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Diastereoselective Synthesis of 2,4-Disubstituted Tetrahydropyranols and Ethers via a Prins-Type Cyclization Catalyzed by Scandium Triflate

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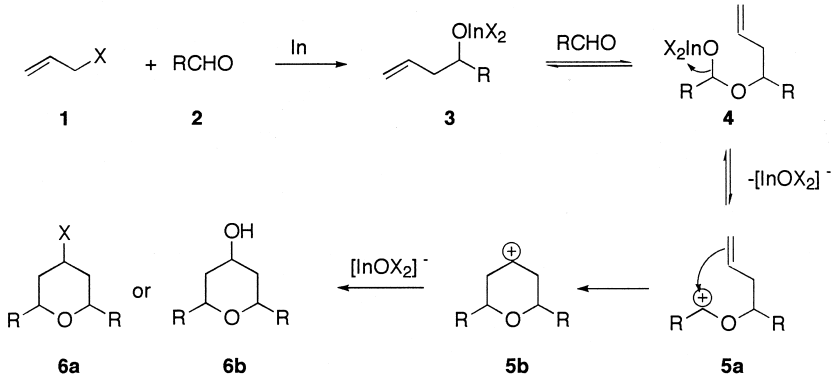
Abstract—The reaction of aldehydes with homoallylic alcohols catalyzed by scandium triflate gives rise to the formation of 2-substituted tetrahydropyran-4-ols and ethers in good overall yields and with 'all-*cis*' configurations and high diastereoselectivities. The stereochemistries of these products were assigned with the assistance of coupling constants and NOE. Factors affecting the reaction have been examined in detail. The reaction was found to be most effective in chloroform. Various aromatic and aliphatic aldehydes underwent the cyclization smoothly. A catalytic cycle for this reaction has been proposed.

Introduction

The condensation of olefins with aldehydes, known as the Prins reaction, is a fundamental reaction for forming carbon–carbon bonds.[1] Under the classical conditions, the reaction was carried out in the presence of strong acids (e.g. sulfuric acid) and at high reaction temperatures, which often generated a mixture of products. The importance of pyrans is exemplified by its presence in the backbone of various carbohydrates and natural products.[2] This prompts extensive studies in forming these pyran structural derivatives.[3] Recently, the potential of Prins-cyclization in forming tetrahydropyran derivatives has been recognized. In the literature, Chan[4] as well as Coppi[5] reported that the coupling between allylsilanes and aldehydes could be used to prepare 2,6-disubstituted 4-halotetrahydropyrans. The mechanism of this reaction was postulated as a cyclization of the hemiacetal formed by condensation of an intermediate homoallyl alcohol derivative with a second molecule of an aldehyde, mediated by the halogenated Lewis acid. Coppi and coworkers found that an analogous condensation could be achieved by directly mixing aldehydes and unsaturated alcohols at 0°C in the presence of a Lewis acid.[5b] Subsequently, several groups have extended the scope of this reaction for various synthetic needs.[6] On the other hand, the formation of oxygenated, instead of halogenated, tetrahydropyran derivatives would often be more desirable synthetically. During our recent investigation of indium-mediated reactions under neat conditions,[7] we accidentally observed the formation of tetrahydropyran-4-ol and



Scheme 1.

Keywords: scandium and compounds; cyclization; diastereoselection; pyrans.

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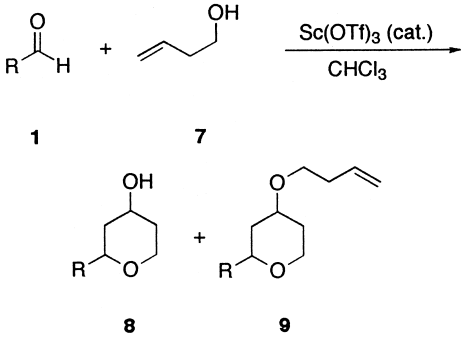
4-bromo derivatives.[8] To explain the formation of the tetrahydropyran derivatives, we postulated that the product was generated through a tandem carbonyl allylation–hemiacetal formation—Prins reaction (Scheme 1).

Subsequently, by controlling the reaction conditions, various 4-chlorotetrahydropyrans were synthesized via the reaction of homoallylic alcohols and aldehydes with indium trichloride as the Lewis acid.[8] From these results, we conceived that by replacing the chloride ion with a non-nucleophilic anion, the synthetically more valuable tetrahydropyranol or its ether would become the major product. Herein, we describe such a reaction catalyzed by scandium triflate (Eq. (1)).[9] Independent of our work, Nishizawa[10] and Overman et al.[11] recently reported preliminary results on related cyclizations.



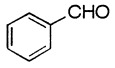
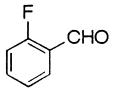
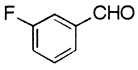
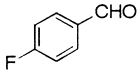
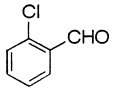
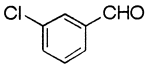
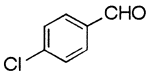
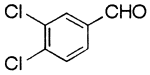
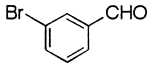
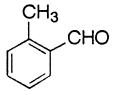
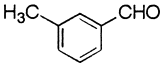
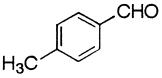
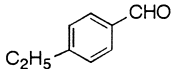
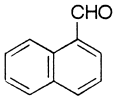
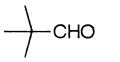
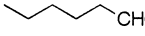
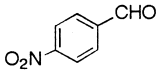
(1)

Results and Discussion

In light of the proposed mechanism, a Lewis acid with a non-nucleophilic counterion is apparently required to facilitate this 'Prins-like' carbonyl addition reaction. For this purpose, it would appear that scandium triflate is an appropriate candidate for forming the desired oxygenated derivatives.[12] When a mixture of benzaldehyde and 3-buten-1-ol was stirred with a catalytic amount of scandium triflate in chloroform under a refluxing temperature, the formation of products was observed by TLC. To ensure the completion of the reaction, the refluxing was kept overnight. After a regular work-up, column chromatography of the crude materials on silica gel provided 2-phenyl-4-hydroxytetrahydropyran (**8a**) and 2-phenyl-4-(3-butenoxy)tetrahydropyran (**9a**) in 14 and 63% yields, respectively.

It appears that the use of scandium triflate is important for the success of the reaction. In the absence of scandium triflate, no reaction was observed. When indium triflate was used as the catalyst, nearly the same results were obtained. With $Yb(OTf)_3$[13] as the Lewis acid, the yield of desired products diminished considerably. The results of this scandium triflate catalyzed Prins-type cyclization between a variety of aromatic aldehydes and 3-buten-1-ol are summarized in Table 1. The uses of different aromatic and aliphatic aldehydes (after further investigation) did not affect the reaction significantly. By using the same standard reaction conditions (CH_3Cl, cat. $Sc(OTf)_3$, reflux), compounds **1a**–**1p** all reacted to give nearly the same yields of products **8a**–**8p** (ca. 20%) and **9a**–**9p** (ca. 60%). Decreasing the amount of alcohol being used did not affect the reaction significantly. When equal equivalents of

Table 1. Tetrahydropyran derivatives via scandium triflate catalyzed Prins-type cyclization

Entry	RCHO	Product **8** (%)	Product **9** (%)	Overall yield (%)
1	 **1a**	**8a** (14) **8a** (12)	**9a** (63) **9a** (58)	77 70[a]
2	 **1b**	**8b** (19)	**9b** (50)	69
3	 **1c**	**8c** (12)	**9c** (57)	69
4	 **1d**	**8d** (16)	**9d** (69)	85
5	 **1e**	**8e** (13)	**9e** (71)	84
6	 **1f**	**8f** (11)	**9f** (65)	76
7	 **1g**	**8g** (15)	**9g** (68)	83
8	 **1h**	**8h** (17)	**9h** (49)	66
9	 **1i**	**8i** (14)	**9i** (72)	86
10	 **1j**	**8j** (20)	**9j** (58)	78
11	 **1k**	**8k** (13)	**9k** (62)	75
12	 **1l**	**8l** (18)	**9l** (64)	82
13	 **1m**	**8m** (10)	**9m** (56)	66
14	 **1n**	**8n** (9)	**9n** (70)	79
15	 **1o**	**8o** (17)	**9o** (54)	71
16	 **1p**	**8p** (12)	**9p** (60)	72
17	 **1q**	**8q** (13)	**9q** (73)	86[b]

[a] Indium triflate was used as the catalyst.
[b] **9q** was a dihydropyran product.

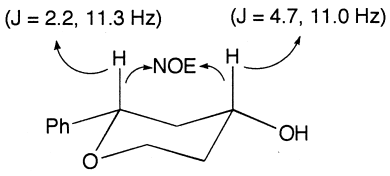


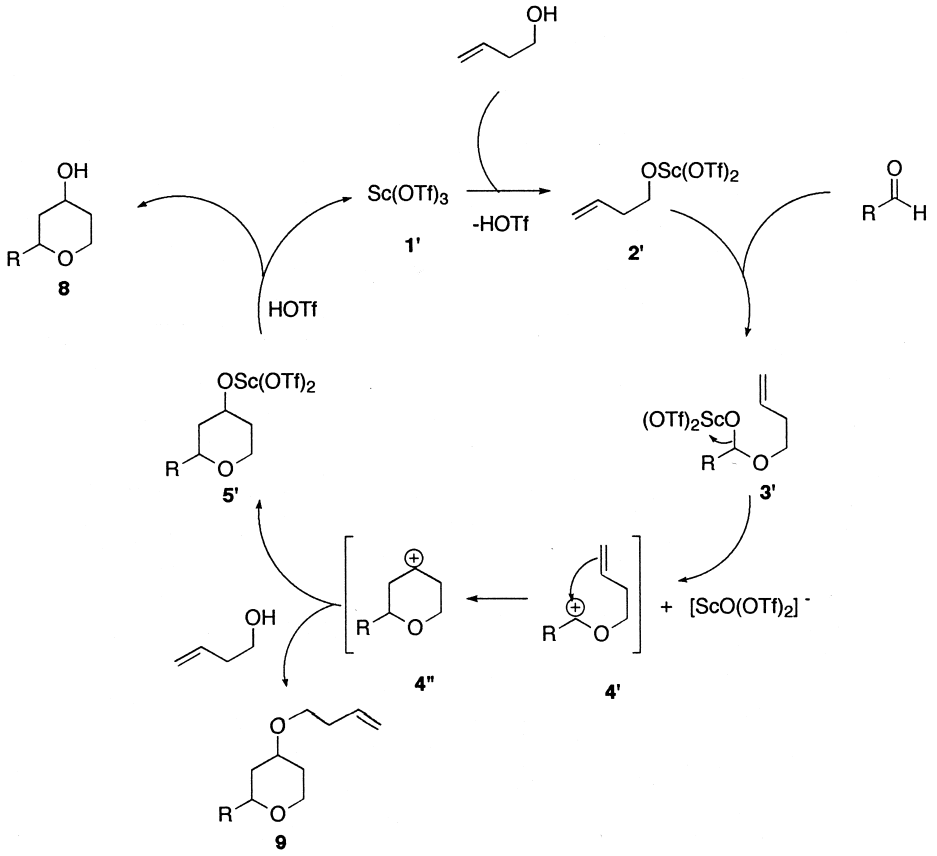
Figure 1.

benzaldehyde and homoallylic alcohol were used for the reaction, the ratio of products is nearly the same as the one obtained under the standard reaction conditions. Interestingly, the reaction of *p*-nitrobenzaldehyde mainly generated a dihydropyran product **9q** (entry 17).

The reaction temperature also has an effect on the yield of the product. At an ambient temperature, the starting material cannot be consumed completely even after reacting for 48 h; whereas under refluxing conditions, no starting aldehyde could be detected either by TLC or ^{1}H NMR after stirring overnight. As a solvent chloroform is more effective than tetrahydrofuran or diethyl ether for the reaction, which is usually the case in Lewis acid catalyzed reactions. The reaction also proceeds slowly in methylene chloride; however, its low boiling point limits temperature changes. No reaction was observed in either toluene or acetonitrile.

In forming multi-substituted tetrahydropyran derivatives, stereochemistry is also important. In the present reaction, only a single diastereomer was formed as judged by ^{1}H spectroscopy of the crude reaction mixture. The substituents in all the products were found *cis*-related in all cases, which was mostly likely due to a thermodynamic control of the reaction. The assignment of the stereochemistry was based on the coupling constants of the protons at the C-2 and C-4 positions. A splitting value of ca. 11 Hz was found for all such protons, indicating the presence of an axial–axial coupling. The two substituents are therefore in the equatorial positions, in agreement with the all-*cis* stereochemistry. The assignment was also confirmed by the ^{1}H NMR chemical shift of the 4-hydrogens in the range of 3.9–4.2 ppm, a typical value for axial protons.[14] The stereochemistry was also corroborated by Nucleus Overhauser Experiments (NOE). NOE measurements were performed at room temperature using the NOESY[15] pulse sequence. The ROESY spectrum of compound **8a** reveals that the signal at 4.31 ppm (H-2) shows a large cross-peak with the signal at 3.91 ppm (H-4) (Fig. 1).

A possible mechanism for this Prins-type cyclization is shown in Scheme 2. The reaction is initiated by scandium triflate (**1′**) to generate the butenoxylated scandium agent (**2′**) which then reacts with the aldehyde to give **3′**. Subsequently, the intermediates **4′** and **4″** could be formed by losing $[ScO(OTf)_2]^-$. The reaction of the latter with 3-buten-1-ol affords the corresponding tetrahydropyran ethers (**9**). Alternatively, the intermediate **4″** could also pick up the $[ScO(OTf)_2]^-$ anion to afford **5′**, which reacts with HOTf to give rise to the formation of corresponding tetrahydropyranols (**8**) and the catalyst (**1′**) itself. A similar mechanism has been used to explain a cross-allylation of aldehyde by Nokami and co-workers very recently.[16]



Scheme 2. Proposed mechanism for the scandium triflate catalyzed tetrahydropyran formations.

Conclusion

In conclusion, the reaction of aldehydes with homoallylic alcohol catalyzed by scandium triflate generates tetrahydropyran-4-ols and ethers in good (overall) yield with *cis* diastereoselectivity. Further investigation of this process and its potential applications to natural product synthesis are currently in progress.

Experimental

All reactions were carried out under a nitrogen atmosphere. Scandium triflate was purchased from Aldrich and was used directly as received. All other chemicals were also used without additional purification. Flash chromatography employed E. Merck silica gel (Kiesegel 60, 230–400 mesh) purchased from Scientific Adsorbents. ^{1}H and ^{13}C NMR measurements were conducted on a GE-400 instrument in $CDCl_3$. GC–Mass spectra were obtained on Hewlett Packard 5890. Elemental analyses were performed at the Center of Instrumental Facility of Tulane University.

General procedure for the scandium triflate catalyzed cyclization

A mixture of benzaldehyde (212 mg, 2 mmol), 3-buten-1-ol (288 mg, 4 mmol) and scandium triflate (98 mg, 0.2 mmol, 5 mol% relative to the alcohol) in chloroform (5 mL) was refluxed under nitrogen overnight. After concentrating in vacuo, the crude reaction mixture was subjected to column chromatography on silica gel eluting with hexane–ethyl acetate (gradient eluent: hexane/EtOAc=27:1 to 3:1) to give product **8a** (50 mg, yield 14%) and product **9a** (292 mg, yield 63%).

***cis*-2-Phenyl-4-hydroxy-tetrahydropyran (8a).** FTIR(film): 3382, 1494, 1445, 1362, 1244, 1136, 1072, 1023, 979, 954, 881, 802, 753, 694, 636 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.30 (m, 5H), 4.31 (dd, J=11.3, 2.2 Hz, 1H), 4.16 (ddd, J=11.8, 4.7, 1.7 Hz, 1H), 3.91 (tt, J=11.0, 4.7 Hz, 1H), 3.57 (dt, J=12.6, 2.2 Hz, 1H), 2.15 (m, 1H), 2.09 (br s, OH, 1H), 1.95 (m, 1H), 1.62 (m, 1H), 1.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=141.8, 128.5, 127.7, 126.0, 78.4, 68.4, 66.4, 43.2, 35.4; GC/MS: *m*/*z* (% base peak) 179 (M^++1, 3), 178 (M^+, 24), 177 (M^+−1, 19), 161 (M^+−OH, 9), 160 (77), 159 (27), 145 (5), 131 (8), 105 (100), 91 (17), 77 (Ph^+, 37), 44 (26), 43 (21), 39 (9); Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.70; H, 7.92.

***cis*-2-(2-Fluorophenyl)-4-hydroxy-tetrahydropyran (8b).** FTIR(film): 3372, 1587, 1494, 1455, 1362, 1229, 1185, 1136, 1077, 1024, 994, 989, 954, 886, 837, 807, 792, 753, 690, 635 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.48 (m, 1H), 7.24 (m, 1H), 7.14 (m, 1H), 7.01 (m, 1H), 4.64 (dd, J=11.5, 1.5 Hz, 1H), 4.17 (ddd, J=11.7, 5.0, 1.5 Hz, 1H), 3.95 (tt, J=11.1, 4.8 Hz, 1H), 3.60 (dt, J=12.3, 2.1 Hz, 1H), 2.20 (m, 1H), 1.96 (m, 1H), 1.79 (br s, OH, 1H), 1.65 (m, 1H), 1.50 (m, 1H), 1.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=160.5, 158.1, 129.2, 129,0, 129.0, 128.9, 127.2, 127.2, 124.4, 124.3, 115.3, 115.1, 71.9, 68.2, 66.4, 42.3, 35.4; GC/MS: *m*/*z* (% base peak) 197 (M^++1, 1), 196 (M^+, 7), 195 (M^+−1, 5), 179 (M^+−OH, 14), 178 (100), 177 (16), 163 (7), 150 (5), 149 (6), 126 (5), 125 (40), 124 (21), 123 (79), 122 (20), 121 (8), 109 (16), 105 (4), 97 (17), 96 (12), 95 (10), 83 (3), 77 (Ph^+, 9), 75 (9), 57 (13), 55 (11), 44 (17), 43 (14), 39 (4); Anal. Calcd for $C_{11}H_{13}O_2F$: C, 67.33; H, 6.68. Found: C, 67.11; H, 6.68.

***cis*-2-(3-Fluorophenyl)-4-hydroxy-tetrahydropyran (8c).** FTIR(film): 3372, 1612, 1592, 1489, 1445, 1362, 1249, 1170, 1136, 1072, 989, 959, 935, 866, 783, 768, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.28 (m, 1H), 7.08 (m, 2H), 6.96 (m, 1H), 4.30 (dd, J=11.4, 2.0 Hz, 1H), 4.15 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 3.90 (tt, J=10.6, 4.6 Hz, 1H), 3.56 (dt, J=12.3, 2.1 Hz, 1H), 2.15 (m, 1H), 2.03 (br s, OH, 1H), 1.94 (m, 1H), 1.61 (m, 1H), 1.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=164.1, 161.7, 144.5, 144.5, 130.0, 129.9, 121.4, 121.4, 114.5, 114.3, 113.0, 112.8, 77.6, 68.2, 66.3, 43.2, 35.3; GC/MS: *m*/*z* (% base peak) 197 (M^++1, 4), 196 (M^+, 29), 195 (M^+−1, 11), 179 (M^+−OH, 14), 178 (100), 177 (21), 163 (7), 150 (5), 149 (7), 126 (5), 125 (28), 124 (24), 123 (83), 122 (23), 121 (11), 109 (16), 105 (4), 101 (11), 97 (23), 96 (20), 95 (17), 83 (5), 77 (Ph^+, 7), 75 (12), 57 (20), 56 (6), 55 (17), 44 (25), 43 (19), 39 (5); Anal. Calcd for $C_{11}H_{13}O_2F$: C, 67.33; H, 6.68. Found: C, 67.44; H, 6.94.

***cis*-2-(4-Fluorophenyl)-4-hydroxy-tetrahydropyran (8d).** FTIR(film): 3382, 1602, 1509, 1362, 1293, 1244, 1219, 1156, 1136, 1072, 984, 881, 832, 807, 777, 596 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.31 (m, 2H), 7.02 (m, 2H), 4.29 (dd, J=11.4, 1.8 Hz, 1H), 4.16 (ddd, J=11.7, 5.0, 1.5 Hz, 1H), 3.93 (tt, J=11.2, 4.4 Hz, 1H), 3.57 (dt, J=12.3, 2.1 Hz, 1H), 2.15 (m, 1H), 1.96 (m, 1H), 1.73 (br s, OH, 1H), 1.64 (m, 1H), 1.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=163.4, 161.0, 137.7, 137.7, 127.7, 127.6, 115.4, 115.2, 77.7, 68.3, 66.4, 43.3, 35.4; GC/MS: *m*/*z* (% base peak) 197 (M^++1, 3), 196 (M^+, 21), 195 (M^+−1, 12), 179 (M^+−OH, 13), 178 (93), 177 (21), 163 (6), 150 (6), 149 (6), 126 (3), 125 (33), 124 (28), 123 (100), 122 (21), 121 (12), 109 (18), 105 (3), 101 (10), 97 (20), 96 (17), 95 (18), 83 (4), 77 (Ph^+, 7), 75 (12), 57 (19), 56 (6), 55 (24), 44 (30), 43 (21), 39 (6); Anal. Calcd for $C_{11}H_{13}O_2F$: C, 67.33; H, 6.68. Found: C, 66.84; H, 6.79.

***cis*-2-(2-Chlorophenyl)-4-hydroxy-tetrahydropyran (8e).** FTIR(film): 3382, 1472, 1433, 1368, 1283, 1244, 1204, 1178, 1125, 1068, 1024, 963, 870, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.48 (m, 1H), 7.24 (m, 1H), 7.14 (m, 1H), 7.01 (m, 1H), 4.65 (dd, J=11.5, 1.5 Hz, 1H), 4.17 (ddd, J=11.7, 5.0, 1.5 Hz, 1H), 3.95 (tt, J=10.6, 4.7 Hz, 1H), 3.60 (dt, J=12.3, 2.1 Hz, 1H), 2.20 (m, 1H), 1.96 (m, 1H), 1.79 (br s, OH, 1H), 1.65 (m, 1H), 1.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=140.5, 131.3, 129.2, 128.3, 127.2, 127.0, 70.7, 64.2, 63.1, 39.6, 32.5; GC/MS: *m*/*z* (% base peak) 215 (^{37}Cl M^++1, 1), 214 (^{37}Cl M^+, 7), 213 (4), 212 (^{35}Cl M^+, 22), 211 (^{35}Cl M^+−1, 4), 196 (33), 195 (M^+−OH, 19), 194 (97), 193 (20), 177 (M^+−Cl, 7), 160 (M^+−Cl−OH, 3), 159 (26), 143 (16), 142 (14), 140 (34), 139 (100), 138 (15), 137 (4), 131 (9), 127 (8), 125 (21), 115 (6), 114 (5), 113 (14), 112 (ClPh$^+$, 11), 111 (9), 105 (7), 103 (20), 102 (6), 91 (4), 89 (6), 77 (Ph^+, 41), 75 (13), 71 (4), 57 (17), 55 (21), 51 (14), 44 (26), 43 (25), 41 (4), 39 (7);

Anal. Calcd for $C_{11}H_{13}O_2Cl$: C, 62.12; H, 6.16. Found: C, 61.91; H, 6.24.

***cis*-2-(3-Chlorophenyl)-4-hydroxy-tetrahydropyran (8f).** FTIR(film): 3372, 1597, 1572, 1469, 1425, 1362, 1244, 1170, 1136, 1072, 984, 954, 881, 851, 783, 714, 685 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.35 (m, 1H), 7.26 (m, 2H), 7.20 (m, 1H), 4.29 (dd, J=11.5, 2.1 Hz, 1H), 4.16 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 3.91 (tt, J=11.3, 4.5 Hz, 1H), 3.56 (dt, J=12.3, 2.1 Hz, 1H), 2.16 (m, 1H), 1.96 (m, 1H), 1.80 (br s, OH, 1H), 1.61 (m, 1H), 1.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=143.9, 134.3, 129.7, 127.7, 126.1, 124.0, 116.5, 77.6, 66.2, 66.3, 43.2, 35.4; GC/MS: *m*/*z* (% base peak) 215 (^{37}Cl M^++1, 2), 214 (^{37}Cl M^+, 14), 213 (9), 212 (^{35}Cl M^+, 41), 211 (^{35}Cl M^+−1, 11), 196 (35), 195 (M^+−OH, 21), 194 (100), 193 (21), 177 (M^+−Cl, 18), 160 (M^+−Cl–OH, 4), 159 (35), 143 (9), 142 (11), 141 (58), 140 (33), 139 (90), 138 (18), 137 (6), 131 (14), 127 (6), 125 (13), 115 (7), 114 (8), 113 (20), 112 ($ClPh^+$, 19), 111 (15), 105 (9), 103 (27), 102 (10), 91 (6), 89 (6), 77 (Ph^+, 39), 75 (17), 71 (5), 57 (22), 55 (20), 51 (15), 44 (29), 43 (27), 41 (5), 39 (8); Anal. Calcd for $C_{11}H_{13}O_2Cl$: C, 62.12; H, 6.16. Found: C, 62.16; H, 6.01.

***cis*-2-(4-Chlorophenyl)-4-hydroxy-tetrahydropyran (8g).** FTIR(film): 3382, 2940, 2842, 1489, 1448, 1409, 1364, 1301, 1249, 1163, 1142, 1085, 1015, 987, 691, 885, 823, 802, 717, 689, 594 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.30 (d, J=8.8 Hz, 2H), 7.26 (d, J=8.8 Hz, 2H), 4.28 (dd, J=11.4, 2.1 Hz, 1H), 4.16 (ddd, J=12.0, 5.0, 1.8 Hz, 1H), 3.92 (tt, J=11.2, 4.4 Hz, 1H), 3.56 (dt, J=12.3, 2.1 Hz, 1H), 2.30 (br s, OH, 1H), 2.14 (m, 1H), 1.97 (m, 1H), 1.62 (m, 1H), 1.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=140.4, 133.3, 128.6, 127.3, 77.6, 68.2, 66.3, 43.2, 35.3; GC/MS: *m*/*z* (% base peak) 215 (^{37}Cl M^++1, 1), 214 (^{37}Cl M^+, 10), 213 (8), 212 (^{35}Cl M^+, 32), 211 (^{35}Cl M^+−1, 11), 196 (32), 195 (M^+−OH, 19), 194 (95), 193 (20), 179 (6), 177 (M^+−Cl, 18), 160 (M^+−Cl–OH, 3), 159 (24), 143 (10), 142 (12), 141 (61), 140 (33), 139 (100), 138 (17), 137 (8), 131 (8), 127 (6), 125 (16), 115 (5), 113 (15), 112 ($ClPh^+$, 19), 111 (13), 105 (10), 103 (24), 89 (6), 77 (Ph^+, 40), 75 (16), 71 (5), 57 (25), 55 (36), 51 (16), 50 (9), 45 (10), 44 (37), 43 (30), 41 (8), 39 (8); Anal. Calcd for $C_{11}H_{13}O_2Cl$: C, 62.12; H, 6.16. Found: C, 62.01; H, 5.95.

***cis*-2-(3,4-Dichlorophenyl)-4-hydroxy-tetrahydropyran (8h).** FTIR(film): 3369, 1472, 1362, 1246, 1130, 1083, 1030, 990, 962, 887, 821, 674, 611 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.45 (m, 1H), 7.40 (m, 1H), 7.15 (m, 1H), 4.28 (dd, J=11.5, 2.0 Hz, 1H), 4.17 (ddd, J=12.0, 5.0, 1.5 Hz, 1H), 3.93 (tt, J=11.2, 4.4 Hz, 1H), 3.55 (dt, J=12.3, 2.0 Hz, 1H), 2.16 (m, 1H), 2.04 (br s, OH, 1H), 1.97 (m, 1H), 1.63 (m, 1H), 1.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=142.2, 132.5, 131.4, 130.4, 127.9, 125.1, 76.9, 68.1, 66.3, 43.2, 35.3; GC/MS: *m*/*z* (% base peak) 248 (^{37}Cl M^+, 26), 247 (15), 246 (^{35}Cl M^+, 38), 245 (^{35}Cl M^+−1, 9), 232 (11), 231 (10), 230 (64), 229 (M^+−OH, 25), 228 (98), 227 (21), 215 (8), 213 (18), 211 (27), 202 (6), 195 (11), 193 (32), 177 (27), 176 (M^+−2Cl 24), 175 (84), 174 (41), 173 (94), 172 (18), 165 (13), 161 (11), 159 (M^+−OH–2Cl, 20), 149 (11), 148 (20), 147 ($ClPh^+$, 23), 146 (27), 145 (11), 139 (23), 137 (24), 123 (9), 111 (23), 102 (18), 101 (16), 85 (7), 77 (Ph^+, 7), 75 (29), 74 (14), 73 (10), 71 (13), 69 (12), 58 (29), 57 (66), 56 (26), 55 (88), 54 (25), 51 (18), 44 (100), 43 (87), 41 (22), 39 (16), 38 (18); Anal. Calcd for $C_{11}H_{12}O_2Cl_2$: C, 53.47; H, 4.93. Found: C, 53.54; H, 4.88.

***cis*-2-(3-Bromophenyl)-4-hydroxy-tetrahydropyran (8i).** FTIR(film): 3370, 1594, 1563, 1470, 1444, 1422, 1359, 1249, 1204, 1138, 1071, 987, 956, 881, 845, 779, 690, 681 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.51 (m, 1H), 7.40 (m, 1H), 7.22 (m, 2H), 4.27 (dd, J=11.4, 1.8 Hz, 1H), 4.16 (ddd, J=11.7, 5.0, 1.5 Hz, 1H), 3.91 (tt, J=11.2, 4.4 Hz, 1H), 3.55 (dt, J=12.3, 2.1 Hz, 1H), 2.15 (m, 1H), 1.95 (m, 1H), 1.91 (br s, OH, 1H), 1.60 (m, 1H), 1.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=144.2, 130.7, 130.0, 129.0, 124.4, 122.5, 77.5, 77.6, 68.2, 66.3, 43.2, 35.3; GC/MS: *m*/*z* (% base peak) 259 (^{81}Br M^++1, 6), 258 (^{81}Br M^+, 46), 257 (14), 256 (^{79}Br M^+, 48), 255 (^{79}Br M^+−1, 8), 241 (12), 240 (^{81}Br M^+−OH, 93), 239 (28), 238 (^{79}Br M^+−OH, 93), 237 (17), 225 (5), 223 (5), 187 (23), 186 (26), 185 (100), 184 (37), 183 (80), 182 (14), 178 (4), 177 (M^+−Br, 26), 171 (12), 169 (12), 159 (M^+−OH–Br, 61), 158 ($^{81}BrPh^+$, 21), 157 (22), 156 ($^{79}BrPh^+$, 19), 155 (10), 131 (24), 120 (5), 105 (30), 104 (18), 103 (36), 102 (16), 101 (9), 91 (10), 89 (7), 78(18), 77 (Ph^+, 64), 76 (19), 75 (18), 71 (10), 58 (16), 57 (52), 56 (14), 55 (49), 54 (13), 51 (25), 50 (14), 45 (18), 44 (57), 43 (48), 41 (10), 39 (11); Anal. Calcd for $C_{11}H_{13}O_2Br$: C, 51.38; H, 5.10. Found: C, 51.45; H, 5.12.

***cis*-2-(2-Methylphenyl)-4-hydroxy-tetrahydropyran (8j).** FTIR(film): 3373, 1490, 1455, 1441, 1362, 1336, 1291, 1243, 1221, 1163, 1141, 1106, 1075, 982, 956, 880, 806, 753, 722 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.43 (m, 1H), 7.19 (m, 3H), 4.48 (dd, J=11.5, 1.8 Hz, 1H), 4.17 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 3.92 (tt, J=11.0, 4.6 Hz, 1H), 3.58 (dt, J=12.3, 2.1 Hz, 1H), 2.33 (s, 3H), 2.12 (m, 1H), 2.02 (br s, OH, 1H), 1.97 (m, 1H), 1.65 (m, 1H), 1.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=139.8, 134.5, 130.3, 127.5, 126.3, 125.5, 75.2, 68.5, 66.4, 41.8, 35.6, 19.0; GC/MS: *m*/*z* (% base peak) 193 (M^++1, 10), 192 (M^+, 65), 191 (M^+−1, 18), 177 (M^+−CH_3, 34), 175 (8), 174 (53), 173 (17), 160 (4), 159 (M^+−OH–CH_3, 31), 121 (28), 120 (28), 119 (100), 118 (18), 117 (19), 115 (8), 105 (28), 103 (7), 93 (18), 92 (15), 91 (CH_3Ph^+, 35), 77 (Ph^+, 11), 65 (12), 57 (11), 55 (23), 44 (13), 43 (13), 41 (6), 39 (9); Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.55; H, 8.46.

***cis*-2-(3-Methylphenyl)-4-hydroxy-tetrahydropyran (8k).** FTIR(film): 3388, 1608, 1590, 1488, 1444, 1426, 1359, 1302, 1249, 1169, 1138, 1076, 1031, 983, 956, 881, 810, 783, 756, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.24 (m, 1H), 7.18 (m, 1H), 7.11 (m, 2H), 4.27 (dd, J=11.5, 1.5 Hz, 1H), 4.16 (ddd, J=11.6, 4.5, 1.5 Hz, 1H), 3.88 (tt, J=11.2, 4.4 Hz, 1H), 3.56 (dt, J=12.3, 2.1 Hz, 1H), 2.52 (br s, OH, 1H), 2.34 (s, 3H), 2.13 (m, 1H), 1.93 (m, 1H), 1.63 (m, 1H), 1.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=141.6, 138.1, 128.5, 128.3, 126.7, 123.0, 78.5, 68.3, 66.4, 43.2, 35.4, 21.5; GC/MS: *m*/*z* (% base peak) 193 (M^++1, 12), 192 (M^+, 78), 191 (M^+−1, 21), 178 (4), 177 (M^+−CH_3, 33), 175 (M^+−OH, 11), 174 (63), 173 (20), 160 (4), 159 (M^+−OH–CH_3, 34), 145 (7), 131 (7), 121 (24), 120 (29), 119 (100), 118 (20), 117 (21),

115 (10), 105 (28), 103 (8), 93 (26), 92 (CH_3Ph^+, 16), 91 (45), 77 (Ph^+, 14), 65 (16), 57 (13), 55 (20), 44 (17), 43 (17), 41 (7), 39 (11); Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.49; H, 8.56.

***cis*-2-(4-Methylphenyl)-4-hydroxy-tetrahydropyran (8l).** FTIR(film): 3381, 1609, 1514, 1444, 1414, 1361, 1309, 1244, 1204, 1161, 1139, 1074, 1030, 982, 956, 877, 812, 769, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.23 (d, J=7.9 Hz, 2H), 7.15 (d, J=7.9 Hz, 2H), 4.27 (dd, J=11.4, 1.8 Hz, 1H), 4.14 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 3.88 (tt, J=10.9, 4.7 Hz, 1H), 3.56 (dt, J=12.3, 2.1 Hz, 1H), 2.34 (s, 3H), 2.32 (br s, OH, 1H), 2.12 (m, 1H), 1.93 (m, 1H), 1.62 (m, 1H), 1.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=138.9, 137.4, 129.1, 125.9, 78.3, 68.4, 66.4, 43.2, 35.4, 21.2; GC/MS: *m*/*z* (% base peak) 193 (M^++1, 10), 192 (M^+, 69), 191 (M^+−1, 19), 178 (5), 177 (M^+−CH_3, 35), 175 (M^+−OH, 8), 174 (57), 173 (17), 160 (4), 159 (M^+−OH−CH_3, 33), 146 (4), 145 (6), 131 (5), 121 (29), 120 (29), 119 (100), 118 (18), 117 (19), 105 (28), 93 (18), 92 (CH_3Ph^+, 15), 91 (36), 77 (Ph^+, 13), 65 (12), 57 (10), 55 (22), 44 (13), 43 (12), 41 (6), 39 (9); Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.52; H, 8.37.

***cis*-2-(4-Ethylphenyl)-4-hydroxy-tetrahydropyran (8m).** FTIR(film): 3366, 1616, 1512, 1463, 1412, 1368, 1247, 1160, 1134, 1073, 1021, 986, 956, 878, 825, 804 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.26 (d, J=7.9 Hz, 2H), 7.17 (d, J=7.9 Hz, 2H), 4.28 (dd, J=11.4, 1.8 Hz, 1H), 4.15 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 3.90 (tt, J=10.8, 4.5 Hz, 1H), 3.56 (dt, J=12.3, 2.3 Hz, 1H), 2.63 (q, J=7.6 Hz, 2H), 2.30 (br s, OH, 1H), 2.15 (m, 1H), 1.95 (m, 1H), 1.64 (m, 1H), 1.56 (m, 1H), 1.22 (t, J=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=143.8, 139.1, 127.9, 126.0, 78.3, 68.4, 66.4, 43.1, 35.5, 28.6, 15.7; GC/MS: *m*/*z* (% base peak) 207 (M^++1, 12), 206 (M^+, 74), 205 (M^+−1, 18), 189 (M^+−OH, 8), 188 (48), 187 (15), 178 (12), 177 (M^+−C_2H_5, 87), 173 (4), 160 (10), 159 (M^+−OH−C_2H_5, 60), 135 (29), 134 (28), 133 (100), 132 (14), 131 (16), 119 (27), 117 (24), 106 (12), 105 (46), 103 (18), 91 (35), 79 (37), 77 (Ph^+, 19), 65 (7), 57 (15), 55 (31), 51 (7), 44 (15), 43 (16), 41 (7), 39 (8); Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.77; H, 9.06.

***cis*-2-(1-Naphthyl)-4-hydroxy-tetrahydropyran (8n).** FTIR(film): 3381, 3041, 1592, 1505, 1444, 1361, 1335, 1308, 1252, 1235, 1174, 1135, 1078, 1025, 973, 956, 819, 799, 777, 729 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=8.02 (d, J=8.2 Hz, 1H), 7.85 (d, J=7.6 Hz, 1H), 7.79 (d, J=7.3 Hz, 1H), 7.62 (d, J=7.3 Hz, 1H), 7.54–7.46 (m, 3H), 5.02 (dd, J=11.5, 1.8 Hz, 1H), 4.26 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 4.05 (tt, J=10.9, 4.7 Hz, 1H), 3.73 (dt, J=12.0, 2.1 Hz, 1H), 2.35 (m, 1H), 2.03 (m, 1H), 1.81 (br s, OH, 1H), 1.72 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=137.3, 133.8, 130.4, 128.9, 128.2, 126.1, 125.5, 125.5, 123.2, 123.1, 75.3, 68.6, 66.6, 42.3, 35.7; GC/MS: *m*/*z* (% base peak) 229 (M^++1, 16), 228 (M^+, 100), 227 (M^+−1, 23), 211 (M^+−OH, 6), 210 (25), 209 (20), 182 (7), 181 (7), 157 (17), 156 (26), 155 (52), 154 (16), 153 (28), 152 (13), 151 (4), 142 (15), 141 (23), 129 (21), 128 (60), 127 (24), 126 (6), 115 (5), 77 (Ph^+, 6), 76 (8), 75 (5), 57 (11), 55 (27), 44 (10), 43 (4), 41 (5), 39 (5), 38 (5), 36 (13); Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.70; H, 6.72.

***cis*-2-*t*-Butyl-4-hydroxy-tetrahydropyran (8o).** FTIR-(film): 3368, 2958, 2855, 1644, 1458, 1362, 1246, 1138, 1074, 1003, 952, 811, 600 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=4.01 (ddd, J=11.7, 5.0, 1.5 Hz, 1H), 3.74 (m, 1H), 3.33 (dt, J=12.3, 2.1 Hz, 1H), 2.85 (dd, J=11.2, 1.5 Hz, 1H), 2.20 (br s, OH, 1H), 1.95 (m, 1H), 1.85 (m, 1H), 1.46 (m, 1H), 1.18 (m, 1H), 0.89 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=84.1, 69.1, 66.1, 35.9, 35.8, 33.9, 26.0; GC/MS: *m*/*z* (% base peak) 157 (M^+−1, 0.4), 143 (3), 125 (8), 101 (100), 83 (21), 73 (9), 57 (90); Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.72; H, 11.34.

***cis*-2-*n*-Pentyl-4-hydroxy-tetrahydropyran (8p).** FTIR-(film): 3381, 2929, 2853, 1360, 1251, 1142, 1078, 1056, 969, 860 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=4.01 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 3.77 (m, 1H), 3.38 (dt, J=12.0, 2.1 Hz, 1H), 3.25 (m, 1H), 1.95 (m, 1H), 1.88 (m, 1H), 1.71 (br s, OH, 1H), 1.57–1.15 (m, 10H), 0.90 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=76.3, 68.3, 65.9, 41.6, 35.9, 35.8, 35.8, 27.7, 22.7, 14.0; GC/MS: *m*/*z* (% base peak) 155 (M^+−OH, 0.4), 101 (100), 83 (6), 69 (9), 57 (33), 44 (20); Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.22; H, 11.44.

***cis*-2-(4-Nitrophenyl)-4-hydroxy-tetrahydropyran (8q).** FTIR(film): 3368, 1599, 1516, 1343, 1247, 1138, 1073, 984, 850, 747, 696, 587 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=8.19 (d, J=8.2 Hz, 2H), 7.50 (d, J=8.2 Hz, 2H), 4.42 (dd, J=11.4, 1.8 Hz, 1H), 4.20 (ddd, J=11.7, 4.7, 1.2 Hz, 1H), 3.95 (tt, J=10.9, 4.7 Hz, 1H), 3.59 (dt, J=12.0, 2.1 Hz, 1H), 2.21 (m, 1H), 2.07 (br s, OH, 1H), 1.99 (m, 1H), 1.65 (m, 1H), 1.44 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=149.4, 147.2, 126.4, 123.7, 77.2, 68.0, 66.4, 43.3, 35.3; GC/MS: *m*/*z* (% base peak) 205 (M^+−OH, 69), 188 (37), 150 (70), 107 (62), 77 (83), 57 (51), 44 (100); Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87. Found: C, 59.46; H, 6.26.

***cis*-2-Phenyl-4-(3-butenoxy)-tetrahydropyran (9a).** FTIR-(film): 1490, 1445, 1352, 1330, 1304, 1260, 1211, 1163. 1144, 1100, 1081, 1037, 1022, 988, 955, 906, 884, 806 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.40–7.27 (m, 5H), 5.86 (m, 1H), 5.13–5.02 (m, 2H), 4.32 (dd, J=11.5, 2.1 Hz, 1H), 4.20 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 3.63 (m, 1H), 3.59 (t, J=6.8 Hz, 2H), 3.56 (m, 1H), 2.37 (q, J=6.8 Hz, 2H), 2.26 (m, 1H), 2.02 (m, 1H), 1.65 (m, 1H), 1.57 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=142.2, 135.3, 128.4, 127.6, 126.0, 116.4, 78.6, 75.5, 67.1, 66.5, 40.4, 34.6, 32.7; GC/MS: *m*/*z* (% base peak) 233 (M^++1, 2), 232 (M^+, 10), 177 (M^+−C_4H_7, 1), 161 (M^+−C_4H_7O, 16), 160(63), 159 (52), 131 (33), 117 (4), 105 (38), 91 (13), 77 (Ph^+, 15), 71 ($C_4H_7O^+$, 3), 55 ($C_4H_7^+$, 100), 43 (10), 41 (10), 39 (13); Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.93; H, 8.43.

***cis*-2-(2-Fluorophenyl)-4-(3-butenoxy)-tetrahydropyran (9b).** FTIR(film): 1695, 1641, 1582, 1489, 1455, 1362, 1254, 1224, 1141, 1077, 1018, 989, 905, 812, 792, 748 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.49 (m, 1H), 7.23 (m, 1H), 7.14 (m, 1H), 7.01 (m, 1H), 5.83 (m, 1H), 5.12–5.02 (m, 2H), 4.65 (dd, J=11.5, 2.0 Hz, 1H), 4.18 (ddd, J=11.7, 4.7, 1.5 Hz, 1H), 3.64 (m, 1H), 3.59 (m,

1H), 3.56 (t, *J*=6.7 Hz, 2H), 2.35 (q, *J*=6.7 Hz, 2H), 2.26 (m, 1H), 2.01 (m, 1H), 1.65 (m, 1H), 1.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=160.5, 158.0, 135.2, 129.4, 129,3, 128.9, 128.8, 127.3, 127.3, 124.4, 124.3, 116.4, 115.2, 115.0, 75.2, 72.1, 67.1, 66.6, 39.4, 34.5, 32.7; GC/MS: *m*/*z* (% base peak) 251 (M^++1, 5), 250 (M^+, 29), 232 (M^+−F, 1), 178 (15), 177 ($M^+-C_4H_7$–F, 100), 149 (8), 125 (5), 124 (10), 123 (23), 112 (5), 109 (5), 98 (20), 97 (5), 83 (9), 77 (Ph^+, 3), 71 ($C_4H_7O^+$, 5), 70 (12), 55 ($C_4H_7^+$, 26), 43 (15), 41 (13), 39 (6); Anal. Calcd for $C_{15}H_{19}O_2F$: C, 71.98; H, 7.65. Found: C, 71.60; H, 7.97.

***cis*-2-(3-Fluorophenyl)-4-(3-butenoxy)-tetrahydropyran (9c).** FTIR(film): 1636, 1612, 1587, 1484, 1440, 1361, 1254, 1175, 1136, 1106, 1082, 1023, 994, 949, 915, 871, 783, 763, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.28 (m, 1H), 7.09 (m, 2H), 6.95 (m, 1H), 5.82 (m, 1H), 5.12-5.02 (m, 2H), 4.30 (dd, *J*=11.7, 2.1 Hz, 1H), 4.18 (ddd, *J*=11.7, 4.7, 1.5 Hz, 1H), 3.61 (m, 1H), 3.55 (t, *J*=6.8 Hz, 2H), 3.52 (m, 1H), 2.33 (q, *J*=6.8 Hz, 2H), 2.23 (m, 1H), 2.00 (m, 1H), 1.62 (m, 1H), 1.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=164.1, 161.7, 144.8, 144.8, 135.2, 129.9, 129.8, 121.4, 121.4, 116.4, 114.4, 114.2, 113.0, 112.8, 77.8, 75.3, 67.1, 66.5, 40.3, 34.5, 32.5; GC/MS: *m*/*z* (% base peak) 250 (M^+, 2), 195 ($M^+-C_4H_7$, 1), 179 ($M^+-C_4H_7O$, 34), 178 (50), 177 ($M^+-C_4H_7$–F, 35), 163 (4), 150 (8), 149 (52), 125 (8), 124 (9), 123 (28), 112 (11), 109 (16), 98 (1), 97 (5), 87 (10), 83 (4), 77 (Ph^+, 2), 71 ($C_4H_7O^+$, 2), 70 (5), 55 ($C_4H_7^+$, 100), 53 (6), 43 (3), 41 (7), 39 (11); Anal. Calcd for $C_{15}H_{19}O_2F$: C, 71.98; H, 7.65. Found: C, 72.72; H, 8.01.

***cis*-2-(4-Fluorophenyl)-4-(3-butenoxy)-tetrahydropyran (9d).** FTIR(film): 1636, 1597, 1509, 1411, 1362, 1219, 1151, 1106, 1082, 1023, 999, 910, 832, 778 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.32 (d, *J*=8.5 Hz, 2H), 7.02 (d, *J*=8.5 Hz, 2H), 5.82 (m, 1H), 5.12–5.02 (m, 2H), 4.28 (dd, *J*=11.7, 2.0 Hz, 1H), 4.17 (ddd, *J*=11.7, 4.7, 1.5 Hz, 1H), 3.61 (m, 1H), 3.55 (t, *J*=6.8 Hz, 2H), 3.52 (m, 1H), 2.33 (q, *J*=6.8 Hz, 2H), 2.20 (m, 1H), 2.01 (m, 1H), 1.61 (m, 1H), 1.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=163.4, 161.0, 137.9, 137.9, 135.2, 127.7, 127.6, 116.4, 115.3, 115.1, 77.9, 75.4, 67.1, 66.5, 40.3, 34.5, 32.5; GC/MS: *m*/*z* (% base peak) 250 (M^+, 2), 249 (M^+−1, 1), 195 ($M^+-C_4H_7$, 1), 179 ($M^+-C_4H_7O$, 29), 178 (100), 177 ($M^+-C_4H_7$–F, 29), 163 (5), 150 (9), 149 (35), 135 (5), 125 (13), 124 (10), 123 (40), 122(14), 109 (15), 97 (5), 96 (5), 95 (7), 87 (4), 83 (4), 77 (Ph^+, 3), 71 ($C_4H_7O^+$, 1), 70 (5), 55 ($C_4H_7^+$, 78), 54 (8), 53 (5), 43 (3), 41 (6), 39 (11); Anal. Calcd for $C_{15}H_{19}O_2F$: C, 71.98; H, 7.65. Found: C, 71.90; H, 7.87.

***cis*-2-(2-Chlorophenyl)-4-(3-butenoxy)-tetrahydropyran (9e).** FTIR(film): 1636, 1568, 1469, 1435, 1357, 1249, 1205, 1146, 1106, 1082, 1053, 1028, 989, 954, 910, 807, 753, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.55 (dd, *J*=7.6, 1.8 Hz, 1H), 7.34–7.17 (m, 3H), 5.82 (m, 1H), 5.12–5.01 (m, 2H), 4.70 (dd, *J*=11.7, 2.0 Hz, 1H), 4.20 (ddd, *J*=11.7, 4.7, 1.5 Hz, 1H), 3.65 (m, 1H), 3.60 (m, 1H), 3.56 (t, *J*=6.8 Hz, 2H), 2.38 (m, 1H), 2.33 (q, *J*=6.8 Hz, 2H), 2.01 (m, 1H), 1.64 (m, 1H), 1.32 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=139.8, 135.2, 131.3, 129.2, 128.5, 127.2, 127.2, 116.4, 75.2, 75.1, 67.1, 66.5, 38.9, 34.5, 32.7; GC/MS: *m*/*z* (% base peak) 268 (^{37}Cl M^+, 14), 267 (7), 266 (^{35}Cl M^+, 41), 231 (M^+−Cl, 3), 221 (4), 196 (5), 195 ($M^+-C_4H_7O$, 35), 194 (14), 193 (100), 177 ($M^+-C_4H_7$–Cl, 1), 163 (1), 141 (11), 140 (12), 139 (19), 138 (7), 128 (7), 127 (5), 125 (3), 112 (13), 111 (8), 110 (3), 105 (3), 99 (4), 98 (29), 97 (3), 83 (10), 77 (Ph^+, 7), 71 ($C_4H_7O^+$, 6), 70 (11), 56 (8), 55 ($C_4H_7^+$, 21), 54 (2), 53 (5), 43 (16), 42 (9), 41 (13), 39 (5); Anal. Calcd for $C_{15}H_{19}O_2Cl$: C, 67.54; H, 7.18. Found: C, 67.02; H, 7.19.

***cis*-2-(3-Chlorophenyl)-4-(3-butenoxy)-tetrahydropyran (9f).** FTIR(film): 1641, 1597, 1573, 1474, 1425, 1362, 1244, 1205, 1146, 1106, 1082, 1028, 989, 910, 778, 709, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.36 (s, 1H), 7.28–7.20 (m, 3H), 5.82 (m, 1H), 5.12–5.02 (m, 2H), 4.27 (dd, *J*=11.7, 1.8 Hz, 1H), 4.17 (ddd, *J*=12.0, 5.0, 1.8 Hz, 1H), 3.60 (m, 1H), 3.55 (t, *J*=7.0 Hz, 2H), 3.52 (m, 1H), 2.32 (q, *J*=7.0 Hz, 2H), 2.22 (m, 1H), 2.00 (m, 1H), 1.61 (m, 1H), 1.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=144.2, 135.2, 134.3, 129.7, 127.7, 126.2, 124.0, 116.5, 77.7, 75.3, 67.1, 66.5, 40.3, 34.5, 32.5; GC/MS: *m*/*z* (% base peak) 269 (^{37}Cl M^++1, 4), 268 (^{37}Cl M^+, 11), 267 (9), 266 (^{35}Cl M^+, 34), 196 (4), 195 ($M^+-C_4H_7O$, 37), 194 (17), 193 (100), 175 (M^+, 4), 165 (12), 143 (5), 142 (9), 141 (9), 140 (15), 139 (16), 138 (10), 131(8), 128 (7), 127 (6), 125 (4), 112 (9), 111 (10), 110 (4), 105 (5), 103 (7), 98 (25), 97 (6), 83 (11), 81 (10), 77 (Ph^+, 8), 71 ($C_4H_7O^+$, 6), 70 (13), 69 (24), 67 (11), 56 (11), 55 ($C_4H_7^+$, 48), 54 (8), 53 (11), 43 (23), 42 (16), 41 (24), 39 (12), 38 (17); Anal. Calcd for $C_{15}H_{19}O_2Cl$: C, 67.54; H, 7.18. Found: C, 67.40; H, 7.19.

***cis*-2-(4-Chlorophenyl)-4-(3-butenoxy)-tetrahydropyran (9g).** FTIR(film): 1636, 1489, 1361, 1244, 1151, 1106, 1082, 1008, 989, 910, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.31 (d, *J*=8.5 Hz, 2H), 7.27 (d, *J*=8.5 Hz, 2H), 5.81 (m, 1H), 5.12–5.02 (m, 2H), 4.28 (dd, *J*=11.7, 2.1 Hz, 1H), 4.17 (ddd, *J*=11.7, 5.0, 1.8 Hz, 1H), 3.59 (m, 1H), 3.55 (t, *J*=6.8 Hz, 2H), 3.53 (m, 1H), 2.32 (q, *J*=6.8 Hz, 2H), 2.20 (m, 1H), 2.00 (m, 1H), 1.60 (m, 1H), 1.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=140.7, 135.2, 133.2, 128.5, 127.3, 116.5, 77.8, 75.3, 67.1, 66.5, 40.3, 34.5, 32.5; GC/MS: *m*/*z* (% base peak) 269 (^{37}Cl M^++1, 1), 268 (^{37}Cl M^+, 6), 267 (3), 266 (^{35}Cl M^+, 20), 231 (M^+−Cl, 1), 196 (6), 195 ($M^+-C_4H_7O$, 37), 194 (17), 193 (100), 175 (M^+, 1), 165 (2), 143 (1), 142 (3), 141 (8), 140 (10), 139 (17), 138 (6), 131(1), 128 (3), 127 (3), 125 (4), 112 (4), 111 (8), 109 (3), 105 (2), 103 (4), 98 (15), 97 (2), 83 (7), 81 (5), 77 (Ph^+, 7), 71 ($C_4H_7O^+$, 4), 70 (9), 69 (5), 67 (6), 56 (9), 55 ($C_4H_7^+$, 28), 54 (6), 53 (6), 43 (19), 42 (13), 41 (17), 39 (9); Anal. Calcd for $C_{15}H_{19}O_2Cl$: C, 67.54; H, 7.18. Found: C, 67.38; H, 7.13.

***cis*-2-(3,4-Dichlorophenyl)-4-(3-butenoxy)-tetrahydropyran (9h).** FTIR(film): 1720, 1639, 1469, 1356, 1244, 1158, 1145, 1127, 1110, 1087, 1024, 993, 961, 916, 899, 818, 759, 732, 701, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.45 (s, 1H), 7.39 (d, *J*=8.5 Hz, 1H), 7.15 (dd, *J*=8.5, 1.8 Hz, 1H), 5.81 (m, 1H), 5.11–5.02 (m, 2H), 4.25 (dd, *J*=11.7, 2.0 Hz, 1H), 4.16 (ddd, *J*=11.7, 4.7, 1.5 Hz, 1H), 3.59 (m, 1H), 3.54 (t, *J*=6.8 Hz, 2H), 3.50 (m, 1H), 2.30 (q, *J*=6.8 Hz, 2H), 2.20 (m, 1H), 2.00 (m, 1H), 1.58 (m, 1H), 1.43 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=142.5, 135.1, 132.4, 131.3, 130.3, 128.0, 125.2, 116.5,

77.4, 75.1, 67.2, 66.5, 40.3, 34.5, 32.4; GC/MS: *m/z* (% base peak) 302 (^{37}Cl M^+, 14), 301 (^{35}Cl M^++1, 4), 300 (^{35}Cl M^+, 23), 231 (11), 230 (M^+−2Cl, 10), 229 (M^+−C_4H_7O, 67), 228 (17), 227 (100), 175 (10), 174 (10), 173 (13), 172 (4), 112 (6), 111 (8), 98 (26), 97 (4), 83 (12), 81 (6), 77 (Ph^+, 2), 75 (4), 71 ($C_4H_7O^+$, 10), 70 (15), 55 ($C_4H_7^+$, 48), 43 (29), 42 (19), 41 (26), 39 (10); Anal. Calcd for $C_{15}H_{18}O_2Cl_2$: C, 59.82; H, 6.02. Found: C, 59.46; H, 5.80.

***cis*-2-(3-Bromophenyl)-4-(3-butenoxy)-tetrahydropyran (9i).** FTIR(film): 1634, 1594, 1563, 1470, 1422, 1359, 1249, 1200, 1164, 1147, 1107, 1080, 1023, 991, 960, 912, 885, 845, 810, 779, 694, 681 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.52 (s, 1H), 7.38 (d, *J*=7.6 Hz, 1H), 7.25 (d, *J*=7.6 Hz, 1H), 7.18 (t, *J*=7.6 Hz, 1H), 5.82 (m, 1H), 5.11–5.02 (m, 2H), 4.26 (dd, *J*=11.7, 2.1 Hz, 1H), 4.16 (ddd, *J*=11.7, 4.7, 1.5 Hz, 1H), 3.59 (m, 1H), 3.54 (t, *J*=6.7 Hz, 2H), 3.50 (m, 1H), 2.32 (q, *J*=6.7 Hz, 2H), 2.22 (m, 1H), 1.99 (m, 1H), 1.59 (m, 1H), 1.46 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=144.5, 135.2, 130.6, 130.0, 129.1, 124.5, 122.5, 116.5, 77.6, 75.2, 67.1, 66.5, 40.3, 34.5, 32.5; GC/MS: *m/z* (% base peak) 312 (^{81}Br M^+, 2), 311 (1), 310 (^{79}Br M^+, 2), 241 (^{79}Br M^+−C_4H_7, 17), 240 (23), 239 (31), 238 (21), 237 (16), 211 (17), 209 (17), 185 (12), 184 (7), 182 (10), 159 (11), 131 (5), 130 (8), 127 (7), 87 (14), 77 (Ph^+, 8), 71 ($C_4H_7O^+$, 4), 55 ($C_4H_7^+$, 100), 54 (8), 43 (3), 41 (5), 39 (9); Anal. Calcd for $C_{15}H_{19}O_2Br$: C, 57.89; H, 6.15. Found: C, 58.01; H, 6.27.

***cis*-2-(2-Methylphenyl)-4-(3-butenoxy)-tetrahydropyran (9j).** FTIR(film): 1639, 1487, 1460, 1442, 1428, 1357, 1249, 1222, 1163, 1141, 1105, 1078, 1020, 988, 957, 912, 809, 750, 719, 638 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.48 (m, 1H), 7.26–7.15 (m, 3H), 5.85 (m, 1H), 5.16–5.02 (m, 2H), 4.50 (dd, *J*=11.4, 1.8 Hz, 1H), 4.21 (ddd, *J*=11.7, 4.7, 1.2 Hz, 1H), 3.66 (m, 1H), 3.59 (t, *J*=6.8 Hz, 2H), 3.57 (m, 1H), 2.38 (q, *J*=6.8 Hz, 2H), 2.37 (s, 3H), 2.22 (m, 1H), 2.05 (m, 1H), 1.68 (m, 1H), 1.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=140.0, 135.3, 134.5, 130.3, 127.4, 126.3, 125.7, 116.5, 75.7, 75.4, 67.1, 66.6, 38.9, 34.6, 32.7, 19.1; GC/MS: *m/z* (% base peak) 247 (M^++1, 1), 246 (M^+, 3), 245 (M^+−1, 1), 231 (M^+−CH_3, 1), 205 (15), 175 (M^+−C_4H_7O, 25), 174 (83), 173 (19), 160 (5), 159 (M^+−C_4H_7O–CH_3, 35), 146 (12), 145 (32), 131 (7), 129 (16), 121 (15), 120 (15), 119 (36), 118 (10), 117 (10), 111 (6), 105 (13), 93 (8), 91 (18), 87 (6), 81 (7), 77 (Ph^+, 6), 71 ($C_4H_7O^+$, 4), 55 ($C_4H_7^+$, 100), 54 (10), 43 (5), 41 (6), 39 (11); Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.93; H, 9.37.

***cis*-2-(3-Methylphenyl)-4-(3-butenoxy)-tetrahydropyran (9k).** FTIR(film): 1636, 1605, 1484, 1439, 1359, 1252, 1171, 1144, 1109, 1082, 1028, 992, 956, 912, 885, 782, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.26–7.20 (m, 2H), 7.15–7.09 (m, 2H), 5.83 (m, 1H), 5.13–5.03 (m, 2H), 4.28 (dd, *J*=11.4, 1.8 Hz, 1H), 4.19 (ddd, *J*=11.7, 4.7, 1.5 Hz, 1H), 3.61 (m, 1H), 3.57 (t, *J*=7.0 Hz, 2H), 3.54 (m, 1H), 2.36 (s, 3H), 2.34 (q, *J*=7.0 Hz, 2H), 2.23 (m, 1H), 2.01 (m, 1H), 1.65 (m, 1H), 1.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=142.0, 138.1, 135.2, 128.4, 128.3, 126.7, 123.1, 116.4, 78.7, 75.5, 67.1, 66.6, 40.2, 34.5, 32.7, 21.5; GC/MS: *m/z* (% base peak) 247 (M^++1, 1), 246 (M^+, 7), 245 (M^+−1, 1), 231 (M^+−CH_3, 1), 175 (M^+−C_4H_7O, 27), 174 (100), 173 (33), 160 (4), 159 (M^+−C_4H_7O–CH_3, 33), 146 (7), 145 (33), 131 (8), 121 (13), 120 (11), 119 (42), 118 (11), 117 (8), 115 (5), 105 (13), 91 (CH_3Ph^+, 17), 77 (Ph^+, 5), 71 ($C_4H_7O^+$, 2), 55 ($C_4H_7^+$, 75), 43 (3), 41 (6), 39 (10); Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.67; H, 9.18.

***cis*-2-(4-Methylphenyl)-4-(3-butenoxy)-tetrahydropyran (9l).** FTIR(film): 1637, 1541, 1439, 1365, 1308, 1246, 1162, 1145, 1110, 1083, 1022, 991, 960, 912, 890, 815, 767, 714 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.26 (d, *J*=8.2 Hz, 2H), 7.17 (d, *J*=8.2 Hz, 2H), 5.86 (m, 1H), 5.16-5.05 (m, 2H), 4.30 (dd, *J*=11.4, 1.8 Hz, 1H), 4.20 (ddd, *J*=11.7, 4.7, 1.8 Hz, 1H), 3.63 (m, 1H), 3.58 (t, *J*=7.0 Hz, 2H), 3.55 (m, 1H), 2.37 (q, *J*=7.0 Hz, 2H), 2.36 (s, 3H), 2.24 (m, 1H), 2.01 (m, 1H), 1.66 (m, 1H), 1.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=139.2, 137.2, 135.3, 129.1, 126.0, 116.4, 78.5, 75.6, 67.1, 66.5, 40.3, 34.6, 32.7, 21.2; GC/MS: *m/z* (% base peak) 247 (M^++1, 2), 246 (M^+, 10), 245 (M^+−1, 1), 175 (M^+−C_4H_7O, 24), 174 (100), 173 (32), 160 (7), 159 (M^+−C_4H_7O–CH_3, 51), 146 (7), 145 (25), 131 (7), 121 (18), 120 (12), 119 (49), 118 (11), 117 (8), 115 (4), 105 (13), 91 (CH_3Ph^+, 16), 77 (Ph^+, 5), 71 ($C_4H_7O^+$, 2), 70 (5), 55 ($C_4H_7^+$, 79), 43 (4), 41 (6), 39 (9); Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.25; H, 8.95.

***cis*-2-(4-Ethylphenyl)-4-(3-butenoxy)-tetrahydropyran (9m).** FTIR(film): 1712, 1642, 1514, 1457, 1444, 1413, 1365, 1246, 1158, 1145, 1105, 1083, 1021, 991, 956, 912, 890, 824 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=7.29 (d, *J*=8.2 Hz, 2H), 7.25 (d, *J*=8.2 Hz, 2H), 5.84 (m, 1H), 5.14–5.04 (m, 2H), 4.30 (dd, *J*=11.5, 1.8 Hz, 1H), 4.19 (ddd, *J*=11.7, 4.7, 1.5 Hz, 1H), 3.63 (m, 1H), 3.57 (t, *J*=6.8 Hz, 2H), 3.55 (m, 1H), 2.65 (q, *J*=7.6 Hz, 2H), 2.38 (q, *J*=6.8 Hz, 2H), 2.25 (m, 1H), 2.03 (m, 1H), 1.67 (m, 1H), 1.58 (m, 1H), 1.26 (t, *J*=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=143.7, 139.4, 135.2, 127.9, 126.1, 116.4, 78.5, 75.6, 67.1, 66.5, 40.2, 34.5, 32.7, 28.6, 15.7; GC/MS: *m/z* (% base peak) 261 (M^++1, 2), 260 (M^+, 12), 259 (M^+−1, 2), 231 (M^+−C_2H_5, 5), 189 (M^+−C_4H_7O, 27), 188 (100), 173 (5), 160 (M^+−C_4H_7O–C_2H_5, 17), 159 (100), 145 (4), 135 (18), 134 (13), 133 (50), 131 (10), 119 (12), 117 (15), 115 (5), 105 (13), 103 (5), 91 (14), 79 (13), 77 (Ph^+, 8), 71 ($C_4H_7O^+$, 3), 70 (5), 55 ($C_4H_7^+$, 84), 54 (9), 43 (4), 41 (6), 39 (9); Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.41; H, 9.40.

***cis*-2-(1-Naphthyl)-4-(3-butenoxy)-tetrahydropyran (9n).** FTIR(film): 1637, 1593, 1505, 1444, 1426, 1356, 1250, 1233, 1176, 1140, 1110, 1079, 1053, 1017, 987, 912, 855, 798, 771, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=8.10 (d, *J*=8.2 Hz, 1H), 7.89 (d, *J*=7.9 Hz, 1H), 7.81 (d, *J*=7.9 Hz, 1H), 7.68 (d, *J*=7.0 Hz, 1H), 7.57–7.49 (m, 3H), 5.87 (m, 1H), 5.17–5.07 (m, 2H), 5.06 (dd, *J*=11.4, 1.2 Hz, 1H), 4.31 (ddd, *J*=11.7, 4.7, 1.2 Hz, 1H), 3.76 (m, 1H), 3.72 (m, 1H), 3.60 (t, *J*=6.7 Hz, 2H), 2.46 (m, 1H), 2.38 (q, *J*=6.7 Hz, 2H), 2.11 (m, 1H), 1.82 (m, 1H), 1.77 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=137.7, 135.3, 133.9, 130.5, 129.0, 128.2, 126.1, 125.7, 125.5, 123.4, 123.4, 116.5, 75.7, 75.6, 67.2, 66.8, 39.4, 34.7, 32.9; GC/MS: *m/z* (% base peak) 283 (M^++1, 12), 282 (M^+, 59), 281 (M^+−1, 2), 211 (M^+−C_4H_7O, 21), 210 (81), 209 (80), 182

(12), 181 (18), 167 (7), 166 (5), 157 (12), 156 (23), 155 (40), 154 (13), 153 (17), 152 (7), 141 (16), 129 (13), 128 (31), 127 (15), 83 (9), 77 (Ph^+, 3), 71 ($C_4H_7O^+$, 4), 55 ($C_4H_7^+$, 100), 54 (10), 53 (6), 43 (6), 41 (5), 39 (8); Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.71; H, 7.73.

***cis*-2-*t*-Butyl-4-(3-butenoxy)-tetrahydropyran (9o).** FTIR-(film): 2955, 2852, 1645, 1467, 1359, 1166, 1142, 1113, 1093, 1058, 999, 911 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=5.85 (m, 1H), 5.07 (m, 2H), 4.06 (ddd, J=12.9, 5.0, 1.5 Hz, 1H), 3.60-3.30 (m, 4H), 2.87 (dd, J=11.4, 1.2 Hz, 1H), 2.35 (m, 2H), 2.01–1.91 (m, 2H), 1.43 (m, 1H), 1.20 (m, 1H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=135.3, 116.4, 84.3, 76.2, 67.0, 66.2, 34.6, 34.0, 32.9, 32.8, 26.1; GC/MS: *m*/*z* (% base peak) 157 ($M^+-C_4H_7$, 16), 155 ($M^+-C_4H_9$, 16), 141 (20), 85 (100), 57 (48), 55 (92), 41 (52); Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 74.02; H, 11.01.

***cis*-2-*n*-Pentyl-4-(3-butenoxy)-tetrahydropyran (9p).** FTIR(film): 3072, 2936, 2854, 1639, 1459, 1355, 1252, 1154, 1104, 1083, 990, 914, 865, 625 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=5.84 (m, J=7.0 Hz, 1H), 5.07 (m, 2H), 4.03 (ddd, J=11.7, 5.0, 1.8 Hz, 1H), 3.53 (dt, J=12.0, 2.1 Hz, 2H), 3.41 (m, 2H), 3.23 (m, 1H), 2.33 (q, J=6.8 Hz, 2H), 1.98 (m, 1H), 1.91 (m, 1H), 1.57–1.14 (m, 10), 0.90 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=135.3, 116.3, 76.4, 75.4, 67.0, 66.0, 38.5, 36.0, 34.5, 32.8, 31.6, 27.7, 22.7, 14.1; GC/MS: *m*/*z* (% base peak) 171 ($M^+-C_4H_7$, 0.4), 170 (0.6), 155 (5), 141 (31), 111 (10), 85 (15), 69 (18), 55 (100), 41 (49); Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 73.90; H, 11.52.

***cis*-2-(4-Nitrophenyl)-2,3-dihydropyran (9q).** FTIR(film): 3035, 2932, 2894, 2829, 1599, 1516, 1343, 1234, 1176, 1086, 1022, 920, 843, 741, 690, 657, 517 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ=8.20 (d, J=8.2 Hz, 2H), 7.50 (d, J=8.2 Hz, 2H), 5.92 (m, 1H), 5.85 (m, 1H), 4.66 (dd, J=10, 4.4 Hz, 1H), 4.39 (m, 2H), 2.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=150.1, 147.2, 126.5, 126.4, 123.8, 123.6, 74.5, 66.5, 32.9; GC/MS: *m*/*z* (% base peak) 205 (M^+, 5), 150 (3), 128 (4), 116 (2), 91 (3), 77 (10), 54 (100), 39 (20); Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40. Found: C, 64.53; H, 5.44.

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