

Revised Mechanism for a Ruthenium-Catalyzed Coupling of Aldehyde and Terminal Alkyne

SUPPORTING INFORMATION

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S.1. Computational investigations.

S.1.1. Gibbs free energy plots for mechanism proposals in schemes 4 and 6

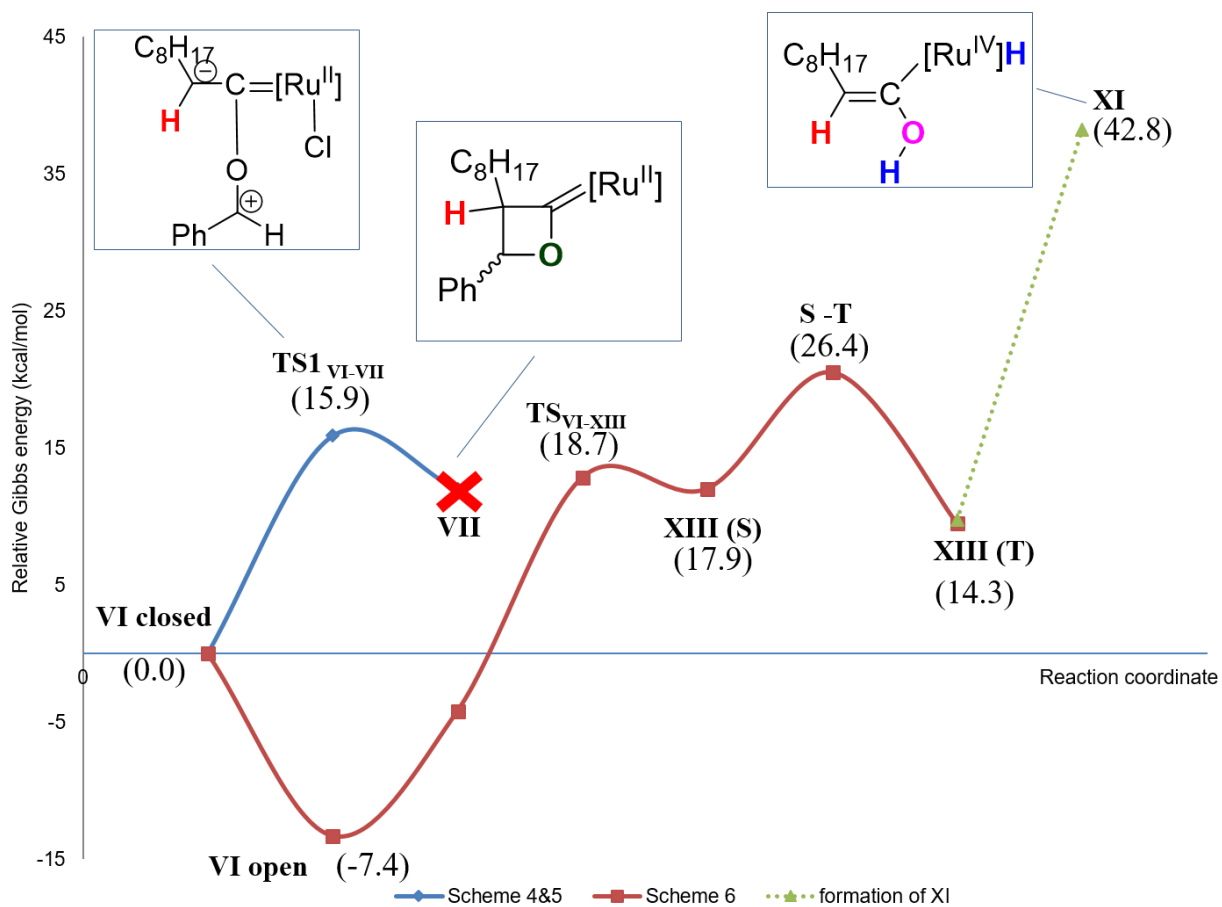


Figure S1. Energies relative to intermediate **VI** are shown for mechanism proposals from schemes 4 (including 5) and 6. The red X indicates that from the **TS1_{VI-VII}** it is not possible to obtain intermediate **VII**, which is illustrated in scheme 5.

S.1.2. CO coordination to ruthenium in XVII

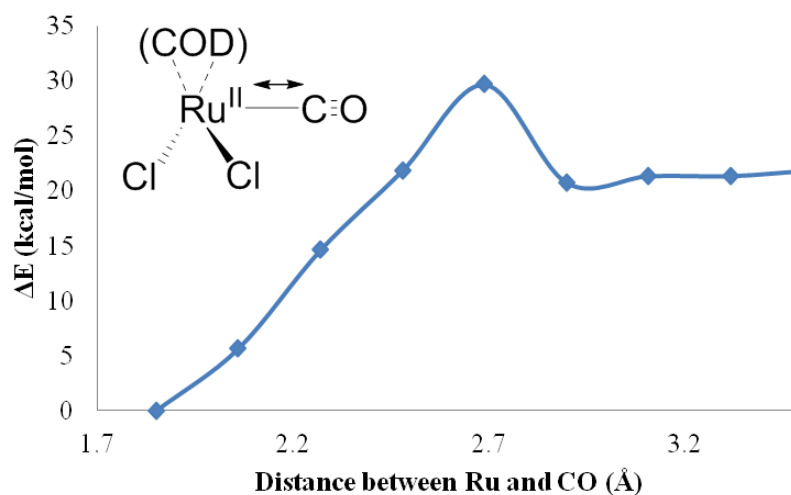


Figure S2. Potential Energy Surface Scan for the loss of CO from XVII.

S.1.3. Cartesian Coordinates

I, Scheme 1(B)

ENERGY = -5814.92026139 a.u.

```

Ru 0.41281 -0.30500 0.10417
Cl 2.48214 0.30494 -0.41973
Cl 0.48769 -2.20770 1.26130
C -0.13543 1.82767 -0.09565
C -1.27112 2.22121 0.81075
C -0.27410 1.25489 -1.37085
C -1.59183 0.96956 -2.05307
C -2.40084 1.19020 0.85867
C -1.89141 -0.22397 0.75369
C -2.04630 -0.46981 -1.81648
C -1.76570 -0.95405 -0.42091
H 0.79192 2.36285 0.09416
H -1.65755 3.20827 0.50657
H -0.85837 2.35614 1.81829
H 0.57962 1.36194 -2.03323
H -2.34856 1.68684 -1.71961
H -2.94893 1.29799 1.80178
H -1.47359 1.14133 -3.12947
H -3.13200 1.37571 0.06582
H -1.87380 -0.79774 1.67486
H -3.11431 -0.60053 -2.05542
H -1.50346 -1.12918 -2.50484
H -1.71544 -2.03348 -0.30986

```

VI, Figure 1(B)

ENERGY = -6010.00553274 a.u.

```

Ru 0.07842 0.20554 0.81788
Cl 1.99338 1.45802 1.20582
Cl 0.66853 -1.28921 2.45936
C -1.78913 0.70099 -1.73050
C -0.67586 1.41201 -0.99359
C -0.85226 2.08245 0.21188
C -2.14905 2.16665 0.97402
C -2.93898 0.85235 1.05922

```

C -2.04478 -0.36417 1.16426
 C -1.61884 -1.10130 0.07790
 C -1.94495 -0.77975 -1.35383
 C 0.98562 -2.21478 -3.75098
 C 0.69086 -1.98612 -5.22590
 C 0.84035 -0.54344 -0.61330
 C 1.50945 -1.15151 -1.54137
 C 1.39141 -0.93372 -3.02097
 H -1.59350 0.77048 -2.80728
 H -2.72449 1.24605 -1.56101
 H 0.19419 1.71136 -1.57812
 H -0.11376 2.83520 0.47175
 H -2.77133 2.95580 0.52950
 H -1.91020 2.51264 1.98392
 H -1.97173 -0.84356 2.14192
 H -1.25867 -2.10859 0.26380
 H -1.27546 -1.37126 -1.98063
 H -2.95939 -1.12727 -1.58917
 H -3.60448 0.74212 0.19573
 H -3.59419 0.88944 1.93709
 H 0.10476 -2.64516 -3.25339
 H 0.40017 -2.91678 -5.72691
 H 1.78387 -2.96076 -3.62921
 H 2.18480 -1.91938 -1.15877
 H -0.13010 -1.27018 -5.35991
 H 0.65437 -0.14478 -3.21710
 H 1.56556 -1.58097 -5.75082
 H 2.34828 -0.56226 -3.41617

VI, Figure 1(C)

ENERGY = -6009.99616485 a.u.

Ru 0.21181 0.15801 0.69895
 Cl 0.95105 1.76009 2.26080
 Cl 0.88160 -1.44246 2.25810
 C -1.63258 0.42704 -1.92365
 C -0.51515 1.20101 -1.26058
 C -0.68959 2.01201 -0.15401
 C -1.99145 2.20397 0.57771
 C -2.74424 0.89724 0.85830
 C -1.81619 -0.27557 1.08601
 C -1.40670 -1.15113 0.06461
 C -1.83832 -0.99136 -1.37146
 C 1.08773 -2.13680 -4.03035
 C 0.97443 -1.71497 -5.48911
 C 0.86769 -0.73209 -0.72680
 C 1.49118 -1.37219 -1.67298
 C 1.58318 -1.00535 -3.12621
 H -1.42117 0.36901 -2.99827
 H -2.55152 1.01755 -1.82944
 H 0.35779 1.41815 -1.86893
 H 0.05763 2.77710 0.02097
 H -2.62853 2.90419 0.01495
 H -1.74802 2.69169 1.52763
 H -1.77683 -0.67189 2.09730
 H -1.13765 -2.15852 0.36790
 H -1.25906 -1.69703 -1.97493
 H -2.89054 -1.29617 -1.47985
 H -3.42983 0.65328 0.03753
 H -3.37070 1.03137 1.74688
 H 0.11013 -2.48451 -3.66674
 H 0.63706 -2.54440 -6.12103
 H 1.76473 -2.99696 -3.93178
 H 1.95740 -2.29793 -1.32596
 H 0.25352 -0.89639 -5.61118
 H 0.99033 -0.10232 -3.31404
 H 1.93700 -1.36348 -5.88296
 H 2.62190 -0.75128 -3.38454

TS_{VI-VII}, Scheme 4

ENERGY = -6355.15893858 a.u.

iFQ = -301.91 and -78.07 cm⁻¹

Ru -0.61336 0.34175 0.95485
Cl 1.58655 0.61231 1.74982
Cl -0.56696 -1.93501 1.50289
O -0.51925 -1.19540 -1.63116
C -2.17033 2.69268 -0.50076
C -0.95494 2.49575 0.37887
C -0.95235 2.33184 1.75404
C -2.14765 2.15176 2.65064
C -3.30735 1.40506 1.98871
C -2.81379 0.22512 1.18267
C -2.56829 0.21412 -0.17584
C -2.69392 1.38845 -1.10312
C 1.21331 3.14542 -2.56770
C 1.85515 4.50387 -2.33205
C 0.10052 0.33726 -0.79945
C 0.91045 0.78968 -1.73725
C 1.71748 2.04808 -1.62875
C 0.06027 -2.27174 -1.76235
C 1.38359 -2.69896 -1.36400
C 2.18214 -2.03838 -0.41492
C 1.85246 -3.87557 -1.97887
C 3.42562 -2.56194 -0.08789
C 3.89437 -3.71661 -0.71848
C 3.11328 -4.37126 -1.67459
H -1.90060 3.37631 -1.31442
H -2.95479 3.20829 0.06376
H -0.03036 2.88114 -0.02697
H -0.03239 2.59259 2.27006
H -2.47636 3.13040 3.03828
H -1.81442 1.58855 3.53534
H -2.92283 -0.74796 1.65375
H -2.55549 -0.75774 -0.65526
H -2.11769 1.15684 -2.00628
H -3.73947 1.50294 -1.43127
H -3.90230 2.07823 1.36361
H -3.98635 1.03665 2.76691
H 0.12353 3.23216 -2.45200
H 1.45061 5.25849 -3.01641
H 1.37745 2.82870 -3.60845
H 1.02576 0.21611 -2.65009
H 1.67031 4.85289 -1.30744
H 1.73858 2.38830 -0.58713
H 2.94224 4.47197 -2.48125
H 2.76188 1.80450 -1.87590
H 4.87016 -4.12009 -0.44973
H 3.48221 -5.27092 -2.16329
H 1.21900 -4.39504 -2.69777
H 4.02541 -2.06250 0.67054
H 1.82764 -1.14899 0.09842
H -0.51608 -3.03432 -2.31027

Intermediate formed after TS_{VI-VII}, Scheme 5

From here, the formation of compound VII is not possible.

ENERGY = -6355.25928229 a.u.

iFQ = -402.01 and -19.02 cm⁻¹

Ru -1.0104380000 0.4976460000 0.5386770000
Cl -0.5903990000 -1.8348520000 1.4028590000
Cl 0.7667090000 1.3409930000 1.8198940000
O -0.0699680000 -1.5834560000 -1.1697280000
C 3.6785340000 -4.0403080000 -0.0941410000
C 4.4177830000 -3.1336680000 0.6634120000
C 3.8126670000 -1.9706500000 1.1436640000
C 2.3310810000 -3.7908390000 -0.3492740000

```

C 2.4703440000 -1.7107350000 0.8811430000
C 1.7223090000 -2.6305770000 0.1385080000
C 0.2706970000 -2.4422610000 -0.1809290000
C 1.7944260000 1.6661920000 -1.4216180000
C 1.2423460000 0.2860880000 -1.5301190000
C 0.1764740000 -0.2259080000 -0.9177080000
C 1.8258540000 3.9977590000 -2.4080630000
C 1.6396820000 2.5147490000 -2.6899790000
C -2.7027390000 0.1450840000 -2.0125940000
C -2.5933290000 -0.4512130000 -0.6415230000
C -3.1040020000 0.1158860000 0.5258450000
C -3.9083450000 1.3994990000 0.6024010000
C -3.0312320000 2.6228640000 0.9067910000
C -1.6530150000 2.5211390000 0.3088300000
C -1.3803070000 2.0216600000 -0.9607610000
C -2.4074830000 1.6459170000 -2.0061520000
H -0.2221560000 -3.3931010000 -0.3813310000
H 2.0015620000 -0.8107360000 1.2731900000
H 4.3862980000 -1.2598960000 1.7361880000
H 1.7448780000 -4.5094840000 -0.9223870000
H 4.1448830000 -4.9483620000 -0.4729460000
H 5.4626370000 -3.3402330000 0.8918330000
H 2.8639350000 1.5921550000 -1.1717500000
H 2.8108090000 4.2013540000 -1.9679110000
H 1.3481940000 2.1715510000 -0.5576080000
H 1.0741730000 4.3521600000 -1.6908860000
H 1.7938700000 -0.4173230000 -2.1530750000
H 2.3523420000 2.1747630000 -3.4540700000
H 1.7275010000 4.6016570000 -3.3180150000
H 0.6439380000 2.3477990000 -3.1269930000
H -4.6663250000 1.2924540000 1.3870600000
H -4.4646070000 1.5411470000 -0.3303480000
H -3.6913860000 -0.0656160000 -2.4517970000
H -1.9721300000 -0.3652170000 -2.6514960000
H -2.4323480000 -1.5234370000 -0.6234000000
H -3.2573380000 -0.5713430000 1.3582680000
H -2.9270920000 2.7427600000 1.9933870000
H -3.5172040000 3.5465690000 0.5522730000
H -0.8904120000 3.1383660000 0.7771530000
H -0.4179680000 2.2884740000 -1.3639190000
H -3.3230720000 2.2270550000 -1.8481870000
H -2.0246370000 1.9512180000 -2.9876770000

```

TS_{VI-VII} (second step), *Scheme 5*

This TS was found using the product as starting point, since the intermediate that should have been the reactant side of the second step was not found. The total energy difference between compound VI and this second TS structure is 24.6 kcal/mol.

ENERGY = -6355.22009723 a.u.

iFQ = -331.08.01

```

Ru -0.7041810000 0.2912830000 0.9475760000
Cl -0.4349500000 -1.9418780000 1.5700190000
Cl 1.4970890000 0.7633280000 1.6408900000
O -0.6793720000 -1.2053280000 -1.5103800000
C 3.3375520000 -3.8703190000 -2.0623300000
C 3.8797730000 -3.5725190000 -0.8100690000
C 3.2952580000 -2.5863430000 -0.0112030000
C 2.2050930000 -3.1960410000 -2.5003500000
C 2.1682700000 -1.9037210000 -0.4425240000
C 1.5910170000 -2.2190350000 -1.6863910000
C 0.3569730000 -1.6809860000 -2.1939080000
C 1.6476610000 1.5931030000 -1.6658990000
C 0.5932720000 0.5724190000 -1.8406730000
C -0.2214900000 -0.0370600000 -0.8970710000
C 2.6922870000 3.7497440000 -2.4955860000
C 1.4635950000 2.8517250000 -2.5142570000
C -3.0618970000 0.9001390000 -0.9915900000
C -2.7257030000 -0.1234490000 0.0556310000

```

```

C -2.8271990000 0.0683990000 1.4214540000
C -3.3293870000 1.3250730000 2.0978880000
C -2.1737260000 2.2318660000 2.5280290000
C -1.0872500000 2.3507800000 1.4916730000
C -1.2346200000 2.2996350000 0.1144030000
C -2.5405750000 2.3031060000 -0.6572470000
H 0.0593640000 -2.0537070000 -3.1758300000
H 1.7612070000 -1.1122030000 0.1821890000
H 3.7246600000 -2.3257280000 0.9543590000
H 1.7679590000 -3.4432420000 -3.4676120000
H 3.7953480000 -4.6300650000 -2.6929160000
H 4.7668590000 -4.0997480000 -0.4618880000
H 2.5968680000 1.1043280000 -1.9566300000
H 3.5619170000 3.2357410000 -2.9246640000
H 1.7679140000 1.8285920000 -0.6007070000
H 2.9552600000 4.0427500000 -1.4711930000
H 0.2931230000 0.3671710000 -2.8722250000
H 1.2242780000 2.5658130000 -3.5498000000
H 2.5280640000 4.6671940000 -3.0728950000
H 0.5902610000 3.4116600000 -2.1508190000
H -3.9094920000 1.0369870000 2.9826610000
H -4.0220260000 1.8643290000 1.4442390000
H -4.1497850000 0.9216950000 -1.1636510000
H -2.6212250000 0.5640000000 -1.9379740000
H -2.6935280000 -1.1526310000 -0.2844980000
H -2.8219500000 -0.8317450000 2.0307270000
H -1.7139000000 1.8205600000 3.4397930000
H -2.5404990000 3.2315590000 2.8135620000
H -0.1456160000 2.7406850000 1.8662430000
H -0.3765740000 2.6561820000 -0.4404910000
H -3.2919170000 2.8751300000 -0.1022290000
H -2.3880490000 2.8566530000 -1.5913850000

```

VI, Figure 2(A)

ENERGY = -6086.47720180 a.u.

```

Ru -0.06960 -0.06855 0.77776
Cl -0.45539 1.28594 2.82643
Cl 0.65655 -1.76213 2.28193
O 1.88772 0.80149 1.23165
C -0.81198 1.78718 -0.11060
C -2.21366 2.06921 0.36372
C -0.53020 0.95924 -1.19528
C -1.61562 0.24587 -1.97308
C -3.03545 0.80816 0.66959
C 1.38140 -1.50495 -5.37119
C -2.19865 -0.40835 1.00197
C 0.72674 -0.95942 -0.60504
C 1.01109 -1.93745 -3.96054
C -1.98017 -1.14427 -1.43016
C -1.73538 -1.30472 0.04770
C 1.79378 -1.19780 -2.88018
C 1.40871 -1.61876 -1.49053
H -0.07138 2.54013 0.14179
H -2.72956 2.69636 -0.38007
H -2.12619 2.66418 1.27612
H 0.39870 1.16162 -1.72011
H -2.49958 0.89502 -1.98398
H -3.69042 1.01748 1.52177
H -1.29170 0.15604 -3.01713
H -3.69716 0.55821 -0.17007
H -2.25616 -0.76939 2.02337
H 1.19049 -0.43395 -5.52128
H -3.03438 -1.37165 -1.65094
H 1.64613 -0.11617 -2.99262
H -1.39081 -1.90120 -1.95541
H -0.06296 -1.77295 -3.79459
H -1.50136 -2.30962 0.38511

```

H 0.79652 -2.05180 -6.11879
H 1.17514 -3.01845 -3.84492
H 2.86936 -1.38093 -3.01717
H 2.44289 -1.68919 -5.58023
H 1.69919 -2.61070 -1.13389
H 2.27037 0.01183 1.65426
H 1.51904 1.30240 1.99675

TS_{VI-XIII}, Figure 2(B), Scheme 7(B)

ENERGY = -6162.90559890 a.u.

iFQ = -250.26 cm⁻¹

Ru -0.01579 0.20999 0.66443
Cl -0.26712 1.11417 2.95820
Cl 1.08405 -1.63454 1.73509
O 2.07959 0.83686 -1.34756
O 2.00012 1.11908 1.23861
C -1.09491 2.08807 0.29572
C -2.46535 2.04666 0.91539
C -0.79107 1.53576 -0.93960
C -1.81431 0.86211 -1.83079
C -3.06280 0.63633 0.96007
C 1.92740 -2.13138 -5.59187
C -2.02093 -0.46305 0.98101
C 0.84993 -0.44142 -0.97256
C 1.52087 -2.40936 -4.15202
C -2.03672 -0.63321 -1.54845
C -1.54837 -1.06376 -0.18673
C 1.76995 -1.22072 -3.22523
C 1.02012 -1.32400 -1.92896
H 2.20191 1.17675 -0.42364
H 2.88370 0.34412 -1.56296
H -0.44933 2.88168 0.66076
H -3.13285 2.72887 0.36490
H -2.38065 2.43482 1.93351
H 0.05943 1.95574 -1.46323
H -2.76125 1.41146 -1.74128
H -3.68977 0.53897 1.85289
H -1.48781 0.98803 -2.86986
H -3.72730 0.47048 0.10150
H -1.93045 -1.02910 1.90204
H 1.33363 -1.31122 -6.01478
H -3.10513 -0.88435 -1.63678
H 1.45652 -0.29692 -3.73454
H -1.53020 -1.22816 -2.31231
H 0.45214 -2.66629 -4.12312
H -1.17691 -2.08134 -0.10119
H 1.77237 -3.01039 -6.22788
H 2.05164 -3.28907 -3.76244
H 2.85765 -1.12283 -3.06740
H 2.98452 -1.84371 -5.66894
H 0.43098 -2.22187 -1.75435
H 2.20756 0.22349 1.60511
H 1.54011 1.55514 2.00137

XIII (S) + 2H₂O, Scheme 7

ENERGY = -6162.90422526 a.u.

Ru -0.04178 0.23961 0.65786
Cl -0.19350 1.12814 2.96215
Cl 1.08959 -1.62123 1.68096
O 2.02844 0.76855 -1.21334
O 2.10974 1.09921 1.25666
C -1.12453 2.11497 0.35746
C -2.48858 2.05055 0.99109
C -0.83000 1.59134 -0.89489

C -1.86476 0.93977 -1.79013
 C -3.07246 0.63393 1.01304
 C 2.01658 -2.24622 -5.57438
 C -2.01418 -0.45042 0.99639
 C 0.89342 -0.31316 -1.03489
 C 1.61046 -2.41569 -4.11868
 C -2.08074 -0.56036 -1.53349
 C -1.54517 -1.01599 -0.19724
 C 1.73034 -1.12853 -3.30459
 C 0.94731 -1.18492 -2.02443
 H 2.19539 1.07477 -0.24720
 H 2.81957 0.31931 -1.55156
 H -0.48452 2.90847 0.73252
 H -3.16860 2.73886 0.46392
 H -2.39466 2.41842 2.01626
 H 0.00675 2.03841 -1.42092
 H -2.81103 1.48587 -1.67522
 H -3.68753 0.51027 1.91097
 H -1.55434 1.08897 -2.83090
 H -3.74593 0.47891 0.15939
 H -1.91284 -1.04059 1.90148
 H 1.37628 -1.50965 -6.07595
 H -3.15247 -0.80804 -1.58733
 H 1.34817 -0.29095 -3.91132
 H -1.60713 -1.14027 -2.32885
 H 0.56690 -2.75868 -4.07534
 H -1.16532 -2.03298 -0.14551
 H 1.92532 -3.18912 -6.12562
 H 2.20447 -3.20540 -3.63897
 H 2.80171 -0.91012 -3.14657
 H 3.05382 -1.89871 -5.67200
 H 0.24596 -2.00490 -1.92349
 H 2.19941 0.17149 1.60821
 H 1.58559 1.54503 1.97566

XIII (S→T), Scheme 7

ENERGY = -6162.89071413 a.u.

Ru -0.34862 0.24316 0.49582
 Cl 1.14149 1.52132 2.00801
 Cl 0.77792 -1.83718 1.11411
 O 2.09816 0.39499 -1.03699
 O 3.15526 -0.27525 1.16387
 C -1.47658 2.06161 0.63862
 C -2.45863 1.93220 1.77627
 C -1.64705 1.57136 -0.65787
 C -2.92223 0.92607 -1.17843
 C -3.20287 0.58825 1.81307
 C 3.17537 -2.47432 -3.63840
 C -2.31132 -0.56048 1.43036
 C 0.72368 0.20957 -1.23498
 C 1.74967 -2.16631 -3.19922
 C -2.95370 -0.59811 -1.03077
 C -2.18920 -1.09147 0.16667
 C 1.30425 -0.71527 -3.48033
 C 0.33845 -0.21521 -2.44399
 H 2.87171 -0.00925 0.21596
 H 2.54875 0.31033 -1.88963
 H -0.76617 2.87272 0.76529
 H -3.18158 2.76422 1.74697
 H -1.89014 2.05669 2.70788
 H -1.03682 2.03786 -1.42173
 H -3.78159 1.38295 -0.67419
 H -3.58389 0.41272 2.82688
 H -3.03621 1.18814 -2.23710
 H -4.08152 0.61036 1.16043
 H -1.83362 -1.10880 2.24127
 H 3.32798 -2.30003 -4.71160

```

H -3.99221 -0.96466 -0.98252
H 0.85829 -0.63323 -4.47990
H -2.51768 -1.06545 -1.92033
H 1.04759 -2.85621 -3.68562
H -1.71990 -2.06726 0.07902
H 3.44108 -3.51719 -3.42648
H 1.64807 -2.35677 -2.12178
H 2.19877 -0.06765 -3.54661
H 3.89551 -1.84400 -3.09903
H -0.71975 -0.32118 -2.63783
H 2.49714 -1.05558 1.29427
H 2.63067 0.45004 1.68298

```

XIII (T), Scheme 7

ENERGY = -5623.51223180 a.u.

```

Ru -0.13860 -0.11728 0.63729
Cl 0.88441 -1.06377 2.46761
O 1.99160 1.59214 -0.19447
C -1.13501 1.42747 -0.49005
C -2.07697 2.20237 0.39596
C -1.39910 0.19798 -1.11749
C -2.73135 -0.52726 -1.11621
C -2.98957 1.33058 1.26899
C 3.97631 -0.42751 -4.59128
C -2.28141 0.12977 1.84191
C 1.51623 0.32655 -0.36950
C 2.81722 -0.51784 -3.61183
C -2.86407 -1.56181 0.00672
C -2.25921 -1.12408 1.30958
C 3.22658 -0.33040 -2.14970
C 2.07616 -0.55620 -1.22196
H 2.82648 1.69700 -0.66985
H -0.34113 2.03463 -0.91735
H -2.68482 2.89267 -0.21178
H -1.46272 2.84269 1.04438
H -0.74612 -0.04635 -1.95058
H -3.54707 0.20225 -1.07112
H -3.37219 1.93889 2.09802
H -2.85109 -1.04029 -2.07817
H -3.86963 1.01098 0.70348
H -1.86706 0.24243 2.84064
H 4.46221 0.55662 -4.55268
H -3.91992 -1.84303 0.14924
H 3.66233 0.67479 -2.03047
H -2.35445 -2.48409 -0.29950
H 2.05271 0.23146 -3.86092
H -1.85958 -1.91260 1.94095
H 3.63278 -0.58997 -5.62012
H 2.32270 -1.49452 -3.71241
H 4.04385 -1.02961 -1.91250
H 4.74458 -1.17917 -4.37074
H 1.61676 -1.54035 -1.26489

```

XI, Scheme 6

ENERGY = -6086.39956781 a.u.

```

Ru 0.1633640000 0.2929200000 0.4951770000
Cl 1.1983640000 -1.6849480000 0.9731070000
Cl 0.4380470000 0.9207430000 2.7862810000
O 2.4985150000 0.1189850000 -1.0675700000
C 0.6574210000 -0.0514180000 -2.5078930000
C 1.5267100000 -0.6158670000 -3.5954070000
C -1.8923230000 -1.0855590000 0.0665420000
C -2.5193570000 -0.5497610000 -1.1874190000
C 1.9620350000 -2.0725380000 -3.3271020000
C 1.1667850000 0.1764400000 -1.2779110000
C -2.0666910000 -0.5731700000 1.3200420000

```

```

C 3.3999610000 -2.3538160000 -3.7339890000
C -2.9760860000 0.5769670000 1.6466090000
C -2.4347810000 0.9754610000 -1.3168430000
C -1.2031480000 1.6240330000 -0.7063680000
C -2.2839050000 1.9501520000 1.6049470000
C -1.1786450000 2.0866810000 0.6024570000
H 1.1517990000 1.4920660000 0.3473290000
H -0.3989470000 0.0928790000 -2.6974680000
H 4.0975850000 -1.7224320000 -3.1671880000
H 2.4283950000 0.0064050000 -3.7201770000
H 1.8378250000 -2.2866390000 -2.2616050000
H 3.6768350000 -3.3949430000 -3.5309980000
H -1.3404850000 -2.0227780000 -0.0181830000
H 1.2828740000 -2.7512930000 -3.8505090000
H -2.0221890000 -1.0255220000 -2.0380890000
H 1.0142470000 -0.5389740000 -4.5571320000
H -3.5714220000 -0.8721550000 -1.2370790000
H 3.5738610000 -2.1572480000 -4.7998680000
H -1.6098360000 -1.1093290000 2.1529410000
H -3.8327120000 0.5583660000 0.9631880000
H -2.4817150000 1.2469030000 -2.3744430000
H -3.3827770000 0.4230350000 2.6526000000
H -3.3114750000 1.4402110000 -0.8585790000
H -0.5275490000 2.1024220000 -1.4116700000
H -1.8539140000 2.1632710000 2.5832960000
H -3.0277880000 2.7328170000 1.4026500000
H -0.4782410000 2.8820270000 0.8394840000
H 2.9568730000 0.0655750000 -1.9165580000

```

TS_{XIII-XIV}(*trans*), Scheme 7

ENERGY = -5968.74278924 a.u.

iFQ = 1114.44 cm⁻¹

```

Ru -1.21326 0.50490 1.02422
Cl -0.16550 -0.55125 2.78218
O 1.17650 1.76264 0.50196
O 3.02803 0.28675 0.60314
C -2.08425 2.07406 -0.19573
C -2.89344 3.02322 0.65097
C -2.50882 0.83372 -0.69707
C -3.91479 0.27544 -0.57553
C -3.83964 2.34239 1.64746
C 3.26299 0.55188 -4.22635
C -3.23248 1.12911 2.30086
C 0.45361 0.84290 -0.04437
C 2.03904 0.08059 -3.45491
C -4.13061 -0.61389 0.65650
C -3.39348 -0.15762 1.88352
C 1.86373 0.82571 -2.13670
C 0.89177 0.18704 -1.18650
C 2.70734 -3.83452 -1.82792
C 3.89764 -3.56478 -2.51082
C 2.21913 -2.92372 -0.89839
C 4.60508 -2.39201 -2.24374
C 2.91037 -1.72920 -0.65245
C 4.11966 -1.47937 -1.31140
C 2.35631 -0.75006 0.28599
H 2.22656 1.16114 0.70103
H -1.25550 2.55107 -0.71274
H -3.46082 3.71112 0.00277
H -2.18482 3.65517 1.20327
H -1.92993 0.44760 -1.53239
H -4.63359 1.10213 -0.58978
H -4.11031 3.06449 2.42732
H -4.13564 -0.31671 -1.47180
H -4.77847 2.06447 1.15891
H -2.75237 1.27844 3.26473
H 3.18774 1.61387 -4.49423

```

H -5.20688 -0.70715 0.87288
 H 1.53925 1.86063 -2.32997
 H -3.78655 -1.62990 0.42581
 H 1.13560 0.20525 -4.07033
 H -3.05653 -0.93912 2.55857
 H 3.40514 -0.01789 -5.15217
 H 2.13260 -0.99620 -3.25494
 H 2.84101 0.93415 -1.64001
 H 4.16796 0.42904 -3.61809
 H 0.29578 -0.64592 -1.54865
 H 2.16341 -4.75646 -2.02677
 H 4.27814 -4.27758 -3.24065
 H 1.29010 -3.12032 -0.36240
 H 1.57353 -1.10390 0.96312
 H 5.53980 -2.18792 -2.76345
 H 4.66313 -0.56662 -1.07748

TS_{xiii-xiv} (*cis*), Scheme 7

ENERGY = -5968.74096835 a.u.

iFQ = -1117.81 cm⁻¹

Ru -1.21768 0.49641 0.98128
 Cl -0.16992 -0.55974 2.73924
 O 1.17208 1.75415 0.45902
 O 3.02361 0.27826 0.56020
 C -2.08867 2.06557 -0.23867
 C -2.89786 3.01473 0.60803
 C -2.51324 0.82523 -0.74001
 C -3.91921 0.26695 -0.61847
 C -3.84406 2.33390 1.60452
 C 3.25857 0.54339 -4.26929
 C -3.23690 1.12062 2.25792
 C 0.44919 0.83441 -0.08731
 C 2.03462 0.07210 -3.49785
 C -4.13503 -0.62238 0.61356
 C -3.39790 -0.16611 1.84058
 C 1.85931 0.81722 -2.17964
 C 0.88735 0.17855 -1.22944
 C 2.70292 -3.84301 -1.87086
 C 3.89322 -3.57327 -2.55376
 C 2.21471 -2.93221 -0.94133
 C 4.60066 -2.40050 -2.28668
 C 2.90595 -1.73769 -0.69539
 C 4.11524 -1.48786 -1.35434
 C 2.35189 -0.75855 0.24305
 H 2.22214 1.15265 0.65809
 H -1.25992 2.54258 -0.75568
 H -3.46524 3.70263 -0.04017
 H -2.18924 3.64668 1.16033
 H -1.93435 0.43911 -1.57533
 H -4.63801 1.09364 -0.63272
 H -4.11473 3.05600 2.38438
 H -4.14006 -0.32520 -1.51474
 H -4.78289 2.05598 1.11597
 H -2.75679 1.26995 3.22179
 H 3.18332 1.60538 -4.53717
 H -5.21130 -0.71564 0.82994
 H 1.53483 1.85214 -2.37291
 H -3.79097 -1.63839 0.38287
 H 1.13118 0.19676 -4.11327
 H -3.06095 -0.94761 2.51563
 H 3.40072 -0.02638 -5.19511
 H 2.12818 -1.00469 -3.29788
 H 2.83659 0.92566 -1.68295
 H 4.16354 0.42055 -3.66103
 H 0.29136 -0.65441 -1.59159
 H 2.15899 -4.76495 -2.06971
 H 4.27372 -4.28607 -3.28359
 H 1.28568 -3.12881 -0.40534
 H 1.56911 -1.11239 0.92018

H 5.53538 -2.19641 -2.80639
H 4.65871 -0.57511 -1.12042

XIV (cis), Scheme 7

ENERGY = -5968.786761964 a.u.

Ru -1.14335 0.46819 0.77324
Cl -0.65960 -1.50082 1.86946
O 1.32935 2.06815 0.47158
O 3.67836 0.75057 -0.23040
C -1.64947 2.55911 0.68878
C -2.75868 2.90429 1.64824
C -1.80693 2.04711 -0.60865
C -3.14494 1.77730 -1.27358
C -3.94168 1.92397 1.65722
C 0.80215 -0.42352 -4.39080
C -3.51999 0.48864 1.49971
C 0.74741 1.02954 0.26433
C 0.96760 -0.86727 -2.94291
C -3.63586 0.34086 -1.06823
C -3.42120 -0.18990 0.32154
C 1.36907 0.28381 -2.02717
C 1.41117 -0.09635 -0.53641
C 3.42964 -3.98928 -0.85201
C 4.41055 -3.90022 -1.84322
C 2.93874 -2.83375 -0.25061
C 4.89571 -2.64954 -2.22281
C 3.41955 -1.57747 -0.63281
C 4.40209 -1.49150 -1.61998
C 2.83777 -0.34538 0.00325
H 3.19291 1.53296 0.07254
H -0.70845 3.06739 0.88895
H -3.12243 3.92211 1.43124
H -2.32157 2.95271 2.65408
H -0.98743 2.24645 -1.29358
H -3.88656 2.49978 -0.91648
H -4.48040 2.03132 2.60582
H -3.05058 1.96596 -2.34990
H -4.66145 2.18117 0.87479
H -3.41906 -0.10068 2.40735
H 0.04980 0.37177 -4.48039
H -4.69631 0.24525 -1.35200
H 0.66486 1.11347 -2.18078
H -3.08938 -0.31693 -1.75706
H 0.02389 -1.30140 -2.57779
H -3.27663 -1.26546 0.39383
H 0.48615 -1.25127 -5.03623
H 1.71447 -1.66945 -2.87030
H 2.35247 0.68423 -2.30916
H 1.74181 -0.02421 -4.79487
H 0.84572 -1.01666 -0.37925
H 3.04864 -4.96085 -0.53878
H 4.80254 -4.80176 -2.31249
H 2.17692 -2.90361 0.52761
H 2.74232 -0.53364 1.08353
H 5.66717 -2.57224 -2.98820
H 4.78298 -0.51199 -1.90053

XIV (trans), Scheme 7

ENERGY = -5968.79112263 a.u.

Ru -0.46217 0.84272 0.66746
Cl 1.00546 0.70837 2.50748
O 1.23314 2.39031 -0.56921
O 2.95597 -0.62169 0.29504
C -1.91587 1.80694 -0.56012
C -3.02572 2.41651 0.26143
C -1.82070 0.46523 -0.97515

C -2.85550 -0.61717 -0.72951
 C -3.62600 1.48387 1.32234
 C 4.50418 0.72889 -4.19944
 C -2.56750 0.71761 2.05712
 C 0.95788 1.21887 -0.65839
 C 3.14049 0.31416 -3.66489
 C -2.74022 -1.35473 0.61623
 C -2.17990 -0.54483 1.74950
 C 2.84024 0.92707 -2.30303
 C 1.67703 0.25454 -1.57860
 C -0.51724 -3.65272 -1.25657
 C -0.70978 -4.10780 0.05053
 C 0.36560 -2.60549 -1.50542
 C -0.02907 -3.49129 1.09812
 C 1.07508 -1.99371 -0.46197
 C 0.86168 -2.44471 0.84531
 C 2.15976 -0.98517 -0.79342
 H 2.42169 -0.15408 0.96281
 H -1.38106 2.53641 -1.16515
 H -3.82112 2.78683 -0.40541
 H -2.62048 3.30592 0.76369
 H -1.22807 0.29909 -1.86953
 H -3.85703 -0.18743 -0.86292
 H -4.20116 2.08234 2.04047
 H -2.74407 -1.36797 -1.52062
 H -4.33687 0.78750 0.86717
 H -2.12513 1.18351 2.93626
 H 4.58114 1.82051 -4.28407
 H -3.71878 -1.76862 0.90946
 H 2.62816 1.99704 -2.41611
 H -2.08691 -2.21714 0.47623
 H 2.35275 0.60956 -4.37443
 H -1.50559 -1.05295 2.43406
 H 4.70288 0.29928 -5.18822
 H 3.09346 -0.78457 -3.60474
 H 3.72004 0.86169 -1.64891
 H 5.30155 0.39677 -3.52285
 H 0.91907 -0.07423 -2.30151
 H -1.04567 -4.12733 -2.08242
 H -1.39326 -4.93168 0.24951
 H 0.53860 -2.28229 -2.53267
 H 2.84256 -1.51020 -1.47306
 H -0.18726 -3.83320 2.12037
 H 1.41474 -1.99235 1.66459

XIV (cis) + LiCl, Figure 3

ENERGY = -6438.73453708 a.u.

Ru -1.27958 0.28067 0.01585
 Cl -1.20457 -2.02553 0.01747
 O 1.08617 1.96943 -0.33350
 O 3.56973 0.89251 -1.22040
 C -1.50131 2.01877 1.26222
 C -2.50969 1.74368 2.34888
 C -1.78237 2.42341 -0.05097
 C -3.15198 2.76283 -0.60400
 C -3.83637 1.14069 1.86247
 C 0.00172 -0.55531 -4.48180
 C -3.63556 0.09155 0.80803
 C 0.63675 0.83569 -0.35700
 C 0.01438 -0.58768 -2.96187
 C -3.81295 1.56595 -1.28847
 C -3.64340 0.27343 -0.53983
 C 1.41021 -0.33132 -2.41231
 C 1.52604 -0.30163 -0.88484
 C 4.12927 -3.68846 0.27264
 C 5.06215 -3.90490 -0.74440
 C 3.46967 -2.46648 0.36433
 C 5.32902 -2.89476 -1.66562

```

C 3.73095 -1.44908 -0.56156
C 4.66424 -1.67047 -1.57562
C 2.98994 -0.13992 -0.43982
H 4.45278 1.11477 -0.89446
H -0.50267 2.24931 1.62622
H -2.70151 2.67168 2.91047
H -2.04669 1.05597 3.06978
H -0.94425 2.87975 -0.56677
H -3.79096 3.17257 0.18474
H -4.34537 0.67715 2.71625
H -3.04182 3.56991 -1.33736
H -4.50939 1.92077 1.49666
H -3.58228 -0.93707 1.15398
H 0.33407 0.41930 -4.86272
H -4.88065 1.76053 -1.47640
H 1.79360 0.61507 -2.81459
H -3.35998 1.43441 -2.28017
H -0.68641 0.17824 -2.57560
H -3.64205 -0.62921 -1.14745
H -0.99569 -0.75968 -4.88707
H -0.36439 -1.54916 -2.59431
H 2.09188 -1.11073 -2.77823
H 0.68497 -1.31026 -4.88980
H 1.16192 -1.24549 -0.48025
H 3.91707 -4.47403 0.99634
H 5.58003 -4.85965 -0.81828
H 2.74130 -2.30084 1.15949
H 2.99301 0.15831 0.61814
H 6.05978 -3.05773 -2.45620
H 4.87295 -0.87797 -2.29198
Li 2.73262 2.66024 -0.98888
Cl 4.22353 4.11852 -0.93669

```

XV(cis), Figure 5

ENERGY = -5892.32509360 a.u.

```

Ru -1.20112 0.53886 0.95002
Cl -1.63561 -1.42759 2.09787
O 1.29749 0.55028 1.88289
C -1.02770 2.67329 0.79248
C -2.22494 3.38960 1.36313
C -0.92426 2.15553 -0.50880
C -2.00702 2.21130 -1.57511
C -3.58742 2.81804 0.93990
C -0.84185 -2.33965 -2.74714
C -3.60031 1.31947 0.91809
C 0.76731 0.26553 0.83274
C -0.10614 -2.02578 -1.45161
C -2.99445 1.03278 -1.54260
C -3.34580 0.53747 -0.16493
C 0.66599 -0.70483 -1.54351
C 1.46353 -0.36285 -0.32524
C 4.52200 -2.75759 -2.71508
C 5.85053 -2.41077 -2.46609
C 3.49151 -2.16858 -1.98771
C 6.14628 -1.47307 -1.47464
C 3.77171 -1.22152 -0.98552
C 5.11815 -0.89573 -0.73926
C 2.77498 -0.58800 -0.13535
H -0.08857 2.94361 1.27320
H -2.16893 4.45721 1.09232
H -2.14975 3.35655 2.45825
H 0.08736 2.11439 -0.90232
H -2.54191 3.16604 -1.50973
H -4.34897 3.16750 1.64670
H -1.52038 2.22118 -2.55819
H -3.88443 3.20681 -0.03848
H -3.90047 0.80882 1.83098
H -1.58644 -1.56803 -2.98236
H -3.91448 1.29177 -2.08988

```

H -0.05830 0.10048 -1.72886
 H -2.55453 0.19231 -2.09262
 H -0.81190 -1.98192 -0.60913
 H -3.55132 -0.52582 -0.06509
 H -1.37091 -3.29815 -2.69280
 H 0.58585 -2.84020 -1.19519
 H 1.32737 -0.71822 -2.41987
 H -0.14644 -2.38384 -3.59585
 H 4.28517 -3.50382 -3.47207
 H 6.65163 -2.88006 -3.03459
 H 2.46932 -2.48662 -2.17035
 H 3.16290 -0.21493 0.81059
 H 7.17890 -1.19894 -1.26288
 H 5.34903 -0.17839 0.04746

XVI (cis), Figure 5

ENERGY = -5778.95694823 a.u.

Ru -1.00806 -0.01671 0.43158
 Cl -0.72127 -1.96119 1.64336
 C -1.16244 2.12629 0.24708
 C -1.90930 2.72141 1.41395
 C -1.73253 1.55607 -0.90302
 C -3.21793 1.51275 -1.21358
 C -3.21480 1.99963 1.77957
 C 0.55620 -2.50462 -3.33244
 C -3.09934 0.50282 1.69176
 C 0.45606 -1.97169 -1.91369
 C -3.90864 0.23329 -0.72515
 C -3.42797 -0.25791 0.61190
 C 0.95680 -0.53020 -1.79009
 C 0.82453 -0.00315 -0.38931
 C 5.43484 -0.97029 0.50169
 C 5.99518 -0.35298 -0.61777
 C 4.10551 -0.73297 0.84115
 C 5.22020 0.51789 -1.38371
 C 3.30210 0.10806 0.05507
 C 3.88688 0.74723 -1.04838
 C 1.87762 0.27531 0.40155
 H -0.14032 2.48229 0.14708
 H -2.10958 3.78752 1.21654
 H -1.23673 2.70134 2.28237
 H -1.08272 1.51550 -1.77265
 H -3.70491 2.40115 -0.79784
 H -3.49368 2.27302 2.80463
 H -3.35220 1.58786 -2.29909
 H -4.03712 2.34507 1.14692
 H -2.85289 -0.02916 2.60721
 H -0.05331 -1.90951 -4.02441
 H -5.00165 0.36986 -0.70963
 H 0.38736 0.10179 -2.48928
 H -3.72187 -0.56816 -1.45170
 H -0.58474 -2.03996 -1.55938
 H -3.45665 -1.33399 0.76259
 H 0.21061 -3.54371 -3.39552
 H 1.03044 -2.60355 -1.22350
 H 2.00147 -0.48467 -2.12700
 H 1.59187 -2.47133 -3.69510
 H 6.03687 -1.64330 1.11092
 H 7.02960 -0.55321 -0.89443
 H 3.66553 -1.22791 1.70633
 H 1.68524 0.54603 1.44072
 H 5.65609 1.02051 -2.24630
 H 3.28393 1.43161 -1.64340

XVII (cis), Scheme 7

ENERGY = -5465.72010299 a.u.

Ru 0.42843 -0.24333 0.03903

```

Cl 0.95472 -2.18984 0.99084
O 3.38979 0.65322 -0.02353
C -0.13706 1.93975 -0.16787
C -1.18135 2.14054 0.89559
C -0.33481 1.35210 -1.40625
C -1.66357 0.99384 -2.02990
C -2.30643 1.09388 0.91856
C -1.83601 -0.32576 0.70966
C 2.31889 0.31498 -0.01875
C -2.01859 -0.48272 -1.85626
C -1.75774 -1.00793 -0.47746
H 0.77588 2.51394 -0.02688
H -1.60668 3.15040 0.78350
H -0.66848 2.15425 1.86701
H 0.49811 1.43627 -2.10586
H -2.44649 1.64250 -1.63004
H -2.79606 1.14152 1.89691
H -1.60848 1.22383 -3.10035
H -3.07959 1.33420 0.18532
H -1.72888 -0.93177 1.60738
H -3.07168 -0.66828 -2.12019
H -1.43988 -1.08760 -2.56683
H -1.61506 -2.08456 -0.40567

```

Product olefin 1 (*cis*), Figure 5

ENERGY = -426.97590268 a.u.

```

C 4.56140 -4.54002 -1.47740
C 5.58630 -4.11864 -2.32669
C 3.67712 -3.61256 -0.93335
C 5.72940 -2.76097 -2.61187
C 3.78606 -2.24867 -1.24114
C 0.77576 -0.62377 -3.59118
C 4.84007 -1.83506 -2.07019
C 2.07761 -0.44387 -1.45468
C 2.78390 -1.30236 -0.72002
C 0.86037 -0.62237 -5.10927
C 2.12294 -0.30518 -2.93934
H 4.44428 -5.59707 -1.24130
H 6.27383 -4.84371 -2.75863
H 2.86968 -3.94760 -0.28289
H 0.01874 0.09692 -3.25004
H 1.34227 0.17262 -0.93931
H 0.43656 -1.60817 -3.23879
H 6.53631 -2.41798 -3.25822
H 2.56495 -1.36308 0.34418
H -0.10629 -0.85576 -5.57086
H 4.96359 -0.77498 -2.28713
H 1.19204 0.35293 -5.48999
H 1.58299 -1.36929 -5.46060
H 2.42338 0.71891 -3.21335
H 2.88364 -0.97469 -3.35595

```

Product olefin 1 (*trans*), Figure 5

ENERGY = -426.98225527 a.u.

```

C -0.92375 -2.42229 0.55153
C 0.10443 -1.75428 -0.10484
C -1.04207 -3.81102 0.45213
C 1.04615 -2.45557 -0.87766
C 2.14737 -1.80833 -1.59355
C -0.11906 -4.52087 -0.31372
C 0.91367 -3.84996 -0.96556
C 2.45221 -0.51145 -1.62066
C 3.57664 0.08272 -2.40017
C 3.09065 1.03226 -3.49666
C 4.22902 1.70647 -4.24813
H 4.23974 0.64358 -1.72111

```

```

H -1.64103 -1.85512 1.14296
H 0.17468 -0.67149 -0.01504
H -1.84726 -4.33408 0.96525
H 2.78161 -2.48440 -2.16671
H -0.20371 -5.60286 -0.40646
H 4.18752 -0.71427 -2.84839
H 1.63599 -4.41181 -1.55818
H 4.88194 0.96715 -4.73057
H 2.45815 0.46748 -4.19640
H 1.84210 0.19635 -1.06184
H 3.85005 2.37566 -5.02944
H 4.85523 2.30392 -3.57229
H 2.43813 1.79529 -3.04688

```

S.2. Experimental investigations

S.2.1. Materials

Benzaldehyde and 4-anisaldehyde were purified by distillation under reduced pressure.¹ 1-Decyne (98%, Aldrich), H₂O¹⁸ (97% O¹⁸) and D₂O (99.9% D, Cambridge Isotope Laboratories) were used as received. 2H-1-Decyne (>95% D incorporation, 86% isolated yield) was synthesized from 1-decyne following an established method.² Solvents were obtained in anhydrous form from a Pure-Solv Multiple Dispensing System. All work-up and purification procedures were carried out with reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm) as visualization method.

S.2.2. Methods

All reactions were carried out under argon atmosphere unless otherwise stated. Flash column chromatography was performed with a Biotage Isolera One System and a Biotage ZIPTM 5g Si (40 – 63 μ M) flash cartridge. Gas chromatography (GC-FID) analysis was conducted on a Shimadzu GC-2014 instrument equipped with a methanizer (a nickel hydrogenation catalyst which transforms CO to methane), a Porapak Q (80/100) column, and a flame-ionization detector (FID). Gas chromatography (GC-MS) were performed with a Restek Rxi®-XLB (30 m, 0.25 mm ID, 0.25 M) column using a Thermo Finnigan gas chromatograph (GC) equipped with a Trace DSQ mass spectrometer, a program-mable temperature vaporization (PTV) injector, and a COMBI PAL autosampler (LEAP technologies, CTC Analytics). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (APCI) in a positive mode. The IR spectra were measured in KBr disks using ABB Bomem MB Series spectrometer with spectral resolution of 2 cm^{-1} . Nuclear magnetic resonance (NMR) spectra were recorded on Varian MERCURY plus-300 spectrometer (¹H 300 MHz, ¹³C 75 MHz) spectrometer or a MERCURY plus-400 spectrometer (¹H 400 MHz, ¹³C 100 MHz) or a MERCURY plus-500 spectrometer (¹H 500 MHz, ¹³C 125 MHz). Chemical shifts for ¹H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ¹³C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl₃: δ 77.0 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of

doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

S.2.3. Optimized Reaction Conditions

Unless otherwise mentioned, all reactions were performed under the previously optimized conditions.³ An oven-dried Biotage microwave tube was charged with [Ru(COD)Cl₂]_n (5.6 mg, 0.02 mmol), CuCl₂·2H₂O (10.2 mg, 0.06 mmol), and LiCl (42.5 mg, 5 equiv.). Toluene (1.0 mL) was then added, followed by the addition of aldehyde (0.2 mmol) and terminal alkyne (0.8 mmol) of choice. The reaction tube was then sealed under argon and placed into a preheated oil bath at 120°C. The reaction was run for 16 h. After the reaction mixture was cooled to room temperature, it was filtered through a short silica gel plug and eluted with dichloromethane. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (SiO₂).

S.2.4. ²H Isotope Labeling (Scheme 8)

The coupling between benzaldehyde and ²H-1-decyne under optimized conditions resulted in the desired product with scrambling of proton isotope information (²H/¹H = 42%/58% by ¹H NMR and 47%/53% by GC-MS) for the hydrogen connected to the olefinic C (C₂) bonded to C₈H₁₇ (Scheme 8A). On the other hand, the hydrogen connected to the olefinic C (C₁) bonded to the phenyl ring contained no deuterium (100% ¹H). When the reaction was performed with benzaldehyde and 1-decyne in the presence of D₂O (4 μL), similar to the previous case, the product exhibited partial incorporation of deuterium (²H/¹H = 14%/86% by ¹H NMR and 18%/82% by GC-MS) on C₂ and the hydrogen on C₁ contained only ¹H (Scheme 8C).

While ¹H NMR uses difference in integration values between the olefinic protons to ascertain percent deuterium incorporation, in a more direct evidence deuterium signals from C₂-²H for both *E* and *Z* isomers of the products were distinctly observed in the corresponding ²H-NMR spectra at 6.26 and 5.69 ppm, respectively (Figure S2).

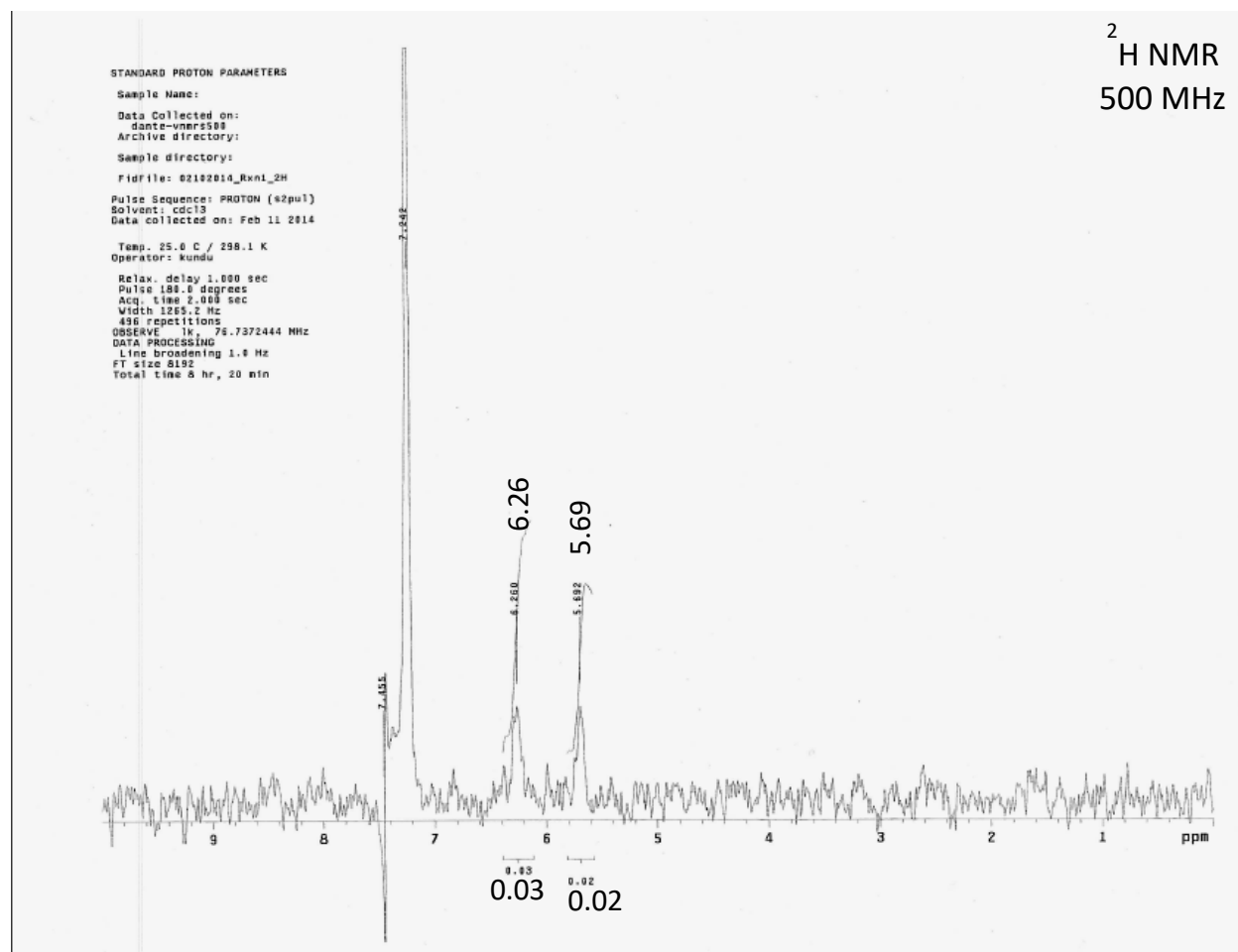


Figure S2. ²H NMR spectrum of partially deuterated *E*- and *Z*-dec-1-en-1-ylbenzene formed in the reaction shown in Scheme 8.

S.2.5. ¹⁸O Isotope Labeling

Reaction head-space analysis and IR spectroscopy were used for these studies. Head-space of the final reaction mixture was analyzed by GC-MS to reveal CO (decarbonylation, GC-MS and GC-FID). The analysis of a typical reaction between 4-anisaldehyde and 1-decyne revealed the presence of CO (*m/z* 28, GC-MS), which was confirmed by matching the retention times of a CO standard and the head-space gas in a GC-FID instrument with an in-line methanizer (Scheme 3C1, Figure 6). When the reaction was performed in the presence of H₂O¹⁸ (6 μL), the head-space analysis revealed (Figure S6) the formation of both CO¹⁶ (100% rel. abundance) and CO¹⁸ (47% rel. abundance).

Moreover, IR spectrum of the solid formed at the end of the reaction revealed multiple metal–CO stretches, indicative of more than one CO occupying the coordination sites of ruthenium. Binding of CO to Ru has previously been implicated for the termination of the catalytic cycle.³ We have investigated the association between the formation of Ru–CO complex and the catalyst

death in the theoretical section of this contribution (see text later). For the reaction in presence of H_2O^{16} (from hygroscopic LiCl or other sources), the IR $\nu(\text{CO})$ bands of the Ru–CO complex were at 1989, 2038, and 2062 cm^{-1} (Figure S4).⁴ The highest intensity $\nu(\text{CO})$ bands for the reaction in presence of H_2O^{18} were at 1975, 2024, 2037, and 2063 cm^{-1} . The appearance of lower frequency IR bands at 1975 and 2024 cm^{-1} is consistent with a Ru–CO¹⁸ complex.

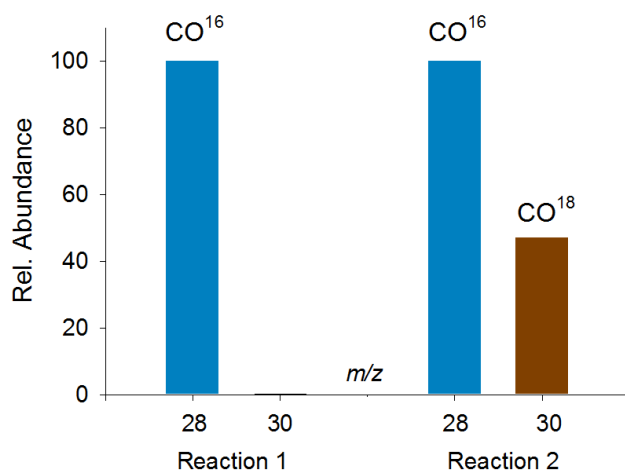


Figure S3. Relative abundances of CO^{16} and CO^{18} produced in reactions in Scheme 3C₁ (Reaction 1, x-axis) and 3C₂ (Reaction 2, x-axis), respectively.

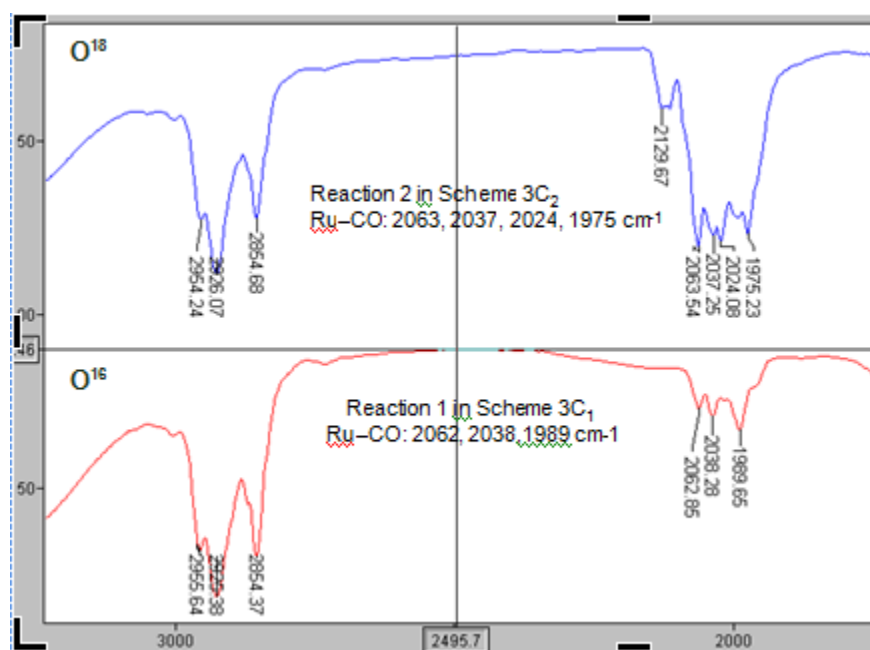


Figure S4. IR spectrum of the solid left over after the reaction.

S.2.6. Control Experiment with Methanol

Drying all the reagents, solvent, reaction tubes, the reactions were conducted in the presence of H_2O and MeOH respectively (at least 0.2 mmol/1.0 equiv each). In the case of H_2O , both

reactions should work; while with MeOH as proton source, if the reaction goes through mechanism in Scheme 6, intermediate XI would not be generated, and no product would be observed; however, the reaction will work following the mechanism in Scheme 4.

In glovebox, an oven-dried Biotage microwave tube were charged with $[\text{Ru}(\text{COD})\text{Cl}_2]_n$ (5.6 mg, 0.02 mmol), CuCl_2 (8.0 mg, 0.06 mmol), LiCl (42.4 mg, 5 equiv.). Then toluene (1.0 mL) was added, followed by injection of p-anisaldehyde (24 μL , 0.2 mmol), 1-decyne (144 μL , 0.8 mmol). The reaction tube was then sealed, moved out from glovebox, placed into the preheat oil bath (120 $^\circ\text{C}$). The stirring rate was set to 750 rpm. The reaction was run for 18 h. After the reaction mixture was cooled to room temperature, it was filtered through a short silica gel plug eluted with EtOAc. The volatiles were removed *in vacuo* and the internal standard CH_3NO_2 (3.6 μL) was injected into the reaction mixture. The reaction yield was measured by crude ^1H NMR recorded by Bruker 400.

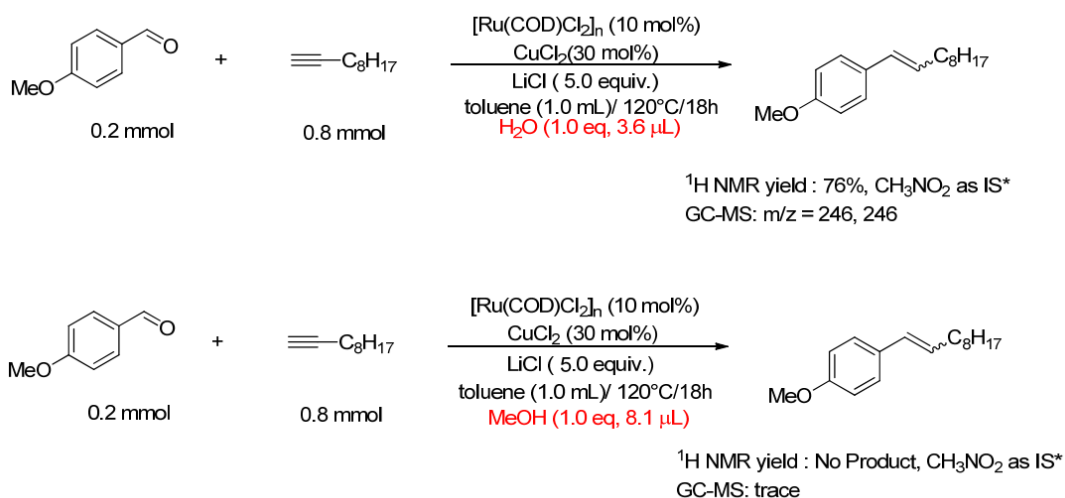


Figure S5. Control experiments with H_2O and Methanol.

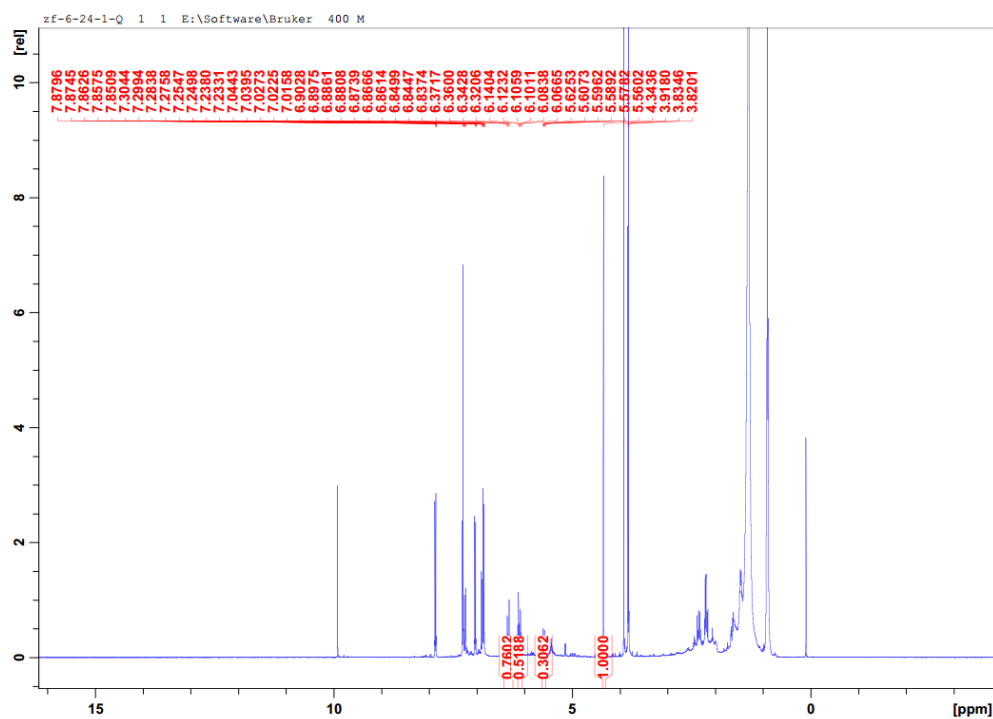


Figure S6. ^1H NMR spectrum of the product of reaction in Figure 9 using 1 eq. of H_2O .

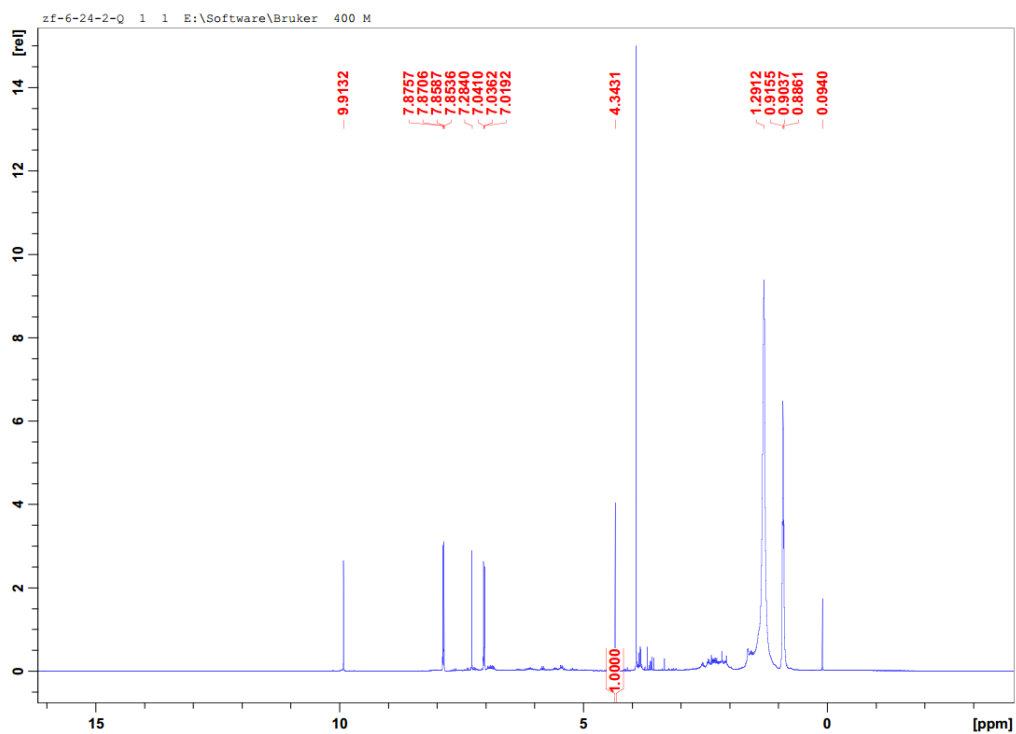


Figure S7. ^1H NMR spectrum of the result of reaction in Figure 9 using 1 eq. of MeOH : no product detected.

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 Sample Name :
 Misc Info :
 Vial Number: 13

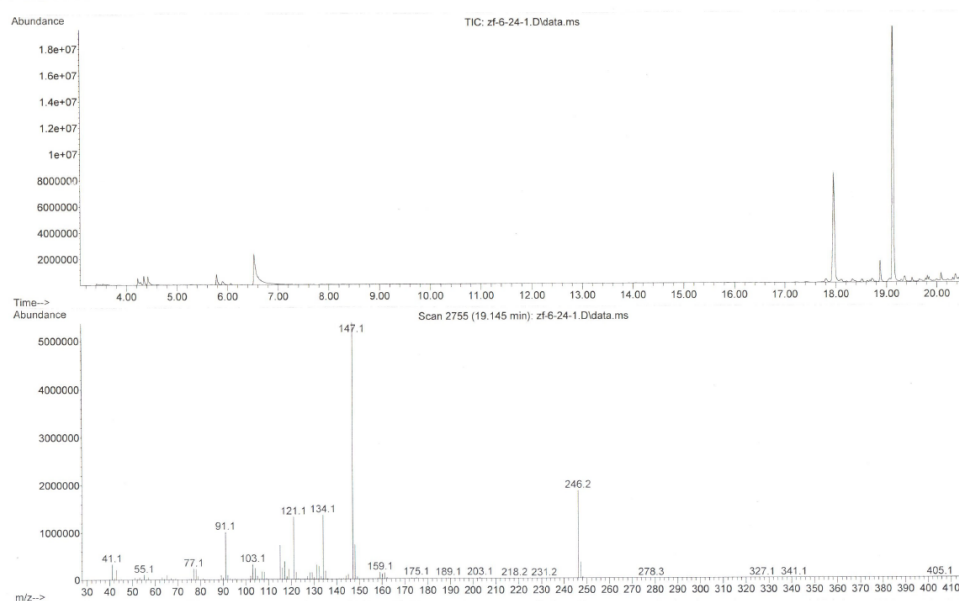


Figure S8. H₂O (1.0 eq., 3.6 μ L) was added and product (m/z =246, 246) was detected by LC-MS.

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 Instrument : 5977A-78908
 Sample Name :
 Misc Info :
 Vial Number: 14

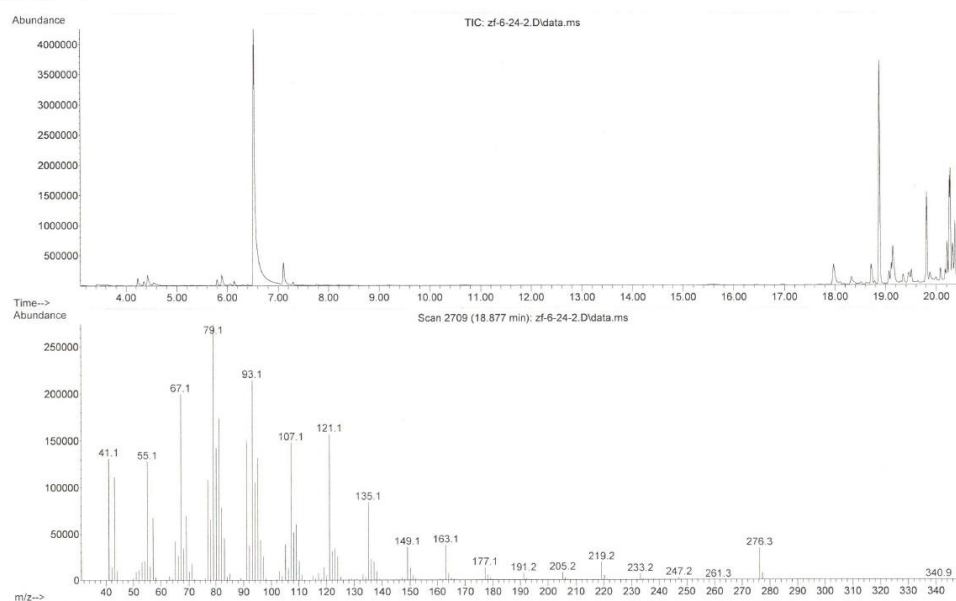
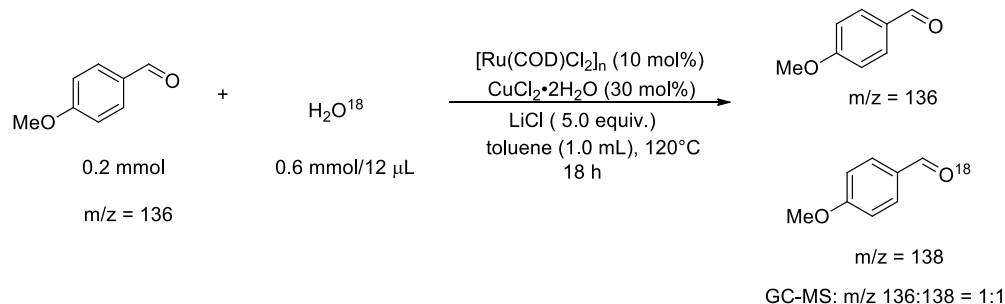


Figure S9. MeOH (1.0 eq., 8.1 μ L) was added and trace amount of product (m/z = 246, 276) was detected by GC-MS.

The two control experiments above were conducted with adding 1.0 equiv. of H₂O and 1.0 equiv. of MeOH to the reaction mixture respectively. The experimental results undoubtedly show that water as proton source is essential for this Ru-catalyzed transformation; while the reaction doesn't work with methanol as proton source. These observations are fully agreement with the experimental design to differentiate the mechanisms outlined above. In view of these results, the reaction mechanism highly favors the one in Scheme 6.

S.2.7. Aldehyde-Water Oxygen Exchange



Scheme S1. Reaction carried out in presence of H₂O¹⁸.

The reaction was conducted with 3 equiv. of H₂O¹⁸ under standard condition in the absence of alkyne for 18 hours. The starting material 4-methoxybenzaldehyde was recovered in 94% yield. The reaction indeed incorporated H₂O¹⁸ into the substrate 4-methoxybenzaldehyde, which was detected by GC-MS with the ratio 1:1.

S.2.8. Role of additives.

The reaction between 4-anisaldehyde and 1-decyne (optimized conditions: Ru(COD)Cl₂, CuCl₂·2H₂O, LiCl) resulted in a 86% product yield (GC-MS). Elimination of LiCl and CuCl₂·dihydrate from the reaction resulted in diminished product yields of 78% and 30% (GC-MS), respectively. On the other hand, a reaction without Ru(COD)Cl₂ and in the presence of CuCl₂·dihydrate (30 mol%) and LiCl (5 equiv) did not result in detectable product formation. This confirms that CuCl₂·dihydrate and LiCl, while beneficial for improving the product yield are not prerequisites for the formation of the target alkenes. The presumed role of copper is likely to assist the removal of CO from Ru, thus improving catalyst turnover and the product yield.⁵

S.3. References

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