Supporting Information for Angew. Chem. Int. Ed. Z 17658

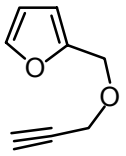
Pt^{II}-Catalyzed Intramolecular Reaction of Furans with Alkynes

Belén Martín-Matute, Diego J. Cárdenas, Antonio M. Echavarren*[a]

Experimental section

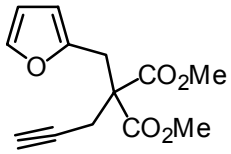
General remarks. The NMR determinations were carried out at 23°C. Only the most significant MS fragmentations are given. Elemental analyses were performed at the SIdI (UAM). All reactions were carried out under an atmosphere of Ar. Solvents were purified and dried by standard methods. Chromatographic purifications were carried out with flash grade silica gel.

Furfuryl Propargyl Ether (1)[1]



Furfuryl alcohol (1.600 g, 16.3 mmol) was added dropwise to a suspension of NaH (720 mg, 17.9 mmol; 60% in mineral oil) in DMF (20 mL) at 0°C. After being stirred for 10 min propargyl bromide (2.70 g, 17.9 mmol; 80% in toluene) was added and the mixture was stirred for 4 h at room temperature. Water (50 mL) was added and the product was extracted with Et_2O (3 x 60 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2, 10:1 hexane/EtOAc) to yield **1** (1.911 g, 86%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 1.2 Hz, 1H), 6.35-6.31 (m, 2H), 4.54 (s, 2H), 4.13 (d, J = 2.4 Hz, 2H), 2.45 (t, J = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 150.68 (C), 143.01 (CH), 110.24 (CH), 110.02 (CH), 79.20 (CH), 74.74 (C), 62.92 (CH_2), 56.61 (CH_2); HRMS-EI calculated for $C_8H_8O_2$: 136.0524; found: 136.0528.

Dimethyl 2-Furylmethylpropargylmalonate (4)



To a stirred suspension of NaH (106 mg, 2.65 mmol; 60% in mineral oil) in dry DMF (10 mL) was added dropwise dimethyl propargylmalonate (406 mg, 2.38 mmol) at 0°C. After being stirred for 10 min (2-furylmethyl)tetramethylenesulfonium

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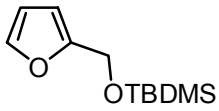
[1] a) H. J. Buttery, J. Moursounidis, D. Wege, Aust. J. Chem., **1995**, 48, 593; b) Y. Baba, T. Sakamoto, S. Soejima, K. Kanematsu, Tetrahedron, **1994**, 50, 5645; c) M. Tsubuki, T. Kamata, H. Okita, M. Arai, A. Shigihara, T. Honda, Chem. Commun., **1999**, 2263.

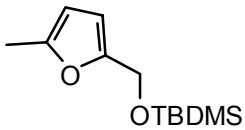
hexafluorophosphate[2] (1.0 g, 3.18 mmol) was added and the mixture was stirred for 15 h at room temperature. Water (20 mL) was added to the flask and the product was extracted with Et_2O (3 x 20 mL) and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2; 5:1 hexane/EtOAc) to yield **4** (400 mg, 67%) as a yellow oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 2.0 Hz, 1H), 6.26 (dd, J = 2.0, 3.2 Hz, 1H), 6.12 (d, J = 3.2 Hz, 1H), 3.75 (s, 6H), 3.44 (s, 2H), 2.75 (d, J = 2.8 Hz, 2H), 2.07 (t, J = 2.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 169.76 (C), 149.87 (C), 142.23 (C), 110.29 (CH), 108.73 (CH), 78.78 (CH), 71.70 (C), 56.81 (C), 52.93 (CH_3), 30.76 (CH_2), 22.70 (CH_2); FAB-MS m/z (%) 251 (M^++1, 16), 250 (M^+, 3), 221 (17), 207 (14).

2-(terc-Butyldimethylsilyloxymethyl)furan



A mixture of furfuryl alcohol (3.7 g, 37.8 mmol), t-butyldimethylsilylchloride (5.20 g, 34.4 mmol), pyridine (3.26 g, 41.3 mmol) and 4-dimethylaminopyridine (50 mg, 0.04 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 12 h at room temperature. The reaction mixture was washed with saturated aqueous NaCl solution (3 x 20 mL), dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2; 10:1 hexane/EtOAc) to yield 2-(terc-butyldimethylsilyloxymethyl)furan (5.48 g, 75 %) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, J = 0.8, 2.0 Hz, 1H), 6.32 (dd, J = 2.0, 3.2 Hz, 1H), 6.23 (dd, J = 0.8, 3.2 Hz, 1H), 4.65 (s, 2H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 154.23 (C), 142.03 (CH), 110.12 (CH), 107.18 (CH), 58.14 (CH_2), 25.86 (CH_3), 18.40 (C), -5.27 (CH_3); MS-EI m/z (%): 211.14 (M^+-1, 4), 171.07 (18), 155.05 (100), 81.04 (71), 75.0 (90).

2-(terc-Butyldimethylsilyloxymethyl)-5-methylfuran



To a stirred solution of 2-(terc-butyldimethylsilyloxymehtyl)furan (3.00 g, 14.0 mmol) in THF (25 mL) was added nBuLi (0.97 mL, 15.5 mmol; 2.5 M in hexanes) at -10°C. After 2 h, the mixture was cooled to -78°C and MeI (2.21 g, 15.5 mmol) was added. The reaction mixture was stirred at room temperature for 4 h and quenched with water. The product was extracted with Et_2O (3 x 30 mL) and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2; 10:1 hexane/EtOAc) to yield 2-(terc-butyldimethylsilyloxymethyl)-5-methylfuran (2.66 g, 84 %) as a yellowish oil: ^1H NMR (300 MHz, $CDCl_3$) δ 6.10 (d, J = 3.2 Hz, 1H), 5.88 (m, 1H), 4.58 (s, 2H), 2.28 (d, J = 0.8 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 152.43 (C), 151.77 (C), 108.13 (CH), 105.97 (CH), 58.17 (CH_2), 25.90

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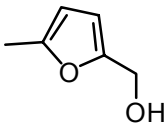
[2] S. Zhang, D. Marshall, L. S. Liebeskind, J. Org. Chem. **1999**, 64, 2729.

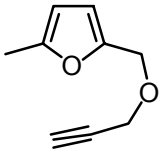
(CH_3), 18.44 (C), 13.55 (CH_3), -5.20 (CH_3); MS-EI m/z (%): 226.12 (M^+, 2), 195.10 (34), 169.06 (59), 95.05 (53), 75.02 (96), 73.04 (100).

2-(5-Methyl)furylmethanol[3]



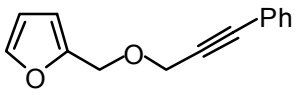
To a stirred solution of 2-(terc-butyldimehtylsilyloxymethyl)-5-methylfuran (2.10 g, 9.3 mmol) in THF (6 mL) was added tetrabutylammonium fluoride hydrate (2.7 g, 10.3 mmol) under argon atmosphere. After being stirred for 1 h water (15 mL) was added. The crude product was extracted with Et_2O (3 x 15 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. After column chromatography (SiO_2; 3:2 hexane/EtOAc) 2-(5-methyl)furylmethanol (999 mg, 96 %) was obtained as a yellowish oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.16 (d, J = 3.2 Hz, 1H), 5.91 (m, 1H), 4.53 (s, 2H), 2.28 (d, J = 1.2 Hz, 3H), 1.89 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 152.38 (C), 152.18 (C), 108.73 (CH), 106.17 (CH), 57.47 (CH_2), 13.52 (CH_3); MS-EI m/z (%): 226.12 (M^+, 27), 11.05 (21), 95.05 (100), 84.00 (16).

2-(5-Methyl)furylmethyl Propargyl Ether (7)



2-(5-Methyl)furylmethanol (620 mg, 5.53 mmol) was added dropwise to a suspension of NaH (244 mg, 6.08 mmol; 60% in mineral oil) in THF (20 mL) at 0°C. After 10 min, propargyl bromide (905 mg, 6.08 mmol; 80% in toluene) was added. The reaction mixture was stirred for 4 h at room temperature and then poured into water (50 mL). The product was extracted with Et_2O (3 x 50 mL), dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2, 10:1 hexane/EtOAc) to yield **7** (825 mg, 99%) as a yellow oil: ^{1}HNMR (300 MHz, $CDCl_3$) δ 6.24 (d, J = 3.2 Hz, 1H), 5.93-5.91 (m, 1H), 4.49 (s, 2H), 4.14 (d, J = 2.4 Hz, 2H), 2.46 (t, J = 2.4 Hz, 1H), 2.28 (d, J = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 152.97(C), 148.78 (C), 111.13 (CH), 106.20 (CH), 79.34 (CH), 74.65 (C), 63.11 (CH_2), 56.47 (CH_2), 13.55 (CH_3); MS-EI m/z (%): 150.09 (M^+, 13), 149.08 (31), 109.05 (32), 95.06 (100), 69.05 (65); HRMS-EI calculated for $C_9H_{10}O_2$: 150.0681; found: 150.0687.

Furfuryl 3-Phenylpropargyl Ether (11)



A solution of furfuryl propargyl ether (1.00 g, 7.35 mmol) in piperidine (25 mL) and PhI (1.50 g, 7.35 mmol) were added to a mixture of CuI (140 mg, .73 mmol) and $Pd(PPh_3)_4$ (425 mg, 0.37

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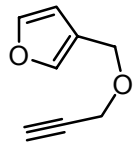
[3] M. Lautens, S. Kumanovic, J. Am. Chem. Soc. **1995**, 117, 1954.

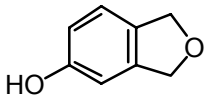
mmol). The reaction mixture was stirred for 15 h at room temperature. Water (25 mL) was added and the product was extracted with Et_2O (3 x 25 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2, 10:1 hexane/EtOAc) to yield **11** as a colourless oil (1.32 g, 85%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48-7.43 (m, 3H), 7.35-7.30 (m, 3H), 6.40 (d, J = 3.2 Hz, 1H), 6.36 (dd, J = 3.2, 1.6 Hz, 1H), 4.63 (s, 2H), 4.39 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 150.98 (C), 143.66 (CH), 131.77 (CH), 128.45 (CH), 128.26 (CH), 122.57 (C), 110.32 (CH), 109.99 (CH), 86.62 (C), 84.64 (C), 63.17 (CH_2), 57.59 (CH_2).

3-Furylmethyl Propargyl Ether (13)



3-Furylmethanol (1.500 g, 15.3 mmol) was added dropwise at 0°C to a stirred suspension of NaH (672 mg, 16.8 mmol; 60% in mineral oil) in THF (15 mL). After 10 min, propargyl bromide (2.50 g, 16.8 mmol; 80% in toluene) was added and the mixture was stirred for 5 h at room temperature. Water (20 mL) was added and the crude product was extracted with Et_2O (3 x 20 mL) and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography purification by column chromatography (SiO_2; 10:1 hexane/EtOAc) **13** was obtained as a colorless oil (1.35 g, 65%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.41 (m, 1H), 7.40 (d, J = 1.6 Hz, 1H), 6.43 (br s, 1H), 4.49 (s, 2H), 4.14 (d, J = 2.4 Hz, 2H), 2.46 (t, J = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 143.43 (CH), 141.14 (CH), 121.23 (C), 110.41 (CH), 79.48 (CH), 74.63 (C), 62.47 (CH_2), 56.59 (CH_2); HRMS-EI calculated for $C_8H_8O_2$: 136.0524; found: 136.0523.

Reaction of 1 with $PtCl_2$. A solution of **1** (50 mg, 0.36 mmol) in acetone (3 mL) was added to $PtCl_2$ (5 mg, 0.018 mmol). The reaction mixture was stirred for 16 h under reflux. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2; 3:1 hexane/EtOAc) to yield a mixture of **2** (22 mg, 44 %) and **3** (8 mg, 16%).



1,3-Dihydro-5-isobenzofuranol (2):[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, J = 8.1 Hz, 1H), 6.75 (dd, J = 2.4, 8.1 Hz, 1H), 6.71 (d, J = 2.4 Hz, 1H), 5.73 (br s, 1H), 5.08 (s, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$; DEPT) δ 155.53 (C), 140.69 (C), 130.66 (C), 121.79 (CH), 114.62 (CH), 107.93 (CH), 73.40 (CH_2), 73.21 (CH_2); HRMS-EI calculated for $C_8H_8O_2$: 135.0524; found: 136.0524.

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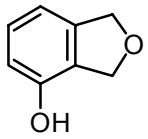
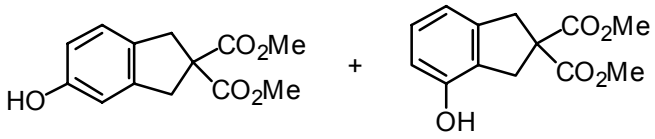
[4] D. R. Shridhar, C. V. R. Sastry, N. K. Vaidya, R. R. Moorty, G. S. Reddi, G. S. Thapar, S. K. Gupta, Indian J. Chem., Sect. B **1978**, 16B, 704-708.



1,3-Dihydro-4-isobenzofuranol (3): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (t, J = 7.7 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 6.66 (d, J 8.0 Hz, 1H), 5.37 (br s, 1H), 5.14-5.12 (m, 4H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$; DEPT) δ 150.15 (C), 141.56 (C), 129.12 (CH), 125.22 (C), 113.73 (CH), 113.23 (CH), 74.04 (CH_2), 71.67 (CH_2); HRMS-EI calculated for $C_8H_8O_2$: 135.0524; found: 136.0526.

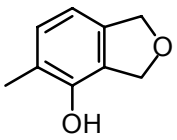
Reaction of 4 with $PtCl_2$



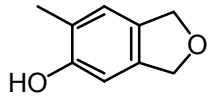
5 **6**

A solution of **4** (100 mg, 0.39 mmol) in acetone (3 mL) was added to $PtCl_2$ (5 mg, 0.02 mmol). The reaction mixture was stirred for 16 h under reflux. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2; 3:1 hexane/EtOAc) to yield 4:1 mixture of **5** and **6** as a yellow oil (80 mg, 79 %): ^{1}H NMR (300 MHz, $CDCl_3$) major isomer (**5**): δ 6.74 (d, J = 7.3 Hz, 1H), 6.62 (br s, 1H), 6.62- 2.58 (m, 1H), 5.80 (br s, 1H), 3.73 (s, 6H), 3.49 (s, 2H), 3.48 (s, 2H); minor isomer (**6**); δ 7.01 (t, J = 7.7 Hz, 1H), 6.74 (br d, J = 7.3 Hz, 1H), 6.59-6.56 (m, 1H), 5.8 (br s, 1H), 3.73 (s ,6H), 3.58 (s, 2H), 3.55 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) mixture of **5** and **6** δ 172.32 (C), 155.17 (C), 151.91 (C), 142.03 (C), 141.31 (C), 131.38 (CH), 128.56 (C), 125.61 (C), 124.86 (CH), 116.37 (CH), 114.17 (CH), 113.50 (CH), 111.16 (CH), 60.77 (C), 60.10 (C), 53.02 (CH_3), 40.83 (CH_2), 40.52 (CH_2), 39.71 (CH_2), 37.06 (CH_2) (two carbons are missing due to overlapping); HRMS-EI calculated for $C_{13}H_{14}O_5$: 250.0841; found: 250.0840.

Reaction of 7 with $PtCl_2$. A solution of **7**(100 mg, 0.66 mmol) in acetone (4 mL) was added to $PtCl_2$ (9 mg, 0.03 mmol). The reaction mixture was stirred for 16 h under reflux. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2; 3:1 hexane/EtOAc) to yield **8** (75 mg, 75%), along with traces of a second phenol tentatively assigned as 1,3-dihydro-6-methyl-5-isobenzofuranol.

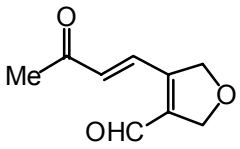


1,3-Dihydro-5-methyl-4-isobenzofuranol (8): m.p. 102-104°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, J = 7.4 Hz, 1H), 6.72 (d, J = 7.4 Hz, 1H), 5.13-5.09 (m, 4H), 4.70 (br s, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 148.17 (C), 139.32 (C), 130.45 (CH), 125.17 (C), 121.48 (C), 112.93 (CH), 73.97 (CH_2), 71.57 (CH_2), 15.01 (CH_3); Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.02; H, 6.69.

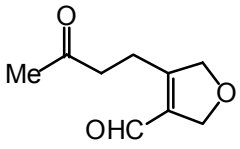


1,3-dihydro-6-methyl-5-isobenzofuranol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (S, 1H), 6.65 (s, 1H), 5.03 (br s, 4H), 4.87 (br s, 1H), 2.26 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$; DEPT) δ 153.36 (C), 138.11 (C), 130.97 (C), 122.99 (CH), 107,40 (CH), 73.37 (CH_2), 73.26 (CH_2), 15.95 (CH_3) (one carbon is missing due to overlapping).

Reaction of 7 with $PtCl_2$ in acetone/H_2O. A solution of **7** (200 mg, 1.33 mmol) in acetone (6 mL) and H_2O (1 mL) was added to $PtCl_2$ (18 mg, 0.66 mmol). The reaction mixture was heated under reflux for 16 h. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2; 5:1 hexane/EtOAc) to yield **8** (76 mg, 38%), aldehyde **9** (9.3 mg, 4%) and aldehyde **10** (21 mg, 10%).

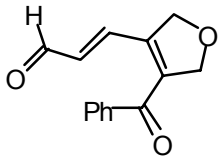


9: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.8 (d, J = 16.1 Hz, 1H), 6.21 (d, J = 16.1 Hz, 1H), 5.05-4.95 (m, 4H), 2.4 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 197.1 (C), 184.7 (CH), 148.3 (C), 141.9 (C), 133.2 (CH), 128.4 (CH), 75.77 (CH_2), 75.3 (CH_2), 28.5 (CH_3); HRMS-EI calculated for $C_9H_{10}O_3$:166.0630; found:166.0633.



10: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H), 4.83-4.70 (m, 4H), 2.85 (bt, J = 7.0 Hz, 2H), 2.64 (t, J = 7.0 Hz, 2H), 22.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 205.81 (C), 185.54 (CH), 157.18 (C), 134.45 (C), 78.45 (CH_2), 74.68 (CH_2), 41.13 (CH_2), 29.64 (CH_3), 18.99 (CH_2); HRMS-EI calculated for $C_9H_{12}O_3$:168.0786; found:168.0781.

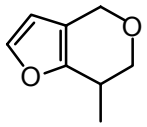
Reaction of 11 with $PtCl_2$



A solution of **11** (100 mg, 0.47 mmol) in acetone (5 mL) was added to $PtCl_2$ (6.3 mg, 0.02 mmol). The reacton mixture was stirred for 32 h under reflux. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2, 6:1 hexane/EtOAc) to yield ketoaldehyde **12** as a yellow solid (25 mg, 24%): m.p. 162-164°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.47 (d, J = 7.3 Hz, 1H), 7.46-7.41 (m, 3H), 7.21-7.14 (m, 3H), 6.30 (dd, J = 16.4, 7.4 Hz, 1H), 4.71 (s, 2H), 4.34 (s, 2H); ^{13} C NMR ($CDCl_3$,

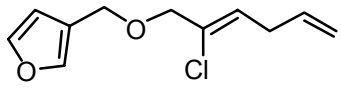
75 MHz; DEPT) δ 192.97 (C), 192.76 (CH), 145.79 (C), 145.35 (C), 132.79 (CH), 130.86 (C), 130.54 (CH), 129.18 (CH), 129.39 (CH), 72.33 (CH_2), 65.33 (CH_2) (one carbon is missing due to overlapping); FAB-HRMS calculated for the M^++1 peak: 229.0869, found 229.0863; Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.03; H, 5.38.

Synthesis of 16 by Pt-catalyzed reaction of 13 followed by hydrogenation



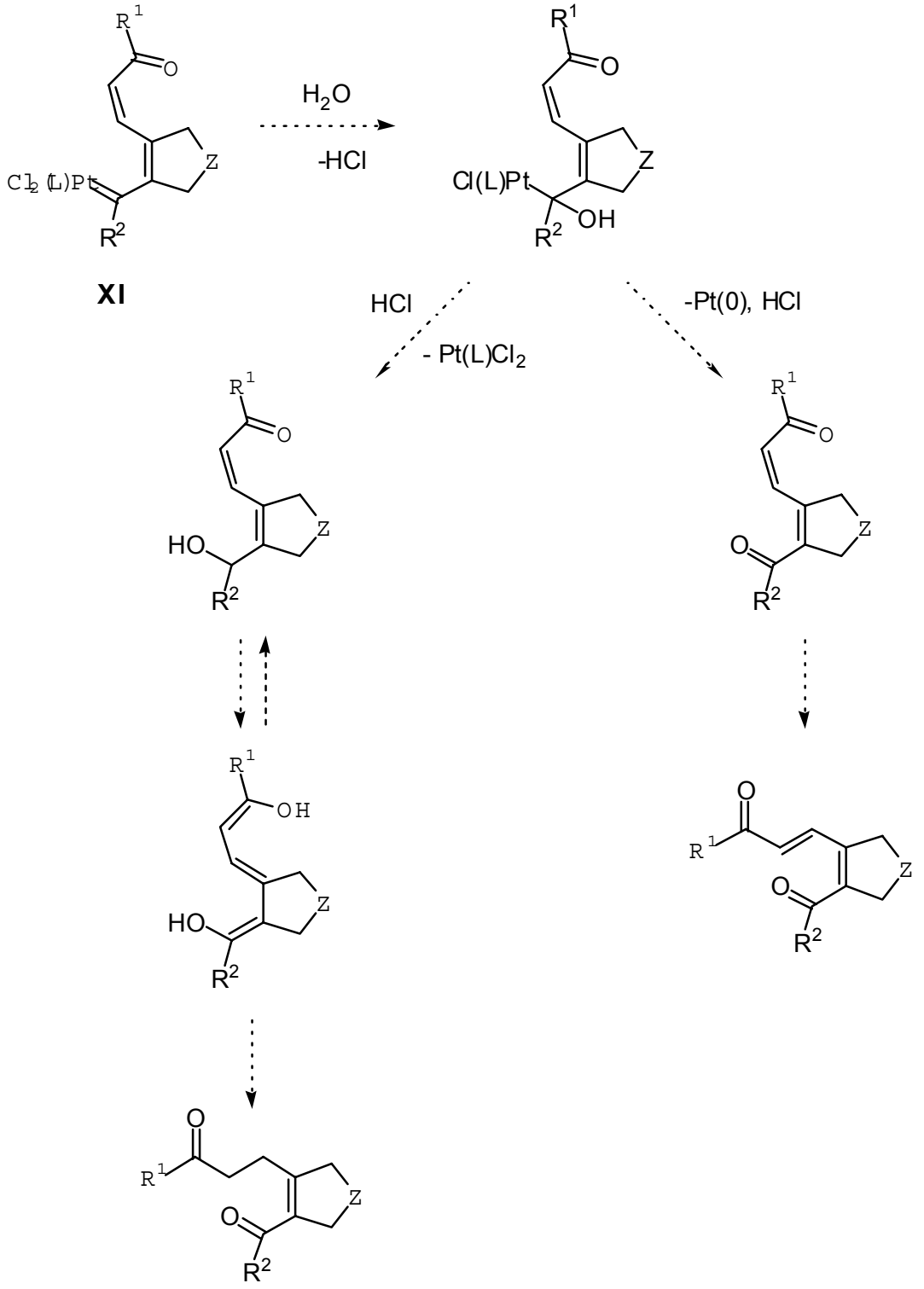
A solution of **13** (400 mg, 2.94 mmol) in Et_2O (10 mL) and an excess of allylchloride (1.6 mL) was added to $PtCl_2$ (160 mg, 0.6 mmol). The reaction mixture was stirred for 15 h at room temperature. The solid was filtered off and the filtrate was evaporated. After evaporation, 389 mg of a yellow oil was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) showed a mixture of **14** [δ 7.34 (d, J = 2.0 Hz, 1H), 6.27 (d, J = 2.0, 1H), 5.27 (br s, 1H), 4.80 (br s, 1H), 4.36 (t, J = 1.4 Hz, 2H)] and polymeric material. To a solution of this yellow oil in $CHCl_3$ (5 mL), 10% Pd/C (10 mg) was added, and the mixture was stirred under H_2 (1 atm) for 4 h. The catalyst was filtered off, and the solution was evaporated to give a yellow oil. The crude product was purified by column chromatography (SiO_2; 20:1 hexane/EtOAc) to yield **15** a colorless oil (139 mg, 34%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 2.0 Hz, 1H), 6.18 (d, J = 2.0 Hz, 1H), 4.58 (s, 1H), 4.57 (s, 1H), 4.00 (dd, J = 11.3, 4.8 Hz, 1H), 3.47 (dd, J = 11.3, 6.5 Hz, 1H), 3-04-2.93 (m, 1H), 1-20 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 151.96 (C), 141.00 (CH), 115.04 (C), 107.06 (CH), 71.59 (CH_2), 64.59 (CH_2), 30.04 (CH), 15.09 (CH_3).

Synthesis of 16 by Pd-catalyzed reaction of 14 with allylchloride.



A solution of **13** (50 mg, 0.36 mmol) in Et_2O (5 mL) and allyl chloride (55 mg, 0.72 mmol) was added to $Pd(MeCN)_2Cl_2$ (5 mg, 0.02 mmol). The reaction mixture was stirred for 16 h under reflux. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2; 10:1 hexane/EtOAc) to give **16** as a yellowish oil (24 mg, 32%): ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, C_6D_6) δ 7.04-7.02 (m, 1H), 6.99 (t, J = 1.6 Hz, 1H), 6.15 (dd, J = 1.6, 0.8 Hz, 1H), 5.65-5.51 (m, 1H), 5.55 (tt, J = 7.28, 1.2 Hz, 1H), 4.93 (dq, J = 16.9, 1.6 Hz, 1H), 4.87 (dq, J = 10.1, 1.6 Hz, 1H), 4.03 (d, J = 0.8 Hz, 2H), 3.75 (q, J = 1.2 Hz, 2H), 2.83-2.77 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6; DEPT) δ 143.51 (CH), 140.86 (CH), 134.86 (CH), 131.96 (C), 125.38 (CH), 122.48 (C), 115.84 (CH_2), 110.57 (CH), 72.84 (CH_2), 63.24 (CH_2), 32.59 (CH_2); the structure was confirmed by HMBC and HMQC experiments.

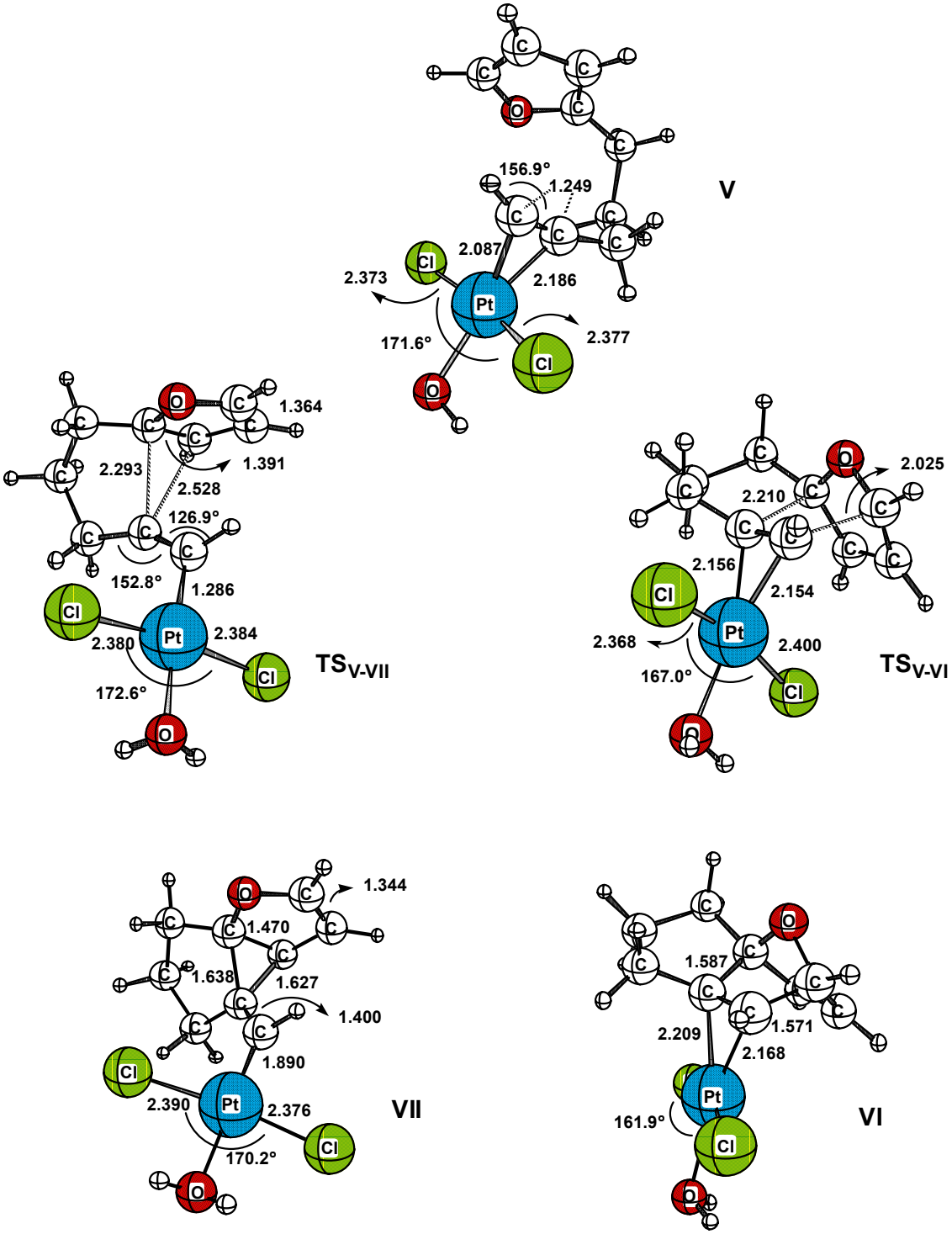
Mechanistic Hypothesis for the Formation of Dihydrofurans



The isomerization of intermediate **XVI** into the final α,β-unsaturated-1,6-dicarbonyl derivative **XVII** is a thermodinamically driven process [ΔH_{calc} = - 12.8 Kcal.mol^{-1} (R^1 = R^2 = H) or - 10.8 Kcal.mol^{-1} starting from the E isomer; PM3 calculations].

Isolation of (E)-isomers can be explained by the facile isomerization of the (Z)-isomers by a conjugate addition-elimination of water or other nucleophile.

Bond distances and angles for stationary points of Figure 1



Atomic coordinates for stationary points of Figure 1

Complex V

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	0.360574	2.115438	0.796990
2	78	0	1.330425	0.149973	-0.111810
3	17	0	2.557658	-1.767534	-0.793802
4	8	0	3.230636	0.940654	0.540043
5	6	0	-0.393766	-0.323478	-1.187995
6	6	0	-0.538508	-0.984473	-0.137617
7	6	0	-0.990105	-1.871339	0.946515
8	6	0	-1.933771	-1.191533	1.966907
9	6	0	-3.401535	-1.096242	1.495561
10	6	0	-3.605853	-0.330122	0.231005
11	6	0	-4.036266	-0.671784	-1.019946
12	6	0	-3.976041	0.521121	-1.815620
13	6	0	-3.514899	1.500131	-0.988545
14	8	0	-3.292218	1.000966	0.259421
15	1	0	3.801460	0.175405	0.744500
16	1	0	3.080174	1.460729	1.351443
17	1	0	-0.669461	0.095125	-2.136869
18	1	0	-0.105095	-2.266140	1.456035
19	1	0	-1.487621	-2.732944	0.478340
20	1	0	-1.551384	-0.193295	2.204090
21	1	0	-1.909335	-1.777721	2.893407
22	1	0	-3.990443	-0.642063	2.304060
23	1	0	-3.803341	-2.105845	1.344092
24	1	0	-4.358522	-1.654089	-1.337969
25	1	0	-4.248064	0.630952	-2.856368
26	1	0	-3.304328	2.550947	-1.115067

Transition state V-VI

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	0.491440	2.261611	-0.786527
2	78	0	1.038363	0.063662	0.006673
3	17	0	2.083748	-1.941860	0.708851
4	6	0	-0.902977	-0.872048	0.057570

5	6	0	-1.240562	-1.956298	-0.915484
6	6	0	-2.889704	0.085689	-0.089008
7	6	0	-0.605048	-0.496045	1.281174
8	6	0	-2.205956	0.574289	1.906295
9	6	0	-2.549099	1.459290	-0.111121
10	8	0	-3.039357	-0.297271	1.224681
11	6	0	-3.457496	-0.815677	-1.143201
12	6	0	-2.146273	1.786135	1.163548
13	6	0	-2.295400	-1.472362	-1.924148
14	1	0	-1.639646	-2.796467	-0.327966
15	1	0	-0.338327	-2.319622	-1.416144
16	1	0	-0.207662	-0.939928	2.183010
17	1	0	-2.236639	0.468182	2.984349
18	1	0	-2.481991	2.072047	-0.998527
19	1	0	-4.113176	-0.259393	-1.822252
20	1	0	-4.063093	-1.585458	-0.650912
21	1	0	-1.685666	2.706706	1.491799
22	1	0	-2.656440	-2.298549	-2.547633
23	1	0	-1.840311	-0.730520	-2.591875
24	8	0	2.998214	0.716257	-0.728499
25	1	0	2.905637	1.691140	-0.762259
26	1	0	3.671080	0.480727	-0.064821

Transition state V-VII

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	2.034943	2.126801	0.821533
2	78	0	1.398064	0.018689	-0.090501
3	17	0	1.030490	-2.190510	-0.896222
4	8	0	3.568179	-0.352719	-0.173331
5	6	0	-0.523632	0.533222	-0.088744
6	6	0	-1.296014	-0.225297	0.605775
7	6	0	-1.558825	-1.393030	1.469877
8	6	0	-3.037553	-1.848370	1.447672
9	6	0	-3.679716	-1.485761	0.103372
10	6	0	-3.450835	-0.032037	-0.153441
11	6	0	-3.460265	1.077944	0.685065
12	6	0	-3.377894	2.227147	-0.152524
13	6	0	-3.335341	1.752528	-1.430907

14	8	0	-3.404012	0.393839	-1.450426
15	1	0	3.718152	-1.221751	0.238746
16	1	0	3.897791	0.331741	0.443053
17	1	0	-0.810960	1.421263	-0.646542
18	1	0	-1.230491	-1.190755	2.496225
19	1	0	-0.913421	-2.182968	1.061032
20	1	0	-3.586458	-1.357809	2.260012
21	1	0	-3.102669	-2.924601	1.630137
22	1	0	-4.753685	-1.713619	0.114269
23	1	0	-3.230778	-2.058428	-0.715316
24	1	0	-3.547472	1.063831	1.762033
25	1	0	-3.328026	3.261509	0.155380
26	1	0	-3.266196	2.229831	-2.397066

Intermediate VI

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	0.046024	-2.162960	0.797882
2	78	0	-0.905266	-0.122900	-0.026967
3	17	0	-2.482880	1.525616	-0.718532
4	8	0	-2.764957	-1.230611	0.401441
5	6	0	1.153345	0.280225	-0.719563
6	6	0	1.569198	-0.438199	-1.983778
7	6	0	2.381886	0.254734	0.285625
8	6	0	0.501157	1.480899	-0.416135
9	1	0	0.005362	2.129926	-1.128058
10	6	0	1.389659	2.107619	0.718519
11	1	0	-2.632299	-1.686669	1.253113
12	1	0	-3.442714	-0.535594	0.514481
13	6	0	1.929626	0.146967	1.735559
14	8	0	2.672091	1.681065	0.200758
15	6	0	3.438873	-0.629024	-0.372767
16	6	0	1.298686	1.294195	2.000521
17	1	0	1.330214	3.193099	0.788750
18	1	0	0.752172	1.585199	2.888651
19	1	0	2.027773	-0.734975	2.351802
20	1	0	3.897737	-1.321490	0.338783
21	1	0	4.229130	0.023766	-0.759518
22	6	0	2.712818	-1.373186	-1.524392

23	1	0	3.389578	-1.628757	-2.345587
24	1	0	1.941829	0.319056	-2.688632
25	1	0	0.750136	-0.968717	-2.474781
26	1	0	2.279797	-2.302833	-1.143657

Intermediate VII

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.849451	-2.186481	-0.889867
2	78	0	-1.298668	0.001845	-0.040596
3	17	0	-2.114922	2.126175	0.643347
4	6	0	2.950188	-1.813488	1.452725
5	6	0	1.577469	-1.100610	1.529891
6	6	0	1.614422	0.077515	0.557071
7	6	0	0.485684	0.625268	-0.063770
8	6	0	3.503978	-1.507000	0.050735
9	6	0	3.039981	-0.102944	-0.229587
10	6	0	2.939298	1.006806	0.728832
11	6	0	3.053745	2.204538	-0.123592
12	8	0	3.221511	0.411647	-1.505649
13	6	0	3.201069	1.781236	-1.390673
14	8	0	-3.433137	-0.691326	-0.053726
15	1	0	2.858267	-2.888678	1.626132
16	1	0	3.636462	-1.424086	2.213810
17	1	0	0.775668	-1.770512	1.212695
18	1	0	1.345667	-0.763416	2.546819
19	1	0	0.648340	1.550853	-0.620177
20	1	0	3.077212	-2.172399	-0.707809
21	1	0	4.596308	-1.577979	-0.006793
22	1	0	3.318109	0.983797	1.746926
23	1	0	3.005773	3.230910	0.211699
24	1	0	3.302093	2.315535	-2.324989
25	1	0	-3.950892	0.035432	-0.442819
26	1	0	-3.424550	-1.428666	-0.692967