Supporting Information

Palladium(II)-Catalyzed Ring Enlargement of 2-(Arylmethylene)cyclopropylcarbinols: Strong Substituent Electronic Nature on the Reaction Pathway

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Content

General Remarks. Melting point instrument is uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Dichloromethane was distilled from CaH_2 under Ar atmosphere. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All of the reactions were monitored by TLC plates coated with Huanghai GF_{254} silica gel. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure.

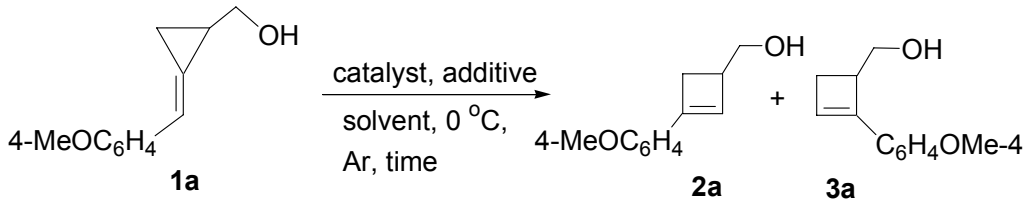
General Procedure for the Preparation of Products 2 and 3.

Compound **1** (0.30 mmol), $PdCl_2$ (0.015 mmol), $CuBr_2$ (0.06 mmol), and $NaHCO_3$ (0.15 mmol) (for compounds **1g**, **1h** and **1i**, 2 mg of MS 4Åwas added) were weighed into an oven-dried test-tube which was sealed with a rubber cap. The tube was then evacuated and back-filled with argon. Then, 1.0 mL of DCM was added into the reaction mixture by a syringe. The mixtures were stirred at zero degree. After completion of the transformations monitored by TLC plates, the reaction mixture was ***directly transferred to silica gel column*** and eluted with mixtures of petroleum ether and ethyl acetate to afford the corresponding products **2** and **3**. These two products are not very stable in air at room temperature. Therefore, they should be stored at < 0 ^{o}C.

General Procedure for the Preparation of Products 4 and 5.

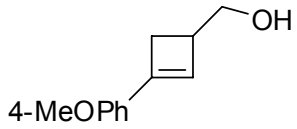
Compound **1** (0.30 mmol), $PdCl_2$ (0.015 mmol), $CuBr_2$ (0.75 mmol), $NaHCO_3$ (0.40 mmol) and 1.0 mL of DCM were added into a test tube. The mixtures were stirred at room temperature with or without a rubber cap. After completion of the transformations monitored by TLC plates, the reaction mixture was directly transferred to silica gel column and eluted with petroleum/ethyl acetate = 30/1 to afford the corresponding products **4** and **5**.

Table S1. Optimization of the Reaction Conditions



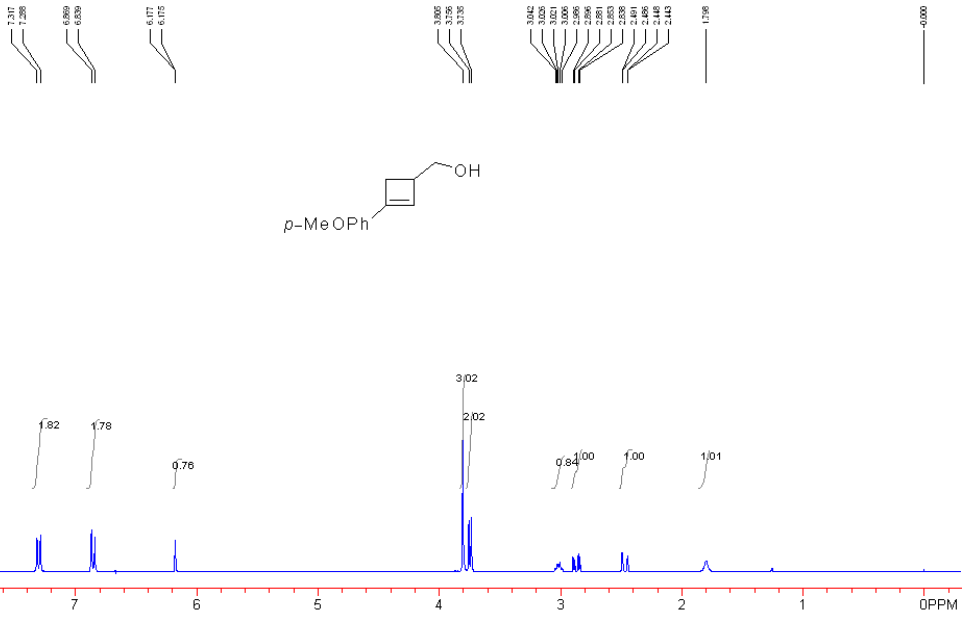
entry[a]	catalyst	additive	solvent	time (h)	conv (%)	yields[b] (%) (**2a**/**3a**)
1[c]	$Pd(OAc)_2$	$CuBr_2$	DCM	0.2	> 99	complex
2	$Pd(OAc)_2$	$CuBr_2$	DCM	0.5	> 99	75 (5:1)
3	$Pd(OAc)_2$	$CuBr_2$	DCE	0.5	> 99	82 (4:1)
4	$Pd(OAc)_2$	$CuBr_2$	PhMe	0.5	42	19 (4:1)
5	$Pd(OAc)_2$	$CuBr_2$	THF	0.5	58	40 (9:1)
6	$Pd(OAc)_2$	$CuBr_2$	EtOEt	0.5	0	—
7	$Pd(OAc)_2$	$CuBr_2$	CH_3CN	1	0	—
8	—	$CuBr_2$	DCM	4	0	—
9	$Pd(OAc)_2$	—	DCM	4	0	—
10	$Pd(OAc)_2$	$Cu(OTf)_2$	DCM	0.5	0	—
11	$Pd(OAc)_2$	$CuBr_2/K_2CO_3$	DCM	0.5	0	—
12	$Pd(OAc)_2$	$CuCl_2$	DCM	1	0	—
13	$Pd(OAc)_2$	$Cu(OAc)_2$	DCM	1	0	—
14	$Pd(OAc)_2$	CuBr	DCM	2	0	—
15	$Pd(OAc)_2$	$NiBr_2$	DCM	2	> 99	88 (6:1)
16	$Pd(OAc)_2$	NaBr	DCM	2	0	—
17	$Pd(OAc)_2$	$MgBr_2$	DCM	2	0	—
18	$Pd(OAc)_2$	$ZnBr_2$	DCM	0.5	40	26 (9:1)
19	$Pd(OAc)_2$	LiBr	DCM	0.5	19	8 (9:1)
20	$Pd(OAc)_2$	$NiBr_2$/LiBr	DCM	1.5	> 99	86 (11:1)
21	$PdBr_2$	—	DCM	0.5	29	23 (5:1)
22	$PdCl_2$	—	DCM	1	81	19 (4:1)
23	$PdCl_2$	$CuBr_2$/AcOH	DCM	0.5	65	35 (4:1)
24[d]	$PdCl_2$	$CuBr_2/NaHCO_3$	DCM	0.5	99	85 (12:1)
25	***$PdCl_2$***	***$CuBr_2/NaHCO_3$***	***DCM***	***0.5***	***> 99***	***89 (12:1)***

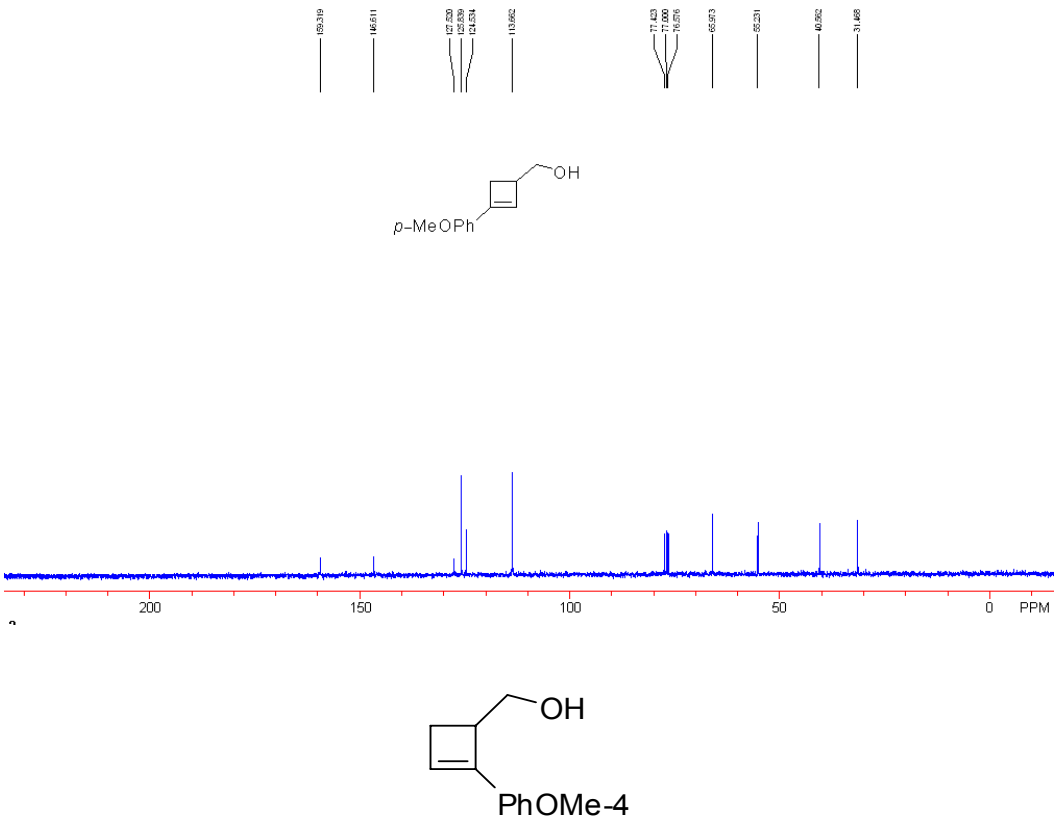
[a] All reactions were carried out with **1a** (0.3 mmol), catalyst (0.015 mmol), additive (0.06 mmol, the second additive such as K_2CO_3, LiBr, AcOH or $NaHCO_3$ was added in 0.15 mmol when necessary), in 1.0 mL of solvent under argon atmosphere. [b] Isolated yields. [c] Carried out at room temperature (20 °C). [d] 0.03 mmol of $CuBr_2$ was added.



[3-(4-Methoxyphenyl)cyclobut-2-enyl]methanol 2a:

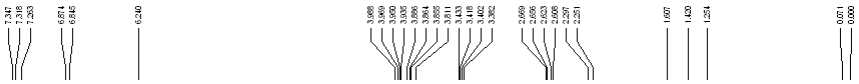
A colorless solid. Mp. 90-92 ^{o}C; IR (film): ν 3369, 2946, 2919, 2837, 1601, 1508, 1303, 1246, 1175, 1106, 1075, 1029, 951, 834, 815, 798, 776 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.80 (s, br, 1H, OH), 2.47 (dd, *J* = 13.2, 1.5 Hz, 1H), 2.87 (dd, *J* = 13.2, 4.5 Hz, 1H), 2.99-3.04 (m, 1H), 3.75 (d, *J* = 6.3 Hz, 2H, CH_2O), 3.81 (s, 3H, CH_3O), 6.18 (d, *J* = 0.6 Hz, 1H, =CH), 6.85 (d, *J* = 9.0 Hz, 2H, ArH), 7.30 (d, *J* = 9.0 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.5, 40.5, 55.2, 66.0, 113.6, 124.6, 125.8, 127.5, 146.6, 159.3; MS (EI) *m/z* (%): 190 (M^+, 39.20), 159 (100.00), 144 (32.54), 129 (19.78), 128 (26.51), 127 (19.78), 116 (23.32), 115 (38.14); Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.54; H, 7.36.

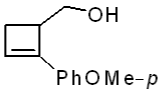




[2-(4-Methoxyphenyl)cyclobut-2-enyl]methanol 3a:

A colorless solid. Mp. 83-85 ^{o}C; IR (film): ν 3450, 2937, 2838, 1672, 1600, 1577, 1512, 1461, 1303, 1250, 1175, 1031, 835 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.61 (s, br, 1H, OH), 2.27 (d, *J* = 13.8 Hz, 1H), 2.64 (dd, *J* = 13.8, 4.2 Hz, 1H), 3.38-3.43 (m, 1H), 3.81 (s, 3H, CH_3O), 3.85-3.89 (m, 1H, CHO), 3.94-4.00 (m, 1H, CHO), 6.24 (s, 1H, =CH), 6.86 (d, *J* = 8.7 Hz, 2H, ArH), 7.33 (d, *J* = 8.7 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 30.1, 44.1, 55.3, 64.7, 113.9, 125.6, 126.1, 127.2, 146.3, 159.2; MS (EI) *m/z* (%): 190 (M^+, 10.45), 147 (16.19), 132 (20.89), 131 (83.55), 103 (40.71), 77 (38.03), 57 (100.00), 51 (19.56), 41 (36.11); HRMS (EI) Calcd. For $C_{12}H_{14}O_2$ 190.0994, Found: 190.0997.

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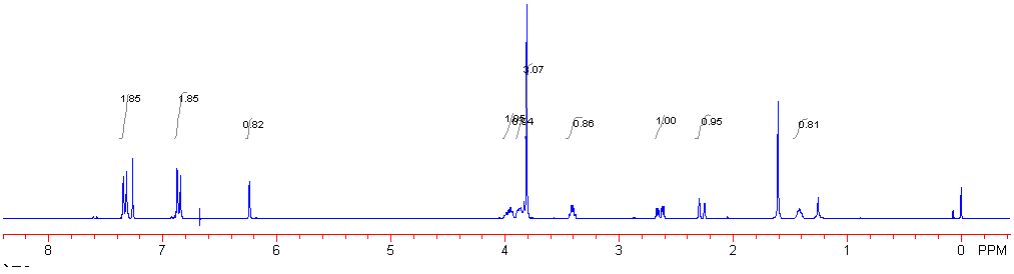
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1.85
0.82
3.07
0.86
1.00
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0.81
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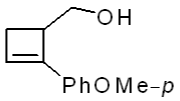
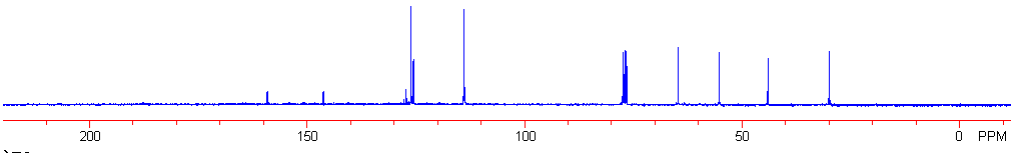
7
6
5
4
3
2
1
0
PPM


OH
PhOMe-p


200
150
100
50
0
PPM

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Ambient temperature
File: NOESY
Mercury-300BB "OMC300"

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Acq. time 0.170 sec
Width 3003.0 Hz
2D Width 3003.0 Hz
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2 x 128 increments
OBSERVE H1, 300.0269630 MHz
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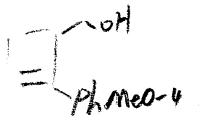
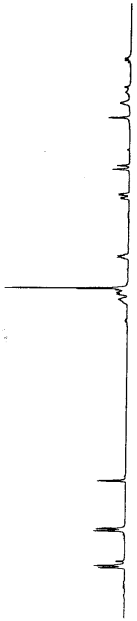
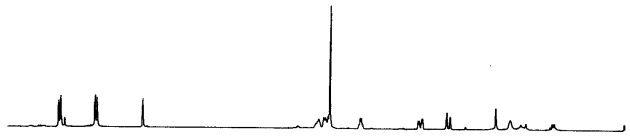
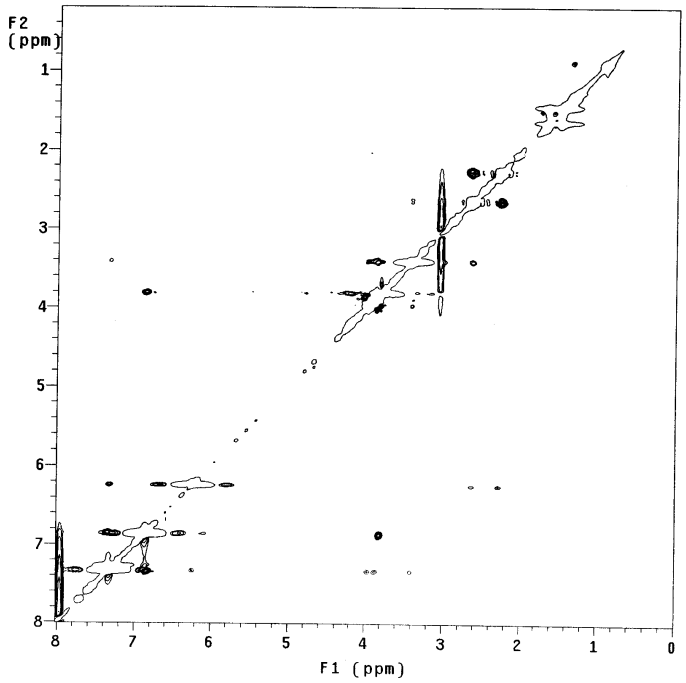
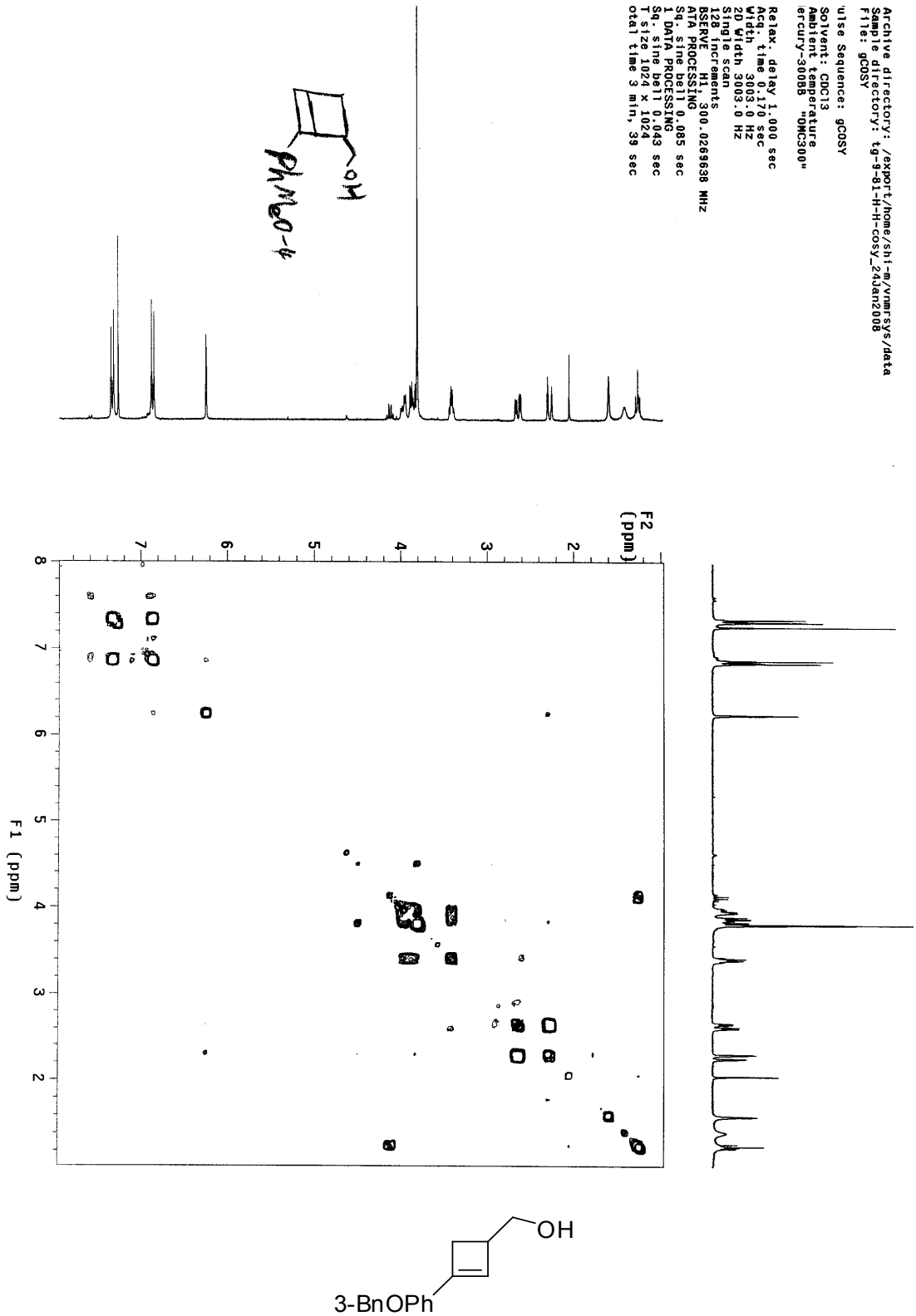






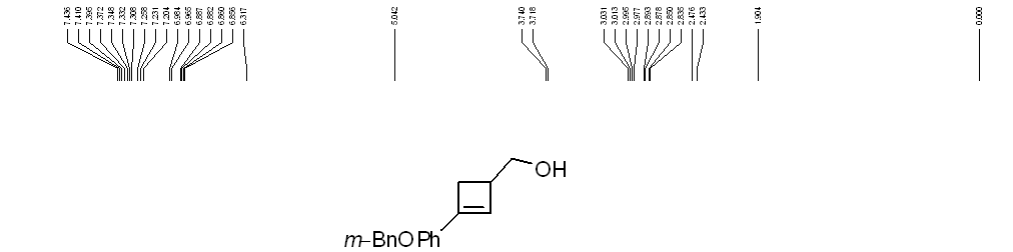


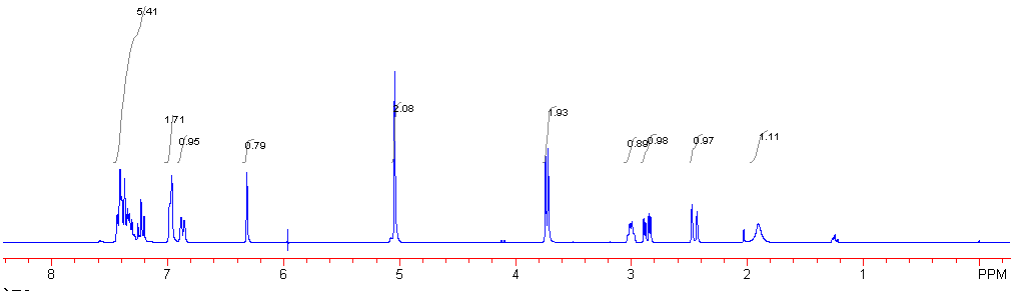


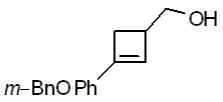
[3-(3-(Benzyloxy)phenyl)cyclobut-2-enyl]methanol 2b:

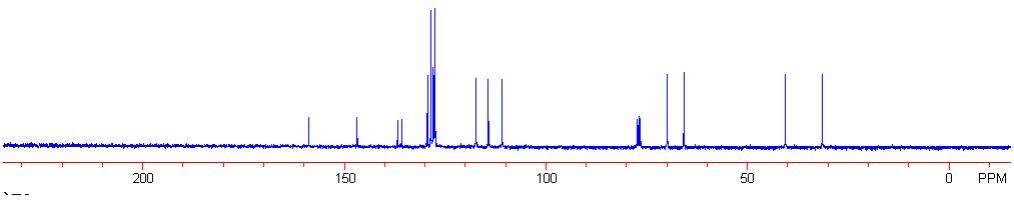
A colorless, viscous liquid. IR (film): ν 3440, 3063, 3032, 2916, 1582, 1486, 1444, 1380, 1319, 1287, 1219, 1027, 777, 738, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.90 (s, br, 1H, OH), 2.45 (d, *J* = 12.9 Hz, 1H), 2.86 (dd, *J* = 12.9, 4.5 Hz, 1H), 2.98-3.03 (m, 1H), 3.73 (d, *J*

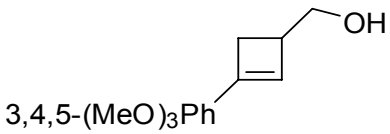
= 6.3 Hz, 2H, CH_2O), 5.04 (s, 2H, $PhCH_2O$), 6.32 (s, 1H, =CH), 6.87 (dd, J = 5.1, 1.2 Hz, 2H, ArH), 6.96-6.98 (m, 2H, ArH), 7.20-7.44 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.5, 40.7, 65.8, 69.9, 110.9, 114.3, 117.3, 127.5, 127.8, 127.9, 128.5, 129.4, 135.8, 136.8, 146.8, 158.8; MS (EI) *m/z* (%): 266 (M^+, 4.93), 235 (5.47), 159 (3.81), 149 (2.87), 131 (2.88), 92 (7.92), 90 (100.00), 65 (8.90); HRMS (EI) Calcd. For $C_{18}H_{18}O$ 266.1307, Found: 266.1301.





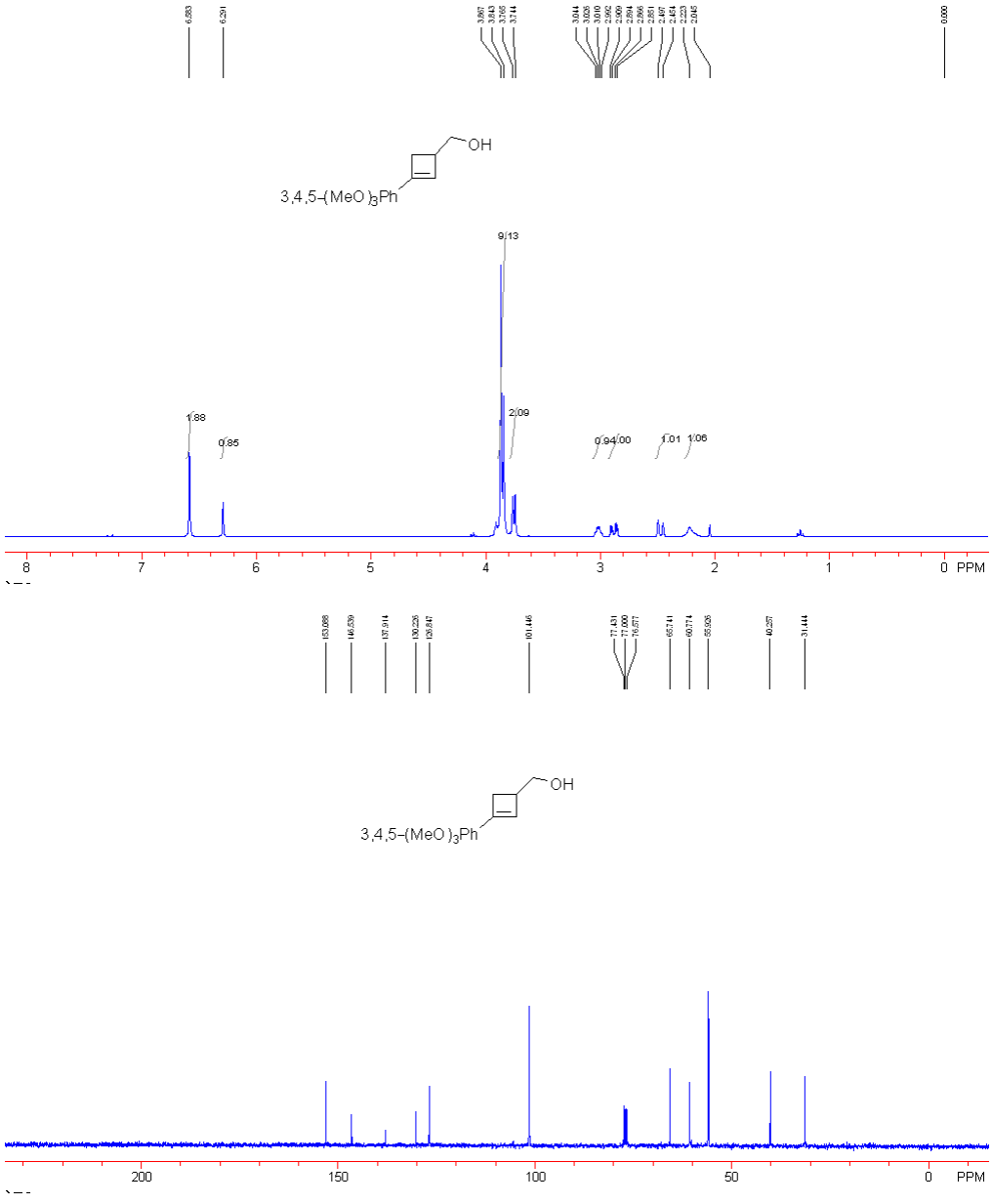


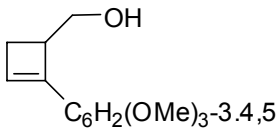




[3-(3,4,5-Trimethoxyphenyl)cyclobut-2-enyl]methanol 2c:

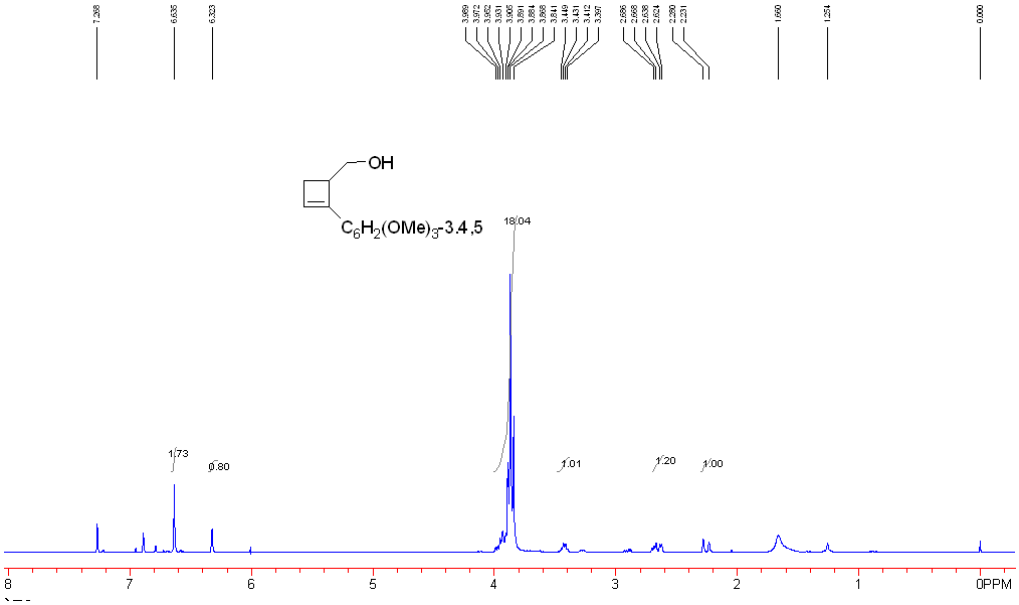
A colorless solid. Mp. 99-101 ^{o}C; IR (film): ν 3442, 2938, 2838, 1579, 1503, 1462, 1415, 1343, 1237, 1126, 1056, 1006, 817 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.22 (s, br, 1H, OH), 2.48 (d, *J* = 13.2 Hz, 1H), 2.88 (dd, *J* = 13.2, 4.5 Hz, 1H), 2.99-3.04 (m, 1H), 3.75 (d, *J* = 6.3 Hz, 2H, CH_2O), 3.84 (s, 3H, CH_3O), 3.87 (s, 6H, $2CH_3O$), 6.29 (s, 1H, =CH), 6.58 (s, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.4, 40.2, 55.9 (2C), 60.8, 65.7, 101.4, 126.9, 130.2, 137.9, 146.5, 153.1; MS (EI) *m/z* (%): 250 (M^+, 76.38), 219 (100.00), 217 (51.34), 201 (92.36), 189 (53.08), 188 (49.55), 174 (26.67), 77 (29.74); HRMS (EI) Calcd. For $C_{14}H_{18}O_4$ 250.1205, Found: 250.1202.

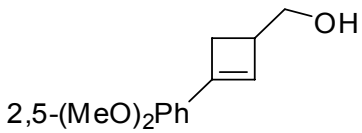




[2-(3,4,5-trimethoxyphenyl)cyclobut-2-enyl]methanol 3c:

A colorless, viscous liquid. IR (film): ν 3496, 2940, 2838, 1678, 1586, 1502, 1459, 1413, 1340, 1235, 1004 839, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.26 (d, *J* = 14.4 Hz, 1H), 2.65 (dd, *J* = 14.4, 4.5 Hz, 1H), 3.40-4.45 (m, 1H), 3.84 (s, 3H, CH_3O), 3.87 (s, 6H, $2CH_3O$), 3.87-3.95 (m, 2H, CH_2O), 6.32 (s, 1H, =CH), 6.64 (s, 2H, ArH); MS (EI) *m/z* (%): 250 (M^+, 13.63), 219 (16.07), 210 (16.78), 195 (64.23), 84 (100.00), 86 (71.94), 49 (19.77), 47 (22.25); HRMS (EI) Calcd. For $C_{14}H_{18}O_4$ 250.1205, Found: 250.1208.

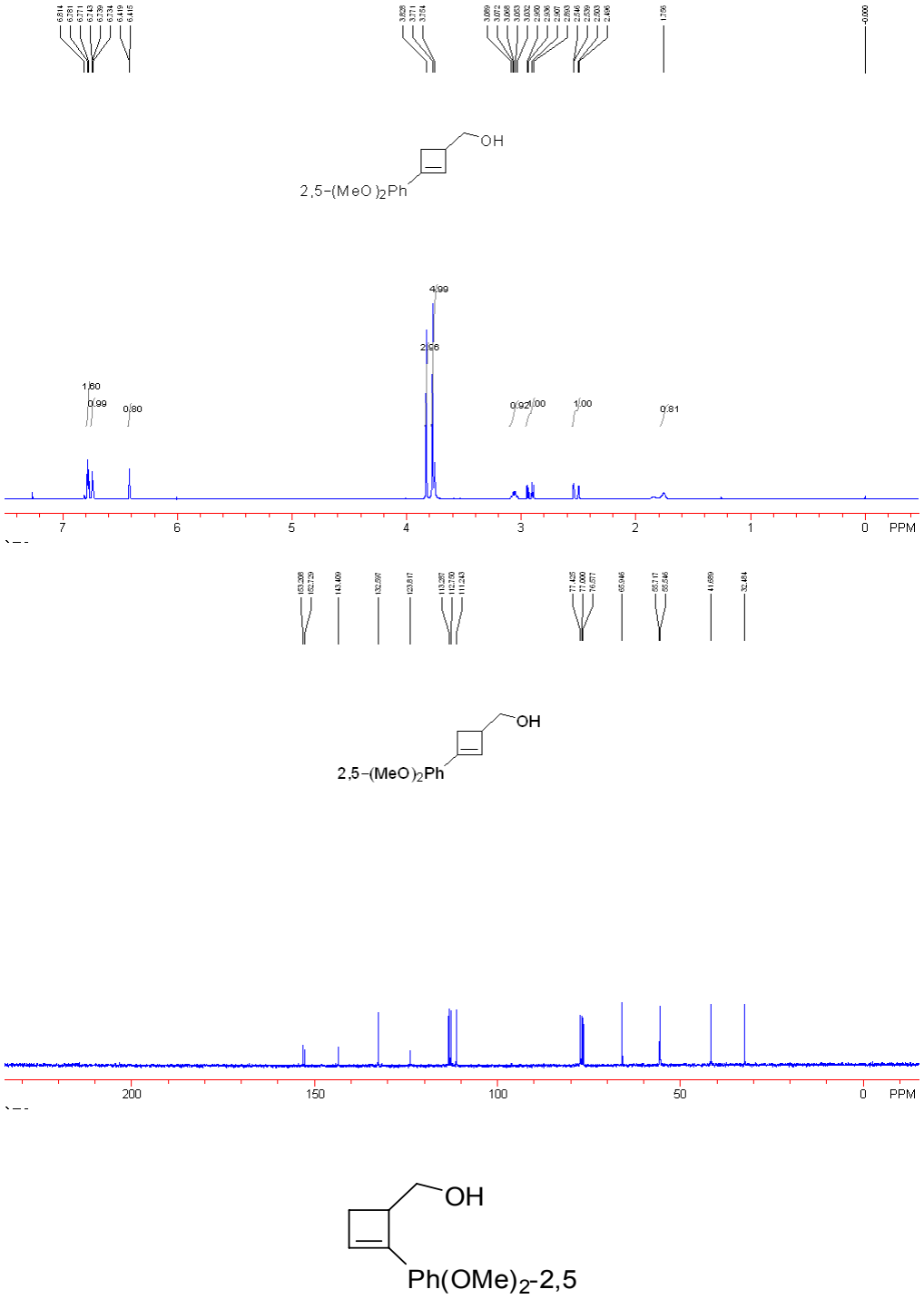




[3-(2,5-Dimethoxyphenyl)cyclobut-2-enyl]methanol 2d:

A colorless, viscous liquid. IR (film): ν 3470, 2996, 2911, 2833, 1582, 1502, 1464, 1278, 1244, 1179, 1023, 827, 803, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.76 (s, br, 1H, OH), 2.52 (dd, *J* = 12.9, 2.1 Hz, 1H), 2.92 (dd, *J* = 12.9, 4.2 Hz, 1H), 3.05-3.07 (m, 1H), 3.76 (d, *J* = 6.3 Hz, 2H, CH_2O), 3.77 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 6.42 (d, *J* = 0.9 Hz, 1H, =CH), 6.73-6.75 (m, 1H, ArH), 6.77 (s, 1H, ArH), 6.78-6.80 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 32.5, 41.7, 55.5, 55.7, 65.9, 111.2, 112.8, 113.3, 123.8, 132.6, 143.4, 152.7,

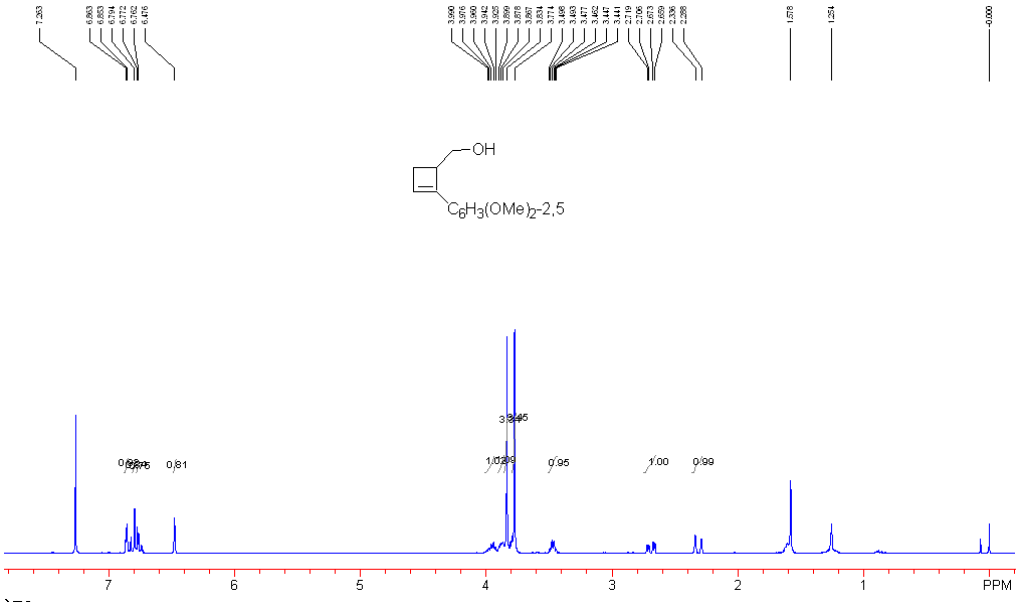
153.2; MS (EI) *m/z* (%): 220 (M^+, 100.00), 189 (74.17), 187 (61.60), 174 (72.45), 161 (66.82), 159 (49.73), 91 (43.55), 77 (51.64); HRMS (EI) Calcd. For $C_{13}H_{16}O_3$ 220.1099, Found: 220.1096.

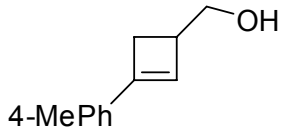


[2-(2,5-Dimethoxyphenyl)cyclobut-2-enyl]methanol 3d:

A colorless, viscous liquid. IR (film): ν 3440, 2938, 2834, 1497, 1464, 1416, 1280, 1224, 1179, 1045, 1023, 808 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.31 (d, *J* = 14.4 Hz, 1H), 2.69 (dd, *J* = 14.4, 4.2 Hz, 1H), 3.44-3.50 (m, 1H), 3.78 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O),

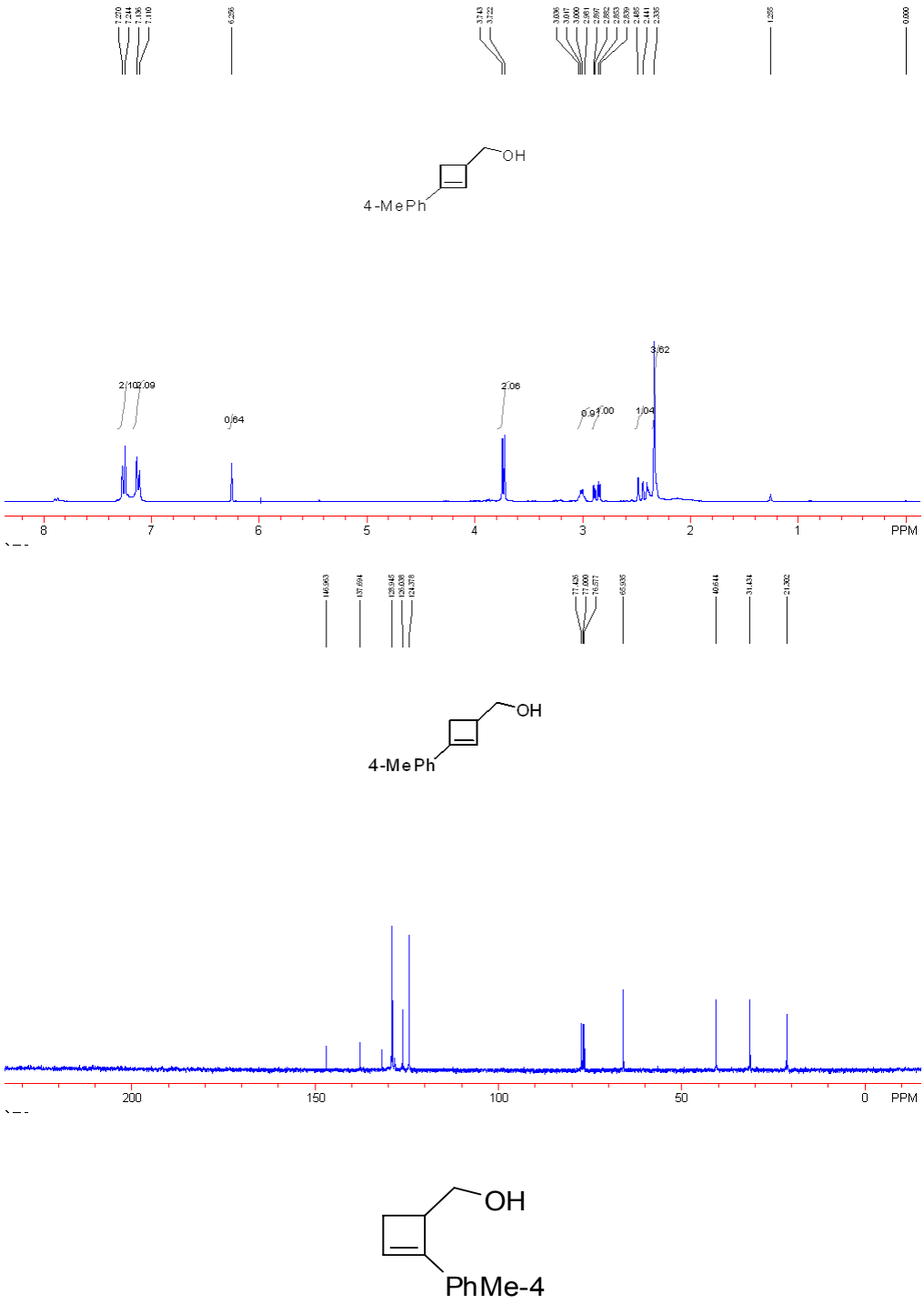
3.86-3.90 (m, 1H, CHO), 3.93-3.98 (m, 1H, CHO), 6.48 (s, 1H, =CH), 6.77 (d, J = 8.7 Hz, 1H, ArH), 6.80 (s, 1H, ArH), 6.86 (d, J = 8.7 Hz, 1H, ArH); HRMS (EI) Calcd. For $C_{13}H_{16}O_3$ 220.1099, Found: 220.1089.





[3-(4-Methyl)cyclobut-2-enyl]methanol 2e:

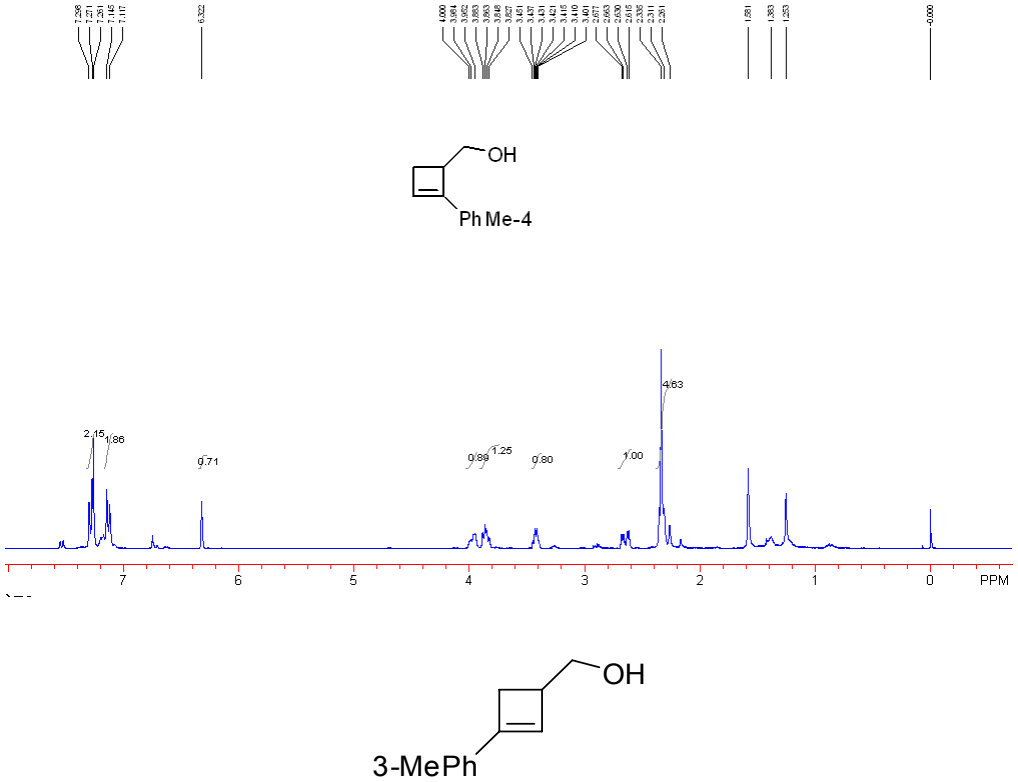
A colorless, viscous liquid. IR (film): ν 3419, 3057, 3028, 2916, 1720, 1686, 1489, 1448, 1275, 1230, 1026, 750, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.33 (s, 3H, CH_3), 2.46 (d, J = 12.9 Hz, 1H), 2.87 (dd, J = 12.9, 4.5 Hz, 1H), 2.98-3.04 (m, 1H), 3.73 (d, J = 6.3 Hz, 2H, CH_2O), 6.26 (s, 1H, =CH), 7.12 (d, J = 7.8 Hz, 2H, ArH), 7.26 (d, J = 7.8 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.3, 31.4, 40.7, 66.0, 124.4, 126.0, 129.0, 131.7, 137.8, 147.1; MS (EI) m/z (%): 174 (M^+, 35.70), 156 (25.03), 145 (23.61), 143 (100.00), 141 (32.23), 128 (91.98), 115 (42.09), 91 (22.42); HRMS (EI) Calcd. For $C_{12}H_{14}O$ 174.1045, Found: 174.1037.



[2-(4-Methoxyphenyl)cyclobut-2-enyl]methanol 3e:

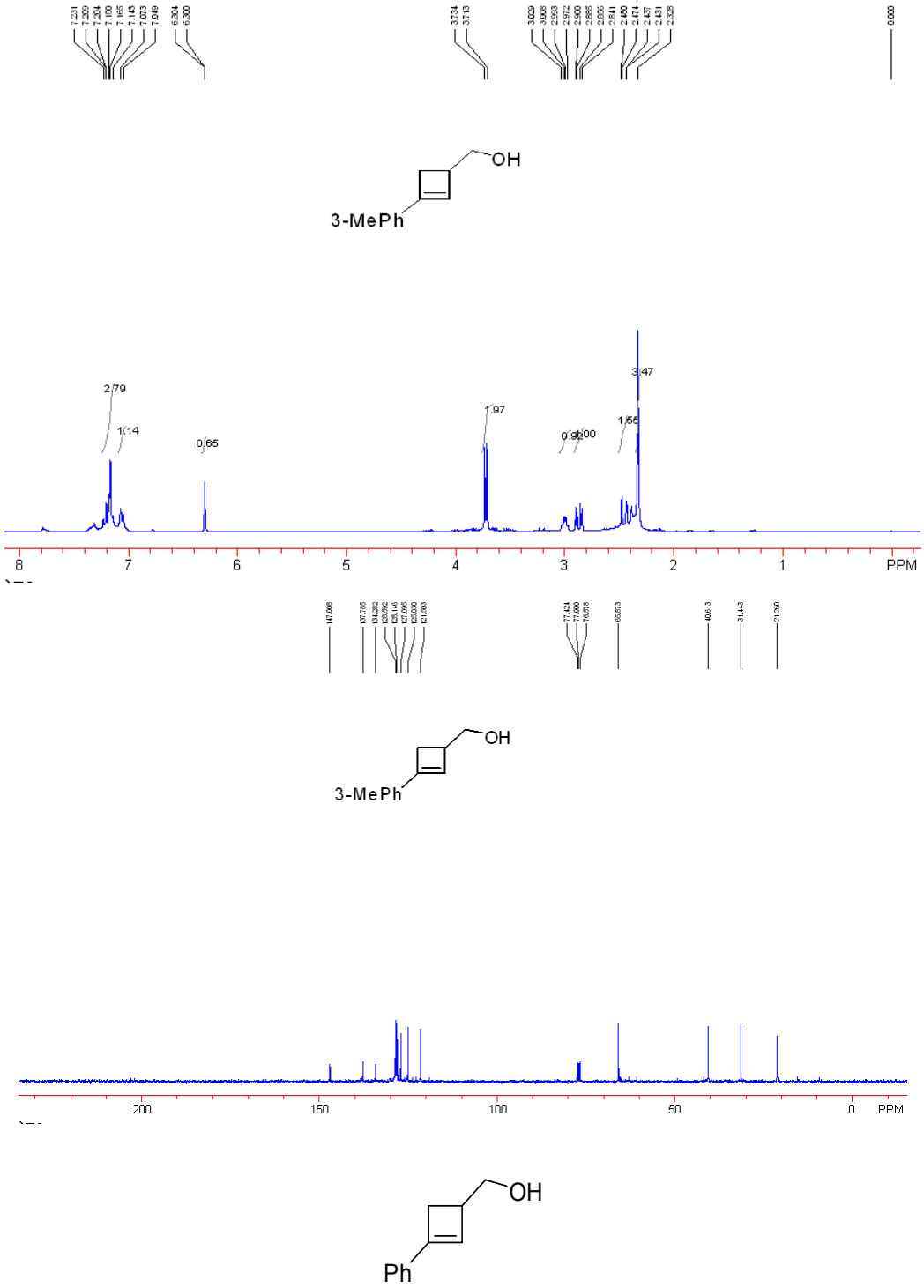
A colorless, viscous liquid. IR (film): ν 3451, 3026, 2922, 2870, 1712, 1681, 1607, 1509, 1446, 1409, 1275, 1182, 1037, 818 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.28 (d, *J* = 14.1 Hz, 1H), 2.34 (s, 3H, CH_3), 2.65 (dd, *J* = 14.1, 4.5 Hz, 1H), 3.41-3.45 (m, 1H), 3.83-3.88 (m, 1H, CHO), 3.95-4.00 (s, 1H, CHO), 6.32 (s, 1H, =CH), 7.13 (d, *J* = 8.4 Hz, 2H, ArH), 7.28 (d, *J* = 8.4 Hz, 2H, ArH); MS (EI) *m/z* (%): 174 (M^+, 45.75), 142 (52.50), 141 (59.31), 131 (64.64),

129 (53.76), 128 (68.24), 119 (48.52), 115 (100.00), 91 (69.06); HRMS (EI) Calcd. For $C_{12}H_{14}O$ 174.1045, Found: 174.1037.



[3-(3-Methyl)cyclobut-2-enyl]methanol 2f:

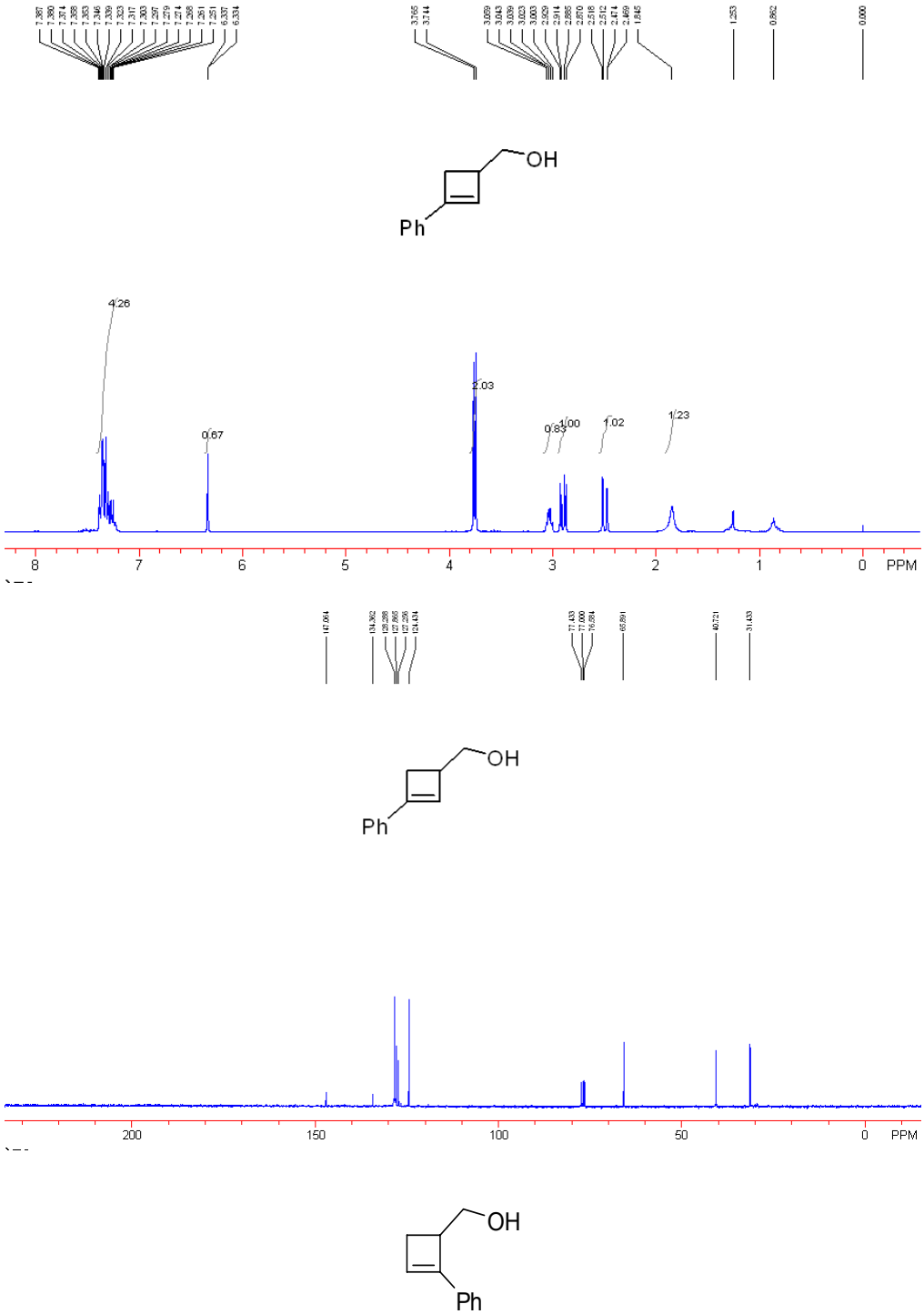
A colorless, viscous liquid. IR (film): ν 3458, 3025, 2922, 1607, 1587, 1488, 1455, 1361, 1254, 1154, 1039, 786 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.33 (s, 3H, CH_3), 2.46 (dd, J = 12.9, 1.8 Hz, 1H), 2.87 (dd, J = 12.9, 4.5 Hz, 1H), 2.97-3.03 (m, 1H), 3.72 (d, J = 6.3 Hz, 2H, CH_2O), 6.30 (d, J = 0.9 Hz, 1H, =CH), 7.06 (d, J = 7.5 Hz, 1H, ArH), 7.14-7.36 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.3, 31.4, 40.6, 65.9, 121.5, 125.0, 127.1, 128.1, 128.6, 134.3, 137.8, 147.0; MS (EI) *m/z* (%): 174 (M^+, 17.05), 143 (88.74), 134 (49.54), 129 (79.11), 128 (100.00), 119 (67.44), 115 (57.07), 92 (51.79), 91 (98.46); HRMS (EI) Calcd. For $C_{12}H_{14}O$ 174.1045, Found: 174.1051.



(3-phenylcyclobut-2-enyl)methanol 2g:

A colorless solid. Mp. 61-63 ^{o}C; IR (film): ν 3420, 3060, 2942, 2885, 1683, 1597, 1448, 1353, 1277, 1215, 1136, 1028, 757, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.84 (s, br, 1H, OH), 2.49 (dd, *J* = 13.5, 1.5 Hz, 1H), 2.90 (dd, *J* = 13.5, 4.8 Hz, 1H), 3.00-3.06 (m, 1H), 3.75 (d, *J* = 6.3 Hz, 2H, CH_2O), 6.34 (d, *J* = 0.9 Hz, 1H, =CH), 7.23-7.39 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.5, 40.7, 65.9, 124.5, 127.3, 127.9, 128.3, 134.4, 147.1; MS (EI) *m/z* (%): 160 (M^+, 17.39), 129 (100.00), 128 (57.40), 127 (29.69), 118 (23.31), 103 (22.24),

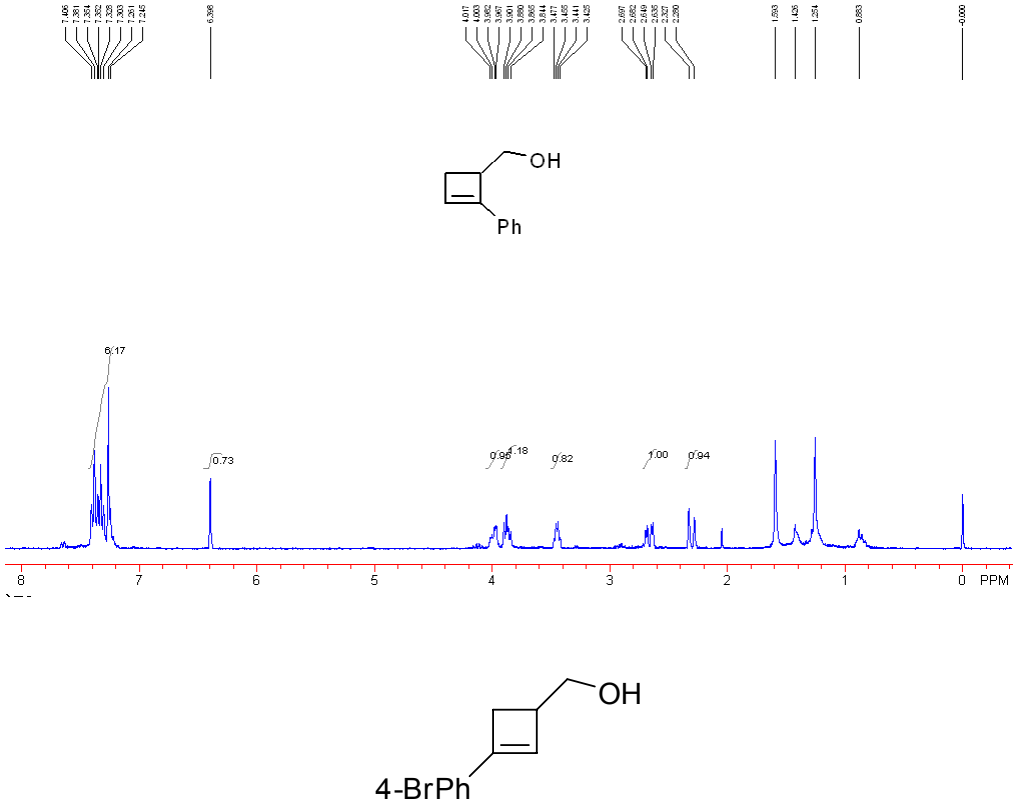
102 (21.41), 77 (27.50), 44 (72.13); Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.40; H, 7.56.



[2-phenylcyclobut-2-enyl]methanol 3g:

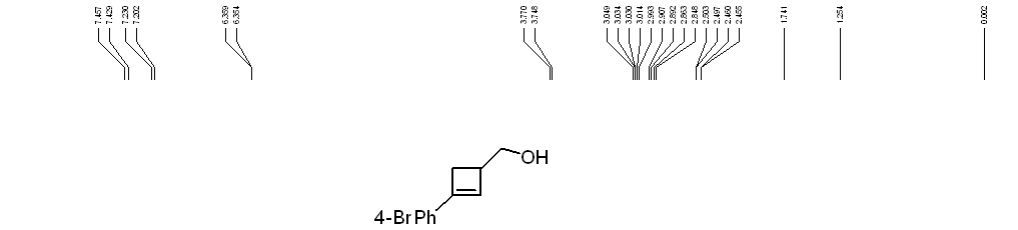
A colorless, viscous liquid. IR (film): ν 3419, 2853, 1590, 1488, 1402, 1270, 1217, 1173, 1093, 1064, 1014, 831 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.31 (d, J = 14.4, Hz, 1H), 2.67 (dd, J = 14.4, 4.8 Hz, 1H), 3.42-3.48 (m, 1H), 3.84-3.90 (m, 1H, CHO), 3.97-4.02 (m, 1H, CHO), 6.40 (s, 1H, =CH), 7.24-7.41 (m, 5H, ArH); MS (EI) *m/z* (%): 160 (M^+, 23.44), 142

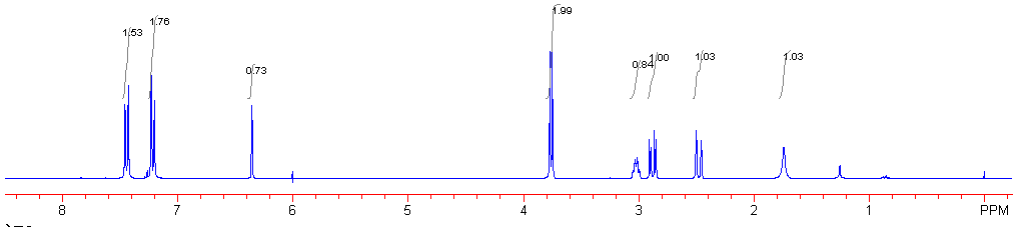
(22.54), 129 (100.00), 128 (67.98), 127 (31.54), 102 (22.24), 77 (27.97), 51 (23.99); HRMS (EI) Calcd. For $C_{11}H_{12}O$ 160.0888, Found: 160.0881.

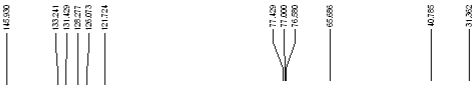


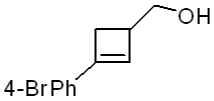
[3-(4-bromophenyl)cyclobut-2-enyl]methanol 2h:

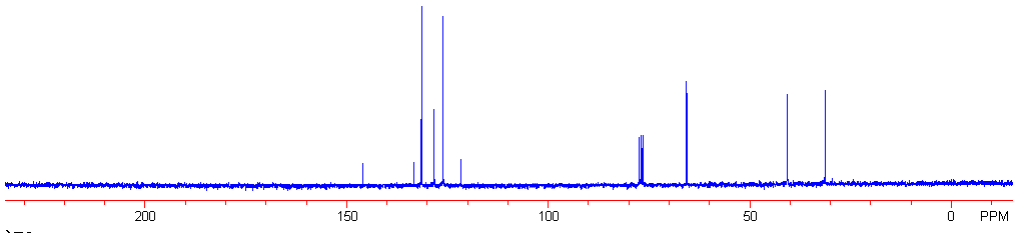
A colorless, viscous liquid. IR (film): ν 3437, 2919, 1688, 1585, 1485, 1398 1361, 1220, 1071, 1009, 817 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.74 (s, br, 1H, OH), 2.47 (dd, *J* = 13.8, 1.8 Hz, 1H), 2.88 (dd, *J* = 13.8, 4.5 Hz, 1H), 2.99-3.05 (m, 1H), 3.76 (d, *J* = 6.6 Hz, 2H, CH_2O), 6.36 (d, *J* = 1.2 Hz, 1H, =CH), 7.22 (d, *J* = 8.4 Hz, 2H, ArH), 7.44 (d, *J* = 8.4 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.4, 40.8, 65.7, 121.7, 126.1, 128.3, 131.4, 133.3, 145.9; MS (EI) *m/z* (%): 238 (M^+, 12.71), 209 (31.00), 207 (27.34), 141 (21.52), 130 (34.69), 129 (24.03), 128 (100.00), 115 (18.12), 102 (25.37); HRMS (EI) Calcd. For $C_{11}H_{11}OBr$ 237.9993, Found: 237.9991.

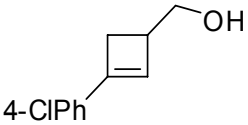








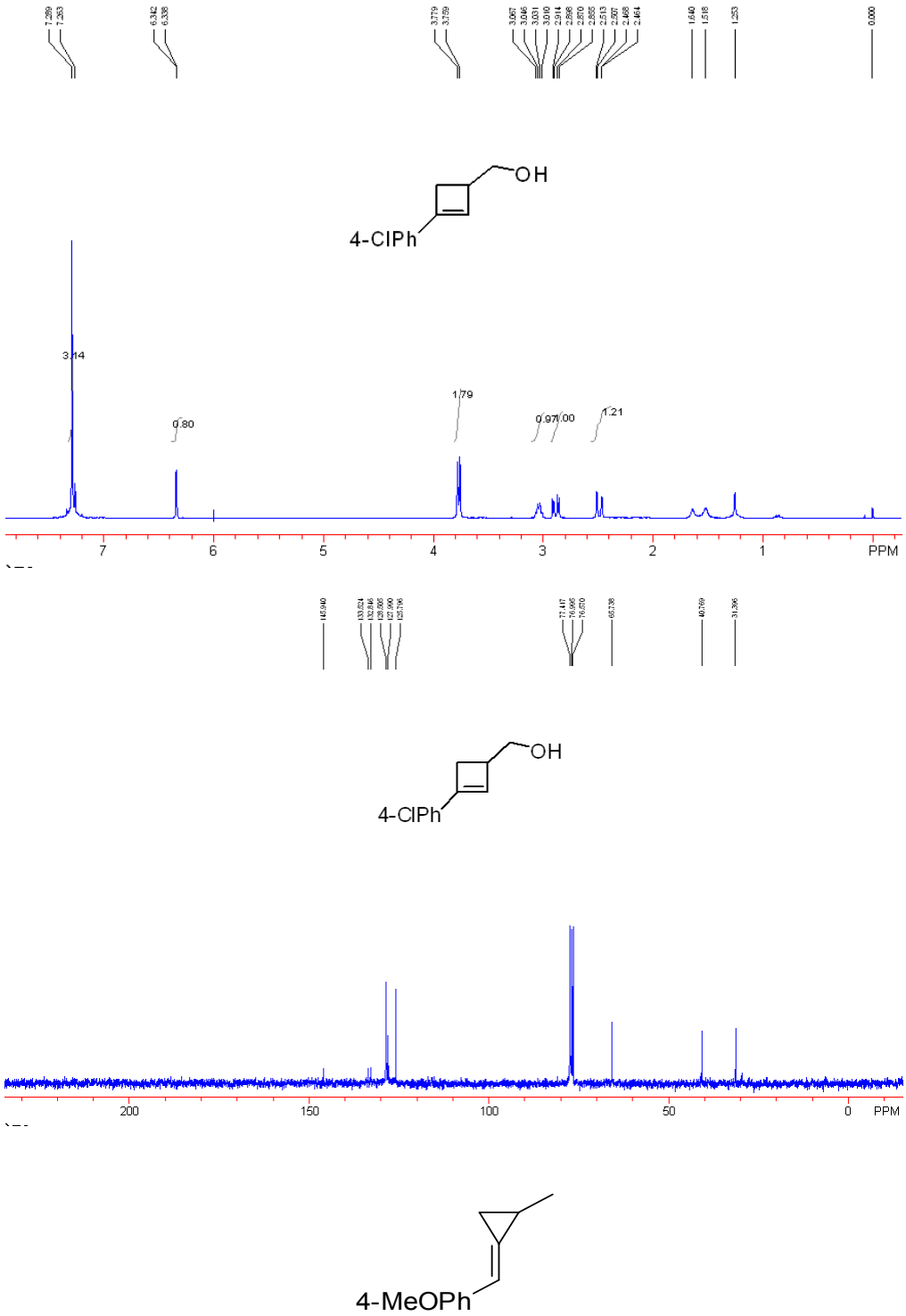




[3-(4-chlorophenyl)cyclobut-2-enyl]methanol 2i:

A colorless, viscous liquid. IR (film): ν 2959, 2935, 2838, 1674, 1601, 1513, 1304, 1250, 1175, 1032, 833 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.49 (dd, J = 12.9, 1.5 Hz, 1H), 2.88 (dd, J = 12.9, 4.5 Hz, 1H), 3.01-3.07 (m, 1H), 3.77 (d, J = 5.7 Hz, 2H, CH_2O), 6.34 (s, 1H, =CH), 7.29 (s, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.4, 40.8, 65.7, 125.8, 128.0, 128.5, 132.9, 133.5, 146.0; MS (EI) *m/z* (%): 194 (M^+, 35.09), 165 (45.67), 163 (68.11), 141 (33.74), 129 (30.86), 128 (100.00), 127 (70.02), 75 (30.61); HRMS (EI) Calcd. For $C_{11}H_{11}OCl$

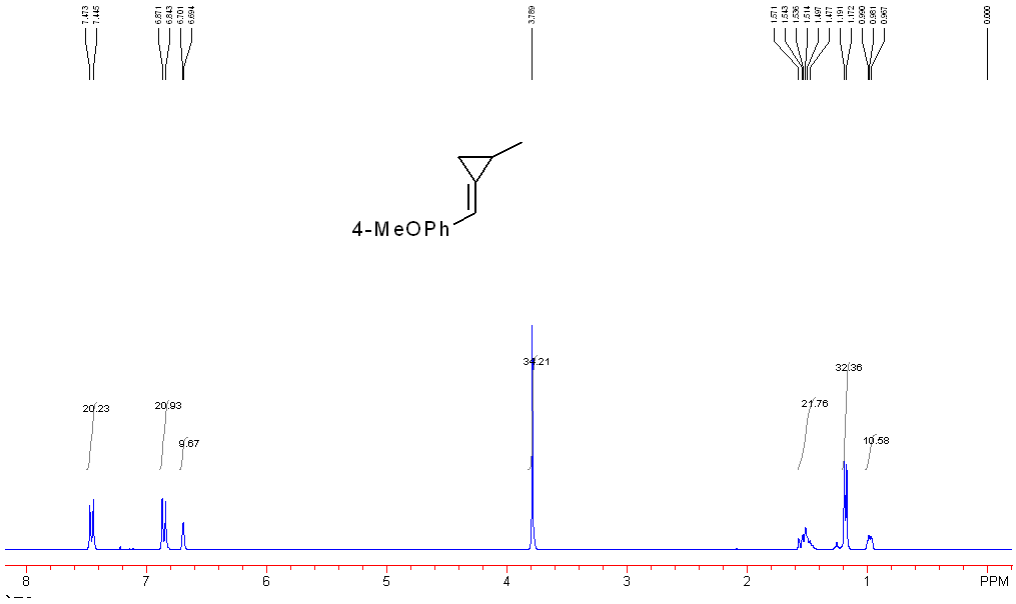
194.0498, Found: 194.0500.

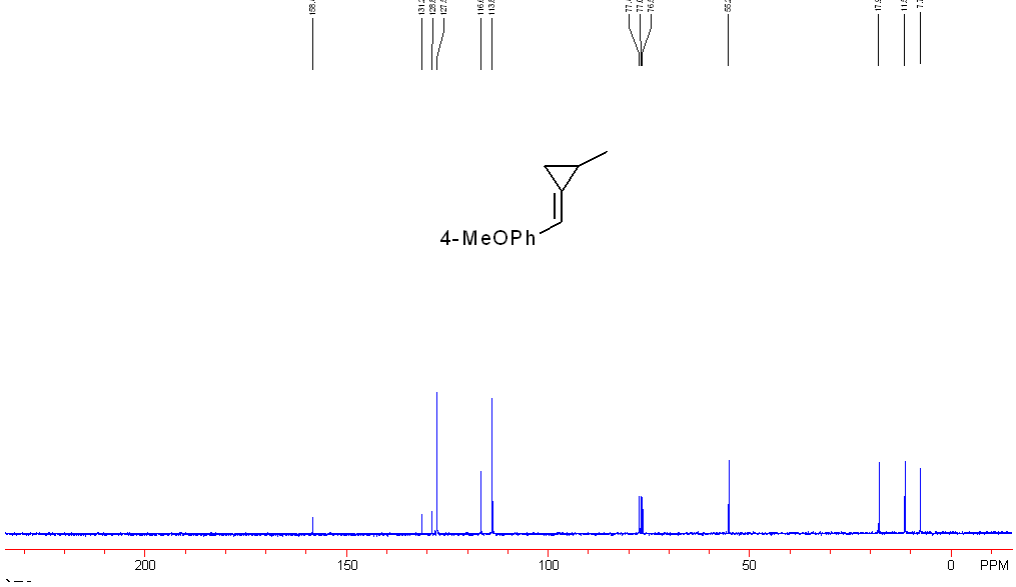


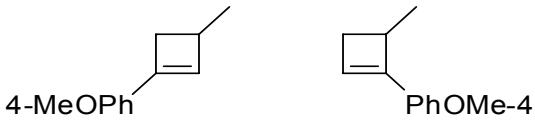
(*E*)-1-methoxy-4-[(2-methylcyclopropylidene)methyl]benzene 1j:

A colorless, viscous liquid. IR (film): ν 2959, 2934, 2838, 1677, 1602, 1513, 1463, 1250, 1175, 1032, 833 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.96-0.99 (m, 1H), 1.18 (d, J = 5.7 Hz, 3H, CH_3), 1.48-1.58 (m, 2H), 3.79 (s, 3H, OCH_3), 6.70 (d, J = 1.8 Hz, 1H, =CHAr), 6.86 (d, J = 8.4 Hz, 2H, ArH), 7.46 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 7.7,

11.5, 18.0, 55.2, 113.8, 116.7, 127.6, 128.8, 131.2, 158.5; MS (EI) *m/z* (%): 174 (M^+, 15.97), 159 (49.03), 148 (100.00), 147 (61.87), 135 (77.56), 134 (63.20), 121 (98.20), 91 (68.00), 77 (69.99); HRMS (EI) Calcd. For $C_{12}H_{14}O$ 174.1045, Found: 174.1053.





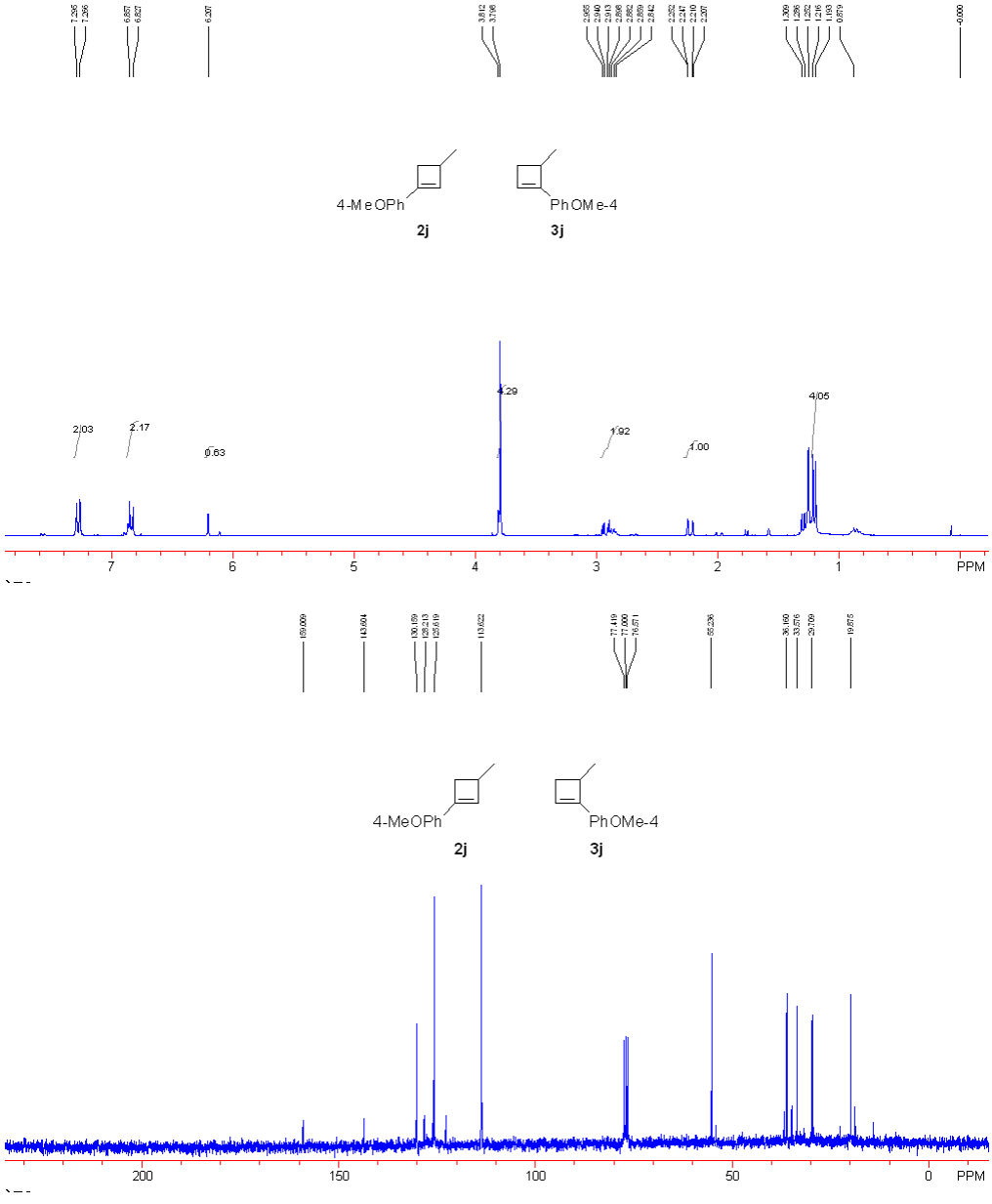


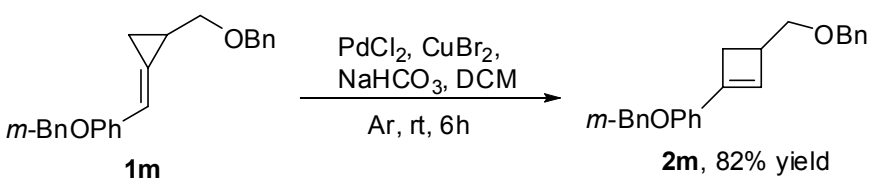
2j **3j**

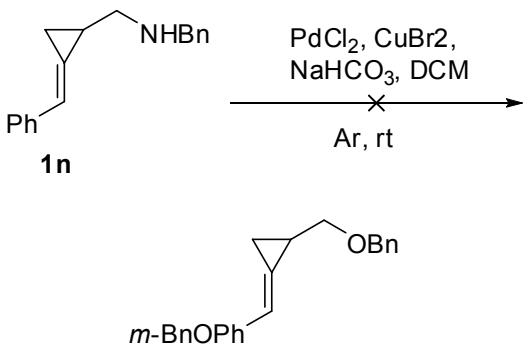
Mixtures of **2j** and **3j** are not stable under air atmosphere:

A colorless, viscous liquid. IR (film): ν 2958, 2934, 1603, 1512, 1303, 1250, 1176, 1032, 832 cm^{-1}; For **2j**: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.20 (d, *J* = 6.9 Hz, 3H, CH_3), 2.23 (dd, *J* = 12.6, 1.2 Hz, 1H), 2.84-2.90 (m, 1H), 2.93 (dd, *J* = 12.6, 4.5 Hz, 1H), 3.80 (s, 3H, OCH_3),

6.21 (d, J = 0.6 Hz, 1H, =CH), 6.84 (d, J = 8.7 Hz,, 2H, ArH), 7.28 (d, J = 8.7 Hz,, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.9, 33.6, 36.2, 55.2, 113.6, 125.6, 128.2, 130.2, 143.6, 159.0; For mixture of **2j** and **3j**: MS (EI) *m/z* (%): 174 (M^+, 92.56), 175 (M^++1, 13.83), 173 (22.41), 160 (12.97), 159 (100.00), 143 (21.47), 115 (15.61), 91 (12.04); HRMS (EI) Calcd. For $C_{12}H_{14}O$ 174.1045, Found: 174.1048.

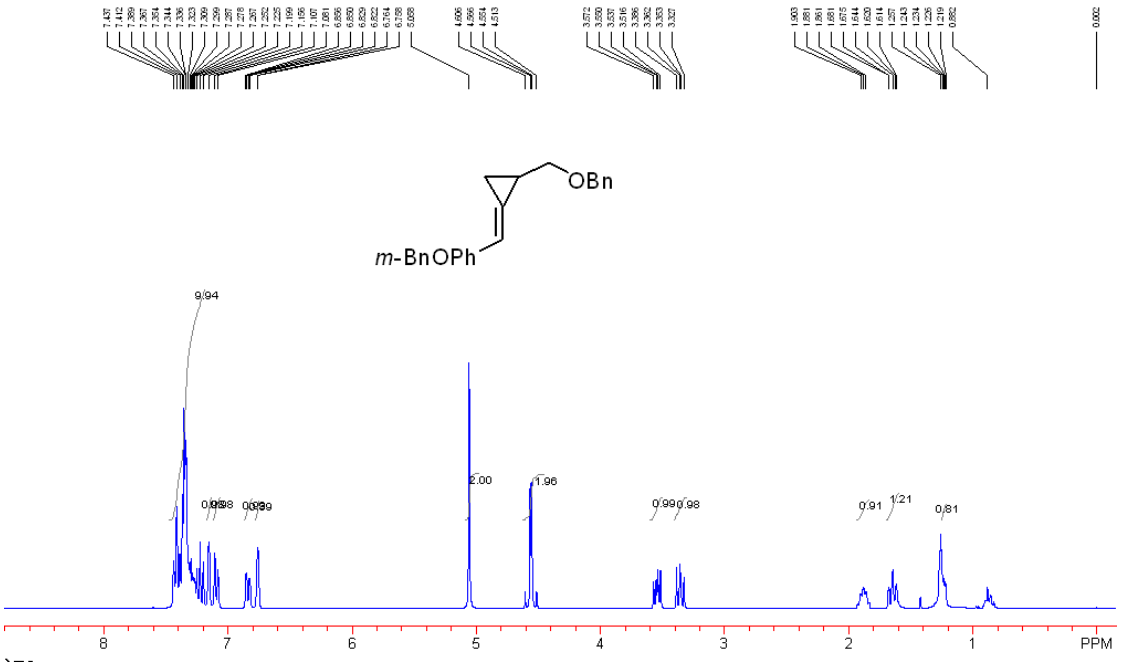


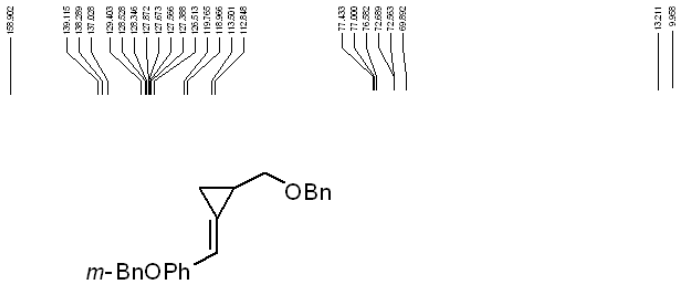


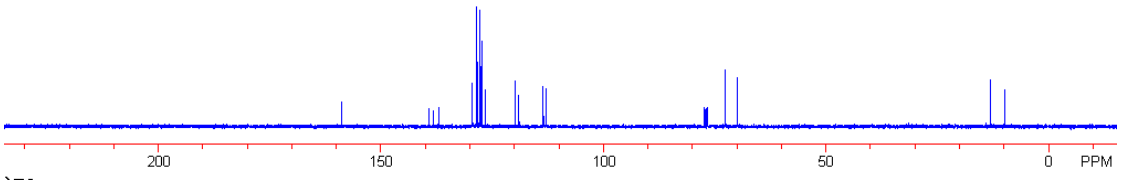


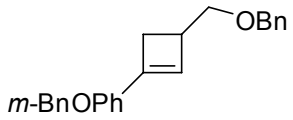
(*E*)-1-(benzyloxy)-3-((2-(benzyloxymethyl)cyclopropylidene)methyl)benzene 1m:

A colorless, viscous liquid. IR (film): ν 3064, 3032, 2927, 2864, 1720, 1686, 1582, 1496, 1453, 1439, 1378, 1363, 1263, 1177, 1098, 1026, 785, 738, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.22-1.26 (m, 1H), 1.64 (td, *J* = 9.0, 1.8 Hz, 1H), 1.86-1.90 (m, 1H), 3.36 (dd, *J* = 10.5, 7.8 Hz, 1H), 3.54 (dd, *J* = 10.5, 6.3 Hz, 1H), 4.53 (d, *J* = 12.3 Hz, 1H), 4.58 (d, *J* = 17.7 Hz, 1H), 5.06 (s, 2H), 6.76 (d, *J* = 1.5 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.20-7.44 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.9, 13.2, 69.9, 72.6, 72.7, 112.9, 113.5, 119.0, 119.8, 126.5, 127.4, 127.6, 127.7, 127.9, 128.4, 128.5, 129.4, 137.0, 138.3, 139.1, 158.9; MS (EI) *m/z* (%): 356 (M^+, 0.10), 265 (3.28), 159 (2.87), 115 (1.32), 92 (7.72), 91 (100.00), 82 (2.26), 77 (1.29), 65 (7.87); HRMS (ESI) Calcd. For $C_{25}H_{24}O_2Na^+$ 379.1670, Found: 379.1669.



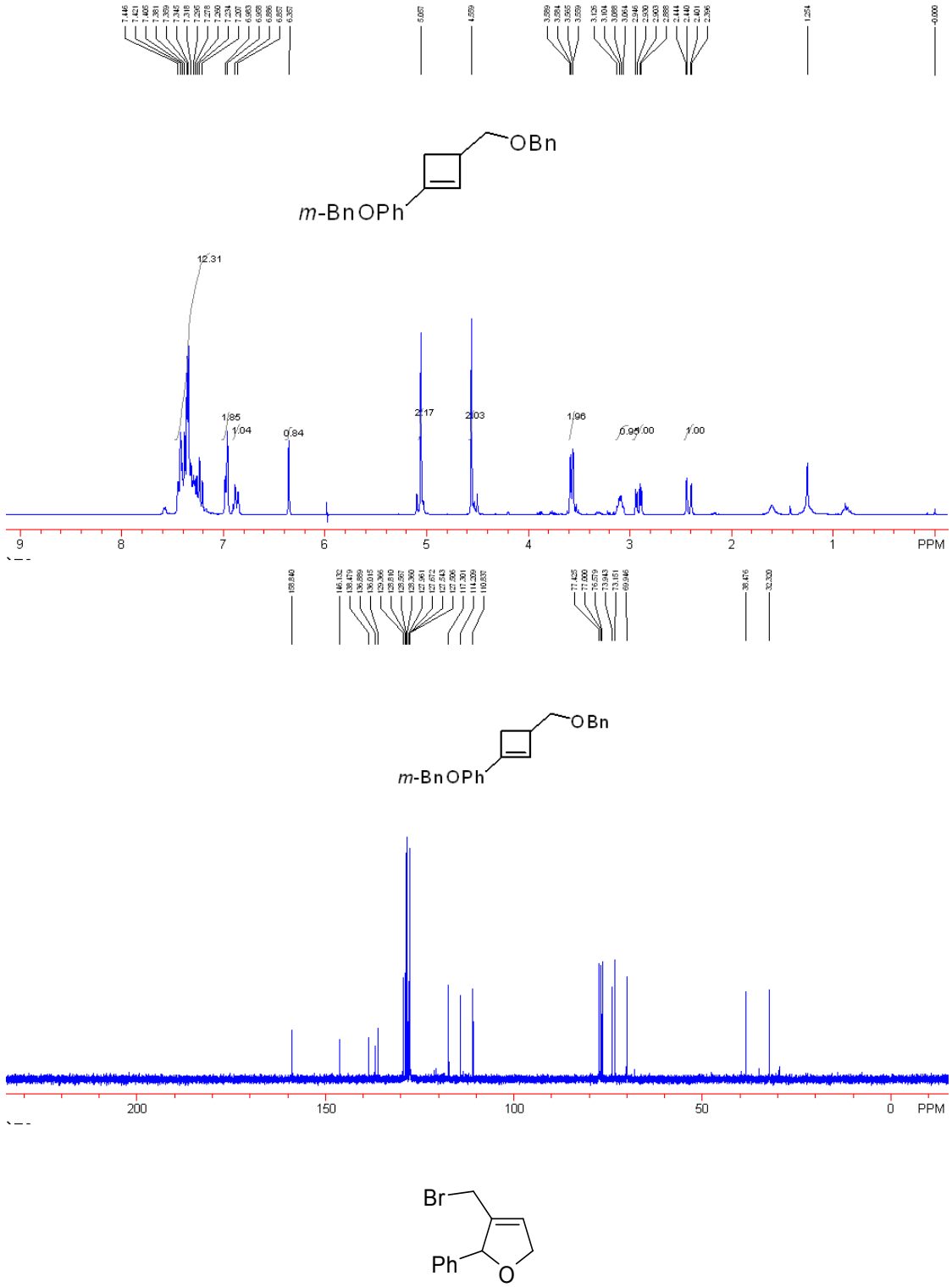






1-(benzyloxy)-3-(3-(benzyloxymethyl)cyclobut-1-enyl)benzene 2m:

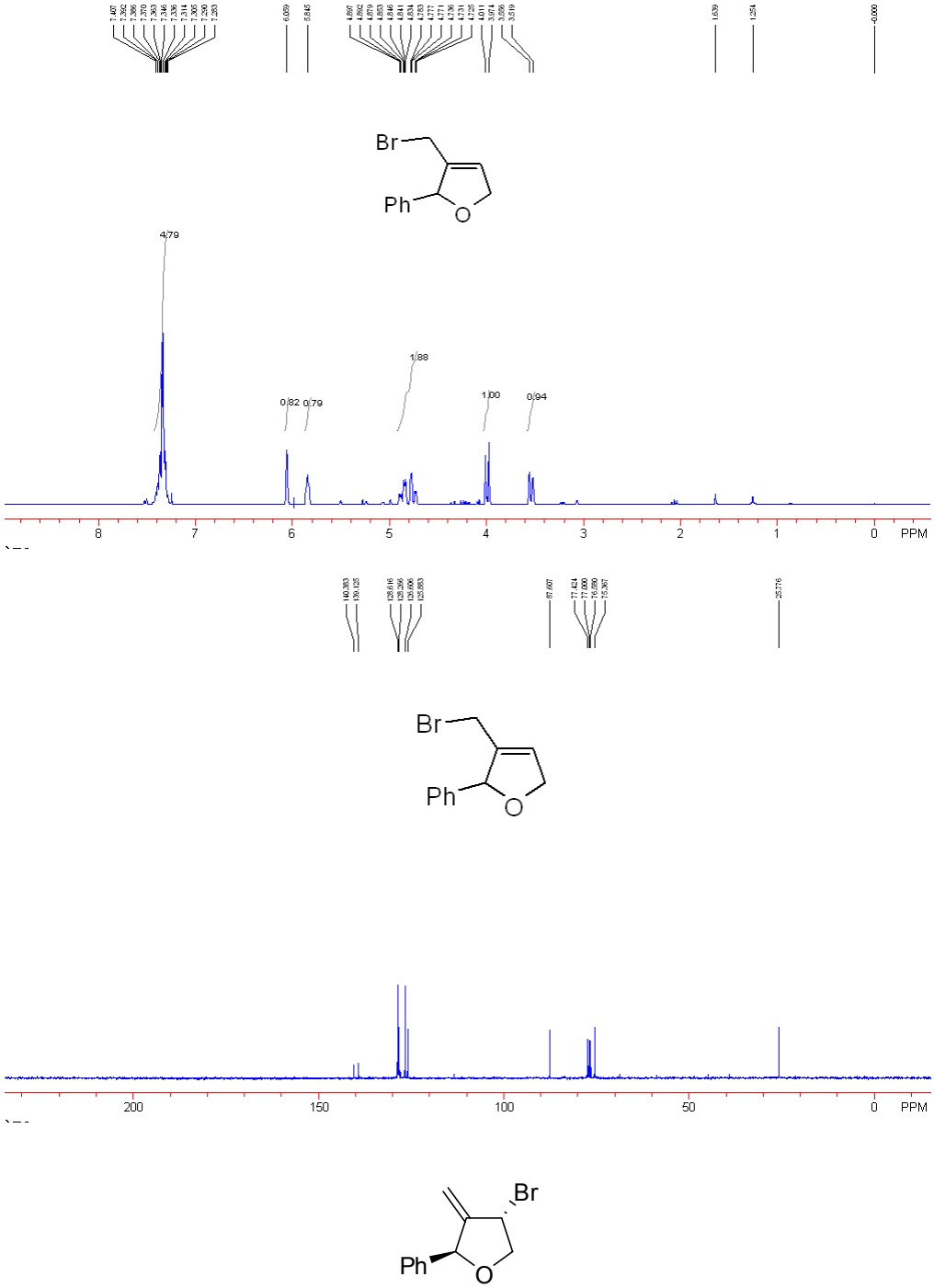
A colorless, viscous liquid. IR (film): ν 3064, 3032, 2930, 2866, 1739, 1598, 1489, 1453, 1381, 1262, 1155, 1097, 1027, 738, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): 2.42 (dd, *J* = 13.2, 1.8 Hz, 1H), 2.92 (dd, *J* = 13.2, 4.2 Hz, 1H), 3.07-3.13 (m, 1H), 3.57 (dd, *J* = 6.9, 1.5 Hz, 2H, CH_2O), 4.56 (s, 2H), 5.06 (s, 2H), 6.36 (s, 1H, =CH), 6.87 (d, *J* = 8.4 Hz, 1H, ArH), 6.97 (d, *J* = 7.2 Hz, 2H, ArH), 7.21-7.45 (m, 11H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 32.3, 38.5, 69.9, 73.2, 73.9, 110.8, 114.2, 117.3, 127.5, 127.6, 127.7, 128.0, 128.4, 128.6, 128.8, 129.4, 136.0, 136.9, 138.5, 145.1, 158.9; MS (EI) *m/z* (%): 265 (M^+-Bn, 0.26), 211 (5.43), 121 (3.56), 106 (4.54), 105 (9.50), 92 (8.70), 91 (100.00), 77 (6.31), 65 (6.91).



3-(bromomethyl)-2-phenyl-2,5-dihydrofuran 4g:

A colorless, viscous liquid. IR (film): ν 3062, 3029, 2852, 1682, 1598, 1491, 1448, 1254, 1216, 1060, 1027, 971, 838, 762, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.54 (d, J = 11.1 Hz, 1H, CHBr), 3.99 (d, J = 11.1 Hz, 1H, CHBr), 4.73-4.90 (m, 2H, CH_2O), 5.85 (s, br, 1H, =CH), 6.06 (s, 1H, ArCHO), 7.25-7.41 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.8, 75.4, 87.6, 125.9, 126.6, 128.3, 128.6, 139.1, 140.4; MS (EI) *m/z* (%): 238 (M^+, 27.66),

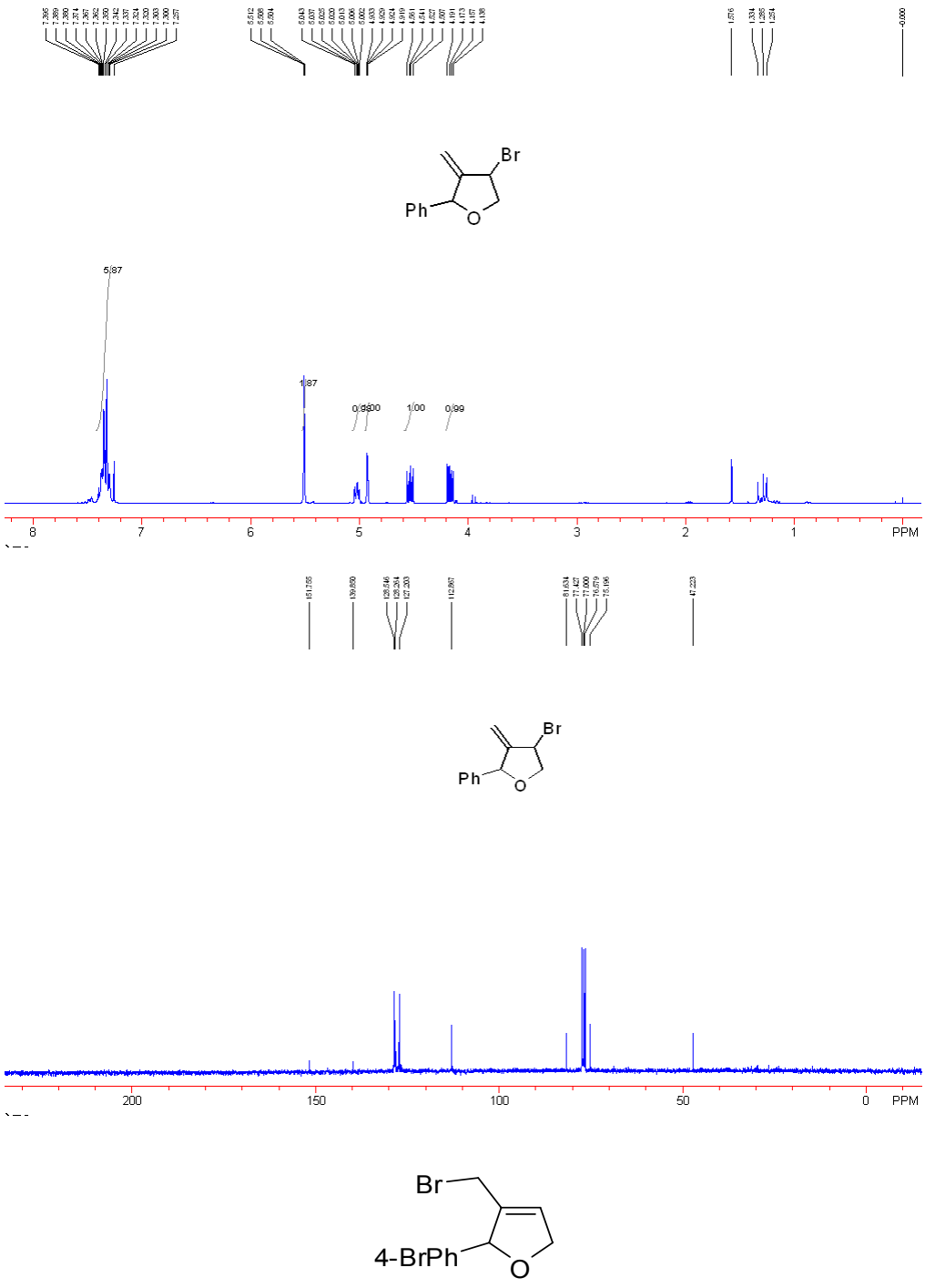
157 (68.96), 145 (70.53), 131 (23.70), 129 (45.16), 128 (33.54), 105 (100.00), 77 (38.77); HRMS (EI) Calcd. For $C_{11}H_{11}OBr$ 237.9993, Found: 237.9995.



(*anti*-2,4)-4-bromo-3-methylene-2-phenyltetrahydrofuran 5g (combined with some amount of unknown products):

A colorless, viscous liquid. IR (film): ν 3062, 3030, 2925, 2854, 1493, 1454, 1216, 1081, 1059, 1028, 965, 912, 753, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.16 (dd, J = 10.2, 5.7 Hz, 1H, CHO), 4.53 (dd, J = 10.2, 6.0 Hz, 1H, CHO), 4.93 (dd, J = 3.0, 1.2 Hz, 1H), 5.00-5.04

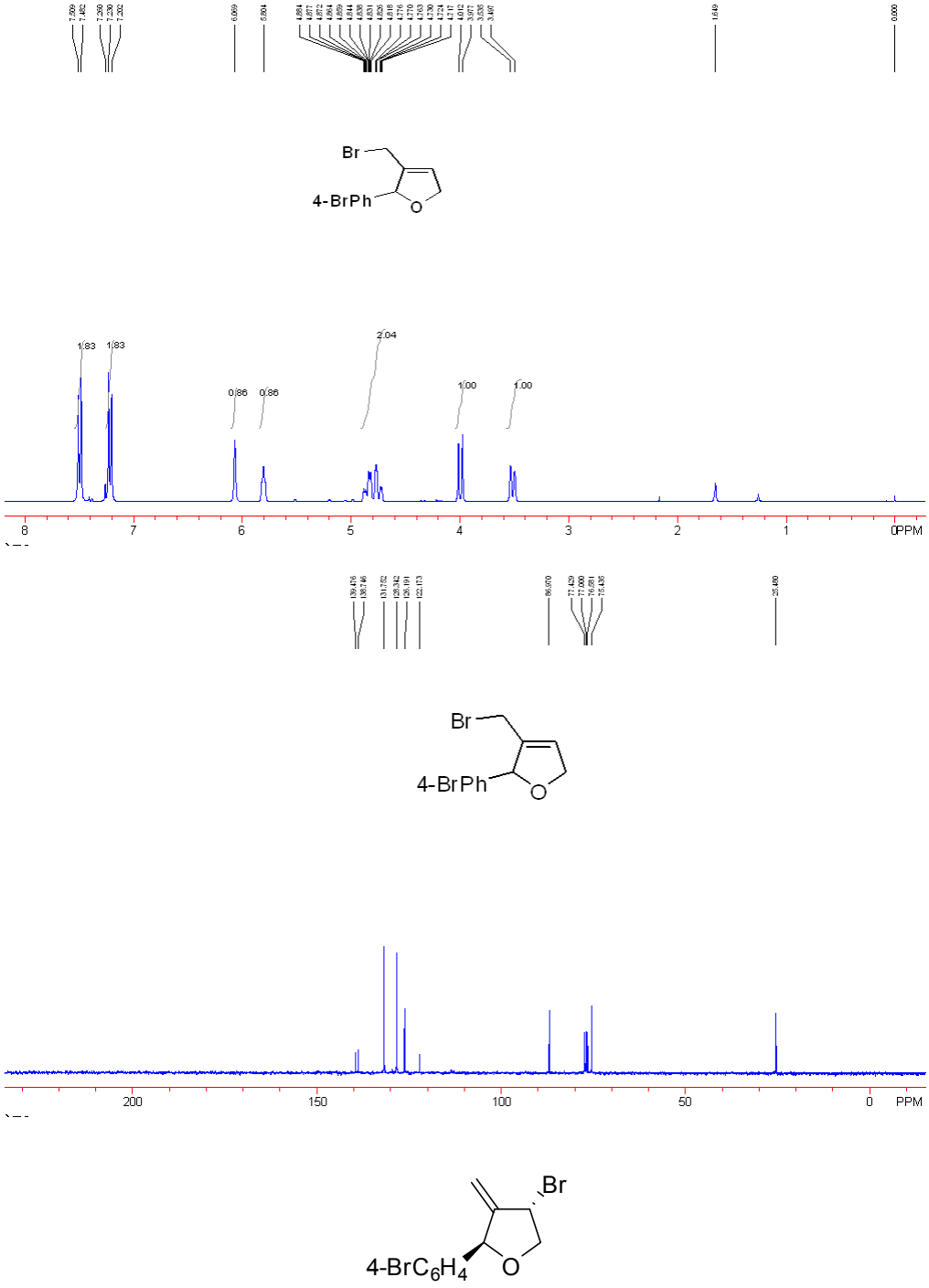
(m, 1H), 5.50 (s, 1H), 5.51 (dd, J = 2.4, 1.2 Hz, 1H), 7.25-7.40 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 47.2, 75.2, 81.6, 112.9, 127.2, 128.3, 128.6, 139.9, 151.8; MS (EI) *m/z* (%): 238 (M^+, 4.64), 159 (23.76), 129 (9.60), 128 (9.17), 106 (9.09), 105 (100.00), 91 (8.55), 77 (12.67), 53 (10.82); HRMS (EI) Calcd. For $C_{11}H_{11}OBr$ 237.9993, Found: 238.0001.



3-(bromomethyl)-2-(4-bromophenyl)-2,5-dihydrofuran 4h:

A colorless solid. Mp. 45-47 ^{o}C; IR (film): ν 3084, 2954, 2852, 1686, 1586, 1484, 1431, 1406, 1252, 1217, 1070, 1010, 816, 632 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.52 (d, J = 11.1

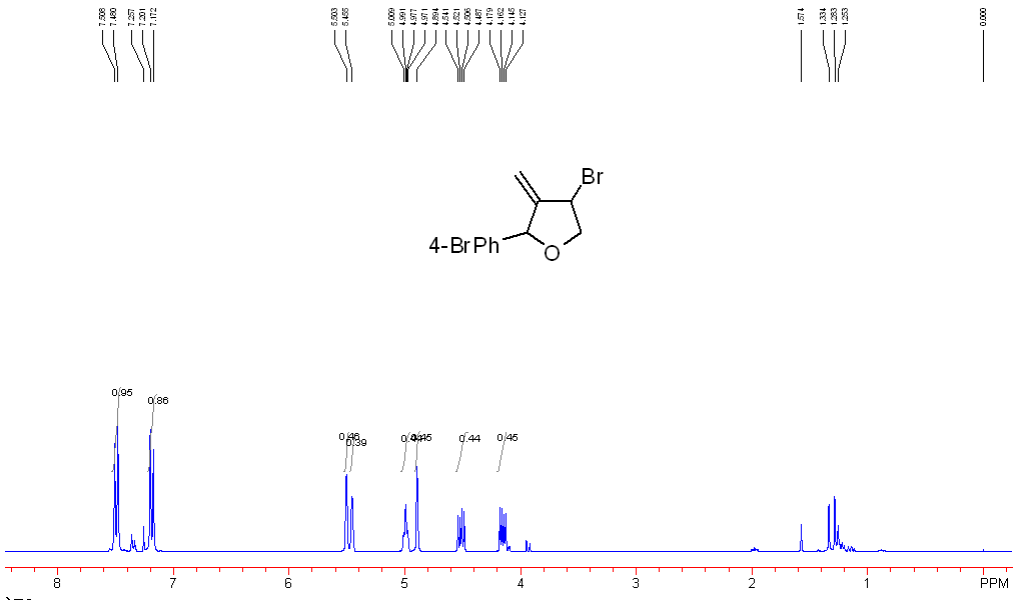
Hz, 1H, CHBr), 3.99 (d, J = 11.1 Hz, 1H, CHBr), 4.72-4.88 (m, 2H, CH_2O), 5.80 (s, br, 1H, =CH), 6.07 (s, 1H, ArCHO), 7.20 (d, J = 8.4 Hz, 2H, ArH), 7.50 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.5, 75.4, 87.0, 122.2, 126.2, 128.3, 131.8, 138.8, 139.5; MS (EI) *m/z* (%): 318 (M^+, 27.66), 237 (62.88), 223 (36.39), 185 (39.57), 183 (35.74), 157 (46.11), 156 (100.00), 129 (64.05), 128 (61.92); HRMS (EI) Calcd. For $C_{11}H_{10}OBr_2$ 315.9098, Found 315.9085. Anal. Calcd for $C_{11}H_{10}OBr_2$: C, 41.44; H, 3.17. Found: C, 41.59; H, 3.29.

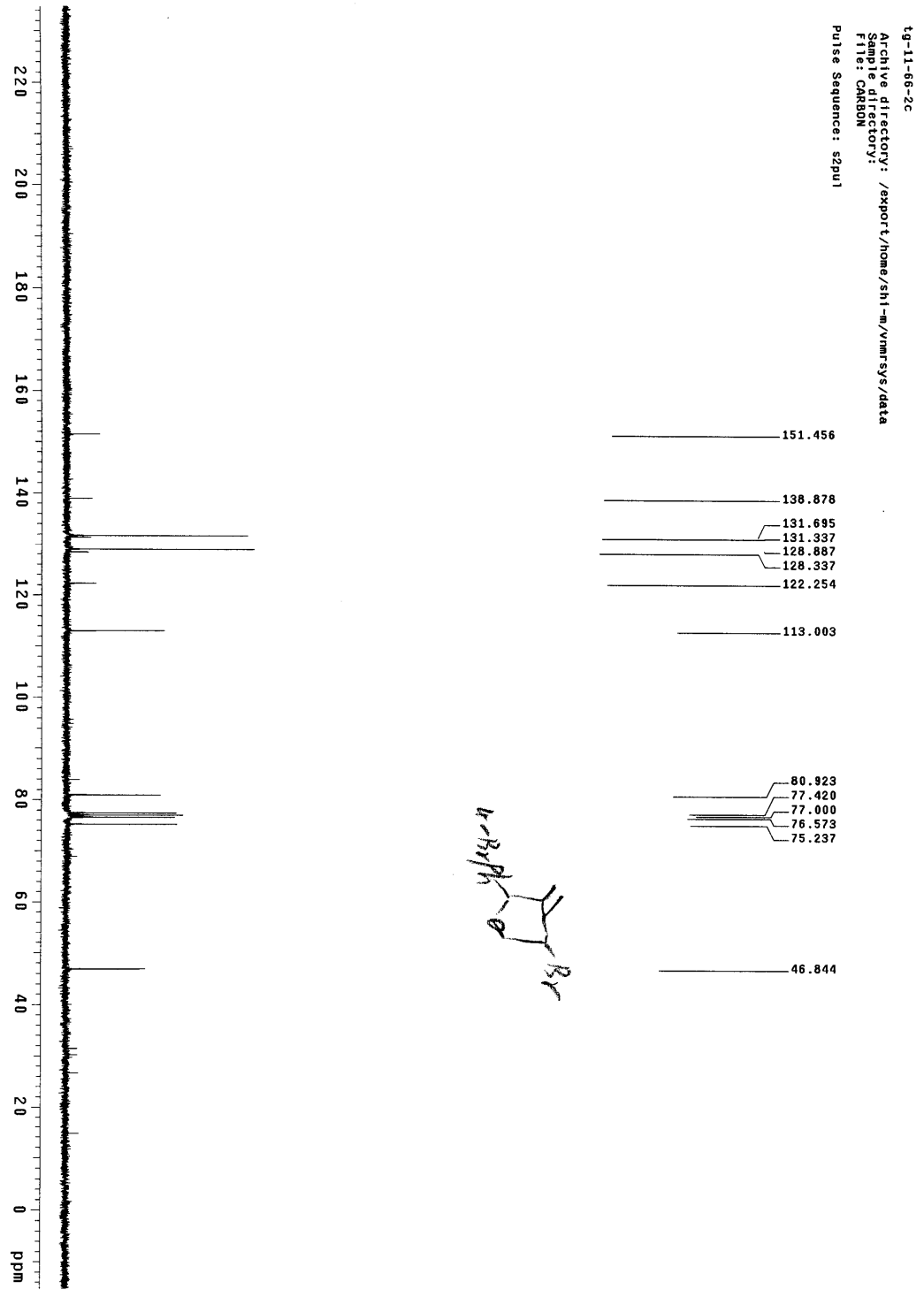


(*anti*-2,4)4-bromo-2-(4-bromophenyl)-3-methylenetetrahydrofuran 5h (combined with

some amount of unknown products):

A colorless, viscous liquid. IR (film): ν 2960, 2856, 1591, 1486, 1404, 1216, 1070, 1010, 965, 846, 814 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.15 (dd, *J* = 10.5, 5.4 Hz, 1H, CHO), 4.51 (dd, *J* = 10.5, 6.0 Hz, 1H, CHO), 4.89 (s, 1H), 4.97-5.01 (m, 1H), 5.46 (s, 1H), 5.50 (s 1H), 7.19 (d, *J* = 8.4 Hz, 2H, ArH), 7.49 (d, *J* = 8.4 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 46.8, 75.2, 80.9, 113.0, 122.3, 128.9, 131.7, 138.9, 151.5; MS (EI) *m/z* (%): 316 (M^+, 6.86), 239 (44.57), 237 (39.90), 185 (92.81), 183 (100.00), 129 (46.02), 128 (42.88), 105 (31.16), 53 (57.09); HRMS (EI) Calcd. For $C_{11}H_{10}OBr_2$ 315.9098, Found: 315.9092.




tg-11-66-2c
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Sample directory:
File: CARBON
Pulse Sequence: s2pul
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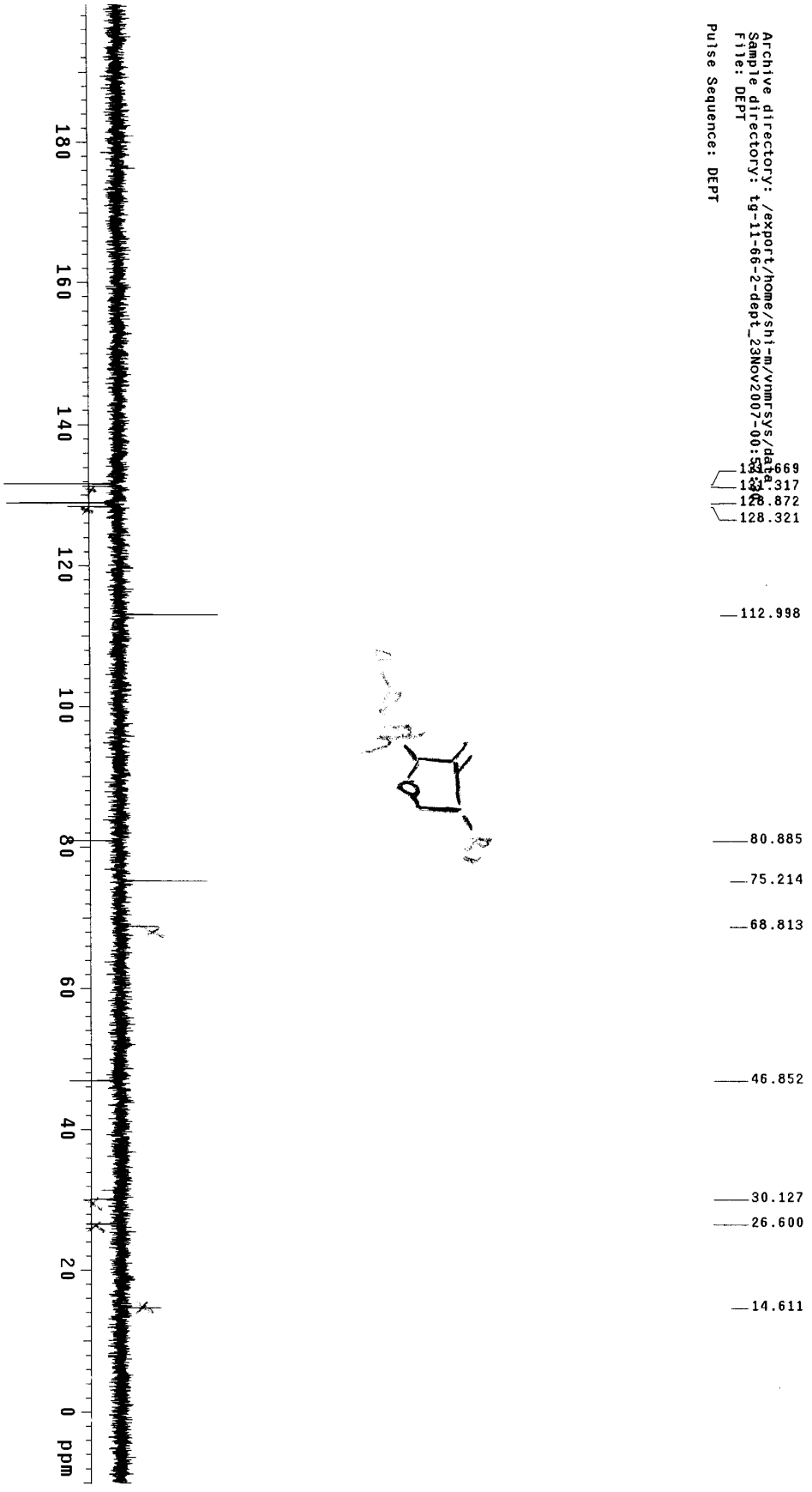
138.878
131.695
131.337
128.887
128.337
122.254
113.003
80.923
77.420
77.000
76.573
75.237
46.844
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Archive directory: /export/home/shi-m/vnmrsys/data
Sample directory: tg-11-66-2-dept_23Nov2007-00:52.fid
File: DEPT
Pulse Sequence: DEPT
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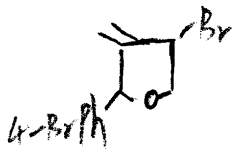
133.317
128.872
128.321
112.998
80.885
75.214
68.813
46.852
30.127
26.600
14.611
180
160
140
120
100
80
60
40
20
0
ppm

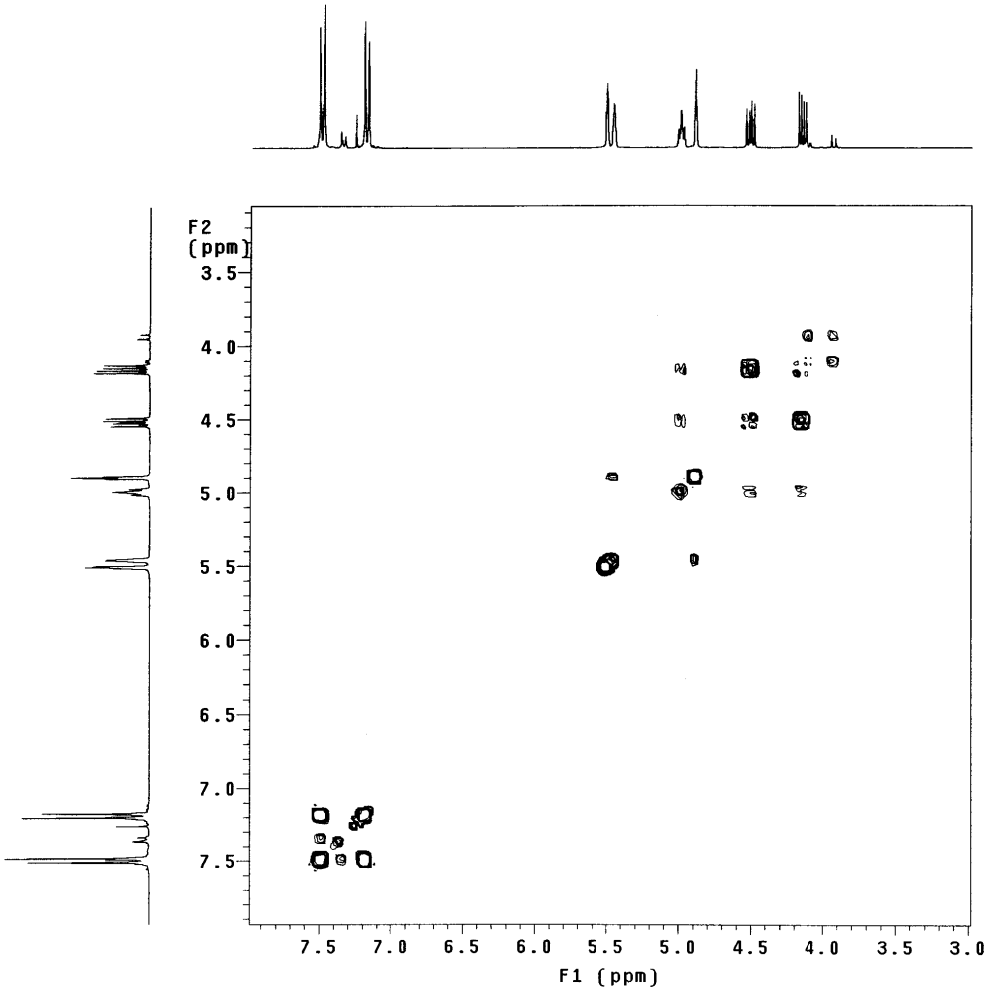
Archive directory: /export/home/shi-m/vnmrsys/data
Sample directory: tg-11-66-2-cosy_19Nov2007
File: gCOSY

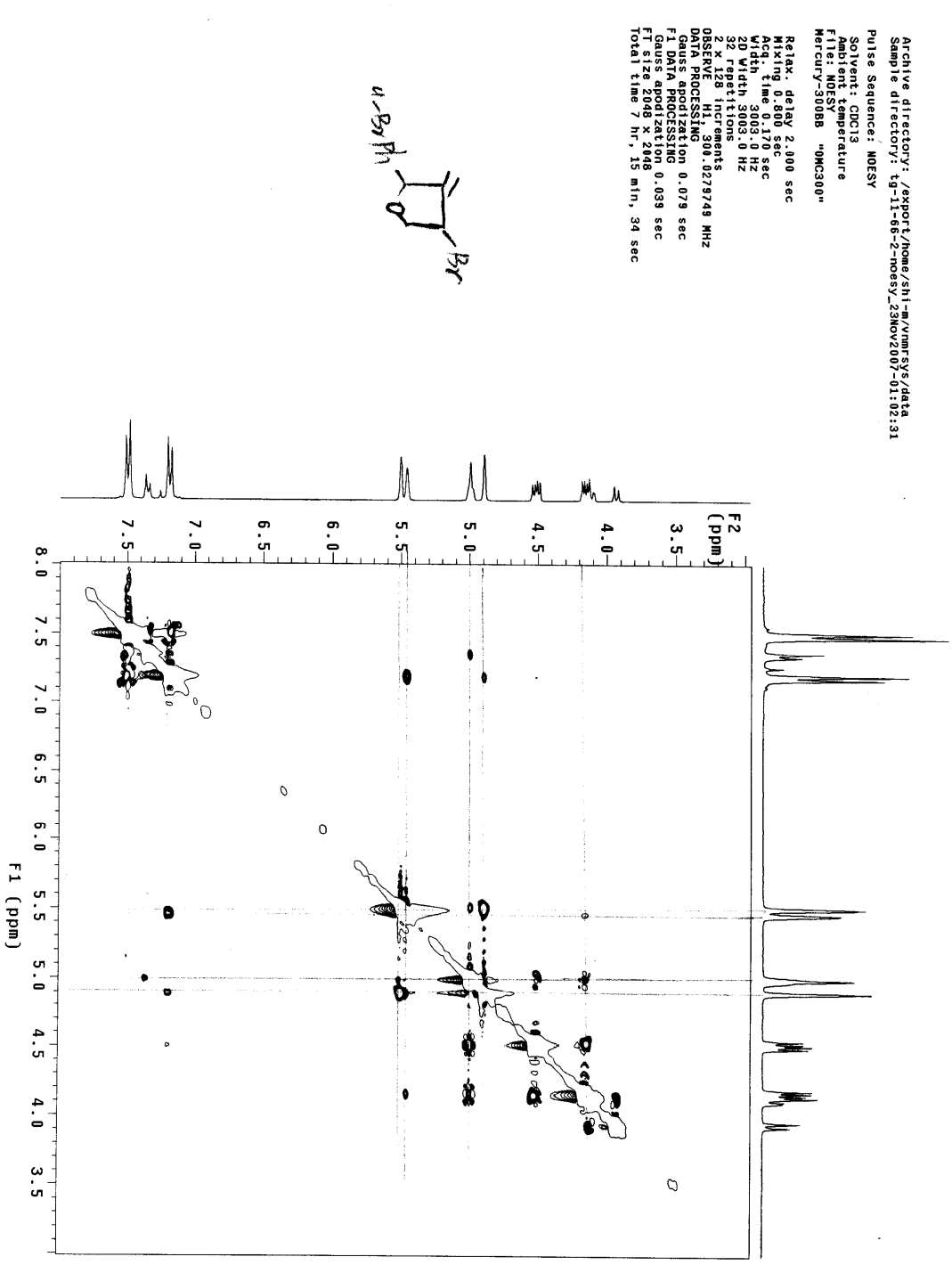
Pulse Sequence: gCOSY

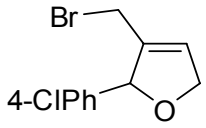
Solvent: CDCl3
Ambient temperature
Mercury-300BB "OMC300"

Relax. delay 1.000 sec
Acq. time 0.170 sec
Width 3003.0 Hz
2D Width 3003.0 Hz
Single scan
128 increments
OBSERVE H1, 300.0279750 MHz
DATA PROCESSING
Sq. sine bell 0.085 sec
F1 DATA PROCESSING
Sq. sine bell 0.043 sec
FT size 1024 x 1024
Total time 3 min, 39 sec





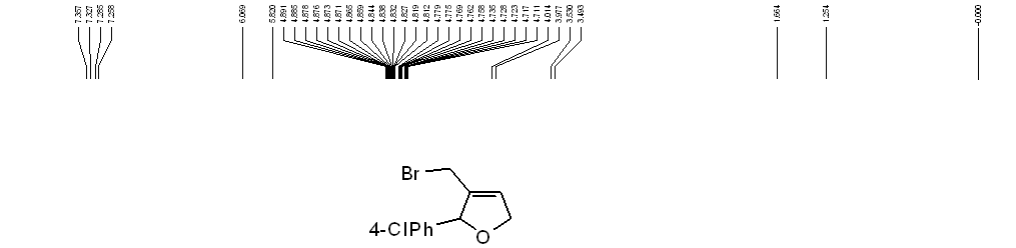


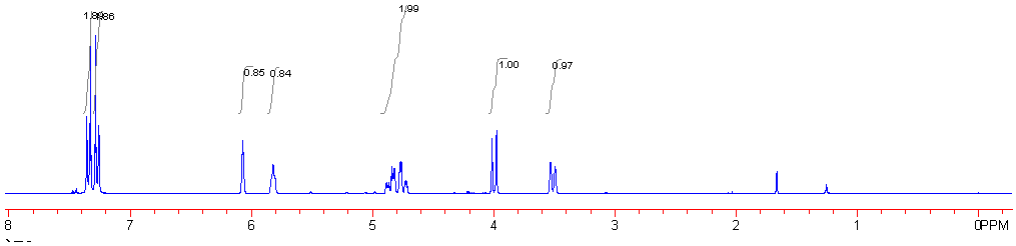


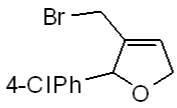
3-(bromomethyl)-2-(4-chlorophenyl)-2,5-dihydrofuran 4i:

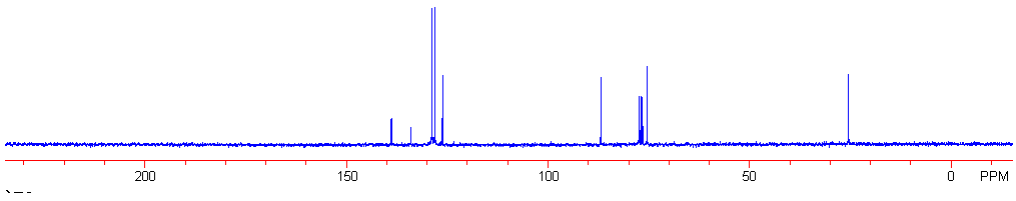
A colorless, viscous liquid. IR (film): ν 2853, 1682, 1590, 1488, 1402, 1270, 1217, 1093, 1064,

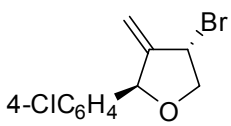
1014, 831 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.51 (d, *J* = 11.1 Hz, 1H, CHBr), 3.99 (d, *J* = 11.1 Hz, 1H, CHBr), 4.71-4.89 (m, 2H, CH_2O), 5.82 (s, br, 1H, =CH), 6.07 (s, 1H, ArCHO), 7.27 (d, *J* = 8.1 Hz, 2H, ArH), 7.34 (d, *J* = 8.1 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.5, 75.4, 86.9, 126.2, 128.0, 128.8, 134.0, 138.8, 138.9; MS (EI) *m/z* (%): 272 (M^+, 30.09), 193 (38.10), 191 (100.00), 179 (49.64), 156 (49.23), 139 (54.92), 129 (35.50), 128 (55.97); HRMS (EI) Calcd. For $C_{11}H_{10}OBrCl$ 271.9604, Found: 271.9603.







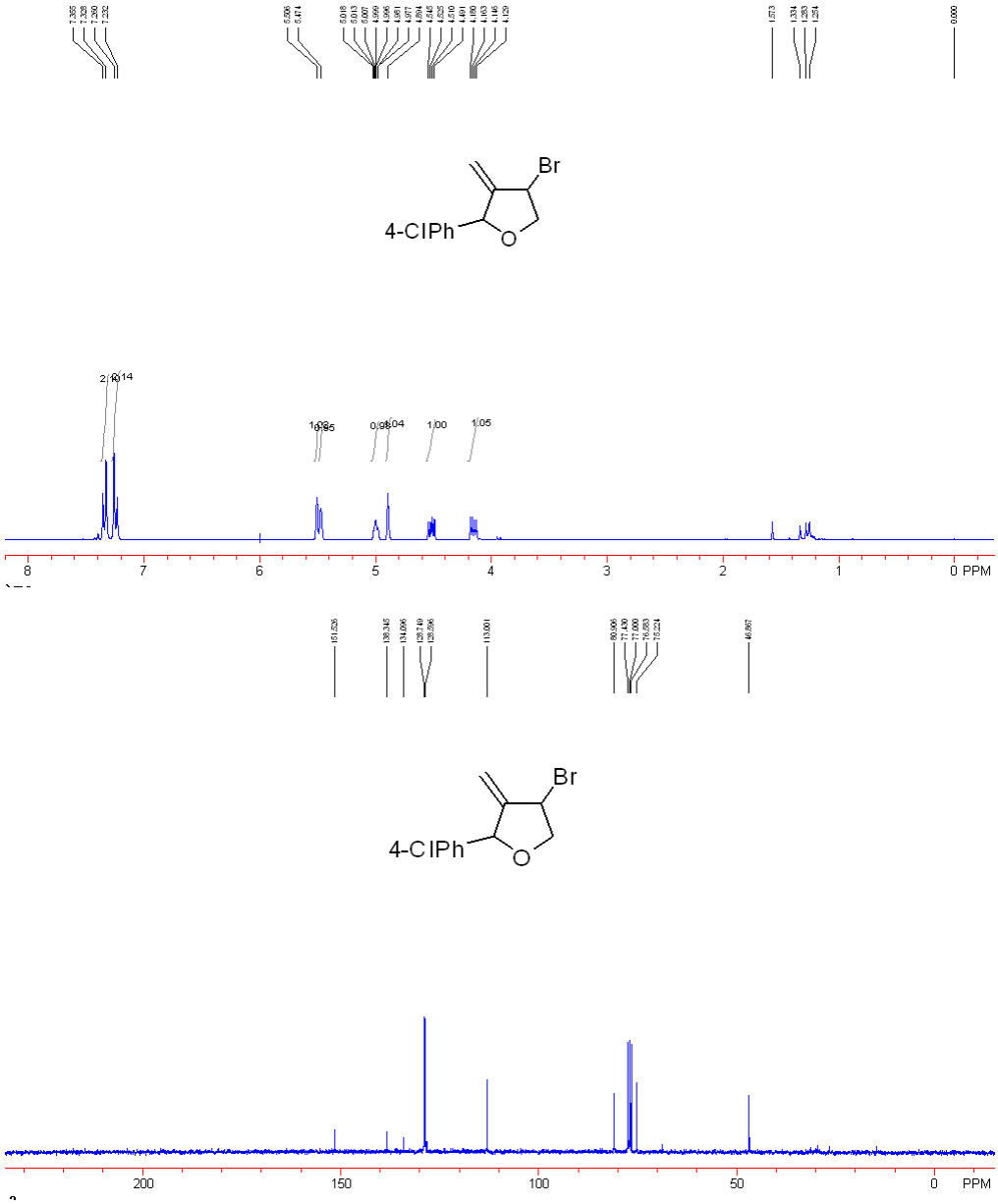


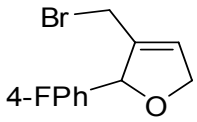


(*anti*-2,4)4-bromo-2-(4-chlorophenyl)-3-methylenetetrahydrofuran 5i (combined with

some amount of unknown products):

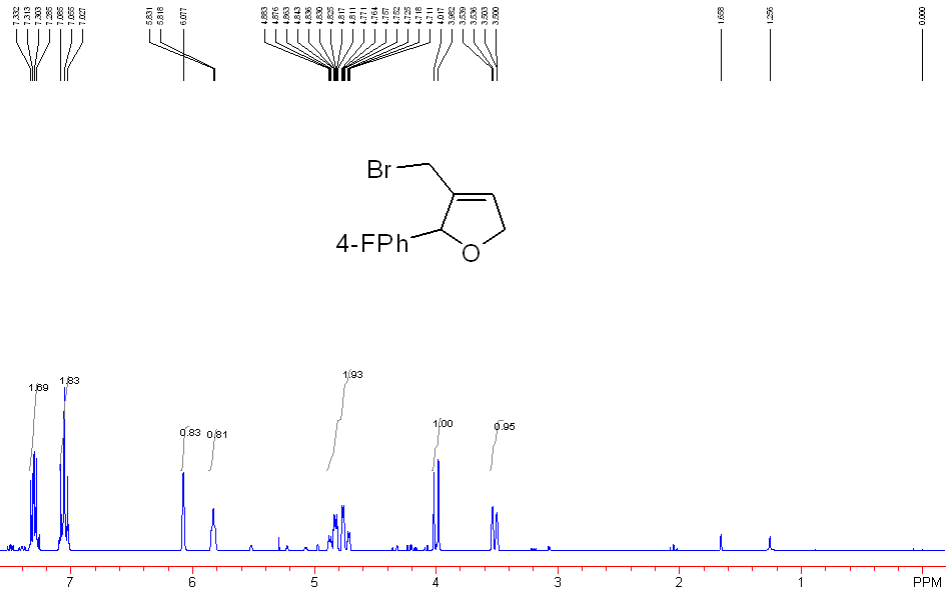
A colorless, viscous liquid. IR (film): ν 2953, 2852, 1597, 1490, 1410, 1218, 1191, 1090, 1066, 1014, 847, 816, 635, 604 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.15 (dd, *J* = 10.2, 5.4 Hz, 1H, CHO), 4.52 (dd, *J* = 10.2, 6.0 Hz, 1H, CHO), 4.89 (s, 1H), 4.98-5.02 (m, 1H), 5.47 (s, 1H), 5.51 (d, *J* = 0.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H, ArH), 7.34 (d, *J* = 8.1 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 46.9, 75.2, 80.9, 113.0, 128.6, 128.7, 134.1, 138.4, 151.5; MS (EI) *m/z* (%): 272 (M^+, 4.29), 239 (12.40), 237 (11.01), 193 (19.19), 141 (40.17), 139 (100.00), 129 (14.27), 128 (14.56), 53 (19.85); HRMS (EI) Calcd. For $C_{11}H_{10}OBrCl$ 271.9604, Found: 271.9613.

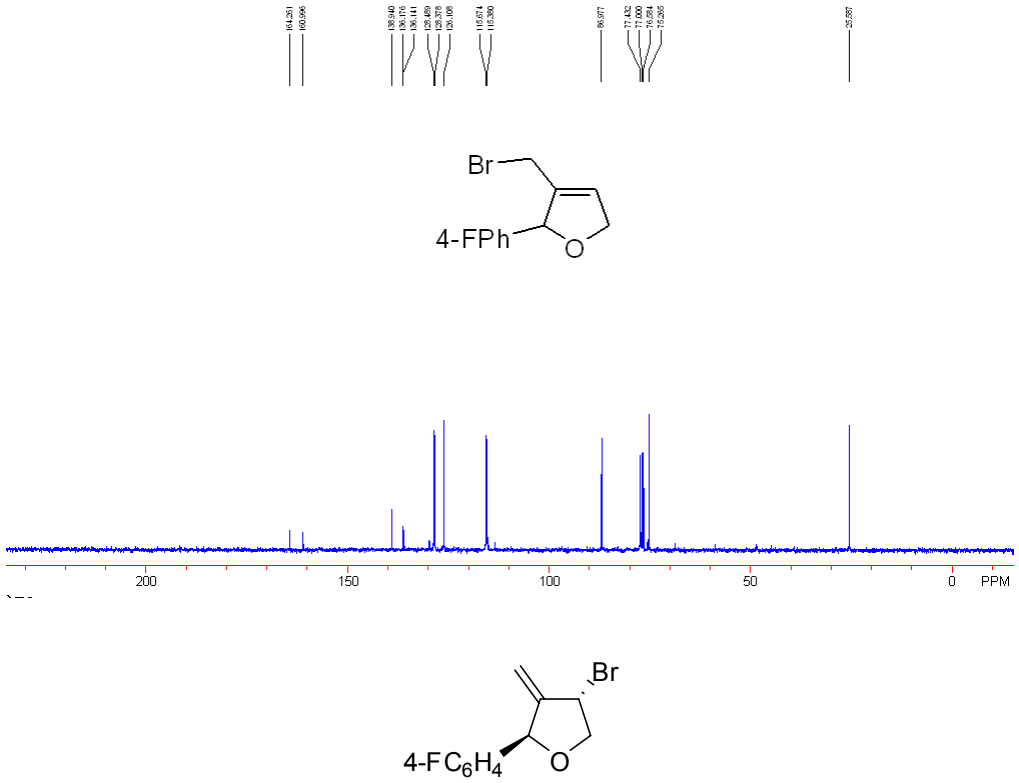




3-(bromomethyl)-2-(4-fluorophenyl)-2,5-dihydrofuran 4k:

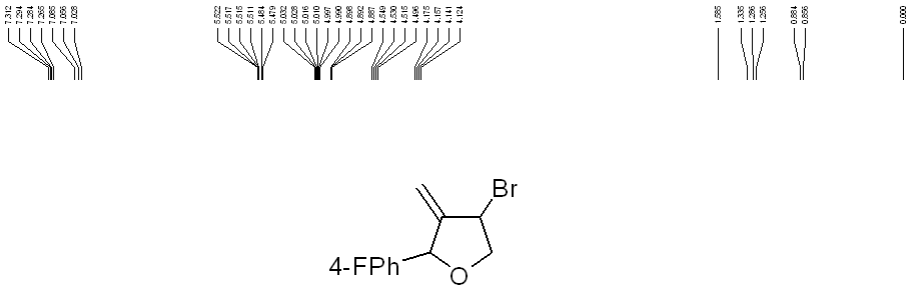
A colorless, viscous liquid. IR (film): ν 3071, 2954, 2852, 1603, 1507, 1429, 1295, 1225, 1192, 1157, 1064, 1014, 856, 832, 611 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.52 (dd, *J* = 10.8, 0.9 Hz, 1H, CHBr), 4.00 (d, *J* = 10.8 Hz, 1H, CHBr), 4.71-4.88 (m, 2H, CH_2O), 5.83 (s, br, 1H, =CH), 6.08 (s, 1H, ArCHO), 7.03-7.10 (m, 2H, ArH), 7.26-7.33 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.6, 75.3, 87.0, 115.5 (d, *J* = 21.8 Hz), 126.1, 128.4 (d, *J* = 8.0 Hz), 136.2 (d, *J* = 3.5 Hz), 138.9, 162.6 (d, *J* = 245.0 Hz); MS (EI) *m/z* (%): 256 (M^+, 18.61), 175 (27.67), 163 (100.00), 149 (25.60), 147 (30.11), 146 (26.39), 123 (80.42), 109 (36.28), 53 (31.14); HRMS (EI) Calcd. For $C_{11}H_{10}BrFO$ 255.9899, Found: 255.9899.

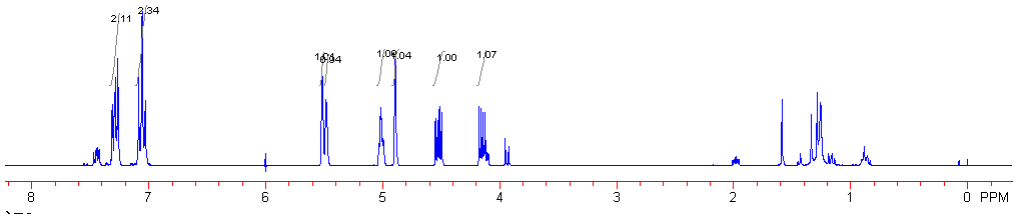


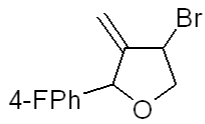


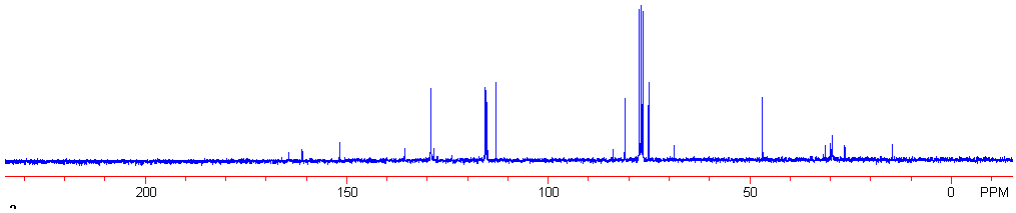
(*anti*-2,4)4-bromo-2-(4-fluorophenyl)-3-methylenetetrahydrofuran 5k (combined with some amount of unknown products):

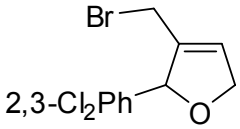
A colorless, viscous liquid. IR (film): ν 3070, 2926, 2853, 1604, 1508, 1467, 1295, 1222, 1191, 1156, 1062, 1014, 856, 829, 642, 611, 534 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.15 (dd, *J* = 10.2, 5.4 Hz, 1H, CHO), 4.52 (dd, *J* = 10.2, 6.0 Hz, 1H, CHO), 4.89 (dd, *J* = 1.8, 1.8 Hz, 1H), 4.99-5.03 (m, 1H), 5.48 (d, *J* = 1.8 Hz, 1H), 5.52 (dd, *J* = 1.8, 1.8 Hz, 1H), 7.03-7.09 (m, 2H, ArH), 7.27-7.31 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 46.9, 75.1, 81.0, 113.0, 115.5 (d, *J* = 21.7 Hz), 129.1 (d, *J* = 10.0 Hz), 135.6 (d, *J* = 3.0 Hz), 151.8, 162.6 (d, *J* = 245.0 Hz); MS (EI) *m/z* (%): 256 (M^+, 21.76), 163 (51.19), 149 (52.38), 123 (100.00), 109 (37.52), 108 (33.37), 57 (40.69), 44 (58.54), 43 (48.17); HRMS (EI) Calcd. For $C_{11}H_{10}BrFO$ 255.9899, Found: 255.9897.







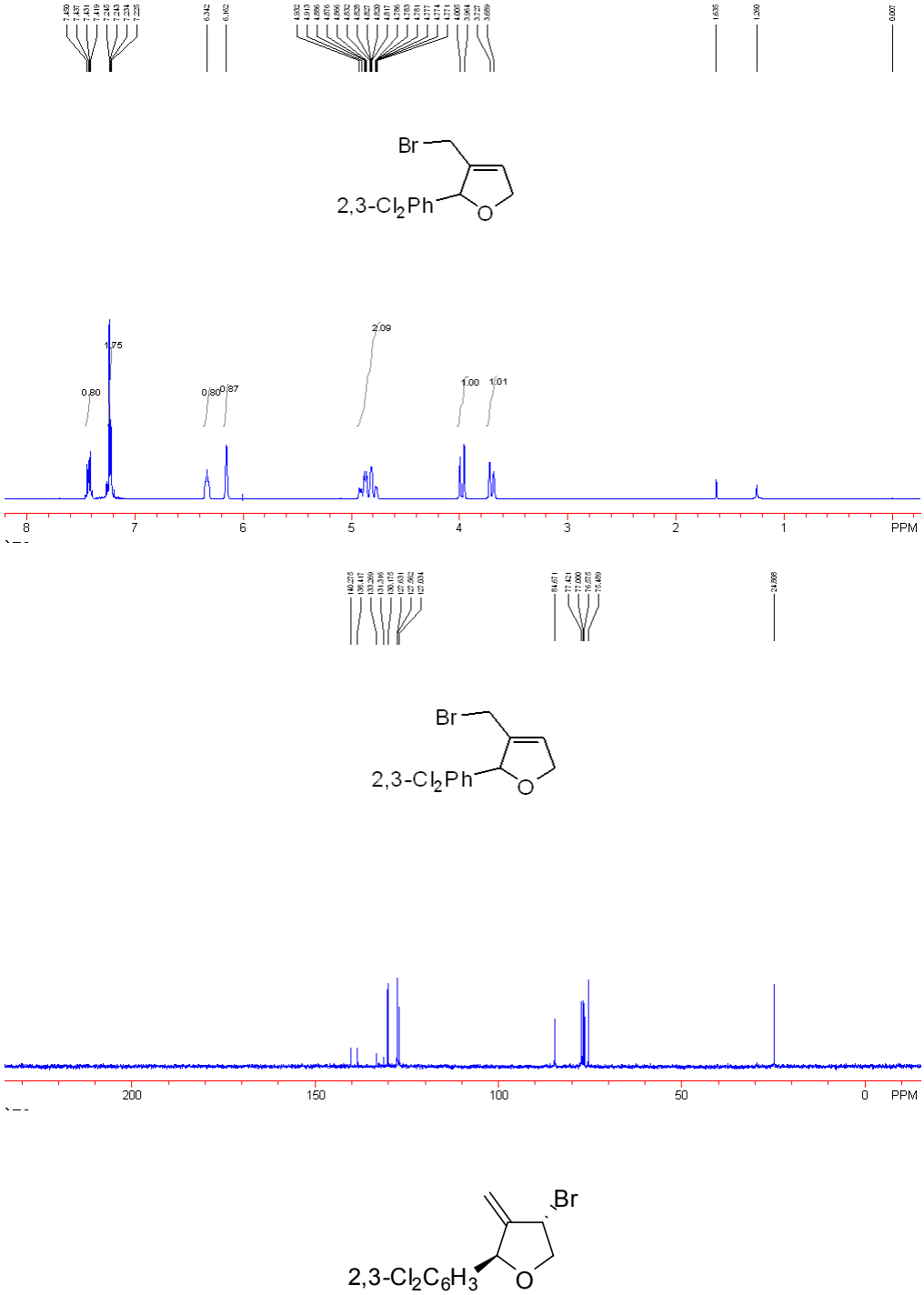




3-(bromomethyl)-2-(2,3-dichlorophenyl)-2,5-dihydrofuran 4l:

A colorless, viscous liquid. IR (film): ν 3116, 3071, 2928, 2854, 1763, 1578, 1509, 1453, 1419, 1284, 1254, 1214, 1158, 1050, 896, 788, 719, 667 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.70 (d, *J* = 11.4 Hz, 1H, CHBr), 3.98 (d, *J* = 11.4 Hz, 1H, CHBr), 4.76-4.93 (m, 2H, CH_2O), 6.16 (s, 1H, ArCHO), 6.34 (s, br, 1H, =CH), 7.23 (d, *J* = 6.0 Hz, 1H, ArH), 7.24 (d, *J* = 3.6 Hz, 1H, ArH), 7.43 (dd, *J* = 6.0, 3.6 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.8, 75.5, 84.7, 127.0, 127.57, 127.64, 130.2, 131.3, 133.3, 138.4, 140.3; MS (EI) *m/z* (%): 306 (M^+,

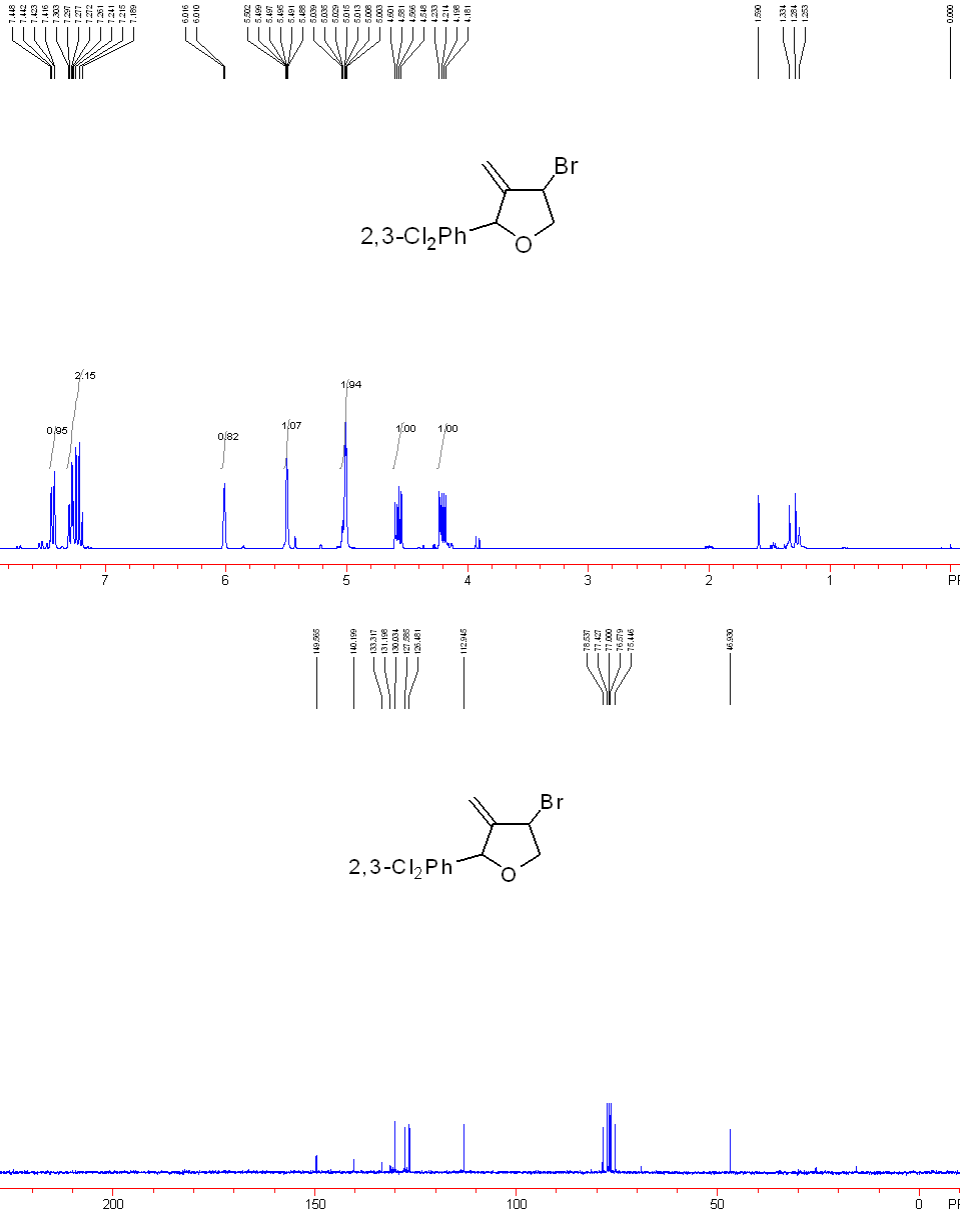
6.00), 227 (56.82), 225 (49.30), 215 (55.41), 213 (81.75), 190 (43.35), 175 (64.22), 173 (100.00), 163 (37.73); HRMS (EI) Calcd. For $C_{11}H_9OBrCl_2$ 305.9214, Found: 305.9212.



(*anti*-2,4)4-bromo-2-(2,3-dichlorophenyl)-3-methylenetetrahydrofuran 5l (combined with some amount of unknown products):

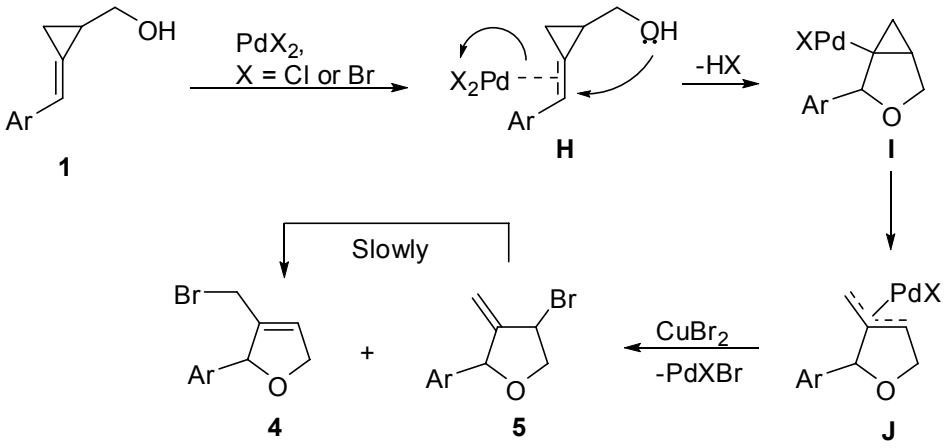
A colorless, viscous liquid. IR (film): ν 3068, 2926, 2858, 1351, 1422, 1213, 1181, 1157, 1103, 1071, 1043, 969, 919, 853, 782, 742, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.21 (dd, *J* = 10.2, 5.4 Hz, 1H, CHO), 4.57 (dd, *J* = 10.2, 6.0 Hz, 1H, CHO), 5.00-5.03 (m, 2H),

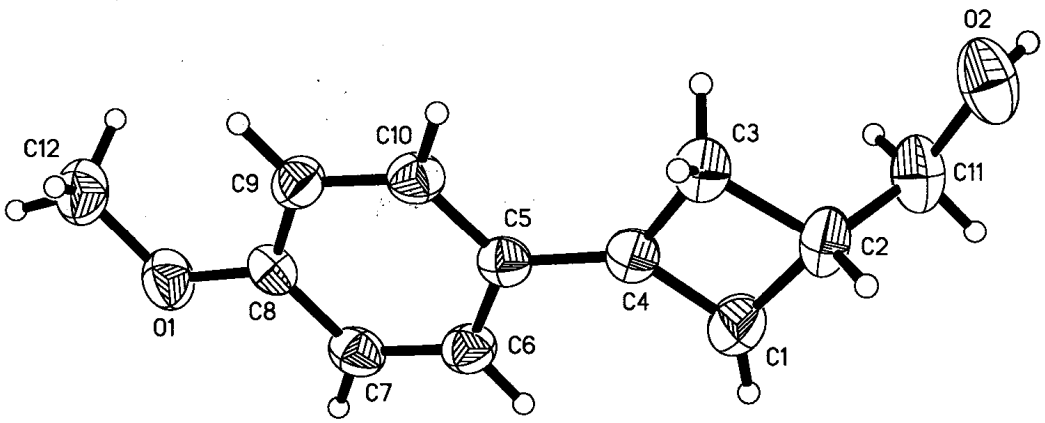
4.49-5.50 (m, 1H), 6.01 (d, J = 2.1Hz, 1H), 7.23 (dd, J = 13.8, 7.5 Hz, 1H, ArH), 7.29 (dd, J = 7.5, 1.8 Hz, 1H, ArH), 7.43 (dd, J = 7.5, 1.8 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 46.9, 75.4, 78.5, 112.9, 126.5, 127.6, 130.0, 131.2, 133.3, 140.2, 149.6; MS (EI) *m/z* (%): 306 (M^+, 0.28), 229 (16.65), 227 (20.48), 177 (13.94), 175 (68.52), 173 (100.00), 128 (10.91), 127 (10.25), 53 (25.32); HRMS (EI) Calcd. For $C_{11}H_9OBrCl_2$ 305.9214, Found: 305.9226.



An alternative mechanism of the reactions under air is provided below. First, PdX_2 coordinates to the carbon-carbon double bonds of substrates **1** to furnish intermediate **H**, then the hydroxyl group attacks at the carbon-carbon double bonds to give cyclopropyl-Pd complex **I**, which undergoes ring-opening reactions to afford π-allylpalladium comples **J**. Bromination of the π-allylpalladium complex delivers brominated furan derivatives **4** and **5**.

Alternative Mechanism (Wacker-type reaction) of the Reactions under Air





The crystal data of **2a** have been deposited in CCDC with number 665100. Empirical Formula: $C_{12}H_{14}O_2$; Formula Weight: 190.23; Crystal Color, Habit: colorless, prismatic; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a = 46.33(2)Å, b = 5.461(3)Å, c = 8.220(4)Å, $\alpha = 90^o$, $\beta = 92.926^o$, $\gamma = 90^o$, V = 2077.2(18)Å^3; Space group: P2(1)/c; Z = 8; D_{calc} = 1.217 g/cm^3; F_{000} = 816; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0677, 0.1706.

Table 1. Crystal data and structure refinement for cd27511.

Identification code	cd27511
Empirical formula	C12 H14 O2
Formula weight	190.23
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 46.33(2) A alpha = 90 deg. b = 5.461(3) A beta = 92.926(11) deg. c = 8.220(4) A gamma = 90 deg.
Volume	2077.2(18) A^3
Z, Calculated density	8, 1.217 Mg/m^3
Absorption coefficient	0.082 mm^-1
F(000)	816
Crystal size	0.435 x 0.415 x 0.211 mm
Theta range for data collection	1.32 to 26.00 deg.
Limiting indices	-57<=h<=50, -6<=k<=6, -10<=l<=9
Reflections collected / unique	10802 / 4047 [R(int) = 0.1159]
Completeness to theta = 26.00	99.1 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.75341
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4047 / 2 / 264
Goodness-of-fit on F^2	0.911
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1706
R indices (all data)	R1 = 0.1197, wR2 = 0.1942
Extinction coefficient	0.0027(13)
Largest diff. peak and hole	0.213 and -0.193 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd27511.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	4660(1)	4610(4)	945(2)	76(1)
O(2)	2647(1)	2672(5)	2667(3)	95(1)
O(3)	338(1)	4946(4)	5847(3)	77(1)
O(4)	2397(1)	4949(5)	5156(3)	92(1)
C(1)	3274(1)	6821(6)	1885(4)	82(1)
C(2)	3052(1)	5365(6)	2785(4)	73(1)
C(3)	3308(1)	3727(5)	3288(3)	66(1)
C(4)	3494(1)	5212(5)	2385(3)	57(1)
C(5)	3800(1)	5047(4)	2063(3)	54(1)
C(6)	3928(1)	6732(5)	1076(3)	62(1)
C(7)	4213(1)	6557(5)	742(3)	63(1)
C(8)	4380(1)	4666(5)	1381(3)	55(1)
C(9)	4259(1)	2973(5)	2382(3)	61(1)
C(10)	3972(1)	3180(5)	2707(3)	59(1)
C(11)	2815(1)	4246(7)	1716(4)	83(1)
C(12)	4830(1)	2576(6)	1458(4)	85(1)
C(13)	1657(1)	6595(5)	3287(3)	68(1)
C(14)	1932(1)	5186(5)	3692(3)	62(1)
C(15)	1746(1)	3599(5)	4743(4)	70(1)
C(16)	1500(1)	5113(4)	4285(3)	54(1)
C(17)	1201(1)	5037(4)	4715(3)	51(1)
C(18)	1100(1)	3227(5)	5713(3)	59(1)
C(19)	816(1)	3116(5)	6126(3)	60(1)
C(20)	624(1)	4870(4)	5534(3)	55(1)
C(21)	720(1)	6714(5)	4538(3)	63(1)
C(22)	1001(1)	6793(5)	4152(3)	59(1)
C(23)	2174(1)	6529(6)	4557(4)	75(1)
C(24)	225(1)	2952(6)	6704(4)	84(1)

Table 3. Bond lengths [A] and angles [deg] for cd27511.

O(1)-C(8)	1.367(3)
O(1)-C(12)	1.414(4)
O(2)-C(11)	1.420(4)
O(2)-H(2)	0.82(2)
O(3)-C(20)	1.367(3)
O(3)-C(24)	1.411(3)
O(4)-C(23)	1.412(4)
O(4)-H(4)	0.855(18)
C(1)-C(4)	1.394(4)
C(1)-C(2)	1.520(4)
C(1)-H(1)	0.9300
C(2)-C(11)	1.501(4)
C(2)-C(3)	1.525(4)
C(2)-H(2A)	0.9800
C(3)-C(4)	1.422(4)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.456(4)
C(5)-C(6)	1.382(4)
C(5)-C(10)	1.383(4)
C(6)-C(7)	1.366(4)
C(6)-H(6)	0.9300
C(7)-C(8)	1.376(4)
C(7)-H(7)	0.9300
C(8)-C(9)	1.374(4)
C(9)-C(10)	1.376(4)
C(9)-H(9)	0.9300
C(10)-H(10)	0.9300
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(16)	1.386(4)
C(13)-C(14)	1.511(4)
C(13)-H(13)	0.9300
C(14)-C(23)	1.492(4)
C(14)-C(15)	1.521(4)
C(14)-H(14)	0.9800
C(15)-C(16)	1.444(4)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.446(4)
C(17)-C(18)	1.381(3)
C(17)-C(22)	1.396(3)
C(18)-C(19)	1.375(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.379(4)
C(19)-H(19)	0.9300
C(20)-C(21)	1.385(4)
C(21)-C(22)	1.355(4)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(8)-O(1)-C(12)	117.5(2)
C(11)-O(2)-H(2)	105(4)
C(20)-O(3)-C(24)	117.2(2)
C(23)-O(4)-H(4)	103(2)
C(4)-C(1)-C(2)	91.7(3)
C(4)-C(1)-H(1)	134.1
C(2)-C(1)-H(1)	134.1
C(11)-C(2)-C(1)	114.8(3)
C(11)-C(2)-C(3)	117.0(3)

C(1)-C(2)-C(3)	84.5(2)
C(11)-C(2)-H(2A)	112.6
C(1)-C(2)-H(2A)	112.6
C(3)-C(2)-H(2A)	112.6
C(4)-C(3)-C(2)	90.4(2)
C(4)-C(3)-H(3A)	113.6
C(2)-C(3)-H(3A)	113.6
C(4)-C(3)-H(3B)	113.6
C(2)-C(3)-H(3B)	113.6
H(3A)-C(3)-H(3B)	110.8
C(1)-C(4)-C(3)	93.3(3)
C(1)-C(4)-C(5)	133.7(3)
C(3)-C(4)-C(5)	133.0(2)
C(6)-C(5)-C(10)	117.3(3)
C(6)-C(5)-C(4)	121.1(2)
C(10)-C(5)-C(4)	121.5(2)
C(7)-C(6)-C(5)	121.4(3)
C(7)-C(6)-H(6)	119.3
C(5)-C(6)-H(6)	119.3
C(6)-C(7)-C(8)	120.2(3)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
O(1)-C(8)-C(9)	124.2(3)
O(1)-C(8)-C(7)	115.9(2)
C(9)-C(8)-C(7)	119.8(3)
C(8)-C(9)-C(10)	119.1(3)
C(8)-C(9)-H(9)	120.4
C(10)-C(9)-H(9)	120.4
C(9)-C(10)-C(5)	122.1(3)
C(9)-C(10)-H(10)	119.0
C(5)-C(10)-H(10)	119.0
O(2)-C(11)-C(2)	109.2(3)
O(2)-C(11)-H(11A)	109.8
C(2)-C(11)-H(11A)	109.8
O(2)-C(11)-H(11B)	109.8
C(2)-C(11)-H(11B)	109.8
H(11A)-C(11)-H(11B)	108.3
O(1)-C(12)-H(12A)	109.5
O(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
O(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(16)-C(13)-C(14)	92.0(2)
C(16)-C(13)-H(13)	134.0
C(14)-C(13)-H(13)	134.0
C(23)-C(14)-C(13)	117.4(2)
C(23)-C(14)-C(15)	116.3(2)
C(13)-C(14)-C(15)	85.4(2)
C(23)-C(14)-H(14)	111.8
C(13)-C(14)-H(14)	111.8
C(15)-C(14)-H(14)	111.8
C(16)-C(15)-C(14)	89.4(2)
C(16)-C(15)-H(15A)	113.8
C(14)-C(15)-H(15A)	113.8
C(16)-C(15)-H(15B)	113.8
C(14)-C(15)-H(15B)	113.8
H(15A)-C(15)-H(15B)	111.0
C(13)-C(16)-C(15)	93.2(2)
C(13)-C(16)-C(17)	134.5(2)
C(15)-C(16)-C(17)	132.4(2)
C(18)-C(17)-C(22)	116.7(3)
C(18)-C(17)-C(16)	121.5(2)
C(22)-C(17)-C(16)	121.8(2)
C(19)-C(18)-C(17)	122.3(2)
C(19)-C(18)-H(18)	118.8
C(17)-C(18)-H(18)	118.8
C(18)-C(19)-C(20)	119.3(3)
C(18)-C(19)-H(19)	120.3
C(20)-C(19)-H(19)	120.3
O(3)-C(20)-C(19)	124.8(3)
O(3)-C(20)-C(21)	115.7(2)

C(19)-C(20)-C(21)	119.5(3)
C(22)-C(21)-C(20)	120.2(2)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	119.9
C(21)-C(22)-C(17)	121.9(3)
C(21)-C(22)-H(22)	119.0
C(17)-C(22)-H(22)	119.0
O(4)-C(23)-C(14)	112.5(3)
O(4)-C(23)-H(23A)	109.1
C(14)-C(23)-H(23A)	109.1
O(4)-C(23)-H(23B)	109.1
C(14)-C(23)-H(23B)	109.1
H(23A)-C(23)-H(23B)	107.8
O(3)-C(24)-H(24A)	109.5
O(3)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
O(3)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd27511.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	58(1)	88(2)	82(1)	7(1)	7(1)	-7(1)
O(2)	69(2)	146(2)	70(2)	-23(2)	14(1)	-18(1)
O(3)	58(1)	81(2)	91(2)	12(1)	1(1)	4(1)
O(4)	61(2)	153(2)	60(1)	-5(1)	-9(1)	32(1)
C(1)	72(2)	74(2)	99(2)	15(2)	-2(2)	11(2)
C(2)	53(2)	96(2)	69(2)	-19(2)	-1(2)	14(2)
C(3)	63(2)	78(2)	56(2)	-9(2)	1(1)	4(2)
C(4)	59(2)	62(2)	51(2)	-10(1)	-2(1)	2(1)
C(5)	62(2)	53(2)	45(2)	-5(1)	-3(1)	-3(1)
C(6)	70(2)	53(2)	62(2)	5(1)	-5(1)	2(1)
C(7)	71(2)	57(2)	62(2)	8(1)	2(2)	-12(1)
C(8)	53(2)	59(2)	53(2)	-3(1)	0(1)	-10(1)
C(9)	59(2)	58(2)	65(2)	7(1)	3(1)	6(1)
C(10)	66(2)	54(2)	58(2)	8(1)	9(1)	-2(1)
C(11)	59(2)	123(3)	68(2)	-9(2)	1(2)	2(2)
C(12)	60(2)	98(2)	97(2)	6(2)	7(2)	7(2)
C(13)	62(2)	76(2)	65(2)	16(2)	-11(1)	-7(2)
C(14)	56(2)	79(2)	52(2)	-5(1)	-3(1)	1(1)
C(15)	73(2)	63(2)	72(2)	-4(2)	-1(2)	6(2)
C(16)	58(2)	54(2)	49(2)	-3(1)	-12(1)	0(1)
C(17)	56(2)	49(2)	46(2)	-2(1)	-12(1)	-2(1)
C(18)	60(2)	55(2)	62(2)	6(1)	-13(1)	9(1)
C(19)	63(2)	59(2)	57(2)	10(1)	-7(1)	-2(1)
C(20)	51(2)	55(2)	59(2)	-4(1)	-10(1)	0(1)
C(21)	59(2)	56(2)	72(2)	5(2)	-12(1)	7(1)
C(22)	65(2)	50(2)	59(2)	9(1)	-11(1)	0(1)
C(23)	58(2)	103(2)	63(2)	-7(2)	-8(2)	5(2)
C(24)	65(2)	102(3)	86(2)	14(2)	11(2)	-4(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd27511.

	x	y	z	U(eq)
H(1)	3265	8231	1250	98
H(2A)	2978	6270	3706	88
H(3A)	3355	3732	4451	79
H(3B)	3289	2065	2880	79
H(6)	3818	8013	629	74
H(7)	4296	7720	80	76
H(9)	4371	1705	2834	73
H(10)	3891	2028	3381	71
H(11A)	2694	5525	1230	100
H(11B)	2898	3323	845	100
H(12A)	4839	2486	2626	127
H(12B)	5022	2759	1083	127
H(12C)	4745	1103	1014	127
H(13)	1611	7935	2625	82
H(14)	1997	4286	2746	75
H(15A)	1727	1919	4369	84
H(15B)	1802	3663	5895	84
H(18)	1229	2042	6120	71
H(19)	755	1870	6797	72
H(21)	592	7900	4134	75
H(22)	1062	8054	3492	70
H(23A)	2254	7700	3815	90
H(23B)	2100	7436	5459	90
H(24A)	268	1453	6157	126
H(24B)	20	3129	6748	126
H(24C)	311	2918	7791	126
H(4)	2451(7)	4240(60)	4300(30)	99(12)
H(2)	2537(11)	1980(110)	2010(60)	120(30)

Table 6. Torsion angles [deg] for cd27511.

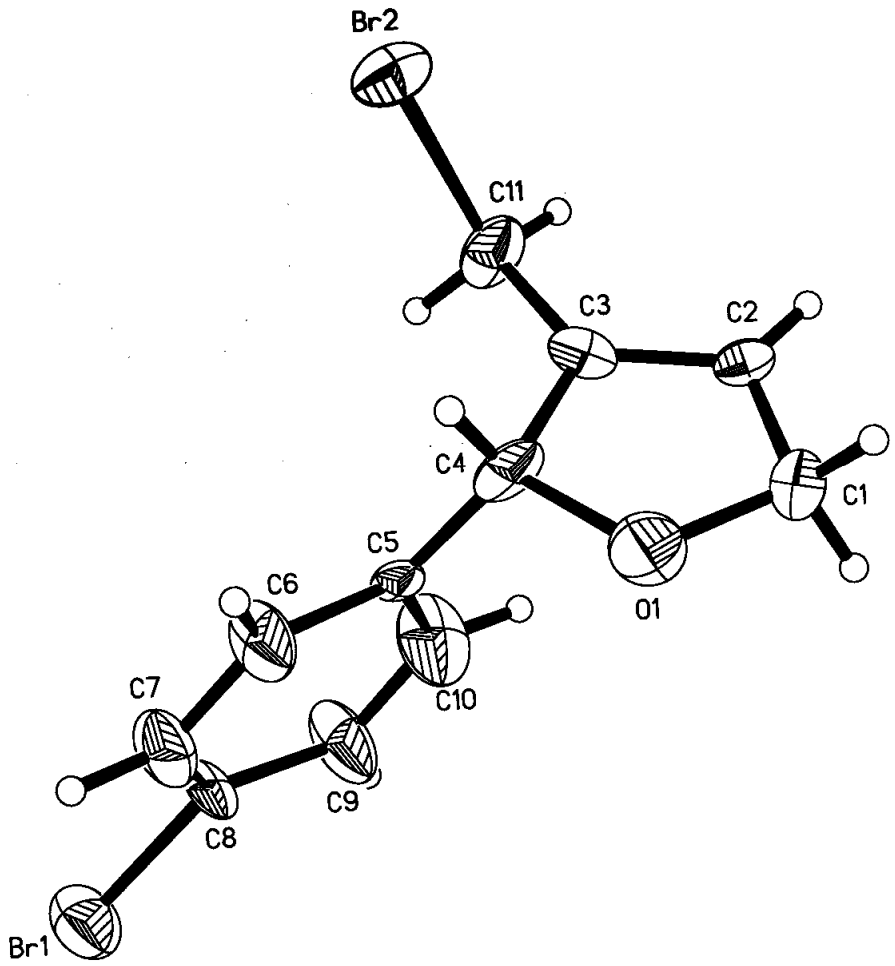
C(4)-C(1)-C(2)-C(11)	-116.6(3)
C(4)-C(1)-C(2)-C(3)	0.7(2)
C(11)-C(2)-C(3)-C(4)	114.4(3)
C(1)-C(2)-C(3)-C(4)	-0.7(2)
C(2)-C(1)-C(4)-C(3)	-0.7(2)
C(2)-C(1)-C(4)-C(5)	177.4(3)
C(2)-C(3)-C(4)-C(1)	0.7(2)
C(2)-C(3)-C(4)-C(5)	-177.4(3)
C(1)-C(4)-C(5)-C(6)	0.4(4)
C(3)-C(4)-C(5)-C(6)	177.8(3)
C(1)-C(4)-C(5)-C(10)	-178.5(3)
C(3)-C(4)-C(5)-C(10)	-1.1(4)
C(10)-C(5)-C(6)-C(7)	0.3(4)
C(4)-C(5)-C(6)-C(7)	-178.6(2)
C(5)-C(6)-C(7)-C(8)	0.5(4)
C(12)-O(1)-C(8)-C(9)	5.1(4)
C(12)-O(1)-C(8)-C(7)	-174.5(3)
C(6)-C(7)-C(8)-O(1)	178.4(2)
C(6)-C(7)-C(8)-C(9)	-1.2(4)
O(1)-C(8)-C(9)-C(10)	-178.5(2)
C(7)-C(8)-C(9)-C(10)	1.1(4)
C(8)-C(9)-C(10)-C(5)	-0.3(4)
C(6)-C(5)-C(10)-C(9)	-0.4(4)
C(4)-C(5)-C(10)-C(9)	178.5(2)
C(1)-C(2)-C(11)-O(2)	172.0(3)
C(3)-C(2)-C(11)-O(2)	75.2(3)
C(16)-C(13)-C(14)-C(23)	-116.4(3)
C(16)-C(13)-C(14)-C(15)	0.9(2)
C(23)-C(14)-C(15)-C(16)	117.5(3)
C(13)-C(14)-C(15)-C(16)	-0.9(2)
C(14)-C(13)-C(16)-C(15)	-1.0(2)
C(14)-C(13)-C(16)-C(17)	179.8(3)
C(14)-C(15)-C(16)-C(13)	1.0(2)
C(14)-C(15)-C(16)-C(17)	-179.8(3)
C(13)-C(16)-C(17)-C(18)	176.9(3)
C(15)-C(16)-C(17)-C(18)	-2.0(4)
C(13)-C(16)-C(17)-C(22)	-3.5(4)
C(15)-C(16)-C(17)-C(22)	177.6(3)
C(22)-C(17)-C(18)-C(19)	0.8(4)
C(16)-C(17)-C(18)-C(19)	-179.6(2)
C(17)-C(18)-C(19)-C(20)	-0.3(4)
C(24)-O(3)-C(20)-C(19)	-6.5(4)
C(24)-O(3)-C(20)-C(21)	173.1(2)
C(18)-C(19)-C(20)-O(3)	179.5(2)
C(18)-C(19)-C(20)-C(21)	-0.1(4)
O(3)-C(20)-C(21)-C(22)	-179.8(2)
C(19)-C(20)-C(21)-C(22)	-0.1(4)
C(20)-C(21)-C(22)-C(17)	0.7(4)
C(18)-C(17)-C(22)-C(21)	-1.0(4)
C(16)-C(17)-C(22)-C(21)	179.3(2)
C(13)-C(14)-C(23)-O(4)	168.3(2)
C(15)-C(14)-C(23)-O(4)	69.3(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd27511 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(4)#1	0.82(2)	1.94(3)	2.723(3)	161(6)
O(4)-H(4)...O(2)	0.855(18)	1.87(2)	2.707(3)	168(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z-1/2



The crystal data of **4h** have been deposited in CCDC with number 674227. Empirical Formula: $C_{11}H_{10}Br_2O$; Formula Weight: 318.01; Crystal Color, Habit: colorless, prismatic; Crystal System: Orthorhombic; Lattice Type: Primitive; Lattice Parameters: a = 6.0931(9)Å, b = 13.8466(19)Å, c = 26.311(4)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2219.8(5)Å^3; Space group: Pna2(1); Z = 8; D_{calc} = 1.903 g/cm^3; F_{000} = 1232; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0928, 0.2064.

Table 1. Crystal data and structure refinement for cd2823.

Identification code	cd2823
Empirical formula	C11 H10 Br2 O
Formula weight	318.01
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pna2(1)
Unit cell dimensions	a = 6.0931(9) A alpha = 90 deg. b = 13.8466(19) A beta = 90 deg. c = 26.311(4) A gamma = 90 deg.
Volume	2219.8(5) A^3
Z, Calculated density	8, 1.903 Mg/m^3
Absorption coefficient	7.267 mm^-1
F(000)	1232
Crystal size	0.341 x 0.261 x 0.157 mm
Theta range for data collection	2.75 to 25.49 deg.
Limiting indices	-7<=h<=7, -14<=k<=16, -31<=l<=27
Reflections collected / unique	10890 / 2117 [R(int) = 0.1919]
Completeness to theta = 25.49	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.2448
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2117 / 12 / 254
Goodness-of-fit on F^2	0.906
Final R indices [I>2sigma(I)]	R1 = 0.0928, wR2 = 0.2064
R indices (all data)	R1 = 0.1267, wR2 = 0.2254
Absolute structure parameter	-10(10)
Extinction coefficient	0.0025(7)
Largest diff. peak and hole	1.574 and -1.169 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd2823.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	11144(5)	6573(2)	-1584(1)	79(1)
Br(2)	10909(5)	3501(2)	1070(1)	66(1)
Br(3)	3735(5)	3558(2)	9815(1)	75(1)
Br(4)	4015(5)	6481(2)	7171(1)	66(1)
O(1)	8250(30)	6648(9)	887(7)	70(5)
O(2)	6810(30)	3295(10)	7314(7)	67(5)
C(1)	6260(40)	6375(15)	1148(11)	63(7)
C(2)	6110(30)	5326(12)	1089(8)	48(5)
C(3)	7910(30)	5021(12)	817(6)	46(5)
C(4)	9370(30)	5859(10)	673(9)	49(6)
C(5)	9770(20)	5974(10)	123(7)	33(4)
C(6)	11730(30)	6335(16)	-45(7)	66(6)
C(7)	12220(30)	6542(14)	-526(7)	74(7)
C(8)	10570(30)	6349(13)	-873(5)	43(5)
C(9)	8480(30)	6046(19)	-731(8)	80(8)
C(10)	8150(40)	5870(20)	-223(7)	86(8)
C(11)	8370(30)	4005(12)	670(10)	64(7)
C(12)	8710(40)	3655(18)	7074(13)	74(8)
C(13)	8710(40)	4716(16)	7158(8)	65(7)
C(14)	7050(30)	4974(12)	7396(8)	49(5)
C(15)	5520(40)	4109(14)	7528(8)	55(6)
C(16)	5150(30)	3927(13)	8075(8)	58(6)
C(17)	3170(30)	4178(16)	8287(8)	75(7)
C(18)	2640(30)	4072(15)	8780(7)	68(6)
C(19)	4260(30)	3729(15)	9118(10)	81(9)
C(20)	6260(40)	3508(18)	8919(8)	89(9)
C(21)	6780(40)	3730(30)	8420(8)	119(12)
C(22)	6500(40)	5979(14)	7572(8)	61(6)

Table 3. Bond lengths [A] and angles [deg] for cd2823.

Br(1)-C(8)	1.926(14)
Br(2)-C(11)	2.00(2)
Br(3)-C(19)	1.88(3)
Br(4)-C(22)	1.97(2)
O(1)-C(4)	1.40(2)
O(1)-C(1)	1.45(3)
O(2)-C(12)	1.41(3)
O(2)-C(15)	1.49(3)
C(1)-C(2)	1.46(3)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.38(2)
C(2)-H(2)	0.9300
C(3)-C(11)	1.49(2)
C(3)-C(4)	1.51(2)
C(4)-C(5)	1.47(3)
C(4)-H(4)	0.9800
C(5)-C(10)	1.35(3)
C(5)-C(6)	1.370(16)
C(6)-C(7)	1.333(17)
C(6)-H(6)	0.9300
C(7)-C(8)	1.385(17)
C(7)-H(7)	0.9300
C(8)-C(9)	1.390(16)
C(9)-C(10)	1.376(17)
C(9)-H(9)	0.9300
C(10)-H(10)	0.9300
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.49(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.24(2)
C(13)-H(13)	0.9300
C(14)-C(22)	1.50(3)
C(14)-C(15)	1.55(2)
C(15)-C(16)	1.48(3)
C(15)-H(15)	0.9800
C(16)-C(21)	1.374(18)
C(16)-C(17)	1.375(17)
C(17)-C(18)	1.345(17)
C(17)-H(17)	0.9300
C(18)-C(19)	1.409(18)
C(18)-H(18)	0.9300
C(19)-C(20)	1.366(18)
C(20)-C(21)	1.385(18)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700

C(4)-O(1)-C(1)	113.2(15)
C(12)-O(2)-C(15)	109.6(17)
O(1)-C(1)-C(2)	105.1(16)
O(1)-C(1)-H(1A)	110.7
C(2)-C(1)-H(1A)	110.7
O(1)-C(1)-H(1B)	110.7
C(2)-C(1)-H(1B)	110.7
H(1A)-C(1)-H(1B)	108.8
C(3)-C(2)-C(1)	108.1(17)
C(3)-C(2)-H(2)	125.9
C(1)-C(2)-H(2)	125.9
C(2)-C(3)-C(11)	125.2(17)
C(2)-C(3)-C(4)	111.3(16)
C(11)-C(3)-C(4)	123.5(17)
O(1)-C(4)-C(5)	112.9(15)
O(1)-C(4)-C(3)	102.3(18)
C(5)-C(4)-C(3)	115.3(15)

O(1)-C(4)-H(4)	108.6
C(5)-C(4)-H(4)	108.6
C(3)-C(4)-H(4)	108.6
C(10)-C(5)-C(6)	117.5(18)
C(10)-C(5)-C(4)	121.8(16)
C(6)-C(5)-C(4)	120.0(17)
C(7)-C(6)-C(5)	125.4(18)
C(7)-C(6)-H(6)	117.3
C(5)-C(6)-H(6)	117.3
C(6)-C(7)-C(8)	115.0(16)
C(6)-C(7)-H(7)	122.5
C(8)-C(7)-H(7)	122.5
C(7)-C(8)-C(9)	123.1(16)
C(7)-C(8)-Br(1)	118.4(12)
C(9)-C(8)-Br(1)	118.4(12)
C(10)-C(9)-C(8)	117(2)
C(10)-C(9)-H(9)	121.6
C(8)-C(9)-H(9)	121.6
C(5)-C(10)-C(9)	122(2)
C(5)-C(10)-H(10)	119.1
C(9)-C(10)-H(10)	119.1
C(3)-C(11)-Br(2)	109.8(14)
C(3)-C(11)-H(11A)	109.7
Br(2)-C(11)-H(11A)	109.7
C(3)-C(11)-H(11B)	109.7
Br(2)-C(11)-H(11B)	109.7
H(11A)-C(11)-H(11B)	108.2
O(2)-C(12)-C(13)	106(2)
O(2)-C(12)-H(12A)	110.4
C(13)-C(12)-H(12A)	110.4
O(2)-C(12)-H(12B)	110.4
C(13)-C(12)-H(12B)	110.4
H(12A)-C(12)-H(12B)	108.6
C(14)-C(13)-C(12)	111.1(19)
C(14)-C(13)-H(13)	124.5
C(12)-C(13)-H(13)	124.5
C(13)-C(14)-C(22)	127(2)
C(13)-C(14)-C(15)	112.2(18)
C(22)-C(14)-C(15)	120.9(19)
C(16)-C(15)-O(2)	108.8(16)
C(16)-C(15)-C(14)	116.1(17)
O(2)-C(15)-C(14)	100.6(18)
C(16)-C(15)-H(15)	110.3
O(2)-C(15)-H(15)	110.3
C(14)-C(15)-H(15)	110.3
C(21)-C(16)-C(17)	115(2)
C(21)-C(16)-C(15)	124.5(18)
C(17)-C(16)-C(15)	119.1(19)
C(18)-C(17)-C(16)	125(2)
C(18)-C(17)-H(17)	117.5
C(16)-C(17)-H(17)	117.5
C(17)-C(18)-C(19)	119(2)
C(17)-C(18)-H(18)	120.7
C(19)-C(18)-H(18)	120.7
C(20)-C(19)-C(18)	117(2)
C(20)-C(19)-Br(3)	119.9(18)
C(18)-C(19)-Br(3)	122.8(15)
C(19)-C(20)-C(21)	121(2)
C(19)-C(20)-H(20)	119.4
C(21)-C(20)-H(20)	119.4
C(16)-C(21)-C(20)	120(2)
C(16)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(14)-C(22)-Br(4)	109.3(12)
C(14)-C(22)-H(22A)	109.8
Br(4)-C(22)-H(22A)	109.8
C(14)-C(22)-H(22B)	109.8
Br(4)-C(22)-H(22B)	109.8
H(22A)-C(22)-H(22B)	108.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd2823.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	75(2)	100(2)	63(2)	15(1)	6(2)	-7(1)
Br(2)	75(2)	47(1)	74(2)	1(1)	-12(2)	15(1)
Br(3)	79(2)	85(2)	61(2)	3(1)	9(2)	-14(1)
Br(4)	73(2)	56(2)	69(2)	5(1)	-6(2)	16(1)
O(1)	94(14)	40(8)	76(11)	-6(7)	17(10)	-4(8)
O(2)	85(13)	36(7)	81(11)	-23(7)	24(10)	-9(8)
C(1)	65(18)	63(13)	60(15)	-1(11)	20(14)	18(12)
C(2)	45(13)	52(11)	46(12)	16(10)	-5(10)	18(8)
C(3)	61(15)	40(11)	37(11)	8(9)	-3(10)	-9(10)
C(4)	48(13)	16(8)	84(16)	-11(9)	-6(11)	2(8)
C(5)	30(10)	16(8)	52(11)	8(7)	2(8)	-2(7)
C(6)	28(9)	94(16)	74(14)	13(12)	-3(9)	-21(10)
C(7)	39(12)	88(16)	94(17)	23(13)	15(11)	-18(11)
C(8)	40(12)	74(12)	14(7)	14(8)	-1(7)	-6(9)
C(9)	32(11)	140(20)	66(15)	29(15)	-4(10)	-25(13)
C(10)	79(18)	150(20)	34(12)	-9(15)	-6(12)	1(15)
C(11)	53(14)	29(10)	110(20)	-5(11)	12(14)	0(9)
C(12)	44(15)	86(17)	90(20)	17(14)	7(15)	-9(13)
C(13)	69(17)	73(15)	53(14)	-9(12)	20(12)	-35(12)
C(14)	31(11)	33(10)	82(15)	8(10)	-11(11)	-10(8)
C(15)	58(15)	60(13)	48(13)	19(10)	-8(11)	-27(11)
C(16)	42(14)	33(10)	100(18)	-6(10)	9(13)	-20(9)
C(17)	55(14)	87(16)	83(16)	14(13)	-8(12)	3(12)
C(18)	46(13)	71(14)	85(16)	11(12)	15(11)	-10(11)
C(19)	50(16)	39(10)	150(30)	11(14)	43(17)	-3(10)
C(20)	58(17)	140(30)	69(15)	39(14)	-22(12)	14(14)
C(21)	30(12)	260(40)	63(18)	30(20)	19(12)	14(17)
C(22)	65(16)	59(13)	59(14)	-1(10)	-34(12)	-15(11)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd2823.

	x	y	z	U(eq)
H(1A)	4997	6689	996	75
H(1B)	6335	6550	1504	75
H(2)	4997	4934	1214	57
H(4)	10782	5786	845	59
H(6)	12815	6444	198	79
H(7)	13571	6797	-622	88
H(9)	7367	5967	-969	97
H(10)	6766	5669	-114	104
H(11A)	8708	3974	310	77
H(11B)	7088	3610	733	77
H(12A)	8678	3510	6714	89
H(12B)	10012	3366	7221	89
H(13)	9804	5132	7047	78
H(15)	4117	4172	7350	66
H(17)	2111	4442	8073	90
H(18)	1240	4222	8896	81
H(20)	7304	3203	9123	107
H(21)	8242	3742	8318	143
H(22A)	7769	6396	7528	73
H(22B)	6119	5971	7929	73

Table 6. Torsion angles [deg] for cd2823.

C(4)-O(1)-C(1)-C(2)	0(3)
O(1)-C(1)-C(2)-C(3)	1(2)
C(1)-C(2)-C(3)-C(11)	-179.2(19)
C(1)-C(2)-C(3)-C(4)	-1(2)
C(1)-O(1)-C(4)-C(5)	124.5(19)
C(1)-O(1)-C(4)-C(3)	0(2)
C(2)-C(3)-C(4)-O(1)	0(2)
C(11)-C(3)-C(4)-O(1)	179.0(18)
C(2)-C(3)-C(4)-C(5)	-122.5(16)
C(11)-C(3)-C(4)-C(5)	56(3)
O(1)-C(4)-C(5)-C(10)	-75(3)
C(3)-C(4)-C(5)-C(10)	42(3)
O(1)-C(4)-C(5)-C(6)	95(2)
C(3)-C(4)-C(5)-C(6)	-147.5(18)
C(10)-C(5)-C(6)-C(7)	-4(3)
C(4)-C(5)-C(6)-C(7)	-174(2)
C(5)-C(6)-C(7)-C(8)	-1(3)
C(6)-C(7)-C(8)-C(9)	6(3)
C(6)-C(7)-C(8)-Br(1)	-177.5(16)
C(7)-C(8)-C(9)-C(10)	-5(4)
Br(1)-C(8)-C(9)-C(10)	178(2)
C(6)-C(5)-C(10)-C(9)	5(3)
C(4)-C(5)-C(10)-C(9)	175(2)
C(8)-C(9)-C(10)-C(5)	-1(4)
C(2)-C(3)-C(11)-Br(2)	-109.4(18)
C(4)-C(3)-C(11)-Br(2)	72(2)
C(15)-O(2)-C(12)-C(13)	3(3)
O(2)-C(12)-C(13)-C(14)	-2(3)
C(12)-C(13)-C(14)-C(22)	177(2)
C(12)-C(13)-C(14)-C(15)	0(3)
C(12)-O(2)-C(15)-C(16)	-125(2)
C(12)-O(2)-C(15)-C(14)	-3(2)
C(13)-C(14)-C(15)-C(16)	119(2)
C(22)-C(14)-C(15)-C(16)	-59(3)
C(13)-C(14)-C(15)-O(2)	2(2)
C(22)-C(14)-C(15)-O(2)	-175.9(17)
O(2)-C(15)-C(16)-C(21)	53(3)
C(14)-C(15)-C(16)-C(21)	-59(3)
O(2)-C(15)-C(16)-C(17)	-142.2(19)
C(14)-C(15)-C(16)-C(17)	105(2)
C(21)-C(16)-C(17)-C(18)	-13(3)
C(15)-C(16)-C(17)-C(18)	-178(2)
C(16)-C(17)-C(18)-C(19)	4(4)
C(17)-C(18)-C(19)-C(20)	-1(3)
C(17)-C(18)-C(19)-Br(3)	179.5(18)
C(18)-C(19)-C(20)-C(21)	8(4)
Br(3)-C(19)-C(20)-C(21)	-173(2)
C(17)-C(16)-C(21)-C(20)	19(4)
C(15)-C(16)-C(21)-C(20)	-176(2)
C(19)-C(20)-C(21)-C(16)	-18(5)
C(13)-C(14)-C(22)-Br(4)	110(2)
C(15)-C(14)-C(22)-Br(4)	-73(2)

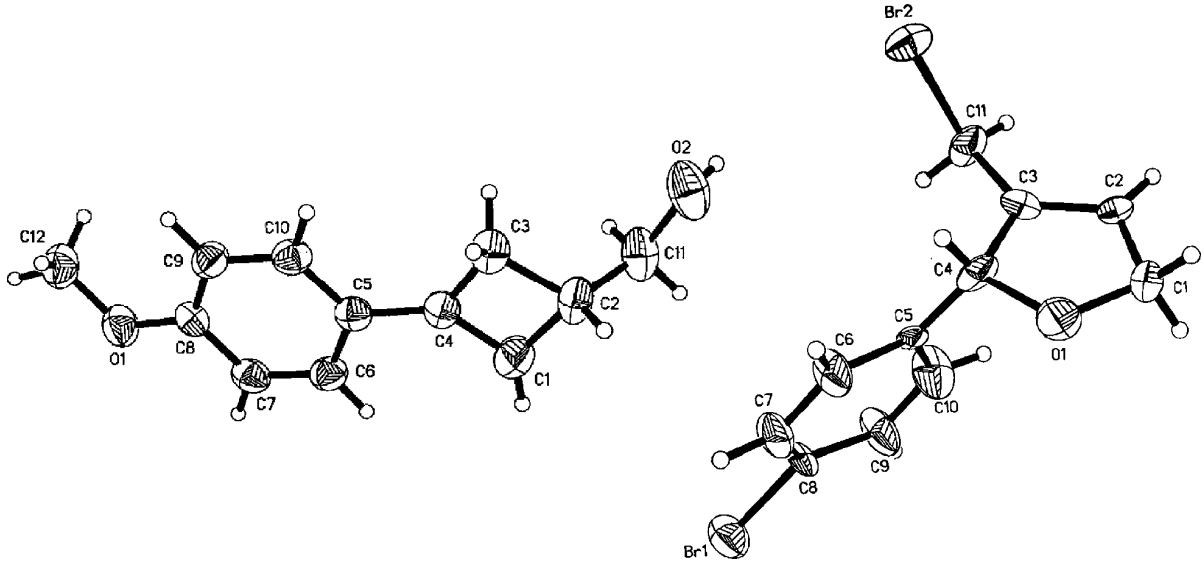
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd2823 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Crystal data

The crystal data of 4h have been deposited with the CCDC, number 674227. Empirical Formula: $C_{11}H_{10}Br_2O$; Formula Weight: 318.01; Crystal Color, Habit: colorless, prismatic; Crystal System: Orthorhombic; Lattice Type: Primitive; Lattice Parameters: a = 6.0931(9)Å, b = 13.8466(19)Å, c = 26.311(4)Å, α = 90°, β = 90°, γ = 90°, V = 2219.8(5)Å^3; Space group: Pna2(1); Z = 8; D_{calc} = 1.903 g/cm^3; F_{000} = 1232; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0928, 0.2064.



ORTEP drawings of **2a** (left) and **4h** (right).