Supporting Information

Iridium Complex-Catalyzed Highly Selective Cross [2+2+2] Cycloaddition of Two Different Monoynes: 2:1 Coupling versus 1:2 Coupling

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General Methods. ^{1}H NMR and ^{13}C NMR spectra were measured on a Brucker AVANCE-400 spectrometer using Me_4Si as an internal standard. Samples were dissolved in $CDCl_3$. GC analyses were performed on a Shimadzu GC-14A using 3-mm x 2-m glass columns packed with 5% OV-17 on 60/80 mesh chromosorb w AW-DMCS. Capillary GC analyses were performed on a Shimadzu GC-17A Ver.2 using SP^{TM}-2331 (0.32 mm i.d. x 60 m). Column chromatography was carried out on 70 - 230 mesh silica gel (Merk; Silica Gel 60). Medium-pressure column chromatography was carried out on a YFLC-540 using an ultrapack Si column. Elemental analyses were carried out on a Yanaco MT-5 CHN analyzer. HRMS measurements were performed on a JEOL SX102A spectrometer.

Materials. All reagents and the solvents were dried and purified before use by the usual procedures. Dimethyl acetylenecarboxylate, methyl 2-octynoate, 1-hexyne, 1-decyne, phenylacetylene, 3-phenyl-1-propyne, 5-chloro-1-pentyne, 5-cyano-1-pentyne, 3-methoxy-1-propyne, trimethylsilylacetylene, *N*,*N*-dimethylpropargylamine, 3-hexyne, 5,7-dodecadiyne, 2-propyn-1-ol, 3-butyn-2-ol, 2-butyn-1-ol were purchased. 1,4-Dimethoxy-2-butyne was prepared by the reaction of disodio-2-butyn-1,4-diol with iodomethane. $[Ir(cod)Cl]_2$ was prepared according to the published method. Triphenylphosphine, 1,1'-bis(diphenylphosphino)ferrocene, bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane and 1,2-bis(dipentafluorophenylphosphino)ethane were purchased.

Cross [2+2+2] cycloaddition of 1 with monoyne. A typical procedure is described (Table 1, entry 2). To a toluene solution (5 mL) of $[Ir(cod)Cl]_2$ (13.4 mg, 0.02 mmol) and dppe (15.9 mg, 0.04 mmol) was added 1-hexyne (0.099 g, 1.2 mmol) via a syringe. Dimethyl acetylenedicarboxylate (0.284 g, 2 mmol) was then added to the solution by a syringe. The reaction mixture was stirred under reflux for 1 h. The progress of the reaction was monitored by GLC. After dimethyl

acetylenedicarboxylate was consumed, toluene was evaporated *in vacuo*. Column chromatography of the residue gave **3a** as a colorless oil (*n*-hexane/AcOEt=80/20, 0.359 g, yield 98%) and **4a** as a colorless oil (*n*-hexane/AcOEt=60/40, 0.003 g, yield 2%).

Tetramethyl 5-(*n*-butyl)-1,2,3,4-benzenetetracarboxylate (3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.36 (sixtet, *J* = 7.4 Hz, 2H), 1.59 (quintet, *J* = 7.4 Hz, 2H), 2.69-2.73 (m, 2H), 3.86 (s, 3H), 3.897 (s, 3H), 3.909 (s, 3H), 3.913 (s, 3H), 7.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 22.2 (CH_2), 32.85 (CH_2), 32.95 (CH_2), 52.5 (OCH_3), 52.7 (2C) (OCH_3), 52.9(OCH_3), 129.7 (arom), 129.9 (arom), 132.8 (arom), 133.6 (arom), 136.6 (arom), 142.7 (arom), 165.0 (C=O), 165.7 (C=O), 167.32 (C=O), 167.40 (C=O). This compound was reported in Reference 3(d) in the text. This compound was analyzed by GLC. t_R= 23.64 min (OV-17; Holding at 140^{o}C for 5 min, then elevating temperature 10^{o}C/min to 280^{o}C).

Tetramethyl 5-(*n*-octyl)-1,2,3,4-benzenetetracarboxylate (3b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.23-1.30 (m, 10H), 1.58-1.62 (m, 2H), 2.68-2.72 (m, 2H), 3.86 (s, 3H), 3.89 (s, 3H), 3.908 (s, 3H), 3.912 (s, 3H), 7.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 22.5 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 30.9 (CH_2), 31.6 (CH_2), 33.2 (CH_2), 52.5 (OCH_3), 52.7 (2C) (OCH_3), 52.9 (OCH_3), 129.7 (arom), 129.9 (arom), 132.9 (arom), 133.6 (arom), 136.6 (arom), 142.8 (arom), 165.0 (C=O), 165.7 (C=O), 167.3 (C=O), 167.4 (C=O). Anal. Calcd for $C_{22}H_{30}O_8$: C, 62.55; H, 7.16; O, 30.30. Found: C, 62.76; H, 7.27. This compound was analyzed by GLC. t_R= 33.84 min (OV-17; Holding at 140^{o}C for 5 min, then elevating temperature 10^{o}C/min to 280^{o}C).

Tetramethyl 5-phenyl-1,2,3,4-benzenetetracarboxylate (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.88 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 7.32-7.34 (m, 2H), 7.40-7.43 (m, 3H), 8.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5 (OCH_3), 52.90(OCH_3), 52.92 (OCH_3), 53.1 (OCH_3), 128.1 (2C) (arom), 128.5 (3C) (arom), 130.0 (arom), 130.1 (arom), 133.85 (arom), 133.97 (arom), 136.6 (arom), 137.9 (arom),

142.1 (arom), 164.8 (C=O), 165.6 (C=O), 167.3 (2C) (C=O). This compound was reported in Reference 3(d) in the text. This compound was analyzed by GLC. t_R= 32.04 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-phenylmethyl-1,2,3,4-benzenetetracarboxylate (3d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.84 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 4.11 (s, 2H), 7.10-7.12 (m, 2H), 7.19-7.21 (m, 1H), 7.22-7.29 (m, 2H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.7 (CH_2), 52.6 (OCH_3), 52.8 (2C) (OCH_3), 53.0 (OCH_3), 126.7 (arom), 128.6 (2C) (arom), 128.9 (2C) (arom), 130.1 (arom), 130.2 (arom), 133.4 (arom), 134.5 (arom), 136.9 (arom), 138.3 (arom), 141.0 (arom), 164.9 (C=O), 165.7 (C=O), 167.2 (C=O), 167.4 (C=O). Anal. Calcd for $C_{21}H_{20}O_8$: C, 63.00; H, 5.03; O, 31.97. Found: C, 63.15; H, 5.17. This compound was analyzed by GLC. t_R= 38.03 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-(3-choloropropyl)-1,2,3,4-benzenetetracarboxylate (3e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07-2.12 (m, 2H), 2.87-2.91 (m, 2H), 3.54 (t, *J* = 6.2 Hz, 2H), 3.87 (s, 3H), 3.91 (s, 3H), 3.92 (s, 6H), 7.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6 (CH_2), 33.6 (CH_2), 43.9 (CH_2), 52.84 (OCH_3), 52.90 (OCH_3), 52.94 (OCH_3), 53.10 (OCH_3), 130.1 (arom), 130.2 (arom), 133.5 (arom), 134.0 (arom), 136.9 (arom), 141.0 (arom), 164.9 (C=O), 165.6 (C=O), 167.3 (C=O), 167.4 (C=O). Anal. Calcd for $C_{17}H_{19}ClO_8$: C, 52.79; H, 4.95; Cl, 9.17; O, 33.09. Found: C, 52.57; H, 4.92; Cl, 9.09. This compound was analyzed by GLC. t_R= 30.12 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-(3-cyanopropyl)-1,2,3,4-benzenetetracarboxylate (3f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (quintet, *J* = 7.6 Hz, 2H), 2.40 (t, *J* = 7.6 Hz, 2H), 2.84-2.88 (m, 2H), 3.87 (s, 3H), 3.92 (s, 9H), 7.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6 (CH_2), 26.6 (CH_2), 32.0 (CH_2), 52.82 (OCH_3), 52.86 (OCH_3), 52.89 (OCH_3),

53.0(OCH_3), 118.8 (CN), 130.2 (arom), 130.3 (arom), 133.6 (2C) (arom), 136.7 (arom), 140.0 (arom), 164.6 (C=O), 165.5 (C=O), 167.0 (C=O), 167.1 (C=O). Anal. Calcd for $C_{18}H_{19}NO_8$: C, 57.29; H, 5.08; N, 3.71; O, 33.92. Found: C, 57.13; H, 5.08; N, 3.70. This compound was analyzed by GLC. t_R= 37.36 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-(methoxymethyl)-1,2,3,4-benzenetetracarboxylate (3g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 3H), 3.87 (s, 3H), 3.90 (s, 3H), 3.93 (s, 6H), 4.58 (s, 2H), 8.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7 (OCH_3), 52.84 (OCH_3), 52.86 (OCH_3), 53.0 (OCH_3), 58.5 (OCH_3), 70.9 (CH_2O), 130.2 (arom), 130.3 (arom), 131.6 (arom), 134.2 (arom), 135.0 (arom), 139.0 (arom), 164.9 (C=O), 165.6 (C=O), 166.7 (C=O), 167.3 (C=O). This compound was reported in Reference 3(d) in the text. This compound was analyzed by GLC. t_R= 22.92 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-trimethylsilyl-1,2,3,4-benzenetetracarboxylate (3h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.34 (s, 9H), 3.87 (s, 3H), 3.88 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 8.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.8 (3C) (CH_3), 52.6 (OCH_3), 52.8 (2C) (OCH_3), 52.9 (OCH_3), 129.3 (arom), 130.2 (arom), 134.9 (arom), 138.0 (arom), 141.4 (arom), 142.3 (arom), 165.4 (C=O), 166.4 (C=O), 167.3 (C=O), 168.4 (C=O). Anal. Calcd for $C_{17}H_{22}O_8Si$: C, 53.39; H, 5.80; O, 33.47; Si, 7.34. Found: C, 53.35; H, 5.84. This compound was analyzed by GLC. t_R= 21.28 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-(*N*,*N*-dimethylaminomethyl)-1,2,3,4-benzenetetracarboxylate (3i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 6H), 3.53 (s, 2H), 3.86 (s, 6H), 3.91 (s, 6H), 8.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.9 (2C) (CH_3), 52.3 (OCH_3), 52.69 (OCH_3), 52.72 (OCH_3), 52.9 (OCH_3), 60.8 (CH_2N), 129.7 (arom), 130.3 (arom), 133.0 (arom), 133.8 (arom), 136.8 (arom), 140.3 (arom), 165.0 (C=O), 165.7 (C=O), 167.1 (C=O), 167.3 (C=O). Anal. Calcd for $C_{17}H_{21}NO_8$: C, 55.58; H, 5.76; N, 3.81; O,

34.84. Found: C, 55.57; H, 5.77; N, 3.65. This compound was analyzed by GLC. t_R= 21.76 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-((*N*-methoxycarbonyl)aminomethyl)-1,2,3,4-benzenetetracarboxylate (3j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 3.91 (s, 6H), 4.40 (d, *J* = 7.1 Hz, 2H), 5.50 (br, 1H), 8.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.8 (CH_2), 52.3 (OCH_3), 52.96 (2C) (OCH_3), 53.06 (OCH_3), 53.12 (OCH_3), 130.9 (arom), 131.1 (arom), 133.4 (arom), 134.2 (arom), 135.3 (arom), 139.3 (arom), 156.8 (C=O), 164.7 (C=O), 165.7 (C=O), 167.1 (2C) (C=O); R_f=0.20 (*n*-hexane : AcOEt=1:6). Anal. Calcd for $C_{17}H_{19}NO_{10}$: C, 51.39; H, 4.82; N, 3.53; O, 40.27. Found: C, 51.31; H, 4.89; N, 3.54.

Tetramethyl 5,6-bis(methoxymethyl)-1,2,3,4-benzenetetracarboxylate (3k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.27 (s, 3H x 2), 3.85 (s, 3H x 2), 3.88 (s, 3H x 2), 4.61 (s, 2H x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.8 (2C) (OCH_3), 53.0 (2C) (OCH_3), 58.2 (2C) (OCH_3), 68.2 (2C) (OCH_2), 130.9 (2C) (arom), 135.1 (2C) (arom), 138.7 (2C) (arom), 166.2 (2C) (C=O), 167.3 (2C) (C=O). HRMS (FAB) Calcd for $C_{18}H_{23}O_{10}$ ($[M+H]^+$) *m/z* 399.1291. Found 399.1286. This compound was reported in Reference 3(d) in the text. This compound was analyzed by GLC. t_R= 26.28 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5,6-bis(acetoxymethyl)-1,2,3,4-benzenetetracarboxylate (3l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H x 2), 3.86 (s, 3H x 2), 3.91 (s, 3H x 2), 5.38 (s, 2H x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4 (2C) (CH_3), 53.0 (2C) (OCH_3), 53.1 (2C) (OCH_3), 59.5 (2C) (CH_2O), 131.9 (2C) (arom), 135.5 (2C) (arom), 136.8 (2C) (arom), 165.9 (2C) (C=O), 166.6 (2C) (C=O), 169.9 (2C) (C=O). Anal. Calcd for $C_{20}H_{22}O_{12}$: C, 52.87; H, 4.88; O, 42.25. Found: C, 52.71; H, 4.97. This compound was analyzed by GLC. t_R= 36.62 min (OV-17; Holding at 140°C for 5 min, then

elevating temperature 10°C/min to 280°C).

Tetramethyl 5,6-diethyl-1,2,3,4-benzenetetracarboxylate (**3m**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.4 Hz, 3H x 2), 2.74 (q, *J* = 7.4 Hz, 2H x 2), 3.84 (s, 3H x 2), 3.89 (s, 3H x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3 (2C) (CH_3), 23.5 (2C) (CH_2), 52.6 (2C) (OCH_3), 52.8 (2C) (OCH_3), 129.0 (2C) (arom), 134.9 (2C) (arom), 143.4 (2C) (arom), 166.6 (2C) (C=O), 167.9 (2C) (C=O). HRMS (FAB) Calcd for $C_{18}H_{23}O_8$ ($[M+H]^+$) *m/z* 367.1393. Found 367.1391. This compound was reported in Reference 3(d) in the text. This compound was analyzed by GLC. t_R= 22.26 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-(*n*-butyl)-6-(1-hexynyl)-1,2,3,4-benzenetetracarboxylate (**3n**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 1.39 (quintet, *J* = 7.3 Hz, 2H), 1.48 (quintet, *J* = 7.3 Hz, 2H), 1.57-1.61 (m, 4H), 2.48 (t, *J* = 7.0 Hz, 2H), 2.82-2.86 (m, 2H), 3.84 (s, 6H), 3.88 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4 (CH_3), 13.6 (CH_3), 19.3 (CH_2), 21.8 (CH_2), 22.9 (CH_2), 30.3 (CH_2), 32.1 (CH_2), 32.3 (CH_2), 52.59 (OCH_3), 52.63 (OCH_3), 52.9 (2C) (OCH_3), 75.2 (C≡C), 102.1 (C≡C), 125.3 (arom), 128.1 (arom), 129.7 (arom), 134.1 (arom), 137.7 (arom), 146.3 (arom), 165.8 (C=O), 166.3 (C=O), 166.9 (C=O), 167.1 (C=O). Anal. Calcd for $C_{24}H_{30}O_8$: C, 64.56; H, 6.77; O, 28.67. Found: C, 64.26; H, 6.78. This compound was analyzed by GLC. t_R= 38.95 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Tetramethyl 5-methyl-6-phenyl-1,2,3,4-benzenetetracarboxylate (**3o**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 3.45 (s, 3H), 3.84 (s, 3H), 3.88 (s, 3H), 3.90 (s, 3H), 7.13-7.16 (m, 2H), 7.37-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8 (CH_3), 52.16 (OCH_3), 52.7 (OCH_3), 52.91 (OCH_3), 52.95 (OCH_3), 128.11 (arom), 128.17 (arom), 128.22 (2C) (arom), 128.7 (2C) (arom), 130.1 (arom), 134.9 (arom), 135.3 (arom), 136.8 (arom), 138.0 (arom), 143.2 (arom), 166.2 (C=O), 166.5 (C=O), 167.1 (C=O), 167.7 (C=O). Anal. Calcd for $C_{21}H_{20}O_8$: C, 63.00; H, 5.03; O, 31.97. Found:

C, 62.82; H, 5.15. This compound was analyzed by GLC. t_R= 35.90 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Trimethyl 1,3-dihydro-3-oxo-4,5,6-isobenzofurantricarboxylate (**6a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.93 (s, 3H), 3.99 (s, 3H), 5.38 (s, 2H), 7.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.18 (OCH_3), 53.22 (OCH_3), 53.26 (OCH_3), 69.1 (OCH_2), 124.9 (arom), 125.5 (arom), 131.8 (arom), 132.6 (arom), 135.6 (arom), 148.5 (arom), 164.5 (C=O), 165.2 (C=O), 165.8 (C=O), 166.8 (C=O). HRMS (FAB) Calcd for $C_{14}H_{13}O_8$ ($[M+H]^+$) *m/z* 309.0610. Found 309.0602. This compound was reported in Reference 3(d) in the text. This compound was analyzed by GLC. t_R= 27.76 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Trimethyl 1-hydro-1-methyl-3-oxo-4,5,6-isobenzofurantricarboxylate (**6b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (d, *J* = 6.7 Hz, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 4.00 (s, 3H), 5.62 (q, *J* = 6.7 Hz, 1H), 7.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9 (CH_3), 53.22 (OCH_3), 53.26 (OCH_3), 53.32 (OCH_3), 77.2 (OCH), 124.2 (arom), 125.6 (arom), 132.1 (arom), 132.8 (arom), 136.0 (arom), 152.9 (arom), 164.6 (C=O), 165.3 (C=O), 165.8 (C=O), 166.1 (C=O). Anal. Calcd for $C_{15}H_{14}O_8$: C, 55.90; H, 4.38; O, 39.72. Found: C, 55.99; H, 4.41. This compound was analyzed by GLC. t_R= 24.65 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

Trimethyl 1,3-dihydro-3-oxo-7-methyl-4,5,6-isobenzofurantricarboxylate (**6c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.89 (s, 3H), 3.94 (s, 3H), 4.00 (s, 3H), 5.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1 (CH_3), 53.0 (OCH_3), 53.19 (OCH_3), 53.25 (OCH_3), 68.7 (OCH_2), 123.5 (arom), 128.8 (arom), 131.3 (arom), 132.3 (arom), 139.3 (arom), 149.4 (arom), 164.7 (C=O), 165.2 (C=O), 167.0 (C=O), 167.4 (C=O). Anal. Calcd for $C_{15}H_{14}O_8$: C, 55.90; H, 4.38; O, 39.72. Found: C, 56.09; H, 4.39. This compound was analyzed by GLC. t_R= 29.71 min (OV-17; Holding at 140°C for 5 min, then elevating temperature 10°C/min to 280°C).

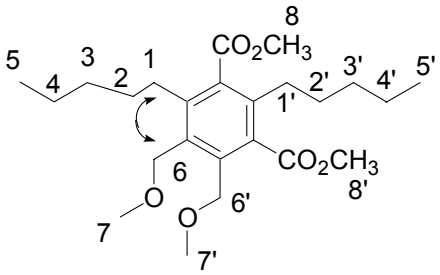
Cross [2+2+2] cycloaddition of 7 with 2k. To a THF solution (5 mL) of $[Ir(cod)Cl]_2$ (13.4 mg, 0.02 mmol) and dppe (15.9 mg, 0.04 mmol) was added **2k** (0.137 g, 1.2 mmol) via a syringe. Ester **7** (0.308 g, 2 mmol) was then added to the solution using a syringe. The reaction mixture was stirred for 1 h at 50°C. The progress of the reaction was monitored by GLC. After **7** was consumed, THF was evaporated *in vacuo*. Column chromatography of the residue gave a mixture of two trimers of **7** as a colorless oil (*n*-hexane/AcOEt=98/2, 34 mg, yield 11%) and a mixture of **8** and **9** as a colorless oil (*n*-hexane/AcOEt=90/10, 0.347 g, yield 82%). The ratio of **8** to **9** was determined using capillary GC. Separation **8** and **9** was carried out using medium-pressure column chromatography. Eluent for **8** was *n*-hexane/AcOEt=90/10**.** Eluent for **9** was *n*-hexane/AcOEt=80/20.

Dimethyl 4,5-bis(methoxymethyl)-2,6-di(*n*-pentyl)-1,3-benzenedicarboxylate (8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 6.9 Hz, 3H), 1.27-1.29 (m, 4H), 1.32-1.38 (m, 4H), 1.48-1.65 (m, 4H), 2.44-2.49 (m, 2H), 2.57-2.60 (m, 2H), 3.31 (s, 3H), 3.39 (s, 3H), 3.88 (s, 6H), 4.47 (s, 2H), 4.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.75 (CH_3), 13.80 (CH_3), 22.0 (CH_2), 22.1 (CH_2), 30.8 (CH_2), 31.3 (2C) (CH_2), 31.8 (CH_2), 32.16 (CH_2), 32.22 (CH_2), 51.7 (2C) (OCH_3), 56.1 (2C) (OCH_3), 67.2 (OCH_2), 69.3 (OCH_2), 132.82 (arom), 132.89 (arom), 135.1 (arom), 136.5 (arom), 136.6 (arom), 140.4 (arom), 169.7 (C=O), 170.0 (C=O). Anal. Calcd for $C_{24}H_{38}O_6$: C, 68.22; H, 9.06; O, 22.72. Found: C, 68.45; H, 9.01. HRMS (GC-EI) Calcd for $C_{24}H_{38}O_6$ ($[M]^+$) *m/z* 422.2668. Found 422.2673. This compound was analyzed by capillary GLC. t_R= 13.89 min (SP™-2331; Holding at 250°C).

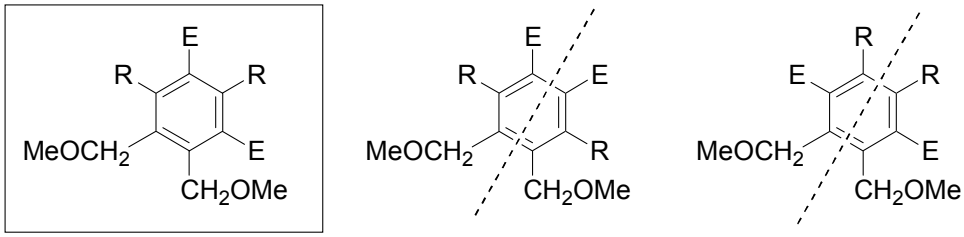
Dimethyl 2,3-bis(methoxymethyl)-5,6-di(*n*-pentyl)-1,4-benzenedicarboxylate (9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.0 Hz, 3H x 2), 1.26-1.40 (m, 4H x 2), 1.47-1.53 (m, 2H x 2), 2.51-2.55 (m, 2H x 2), 3.28 (s, 3H x 2), 3.89 (s, 3H x 2), 4.45 (s, 2H x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (2C) (CH_3), 22.2 (2C) (CH_2), 30.6 (2C) (CH_2), 31.0 (2C) (CH_2), 32.4 (2C) (CH_2), 51.9 (2C) (OCH_3), 58.1 (2C) (OCH_3), 69.1

(2C) (OCH_2), 131.9 (2C) (arom), 136.2 (2C) (arom), 138.1 (2C) (arom), 170.2 (2C) (C=O). Anal. Calcd for $C_{24}H_{38}O_6$: C, 68.22; H, 9.06; O, 22.72. Found: C, 68.09; H, 8.86. This compound was analyzed by capillary GLC. t_R= 13.12 min (SP^{TM}-2331; Holding at 250°C).

Assignment of 8

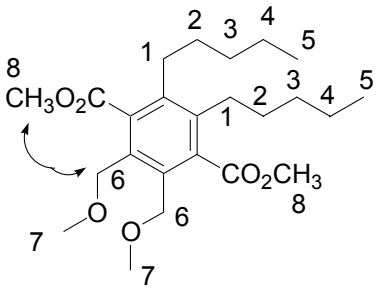


The 2D NOESY spectrum reveals a cross-peak of methylene proton H-1 with methylene proton H-6. This suggests a short distance between H-1 and H-6. The reaction of **7** with **2k** can give three isomers. Two of these three isomers have a symmetrical aromatic ring. The ^{13}C spectrum of **8** reveals that six aromatic carbons are magnetically nonequivalent. From the ^{13}C-NMR spectrum, it is clear that **8** has an unsymmetrical aromatic ring. Product **8** can be assigned as above.



R=*n*-Pentyl E=CO_2Me

Assignment of 9



The 2D NOESY spectrum reveals a cross-peak of methyl proton H-8 with methylene

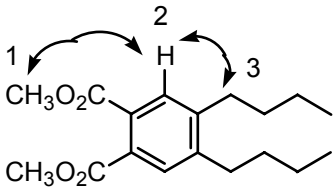
proton H-6. This suggests a short distance between H-6 and H-8.

Dimethyl 3,4,5,6-tetrakis(methoxymethyl)-1,2-benzenedicarboxylate (11k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.27 (s, 3H x 2), 3.38 (s, 3H x 2), 3.84 (s, 3H x 2), 4.59 (s, 2H x 2), 4.62 (s, 2H x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2 (2C) (OCH_3), 57.9 (2C) (OCH_3), 58.1 (2C) (OCH_3), 67.1 (2C) (CH_2O), 68.1 (2C) (CH_2O), 133.1 (2C) (arom), 136.1 (2C) (arom), 138.6 (2C) (arom), 168.2 (2C) (C=O). Anal. Calcd for $C_{18}H_{26}O_8$: C, 58.37; H, 7.08; O, 34.56. Found: C, 58.16; H, 7.01. This compound was analyzed by GLC. t_R= 19.54 min (OV-17; Holding at 140^{o}C for 3 min, then elevating temperature 10^{o}C/min to 280^{o}C).

Dimethyl 3,4,5,6-tetraethyl-1,2-benzenedicarboxylate (11m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, *J* = 7.5 Hz, 3H x 2), 1.19 (t, *J* = 7.5 Hz, 3H x 2), 2.69 (q, *J* = 7.5 Hz, 2H x 2), 2.71 (q, *J* = 7.5 Hz, 2H x 2), 3.84 (s, 3H x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4 (2C) (CH_3), 15.9 (2C) (CH_3), 22.0 (2C) (CH_2), 23.4 (2C) (CH_2), 52.0 (2C) (OCH_3), 130.4 (2C) (arom), 138.0 (2C) (arom), 143.1 (2C) (arom), 169.6 (2C) (C=O). This compound was reported in Reference 3(a) in the text. This compound was analyzed by GLC. t_R= 15.52 min (OV-17; Holding at 140^{o}C for 3 min, then elevating temperature 10^{o}C/min to 280^{o}C).

Dimethyl 3,4-di(*n*-butyl)-1,2-benzenedicarboxylate (12a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 6H), 1.40 (sixtet, *J* = 7.3 Hz, 4H), 1.57 (quintet, *J* = 7.3 Hz, 4H), 2.63-2.67 (m, 4H), 3.88 (s, 6H), 7.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (2C) (CH_3), 22.6 (2C) (CH_2), 32.2 (2C) (CH_2), 32.9 (2C) (CH_2), 52.4 (2C) (OCH_3), 129.3 (2C) (arom), 129.6 (2C) (arom), 144.2 (2C) (arom), 168.3 (2C) (C=O). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55; O, 20.89. Found: C, 70.68; H, 8.42. This compound was analyzed by GLC. t_R= 16.23 min (OV-17; Holding at 140^{o}C for 3 min, then elevating temperature 10^{o}C/min to 280^{o}C).

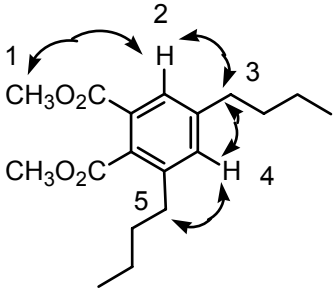
Assignment of 12a



The 2D NOESY spectrum reveals cross-peaks of proton H-2 with methyl proton H-1 and methylene proton H-3. This suggests a short distance between H-1, H-2 and H-3.

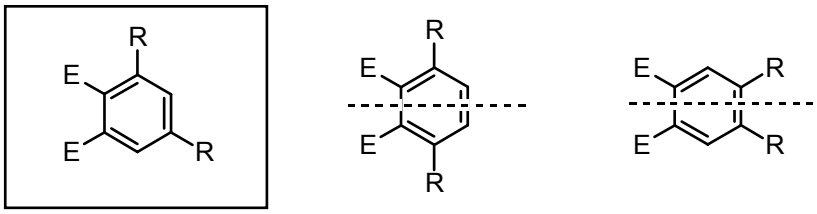
Dimethyl 3,5-di(*n*-butyl)-1,2-benzenedicarboxylate (12b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H), 1.31-1.38 (m, 4H), 1.53-1.62 (m, 4H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 3.87 (s, 3H), 3.91 (s, 3H), 7.22 (d, *J* = 1.6 Hz), 7.63 (d, *J* = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (2C) (CH_3), 22.2 (CH_2), 22.5 (CH_2), 33.0 (CH_2), 33.3 (CH_2), 33.5 (CH_2), 35.2 (CH_2), 52.29 (OCH_3), 52.33 (OCH_3), 127.5 (arom), 128.0 (arom), 132.3 (arom), 133.7 (arom), 140.5 (arom), 144.1 (arom), 166.6 (C=O), 170.0 (C=O). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55; O, 20.89. Found: C, 70.60; H, 8.55. This compound was analyzed by GLC. t_R= 15.48 min (OV-17; Holding at 140°C for 3 min, then elevating temperature 10°C/min to 280°C).

Assignment of 12b



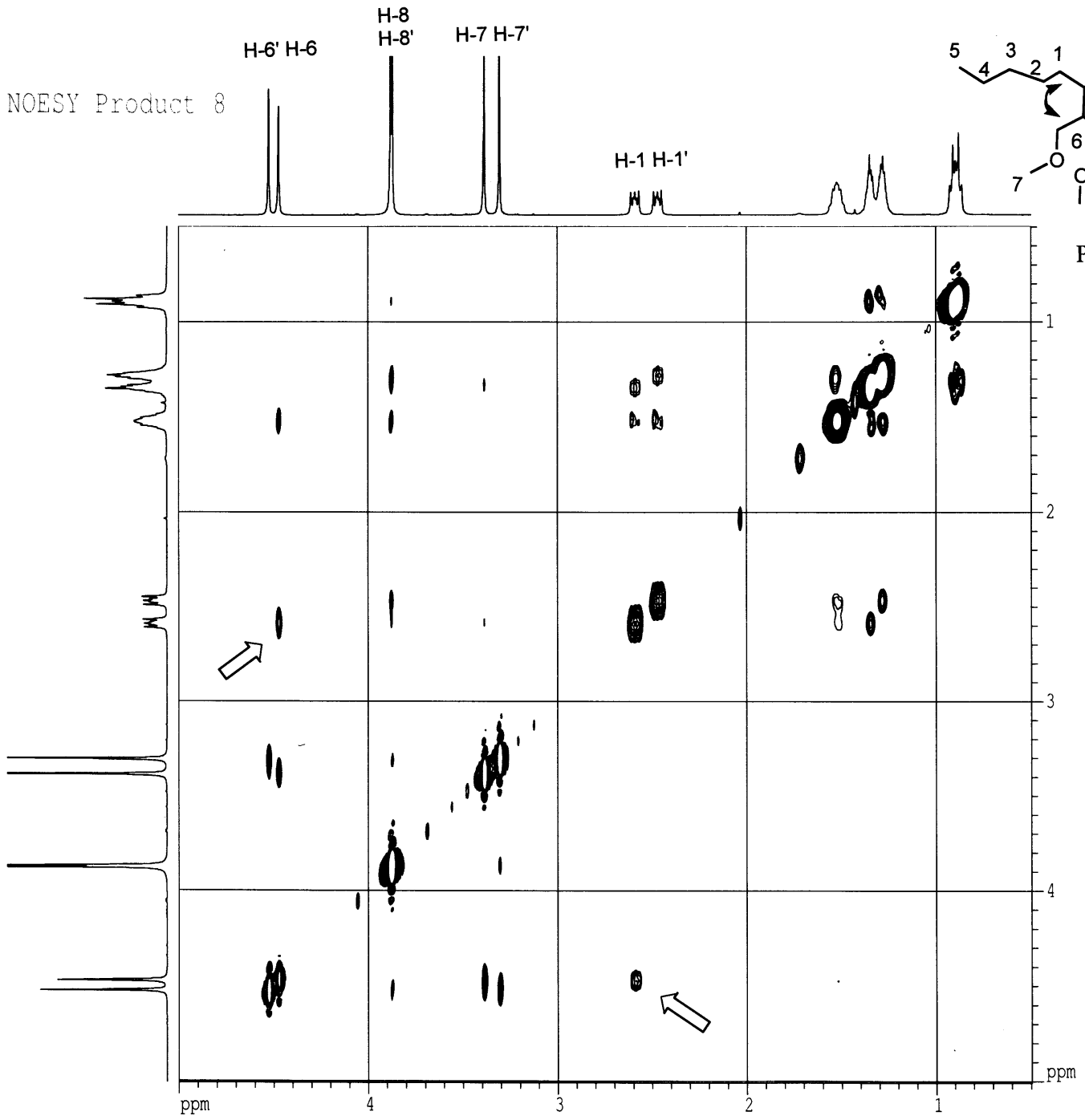
The 2D NOESY spectrum reveals cross-peaks of proton H-2 with methyl proton H-1 and methylene proton H-3. This suggests a short distance between H-1, H-2 and H-3. Cross-peaks of proton H-4 with methylene proton H-3 and methylene proton H-5 were observed. This suggests a short distance between H-3, H-4 and H-5. The reaction of one molecule of DMAD with two molecule of 1-hexyne can give three isomers. Two

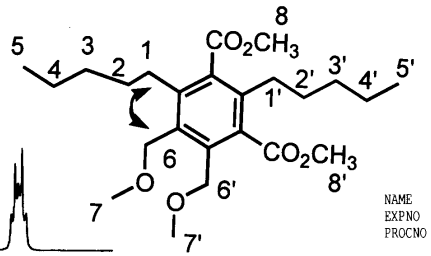
of these three isomers have a symmetrical aromatic ring. The ^{13}C spectrum of **12b** reveals that six aromatic carbons are magnetically nonequivalent. From the ^{13}C-NMR spectrum, it is clear that **12b** has an unsymmetrical aromatic ring. Product **12b** can be assigned as above.



R=*n*-Butyl E=CO_2Me

NOESY Product 8





Product 8

Current Data Parameters

NAME	tomoaki
EXPNO	76
PROCNO	1

F2 - Acquisition Parameters

Date_	20020722
Time	21.13
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PROBHD	5 mm QNP 1H/13
PULPROG	noesytp
TD	2048
SOLVENT	CDCl3
NS	80
DS	8
SWH	5208.333 Hz
FIDRES	2.543132 Hz
AQ	0.1966580 sec
RG	32
DW	96.000 usec
DE	6.00 usec
TE	300.0 K
D0	0.00000300 sec
D1	1.00000000 sec
D8	1.00000000 sec
IN0	0.00009600 sec

======== CHANNEL f1 ========

NUC1	1H
P1	10.50 usec
PL1	-3.00 dB
SFO1	400.1322007 MHz

F1 - Acquisition parameters

ND0	2
TD	256
SFO1	400.1322 MHz
FIDRES	20.345053 Hz
SW	13.017 ppm

F2 - Processing parameters

SI	2048
SF	400.1300035 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

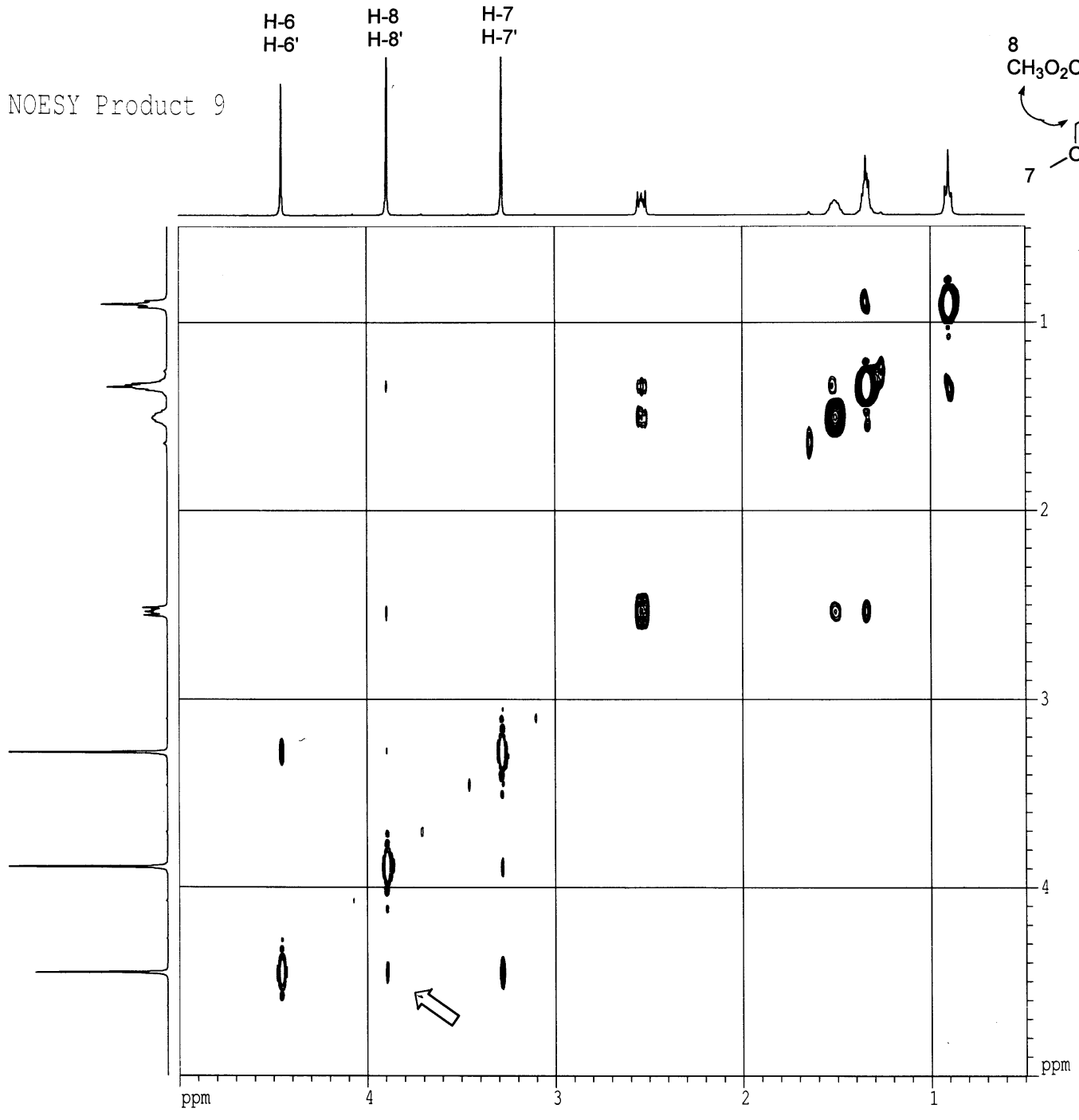
F1 - Processing parameters

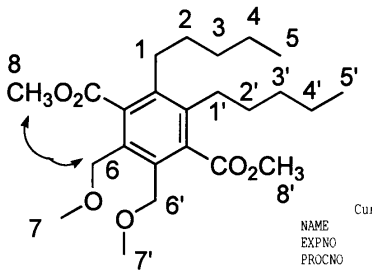
SI	1024
MC2	TPPI
SF	400.1300035 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	5.002 ppm
F2LO	2001.43 Hz
F2PHI	0.496 ppm
F2HI	198.35 Hz
F1PLO	5.008 ppm
F1LO	2003.97 Hz
F1PHI	0.496 ppm
F1HI	198.35 Hz
F2PPMCM	0.30042 ppm/cm
F2HZCM	120.20535 Hz/cm
F1PPMCM	0.30084 ppm/cm
F1HZCM	120.37489 Hz/cm

NOESY Product 9





Product 9

Current Data Parameters

NAME	tomoaki
EXPNO	78
PROCNO	1

F2 - Acquisition Parameters

Date_	20020724
Time	20.54
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PROBHD	5 mm QNP 1H/13
PULPROG	noesytp
TD	2048
SOLVENT	CDCl3
NS	80
DS	8
SWH	5208.333 Hz
FIDRES	2.543132 Hz
AQ	0.1966580 sec
RG	71.8
DW	96.000 usec
DE	6.00 usec
TE	300.0 K
D0	0.00000300 sec
D1	1.00000000 sec
D8	1.00000000 sec
IN0	0.00009600 sec

======== CHANNEL f1 ========

NUC1	1H
P1	10.50 usec
PL1	-3.00 dB
SFO1	400.1322007 MHz

F1 - Acquisition parameters

ND0	2
TD	256
SFO1	400.1322 MHz
FIDRES	20.345053 Hz
SW	13.017 ppm

F2 - Processing parameters

SI	2048
SF	400.1300065 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

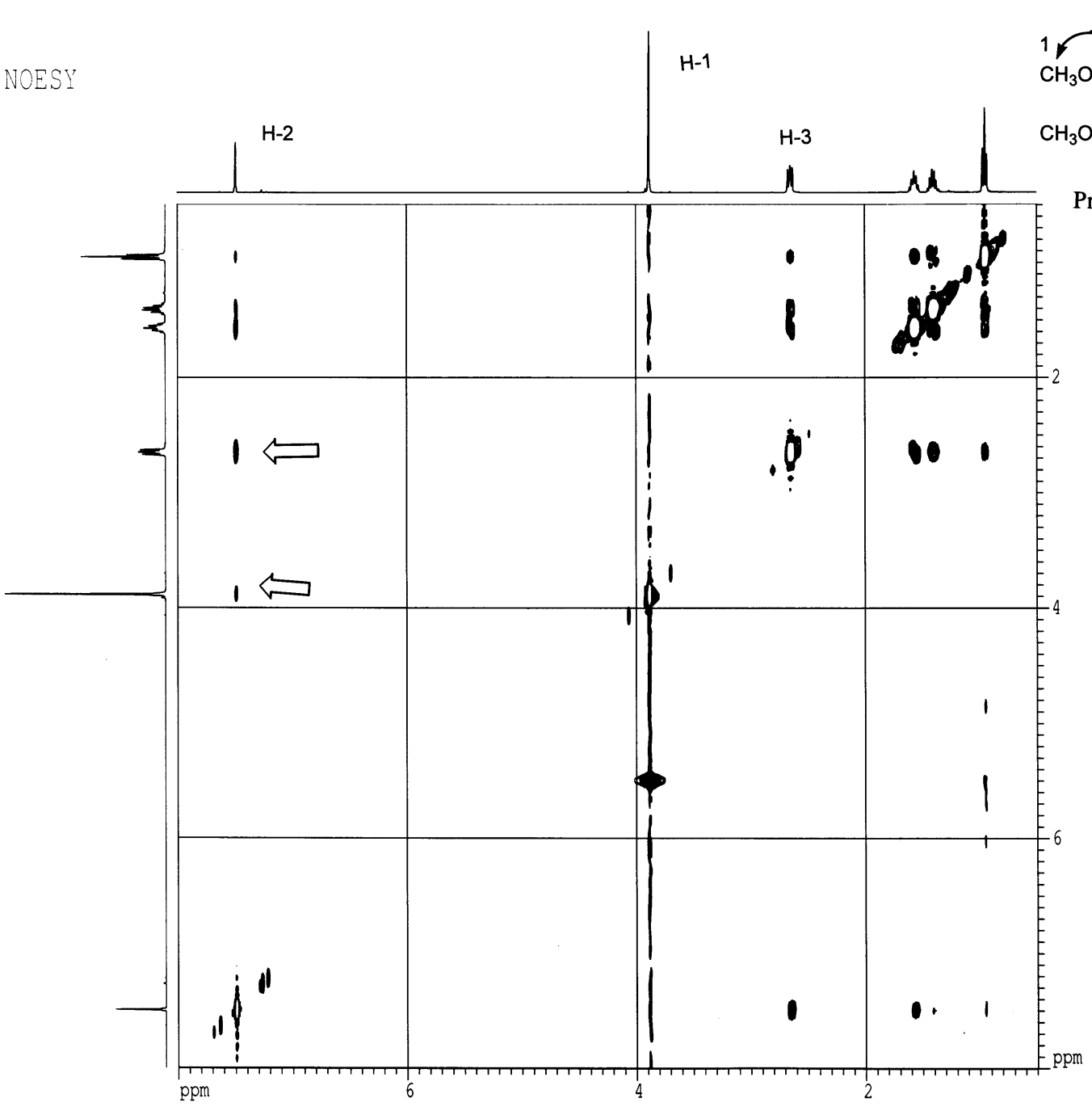
F1 - Processing parameters

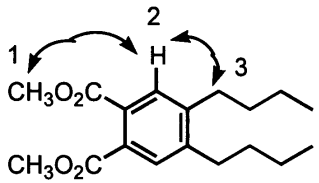
SI	1024
MC2	TPPI
SF	400.1300065 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	5.001 ppm
F2LO	2000.95 Hz
F2PHI	0.495 ppm
F2HI	197.87 Hz
F1PLO	5.001 ppm
F1LO	2000.95 Hz
F1PHI	0.488 ppm
F1HI	195.33 Hz
F2PPMCM	0.30042 ppm/cm
F2HZCM	120.20535 Hz/cm
F1PPMCM	0.30084 ppm/cm
F1HZCM	120.37489 Hz/cm

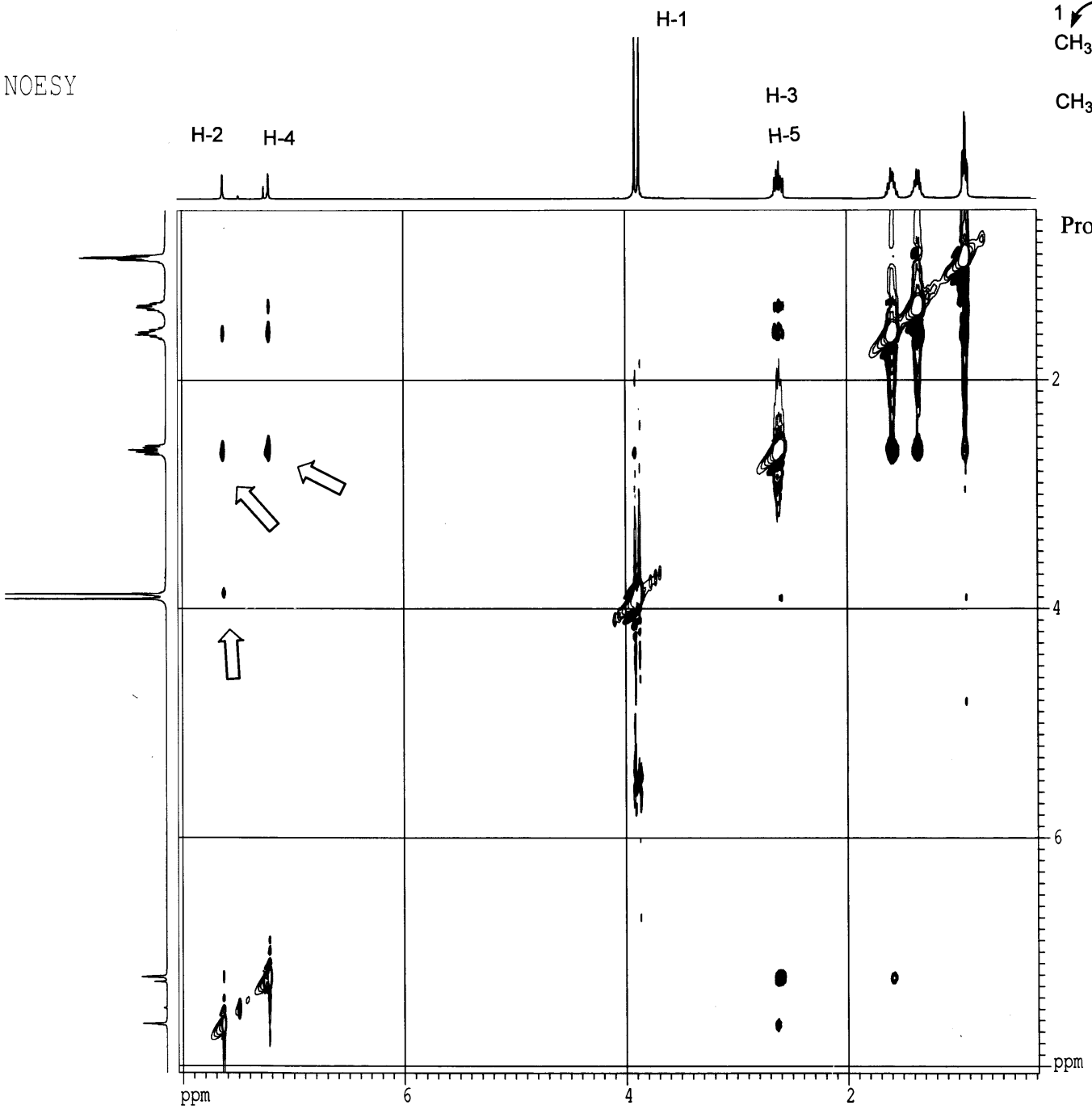
NOESY

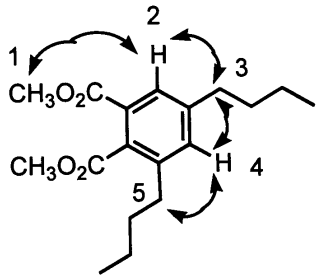




Product **12a**

NOESY





Product **12b**