Stereoselective Preparation of Functionalised Acyclic Alkenylmagnesium Reagents Using *i*-PrMgCl·LiCl

Hongjun Ren, Arkady Krasovskiy, Paul Knochel *

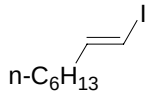
Department Chemie, Ludwig-Maximilians-Universität, Butenandtstrasse 5-13, 81377, München (Germany).
Paul.Knochel@cup.uni-muenchen.de

Supporting Information

General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and, if air or moisture sensitive, in flame-dried glassware under argon. Syringes used to transfer reagents and solvent were purged with argon prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC).

Preparation of the reagent *i*-PrMgCl·LiCl:
Magnesium turnings (110 mmol) and anhydrous LiCl (100 mmol) were placed in an Ar-flushed flask and THF (25 mL) was added. A solution of *i*-PrCl (100 mmol) in THF (25 mL) was slowly added at rt. The reaction starts within a few minutes. After addition, the reaction mixture was stirred for 12 h at rt. The grey solution of *i*-PrMgCl·LiCl was cannulated to an other flask under Ar and removed in this way from excess of magnesium. A yield of ca. 95-98% of *i*-PrMgCl·LiCl is obtained.



(*E*)-1-Iodo-1-octene (3a).[1] To a solution of 1-octyne (2.75 g, 25 mmol, in 50 mL of dry hexane) was added neat DIBAL (2.85 g, 25 mmol) slowly so the temperature stays below 40 ^{o}C. The reaction was then heated at 50 ^{o}C for 4 hr, and then cooled down to rt and hexane was removed under vacuum. THF (20 mL) was added and the solution was cooled to –50 ^{o}C, and iodine (6.35 g, 25 mmol) in THF (20 mL) was slowly added. The mixture was then warmed to

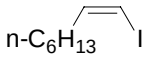
rt change color from brownish-red to almost colorless. The reaction mixture was then quenched by dropwise addition of 20 % sulfuric acid and was poured in a mixture of ice and 20 % sulfuric acid. The mixture was then extracted with pentane, and the organic extracts were washed with sodium thiosulfate, sodium bicarbonate solutions, and dried ($MgSO_4$), and the solvents were removed *in vacuo*. Purification by flash chromatography (pentane) yielded the pure product **3a** (5.68 g, 95 %) as a colorless oil. GC and ^{1}H NMR analysis indicated 99% isomeric purity (*E*:*Z* = 99:1).

^{1}H NMR ($CDCl_3$, 300 MHz): 6.49 (dt, J_1 = 14.4 Hz, J_2 = 7.2 Hz, 1 H), 5.95 (dt, J_1 = 14.4 Hz, J_2 = 1.5 Hz , 1 H), 2.03 (dq, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 2 H), 1.18-1.44 (m, 8 H), 0.86 (t, J = 6.9 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 146.8, 74.2, 36.0, 31.5, 28.6, 28.3, 22.5, 14.0;

IR (film): 2926, 1606, 1465, 943 cm^{-1};

MS (EI, 70 ev), m/z (%): 238 (M^+, 50 %), 167 (35 %), 154 (34 %), 69 (100 %).



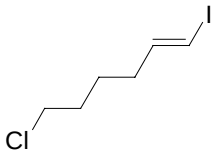
(*Z*)-1-Iodo-1-octene (3b).[2] To a solution of 1-octyne (550 mg, 5 mmol) in anhydrous CH_2Cl_2 was slowly added $HBBr_2{\cdot}SMe_2$ (5 mL, 1.0 M in CH_2Cl_2) and the mixture was stirred for 10 h. Water (0.9 mL) and ether (2.5 mL) was added to the reaction mixture at 0 ^{o}C. The reaction mixture was stirred for about 20 min after the addition and more ether (25 mL) was added. The organic layer was washed with cold water, brine and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the boronic acid was obtained in satisfactory purity. The boronic acid was then dissolved in the mixture solvent of ether and tetrahydrofuran (5 mL, 1:1) in a 25-mL flask and cooled down to 0 ^{o}C. Elemental iodine (13 mmol) was added and the mixture was stirred for 8 h at 0 ^{o}C. Aqueous sodium thiosulfate was added until iodine color disappeared, the mixture was extracted with pentane, washed with brine and dried over $MgSO_4$. Purification by flash chromatography (pentane) yielded the pure product **3b** (800 mg, 67 %) as a colorless oil. GC and ^{1}H NMR analysis indicated 98 % isomeric purity (*E*:*Z* = 2:98).

^{1}H NMR ($CDCl_3$, 300 MHz): 6.11-6.19 (m, 2 H), 2.07-2.16 (m, 2 H), 1.18-1.50 (m, 8 H), 0.87 (t, J = 6.9 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 141.5, 82.1, 34.7, 31.6, 28.8, 27.9, 22.6, 14.0;

IR (film): 2926, 1610, 1465, 1285 cm^{-1};

MS (EI, 70 ev), m/z (%): 238 (M^+, 52%), 167 (25 %), 154 (30 %), 69 (100%).



(*E*)-6-Chloro-1-iodo-hex-1-ene (3c). The reaction was carried out according to the procedure for (*E*)-1-iodo-1-octene (**3a**). 6-Chloro-1-hexyne (2.33 g, 20 mmol), neat DIBAL (2.28 g, 20 mmol) and I_2 (5.08 g, 20 mmol) yielded the product (*E*)- 6-chloro-1-iodo-hex-1-ene (**3c**) (3.98 g, 81 %) as a colorless oil. GC and ^{1}H NMR analysis indicated 99% isomeric purity (*E*:*Z* = 99:1).

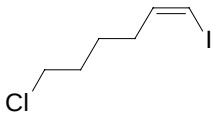
^{1}H NMR ($CDCl_3$, 300 MHz): 6.48 (dt, J_1 = 14.7 Hz, J_2 = 7.2 Hz, 1 H), 6.01 (dt, J_1 = 14.7 Hz, J_2 = 1.8 Hz, 1 H), 3.51 (t, J = 6.6 Hz, 2 H), 2.07 (qd, , J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1 H, 2 H), 1.75 (m, 2 H), 1.54 (m, 2 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 145.7, 75.1, 44.6, 35.2, 31.7, 25.5;

IR (film): 2937, 1606, 1454, 1230, 947 cm^{-1};

MS (EI, 70 ev): 246 (M^+,^{37}Cl, 33%), 244 (M^+, ^{35} Cl, 100%), 180 (9%), 167 (59 %), 154 (32 %), 127 (14 %), 81 (52 %);

HRMS (EI): calcd. for $C_6H_{10}ClI$: 243.9516, found: 243.9512.



(*Z*)-6-Chloro-1-iodo-hex-1-ene (3d). The reaction was carried out according to the procedure of (*Z*)-1-iodo-1-octene. 6-Chloro-1-hexyne (291 mg, 2.5 mmol), $HBBr_2{\cdot}SMe_2$ (2.5 mL, 1.0 M in CH_2Cl_2) and I_2 (1.7 g, 6.75 mmol) yielded the product (*Z*)-6-chloro-1-iodo-hex-1-ene (**3d**) (469 mg, 77 %) as a colorless oil . GC and ^{1}H NMR analysis indicated 97 % isomeric purity (*E*:*Z* = 3:97).

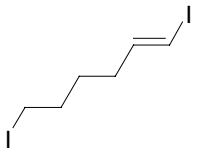
^{1}H NMR ($CDCl_3$, 300 MHz): 6.11- 6.23 (m, 2 H), 3.53 (t, J = 6.3 Hz, 2 H), 2.16 (q, J = 7.2 Hz, 2 H), 1.80 (m, 2 H), 1.57 (m, 2 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 140.5, 83.0, 44.7, 33.8, 31.8, 25.1;

IR (film): 2939, 1610, 1454, 1297, 1284, 690 cm^{-1};

MS (EI, 70 ev): 246 (M^+, ^{37}Cl, 16 %), 244 (M^+, ^{35}Cl, 49 %), 167 (35 %), 154 (28 %), 117 (13 %), 81 (100 %);

HRMS (EI): calcd. for $C_6H_{10}ClI$: 243.9516, found: 243.9521.



(*E*)-1,6-Diiodo-hex-1-ene (3e). A mixture of (*E*)- 6-chloro-1-iodo-hex-1-ene (**3c**) (732 mg, 3.0 mmol), NaI (900 mg, 6.0 mmol) and acetone (5 mL) was stirred at 70 °C overnight. After cooling to room temperature, water (10 mL) was added. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 100:1) yielded the product **3e** (912 mg, 90 %) as a colorless oil. GC and ^{1}H NMR analysis indicated 99% isomeric purity (*E*:*Z* = 99:1).

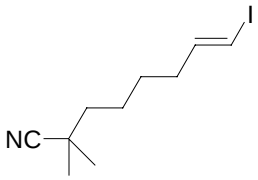
^{1}H NMR ($CDCl_3$, 300 MHz): 6.47 (dt, J_1 = 14.6 Hz, J_2 = 6.6 Hz, 1 H), 6.00 (d, J = 14.6 Hz, 1 H), 3.15 (t, J = 6.3 Hz, 2 H), 2.01-2.10 (m, 2 H), 1.70-1.85 (m, 2 H), 1.49 (m, 2 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 145.6, 75.3, 34.8, 32.5, 29.1, 6.3;

IR (film): 2928, 1605, 1450, 1219, 1187, 943;

MS (EI, 70 ev): 336 (20 %), 209 (79 %), 167 (94 %), 81 (100 %);

HRMS (EI): calcd. for $C_6H_{10}I_2$: 335.8872, found: 335.8894.



(*E*)-8-Iodo-2,2-dimethyl-oct-7-enenitrile (3f). To a solution of isobutyronitrile (104 mg, 1.5 mmol) in THF (3 mL) was added LDA (1.5 mmol, in 3 mL of THF, prepared from *n*-BuLi and HN(*i*-Pr)$_2$) at –78 ^{o}C and the mixture was stirred for 1 h. Then, the solution of **3e** (336 mg, 1.0 mmol, in 1 mL of THF) was added and stirred for 2 h at this temperature.The reaction mixture was warmed to room temperature and stirred for 1 h, then quenched with NH_4Cl (aq). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 50:1) yielded the pure product **3f** (191 mg, 69 %) as a colorless oil. GC and ^{1}H NMR analysis indicated 99% isomeric purity (*E*:*Z* = 99:1).

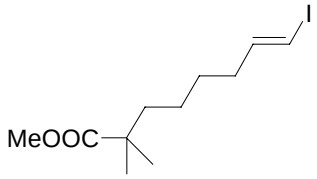
^{1}H NMR ($CDCl_3$, 300 MHz): 6.47 (dt, J_1 = 14.1 Hz, J_2 = 7.2 Hz, 1 H), 5.98 (dt, J_1 = 14.1 Hz, J_2 = 1.2 Hz, 1 H), 2.02-2.10 (m, 2 H), 1.36-1.51 (m, 6 H), 1.30 (s, 6 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 145.9, 125.0, 74.8, 40.7, 35.7, 32.2, 28.2, 26.6, 24.5;

IR (film): 2938, 2234, 1606, 1462, 1207, 949;

MS (EI, 70 ev): 277 (11 %), 180 (26 %), 167 (58 %), 150 (100 %), 123 (17 %);

HRMS (EI): calcd. for $C_{10}H_{16}IN$: 277.0327, found: 277.0359.



(*E*)-8-Iodo-2,2-dimethyl-oct-7-enoic acid methyl ester (3g). To a solution of methyl isobutyrate (174 mg, 1.5 mmol) in THF (3 mL) was added LDA (1.5 mmol, in 3 mL of THF, prepared from *n*-BuLi and HN(*i*-Pr)$_2$) at –78 ^{o}C and the mixture was stirred for 1 h. Then, the solution of **3e** (336 mg, 1.0 mmol, in 1 ml of THF) was added and the mixture was stirred for 2 h at this temperature. The reaction mixture was warmed to room temperature and stirred for 1 h, then quenched with NH_4Cl (aq). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 25:1) yielded the pure product **3g** (224 mg, 81 %) as a colorless oil. GC and ^{1}H NMR analysis indicated 99% isomeric purity (*E*:*Z* = 99:1).

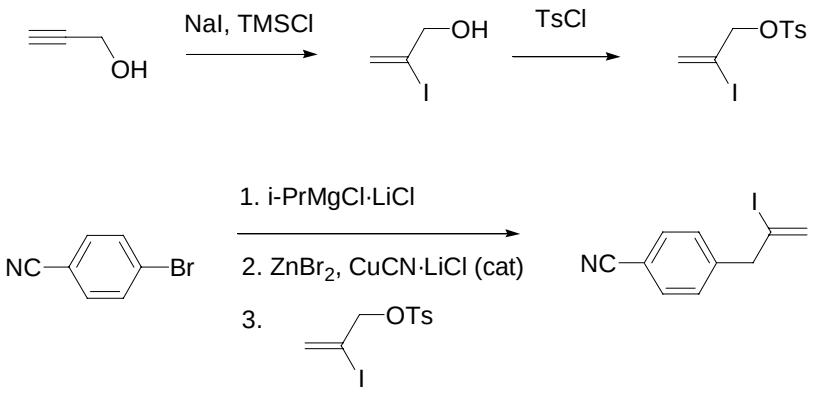
^{1}H NMR ($CDCl_3$, 300 MHz): 6.46 (dt, J_1 = 14.1 Hz, J_2 = 6.9 Hz, 1 H), 5.95 (dt, J_1 = 14.1 Hz, J_2 = 1.5 Hz, 1 H), 3.63 (s, 3 H), 1.98-2.06 (m, 2 H), 1.40-1.50 (m, 2 H), 1.26-1.40 (m, 2 H), 1.13-1.23 (m, 2 H), 1.13 (s, 6 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 178.4, 146.4, 74.5, 51.7, 42.2, 40.4, 35.8, 28.7, 25.1, 24.2;

IR (film): 2938, 1732, 1606, 1473, 1193, 1156, 948;

MS (EI, 70 ev): 311 (M^++1, 0.7 %), 251 (0.8 %), 195 (3.3 %), 183 (33.9 %), 123 (100 %), 102 (77 %);

HRMS (EI): calcd. for $C_{11}H_{20}IO_2$ (M^++H): 311.0508, found: $C_{11}H_{20}IO_2$: 311.0488 (M^++H).



4-(2-Iodo-allyl)-benzonitrile (3h). 2-Iodo-prop-2-en-1-ol was obtained according to a literature procedure.[3] The mixture of 2-iodo-prop-2-en-1-ol (2.13 g, 11.6 mmol) , TsCl (2.43 g, 12.8 mmol) and Et_3N (1.74 g, 17.4 mmol) in CH_2Cl_2 (25 mL) were stirred at 0 ^oC for 7 h. Then, the mixture was washed with brine and dried ($MgSO_4$). The crude product was purified on silica gel yielding the 2-iodoallyl tosylate (3.33 g, 85 %) as a colorless oil.

To a solution of 4-bromobenzonitrile (1.82 g, 10 mmol) in THF (10 mL) was added the *i*-PrMgCl·LiCl (5.5 mL, 2.0 M in THF, 11.0 mmol) at –10 ^oC and stirred for 4 h. $ZnBr_2$ (11.0 mL, 1.0 M in THF) was added and the reaction mixture was stirred at this temperature for 30 min. Then the solution of 2-iodoallyl tosylate (3.38 g, 10 mmol) in THF (5 mL), CuCN·2LiCl (2.0 mL, 1.0 M in THF) and NMP (4 mL) were added subsequently to the reaction mixture. The reaction mixture was stirred at room temperature overnight then quenched with NH_4Cl (aq) (5 mL). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 15:1) yielded the pure product **3h** (1.69 g, 63 %) as a colorless oil.

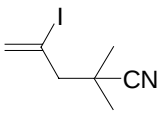
^1H NMR ($CDCl_3$, 300 MHz): 7.60 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 6.09-6.10 (m, 1 H), 5.84 (s, 1 H), 3.81 (s, 2 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 143.2, 132.3, 129.7, 128.1, 118.7, 110.9, 107.2, 51.4;

IR (film): 2976, 2228, 1607, 1504, 1188 cm^{-1};

MS (EI, 70 ev): 269 (M^+, 78 %), 142 (100 %), 115 (81 %);

HRMS (EI): calcd. for $C_{10}H_8IN$: 268.9701, found: 268.9726.



4-Iodo-2,2-dimethyl-pent-4-enenitrile (3i). To a solution of isobutyronitrile (104 mg, 1.5 mmol) in THF (3 mL) was added LDA (1.5 mmol, in 3 mL of THF, prepared from *n*-BuLi and HN(*i*-Pr)$_2$) at –78 ^{o}C and stirred for 1 h. Then, the solution of 2-iodoallyl tosylate (338 mg, 1.0 mmol) in THF (1 mL) was added and the mixture was stirred for 2 h at this temperature then quenched with NH_4Cl (aq). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 25:1) yielded the pure product **3i** (134 mg, 57 %) as a solid; m.p.: 36.9-37.5 ^{o}C.

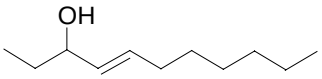
^{1}H NMR ($CDCl_3$, 300 MHz): 6.25-6.28 (m, 1 H), 6.03 (d, *J* = 1.8 Hz, 1 H), 2.73 (d, *J* = 1.3 Hz, 2 H), 1.44 (s, 6 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 131.7, 124.1, 99.5, 53.9, 33.1, 26.8;

IR (KBr): 2977, 2234, 1611, 1184, 909 cm^{-1};

MS (EI, 70 ev): 235 (M^+, 100 %), 167 (21 %), 127 (10 %), 108 (11 %), 81 (32 %);

HRMS (EI): calcd. for $C_7H_{10}IN$: 234.9858, found: 234.9844.



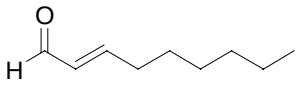
(*E*)-Undec-4-en-3-ol (5a).[4] To a solution of (*E*)-1-iodo-1-octene (**3a**) (119 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40 °C. After 7 h, a complete conversion to the Grignard reagent (**4a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Propionaldehyde (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 3:1) yielded the pure product **5a** (70 mg, 82 % yield) as a colorless oil. ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

^{1}H NMR ($CDCl_3$, 300 MHz): 5.61 (ddt, J_1 = 15.5 Hz, J_2 = 6.6 Hz, J_3 = 0.9 Hz, 1 H), 5.41 (ddt, J_1 = 15.5 Hz, J_2 = 6.6 Hz, J_3 = 1.3 Hz, 1 H), 3.94 (q, *J* = 6.6 Hz, 1 H), 1.97-2.03 (m, 2 H), 1.17-1.60 (m, 7 H), 0.81-0.90 (m, 6 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 132.7, 132.4, 74.5, 32.2, 31.7, 30.1, 29.2, 28.8, 22.6, 14.0, 9.7;

IR (film): 3350, 2960, 1670, 1464, 966 cm^{-1};

MS (EI, 70 ev): 170 (M^+, 0.4 %), 152 (11 %), 141 (54 %), 123 (26 %), 85 (83 %), 57 (100 %).



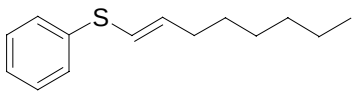
(*E*)-Non-2-enal (5b).[5] To a solution of (*E*)-1-iodo-1-octene (**3a**) (119 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40 °C. After 7 h, a complete conversion to the Grignard reagent (**4a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. DMF (0.75 mmol in 0.5 ml of THF) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 30:1) yielded the pure product **5b** (50 mg, 71 % yield) as a colorless oil. ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

^{1}H NMR ($CDCl_3$, 300 MHz): 9.46 (d, J = 7.9 Hz, 1 H), 6.81 (dt, J_1 = 15.5 Hz, J_2 = 6.6 Hz, 1 H), 6.08 (ddt, J_1 = 15.9 Hz, J_2 = 7.9 Hz, J_3 = 1.3 Hz, 1 H), 2.25-2.34 (m, 2 H), 1.20-1.52 (m, 8 H), 0.85 (t, J = 6.6 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 194.1, 159.0, 132.9, 32.7, 31.5, 28.7, 27.7, 22.5, 14.0;

IR (film): 2928, 1697, 1421, 1308, 977 cm^{-1};

MS (EI, 70 ev): 139 (M^+-H, 0.6 %), 122 (6 %), 111 (13 %), 96 (35 %), 70 (100 %).



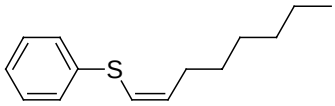
(*E*)-Oct-1-enylsulfanyl-benzene (5c).[6] To a solution of (*E*)-1-iodo-1-octene (**3a**) (119 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 7 h, a complete conversion to the Grignard reagent (**4a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Diphenyl disulfide (120 mg, 0.55 mmol, 1.1 equiv.) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with 2 N NaOH (10 ml) thoroughly and brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane) yielded the pure product **5c** (86 mg, 78 % yield) as a colorless oil. ^{1}H NMR analysis indicated 99% isomeric purity (*E*:*Z* = 99:1).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.16-7.36 (m, 5 H), 6.16 (dt, J_1 = 14.8 Hz, J_2 = 0.9 Hz, 1 H), 6.03 (dt, J_1 = 14.8 Hz, J_2 = 6.6 Hz, 1 H), 2.19 (m, 2 H), 1.24-1.50 (m, 8 H), 0.93 (t, J = 6.6 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 137.8, 136.7, 128.9, 128.4, 126.0, 120.6, 33.1, 31.6, 29.0, 28.8, 22.6, 14.1;

IR (film): 2926, 1738, 1584, 1439, 738;

MS (EI, 70 ev): 220 (M^+, 83 %), 149 (100 %), 134 (31 %), 116 (84 %).



(*Z*)-Oct-1-enylsulfanyl-benzene (5d).[7] To a solution of (*Z*)-1-iodo-1-octene (**3b**) (119 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 20 h, a complete conversion to the Grignard reagent (**4b**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Diphenyl disulfide (120 mg, 0.55 mmol, 1.1 equiv.) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with 2 N NaOH (10 ml) thoroughly and brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane) yielded the pure product **5d** (76 mg, 69 % yield) as a colorless oil. ^{1}H NMR analysis indicated 98 % isomeric purity (*E*:*Z* = 2:98).

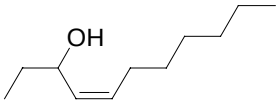
^{1}H NMR ($CDCl_3$, 300 MHz): 7.08-7.29 (m, 5 H), 6.11 (dt, J_1 = 8.8 Hz, J_2 = 1.3 Hz, 1 H), 5.75 (dt, J_1 = 8.8 Hz, J_2 = 7.5 Hz, 1 H), 2.13-2.22 (m, 2 H), 1.17-1.14 (m, 8 H), 0.82 (t, J = 6.6 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 136.6, 133.8, 128.9, 128.7, 126.1, 122.5, 31.7, 29.1, 29.0, 28.9, 22.6, 14.1;

IR (film): 2926, 1609, 1585, 1479, 736 cm^{-1};

MS (EI, 70 ev): 220 (M^+, 60 %), 149 (100 %), 134 (25 %), 116 (67 %), 110 (51 %), 91 (12 %), 69 (56 %);

HRMS (EI): calcd. for $C_{14}H_{20}S$, 220.1286; found: 220.1302.



(*Z*)-Undec-4-en-3-ol (5e). To a solution of (*Z*)-1-iodo-1-octene (**3b**) (119 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40 °C. After 20 h, a complete conversion to the Grignard reagent (**4b**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Propionaldehyde (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 3:1) yielded the pure product **5e** (59 mg, 70 % yield) as a colorless oil. ^{1}H NMR analysis indicated 98 % isomeric purity (*E*:*Z* = 2:98).

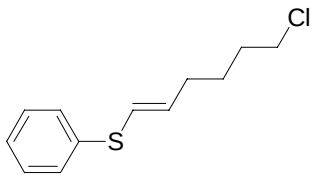
^{1}H NMR ($CDCl_3$, 300 MHz): 5.48 (ddt, J_1 = 11.1 Hz, J_2 = 7.5 Hz, J_3 = 0.9 Hz, 1 H), 5.33 (m, 1 H), 4.33 (m, 1 H), 1.97-2.13 (m, 2 H), 1.12-1.67 (m, 10 H), 0.87 (m, 6 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 132.7, 132.2, 69.1, 31.7, 30.4, 29.7, 28.9, 27.7, 22.6, 14.1, 9.7;

IR (film): 3339, 2959, 1658, 1464, 1007 cm^{-1};

MS (EI, 70 ev): 170 (M^+, 0.4 %), 152 (13 %), 141 (51 %), 123 (36 %), 85 (87 %), 81 (95 %), 57 (100 %);

HRMS (EI): calcd. for $C_{11}H_{22}O$, 170.1671; found: 170.1621.



(*E*)-(6-Chloro-hex-1-enylsulfanyl)-benzene (5f). To a solution of (*E*)- 6-chloro-1-iodo-hex-1-ene (**3c**) (122 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40 °C. After 7 h, a complete conversion to the Grignard reagent (**4c**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Diphenyl disulfide (120 mg, 0.55 mmol, 1.1 equiv.) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with 2 M NaOH (10 mL) thoroughly and brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 100:1) yielded the pure product **5f** (85 mg, 75 %) as a colorless oil. ^{1}H NMR analysis indicated 99% isomeric purity (*E*:*Z* = 99:1).

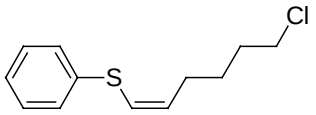
^{1}H NMR ($CDCl_3$, 300 MHz): 7.08-7.27 (m, 5 H), 6.09 (dt, J_1 = 15.0 Hz, J_2 = 1.3 Hz, 1 H), 5.86 (dt, J_1 = 15.0 Hz, J_2 = 6.6 Hz, 1 H), 3.47 (t, J = 6.6 Hz, 2 H), 2.08-2.16 (m, 2 H), 1.68-1.79 (m, 2 H), 1.44-1.56 (m, 2 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 136.2, 135.8, 128.9, 128.7, 126.2, 121.9, 44.7, 32.2, 31.9, 26.2;

IR (film): 2936, 1731, 1583, 1479,1439, 951, 739 cm^{-1};

MS (EI, 70 ev): 228 (M^+, ^{37}Cl, 10 %), 226 (M^+, ^{35}Cl, 39 %), 149 (100 %), 134 (19 %), 116 (58 %), 59 (88 %);

HRMS (EI): calcd. for $C_{12}H_{15}ClS$, 226.0583; found: 226.0582.



(*Z*)-(6-Chloro-hex-1-enylsulfanyl)-benzene (5g). To a solution of (*Z*)- 6-chloro-1-iodo-hex-1-ene (**3d**) (122 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 20 h, a complete conversion to the Grignard reagent (**4d**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Diphenyl disulfide (120 mg, 0.55 mmol, 1.1 equiv.) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with 2 M NaOH (10 mL) thoroughly and brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 100:1) yielded the pure product **5g** (92 mg, 81 %) as a colorless oil. ^{1}H NMR analysis indicated 97 % isomeric purity (*E*:*Z* = 3:97).

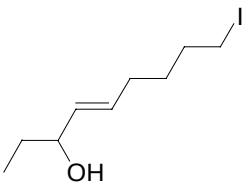
^{1}H NMR ($CDCl_3$, 300 MHz): 7.10-7.28 (m, 5 H), 6.16 (dt, J_1 = 9.0 Hz, J_2 = 1.3 Hz, 1 H), 5.72 (dt, J_1 = 9.3 Hz, J_2 = 7.5 Hz, 1 H), 3.49 (t, J = 6.6 Hz, 2 H), 2.17-2.26 (m, 2 H), 1.70-1.81 (m, 2 H), 1.48-1.58 (m, 2 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 136.2, 132.3, 129.0, 128.8, 126.3, 123.7, 44.8, 32.0, 28.2, 26.2;

IR (film): 2934, 1731, 1584, 1479, 1439 cm^{-1};

MS (EI, 70 ev): 228 (M^+, ^{37}Cl, 15 %), 226 (M^+, ^{35}Cl, 44 %), 149 (100 %), 116 (45 %), 110 (63 %), 91 (37 %);

HRMS (EI): calcd. for $C_{12}H_{15}ClS$, 226.0583; found: 226.0585.



(*E*)-9-Iodo-non-4-en-3-ol (5h). To a solution of (*E*)- 1,6-diiodo-hex-1-ene **(3e**) (168 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 7 h, a complete conversion to the Grignard reagent (**4e**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Propionaldehyde (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 4:1) yielded the pure product **5h** (112 mg, 84 %) as a colorless oil. ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

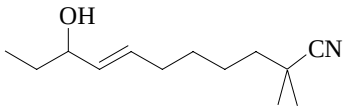
^{1}H NMR ($CDCl_3$, 300 MHz): 5.59 (dt, J_1 = 15.0 Hz, J_2 = 6.6 Hz, 1 H), 5.44 (ddt, J_1 = 15.0 Hz, J_2 = 6.6 Hz, J_3 = 1.3 Hz, 1 H), 3.95 (m, 1 H), 3.16 (t, *J* = 7.2 Hz, 2 H), 2.04 (q, *J* = 7.2 Hz, 2 H), 1.74-1.86 (m, 2 H), 1.40-1.58 (m, 4 H), 0.87 (t, *J* = 7.5 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 133.5, 131.1, 74.3, 32.9, 31.0, 30.1, 29.9, 9.7, 6.7;

IR (film): 3368, 2930, 1669, 1455, 966 cm^{-1};

MS (EI, 70 ev): 267 (M^+-H, 0.4 %), 250 (30 %), 239 (50 %), 155 (14 %), 81 (54 %), 57 (100 %);

HRMS (EI): calcd. for $C_9H_{16}IO$: 267.0246 (M^+-H); found: 267.0242 (M^+-H).



(*E*)-9-Hydroxy-2,2-dimethyl-undec-7-enenitrile (5i). To a solution of (*E*)-8-iodo-2,2-dimethyl-oct-7-enenitrile (**3f**) (139 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 7 h, a complete conversion to the Grignard reagent (**4f**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Propionaldehyde (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 2:1) yielded the pure product **5i** (80 mg, 77 %) as a colorless oil. ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

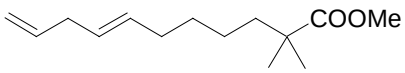
^{1}H NMR ($CDCl_3$, 300 MHz): 5.59 (dt, J_1 = 15.6 Hz, J_2 = 6.6 Hz, 1 H), 5.43 (ddt, J_1 = 15.6 Hz, J_2 = 6.6 Hz, J_3 = 1.3 Hz, 1H), 3.92-3.96 (m, 1 H), 2.04 (q, *J* = 6.6 Hz, 2 H), 1.35-1.66 (m, 8 H), 1.30 (s, 6 H), 0.87 (t, J = 7.5 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 133.3, 131.4, 125.1, 74.3, 40.8, 32.3, 31.8, 30.1, 28.9, 26.63, 26.58, 24.6, 9.7;

IR (film): 3436, 2974, 2235, 1730, 1669, 1463, 968 cm^{-1};

MS (EI, 70 ev): 208 (M^+-H, 0.1 %), 192 (2 %), 180 (100 %), 162 (29 %), 135 (32 %), 85 (96 %);

HRMS (EI): calcd. for $C_{13}H_{22}NO$: 208.1701 (M^+-H); found: 208.1681 (M^+-H).



(*E*)-2,2-Dimethyl-undeca-7,10-dienoic acid methyl ester (5j). To a solution of (*E*)-8-iodo-2,2-dimethyl-oct-7-enoic acid methyl ester (**3g**). (155 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 12 h, a complete conversion to the Grignard reagent (**4g**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Allyl bromide (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 25:1) yielded the pure product **5j** (80 mg, 71 %) as a colorless oil. GC and ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

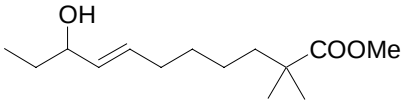
^{1}H NMR ($CDCl_3$, 300 MHz): 5.73-5.86 (m, 1 H), 5.34-5.43 (m, 2 H), 4.90-5.04 (m, 2 H), 3.63 (s, 3 H), 2.64-2.79 (m, 2 H), 1.90-2.01 (m, 2 H), 1.16-1.51 (m, 6 H), 1.13 (s, 6 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 178.5, 137.4, 131.4, 127.7, 114.7, 51.6, 42.3, 40.6, 36.7, 32.3, 29.8, 25.1, 24.4;

IR (film): 3079, 2935, 1734, 1639, 1154, 969, 912 cm^{-1}

MS (EI, 70 ev): 224 (M^+, 0.1 %), 192 (10 %), 123 (11 %), 102 (100 %), 81 (48 %);

HRMS (EI): calcd. for $C_{14}H_{24}O_2$: 224.1776; found: 224.1775.



(*E*)-9-Hydroxy-2,2-dimethyl-undec-7-enoic acid methyl ester (5k). To a solution of (*E*)-8-iodo-2,2-dimethyl-oct-7-enoic acid methyl ester (**3g**). (155 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 12 h,

a complete conversion to the Grignard reagent (**4g**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Propionaldehyde (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 2:1) yielded the pure product **5k** (99 mg, 82 %) as a colorless oil. ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

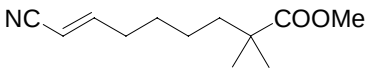
^{1}H NMR ($CDCl_3$, 300 MHz): 5.58 (dt, J_1 = 15.6 Hz, J_2 = 6.6 Hz, 1 H), 5.40 (ddt, J_1 = 15.6 Hz, J_2= 6.6 Hz, J_3 = 1.3 Hz, 1 H), 3.93 (q, J = 6.6 Hz, 1 H), 3.62 (s, 3 H), 1.99 (q, J = 7.2 Hz, 2 H), 1.12-1.59 (m, 6 H), 1.12 (s, 8 H), 0.86 (t, J = 7.2 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 178.5, 132.9, 131.9, 74.4, 51.6, 42.2, 40.5, 31.9, 30.1, 29.5, 25.2, 25.1, 24.3, 9.7;

IR (film): 3498, 2970, 1733, 1194, 1148 cm^{-1}

MS (EI, 70 ev): 224 (M^+-H_2O, 1 %), 213 (15 %), 192 (64 %), 153 (76 %), 102 (100 %);

HRMS (EI): calcd. for $C_{14}H_{24}O_2$ (M^+-H_2O): 224.1776; found: 224.1728 (M^+-H_2O).



8-Cyano-2,2-dimethyl-oct-7-enoic acid methyl ester (5l). To a solution of (*E*)-8-iodo-2,2-dimethyl-oct-7-enoic acid methyl ester (**3g**). (155 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 12 h, a complete conversion to the Grignard reagent (**4g**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. TsCN (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 4:1) yielded the pure product **5l** (78 mg, 75 %) as a colorless oil. GC and ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

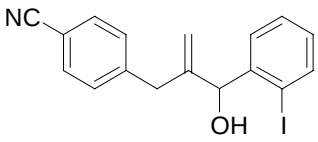
^{1}H NMR ($CDCl_3$, 300 MHz): 6.67 (dt, J_1 = 16.3 Hz, J_2 = 6.9 Hz, 1 H), 5.29 (dt, J_1 = 16.3 Hz, J_2 = 1.8 Hz, 1 H), 3.63 (s, 3 H), 2.15-2.22 (m, 2 H), 1.16-1.51 (m, 6 H), 1.13 (s, 6 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 178.2, 155.7, 117.4, 99.8, 51.7, 42.1, 40.2, 33.0, 27.9, 25.1, 24.3;

IR (film): 2975, 2223, 1729, 1633, 1474, 971 cm^{-1};

MS (EI, 70 ev): 210 (M^++1, 1 %), 194 (1 %), 150 (52 %), 134 (23 %), 102 (100 %);

HRMS (EI): calcd. for $C_{12}H_{20}NO_2$ (M^+ + H): 210.1494; found: 210.1464 (M^+ + H).



4-{2-[Hydroxy-(2-iodo-phenyl)-methyl]-allyl}-benzonitrile (5m). To a solution of 4-(2-iodo-allyl)-benzonitrile (**3h**) (135 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40 °C. After 5 h, a complete conversion to the Grignard reagent (**4h**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. 2-Iodobenzaldehyde (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:1) yielded the pure product **5m** (170 mg, 91 %) as a colorless oil.

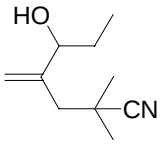
^{1}H NMR ($CDCl_3$, 300 MHz): 7.72 (d, *J* = 8.0 Hz, 1 H), 7.45 (d, *J* = 8.1 Hz, 2 H), 7.38 (d, *J* = 7.8 Hz, 1 H), 7.27 (t, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2 H), 6.91 (t, *J* = 7.5 Hz, 1 H), 5.22 (s, 1 H), 5.28 (s, 1 H), 4.88 (s, 1 H), 3.40 (d, *J* = 15.6 Hz, 1 H), 3.24 (d, *J* = 15.6 Hz, 1 H), 2.16 (bs, 1 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 147.7, 144.6, 143.3, 139.5, 132.0, 130.0, 129.7, 128.6, 128.2, 119.0, 115.1, 110.0, 99.4, 79.1, 39.6;

IR (film): 3430, 2228, 1647, 1607, 1434, 1009 cm^{-1};

MS (EI, 70 ev): 375 (M^+, 10 %), 357 (10 %), 259 (67 %), 231 (34 %), 132 (100 %);

HRMS (EI): calcd. for $C_{17}H_{14}INO$: 375.0120; found: 375.0144.



4-(1-Hydroxy-propyl)-2,2-dimethyl-pent-4-enenitrile (5n). To a solution of 4-iodo-2,2-dimethyl-pent-4-enenitrile (**3i**) (118 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40°C. After 7 h, a complete conversion to the Grignard reagent (**4i**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Propionaldehyde (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10

mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 2:1) yielded the pure product **5n** (59 mg, 70 %) as a colorless oil.

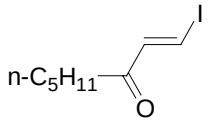
^{1}H NMR ($CDCl_3$, 300 MHz): 5.29 (t, *J* = 1.2 Hz, 1 H), 5.15 (s, 1 H), 4.10 (m, 1 H), 2.34 (d, *J* = 14.6 Hz, 1 H), 2.18 (d, *J* = 14.6 Hz, 1 H), 1.83 (bs, 1 H), 1.43-1.70 (m, 2 H), 1.37 (s, 3 H), 1.36 (s, 3 H), 0.91 (t, *J* = 7.5 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 146.5, 125.3, 114.6, 75.7, 42.5, 31.8, 28.6, 27.4, 26.9, 9.8;

IR (film): 3436, 2975, 2235, 1646, 1456, 982, 913 cm^{-1};

MS (EI, 70 ev): 167 (M^+, 1 %), 152 (12 %), 138 (62 %), 111 (100 %), 93 (65 %);

HRMS (EI): calcd. for $C_{10}H_{17}NO$: 167.1310; found: 167.1324.



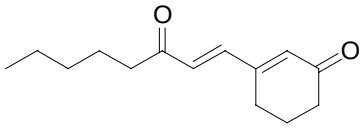
1-Iodo-oct-1-en-3-one (6). A mixture of oct-1-yn-3-one (496 mg, 4.0 mmol), LiI (643 mg, 4.8 mmol) and HOAc (4 mL) was stirred at room temperature for 3 h.[8] Water (10 mL) was added and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with saturated aqueous $NaHCO_3$, brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 15:1) yielded the product **6** (927 mg, 92 %) as a white solid; m.p.: 37.7-38.4 ^{o}C (lit.[9] 36-37 ^{o}C). GC and ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.78 (d, *J* = 15.0 Hz, 1 H), 7.13 (d, *J* = 15.0 Hz, 1 H), 2.47 (t, *J* = 7.3 Hz, 2 H), 1.50-1.65 (m, 2 H), 1.18-1.35 (m, 4 H), 0.86 (t, *J* = 6.9 Hz, 3 H)

^{13}C NMR ($CDCl_3$, 75 MHz): 197.5, 144.6, 98.6, 40.4, 31.3, 23.4, 22.4, 13.9;

IR (KBr): 2955, 1695, 1675, 1572, 1466, 955 cm^{-1};

MS (EI, 70 ev): 253 (M^+ + 1, 0.4 %), 196 (95 %), 181 (100 %), 153 (19 %), 125 (46 %).



3-(3-Oxo-oct-1-enyl)-cyclohex-2-enone (9a). To a stirred solution of 1-iodo-oct-1-en-3-one (**6**) (126 mg, 0.5 mmol) and CsF (11 mg, 0.07 mmol) in dry CH_3CN (0.5 mL) was added TMSCN (75 mg, 0.75 mmol) dropwise.[10] The resulting solution was stirred continuously and the reaction conversion was monitored by TLC. Water (5 mL) was added after 1 h and the

aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. GC and ^{1}H NMR analysis indicated a high purity of the product.

To a solution of the corresponding silylated cyanhydrine derivative **7** in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40 °C. After 2 h, a complete conversion to the Grignard reagent (**8**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. THF (1.0 mL) and CuCN·2LiCl (0.55 mmol, 0.55 mL, 1.0 M in THF) was added at this temperature and stirred for 15 min. 3-Iodo-cyclohex-2-enone (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was stirred continuously 4 h at –30 °C. The reaction minxture was warmed up to 25 °C, TBAF (0.5 mL, 0.5 mmol, 1.0 M in THF) and HCl (1.0 mL, 2 M in H_2O) were added. The mixture was stirred for another 2 h before the addition of aq. NH_3 (2 ml). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 2:1) yielded the pure product **9a** (85 mg, 77 %) as a pale yellow solid; m.p.: 52.9-53.4 °C. GC and ^{1}H NMR analysis indicated 99% isomeric purity (*E*:*Z* = 99:1).

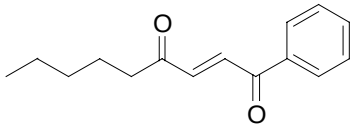
^{1}H NMR ($CDCl_3$, 300 MHz): 7.17 (d, *J* = 16.2 Hz, 1 H), 6.47 (d, *J* = 16.2 Hz, 1 H), 6.16 (s, 1 H), 2.59 (t, *J* = 7.2 Hz, 2 H), 2.41-2.50 (m, 4 H), 2.01-2.10 (m, 2 H), 1.56-1.67 (m, 2 H), 1.22-1.36 (m, 4 H), 0.87 (t, *J* = 6.9 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 200.0, 199.5, 154.2, 141.7, 132.9, 131.1, 41.0, 37.6, 31.3, 24.8, 23.7, 22.4, 22.0, 13.9;

IR (KBr): 2954, 1691, 1661, 1605, 1581, 1467 cm^{-1};

MS (EI, 70 ev): 220 (M^+, 11 %), 191 (9 %), 164 (95 %), 149 (100 %), 136 (43 %), 121 (51 %);

HRMS (EI): calcd. for $C_{14}H_{20}O_2$: 220.1463; found: 260.1451.



1-Phenyl-non-2-ene-1,4-dione (9b). To a stirred solution of 1-iodo-oct-1-en-3-one (**6**) (126 mg, 0.5 mmol) and CsF (11 mg, 0.07 mmol) in dry CH_3CN (0.5 mL) was added TMSCN (75 mg, 0.75 mmol) dropwise.[10] The resulting solution was stirred continuously and the reaction conversion was monitored by TLC. Water (5 mL) was added after 1 h and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine

(10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. GC and ^{1}H NMR analysis indicated it was very pure.

To a solution of the corresponding silylated cyanhydrine derivative **7** in THF (0.2 ml) was slowly added *i*-PrMgCl·LiCl (0.28 mL, 0.55 mmol, 2.00 M in THF) at –40 °C. After 2 h, a complete conversion to the Grignard reagent (**8**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. THF (1.0 mL) and CuCN·2LiCl (0.55 mmol, 0.55 mL,1.0 M in THF) was added at this temperature and stirred for 15 min. Benzoyl chloride (0.7 mmol in 0.5 mL of THF) was added and the reaction mixture was stirred at –40 ^{o}C for 1 h, then warmed up to rt and stirred for 1 h. TBAF (0.5 mL, 0.5 mmol, 1.0 M in THF) and HCl (1.0 mL, 2 M in H_2O) were added and the mixture was stirred for another 2 h before the addition of aq. NH_3 (2 mL). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 3:1) yielded the pure product **9b** (85 mg, 74 %) as a pale yellow oil. GC and ^{1}H NMR analysis indicated 99 % isomeric purity (*E*:*Z* = 99:1).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.90-8.00 (m, 2 H), 7.71 (d, *J* = 15.9 Hz, 1 H), 7.55-7.63 (m, 1 H), 7.44-7.52 (m, 2 H), 7.10 (d, *J* = 15.9 Hz, 1 H), 2.66 (t, *J* = 7.5 Hz, 2 H), 1.61-1.71 (m, 2 H), 1.22-1.39 (m, 4 H), 0.88 (t, *J* = 6.9 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 75 MHz): 200.2, 190.3, 137.8, 136.8, 133.8, 133.1, 128.83, 127.78, 42.4, 31.3, 23.4, 22.4, 13.8;

IR (film): 2957, 1701, 1666, 1597, 1580, 1287 cm^{-1};

MS (EI, 70 ev): 230 (M^+, 9 %), 201 (14 %), 174 (20 %), 159 (51 %), 131 (100 %), 105 (89 %);

HRMS (EI): calcd. for $C_{15}H_{18}O_2$: 230.1307; found: 230.1339.

References:

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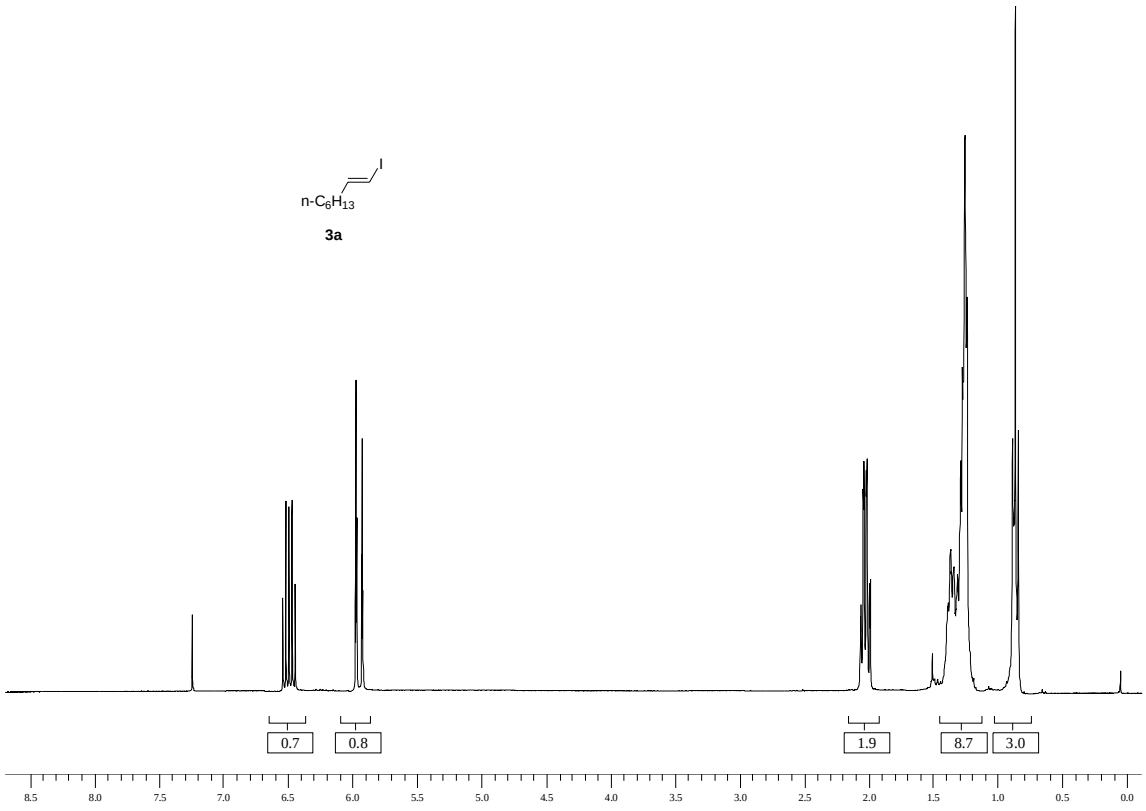
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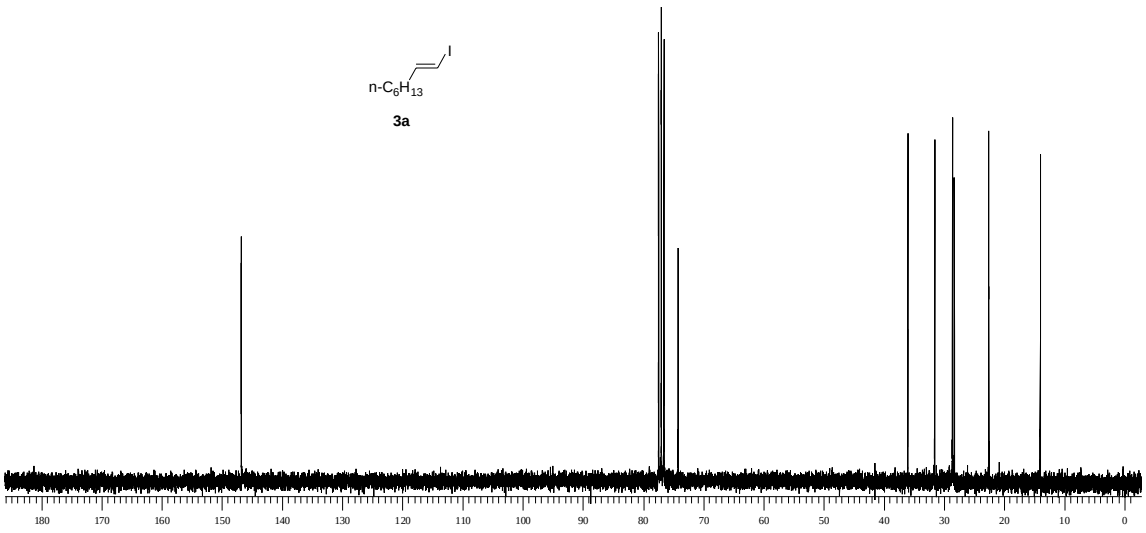
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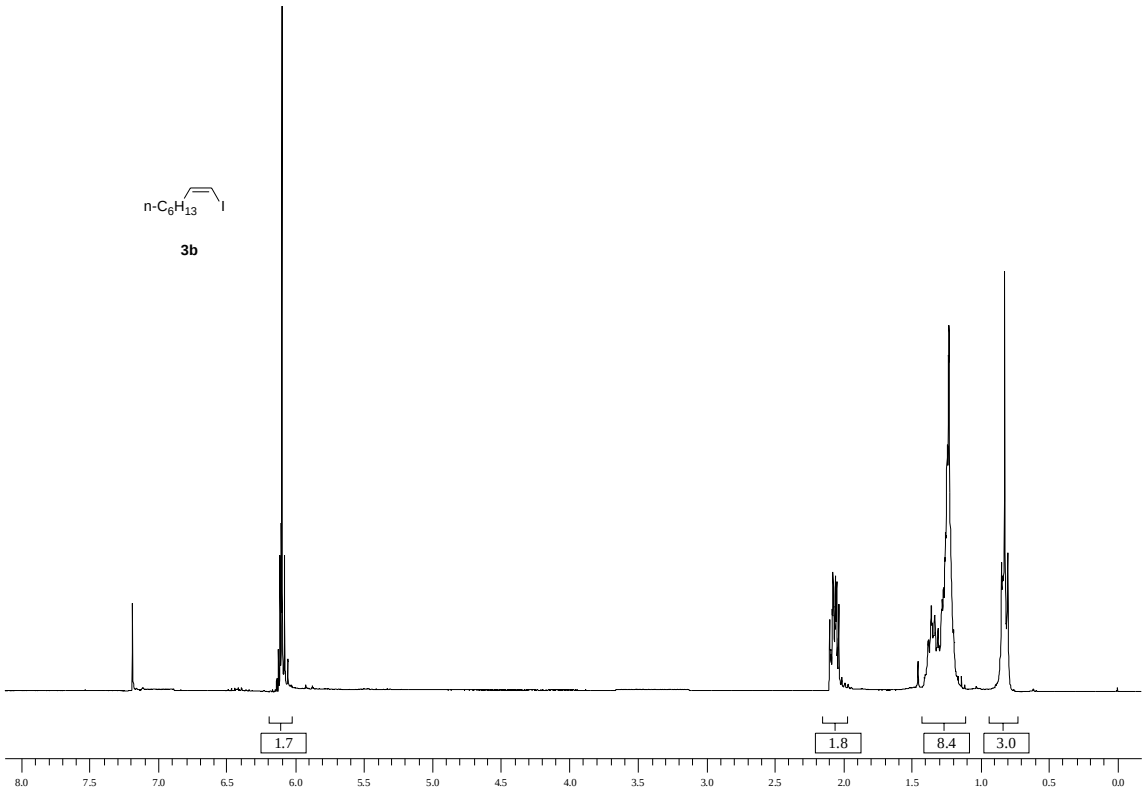
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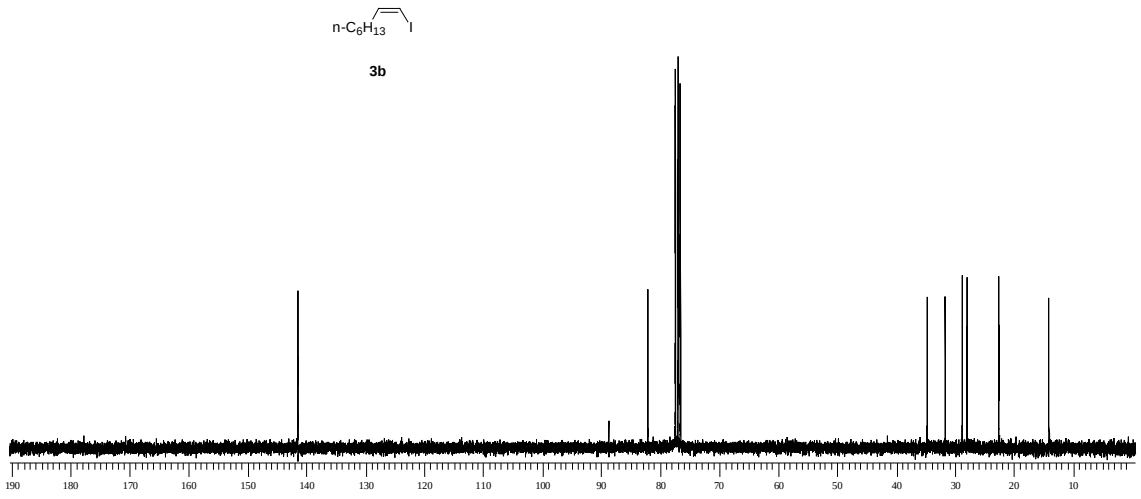
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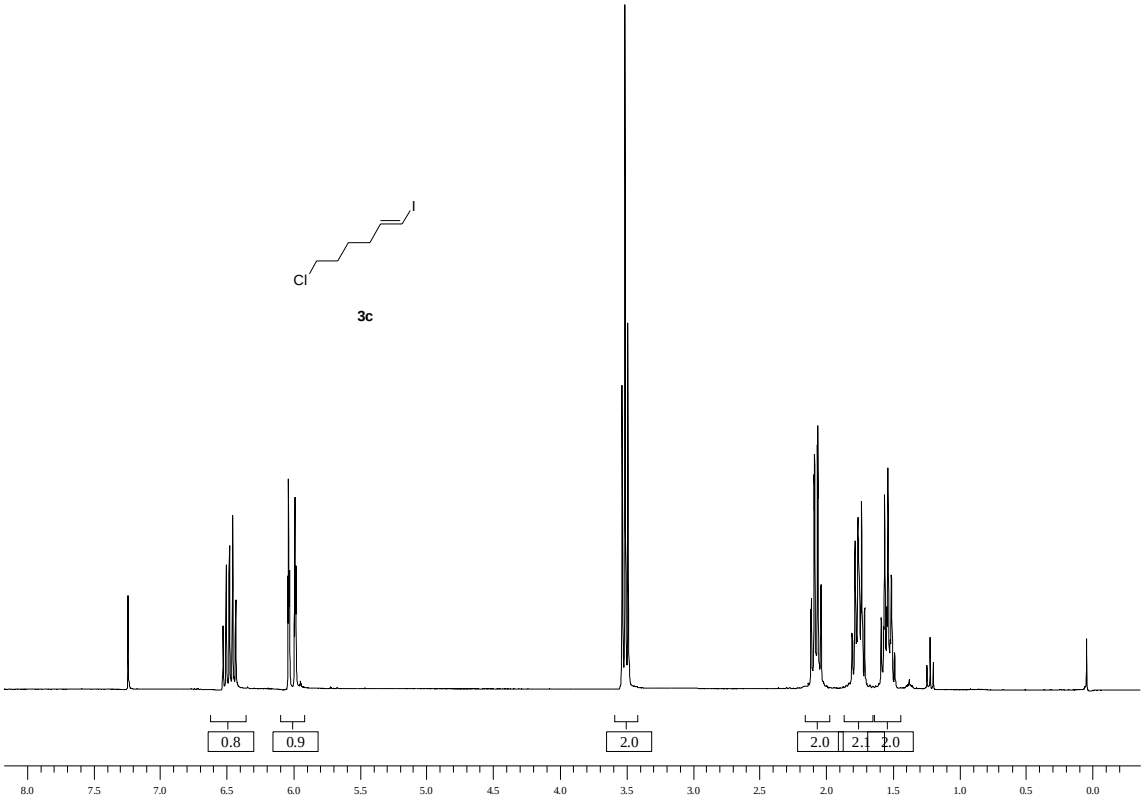
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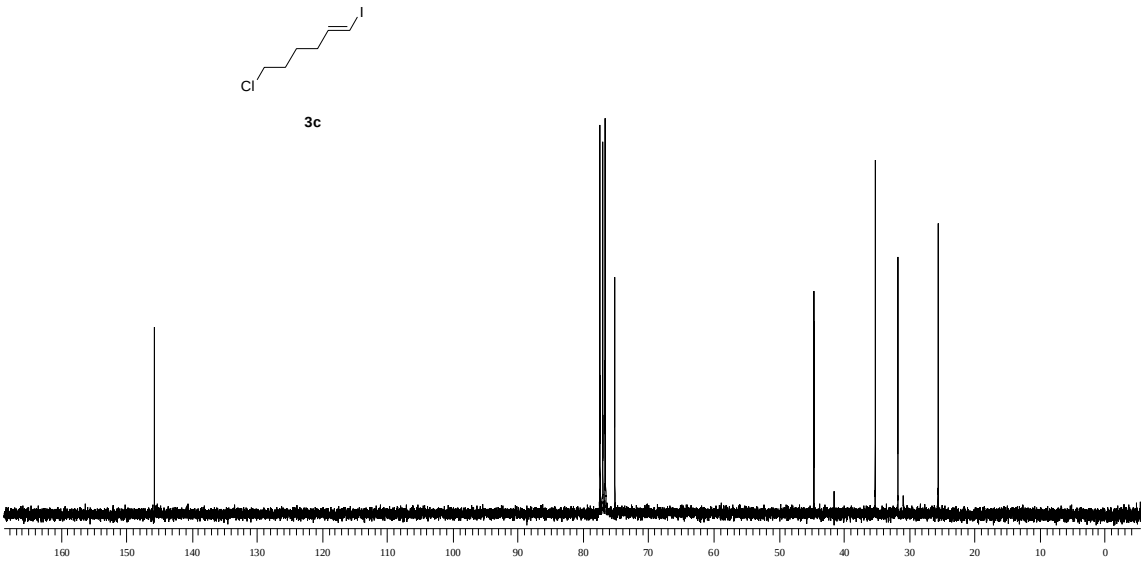
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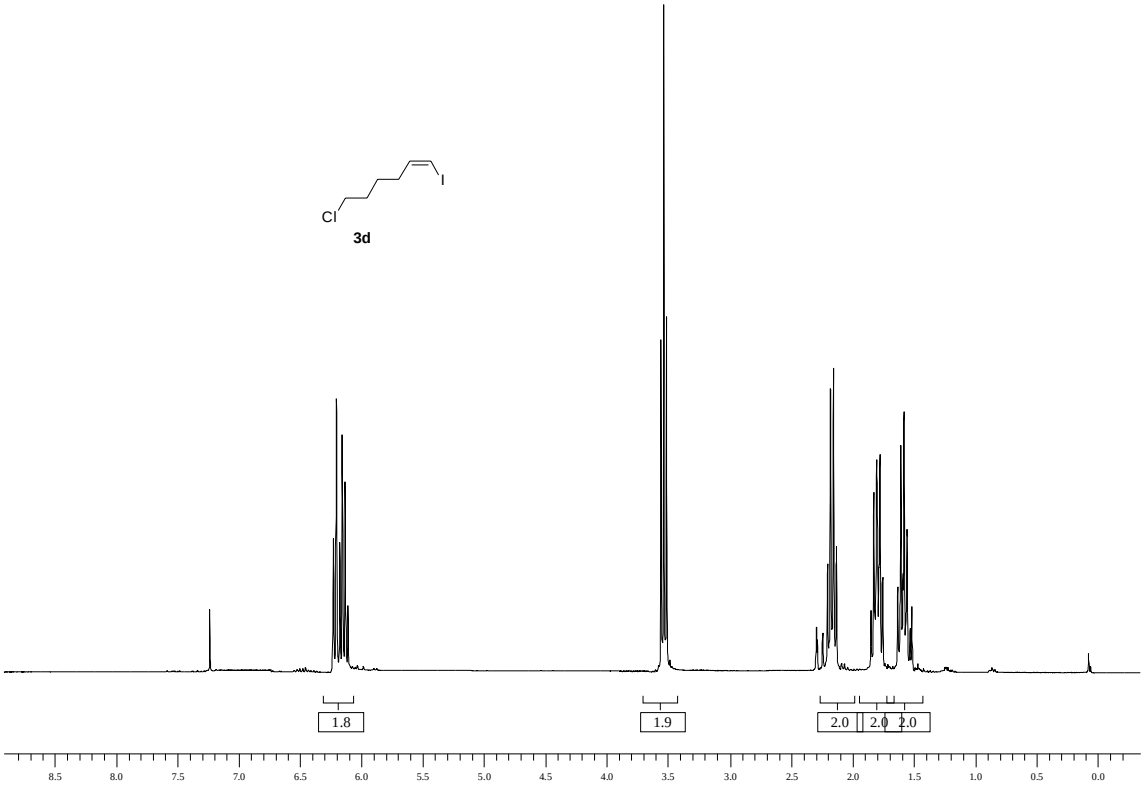
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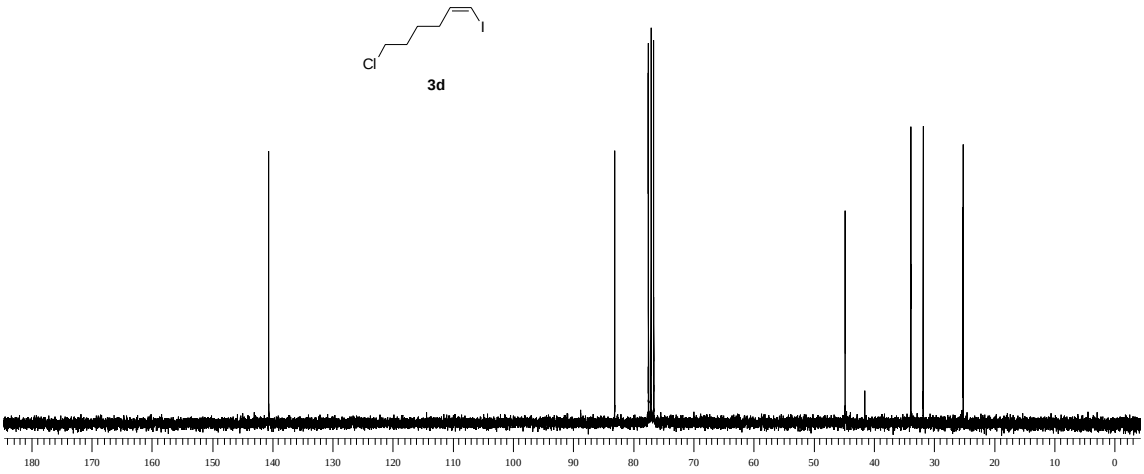
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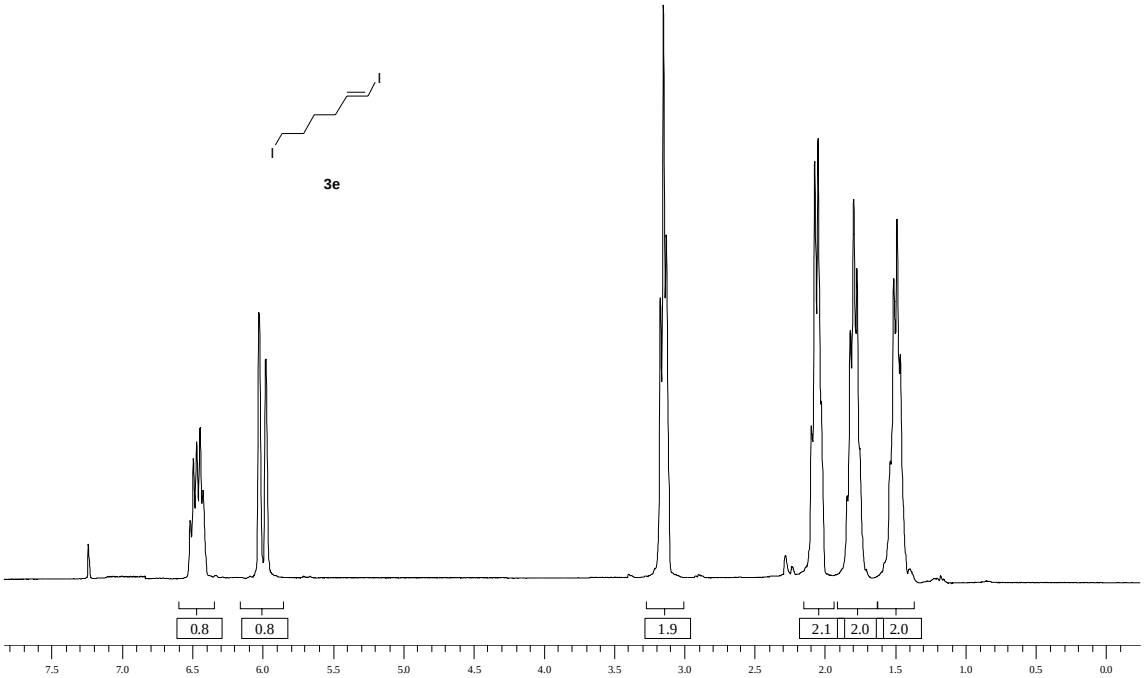
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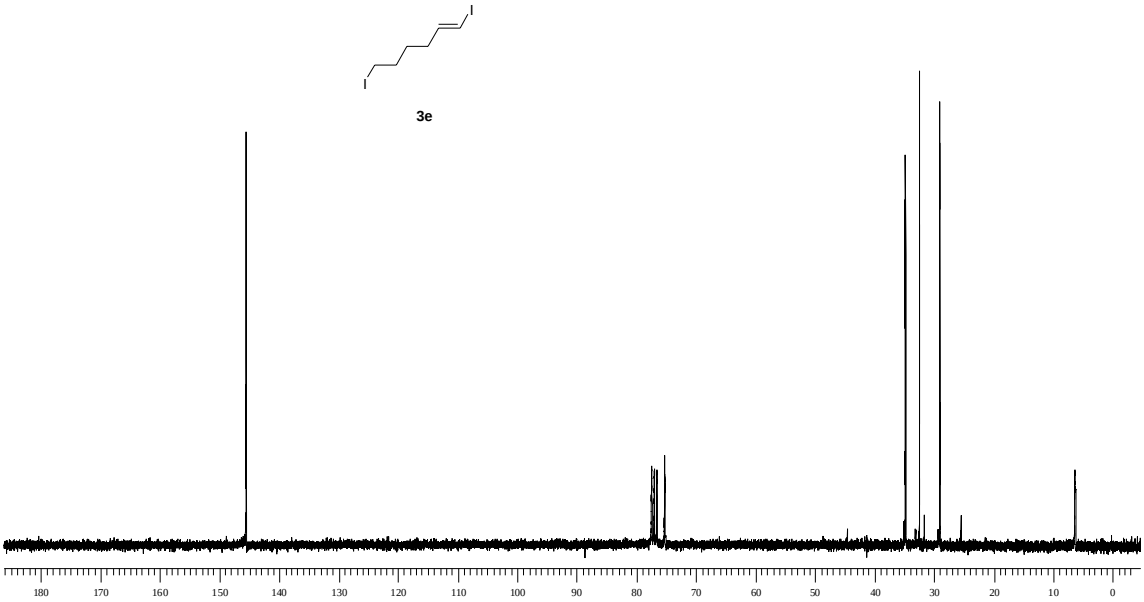
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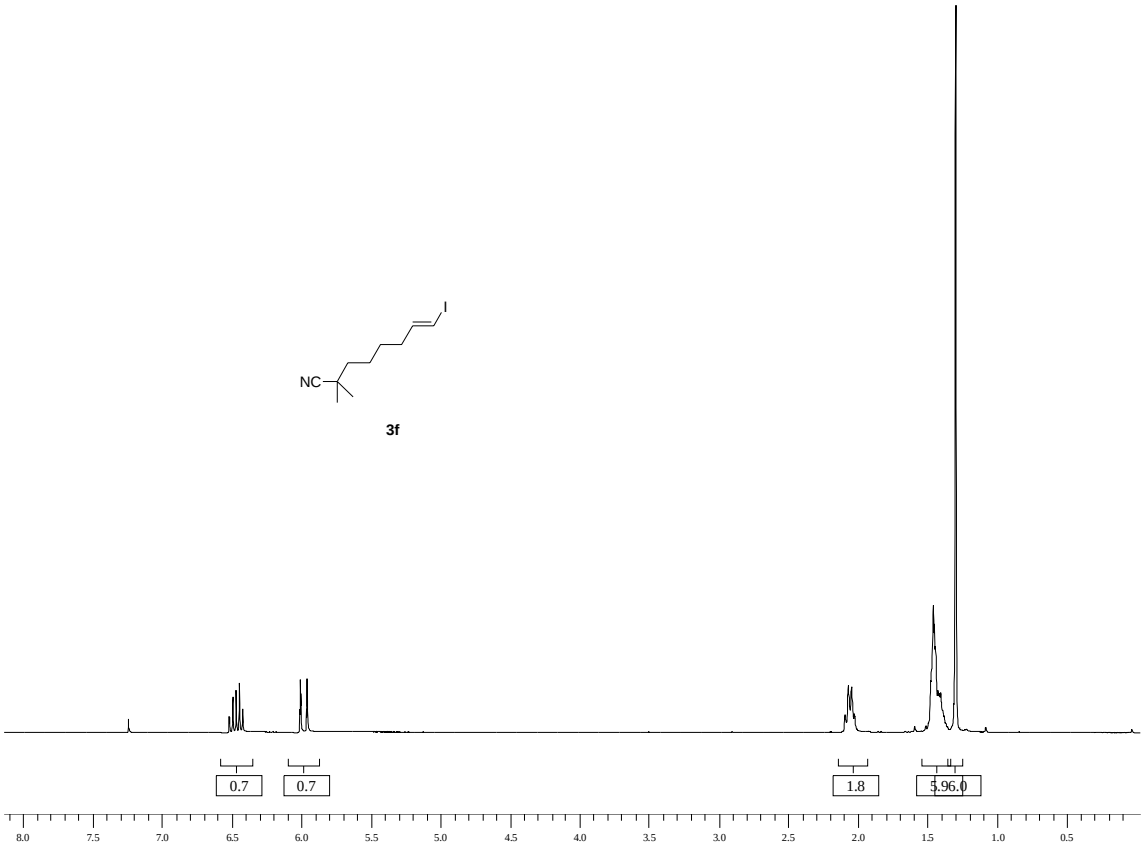
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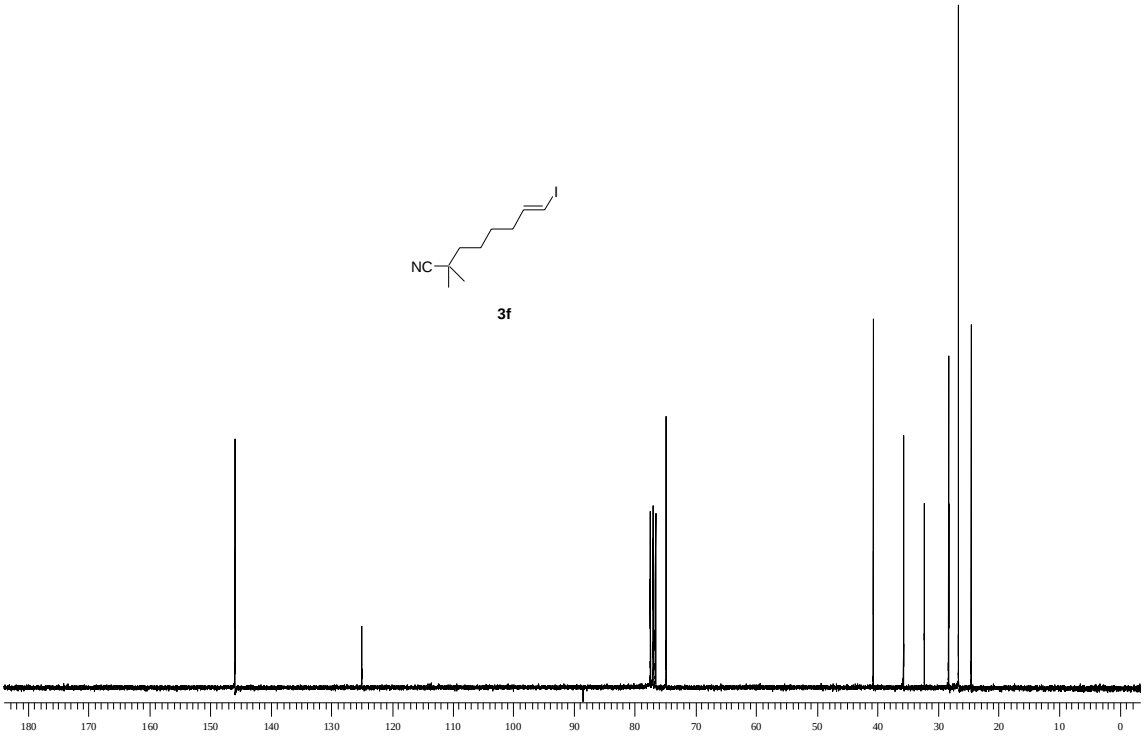
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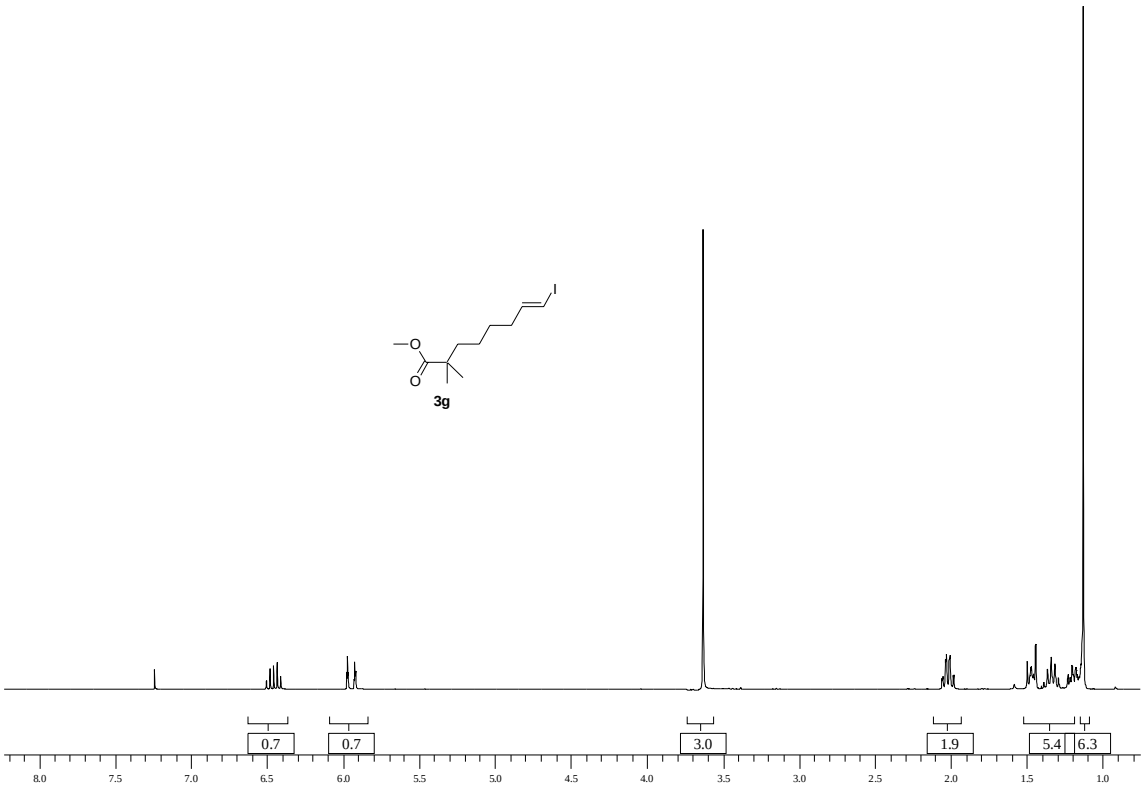
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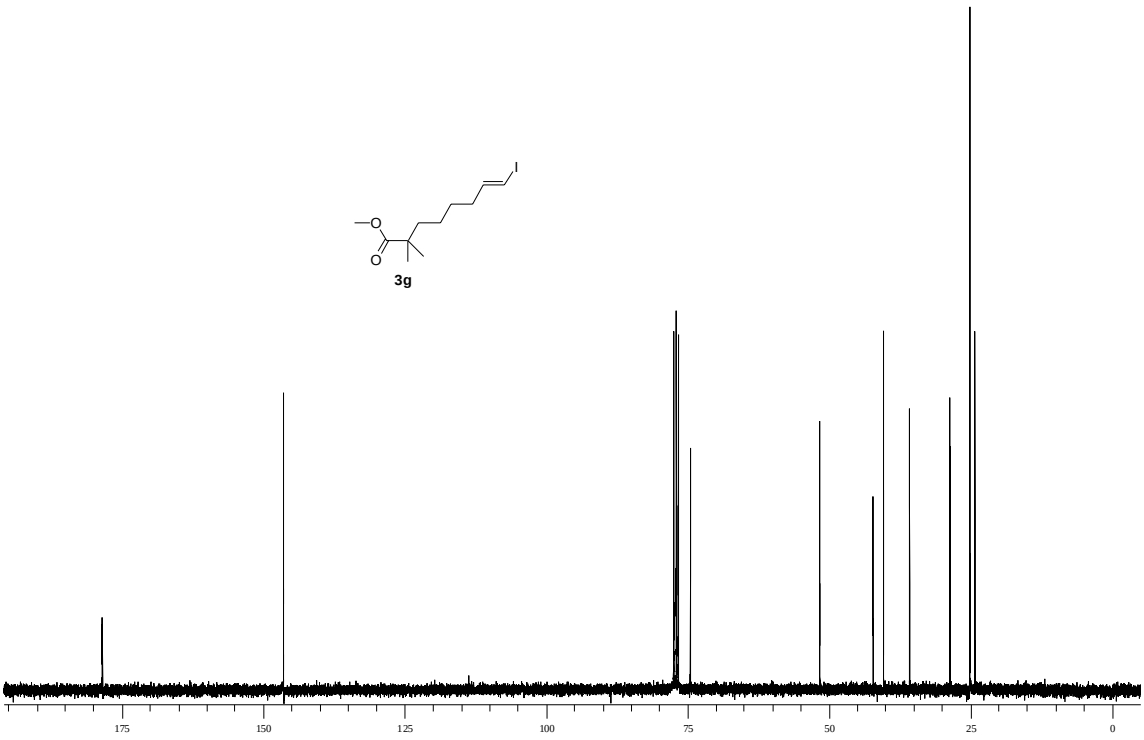
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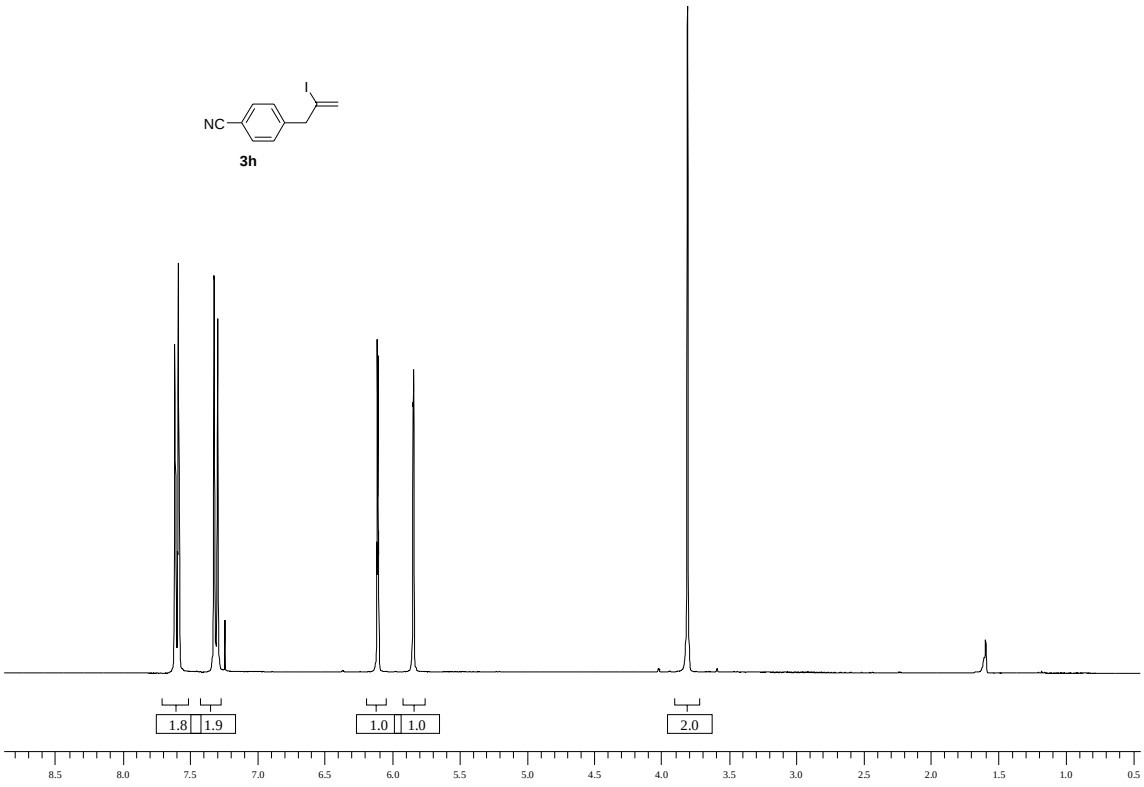
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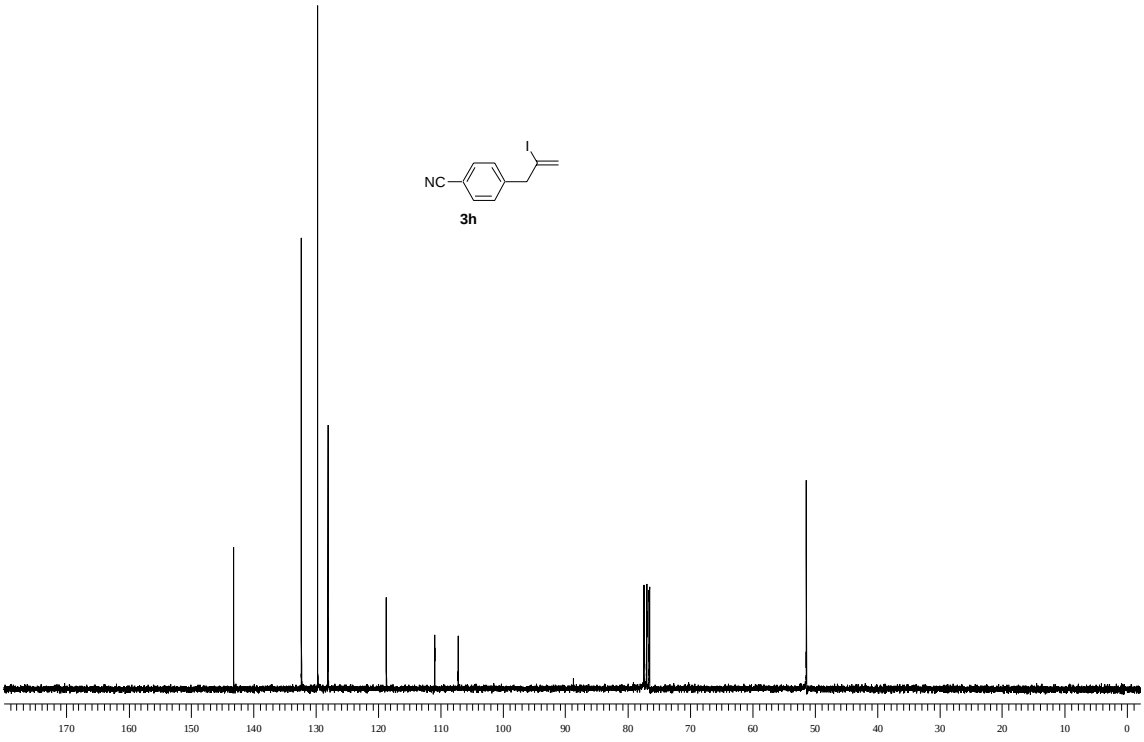
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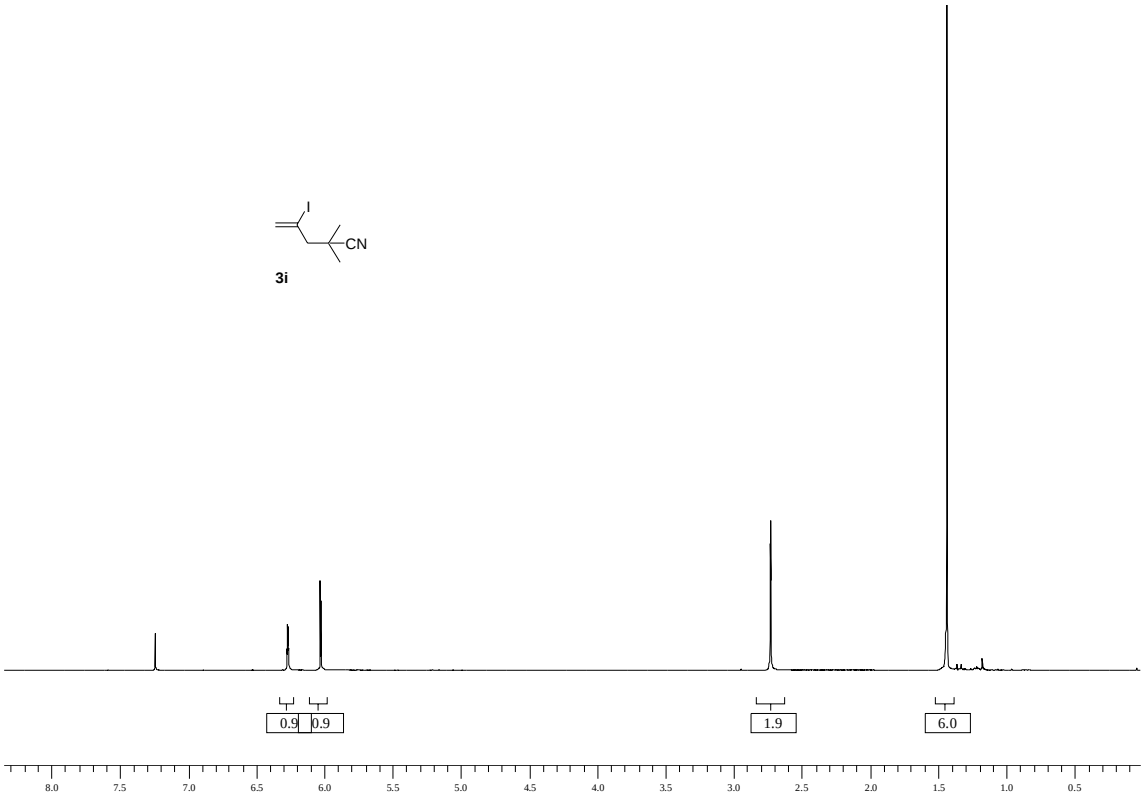
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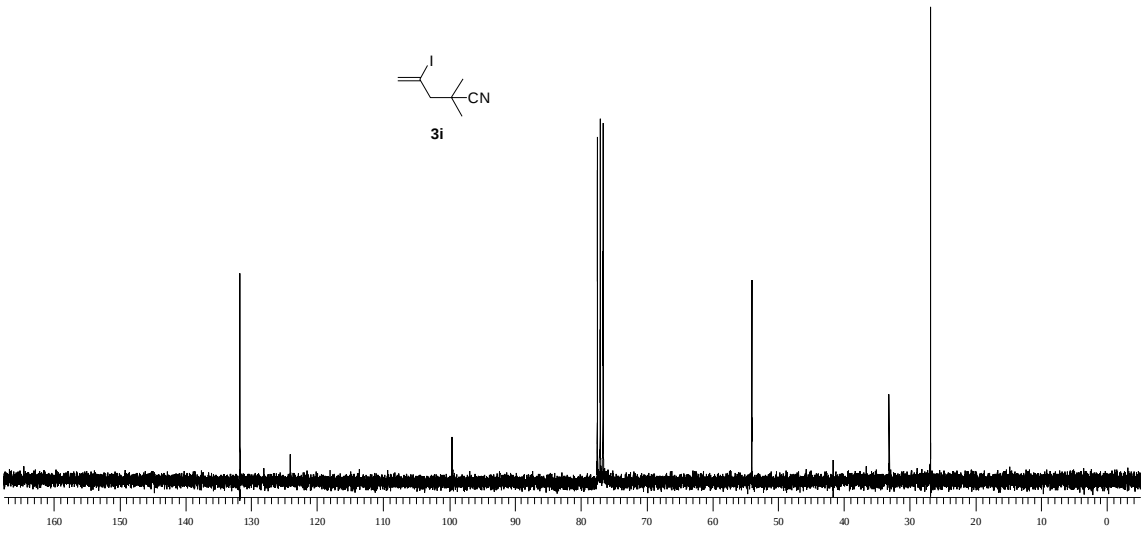
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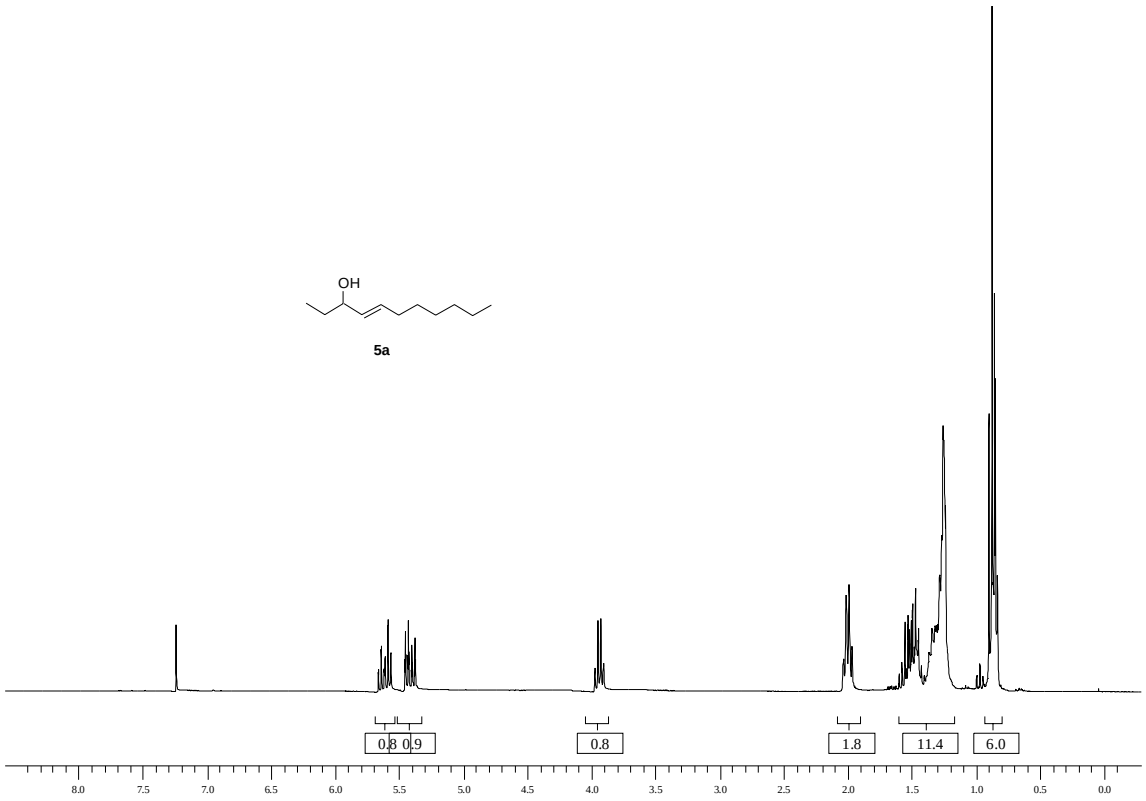
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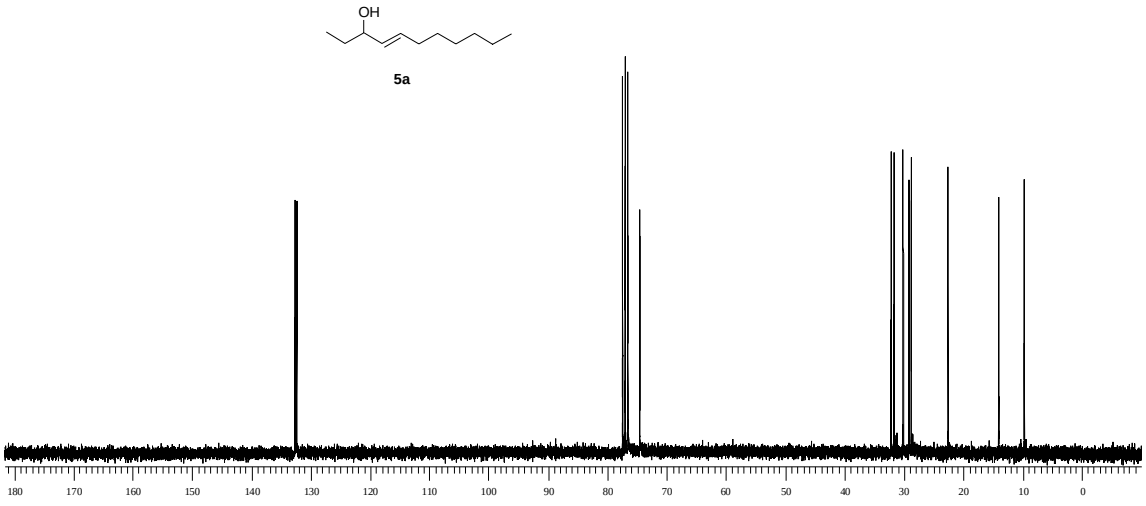
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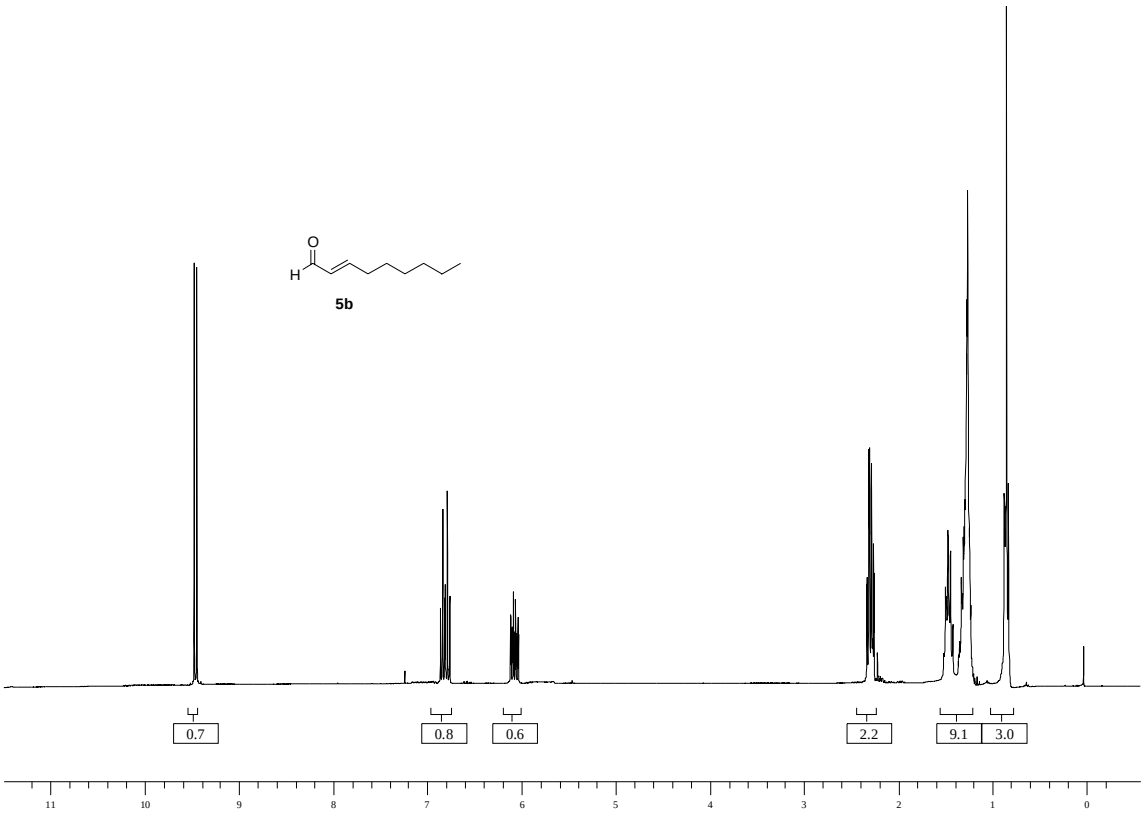
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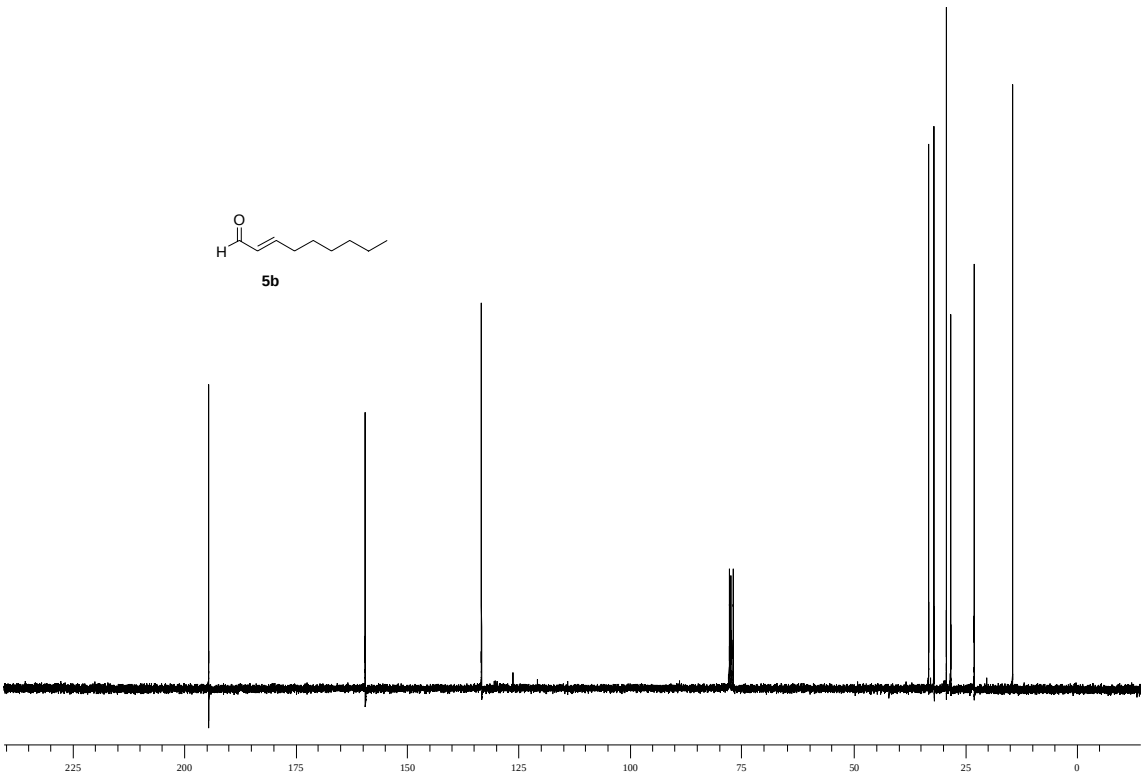
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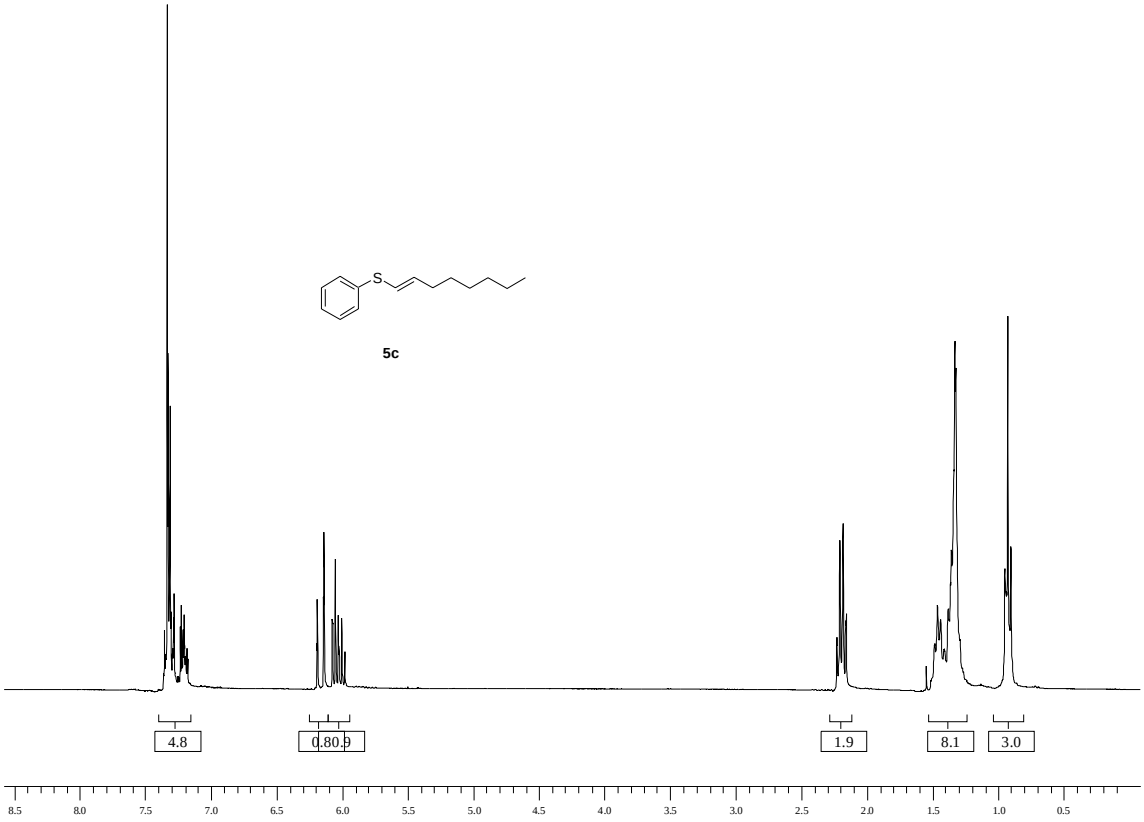
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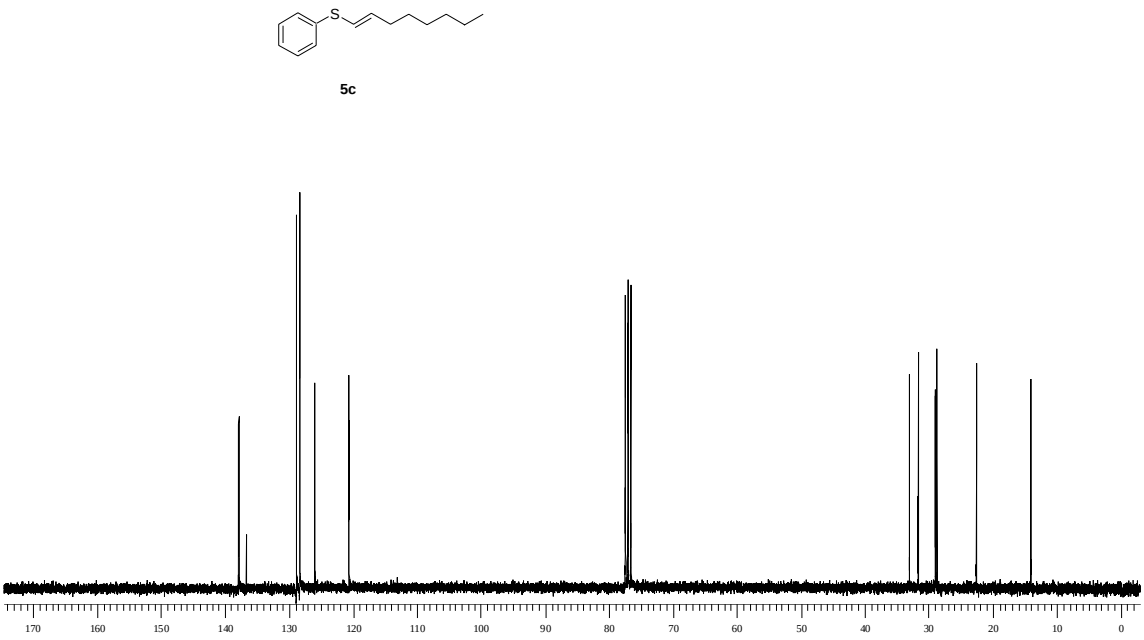
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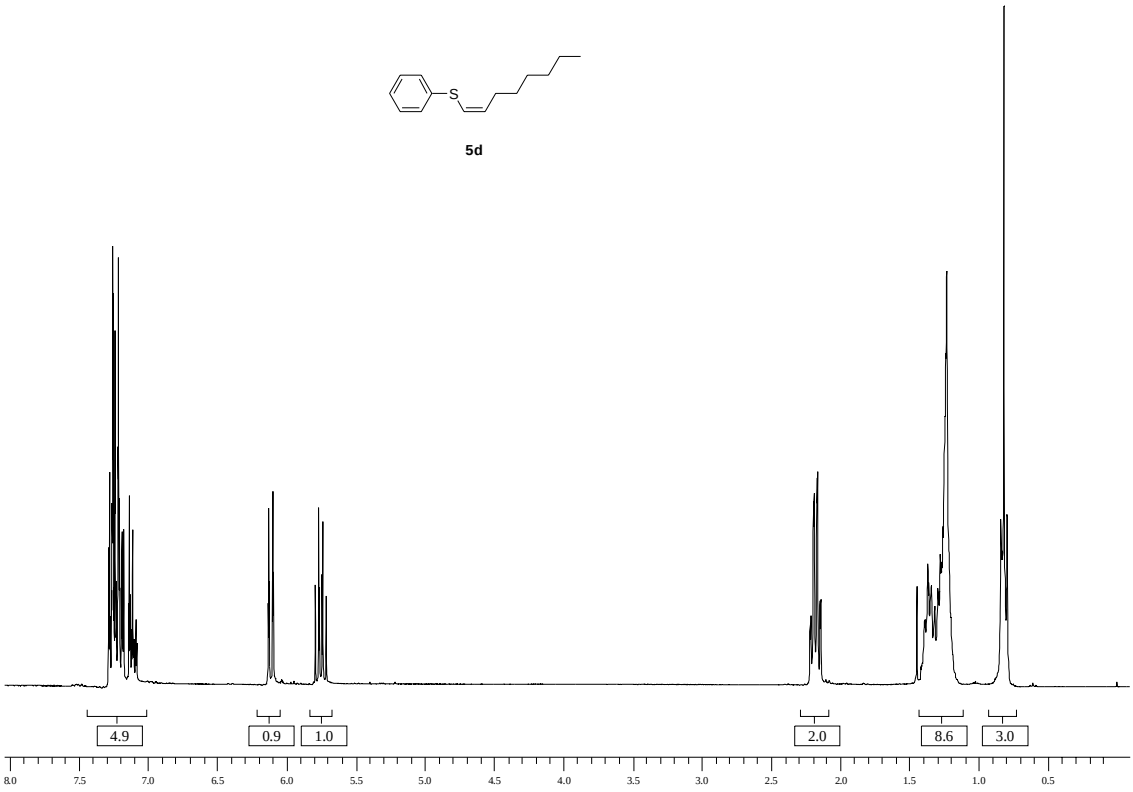
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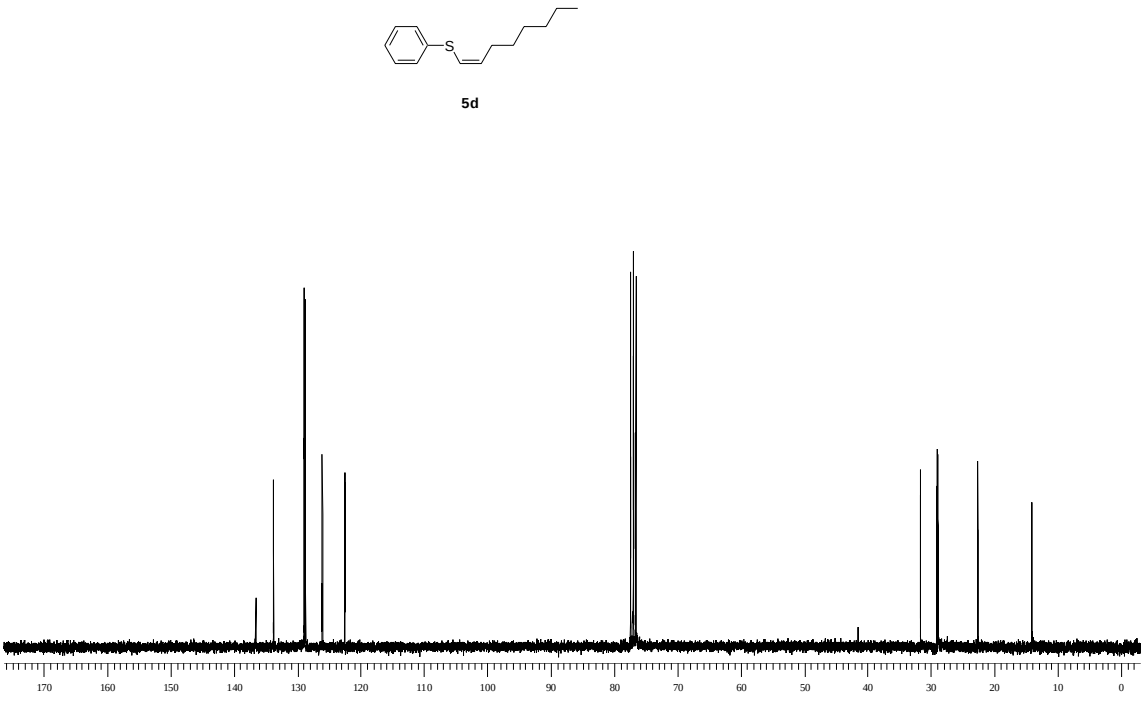
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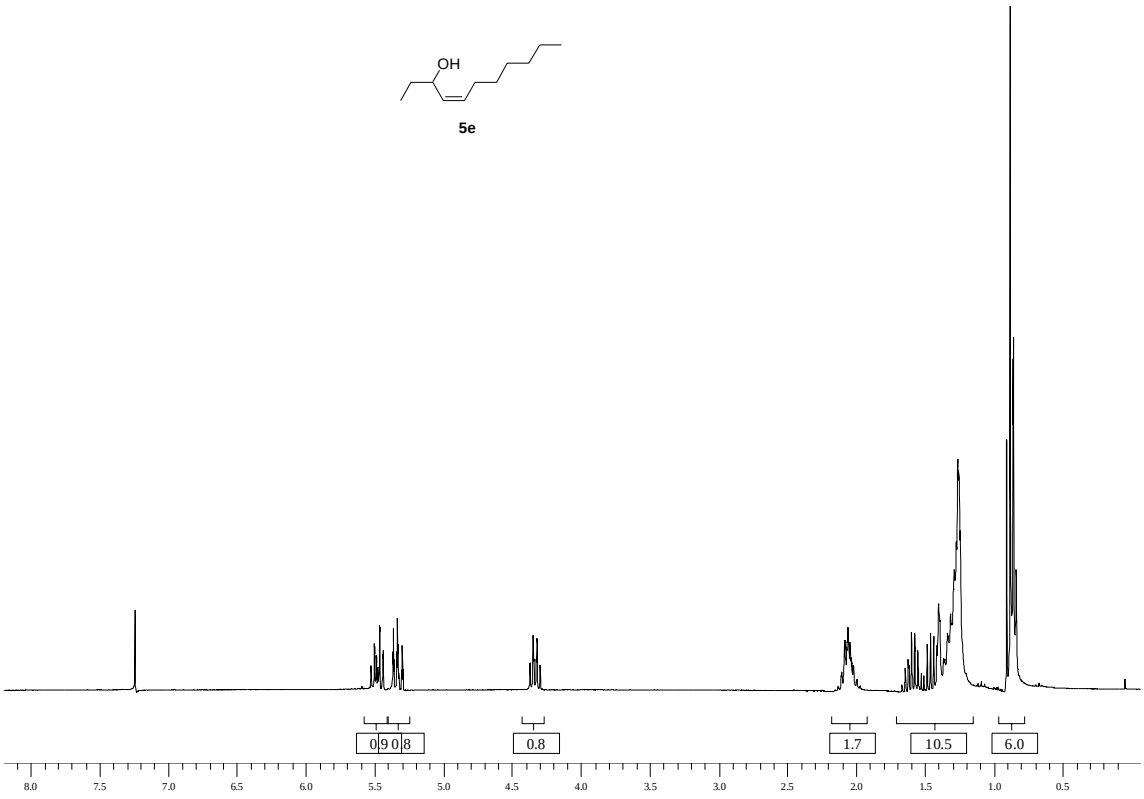
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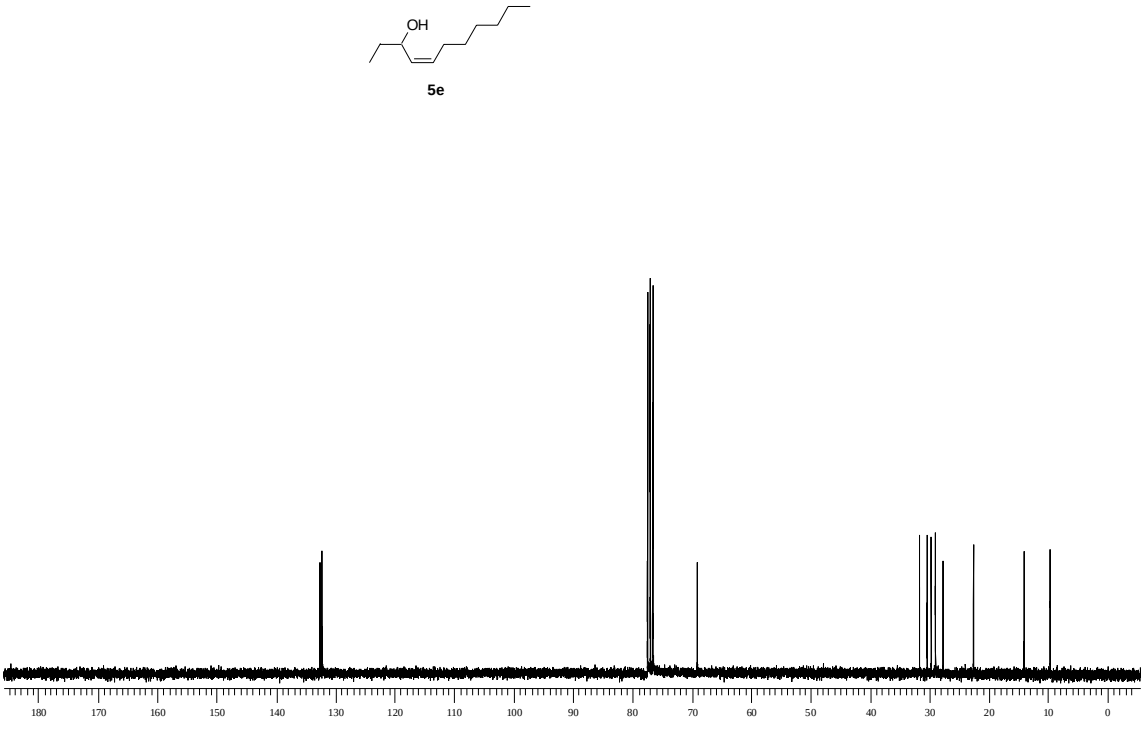
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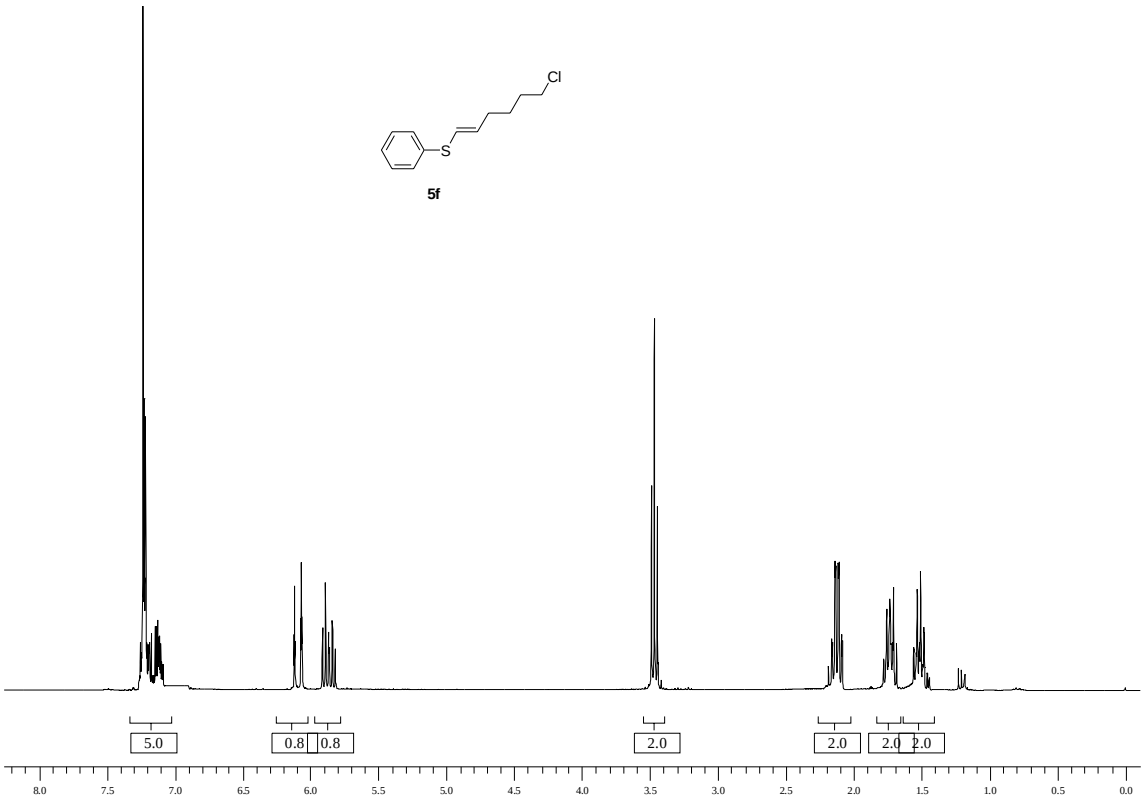
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S
5f
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6.0
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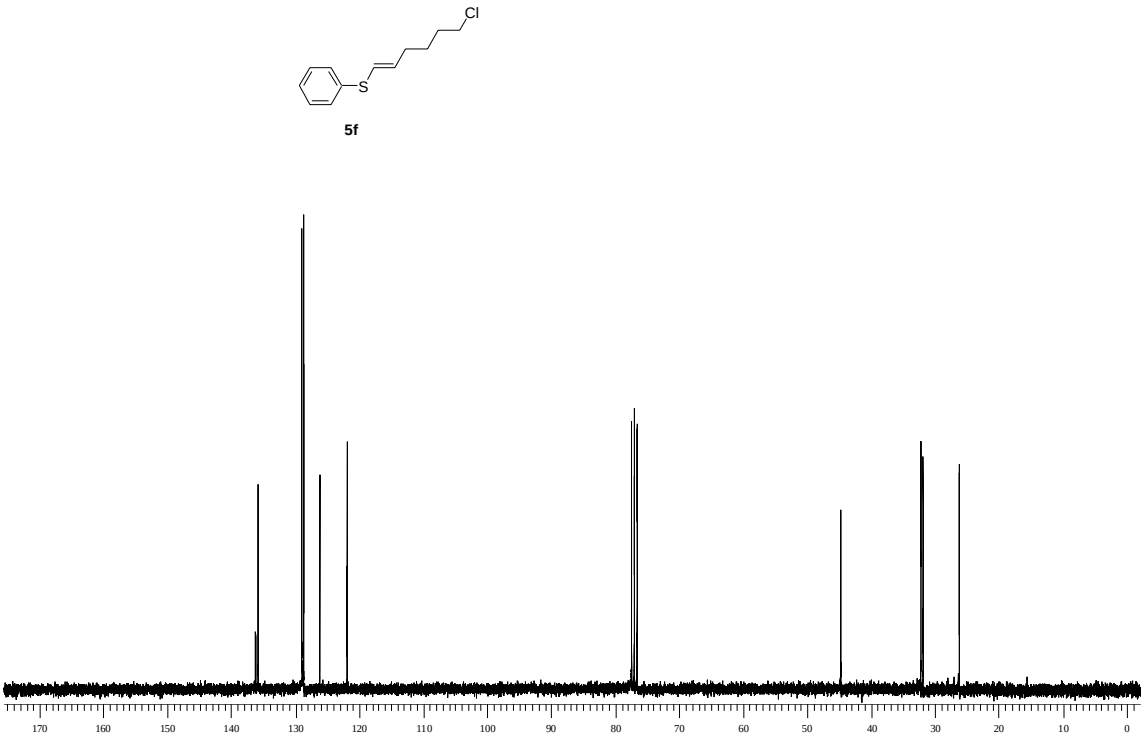
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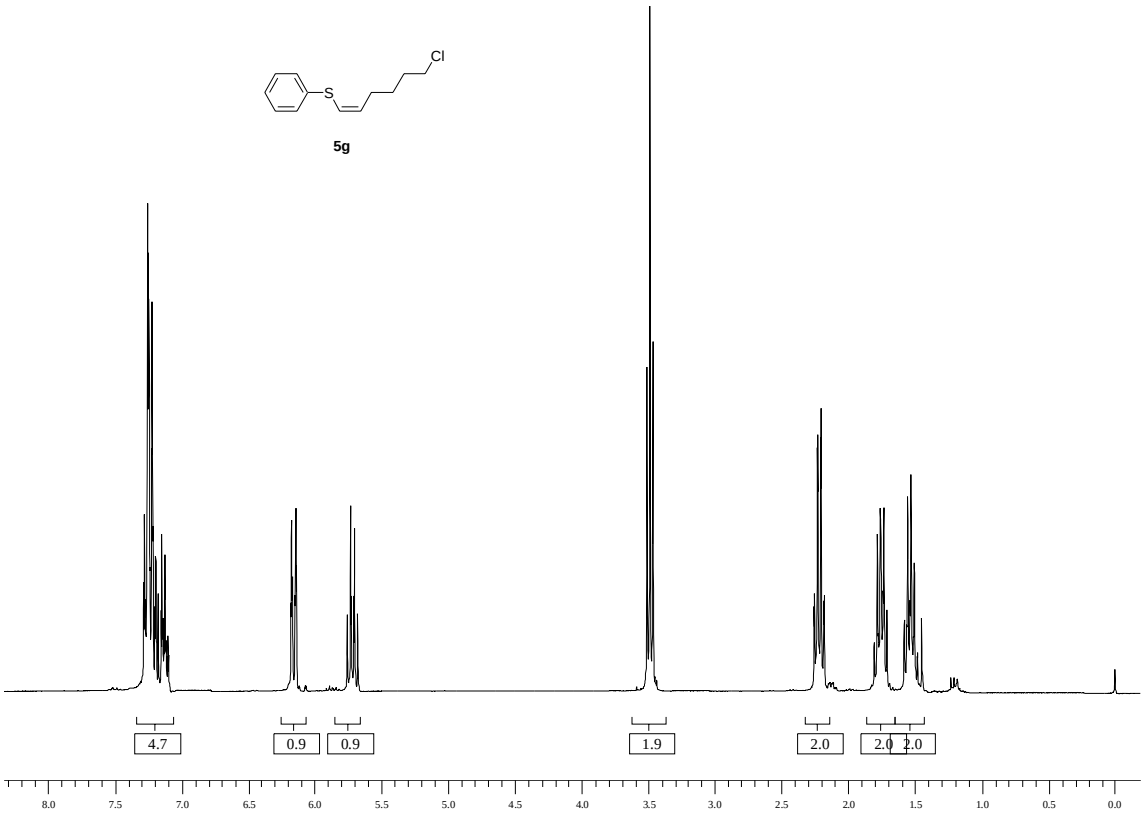
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S
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6.0
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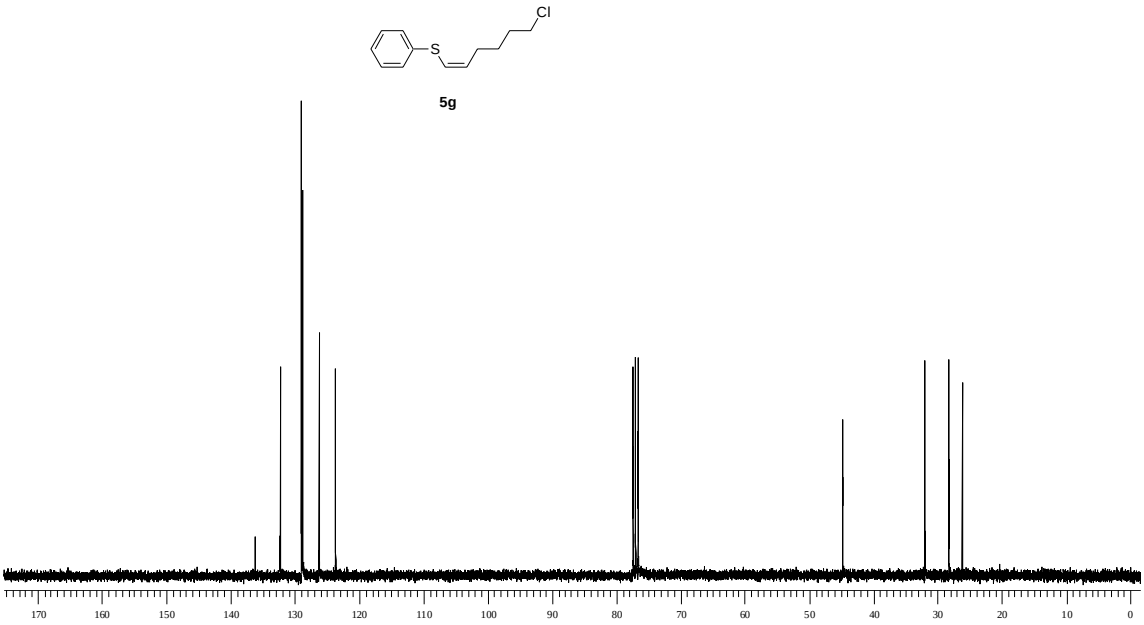
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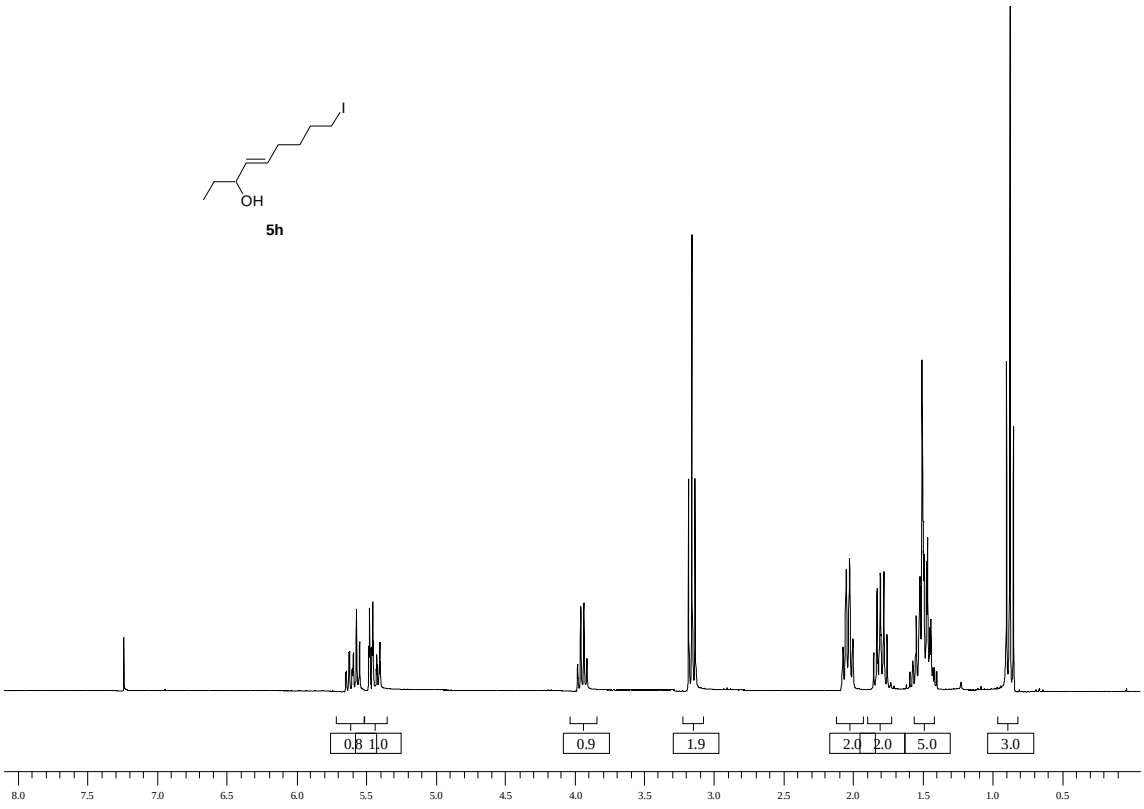
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OH
5h
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0.9
1.9
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2.0
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8.0
7.5
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6.5
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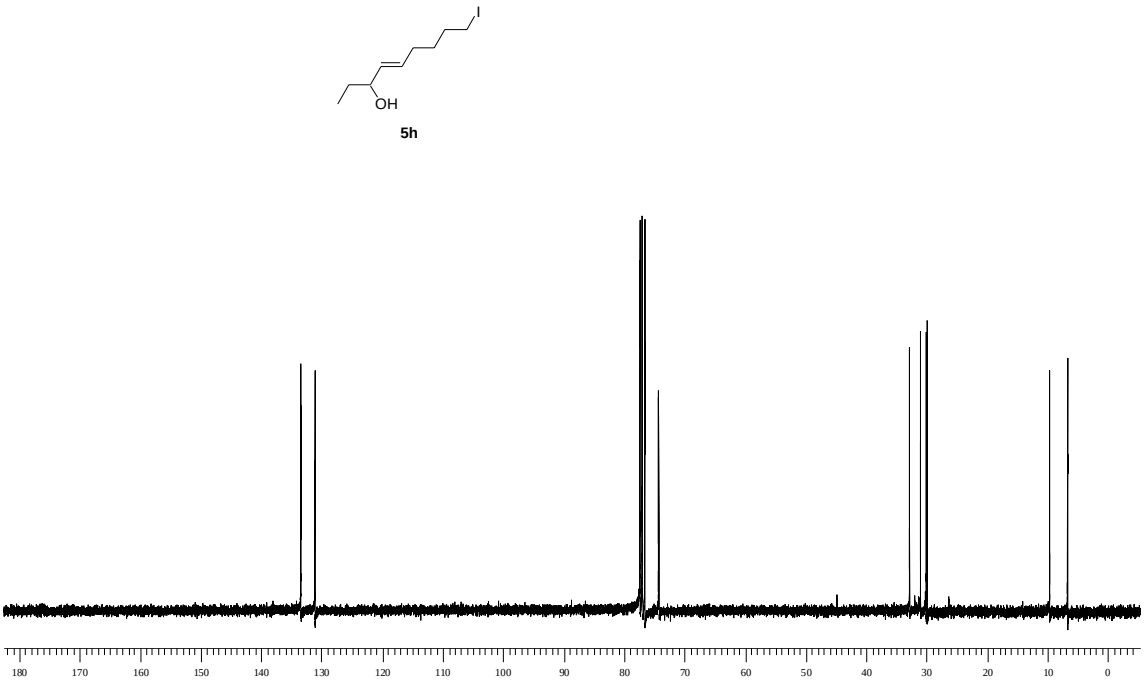
I
OH
5h
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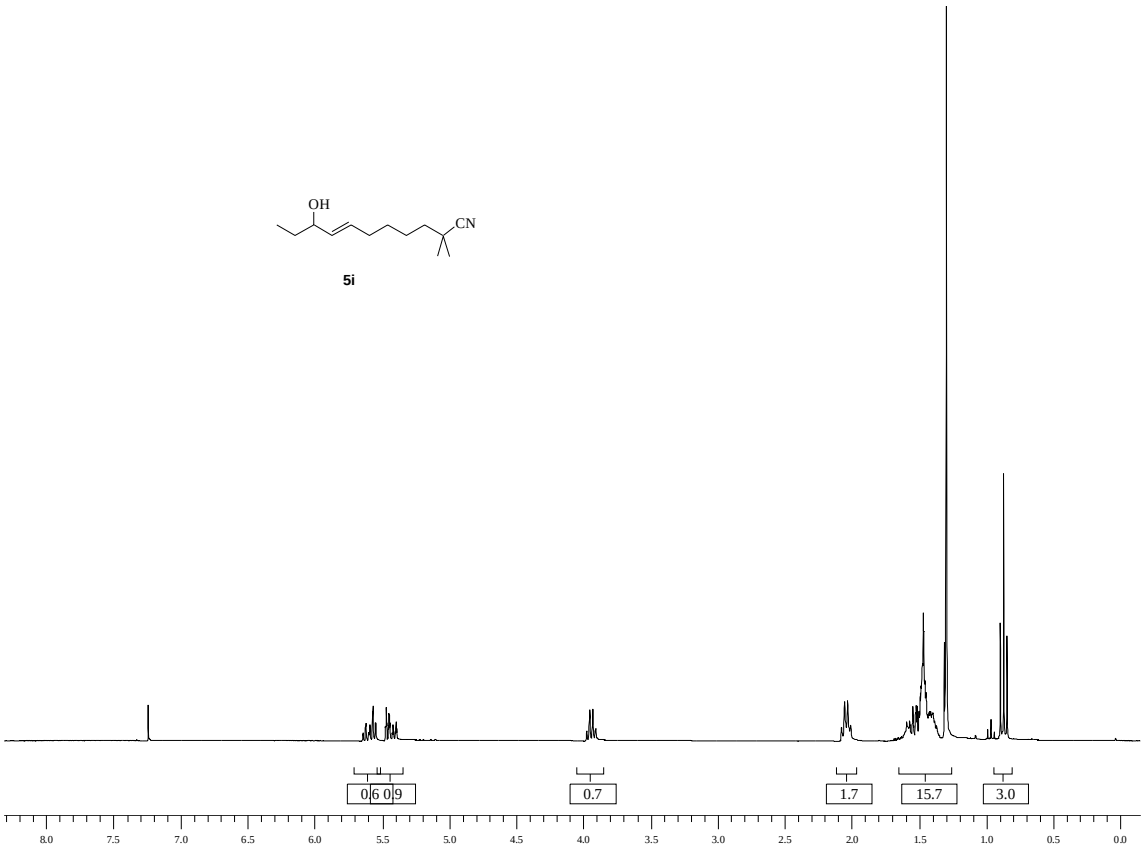
OH
CN
5i
0.6
0.9
0.7
1.7
15.7
3.0
8.0
7.5
7.0
6.5
6.0
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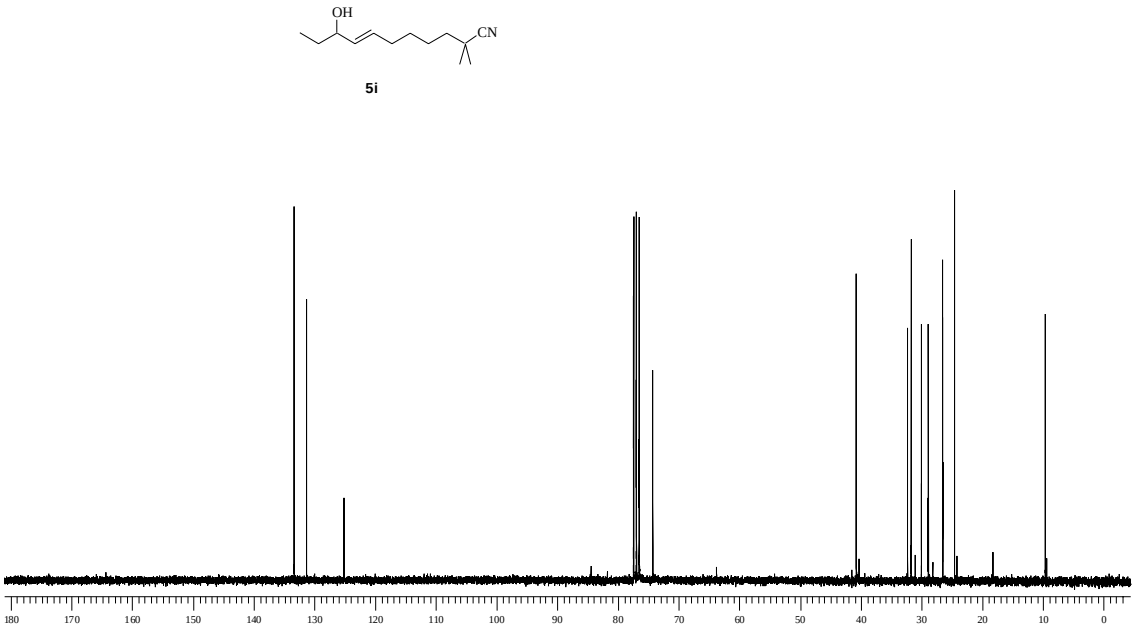
OH
CN
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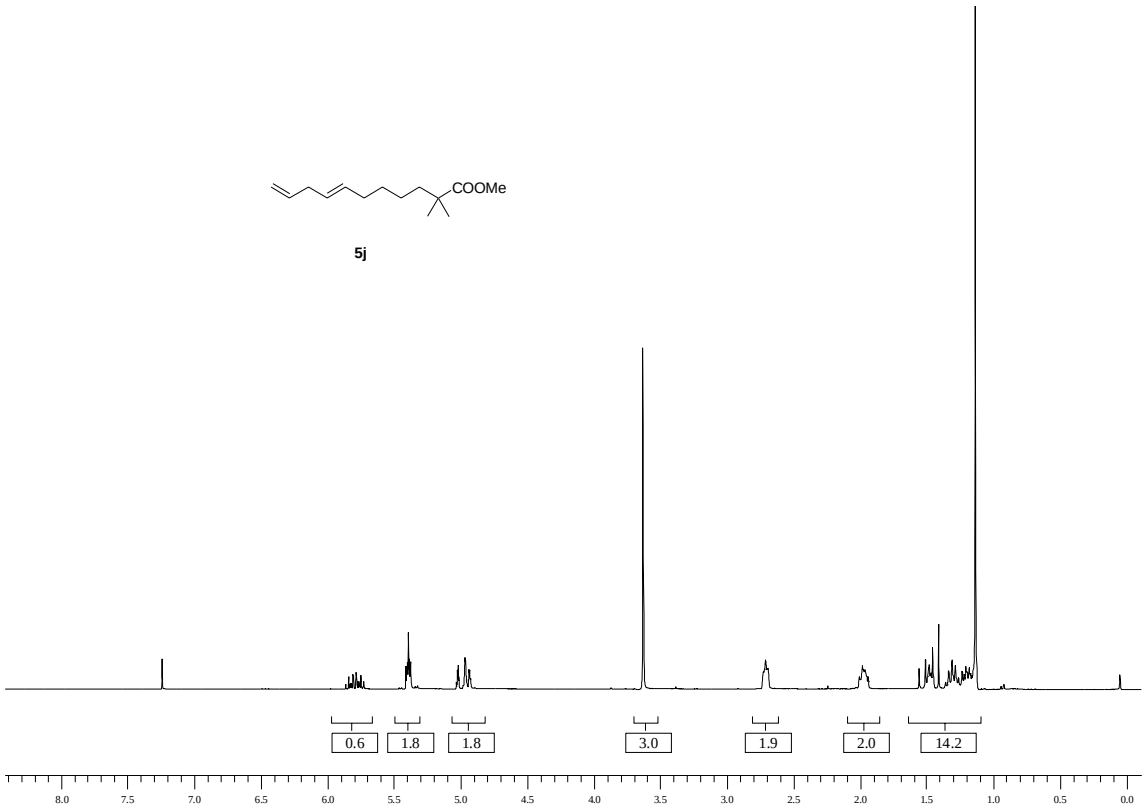
COOMe
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1.8
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1.9
2.0
14.2
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7.0
6.5
6.0
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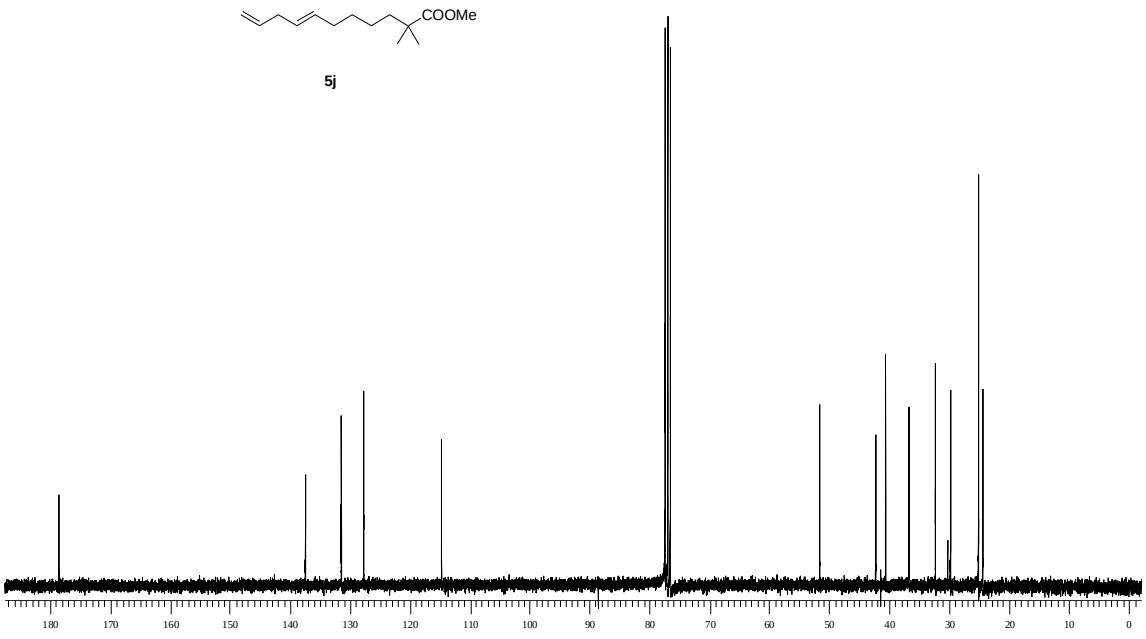
COOMe
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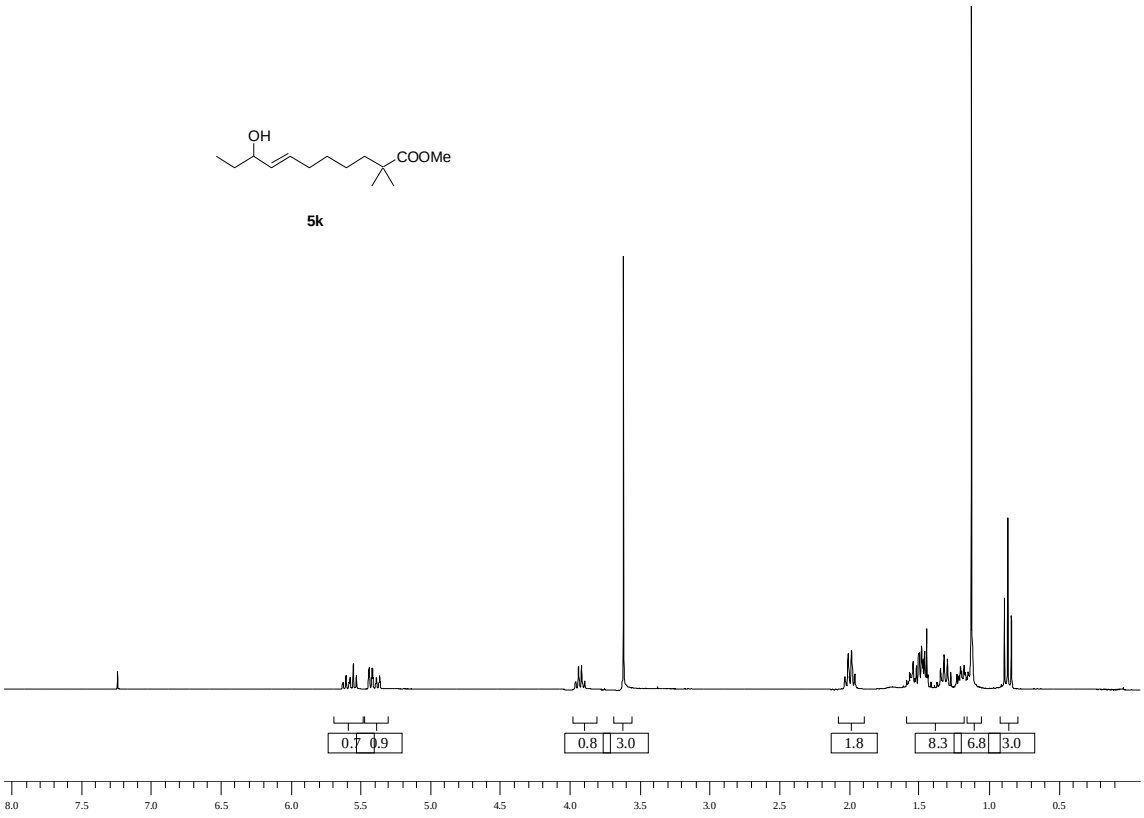
OH
COOMe
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3.0
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8.3
6.8
3.0
8.0
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6.5
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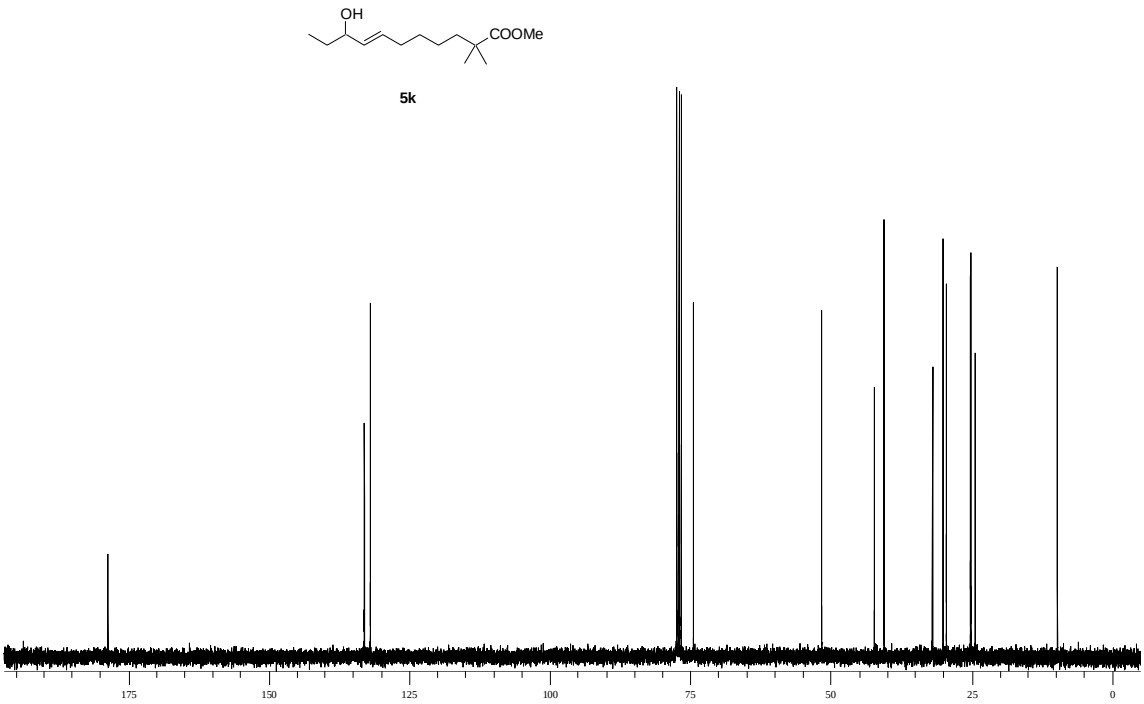
OH
COOMe
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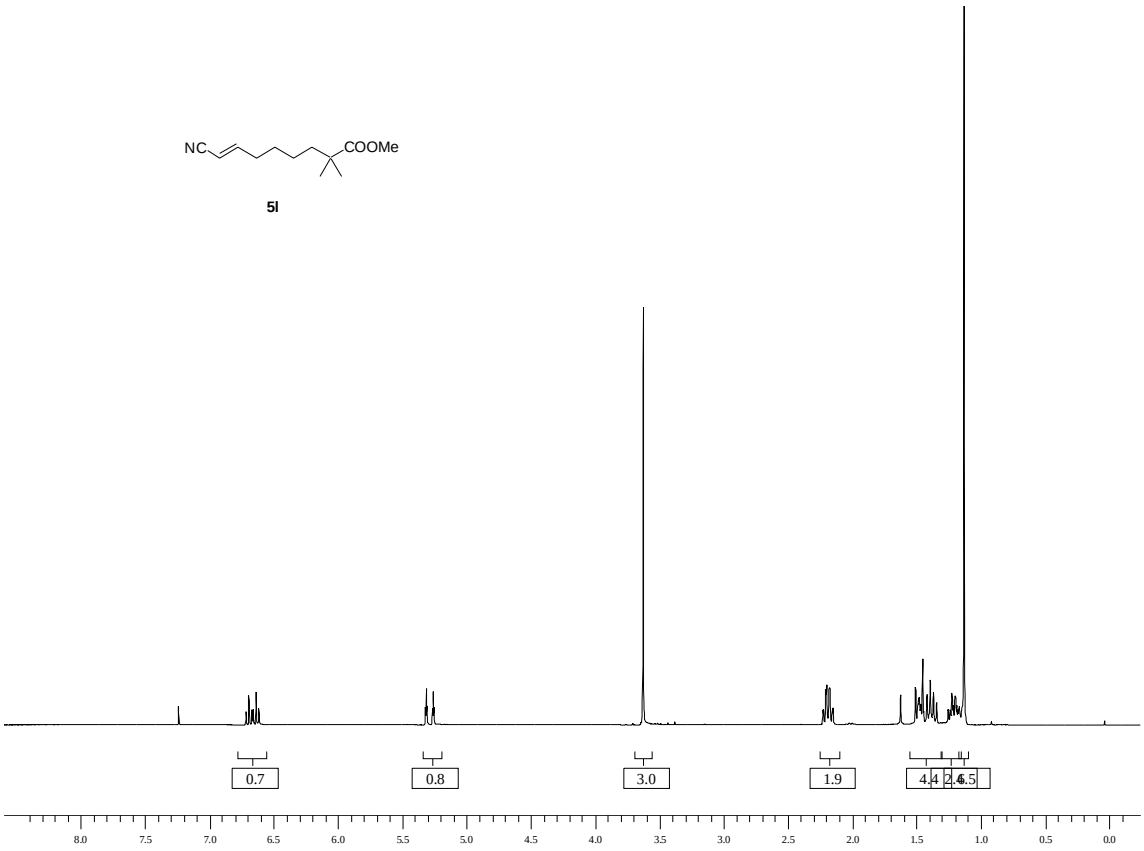
NC
COOMe
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2.4
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8.0
7.5
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6.5
6.0
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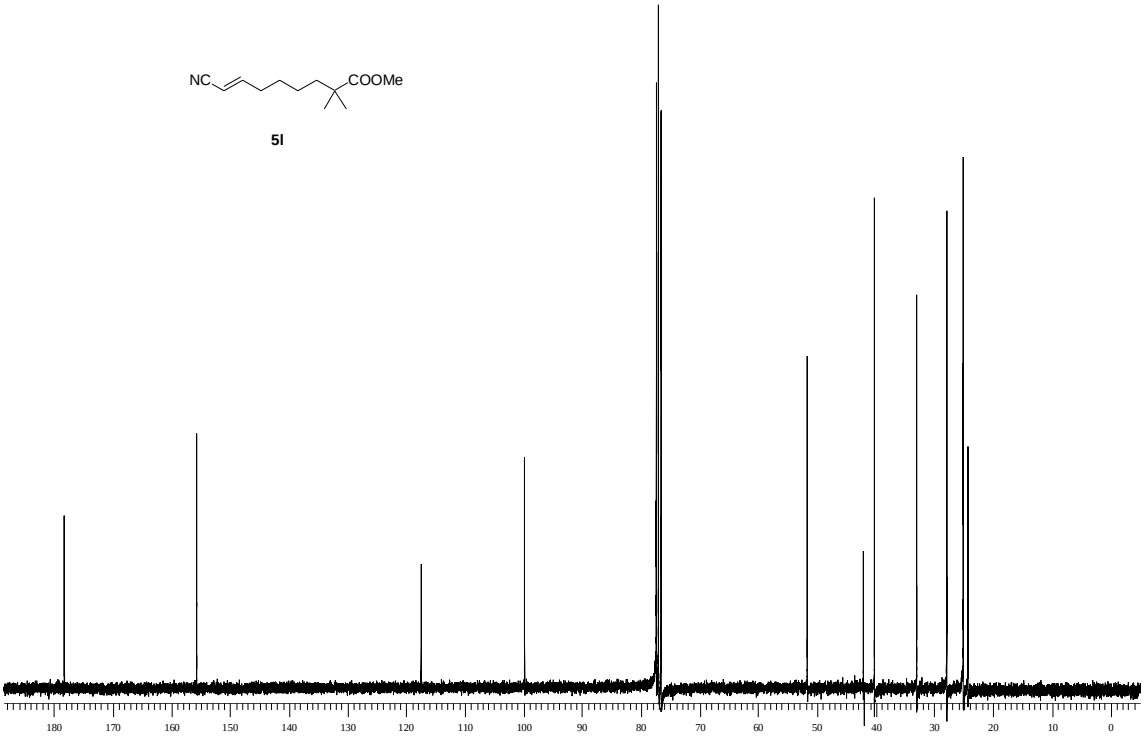
NC
COOMe
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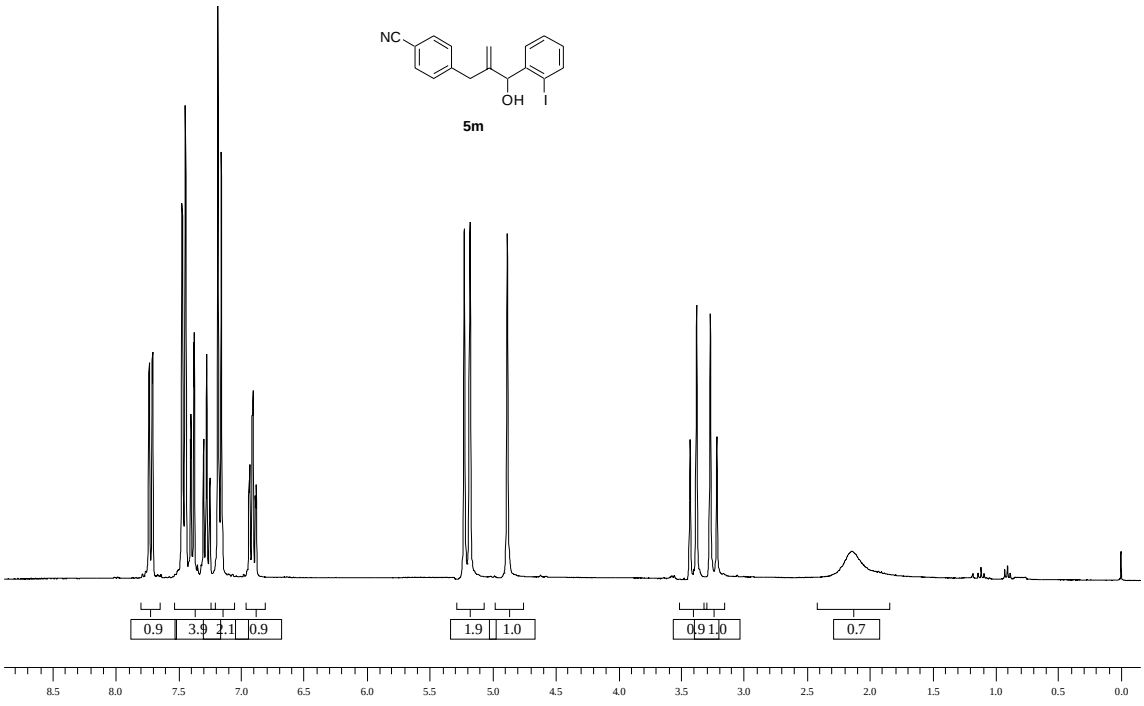
NC
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0.9
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8.0
7.5
7.0
6.5
6.0
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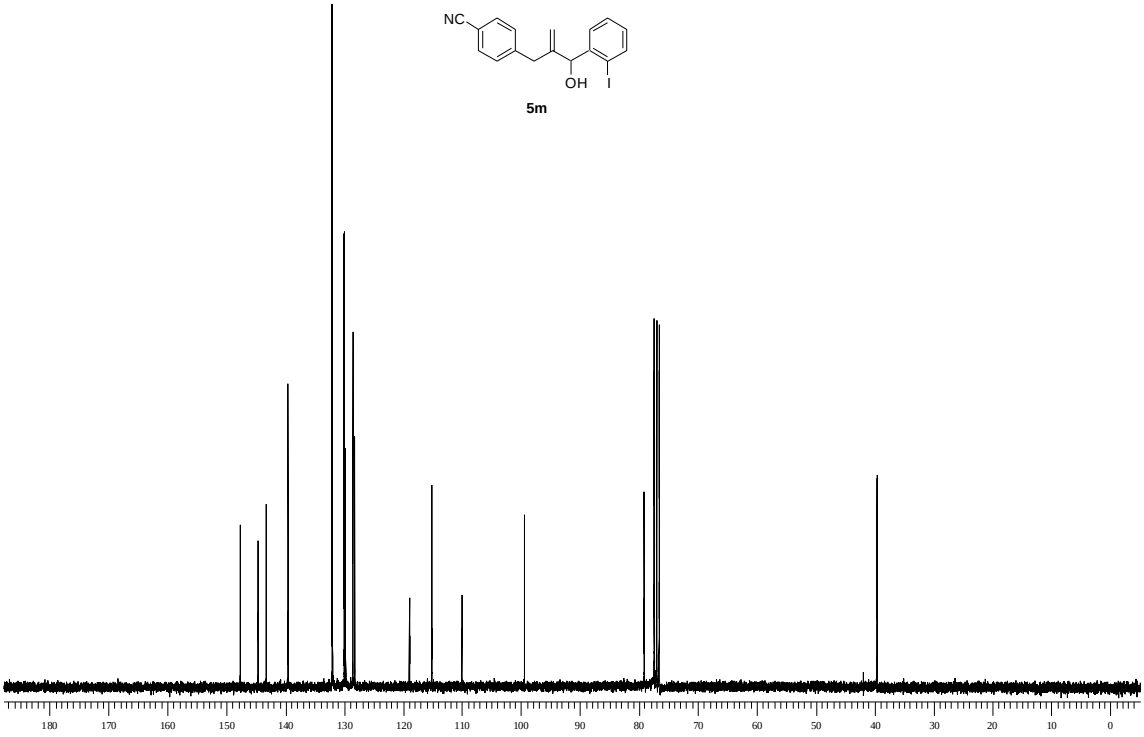
NC
OH
I
5m
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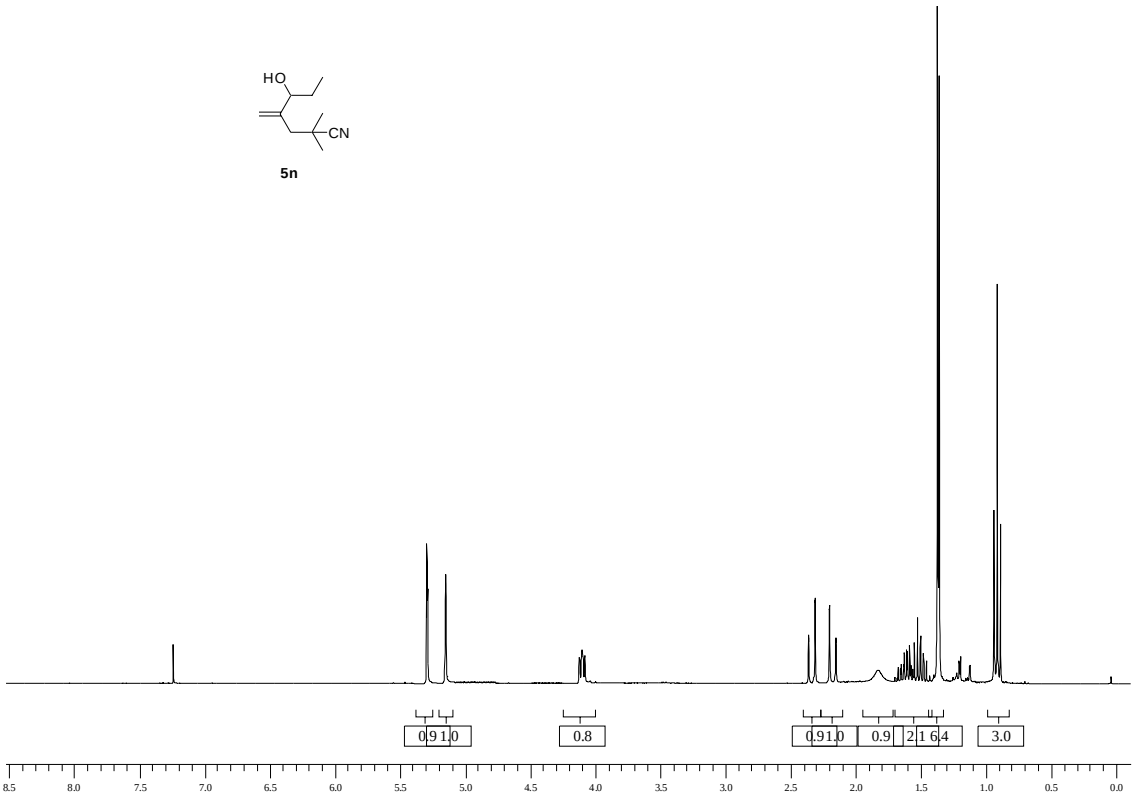
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8.0
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7.0
6.5
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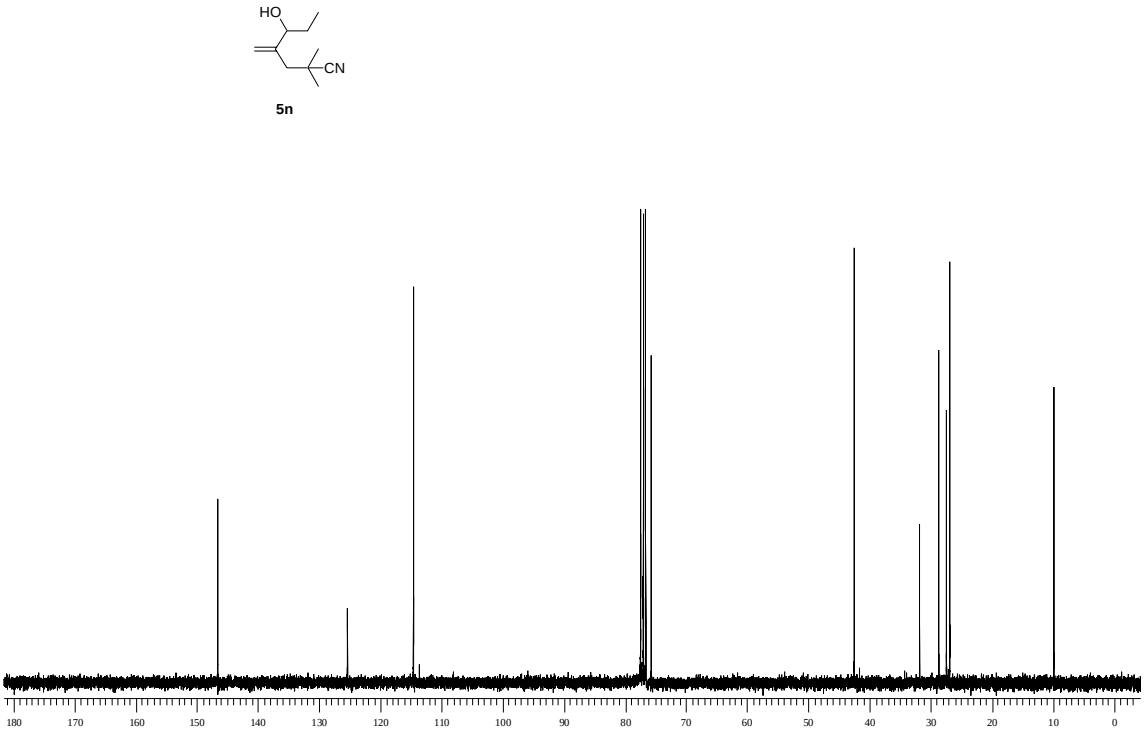
HO
CN
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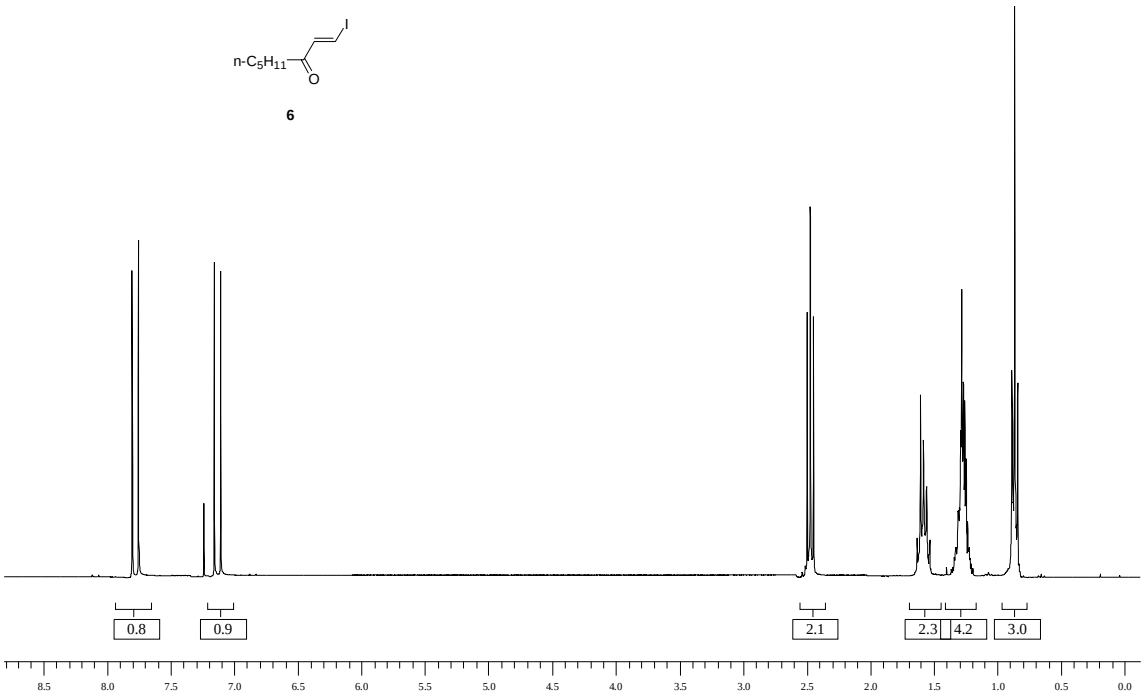
n-C5H11
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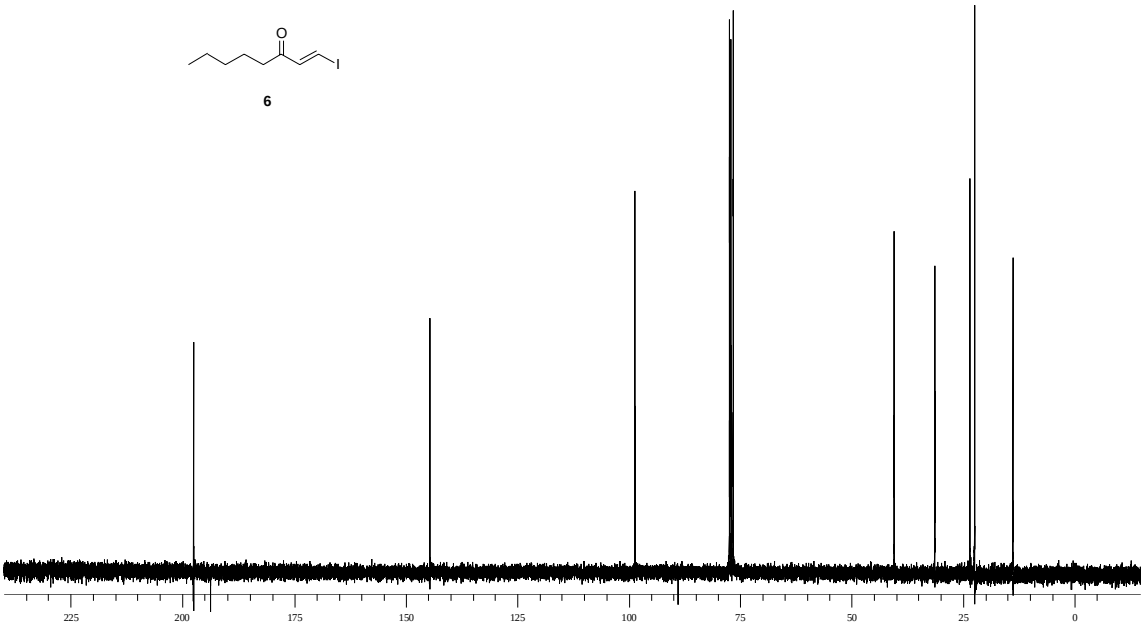
O
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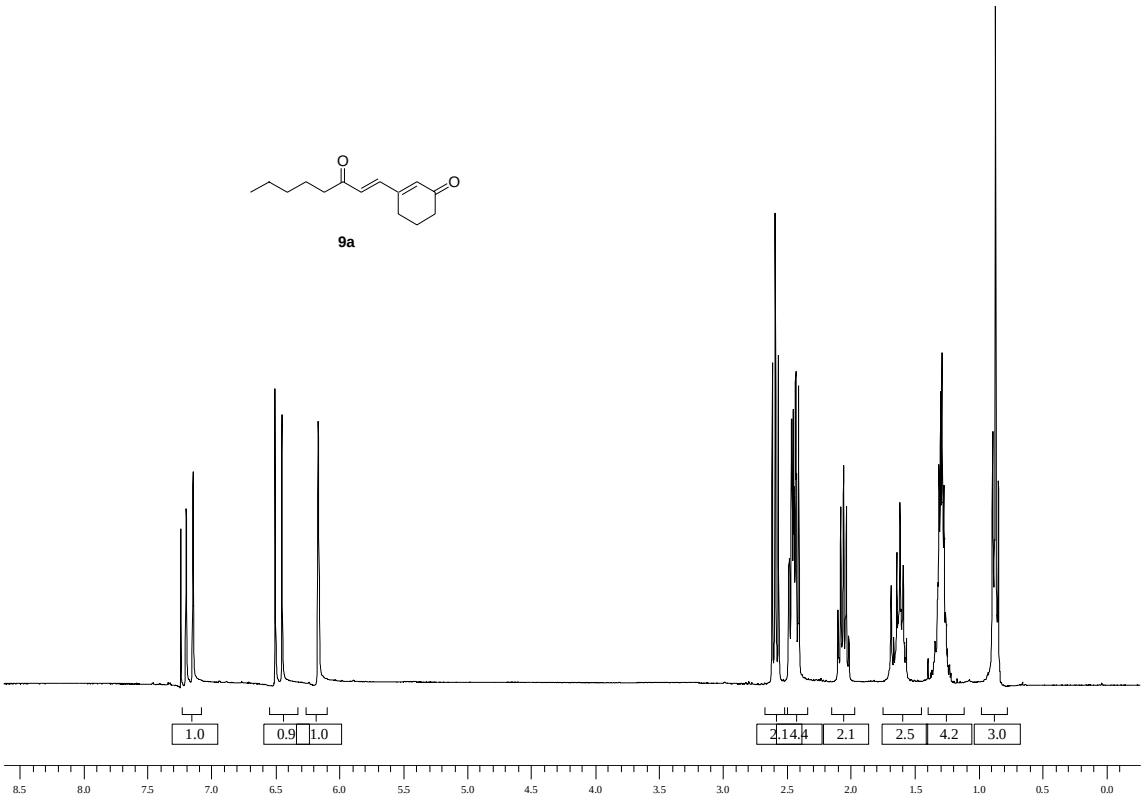
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O
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2.1
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8.0
7.5
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6.5
6.0
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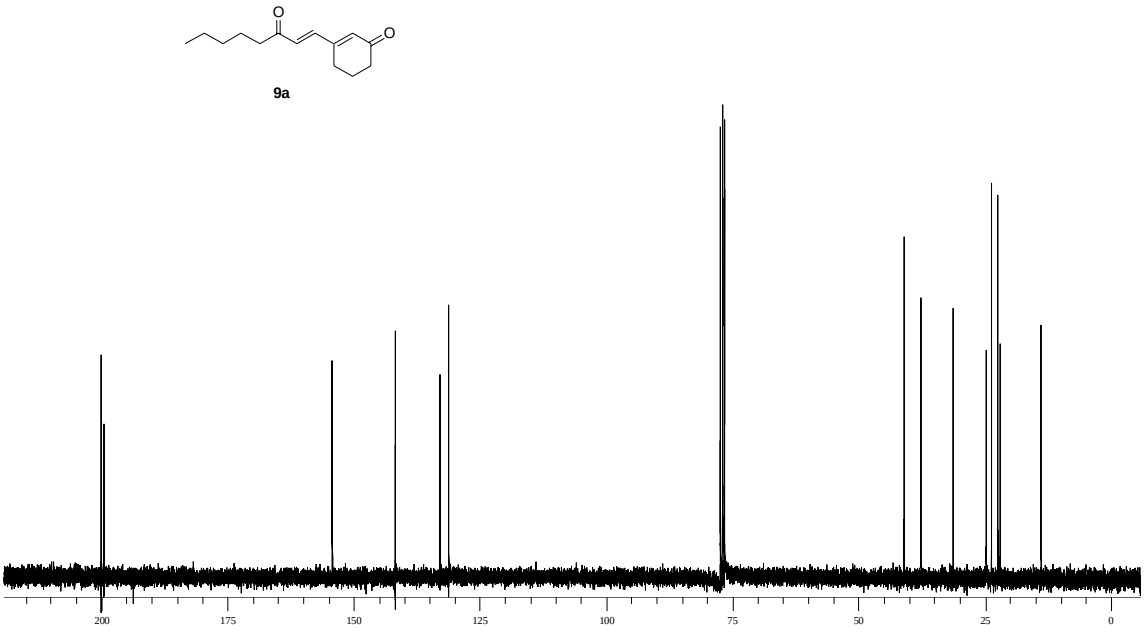
O
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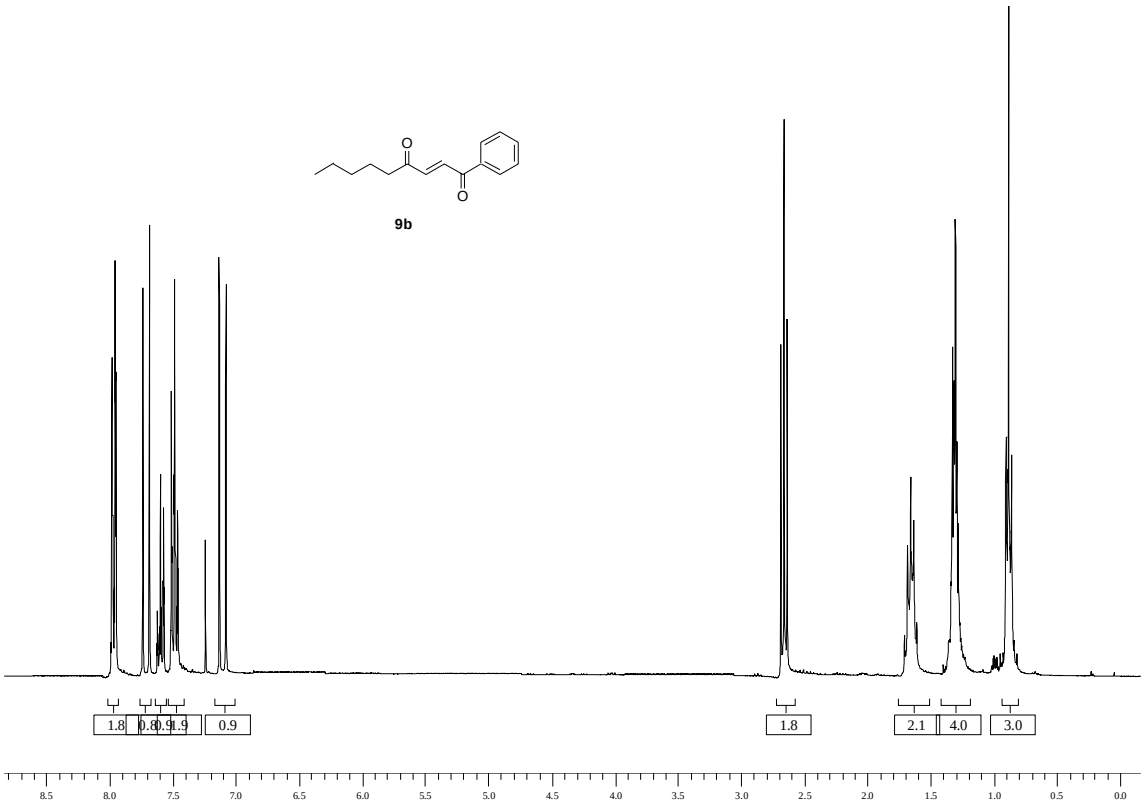
O
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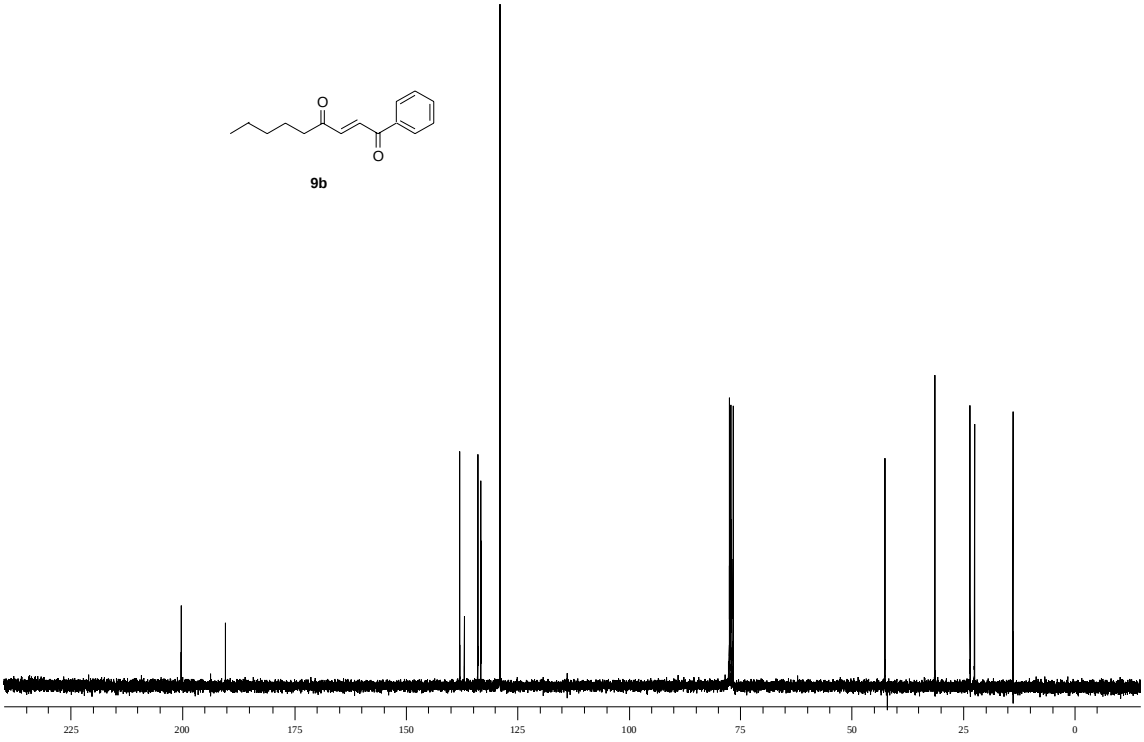
O
O
9b
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150
125
100
75
50
25
0