Supplementary Material (ESI)

Ambiphilic Allenes: Synthesis and Reactivity

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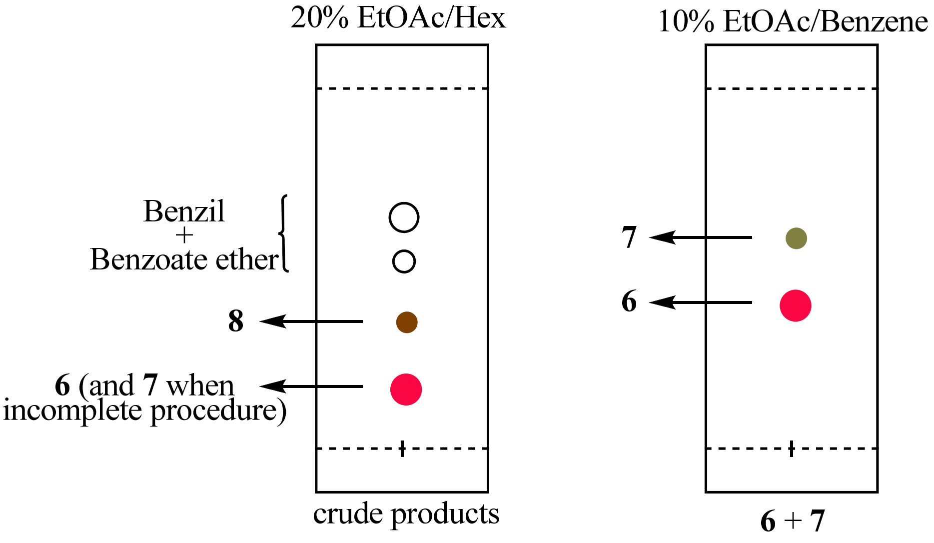
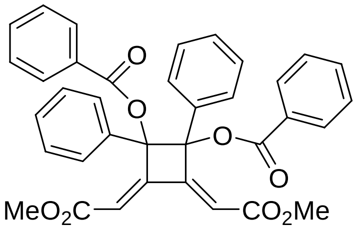
General remarks. ^{1}H NMR and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded either at 400 and 100 MHz or at 500 and 125 MHz (Bruker Ac 200 and AMX2-500), respectively. FT-IR spectra were measured in chloroform solutions using a Perkin Elmer FT-IR Spectrum BX spectrophotometer. Mass spectra (low resolution) (EI/CI) were obtained with a Hewlett-Packard 5995 gas chromatograph/mass spectrometer. High-resolution mass spectra were recorded with a Micromass Autospec mass spectrometer. Microanalyses were performed with a Fisons Instruments EA 1108 carbon, hydrogen, and nitrogen analyzer. Analytical thin-layer chromatography plates used were E. Merck Brinkman UV-active silica gel (Kieselgel 60 F254) on aluminum. Flash column chromatography was carried out with E. Merck silica gel 60 (particle size less than 0.020 mm) using appropriate mixtures of ethyl acetate and hexanes as eluent. All reactions were performed in oven-dried glassware under nitrogen unless otherwise stated. Dichloromethane was distilled from CaH_2. Triethylamine was distilled from potassium hydroxide pellets. All other materials were obtained from commercial suppliers and used as received. Melting points are uncorrected.

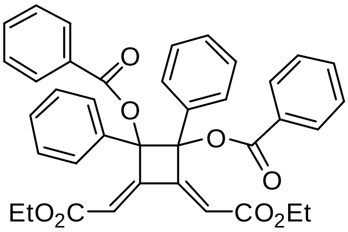
Experimental section

Synthesis of substituted cyclobutanes 6 and 8: (representative example): Benzil **2a** (3.00 mmol) and methyl propiolate **3a** (3.00 mmol) were dissolved in 5 mL of CH_2Cl_2 and the solution was cooled to 0ºC in an ice bath. Et_3N (0.30 mmol) was added and the reaction was allowed to react overnight without further cooling. Et_3N (3 mmol) was added and the reaction was allowed to react for one additional day (this step simplifies the isolation of **6** while transform **7** *cis*/*trans* into **8**. Purification of products **6** *trans*/*cis* and **8** was carried out by flash column chromatography (silica gel, n-hexane/EtOAc 80/20 to 60/40). In certain occasions product **8** is not analytically pure after this chromatography. It can be further purified by a second flash column chromatography (silica gel, n-hexane/CH_2Cl_2 50/50). Cyclobutane **6** *trans* can be separated from the minor **6** *cis*-isomer by recrystallization in CH_2Cl_2 - 20% EtOAc/Hex.

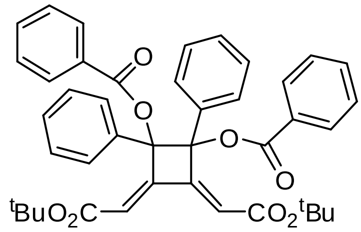


(3Z,4Z)-3,4-bis(2-methoxy-2-oxoethylidene)-1,2-diphenylcyclobutane-1,2-diyl dibenzoate (6aa) *trans*-isomer (major): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.37 (s, 6H), 6.86 (s, 2H), 7.16-7.29 (m, 10H), 7.41 (tt, 2H, J = 7.4 and 1.3 Hz), 7.56 (m, 4H), 7.69 (m, 4H). Characteristic data for *cis*-isomer (minor): δ 3.42 (s, 6H), 6.79 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 51.5, 92.4, 117.8, 127.6, 128.0, 128.1, 128.2, 129.2, 129.9, 132.5, 134.8, 151.2, 163.3, 164.7. IR ($CHCl_3$, cm^{-1}) 3027.8, 1730.3, 1449.9, 1436.1, 1343.8, 1268.1, 1222.3, 1108.6. Anal. Calcd. for $C_{36}H_{28}O_8$: C, 73.46; H, 4.79. Found: C, 73.47; H, 4.71. MS, *m/z* (relative intensities) 588 (M+, 0.3), 362 (8.4), 162 (28), 130 (19), 105 (100), 77 (32). White solid, mp = 181.0-182.6 ºC.

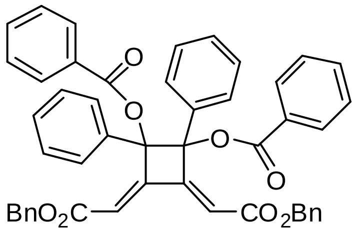




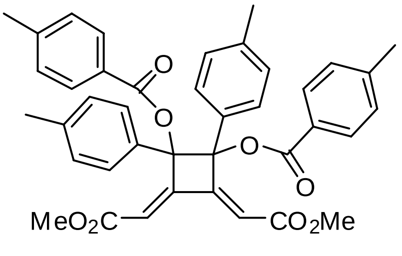
(3Z,4Z)-3,4-bis(2-ethoxy-2-oxoethylidene)-1,2-diphenylcyclobutane-1,2-diyl dibenzoate (6ab) *trans*-isomer (major): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.69 (t, 6H, *J* = 7.2 Hz), 3.75 (dq, 2H, *J* = 10.9 and 7.2 Hz), 3.84 (dq, 2H, *J* = 10.9 and 7.2 Hz), 6.84 (s, 2H), 7.15 (tt, 2H, *J* = 7.2 and 1.3 Hz), 7.22-7.27 (m, 8H), 7.41 (tt, 2H, *J* = 7.6 and 1.3 Hz), 7.58 (m, 4H), 7.70 (m, 4H). Characteristic data for *cis*-isomer (minor): δ 6.77 (s, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 13.4, 60.6, 92.6, 118.3, 127.6, 128.0, 128.21 (2), 129.2, 129.9, 132.6, 135.0, 151.0, 163.2, 164.4. IR (CHCl$_3$, cm^{-1}) 3028.1, 1730.0, 1709.5, 1449.9, 1370.1, 1337.5, 1267.2, 1109.2. Anal. Calcd. for $C_{38}H_{32}O_8$: C, 74.01; H, 5.23. Found: C, 74.22; H, 5.25. MS, *m/z* (relative intensities) 616 (M+, 4.2), 494 (13), 390 (49), 106 (29), 105 (100), 77 (68). White solid, mp = 200.6-201.1 ºC.



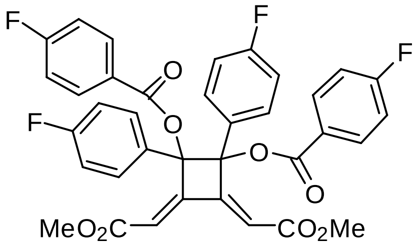
(3Z,4Z)-3,4-bis(2-tert-butoxy-2-oxoethylidene)-1,2-diphenylcyclobutane-1,2-diyl dibenzoate (6ac) *trans*-isomer (major): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.89 (s, 18H), 6.72 (s, 2H), 7.11 (tt, 2H, *J* = 7.4 and 1.2 Hz), 7.21-7.27 (m, 8H), 7.41 (tt, 2H, *J* = 7.3 and 1.3 Hz), 7.61 (m, 4H), 7.72 (m, 4H). Characteristic data for *cis*-isomer (minor): δ 6.65 (s, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 27.3, 81.2, 92.7, 120.0, 127.4, 127.9, 128.2, 128.5, 129.1, 130.0, 132.5, 135.1, 149.9, 163.0, 163.7. IR (CHCl$_3$, cm^{-1}) 2981.8, 1731.7, 1697.2, 1450.1, 1369.8, 1290.6, 1265.5, 1215.9, 1158.2, 1108.3. Anal. Calcd. for $C_{42}H_{40}O_8$: C, 74.98; H, 5.99. Found: C, 74.92; H, 6.31. MS, *m/z* (relative intensities) 672 (M+, 0.09), 438 (18), 333 (17), 316 (79), 288 (18), 106 (24), 105 (100), 77 (42). White solid, mp = 193.0-193.8 ºC.



(3Z,4Z)-3,4-bis(2-(benzyloxy)-2-oxoethylidene)-1,2-diphenylcyclobutane-1,2-diyl dibenzoate (6ad) *trans*-isomer (major): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.76 (d, 2H, *J* = 12.2 Hz), 4.85 (d, 2H, *J* = 12.2 Hz), 6.73 (dt, 4H, J = 6.9 and 1.3), 6.91 (s, 2H), 7.01 (tt, 4H, *J* = 7.6 and 1.5 Hz), 7.12 (tt, 2H, *J* = 7.5 and 2.0 Hz), 7.14-7.26 (m, 10H), 7.35-7.40 (m, 6H), 7.64 (dt, 4H, *J* = 7.2 and 1.3 Hz). Characteristic data for *cis*-isomer (minor): δ 6.80 (s, 2H**)**. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 66.8, 92.4, 118.0, 127.6, 127.78, 127.84, 128.1, 128.8, 128.30, 129.2, 129.6, 132.4, 134.8, 134.9, 151.4, 163.3, 164.3. IR (CHCl$_3$, cm^{-1}) 3032.0, 1729.8, 1708.3, 1450.1, 1267.3, 1108.4. Anal. Calcd. for $C_{48}H_{36}O_8$: C, 77.82; H, 4.90. Found: C, 77.96; H, 4.91. MS, *m/z* (relative intensities) 740 (M+, 0.7), 618 (0.7), 498 (0.9), 423 (10), 105 (100), 91 (43), 77 (18). White solid, mp = 161.0-162.3 ºC.

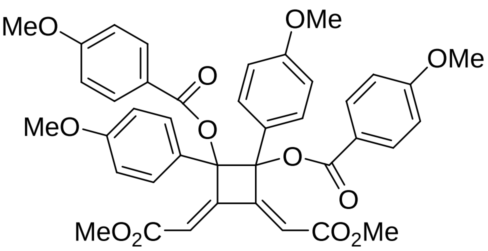


((3Z,4Z)-3,4-bis(2-methoxy-2-oxoethylidene)-1,2-dip-tolylcyclobutane-1,2-diyl bis(4-methylbenzoate) (6ba) *trans*-isomer (major): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2. 21 (s, 6H), 2.31 (s, 6H), 3.37 (s, 6H), 6.80 (s, 2H), 7.04 (d, 4H, *J* = 7.8 Hz), 7.05 (d, 4H, *J* = 7.8 Hz), 7.45 (d, 4H, *J* = 8.3 Hz), 7.53 (d, 4H, *J* = 8.3 Hz). Characteristic data for *cis*-isomer (minor): δ 6.71 (s, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 21.0, 21.5, 51.5, 92.3, 117.4, 127.4, 128.0, 128.3, 128.6, 129.3, 132.1, 137.7, 143.0, 151.6, 163.4, 164.8. IR (CHCl$_3$, cm^{-1}) 3027.1, 1728.9, 1612.2, 1436.1, 1341.8, 1269.9, 1177.5, 1104.9. Anal. Calcd. for $C_{40}H_{36}O_8$: C, 74.52; H, 5.63. Found: C, 74.71; H, 5.58. MS, *m/z* (relative intensities) 644 (M+, 8.2), 508 (9.9), 390 (10), 331 (11), 136 (14), 120 (29), 119 (100), 91 (70). White solid, mp = 175.5-176.8 ºC.

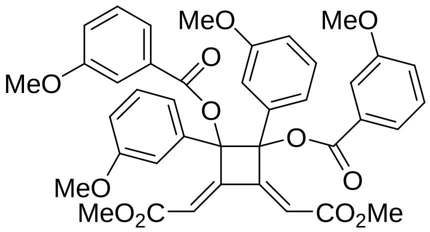


(3Z,4Z)-1,2-bis(4-fluorophenyl)-3,4-bis(2-methoxy-2-oxoethylidene)cyclobutane-1,2-diyl bis(4-fluorobenzoate) (6ca) *trans*-isomer (major): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.42 (s, 6H), 6.86 (s, 2H), 6.93-6.99 (m, 8H), 7.58-7.65 (m, 8H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.7, 91.9, 114.7 (d, J_{CF} = 21.9 Hz), 115.4 (d, J_{CF} = 22.6 Hz), 118.0, 125.7 (d, J_{CF} = 2.8 Hz), 130.0 (d, J_{CF} = 8.5 Hz), 130.5 (d, J_{CF} = 3.5 Hz), 131.7 (d, J_{CF} = 9.2 Hz), 150.9, 162.3, 162.6 (d, J_{CF} = 248 Hz), 164.5, 165.6 (d, J_{CF} = 254 Hz). IR (CHCl$_3$, cm^{-1}) 2953.9, 1732.3, 1605.4, 1508.6, 1266.2, 1239.5, 1222.0. Anal. Calcd. for $C_{36}H_{24}F_4O_8$: C, 65.46; H, 3.66. Found: C, 65.34; H, 3.86. MS, *m/z* (relative intensities) 660 (M+, 7.4), 520 (13), 398 (35), 123 (100), 95 (24). Yellow solid, mp = 181-184 ºC.

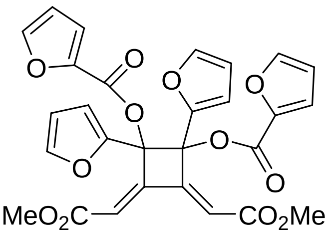
(3Z,4Z)-3,4-bis(2-methoxy-2-oxoethylidene)-1,2-bis(4-methoxyphenyl)cyclobutane-1,2-diyl bis(4-methoxybenzoate) (6da) *trans*-isomer (major): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.37 (s, 6H), 3.68 (s, 6H), 3.76 (s, 6H), 6.73 (d, 4H, *J* = 9.0 Hz), 6.77 (d, 4H, *J* = 9.0 Hz), 6.79 (s, 2H), 7.55 (d, 4H, *J* = 8.7 Hz), 7.56 (d, 4H, *J* = 8.7 Hz). Characteristic data for *cis*-isomer (minor): δ 3.38 (s, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.4, 55.1, 55.2, 92.1, 113.0, 113.2, 117.3, 122.4, 127.3, 129.4, 131.3, 152.0, 159.3, 162.98, 163.00, 164.8. IR (CHCl$_3$, cm^{-1}) 3013.6, 1725.7, 1608.0,



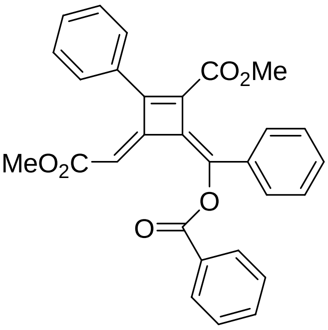
1511.7, 1254.6, 1167.9, 1100.3, 1033.1. Anal. Calcd. for $C_{40}H_{36}O_{12}$: C, 67.79; H, 5.12. Found: C, 67.56; H, 5.40. MS, *m/z* (relative intensities) 708 (M+, 9.5), 422 (6.0), 363 (3.6), 152 (9.8), 136 (27), 135 (100), 77 (13). Yellow solid, mp = 147.1-147.8 ºC.



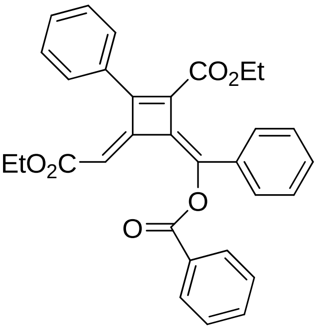
(3Z,4Z)-3,4-bis(2-methoxy-2-oxoethylidene)-1,2-bis(3-methoxyphenyl)cyclobutane-1,2-diyl bis(3-methoxybenzoate) (6ea) *trans*-isomer (major): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.40 (s, 6H), 3.71 (s, 6H), 3.73 (s, 6H), 6.72 (ddd, 2H, *J* = 8.0, 2.7 and 1.1 Hz), 6.82 (s, 2H), 6.96 (ddd, 2H, *J* = 7.6, 2.6 and 1.5 Hz), 7.10 (dd, 2H, *J* = 2.3 and 1.4Hz), 7.14-7.25 (m, 10H). Characteristic data for *cis*-isomer (minor): δ 6.76 (s, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.5, 55.20, 55.23, 92.3, 113.86 (2), 114.3, 117.7, 119.0, 120.3, 121.7, 128.7, 129.0, 131.2, 136.3, 151.1, 159.0, 159.2, 163.3, 164.7. IR (CHCl$_3$, cm^{-1}) 3013.5, 2964.6, 1731.3, 1488.5, 1435.8, 1262.3, 1099.1, 1045.2. Anal. Calcd. for $C_{40}H_{36}O_{12}$: C, 67.79; H, 5.12. Found: C, 67.60; H, 5.31. MS, *m/z* (relative intensities) 708 (M+,25), 556(60), 363 (22), 152 (33), 136 (77), 135 (100), 77 (40). Yellow solid, mp = 110.4-111.6 ºC.



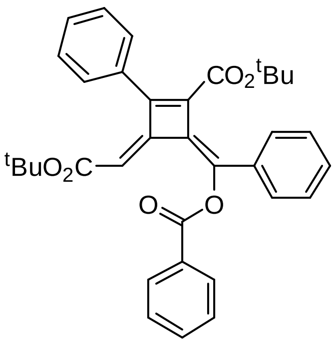
(3Z,4Z)-1,2-di(furan-2-yl)-3,4-bis(2-methoxy-2-oxoethylidene)cyclobutane-1,2-diyl difuran-2-carboxylate (6fa) *trans*-isomer (major): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.54 (s, 6H), 6.25 (dd, 2H, *J* = 3.3 and 1.7 Hz), 6.42 (dd, 2H, *J* = 3.5 and 1.6 Hz), 6.62 (s, 2H), 6.64 (dd, 2H, *J* = 3.5 and 1.1 Hz), 7.07 (dd, 2H, *J* = 3.5 and 1.1 Hz), 7.30 (dd, 2H, *J* = 1.9 and 1.1 Hz), 7.49 (dd, 2H, *J* = 1.9 and 0.8 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.7, 86.6, 110.7, 111.6, 112.1, 118.0, 118.4, 142.9, 143.8, 146.6, 147.2, 149.3, 155.0, 164.3. IR (CHCl$_3$, cm^{-1}) 3026.3, 2956.3, 1733.9, 1471.7, 1295.3, 1177.9, 1113.6. Anal. Calcd. for $C_{28}H_{20}O_{12}$: C, 61.32; H, 3.68. Found: C, 61.48; H, 3.99. MS, *m/z* (relative intensities) 548 (M+, 5.3), 436 (7.6), 377 (6.1), 283 (6.1), 95 (100). Brown solid, mp = 67.0-67.9 ºC.



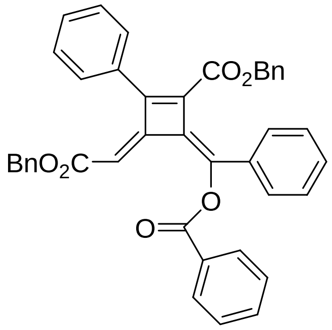
(E)-((E)-4-(2-methoxy-2-oxoethylidene)-2-(methoxycarbonyl)-3-phenylcyclobut-2-enylidene)(phenyl)methyl benzoate (8aa): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.32 (s, 3H), 3.38 (s, 3H), 6.08 (s, 1H), 7.33-7.41 (m, 6H), 7.46-7.54 (m, 6H), 7.65 (tt, 1H, *J* = 7.5 and 1.3 Hz), 8.19 (m, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.0, 51.5, 110.4, 126.5, 127.5, 127.9, 128.0, 128.6, 128.77, 128.79, 129.0, 129.5, 130.1, 131.1, 133.9, 134.4, 136.5, 142.2, 149.5, 156.6, 161.5, 164.6, 165.4. IR (CHCl$_3$, cm^{-1}) 3028.2, 2953.0, 1731.6, 1435.9, 1258.0, 1063.4. Anal. Calcd. for $C_{29}H_{22}O_6$: C, 74.67; H, 4.75. Found: C, 74.77; H, 5.00. MS, *m/z* (relative intensities) 466 (M+, 24), 330 (10), 215 (17), 106 (19), 105 (100), 77 (60). Yellow solid, mp = 156.5-157.9 ºC.



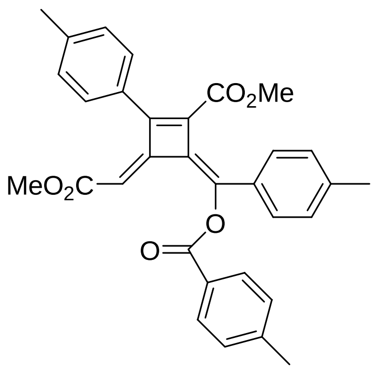
(E)-((E)-4-(2-ethoxy-2-oxoethylidene)-2-(ethoxycarbonyl)-3-phenylcyclobut-2-enylidene)(phenyl)methyl benzoate (8ab): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.77 (t, 3H, *J* = 7.1), 0.83 (t, 3H, *J* = 7.1), 3.80 (q, 2H, *J* = 7.1), 3.88 (q, 2H, *J* = 7.1), 6.06 (s, 1H), 7.33-7.38 (m, 6H), 7.46-7.52 (m, 6H), 7.65 (tt, 1H, *J* = 7.5 and 1.3 Hz), 8.18 (m, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 13.30 (2), 60.4, 61.0, 110.7, 126.6, 127.5, 127.9, 128.0, 128.72, 128.79, 128.83, 129.1, 129.5, 130.2, 131.4, 133.9, 134.6, 136.4, 142.3, 148.9, 156.3, 161.2, 164.7, 165.3. IR (CHCl$_3$, cm^{-1}) 3029.8, 1731.4, 1446.2, 1372.5, 1258.2, 1245.4, 1063.5. HRMS (*m/z*): [M]$^{+}$ calcd for $C_{31}H_{26}O_6$, 494.1729; found, 494.1720. MS, *m/z* (relative intensities) 494 (M+, 15), 344 (10), 215 (15), 106 (22), 105 (100), 77 (62).



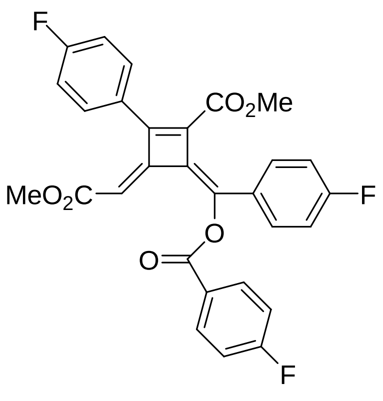
(E)-((E)-4-(2-tert-butoxy-2-oxoethylidene)-2-(tert-butoxycarbonyl)-3-phenylcyclobut-2-enylidene)(phenyl)methyl benzoate (8ac): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.15 (s, 9H), 1.23 (s, 9H), 5.97 (s, 1H), 7.32-7.37 (m, 6H), 7.44-7.53 (m, 6H), 7.64 (tt, 1H, *J* = 7.4 and 1.3 Hz), 8.18 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.58, 27.61, 81.1, 82.7, 112.2, 126.9, 127.5, 128.0, 128.2, 128.75, 128.85, 128.90, 128.98, 129.3, 130.2, 131.6, 133.8, 134.7, 135.9, 143.3, 147.5, 155.2, 160.5, 164.6, 164.8. IR ($CHCl_3$, cm^{-1}) 2982.0, 1730.7, 1709.0, 1452.1, 1369.7, 1258.3, 1148.3, 1112.8, 1081.3, 1063.7. Anal. Calcd. for $C_{35}H_{34}O_6$: C, 76.34; H, 6.22. Found: C, 76.34; H, 6.28. MS, *m/z* (relative intensities) 550 (M+, 0.7), 372 (19), 316 (73), 215 (7.8), 105 (100), 77 (25).



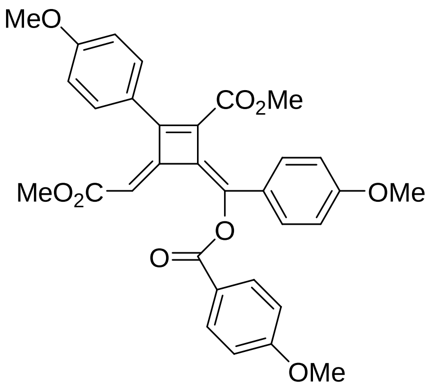
(E)-((E)-4-(2-(benzyloxy)-2-oxoethylidene)-2-(benzyloxycarbonyl)-3-phenylcyclobut-2-enylidene)(phenyl)methyl benzoate (8ad): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.70 (s, 2H), 4.81 (s, 2H), 6.03 (s, 1H), 6.82-6.88 (m, 4H), 7.11-7.25 (m, 10H), 7.32-7.44 (m, 6H), 7.55 (tt, 1H, *J* = 7.4 and 1.3 Hz), 8.08 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 66.0, 66.8, 110.5, 126.5, 127.6, 127.93, 127.97, 127.98, 128.03, 128.21, 128.24, 128.3, 128.7, 128.8, 129.2, 129.5, 130.2, 131.1, 133.9, 134.3, 134.6, 135.4, 136.6, 142.2, 149.4, 156.4, 161.0, 164.7, 164.9. IR ($CHCl_3$, cm^{-1}) 3026.3, 1733.8, 1601.4, 1452.1, 1258.7, 1244.5, 1222.4, 1177.3, 1106.9, 1081.1, 1064.0. Anal. Calcd. for $C_{41}H_{30}O_6$: C, 79.60; H, 4.89. Found: C, 79.35; H, 5.29. MS, *m/z* (relative intensities) 618 (M+, 1.5), 406 (5.8), 301 (1.8), 215 (2.8), 105 (100), 91 (84).



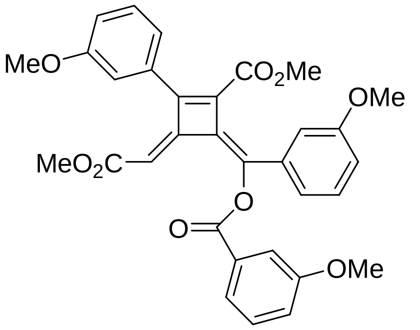
(E)-((E)-4-(2-methoxy-2-oxoethylidene)-2-(methoxycarbonyl)-3-p-tolylcyclobut-2-enylidene)(p-tolyl)methyl 4-methylbenzoate (8ba): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.34 (s, 3H), 2.37 (s, 3H), 2.44 (s, 3H), 3.36 (s, 3H), 3.41 (s, 3H), 6.06 (s, 1H), 7.13 (d, 2H, *J* = 7.7), 7.18 (d, 2H, *J* = 7.9), 7.30-7.37 (m, 6H), 8.06 (d, 2H, *J* = 8.2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 21.5, 21.7, 51.1, 51.5, 110.2, 126.0, 126.2, 127.8, 128.2, 128.3, 128.6, 128.7, 129.5, 130.2, 131.7, 136.4, 139.0, 139.7, 141.8, 144.7, 149.9, 156.2, 161.8, 164.7, 165.5. IR ($CHCl_3$, cm^{-1}) 3018.4, 1730.7, 1611.7, 1435.9, 1260.2, 1222.3, 1178.4, 1105.0, 1070.9. Anal. Calcd. for $C_{32}H_{28}O_9$: C, 75.57; H, 5.55. Found: C, 75.53; H, 5.66. MS, *m/z* (relative intensities) 508 (M+, 23), 330 (16), 243 (18), 152 (15), 119 (100), 91 (16). Yellow solid, mp = 162.5-164.0 ºC.



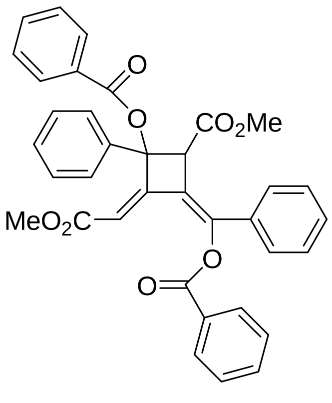
(E)-(4-fluorophenyl)((E)-3-(4-fluorophenyl)-4-(2-methoxy-2-oxoethylidene)-2-(methoxycarbonyl)cyclobut-2-enylidene)methyl 4-fluorobenzoate (8ca): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.39 (s, 3H), 3.42 (s, 3H), 6.02 (s, 1H), 7.02-7.09 (m, 4H), 7.19 (t, 2H, *J* = 8.6), 7.43-7.49 (m, 4H), 8.18 (dd, 2H, *J* = 8.7 and 5.3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 51.3, 51.7, 110.7, 114.7 (d, J_{CF} = 21.9 Hz), 115.0 (d, J_{CF} = 21.9 Hz), 116.2 (d, J_{CF} = 22.6 Hz), 124.9 (d, J_{CF} = 2.8 Hz), 126.6, 127.1 (d, J_{CF} = 3.5 Hz), 130.3 (d, J_{CF} = 8.5 Hz), 130.5 (d, J_{CF} = 3.5 Hz), 131.1 (d, J_{CF} = 8.5 Hz), 132.8 (d, J_{CF} = 9.2 Hz), 135.53, 141.8, 149.4, 156.3, 161.2, 163.2 (d, J_{CF} = 250 Hz), 163.4 (d, J_{CF} = 251 Hz), 163.7, 165.2, 166.5 (d, J_{CF} = 256 Hz). IR ($CHCl_3$, cm^{-1}) 3015.3, 1732.1, 1604.2, 1508.3, 1436.0, 1254.0, 1239.9, 1156.2, 1067.4. Anal. Calcd. for $C_{29}H_{19}$ F_3O_6: C, 66.92; H, 3.68. Found: C, 67.00; H, 3.84. MS, *m/z* (relative intensities) 520 (M+, 17), 365 (2.2), 251 (1.8), 123 (100), 95 (11). Yellow solid, mp = 157.0-158.4 ºC.



(E)-((E)-4-(2-methoxy-2-oxoethylidene)-2-(methoxycarbonyl)-3-(4-methoxyphenyl)cyclobut-2-enylidene)(4-methoxyphenyl)methyl 4-methoxybenzoate (8da): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.40 (s, 3H), 3.42 (s, 3H), 3.78 (s, 3H), 3.82 (s, 3H), 3.87 (s, 3H), 6.05 (s, 1H), 6.85 (d, 2H, *J* = 8.8), 6.89 (d, 2H, *J* = 9.0), 6.98 (d, 2H, *J* = 9.0), 7.38 (d, 2H, *J* = 9.0), 7.46 (d, 2H, *J* = 8.8), 8.12 (d, 2H, *J* = 9.0). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.2, 51.5, 55.19, 55.21, 55.5, 110.1, 112.9, 113.3, 114.1, 121.2, 123.6, 125.6, 127.2, 129.4, 130.7, 132.3, 135.8, 140.8, 150.1, 155.7, 160.0, 160.6, 161.9, 164.1, 164.5, 165.6. IR (CHCl$_3$, cm^{-1}) 3017.6, 2973.8, 1726.7, 1606.3, 1511.6, 1253.0, 1173.6, 1032.6. HRMS (*m*/*z*): [M]$^+$ calcd for $C_{32}H_{28}O_9$, 556.1733; found, 556.1743. MS, *m/z* (relative intensities) 556 (M+, 50), 421 (13), 393 (5.3), 136 (47), 135 (100), 77 (22).



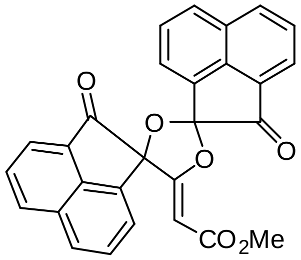
(E)-((E)-4-(2-methoxy-2-oxoethylidene)-2-(methoxycarbonyl)-3-(3-methoxyphenyl)cyclobut-2-enylidene)(3-methoxyphenyl)methyl 3-methoxybenzoate (8ea): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.37 (s, 3H), 3.44 (s, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 3.87 (s, 3H), 6.08 (s, 1H), 6.90 (ddd, 1H, *J* = 8.2, 2.6 and 1.1), 6.94 (ddd, 1H, *J* = 8.2, 2.6 and 1.1), 7.01-7.08 (m, 4H), 7.20 (ddd, 1H, *J* = 8.4, 2.6 and 1.1), 7.25 (t, 1H, *J* = 8.0), 7.29 (t, 1H, *J* = 8.0), 7.43 (t, 1H, *J* = 8.0), 7.67 (dd, 1H, *J* = 2.4 and 1.3), 7.80 (dt, 1H, *J* = 8.0 and 1.3). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.1, 51.6, 55.15, 55.20, 55.4, 110.3, 113.2, 113.8, 114.5, 115.1, 115.7, 120.2, 120.6, 121.1, 122.5, 126.6, 128.6, 129.0, 129.8, 130.0, 132.2, 135.6, 136.3, 142.4, 149.2, 155.9, 158.8, 159.2, 159.9, 161.7, 164.5, 165.5. IR (CHCl$_3$, cm^{-1})2927.5, 1732.3, 1600.1, 1587.2, 1488.3, 1465.8, 1435.5, 1272.4, 1040.8. HRMS (*m*/*z*): [M]$^+$ calcd for $C_{32}H_{28}O_9$, 556.1733; found, 556.1741. MS, *m/z* (relative intensities) 556 (M+,10), 421 (13), 436 (2.9), 390 (2.5), 135 (100), 107 (15).



(2Z,3Z)-3-(benzoyloxy(phenyl)methylene)-2-(2-methoxy-2-oxoethylidene)-4-(methoxycarbonyl)-1-phenylcyclobutyl benzoate (7aa) major isomer: 7aa was obtained with a combined yield of 19% as an inseparable mixture of two isomers when the reaction of benzil and methyl propiolate was carried out with 5 mol% of Bu_3N with overnight stirring to avoid as much as possible the conversion of **7aa** into **8aa**. If longer reaction times or Et_3N is used instead of Bu_3N lower yields of **7aa** are obtained. **7aa** and **6aa** have the same Rf in 20% EtOAc/Hex but quite different in 10% EtOAc/Benzene. Two flash chromatographies using the previously mentioned solvent mixtures were performed to successfully isolate **7aa**. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.40 (s, 3H), 3.45 (s, 3H), 4.82 (s, 1H), 6.27 (s, 1H), 7.30-7.50 (m, 9H), 7.54-7.70 (m, 7H), 8.15 (m, 2H), 8.28 (m, 2H). Characteristic data for minor isomer: δ 2.91 (s, 3H), 3.25 (s, 3H), 5.41 (s, 1H), 6.29 (s, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.1, 52.1, 59.3, 83.8, 114.7, 125.2, 126.4, 128.0, 128.47(2), 128.52, 128.7, 129.0, 130.3, 133.2, 133.3, 134.2, 140.0, 148.42, 148.49, 155.3, 163.6, 164.9, 165.2, 168.1. IR (CHCl$_3$, cm^{-1}) 3025.2, 2953.7, 1735.6, 1636.5, 1601.6, 1451.7, 1436.0, 1283.2, 1241.7, 1159.2, 1093.8. Anal. Calcd. for $C_{36}H_{28}O_8$: C, 73.46; H, 4.79. Found: C, 73.35; H, 4.78. MS, *m/z* (relative intensities) 588 (M+, 0.3), 384 (44), 213 (25), 199 (24), 126 (30), 105 (100), 77 (32). On the basis of their ^{1}H NMR spectroscopic data, we estimated that the t*rans*-isomer, which places both the hydrogen and the acyloxy group on the same side of the ring, would show an important unshielding effect on the hydrogen resonance with regarding to the other isomer. On this premise, we tentatively assigned the *trans*-configuration to the minor isomer (δ_H = 5.41 ppm) and the *cis* to the major isomer (δ_H = 4.82 ppm).

Synthesis 1,3-dioxolane (9): Following the standard procedure for the synthesis of cyclobutane products (equimolar amounts of starting materials) clearly showed that the formation of 1,3-dioxolanic products is favored over other processes (^{1}H NMR of the crude products). Therefore, based on our previous experience (see reference 6b and references cited therein), we changed the reaction parameters to maximize the formation of these compounds. Acenaphthenequinone **2g** (4.00 mmol) and methyl propiolate **3a** (2.00 mmol) were dissolved in 5 mL of CH_2Cl_2 and the solution was cooled to -78ºC. Et_3N (0.20 mmol) was added and the reaction was allowed to react overnight without further cooling. ^{1}H NMR of the crude products showed characteristic signals for the 1,3-dioxolanic products and very small amounts of the cyclobutane products **6ga** *cis*/*trans* (7.29 and 7.12 ppm). Purification of products **9** was carried out by flash column chromatography (silica gel, n-hexane/EtOAc 80/20 to 60/40) giving an overall yield of 70%.

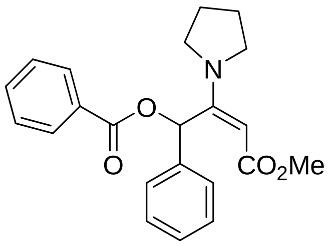
Substituted 1,3-dioxolane (9), four isomers: ^{1}H NMR ($CDCl_3$, 400 MHz): δ (isomer 1st of 4) 2.84 (s, 3H), 5.76 (s, 1H), 7.73-7.80 (m, 4H), 7.93 (d, 1H, J = 10.9 Hz), 7.95 (t, 2H, J = 9.3 Hz), 8.06 (d, 1H, J = 7.1 Hz), 8.12 (d, 2H, J = 8.3 Hz), 8.21 (d, 1H, J = 6.9 Hz), 8.29 (d, 1H, J = 6.9 Hz). (isomer 2nd of 4) 3.55 (s, 3H), 4.37 (s, 1H), 7.73-7.84 (m, 4H), 7.99-8.06 (m, 4H), 8.17 (t, 2H, J = 8.5 Hz), 8.36 (d, 1H, J = 7.3 Hz), 8.47 (d, 2H, J = 6.9 Hz). (isomer 3rd of 4) 3.03 (s, 3H), 5.84 (s, 1H), 7.70-7.77 (m, 4H), 7.83 (d, 1H, J = 6.9 Hz), 7.87 (d, 1H, J = 6.9 Hz), 7.95 (d, 1H, J = 8.4 Hz), 7.99 (t, 2H, J = 8.2 Hz), 8.09 (t, 2H, J = 7.1 Hz), 8.10 (d, 1H, J = 8.3 Hz). (isomer 4th of 4) 3.56 (s, 3H), 4.51 (s, 1H), 7.75-7.83 (m, 4H), 7.88 (d, 1H, J = 7.2 Hz), 8.00-8.10 (m, 5H), 8.17 (t, 2H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (isomer 1st of 4). 50.4, 89.7, 93.2, 107.6, 122.3, 122.5, 122.6, 122.9, 126.3, 127.7, 128.0, 128.3, 128.4, 129.1, 129.2, 130.3 (2), 131.0, 131.70, 131.74, 132.5, 135.7, 142.9, 143.6, 165.4, 166.0, 196.5, 196.7. (isomer 2nd of 4) 51.1, 90.3, 90.6, 110.0, 121.9, 122.6, 123.4, 123.8, 123.9, 126.8, 127.9, 128.3, 128.5, 129.2, 129.3, 129.7, 130.4, 130.6, 131.2, 132.5, 132.6, 134.6, 143.39, 143.41, 163.8, 164.7, 196.7, 197.7. (isomer 3rd of 4) 50.7, 89.1, 93.6, 107.4, 119.4, 121.4, 122.7, 122.8, 126.6, 128.0, 128.5, 128.6, 128.7, 130.4, 130.5, 131.1, 131.7, 131.8, 132.0, 137.7, 142.3, 142.7, 165.6, 165.7, 193.0, 194.7, (2 peaks buried under peaks at 128.5-128.7). (isomer 4th of 4) 51.1, 89.8, 90.8, 110.2, 120.8, 121.3, 122.9, 123.5, 127.0, 128.1, 128.6, 128.8, 129.0, 129.1, 130.3, 130.5, 130.7, 132.0, 132.1, 132.3, 136.7, 142.4, 142.6, 164.1, 164.7, 193.8, 195.1. IR ($CHCl_3$, cm^{-1}) (isomer 2nd of 4) 3015.8, 1736.6, 1673.7, 1437.3, 1290.3, 1264.3, 1075.9, 1031.8. Anal. Calcd. for $C_{28}H_{16}O_6$: (isomer 2nd of 4) C, 75.00; H, 3.60. Found: C, 75.05; H, 3.62. MS, *m/z* (relative intensities) (isomer 2nd of 4) 448 (M+, 17), 235 (66), 207 (41), 179 (25), 154 (71), 151 (38), 126 (100). Isomer 2nd of 4, white solid, mp = 263.0-265.0 ºC. The relative intensities of the four isomers are 2.5:6.0:1.0:3.3. The 1st isomer is the least polar and the 4th isomer is the most polar. Based on our previous experience with 1,3-dioxolanes (Z syn always the major isomer and E anti always the minor isomer) we tentatively assign the following isomers: Isomer 1st of 4 = E syn. Isomer 2nd of 4 = Z syn. Isomer 3rd of 4 = E anti. Isomer 4th of 4 = Z anti.



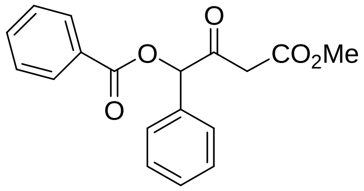
Scale up synthesis of substituted cyclobutanes 6aa and 8aa: Benzil **2a** (100 mmol) and methyl propiolate **3a** (100 mmol) were dissolved in 166 mL of CH_2Cl_2 and the solution was cooled to 0ºC in an ice bath. Et_3N (10 mmol) was added and the reaction was allowed to react overnight without further cooling. Et_3N (100 mmol) was added and the reaction was allowed to react for one additional day. The reaction was quenched with 100mL of 1M HCl. The organic layer was separated and the aqueous layer extracted once with 50mL of CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was dissolved in approximately 30mL of CH_2Cl_2 and then enough 20% EtOAc/Hex was added to just maintain a clear dark red solution. On standing, **6aa** quickly began to precipitate and the mixture was allowed to rest for 2 hours. The dark red solution was decanted (keep aside) and the solid washed a few times with a 20% EtOAc/Hex. The solid was redissolved in CH_2Cl_2 and Hexane was added before concentrating in vacuo to give a light yellowish solid which was washed with hexanes in order to obtain a white crystalline product (11.77g of **6aa** (40%), pure *trans* isomer). The remaining products (approximately 20g in the dark red solution) were purified by column chromatography. A first chromatography using increasing amounts of EtOAc in Hexanes (10%, 20%, 30%, 50%) yielded three large fractions. The first fraction contained an unwanted side product and unreacted benzil. The second fraction contained **8aa** and **6aa**. The third fraction contained a mixture of **6aa**, **8aa** and some unidentified side products. Product **8aa** and **6aa** from the second and third fractions were further purified by column chromatographies (CH_2Cl_2 or EtOAc/Hex mixtures). The total amounts of recovered products were: 13.82g of **6aa** (47%, overall 98:2 *trans*/*cis* although recrystallized product is pure *trans* isomer) and 4.81g of **8aa** (21%).

Evidences for the formation of an allene intermediate

Reaction of allene intermediate with pyrrolidine. Synthesis of 4 and 5: Benzil **2a** (2.00 mmol) and methyl propiolate **3a** (2.00 mmol) were dissolved in 5 mL of CH_2Cl_2 and the solution was cooled to 0ºC in an ice bath. Et_3N (0.20 mmol) was added and the reaction was allowed to react for 10 minutes. Pyrrolidine (2.00 mmol) was added and the reaction was stirred for a few minutes. After removing the solvent at reduced pressure the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 80/20, 2% Et_3N to avoid hydrolysis of the enamine) to yield **4** (77%). **4** was quantitatively transformed into **5** simply by stirring a solution of **4** in CH_2Cl_2 with 1M HCl. After extracting with CH_2Cl_2 and removing the solvent at reduced pressure the product was purified by flash column chromatography (silica gel, n-hexane/EtOAc 80/20).



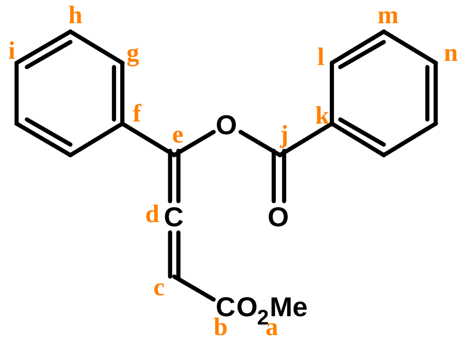
(E)-4-methoxy-4-oxo-1-phenyl-2-(pyrrolidin-1-yl)but-2-enyl benzoate (4): ^1H NMR ($CDCl_3$, 400 MHz): δ 1.62-1.72 (m, 2H), 1.77-1.86 (m, 2H), 3.21-3.26 (m, 2H), 3.29-3.36 (m, 2H), 3.68 (s, 3H), 4.81 (s, 1H), 7.24-7.29 (m, 1H), 7.32-7.40 (m, 4H), 7.48 (tt, 2H, *J* = 7.8 and 1.6 Hz), 7.59 (tt, 1H, *J* = 7.8 and 1.4 Hz), 8.15 (dd, 2H, *J* = 8.5 and 1.3 Hz), 8.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.0, 49.1, 50.4, 70.3, 87.0, 125.4, 128.52, 128.54, 129.8, 129.9, 133.2, 136.8, 156.4, 164.9, 168.5. IR ($CHCl_3$, cm^{-1}) 3012.8, 1726.9, 1678.8, 1578.0, 1451.5, 1427.2, 1267.6, 1214.3, 1148.6, 1095.9. Anal. Calcd. for $C_{20}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.54; H, 6.39; N, 3.85. MS, *m/z* (relative intensities) 365 (M+, 21), 260 (38), 244 (53), 243 (100), 228 (69), 154 (29), 105 (80), 77 (39).

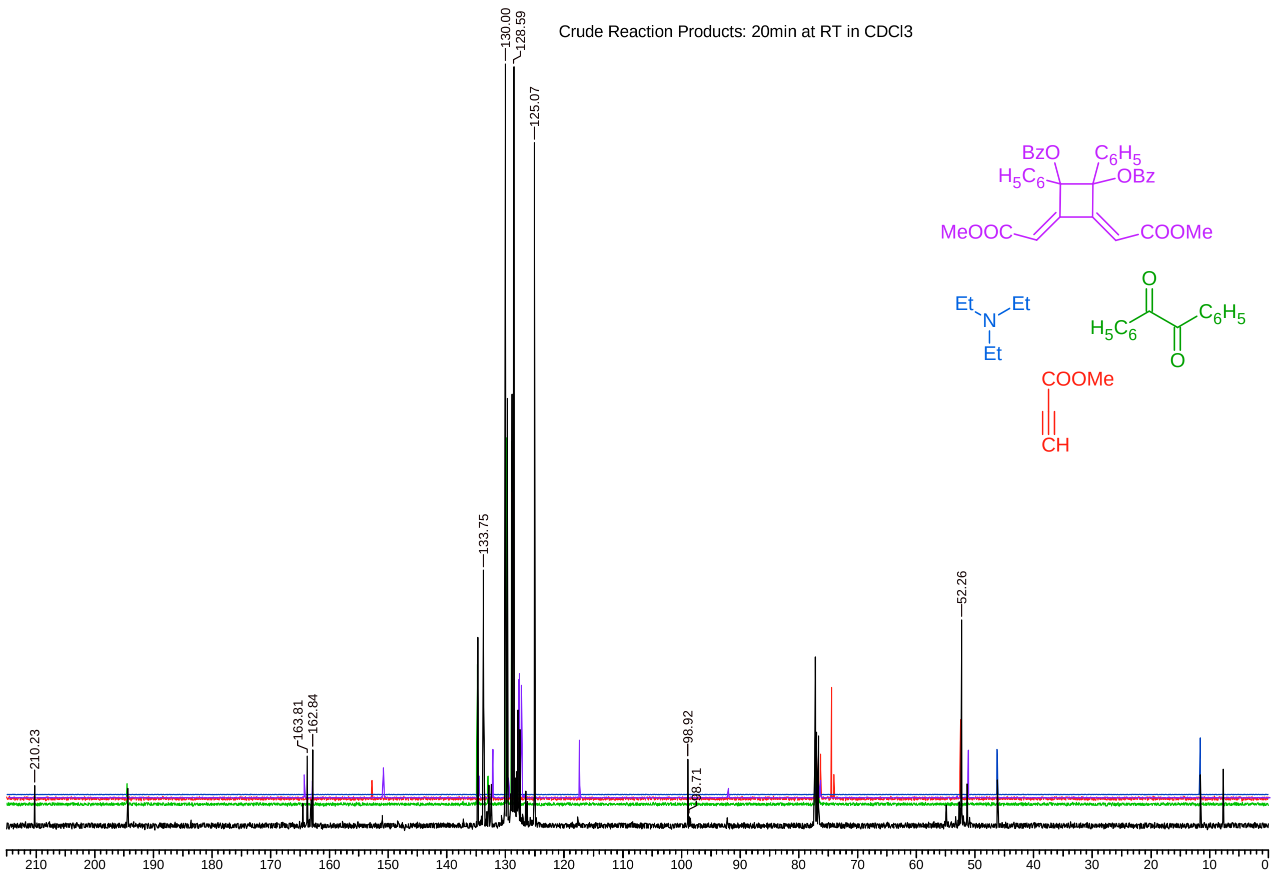


3-(methoxycarbonyl)-2-oxo-1-phenylpropyl benzoate (5): ^1H NMR ($CDCl_3$, 400 MHz): δ 3.53 (d, 1H, *J* = 15.4 Hz), 3.60 (d, 1H, *J* = 15.4 Hz), 3.64 (s, 3H), 6.39 (s, 1H), 7.40-7.47 (m, 5H), 7.52 (dd, 2H, *J* = 8.0 and 1.6), 7.58 (tt, 1H, *J* = 7.4 and 1.3), 8.10 (dd, 2H, *J* = 8.5 and 1.3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 45.6, 52.4, 80.3, 128.1, 128.5, 129.0, 129.1, 129.6, 129.9, 132.8, 133.5, 165.4, 166.5, 196.4. IR ($CHCl_3$, cm^{-1}) 3030.7, 1726.6, 1452.1, 1264.5, 1110.0. Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.41; H, 5.05. MS, *m/z* (relative intensities) 312 (M+, 1.2), 211 (21), 105 (100), 77 (17).

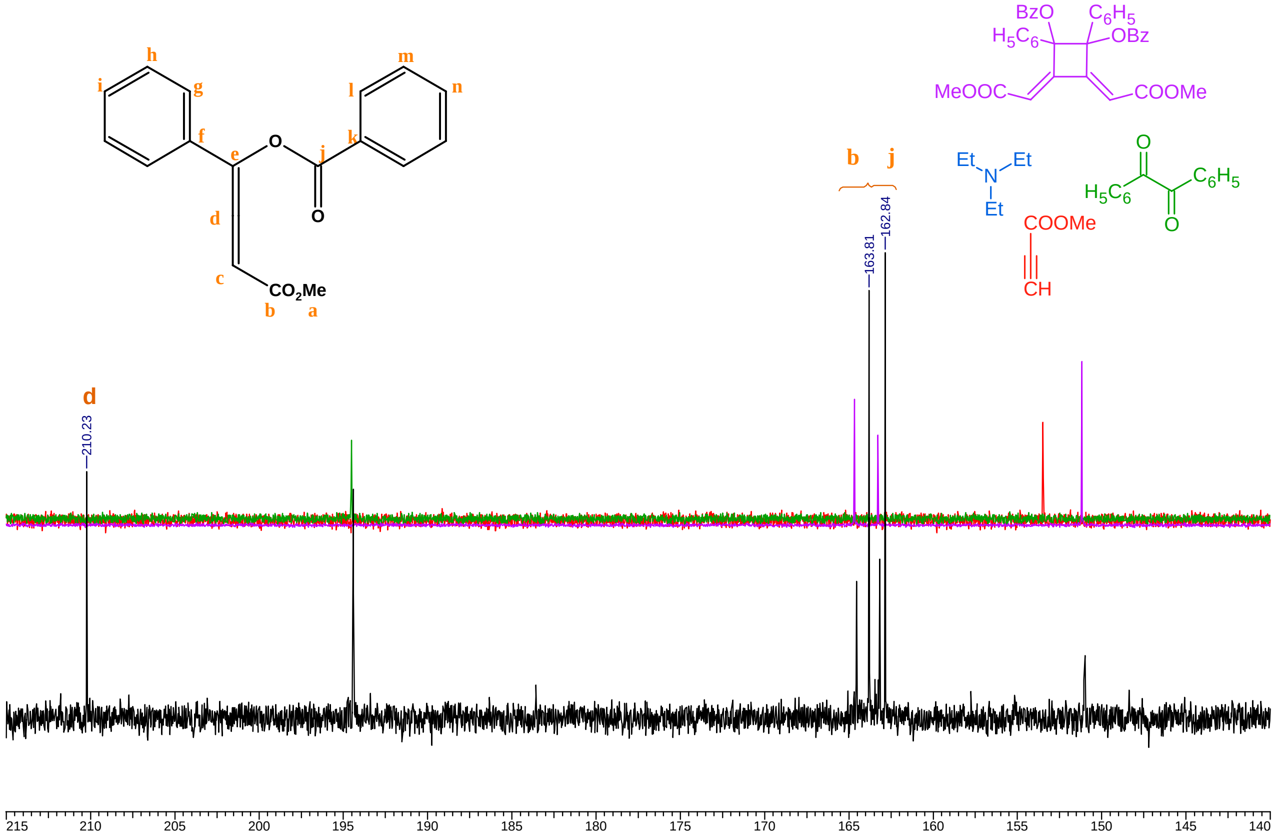
Reaction of Benzil and Methyl Propiolate catalyzed by Et_3N in $CDCl_3$: 2a (2.00 mmol) and **3a** (2.00 mmol) were dissolved in 3.3 mL of $CDCl_3$ and the solution was cooled to 0ºC in an ice bath. Et_3N (0.20 mmol) was added and the reaction was allowed to react for 5 minutes. Part of the reaction mixture was transferred into an NMR tube with a pipette and it was directly taken for the acquisition of its ^{13}C NMR spectrum at RT (the acquisition required 256 scans and 20 minutes). The following spectra show: 1) the formation of a major intermediate, 2) the disappearance of methyl propiolate and most of benzyl, 3) the formation of a small amount of the main cyclobutane product, and 4) the catalyst in the form of Et_3N and an ammonium salt (7.7 and 54.9 ppm). We can assign peaks to all of the C atoms of the allene except for C(e) which must be buried under a larger peak in the aromatic region.

C	**δ**
a	52.3
b	163.8
c	98.9
d	210.2
e	
f	130.1
g	125.1
h	128.6
i	129.0
j	162.8
k	128.7
l	130.0
m	128.6
n	133.8





Crude Reaction Products: 20min at RT in CDCl3



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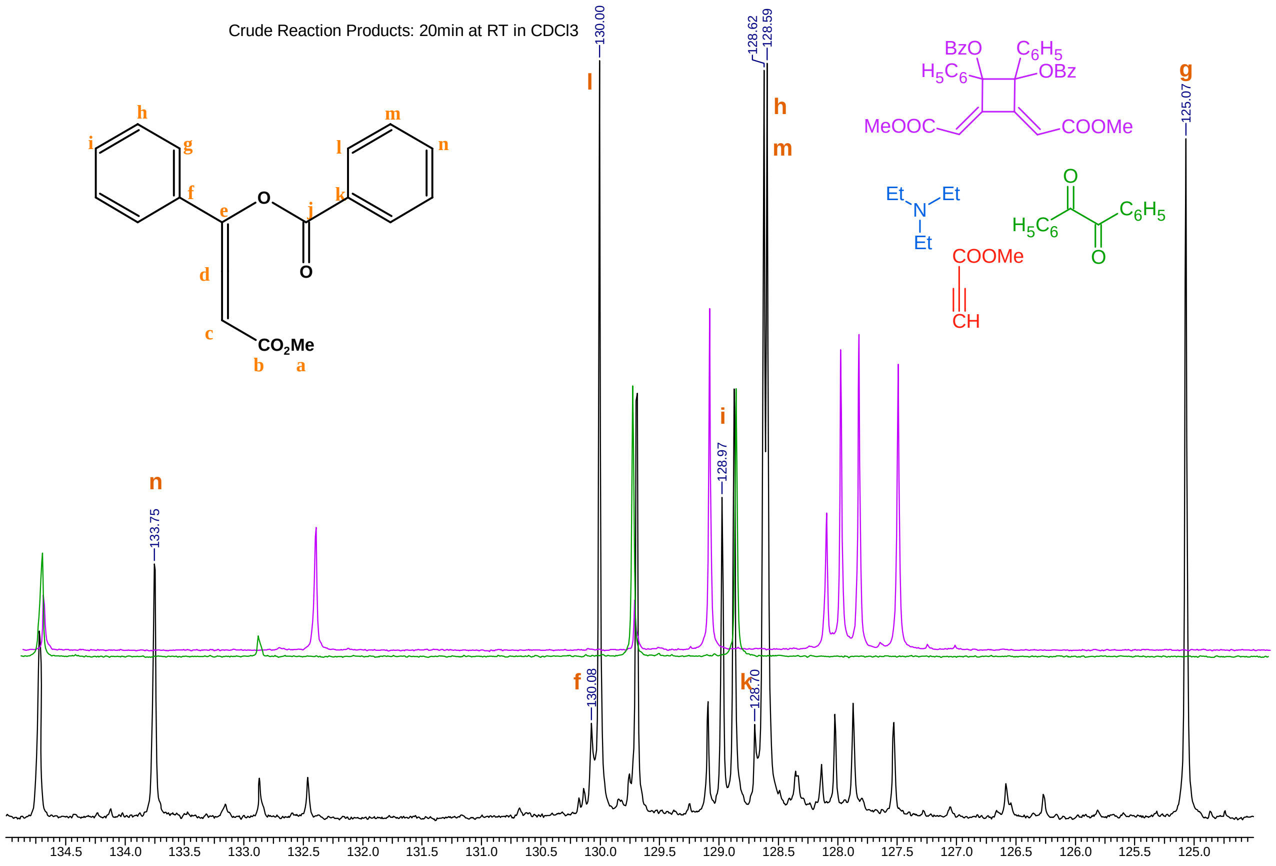
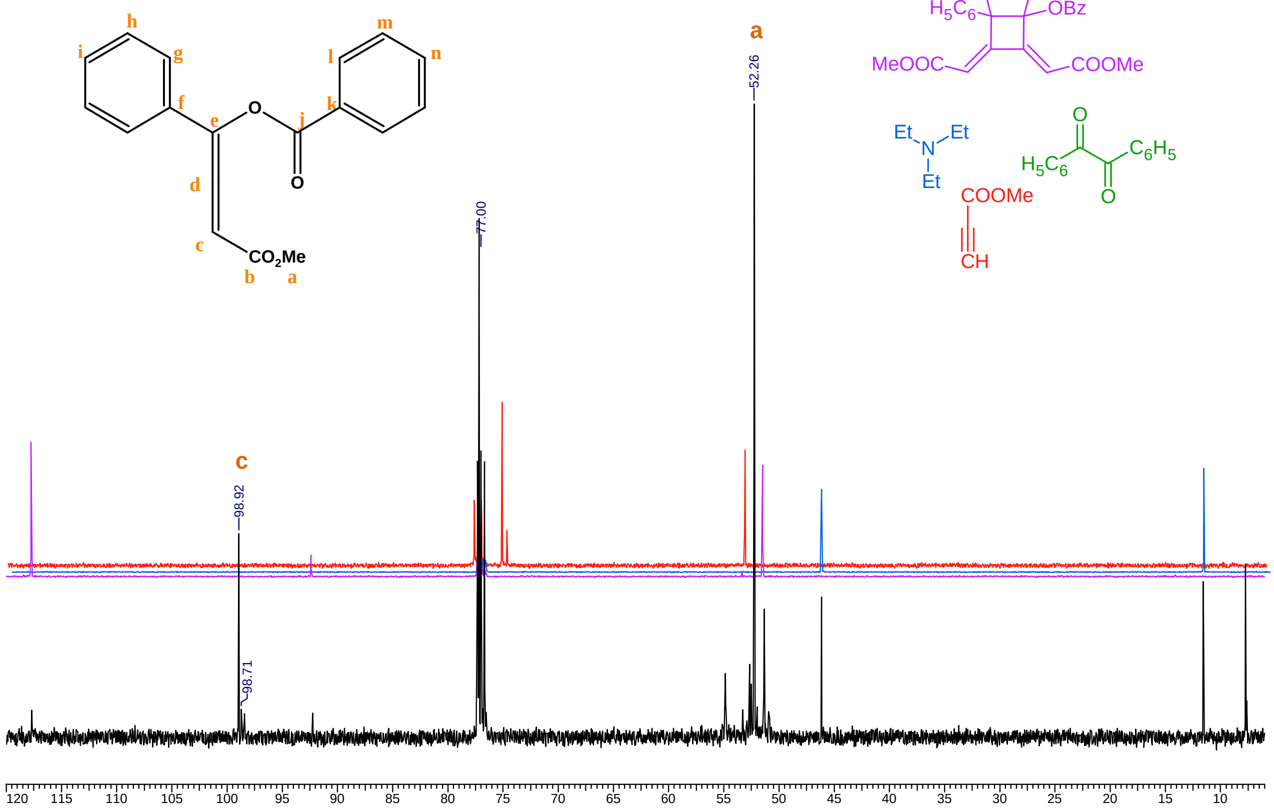
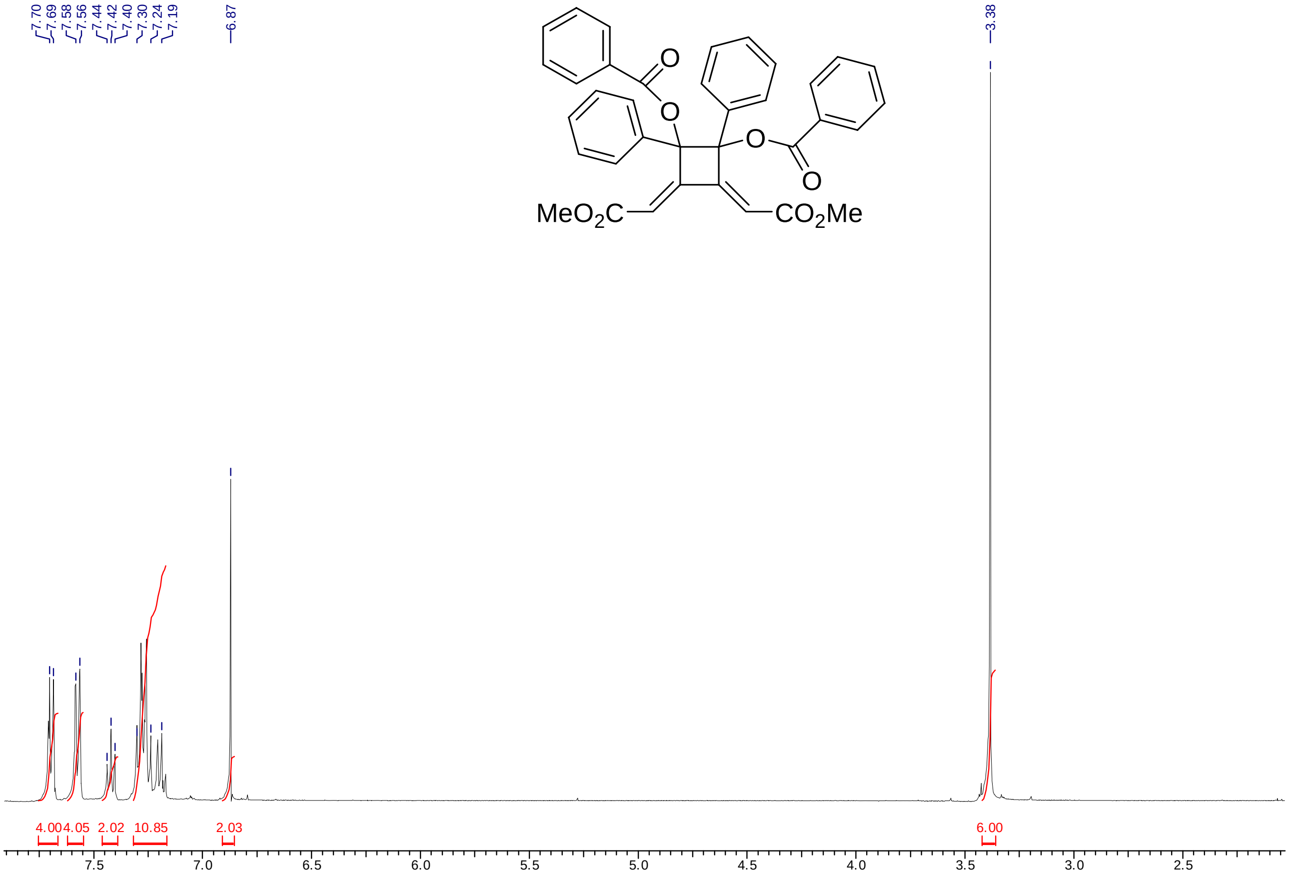
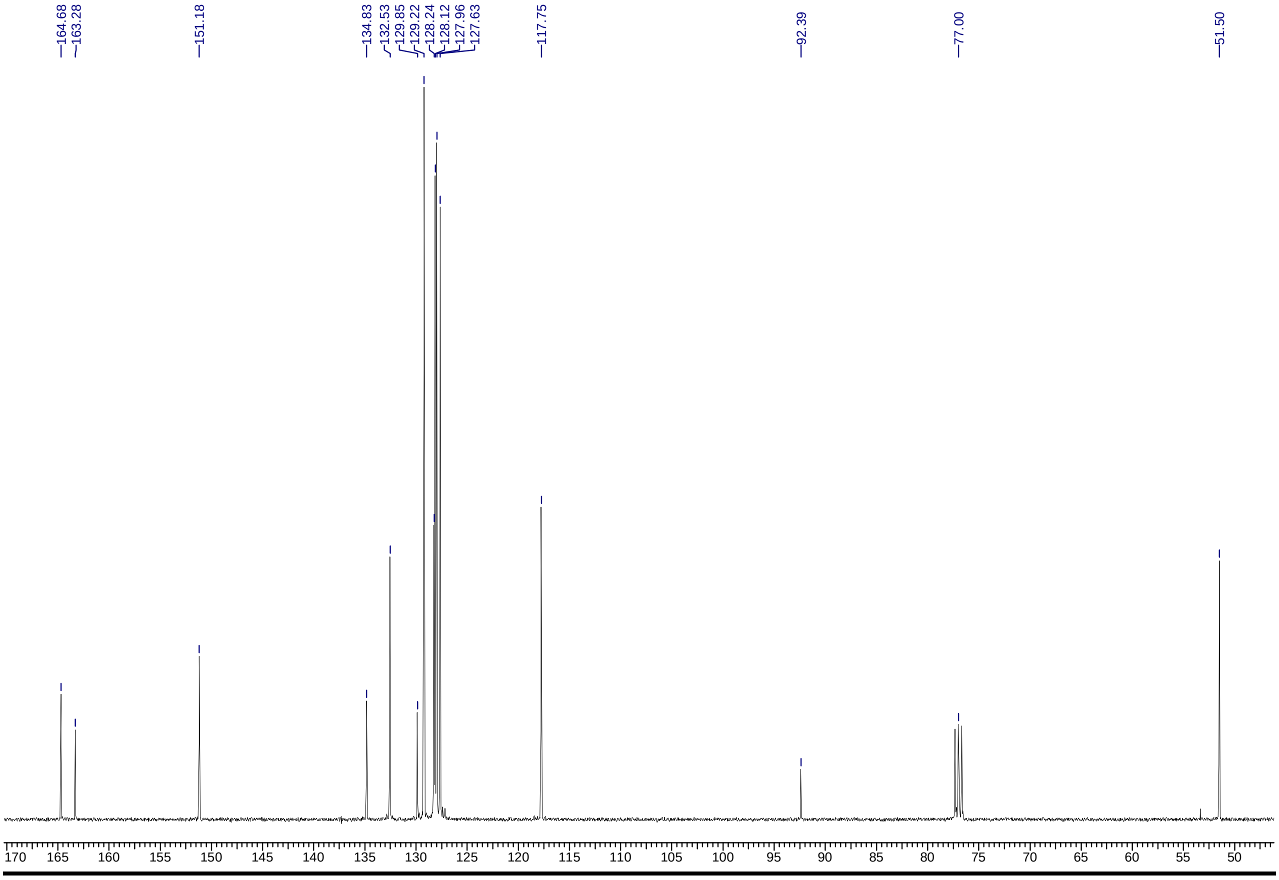
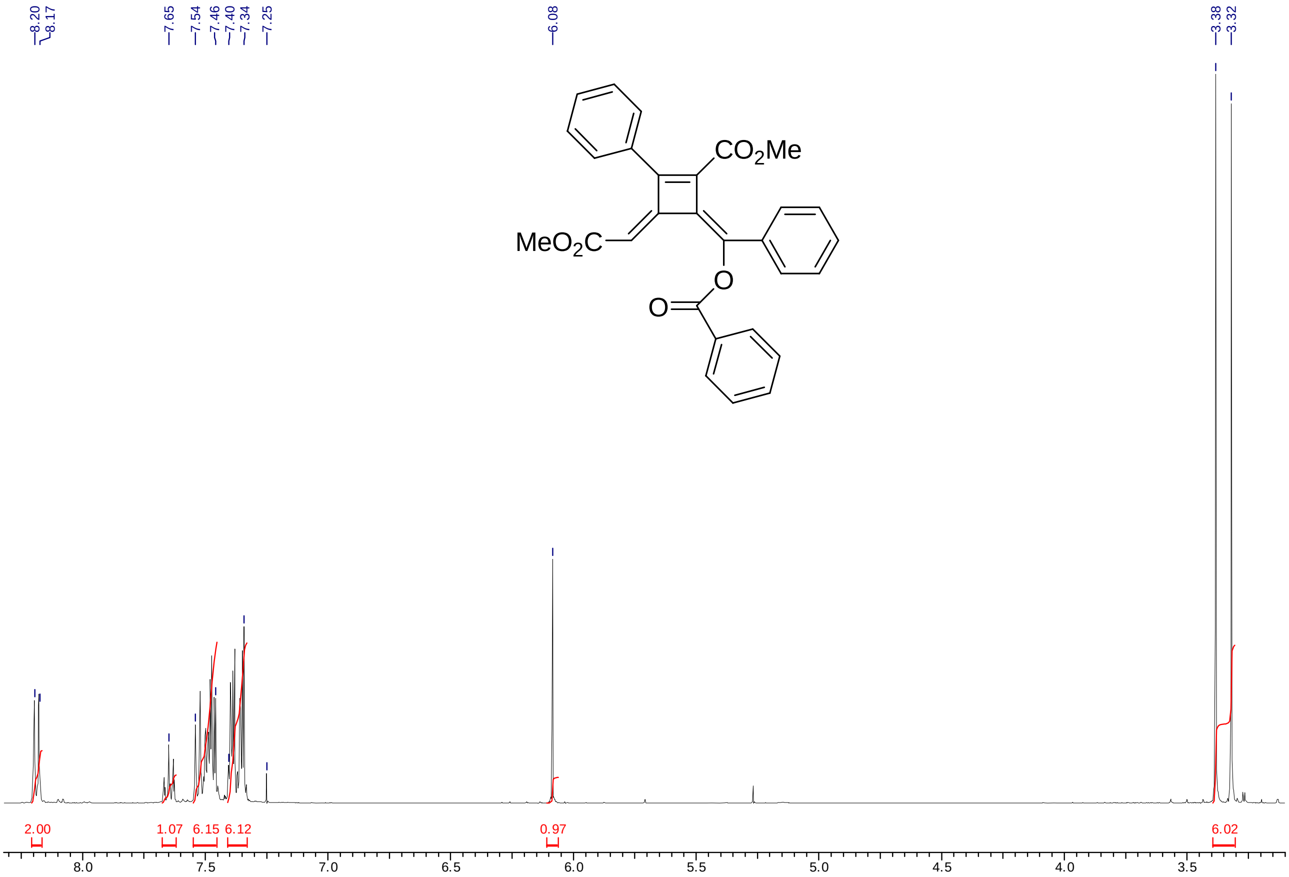


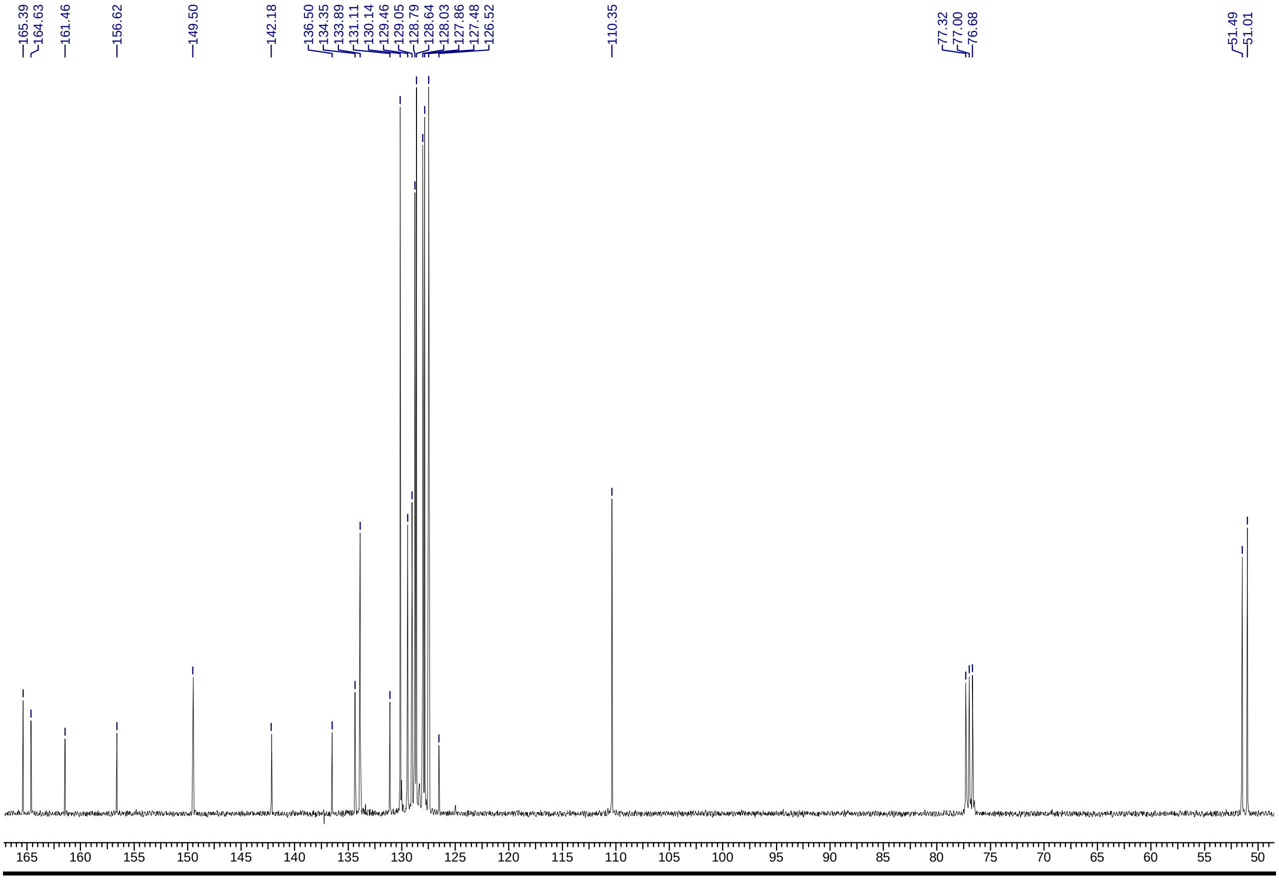
Crude Reaction Products: 20min at RT in CDCl3




7.70
7.69
7.58
7.56
7.44
7.42
7.40
7.30
7.24
7.19
6.87
3.38
O
O
O
O
MeO2C
CO2Me
4.00
4.05
2.02
10.85
2.03
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5


164.68
163.28
151.18
134.83
132.53
129.85
129.22
128.24
128.12
127.96
127.63
117.75
92.39
77.00
51.50
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50


8.20
8.17
7.65
7.54
7.46
7.40
7.34
7.25
6.08
3.38
3.32
CO2Me
MeO2C
O
O
2.00
1.07
6.15
6.12
0.97
6.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5


165.39
164.63
161.46
156.62
149.50
142.18
136.50
134.35
133.89
131.11
130.14
129.46
129.05
128.79
128.64
128.03
127.86
127.48
126.52
110.35
77.32
77.00
76.68
51.49
51.01
165
160
155
150
145
140
135
130
125
120
115
110
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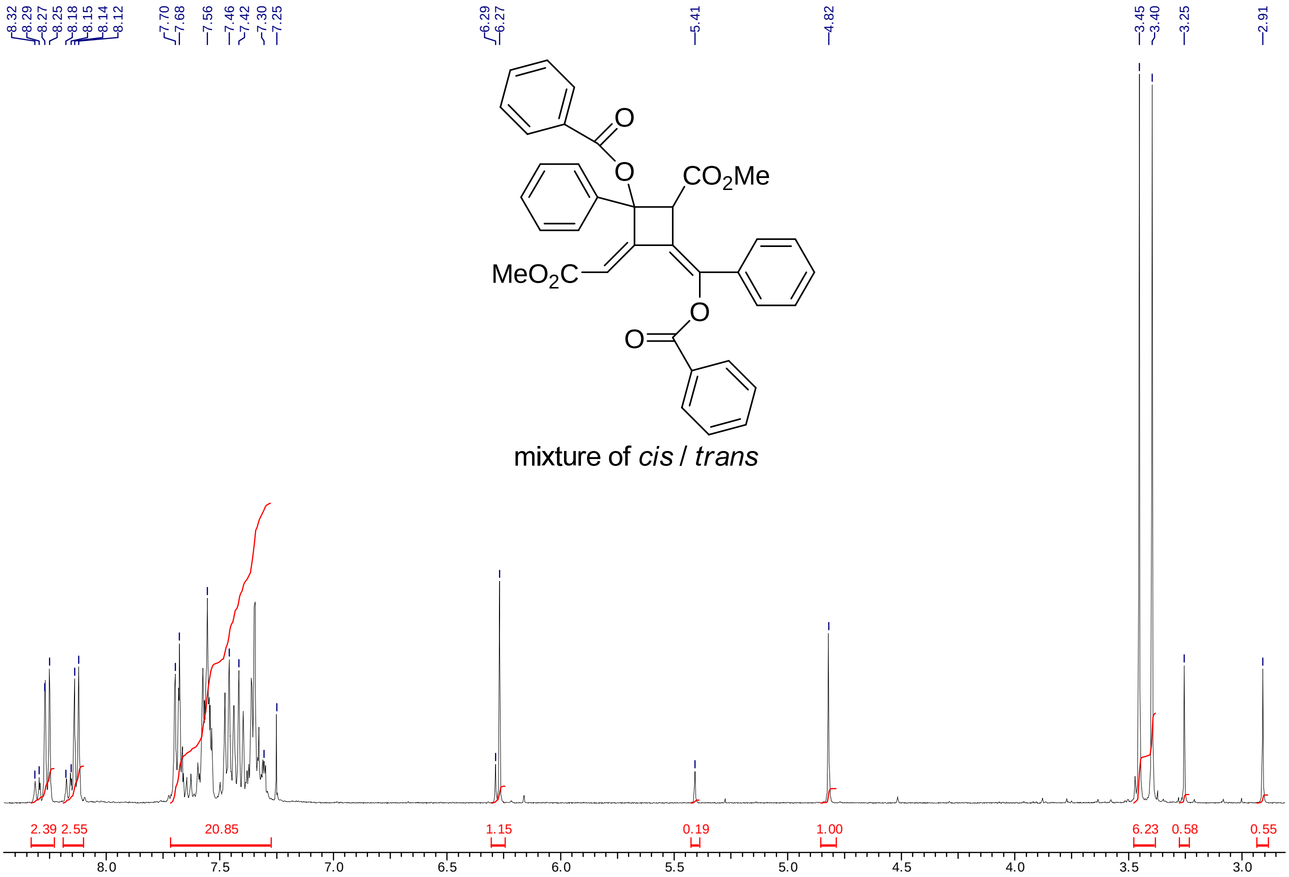
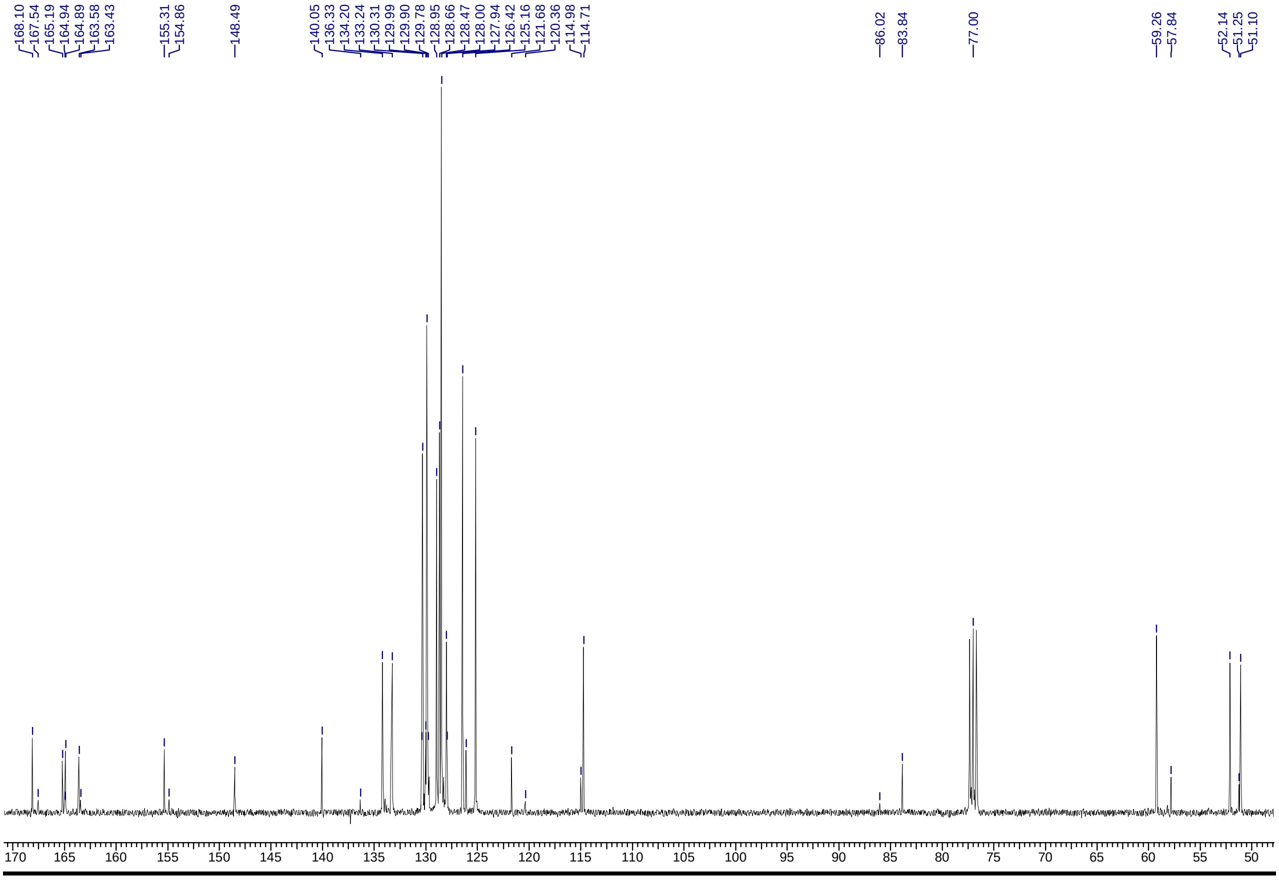
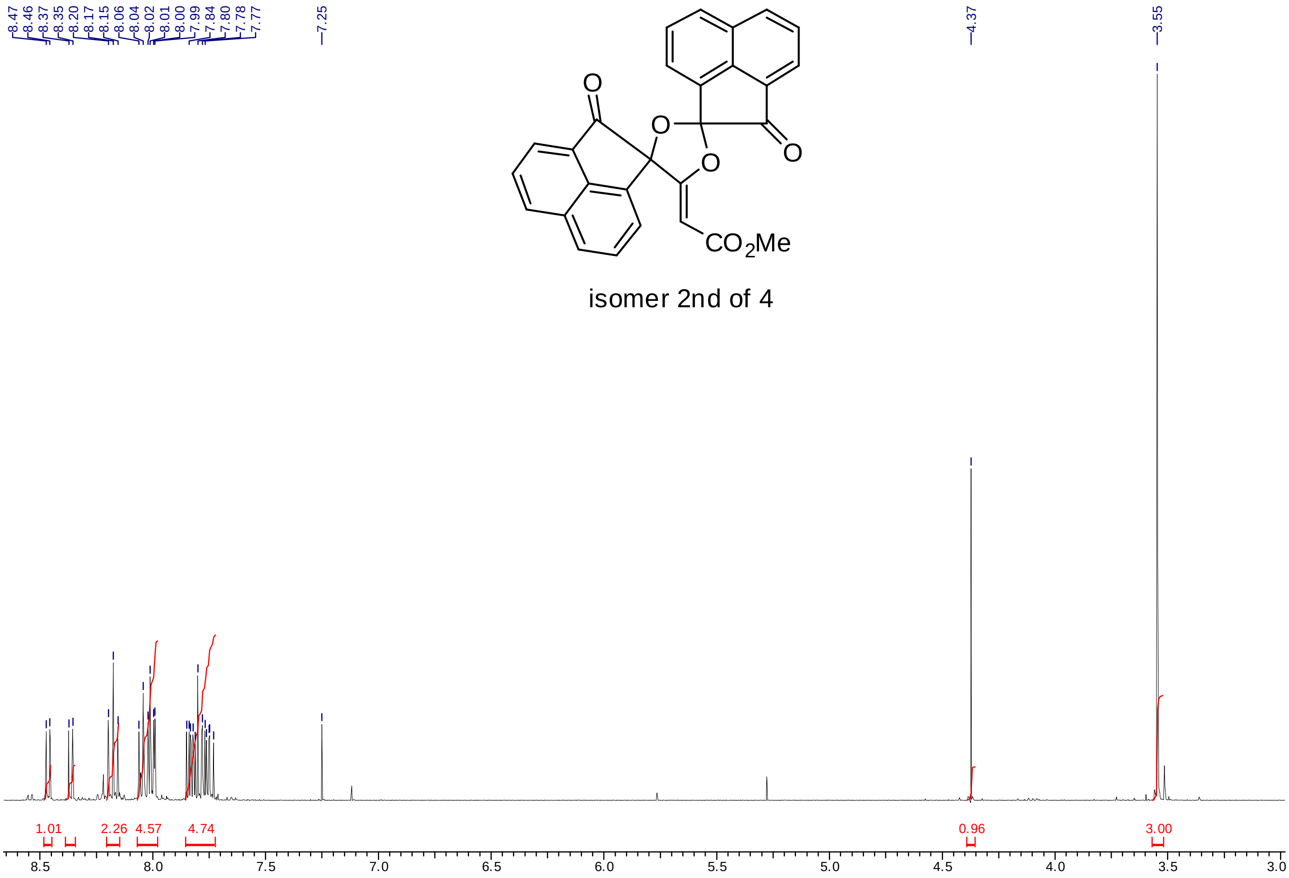
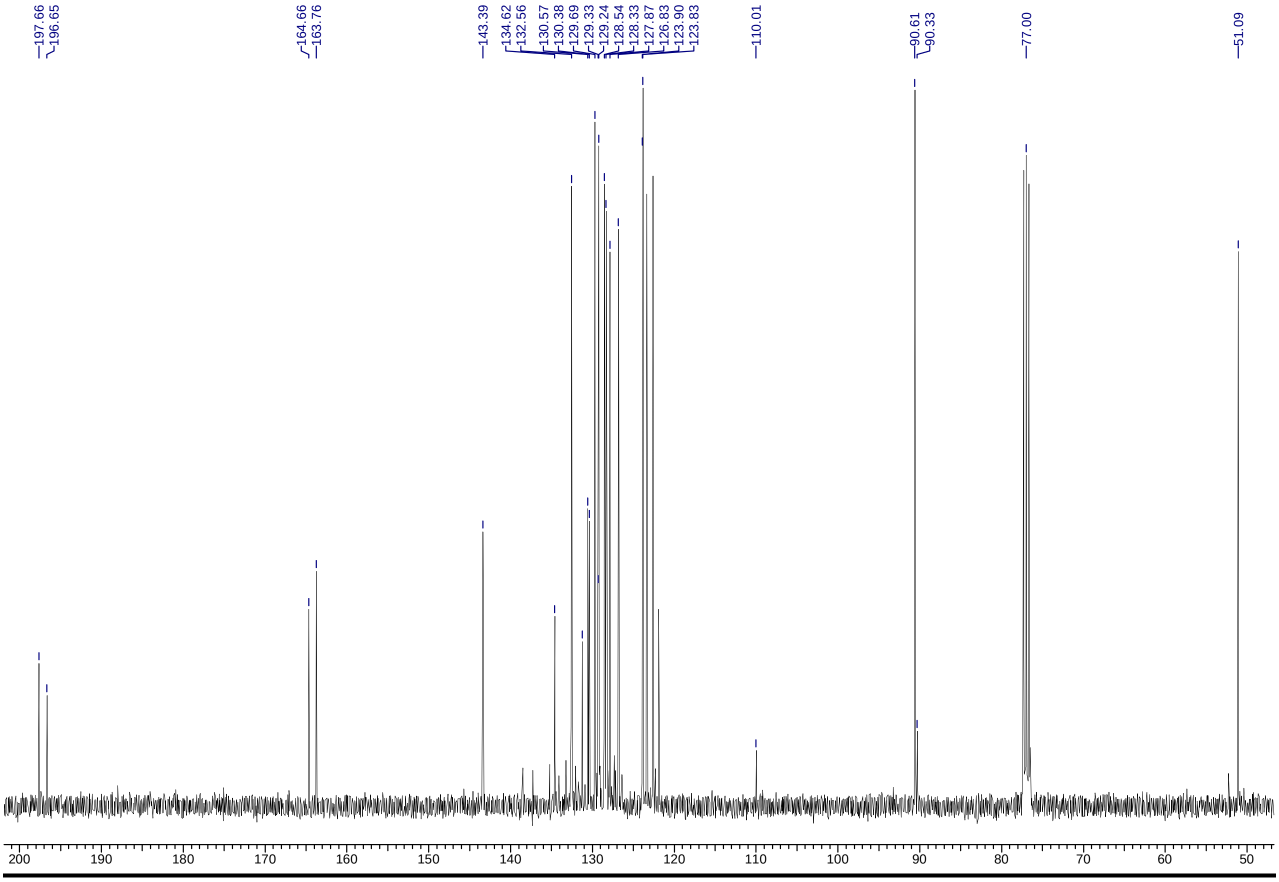
75
70
65
60
55
50



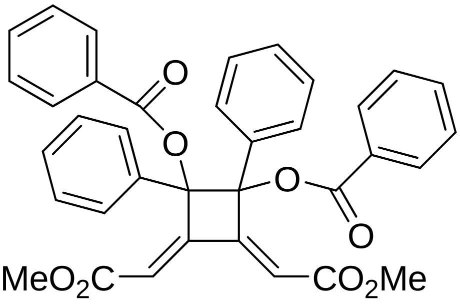
mixture of *cis* / *trans*

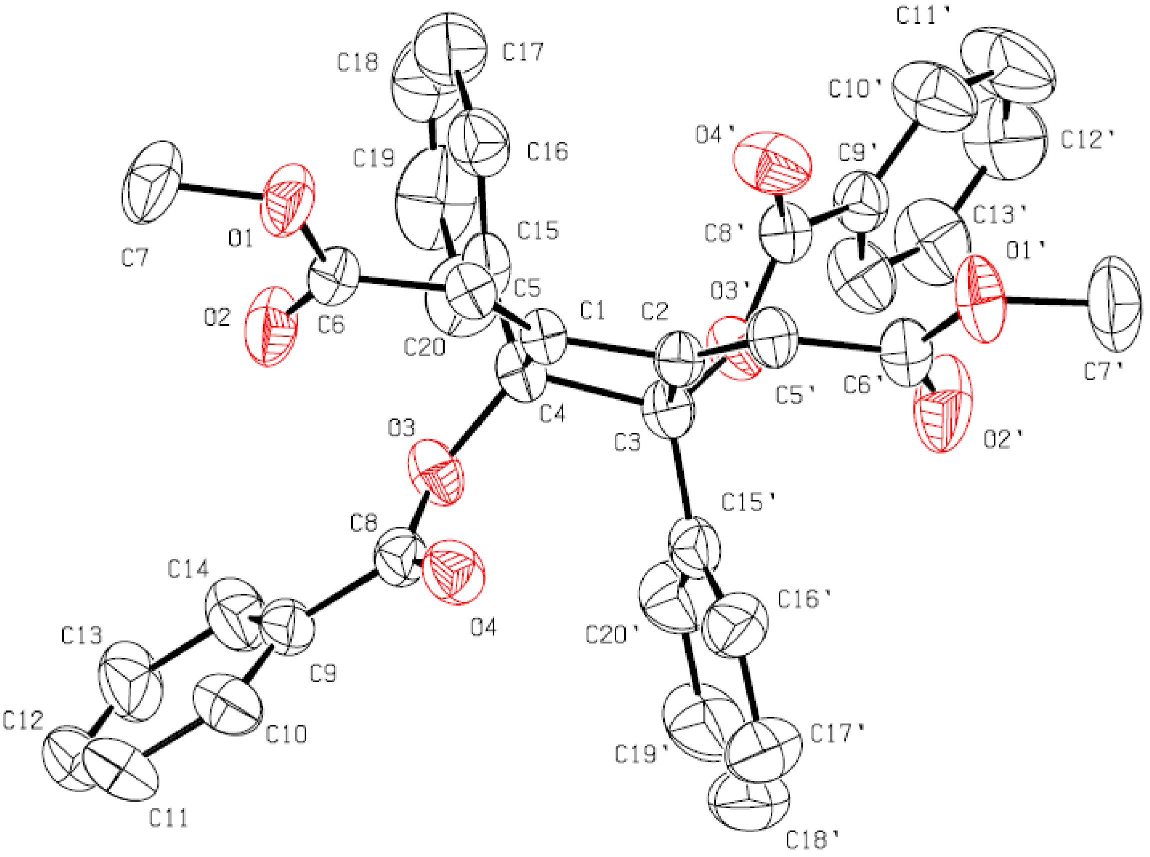



8.47
8.46
8.37
8.35
8.20
8.17
8.15
8.06
8.04
8.02
8.01
8.00
7.99
7.84
7.80
7.78
7.77
7.25
4.37
3.55
O
O
O
O
O
CO_2Me
isomer 2nd of 4
1.01
2.26
4.57
4.74
0.96
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0


197.66
196.65
164.66
163.76
143.39
134.62
132.56
130.57
130.38
129.69
129.33
129.24
128.54
128.33
127.87
126.83
123.90
123.83
110.01
90.61
90.33
77.00
51.09
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50

Crystal data for **6aa**: $C_{36}H_{28}O_8$, *M*=588.58, monoclinic, *a*=31.764(3), *b*=10.8730(10), *c*=18.823(2) Å, *β*=91.707(5)°, *V*=6498.0(11)Å^3, *T*=293K, space group C2/c (no. 15), *Z*=8, 34744 reflections measured, 5184 unique (R_{int}=0.064). All non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least squares procedures on F^2. The solvent molecule (dichloromethane) presented a higher disorder and it was impossible to establish a good model even using an isotropic refinement. Therefore a SQUEZZE procedure was made in order to eliminate the contribution of the solvent molecule. In any case it does not play an important role in the structure. All H atoms were placed in geometrically calculated positions. The methyl-H atoms were refined as rigid groups, which were allowed to rotate but not to tip, with $U_{iso}(H)=1.5U_{eq}(C)$. All other H atoms were allowed to ride on their parent atoms with $U_{iso}(H)=1.2U_{eq}(C)$. The final *R* and wR^2 were 0.0770 and 0.2019 respectively. CCDC 704023.





Crystal data for **8aa:** $C_{29}H_{22}O_6$, *M*=466.47, monoclinic, *a*=10.769(1), *b*=9.678(1), *c*=23.311(1) Å, *β*=96.400(2)º, *V*=2414.4(4)Å^3, *T*=293K, space group P21/c (no. 14), *Z*=4, 27643 reflections measured, 3454 unique (R_{int}=0.047). Only the reflections up to 0.9 Å were considered in the refinement process. All non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least squares procedures on F^2. The molecule presents a moderate disorder in one carboxylic group (O4-C20-03-C21) that was modeled using two sites with occupancy levels of 70% and 30% of probability. All H atoms were placed in geometrically calculated positions. The methyl-H atoms were refined as rigid groups, which were allowed to rotate but not to tip, with U_{iso}(H)=1.5U_{eq}(C). All other H atoms were allowed to ride on their parent atoms with U_{iso}(H)=1.2U_{eq}(C). The final *R* and *wR*^{2} were 0.0699 and 0.1955 respectively. CCDC 704024.