Iridium(III)-bis(oxazolinyl)phenyl Catalysts for Enantioselective C-H Functionalization

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Supporting Information (SI 1) – Experimental Procedures and Characterization

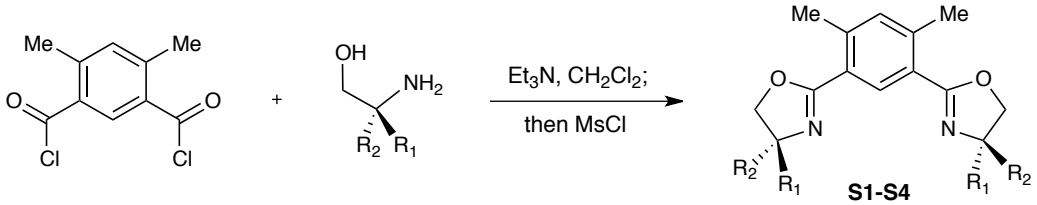
I. General Information

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 600 spectrometer (600 MHz ^{1}H, 150 MHz ^{13}C), a Varian Unity plus 600 spectrometer (600 MHz ^{1}H, 150 MHz ^{13}C), and a Varian Inova 400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C) at room temperature in $CDCl_3$ (neutralized and dried with anhydrous K_2CO_3) with internal $CHCl_3$ as the reference (7.26 ppm for ^{1}H and 77.23 ppm for ^{13}C), unless otherwise stated. Chemical shifts (δ values) were reported in parts per million (ppm) and

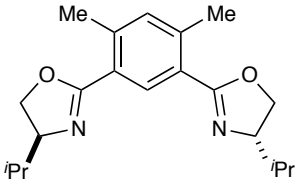
coupling constants (*J* values) in Hz. Multiplicity was indicated using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, b = broad. Infrared (IR) spectra were recorded using a Thermo Electron Corporation Nicolet 380 FT-IR spectrometer. High-resolution mass spectra were obtained using a Thermo Electron Corporation Finigan LTQFTMS (at the Mass Spectrometry Facility, Emory University). Melting points were taken using a Fisher Johns melting point apparatus and are uncorrected (dec. = decomposition). High-pressure liquid chromatography (HPLC) was carried out on a Varian Prostar 210 equipped with Daicel OD, OJ, OD-H, OJ-H, AD-H, and SS Whelk columns and a variable wavelength detector or an Agilent 1100 Series equipped with Daicel AD-H, AS-H, OD-H, and OJ-H columns and a variable wavelength detector. Analytical thin layer chromatography (TLC) was performed on precoated glass backed EMD 0.25 mm silica gel 60 plates. TLC visualization was accomplished by fluorescence quenching and staining with ethanolic anisaldehyde or $KMnO_4$. Flash column chromatography was carried out using Silicycle SiliaFlash® F60 silica gel (40-63 μm). All reactions were conducted in oven dried and nitrogen charged glassware. Anhydrous solvents were obtained by passage through activated alumina columns using a *Glass Contours* solvent purification system unless otherwise noted. Solvents used in workup, extraction, and column chromatography were used as received from commercial suppliers without further purification. Chloroform used in chromatography was neutralized with anhydrous K_2CO_3 prior to use. All reagents were purchased from Sigma Aldrich or Strem and used as received unless otherwise noted. 1,4-cyclohexadiene (Sigma Aldrich) contained ~ 0.1-0.2 % of hydroquinone or BHT (3,5-di-*tert*-butyl-4-hydroxytoluene) radical inhibitors. All diazoesters were prepared according to the literature procedure.[1] 4Å powdered molecular sieves were activated by heating to 100 °C under reduced pressure (0.2 torr) for at least 12 hours. We acknowledge the use of shared instrumentation provided by grants from the National Institutes of Health and the National Science Foundation. Detailed computational analysis (SI 2) and full crystallographic data (CIF, SI 3) are available as separate files.

II. Procedures and Characterization for Phebox Ligands and Iridium PheBox Complexes

*a.) General Procedure **A** for the Synthesis of diMePhebox Ligands **S1 – S4**.*



A procedure was adapted from the literature[2] as follows: a solution of 4,6-dimethylisophthaloyldichloride[3,4] (1.0 equiv.) in CH_2Cl_2 (0.25 M in acid chloride) was slowly added to a solution of amino alcohol (2.0 equiv.) and Et_3N (15 equiv.) in anhydrous CH_2Cl_2 (0.25 M in amino alcohol) at 0° C. The solution was warmed to room temperature and stirred for one hour. The mixture was again cooled to 0° C and methanesulfonyl chloride (2.2 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred 5.5 hours. Then, 1M K_2CO_3 (~50 mL/1g acid chloride) was added at 0° C and the mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified as indicated.

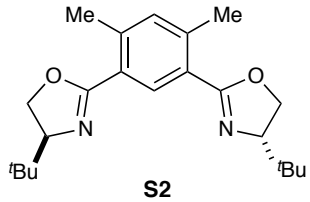


S1

(*S,S*)-diMePhebox-^{i}Pr **S1**.[5]

Prepared according to general procedure **A**; 4,6-dimethylisophthaloyl chloride (1.2 g, 5.2 mmol) in CH_2Cl_2 (21 mL), L-valinol (1.10 g, 10.4 mmol), Et_3N (11 mL, 78 mmol) in CH_2Cl_2 (42 mL), and methanesulfonyl chloride (0.90 mL, 11.4 mmol)) gave (*S,S*)-diMePhebox-^{i}Pr **S1** as a colorless oil following purification by flash chromatography (SiO_2, 15 % → 20 % → 30 % EtOAc:pentane) (550 mg, 32 %).

^{1}H NMR (600 MHz; $CDCl_3$): δ 8.20 (s, 1H), 7.10 (s, 1H), 4.32 (dd, *J* = 9.4, 8.0, 2H), 4.10 (ddd, *J* = 9.4, 7.7, 6.3, 2H), 4.04 (t, *J* = 7.7, 2H), 2.58 (s, 6H), 1.82 (oct, *J* = 6.6, 2H), 1.01 (d, *J* = 6.8, 6H), 0.92 (d, *J* = 6.8, 6H)
^{13}C NMR (150 MHz, $CDCl_3$): δ 163.2, 141.3, 134.4, 131.5, 125.0, 73.4, 69.4, 33.1, 21.9, 19.1, 18.5
HRMS [+ APCI] calculated for 329.2224, found 329.2222 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 2959, 2952, 1646, 1067, 999, 570
$[\alpha]_D^{22}$ -108 (*c* = 1.00, $CHCl_3$)
R_f 0.42 (30 % EtOAc:hexanes)

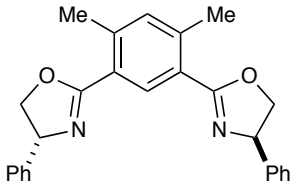


S2

(*S,S*)-diMePhebox-^{t}Bu **S2**.

Prepared according to general procedure **A**, with anhydrous THF as solvent; 4,6-dimethylisophthaloyl chloride (1.0 g, 4.3 mmol) in THF (9 mL), (*S*)-*tert*-leucinol (1.0 g, 8.6 mmol), Et_3N (17 mL, 123 mmol) in THF (26 mL), and methanesulfonyl chloride (1.8 mL, 22.4 mmol) gave (*S,S*)-diMePhebox-^{t}Bu **S2** as a pale yellow oil which solidified upon standing following purification by flash chromatography (SiO_2, 10 % → 15 % → 30 % EtOAc:pentane) (460 mg, 31 %).

^{1}H NMR (400 MHz; $CDCl_3$): δ 8.19 (s, 1H), 7.11 (s, 1H), 4.26 (dd, *J* = 10.1, 8.5, 2H), 4.14 (t, *J* = 8.0, 2H), 4.06 (dd, *J* = 10.1, 7.6, 2H), 2.60 (s, 6H), 0.90 (s, 18H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 141.4, 134.4, 131.4, 124.9, 77.1, 67.9, 34.1, 26.1, 21.9
HRMS [+ ESI] calculated for 357.2537, found 357.2532 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 2955, 2902, 2868, 1648, 1364, 1078, 1007, 955
$[\alpha]_D^{22}$ -103 (*c* = 1.00, $CHCl_3$)
m.p. 91-92 °C
R_f 0.43 (15 % EtOAc:hexanes)

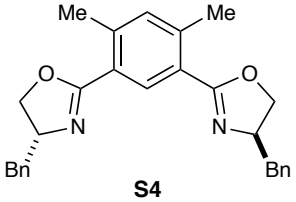


S3

(*R,R*)-diMePhebox-Ph **S3**.

Prepared according to general procedure **A**; 4,6-dimethylisophthaloyl chloride (700 mg, 3.0 mmol) in CH_2Cl_2 (12 mL), D-phenylglycinol (820 mg, 6.0 mmol), Et_3N (6.4 mL, 45 mmol) in CH_2Cl_2 (24 mL), and methanesulfonyl chloride (0.52 mL, 6.6 mmol) gave (*S,S*)-diMePhebox-Ph **S3** as a white solid following purification by flash chromatography (SiO_2, 20 % → 30 % EtOAc:pentane) (500 mg, 42 %).

^{1}H NMR (600 MHz; $CDCl_3$): δ 8.50 (s, 1H), 7.39-7.29 (m, 10H), 7.22 (s, 1H), 5.46 (dd, *J* = 10.1, 8.3, 2H), 4.75 (dd, *J* = 10.1, 8.3, 2H), 4.21 (t, *J* = 8.3, 2H), 2.72 (s, 6H)
^{13}C NMR (150 MHz, $CDCl_3$): δ 164.5, 142.8, 142.1, 134.7, 132.0, 128.9, 127.7, 126.8, 124.5, 74.1, 70.8, 22.2
HRMS [+ APCI] calculated for 397.1911, found 397.1909 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 3057, 2894, 1634, 1064, 1033, 760, 696, 535
$[\alpha]_D^{22}$ +80.6 (*c* = 1.00, $CHCl_3$)
m.p. 103-104 °C
R_f 0.40 (30 % EtOAc:hexanes)



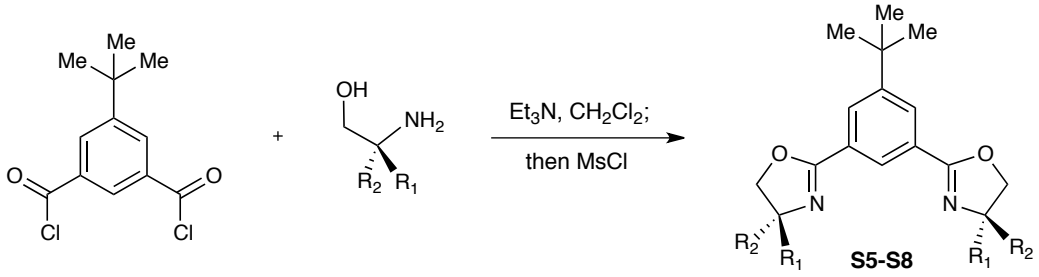
S4

(*R,R*)-diMePhebox-Bn **S4**.

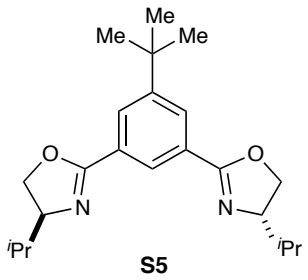
Prepared according to general procedure **A**; 4,6-dimethylisophthaloyl chloride (500 mg, 2.16 mmol) in CH_2Cl_2 (9 mL), D-phenylalaninol (650 mg, 4.32 mmol), Et_3N (4.4 mL, 32 mmol) in CH_2Cl_2 (18 mL), and methanesulfonyl chloride (0.37 mL, 4.8 mmol) gave (*R,R*)-diMePhebox-Bn **S4** as an off-white solid following purification by flash chromatography (SiO_2, 30 % → 50 % EtOAc:pentane) (550 mg, 60 %).

^{1}H NMR (400 MHz; $CDCl_3$): δ 8.23 (s, 1H), 7.32-7.20 (m, 10H), 7.11 (s, 1H), 4.59 (tdd, *J* = 8.9, 7.1, 5.3, 2H), 4.27 (t, *J* = 8.9, 2H), 4.08 (dd, *J* = 8.4, 7.2, 2H), 3.20 (dd, *J* = 13.7, 5.2, 2H), 2.75-2.70 (m, 2H), 2.56 (s, 6H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 141.6, 138.3, 134.5, 131.8, 129.5, 128.7, 126.7, 124.8, 71.0, 68.6, 42.1, 21.9
HRMS [+ APCI] calculated for 425.2224, found 425.2219 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 3026, 2923, 1642, 1347, 700
$[\alpha]_D^{22}$ +9.1 (*c* = 1.00, $CHCl_3$)
m.p. 92-93 °C
R_f 0.30 (30 % EtOAc:hexanes)

*b.) General Procedure **B** for the Synthesis of ^{t}BuPhebox Ligands **S5 – S8**.*



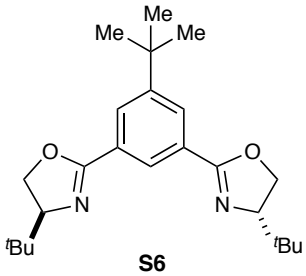
A procedure was adapted from the literature[2] as follows: a solution of 5-^{t}butylisophthaloyl dichloride (1.0 equiv.) in anhydrous CH_2Cl_2 (0.25 M in acid chloride) was slowly added to a solution of amino alcohol (2.0 equiv.) and Et_3N (15 equiv.) in CH_2Cl_2 (0.25 M in amino alcohol) at 0° C. The solution was warmed to room temperature and stirred for one hour. The mixture was again cooled to 0° C and methanesulfonyl chloride (2.2 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred 5.5 hours. Then, 1M K_2CO_3 (~50 mL/1g acid chloride) was added at 0° C and the mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified as indicated.



(*S,S*)-^{t}BuPhebox-^{i}Pr **S5**.[6]

Prepared according to general procedure **B**; 5-^{t}butylisophthaloyl dichloride (2.6 g, 10 mmol) in CH_2Cl_2 (40 mL), L-valinol (2.00 g, 19.5 mmol), Et_3N (21.0 mL, 151 mmol) in CH_2Cl_2 (80 mL), and methanesulfonyl chloride (1.7 mL, 22 mmol) gave (*S,S*)-^{t}BuPhebox-^{i}Pr **S5** as a white solid following purification by flash chromatography (SiO_2, 30 % EtOAc:pentane) (2.2 g, 63 %).

^{1}H NMR (400 MHz; $CDCl_3$): δ 8.34 (t, *J* = 1.6, 1H), 8.09 (d, *J* = 1.6, 2H), 4.43-4.39 (m, 2H), 4.17-4.09 (m, 4H), 1.90-1.85 (m, 2H), 1.37 (s, 9H), 1.04 (d, *J* = 6.8, 3H), 0.93 (d, *J* = 6.8, 3H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 163.3, 151.8, 128.1, 125.8, 72.9, 70.3, 35.2, 33.0, 31.5, 19.2, 18.2
HRMS [+ APCI] calculated for calculated for 357.25366, found 357.25349 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 2959, 2903, 1653, 1593, 1235, 983
$[\alpha]_D^{22}$ -95.0 (*c* = 1.00, $CHCl_3$)
m.p. 84-86 °C
R_f 0.15 (3 % EtOAc:CH_2Cl_2)

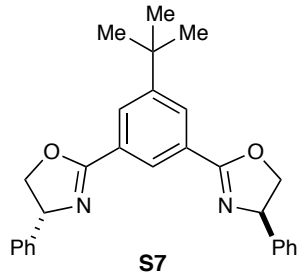


S6

(*S,S*)-^{t}BuPhebox-^{t}Bu **S6**.[6]

Prepared according to general procedure **B**; 5-^{t}butylisophthaloyl dichloride (2.3 g, 9.0 mmol) in CH_2Cl_2 (35 mL), L-*tert*-leucinol (2.1 g, 18 mmol), Et_3N (19.0 mL, 134 mmol) in CH_2Cl_2 (75 mL), and methanesulfonyl chloride (1.6 mL, 20 mmol) gave (*S,S*)-^{t}BuPhebox-^{t}Bu **S6** as a white solid following purification by flash chromatography (SiO_2, 30 % EtOAc:pentane) (1.7 g, 54 %).

^{1}H NMR (400 MHz; $CDCl_3$): δ 8.37 (t, *J* = 1.6, 1H), 8.06 (d, *J* = 1.6, 2H), 4.35 (dd, *J* = 10.1, 8.6, 2H), 4.24 (dd, *J* = 8.6, 7.6, 2H), 4.06 (dd, *J* = 10.1, 7.6, 2H), 1.37 (s, 9H), 0.96 (s, 18H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 163.1, 151.7, 128.1, 125.8, 76.4, 68.8, 35.1, 34.2, 26.0
HRMS [+ APCI] calculated for 385.2846, found 385.2850 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 2954, 1650, 1360, 1245, 1113, 976, 593
$[\alpha]_D^{22}$ -103 (*c* = 1.00, $CHCl_3$)
m.p. 166-168 °C
R_f 0.26 (3 % EtOAc:CH_2Cl_2)

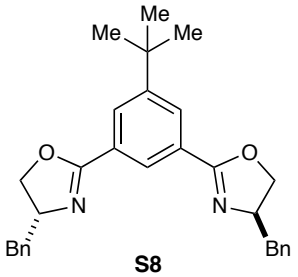


S7

(*R,R*)-^{t}BuPhebox-Ph **S7**.

Prepared according to general procedure **B**; 5-^{t}butylisophthaloyl dichloride (2.6 g, 10 mmol) in CH_2Cl_2 (40 mL), D-phenylglycinol (2.74 g, 20.0 mmol), Et_3N (21.0 mL, 150 mmol) in CH_2Cl_2 (80 mL), and methanesulfonyl chloride (0.90 mL, 11 mmol) gave (*R,R*)-^{t}BuPhebox-Ph **S7** as a white solid following purification by flash chromatography (SiO_2, 30 % → 50 % EtOAc:pentane) (1.34 g, 54 %).

^{1}H NMR (400 MHz; $CDCl_3$): δ 8.51 (t, *J* = 1.6, 1H), 8.23 (d, *J* = 1.6, 2H), 7.39-7.28 (m, 10H), 5.41 (dd, *J* = 10.1, 8.2, 2H), 4.81 (dd, *J* = 10.1, 8.4, 2H), 4.29 (t, *J* = 8.3, 2H), 1.39 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 142.5, 129.0, 128.8, 127.9, 127.0, 126.2, 75.2, 70.5, 35.3, 31.5.
HRMS [+ APCI] calculated for 425.22235, found 425.22210 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 3030, 2962, 2897, 1646, 1236, 980, 697, 574
$[\alpha]_D^{22}$ +66.1 (*c* = 1.00, $CHCl_3$)
m.p. 152-154 °C
R_f 0.39 (50 % EtOAc:hexanes)



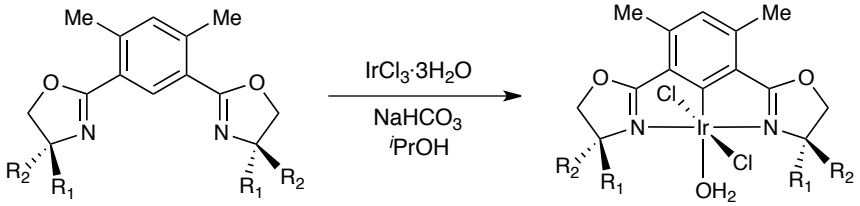
S8

(*R,R*)-^{t}BuPhebox-Bn **S8**.

Prepared according to general procedure **B**; 5-^{t}butylisophthaloyl dichloride (1.3 g, 5.0 mmol) in CH_2Cl_2 (20 mL), D-phenylalaninol (1.51 g, 10.0 mmol), Et_3N (10.4 mL, 75 mmol) in CH_2Cl_2 (40 mL), and methanesulfonyl chloride (0.9 mL, 11 mmol) gave (*R,R*)-^{t}BuPhebox-Bn **S8** as an amorphous solid following purification by flash chromatography (SiO_2, 30 % → 50 % EtOAc:pentane) (1.7 g, 74 %).

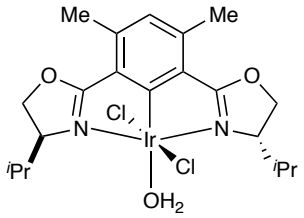
^{1}H NMR (400 MHz; $CDCl_3$): δ 8.38 (t, *J* = 1.5, 1H), 8.18 (d, *J* = 1.5, 2H), 7.37-7.25 (m, 10H), 4.64 (tdd, *J* = 9.2, 7.3, 4.9, 2H), 4.38 (t, *J* = 8.9, 2H), 4.19 (dd, *J* = 8.4, 7.4, 2H), 3.32 (dd, *J* = 13.7, 4.9, 2H), 2.76 (dd, *J* = 13.7, 9.2, 2H), 1.43 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 152.0, 138.2, 129.5, 128.8, 128.4, 128.1, 126.8, 125.8, 72.1, 68.3, 42.1, 35.2, 31.5
HRMS [+ APCI] calculated for 453.2534, found 453.2537 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 3026, 2963, 1648, 1239, 977, 701
$[\alpha]_D^{22}$ -13.2 (*c* = 1.00, $CHCl_3$)
R_f 0.40 (30 % EtOAc:hexanes)

*c.) General Procedure **C** for the Synthesis of diMePhebox Iridium Complexes **1-4**.*



S1-S4 **1-4**

A procedure was adapted from the literature[5] as follows: A round-bottom flask was charged with $IrCl_3{\cdot}3H_2O$ (1.1 equiv.), $NaHCO_3$ (1.1 equiv.), and diMePhebox ligand (1.0 equiv.). Isopropanol (0.03 M) was added and the mixture was refluxed for the indicated time. The crude reaction mixture was concentrated, adsorbed onto SiO_2 using a rotary evaporator, and immediately purified by column chromatography (SiO_2, eluent as indicated). The residue was then crystallized or triturated as indicated to give the iridium diMePhebox complexes **1-4**.

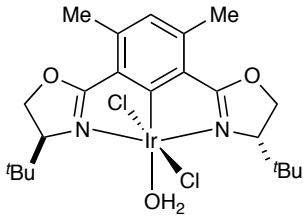


1

[(*S,S*)-^{t}BuPhebox-^{i}Pr]IrCl$_2$(H$_2$O) **1**.[5]

Following general procedure **C**, a mixture of (*S,S*)-diMePheBox-^{i}Pr **S1** (350 mg, 1.0 mmol), IrCl$_3$·3H$_2$O (300 mg, 1.0 mmol), sodium bicarbonate (84 mg, 1.0 mmol), and isopropanol (30 mL) was refluxed for 11 hours. The resulting mixture was purified by flash column chromatography (SiO$_2$, 20 % → 50 % EtOAc:hexanes). The orange fractions at R$_f$ 0.33 (50 % EtOAc:hexanes) were collected and concentrated. The oil was crystallized by slow evaporation of a concentrated CH$_2$Cl$_2$ solution to give [(*S,S*)-diMePhebox-^{i}Pr]IrCl$_2$(H$_2$O) **1** as an orange solid (320 mg, 56 %).

^{1}H NMR (400 MHz; 50 °C, CDCl$_3$): δ 6.64 (s, 1H), 4.83-4.75 (m, 4H), 4.20 (t, *J* = 6.4, 2H), 2.63 (s, 6H), 2.45 (s, 2H), 2.25 (s, 2H), 0.97 (dd, *J* = 10.4, 7.0, 12H)
^{13}C NMR (150 MHz; CDCl$_3$): δ 176.2, 141.2, 126.7, 126.2, 71.0, 67.3, 29.1, 19.7, 18.9, 15.5
HRMS [+ APCI] calculated for 596.16558, found 596.16548 [M-Cl,-H$_2$O, +CH$_3$CN]$^{+}$
IR (thin film, cm^{-1}) ν = 3364, 2958, 2930, 1603, 1383, 1219, 943, 570
[α]$_D^{22}$ +232 (*c* = 0.46, CHCl$_3$)
m.p. 200 °C (dec.)
R$_f$ 0.33 (50 % EtOAc:hexanes)

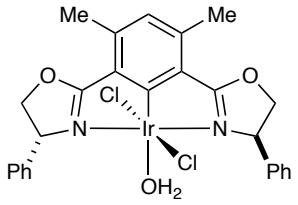


2

[(*S,S*)-diMePhebox-^{t}Bu]IrCl$_2$(H$_2$O) **2**.

Following general procedure **C**, a mixture of (*S,S*)-diMePheBox-^{t}Bu **S2** (350 mg, 0.98 mmol), IrCl$_3$·3H$_2$O (330 mg, 1.1 mmol), NaHCO$_3$ (90 mg, 1.1 mmol), and isopropanol (33 mL) was refluxed for 12 hours. The resulting mixture was purified by flash column chromatography (SiO$_2$, 30 % → 50 % → 65 % EtOAc:hexanes) followed by trituration with dry Et$_2$O to give [(*S,S*)-diMePhebox-^{t}Bu]IrCl$_2$(H$_2$O) **2** as an orange solid (174 mg, 28 %).

^{1}H NMR (600 MHz; CDCl$_3$): δ 6.60 (s, 1H), 4.99-4.94 (m, 2H), 4.78-4.73 (m, 2H), 4.13-4.08 (m, 2H), 2.61 (s, 6H), 2.19 (s, 2H), 1.22 (s, 18H)
^{13}C NMR (100 MHz; CDCl$_3$): δ 177.1, 141.9, 127.2, 126.4, 72.9, 71.9, 34.1, 26.8, 19.1
HRMS [+ APCI] calculated for 656.22309, found 656.22242 [M-Cl, -H$_2$O, +CH$_3$CN, +MeOH]$^{+}$
IR (thin film, cm^{-1}) ν = 2962, 2880, 1594, 1488, 1392, 1323, 1220, 1072, 945, 855
[α]$_D^{22}$ +408 (*c* = 1.00, CHCl$_3$)
m.p. 340 °C (dec.)
R$_f$ 0.21 (30 % EtOAc:hexanes)

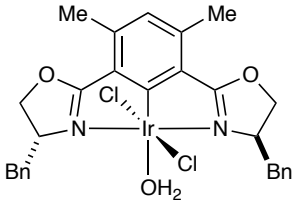


3

[(*R,R*)-diMePhebox-Ph]$IrCl_2(H_2O)$ **3**.

Following general procedure **C**, a mixture of (*R,R*)-diMePhebox-Ph **S3** (300 mg, 0.76 mmol), $IrCl_3 \cdot 3H_2O$ (250 mg, 0.84 mmol), $NaHCO_3$ (70 mg, 0.84 mmol), and isopropanol (25 mL) was refluxed for 10 hours. The resulting mixture was purified by flash column chromatography (SiO_2, 30 % → 50 % EtOAc:hexanes)
The orange fractions at Rf 0.46 (30 % EtOAc:hexanes) were collected and concentrated to give an orange powder which was crystallized by slow diffusion of pentane into a saturated $CHCl_3$ solution to give [(*R,R*)-diMePhebox-Ph]$IrCl_2(H_2O)$ **3** as an orange solid (254 mg, 51 %).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.50-7.49 (m, 4H), 7.37-7.33 (m, 6H), 6.68 (s, 1H), 5.28-5.17 (m, 4H), 4.63-4.58 (m, 2H), 2.70 (s, 6H), 1.86 (bs, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 181.2, 142.2, 137.8, 129.1, 129.0, 126.3, 126.2, 77.9, 67.1, 19.1
HRMS [+ APCI] calculated for 656.22309, found 656.22242 $[M\text{-}Cl, -H_2O, +CH_3CN, +MeOH]^+$
IR (thin film, cm^{-1}) ν = 3273, 2967, 1599, 1480, 1386, 1218, 1020, 753, 698.
$[\alpha]_D^{22}$ -464 (*c* = 1.01, $CHCl_3$)
m.p. 195 °C (dec.)
R_f 0.46 (30 % EtOAc:hexanes)



4

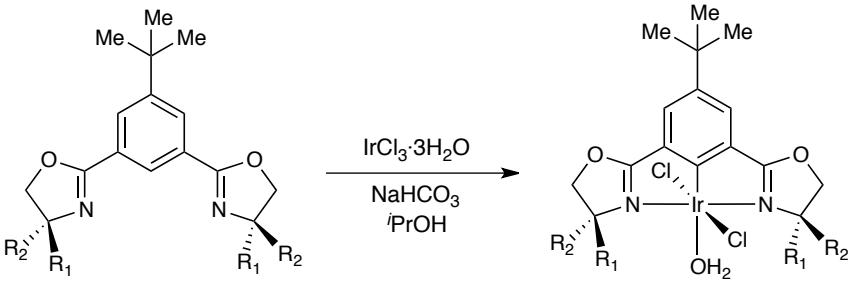
[(*R,R*)-diMePhebox-Bn]$IrCl_2(H_2O)$ **4**.

Following general procedure **C**, a mixture of (*R,R*)-diMePheBox-Bn **S4** (120 mg, 0.28 mmol), $IrCl_6 \cdot 6H_2O$ (160 mg, 0.31 mmol), $NaHCO_3$ (77 mg, 0.92 mmol, 3.3 equiv.), and isopropanol (11 mL) was refluxed for 8 hours. The resulting mixture was purified by flash column chromatography (SiO_2, 30 % EtOAc:hexanes). The orange fractions at R_f 0.33 (5 % EtOAc:CH_2Cl_2) (SiO_2, 30 % EtOAc:hexanes) were collected and concentrated to give [(*R,R*)-diMePhebox-Bn]$IrCl_2(H_2O)$ **4** as an orange solid (60 mg, 30 %).

^{1}H NMR (600 MHz; $CDCl_3$): δ 7.35-7.21 (m, 10H), 6.66 (s, 1H), 4.75 (t, *J* = 8.9, 2H), 4.61 (t, *J* = 7.8, 2H), 4.55-4.52 (m, 2H), 3.64 (dd, *J* = 14.0, 3.9, 2H), 2.83 (dd, *J* = 14.1, 10.4, 2H), 2.64 (s, 6H), 2.17 (bs, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 177.9, 141.7, 137.3, 129.4, 129.1, 127.1, 126.2, 75.2, 63.7, 40.5, 19.0
HRMS [+ APCI] calculated for 615.16099, found 615.16100 $[M\text{-}2Cl, -H_2O]^+$
IR (thin film, cm^{-1}) ν = 3303, 3026, 2963, 1602, 1482, 1388, 1219, 751, 702

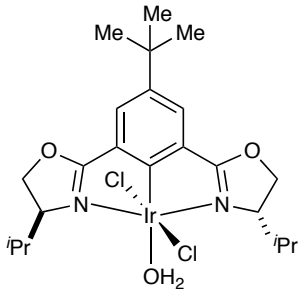
$[\alpha]_D^{22}$ -123 (c = 0.50, $CHCl_3$)
m.p. 216 °C (dec.)
R_f 0.33 (5 % EtOAc:CH_2Cl_2)

*d.) General Procedure **D** for the Synthesis of ^{t}BuPhebox Iridium Complexes **5-8**.*



S5-S8 **5-8**

A procedure was adapted from the literature[5] as follows: A round-bottom flask was charged with $IrCl_3{\cdot}3H_2O$ (1.1 equiv.), $NaHCO_3$ (1.1 equiv.), and ^{t}BuMePhebox ligand (1.0 equiv.). Isopropanol (0.03 M) was added and the mixture was refluxed for the indicated time. The crude reaction mixture was concentrated then adsorbed onto SiO_2 using a rotary evaporator, immediately purified by column chromatography (SiO_2, eluent as indicated), and crystallized as indicated to give the iridium ^{t}BuPhebox complexes **5-8**.

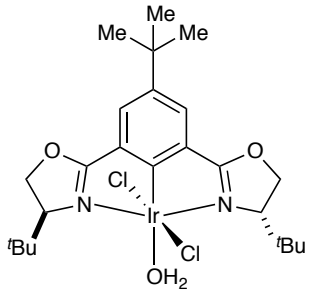


5

[(*S,S*)-^{t}BuPhebox-^{i}Pr]$IrCl_2(H_2O)$ **5**.

Following general procedure **D**, a mixture of (*S,S*)-^{t}BuPhebox-^{i}Pr **S5** (200 mg, 0.561 mmol), $IrCl_3{\cdot}3H_2O$ (219 mg, 0.62 mmol), sodium bicarbonate (52 mg, 0.62 mmol), and isopropanol (22 mL) was refluxed for 2 hours. The resulting mixture was purified by flash column chromatography (SiO_2, 30 % EtOAc:hexanes → 50 % → 75 %). The orange fractions at R_f 0.33 (30 % EtOAc:hexanes) were collected and concentrated to give [(*S,S*)-^{t}BuPhebox-^{i}Pr]$IrCl_2(H_2O)$ **5** as an orange solid (147 mg, 41 %).

^{1}H NMR (600 MHz; $CDCl_3$): δ 7.50 (s, 2H), 4.82 (d, J = 7.6, 4H), 4.27-4.09 (bm, 2H), 2.43 (bs, 2H), 1.36 (s, 9H), 0.94 (bs, 12H)
^{13}C NMR (150 MHz, $CDCl_3$): δ 176.6, 145.1, 129.1, 125.5, 71.3, 68.0, 35.1, 32.0, 29.2, 19.7, 15.4
HRMS [+ APCI] calculated for 548.20148, found 548.19698 $[M\text{-}2Cl,\text{-}H_2O]^+$
IR (thin film, cm^{-1}) ν = 3321, 2955, 1620, 1442, 1377, 1285, 968
$[\alpha]_D^{22}$ +188 (c = 1.00, $CHCl_3$)
m.p. 204 °C (dec.)
R_f 0.33 (30 % EtOAc:hexanes)

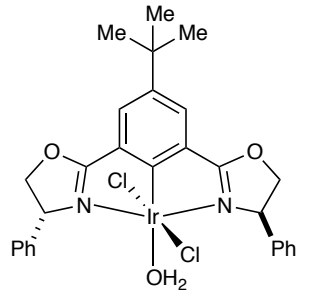


6

[(*S,S*)-^{t}BuPhebox-^{t}Bu]$IrCl_2(H_2O)$ **6**.

Following general procedure **D**, a mixture of (*S,S*)-^{t}BuPhebox-^{t}Bu **S6** (216 mg, 0.561 mmol), $IrCl_3 \cdot 3H_2O$ (219 mg, 0.62 mmol), sodium bicarbonate (52 mg, 0.62 mmol), and isopropanol (22 mL) was refluxed for 4.5 hours. The resulting mixture was purified by flash column chromatography (SiO_2, 30 % EtOAc:hexanes). The orange fractions at R_f 0.15 (30 % EtOAc:hexanes, 2 runs) were collected and concentrated to give [(*S,S*)-^{t}BuPhebox-^{t}Bu]$IrCl_2(H_2O)$ **6** as a bright orange solid (100 mg, 27 %).

^{1}H NMR (600 MHz; $CDCl_3$): δ 7.48 (d, *J* = 1.3, 2H), 4.89-4.87 (d, *J* = 8.4, 4H), 3.98 (m, 2H), 2.92 (s, 2H), 1.37 (s, 9H), 1.16 (m, 18H)
^{13}C NMR (150 MHz, $CDCl_3$): δ 177.4, 145.2, 129.4, 125.9, 73.4, 72.3, 35.0, 34.7, 31.9, 26.6
HRMS [+ APCI] calculated for 576.22844, found 575.22470 [M-2Cl,-H_2O]
IR (thin film, cm^{-1}) ν = 3338, 2954, 1695, 1447, 1379, 1261, 982
$[\alpha]_D^{22}$ +174 (*c* = 0.10, $CHCl_3$)
m.p. 370 °C (dec.)
R_f 0.15 (30 % EtOAc:hexanes, 2 runs)



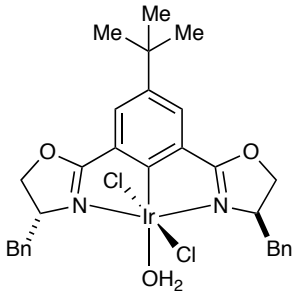
7

[(*R,R*)-^{t}BuPhebox-Ph]$IrCl_2(H_2O)$ **7**.

Following general procedure **D**, a mixture of (*R,R*)-^{t}BuPhebox-Ph **S7** (84 mg, 0.20 mmol), $IrCl_3 \cdot 3H_2O$ (78 mg, 0.22 mmol), sodium bicarbonate (19 mg, 0.22 mmol), and isopropanol (8 mL) was refluxed for 7 hours. The resulting mixture was purified by flash column chromatography (SiO_2, 30 % EtOAc:hexanes). The orange fractions at R_f 0.28 (3 % EtOAc:$CHCl_3$) was collected and concentrated to give [(*R,R*)-^{t}BuPhebox-Ph]$IrCl_2(H_2O)$ **7** as an orange solid (20 mg, 14 %).

^{1}H NMR (600 MHz; $CDCl_3$): δ 7.63 (s, 2H), 7.46-7.45 (m, 4H), 7.35-7.30 (m, 6H), 5.30-5.22 (m, 4H), 4.67-4.61 (m, 2H), 1.65 (bs, 4H), 1.39 (s, 9H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 180.6, 145.1, 138.0, 129.2, 129.0, 128.9, 128.4, 126.2, 78.5, 67.3, 35.1, 32.0
HRMS [+ APCI] calculated for 616.17018, found 616.16588 [M-2Cl,-H_2O]$^+$
IR (thin film, cm^{-1}) ν = 3321, 3032, 2963, 1618, 1549, 1476, 1444, 1379, 1289, 981, 730, 699

$[\alpha]_D^{22}$ -372 (c = 0.50, $CHCl_3$)
m.p. 202 °C (dec.)
$\mathbf{R_f}$ 0.28 (3 % EtOAc:$CHCl_3$)



8

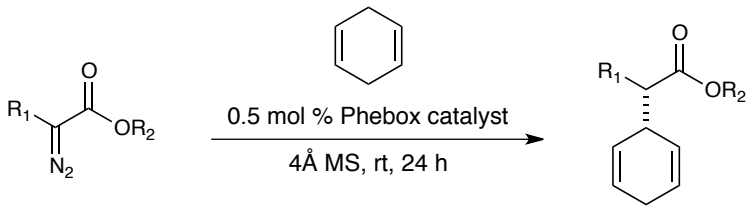
[(*R,R*)-^{t}BuPhebox-Bn]$IrCl_2(H_2O)$ **8**.

Following general procedure **D**, a mixture of (*R,R*)-^{t}BuPhebox-Bn **S8** (1.60 g, 3.54 mmol), $IrCl_3 \cdot 3H_2O$ (1.37 g, 3.89 mmol), sodium bicarbonate (330 mg, 3.89 mmol), and isopropanol (118 mL) was refluxed for 2 hours. The resulting mixture was purified by flash column chromatography (SiO_2, 3 % → 6 % → 8 % → 10 % EtOAc:CH_2Cl_2). The orange fractions at Rf 0.38 (30 % EtOAc:hexanes) were collected and concentrated to give an orange powder which was crystallized by slow diffusion of pentane into a saturated CH_2Cl_2 solution to give [(*R,R*)-^{t}BuPhebox-Bn]$IrCl_2(H_2O)$ **8** as an orange solid (1.4 g, 54 %).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.54 (s, 2H), 7.31-7.20 (m, 10H), 4.79 (m, 2H), 4.60 (m, 4H), 3.64 (dd, J = 13.8, 3.1, 2H), 2.84 (dd, J = 14.1, 9.7, 2H), 2.20 (s, 2H), 1.35 (s, 9H)
^{13}C NMR (150 MHz, $CDCl_3$): δ 177.4, 145.0, 137.2, 129.4, 126.9, 125.6, 75.4, 64.1, 40.3, 35.0, 31.9
HRMS [+ APCI] calculated for 643.1931, found 643.1933 $[M\text{-}2Cl,\text{-}H_2O]^+$
IR (thin film, cm^{-1}) ν = 3330, 2957, 1619, 1447, 1378, 1286, 975, 728, 699
$[\alpha]_D^{22}$ -142 (c = 0.50, $CHCl_3$)
m.p. 220 °C (dec.)
$\mathbf{R_f}$ 0.38 (30 % EtOAc:hexanes)

III. Procedure and Characterization Data for C-H Insertion Reactions

*a.) General procedure **E** for the C-H insertion reactions of donor/acceptor carbenoids into 1,4-cyclohexadiene (Table 2).*



A dry 7 mL vial was charged with diazoester (0.82 mmol), 4Å powdered molecular sieves (164 mg, 200 mg/1 mmol diazo) and a PTFE coated magnetic stir bar. The vial was capped with a PTFE septum then evacuated and backfilled with dry nitrogen three times. 1,4-cyclohexadiene (1.64 mL, 0.5 M in diazo) was added via syringe. The cap was removed and the iridium catalyst (0.5 mol %, 4.1 μmol) was added in a single portion. The cap was quickly replaced, the vial headspace purged with dry

nitrogen, and the mixture was stirred for 24 hours at ambient temperature (~ 22 °C). The reaction mixture was concentrated and the residue was purified by flash column chromatography (SiO_2, 5 % Et_2O:pentane) to furnish the title compound. The enantiomeric excess of the product was determined by chiral HPLC.

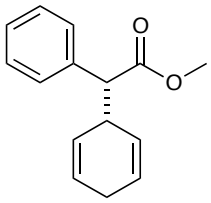


Table 2, Entry 1. Methyl-(*R*)-(2,5-cyclohexadienyl)phenylacetate[7]; colorless oil, 93 %, 97 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.34-7.23 (m, 5H), 5.80 (m, 1H), 5.73-5.65 (m, 2H), 5.27-5.23 (m, 1H), 3.66 (s, 3H), 3.47 (m, 1H), 3.41 (d, *J* = 10.4, 1H), 2.62-2.58 (m, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 173.6, 136.9, 128.8, 128.7, 127.6, 126.8, 126.5, 126.1, 126.0, 58.5, 52.2, 38.7, 26.6
HPLC (Daicel OJ, 230 nm detection, 0.5 % 2-propanol:hexanes, 1 mL/min); t_R = 8.72 min (major) and 10.32 min (minor)
$[\alpha]_D^{22}$ -105.5 (*c* = 1.00, $CHCl_3$)

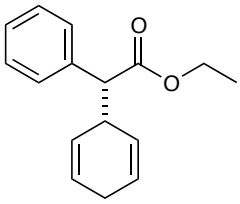


Table 2, Entry 2. Ethyl-(*R*)-(2,5-cyclohexadienyl)phenylacetate; colorless oil, 93 %, 96 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.35-7.23 (m, 5H), 5.81-5.77 (m, 1H), 5.74-5.64 (m, 2H), 5.27-5.22 (m, 1H), 4.21-4.04 (m, 2H), 3.50-3.44 (m, 1H), 3.38 (d, *J* = 10.4, 1H), 2.62-2.58 (m, 2H), 1.21 (t, *J* = 7.1, 3H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 173.1, 137.0, 128.8, 128.7, 127.5, 126.8, 126.4, 126.1, 126.0, 60.9, 58.7, 38.7, 26.6, 14.4
HRMS [+ APCI] calculated for 169.10118, found 169.10098 $[M\text{-}CO_2Et]^+$
IR (thin film, cm^{-1}) ν = 3030, 2980, 1729, 1153, 697
HPLC (Daicel OD, 230 nm detection, 0.5 % 2-propanol:hexanes, 1 mL/min); t_R = 6.68 min (major) and 8.77 min (minor)
$[\alpha]_D^{22}$ -95.0 (*c* = 1.00, $CHCl_3$)

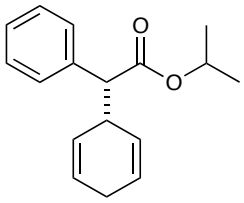


Table 2, Entry 3. isopropyl-(*R*)-(2,5-cyclohexadienyl)phenylacetate; colorless oil, 86 %, 96 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.34-7.22 (m, 5H), 5.81-5.77 (m, 1H), 5.74-5.70 (m, 1H), 5.68-5.63 (m, 1H), 5.28-5.23 (m, 1H), 5.00 (sept, *J* = 6.3, 1H), 3.51-3.42 (m, 1H), 3.35 (d, *J* = 10.4, 1H), 2.62-2.57 (m, 2H), 1.23 (d, *J* = 6.3, 3H), 1.13 (d, *J* = 6.3, 3H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.6, 137.2, 128.8, 128.6, 127.4, 126.9, 126.3, 126.2, 125.9, 68.3, 58.9, 38.8, 26.6, 22.0, 21.8
HRMS [+ APCI] calculated for 215.10666, found 215.10649 $[M-((H_3C)_2CH)+H]^+$
IR (thin film, cm^{-1}) ν = 3030, 2979, 1725, 1163, 1106, 697
HPLC (Daicel AD-H, 230 nm detection, 0.3 % 2-propanol:hexanes, 1 mL/min); t_R = 6.35 min (minor) and 6.99 min (major)
$[\alpha]_D^{22}$ -78.7 (*c* = 2.00, $CHCl_3$)

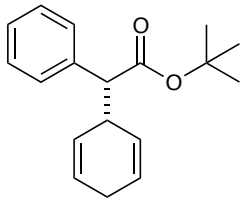


Table 2, Entry 4. *tert*-butyl-(*R*)-(2,5-cyclohexadienyl)phenylacetate; pale yellow oil, 71 %, 88 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.33-7.22 (m, 5H), 5.81-5.73 (m, 2H), 5.67-5.63 (m, 1H), 5.26-5.22 (m, 1H), 3.46-3.37 (m, 1H), 3.29 (d, *J* = 10.4, 1H), 2.61-2.57 (m, 2H), 1.40 (s, 9H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.3, 137.5, 128.8, 128.5, 127.3, 127.0, 126.4, 126.1, 125.8, 81.0, 59.6, 38.8, 28.2, 26.6
HRMS [+ APCI] calculated for 169.10118, found 169.10091 $[M-CO_2{}^tBu]^+$
IR (thin film, cm^{-1}) ν = 3030, 2926, 2856, 1725, 1143, 697
HPLC (Daicel OJ-H, 230 nm detection, 0.5 % 2-propanol:hexanes, 1 mL/min); t_R = 4.25 min (major) and 4.69 min (minor)
$[\alpha]_D^{22}$ -59.5 (*c* = 1.00, $CHCl_3$)

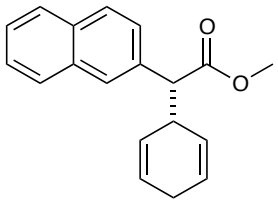


Table 2, Entry 5. methyl-(*R*)-(2,5-cyclohexadienyl)-(2-naphthalenyl)acetate; pale-yellow wax, 97 %, 95 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.84-7.81 (m, 3H), 7.79 (d, *J* = 1.5, 1H), 7.52 (dd, *J* = 8.6, 1.8, 1H), 7.49-7.46 (m, 2H), 5.87-5.82 (m, 1H), 5.80-5.76 (m, 1H), 5.68 (dtd, *J* = 10.2, 3.3, 1.6, 1H), 5.30-5.26 (m, 1H), 3.69 (s, 3H), 3.64-3.59 (m, 2H), 2.66-2.61 (m, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 173.6, 134.4, 128.4, 128.08, 127.95, 127.83, 126.8, 126.6, 126.5, 126.3, 126.20, 126.1, 126.0, 58.7, 52.2, 38.7, 26.6
HRMS [+ APCI] calculated for 279.13796, found 279.13773 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 3028, 2950, 1733, 1156, 754
HPLC (Daicel AD-H, 230 nm detection, 0.3 % 2-propanol:hexanes, 1 mL/min); t_R = 10.90 min (major) and 12.70 min (minor)
$[\alpha]_D^{22}$ -159.2 (*c* = 1.00, $CHCl_3$)

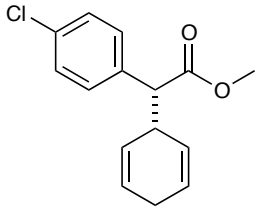


Table 2, Entry 7. methyl-(*R*)-(2,5-cyclohexadienyl)(4-chlorophenyl)acetate[7]; colorless oil, 93 %, 97 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.29-7.23 (m, 4H), 5.81-5.76 (m, 1H), 5.70-5.63 (m, 2H), 5.28-5.23 (m, 1H), 3.66 (s, 3H), 3.45-3.38 (m, 2H), 2.60-2.55 (m, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 173.2, 135.3, 133.5, 130.2, 128.8, 126.7, 126.5, 126.4, 125.5, 57.7, 52.3, 38.7, 26.5
HPLC (Daicel OD, 230 nm detection, 0.5 % 2-propanol:hexanes, 1 mL/min); t_R = 5.30 min (minor) and 7.36 min (minor)
$[\alpha]_D^{22}$ -147.9 (*c* = 1.00, $CHCl_3$)

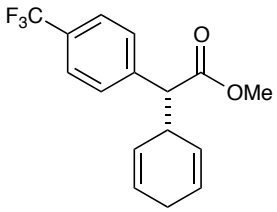


Table 2, Entry 8. methyl-(*R*)-(2,5-cyclohexadienyl)(4-trifluoromethylphenyl)acetate; colorless oil, 88 %, 88 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.58 (d, *J* = 8.2, 2H), 7.46 (d, *J* = 8.2, 2H), 5.83-5.80 (m, 1H), 5.73-5.67 (m, 2H), 5.26-5.23 (m, 1H), 3.69 (s, 3H), 3.51 (s, 2H), 2.61-2.57 (m, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): 172.9, 140.9, 129.3, 126.9, 126.8, 126.3, 125.6, 125.3, 58.2, 52.4, 38.8, 26.5.
HRMS [+APCI] calculated for 237.08856, found 237.08869 $[M\text{-}CO_2Me]^+$
IR (thin film, cm^{-1}) ν = 3031, 2954, 1736, 1324, 1160, 1124, 1069, 834, 696.
HPLC (Daicel OD-H, 230 nm detection, 0.3% IPA:hexane, 0.8 mL/min); t_R = 4.88 min (minor) and 5.75 min (major).
$[\alpha]_D^{22}$ -83.3 (*c* = 3.00, $CHCl_3$)

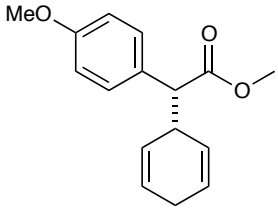


Table 2, Entry 9. methyl-(*R*)-(2,5-cyclohexadienyl)(4-methoxyphenyl)acetate[7]; colorless oil, 74 %, 83 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.25-7.22 (m, 2H), 6.86-6.82 (m, 2H), 5.80-5.76 (m, 1H), 5.71-5.64 (m, 2H), 5.29-5.24 (m, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 3.47-3.39 (m, 1H), 3.35 (d, *J* = 10.4, 1H), 2.62-2.57 (m, 2H)

^{13}C NMR (100 MHz; $CDCl_3$): δ 173.9, 159.1, 129.8, 129.0, 126.9, 126.4, 126.1, 126.0, 114.1, 57.6, 55.4, 52.1, 38.8, 26.6
HPLC (Daicel OJ, 230 nm detection, 0.5 % 2-propanol:hexanes, 1 mL/min); t_R = 13.68 min (major) and 17.88 min (minor)
$[\alpha]_D^{22}$ -111.7 (*c* = 1.00, $CHCl_3$)

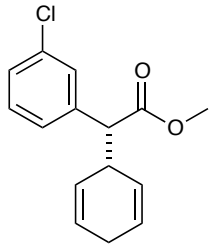


Table 2, Entry 10. methyl-(*R*)-(2,5-cyclohexadienyl)(3-chlorophenyl)acetate[7]; colorless oil, 99 %, 91 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.32 (s, 1H), 7.24-7.19 (m, 3H), 5.81-5.77 (m, 1H), 5.72-5.64 (m, 2H), 5.27-5.22 (m, 1H), 3.67 (s, 3H), 3.48-3.40 (m, 1H), 3.38 (d, *J* = 10.2, 1H), 2.61-2.56 (m, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 173.1, 138.8, 134.5, 129.9, 129.0, 127.8, 127.1, 126.8, 126.6, 126.4, 125.5, 58.0, 52.3, 38.7, 26.5
HPLC (Daicel OD-H, 230 nm detection, 0.5 % 2-propanol:hexanes, 1 mL/min); t_R = 4.26 min (minor) and 4.90 min (major)
$[\alpha]_D^{22}$ -105.3 (*c* = 2.00, $CHCl_3$)

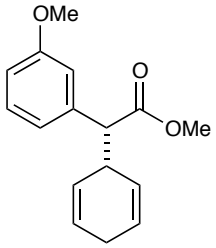


Table 2, Entry 11. methyl-(*R*)-(2,5-cyclohexadienyl)-(3-methoxyphenyl)acetate[7]; colorless oil, 88 %, 99 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.24 (t, *J* = 7.9, 1H), 6.93-6.90 (m, 2H), 6.82 (ddd, *J* = 8.2, 2.5, 1.0, 1H), 5.81 (m, 1H), 5.70 (m, 2H), 5.27 (m, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 3.46 (m, 1H), 3.38 (d, *J* = 10.6, 1H), 2.62 (m, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 173.5, 159.8, 138.4, 129.7, 126.8, 126.5, 126.0, 121.2, 114.3, 113.0, 58.5, 55.4, 52.2, 38.7, 26.6
HPLC (Daicel AD-H, 230 nm detection, 0.5 % 2-propanol:hexanes, 1 mL/min); t_R = 11.25 min (major) and 18.24 min (minor)
$[\alpha]_D^{22}$ -122.4 (*c* = 2.00, $CHCl_3$)

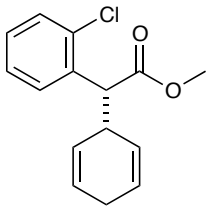


Table 2, Entry 12. methyl-(*R*)-(2,5-cyclohexadienyl)(2-chlorophenyl)acetate[7]; colorless oil, 10 %.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.55 (dd, *J* = 7.9, 1.8, 1H), 7.38 (dd, *J* = 7.9, 1.5, 1H), 7.27-7.17 (m, 2H), 5.83-5.78 (m, 1H), 5.76-5.70 (m, 2H), 5.34-5.29 (m, 1H), 4.24 (d, J = 9.5, 1H), 3.68 (s, 3H), 3.56-3.49 (m, 1H), 2.60 (m, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 173.0, 134.7, 129.8, 129.4, 128.6, 127.1, 126.71, 126.67, 126.4, 125.3, 52.7, 52.2, 38.7, 26.6

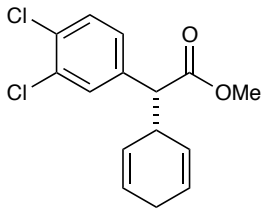
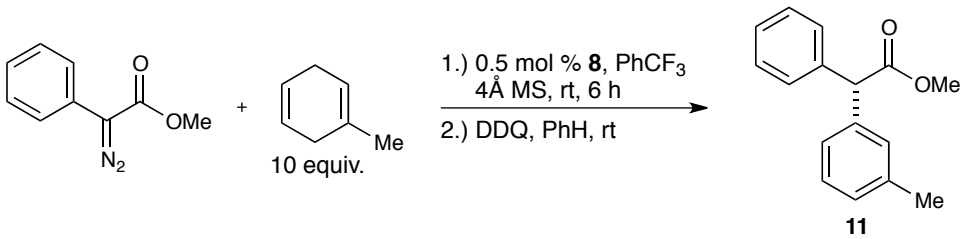


Table 2, Entry 13. methyl-(*R*)-(2,5-cyclohexadienyl)(3,4-dichlorophenyl)acetate[7]; colorless oil, 99 %, 93 % ee.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.43 (d, *J* = 2.1, 1H), 7.39 (d, *J* = 8.3, 1H), 7.18 (dd, *J* = 8.3, 2.1, 1H), 5.81 (dtt, *J* = 10.1, 3.3, 1.7, 1H), 5.73 (dtt, *J* = 10.2, 3.3, 1.7, 1H), 5.67-5.62 (m, 1H), 5.32-5.27 (m, 1H), 3.70 (s, 3H), 3.46-3.38 (m, 2H), 2.62-2.56 (m, 2H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.8, 137.0, 132.7, 131.8, 130.9, 130.5, 128.3, 127.0, 126.9, 126.2, 125.2, 57.4, 52.4, 38.8, 26.5
HPLC (Daicel OD-H, 230 nm detection, 0.5 % 2-propanol:hexanes, 0.5 mL/min); t_R = 8.24 min (minor) and 10.23 min (major)
$[\alpha]_D^{22}$ -120.9 (*c* = 1.00, $CHCl_3$)

b.) Procedures and characterization for C-H insertion reactions into cyclic dienes (Scheme 2).

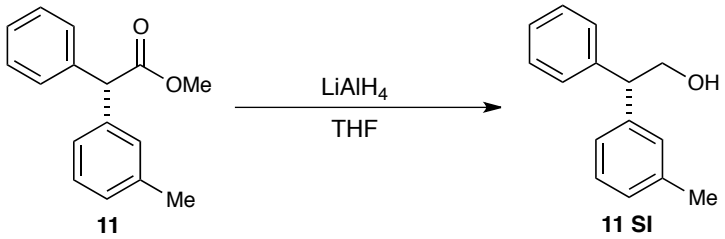


methyl-(*S*)-2-phenyl-2-(3-methylphenyl)acetate **11**.

A dry 7 mL vial was charged with methyl-phenyldiazoacetate (144 mg, 0.82 mmol), 4Å powdered molecular sieves (164 mg, 200 mg/1 mmol diazo) and a PTFE coated magnetic stir bar. The vial was capped with a PTFE septum then evacuated and backfilled with dry nitrogen three times. 1-methyl-1,4-cyclohexadiene (772 mg, 8.2 mmol) and α-α-α-trifluorotoluene (0.82 mL, 1 M in diazo) were added via syringe. The cap was removed and iridium catalyst **8** (0.5 mol %, 3.0 mg, 4.1 μmol) was added in a single portion. The cap was quickly replaced, the vial headspace purged with dry nitrogen, and the mixture was stirred for 6 hours at ambient temperature (~ 22 °C). The reaction mixture was concentrated and the residue was purified by flash column chromatography to give a colorless oil (SiO_2, 5 % Et_2O:pentane, R_f 0.37). ^{1}H NMR analysis indicated a 1.3:1 mixture of inseparable diastereomers (133 mg, 67 %). A portion of the oil (63 mg, 0.26 mmol) was dissolved in benzene (9

mL, 0.03 M) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (125 mg, 0.55 mmol) was added in a single portion. The mixture was stirred for 10 minutes then filtered through Celite, washing with $CHCl_3$ until the filtrate ran clear. The filtrate was concentrated and the residue was purified by flash column chromatography (SiO_2, 5 % → 10 % Et_2O:pentane) to give methyl-(*S*)-2-phenyl-2-(3-methylphenyl)acetate **11** as a colorless oil (60 mg, 95 %, 64 % over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.31-7.28 (m, 4H), 7.26-7.18 (m, 2H), 7.10-7.05 (m, 3H), 4.98 (s, 1H), 3.73 (s, 3H), 2.31 (s, 3H)
^{13}C NMR (100 MHz; $CDCl_3$): 173.3, 138.9, 138.7, 138.5, 129.5, 128.8, 128.70, 128.3, 127.4, 125.8, 57.1, 52.5, 21.7
HRMS [+NSI] calculated for 279.07819, found 279.07814 $[M+K]^+$
IR (thin film, cm^{-1}) ν = 3028, 2950, 1736, 1159, 700
$[\alpha]_D^{22}$ +12.3 (*c* = 1.00, $CHCl_3$)
R_f 0.19 (5 % Et_2O:pentane)

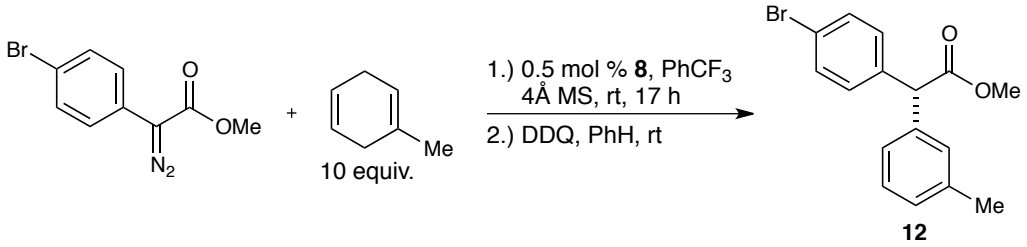


11 **11 SI**

(*S*)-2-phenyl-2-(3-methylphenyl)ethanol **11 SI**.

A solution of $LiAlH_4$ in Et_2O (1.0 M, 0.38 mL, 0.38 mmol) was added slowly to a solution of **11** (60 mg, 0.25 mmol) in THF (1.5 mL, 0.17 M) at room temperature and the reaction mixture was stirred for 14 hours. At room temperature, water (0.5 mL), 1M NaOH (0.6 mL), diethyl ether (6 mL), and water (2 mL) were added sequentially and the mixture was stirred for 5 minutes. The phases were separated and the aqueous phase was extracted with diethyl ether (3 x 5 mL). The ethereal phases were combined, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (SiO_2, 20 % → to 30 % EtOAc:hexanes) to give (*S*)-2-phenyl-2-(3-methylphenyl)ethanol **11 SI** as a colorless oil (50 mg, 94 %, > 99 % ee).

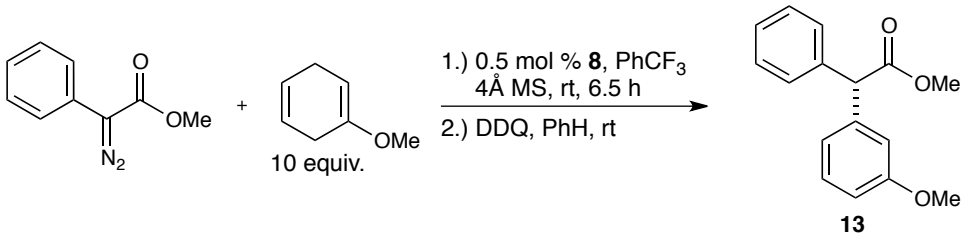
^{1}H NMR (600 MHz; $CDCl_3$): δ 7.32-7.30 (m, 2H), 7.26-7.19 (m, 4H), 7.06-7.03 (m, 3H), 4.16-4.14 (m, 3H), 2.31 (s, 3H), 1.49 (bs, 1H)
^{13}C NMR (150 MHz; $CDCl_3$): 141.6, 141.4, 138.6, 129.3, 128.9, 128.8, 128.5, 127.8, 127.0, 125.4, 66.4, 53.8, 21.7
HRMS [+NSI] calculated for 235.10934, found 235.10927 $[M+Na]^+$
IR (thin film, cm^{-1}) ν = 3370, 3026, 2922, 1604, 1492, 1059, 700
HPLC (Daicel OJ, 230 nm detection, 10 % 2-propanol:hexanes, 0.7 mL/min); t_R = 29.50 min (major) and 33.95 min (minor)
$[\alpha]_D^{22}$ +1.0 (*c* = 0.50, $CHCl_3$)
R_f 0.24 (20 % EtOAc:hexanes)



methyl-(*S*)-2-(4-bromophenyl)-2-(3-methylphenyl)acetate **12**.

A dry 7 mL vial was charged with methyl *p*-bromophenyldiazoacetate (105 mg, 0.41 mmol), 4Å powdered molecular sieves (82 mg, 200 mg/1 mmol diazo) and a PTFE coated magnetic stir bar. The vial was capped with a PTFE septum then evacuated and backfilled with dry nitrogen three times. 1-methyl-1,4-cyclohexadiene (386 mg, 4.1 mmol) and α-α-α-trifluorotoluene (0.2 mL, 1 M in diazo) were added via syringe. The cap was removed and iridium catalyst **8** (0.5 mol %, 1.5 mg, 2.1 μmol) was added in a single portion. The cap was quickly replaced, the vial headspace purged with dry nitrogen, and the mixture was stirred for 17 hours at ambient temperature (~ 22 °C). The reaction mixture was concentrated and the residue was purified by flash column chromatography (SiO_2, 5 % Et_2O:pentane, R_f 0.57). ^{1}H NMR analysis indicated a 1.3:1 mixture of inseparable diastereomers as a colorless oil (128 mg, 97 %). A portion of the oil (62 mg, 0.19 mmol) was dissolved in benzene (6.5 mL, 0.03 M) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (52 mg, 0.23 mmol) was added in a single portion. The mixture was stirred for 2 hours then filtered through Celite, washing with $CHCl_3$ until the filtrate ran clear. The filtrate was concentrated and the residue was purified by flash column chromatography (SiO_2, 5 % → 10 % Et_2O:pentane) to give methyl-(*S*)-2-(4-bromophenyl)-2-(3-methylphenyl)acetate **12** as a colorless oil (62 mg, 99 %, 95 % ee, 96 % over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.43 (d, *J* = 8.5, 2H), 7.24-7.21 (m, 1H), 7.18 (d, *J* = 8.5, 2H), 7.07 (t, *J* = 6.2, 3H), 4.93 (s, 1H), 3.73 (s, 3H), 2.32 (s, 3H)
^{13}C NMR (100 MHz; $CDCl_3$): 172.8, 138.7, 138.1, 137.9, 131.9, 130.6, 129.3, 128.8, 128.5, 125.6, 121.5, 56.5, 52.7, 21.7
HRMS [+APCI] calculated for 259.01169, found 259.01192 $[M\text{-}CO_2Me]^+$
IR (thin film, cm^{-1}) ν = 2950, 1738, 1488, 1161, 1011
HPLC (Daicel SS WHELK, 230 nm detection, 1.0 % 2-propanol:hexanes, 1 mL/min); t_R = 11.35 min (minor) and 14.68 min (major)
$[\alpha]_D^{22}$ +19.8 (*c* = 1.00, $CHCl_3$)
R_f 0.29 (5 % Et_2O:pentane)

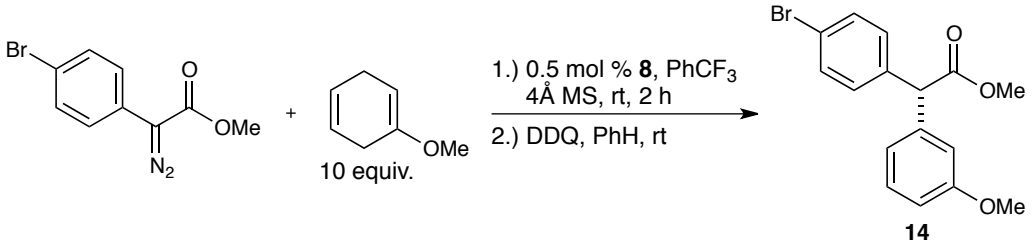


methyl-(*S*)-2-phenyl-2-(3-methoxyphenyl)acetate **13**.

A dry 7 mL vial was charged with methyl phenyldiazoacetate (72 mg, 0.41 mmol), 4Å powdered molecular sieves (82 mg, 200 mg/1 mmol diazo) and a PTFE coated magnetic stir bar. The vial was capped with a PTFE septum then evacuated and backfilled with dry nitrogen three times. 1-methoxy-

1,4-cyclohexadiene (534 mg, 4.1 mmol) and α-α-α-trifluorotoluene (0.2 mL, 1 M in diazo) were added via syringe. The cap was removed and iridium catalyst **8** (0.5 mol %, 1.5 mg, 2.1 μmol) was added in a single portion. The cap was quickly replaced, the vial headspace purged with dry nitrogen, and the mixture was stirred for 6.5 hours at ambient temperature (~ 22 °C). The reaction mixture was concentrated and the residue was filtered through a pad of silica, washing first with hexanes (to remove excess diene) then washing with 1:1 Et_2O:pentane to collect the insertion product (5 % Et_2O:pentane, R_f 0.21) as a colorless oil. ^{1}H NMR of the mixture showed a 1.1:1 mixture of inseparable diastereomers. The oil was dissolved in benzene (10 mL, 0.04 M) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (111 mg, 0.49 mmol) was added in a single portion. The mixture was stirred for 2 hours then filtered through Celite, washing with $CHCl_3$ until the filtrate ran clear. The filtrate was concentrated and the residue was purified by flash column chromatography (SiO_2, 5 % → 10 % Et_2O:pentane) to give methyl-(*S*)-2-phenyl-2-(3-methoxyphenyl)acetate **13** as a colorless oil (103 mg, 98 %, 94 % ee).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.31-7.29 (m, 4H), 7.27-7.21 (m, 3H), 6.89-6.87 (m, 1H), 6.86-6.85 (m, 1H), 6.81-6.78 (m, 1H), 4.99 (s, 1H), 3.76 (s, 3H), 3.73 (s, 3H)
^{13}C NMR (100 MHz; $CDCl_3$): 173.1, 159.9, 140.2, 138.6, 129.8, 128.8, 127.5, 121.2, 114.8, 112.7, 57.1, 55.4, 52.6
HRMS [+NSI] calculated for 295.07310, found 295.07297 $[M+K]^+$
IR (thin film, cm^{-1}) ν = 2950, 1733, 1597, 1489, 1261, 1144, 696
HPLC (Daicel ChiralPak AS-H, 230 nm detection, 1.0 % 2-propanol:hexanes, 0.5 mL/min); t_R = 16.69 min (major) and 18.56 min (minor)
$[\alpha]_D^{22}$ +10.4 (*c* = 1.00, $CHCl_3$)
R_f 0.24 (10 % Et_2O:pentane)

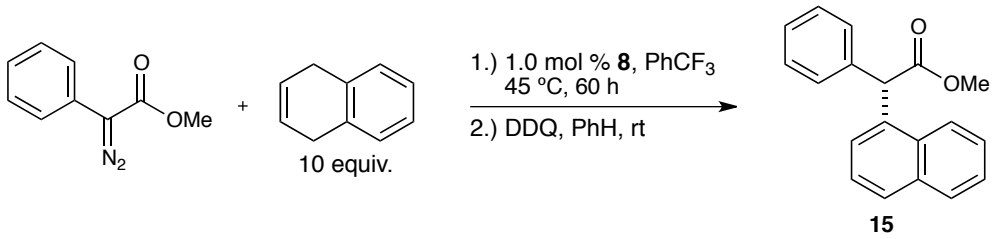


methyl-(*S*)-2-(4-bromophenyl)-2-(3-methoxyphenyl)acetate **14**.

A dry 7 mL vial was charged with methyl *p*-bromophenyldiazoacetate (105 mg, 0.41 mmol), 4Å powdered molecular sieves (82 mg, 200 mg/1 mmol diazo) and a PTFE coated magnetic stir bar. The vial was capped with a PTFE septum then evacuated and backfilled with dry nitrogen three times. 1-methoxy-1,4-cyclohexadiene (452 mg, 4.1 mmol) and α-α-α-trifluorotoluene (0.2 mL, 1 M in diazo) were added via syringe. The cap was removed and iridium catalyst **8** (0.5 mol %, 1.5 mg, 2.1 μmol) was added in a single portion. The cap was quickly replaced, the vial headspace purged with dry nitrogen, and the mixture was stirred for 2 hours at ambient temperature (~ 22 °C). The reaction mixture was concentrated and the residue was filtered through a pad of silica, washing first with hexanes (to remove excess diene) then washing with 1:1 Et_2O:pentane to collect the insertion product (10 % Et_2O:pentane, R_f 0.33) as a colorless oil. ^{1}H NMR of the mixture showed a 4.3:1 mixture of inseparable diastereomers. The oil was dissolved in benzene (14 mL, 0.03 M) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (111 mg, 0.49 mmol) was added in a single portion. The mixture was stirred for 8 hours then filtered through Celite, washing with $CHCl_3$ until the filtrate ran clear. The filtrate was concentrated and the residue was purified by flash column chromatography (SiO_2, 5 % →

10 % Et_2O:pentane) to give methyl-(*S*)-2-(4-bromophenyl)-2-(3-methoxyphenyl)acetate **14** as a colorless oil (113 mg, 82 %, 90 % ee).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.44 (d, *J* = 8.5, 2H), 7.27-7.23 (m, 2H), 7.19 (m, *J* = 8.5, 2H), 6.87-6.85 (m, 1H), 6.83-6.80 (m, 2H), 4.95 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H)
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.6, 160.0, 139.7, 137.7, 131.9, 130.5, 130.0, 121.6, 121.0, 114.7, 112.8, 56.5, 55.4, 52.7
HRMS [+NSI] calculated for 372.98362, found 372.98351 $[M+K]^+$
IR (thin film, cm^{-1}) ν = 2951, 1737, 1489, 1262, 1162, 1011
HPLC (Chiralcel OJ-H, 230 nm detection, 25 % 2-propanol:hexanes, 1 mL/min); t_R = 20.66 min (minor) and 22.74 min (major)
$[\alpha]_D^{22}$ +20.5 (*c* = 1.00, $CHCl_3$)
R_f 0.23 (10 % Et_2O:pentane)



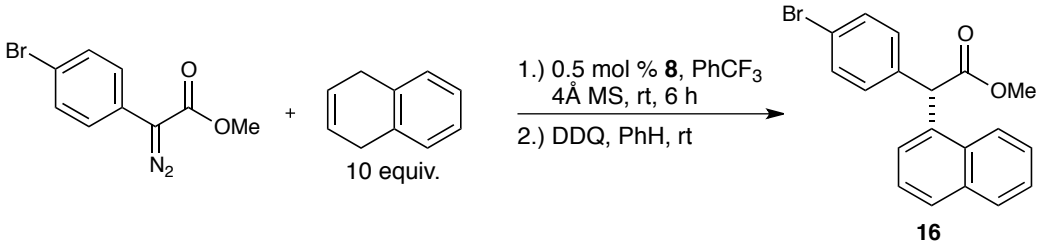
15

methyl-(*S*)-2-(1-naphthalenyl)-2-phenylacetate **15**.

A dry 7 mL vial was charged with 4Å powdered molecular sieves (84 mg, 200 mg/1 mmol diazo), 1,4-dihydronapthalene (549 mg, 4.22 mmol), iridium catalyst **8** (1 mol %, 3.0 mg, 4.2 μmol) and a PTFE coated magnetic stir bar. The vial was capped with a PTFE septum then evacuated and backfilled with dry nitrogen three times. The mixture was submerged in a preheated 45 °C oil bath, then a solution of methyl phenyldiazoacetate (74 mg, 0.42 mmol) and 1,4-dihydronaphthalene (0.11 mL, 0.26 M in diazo) in α-α-α-trifluorotoluene (0.73 mL, 0.58 M in diazo) was added over the course of 42 hours *via* syringe pump. The mixture was allowed to stir an additional 18 hours then filtered through a plug of silica gel, washing with a 1:1 mixture of Et_2O:pentane. The filtrate was concentrated and the residue was purified by flash column chromatography [SiO_2, 0 % → 5 % Et_2O:pentane (R_f 0.37 in 5 % Et_2O:pentane)] to collect the insertion product as a colorless oil (68 mg, 58 %). ^{1}H NMR of the oil showed a 8:1 mixture of inseparable diastereomers. The oil was dissolved in benzene (14 mL, 0.03 M) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (111 mg, 0.50 mmol) was added in a single portion. The mixture was stirred for 2 hours, then a second portion of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (76 mg, 0.34 mmol) was added. The mixture was stirred for 4 hours then a third portion of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (26 mg, 0.11 mmol) was added. The reaction was stirred an additional 14 h, at which time the entire mixture was filtered through a pad of silica gel, washing with a 1:1 mixture of Et_2O:pentane until the filtrate ran clear. The filtrate was concentrated and the residue was purified by flash column chromatography (SiO_2, 0 % → 5 % → 10 % Et_2O:pentane) to give methyl-(*S*)-2-(1-naphthalenyl)-2-phenylacetate **15** as a colorless oil (62 mg, 53 %, 95 % ee)

^{1}H NMR (400 MHz; $CDCl_3$): δ 8.01-7.98 (m, 1H), 7.89-7.87 (m, 1H), 7.81 (d, *J* = 8.2, 1H), 7.52-7.48 (m, 2H), 7.44 (t, *J* = 7.7, 1H), 7.37-7.27 (m, 6H), 5.81 (s, 1H), 3.77 (s, 3H)
^{13}C NMR (100 MHz; $CDCl_3$): 173.5, 138.1, 134.6, 134.2, 131.8, 129.2, 128.9, 128.4, 127.6, 126.8, 126.5, 125.9, 125.6, 123.3, 77.4, 53.8, 52.7

HRMS [+APCI] calculated for 299.10425, found 299.10414 $[M+Na]^+$
IR (thin film, cm^{-1}) ν = 3060, 2950, 1735, 1195, 1151, 778, 698
HPLC (Daicel Chiralpak AS-H, 210 nm detection, 1.0 % 2-propanol:hexanes, 1 mL/min); t_R = 6.53 min (major) and 7.54 min (minor)
$[\alpha]_D^{22}$ +7.4 (*c* = 1.00, $CHCl_3$)
R_f 0.40 (10 % Et_2O:pentane)



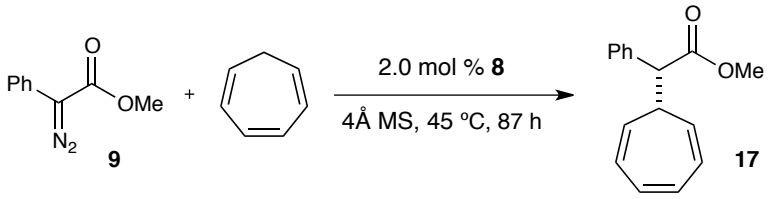
16

methyl-(*S*)-2-(4-bromophenyl)-2-(1-naphthalenyl)acetate **16**.

A dry 7 mL vial was charged with 4Å powdered molecular sieves (42 mg, 200 mg/1 mmol diazo), 1,4-dihydronapthalene (275 mg, 2.11 mmol), iridium catalyst **8** (1 mol %, 1.5 mg, 2.1 μmol) and a PTFE coated magnetic stir bar. The vial was capped with a PTFE septum then evacuated and backfilled with dry nitrogen three times. The mixture was submerged in a preheated 45 °C oil bath, then a solution of methyl 4-bromophenyldiazoacetate (54 mg, 0.21 mmol) in α-α-α-trifluorotoluene (0.42 mL, 0.5 M in diazo) was added over the course of 42 hours *via* syringe pump. The mixture was allowed to stir an additional 24 hours then filtered through a pad of silica gel, washing with a 1:1 mixture of Et_2O:pentane. The filtrate was concentrated and the residue was purified by flash column chromatography [SiO_2, 0 % → 5 % Et_2O:pentane (R_f 0.28 in 5 % Et_2O:pentane)] to collect the insertion product as a colorless oil (68 mg, 58 %). The oil was dissolved in benzene (7 mL, 0.03 M) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (57 mg, 0.50 mmol) was added in a single portion. The mixture was stirred for 2 hours, then a second portion of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (25 mg, 0.11 mmol) was added. The mixture was stirred for an additional 16 hours, at which time the entire mixture was filtered through a pad of silica gel, washing with a 1:1 mixture of Et_2O:pentane until the filtrate ran clear. The filtrate was concentrated and the residue was purified by flash column chromatography (SiO_2, 0 % → 5 % → 10 % Et_2O:pentane) to give methyl-(*S*)-2-(4-bromophenyl)-2-(1-naphthalenyl)acetate **16** as a colorless oil (37 mg, 52 %, 88 % ee).

^{1}H NMR (600 MHz; $CDCl_3$): δ 7.93-7.91 (m, 1H), 7.88-7.87 (m, 1H), 7.82 (d, *J* = 8.3, 1H), 7.50-7.48 (m, 2H), 7.45 (dt, *J* = 8.0, 3.8, 3H), 7.35 (d, *J* = 7.1, 1H), 7.19 (d, *J* = 8.3, 2H), 5.74 (s, 1H), 3.77 (s, 3H)
^{13}C NMR (150 MHz; $CDCl_3$): 173.1, 137.2, 134.2, 134.0, 132.0, 131.6, 130.9, 129.3, 128.7, 126.9, 126.3, 126.1, 125.6, 123.3, 121.7, 53.2, 52.9
HRMS [+NSI] calculated for 392.98870, found 392.98858 $[M+K]^+$
IR (thin film, cm^{-1}) ν = 3049, 2950, 1735, 1487, 1162, 778
HPLC (Daicel Chiralcel OJ-H, 230 nm detection, 25 % 2-propanol:hexanes, 1 mL/min); t_R = 15.79 min (major) and 19.39 min (minor)
$[\alpha]_D^{22}$ -1.6 (*c* = 1.00, $CHCl_3$)
R_f 0.39 (10 % Et_2O:pentane)

c.) Procedure and characterization for C-H insertion into cycloheptatriene (Equation 2).



methyl-(*R*)-2-(cyclohepta-2,4,6-trien-1-yl)-2-phenylacetate **17**.

A solution of **9** (72 mg, 0.41 mmol) in cycloheptatriene (1.44 mL) was added over the course of 72 hours to a stirring mixture of iridium catalyst **8** (6.0 mg, 8.2 µmol, 2.0 mol %), 4Å powdered molecular sieves (82 mg, 200 mg/1 mmol diazo), and cycloheptatriene (0.82 mL) at 45 °C. Upon addition of the diazoester, the reaction was stirred for an additional 15 hours. The reaction mixture was filtered through Celite, the filter cake was washed with $CHCl_3$, and the filtrate was concentrated. The residue was purified by flash column chromatography (SiO_2, 5 % Et_2O:pentane) to give methyl-(*R*)-2-(cyclohepta-2,4,6-trien-1-yl)-2-phenylacetate **17** as a colorless oil (50 mg, 51 %, 86 % ee).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.35-7.26 (m, 5H), 6.68 (qd, *J* = 11.7, 5.4, 2H), 6.27 (dd, *J* = 9.5, 5.4, 1H), 6.10 (dd, *J* = 9.5, 5.5, 1H), 5.37 (dd, *J* = 9.5, 6.1, 1H), 5.00 (dd, *J* = 9.5, 6.1, 1H), 3.84 (d, *J* = 11.7, 1H), 3.67 (s, 3H), 2.67 (dt, *J* = 11.7, 6.0, 1H).
^{13}C NMR (100 MHz; $CDCl_3$): 173.7, 137.2, 131.21, 131.10, 128.9, 128.8, 127.8, 125.9, 125.7, 124.4, 123.4, 53.2, 52.3, 41.9.
HRMS [+NSI] calculated for 241.12231, found 241.12220 $[M+H]^+$
IR (thin film, cm^{-1}) ν = 3016, 2951, 1733, 1155, 695.
HPLC (Daicel Chiralcel OJ-H, 210 nm detection, 5.0 % 2-propanol:hexanes, 1 mL/min); t_R = 15.40 min (major) and 25.64 min (minor).
$[\alpha]_D^{22}$ +8.0 (*c* = 0.50, $CHCl_3$).
R_f 0.32 (5 % Et_2O:pentane)

*d.) Procedure and characterization for the oxidation of methyl-(R)-(2,5-cyclohexadienyl)-(3-methoxyphenyl)acetate (Table 2, Entry 11) to methyl-(R)-2-phenyl-2-(3-methoxyphenyl)acetate (**epi-13**).*

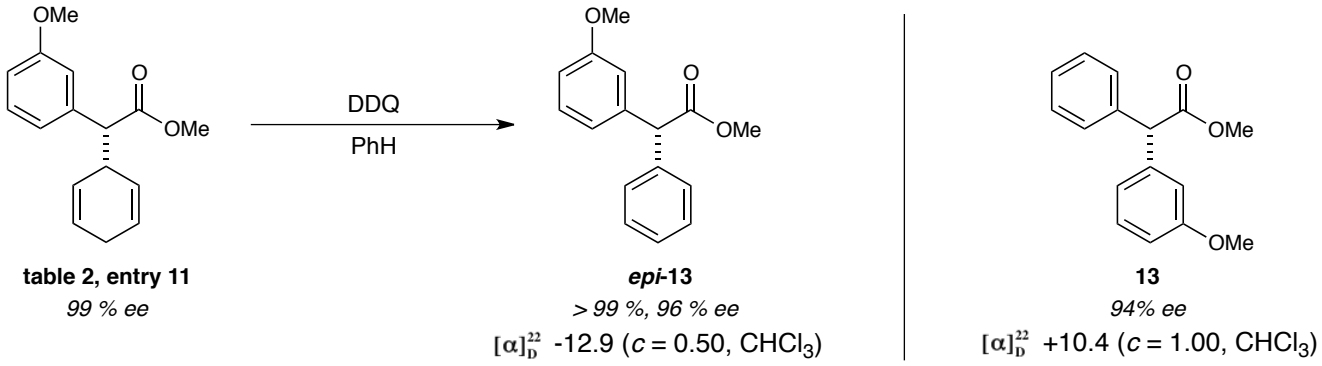


table 2, entry 11
99 % ee

***epi*-13**
> 99 %, 96 % ee
$[\alpha]_D^{22}$ -12.9 (*c* = 0.50, $CHCl_3$)

13
94% ee
$[\alpha]_D^{22}$ +10.4 (*c* = 1.00, $CHCl_3$)

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (44 mg, 0.19 mmol) was added in a single portion to a stirring mixture of methyl-(*R*)-(2,5-cyclohexadienyl)-(3-methoxyphenyl)acetate (41 mg, 0.16 mmol). The mixture was stirred for 18 hours, and the entire mixture was filtered through a pad of silica gel, washing with a 1:1 mixture of Et_2O:pentane until the filtrate ran clear. The filtrate was concentrated and the residue was purified by flash column chromatography (SiO_2, 5 % → 10 % Et_2O:pentane) to give methyl-(R)-2-phenyl-2-(3-methoxyphenyl)acetate (***epi*-13**) as a colorless oil (41 mg, > 99 %, 96 % ee).

HPLC (Daicel ChiralPak AS-H, 230 nm detection, 1.0 % 2-propanol:hexanes, 0.5 mL/min); t_R = 16.27 min (minor) and 18.48 min (major).
$[\alpha]_D^{22}$ -12.9 (*c* = 0.50, $CHCl_3$).

IV. References

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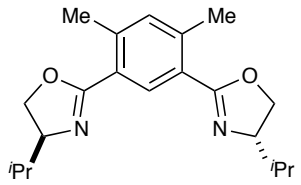

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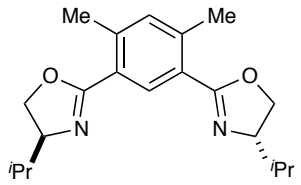

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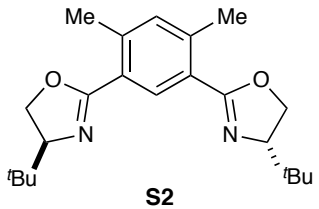

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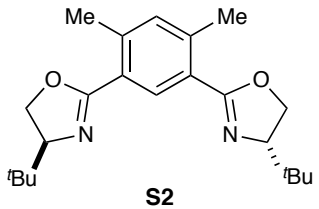
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S2

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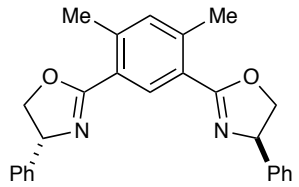

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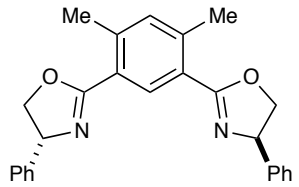

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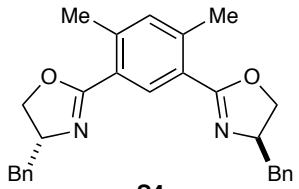

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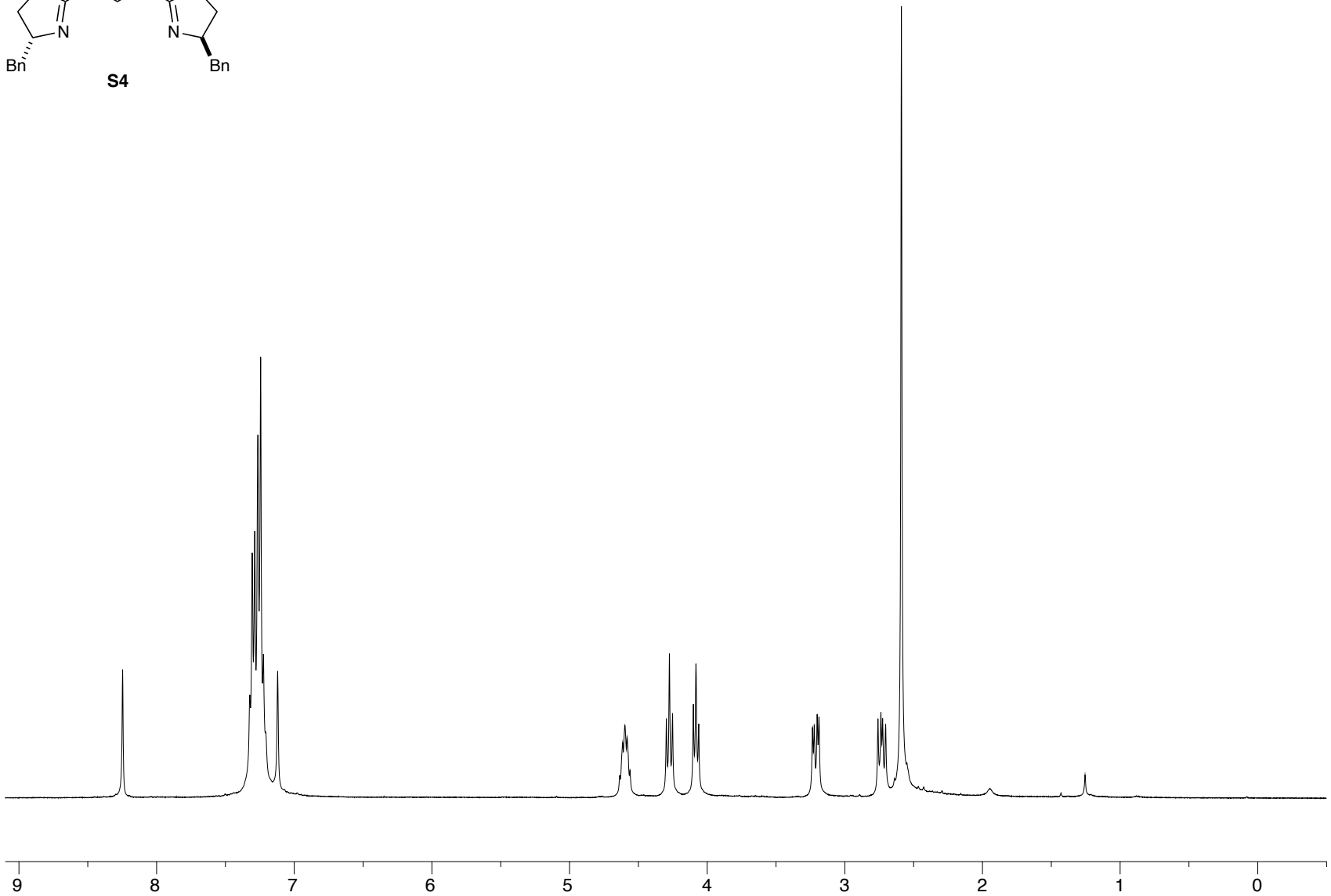

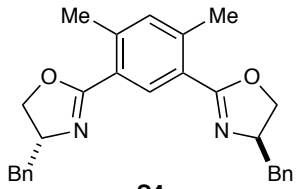

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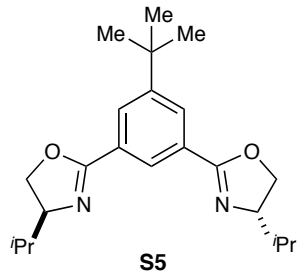

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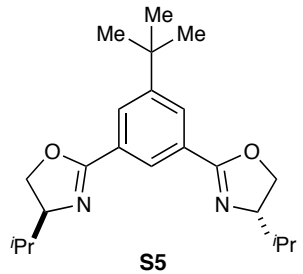

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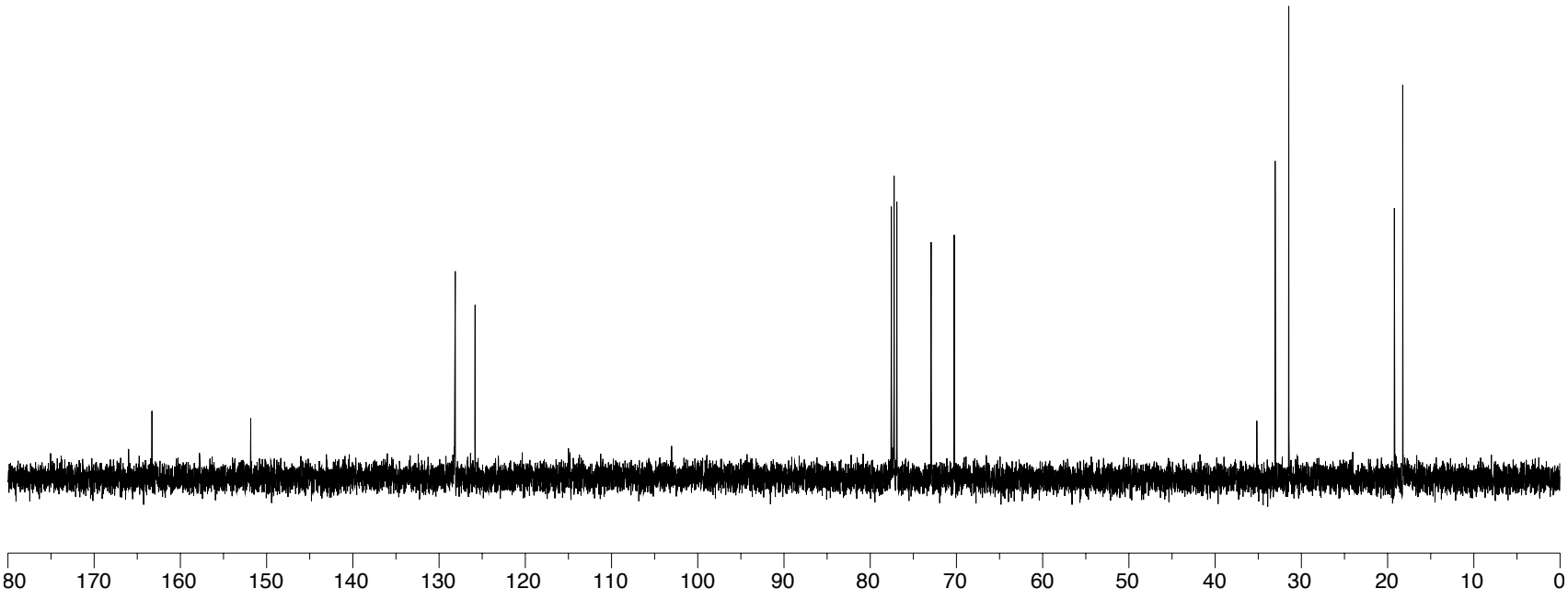

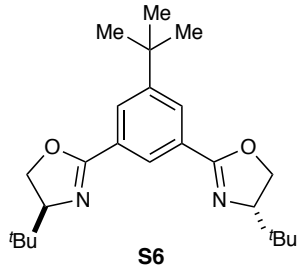

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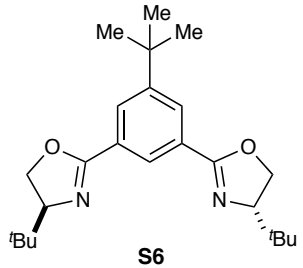

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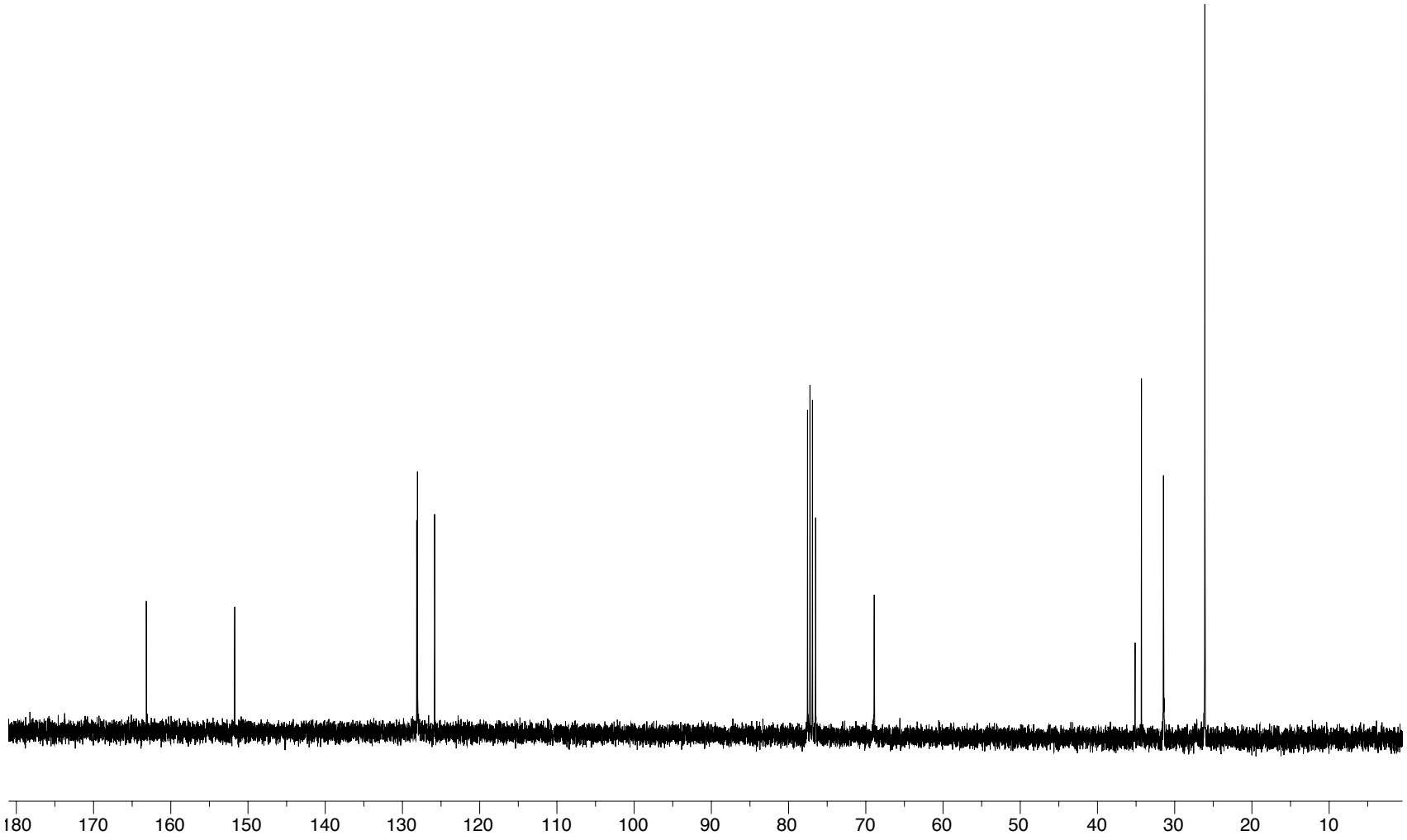

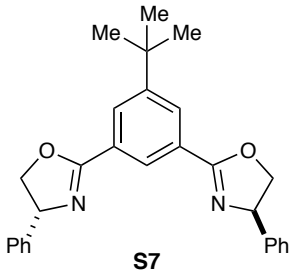

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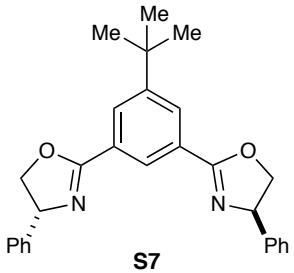

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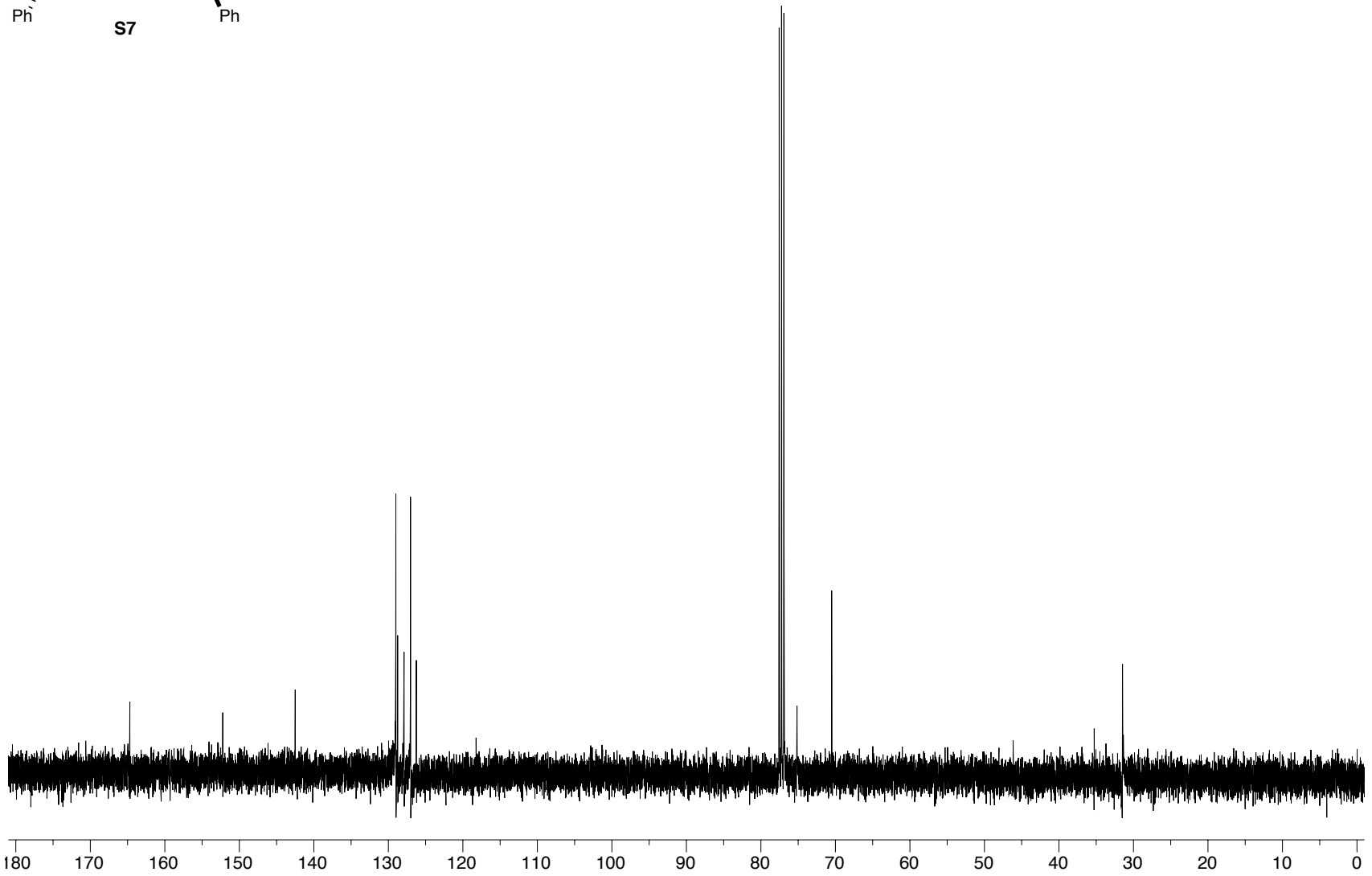

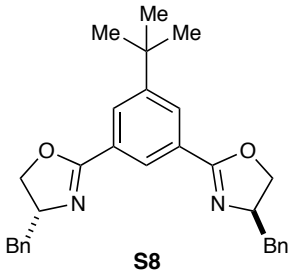

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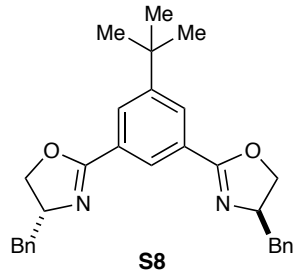

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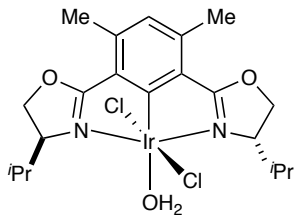

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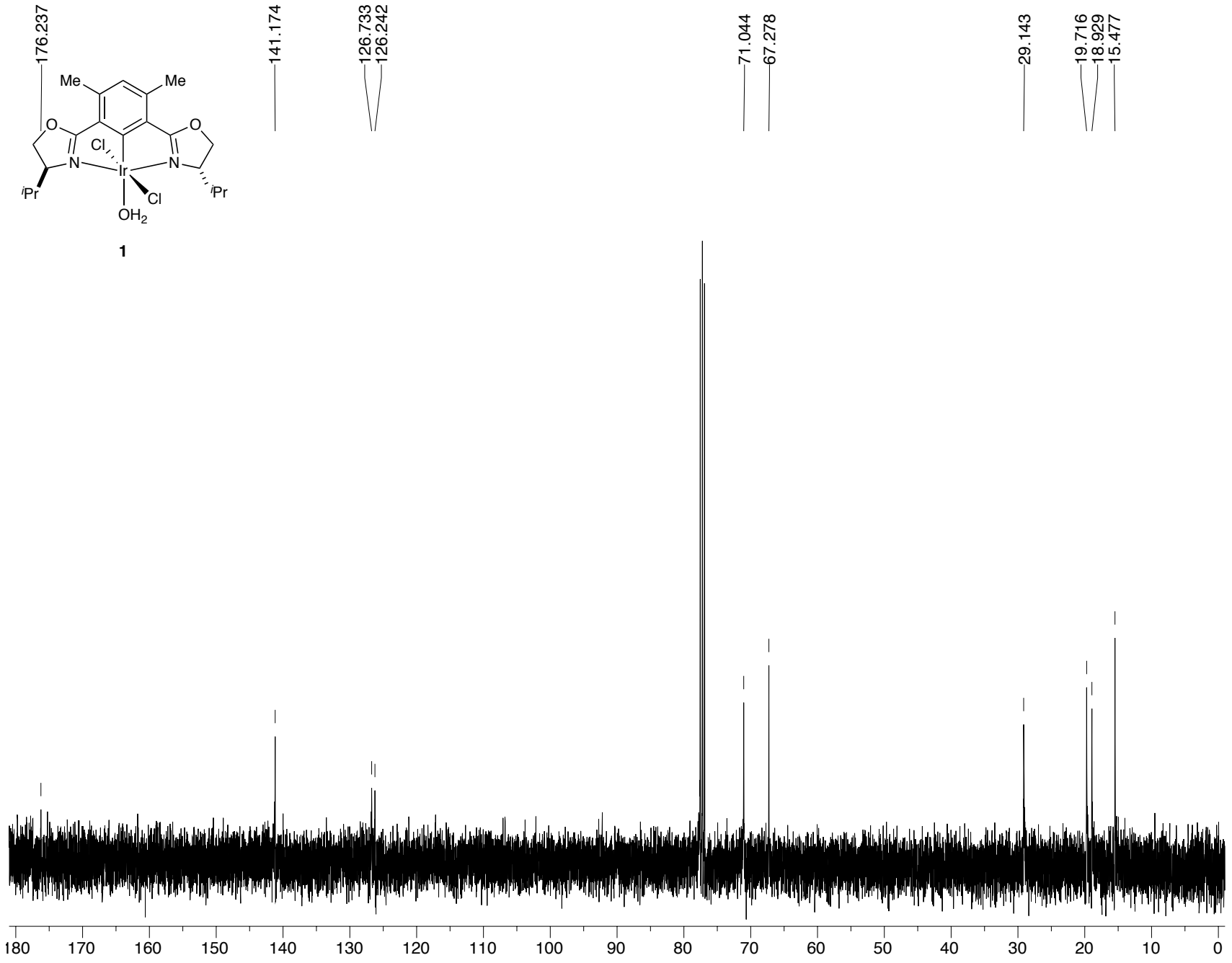

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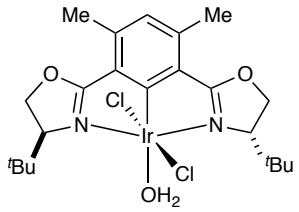

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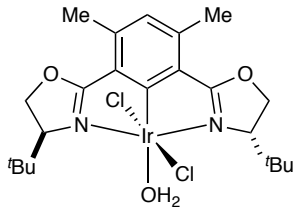

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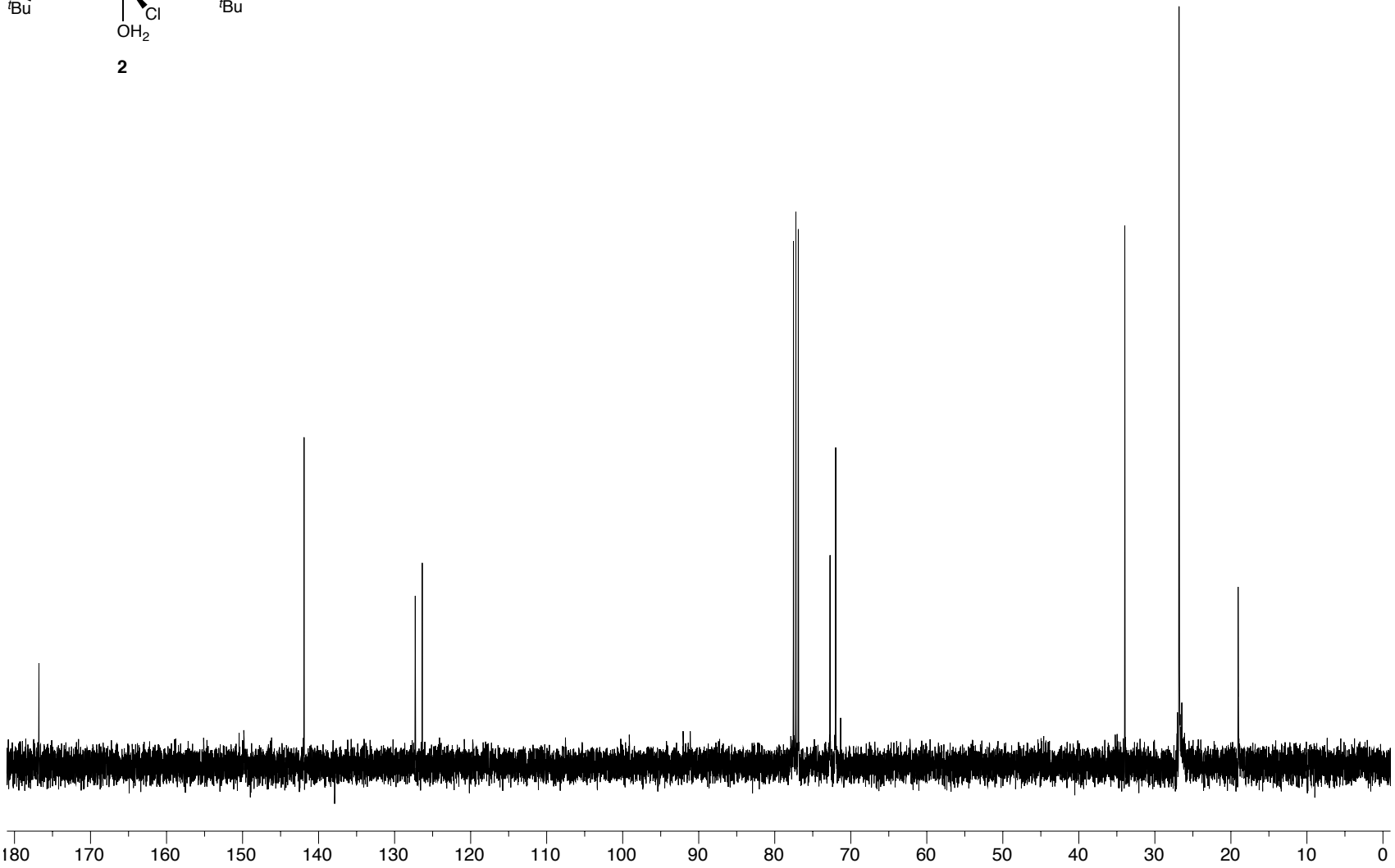

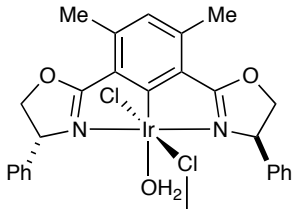

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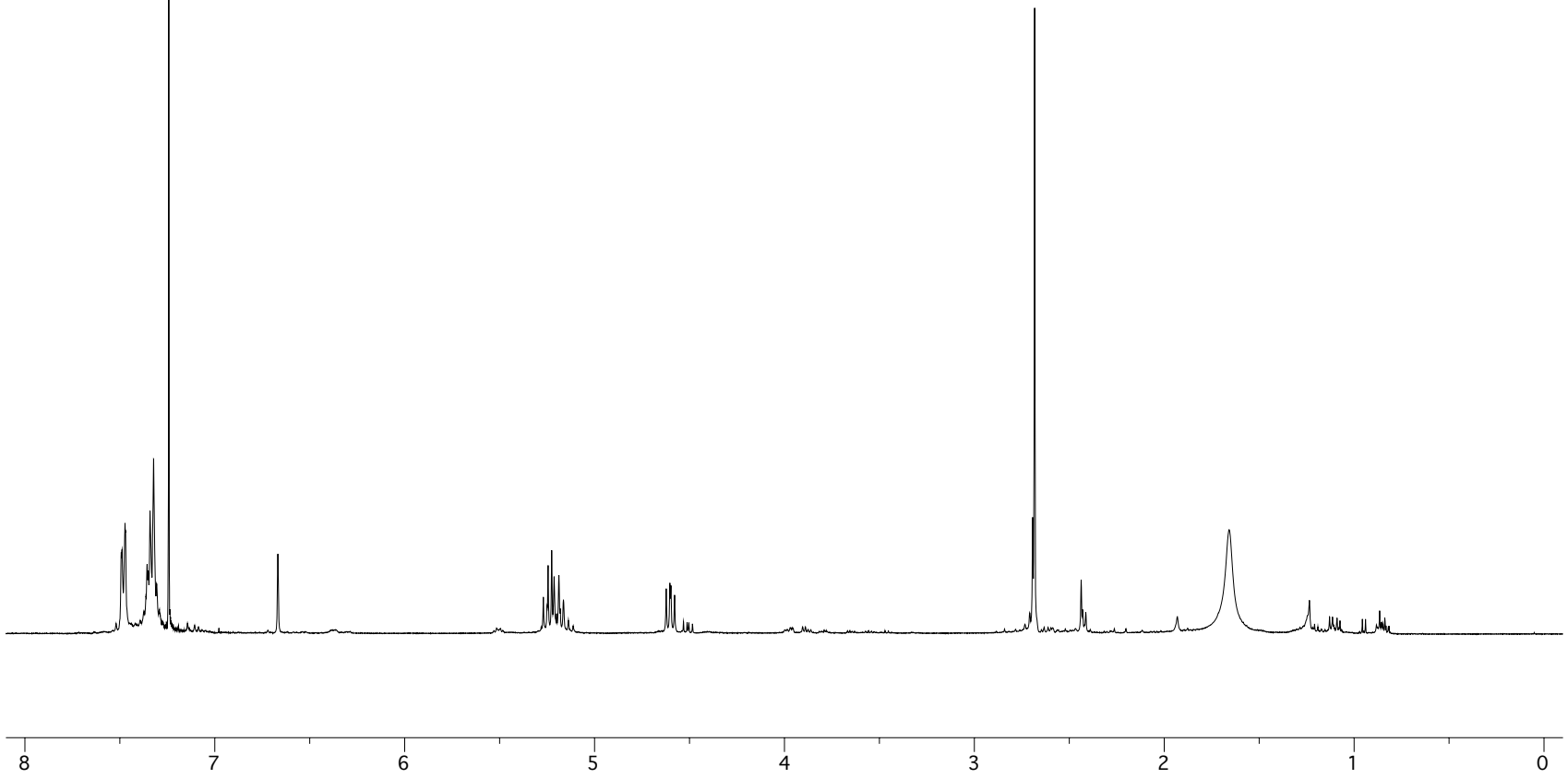

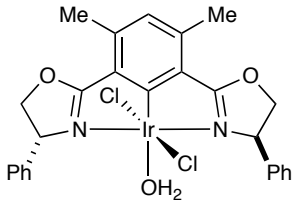

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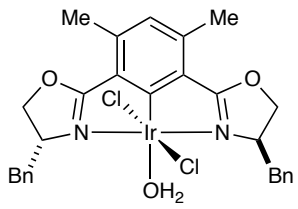

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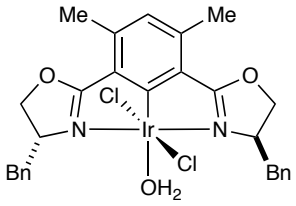

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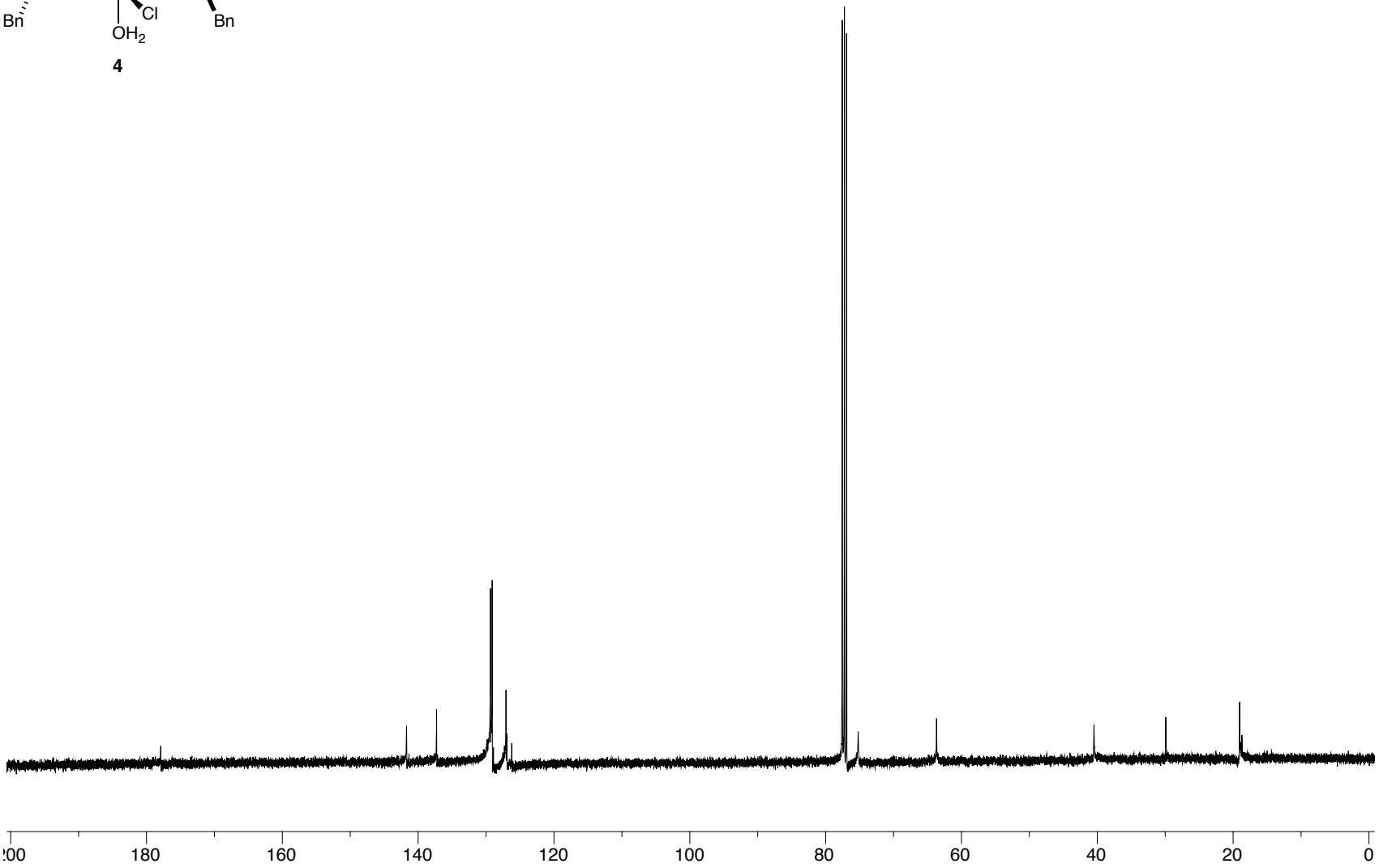

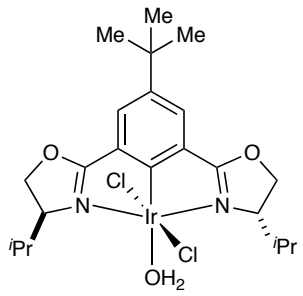

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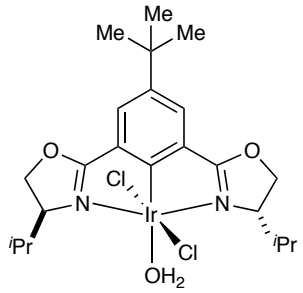

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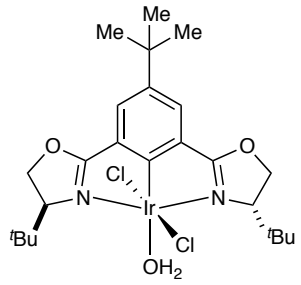

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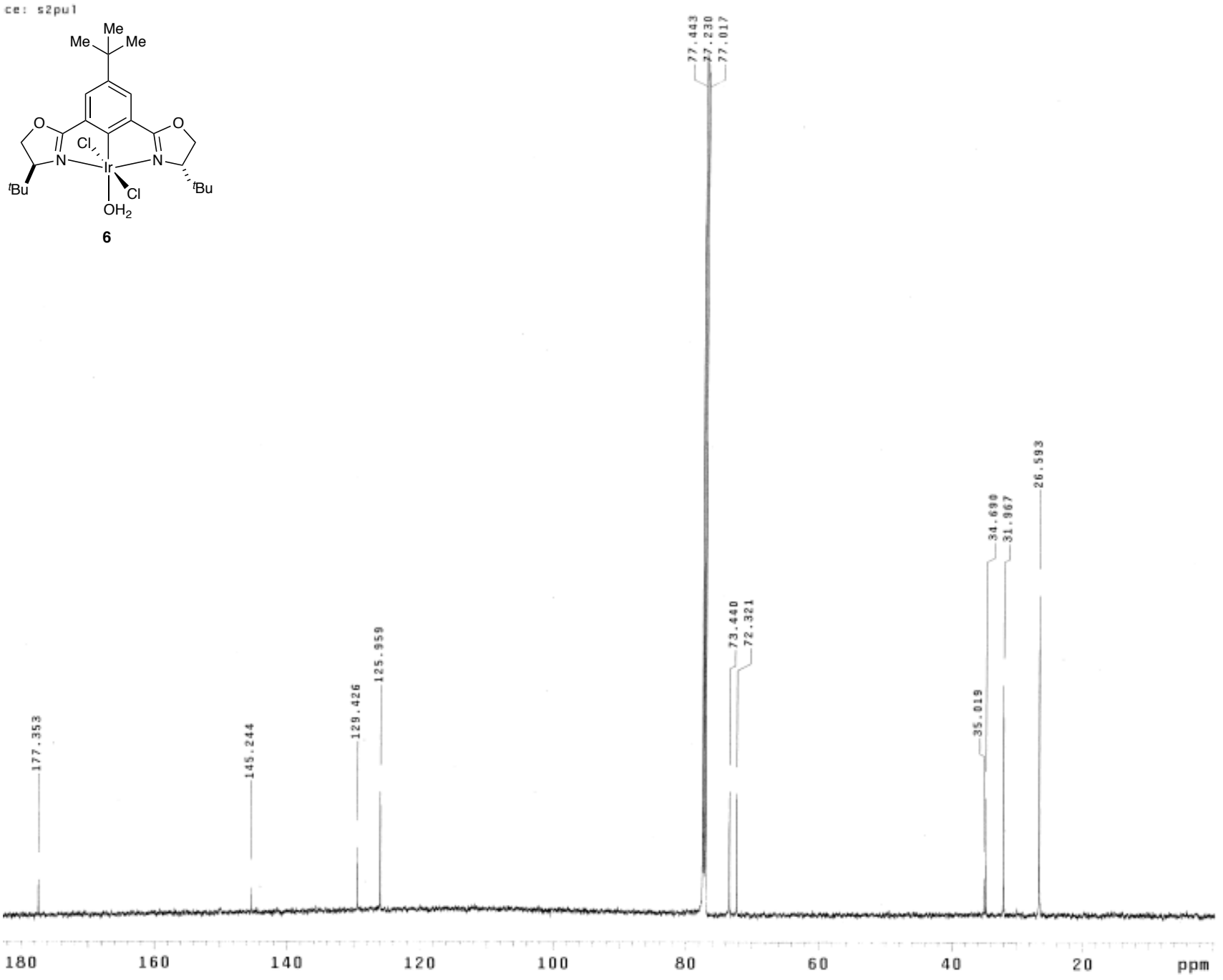

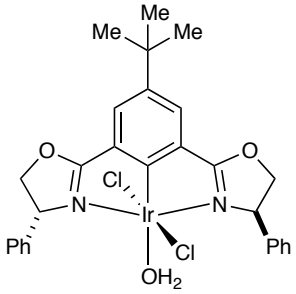

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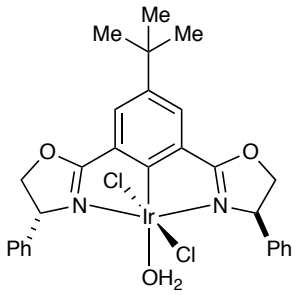

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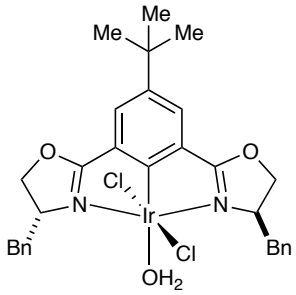

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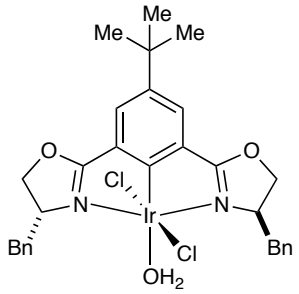

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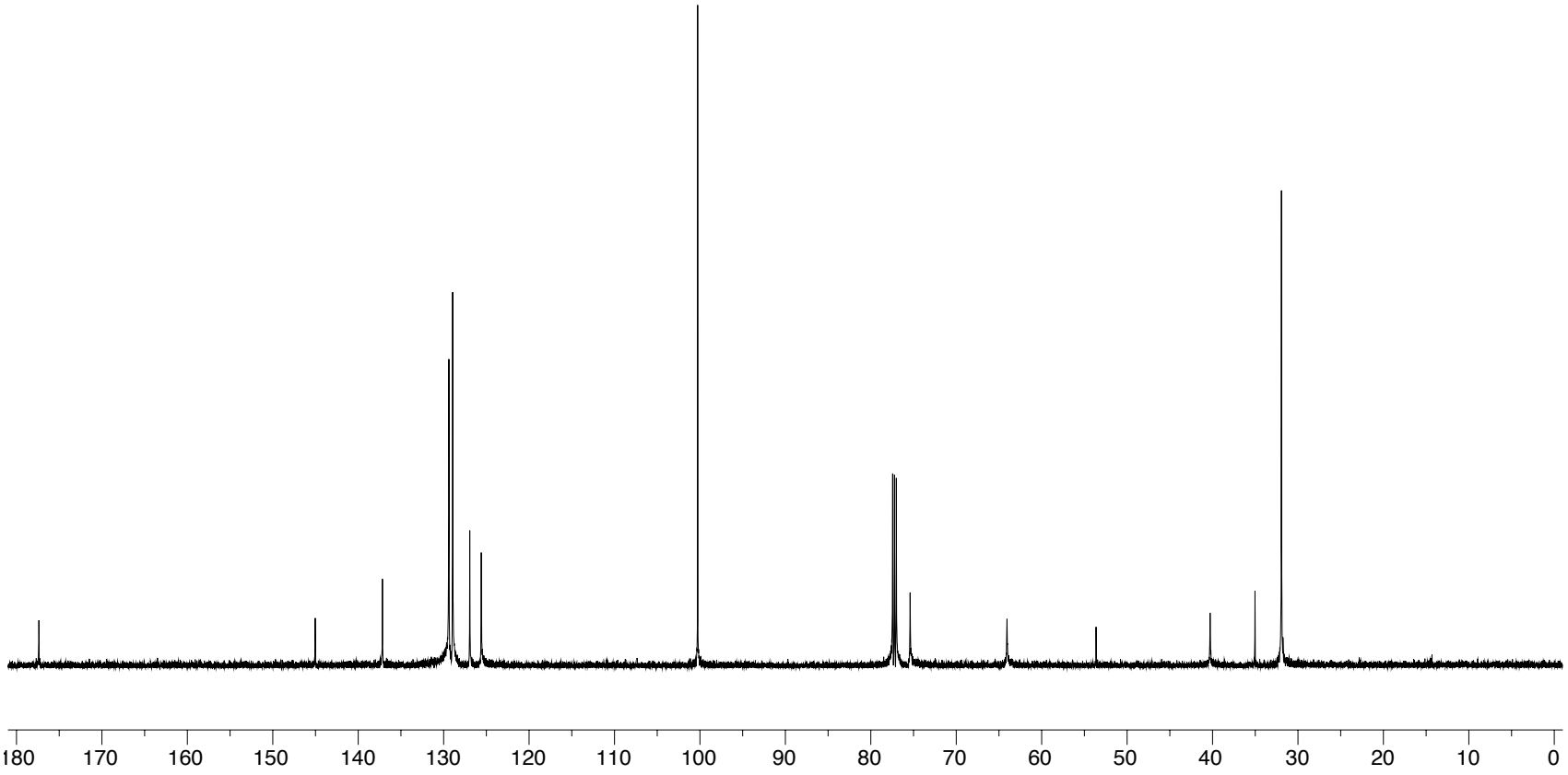

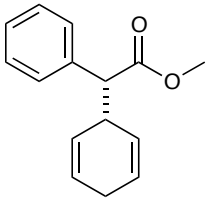

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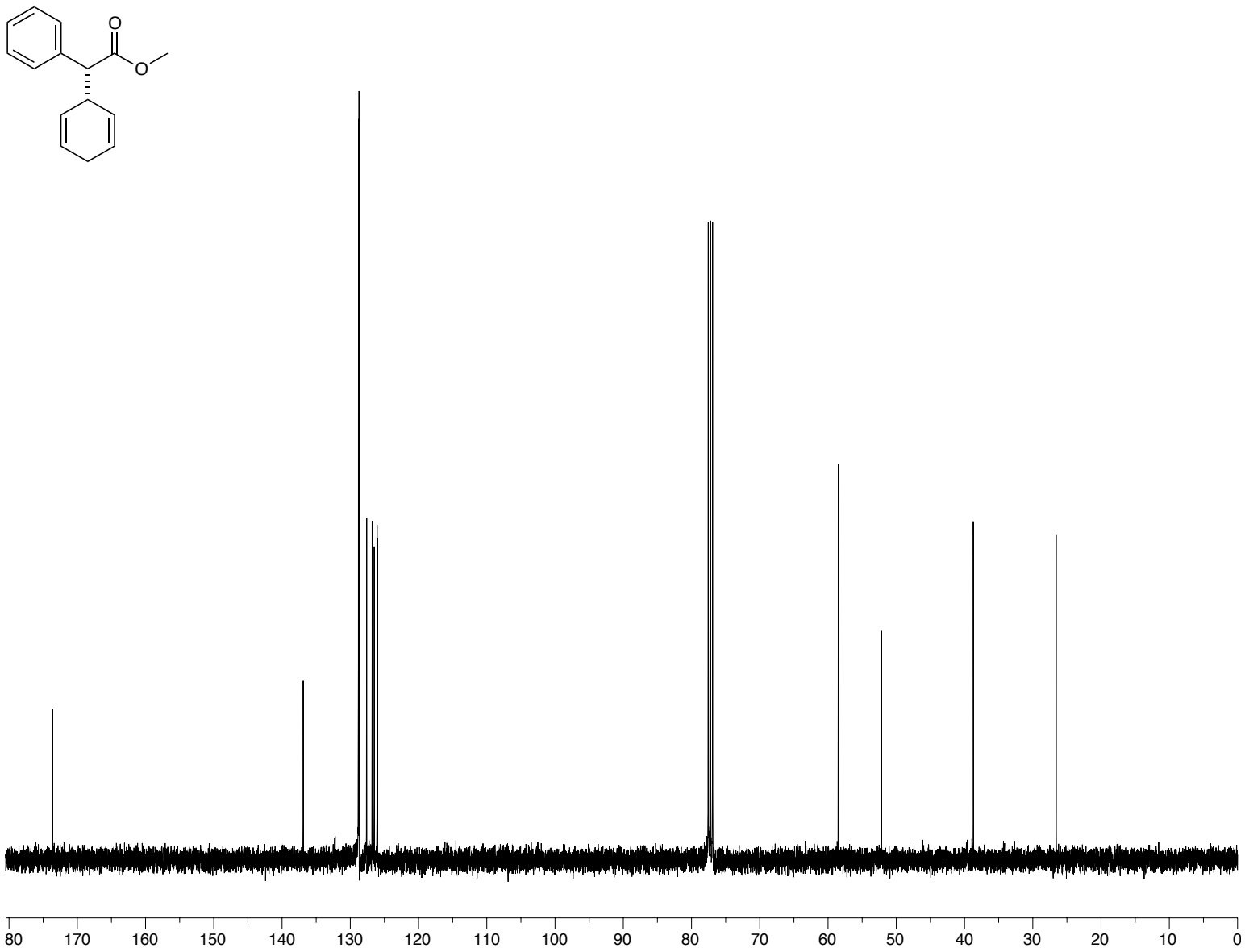

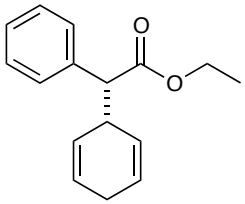

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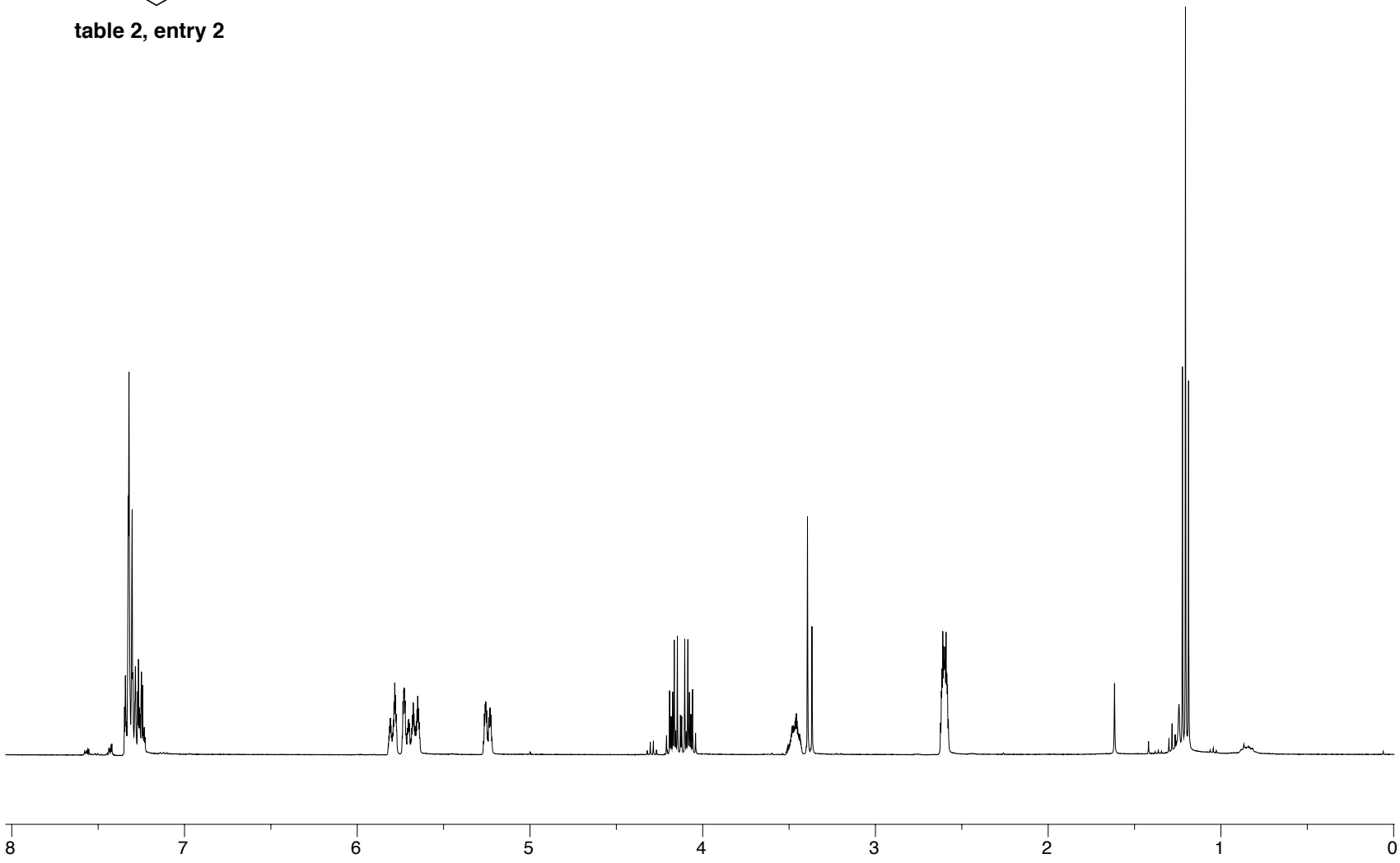

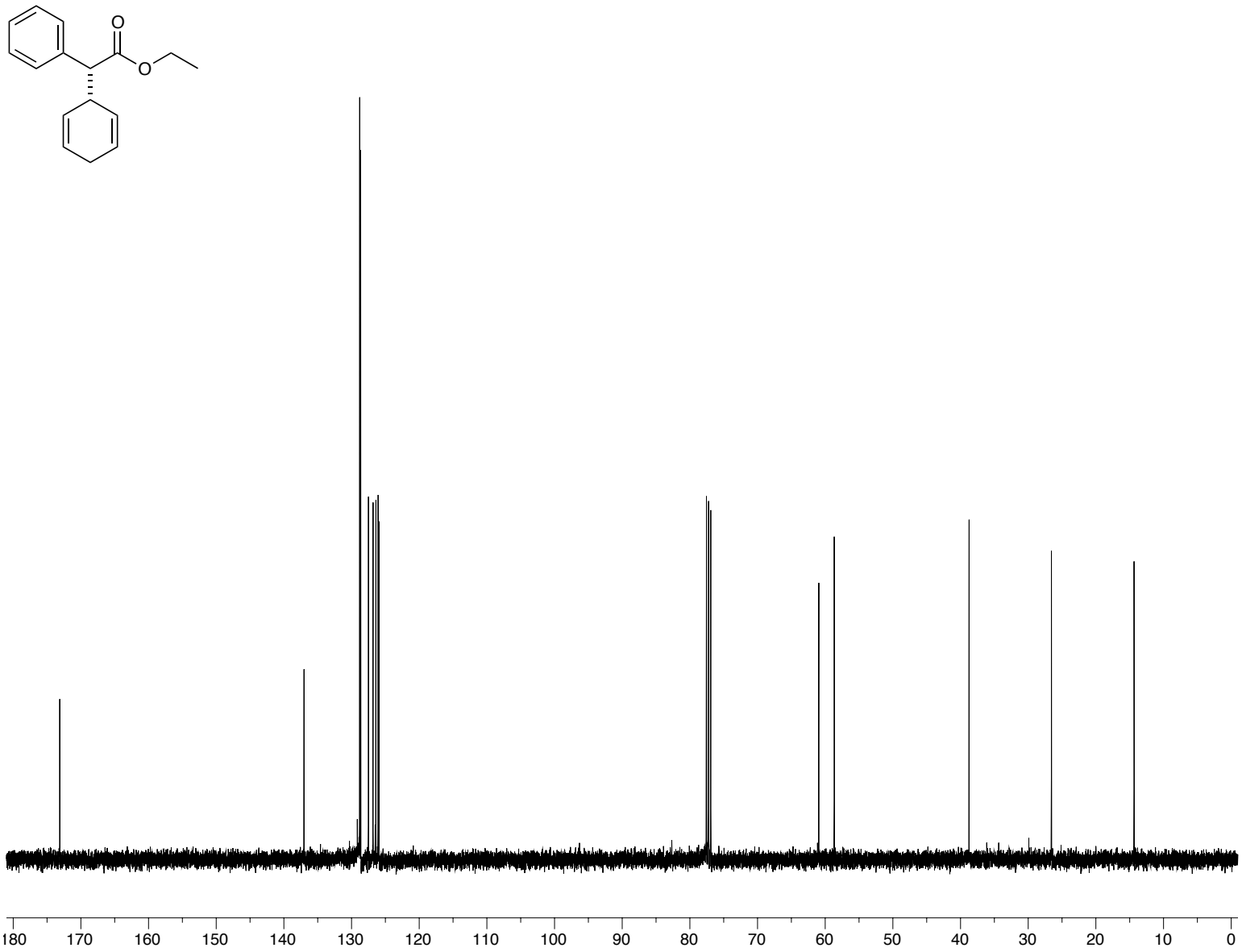

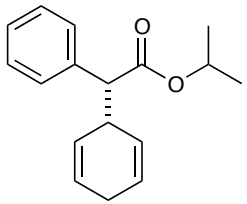

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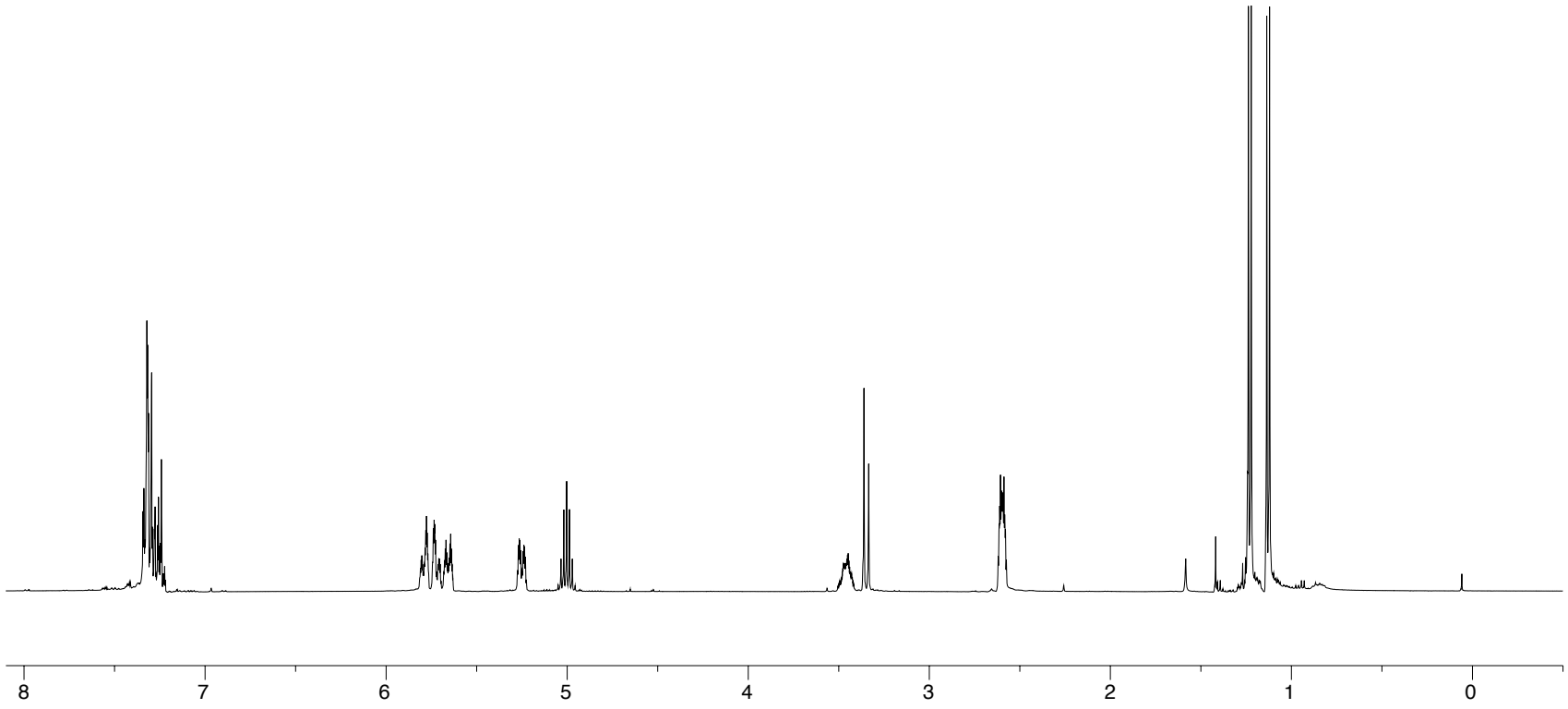

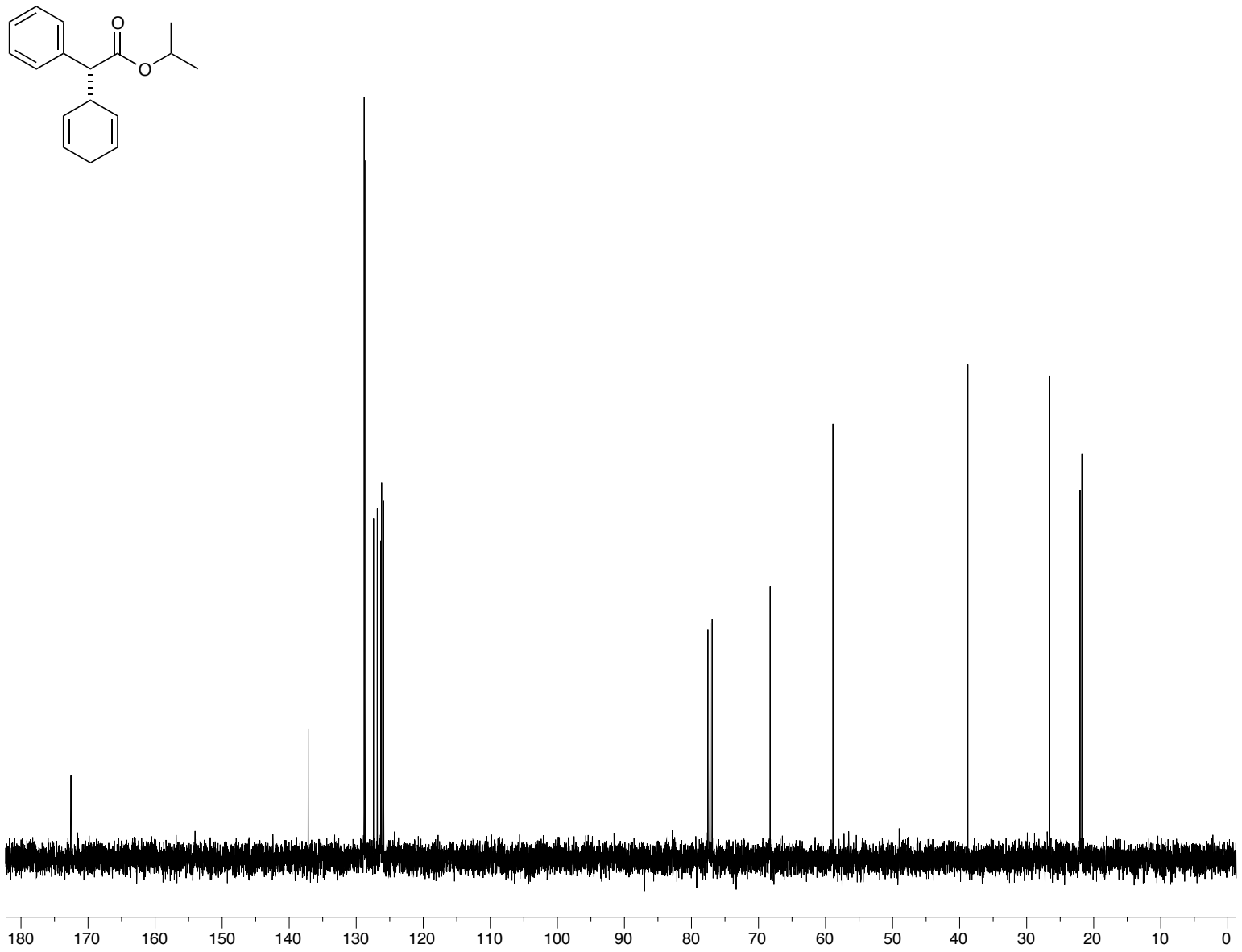

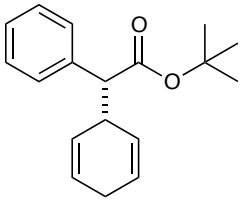

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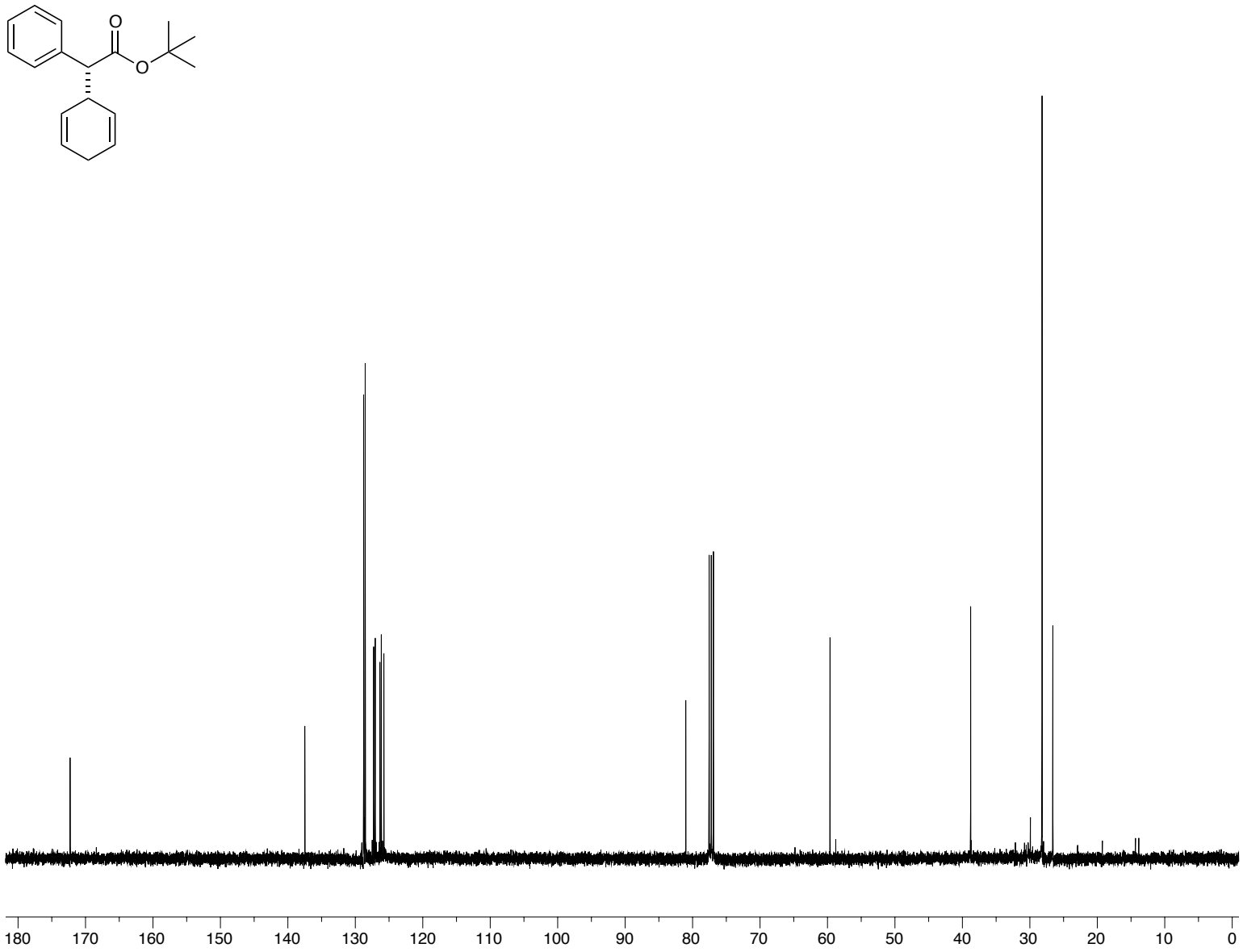

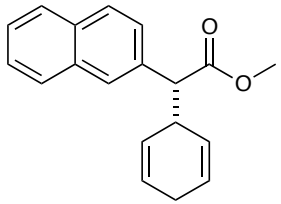

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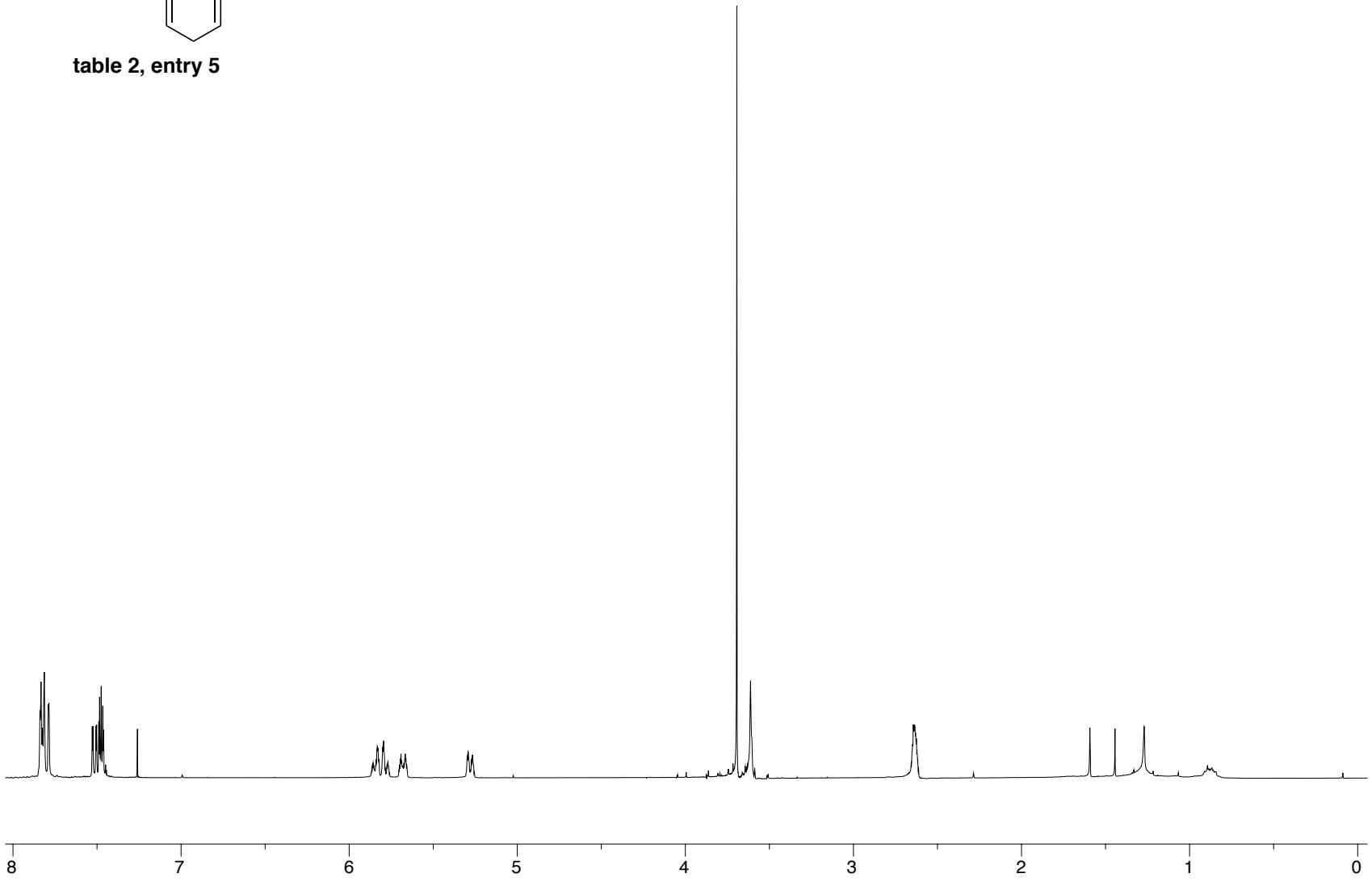

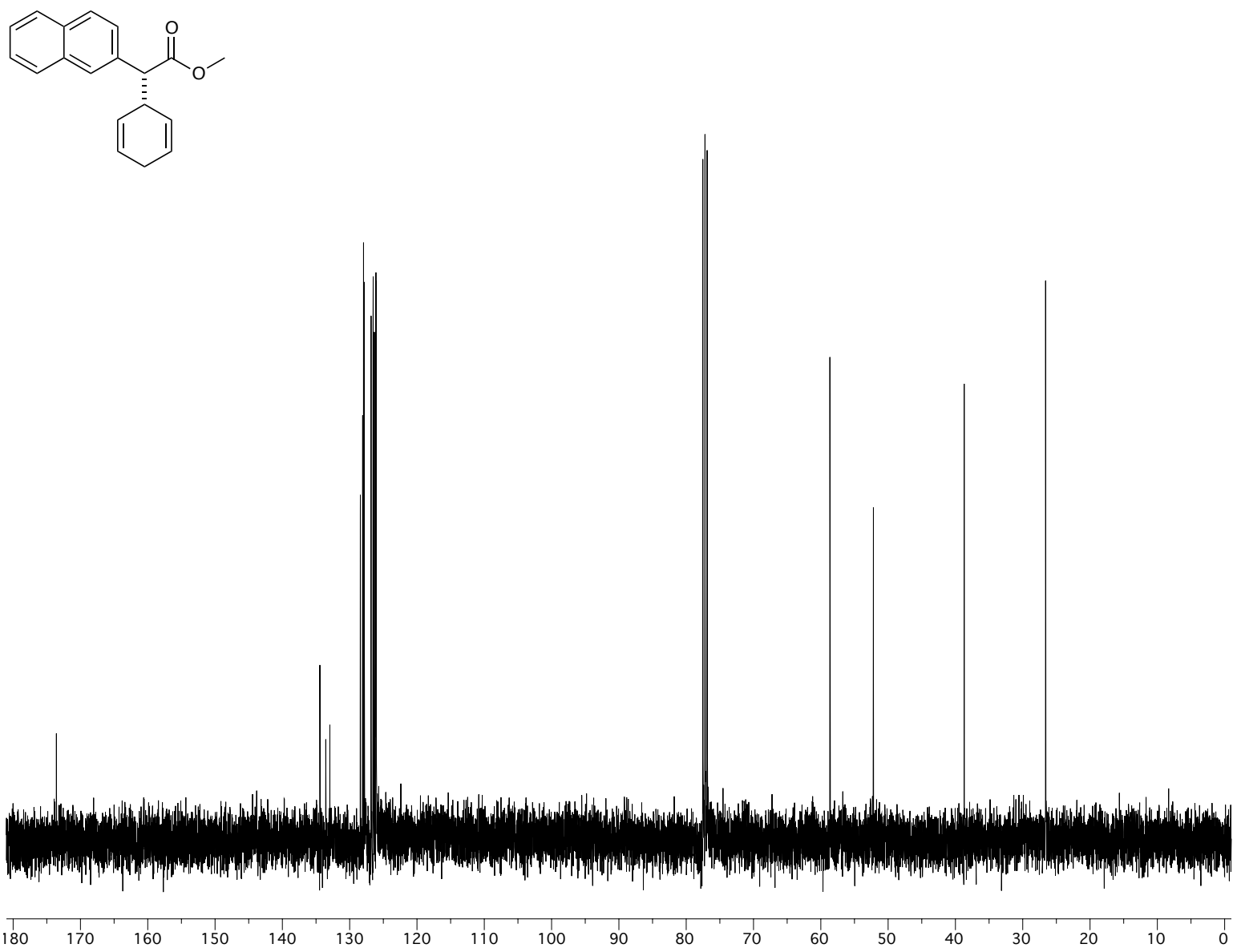

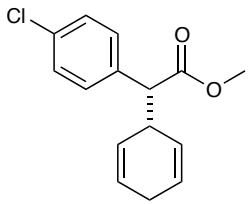

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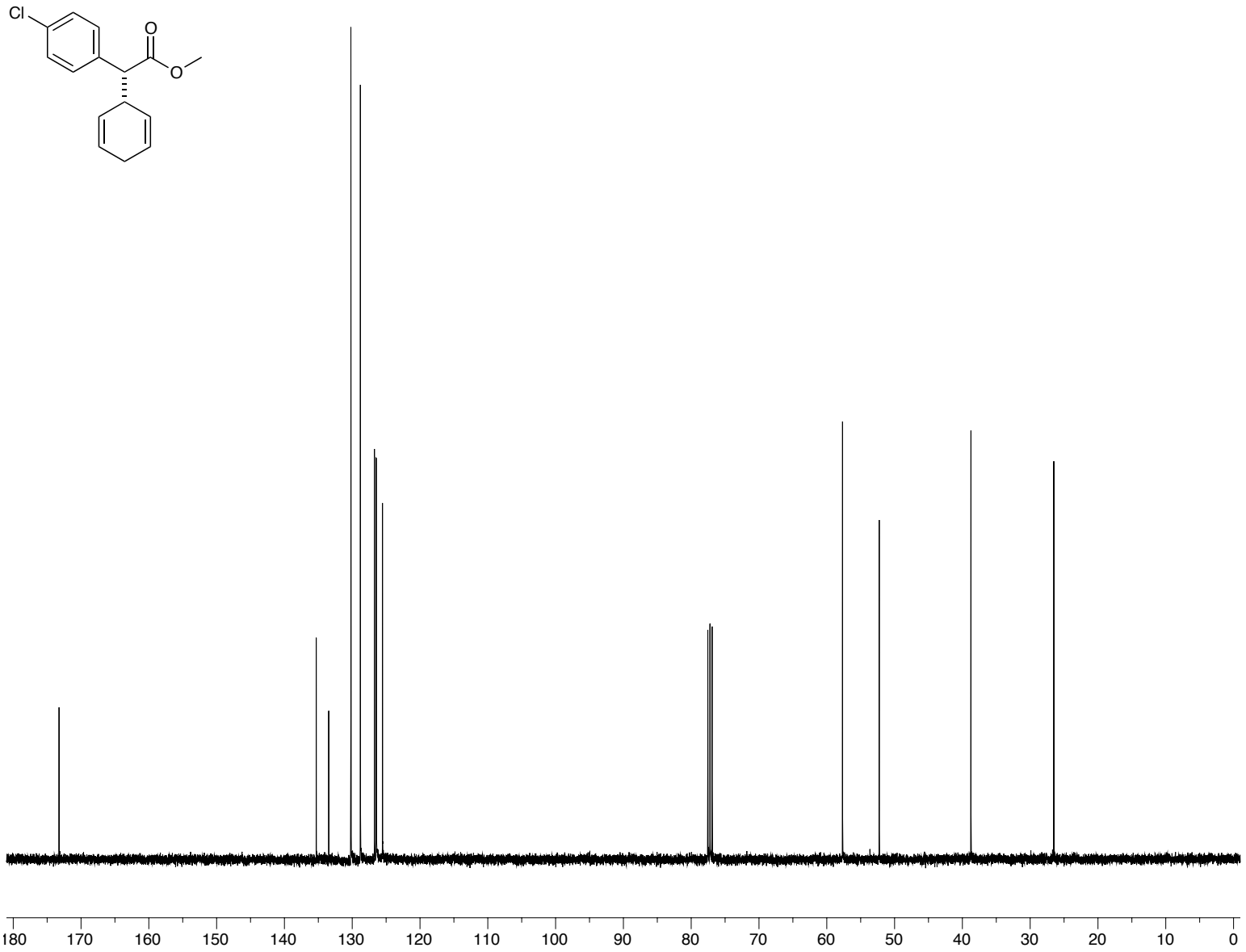

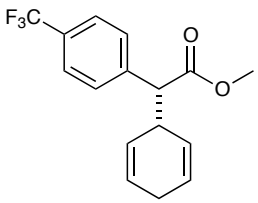

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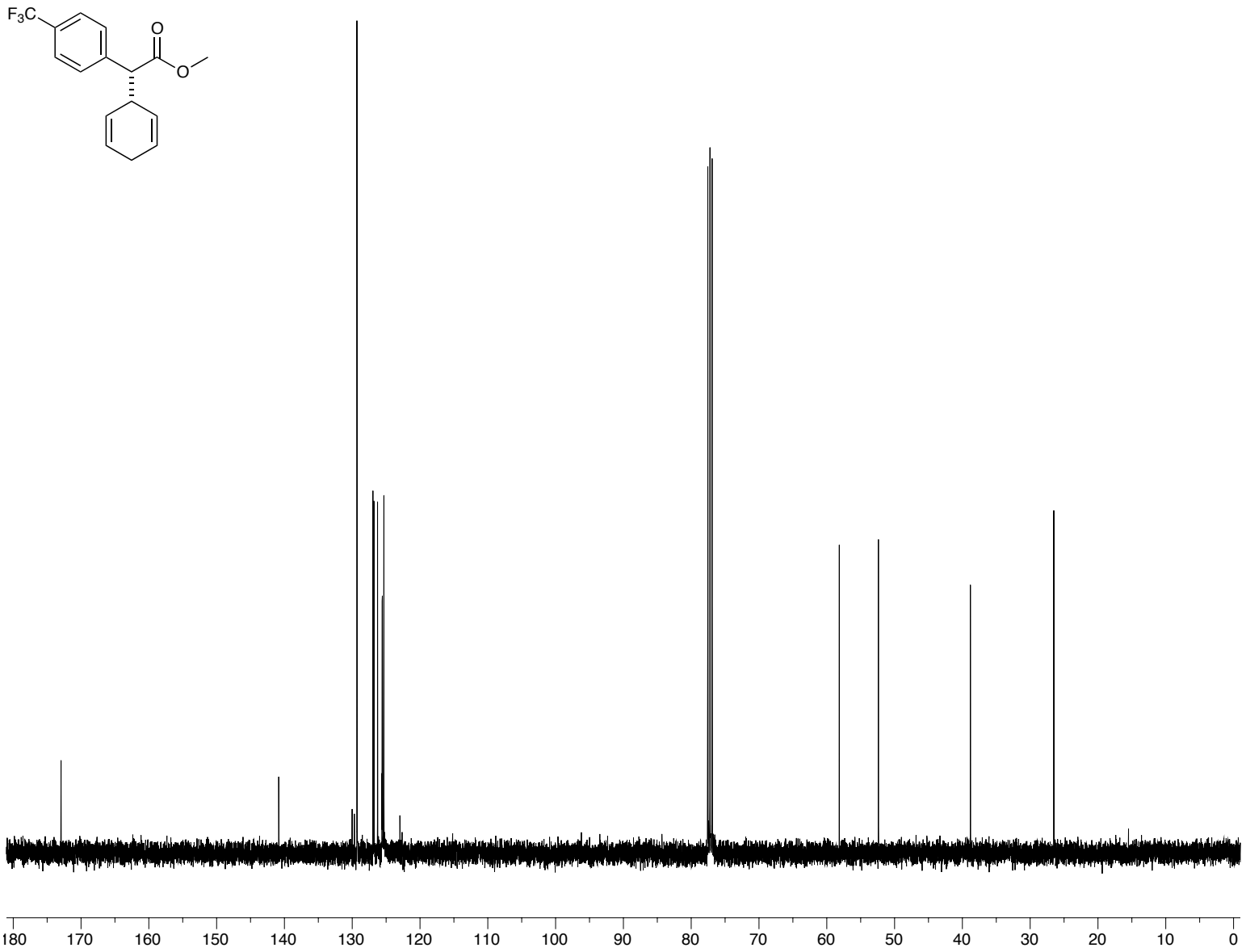

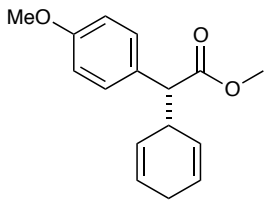

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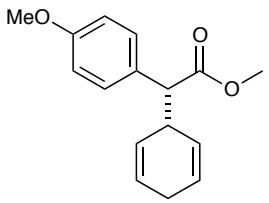

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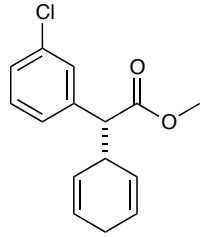

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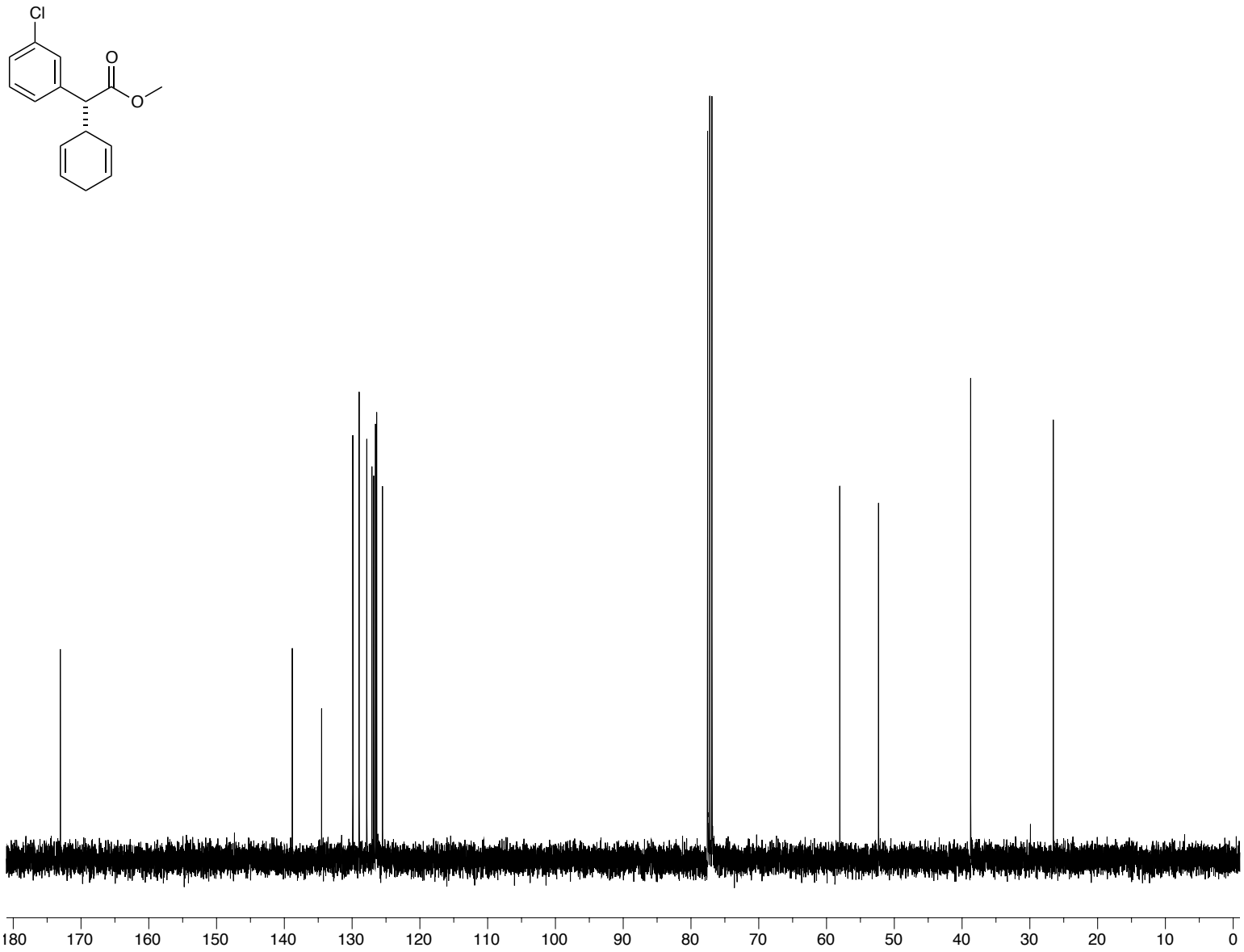

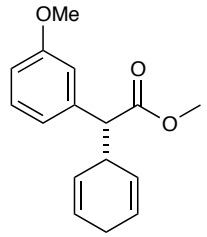

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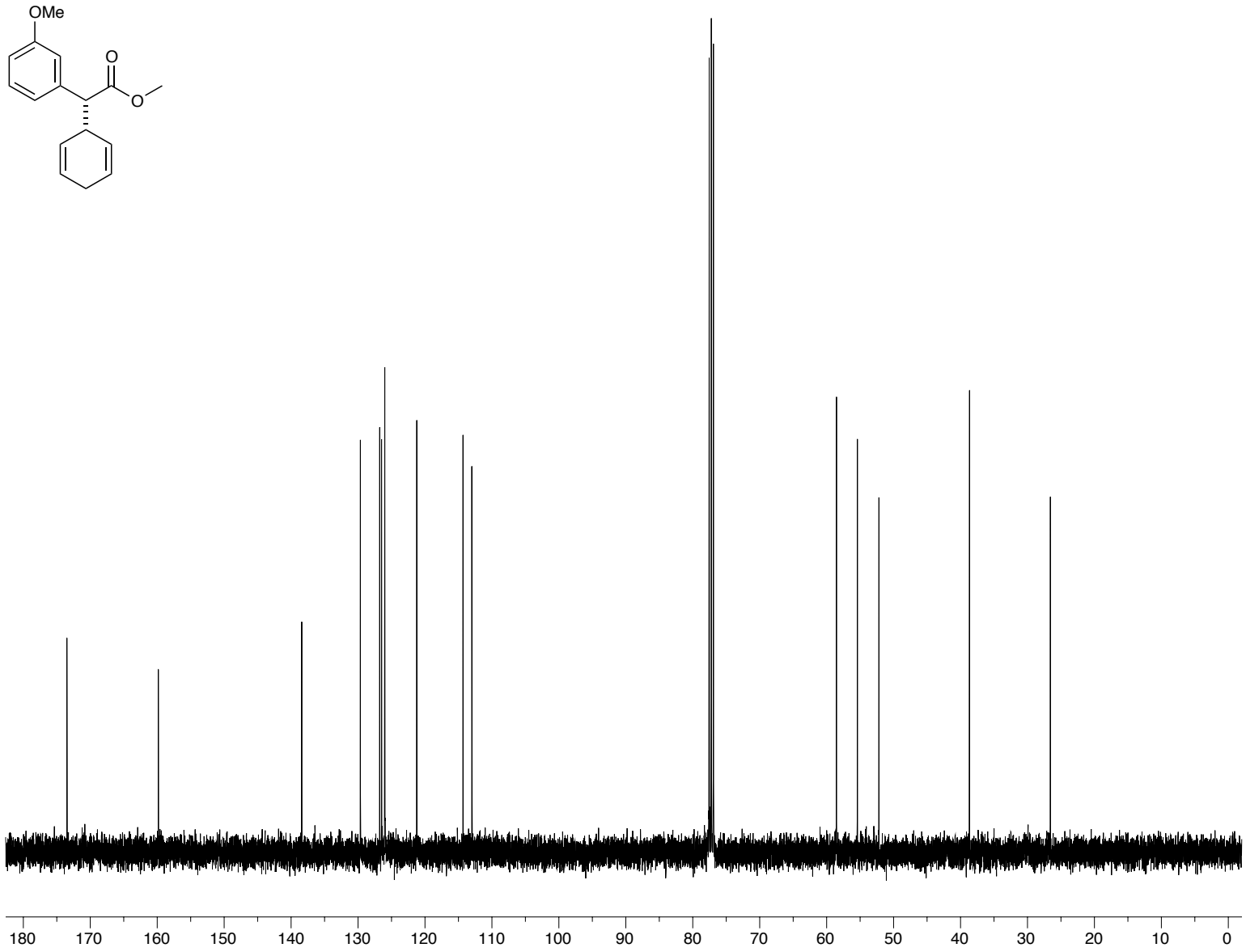

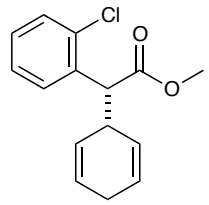

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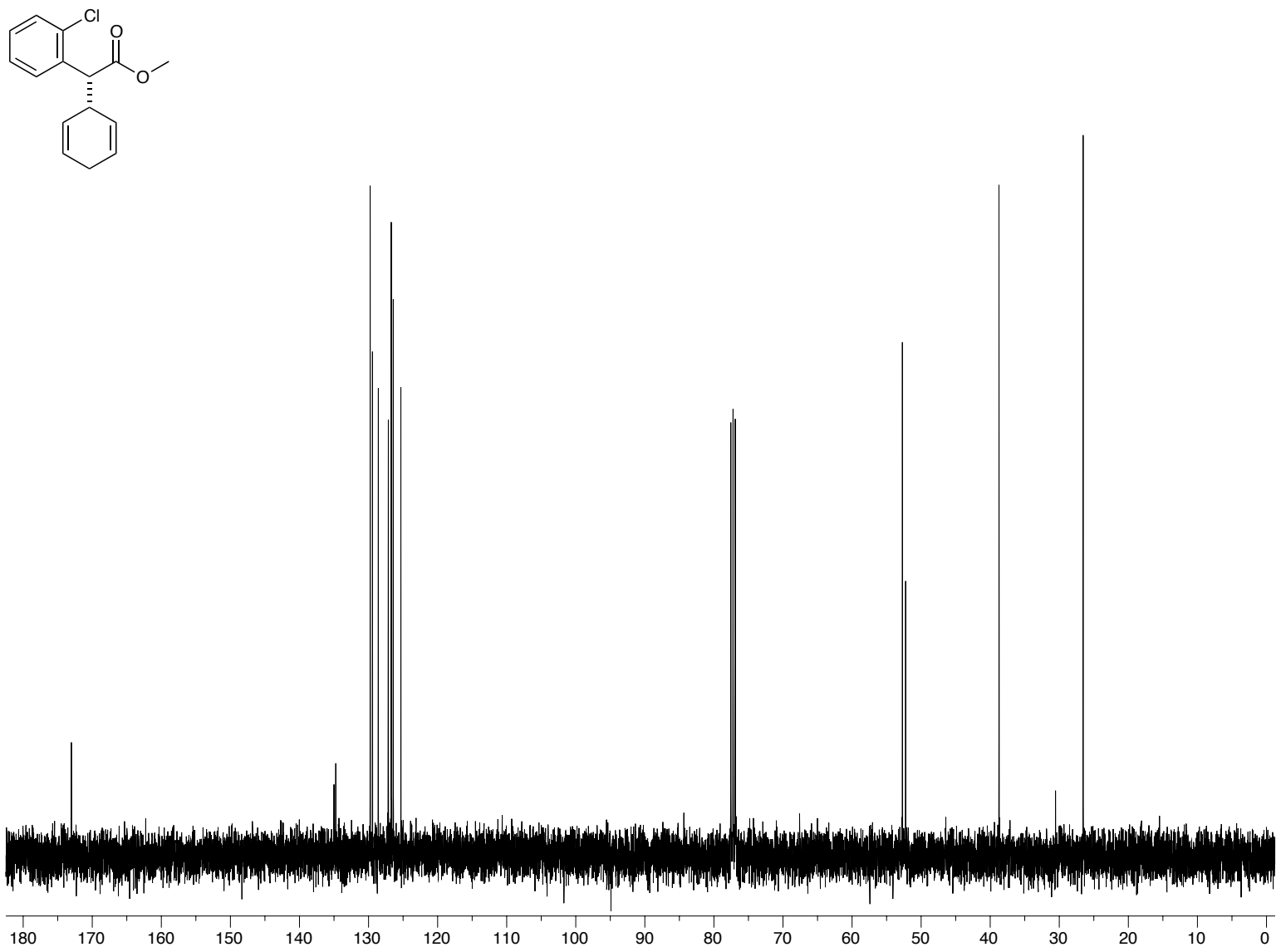

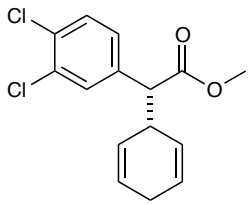

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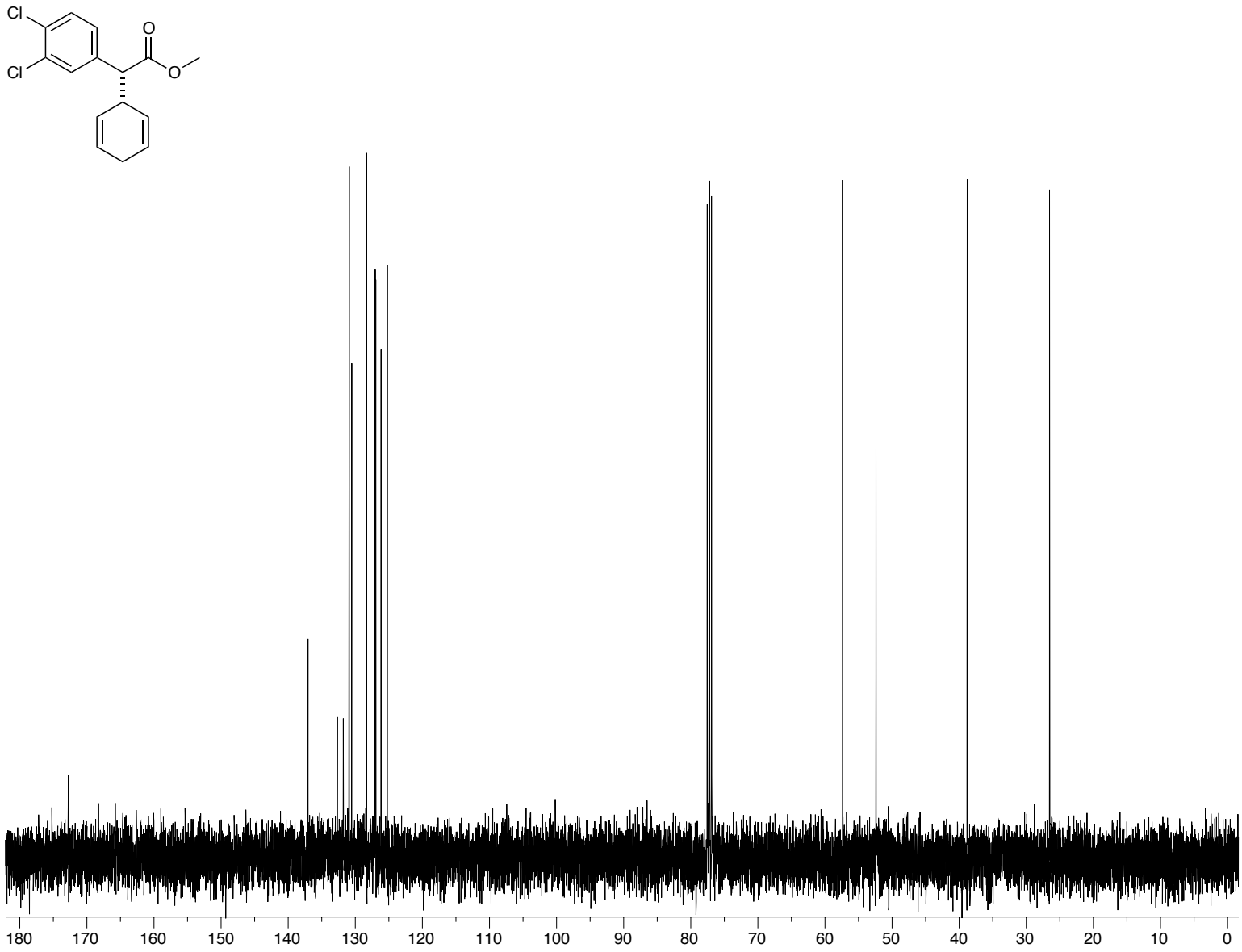

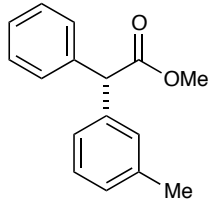

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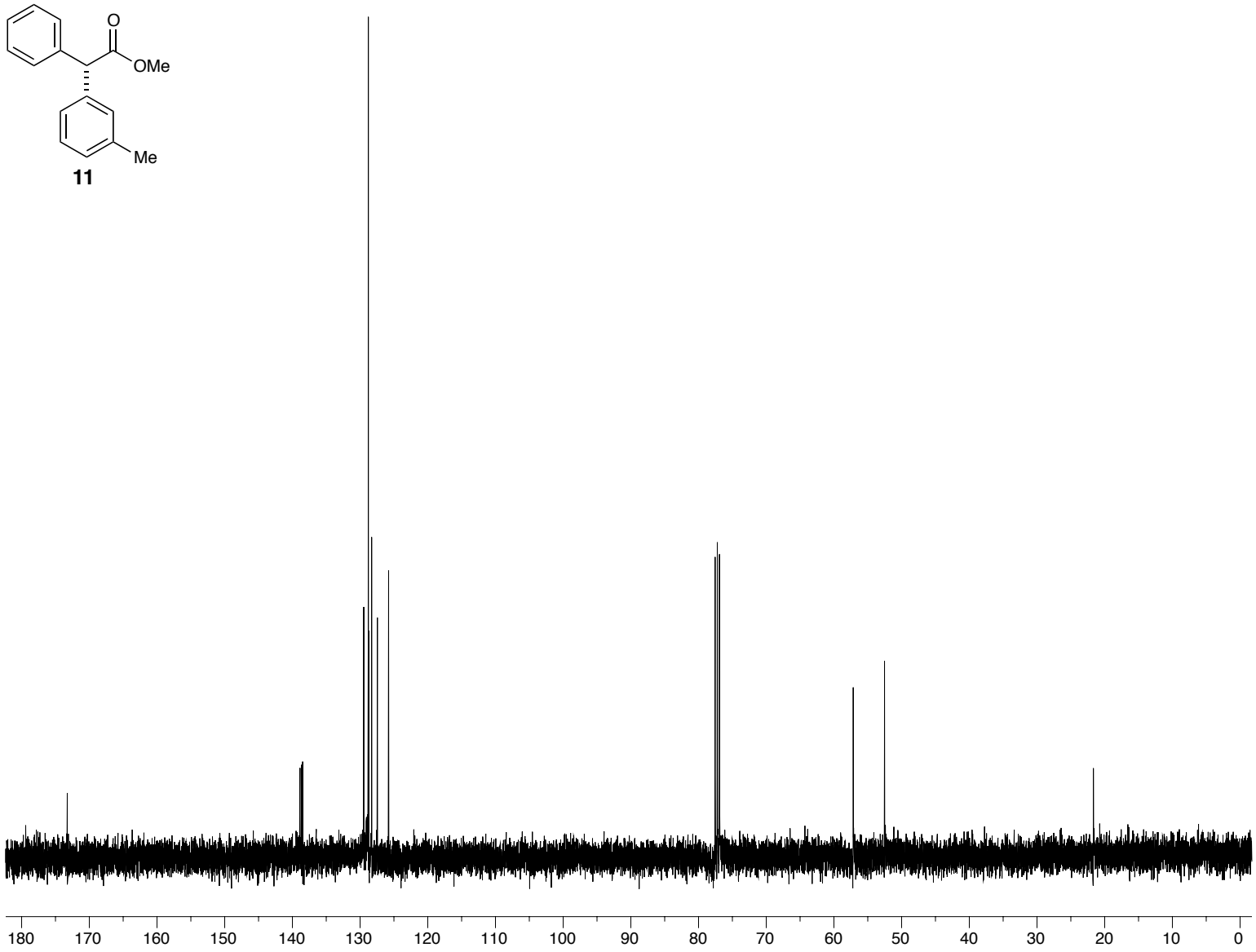

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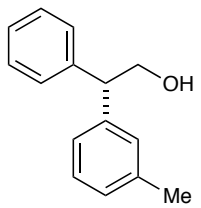

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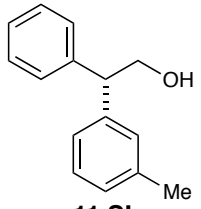

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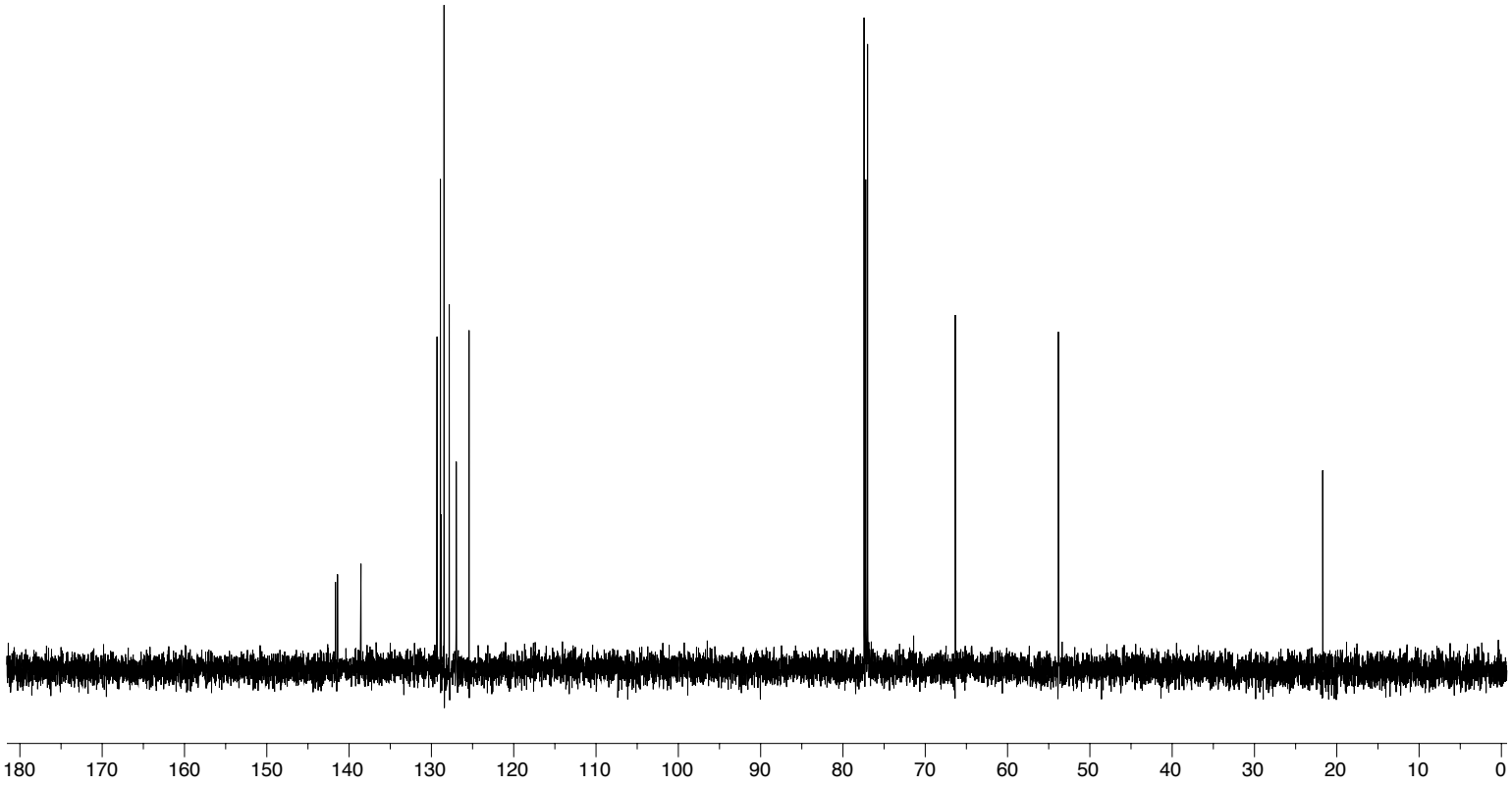

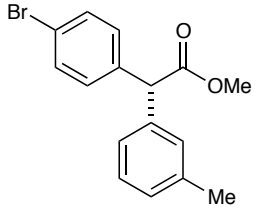

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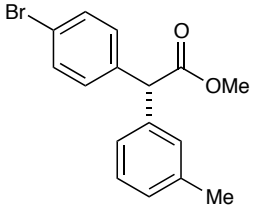

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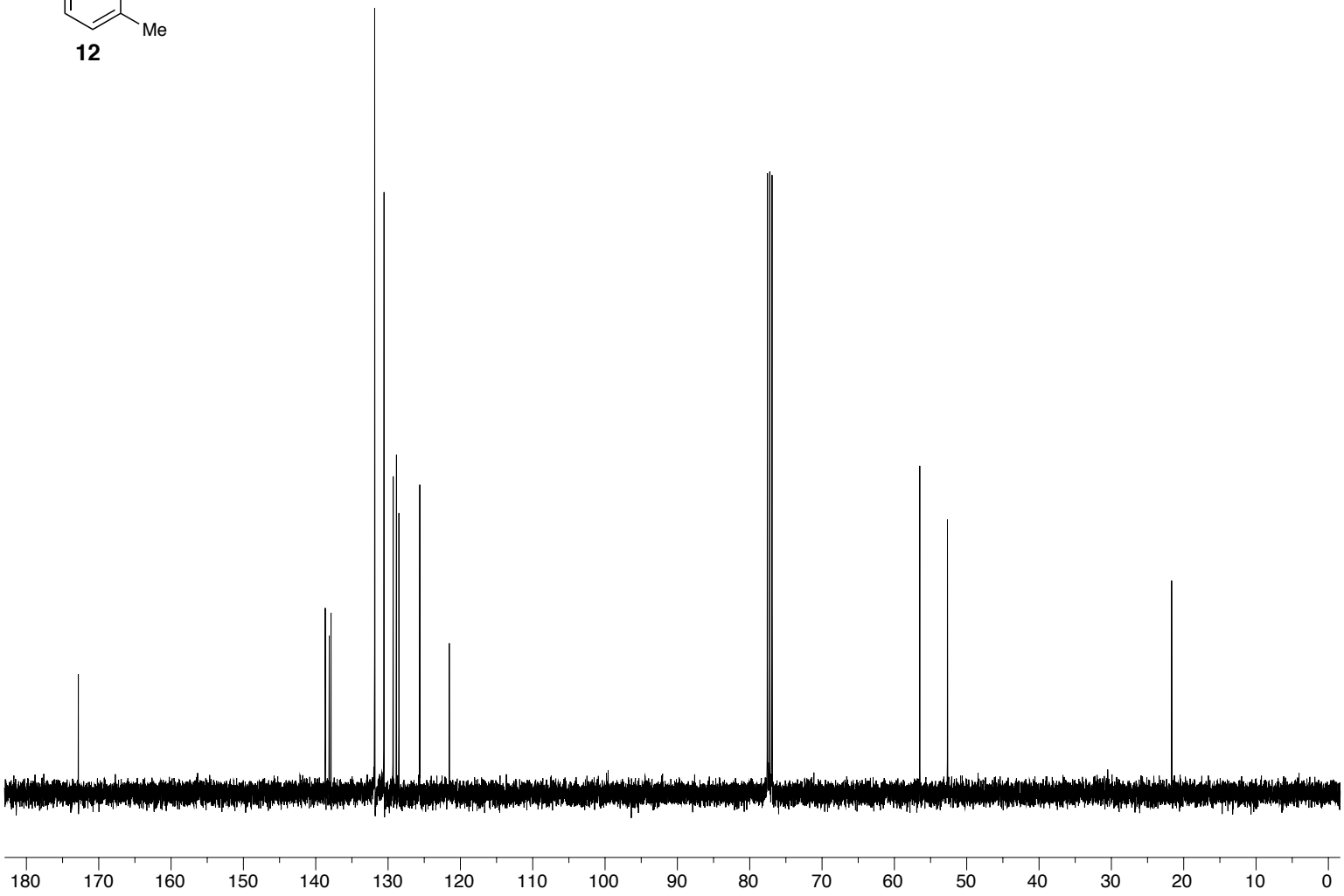

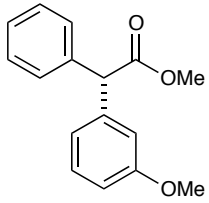

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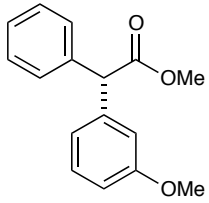

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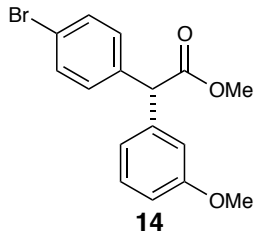

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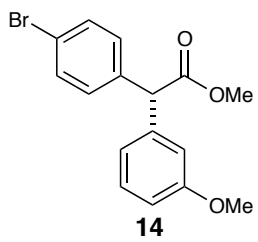

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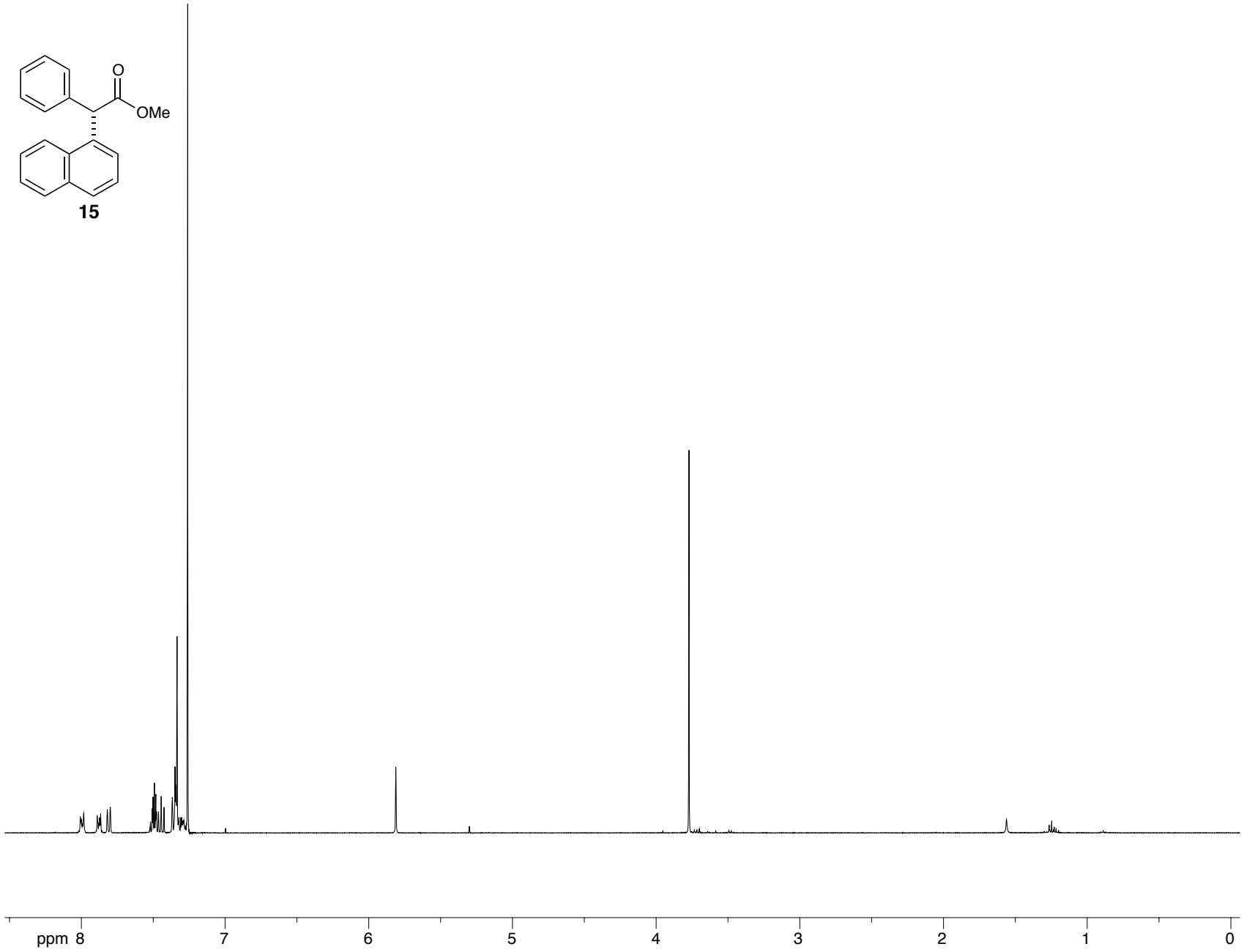

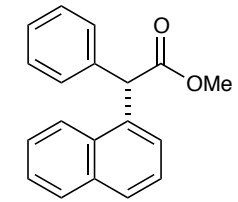

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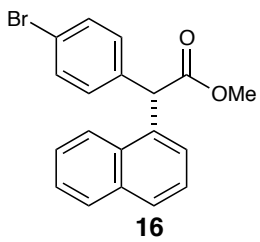

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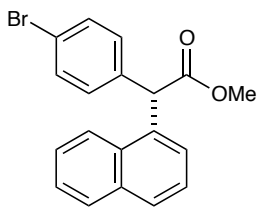

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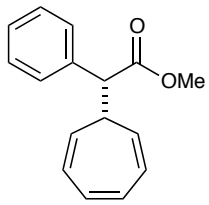

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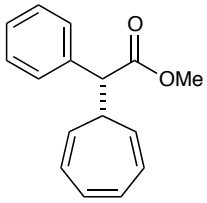

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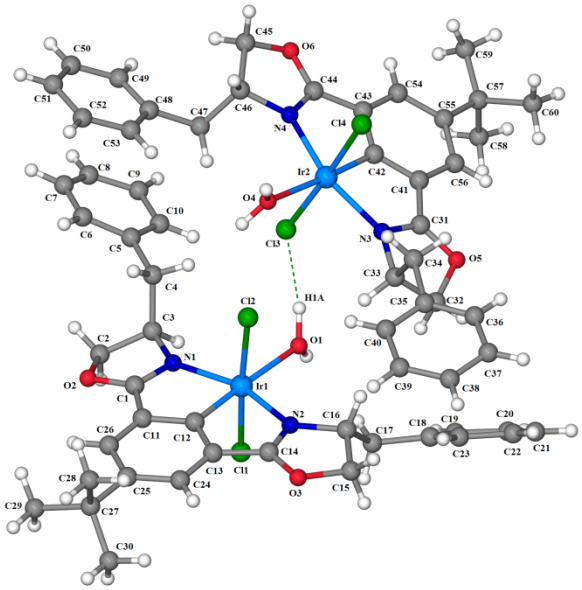
VI. X-ray Crystallographic Data

Crystal structure data for the absolute structure determination of [(*R*,*R*)-^{t}BuPheBox-Bn]IrCl$_2$(H$_2$O) **8** has been deposited in the Cambridge Crystallographic Data Centre (CCDC) and is available free of charge.

CCDC #904665

$C_{32}H_{37}Cl_6IrN_2O_3$ M = 902.54 orange prism 0.56 ´ 0.37 ´ 0.32 mm^3 orthorhombic, space group $P2_12_12_1$ a = 8.5561(12), b = 28.710(4), c = 29.726(4) Å V = 7302.1(17) Å^3 Z = 8 D_c = 1.642 g/cm^3 MoKa radiation, l = 0.71073 Å T = 173(2)K $2q_{max}$ = 59.3º 54198 reflections collected, 20318 unique Numerical absorption correction R_{int} = 0.0413 Final *GooF* = 1.050 *R1* = 0.0465 *wR2* = 0.1062 814 parameters, 75 restraints μ = 4.130 mm^{-1}	

General Information

There are two iridium molecules in the asymmetric unit. There are also two CH_2Cl_2 molecules that have been omitted for clarity. The absolute structure is correct, and the atoms C3, C16, C33 and C46 are the chiral centres and have the (*R*) configuration.

The crystals grew as large orange prisms. A suitable single crystal was selected from the sample and mounted onto a nylon fibre with paratone oil and placed under a cold stream at 173K. Single crystal X-ray data were collected on a Bruker APEX2 diffractometer with 1.6 kW graphite monochromated Mo radiation. The detector to crystal distance was 5.1 cm. Exposure times of 10s per frame and scan widths of 0.5º were used throughout the data collection. The data collection was performed using a combination of 2 sets of ω scans with different φ values yielding data in the θ range 1.97 to 29.63° and with an average completeness of 99.7%. The frames were integrated with the

SAINT v7.68a (Bruker, 2009).[1] A numerical absorption correction was carried out using the program SADABS V2008-1 (Bruker, 2008)[2]. The structure was solved and refined with Olex2[3] and SHELX (Sheldrick, 2008).[4] In the final cycles of refinement all non-hydrogen atoms, except the disordered atoms were refined anisotropically. The structure contains disordered phenyl rings, t-butyl groups and dichloromethane solvent molecules of crystallisation. The disorder for each disordered group was treated the same way: modeled using two components with similarity restraints and restraints/constraints on thermal parameters for individual split atoms. The populations of individual components were refined or fixed at 50%.

For clarity, Figure 1 shows the plot of only one of the two molecules in the asymmetric unit

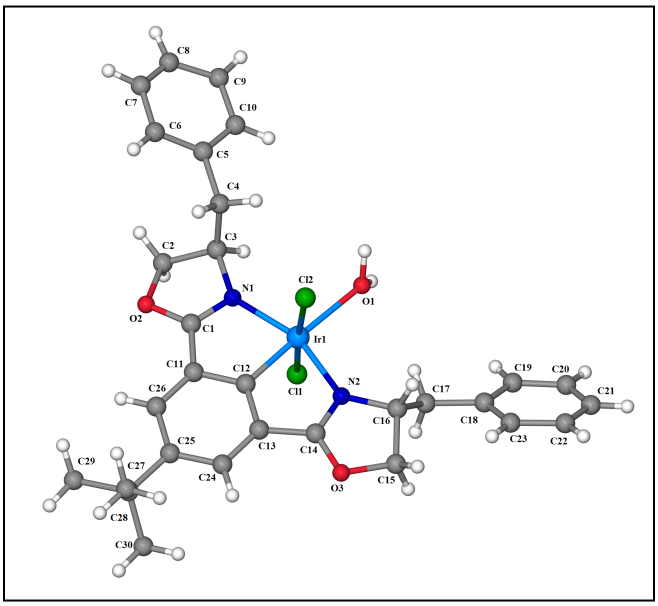


Figure 1

References

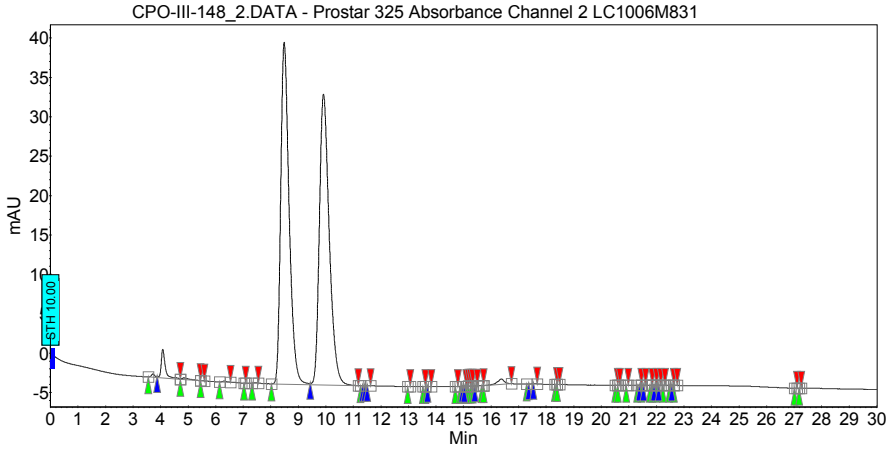
(1) Bruker (2009). SAINT V7.68a, BRUKER AXS Inc., Madison, WI, USA.
(2) Bruker (2008), SADABS V2008-1, BRUKER AXS Inc., Madison, WI, USA.
(3) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann (2009). OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst. 42*, 339-341. *Supramol. Chem.* **2001**, *1,* 189-191
(4) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

VII. HPLC Traces

Chromatogram : CPO-III-148_2_channel2

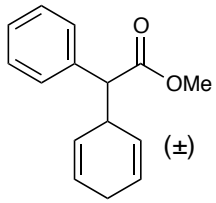
System : Prostar LC System
Method : OJ_30min_1mL_0.5%-230nm
User : User1

Acquired : 8/3/2011 4:47:33 PM
Processed : 8/3/2011 5:18:13 PM
Printed : 8/4/2011 9:01:14 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.72	0.20	0.4	0.1	0.202
2	UNKNOWN	4.08	2.00	3.6	0.6	2.003
3	UNKNOWN	4.85	0.20	0.2	0.1	0.205
4	UNKNOWN	5.56	0.00	0.0	0.0	0.002
5	UNKNOWN	6.29	0.07	0.1	0.0	0.070
6	UNKNOWN	7.06	0.00	0.0	0.0	0.001
7	UNKNOWN	7.45	0.01	0.0	0.0	0.014
8	UNKNOWN	8.49	48.48	43.4	15.3	48.477
9	UNKNOWN	9.91	48.30	36.9	15.3	48.298
10	UNKNOWN	11.30	0.00	0.0	0.0	0.002
11	UNKNOWN	11.37	0.00	0.0	0.0	0.003
12	UNKNOWN	11.45	0.01	0.0	0.0	0.005
13	UNKNOWN	11.53	0.00	0.0	0.0	0.003
14	UNKNOWN	13.02	0.00	0.0	0.0	0.001
15	UNKNOWN	13.57	0.00	0.0	0.0	0.001
16	UNKNOWN	13.65	0.00	0.0	0.0	0.002
17	UNKNOWN	13.73	0.00	0.0	0.0	0.003
18	UNKNOWN	14.74	0.00	0.0	0.0	0.001
19	UNKNOWN	14.91	0.00	0.0	0.0	0.002
20	UNKNOWN	14.98	0.00	0.0	0.0	0.002
21	UNKNOWN	15.06	0.00	0.0	0.0	0.002
22	UNKNOWN	15.14	0.00	0.0	0.0	0.001
23	UNKNOWN	15.21	0.00	0.0	0.0	0.001
24	UNKNOWN	15.29	0.00	0.0	0.0	0.001
25	UNKNOWN	15.38	0.00	0.0	0.0	0.001
26	UNKNOWN	15.45	0.00	0.0	0.0	0.002



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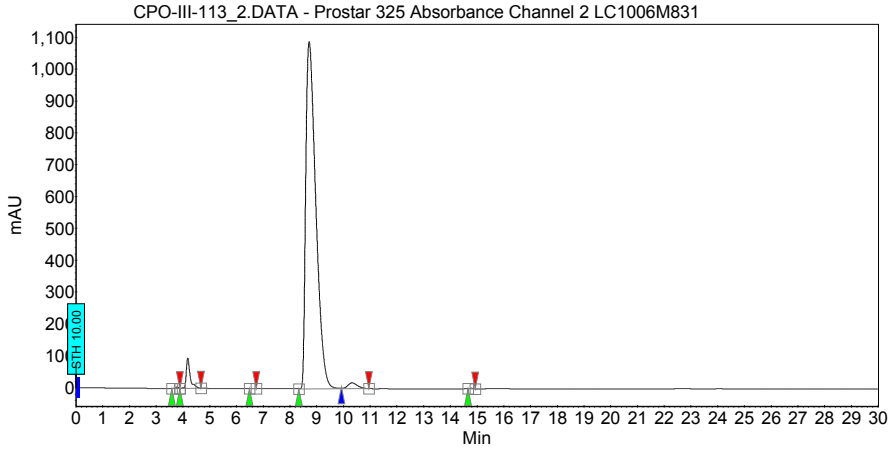
PAGECOUNT

Chromatogram : CPO-III-113_2_channel2

System : Prostar LC System
Method : OJ_30min_1mL_0.5%-230nm
User : User1

Acquired : 6/21/2011 5:46:42 PM
Processed : 6/21/2011 6:17:20 PM
Printed : 6/22/2011 8:38:56 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.79	0.11	5.4	0.6	0.111
2	UNKNOWN	4.18	3.19	95.5	15.9	3.188
3	UNKNOWN	6.60	0.02	0.6	0.1	0.019
4	UNKNOWN	8.72	95.10	1089.8	475.2	95.097
5	UNKNOWN	10.32	1.55	18.4	7.7	1.549
6	UNKNOWN	14.79	0.04	1.4	0.2	0.035
Total			100.00	1211.2	499.7	100.000

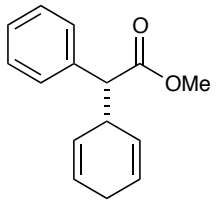


table 2, entry 1

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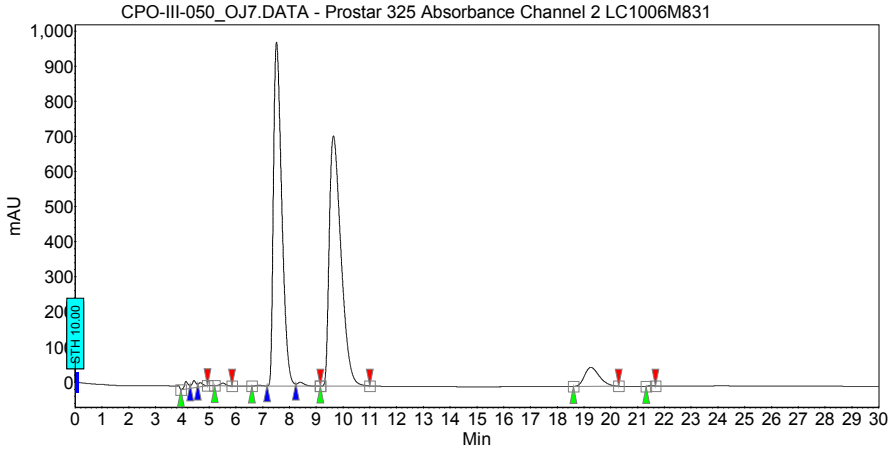
PAGECOUNT

Chromatogram : CPO-III-050_OJ7_channel2

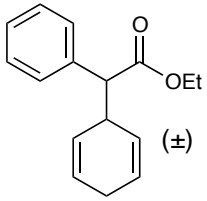
System : Prostar LC System
Method : OJ_30min_1mL_0.5%-230nm
User : User1

Acquired : 4/21/2011 3:18:01 PM
Processed : 4/21/2011 3:48:20 PM
Printed : 4/21/2011 4:49:02 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.13	0.49	21.9	3.7	0.486
2	UNKNOWN	4.43	0.49	20.7	3.7	0.487
3	UNKNOWN	4.66	0.30	11.8	2.3	0.296
4	UNKNOWN	5.52	0.25	8.3	1.9	0.251
5	UNKNOWN	6.85	0.10	2.5	0.7	0.097
6	UNKNOWN	7.52	45.99	979.7	351.9	45.992
7	UNKNOWN	8.41	0.46	11.3	3.5	0.460
8	UNKNOWN	9.64	47.36	713.1	362.4	47.359
9	UNKNOWN	19.25	4.53	54.1	34.7	4.533
10	UNKNOWN	21.48	0.04	2.0	0.3	0.038
Total			100.00	1825.1	765.2	100.000



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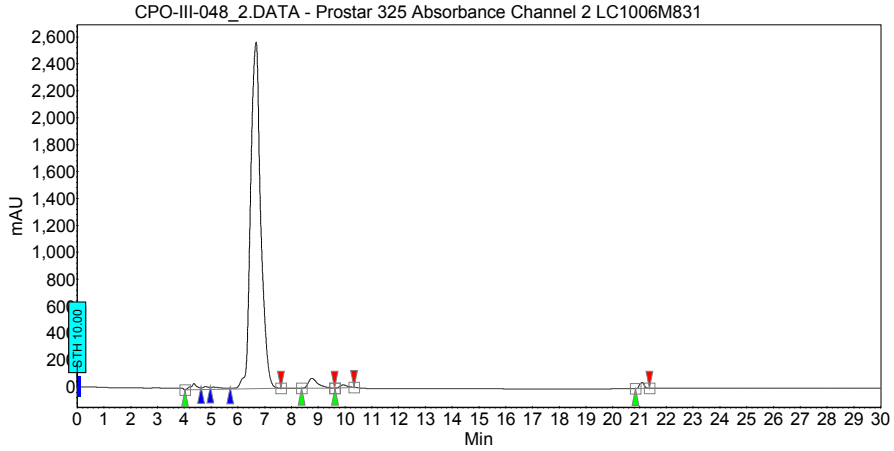
PAGECOUNT

Chromatogram : CPO-III-048_2_channel2

System : Prostar LC System
Method : OD_30min_1mL_0.5%_230nm
User : User1

Acquired : 4/21/2011 1:37:43 PM
Processed : 4/21/2011 2:08:01 PM
Printed : 4/21/2011 2:36:07 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.36	1.06	45.9	12.7	1.059
2	UNKNOWN	4.78	0.49	21.2	5.9	0.493
3	UNKNOWN	5.09	0.68	16.7	8.1	0.679
4	UNKNOWN	6.68	93.90	2574.6	1123.9	93.904
5	UNKNOWN	8.77	2.58	73.6	30.9	2.583
6	UNKNOWN	9.93	0.57	21.8	6.8	0.565
7	UNKNOWN	21.10	0.72	43.7	8.6	0.716
Total			100.00	2797.4	1196.8	100.000

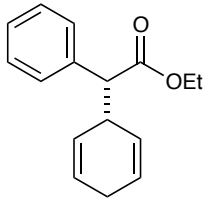


table 2, entry 2

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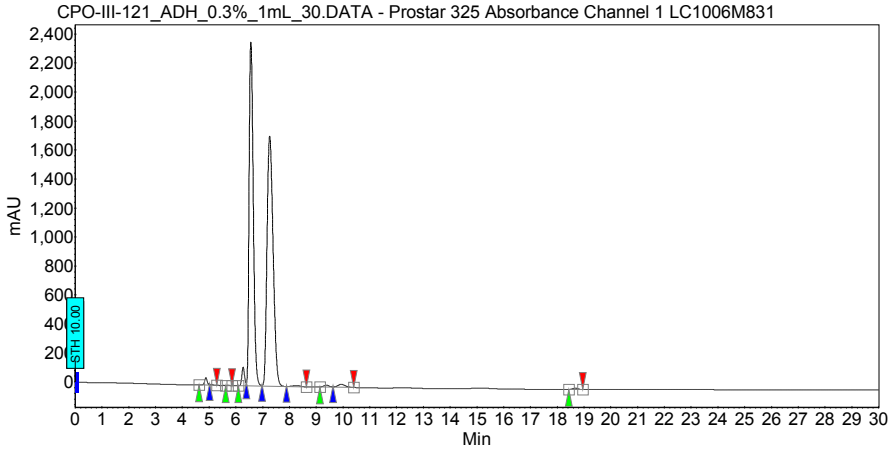
PAGECOUNT

Chromatogram : CPO-III-121_ADH_0.3%_1mL_30_channel1

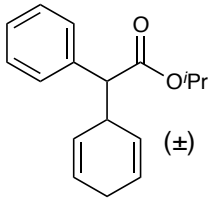
System : Prostar LC System
Method : ADH_30min_1mL_0.3%-230nm
User : User1

Acquired : 6/24/2011 2:29:17 AM
Processed : 6/24/2011 2:59:56 AM
Printed : 6/24/2011 9:24:35 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.88	0.64	51.5	5.9	0.640
2	UNKNOWN	5.09	0.06	4.9	0.6	0.064
3	UNKNOWN	5.72	0.03	2.2	0.2	0.025
4	UNKNOWN	6.27	1.65	129.6	15.2	1.655
5	UNKNOWN	6.56	46.67	2371.0	428.9	46.670
6	UNKNOWN	7.26	49.40	1726.9	454.1	49.405
7	UNKNOWN	8.27	0.30	7.8	2.8	0.302
8	UNKNOWN	9.38	0.32	13.0	2.9	0.319
9	UNKNOWN	9.94	0.72	20.1	6.6	0.717
10	UNKNOWN	18.68	0.20	8.8	1.9	0.203
Total			100.00	4335.9	919.1	100.000



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PAGECOUNT

Chromatogram : CPO-III-125_c_2_channel2

System : Prostar LC System
Method : ADH_30min_1mL_0.3%-230nm
User : User1

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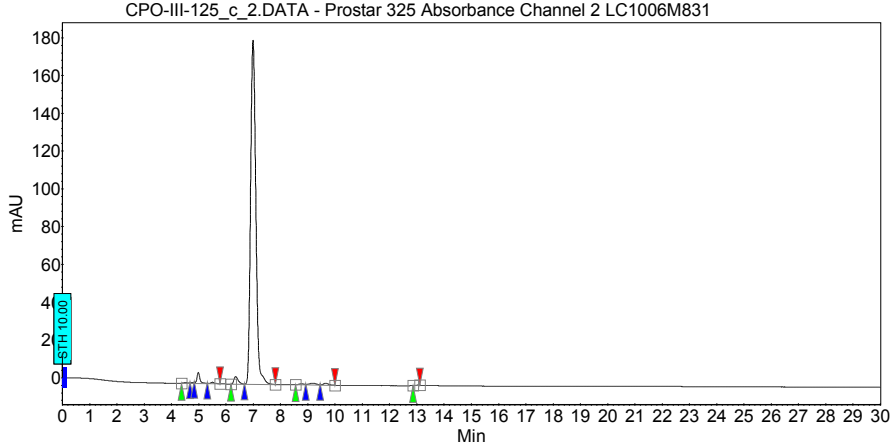
Processed : 6/29/2011 12:22:33 PM
Printed : 6/29/2011 4:00:36 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.51	0.13	0.4	0.1	0.128
2	UNKNOWN	4.79	0.13	0.5	0.1	0.130
3	UNKNOWN	4.98	1.72	5.8	0.7	1.719
4	UNKNOWN	5.50	0.27	0.8	0.1	0.271
5	UNKNOWN	6.35	1.71	4.1	0.7	1.709
6	UNKNOWN	6.99	94.56	182.3	40.6	94.560
7	UNKNOWN	8.78	0.27	0.5	0.1	0.268
8	UNKNOWN	9.18	0.66	0.9	0.3	0.664
9	UNKNOWN	9.66	0.53	1.0	0.2	0.532
10	UNKNOWN	13.02	0.02	0.1	0.0	0.017
Total			100.00	196.3	43.0	100.000

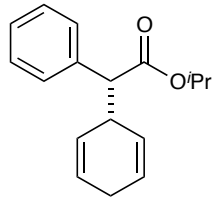


table 2, entry 3

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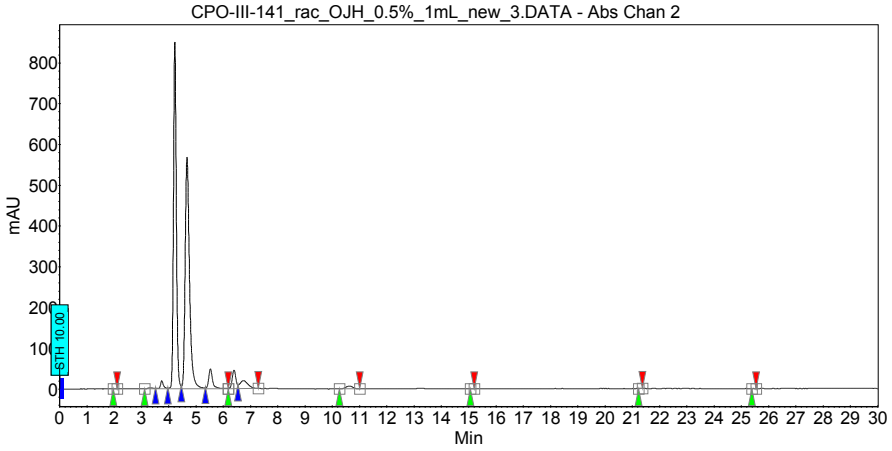
PAGECOUNT

Chromatogram :
CPO-III-141_rac_OJH_0.5%_1mL_new_3_channe
l2

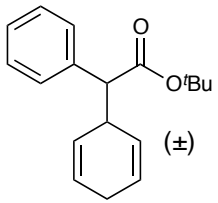
System : System_1
Method : OJH_30min_1mL_0.5%_230nm
User : User1

Acquired : 7/20/2011 2:37:30 PM
Processed : 7/20/2011 3:08:15 PM
Printed : 7/21/2011 8:27:30 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	2.01	0.01	0.3	0.0	0.009
2	UNKNOWN	3.36	0.25	2.6	0.6	0.253
3	UNKNOWN	3.74	1.06	19.6	2.5	1.060
4	UNKNOWN	4.22	44.05	850.5	103.4	44.051
5	UNKNOWN	4.67	44.59	567.7	104.6	44.586
6	UNKNOWN	5.53	3.36	48.4	7.9	3.362
7	UNKNOWN	6.39	2.99	45.4	7.0	2.993
8	UNKNOWN	6.74	2.79	19.4	6.5	2.790
9	UNKNOWN	10.62	0.88	6.8	2.1	0.875
10	UNKNOWN	15.11	0.01	0.2	0.0	0.006
11	UNKNOWN	21.28	0.01	0.2	0.0	0.007
12	UNKNOWN	25.44	0.01	0.3	0.0	0.008
Total			100.00	1561.4	234.7	100.000



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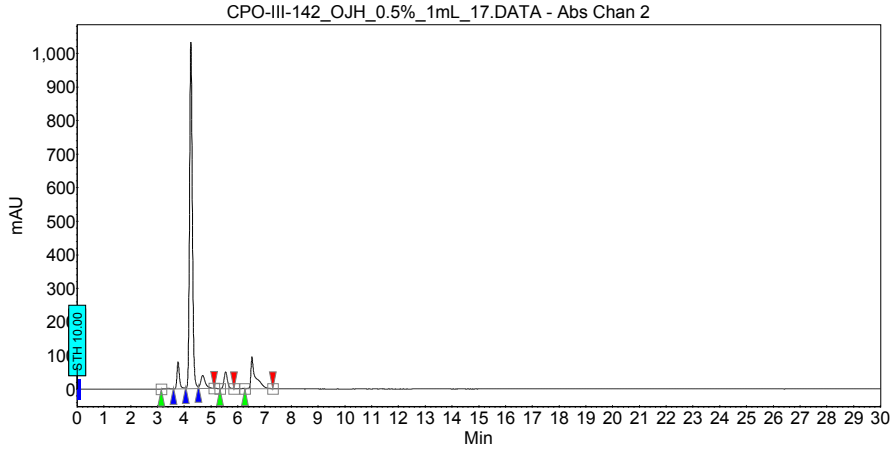
PAGECOUNT

Chromatogram :
CPO-III-142_OJH_0.5%_1mL_17_channel2

System : System_1
Method : OJH_30min_1mL_0.5%_230nm
User : User1

Acquired : 7/21/2011 9:27:18 AM
Processed : 7/21/2011 9:58:04 AM
Printed : 7/21/2011 10:56:23 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.40	0.28	2.7	0.5	0.284
2	UNKNOWN	3.77	5.24	80.6	8.8	5.237
3	UNKNOWN	4.25	74.41	1033.3	125.4	74.414
4	UNKNOWN	4.69	4.64	39.2	7.8	4.644
5	UNKNOWN	5.54	4.33	50.2	7.3	4.325
6	UNKNOWN	6.53	11.10	94.9	18.7	11.096
Total			100.00	1300.7	168.5	100.000

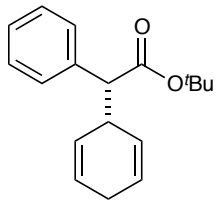


table 2, entry 4

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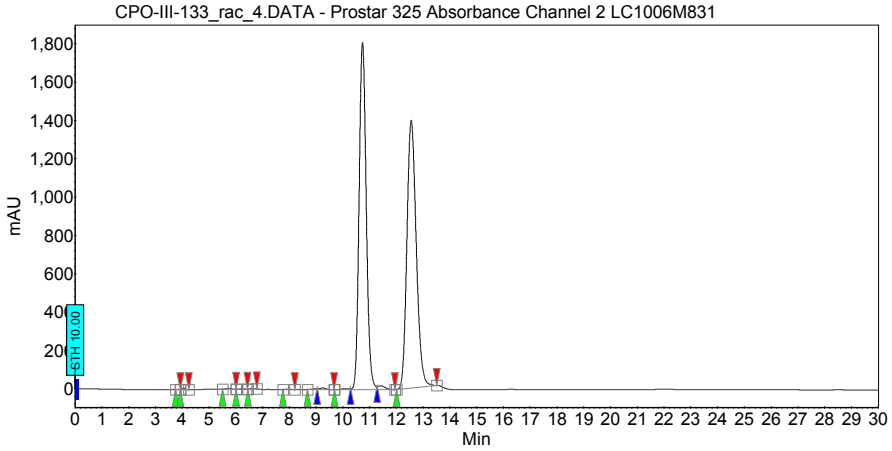
PAGECOUNT

Chromatogram : CPO-III-133_rac_4_channel2

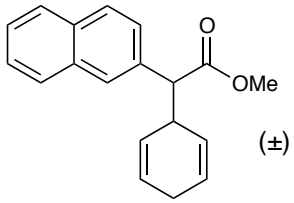
System : Prostar LC System
Method : ADH_30min_1mL_0.3%-230nm
User : User1

Acquired : 7/14/2011 8:11:09 PM
Processed : 7/14/2011 8:41:50 PM
Printed : 7/14/2011 10:27:51 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.86	0.01	1.5	0.1	0.009
2	UNKNOWN	4.04	0.08	9.1	0.9	0.081
3	UNKNOWN	5.71	0.10	5.6	1.2	0.104
4	UNKNOWN	6.25	0.05	3.1	0.6	0.053
5	UNKNOWN	6.61	0.04	2.8	0.5	0.040
6	UNKNOWN	7.98	0.05	2.4	0.6	0.050
7	UNKNOWN	8.98	0.08	3.9	0.9	0.082
8	UNKNOWN	9.25	0.23	9.7	2.7	0.235
9	UNKNOWN	10.14	0.16	4.9	1.8	0.158
10	UNKNOWN	10.74	49.17	1811.3	559.5	49.169
11	UNKNOWN	11.42	0.56	20.2	6.4	0.558
12	UNKNOWN	12.55	49.46	1396.6	562.8	49.461
Total			100.00	3271.0	1137.9	100.000

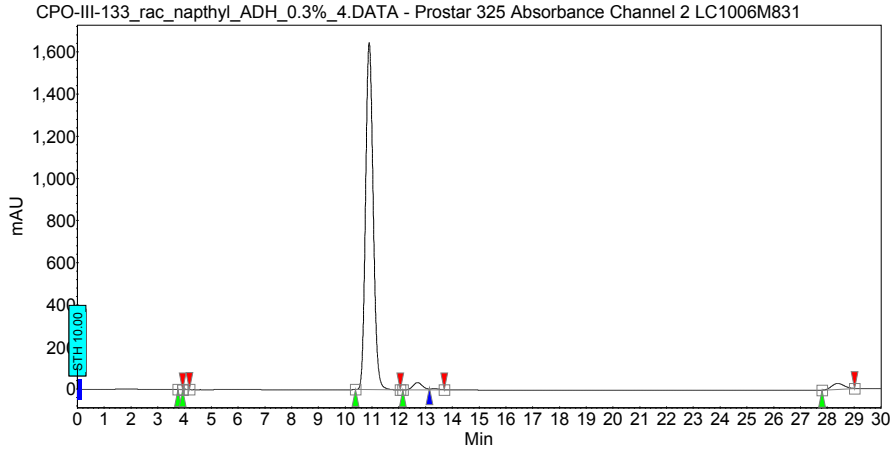


(±)

Chromatogram : CPO-III-133_rac_napthyl_ADH_0.3%_4_channel2

System : Prostar LC System
Method : ADH_30min_1mL_0.3%-230nm
User : User1

Acquired : 7/11/2011 6:41:58 PM
Processed : 7/11/2011 7:12:38 PM
Printed : 7/12/2011 5:22:15 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.86	0.02	1.5	0.1	0.019
2	UNKNOWN	4.03	0.04	2.4	0.2	0.041
3	UNKNOWN	10.90	94.57	1647.1	543.8	94.567
4	UNKNOWN	12.70	2.45	34.6	14.1	2.452
5	UNKNOWN	13.33	0.31	5.1	1.8	0.306
6	UNKNOWN	28.38	2.62	27.7	15.0	2.616
Total			100.00	1718.4	575.1	100.000

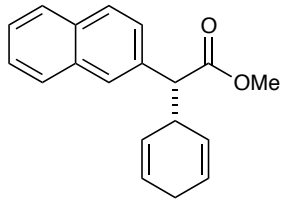
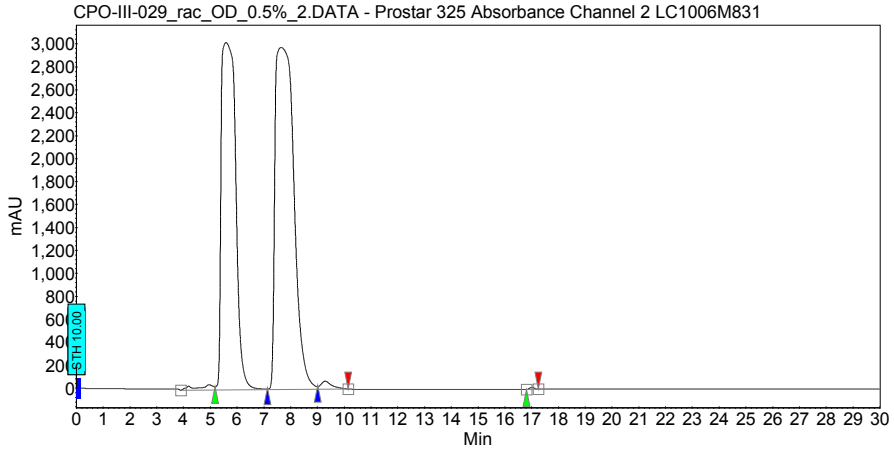


table 2, entry 5

Chromatogram : CPO-III-029_rac_OD_0.5%_2_channel2

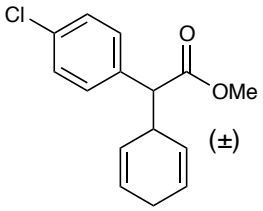
System : Prostar LC System
Method : OD_30min_1mL_0.5%_230nm
User : User1

Acquired : 4/11/2011 12:43:02 PM
Processed : 4/11/2011 1:13:42 PM
Printed : 4/11/2011 6:43:46 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.58	43.44	3027.4	1886.5	43.443
2	UNKNOWN	7.65	55.70	2981.7	2418.7	55.700
3	UNKNOWN	9.28	0.78	70.1	33.8	0.779
4	UNKNOWN	17.02	0.08	18.7	3.4	0.078
Total			100.00	6098.0	4342.4	100.000



Page
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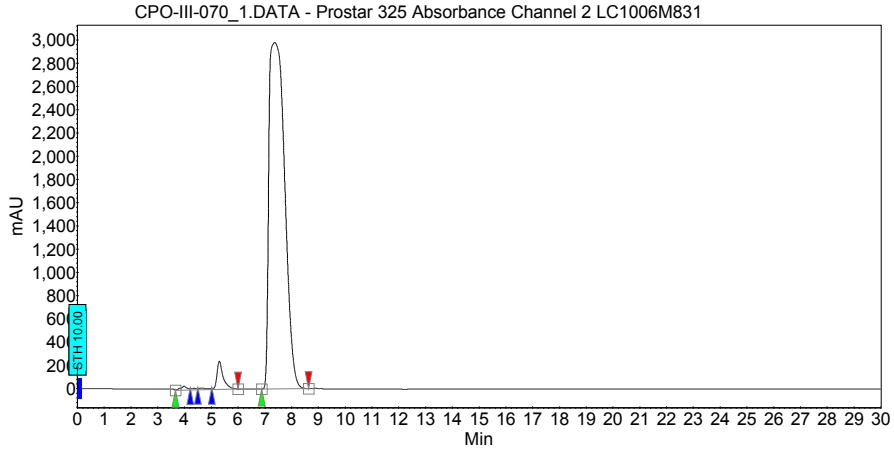
PAGECOUNT

Chromatogram : CPO-III-070_1_channel2

System : Prostar LC System
Method : OD_30min_1mL_0.5%_230nm
User : User1

Acquired : 5/6/2011 11:35:26 AM
Processed : 5/6/2011 12:06:04 PM
Printed : 5/6/2011 1:51:15 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.98	0.43	34.9	9.1	0.429
2	UNKNOWN	4.35	0.16	12.8	3.3	0.156
3	UNKNOWN	4.64	0.25	14.1	5.3	0.251
4	UNKNOWN	5.30	3.07	242.1	64.8	3.072
5	UNKNOWN	7.36	96.09	2982.7	2026.2	96.091
Total			100.00	3286.6	2108.6	100.000

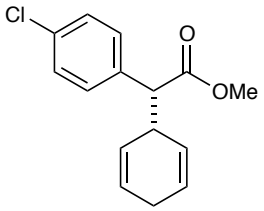


table 2, entry 7

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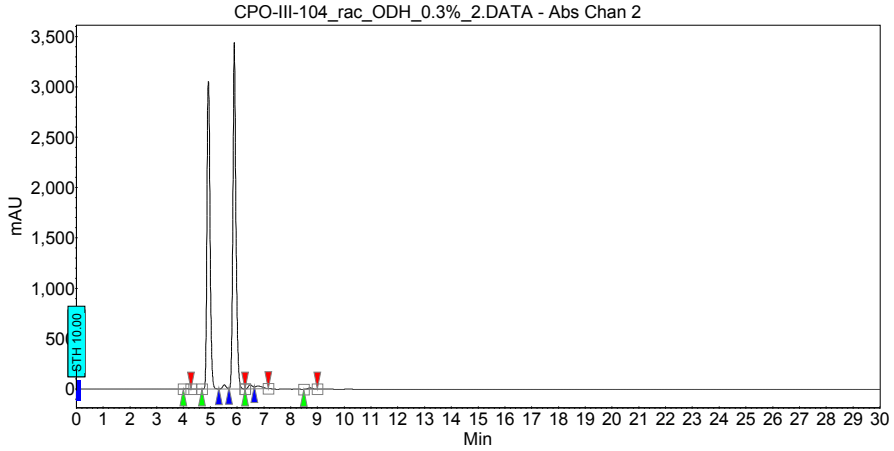
Chromatogram : CPO-III-104_rac_ODH_0.3%_2_channel2

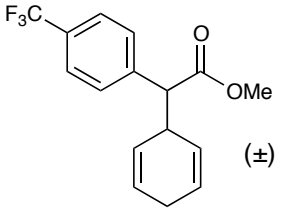
System : System_1
Method : ODH_30min_0.8mL_0.3%_230nm
User : User1

Acquired : 6/11/2011 3:36:05 PM
Processed : 6/11/2011 4:06:52 PM
Printed : 6/12/2011 3:57:18 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.11	0.06	5.6	0.6	0.065
2	UNKNOWN	4.93	46.10	3059.1	411.4	46.096
3	UNKNOWN	5.52	0.72	41.6	6.4	0.717
4	UNKNOWN	5.90	50.92	3443.0	454.4	50.919
5	UNKNOWN	6.48	0.91	41.8	8.1	0.912
6	UNKNOWN	6.78	0.99	29.5	8.9	0.994
7	UNKNOWN	8.72	0.30	12.7	2.6	0.296
Total			100.00	6633.3	892.5	100.000



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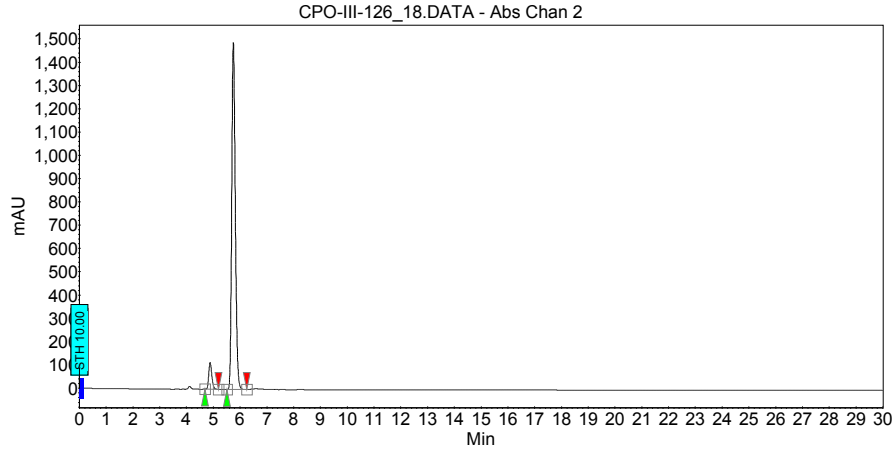
Chromatogram : CPO-III-126_18_channel2

System : System_1
Method : ODH_30min_0.8mL_0.3%_230nm
User : User1

Acquired : 6/27/2011 4:53:53 PM
Processed : 6/27/2011 5:24:30 PM
Printed : 6/29/2011 9:04:16 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.88	6.17	114.6	15.2	6.173
2	UNKNOWN	5.75	93.83	1489.4	230.8	93.827
Total			100.00	1604.0	246.0	100.000

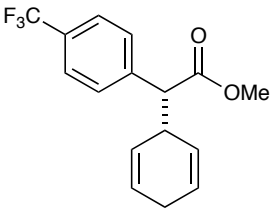


table 2, entry 8

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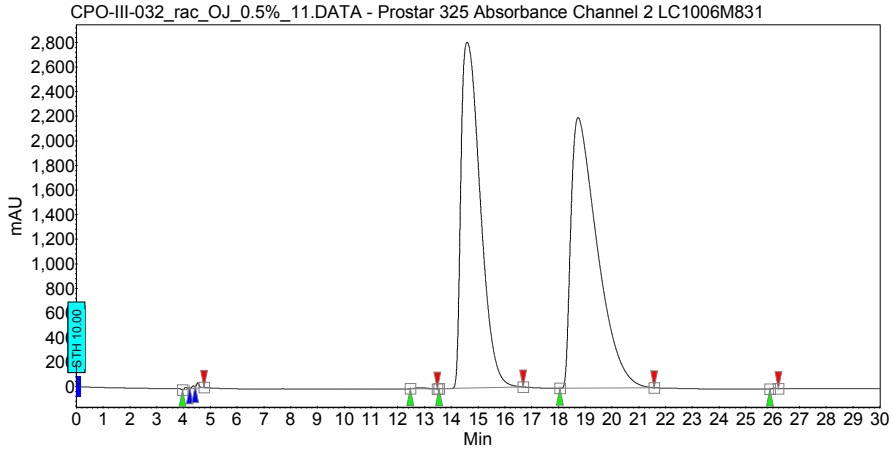
Chromatogram : CPO-III-032_rac_OJ_0.5%_11_channel2

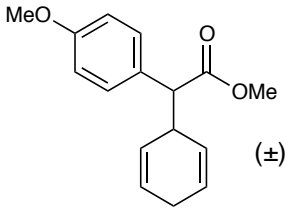
System : Prostar LC System
Method : OJ_30min_1mL_0.5%-230nm
User : User1

Acquired : 4/11/2011 3:53:55 PM
Processed : 4/11/2011 4:24:34 PM
Printed : 4/11/2011 6:50:08 PM



Peak results :

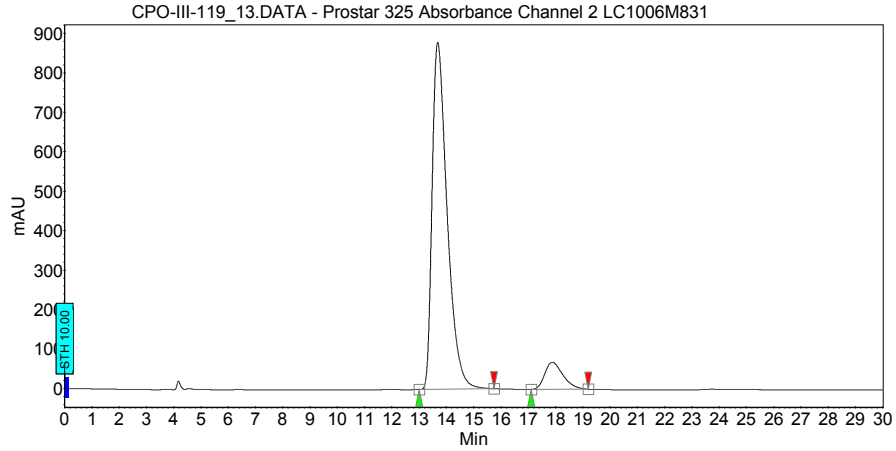
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.08	0.05	16.4	2.6	0.053
2	UNKNOWN	4.36	0.06	22.8	3.1	0.063
3	UNKNOWN	4.53	0.11	44.1	5.3	0.109
4	UNKNOWN	12.86	0.09	9.2	4.5	0.092
5	UNKNOWN	14.59	48.20	2815.1	2344.9	48.199
6	UNKNOWN	18.73	51.47	2203.1	2503.9	51.469
7	UNKNOWN	26.04	0.02	5.2	0.8	0.015
Total			100.00	5115.9	4865.0	100.000



Chromatogram : CPO-III-119_13_channel2

System : Prostar LC System
Method : OJ_30min_1mL_0.5%-230nm
User : User1

Acquired : 6/27/2011 2:31:24 PM
Processed : 6/27/2011 5:00:19 PM
Printed : 6/27/2011 5:00:45 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.68	91.34	880.2	560.9	91.338
2	UNKNOWN	17.88	8.66	68.5	53.2	8.662
Total			100.00	948.6	614.1	100.000

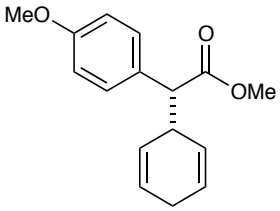
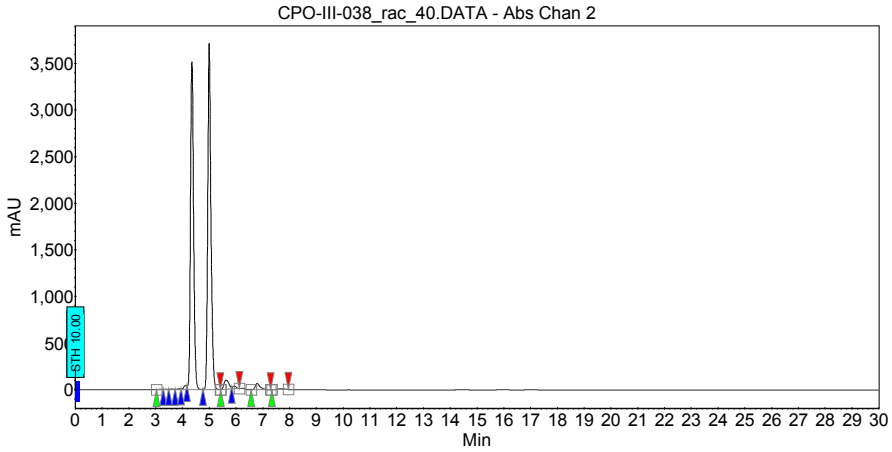


table 2, entry 9

Chromatogram : CPO-III-038_rac_40_channel2

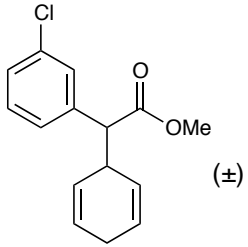
System : System_1
Method : ODH_30min_1mL_0.5%_230nm
User : User1

Acquired : 6/11/2011 2:42:40 AM
Processed : 6/11/2011 3:13:29 AM
Printed : 6/11/2011 2:19:28 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.16	0.07	5.9	0.8	0.073
2	UNKNOWN	3.36	0.06	4.0	0.6	0.060
3	UNKNOWN	3.59	0.11	8.1	1.2	0.115
4	UNKNOWN	3.85	0.13	9.3	1.3	0.129
5	UNKNOWN	4.11	0.58	43.7	6.0	0.579
6	UNKNOWN	4.35	45.75	3517.8	476.0	45.750
7	UNKNOWN	5.00	49.28	3717.0	512.7	49.284
8	UNKNOWN	5.63	1.99	97.1	20.7	1.992
9	UNKNOWN	5.93	0.38	27.0	4.0	0.380
10	UNKNOWN	6.79	1.40	67.6	14.5	1.397
11	UNKNOWN	7.69	0.24	9.2	2.5	0.243
Total			100.00	7506.7	1040.4	100.000



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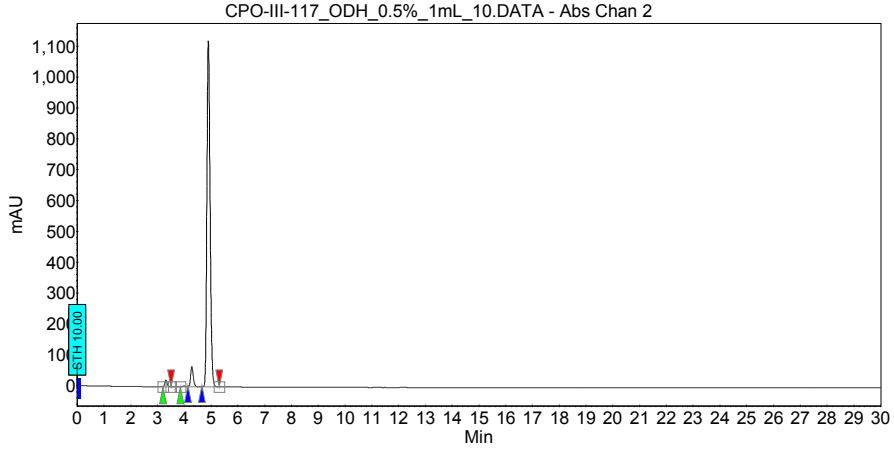
Chromatogram : CPO-III-117_ODH_0.5%_1mL_10_channel2

System : System_1
Method : ODH_30min_1mL_0.5%_230nm
User : User1

Acquired : 6/23/2011 10:51:06 AM
Processed : 6/23/2011 11:21:42 AM
Printed : 6/23/2011 6:56:24 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.31	1.27	21.5	2.1	1.270
2	UNKNOWN	3.99	0.21	2.8	0.3	0.211
3	UNKNOWN	4.28	4.64	65.4	7.6	4.635
4	UNKNOWN	4.90	93.88	1122.4	154.3	93.884
Total			100.00	1212.0	164.4	100.000

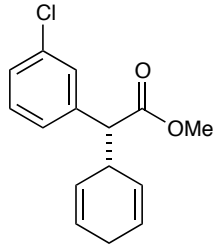


table 2, entry 10

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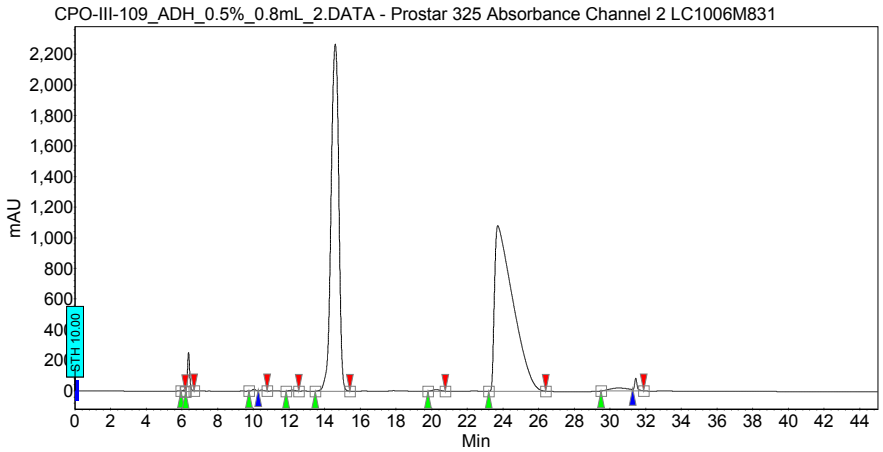
Chromatogram : CPO-III-109_ADH_0.5%_0.8mL_2_channel2

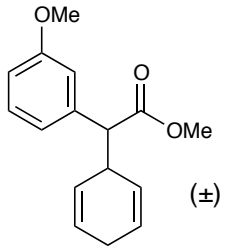
System : Prostar LC System
Method : ADH_45min_0.8mL_0.5%_230nm
User : User1

Acquired : 6/17/2011 11:12:38 AM
Processed : 6/17/2011 11:58:17 AM
Printed : 6/17/2011 5:43:06 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.09	0.04	9.0	1.0	0.039
2	UNKNOWN	6.36	1.40	254.1	35.2	1.402
3	UNKNOWN	10.03	0.11	10.8	2.7	0.109
4	UNKNOWN	10.46	0.07	6.3	1.7	0.069
5	UNKNOWN	12.16	0.10	6.1	2.4	0.096
6	UNKNOWN	14.59	45.20	2269.9	1135.9	45.197
7	UNKNOWN	20.25	0.20	9.9	5.1	0.202
8	UNKNOWN	23.70	51.47	1083.8	1293.5	51.467
9	UNKNOWN	30.47	0.88	18.8	22.0	0.876
10	UNKNOWN	31.44	0.54	82.0	13.7	0.543
Total			100.00	3750.7	2513.2	100.000



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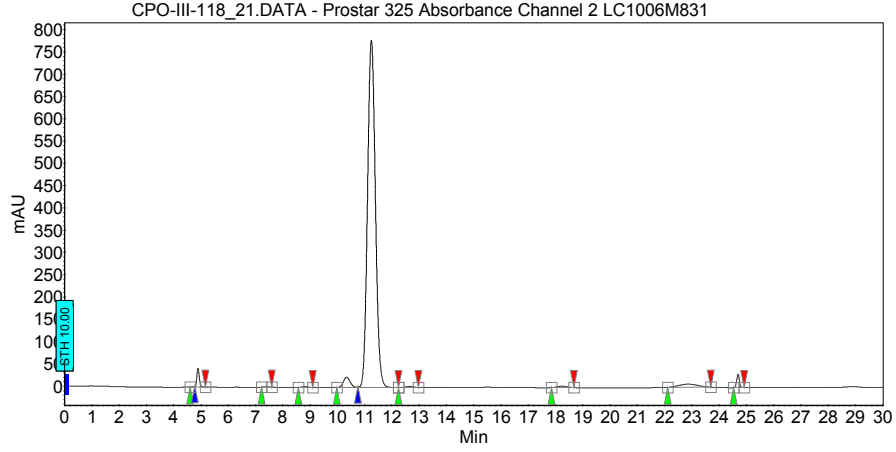
Chromatogram : CPO-III-118_21_channel2

System : Prostar LC System
Method : ADH_30min_1mL_0.5%-230nm
User : User1

Acquired : 6/23/2011 5:27:40 AM
Processed : 6/23/2011 5:58:21 AM
Printed : 6/23/2011 8:32:36 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.71	0.03	1.2	0.1	0.034
2	UNKNOWN	4.89	1.58	41.7	4.5	1.576
3	UNKNOWN	7.40	0.08	1.3	0.2	0.076
4	UNKNOWN	8.82	0.16	1.8	0.4	0.159
5	UNKNOWN	10.34	2.39	23.3	6.8	2.391
6	UNKNOWN	11.25	91.83	779.6	259.7	91.833
7	UNKNOWN	12.64	0.28	2.4	0.8	0.277
8	UNKNOWN	18.24	0.45	3.1	1.3	0.450
9	UNKNOWN	22.86	2.02	7.1	5.7	2.019
10	UNKNOWN	24.70	1.19	30.1	3.4	1.186
Total			100.00	891.7	282.8	100.000

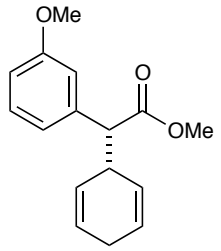


table 2, entry 11

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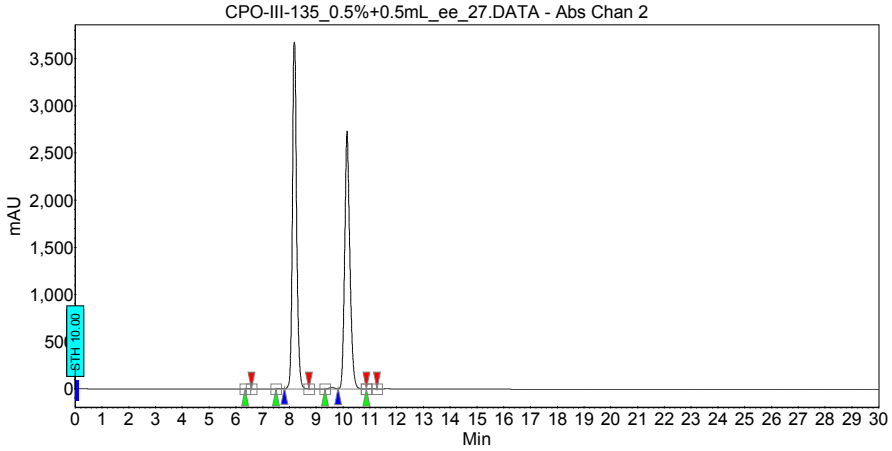
Chromatogram : CPO-III-135_0.5%+0.5mL_ee_27_channel2

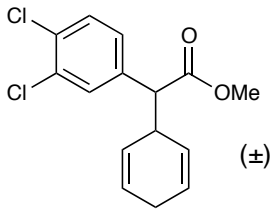
System : System_1
Method : ODH_30min_0.5mL_0.5%_280_230nm
User : User1

Acquired : 7/13/2011 8:45:14 PM
Processed : 7/13/2011 9:16:03 PM
Printed : 7/14/2011 5:56:50 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.45	0.02	2.5	0.3	0.025
2	UNKNOWN	7.67	0.07	4.7	0.9	0.067
3	UNKNOWN	8.18	52.24	3676.4	675.5	52.237
4	UNKNOWN	9.58	0.33	18.7	4.2	0.325
5	UNKNOWN	10.15	47.29	2735.4	611.5	47.293
6	UNKNOWN	11.09	0.05	3.4	0.7	0.053
Total			100.00	6441.0	1293.1	100.000



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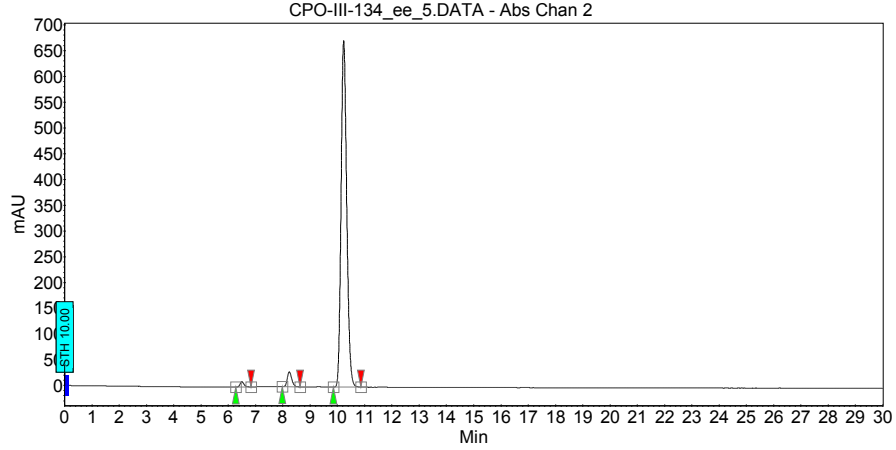
Chromatogram : CPO-III-134_ee_5_channel2

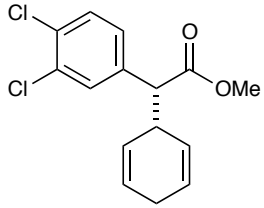
System : System_1
Method : ODH_30min_0.5mL_0.5%_280_230nm
User : User1

Acquired : 7/14/2011 8:33:23 PM
Processed : 7/14/2011 9:04:11 PM
Printed : 8/17/2011 5:58:00 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.50	1.02	10.4	1.7	1.020
2	UNKNOWN	8.24	3.27	29.0	5.5	3.273
3	UNKNOWN	10.23	95.71	672.5	161.4	95.706
Total			100.00	711.8	168.6	100.000



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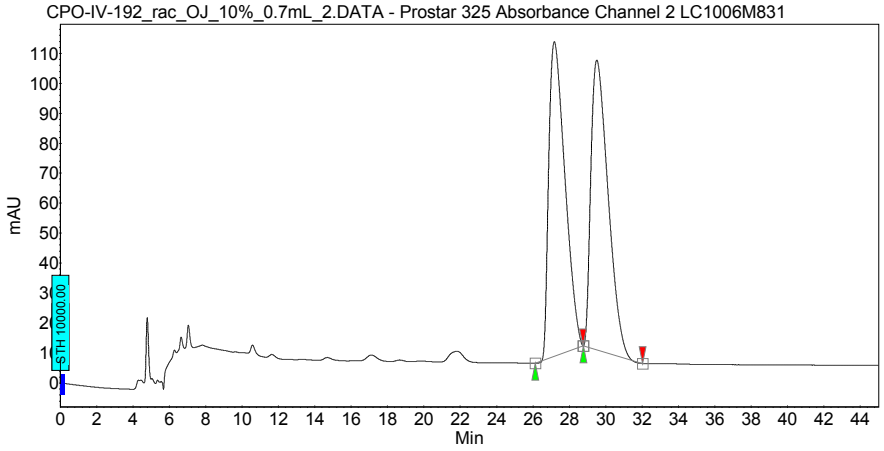
Chromatogram :
CPO-IV-192_rac_OJ_10%_0.7mL_2_channel2

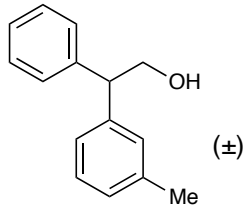
System : Prostar LC System
Method : OJ_45min_0.7mL_10%-230nm_NEW
User : User1

Acquired : 3/11/2013 10:23:39 AM
Processed : 3/11/2013 2:07:37 PM
Printed : 3/13/2013 10:10:34 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	27.17	50.46	105.0	108.1	50.464
2	UNKNOWN	29.51	49.54	96.8	106.1	49.536
Total			100.00	201.8	214.2	100.000



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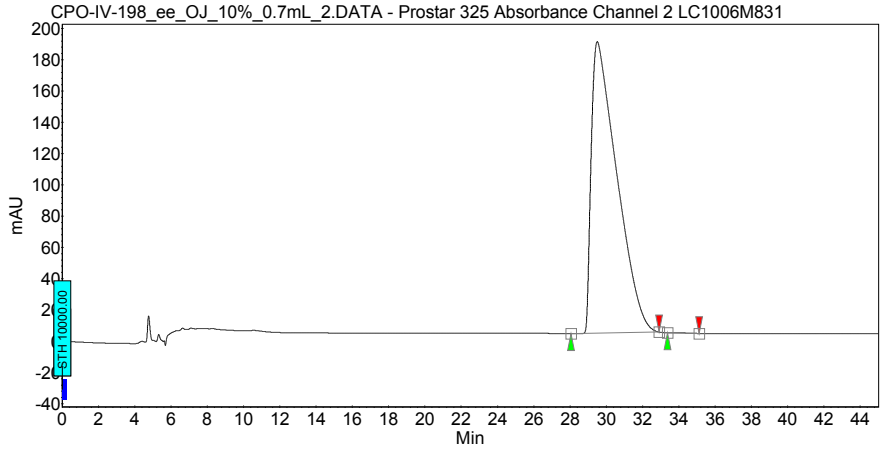
Chromatogram :
CPO-IV-198_ee_OJ_10%_0.7mL_2_channel2

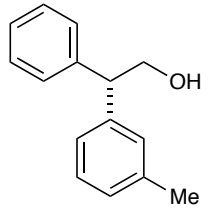
System : Prostar LC System
Method : OJ_45min_0.7mL_10%-230nm_NEW
User : User1

Acquired : 3/12/2013 5:09:17 PM
Processed : 3/13/2013 10:10:00 AM
Printed : 3/13/2013 10:12:58 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	29.50	99.96	186.5	303.8	99.958
2	UNKNOWN	33.95	0.04	0.2	0.1	0.042
Total			100.00	186.7	303.9	100.000



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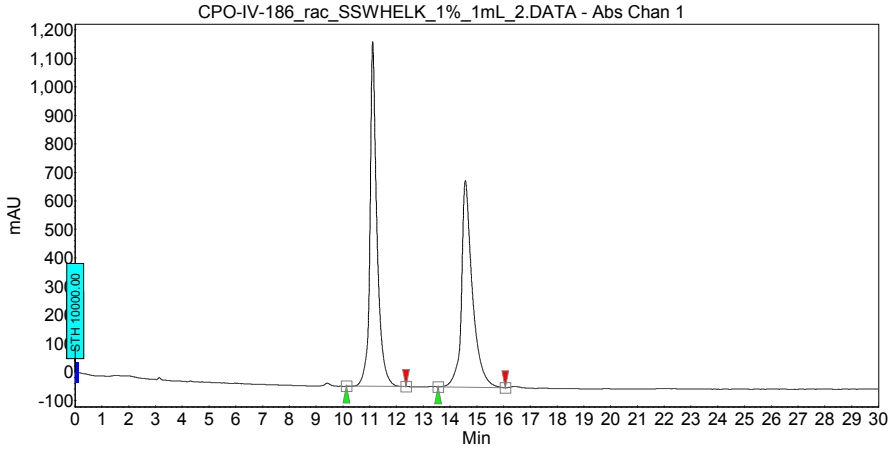
Chromatogram :
CPO-IV-186_rac_SSWHELK_1%_1mL_2_channe
l1

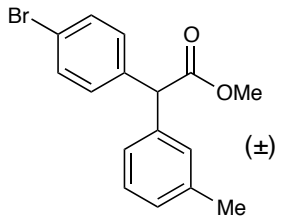
System : System_1
Method : SS_WHELK_30min_1mL_1%_230nm
User : User1

Acquired : 1/18/2013 7:05:22 PM
Processed : 1/19/2013 11:55:49 AM
Printed : 1/19/2013 11:58:26 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.11	51.85	1209.5	366.6	51.850
2	UNKNOWN	14.57	48.15	724.9	340.4	48.150
Total			100.00	1934.4	707.1	100.000



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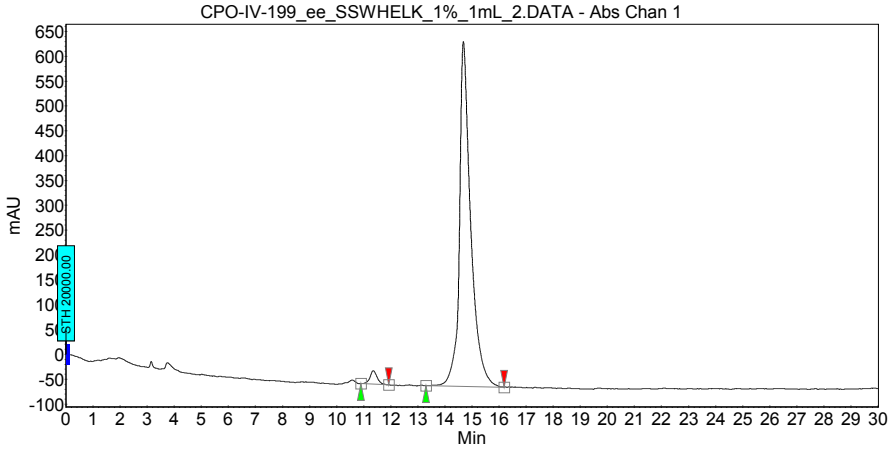
Chromatogram :
CPO-IV-199_ee_SSWHELK_1%_1mL_2_channel1

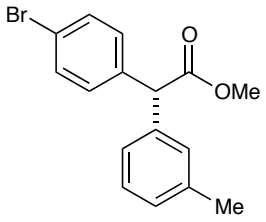
System : System_1
Method : SS_WHELK_30min_1mL_1%_230nm
User : User1

Acquired : 2/1/2013 9:59:17 AM
Processed : 2/1/2013 10:33:38 AM
Printed : 2/1/2013 10:35:28 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.35	2.41	27.0	8.3	2.408
2	UNKNOWN	14.68	97.59	693.9	335.2	97.592
Total			100.00	721.0	343.5	100.000



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