Lewis Acid-Induced Intramolecular Friedel-Crafts Cyclization of 1,3-bis-Exocyclic Dienes. A New Route to 4a-Methyltetrahydrofluorenes.

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Supplementary Information & Experimental.

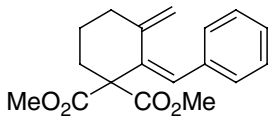
General. Proton magnetic resonance (^{1}H NMR) and carbon magnetic (^{13}C NMR) resonance spectra were measured at 300 MHz with a Bruker AM 300 and ALS 300 spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (scale). The multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, number of protons and coupling constants (reported in Hz)) are indicated in parentheses. High-resolution mass spectra were recorded on a Thermoquest Finnigan MAT 95 Xl. Elemental analyses were performed by Service Central d'Analyses du CNRS de Solaize, FRANCE. Infrared spectra were recorded on a Perkin-Elmer 298 or Perkin-Elmer FT-IR PARAGON 500. Melting points were measured on a BUCHI B-540 and are uncorrected.

All reactions were performed under an atmosphere of dry nitrogen or dry argon in glassware equipped with a magnetic stirring bar and a rubber septum. Standard inert atmosphere techniques were used in handling all air and moisture sensitive reagents. Reaction were monitored by analytical thin layer chromatography (TLC) using commercial aluminium sheets pre-coated (0.2 mm layer thickness) with silica gel $60F_{254}$ (Merck). Product purification by flash column chromatography was performed using Merck Silica Gel 60 Å (40-63 m). Anhydrous toluene was freshly distilled from CaH_2, THF from sodium-benzophenone ketyl radical. Chloroform ($CHCl_3$) was used as received without purification.

Starting material :
Experimental procedure for the synthesis of 1,3-bis-exocyclic dienes:
Potassium hydride (35% in mineral oil) was washed with anhydrous THF, dried and stored under nitrogen prior to use.
To a suspension of KH (48 mg, 1.2 mmol) in 3 ml of anhydrous THF was added 18-C-6 (53 mg, 0.2 mmol), 2-(4-methylene-hex-5-ynyl)-malonic acid dimethyl ester (191 mg, 1 mmol) in 4 ml of THF, and iodobenzene (170 µl, 1.5 mmol). This mixture was stirred at room temperature for 15 min. In a separate flask, *n*BuLi (2M in hexanes) was added dropwise at room temperature to a suspension of $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in 3 ml of THF until the mixture becomes dark green. After heating at reflux for 5 min and cooling, the mixture turned to a dark red homogeneous solution and was added at room temperature *via* a cannula to the anion solution prepared above. The resulting mixture was then stirred at 30 °C for 3 h (monitored by TLC until completion). The solution was then filtered through a short pad of silica gel (eluting with diethyl ether) and the solvent was removed under reduced pressure.

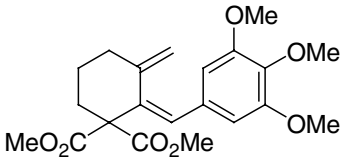
The residue was purified by flash chromatography with petroleum ether/Et_2O 80/20 to afford **1a** as a pale yellow solid (182 mg, 61%).

(*E*)-3-Methylene-2-methylene-cyclohexane-1,1-dicarboxylic acid dimethyl ester 1a



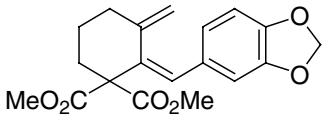
Mp 91-92°C. IR (KBr): 3050, 3020, 2990, 2930, 2860, 1735, 1720, 1630, 1435, 1280, 1240, 1190, 1115, 1080, 990, 910, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.71 (m, 2H), 2.40 (t, *J* = 6.1 Hz, 4H), 3.79 (s, 6H), 4.76 (d, *J* = 2.2 Hz, 1H), 5.02 (m, 1H), 6.12 (s, 1H), 7.13-7.26 (m, 3H), 7.31 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.31, 33.96, 36.26, 52.73, 65,00, 116.58, 126.73, 126.77, 127.89, 129.04, 137.03, 139.72, 143.07, 170.80. Microanalysis (%) : found : C 71.93, H 6.65; calcd. for $C_{21}H_{26}O_7$: C 71.98, H 6.71.

(*E*)-3-Methylene-2-(3,4,5-trimethoxy-benzylidene)-cyclohexane-1,1-dicarboxylic acid dimethyl ester 1b



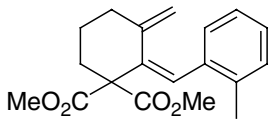
Brown solid, yield 83%. Mp 93-95°C. IR (KBr): 3008, 2954, 2939, 2839, 1742, 1729, 1580, 1508, 1457, 1430, 1334, 1288, 1263, 1232, 1126, 1001, 903, 875, 816 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.73 (m, 2H), 2.41 (t, *J* = 6.0 Hz, 4H), 3.80 (s, 6H), 3.82 (s, 6H), 3.84 (s, 3H), 4.85 (d, *J* = 1.5 Hz, 1H), 4.98 (s, 1H), 6.05 (s, 1H), 6.59 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.40, 34.02, 36.27, 52.90, 56.14, 61.03, 65.13, 106.45, 116.62, 126.60, 132.40, 137.18, 139.45, 143.31, 152.72, 170.85. Microanalysis (%) : found : C 64.74, H 6.57; calcd. for $C_{18}H_{20}O_4$: C 64.60, H 6.71.

(*E*)-2-Benzo[1,3]dioxol-5-ylmethylene-3-methylene-cyclohexane-1,1- dicarboxylic acid dimethyl ester 1c



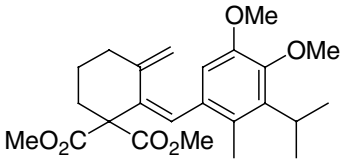
Yellow oil, yield 79%. IR (film): 3082, 2952, 1732, 1634, 1606, 1505, 1488, 1445, 1247, 1155, 1039, 935, 911, 807, 733 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.70 (m, 2H), 2.37 (t, *J* = 6.1 Hz, 4H), 3.78 (s, 6H), 4.82 (d, *J* = 2.1 Hz, 1H), 4.95 (d, *J* = 0.9 Hz, 1H), 5.91 (s, 2H), 6.00 (s, 1H), 6.70 (m, 2H), 6.89 (d, *J* = 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.40, 34.03, 36.28, 52.82, 65,07, 101.00, 107.97, 109.12, 116.59, 123.31, 126.27, 130.92, 138.61, 143.25, 146.48, 147.19, 170.90. HRMS calcd for $C_{19}H_{20}O_6$ (MH^+) 345.1338, found 345.1340.

(*E*)-2-(2-Methyl-benzylidene)-3-methylene-cyclohexane-1,1- dicarboxylic acid dimethyl ester 1d



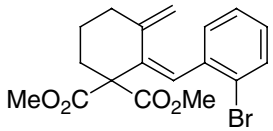
White solid, yield 63%. Mp 69-71°C. IR (KBr): 3080, 2980, 2953, 2935, 1735, 1638, 1478, 1459, 1446, 1432, 1283, 1256, 1230, 1199, 1098, 995, 901, 753 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.68 (m, 2H), 2.27 (s, 3H), 2.31 (t, J = 6.1 Hz, 2H), 2.41 (m, 2H), 3.78 (s, 6H), 4.50 (d, J = 2.0 Hz, 1H), 4.78 (m, 1H), 6.18 (s, 1H), 7.01-7.13 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 19.93, 24.08, 33.65, 36.11, 52.75, 64.54, 116.37, 125.37, 126.81, 126.87, 126.88, 129.56, 136.25, 136.97, 139.49, 142.71, 171.07. HRMS calcd for $C_{19}H_{22}O_4$ (MH^+) 315.1596, found 315.1596.

(*E*)-2-(3-Isopropyl-4,5-dimethoxy-2-methyl-benzylidene)-3-methylene-cyclohexane-1,1-dicarboxylic acid dimethyl ester 1e



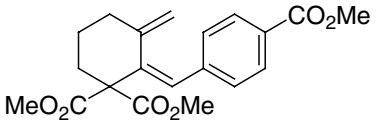
Brown oil, yield 76%. IR (film): 3084, 2952, 2872, 1739, 1634, 1590, 1455, 1434, 1314, 1252, 1154, 1121, 1083, 903, 783 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.31 (d, J = 7.2Hz, 6H), 1.67 (m, 2H), 2.20 (s, 3H), 2.29 (t, J = 6.4 Hz, 2H), 2.41 (m, 2H), 3.34 (s, 1H), 3.76 (s, 3H), 3.78 (s, 6H), 3.80 (s, 3H), 4.51(d, J = 2.0 Hz, 1H), 4.79 (d, J = 1.9 Hz, 1H), 6.19 (s, 1H), 6.50 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 16.58, 21.57, 23.99, 28.42, 33.53, 35.97, 52.69, 55.66, 60.79, 64.37, 110.87, 116.30, 126.64, 128.28, 132.77, 138.63, 139.58, 142.44, 147.21, 150.38, 171.12. HRMS calcd for $C_{24}H_{32}O_6$ (MH^+) 416.2198, found 416.2194.

(*E*)-2-(2-bromo-benzylidene)-3-methylene-cyclohexane-1,1- dicarboxylic acid dimethyl ester 1f



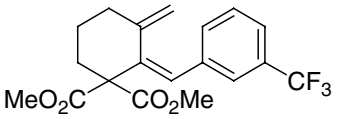
White solid, yield 34%. Mp 100-102°C. IR (KBr): 3011, 2958, 2939, 2873, 1748, 1726, 1635, 1465, 1442, 1258, 1230, 1156, 1084, 906, 748 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.69 (m, 2H), 2.34 (t, J = 6.1 Hz, 2H), 2.40 (t, J = 6.0 Hz, 2H), 3.79 (s, 6H), 4.62 (d, J = 1.7 Hz, 1H), 4.82 (s, 1H), 6.18 (s, 1H), 7.04 (m, 1H), 7.13-7.24 (m, 3H), 7.50 (d, J =7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.00, 33.66, 36.01, 52.82, 64,38, 116.75, 124.14, 126.78, 126.90, 128.32, 130.73, 132.27, 138.04, 140.76, 142.57, 170.81. Microanalysis (%) : found : C 57.30, H 5.05; calcd. for $C_{18}H_{19}BrO_4$: C 57.01, H 5.05.

(*E*)-2-(4-methoxycarbonyl-benzylidene)-3-methylene-cyclohexane-1,1- dicarboxylic acid dimethyl ester 1g



White solid, yield 67%. Mp 62-64°C. IR (KBr): 3084, 2953, 1764, 1735, 1717, 1605, 1456, 1436, 1277, 1239, 1147, 1107, 1013, 938, 902, 888, 786, 766, 716 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.74 (m, 2H), 2.40 (d, J = 6.1 Hz, 4H), 3.79 (s, 6H), 3.89 (s, 3H), 4.72 (d, J = 1.9 Hz, 1H), 4.90 (s, 1H), 6.14 (s, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.9 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.20, 33.97, 36.20, 52.03, 52.82, 64.98, 117.17, 125.94, 128.32, 129.04, 129.25, 141.98, 141.98, 142.80, 166.95, 170.57. Microanalysis (%) : found : C 66.88, H 6.25; calcd. for $C_{20}H_{22}O_6$: C 67.03, H 6.19.

(*E*)-3-Methylene-2-(3-trifluoromethyl-benzylidene)-cyclohexane-1,1- dicarboxylic acid dimethyl ester 1h



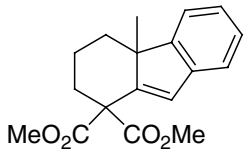
Colorless solid, yield 52%. Mp 75-77°C. IR (KBr): 3080, 2943, 1729, 1638, 1593, 1436, 1331, 1289, 1261, 1237, 1164, 1127, 1074, 998, 911, 805, 701 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.74 (m, 2H), 2.41 (t, J = 6.0 Hz, 4H), 3.79 (s, 6H), 4.71 (d, J = 1.9 Hz, 1H), 4.92 (s, 1H), 6.13 (s, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.55 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.52, 34.28, 36.49, 52.70, 65.25, 117.47, 123.75, 124.52, 125.64, 126.22, 128.66, 130.67, 132.61, 138.14, 141.95, 143.01, 170.90.

Friedel-Crafts cyclizations :

With $BF_3.Et_2O$: diene **1a** (R = H) (60 mg, 0.2 mmol) was dissolved in 2.5 ml of $CHCl_3$ at 0°C. $BF_3.Et_2O$ (152 l, 1.2 mmol) was slowly added and the resulting solution stirred at 40°C for 6 hours. The reaction mixture was then quenched with 2 ml of water and 5 ml of CH_2Cl_2 were added, aqueous phase was extracted with 5 ml of CH_2Cl_2. Combined organic phases were dried ($MgSO_4$) and evaporated to yield a crude product. Purification by gel flash column chromatography yielded **2a** as a white solid (56 mg, 93%).

With $Sc(OTf)_3$: diene **1a** (R = H) (30 mg, 0.1 mmol) was dissolved in 1 ml of toluene and $Sc(OTf)_3$ (10 mg, 0.02 mmol) was added. After 4 hours at reflux, the reaction was stopped and the resulting mixture directly purified by gel flash column chromatography to yield **2a** as a white solid (29 mg, 96%).

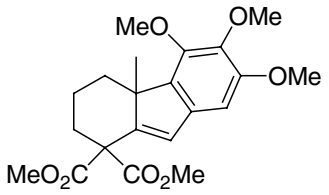
4a-Methyl-2,3,4,4a-tetrahydro-fluorene-1,1-dicarboxylic acid dimethyl ester 2a



Mp 98-100°C. IR (KBr): 2990, 2918, 2847, 1748, 1731, 1466, 1451, 1436, 1292, 1265, 1245, 1225, 1178, 1122, 1089, 994, 893, 754 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.08 (td, J = 13.2, 3.8 Hz, 1H), 1.16 (s, 3H), 1.71 (m, 2H), 1.88 (m, 1H), 2.14 (dd, J = 12.8, 1.7 Hz, 1H), 2.68 (dd, J = 12.8, 1.7 Hz, 1H), 3.73 (s, 3H), 3.84 (s, 3H), 6.63 (s, 1H), 7.17-7.25 (m, 3H),

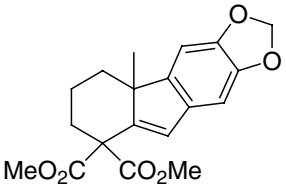
7.34 (d, J = 6.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 19.4, 22.1, 34.4, 37.4, 51.2, 52.7, 53.0, 58.9, 121.1, 121.7, 125.1, 126.2, 126.8, 141.2, 149.5, 154.1, 170.5, 171.2. HRMS calcd for $C_{18}H_{20}O_4$ (MH^+) 301.1439, found 301.1440.

5,6,7-Trimethoxy-4a-methyl-2,3,4,4a-tetrahydro-fluorene-1,1-dicarboxylic acid dimethyl ester 2b



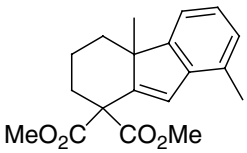
scale : diene **1b** (100 mg, 0.26 mmol); purification: flash chromatography on silica gel (eluent : PE:Et_2O 50:50); yield: 94%. Mp 120-122°C. IR (KBr): 2978, 2940, 1754, 1737, 1608, 1571, 1471, 1450, 1408, 1356, 1292, 1251, 1231, 1136, 1114, 1100, 1076, 1034, 1018, 982, 922, 878 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.14 (td, J = 13.4, 3.8 Hz, 1H), 1.23 (s, 3H), 1.86 (m, 3H), 2.45 (d, J = 12.6 Hz, 1H), 2.68 (d, J = 12.6 Hz, 1H), 3.73 (s, 3H), 3.82 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 3.93 (s, 3H), 6.48 (s, 1H), 6.68 (s, H). ^{13}C NMR ($CDCl_3$, 75 MHz): 19.5, 20.5, 34.7, 36.5, 52.6, 59.9, 53.3, 56.6, 59.1, 61.3, 101.5, 126.1, 137.4, 137.8, 140.7, 150.0, 150.4, 153.7, 170.8, 171.6. Microanalysis (%) : found : C 64.55, H 6.58; calcd. for $C_{21}H_{26}O_7$: C 64.60, H 6.71.

4b-Methyl-4b,5,6,7-tetrahydro-1,3-dioxa-cyclopenta[b]fluorene-8,8-dicarboxylic acid dimethyl ester 2c



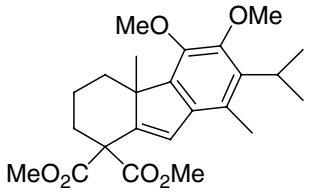
scale : diene **1c** (80 mg, 0.23 mmol); purification: flash chromatography on silica gel (eluent : PE:Et_2O 75:25); yield: 81%. Mp 109-111°C. IR (KBr): 2982, 2964, 2938, 2865, 1743, 1720, 1496, 1474, 1439, 1294, 1267, 1245, 1218, 1145, 1044, 941, 872, 830 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.04 (td, J = 13.0, 3.9 Hz, 1H), 1.11 (s, 3H), 1.68-1.75 (m, 2H), 1.84 (tt, J = 13.8, 3.5 Hz, 1H), 2.06 (br.d, J = 12 Hz, 1H), 2.66 (br.d, J = 11.8 Hz, 1H), 3.73 (s, 3H), 3.83 (s, 3H), 5.93 (s, 2H), 6.52 (s, 1H), 6.78 (s, 1H), 6.82 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 19.5, 22.2, 34.5, 37.7, 51.0, 52.7, 53.0, 58.9, 101.0, 102.6, 102.8, 125.7, 134.7, 146.0, 146.6, 148.2, 148.5, 170.5, 171.2. Microanalysis (%) : found : C 66.20, H 5.93; calcd. for $C_{19}H_{20}O_6$: C 66.27, H 5.85.

4a,8-dimethyl-2,3,4,4a-tetrahydro-fluorene- dicarboxylic acid dimethyl ester 2d



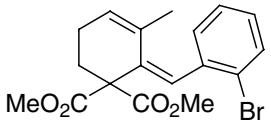
scale : diene **1d** (120 mg, 0.38 mmol); purification: flash chromatography on silica gel (eluent : PE:Et_2O 80:20); yield: 97%. Mp 45-47°C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.09 (td, *J* = 13.2, 3.4 Hz, 1H), 1.15 (s, 3H), 1.70 (m, 2H), 1.88 (m, 1H), 2.12 (dd, *J* = 12.8, 1.5 Hz, 1H), 2.42 (s, 3H), 2.68 (dd, *J* = 12.8, 1.7 Hz, 1H), 3.73 (s, 3H), 3.85 (s, 3H), 6.73 (s, 1H), 7.02-7.08 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 18.6, 19.5, 22.1, 34.6, 37.5, 51.4, 52.6, 53.0, 58.9, 118.5, 124.3, 125.3, 127.9, 130.9, 139.0, 148.9, 154.0, 170.5, 171.2. HRMS calcd for $C_{19}H_{22}O_4$ (MH^+) 315.1596, found 315.1594.

7-Isopropyl-5,6-dimethoxy-4a,8-dimethyl-2,3, 4,4a-tetrahydro-fluorene- dicarboxylic acid dimethyl ester 2e



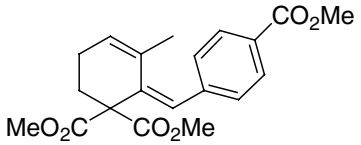
scale : diene **1e** (428 mg, 1.03 mmol); purification: flash chromatography on silica gel (eluent : PE:Et_2O 80:20); yield: 73%. Mp 145-147°C IR (KBr): 2944, 1740, 1722, 1613, 1452, 1318, 1304, 1271, 1246, 1223, 1203, 1171, 1123, 1045, 1031, 974, 914, 856, 837, 774 cm^{-1}.^{1}H NMR ($CDCl_3$, 300 MHz): 1.17-1.28 (m, 1H), 1.24 (s, 3H), 1.32 (d, *J* = 7 Hz, 3H), 1.35 (d, *J* = 7 Hz, 3H), 1.69 (m, 2H), 1.88 (m, 1H), 2.34 (s, 3H), 2.43 (d, *J* = 12.8 Hz, 1H), 2.65 (d, *J* = 12.8 Hz, 1H), 3.37 (m, 1H), 3.72 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 3.84 (s, 3H), 6.62 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 16.0, 19.1, 20.4, 21.7, 21.8, 28.3, 34.4, 36.1, 52.2, 52.5, 52.9, 58.7, 60.1, 60.3, 124.2, 124.7, 136.8, 138.9, 142.7, 147.7, 147.9, 150.6, 170.6, 171.4. HRMS calcd for $C_{24}H_{32}O_6$ 416.21989, found 416.21898.

2-(2-Bromo-benzylidene)-3-methyl-cyclohex-3-ene-1,1- dicarboxylic acid dimethyl ester 2f



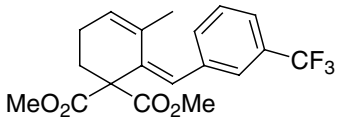
scale : diene **1f** (60 mg, 0.16 mmol); purification: flash chromatography on silica gel (eluent : PE:Et_2O : 90:10); yield: 67%. Mp 106-108°C. IR (KBr): 2924, 2854, 1728, 1560, 1455, 1434, 1252, 1233, 1166, 1075, 980, 856, 763 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.01 (s, 3H), 2.20 (m, 2H), 2.31 (t, *J* = 5.8 Hz, 2H), 3.39 (s, 6H), 5.78 (br. s, 1H), 6.65 (s, 1H), 7.08 (m, 1H), 7.21 (m, 1H), 7.55 (dd, *J* = 7.9, 1.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 22.0, 23.4, 31.9, 52.3, 58.9, 124.6, 126.7, 127.2, 127.9, 128.8, 131.2, 131.8, 132.9, 134.6, 137.3, 171.1.

2-(4-Methoxycarbonyl-benzylidene)-3-methyl-cyclohex-3-ene-1,1-dicarboxylic acid dimethyl ester 2g



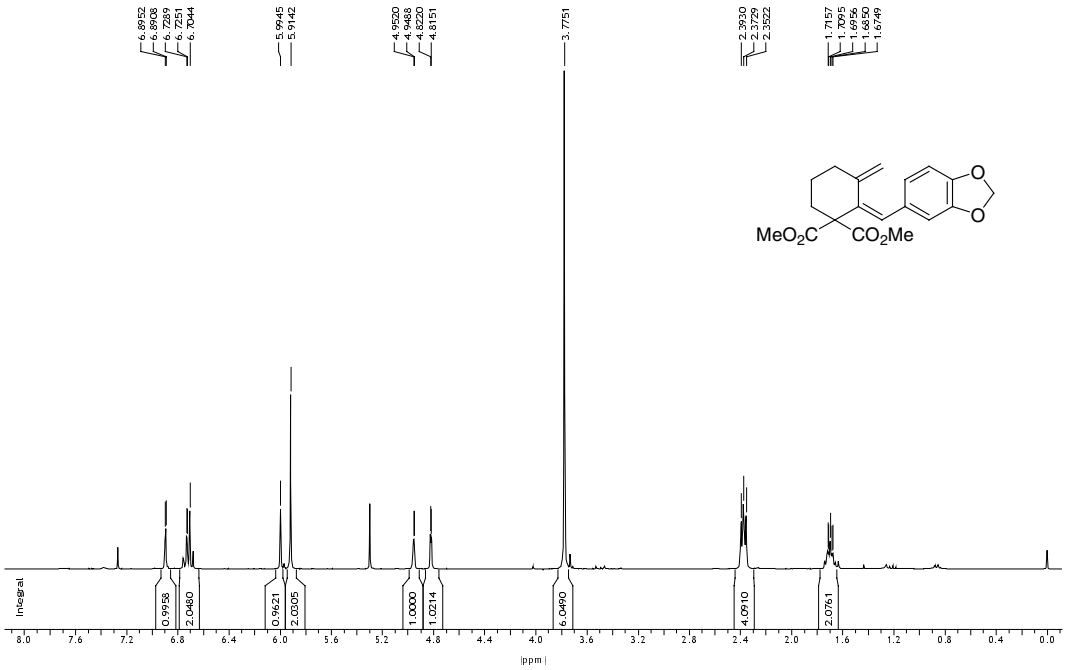
scale : diene **1g** (76 mg, 0.2 mmol); purification: flash chromatography on silica gel (eluent : PE:Et_2O : 75:25); yield: 60%. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.98 (s, 3H), 2.22 (m, 2H), 2.28 (m, 2H), 3.37 (s, 6H), 3.90 (s, 3H), 5.80 (br. s, 1H), 6.83 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 22.0, 23.3, 32.2, 52.2, 52.5, 58.7, 127.5, 127.8, 128.5, 128.8, 129.0, 132.8, 135.4, 142.3, 167.1, 171.0. Microanalysis (%) : found : C 67.03, H 6.19; calcd. for $C_{20}H_{22}O_6$: C 67.01, H 6.58.

3-Methyl-2-(3-trifluoromethyl-benzylidene)-cyclohex-3-ene-1,1-dicarboxylic acid dimethyl ester 2h

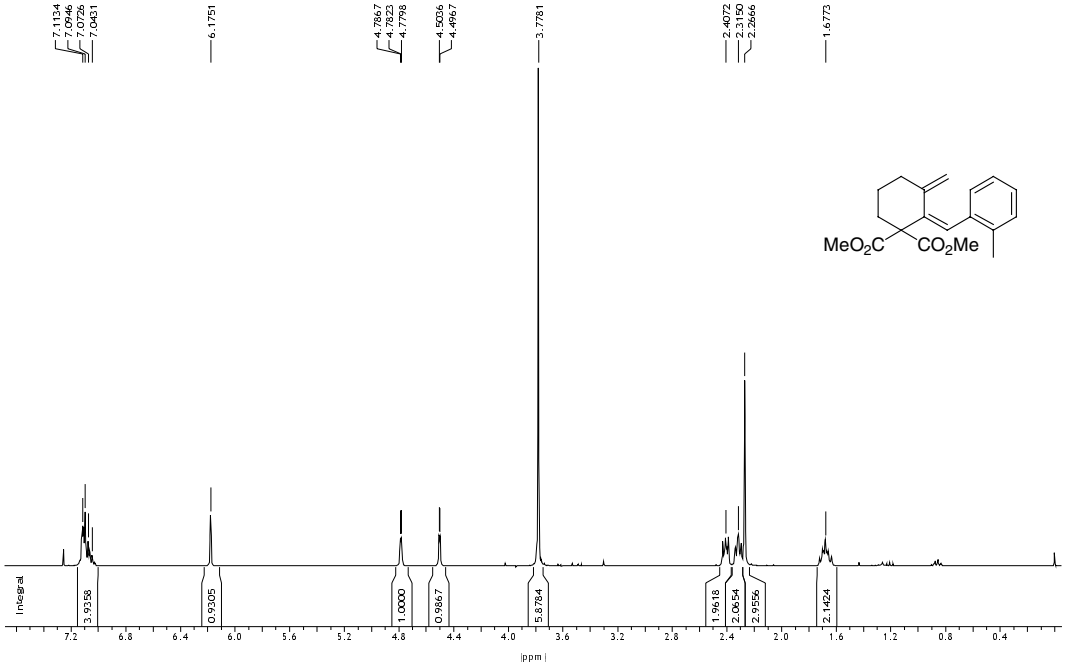


scale : diene **1h** (37 mg, 0.1 mmol); purification: flash chromatography on silica gel (eluent : PE:Et_2O : 90:10); yield: 65%. IR (KBr): 2953, 2847, 1747, 1732, 1622, 1590, 1486, 1435, 1335, 1248, 1164, 1124, 1074, 1017, 991, 912, 805, 777, 735, 704, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.98 (d, J = 1.3 Hz, 3H), 2.21 (m, 2H), 2.29 (m, 2H), 3.38 (s, 6H), 5.80 (br.s, 1H), 6.81 (s, 1H), 7.42-7.52 (m, 3H), 7.63 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 22.2, 23.5, 32.4, 52.7, 58.9, 124.6, 124.8, 126.0, 127.1, 128.2, 128.5, 130.3, 132.7, 132.9, 135.8, 138.3, 171.2. HRMS calcd for $C_{19}H_{19}F_3O_4$ (MH^+) 369.1313, found 369.1317.

^{1}H NMR **1c**



^{1}H NMR **1d**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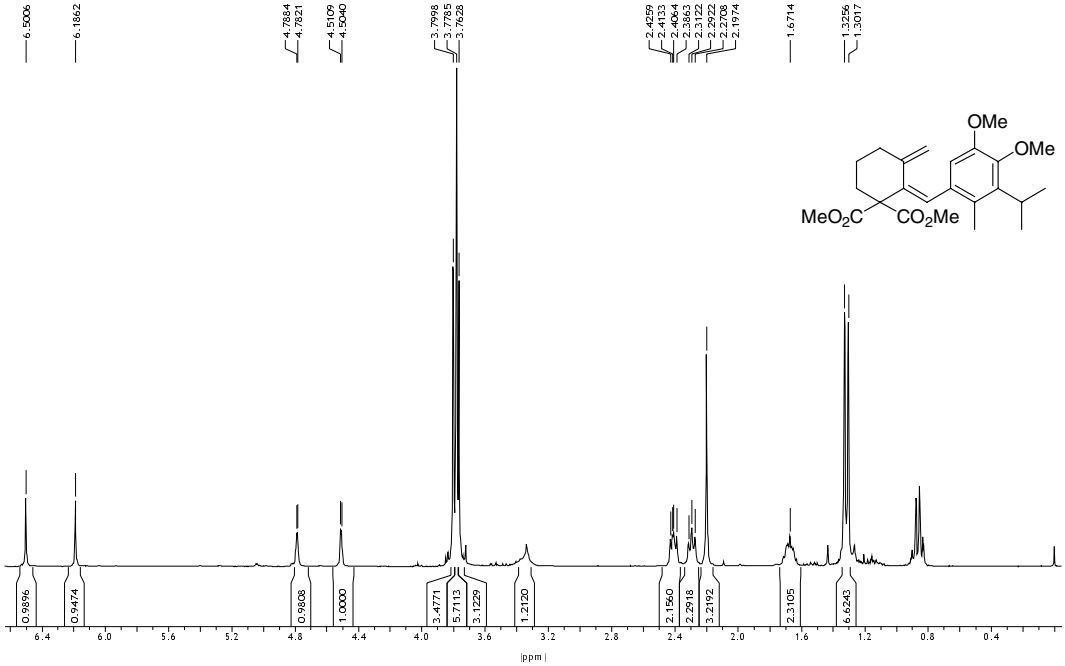
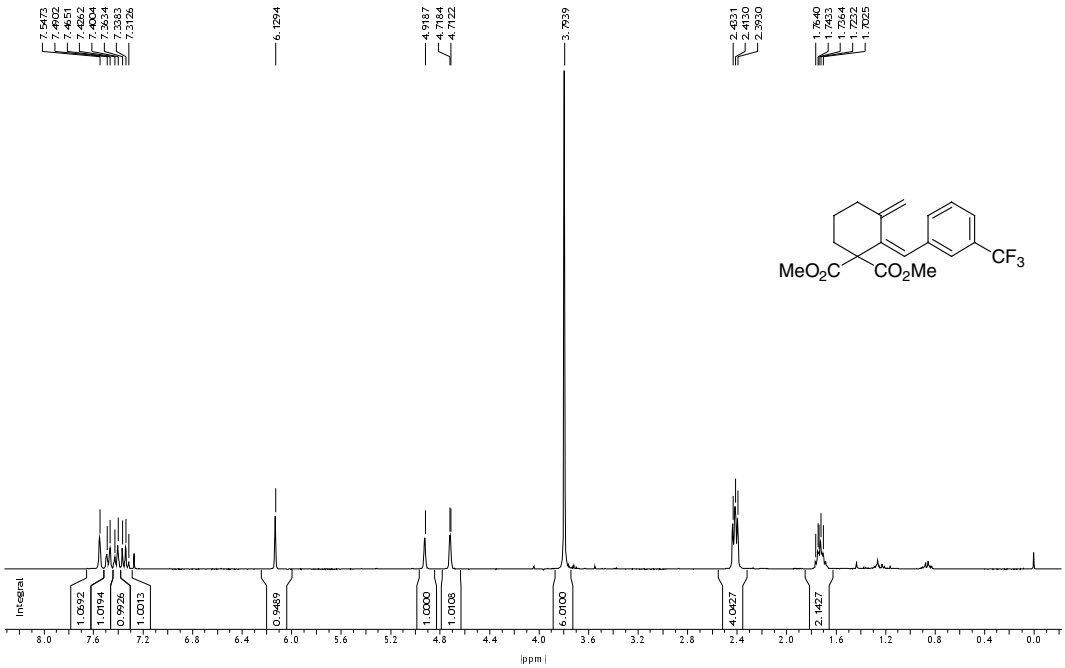
7.0431
6.1751
4.7867
4.7823
4.7798
4.5036
4.4967
3.7781
2.4072
2.3150
2.2866
1.6773
MeO2C
CO2Me
Integral
3.9358
0.9305
1.0000
0.9867
5.8784
1.9618
2.0654
2.9556
2.1424
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
|ppm|

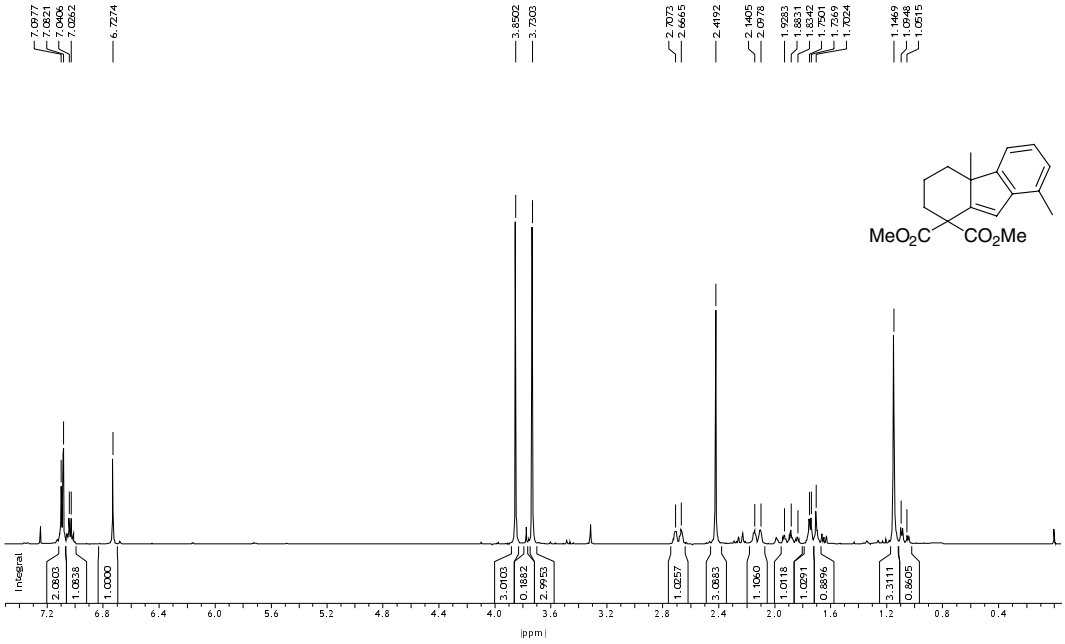
^{1}H NMR **1e**



^{1}H NMR **1h**



^{1}H NMR **2d**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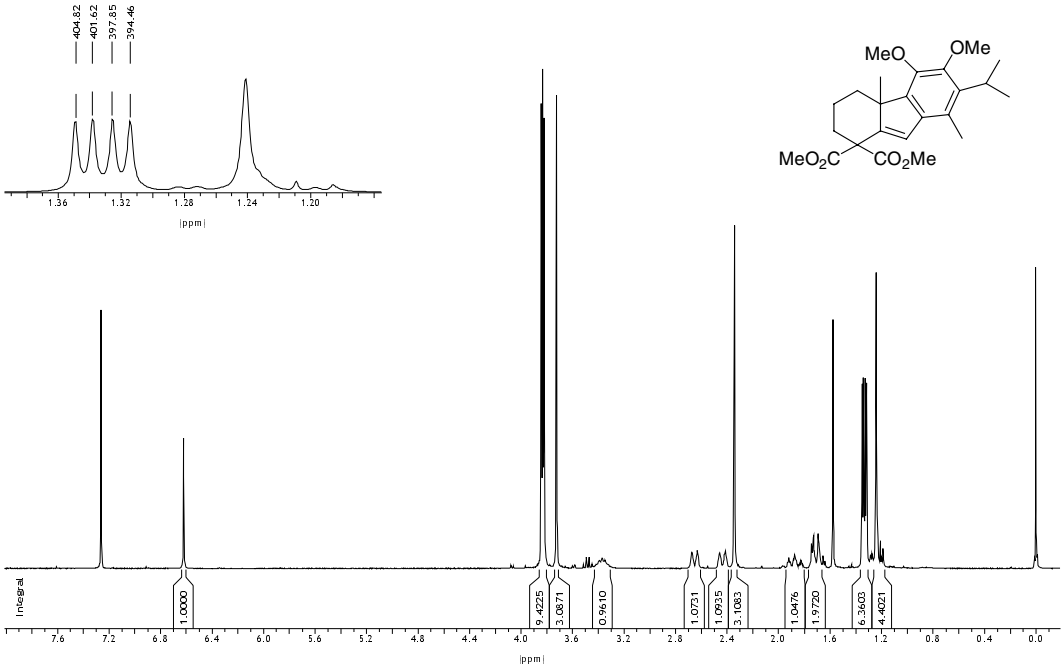
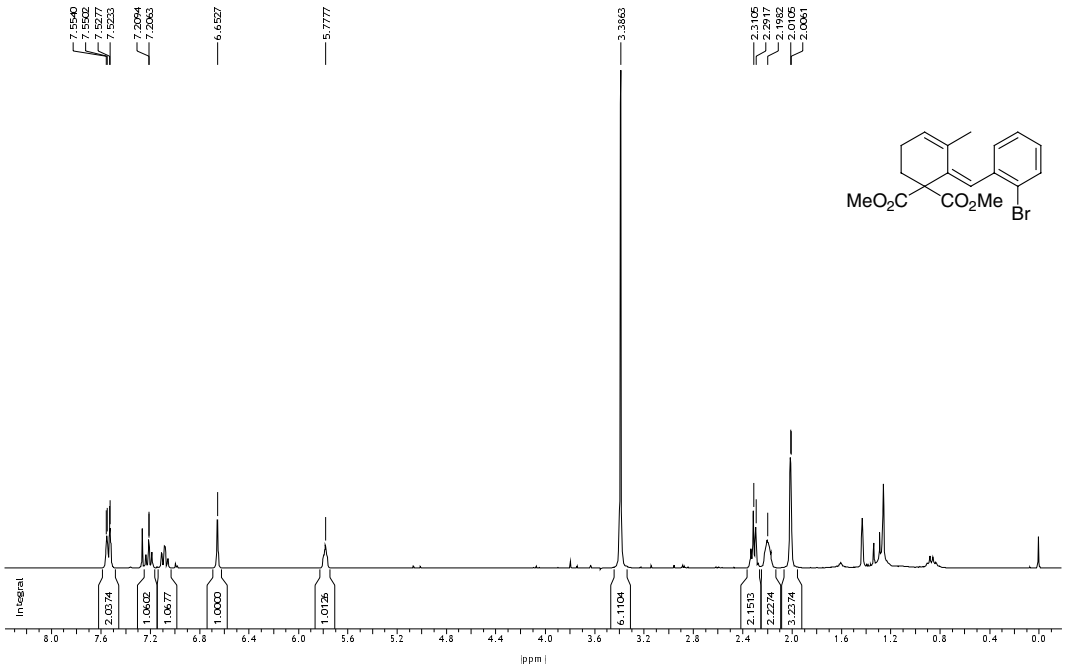
7.0262
6.7274
3.8502
3.7403
2.7073
2.6665
2.4192
2.1405
2.0978
1.9283
1.8831
1.8342
1.7901
1.7369
1.7024
1.1469
1.0946
1.0515
MeO2C
CO2Me
Integral
2.0603
1.0838
1.0000
3.0103
0.1882
2.9153
1.0257
3.0383
1.1060
1.0118
1.0291
0.8916
3.3111
0.8605
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
[ppm]

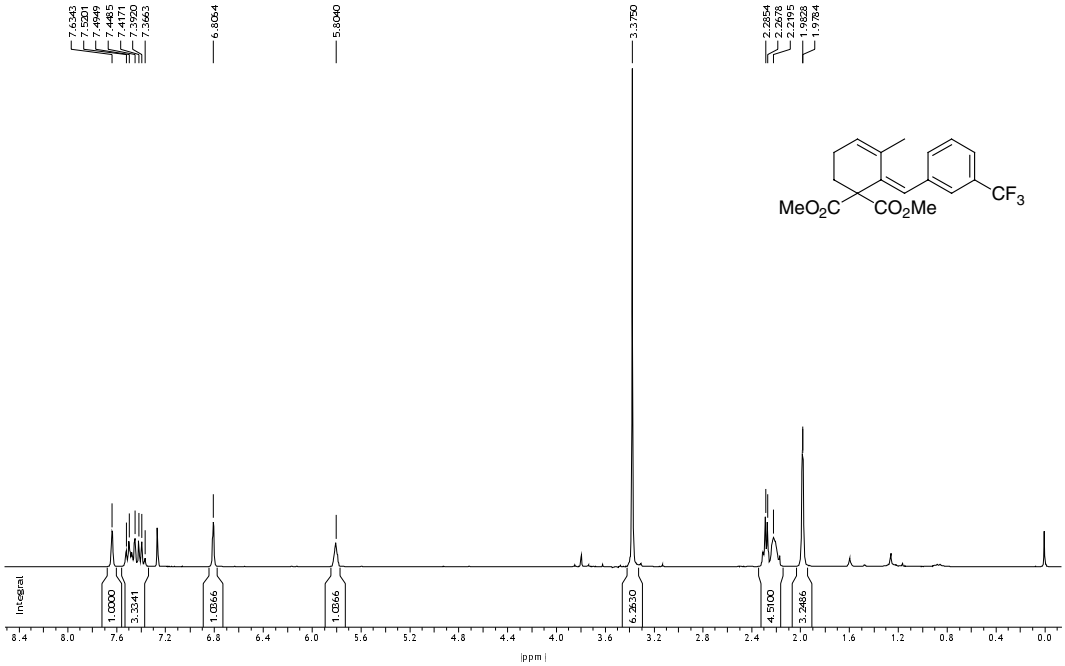
^{1}H NMR **2e**



^{1}H NMR **2f**



^{1}H NMR **2h**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2.2678
2.2195
1.9828
1.9784
MeO2C
CO2Me
CF3
Integral
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3.3341
1.0066
1.0066
6.2630
4.5100
3.2486
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
|ppm|