Supporting Information
for
Gold(III) Porphyrin-Catalyzed Cycloisomerization of Allenones

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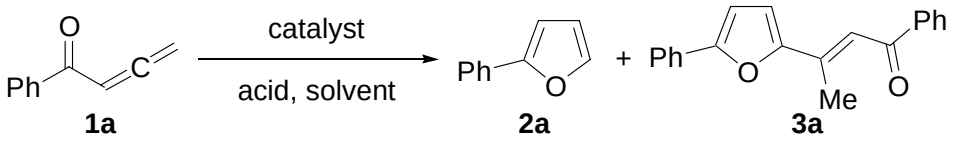
General Experimental Section: Reagents were obtained commercially and used without further purification unless indicated otherwise. The gold(III) porphyrin catalysts and allenone starting materials **1** were prepared following literature procedures.[S1, S2] Solvent was removed under reduced pressure and the residue obtained was chromatographed on a silica gel column (230-400 mesh) using a gradient solvent system (EtOAc: *n*-hexane as eluant unless specified otherwise). ^{1}H and ^{13}C NMR spectra were measured on either a Bruker DPX-400 or DPX-300 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Mass spectra were determined on a Finnigan MAT 95 mass spectrometer. IR spectra were recorded on Bio-RAD PTS-165 spectrometer.

General Procedure for Gold(III) Porphyrin-catalyzed Cycloisomerization of Allenones 1 to Furans 2

To a acetone solution (3 mL) containing allenone **1** (0.5 mmol) was added gold(III) porphyrin (5 μmol) and Brønsted acid (0.05 mmol) and the resultant mixture was stirred at 60^{o}C for 30 mins. The solvent was removed and the crude residue was purified by silica gel column chromatography to give the furan product **2**. The same procedure was used for reactions with other Au(III) or Ag(I) catalysts.

Table S1. Optimization of Reaction Conditions[a]



1a **2a** **3a**

entry	acid	catalyst	solvent	time (h)	yield (%)[b, c]
1	TFA	[Au(TPP)]Cl[d]	acetone	0.5	88[e]
2	TFA	[Au(F_{20}-TPP)]Cl[f]	acetone	0.25	78
3	TFA	[Au(TPP)]Cl	EtOH	0.5	87
4	TFA	[Au(TPP)]Cl	1,2-dichloroethane	1	79
5	TFA	[Au(TPP)]Cl	DMF	0.5	78
6	TFA	[Au(TPP)]Cl	DMSO	0.5	81
7	TFA	[Au(TPP)]Cl	CH_3CN	1	82
8	TFA	[Au(TPP)]Cl	C_6H_6	2	28
9	TFA	[Au(TPP)]Cl	EtOAc	2	17
10[g]	TFA	[Au(TPP)]Cl	acetone	2	28[h]
11	TsOH	[Au(TPP)]Cl	acetone	0.5	87
12	CH_3CO_2H	[Au(TPP)]Cl	acetone	1	29
13	-	[Au(TPP)]Cl	acetone	2	-[i]
14	-	[Au(TPP)]OTf	acetone	2	-[i]
15	TFA	$AuCl_3$	acetone	0.5	49[j]
16	TFA	$AuPPh_3Cl$	acetone	0.5	48[k]
17	TFA	[Au(salen)]Cl[l]	acetone	0.5	38[m]
18[n]	TFA	$AgNO_3$	acetone	0.5	10[o]

[a]Reactions were performed with 1 mol% catalyst at 60°C. [b]^{1}H NMR yield. [c]All substrate conversions were quantitative based on ^{1}H NMR analysis. [d]H_2(TPP) = *meso*-tetraphenylporphyrin. [e]Isolated yield. [f]H_2(F_{20}-TPP) = *meso*-tetrakis(pentafluorophenyl)porphyrin. [g]Reaction conducted at room temperature. [h]31% substrate conversion as determined by ^{1}H NMR analysis. [i]No reaction. [j]The dimer **3a** was also isolated in 16% yield. [k]58% substrate conversion based on ^{1}H NMR analysis. [l]H_2(salen) = *N*,*N*'-bis(salicylidene)ethylenediamine. [m]47% substrate conversion based on ^{1}H NMR analysis. [n]Conducted with 2 mol% $AgNO_3$ catalyst. [o]21% substrate conversion based on ^{1}H NMR analysis. The dimer **3a** was also isolated in 2% yield.

2-Phenyl-furan 2a.[S3] Yield 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, 2H, J = 7.9 Hz), 7.46 (d, 1H, J = 1.8 Hz), 7.37 (t, 2H, J = 7.9 Hz), 7.22-7.27 (m, 1H), 6.64 (d, 1H, J = 3.4 Hz), 6.46 (dd, 1H, J = 3.4, 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 142.0, 130.9, 128.6, 127.3, 123.8, 111.6, 104.9; MS (EI) *m/z* 144 [M^+]; HRMS (EI) calcd. for $C_{10}H_8O$ 144.0575, found 144.0572.

2-*p*-Tolyl-furan 2b. Yield 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, 2H, J = 8.2 Hz), 7.41 (d, 1H, J = 1.8 Hz), 7.14 (d, 2H, J = 8.2 Hz), 6.55 (d, 1H, J = 3.3Hz), 6.42 (dd, 1H, J = 3.3, 1.8 Hz), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 141.6, 137.1, 129.3, 128.2, 123.7, 111.5, 104.2, 21.2; IR (neat, cm^{-1}) 3292, 1633, 1435, 1340, 1287, 1131, 1096, 1058, 642; MS (EI) *m/z* 158 [M^+]; HRMS (EI) calcd. for $C_{11}H_{10}O$ 158.0731, found 158.0726.

2-(4-Methoxy-phenyl)-furan 2c.[S3] Yield 81%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, 2H, J = 8.9Hz), 7.41 (d, 1H, J = 1.6 Hz), 6.90 (d, 2H, J = 8.9Hz), 6.50 (d, 1H, J = 3.3Hz), 6.43 (dd, 1H, J = 3.3, 1.6 Hz), 3.81(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 153.9, 141.3, 125.2, 123.9, 114.1, 114.5, 103.3, 55.2; MS (EI) *m/z* 174 [M^+]; HRMS (EI) calcd. for $C_{11}H_{10}O_2$ 174.0681, found 174.0685.

2-(4-Bromo-phenyl)-furan 2d.[S4] Yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.51 (m, 5H), 6.63 (d, 1H, J = 3.4Hz), 6.45 (dd, 1H, J = 3.4, 1.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 142.3, 131.8, 129.7, 125.3, 121.0, 111.8, 105.5; MS (EI) *m/z* 222 [M^+]; HRMS (EI) calcd. for $C_{10}H_7BrO$ 221.9680, found 221.9679.

2-(3-Bromo-phenyl)-furan 2e.[S3] Yield 87%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.57 (d, 1H, J = 7.8 Hz), 7.46 (t, 1H, J = 0.9 Hz), 7.38 (dt, 1H, J = 7.8, 0.9 Hz), 7.23 (t, 1H, J = 7.8Hz), 6.66 (d, 1H, J = 3.4Hz), 6.46-6.48 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 142.5, 132.7, 130.2, 130.1, 126.7, 122.8, 122.2, 111.8, 106.1; MS (EI) *m/z* 222 [M^+]; HRMS (EI) calcd. for $C_{10}H_7OBr$ 221.9680, found 221.9682.

2-(2-Bromo-phenyl)-furan 2f.[S5] Yield 98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (dd, 1H, J = 7.9, 1.6 Hz), 7.64 (dd, 1H, J = 7.9, 1.0 Hz), 7.51(dd, 1H, J = 1.8, 0.7 Hz), 7.35 (dt, 1H, J = 7.4, 1.2 Hz), 7.08-7.17 (m, 2H), 6.51 (dd, 1H, J = 3.5, 1.8Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 112.2, 134.1, 131.2, 128.8, 128.3, 127.3, 119.6, 111.3, 110.5; MS (EI) *m/z* 222 [M^+]; HRMS (EI) calcd. for $C_{10}H_7OBr$ 221.9680, found 221.9683.

2-(4-Chloro-phenyl)-furan 2g.[S3] Yield 86% ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 2H, J = 8.7 Hz), 7.44 (d, 1H, J = 1.7 Hz), 7.34(d, 2H, J = 8.7 Hz), 6.61 (d, 1H, J = 3.4 Hz), 6.45 (dd, 1H, J = 3.4, 1.7Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 142.2, 132.9, 129.3, 128.8, 124.9, 111.7, 105.4; MS (EI) *m/z* 178 [M^+]; HRMS (EI) calcd. for $C_{10}H_7OCl$ 178.0185, found 178.0187.

4-Furan-2-yl-benzoic acid methyl ester 2h.[S3] Yield 92%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03(d, 2H, J = 8.4Hz), 7.72(d, 2H, J = 8.4Hz), 7.51(d, 1H, J = 1.7Hz), 6.78(d, 1H, J = 3.4Hz), 6.50(dd, 1H, J = 3.4, 1.7Hz), 3.92(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 152.8, 143.0, 134.7, 129.9, 128.4, 123.3, 111.9, 107.1, 51.9; MS (EI) *m/z* 171 [M^+ – Me]; HRMS (EI) calcd. for $C_{11}H_7O_2$ 171.0446, found 171.0445.

2-(4-Nitro-phenyl)-furan 2i.[S6] Yield 91%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, 2H, J = 8.9Hz), 7.79 (d, 2H, J = 8.9 Hz), 7.57 (d, 1H, J = 1.6 Hz), 6.88 (d, 1H, J = 3.4Hz), 6.55 (dd, 1H, J = 3.4, 1.6Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 144.1, 136.4, 129.1, 124.3, 123.9, 112.4, 108.9; MS (EI) *m/z* 189 [M^+]; HRMS (EI) calcd. for $C_{10}H_7NO_3$ 189.0426, found 189.0424.

2-Naphthalen-2-yl-furan 2j.[S7] Yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.75-7.86 (m, 4H), 7.52 (d, 1H, J = 1.7 Hz), 7.41-7.49 (m, 2H), 6.77 (d, 1H, J = 3.3Hz), 6.52 (dd, 1H, J = 3.3, 1.7Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 142.3, 133.5, 132.6, 128.3, 128.2, 128.1, 127.7, 126.4, 125.9, 122.3, 122.1, 111.8, 105.7; MS (EI) *m/z* 194 [M^+]; HRMS (EI) calcd. for $C_{14}H_{10}O$ 194.0732, found 194.0738.

2-(6-Bromo-naphthalen-2-yl)-furan 2k. Yield 85%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.93 (s, 1H), 7.67-7.76 (m, 3H), 7.50-7.53 (m, 2H), 6.75 (d, 1H, J = 3.3 Hz), 6.50 (dd, 1H, J = 3.3, 1.7Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 142.5, 133.5, 131.9, 129.8, 129.77, 129.70, 128.5, 127.4, 123.8, 121.8, 119.7, 111.8, 105.9; IR (KBr, cm^{-1}) 3057, 1699, 1470, 1429, 1215, 1161, 1007, 758; MS (EI) *m/z* 272 [M^+]; HRMS (EI) calcd. for $C_{14}H_9OBr$ 271.9836, found 271.9835.

6-Furan-2-yl-naphthalene-2-carboxylic acid methyl ester 2l. Yield 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.14 (s, 1H), 8.04 (d, 1H, J = 8.6Hz), 7.79-7.94 (m, 3H), 7.54 (d, 1H, J = 1.6 Hz), 6.82 (d, 1H, J = 3.3 Hz), 6.53 (dd, 1H, J = 3.3, 1.6 Hz), 3.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 153.5, 142.8, 135.7, 131.8, 130.8, 130.3, 129.7, 128.3, 127.2, 125.8, 123.0, 121.8, 111.9, 106.7, 52.2; IR (KBr, cm^{-1}) 3293, 1707, 1425, 1286, 1057, 630; MS (EI) *m/z* 252 [M^+]; HRMS (EI) calcd. for $C_{16}H_{12}O_3$ 252.0786, found 252.0791.

2-Anthracen-2-yl-furan 2m. Yield 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.36 (s, 1H), 8.29 (s, 1H), 7.97-8.00 (m, 3H), 7.74 (dd, 1H, J = 8.9, 1.6 Hz), 7.54 (d, 1H, J = 1.2 Hz), 7.43-7.46 (m, 2H), 6.68 (d, 1H, J = 3.3Hz), 6.53 (dd, 1H, J = 3.3, 1.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 142.4, 132.2, 131.8, 131.6, 130.8, 128.6, 128.2, 128.1, 127.4, 126.5, 126.1, 125.5, 125.4, 122.3, 121.8, 111.8, 105.3; IR (KBr, cm^{-1}) 3025, 1686, 1443, 1356, 1201, 1007, 758, 690; MS (EI) *m/z* 244 [M^+]; HRMS (EI) calcd. for $C_{18}H_{12}O$ 244.0888, found 244.0887.

1,4-Difurylbenzene 2n. Yield 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.47 (dd, 2H, J = 1.8, 0.7Hz), 6.66 (dd, 2H, J = 3.4, 0.7 Hz), 6.47 (dd, 2H, J = 3.4, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 142.1, 129.7, 124.0, 111.7, 105.1; IR (KBr, cm^{-1}) 3010, 1611, 1440, 1342, 1208, 1123, 1008, 769; MS (EI) *m/z* 210 [M^+]; HRMS (EI) calcd. for $C_{14}H_{10}O_2$ 210.0681, found 210.0681.

[2,2']Bifuranyl 2o.[S8] Yield 82%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40(d, 2H, J = 1.6 Hz), 6.54 (d, 2H, J = 3.3 Hz), 6.44 (dd, 2H, J = 3.3, 1.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 146.6, 111.3, 105.1; MS (EI) *m/z* 134 [M^+]; HRMS (EI) calcd. for $C_8H_6O_2$ 134.0367, found 134.0147.

2-Thiophen-2-yl-furan 2p.[S9] Yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, 1H, J = 1.8, 0.6 Hz), 7.25 (dd, 1H, J = 3.6, 1.1 Hz), 7.22 (dd, 1H, J = 5.1, 1.1 Hz), 7.03 (dd, 1H, J = 5.1, 3.6Hz), 6.49 (d, 1H, J = 3.3Hz), 6.44 (dd, 1H, J = 3.3, 1.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 141.6, 133.8, 127.6, 124.1, 122.5, 111.6, 104.9; MS (EI) *m/z* 150 [M^+]; HRMS (EI) calcd. for C_8H_6OS 150.0139, found 150.0150.

2-Methyl-furan 2q.[S3] Yield 89%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, 1H, J = 1.7 Hz), 6.26 (dd, 1H, J = 2.9, 1.7 Hz), 5.96 (d, 1H, J = 2.9 Hz), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 140.7, 110.2, 105.3, 13.3; MS (EI) *m/z* 82 [M^+]; HRMS (EI) calcd. for C_5H_6O 82.0419, found 82.0423.

2-Benzyl-furan 2r.[S3] Yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.31 (m, 6H), 6.28 (dd, 1H, J = 3.0, 1.9 Hz), 5.99 (d, 1H, J = 3.0Hz), 3.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 141.4, 138.1, 128.7, 128.5, 126.4, 110.2, 106.2, 34.4; MS (EI) *m/z* 158 [M^+]; HRMS (EI) calcd. for $C_{11}H_{10}O$ 158.0731, found 158.0715.

3-Butyl-2-methyl-furan 2s.[S10] Yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, 1H, J = 1.7 Hz), 6.18 (d, 1H, J = 1.7 Hz), 2.28-2.33 (m, 2H), 2.20 (s, 3H), 1.42-1.49 (m, 2H), 1.26-1.36 (m, 2H), 0.91 (t, 3H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 139.6, 118.9, 111.5, 32.6, 24.4, 22.3, 13.9, 11.4; MS (EI) *m/z* 138 [M^+]; HRMS (EI) calcd. for $C_9H_{14}O$ 138.1044, found 138.1038.

2-Methyl-5-pentyl-furan 2t. Yield 97%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (s, 2H), 2.55 (t, 2H, J = 7.6 Hz), 2.24 (s, 3H), 1.57-1.64 (m, 2H), 1.24-1.35 (m, 4H), 0.90 (t, 3H, J = 6.9Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 149.9, 105.6, 105.0, 31.4, 28.0, 27.8,

22.4, 13.9, 13.4; IR (neat, cm^{-1}) 2958. 2932, 1715, 1470, 1377, 1101; MS (EI) *m/z* 152 [M^+]; HRMS (EI) calcd. for $C_{10}H_{16}O$ 152.1201, found 152.1209.

2-Hexyl-5-styryl-furan 2u. Yield 95%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 2H, J = 7.5Hz), 7.31 (t, 2H, J = 7.3 Hz), 7.20 (t, 1H, J = 7.3 Hz), 6.95 (d, 1H, J = 6.2 Hz), 6.82 (d, 1H, J = 6.2 Hz), 6.23 (d, 1H, J = 3.1 Hz), 6.00 (d, 1H, J = 3.1 Hz), 2.64 (t, 2H, J = 7.6 Hz), 1.62-1.70 (m, 2H), 1.25-1.40 (m, 6H), 0.89 (t, 3H, J = 6.7 Hz)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 151.5, 137.8, 128.6, 127.1, 126.1, 125.4, 116.7, 109.6, 106.8, 31.5, 28.8, 28.2, 27.9, 22.5, 14.0; IR (neat, cm^{-1}) 2929, 1598, 1530, 1494, 1447, 1017, 955, 778, 747, 691; MS (EI) *m/z* 254 [M^+]; HRMS (EI) calcd. for $C_{18}H_{22}O$ 254.16706, found 254.1669.

3-Butyl-5-pentyl-2-styryl-furan 2v. Yield 90%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, 2H, J = 7.6 Hz), 7.32 (t, 2H, J = 7.3 Hz), 7.19 (t, 1H, J = 7.3 Hz), 6.90 (d, 1H, J = 6.2 Hz), 6.83 (d, 1H, J = 6.2 Hz), 5.91 (s, 1H), 2.62 (t, 2H, J = 7.5 Hz), 2.44 (t, 2H, J = 7.5 Hz), 1.62-1.71 (m, 2H), 1.50-1.60 (m, 2H), 1.28-1.46 (m, 6H), 0.87-0.97 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0, 146.8, 137.9, 128.5, 126.8, 125.9, 125.3, 123.7, 114.8, 108.3, 32.5, 31.5, 30.1, 27.9, 24.8, 22.5, 22.3, 14.0, 13.8; IR (neat, cm^{-1}) 2934, 1599, 1533, 1495, 1443, 1018, 945, 775, 684; MS (EI) *m/z* 296 [M^+]; HRMS (EI) calcd. for $C_{21}H_{28}O$ 296.2140, found 296.2132.

3-Butyl-2-methyl-5-pentyl-furan 2w. Yield 93%; ^1H NMR (300 MHz, $CDCl_3$) δ 5.76 (s, 1H), 2.51 (t, 2H, J = 7.6Hz), 2.26 (t, 2H, J = 7.5 Hz), 2.15 (s, 3H), 1.54-1.65 (m, 2H), 1.40-1.52 (m, 2H), 1.25-1.38 (m, 6H), 0.87-0.94 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 144.7, 119.4, 106.4, 32.6, 31.5, 28.0, 27.8, 24.5, 22.4, 22.3, 13.98, 13.90, 11.3; IR (neat, cm^{-1}) 2958, 2931, 1693, 1466, 1378, 1148, 929; MS (EI) *m/z* 208 [M^+]; HRMS (EI) calcd. for $C_{14}H_{24}O$ 208.1827, found 208.1819.

Procedure for Recycling of [Au(TPP)]Cl for Allenone Cycloisomerization

To an acetone solution (30 mL) containing allenone **1a** (15 mmol) was added [Au^{III}(TPP)]Cl (15 μmol) and CF_3CO_2H (1.5 mmol) and the resultant mixture was stirred at 60^{o}C for 2 h. About 27 mL of solvent was removed under reduced pressure and *n*-hexane was added to the mixture to precipitate out the gold(III) porphyrin catalyst, which was filtered and washed with *n*-hexane (3 x 40 mL). Excess solvent was removed under reduced pressure and the product yield was determined by ^{1}H NMR analysis. After each reaction, the catalyst recovered by filtration was dried under reduced pressure. The Cycloisomerization of allenone **1a** was repeated a further nine times using the recovered catalyst under the same reaction conditions.

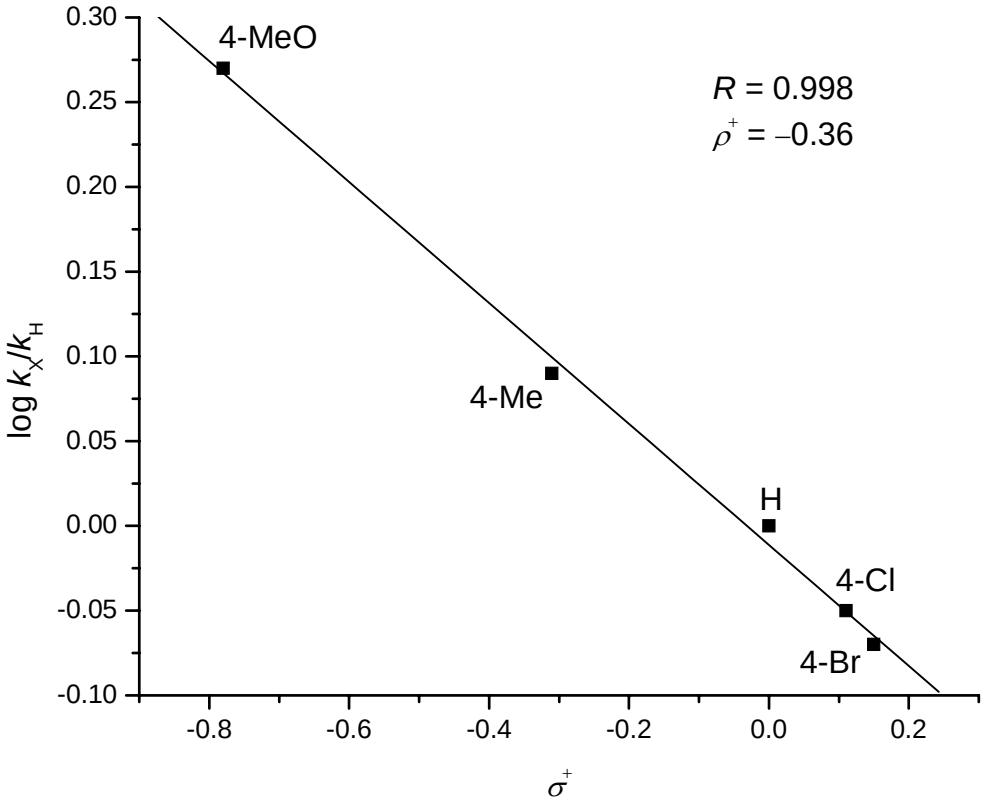
Competitive Allenone Cycloisomerizations Catalyzed by [Au(TPP)]Cl

To a solution of **1a** (0.5 mmol) and substituted phenyl allenone (0.5 mmol) in acetone (3 mL) was added [Au(TPP)]Cl (5 μmol) and TFA (0.05 mmol). The mixture was stirred at 50^{o}C for 30 mins. The amount of substrate conversions were determined by ^{1}H NMR analysis.

Table S2. Variation of log k_X/k_H with σ^+ for [Au(TPP)]Cl-catalyzed Cycloisomerization of *Para*-substituted Allenones *p*-X-$C_6H_4C(O)CH=C=CH_2$ **1a-d** and **1g**.

allenone	X	k_X/k_H	log $k_X/k_{H(exptl)}$	σ^+
1c	OMe	1.86	0.27	–0.78
1b	Me	1.23	0.09	–0.31
1a	H	1	0	0
1g	Cl	0.89	–0.05	0.11
1d	Br	0.85	–0.07	0.15

Figure S1. Linear Free-energy Correlation of log k_X/k_H vs. σ^+ Plot for Cycloisomerization of *Para*-substituted Allenones *p*-X-$C_6H_4C(O)CH=C=CH_2$ **1a-d** and **1g** Catalyzed by [Au(TPP)]Cl.



Hydroamination of Phenylacetlyene Catalyzed by [Au(TPP)]Cl[S11]

Phenylacetlyene (0.5 mmol), *p*-anisidine (0.55 mmol) and [Au(TPP)]Cl (25 μmol) was placed in a round bottom flask and stirred at 80 ^oC for 12 h. On cooling the reaction mixture to room temperature, (4-methoxyphenyl)(1-phenylethylidene)amine **5** was obtained by re-crystallized by slowly diffusing *n*-hexane to a CH_2Cl_2 solution containing the reaction mixture. Yield 73%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97-8.00 (m, 2H), 7.42-

7.46 (m, 3H), 6.93 (d, 2H, J = 8.5 Hz), 6.78 (d, 2H, J = 8.5Hz), 3.80 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 156.0, 152.0, 139.8, 130.3, 128.3, 127.1, 120.7, 114.3, 55.4, 17.3; MS (EI) *m/z* 225 [M^+].

Hydrolysis of Phenylacetlyene Catalyzed by [Au(TPP)]Cl[S12]

To a solution of phenylacetlyene (0.5 mmol) and water (2.5 mmol) in ethanol (3 mL) was added [Au(TPP)]Cl (25 μmol) and H_2SO_4 (0.05 mmol). The mixture was stirred at reflux for 18 h. The reaction mixture was diluted with sat. $NaHCO_3$ and extracted with Et_2O, washed with brine, dried over $MgSO_4$. and filtered. Removel of the solvent under eeduced pressure and purification of the resultant residue by flash chromatography gave acetophenone **6**. Yield 87%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, 2H, J = 7.3Hz), 7.56 (t, 1H, J = 7.9 Hz), 7.46(t, 2H, J = 7.9 Hz), 2.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9, 137.1, 133.0, 128.5, 128.2, 26.5; MS (EI) *m/z* 120 [M^+].

Deuterium Labeling Experiments

Gold(III) Porphyrin-catalyzed Cycloisomerization of 1r to 2r

To a solution of **1r** (0.5 mmol) in $(CD_3)_2CO$ (3 mL) and D_2O (0.2 mL) was added [Au^{III}(TPP)]Cl (5 μmol) and CF_3CO_2D (0.1 mmol). The mixture was stirred at 60^{o}C for 30 mins. The solvent was removed and the crude residue was purified by silica gel column chromatography to **2r** in 84% yield with complete substrate conversion and with a deuterium content of 83% at C-3 as determined by ^{1}H NMR analysis (Figure S1a). Yield 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.31 (m, 6H), 6.28 (dd, 0.17H, J = 3.0, 1.9 Hz), 5.99 (s, 1H), 3.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 141.4, 138.1,

128.7, 128.5, 126.5, 110.2, 106.1, 34.4; IR (neat, cm^{-1}) 3032, 2926, 1587, 1502, 1456, 1155, 1070, 991, 939, 704; MS (EI) *m/z* 159 [M^+]; HRMS (EI) calcd. for $C_{11}H_9DO$ 159.0793, found 159.0788.

Treatment of 1r with CF_3CO_2D in $(CD_3)_2CO$ and D_2O

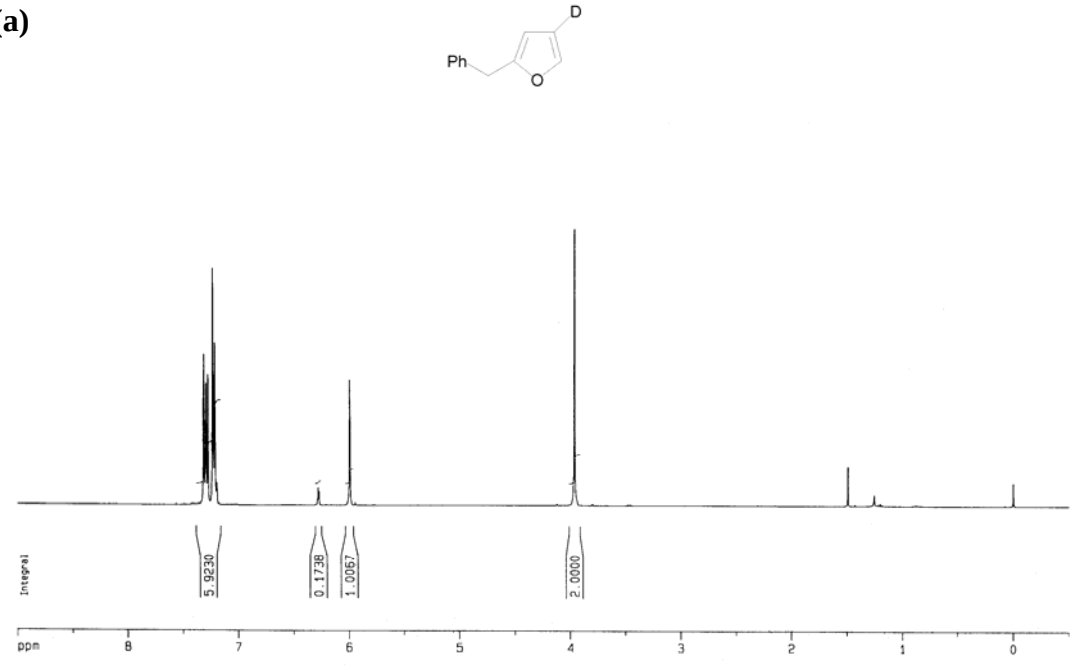
To a solution of **1r** (0.5 mmol) in in $(CD_3)_2CO$ (3 mL) and D_2O (0.2 mL) was added CF_3CO_2D (0.1 mmol). The mixture was stirred at 60°C for 30 mins. The solvent was removed. ^1H NMR analysis of the crude residue revealed no deuterium exchange in **1r** was observed.

Treatment of 2r with [Au(TPP)]Cl and CF_3CO_2D in $(CD_3)_2CO$ and D_2O

To a solution of deuterium-free **2r** (0.5 mmol) in $(CD_3)_2CO$ (3 mL) and D_2O (0.2 mL) was added $[Au^{III}(TPP)]Cl$ (5 μmol) and CF_3CO_2D (0.1 mmol). The mixture was stirred at 60°C for 30 mins. The solvent was removed and the remaining residue was purified by silica gel column chromatography. ^1H NMR analysis of **2r** revealed no deuterium exchange in the furan product was found, as shown in Figure S2.

Figure S2. 1H NMR Spectra of (a) **2r** obtained from [Au^{III}(TPP)]Cl-catalyzed cycloisomerization of **1r** in the presence of $(CD_3)_2CO$, D_2O, and CF_3CO_2D, and (b) deuterium-free **2r** treated with [Au^{III}(TPP)]Cl and CF_3CO_2D in $(CD_3)_2CO$ and D_2O.

(a)



(b)

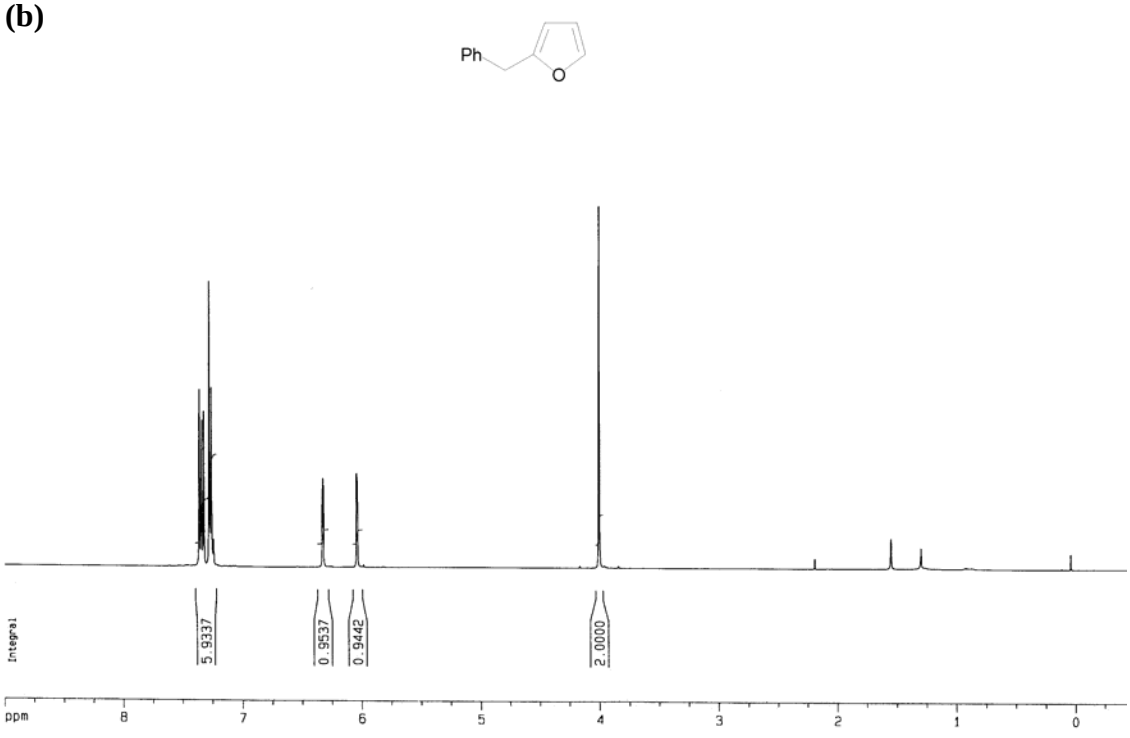


Figure S3. ^{1}H NMR of 2-*p*-Tolyl-furan **2b**.

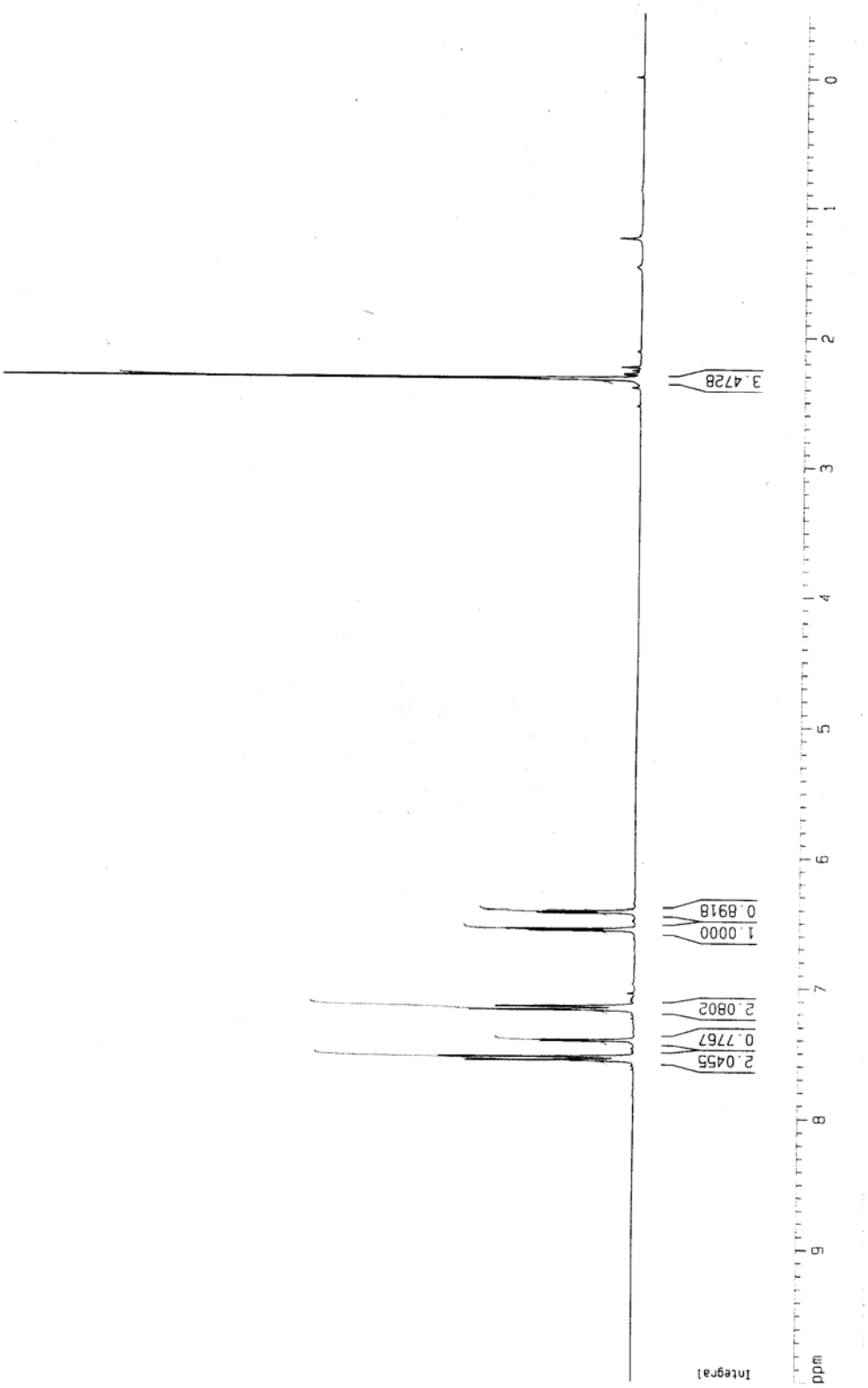


Figure S4. [1]H NMR of 2-(6-Bromo-naphthalen-2-yl)-furan **2k**.

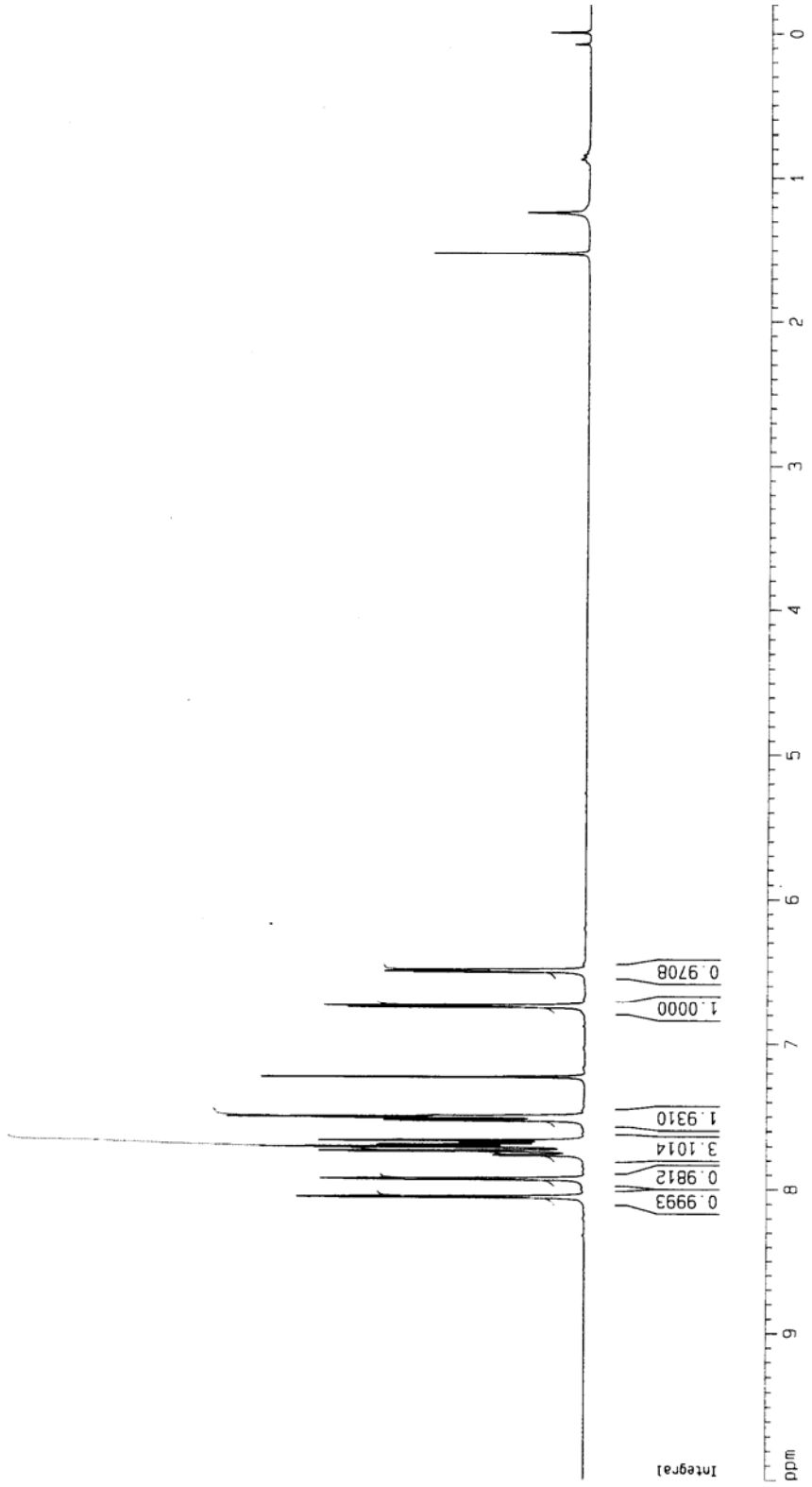


Figure S5. ^{1}H NMR of 6-Furan-2-yl-naphthalene-2-carboxylic acid methyl ester **2l**.

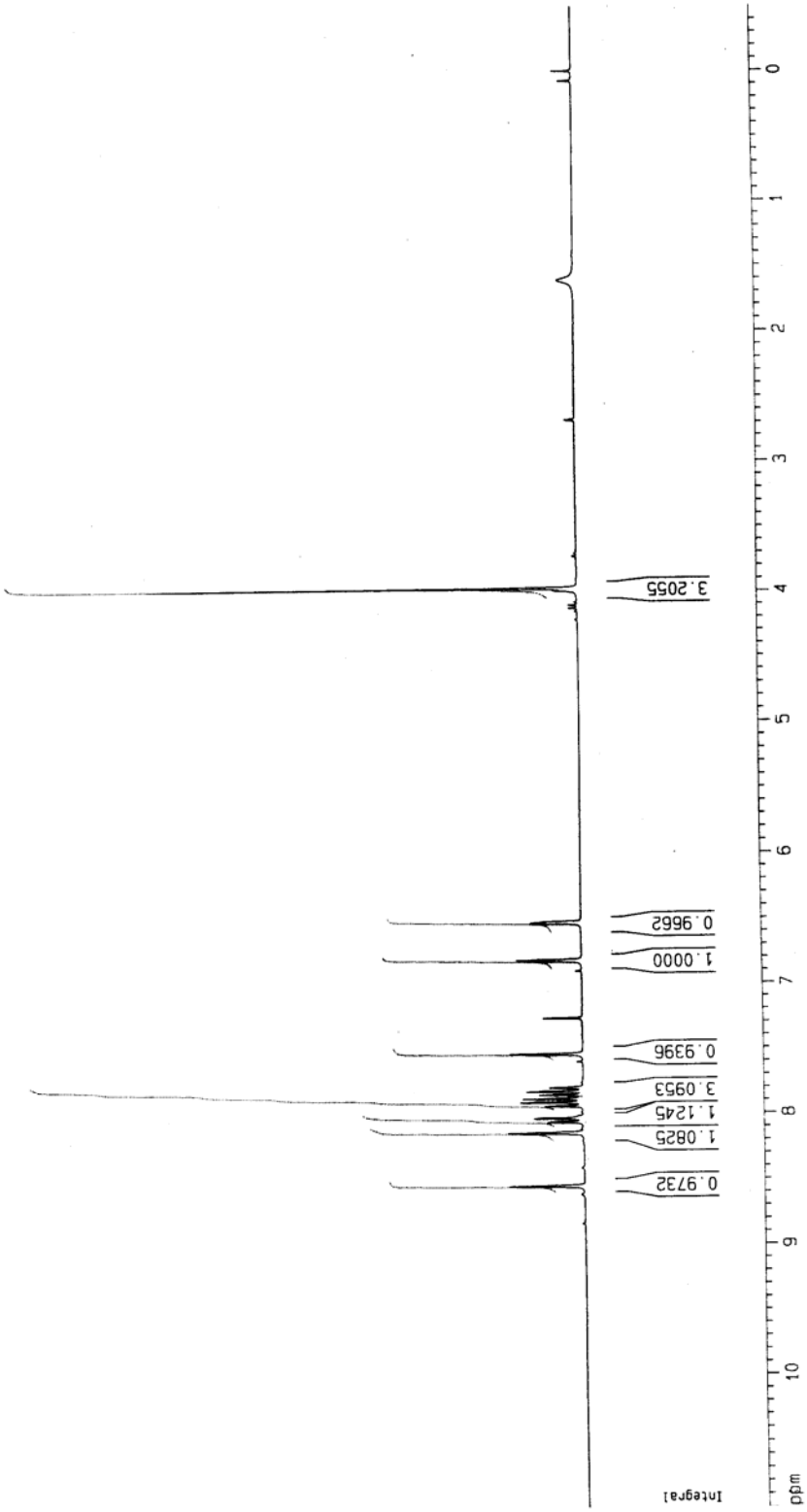


Figure S6. ^{1}H NMR of 2-Anthracen-2-yl-furan **2m**.

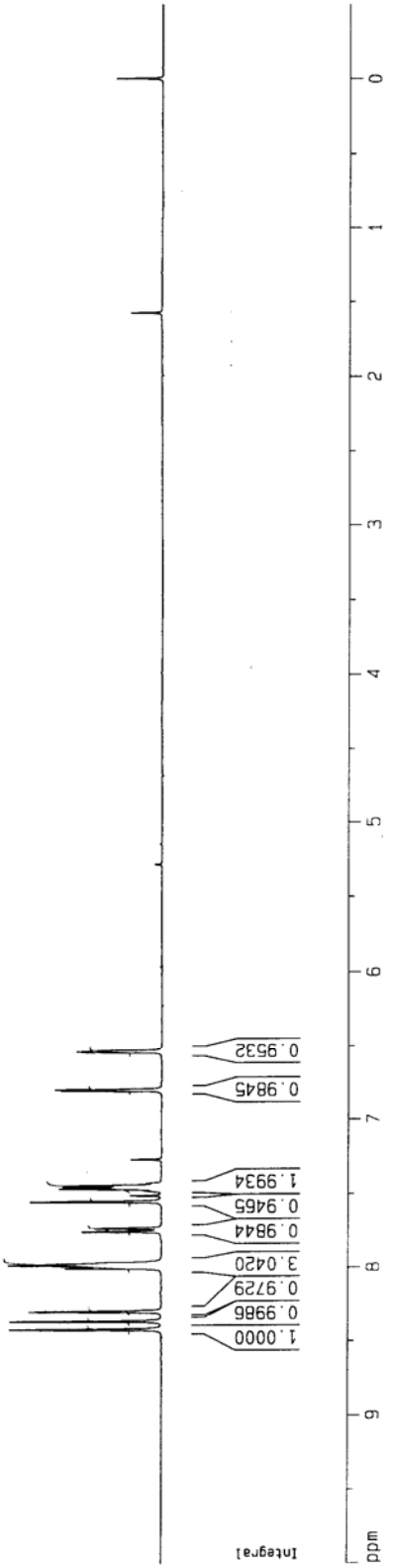


Figure S7. ^{1}H NMR of 1,4-difurylbenzene **2n**.

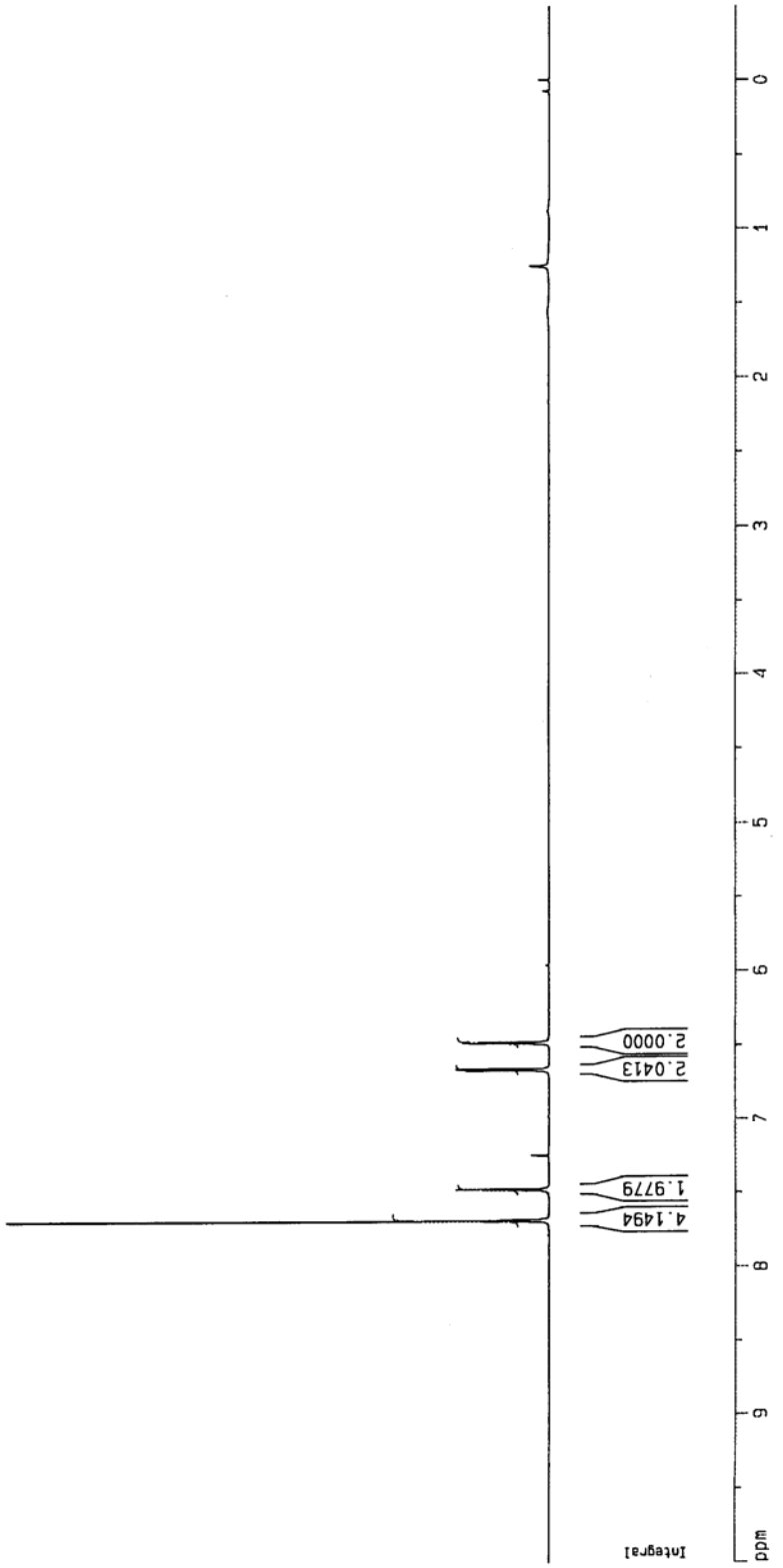


Figure S8. [1]H NMR of 2-Methyl-5-pentyl-furan **2t**.

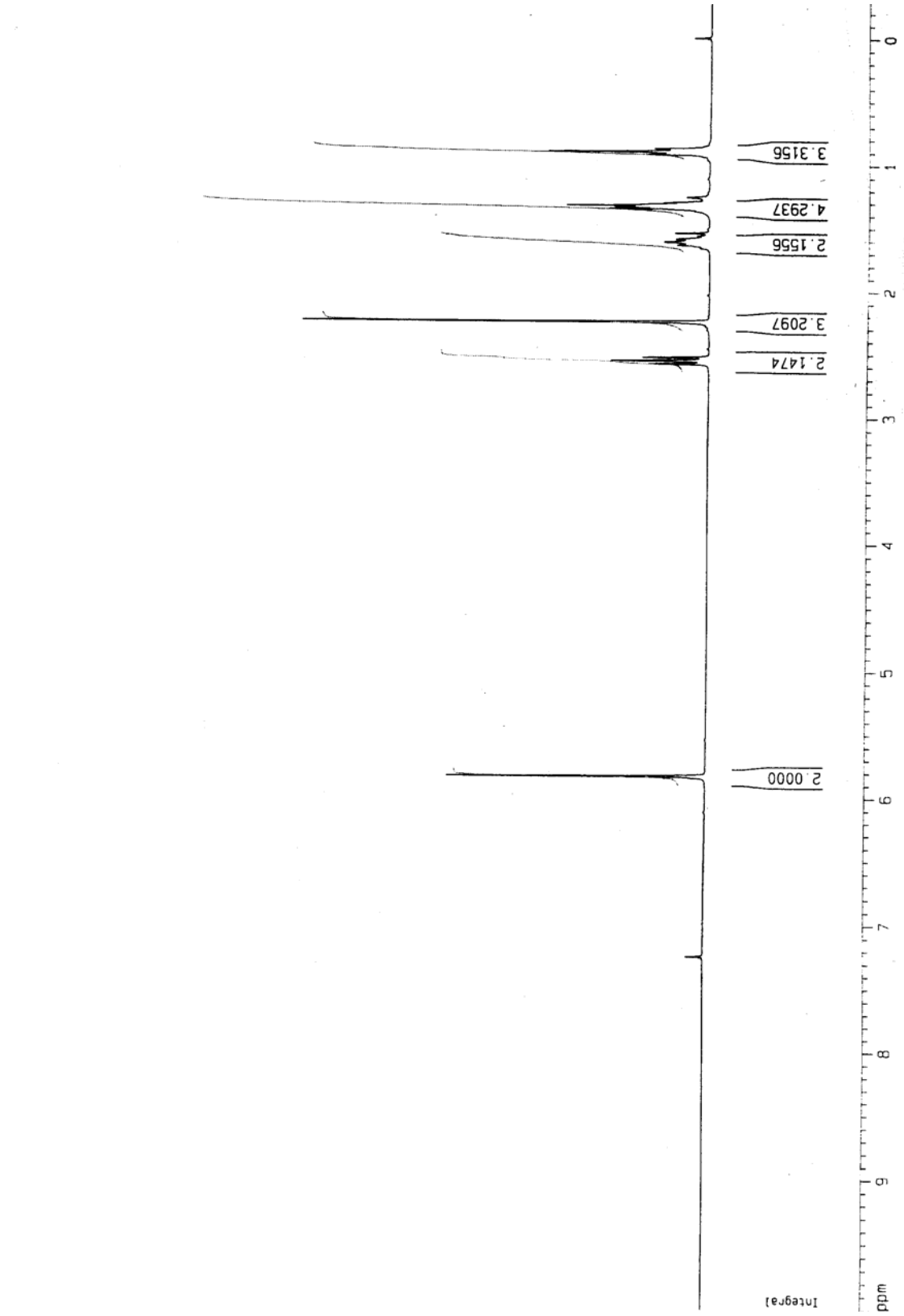


Figure S9. ^{1}H NMR of 2-Hexyl-5-styryl-furan **2u**.

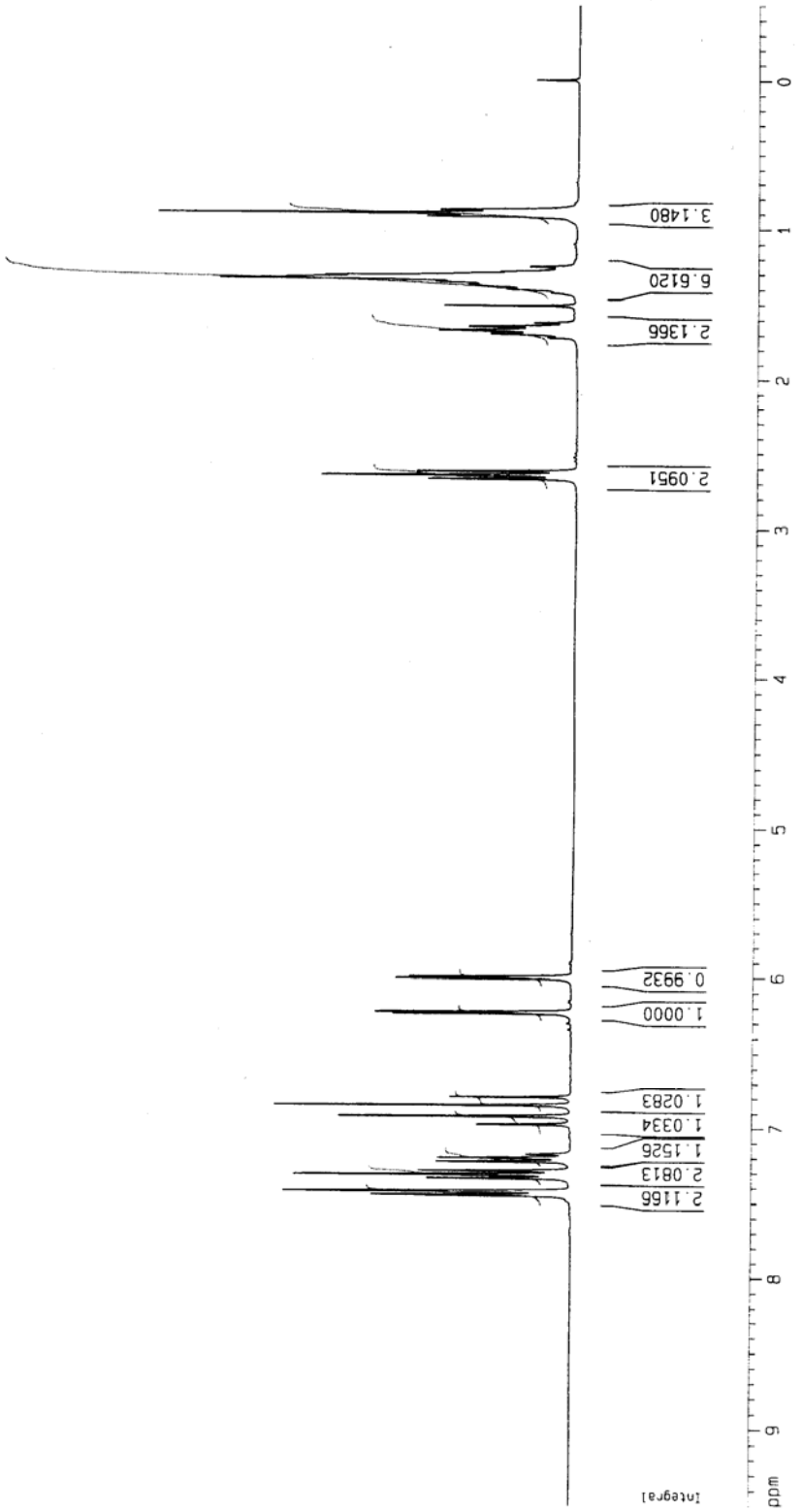


Figure S10. ^{1}H NMR of 3-Butyl-5-pentyl-2-styryl-furan **2v**.

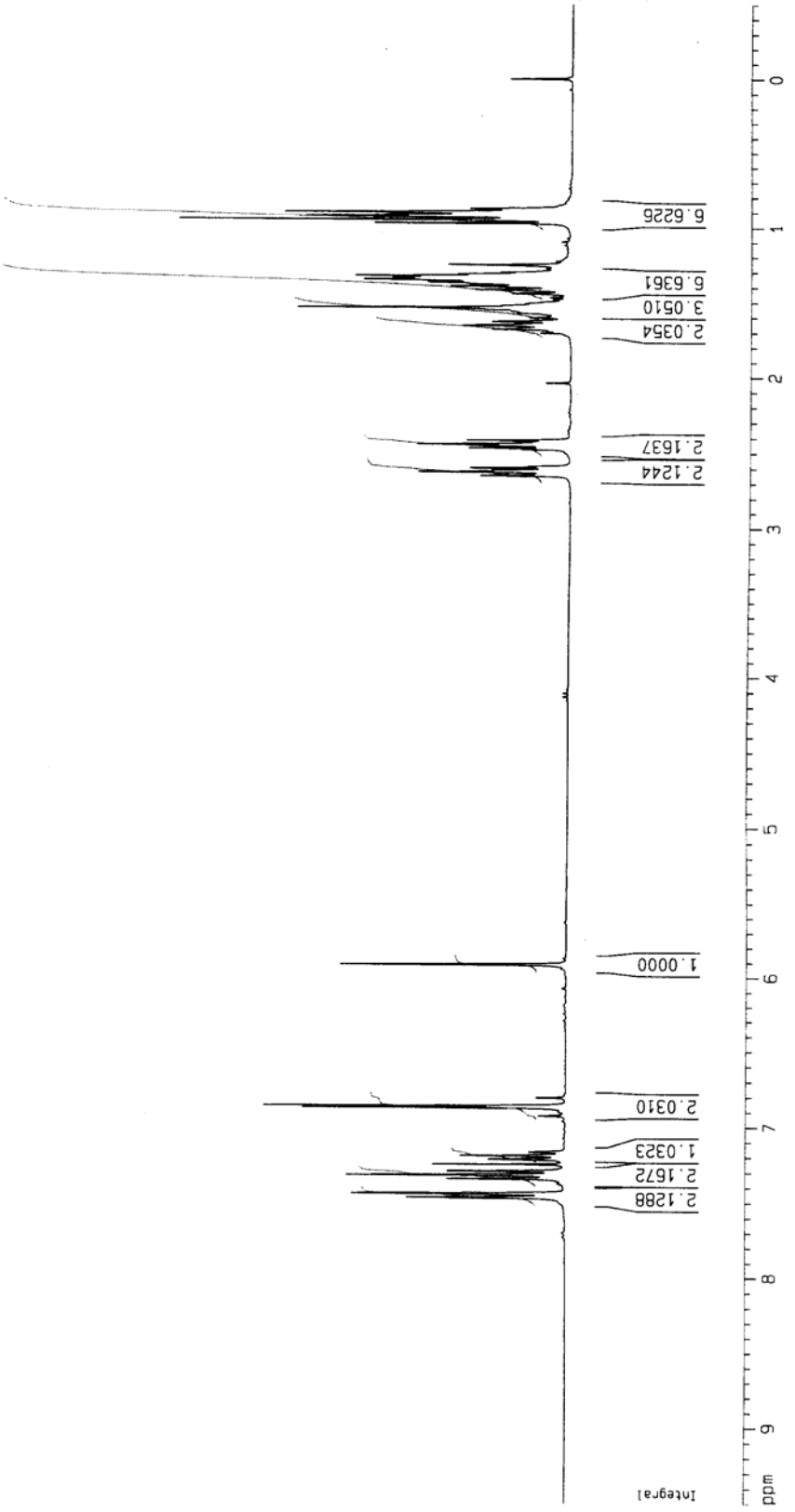
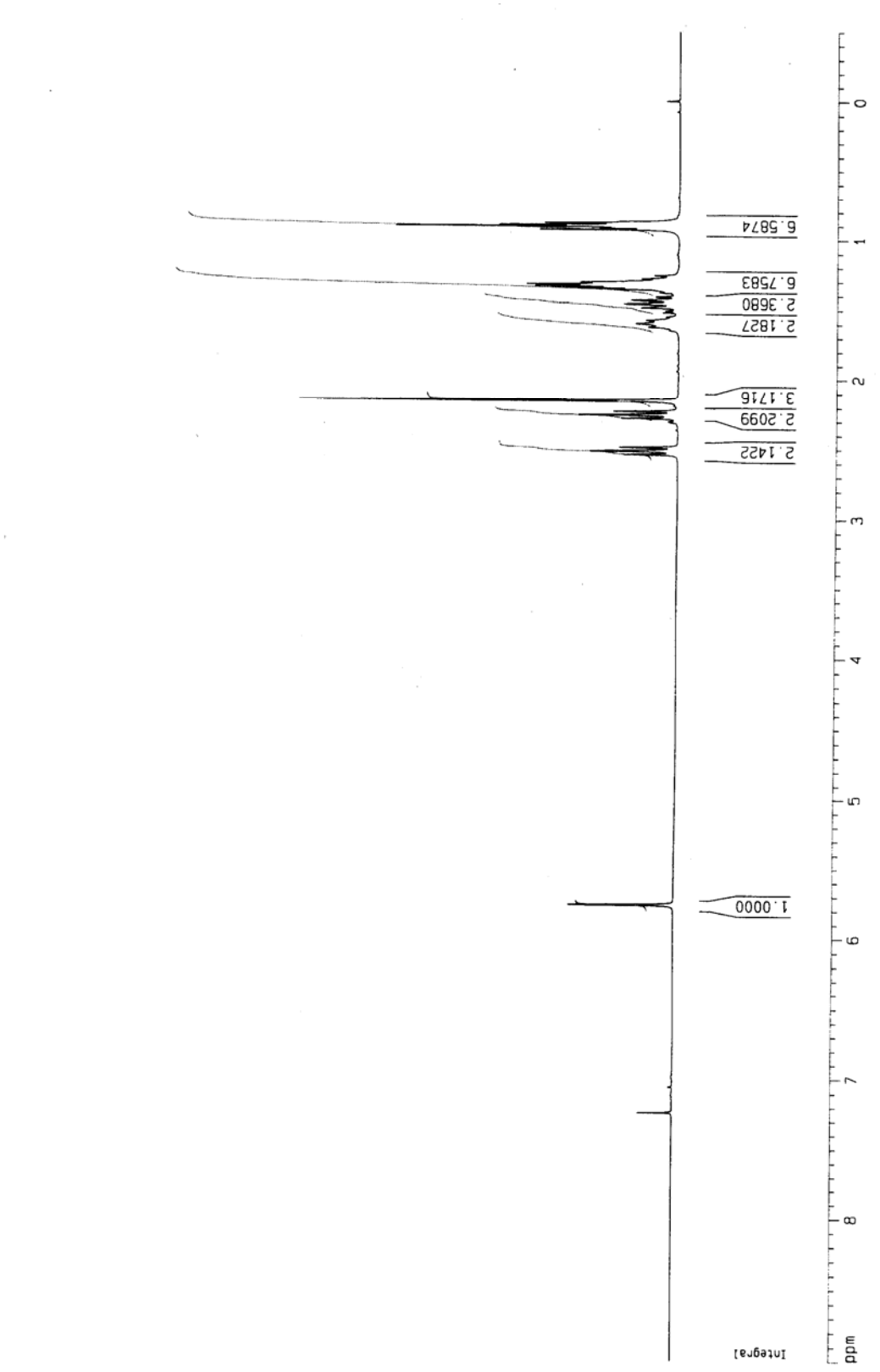


Figure S11. ^{1}H NMR of 3-Butyl-2-methyl-5-pentyl-furan **2w**.



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