	
Empirical formula	C34 H40 N4 O	
Formula weight	520.70	
Temperature	100.0(3) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.59380(10) Å	α= 90°.
	b = 12.2141(2) Å	β= 90°.
	c = 24.9699(4) Å	γ = 90°.
Volume	2925.96(7) $Å^3$	
Z	4	
Density (calculated)	1.182 Mg/m^3	
Absorption coefficient	0.558 mm^{-1}	
F(000)	1120	
Crystal size	0.160 x 0.150 x 0.120 mm^3	
Theta range for data collection	3.540 to 73.366°.	

Index ranges	-11<=h<=9, -14<=k<=15, -29<=l<=30
Reflections collected	12308
Independent reflections	5479 [R(int) = 0.0227]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.96883
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5479 / 0 / 370
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0763
R indices (all data)	R1 = 0.0376, wR2 = 0.0798
Absolute structure parameter	-0.09(13)
Extinction coefficient	n/a
Largest diff. peak and hole	0.145 and -0.212 e.$Å^{-3}$

VII CD Spectra of Λ-Rh3

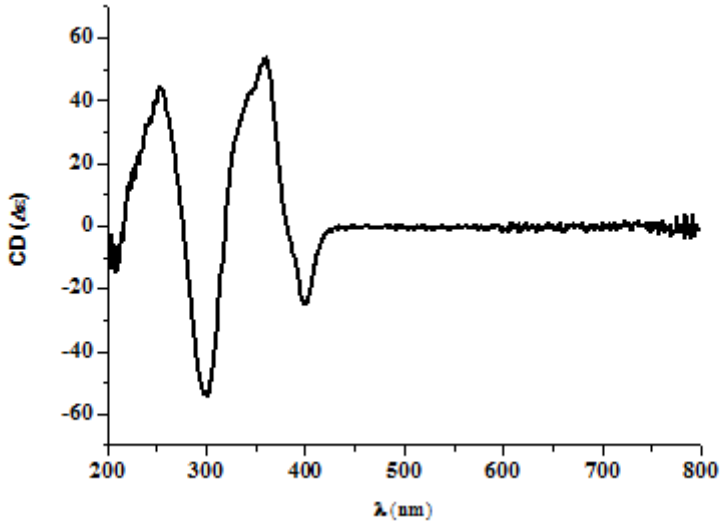


Figure 1. CD spectra of Λ-Rh3 recorded in CH_3OH (0.2 mM)