Iridium-Catalyzed Enantioselective Allylic Substitution of Enol Silanes from Vinylogous Esters and Amides

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Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data, ^{1}H and ^{13}C Spectra of New Compounds

General Experimental Details. All reaction solvents were purified before use. Tetrahydrofuran, dichloromethane, diethyl ether and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of nitrogen using flame-dried or oven-dried (150 °C) glassware. The term "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator with the water bath temperature below 30 °C, followed by removal of residual solvent at high vacuum (< 0.2 mbar). $[Ir(cod)Cl]_2$ was obtained from Johnson-Matthey and used without further purification.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on commercial instruments (400, 500 and 600 MHz) at University of California, Berkeley NMR facility. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 100, 126 and 151 MHz. The proton signal for residual non-deuterated solvent (δ 7.26 for $CHCl_3$) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ77.36 resonance of $CHCl_3$. Coupling constants are reported in Hz. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer via the Micro Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F_{254} glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or $KMnO_4$. Column chromatography was generally performed using Kieselgel 60 (230-400 mesh) silica gel, typically using a 50-100:1 weight ratio of silica gel to crude product.

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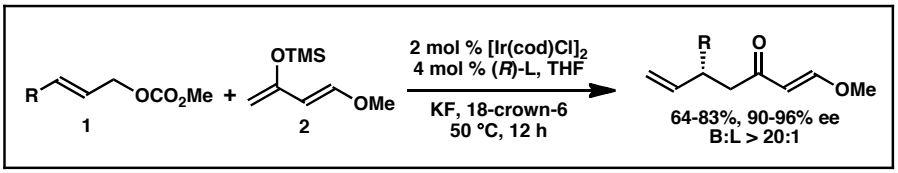
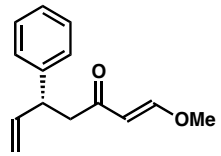
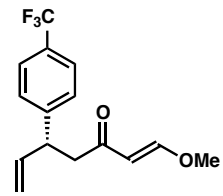


General Procedure for Ir-catalyzed Asymmetric Allylic Substitution with Enol Silane 2. In a nitrogen-filled dry-box, $[Ir(cod)Cl]_2$ (2.7 mg, 0.0040 mmol), the phosphoramidite ligand (R_a, R_c, R_c)-**L** (4.3 mg, 0.0080 mmol), KF (12 mg, 0.20 mmol), 18-crown-6 (53 mg, 0.20 mmol) and a Teflon-coated magnetic stirring bar were added to a 1-dram vial. Then, anhydrous THF (0.40 mL) was added. The mixture was stirred for 5 minutes at ambient temperature before the carbonate **1** (0.20 mmol) and the enol silane **2** (0.40 mmol, 2.0 equiv) were added. The vial was sealed with a cap containing a PTFE-lined silicone septum, removed from the dry-box and stirred at 50 ˚C for 12 h. The reaction progress was monitored by TLC and ^{1}H-NMR spectroscopy. When the reaction was judged to be complete, the reaction mixture was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution: hexane:Et_2O = 50:1 to 5:1) to provide the product **4**.

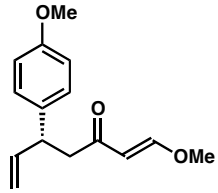


(*R*,*E*)-1-methoxy-5-phenylhepta-1,6-dien-3-one (4a). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as colorless oil in 81% yield (36 mg, 83%; 34 mg, 79%). The enantiomeric excess was determined by HPLC analysis to be 94% ee (254 nm, 25 °C); t_1 = 9.15 min, t_2 = 10.4 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 3.69˚ (*c* 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 12.8 Hz, 1H), 7.28-7.32 (m, 2H), 7.18-7.23 (m, 3H), 5.99 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.54 (d, *J* = 12.8 Hz, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 3.97 (app. q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 2.90 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.84 (dd, *J* = 15.6, 7.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 163.1, 143.5, 141.1, 128.9, 128.0, 126.8, 114.9, 106.2, 57.8, 47.1, 45.2; IR (neat) 3081, 3061, 3027, 2925, 2850, 1683, 1639, 1621, 1594, 1493, 1453, 1438, 1410, 1338, 1311, 1230, 1189, 1136, 1070, 1031, 956, 921 cm^{-1}; HRMS (EI): *m/z* for $C_{14}H_{16}O_2$ $[M]^+$ calcd. 216.1150, found: 216.1149.

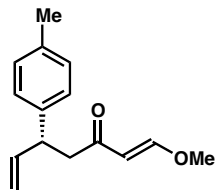


(*R*,*E*)-1-methoxy-5-(4-(trifluoromethyl)phenyl)hepta-1,6-dien-3-one (4b). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as colorless oil in 64% yield (35 mg, 62%; 38 mg, 67%). The enantiomeric excess was determined by HPLC analysis to be 92% ee (254 nm, 25 °C); t_1 = 8.96 min, t_2 = 11.1 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 6.41˚ (*c* 1.05,

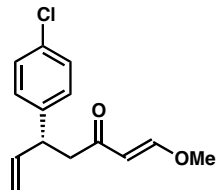
$CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 12.5 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 5.97 (ddd, J = 17.0, 10.5, 6.5 Hz, 1H), 5.54 (d, J = 12.5 Hz, 1H), 5.10 (d, J = 10.5 Hz, 1H), 5.03 (d, J = 17.0 Hz, 1H), 4.06 (app. q, J = 7.0 Hz, 1H), 3.68 (s, 3H), 2.92 (dd, J = 16.0, 7.0 Hz, 1H), 2.85 (dd, J = 16.0, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 163.3, 147.6, 140.3, 129.1 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.5, 125.8 (q, $J_{C\text{-}F}$ = 3.9 Hz), 124.5 (q, $J_{C\text{-}F}$ = 272.6 Hz), 115.6, 105.9, 57.9, 46.6, 44.7; IR (neat) 3082, 3017, 2979, 2940, 2846, 1683, 1640, 1621, 1595, 1456, 1439, 1418, 1327, 1233, 1165, 1123, 1069, 1018, 955, 922 cm^{-1}; HRMS (EI): *m/z* for $C_{15}H_{15}F_3O_2$ $[M]^+$ calcd. 284.1024, found: 284.1018.



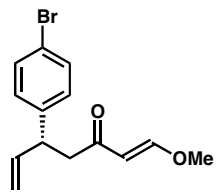
(*R*,*E*)-1-methoxy-5-(4-methoxyphenyl)hepta-1,6-dien-3-one (4c). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as colorless oil in 69% yield (33 mg, 67%; 35 mg, 71%). The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 °C); t_1 = 11.3 min, t_2 = 14.3 min [(Chiralpak AD-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 9.46° (*c* 0.93, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 12.5 Hz, 1H), 7.12-7.14 (m, 2H), 6.83-6.85 (m, 2H), 5.97 (ddd, J = 17.0, 10.5, 6.5 Hz, 1H), 5.54 (d, J = 12.5 Hz, 1H), 5.03 (dt, J = 10.5, 1.5 Hz, 1H), 5.00 (dt, J = 17.0, 1.5 Hz, 1H), 3.92 (app. q, J = 7.0 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 2.87 (dd, J = 15.5, 7.5 Hz, 1H), 2.80 (dd, J = 15.5, 7.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.0, 163.1, 158.5, 141.4, 135.4, 128.9, 114.5, 114.2, 106.1, 57.8, 55.5, 47.2, 44.3; IR (neat) 3077, 2936, 2837, 1747, 1683, 1639, 1594, 1512, 1462, 1441, 1304, 1249, 1179, 1079, 1034, 958, 920 cm^{-1}; HRMS (EI): *m/z* for $C_{15}H_{18}O_3$ $[M]^+$ calcd. 246.1256, found: 246.1254.



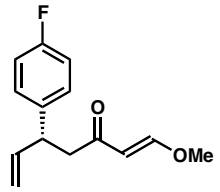
(*R*,*E*)-1-methoxy-5-(*p*-tolyl)hepta-1,6-dien-3-one (4d). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 77% yield (35 mg, 76%; 36 mg, 78%). The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 °C); t_1 = 9.34 min, t_2 = 11.8 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 12.1° (*c* 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 12.4 Hz, 1H), 7.11 (app. s, 4H), 5.98 (ddd, J = 17.2, 10.4, 6.4 Hz, 1H), 5.55 (d, J = 12.4 Hz, 1H), 5.04 (dt, J = 10.4, 1.2 Hz, 1H), 5.02 (dt, J = 17.2, 1.2 Hz, 1H), 3.94 (app. q, J = 7.2 Hz, 1H), 3.66 (s, 3H), 2.89 (dd, J = 15.6, 7.6 Hz, 1H), 2.82 (dd, J = 15.6, 7.2 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 163.1, 141.2, 140.4, 136.3, 129.5, 127.8, 114.6, 106.1, 57.8, 47.1, 44.8, 21.3; IR (neat) 3079, 3020, 2977, 2923, 1685, 1638, 1620, 1594, 1438, 1411, 1338, 1310, 1231, 1187, 1134, 1077, 1031, 996, 956, 919 cm^{-1}; HRMS (EI): *m/z* for $C_{15}H_{18}O_2$ $[M]^+$ calcd. 230.1307, found: 230.1309.



(*R*,*E*)-5-(4-chlorophenyl)-1-methoxyhepta-1,6-dien-3-one (4e). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as white solid in 79% yield (43 mg, 86%; 36 mg, 72%). The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 °C); t_1 = 10.9 min, t_2 = 13.5 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 5.52° (*c* 1.05, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 12.5 Hz, 1H), 7.25-7.27 (m, 2H), 7.13-7.16 (m, 2H), 5.95 (ddd, *J* = 17.0, 10.0, 6.5 Hz, 1H), 5.54 (d, *J* = 12.5 Hz, 1H), 5.07 (dt, *J* = 10.0 Hz, 1H), 5.00 (d, *J* = 17.0 Hz, 1H), 3.96 (app. q, *J* = 7.0 Hz, 1H), 3.68 (s, 3H), 2.88 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.81 (dd, *J* = 16.0, 7.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 163.2, 141.9, 140.8, 132.4, 129.4, 128.9, 115.2, 106.0, 57.9, 46.8, 44.3; IR (neat) 3081, 3010, 2977, 2937, 2842, 1683, 1639, 1621, 1593, 1491, 1455, 1438, 1408, 1340, 1311, 1231, 1189, 1136, 1091, 1037, 1014, 957, 920 cm^{-1}; HRMS (EI): *m/z* for $C_{14}H_{15}ClO_2$ $[M]^+$ calcd. 250.0761, found: 250.0756.

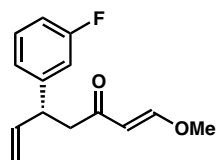


(*R*,*E*)-5-(4-bromophenyl)-1-methoxyhepta-1,6-dien-3-one (4f). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as white solid in 71% yield (44 mg, 75%; 40 mg, 68%). Melting point: 43-46 °C. The enantiomeric excess was determined by HPLC analysis to be 96% ee (254 nm, 25 °C); t_1 = 11.5 min, t_2 = 14.4 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 4.06° (*c* 1.43, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 12.5 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 5.94 (ddd, *J* = 17.0, 10.0, 6.5 Hz, 1H), 5.53 (d, *J* = 12.5 Hz, 1H), 5.07 (dt, *J* = 10.0 Hz, 1H), 5.00 (d, *J* = 17.0 Hz, 1H), 3.95 (app. q, *J* = 7.0 Hz, 1H), 3.68 (s, 3H), 2.88 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.80 (dd, *J* = 16.0, 7.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 163.2, 142.4, 140.5, 131.9, 129.8, 120.5, 115.2, 106.0, 57.9, 46.7, 44.4; IR (neat) 3080, 3021, 2977, 2937, 2841, 1682, 1659, 1651, 1643, 1621, 1593, 1488, 1455, 1437, 1404, 1339, 1311, 1231, 1190, 1136, 1074, 1010, 957, 921 cm^{-1}; HRMS (EI): *m/z* for $C_{14}H_{15}BrO_2$ $[M]^+$ calcd. 294.0255, found: 294.0258. A single crystal suitable for X-ray analysis was prepared by slow diffusion of hexane into a saturated solution of the compound in ether at ambient temperature.

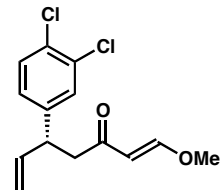


(*R*,*E*)-5-(4-fluorophenyl)-1-methoxyhepta-1,6-dien-3-one (4g). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 83% yield (41 mg, 88%; 37 mg, 79%). The enantiomeric excess was determined by HPLC analysis to be 96% ee (254 nm, 25 °C); t_1 = 10.4 min, t_2 = 12.1 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 18.0° (*c* 1.20, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.55 (d, J = 12.8 Hz, 1H), 7.15-7.19 (m, 2H), 6.96-7.00 (m, 2H), 5.96 (ddd, J = 17.2, 10.4, 6.4 Hz, 1H), 5.54 (d, J = 12.8 Hz, 1H), 5.06 (dt, J = 10.4, 1.2 Hz, 1H), 5.00 (dt, J = 17.2, 1.2 Hz, 1H), 3.97 (app. q, J = 7.2 Hz, 1H), 3.67 (s, 3H), 2.88 (dd, J = 15.6, 7.2 Hz, 1H), 2.80 (dd, J = 15.6, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 163.2, 161.8 (d, $J_{C\text{-}F}$ = 244.5 Hz), 140.9, 139.0 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.1 Hz), 114.9, 106.0, 57.8, 47.0, 44.2; IR (neat) 3079, 2978, 2937, 2844, 1685, 1638, 1621, 1594, 1509, 1455, 1438, 1411, 1340, 1311, 1222, 1159, 1136, 1077, 1036, 1015, 957, 920 cm^{-1}; HRMS (EI): *m/z* for $C_{14}H_{15}FO_2$ $[M]^+$ calcd. 234.1056, found: 234.1051.

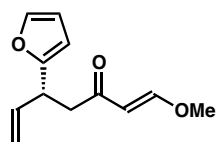


(*R*,*E*)-5-(3-fluorophenyl)-1-methoxyhepta-1,6-dien-3-one (4h). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as colorless oil in 69% yield (33 mg, 71%; 32 mg, 68%). The enantiomeric excess was determined by HPLC analysis to be 96% ee (254 nm, 25 °C); t_1 = 9.42 min, t_2 = 10.1 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 9.36° (*c* 0.94, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 12.5 Hz, 1H), 7.23-7.27 (m, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.87-6.93 (m, 2H), 5.95 (ddd, J = 17.0, 10.0, 6.5 Hz, 1H), 5.55 (d, J = 12.5 Hz, 1H), 5.08 (dt, J = 10.0 Hz, 1H), 5.03 (d, J = 17.0 Hz, 1H), 3.99 (app. q, J = 7.0 Hz, 1H), 3.68 (s, 3H), 2.89 (dd, J = 16.0, 7.5 Hz, 1H), 2.82 (dd, J = 16.0, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 163.24, 163.23 (d, $J_{C\text{-}F}$ = 245.5 Hz), 146.1 (d, $J_{C\text{-}F}$ = 6.0 Hz), 140.4, 130.3 (d, $J_{C\text{-}F}$ = 9.1 Hz), 123.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 115.3, 114.9 (d, $J_{C\text{-}F}$ = 21.1 Hz), 113.6 (d, $J_{C\text{-}F}$ = 21.1 Hz), 106.0, 57.9, 46.7, 44.7; IR (neat) 3080, 3015, 2977, 2938, 2844, 1683, 1640, 1592, 1488, 1448, 1414, 1340, 1311, 1232, 1141, 1072, 974, 921 cm^{-1}; HRMS (EI): *m/z* for $C_{14}H_{15}FO_2$ $[M]^+$ calcd. 234.1056, found: 234.1051.

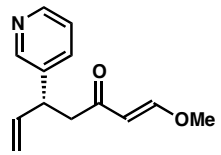


(*R*,*E*)-5-(3,4-dichlorophenyl)-1-methoxyhepta-1,6-dien-3-one (4i). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as colorless oil in 72% yield (40 mg, 70%; 42 mg, 74%). The enantiomeric excess was determined by HPLC analysis to be 94% ee (254 nm, 25 °C); t_1 = 9.75 min, t_2 = 11.3 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 3.37° (*c* 0.95, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 12.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 2.0 Hz, 1H), 7.06 (dd, J = 8.0, 2.0 Hz, 1H), 5.92 (ddd, J = 17.0, 10.0, 6.5 Hz, 1H), 5.55 (d, J = 12.5 Hz, 1H), 5.09 (d, J = 10.0 Hz, 1H), 5.02 (d, J = 17.0 Hz, 1H), 3.96 (app. q, J = 7.0 Hz, 1H), 3.69 (s, 3H), 2.88 (dd, J = 16.0, 7.0 Hz, 1H), 2.80 (dd, J = 16.0, 7.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 163.4, 143.8, 140.0, 132.7, 130.72, 130.69, 130.0, 127.9, 115.7, 105.9, 57.9, 46.5, 44.0; IR (neat) 3081, 3013, 2976, 2936, 2842, 1683, 1640, 1621, 1594, 1470,

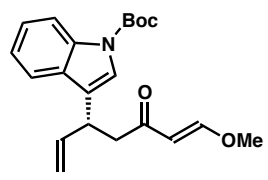
1437, 1397, 1340, 1311, 1251, 1231, 1192, 1133, 1076, 1030, 948, 921 cm^{-1}; HRMS (EI): *m/z* for $C_{14}H_{14}Cl_2O_2$ $[M]^+$ calcd. 284.0371, found: 284.0377.



(*R*,*E*)-5-(furan-2-yl)-1-methoxyhepta-1,6-dien-3-one (4j). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 67% yield (29 mg, 70%; 26 mg, 63%). The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 °C); t_1 = 9.30 min, t_2 = 10.3 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = –30.6° (*c* 0.93, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 12.5 Hz, 1H), 7.32 (d, *J* = 1.0 Hz, 1H), 6.28 (dd, *J* = 3.0, 2.0 Hz, 1H), 6.04 (d, *J* = 3.0 Hz, 1H), 5.91 (ddd, *J* = 17.0, 10.0, 7.5 Hz, 1H), 5.57 (d, *J* = 12.5 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 5.08 (d, *J* = 17.0 Hz, 1H), 4.07 (app. q, *J* = 7.0 Hz, 1H), 3.69 (s, 3H), 2.95 (dd, *J* = 16.0, 7.5 Hz, 1H), 2.79 (dd, *J* = 16.0, 7.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 163.3, 156.2, 141.7, 138.1, 116.2, 110.5, 106.0, 105.7, 57.8, 44.7, 39.0; IR (neat) 3082, 2938, 2845, 1782, 1682, 1640, 1621, 1593, 1505, 1455, 1439, 1410, 1342, 1312, 1228, 1195, 1146, 1082, 1011, 922 cm^{-1}; HRMS (EI): *m/z* for $C_{12}H_{14}O_3$ $[M]^+$ calcd. 206.0943, found: 206.0939.

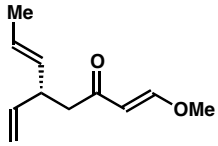


(*R*,*E*)-1-methoxy-5-(pyridin-3-yl)hepta-1,6-dien-3-one (4k). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 73% yield (33 mg, 76%; 31 mg, 71%). The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 °C); t_1 = 28.9 min, t_2 = 33.4 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = 2.62° (*c* 1.03, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 2.0 Hz, 1H), 8.46 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.57 (d, *J* = 12.5 Hz, 1H), 7.53 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.23 (dd, *J* = 8.0, 5.0 Hz, 1H), 5.98 (ddd, *J* = 17.0, 10.0, 6.5 Hz, 1H), 5.55 (d, *J* = 12.5 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 4.03 (app. q, *J* = 7.0 Hz, 1H), 3.68 (s, 3H), 2.94 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.85 (dd, *J* = 16.0, 7.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 163.4, 149.5, 148.0, 140.0, 138.9, 135.9, 123.8, 115.8, 105.8, 57.9, 46.5, 42.4; IR (neat) 2917, 1638, 1620, 1592, 1474, 1455, 1354, 1299, 1251, 1109, 960 cm^{-1}; HRMS (ESI): *m/z* for $C_{13}H_{16}NO_2$ $[M+H]^+$ calcd. 218.1176, found: 218.1176.

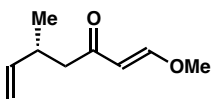


(*R*,*E*)-*tert*-butyl 3-(7-methoxy-5-oxohepta-1,6-dien-3-yl)-1*H*-indole-1-carboxylate (4l). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 78% yield (53 mg, 75%; 58 mg, 82%). The enantiomeric excess was determined by HPLC analysis to be 93% ee (254 nm, 25 °C); t_1 = 9.27 min, t_2 = 11.0 min [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0

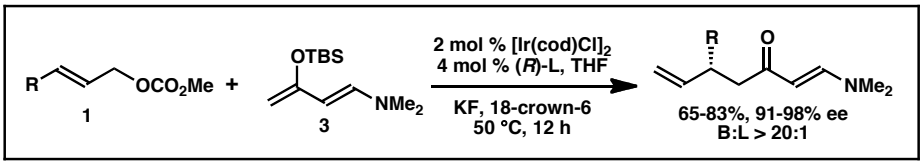
mL/min]; $[\alpha]_D^{25}$ = –20.4° (*c* 1.40, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (bs, 1H), 7.59 (d, *J* = 12.5 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.38 (bs, 1H), 7.30 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.22 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.02 (ddd, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.60 (d, *J* = 12.5 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.23 (app. q, *J* = 7.0 Hz, 1H), 3.67 (s, 3H), 2.99 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.94 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 163.2, 150.1, 139.7, 136.0, 129.9, 124.7, 122.6, 122.5, 120.0, 115.6, 115.5, 106.1, 83.8, 77.6, 57.8, 45.8, 36.3, 28.5; IR (neat) 2977, 2924, 1731, 1687, 1658, 1640, 1621, 1595, 1453, 1372, 1309, 1256, 1158, 1082 cm^{-1}; HRMS (ESI): *m/z* for $C_{21}H_{26}NO_4$ $[M+H]^+$ calcd. 356.1856, found: 356.1859.



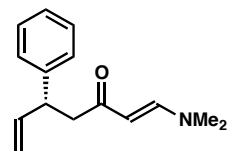
(*R*,1*E*,6*E*)-1-methoxy-5-vinylocta-1,6-dien-3-one (4m). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as colorless oil in 79% yield (29 mg, 81%; 28 mg, 78%). The enantiomeric excess was determined by HPLC analysis to be 92% ee (254 nm, 25 °C); t_1 = 9.90 min, t_2 = 11.3 min [(Chiralpak AS-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = 1.56° (*c* 0.96, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 12.5 Hz, 1H), 5.76 (ddd, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.58 (d, *J* = 12.5 Hz, 1H), 5.47 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.37 (ddq, *J* = 15.5, 7.0, 1.5 Hz, 1H), 5.02 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.99 (d, *J* = 10.0, Hz, 1H), 3.70 (s, 3H), 3.32-3.26 (m, 1H), 2.54 (app. d, *J* = 7.0 Hz, 2H), 1.65 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.3, 163.1, 140.8, 132.6, 126.0, 114.5, 106.3, 57.8, 46.4, 42.6, 18.3; IR (neat) 3079, 2968, 2937, 2856, 1683, 1640, 1621, 1594, 1439, 1411, 1338, 1311, 1221, 1139, 1074, 969, 919 cm^{-1}; HRMS (EI): *m/z* for $C_{11}H_{16}O_2$ $[M]^+$ calcd. 180.1150, found: 180.1146.



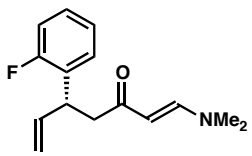
(*R*,*E*)-1-methoxy-5-methylhepta-1,6-dien-3-one (4n). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 75% yield (24 mg, 78%; 22 mg, 71%). The enantiomeric excess was determined by HPLC analysis to be 90% ee (254 nm, 25 °C); t_1 = 10.1 min, t_2 = 11.5 min [(Chiralpak AS-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min]; $[\alpha]_D^{25}$ = –8.96° (*c* 0.87, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 12.5 Hz, 1H), 5.79 (ddd, *J* = 17.0, 10.5, 7.0 Hz, 1H), 5.59 (d, *J* = 12.5 Hz, 1H), 5.00 (dt, *J* = 17.5, 1.5 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 3.71 (s, 3H), 2.78-2.72 (m, 1H), 2.50 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.38 (dd, *J* = 15.0, 7.5 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.9, 163.0, 143.4, 113.2, 106.3, 57.8, 48.2, 34.2, 20.0; IR (neat) 3080, 2964, 2935, 1683, 1640, 1621, 1595, 1455, 1439, 1417, 1340, 1311, 1243, 1223, 1196, 1170, 1138, 1046, 996, 978, 915 cm^{-1}; HRMS (EI): *m/z* for $C_9H_{14}O_2$ $[M]^+$ calcd. 154.0994, found: 154.0992.



General Procedure for Ir-catalyzed Asymmetric Allylic Substitution with silane 3. In a nitrogen-filled dry-box, $[Ir(cod)Cl]_2$ (2.7 mg, 0.0040 mmol), the phosphoramidite ligand (R_a, R_c, R_c)-**L** (4.3 mg, 0.0080 mmol), KF (12 mg, 0.20 mmol), 18-crown-6 (53 mg, 0.20 mmol) and a Teflon-coated magnetic stirring bar were added to a 1-dram vial. Then, anhydrous THF (0.40 mL) was added. The mixture was stirred for 5 minutes at ambient temperature before the carbonate **1** (0.20 mmol) and enol silane **3** (0.40 mmol, 2.0 equiv) were added. The vial was sealed with a cap containing a PTFE-lined silicone septum, removed from the dry-box and stirred at 50 ˚C for 12 h. The reaction progress was monitored by TLC and ^{1}H-NMR spectroscopy. When the reaction was judged to be complete, the reaction mixture was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution: hexane:EtOAc = 10:1 to 1:5) to provide product **5**.[2]

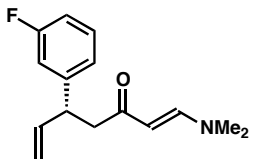


(*R*,*E*)-1-methoxy-5-phenylhepta-1,6-dien-3-one (5a). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 79% yield (35 mg, 76%; 38 mg, 83%). The enantiomeric excess was determined by HPLC analysis to be 92% ee (254 nm, 25 °C); t_1 = 20.7 min, t_2 = 24.8 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = 15.1˚ (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 12.4 Hz, 1H), 7.29-7.35 (m, 5H), 6.06 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.04 -5.09 (m, 2H), 5.02 (d, *J* = 12.4 Hz, 1H), 4.02 (app. q, *J* = 7.2 Hz, 1H), 3.06 (bs, 3H), 2.83 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.79 (bs, 3H), 2.76 (dd, *J* = 14.4, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.9, 153.0, 144.1, 141.6, 128.7, 128.1, 126.5, 114.5, 96.5, 47.5, 46.0, 45.1, 37.3; IR (neat) 3061, 3027, 2925, 2808, 1722, 1651, 1574, 1492, 1435, 1420, 1360, 1282, 1115, 1073, 1030, 986, 950, 915 cm^{-1}; HRMS (ESI): *m/z* for $C_{15}H_{20}NO$ $[M+H]^+$ calcd. 230.1539, found: 230.1541.

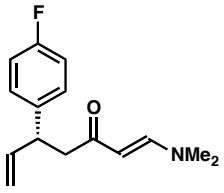


(*R*,*E*)-1-(dimethylamino)-5-(2-fluorophenyl)hepta-1,6-dien-3-one (5b). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 69% yield (33 mg, 67%; 35 mg, 71%). The enantiomeric excess was determined by HPLC analysis to be 91% ee (254 nm, 25 °C); t_1 = 20.4 min, t_2 = 22.2 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = 2.47˚ (*c* 0.93, $CHCl_3$); ^{1}H

NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 12.6 Hz, 1H), 7.22-7.25 (m, 1H), 7.14-7.18 (m, 1H), 7.05-7.07 (m, 1H), 6.98-7.01 (m, 1H), 6.03 (ddd, J = 16.8, 10.2, 7.2 Hz, 1H), 4.99-5.04 (m, 3H), 4.22 (app. q, J = 7.2 Hz, 1H), 3.03 (bs, 3H), 2.76-2.83 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.4, 161.0 (d, $J_{C\text{-}F}$ = 246.0 Hz), 152.9, 140.1, 130.9 (d, $J_{C\text{-}F}$ = 14.3 Hz), 129.7 (d, $J_{C\text{-}F}$ = 5.1 Hz), 128.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 124.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.6 Hz), 115.0, 96.2, 46.3, 45.1, 40.4, 37.3; IR (neat) 3079, 2922, 2808, 1651, 1574, 1490, 1435, 1359, 1282, 1229, 1084, 1037, 987, 949, 918 cm^{-1}; HRMS (ESI): *m/z* for $C_{15}H_{19}FNO$ $[M+H]^+$ calcd. 248.1445, found: 248.1447.

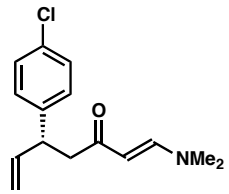


(*R*,*E*)-1-(dimethylamino)-5-(3-fluorophenyl)hepta-1,6-dien-3-one (5c). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 65% yield (31 mg, 63%; 33 mg, 67%). The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 °C); t_1 = 20.5 min, t_2 = 22.1 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = 10.2˚ (*c* 1.07, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 12.6 Hz, 1H), 7.20-7.24 (m, 1H), 7.01 (d, J = 7.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.85 (dt, J = 8.4, 2.4 Hz, 1H), 5.96 (ddd, J = 16.8, 10.2, 6.6 Hz, 1H), 5.00-5.04 (m, 2H), 4.95 (d, J = 12.6 Hz, 1H), 3.98 (app. q, J = 7.2 Hz, 1H), 3.02 (bs, 3H), 2.76 (bs, 3H), 2.75 (dd, J = 14.4, 7.8 Hz, 1H), 2.69 (dd, J = 14.4, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 163.2 (d, $J_{C\text{-}F}$ = 245.5 Hz), 152.9, 146.8 (d, $J_{C\text{-}F}$ = 7.0 Hz), 141.1, 130.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 123.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 114.9, 114.88 (d, $J_{C\text{-}F}$ = 21.1 Hz), 113.3 (d, $J_{C\text{-}F}$ = 21.1 Hz), 96.4, 47.2, 45.5, 45.0, 37.2; IR (neat) 3078, 2919, 2809, 1651, 1557, 1487, 1435, 1360, 1281, 1238, 1138, 1114, 1090, 987, 950, 919 cm^{-1}; HRMS (ESI): *m/z* for $C_{15}H_{19}FNO$ $[M+H]^+$ calcd. 248.1445, found: 248.1446.

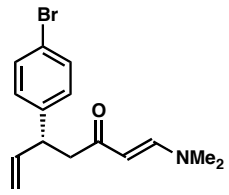


(*R*,*E*)-1-(dimethylamino)-5-(4-fluorophenyl)hepta-1,6-dien-3-one (5d). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 73% yield (34 mg, 69%; 38 mg, 77%). The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 °C); t_1 = 15.8 min, t_2 = 18.2 min [(Chiralpak AD-H) hexane/*i*-PrOH, 85:15, 0.5 mL/min]; $[\alpha]_D^{25}$ = 14.6˚ (*c* 0.83, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 12.6 Hz, 1H), 7.18-7.120 (m, 2H), 6.95-6.97 (m, 2H), 5.98 (ddd, J = 16.8, 10.2, 6.6 Hz, 1H), 4.99-5.04 (m, 2H), 4.95 (d, J = 12.6 Hz, 1H), 3.97 (app. q, J = 7.2 Hz, 1H), 3.03 (bs, 3H), 2.76 (bs, 3H), 2.75 (dd, J = 15.0, 7.2 Hz, 1H), 2.69 (dd, J = 15.0, 7.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.5, 161.7 (d, $J_{C\text{-}F}$ = 242.9 Hz), 152.9, 141.7, 139.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 114.6, 96.6, 47.6, 45.2, 45.1, 37.3; IR (neat) 3076, 3002, 2918, 2810, 1651, 1574, 1557, 1509, 1435,

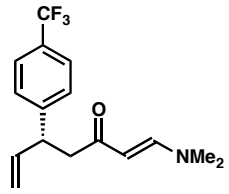
1422, 1359, 1282, 1220, 1159, 1114, 1015, 987, 953, 918 cm^{-1}; HRMS (ESI): *m/z* for $C_{15}H_{19}FNO$ $[M+H]^+$ calcd. 248.1445, found: 248.1446.



(*R*,*E*)-5-(4-chlorophenyl)-1-(dimethylamino)hepta-1,6-dien-3-one (5e). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 72% yield (39 mg, 74%; 37 mg, 70%). The enantiomeric excess was determined by HPLC analysis to be 93% ee (254 nm, 25 °C); t_1 = 16.5 min, t_2 = 20.7 min [(Chiralpak AD-H) hexane/*i*-PrOH, 85:15, 0.5 mL/min]; $[\alpha]_D^{25}$ = 8.17° (*c* 1.20, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 12.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.97 (ddd, *J* = 17.4, 10.2, 6.6 Hz, 1H), 5.04 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 17.4 Hz, 1H), 4.95 (d, *J* = 12.6 Hz, 1H), 3.96 (app. q, *J* = 7.2 Hz, 1H), 3.03 (bs, 3H), 2.76 (bs, 3H), 2.75 (dd, *J* = 15.0, 7.8 Hz, 1H), 2.68 (dd, *J* = 15.0, 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.3, 152.9, 142.6, 141.3, 132.1, 129.6, 128.7, 114.8, 96.4, 47.3, 45.2, 45.1, 37.3; IR (neat) 3079, 2924, 2807, 1651, 1574, 1557, 1490, 1435, 1419, 1360, 1282, 1089, 1014, 987, 950, 918 cm^{-1}; HRMS (ESI): *m/z* for $C_{15}H_{19}ClNO$ $[M+H]^+$ calcd. 264.1150, found: 264.1150.

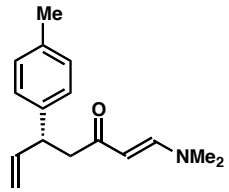


(*R*,*E*)-5-(4-bromophenyl)-1-(dimethylamino)hepta-1,6-dien-3-one (5f). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 72% yield (45 mg, 73%; 44 mg, 71%). The enantiomeric excess was determined by HPLC analysis to be 91% ee (254 nm, 25 °C); t_1 = 17.4 min, t_2 = 22.4 min [(Chiralpak AD-H) hexane/*i*-PrOH, 85:15, 0.5 mL/min]; $[\alpha]_D^{25}$ = 7.32° (*c* 1.27, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 12.6 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.97 (ddd, *J* = 17.4, 10.2, 6.6 Hz, 1H), 5.04 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 17.4 Hz, 1H), 4.94 (d, *J* = 12.6 Hz, 1H), 3.95 (app. q, *J* = 7.2 Hz, 1H), 3.04 (bs, 3H), 2.76 (bs, 3H), 2.75 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.68 (dd, *J* = 14.4, 7.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.2, 152.9, 143.1, 141.2, 131.7, 129.9, 120.2, 114.8, 96.3, 47.2, 45.2, 45.1, 37.3; IR (neat) 3078, 2923, 1651, 1568, 1487, 1435, 1420, 1360, 1280, 1086, 1010 cm^{-1}; HRMS (ESI): *m/z* for $C_{15}H_{19}BrNO$ $[M+H]^+$ calcd. 308.0645, found: 308.0644.

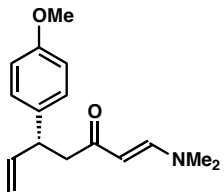


(*R*,*E*)-1-(dimethylamino)-5-(4-(trifluoromethyl)phenyl)hepta-1,6-dien-3-one (5g). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 63% yield (37 mg, 62%; 38 mg, 64%). The enantiomeric excess was determined by HPLC analysis to be 92% ee (254 nm, 25 °C); t_1 = 25.5 min, t_2 = 28.2 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = 4.56° (*c*

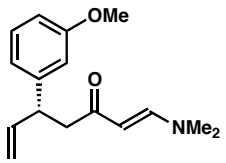
1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 12.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 5.99 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 12.4 Hz, 1H), 4.06 (app. q, *J* = 7.2 Hz, 1H), 3.04 (bs, 3H), 2.80 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.76 (bs, 3H), 2.72 (dd, *J* = 14.8, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 153.1, 148.2, 140.9, 128.7 (q, J_{C-F} = 32.2 Hz), 128.5, 125.6 (q, J_{C-F} = 4.0 Hz), 124.6 (q, J_{C-F} = 271.6 Hz), 115.2, 96.2, 47.1, 45.7, 45.1, 37.3; IR (neat) 3079, 2923, 2853, 1653, 1617, 1571, 1437, 1421, 1360, 1327, 1282, 1163, 1119, 1068, 1017 cm^{-1}; HRMS (ESI): *m/z* for $C_{16}H_{19}F_3NO$ $[M+H]^+$ calcd. 298.1413, found: 298.1411.



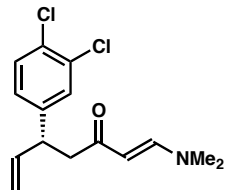
(*R*,*E*)-1-(dimethylamino)-5-(*p*-tolyl)hepta-1,6-dien-3-one (5h). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 80% yield (38 mg, 78%; 40 mg, 82%). The enantiomeric excess was determined by HPLC analysis to be 94% ee (254 nm, 25 °C); t_1 = 14.7 min, t_2 = 19.3 min [(Chiralpak AD-H) hexane/*i*-PrOH, 85:15, 0.5 mL/min]; $[\alpha]_D^{25}$ = 10.4° (*c* 1.13, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 12.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.99 (ddd, *J* = 17.4, 10.8, 7.2 Hz, 1H), 4.98-5.03 (m, 3H), 3.93 (app. q, *J* = 7.2 Hz, 1H), 3.03 (bs, 3H), 2.77 (bs, 3H), 2.76 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.70 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.9, 152.8, 141.9, 141.1, 135.9, 129.4, 127.9, 114.3, 96.5, 47.6, 45.6, 45.1, 37.3, 21.3; IR (neat) 3077, 2921, 2807, 1651, 1574, 1513, 1487, 1435, 1359, 1283, 1186, 1113, 1086, 1021, 987, 950, 914 cm^{-1}; HRMS (ESI): *m/z* for $C_{16}H_{22}NO$ $[M+H]^+$ calcd. 244.1696, found: 244.1696.



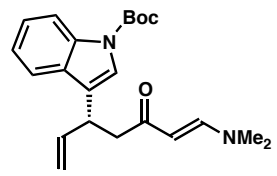
(*R*,*E*)-1-(dimethylamino)-5-(4-methoxyphenyl)hepta-1,6-dien-3-one (5i). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 69% yield (35 mg, 68%; 37 mg, 71%). The enantiomeric excess was determined by HPLC analysis to be 94% ee (254 nm, 25 °C); t_1 = 19.4 min, t_2 = 25.7 min [(Chiralpak AD-H) hexane/*i*-PrOH, 85:15, 0.5 mL/min]; $[\alpha]_D^{25}$ = 12.7° (*c* 0.85, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 12.6 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.99 (ddd, *J* = 17.4, 10.8, 6.6 Hz, 1H), 4.96-5.01 (m, 3H), 3.92 (app. q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 3.02 (bs, 3H), 2.76 (bs, 3H), 2.75 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.69 (dd, *J* = 14.4, 7.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.8, 158.2, 152.7, 142.0, 136.2, 128.9, 115.1, 115.0, 96.5, 55.5, 47.6, 45.1, 45.0, 37.2; IR (neat) 3078, 2999, 2910, 1651, 1568, 1512, 1436, 1421, 1355, 1282, 1249, 1179, 1112, 1034, 987, 955, 917 cm^{-1}; HRMS (ESI): *m/z* for $C_{16}H_{22}NO_2$ $[M+H]^+$ calcd. 260.1645, found: 260.1647.



(*R*,*E*)-1-(dimethylamino)-5-(3-methoxyphenyl)hepta-1,6-dien-3-one (5j). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 72% yield (37 mg, 71%; 38 mg, 73%). The enantiomeric excess was determined by HPLC analysis to be 96% ee (254 nm, 25 °C); t_1 = 25.9 min, t_2 = 31.2 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = 6.60° (*c* 1.03, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 12.6 Hz, 1H), 7.20 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 6.72 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.99 (ddd, *J* = 17.4, 10.8, 7.2 Hz, 1H), 5.01-5.05 (m, 2H), 4.98 (d, *J* = 12.6 Hz, 1H), 3.95 (app. q, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 3.03 (bs, 3H), 2.76 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.75 (bs, 3H), 2.71 (dd, *J* = 15.0, 6.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.7, 159.9, 152.8, 146.0, 141.5, 129.6, 120.5, 114.6, 113.9, 111.8, 96.6, 55.5, 47.5, 46.0, 45.0, 37.3; IR (neat) 2915, 1651, 1567, 1471, 1455, 1354, 1285, 1252, 1108, 960 cm^{-1}; HRMS (ESI): *m/z* for $C_{16}H_{22}NO_2$ $[M+H]^+$ calcd. 260.1645, found: 260.1646.

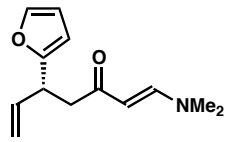


(*R*,*E*)-5-(3,4-dichlorophenyl)-1-(dimethylamino)hepta-1,6-dien-3-one (5k). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 75% yield (46 mg, 77%; 44 mg, 74%). The enantiomeric excess was determined by HPLC analysis to be 92% ee (254 nm, 25 °C); t_1 = 21.2 min, t_2 = 27.3 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = 8.64° (*c* 1.10, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 12.6 Hz, 1H), 7.29-7.32 (m, 2H), 7.06 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.92 (ddd, *J* = 17.4, 10.2, 6.6 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 5.00 (d, *J* = 17.4 Hz, 1H), 4.93 (d, *J* = 12.6 Hz, 1H), 3.94 (app. q, *J* = 7.2 Hz, 1H), 3.02 (bs, 3H), 2.75 (bs, 3H), 2.73 (dd, *J* = 15.0, 7.2 Hz, 1H), 2.66 (dd, *J* = 15.0, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 153.0, 144.4, 140.7, 132.4, 130.5, 130.3, 130.1, 127.8, 115.3, 96.6, 47.1, 45.0, 44.9, 37.3; IR (neat) 3080, 2923, 2807, 1652, 1574, 1470, 1435, 1420, 1359, 1282, 1132, 1114, 1086, 1029, 986, 949, 919 cm^{-1}; HRMS (ESI): *m/z* for $C_{15}H_{18}Cl_2NO$ $[M+H]^+$ calcd. 298.0760, found: 298.0759.

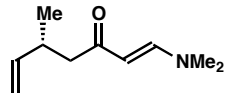


(*R*,*E*)-*tert*-butyl 3-(7-(dimethylamino)-5-oxohepta-1,6-dien-3-yl)-1*H*-indole-1-carboxylate (5l). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 83% yield (63 mg, 86%; 59 mg, 80%). The enantiomeric excess was determined by HPLC analysis to be 94% ee (254 nm, 25 °C); t_1 = 19.5 min, t_2 = 23.1 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = –21.5° (*c* 1.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (bs, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 12.5 Hz, 1H), 7.39 (bs, 1H), 7.28 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.20 (dd, *J* = 7.6, 7.6 Hz,

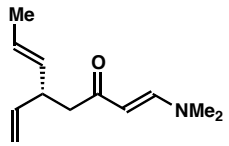
1H), 6.03 (ddd, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.11 (d, *J* = 17.2 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 5.03 (d, *J* = 12.4 Hz, 1H), 4.22 (app. q, *J* = 7.2 Hz, 1H), 3.01 (bs, 3H), 2.89 (dd, *J* = 14.8, 6.4 Hz, 1H), 2.81 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.76 (bs, 3H), 1.66 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.8, 153.2, 150.1, 140.2, 136.0, 130.2, 124.5, 123.1, 122.6, 122.5, 120.2, 115.5, 115.1, 96.5, 83.6, 46.1, 45.0, 37.3, 28.5; IR (neat) 3052, 2978, 2929, 2810, 1731, 1651, 1574, 1476, 1453, 1435, 1421, 1372, 1309, 1256, 1219, 1158, 1085, 1017, 990, 950, 917 cm^{-1}; HRMS (ESI): *m/z* for $C_{22}H_{29}N_2O_3$ $[M+H]^+$ calcd. 369.2173, found: 369.2171.



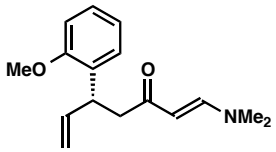
(*R*,*E*)-1-(dimethylamino)-5-(furan-2-yl)hepta-1,6-dien-3-one (5m). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as yellow oil in 68% yield (29 mg, 66%; 31 mg, 71%). The enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 °C); t_1 = 20.3 min, t_2 = 22.4 min [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = –45.0° (*c* 1.30, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 12.6 Hz, 1H), 7.31 (d, *J* = 1.2 Hz, 1H), 6.26 (dd, *J* = 3.0, 2.4 Hz, 1H), 6.03 (d, *J* = 3.0 Hz, 1H), 5.91 (ddd, *J* = 17.4, 10.2, 7.2 Hz, 1H), 5.06 (d, *J* = 17.4 Hz, 1H), 5.05 (d, *J* = 10.8 Hz, 1H), 4.99 (d, *J* = 12.6 Hz, 1H), 4.05 (app. q, *J* = 7.2 Hz, 1H), 3.04 (bs, 3H), 2.81 (dd, *J* = 15.0, 7.2 Hz, 1H), 2.77 (bs, 3H), 2.66 (dd, *J* = 15.0, 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.1, 157.0, 152.9, 141.4, 138.8, 115.7, 110.4, 105.4, 96.3, 45.1, 39.9, 37.2; IR (neat) 3112, 3080, 2922, 2809, 1651, 1557, 1504, 1488, 1435, 1360, 1283, 1233, 1148, 1092, 1010, 950, 920 cm^{-1}; HRMS (ESI): *m/z* for $C_{13}H_{18}NO_2$ $[M+H]^+$ calcd. 220.1332, found: 220.1331.



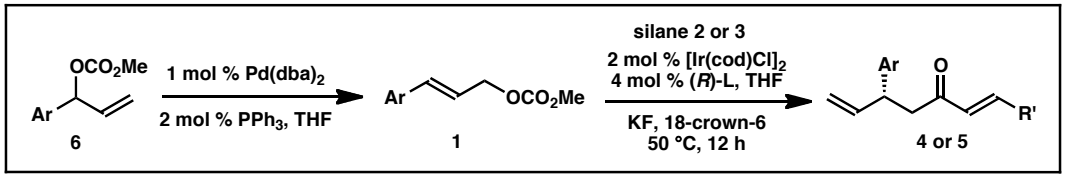
(*R*,*E*)-1-(dimethylamino)-5-methylhepta-1,6-dien-3-one (5n). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 69% yield (22 mg, 66%; 24 mg, 72%). The enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 °C); t_1 = 13.9 min, t_2 = 15.2 min [(Chiralpak OJ-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]; $[\alpha]_D^{25}$ = –2.53° (*c* 0.75, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 12.6 Hz, 1H), 5.82 (ddd, *J* = 17.4, 10.2, 6.6 Hz, 1H), 5.03 (d, *J* = 12.6 Hz, 1H), 5.00 (d, *J* = 17.4 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 3.06 (bs, 3H), 2.80 (bs, 3H), 2.71-2.76 (m, 1H), 2.39 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.25 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.03 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.1, 152.7, 144.3, 112.6, 96.7, 48.9, 45.1, 37.3, 35.0, 20.0; IR (neat) 3078, 2958, 2926, 2810, 1725, 1651, 1626, 1574, 1489, 1435, 1421, 1359, 1281, 1231, 1113, 1075, 982, 912 cm^{-1}; HRMS (ESI): *m/z* for $C_{10}H_{18}NO$ $[M+H]^+$ calcd. 168.1383, found: 168.1384.



(*R*,1*E*,6*E*)-1-(dimethylamino)-5-vinylocta-1,6-dien-3-one (5o). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 68% yield (26 mg, 67%; 27 mg, 70%). The enantiomeric excess was determined by HPLC analysis to be 93% ee (254 nm, 25 °C); t_1 = 26.5 min, t_2 = 30.3 min [(Chiralpak AS-H) hexane/*i*-PrOH, 85:15, 0.5 mL/min]; $[\alpha]_D^{25}$ = 4.96° (*c* 1.15, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 12.6 Hz, 1H), 5.79 (ddd, *J* = 17.4, 10.2, 7.2 Hz, 1H), 5.47 (dq, *J* = 15.6, 6.0 Hz, 1H), 5.39 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.02 (d, *J* = 12.6 Hz, 1H), 5.01 (d, *J* = 16.8 Hz, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 3.30-3.28 (m, 1H), 3.05 (bs, 3H), 2.80 (bs, 3H), 2.42 (app. d, *J* = 7.8 Hz, 2H), 1.65 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.3, 152.7, 141.5, 133.3, 125.3, 114.0, 96.7, 47.0, 45.0, 43.4, 37.3, 18.3; IR (neat) 3024, 2918, 2857, 1651, 1574, 1557, 1488, 1435, 1359, 1283, 1079, 969, 913 cm^{-1}; HRMS (ESI): *m/z* for $C_{12}H_{20}NO$ $[M+H]^+$ calcd. 194.1539, found: 194.1539.

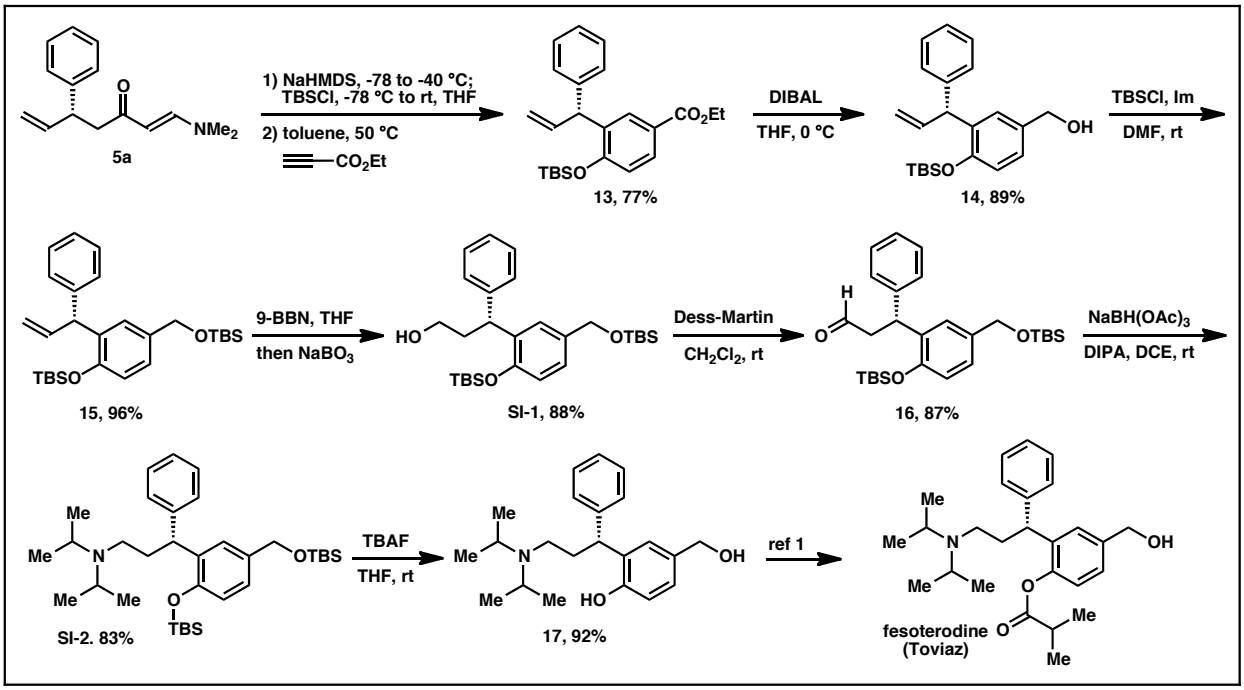


(*R*,*E*)-1-(dimethylamino)-5-(2-methoxyphenyl)hepta-1,6-dien-3-one (5p). The crude mixture was purified by flash column chromatography to give the title compound as light yellow oil in 70% yield (35 mg, 68%; 38 mg, 73%). The enantiomeric excess was determined by HPLC analysis to be 89% ee (254 nm, 25 °C); t_1 = 8.65 min, t_2 = 9.19 min [(Chiralpak AD-H) hexane/*i*-PrOH, 85:15, 1.0 mL/min]; $[\alpha]_D^{25}$ = 10.7° (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 13 Hz, 1H), 7.14-7.17 (m, 2H), 6.89 (t, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.05 (ddd, *J* = 17.0, 10.0, 7.5 Hz, 1H), 4.99-5.04 (m, 3H), 4.32 (app. q, *J* = 7.0 Hz, 1H), 3.82 (s, 3H), 3.00 (bs, 3H), 2.73-2.78 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 157.2, 152.7, 140.9, 132.5, 128.5, 127.5, 120.8, 114.4, 111.0, 96.4, 55.7, 46.4, 44.9, 39.9, 37.2; IR (neat) 3075, 2921, 2836, 1657, 1574, 1492, 1435, 1357, 1286, 1242, 1085, 1028, 755 cm^{-1}; HRMS (ESI): *m/z* for $C_{16}H_{22}NO_2$ $[M+H]^+$ calcd. 260.1651, found: 260.1647.



General Procedure for Sequential Pd-Catalyzed Isomerization of Branched Allylic Carbonates 6 and Ir-Catalyzed Asymmetric Allylic Substitution with Silanes 2 and 3. In a nitrogen-filled dry-box, $Pd(dba)_2$ (2.3 mg, 0.0040 mmol), PPh_3 (2.1 mg, 0.0080 mmol) and a Teflon-coated magnetic stirring bar were added to a 1-dram vial. Anhydrous THF (0.40 mL) was

added. The mixture was stirred for 10 minutes at ambient temperature before the branched allylic carbonate **6** (0.40 mmol) was added. The vial was sealed with a cap containing a PTFE-lined silicone septum, and stirred at ambient temperature in the dry-box. The reaction progress was monitored by ^{1}H-NMR spectroscopy. When the isomerization reaction was judged to be complete, the reaction mixture was filtered through a short pad of silica into a 1-dram vial (rinsed with 0.4 mL of THF). The resulting crude linear carbonate in THF was subjected to the Ir-catalyzed allylic substitution with silanes **2** or **3** under the standard reaction conditions. This reaction sequence provided the allylated products **4** and **5** in 65-79% yield and 91-93% ee.



Enantioselective Synthesis of Fesoterodine. Step 1. Synthesis of 13: NaHMDS (403 mg, 2.20 mmol) was weighed into an oven-dried, 200 mL round bottom flask containing a stir bar in a glove box. The flask was capped with a rubber septum and removed from the glove box and placed in a cold bath. THF (7.0 mL) was added to the flask and the resulting solution was cooled to –78 ˚C. After stirring for 5 minutes, a solution of compound **5a** (500 mg, 2.18 mmol) in THF (2.0 mL) was added slowly. The reaction mixture was stirred at –78 ˚C for 60 min, and TBSCl (350 mg, 2.32 mmol) in THF (1.0 mL) was added via a syringe. After 2 h at –78 ˚C, the solution was warmed to ambient temperature, and stirring was continued for 3 h. The reaction mixture was concentrated under reduced pressure. Anhydrous pentane (100 mL) was added to the flask, and the resulting suspension was filtered under Ar. The solution was concentrated under reduced pressure to give the crude reaction product as yellow oil. Toluene (3 mL) was

added to the flask containing the crude product followed by the addition of ethyl propionate (286 mg, 2.92 mmol). The mixture was heated at 50 ˚C, and the reaction progress was monitored by TLC and ^{1}H-NMR spectroscopy. When the reaction was judged to be complete, the reaction mixture was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution: hexane:Et_2O = 50:1 to 10:1) to provide the product **13** as a light yellow oil (620 mg, 77% over two steps). $[\alpha]_D^{25}$ = 2.62˚ (*c* 2.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.86 (m, 2H), 7.24-7.27 (m, 2H), 7.17-7.19 (m, 1H), 7.11-7.14 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.28 (ddd, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.23 (dt, *J* = 10.0, 1.5 Hz, 1H), 5.13 (d, *J* = 7.0 Hz, 1H), 4.89 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.32 (q, *J* = 7.0 Hz, 2H), 1.35 (t, *J* = 7.0 Hz, 3H), 0.91 (s, 9H), 0.23 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 157.8, 142.7, 140.4, 133.8, 132.0, 129.7, 128.9, 128.5, 126.5, 123.5, 118.3, 116.9, 60.9, 48.0, 26.0, 18.6, 14.7, -3.76, -3.84; IR (neat) 3061, 3027, 2956, 2930, 2897, 2858, 1716, 1604, 1494, 1365, 1278, 1231, 1113, 900, 841, 782, 721 cm^{-1}; HRMS (EI): *m/z* for $C_{24}H_{32}O_3Si$ $[M]^+$ calcd. 396.2120, found: 396.2118.

Step 2. Synthesis of 14: Ether ester **13** (396 mg, 1.0 mmol) was weighed into an oven-dried, 100 mL flask containing a stir bar. The flask was capped with a rubber septum and placed in a cold bath. Anhydrous THF (5 mL) was added to the flask under the Argon atmosphere and the resulting solution was cooled to 0 ˚C. After stirring for 5 minutes, a solution of DIBAL in THF (1 M, 2.4 mL, 2.4 mmol) was added at 0 ˚C. The mixture was stirred at 0 ˚C for 4 h and ethyl acetate (2 mL) was added slowly. After stirring for 10 minutes, a saturated aqueous solution of Rochelle's salt (50 mL) was added, and the resulting solution was stirred vigorously at ambient temperature for 12 h. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution: hexane:Et_2O = 20:1 to 1:1) to give product **14** (315 mg, 89%) as a colorless oil. $[\alpha]_D^{25}$ = −31.9˚ (*c* 2.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.28 (m, 2H), 7.09-7.19 (m, 5H), 6.28 (d, *J* = 8.5 Hz, 1H), 6.26 (ddd, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.21 (dt, *J* = 10.0, 1.5 Hz, 1H), 5.17 (d, *J* = 7.0 Hz, 1H), 4.88 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.57 (s, 2H), 1.56 (bs, 1H), 0.93 (s, 9H), 0.21 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.2, 143.2, 140.7, 133.8, 133.6, 129.4, 129.0, 128.5, 126.7, 126.4, 118.8, 116.6, 65.5, 47.9, 26.1, 18.6, -3.75, -3.82; IR (neat) 3334, 3082, 3060, 3027, 2956, 2929, 2885, 2857, 1609, 1495, 1471, 1463, 1267, 1006, 915, 840, 781 cm^{-1}; HRMS (ESI): *m/z* for $C_{22}H_{31}O_2Si$ $[M+H]^+$ calcd. 355.2093, found: 355.2091.

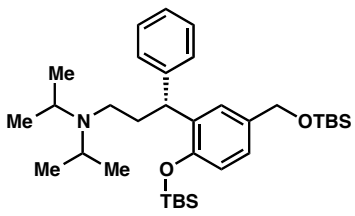
Step 3. Synthesis of 15: Alcohol **14** (240 mg, 0.68 mmol) was weighed into an oven-dried, 50 mL flask containing a stir bar and DMF (4 mL) was added to the flask, followed by the addition of imidazole (93 mg 1.37 mmol). After 5 minutes, TBSCl (154 mg, 1.02 mmol) was

added and the reaction mixture was stirred at ambient temperature for 8 h. Water (30 mL) and ether (10 mL) were added to the reaction flask. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution: hexane:Et_2O = 100:1 to 10:1) to give silyl ether **15** (306 mg, 96%) as a colorless oil. $[\alpha]_D^{25}$ = 1.1˚ (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.25 (m, 2H), 7.14-7.18 (m, 3H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.24 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.18 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.16 (d, *J* = 6.5 Hz, 1H), 4.84 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.63 (s, 2H), 0.93 (s, 9H), 0.89 (s, 9H), 0.19 (s, 3H), 0.12 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 143.4, 140.9, 134.1, 133.3, 129.1, 128.43, 128.41, 126.3, 125.4, 118.5, 116.4, 65.2, 47.9, 26.3, 26.2, 18.7, 18.6, -3.72, -3.80, -4.83, -4.85; IR (neat) 3027, 2956, 2929, 2885, 2857, 1610, 1496, 1463, 1362, 1255, 1091, 916, 838, 778 cm^{-1}; HRMS (EI): *m/z* for $C_{28}H_{44}O_2Si_2$ $[M]^+$ calcd. 468.2880, found: 468.2882.

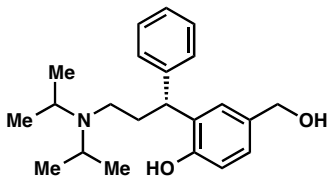
Step 4. Synthesis of SI-1: 9-BBN dimer (160 mg, 0.65 mmol) was weighed into an oven-dried, 50 mL flask containing a stir bar in a glove box. The flask was capped with a rubber septum and removed from the glove box and placed in a cold bath. THF (5 mL) was added to the flask, and the resulting solution was cooled to 0 ˚C. After stirring for 5 minutes, a solution of silyl ether **15** (188 mg, 0.40 mmol) in THF (5 mL) was added to the reaction flask at 0 ˚C. The reaction mixture was stirred at 0 ˚C for 8 h. $NaBO_3$ (800 mg) in 10 mL water was added to the reaction flask, and the resulting mixture was stirred at ambient temperature for 6 h. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution: hexane:Et_2O = 50:1 to 2:1) to give alcohol product **SI-1** (172 mg, 88%) as a colorless oil. $[\alpha]_D^{25}$ = 21.2˚ (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.28 (m, 4H), 7.14-7.18 (m, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.62-4.65 (m, 1H), 4.61 (s, 2H), 3.59-3.64 (m, 1H), 3.51-3.57 (m, 1H), 2.29-2.37 (m, 1H), 2.11-2.19 (m, 1H), 1.02 (s, 9H), 0.89 (s, 9H), 0.28 (s, 3H), 0.21 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.3, 144.8, 134.7, 134.6, 128.6, 128.43 127.0, 126.3, 125.2, 118.6, 65.1, 61.6, 39.2, 38.6, 26.31, 26.29, 18.71, 18.70, -3.49, -3.73, -4.88, -4.86; IR (neat) 3366, 2954, 2930, 2884, 2858, 1495, 1471, 1255, 1100, 936, 838, 779 cm^{-1}; HRMS (ESI): *m/z* for $C_{28}H_{47}O_3Si_2$ $[M+H]^+$ calcd. 487.3064, found: 487.3063.

Step 5. Synthesis of 16: A 50-mL, pear-shaped flask equipped with a rubber septum and argon inlet needle was charged with alcohol **SI-1** (100 mg, 0.21 mmol), $NaHCO_3$ (250 mg, 3.0 mmol) and 5 mL of CH_2Cl_2. Dess-Martin periodinane (223 mg, 0.53 mmol) was added in one

portion, and the resulting white slurry was stirred at room temperature. The reaction progress was monitored by TLC and ^{1}H-NMR spectroscopy. When the reaction was judged to be complete, the reaction mixture was diluted with 20 mL of Et_2O, and the resulting mixture was filtrated through a pad of Celite. The solution was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution: hexane:Et_2O = 50:1 to 5:1), which provided aldehyde **16** (86 mg, 86% yield) as a colorless oil. $[\alpha]_D^{25}$ = 22.7° (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (t, *J* = 2.0 Hz, 1H), 7.25-7.29 (m, 2H), 7.17-7.21 (m, 3H), 7.02 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.97 (d, *J* = 1.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.05 (t, *J* = 8.0 Hz, 1H), 4.59 (s, 2H), 3.01-3.10 (m, 2H), 0.99 (s, 9H), 0.88 (s, 9H), 0.26 (s, 3H), 0.21 (s, 3H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.0, 152.1, 143.0, 134.4, 133.6, 128.9, 128.4, 127.0, 126.8, 125.6, 118.5, 65.0, 49.1, 38.3, 26.3, 26.2, 18.71, 18.70, -3.6, -3.7, -4.90, -4.89; IR (neat) 2955, 2929, 2885, 1727, 1496, 1471, 1256, 1101, 895, 837, 779 cm^{-1}; HRMS (EI): *m/z* for $C_{28}H_{44}O_3Si_2$ $[M]^+$ calcd. 484.2829, found: 484.2828.



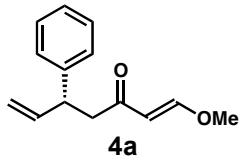
Step 6. Synthesis of SI-2: Aldehyde **16** (86 mg, 0.18 mmol) was weighed into an oven-dried, 50 mL flask containing a stir bar. The flask was capped with a rubber septum. Diisopropylamine (60 μL) and 1,2-dichloroethane (5 mL) were added to the flask. After stirring at 0 °C for 2 h, sodium triacetoxyborohydride (95 mg, 0.45 mmol) was added to the flask. The resulting mixture was stirred at ambient temperature until the aldehyde was consumed, as determined by TLC analysis (12 h). An aqueous saturated $NaHCO_3$ (5 mL) solution was added. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution: hexane:EtOAc = 10:1 to 1:5) to give alcohol product **SI-2** (84 mg, 83%) as a colorless oil. $[\alpha]_D^{25}$ = 18.7° (*c* 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.28 (m, 4H), 7.12-7.16 (m, 2H), 7.02 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 4.59-4.66 (m, 2H), 4.44 (t, *J* = 8.0 Hz, 1H), 3.07-3.14 (m, 2H), 2.37-2.50 (m, 2H), 2.14-2.28 (m, 2H), 1.02 (s, 9H), 0.99-1.01 (m, 12H), 0.91 (s, 9H), 0.26 (s, 3H), 0.21 (s, 3H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.3, 145.3, 135.0, 134.2, 128.5, 128.3, 126.8, 126.1, 125.0, 118.3, 65.2, 49.9, 44.7, 41.3, 36.9, 26.3, 20.7, 20.3, 18.71, 18.7, -3.60, -3.64, -4.88; IR (neat) 3026, 2958, 2930, 2885, 2858, 1609, 1495, 1472, 1463, 1423, 1389, 1361, 1326, 1255, 1206, 1160, 1102, 1006, 937, 915 cm^{-1}; HRMS (ESI): *m/z* for $C_{34}H_{60}NO_2Si_2$ $[M+H]^+$ calcd. 510.4157, found: 510.4150.



Step 7. Synthesis of 17: To a solution of silyl ether **SI-2** (29 mg, 0.051 mmol) in THF (2 mL) were added TBAF (1.0 M in THF, 250 μL). The reaction mixture was stirred at ambient temperature until the starting material was consumed, as determined by TLC analysis (24 h). The reaction mixture was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution; CH_2Cl_2:MeOH = 100:1 to 100:5) to give alcohol **17** (16 mg, 92% yield) as a colorless oil. $[\alpha]_D^{25} = 3.81^\circ$ (*c* 1.05, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.33 (m, 4H), 7.21-7.25 (m, 1H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.76 (bs, 1H), 4.50 (dd, *J* = 11.0, 4.5 Hz 1H), 4.43 (s, 2H), 3.24-3.31 (m, 3H), 2.72-2.78 (m, 1H), 2.35-2.43 (m, 2H), 2.11-2.19 (m, 1H), 1.60 (d, *J* = 6.5 Hz, 6H), 1.11 (d, *J* = 6.5 Hz, 6H); IR (neat) 3295, 2962, 2926, 2854, 2673, 1770, 1644, 1611, 1556, 1494, 1453, 1385, 1260, 1218, 1177, 1101, 1019, 818 cm^{-1}; HRMS (ESI): *m/z* for $C_{22}H_{32}NO_2$ $[M+H]^+$ calcd. 342.2433, found: 342.2431.

References:

1. Dirat, O.; Bibb, A. J.; Burns, C. M.; Checksfield, G. D.; Dillon, B. R.; Field, S. E.; Fussell, S. J.; Green, S. P.; Mason, C.; Mathew, J.; Mathew, S.; Moses, I. B.; Nikiforov, P. I.; Pettman, A. J.; Susanne, F. *Org. Process Res. Dev.* **2011**, 15, 1010.
2. Low intensity of ^{13}C signals of two N-methyl and two enamine carbons were observed in the allylated products **5**.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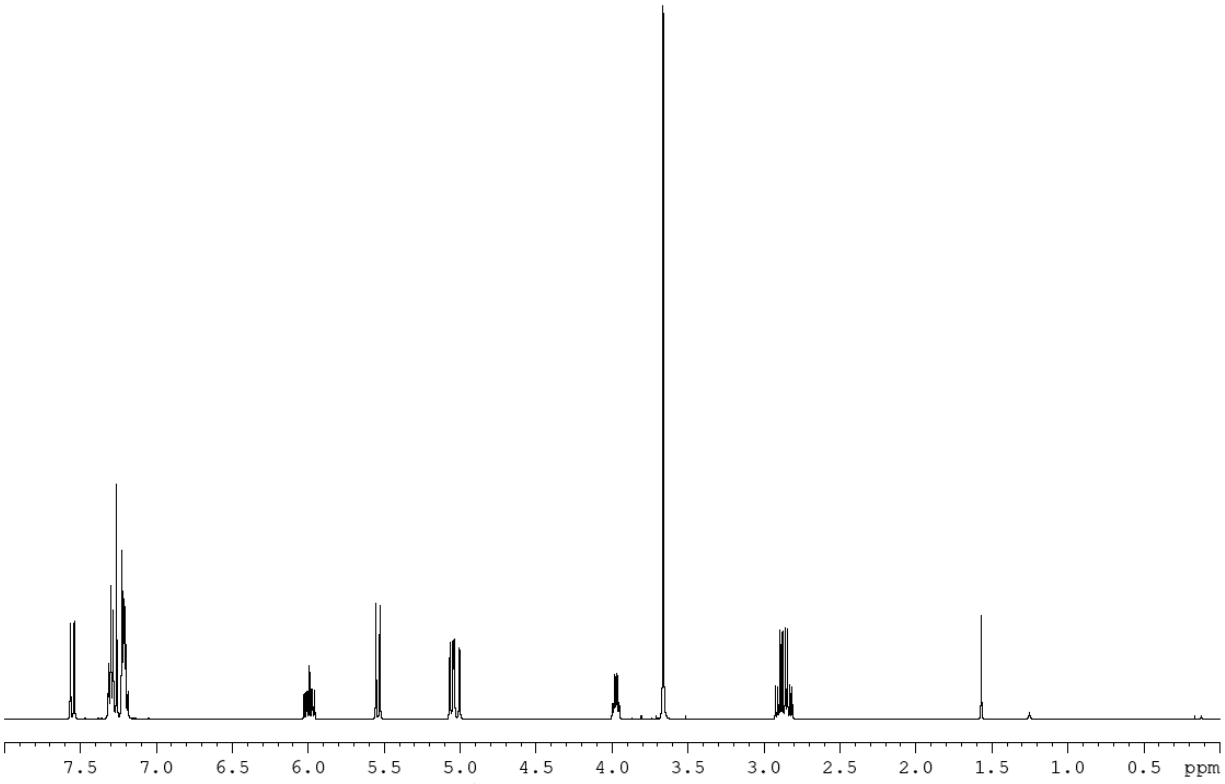
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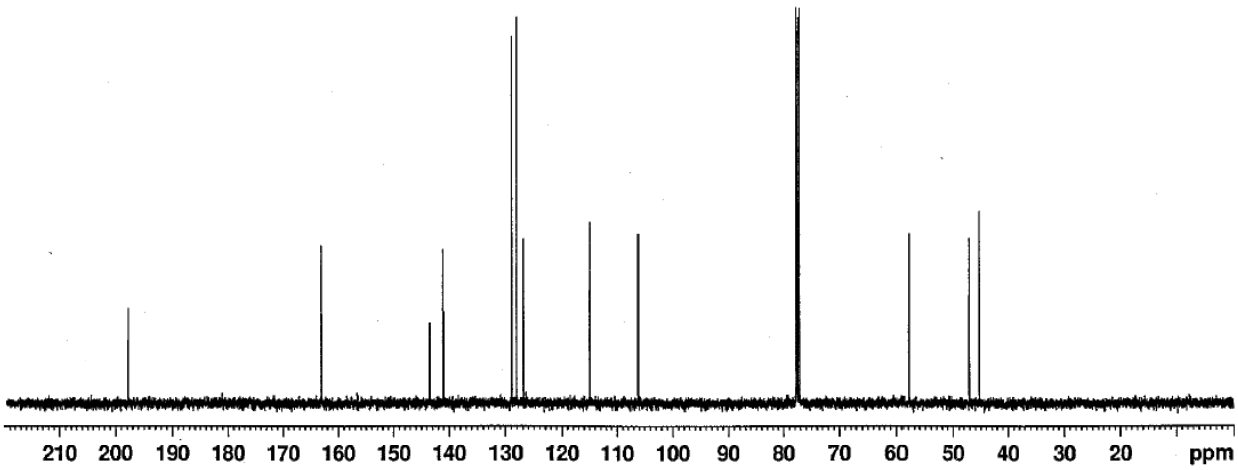
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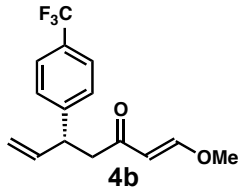
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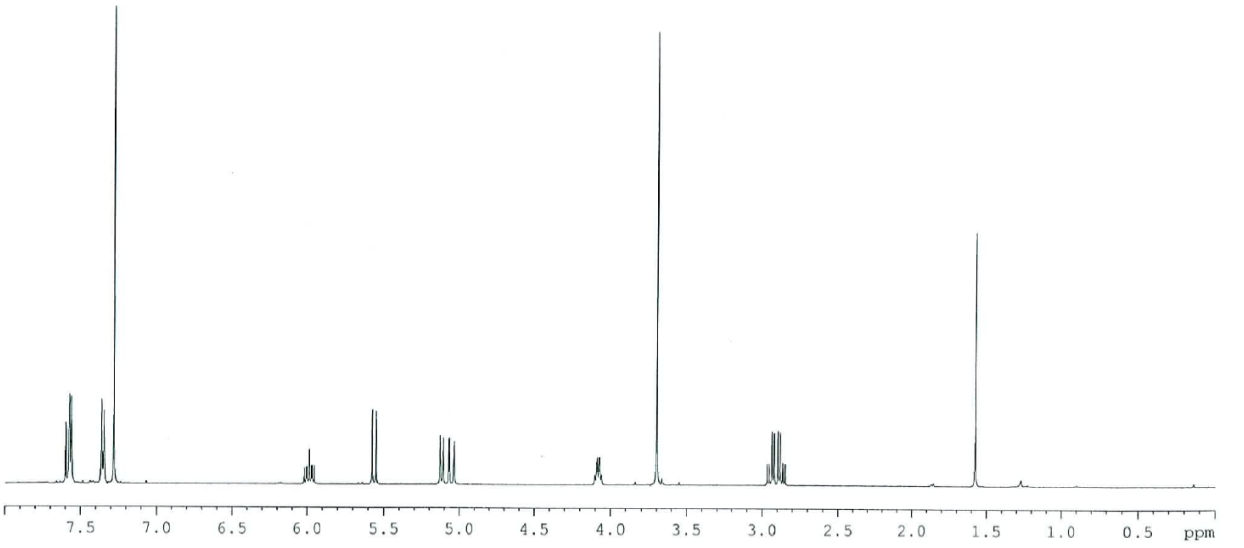
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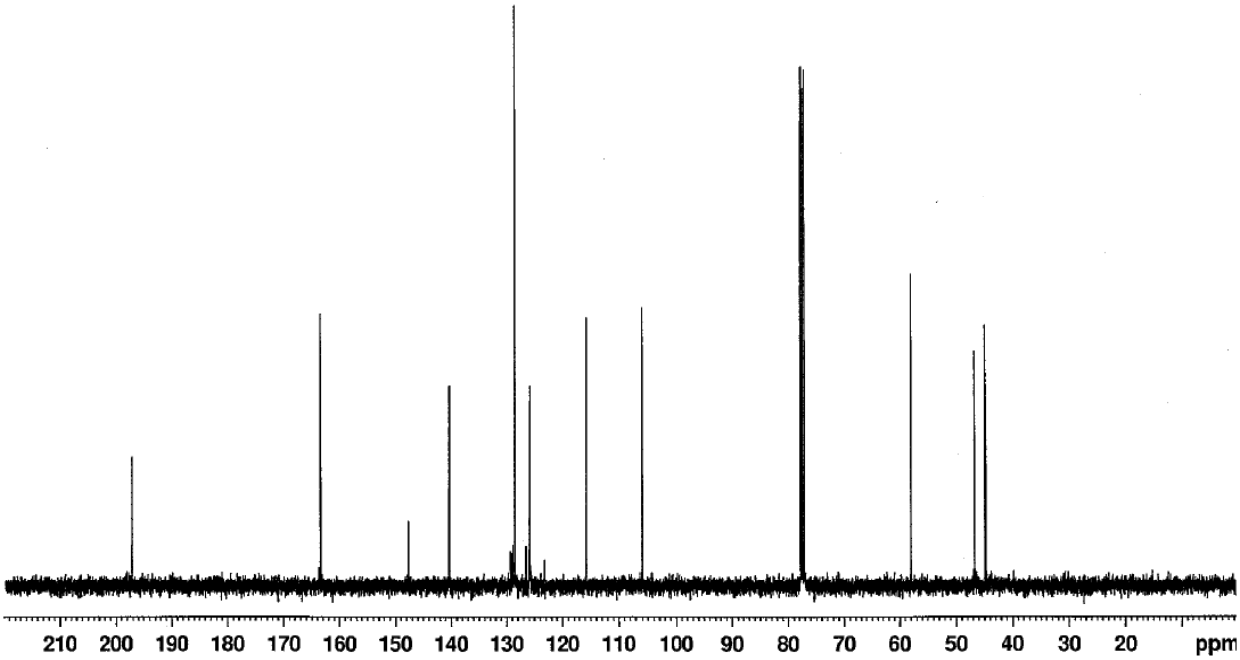
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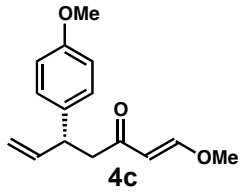
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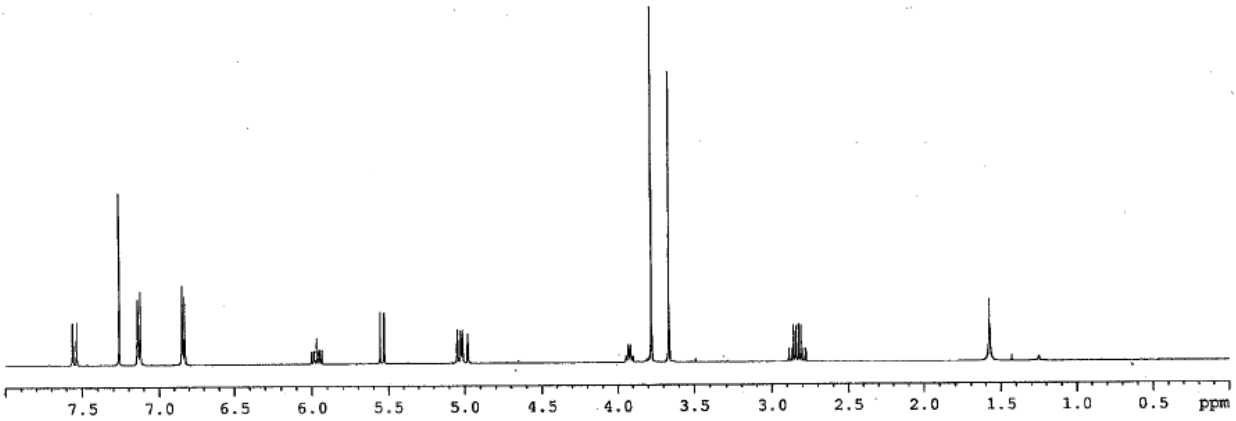
O
OMe

4c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1.0
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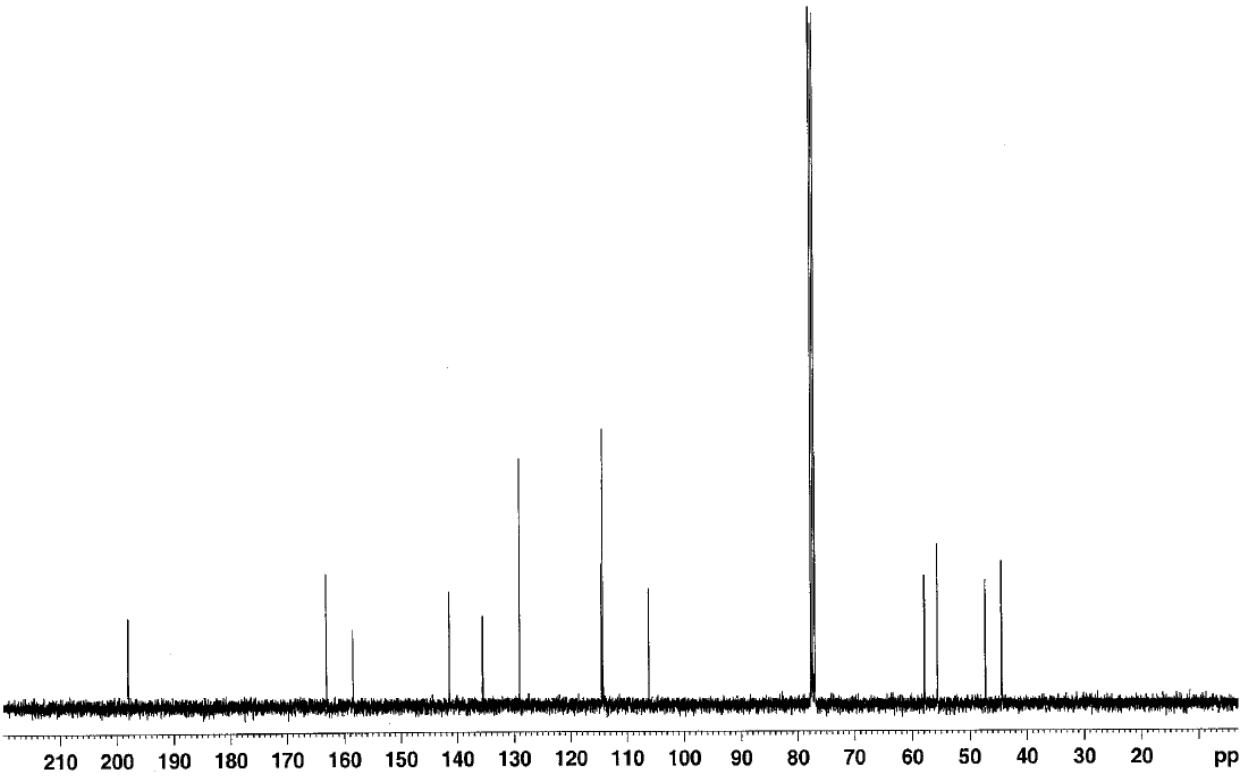
ppm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20
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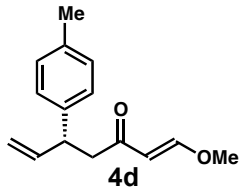
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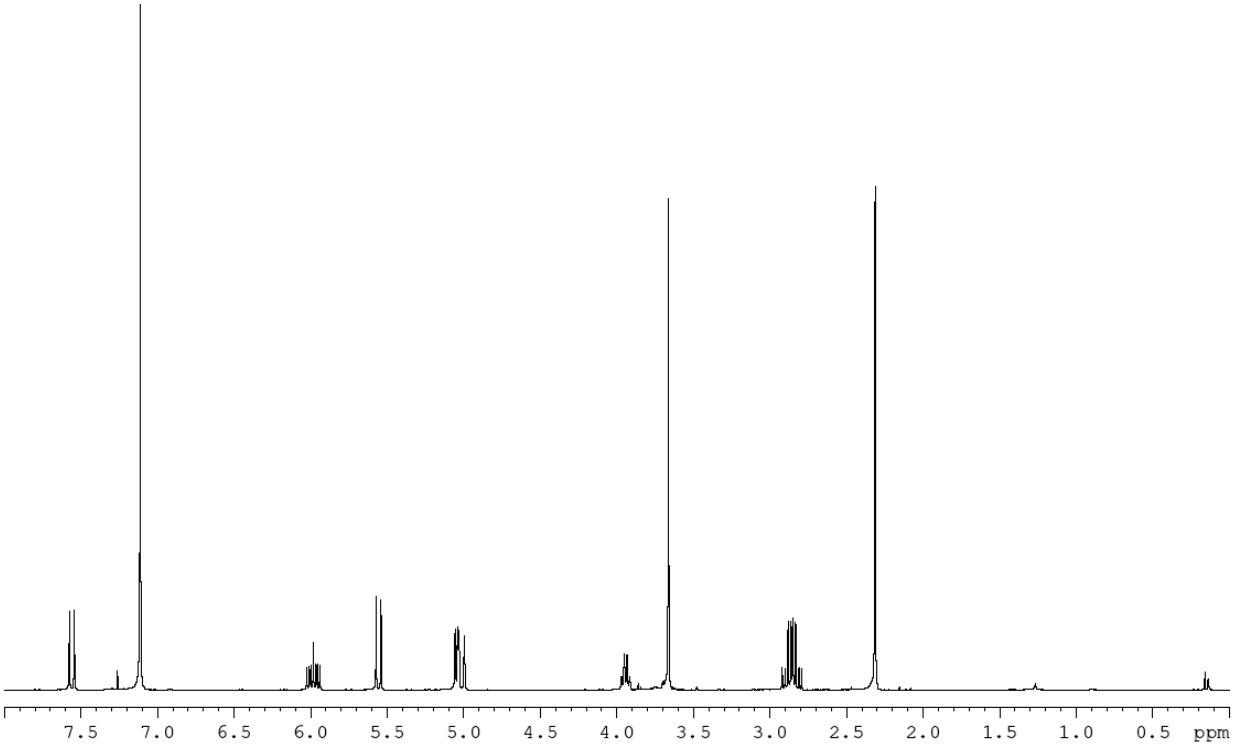
O
OMe

4d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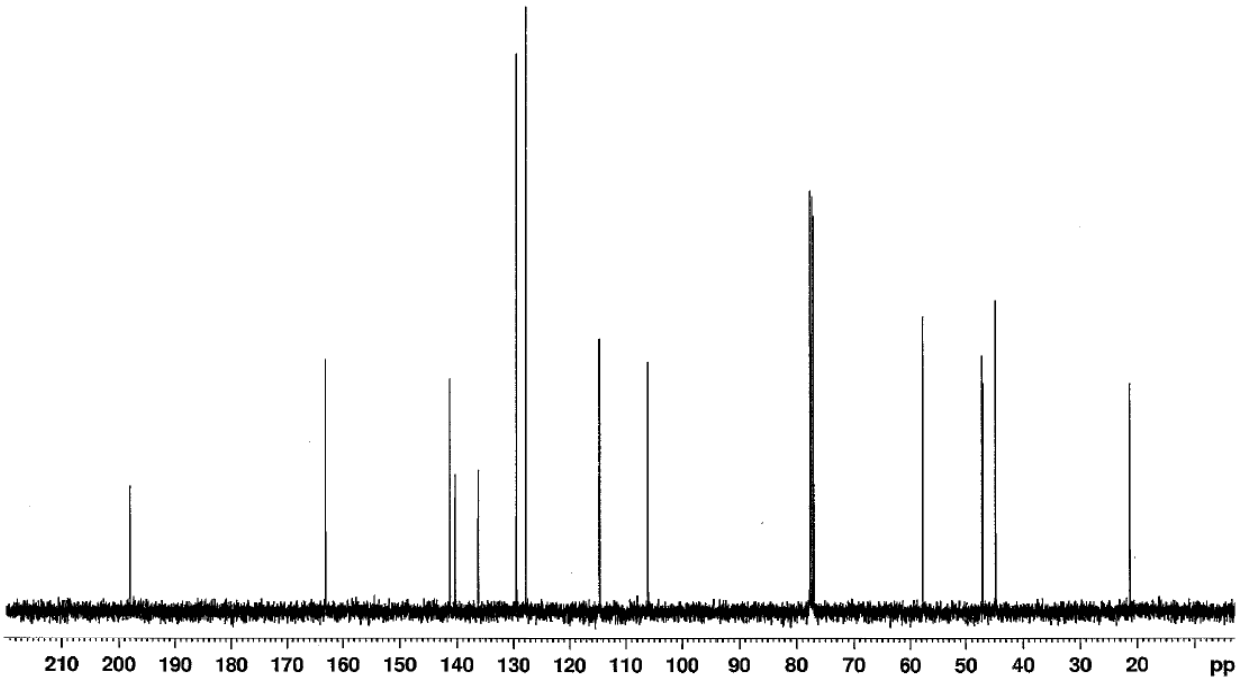
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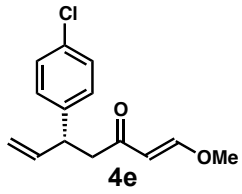
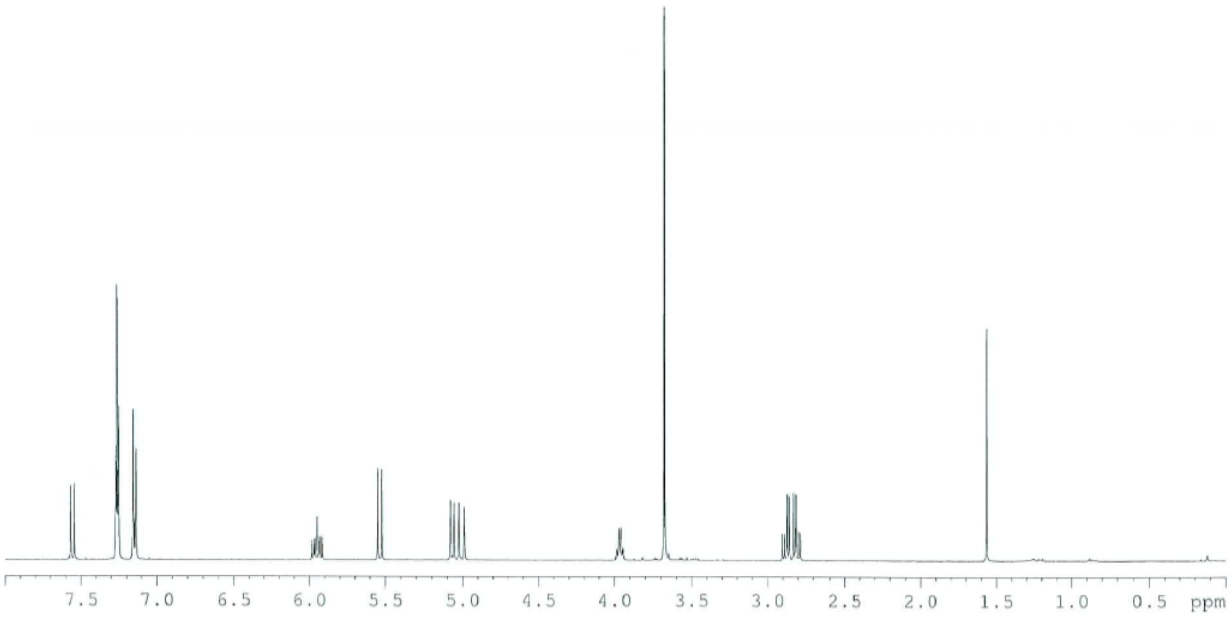

Cl
O
OMe

4e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1.0
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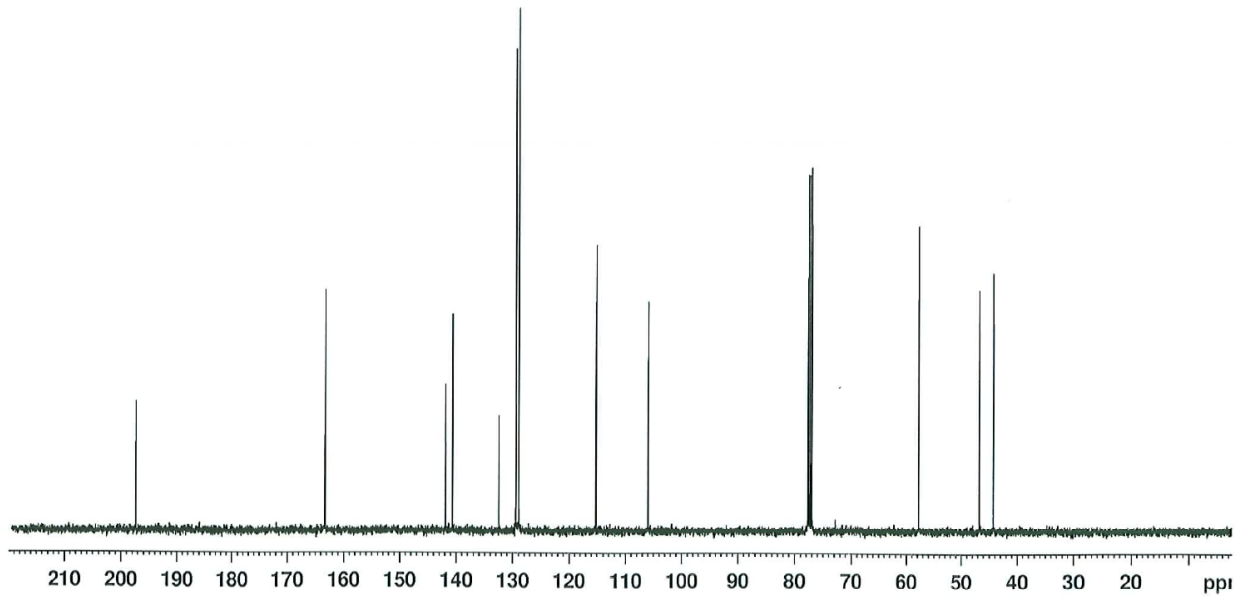
ppm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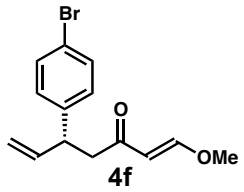
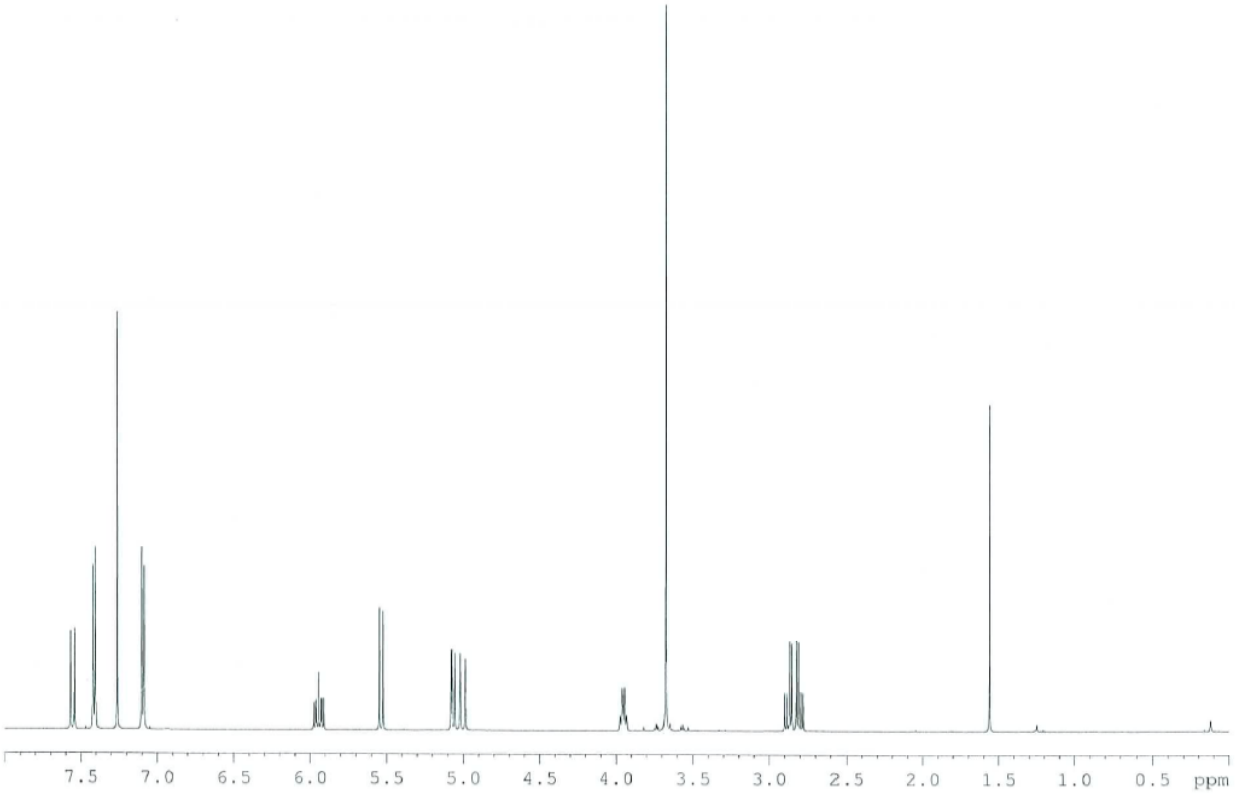
ppı


Br
O
OMe

4f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1.5
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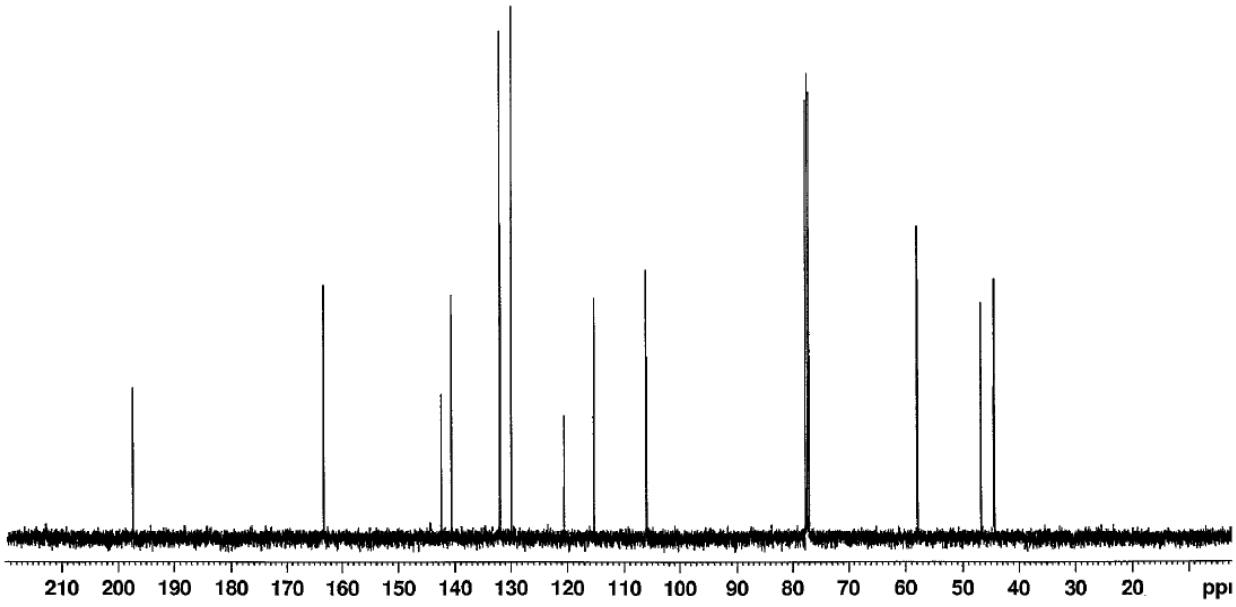
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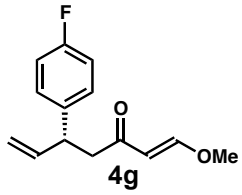
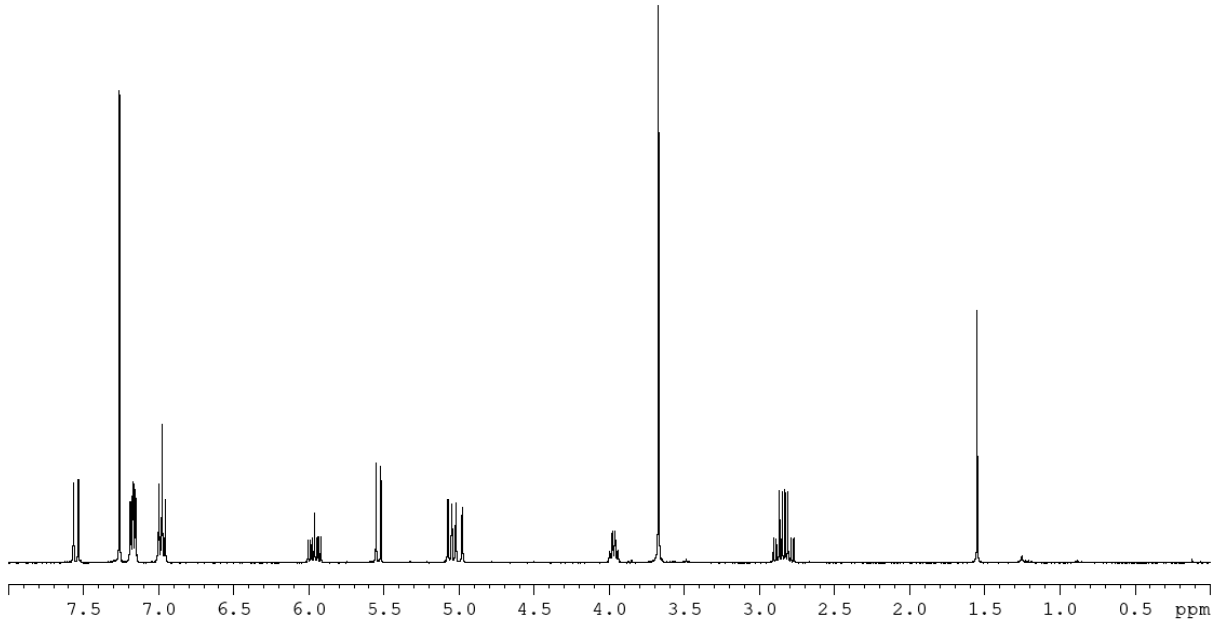
ppı


F
O
OMe

4g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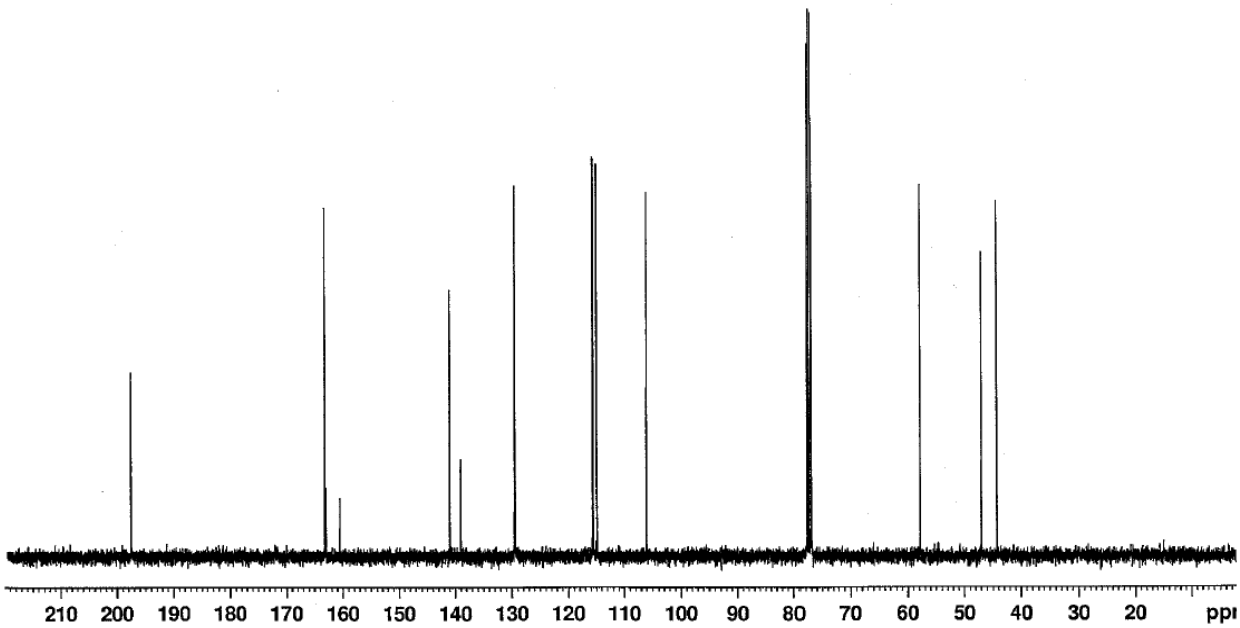
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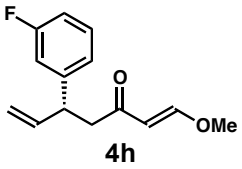
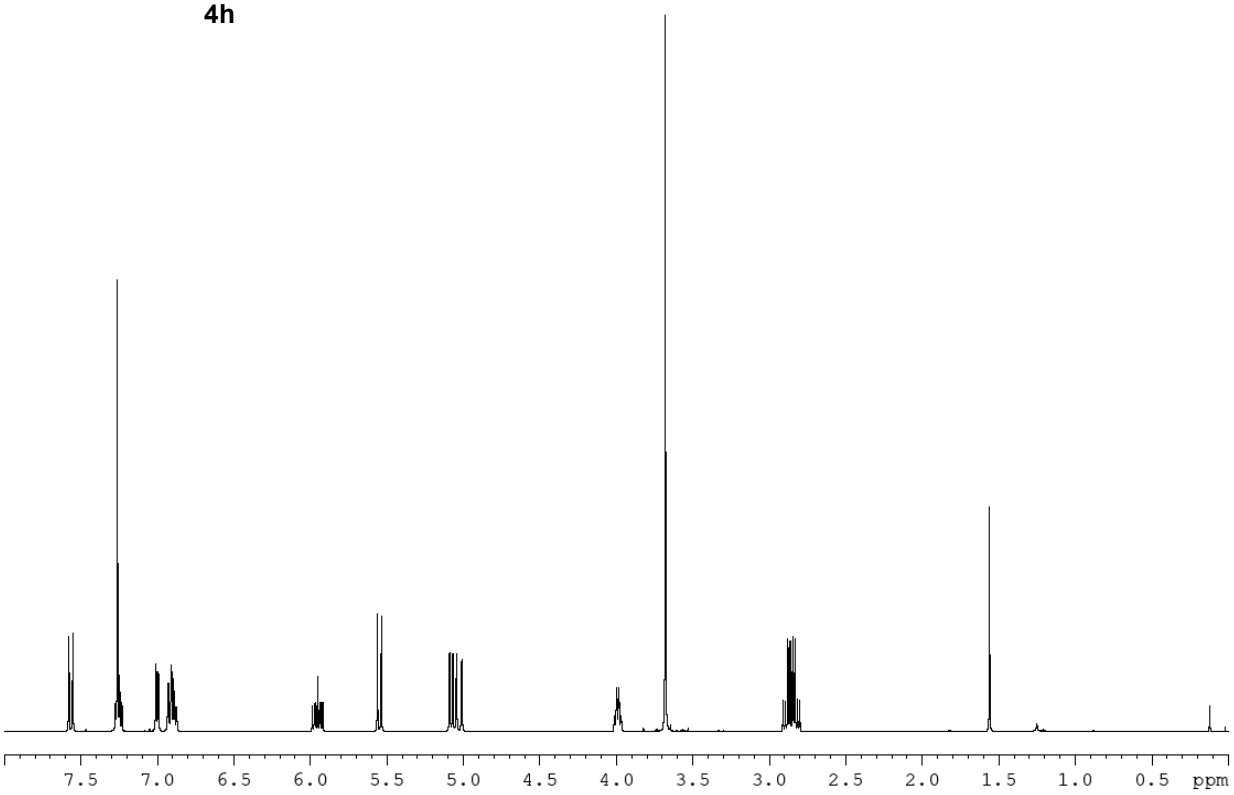

F
O
OMe

4h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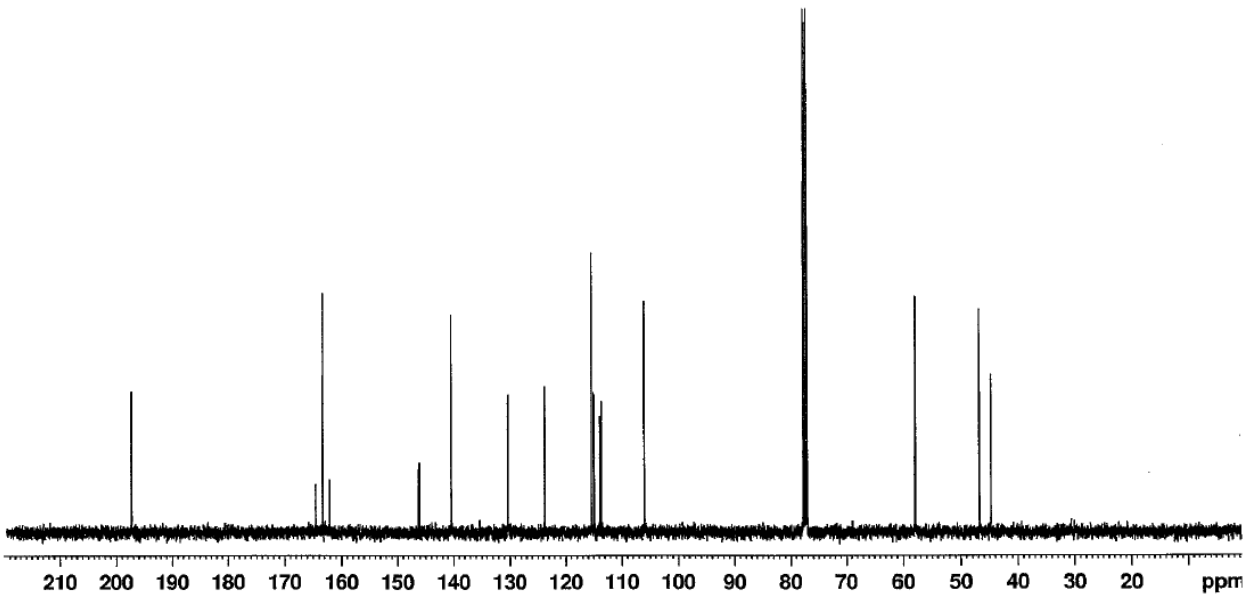
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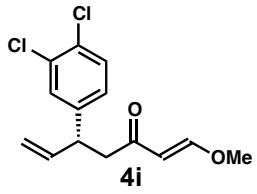
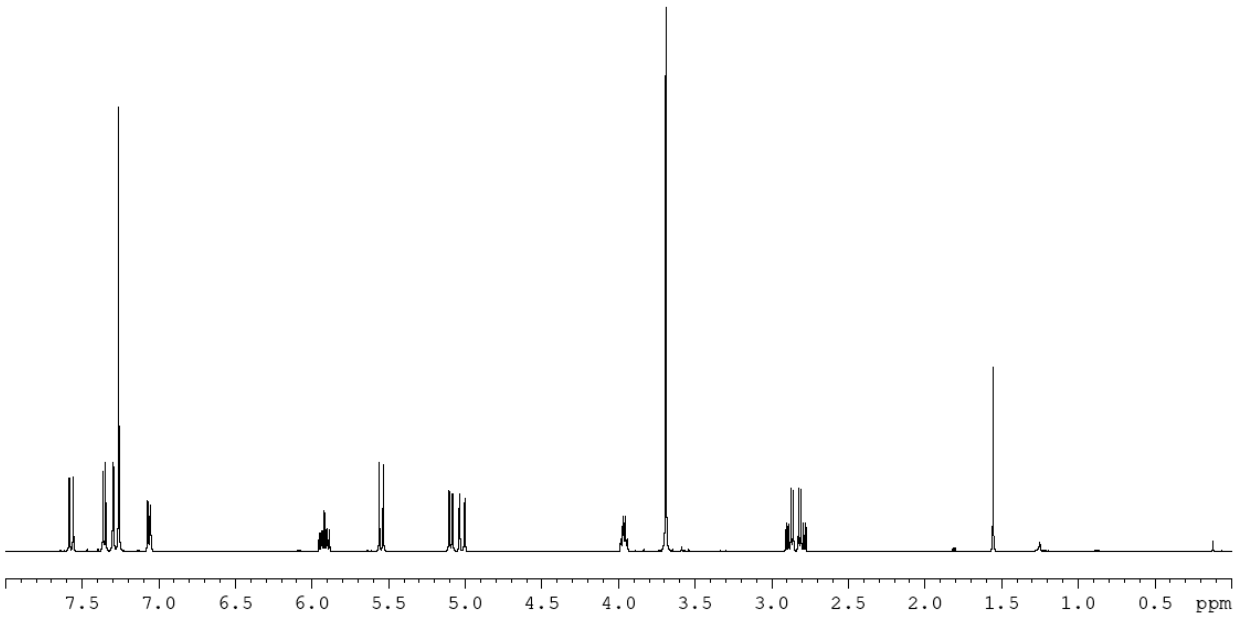

Cl
Cl
O
OMe

4i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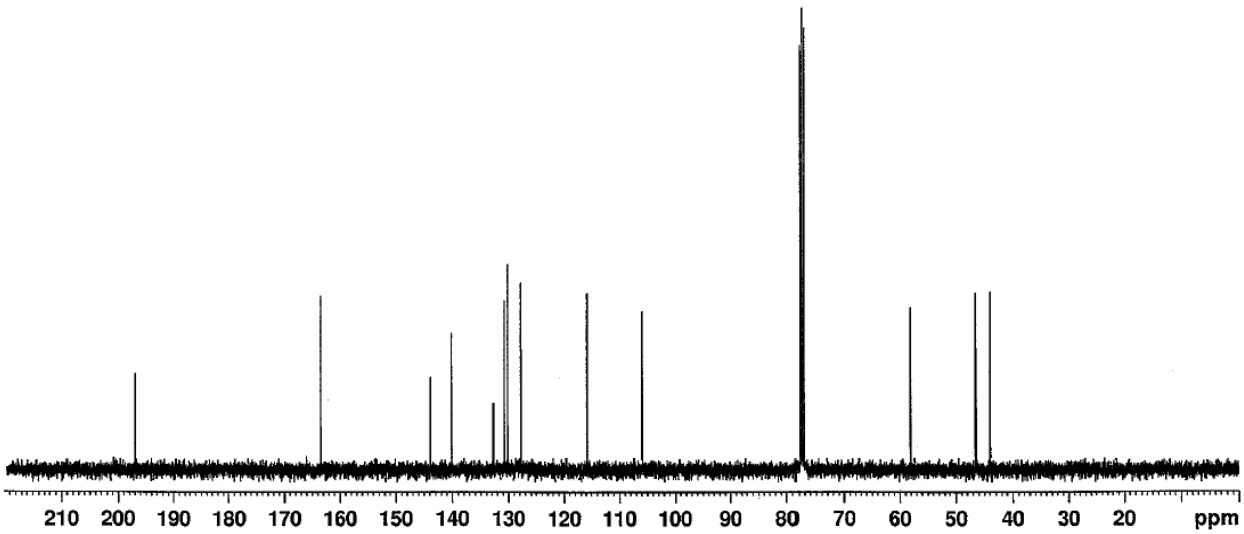
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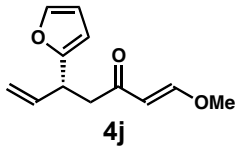
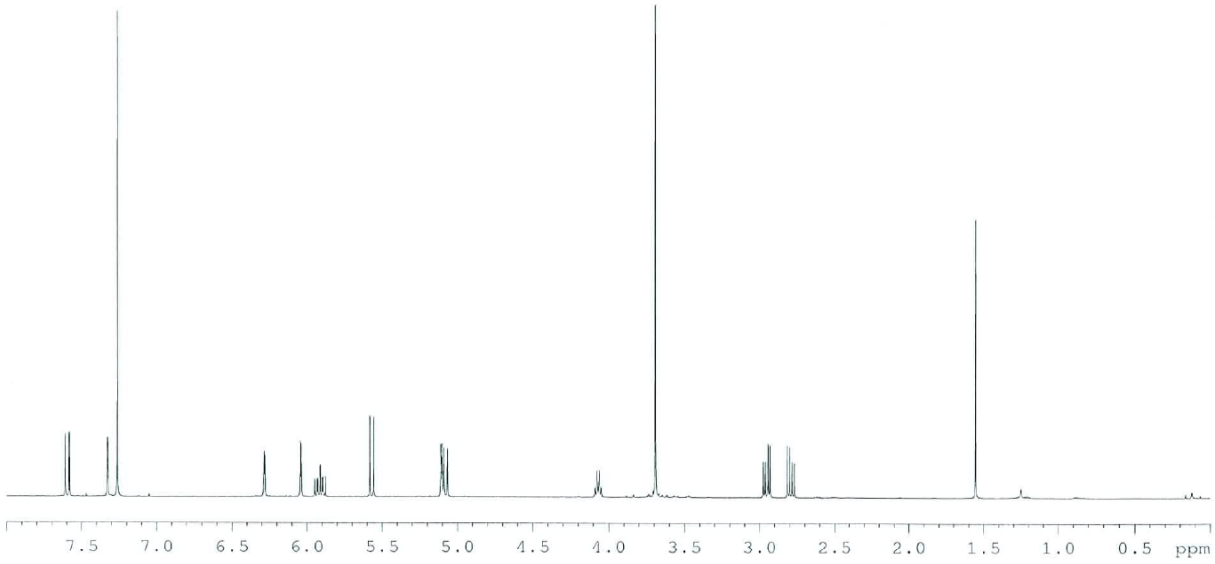

O
O
OMe

4j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4.5
4.0
3.5
3.0
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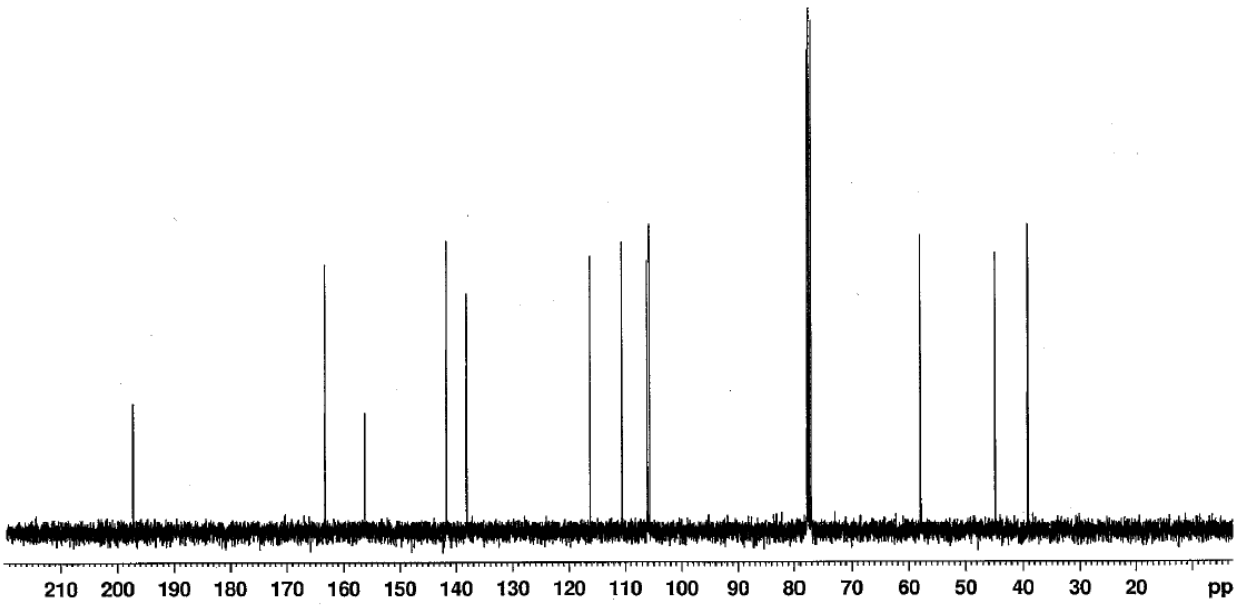
2.0
1.5
1.0
0.5
ppm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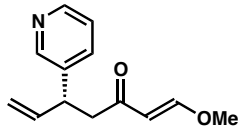
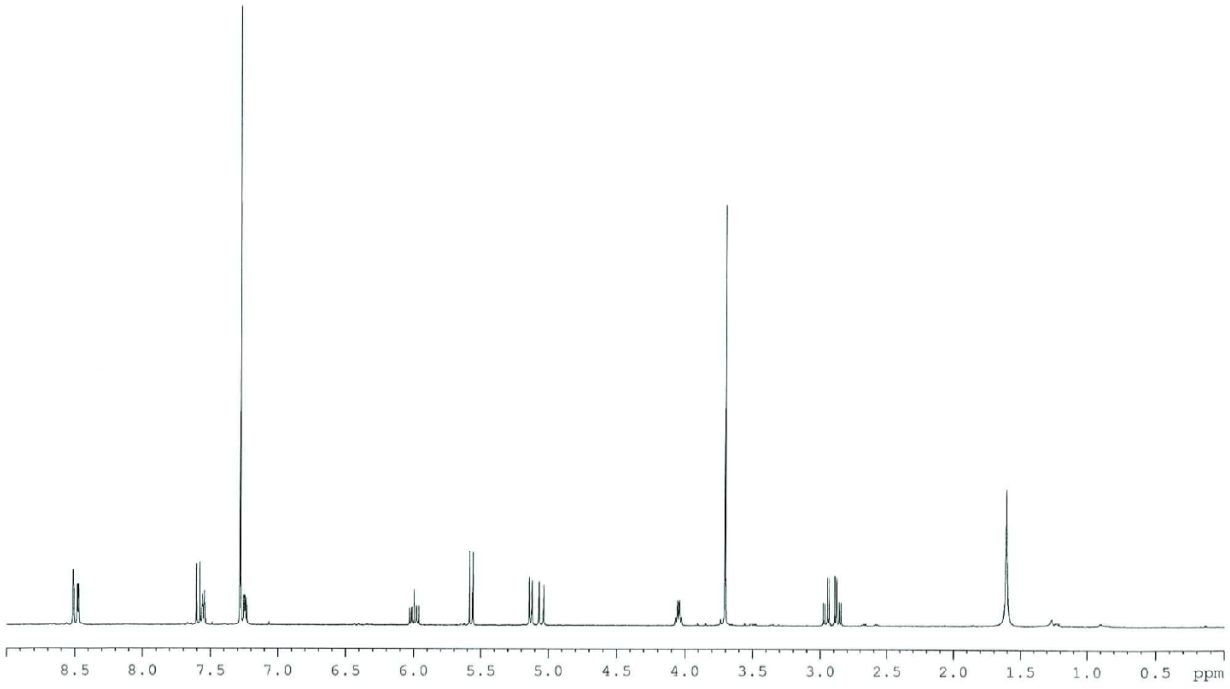
pp


N
O
OMe

4k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4.0
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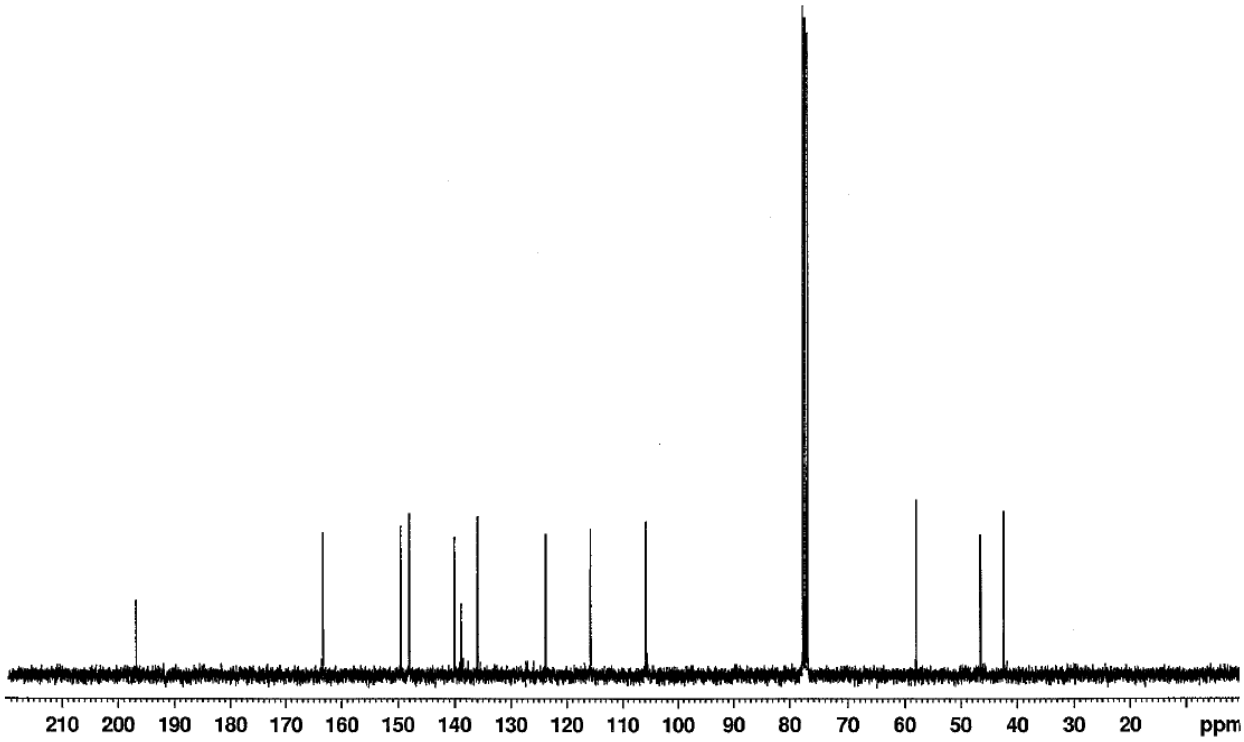
1.0
0.5
ppm


210
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80
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50
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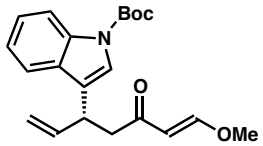
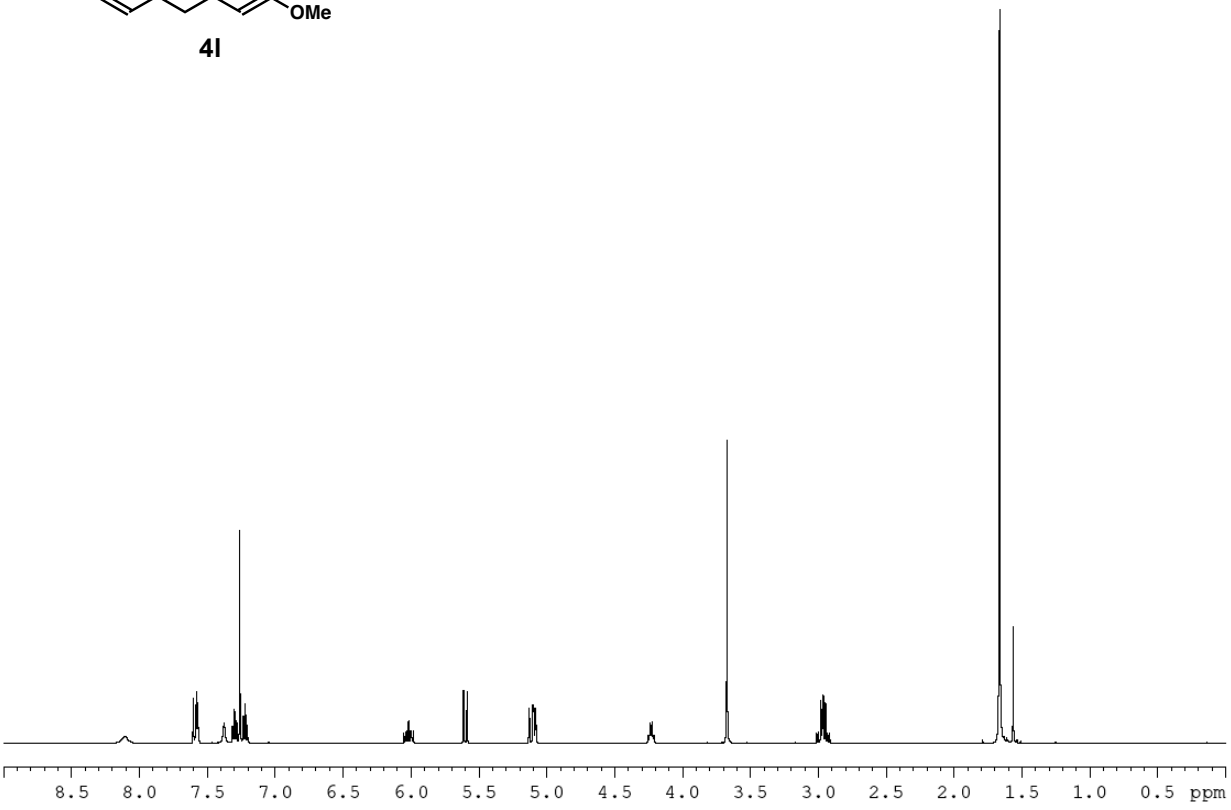
30
20
ppm


Boc
N
O
OMe

4l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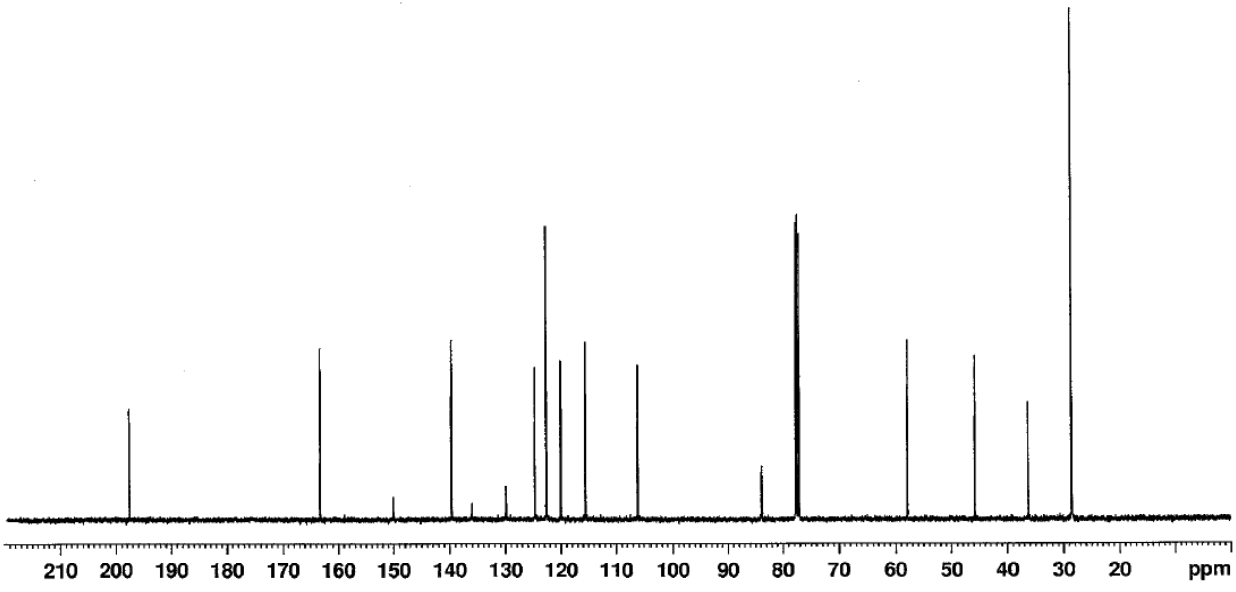
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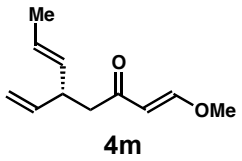
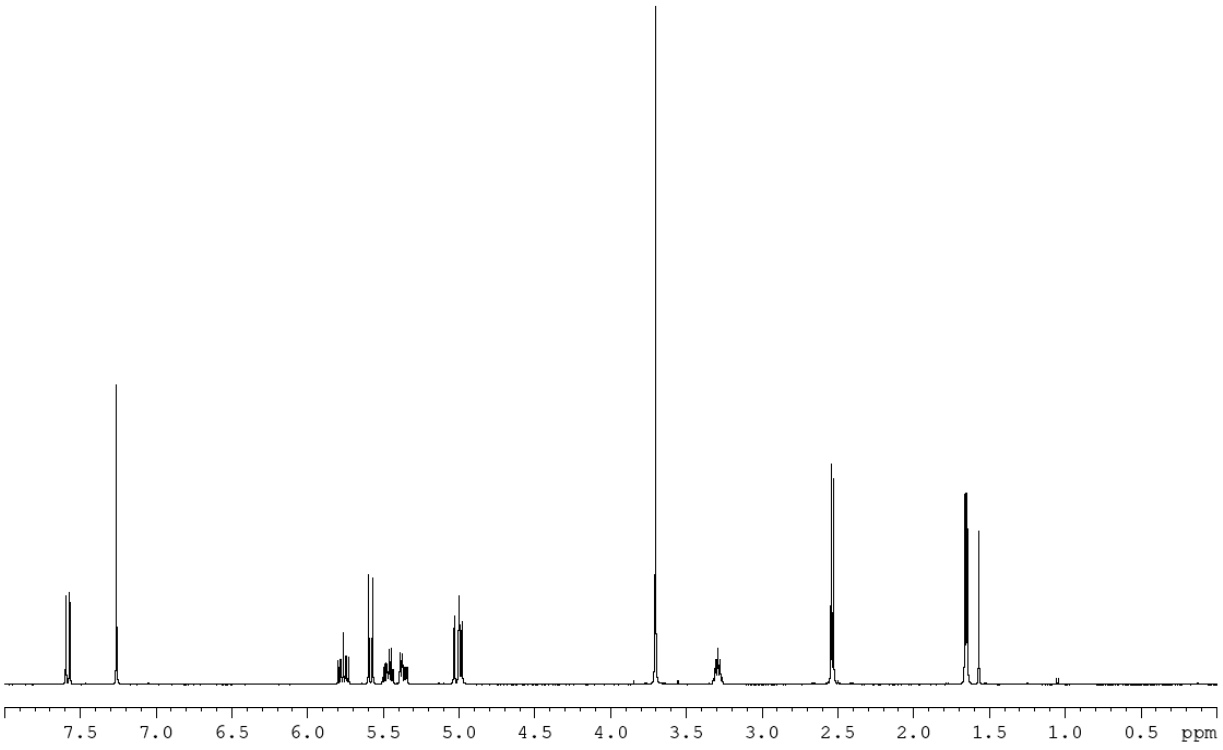

Me
O
OMe

4m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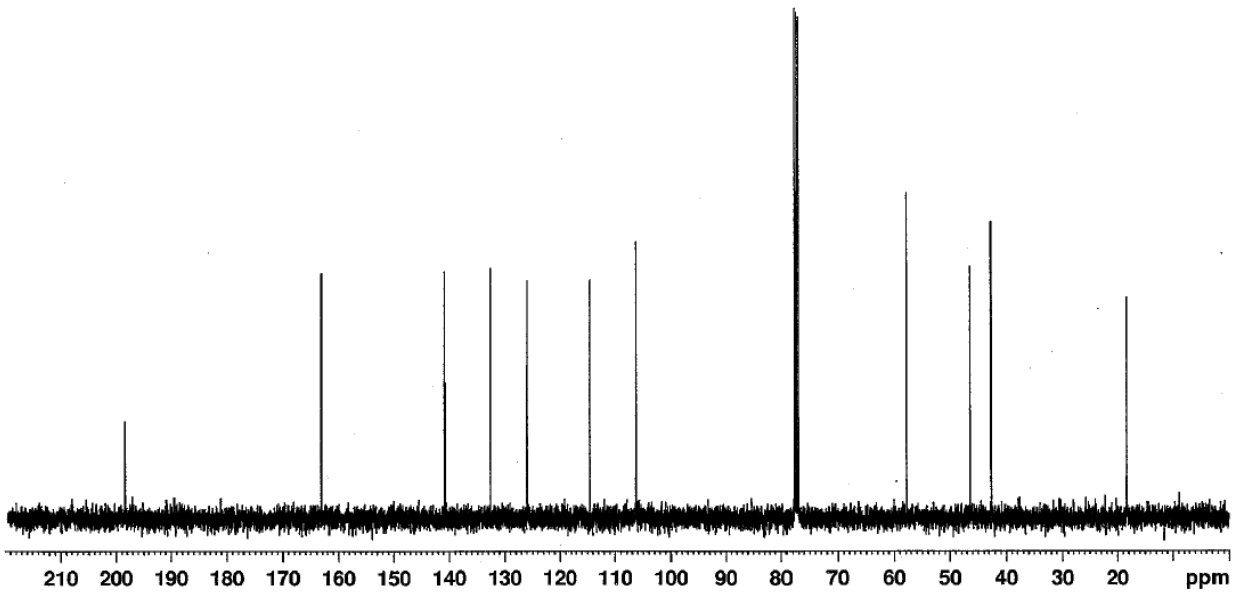
1.5
1.0
0.5
ppm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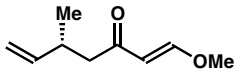
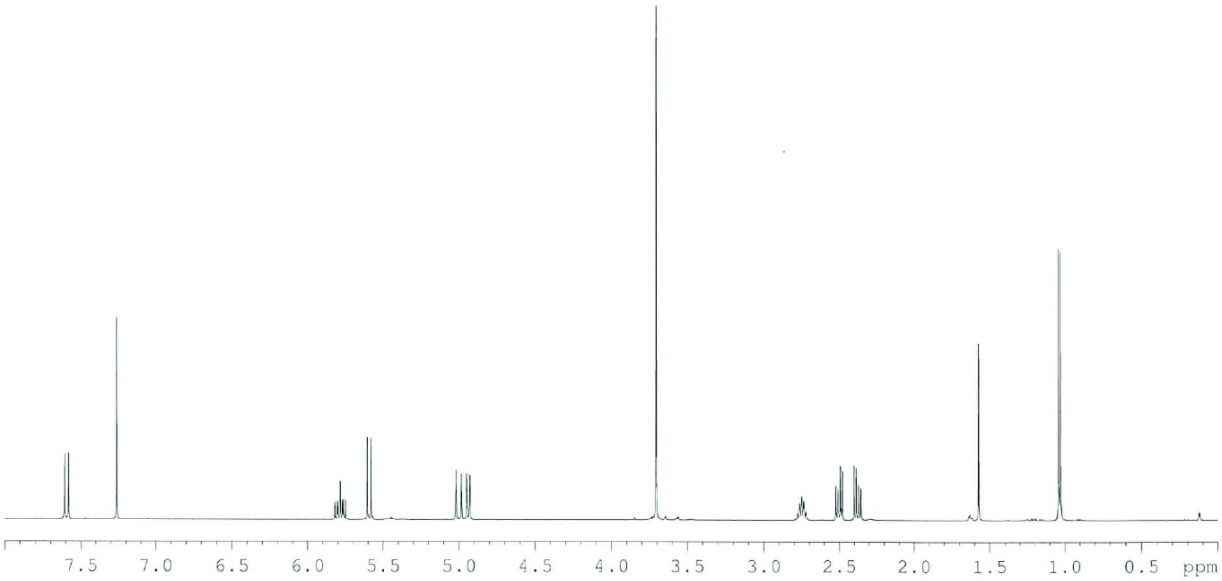
ppm


Me
O
OMe

4n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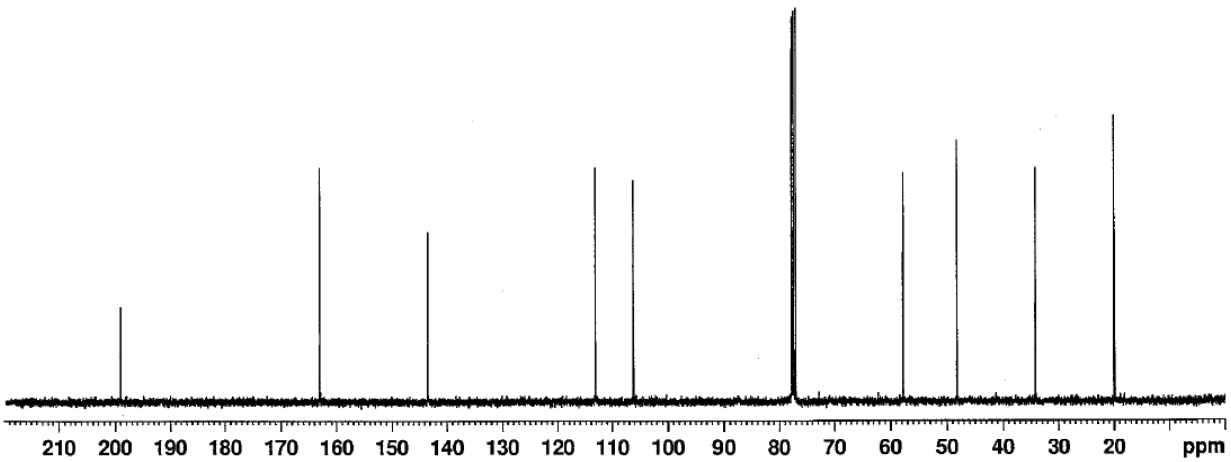
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


210
200
190
180
170
160
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140
130
120
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100
90
80
70
60
50
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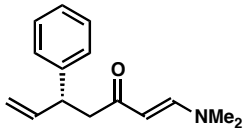
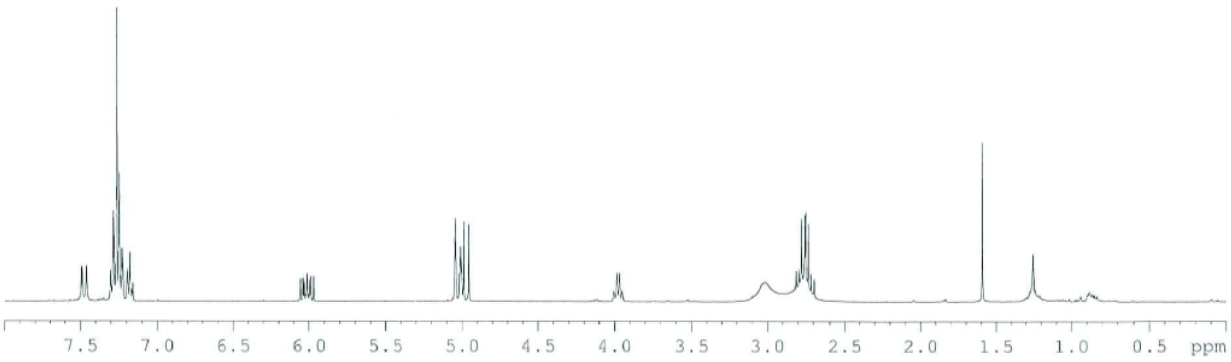
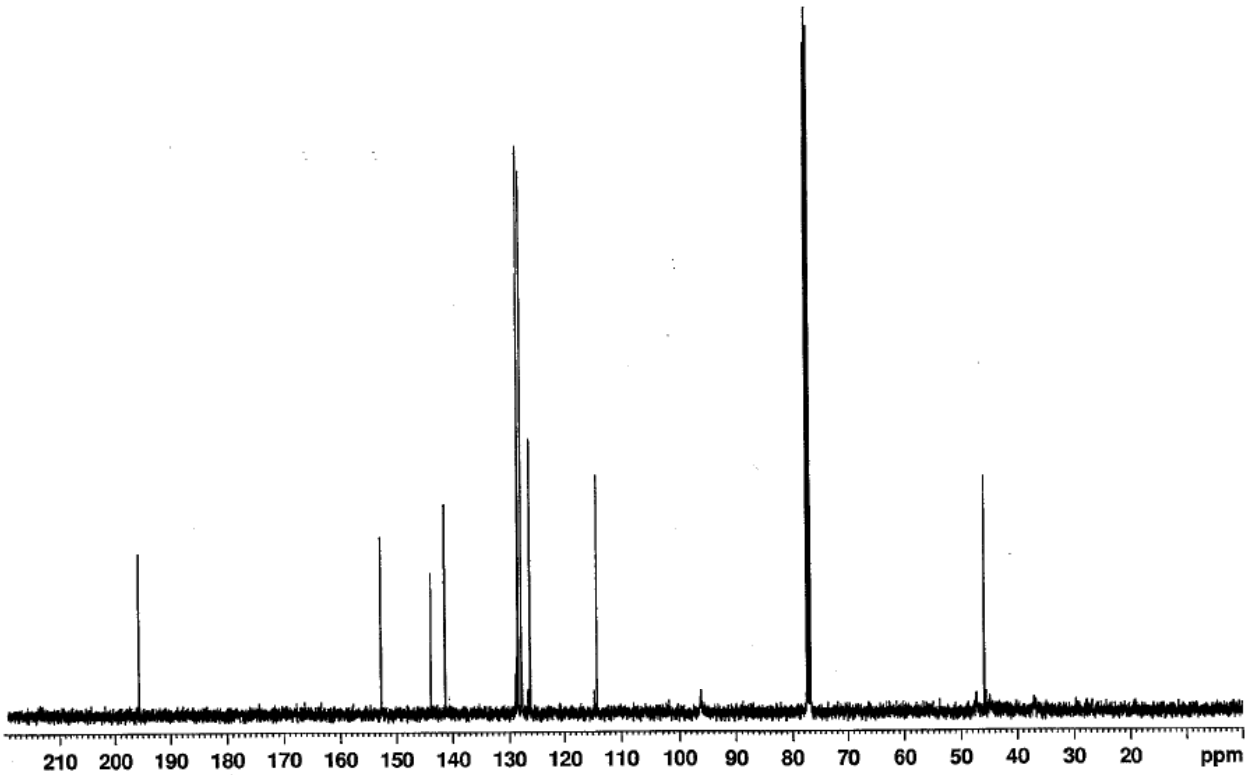
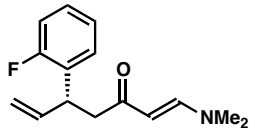
30
20
ppm


O
NMe2

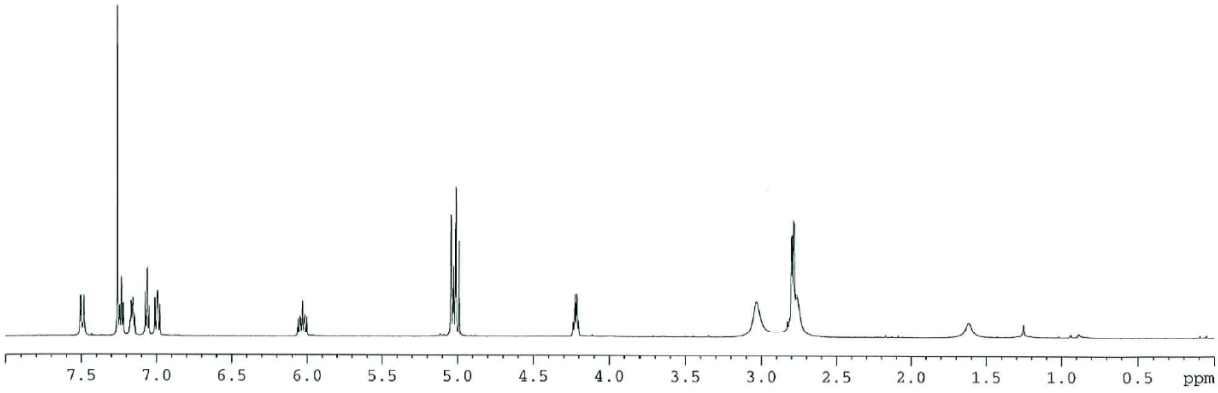
5a


7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


F
O
NMe2

5b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7.0
6.5
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5.5
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4.5
4.0
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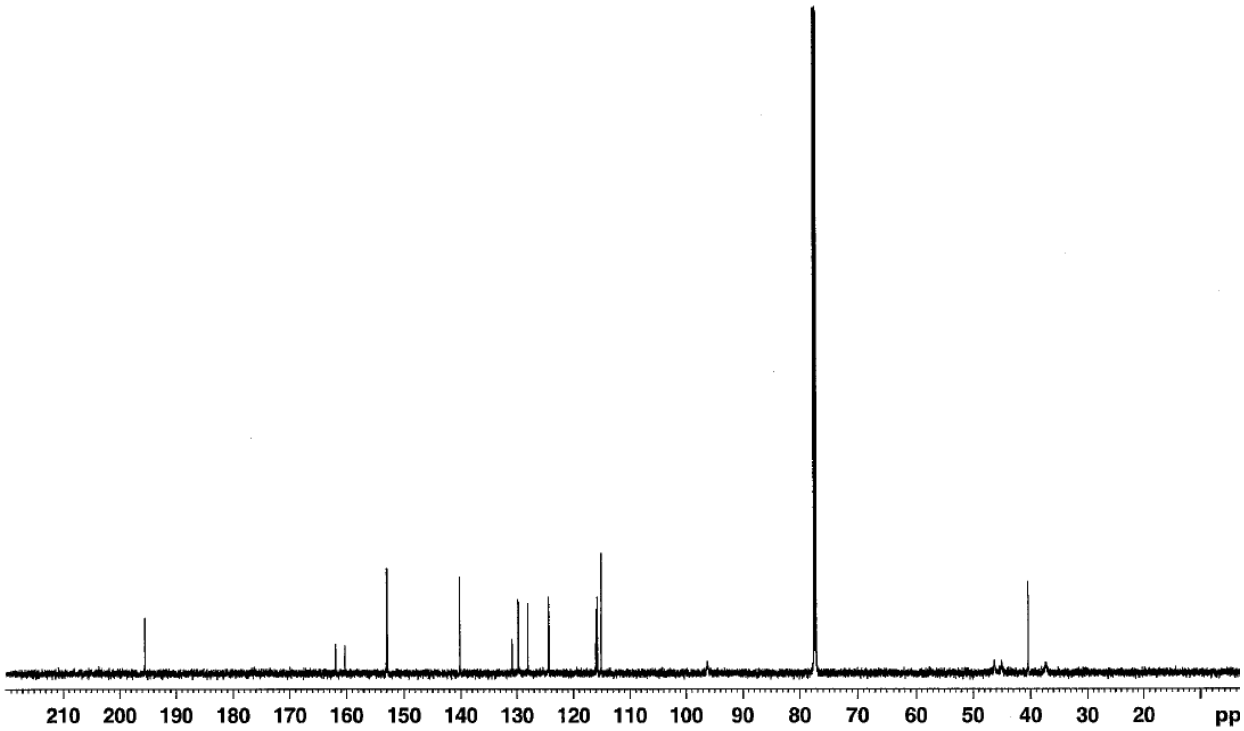
3.0
2.5
2.0
1.5
1.0
0.5
ppm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140
130
120
110
100
90
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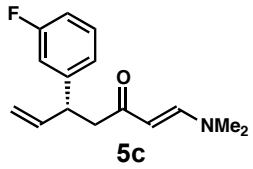
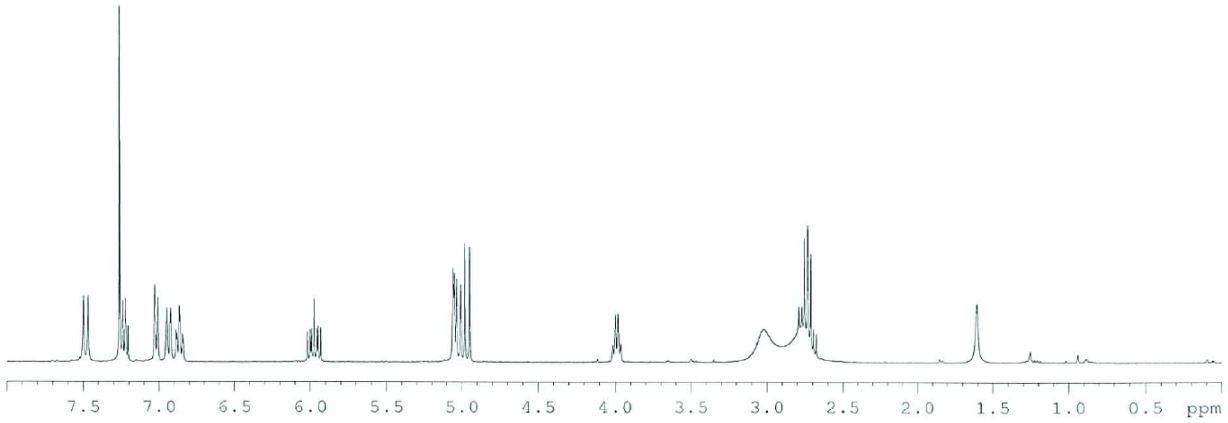
60
50
40
30
20
pp


F
O
NMe2

5c


7.5
7.0
6.5
6.0
5.5
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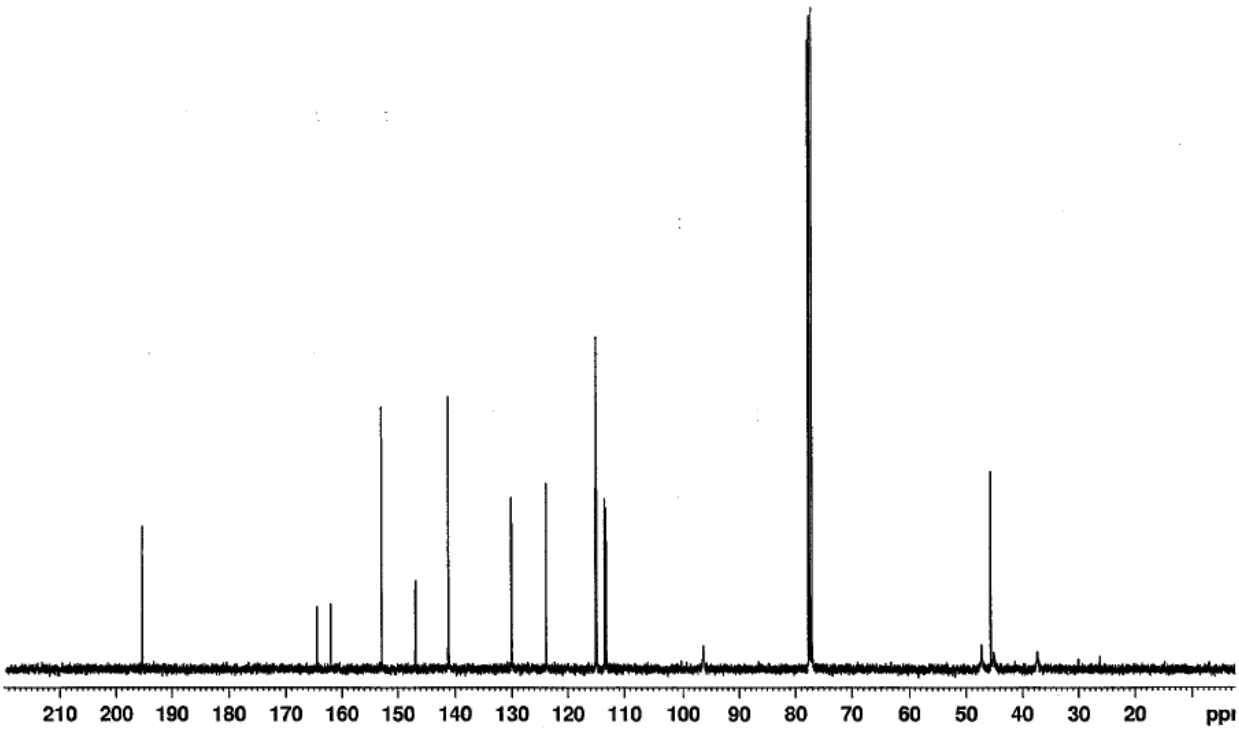
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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100
90
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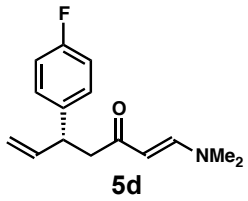
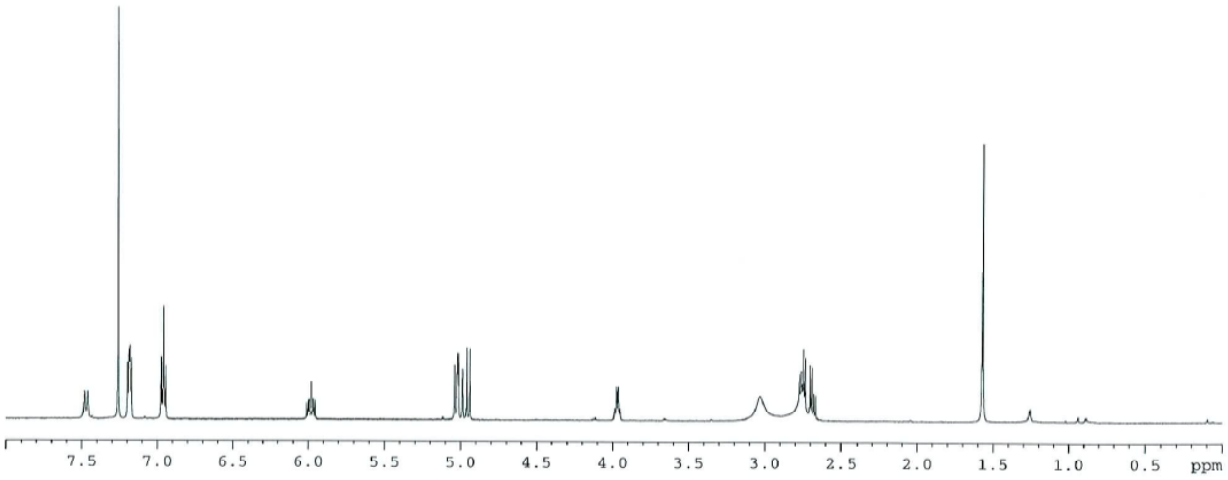
30
20


F
O
NMe2

5d


7.5
7.0
6.5
6.0
5.5
5.0
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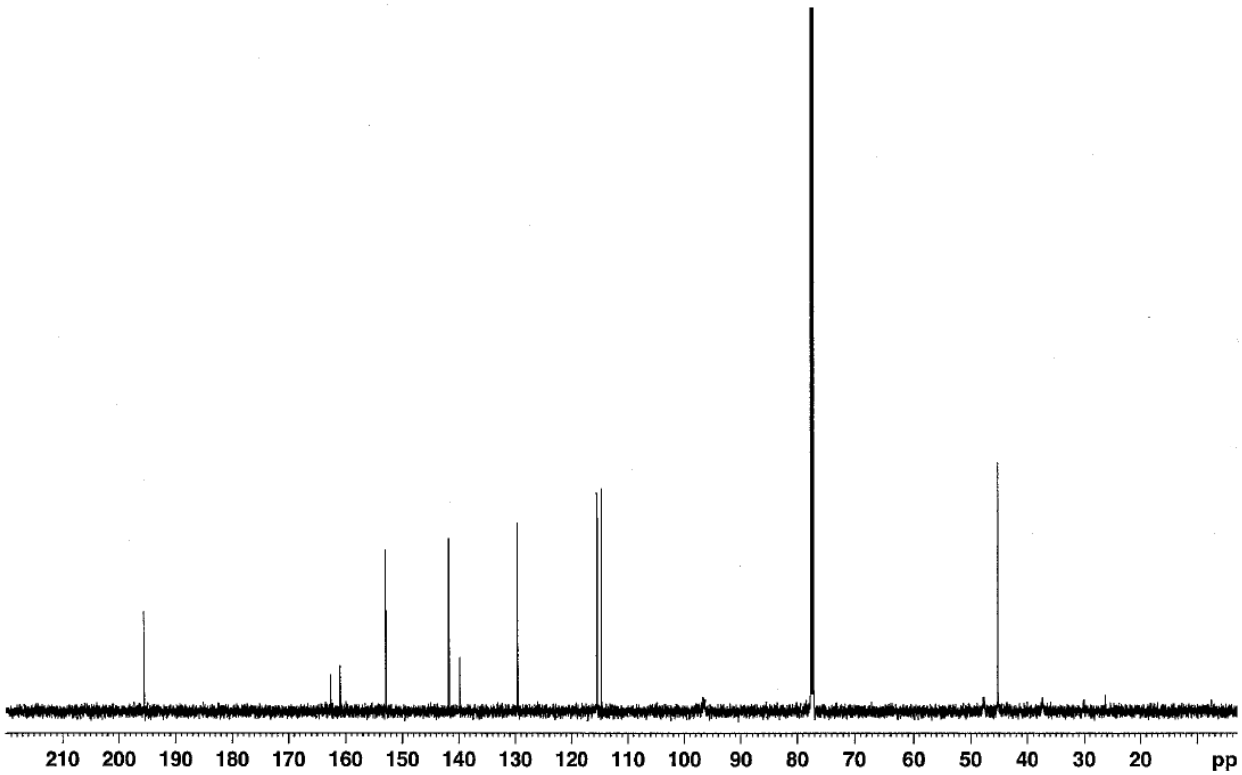
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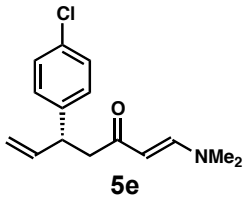
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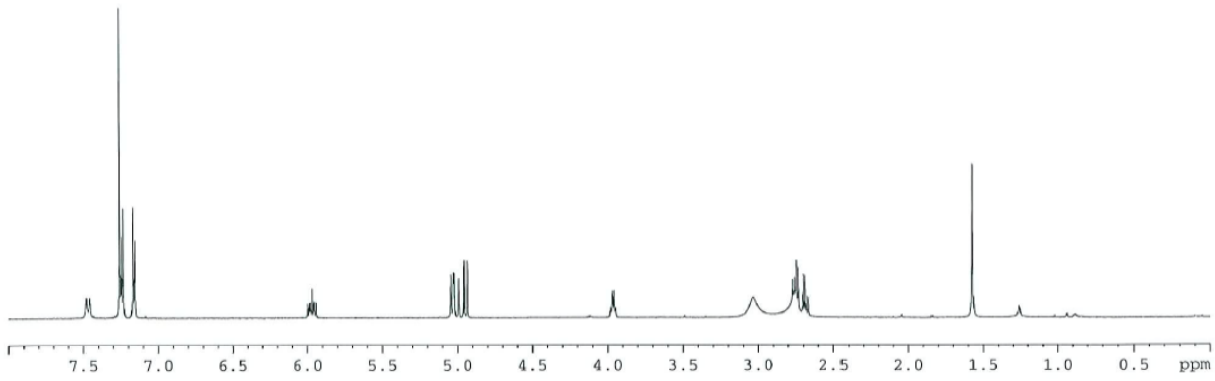
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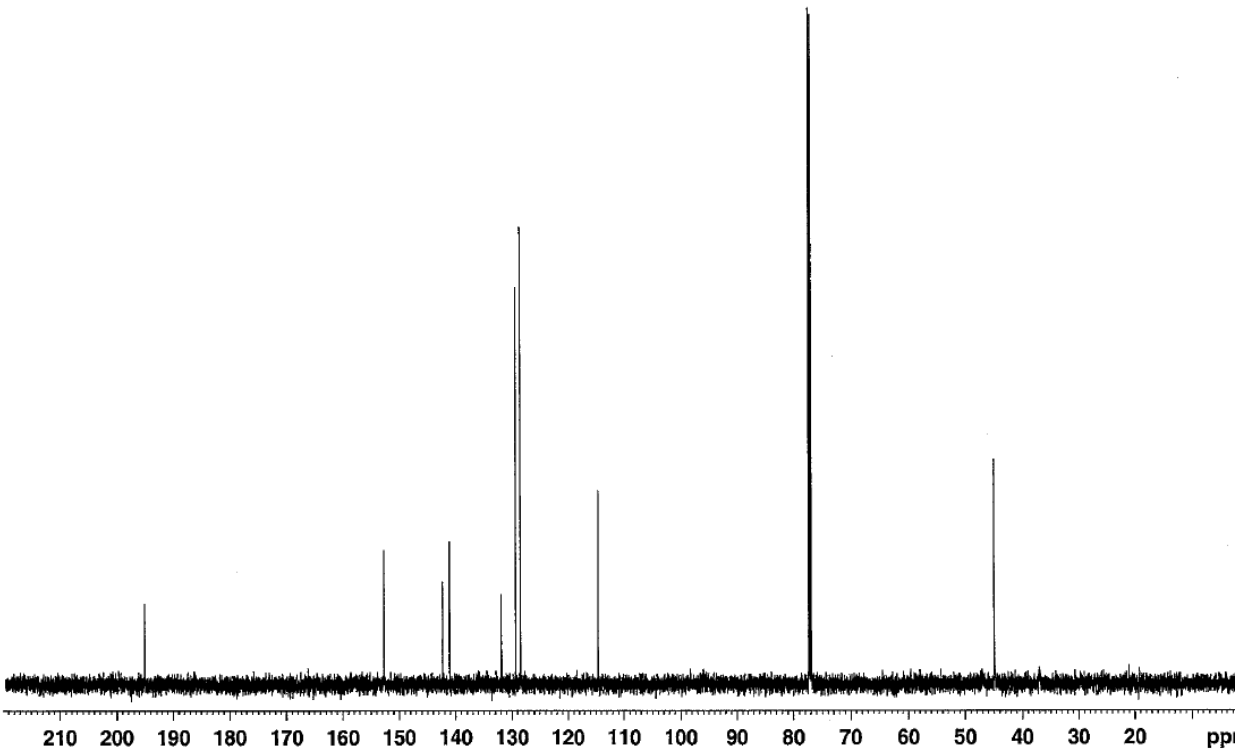
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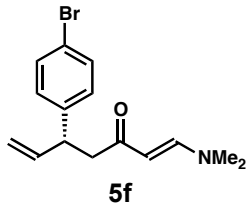
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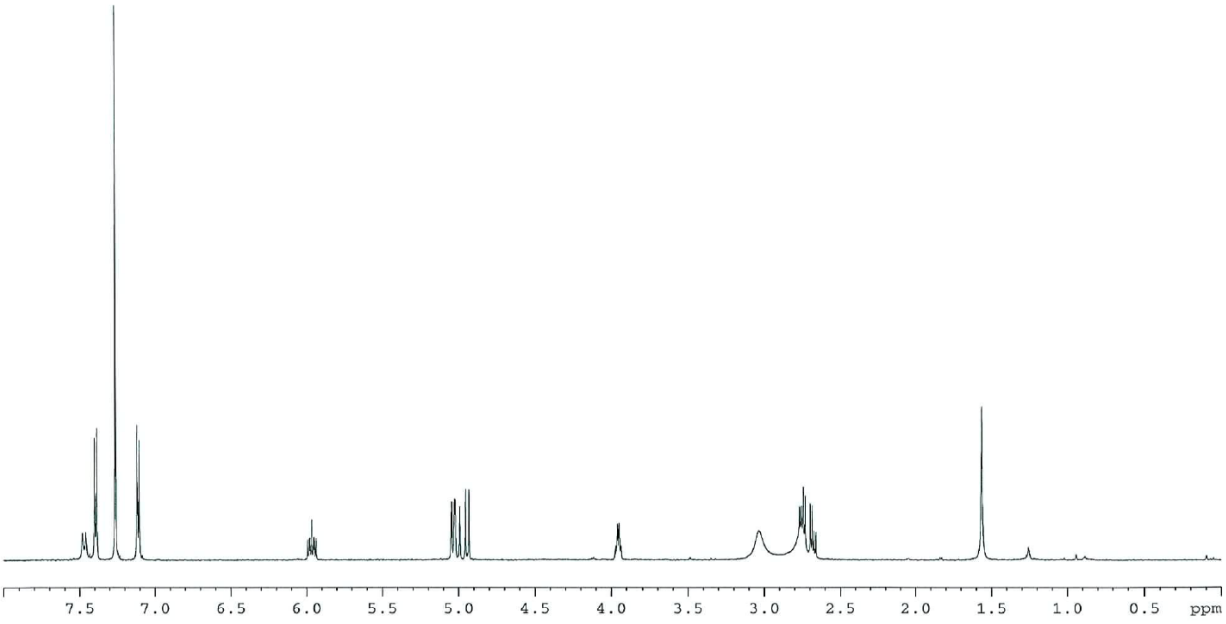
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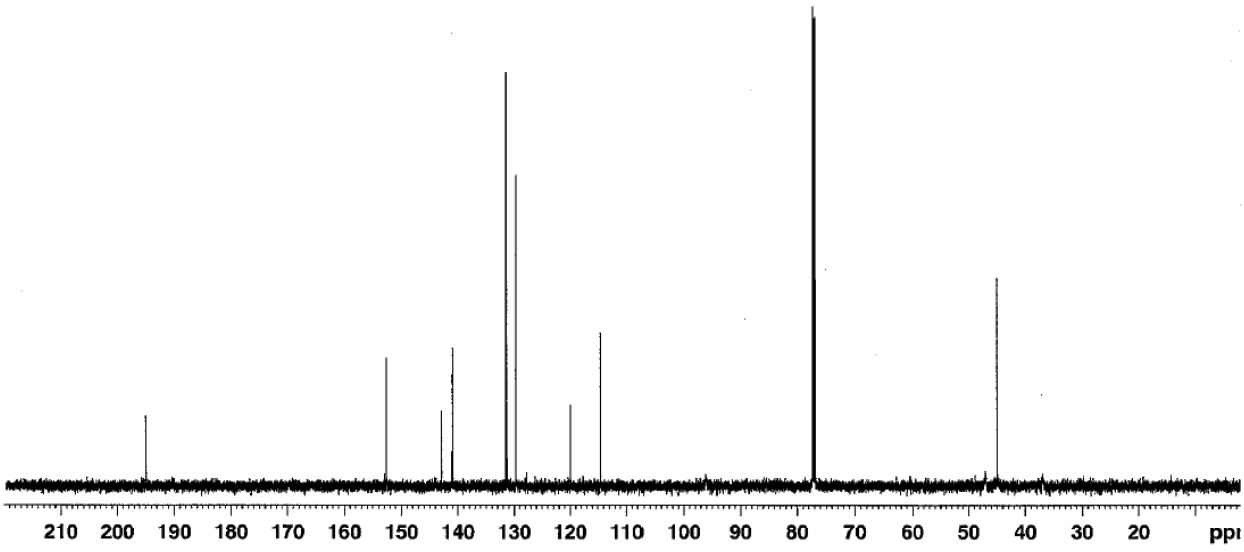
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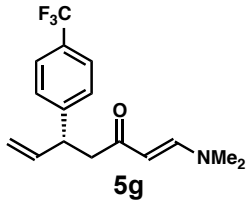
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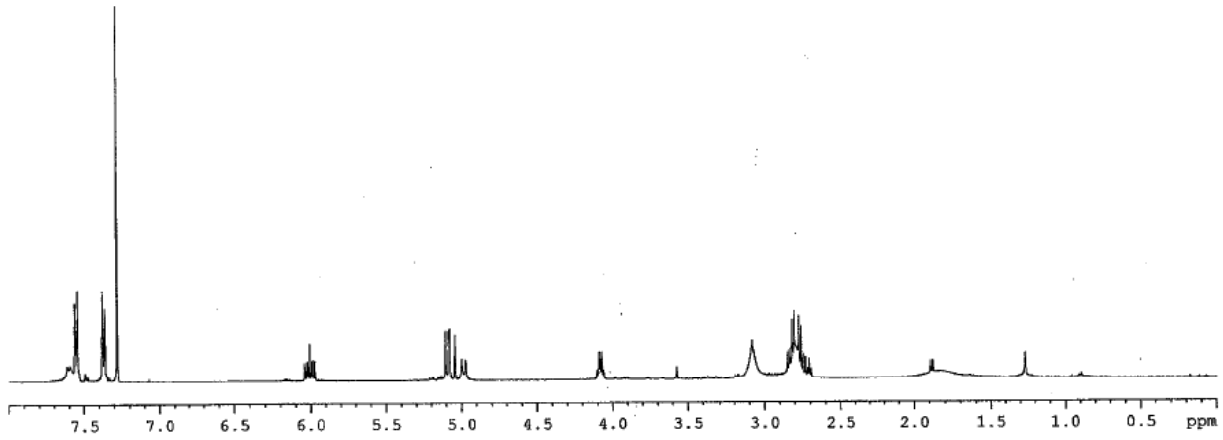
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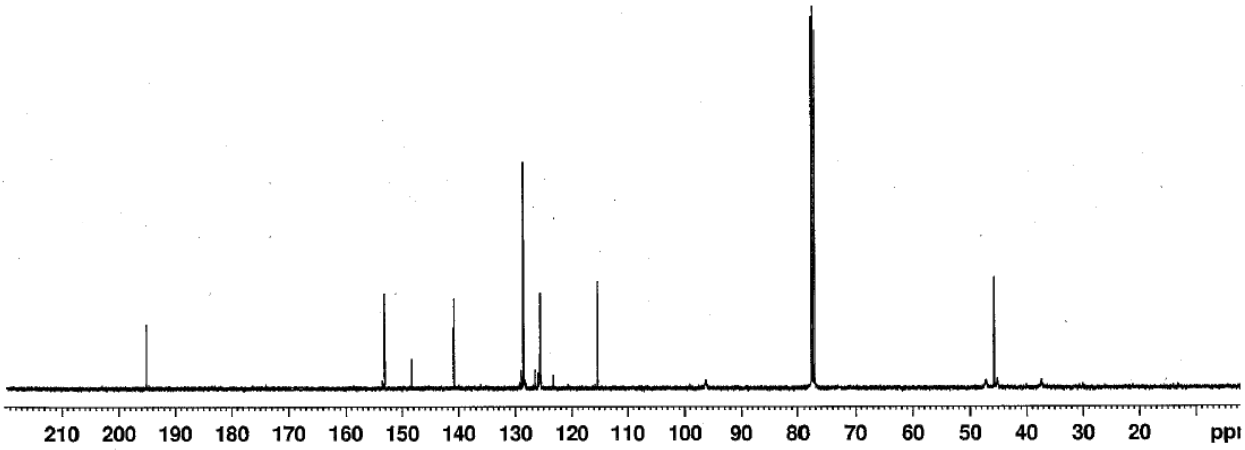
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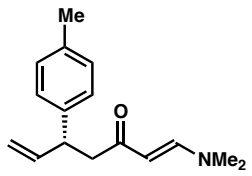
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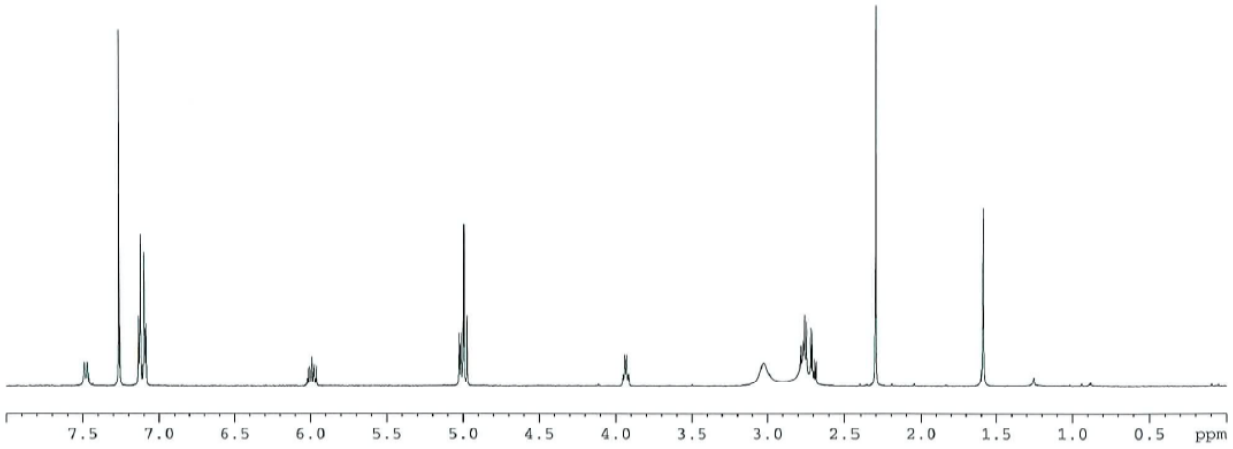
5h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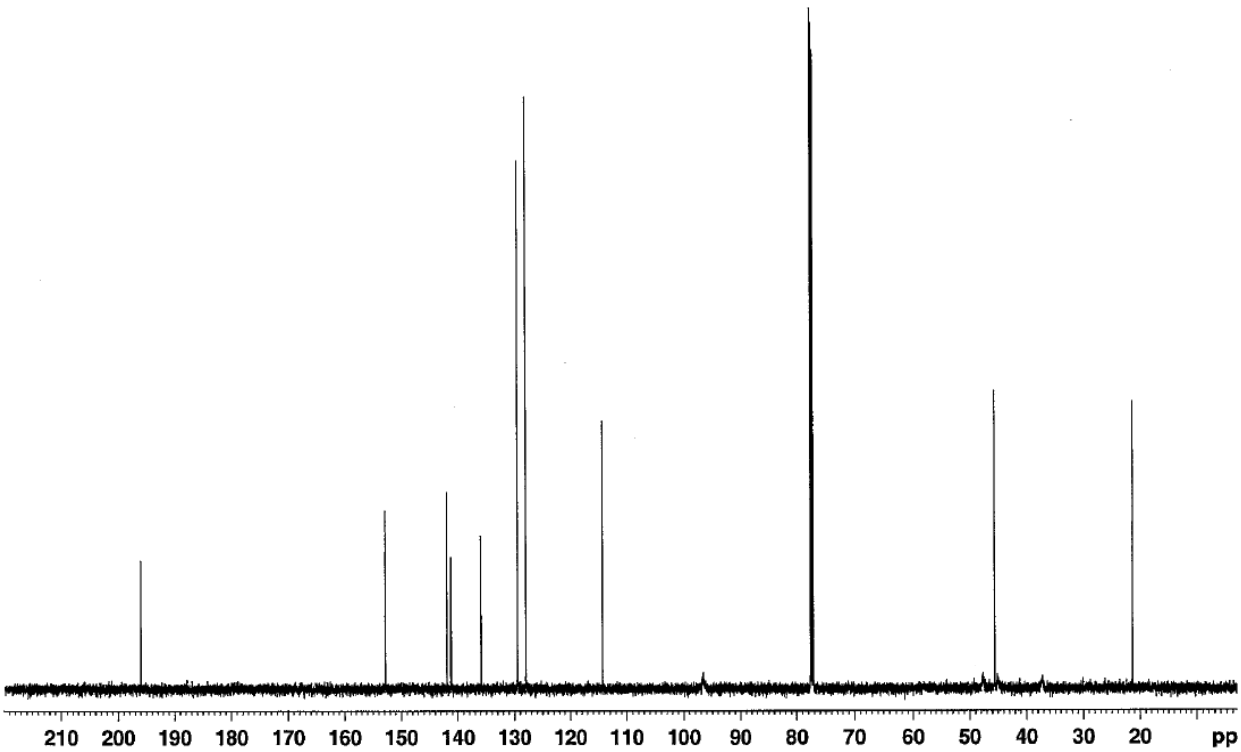
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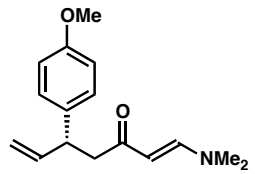
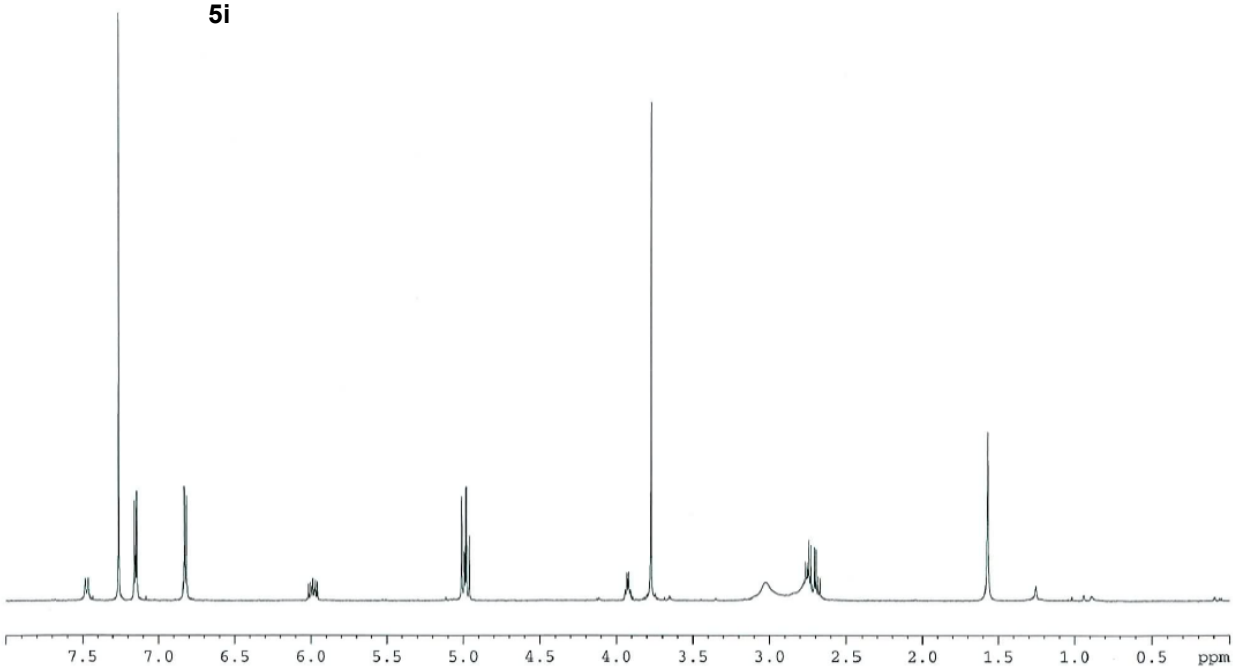

OMe
O
NMe2

5i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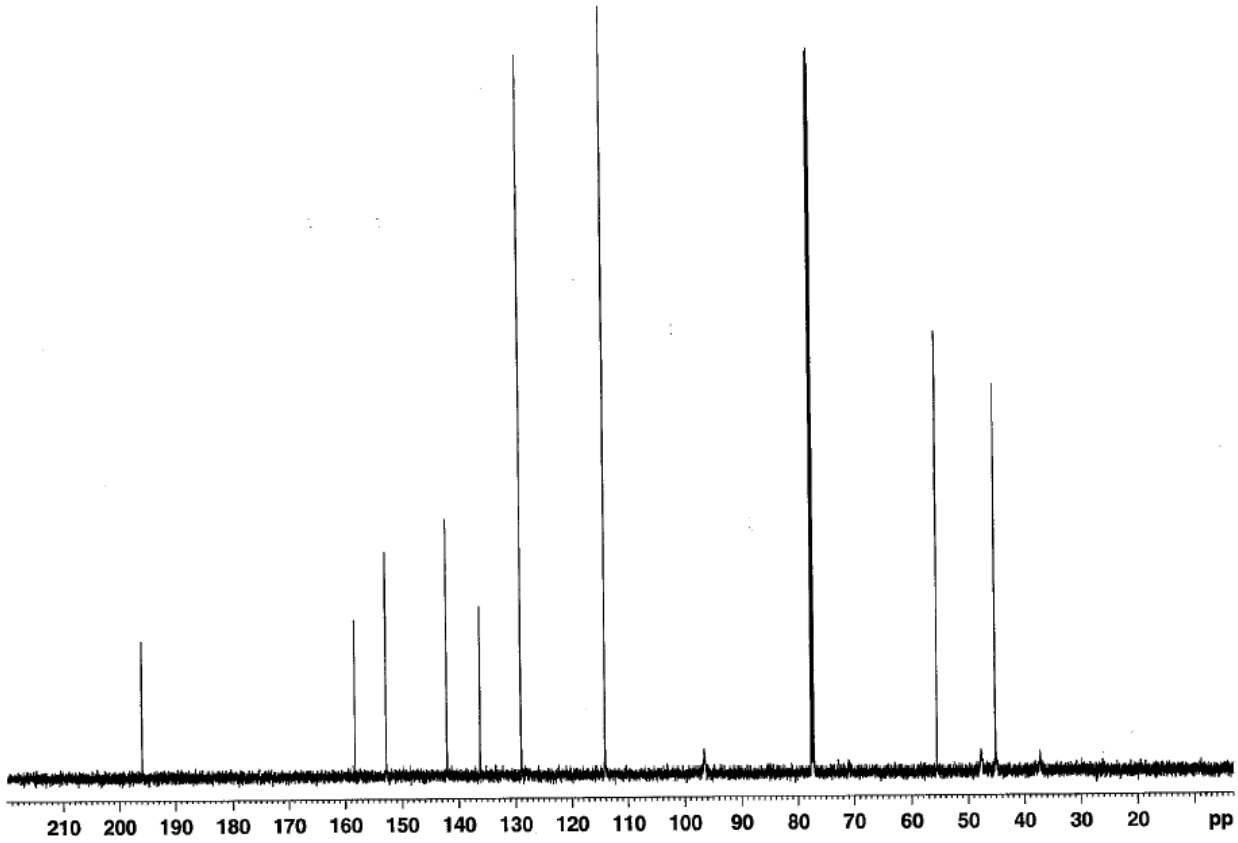
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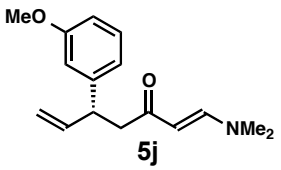
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O
NMe2

5j

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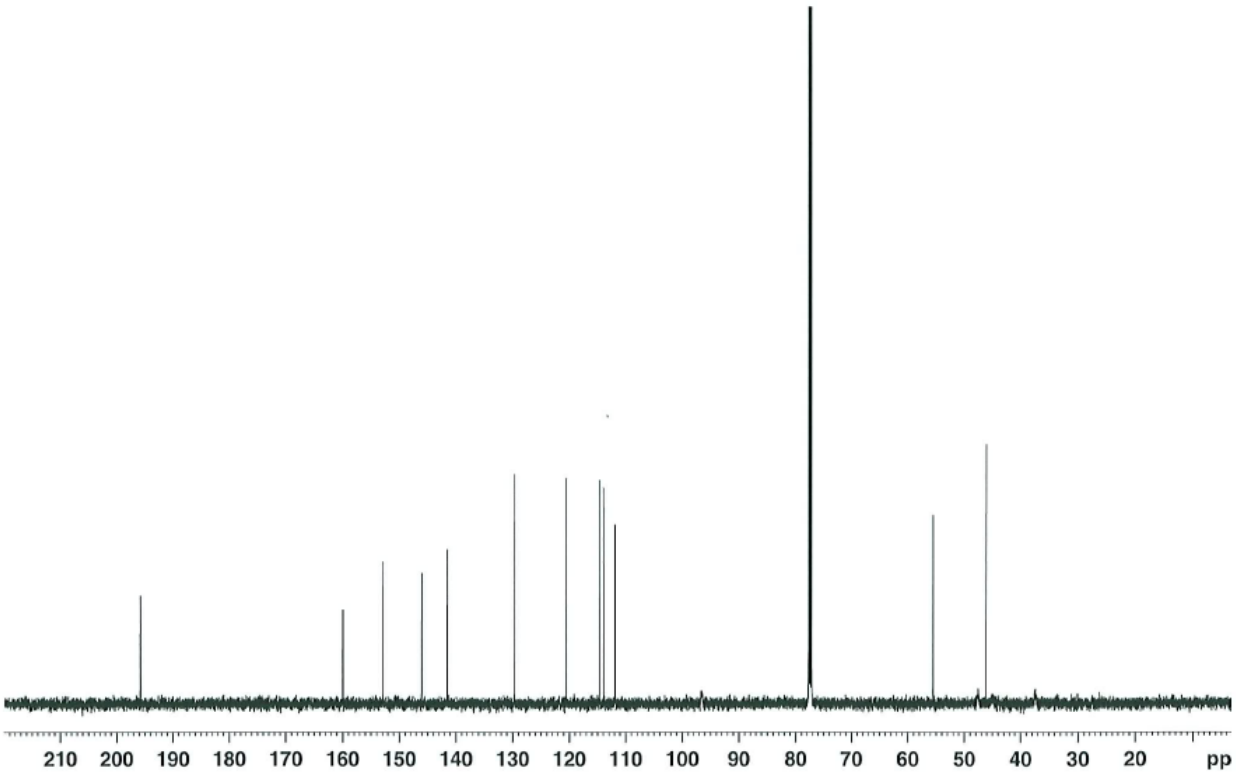
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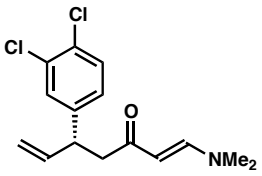
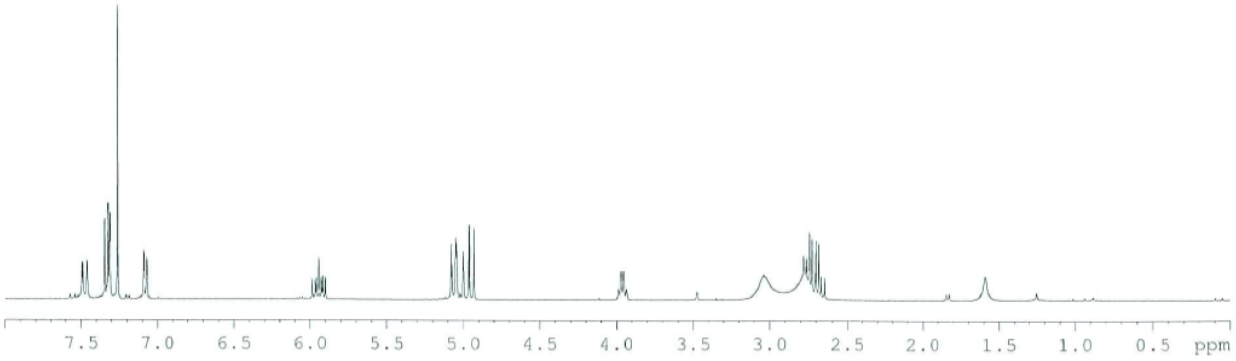

Cl
Cl
O
NMe2

5k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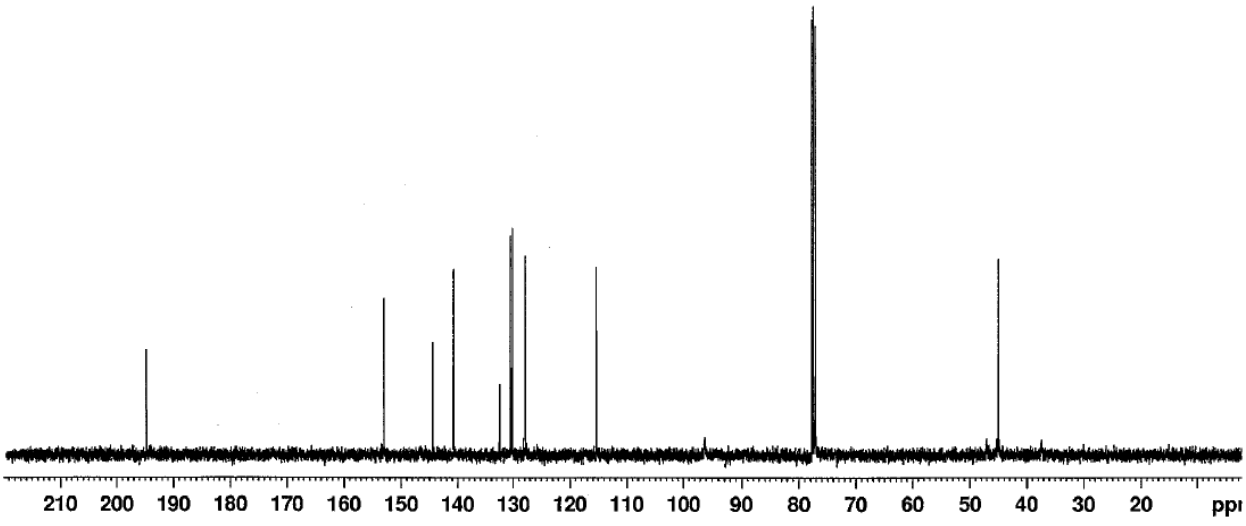
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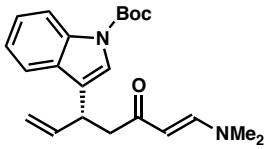
Boc
N
O
NMe2

5l

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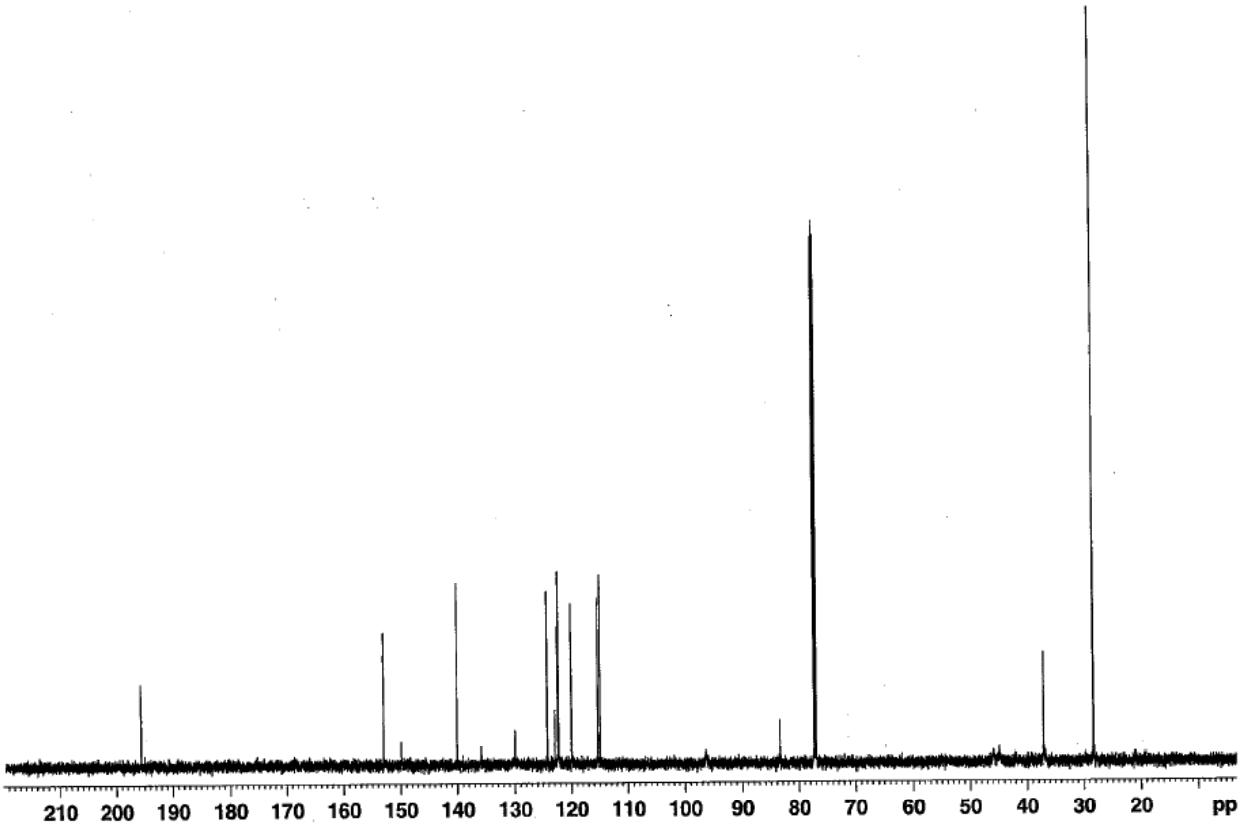
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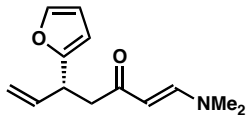
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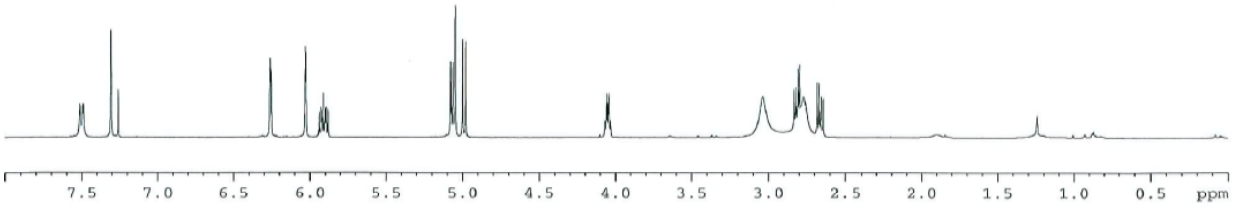
5m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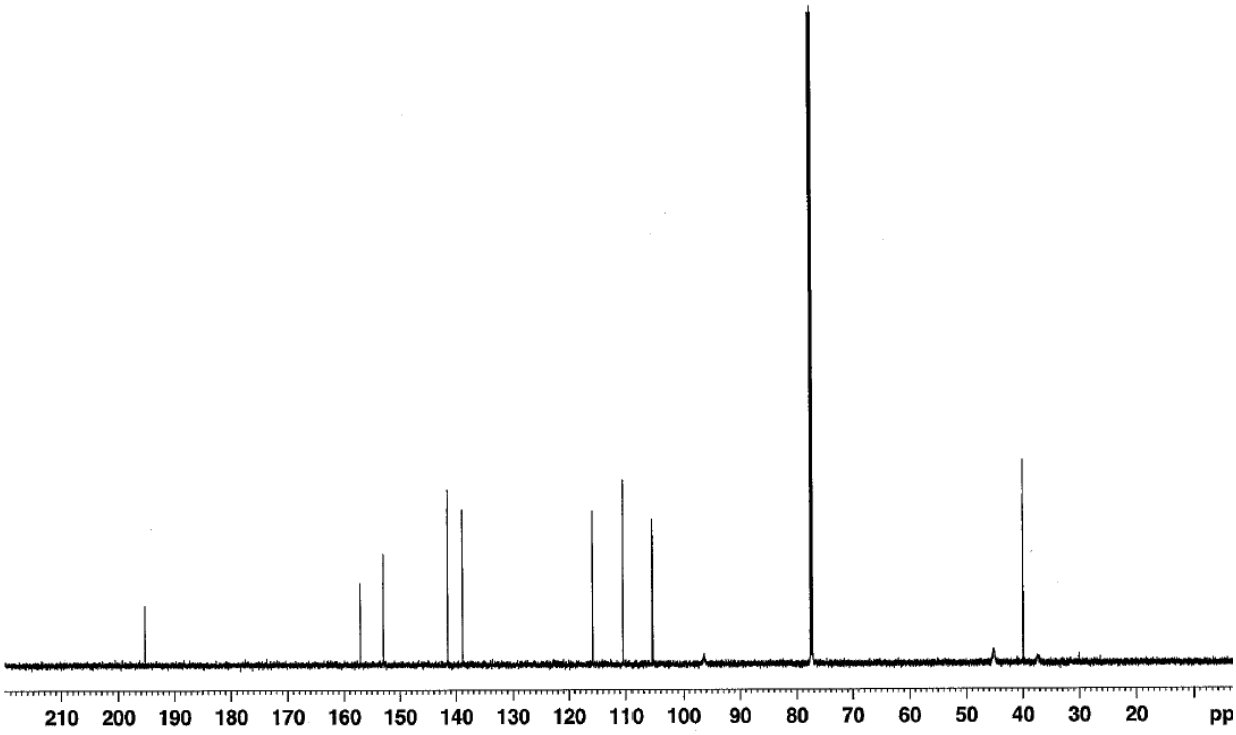
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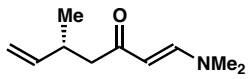
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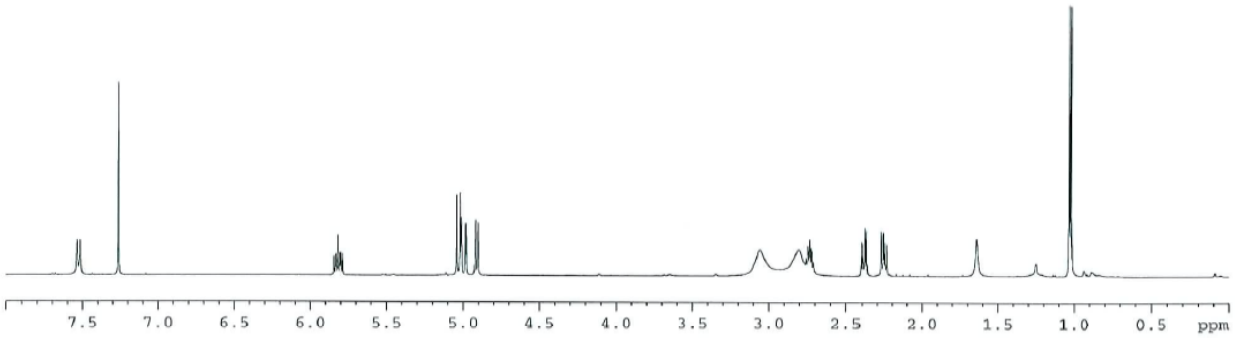
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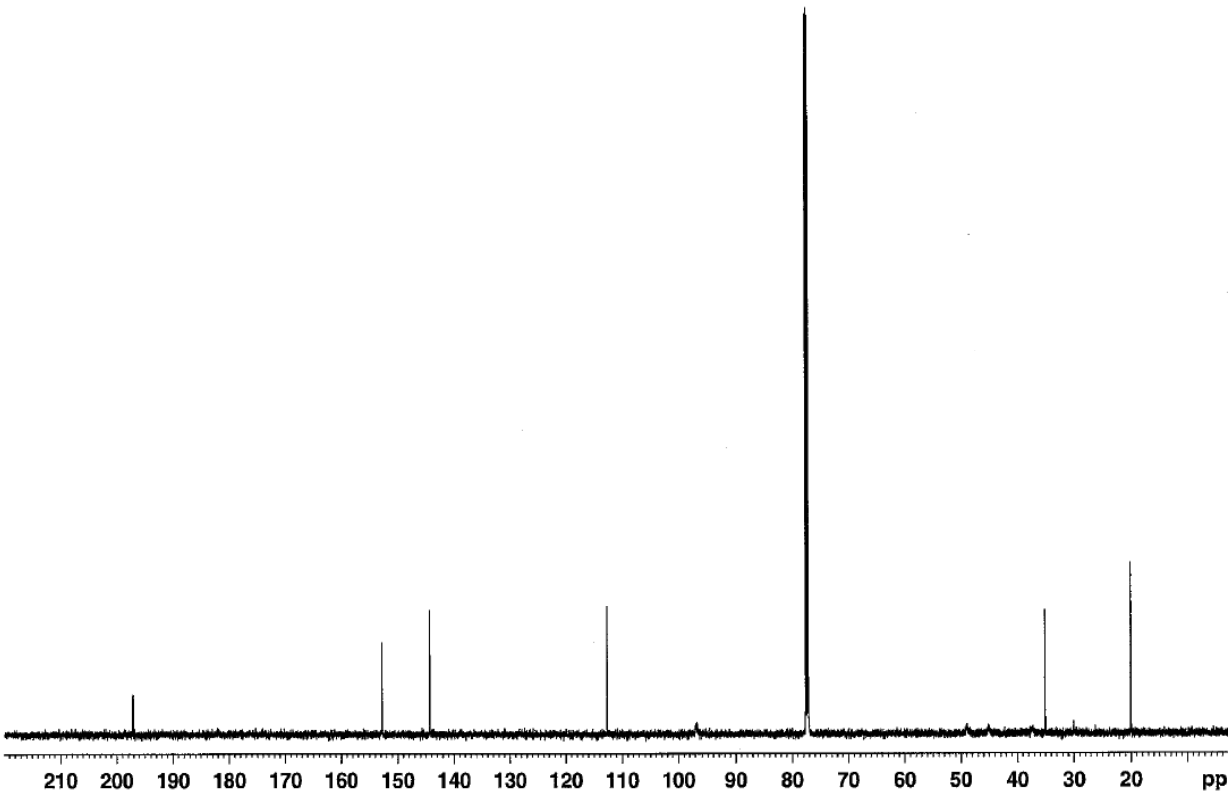
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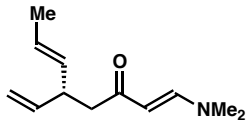
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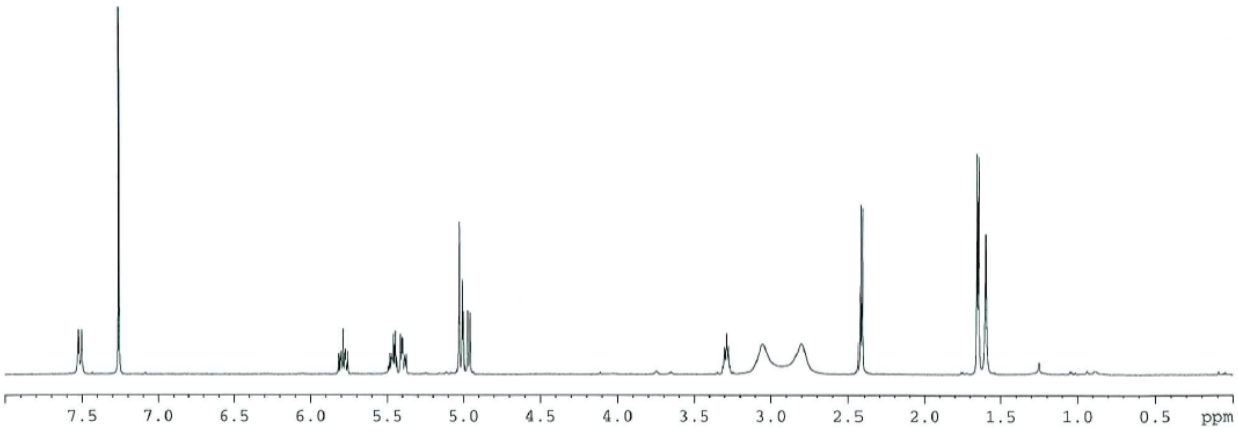
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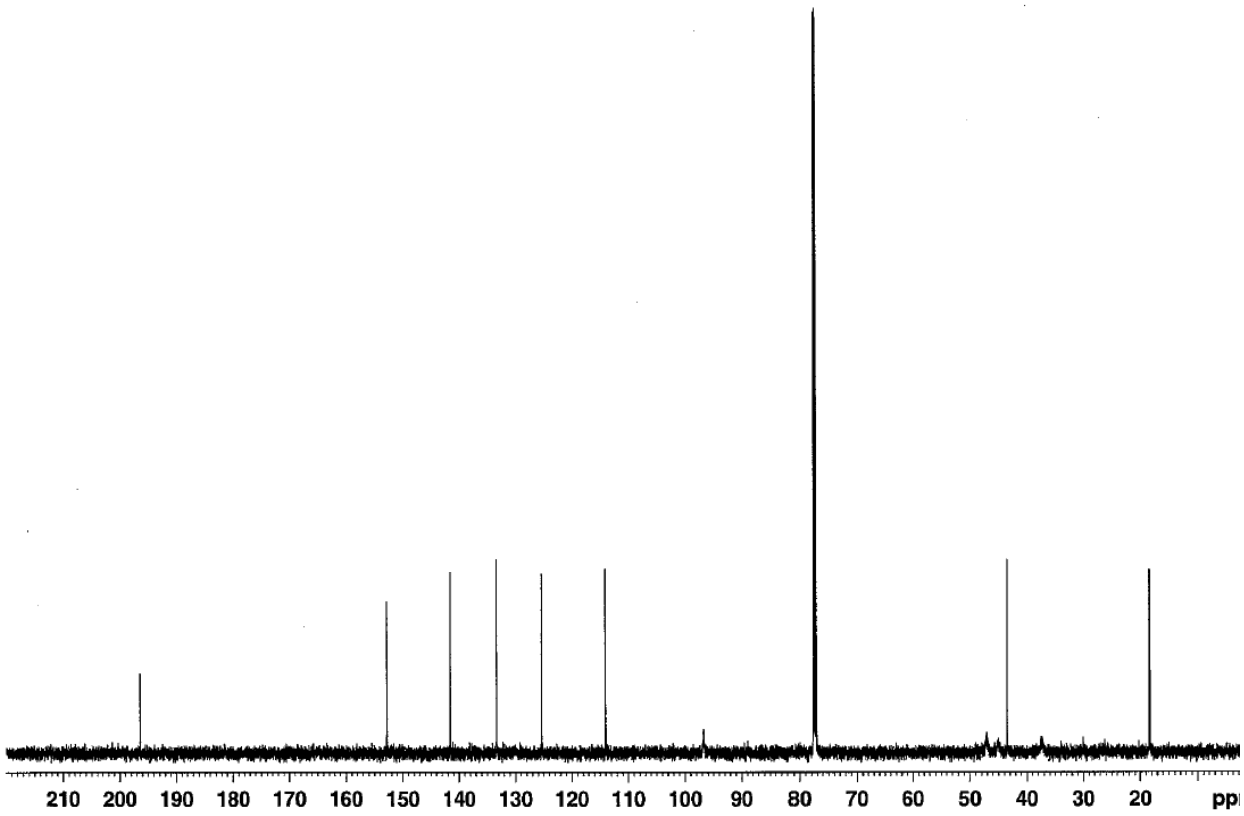
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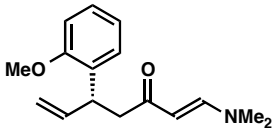
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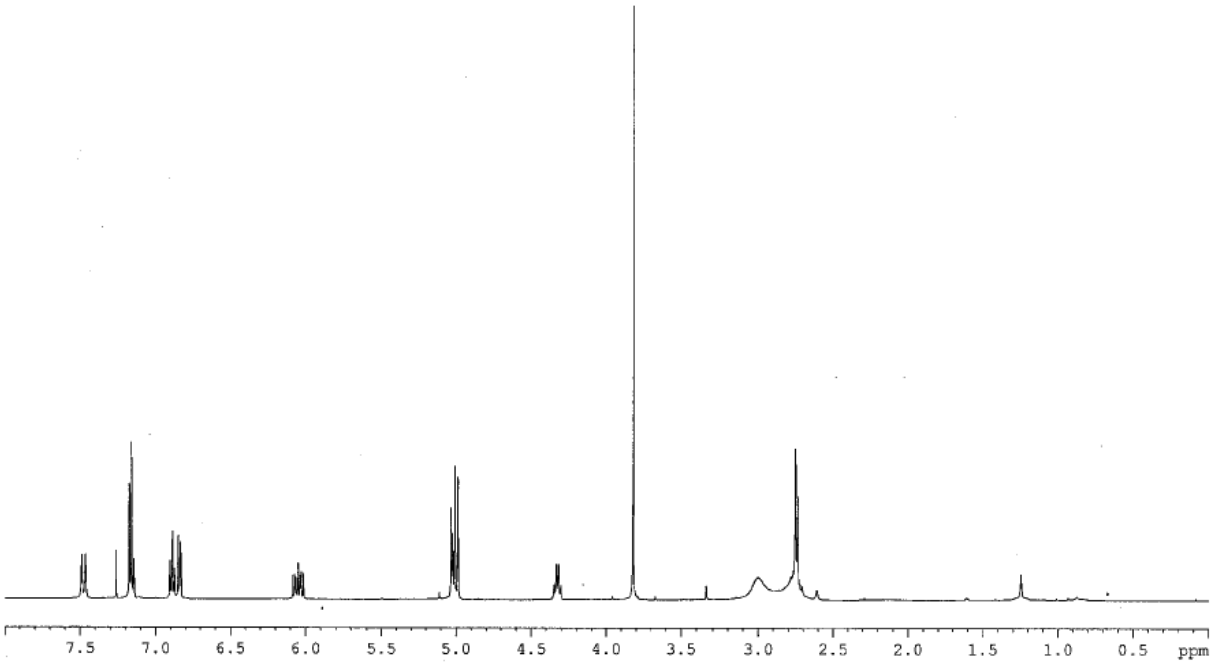
5p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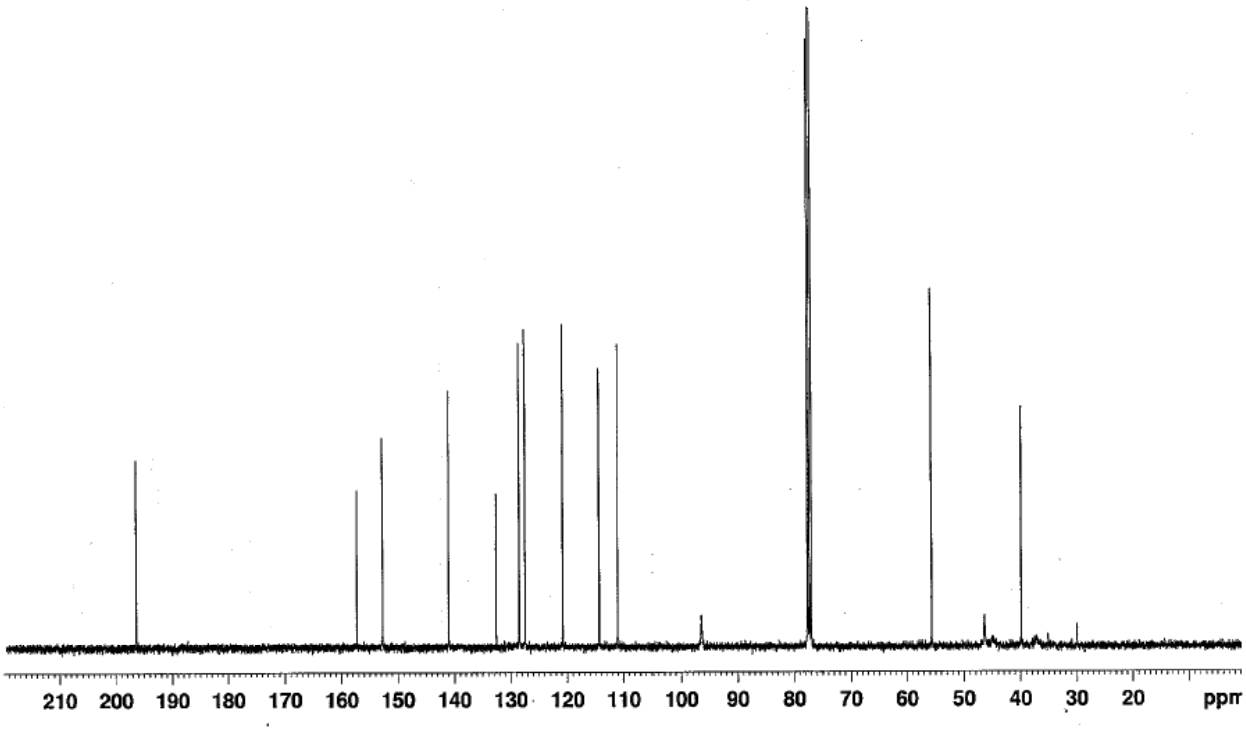
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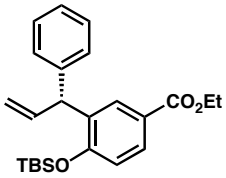
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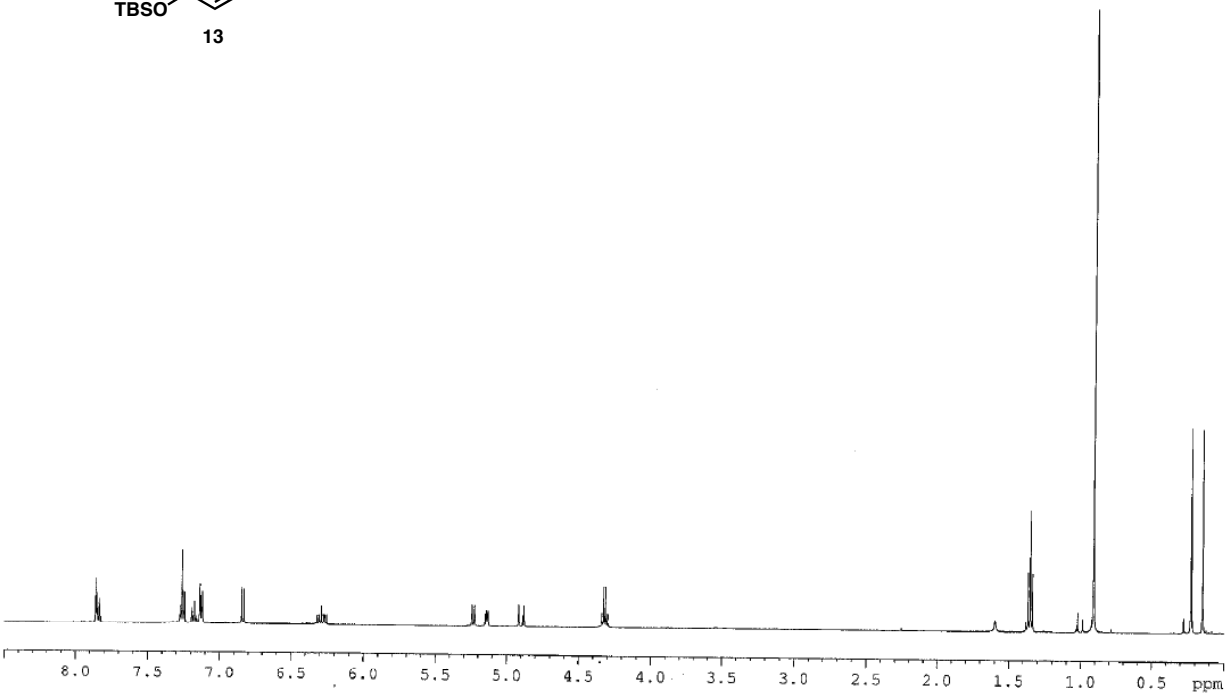
TBSO

13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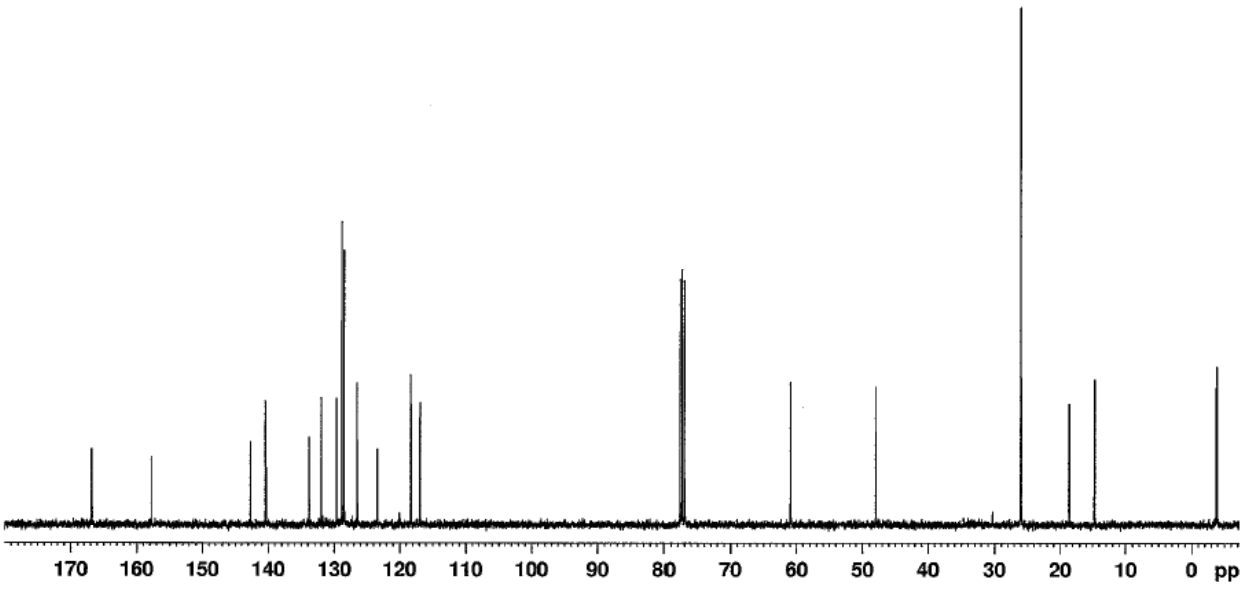
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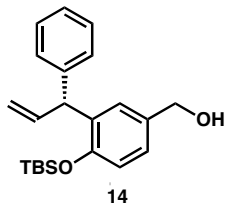
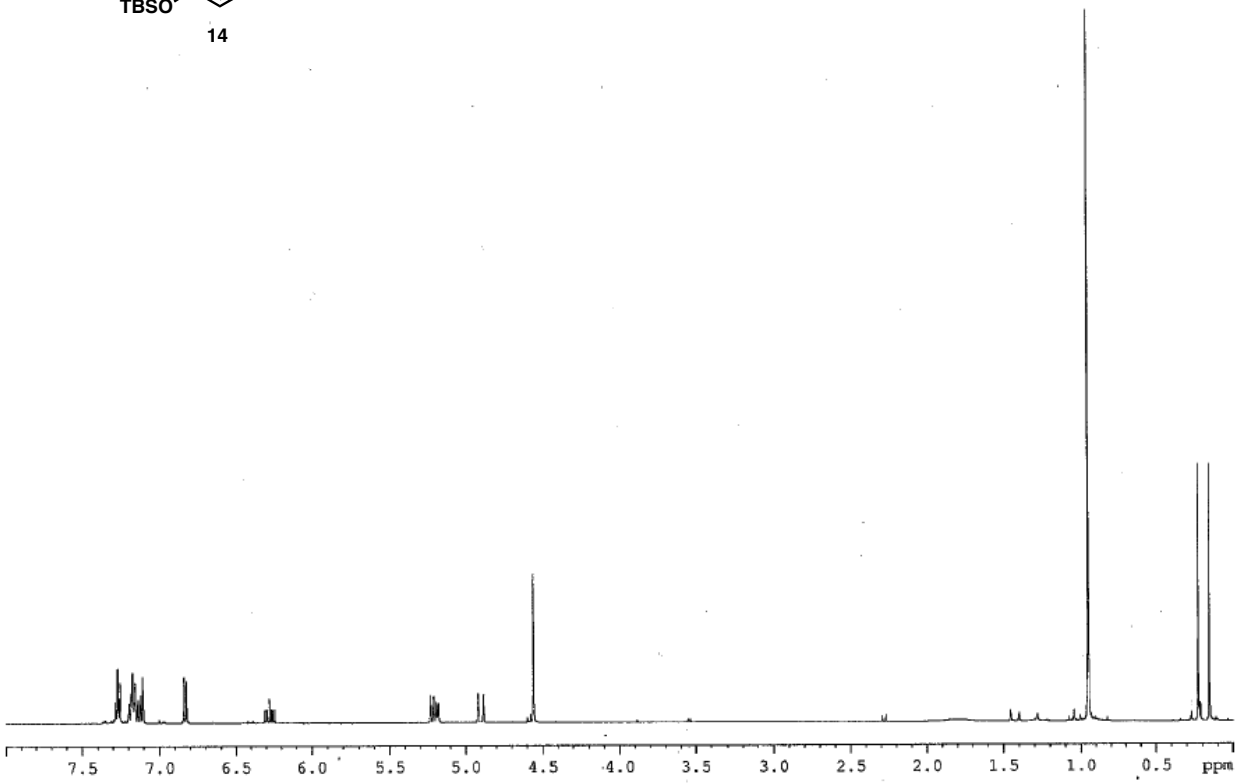

OH
TBSO

14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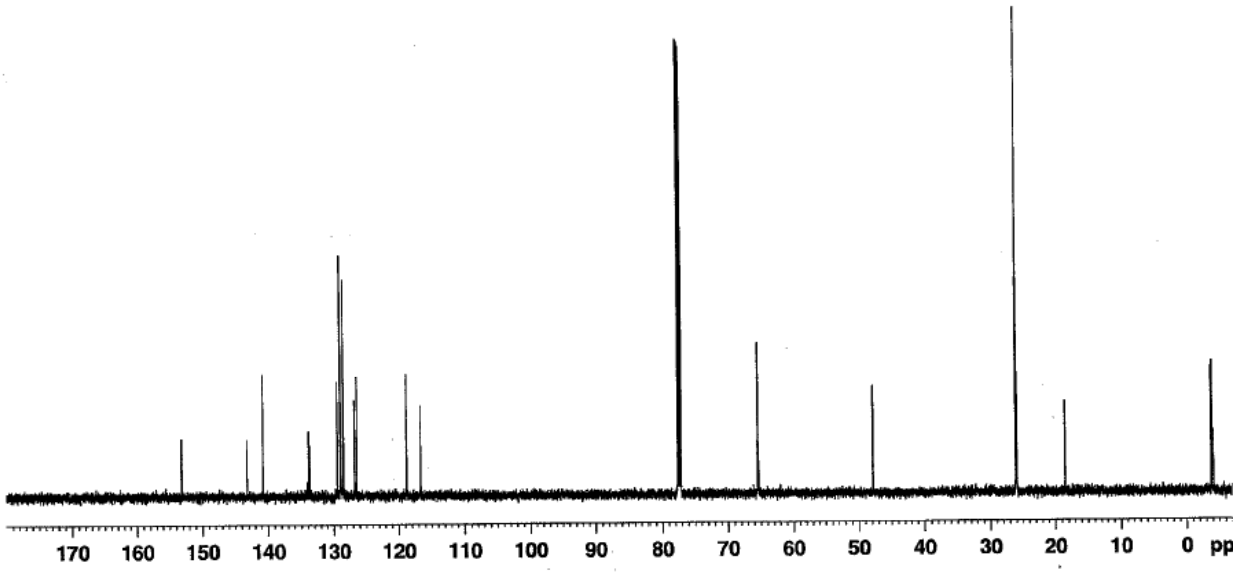
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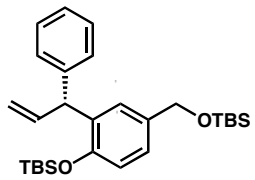
OTBS
TBSO

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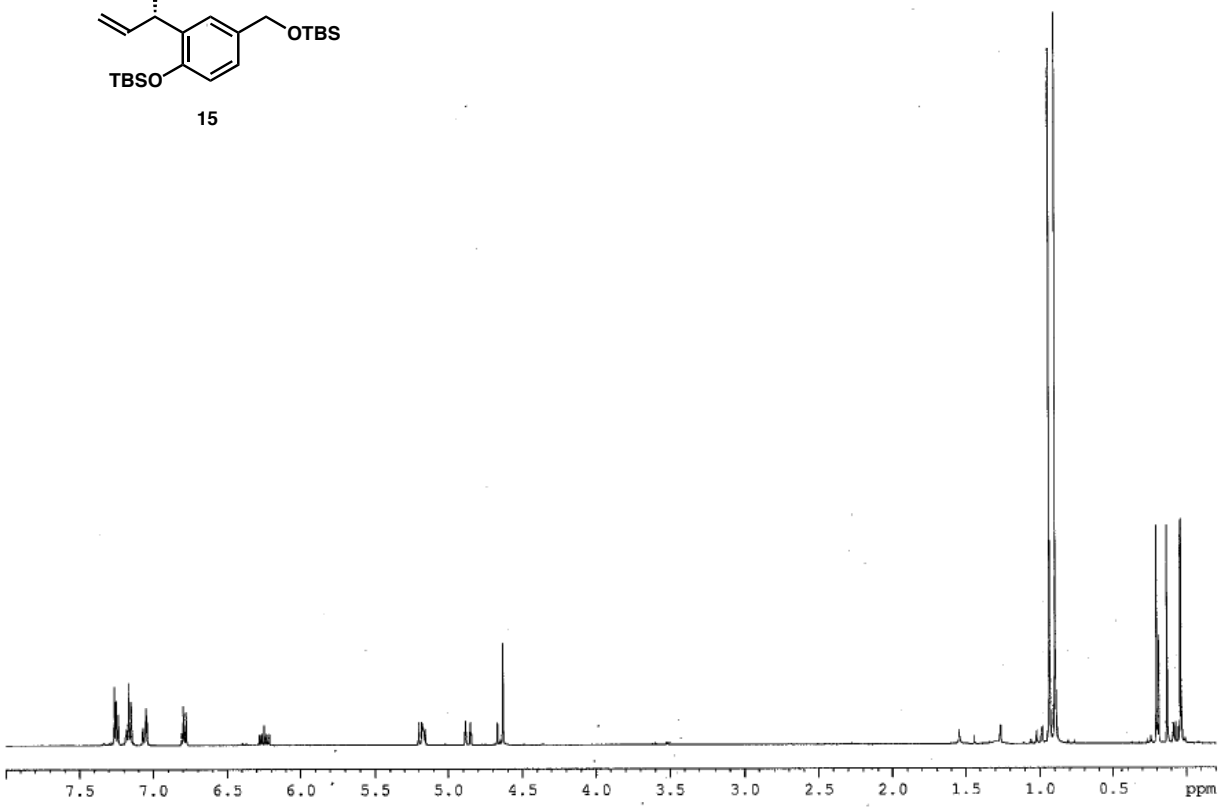
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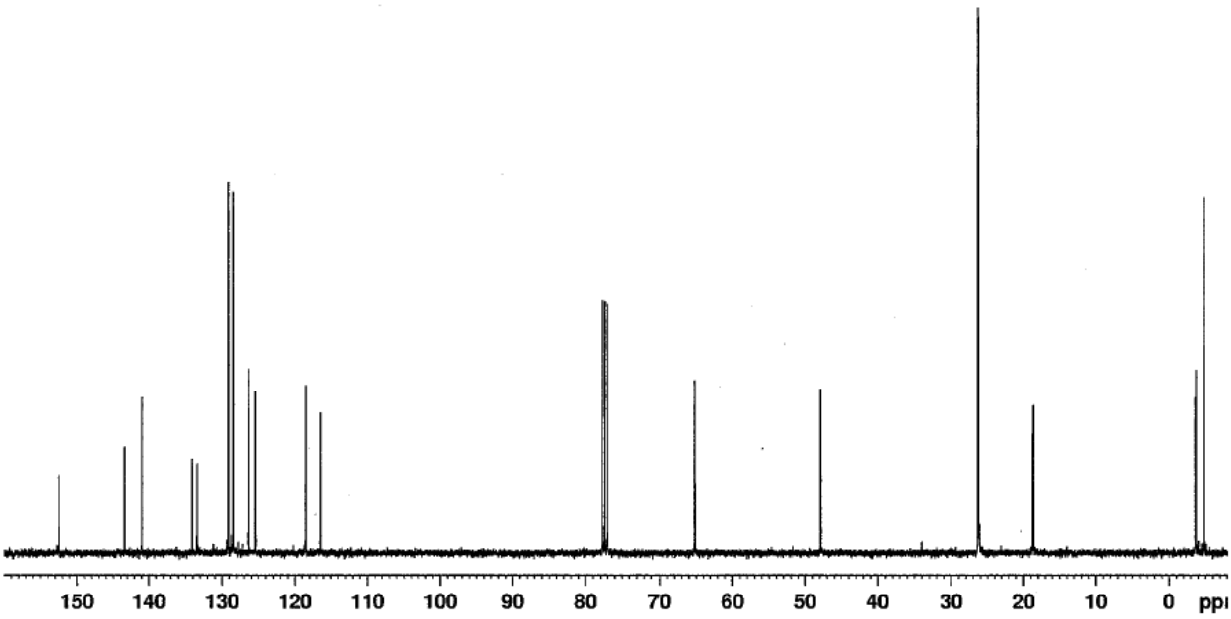
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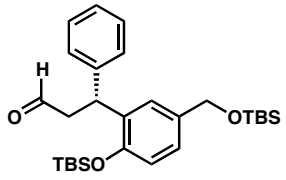
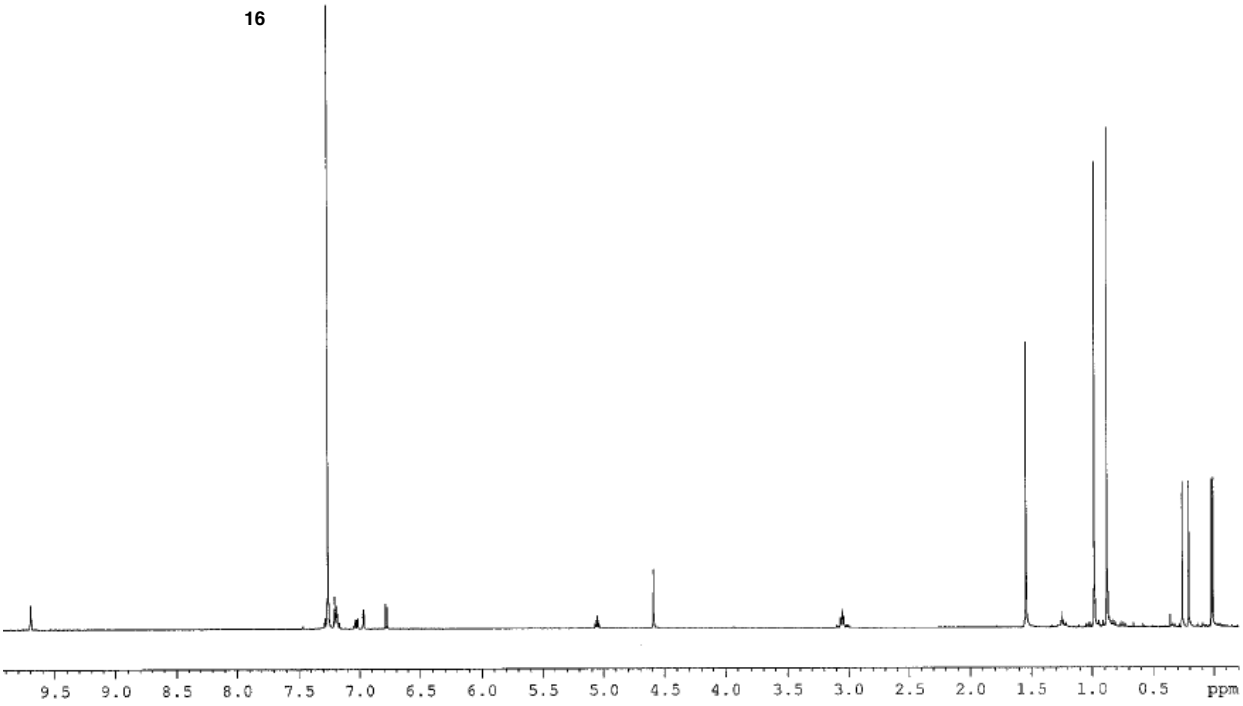
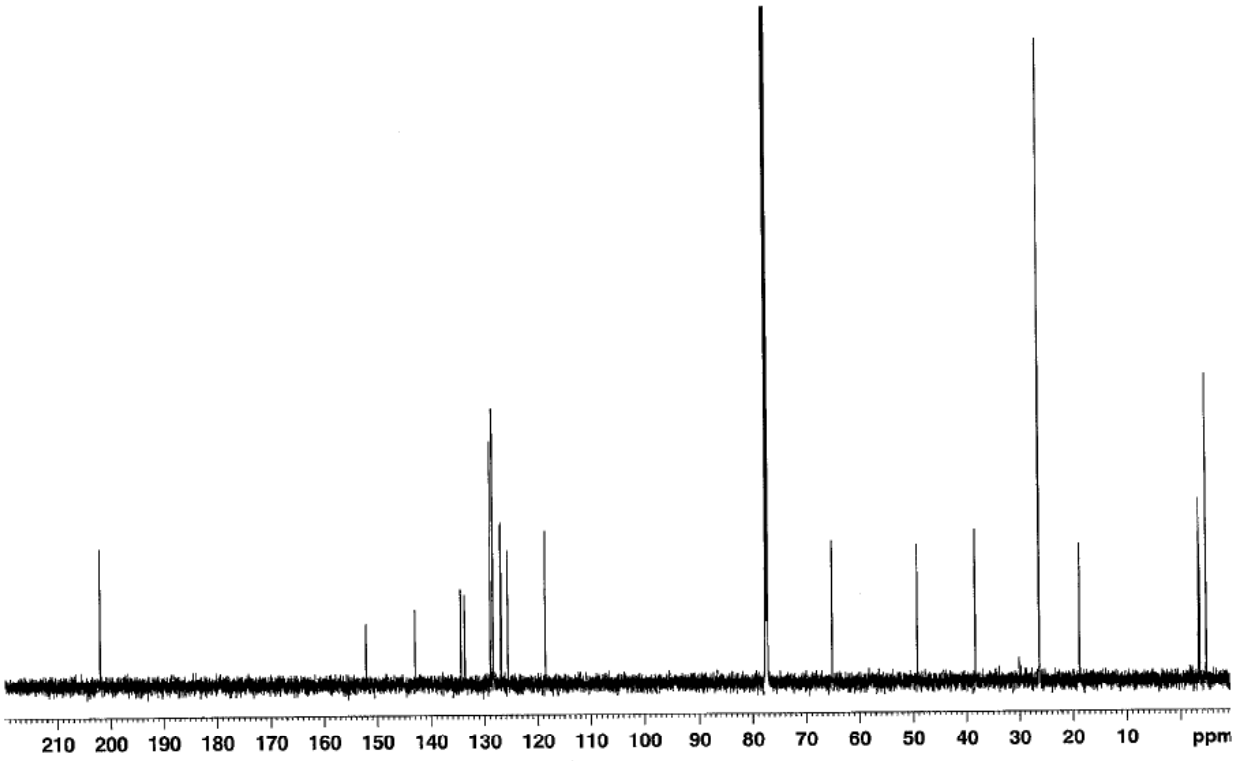
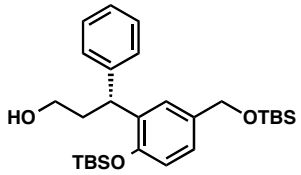
0
ppm


H
O
OTBS
TBSO

16

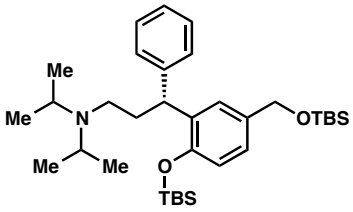

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


HO
OTBS
TBSO

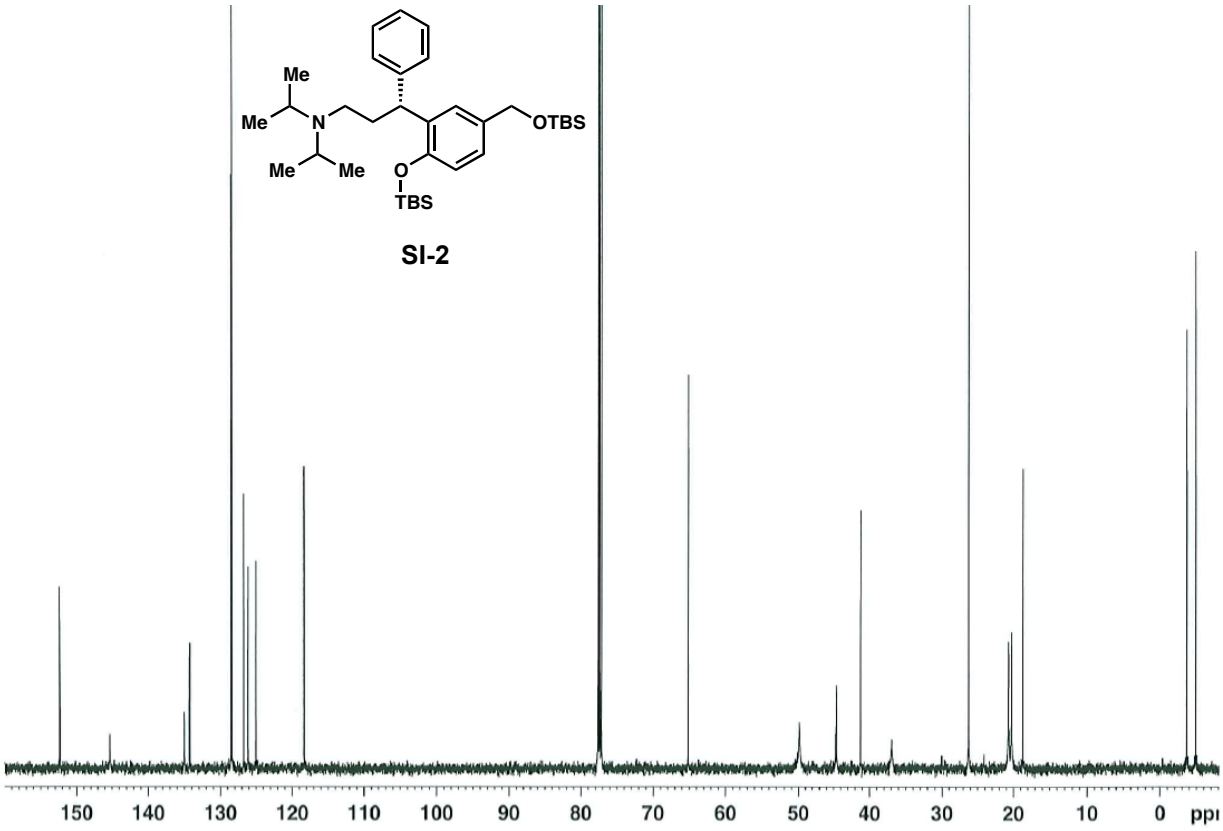
SI-1

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

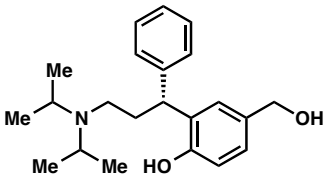

Me
Me
N
OTBS
Me
Me
O
TBS

SI-2

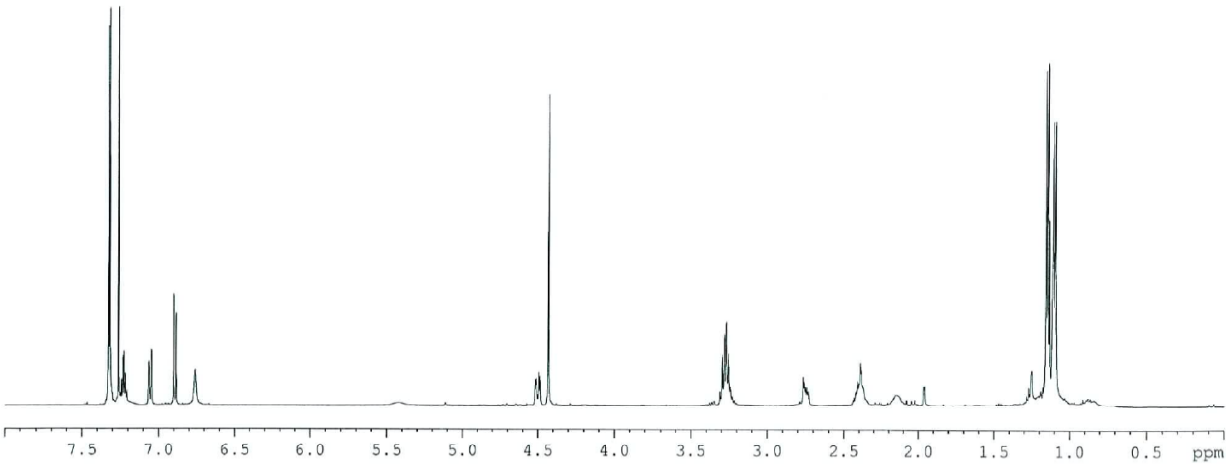
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


Me
Me
N
Me
Me
O
TBS
OTBS
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppı

SI-2


Me
Me
N
Me
Me
HO
OH

17


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm