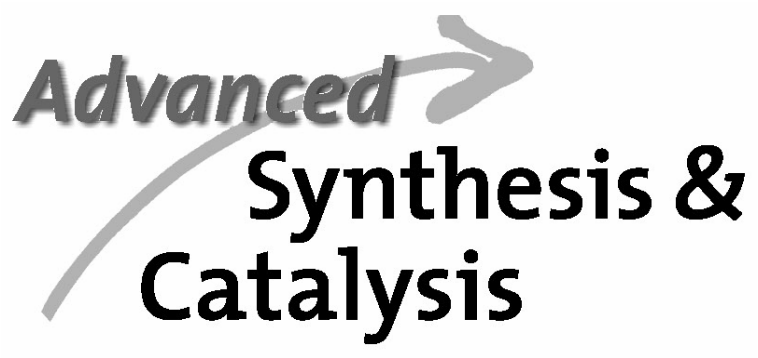

Supporting Information

Supporting Information

Metal Triflate-Catalyzed Regio- and Stereoselective Friedel-Crafts Alkenylation of Arenes with Alkynes in an Ionic Liquid: Scope and Mechanism

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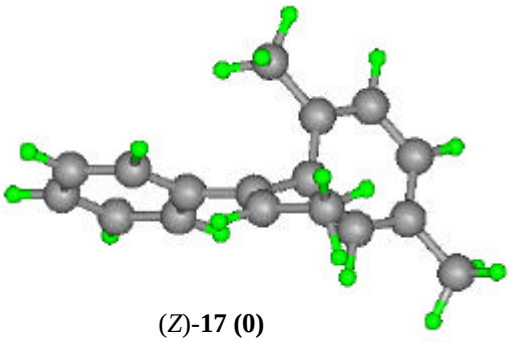
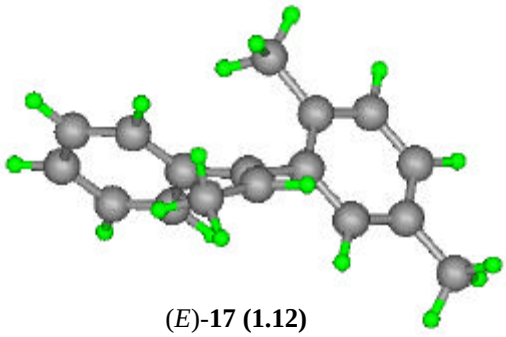
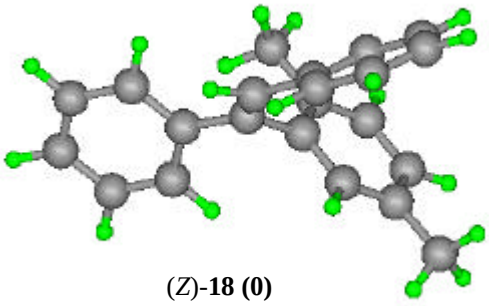
Computational Calculation of the Relative Energies of the (*E*)/(*Z*) Stereoisomers.



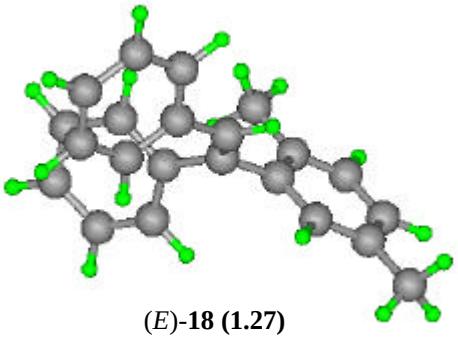
(*Z*)-**17 (0)**



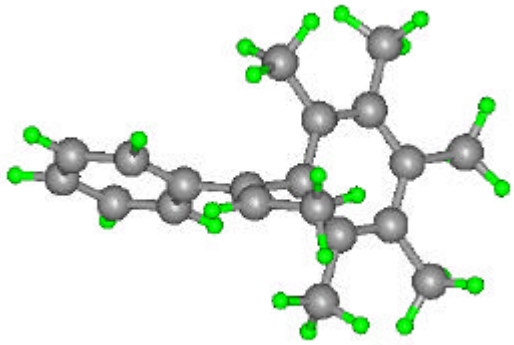
(*E*)-**17 (1.12)**



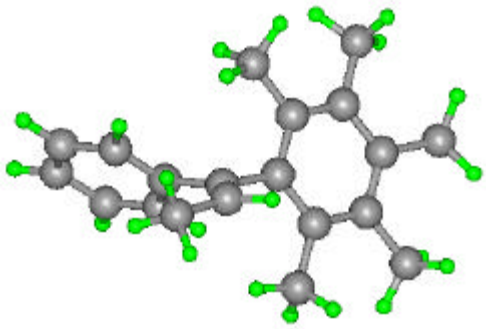
(*Z*)-**18 (0)**



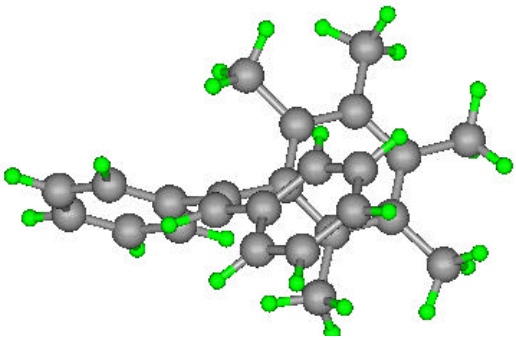
(*E*)-**18 (1.27)**



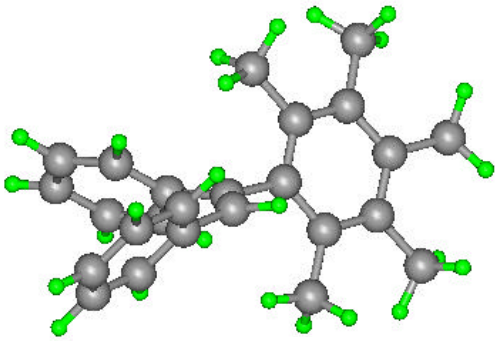
(*Z*)-**24 (0)**



(*E*)-**24 (2.19)**



(*Z*)-**25 (0)**



(*E*)-**25 (2.97)**

Figure. MP2/6-31G* optimized structures of (*Z*)- and (*E*)-isomers of 1-phenyl-1-(*p*-xylyl)propene (**17**), 1,2-diphenyl-1-(*p*-xylyl)ethene (**18**), 1-pentamethylphenyl-1-phenylpropene (**24**) and 1-pentamethylphenyl-1,2-diphenylpropene (**25**). The values in parentheses are relative energies (kcal/mol) of the (*E*)-isomers with respect to the corresponding (*Z*)-isomers.

Spectroscopic data of compounds

1,1-Diphenylpropene (6). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (d, *J* = 7.0 Hz, 3H), 6.17 (q, *J* = 7.0 Hz, 1H), 7.17-7.40 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 16.21, 124.65, 127.19, 127.31, 127.68, 128.54, 128.62, 130.54, 140.48, 142.92, 143.44.

1,1-Diphenylethene (7). ^{1}H NMR (300 MHz, $CDCl_3$): d 5.45 (s, 2H), 7.29-7.35 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 114.76, 128.16, 128.61, 128.72, 141.92, 150.48.

1-Phenyl-1-(*p*-xylyl)ethene (8). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.99 (s, 3H), 2.30 (s, 3H), 5.16 (d, *J* = 1.4 Hz, 1H), 5.73 (d, *J* = 1.4 Hz, 1H), 7.04-7.28 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): d 20.12, 21.42, 115.13, 127.00, 128.01, 128.71, 128.81, 130.49, 131.17, 133.43, 135.53, 141.16, 141.97, 150.09.

1-Ferrocenyl-1-mesitylethene (9). ^{1}H NMR (300 MHz, $CDCl_3$): d 2.21 (s, 6H), 2.29 (s, 3H), 4.11 (s, 5H), 4.12-4.18 (pseudo s, AA'BB', 4H), 5.03 (d, *J* = 2.1 Hz, 1H), 5.78 (d, *J* = 2.1 Hz, 1H), 6.86 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): d 20.56, 21.28, 67.92, 68.29, 69.87, 86.86, 113.37, 128.27, 135.75, 136.28, 139.18, 143.95, 146.08.

1-Ferrocenyl-1-pentamethylphenylethene (10). ^{1}H NMR (300 MHz, $CDCl_3$): d 2.20 (s, 6H), 2.21(s, 6H), 2.25 (s, 3H), 4.11 (s, 5H), 4.13-4.16 (m, AA'BB', 4H), 5.00 (d, *J* = 2.1 Hz, 1H), 5.78 (d, *J*=2.1 Hz, 1H); ^{13}C NMR (75MHz, $CDCl_3$): d 16.87, 16.98, 18.57, 67.95, 68.24, 69.77, 87.80, 113.34, 131.21, 132.41, 133.62, 139.81, 147.64.

1-(*p*-Trifluoromethylphenyl)-1-(*p*-xylyl)ethene (11). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.98 (s, 3H), 2.34, (s, 3H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.80 (d, *J* = 1.1 Hz, 1H), 7.02 – 7.58 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): d 20.10, 21.38, 116.82, 123.50 (q, ^{3}J(C-C-C-F) = 3.8 Hz), 124.65 (q, ^{1}J(C-F) = 272.4 Hz), 124.67 (q, ^{3}J(C-C-C-F) = 3.8 Hz), 129.12, 129.28, 130.39, 130.69, 131.16, 131.31 (q, ^{2}J(C-C-F) = 32.0 Hz), 133.26, 135.83, 140.96, 142.05, 149.00.

1-(*p*-Chlorophenyl)-1-(*p*-xylyl)ethene (12). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.99 (s, 3H), 2.33 (s, 3H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.71 (d, *J* = 1.2 Hz, 1H), 7.01 – 7.25 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): d 19.99, 21.31, 115.52, 128.22, 128.83, 128.88, 130.50, 131.02, 133.25, 133.78, 135.62, 139.60, 141.35, 148.94.

(*E*)-4-Mesityl-3-buten-2-one (13). ^{1}H NMR (300 MHz, $CDCl_3$):?d 2.28 (s, 3H, CH_3), 2.32 (s, 6H, $2CH_3$), 2.38 (s, 3H, CH_3), 6.33 (d, *J* = 16.5 Hz, 1H), 6.89 (s, 2H), 7.67 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): d 20.70, 20.73, 27.04, 128.96, 130.52, 131.99, 136.41, 138.11, 141.54, 197.89.

(*E*)-4-Pentamethylphenyl-3-buten-2-one (14). ^{1}H NMR (300 MHz, $CDCl_3$): d 2.21 (s, 12H), 2.25 (s, 3H), 2.39 (s, 3H), 6.15 (d, *J* = 16 Hz, 1H), 7.72 (d, *J* = 16 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): d 16.24, 16.66, 17.71, 27.14, 130.85, 132.42, 132.59, 133.65, 135.07, 144.86, 197.94.

1,1,2-Triphenylethene (15). ^{1}H NMR (300 MHz, $CDCl_3$): d 6.94-7.33 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): d 53.76, 126.94, 127.62, 127.72, 128.14, 128.27, 128.39, 128.83, 129.69, 130.48, 137.48, 140.47, 142.70, 143.51.

Ethyl 3,3-diphenylpropenoate (16). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.11 (t, *J* = 7.1 Hz, 3H), 4.05 (q, *J* = 7.1 Hz, 2H), 6.36 (s, 1H), 7.21 – 7.39 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): d 14.37, 60.42, 117.92, 128.24, 128.47, 128.67, 128.95, 129.52, 129.75, 139.4, 141.22, 156.82, 166.51.

(*Z*)-1-Phenyl-1-(*p*-xylyl)propene (17). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.59 (d, *J* = 6.9 Hz, 3H), 2.03 (s, 3H), 2.31 (s, 3H), 6.27 (q, *J* = 6.9 Hz ,1H), 6.82-7.35 (m, 7H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 15.91, 19.49, 21.46, 124.09, 126.56, 127.04, 128.28, 128.32, 128.66, 130.35, 131.08, 133.86, 135.52, 139.57, 142.00.

(*Z*)-1,2-Diphenyl-1-(*p*-xylyl)ethene (18). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.99 (s, 3H), 2.27 (s, 3H), 6.94-7.32 (m, 14H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 19.51, 21.38, 127.02, 127.25, 127.70, 128.39, 128.50, 128.73, 128.78, 129.39, 130.78, 130.90, 133.70, 136.18, 137.79, 139.87, 141.79, 142.88.

Ethyl (*Z*)-3-Phenyl-3-(*p*-xylyl)propenoate (19). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.07 (t, *J* = 7.1 Hz, 3H), 2.04 (s, 3H), 2.31 (s, 3H), 4.01 (q, *J* = 7.1 Hz, 2H), 6.49 (s, 1H), 6.85 (s, 1H), 7.03 – 7.13 (m, 2H), 7.25 - 7.32 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 14.33, 19.34, 21.36, 60.27, 117.95, 127.82, 128.86, 128.90, 129.31, 129.74, 130.03, 132.62, 135.08, 138.87, 139.85, 156.31, 166.25.

(*Z*)-1-Mesityl -1-phenylpropene (20). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.52 (d, *J* = 6.9 Hz, 3H), 2.04 (s, 6H), 2.31 (s, 3H), 6.36 (q, *J* = 6.9 Hz, 1H), 6.91 (s, 2H), 7.11 – 7.32 (m, 5H); ^{13}C NMR (75.5 MHz): d 15.0, 15.4, 19.7, 20.5, 21.0, 21.1, 123.3, 125.5, 126.2, 126.4, 126.6, 127.8, 128.1, 128.2, 128.3, 129.1, 135.6, 136.0, 136.2, 136.3, 136.4, 139.4, 139.5, 139.9, 140.5, 140.9.

(*Z*)-1,2-Diphenyl-1-mesitylethene (21). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.99 (s, 6H), 2.04 (s, 6H), 2.33 (s, 3H), 6.91 (s, 1H), 6.80 – 7.47 (m, 12H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): d 20.01, 21.40, 126.21, 127.16, 127.48, 128.26, 128.42, 128.64, 128.65, 128.92, 136.12, 136.25, 137.07, 137.70, 140.02, 141.73.

(*Z*)-4-Mesityl-4-phenyl-3-buten-2-one (22). ^{1}H NMR (300 MHz, $CDCl_3$):?d 1.77 (s, 3H, CH_3), 2.05 (s, 6H, $2CH_3$), 2.33 (s, 3H, CH_3), 6.82 (s, 1H), 6.94 (s, 2H), 7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): d 19.80, 21.12, 29.31, 127.08, 127.89, 128.60, 128.70, 129.58, 134.89, 135.12, 137.68, 138.50, 152.66, 199.51.

Ethyl (*Z*)-3-mesityl-3-phenylpropenoate (23). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.09 (t, *J* = 7.1 Hz, 3H), 2.02 (s, 6H), 2.31 (s, 3H), 4.02(q, *J* = 7.1 Hz, 2H), 6.61 (s, 1H), 6.89(s, 2H), 7.15 – 7.65 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): d 13.99, 19.74, 21.15, 59.85, 117.54, 126.94, 127.99, 128.64, 129.46, 134.62, 135.22, 136.68, 138.35, 155.06, 165.67.

(*Z*)-1-Pentamethylphenyl-1-phenyl-1-propene (24). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.48 (d, *J* = 6.6 Hz, 3H), 2.03 (s, 6H), 2.22 (s, 6H), 2.27 (s, 3H), 6.36 (q, *J* = 6.8 Hz, 1H), 7.11-7.31 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): d 15.15, 16.63, 16.75, 17.17, 123.24, 125.73, 126.42, 128.22, 131.52, 132.19, 133.32, 135.96, 141.19, 141.79.

(*Z*)-1,2-Diphenyl-1-pentamethylphenylethene (25). ^{1}H NMR (300 MHz, $CDCl_3$): d 2.00 (s, 6H), 2.21 (s, 6H), 2.30 (s, 3H), 7.13 (s, 1H), 6.36 (q, *J* = 6.8 Hz, 2H), 6.87-7.40 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): d 16.62, 16.86, 17.18, 126.18, 126.71, 127.09, 127.82, 128.12, 128.35, 128.59, 131.11, 132.72, 133.90, 136.28, 137.63, 141.70, 142.18.

(*Z*)-4-Pentamethylphenyl-4-phenyl-3-buten-2-one (26). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.68 (s, 3H), 2.03 (s, 6H), 2.23 (s, 6H), 2.29 (s, 3H), 6.82 (s, 1H), 7.28-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): d 16.46, 16.83, 17.67, 29.29, 127.30, 128.03, 128.65, 129.47, 130.37, 132.85, 134.84, 135.19, 139.18, 154.80, 200.18.

Ethyl (*Z*)-3-pentamethylphenyl-3-phenylpropenoate (27). ^{1}H NMR (300 MHz, $CDCl_3$): d 1.07 (t, *J* = 7.1 Hz, 3H, (*Z*)-isomer), 1.16 (t, *J* = 7.1 Hz, 3H, (*E*)-isomer), 2.00 (s, 6H, (*Z*)-isomer), 2.21 (s, 6H, (*Z*)-isomer), 2.26 (s, 3H, (*Z*)-isomer), 4.00 (q, *J* = 7.1 Hz, 2H, (*Z*)-isomer), 4.30 (q, *J* =7.1 Hz, 2H, (*E*)-isomer), 5.86 (s, 1H, (*E*)-isomer), 6.62 (s, 1H, (*Z*)-isomer), 7.21–7.40 (m, 5H); ^{13}C NMR($CDCl_3$, 75.5 MHz): d 13.89, 16.44, 16.79, 17.44, 59.65, 117.37, 127.09, 128.53, 129.24, 129.86, 131.89, 133.75, 135.47, 139.05, 156.88, 165.68.

(Z)-1-(1-Naphthyl)-1-phenylpropene (28). The reaction gave an inseparable mixture of four isomers of 1-naphthyl and 2-naphthyl regioisomers, including the corresponding *E*/*Z* isomers. The isomer ratio determined by GC-MS analysis was 75/19/4/1.

^{1}H NMR (300 MHz, $CDCl_3$): δ?.55 (d, *J* = 7.1 Hz, 3H, (*Z*)-isomer), 6.52 (q, *J* = 7.1 Hz, 1H, (*Z*)-isomer), 7.11~ 7.98 (m, 12H).

(Z)-1-(Chlorophenyl)-1-phenylpropene (29). The reaction gave an inseparable mixture of four isomers of ortho and para regioisomers, including the corresponding *E*/*Z* isomers. The isomer ratio determined by GC-MS analysis was 11/15/31/39.

(Z)-1-(Chlorophenyl)-1,2-diphenylethene (30). The reaction gave an inseparable mixture of four isomers of ortho and para regioisomers, including the corresponding *E*/*Z* isomers. The isomer ratio determined by GC-MS analysis was 8/18/34/40.

Compound 31. ^{1}H NMR (300 MHz. $CDCl_3$): δ 7.1-7.7 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 80.63, 89.08, 119.68, 121.85, 126.78. 129.05, 129.97, 131.41, 133.57, 150.57.

Compound 33. ^{1}H NMR (300 MHz. $CDCl_3$): δ 2.09 (s, 3H), 7.26-7.28 (m, 1H), 7.48-7.50 (m, 2H), 7.61 (s, 1H), 7.80-7.88 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 4.42, 72.58, 88.72, 118.99, 121.16, 126.42, 127.15, 128.19, 128.23, 130.02, 132.07, 134.09, 148.13, 152.52.

Compound 35. ^{1}H NMR (300 MHz. $CDCl_3$): δ 7.35-7.91 (m, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 80.78, 89.29, 119.11, 119.72, 121.20, 126.51, 127.23, 128.26, 128.29, 129.16, 130.12, 131.55, 132.16, 133.70, 134.15, 148.22, 152.96.

Compound 37. ^{1}H NMR (300 MHz. $CDCl_3$): δ 3.75-3.78 (br s, 9H), 6.81-6.83 (br s, 2H), 7.20-7.48 (m, 5H), 7.76 (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 56.65, 61.48, 83.87, 86.23, 98.17, 120.37, 129.10, 130.86, 133.08, 133.93, 135.61, 151.39, 153.86.

Compound 39. ^{1}H NMR (300 MHz. $CDCl_3$): δ 5.95 (s, 2H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 7.26-7.54 (m, 6H), 7.88 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 83.85, 86.23, 101.83, 103.27, 108.59, 113.77, 120.42, 129.00, 130.71, 132.01, 133.05, 145.16, 148.29, 151.50.

4-Phenylcoumarin (32). ^{1}H NMR (300 MHz, $CDCl_3$): d 6.38 (s, 1H), 7.20–7.59 (m, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 115.59, 117.73, 124.56, 127.41, 128.84, 129.27, 130.08, 132.32, 135.61, 154.60, 156.09, 161.17.

1-Methyl-3*H*-benzo[*f*]chromen-3-one (34). ^{1}H NMR (300 MHz, $CDCl_3$): d 2.95 (s, 3H), 6.40 (s, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.65 (t, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 8.60 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 26.92, 114.95, 117.01, 118.29, 125.46, 125.86, 128.32, 130.17, 130.70, 131.81, 134.12, 154.59.

1-Phenyl-3*H*-benzo[*f*]chromen-3-one (36). ^{1}H NMR (300 MHz. $CDCl_3$): d 6.32 (s, 1H), 7.00-7.50 (m, 9H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 113.56, 117.34, 118.01, 125.87, 126.42, 127.21, 127.97, 129.51, 129.65, 129.72, 129.86, 131.82, 134.46, 140.09, 155.29, 156.99, 160.85.

5,6,7-Trimethoxy-4-phenylquinolin-2(1*H*)-one (38). ^{1}H NMR (300 MHz. $CDCl_3$): d 3.25 (s, 3H), 3.79 (s, 3H), 3.98 (s, 3H), 6.39 (s, 1H), 6.77 (s, 1H), 7.2-7.5 (m, 7H), 13.03 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 56.22, 60.74, 61.05, 94.36, 108.52, 119.86, 127.22, 127.53, 136.98, 138.61, 141.04, 150.94, 152.50, 156.59, 163.89.

8-Phenyl-[1,3]dioxolo[4,5-*g*]quinolin-6(5*H*)-one (40). ^{1}H NMR (300 MHz. $CDCl_3$): d 6.01 (s, 2H), 6.56 (s, 1H), 6.90 (s, 1H), 7.00 (s, 1H), 7.4-7.5 (m, 5H), 12.71 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): d 96.84, 102.04, 104.00, 114.82, 128.65, 128.71, 128.95, 135.83, 137.30, 145.09, 151.24, 154.27.

^{1}H NMR data of compounds isolated from isomerization experiment.

^{1}H NMR (300 MHz, $CDCl_3$) of (*Z*)-(**18**). d 1.99 (s, 3H), 2.27 (s, 3H), 6.94-7.32 (m, 14H); ^{1}H NMR (300 MHz, $CDCl_3$) of (*E*)-(**18**). d 2.07 (s, 3H), 2.32 (s, 3H), 6.94-7.32 (m, 14H).