Cross-Couplings of Alkyl Electrophiles Under "Ligandless" Conditions: Negishi Reactions of Organozirconium Reagents

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Supporting Information

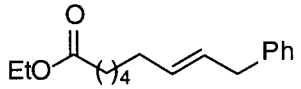
I. General

$Pd(acac)_2$ (Strem), LiBr (Aldrich, dried under vacuum at 120 °C for 24 hours), Cp_2ZrHCl (Strem), and NMP (Aldrich/Sure-Seal) were used without purification. THF was passed through a neutral alumina column. 1-Bromodecane (Avocado), ethyl 6-bromohexanoate (Aldrich), benzyl 4-bromobutyl ether (Aldrich), 4-bromobutyronitrile (Aldrich), 2-(3-bromopropoxy)tetrahydro-2*H*-pyran (Aldrich), 5-bromo-1-pentene (Avocado), (bromomethyl)cyclohexane (TCI), 1-octyne (Aldrich), 3-phenyl-1-propyne (Aldrich), 3,3-dimethyl-1-butyne (Aldrich), ethyl ethynyl ether (Aldrich/40 wt% solution in hexanes), 2-(3-butynyloxy)tetrahydro-2*H*-pyran (Aldrich), and 4,4-dimethyl-2-pentyne (Lancaster) were sparged with argon before use (if a liquid). All other compounds were prepared according to literature procedures.

II. Negishi Cross-Coupling Reactions

Representative Procedure 1 (with a glove box). In a glove box, the alkyne (2.0 mmol) was added to a suspension of Cp_2ZrHCl (2.0 mmol) in THF (2.0 mL) in a 20-mL vial. The resulting mixture was allowed to stir for one hour at room temperature. Then, NMP (2.0 mL) was added, and the mixture was transferred to a 20-mL vial that contained $Pd(acac)_2$ (7.5 mg, 0.025 mmol) and LiBr (0.174 g, 2.0 mmol). Next, the alkyl bromide (1.0 mmol) was added, and then the vial was sealed with electrical tape, removed from the glove box, and heated at 55 °C for 24 hours. At the conclusion of the reaction, the mixture was passed through a short pad of silica gel (with Et_2O) to remove polar compounds (e.g., salts and metals). The filtrate was concentrated, and the residue was purified by flash chromatography.

Procedure without a glove box (Table 2, entry 1). In air, Cp_2ZrHCl (0.542 g, 2.0 mmol) was added to a 20-mL vial, which was evacuated and refilled with argon three times. THF (2.0 mL) and then 3-phenyl-1-propyne (249 μL, 2.0 mmol) were added, and the resulting mixture was allowed to stir for one hour at room temperature. Then, NMP (2.0 mL) was added, and the mixture was transferred to a 20-mL vial that contained $Pd(acac)_2$ (7.5 mg, 0.025 mmol) and LiBr (0.174 g, 2.0 mmol) (both were weighed in the air). Next, ethyl 6-bromohexanoate (228 μL, 1.0 mmol) was added, and the reaction vial was purged with argon, sealed with electrical tape, and heated at 55 °C for 24 hours. At the conclusion of the reaction, the mixture was passed through a short pad of silica gel (with Et_2O) to remove polar compounds (e.g., salts and metals). The filtrate was concentrated, and the residue was purified by flash chromatography.



Ethyl 9-phenyl-7*E*-nonenoate (Table 2, entry 1). Procedure 1 was followed: ethyl 6-bromohexanoate (228 μL, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless oil (0.256 g, 98%).

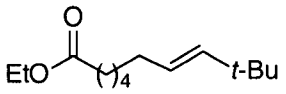
A second run was performed on the same scale, and the product was isolated in 99% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.16 (m, 5H), 5.60-5.47 (m, 2H), 4.13 (q, J=7.2 Hz, 2H), 3.33 (d, J=5.7 Hz, 2H), 2.29 (t, J=7.5 Hz, 2H), 2.07-2.00 (m, 2H), 1.68-1.58 (m, 2H), 1.43-1.28 (m, 4H), 1.26 (t, J=7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz):δ 174.5, 141.7, 132.4, 129.7, 129.2, 129.1, 126.6, 60.9, 39.8, 35.0, 33.0, 29.8, 29.4, 25.6, 15.0.

HRMS (EI) calc. for $C_{17}H_{24}O_2$: 260.1771, found: 260.1775.

IR (neat): 3028, 2980, 2930, 2855, 1735, 1603, 1180 cm^{-1}.



Ethyl 9,9-dimethyl-7*E*-decenoate (Table 2, entry 2). Procedure 1 was followed: ethyl 6-bromohexanoate (228 μL, 1.0 mmol), 3,3-dimethyl-1-butyne (246 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless liquid (0.192 g, 85%).

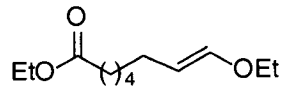
A second run was performed on the same scale, and the product was isolated in 86% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.43 (d, J=15.6 Hz, 1H), 5.28 (dt, J=15.6, 6.3 Hz, 1H), 4.12 (q, J=6.9 Hz, 2H), 2.28 (t, J=7.2 Hz, 2H), 1.97-1.93 (m, 2H), 1.64-1.57 (m, 2H), 1.38-1.29 (m, 4H), 1.25 (t, J=6.9 Hz, 3H), 0.98 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.2, 141.8, 124.5, 60.3, 34.5, 32.9, 32.6, 29.9, 29.5, 28.7, 25.0, 14.4.

HRMS (ESI) calc. for $C_{14}H_{26}O_2Na$ [M+Na]: 249.1825, found: 249.1831.

IR (neat): 2958, 2863, 1739, 1183 cm^{-1}.



Ethyl 8-ethoxy-7*E*-octenoate (Table 2, entry 3). Procedure 1 was followed: ethyl 6-bromohexanoate (228 μL, 1.0 mmol), ethyl ethynyl ether (0.350 g, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (3% Et_2O in hexanes) as a colorless liquid (0.212 g, 99%).

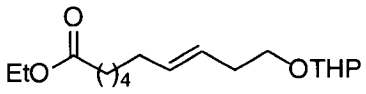
A second run was performed on the same scale, and the product was isolated in 93% yield.

^{1}H NMR (C_6D_6, 300 MHz): δ 6.24 (d, J=12.6 Hz, 1H), 4.72 (dt, J=12.6, 7.5 Hz, 1H), 3.97 (q, J=7.2 Hz, 2H), 3.42 (q, J=6.9 Hz, 2H), 2.13 (t, J=7.5 Hz, 2H), 1.86-1.79 (m, 2H), 1.59-1.55 (m, 2H), 1.25-1.18 (m, 4H), 1.06 (t, J=6.9 Hz, 3H), 0.97 (t, J=7.2 Hz, 3H).

^{13}C NMR (C_6D_6, 125 MHz): δ 173.3, 147.2, 103.8, 64.6, 60.3, 34.7, 31.2, 29.1, 28.4, 25.5, 15.2, 14.7.

HRMS (ESI) calc. for $C_{12}H_{22}O_3Na$ [M+Na]: 237.1461, found: 237.1468.

IR (neat): 2980, 2931, 2856, 1737, 1673, 1654, 1184 cm^{-1}.



Ethyl 10-(2-tetrahydro-2*H*-pyranoxy)-7*E*-decenoate (Table 2, entry 4). Procedure 1 was followed: ethyl 6-bromohexanoate (228 μL, 1.0 mmol), 2-(3-butynyloxy)tetrahydro-2*H*-pyran (235 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (8-10% Et_2O in hexanes gradient) as a colorless liquid (0.205 g, 69%).

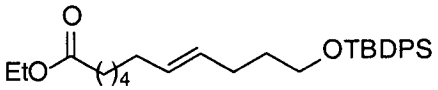
A second run was performed on the same scale, and the product was isolated in 74% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.50-5.36 (m, 2H), 4.57-4.55 (m, 1H), 4.09 (q, J=7.2 Hz, 2H), 3.87-3.80 (m, 1H), 3.74-3.66 (m, 1H), 3.50-3.34 (m, 2H), 2.29-2.22 (m, 4H), 1.99-1.93 (m, 2H), 1.82-1.46 (m, 8H), 1.35-1.26 (m, 4H), 1.22 (t, J=7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0, 132.3, 126.6, 98.8, 67.4, 62.3, 60.3, 34.4, 33.1, 32.5, 30.8, 29.1, 28.7, 25.6, 24.9, 19.7, 14.3.

HRMS (ESI) calc. for $C_{17}H_{30}O_4Na$ [M+Na]: 321.2036, found: 321.2036.

IR (neat): 2939, 2868, 1736, 1183, 1121, 971 cm^{-1}.



Ethyl 11-(*t*-butyldiphenylsilanyl)-7*E*-undecenoate (Table 2, entry 5). Procedure 1 was followed: ethyl 6-bromohexanoate (228 μL, 1.0 mmol), *t*-butyl(pent-4-ynyloxy)diphenylsilane (0.646 g, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless liquid (0.463 g, 99%).

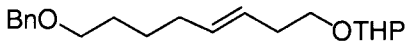
A second run was performed on the same scale, and the product was isolated in 99% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69-7.66 (m, 4H), 7.43-7.38 (m, 6H), 5.39-5.35 (m, 2H), 4.14 (q, J=7.2 Hz, 2H), 3.66 (t, J=6.3 Hz, 2H), 2.28 (t, J=7.5 Hz, 2H), 2.08-2.07 (m, 2H), 1.96-1.95 (m, 2H), 1.64-1.58 (m, 4H), 1.33-1.29 (m, 4H), 1.26 (t, J=7.2 Hz, 3H), 1.05 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.1, 135.8, 134.3, 130.6, 130.1, 129.7, 127.8, 63.5, 60.4, 34.5, 32.6, 29.4, 29.0, 28.8, 27.1, 27.0, 25.0, 19.4, 14.5.

HRMS (ESI) calc. for $C_{29}H_{42}O_3SiNa$ [M+Na]: 489.2795, found: 489.2809.

IR (neat): 3071, 2931, 2857, 1737, 1590, 1185, 1111 cm^{-1}.



8-Benzyloxy-1-(2-tetrahydro-2*H*-pyranoxy)-3*E*-octenoate (Table 2, entry 6). Procedure 1 was followed: benzyl 4-bromobutyl ether (212 μL, 1.0 mmol), 2-(3-butynyloxy)tetrahydro-2*H*-pyran (235 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (15 mg, 0.050 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (6% Et_2O in hexanes) as a colorless liquid (0.235 g, 74%).

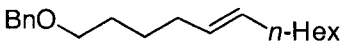
A second run was performed on the same scale, and the product was isolated in 71% yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36-7.27 (m, 5H), 5.52-5.39 (m, 2H), 4.60-4.56 (m, 1H), 4.50 (s, 2H), 3.88-3.85 (m, 1H), 3.75-3.71 (m, 1H), 3.50-3.36 (m, 4H), 2.31-2.27 (m, 2H), 2.06-1.99 (m, 3H), 1.85-1.40 (m, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.4, 128.6, 127.8, 127.7, 126.8, 125.0, 96.0, 73.1, 70.5, 67.6, 62.5, 33.3, 32.6, 30.9, 29.4, 26.2, 25.7, 19.8.

HRMS (ESI) calc. for $C_{20}H_{30}O_3Na$ [M+Na]: 341.2087, found: 341.2086.

IR (neat): 3030, 2939, 2856, 1454, 1119, 1033, 970 cm^{-1}.



1-Benzyloxy-5*E*-dodecene (Table 2, entry 7). Procedure 1 was followed: benzyl 4-bromobutyl ether (212 μL, 1.0 mmol), 1-octyne (300 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (1% Et_2O in hexanes) as a colorless liquid (0.229 g, 84%).

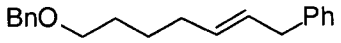
A second run was performed on the same scale, and the product was isolated in 80% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.26 (m, 5H), 5.40-5.37 (m, 2H), 4.50 (s, 2H), 3.47 (t, J=6.6 Hz, 2H), 2.01-1.97 (m, 4H), 1.65-1.60 (m, 2H), 1.45-1.40 (m, 2H), 1.32-1.25 (m, 8H), 0.88 (t, J=7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 131.0, 131.1, 128.6, 127.8, 127.7, 73.1, 70.6, 32.8, 32.6, 32.0, 29.8, 29.5, 29.1, 26.4, 22.9, 14.4.

HRMS (ESI) calc. for $C_{19}H_{30}ONa$ [M+Na]: 297.2189, found: 297.2184.

IR (neat): 3029, 2926, 2855, 1454, 1105 cm^{-1}.



7-Phenyl-hept-5*E*-enyloxymethylbenzene (Table 2, entry 8). Procedure 1 was followed: benzyl 4-bromobutyl ether (212 μL, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless liquid (0.240 g, 95%).

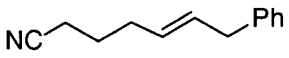
A second run was performed on the same scale, and the product was isolated in 99% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37-7.18 (m, 10H), 5.64-5.46 (m, 2H), 4.51 (s, 2H), 3.48 (t, J=6.3 Hz, 2H), 3.34 (d, J=5.7 Hz, 2H), 2.10-2.03 (m, 2H), 1.70-1.60 (m, 2H), 1.53-1.45 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.2, 138.8, 131.8, 129.3, 128.7, 128.5, 127.8, 127.7, 126.0, 73.0, 70.4, 39.2, 32.5, 29.4, 26.2.

HRMS (ESI) calc. for $C_{20}H_{24}ONa$ [M+Na]: 303.1719, found: 303.1716.

IR (neat): 3028, 2933, 2856, 1453, 1103 cm^{-1}.

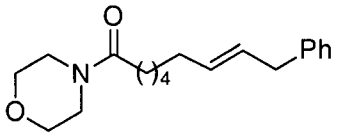


7-Phenyl-5*E*-heptenenitrile (Table 2, entry 9). [129266-49-5] Procedure 1 was followed: 4-bromobutyronitrile (99 μL, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (6% Et_2O in hexanes) as a yellow liquid (0.125 g, 68%).

A second run was performed on the same scale, and the product was isolated in 68% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34-7.26 (m, 2H), 7.24-7.16 (m, 3H), 5.74-5.64 (m, 1H), 5.49-5.39 (m, 1H), 3.37 (d, J=6.9 Hz, 2H), 2.33 (t, J=7.2 Hz, 2H), 2.24-2.16 (m, 2H), 1.79-1.70 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.2, 132.2, 129.6, 129.2, 126.8, 120.4, 39.7, 31.9, 25.7, 17.0.



***N*-Morpholinyl 9-phenyl-7*E*-nonenamide (Table 2, entry 10).** Procedure 1 was followed: *N*-morpholinyl 6-bromohexanamide (0.264 g, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (20 → 35% EtOAc in hexanes) as a colorless liquid (0.224 g, 74%).

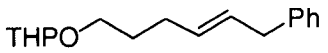
A second run was performed on the same scale, and the product was isolated in 79% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31-7.25 (m, 2H), 7.21-7.16 (m, 3H), 5.59-5.46 (m, 2H), 3.67-3.61 (m, 6H), 3.48-3.43 (m, 2H), 3.33 (d, J=6.0 Hz, 2H), 2.30 (t, J=7.2 Hz, 2H), 2.06-2.00 (m, 2H), 1.68-1.58 (m, 2H), 1.43-1.31 (m, 4 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.9, 141.2, 131.8, 129.1, 128.6, 128.5, 126.0, 67.1, 66.8, 46.1, 42.0, 39.2, 33.2, 32.5, 29.3, 29.1, 25.2.

HRMS (EI) calc. for $C_{19}H_{27}NO_2$: 301.2036, found: 301.2051.

IR (neat): 3026, 2924, 2853, 1650, 1454, 1431, 1272, 1116 cm^{-1}.



6-Phenyl-1-(2-tetrahydro-2*H*-pyran)-4*E*-hexene (Table 2, entry 11). Procedure 1 was followed: 2-(3-bromopropoxy)tetrahydro-2*H*-pyran (169 μL, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (3% Et_2O in hexanes) as a colorless liquid (0.207 g, 80%).

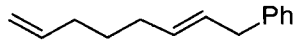
A second run was performed on the same scale, and the product was isolated in 74% yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.31-7.26 (m, 2H), 7.21-7.16 (m, 3H), 5.63-5.49 (m, 2H), 4.58-4.55 (m, 1H), 3.89-3.82 (m, 1H), 3.79-3.71 (m, 1H), 3.52-3.46 (m, 1H), 3.43-3.53 (m, 1H), 3.34 (d, J=6.0 Hz, 2H), 2.13 (q, J=6.0 Hz, 2H), 1.83-1.64 (m, 4H), 1.61-1.48 (m, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.1, 131.4, 129.5, 128.6, 128.5, 126.1, 99.0, 67.1, 62.4, 39.2, 30.9, 29.7, 29.3, 25.7, 19.8.

HRMS (ESI) calc. for $C_{17}H_{24}O_2Na$ [M+Na]: 283.1669, found: 283.1679.

IR (neat): 3027, 2941, 2870, 1453, 1121, 1034, 969 cm^{-1}.

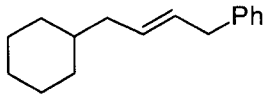


1-Phenyl-2*E*,7-octadiene (Table 2, entry 12). [70603-44-0] Procedure 1 was followed: 5-bromo-1-pentene (119 μL, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (pentane) as a colorless liquid (0.136 g, 73%).

A second run was performed on the same scale, and the product was isolated in 75% yield.

^{1}H NMR (C_6D_6, 300 MHz): δ 7.16-7.01 (m, 5H), 5.74 (ddt, J=17.1, 10.2, 6.6 Hz, 1H), 5.53-5.43 (m, 1H), 5.39-5.28 (m, 1H), 5.00-4.90 (m, 2H), 3.19 (d, J=6.6 Hz, 2H), 1.94-1.85 (m, 4H), 1.34 (quin., J=7.2 Hz, 2H).

^{13}C NMR (C_6D_6, 125 MHz): δ 141.5, 139.2, 132.0, 130.0, 129.2, 12.0, 126.6, 115.09, 39.8, 33.9, 32.6, 29.3.

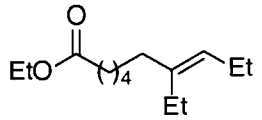


(4-Phenyl-2*E*-butenyl)cyclohexane (Table 2, entry 13). [121253-59-6] Procedure 1 was followed: (bromomethyl)cyclohexane (140 μL, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (15 mg, 0.050 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The reaction was quenched with iodine in THF, and the product was isolated by flash chromatography (pentane) as a colorless liquid (0.133 g, 62%).

A second run was performed on the same scale, and the product was isolated in 57% yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33-7.26 (m, 2H), 7.22-7.20 (m, 3H), 5.59-5.50 (m, 2H), 3.37 (d, J=3.6 Hz, 2H), 1.95 (t, J=4.2 Hz, 2H), 1.75-1.65 (m, 5H), 1.34-1.14 (m, 4H), 0.95-0.88 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.9, 131.4, 130.4, 129.2, 129.0, 126.6, 41.3, 39.9, 38.8, 33.9, 27.3, 27.1.



Ethyl 7-ethyl-7*E*-decenoate (Table 2, entry 14). Procedure 1 was followed: ethyl 6-bromohexanoate (228 μL, 1.0 mmol), 3-hexyne (233 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless oil (0.183 g, 81%).

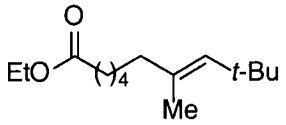
A second run was performed on the same scale, and the product was isolated in 89% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.04 (t, J=7.2 Hz, 1H), 4.10 (q, J=7.2 Hz, 2H), 2.27 (t, J=7.5 Hz, 2H), 2.02-1.92 (m, 6H), 1.66-1.56 (m, 2H), 1.40-1.21 (m, 7H), 0.92 (t, J=7.5 Hz, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0, 140.4, 126.1, 60.3, 36.5, 34.5, 29.1, 28.0, 25.1, 23.1, 21.0, 15.0, 14.4, 13.5.

HRMS (EI) calc. for $C_{14}H_{26}O_2$: 226.1927, found: 226.1922.

IR (neat): 2964, 2873, 1739, 1181 cm^{-1}.



Ethyl 9,9-dimethyl-7-methyl-7*E*-decenoate (Table 2, entry 15). Procedure 1 was followed: ethyl 6-bromohexanoate (228 μL, 1.0 mmol), 4,4-dimethyl-2-pentyne (269 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (15 mg, 0.050 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). Reaction time: 48 h. The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless liquid (0.181 g, 75%).

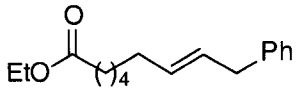
A second run was performed on the same scale, and the product was isolated in 76% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.13 (s, 1H), 4.13 (q, J=7.2 Hz, 2H), 2.28 (t, J=7.8 Hz, 2H), 1.90 (t, J=6.9 Hz, 2H), 1.67 (s, 3H), 1.65-1.59 (m, 2H), 1.38-1.25 (m, 4H), 1.25 (t, J=7.2 Hz, 3H), 1.07 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0, 135.2, 133.9, 60.3, 41.7, 34.6, 32.2, 31.3, 28.8, 28.0, 25.1, 17.0, 14.4.

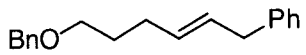
HRMS calc. for $C_{15}H_{28}O_2Na$ [M+Na]: 263.1892, found: 263.1893.

IR: 2954, 2863, 1739, 1180 cm^{-1}.



Ethyl 9-phenyl-7*E*-nonenoate (Table 3, entry 1). Procedure 1 was followed: ethyl 6-iodohexanoate (0.270 g, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless oil (0.216 g, 83%).

A second run was performed on the same scale, and the product was isolated in 81% yield.



6-Phenyl-hex-4*E*-enyloxymethylbenzene (Table 3, entry 2). Procedure 1 was followed: benzyl 3-(*p*-toluenesulfonyloxy)propyl ether (0.320 g, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless liquid (0.198 g, 83%).

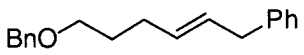
A second run was performed on the same scale, and the product was isolated in 84% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.17 (m, 10H), 5.63-5.49 (m, 2H), 4.50 (s, 2H), 3.49 (t, J=6.6 Hz, 2H), 3.34 (d, J=5.7 Hz, 2H), 2.18-2.11 (m, 2H), 1.77-1.68 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.3, 139.0, 131.5, 129.8, 128.8, 128.7, 128.0, 127.9, 126.3, 73.2, 70.1, 39.4, 30.0, 29.4.

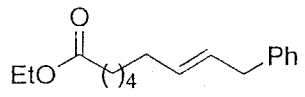
HRMS (ESI) calc. for $C_{19}H_{22}ONa$ [M+Na]: 289.1563, found: 289.1570.

IR (neat): 3028, 2935, 2853, 1453, 1103 cm^{-1}.



6-Phenyl-hex-4*E*-enyloxymethylbenzene (Table 3, entry 3). Procedure 1 was followed: benzyl 3-chloropropyl ether (0.185 g, 1.0 mmol), 3-phenyl-1-propyne (249 μL, 2.0 mmol), Cp_2ZrHCl (0.542 g, 2.0 mmol), $Pd(acac)_2$ (7.5 mg, 0.025 mmol), LiBr (0.174 g, 2.0 mmol), NMP (2.0 mL), and THF (2.0 mL). The product was isolated by flash chromatography (2% Et_2O in hexanes) as a colorless liquid (0.105 g, 44%).

A second run was performed on the same scale, and the product was isolated in 48% yield.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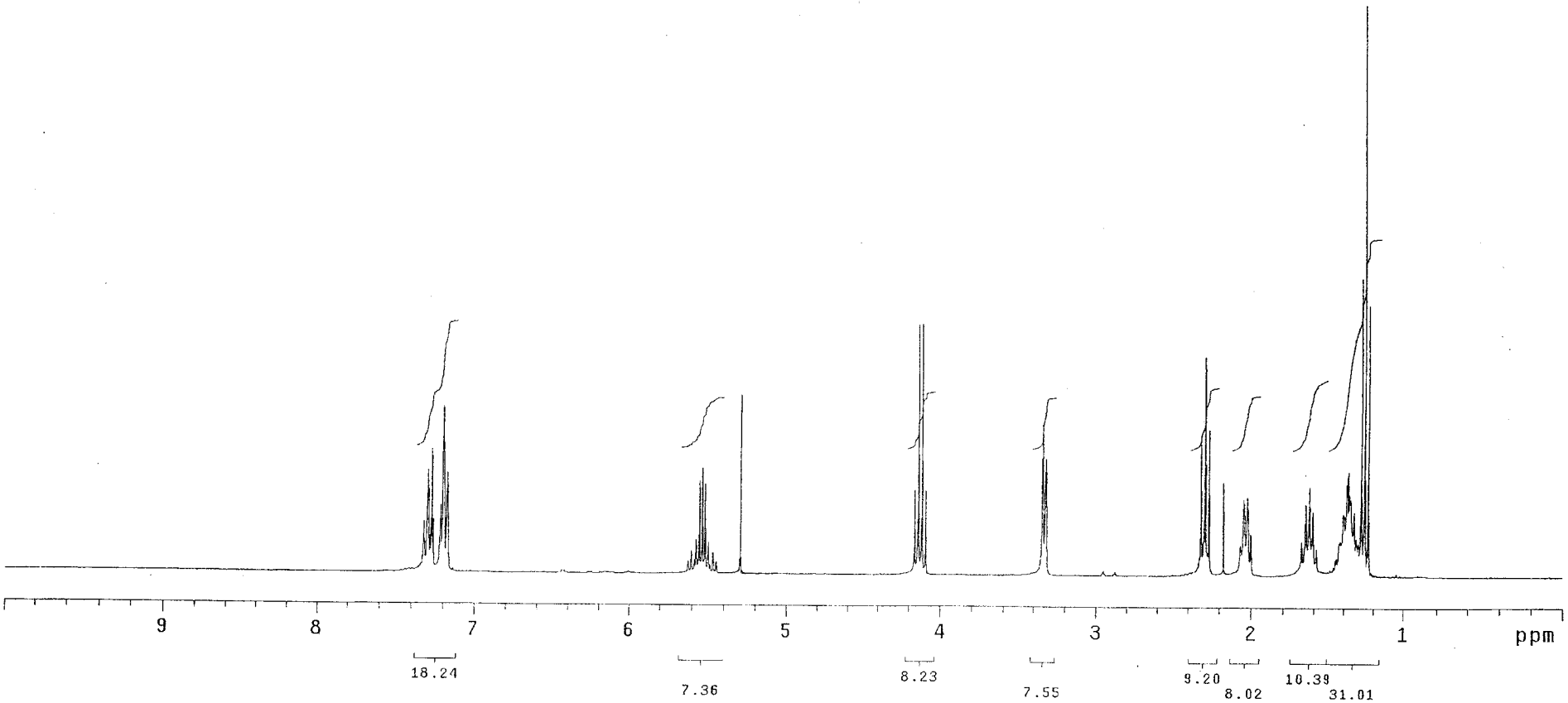
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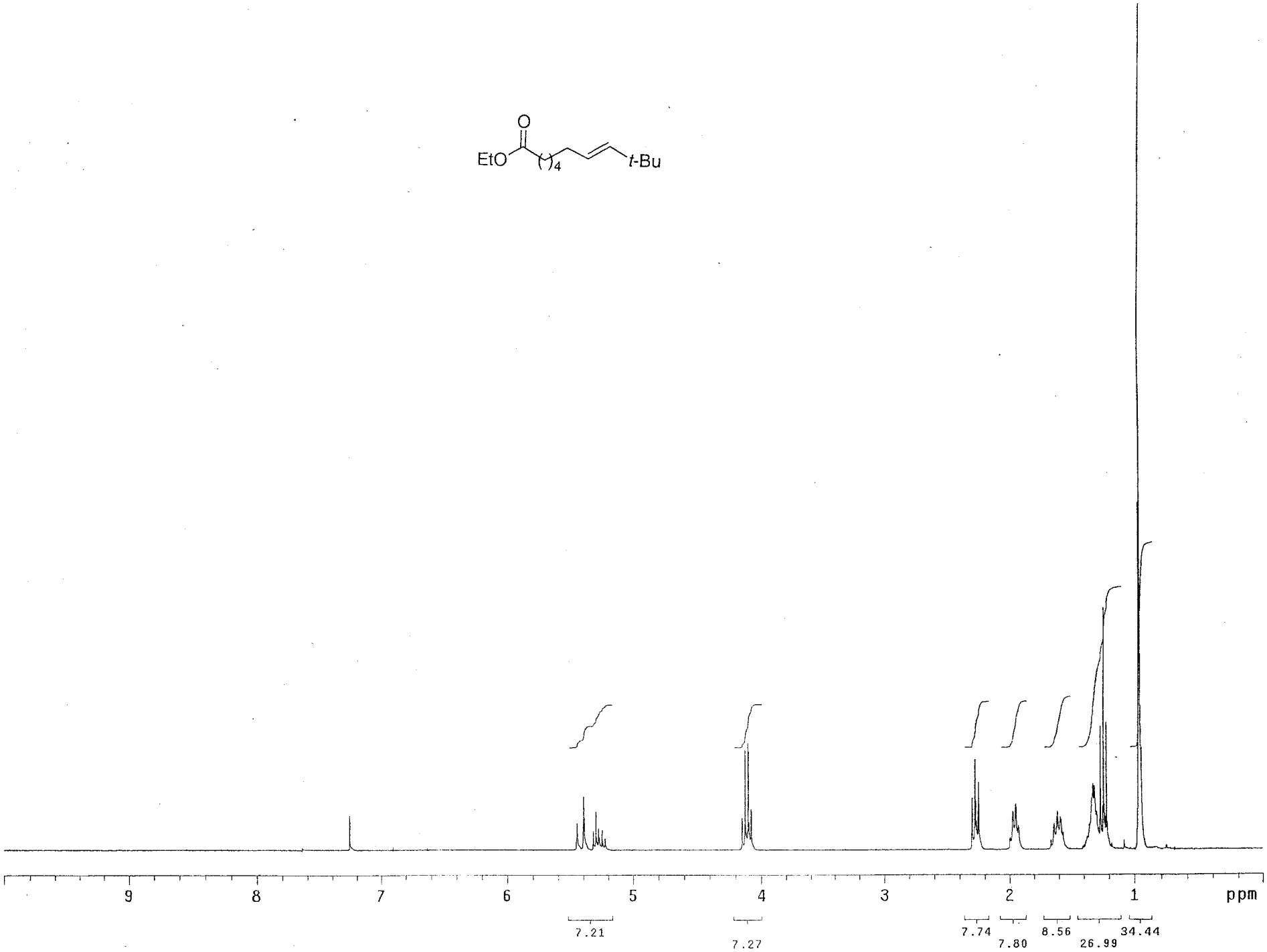
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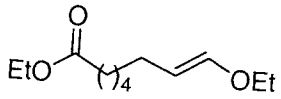
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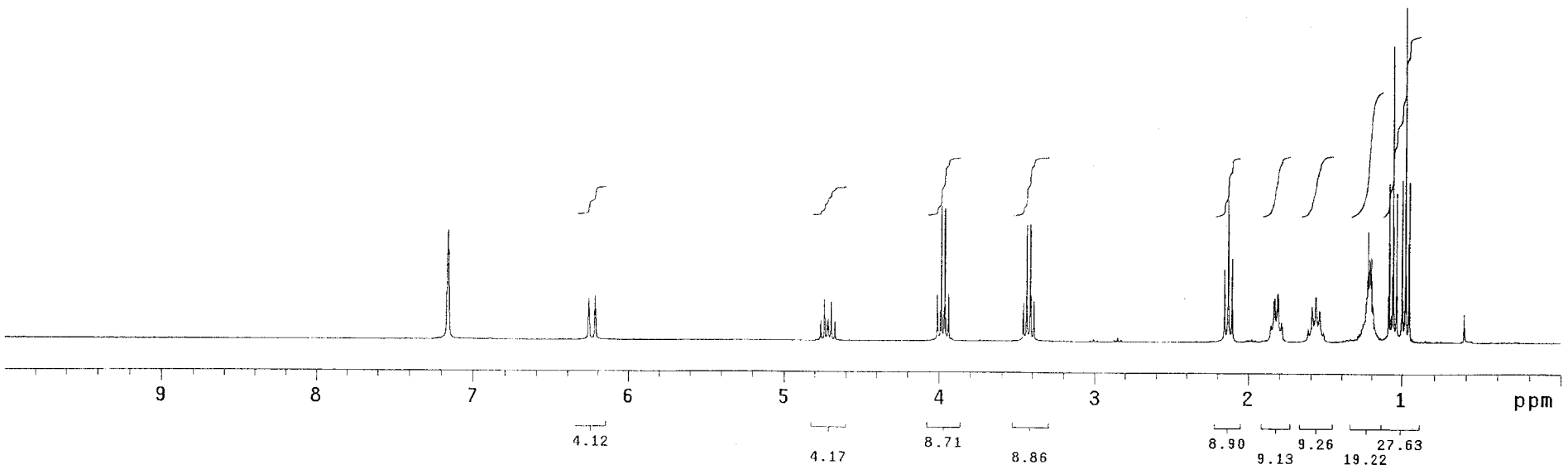
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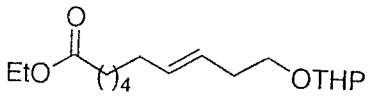
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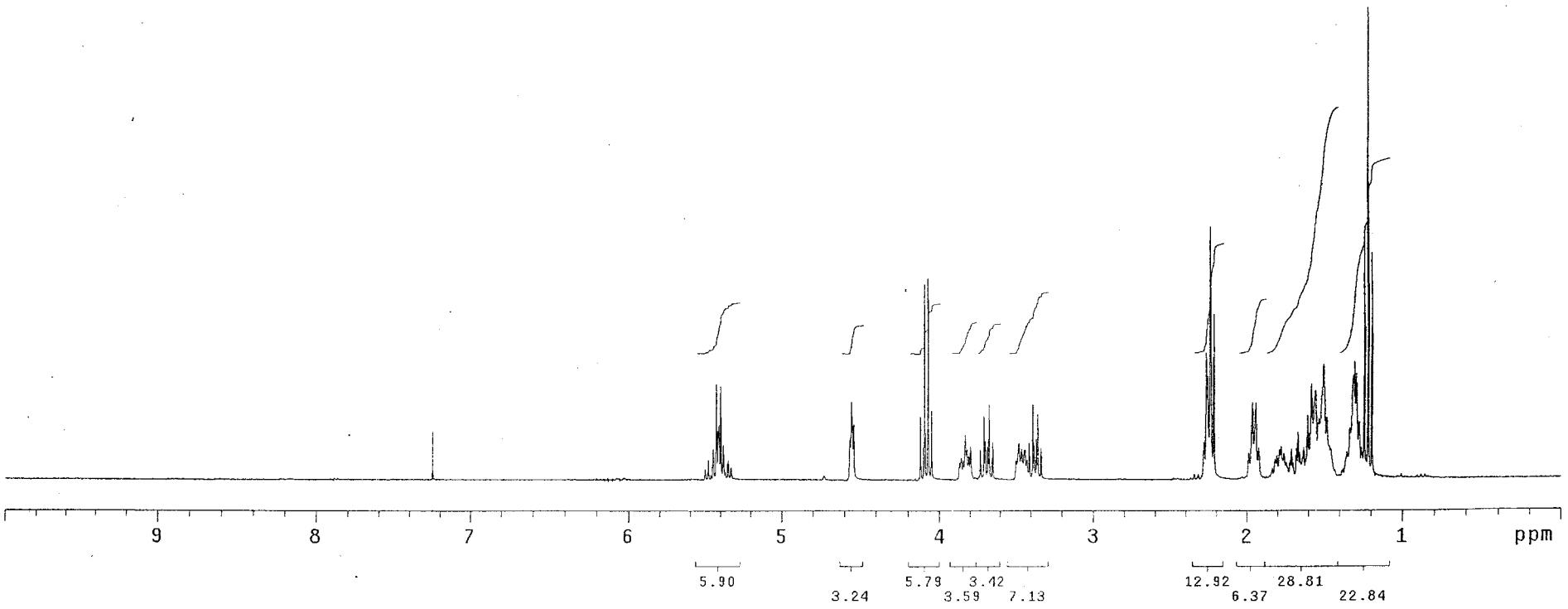
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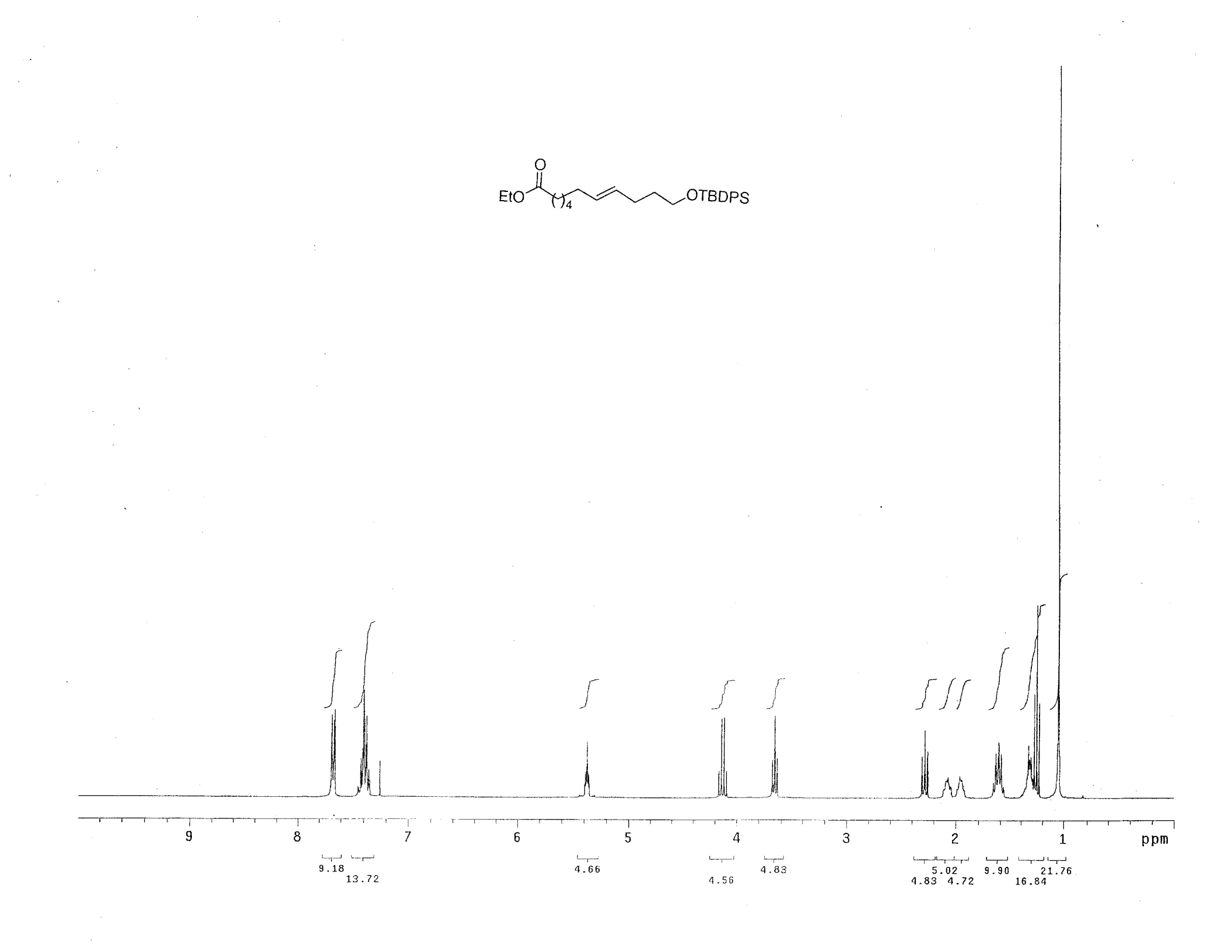
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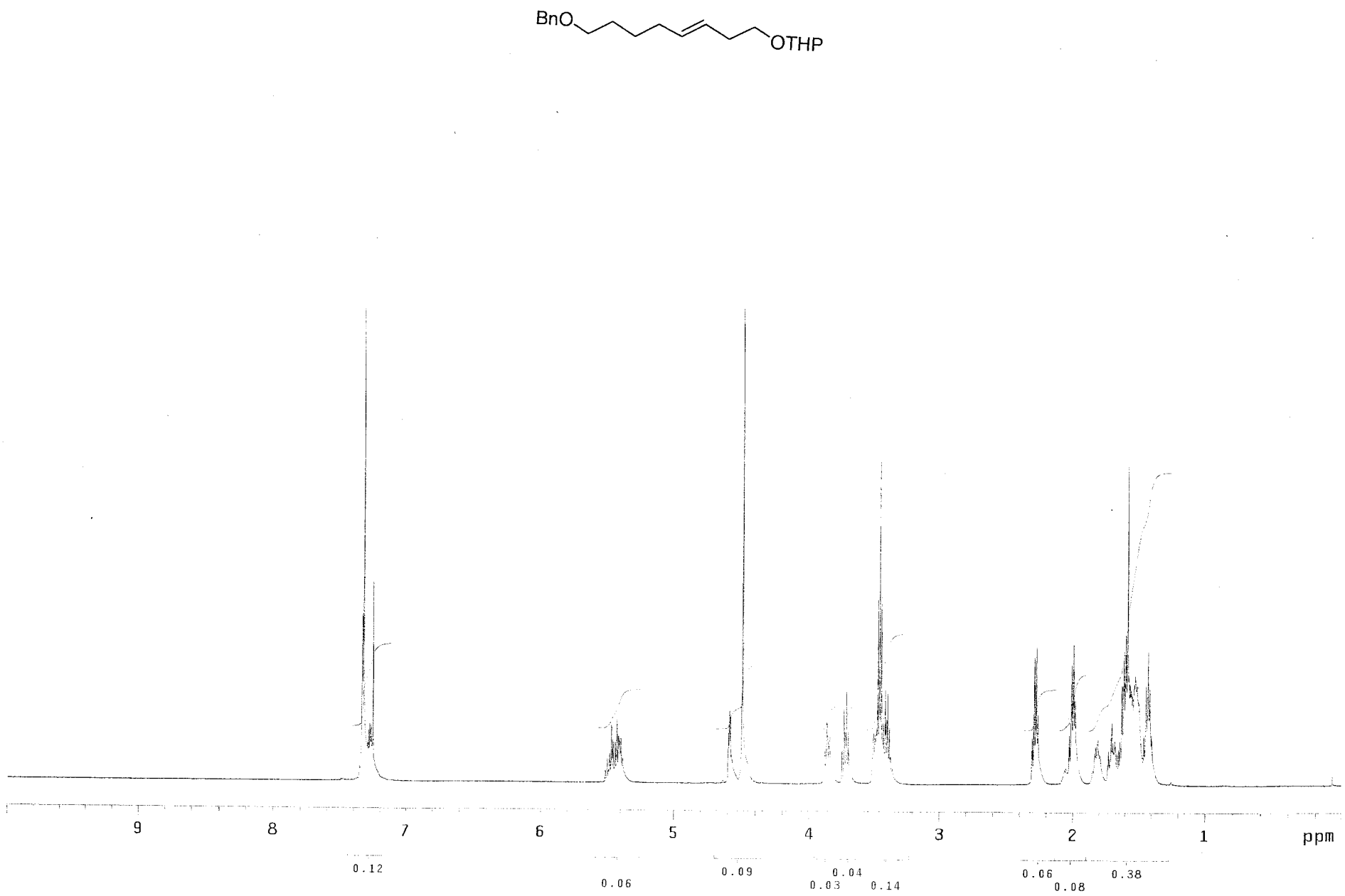
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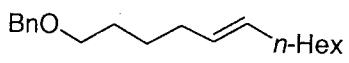
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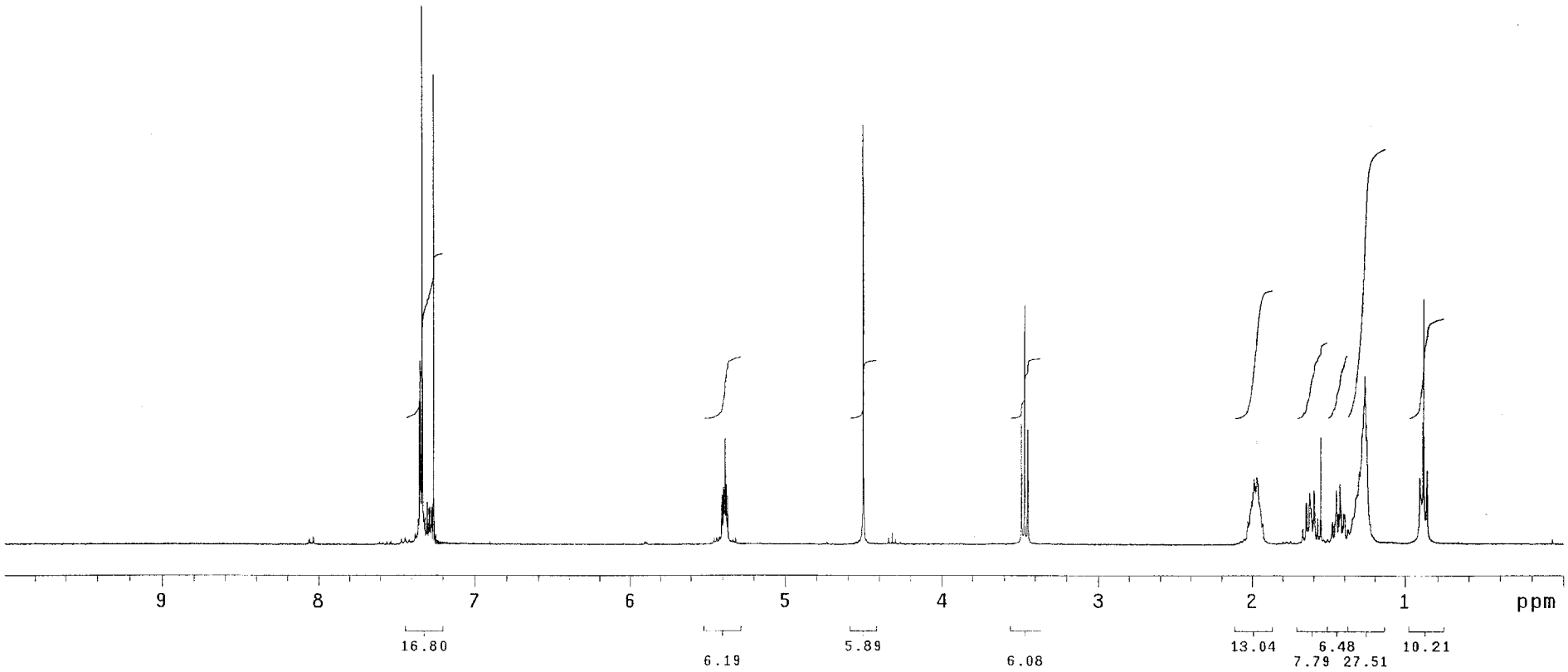
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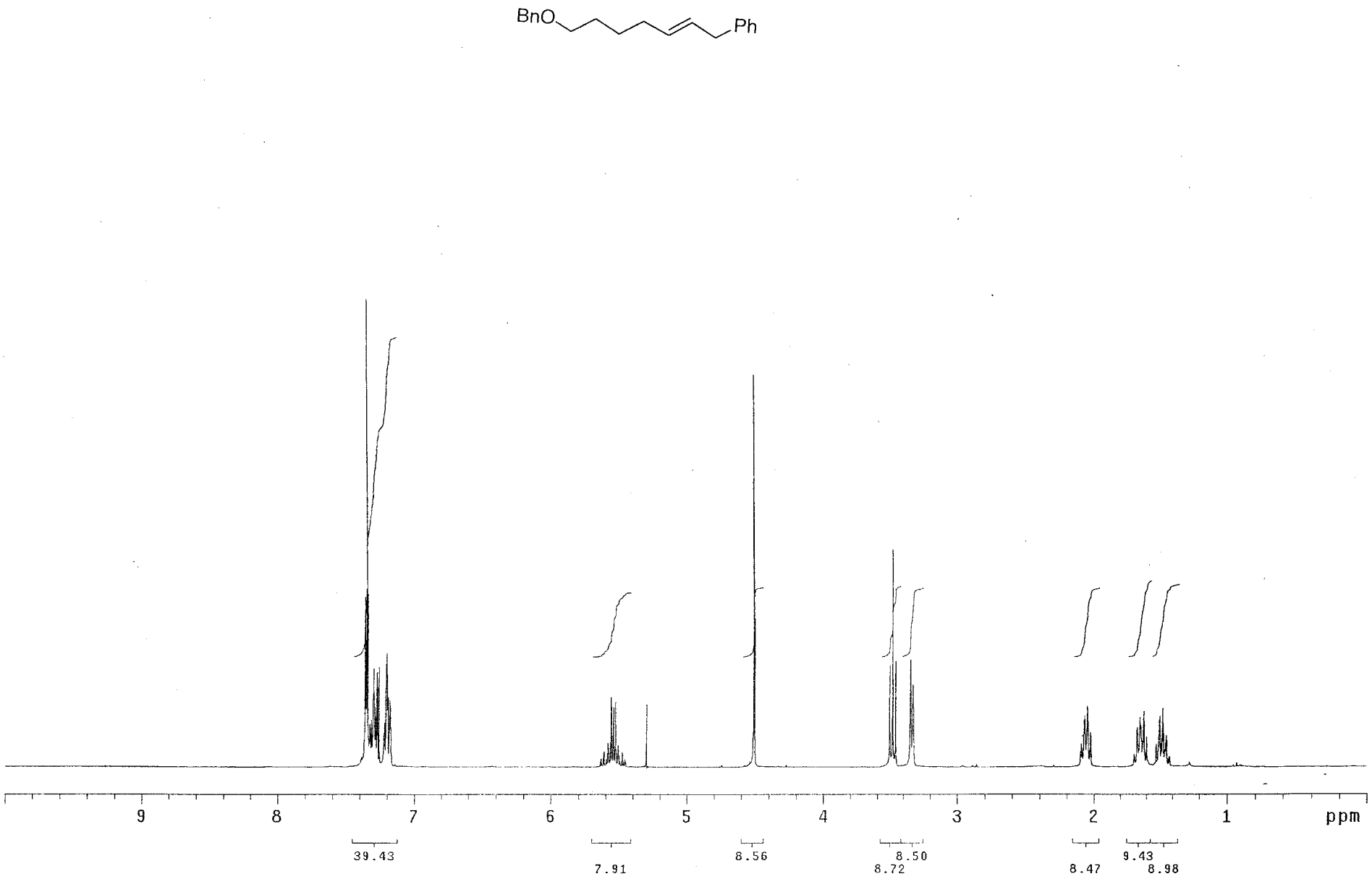
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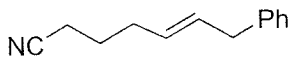
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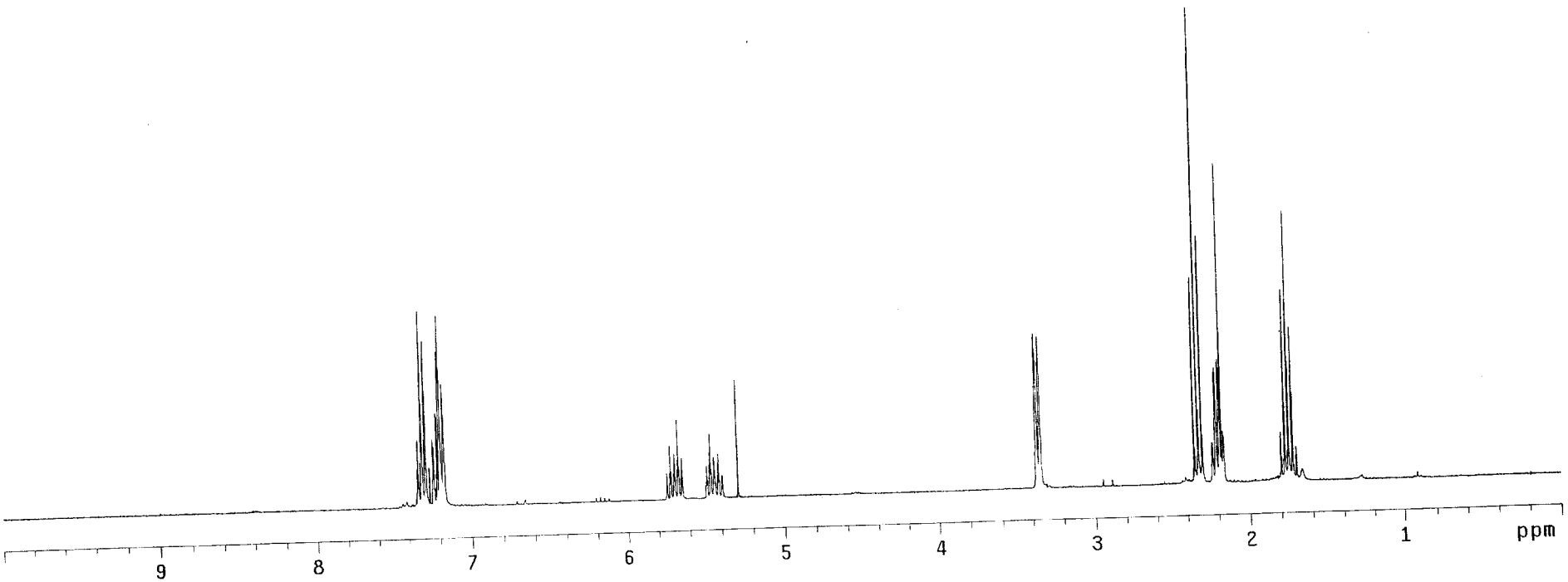
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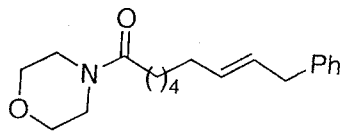
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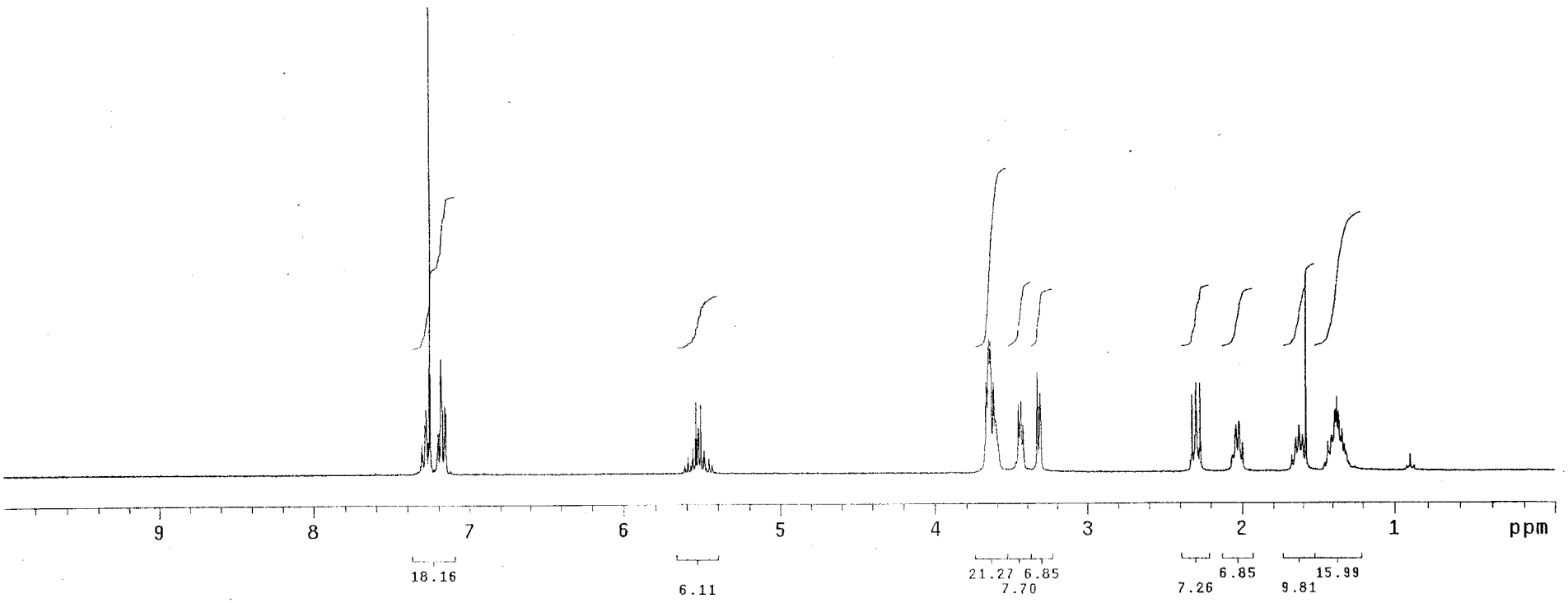
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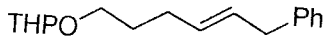
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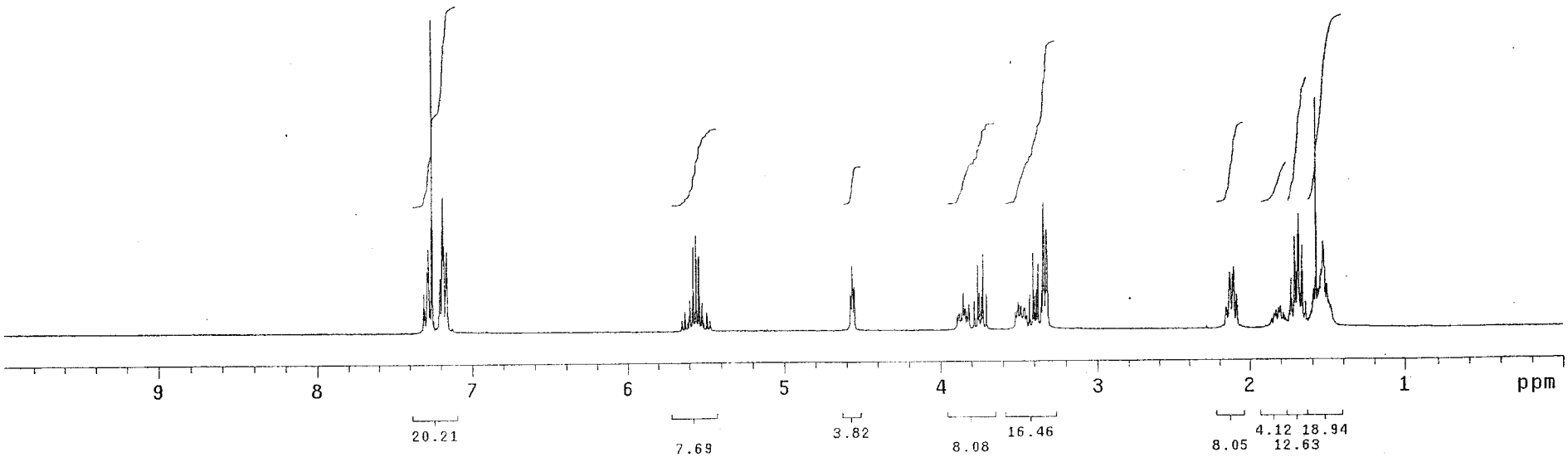
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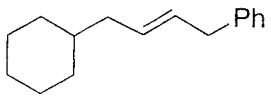
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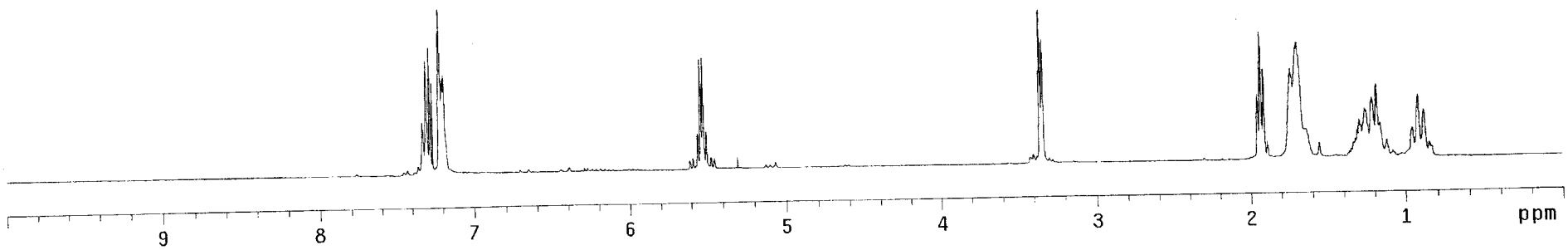
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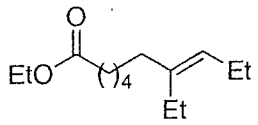
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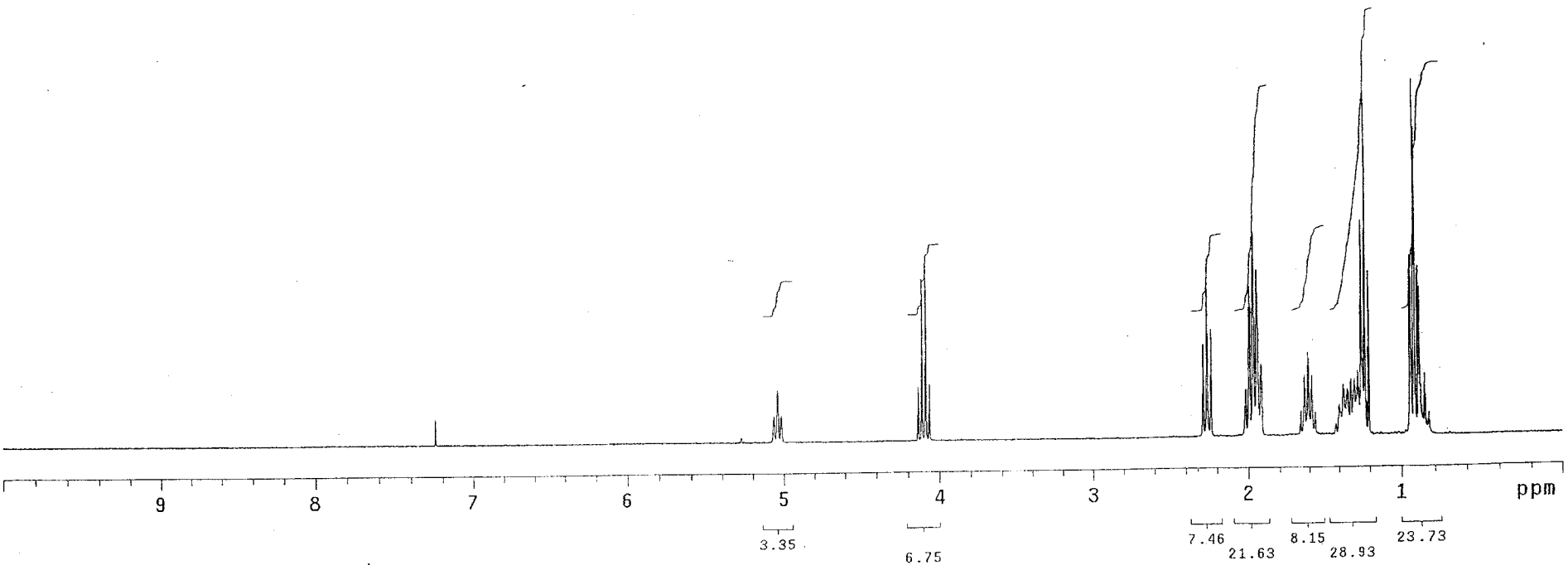
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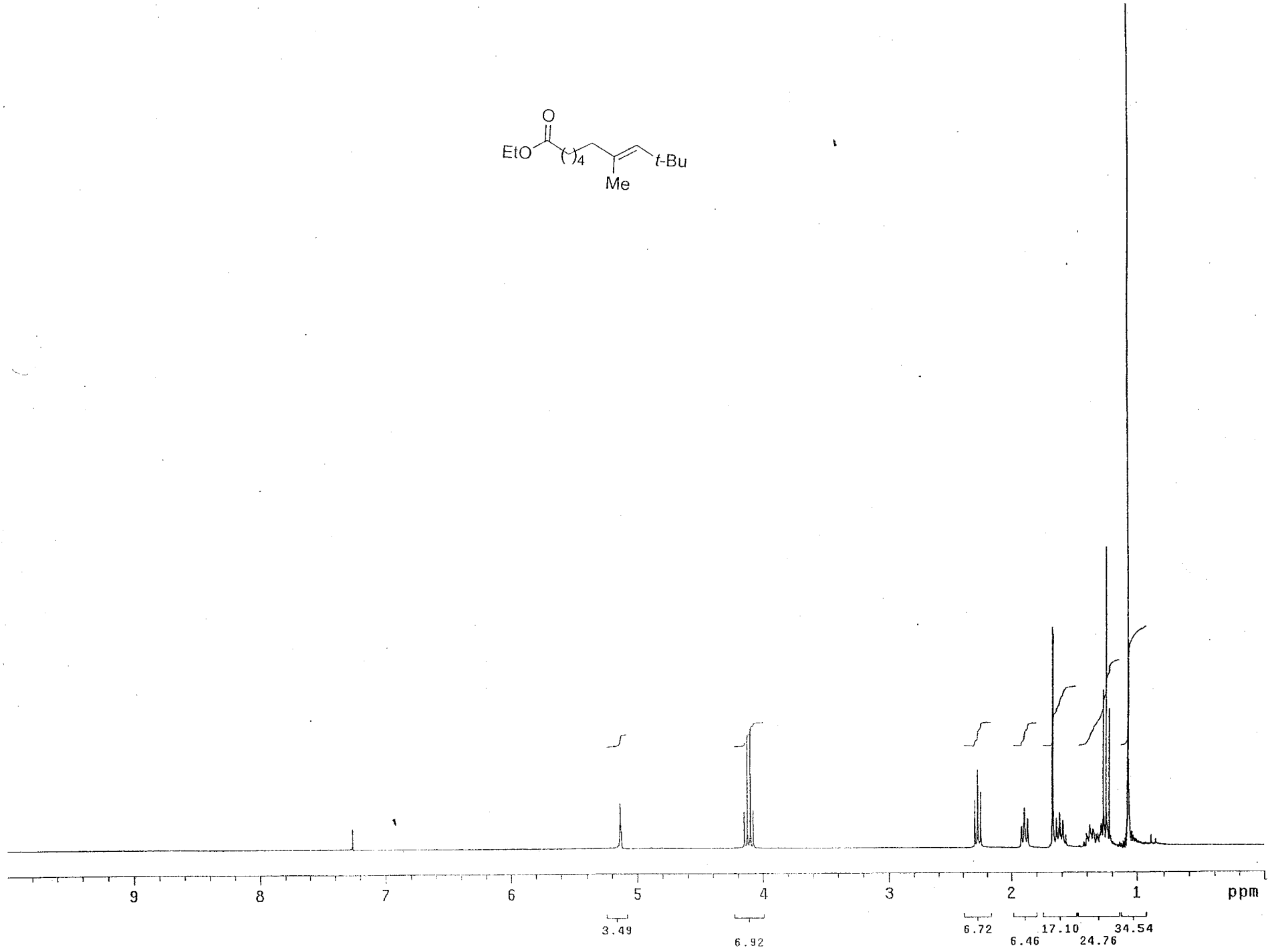
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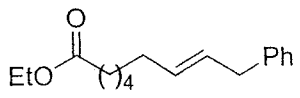
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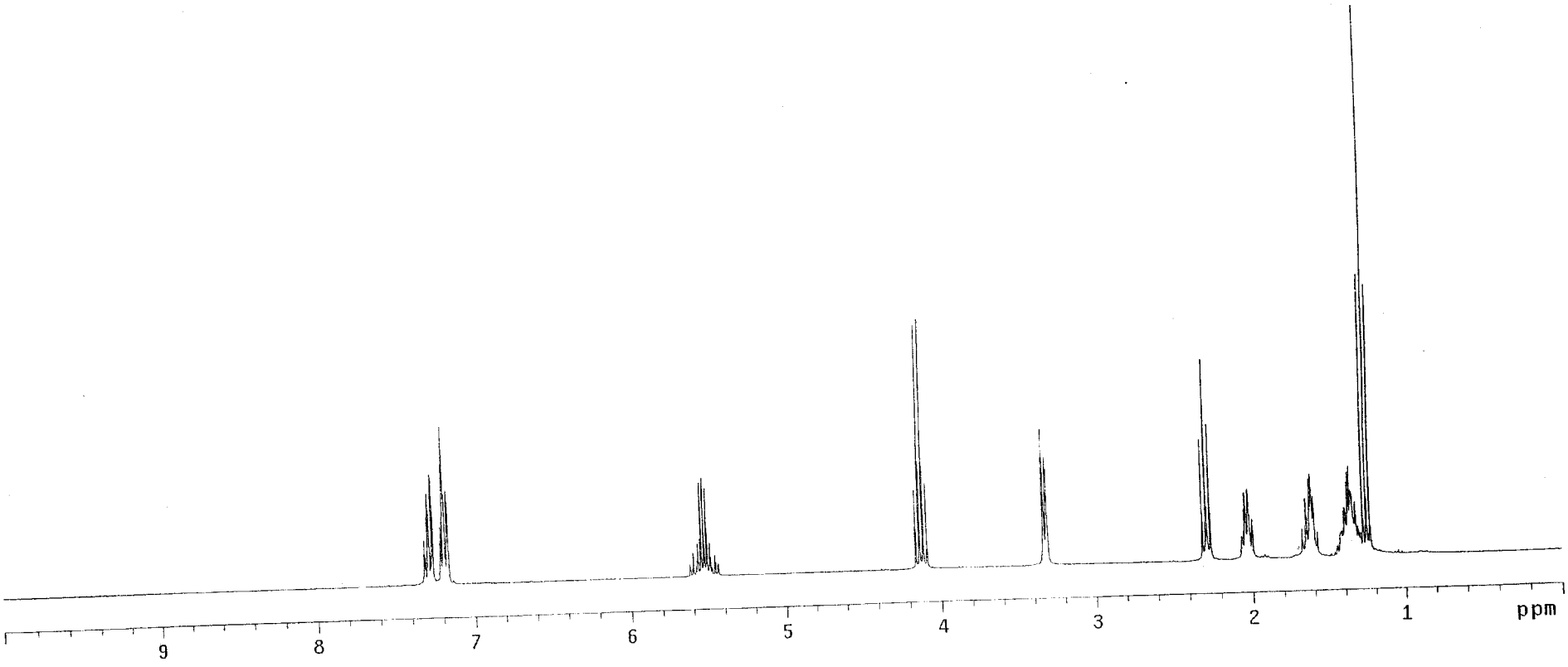
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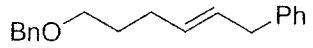
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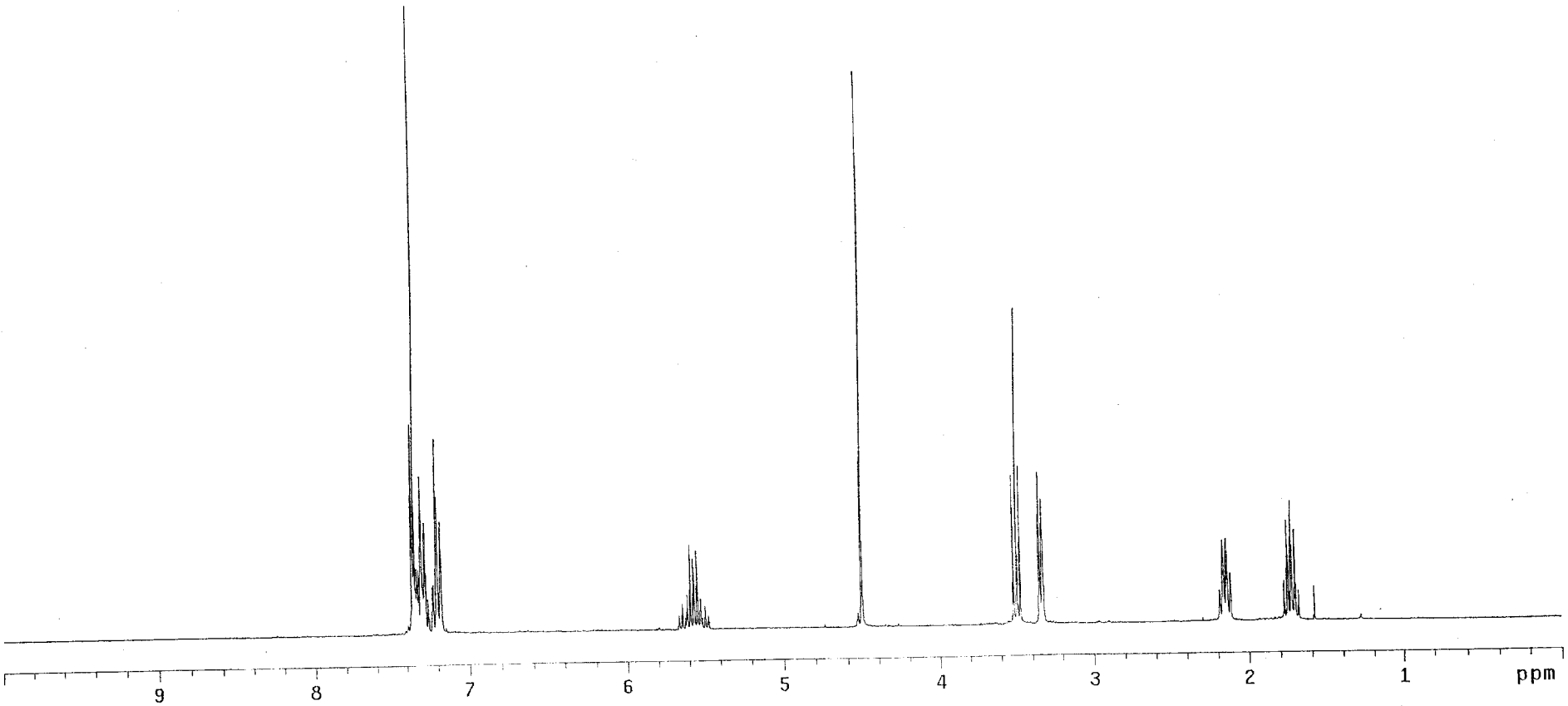
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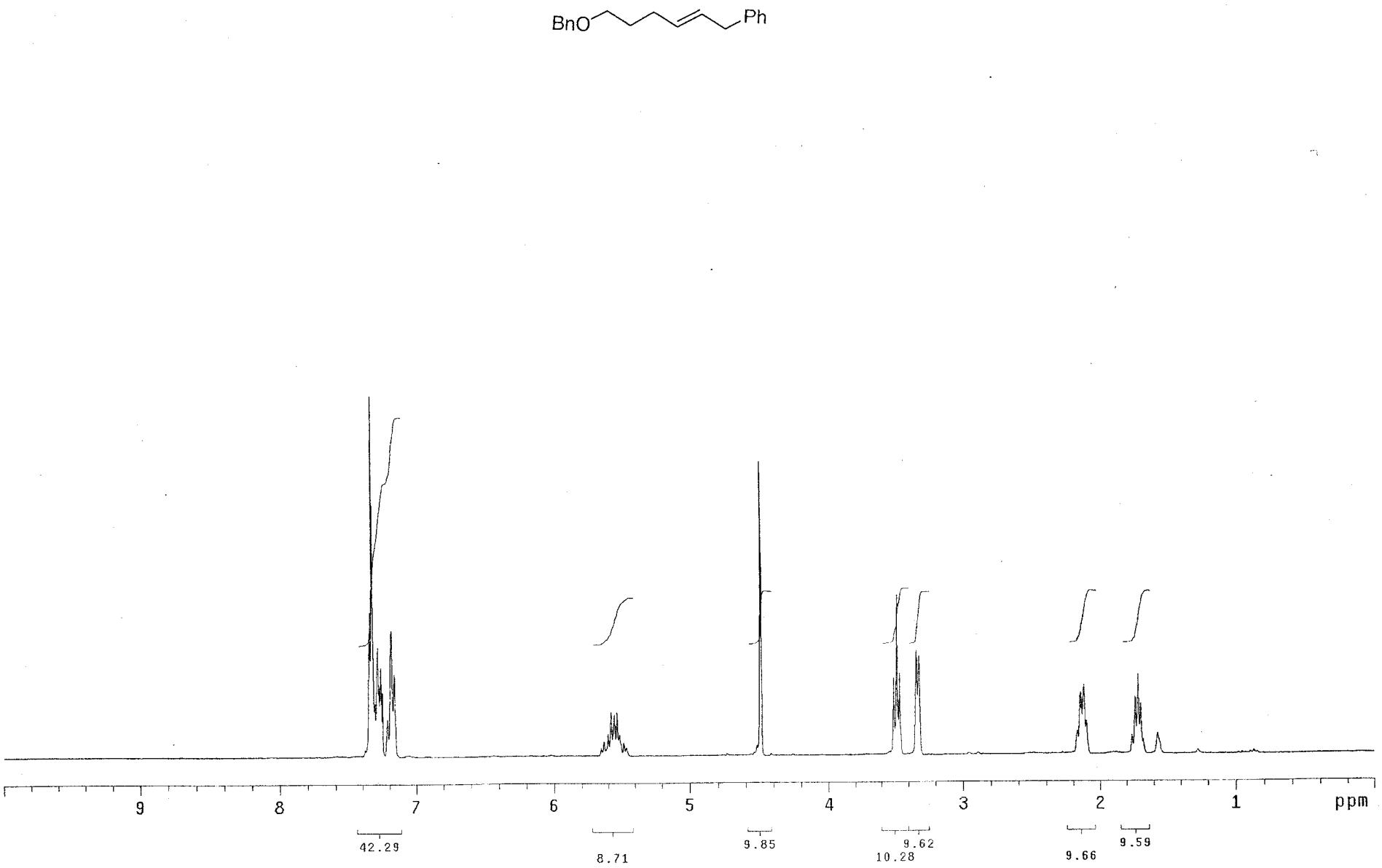
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