Supporting Information

Highly Enantioselective Diels-Alder Reactions of Danishefsky's-type Dienes with Electron-Deficient Alkenes Catalyzed by Yb(III)-BINAMIDE Complexes

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General Methods: All reactions involving air- or moisture-sensitive reagents or intermediates were performed under an inert atmosphere of argon in glassware. Unless otherwise noted, solvents and reagents were reagent grade and used without further purification. *i*Pr_2NEt and DBU were distilled from CaH_2. CH_2Cl_2 was used as received from Kanto, Chemical CO., INC. Analytical and preparative TLC was carried out on E. Merck 0.25 mm silica gel 60 GF_{254} plates. Silica gel column chromatography was performed using Fuji Silysia Chemical Ltd. silica gel PSQ 60B. Celite® was used with Celite® 545. The phrase "usual workup" refers to the following procedure: The combined organic layers were washed with brine, dried over $MgSO_4$ or Na_2SO_4, and concentrated under reduced pressure.

Melting points are uncorrected. Optical rotations were measured on a JASCO P-1000 polarimeter at 589 nm. Data are reported as follows: $[\alpha]_D^{temp}$, concentration (*c* g/100 mL), and solvent. ^{1}H NMR and ^{13}C NMR spectra were taken on 400 MHz and 100 MHz instruments (JEOL LNM-GSX 400α, JEOL JMN-ECP 400) in the indicated solvent at rt. Chemical shifts are reported in parts per million (ppm) downfield from $(CH_3)_4Si$ (TMS). Coupling constants are reported in hertz (Hz). Spectral splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a JASCO FT/IR-230 spectrometer either neat on sodium chloride plates or on a KBr pellet. MS spectrometry was carried out at the Chemical Analysis Center of Chiba University. High performance liquid chromatography (HPLC) analyses were performed on a Shimadzu LC-2010C (Shimadzu Ind., Ltd.), with detection at 254 nm, and on a Daicel chiral column (Chiralcel OJ-H or Chiralpak AD-H, Daicel Chemical Ind., Ltd.). (*S*)-1,1'-Binaphtyl-2,2'-diamine was purchased from Aldrich and used without further purification.

Preparation of Dienes

Diens **1a-c**[1] were prepared according to the reported procedures.

Preparation of BINAMIDEs

BINAMIDE 3a: To a solution of (*S*)-1,1'-binaphtyl-2,2'-diamine (227 mg, 0.8 mmol) and *i*Pr_2NEt (0.42 mL, 2.4 mmol) in CH_2Cl_2 (8 mL) was added benzoyl chloride (0.23 mL, 2.0 mmol) at 0 °C.

After being stirred for 2 h at room temperature, the reaction was quenched with 1N HCl (3 mL). This mixture was extracted with CH_2Cl_2. The usual workup gave a residue that was purified by column chromatography (SiO_2, hexane/AcOEt: 4/1 to 2/1) to give **3a** (399 mg, quant) as a colorless amorphous solid. mp 188-189 °C; $[\alpha]_D^{23}$ –81.9 (*c* 1.00, $CHCl_3$); IR (KBr) 1677, 1594, 1500, 1427, 1282, 1072, 867 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23-7.29 (10H, m), 7.35-7.39 (4H, m), 7.51 (2H, dd, *J* = 6.9, 7.0 Hz), 7.75 (2H, brs), 7.99 (2H, d, *J* = 8.0 Hz), 8.13 (2H, d, *J* = 9.1 Hz), 8.75 (2H, d, *J* = 9.1 Hz); ^{13}C NMR ($CDCl_3$) δ 120.6, 121.4, 125.0, 125.7, 126.7, 127.6, 128.5, 128.6, 130.2, 131.3, 131.8, 132.2, 134.2, 135.3, 165.7; LRMS (FAB) *m/z* 493 $(M+H)^+$; HRMS (FAB) Calcd for $C_{34}H_{25}N_2O_2$ $(M+H)^+$ 493.1873, found 493.1873.

BINAMIDE 3b: BINAMIDE **3b** was prepared in 92% yield according to the procedure described for synthesis of **3a**. Colorless amorphous solid; $[\alpha]_D^{24}$ +7.3 (*c* 1.00, $CHCl_3$); IR (KBr) 1654, 1590, 1504, 1481, 1427, 1280, 1108, 1072, 1010, 906, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23-7.29 (10H, m), 7.04-7.06 (4H, m), 7.25 (2H, d, *J* = 7.9 Hz), 7.33-7.36 (6H, m,), 7.49 (2H, dt, *J* = 1.3, 7.0 Hz), 7.73 (2H, brs), 7.99 (2H, d, *J* = 8.2 Hz), 8.11 (2H, d, *J* = 8.8 Hz), 8.59 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 121.5, 121.7, 124.9, 125.9, 126.7, 127.8, 128.3, 128.6, 130.2, 131.4, 131.8, 132.1, 132.9, 134.9, 164.9; LRMS (FAB) *m/z* 653, 651, 649 $(M+H)^+$; HRMS (FAB) Calcd for $C_{34}H_{23}{}^{79}Br^{81}BrN_2O_2$ $(M+H)^+$ 651.0105, found 651.0081.

BINAMIDE 3c: BINAMIDE **3c** was prepared in 82% yield according to the procedure described for synthesis of **3a**. Colorless solid; mp 215-217 °C; $[\alpha]_D^{22}$ –68.4 (*c* 0.99, $CHCl_3$); IR (KBr) 1654, 1489, 1260, 813 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05-7.09 (4H, m), 7.29-7.31 (4H, m), 7.38 (2H, dd, *J* = 8.8, 8.8 Hz), 7.46-7.54 (4H, m), 7.70 (2H, brs), 8.02 (2H, d, *J* = 8.0 Hz), 8.14 (2H, d, *J* = 8.8 Hz), 8.61 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 121.6, 121.7, 122.8, 124.9, 125.1, 126.0, 127.8, 128.7, 130.1, 130.3, 131.5, 132.0, 134.7, 134.8, 136.1, 164.4; LRMS (EI) *m/z* 652, 650, 648 (M^+), 451, 185 (base); HRMS (FAB) Calcd for $C_{34}H_{23}{}^{79}Br^{81}Br\ N_2O_2$ (M^+) 651.0109, found 651.0038.

BINAMIDE 3d: BINAMIDE **3d** was prepared quantitatively according to the procedure described for synthesis of **3a**. Colorless amorphous solid; $[\alpha]_D^{23}$ –104 (*c* 1.00, $CHCl_3$); IR (KBr) 1670, 1589, 1488, 1425, 1288 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85 (2H, d, *J* = 8.0 Hz), 6.99-7.08 (4H, m), 7.13-7.19 (2H, m), 7.27 (2H, d, *J* = 8.8 Hz), 7.37 (2H, dd, *J* = 8.0, 8.0 Hz), 7.51 (2H, dd, *J* = 6.8, 8.0 Hz), 7.73 (2H, brs), 8.01 (2H, d, *J* = 8.8 Hz), 8.13 (2H, d, *J* = 8.8 Hz), 8.58-8.63 (2H, m); ^{13}C NMR ($CDCl_3$) δ; 114.3 (d, *J* = 23.1 Hz), 118.9 (d, *J* = 20.6 Hz), 121.7 (d, *J* = 4.2 Hz), 121.9 (d, *J* = 2.5 Hz), 124.9, 126.0, 127.8, 128.6, 130.2, 130.3, 131.5, 132.0, 134.8, 136.4 (d, *J* = 6.6 Hz), 162.6 (d, *J* = 246.8 Hz), 164.6; LRMS (FAB) *m/z* 529 $(M+H)^+$; HRMS (FAB) Calcd for $C_{34}H_{23}F_2N_2O_2$ $(M+H)^+$ 529.1728, found 529.1684.

BINAMIDE 3e: BINAMIDE **3e** was prepared quantitatively according to the procedure described for synthesis of **3a**. Colorless amorphous solid; mp 186-186.5 °C; $[\alpha]_D^{22}$ –107 (*c* 1.00, $CHCl_3$); IR (KBr) 1660, 1504, 1430, 1332, 1274, 1128 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31-7.42 (10H, m), 7.52 (2H, ddd, *J* = 1.2, 6.8, 8.0 Hz), 7.61 (2H, d, *J* = 7.6 Hz), 7.79 (2H, brs), 8.02 (2H, d, *J* = 8.4 Hz), 8.15

(2H, d, J = 8.8 Hz), 8.60 (2H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 121.7, 121.8 (q, J = 6.6 Hz), 123.7 (q, J = 4.1 Hz), 124.7, 124.8, 126.1, 127.9, 128.3 (q, J = 3.3 Hz), 128.7, 129.3, 130.0, 130.4, 131.1, (q, J = 32.9 Hz), 131.6, 131.9, 134.7, 135.0, 164.4; LRMS (EI) *m/z* 628 (M^+), 439, 267, 173 (base); HRMS (FAB) Calcd for $C_{36}H_{23}F_6N_2O_2$ (M^+) 629.1664, found 629.1639.

BINAMIDE 3f: BINAMIDE **3f** was prepared according to the procedure described for synthesis of **3a**. Colorless solid; mp 111-112 °C; $[\alpha]_D^{22}$ –52.6 (*c* 1.02, $CHCl_3$); IR (KBr) 1654, 1590, 1490, 1425, 1280, 1025, 811 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.11-7.20 (6H, m), 7.27-7.33 (4H, m), 7.36 (2H, dd, J = 1.2, 8.0 Hz), 7.47 (2H, ddd, J = 1.2, 8.0, 8.0 Hz), 7.68 (2H, brs), 7.96 (2H, d, J = 8.0 Hz), 8.10 (2H, d, J = 9.2 Hz), 8.66 (2H, d, J = 9.2 Hz); ^{13}C NMR ($CDCl_3$) δ ; LRMS (EI) *m/z* 652, 650, 648 (M^+), 451, 183 (base); HRMS (FAB) Calcd for $C_{34}H_{22}{}^{79}Br^{81}Br\,N_2O_2$ (M^+) 650.0028, found 649.9974.

BINAMIDE 3g: To a solution of (*S*)-1,1'-binaphtyl-2,2'-diamine (314 mg, 1.1 mmol) in CH_2Cl_2 (11 mL) was added aqueous 10% NaOH (7 mL). To this mixture was added 3,5-difluorobenzoyl chloride (0.42 mL, 3.3 mmol) at 0 °C. After being stirred for 0.5 h at the same temperature, the separated aqueous layer was extracted with CH_2Cl_2. Usual workup gave a residue which was purified by column chromatography (SiO_2, hexane/AcOEt: 4/1) to give **3g** (593 mg, 95%) as a colorless amorphous solid. $[\alpha]_D^{19}$ –117 (*c* 0.99, $CHCl_3$); IR (KBr) 1654, 1596, 1506, 1322, 1126 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.68-6.70 (4H, m), 6.78-6.83 (2H, m), 7.29 (2H, d, J = 8.0 Hz), 7.39 (2H, ddd, J = 1.2, 8.0, 8.0 Hz), 7.53 (2H, ddd, J = 1.2, 8.0, 8.0 Hz), 7.73 (2H, brs), 8.02 (2H, d, J = 8.0 Hz), 8.13 (2H, d, J = 8.8 Hz), 8.46 (2H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 107.2 (t, J = 25.6 Hz), 110.1 (dd, J = 7.4, 18.9 Hz), 122.3, 123.1, 124.9, 126.2, 127.8, 128.6, 130.3, 131.7, 132.0, 134.3, 137.3 (t, J = 8.3 Hz), 162.7 (dd, J = 11.5 and 250.1 Hz), 163.6; LRMS (FAB) *m/z* 565 $(M+H)^+$; HRMS (FAB) Calcd for $C_{34}H_{21}F_4N_2O_2$ $(M+H)^+$ 565.1539, found 565.1495.

BINAMIDE 3h: To a solution of (*S*)-1,1'-binaphtyl-2,2'-diamine (142 mg, 0.50 mmol) and Et_3N (0.17 mL, 1.25 mmol) in CH_2Cl_2 (5 mL) was added 3,5-bistrifluoromethylbenzoyl chloride (0.20 mL, 1.10 mmol) at 0 °C. After being stirred for 2 h at the same temperature, the reaction was quenched with 1N HCl (2 mL). This mixture was extracted with CH_2Cl_2. Usual workup gave a residue that was purified by column chromatography (SiO_2, hexane/AcOEt: 8/1 to 5/1) to give **3h** (350 mg, 92%) as a colorless amorphous solid. mp 216-217 °C; $[\alpha]_D^{20}$ –104 (*c* 1.00, $CHCl_3$); IR (KBr) 1662, 1621, 1506, 1373, 1276, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.36 (2H, d, J = 8.4 Hz), 7.43 (2H, dd, J = 8.0, 8.0 Hz), 7.53-7.57 (6H, m), 7.82-7.88 (4H, m), 8.04 (2H, d, J = 8.4 Hz), 8.16 (2H, d, J = 8.8 Hz), 8.47 (2H, dd, J = 2.4, 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 121.2, 122.1, 123.0, 123.9, 124.7, 125.2 (septet, J = 3.3 Hz), 126.5, 127.1 (q, J = 2.5 Hz), 128.1, 128.9, 130.6, 131.8 (q, J = 33.8 Hz), 134.2, 136.2, 163.1; LRMS (FAB) *m/z* 765 $(M+H)^+$; HRMS (FAB) Calcd for $C_{38}H_{21}F_{12}N_2O_2$ $(M+H)^+$ 765.1411, found 765.1461.

Preparation of Dienophiles

Dienophiles **2a-c**[2a], **2d**[2b], **2e**[2c], and **2i**[2d] were prepared according to the reported procedures.

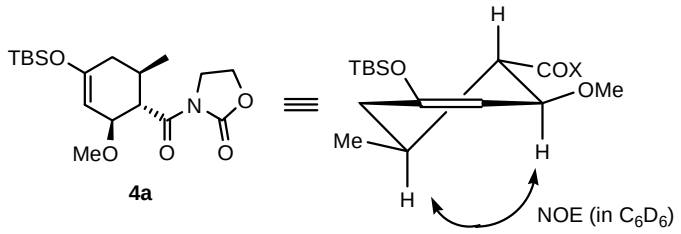
Dienophile 2f: To a mixture of (*E*)-4-chloro-2-butenoic acid (1.50 g, 12.4 mmol) in CH_2Cl_2 (5 mL) were added DMF (5 drops) and oxalyl chloride (1.2 mL, 13.7 mmol) at room temperature. Then the mixture was stirred for 3 h at the same temperature. To a solution of 1,3-oxazolidin-2-one (1.30 g, 14.9 mmol) in THF (60 mL) was added NaH [0.66 g (60% in mineral oil), 16.4 mmol] at 0 °C. The mixture was stirred for 0.5 h at 0 °C and then for 1 h at room temperature. To this suspension was added a solution of (*E*)-4-chloro-2-butenoyl chloride at 0 °C, and the mixture was stirred for 5 h at room temperature. The reaction was quenched with water (20 mL) and the mixture was extracted with AcOEt. After the usual workup, a crude product was purified by column chromatography (SiO_2, hexane/AcOEt: 2/1) to give **2f** (1.26 g, 53%) as a colorless solid. mp 91.5-92 °C; IR (KBr) 1778, 1671, 1388, 1367, 1220, 1112, 1045, 971 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.09 (2H, t, *J* = 8.0 Hz), 4.22-4.24 (2H, m), 4.45 (2H, t, *J* = 8.0 Hz), 7.09-7.16 (1H, m), 7.50 (1H, ddd, *J* = 1.2, 2.8, 15.2 Hz); ^{13}C NMR ($CDCl_3$) δ 42.6, 42.7, 62.1, 122.5, 143.3, 153.3, 164.2; LRMS (FAB) *m/z* 190 $(M+H)^+$; HRMS (FAB) Calcd for $C_7H_9ClNO_3$ $(M+H)^+$ 190.0271, found 190.0275.

Dienophile 2g: According to the procedure described for the synthesis of **2f**, **2g** was prepared in 61% yield: Colorless solid; mp 77-78.5 °C; IR (KBr) 1768, 1675, 1627, 1365, 1280, 1205, 1116, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.59-2.64 (2H, m), 2.81 (2H, t, *J* = 7.6 Hz), 4.06 (2H, t, *J* = 8.0 Hz), 4.41 (2H, t, *J* = 8.0 Hz), 7.17-7.31 (7H, m); ^{13}C NMR ($CDCl_3$) δ 34.27, 34.29, 42.7, 62.0, 120.4, 126.1, 128.3, 128.5, 140.7, 150.3, 153.5, 165.1; LRMS (EI) *m/z* 245 (M^+), 158, 91 (base); HRMS (FAB) Calcd for $C_{14}H_{16}NO_3$ $(M+H)^+$ 246.1130, found 246.1139.

Dienophile 2h: According to the procedure described for the synthesis of **2f**, **2h** was prepared in 53% yield: Colorless solid; mp 57-58 °C; IR (KBr) 1762, 1683, 1369, 1336, 1209, 1116, 1041 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.08 (2H, t, *J* = 8.0 Hz), 4.23-4.25 (2H, m), 4.43 (2H, t, *J* = 8.0 Hz), 4.58 (2H, s), 7.16 (1H, dt, *J* = 4.4, 15.2 Hz), 7.28-7.37 (5H, m), 7.52 (1H, ddd, *J* = 1.6, 2.8, 15.2 Hz); ^{13}C NMR ($CDCl_3$) δ 42.6, 62.1, 68.9, 72.8, 120.1, 127.7, 127.8, 128.5, 137.7, 146.2, 153.3, 164.9; LRMS (EI) *m/z* 261 (M^+), 155, 91 (base); HRMS (FAB) Calcd for $C_{14}H_{16}NO_4$ $(M+H)^+$ 262.1079, found 262.1082.

Synthesis of 4a Using Asymmetric DA Reaction Catalyzed by Yb(III)-BINAMIDE Complex: A mixture of $Yb(OTf)_3$ (620 mg, 1.0 mmol) and BINAMIDE **3g** (677 mg, 1.2 mmol) was dried at 90 °C under reduced pressure (<0.1 mmHg) for 0.5 h with stirring. After the mixture was allowed to cool to room temperature, CH_2Cl_2 (45 ml) and DBU (0.36 mL, 2.4 mmol) were added successively and the mixture was stirred for 2 h. Dienophile **2a** (1.55 g, 10 mmol) in CH_2Cl_2 (5.0 mL) and diene **1b** (5.0 mL, 20 mmol) were added successively at 0 °C, and the mixture was stirred for 4 h at the same temperature. Water (10 mL) was then added to quench the reaction, and the insoluble materials were filtered through a pad of Celite. After usual workup, the crude product was purified by column chromatography (SiO_2, hexane/acetone: 5/1) to give **4a** (3.70 g, quant) as a colorless oil which was solidified on standing. The enantiomeric excess of the product was determined to be 91% ee by HPLC analysis (Daicel Chiralcel OJ-H) after conversion to the cyclohexenone **5a** (vide ínfra), and its ee value was enriched to 99% ee by single recrystallization from *n*-hexane. Colorless

needle; mp 67.5-68.5 °C; $[\alpha]_D^{24}$ +30.8 (*c* 0.50, $CHCl_3$, 81% ee); IR (neat) 2929, 2858, 1775, 1693, 1664, 1462, 1384, 1321, 1197, 1088, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (6H, s), 0.93 (9H, s), 0.96 (3H, d, *J* = 6.4 Hz), 1.99-2.11 (3H, m), 3.24 (3H, s), 4.02-4.15 (3H, m), 4.40 (2H, t, *J* = 8.0 Hz), 4.47 (1H, d, *J* = 8.8 Hz), 4.94 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.4, 17.9, 18.4, 25.6, 31.8, 38.1, 42.8, 48.6, 54.2, 61.6, 79.0, 103.4, 152.4, 153.3, 176.1; LRMS (FAB) *m/z* 408 $(M+K)^+$; HRMS (FAB) Calcd for $C_{18}H_{31}NO_5SiK$ $(M+K)^+$ 408.1609, found 408.1648.



Synthesis of 5a by Asymmetric DA Catalyzed by Yb(III)-BINAMIDE Complex: A mixture of $Yb(OTf)_3$ (18.6 mg, 0.030 mmol) and BINAMIDE **3g** (20.3 mg, 0.036 mmol) was dried at 90 °C under reduced pressure (<0.1 mmHg) for 0.5 h with stirring. After the mixture was allowed to cool to room temperature, CH_2Cl_2 (2.0 ml) and DBU (11 μL, 0.072 mmol) were successively added and the mixture was stirred for 2 h. Dienophile **2a** (93 mg, 0.60 mmol) in CH_2Cl_2 (1.0 mL) and diene **1b** (0.30 mL, 1.20 mmol) were added successively at 0 °C, and the mixture was stirred for 5 h at the same temperature. Water (1 mL) was then added to quench the reaction, and the insoluble materials were filtered through a pad of Celite. The usual workup gave a residue which was dissolved in a mixture of 1,2-dichloroethane (6 mL) and TFA (0.12 mL). The resulting solution was stirred at 60 °C for 0.5 h. The reaction was quenched with aqueous saturated $NaHCO_3$ (2 mL) and the mixture was extracted with CH_2Cl_2. The usual workup gave a residue that was purified by column chromatography (SiO_2, hexane/AcOEt: 1/1) to give **5a** (125.6 mg, 94%) as a colorless solid. The enantiomeric excess of the product was determined to be 94% ee by HPLC analysis. mp 108-109 °C; $[\alpha]_D^{23}$ –188 (*c* 0.99, $CHCl_3$, >99% ee); IR (KBr) 1781, 1695, 1678, 1393, 1373, 1225, 1119 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (3H, d, *J* = 6.8 Hz), 2.27 (1H, dd, *J* = 11.6, 17.2 Hz), 2.61-2.71 (2H, m), 4.06-4.16 (2H, m), 4.50 (2H, t, *J* = 8.0 Hz), 4.56 (1H, ddd, *J* = 2.8, 2.8, 8.0 Hz), 6.12 (1H, dd, *J* = 2.8, 10.4 Hz), 6.75 (1H, dd, *J* = 2.8, 10.4 Hz); ^{13}C NMR ($CDCl_3$) δ 19.7, 32.6, 42.8, 44.1, 47.6, 62.1, 130.4, 144.9, 153.3, 171.9, 198.3; LRMS (EI) *m/z* 223 (M^+), 208, 181, 153, 136 (base); HRMS (FAB) Calcd for $C_{11}H_{14}NO_4$ (M^+) 224.0923, found 224.0919; HPLC: Daicel Chiralcel OJ-H, 254 nm, flow rate: 1.0 mL/min, *n*-Hexane:*i*PrOH=65:35, retention time: 23.9 min (major) and 29.8 min (minor).

Compound 5b: A mixture of $Yb(OTf)_3$ (18.6 mg, 0.030 mmol) and BINAMIDE **3g** (20.3 mg, 0.036 mmol) was dried at 90 °C under reduced pressure (<0.1 mmHg) for 0.5 h. After the mixture was allowed to cool to room temperature, CH_2Cl_2 (1.0 ml) and DBU (11 μL, 0.072 mmol) were successively added and the mixture was stirred for 2 h. Dienophile **2b** (42 mg, 0.30 mmol) in CH_2Cl_2 (0.5 mL) and diene **1c** (0.17 mL, 0.60 mmol) were successively added at –20 °C, and the mixture was stirred for 3 h at the same temperature. Water (1 mL) was then added to quench the reaction, and the insoluble materials were filtered through a pad of Celite. After a usual workup, to

the crude product was added DCE (3 mL) and TFA (60 μL). The resulting mixture was stirred at 60 °C for 0.5 h. The reaction was quenched with aqueous saturated $NaHCO_3$ (1 mL) and the mixture was extracted with CH_2Cl_2. Usual workup gave a residue which was purified by column chromatography (SiO_2, hexane/AcOEt: 3/5) to give **5b** (58.5 mg, 93%) as a colorless solid. The enantiomeric excess of the product was determined to be 71% ee by HPLC analysis. mp 95-96 °C; $[\alpha]_D^{22}$ –45.8 (*c* 1.01, $CHCl_3$, 54% ee); IR (KBr) 1772, 1671, 1386, 1368, 1224, 1114, 1041 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15-2.24 (1H, m), 2.36-2.43 (1H, m), 2.50 (1H, ddd, *J* = 5.2, 11.6, 16.4 Hz), 2.67 (1H, ddd, *J* = 4.4, 6.0, 16.4 Hz), 4.09 (2H, t, *J* = 8.0 Hz), 4.49 (2H, t, *J* = 8.0 Hz), 4.63-4.68 (1H, m), 6.13 (1H, dd, *J* = 2.4, 10.4 Hz), 6.96 (1H, dd, *J* = 2.8, 10.4 Hz); ^{13}C NMR ($CDCl_3$) δ 26.3, 36.2, 40.9, 42.7, 62.2, 130.7, 145.8, 153.2, 172.2, 198.1; LRMS (EI) *m/z* 209 (M^+, 29), 181 (31), 163 (19), 122 (100); HRMS *m/z* Calcd for $C_{10}H_{12}NO_4$ 210.0766, found 210.0750; HPLC: Daicel Chiralcel OJ-H, 254 nm, flow rate: 0.75 mL/min, *n*-Hexane:*i*PrOH=60:40, retention time: 37.4 min for (4*R*)-**5b** and 39.0 min for (4*S*)-**5b**.

Compound 5c: A mixture of $Yb(OTf)_3$ (18.6 mg, 0.030 mmol) and BINAMIDE **3g** (20.3 mg, 0.036 mmol) was dried at 90 °C under reduced pressure (<0.1 mmHg) for 0.5 h with stirring. After the mixture was allowed to cool to room temperature, CH_2Cl_2 (1.0 ml) and DBU (11 μL, 0.072 mmol) were added successively and the mixture was stirred for 2 h. Dienophile **2c** (55 mg, 0.30 mmol) in CH_2Cl_2 (0.5 mL) and diene **1b** (0.15 mL, 0.60 mmol) were added successively at room temperature, and the mixture was stirred for 6 h at the same temperature. Water (1 mL) was then added to quench the reaction, and the insoluble materials were filtered through a pad of Celite. After usual workup, the crude product was dissolved in a mixture of DCE (3 mL) and TFA (60 μL). The solution was stirred at 60 °C for 0.5 h. The reaction was quenched with aqueous saturated $NaHCO_3$ (1 mL) and the mixture was extracted with CH_2Cl_2. Usual workup gave a residue which was purified by column chromatography (SiO_2, hexane/AcOEt: 5/4) to give **5c** (70.1 mg, 93%) as a colorless oil. The enantiomeric excess of the product was determined to be 97% ee by HPLC analysis. $[\alpha]_D^{24}$ –174 (*c* 1.57, $CHCl_3$, 90% ee); IR (neat) 1778, 1694, 1384, 1224, 1115, 1041 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (3H, t, *J* = 6.8 Hz), 1.22-1.47 (4H, m), 2.25 (1H, dd, *J* = 10.0, 16.4 Hz), 2.53-2.62 (1H, m), 2.77 (1H, dd, *J* = 4.4, 16.4 Hz), 4.05-4.16 (2H, m), 4.50 (2H, t, *J* = 8.0 Hz), 4.62 (1H, ddd, *J* = 2.4, 2.8, 7.6 Hz), 6.12 (1H, dd, *J* = 2.4, 10.0 Hz), 6.73 (1H, dd, *J* = 2.8, 10.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 19.6, 36.0, 36.8, 41.1, 42.8, 46.5, 62.1, 130.6, 144.7, 153.2, 171.9, 198.4; LRMS (FAB) *m/z* 252 $(M+H)^+$; HRMS (FAB) Calcd for $C_{13}H_{18}NO_4$ 252.1236, found 252.1237; HPLC: Daicel Chiralcel OJ-H, 254 nm, flow rate: 0.75 mL/min, *n*-Hexane:*i*PrOH=75:25, retention time: 31.0 min (major isomer) and 33.6 min (minor isomer).

Compound 5d: Dienophile **2d** (59 mg, 0.30 mmol) was converted to **5d** (70 mg, 88%, 87% ee) according to the procedure for **5c**. **5d**: $[\alpha]_D^{20}$ –176 (*c* 1.01, $CHCl_3$, 87% ee); IR (KBr) 1789, 1681, 1470, 1378, 1241, 1109, 1042 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (3H, d, *J* = 6.4 Hz), 0.89 (3H, d, *J* = 6.4 Hz), 1.12 (1H, ddd, *J* = 4.4, 9.6, 14.0 Hz), 1.35 (1H, ddd, *J* = 4.4, 9.6, 14.0 Hz), 1.61-1.71 (1H, m), 2.22 (1H, dd, *J* = 10.0, 16.4 Hz), 2.60-2.69 (1H, m), 2.78 (1H, dd, *J* = 4.4, 16.4 Hz), 4.05-4.16 (2H, m), 4.50 (2H, t, *J* = 8.0 Hz), 4.58 (1H, ddd, *J* = 2.8, 2.8, 7.2 Hz), 6.12 (1H, dd, *J* = 2.8, 10.0

Hz), 6.74 (1H, dd, *J* = 2.8, 10.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.6, 24.6, 34.8, 41.1, 42.8, 43.1, 46.8, 62.1, 130.6, 144.7, 153.2, 171.8, 198.4; LRMS (EI) *m/z* 265 (M^+, 26), 208 (48), 178 (61), 121 (100); HRMS (FAB) Calcd for $C_{14}H_{20}NO_4$ 266.1392, found 266.1400; HPLC: Daicel Chiralpak AD-H, 254 nm, flow rate: 1.0 mL/min, *n*-Hexane:*i*PrOH=90:10, retention time: 22.3 min (minor isomer) and 23.4 min (major isomer).

Compound 5e: According to the procedure described for the synthesis of **5d**, **5e** was obtained in 29% yield with 56% ee. **5e**: Colorless solid; mp 93-94 °C; $[\alpha]_D^{23}$ –111 (*c* 0.82, $CHCl_3$, 56% ee); IR (KBr) 1778, 1694, 1391, 1223, 1113, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, d, *J* = 6.8 Hz), 0.96 (3H, d, *J* = 6.8 Hz), 1.68-1.76 (1H, m), 2.31 (1H, dd, *J* = 10.8, 15.2 Hz), 2.54-2.63 (2H, m), 4.10 (2H, t, *J* = 8.0 Hz), 4.50 (2H, t, *J* = 8.0 Hz), 4.86 (1H, ddd, *J* = 2.4, 2.8, 8.0 Hz), 6.11 (1H, dd, *J* = 2.4, 10.0 Hz), 6.71 (1H, dd, *J* = 2.8, 10.0 Hz); ^{13}C NMR ($CDCl_3$) δ 17.6, 20.7, 29.6, 37.0, 42.5, 42.9, 45.0, 62.1, 130.5, 145.1, 153.2, 172.1, 198.9; LRMS (EI) *m/z* 251 (M^+, 9), 208 (38), 164 (24), 121 (100); HRMS (FAB) Calcd for $C_{13}H_{18}NO_4$ 252.1236, found 252.1237; HPLC: Daicel Chiralcel OJ-H, 254 nm, flow rate: 1.0 mL/min, *n*-Hexane:*i*PrOH=75:25, retention time: 21.4 min (major isomer) and 31.5 min (minor isomer).

Compound 5f: According to the procedure described for the synthesis of **5a**, **5f** was obtained in 79% yield with 88% ee. **5f**: $[\alpha]_D^{24}$ –156 (*c* 2.67, $CHCl_3$, 88% ee); IR (KBr) 1777, 1681, 1379, 1236, 1114, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.60 (1H, dd, *J* = 3.2, 16.4 Hz), 2.70 (1H, dd, *J* = 4.4, 16.4 Hz), 2.99-3.08 (1H, m), 3.58 (1H, dd, *J* = 4.8, 11.2 Hz), 3.64 (1H, dd, *J* = 5.2, 11.2 Hz), 4.04-4.16 (2H, m), 4.49-4.53 (2H, m), 4.87 (1H, ddd, *J* = 2.8, 2.8, 8.4 Hz), 6.11 (1H, dd, *J* = 2.8, 10.4 Hz), 6.76 (1H, dd, *J* = 2.8, 10.4 Hz); ^{13}C NMR ($CDCl_3$) δ 38.3, 39.7, 42.8, 43.8, 46.9, 62.3, 130.2, 144.3, 153.1, 170.7, 196.8; LRMS (EI) *m/z* 257 (M^+, 12), 221 (5), 121 (100); HRMS (FAB) Calcd for $C_{11}H_{13}ClNO_4$ 258.0533, found 258.0532; HPLC: Daicel Chiralcel OJ-H, 254 nm, flow rate: 1.0 mL/min, *n*-Hexane:*i*PrOH=60:40, retention time: 32.1 min (major isomer) and 37.8 min (minor isomer).

Compound 5g: According to the procedure described for the synthesis of **5c**, **5g** was obtained in 96% yield with 94% ee. **5g**: Colorless solid; mp 106-108 °C; $[\alpha]_D^{23}$ –157 (*c* 1.01, $CHCl_3$, 94% ee); IR (KBr) 1765, 1680, 1476, 1454, 1382, 1235, 1112 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.67-1.86 (2H, m), 2.34 (1H, dd, *J* = 10.0, 16.4 Hz), 2.56 (1H, ddd, *J* = 6.4, 10.4, 13.6 Hz), 2.61-2.68 (1H, m), 2.74 (1H, ddd, *J* = 5.6, 10.4, 13.6 Hz), 2.84 (1H, dd, *J* = 4.4, 16.4 Hz), 4.04-4.08 (2H, m), 4.44-4.48 (2H, m), 4.65 (1H, dt, *J* = 2.8, 2.8, 7.2 Hz), 6.13 (1H, dd, *J* = 2.8, 10.4 Hz), 6.73 (1H, dd, *J* = 2.8, 10.4 Hz), 7.15-7.20 (3H, m), 7.26-7.30 (2H, m); ^{13}C NMR ($CDCl_3$) δ 32.6, 35.4, 36.6, 41.0, 42.8, 46.4, 62.1, 126.0, 128.3, 128.4, 130.7, 141.2, 144.6, 153.2, 171.5, 198.0; LRMS (EI) *m/z* 313 (M^+, 18), 226 (45), 208 (52), 91 (100); HRMS (FAB) Calcd for $C_{18}H_{20}NO_4$ 314.1392, found 314.1393; HPLC: Daicel Chiralpak AD-H, 254 nm, flow rate: 1.0 mL/min, *n*-Hexane:*i*PrOH=85:15, retention time: 27.4 min (major) and 29.4 min (minor).

Compound 5h: According to the procedure described for the synthesis of **5a**, **5h** was obtained in

97% yield with 89% ee. **5h**: Colorless solid; mp 78-79 °C; $[\alpha]_D^{22}$ –78.9 (*c* 1.01, $CHCl_3$, 84% ee); IR (KBr) 1778, 1695, 1388, 1224, 1112, 1043 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (1H, dd, *J* = 12.8, 16.4 Hz), 2.57 (1H, dd, *J* = 4.0, 16.4 Hz), 2.93-3.03 (1H, m), 3.40 (1H, ddd, *J* = 6.8, 8.8, 10.0 Hz), 3.54-3.57 (2H, m), 3.78-3.90 (2H, m), 4.21 (1H, dd, *J* = 8.8, 16.4 Hz), 4.37 (1H, d, *J* = 11.2 Hz), 4.46 (1H, d, *J* = 11.2 Hz), 4.96 (1H, ddd, *J* = 2.4, 2.8, 9.2 Hz), 6.12 (1H, dd, *J* = 2.8, 10.0 Hz), 6.69 (1H, dd, *J* = 2.4, 10.0 Hz), 7.28-7.37 (5H, m); ^{13}C NMR ($CDCl_3$) δ 38.7, 39.0, 42.5, 43.9, 61.7, 73.0, 73.2, 127.7, 127.9, 128.3, 130.1, 137.9, 145.9, 153.5, 172.6, 197.4; LRMS (EI) *m/z* 329 (M^+, 1), 221 (17), 208 (19), 121 (31), 91 (100); HRMS (FAB) Calcd for $C_{18}H_{20}NO_5$ 330.1341, found 330.1342; HPLC: Daicel Chiralcel OJ-H, 254 nm, flow rate: 1.0 mL/min, *n*-Hexane:*i*PrOH=55:45, retention time: 30.3 min (major) and 41.8 min (minor).

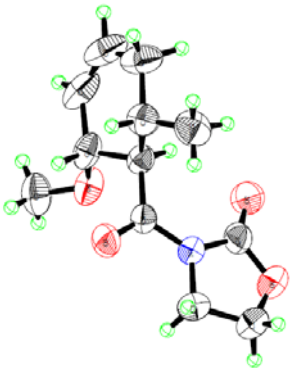
Compound 5i: A mixture of $Yb(OTf)_3$ (18.6 mg, 0.030 mmol) and BINAMIDE **3g** (20.3 mg, 0.036 mmol) was dried at 90 °C under reduced pressure (<0.1 mmHg) for 0.5 h. After the mixture was allowed to cool to room temperature, CH_2Cl_2 (1.0 ml), dienophile **2i** in CH_2Cl_2 (0.5 mL), and DBU (11 μL, 0.072 mmol) were successively added and the mixture was stirred for 2 h. Then diene **1a** (0.12 mL, 0.60 mmol) was added at 0 °C, and the mixture was stirred for 2 h at the same temperature. H_2O (1 mL) was then added to quench the reaction, and the insoluble materials were filtered through a pad of Celite. After a usual workup, the crude product was dissolved in CH_2Cl_2 (3.0 mL). To this solution was added BF_3-OEt_2 (42 μL, 0.33 mmol) at –78 °C, and then stirred at the same temperature for 1 h. The reaction was quenched with brine (1 mL) and the mixture was extracted with CH_2Cl_2. Usual workup gave a residue which was purified by column chromatography (SiO_2, hexane/AcOEt: 2/3) to give **5i** (74.8 mg, 93%) as a colorless oil. The enantiomeric excess of the product was determined to be 92% ee by HPLC analysis. $[\alpha]_D^{21}$ –102 (*c* 1.01, $CHCl_3$, 81% ee); IR (KBr) 1778, 1697, 1680, 1384, 1310, 1226, 1115, 1037 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.59 (1H, dd, *J* = 13.2, 16.4 Hz), 2.97 (1H, dd, *J* = 4.4, 16.4 Hz), 3.63 (1H, ddd, *J* = 4.4, 9.2, 13.2 Hz), 3.73 (3H, s), 4.02-4.17 (2H, m), 4.48-4.54 (2H, m), 5.04 (1H, ddd, *J* = 2.8, 2.8, 9.2 Hz), 6.13 (1H, dd, *J* = 2.8, 10.4 Hz), 6.81 (1H, dd, *J* = 2.8, 10.4 Hz); ^{13}C NMR ($CDCl_3$) δ 38.4, 41.7, 42.8, 43.5, 52.5, 62.4, 130.2, 144.1, 153.2, 170.8, 172.5, 195.5; LRMS (EI) *m/z* 267 (M^+, 3), 236 (9), 208 (9), 180 (100); HRMS (FAB) Calcd for $C_{12}H_{14}NO_6$ 268.0821, found 268.0826; HPLC: Daicel Chiralpak AD-H, 254 nm, flow rate: 1.0 mL/min, *n*-Hexane:*i*PrOH=85:15, retention time: 34.9 min (major) and 47.2 min (minor).

Experimental Procedures for the Synthesis of Compounds 6-10

Compound 6: To a solution of **4a** (2.82 g, 7.63 mmol) and *n*-$Bu_4NSiPh_3F_2$ (2.03 mL, 3.82 mmol) in CH_2Cl_2 (25 mL) was added NfF (2.74 mL, 15.3 mmol) at 0 °C. After being stirred for 0.5 h at the same temperature, the reaction was quenched with aqueous saturated $NaHCO_3$ (5 mL). This mixture was extracted with CH_2Cl_2. Usual workup gave a residue which was purified by column chromatography (SiO_2, hexane/AcOEt: 2/1) to give **6** (3.39 g, 83%) as a yellow oil. $[\alpha]_D^{22}$ +33.9 (*c* 1.00, $CHCl_3$, 90% ee); IR (neat) 3055, 2987, 1783, 1697, 1421, 1387, 1265, 1241, 1206, 1145, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (3H, d, *J* = 6.4 Hz), 2.17-2.43 (3H, m), 3.31 (3H, s), 3.97-4.19 (3H,

m), 4.42-4.51 (3H, m), 5.92 (1H, brs); ^{13}C NMR ($CDCl_3$) δ 17.9, 31.7, 35.4, 42.7, 47.8, 55.8, 61.7, 77.9, 109-118 (m, $CF_2CF_2CF_2CF_3$), 117.7, 148.9, 153.2, 174.5; LRMS (FAB) *m/z* 576 $(M+K)^+$; HRMS (FAB) Calcd for $C_{16}H_{16}F_9N_2O_7SK$ 576.0141, found 576.1040.

Compound 7: To a solution of **6** (3.39 g, 6.30 mmol) in DMF (21 mL) was successively added Et_3N (3.5 mL, 25.2 mmol), HCO_2H (0.7 mL, 18.9 mmol), PPh_3 (83 mg, 0.32 mmol) and $Pd(PPh_3)_2Cl_2$ (224 mg, 0.32 mmol) at room temperature. After being stirred for 6 h at 65 °C, the mixture was filtered through a pad of Celite, and the residue was washed with AcOEt. This mixture was extracted with AcOEt. Usual workup gave a residue that was purified by column chromatography (SiO_2, hexane/AcOEt: 2/1) to give **7** (1.33 g, 88%) as a yellow solid. mp 67.5-71 °C; $[\alpha]_D^{24}$ +73.3 (*c* 0.96, $CHCl_3$, 90% ee); IR (KBr) 3055, 2985, 2831, 1780, 1694, 1386 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (3H, d, *J* = 6.8 Hz), 1.91 (1H, ddd, *J* = 3.6, 10.4, 19.2 Hz), 1.98-2.08 (1H, m), 2.14 (1H, ddd, *J* = 3.2, 4.8, 19.2 Hz), 3.30 (3H, s), 4.03-4.16 (3H, m), 4.34 (1H, ddd, *J* = 1.6, 3.2, 9.2 Hz), 4.41 (2H, t, *J* = 8.0 Hz), 5.77-5.83 (2H, m); ^{13}C NMR ($CDCl_3$) δ 18.4, 32.4, 33.8, 42.7, 48.7, 55.3, 61.5, 79.1, 126.5, 128.6, 153.3, 176.2; LRMS (FAB) *m/z* 278 $(M+K)^+$; HRMS (FAB) Calcd for $C_{12}H_{17}NO_4K$ 278.0795, found 278.0814.



X-ray structure of compound **7** shown as an enantiomer.

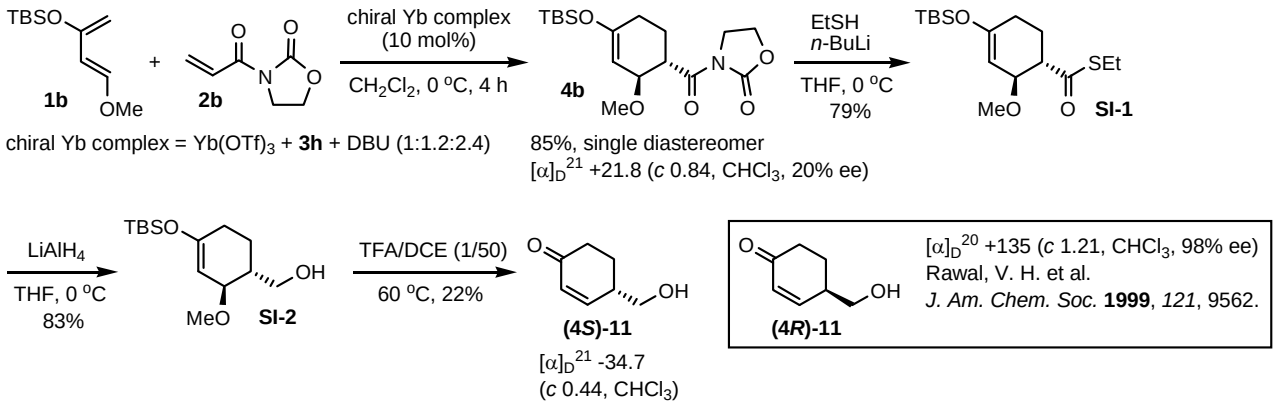
Compound 8: To a solution of **6** (40 mg, 74 μmol) and $Pd(PPh_3)_4$ (2.2 mg, 1.9 μmol) in DME (7 mL) was successively added $PhB(OH)_2$ (28 mg, 228 μmol) in EtOH (0.15 mL) and 2 M aqueous $NaHCO_3$ (38 μL) at room temperature. After being stirred for 20 h under reflux, the mixture was filtered through a pad of Celite, and the residue was washed with CH_2Cl_2. This mixture was extracted with CH_2Cl_2. Usual workup gave a residue which was purified by column chromatography (SiO_2, hexane/AcOEt: 2/1) to give **8** (20.0 mg, 86%) as a colorless oil. $[\alpha]_D^{23}$ +70.7 (*c* 0.80, $CHCl_3$, 90% ee); IR (neat) 3055, 2986, 2830, 1781, 1696, 1386 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (3H, d, *J* = 6.8 Hz), 2.12-2.24 (1H, m), 2.31-2.40 (1H, m), 2.53 (1H, dd, *J* = 4.8, 17.2 Hz), 3.37 (3H, s), 4.06-4.22 (3H, m), 4.43 (2H, t, *J* = 7.6 Hz), 4.51-4.54 (1H, m), 6.15 (1H, brs), 7.25-7.42 (5H, m); ^{13}C NMR ($CDCl_3$) δ 18.6, 32.7, 36.3, 42.8, 48.5, 55.4, 61.6, 79.9, 123.3, 125.4, 127.5, 128.3, 138.7, 140.5, 153.3, 176.2; LRMS (FAB) *m/z* 354 $(M+K)^+$; HRMS (FAB) Calcd for $C_{18}H_{21}NO_4K$ 354.1108, found 354.1117.

Compound 9: To a solution of **6** (74 mg, 0.14 mmol), $Pd(PPh_3)_4$ (2.2 mg, 1.9 μmol), and CuI (1.3

mg, 7.0 μmol) in DME (0.28 mL) was successively added Et_3N (78 μL, 0.56 μmol) and phenylacetylene (31 μL, 0.28 mmol) at room temperature. After being stirred for 0.5 h at the same temperature, the mixture was filtered through a pad of Celite, and the residue was washed with AcOEt. This mixture was extracted with AcOEt. Usual workup gave a residue that was purified by column chromatography (SiO_2, hexane/AcOEt: 2/1) to give **9** (47.2 mg, 99%) as a yellow oil. $[\alpha]_D^{24}$ +54.3 (*c* 1.20, $CHCl_3$, 90% ee); IR (neat) 3054, 2984, 1782, 1696, 1386, 896 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (3H, d, *J* = 6.4 Hz), 2.06-2.21 (2H, m), 2.34-2.39 (1H, m), 3.34 (3H, s), 4.04-4.17 (3H, m), 4.41-4.45 (3H, m), 6.25 (1H, brs), 7.30-7.33 (3H, m), 7.41-7.45 (2H, m); ^{13}C NMR ($CDCl_3$) δ 18.2, 32.4, 37.9, 42.8, 48.1, 55.7, 61.6, 79.1, 89.0, 122.6, 123.1, 128.2, 128.3, 131.6, 132.6, 153.3, 175.8; LRMS (EI) *m/z* 339 (M^+, 33), 307 (44), 252 (48), 205 (100); HRMS (FAB) Calcd for $C_{20}H_{21}NO_4K$ 378.1108, found 378.1140.

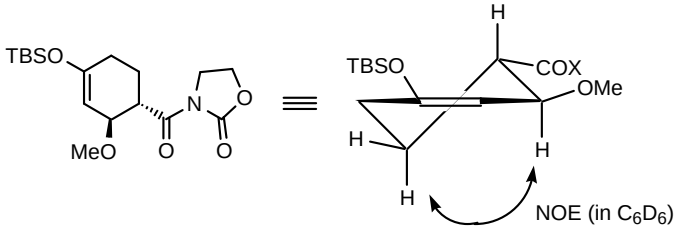
Compound 10: To a solution of **6** (52 mg, 96 μmol) in DMF (0.96 mL) was successively added Et_3N (40 μL, 288 μmol), methyl acrylate (11 μL, 192 μmol), and $Pd(PPh_3)_2Cl_2$ (3.4 mg, 4.8 μmol) at room temperature. After being stirred for 4 h at 70 °C, the mixture was filtered through a pad of Celite, and the pad was eluted with AcOEt. This mixture was extracted with AcOEt. Usual workup gave a residue that was purified by column chromatography (SiO_2, hexane/AcOEt: 2/1) to give **10** (22.0 mg, 71%) as a yellow solid. mp 112-113.5 °C; $[\alpha]_D^{20}$ +145 (*c* 1.03, $CHCl_3$, 99% ee); IR (KBr) 3055, 2987, 2832, 1782, 1718, 1699, 1386 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (3H, d, *J* = 5.6 Hz), 1.97-2.12 (2H, m), 2.32 (1H, dd, *J* = 3.6, 16.8 Hz), 3.34 (3H, s), 3.78 (3H, s), 4.04-4.16 (3H, m), 4.41-4.45 (3H, m), 5.86 (1H, d, *J* = 15.6 Hz), 6.19 (1H, brs), 7.31 (1H, d, *J* = 15.6 Hz); ^{13}C NMR ($CDCl_3$) δ 18.3, 32.0, 32.9, 42.7, 48.5, 51.6, 55.9, 61.6, 79.4, 117.5, 135.3, 135.7, 145.7, 153.3, 167.4, 175.5; LRMS (FAB) *m/z* 362 $(M+K)^+$; HRMS (FAB) Calcd for $C_{16}H_{21}NO_6K$ 362.1006, found 362.0987.

Determination of the Absolute Configuration of 4b.



Compound 4b: A mixture of $Yb(OTf)_3$ (37.2 mg, 0.060 mmol) and BINAMIDE **3h** (55.0 mg, 0.072 mmol) was dried at 90 °C under reduced pressure (<0.1 mmHg) for 0.5 h. After the mixture was allowed to cool to room temperature, CH_2Cl_2 (2.0 ml) and DBU (22 μL, 0.072 mmol) were successively added and the mixture was stirred for 2 h. Dienophile **2b** (85 mg, 0.60 mmol) in

CH_2Cl_2 (1.0 mL) and diene **1b** (0.30 mL, 1.20 mmol) were successively added at 0 °C, and the mixture was stirred for 4 h at the same temperature. H_2O (1 mL) was then added to quench the reaction, and the insoluble materials were filtered. After a usual workup, the crude product was purified by column chromatography (SiO_2, hexane/Et_2O: 1/2) to give **4b** (181.8 mg, 85%) as a colorless oil. The enantiomeric excess of the product was determined to be 20% ee by HPLC analysis (Daicel Chiralcel OJ-H) after conversion to the cyclohexenone **5b**. $[\alpha]_D^{21}$ +21.8 (*c* 0.84, $CHCl_3$, 20% ee); IR (neat) 2930, 2857, 1771, 1698, 1652, 1472, 1458, 1395 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (6H, s), 0.92 (9H, s), 1.63-1.74 (1H, m), 1.98-2.05 (2H, m), 2.26-2.36 (1H, m), 3.31 (3H, s), 3.80 (1H, ddd, *J* = 2.8, 8.4, 8.4 Hz), 3.98-4.13 (2H, m), 4.37-4.47 (3H, m), 4.99 (1H, dd, *J* = 2.0, 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.4, 17.9, 24.5, 25.6, 29.2, 42.8, 43.7, 55.4, 61.9, 76.3, 103.3, 153.0, 153.1, 174.6; LRMS (FAB) *m/z* 394 $(M+K)^+$; HRMS (FAB) Calcd for $C_{17}H_{29}NO_5SiK$ 394.1452, found 394.1457.



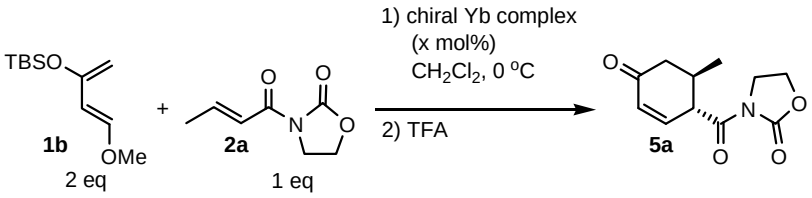
Compound SI-1: To a solution of EtSH (115 μL, 1.55 mmol) in THF (5 mL), *n*-BuLi [0.65 mL (1.6 M solution of hexane), 1.04 mmol] was added dropwise at –78 °C. After being stirred at 0 °C for 0.5 h, **4b** (184 mg, 0.52 mmol) in THF (2 mL) was added at the same temperature. Then the mixture was stirred at the same temperature for 0.5 h before adding aqueous saturated NH_4Cl (1 mL) to quench the reaction. The mixture was extracted with Et_2O. After a usual workup, the crude product was purified by column chromatography (SiO_2, hexane/AcOEt: 20/1) to give **SI-1** (135.6 mg, 79%) as a colorless oil. $[\alpha]_D^{21}$ +20.1 (*c* 1.04, $CHCl_3$, 20% ee); IR (neat) 2931, 2858, 1681, 1667, 1465, 1363, 1259, 1209, 1093 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (6H, s), 0.91 (9H, s), 1.26 (3H, t, *J* = 7.2 Hz), 1.80-1.90 (1H, m), 1.93-2.08 (2H, m), 2.11-2.20 (1H, m), 2.74 (1H, ddd, *J* = 3.6, 7.2, 11.2 Hz), 2.84-2.97 (2H, m), 3.32 (3H, s), 4.28-4.32 (1H, m), 4.96-4.97 (1H, m); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.4, 14.6, 18.0, 23.2, 24.5, 25.6, 28.7, 53.6, 55.8, 76.5, 103.5, 153.4, 201.3; LRMS (FAB) *m/z* 369 $(M+K)^+$; HRMS (FAB) Calcd for $C_{16}H_{30}O_3SSiK$ 369.1322, found 369.1343.

Compound SI-2: To a suspension of $LiAlH_4$ (75 mg, 1.98 mmol) in THF (3 mL), **SI-1** (131 mg, 0.40 mmol) in THF (2 mL) was added at 0 °C and the mixture was stirred at the same temperature for 0.5 h. H_2O (5 drops), 10% aqueous NaOH (5 drops) and H_2O (15 drops) were added carefully. The mixture was filtered through a pad of Celite, and the residue was washed with CH_2Cl_2. The filtrate was concentrated to give a residue, which was purified by column chromatography (SiO_2, hexane/AcOEt: 2/1) to give **SI-2** (89.9 mg, 83%) as a colorless oil. $[\alpha]_D^{22}$ +5.7 (*c* 1.00, $CHCl_3$, 20% ee); IR (neat) 3388, 2930, 2858, 1662, 1472, 1362, 1254, 1207 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (6H, s), 0.92 (9H, s), 1.35-1.45 (1H, m), 1.71-1.88 (2H, m), 1.97 (1H, dt, *J* = 4.0, 8.8 Hz), 2.12-2.21 (1H, m), 2.66 (1H, dd, *J* = 2.8, 7.2 Hz), 3.34 (3H, s), 3.58-3.71 (2H, m), 3.91-3.93 (1H, m), 4.98 (1H, dd,

J = 2.0, 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.4, 18.0, 22.8, 25.6, 29.0, 40.2, 54.5, 66.8, 80.0, 103.1, 154.2; LRMS (FAB) 311 $(M+K)^+$; HRMS (FAB)*m/z* Calcd for $C_{14}H_{28}NO_3SiK$ 311.1445, found 311.1446.

Compound 11: To a solution of **SI-2** (85 mg, 0.31 mmol) in DCE (3 mL), TFA (60 μL) was added and the mixture was stirred at 60 °C for 0.5 h. The reaction was quenched with aqueous saturated $NaHCO_3$ (1 mL) and the mixture was extracted with CH_2Cl_2. Usual workup gave a residue that was purified by column chromatography (SiO_2, hexane/AcOEt: 1/2 to 1/3) to give **11** (8.8 mg, 22%) as a Colorless solid. $[\alpha]_D^{22}$ –34.7 (*c* 0.44, $CHCl_3$, 20% ee); ^{1}H NMR ($CDCl_3$) δ 1.67 (1H, brs), 1.77-1.87 (1H, m), 2.11-2.18 (1H, m), 2.41 (1H, ddd, J = 4.8, 12.4, 16.8 Hz), 2.56 (1H, ddd, J = 4.8, 4.8, 16.8 Hz), 2.61-2.69 (1H, m), 3.66-3.76 (2H, m), 6.08 (1H, dd, J = 2.4, 10.0 Hz), 6.97 (1H, ddd, J = 1.2, 2.4, 10.0 Hz).

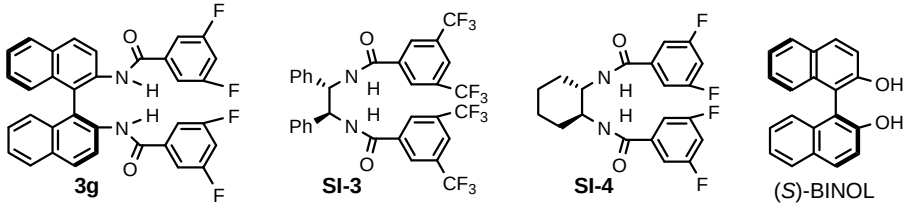
Application of Various Ligands to the Asymmetric Diels-Alder Reaction.[a]



chiral Yb complex = $Yb(OTf)_3$ + ligand + amine (1:1.2:2.4)

entry[a]	ligand	amine	x (mol%)	time (h)	yield (%)	ee (%)
1	**3g**	DBU	5	5	94	94
2	**SI-3**	DBU	10	30	58	43
3	**SI-4**	DBU	10	48	trace	-
4[b]	(*S*)-BINOL	*i*Pr_2NEt	10	4	9	-63[c]

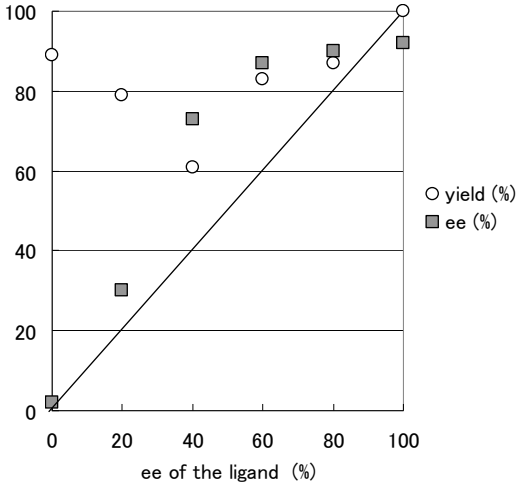
[a] In entries 1-3, the catalysts were prepared at room temperature for 2 h. [b] The catalyst was prepared at 0 °C for 0.5 h (Kobayashi, S. *et al. Tetrahedron Lett*. **1994**, *35*, 4639.). [c] Opposite enantiomer was obtaind.



SI-3: To a solution of (1*S*, 2*S*)-1,2-diamino-1,2-diphenylethane (127 mg, 0.60 mmol) and Et_3N (0.21 mL, 1.50 mmol) in CH_2Cl_2 (6 mL) was added 3,5-bistrifluoromethylbenzoylchloride (0.24 mL, 1.32 mmol) at 0 °C. After being stirred for 12 h at the same temperature, the reaction was quenched with 1N HCl (2 mL). This mixture was extracted with AcOEt. Usual workup gave a residue that was purified by column chromatography (SiO_2, hexane/acetone: 3/1) to give **SI-3** (380 mg, 92%) as a white solid. mp 258-261 °C; $[\alpha]_D^{22}$ –7.4 (*c* 0.50, acetone); IR (KBr) 1643, 1535, 1278, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.57 (2H, s), 7.14-7.28 (10, m), 8.29 (2H, s), 8.38 (4H, s), 9.67 (2H, brs); ^{13}C NMR ($CDCl_3$) δ 58.5, 121.6, 124.3, 124.8, 127.1, 127.3, 128.1 (d, J = 16.5 Hz), 130.5 (q, J = 32.9 Hz), 136.6, 139.5, 163.6; LRMS (EI) *m/z* 692 (M^+, 1), 673 (3), 346 (100), 241 (95); HRMS (FAB) Calcd for $C_{32}H_{21}F_{12}N_2O_2$ 693.1411, found 693.1375.

SI-4: To a solution of (1*S*, 2*S*)-1,2-diaminocyclohexane (91 mg, 0.80 mmol) and Et_3N (0.28 mL, 2.00 mmol) in CH_2Cl_2 (8 mL) was added 3,5-difluorobenzoylchloride (0.22 mL, 1.76 mmol) at 0 ^oC. After being stirred for 2 h at at the same temperature, the reaction was quenched with 1N HCl (2 mL). This mixture was extracted with AcOEt/acetone. Usual work up gave a residue which was purified by recrystallization from EtOH to give **SI-4** (219 mg, 70%) as a colorless needle. mp 263-265 ^oC; $[\alpha]_D^{22}$ +140 (*c* 0.51, acetone); IR (KBr) 1637, 1592, 1542, 1336, 1122, 981 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.27-1.35 (2H, m), 1.49-1.57 (2H, m), 1.76 (2H, d, *J* = 8.0 Hz), 1.87 (2H, d, *J* = 8.0 Hz), 3.89-3.99 (2H, m), 7.37-7.42 (6H, m), 8.50 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (DMSO-d_6) δ 24.6, 31.2, 53.0, 106.3 (t, *J* = 25.0 Hz), 110.4 (dd, *J* = 7.4, 18.9 Hz), 138.4 (t, *J* = 8.3 Hz), 162.0 (dd, *J* = 13.1, 246.0 Hz), 163.7; LRMS (EI) *m/z* 394 (M^+, 21), 237 (100), 210 (40), 141 (100); HRMS (FAB) Calcd for $C_{20}H_{19}F_4N_2O_2$ 395.1383, found 395.1368.

(+)-Nonlinear Effect of BINAMIDE (2g) in Asymmetric Diels-Alder Reaction



ligand ee (%)	yield (%)	product ee (%)
20	79	30
40	61	73
60	83	87
80	87	90
100	100	92
0	89	2

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1. (a) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807. (b) Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451. (c) Myles, D. C.; Bigham, M. H. *Organic Synthesis* Vol. 70, Meyers, A. I. Eds., 231. (d) Burger, M. T.; Still, W. C. *J. Org. Chem.* **1996**, *61*, 775.

2. (a) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340. (b) Horst, K.; Juergen, K. *J. Chem. Soc.*, *Perkin Trans. 1* **1989**, 1168. (c) Sibi, M. P.; Rheault, T. R.; Chandramouli, S. V.; Jasperse, C. P. *J. Am. Chem. Soc.* **2002**, *124*, 2924. (d) Knol, J.; Feringa, B. L. *Synlett* **1995**, 1025.

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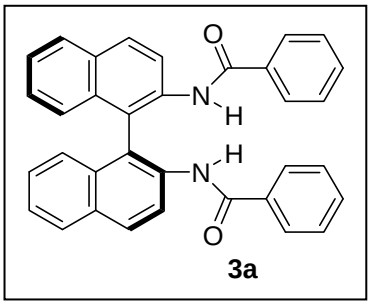

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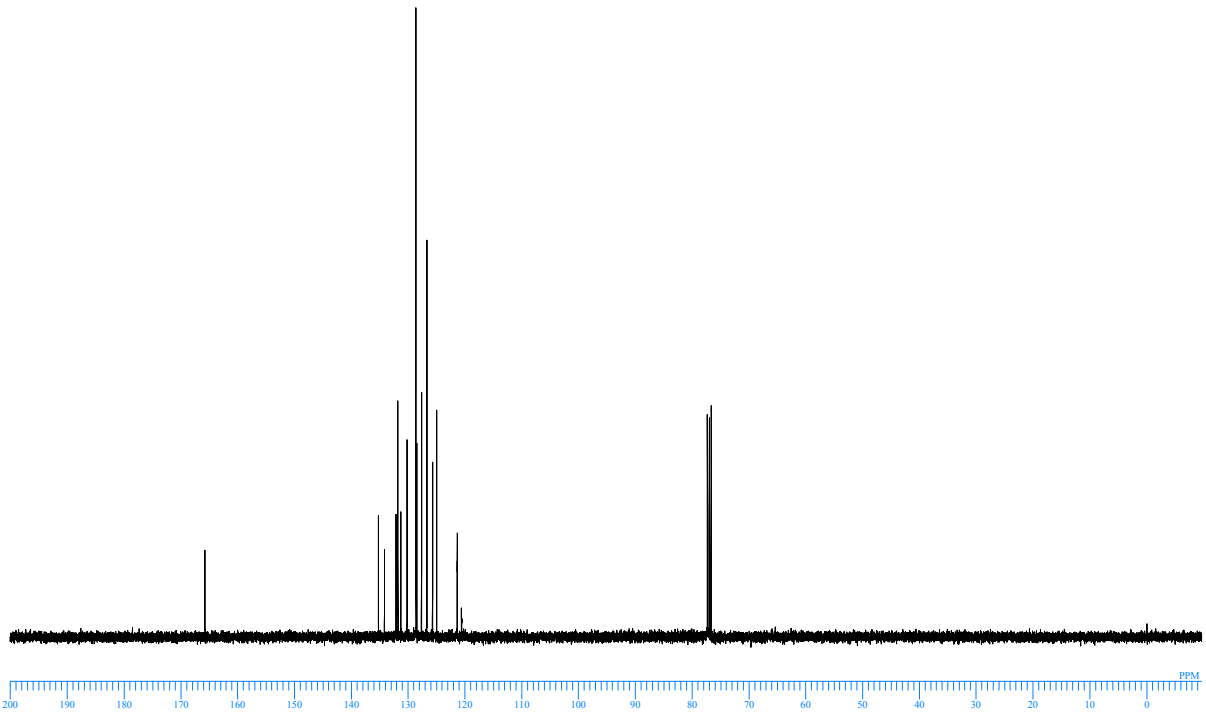

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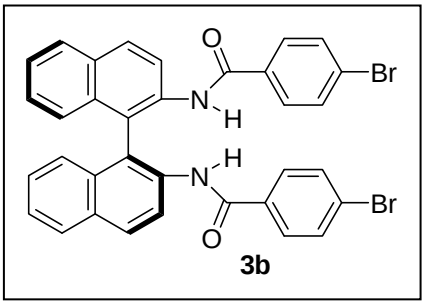

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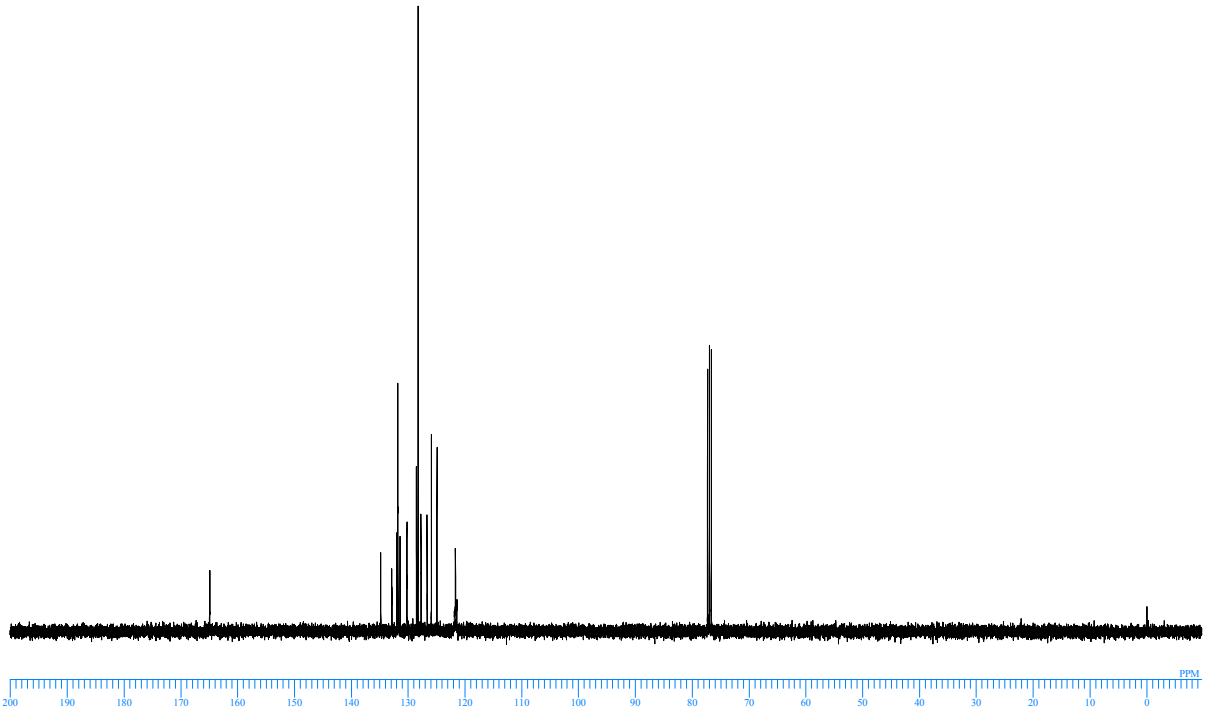

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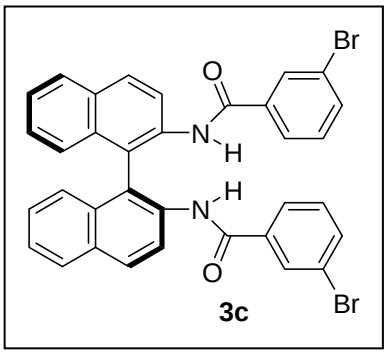

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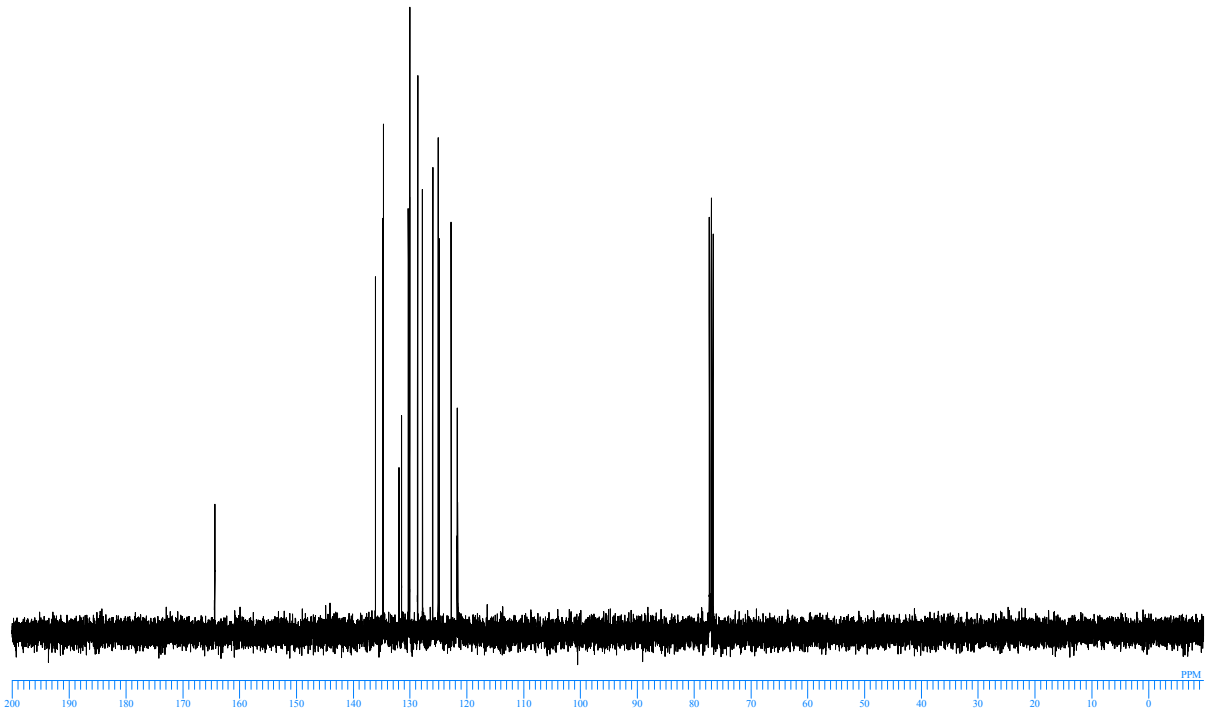

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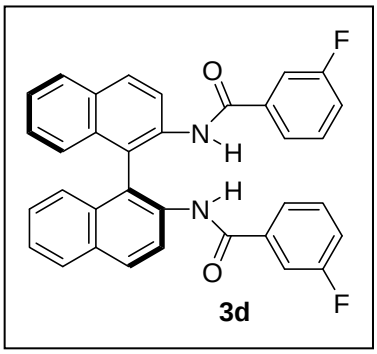

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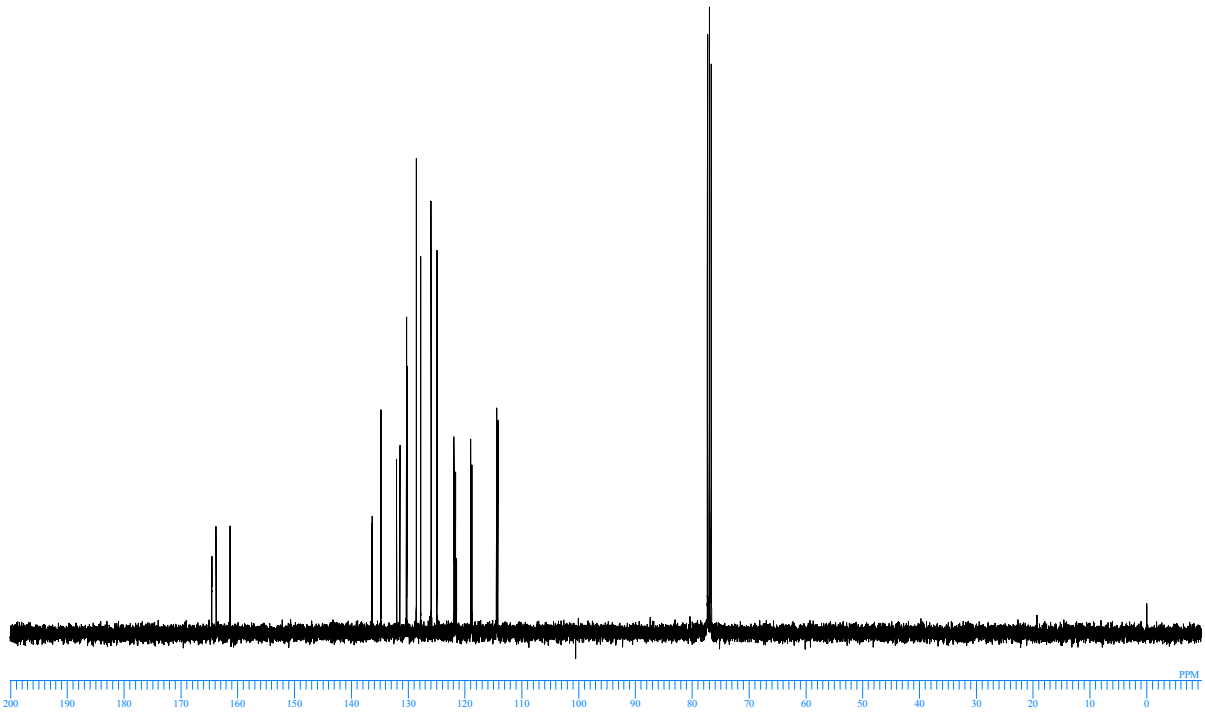

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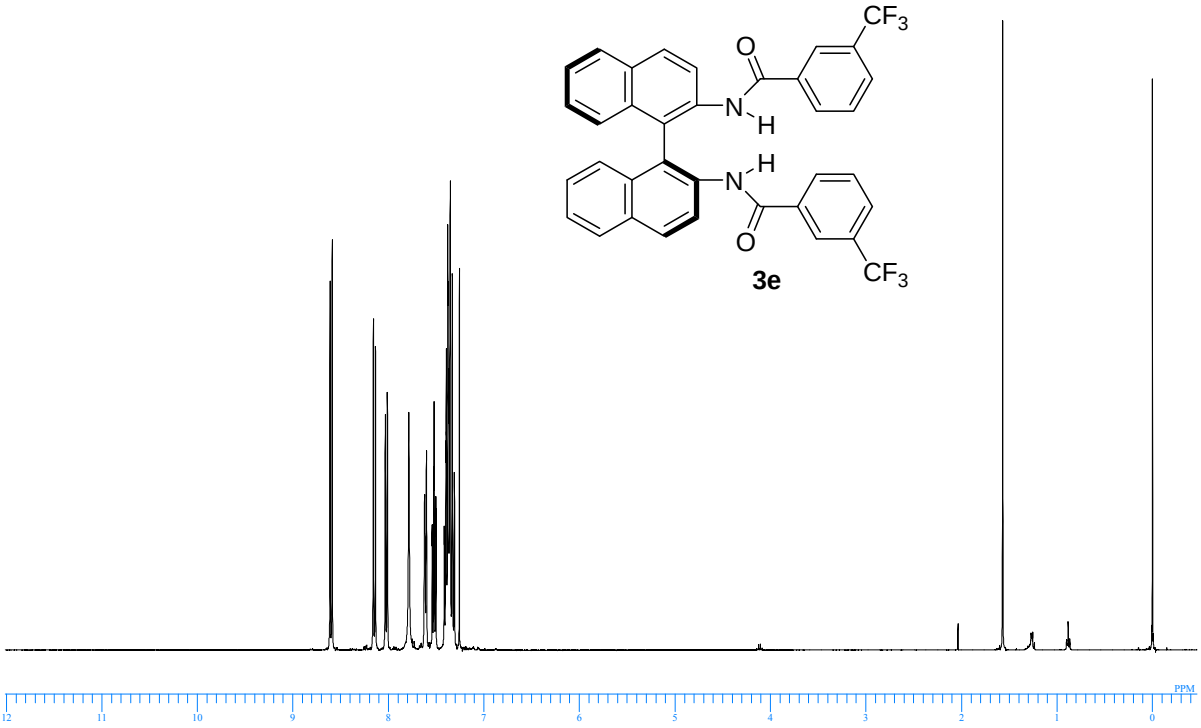

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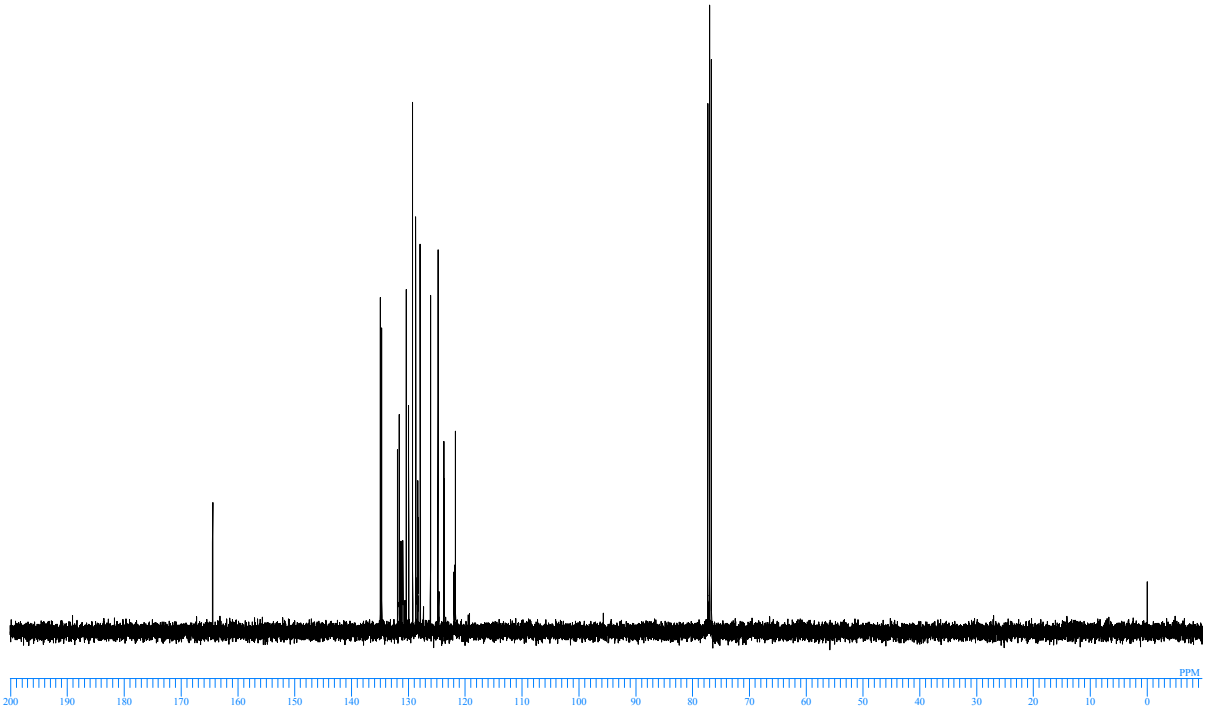

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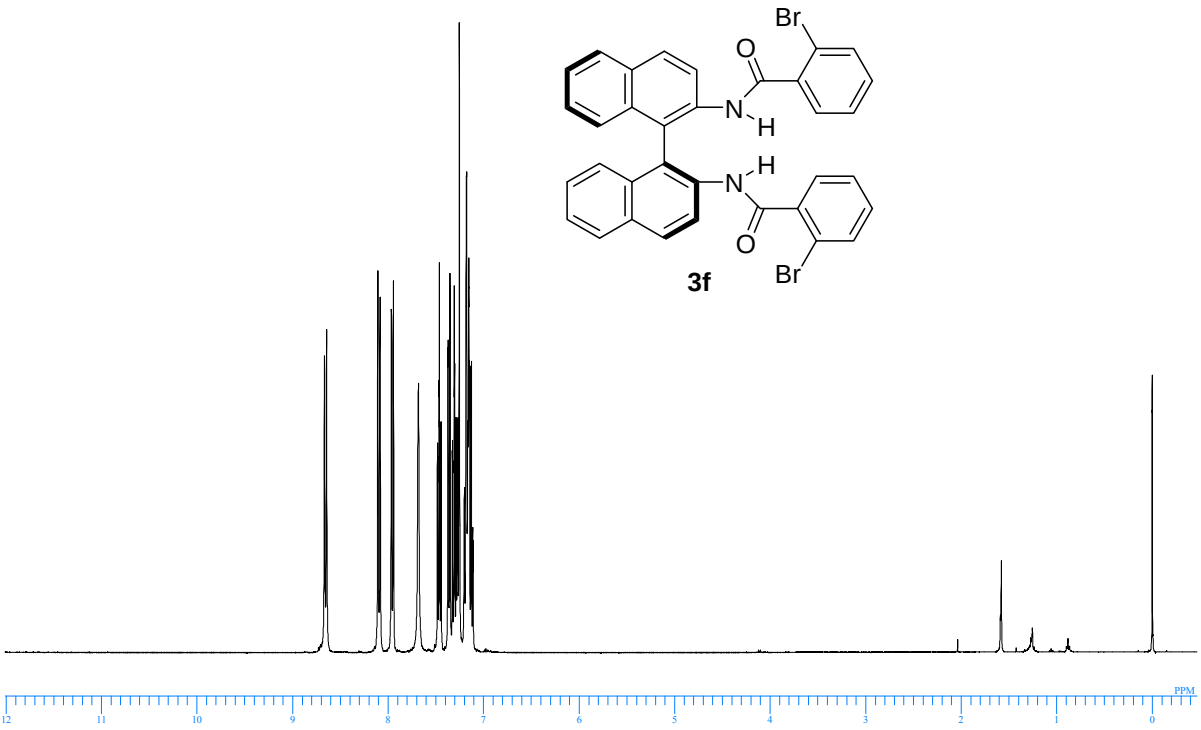

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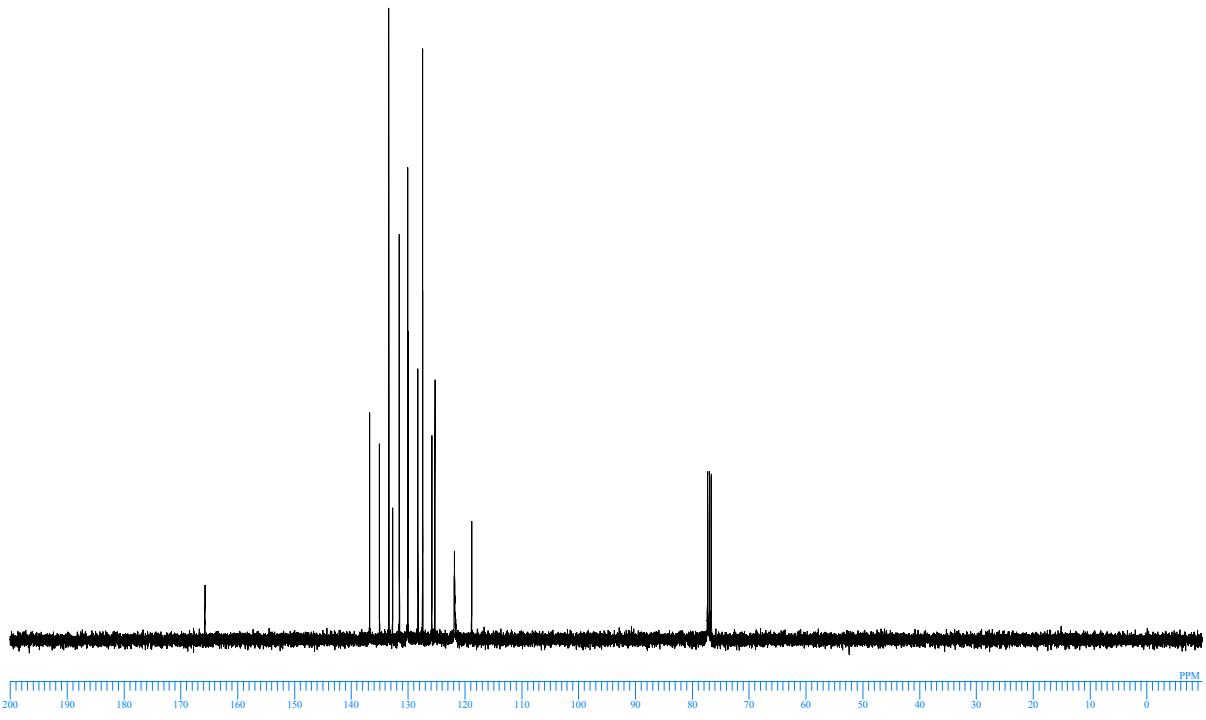

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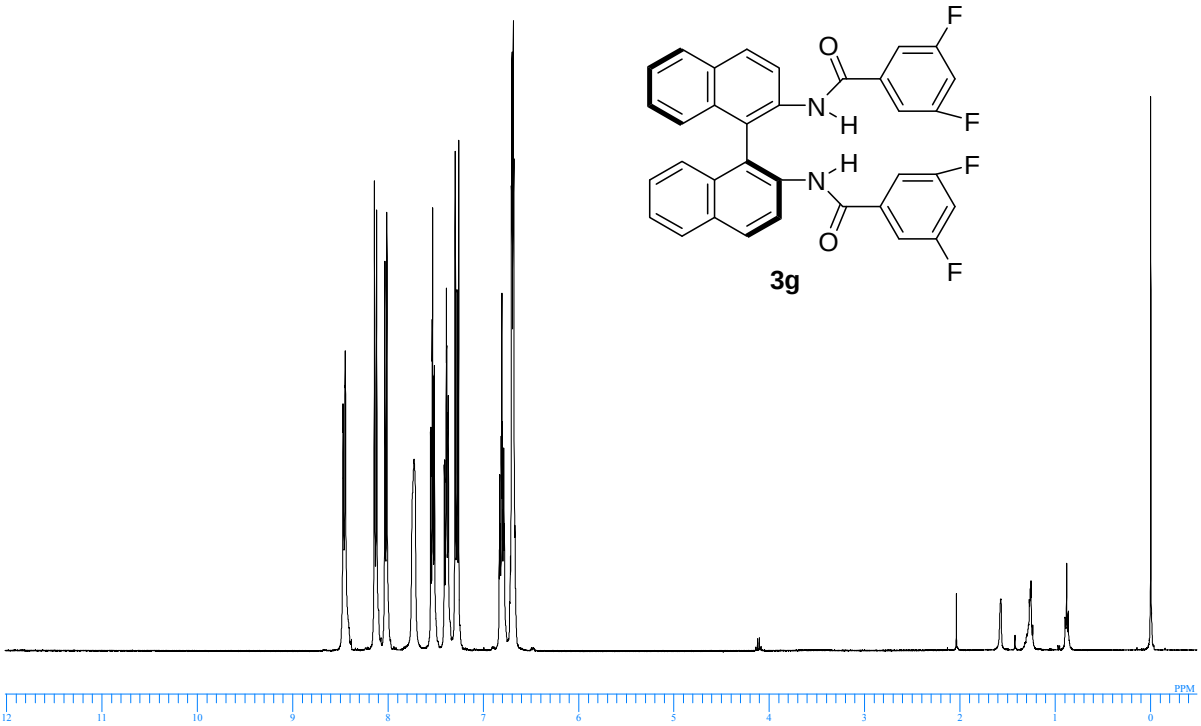

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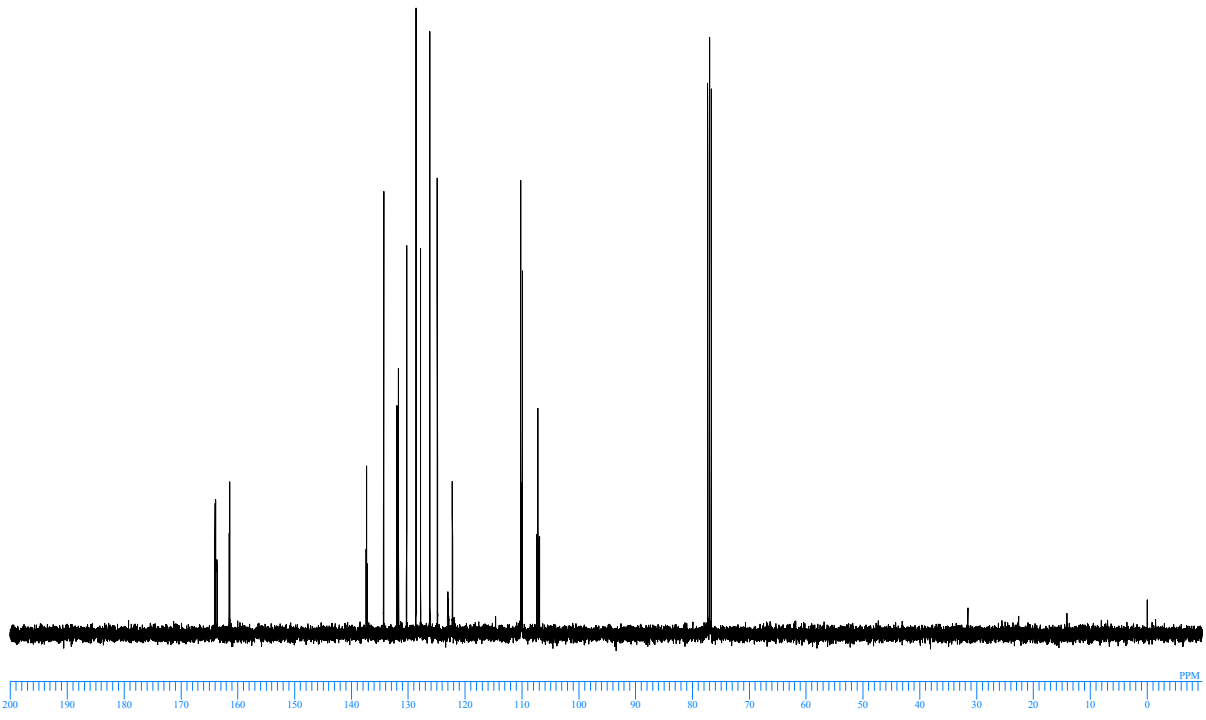

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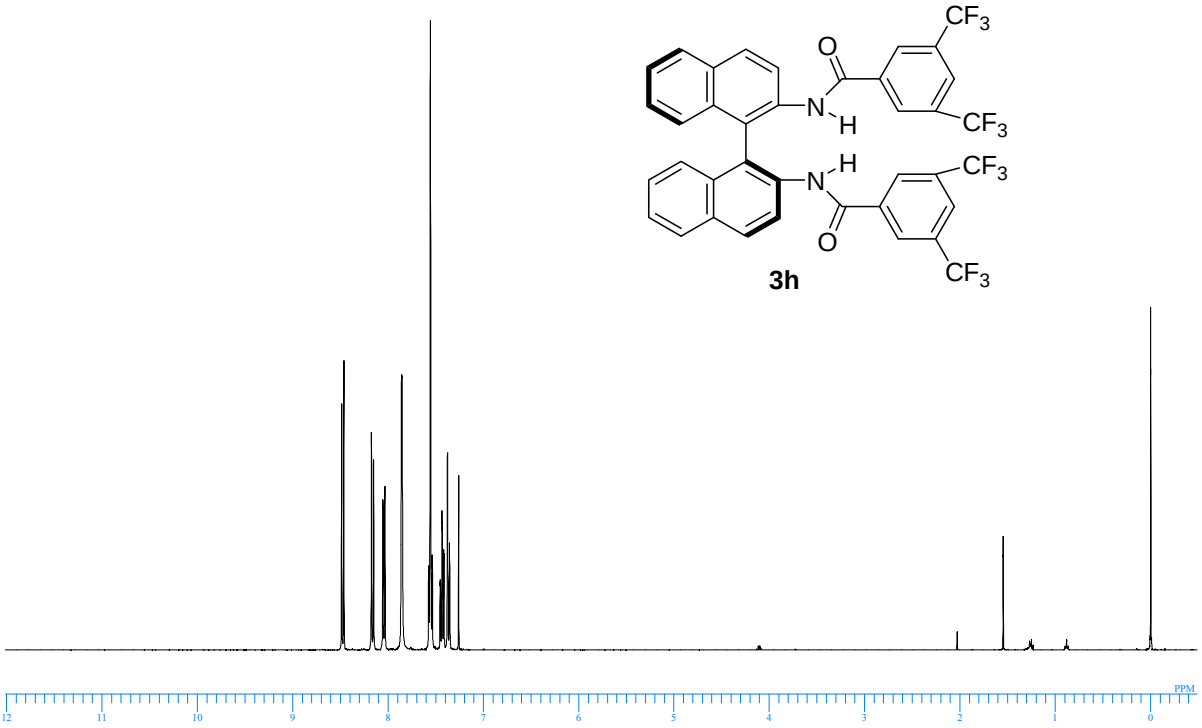

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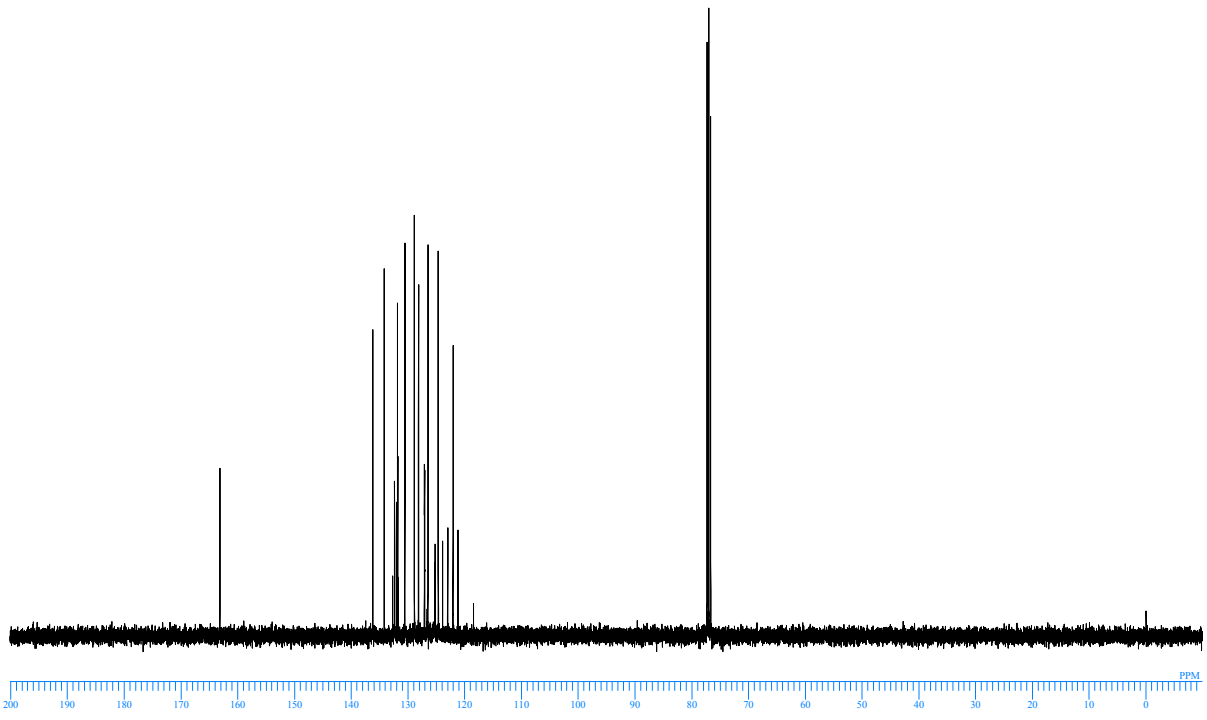

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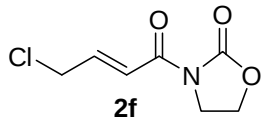

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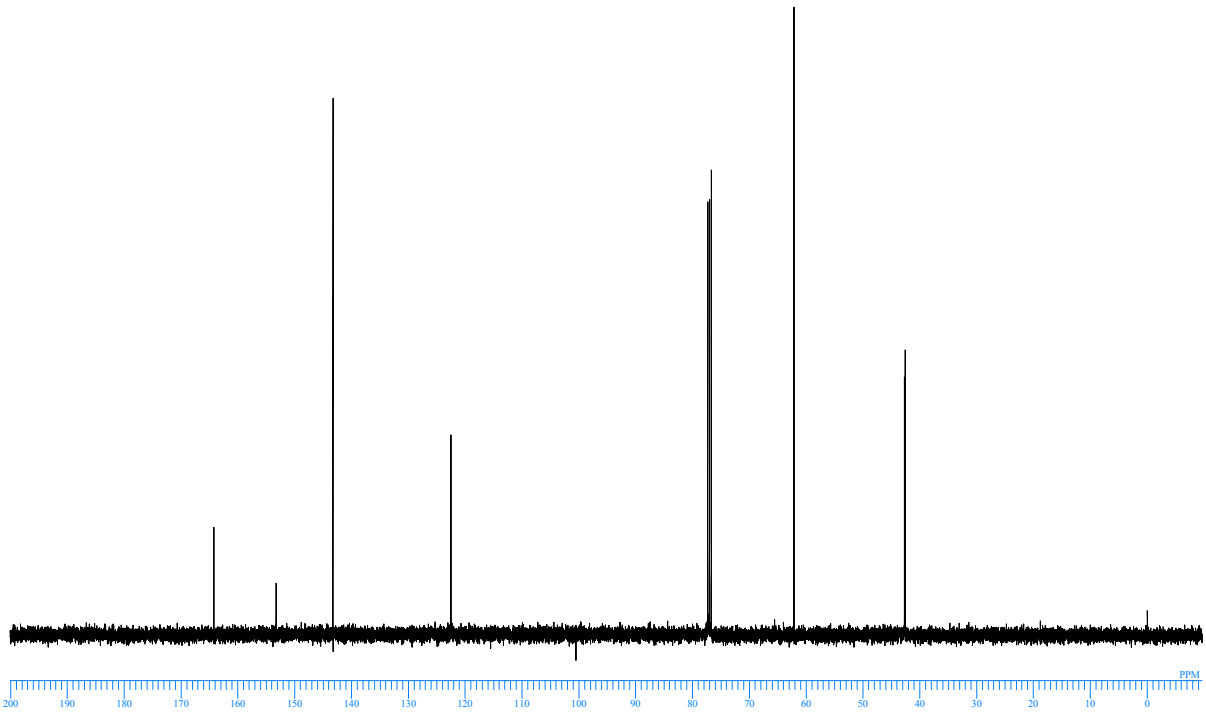

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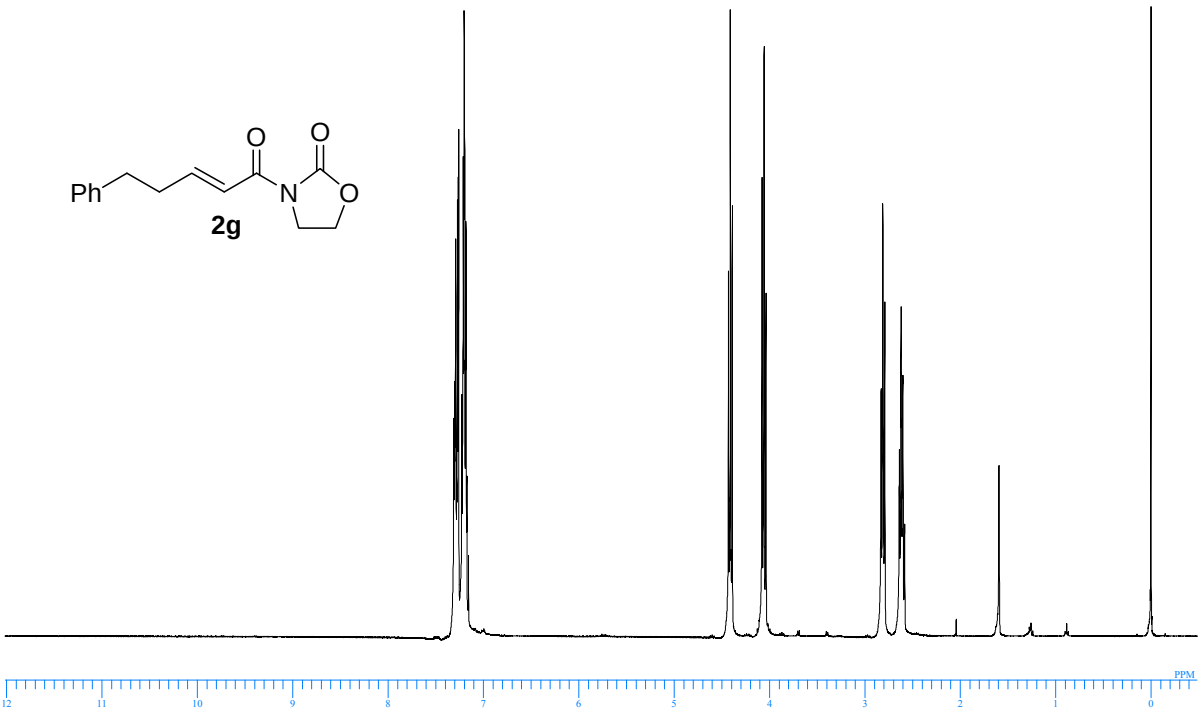

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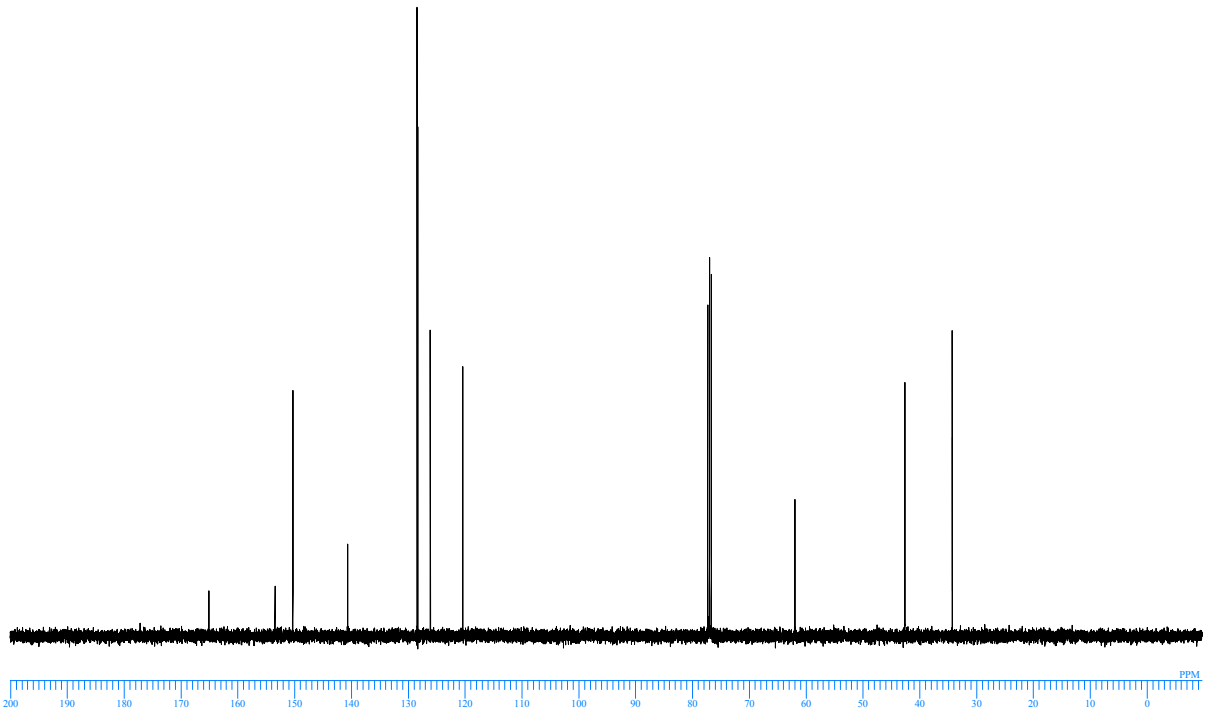

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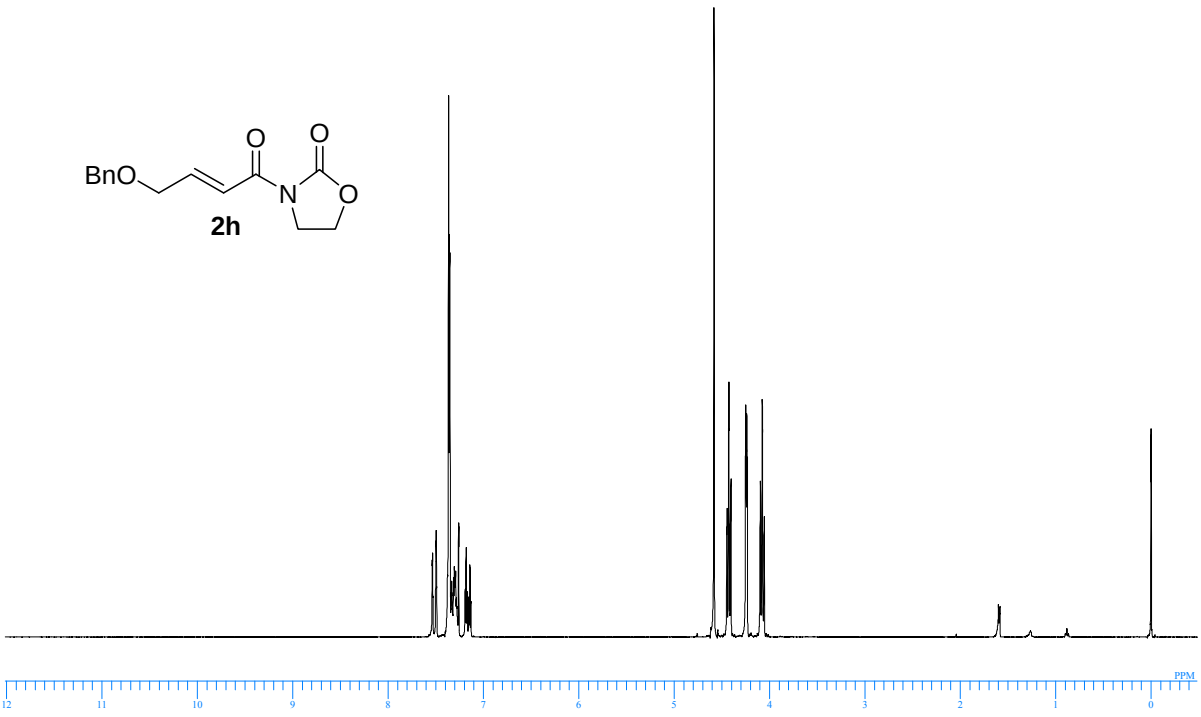

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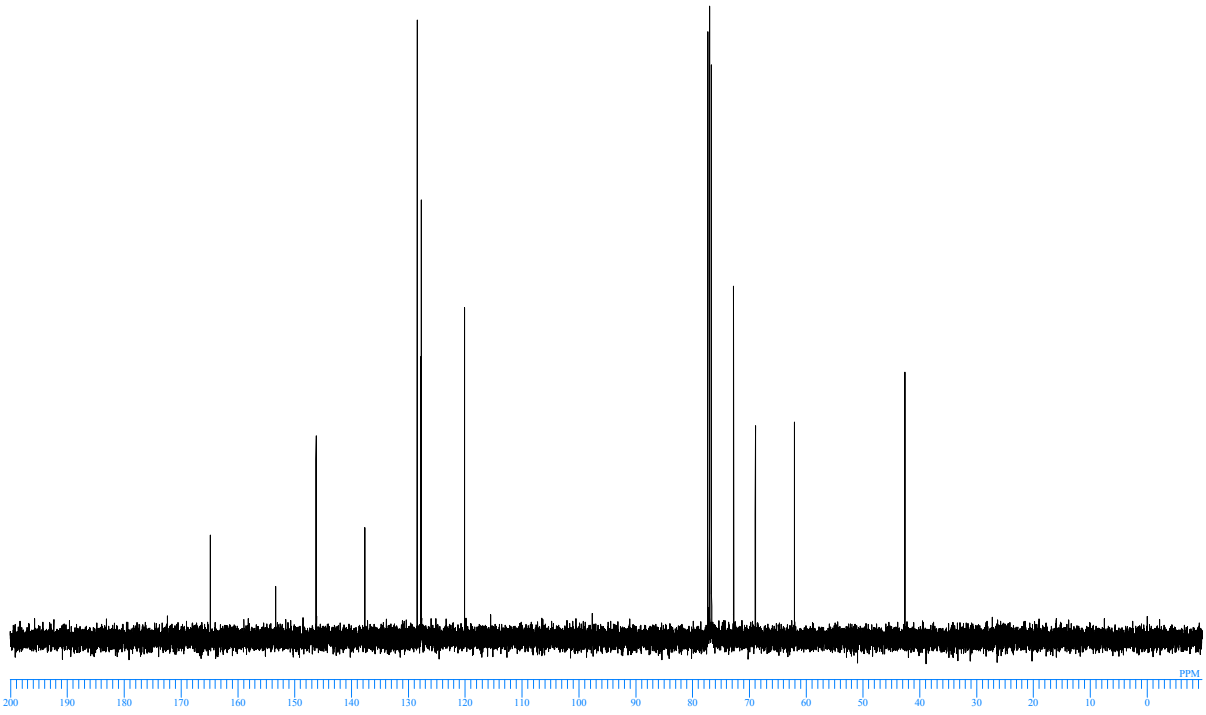

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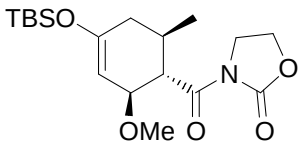

4a

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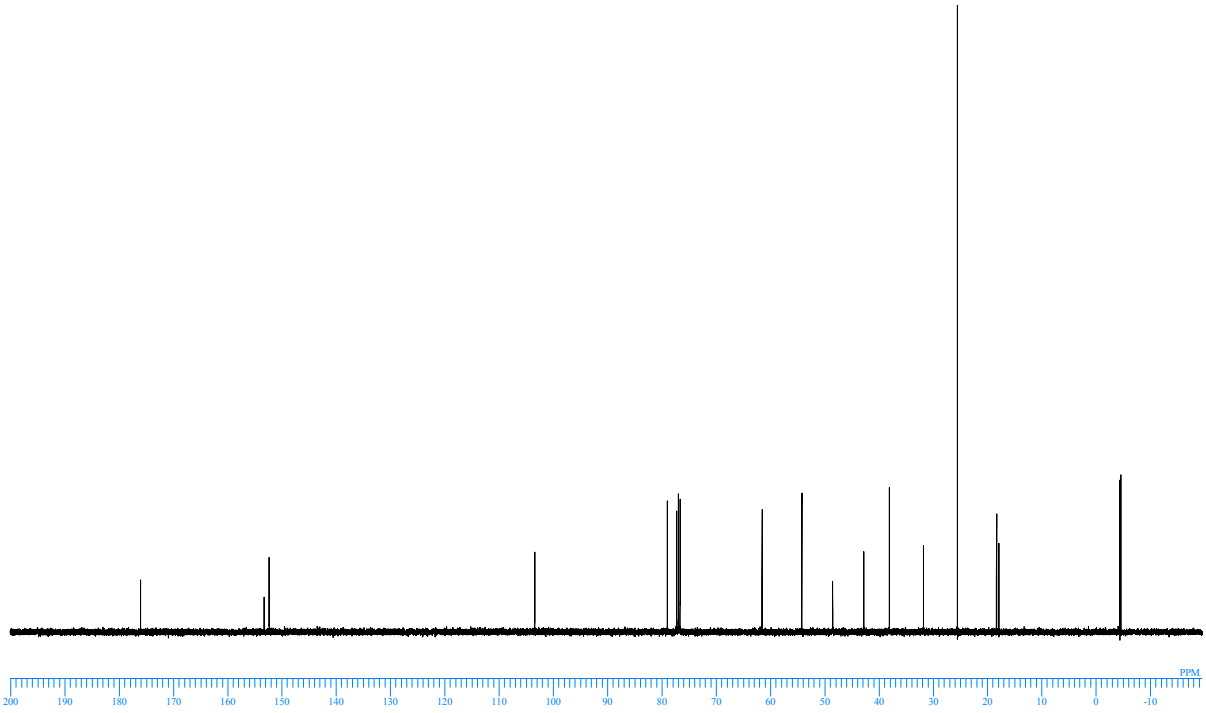

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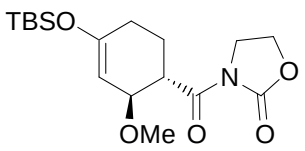

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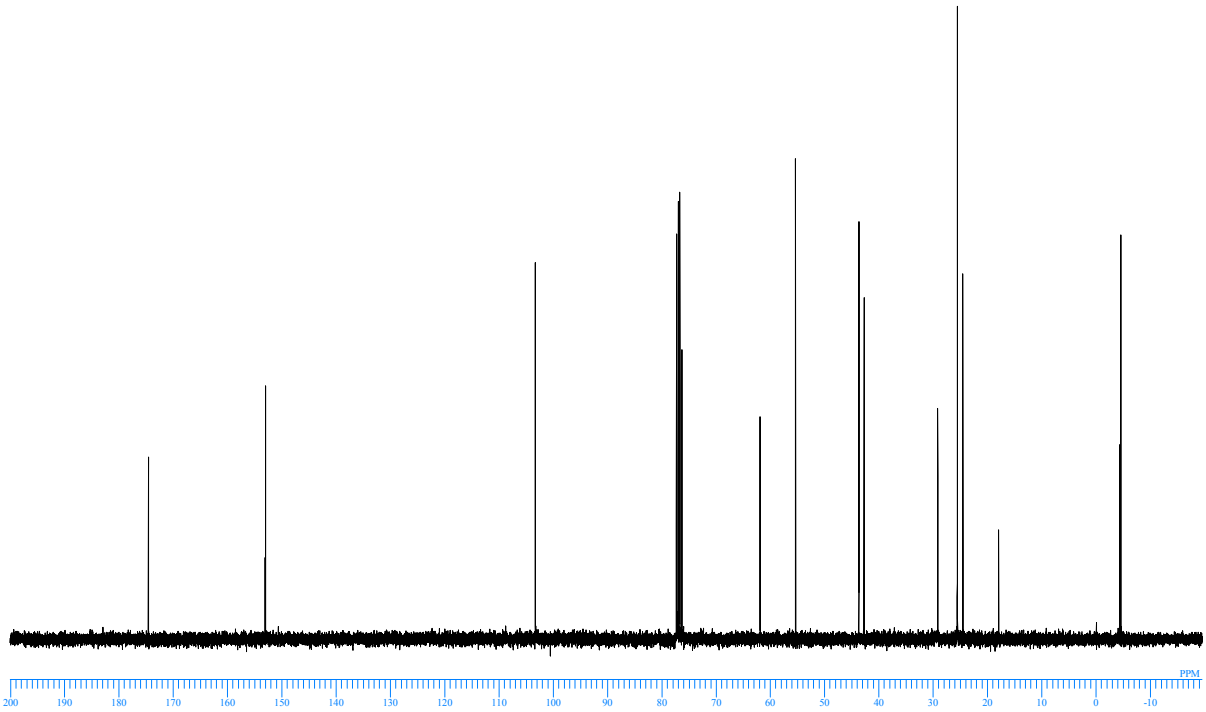

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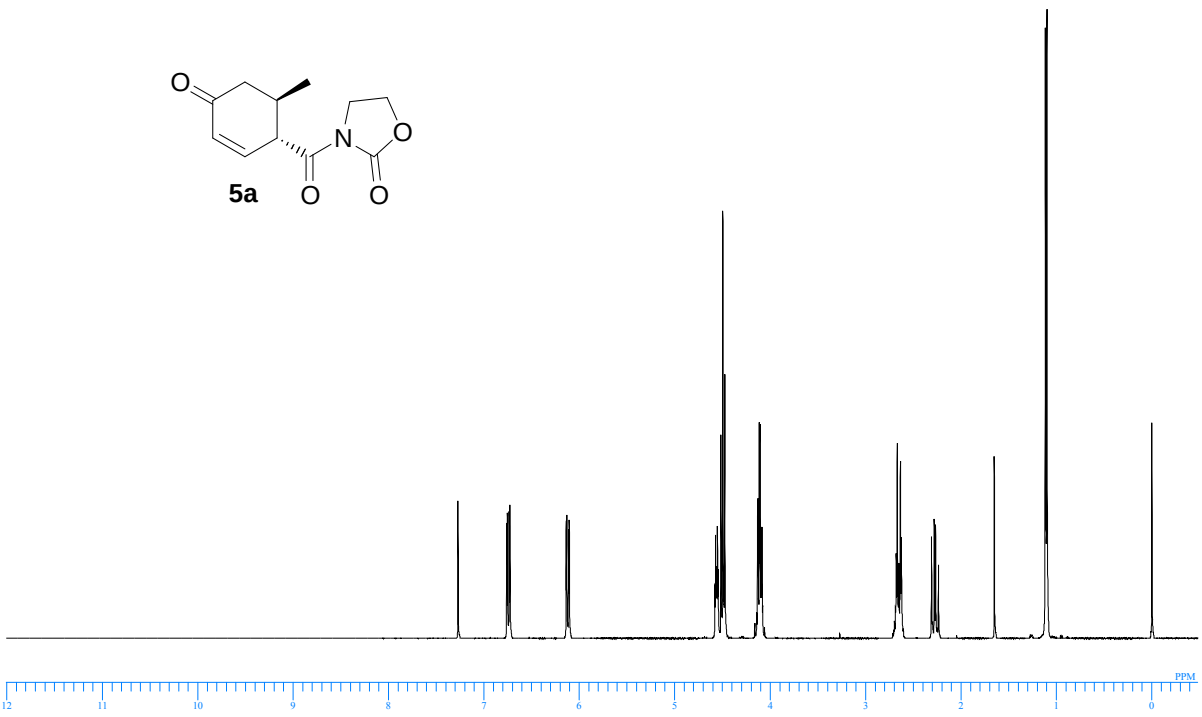

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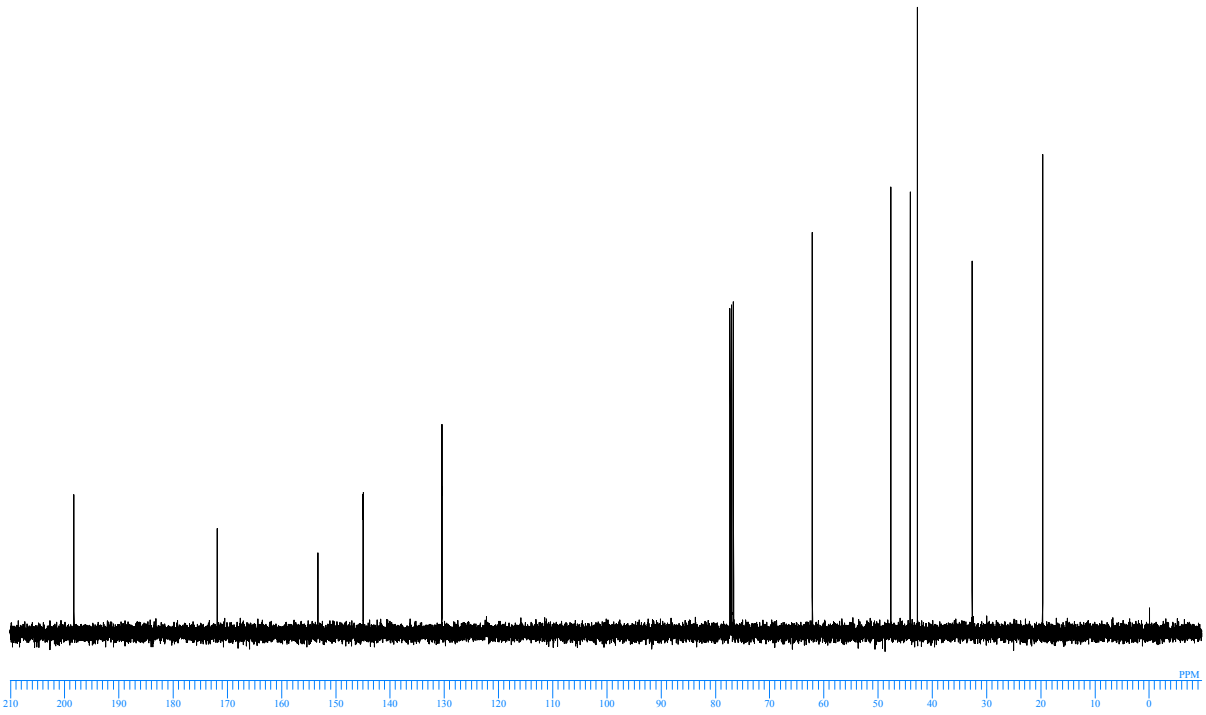

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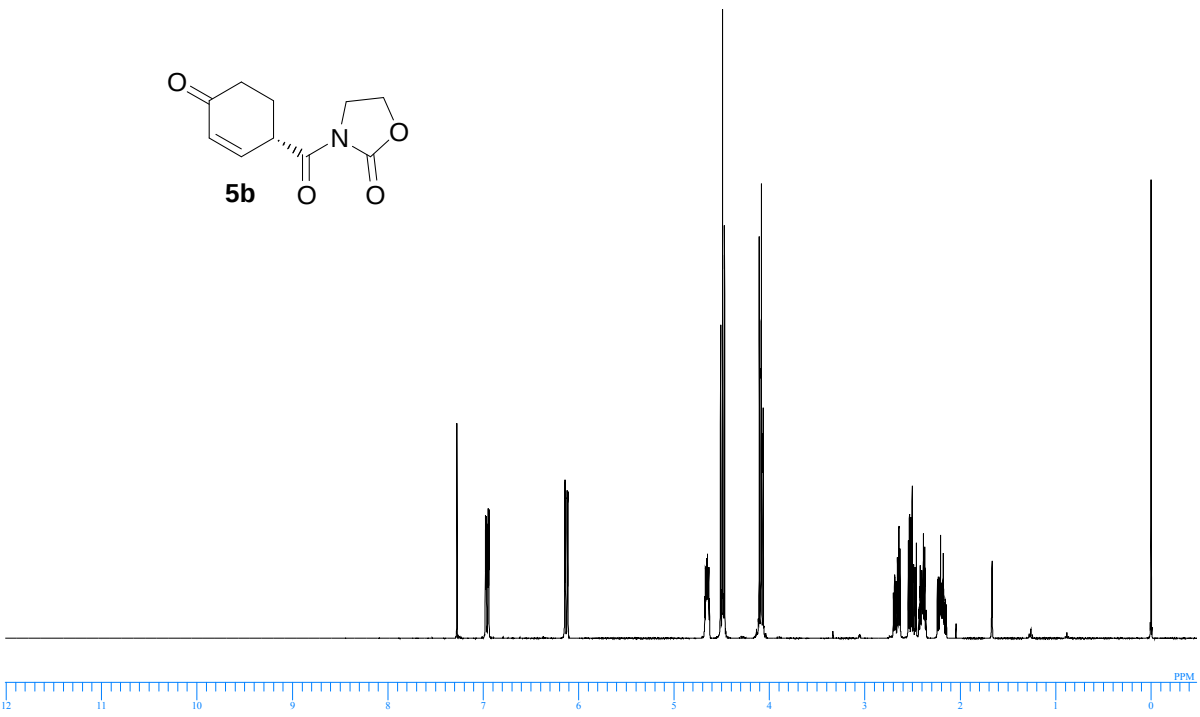

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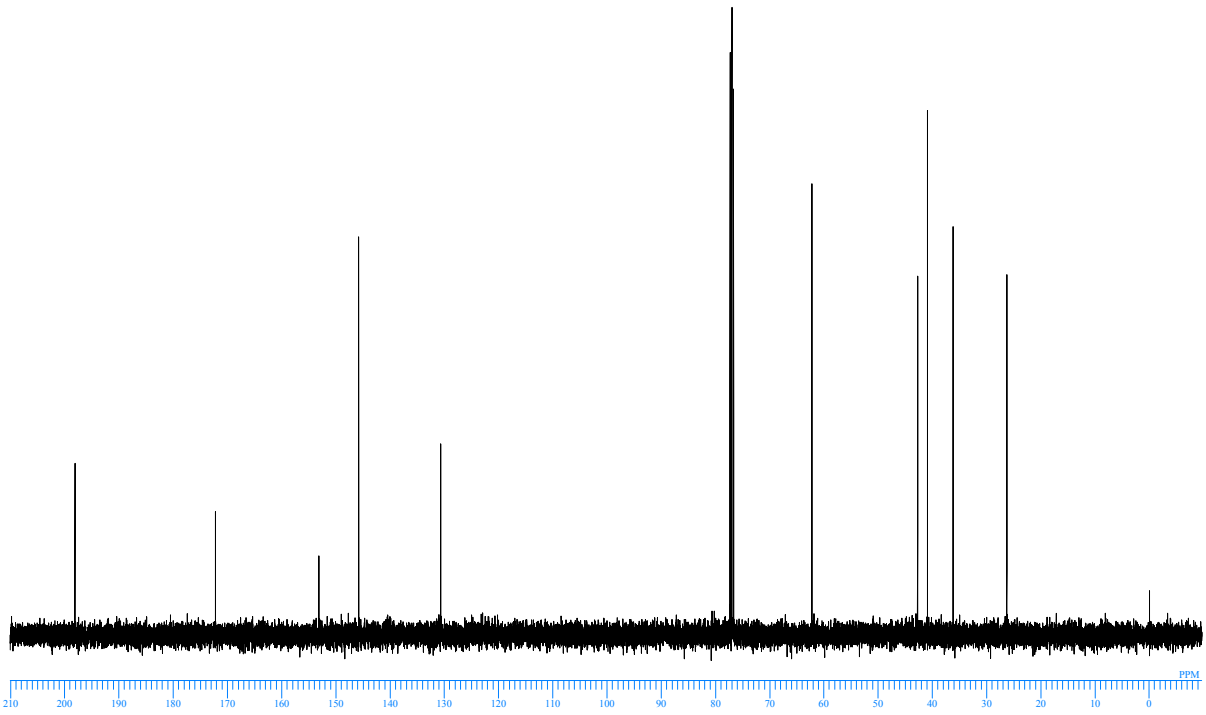

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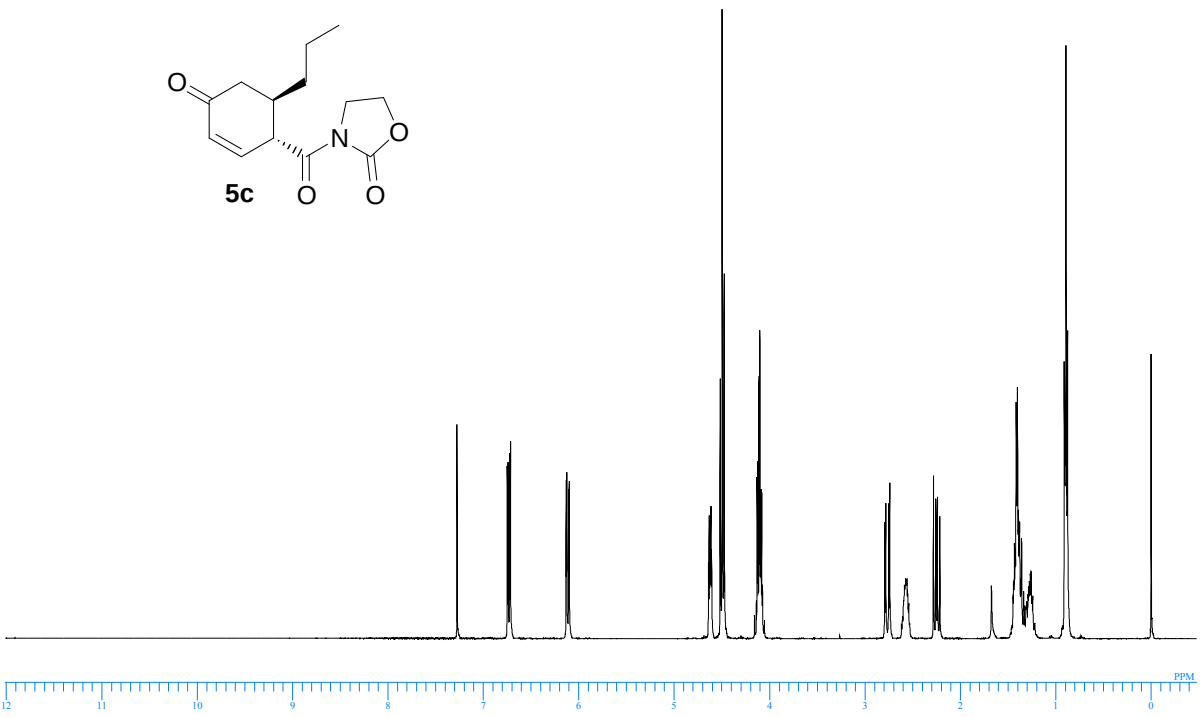

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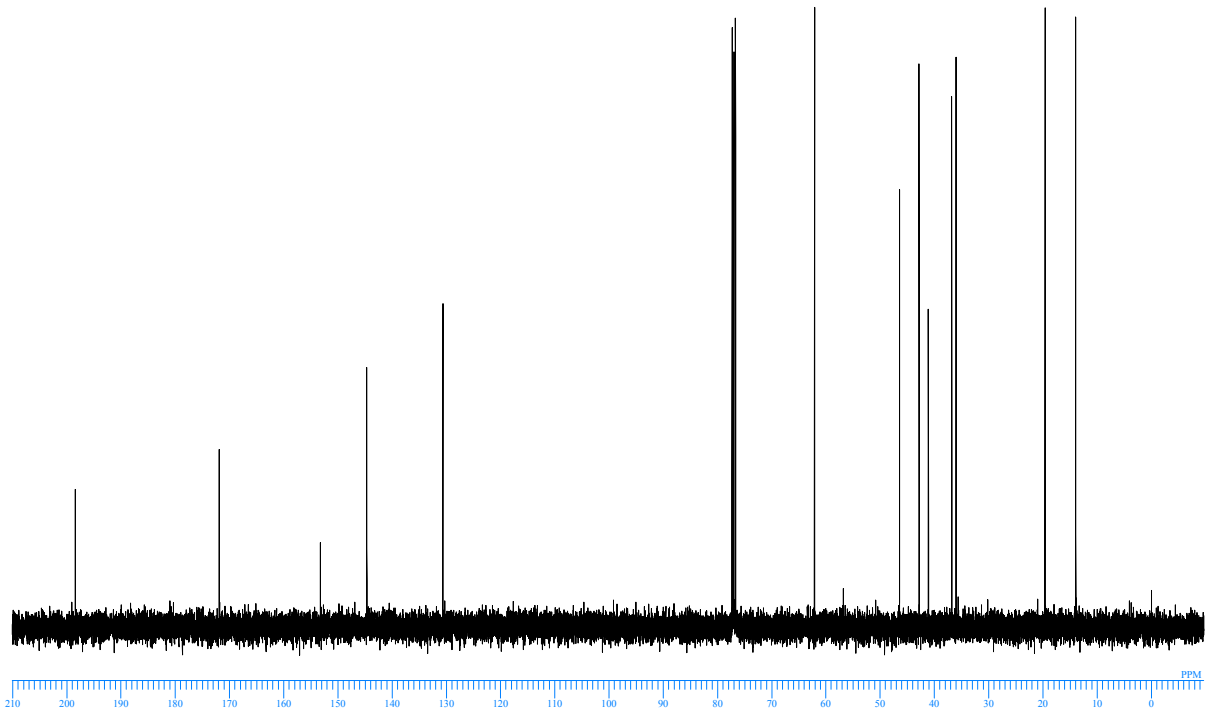

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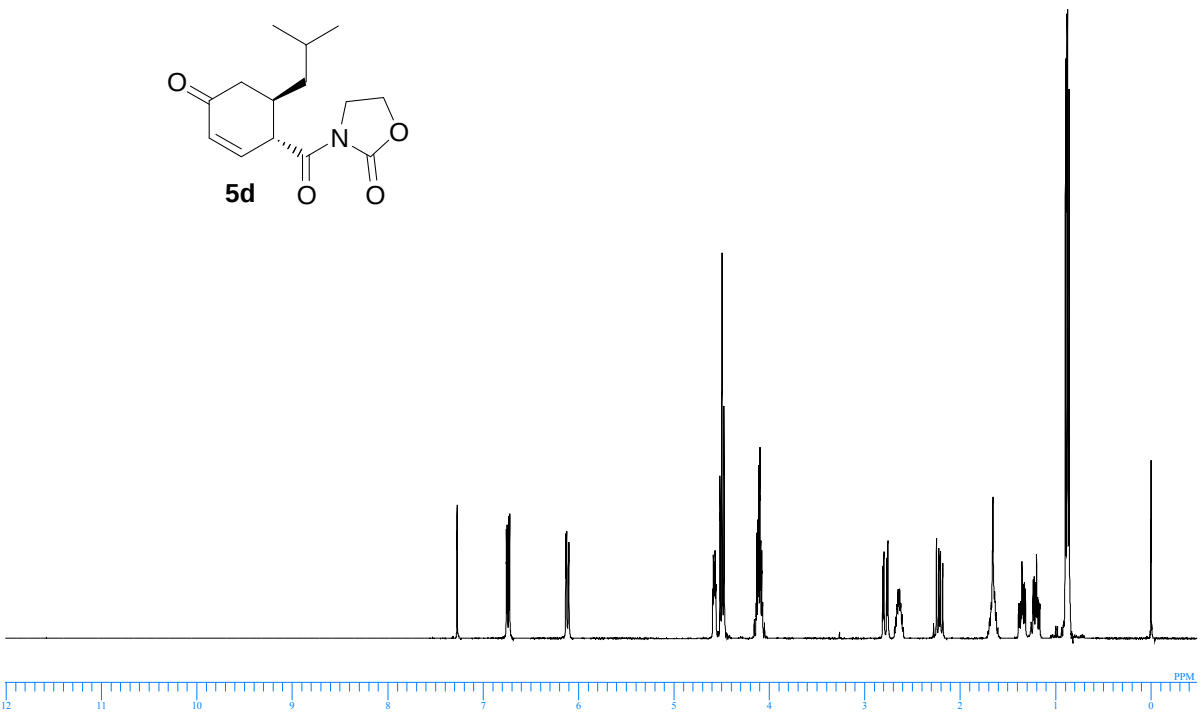

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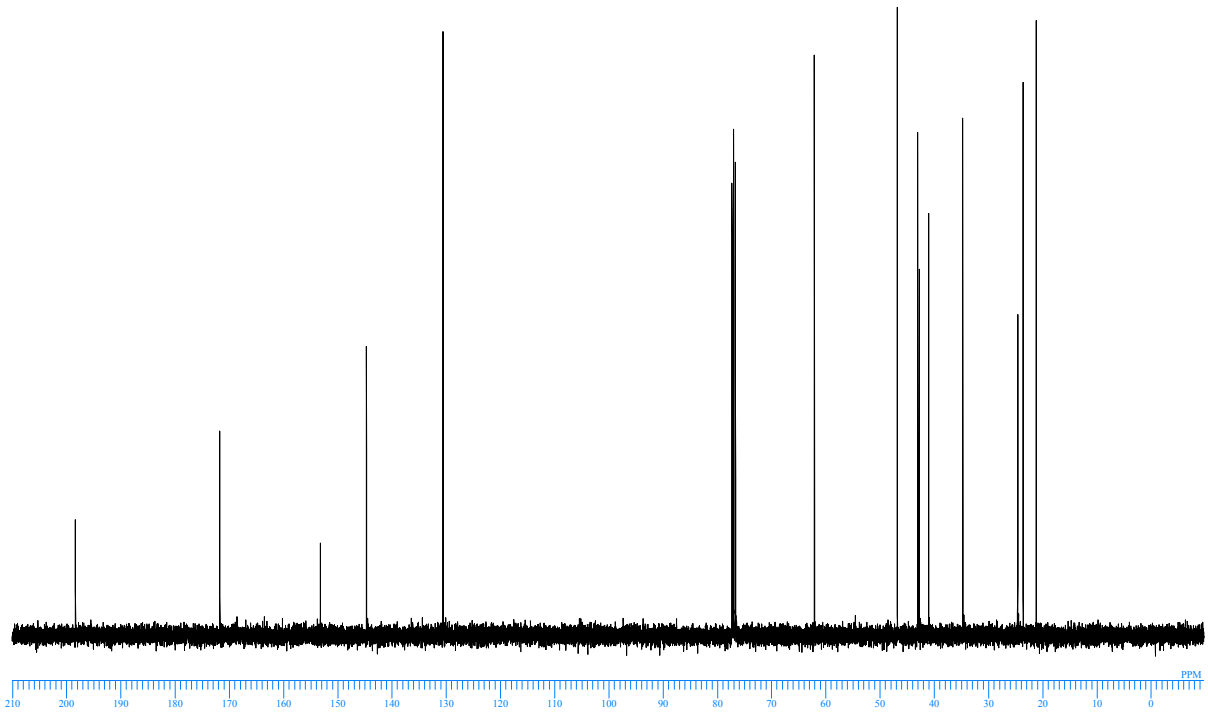

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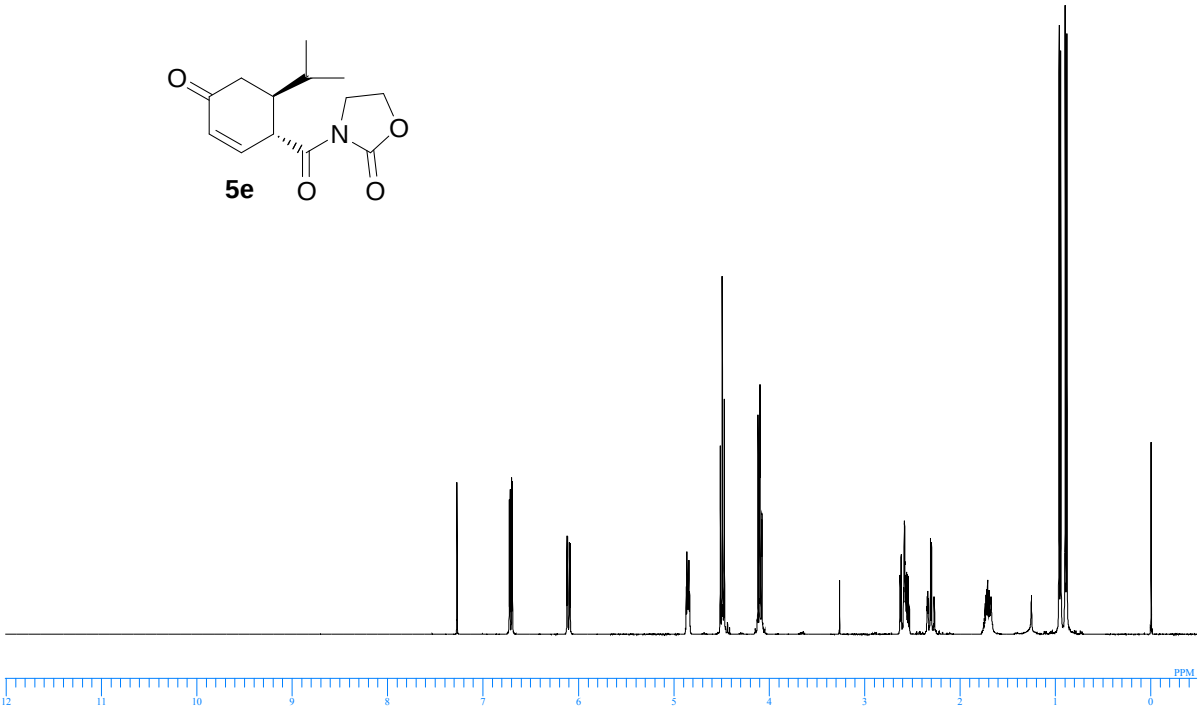

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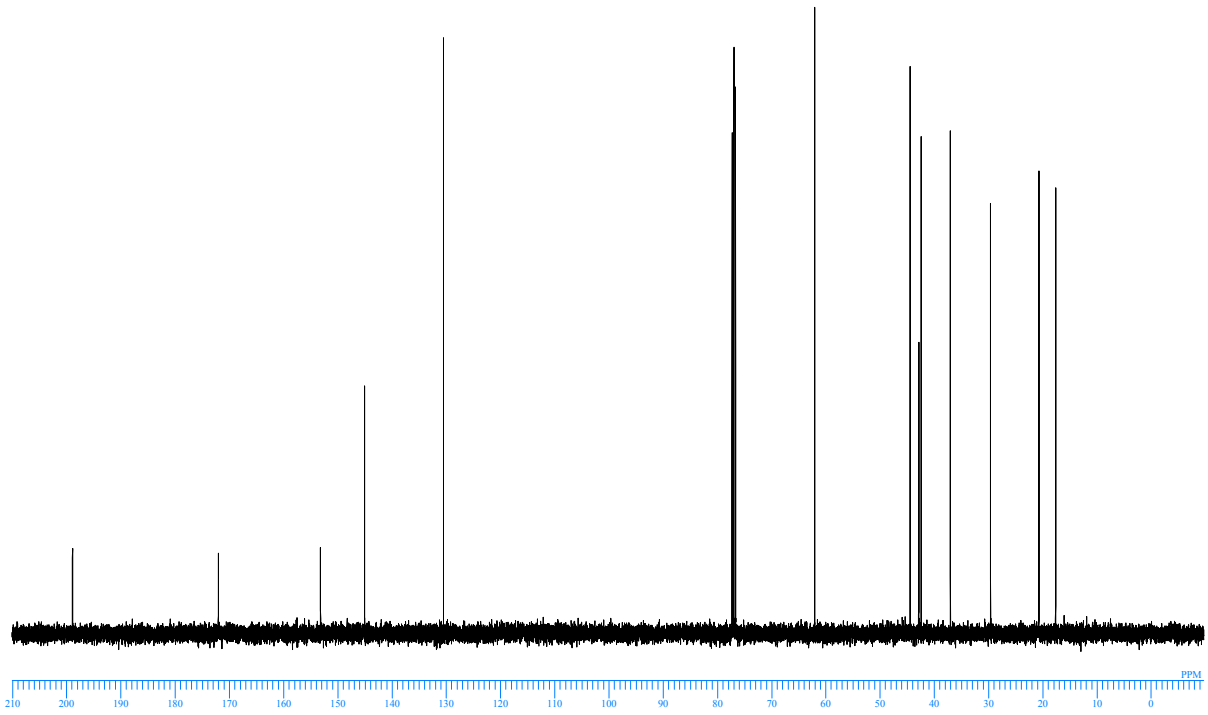

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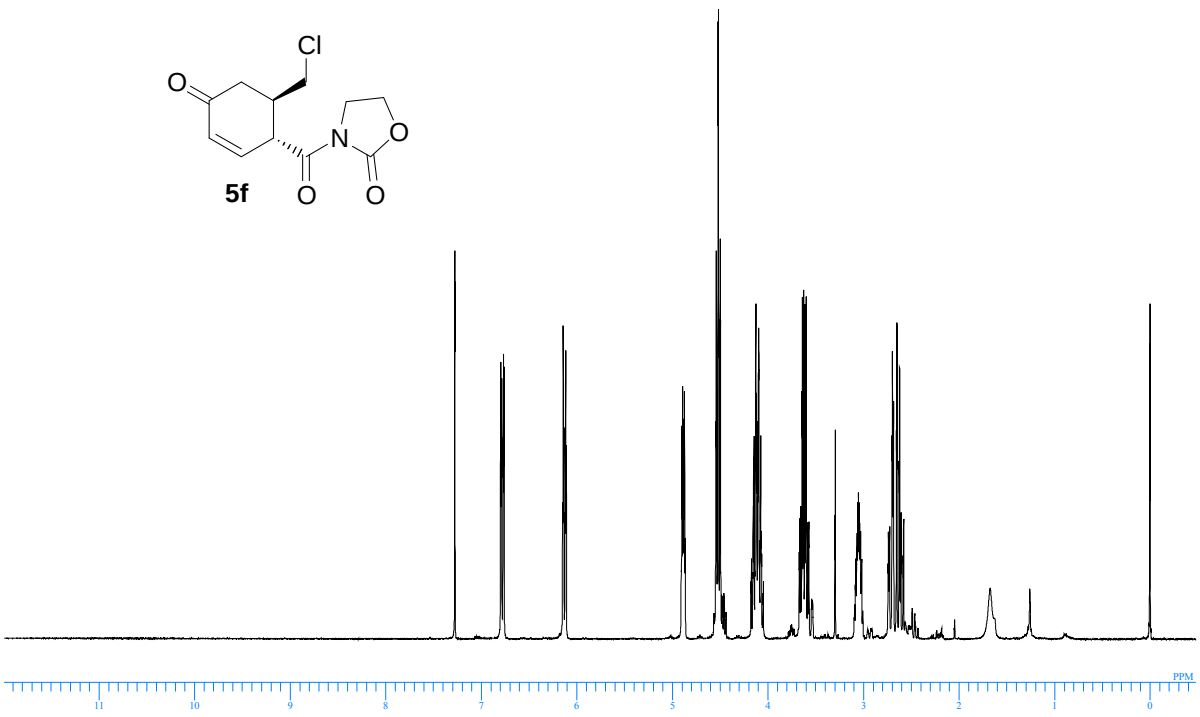

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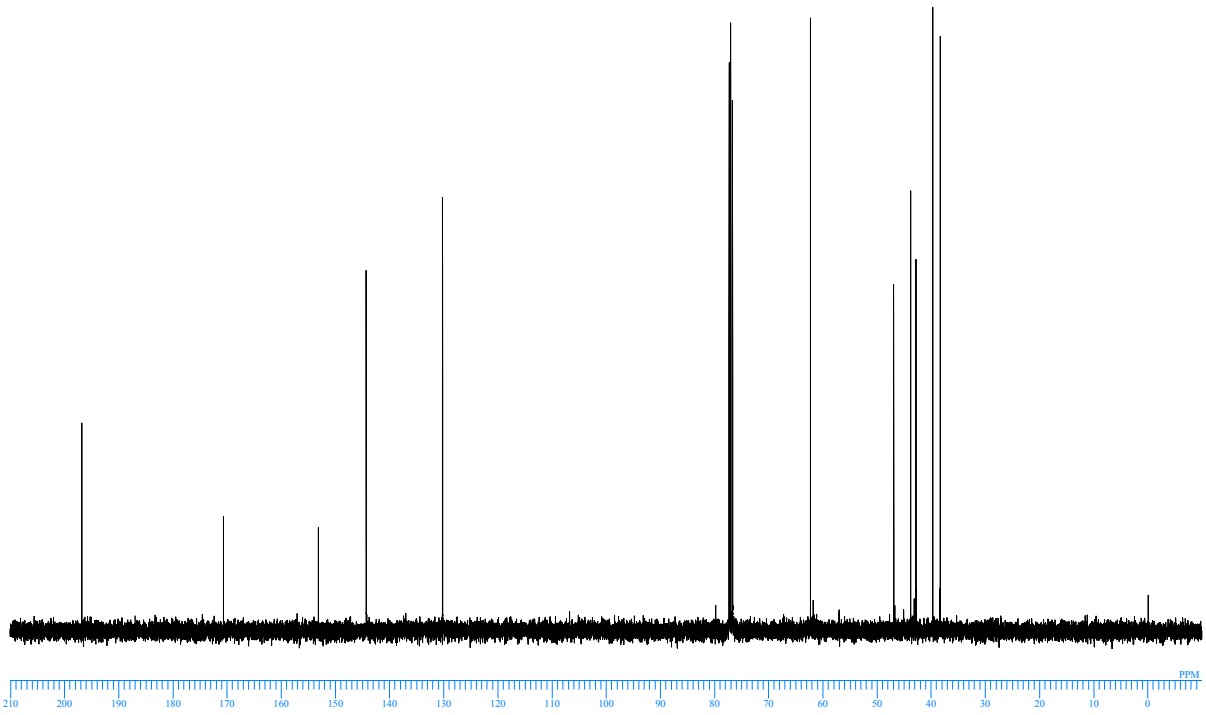

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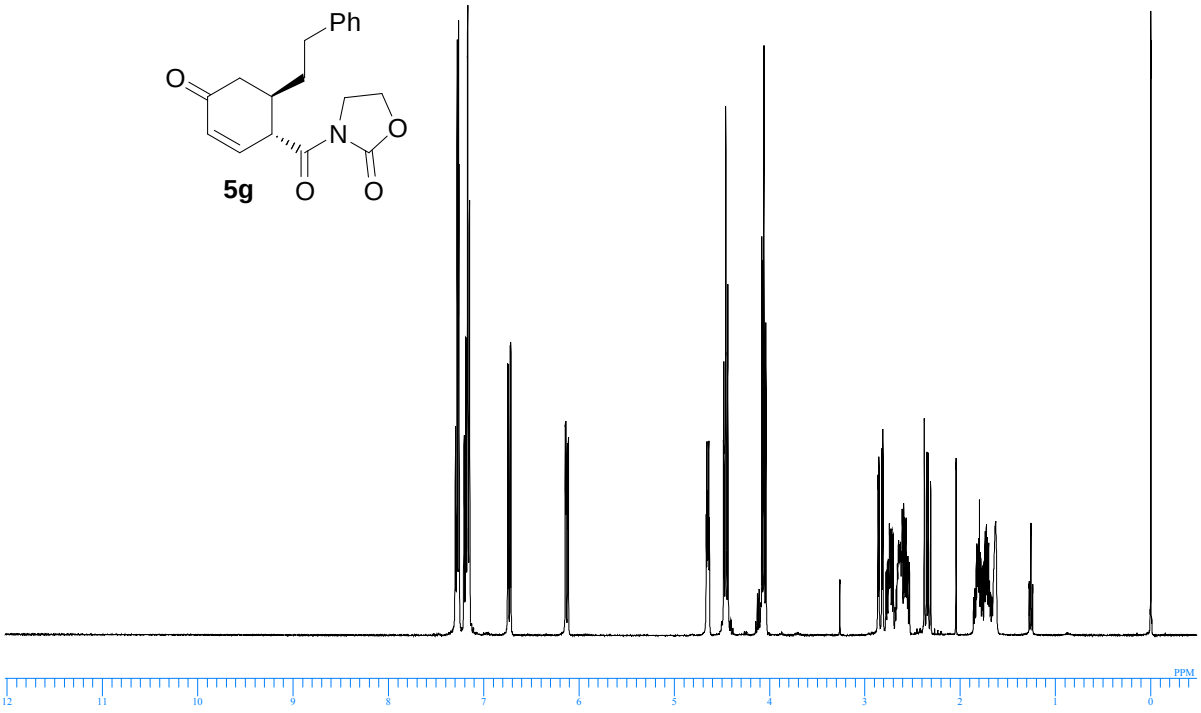

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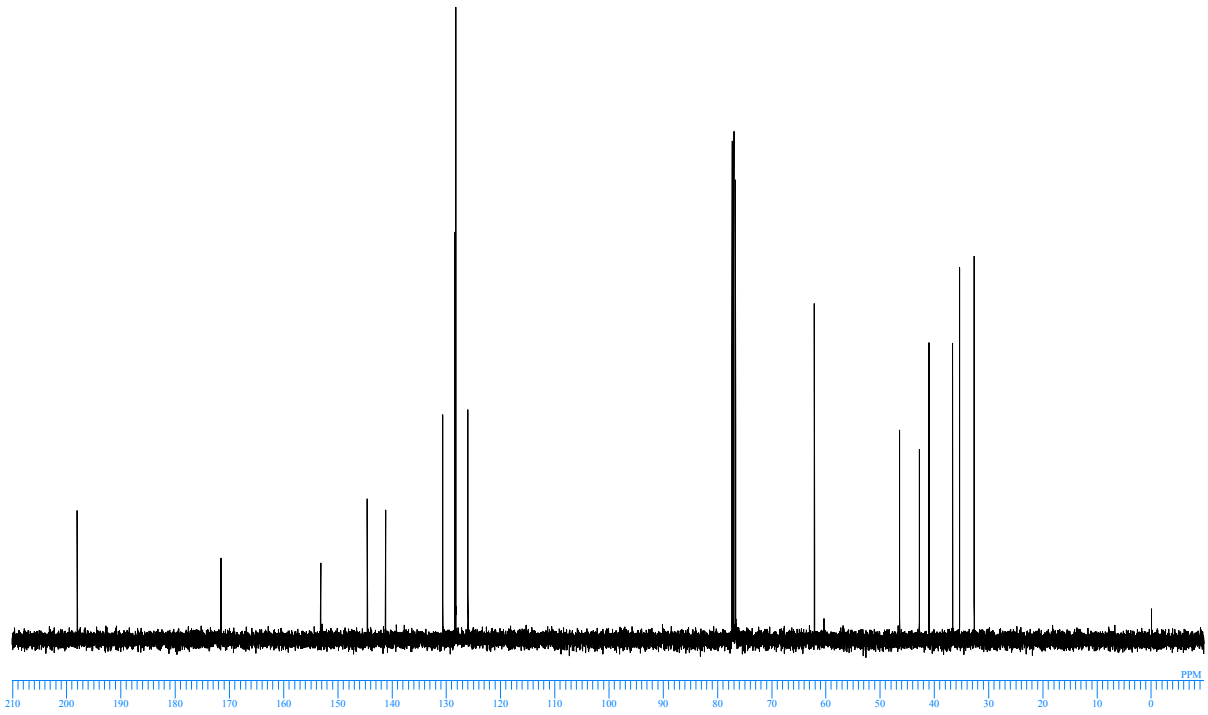

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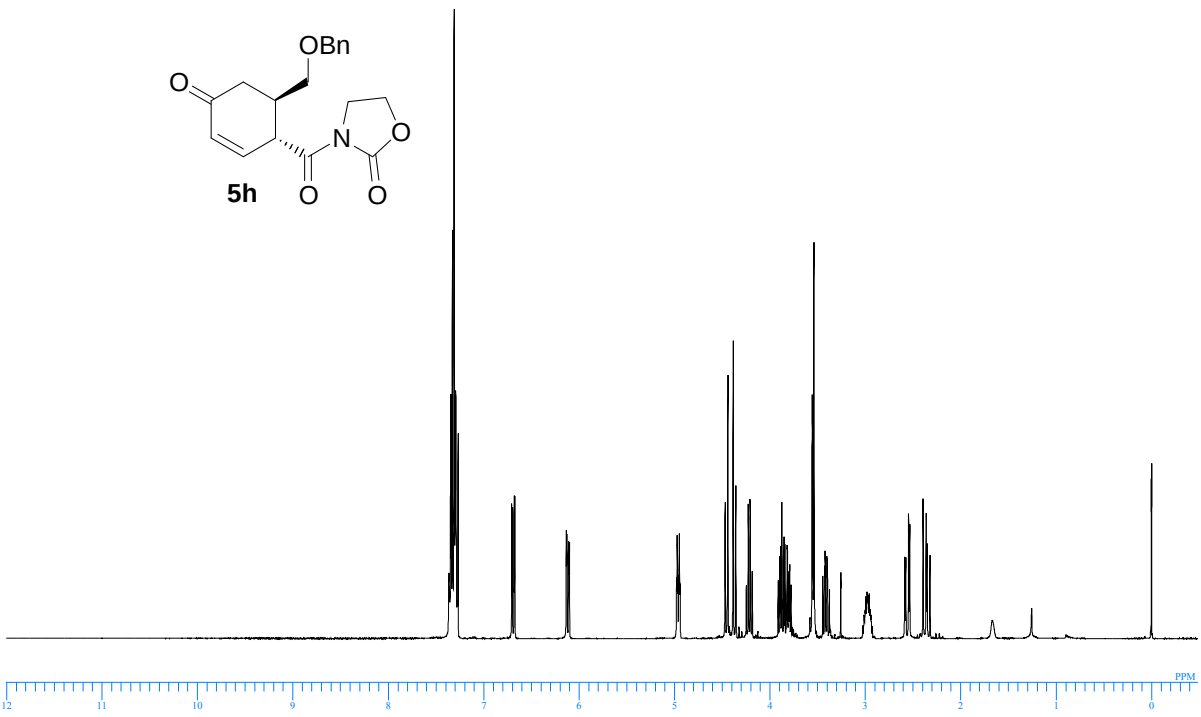

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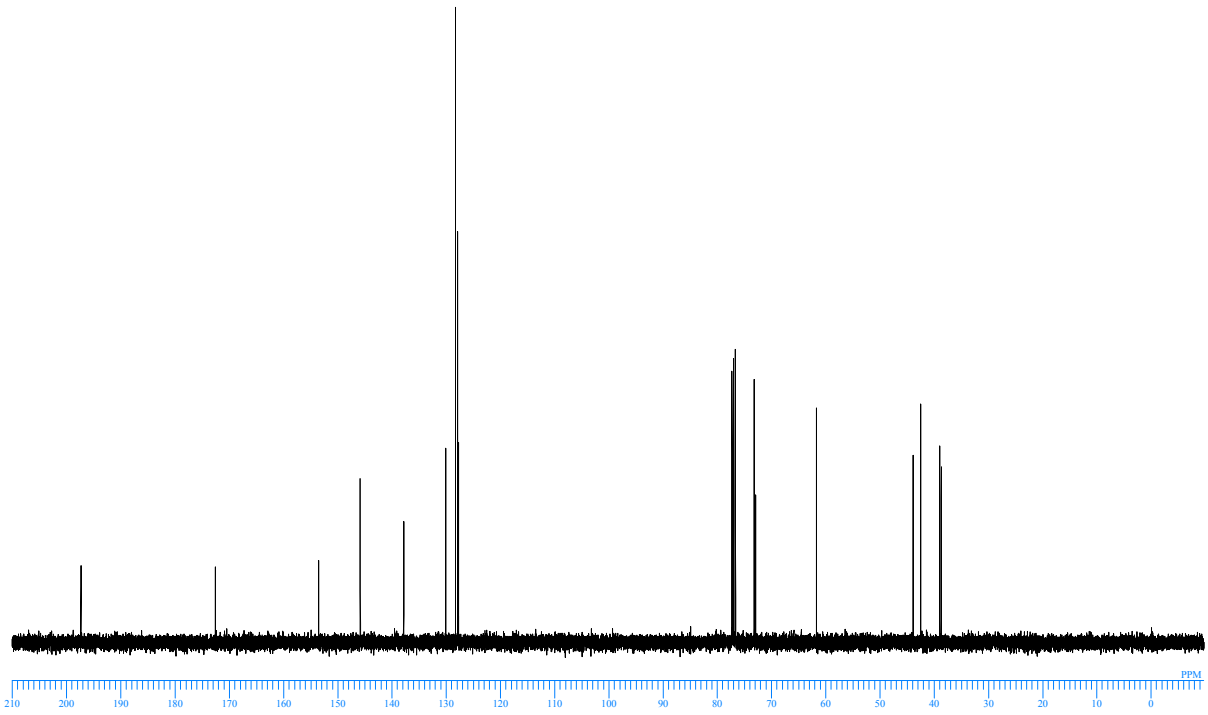

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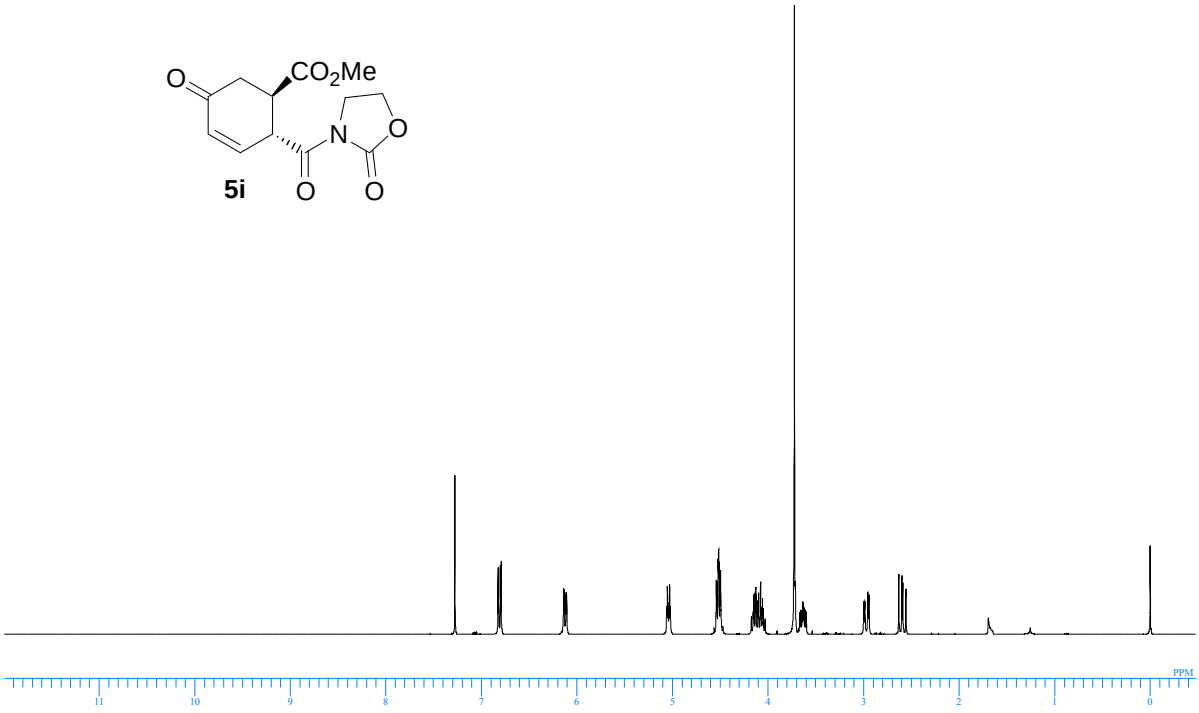

5i

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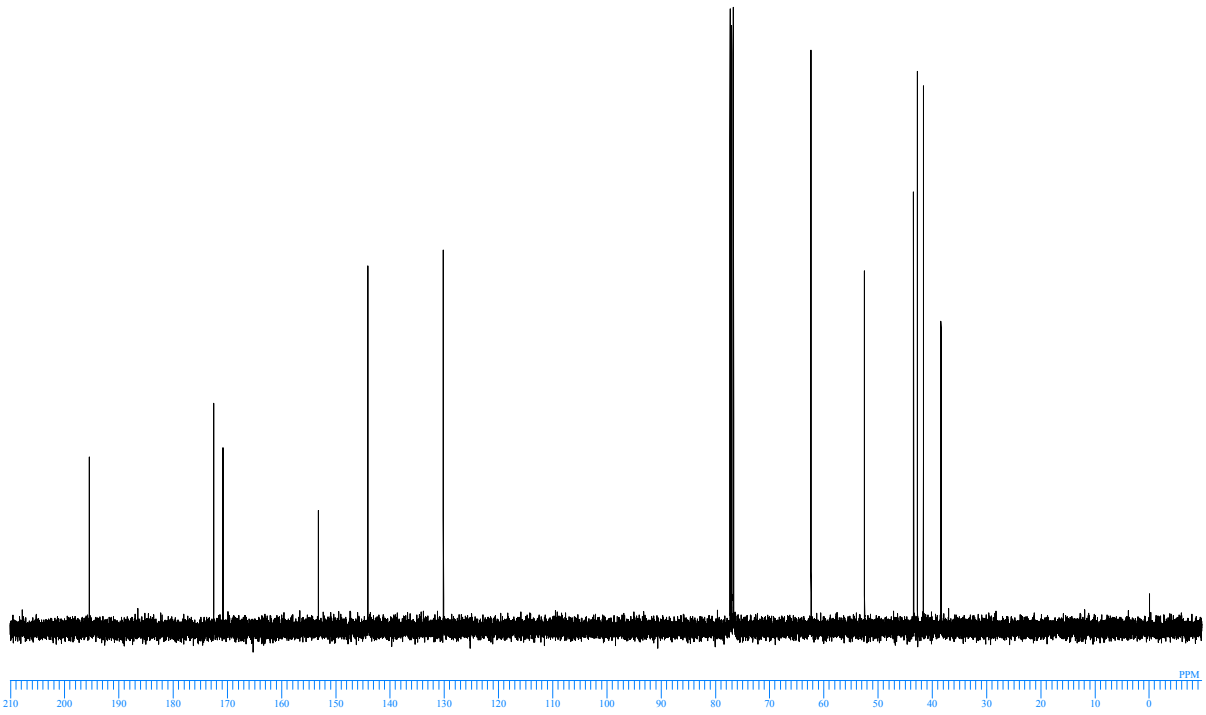

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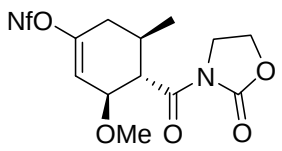

6

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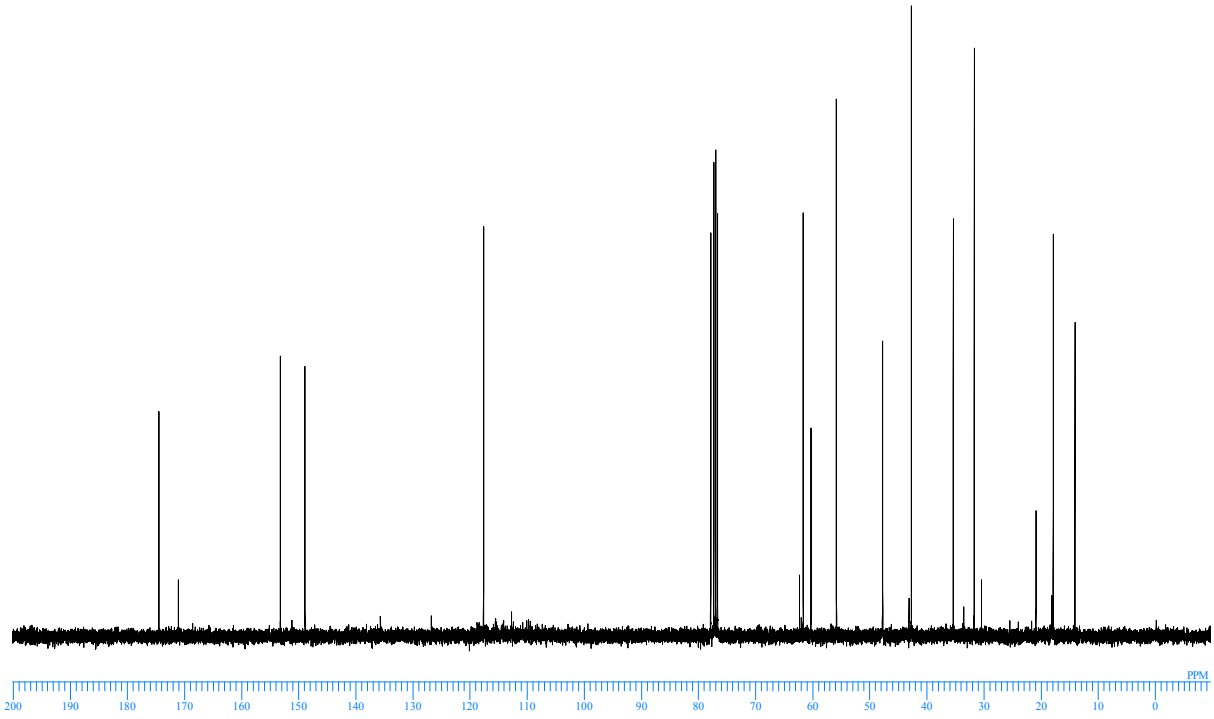

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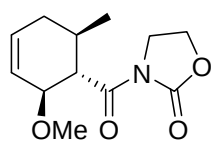

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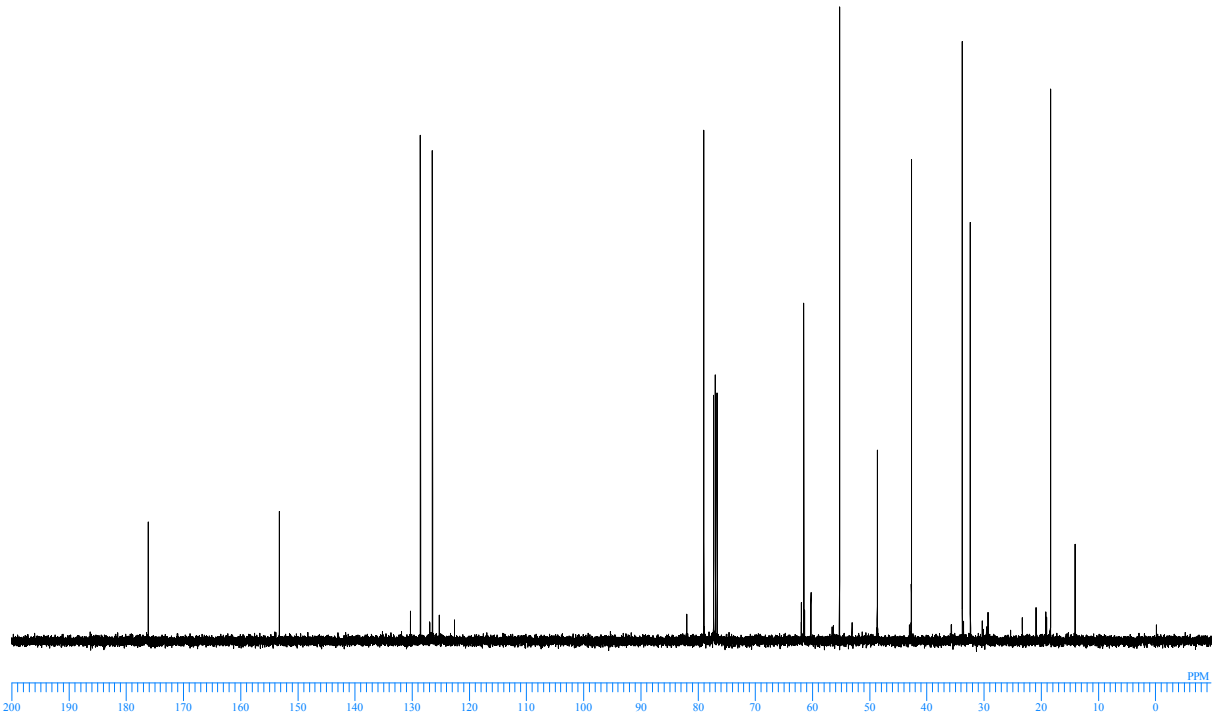

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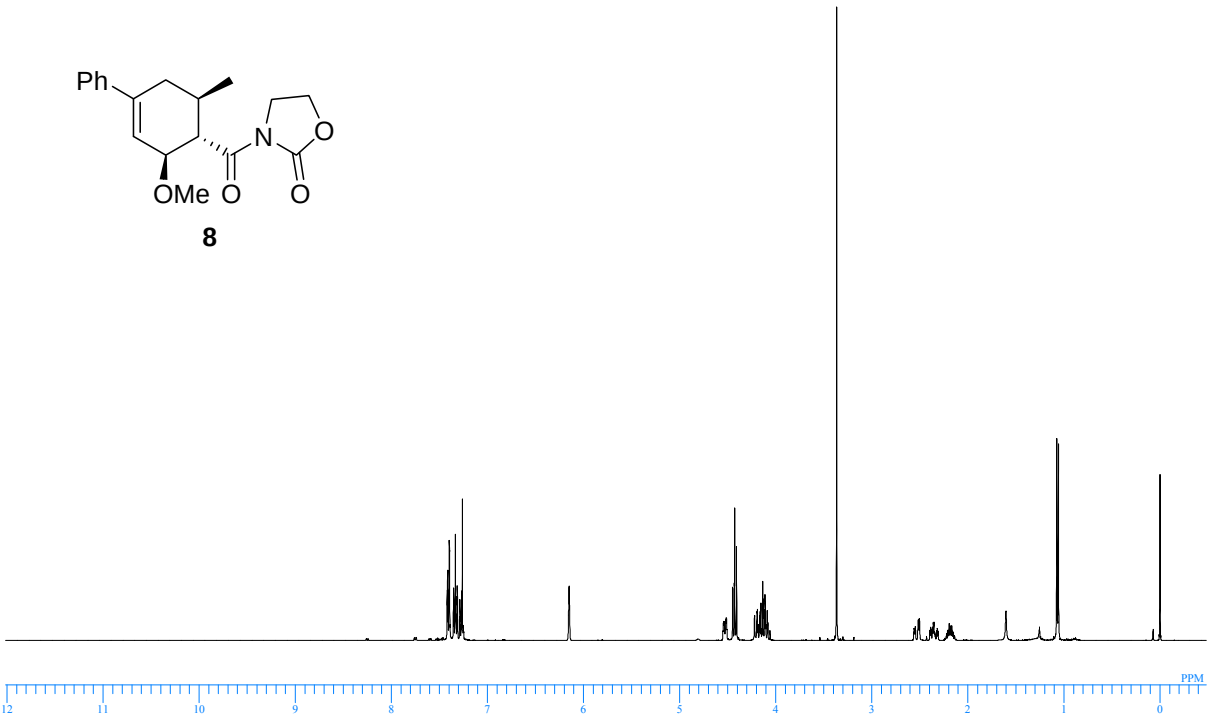

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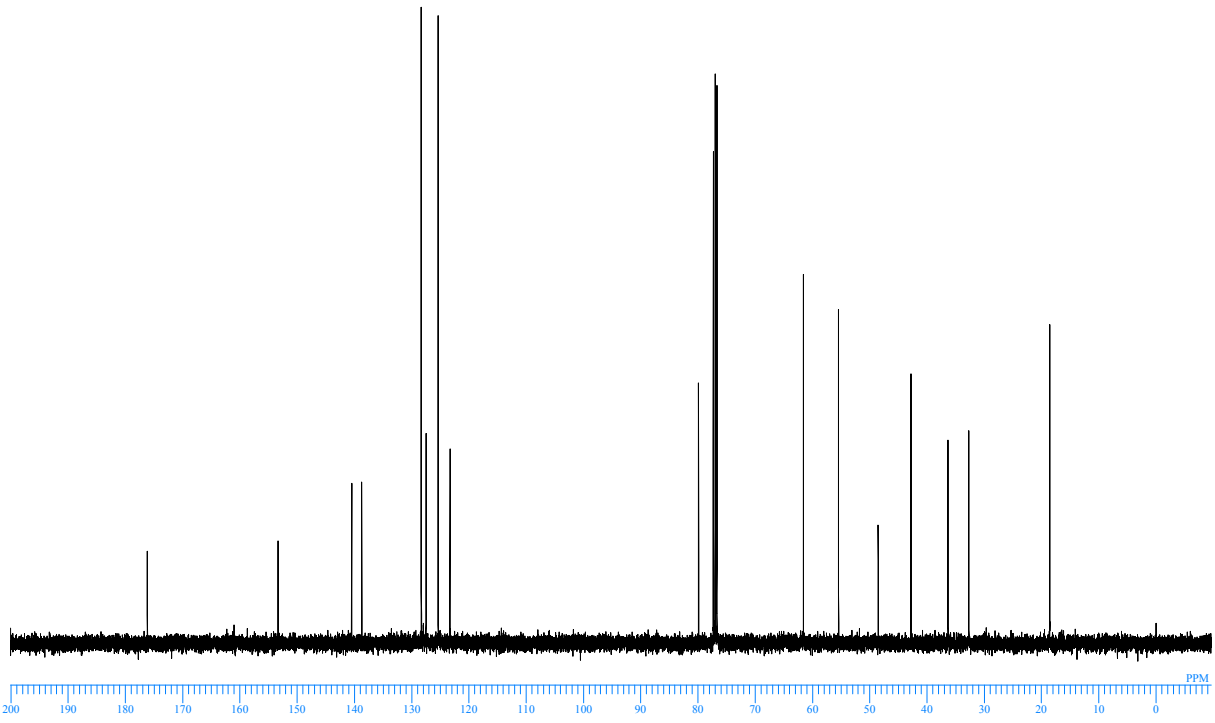

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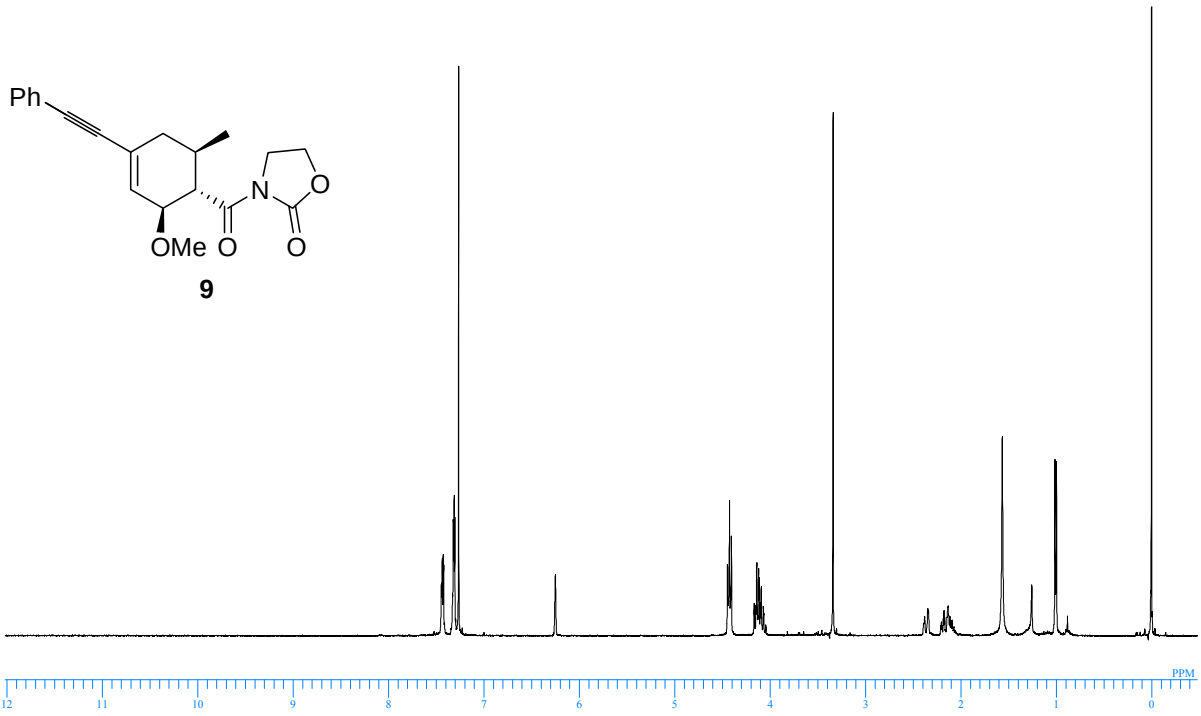

9

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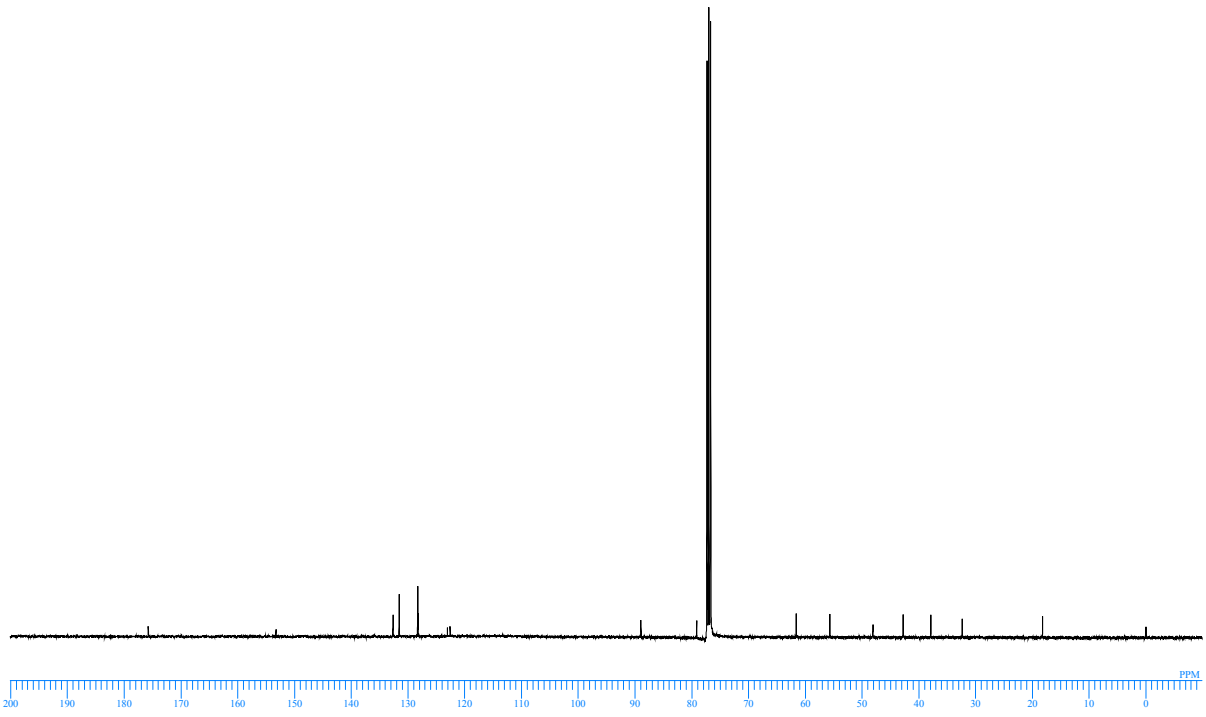

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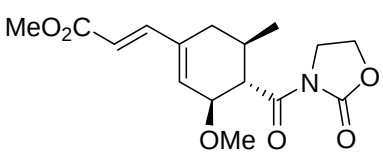

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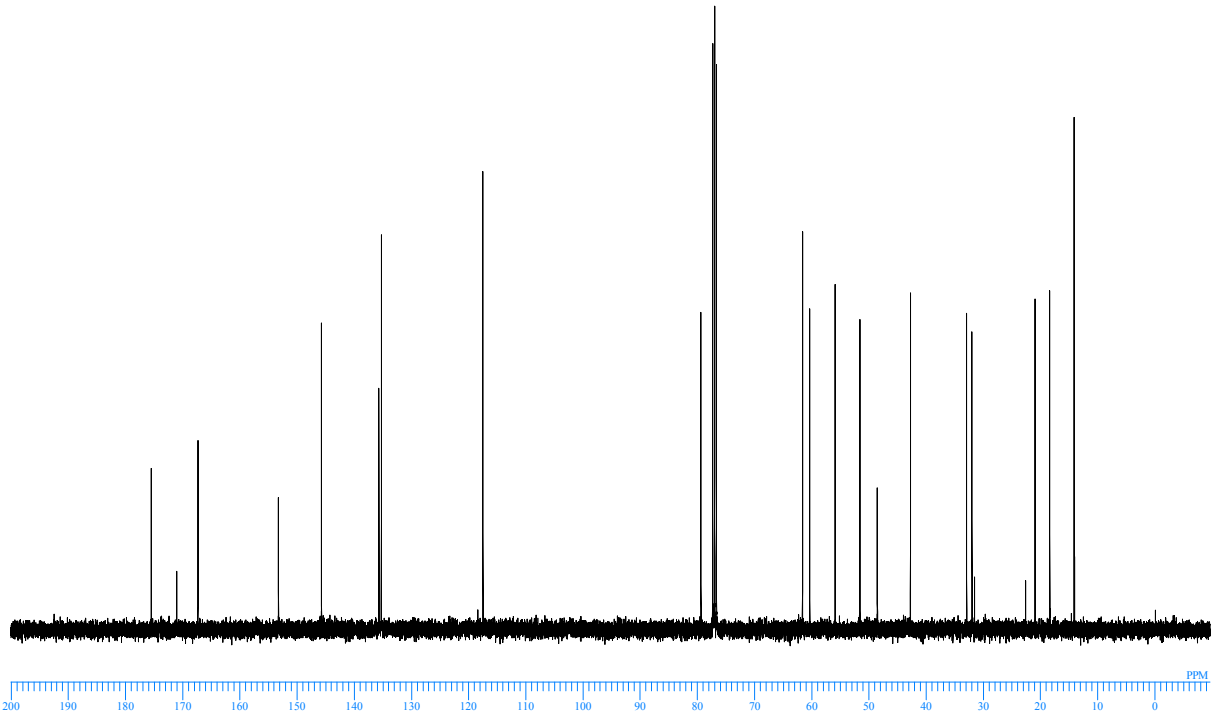

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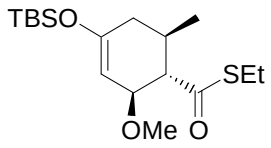

SI-1

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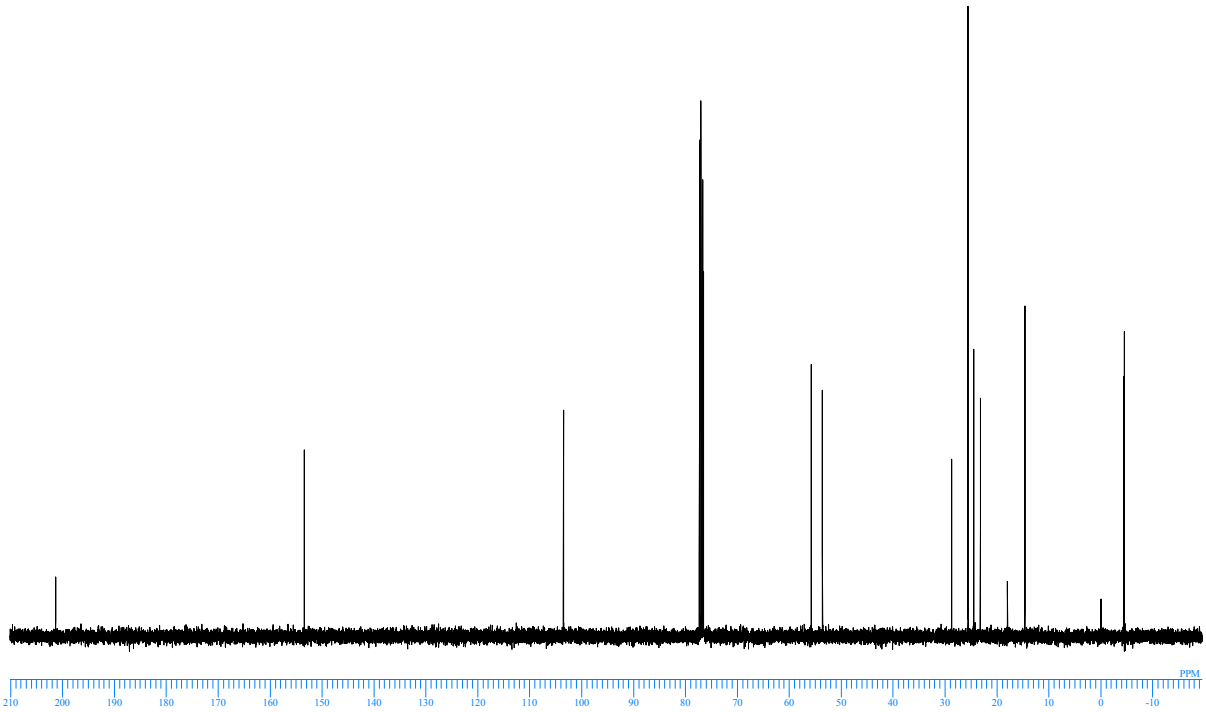

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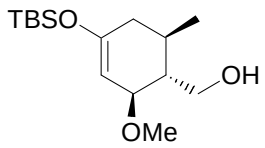

SI-2

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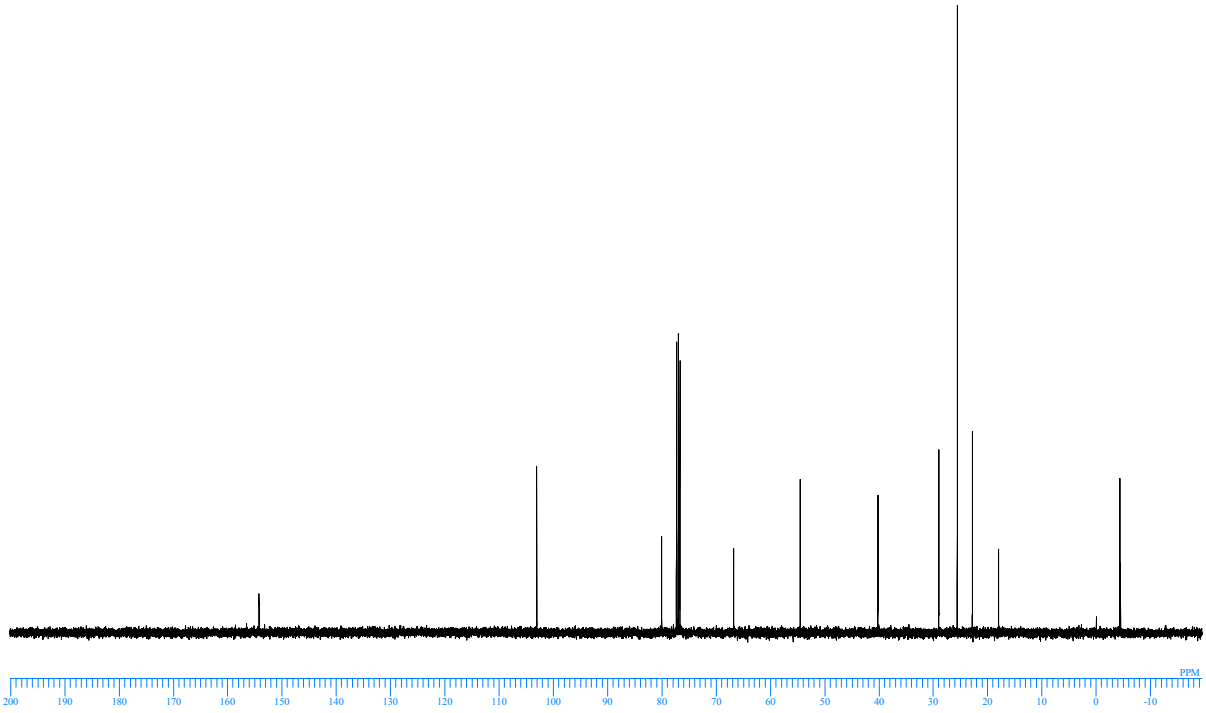

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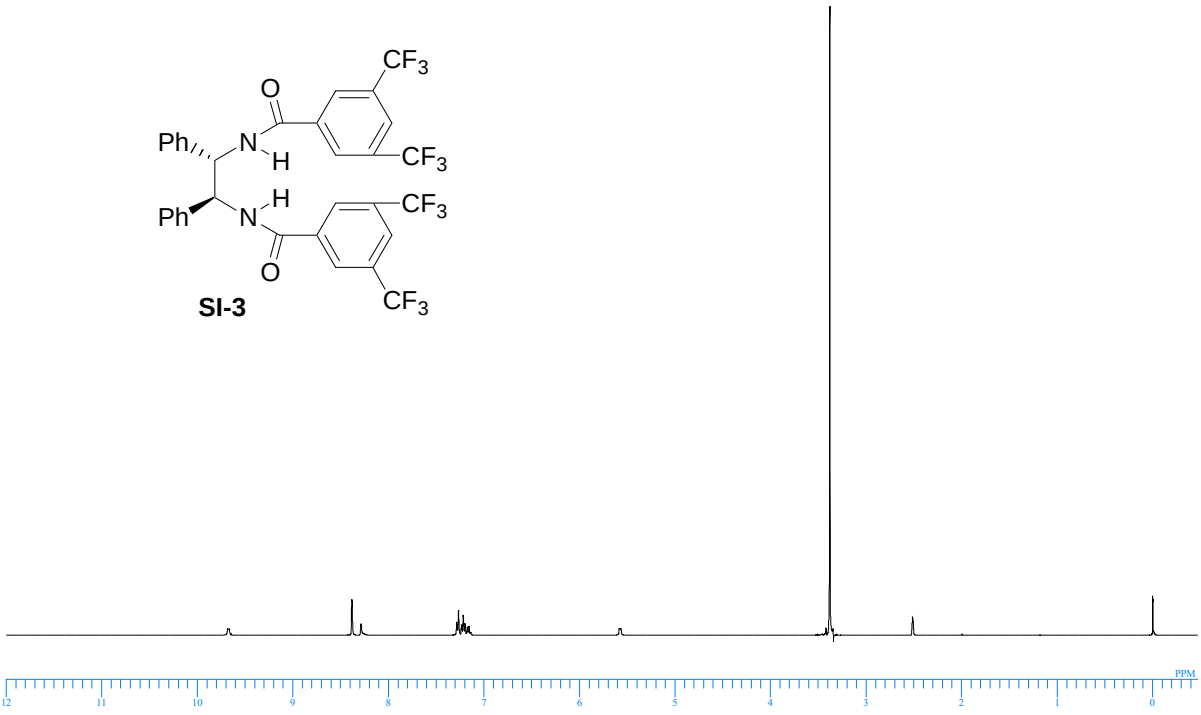
YKSHI-12-043002-CUDE



SI-3

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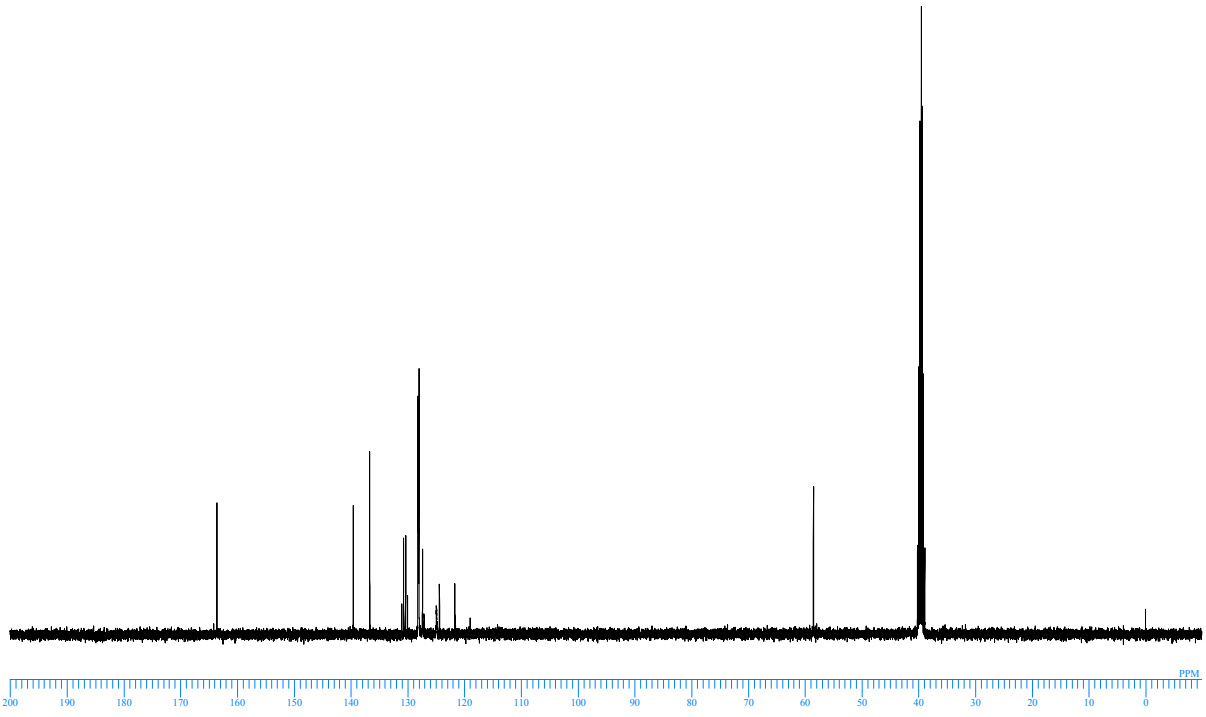
13C-COM



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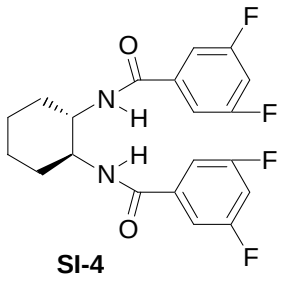

SI-4

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