An Efficient C=C Double Bonds Formation Reaction via a New Synthetic Strategy: Self-Sorting Tandem Reaction

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In order to support the hypothetic mechanism (Scheme 3 in the text), following experiments were carried out.

- (1) A mixture of acetophenone **1** (1 equiv), CuO (1 equiv), and iodine (1 equiv) in methanol was heated at 65 °C for 1 h, compound **2** was obtained in 96% yield. Similarly, compound **12a** yielded **12a'** in 92% yield (Scheme 4). Experimental results showed that other aryl methyl ketones also could afford the corresponding α -iodoketones in excellent yields, these results will be reported in another paper. The solvent could not be DMSO, otherwise, compound **2** would be transformed into **6b/c** as reported in the paper. Based on this, we believe that the α -iodoketones might be the key intermediates in this type of reaction.

- (2) When heating the mixture of **2** (2.5 mmol), iodine (2.5 mmol), CuO (5.0 mmol) in DMSO (15 mL) at 65 °C for 12 h, the olefinic products **6b/c** were also obtained (83%). Similarly, **12a'** gave isomers **12b/c** in 85% yield under the same conditions. In addition, heating the mixture of **2** (2.5 mmol), HI solution (45%, 5 mmol) in DMSO (15 mL) at 65 °C for 12 h, the olefinic products **6b/c** were obtained only in 18% yield. These results indicated the reaction underwent intermediates α -iodoketones (**2** and **12a'**), sequentially generated target products via self-sorting tandem reaction (Scheme 5).

- (3) We also successfully got compound **12a''** from **12a'** in DMSO at 65 °C for 8 h (yield, 87%). To our surprise, in the presence of CuO (1 equiv), **12a''** was obtained in shorter reaction time (2.5 h vs 8 h) and slightly higher yield (89% vs 87%) (Scheme 6). Probably, oxidant CuO could promote the transformation from **12a'** to **12a''**. This test showed that α -iodoketones could be oxidized to the corresponding aldehyde in the absence of iodine.

(4) If the reaction temperature was in the range of 60-65 °C using **12a** as starting material, the target products **12b/c** were obtained in 81% overall yield. However, when the temperature was elevated to 90 °C, the corresponding aromatic acid **12a'''** was the major product (3 h, 88%) (**Scheme 7**). Probably, the α -iodoketone was rapidly oxidized to **12a'''** in short reaction time, and this step was the main fast reaction. So the reaction temperature should play a crucial role in controlling reactive rates between the oxidation of α -iodoketones to aldehyde and the formation of sulfonium salt.

(5) When the substrate was alkaline 4-acetylpyridine **19a**, no expected products were observed. It was supposed that HI formed in the first step combined with N-atom of 4-acetylpyridine to form ammonium salt **19a'** which prevented the further reaction (**Scheme 8**). This experiment was another evidence in support of the hypothesis.

(6) When compound **20a** was used as substrate (Table 1, Entry 15 in the text), no olefinic products were obtained and gave complicated mixture. This experiment further indicated our hypothetic mechanism was reasonable since intramolecular self-sorting reaction (from **21** to **22**) was impossible in theory (**Scheme 9**).

Scheme 9 intramolecular coupling reaction experiment.

(7) Compound **26** was obtained nearly quantitatively (98%) from **24**. Owing to the well-conjugated structure of the molecule **24**, it was rapidly transformed into **26** undergoing the α -iodoketones intermediate **25** (**Scheme 10**). This experiment showed the whole reaction process underwent intermediate α -iodoketones, and the reactive rates to form **26** was much faster than the formation of sulfonium salt.

Scheme 10 α -arylketone experiment

In Summary, according to the above experiments and analysis, it was certain that the hypothetical mechanism proposed in the text (**Scheme 3**) was reasonable.

Other substrates experiments

(1) No olefinic products were obtained when compound **27** was used as substrate. Probably, it was different to yield intermediate. And no reaction took place using **28** as reactant.

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(2) A mixture of **29** (2.5 mmol), iodine (5 mmol) and CuO (7.5 mmol) in DMSO (20 mL) was heated at 65 °C for 12 h, compound **31** was the major product (48%), and its structure was confirmed by ¹H NMR and GC-MS.

Y1110a#120 RT: 0.64 AL: 1 NL: 1.31E7
T: [0.0] + c El det=350.00 Full ms [40.00-350.00]

S6

y060106c cdc13

y060106a cdc13

S7

Y1110c #221 RT 1.15 AV 1 NL 124E7
T (D) + e El det=350.00 Full ms [40.00-350.00]

ypome-a cdc13
20050831

S8

y1009b cdcl3

S9

C:\Xcalibur\data\Y1009b

10/12/05 08:30:28 AM

RT: 0.00 - 11.80

Y1009b #706 RT: 5.53 AV: 1 NL: 4.63E6
T: {0.0} + c EI det=350.00 Full ms [50.00-350.00]

#Detailed experimental procedure

All methyl ketones must be freshly distilled or recrystallized under nitrogen atmosphere before use. Dimethyl sulfoxide was freshly distilled from calcium hydride. Column chromatography was performed using 200-300 mesh silica gel. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer as KBr film with absorption in cm^{-1} . NMR spectra were measured on instruments operating at 400 MHz for ^1H and 100 MHz for ^{13}C . Mass spectra were measured on a Finnigan Trace MS spectrometer. All melting points are uncorrected.

Compounds **6–18b/c** were prepared analogous to the following procedure: A solution of aryl or heteroaryl methyl ketones (5 mmol), iodine (10 mmol) and CuO (15 mmol) in DMSO (25 mL) was heated at 65 °C for 18 h. After filtration then the reaction mixture was then poured into 150 mL brine and the aqueous layer was extracted with EtOAc (3×100 mL). The extract was washed with $\text{Na}_2\text{S}_2\text{O}_3$ and NaOH solution, dried over anhydrous Na_2SO_4 then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc-hexane as eluent to give the expected compounds.

Crystal data of compounds 6b, 6c and 7c

Crystal data for 6b: (CCDC-290865). $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}$, Mr = 282.34, monoclinic, space group $\text{P2}_1/\text{c}$, $a = 8.856(5)$, $b = 19.688(12)$, $c = 9.065(5)$ Å, $\alpha = 90^\circ$, $\beta = 98.531(9)^\circ$, $\gamma = 90^\circ$, $V = 1563.2(16)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.200$ g cm⁻³, $F(000) = 592$, $\mu(\text{MoK}\alpha) = 0.205$ mm⁻¹, crystal dimensions 0.30×0.30×0.30 mm, 6896 reflections measured, 2692 unique ($R_{\text{int}} = 0.0343$) which were used in all calculations. The final $wR_2(F^2)$ was 0.1713 (all data).

Crystal data for 6c: (CCDC-290866). $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}$, Mr = 282.34, monoclinic, space group $\text{P2}_1/\text{c}$, $a = 9.6295(9)$, $b = 10.5087(10)$, $c = 15.1393(14)$ Å, $\alpha = 90^\circ$, $\beta = 105.982(2)^\circ$, $\gamma = 90^\circ$, $V = 1472.8(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.273$ g cm⁻³, $F(000) = 592$, $\mu(\text{MoK}\alpha) = 0.218$ mm⁻¹, crystal dimensions 0.30 × 0.28 × 0.20 mm, 9992 reflections measured, 3477 unique ($R_{\text{int}} = 0.0219$) which were used in all calculations. The final $wR_2(F^2)$ was 0.1250 (all data).

Crystal data for 7c: (CCDC-290867). $\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{O}_2\text{S}$, Mr = 351.23, monoclinic, space group $\text{P2}_1/\text{c}$, $a = 16.0885(17)$, $b = 9.0949(10)$, $c = 11.4633(12)$ Å, $\alpha = 90^\circ$, $\beta = 104.433(2)^\circ$, $\gamma = 90^\circ$, $V = 1624.4(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.436$ g cm⁻³, $F(000) = 720$, $\mu(\text{MoK}\alpha) = 0.531$ mm⁻¹, crystal dimensions 0.30 × 0.20 × 0.20 mm, 8962 reflections measured, 3176 unique ($R_{\text{int}} = 0.0376$) which were used in all calculations. The final $wR_2(F^2)$ was 0.1053 (all data).

¹H NMR, ¹³C NMR, MS, M. p. and IR spectra of compounds 6–18b/c(Z)-2-(methylthio)-1,4-diphenylbut-2-ene-1,4-dione
(6b)

Yellow solid, m.p.: 65-66°C; ¹H NMR (CDCl₃, 400MHz): δ (ppm) 8.06 (d, *J*=8.8 Hz, 2H), 7.94 (d, *J*=8.8 Hz, 2H), 7.69-7.42 (m, 6H), 7.09 (s, 1H), 2.16 (s, 3H); ¹³C NMR (CDCl₃, 100MHz): δ (ppm) 191.9, 188.2, 160.6, 137.8, 134.9, 134.8, 132.7, 130.0, 129.1, 128.6, 128.1, 116.0, 15.4; IR (KBr, cm⁻¹): 3417 m, 1666 s, 1632 s, 1596 m, 1531 m, 1246 s, 1022 m, 699 m; MS (EI) m/z: 282 (71%), 266 (34), 236 (38), 234 (43), 103 (92), 76 (100), 51 (62).

(E)-2-(methylthio)-1,4-diphenylbut-2-ene-1,4-dione
(6c)

Yellow solid, m.p.: 94-95°C; ¹H NMR (CDCl₃, 400MHz): δ (ppm) 8.01 (d, *J*=7.2 Hz, 2H), 7.90 (d, *J*=7.2 Hz, 2H), 7.57-7.40 (m, 6H), 7.04 (s, 1H), 2.46 (s, 3H); ¹³C NMR (CDCl₃, 100MHz): δ (ppm) 193.8, 185.1, 160.8, 137.1, 134.8, 133.6, 133.0, 128.8, 128.7, 128.6, 128.4, 115.7, 14.9; IR (KBr, cm⁻¹): 3422 m, 1672 s, 1636 s, 1539 s, 1219 s, 780 m, 698 m, 630 m; MS (EI) m/z: 282 (95%), 266 (45), 236 (37), 234 (44), 178 (51), 176 (47), 162 (46), 101 (89), 74 (100), 49 (97).

(Z)-1,4-bis(4-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione
(7b)

Yellow solid, m.p.: 120-121°C; ¹H NMR (CDCl₃, 400MHz): δ (ppm) 7.97 (d, *J*=8.4 Hz, 2H), 7.85 (d, *J*=8.4 Hz, 2H), 7.48 (d, *J*=8.4 Hz, 2H), 7.39 (d, *J*=8.4 Hz, 2H), 7.01 (s, 1H), 2.13 (s, 3H); ¹³C NMR (CDCl₃, 100MHz): δ (ppm) 190.4, 186.7, 160.7, 141.5, 139.1, 136.0, 133.0, 131.2, 129.5, 129.4, 128.9, 115.5, 15.4; IR (KBr, cm⁻¹): 3423 m, 1671 s, 1635 m, 1586 s, 1534 s, 1255 s, 1089 s, 818 m, 795 m; MS (EI) m/z: 353 (M+1, 38%), 352 (28), 350 (68), 199 (7), 197 (14), 196 (26), 136 (97), 109 (100), 72 (97), 50 (64).

(E)-1,4-bis(4-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione
(7c)

Yellow solid, m.p.: 140-141°C; ¹H NMR (CDCl₃, 400MHz): δ (ppm) 7.92 (d, *J*=8.4 Hz, 2H), 7.83 (d, *J*=8.4 Hz, 2H), 7.44 (d, *J*=8.4 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 2H), 6.96 (s, 1H), 2.46 (s, 3H); ¹³C NMR (CDCl₃, 100MHz): δ (ppm) 192.4, 183.7, 161.2, 140.0, 139.5, 135.1, 133.0, 129.9, 129.8, 129.1, 128.9, 115.1, 14.9; IR (KBr, cm⁻¹): 3422 m, 1680 s, 1633 s, 1586 s, 1535 s, 1401 m, 1253 m, 1215 m, 1090 s, 1051 m, 917 m, 828 m, 654 m; MS (EI) m/z: 353 (M+1, 26%), 352 (29), 350 (56), 136 (93), 109 (95), 74 (100), 50 (62).

(Z)-1,4-bis(4-bromophenyl)-2-(methylthio)but-2-ene-1,4-dione
(8b)

Yellow solid, m.p.: 122-123°C; ¹H NMR (CDCl₃, 400MHz): δ (ppm) 7.91 (d, *J*=8.8 Hz, 2H), 7.79 (d, *J*=8.8 Hz, 2H), 7.68 (d, *J*=8.4 Hz, 2H), 7.59 (d, *J*=8.4 Hz, 2H), 7.01 (s, 1H), 2.15 (s, 3H); ¹³C NMR (CDCl₃, 100MHz): δ (ppm) 190.7, 187.0, 160.8, 136.4, 133.5, 132.6, 132.0, 131.3, 130.5, 129.6, 127.9, 115.5, 15.5; IR (KBr, cm⁻¹): 3424 m, 1671 s, 1635 m, 1584 s, 1532 s, 1252 s, 1009 m, 816 m, 792 m; MS (EI) m/z: 443 (M+1, 20%), 441 (41), 438 (19), 185 (98), 183 (100), 157 (42), 155 (42).

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(E)-1,4-bis(4-bromophenyl)-2-(methylthio)but-2-ene-1,4-dione
(8c)

Yellow solid, m.p.: 134-136°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 7.84 (d, $J=8.4$ Hz, 2H), 7.75 (d, $J=8.4$ Hz, 2H), 7.61 (d, $J=8.4$ Hz, 2H), 7.58 (d, $J=8.4$ Hz, 2H), 6.95 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 192.6, 184.0, 161.3, 135.6, 133.5, 132.2, 131.9, 130.0, 129.9, 128.9, 128.3, 115.2, 15.0; IR (KBr, cm^{-1}): 3422 w, 1671 s, 1640 s, 1584 s, 1539 s, 1219 s, 1069 s, 1047 s, 1007 s, 924 s, 805 s; MS (EI) m/z : 443 ($M+1$, 24%), 441 (42), 438 (26), 186 (92), 185 (100), 183 (90), 182 (93), 157 (45), 155 (45).

(Z)-2-(methylthio)-1,4-bis(4-nitrophenyl)but-2-ene-1,4-dione
(9b)

Yellow solid, m.p.: 189-191°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 8.39 (d, $J=8.8$ Hz, 2H), 8.31 (d, $J=8.8$ Hz, 2H), 8.24 (d, $J=8.8$ Hz, 2H), 8.08 (d, $J=8.8$ Hz, 2H), 7.08 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 189.9, 186.1, 161.8, 151.3, 150.1, 142.1, 138.8, 130.9, 129.0, 124.4, 124.0, 115.7, 15.6; IR (KBr, cm^{-1}): 3423 w, 3101 w, 1677 s, 1638 m, 1598 m, 1515 s, 1347 s, 1251 s, 1228 s, 1042 m, 852 m, 706 m; MS (EI) m/z : 372 (21%), 357 (12), 150 (100), 104 (33), 92 (36).

(E)-2-(methylthio)-1,4-bis(4-nitrophenyl)but-2-ene-1,4-dione
(9c)

Yellow solid, m.p.: 190-192°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 8.33 (d, $J=8.4$ Hz, 2H), 8.30 (d, $J=8.4$ Hz, 2H), 8.14 (d, $J=8.4$ Hz, 2H), 8.03 (d, $J=8.4$ Hz, 2H), 7.01 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 191.6, 183.5, 163.0, 150.6, 150.4, 141.4, 139.1, 129.5, 129.4, 124.2, 123.9, 115.1, 15.3; IR (KBr, cm^{-1}): 3421 m, 1677 s, 1639 m, 1598 s, 1514 s, 1347 s, 1318 s, 1252 s, 1228 s, 1042 m, 853 m, 706 m; MS (EI) m/z : 372 (12%), 205 (25), 165 (39), 150 (44), 145 (100), 102 (58), 92 (28), 76 (39).

(Z)-1,4-bis(3,4-dichlorophenyl)-2-(methylthio)but-2-ene-1,4-dione
(10b)

Yellow solid, m.p.: 124-125°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 8.12 (d, $J=2.0$ Hz, 1H), 8.00 (d, $J=2.0$ Hz, 1H), 7.87 (dd, $J_1=8.4$ Hz, $J_2=2.0$ Hz, 1H), 7.75 (dd, $J_1=8.4$ Hz, $J_2=2.0$ Hz, 1H), 7.63 (d, $J=8.4$ Hz, 1H), 7.54 (d, $J=8.4$ Hz, 1H), 6.96 (s, 1H), 2.17 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 189.3, 185.4, 160.9, 139.8, 137.2, 137.1, 134.1, 134.0, 133.2, 131.3 (2C), 130.7, 129.9, 128.8, 127.0, 115.2, 15.5; IR (KBr, cm^{-1}): 3419 w, 3088 w, 1677 s, 1635 m, 1581 m, 1539 m, 1266 s, 1228 s, 1215 s, 1084 s, 1025 s, 811 m, 741 m; MS (EI) m/z : 423 ($M+1$, 8%), 421 (16), 418 (12), 177 (13), 175 (80), 173 (100), 147 (30), 145 (44).

(E)-1,4-bis(3,4-dichlorophenyl)-2-(methylthio)but-2-ene-1,4-dione
(10c)

Yellow solid, m.p.: 140-142°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 8.03 (d, $J=2.0$ Hz, 1H), 7.97 (d, $J=2.0$ Hz, 1H), 7.79 (dd, $J_1=8.0$ Hz, $J_2=2.0$ Hz, 1H), 7.72 (dd, $J_1=8.4$ Hz, $J_2=2.0$ Hz, 1H), 7.55 (d, $J=8.4$ Hz, 1H), 7.53 (d, $J=8.4$ Hz, 1H), 6.91 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 191.2, 182.7, 161.9, 138.2, 137.8, 136.3, 134.3, 133.5, 133.3, 131.0, 130.8, 130.3, 130.2, 127.5, 127.4, 114.8, 15.1; IR (KBr, cm^{-1}): 3448 w, 3097 w, 1675 s, 1638 s, 1582 m, 1530 s, 1232 m, 1207 s, 1053 m, 1026 m, 937 m, 826 m, 732 m, 657 m; MS (EI) m/z : 423 ($M+1$, 3%), 420 (6), 418 (5), 177 (10), 175 (82), 173 (100), 147 (29), 145 (42).

Yellow solid, m.p.: 106-107°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 7.95 (d, $J=8.4$ Hz, 2H), 7.84 (d, $J=8.4$ Hz, 2H), 7.32 (d, $J=8.4$ Hz, 2H), 7.24 (d, $J=8.4$ Hz, 2H), 7.06 (s, 1H), 2.45 (s, 3H), 2.39 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) 191.2, 187.5, 160.1, 145.8, 143.2, 135.1, 132.3, 129.9, 129.6, 129.1, 127.9, 115.6, 21.6, 21.4, 15.1; IR (KBr, cm^{-1}): 3422 s, 1668 s, 1631 s, 1604 s, 1539 s, 1251 s, 1207 s, 1180 s, 1080 m, 1041 m, 807 m, 750 m; MS (EI) m/z: 311(M+1, 25%), 294 (15), 189 (16), 176 (17), 147 (17), 118 (100), 114 (51), 89 (97), 63 (93).

Yellow solid, m.p.: 95-97°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 7.90 (d, $J=8.0$ Hz, 2H), 7.82 (d, $J=8.0$ Hz, 2H), 7.24 (d, $J=8.0$ Hz, 2H), 7.21 (d, $J=8.0$ Hz, 2H), 7.02 (s, 1H), 2.43 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 193.4, 184.5, 160.2, 144.3, 143.6, 134.5, 132.3, 129.3, 129.1, 128.7, 128.4, 115.5, 21.6, 21.5, 14.7; IR (KBr, cm^{-1}): 3421 w, 1667 s, 1640 s, 1605 s, 1546 s, 1252 s, 1229 s, 1178 s, 1050 s, 926 m, 808 m; MS (EI) m/z: 311(M+1, 6%), 262 (11), 190 (22), 176 (25), 147 (28), 115 (98), 88 (100), 63 (96).

Yellow solid, m.p.: 106-107°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 8.04 (d, $J=8.8$ Hz, 2H), 7.93 (d, $J=8.8$ Hz, 2H), 7.05 (s, 1H), 6.98 (d, $J=8.8$ Hz, 2H), 6.92 (d, $J=8.8$ Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 190.5, 186.9, 164.8, 163.2, 159.9, 132.5, 130.9, 130.3, 127.9, 115.7, 114.3, 113.8, 55.6, 55.4, 15.3; IR (KBr, cm^{-1}): 3421 m, 1658 s, 1628 s, 1602 s, 1574 s, 1534 s, 1508 s, 1422 m, 1345 s, 1255 s, 1167 s, 1020 s, 813 m; MS (EI) m/z: 342 (100%), 326 (26), 296 (60), 134 (99), 107 (63), 92 (59), 77 (75).

Yellow solid, m.p.: 93-95°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 7.95 (d, $J=8.8$ Hz, 2H), 7.89 (d, $J=8.8$ Hz, 2H), 6.98 (s, 1H), 6.91 (d, $J=9.2$ Hz, 2H), 6.89 (d, $J=9.2$ Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 192.5, 183.6, 163.8, 163.4, 159.6, 131.0, 130.7, 130.1, 128.0, 115.5, 114.0, 113.7, 55.4 (2C), 14.8; IR (KBr, cm^{-1}): 3442 m, 1663 s, 1598 s, 1544 s, 1258 s, 1226 s, 1166 s, 1023 s, 822 m, 747 m, 602 m; MS (EI) m/z: 342 (94%), 326 (33), 296 (37), 294 (42), 192 (33), 132 (93), 106 (96), 92 (100), 75 (97), 62 (93).

Yellow solid, m.p.: 107-108°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 8.02 (d, $J=8.8$ Hz, 2H), 7.92 (d, $J=8.8$ Hz, 2H), 7.04 (s, 1H), 6.96 (d, $J=8.8$ Hz, 2H), 6.90 (d, $J=8.8$ Hz, 2H), 4.14-4.06 (m, 4H), 2.14 (s, 3H), 1.48-1.40 (m, 6H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 190.4, 186.9, 164.2, 162.5, 159.8, 132.4, 130.6, 130.2, 127.6, 115.6, 114.6, 114.1, 63.9, 63.6, 15.2, 14.54, 14.49; IR (KBr, cm^{-1}): 3405 w, 2983 w, 1650 s, 1627 s, 1603 s, 1573 s, 1540 s, 1508 s, 1261 s, 1235 s, 1180 s, 1037 s, 839 m; MS (EI) m/z: 371 (12%), 206 (9), 147 (93), 120 (100), 92 (98), 76 (34), 64 (95).

(Z)-1,4-di(benzo)[1,3]dioxol-5-yl)-2-(methylthio)but-2-ene-1,4-dione

(14b)

Yellow solid, m.p.: 145-147°C; ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 7.64 (dd, $J_1=8.4$ Hz, $J_2=2.0$ Hz, 1H), 7.52-7.44 (m, 3H), 6.97 (s, 1H), 6.89 (d, $J=8.0$ Hz, 1H), 6.82 (d, $J=8.0$ Hz, 1H), 6.04 (s, 2H), 6.03 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 189.9, 186.2, 156.0, 153.3, 151.4, 148.6, 148.2, 132.7, 129.6, 127.7, 124.0, 115.6, 108.5, 108.3, 107.9, 107.8, 102.2, 101.8, 15.3; IR (KBr, cm^{-1}): 3426 w, 2900 w, 1661 s, 1628 s, 1599 s, 1442 s, 1246 s, 1113 m, 1039 s, 931 m, 809 m; MS (EI) m/z: 371 (M+1, 25%), 324 (24), 174 (25), 149 (100), 121 (57), 65 (38).

(E)-1,4-di(benzo)[1,3]dioxol-5-yl)-2-(methylthio)but-2-ene-1,4-dione

(14c)

Yellow solid, m.p.: 153-154°C; ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 7.56 (dd, $J_1=8.0$ Hz, $J_2=1.6$ Hz, 1H), 7.54 (dd, $J_1=8.0$ Hz, $J_2=1.6$ Hz, 1H), 7.48 (d, $J=1.6$ Hz, 1H), 7.37 (d, $J=1.6$ Hz, 1H), 6.92 (s, 1H), 6.84 (d, $J=3.2$ Hz, 1H), 6.82 (d, $J=3.6$ Hz, 1H), 6.03 (s, 2H), 6.02 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) 191.9, 183.2, 159.9, 152.3, 151.8, 148.3, 148.2, 132.0, 129.8, 125.5, 124.6, 115.5, 108.3, 108.2, 108.1, 107.8, 101.9, 101.8, 14.8; IR (KBr, cm^{-1}): 3422 w, 2909 w, 1651 s, 1600 s, 1545 s, 1492 s, 1444 s, 1251 s, 1110 s, 1033 s, 931 m, 809 m; MS (EI) m/z: 371 (M+1, 38%), 324 (38), 221 (9), 174 (20), 149 (100), 121 (54), 65 (40).

(Z)-2-(methylthio)-1,4-di(naphthalen-1-yl)but-2-ene-1,4-dione

(15b)

Yellow solid, m.p.: 133-134°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 9.18 (d, $J=8.8$ Hz, 1H), 8.67 (d, $J=8.8$ Hz, 1H), 8.24 (d, $J=7.6$ Hz, 1H), 8.11 (d, $J=8.0$ Hz, 1H), 7.95-7.39 (m, 10H), 7.06 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 193.4, 191.7, 161.5, 136.6, 135.6, 134.2, 134.0, 133.7, 132.2, 131.0, 130.7, 130.1, 129.2, 128.8, 128.3, 127.5 (2 C), 126.9, 126.3, 125.7 (2 C), 124.42, 124.39, 120.9, 15.5; IR (KBr, cm^{-1}): 3424 m, 1640 s, 1568 s, 1533 s, 1505 m, 1232 s, 1122 m, 781 s; MS (EI) m/z: 383 (M+1, 23%), 366 (23), 336 (44), 334 (65), 228 (16), 226 (22), 152 (96), 125 (100), 101 (25), 77 (30).

(E)-2-(methylthio)-1,4-di(naphthalen-1-yl)but-2-ene-1,4-dione

(15c)

Yellow solid, m.p.: 107-108°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 9.23 (d, $J=8.4$ Hz, 1H), 8.13 (dd, $J_1=7.6$ Hz, $J_2=1.2$ Hz, 1H), 8.06 (d, $J=8.0$ Hz, 1H), 8.00 (d, $J=8.4$ Hz, 1H), 7.99-7.34 (m, 10H), 6.82 (s, 1H), 2.52 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 195.0, 189.3, 161.5, 136.4, 134.4, 133.9, 133.6, 132.2, 131.7, 131.3, 131.0, 130.0, 128.7, 128.2, 127.42 (2 C), 127.35, 126.5 (2 C), 126.2, 125.3, 124.3, 124.0, 119.8, 15.1; IR (KBr, cm^{-1}): 3425 m, 3049 m, 1666 s, 1641 s, 1541 s, 1505 s, 1229 s, 1098 s, 801 m, 755 s; MS (EI) m/z: 383 (M+1, 46%), 334 (99), 308 (30), 228 (32), 226 (45), 211 (33), 206 (23), 179 (33), 150 (100), 124 (91), 101 (65), 77 (45).

(Z)-2-(methylthio)-1,4-di(naphthalen-2-yl)but-2-ene-1,4-dione
(**16b**)

Yellow solid, m.p.: 126-127°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 8.61 (s, 1H), 8.45 (s, 1H), 8.16 (dd, $J_1=8.4$ Hz, $J_2=1.6$ Hz, 1H), 8.09 (dd, $J_1=8.4$ Hz, $J_2=1.6$ Hz, 1H), 8.00-7.51 (m, 10H), 7.35 (s, 1H), 2.22 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ ppm 191.7, 187.8, 160.5, 136.0, 135.1, 135.0, 133.1, 132.3, 132.2, 132.0, 129.7, 129.3 (2 C), 129.2, 129.0, 128.3, 128.1, 127.7, 127.5, 127.0, 126.5, 123.8, 123.7, 116.1, 15.3; IR (KBr, cm^{-1}): 3421 w, 3039 w, 1660 s, 1620 s, 1539 s, 1284 m, 1183 s, 816 s, 749 s; MS (EI) m/z : 382 (82%), 366 (41), 335 (100), 308 (30), 212 (37), 179 (98), 150 (98), 124 (92), 99 (47), 77 (71).

(E)-2-(methylthio)-1,4-di(naphthalen-2-yl)but-2-ene-1,4-dione
(**16c**)

Yellow solid, m.p.: 98-99°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 8.42 (s, 1H), 8.38 (s, 1H), 8.06 (d, $J=7.2$ Hz 1H), 7.86-7.73 (m, 7H), 7.52-7.41 (m, 4H), 7.20 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 193.8, 184.9, 160.8, 135.9, 135.4, 134.4, 132.6, 132.4, 130.7, 130.0, 129.7, 129.4, 128.8, 128.6, 128.5, 128.4, 127.8, 127.7, 126.7, 126.6, 124.2, 123.9, 118.1, 116.0, 15.0; IR (KBr, cm^{-1}): 3420 m, 3056 m, 1666 s, 1624 s, 1540 s, 1277 s, 1178 s, 1124 s, 816 m, 752 s; MS (EI) m/z : 382 (77%), 367 (31), 335 (100), 181 (41), 179 (69), 150 (99), 123 (99), 102 (34), 100 (36), 76 (37).

(Z)-1,4-Di-furan-2-yl-2-methylsulfonyl-but-2-ene-1,4-dione (**17b**)

Yellow solid, m.p.: 152-153°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 7.78 (d, $J=1.6$ Hz, 1H), 7.57 (d, $J=1.6$ Hz, 1H), 7.34 (d, $J=3.6$ Hz, 1H), 7.23 (d, $J=3.6$ Hz, 1H), 7.07 (s, 1H), 6.64 (dd, $J_1=3.6$ Hz, $J_2=1.6$ Hz, 1H), 6.56 (dd, $J_1=3.6$ Hz, $J_2=1.6$ Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 178.4, 176.7, 158.1, 153.2, 150.5, 149.4, 146.1, 123.3, 116.9, 116.8, 113.0, 112.6, 15.4. IR (KBr, cm^{-1}): 3419 m, 3115 m, 1646 s, 1624 s, 1542 s, 1461, 1395 s, 1269 s, 1107 s, 1056 s, 1015 s, 768 s.

(Z)-2-Methylsulfonyl-1,4-di-thiophen-2-yl-but-2-ene-1,4-dione (**18b**)

Yellow solid, m.p.: 124-125°C; ^1H NMR (CDCl_3 , 400MHz): δ (ppm) 7.86 (dd, $J_1=4.8$ Hz, $J_2=1.2$ Hz, 1H), 7.83 (dd, $J_1=4.0$ Hz, $J_2=0.8$ Hz, 1H), 7.69 (dd, $J_1=4.0$ Hz, $J_2=1.2$ Hz, 1H), 7.65 (dd, $J_1=4.8$ Hz, $J_2=0.8$ Hz, 1H), 7.21 (dd, $J_1=4.8$ Hz, $J_2=4.0$ Hz, 1H), 7.13 (dd, $J_1=4.8$ Hz, $J_2=4.0$ Hz, 1H), 7.02 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz): δ (ppm) 183.5, 180.6, 159.0, 145.1, 141.7, 137.1, 136.6, 133.8, 131.0, 128.8, 128.2, 116.4, 15.4. IR (KBr, cm^{-1}): 3088 w, 1638 s, 1613 s, 1538 s, 1411 s, 1267 s, 1247 s, 922 m, 730 s.

S16

xyPh-1 CDCl₃
20050909

S17

S18

CSC1=C(C(=O)c2ccc(Cl)cc2)C(=O)c3ccc(Cl)cc3

S20

xyprf-1.cdc13
20050309

2.152

1.555

S21

xyPBr-2 CDCl₃
20050909

—2.459

S23

MPN02-b CDCl₃
20050508

S24

S25

10c

Y9Pmefdc13

S27

yyyme2 CDC13
20050827
H1 NMR

S28

yyPome-b cdc13

S29

EBT cdc13

S30

xy poet-1

8.026
8.004
7.927
7.904

7.260
7.040
6.966
6.944
6.911
6.889

4.133
4.116
4.092
4.074

2.140
1.580
1.471
1.453
1.444
1.436
1.426
1.409

yydl0-1 cdc13

yydio-2 cdc13

14c

7.568
7.564
7.548
7.544
7.528
7.524
7.484
7.480
7.368
7.364
7.261
6.920
6.844
6.836
6.824
6.815
6.031
6.024

— 2.426

S32

S33

S34

hyana-2 CDCl₃
20050916

— 2.515

— 1.548

15c

S35

kybna-1 CDCl₃
20050916

S36

yybna-2 cdc13
20050930

2.442

S37

Y060222 cdcl320060222