Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information (Spectra) for:

Two-Stage Optimization of a Supramolecular Catalyst for Catalytic Asymmetric Hydroboration

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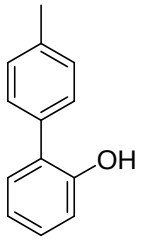
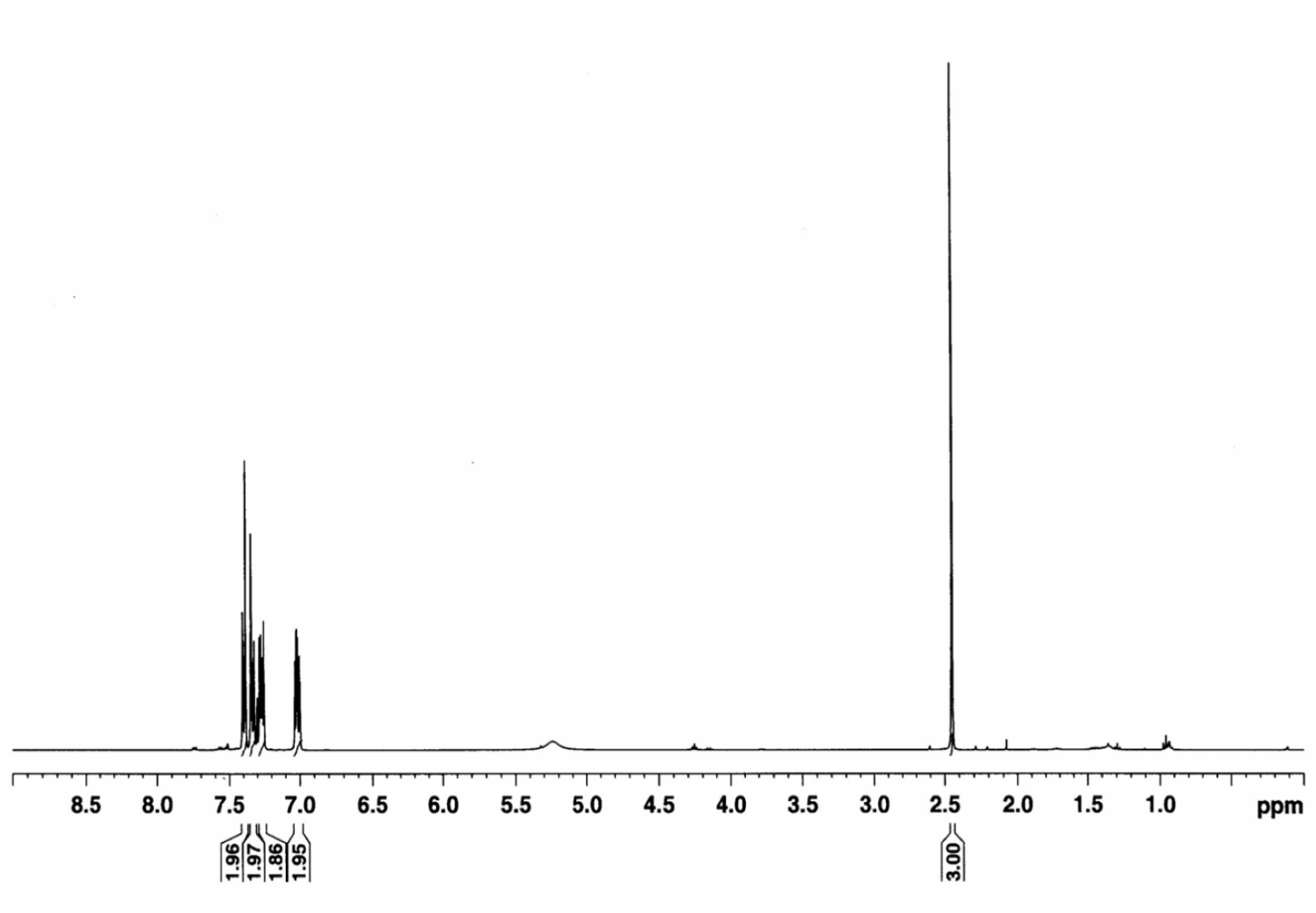


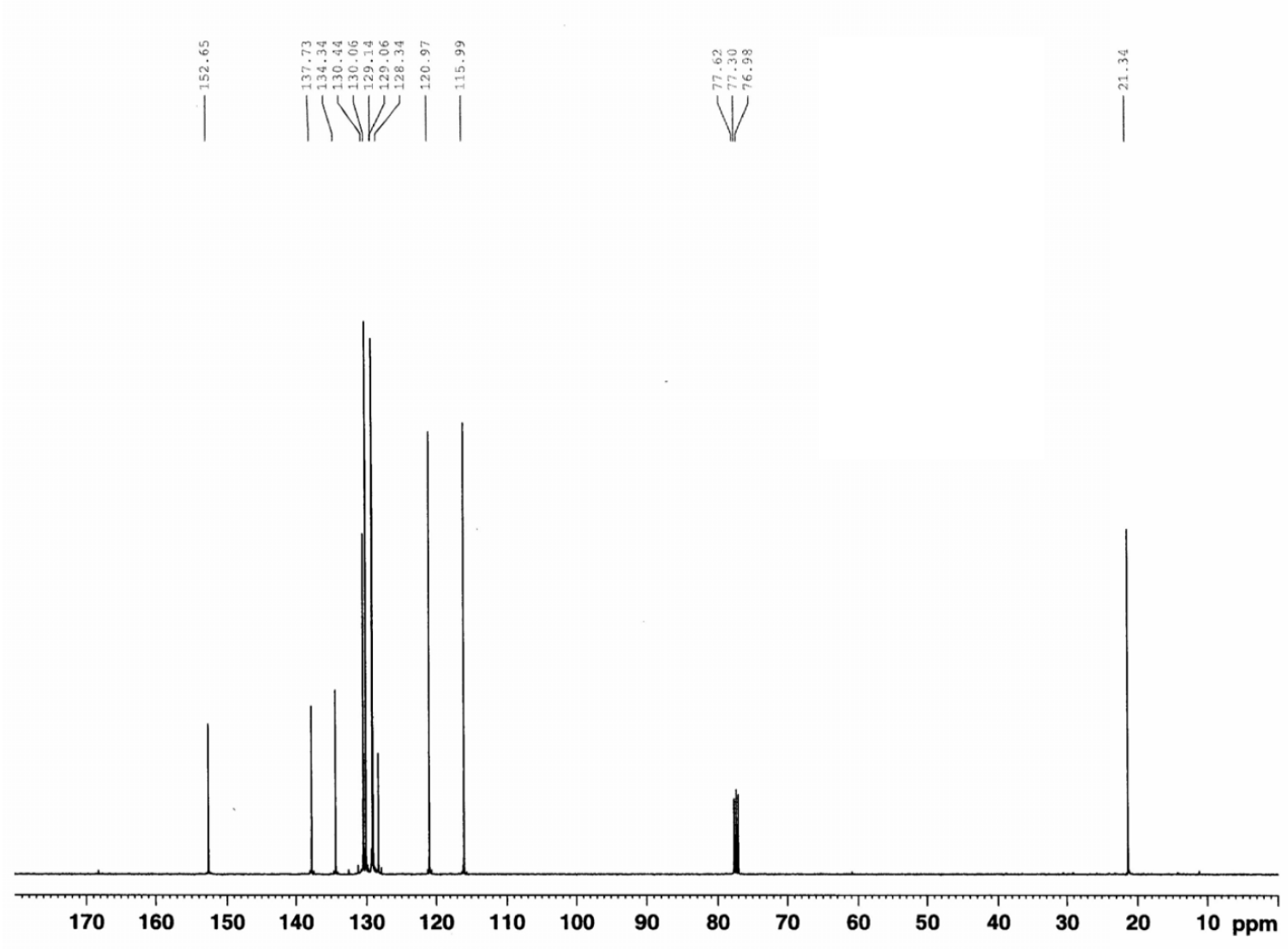
The general procedure for the synthesis of tethers affords, after flash chromatography on silica gel (10:90 ethyl acetate:hexane), the compound pictured (90%) as a colorless oil.

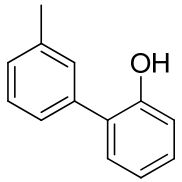
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.40-7.38 (2H, m), 7.34-7.30 (2H, m), 7.28-7.25 (2H, m), 7.03-6.99 (2H, m), 2.45 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 152.7, 137.7, 134.3, 130.4, 130.1, 129.1, 129.1, 128.3, 121.0, 116.0, 21.3 ppm
HRMS (FABS)	calcd. for $C_{13}H_{12}O$ (M+), 184.0888; found, 184.0893 *m/z*

^{1}H NMR of A(I)



^{13}C NMR of A(I)

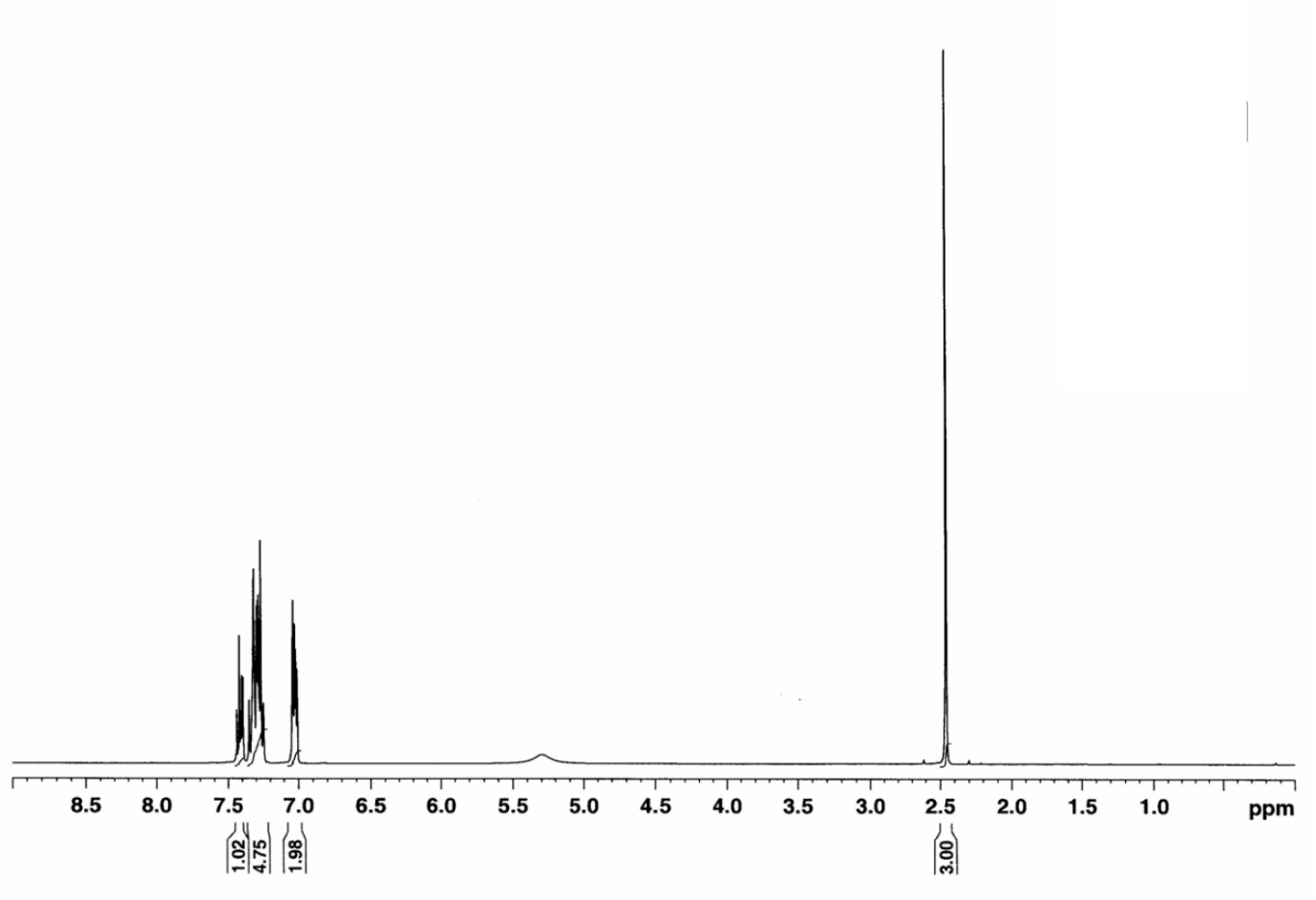




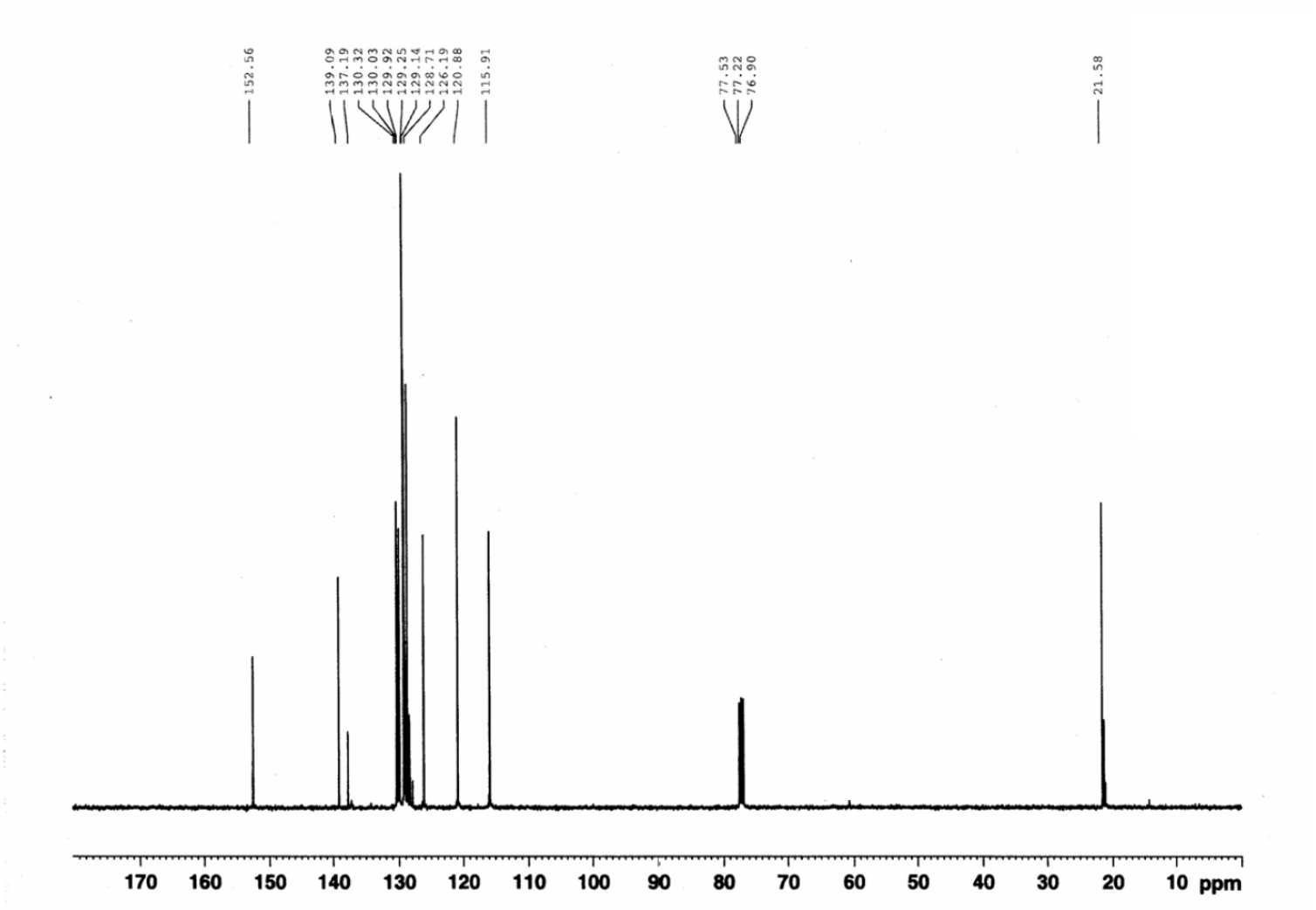
The general procedure for the synthesis of tethers affords, after flash chromatography on silica gel (10:90 ethyl acetate:hexane), the compound pictured (96%) as a colorless oil.

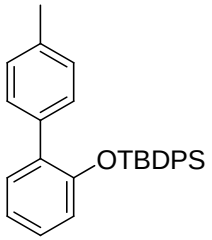
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.44-7.35 (1H, m), 7.32-7.25 (5H, m), 7.05-7.00 (2H, m), 2.46 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 152.6, 139.1, 137.2, 130.3, 130.0, 129.9, 129.3, 129.1, 128.7, 126.2, 120.9, 115.9, 21.6 ppm
HRMS (FABS)	calcd. for $C_{13}H_{12}O$ (M^+), 184.0888; found, 184.0886 *m/z*

^{1}H NMR of B(I)



^{13}C NMR of B(I)

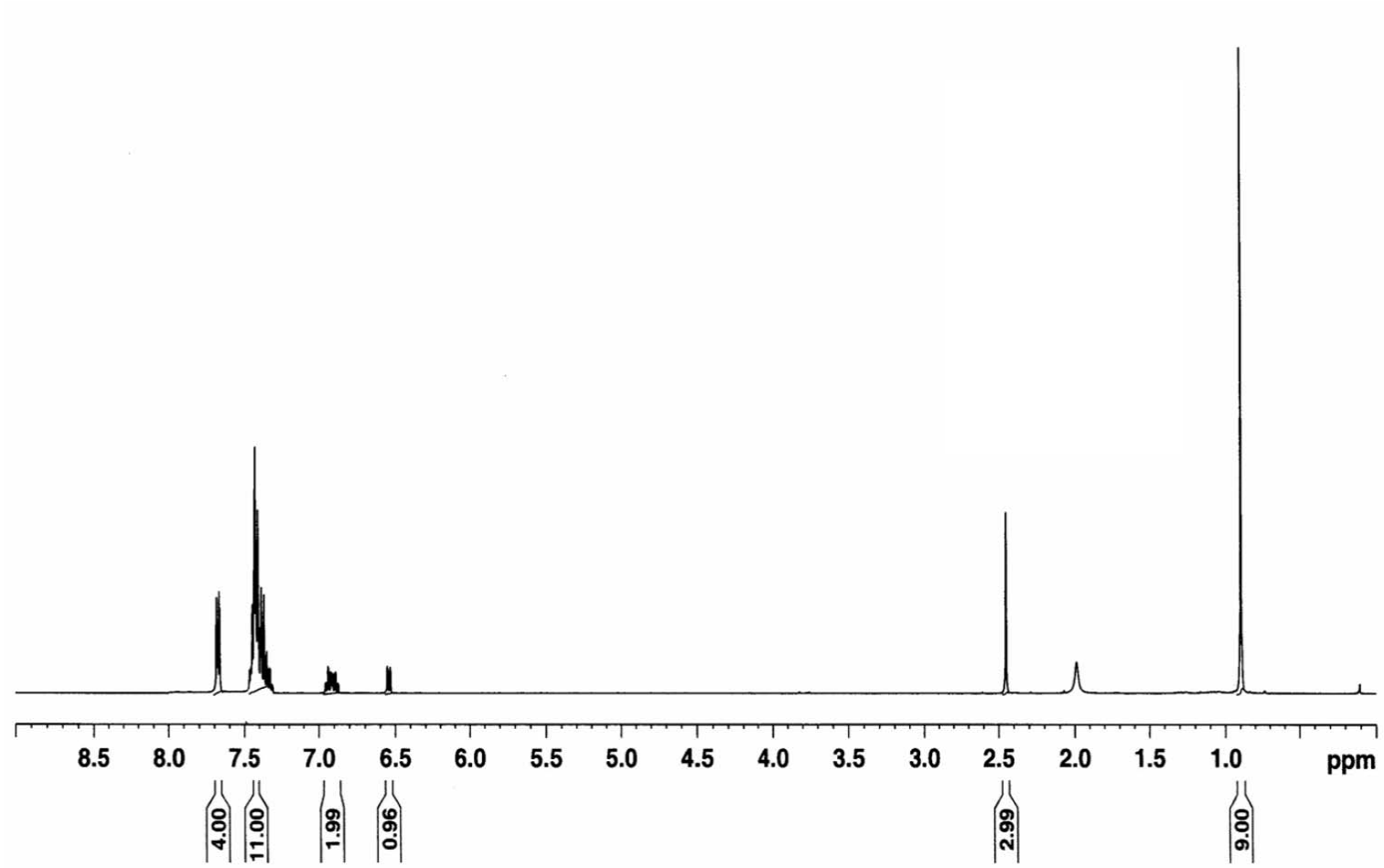




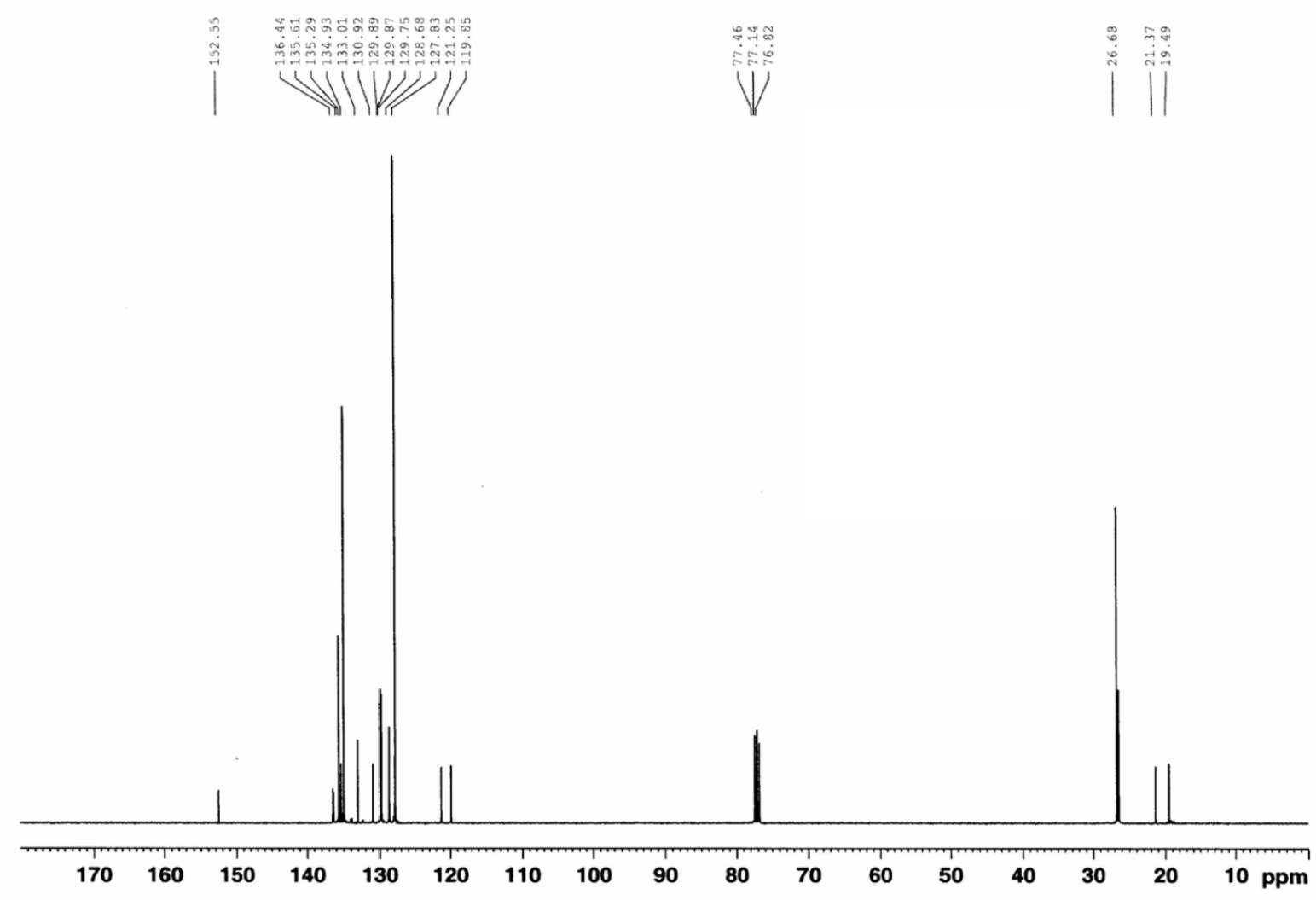
The general procedure for the synthesis of tethers affords, after flash chromatography on silica gel (5:95 ethyl acetate:hexane), the compound pictured (93%) as a colorless oil.

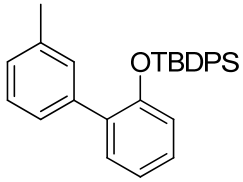
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.69-7.66 (4H, dd, *J* = 9.6 Hz, 1.8 Hz), 7.45-7.36 (11H, m), 6.96-6.86 (2H, m), 6.57-6.51 (1H, dd, *J* = 7.9, 1.3 Hz), 2.45 (3H, s), 0.89 ppm (9H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 152.6, 136.4, 135.6, 135.3, 134.9, 133.0, 130.9, 129.9, 129.8, 129.7, 128.7, 127.8, 121.3, 119.9, 26.7, 21.4, 19.5 ppm
HRMS (FABS)	calcd. for $C_{29}H_{30}OSiLi$ $[(M+Li)^+]$, 429.2226; found, 429.2215 *m/z*

^{1}H NMR of A(II)



^{13}C NMR of A(II)

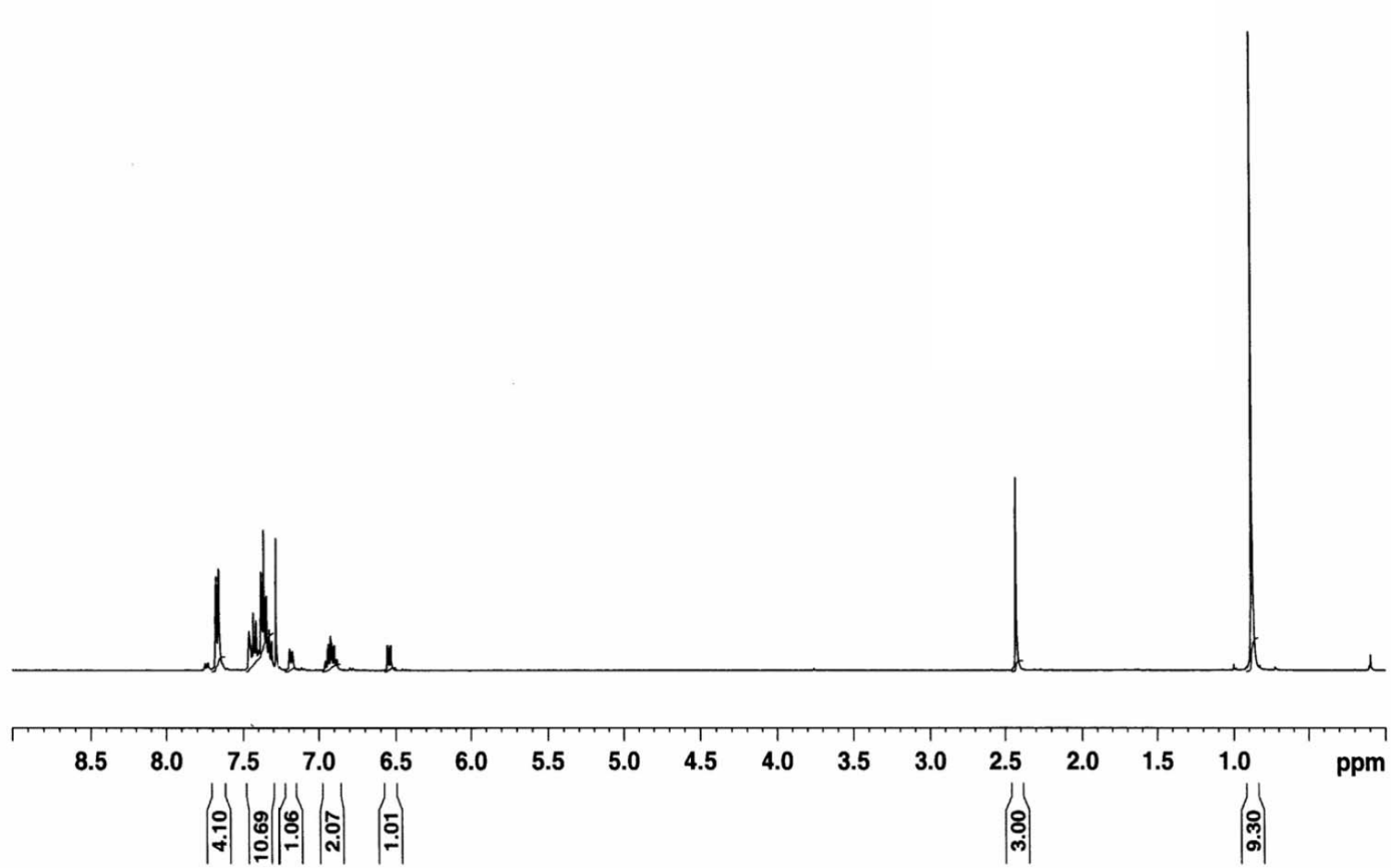




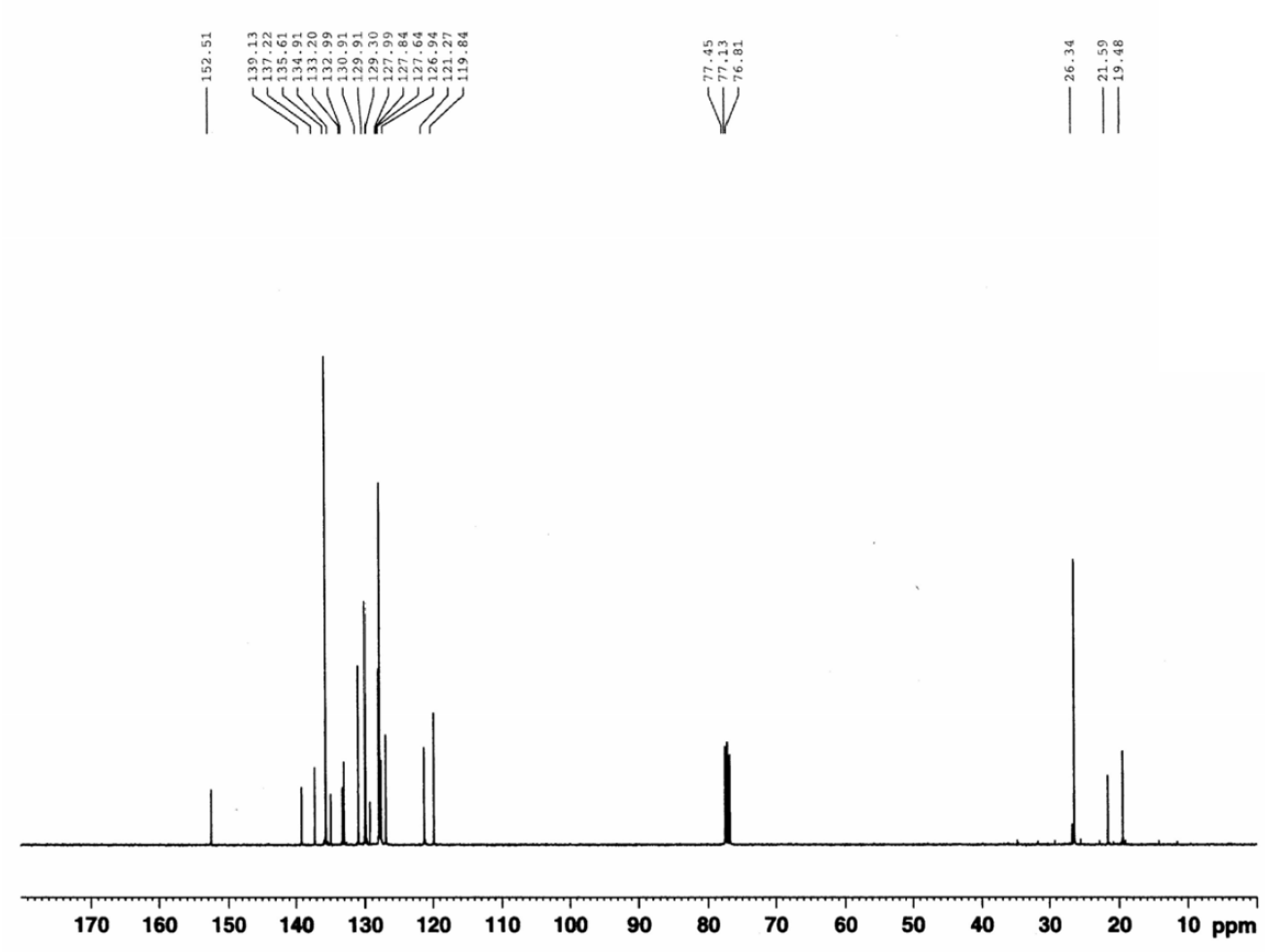
The general procedure for the synthesis of tethers affords, after flash chromatography on silica gel (5:95 ethyl acetate:hexane), the compound pictured (98%) as a colorless oil.

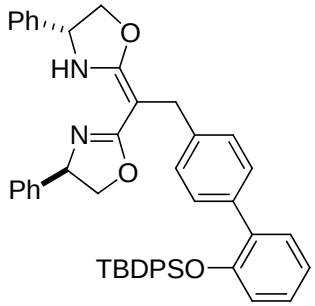
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.68-7.63 (4H, dd, *J* = 9.6, 1.9 Hz), 7.46-7.28 (10H, m), 7.18 (1H, d, *J* = 7.2 Hz), 6.96-6.88 (2H, m), 6.54-6.50 (1H, dd, *J* = 7.7, 1.5 Hz), 2.43 (3H, s), 0.88 ppm (9H, s);
^{13}C NMR (100 MHz, $CDCl_3$)	δ 152.5, 139.1, 137.2, 135.6, 134.9, 133.2, 133.0, 130.9, 129.9, 129.3, 128.0, 127.8, 127.6, 126.9, 121.3, 119.8, 26.3, 21.6, 19.5 ppm
HRMS (FABS)	calcd. for $C_{29}H_{30}OSiLi$ $[(M+Li)^+]$, 429.2226; found, 429.2217 *m/z*

^{1}H NMR of B(II)



^{13}C NMR of B(II)

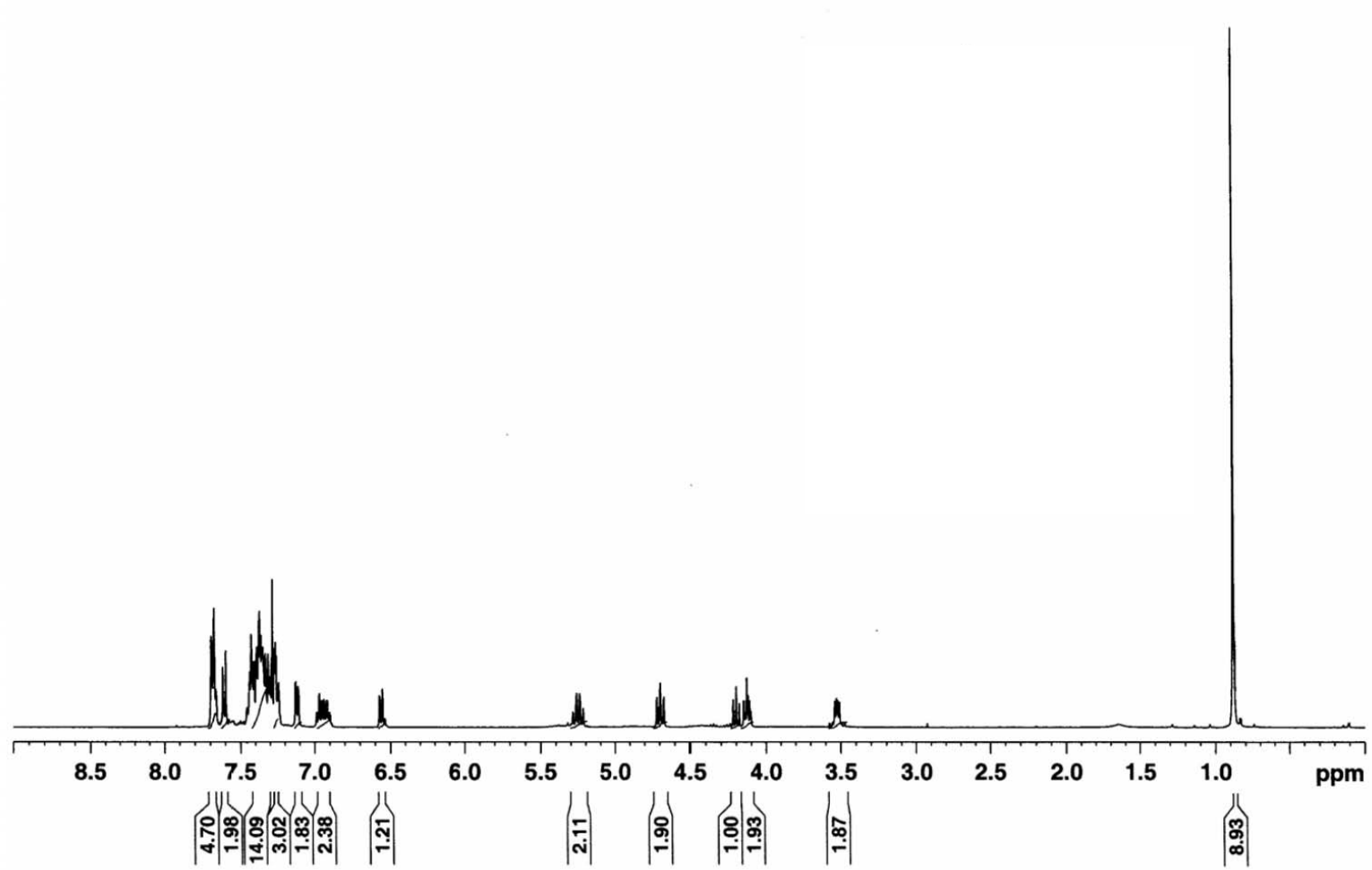




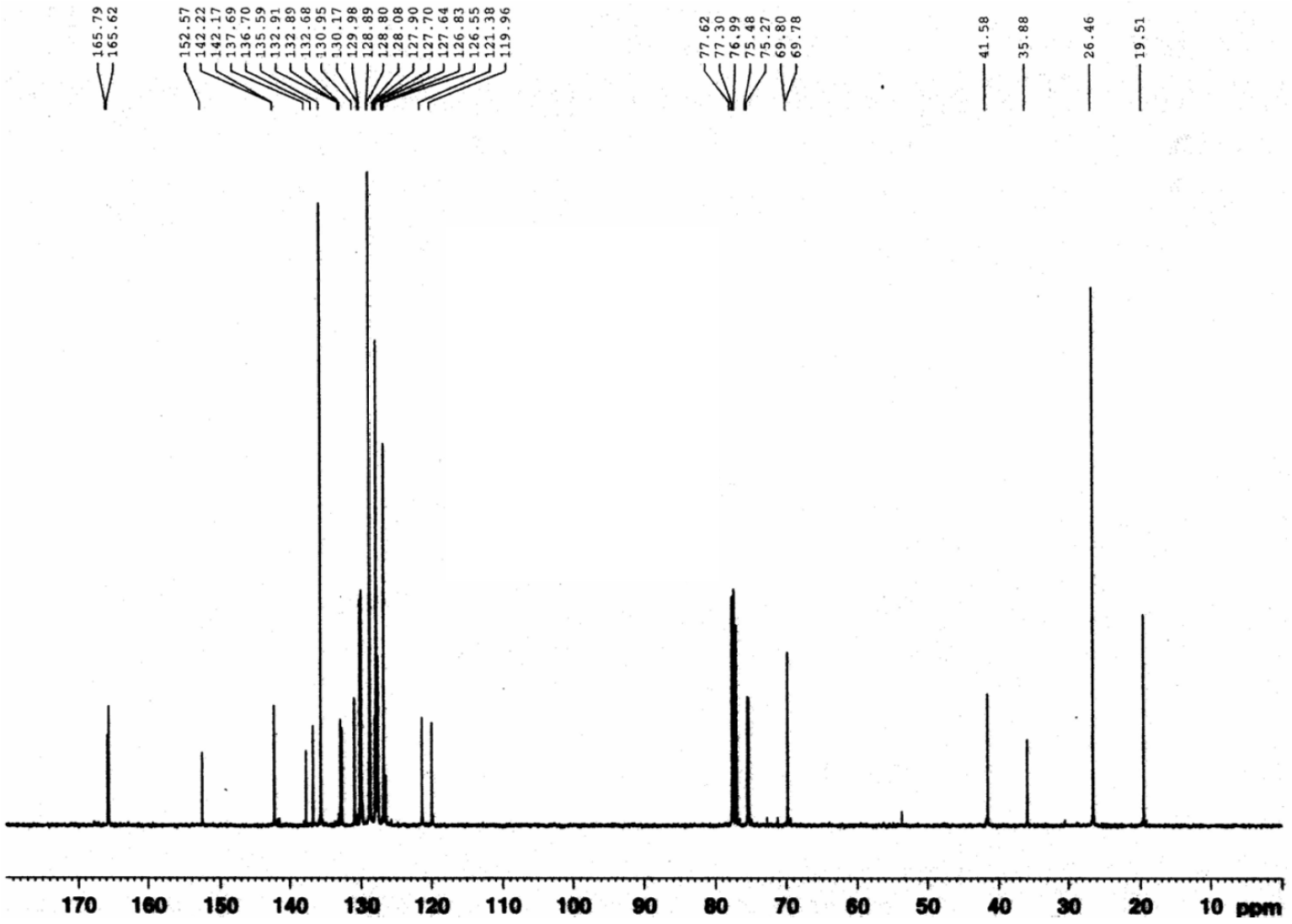
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (85%) as a white foamy solid.

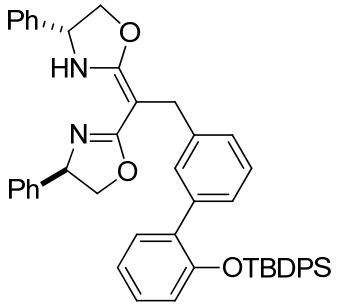
m.p.	84 - 85 °C
Optical rotation	$[\alpha]D^{25}$ = +28.0 (c = 1.1, CH_2Cl_2);
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.71-7.65 (5H, m), 7.63-7.58 (2H, m), 7.44-7.24 (14H, m), 7.13-7.11 (2H, dd, *J* = 8.1, 8.0 Hz), 6.97-6.87 (2H, m), 6.57-6.54 (1H, dd, *J* = 8.0, 7.9 Hz), 5.28 and 5.22 (2H, t, *J*= 10.0, 10.0 Hz), 4.71 and 4.68 (2H, dd, *J*= 10.4, 10.3 Hz), 4.25-4.18 (1H, dd, *J* = 8.1, 8.1 Hz), 4.17-4.10 (2H, m), 3.59-3.51 (2H, m), 0.88 ppm (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.8, 165.6, 152.6, 142.2, 142.2, 137.7, 136.7, 135.6, 132.91, 132.89, 132.7, 131.0, 130.2, 130.0, 128.9, 128.8, 128.1, 127.9, 127.7, 127.6, 126.8, 126.6, 121.4, 120.0, 75.5, 75.3, 69.80, 69.78, 41.6, 35.9, 26.5, 19.5 ppm
HRMS (FAB)	calcd. for $C_{48}H_{47}N_2O_3Si$ $[(M+H)^+]$, 727.3356; found, 727.3373 *m/z*

^{1}H NMR of ^{R}A(IV)



^{13}C NMR of ^{R}A(IV)

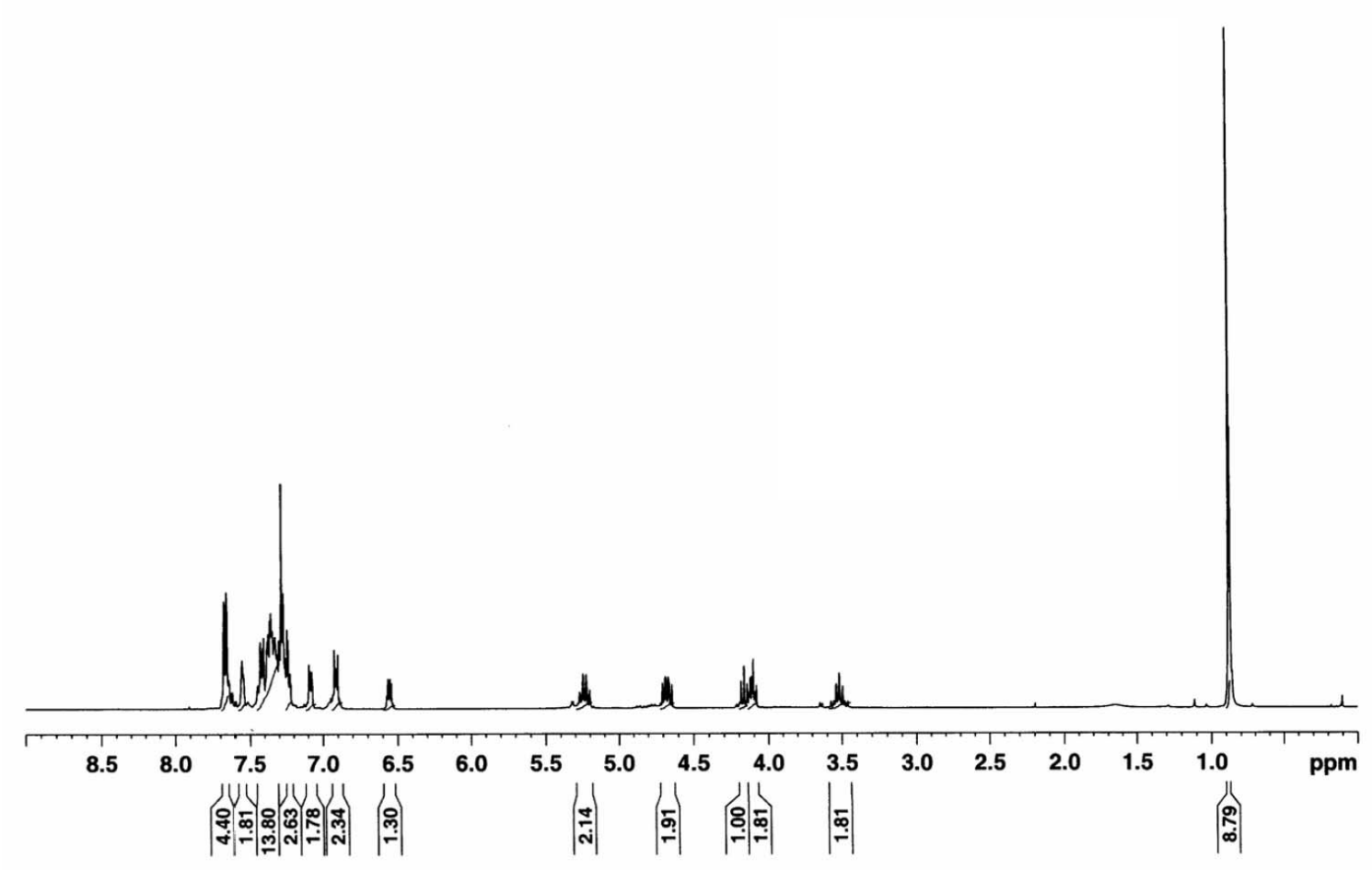




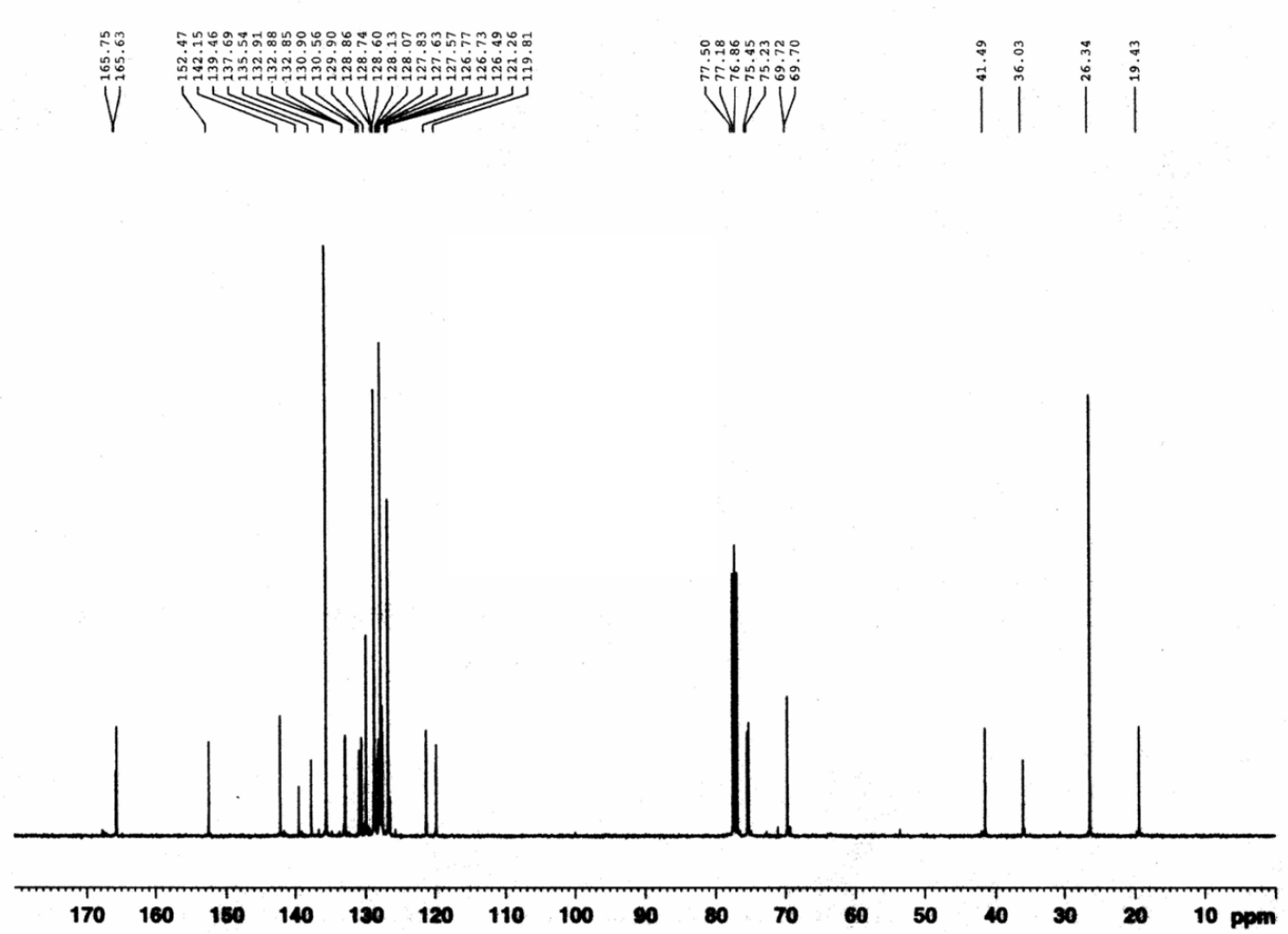
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (82%) as a white foamy solid.

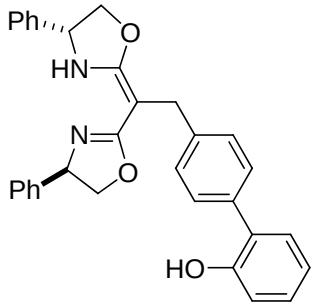
m.p.	89 - 90 °C
Optical rotation	[α]D ^{25} = +24.2 (c = 0.8, CH_2Cl_2);
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.56-7.54 (2H, m), 7.45-7.22 (17H, m), 7.09-7.07 (2H, dd, *J* = 7.9, 7.8 Hz), 6.92-6.90 (2H, m), 6.57-6.54 (2H, m), 5.28 and 5.20 (2H, t, *J*= 10.0, 10.0 Hz), 4.68 and 4.65 (2H, dd, *J*= 10.1, 10.1 Hz), 4.19-4.15 (1H, dd, *J* = 8.2, 8.1 Hz), 4.13-4.08 (2H, m), 3.57-3.46 (2H, m), 0.87 ppm (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.8, 165.6, 152.5, 142.2, 139.5, 137.7, 135.5, 132.91, 132.88, 132.85, 130.9, 130.6, 129.9, 128.9, 128.7, 128.6, 128.13, 128.07, 127.8, 127.63, 127.57, 126.8, 126.7, 126.5, 121.3, 119.8, 75.5, 75.2, 69.72, 69.70, 41.5, 36.0, 26.34, 19.4 ppm
HRMS (FAB)	calcd. for $C_{48}H_{47}N_2O3Si$ [$(M+H)^+$], 727.3356; found, 727.3349 *m/z*.

^{1}H NMR of ^{R}B(IV)



^{13}C NMR of ^{R}B(IV)

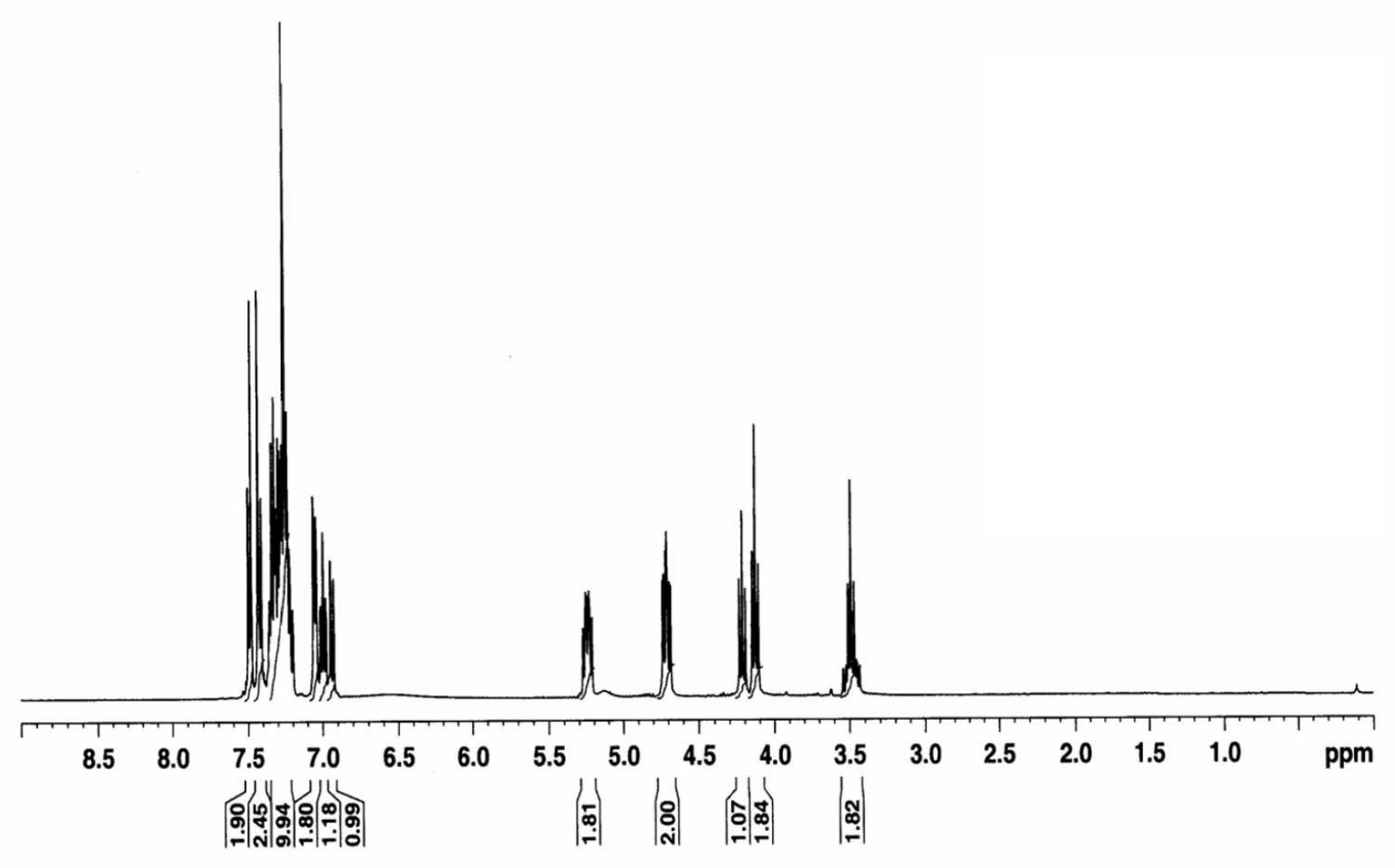




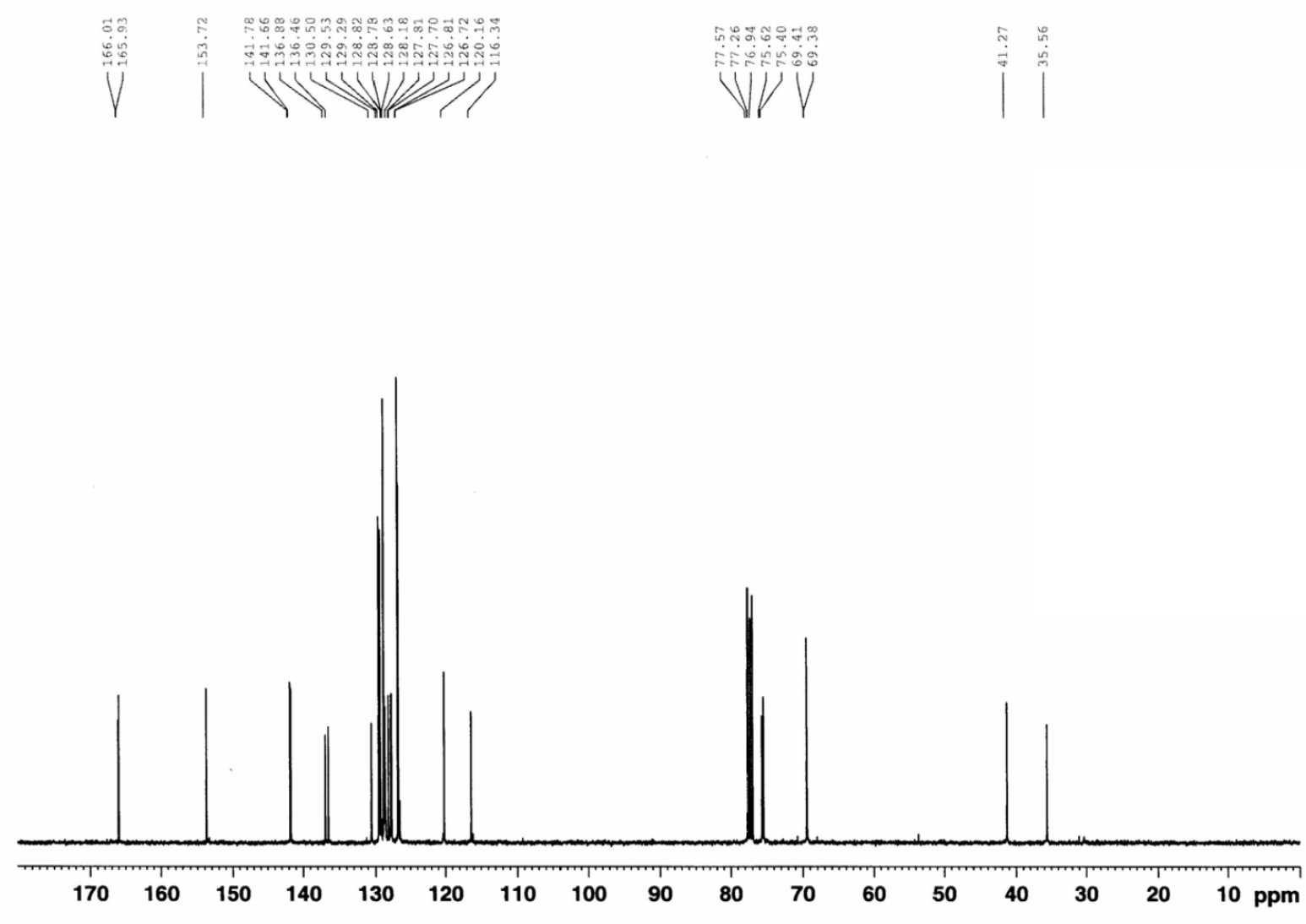
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (96%) as a white foamy solid.

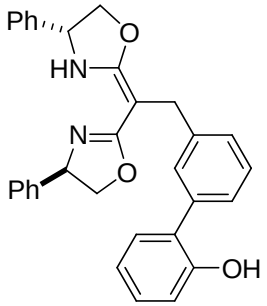
m.p.	120 - 122 °C
Optical rotation	$[\alpha]D^{25}$ = +18.7 (c = 0.7, CH_2Cl_2);
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.50-7.41 (4H, dd, *J* = 19.6, 8.1 Hz), 7.36-7.19 (10H, m), 7.06-7.03 (2H, dd, *J* = 7.8, 7.0 Hz), 7.03-6.98 (1H, dd, *J* = 8.6, 8.4 Hz), 6.95-6.92 (1H, d, *J* = 8.0 Hz), 5.27-5.21 (2H, m), 4.74 and 4.68 (2H, dd, *J* = 8.5, 8.3 Hz), 4.24-4.19 (2H, dd, *J* = 8.2, 8.1 Hz), 4.15-4.10 (1H, dd, *J* = 8.5, 8.5 Hz), 3.54-3.43 ppm (2H, m)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 166.0, 165.9, 153.7, 141.8, 141.7, 136.9, 136.5, 130.5, 129.5, 129.3, 128.82, 128.78, 128.6, 128.2, 127.8, 127.7, 126.8, 126.7, 120.2, 116.3, 75.6, 75.4, 69.41, 69.38, 41.3, 35.6 ppm
HRMS (FAB)	calcd. for $C_{32}H_{29}N_2O_3$ $[(M+H)^+]$, 489.2178; found, 489.2170 *m/z*

^{1}H NMR of ^{R}A(V)



^{13}C NMR of ^{R}A(V)

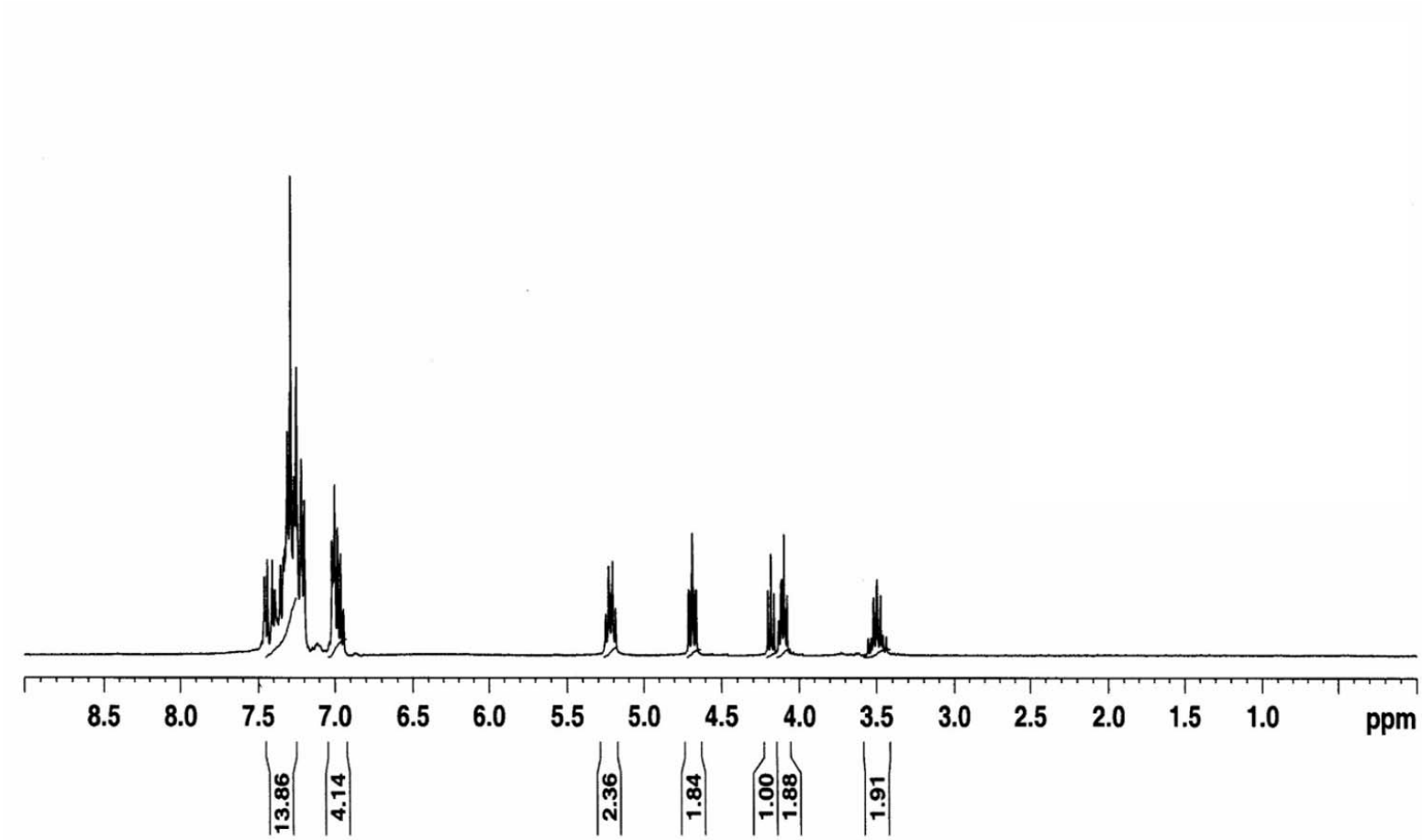




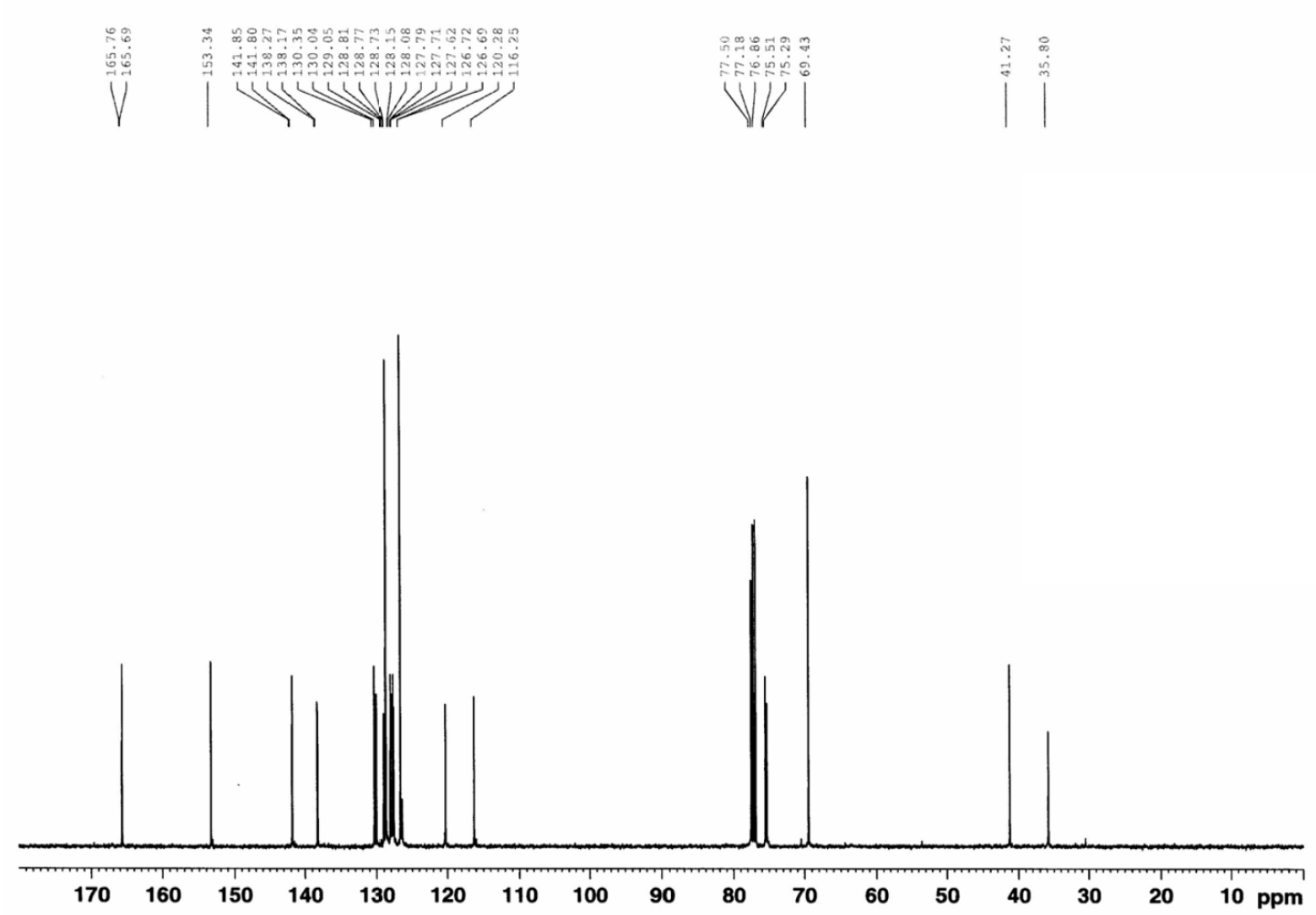
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (91%) as a white foamy solid.

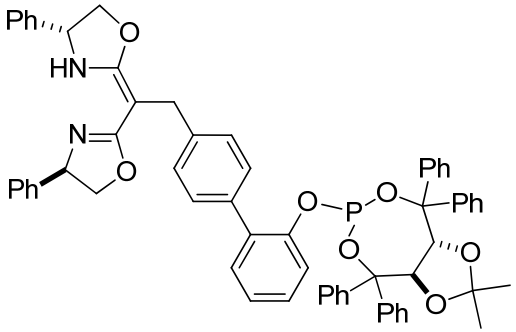
m.p.	124 - 126 °C
Optical rotation	$[\alpha]D^{25}$ = +18.8 (c = 0.6, CH_2Cl_2);
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.44-7.20 (14H, m), 7.02-6.96 (4H, m), 5.24 and 5.20 (2H, t, *J* = 10.8, 10.8 Hz), 4.71 and 4.66 (2H, dd, *J* = 8.5, 8.5 Hz), 4.21-4.17 (1H, dd, *J* = 8.2, 8.1 Hz), 4.14-4.07 (2H, m), 3.55-3.43 ppm (2H, m)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.8, 165.7, 153.3, 141.9, 141.8, 138.3, 138.2, 130.4, 130.0, 129.1, 128.81, 128.77, 128.71, 128.2, 128.1, 127.8, 127.7, 127.6, 126.72, 126.69, 120.3, 116.3, 75.5, 75.3, 69.4, 41.3, 35.8 ppm
HRMS (FAB)	calcd. for $C_{32}H_{29}N_2O_3$ $[(M+H)^+]$, 489.2178; found, 489.2180 *m/z*.

^{1}H NMR of ^{R}B(V)



^{13}C NMR of ^{R}B(V)

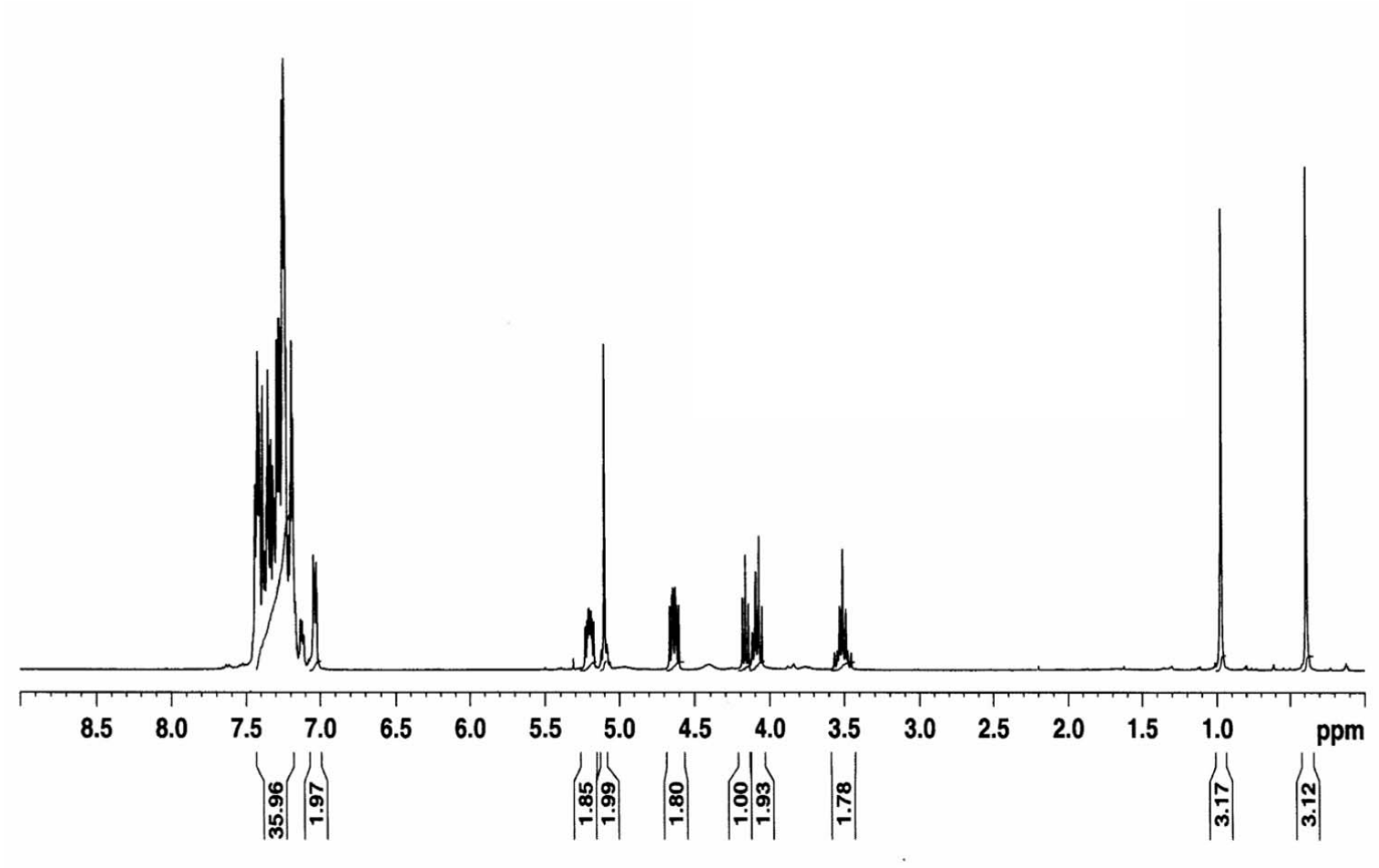




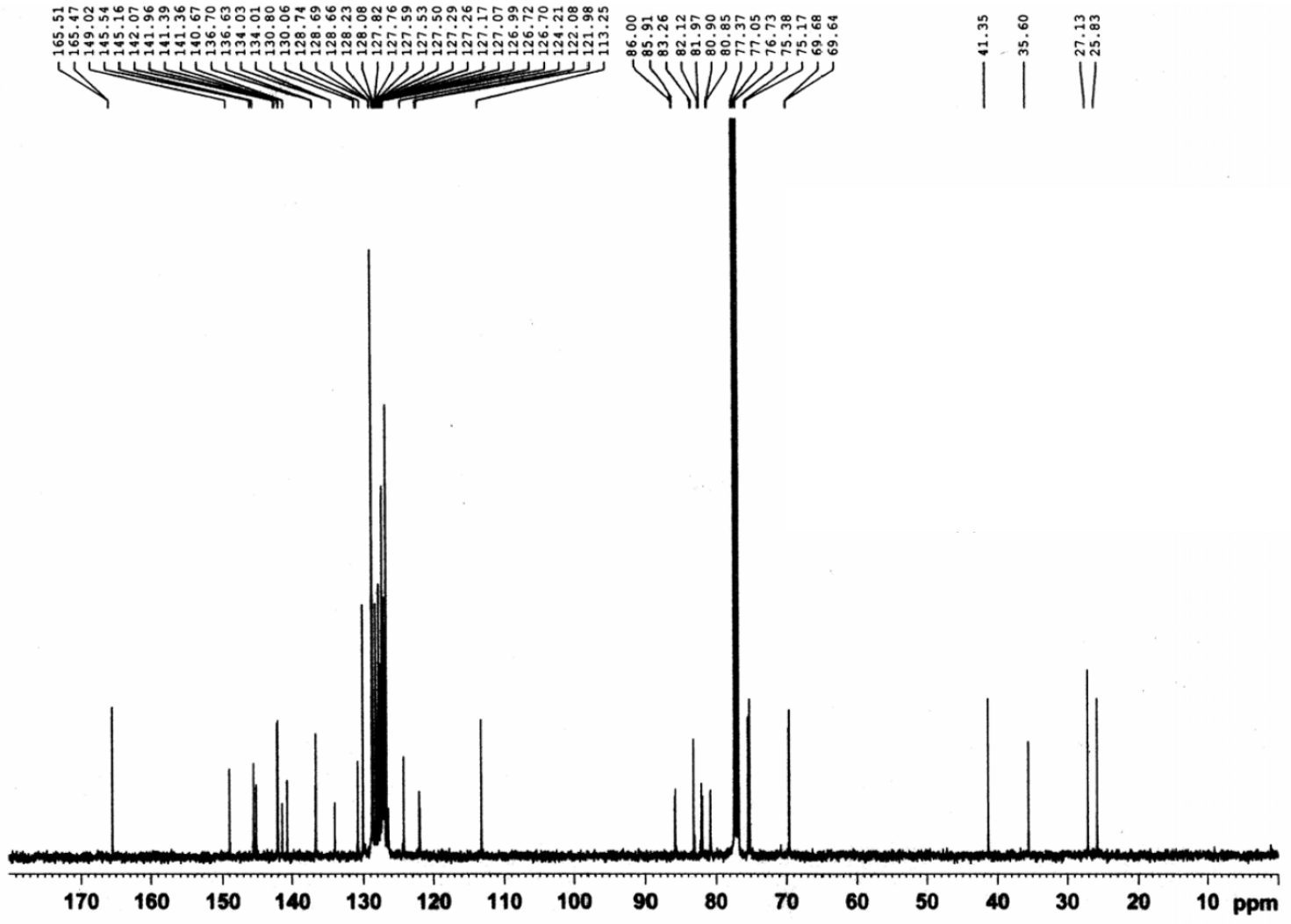
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (77%) as a white foamy solid.

m.p.	138 - 139 °C
Optical rotation	$[\alpha]D^{25}$ = -158.0 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.44-7.12 (36H, m), 7.04-7.02 (2H, m), 5.23-5.18 (2H, m), 5.10 (2H, s), 4.66-4.60 (2H, m), 4.19-4.15 (1H, dd, *J* = 8.2, 8.2 Hz), 4.12-4.05 (2H, m), 3.57-3.45 (2H, m), 0.98 (3H, s), 0.39 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.5, 165.47, 149.0, 145.5, 145.2, 142.1, 142.0, 141.39, 141.36, 140.7, 136.7, 136.6, 134.03, 134.01, 130.8, 130.1, 128.7, 128.69, 128.66, 128.2, 128.1, 127.8, 127.76, 127.6, 127.53, 127.50, 127.29, 127.26, 127.17, 127.07 126.99, 126.72, 126.70, 124.2, 122.1, 122.0, 113.2, 86.0 (d, *J*CP = 8.9 Hz), 83.3, 82.1 (d, *J*CP = 14.5 Hz), 80.9 (d, *J*CP = 4.5 Hz), 75.4, 75.2, 69.7, 69.6, 41.4, 35.6, 27.1, 25.8 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 134.9 ppm
HRMS (FAB)	calcd. for $C_{63}H_{56}N_2O_7P$ $[(M+H)^+]$, 983.3825; found, 983.3840 *m/z*.

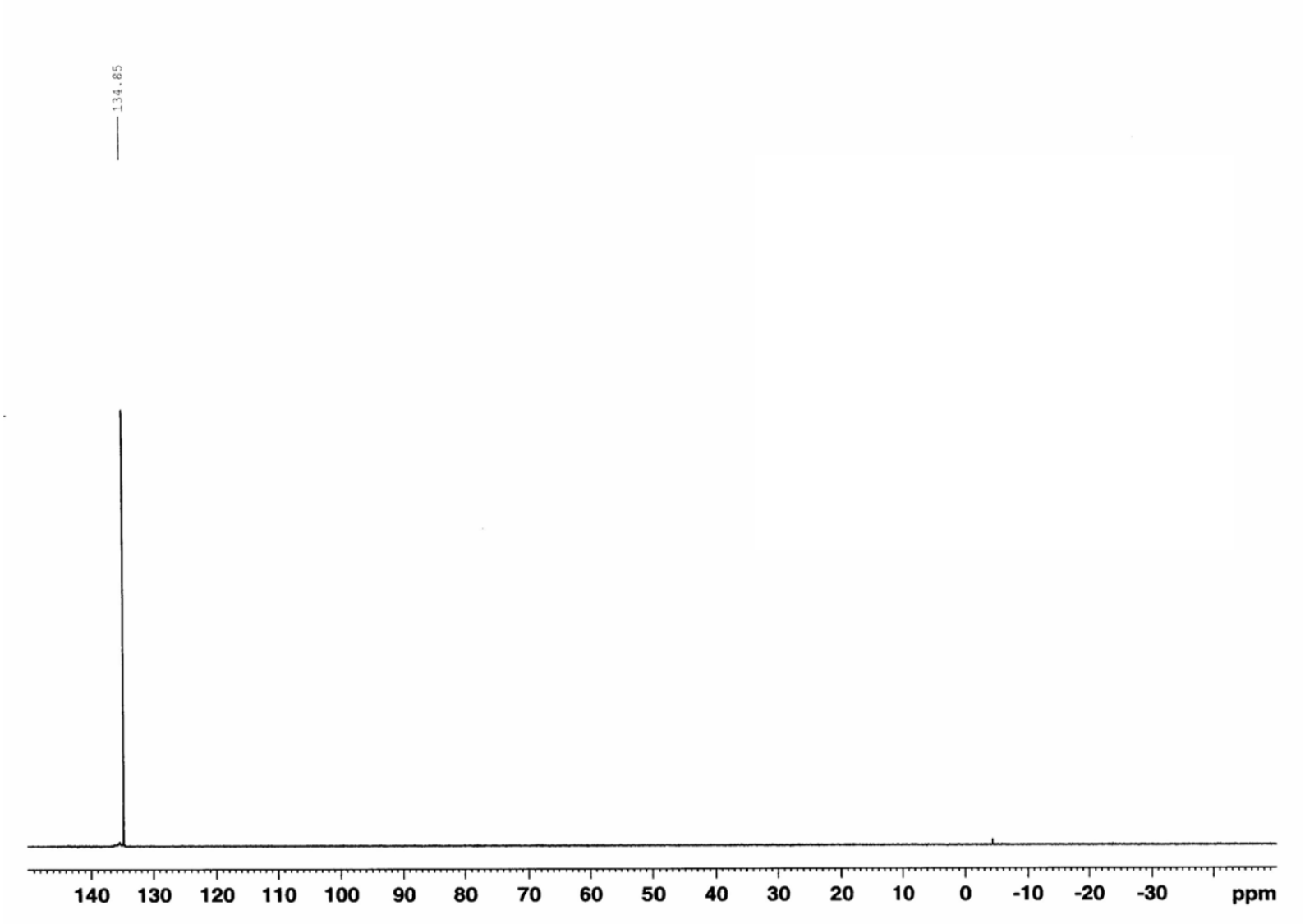
^{1}H NMR of ^{R}Aa

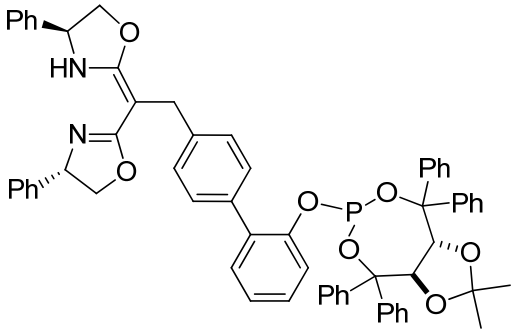


^{13}C NMR of ^{R}Aa



^{31}P NMR of ^{R}Aa

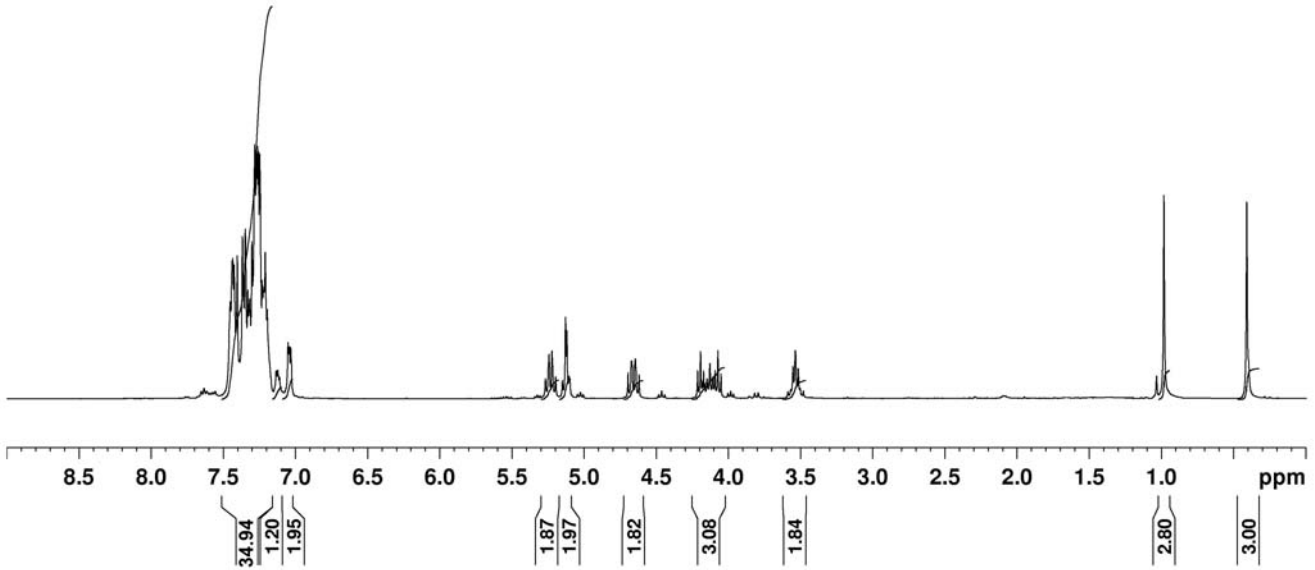




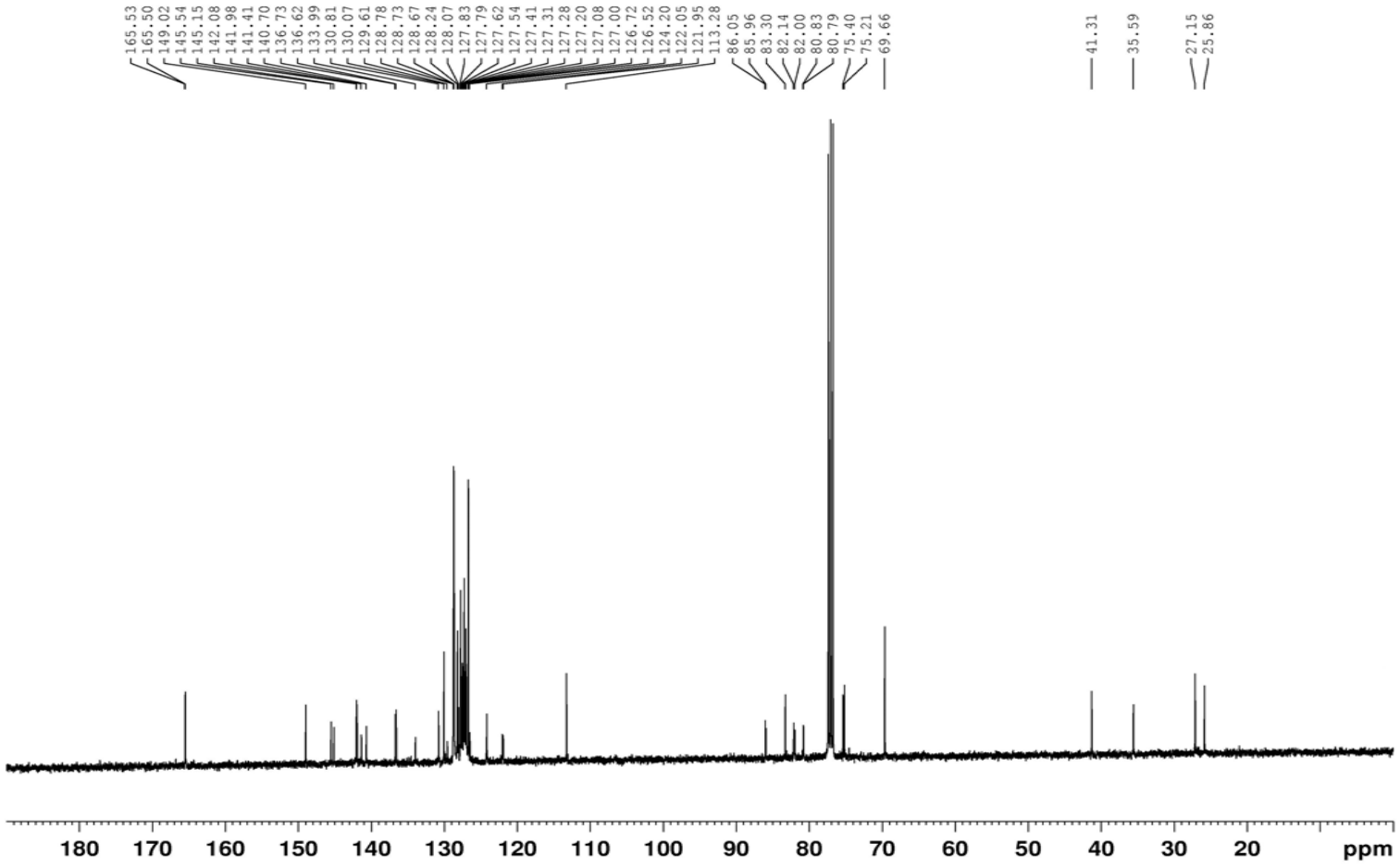
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (77%) as a white foamy solid.

m.p.	139 - 140 °C
Optical rotation	$[\alpha]D^{25}$ = -158.0 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.45-7.21 (35H, m), 7.20 (1H, m), 7.05-7.03 (2H, m), 5.24-5.22 (2H, m), 5.13-5.12 (2H, m), 4.68-4.64 (2H, m), 4.19-4.07 (3H, m), 3.55-3.54 (2H, m), 0.98 (3H, s), 0.408 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.53, 165.50, 149.02, 145.54, 145.15, 142.08, 141.98, 141.41, 140.70, 136.73, 136.62, 133.99, 130.81, 130.07, 129.61, 128.78, 128.73, 128.67, 128.24, 128.07, 127.83, 127.79, 127.62, 127.54, 127.41, 127.31, 127.28, 127.20, 127.08, 127.00, 126.72, 126.52, 124.20, 121.95, 113.28, 86.05, 85.96, 83.30, 82.14, 82.00, 80.83, 80.79, 75.40, 75.21, 69.66, 41.31, 35.59, 27.15, 25.86 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 134.7 ppm
HRMS (ESI)	calcd. for $C_{63}H_{55}N_2O_7P$ $[(M+Na)^+]$, 1005.3747; found, 1005.3635 *m/z*.

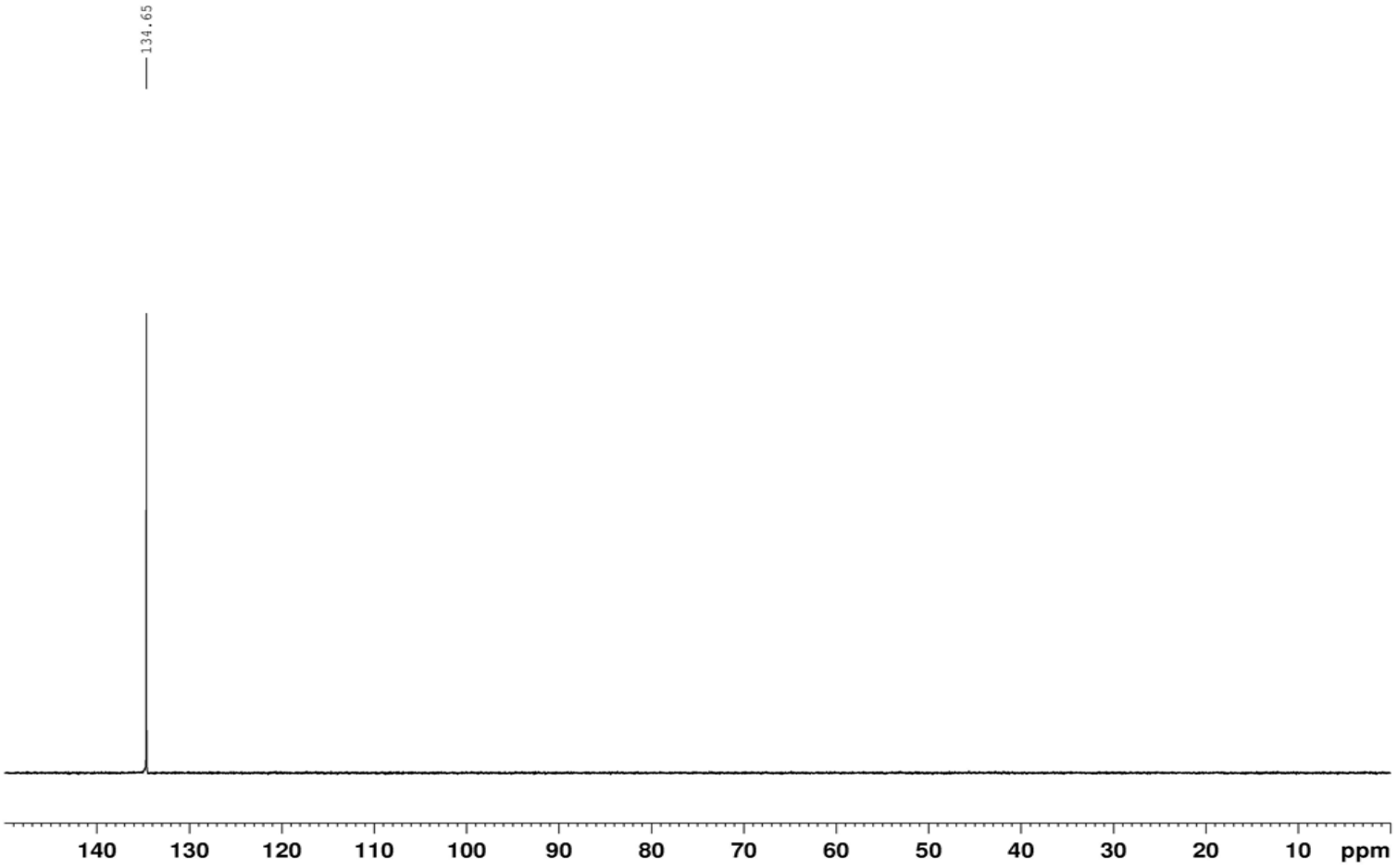
^{1}H NMR of ^{S}Aa

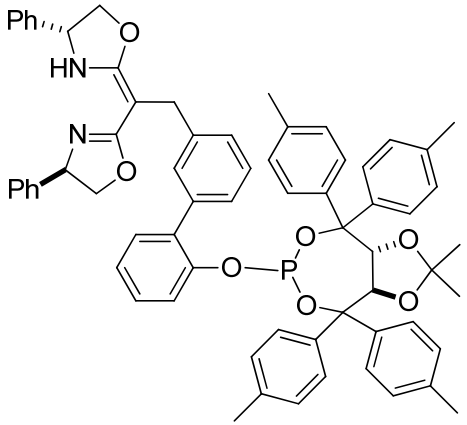


^{13}C NMR of ^{S}Aa



^{31}P NMR of ^{S}Aa

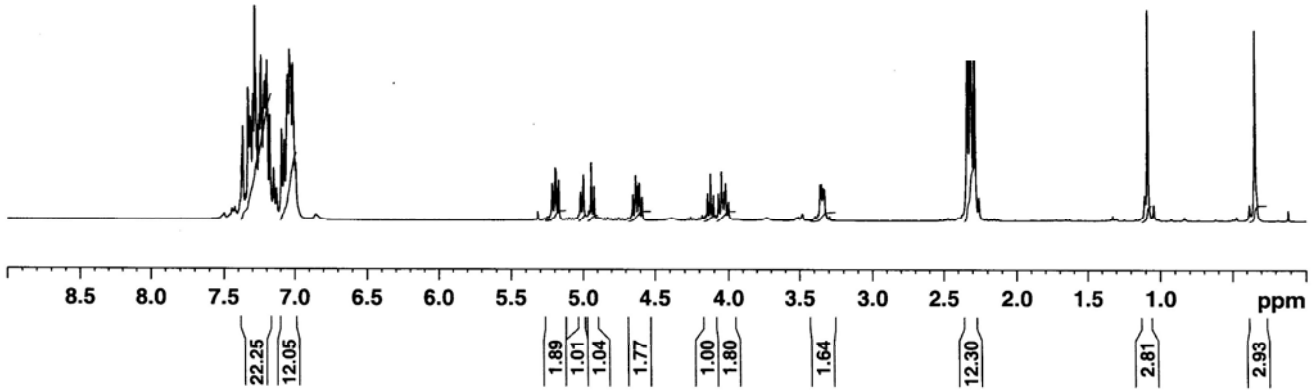




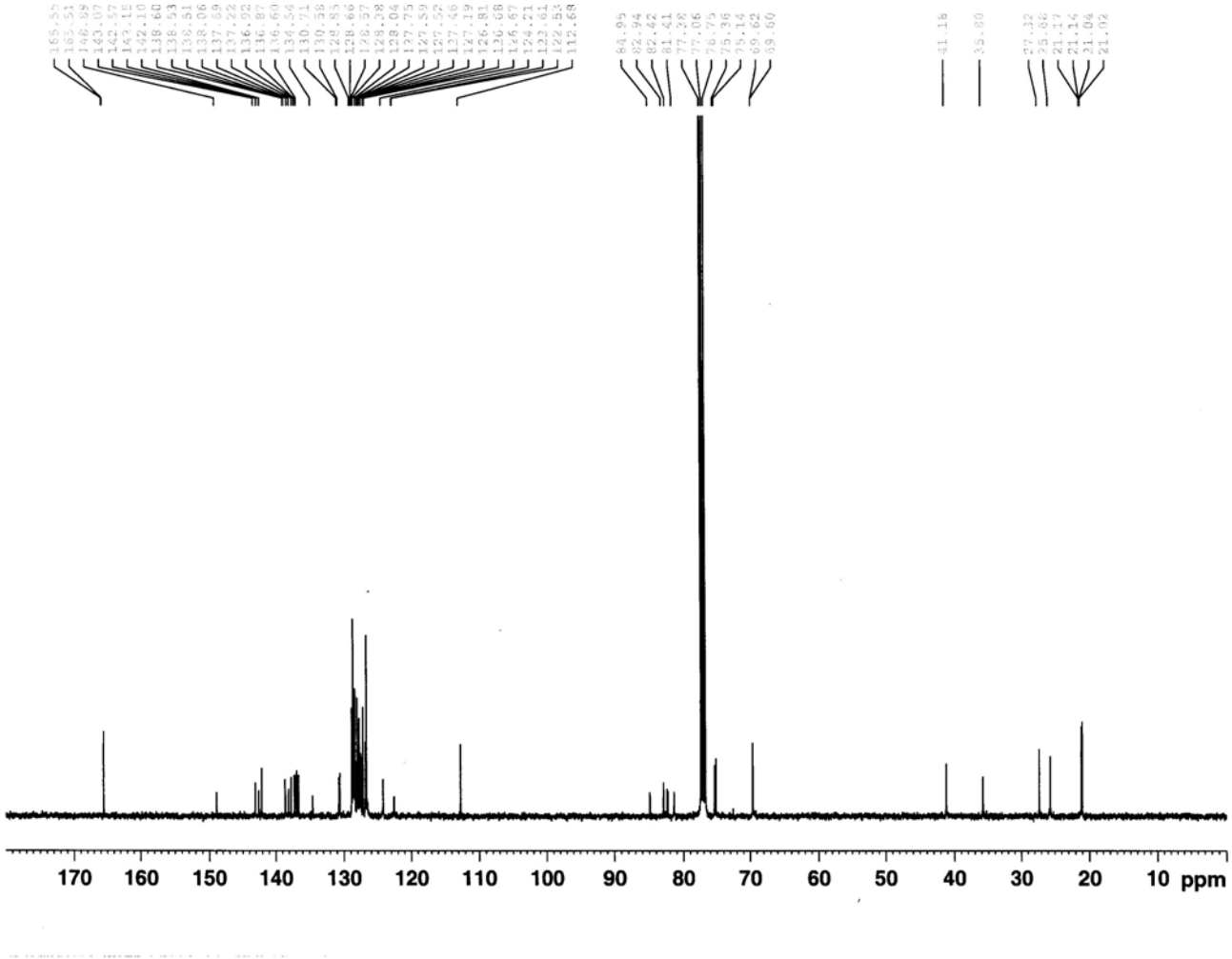
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (78%) as a white foamy solid.

m.p.	126 - 130 °C
Optical rotation	$[\alpha]D^{25}$ = -118.2 (c = 0.4, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.39-7.17 (22H, m), 7.09-7.00 (12H, m), 5.20-5.18 (2H, m), 5.00 (1H, d, *J* = 7.8 Hz), 4.91 (1H, d, *J* = 8.2 Hz), 4.63-4.60 (2H, m), 4.14-4.12 (1H, dd, *J* = 8.3, 8.3 Hz), 4.04-4.00 (2H, m), 3.36-3.34 (2H, m), 2.34-2.28 (12H, m) 1.10 (3H, s), 0.34 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.54, 165.51, 148.87, 148.85, 143.1, 142.5, 142.2, 142.1, 138.6, 138.5, 138.4, 138.0, 137.7, 137.2, 136.9, 136.6, 134.63, 134.60, 130.7,130.6, 128.8, 128.7, 128.6, 128.4, 128.1, 127.8, 127.6, 127.52, 127.46, 127.22, 126.8, 126.7, 124.3, 122.73, 122.66, 112.6 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 135.3 ppm
HRMS (FAB)	calcd. for $C_{67}H_{63}N_2O_7P$ $[(M+H)^+]$, 1039.2001; found, 1039.4435 *m/z*

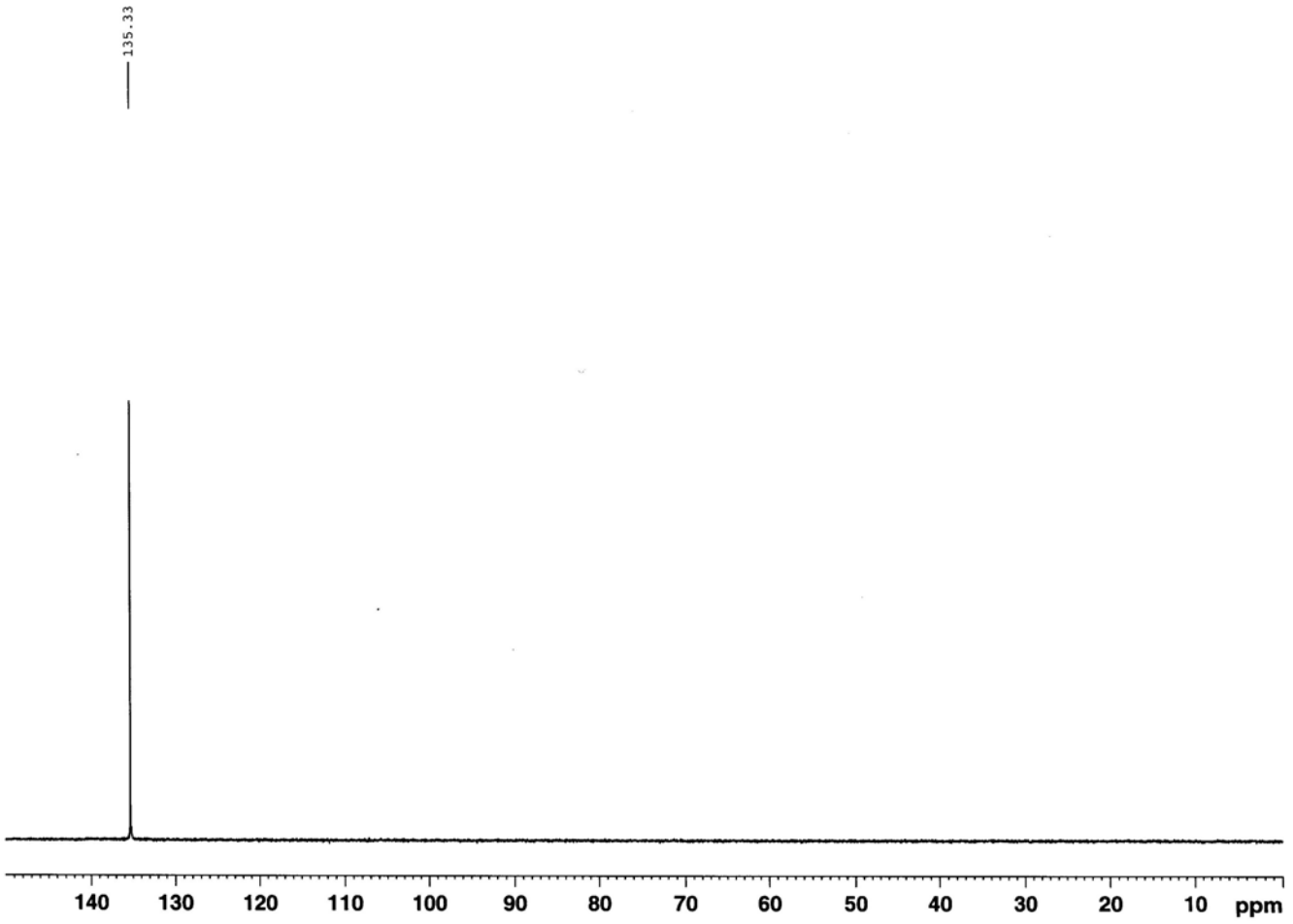
^{1}H NMR of ^{R}Bb

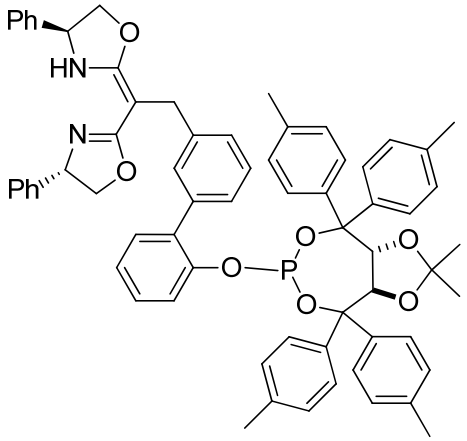


^{13}C NMR of ^{R}Bb



^{31}P NMR of ^{R}Bb

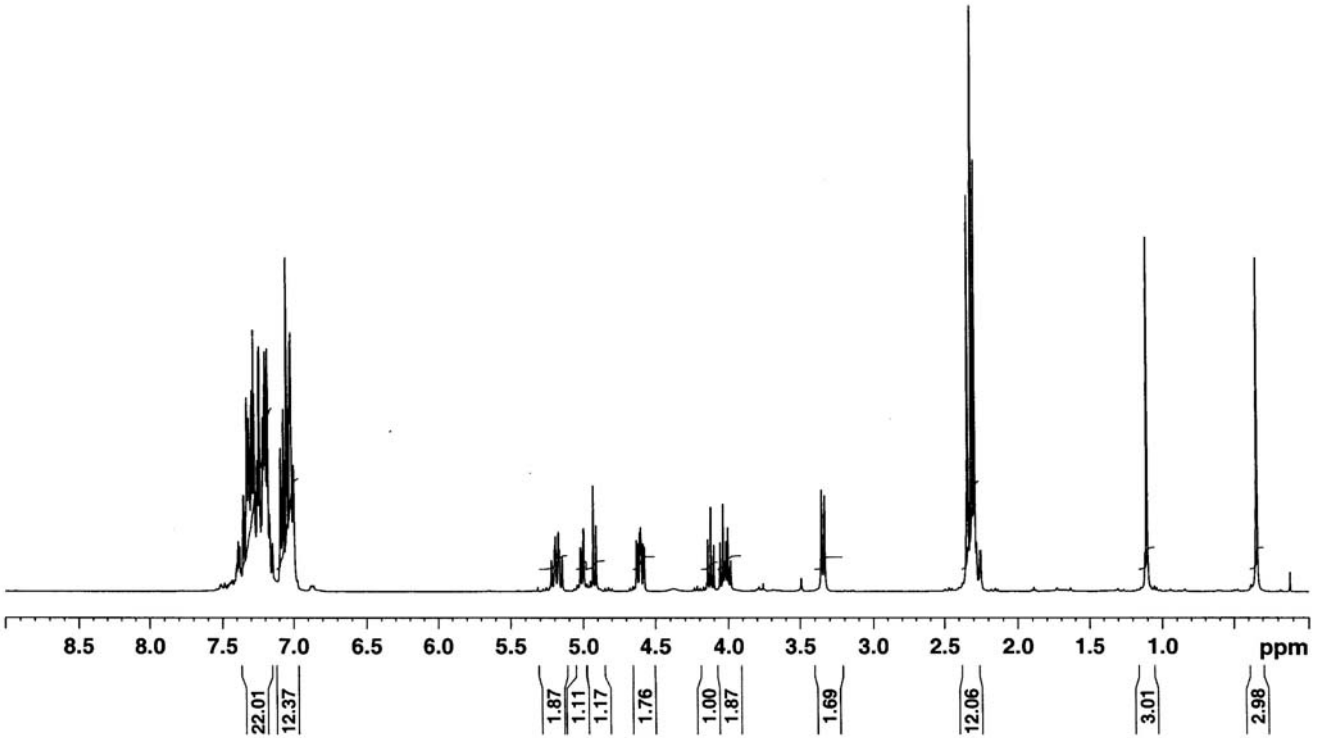




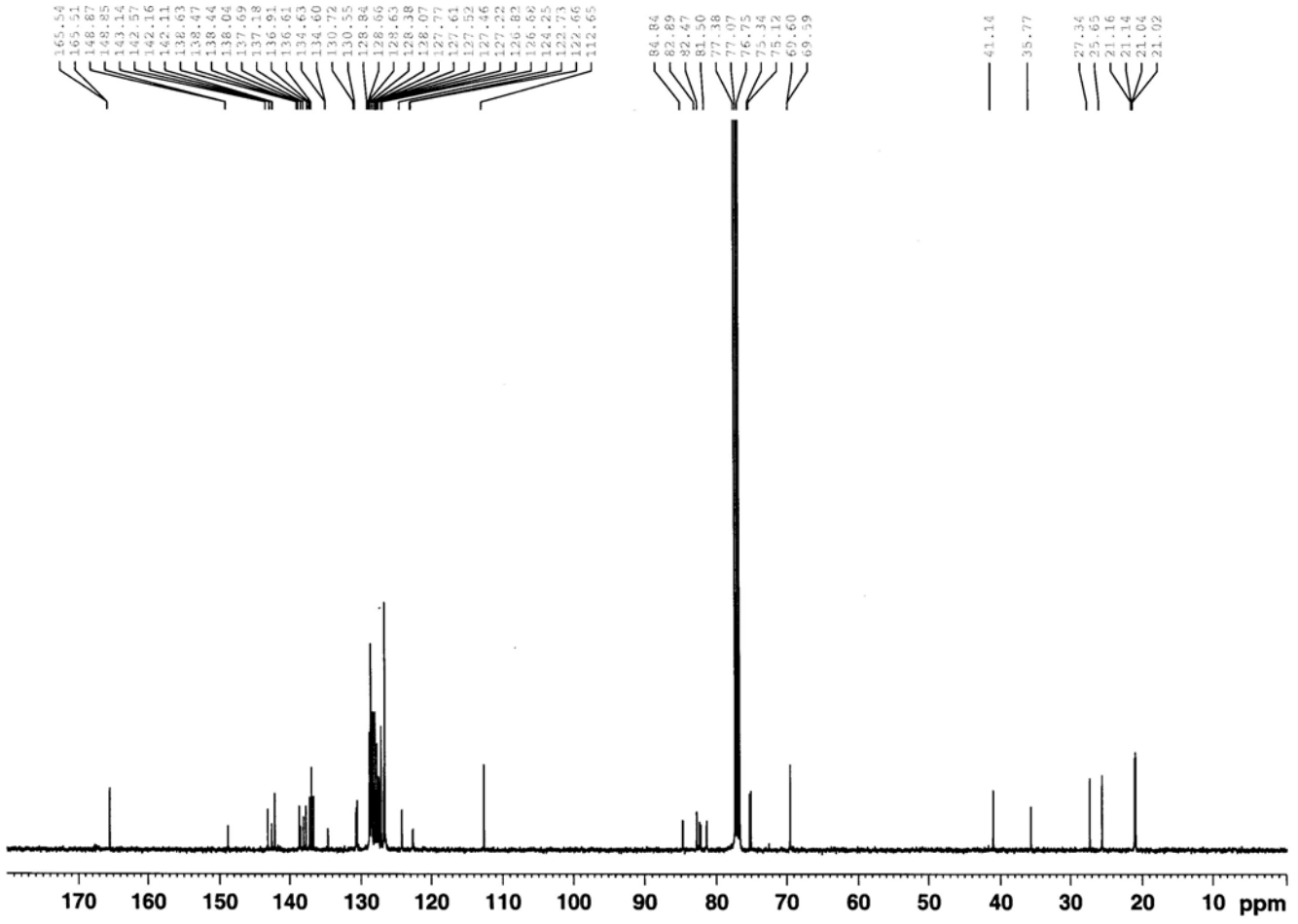
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (81%) as a white foamy solid.

m.p.	126 - 129 °C
Optical rotation	$[\alpha]D^{25}$ = -103.5 (c = 0.4, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ7.37-7.13 (22H, m), 7.09-6.99 (12H, m), 5.22-5.17 (2H, m), 4.98 (1H, d, *J* = 7.8 Hz), 4.90 (1H, d, *J* = 8.2 Hz), 4.63-4.61 (2H, m), 4.13-4.10 (1H, dd, *J* = 8.3, 8.3 Hz), 4.05-4.03 (2H, m), 3.36-3.33 (2H, m), 2.34-2.29 (12H, m) 1.08 (3H, s), 0.34 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.55, 165.51, 148.9 (2C), 143.1, 142.6, 142.2, 142.1, 138.6, 138.53, 138.51, 138.1, 137.7, 137.2, 136.9, 136.6, 134.5, 130.7,130.6, 128.9, 128.7, 128.6, 128.4, 128.1, 127.8, 127.6, 127.52, 127.46, 127.2, 126.8, 126.68, 127.67, 124.2, 122.6, 122.5, 112.67, 85.0 (d, *J*CP = 8.8 Hz), 82.9, 82.4 (d, *J*CP = 14.3 Hz), 81.4 (d, *J*CP = 4.4 Hz), 75.4, 75.1, 69.62, 69.60, 41.2, 35.8, 27.3, 25.7, 21.17, 21.14, 21.04, 21.02 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 135.3 ppm
HRMS (FAB)	calcd. for $C_{67}H_{63}N_2O_7P$ $[(M+H)^+]$, 1039.2001; found, 1039.4435 *m/z*

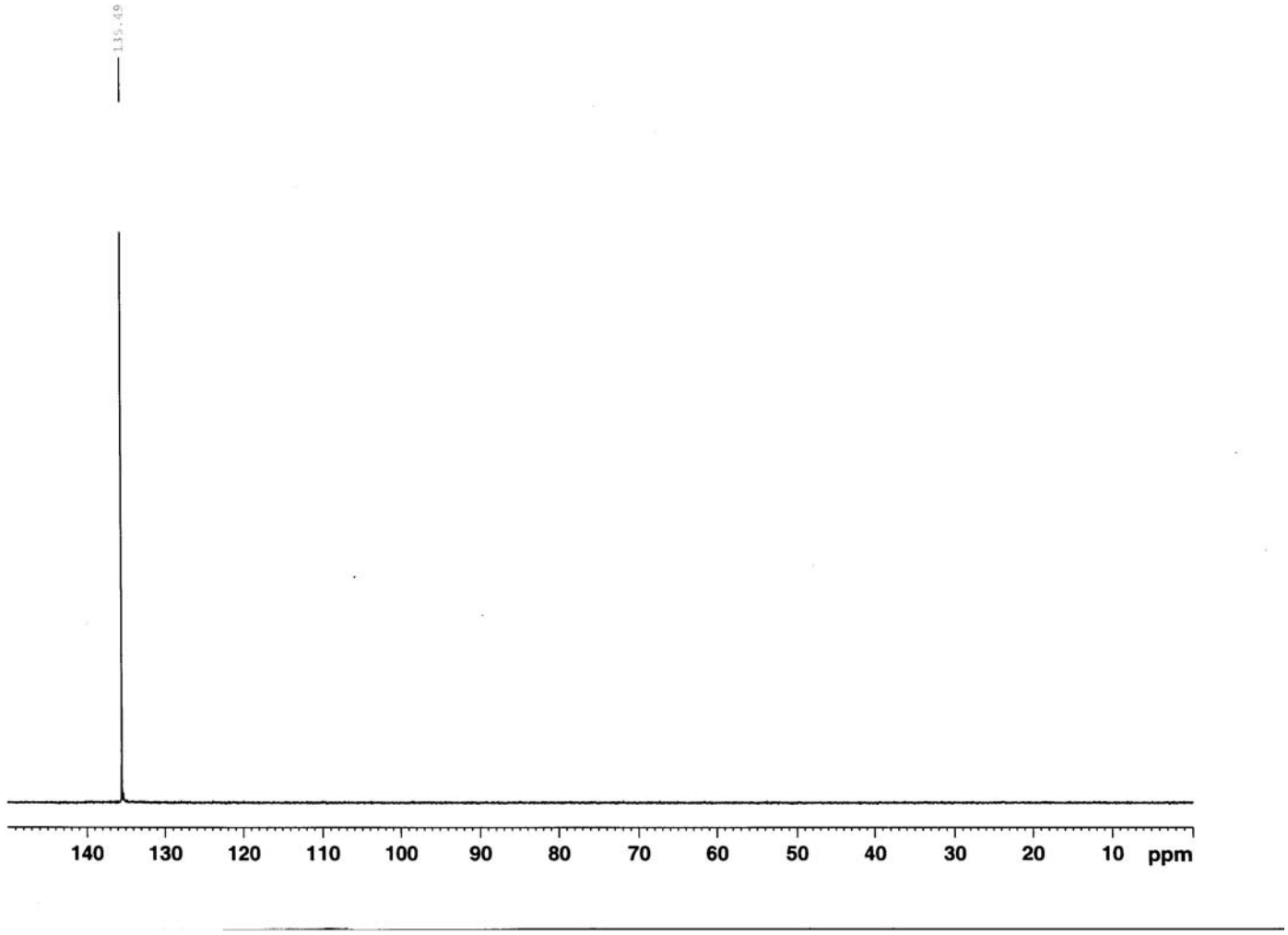
^{1}H NMR of ^{S}Bc

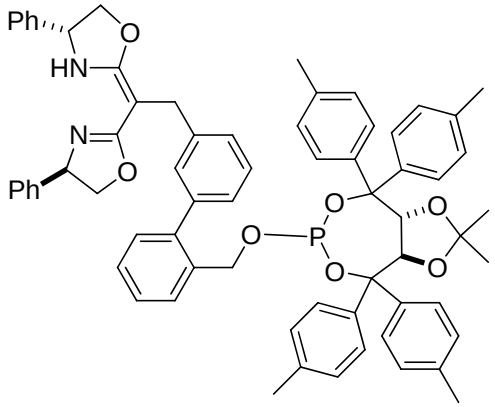


^{13}C NMR of ^{S}Bc



^{31}P NMR of ^{S}Bc

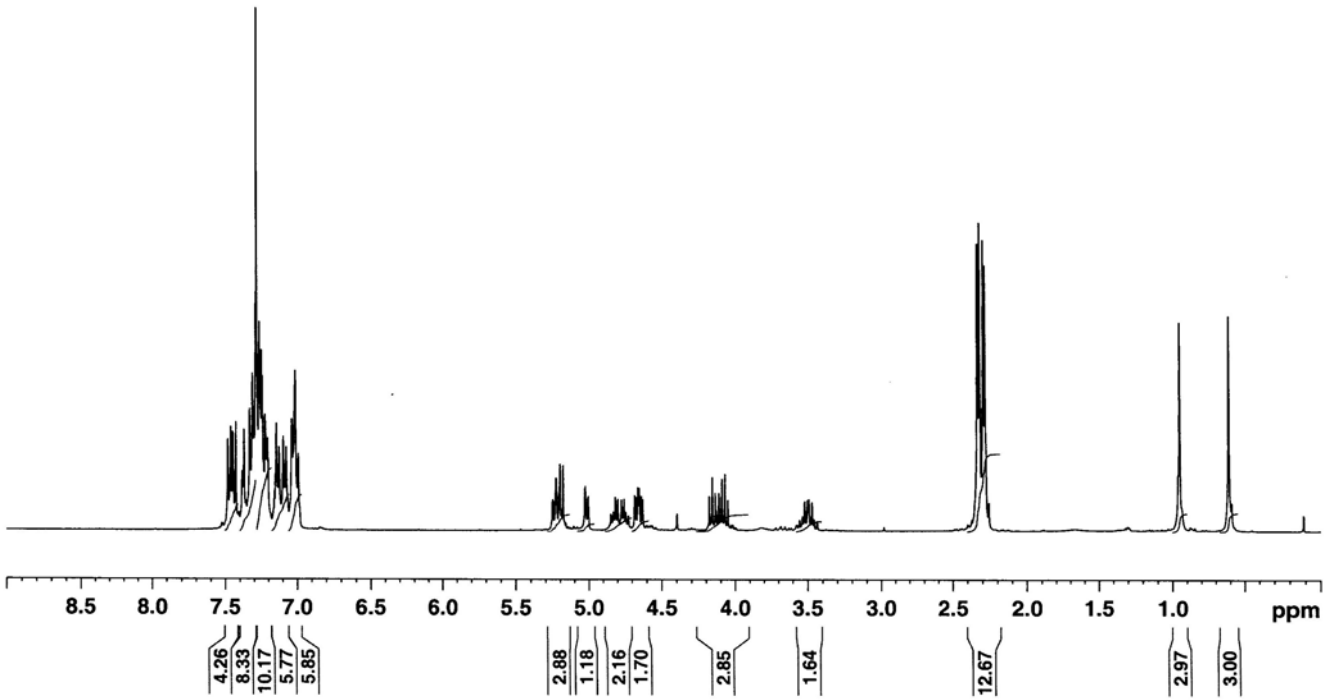




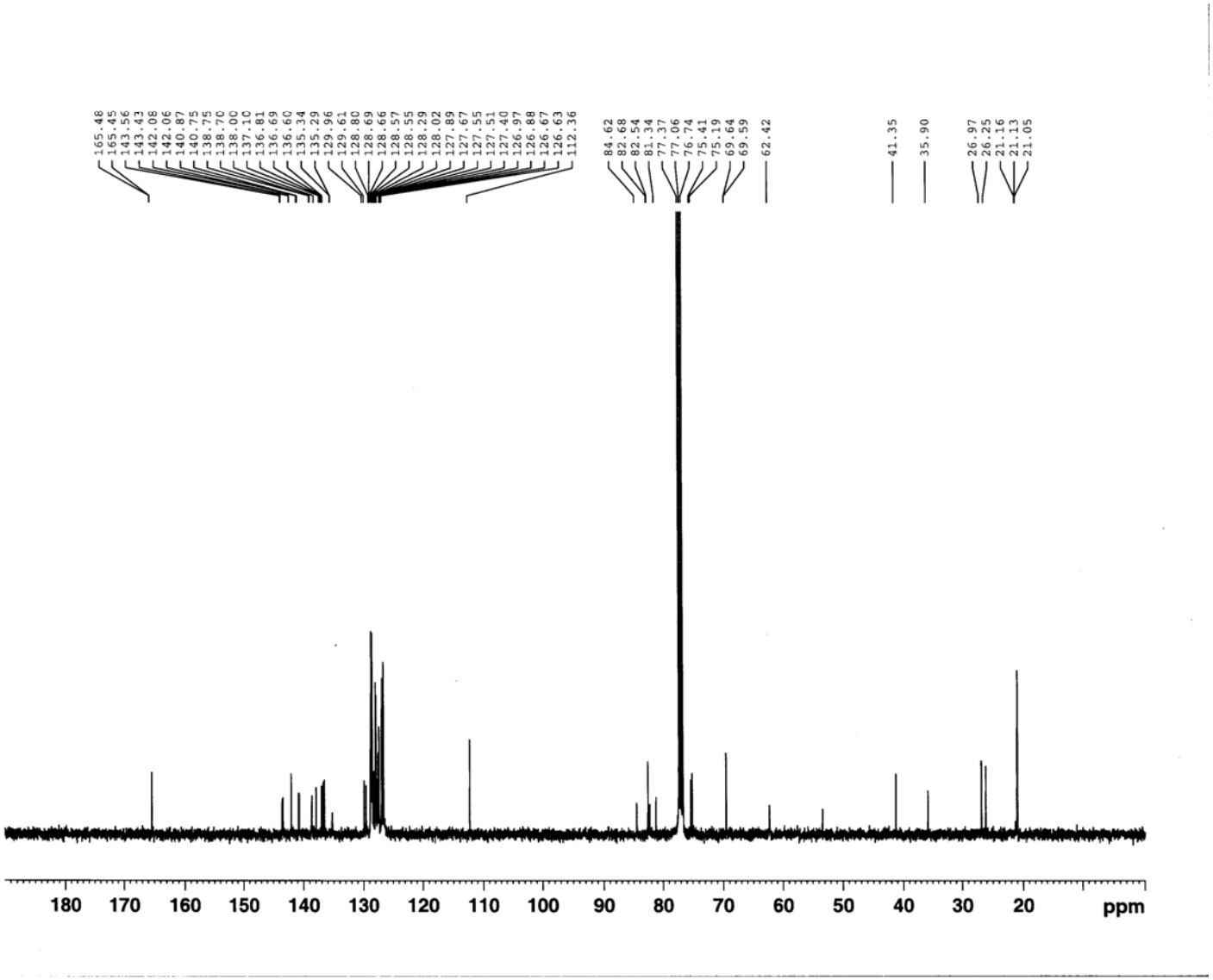
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (82%) as a white foamy solid.

m.p.	133 - 136 °C
Optical rotation	$[\alpha]D^{25}$ = -118.0 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.48-7.43 (4H, m), 7.39-7.20 (18H, m), 7.15-7.13 (6H, m), 7.10-6.99 (6H, m), 5.32-5.19 (3H, m), 5.03 (1H, d, *J* = 8.2 Hz), 4.91-4.75 (2H, m), 4.66-4.65 (2H, m), 4.16-4.07 (3H, m), 3.53-3.47 (2H, m), 2.33 (3H, s), 2.32 (3H, s), 2.29 (3H, s), 2.28 (3H, s), 0.96 (3H, s), 0.61 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.51, 165.48, 149.1, 143.0, 142.5, 142.1, 142.0, 138.6, 138.5, 138.0, 137.3, 136.90, 136.86, 136.72, 136.6, 136.5, 130.7,130.1, 128.8, 128.70, 128.64, 128.55, 128.37, 128.0, 127.8, 127.6, 127.5, 127.1, 126.9, 126.7, 124.2, 122.4, 122.3, 112.8, 85.3 (d, *J*CP = 8.8 Hz), 83.0, 82.3 (d, *J*CP = 14.3 Hz), 81.2 (d, *J*CP = 4.4 Hz), 75.4, 75.2, 69.7, 69.6, 41.3, 35.6, 27.3, 25.8, 21.16, 21.12, 21.01 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 131.5 ppm
HRMS (FAB)	calcd. for $C_{68}H_{65}N_2O_7P$ $[(M+H)^+]$, 1053.2267; found, 1053.4563 *m/z*

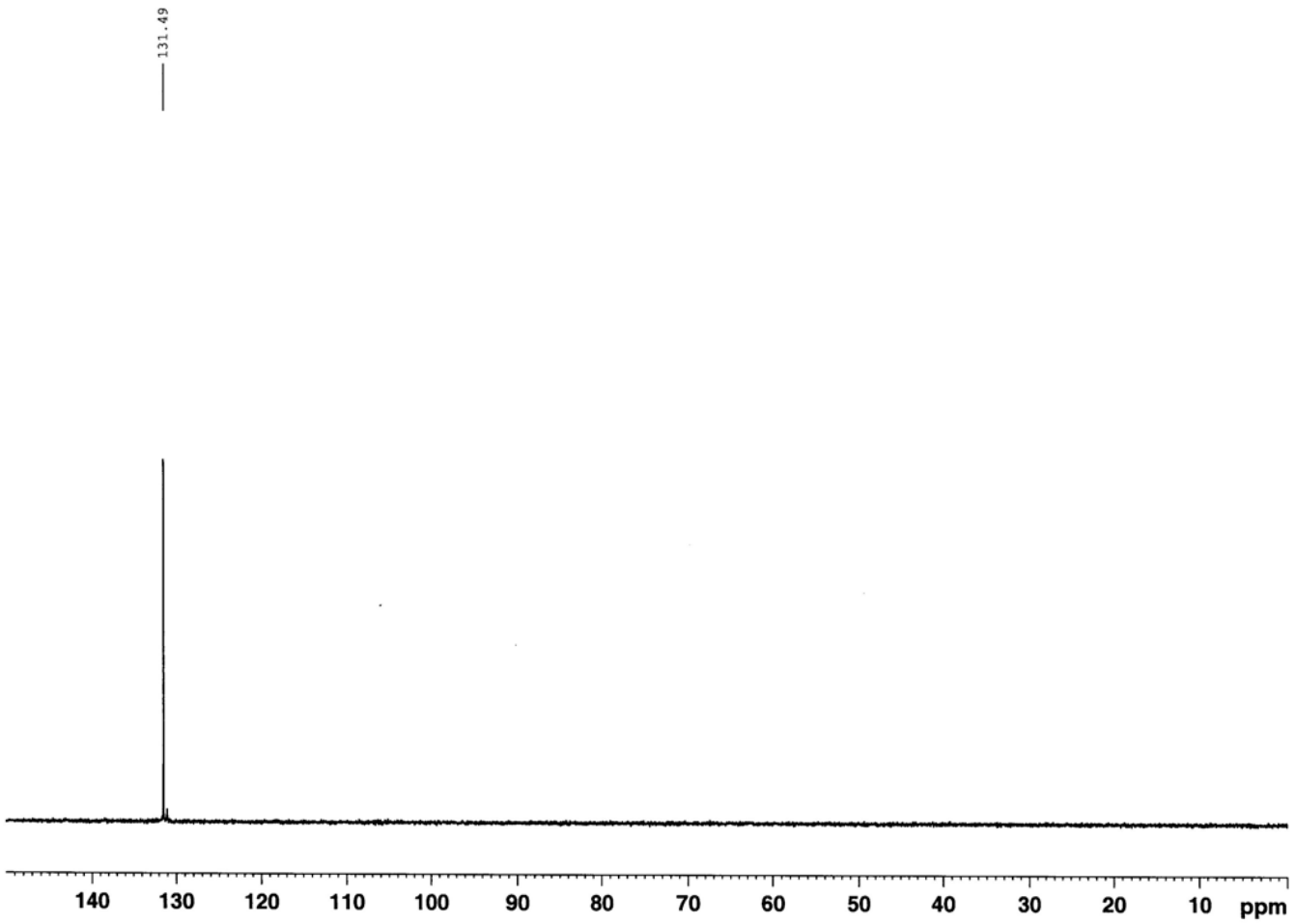
^{1}H NMR of ^{R}Cc

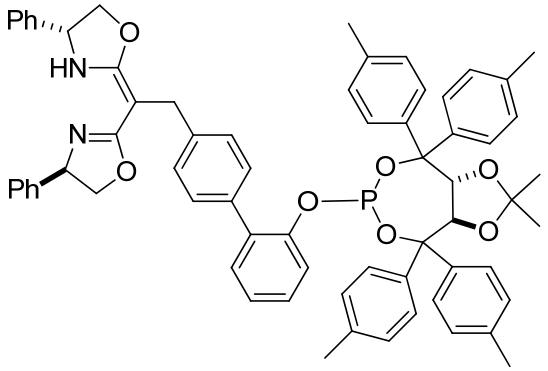


^{13}C NMR of ^{R}Cc



^{31}P NMR of ^{R}Cc

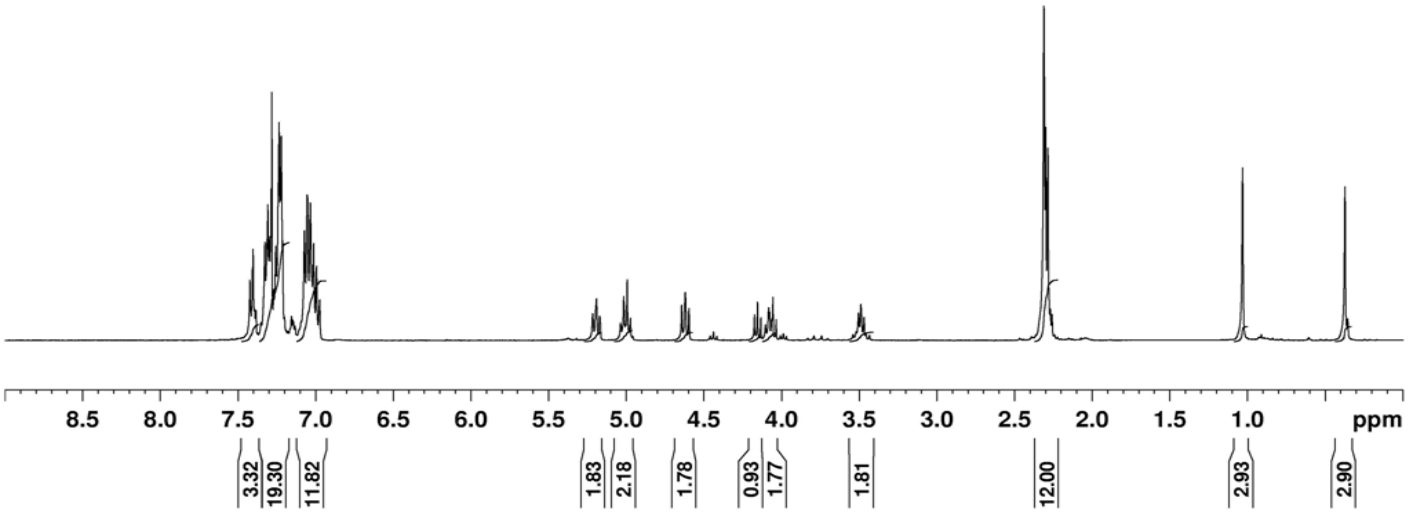




The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (85%) as a white foamy solid.

m.p.	121 - 125 °C
Optical rotation	[α]D ^{25} = -141.0 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.42-7.40 (4H, m), 7.39-7.22 (18H, m), 7.08-6.98 (12H, m), 5.20-5.17 (2H, m), 5.01-4.96 (2H, m), 4.64-4.60 (2H, m), 4.18-4.14 (1H, dd, *J* = 8.1, 8.1 Hz), 4.09-4.03 (2H, m), 3.50-3.47 (2H, m), 2.31-2.25 (12H, m) 1.04 (3H, s), 0.36 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.55, 165.50, 149.1, 143.0, 142.5, 142.1, 142.0, 138.6, 138.5, 138.0, 137.3, 136.93, 136.87, 136.75, 136.6, 136.5, 134.2,130.7,130.1, 128.8, 128.70, 128.64, 128.59, 128.55,128.4, 128.0, 127.8, 127.6, 127.5, 127.1, 126.9, 126.7, 124.2, 122.4, 122.3, 112.8, 85.3 (d, *J*CP = 8.8 Hz), 83.0, 82.3 (d, *J*CP = 14.3 Hz), 81.2 (d, *J*CP = 4.4 Hz), 75.4, 75.1, 69.7, 69.6, 41.3, 35.6, 27.3, 25.8, 21.16, 21.12, 21.01,14.2 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 136.4 ppm
HRMS (FAB)	calcd. for $C_{67}H_{63}N_2O_7P$ $[(M+H)^+]$, 1039.2001; found, 1039.4461 *m/z*.

^{1}H NMR of ^{R}Ac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3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.32
19.30
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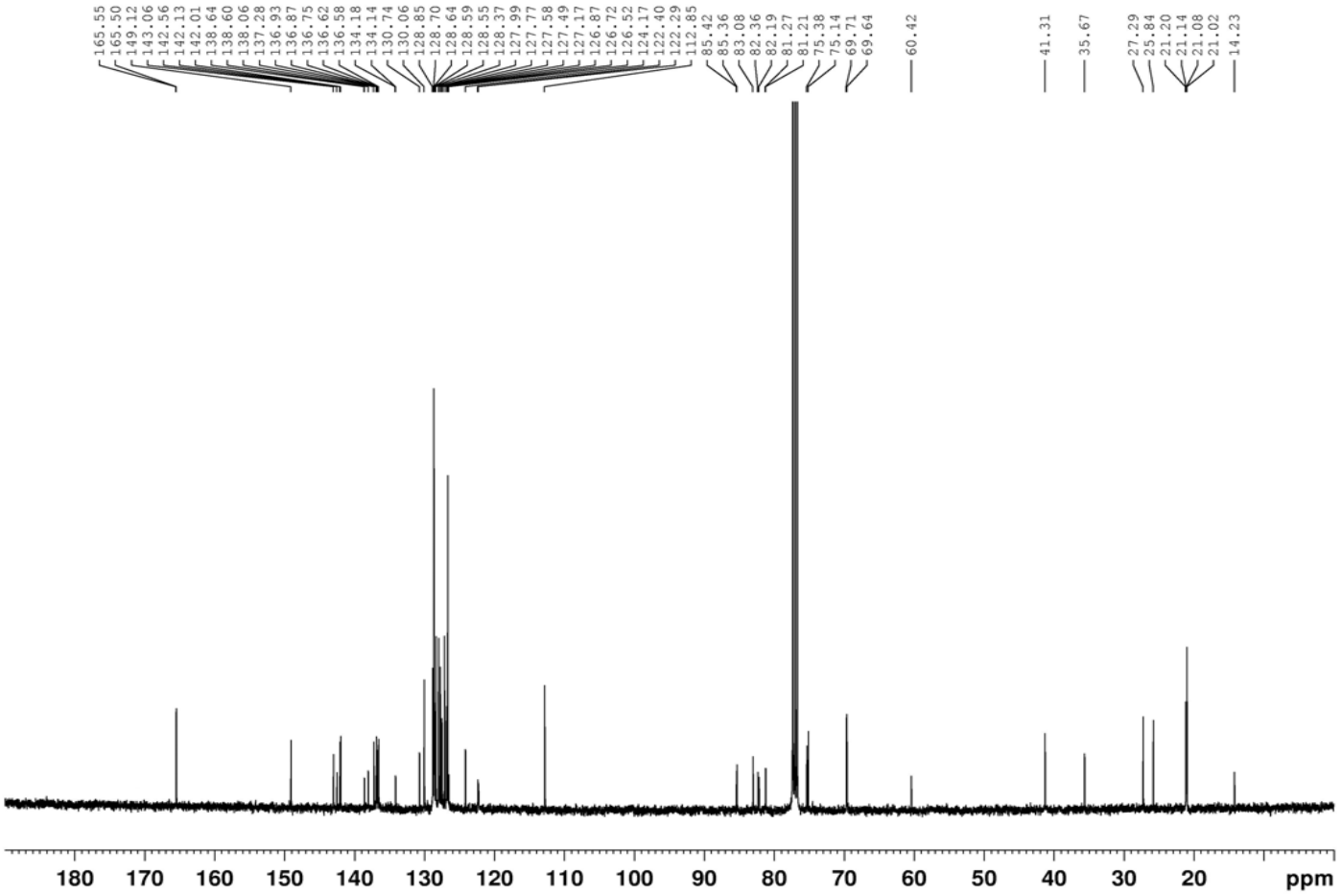
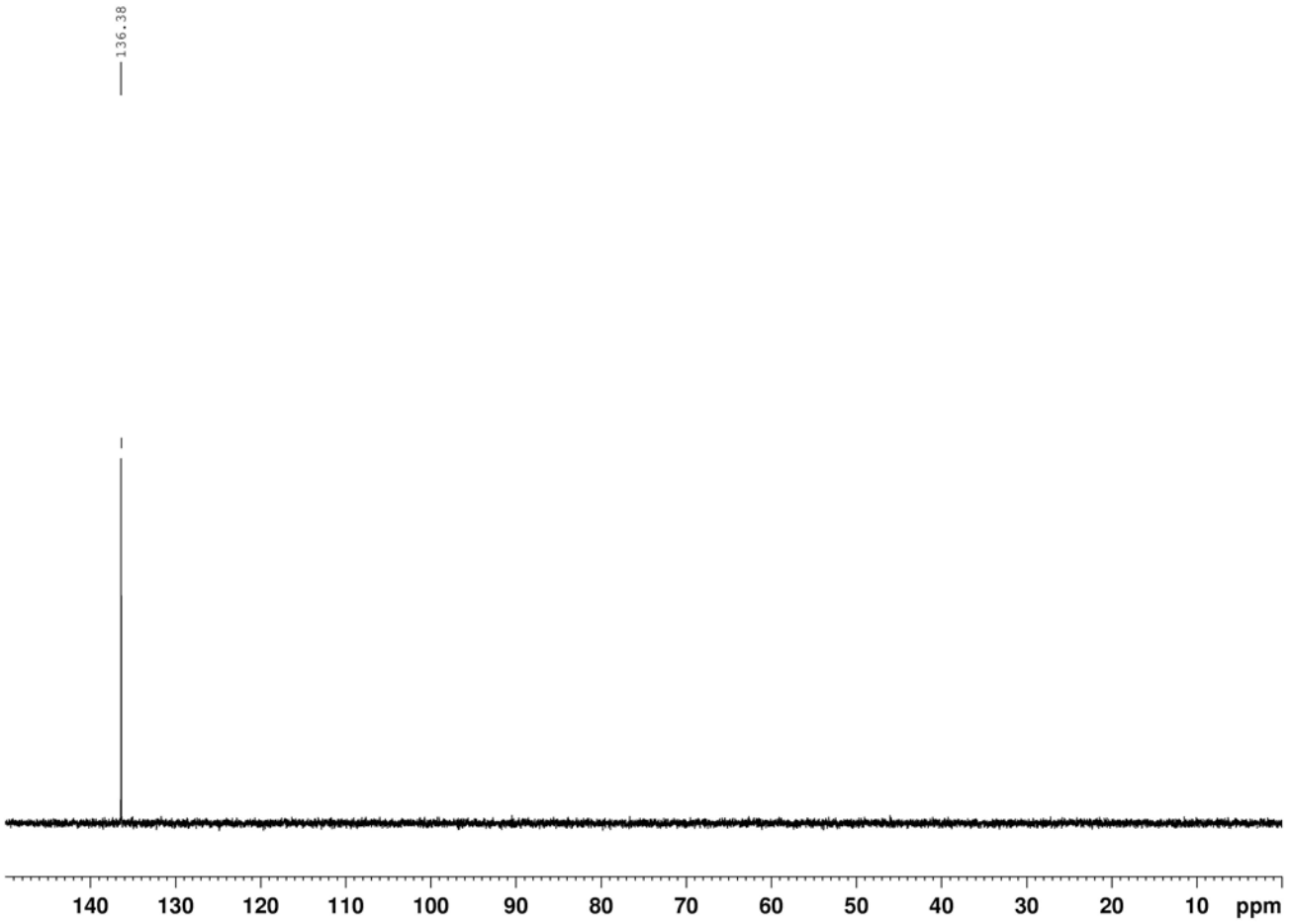
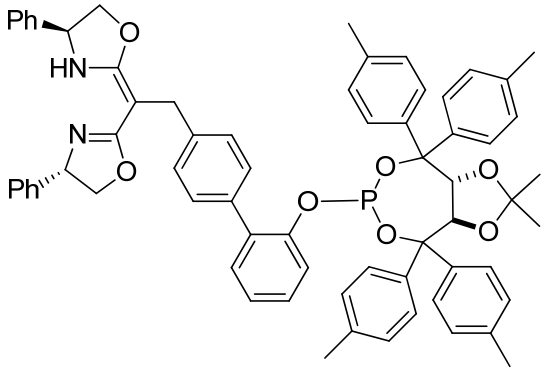
1.83
2.18
1.78
0.93
1.77
1.81
12.00
2.93
2.90

^{13}C NMR of ^{R}Ac



^{31}P NMR of ^{R}Ac

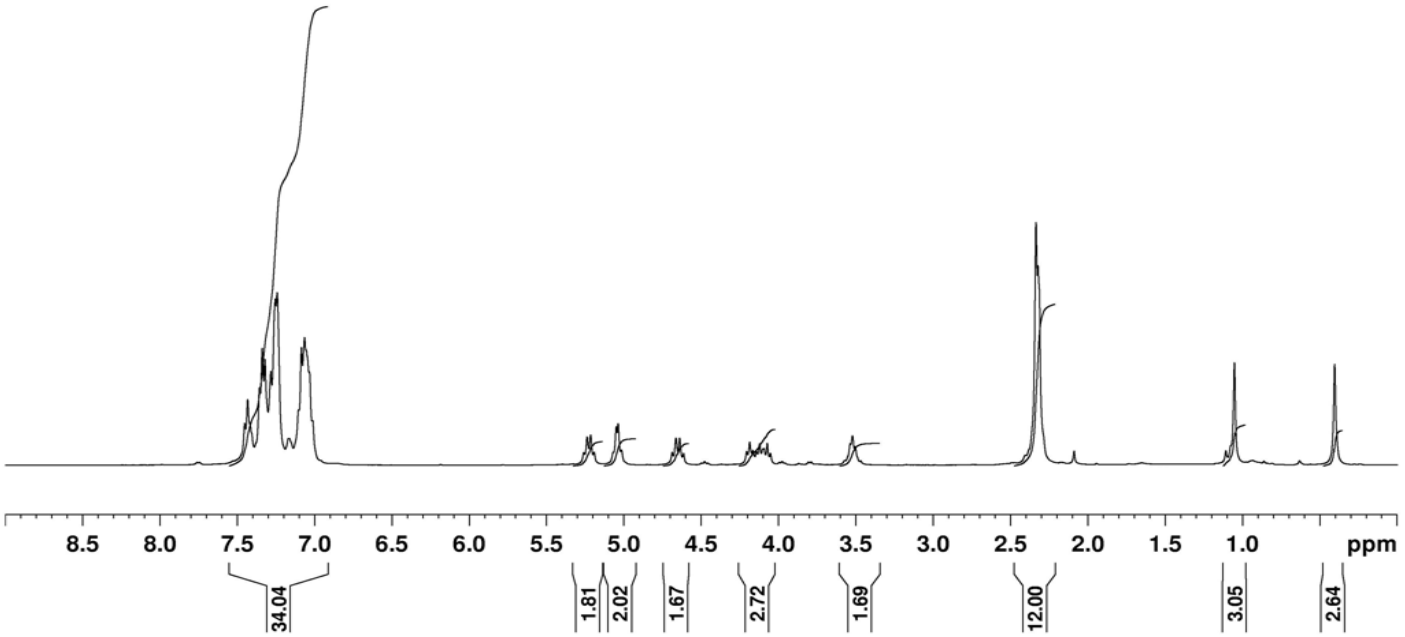




The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (82%) as a white foamy solid.

m.p.	120 - 125 °C
Optical rotation	[α]D ^{25} = -128.7 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.45-7.41 (4H, m), 7.40-7.20 (18H, m), 7.07-6.99 (12H, m), 5.22-5.20 (2H, m), 5.02-5.00 (2H, m), 4.63-4.62 (2H, m), 4.17-4.14 (1H, dd, *J* = 8.2, 8.2 Hz), 4.09-4.03 (2H, m), 3.50-3.47 (2H, m), 2.32-2.26 (12H, m) 1.05 (3H, s), 0.40 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.55, 165.51, 149.1, 143.0, 142.5, 142.1, 142.0, 138.66, 138.61, 138.1, 137.3, 136.9, 136.9, 136.8, 136.6, 136.5, 134.11, 134.08, 130.1, 128.8, 128.70, 128.65, 128.4, 128.0, 127.8, 127.6, 127.5, 127.2, 126.9, 126.7, 124.2, 122.33, 122.22, 112.9, 85.3 (d, *J*CP = 8.8 Hz), 83.1, 82.4 (d, *J*CP = 14.3 Hz), 81.2 (d, *J*CP = 4.4 Hz), 75.4, 75.2, 69.7, 69.6, 41.3, 35.6, 27.3, 25.8, 21.18, 21.14, 21.03 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 136.2 ppm
HRMS (FAB)	calcd. for $C_{67}H_{63}N_2O_7P$ [(M+H)+], 1039.2001; found,1039.4430 *m/z*

^{1}H NMR of ^{S}Ac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1.5
1.0
ppm
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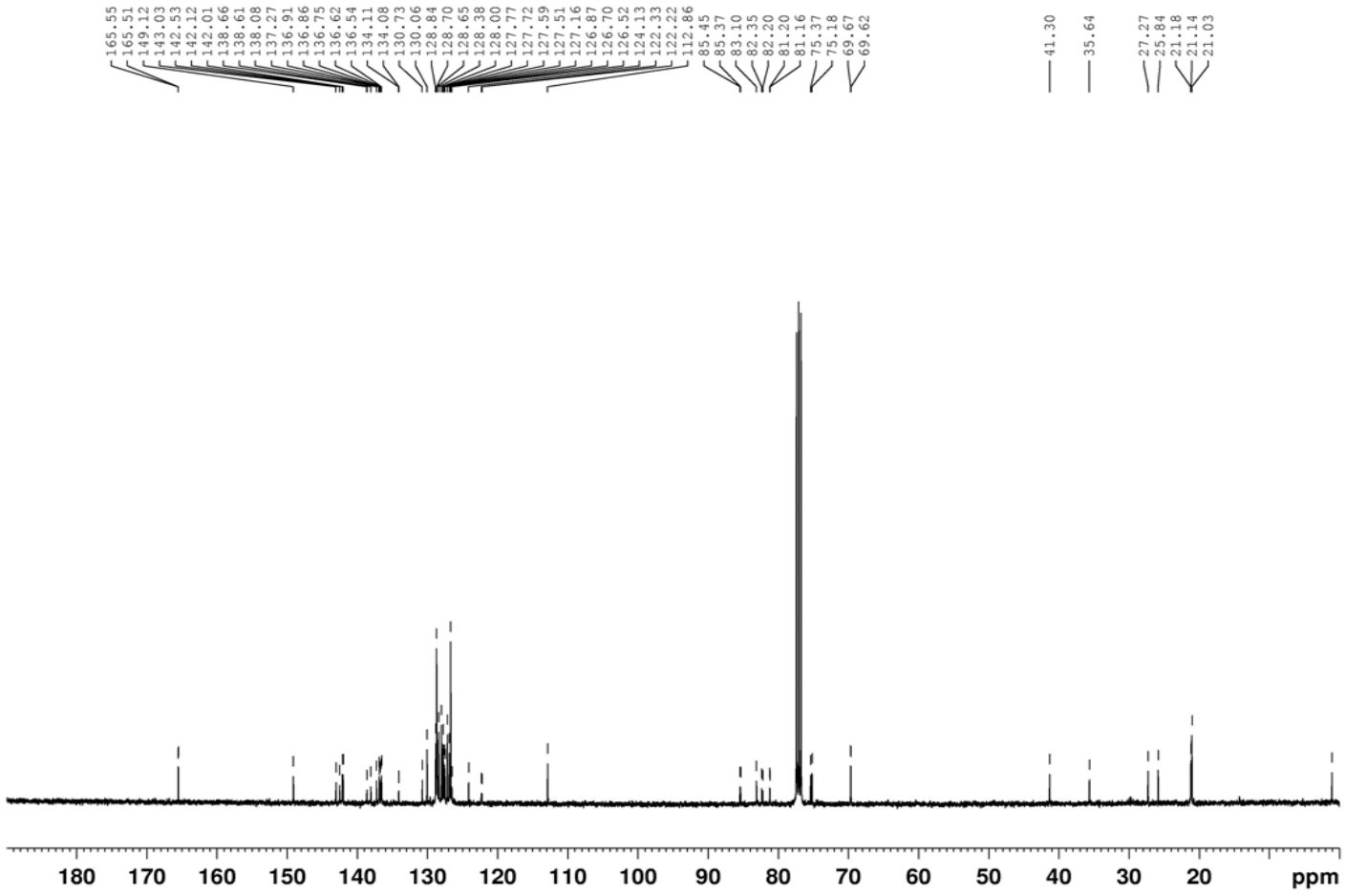
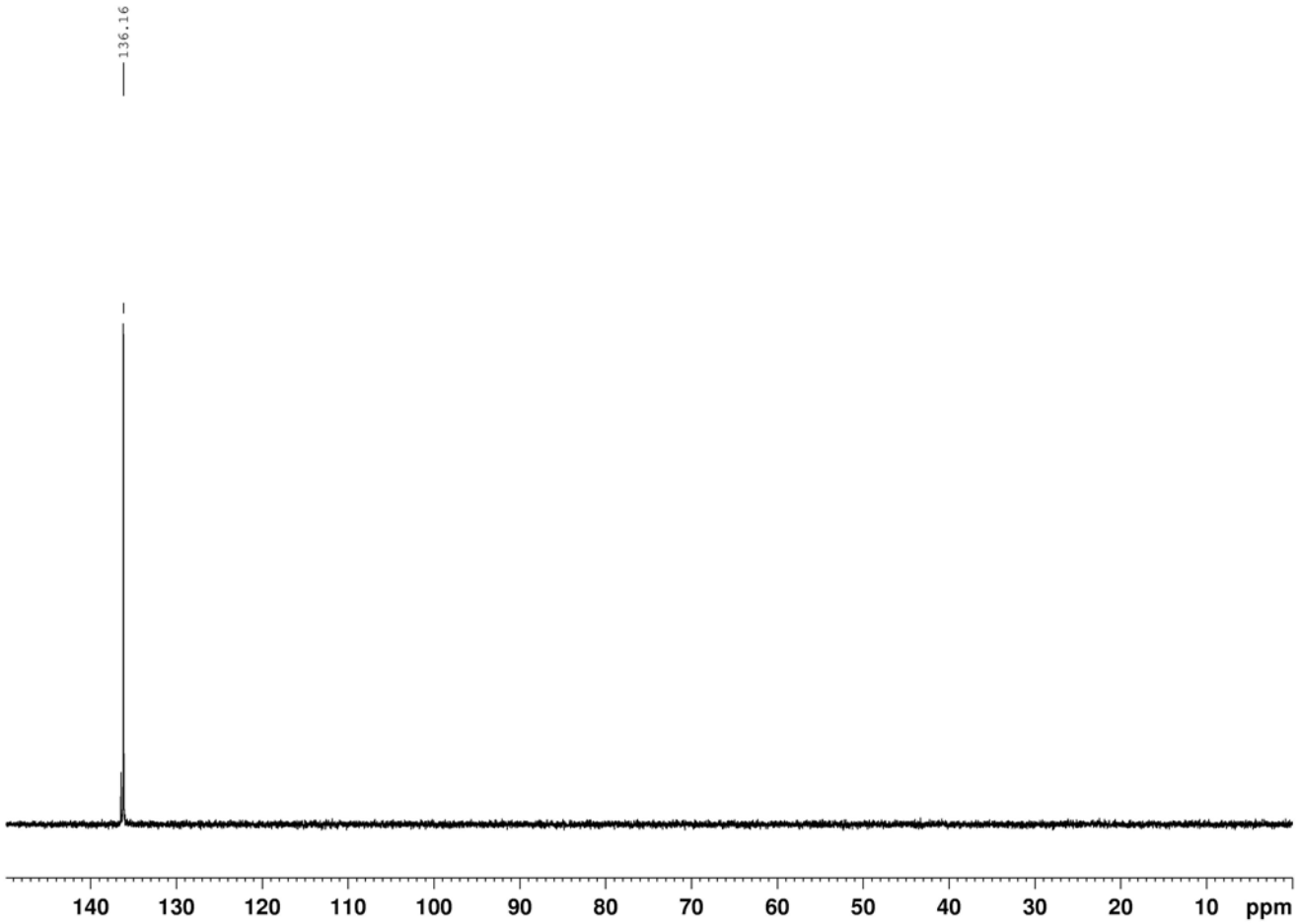
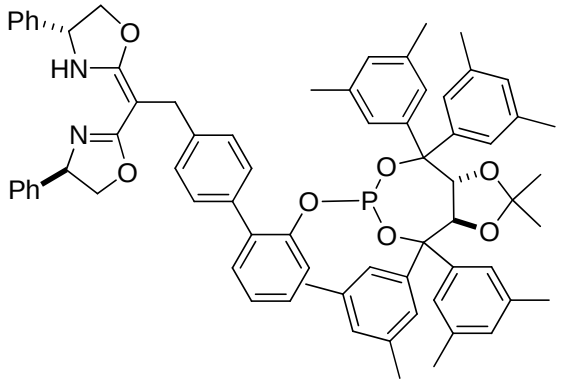
2.02
1.67
2.72
1.69
12.00
3.05
2.64

^{13}C NMR of ^{S}Ac



^{31}P NMR of ^{S}Ac

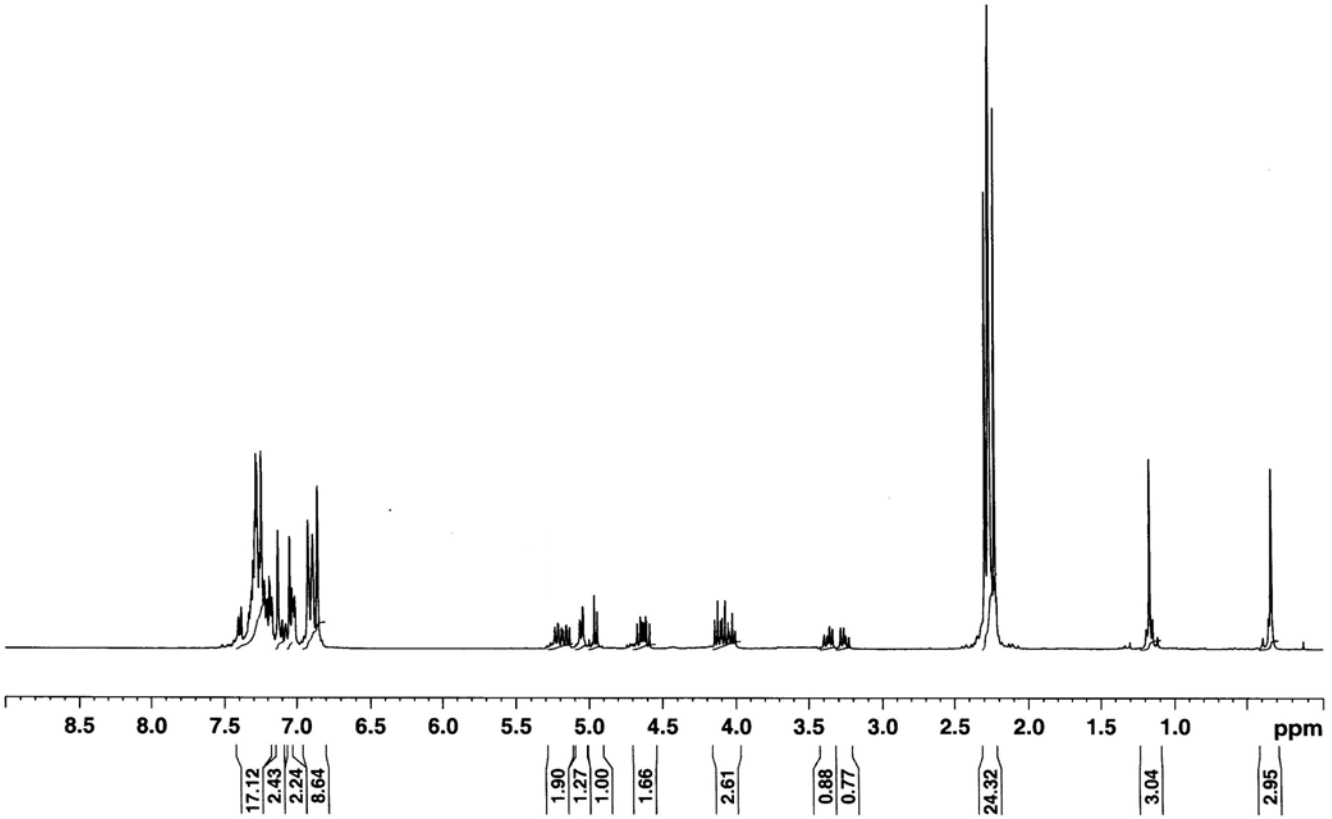




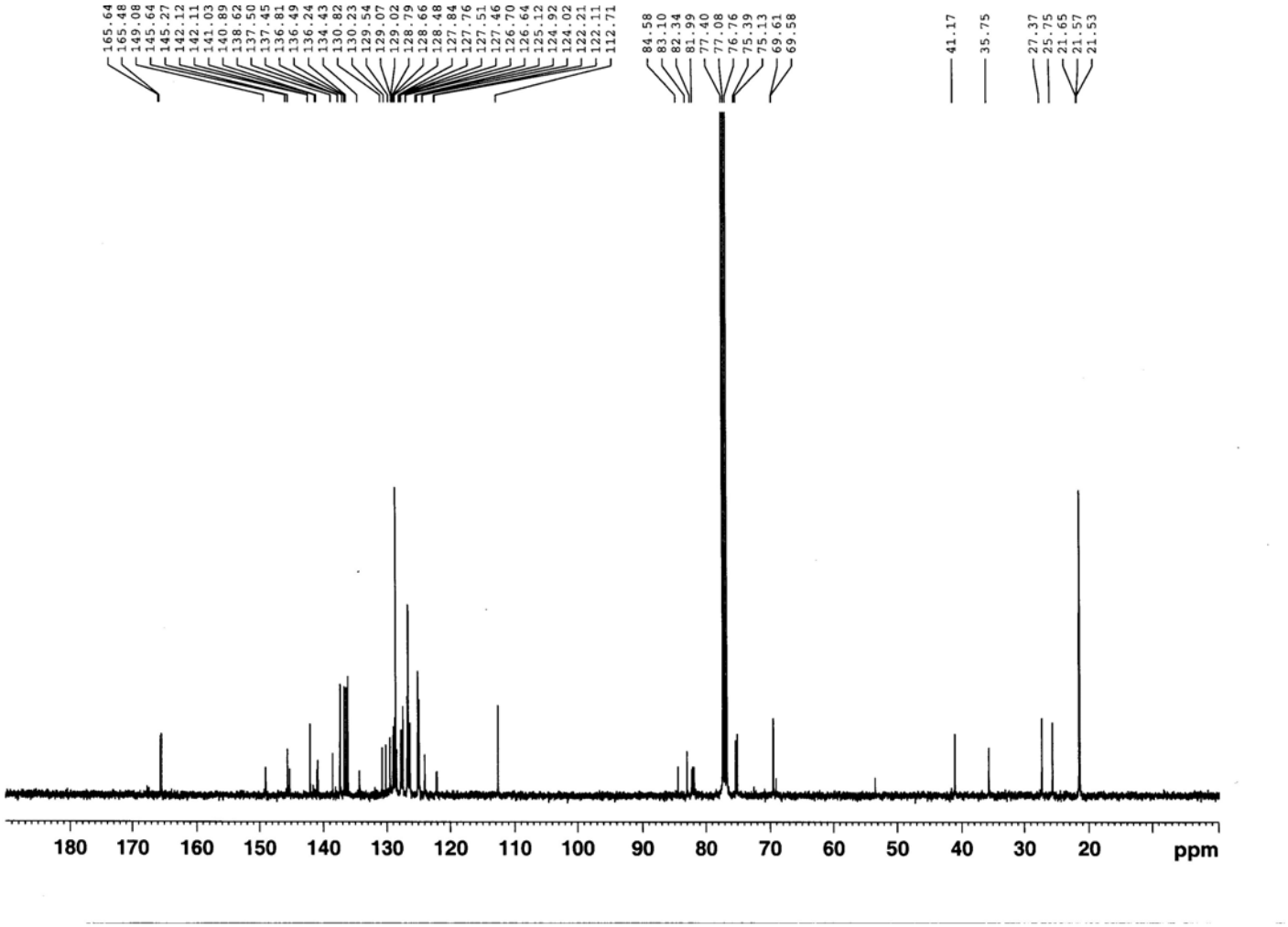
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (89%) as a white foamy solid.

m.p.	120 - 125°C
Optical rotation	$[\alpha]D^{25}$ = -163.0 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.33-7.21 (17H, m), 7.19-7.16 (2H, m), 7.13-7.05 (2H, m), 7.01-6.86 (9H, m), 5.07 (1H, d, *J* = 7.9 Hz), 4.96 (1H, d, *J* = 8.3 Hz), 4.67-4.59 (2H, m), 4.15-4.03 (3H, m), 3.36-3.27 (2H, m), 2.29-2.23 (24H, m) 1.17 (3H, s), 0.34 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.6, 165.5, 149.1, 145.6, 145.3, 142.12, 142.11, 141.0, 140.9, 138.6, 137.50, 137.45, 136.8, 136.5, 136.2, 134.4, 130.8, 130.2, 129.5, 129.1, 129.0 128.8, 128.7, 128.5, 127.84, 127.76, 127.51, 127.46, 126.7, 126.6, 125.1, 124.9, 124.0, 122.2, 122.1, 112.7, 84.5 (d, *J*CP = 8.3 Hz), 83.1, 82.3 (d, *J*CP = 14.0 Hz), 82.0 (d, *J*CP = 4.3 Hz), 75.4, 75.1, 69.61, 69.58, 41.2, 35.8, 27.4, 25.8, 21.65, 21.57, 21.53 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 134.7 ppm
HRMS (FAB)	calcd. For $C_{71}H_{71}N_2O_7P$ $[(M+H)^+]$, 1095.3064; found, 1095.5075 *m/z*

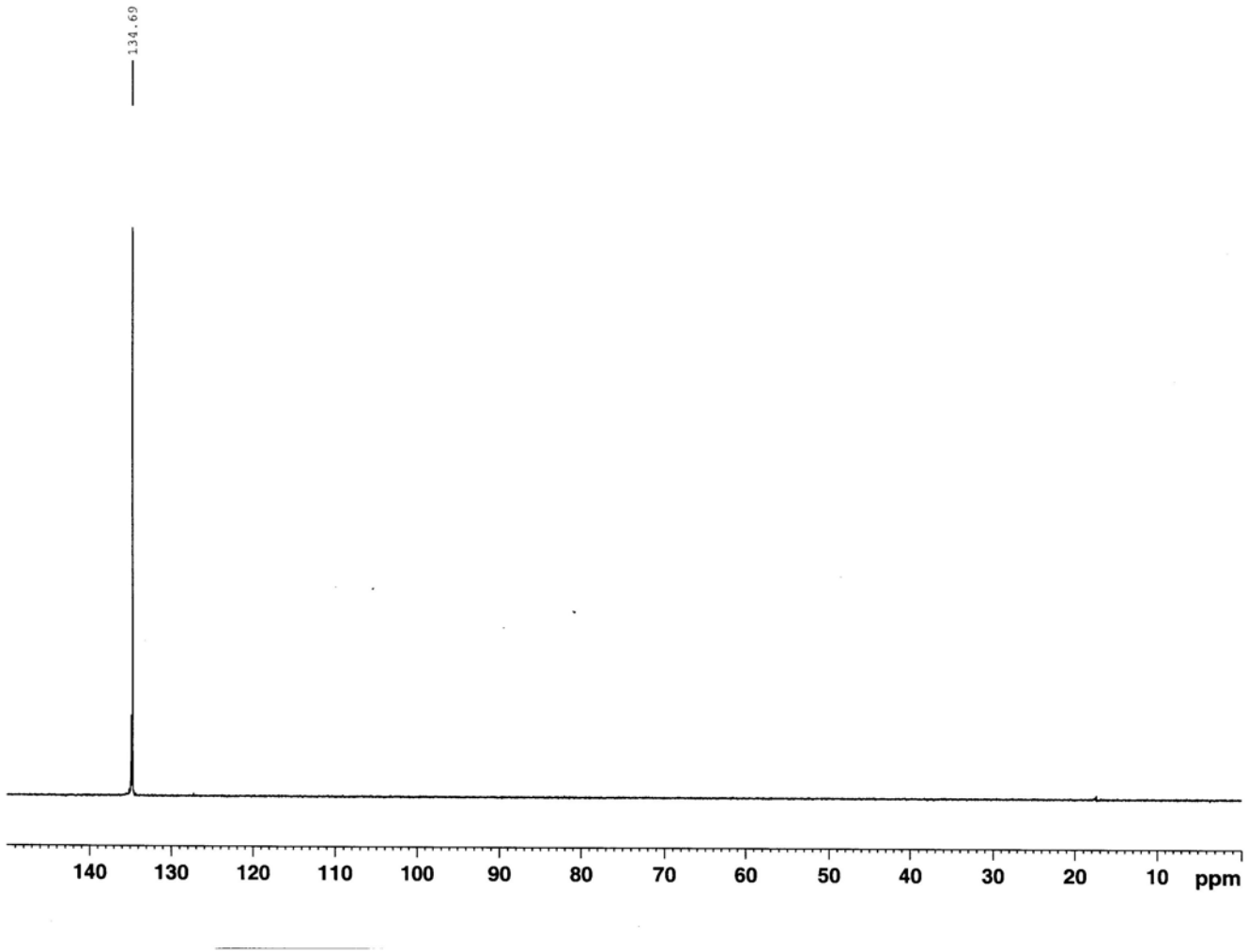
^{1}H NMR of ^{R}Ab

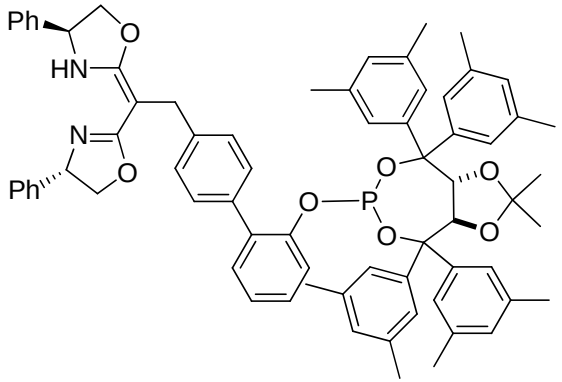


^{13}C NMR of ^{R}Ab



^{31}P NMR of ^{R}Ab

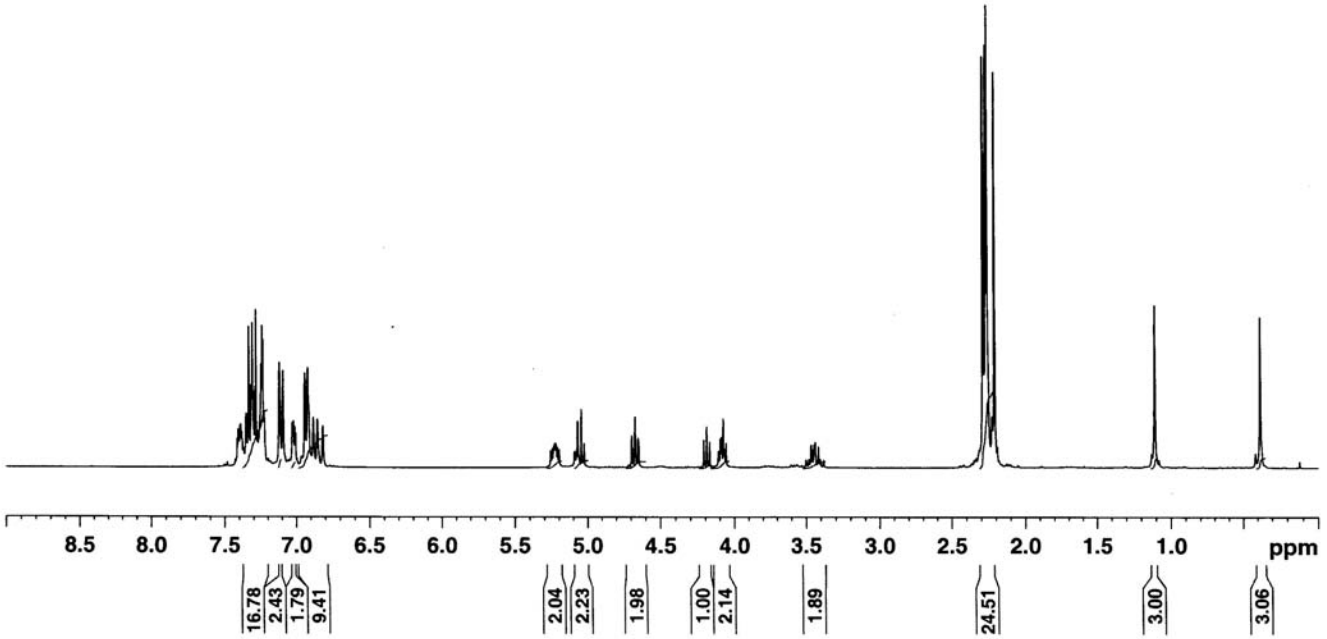




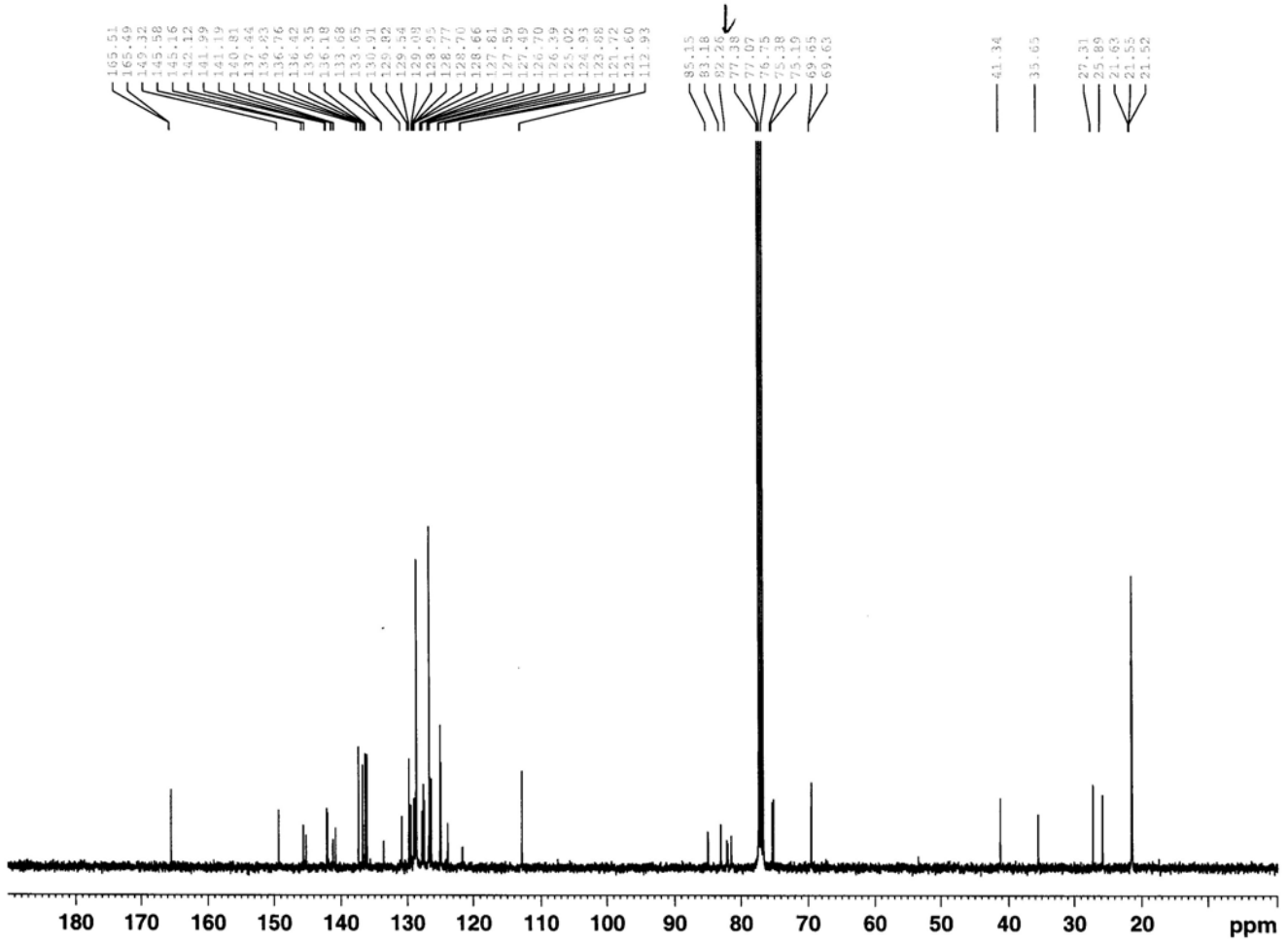
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (87%) as a white foamy solid.

m.p.	120 - 125 °C
Optical rotation	$[\alpha]D^{25}$ = -149.0 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.41-7.23 (17H, m), 7.12-7.09 (2H, m), 7.03-7.00 (2H, m), 6.94-6.82 (9H, m), 5.32-5.17 (2H, m), 5.07-5.05 (2H, m), 4.70-4.65 (2H, m), 4.21-4.17 (1H, dd, *J* = 8.3, 8.3 Hz), 4.10-4.08 (2H, m), 3.50-3.47 (2H, m), 2.29-2.23 (24H, m) 1.10 (3H, s), 0.35 ppm (3H,s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.51, 165.49, 149.3, 145.6, 145.2, 142.1, 142.0, 141.2, 137.4, 136.83, 136.76, 136.42, 136.35, 136.2, 133.68, 133.65, 130.9, 129.8, 129.5, 129.1, 129.0, 128.8, 128.70, 128.66, 127.8, 127.6, 127.5, 126.7, 126.4, 125.0, 124.9, 123.9, 121.7, 121.6, 112.9, 85.2 (d, *J*CP = 8.8 Hz), 83.2, 82.6 (d, *J*CP = 14.3 Hz), 81.2 (d, *J*CP = 4.4 Hz), 75.4, 75.2, 69.65, 69.63, 41.3, 35.7, 27.3, 25.9, 21.63, 21.55, 21.52 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 136.4 ppm
HRMS (FAB)	calcd. for $C_{71}H_{71}N_2O_7P$ $[(M+H)^+]$, 1095.3064; found, 1095.5059 *m/z*

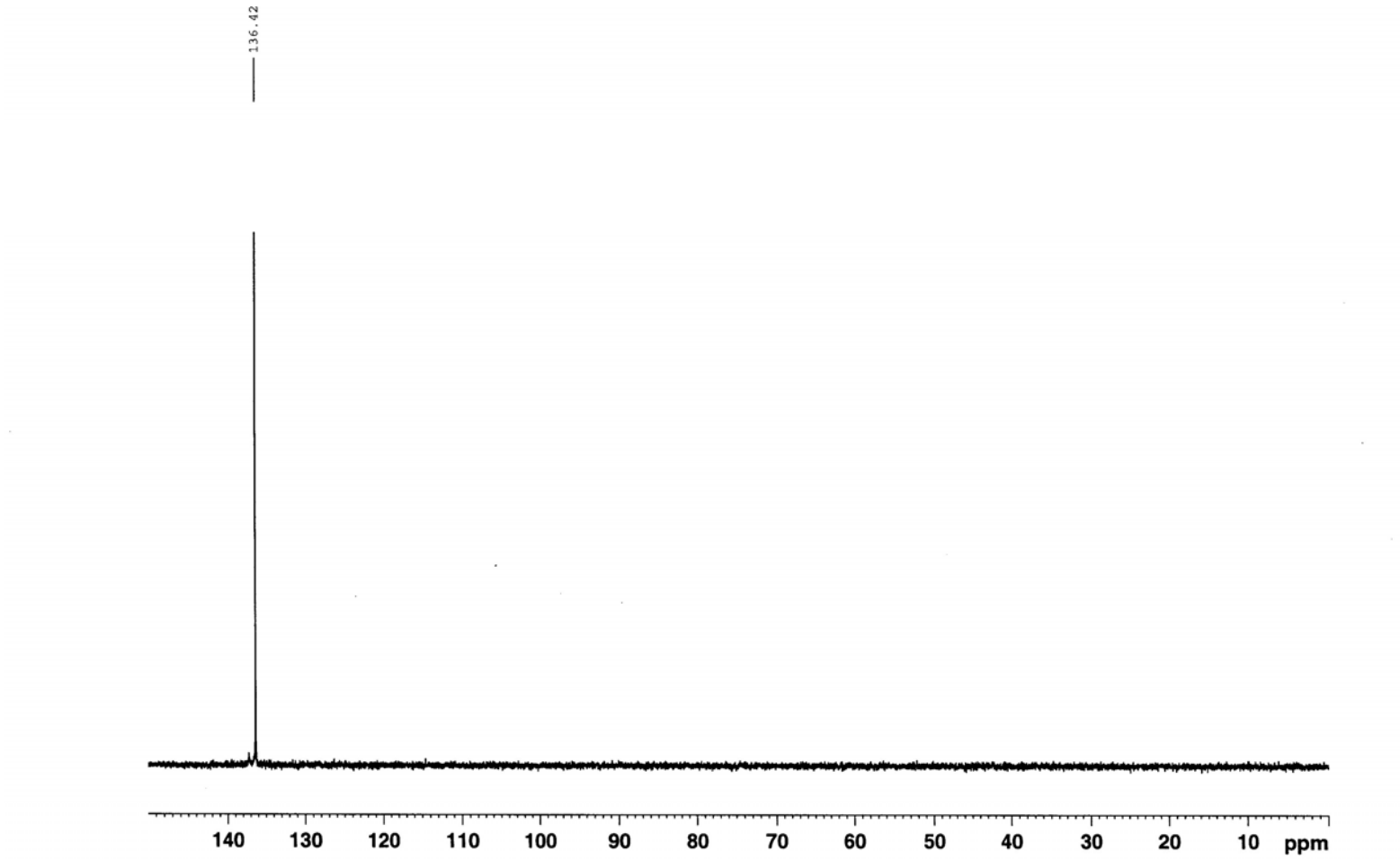
^{1}H NMR of ^{S}Ab

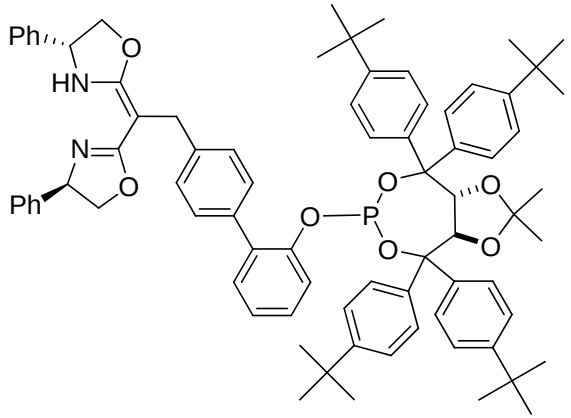


^{13}C NMR of ^{S}Ab



^{31}P NMR of ^{S}Ab

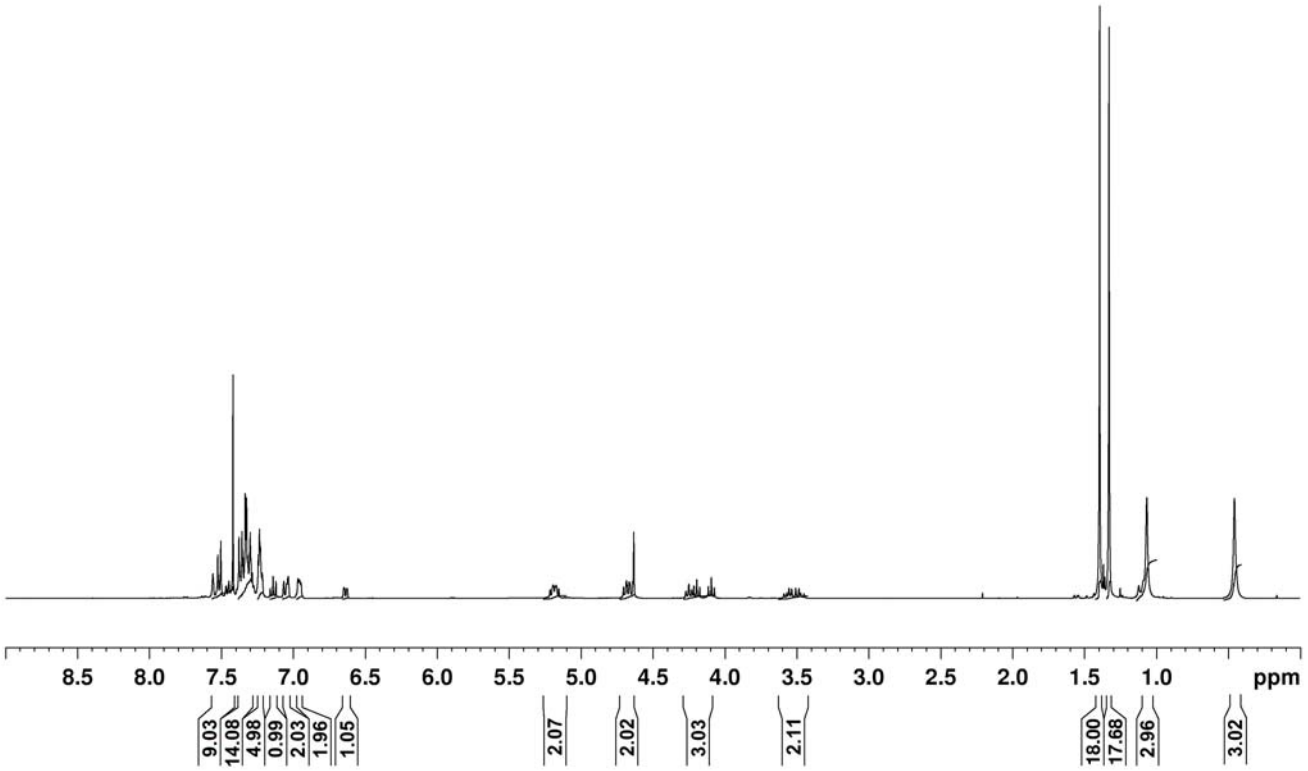




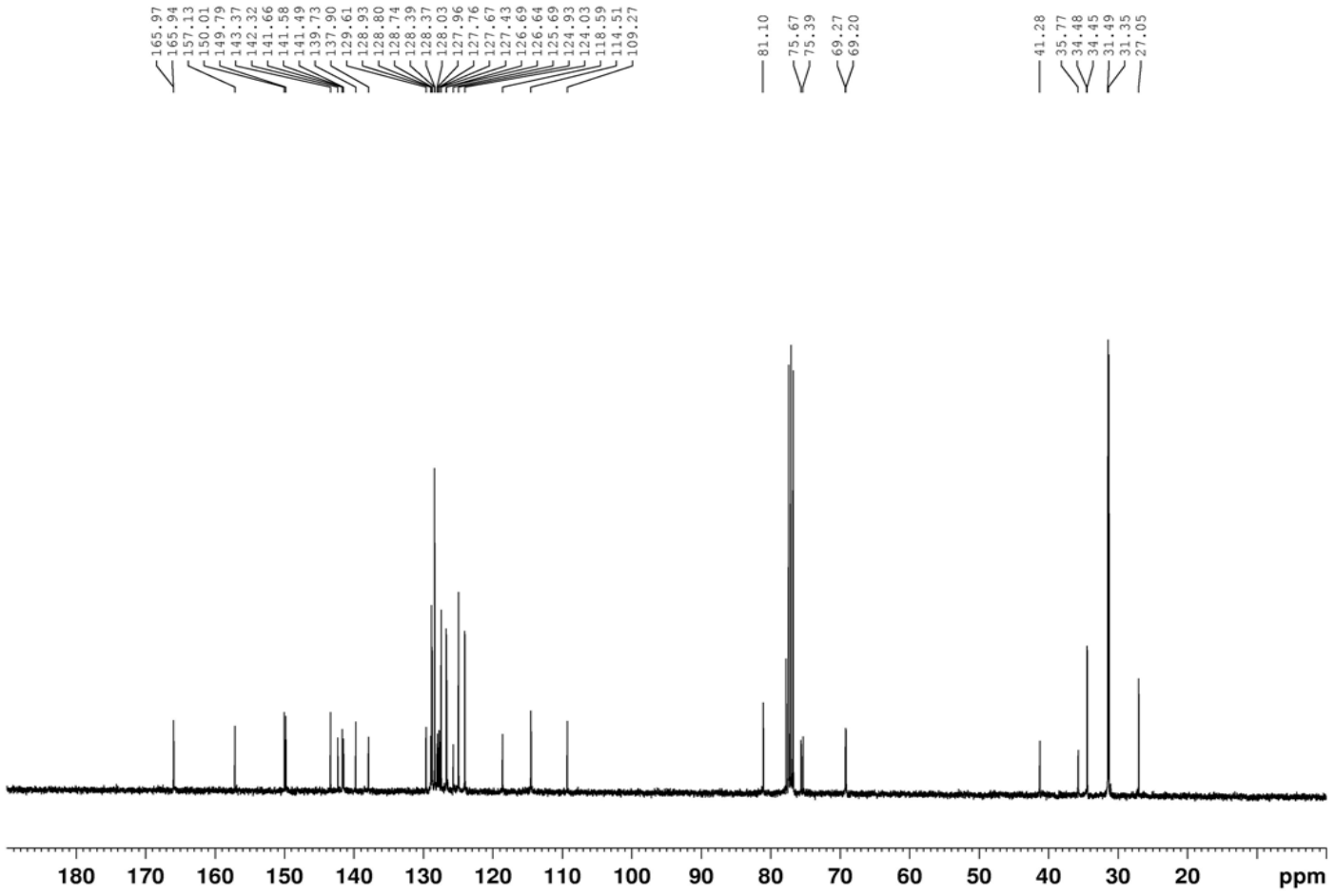
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (80%) as a white foamy solid.

m.p.	123 - 127 °C
Optical rotation	$[\alpha]D^{25}$ = -141.0 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.56-7.28 (23H, m), 7.24-7.23 (5H, m), 7.22-7.12 (2H, m), 7.06-7.03 (2H, m), 6.97-6.94 (2H, m), 6.67-6.63 (1H, m), 5.25-5.13 (2H, m), 4.69-4.64 (2H, m), 4.25-4.10 (3H, m), 3.60-3.47 (2H, m), 1.40 (18H, s), 1.33 (18H, s), 1.06 (3H, s), 0.45 ppm (3H,s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.97, 165.94, 157.13, 150.01, 149.79, 143.37, 142.32, 141.66, 141.58, 141.49, 139.73, 137.90, 129.61, 128.93, 128.80, 128.74, 128.39, 128.37, 128.03, 127.96, 127.76, 127.67, 127.43, 126.69, 126.64, 125.69, 124.93, 124.03, 118.59, 114.51, 109.27, 81.10, 75.67, 75.39, 69.27, 69.20, 41.28, 35.77, 34.48, 34.45, 31.49, 31.35, 27.05 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 133.5 ppm
HRMS (ESI)	calcd. for $C_{79}H_{83}N_2O_7P$ $[(M+Na)^+]$, 1230.5085; found, 1230.7161 *m/z*

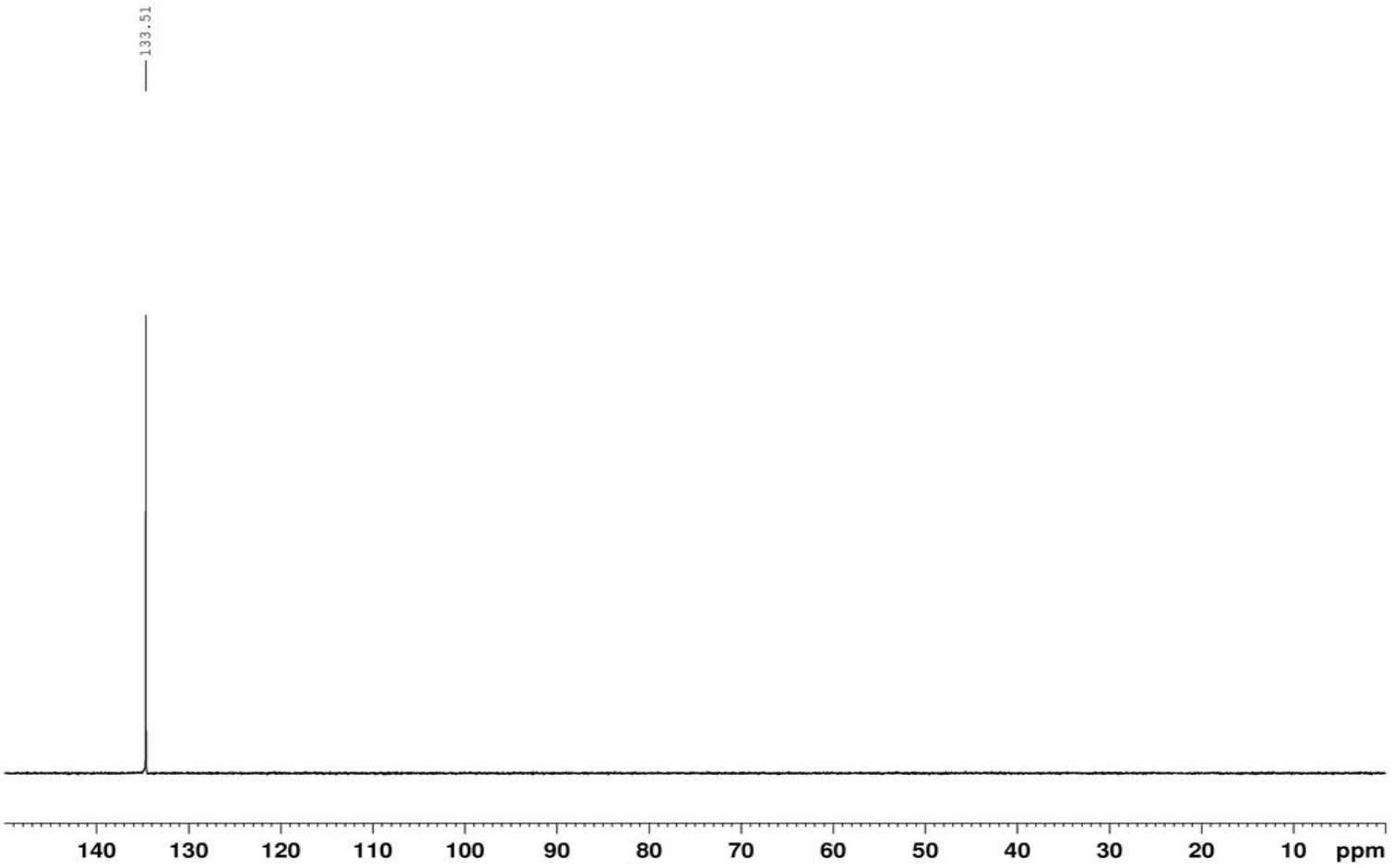
^{1}H NMR of ^{R}Ad

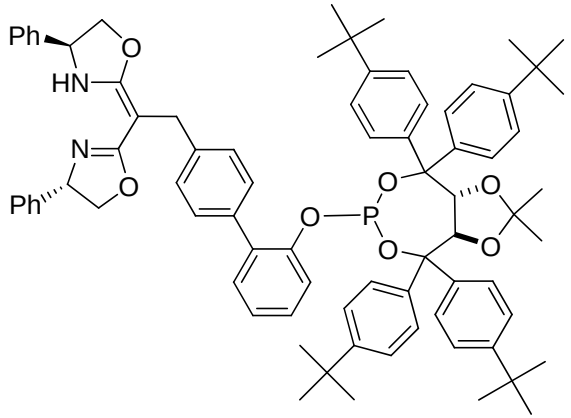


^{13}C NMR of ^{R}Ad



^{31}P NMR of ^{R}Ad

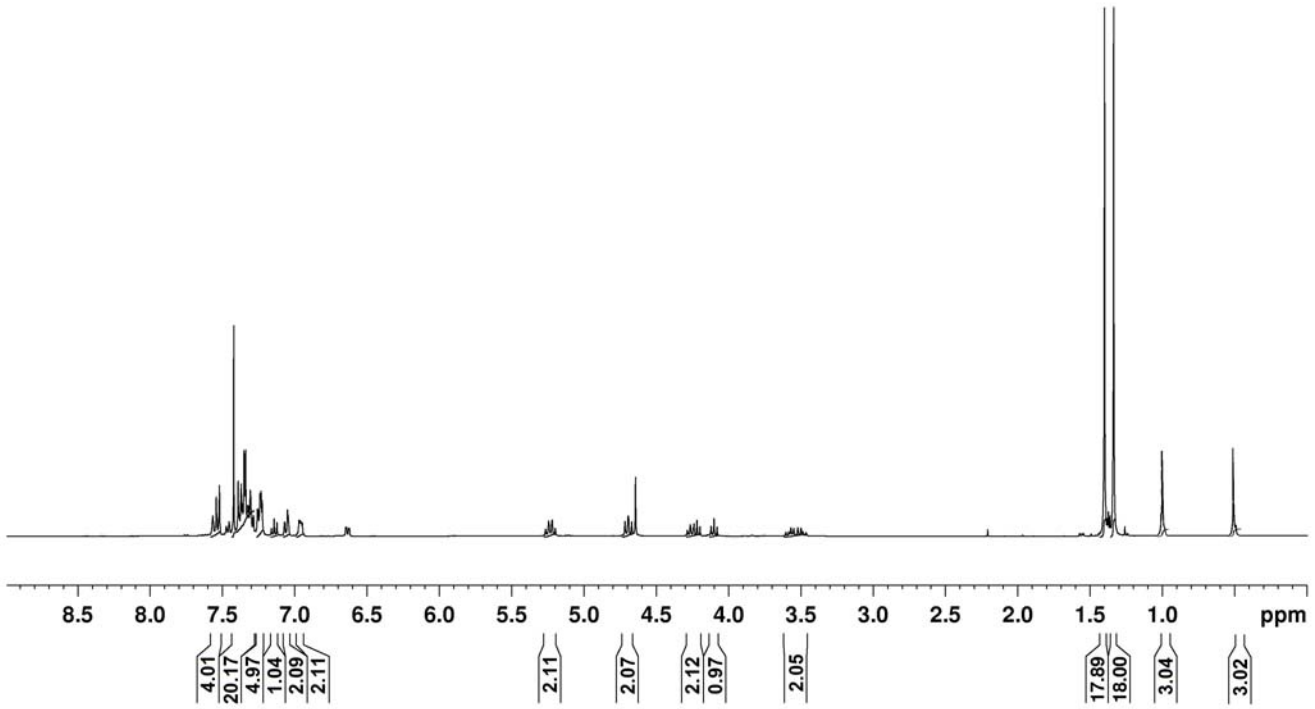




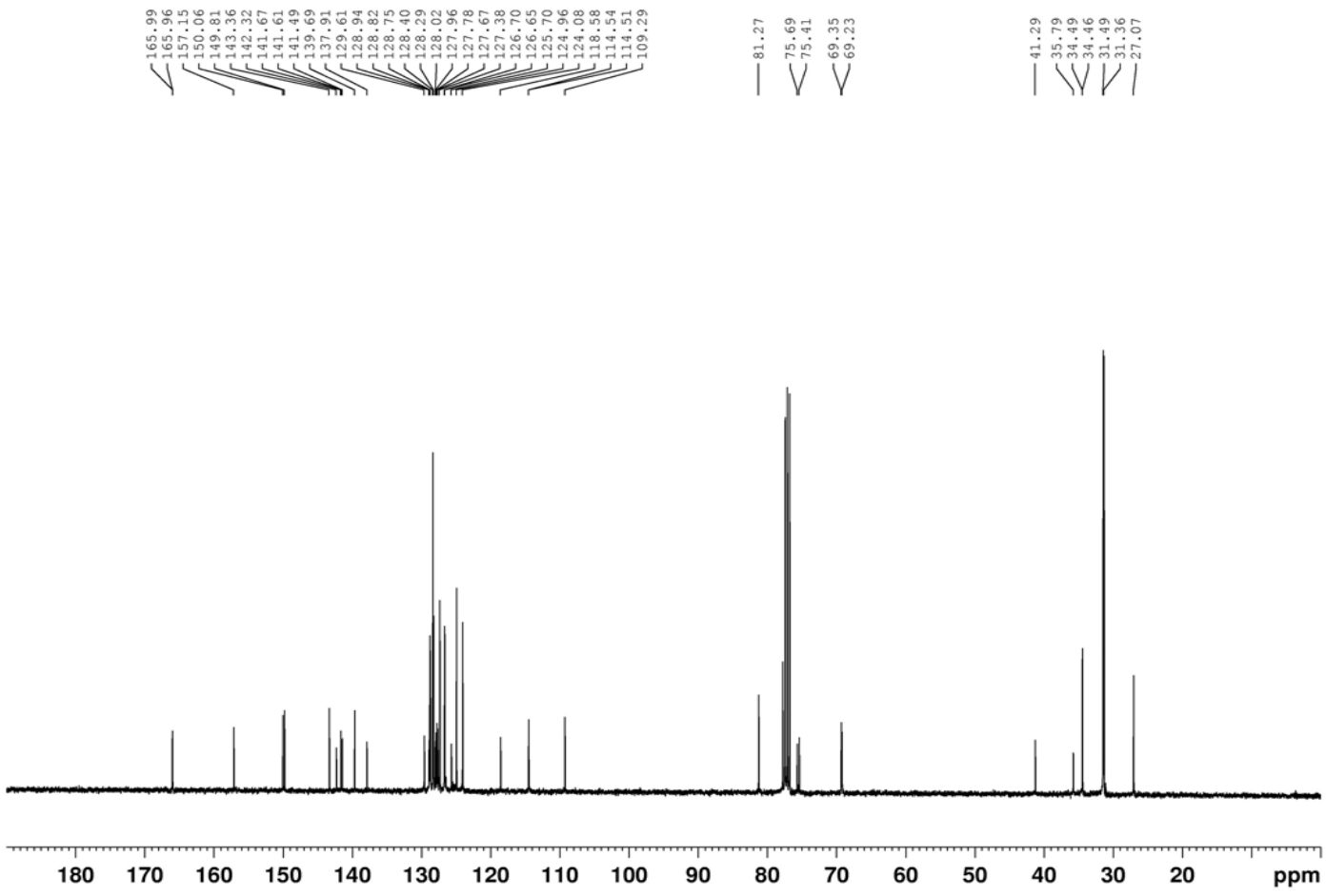
The general procedure for the synthesis of tether affords, after flash chromatography on silica gel (5:95 methanol:dichloromethane), the compound pictured (80%) as a white foamy solid.

m.p.	124 - 126 °C
Optical rotation	$[\alpha]D^{25}$ = -128.0 (c = 0.5, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.57-7.52 (4H, m), 7.45-7.28 (20H, m), 7.26-7.22 (5H, m), 7.14-7.12 (1H, m), 7.07-7.04 (2H, m), 6.97-6.95 (2H, m), 5.25-5.22 (2H, m), 4.72-4.67 (2H, m), 4.27-4.22 (2H, m), 4.10 (1H, m), 3.63-3.62 (2H, m), 1.40 (18H, s), 1.34 (18H, s), 0.98 (3H, s), 0.53 ppm (3H,s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 165.99, 165.96, 157.15, 150.06, 149.81, 143.36, 142.32, 141.67, 141.61, 141.49, 139.69, 137.91, 129.61, 128.94, 128.82, 128.75, 128.40, 128.29, 128.02, 127.96, 127.78, 127.67, 127.38, 126.70, 126.65, 125.70, 124.96, 124.08, 118.58, 114.54, 114.51, 109.29, 81.27, 75.69, 75.41, 69.35, 69.23, 41.29. 35.79, 34.49, 34.46, 31.49, 31.36, 27.07 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ133.6 ppm
HRMS (ESI)	calcd. for $C_{79}H_{83}N_2O_7P$ $[(M+Na)^+]$, 1230.5085; found, 1230.7059 *m/z*

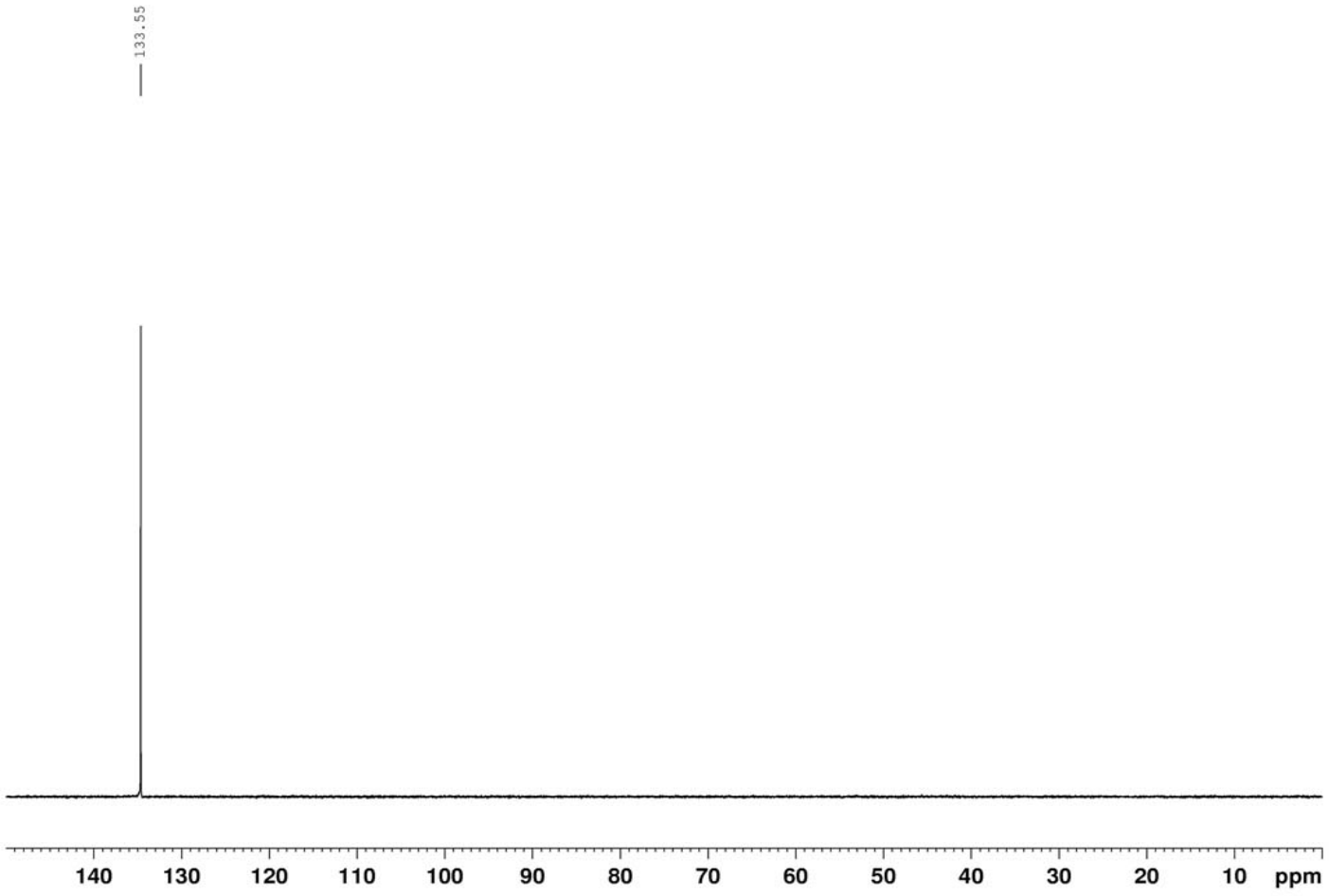
^{1}H NMR of ^{S}Ad

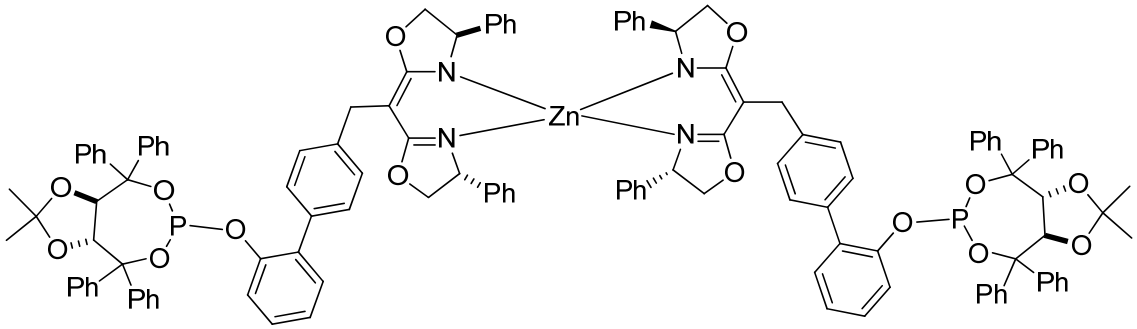


^{13}C NMR of ^{S}Ad



^{31}P NMR of ^{S}Ad

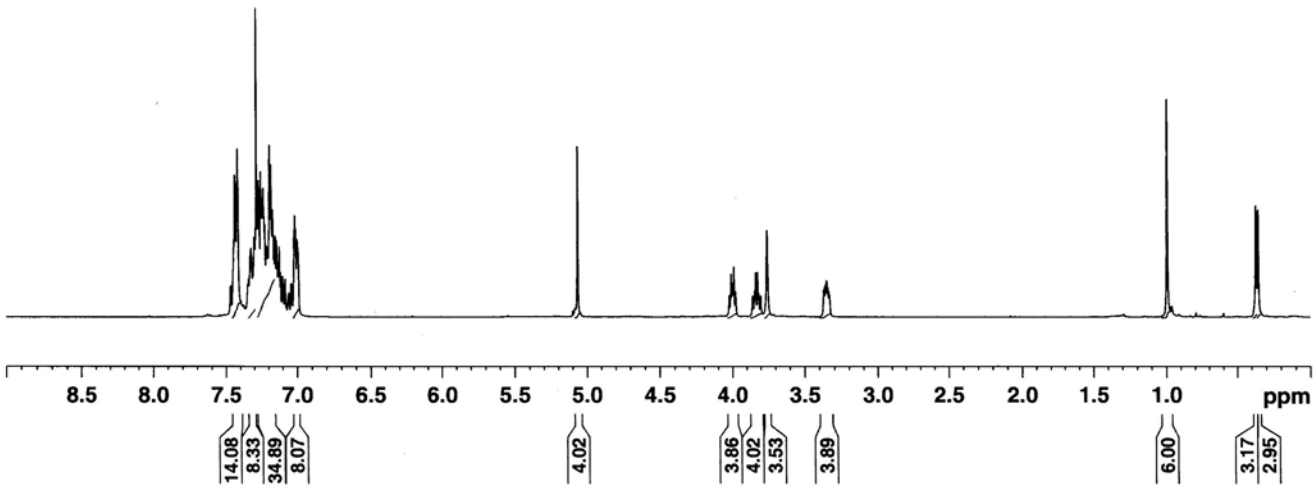




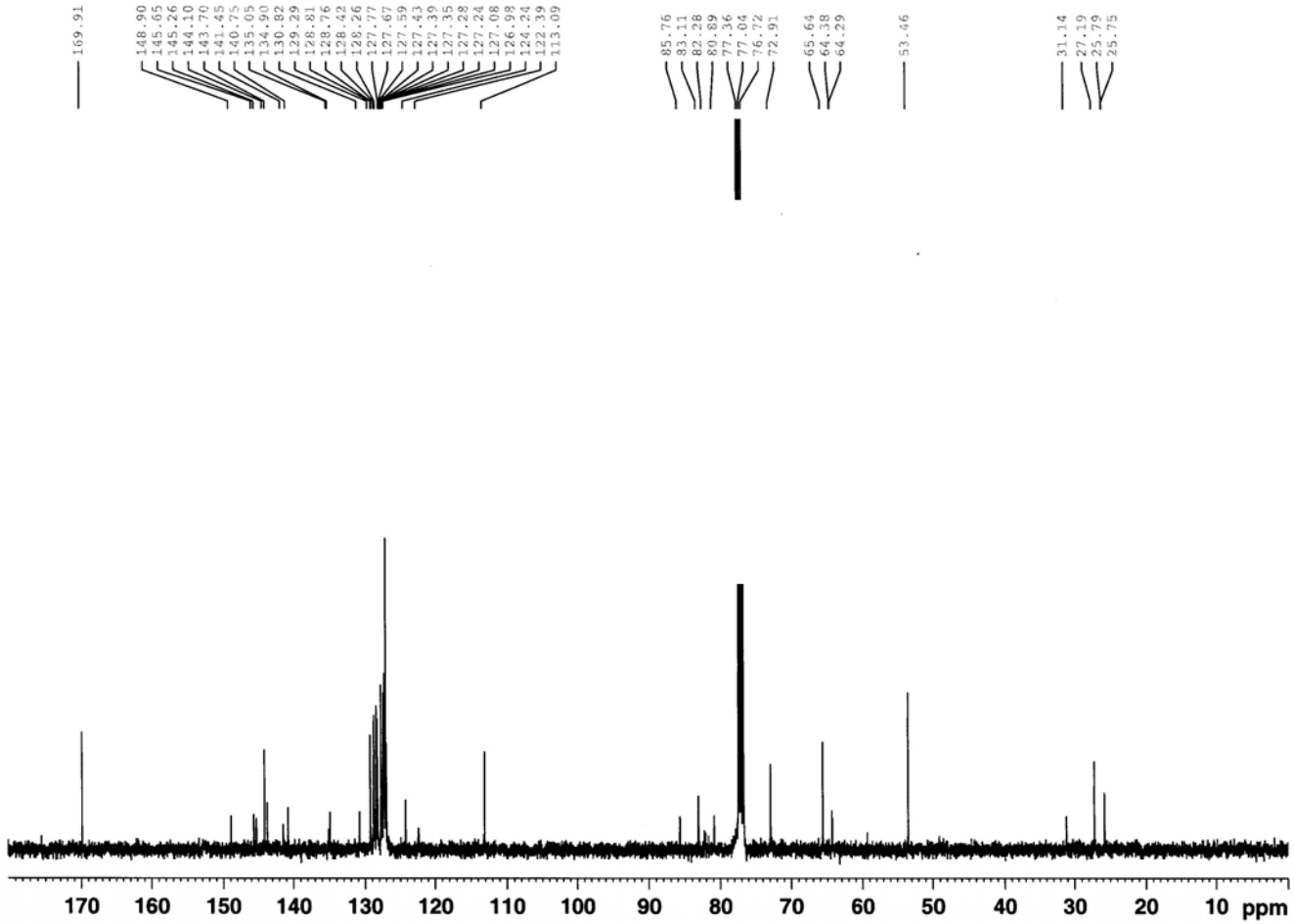
The general procedure for the synthesis of self-assembled ligands affords the compound pictured (99%) as a white solid.

m.p.	171 - 173 °C
Optical rotation	$[\alpha]D^{25}$ = -67.5 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.47-7.42 (16H, m), 7.34-7.12 (52H, m), 7.03-6.98, (8H, m), 5.06 (4H, s), 4.02-3.98, (4H, m), 3.86-3.80 (4H, m), 3.76 (4H, s), 3.37-3.33 (4H, m), 0.99 (6H, s), 0.37 (3H, s), 0.35 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 169.9, 149.0, 148.9, 145.7, 145.6, 145.3, 144.1, 143.7, 141.50, 141.45, 140.8, 140.7, 135.14, 135.05, 135.0, 134.9, 130.8, 129.3, 129.1, 128.81, 128.76, 128.4, 128.3, 127.8, 127.7, 127.6, 127.43, 127.39, 127.4, 127.3, 127.2, 127.1,, 127.0, 125.0, 124.2, 122.4, 122.2, 113.24, 113.1, 85.8, 85.7, 83.1, 83.0, 82.3, 82.1, 80.9, 80.8, 72.9, 65.6, 64.4, 64.3, 53.5, 31.1, 27.2, 25.79, 25.75 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 133.7 ppm
HRMS (FAB)	calcd. for $C_{138}H_{132}N_4O_{14}P_2Zn$ $[(M+Li)^+]$, 2197.8508; found, 2197.8728 *m/z*

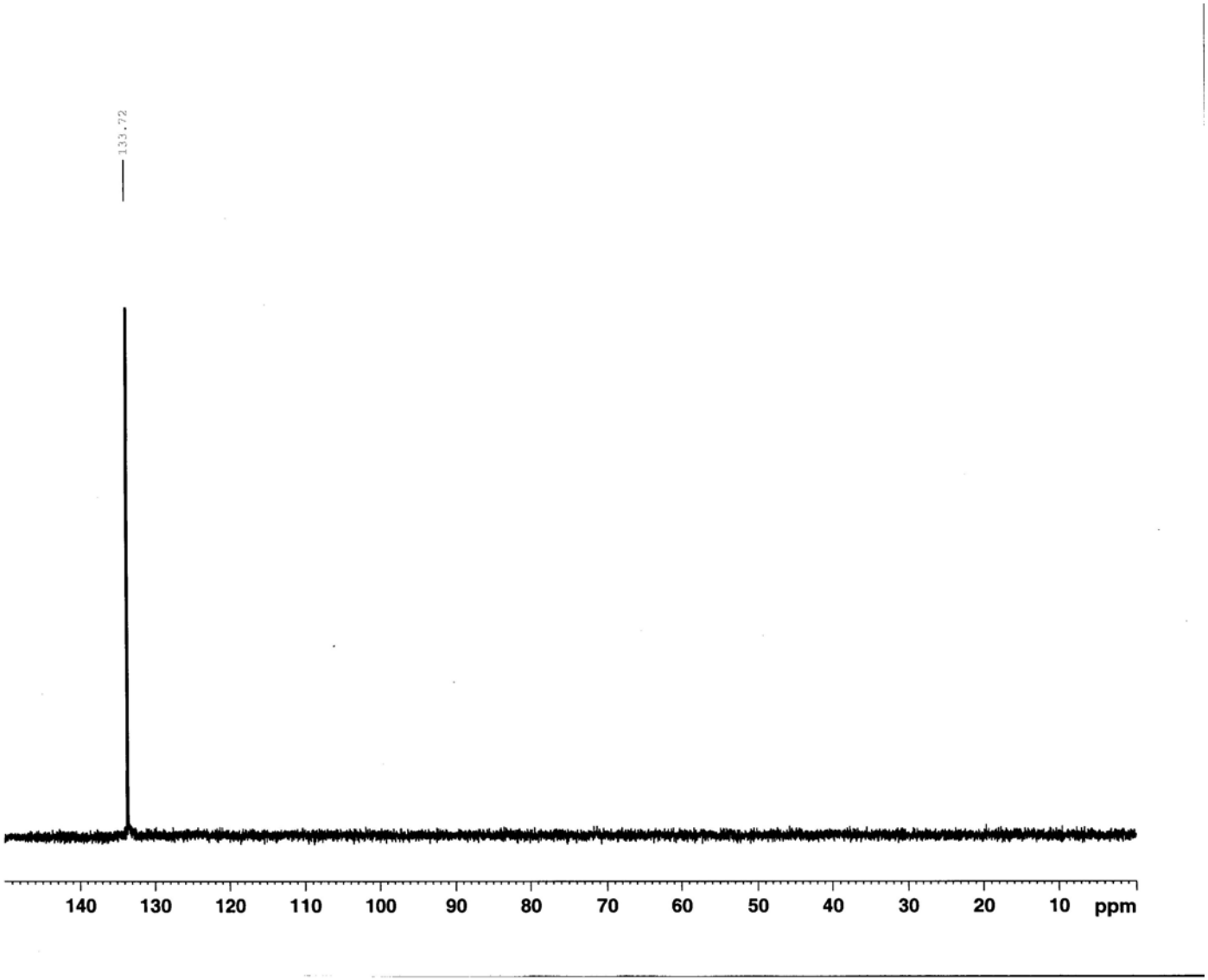
^{1}H NMR of Zn(^{S}Aa, ^{R}Aa)

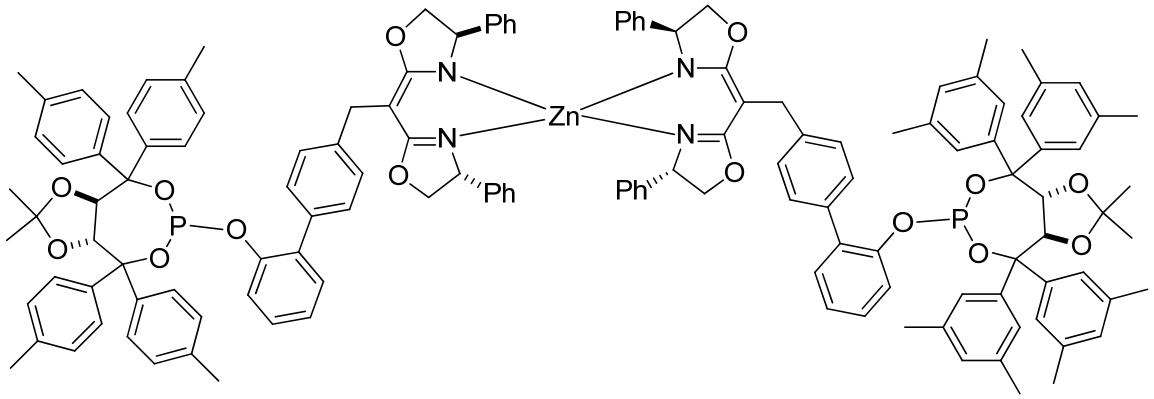


^{13}C NMR of Zn(^{S}Aa, ^{R}Aa)



^{31}P NMR of Zn(^{S}Aa, ^{R}Aa)

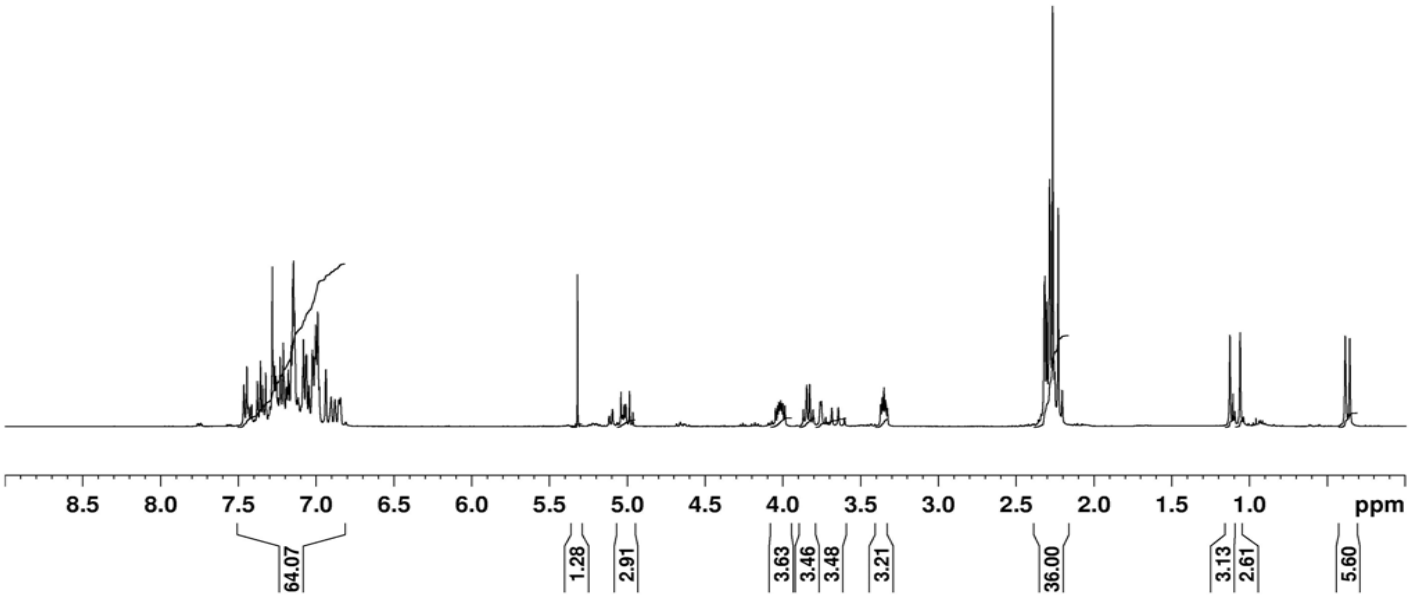




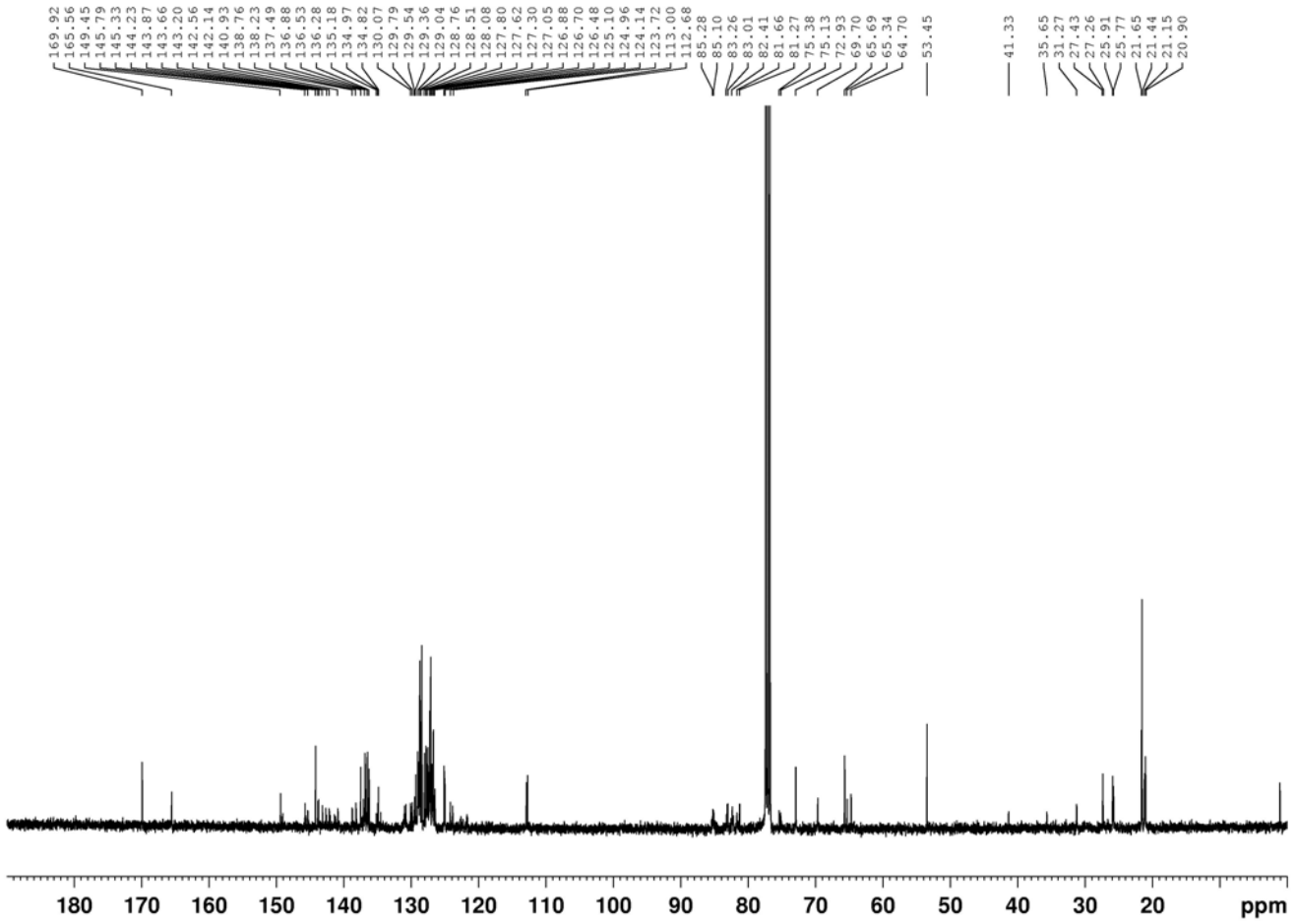
The general procedure for the synthesis of self-assembled ligands affords the compound pictured (99%) as a white solid.

m.p.	171 - 173 °C
Optical rotation	$[\alpha]D^{25}$ = -67.5 (c = 0.2, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.47 – 6.91 (68H, m), 5.32 (1H, s), 5.04 – 4.99 (3H, m), 4.05 – 3.83 (4H, m), 3.86 – 3.80 (4H, m), 3.76 – 3.60 (4H, m), 3.38 – 3.33 (4H, m), 2.32 – 2.23 (36H, m), 1.13 (3H, s), 1.06 (3H, s), 0.39 (3H, s), 0.36 ppm (3H, s)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 169.9, 165.6, 149.5, 145.8, 145.3, 144.2, 143.9, 143.7, 143.2, 142.6, 142.1, 140.9, 138.8, 138.2, 137.5, 136.9, 136.5, 136.3, 135.2, 134.9, 134.8, 130.1, 129.8, 129.5, 129.4, 129.0, 128.8, 128.5, 128.1, 127.8, 127.6, 127.1, 126.9, 126.7, 126.5, 125.1, 125.0, 124.1, 112.7, 85.3, 85.1, 83.3, 83.0, 82.4, 81.7, 81.3, 75.4, 75.1, 72.9, 69.7, 65.7, 65.3, 64.7, 53.5, 41.3, 35.7, 31.3, 27.4, 27.3, 25.9, 25.8, 21.7, 21.4, 21.2, 20.9 ppm
^{31}P NMR (162 MHz, $CDCl_3$)	δ 135.5, 135.0 ppm
HRMS (ESI)	calcd. for $C_{138}H_{132}N_4O_{14}P_2Zn$ $[(M+Li)^+]$, 2197.8508; found, 2197.8728 *m/z*

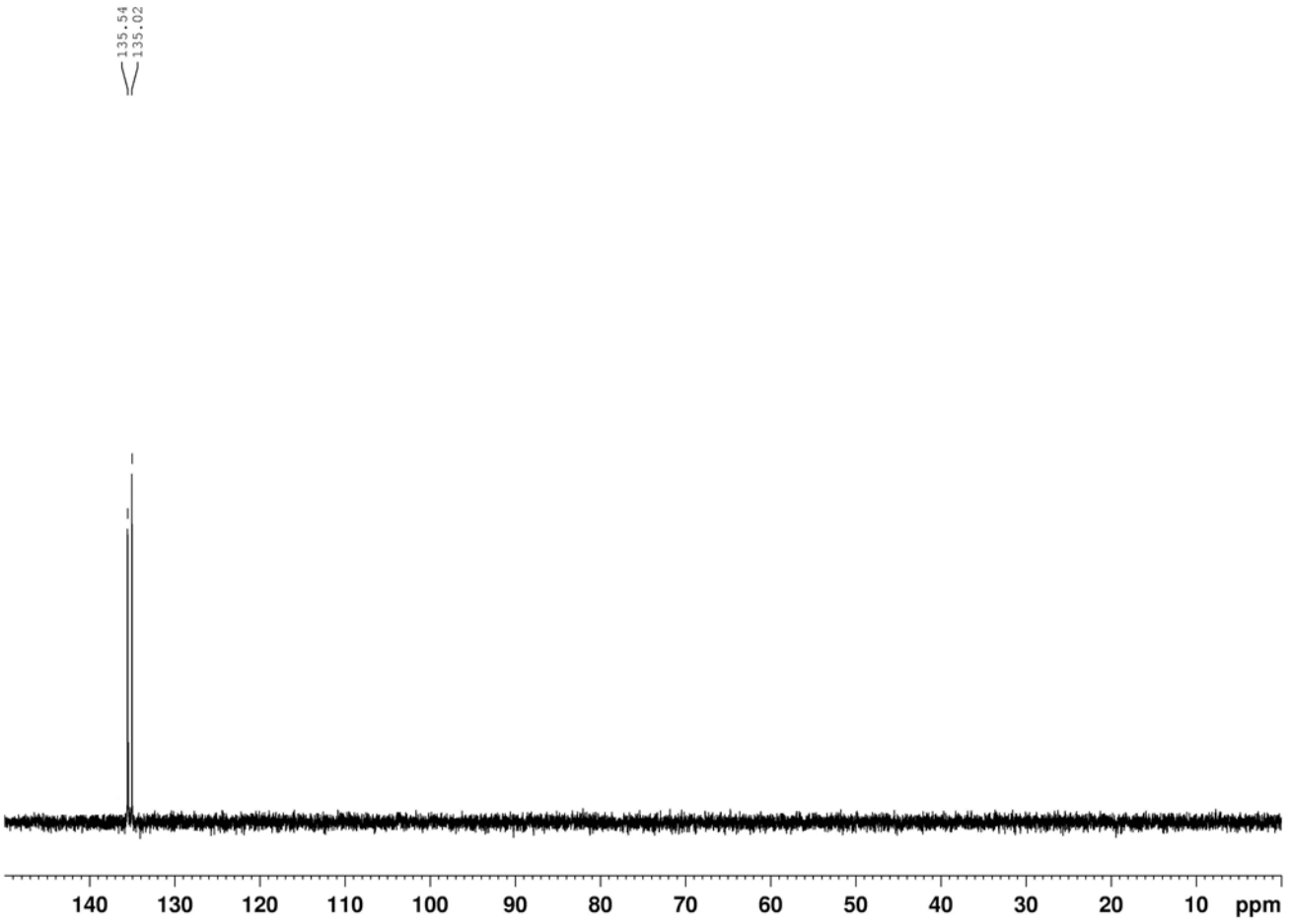
^{1}H NMR of Zn(^{S}Ab, ^{R}Ac)

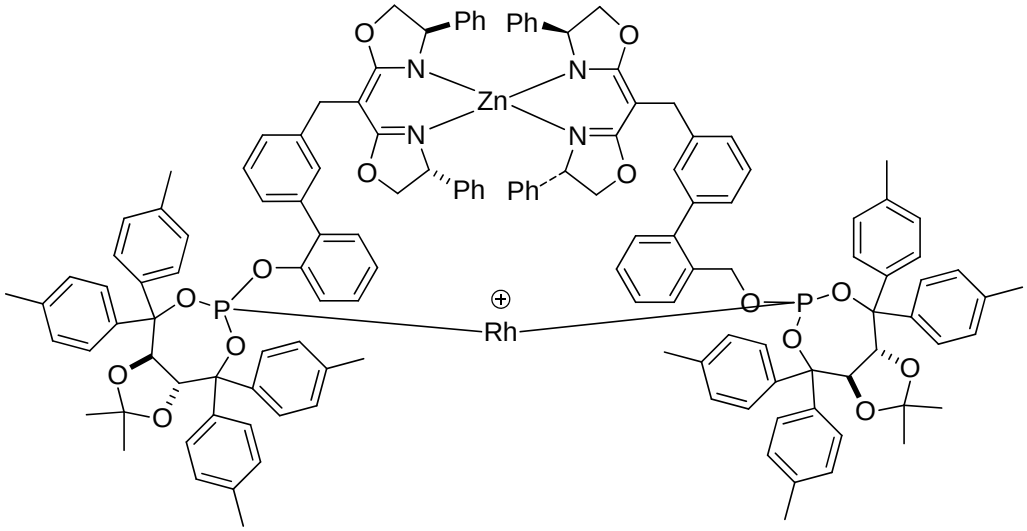


^{13}C NMR of Zn(^{S}Ab, ^{R}Ac)



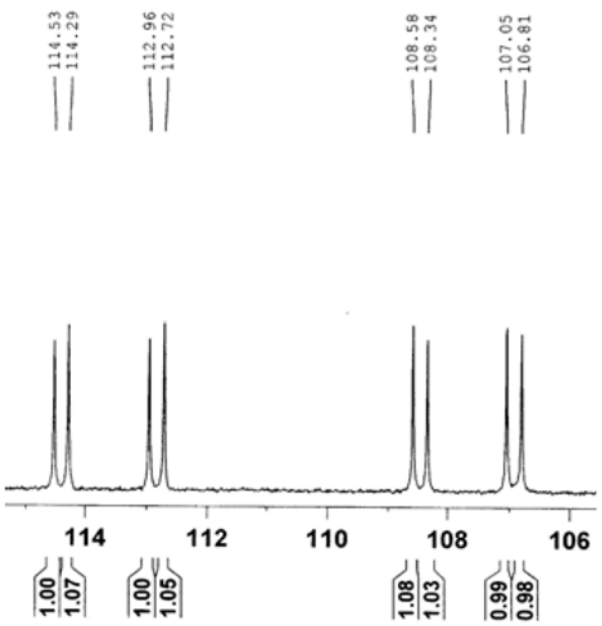
^{31}P NMR of Zn(^{S}Ab, ^{R}Ac)

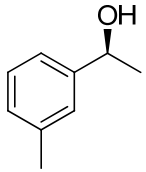




^{31}P NMR (162 MHz, CD_2Cl_2)	δ 107.7 (dd, $J_{P\text{-}Rh}$ = 249 Hz, $J_{P\text{-}P}$ = 39 Hz), 113.16 (dd, $J_{P\text{-}Rh}$ = 254 Hz, $J_{P\text{-}P}$ = 39 Hz)

^{31}P NMR of Zn(^{S}Bc, ^{R}Cc)

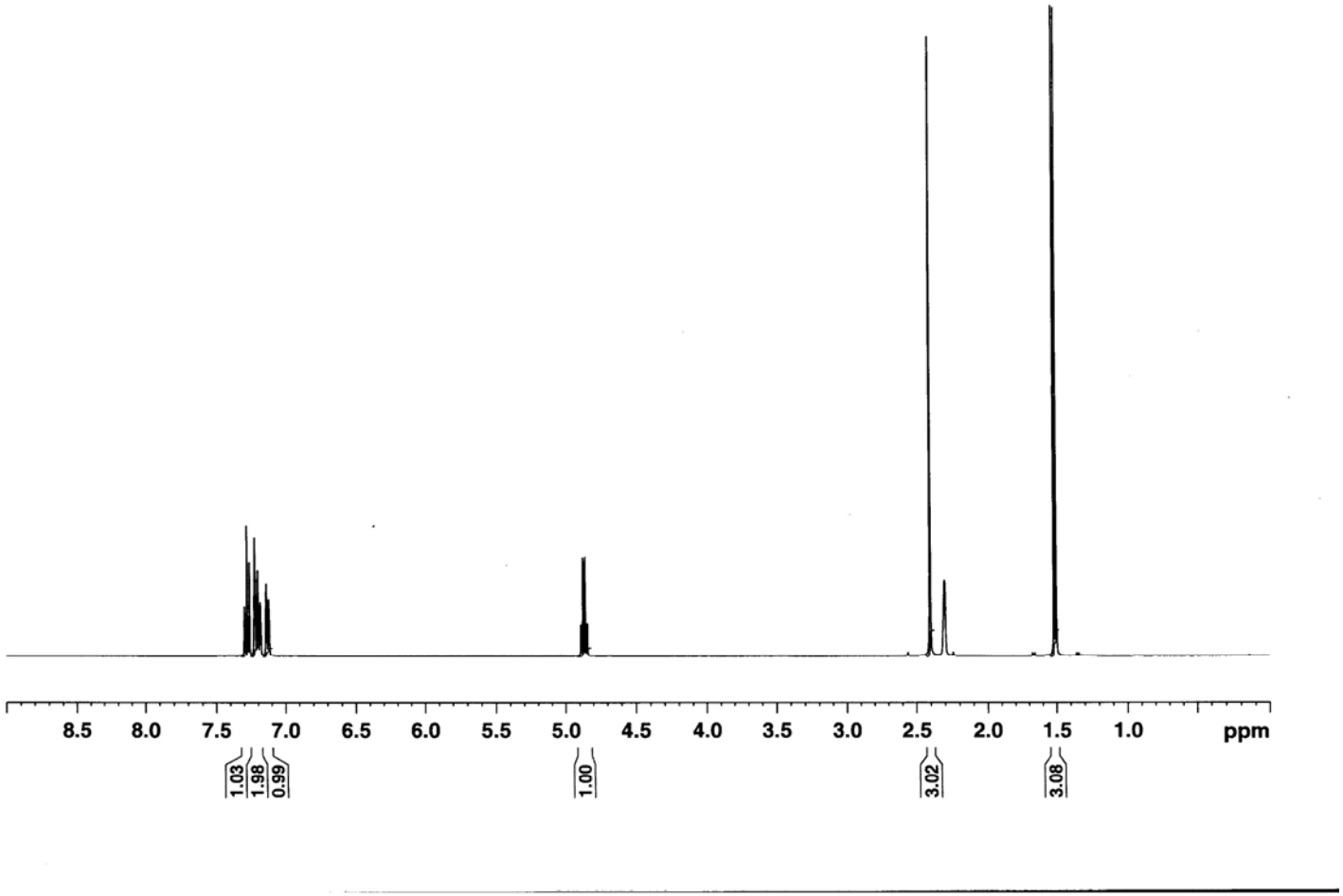




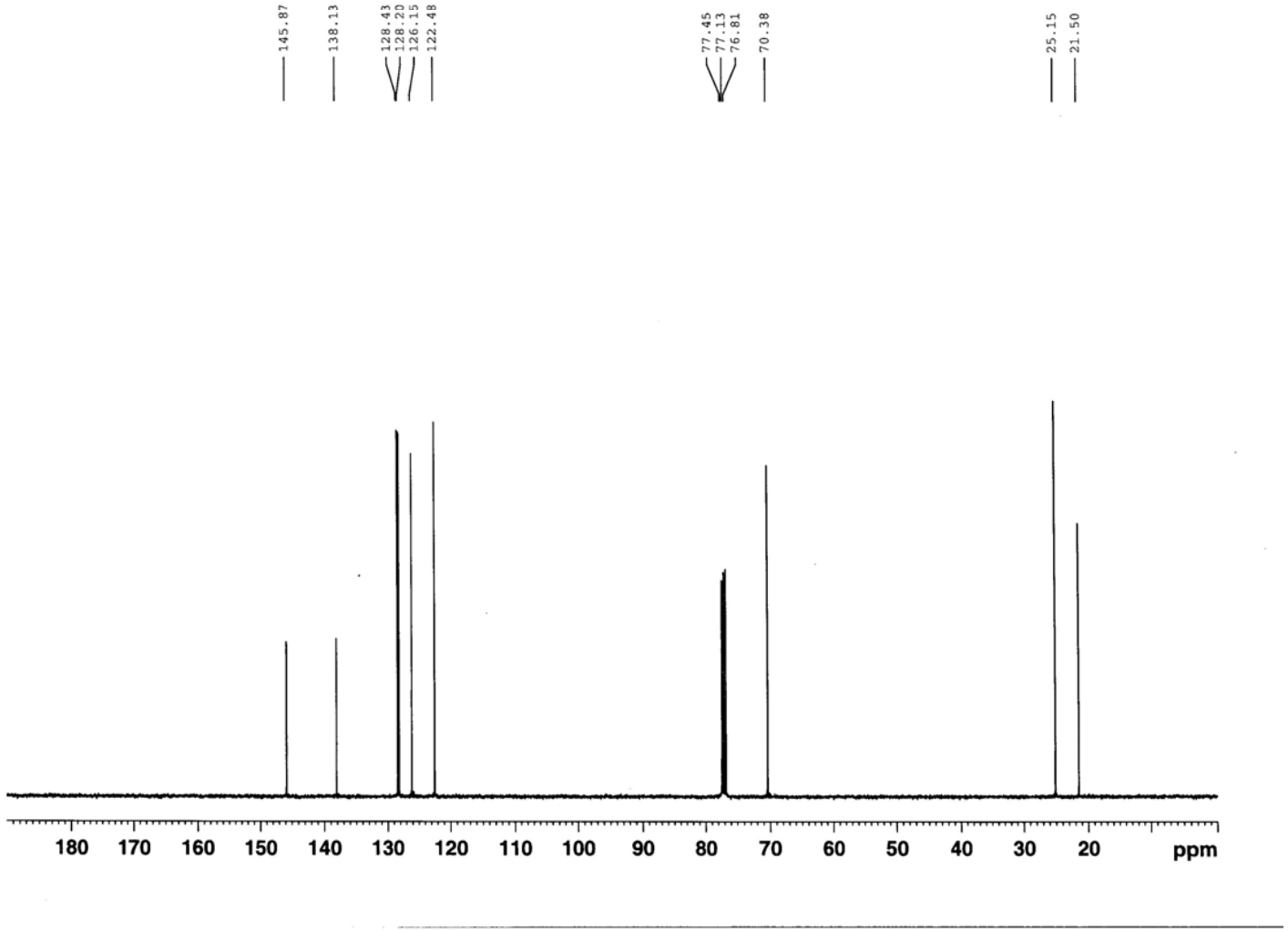
The general procedure for the preparative scale reaction affords, after flash chromatography on silica gel (10:90 ethyl acetate:hexane), the compound pictured (93%) as a clear oil.

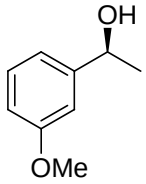
Optical rotation	$[\alpha]D^{25}$ = +65.3 (c = 1.0, $CHCl_3$)
GC analysis	J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β, 120 °C (1 min hold) to 130°C @ 1°C/min then165°C @ 2°C/min) found peaks at 15.19 (2.8%, (R)) and 15.74 (97.2%, (S))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.28 (1H, t, J = 7.6 Hz), 7.26 (1H, s), 7.22 (1H, dd, J = 9.6, 4.1 Hz), 7.13 (1H, d, J = 7.6 Hz), 4.89-4.84 (1H, q, J = 12.8, 6.4 Hz), 2.40 (3H, s) 1.51 ppm (3H, d, J = 6.8 Hz);
^{13}C NMR (100 MHz, $CDCl_3$)	δ 145.9, 138.1, 128.4, 128.2, 126.2, 122.5, 70.4, 25.2, 21.5 ppm
HRMS (FABS)	calcd. for $C_9H_{12}O$ $[(M+H)^+]$, 136.0888; found: 136.0886 m/z

^{1}H NMR of 4a



^{13}C NMR of 4a

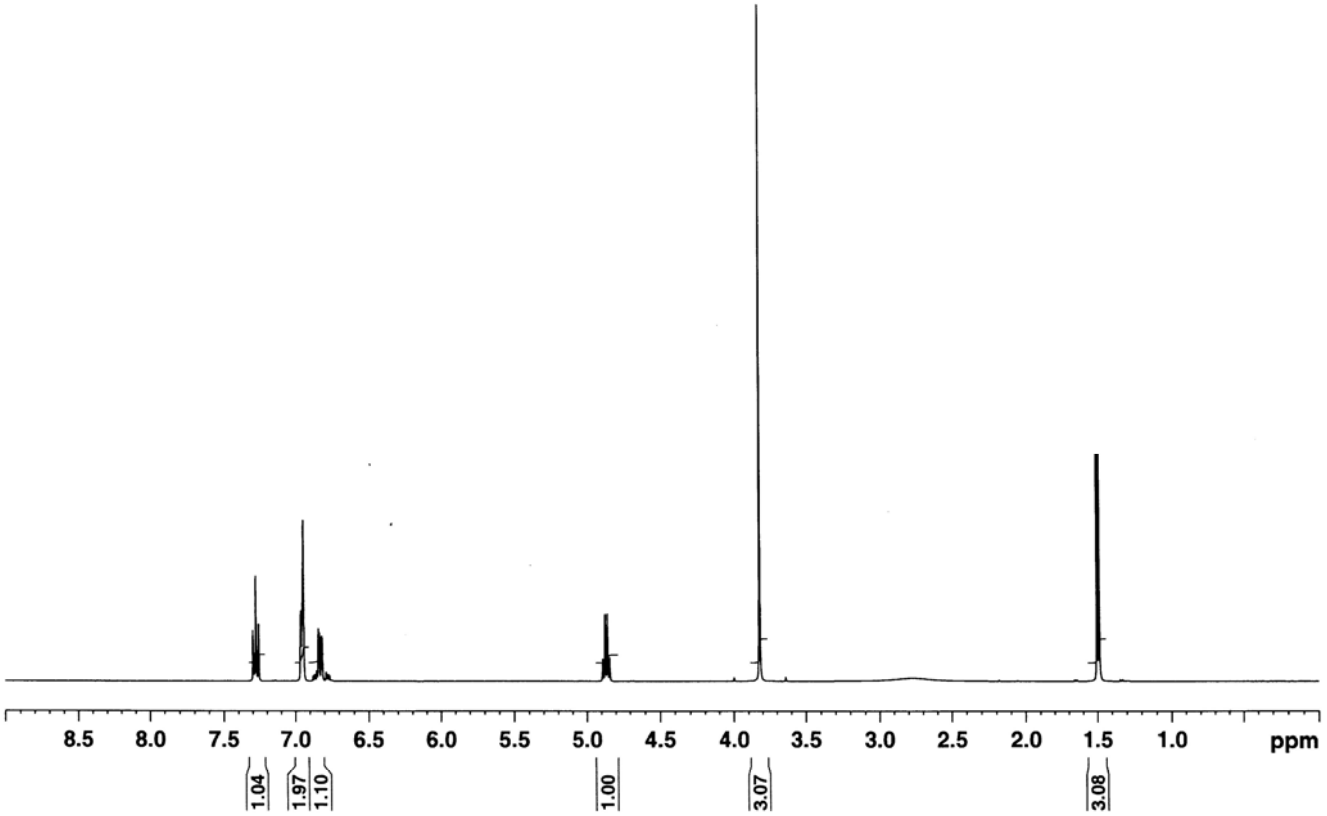




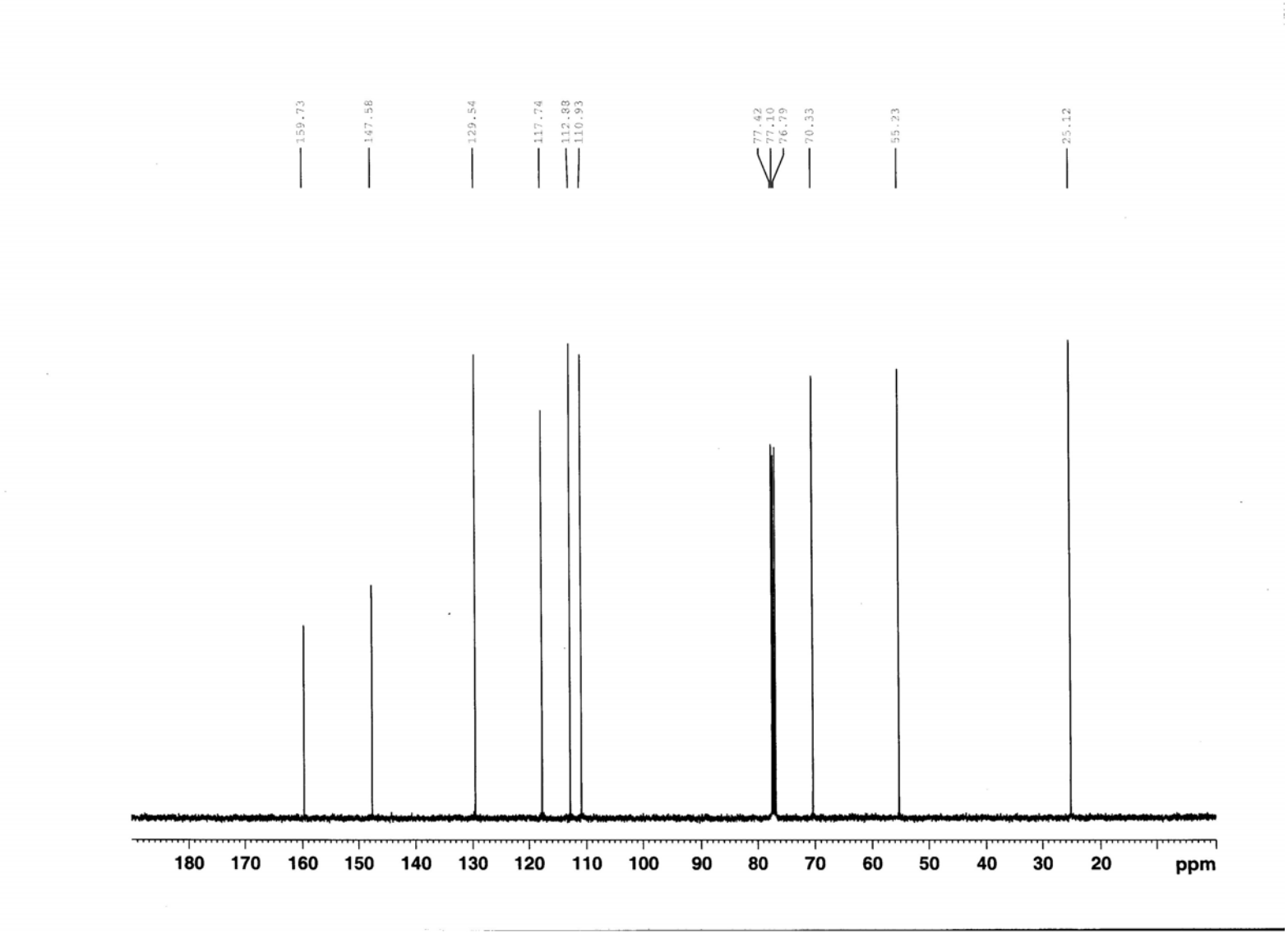
The general procedure for the preparative scale reaction affords, after flash chromatography on silica gel (10:90 ethyl acetate:hexane), the compound pictured (90%) as a clear oil.

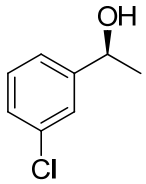
Optical rotation	$[\alpha]D^{25}$ = +40.4 (c = 1.1, $CHCl_3$)
GC analysis	J&W Scientific 30 m x 0.25 mm ID Cyclosil β, 120 °C (1 min hold) to 130°C @ 1°C/min then to 165°C @ 2°C/min) found peaks at 24.15 (2.5%, (*R*)) and 24.53 (97.5%, (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.28 (1H, t, *J* = 8.0 Hz), 6.96-6.95 (2H, m), 6.84-6.82 (1H, dd, *J* = 7.7, 2.4 Hz), 4.89-4.84 (1H, q, *J* = 12.8, 6.4 Hz), 3.82 (3H, s) 1.49 ppm (3H, d, *J* = 6.4 Hz)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 159.7, 147.6, 129.5, 117.7, 112.9, 110.9, 70.3, 55.2, 25.1 ppm
HRMS (FABS)	calcd. for $C_9H_{12}O_2$ [$(M+H)^+$], 152.0837; found: 152.0835 *m/z*

^{1}H NMR of 4b



^{13}C NMR of 4b

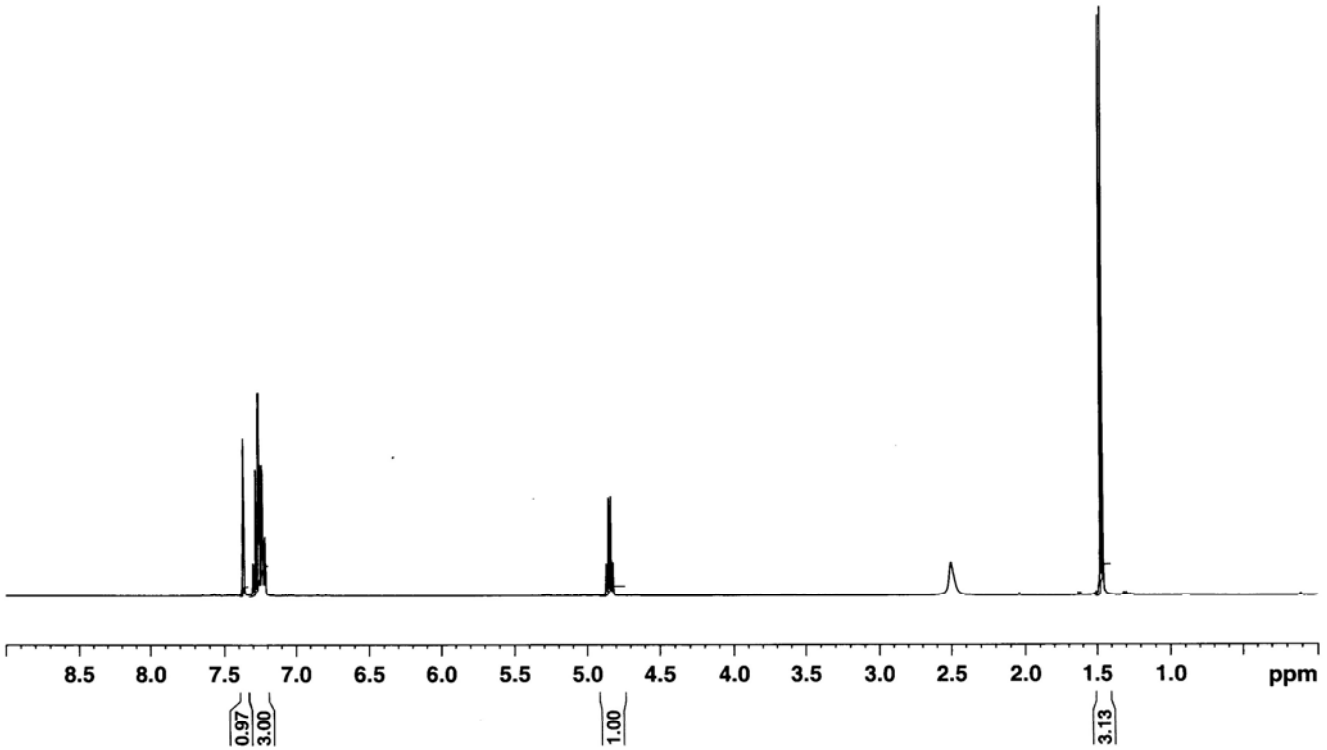




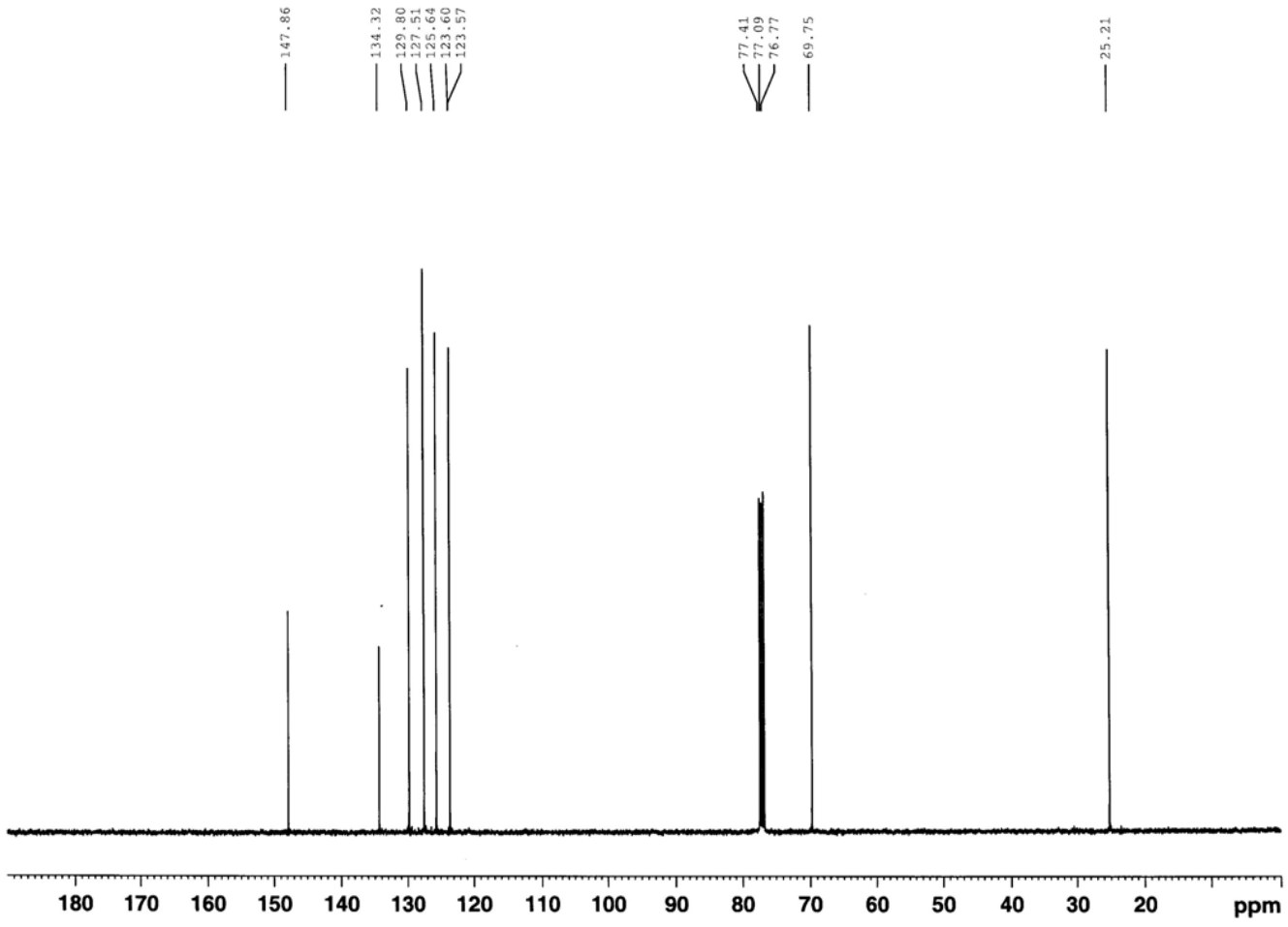
The general procedure for the preparative scale reaction affords, after flash chromatography on silica gel (10:90 ethyl acetate:hexane), the compound pictured (89%) as a clear oil.

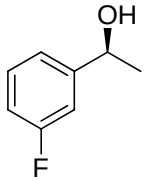
Optical rotation	$[\alpha]D^{25}$ = +50.3 (c = 1.2, $CHCl_3$)
GC analysis	(J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β, 120 °C (1 min hold) to 130°C @ 1°C/min then 165°C @ 2°C/min) found peaks at 23.73 (1.8%, (R)) and 23.99 (98.2%, (S))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.37 (1H, s), 7.30-7.21 (3H, m), 4.87-4.82 (1H, q, J = 12.8, 6.4 Hz), 1.46 ppm (3H, d, J = 6.4 Hz)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 147.9, 134.2, 129.8, 127.5, 125.6, 123.6, 69.8, 25.2 pm
HRMS (FABS)	calcd. for C_8H_9ClO $[(M+H)^+]$, 156.0342; found: 156.10338 m/z.

^{1}H NMR of 4c



^{13}C NMR of 4c

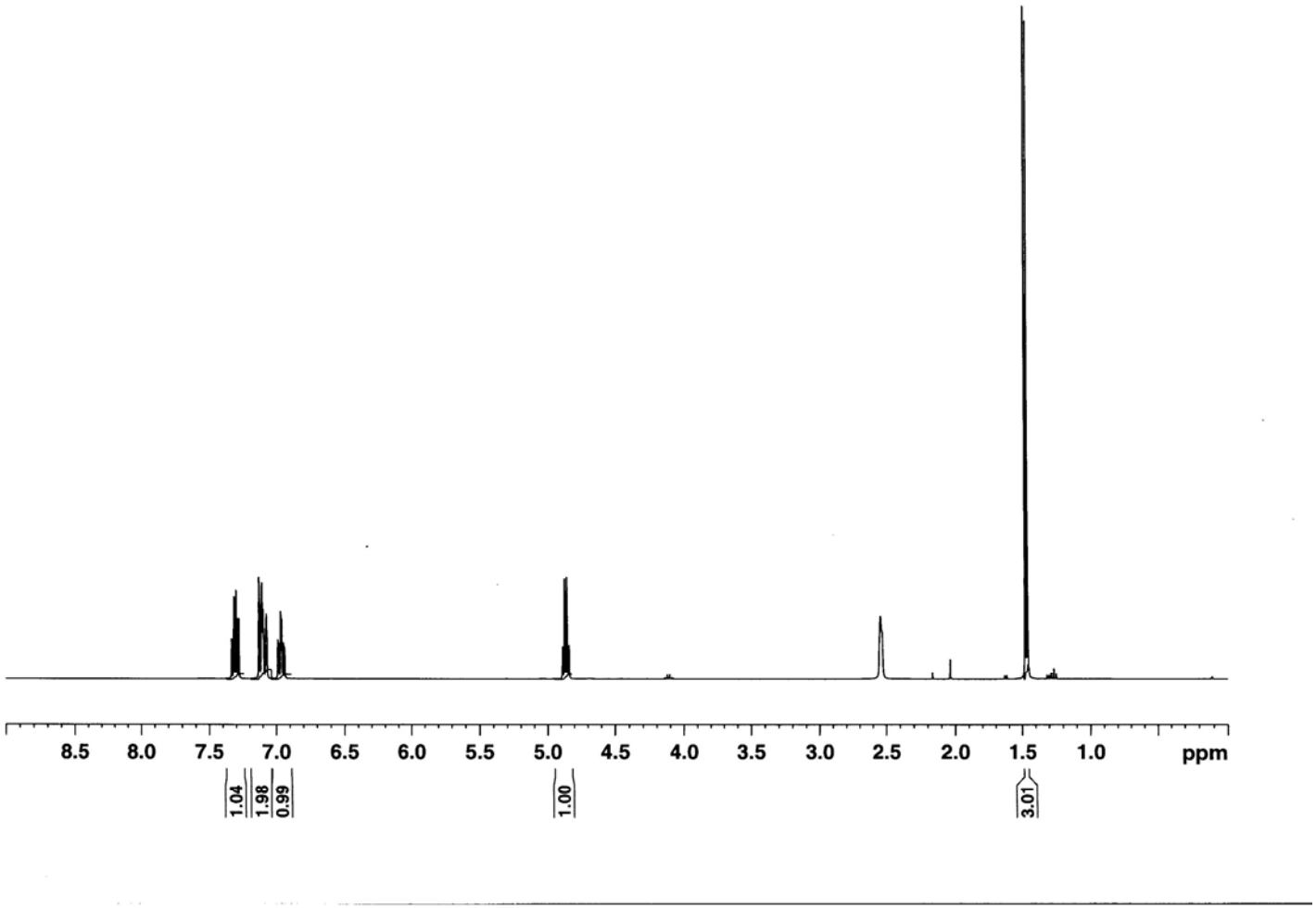




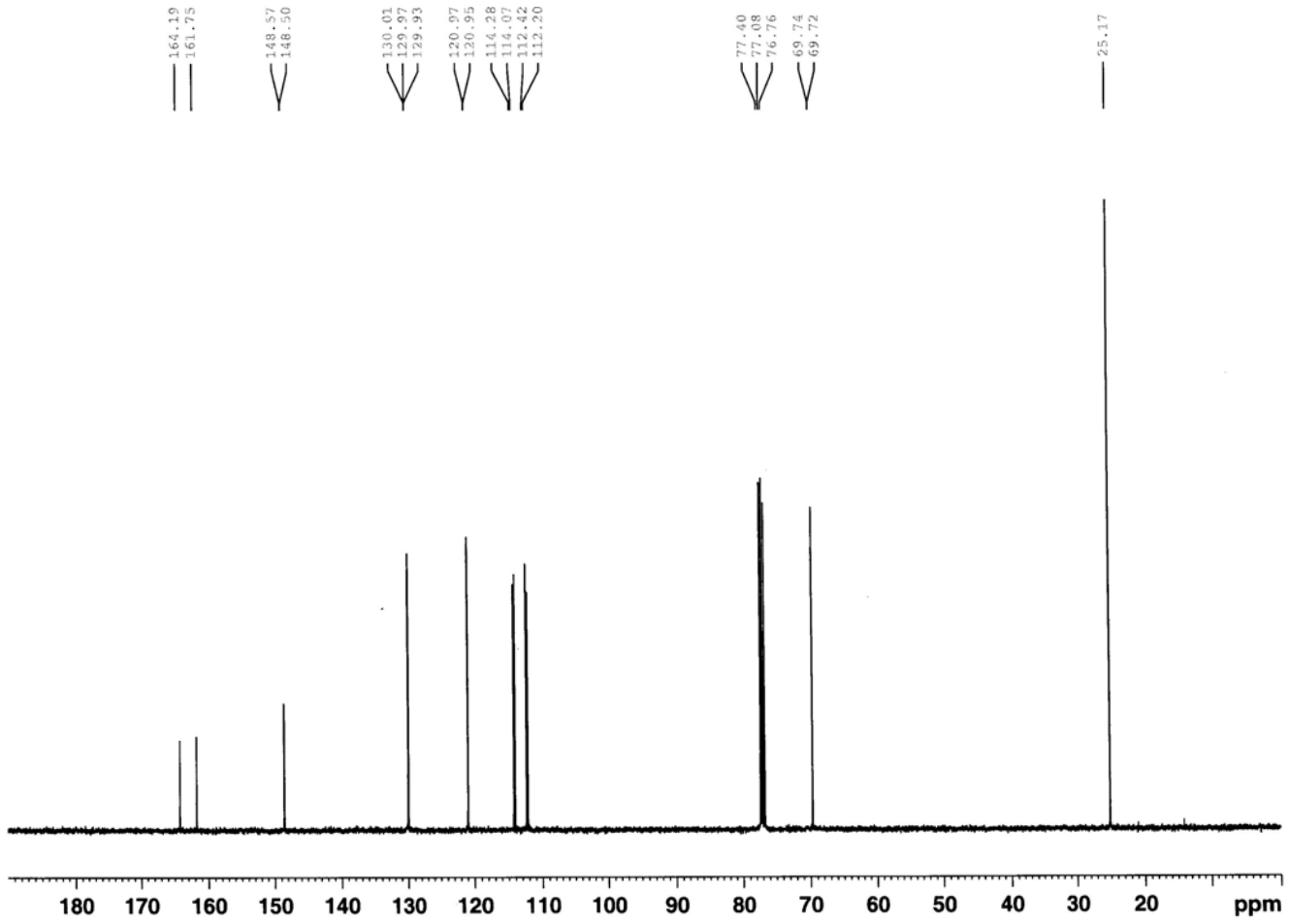
The general procedure for the preparative scale reaction affords, after flash chromatography on silica gel (10:90 ethyl acetate:hexane), the compound pictured (89%) as a clear oil.

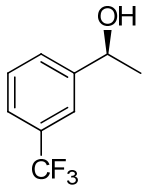
Optical rotation	$[\alpha]D^{25}$ = +39.8 (c = 1.8, $CHCl_3$)
GC analysis	(J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β, 120 °C (1 min hold) to 130°C @ 1°C/min then 165°C @ 2°C/min) found peaks at 13.23 (2.2%, (*R*)) and 13.52 (97.8%, (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.29 (1H, dt, *J* = 8.0, 2.1 Hz), 7.13-7.07 (2H, m), 6.99-6.94 (1H, dt, *J* = 9.2, 3.6 Hz), 4.86 (1H, q, *J* = 12.8, 6.4 Hz), 1.48 ppm (3H, d, *J* = 6.5 Hz)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 163.0 (d, *J*CF = 245.5 Hz), 148.5 (d, *J*CF = 7.0 Hz), 130.0 (t, *J*CF = 14.1 Hz), 121.0 (d, *J*CF = 2.0 Hz), 114.2 (d, *J*CF = 21.1 Hz), 112.3 (d, *J*CF = 22.1 Hz), 69.7 (d, *J*CF = 2.0 Hz), 25.2 ppm
HRMS (FABS)	calcd. for C_8H_9FO $[(M+H)^+]$, 140.0639; found: 140.0639 *m/z*

^{1}H NMR of 4d



^{13}C NMR of 4d

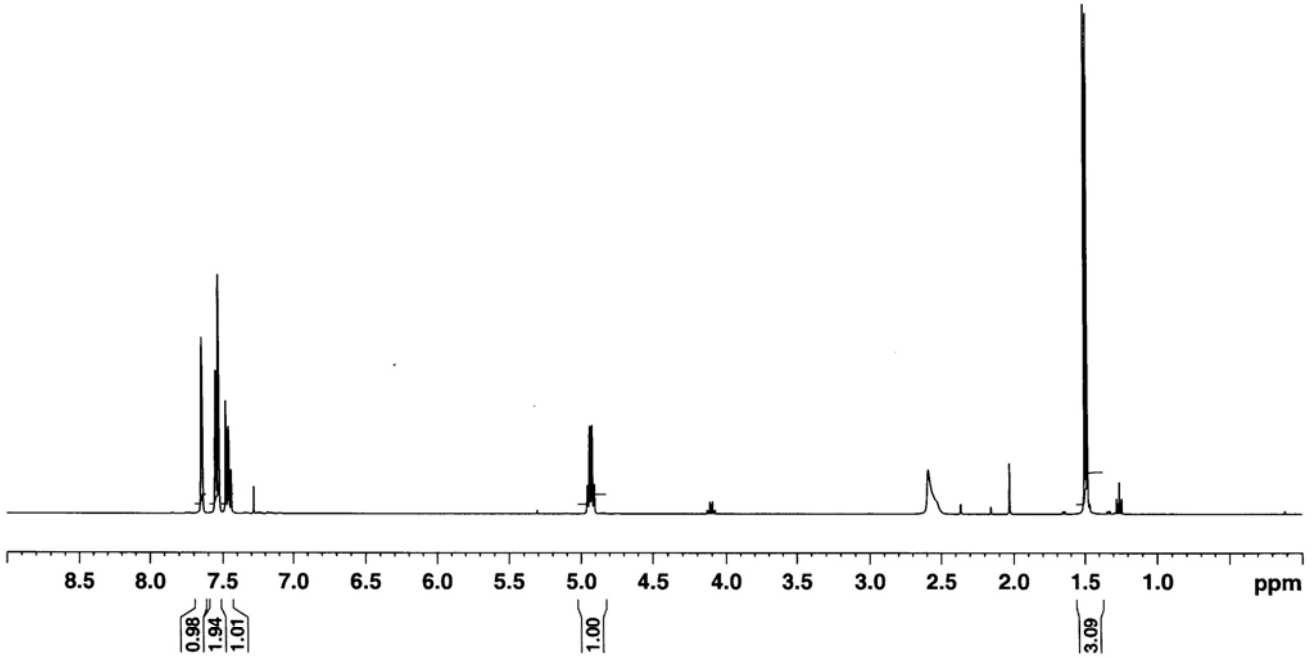




The general procedure for the preparative scale reaction affords, after flash chromatography on silica gel (10:90 ethyl acetate:hexane), the compound pictured (87%) as a clear oil.

Optical rotation	$[\alpha]D^{25}$ = +39.1 (c = 0.9, $CHCl_3$)
GC analysis	(J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β, 120 °C (1 min hold) to 130°C @ 1°C/min then 165°C @ 2°C/min) found peaks at 13.34 (1.3%, (*R*)) and 13.59 (98.7%, (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.65 (1H, s), 7.55-7.53 (2H, m), 7.47 (1H, d, *J* = 7.7 Hz), 4.93 (1H, q, *J* = 12.8, 6.4 Hz), 2.37 (3H, s) 1.49 ppm (3H, d, *J* = 6.4 Hz)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 146.7, 130.7 (q, *J*CF = 32.2 Hz), 128.9, 128.8, 124.2 (t, *J*CF = 4.0 Hz), 125.5 (d, *J*CF = 271.7 Hz), 122.2 (q, *J*CF = 4.0 Hz), 69.8, 25.3 ppm
HRMS (FABS)	calcd. for $C_9H_9F_3O$ $[(M+H)^+]$, 190.0606; found: 190.0599 *m/z*

^{1}H NMR of 4e



^{13}C NMR of 4e