Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Catalytic Asymmetric Hydroboration of *β,γ*-Unsaturated Weinreb Amides: Surprising Influence of the Borane.

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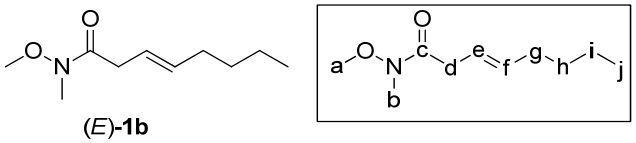
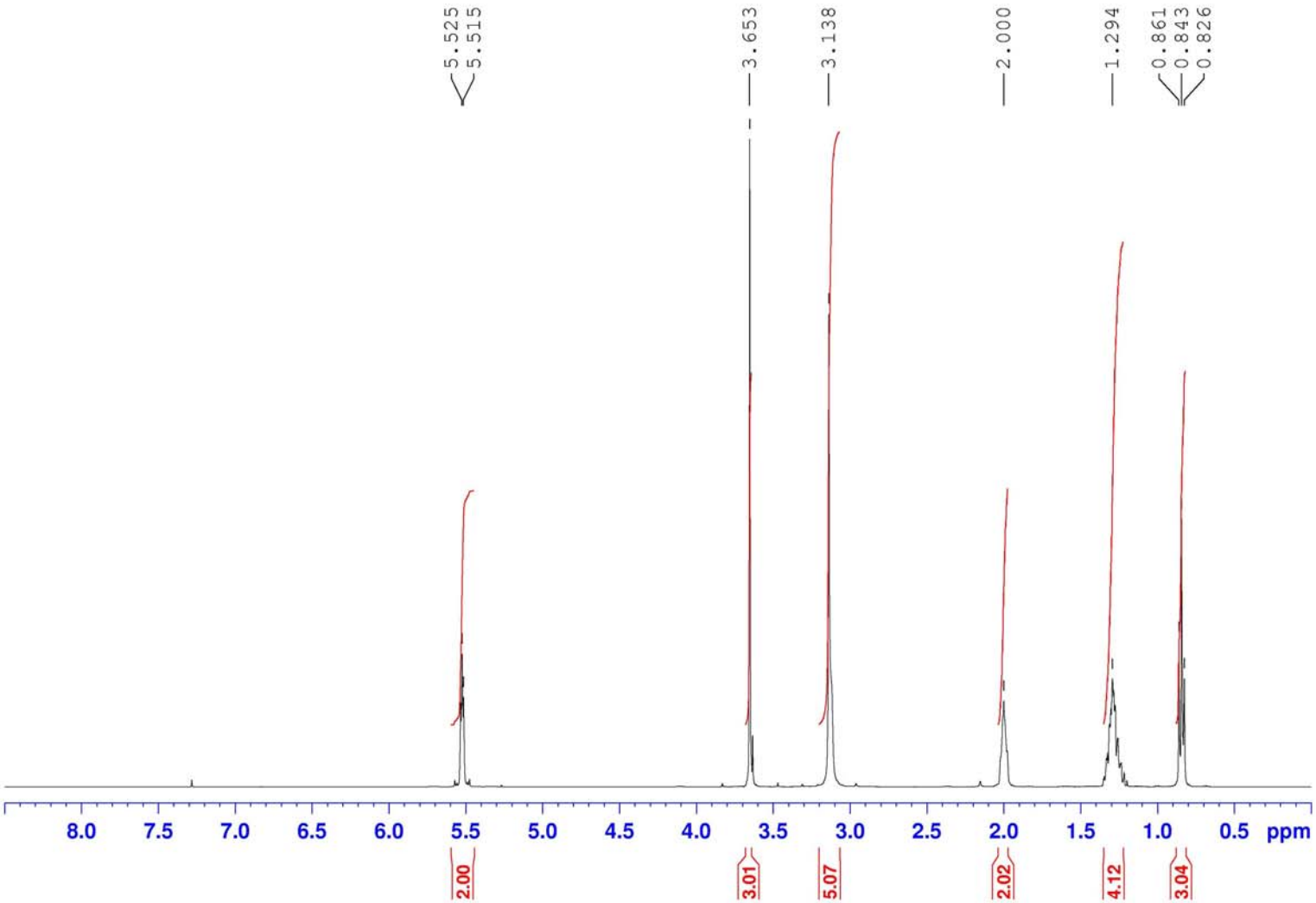


(*E*)-**1b**

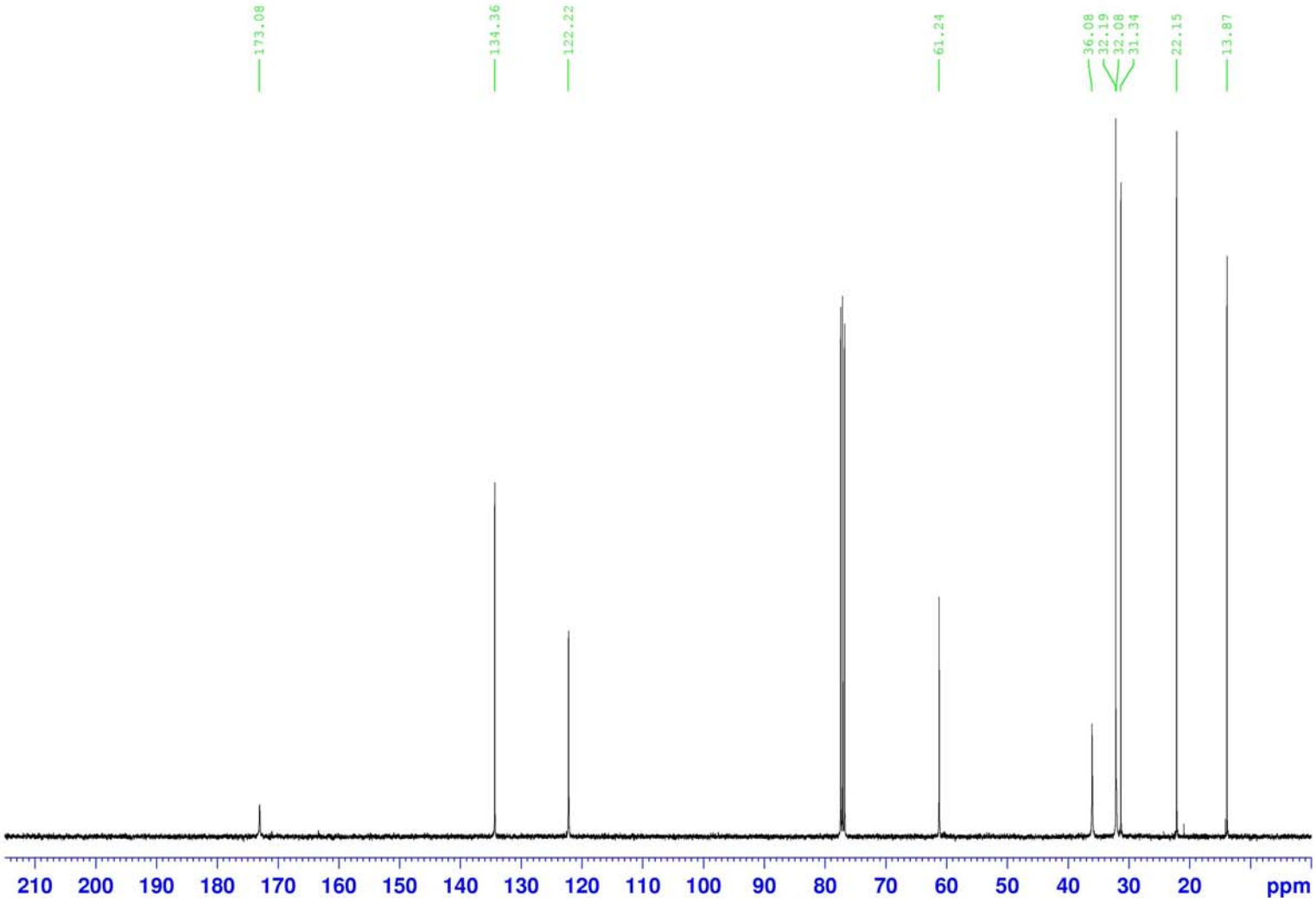
The general procedure for the synthesis of *β*,*γ*-unsaturated Weinreb amides affords, after flash chromatography on silica gel (85:15 hexanes:ethyl acetate), the title compound (85%) as a colorless oil.

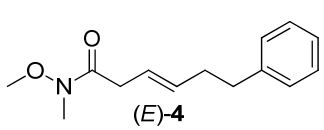
TLC analysis	R_f 0.6 (50:50 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 5.60–5.40 (2H, m, e,f), 3.65 (3H, s, a), 3.15–3.05 (2H, suspected d, d), 2.05–1.95 (2H, m, g), 1.40–1.20 (4H, m, h,i), 0.84 (3H, t, J = 7.0 Hz, j).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.08 (c), 134.36 (f), 122.22 (e), 61.24 (a), 36.08 (d), 32.19 (g), 32.08 (b), 31.34 (h), 22.15 (i), 13.87 (j).
IR (neat)	2958 (CH sp^2 stretch), 2929 (CH sp^3 stretch), 2873, 1667 (C=O stretch), 1465, 1414, 1379 (C-N stretch), 1175, 1102 (C-O stretch), 999, 969, 933 cm^{-1}.
HRMS (CI)	Calcd. for $C_{10}H_{20}NO_2$ (M+H): 186.1494, found 186.1488 *m/z*.

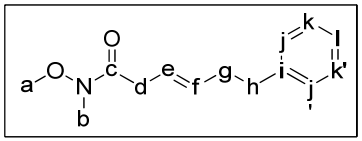
^{1}H NMR of (*E*)-1b



^{13}C NMR of (*E*)-1b



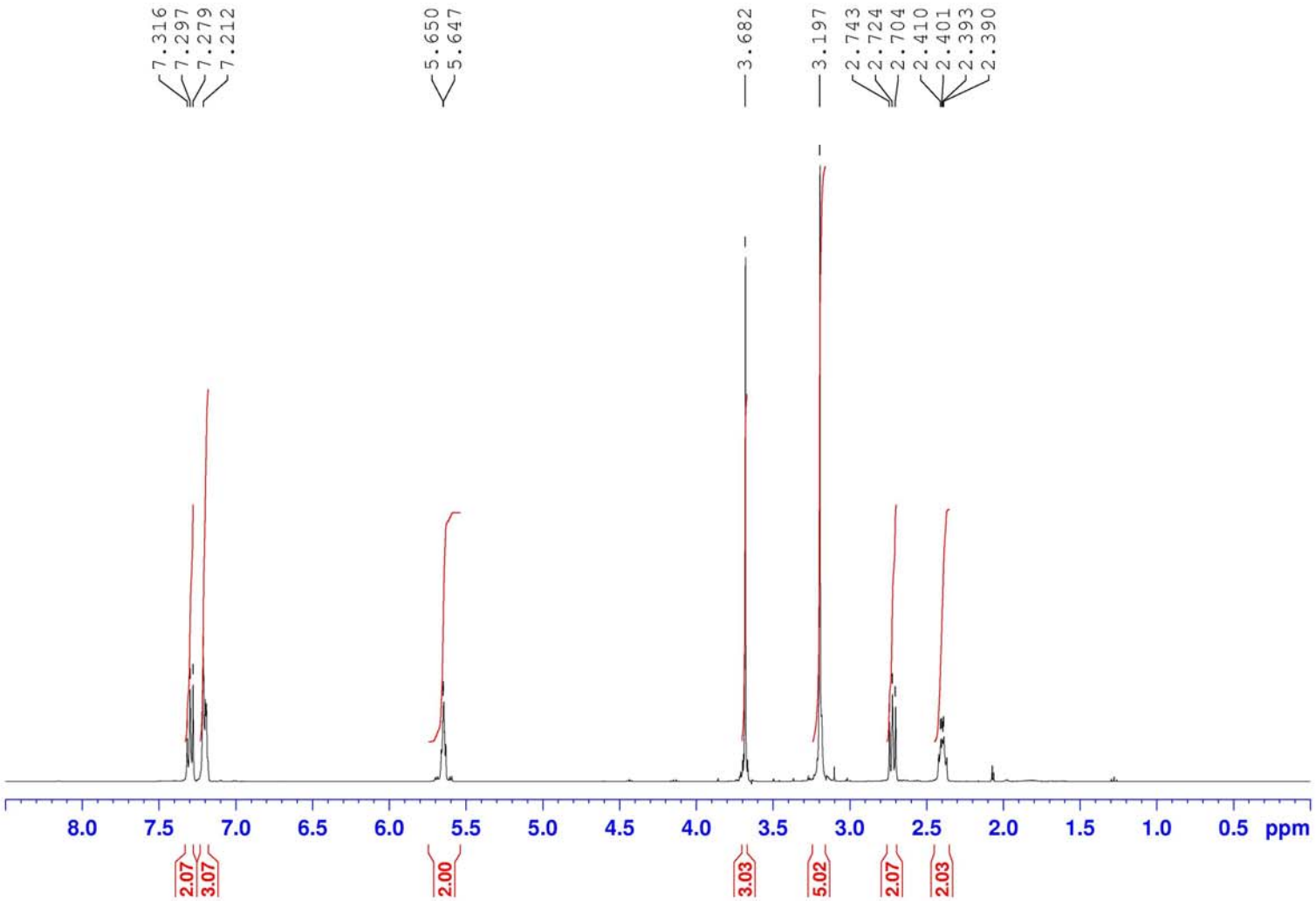




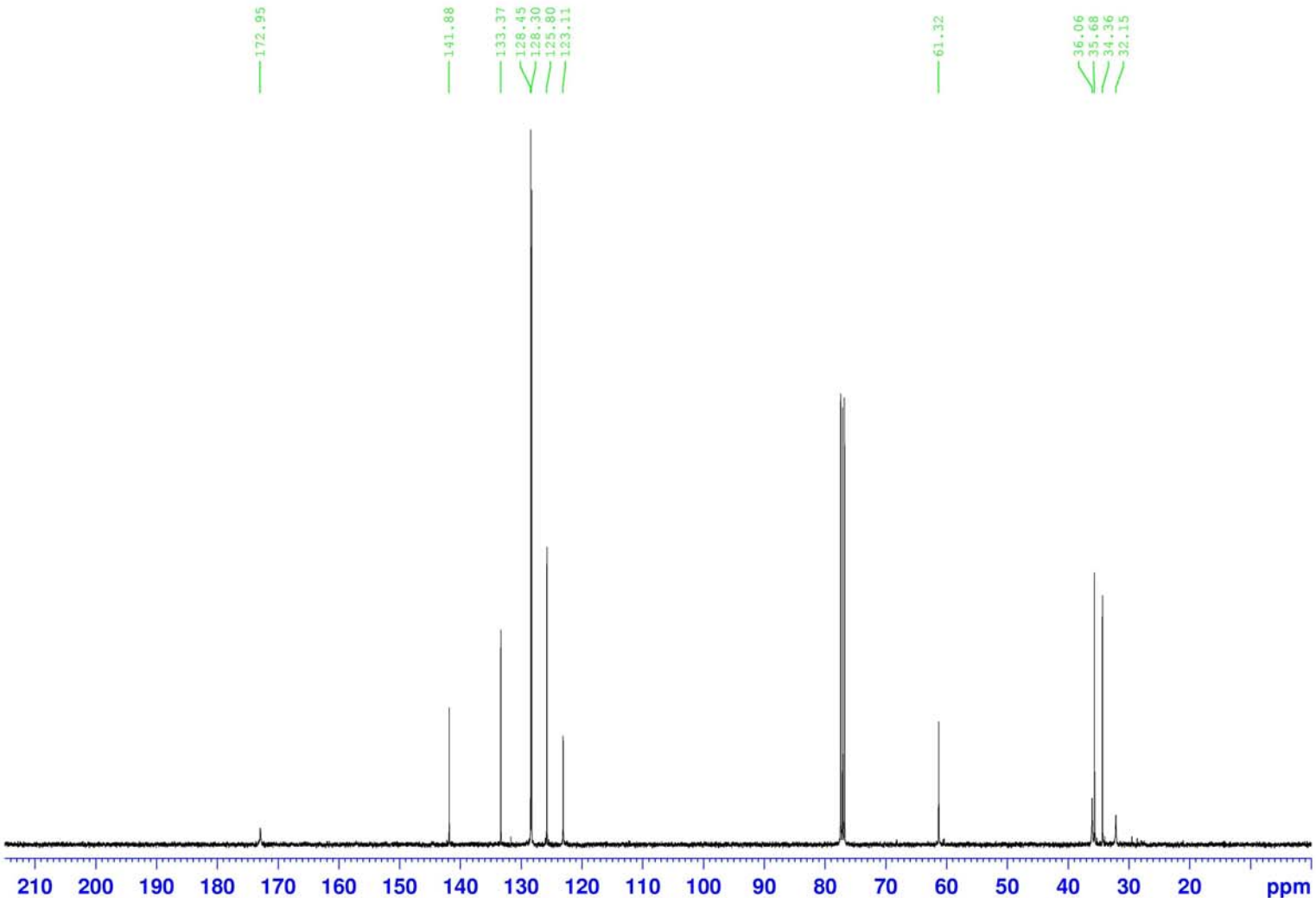
The general procedure for the synthesis of *β*,*γ*-unsaturated Weinreb amides affords, after flash chromatography on silica gel (85:15 hexanes:ethyl acetate), the title compound (78%) as a colorless oil.

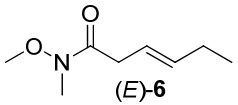
TLC analysis	R_f 0.60 (50:50 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.35–7.25 (2H, m, k,k'), 7.25–7.15 (3H, m, j,j',l), 5.20–5.10 (2H, m, e,f), 3.68 (3H, s, a), 3.15–3.05 (2H, suspected d, d), 3.20 (3H, s, b), 2.72 (2H, t, J = 7.5 Hz, h), 2.45–2.35 (2H, m, g).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.95 (c), 141.88 (i), 133.37 (f), 128.45 (j,j'), 128.30 (k,k'), 125.80 (l), 123.11 (e), 61.32 (a), 36.06 (d), 35.68 (h), 34.36 (g), 32.15 (b).
IR (neat)	3026 (CH sp^2 stretch), 2936 (CH sp^3 stretch), 1657 (C=O stretch), 1454, 1382 (C-N stretch), 1176, 1108 (C-O stretch), 1000, 967, 746, 699 cm^{-1}.
HRMS (CI)	Calcd. for $C_{14}H_{20}NO_2$ (M+H): 234.1495, found 234.1504 *m/z*.

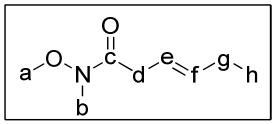
^{1}H NMR of (*E*)-4



^{13}C NMR of (*E*)-4



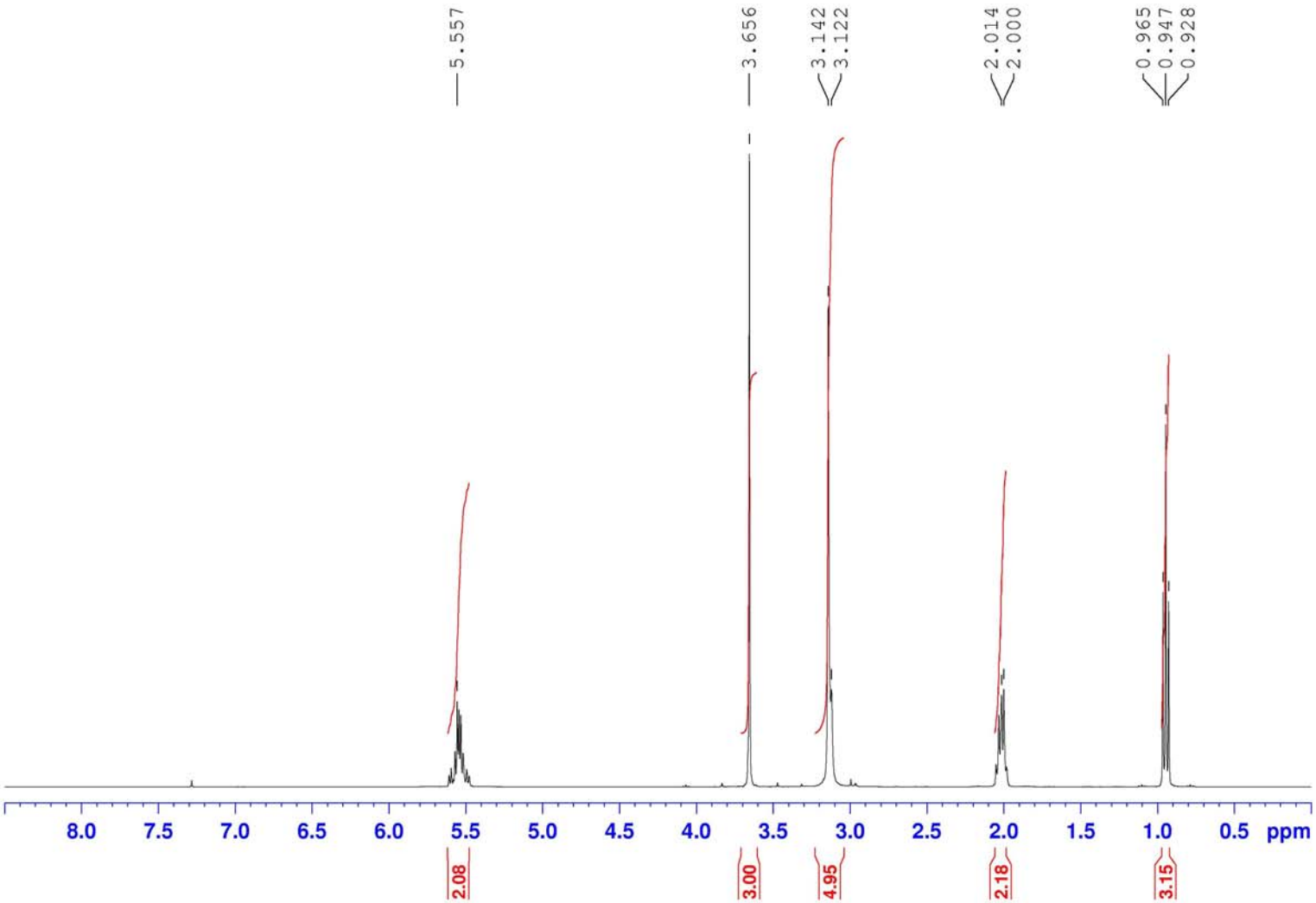




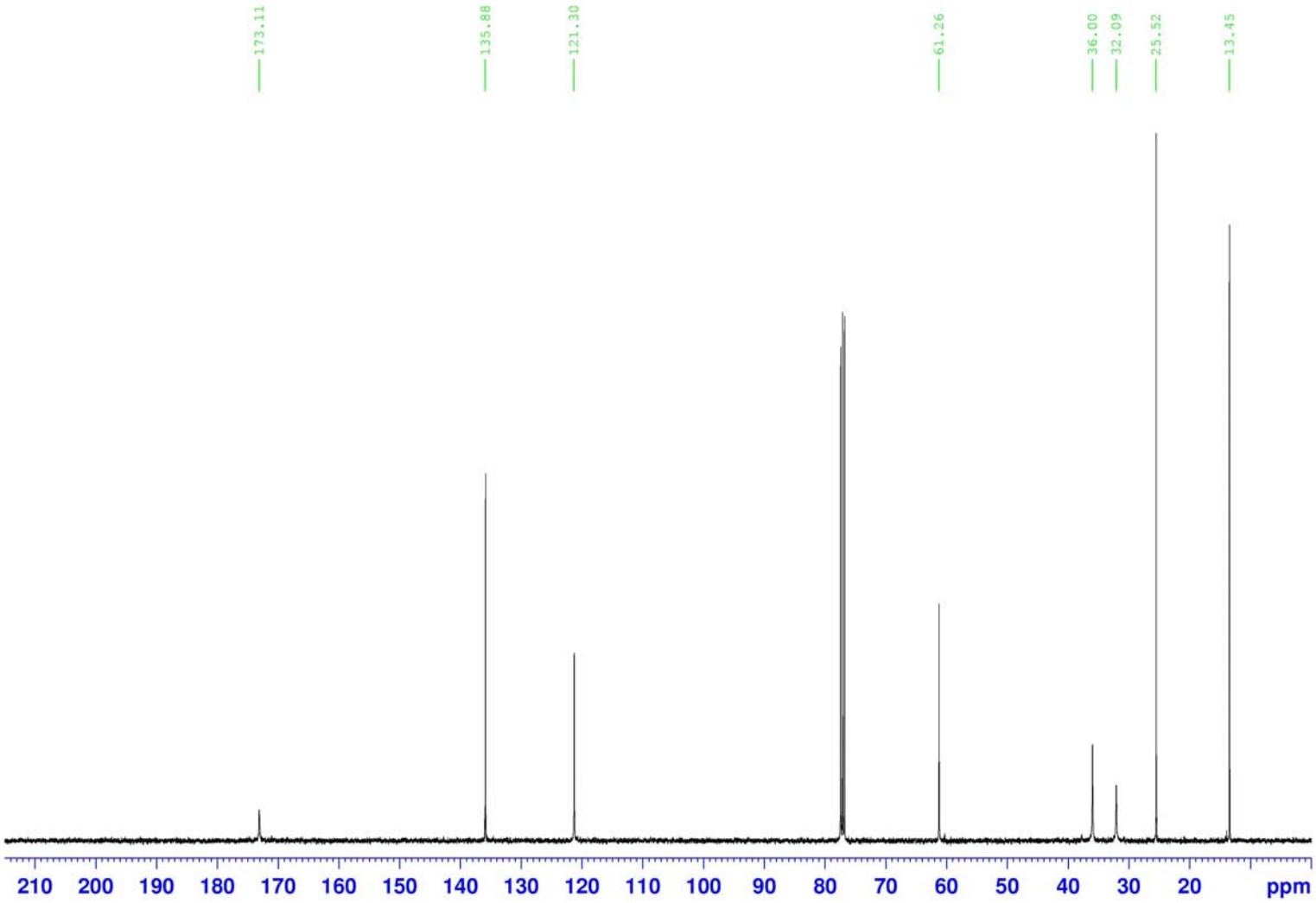
The general procedure for the synthesis of *β*,*γ*-unsaturated Weinreb amides affords, after flash chromatography on silica gel (85:15 hexanes:ethyl acetate), the title compound (83%) as a colorless oil.

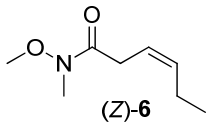
TLC analysis	R_f 0.5 (50:50 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 5.60–5.40 (2H, m, e,f), 3.66 (3H, s, a), 3.15–3.10 (2H, suspected d, d), 3.14 (3H, s, b), 2.05–1.95 (2H, m, g), 0.95 (3H, t, J = 7.4 Hz, h).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.11 (c), 135.88 (f), 121.30 (e), 61.26 (a), 36.00 (d), 32.09 (b), 25.52 (g), 13.45 (h).
IR (neat)	2964 (CH sp^2 stretch), 2937 (CH sp^3 stretch), 1660 (C=O stretch), 1462, 1411, 1381 (C-N stretch), 1175, 1102, 1013 (C-O stretch), 967, 937, 820, 780 cm^{-1}.
HRMS (CI)	Calcd. for $C_8H_{16}NO_2$ (M+H): 158.1181, found 158.1176 *m/z*.

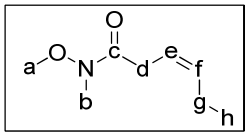
^{1}H NMR of (*E*)-6



^{13}C NMR of (*E*)-6



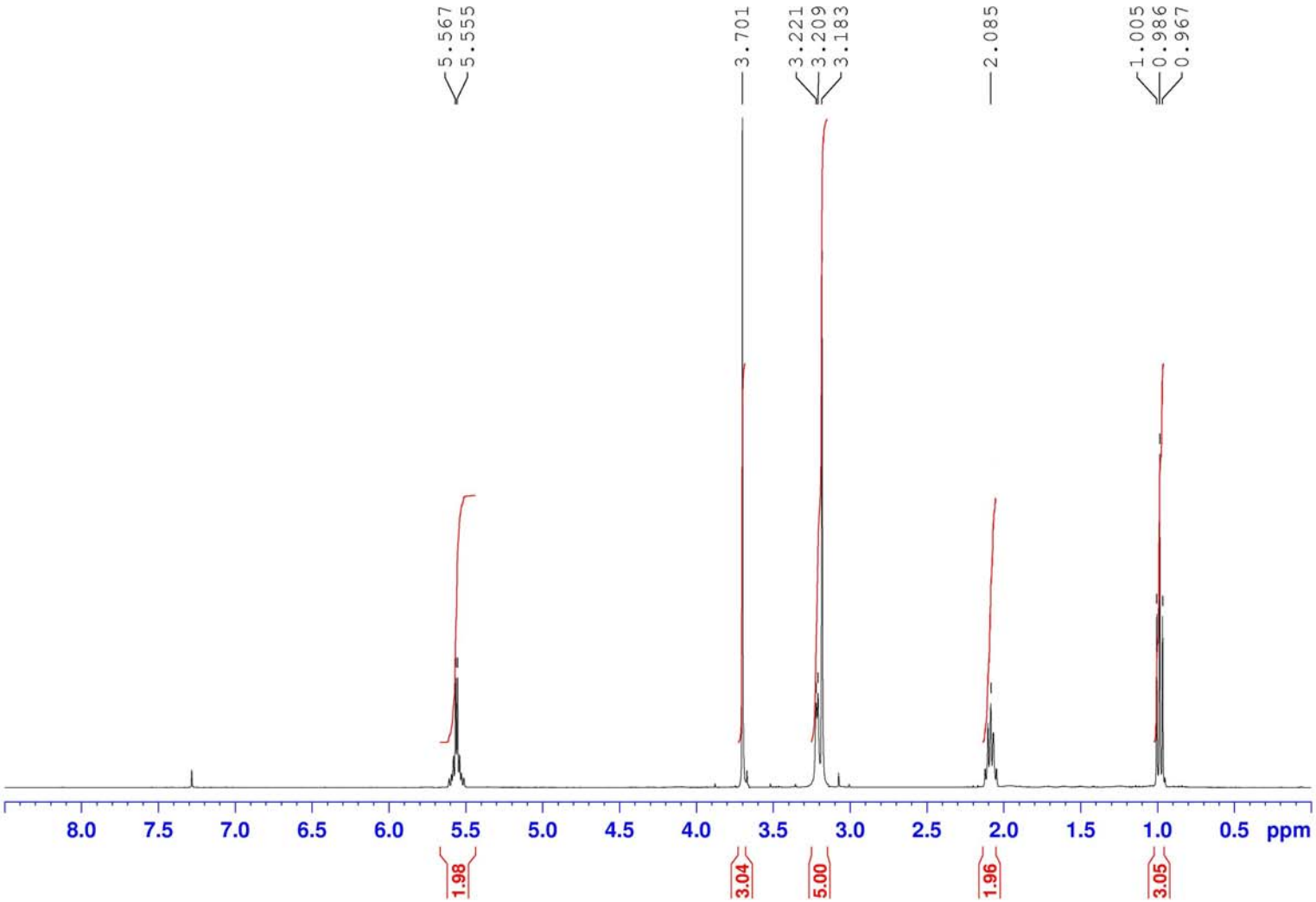




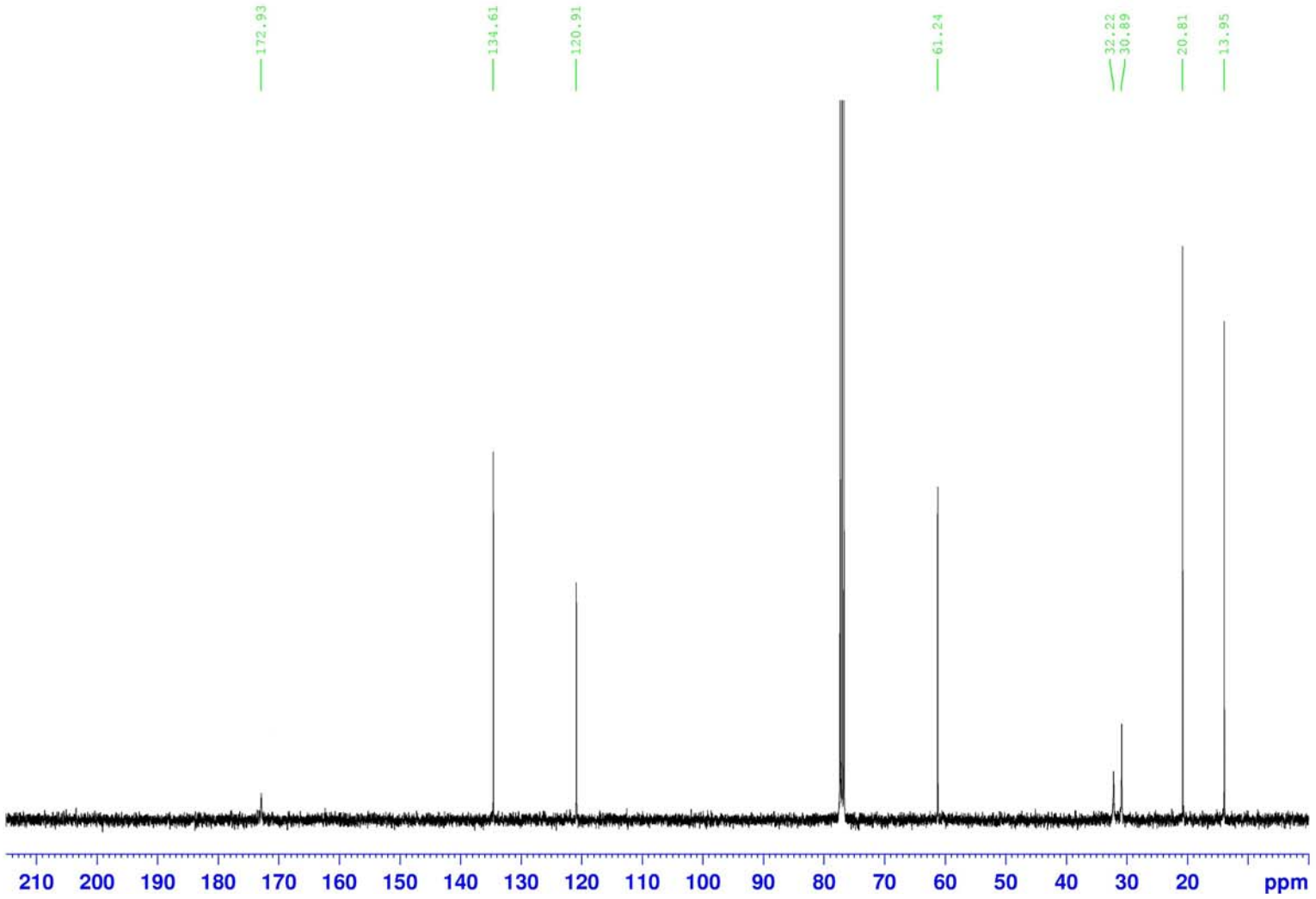
The general procedure for the synthesis of *β*,*γ*-unsaturated Weinreb amides affords, after flash chromatography on silica gel (85:15 hexanes:ethyl acetate), the title compound (80%) as a colorless oil.

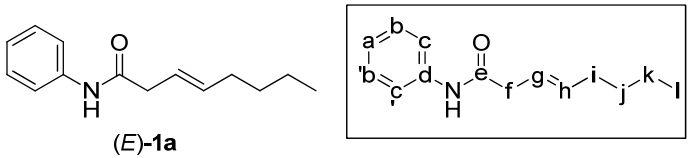
TLC analysis	R_f 0.5 (50:50 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 5.60–5.50 (2H, m, e,f), 3.70 (3H, s, a), 3.21 (2H, d, J = 4.9 Hz, d), 3.18 (3H, s, b), 2.15–2.05 (2H, m, g), 0.99 (3H, t, J = 7.5 Hz, h).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.93 (c), 134.61 (f), 120.91 (e), 61.24 (a), 32.22 (b), 30.89 (d), 20.81 (g), 13.95 (h).
IR (neat)	2965 (CH sp^2 stretch), 2937 (CH sp^3 stretch), 1665 (C=O stretch), 1463, 1376 (C-N stretch), 1241, 1176, 1119 (C-O stretch), 989, 924, 785, 703 cm^{-1}.
HRMS (CI)	Calcd. for $C_8H_{16}NO_2$ (M+H): 158.1181, found 158.1176 *m/z*.

^{1}H NMR of (*Z*)-6



^{13}C NMR of (*Z*)-6



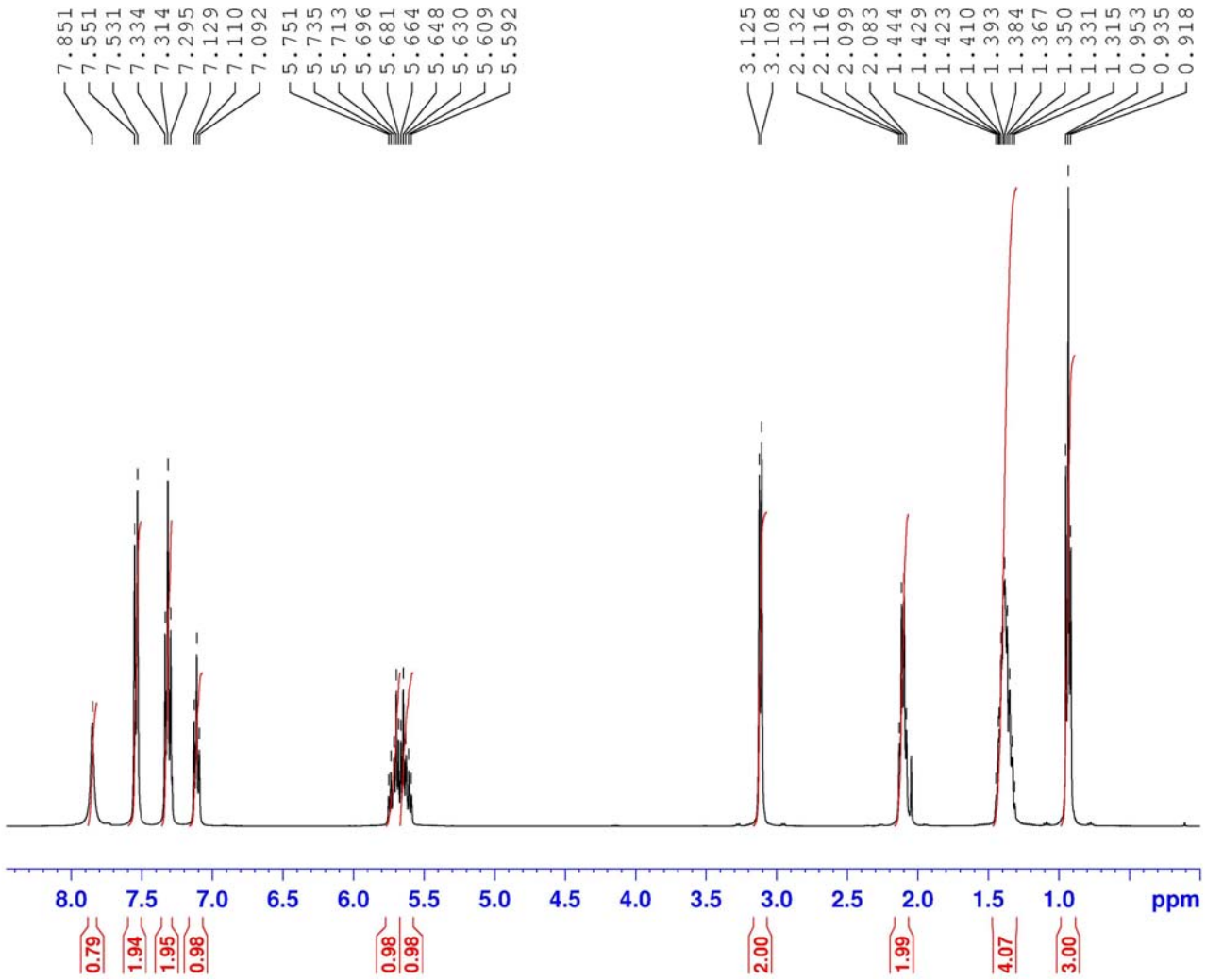


(*E*)-**1a**

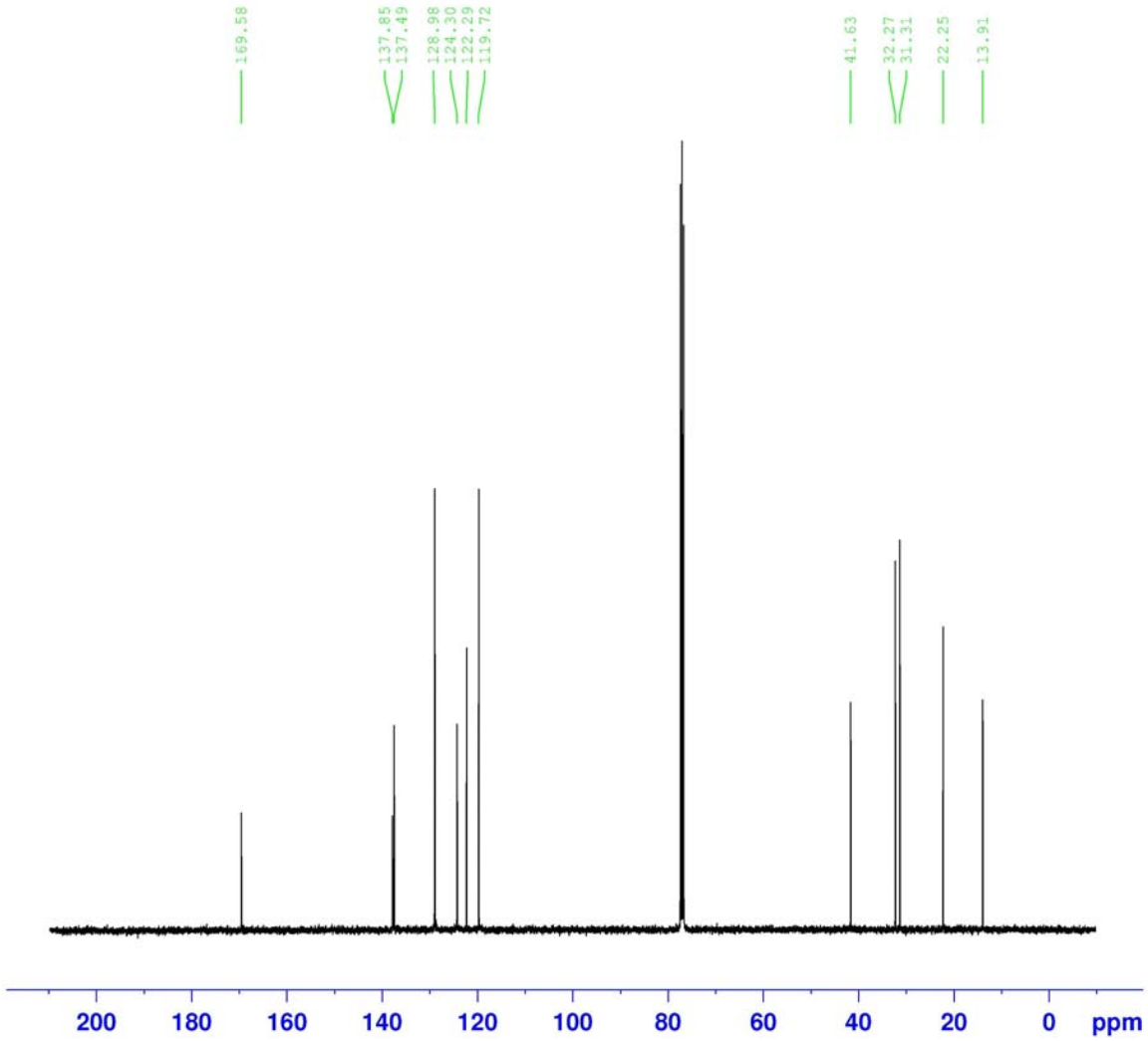
The general procedure for the synthesis of *β*,*γ*-unsaturated phenyl amides affords, after flash chromatography on silica gel (75:25 hexanes:ethyl acetate), the title compound (85%) as a colorless oil.

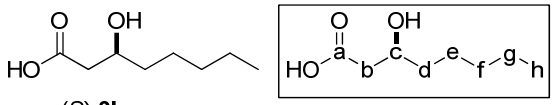
m.p.	47–49 °C
TLC analysis	R_f 0.54 (75:25 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.85 (1H, br s, NH), 7.54 (2H, d, *J* = 8.0 Hz, c,c'), 7.31 (2H, t, *J* = 7.8 Hz, b,b'), 7.11 (1H, t, *J* = 7.4 Hz, a), 5.76-5.59 (2H, m, g,h), 3.12 (2H, d, *J* = 6.7 Hz, f), 2.14–2.08 (2H, m, i), 1.44–1.33 (4H, m, j,k), 0.94 (3H, t, *J* = 7.01 Hz, l).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 169.58 (e), 137.85 (d), 137.49 (g), 128.98 (b,b'), 124.20 (a), 122.29 (h), 119.72 (c,c'), 41.63 (f), 32.27 (i), 31.31 (j), 22.25 (k), 13.91 (l).
IR (neat)	3292 (N-H stretch), 2948, 2923, 2864, 6959, 1596, 1525 (N-H bend), 1498, 1440, 1357, 1250, 1187 cm^{-1}.
HRMS (FAB)	Calcd. for $C_{14}H_{19}NO$ (M+H): 218.1545, found 218.1536 *m/z*.

^{1}H NMR of (*E*)-1a



^{13}C NMR of (*E*)-1a



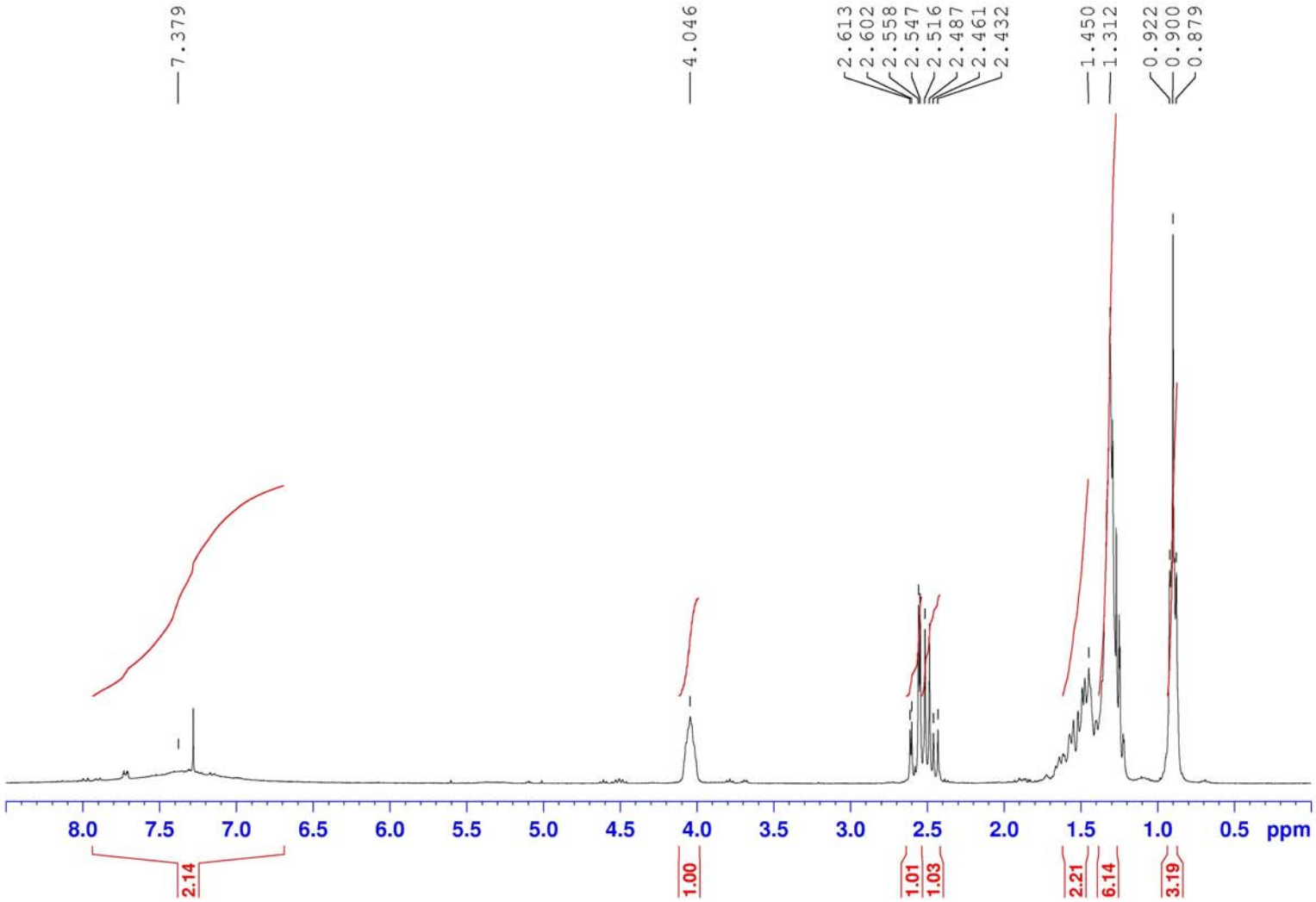


(*S*)-**3b**

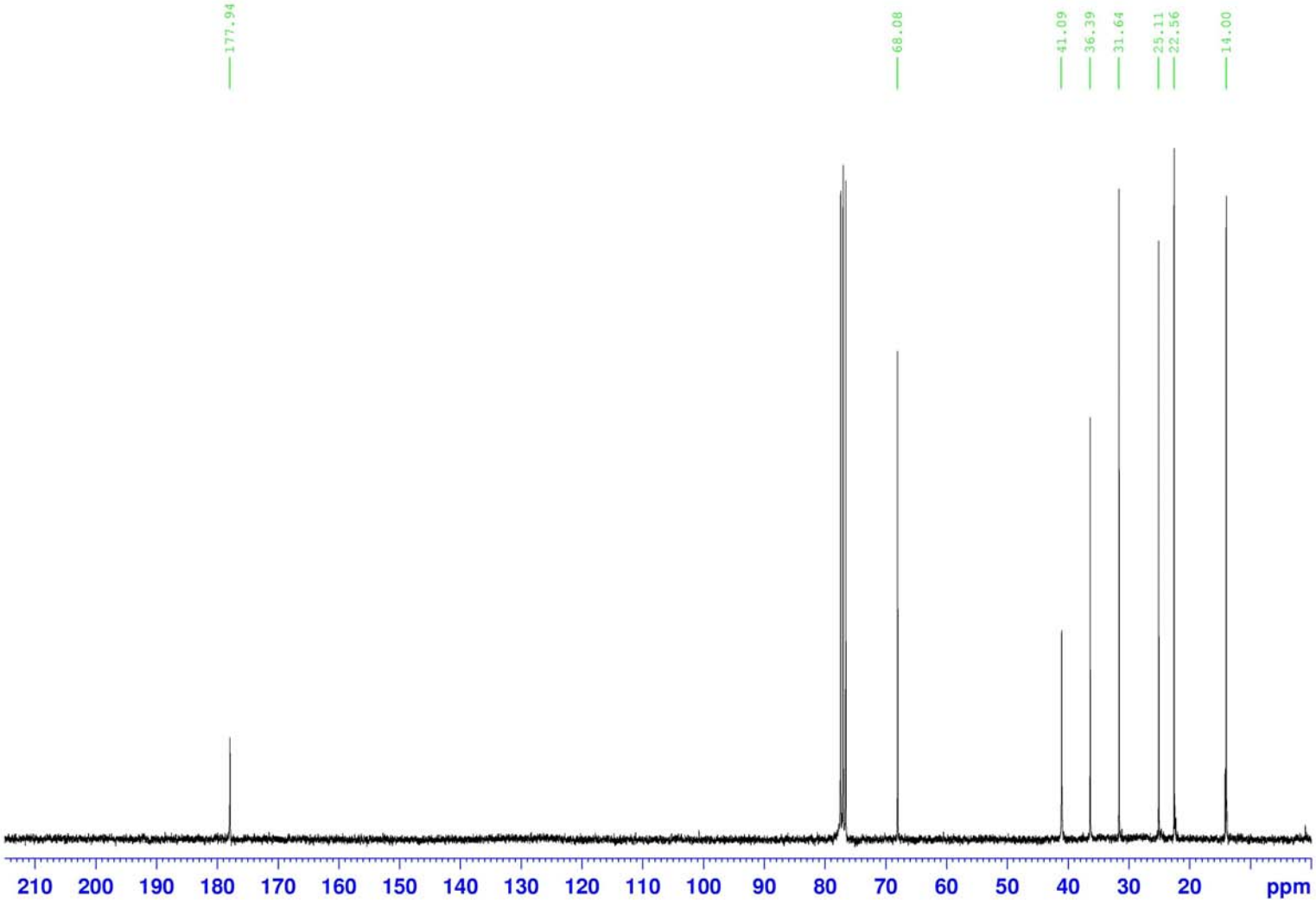
Catalytic asymmetric hydroboration of (*E*)-**1b** affords, after flash chromatography on silica gel (60:40 hexanes:ethyl acetate), the title compound (81%) as a colorless oil.

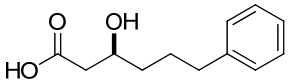
TLC analysis	R_f 0.4 (30:70 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20} = +14.2°$ (*c* 0.5, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.37 (2H, br s, COOH, OH), 4.10–4.00 (1H, m, c), 2.57 and 2.47 (2H, overlapping dd's, J_1 = 16.5 Hz, 3.3 Hz, J_2 = 16.5 Hz, 8.8 Hz, b), 1.60–1.40 (2H, m, d), 1.40–1.20 (6H, m, e,f,g), 0.90 (3H, t, J = 6.5 Hz, h).
^{13}C NMR (75 MHz, $CDCl_3$)	δ 177.94 (a), 68.08 (c), 41.09 (b), 36.39 (d), 31.64 (e), 25.11 (f), 22.56 (g), 14.00 (h).
IR (neat)	3391 (OH stretch), 2930, 2860 (CH sp^3 stretch), 1709 (C=O stretch), 1378 (C- N stretch), 1156, 1126, 1080 (C-O stretch), 1044, 950, 883, 828 cm^{-1}.

^{1}H NMR of (*S*)-3b

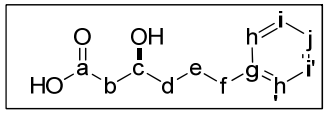


^{13}C NMR of (*S*)-3b





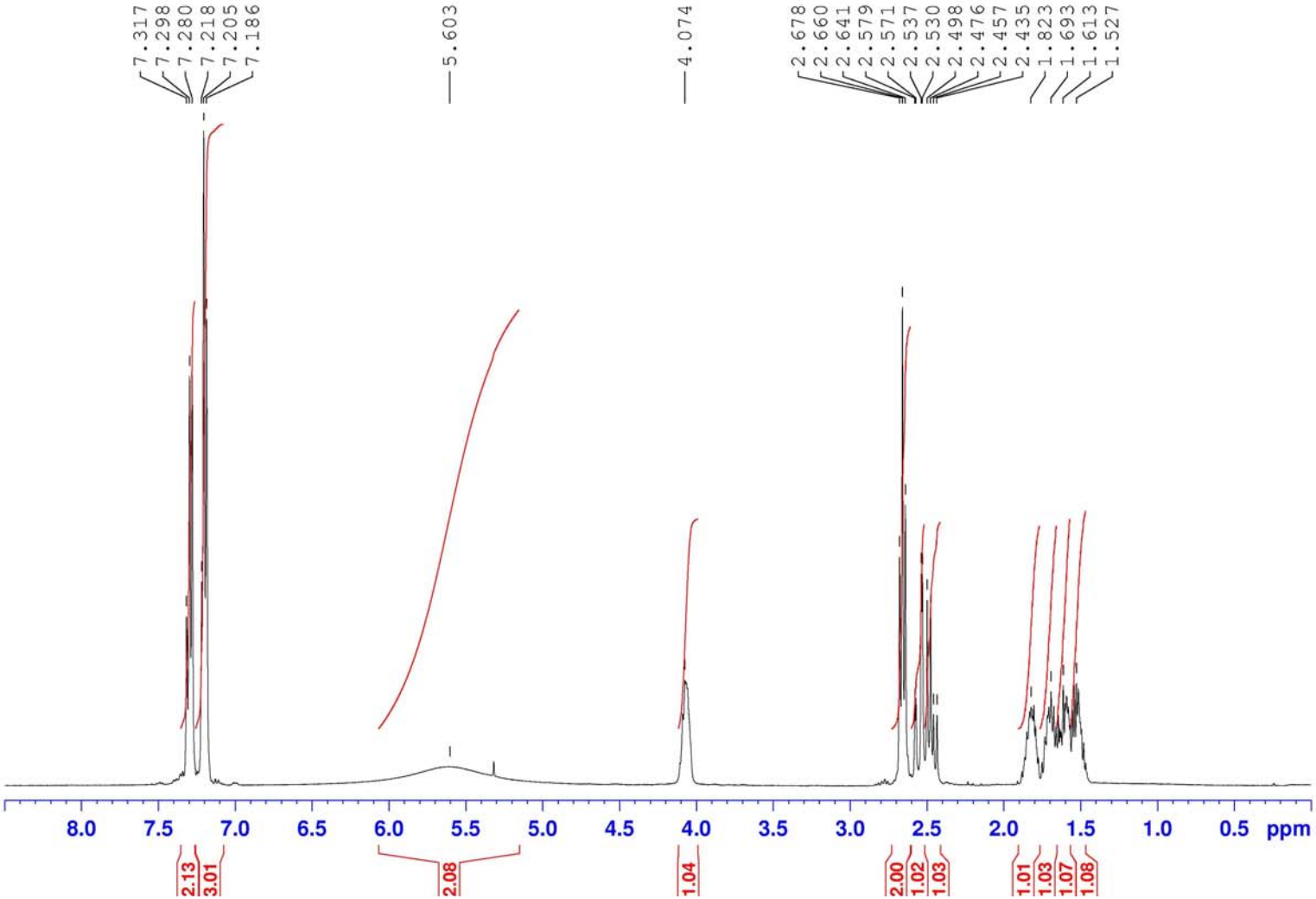
(*S*)-**5**



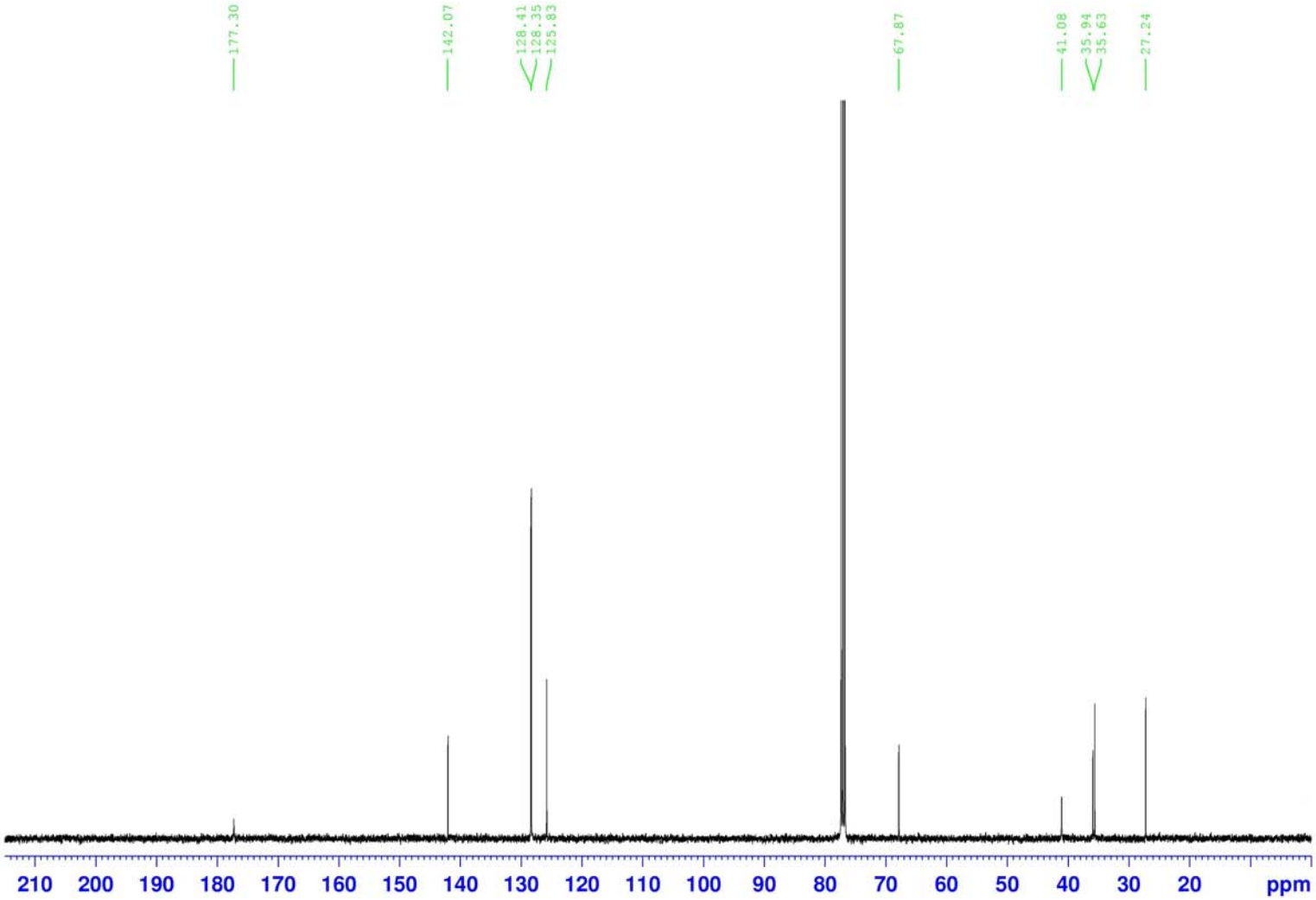
Catalytic asymmetric hydroboration of (*E*)-**4** affords, after flash chromatography on silica gel (60:40 hexanes:ethyl acetate), the title compound (76%) as a colorless oil.

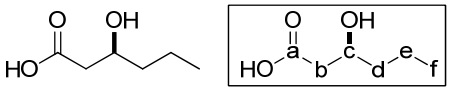
TLC analysis	R_f 0.5 (30:70 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20}$ = +13.8° (*c* 0.5, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.35–7.25 (2H, m, i,i'), 7.25–7.15 (3H, m, h,h',j), 5.60 (2H, br s, COOH, OH), 4.10–4.00 (1H, m, c), 2.66 (2H, t, J = 7.5 Hz, f), 2.55 and 2.46 (2H, overlapping dd's, J_1 = 16.6 Hz, 2.9 Hz, J_2 = 16.6 Hz, 8.9 Hz, b), 1.90–1.75 (1H, m, d), 1.75–1.65 (1H, m, d), 1.65–1.60 (1H, m, e), 1.60–1.50 (1H, m, e).
^{13}C NMR (75 MHz, $CDCl_3$)	δ 177.30 (a), 142.07 (g), 128.41 (h,h'), 128.35 (i,i'), 125.83 (j), 67.87 (c), 41.08 (b), 35.94 (d), 35.63 (f), 27.24 (e).
IR (neat)	3230 (OH stretch), 2932 (CH sp^3 stretch), 2547, 1689 (C=O stretch), 1447, 1407, 1311, 1291, 1194 (C-O stretch), 1075, 938, 877, 736, 699 cm^{-1}.

^{1}H NMR of (*S*)-5



^{13}C NMR of (*S*)-5



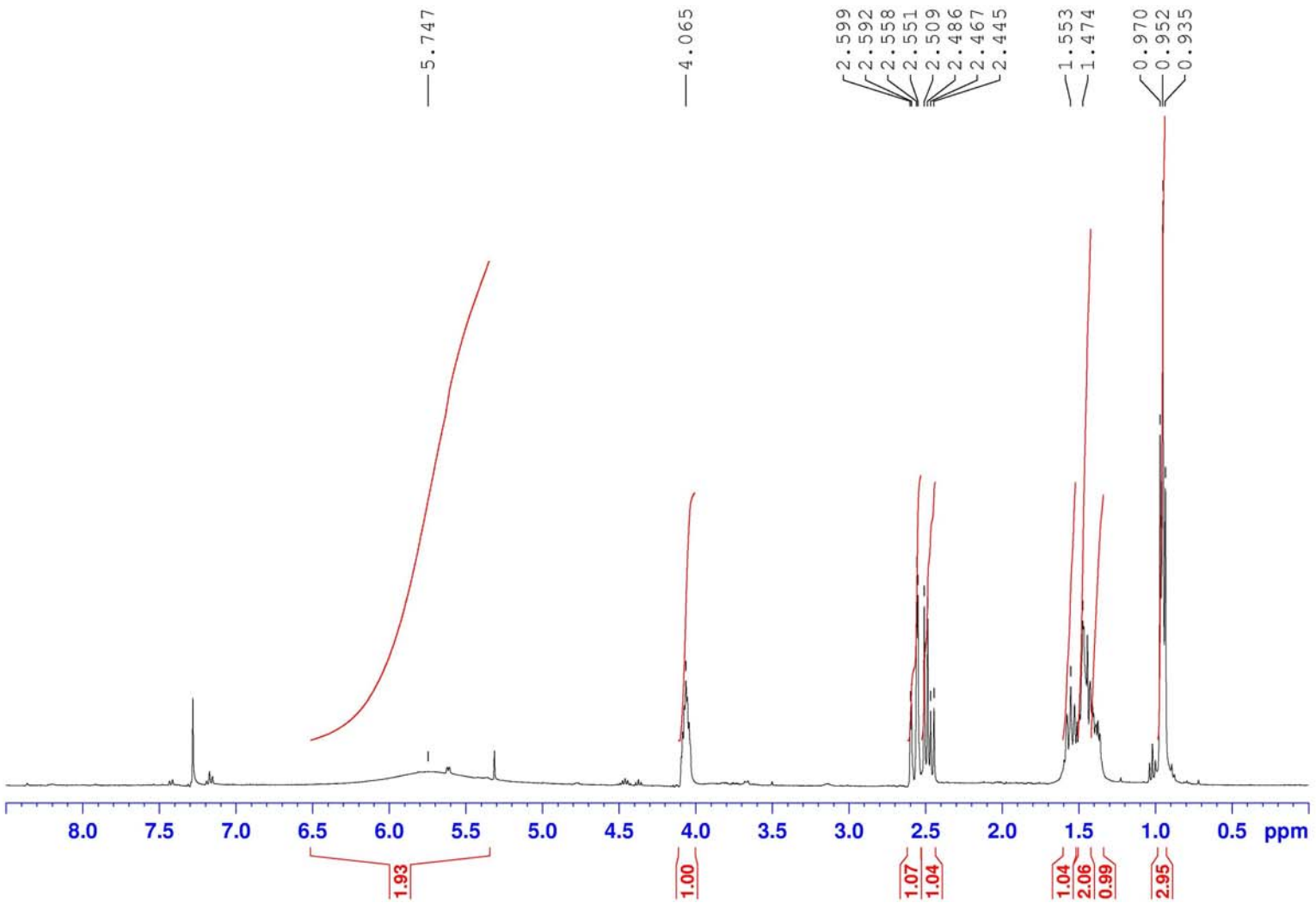


(*S*)-**7**

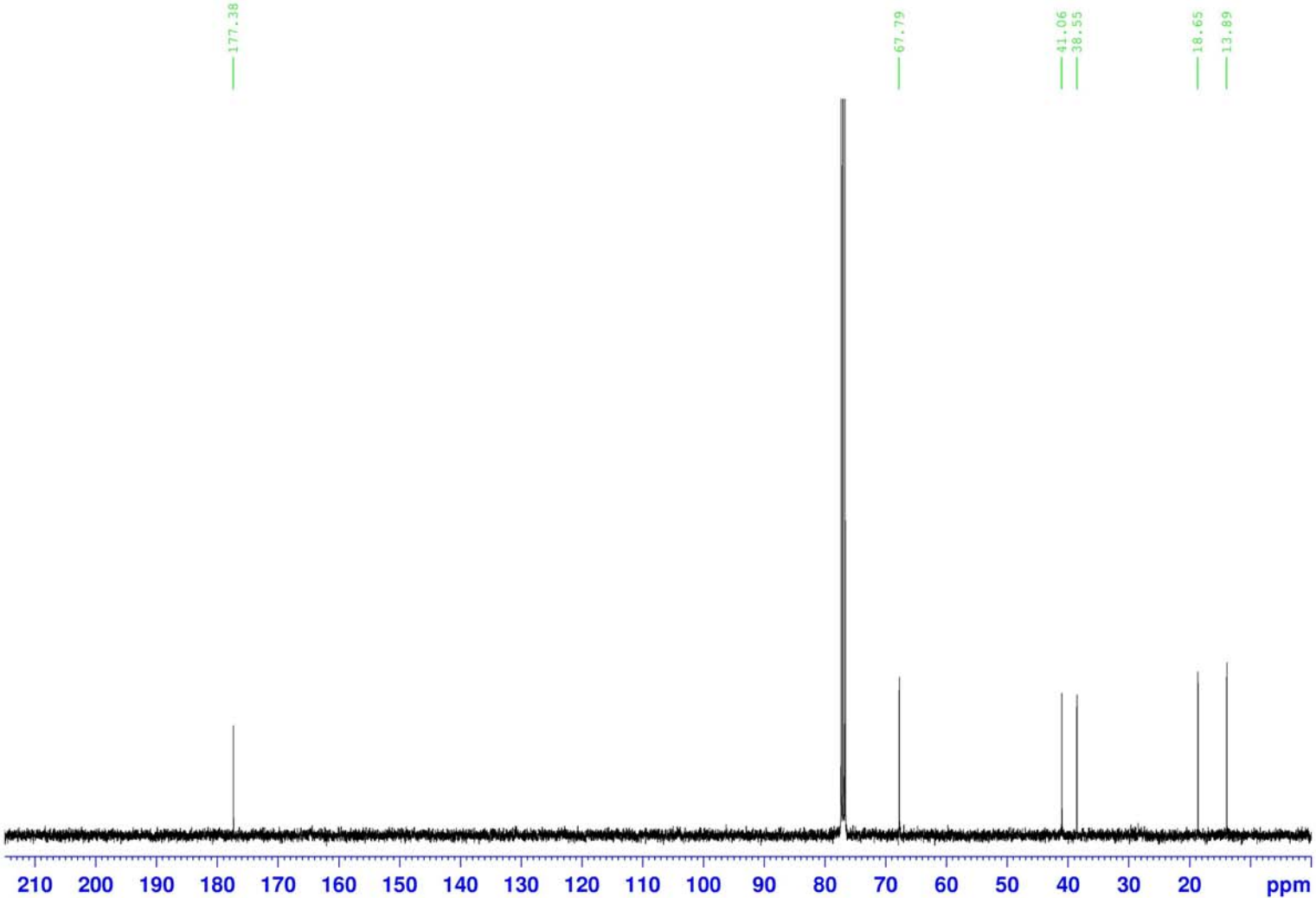
Catalytic asymmetric hydroboration of (*E*)-**6** affords, after flash chromatography on silica gel (60:40 hexanes:ethyl acetate), the title compound (73%) as a colorless oil.

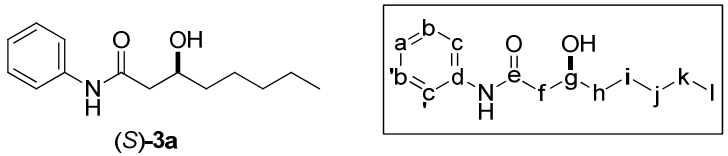
TLC analysis	R_f 0.3 (30:70 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20}$ = +13.0º (*c* 0.5, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 5.75 (2H. br s, COOH, OH), 4.10–4.00 (1H, m, c), 2.57 and 2.47 (2H, overlapping dd's, J_1 = 16.5 Hz, 3.0 Hz, J_2 = 16.5 Hz, 8.9 Hz), 1.60–1.50 (1H, m, d),1.50–1.40 (2H, m, d,e), 1.40–1.35 (1H, m, e), 0.95 (3H, t, *J* = 7.0 Hz, f).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 177.38 (a), 67.79 (c), 41.06 (b), 38.55 (d), 18.65 (e), 13.89 (f).
IR (neat)	3522 (OH stretch), 2959 (CH sp^3 stretch), 2932, 2874, 1708 (C=O stretch), 1467, 1380, 1177 (C-O sretch), 1122, 1075, 1019, 952, 883, 827 cm^{-1}.

^{1}H NMR of (*S*)-7



^{13}C NMR of (*S*)-7



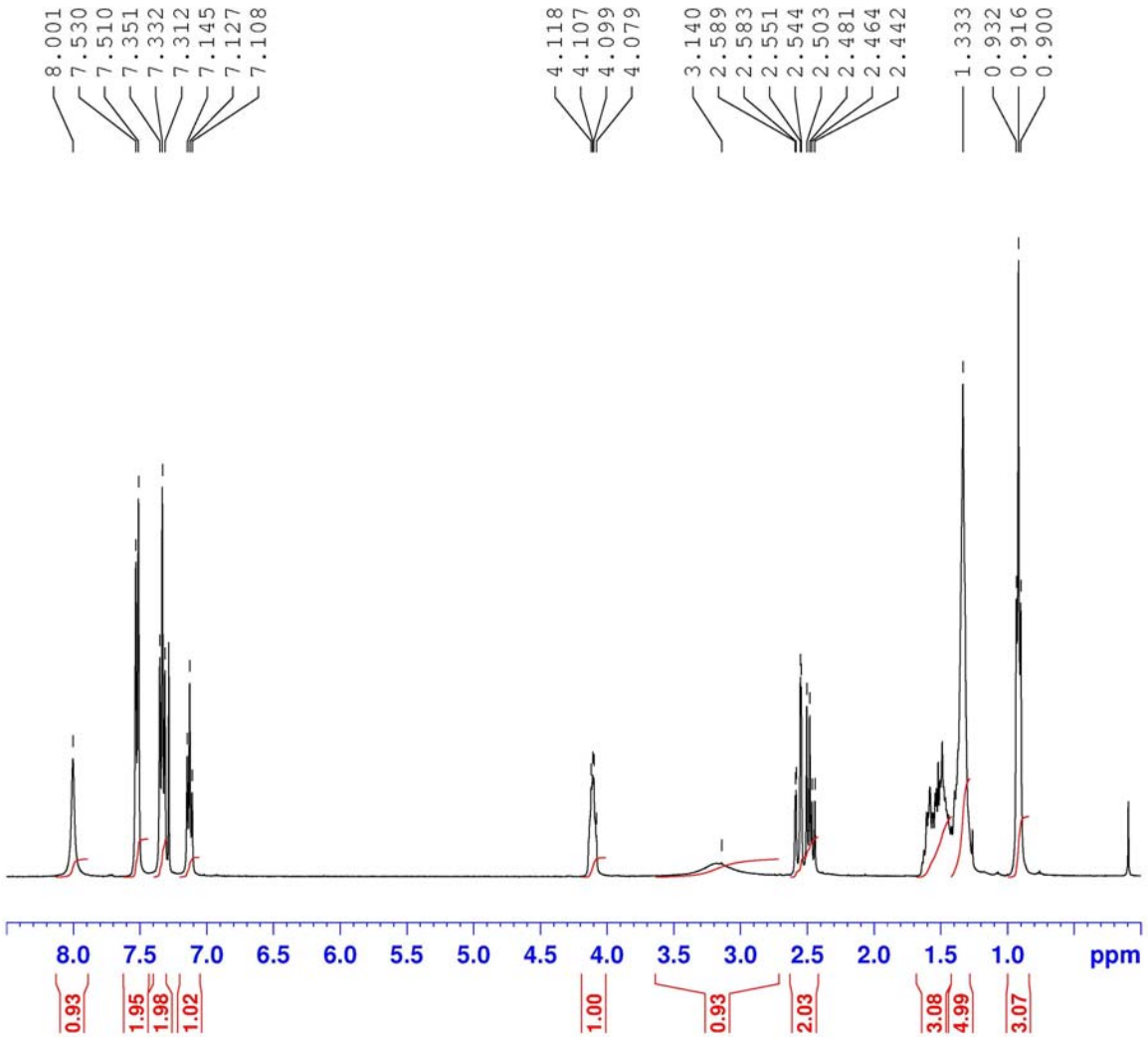


(*S*)-**3a**

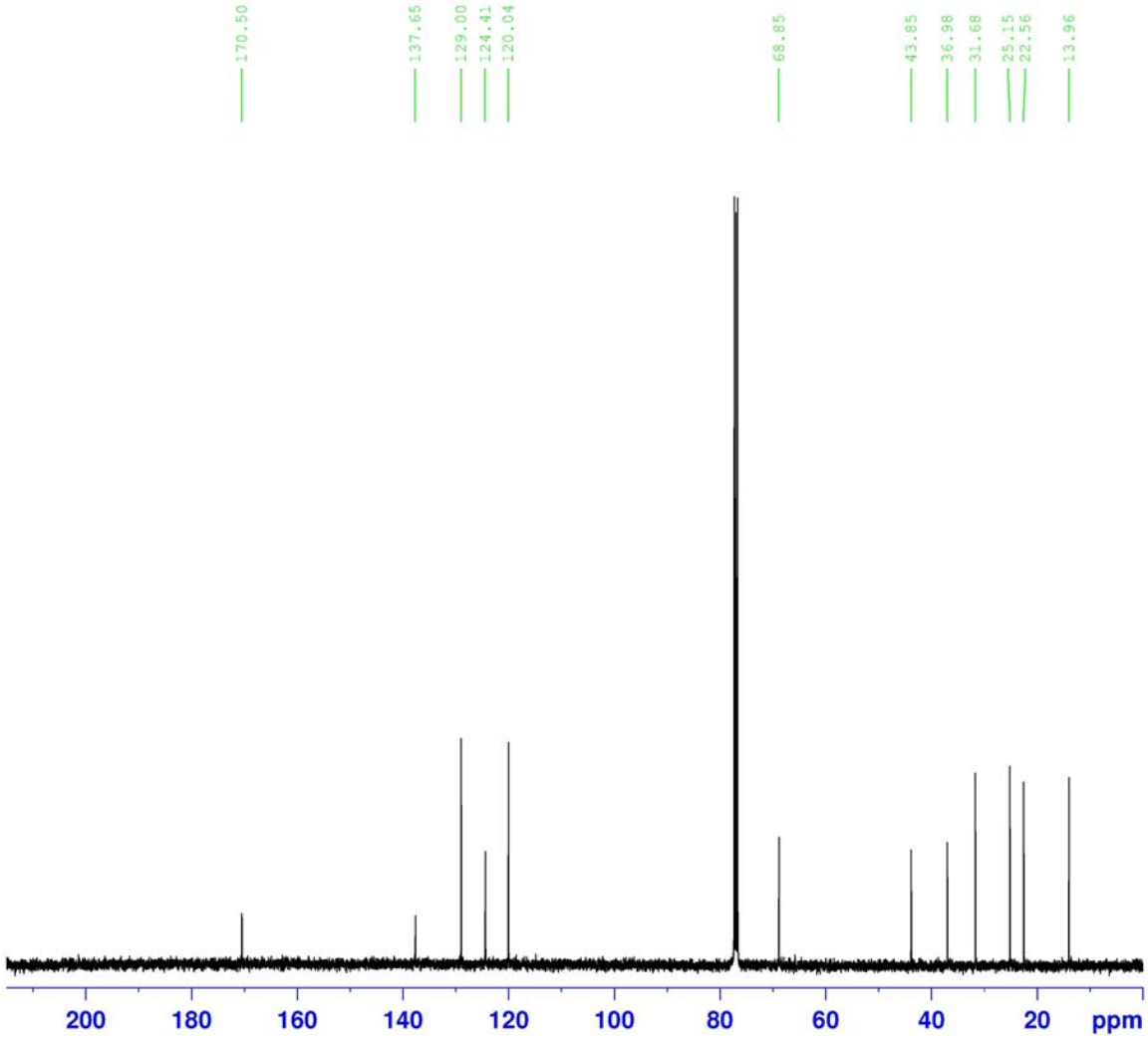
Catalytic asymmetric hydroboration of (*E*)-**1a** affords, after flash chromatography on silica gel (75:25 hexanes:ethyl acetate), the title compound (78%) as a colorless oil.

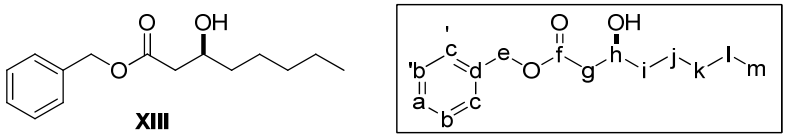
TLC analysis	R_f 0.60 (50:50 hexanes:ethyl acetate)
m.p.	113–114 ^{o}C
Optical rotation	$[\alpha]_D^{20} = +7.0^{o}$ (*c* 0.5, ethanol)
HPLC analysis	HPLC analysis (Chiralpak-AD, 85:15 hexanes:isopropanol) showed peaks at 23.5 minutes (3.5% (R)) and 26.5 minutes (96.5% (S)).
^{1}H NMR (400 MHz, $CDCl_3$)	δ 8.00 (1H, br s, NH), 7.52 (2H, d, *J* = 8.0 Hz, c, c'), 7.33 (2H, t, *J* = 7.7 Hz, b, b'), 7.13 (1H, t, *J* = 7.3 Hz, a), 4.20-4.00 (1H, m, g), 3.14 (1H, br s, OH), 2.57 and 2.47 (2H, overlapping dd's, J_1 = 15.4 Hz, 2.5 Hz, J_2 = 15.4 Hz, 8.8 Hz, f), 1.70-1.20 (8H, m, h,i,j,k), 0.92 (3H, t, *J* = 6.6 Hz, l).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 170.50 (e), 137.65 (d), 129.00 (c,c'), 124.41 (a), 120.04 (b,b'), 68.85 (g), 43.85 (f), 36.98 (h), 31.68 (i), 25.15 (j), 22.56 (k), 13.96 (l).
IR (neat)	3304 (N-H stretch), 2951, 2928, 2868, 1661 (C=O stretch), 1598, 1537 (N-H bend), 1498, 1442, 1308 (C-N stretch), 1253, 1123 (C-OH stretch), 1071, 756, 690 cm^{-1}.
HRMS (FAB)	Calcd. for $C_{14}H_{22}NO_2$ (M+H): 236.1651, found 236.1661 *m/z*..

^{1}H NMR of (*S*)-3a



^{13}C NMR of (*S*)-3a

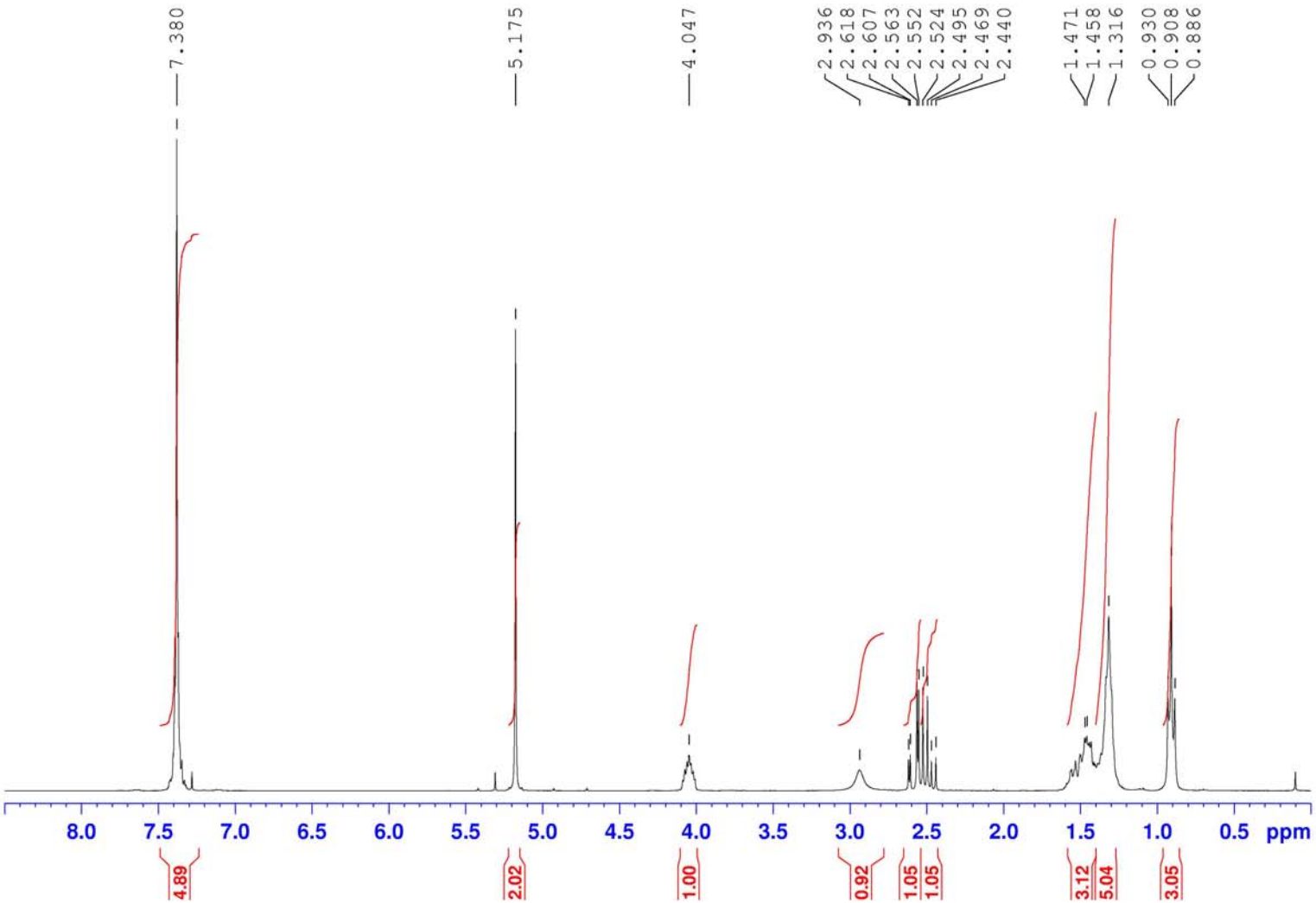




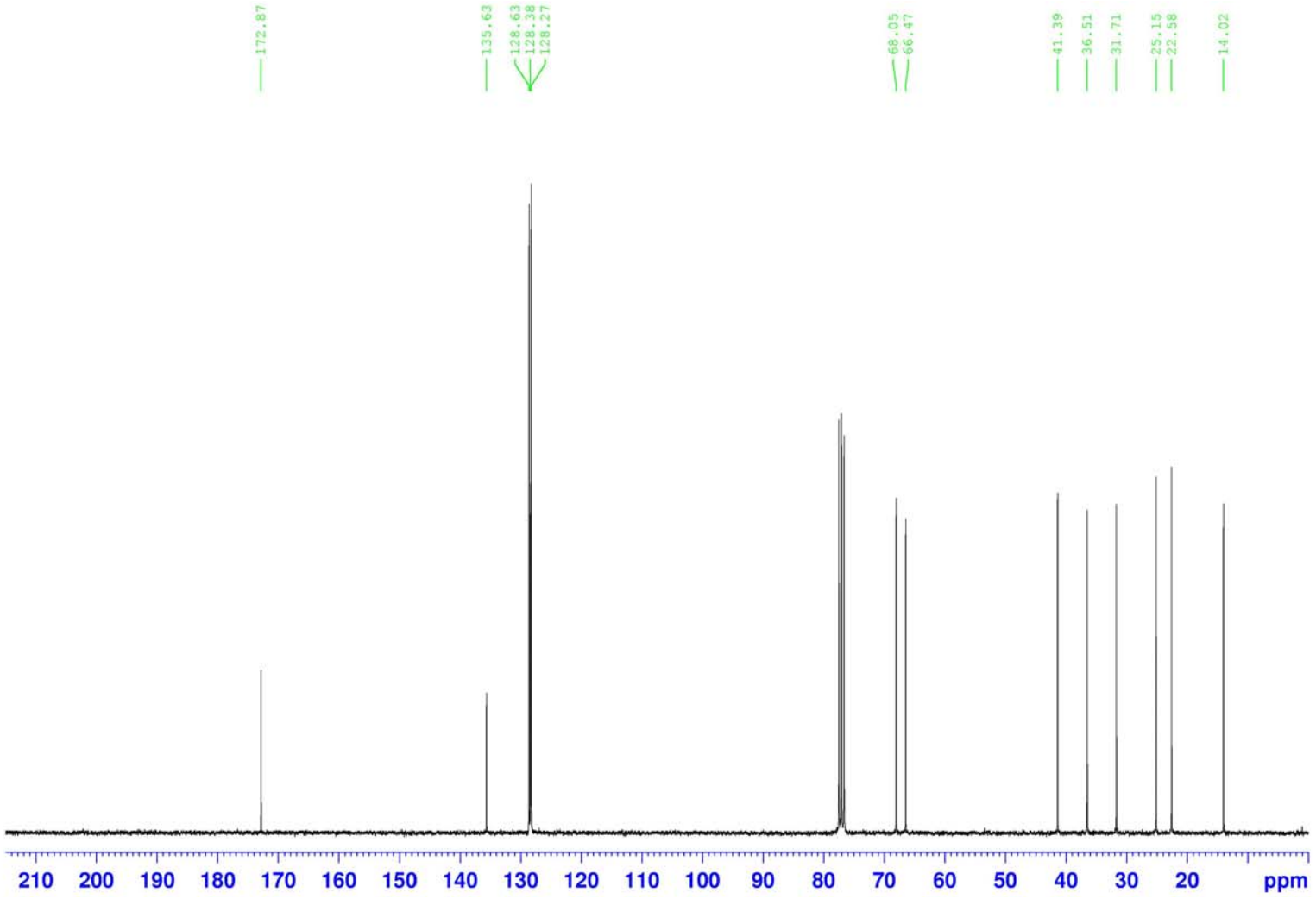
Benzylation of *β*-hydroxyacid (*S*)-**3b** affords, after flash chromatography on silica gel (90:10 hexanes:ethyl acetate), the title compound (82%) as a light yellow oil.

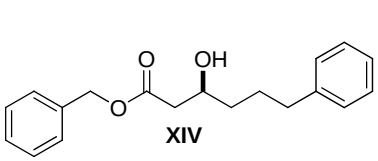
TLC analysis	R_f 0.6 (80:20 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20}$ = +14.2° (*c* 0.5, $CHCl_3$)
HPLC analysis	HPLC analysis (Chiralcel-OD, 80:20 hexanes: isopropanol) showed peaks at 11 minutes (1.5% (R)) and 14 minutes (98.5% (S)).
^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.45–7.30 (5H, m, a,b,b',c,c'), 5.18 (2H, s, e), 4.10–4.00 (1H, m, h), 2.94 (1H, br s, OH), 2.58 and 2.48 (2H, overlapping dd's, J_1 = 16.4 Hz, 3.4 Hz, J_2 = 16.4 Hz, 8.8 Hz, g), 1.60–1.40 (3H, m, i,j), 1.40–1.20 (5H, m, j,k,l), 0.91 (3H, t, *J* = 6.6 Hz, m).
^{13}C NMR (75 MHz, $CDCl_3$)	δ 172.87 (f), 135.63 (d), 128.63 (c,c'), 128.38 (a), 128.27 (b,b'), 68.05 (h), 66.47 (e), 41.39 (g), 36.51 (i), 31.71 (j), 25.15 (k), 22.58 (l), 14.02 (m).
IR (neat)	3441 (OH stretch), 2954 (CH sp^3 stretch), 2930, 2859, 1728 (C=O stretch), 1456, 1278, 1160 (C-O stretch), 969, 736, 695 cm^{-1}.

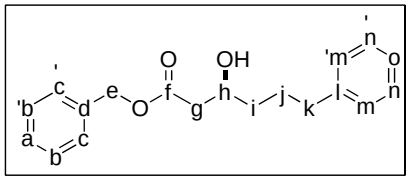
^{1}H NMR of XIII



^{13}C NMR of XIII



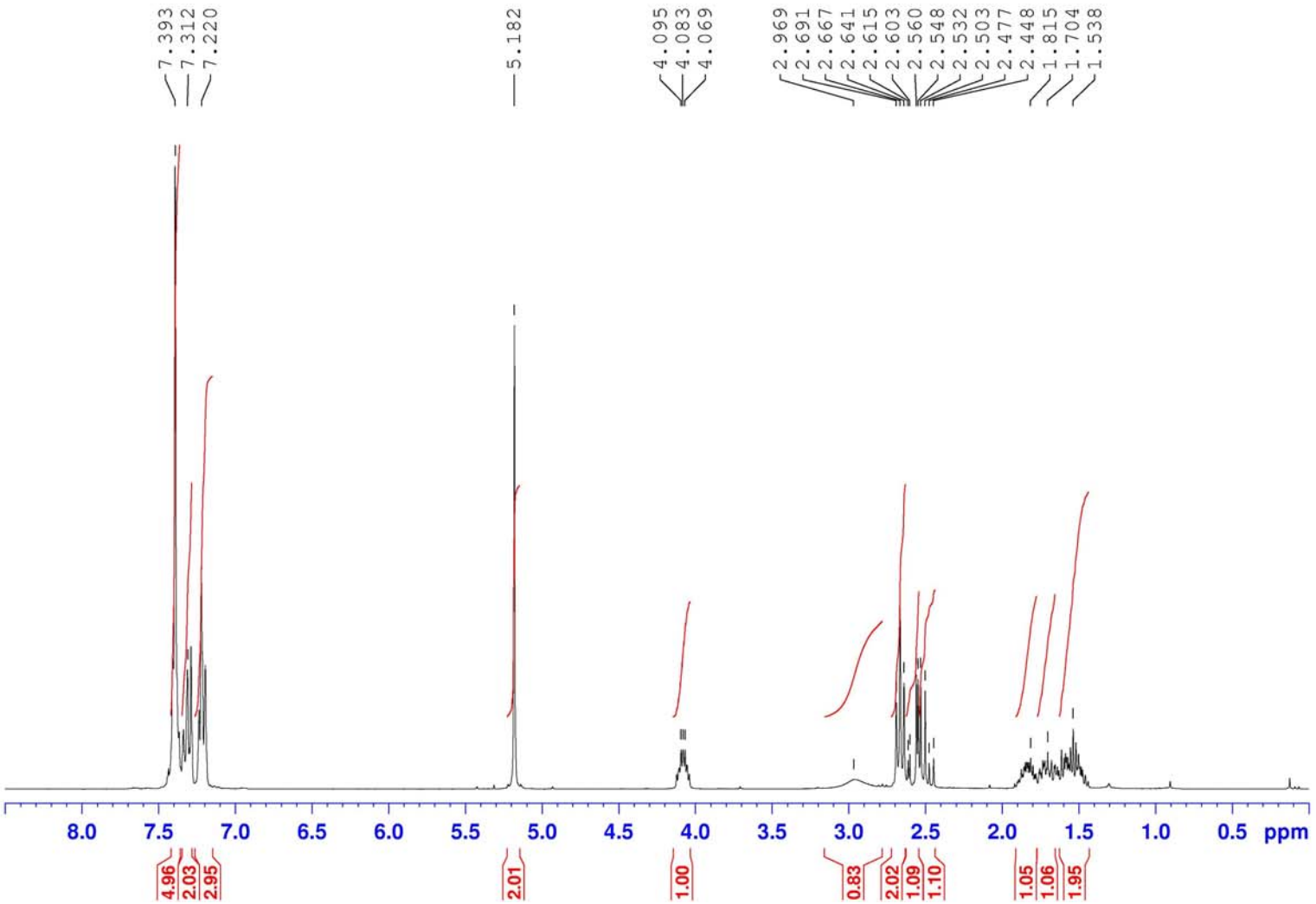




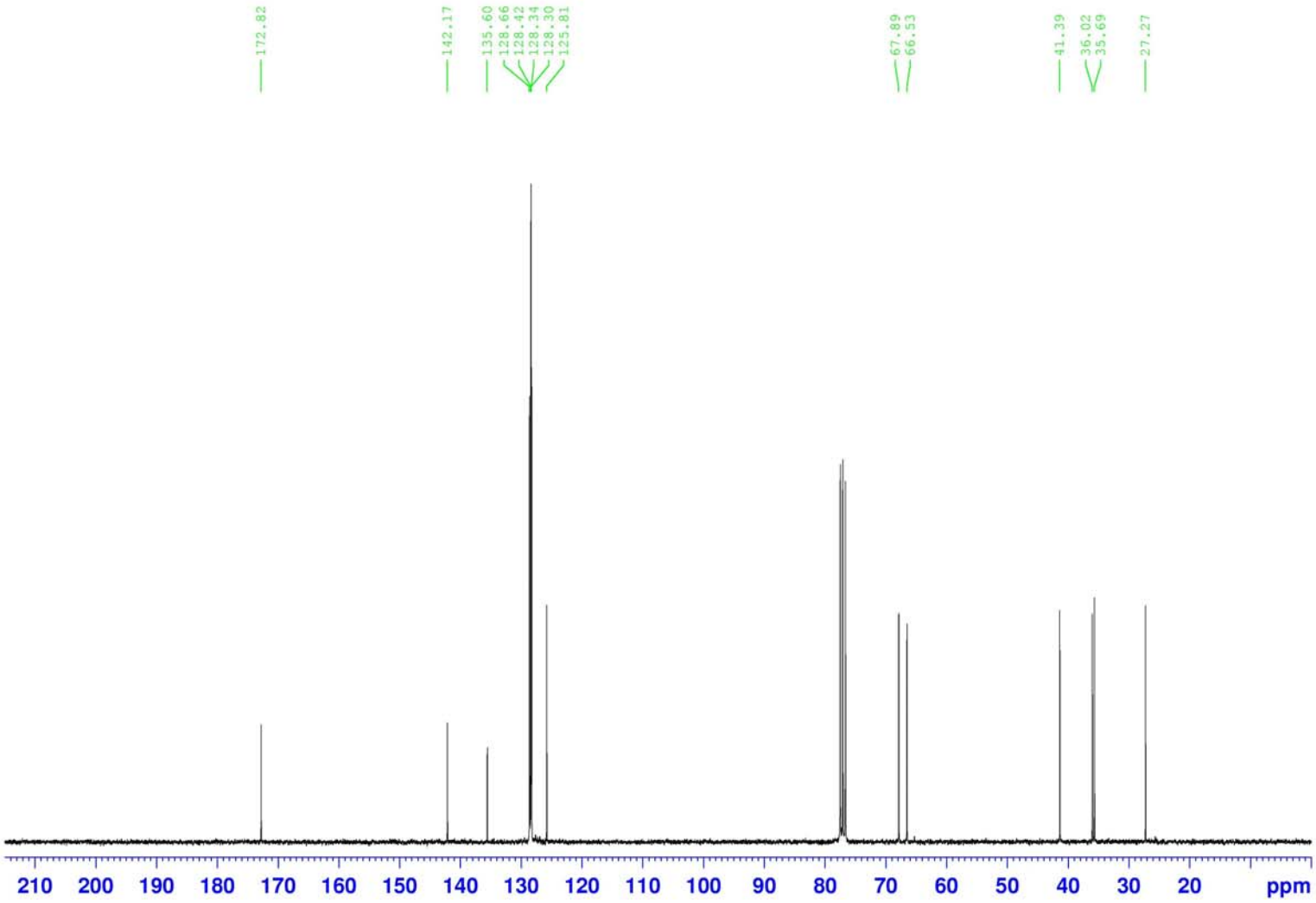
Benzylation of *β*-hydroxyacid (*S*)-**5** affords, after flash chromatography on silica gel (90:10 hexanes:ethyl acetate), the title compound (84%) as a light yellow oil.

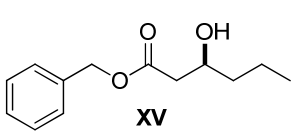
TLC analysis	R_f 0.5 (80:20 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20}$ = +15.9º (*c* 0.5, $CHCl_3$)
HPLC analysis	HPLC analysis (Chiralcel-OD, 80:20 hexanes: isopropanol) showed peaks at 22 minutes (2.0% (R)) and 31 minutes (98.0% (S)).
^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.45–7.35 (5H, m, a,b,b',c,c'), 7.35–7.25 (2H, m, n,n'), 7.25–7.15 (3H, m, m,m',o), 5.18 (2H, s, e), 4.15–4.00 (1H, m, h), 2.97 (1H, br s, OH), 2.67 (2H, t, J = 7.4 Hz, k), 2.58 and 2.49 (2H, overlapping dd's, J_1 = 16.5 Hz, 3.6 Hz, J_2 = 16.5 Hz, 8.6 Hz, g), 1.90–1.80 (1H, m, i), 1.75–1.60 (1H, m, i), 1.60–1.40 (2H, m, j).
^{13}C NMR (75 MHz, $CDCl_3$)	δ 172.82 (f), 142.17 (l), 135.60 (d), 128.66 (c,c'), 128.42 (m,m',a), 128.34 (n,n'), 128.30 (b,b'), 125.81 (o), 67.89 (h), 66.53 (e), 41.39 (g), 36.02 (i), 35.69 (k), 27.27 (j).
IR (neat)	3434 (OH stretch), 2938 (CH sp^3 stretch), 2859, 1728 (C=O stretch), 1496, 1454, 1168 (C-O stretch), 1087, 967, 748, 696 cm^{-1}.
HRMS (CI)	Calcd. for $C_{19}H_{22}NaO_3$ (M+Na): 321.1467, found 321.1472 *m/z*.

^{1}H NMR of XIV

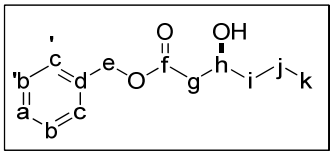


^{13}C NMR of XIV





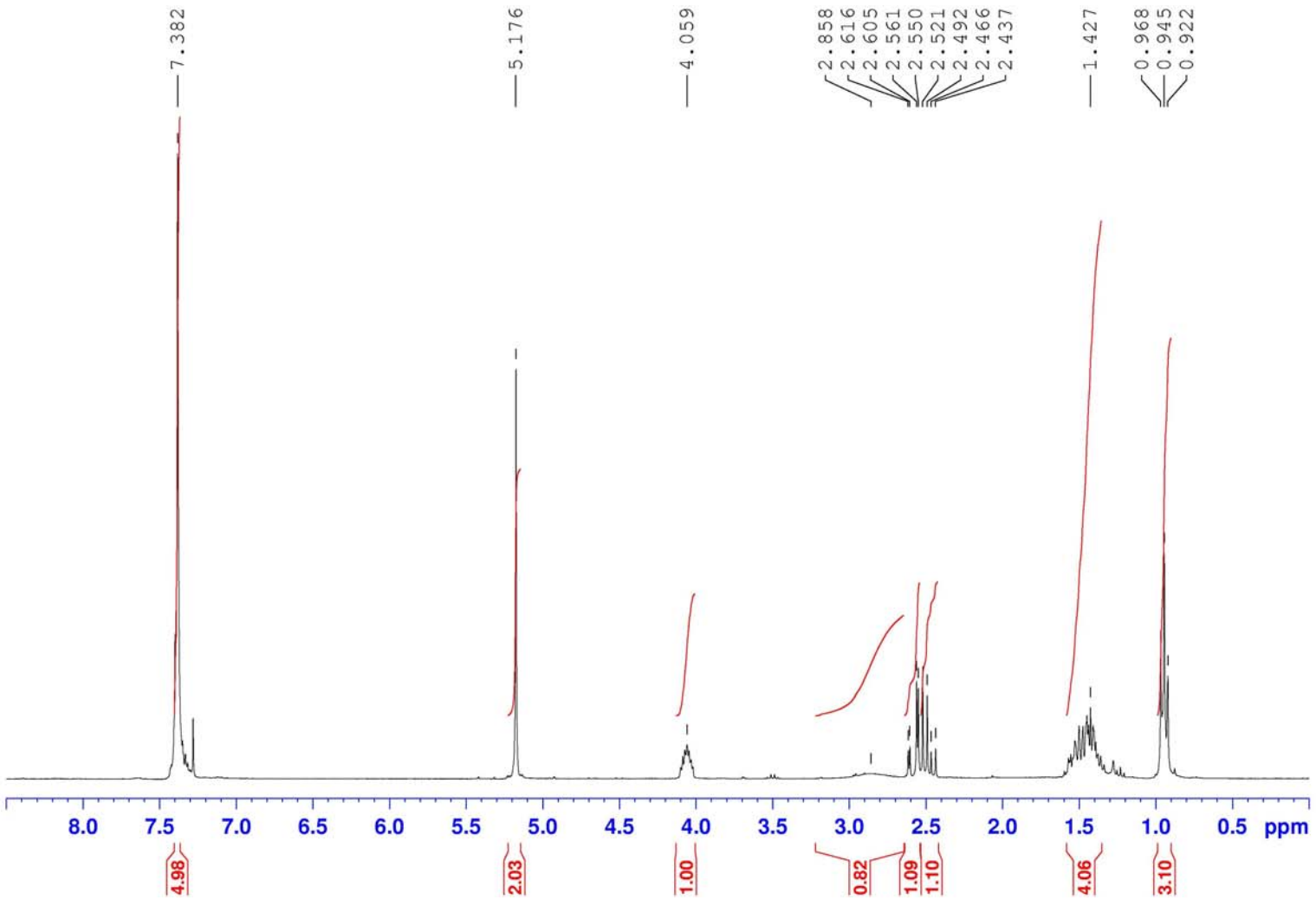
XV



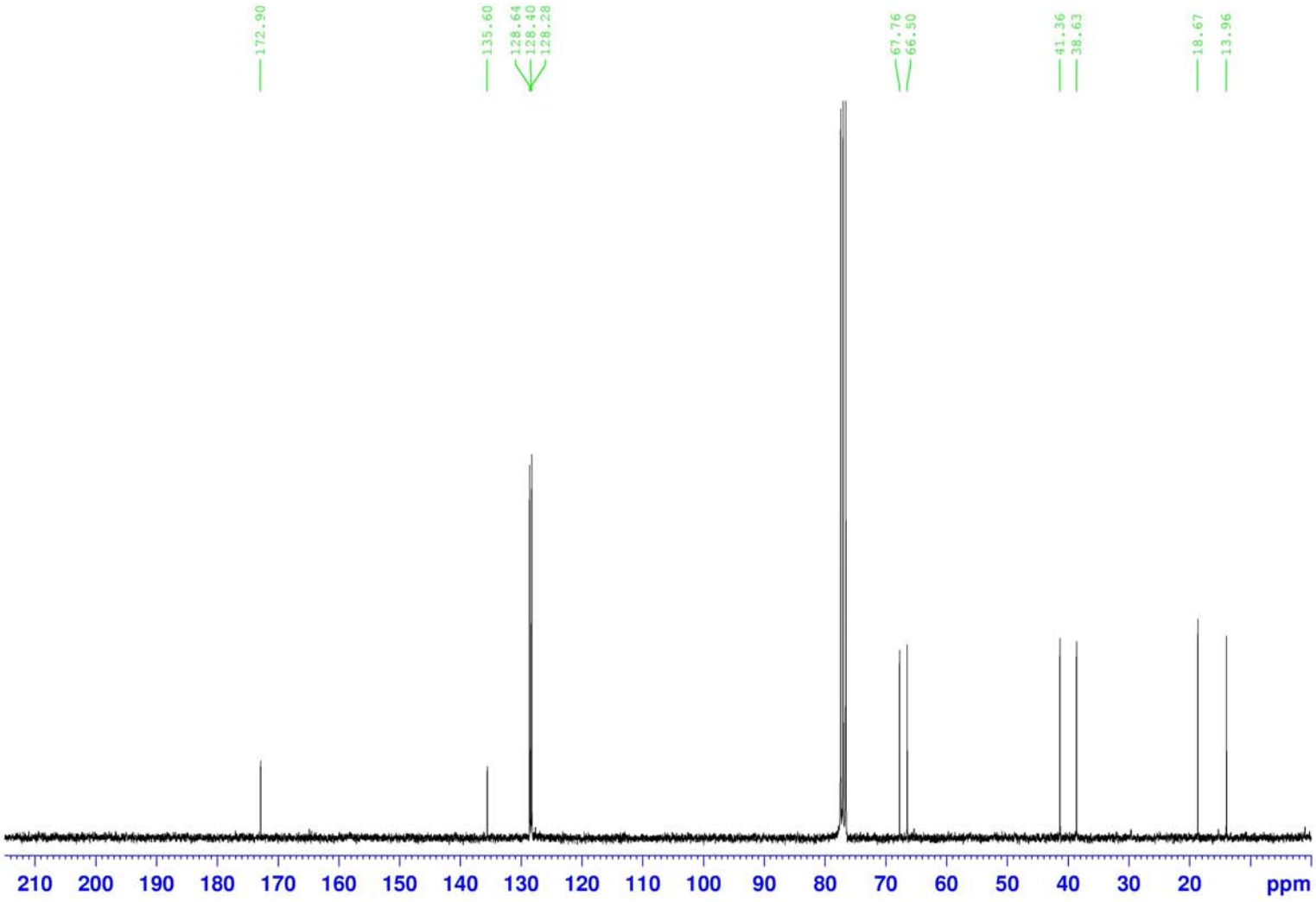
Benzylation of *β*-hydroxyacid (*S*)-**7** affords, after flash chromatography on silica gel (90:10 hexanes:ethyl acetate), the title compound (78%) as a light yellow oil.

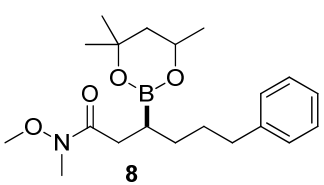
TLC analysis	R_f 0.5 (80:20 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20} = +13.8°$ (*c* 0.5, $CHCl_3$)
HPLC analysis	HPLC analysis (Chiralcel-OD, 80:20 hexanes: isopropanol) showed peaks at 9 minutes (1.5% (R)) and 12 minutes (98.5% (S)).
^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.45–7.35 (5H, m, a,b,b',c,c'), 5.18 (2H, s, e), 4.10–4.00 (1H, m, h), 2.86 (1H, br s, OH), 2.58 and 2.48 (2H, overlapping dd's, J_1 = 16.5 Hz, 3.4 Hz, J_2 = 16.5 Hz, 8.8 Hz, g), 1.60–1.35 (4H, m, i,j), 0.95 (3H, t, J = 7.0 Hz, k).
^{13}C NMR (75 MHz, $CDCl_3$)	δ 172.90 (f), 135.60 (d), 128.64 (c,c'), 128.40 (a), 128.28 (b,b'), 67.76 (h), 66.50 (e), 41.36 (g), 38.63 (i), 18.67 (j), 13.96 (k).
IR (neat)	3444 (OH stretch), 2958 (CH sp^3 stretch), 2932, 2872, 1728 (C=O stretch), 1455, 1381, 1262, 1163 (C-O stretch), 980, 906, 736, 696 cm^{-1}.

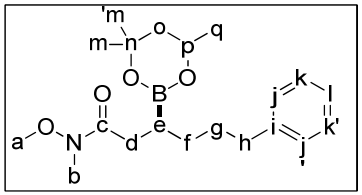
^{1}H NMR of XV



^{13}C NMR of XV



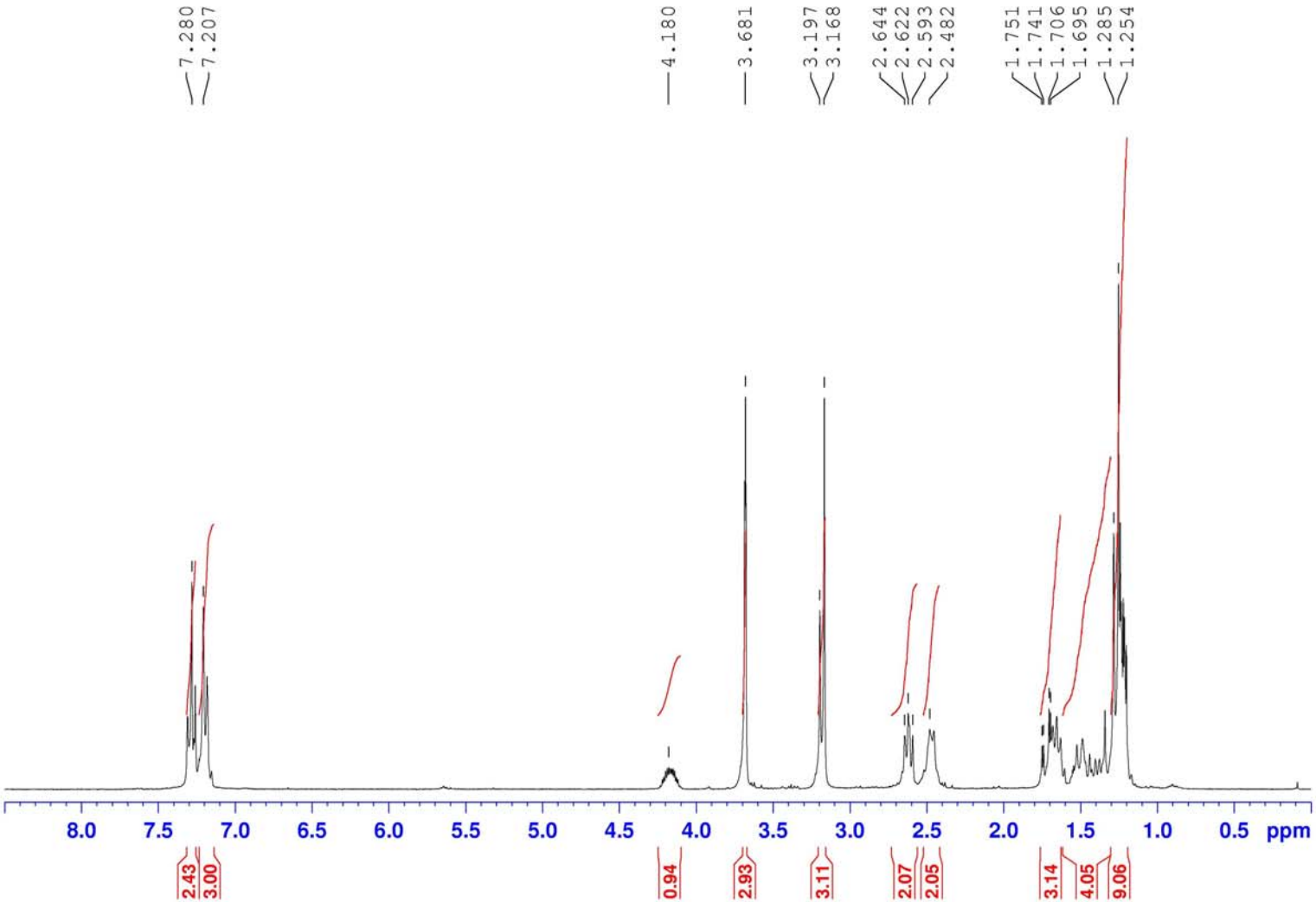




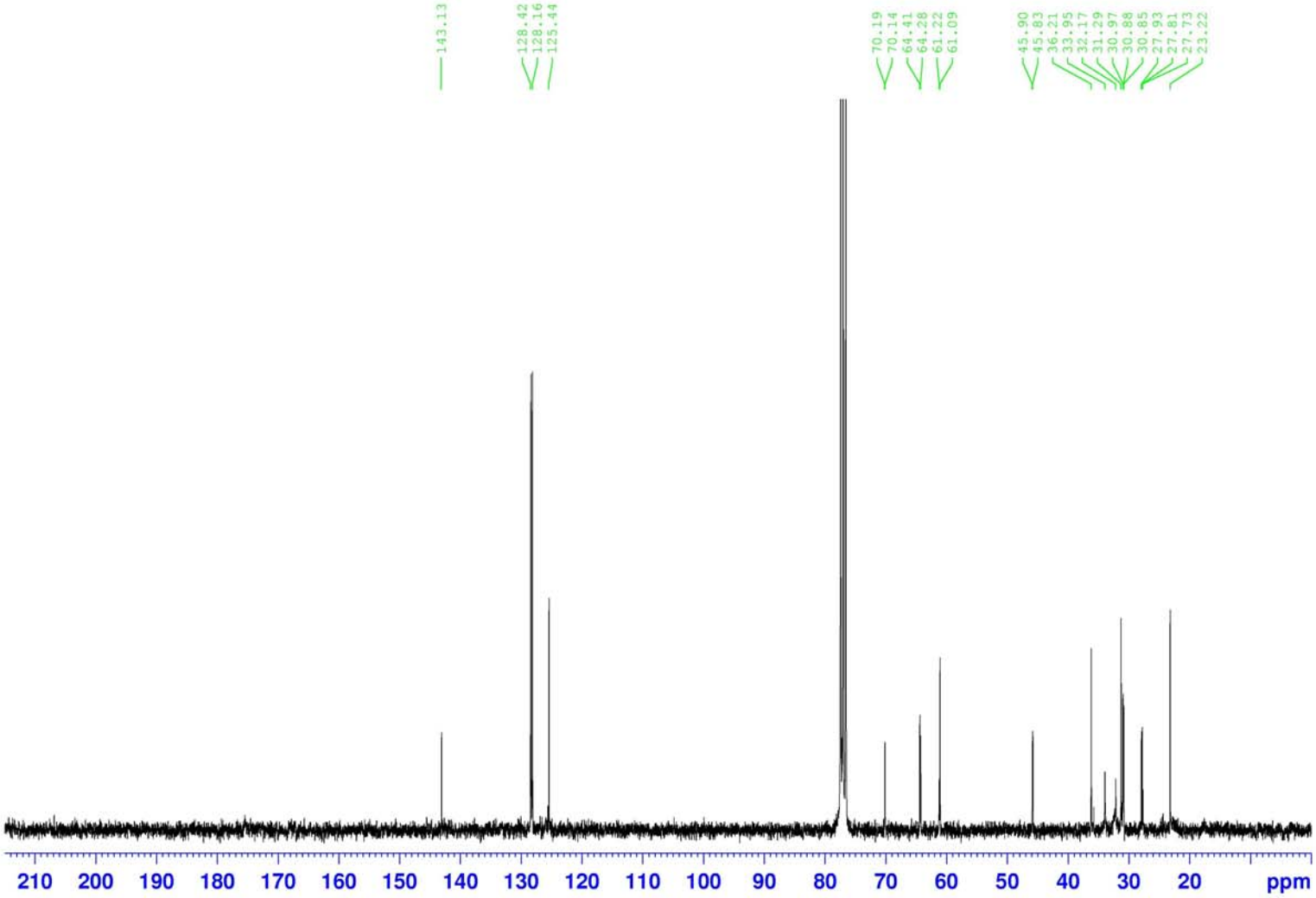
Catalytic asymmetric hydroboration of (*E*)-**4** without oxidative workup affords, after flash chromatography on silica gel (85:15 hexanes:ethyl acetate), the title compound (79%) as a light yellow oil.

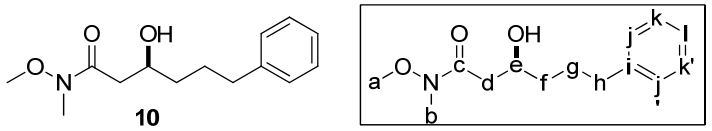
TLC analysis	R_f 0.5 (60:40 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20}$ = -8.0º (*c* 0.5, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.35–7.25 (2H, m, k,k'), 7.25–7.15 (3H, m, j,j',l), 4.25–4.10 (1H, m, q), 3.68 (3H, s, a), 3.20 and 3.17 (3H, s's, b), 2.62 (2H, t, *J* = 6.8 Hz, h), 2.50–2.40 (2H, m, d), 1.72 (1H, dd, *J* = 13.7 Hz, 3.0 Hz, o), 1.70–1.60 (2H, m, f), 1.60–1.30 (4H, m, o,g,e), 1.29 (3H, s, m), 1.25 (3H, s, m'), 1.25–1.20 (3H, m, q).
^{13}C NMR (75 MHz, $CDCl_3$)	δ 143.13 (i), 128.42 (j,j'), 128.16 (k,k'), 125.44 (l), 70.19 and 70.14 (n), 64.41 and 64.28 (p), 61.22 and 61.09 (a), 45.90 and 45.83 (o), 36.21 (h), 33.95 (d), 32.17 (b), 31.29 (m), 30.97 (g), 30.88 and 30.85 (f), 27.93 and 27.81 (m'), 27.73 (e), 23.22 (q).
IR (neat)	2858 (CH sp^3 stretch), 2926, 2856, 1662 (C=O stretch), 1454, 1378, 1314, 1144 (C-O stretch), 1001, 967, 867, 670 cm^{-1}.
HRMS (CI)	Calcd. for $C_{20}H_{33}BNO_4$ (M+H): 362.2503, found 362.2511 *m/z*.

^{1}H NMR of 8



^{13}C NMR of 8

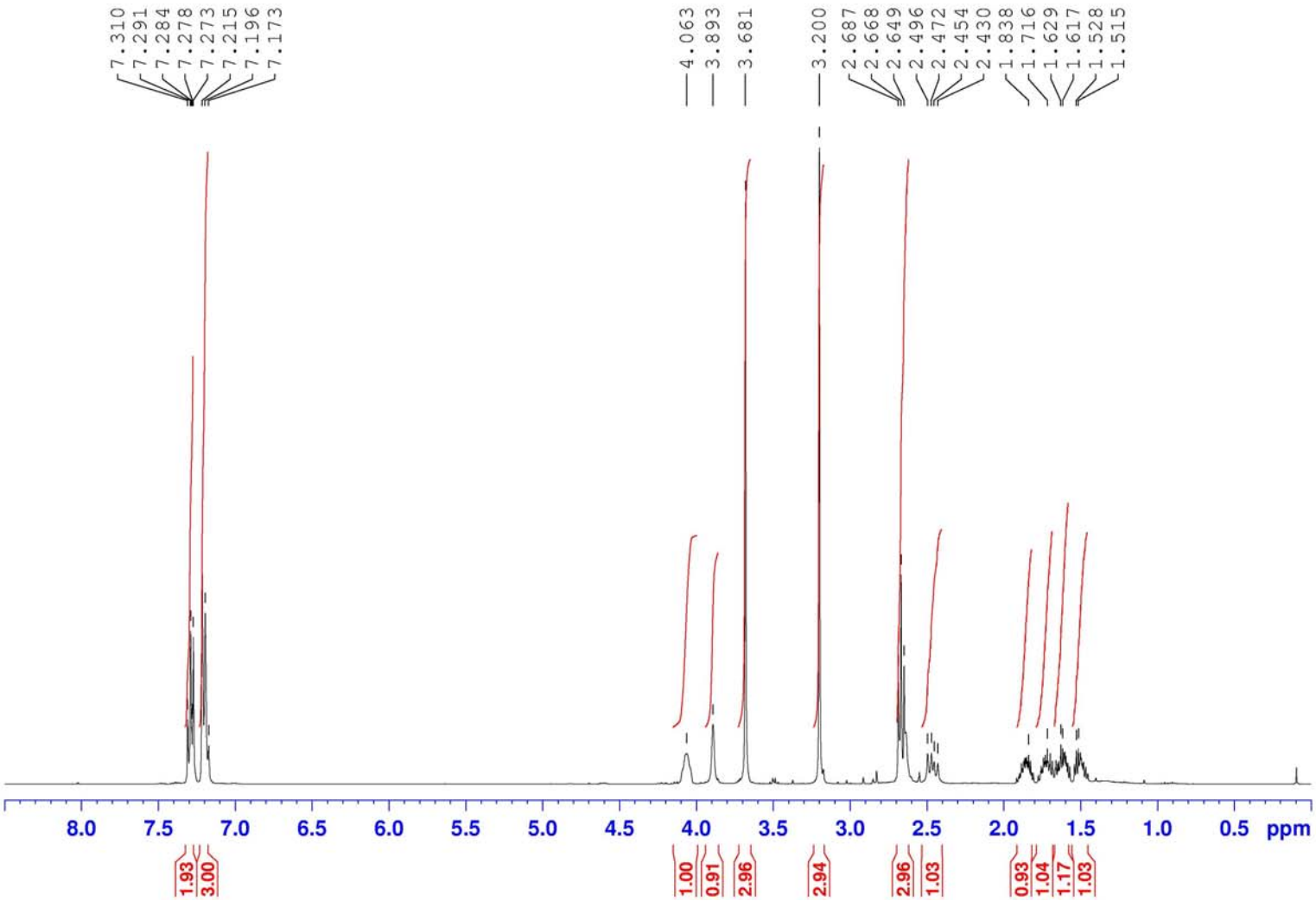




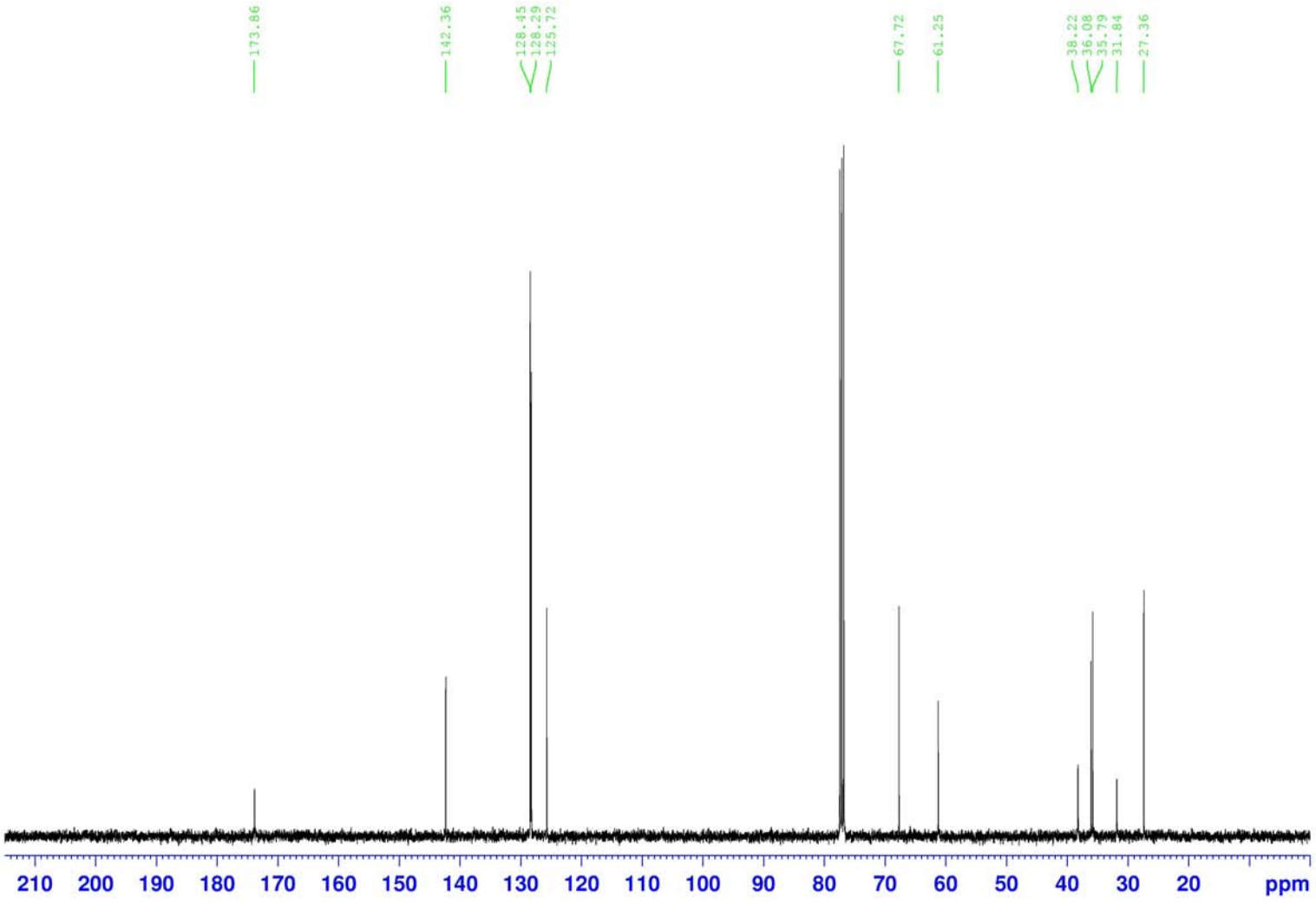
Catalytic asymmetric hydroboration of (*E*)-**4** with mild oxidative workup ($NaBO_3$) affords, after flash chromatography on silica gel (60:40 hexanes:ethyl acetate), the title compound (97%) as a light yellow oil.

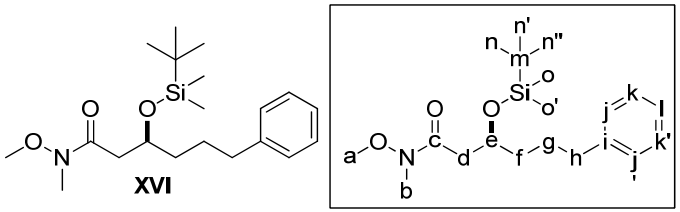
TLC analysis	R_f 0.4 (25:75 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20}$ = +21.5º (*c* 0.5, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.35–7.25 (2H, m, k,k'), 7.25–7.15 (3H, m, j,j',l), 4.10–4.00 (1H, m, e), 3.89 (1H, br s, OH), 3.68 (3H, s, a), 3.68 (3H, s, b), 2.67 (2H, t, *J* = 7.5 Hz, h), 2.70–2.60 (1H, suspected dd, d), 2.46 (1H, dd, *J* = 16.8 Hz, 9.6 Hz, d), 1.90–1.80 (1H, m, f), 1.80–1.70 (1H, m, f), 1.70–1.60 (1H, m, g), 1.60–1.45 (1H, m, g).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.86 (c), 142.36 (i), 128.45 (j,j'), 128.29 (k,k'), 125.72 (l), 67.72 (e), 61.25 (a), 38.22 (d), 36.08 (f), 35.79 (h), 31.84 (b), 27.36 (g).
IR (neat)	3427 (OH stretch), 2962 (CH sp^3 stretch), 1639 (C=O stretch), 1453, 1387 (C-N stretch), 1258, 1088 (C-O stretch), 1004, 870, 789, 699 cm^{-1}.
HRMS (ESI)	Calcd. for $C_{14}H_{21}NaNO_3$ (M+Na): 274.1419, found 274.1414 *m/z*.

^{1}H NMR of 10



^{13}C NMR of 10

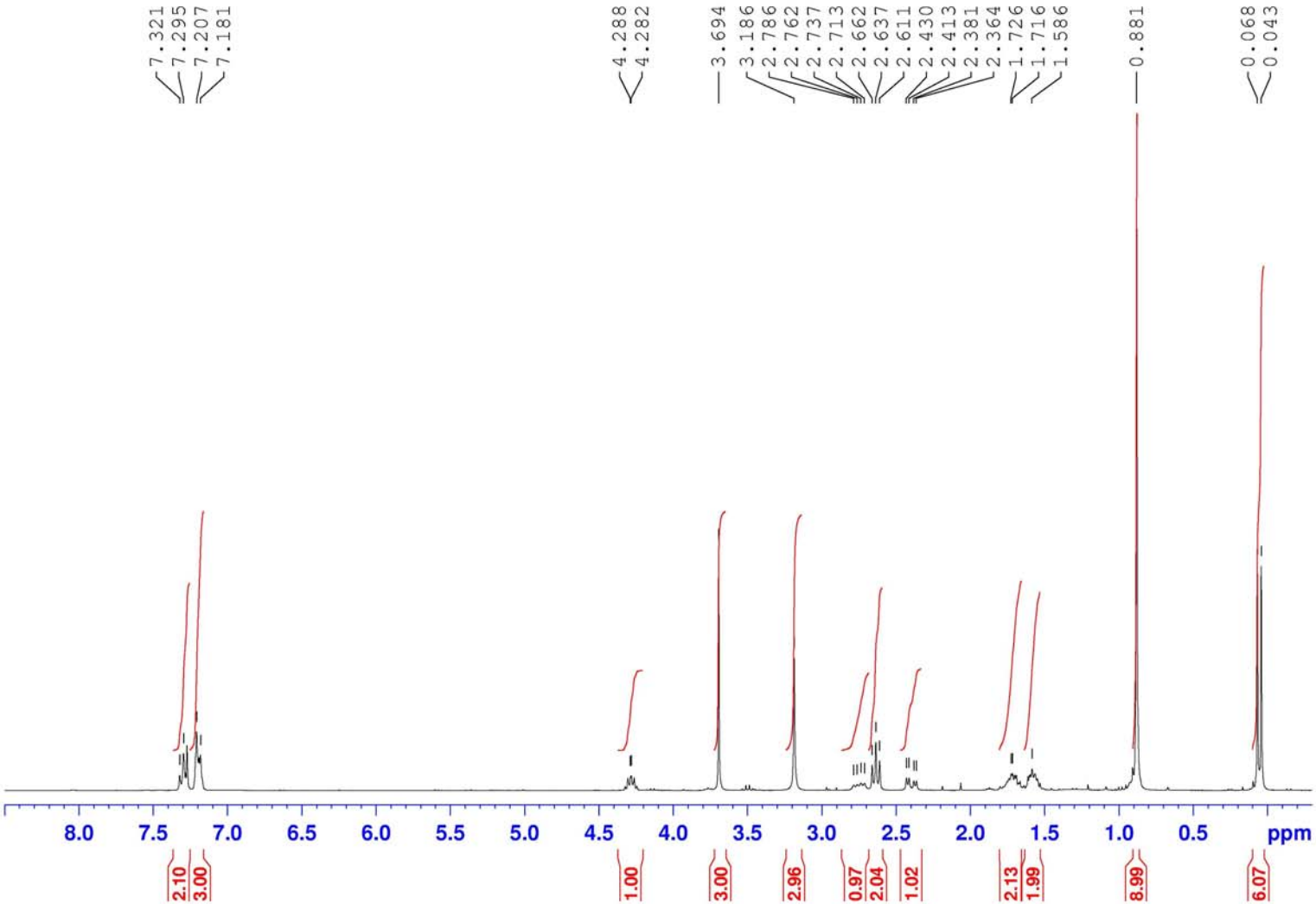




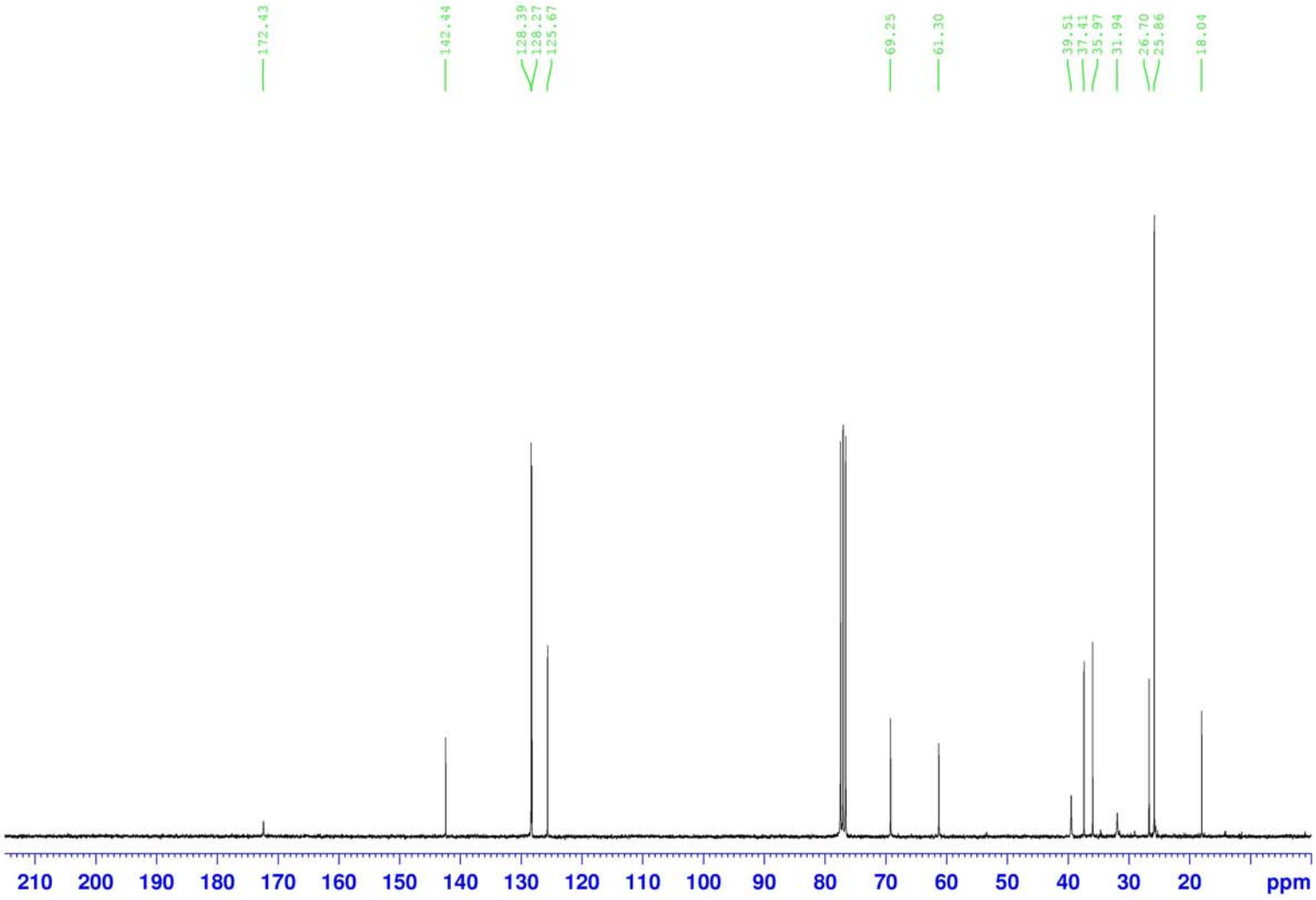
TBS-protection of **10** affords, after flash chromatography on silica gel (90:10 hexanes:ethyl acetate), the title compound (82%) as a light yellow oil.

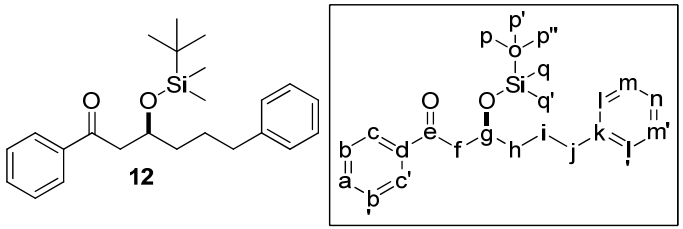
TLC analysis	R_f 0.30 (90:10 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20}$ = +° (*c* 0.5, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.35–7.25 (2H, m, k,k'), 7.25–7.15 (3H, m, j,j',l), 4.35–4.25 (1H, m, e), 3.69 (3H, s, a), 3.19 (3H, s, b), 2.75 and 2.39 (2H, overlapping dd's, J_1 = 14.6 Hz, 7.3 Hz, J_2 = 14.6 Hz, 5.3 Hz, d), 2.64 (2H, t, *J* = 7.5 Hz, h), 1.80–1.65 (2H, m, f), 1.65–1.50 (2H, m, g), 0.88 (9H, s, n,n',n''), 0.07 (3H, s, o), 0.04 (3H, s, o').
^{13}C NMR (75 MHz, $CDCl_3$)	δ 172.43 (c), 142.44 (i), 128.39 (j,j'), 128.27 (k,k'), 125.67 (l), 69.25 (e), 61.30 (a), 39.51 (d), 37.41 (f), 35.97 (h), 31.94 (b), 26.70 (g), 25.86 (n,n',n''), 18.04 (m), -4.65 (o), -4.71 (o').
IR (neat)	2929 (CH sp^3 stretch), 2855, 1661 (C=O stretch), 1472, 1385, 1252, 1090 (C-O stretch), 1004, 939, 834, 775, 732, 698 cm^{-1}.
HRMS (ESI)	Calcd. for $C_{20}H_{35}NNaO_3Si$ (M+Na): 388.2284, found 388.2283 *m/z*.

^{1}H NMR of XVI



^{13}C NMR of XVI

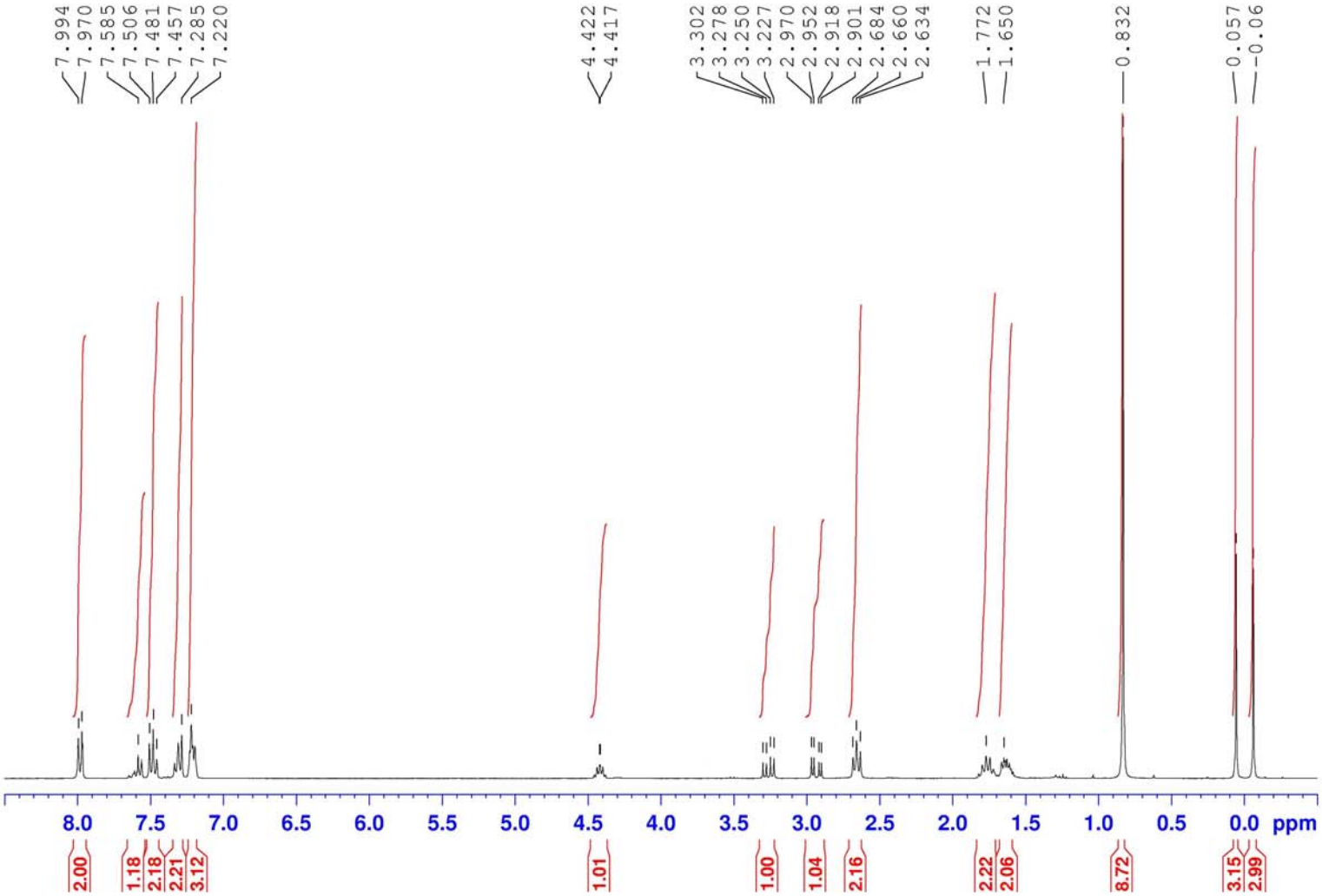




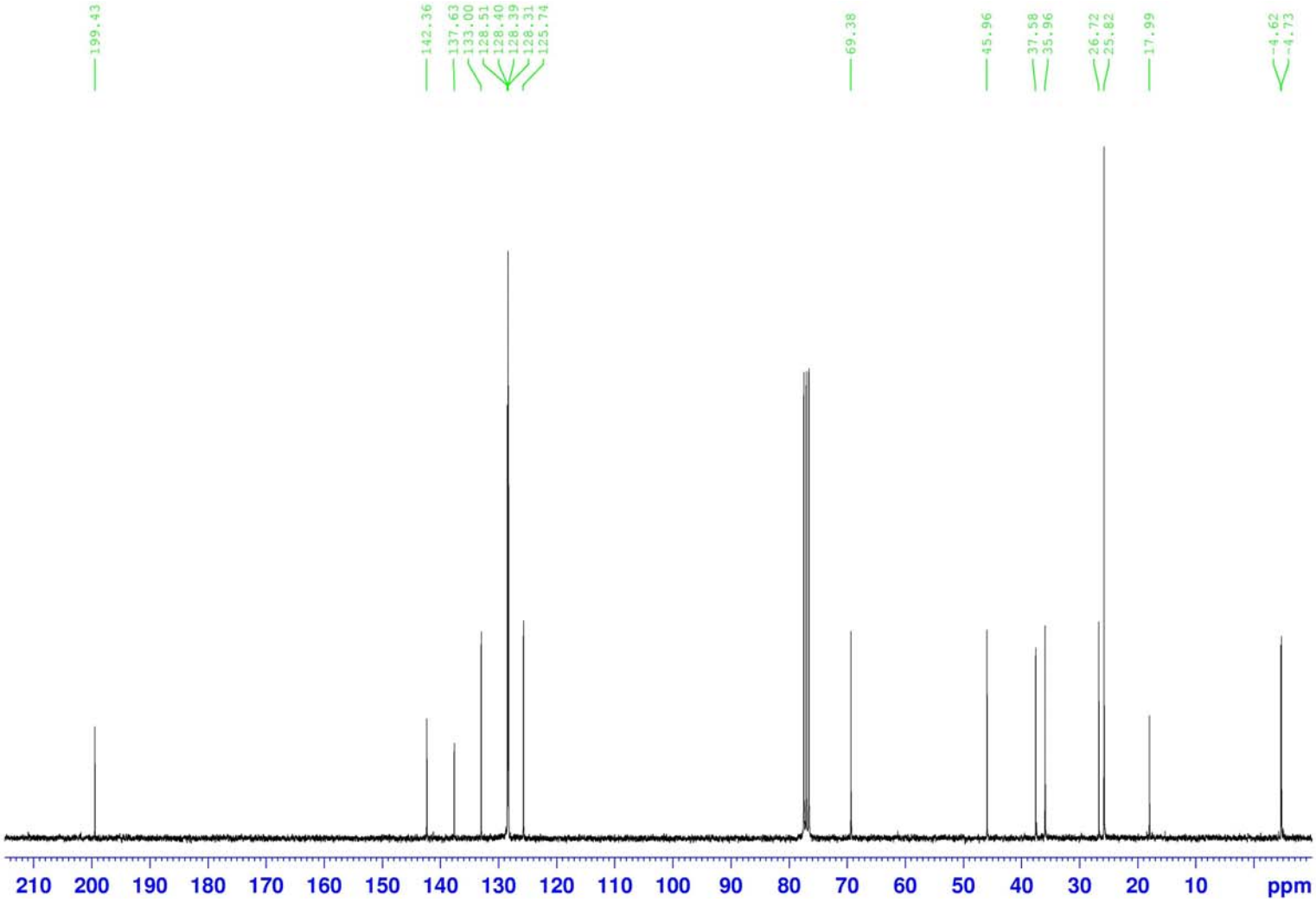
Treatment of *β*-siloxy Weinreb amide **XVI** with phenylmagnesium bromide affords, after flash chromatography on silica gel (95:5 hexanes:ethyl acetate), the title compound (94%) as a light yellow oil.

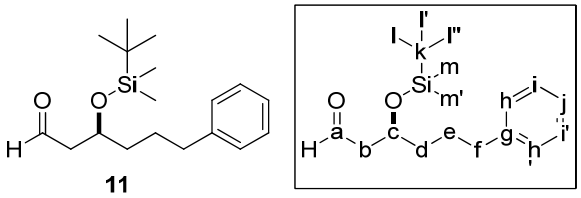
TLC analysis	R_f 0.6 (90:10 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20}$ = +21.2° (*c* 0.5, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$)	δ 8.05–7.95 (2H, m, c,c'), 7.60–7.55 (1H, m, a), 7.55–7.45 (2H, m, b,b'), 7.35–7.25 (2H, m, m,m'), 7.25–7.15 (3H, m, l,l',n), 4.45–4.35 (1H, m, g), 3.26 and 2.93 (2H, overlapping dd's, J_1 = 15.4 Hz, 7.1 Hz, J_2 = 15.4 Hz, 5.3 Hz, f), 2.66 (2H, t, J = 7.3 Hz, j), 1.80–1.70 (2H, m, h), 1.70–1.55 (2H, m, i), 0.83 (9H, s, p,p',p''), 0.06 (3H, s, q), -0.06 (3H, s, q').
^{13}C NMR (75 MHz, $CDCl_3$)	δ 199.43 (e), 142.36 (k), 137.63 (d), 133.00 (a), 128.51 (b,b'), 128.40 (l,l'), 128.39 (m,m'), 128.31 (c,c'), 125.74 (n), 69.38 (g), 45.96 (f), 37.58 (h), 35.96 (j), 26.72 (i), 25.82 (p,p',p''), 17.99 (o), -4.62 (q), -4.73 (q').
IR (neat)	2928 (CH sp^3 stretch), 2855, 1684 (C=O stretch), 1598, 1474, 1448, 1360, 1252, 1210, 1090 (C-O stretch), 1019, 1003, 833, 775, 669 cm^{-1}.
HRMS (ESI)	Calcd. for $C_{24}H_{34}NaO_2Si$ (M+Na): 405.2226, found 405.2223 *m/z*.

^{1}H NMR of 12



^{13}C NMR of 12



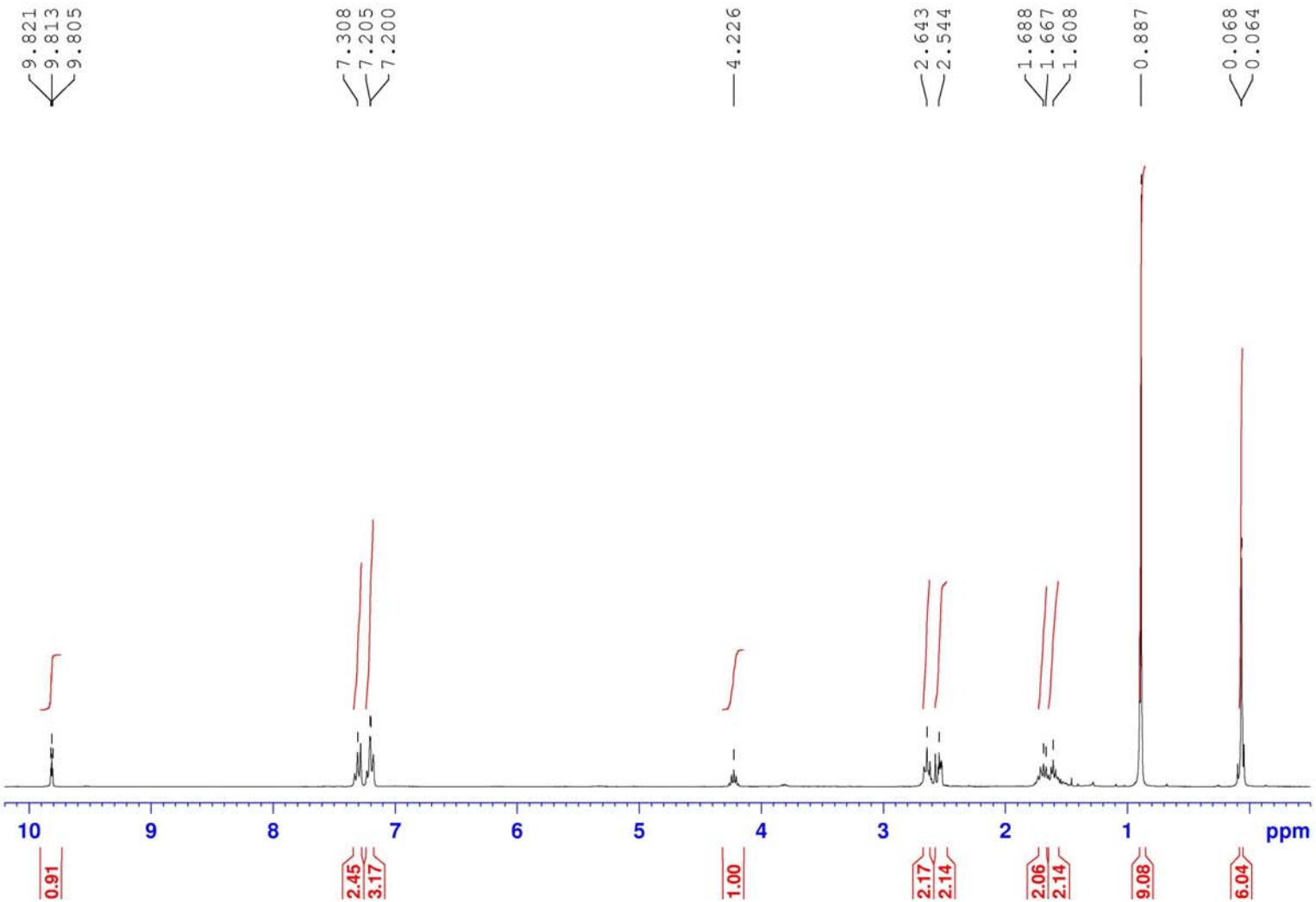


11

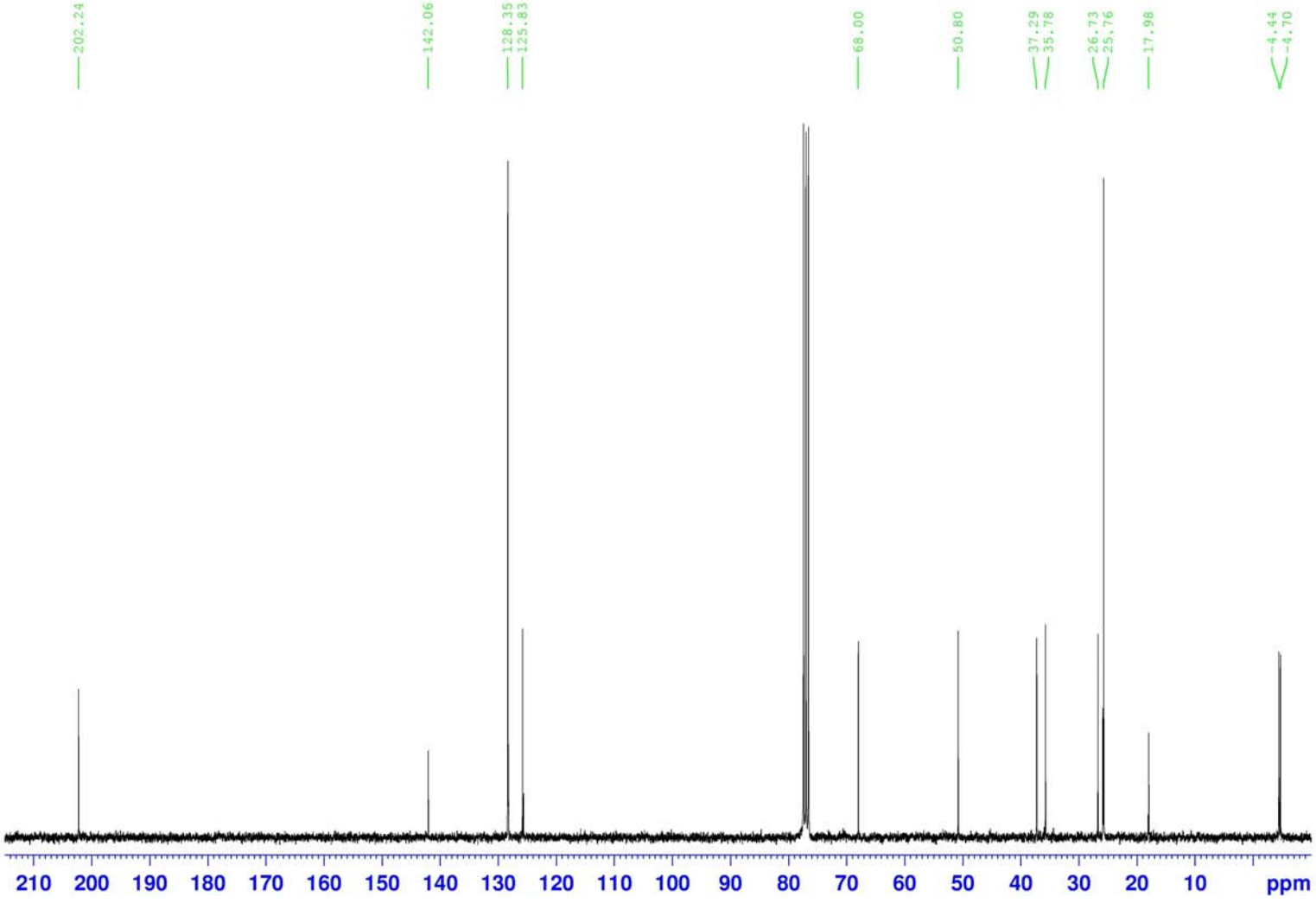
Half reduction of *β*-siloxy Weinreb amide **XVI** with DIBAL-H affords, after flash chromatography on silica gel (95:5 hexanes:ethyl acetate), the title compound (91%) as a light yellow oil.

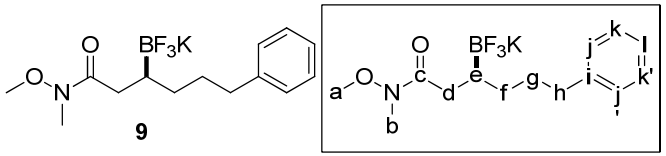
TLC analysis	R_f 0.4 (90:10 hexanes:ethyl acetate)
Optical rotation	$[\alpha]_D^{20} = +5.5°$ (*c* 0.5, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$)	δ 9.81 (1H, t, *J* = 2.3 Hz, a), 7.35–7.25 (2H, m, i,i'), 7.25–7.15 (3H, m, h,h',j), 4.25–4.15 (1H, m, c), 2.70–2.60 (2H, m, f), 2.60–2.50 (2H, m, b), 2.75–2.65 (2H, m, d), 2.65–2.55 (2H, m, e), 0.89 (9H, s, l,l',l"), 0.07 (3H, s, m), 0.06 (3H, s, m').
^{13}C NMR (75 MHz, $CDCl_3$)	δ 202.24 (a), 142.06 (g), 128.35 (h,h',i,i'), 125.83 (j), 68.00 (c), 50.80 (b), 37.29 (d), 35.78 (f), 26.73 (e), 25.76 (l,l',l"), 17.98 (k), -4.44 (m), -4.70 (m').
IR (neat)	2929 (CH sp^3 stretch), 2857, 1725 (C=O stretch), 1471, 1361, 1253, 1095 (C-O stretch), 1027, 1005, 834, 774, 698 cm^{-1}.

^{1}H NMR of 11



^{13}C NMR of 11

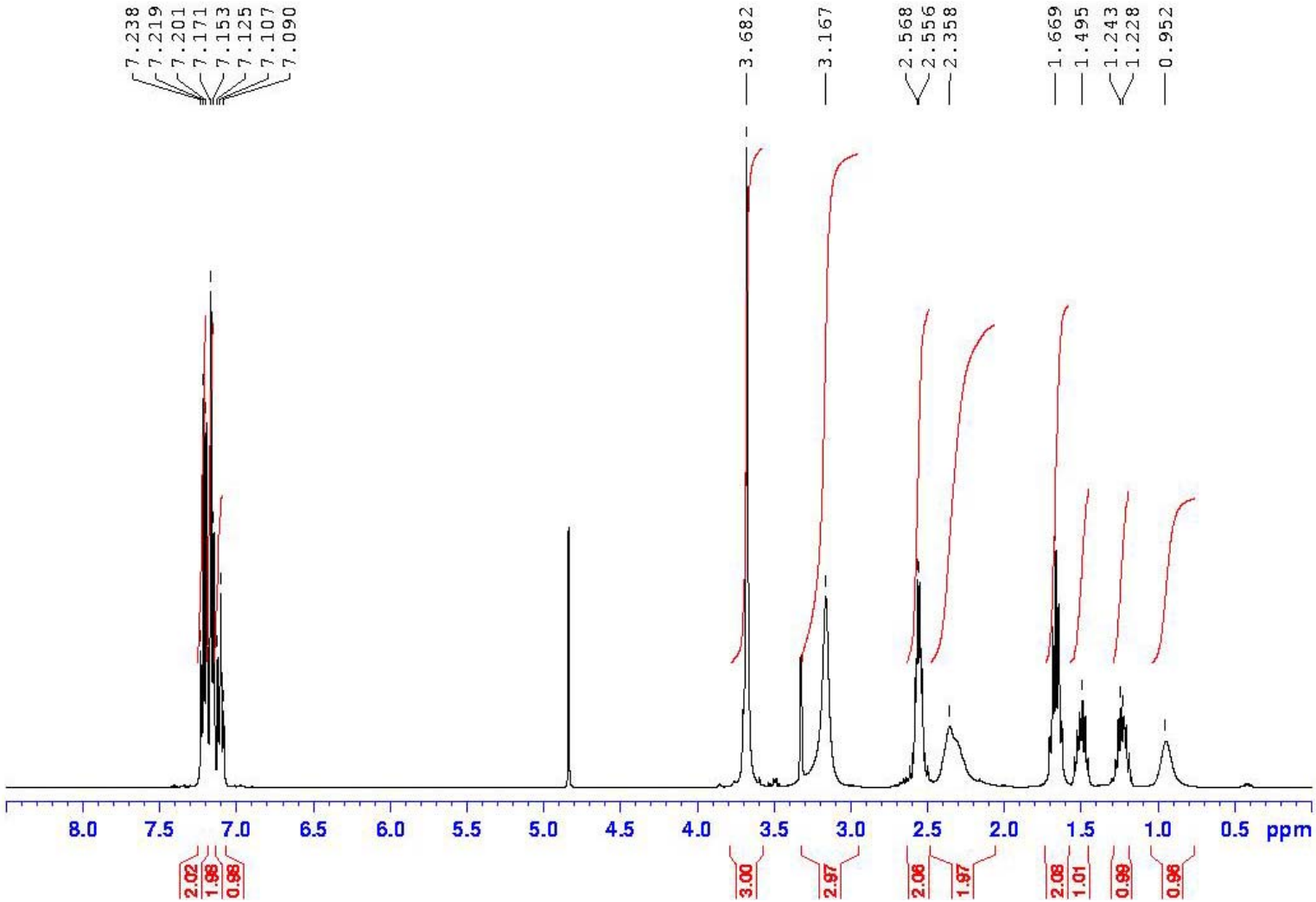




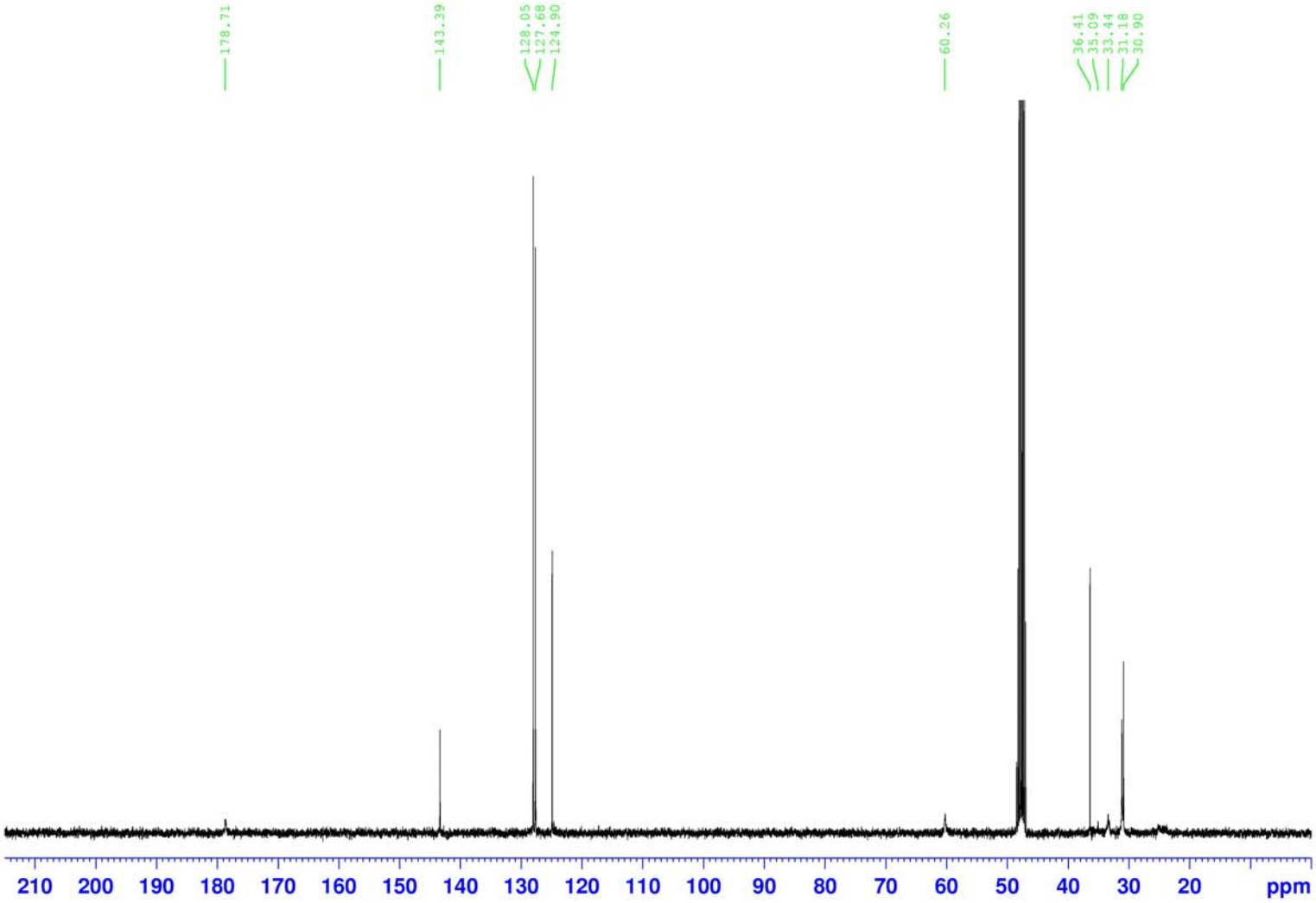
Treatment of *β*-borato Weinreb amide **8** with satd. aq KHF_2 affords the title compound (82%) as a white solid.

m.p.	235–236 °C
Optical rotation	$[\alpha]_D^{20}$ = -10.2° (*c* 0.5, MeOH)
^{1}H NMR (300 MHz, MeOD)	δ 7.25–7.20 (2H, m, k,k'), 7.20–7.15 (2H, m, j,j'), 7.15–7.05 (1H, m, l), 3.68 (3H, s, a), 3.17 (3H, s, b), 2.60–2.50 (2H, m, h), 2.40–2.20 (2H, m, d), 1.70–1.60 (2H, m, g), 1.55–1.45 (1H, m, f), 1.30–1.15 (1H, m, f), 0.95 (1H, br s, e).
^{13}C NMR (75 MHz, MeOD)	δ 178.71 (c), 143.39 (i), 128.05 (j,j'), 127.68 (k,k'), 124.90 (l), 60.26 (a), 36.41 (h), 33.44 (d), 31.18 (e,f), 30.90 (b,g).
^{19}F NMR (376 MHz, MeOD)	δ -146.53.
IR (neat)	2958 (CH sp^3 stretch), 2856, 1668 (C=O stretch), 1454, 1390, 1300, 1144 (C-O stretch), 1000, 955, 854, 660 cm^{-1}.
HRMS (CI)	Calcd. for (M-BF_3K+2H): 236.1651, found 236.1654 *m/z*.

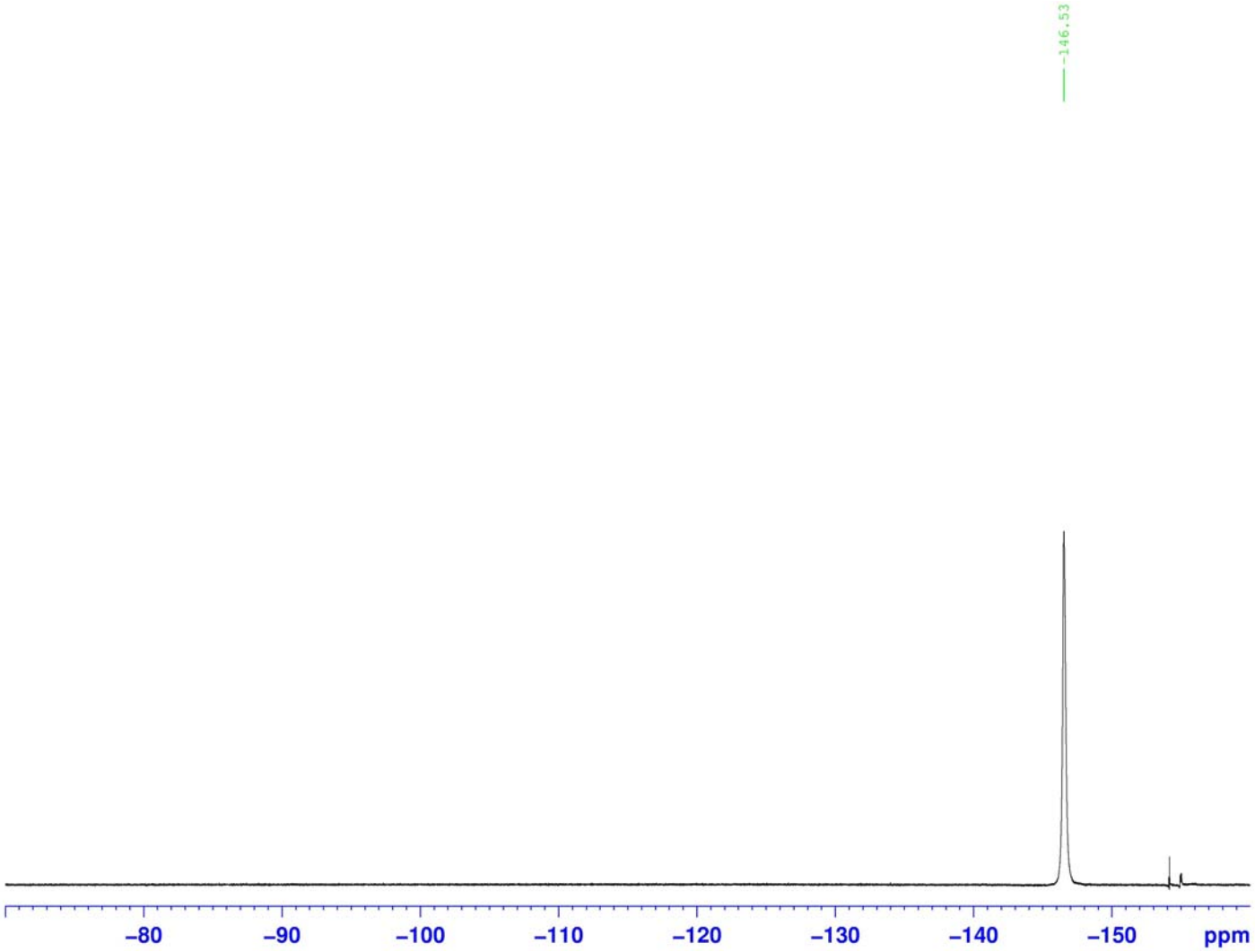
^{1}H NMR of 9

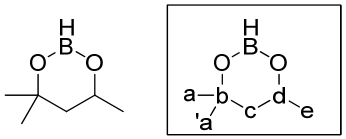


^{13}C NMR of 9



^{19}F NMR of 9



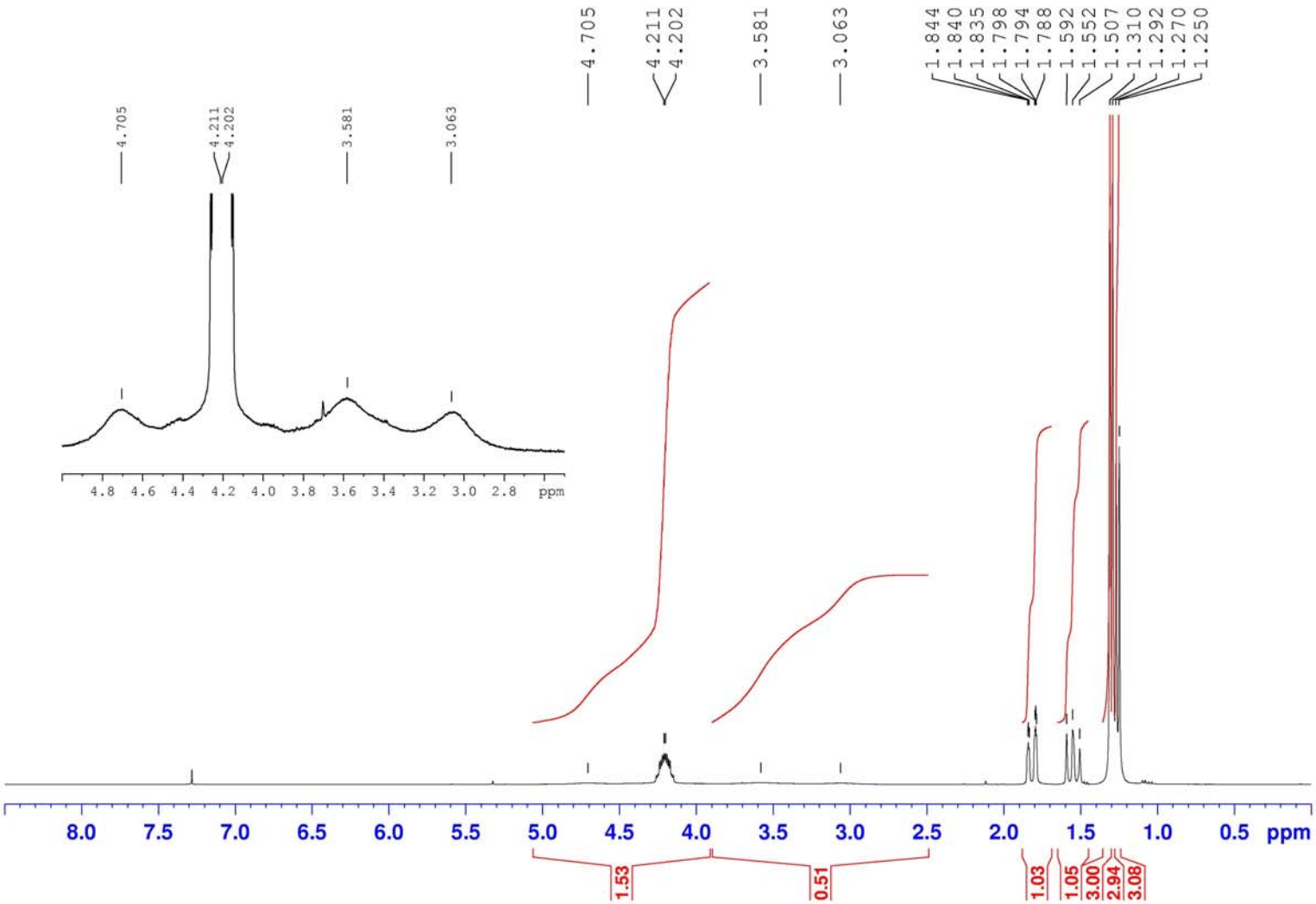


B7

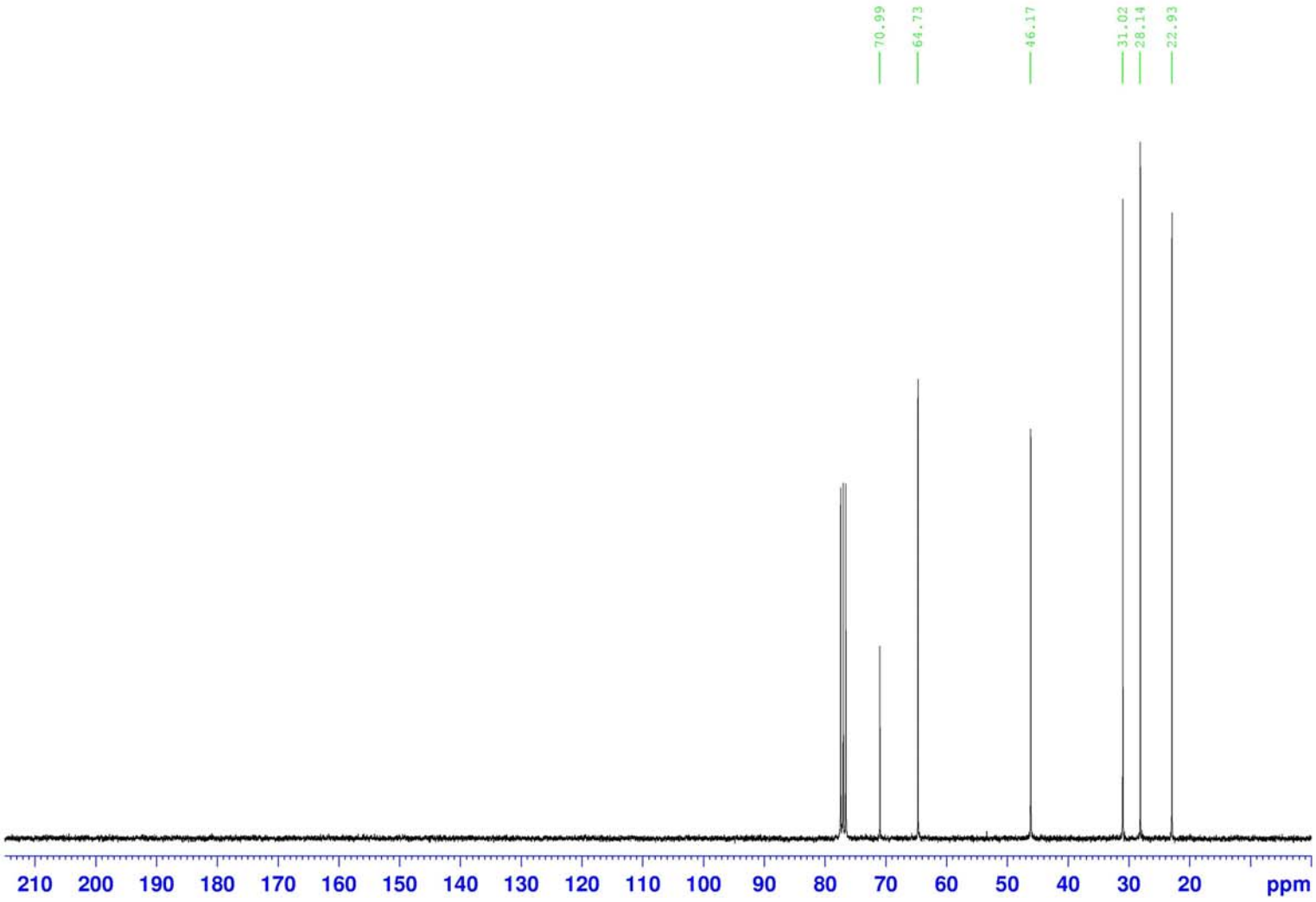
The general procedure for the preparation of 1,3,2-dioxaborolanes affords, after bulb-to-bulb distillation, the title compound (75%) as a colorless liquid.

b.p.	160–165 ^{o}C
^{1}H NMR (300 MHz, $CDCl_3$)	δ 4.30–4.15 (1H, m, d), 3.84 (1H, q, *J* = 155.6 Hz, BH), 1.90–1.75 (1H, m, c), 1.60–1.45 (1H, m, c), 1.31 (3H, s, a), 1.29 (3H, s, a'), 1.26 (3H, d, *J* = 6.2 Hz, e).
^{13}C NMR (75 MHz, $CDCl_3$)	δ 70.99 (b), 64.73 (d), 46.17 (c), 31.02 (a), 28.14 (a'), 22.93 (e).
^{11}B NMR (193 MHz, THF with residual $CDCl_3$)	δ 24.96 (d, *J* = 169.1 Hz).
IR (neat)	2976 (CH sp^3 stretch), 2879, 2400, 1495, 1427, 1384, 1291, 1156 (C-O stretch), 1094, 1024, 889, 789, 666 cm^{-1}.
HRMS (CI)	Calcd. for $C_6H_{14}BO_2$ (M+H): 129.1087, found 129.1082 *m/z*.

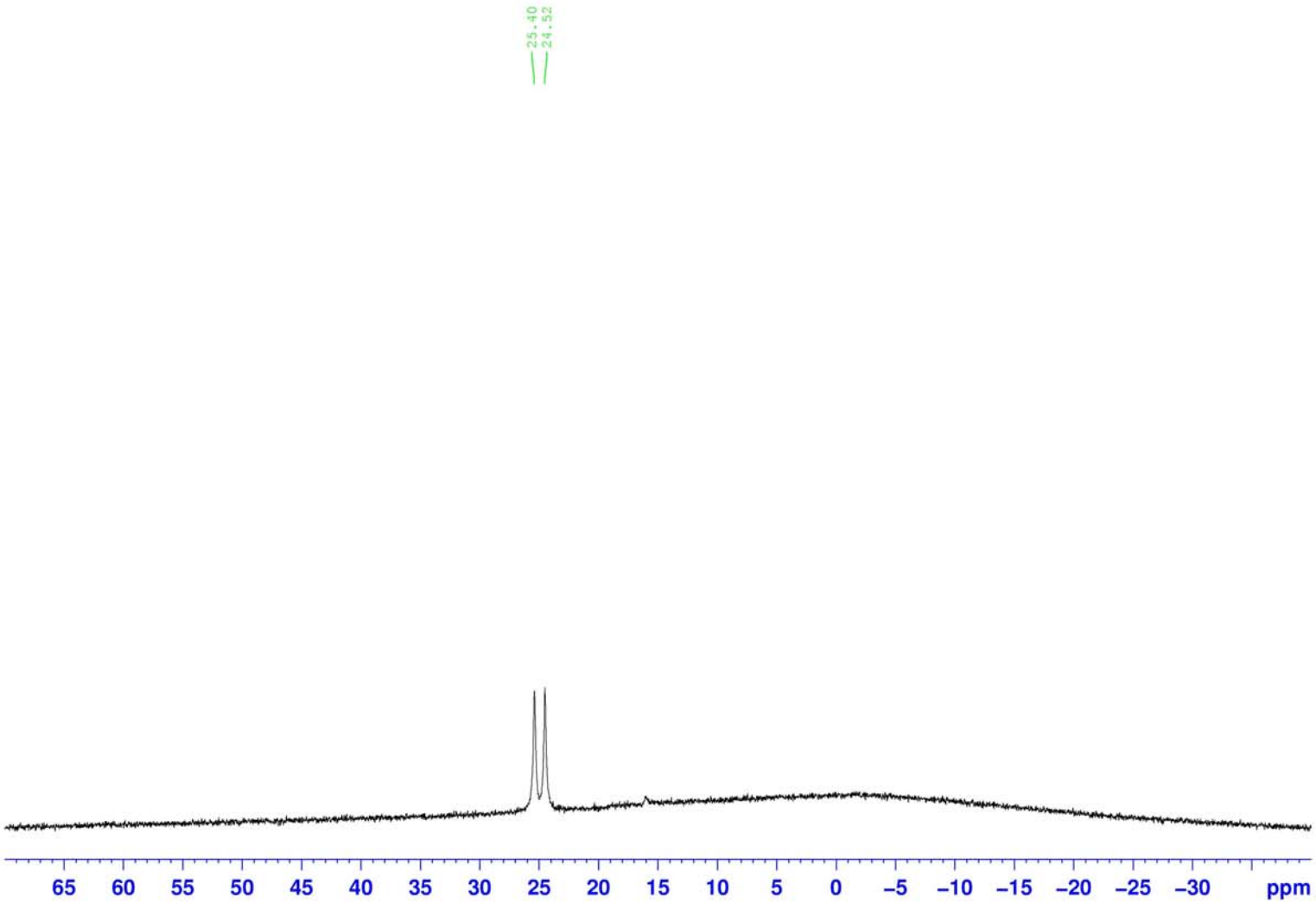
^{1}H NMR of B7

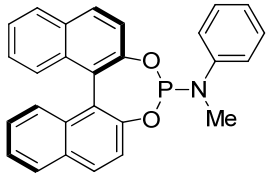


^{13}C NMR of B7



^{11}B NMR of B7



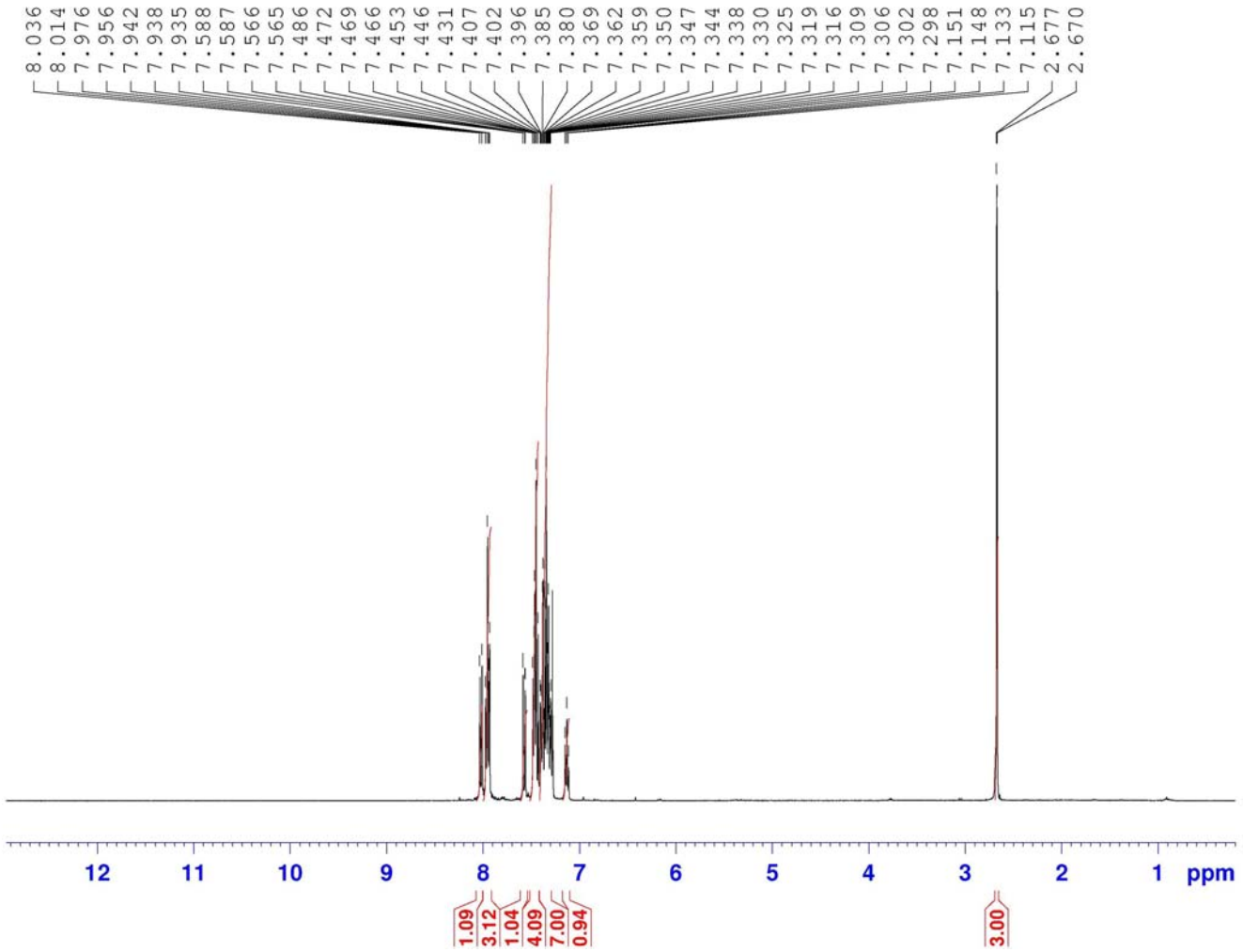


L

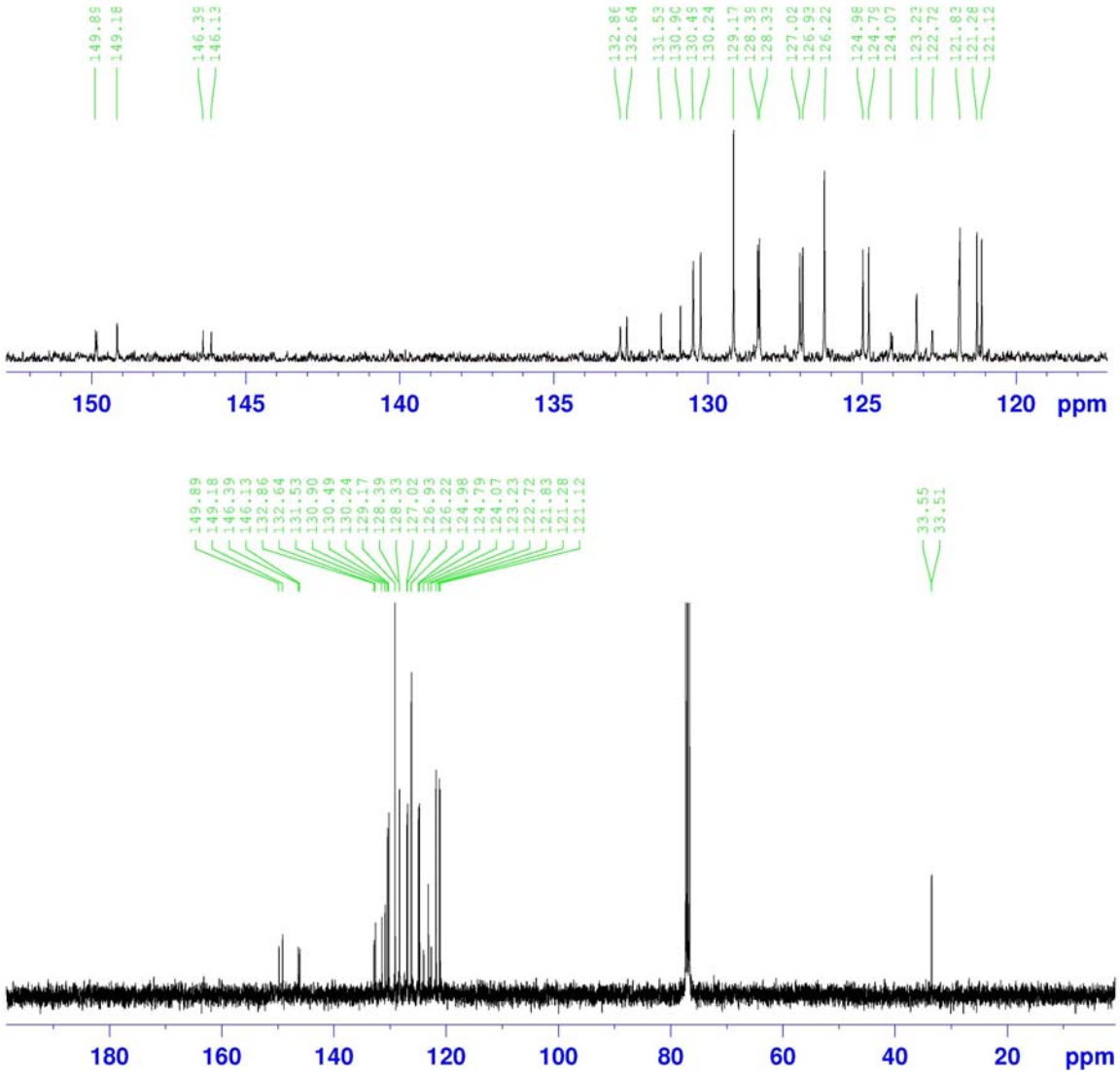
The general procedure for the preparation of phosphoramidites affords, after flash chromatography on silica gel (92:8 hexanes:ethyl acetate), the title compound (68%) as a white foamy solid.

m.p.	94–95 °C
Optical rotation	$[\alpha]_D^{20}$ = -87.2° (*c* 0.5, ethanol)
TLC analysis	R_f 0.60 (75:25 hexanes: DCM)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 8.03 (1H, d, *J* = 8.8 Hz), 8.00-7.90 (3H, m), 7.60-7.55 (1H, m), 7.50-7.41 (4H, m), 7.41-7.25 (7H, m), 7.17-7.10 (1H, m), 2.67 (3H, d, *J* = 2.51 Hz).
^{13}C NMR (100 MHz, $CDCl_3$)	δ 149.89, 149.18, 146.39, 146.13 132.86, 132.64, 131.53, 130.90, 130.49, 130.24, 129.17, 128.39, 128.33, 127.02, 126.93, 126.22, 124.98, 124.79, 124.07, 123.23, 122.72, 121.83, 121.28, 121.12, 33.53 (J_{CP} = 4.02 Hz).
^{31}P NMR (162 MHz, $CDCl_3$)	δ 143.76.
IR (neat)	3061, 2935 (P-O stretch), 1589, 1489, 1330, 1269, 1226, 1061, 938, 804, 769 cm^{-1}.
HRMS (FAB)	Calcd. for $C_{27}H_{20}NO_2P$ (M+H): 422.1310, found 422.1307 *m/z*..

^{1}H NMR of L



^{13}C NMR of L



^{31}P NMR of L