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Supporting Information

69451 Weinheim, Germany

Highly Enantioselective Diphenylzinc Addition to Aliphatic and Aromatic Aldehydes Catalyzed by a Readily Available H_8BINOL Derivative

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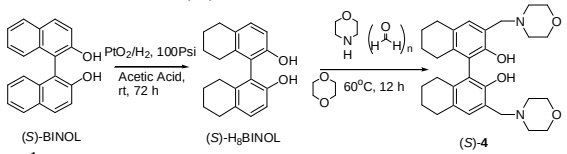
Contents:

Instruments:

NMR: Varian 300MHz and 500MHz NMR system.
Polarimeter: JASCO digital polarimeter DIP-1000.
Chiral GC: HP 6890 series GC; Supelco Beta-Dex 120 Fused silica capillary Column (30 m Length × 0.25 mm ID× 0.25 μm film thickness).
HPLC: Waters 600 pump and Waters 486 TUNABLE ABSORBANCE DETECTOR (254nm), Chiralcel OD and Chiralpak AD columns.

Synthesis and Characterization of (*S*)-4:



Preparation of (*S*)-H_8BINOL:[1]

A beaker containing (*S*)-BINOL (10 g, 0.035mol), PtO_2 (0.88 g, 0.0022 mol), glacial acetic acid (180 mL) and a stir bar was placed in a Parr Non-Stirred Pressure Vessel, and 100psi hydrogen was charged. After the reaction mixture was stirred at room temperature for 72 h, it was filtered through a thin pad of celite to remove the catalyst and concentrated with roto-evaporation. CH_2Cl_2 (250 mL) and water (200 mL) were added into the residue and the CH_2Cl_2 layer was separated. The water phase was extracted with CH_2Cl_2 (2 x 50 mL), and the combined organic layers were washed with water (2 x 100 mL), $NaHSO_3$ (10% aq., 100 mL) and dried over Na_2SO_4. After removal of the solvents, the remaining solid was recrystallized from heptanes (75 mL) to give (*S*)-H_8BINOL as white needle crystals (9.6 g, 92% yield).

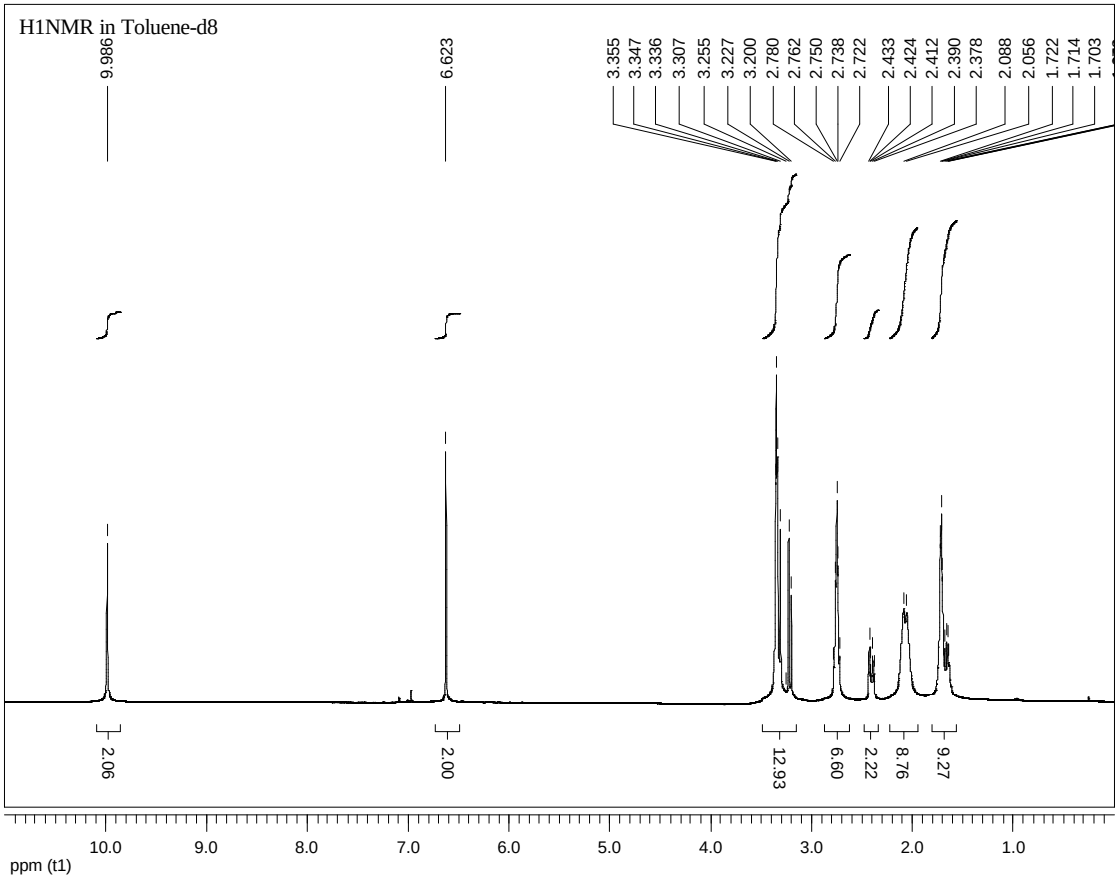
Preparation of (*S*)-**4**:

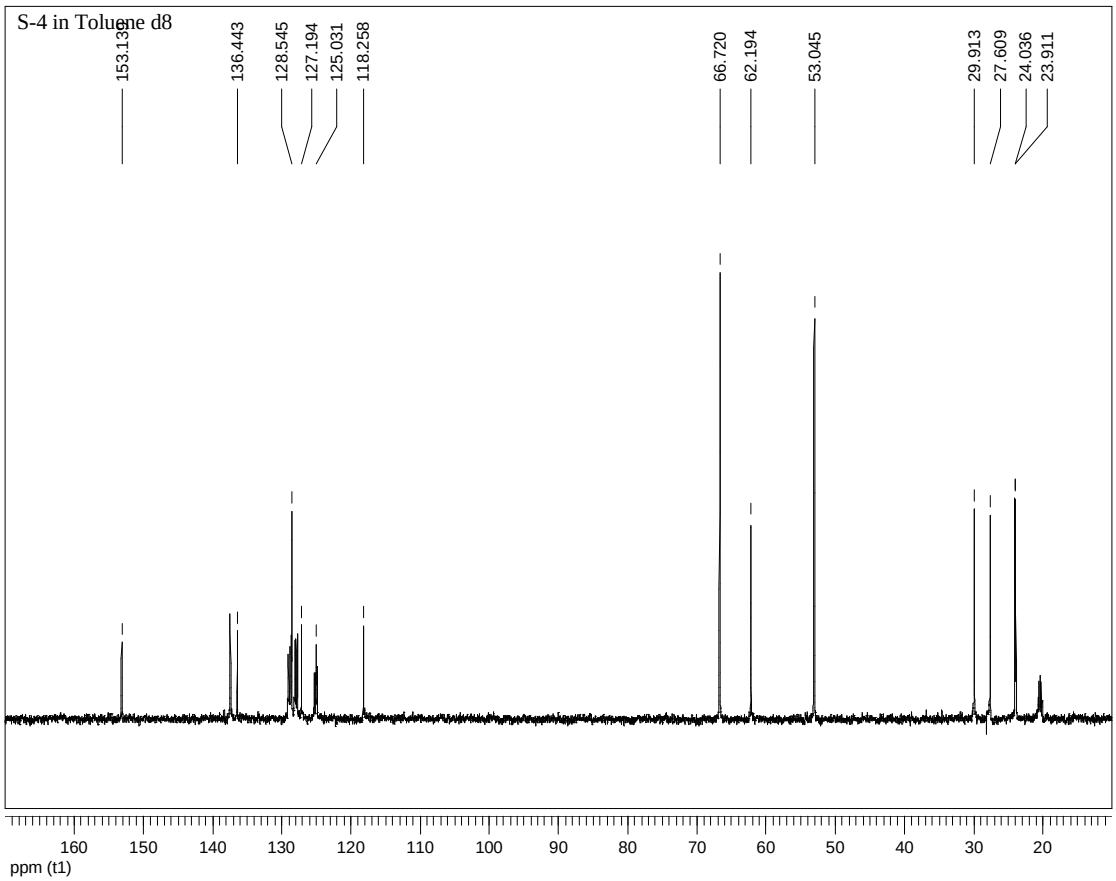
(*S*)-H_8BINOL (5.0 g, 0.017mol), morpholinomethanol (50 mL, see the preparation below) and 1,4-dioxane (30 mL) were mixed in a 250 mL round bottom flask at room temperature. After the mixture was heated at 60 °C for 12 h with stirring, it was cooled down to room temperature and combined with ethyl acetate (150 mL) in a separation funnel. The organic layer was then washed with saturated $NaHCO_3$ (3 x 100 mL) and water (2 x 100 mL). Removal of ethyl acetate gave (*S*)-**4** as a white solid (8.0 g, 95% yield). Recrystalization of this compound from ethanol gave white needle crystals.[2,3]

Preparation of Morpholinomethanol:

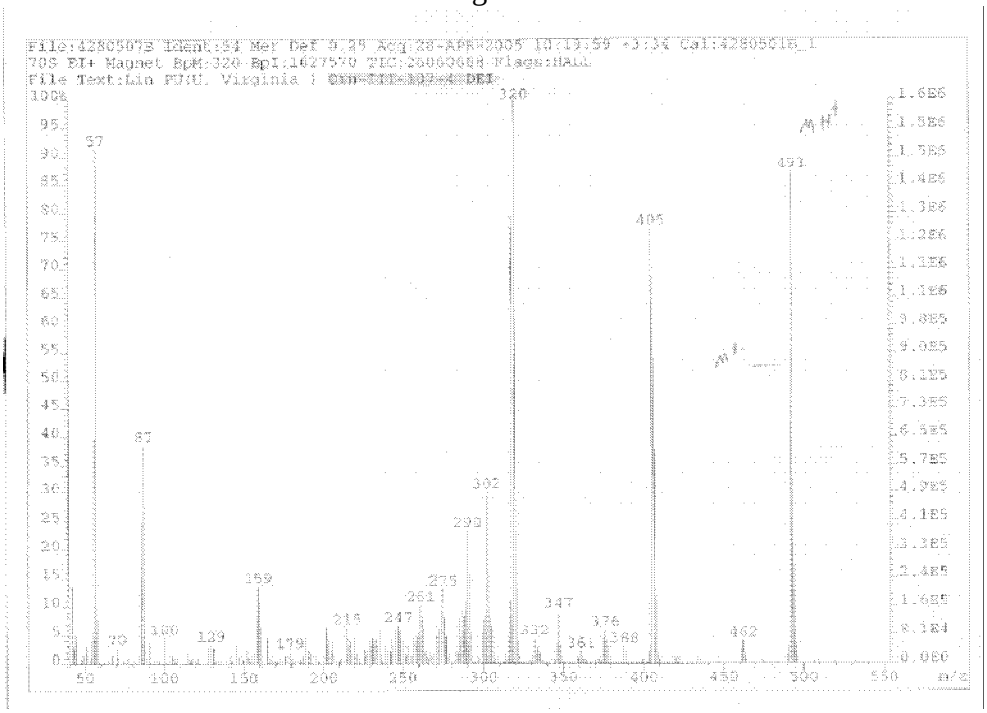
To a 250 mL round bottom flask containing paraformaldehyde (30.0 g, 1.0 mol), morpholine (88 mL, 1.0 mol) was added dropwise at 0 °C over 1 h with vigorous stirring. (Caution: this was a highly exothermic reaction.) The reaction mixture was allowed to warm up to room temperature. After 4 h, the mixture was slowly heated to 60 °C and maintained at the temperature for 10 h. This led to the formation of morpholinomethanol as a clear syrup-like liquid.

Characterization of (*S*)-**4**, (*S*)-3,3'-bismorpholinylmethyl-5,5', 6,6',7,7',8,8'-octahydro-1,1'-bi-2- naphthol.
^{1}H NMR (500 MHz, toluene-d_8) δ 9.99 (s, 2H), 6.62 (s, 2H), 3.20 to 3.36 (m, 12H), 2.75 (m, 6H), 2.42 (m, 2H), 2.07 (m, 8H), 1.63 to 1.72 (m, 8H).
^{13}C NMR (125 MHz, toluene-d_8) δ 153.14, 136.44, 128.54, 127.19, 125.031, 118.26, 66.72, 62.19, 53.04, 29.91, 27.61, 24.04, 23.91.
$[\alpha]_D^{25}$ = -35.4 (c = 1.04, THF).
Anal. Calcd. for $C_{30}H_{40}N_2O_4$: C, 73.14; H, 8.18; N, 5.69. Found: C, 73.22; H, 8.20; N, 5.66. HRMS Calcd for $C_{30}H_{40}N_2O_4$: 492.2988. Found. 492.2969.

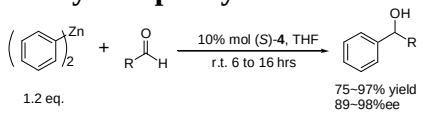

H1NMR in Toluene-d8
9.986
6.623
3.355
3.347
3.336
3.307
3.255
3.227
3.200
2.780
2.762
2.750
2.738
2.722
2.433
2.424
2.412
2.390
2.378
2.088
2.056
1.722
1.714
1.703
2.06
2.00
12.93
6.60
2.22
8.76
9.27
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)



High resolution MS

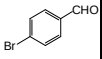
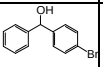
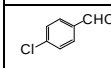
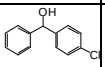
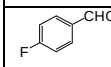
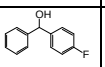
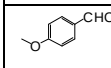
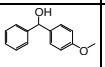
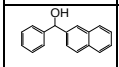
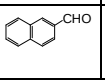


General procedure for the catalytic diphenylzinc addition to aldehydes.



Under nitrogen to a 10 mL round bottom flask (flame dried under vacuum), diphenylzinc (66 mg, 0.3 mmol, 1.2 equiv), (*S*)-**4** (12.3 mg, 0.025 mmol, 0.1 equiv) and THF (2.0 mL, anhydrous) were added sequentially. After the resulting solution was stirred at room temperature for 1 h, an aldehyde (0.25 mmol) was added and the reaction was monitored by TLC. At the completion of the reaction, ammonium chloride (saturated, aq.) was added to quench the reaction. The mixture was extracted with methylene chloride three times. After removal of the solvents, the residue was purified by column chromatograph on silica gel eluted with hexanes/ethyl acetate (12:1) to give the product as either colorless oil or white solid in 75 - 97% yield.

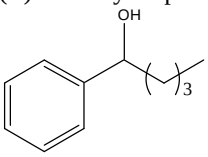
Chiral HPLC or GC conditions for the ee determination of the alcohol products.

aldehyde	product	time	yield	ee	instrument	method	t_S(min)	t_R(min)	config	ref
		12h	87%	92%	HPLC chiralcel OD column	98:2 Hexanes:^{i}PrOH, 1 mL/min	16.4	12.9	R[a]	4,5
		12h	78%	93%	HPLC chiralcel OD column	98:2 Hexanes: ^{i}PrOH, 1 mL/min	14.6	12.2	R[b]	5
		12h	75%	92%	HPLC chiralcel OD column	98:2 Hexanes: ^{i}PrOH, 1 mL/min	17.0	14.6	R[b]	6
		16h	82%	92%	GC Supelco Beta-Dex 120	145°C isotherm, 1 mL/min	13.0	13.3	R[b]	6
		6h	93%	98%	GC Supelco Beta-Dex 120	120°C isotherm, 1 mL/min	39.4	40.4	R[a]	7,8
		12h	88%	96%	HPLC chiralcel OD column	98:2 Hexanes: ^{i}PrOH, 1 mL/min	15.1	13.5	R[b]	9
		8h	96%	98%	HPLC chiralcel OD column	99:1 Hexanes: ^{i}PrOH, 0.4 mL/min	46.0	60.1	R[b]	7
		16h	90%	89%	HPLC chiralcel OD column	95:5 Hexanes: ^{i}PrOH, 1 mL/min	16.8	14.7	S[b]	10
		16h	91%	89%	HPLC chiralcel OD column	98:2 Hexanes: ^{i}PrOH, 1 mL/min	29.8	34.0	S[b]	10
		16h	90%	89%	HPLC chiralcel OD column	98:2 Hexanes: ^{i}PrOH, 1 mL/min	29.7	35.4	S[a]	11
		16h	92%	94%	HPLC chiralcel OD column	98:2 Hexanes: ^{i}PrOH, 1 mL/min	28.8	32.1	S[a]	10, 12
		16h	91%	91%	HPLC chiralpak AD column	98:2 Hexanes: ^{i}PrOH, 1 mL/min	44.0	40.7	S[b]	13
		16h	97%	89%	HPLC chiralcel OD column	90:10 Hexanes: ^{i}PrOH, 1 mL/min	16.3	19.7	S[b]	11

Note: Configurations: a. Determined by comparison with literature values, b. assigned by assuming the same reaction pathway as others.

Characterization of the diphenylzinc addition products:

(*R*)-1-Phenyl-1-pentanol [reference 4,5]

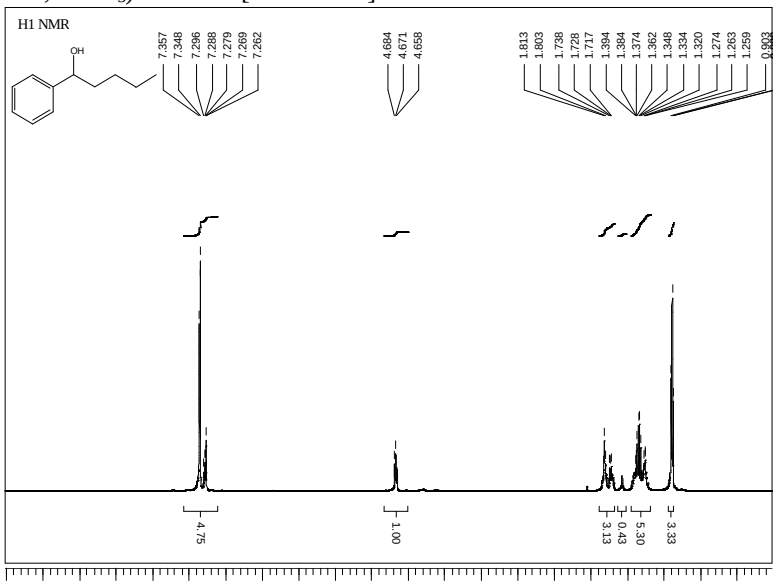


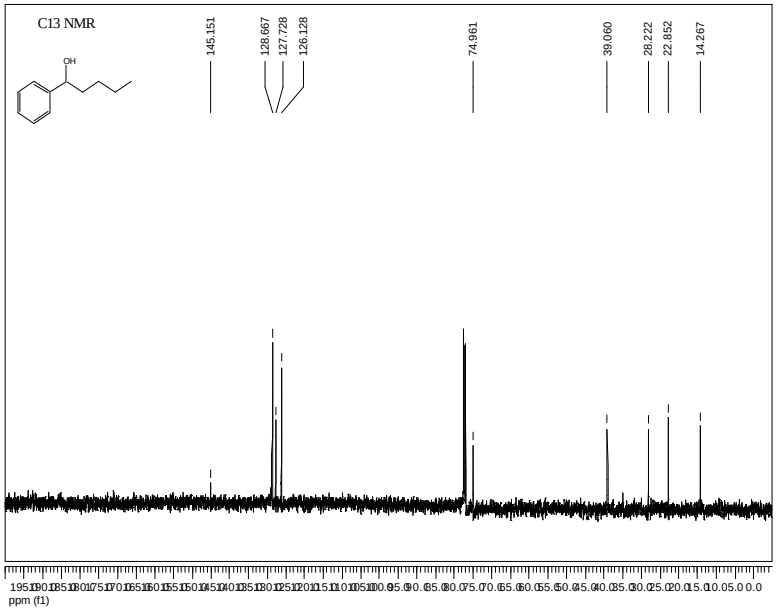
87% yield, 92%ee

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.269 to 7.356 (m, 5H), 4.671 (m, 1H), 1.717 to 1.813 (m, 2H), 1.258 to 1.394(m, 4H), 0.889(m, 3H).

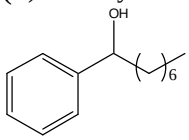
^{13}C NMR (75 MHz, $CDCl_3$) *d* 145.15, 128.67, 127.73, 126.13, 74.96, 39.06, 28.22, 22.85, 14.27.

$[\alpha]_D^{25}$=+ 7.9 (c=0.14, $CHCl_3$) 92%ee R [reference 5].





(*R*)-1-Phenyl-1-octanol [reference 5]

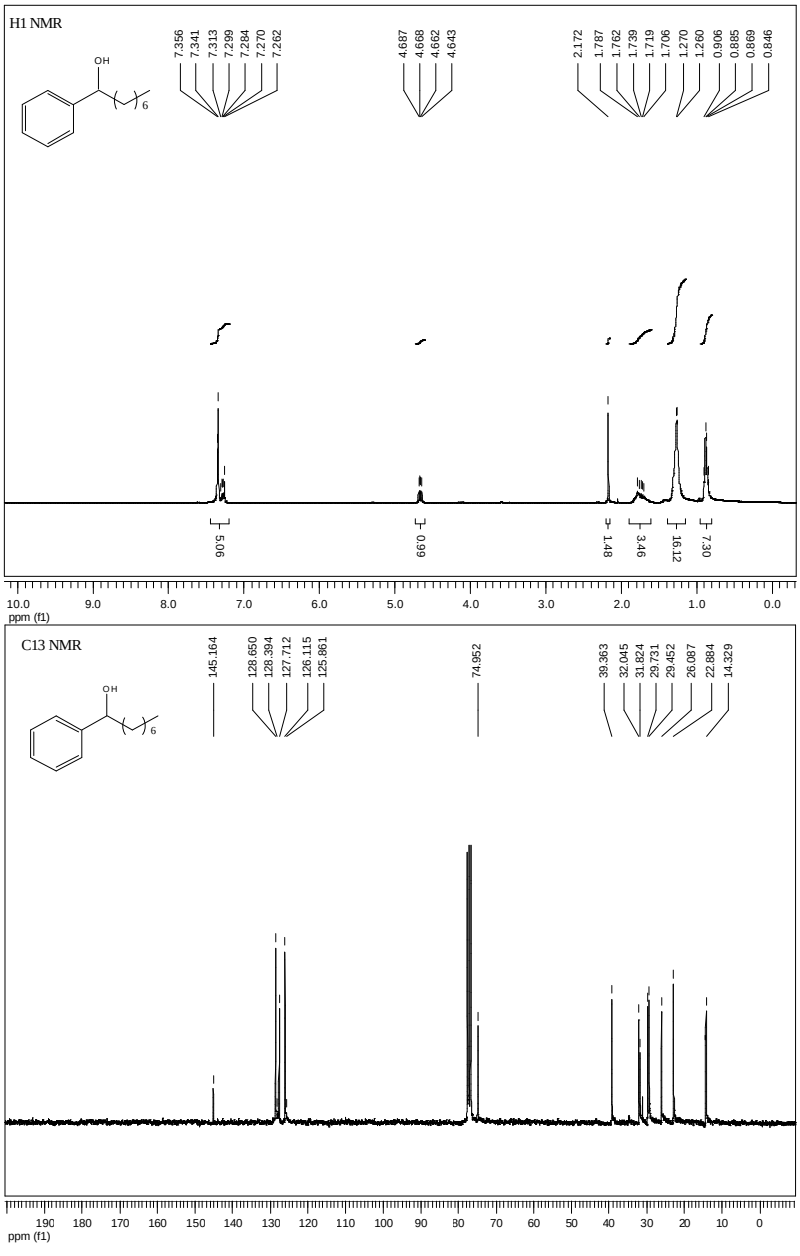


78% yield, 93%ee.

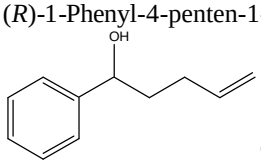
^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.270 to 7.355 (m, 5H), 4.642 to 4.687 (m, 1H), 2.171(s, 1H), 1.705 to 1.786 (m, 2H), 1.260 to 1.270(m, 10H), 0.845 to 0.885 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *d* 145.164, 128.650, 128.394, 127.711, 126.115, 125.860, 74.951, 39.363, 32.044, 31.823, 29.730, 29.451, 26.086, 22.883, 14.328.

$[\alpha]_D^{25}$=+ 7.9 (c=0.14, $CHCl_3$) 92%ee R [reference 5]



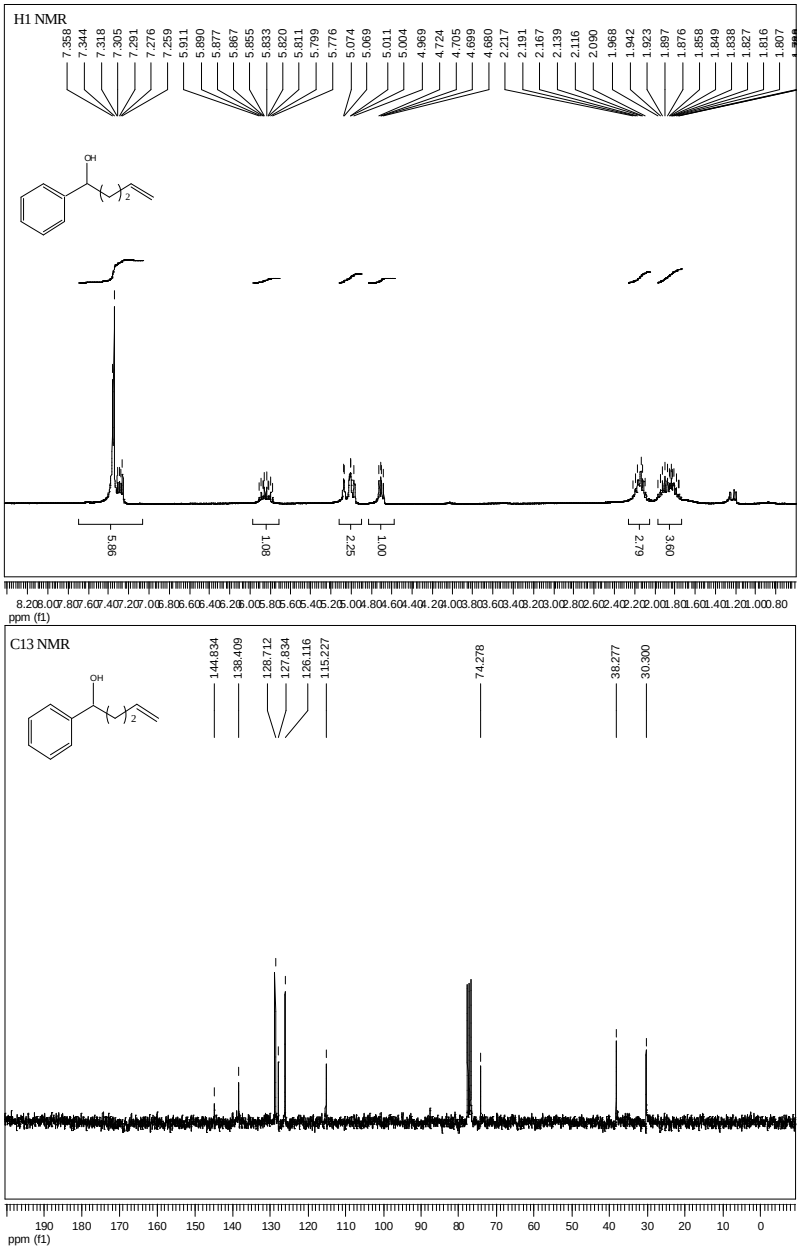
(*R*)-1-Phenyl-4-penten-1-ol [reference 6]



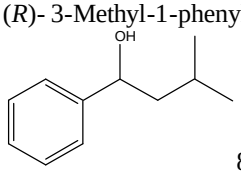
75% yield, 92%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.275 to 7.358(m, 5H), 5.776 to 5.911(m, 1H), 4.969 to 5.074(m, 2H), 4.679 to 4.723 (m, 1H), 1.762 to 2.217(m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) *d* 144.834, 138.409, 128.711, 127.834, 126.116, 115.226, 74.278, 38.276, 30.299.



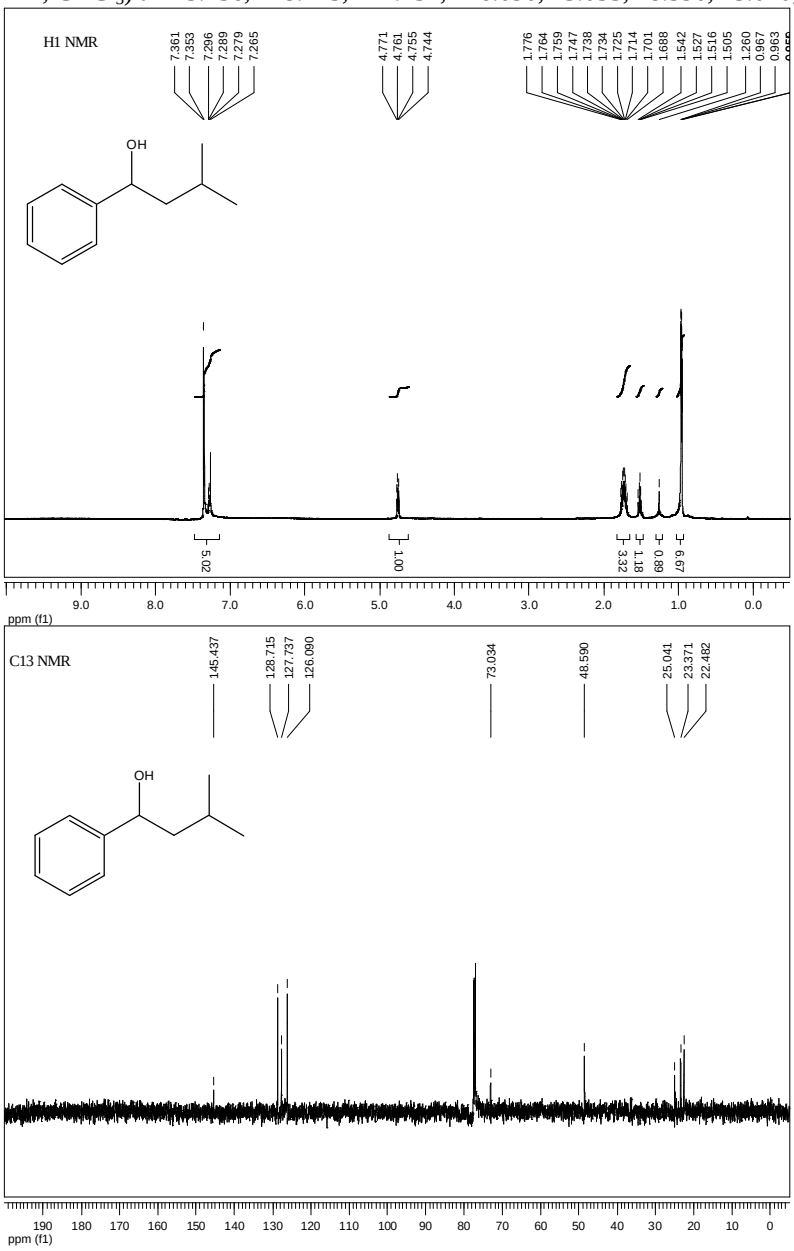
(*R*)- 3-Methyl-1-phenyl-1-butanol [reference 6]



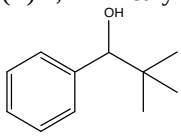
82%yield, 92%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.264 to 7.361 (m, 5H), 4.743 to 4.770 (m, 1H) , 1.687 to 1.776(m, 2H), 1.504 to 1.541(m, 1H) , 1.259 (s, 1H), 0.950 to 0.967 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) *d* 145.436, 128.715, 127.737, 126.090, 73.033, 48.590, 25.040, 23.370, 22.482.



(*R*)-2,2-Dimethyl-1-phenylpropanol [reference 7,8]

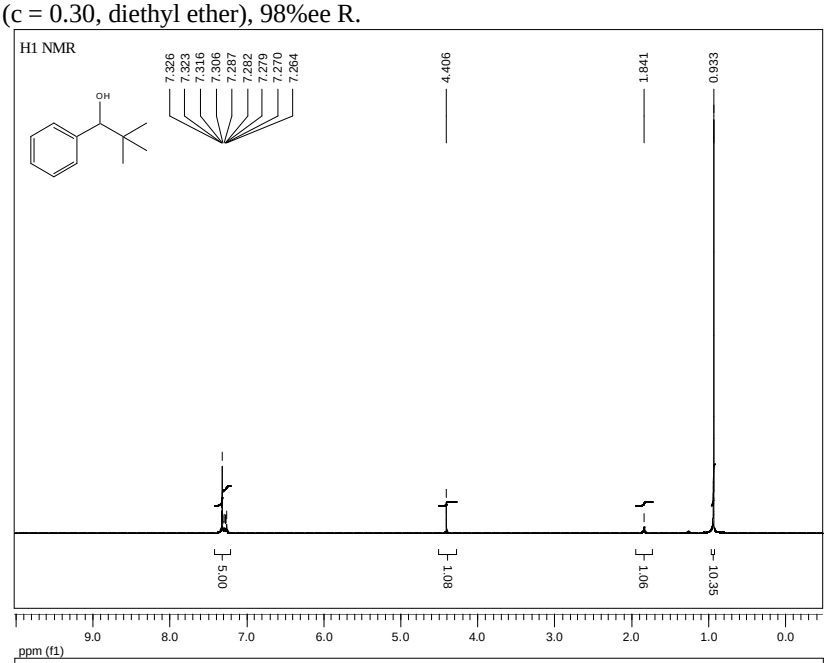


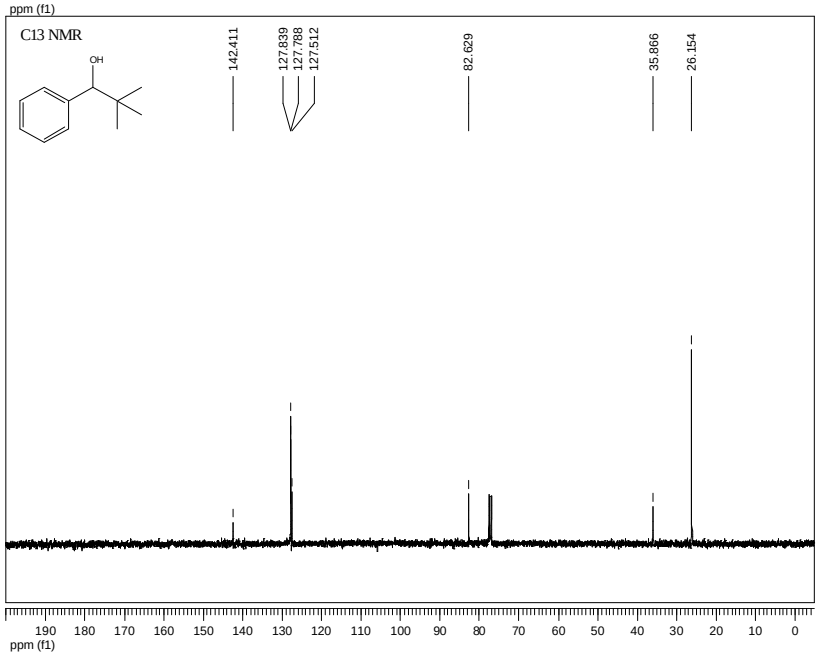
93%yield, 98%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.269 to 7.325 (m, 5H), 4.406 (s, 1H), 1.841 (s, 1H), 0.933 (s, 9H).

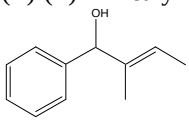
^{13}C NMR (75 MHz, $CDCl_3$) *d* 142.410, 127.838, 127.788, 127.512, 82.628, 35.865, 26.154.

$[\alpha]_D^{25}$ = 10.2 (c = 0.30, diethyl ether), 98%ee R.





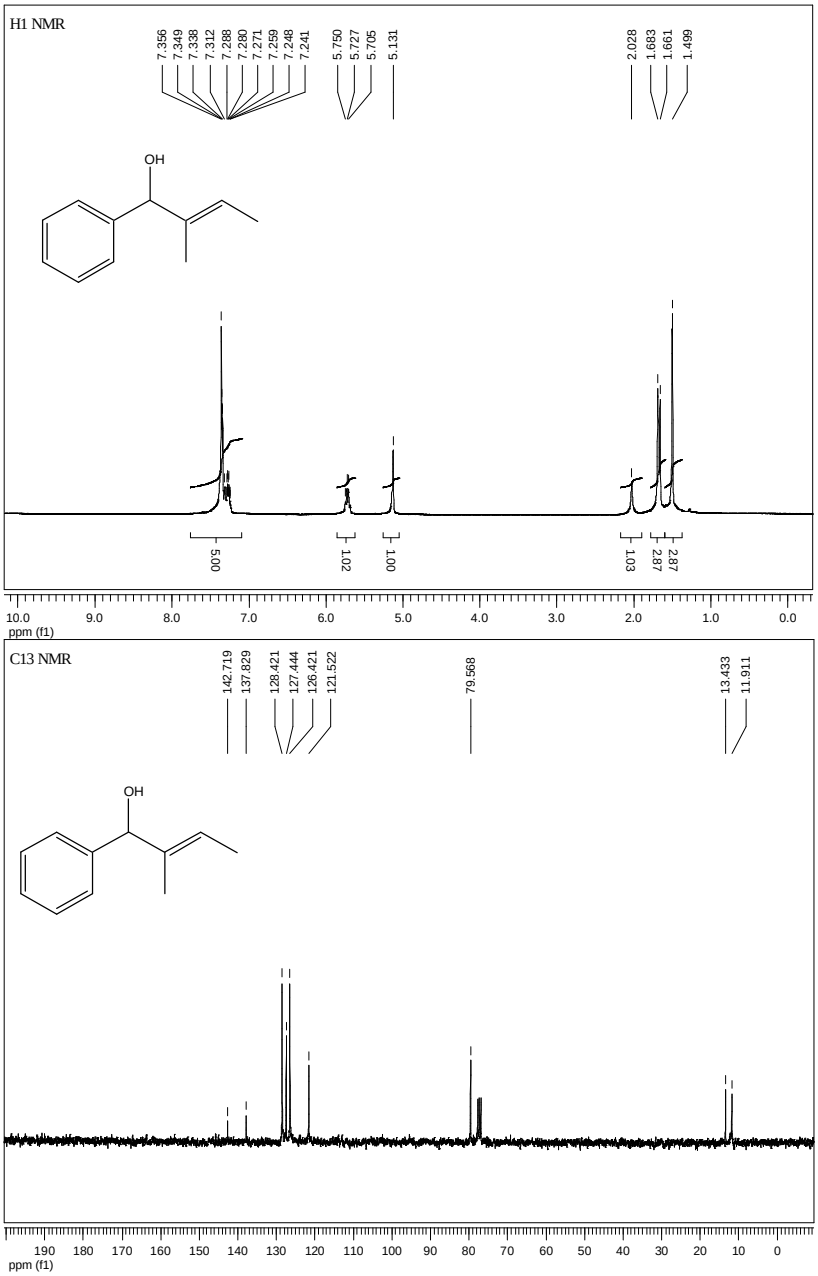
(*R*)-(*E*)-2-Methyl-1-phenylbut-2-en-1-ol [reference 9]



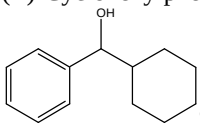
88%yield, 96%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.240 to 7.356 (m, 5H), 5.704 to 5.749 (m, 1H), 5.130 (s, 1H), 2.028 (s, 1H), 1.661 to 1.683 (m, 3H), 1.498 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *d* 142.719, 137.828, 128.421, 127.443, 126.421, 121.521, 79.567, 13.433, 11.911.



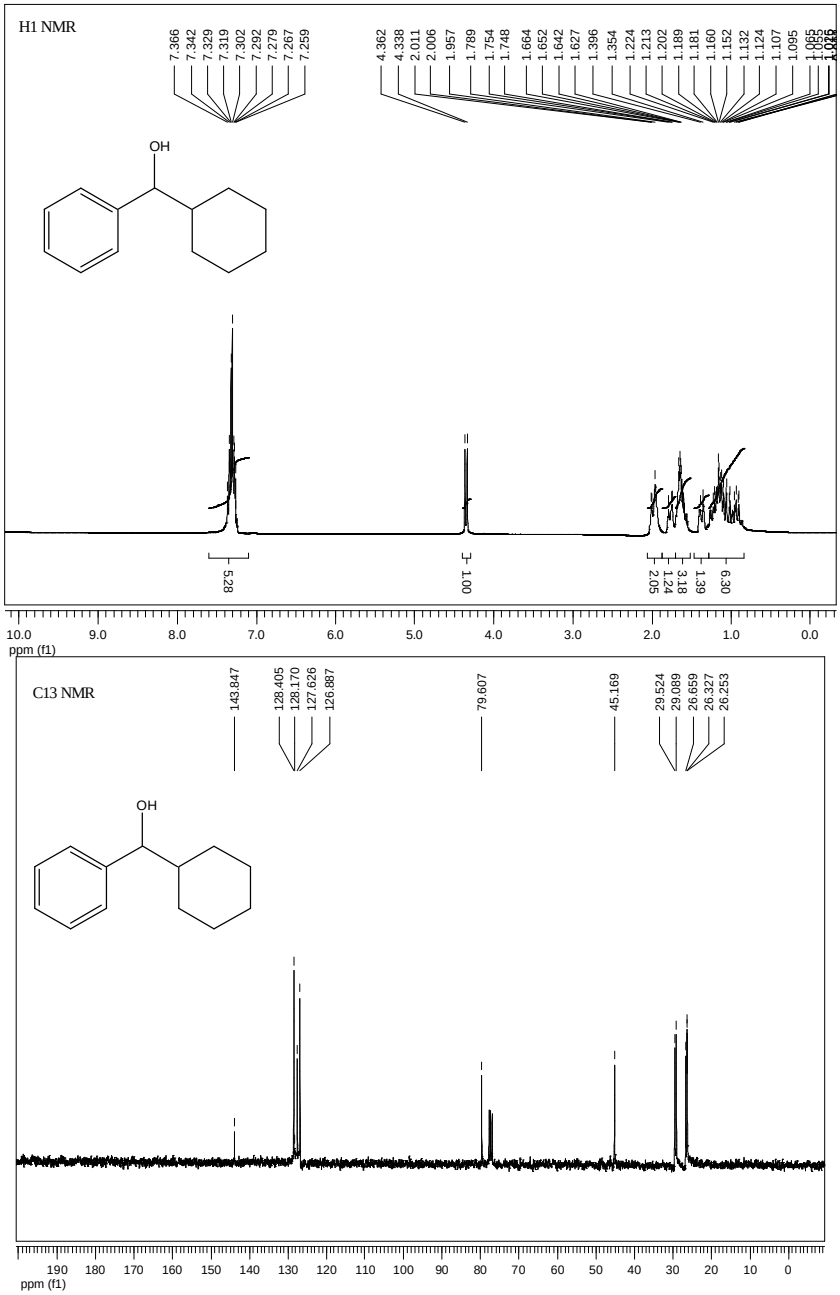
(*R*)-Cyclohexylphenylmethanol [reference 7]



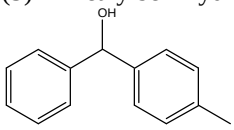
96% yield, 98%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.266 to 7.365 (m, 5H), 4.362 (s, 1H), 4.338, 0.901 to 2.011 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$) *d* 143.846, 128.405, 127.625, 126.886, 79.607, 45.168, 29.524, 29.089, 26.659, 26.327, 26.252.



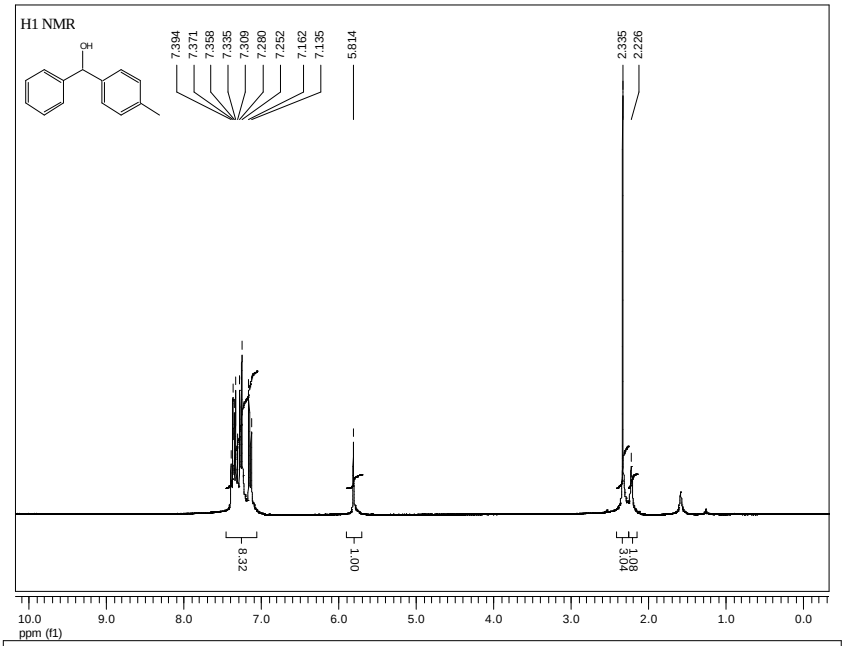
(*S*)-4-Methylbenzhydrol [reference 10]

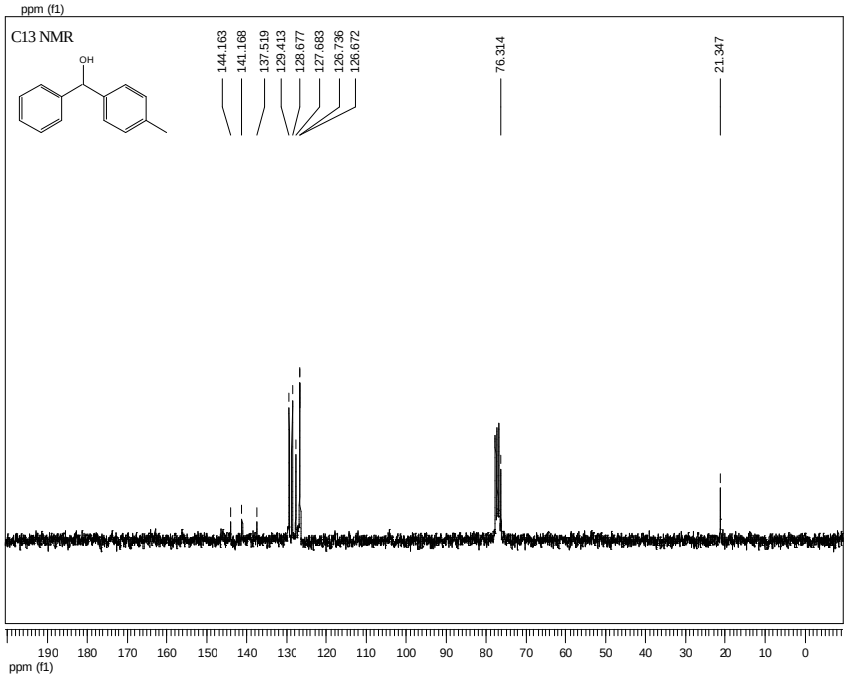


90% yield, 89% ee.

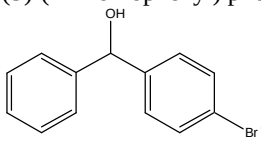
^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.135 to 7.394 (m, 9H), 5.814(s, 1H), 2.335 (s, 1H), 2.226 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) *d* 144.162, 141.167, 137.518, 129.412, 128.676, 127.682, 126.736, 126.672, 76.314, 21.346.





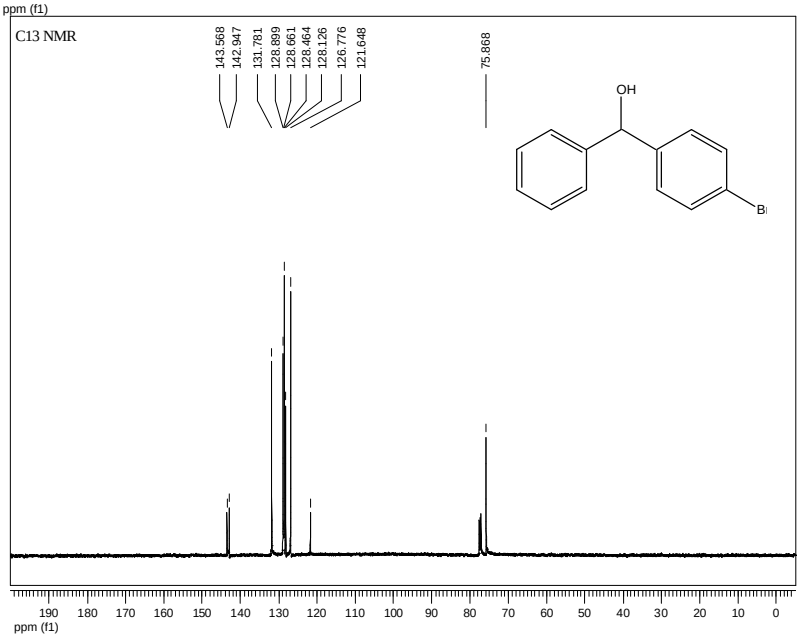
(*S*)-(4-Bromophenyl) phenylmethanol [reference 10]



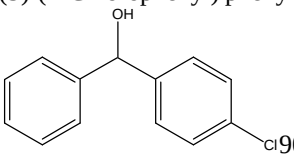
91%yield, 89%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.234 to 7.470 (m, 9H), 5.770 (s, 1H), 2.401 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) *d* 143.568, 142.947, 131.781, 128.898, 128.660, 128.464, 128.125, 126.775, 121.648, 75.867.



(*S*)-(4-Chlorophenyl) phenylmethanol [reference 11]

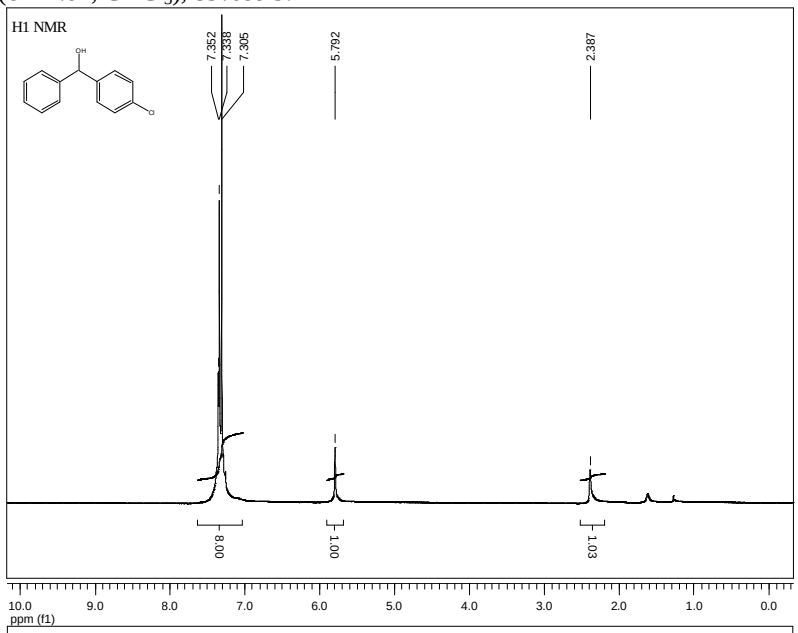


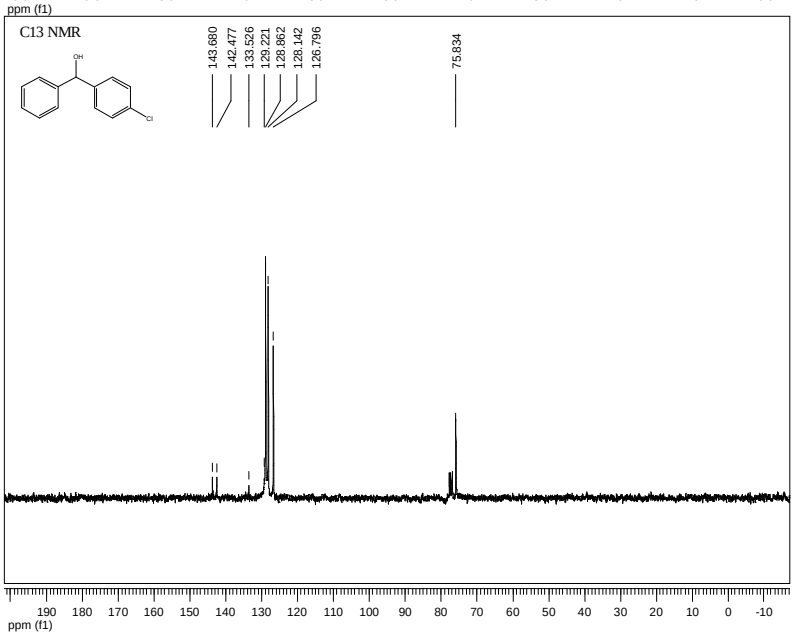
90%yield, 89%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.305 to 7.352 (m, 9H), 5.791(s, 1H), 2.386(s, 1H).

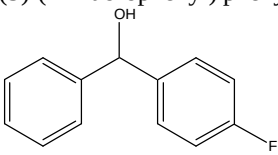
^{13}C NMR (75 MHz, $CDCl_3$) *d* 143.680, 142.477, 133.525, 129.220, 128.861, 128.141, 126.796, 75.833.

$[\alpha]_D^{25}$ = +24.4 (c = 1.62, $CHCl_3$), 89%ee S.





(*S*)-(4-Fluorophenyl) phenylmethanol [reference 10,12]

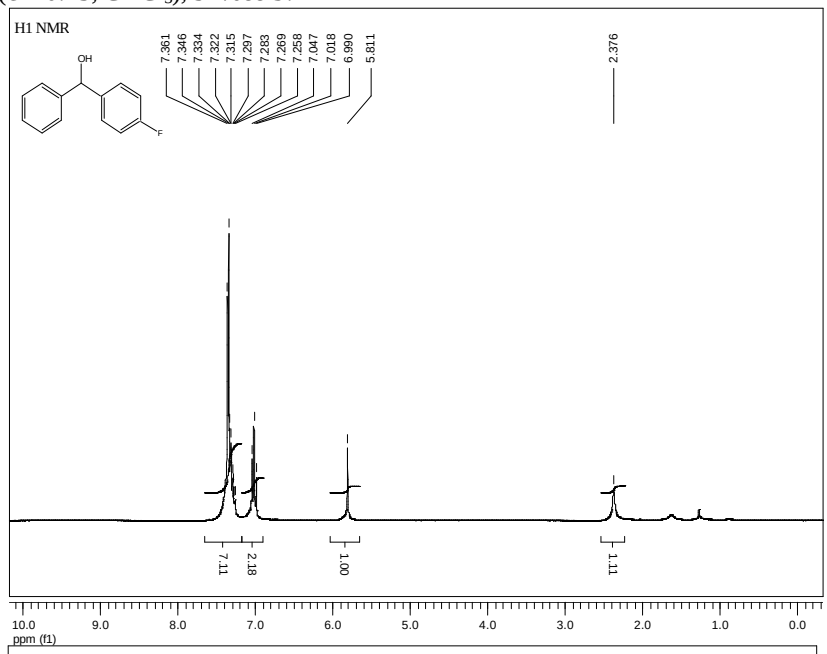


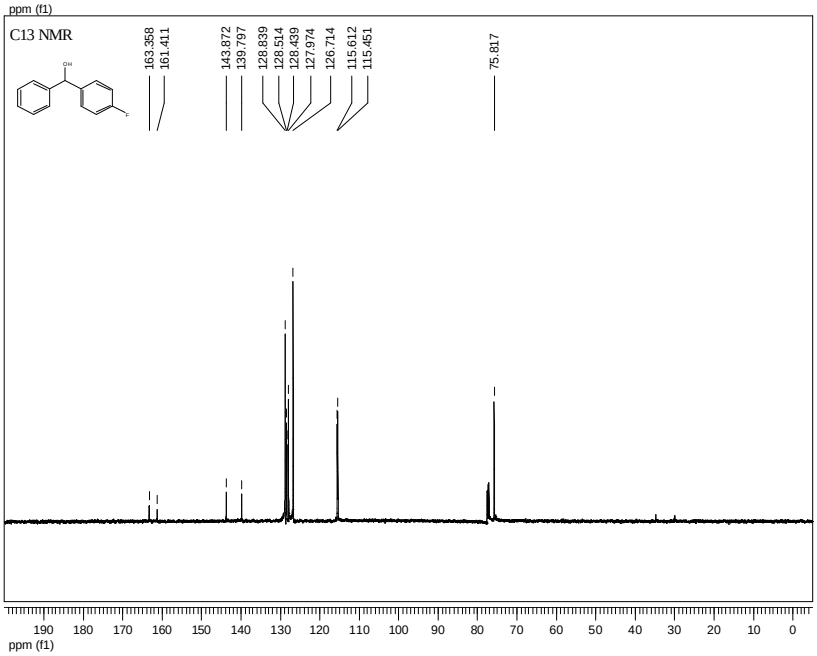
92%yield, 94%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 6.989 to 7.361 (m, 9H), 5.810 (s, 1H), 2.375 (s, 1H).

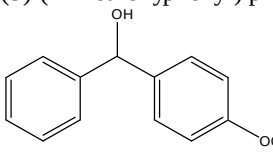
^{13}C NMR (75 MHz, $CDCl_3$) *d* 163.357, 161.411, 143.871, 139.796, 128.839, 128.514, 128.438, 127.974, 126.713, 115.611, 115.450, 75.817.

$[\alpha]_D^{25}$ = +1.5 (c = 0.13, $CHCl_3$), 94%ee S.



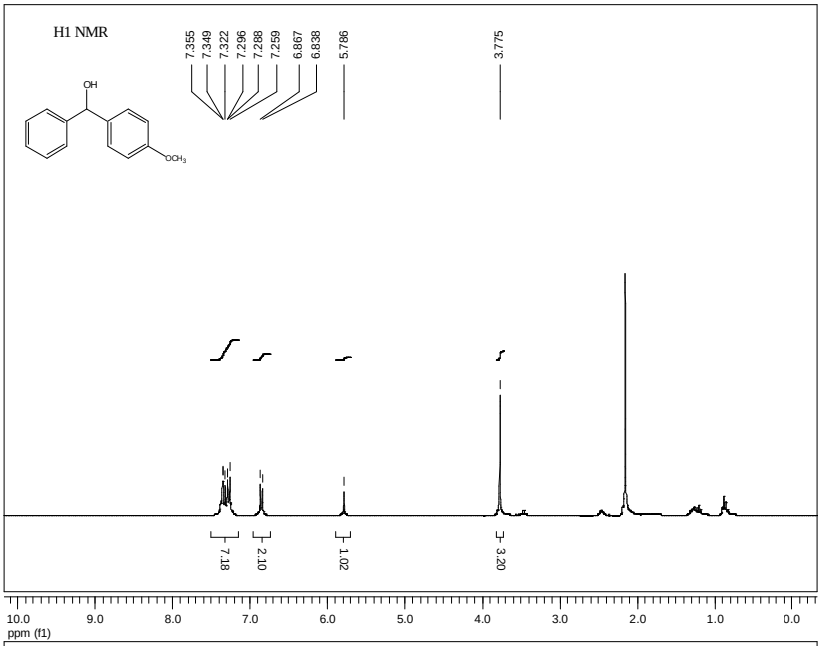


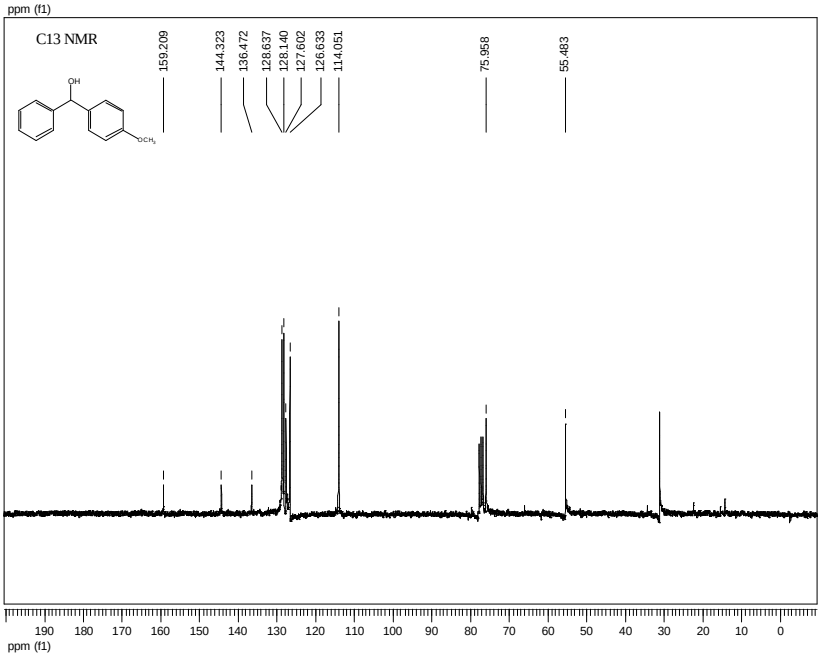
(*S*)-(4-Methoxyphenyl) phenylmethanol [reference 13]



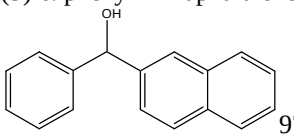
91%yield, 91%ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.287 to 7.354 (m, 7H), 6.838 to 6.866 (m, 2H), 5.785 (s, 1H), 3.774 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) *d* 159.208, 144.322, 136.472, 128.637, 128.140, 127.602, 126.633, 114.051, 75.957, 55.482.





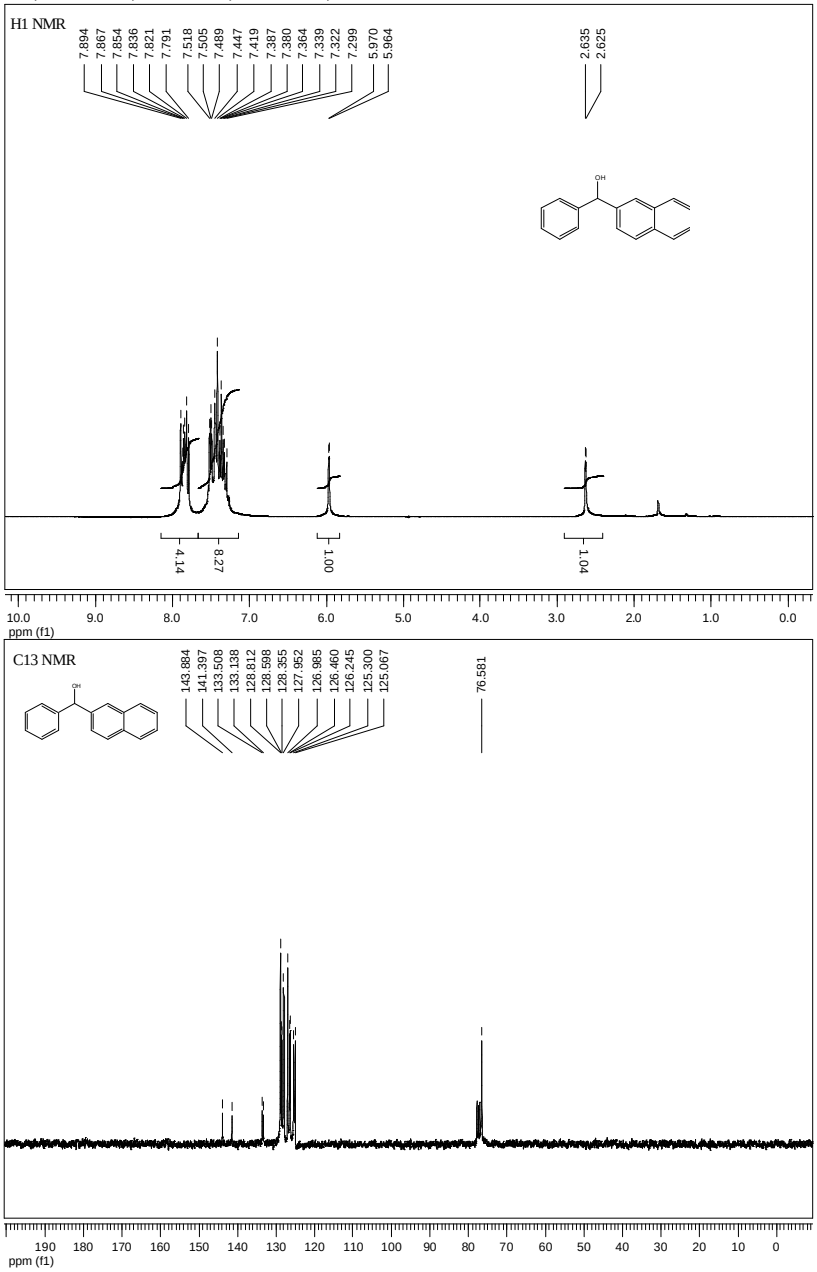
(*S*)-α-phenyl-2-Naphthalenemethanol [reference 11]



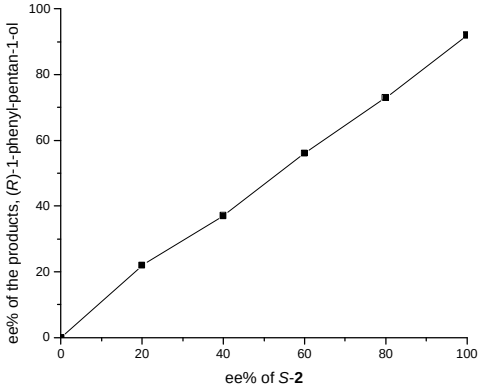
97%yield, 89% ee.

^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.299 to 7.893 (m, 12H), 5.968(m, 1H), 2.629(m, 1H).

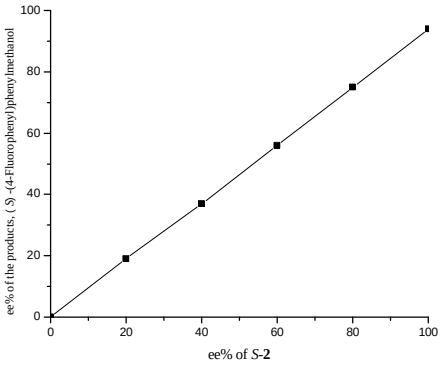
^{13}C NMR (75 MHz, $CDCl_3$) *d* 143.884, 141.396, 133.507, 133.138, 128.812, 128.597, 128.354, 127.951, 126.984, 126.460, 126.244, 125.299, 125.067, 76.580.



Correlation of the ee of (*S*)-4 and that of Its Catalytic Product from the Reaction of valeraldehyde and 4-fluorbenzaldehyde with diphenylzinc.

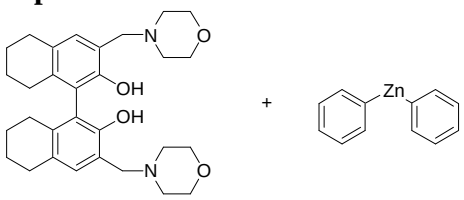


ee% of S-4	ee% of the products, (*R*)-1-phenyl-1-pentanol
0	0
20	22
40	37
60	56
80	73
100	92



ee% of S-4	ee% of the products, (*S*)-(4-Fluorophenyl)phenylmethanol
0	0
20	19
40	37
60	56
80	75
100	94

NMR study of the zinc complexes:



(*S*)-**4**

All NMR spectra were taken in toluene-d_8 and the spectrum windows shown bellow are all from 6 ppm to 10.5 ppm for ^{1}H NMR and 10 ppm to 170 ppm for ^{13}C NMR unless specified. Frequency is 500MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR.

Observations:

(1) Treating (*S*)-**4** with various amount of diphenylzinc (0 equiv to 12 equiv) in toluene-d_8 to study the structures of the resulting zinc complexes.

In the ^{1}H NMR spectrum of the pure ligand, two singlets (-OH at δ 9.99; the only aromatic proton at δ 6.62) were observed. Addition of diphenylzinc started diminishing the two singlets with new and broad peaks growing in the region. Benzene signal at δ 7.14 also appeared. A series of spectra were recorded for diphenylzinc versus (*S*)-**4** at 0, 0.3 equiv, 1.0 equiv, 1.2 equiv, and 1.5 equiv.

In the presence of 1.5 equiv diphenylzinc, the following new and sharp peaks of aromatic protons were observed: δ 7.68 (d, *J* = 7.2 Hz, 2H) 7.55 (s, 1H) 7.48 (d, *J* = 7.2 Hz, 2H) 7.27 (t, *J* = 7.2Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.10-7.18 (m, overlapping with the free benzene signal), 6.57 (s, 1H), 6.47 (s, 1H), 6.45 (s, 1H). ^{13}C NMR, gDQ-COSY and gHSQC NMR measurements were conducted to study this complex. In the gDQ-COSY spectrum, the following correlations were observed: protons at δ 7.68 (d, *J* = 7.2 Hz, 2H) and 7.27 (t, *J* = 7.2Hz, 2H) are coupled with each other; protons at δ 7.48 (d, *J* = 7.2 Hz, 2H) and 7.20 (t, *J* = 7 Hz, 2H) are coupled with each other; both peaks at δ 7.27 (t, J=7.2Hz, 2H) and 7.20 (t, J=7.2Hz, 2H) are coupling with the multiplets overlapped with benzene (δ 7.12 to 7.16); no coupling among the following four signals: δ 7.55 (s, 1H), 6.57 (s, 1H), 6.47 (s, 1H) and 6.45 (s, 1H). There must be two different phenyl groups: one shows signals at δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 2H) and 7.10-7.18 (m), and the other at δ 7.48 (d, J = 7.2 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H) and 7.10-7.18 (m). The gHSQC gave similar information.

On the basis of the stoichiometry of diphenylzinc versus (*S*)-**4** and the NMR information, formation of a [2+3] complex was proposed. That is, this complexes should contain two (*S*)-**4** ligands, three zinc centers and a total of two phenyl groups on Zn in an unsymmetrical arrangement. The six most down field carbon signals in the ^{13}C NMR spectrum (δ 160.07, 158.45, 157.14, 156.73, 155.95 and 154.77) were assigned to the two phenyl carbons connected to the zinc atoms and the four carbons bearing the oxygen atoms in the two unsymmetrical ligands.

More aromatic peaks appeared when the amount of diphenylzinc increased to 2 equiv. Similar doublets from phenyl protons (δ 8.10 and 7.90) were observed. This indicates two additional and different phenyl groups. When up to 12.0 equiv of diphenylzinc was added, one singlet at δ 6.65 for the aromatic proton of the ligand appeared which indicates the formation of a C_2 symmetric complex.

(2) Monitoring the progress of the reaction with trimethylacetaldehyde with ^{1}H NMR.

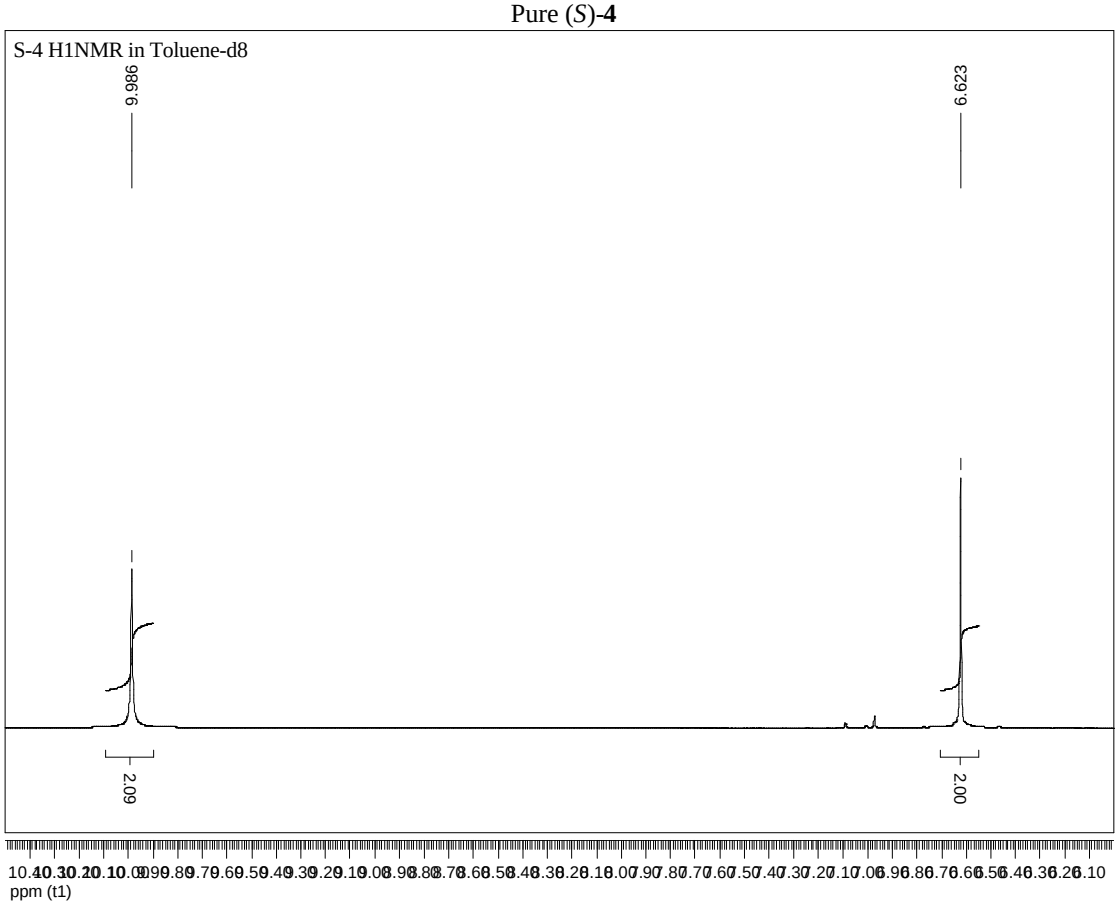
A mixture of (*S*)-**4**, diphenylzinc (1.0 equiv versus the ligand) and the aldehyde (excess) in toluene-d_8 showed no reaction after overnight. A mixture of (*S*)-**4**, diphenylzinc (1.5 equiv versus the ligand) and the aldehyde (excess) in toluene-d_8 showed no reaction after overnight. For the mixtures of (*S*)-**4** + diphenylzinc (2.0 equiv versus the ligand) and (*S*)-**4** + diphenylzinc (4.0 equiv versus the ligand), once a large excess of 2,2-dimethyl-propanal was added, the diphenylzinc signals started decreasing, and the aromatic signals at δ 8.10 and 7.90 became smaller and smaller. When the reaction stopped, the stable [2+3] complex was regenerated as shown by ^{1}H and ^{13}C NMR data..

The ^{1}H NMR spectrum of (*S*)-**4** + 12.0 eq. diphenylzinc (12.0 equiv) + trimethylacetaldehyde (12.0 equiv) showed the formation of multiple zinc alkoxides generated from the phenyl addition (multiple

singlets from δ 4.25 to 4.85 for *H*-CPh^{t}Bu and from δ 0.60 to 0.95 for -^{t}Bu. Addition of D_2O released 2,2-dimethyl-1-phenyl-1-propanol with two singlets at δ 4.01 and 0.89. The ligand (*S*)-**4** was regenerated.

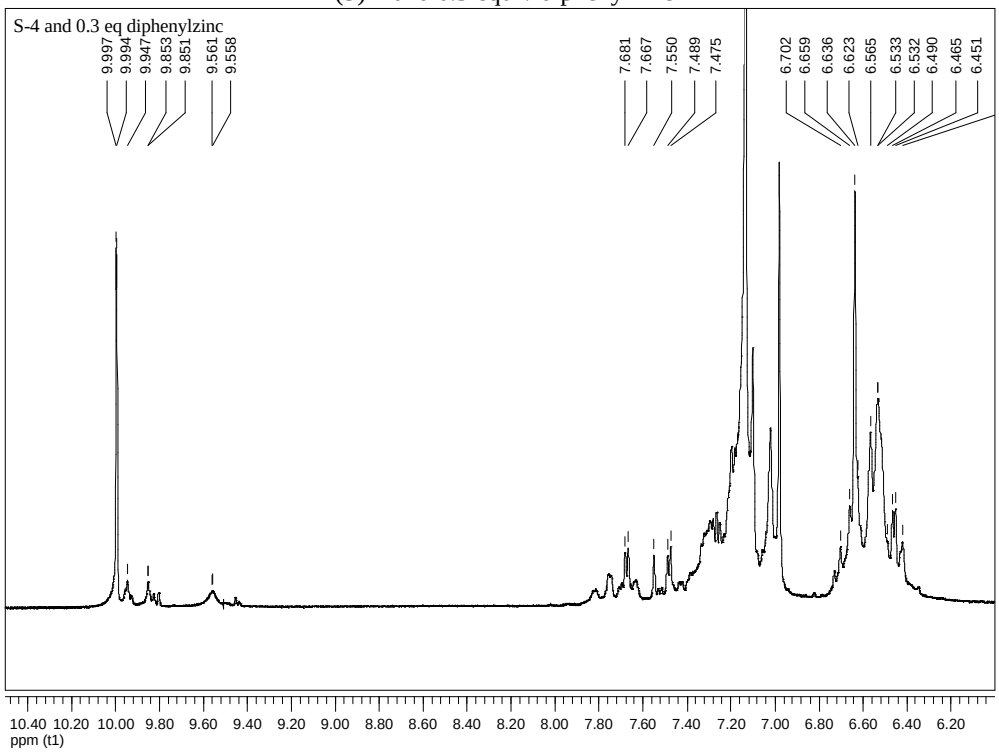
NMR Spectra:

Pure (*S*)-**4**

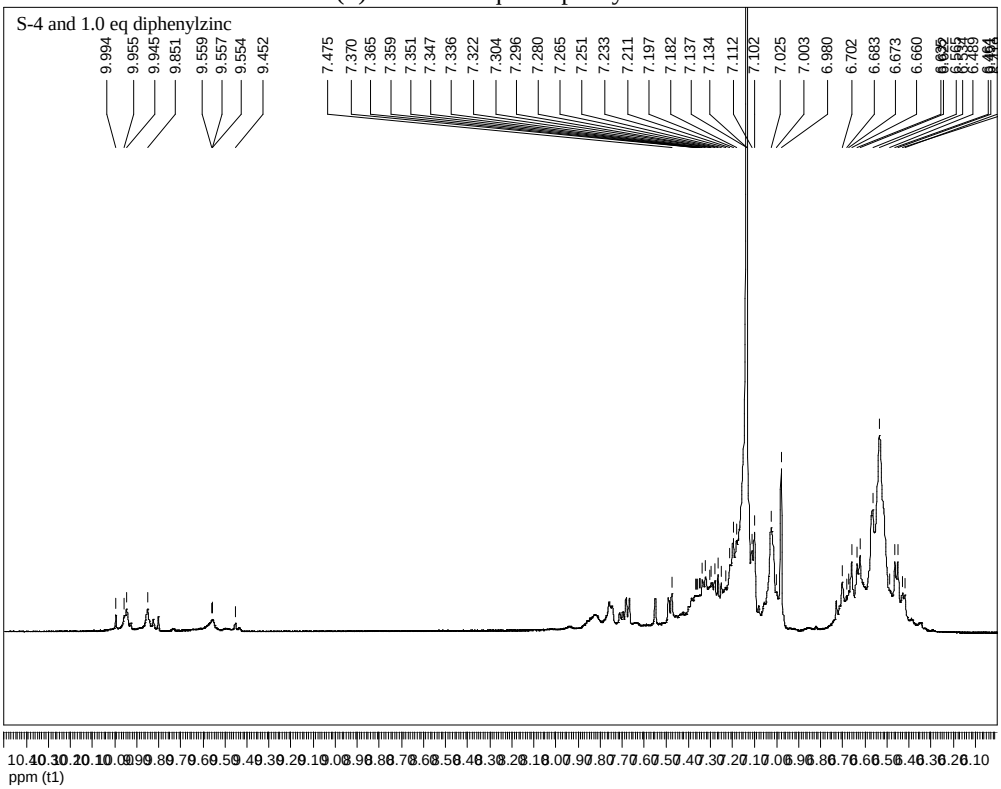


d 9.985(s, 2H), 6.623(s, 2H).

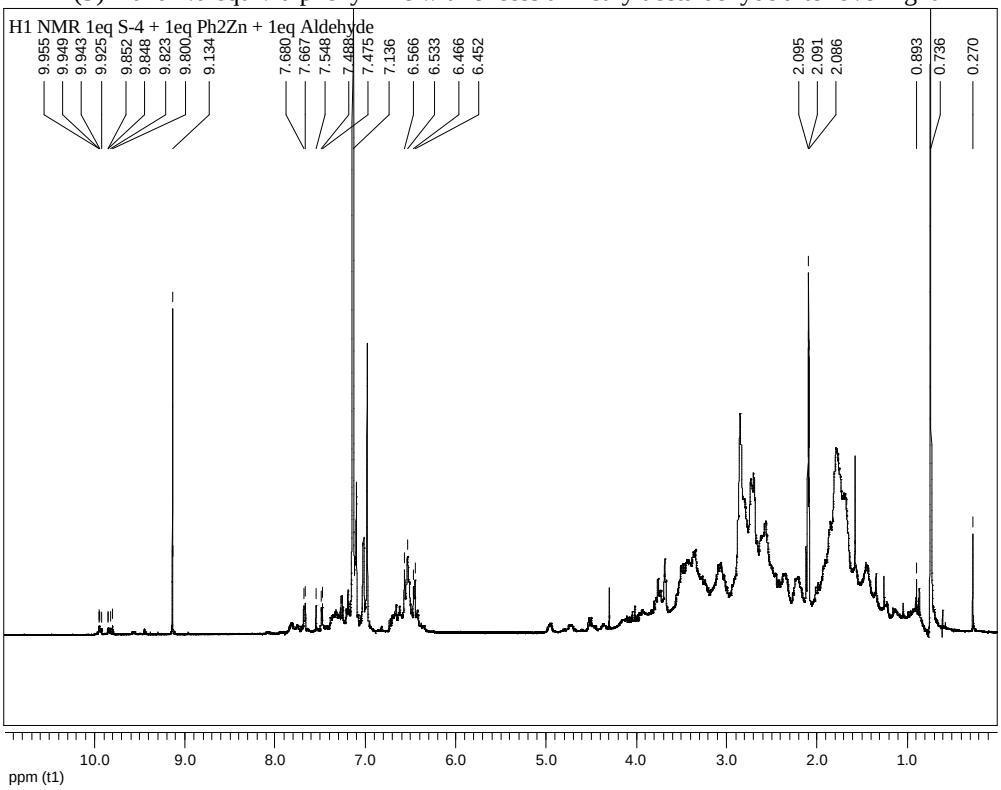
(*S*)-**4** and 0.3 equiv diphenylzinc



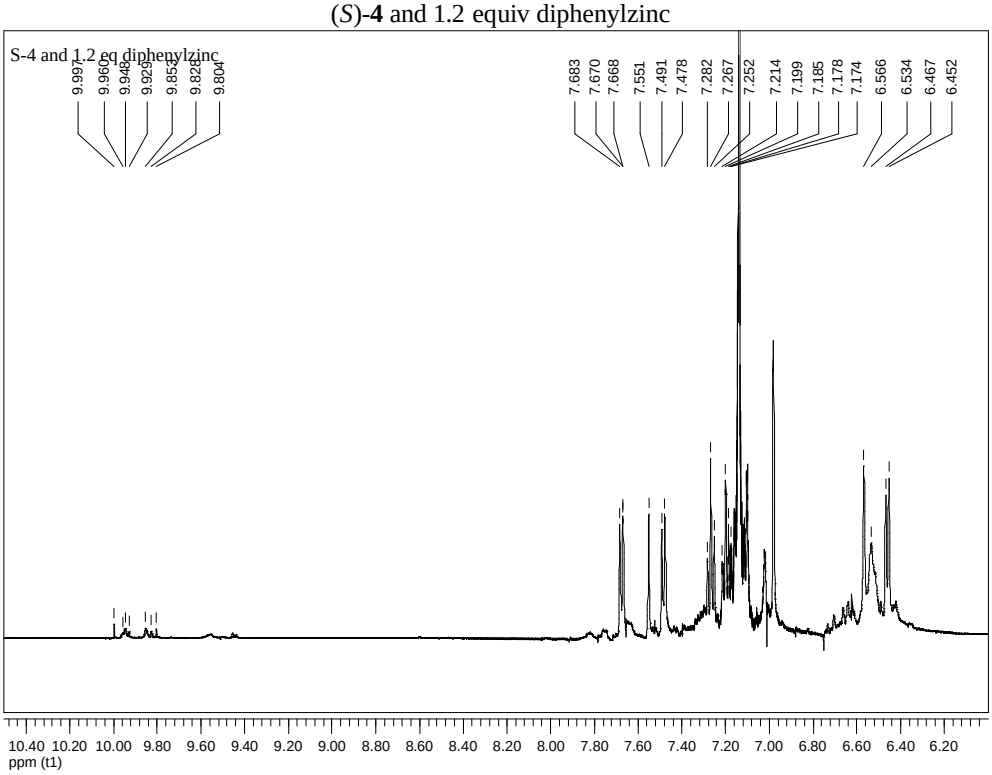
(*S*)-**4** and 1.0 equiv diphenylzinc



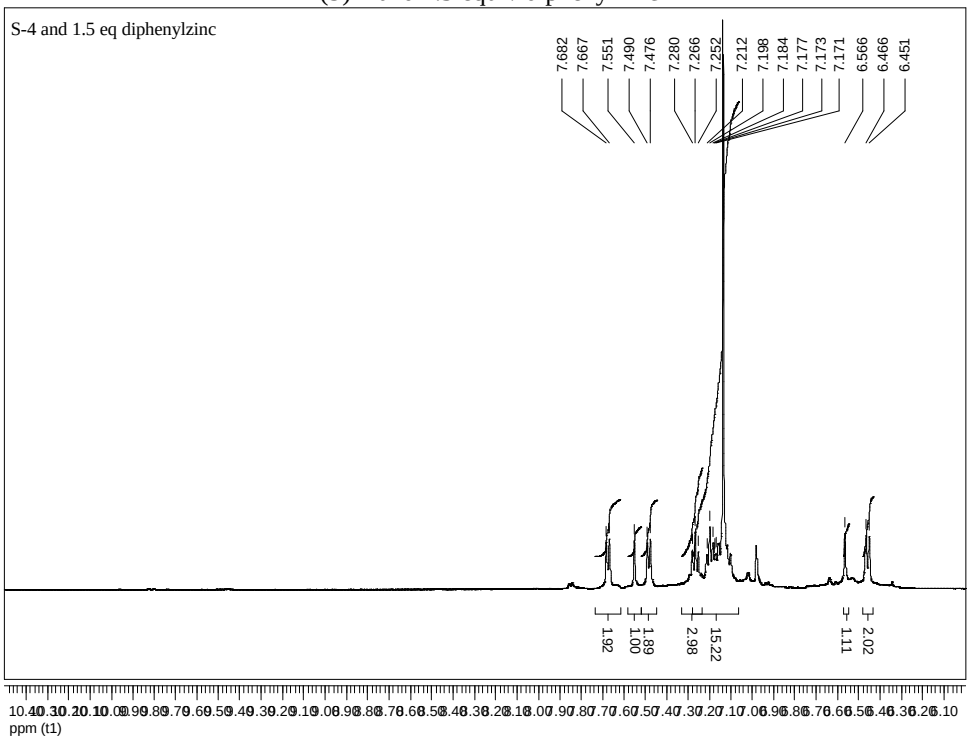
(*S*)-**4** and 1.0 equiv diphenylzinc with excess trimethylacetaldehyde after overnight



(*S*)-**4** and 1.2 equiv diphenylzinc

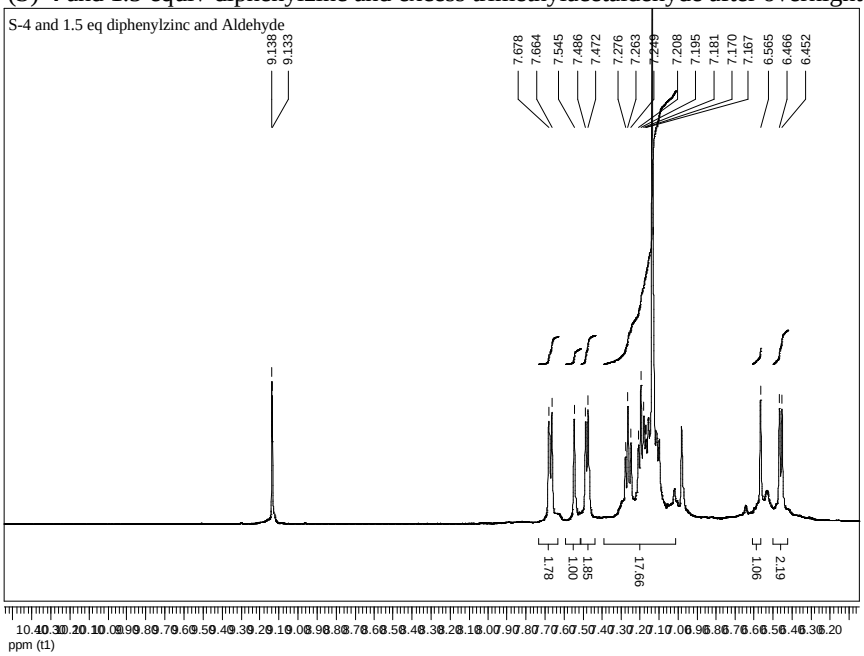


(*S*)-**4** and 1.5 equiv diphenylzinc



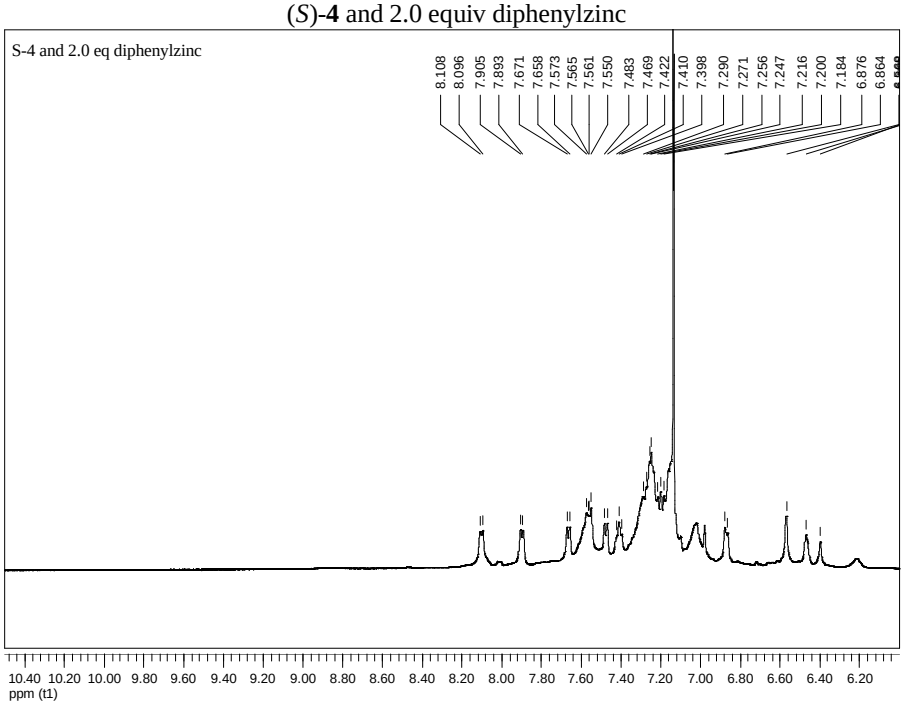
δ ppm 7.675(d, J=7.2Hz, 2H) 7.550, (s, 1H) 7.483, (d, J=7.2Hz, 2H) 7.266, (t, J=7.2Hz, 2H) 7.198, (t, J=7.2Hz, 2H) 6.565, (s, 1H) 6.466 (s, 1H), 6.451 (s, 1H).

(*S*)-**4** and 1.5 equiv diphenylzinc and excess trimethylacetaldehyde after overnight



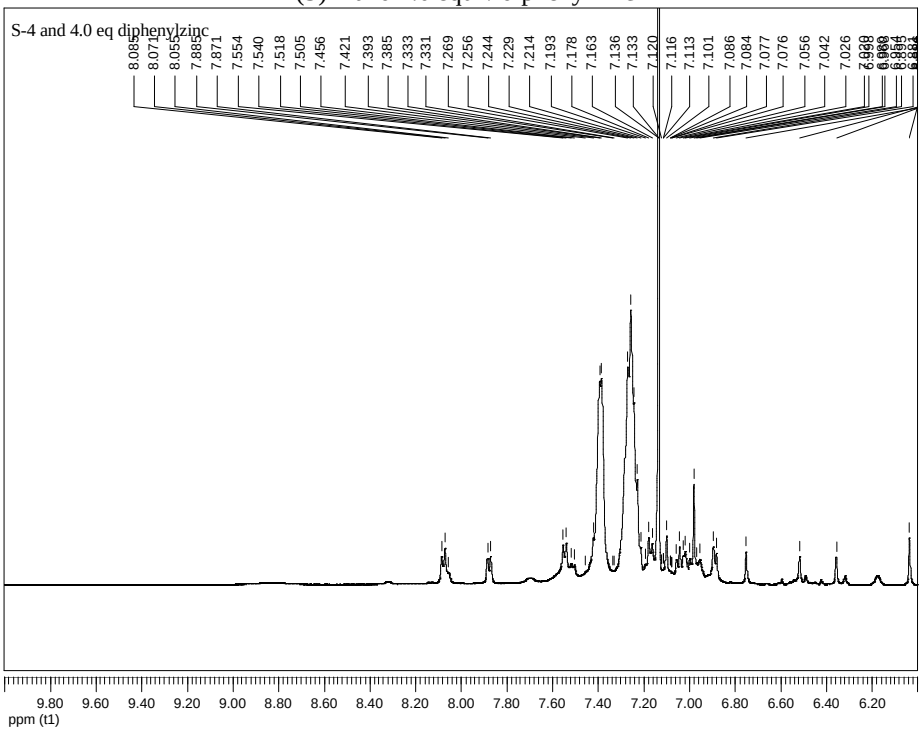
δ 9.138, aldehyde proton, δ 7.675(d, J=7.2Hz, 2H) 7.550, (s, 1H) 7.483, (d, J = 7.2Hz, 2H) 7.266, (t, J = 7.2Hz, 2H) 7.198, (t, J = 7.2Hz, 2H) 6.565, (s, 1H) 6.466 (s, 1H), 6.451 (s, 1H).

(*S*)-**4** and 2.0 equiv diphenylzinc

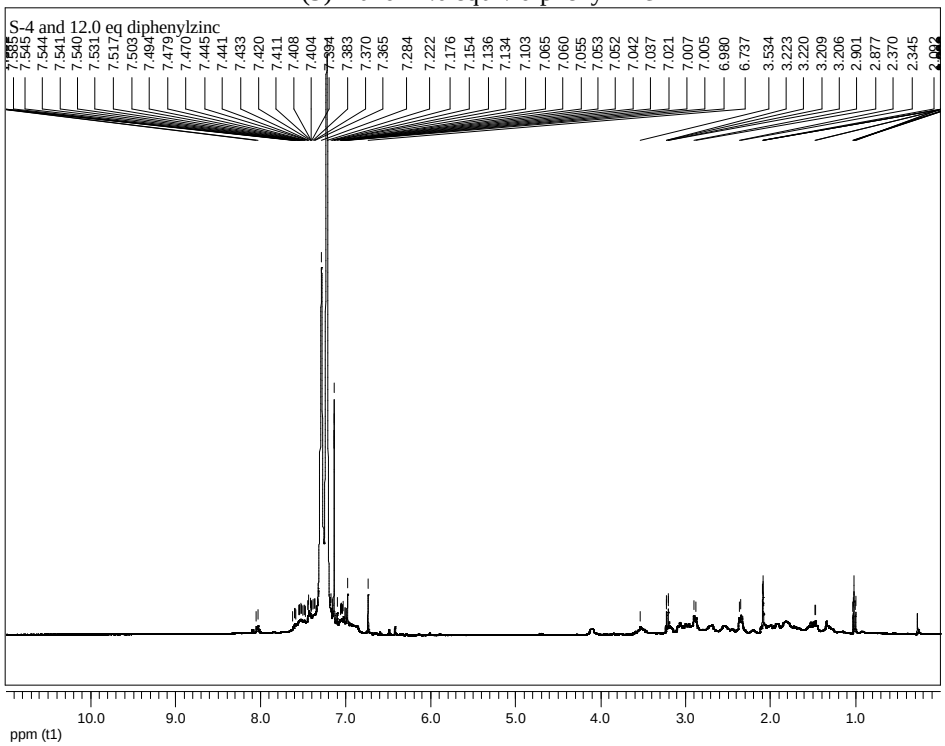


δ 8.107, 8.096, 7.905, 7.892, 7.671, 7.657, 7.572, 7.565, 7.561, 7.550, 7.482, 7.468, 7.422, 7.409, 7.397, 7.290, 7.271, 7.256, 7.246, 7.215, 7.199, 7.183, 6.876, 6.864, 6.567, 6.470, 6.397.

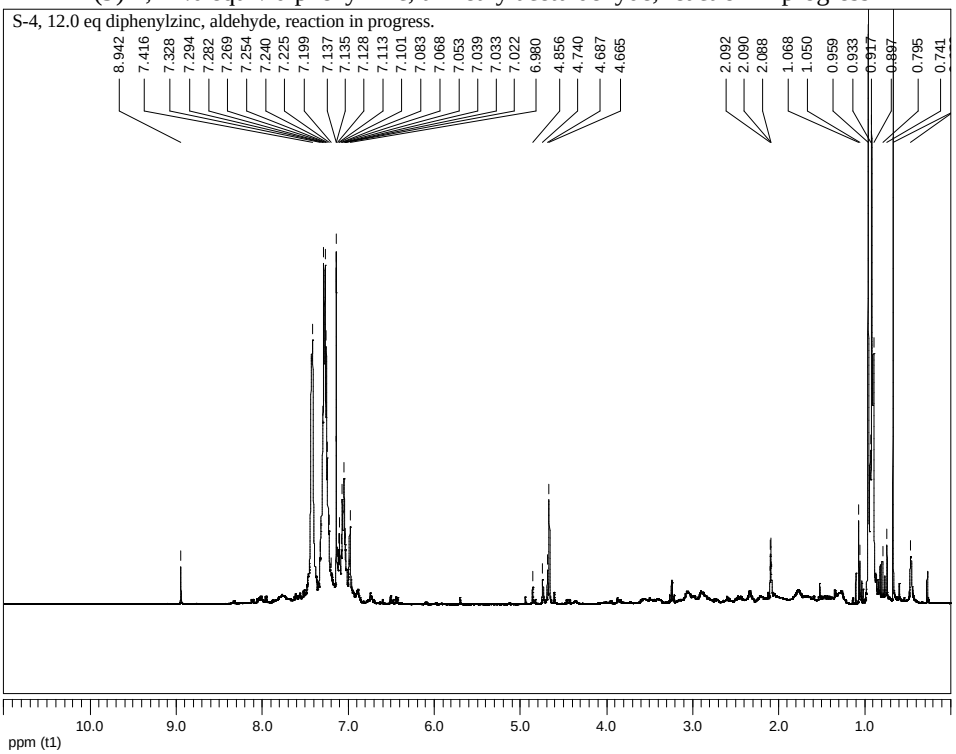
(*S*)-**4** and 4.0 equiv diphenylzinc



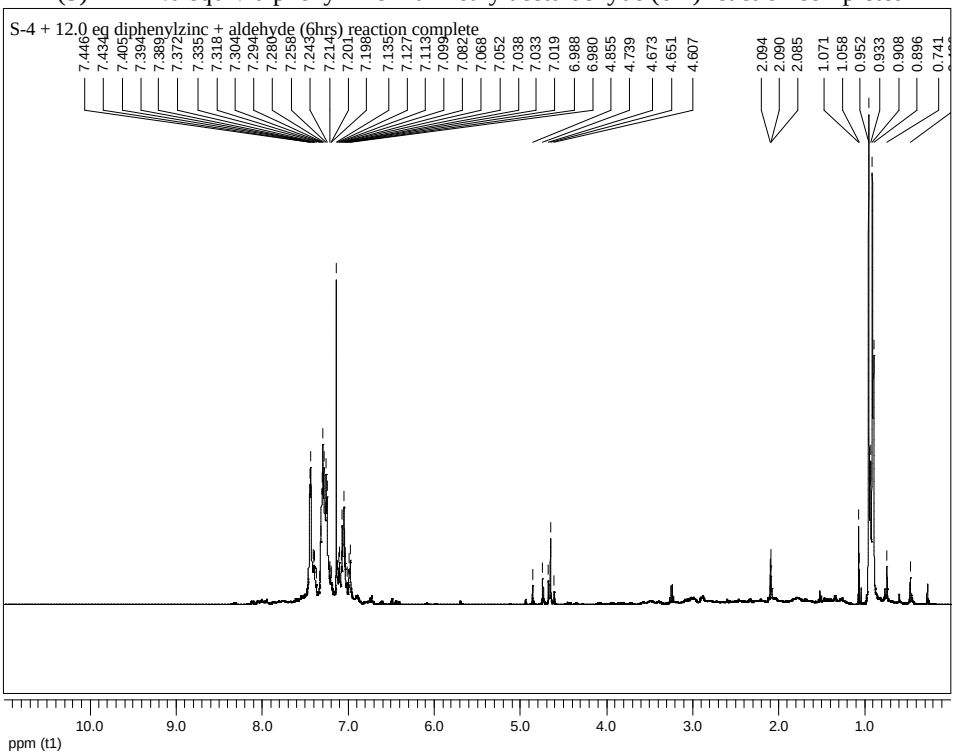
(*S*)-**4** and 12.0 equiv diphenylzinc



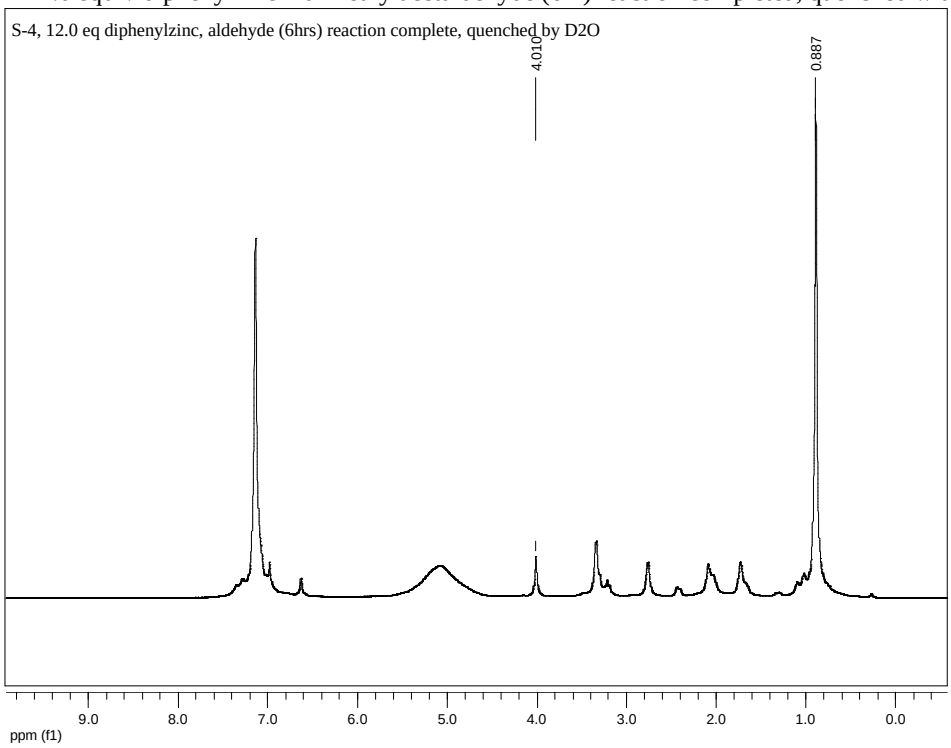
(*S*)-**4**, 12.0 equiv diphenylzinc, trimethylacetaldehyde, reaction in progress



(*S*)-**4** + 12.0 equiv diphenylzinc + trimethylacetaldehyde (6 h) reaction completed

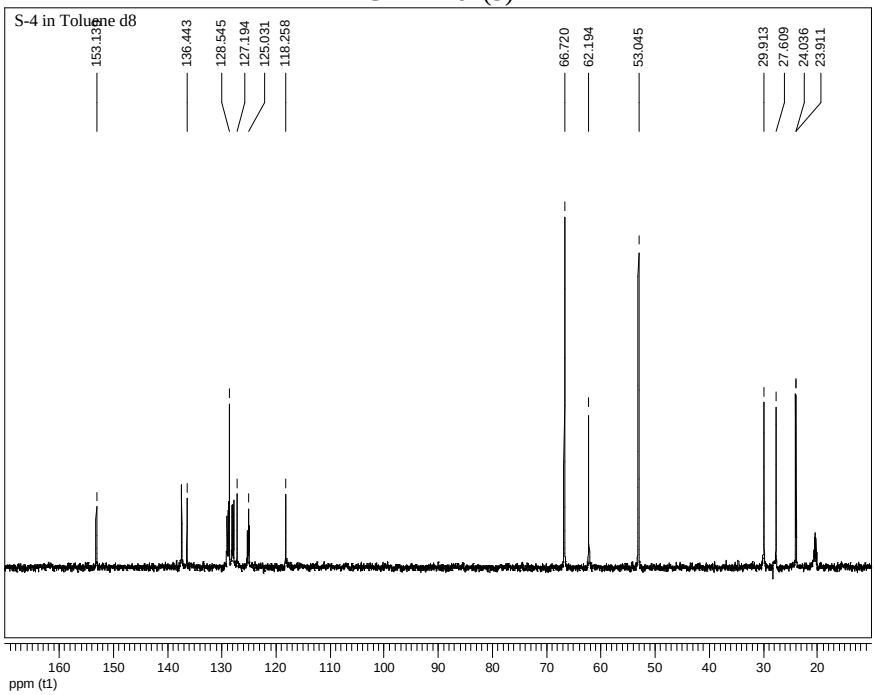


(*S*)-**4** + 12.0 equiv diphenylzinc + trimethylacetaldehyde (6 h) reaction completed, quenched with D_2O



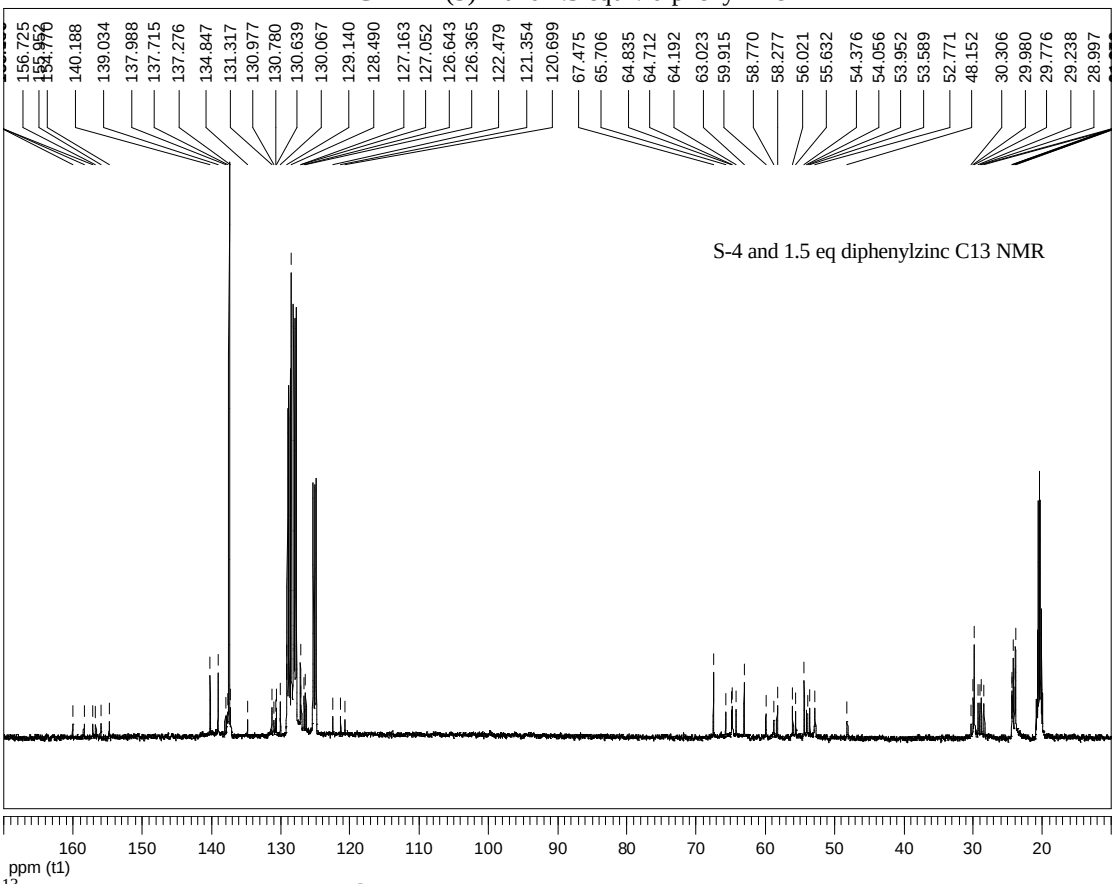
d C*H*OH (4.010) and (CH_3)$_3$C (0.887)

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



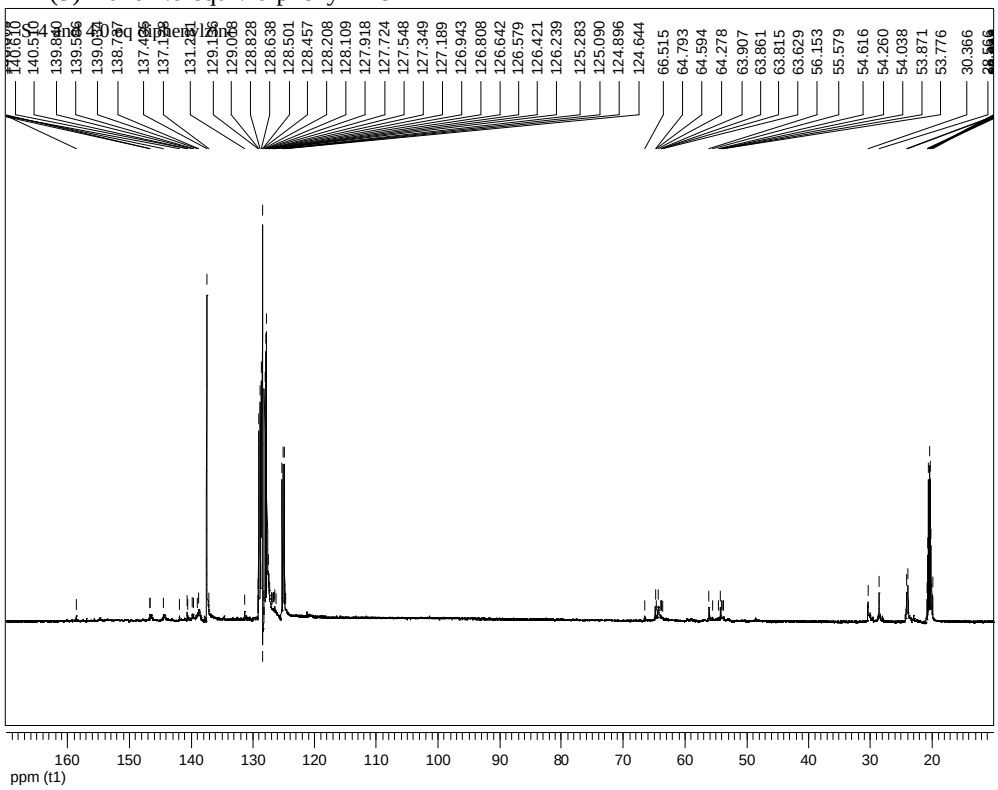
^{13}C NMR (125 MHz, toluene-d_8) *d* 153.138, 136.443, 128.544, 127.194, 125.031, 118.257, 66.719, 62.193, 53.044, 29.913, 27.609, 24.035, 23.911.

^{13}C NMR (*S*)-**4** and 1.5 equiv diphenylzinc

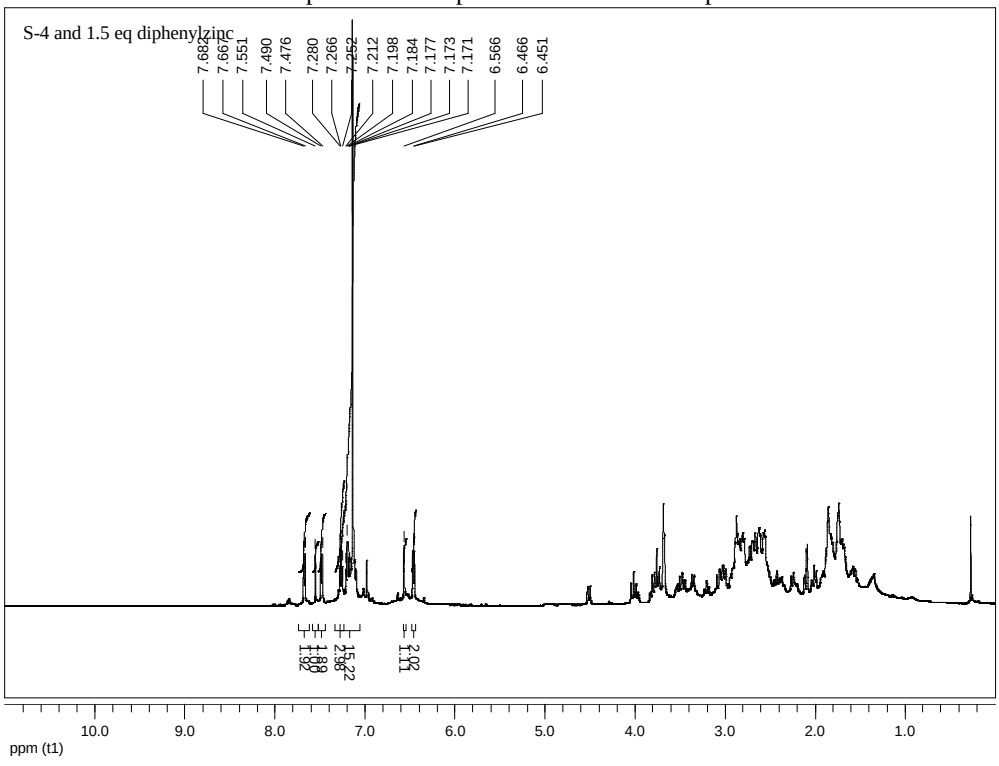


^{13}C NMR (125 MHz, toluene-d_8) *d* 160.066, 158.445, 157.139, 156.725, 155.952, 154.769, 140.187, 139.033, 137.987, 137.715, 137.275, 134.847, 131.316, 130.977, 130.780, 130.638, 130.066, 129.139, 128.490, 127.162, 127.052, 126.643, 126.365, 122.479, 121.354, 120.699, 67.474, 65.706, 64.835, 64.711, 64.192, 63.022, 59.914, 58.770, 58.276, 56.021, 55.631, 54.376, 54.055, 53.951, 53.589, 52.770, 48.152, 30.306, 29.980, 29.775, 29.237, 28.997, 28.767, 28.375, 24.377, 24.289, 24.200, 23.969, 23.861.

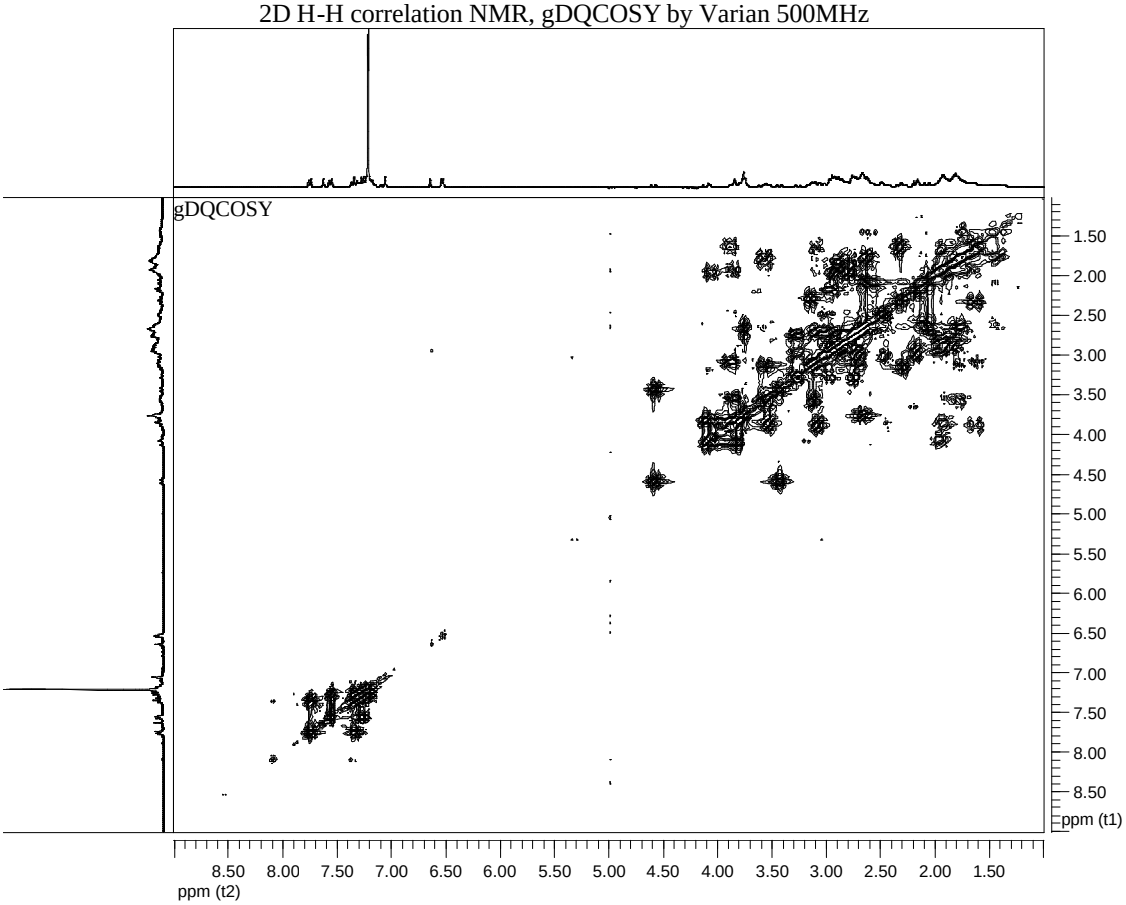
^{13}C NMR (*S*)-**4** and 4.0 equiv diphenylzinc



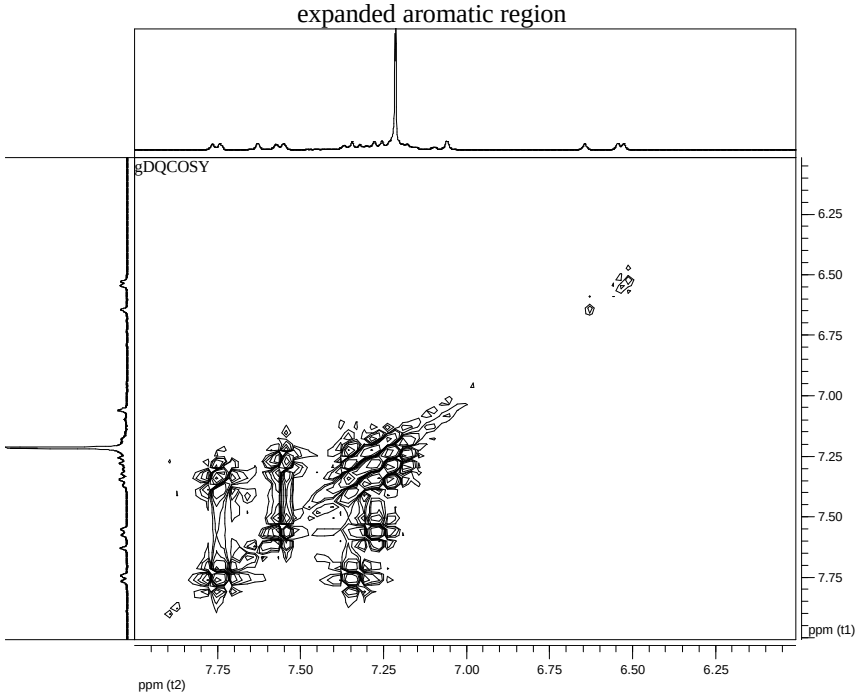
Full proton NMR spectrum of the 2+3 complex



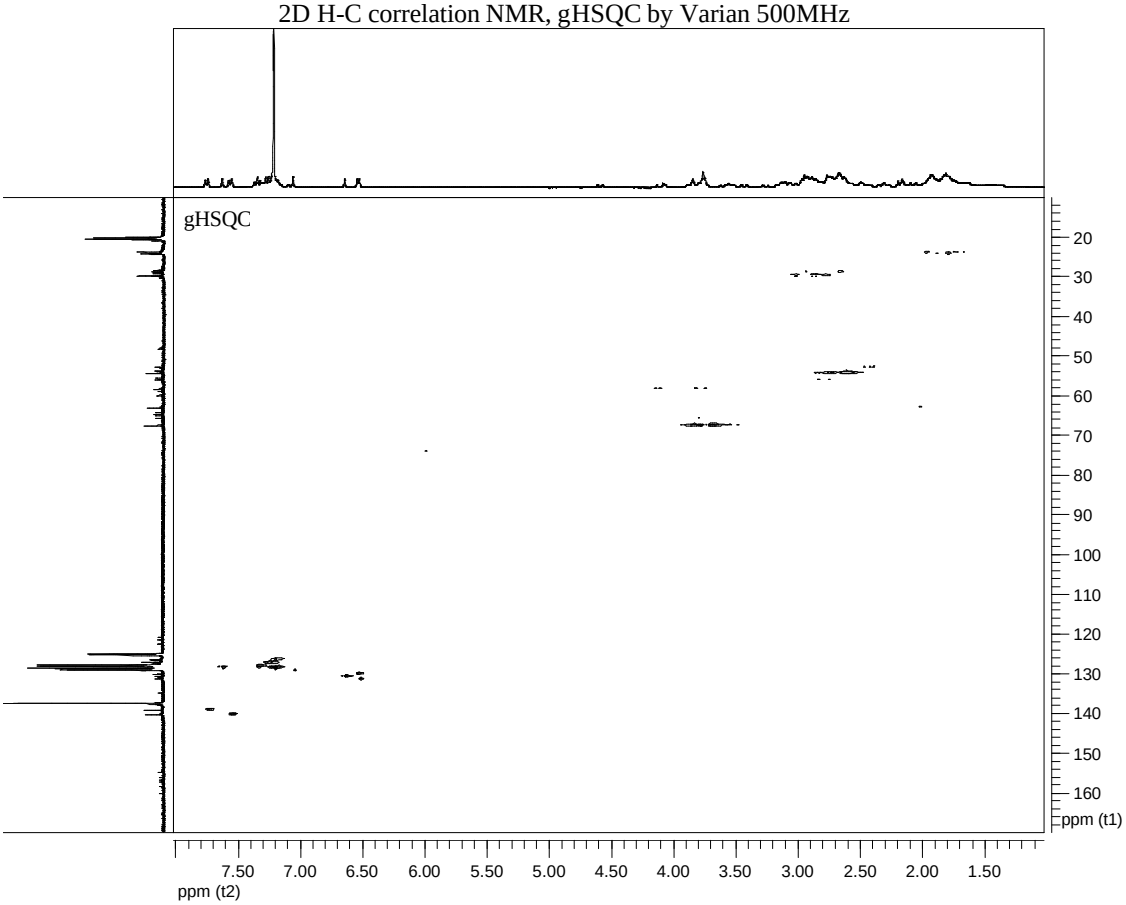
2D H-H correlation NMR, gDQCOSY by Varian 500MHz



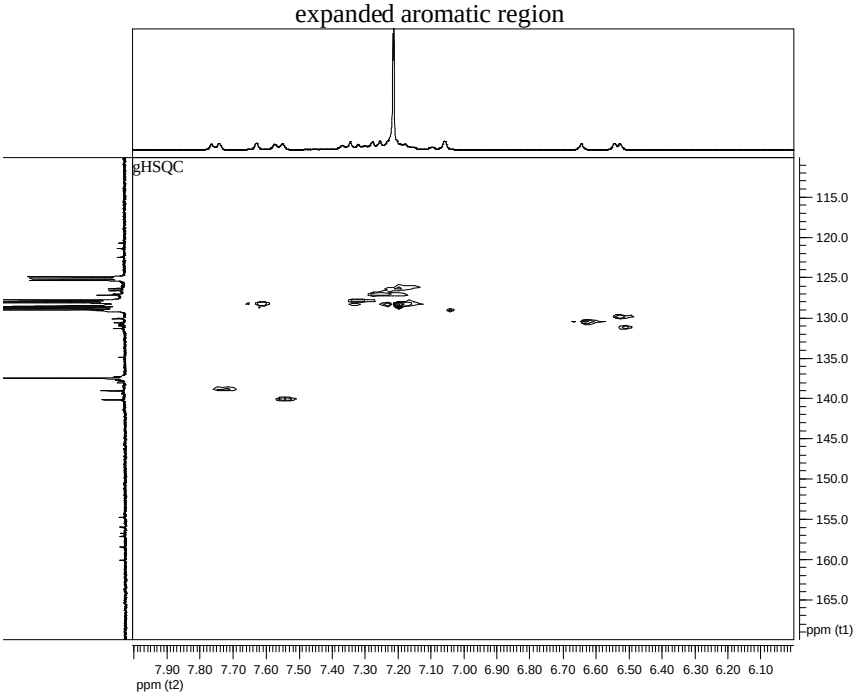
expanded aromatic region



2D H-C correlation NMR, gHSQC by Varian 500MHz



expanded aromatic region



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