A Mild, Palladium-Catalyzed Method for the Dehydrohalogenation of Alkyl Bromides: Synthetic and Mechanistic Studies

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Supporting Information

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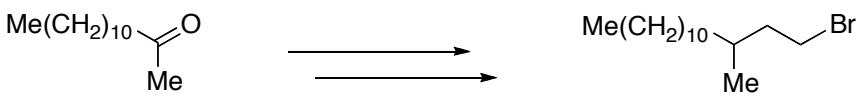
I. General

The following reagents were purchased and used as received: P(*t*-Bu)$_2$Me (Aldrich), $Pd_2(dba)_3$ (Strem), [HP(*t*-Bu)$_2$Me]BF_4, (Aldrich), Cy_2NH (Aldrich), 2,2,6,6-tetramethylpiperidine (TMP; Aldrich), KO*t*-Bu (Strem), LiOMe (Aldrich), and 1,4-dioxane (Aldrich, anhydrous). Pd(P(*t*-Bu)$_2$Me)$_2$ [479210-19-0] was prepared according to a literature procedure.[1]

Unless otherwise specified, reactions were conducted with magnetic stirring in oven-dried glassware under an inert atmosphere.

II. Preparation of Materials

These procedures have not been optimized.



1-Bromo-3-methyltetradecane

Triethyl phosphonoacetate (11.9 mL, 60.0 mmol) was added dropwise to a mixture of NaH (1.44 mg, 60.0 mmol) in THF (100 mL) at 0 °C. After 1 h of stirring, a solution of 2-tridecanone

(1) Hills, I. D.; Netherton, M. R.; Fu, G. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 5749–5752.

(9.90 g, 50.0 mmol) in THF (50 mL) was added dropwise to the solution of olefinating agent, and the resulting mixture was allowed to slowly warm to r.t. After 12 h, H_2O (40 mL) was added, the phases were separated, and the aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was then filtered through a pad of silica (~5 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with a 5% EtOAc/hexane solution (300 mL). The combined filtrates were concentrated under reduced pressure, and the resulting oil was subjected to flash chromatography (silica; 5% EtOAc/hexane), which provided (*E*)-ethyl 3-methyltetradec-2-enoate (10.3 g, 77%) as a clear, colorless oil.

A solution of (*E*)-ethyl 3-methyltetradec-2-enoate (4.50 g, 15.9 mmol) in MeOH (100 mL) was treated with 10% palladium on carbon (500 mg), and the resulting mixture was maintained under a hydrogen atmosphere (1 atm) at r.t. for 18 h. Next, the reaction mixture was filtered through Celite™ (~3 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with CH_2Cl_2 (50 mL). The combined filtrates were concentrated under reduced pressure to afford ethyl 3-methyltetradecanoate, which was used without purification in the next reaction.

A solution of ethyl 3-methyltetradecanoate in Et_2O (20 mL) was added dropwise to a suspension of $LiAlH_4$ (1.90 g, 50.1 mmol) in Et_2O (120 mL) at 0 °C. The resulting mixture was allowed to slowly warm to r.t. After 22 h, the reaction mixture was cooled to 0 °C, and Et_2O (50 mL), H_2O (1.9 mL), NaOH (6 M aqueous solution; 1.9 mL), and H_2O (5.7 mL) were added in this order. The resulting mixture was allowed to warm to r.t., maintained at this temperature for 15 min, and then dried ($MgSO_4$). After 15 min, the reaction mixture was filtered, and the solids thus retained were washed with CH_2Cl_2 (100 mL). The combined filtrates were concentrated under reduced pressure to afford 3-methyltetradecan-1-ol (8.6 g, 98% over 2 steps from (*E*)-ethyl 3-methyltetradec-2-enoate) as a clear, colorless oil.

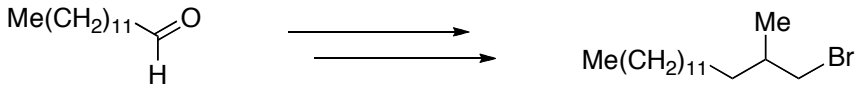
PPh_3Br_2 (6.60 g, 15.7 mmol) was added to a solution of 3-methyltetradecan-1-ol (3.00 g, 13.1 mmol) and imidazole (1.07 g, 15.7 mmol) in CH_2Cl_2 (30 mL) at 0 °C. Next, the reaction mixture was allowed to slowly warm to r.t. After 19 h, $Na_2S_2O_3$ (saturated aqueous solution; 10 mL) and NaOH (6 M aqueous solution; 5 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was filtered through a pad of silica (~5 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with a 5% EtOAc/hexane solution (300 mL). The combined filtrates were concentrated under reduced pressure, and the resulting oil was subjected to flash chromatography (silica; hexane), which provided the title compound (2.80 g, 74%) as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.49-3.38 (m, 2H), 1.92-1.85 (m, 1H), 1.71-1.55 (m, 2H), 1.26 (br s, 20H), 0.89 (d, 6H, J = 3.9 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 36.3, 32.15, 32.09, 31.8, 30.0, 29.8, 29.5, 27.0, 22.9, 19.1, 14.3.

FT-IR (neat) 2976, 2924, 2854, 1466, 1379, 1262, 1216, 721 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{15}H_{31}Br$: 290, found: 290.



1-Bromo-2-methylpentadecane

Triethyl 2-phosphonopropionate (5.80 g, 24.2 mmol) was added dropwise to a mixture of NaH (580 mg, 24.2 mmol) in THF (70 mL) at 0 °C. After 1 h, a solution of tridecanal (4.00 g, 20.2 mmol) in THF (50 mL) was added dropwise to the solution of olefinating agent, and the resulting mixture was allowed to slowly warm to r.t. After 16 h, H_2O (30 mL) was added, the phases were separated, and the aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was filtered through a pad of silica (~5 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with a 5% EtOAc/hexane solution (300 mL). The combined filtrates were concentrated under reduced pressure, and the resulting oil was subjected to flash chromatography (silica; 5% EtOAc/hexane), which provided (*E*)-ethyl 2-methylpentadec-2-enoate (4.60 g, 81%) as a clear, colorless solid.

A solution of (*E*)-ethyl 2-methylpentadec-2-enoate (4.50 g, 15.9 mmol) in MeOH (50 mL) was treated with 10% palladium on carbon (250 mg), and the resulting mixture was maintained under a hydrogen atmosphere (1 atm) at r.t. for 18 h. Next, the reaction mixture was filtered through Celite™ (~3 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with CH_2Cl_2 (30 mL). The combined filtrates were concentrated under reduced pressure to afford ethyl 2-methylpentadecanoate, which was used without purification in the next reaction.

A solution of ethyl 2-methylpentadecanoate in Et_2O (10 mL) was added dropwise to a suspension of $LiAlH_4$ (600 mg, 15.8 mmol) in Et_2O (60 mL) at 0 °C. The resulting mixture was allowed to slowly warm to r.t. After 20 h, the mixture was cooled to 0 °C, and Et_2O (30 mL), H_2O (0.6 mL), NaOH (6 M aqueous solution; 0.6 mL), and H_2O (1.8 mL) were added in this order. The resulting mixture was warmed to r.t., maintained at this temperature for 15 min, then dried ($MgSO_4$). After 15 min, the reaction mixture was filtered, and the solids thus retained were washed with CH_2Cl_2 (50 mL). The combined filtrates were concentrated under reduced pressure to afford 2-methylpentadecan-1-ol (2.70 g, 70% over 2 steps from (*E*)-ethyl 2-methylpentadec-2-enoate) as a clear, colorless oil.

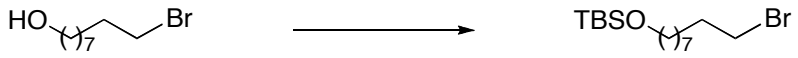
PPh_3Br_2 (2.50 g, 5.94 mmol) was added to a solution of 2-methylpentadecan-1-ol (1.20 g, 4.95 mmol) and imidazole (400 mg, 5.94 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was allowed to slowly warm to r.t. After 16 h, $Na_2S_2O_3$ (saturated aqueous solution; 10 mL) and NaOH (6 M aqueous solution; 5 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was then filtered through a pad of silica (~5 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with a 5% EtOAc/hexane solution (300 mL). The combined filtrates were concentrated under reduced pressure, and the resulting oil was subjected to flash chromatography (silica; hexane), which provided the title compound (1.45 g, 95%) as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40 (dd, 1H, J = 5.0, 10.0 Hz), 3.33 (dd, 1H, J = 5,0, 10.0 Hz), 1.82-1.76 (m, 1H), 1.46-1.41 (m, 1H), 1.26 (br s, 23H), 1.01 (d, 3H, J = 7.0 Hz), 0.89 (t, 3H, J = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 41.4, 35.3, 35.0, 32.1, 29.90, 29.88, 29.87, 29.83, 29.79, 29.6, 27.1, 22.9, 18.9, 14.3.

FT-IR (neat) 2957, 2925, 2854, 1466, 1378, 1230, 721 cm^{-1}.

MS (EI) *m*/*z* ($M-Br^+$) calcd for $C_{16}H_{33}$: 225, found: 225.



9-Bromo-1-(*tert*-butyldimethylsilyloxy)nonane

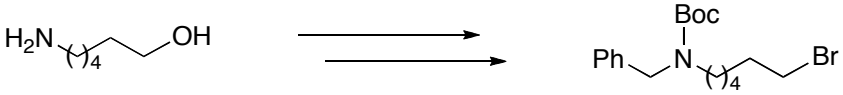
TBSCl (675 mg, 4.48 mmol) was added to a solution of 9-bromononan-1-ol (1.00 g, 4.48 mmol), imidazole (460 mg, 6.72 mmol), and DMAP (55 mg, 0.45 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 18 h, NH_4Cl (saturated aqueous solution; 10 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash chromatography (silica; 1% EtOAc/hexane), which provided the title compound (1.30 g, 86%) as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59 (t, 2H, *J* = 11.0 Hz), 3.40 (t, 2H, *J* = 11.0 Hz), 1.85 (pentet, 2H, *J* = 12.0 Hz), 1.53-1.29 (m, 12H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 63.4, 34.0, 32.96, 32.95, 29.5, 29.4, 28.8, 28.3, 26.1, 25.9, 18.5, –5.2.

FT-IR (neat) 2930, 2856, 1737, 1472, 1255, 1100, 836, 775 cm^{-1}.

MS (EI) *m*/*z* ($M+H^+$) calcd for $C_{15}H_{34}BrOSi$: 337, found: 337.



***tert*-Butyl-*N*-benzyl(6-bromohexyl)carbamate**

A mixture of benzaldehyde (1.83 mL, 18.0 mmol), 6-amino-hexan-1-ol (2.00 g, 17.1 mmol), and 4Å molecular sieves (4 g) in toluene (20 mL) was heated at reflux. After 20 h, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to provide 6-(benzylideneamino)hexan-1-ol. This somewhat unstable material was used without purification in the next reaction.

$NaBH_4$ (800 mg, 21.1 mmol) was added to a solution of 6-(benzylideneamino)hexan-1-ol in MeOH (20 mL) at 0 °C. After 16 h, the mixture was concentrated, CH_2Cl_2 (20 mL) and H_2O (10 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide 6-(benzylamino)hexan-1-ol, which was used without purification in the next reaction.

A solution of di-*tert*-butyl dicarbonate (3.80 g, 17.4 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of 6-(benzylamino)hexan-1-ol in CH_2Cl_2 (20 mL) and NaOH (1 M aqueous solution; 16 mL). After 18 h, H_2O (10 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide *tert*-butyl benzyl(6-hydroxyhexyl)carbamate, which was used without purification in the next reaction.

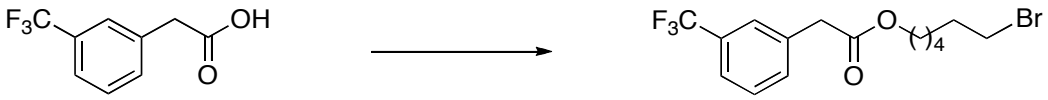
PPh_3Br_2 (8.70 g, 20.6 mmol) was added to a solution of *tert*-butyl benzyl(6-hydroxyhexyl)carbamate and imidazole (1.40 g, 20.6 mmol) in CH_2Cl_2 (60 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 20 h, $Na_2S_2O_3$ (saturated aqueous solution; 20 mL) and NaOH (6 M aqueous solution; 10 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash chromatography (silica; 95:5:1 *v*/*v* hexane/EtOAc/Et_3N), which provided the title compound (3.2 g, 51% over 4 steps from 6-amino-hexan-1-ol) as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.24 (m, 5H), 4.45 (br s, 1H), 4.41 (br s, 1H), 3.38 (t, 2H, *J* = 7.0 Hz), 3.22 (br s, 1H), 3.13 (br s, 1H), 1.85-1.79 (m, 2H), 1.51 (br s, 6H), 1.44 (br s, 6H), 1.27 (br s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 138.7, 128.4, 127.7, 127.1, 79.5, 50.6, 50.0, 46.5, 33.7, 32.7, 28.5, 27.9, 26.0.

FT-IR (neat) 2974, 2933, 2859, 1695, 1455, 1416, 1365, 1243, 1170, 880, 730, 700 cm^{-1}.

MS (EI) *m*/*z* ($M-isobutylene^+$) calcd for $C_{14}H_{20}BrNO_2$: 313, found: 313.



6-Bromohexyl 2-(3-(trifluoromethyl)phenyl)acetate

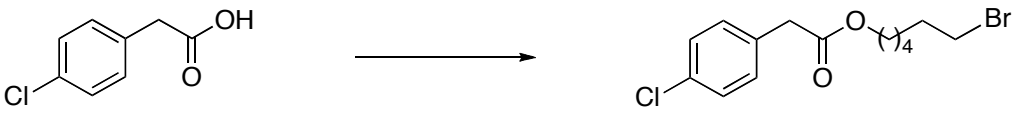
A mixture of 2-(3-(trifluoromethyl)phenyl)acetic acid (1.22 g, 6.00 mmol), 1,6-dibromohexane (4.40 g, 18.0 mmol), and K_2CO_3 (2.50 g, 18.0 mmol) in acetone (40 mL) was heated at reflux. After 24 h, the mixture was allowed to cool to r.t., and it was filtered through Celite™ (~2 cm deep pad contained in a sintered glass funnel); the solids thus retained were washed with acetone (40 mL). The combined filtrates were then concentrated under reduced pressure, and the resulting residue was subjected to flash chromatography (silica; 5% EtOAc/hexane), which provided the title compound (1.60 g, 79%) as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.44 (m, 4H), 4.11 (t, 2H, *J* = 7.0 Hz), 3.69 (s, 2H), 3.39 (t, 2H, *J* = 7.0 Hz), 1.83 (pentet, 2H, *J* = 8.0 Hz), 1.64 (pentet, 2H, *J* = 8.0 Hz), 1.43 (pentet, 2H, *J* = 8.0 Hz), 1.34 (pentet, 2H, *J* = 8.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 135.1, 132.8, 131.9 (q, *J* = 32 Hz), 129.1, 126.2, 124.12 (q, *J* = 271 Hz), 124.04, 65.1, 41.1, 33.8, 28.4, 27.8, 25.1.

FT-IR (neat) 2939, 2861, 1737, 1452, 1332, 1164, 1125, 1077, 701 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{15}H_{18}BrF_3O_2$: 368, found: 368.



6-Bromohexyl 2-(4-chlorophenyl)acetate

6-Bromohexyl 2-(4-chlorophenyl)acetate was prepared in the same manner as described for the synthesis of 6-bromohexyl 2-(3-(trifluoromethyl)phenyl)acetate, but now using 2-(4-chlorophenyl)acetic acid. In this way, the title compound (1.40 g, 72%) was obtained as a clear,

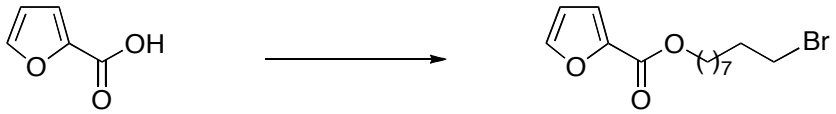
colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, 2H, *J* = 8.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 4.08 (t, 2H, *J* = 7.0 Hz), 3.58 (s, 2H), 3.38 (t, 2H, *J* = 7.0 Hz), 1.83 (pentet, 2H, *J* = 7.0 Hz), 1.63 (pentet, 2H, *J* = 7.0 Hz), 1.43 (pentet, 2H, *J* = 7.0 Hz), 1.33 (pentet, 2H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 133.0, 132.6, 130.7, 128.7, 64.9, 40.7, 33.7, 32.6, 28.4, 27.7, 25.0.

FT-IR (neat) 2938, 2860, 1736, 1493, 1252, 1159, 1091, 1017, 807 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{14}H_{18}BrClO_2$: 334, found: 334.



9-Bromononyl furan-2-carboxylate

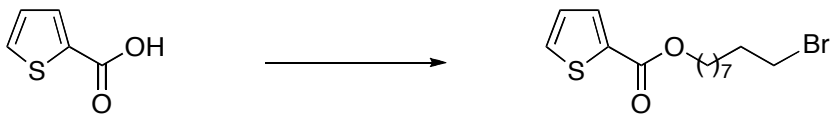
A mixture of furan-2-carboxylic acid (807 mg, 7.20 mmol), 1,9-dibromononane (2.47 g, 8.63 mmol), and K_2CO_3 (1.50 g, 10.8 mmol) in acetone (30 mL) was heated at reflux. After 14 h, the mixture was allowed to cool to r.t., and it was filtered through Celite™ (~2 cm deep pad contained in a sintered glass funnel); the solids thus retained were washed with acetone (20 mL). The combined filtrates were then concentrated under reduced pressure, and the resulting residue was subjected to flash chromatography (silica; 97:2:1 *v*/*v* hexane/EtOAc/Et_3N), which provided the title compound (260 mg, 12%) as a clear, light-yellow oil.

^{1}H NMR (500 MHz, CCl_3) δ 7.58 (dd, 1H, *J* = 1.0, 2.0 Hz), 7.17 (dd, 1H, *J* = 1.0, 7.0 Hz), 6.51 (dd, 1H, *J* = 2.0, 3.5 Hz), 4.30 (t, 2H, *J* = 7.0 Hz), 3.41 (t, 2H, *J* = 7.0 Hz), 1.85 (pentet, 2H, *J* = 7.0 Hz), 1.75 (pentet, 2H, *J* = 7.0 Hz), 1.48-1.24 (m, 10H).

^{13}C NMR (125 MHz, C_6D_6) δ 158.6, 146.1, 145.7, 117.7, 111.9, 64.9, 33.9, 33.0, 29.6, 29.4, 29.0, 28.9, 28.3, 26.1.

FT-IR (neat) 2930, 2856, 1718, 1474, 1296, 1180, 1119, 763 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{14}H_{21}BrO_3$: 314, found: 314.



9-Bromononyl thiophene-2-carboxylate

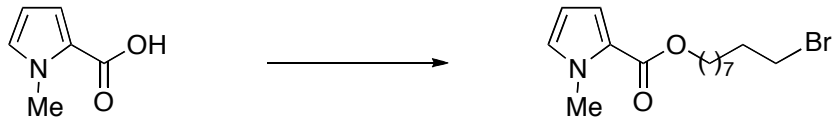
9-Bromononyl thiophene-2-carboxylate was prepared in the same manner as described for the synthesis of 9-bromononyl furan-2-carboxylate, but now using thiophene-2-carboxylic acid. In this way, the title compound (510 mg, 20%) was obtained as a clear, light-yellow oil.

^{1}H NMR (500 MHz, C_6D_6) δ 7.74 (dd, 1H, *J* = 1.5, 4.0 Hz), 6.76 (dd, 1H, *J* = 1.0, 5.0 Hz), 6.52-6.50 (m, 1H), 4.12 (t, 2H, *J* = 7.0 Hz), 2.93 (t, 2H, *J* = 7.0 Hz), 1.48-1.41 (m, 4H), 1.34-1.22 (m, 1H), 1.14-0.95 (m, 9H).

^{13}C NMR (125 MHz, C_6D_6) δ 162.1, 134.7, 133.4, 132.1, 128.4, 65.2, 33.8, 33.0, 29.5, 29.4, 29.0, 28.9, 28.3, 26.2.

FT-IR (neat) 2929, 2855, 1710, 1527, 1420, 1260, 1095 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{14}H_{21}BrO_2S$: 334, found: 334.



9-Bromononyl *N*-methylpyrrole-2-carboxylate

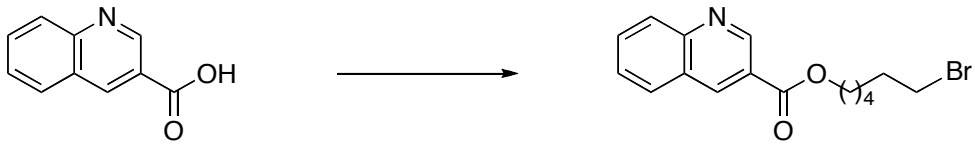
9-Bromononyl *N*-methylpyrrole-2-carboxylate was prepared in the same manner as described for the synthesis of 9-bromononyl furan-2-carboxylate, but now using *N*-methylpyrrole-2-carboxylic acid. In this way, the title compound (750 mg, 57%) was obtained as a clear, light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (dd, 1H, *J* = 1.5, 4.0 Hz), 6.79-6.76 (m, 1H), 6.11 (dd, 1H, *J* = 1.0, 5.0 Hz), 4.21 (t, 2H, *J* = 7.0 Hz), 3.93 (s, 3H), 3.41 (t, 2H, *J* = 7.0 Hz), 1.84 (pentet, 2H, *J* = 7.0 Hz), 1.72 (pentet, 2H, *J* = 7.0 Hz), 1.44-1.33 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 129.4, 122.7, 117.6, 107.8, 63.9, 36.8, 34.0, 32.8, 29.3, 29.2, 28.8, 28.7, 28.2, 26.0.

FT-IR (neat) 2929, 2855, 1701, 1532, 1466, 1416, 1321, 1246, 1114, 737 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{15}H_{24}BrNO_2$: 329, found: 329.



6-Bromohexyl quinoline-3-carboxylate

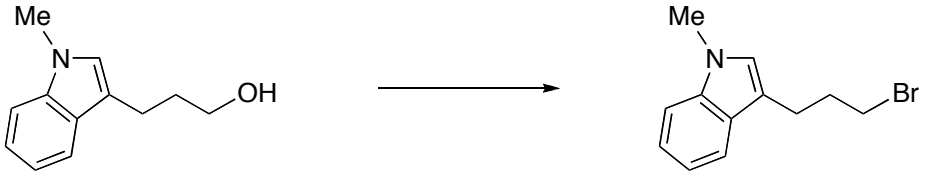
6-Bromohexyl quinoline-3-carboxylate was prepared in the same manner as described for the synthesis of 6-bromohexyl 2-(3-(trifluoromethyl)phenyl)acetate, but now using quinoline-3-carboxylic acid. In this way, the title compound (1.10 g, 63%) was obtained as a bright-yellow solid.

^{1}H NMR (500 MHz, C_6D_6) δ 9.76 (s, 1H), 8.68 (s, 1H), 8.22 (d, 1H, *J* = 8.5 Hz), 7.32 (d, 1H, *J* = 8.0 Hz), 7.27 (dt, 1H, *J* = 1.0, 7.0 Hz), 7.04 (dt, 1H, *J* = 1.0, 7.0 Hz), 4.08 (t, 2H, *J* = 7.0 Hz), 2.88 (t, 2H, *J* = 7.0 Hz), 1.38-1.30 (m, 4H), 1.04-0.93 (m, 4H).

^{13}C NMR (125 MHz, C_6D_6) δ 165.2, 150.5, 150.3, 138.5, 131.7, 130.1, 129.2, 127.3, 127.1, 123.7, 65.2, 33.7, 32.8, 28.7, 27.9, 25.3.

FT-IR (neat) 2936, 1719, 1367, 1287, 1238, 1199, 1104 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{16}H_{18}BrNO_2$: 335, found: 335.



3-(3′-Bromopropyl)-*N*-methylindole

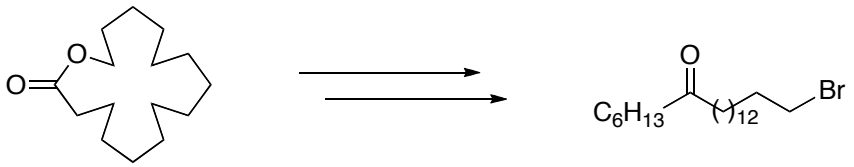
PPh_3Br_2 (3.70 g, 8.80 mmol) was added to a solution of 3-(*N*-methylindol-3′-yl)propan-1-ol[2] (1.85 g, 7.34 mmol) and imidazole (600 mg, 8.80 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 16 h, $Na_2S_2O_3$ (saturated aqueous solution; 10 mL) and NaOH (6 M aqueous solution; 10 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was filtered through a pad of silica (~5 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with a 10% EtOAc/hexane solution (300 mL). The combined filtrates were concentrated under reduced pressure, and the resulting oil was subjected to flash chromatography (silica; 95:5:1 *v*/*v* hexane/EtOAc/Et_3N), which provided the title compound (1.55 g, 63%) as a clear, light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, 1H, *J* = 1.0, 8.0 Hz), 7.35 (dd, 1H, *J* = 1.0, 8.0 Hz), 7.29 (dt, 1H, *J* = 1.0, 8.0 Hz), 7.18 (dt, 1H, *J* = 1.0, 8.0 Hz), 6.93 (s, 1H), 3.78 (s, 3H), 3.49 (t, 2H, *J* = 7.0 Hz), 2.98 (t, 2H, *J* = 7.0 Hz), 2.29 (pentet, 2H, *J* = 8.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 127.8, 126.7, 121.6, 119.0, 118.8, 113.0, 109.3, 34.0, 33.2, 32.6, 23.3.

FT-IR (neat) 3054, 2933, 1615, 1473, 1377, 1326, 1252, 1239, 804, 740 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{12}H_{14}BrN$: 251, found: 251.



21-Bromohenicosan-7-one

Isopropylmagnesium chloride (2.0 M solution in Et_2O; 30 mL, 60 mmol) was added dropwise to a mixture of pentadecanolide (2.60 g, 10.0 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (3.00 g, 30.2 mmol) in THF (60 mL) at 0 °C. The resulting mixture was then warmed to r.t. After 1 h, it was cooled to 0 °C, and NH_4Cl (saturated aqueous solution; 20 mL) was added. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide 15-hydroxy-*N*-methoxy-*N*-methylpentadecanamide, which was used without purification in the next reaction.

Hexylmagnesium bromide (2.0 M solution in Et_2O; 25 mL, 50 mmol,) was added to a solution of 15-hydroxy-*N*-methoxy-*N*-methylpentadecanamide in THF (50 mL) at 0 °C. After 16 h, NH_4Cl (saturated aqueous solution; 20 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide 21-hydroxyhenicosan-7-one, which was used without purification in the next reaction.

PPh_3Br_2 (1.55 g, 3.67 mmol) was added to a solution of 21-hydroxyhenicosan-7-one and imidazole (250 mg, 3.67 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 20 h, $Na_2S_2O_3$ (saturated aqueous solution; 10 mL) and NaOH (6 M aqueous

(2) Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2003**, *125*, 9578–9579.

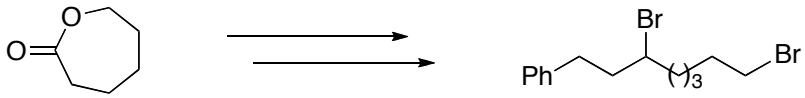
solution; 10 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was then filtered through a pad of silica (~5 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with a 10% EtOAc/hexane solution (300 mL). The combined filtrates were concentrated under reduced pressure, and the resulting residue was subjected to flash chromatography (silica; 5% EtOAc/hexane), which provided the title compound (1.04 g, 27% over 3 steps from pentadecanolide) as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.42 (t, 2H, J = 7.0 Hz), 2.39 (t, 4H, J = 7.5 Hz), 1.79 (pentet, 2H, J = 7.0 Hz), 1.57-1.53 (m, 4H), 1.43 (pentet, 2H, J = 7.5 Hz), 1.26 (br s, 24H), 0.88 (t, 3H, J = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 211.8, 42.9, 34.2, 32.9, 31.7, 29.71, 29.70, 29.64, 29.58, 29.54, 29.4, 29.0, 28.9, 28.3, 24.0, 23.9, 22.6, 14.2.

FT-IR (neat) 3447, 2915, 2850, 1702, 1472 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{21}H_{41}BrO$: 390, found: 390.



(3,8-Dibromooctyl)benzene

Isopropylmagnesium chloride (2.0 M solution in Et_2O; 72 mL, 144 mmol) was added dropwise to a mixture of 2-oxepanone (2.70 g, 23.9 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (7.00 g, 71.8 mmol) in THF (100 mL) at 0 °C. The resulting mixture was then warmed to r.t. After 1 h, it was cooled to 0 °C, and NH_4Cl (saturated aqueous solution; 30 mL) was added. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide 6-hydroxy-*N*-methoxy-*N*-methylhexanamide, which was used without purification in the next reaction.

2-Phenethylmagnesium chloride (1.0 M solution in Et_2O; 60 mL, 60 mmol) was added to a solution of 6-hydroxy-*N*-methoxy-*N*-methylhexanamide in THF (50 mL) at 0 °C. After 2 h of stirring, NH_4Cl (saturated aqueous solution; 20 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash chromatography (silica; 30% EtOAc/hexane), which provided 8-hydroxy-1-phenyloctan-3-one (3.40 g, 51% over 2 steps from 2-oxepanone) as a clear, colorless oil.

PPh_3Br_2 (6.90 g, 16.3 mmol) was added to a solution of 8-hydroxy-1-phenyloctan-3-one (3.0 g, 13.6 mmol) and imidazole (1.1 g, 16.3 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 12 h, $Na_2S_2O_3$ (saturated aqueous solution; 20 mL) and NaOH (6 M aqueous solution; 10 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was filtered through a pad of silica (~5 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with a 10% EtOAc/hexane solution (300 mL). The combined filtrates were concentrated under reduced pressure to provide 8-bromo-1-phenyloctan-3-one, which was used without purification in the next reaction.

$NaBH_4$ (351 mg, 9.27 mmol) was added to a solution of 8-bromo-1-phenyloctan-3-one in MeOH (20 mL) at 0 °C. After 15 h, the mixture was concentrated, CH_2Cl_2 (20 mL) and H_2O (10 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide 8-bromo-1-phenyloctan-3-ol, which was used without purification in the next reaction.

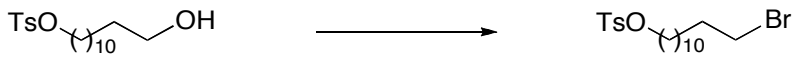
PPh_3Br_2 (3.10 g, 7.42 mmol) was added to a solution of 8-bromo-1-phenyloctan-3-ol and imidazole (505 mg, 7.42 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 16 h, $Na_2S_2O_3$ (saturated aqueous solution; 10 mL) and NaOH (6 M aqueous solution; 5 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was filtered through a pad of silica (~5 cm deep pad contained in a sintered glass funnel), and the solids thus retained were washed with a 5% EtOAc/hexane solution (300 mL). The combined filtrates were concentrated under reduced pressure, and the resulting residue was subjected to flash chromatography (silica; 2% EtOAc/hexane), which provided the title compound (1.00 g, 27% over 3 steps from 8-hydroxy-1-phenyloctan-3-one) as a clear, light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 3.98 (pentet, 1H, J = 8.0 Hz), 3.41 (t, 2H, J = 6.5 Hz), 2.94-2.88 (m, 1H), 2.79-2.73 (m, 1H), 2.18-2.07 (m, 2H), 1.88-1.80 (m, 4H), 1.61-1.44 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 128.60, 128.56, 126.2, 57.5, 40.8, 39.0, 33.8, 32.6, 27.6, 26.8.

FT-IR (neat) 3450, 3026, 2937, 2859, 1603, 1496, 1454, 1240, 749 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{14}H_{20}Br_2$: 348, found: 348.



12-Bromo-1-(tosyloxy)dodecane

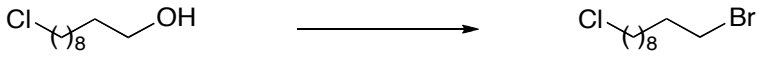
Tosyl chloride (863 mg, 4.52 mmol) was added to a solution of 12-bromododecan-1-ol (1.00 g, 3.77 mmol), Et_3N (1.60 mL, 11.3 mmol), and DMAP (46 mg, 0.38 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 16 h, $Na_2S_2O_3$ (saturated aqueous solution; 10 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (1 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash chromatography (silica; 10% EtOAc/hexane), which provided the title compound (1.50 g, 95%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 8.5 Hz), 7.35 (d, 2H, J = 8.5 Hz), 4.02 (t, 2H, J = 6.5 Hz), 3.41 (t, 2H, J = 7.0 Hz), 2.46 (s, 3H), 1.85 (pentet, 2H, J = 7.0 Hz), 1.63 (pentet, 2H, J = 7.0 Hz), 1.42 (pentet, 2H, J = 7.5 Hz), 1.29-1.22 (m, 14H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 133.2, 129.9, 128.0, 70.8, 34.2, 32.9, 29.52, 29.50, 29.47, 29.4, 29.0, 28.9, 28.8, 28.2, 25.4, 21.7.

FT-IR (neat) 2920, 2852, 1600, 1471, 1357, 1173, 955, 842, 812 cm^{-1}.

MS (EI) m/z (M–OTs^+) calcd for $C_{12}H_{24}Br$: 247, found: 247.



1-Bromo-10-chlorodecane

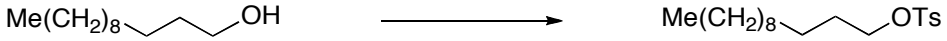
1-Bromo-10-chlorodecane was prepared in the same manner as described for the synthesis of 3-(3′-bromopropyl)-*N*-methylindole, but now using 10-bromodecan-1-ol. In this way, the title compound (2.30 g, 86%) was obtained as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (t, 2H, *J* = 7.0 Hz), 3.42 (t, 2H, *J* = 7.0 Hz), 1.86 (pentet, 2H, *J* = 7.0 Hz), 1.77 (pentet, 2H, *J* = 7.0 Hz), 1.44-1.41 (m, 4H), 1.31 (br s, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 45.2, 34.0, 32.8, 32.7, 29.38, 29.36, 28.9, 28.8, 28.2, 26.9.

FT-IR (neat) 2929, 2855, 2361, 1465, 723 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{10}H_{20}BrCl$: 256, found: 256.



1-(Tosyloxy)dodecane

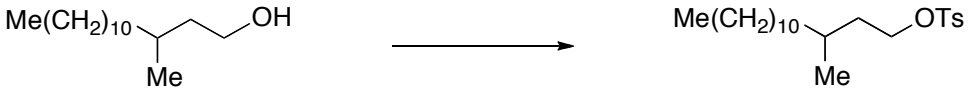
1-(Tosyloxy)dodecane was prepared in the same manner as described for the synthesis of 12-bromo-1-(tosyloxy)dodecane, but now using dodecan-1-ol. In this way, the title compound (7.80 g, 87%) was obtained as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, 2H, *J* = 7.0 Hz), 7.35 (d, 2H, *J* = 8.5 Hz), 4.02 (t, 2H, *J* = 6.5 Hz), 2.45 (s, 3H), 1.63 (pentet, 2H, *J* = 7.0 Hz), 1.30-1.22 (m, 18H), 0.88 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 133.3, 129.9, 128.0, 70.8, 32.0, 29.7, 29.6, 29.5, 29.4, 29.0, 28.9, 25.4, 22.8, 21.7, 14.2.

FT-IR (neat) 2925, 2855, 1599, 1467, 1363, 1178, 1098, 953, 815 cm^{-1}.

MS (ESI) *m*/*z* ($M+Na^+$) calcd for $C_{19}H_{32}NaO_3S$: 363, found: 363.



3-Methyl-1-(tosyloxy)tetradecane

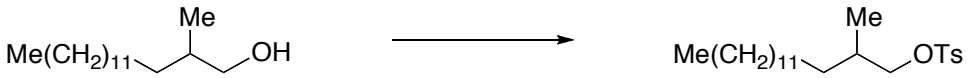
3-Methyl-1-(tosyloxy)tetradecane was prepared in the same manner as described for the synthesis of 12-bromo-1-(tosyloxy)dodecane, but now using 3-methyltetradecan-1-ol. In this way, the title compound (3.20, 64%) was obtained as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H, *J* = 8.5 Hz), 7.35 (d, 2H, *J* = 8.5 Hz), 4.10-4.03 (m, 2H), 2.46 (s, 3H), 1.67 (pentet, 1H, *J* = 7.0 Hz), 1.52-1.39 (m, 2H) 1.30-1.19 (m, 20H), 0.89 (t, 3H, *J* = 7.0 Hz), 0.89 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 133.2, 129.8, 127.9, 69.1, 36.6, 35.7, 32.0, 29.9, 29.73, 29.70, 29.4, 29.2, 26.8, 22.7, 21.6, 19.2, 14.2.

FT-IR (neat) 2925, 2854, 1599, 1466, 1365, 1189, 1178, 1098, 945, 814 cm^{-1}.

MS (ESI) *m*/*z* ($M+Na^+$) calcd for $C_{22}H_{38}NaO_3S$: 405, found: 405.



2-Methyl-1-(tosyloxy)pentadecane

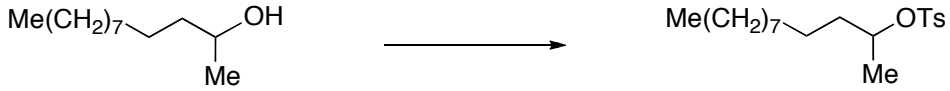
2-Methyl-1-(tosyloxy)pentadecane was prepared in the same manner as described for the synthesis of 12-bromo-1-(tosyloxy)dodecane, but now using 2-methylpentadecan-1-ol. In this way, the title compound (2.10 g, 86%) was obtained as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, 2H, *J* = 8.5 Hz), 7.35 (d, 2H, *J* = 8.5 Hz), 3.87 (dd, 1H, *J* = 5.5, 9.5 Hz), 3.80 (dd, 1H, *J* = 5.0, 10.0 Hz), 2.45 (s, 3H), 1.76 (pentet, 1H, *J* = 6.5 Hz) 1.26-1.07 (m, 24H), 0.90-0.87 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 133.2, 129.8, 127.9, 75.2, 32.9, 32.7, 32.0, 29.77, 29.74, 29.69, 29.61, 29.4, 26.6, 22.8, 21.7, 16.5, 14.2.

FT-IR (neat) 2924, 2853, 1599, 1467, 1364, 1189, 1177, 1098, 968, 813 cm^{-1}.

MS (EI) *m*/*z* (M–OTs$^+$) calcd for $C_{16}H_{33}$: 225, found: 225.



2-(Tosyloxy)dodecane

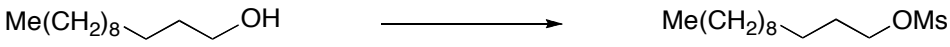
Tosyl chloride (1.90 g, 9.80 mmol) was added to a solution of 2-dodecanol (2.00 mL, 8.91 mmol), pyridine (2.50 mL, 17.8 mmol) in CH_2Cl_2 (24 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 16 h, $NaHCO_3$ (saturated aqueous solution; 10 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (1 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash chromatography (silica; 2% EtOAc/hexane), which provided the title compound (2.50 g, 77%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H, *J* = 8.5 Hz), 7.33 (d, 2H, *J* = 8.5 Hz), 4.60 (sextet, 1H, *J* = 6.0 Hz), 2.45 (s, 3H), 1.64-1.56 (m, 1H), 1.48-1.45 (m, 1H), 1.31-1.16 (m, 19H), 0.88 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 134.5, 129.6, 127.6, 80.5, 36.4, 31.8, 29.5, 29.4, 29.34, 29.26, 29.1, 24.8, 22.6, 21.5, 20.8, 14.0.

FT-IR (neat) 2926, 2855, 2361, 1599, 1496, 1466, 1364, 1177, 1098, 912, 815 cm^{-1}.

MS (ESI) *m*/*z* (M+NH_4^+) calcd for $C_{19}H_{36}NO_3S$: 358, found: 358.



1-(Mesyloxy)dodecane

Mesyl chloride (2.07 mL, 26.8 mmol) was added to a solution of dodecan-1-ol (3.00 mL, 13.4 mmol), Et_3N (5.60 mL, 40.2 mmol), and DMAP (40 mg, 0.33 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 16 h, $NaHCO_3$ (saturated aqueous solution; 10 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash

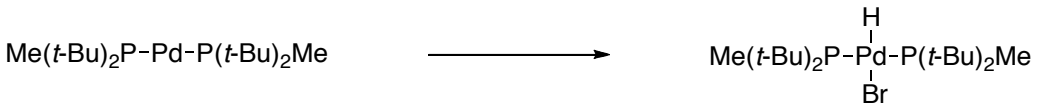
chromatography (silica; 5% EtOAc/hexane), which provided the title compound (3.25 g, 92%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.22 (t, 2H, J = 7.0 Hz), 3.00 (s, 3H), 1.74 (pentet, 2H, J = 7.0 Hz), 1.41-1.26 (m, 18H), 0.88 (t, 3H, J = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 70.3, 37.3, 32.0, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 25.5, 22.7, 14.2.

FT-IR (neat) 3034, 2921, 2853, 1473, 1343, 1329, 1169, 984, 948 cm^{-1}.

MS (ESI) m/z ($M+Na^+$) calcd for $C_{13}H_{28}NaO_3S$: 287, found: 287.



***trans*-Pd(P(*t*-Bu)$_2$Me)$_2$HBr**

In a nitrogen-filled glovebox, 1-bromohexane (74 μL, 0.53 mmol) was added to an oven-dried 20-mL vial containing a solution of Pd(P(*t*-Bu)$_2$Me)$_2$ (205 mg, 0.48 mmol) in Et_2O (2 mL). The vial was capped, the joint was wrapped with electrical tape, and the vial was removed from the glovebox. After 16 h of stirring at r.t., the mixture was filtered through a Büchner funnel, and the solids thus retained were washed with pentane (10 mL). The filtrate was concentrated, pentane (10 mL) was added, and the resulting mixture was filtered through a Büchner funnel once more. The solids were combined and dried under reduced pressure to provide the title compound (170 mg, 70%) as a yellow solid.

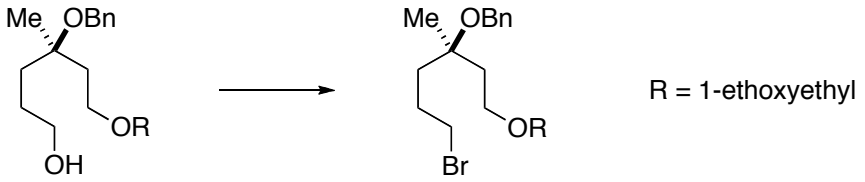
^{1}H NMR (300 MHz, THF–d_8) δ 1.63 (t, 6H, J = 2.5 Hz), 1.27 (t, 36H, J = 8.0 Hz), –12.71 (t, 1H, J = 6.5 Hz).

^{13}C NMR (125 MHz, dioxane–d_8) δ 33.6 (t, J = 10 Hz), 29.3 (t, J = 3 Hz), 6.2 (t, J = 10 Hz).

^{31}P NMR (128 MHz, THF–d_8) δ 53.5.

FT-IR (neat) 2941, 2032, 1465, 1388, 1362, 1290, 1181, 1020, 871, 814 cm^{-1}.

MS (FAB) m/z ($M–HBr^+$) calcd for $C_{18}H_{42}P_2Pd$: 426.1797, found: 426.1795.



(*R*)-{[(6-Bromo-1-(1-ethoxyethoxy)-3-methylhexan-3-yl)oxy]methyl}benzene

A solution of PPh_3Br_2 in CH_2Cl_2 (10 mL) was added dropwise to a solution of (*R*)-4-(benzyloxy)-6-(1-ethoxyethoxy)-4-methylhexan-1-ol[3] (210 mg, 0.68 mmol), imidazole (129 mg, 1.90 mmol), pyridine (0.15 mL, 1.9 mmol), and Et_3N (0.40 mL, 2.8 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 16 h, $Na_2S_2O_3$ (saturated aqueous solution; 5 mL) and $NaHCO_3$ (saturated aqueous solution; 5 mL) were added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic

(3) Ray, N. C.; Raveendranath, P. C.; Spencer, T. A. *Tetrahedron* **1992**, *48*, 9427–9432.

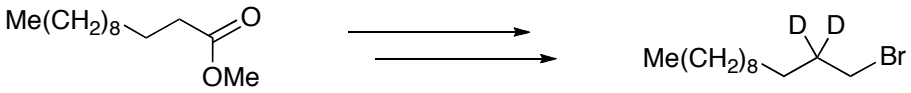
phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash chromatography (silica; 95:5:1 *v*/*v* hexane/EtOAc/Et_3N), which provided the title compound (216 mg, 86%) as a clear, light-yellow oil.

^{1}H NMR (500 MHz, C_6D_6) δ 7.30 (d, 2H, *J* = 8.5 Hz), 7.17 (t, 2H, *J* = 7.5 Hz), 7.07 (t, 1H, *J* = 7.5 Hz), 4.54 (q, 1H, *J* = 5.0 Hz), 4.18 (s, 2H), 3.71 (q, 1H, *J* = 6.0 Hz), 3.51-3.47 (m, 2H), 3.40-3.22 (m, 1H), 2.93 (t, 2H, *J* = 6.5 Hz), 1.85-1.71 (m, 2H), 1.68-1.62 (m, 2H), 1.52-1.36 (m, 2H), 1.24 (d, 3H, *J* = 5.0 Hz), 1.09 (t, 3H, *J* = 7.5 Hz), 0.99 (s, 3H).

^{13}C NMR (125 MHz, C_6D_6) δ 140.1, 128.5, 127.5, 127.3, 99.8, 75.7, 63.4, 61.2, 60.52, 60.50, 38.3, 37.37, 37.32, 34.7, 27.4, 23.64, 23.59, 20.1, 15.7.

FT-IR (neat) 2974, 2921, 2934, 2361, 2341, 1455, 1380, 1131, 1088, 1059 cm^{-1}.

MS (EI) *m*/*z* (M–$C_4H_9O^+$) calcd for $C_{14}H_{20}BrO_2$: 299, found: 299.



1-Bromo-2,2-dideuterododecane

A solution of methyl dodecanoate (1.80 g, 8.40 mmol) in MeOD (8 mL) was added to a mixture of NaOMe (1.00 g, 18.5 mmol) in MeOD (8 mL), and the resulting mixture was heated at reflux. After 90 h, the mixture was allowed to cool to r.t., D_2O (2 mL) was added, and the resulting mixture was filtered through a short pad of silica (Et_2O elution), which provided methyl 2,2-dideuterododecanoate, which was used without purification in the next reaction.

A solution of methyl 2,2-dideuterododecanoate in Et_2O (10 mL) was added dropwise to a suspension of $LiAlH_4$ (450 mg, 11.6 mmol) in Et_2O (15 mL) at 0 °C. The resulting mixture was allowed to slowly warm to r.t. After 16 h, the reaction mixture was cooled to 0 °C, and Et_2O (50 mL), H_2O (0.45 mL), NaOH (6 M aqueous solution; 0.45 mL), and H_2O (1.35 mL) were added in this order. The resulting mixture was warmed to r.t., maintained at this temperature for 15 min, and then dried ($MgSO_4$). After 15 min, the reaction mixture was filtered, and the solids thus retained were washed with CH_2Cl_2 (50 mL). The combined filtrates were concentrated under reduced pressure to afford 2,2-dideuterododecan-1-ol, which was used without purification in the next reaction.

Mesyl chloride (0.42 mL, 5.4 mmol) was added to a solution of 2,2-dideuterododecan-1-ol (840 mg, 4.46 mmol), Et_3N (1.25 mL, 8.92 mmol), and DMAP (110 mg, 0.89 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was allowed to slowly warm to r.t. After 16 h, $NaHCO_3$ (saturated aqueous solution; 10 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide 1-(mesyloxy)-2,2-dideuterododecane, which was used without purification in the next reaction.

LiBr (775 mg, 8.92 mmol) was added to a solution of 1-(mesyloxy)-2,2-dideuterododecane in acetone (15 mL), and the resulting mixture was heated at reflux. After 16 h, the mixture was allowed to cool to r.t., and it was filtered through a short pad of silica (hexane). The resulting residue was then subjected to flash chromatography (silica; hexane), which provided the title compound (500 mg, 24% over 4 steps from methyl dodecanoate) as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40 (s, 2H), 1.48-1.20 (m, 18H), 0.88 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 34.0, 32.1, 29.8, 29.7, 29.6, 29.5, 28.9, 28.2, 22.8, 14.3.

FT-IR (neat) 2924, 2854, 2361, 2341, 1457, 1238 cm^{-1}.
MS (EI) *m*/*z* (M^+) calcd for $C_{12}H_{23}D_2Br$: 250, found: 250.

III. Palladium-Catalyzed Dehydrohalogenation Reactions

General Procedure (alkyl bromides) (conducted in a glovebox; however, see the next procedure). Outside of a glovebox, the alkyl bromide (0.60 mmol) was added to an oven-dried 4-mL vial (containing a stir bar). This vial was then transferred into a glovebox, where dioxane (520 μL), Cy_2NH (140 μL, 0.72 mmol), KO*t*-Bu (480 μL of a 125 mM solution in dioxane; 60 μmol), and $Pd(P(t\text{-}Bu)_2Me)_2$ (the specified amount, in 200 μL of dioxane) were added in turn. The vial was then capped, the joint was wrapped with electrical tape, and the vial was removed from the glovebox. The reaction mixture was stirred at r.t. for 24 h, and then it was filtered through silica (~3 cm height, contained in a sintered glass funnel (1.5 cm diameter)), and the silica was washed with 5% Et_2O/pentane (50 mL). The filtrate was then concentrated under reduced pressure, and the residue was purified by chromatography.

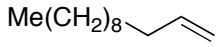
Notes: (a) Although a reaction time of 24 h is employed in the General Procedure, in most cases the reaction is essentially complete within 8–10 h. (b) In order to remove a yellow impurity that is not visible by ^1H, ^{13}C, or ^{31}P NMR spectroscopy, reverse-phase chromatography was used to purify certain reaction products. Alternatively, this unidentified impurity can easily be removed by passing the product obtained by normal-phase flash chromatography through a short pad of $AgNO_3$-impregnated silica gel (25% by weight).

Procedure (alkyl bromides) (without a glovebox). $Pd_2(dba)_3$ (19.2 mg, 21 μmol), $[HP(t\text{-}Bu)_2Me)]BF_4$ (20.9 mg, 84 μmol), and a stir bar were added to an oven-dried 25-mL flask. A rubber septum was fitted to the flask, which was then evacuated and backfilled with argon (3 cycles). The flask was detached from the argon line, and KO*t*-Bu (1.20 mL of a 125 mM solution in dioxane; 0.15 mmol) and Cy_2NH (140 μL, 0.72 mmol) were added in turn via syringe. The puncture holes of the septum were then covered with vacuum grease, and the mixture was stirred at r.t. for 2 h. The vacuum grease was then wiped off, 1-bromododecane (150 mg, 0.60 mmol) was added via syringe, and the puncture holes of the septum were covered with vacuum grease. The reaction mixture was stirred for 24 h, and then it was filtered through silica (~3 cm height, contained in a sintered glass funnel (1.5 cm diameter)), and the silica was washed with 5% Et_2O/pentane (50 mL). The filtrate was then concentrated under reduced pressure, and the residue was purified by chromatography (100% pentane), which afforded 1-dodecene as a clear, colorless oil. First run: 97 mg (96%). Second run (6.0 mmol scale): 902 mg (89%). The product was identical to authentic material (Aldrich) by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, and GC analysis.

Notes: (a) Stirring $Pd_2(dba)_3$ and $[HP(t\text{-}Bu)_2Me]BF_4$ in the presence of Cy_2NH and KO*t*-Bu for 2 h prior to the addition of 1-dodecene is required in order to achieve full conversion. (b) When the reaction is performed under a nitrogen atmosphere, the dehydrohalogenation proceeds in ~90% yield. Thus, the use of argon and the scrupulous removal of air from the reaction vessel is important for optimal and reproducible results, particularly for small-scale reactions.

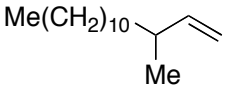
General Procedure (alkyl sulfonates) (conducted in a glovebox). Outside of a glovebox, the alkyl sulfonate (0.60 mmol) was added to an oven-dried 4-mL vial (containing a stir bar). This

vial was then transferred into a glovebox, where TMP (122 μL, 0.72 mmol), LiOMe (the specified volume of a 125 mM solution in dioxane), and $Pd(P(t\text{-}Bu)_2Me)_2$ (the specified amount, in the amount of dioxane that generates a 0.50 M solution) were added in turn. The vial was then capped, the joint was wrapped with electrical tape, and the vial was removed from the glovebox. The reaction mixture was stirred at the specified temperature for the specified time, and then it was filtered through silica (~3 cm height, contained in a sintered glass funnel (1.5 cm diameter)), and the silica was washed with pentane (50 mL). The filtrate was then concentrated under reduced pressure, and the residue was purified by chromatography (pentane).



1-Dodecene [112-41-4] (Table 2, entry 1)

$Pd(P(t\text{-}Bu)_2Me)_2$ (15.4 mg, 36 μmol, 6.0 mol%). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 91 mg (90%). Second run: 98 mg (97%). This product was identical to authentic material (Aldrich) by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and GC analysis.



3-Methyltetradec-1-ene (Table 2, entry 2)

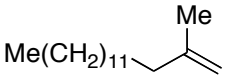
$Pd(P(t\text{-}Bu)_2Me)_2$ (34.6 mg, 81 μmol, 13.5 mol%). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 125 mg (99%). Second run: 124 mg (98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (ddd, 1H, J = 7.5, 10.0, 17.5 Hz), 4.96 (ddd, 1H, J = 1.0, 2.0, 18.0 Hz), 4.90 (ddd, 1H, J = 1.0, 2.0, 10.0 Hz), 2.16-2.06 (m, 1H), 1.26 (br, 20H), 0.97 (d, 3H, J = 7.0 Hz), 0.88 (t, 3H, J = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 112.4, 38.0, 36.9, 32.2, 30.0, 29.93, 29.91, 29.6, 27.5, 22.9, 20.4, 14.3.

FT-IR (neat) 2925, 2854, 1640, 1496, 910 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{15}H_{30}$: 210, found: 210.



2-Methylpentadec-1-ene (Table 2, entry 3)

$Pd(P(t\text{-}Bu)_2Me)_2$ (76.8 mg, 0.18 mmol, 30 mol%). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 133 mg (99%). Second run: 133 mg (99%).

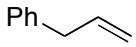
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (d, 2H, J = 11.0 Hz), 2.00 (t, 2H, J = 7.5 Hz), 1.72 (s, 3H), 1.46-1.38 (m, 2H), 1.34-1.24 (m, 20H), 0.89 (t, 3H, J = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 109.7, 38.0, 32.1, 29.88, 29.85, 29.84, 29.75, 29.6, 27.8, 22.9,

22.6, 14.3.

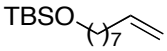
FT-IR (neat) 2925, 2854, 1652, 1457, 886, cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{16}H_{32}$: 224, found: 224.



Allylbenzene [300-57-2] (Table 2, entry 4)

$Pd(P(t\text{-}Bu)_2Me)_2$ (21.8 mg, 51 μmol, 8.5 mol%). First run: 100% calibrated GC yield (*n*-decane used as an internal standard). Second run: 100% calibrated GC yield (*n*-decane used as an internal standard). This product was identical to authentic material (Aldrich) by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, and GC analysis.



1-(*tert*-Butyldimethylsilyloxy)non-8-ene (Table 2, entry 5)

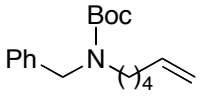
$Pd(P(t\text{-}Bu)_2Me)_2$ (20.5 mg, 48 μmol, 8.0 mol%). The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, colorless oil. First run: 138 mg (90%). Second run: 133 mg (86%).

^1H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, 1H, *J* = 6.5, 10.0, 17.0 Hz), 5.00 (d, 1H, *J* = 17.0 Hz), 4.93 (d, 1H, *J* = 10.0 Hz), 3.60 (t, 2H, *J* = 6.5 Hz), 2.04 (q, 2H, *J* = 6.5 Hz), 1.56-1.46 (m, 2H), 1.44-1.22 (m, 8H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 114.3, 63.4, 33.4, 33.0, 29.5, 29.3, 29.1, 26.1, 25.9, 18.5, –5.1.

FT-IR (neat) 2929, 2857, 1472, 1255, 1102, 836, 775 cm^{-1}.

MS (EI) *m*/*z* ($M–Me^+$) calcd for $C_{14}H_{29}OSi$: 241, found: 241.



***tert*-Butyl-*N*-benzyl(hex-5-en-1-yl)carbamate (Table 2, entry 6)**

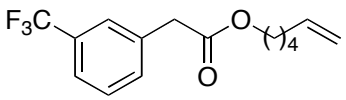
$Pd(P(t\text{-}Bu)_2Me)_2$ (20.5 mg, 48 μmol, 8.0 mol%). The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, colorless oil. First run: 168 mg (97%). Second run: 170 mg (98%).

^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.16 (m, 5H), 5.81-5.73 (m, 1H), 4.99 (d, 1H, *J* = 17.0 Hz), 4.94 (d, 1H, *J* = 10.5 Hz), 4.42 (br s, 2H), 3.22 (br s, 1H), 3.13 (br s, 1H), 2.04 (br s, 2H), 1.58-1.26 (m, 4H), 1.50 (br s, 9/2H), 1.48 (br s, 9/2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 138.6, 128.4, 127.7, 127.1, 114.6, 79.5, 50.5, 49.9, 46.4, 33.4, 28.5, 27.5, 26.1.

FT-IR (neat) 2976, 2931, 1695, 1455, 1416, 1366, 1250, 1170, 910, 881 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{18}H_{27}NO_2$: 289, found: 289.



Hex-5-en-1-yl 2-(3-(trifluoromethyl)phenyl)acetate (Table 2, entry 7)

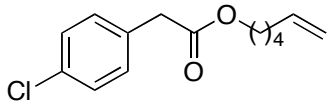
$Pd(P(t\text{-}Bu)_2Me)_2$ (19.2 mg, 45 μmol, 7.5 mol%). The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, colorless oil. First run: 146 mg (84%). Second run: 151 mg (88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.48 (m, 4H), 5.77 (ddt, 1H, *J* = 7.0, 13.5, 17.0 Hz), 5.02-4.95 (m, 2H), 4.12 (t, 2H, *J* = 7.5 Hz), 3.68 (s, 2H), 2.06 (q, 2H, *J* = 7.5 Hz), 1.65 (pentet, 2H, *J* = 7.5 Hz), 1.42 (pentet, 2H, *J* = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 138.3, 135.1, 132.8, 131.0 (q, *J* = 32 Hz), 129.1, 126.2 (q, *J* = 4 Hz), 124.2 (q, *J* = 271 Hz), 124.1 (q, *J* = 4 Hz), 115.0, 65.2, 41.2, 33.3, 28.0, 25.2.

FT-IR (neat) 2939, 1738, 1453, 1332, 1165, 1126, 1077, 914, 701 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{15}H_{17}F_3O_2$: 286, found: 286.



Hex-5-en-1-yl 2-(4-chlorophenyl)acetate (Table 2, entry 8)

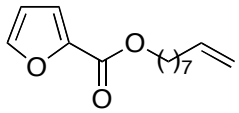
$Pd(P(t\text{-}Bu)_2Me)_2$ (12.8 mg, 30 μmol, 5.0 mol%). The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, colorless oil. First run: 137 mg (90%). Second run: 140 mg (92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, 2H, *J* = 14.0 Hz), 7.21 (d, 2H, *J* = 14.0 Hz), 5.77 (ddt, 1H, *J* = 11.0, 16.5, 21.5 Hz), 5.03-4.94 (m, 2H), 4.09 (t, 2H, *J* = 16.5 Hz), 3.58 (s, 2H), 2.05 (q, 2H, *J* = 12.0 Hz), 1.62 (pentet, 2H, *J* = 12.0 Hz), 1.41 (pentet, 2H, *J* = 12.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 138.2, 133.0, 132.6, 130.6, 128.7, 114.9, 64.9, 40.7, 33.2, 28.0, 25.1.

FT-IR (neat) 2938, 1737, 1493, 1359, 1251, 1159, 1091 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{14}H_{17}ClO_2$: 252, found: 252.



Non-8-en-1-yl furan-2-carboxylate (Table 2, entry 9)

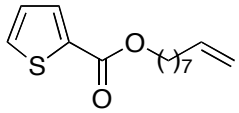
$Pd(P(t\text{-}Bu)_2Me)_2$ (19.2 mg, 45 μmol, 7.5 mol%). The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, yellow oil. First run: 126 mg (89%). Second run: 119 mg (84%).

^{1}H NMR (500 MHz, C_6D_6) δ 7.02 (s, 1H), 6.90 (s, 1H), 5.85 (s, 1H), 5.82-5.72 (m, 1H), 5.04 (d, 1H, *J* = 17.0 Hz), 5.00 (d, 1H, *J* = 10.0 Hz), 4.14 (t, 2H, *J* = 7.0 Hz), 1.94 (pentet, 2H, *J* = 7.0 Hz), 1.47 (pentet, 2H, *J* = 7.0 Hz), 1.24 (pentet, 2H, *J* = 7.0 Hz), 1.19-1.09 (m, 6H).

^{13}C NMR (125 MHz, C_6D_6) δ 158.6, 146.1, 145.7, 139.2, 117.7, 114.6, 111.8, 64.9, 34.2, 29.4, 29.3, 29.2, 29.0, 26.2.

FT-IR (neat) 2929, 2856, 1732, 1581, 1475, 1399, 1296, 1180, 1119, 763 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{14}H_{20}O_3$: 236, found: 236.



Non-8-en-1-yl thiophene-2-carboxylate (Table 2, entry 10)

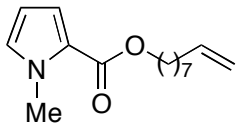
$Pd(P(t\text{-}Bu)_2Me)_2$ (19.2 mg, 45 μmol, 7.5 mol%). The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, light-yellow oil. First run: 146 mg (96%). Second run: 146 mg (96%).

^1H NMR (500 MHz, C_6D_6) δ 7.74 (d, 1H, *J* = 3.5 Hz), 6.74 (s, 1H), 6.51 (d, 1H, *J* = 3.5 Hz), 5.74 (ddt, 1H, *J* = 5.0, 6.5, 17.0 Hz), 5.02 (ddd, 1H, *J* = 1.0, 1.5, 17.0 Hz), 4.96 (ddd, 1H, *J* = 1.0, 1.5, 6.5 Hz), 4.10 (t, 2H, *J* = 7.0 Hz), 1.91 (pentet, 2H, *J* = 7.0 Hz), 1.42 (pentet, 2H, *J* = 7.0 Hz), 1.22 (pentet, 2H, *J* = 7.0 Hz), 1.15-1.04 (m, 6H).

^{13}C NMR (125 MHz, C_6D_6) δ 162.0, 139.2, 134.8, 133.4, 132.1, 127.8, 114.6, 65.2, 34.2, 29.4, 29.3, 29.2, 29.0, 26.2.

FT-IR (neat) 2928, 2856, 1713, 1526, 1420, 1359, 1094 cm^{-1}.

MS (ESI) *m*/*z* ($M+Na^+$) calcd for $C_{14}H_{20}NaO_2S$: 275, found: 275.



Non-8-en-1-yl *N*-methylpyrrole-2-carboxylate (Table 2, entry 11)

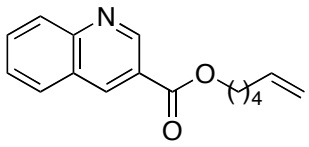
$Pd(P(t\text{-}Bu)_2Me)_2$ (19.2 mg, 45 μmol, 7.5 mol%). For this dehydrobromination, 2.5 mol% KO*t*-Bu (120 μL of a 125 mM solution in dioxane; 15 μmol) was used. The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, colorless oil. First run: 137 mg (92%). Second run: 139 mg (93%). Olefin isomerization was observed (17:1 ratio of terminal to internal alkenes, as determined by ^1H NMR spectroscopy).

^1H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, 1H, *J* = 1.5, 4.0 Hz), 6.78 (s, 1H), 6.12-6.11 (m, 1H), 5.81 (ddt, 1H, *J* = 6.5, 10.0, 17.0 Hz), 5.00 (ddd, 1H, *J* = 1.5, 1.5, 17.0 Hz), 4.94 (ddd, 1H, *J* = 0.5, 1.0, 10.0 Hz), 4.22 (t, 2H, *J* = 6.5 Hz), 3.93 (s, 3H), 2.05 (q, 2H, *J* = 6.5 Hz), 1.72 (pentet, 2H, *J* = 7.0 Hz), 1.43-1.32 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 139.1, 129.4, 122.7, 117.7, 114.3, 107.8, 63.9, 36.9, 33.8, 29.2, 29.1, 28.9, 26.1.

FT-IR (neat) 3076, 2929, 2856, 1705, 1641, 1532, 1468, 1415, 1321, 1247, 1116, 910, 736 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{15}H_{23}NO_2$: 249, found: 249.



Hex-5-en-1-yl quinoline-3-carboxylate (Table 2, entry 12)

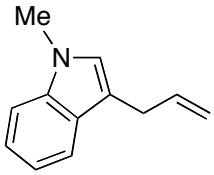
$Pd(P(t\text{-}Bu)_2Me)_2$ (30.7 mg, 72 μmol, 12 mol%). The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, yellow oil. First run: 149 mg (97%). Second run: 147 mg (96%).

^{1}H NMR (500 MHz, C_6D_6) δ 9.73 (d, 1H, J = 2.0 Hz), 8.64 (d, 1H, J = 2.0 Hz), 8.22 (d, 1H, J = 8.5 Hz), 7.30-7.26 (m, 2H), 7.04 (td, 1H, J = 1.0, 8.5 Hz), 5.64 (ddt, 1H, J = 7.0, 10.5, 17.0 Hz), 4.98-4.92 (m, 2H), 4.11 (t, 2H, J = 6.5 Hz), 1.87-1.82 (m, 2H), 1.46-1.41 (m, 2H), 1.28-1.19 (m, 2H).

^{13}C NMR (125 MHz, C_6D_6) δ 165.2, 150.5, 150.4, 138.5, 138.4, 131.6, 130.1, 129.2, 127.2, 127.1, 123.7, 115.1, 65.2, 33.6, 28.4, 25.5.

FT-IR (neat) 3411, 2934, 1721, 1620, 1286, 1238, 790, 769 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{16}H_{17}NO_2$: 255, found: 255.



3-Allyl-*N*-methylindole (Table 2, entry 13)

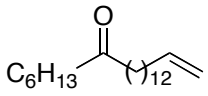
$Pd(P(t\text{-}Bu)_2Me)_2$ (17.9 mg, 42 μmol, 7.0 mol%). The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, light-yellow oil. First run: 88 mg (85%). Second run: 85 mg (83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dt, 1H, J = 1.5, 7.0 Hz), 7.44-7.24 (m, 3H), 6.95 (s, 1H), 6.23 (ddt, 1H, J = 11.0, 16.5, 27.5 Hz), 5.33 (ddd, 1H, J = 2.0, 2.5, 27.5 Hz), 5.23 (ddd, 1H, J = 2.0, 2.5, 16.5 Hz), 3.82 (s, 3H), 3.67 (d, 2H, J = 11.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 137.2, 127.9, 126.6, 121.6, 119.3, 118.8, 115.1, 113.0, 109.3, 32.7, 29.9.

FT-IR (neat) 3056, 2912, 2361, 1637, 1473, 1424, 1374, 1328, 911, 738 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{12}H_{13}N$: 171, found: 171.



Henicos-20-en-7-one (Table 2, entry 14)

$Pd(P(t\text{-}Bu)_2Me)_2$ (38.4 mg, 90 μmol, 15 mol%). The product was purified by flash chromatography on silica gel (2% Et_2O/pentane). The residue was then passed through a short pad of $AgNO_3$-doped silica gel (25% by weight; 10% Et_2O/pentane). Colorless solid. First run: 176 mg (95%). Second run: 167 mg (90%).

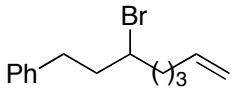
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, 1H, J = 6.5, 10.0, 17.0 Hz), 5.00 (ddd, 1H, J = 1.5, 1.5,

17.0 Hz), 4.93 (ddd, 1H, J = 1.0, 1.5, 10.0 Hz), 2.38 (t, 4H, J = 7.0 Hz), 2.04 (q, 2H, J = 7.0 Hz), 1.56 (pentet, 4H, J = 6.5 Hz), 1.26 (br s, 24H), 0.88 (t, 3H, J = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 211.5, 139.2, 114.1, 42.8, 33.9, 31.7, 29.69, 29.67, 29.57, 29.55, 29.5, 29.3, 29.2, 29.0, 23.92, 23.88, 22.6, 14.1.

FT-IR (neat) 2917, 2849, 1705 cm^{-1}.

MS (EI) m/z (M^+) m/z (M_+) calcd for $C_{21}H_{40}O$: 308, found: 308.



(3-Bromooct-7-en-1-yl)benzene (Table 2, entry 15)

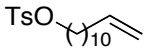
$Pd(P(t\text{-}Bu)_2Me)_2$ (30.7 mg, 72 μmol, 12 mol%). For this dehydrobromination, 20 mol% KO*t*-Bu (960 μL of a 125 mM solution in dioxane; 120 μmol) was used. The product was purified by reverse-phase chromatography (10% MeCN/H_2O → MeCN) twice. Clear, yellow oil. First run: 121 mg (75%). Second run: 128 mg (80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.18 (m, 5H), 5.79 (ddt, 1H, J = 6.5, 10.0, 17.0 Hz), 5.01 (d, 1H, J = 17.0 Hz), 4.97 (d, 1H, J = 10.0 Hz), 3.99 (septet, 1H, J = 4.5 Hz), 2.94-2.88 (m, 1H), 2.79-2.73 (m, 1H), 2.19-2.02 (m, 4H), 1.92-1.80 (m, 2H), 1.71-1.62 (m, 1H), 1.56-1.48 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 138.3, 128.63, 128.57, 126.2, 115.1, 57.5, 40.8, 38.7, 33.8, 33.2, 26.8.

FT-IR (neat) 3064, 3027, 2941, 2860, 1641, 1603, 1496, 1454, 1229, 993, 912, 749 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{14}H_{19}Br$: 268, found: 268.



1-(Tosyloxy)dodec-11-ene (Table 2, entry 16)

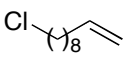
$Pd(P(t\text{-}Bu)_2Me)_2$ (28.2 mg, 66 μmol, 11 mol%). The product was purified by flash chromatography on silica gel (5% EtOAc/hexane), followed by reverse-phase chromatography (10% MeCN/H_2O → MeCN). Clear, colorless solid. First run: 173 mg (85%). Second run: 178 mg (88%). Olefin isomerization was observed (6:1 ratio of terminal to internal alkenes, as determined by ^{1}H NMR spectroscopy).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.5 Hz), 7.34 (d, 2H, J = 8.5 Hz), 5.81 (ddt, 1H, J = 6.5, 10.0, 17.0 Hz), 4.91 (d, 1H, J = 17.0 Hz), 4.95 (d, 1H, J = 10.0 Hz), 4.02 (t, 2H, J = 6.5 Hz), 2.45 (s, 3H), 2.04 (pentet, 2H, J = 6.5 Hz), 1.66-1.59 (m, 2H), 1.42-1.16 (m, 14H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 139.2, 133.2, 129.9, 127.9, 114.2, 70.8, 33.8, 29.5, 29.4, 29.1, 28.9, 28.8, 25.3, 21.7.

FT-IR (neat) 3075, 2927, 2855, 1640, 1599, 1466, 1363, 1179, 1099, 959, 815 cm^{-1}.

MS (ESI) m/z ($M+Na^+$) calcd for $C_{19}H_{30}NaO_3S$: 361, found: 361.



10-Chlorodec-1-ene (Table 2, entry 17)

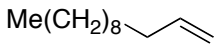
$Pd(P(t\text{-}Bu)_2Me)_2$ (16.6 mg, 39 μmol, 6.5 mol%). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 91 mg (87%). Second run: 95 mg (91%).

^1H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, 1H, J = 7.0, 10.0, 17.0 Hz), 5.00 (ddd, 1H, J = 1.0, 1.5, 17.0 Hz), 4.96 (ddd, 1H, J = 1.0, 1.0, 10.0 Hz), 3.54 (t, 2H, J = 7.0 Hz), 2.04 (q, 2H, J = 7.0 Hz), 1.76 (pentet, 2H, J = 7.0 Hz), 1.48-1.24 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 114.3, 45.2, 33.9, 32.8, 29.4, 29.1, 28.99, 28.97, 27.0.

FT-IR (neat) 3077, 2928, 2856, 1641, 1463, 1310, 993, 910, 725 cm^{-1}.

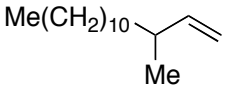
MS (EI) m/z (M^+) calcd for $C_{10}H_{19}Cl$: 174, found: 174.



1-Dodecene [112-41-4] (Table 3, entry 1)

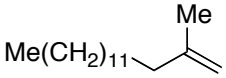
$Pd(P(t\text{-}Bu)_2Me)_2$ (15.4 mg, 36 μmol, 6.0 mol%), LiOMe (288 μL of a 125 μM solution in dioxane; 6.0 mol%), 80 °C (8 h). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 99 mg (98%). Second run: 100 mg (99%). This product was identical to authentic material (Aldrich) by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, and GC analysis.

Olefin isomerization was observed (18:1 ratio of terminal to internal alkenes, as determined by ^1H NMR spectroscopy).



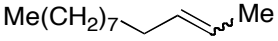
3-Methyltetradec-1-ene (Table 3, entry 2)

$Pd(P(t\text{-}Bu)_2Me)_2$ (15.4 mg, 36 μmol, 6.0 mol%), LiOMe (288 μL of a 125 μM solution in dioxane; 6.0 mol%), 90 °C (24 h). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 122 mg (97%). Second run: 123 mg (97%).



2-Methylpentadec-1-ene (Table 3, entry 3)

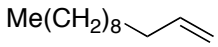
$Pd(P(t\text{-}Bu)_2Me)_2$ (43.5 mg, 100 μmol, 17 mol%), LiOMe (816 μL of a 125 μM solution in dioxane; 6.0 mol%), 100 °C (24 h). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 129 mg (96%). Second run: 130 mg (97%).



2-Dodecene and 1-dodecene (Table 3, entry 4)

$Pd(P(t\text{-}Bu)_2Me)_2$ (64 mg, 150 μmol, 25 mol%), LiOMe (1.2 mL of a 125 μM solution in dioxane;

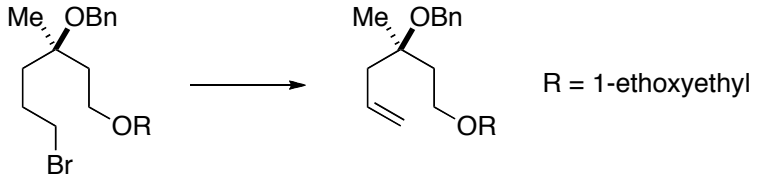
25 mol%), 100 °C (24 h). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 97 mg (96%). Second run: 93 mg (92%). Olefin isomerization was observed (1:2 ratio of terminal to internal alkenes, as determined by ^{1}H NMR spectroscopy).



1-Dodecene [112-41-4] (Table 3, entry 5)

$Pd(P(t\text{-}Bu)_2Me)_2$ (30.7 mg, 72 μmol, 12 mol%), LiOMe (576 μL of a 125 μM solution in dioxane; 12 mol%), 80 °C (8 h). The product was purified by flash chromatography on silica gel (100% pentane). Clear, colorless oil. First run: 88 mg (87%). Second run: 95 mg (94%). This product was identical to authentic material (Aldrich) by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and GC analysis.

Olefin isomerization was observed (14:1 ratio of terminal to internal alkenes, as determined by ^{1}H NMR spectroscopy).



(*R*)-{[(1-(1-Ethoxyethoxy)-3-methylhex-5-en-3-yl)oxy]methyl}benzene (Figure 2)

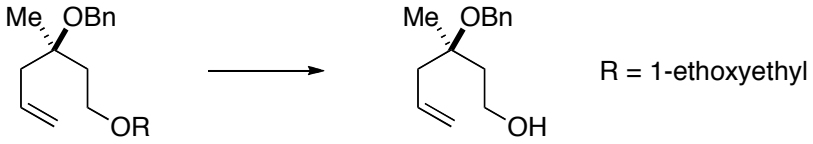
The title compound was prepared according to the general procedure from (*R*)-{[(6-bromo-1-(1-ethoxyethoxy)-3-methylhexan-3-yl)oxy]methyl}benzene (160 mg, 0.43 mmol) with $Pd(P(t\text{-}Bu)_2Me)_2$ (18.3 mg, 43 μmol, 10 mol%). The product was purified by flash chromatography (25% by weight $AgNO_3$-doped silica/silica; 90:10:1 *v*/*v* hexane/EtOAc/Et_3N) and isolated as a clear, light-yellow oil (117 mg, 93%).

^{1}H NMR (500 MHz, C_6D_6) δ 7.37 (d, 2H, *J* = 8.0 Hz), 7.21 (t, 2H, *J* = 7.5 Hz), 7.11 (t, 1H, *J* = 7.0 Hz), 5.94-5.86 (m, 1H), 5.06-5.00 (m, 2H), 4.63-4.57 (m, 1H), 4.28 (s, 2H), 3.87-3.79 (m, 1H), 3.70-3.51 (m, 2H), 3.37-3.25 (m, 1H), 2.31-2.20 (m, 2H), 1.99-1.84 (m, 2H), 1.27 (t, 3H, *J* = 5.5 Hz), 1.13 (s, 6H).

^{13}C NMR (125 MHz, C_6D_6) δ 140.2, 134.8, 128.5, 127.5, 127.3, 117.6, 100.0, 99.8, 76.0, 63.5, 61.3, 61.2, 43.8, 43.7, 38.2, 23.7, 23.6, 20.0, 15.7.

FT-IR (neat) 2976, 2932, 2361, 2341, 1718, 1455, 1381, 1274, 1131, 1098, 1060, 914 cm^{-1}.

MS (EI) *m*/*z* ($M-C_4H_9O^+$) calcd for $C_{14}H_{19}O_2$: 219, found: 219.



(*R*)-3-(Benzyloxy)-3-methylhex-5-en-1-ol (Figure 2)

A solution of HCl (4 M aqueous solution; 0.2 mL) was added dropwise to a mixture of silica

gel (1 g) in CH_2Cl_2 (5 mL). The mixture was cooled to 0 °C, and a solution of (*R*)-{[(1-(1-ethoxyethoxy)-3-methylhex-5-en-3-yl)oxy]methyl}benzene (89 mg, 0.30 mmol) in CH_2Cl_2 (3 mL) was added dropwise. After 4 h of stirring at 0 °C, the mixture was filtered through a short pad of silica (Et_2O). The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica; 7:3 *v*/*v* hexane/Et_2O), which provided the title compound as a clear, colorless oil (66 mg, 98%).[4]

^{1}H NMR (500 MHz, C_6D_6) δ 7.25 (d, 2H, *J* = 7.0 Hz), 7.14 (m, 2H), 7.05 (t, 1H, *J* = 7.0 Hz), 5.70 (ddt, 1H, *J* = 3.0, 10.0, 17.5 Hz), 4.99-4.91 (m, 2H), 4.15 (s, 2H), 3.66 (m, 2H), 2.13 (m, 2H) 1.72 (m, 1H), 1.44 (m, 1H), 1.28 (br s, 1H), 0.98 (s, 3H).

^{13}C NMR (125 MHz, C_6D_6) δ 137.7, 132.5, 126.6, 125.63, 125.56, 115.8, 75.6, 61.8, 57.0, 41.3, 38.6, 21.0.

FT-IR (neat) 3419, 2929, 1718, 1640, 1455, 1382, 1051, 914 cm^{-1}.

MS (ESI) *m*/*z* ($M+Na^+$) calcd for $C_{14}H_{20}NaO_2$: 243, found: 243.

$[\alpha]^{23}_D = -3.2°$ (c = 0.0145, CH_2Cl_2).

IV. Mechanistic Studies

Determination of the Rate Law for 1-Bromododecane. 1-Bromododecane (25 mg, 0.10 mmol) and *n*-decane (19.5 μL, 0.10 mmol; internal standard) were added to a 4-mL vial equipped with a stir bar. This vial was transferred into a glovebox, where dioxane (150 μL), Cy_2NH (24 μL, 0.12 mmol), and $Pd(P(t\text{-}Bu)_2Me)_2$ (the specified amount, in 50 μL of dioxane) were added in turn. The vial was then capped, and the reaction mixture was stirred at room temperature in the glovebox. An aliquot was taken from the reaction mixture every 10 min over a period of 60 min. The aliquots thus obtained were quenched upon removal from the glovebox, and after dilution with Et_2O the mixtures were passed through Acrodisc filters. The amount of product and starting material was determined by GC analysis (calibrated with *n*-decane as an internal standard). The initial rate was measured by plotting the yield of 1-dodecene over the first 60 min of the reaction.

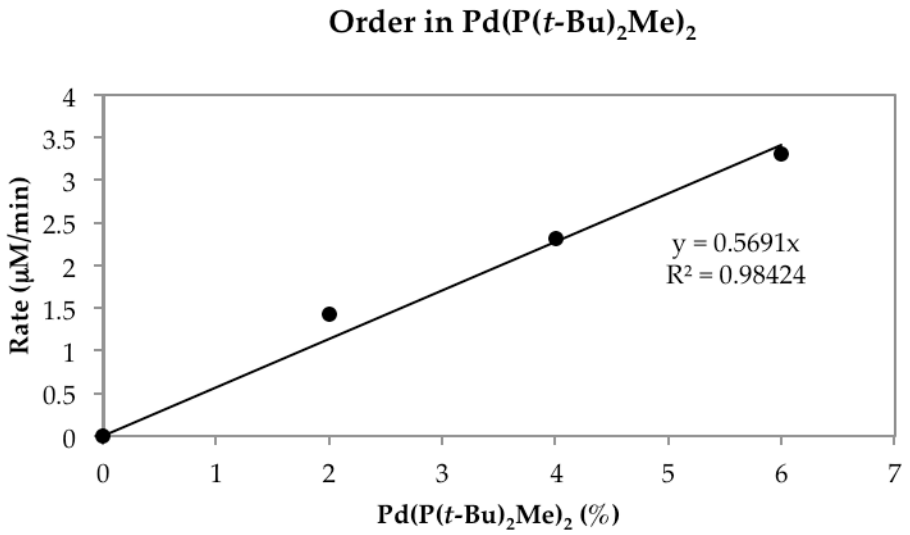
Order in $Pd(P(t\text{-}Bu)_2Me)_2$

Table S1. Observed Initial Rates.

$Pd(P(t\text{-}Bu)_2Me)_2$ (%)	k_{obs} (μM/min)
0	0
2	1.4
4	2.3
6	3.3

(4) Ray, N. C.; Raveendrath, P. C.; Spencer, T. A. *Tetrahedron* **1992**, *48*, 9427–9432.

Figure S1.

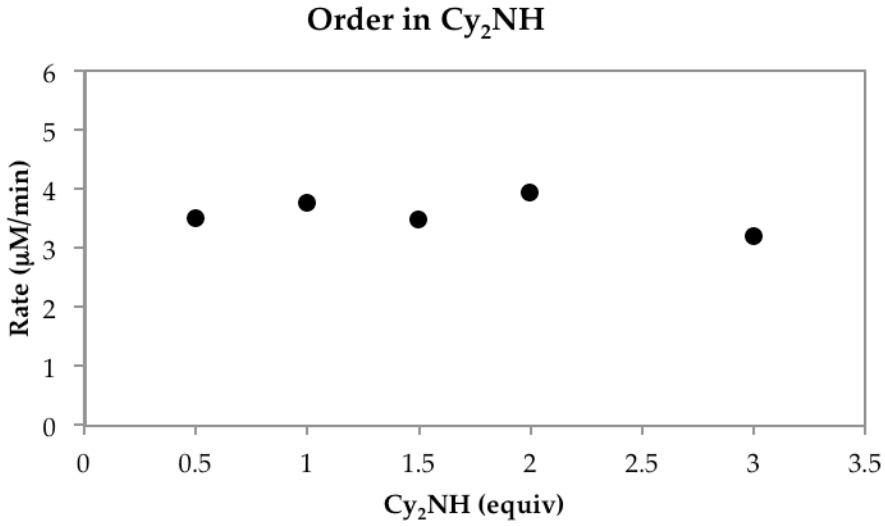


Order in Cy_2NH

Table S2. Observed Initial Rates.

Cy_2NH (equiv)	k_{obs} (μM/min)
0.5	3.5
1	3.8
1.5	3.5
2	3.9
3	3.2

Figure S2.

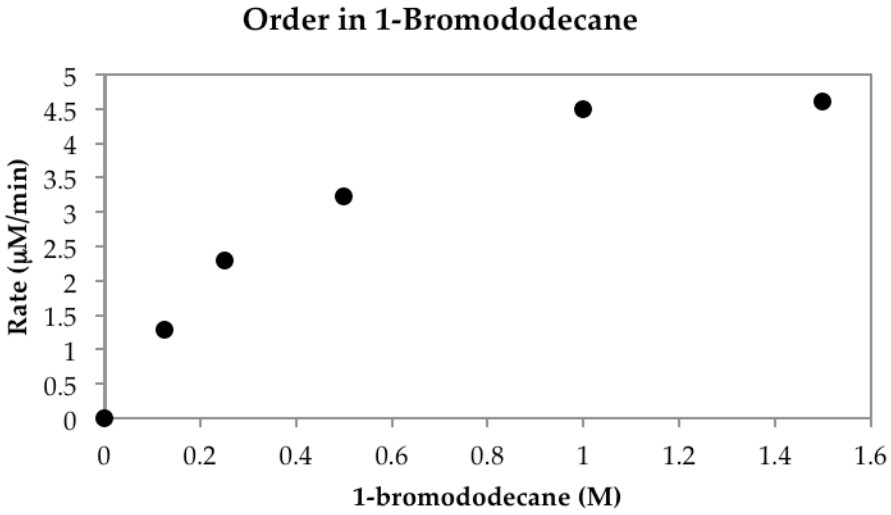


Order in 1-Bromododecane

Table S3. Observed Initial Rates.

1-bromododecane (mM)	k_{obs} (μM/min)
0	0
0.125	1.3
0.25	2.3
0.5	3.2
1	4.5
1.5	4.6

Figure S3.



eq 4

In a glovebox, 1-bromododecane (9.0 mg, 36 μmol) and Pd(P(*t*-Bu)$_2$Me)$_2$ (12.2 mg, 29 μmol; in 480 μL of dioxane) were added to a screw-cap NMR tube. The progress of the reaction was monitored periodically by ^{31}P NMR spectroscopy.

Table S4. Relative amounts of palladium compounds.

Time (h)	L_2Pd	L_2PdRBr	L_2PdHBr
0.08	70	17	13
0.33	38	25	38
0.58	20	22	58
0.83	5	25	70
1.1	5	20	75
1.5	trace	17	83
2.0	–	12	88
2.5	–	10	90
3.0	–	–	100

L = P(*t*-Bu)$_2$Me

eq 5

In a glovebox, 1-bromododecane (9.0 mg, 36 μmol), P(*t*-Bu)$_2$Me (8.4 mg, 43 μmol), Pd(P(*t*-Bu)$_2$Me)$_2$ (12.2 mg, 29 μmol; in 240 μL of dioxane), $OPPh_3$ (7.9 mg, 29 μmol; in 240 μL of dioxane solution; internal standard) were added to a screw-cap NMR tube. The progress of the reaction was monitored periodically by ^{31}P NMR spectroscopy.

Table S5. Relative amounts of palladium compounds.

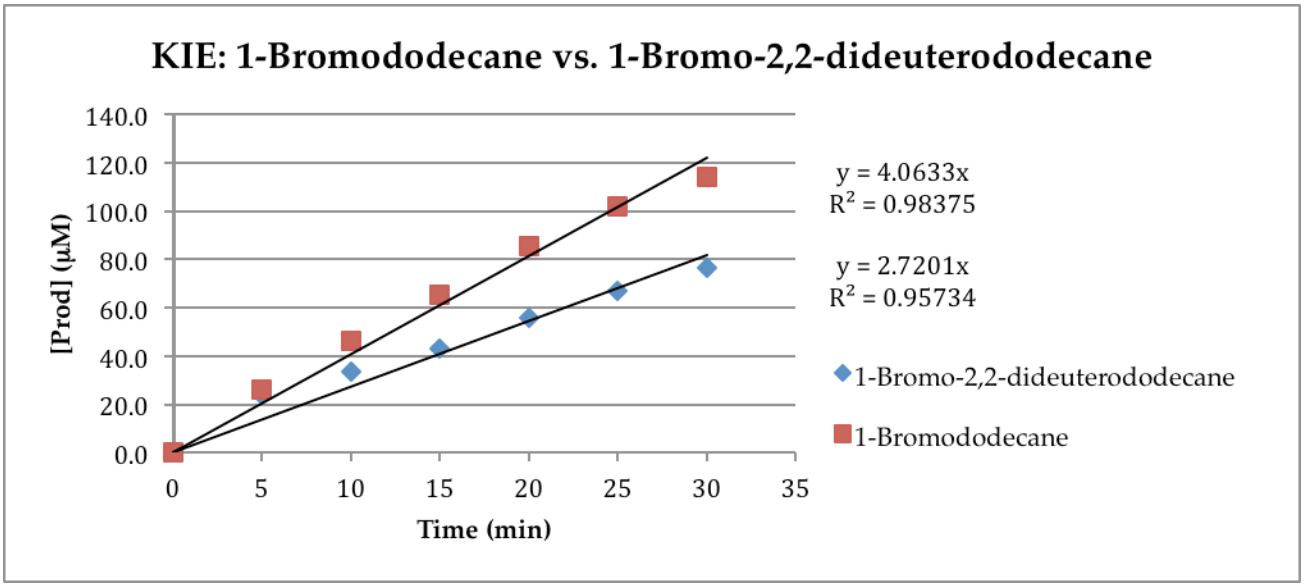
Time (h)	L_2Pd	L_2PdRBr	L_2PdHBr
1.0	10	78	12
1.5	trace	80	20
2.0	–	75	25
3.0	–	62	38
6.0	–	34	66
10.0	–	14	86
12.0	–	–	100

L = P(*t*-Bu)$_2$Me

Procedure for Kinetic Isotope Effect Experiments (1-bromododecane vs. 1-bromododecane-2,2-d$_2$) (eq 6). 1-Bromododecane (24 μL, 0.10 mmol) and *n*-decane (19.5 μL, 0.10 mmol; internal standard) were added to a 4-mL vial equipped with a stir bar. This vial was transferred into a glovebox, where dioxane (150 μL), Cy_2NH (24 μL, 0.12 mmol), and Pd(P(*t*-Bu)$_2$Me)$_2$ (2.6 mg, 6.0 μmol; in 50 μL of dioxane) were added in turn. The vial was then capped, and the reaction mixture was stirred at room temperature in the glovebox. An aliquot was taken from the reaction mixture every 5 min over a period of 30 min. The aliquots thus obtained were quenched upon removal from the glovebox, and after dilution with Et_2O the mixtures were passed through Acrodisc filters. The amount of product and starting material was determined by GC analysis (calibrated with *n*-decane as an internal standard). The initial rate was measured by plotting the yield of 1-dodecene over the first 30 min of the reaction.

This procedure was repeated, but with 1-bromododecane-2,2-d$_2$ rather than with 1-bromododecane.

Figure S4.



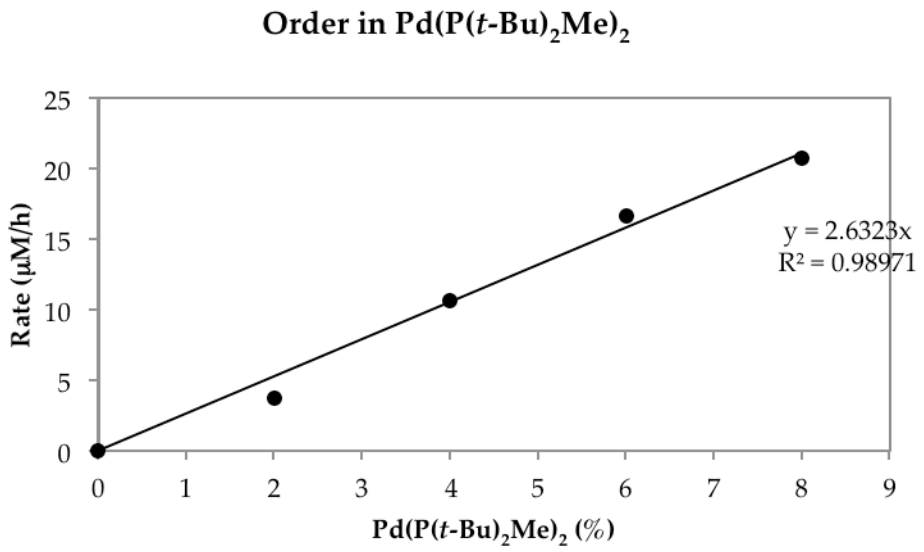
Determination of the Rate Law for 1-Bromo-2-methylpentadecane (eq 7). 1-Bromo-2-methylpentadecane (31 mg, 0.10 mmol) and *n*-decane (19.5 μL, 0.10 mmol; internal standard) were added to a 4-mL vial equipped with a stir bar. This vial was transferred into a glovebox, where dioxane (150 μL), Cy_2NH (24 μL, 0.12 mmol), and $Pd(P(t\text{-}Bu)_2Me)_2$ (the specified amount, in 50 μL of dioxane) were added in turn. The vial was then capped, and the reaction mixture was stirred at room temperature in the glovebox. An aliquot was taken from the reaction mixture every 10 min over a period of 2.5 h. The aliquots thus obtained were quenched upon removal from the glovebox, and after dilution with Et_2O the mixtures were passed through Acrodisc filters. The amount of product and starting material was determined by GC analysis (calibrated with *n*-decane as an internal standard). The initial rate was measured by plotting the yield of 1-dodecene over the first 2.5 h of the reaction.

Order in $Pd(P(t\text{-}Bu)_2Me)_2$

Table S6. Observed Initial Rates.

$Pd(P(t\text{-}Bu)_2Me)_2$ (%)	k_{obs} (μM/h)
0	0
2	3.8
4	10.6
6	16.6
8	20.8

Figure S5.

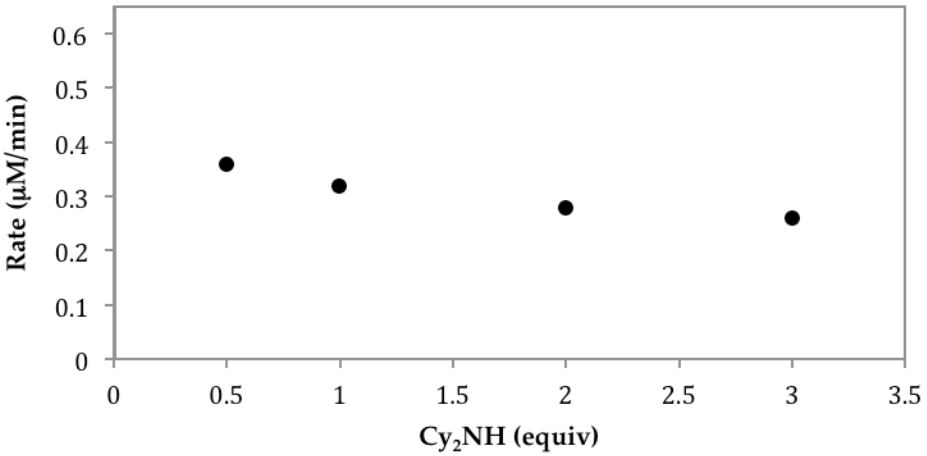


Order in Cy_2NH (aliquots taken every 10 min for 50 min)

Table S7. Observed Initial Rates.

Cy_2NH (equiv)	k_{obs} (μM/min)
0.5	0.36
1	0.32
2	0.28
3	0.26

Figure S6.

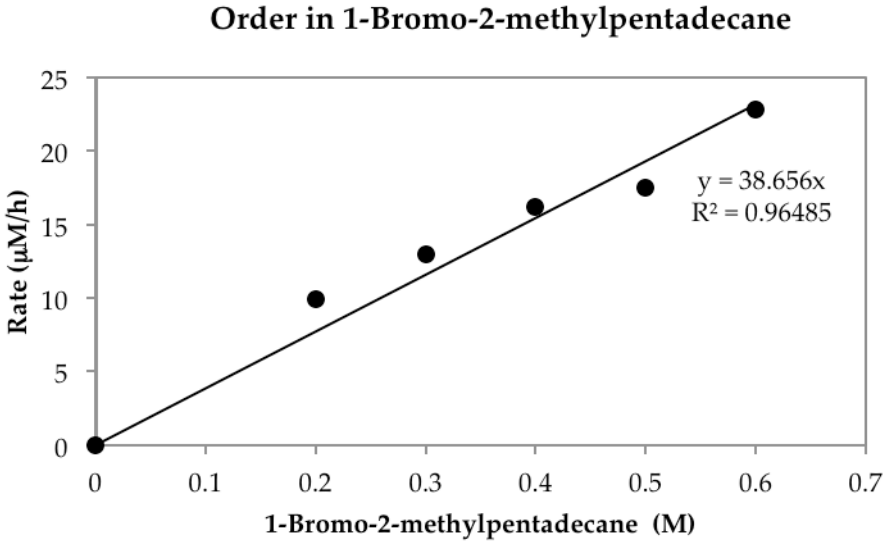


Order in 1-Bromo-2-methylpentadecane

Table S8. Observed Initial Rates.

1-bromo-2-methylpentadecane (M)	k_{obs} (μM/h)
0	0
0.2	9.9
0.3	13
0.4	16.2
0.5	17.5
0.6	22.8

Figure S7.



eq 9

In a glovebox, Cy_2NH (118 mg, 0.59 mmol) and *trans*-$Pd(P(t\text{-}Bu)_2Me)_2HBr$ (15.0 mg, 30 μmol; in 480 μL of dioxane) were added to a screw-cap NMR tube. The progress of the reaction was monitored periodically by ^{31}P NMR spectroscopy.

Table S9. Relative ratios of palladium compounds.

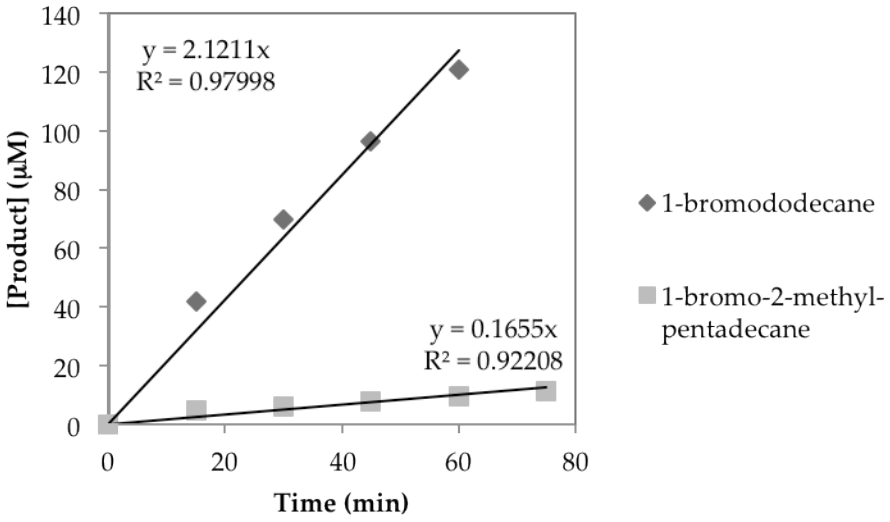
Time (h)	**L_2PdHBr**	**L_2Pd**
24	40	1

L = $P(t\text{-}Bu)_2Me$

General Procedure for Competition Experiments: Reactivity as a Function of the Steric Demand of the Alkyl Bromide. 1-Bromododecane (24 mg, 0.10 mmol), the second alkyl bromide (0.10 mmol), and *n*-decane (19.5 μL, 0.10 mmol; internal standard) were added to a 4-mL vial equipped with a stir bar. This vial was transferred into a glovebox, where dioxane (140 μL), Cy_2NH (48 μL, 0.24 mmol), KO*t*-Bu (160 μL of a 125 μM dioxane solution, 20 μmol), and $Pd(P(t\text{-}Bu)_2Me)_2$ (5.2 mg, 12 μmol, in 100 μL of dioxane) were added. The vial was then capped, and the reaction mixture was stirred at room temperature in the glovebox. An aliquot was taken from the reaction mixture every 15 minutes over a period of 60-75 minutes. The aliquots thus obtained were quenched upon removal from the glovebox, and after dilution with Et_2O the mixtures were passed through Acrodisc filters. The amount of product and starting material was determined by GC analysis (calibrated with *n*-decane as an internal standard). The initial rate was measured by plotting the yield of 1-dodecene and the yield of the other alkene over the first 60-75 min of the reaction.

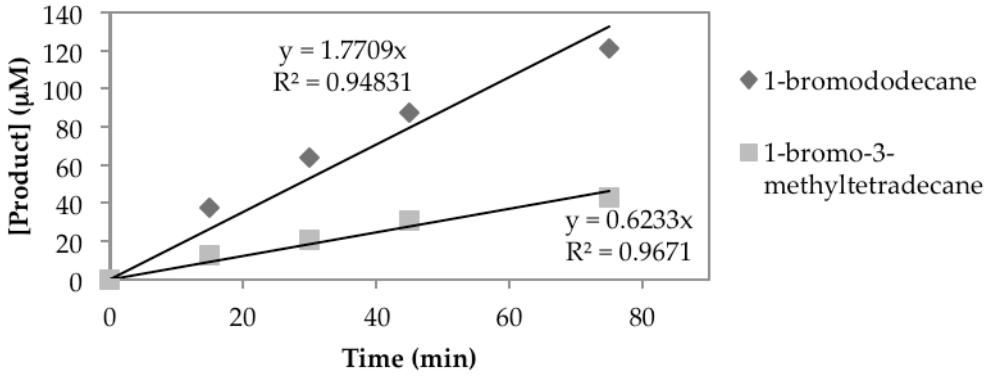
1-Bromododecane vs. 1-Bromo-2-methylpentadecane

Figure S8.



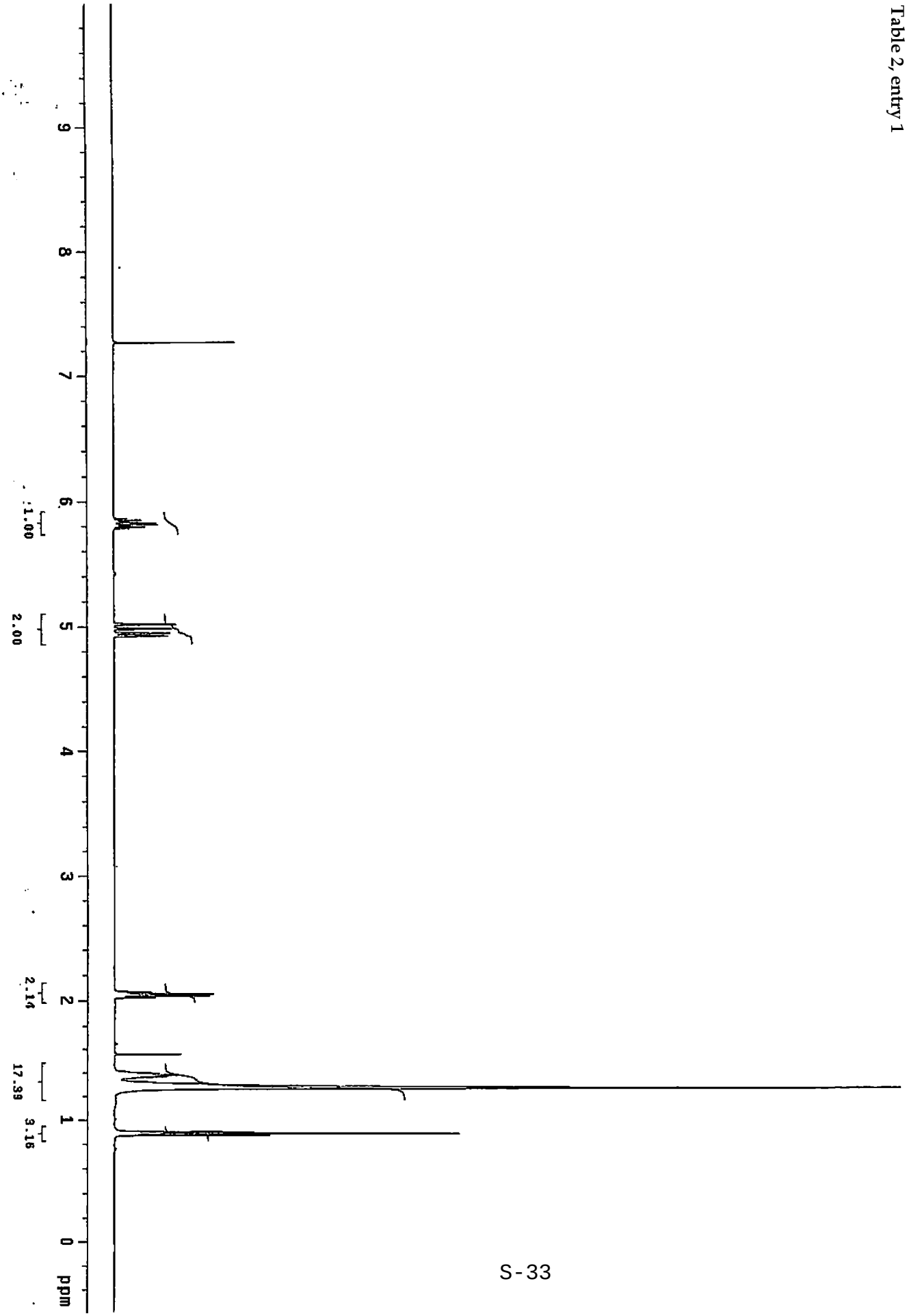
1-Bromododecane vs. 1-Bromo-3-methyltetradecane

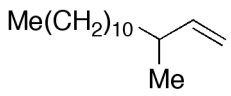
Figure S9.



IV. ^{1}H NMR Spectra

Table 2, entry 1





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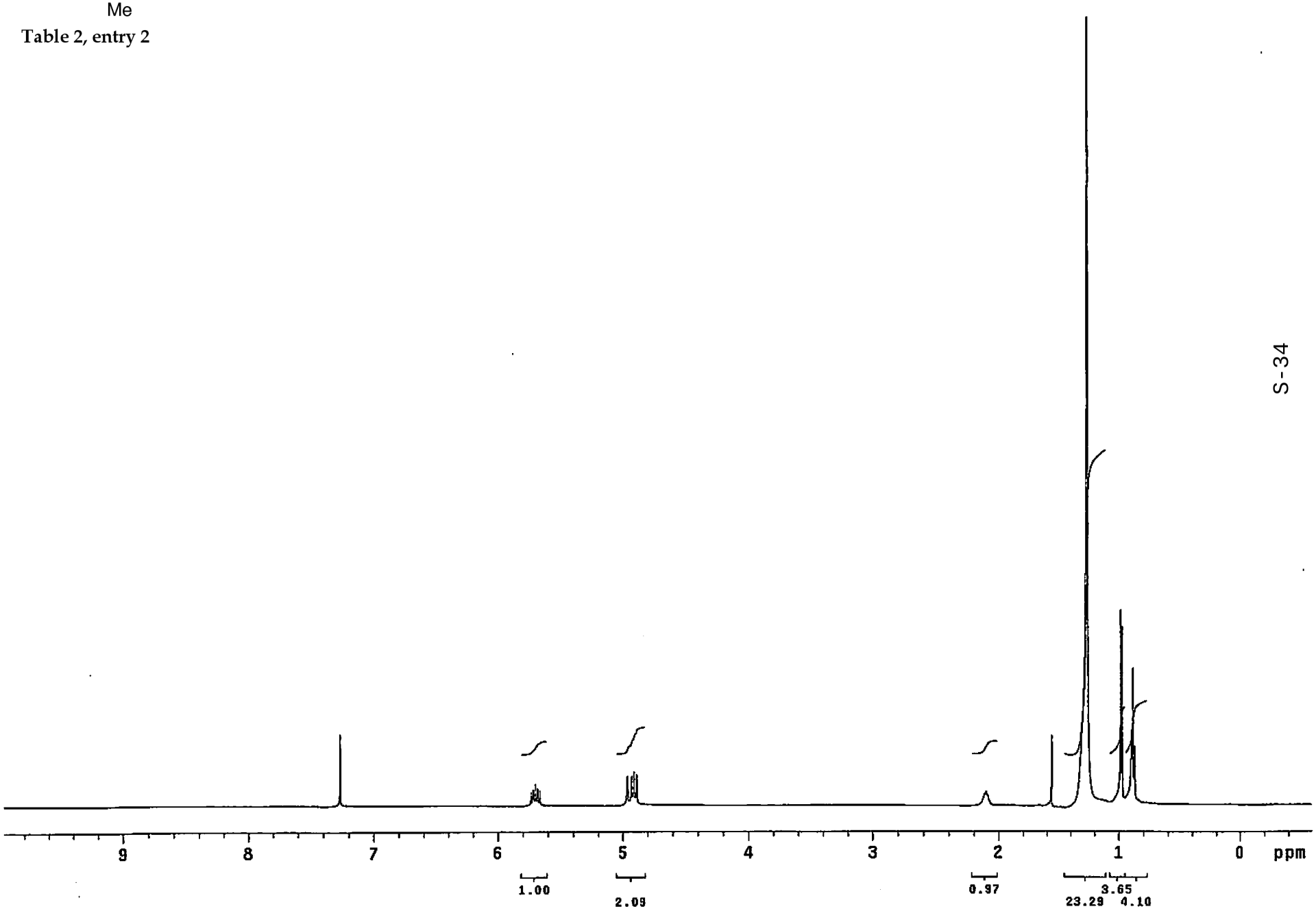

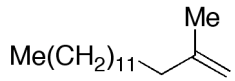

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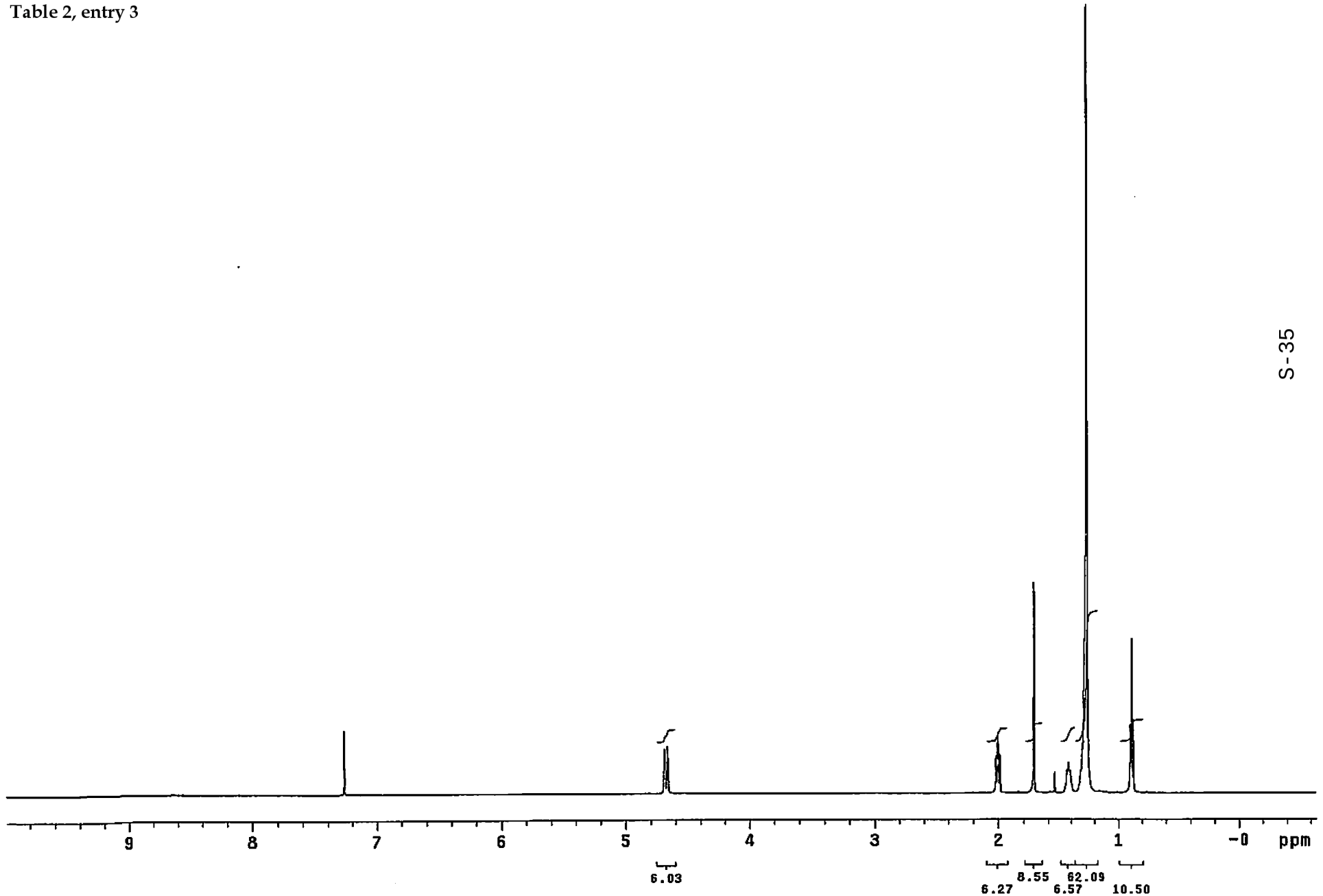


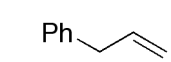
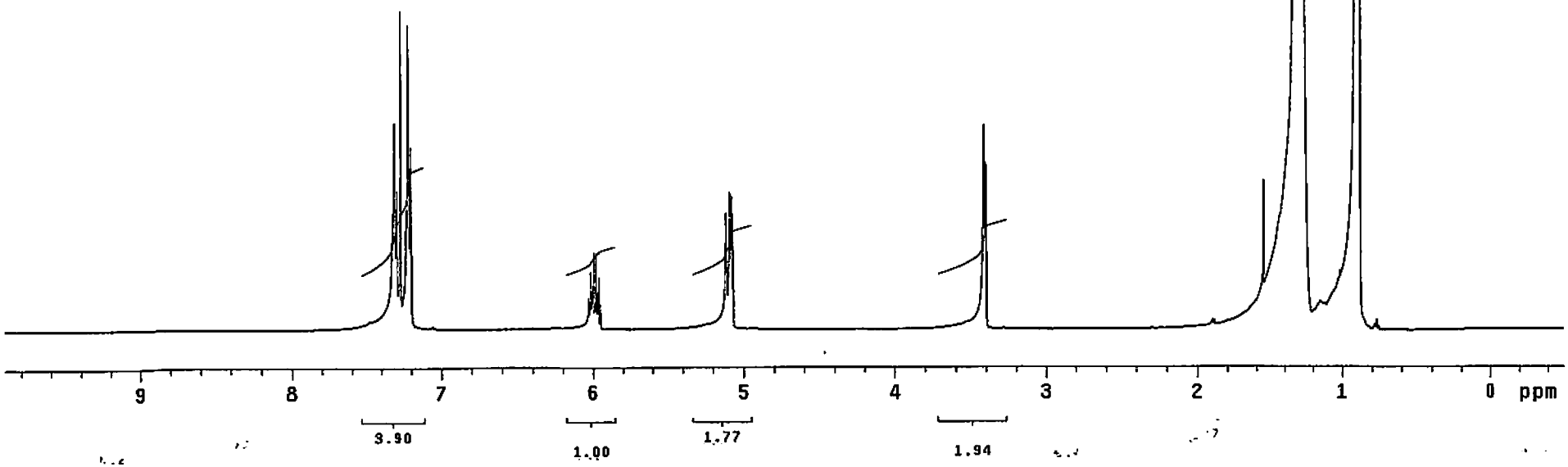
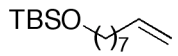


Table 2, entry 4

n-decane
(internal standard)





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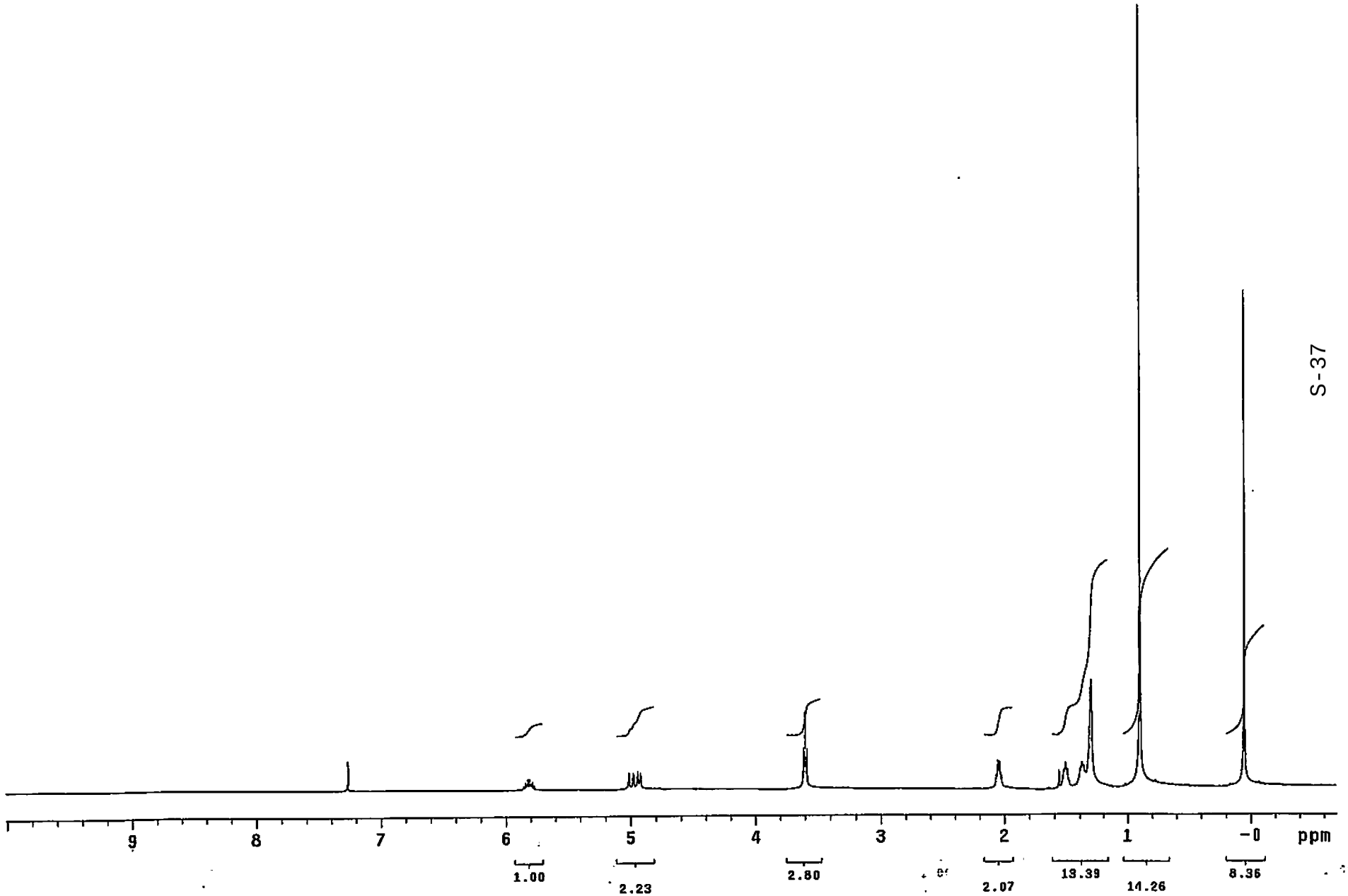

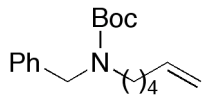

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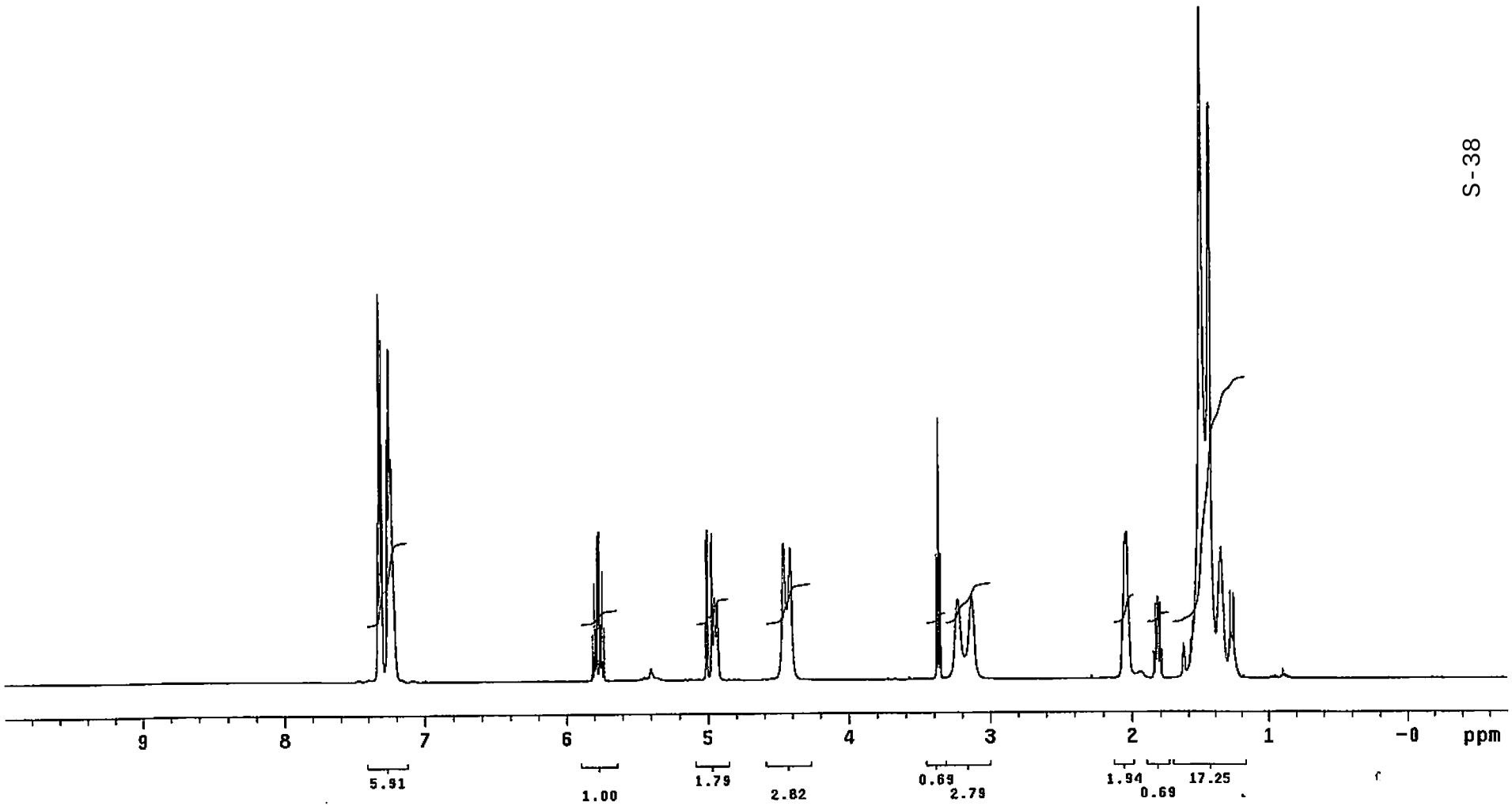

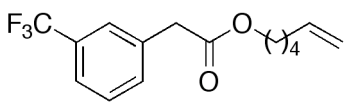

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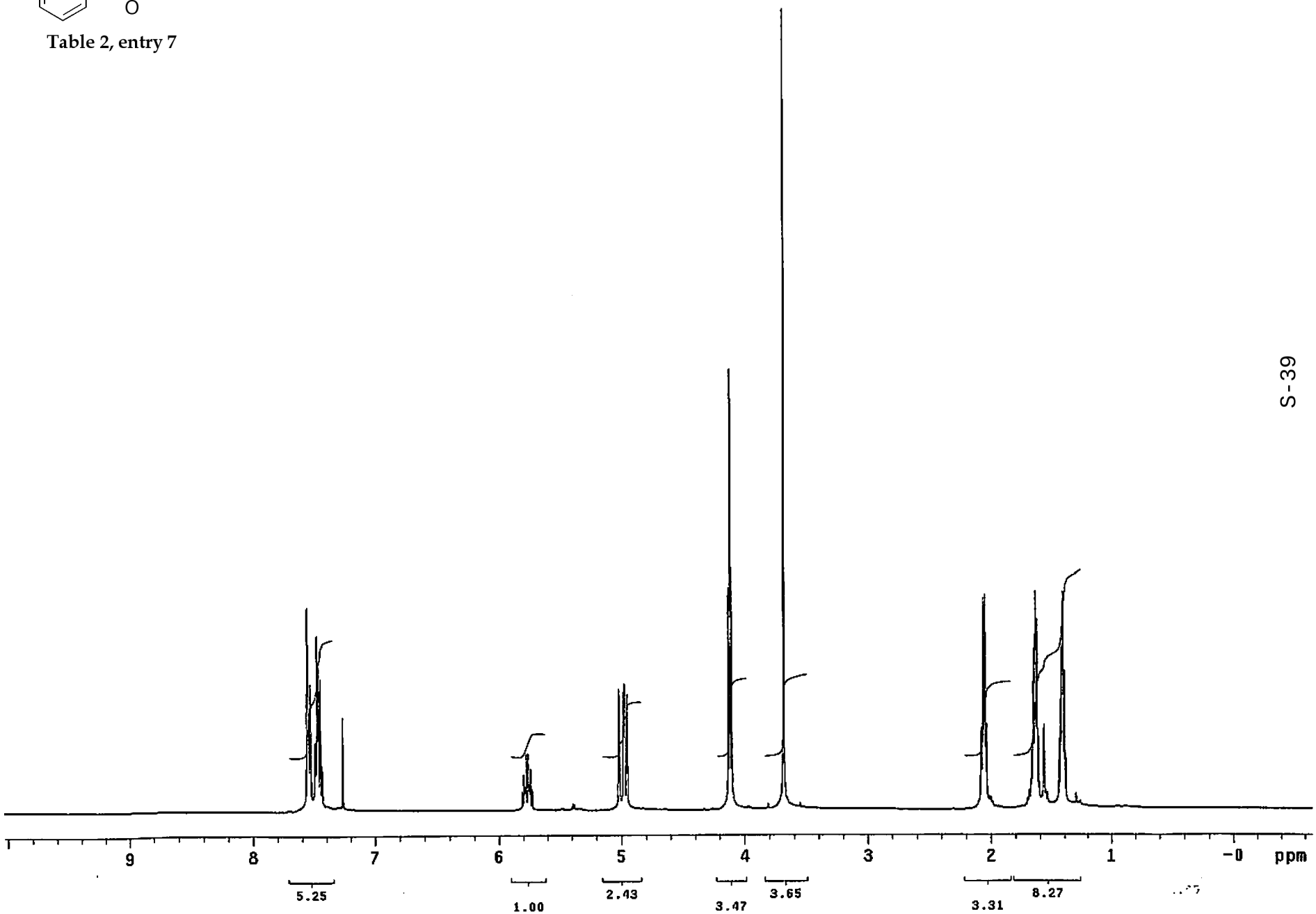

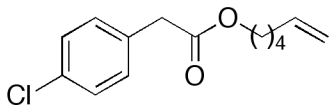

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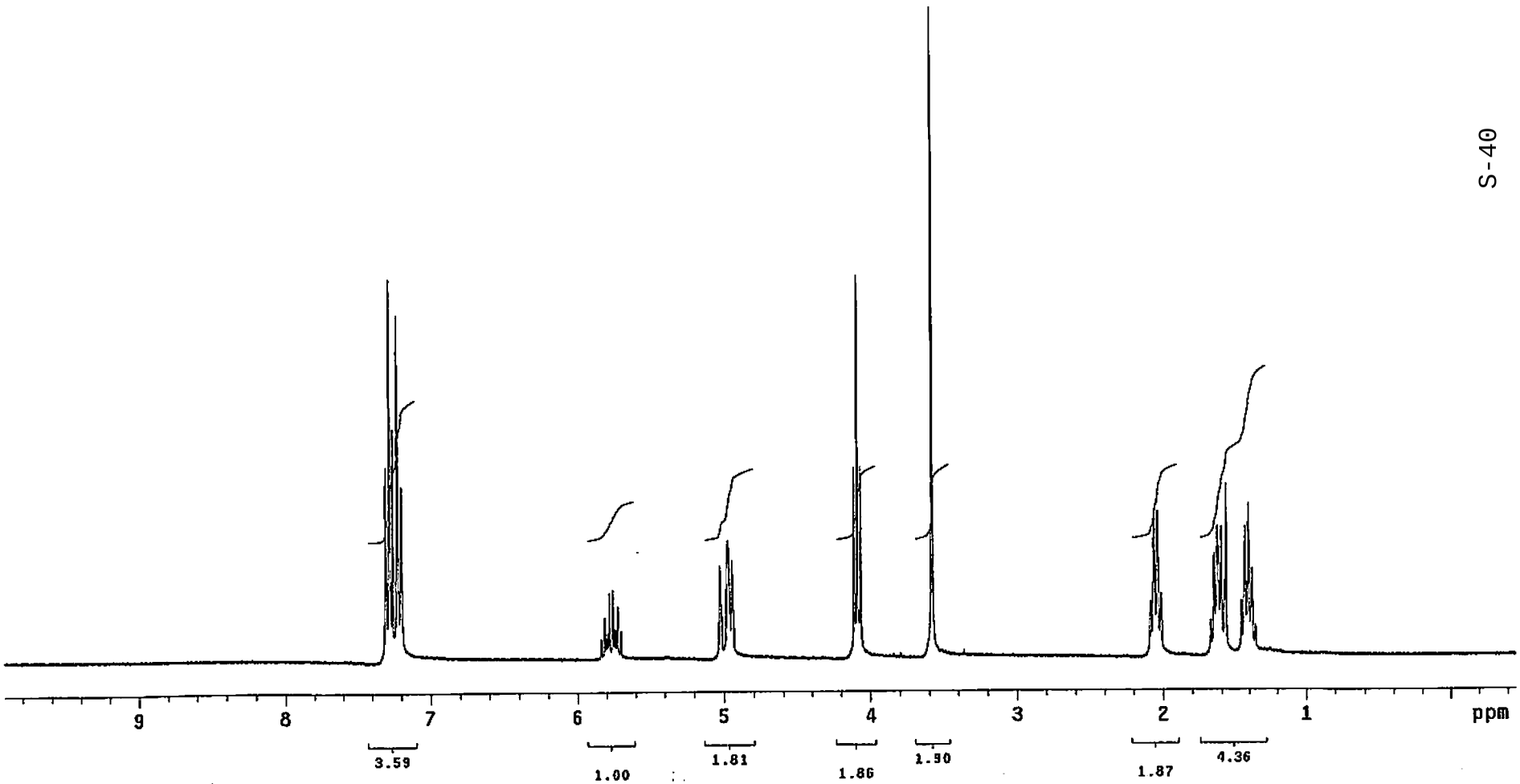

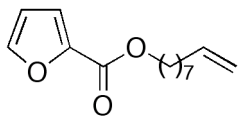

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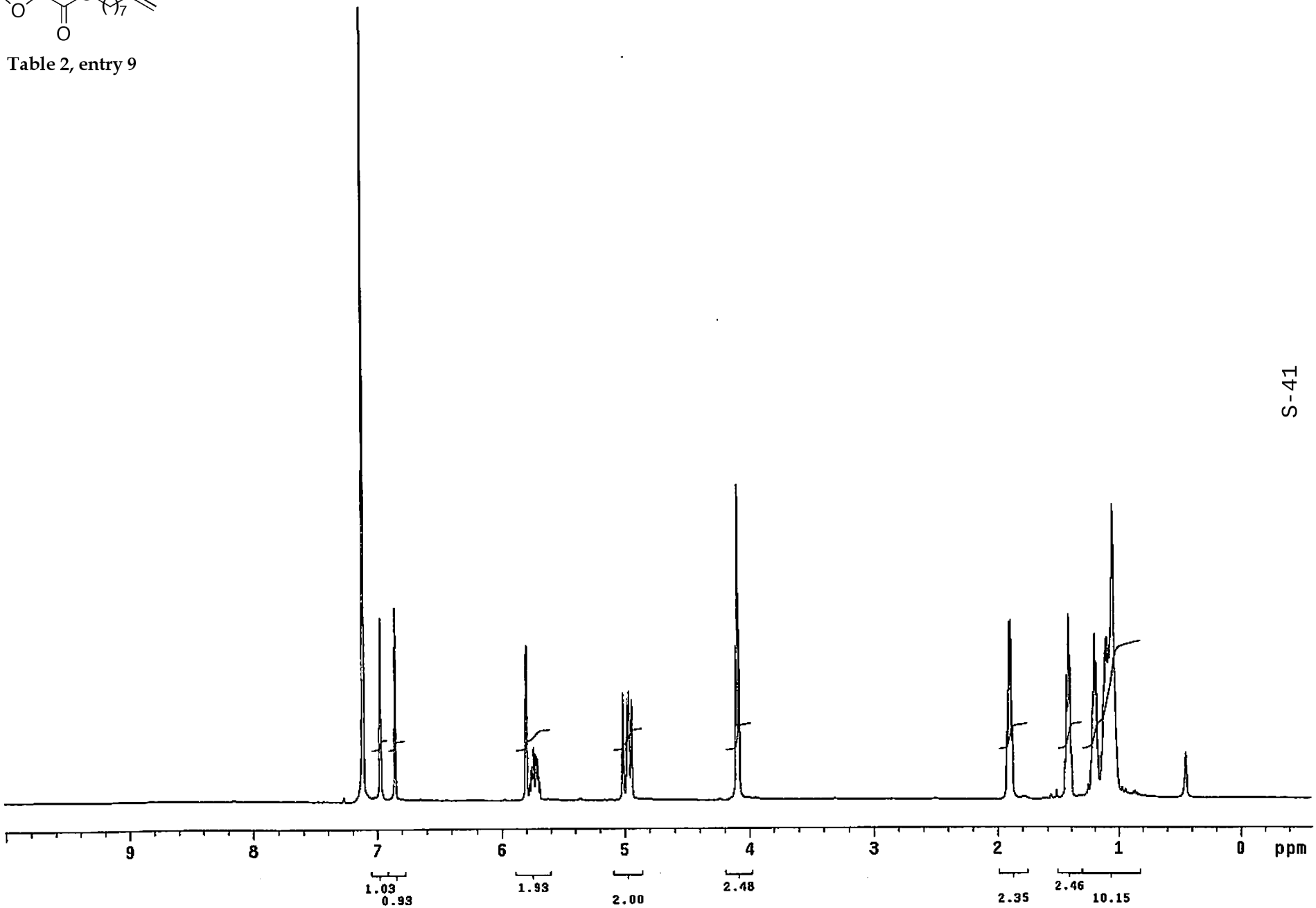

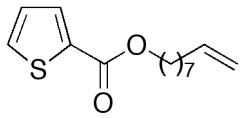

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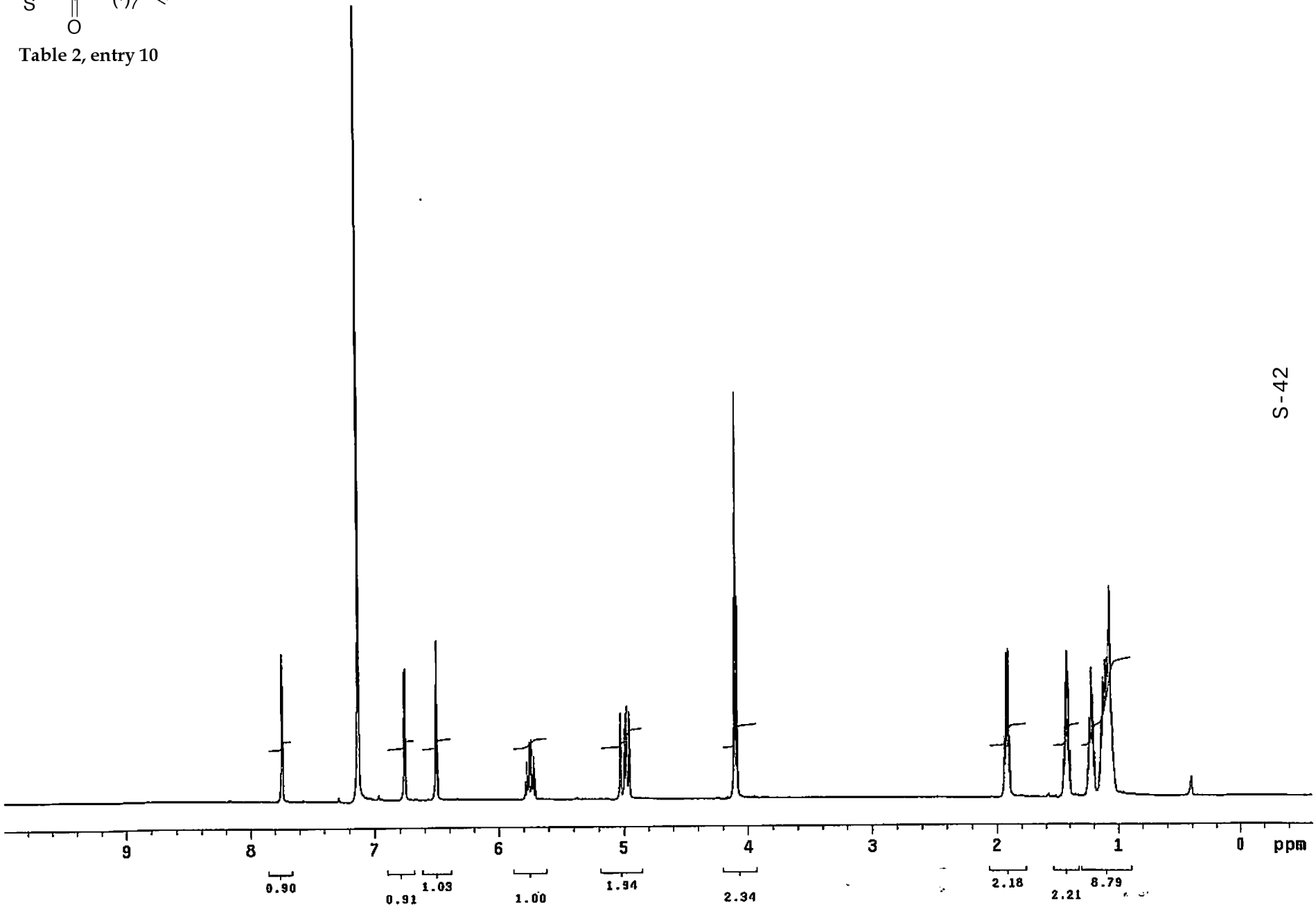

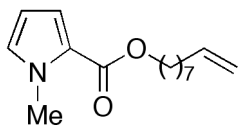

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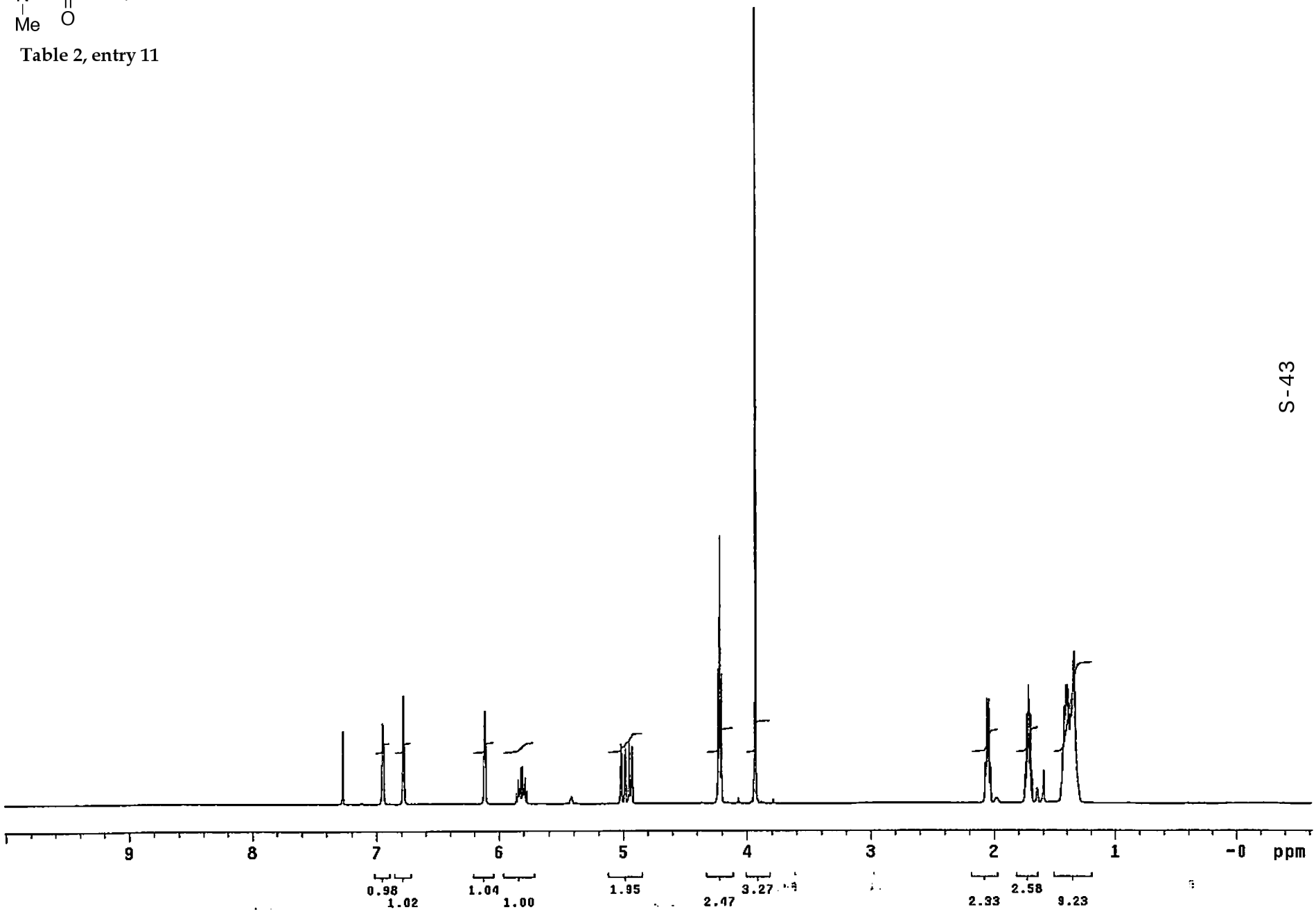

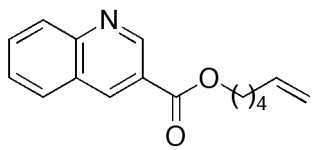

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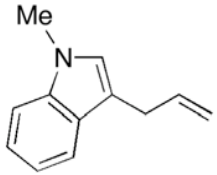

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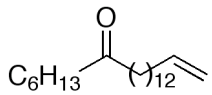

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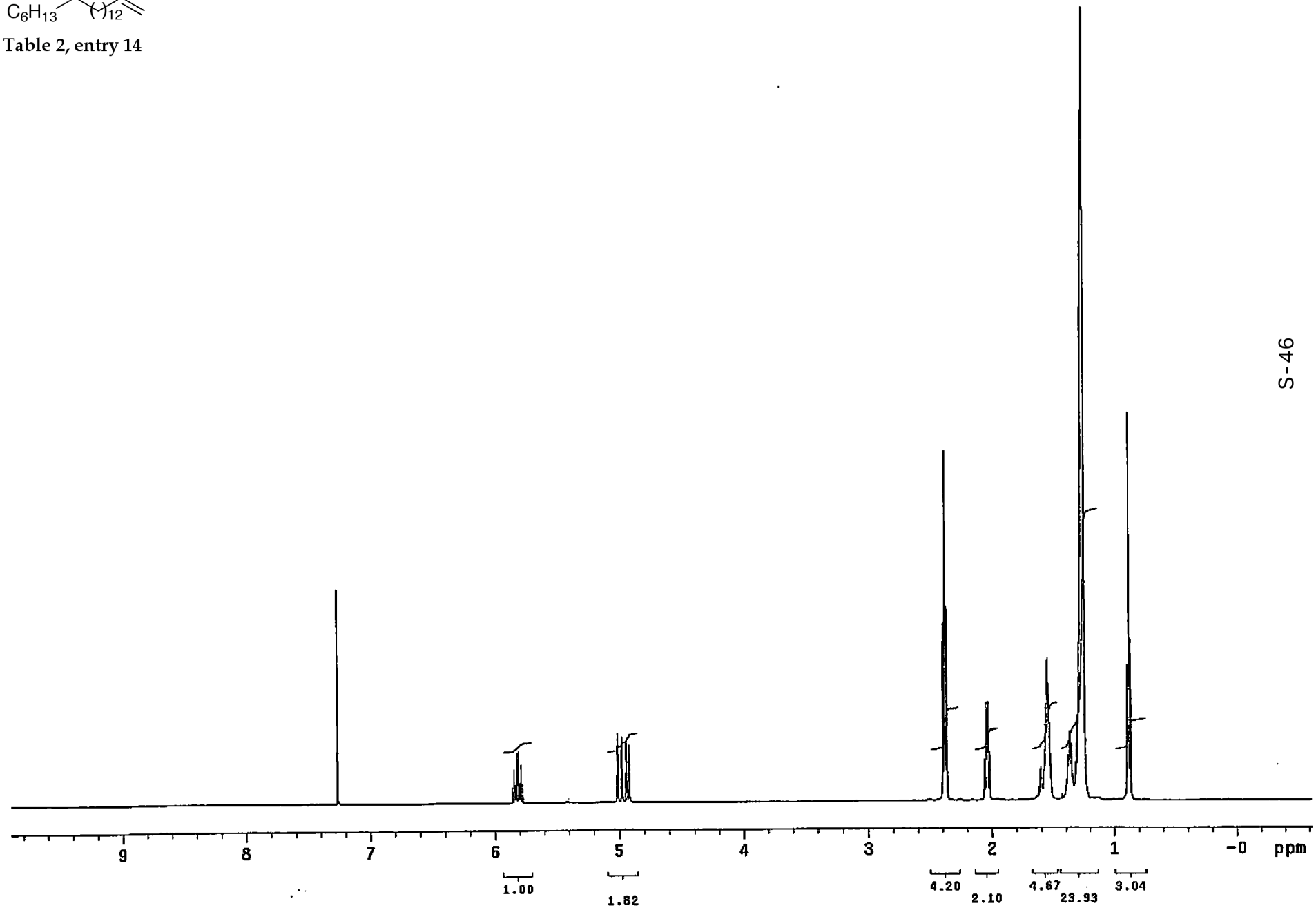

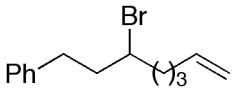

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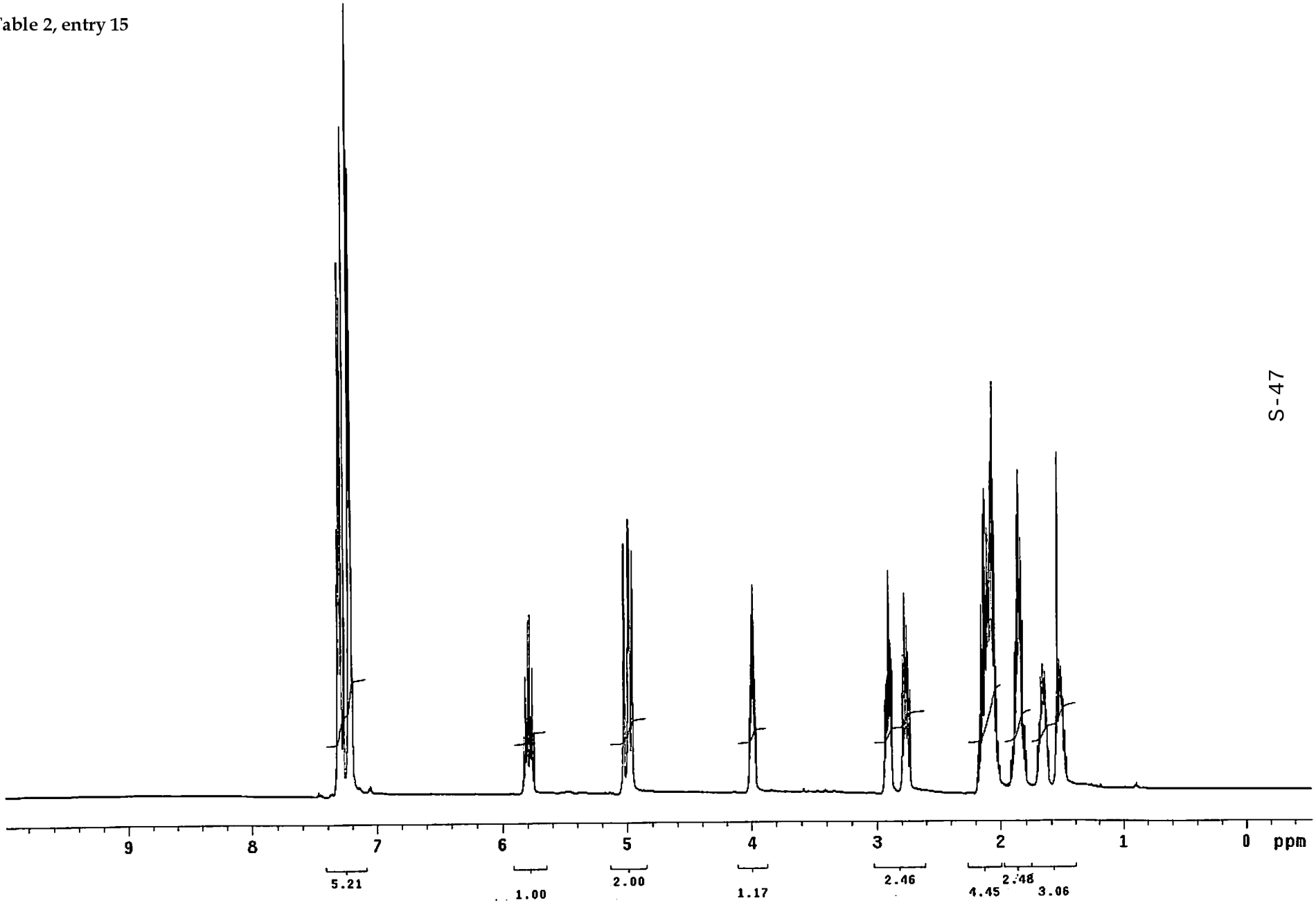

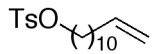

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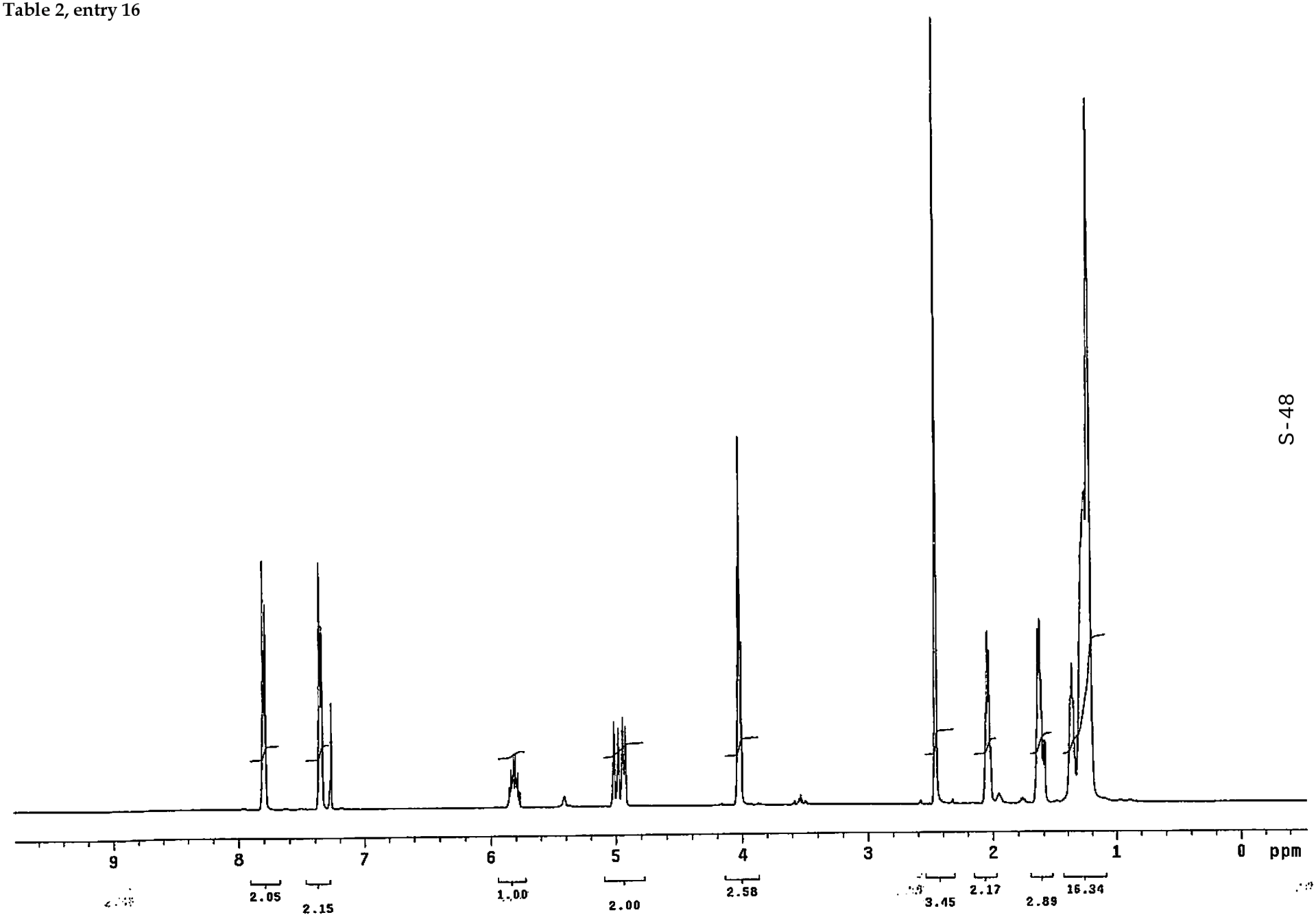

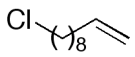

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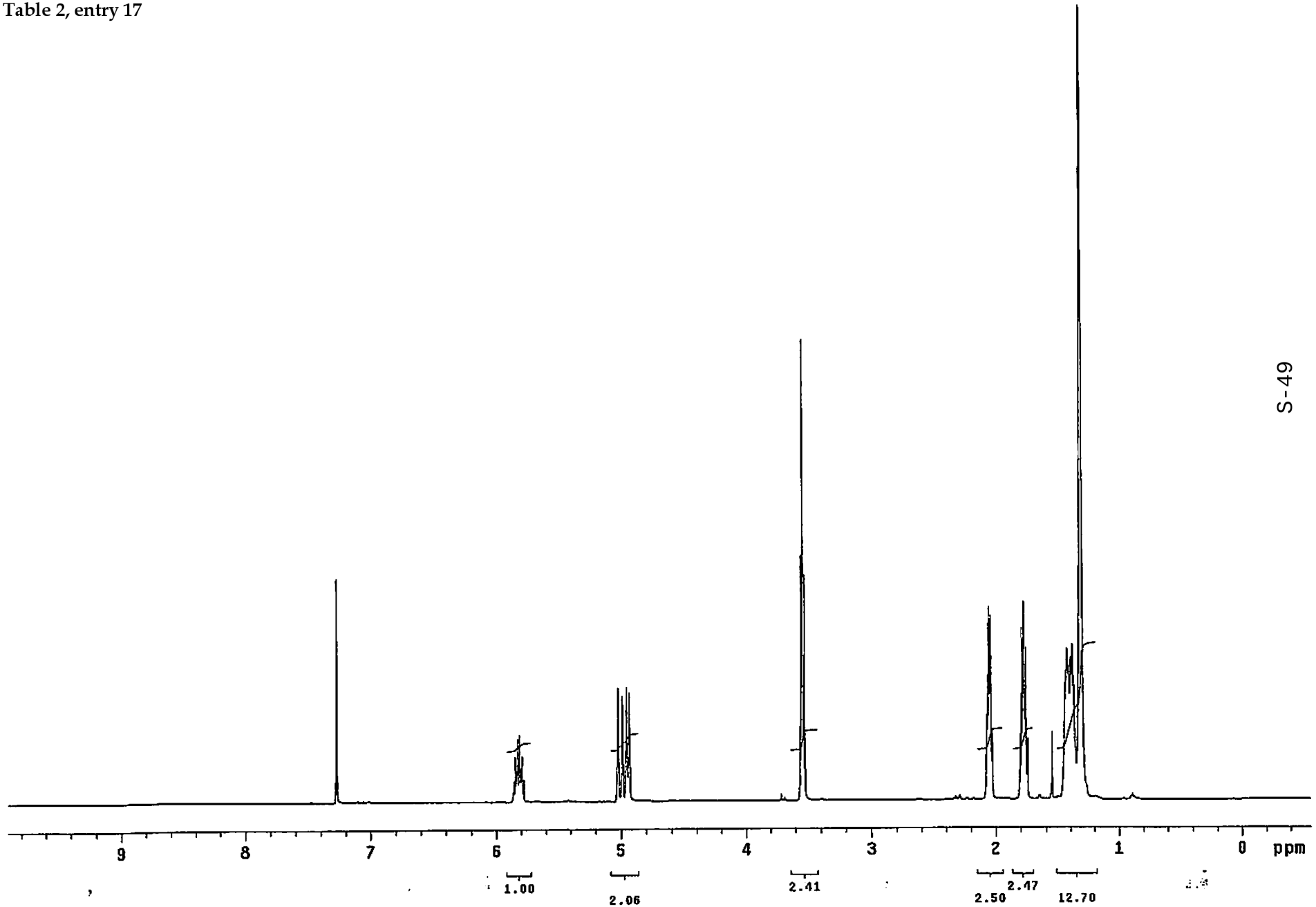

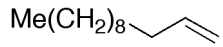

Table 3, entry 1

STANDARD PROTON PARAMETERS

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	H.fid	dmm	w
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tn	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
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fb	not used	proc	ft
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tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	8	wbs	
ct	8	wnt	wft
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gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
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ai cdc ph

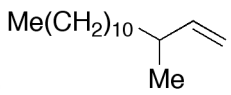
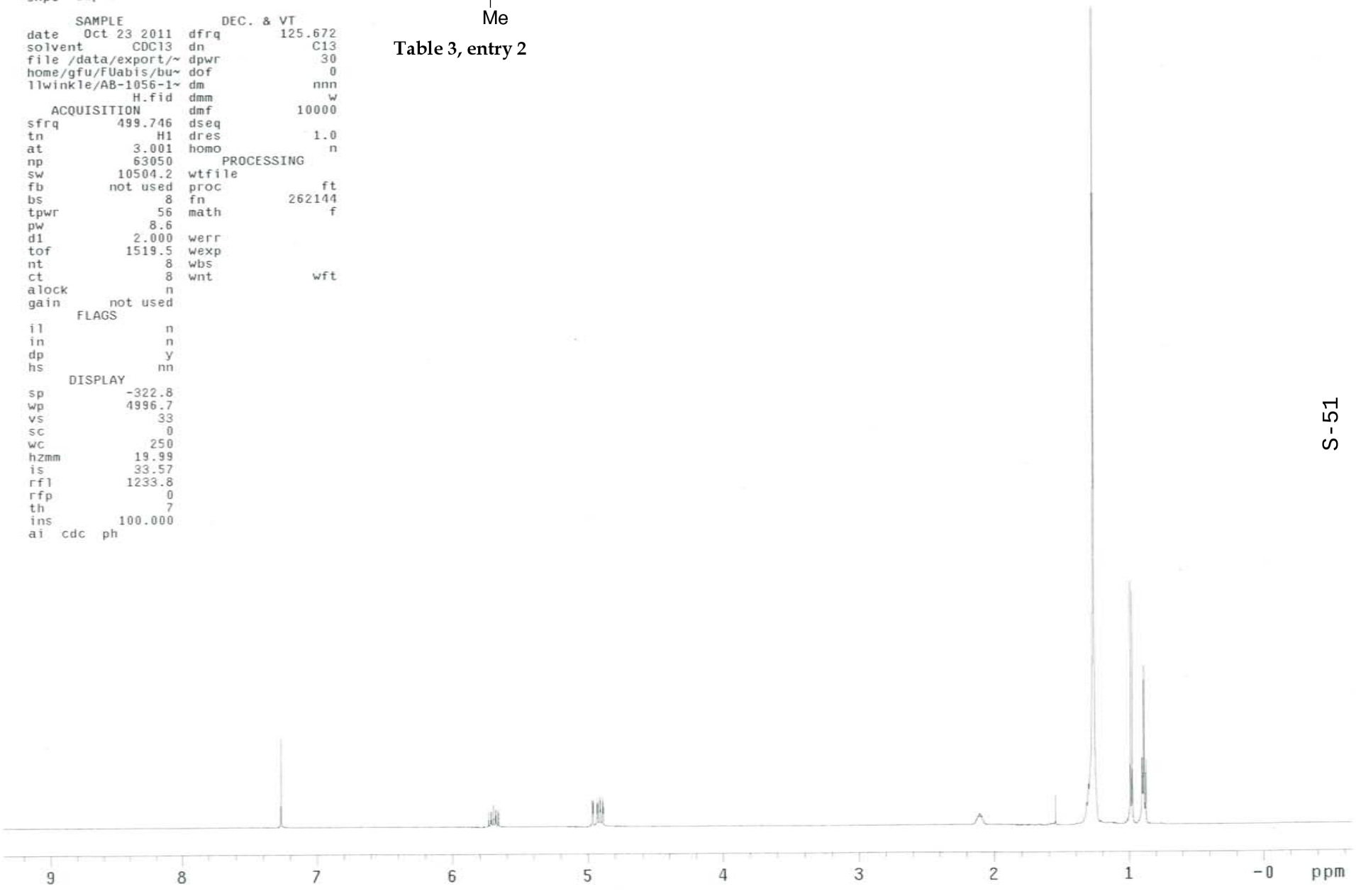


Table 3, entry 2



STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 15 2011	dfrq	125.672
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUabis/bu~		dof	0
llwinkle/AB-1053-1~		dm	nnn
	H.fid	dmm	w
ACQUISITION		dmf	10000
sfrq	499.746	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	8	wbs	
ct	8	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-129.6		
wp	6142.3		
vs	77		
sc	0		
wc	250		
hzmm	24.57		
is	33.57		
rfl	1233.8		
rfp	0		
th	7		
ins	100.000		

ai` cdc ph

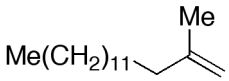
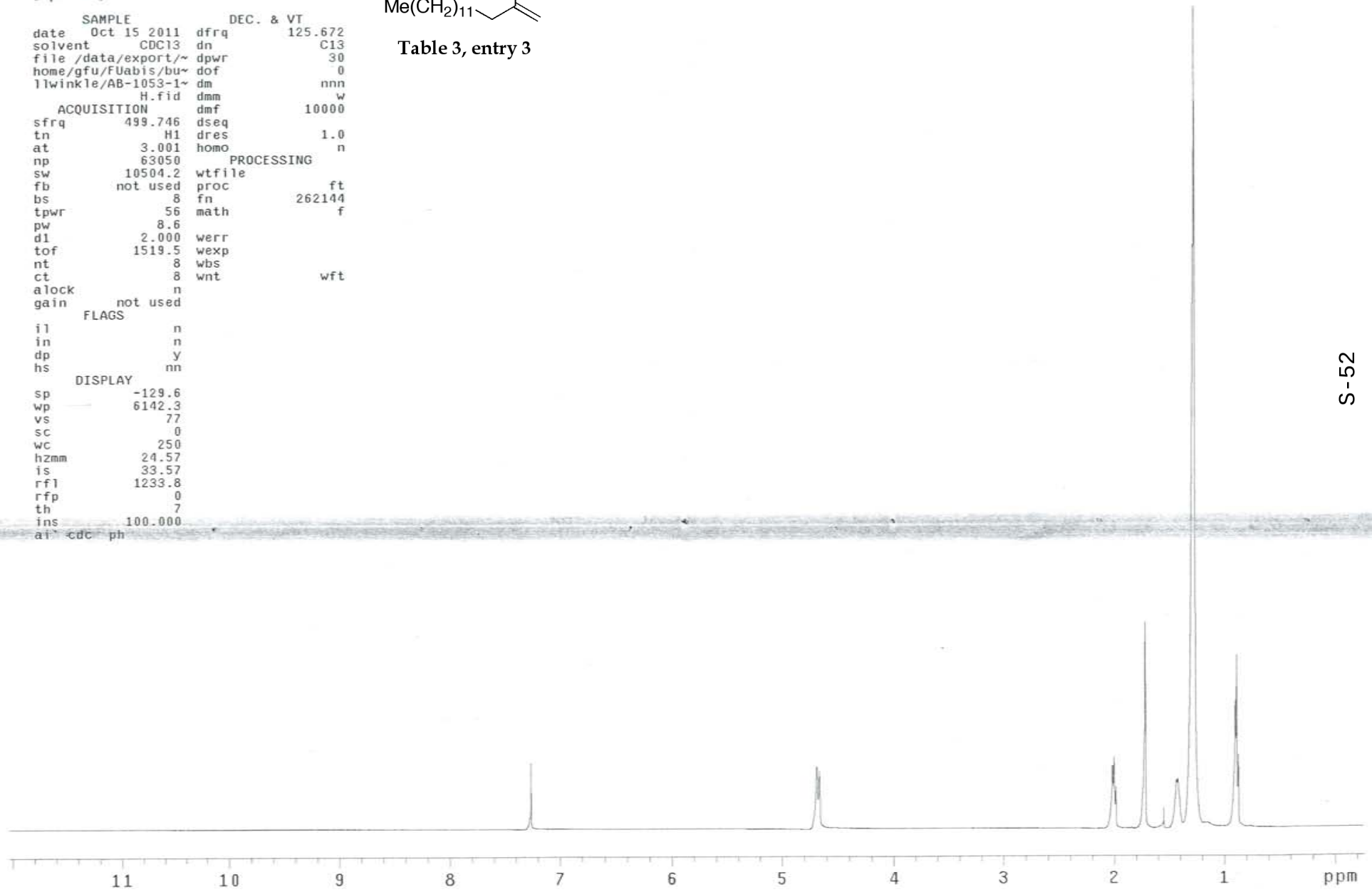


Table 3, entry 3



STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 19 2011	dfrq	125.672
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUabis/bu~		dof	0
llwinkle/AB-1145-1~		dm	nnn
	H.fid	dmm	w
ACQUISITION		dmf	10000
sfrq	499.746	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	8	wbs	
ct	8	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-46.7		
wp	4831.0		
vs	76		
sc	0		
wc	250		
hzmm	19.32		
is	33.57		
rfl	1233.8		
rfp	0		
th	7		
ins	100.000		
ai cdc ph			

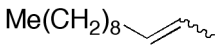
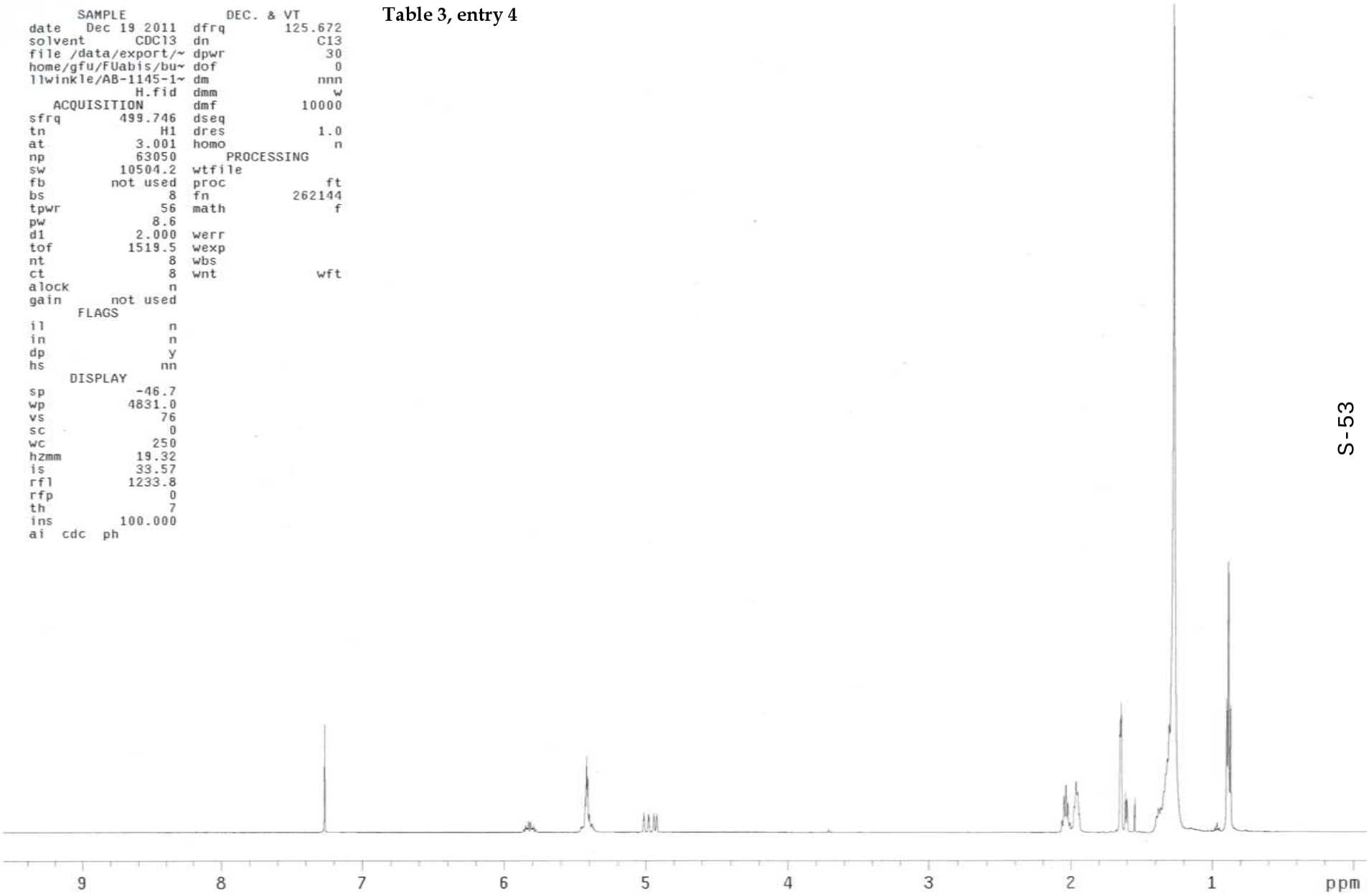


Table 3, entry 4



STANDARD PROTON PARAMETERS

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 26 2011	dfrq	125.672
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUabis/bu~		dof	0
llwinkle/AB-1065-1~		dm	nnn
	H.fid	dmm	w
ACQUISITION		dmf	10000
sfrq	499.746	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	8	wbs	
ct	8	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-170.9		
wp	4817.3		
vs	77		
sc	0		
wc	250		
hzmm	19.27		
is	33.57		
rfl	1233.8		
rfp	0		
th	7		
ins	100.000		
ai cdc ph			

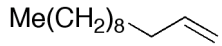
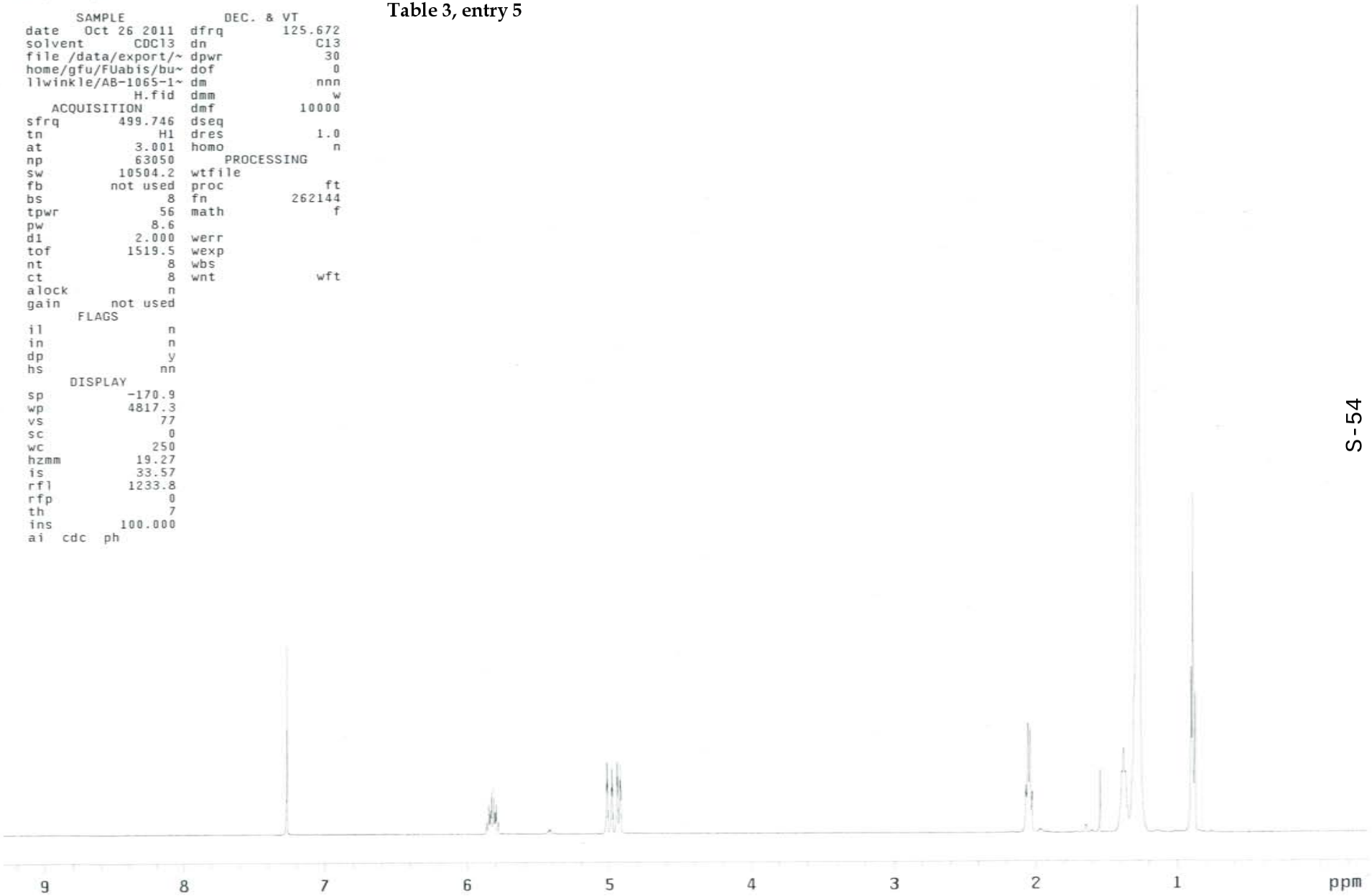
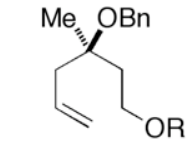


Table 3, entry 5





R = 1-ethoxyethyl

Figure 2

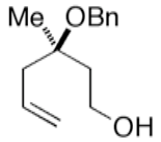


Figure 2