

Supporting Information

Reaction control in heterogeneous catalysis using montmorillonite: Switching between acid-catalysed and red-ox processes

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1. General methods

All the chemicals were purchased from Aldrich Chemical Co and used without further purification unless stated otherwise. Yields refer to the chromatographically and spectroscopically (^1H and ^{13}C) homogeneous materials, unless otherwise stated. All glassware utilized was flame-dried before use. Reactions were monitored by TLC carried out on 0.25 mm Macherey Nagel silica gel plates. Developed TLC plates were visualized under a short-wave UV lamp and by heating plates that were dipped in $\text{Ce}(\text{SO}_4)_2$. Flash column chromatography (FCC) was performed using flash silica gel (230–400) and employed a solvent polarity correlated with TLC mobility. NMR experiments were conducted on a Varian Unity and Bruker Avance 300 MHz instruments using CDCl_3 (99.9% D) as the solvent, with chemical shifts (δ) referenced to internal standards residual CHCl_3 and CDCl_3 , (7.26 ppm ^1H , 77.0 ppm ^{13}C) or Me_4Si as an internal reference (0.00 ppm). Chemical shifts are in parts per million (ppm). Mass spectra were recorded on Jeol JS102 high-resolution mass spectrometer. The measurements of EPR were made with a Jeol JES-TE300 X band fashion spectrometer with a cylindrical cavity in the mode TE_{011} . The external calibration of the magnetic field was made with a precision gaussmeter, Jeol ES-FC5.

2. Experimental procedures

Preparation of modified montmorillonite

The natural montmorillonite sample was the same as we described previously.¹ Modification and characterization of montmorillonite with $\text{CF}_3\text{SO}_3\text{H}$ was realized according to the method previously reported.¹

General procedure for the synthesis of tetrasubstituted furans

A solution of hydroquinone (50% mmol) and modified montmorillonite (20%w) in anhydrous benzene (30 mL) was deoxygenated under an argon atmosphere. Then a solution of α -hydroxyl ketones **1** (1 mmol) in deoxygenated benzene (5 mL) was added at room temperature. The reaction mixture was stirred for 12 h at reflux under argon atmosphere. After that time, the reaction mixture was filtered and concentrated in vacuum. The resulting residue was purified by flash column chromatography on silica gel.

General procedure for the synthesis of 1,2-diketones

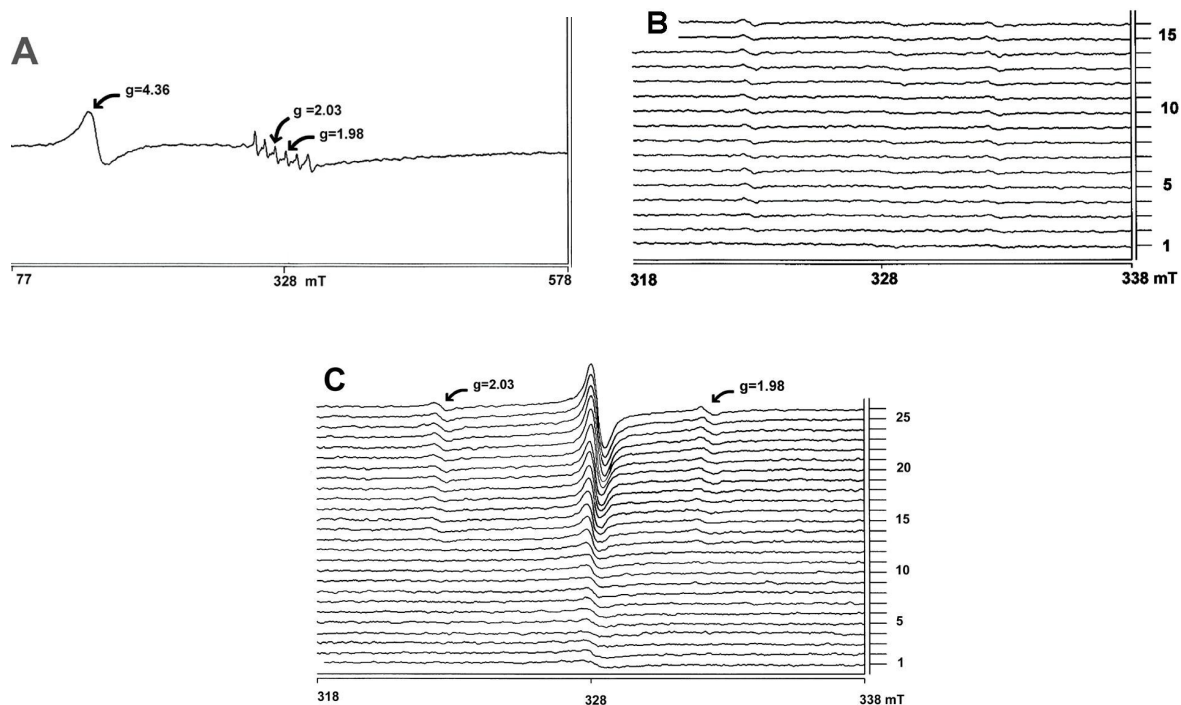
A solution of α -hydroxyl ketones **1** (1 mmol) and modified montmorillonite (20%w) in anhydrous benzene (30 mL) was stirred for 6 h at reflux under argon atmosphere. After that time, the reaction mixture was filtered and concentrated in vacuum. The resulting residue was purified by flash column chromatography on silica gel.

Reuse of the catalyst

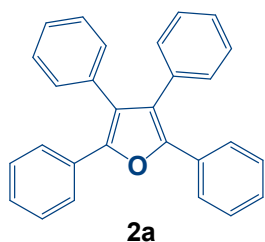
When the organic reactions were complete, the montmorillonite catalyst was removed by filtration, washed with ethyl acetate, dried overnight in an oven at 100 °C, and subjected to a second experimental run with the same substrate. After the completion of four runs, results indicated no significant variation in yield.

EPR analysis

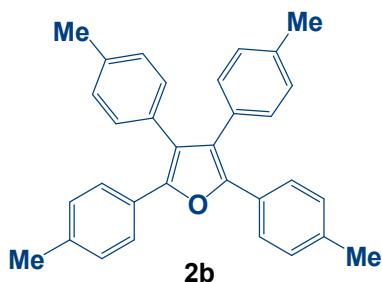
A tube was prepared adding 40 mg of the modified montmorillonite and dried at 70 °C under vacuum; the tube was analyzed by EPR (Figure **S1A**). Then 2 mL of anhydrous benzene were added and the sample was analyzed (Figure **S1B**). The last experiment was carried out after adding benzoine to the tube, scanning every 5 minutes (Figure **S1C**).

**Figure S1**

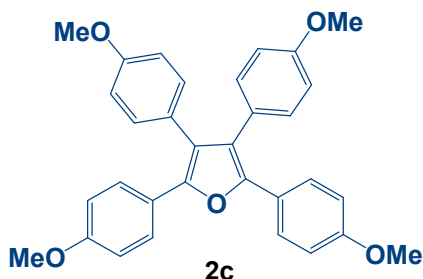
3. Characterization data



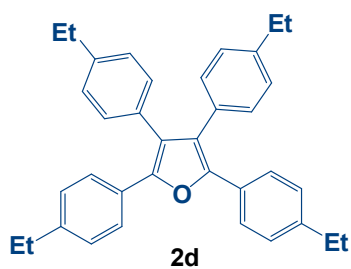
2,3,4,5-tetraphenylfuran 2a:² Following the general procedure for the synthesis of tetrasubstituted furans, the reaction was carried out starting from benzoin **1a** (212 mg, 1 mmol), hydroquinone (55 mg, 0.5 mmol) and modified montmorillonite (42 mg), to give 111 mg of a white solid (60%, mp 173-174 °C); ¹H NMR (CDCl₃): δ 7.51-7.49 (m, 4H), 7.26-7.20 (m, 12H), 7.16-12.13 (m, 4H); ¹³C NMR (CDCl₃): δ 147.7, 133.1, 130.9, 130.4, 128.5, 128.3, 127.3, 127.1, 125.8, 125.1. HRMS (FAB) calcd for C₂₈H₂₀O 372.1514, found 372.1518.



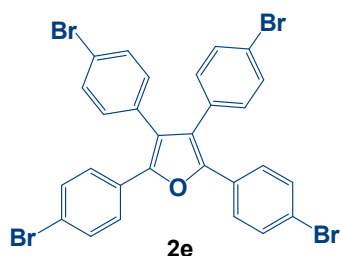
2,3,4,5-tetra-*p*-tolylfuran 2b:² Following the general procedure for the synthesis of tetrasubstituted furans, the reaction was carried out starting from benzoin **1b** (240 mg, 1 mmol), hydroquinone (55 mg, 0.5 mmol) and modified montmorillonite (48 mg), to give 133 mg of a white solid (62%, mp 185-186 °C); ¹H NMR (CDCl₃): δ 7.37 (d, *J* = 8.4 Hz, 4H), 7.04 (d, *J* = 8.0 Hz, 4H), 7.02 (s, 8H), 2.36 (s, 12H); ¹³C NMR (CDCl₃): δ 147.5, 136.9, 136.5, 130.3, 130.2, 129.0, 128.7, 128.4, 125.8, 124.3, 29.7, 21.3. HRMS (FAB) calcd for C₃₂H₂₈O 428.2141, found 428.2139.



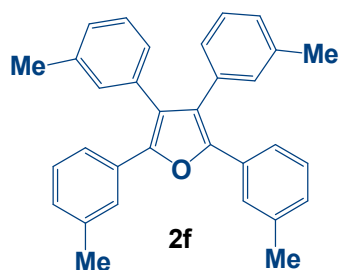
2,3,4,5-tetrakis(4-methoxyphenyl)furan 2c:³ Following the general procedure for the synthesis of tetrasubstituted furans, the reaction was carried out starting from benzoin **1c** (272 mg, 1 mmol), hydroquinone (55 mg, 0.5 mmol) and modified montmorillonite (54 mg), to give 160 mg of a white solid (65%, mp 207-209 °C); ¹H NMR (CDCl₃): δ 7.42 (d, *J* = 8.8 Hz, 4 H), 7.04 (d, *J* = 8.8 Hz, 4 H), 6.79 (d, *J* = 8.2 Hz, 4 H), 6.77 (d, *J* = 8.4 Hz, 4 H), 3.78 (s, 12H); ¹³C NMR (CDCl₃): δ 147.7, 133.1, 130.9, 130.4, 128.5, 128.3, 127.3, 127.1, 125.8, 125.1, 55.1, 55.0. HRMS (FAB) calcd for C₃₂H₂₈O₅ 492.1937, found 492.1941.



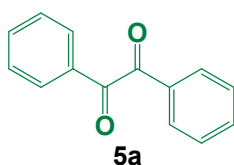
2,3,4,5-tetrakis(4-ethylphenyl)furan 2c:⁴ Following the general procedure for the synthesis of tetrasubstituted furans, the reaction was carried out starting from benzoin **1d** (268 mg, 1 mmol), hydroquinone (55 mg, 0.5 mmol) and modified montmorillonite (52 mg), to give 157 mg of a white solid (65%, mp 194-196 °C); ¹H NMR (CDCl₃): δ 7.35 (d, *J* = 8.2 Hz, 4 H), 7.03-6.89 (m, 12H), 2.58-2.51 (m, 8H), 1.16 (t, *J* = 7.6 Hz, 6H), 1.15 (t, *J* = 7.6 Hz, 6H); ¹³C NMR (CDCl₃): δ 145.5, 143.2, 142.7, 130.6, 130.3, 128.7, 127.8, 127.7, 125.8, 124.4, 28.6, 28.5, 15.3, 15.1. HRMS (FAB) calcd for C₃₆H₃₆O 484.2766, found 484.2769.



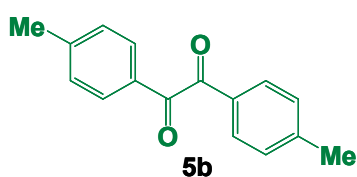
2,3,4,5-tetrakis(4-bromophenyl)furan 2e:² Following the general procedure for the synthesis of tetrasubstituted furans, the reaction was carried out starting from benzoin **1e** (368 mg, 1 mmol), hydroquinone (55 mg, 0.5 mmol) and modified montmorillonite (72 mg), to give 205 mg of a white solid (60%, mp 165-167 °C); ¹H NMR (CDCl₃): δ 7.42 (d, *J* = 8.0 Hz, 8 H), 7.32 (d, *J* = 8.0 Hz, 4 H), 6.98 (d, *J* = 8.0 Hz, 4 H); ¹³C NMR (CDCl₃): δ 147.3, 131.9, 131.7, 131.1, 128.9, 127.3, 121.9, 121.8 HRMS (FAB) calcd for C₂₈H₁₆BrO 683.7935, found 683.7939.



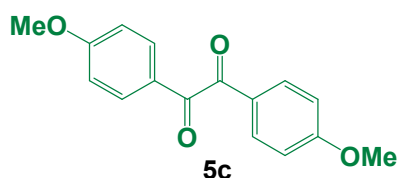
2,3,4,5-tetra-*m*-tolylfuran:² Following the general procedure for the synthesis of tetrasubstituted furans, the reaction was carried out starting from benzoin **1f** (240 mg, 1 mmol), hydroquinone (55 mg, 0.5 mmol) and modified montmorillonite (48 mg), to give 128 mg of a white solid (60%, mp 100-102 °C); ¹H NMR (CDCl₃): δ 7.41 (s, 2 H), 7.25 (d, *J* = 5.6 Hz, 2 H), 7.12 (t, *J* = 7.6 Hz, 4 H), 7.04-6.94 (m, 8 H), 2.30 (s, 6 H), 2.23 (s, 6 H); ¹³C NMR (CDCl₃): δ 147.6, 137.9, 137.7, 133.2, 131.1, 128.1, 127.8, 127.5, 126.4, 125.1, 123.1, 21.5, 21.3. HRMS (FAB) calcd for C₃₂H₂₈O 428.2140, found 428.2145.



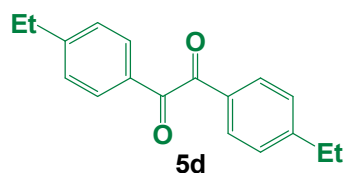
Benzil 5a:⁵ Following the general procedure for the synthesis of 1,2-diketones, the reaction was carried out starting from benzoin **1a** (212 mg, 1 mmol) and modified montmorillonite (42 mg), to give 199 mg of a white solid (95%, mp 92-94 °C); ¹H NMR (CDCl₃): δ 8.01-7.94 (m, 4H), 7.70-7.64 (m, 2H), 7.56-7.50 (m, 4H); ¹³C NMR (CDCl₃): δ 194.6, 134.9, 133.0, 129.9, 129.0. HRMS (FAB) calcd for C₁₄H₁₀O₂ 210.0681, found 210.0682.



Benzil 5b:⁵ Following the general procedure for the synthesis of 1,2-diketones, the reaction was carried out starting from benzoin **1b** (240 mg, 1 mmol) and modified montmorillonite (48 mg), to give 226 mg of a white solid (95%, mp 102-104 °C); ¹H NMR (CDCl₃): δ 7.68 (d, *J* = 8 Hz, 4H), 7.28 (d, *J* = 8 Hz, 4H), 2.40 (s, 6H); ¹³C NMR (CDCl₃): δ 194.6, 146.2, 130.9, 130.1, 129.8, 22.0. HRMS (FAB) calcd for C₁₆H₁₄O₂ 238.0994, found 238.0996.

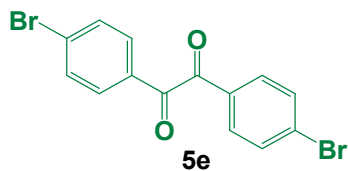


Benzil 5c:⁵ Following the general procedure for the synthesis of 1,2-diketones, the reaction was carried out starting from benzoin **1c** (272 mg, 1 mmol) and modified montmorillonite (54 mg), to give 256 mg of a white solid (95%, mp 131-133 °C); ¹H NMR (CDCl₃): δ 7.69 (d, *J* = 8 Hz, 4H), 6.92 (d, *J* = 8 Hz, 4H), 3.88 (s, 6H); ¹³C NMR (CDCl₃): δ 193.6, 165.0, 132.5, 126.5, 114.4, 55.8. HRMS (FAB) calcd for C₁₆H₁₄O₄ 270.0892, found 270.0893.



Benzil 5d:⁵ Following the general procedure for the synthesis of 1,2-diketones, the reaction was carried out starting from benzoin **1d** (268 mg, 1 mmol) and modified montmorillonite (52 mg), to give 253 mg of a white solid (95%, mp 122-124 °C); ¹H NMR (CDCl₃): δ 7.80 (d, *J* = 8 Hz, 4H), 7.23 (d, *J* = 8 Hz, 4H), 2.62 (q, *J* = 7.6 Hz, 4H), 1.15 (t, *J* = 7.6 Hz, 6H); ¹³C

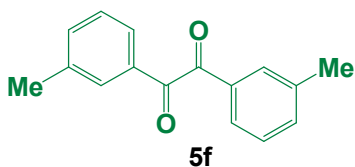
NMR (CDCl₃): δ 194.7, 152.3, 130.9, 130.2, 128.6, 29.3, 15.2. HRMS (FAB) calcd for C₁₈H₁₈O₂ 266.1307, found 266.1309.



Benzil 5e:⁵ Following the general procedure for the synthesis of 1,2-diketones, the reaction was carried out starting from benzoin **1e** (368 mg, 1 mmol) and modified montmorillonite (72 mg), to give 328 mg of a white solid (90%, mp 223-225 °C); ¹H NMR (CDCl₃): δ 7.83 (d, J = 8 Hz, 4H), 7.67 (d, J = 8 Hz, 4H); ¹³C NMR (CDCl₃): δ 192.7, 132.7,

131.7, 131.4, 130.9. HRMS (FAB) calcd for C₁₄H₈Br₂O₂ 365.8891, found 365.8893.

Benzil 5f:⁵ Following the general procedure for the synthesis of 1,2-diketones, the reaction was carried out starting from benzoin **1f** (240 mg, 1



mmol) and modified montmorillonite (48 mg), to give 226 mg of a white solid (95%, mp 125-127 °C); ¹H NMR (CDCl₃): δ 7.82-7.73 (m, 4H), 7.47 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 2.40 (s, 6H); ¹³C NMR (CDCl₃): δ 195.1,

139.1, 135.8, 133.2, 130.4, 129.0, 127.4, 21.4. HRMS (FAB) calcd for C₁₆H₁₄O₂ 238.0994, found 238.0998.

4. References

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