Supporting Information for
Remarkably Mild and Efficient Intramolecular Friedel-Crafts Cyclization
Catalyzed by In(III)

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General Experimental:

Thin layer chromatography (TLC) was performed on silica gel Whatman-60F glass plates, and components were visualized by illumination with UV light or by staining with potassium permanganate solution. Chromatography was performed using silica E. Merck silica gel 60 (230-400 mesh). NMR spectra were recorded in CDCl₃ on a Varian Inova 500 MHz, 400 MHz, or Varian Mercury 300 MHz spectrometer. ¹³C NMR was recorded using broad band proton decoupling. Chemical shifts are reported in δ relative to TMS and coupling constants in Hz. Optical rotations were recorded on a JASCO-CIP-370 instrument. High-resolution mass spectra (HRMS) [Positive Ion FAB (FAB⁺) or Electrospray (ES)] were in the Department of Chemistry and Molecular Biology at North Dakota State University. Melting points were determined without correction. Solvents were dried using a nitrogen pressurized alumina column system from Solvtek.

Representative Procedure:

Substrate (0.1 mmol) and dichloromethane (2 ml, 0.05M) were placed in a small screw-cap scintillation vial equipped with a magnetic stirbar. Powdered 4Å molecular sieves (50 mg) and Lewis acid catalyst (0.01 mmol) were added and the reaction was allowed to stir at room temperature. Upon completion of the reaction (usually 16 hr), the mixture was loaded onto a silica gel column directly and eluted using 10:1 hexane-ethyl acetate solution to afford the cyclic product.

Characterization Data for 3a-3q, 4a-4p:

Cis-2-(4-bromo-but-2-enyl)-2-(3,5-dimethoxy-benzyl)-malonic acid diethyl ester (3a). IR (neat) cm^{-1} : 2980, 2838, 1730, 1596, 1462, 1289, 1203, 1070, 857; ^1H NMR (400 MHz, CDCl_3) δ 6.31 (t, $J = 2.4$ Hz, 1H), 6.20 (d, $J = 2.4$ Hz, 2H) 5.84 (ddd, $J = 1.6, 8.4, 16.4$ Hz, 1H), 5.56 (dt, $J = 7.2, 14.8$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 4H), 3.91 (d, $J = 8.4$ Hz, 2H), 3.72 (s, 6H), 3.18 (s, 2H), 2.63 (dd, $J = 1.6, 7.6$ Hz, 2H), 1.24 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 160.9, 138.0, 129.0, 128.6, 108.4, 99.0, 61.8, 58.4, 55.4, 38.7, 29.7, 26.8, 14.4, 14.3; HRMS Calcd for $\text{C}_{20}\text{H}_{27}\text{BrNaO}_6$ ($\text{M} + \text{Na}^+$): 465.0889, found 465.0897.

R12P001-2
Pulse Sequence: s2pu1
Solvent: cdcl_3
Temp: 25.0 C / 298.1 K
INOVA-400 "vnmr400"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.334 sec
VIA 4882.0 Hz
4 repetitions
OBSERVE H1, 399.9356500 MHz
DATA PROCESSING
FT size 262144
Total time 8 min, 14 sec

R02000M-2
Pulse Sequence: s2pu1
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-2-231-1c
INOVA-400 "vnmr400"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.728 sec
VIA 4882.0 Hz
484 repetitions
OBSERVE H1, 100.626752 MHz
DECOUPLE H1, 399.9376499 MHz
Power 35 dB
on during acquisition
off during delay
VAT2-16 modulated
Data PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 48 sec

Cis-2-(4-bromo-but-2-enyl)-2-(3-dimethoxy-benzyl)-malonic acid diethyl ester (3b). IR (neat) cm^{-1} : 2981, 2836, 1728, 1585, 1490, 1264, 1203, 1046, 859, 700; ^1H NMR (400 MHz, CDCl_3) δ 7.16 (t, $J = 8.0$ Hz, 1H), 6.75 (dd, $J = 2.0, 8.0$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 1H), 6.59 (t, $J = 2.0$ Hz, 1H), 5.83 (ddd, $J = 2.0, 8.0, 18.8$ Hz, 1H), 5.56 (dt, $J = 7.6, 14.8$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 4H), 3.91 (d, $J = 8.4$ Hz, 2H), 3.74 (s, 3H), 3.21 (s, 2H), 2.61 (dd, $J = 1.6, 7.6$ Hz, 2H), 1.23 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 159.7, 137.4, 129.5, 129.0, 128.6, 122.5, 116.1, 112.4, 61.8, 58.5, 55.3, 38.4, 29.6, 26.8, 14.3, 14.2; HRMS Calcd for $\text{C}_{19}\text{H}_{25}\text{BrNaO}_5$ ($\text{M} + \text{Na}^+$): 436.2926, found 436.2920.

Trans-2-(4-bromo-but-2-enyl)-2-naphthalene-2-ylmethyl-malonic acid diethyl ester (3c). IR (neat) cm^{-1} : 2980, 1728, 1463, 1367, 1200, 1051, 968, 908, 860, 824, 744; ^1H NMR (500 MHz, CDCl_3) δ 7.80 (m, 3H), 7.63 (s, 1H), 7.48 (m, 2H), 7.25 (dd, $J = 1.5, 8.0$, 1H), 5.81 (ddd, $J = 6.5, 15.0, 22.0$ Hz, 2H), 4.25 (q, $J = 7.0$ Hz, 4H), 4.00 (d, $J = 6.5$ Hz, 2H), 3.44 (s, 2H), 2.63 (d, $J = 6.0$ Hz, 2H), 1.29 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.6, 133.3, 132.4, 130.8, 130.0, 128.9, 128.0, 127.9, 127.6, 127.5, 126.0, 125.7, 61.6, 61.5, 60.4, 58.8, 38.6, 35.1, 32.5, 21.0, 14.1; HRMS Calcd for $\text{C}_{22}\text{H}_{25}\text{BrNaO}_4$ ($M + \text{Na}^+$): 455.0834, found 455.0838.

R-4-121
Pulse Sequence: zgpg30
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-121
INOVAS-500 "delta5"
PULSE SEQUENCE
Relax: delay 8.380 sec
Pulprg: zgpg30
Acq: time 2.988 sec
VIA: 650.9 Hz
4 repetitions
OBSERVE F1: 499.671619 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 8 min, 12 sec

R-4-121
Pulse Sequence: zgpg30
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-121
INOVAS-500 "delta5"
PULSE SEQUENCE
Relax: delay 8.380 sec
Pulprg: zgpg30
Acq: time 6.579 sec
VIA: 27685.4 Hz
384 repetitions
OBSERVE F1: 125.6425171 MHz
DECOUPLE H1: 499.6741943 MHz
Power: 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 7 min, 35 sec

Cis-2-(4-bromo-but-2-enyl)-2-(3-methyl-benzyl)-malonic acid diethyl ester (3d). IR (neat) cm^{-1} : 2980, 1731, 1608, 1463, 1367, 1281, 1202, 1097, 1043, 858, 703; ^1H NMR (400 MHz, CDCl_3) δ 7.13 (t, $J = 8.0$ Hz, 1H), 7.03 (d, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 6.4$ Hz, 2H), 5.85 (ddd, $J = 2.0, 8.4, 18.8$ Hz, 1H), 5.56 (dt, $J = 7.6, 18.4$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 4H), 3.92 (d, $J = 8.4$ Hz, 2H), 3.19 (s, 2H), 2.60 (dd, $J = 2.0, 7.6$ Hz, 2H), 2.28 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 138.1, 135.7, 130.9, 129.0, 128.6, 128.5, 127.1, 61.7, 58.5, 38.2, 29.5, 26.9, 21.6, 14.3; HRMS Calcd for $\text{C}_{19}\text{H}_{25}\text{BrNaO}_4$ ($\text{M} + \text{Na}^+$): 419.0834, found 419.0854.

Cis-2-(4-bromo-but-2-enyl)-2-(4-methyl-benzyl)-malonic acid diethyl ester (3e).

IR (neat) cm^{-1} : 2981, 1729, 1515, 1445, 1390, 1240, 1043, 863, 729; ^1H NMR (400 MHz, CDCl_3) δ 7.06 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 8.0$ Hz, 2H), 5.85 (ddd, $J = 2.0$, 8.4, 16.8 Hz, 1H), 5.56 (dt, $J = 7.2$, 18.0 Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 4H), 3.91 (d, $J = 8.0$ Hz, 2H), 3.19 (s, 2H), 2.60 (dd, $J = 1.6$, 7.2 Hz, 2H), 2.28 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 136.9, 132.6, 129.9, 129.3, 129.0, 128.6, 61.7, 58.6, 37.9, 29.5, 27.0, 21.2, 14.3; HRMS Calcd for $\text{C}_{19}\text{H}_{25}\text{BrNaO}_4$ ($\text{M} + \text{Na}^+$): 419.0834, found 419.0830.

Trans-2-(4-bromo-but-2-enyl)-2-(3-fluorobenzyl)-malonic acid diethyl ester (3f).
 IR (neat) cm^{-1} : 2982, 1728, 1660, 1615, 1488, 1447, 1390, 1272, 1202, 1094, 1049, 969, 859, 788, 695; ^1H NMR (400 MHz, CDCl_3) δ 7.21 (m, 1H), 6.92-6.78 (m, 3H), 5.75 (ddd, $J = 7.2, 14.8, 22.0$ Hz, 1H), 5.69 (ddd, $J = 7.2, 14.8, 22.4$ Hz, 1H), 4.17 (m, 4H), 3.91 (d, $J = 7.2$ Hz, 2H), 3.19 (s, 2H), 2.54 (d, $J = 6.8$ Hz, 2H), 1.23 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 164.1, 138.6, 131.1, 130.0, 129.9, 125.9, 125.9, 117.2, 117.0, 114.3, 114.1, 61.8, 58.8, 38.3, 35.3, 32.4, 14.3; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{BrFNaO}_4$ ($\text{M} + \text{Na}^+$): 423.0583, found 423.0577.

R-4-174
 Pulse Sequence: szpu1
 Solvent: cdcl_3
 Temp: 25.0 C / 298.1 K
 File: R-4-174
 INOVA-500 "deltas"
 PULSE SEQUENCE
 Relax delay 0.300 sec
 Pulse 45.0 degrees
 Acq. time 0.334 sec
 VSWR 4852.0 Hz
 4 repetitions
 OBSERVE H1, 399.9356384 MHz
 DATA PROCESSING
 FT size 252144
 Total time 0 min, 14 sec

B2B0EPN
 Pulse Sequence: szpu1
 Solvent: CDCl_3
 Temp: 25.0 C / 298.1 K
 File: R-4-174c
 INOVA-500 "deltas"
 PULSE SEQUENCE
 Relax delay 0.300 sec
 Pulse 45.0 degrees
 Acq. time 0.770 sec
 Width 22222.2 Hz
 384 repetitions
 OBSERVE C13, 100.6263733 MHz
 DECOUPLE H1, 399.9356384 MHz
 Power 35 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 32768
 Total time 0 min, 49 sec

***Trans*-2-(4-bromo-but-2-enyl)-2-(4-fluorobenzyl)-malonic acid diethyl ester (3g).**

IR (neat) cm^{-1} : 2982, 1728, 1605, 1511, 1444, 1367, 1205, 1010, 969, 852; ^1H NMR (400 MHz, CDCl_3) δ 7.05 (dd, $J = 5.6, 8.8$ Hz, 2H), 6.92 (t, $J = 8.4$ Hz, 2H), 5.73 (ddd, $J = 7.2, 14.4, 22.4$ Hz, 1H), 5.68 (ddd, $J = 6.8, 14.8, 22.0$ Hz, 1H), 4.16 (m, 4H), 3.91 (d, $J = 7.2$ Hz, 2H), 3.17 (s, 2H), 2.53 (d, $J = 7.2$ Hz, 2H), 1.22 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 131.7, 131.6, 131.0, 129.9, 115.5, 115.3, 61.7, 58.9, 37.9, 35.2, 32.5, 14.2; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{BrFNaO}_4$ ($\text{M} + \text{Na}^+$): 423.0583, found 423.0585.

R-4-166
Pulse Sequence: szpul
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
File: R-4-166
INNOVA-500 "delta5"
PULSE SEQUENCE
Relax. delay 8.388 sec
Pulse 45.0 degrees
Acq. time 3.334 sec
Width 4882.0 Hz
6 repetitions
OBSERVE H1, 399.9356384 MHz
DATA PROCESSING
FT size 262144
Total time 8 min, 14 sec

0240098
Pulse Sequence: szpul
Solvent: CDCl3
Temp: 25.0 C / 298.1 K
File: R-4-166C
INNOVA-500 "delta5"
PULSE SEQUENCE
Relax. delay 8.388 sec
Pulse 45.0 degrees
Acq. time 6.728 sec
Width 22232.2 Hz
384 repetitions
OBSERVE C13, 100.5638733 MHz
DECOUPLE H1, 399.9376528 MHz
Power 35 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 9 min, 49 sec

***Trans*-2-(4-bromo-but-2-enyl)-2-(3-chloro-benzyl)-malonic acid diethyl ester (**3h**).**

IR (neat) cm^{-1} : 2981, 1727, 1598, 1573, 1478, 1444, 1367, 1202, 1082, 968, 856, 790, 733, 697; ^1H NMR (500 MHz, CDCl_3) δ 7.22 (m, 2H), 7.12 (s, 1H), 7.01 (d, $J = 6.5$ Hz, 1H), 5.78 (ddd, $J = 7.5, 15.0, 23.0$ Hz, 1H), 5.71 (ddd, $J = 7.5, 15.0, 22.5$ Hz, 1H), 4.20 (m, 4H), 3.95 (d, $J = 7.0$ Hz, 2H), 3.20 (s, 2H), 2.57 (d, $J = 7.0$ Hz, 2H), 1.26 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.3, 137.9, 134.1, 130.9, 130.1, 129.6, 129.5, 128.2, 127.3, 61.6, 58.6, 38.1, 35.1, 32.2, 14.0; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{ClBrNaO}_4$ ($M + \text{Na}^+$): 439.0288, found 439.0287.

R-4-154
Pulse Sequence: szpul
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
F1file: R-4-154
INDVA-500 "delta5"
PULSE SEQUENCE
Relax: delay 0.300 sec
Pulse: 45.0 degrees
Acq: time 2.910 sec
Width: 6550.0 Hz
4 repetitions
OBSERVE F1: 499.6716919 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 9 min, 12 sec

R-4-154
Pulse Sequence: szpul
Solvent: CDCl3
Temp: 25.0 C / 298.1 K
User: j-lia-07
F1file: R-4-154
INDVA-500 "delta5"
PULSE SEQUENCE
Relax: delay 0.300 sec
Pulse: 45.0 degrees
Acq: time 0.570 sec
Width: 27643.4 Hz
256 repetitions
OBSERVE C13: 125.6425171 MHz
DECOUPLE H1: 499.6741943 MHz
Power 40 dB
on during acquisition
off during delay
VOLT2-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 7 min, 35 sec

***Trans*-2-(4-bromo-but-2-enyl)-2-(4-chloro-benzyl)-malonic acid diethyl ester (**3i**).**

IR (neat) cm^{-1} : 2981, 1728, 1492, 1444, 1367, 1203, 1094, 1016, 968, 847; ^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 5.73 (ddd, $J = 7.2, 14.8, 22.4$ Hz, 1H), 5.67 (ddd, $J = 7.2, 15.2, 22.4$ Hz, 1H), 4.16 (m, 4H), 3.91 (d, $J = 7.2$ Hz, 2H), 3.16 (s, 2H), 2.52 (d, $J = 7.2$ Hz, 2H), 1.22 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 134.5, 133.2, 131.5, 131.1, 129.9, 128.7, 61.7, 58.8, 38.0, 35.3, 32.5, 14.2; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{ClBrNaO}_4$ ($\text{M} + \text{Na}^+$): 439.0288, found 439.0278.

R-4-175
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-175
INOVA-500 "deltas"
PULSE SEQUENCE
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 3.334 sec
Width 4862.5 Hz
4 repetitions
OBSERVE H1, 399.9356384 MHz
DATA PROCESSING
FT size 262144
Total time 0 min, 14 sec

S225979
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-175c
INOVA-500 "deltas"
PULSE SEQUENCE
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.770 sec
Width 2222.2 Hz
256 repetitions
OBSERVE C13, 100.626183 MHz
DECOUPLE H1, 399.9376526 MHz
Power 35 dB
off during acquisition
WALTZ-16 Modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 0 min, 49 sec

***Trans*-2-(4-bromo-but-2-enyl)-2-(3-bromo-benzyl)-malonic acid diethyl ester (**3j**).**

IR (neat) cm^{-1} : 2981, 1728, 1595, 1567, 1476, 1444, 1367, 1270, 1202, 1096, 1074, 968, 696, 668; ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, $J = 7.5$ Hz, 1H), 7.28 (d, $J = 2.5$ Hz, 1H), 7.14 (t, $J = 8.0$ Hz, 1H), 7.06 (d, $J = 7.5$ Hz, 1H), 5.78 (ddd, $J = 7.5$, 15.0, 22.5 Hz, 1H), 5.71 (ddd, $J = 7.0$, 14.5, 22.5 Hz, 1H), 4.21 (m, 4H), 3.95 (d, $J = 7.5$ Hz, 2H), 3.19 (s, 2H), 2.57 (d, $J = 7.0$ Hz, 2H), 1.26 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.3, 138.2, 133.0, 131.0, 130.2, 130.2, 129.8, 129.6, 128.6, 61.6, 58.6, 38.0, 37.8, 35.1, 32.2, 14.1; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{Br}_2\text{NaO}_4$ ($\text{M} + \text{Na}^+$): 482.9782, found 482.9777.

R-4-155
Pulse Sequence: szpu1
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-155
INNOVA-500 "delta5"
PULSE SEQUENCE
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 2.958 sec
Width 6558.0 Hz
4 repetitions
OBSERVE F1: 499.6716919 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 12 sec

R-4-155
Pulse Sequence: szpu1
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
User: 1-14-07
File: R-4-155c
INNOVA-500 "delta5"
PULSE SEQUENCE
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.579 sec
Width 27463.4 Hz
384 repetitions
OBSERVE C13: 125.6425171 MHz
DECOUPLE H1: 499.6741943 MHz
Power 40 dB
on during acquisition
off during delay
VALT2-15 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 7 min, 35 sec

Trans-2-(4-bromo-but-2-enyl)-2-(4-bromo-benzyl)-malonic acid diethyl ester (3k). IR (neat) cm^{-1} : 2981, 1727, 1593, 1488, 1444, 1367, 1270, 1204, 1106, 1073, 1012, 968, 912, 863, 807, 733; ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 8.4$ Hz, 2H), 7.14 (t, $J = 8.0$ Hz, 1H), 6.97 (d, $J = 8.4$ Hz, 2H), 5.73 (ddd, $J = 7.6, 15.2, 22.4$ Hz, 1H), 5.67 (ddd, $J = 7.2, 14.8, 22.4$ Hz, 1H), 4.16 (m, 4H), 3.91 (d, $J = 7.6$ Hz, 2H), 3.15 (s, 2H), 2.57 (d, $J = 6.8$ Hz, 2H), 1.22 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 135.0, 131.9, 131.6, 131.1, 129.8, 121.3, 61.7, 58.8, 38.1, 35.3, 32.5, 14.3; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{Br}_2\text{NaO}_4$ ($\text{M} + \text{Na}^+$): 482.9782, found 482.9786.

0240000
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: 8-4-187
INDVA=500 "delta5"
PULSE SEQUENCE
Relax: delay 8.300 sec
Pulse 45.0 degrees
Acq: time 3.354 sec
Width 4022.0 Hz
4 repetitions
OBSERVE H1, 500.1337533 MHz
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 14 sec

0240000
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: 8-4-187
INDVA=500 "delta5"
PULSE SEQUENCE
Relax: delay 8.300 sec
Pulse 45.0 degrees
Acq: time 8.720 sec
Width 22222.0 Hz
384 repetitions
OBSERVE C13, 100.628723 MHz
DECOUPLE H1, 500.1337533 MHz
Power 35 dB
on during acquisition
off during delay
WALTZ16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 49 sec

Cis-2-benzyl-2-(4-bromo-but-2-enyl)-malonic acid diethyl ester (3l). IR (neat) cm^{-1} : 2981, 1728, 1445, 1390, 1203, 1090, 1041, 862, 702; ^1H NMR (400 MHz, CDCl_3) δ 7.24 (m, 3H), 7.06 (m, 2H), 5.85 (ddd, $J = 2.0, 8.4, 16.4$ Hz, 1H), 5.56 (dt, $J = 7.2, 18.0$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 4H), 3.91 (d, $J = 8.0$ Hz, 2H), 3.23 (s, 2H), 2.60 (dd, $J = 2.0, 7.6$ Hz, 2H), 1.23 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 135.9, 130.1, 129.0, 128.6, 128.5, 127.3, 61.8, 58.6, 38.4, 29.6, 26.9, 14.3; HRMS Calcd for $\text{C}_{18}\text{H}_{23}\text{BrNaO}_4$ ($\text{M} + \text{Na}^+$): 405.0677, found 405.0671.

***Trans*-N-(4-bromo-but-2-enyl)-N-(3,5-dimethoxy-benzyl)-4-methylbenzenesulfonamide (3m).** IR (neat) cm^{-1} : 3054, 2986, 2841, 2305, 1598, 1432, 1340, 1265, 1206, 1159, 1066, 897, 739; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 6.33 (s, 3H), 5.63 (dt, $J = 7.2, 15.2$ Hz, 1H), 5.43 (dt, $J = 6.4, 15.2$ Hz, 1H), 4.23 (s, 2H), 3.77-3.71 (m, 10H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.2, 143.7, 138.3, 137.5, 131.1, 130.1, 129.4, 127.4, 106.4, 100.2, 55.6, 50.8, 47.9, 31.6, 21.8; HRMS Calcd for $\text{C}_{20}\text{H}_{24}\text{BrNNaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 476.0507, found 476.0507.

R13P2801
Pulse Sequence: s2pul
Solvent: cdcl_3
Temp: 25.0 C / 298.1 K
INDVX=400 "nuclr400"

Relax. delay 8.300 sec
Pulse 45.0 degrees
Acq. time 3.350 sec
Width 4662.0 Hz
4 repetitions
OBSERVE H1, 399.9354500 MHz
DATA PROCESSING
FT size 262144
Total time 8 min, 14 sec

R-3-388
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
INDVX=400 "nuclr400"

Relax. delay 8.300 sec
Pulse 45.0 degrees
Acq. time 6.750 sec
Width 22232.2 Hz
128 repetitions
OBSERVE C13, 100.628752 MHz
DECOUPLE H1, 399.9376499 MHz
Power 35 dB
on during acquisition
off during delay
WALTZ-16 Modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 48 sec

***Trans*-N-(4-bromo-but-2-enyl)-N-(3-methoxy-benzyl)-4-methyl-benzenesulfonamide (3n).** IR (neat) cm^{-1} : 2922, 2836, 1737, 1600, 1440, 1336, 1264, 1158, 1094, 1042, 920, 752, 694, 658; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (dt, $J = 2.0$, 8.4 Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 8.0$ Hz, 1H), 6.78 (dt, $J = 2.0$, 8.0 Hz, 3H), 5.61 (dt, $J = 7.6$, 15.2 Hz, 1H), 5.43 (dt, $J = 6.8$, 13.2 Hz, 1H), 4.27 (s, 2H), 3.76-3.72 (m, 7H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 143.7, 137.5, 137.4, 131.0, 130.1, 129.8, 129.4, 127.4, 121.0, 113.9, 113.8, 106.4, 55.4, 50.7, 48.0, 31.6, 21.8; HRMS Calcd for $\text{C}_{19}\text{H}_{22}\text{BrNNaO}_3\text{S}$ ($\text{M} + \text{Na}^+$): 446.0401, found 446.0400.

R-3-301
Pulse Sequence: szpul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
INNOVA-400 "vnmr400"
Relax. delay 2.200 sec
Pulse 45.0 degrees
Acq. time 3.350 sec
Width 4602.0 Hz
6 repetitions
OBSERVE H1, 399.9356500 MHz
DATA PROCESSING
FT size 25144
Total time 0 min, 14 sec

0200000
Pulse Sequence: szpul
Solvent: CDCl_3
Temp: 25.4 C / 298.1 K
INNOVA-400 "vnmr400"
Relax. delay 8.350 sec
Pulse 45.0 degrees
Acq. time 8.750 sec
Width 2222.2 Hz
128 repetitions
OBSERVE C13, 100.6263752 MHz
DECOUPLE H1, 399.9376499 MHz
Power 35 dB
on during acquisition
off during delay
WALTZ-16 modulated
Data PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 48 sec

Trans-N-(4-bromo-but-2-enyl)-N-(3-methyl-benzyl)-4-methyl-benzenesulfonamide (3o). IR (neat) cm^{-1} : 3028, 2921, 1598, 1492, 1441, 1336, 1251, 1158, 1092, 1042, 923, 815, 736, 696, 657; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 7.00 (d, $J = 6.4$ Hz, 2H), 5.59 (dt, $J = 7.6, 15.2$ Hz, 1H), 5.40 (dt, $J = 6.8, 13.6$ Hz, 1H), 4.26 (s, 2H), 3.74 (dd, $J = 7.6, 14.4$ Hz, 4H), 2.43 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 138.5, 137.5, 135.7, 130.9, 130.0, 129.5, 128.8, 128.7, 127.4, 125.8, 50.7, 48.0, 31.6, 21.8, 21.5; HRMS Calcd for $\text{C}_{19}\text{H}_{22}\text{BrNNaO}_2\text{S}$ ($\text{M} + \text{Na}^+$): 430.0452, found 430.0457.

Trans-N-Benzyl-N-(4-bromo-but-2-enyl)-4-methyl-benzenesulfonamide (3p). IR (neat) cm^{-1} : 3030. 2921, 1598. 1494. 1454. 1337. 1206. 1158. 1094. 968. 923. 815. 764. 732. 698; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.32-7.21 (m, 7H), 5.58 (dt, $J = 7.2, 14.8$ Hz, 1H), 5.40 (dt, $J = 6.4, 14.0$ Hz, 1H), 4.30 (s, 2H), 3.73 (t, $J = 8.0$ Hz, 4H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 137.4, 135.9, 130.9, 130.0, 129.4, 128.8, 128.8, 128.1, 127.5, 50.8, 48.1, 31.5, 21.8; HRMS Calcd for $\text{C}_{18}\text{H}_{20}\text{BrNNaO}_2\text{S}$ ($\text{M} + \text{Na}^+$): 416.0296, found 416.0304.

Trans-N-(4-chloro-but-2-enyl)-N-(3,5-dimethoxy-benzyl)-4-methyl-benzenesulfonamide (3q). IR (neat) cm^{-1} : 3020, 2960, 2840, 1597, 1459, 1338, 1205, 1157, 1097, 1066, 919, 815, 770, 667; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 6.33 (s, 3H), 5.59 (dt, $J = 6.8, 15.2$ Hz, 1H), 5.43 (dt, $J = 6.4, 12.8$ Hz, 1H), 4.23 (s, 2H), 3.88 (d, $J = 6.8$ Hz, 2H), 3.74 (d, $J = 6.4$ Hz, 2H), 3.71 (s, 6H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.2, 143.7, 138.3, 137.5, 130.7, 130.0, 129.0, 127.5, 106.4, 100.2, 55.5, 50.9, 48.1, 44.0, 21.7; HRMS Calcd for $\text{C}_{20}\text{H}_{24}\text{ClNNaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 432.1012, found 432.1012.

6,8-Dimethoxy-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (4a). IR (neat) cm^{-1} : 2978, 2359, 1729, 1607, 1491, 1390, 1198, 1101, 1049, 939, 861, 731, 668; ^1H NMR (400 MHz, CDCl_3) δ 6.30 (s, 2H), 5.78 (ddd, J = 5.2, 8.4, 13.6 Hz, 1H), 4.92 (bd, J = 8.4 Hz, 1H), 4.79 (bd, J = 13.6 Hz), 4.29-4.06 (m, 4H), 3.78 (s, 3H), 3.72 (s, 3H), 3.32 (d, J = 12.4 Hz, 1H), 3.06 (d, J = 12.8 Hz, 1H), 2.53 (dd, J = 6.0, 10.8 Hz, 1H), 2.24 (dd, J = 4.8, 11.2 Hz, 1H), 1.24 (t, J = 5.6 Hz, 3H), 1.16 (t, J = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 171.4, 159.2, 158.8, 141.7, 136.2, 117.8, 113.5, 104.5, 97.3, 61.5, 55.5, 55.4, 53.2, 35.7, 35.3, 34.6, 14.2, 14.1; HRMS Calcd for $\text{C}_{20}\text{H}_{26}\text{NaO}_6$ ($\text{M} + \text{Na}^+$): 385.1627, found 385.1630.

Mixture of 7-methoxy-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester and 5-methoxy-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (para-, ortho-4b). IR (neat) cm^{-1} : 2980, 1730, 1639, 1502, 1467, 1242, 918, 863, 737, 702; ^1H NMR (400 MHz, CDCl_3) δ 7.06 (d, $J = 8.4$ Hz, 1H), 6.69 (dd, $J = 2.8, 8.4$ Hz, 1H), 6.64 (d, $J = 2.4$ Hz, 1H), 5.70 (dd, $J = 10.0, 17.2$ Hz, 1H), 5.13 (ddt, $J = 0.8, 8.0, 15.2$ Hz, 2H), 4.21-4.05 (m, 4H), 3.75 (s, 3H), 3.43 (dd, $J = 10.0, 15.6$ Hz, 1H), 3.40 (d, 18.4 Hz, 1H), 3.13 (d, $J = 16$ Hz, 1H), 2.55 (ddd, $J = 2.0, 6.0, 13.6$ Hz, 1H), 1.96 (dd, $J = 11.6, 13.6$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 170.8, 158.3, 141.8, 135.7, 134.9, 129.8, 128.6, 127.4, 121.4, 116.3, 113.7, 113.5, 112.8, 108.7, 61.8, 61.5, 61.5, 61.4, 55.5, 55.4, 53.7, 41.0, 35.6, 35.5, 35.4, 35.2, 34.5, 14.2, 14.2, 14.1; HRMS Calcd for $\text{C}_{19}\text{H}_{24}\text{NaO}_5$ ($\text{M} + \text{Na}^+$): 355.1521, found 355.1530.

4-vinyl-3,4-dihydro-1 *H*-phenanthrene-2,2-dicarboxylic acid diethyl ester (4c). IR (neat) cm^{-1} : 3053, 2980, 1730, 1632, 1601, 1510, 1446, 1391, 1298, 1186, 1074, 916, 863, 739, 658; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.0$ Hz, 1H), 7.76 (dd, $J = 1.6, 7.6$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.40 (ddd, $J = 1.6, 6.8, 14.8$ Hz, 2H), 7.26 (d, $J = 8.8$ Hz, 1H), 5.87, (ddd, $J = 6.8, 10.4, 17.2$ Hz, 1H), 5.03 (dt, $J = 1.2, 10.0$ Hz, 1H), 4.81 (dt, $J = 1.2, 18.4$ Hz, 1H), 4.36 (dd, $J = 6.4, 12.4$ Hz, 1H), 4.20-4.03 (m, 4H), 3.59 (d, $J = 16.4$ Hz, 1H), 3.24 (d, $J = 16.4$ Hz, 1H), 2.72 (dq, $J = 1.2, 7.2$ Hz, 1H), 2.45 (dd, $J = 4.8, 13.6$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.12 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 171.4, 141.9, 133.0, 132.1, 132.1, 131.1, 128.6, 127.8, 127.5, 125.9, 125.1, 124.9, 116.1, 61.6, 52.8, 37.9, 36.0, 35.6, 35.2, 14.2, 14.1; HRMS Calcd for $\text{C}_{22}\text{H}_{24}\text{NaO}_4$ ($M + \text{Na}^+$): 375.1572, found 375.1584.

R=4-122
Pulse Sequence: szpul
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
File: R=4-122
INOVAS88 "delias"
PULSE SEQUENCE
Relax: delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.254 sec
Width 4882.0 Hz
4 repetitions
OBSERVE H1, 399.9356384 MHz
DATA PROCESSING
FT size 26244
Total time 0 min, 14 sec

0000000
Pulse Sequence: szpul
Solvent: CDCl3
Temp: 25.0 C / 298.1 K
File: R=4-122
INOVAS88 "delias"
PULSE SEQUENCE
Relax: delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.724 sec
Width 22122.2 Hz
384 repetitions
OBSERVE C13, 100.6261723 MHz
DECOUPLE H1, 399.9356384 MHz
Power 35 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 0 min, 49 sec

Mixture of 7-methyl-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester and 5-methyl-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (para-, ortho-4d). IR (neat) cm^{-1} : 2979, 1732, 1639, 1502, 1367, 1241, 1182, 1056, 917, 863, 821, 737, 703; ^1H NMR (400 MHz, CDCl_3) δ

7.07-6.92 (m, 3H), 5.72 (m, 1H), 5.14 (ddt, $J = 0.8, 7.6, 15.2$ Hz, 2H), 4.21-4.04 (m, 4H), 3.46 (dd, $J = 9.6, 16.4$ Hz, 1H), 3.36 (ddd, $J = 2.0, 6.8, 16.4$ Hz, 1H), 3.09 (dd, $J = 10.4, 16.4$ Hz, 1H), 2.56 (ddd, $J = 1.2, 7.6, 14.0$ Hz, 1H), 2.27 (s, 3H), 1.97 (dd, $J = 11.2, 13.6$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.0, 170.9, 141.6, 140.7, 137.2, 136.2, 134.8, 134.3, 133.4, 133.4, 129.6, 128.8, 128.5, 127.4, 127.0, 126.5, 116.4, 115.1, 61.8, 61.5, 61.5, 61.5, 53.7, 53.2, 41.3, 38.8, 35.6, 35.3, 35.2, 35.1, 21.1, 19.9, 14.2, 14.2, 14.1; HRMS Calcd for $\text{C}_{19}\text{H}_{24}\text{NaO}_4$ ($M + \text{Na}^+$): 339.1572, found 339.1574.

6-Methyl-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (4e). IR (neat) cm^{-1} : 2980, 1731, 1640, 1503, 1447, 1367, 1246, 1095, 918, 864, 809, 737, 703; ^1H NMR (400 MHz, CDCl_3) δ 7.01 (d, $J = 7.6$ Hz, 1H), 6.95 (dd, $J = 3.2, 11.2$ Hz, 2H), 5.74 (ddd, $J = 9.6, 16.8, 18.4$ Hz, 1H), 5.16 (ddt, $J = 1.6, 6.4, 16.8$ Hz, 2H), 4.21-4.09 (m, 4H), 3.46 (dd, $J = 10.0, 16.0$ Hz, 1H), 3.36 (dd, $J = 1.2, 16.0$ Hz, 1H), 3.11 (d, $J = 16.4$ Hz, 1H), 2.56 (ddd, $J = 2.0, 6.0, 13.6$ Hz, 1H), 2.25 (s, 3H), 1.97 (dd, $J = 11.2, 13.2$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.0, 170.9, 141.6, 136.2, 135.9, 130.5, 130.0, 129.1, 128.9, 127.6, 116.6, 61.8, 61.5, 53.7, 41.6, 35.3, 34.9, 21.3, 14.2, 14.2; HRMS Calcd for $\text{C}_{19}\text{H}_{24}\text{NaO}_4$ ($M + \text{Na}^+$): 339.1572, found 339.1563.

Q2469BH
Pulse Sequence: szpu1
Solvent: CDCl_3
Temp. 25.0 C / 298.1 K
File: R-4-65
INNOVA-500 "delta5"
PULSE SEQUENCE
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.778 sec
Width 22322.0 Hz
256 repetitions
OBSERVE C13, 100.5638733 MHz
DECOUPLE H1, 399.9376526 MHz
Power 35 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 35768
Total time 8 min, 49 sec

Mixture of 7-fluoro-4-vinyl-3,4-dihydro-1H-naphthalene-2,2-dicarboxylic acid diethyl ester and 5-fluoro-4-vinyl-3,4-dihydro-1H-naphthalene-2,2-dicarboxylic acid diethyl ester (para-, ortho-4f). IR (neat) cm^{-1} : 2982, 2258, 1731, 1640, 1614, 1591, 1498, 1463, 1368, 1242, 1105, 1057, 1033, 912, 863, 820, 734, 649; ^1H

NMR (400 MHz, CDCl_3) δ 7.11 (m, 1H), 6.81 (m, 2H), 5.70 (ddd, $J = 8.8, 10.0, 17.2$, 1H), 5.18-5.13 (m, 2H), 4.21-4.06 (m, 4H), 3.44 (dd, $J = 9.6, 16.4$ Hz, 1H), 3.36 (dd, $J = 2.0, 16.4$ Hz, 1H), 3.13 (t, $J = 16.4$ Hz, 1H), 2.56 (ddd, $J = 2.4, 6.0, 12.0$ Hz, 1H), 1.97 (dd, $J = 11.2, 13.6$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 170.7, 162.8, 160.3, 141.2, 140.3, 135.9, 135.8, 132.1, 130.3, 130.2, 127.9, 127.8, 124.7, 116.8, 115.2, 115.0, 114.8, 113.7, 113.6, 113.5, 113.3, 61.9, 61.7, 61.6, 61.6, 53.5, 41.1, 35.8, 35.3, 35.2, 35.1, 34.5, 14.2, 14.2, 14.1; HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{FNaO}_4$ ($\text{M} + \text{Na}^+$): 343.1322, found 343.1314.

6-Fluoro-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (4g). IR (neat) cm^{-1} : 2982, 2258, 1731, 1613, 1497, 1466, 1368, 1259, 1138, 1056, 913, 875, 811, 733, 649; ^1H NMR (400 MHz, CDCl_3) δ 7.05 (dd, $J = 6.0, 8.4$ Hz, 1H), 6.84 (m, 2H), 5.71 (dddd, $J = 8.4, 10.0, 16.4, 17.6$ Hz, 1H), 5.19 (dd, $J = 6.4, 16.8$ Hz, 2H), 4.19 (q, $J = 7.2$ Hz, 2H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.47 (dd, $J = 10.4$ Hz, 1H), 3.36 (dd, $J = 1.6, 16.4$ Hz, 1H), 3.09 (dd, $J = 0.8, 16.0$ Hz, 1H), 2.56 (ddd, $J = 2.0, 6.0, 13.6$ Hz, 1H), 1.96 (dd, $J = 11.2, 13.6$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.15 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 170.7, 162.8, 160.4, 140.7, 138.7, 138.6, 130.4, 130.3, 129.2, 117.3, 115.1, 114.9, 114.0, 113.7, 61.9, 61.6, 53.7, 41.8, 34.9, 34.5, 14.2, 14.2; HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{FNaO}_4$ ($M + \text{Na}^+$): 343.1322, found 343.1327.

R-4-176
Pulse Sequence: szpu1
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
File: R-4-176
INVOA-500 "deltaS"
PULSE SEQUENCE
Relax: delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.354 sec
Width 4662.0 Hz
4 repetitions
OBSERVE H1, 399.9356384 MHz
DATA PROCESSING
FT size 262144
Total time 0 min, 14 sec

R2208PM
Pulse Sequence: szpu1
Solvent: CDCl3
Temp: 25.0 C / 298.1 K
File: R-4-176
INVOA-500 "deltaS"
PULSE SEQUENCE
Relax: delay 0.300 sec
Pulse 45.0 degrees
Acq. time 0.720 sec
Width 2222.0 Hz
384 repetitions
OBSERVE C13, 101.5638733 MHz
DECOUPLE H1, 399.9376526 MHz
Power 35 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 0 min, 49 sec

Mixture of 7-chloro-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester and 5-chloro-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (para-, ortho-4h). IR (neat) cm^{-1} : 2981, 2257, 1731, 1639, 1598, 1571, 1511, 1445, 1368, 1247, 1096, 1054, 913, 864, 734, 649; ^1H

NMR (400 MHz, CDCl_3) δ 7.23 (d, $J = 6.0\text{Hz}$, 1H), 7.12-7.07 (m, 2H), 5.78 (ddd, $J = 4.8, 8.4, 13.2$, 1H), 5.19 (dd, $J = 6.0, 14.0$ Hz, 2H), 4.23-4.07 (m, 4H), 4.04 (dd, $J = 1.2, 6.0$ Hz, 1H), 3.37 (dd, $J = 1.6, 12.8$ Hz, 1H), 3.10 (t, $J = 13.2$ Hz, 1H), 2.57 (ddd, $J = 2.0, 5.2, 11.2$ Hz, 1H), 2.42 (dd, $J = 3.2, 11.2$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.14 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 171.3, 171.1, 170.4, 140.7, 139.1, 136.7, 135.4, 134.8, 134.6, 134.4, 132.0, 129.9, 128.5, 127.8, 127.5, 127.5, 116.9, 115.1, 61.7, 61.5, 61.4, 53.3, 52.9, 41.0, 38.5, 35.0, 34.8, 34.8, 34.0 ; HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{ClNaO}_4$ ($\text{M} + \text{Na}^+$): 359.1026, found 359.1030.

6-Chloro-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (4i). IR (neat) cm^{-1} : 2981, 2257, 1731, 1640, 1596, 1482, 1447, 1390, 1300, 1185, 1140, 1095, 1059, 1033, 913, 866, 811, 733; ^1H NMR (400 MHz, CDCl_3) δ 7.13-7.02 (m, 3H), 5.70 (dd, $J = 9.2, 17.6$ Hz, 1H), 5.20 (dd, $J = 3.6, 15.2$ Hz, 2H), 4.21-4.10 (m, 4H), 3.46 (dd, $J = 10.4, 16.0$ Hz, 1H), 3.36 (dd, $J = 2.0, 16.4$ Hz, 1H), 3.09 (d, $J = 16.4$ Hz, 1H), 2.56 (ddd, $J = 2.4, 6.4, 13.6$ Hz, 1H), 1.95 (dd, $J = 11.2, 13.6$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 170.7, 140.5, 138.5, 132.2, 130.3, 128.5, 126.9, 117.5, 61.9, 61.7, 53.6, 41.6, 34.9, 34.7, 14.2, 14.2; HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{ClNaO}_4$ ($\text{M} + \text{Na}^+$): 359.1026, found 359.1030.

R-4-189
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-189
INOVA-500 "delta5"
PULSE SEQUENCE
Relax. delay 8.380 sec
Pulse 45.0 degrees
Acq. time 0.334 sec
Width 4882.0 Hz
4 repetitions
OBSERVE M1, 399.9358384 MHz
DATA PROCESSING
FT size 262144
Total time 8 min, 14 sec

00000000
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-189c
INOVA-500 "delta5"
PULSE SEQUENCE
Relax. delay 8.380 sec
Pulse 45.0 degrees
Acq. time 0.720 sec
Width 22222.0 Hz
255 repetitions
OBSERVE C13, 100.6263733 MHz
DECOUPLE H1, 399.9276526 MHz
Power 35 dB
on during acquisition
off during delay
VOLTAGE modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 49 sec

Mixture of 7-bromo-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester and 5-bromo-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (para-, ortho-4j). IR (neat) cm^{-1} : 2981, 1731, 1639, 1592, 1565, 1446, 1390, 1248, 1184, 1054, 915, 863, 821, 736; ^1H NMR (400 MHz, CDCl_3) δ 7.26 (t, $J = 6.8$ Hz, 1H), 7.03 (dd, $J = 1.2, 5.6$ Hz, 1H), 5.78 (ddd, $J = 4.4, 8.0, 13.2$, 1H), 5.19 (dd, $J = 5.6, 13.6$ Hz, 2H), 4.23-4.07 (m, 4H), 4.03 (bs, 1H), 3.37 (t, $J = 12.4$ Hz, 1H), 3.10 (t, $J = 13.2$ Hz, 1H), 2.57 (m, 1H), 2.48 (dd, $J = 3.2, 11.6$ Hz, 1H), 1.28-1.13 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 171.2, 170.4, 140.5, 139.0, 136.9, 136.1, 135.8, 135.4, 131.4, 131.2, 130.2, 129.4, 128.2, 127.9, 125.3, 120.2, 117.0, 115.4, 61.7, 61.5, 61.4, 53.2, 53.1, 41.0, 40.9, 35.1, 34.8, 34.7, 33.9, 14.0, 13.9, 13.9, 13.9; HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{BrNaO}_4$ ($\text{M} + \text{Na}^+$): 403.0521, found 403.0514.

6-Bromo-4-vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (4k). IR (neat) cm^{-1} : 2982, 2256, 1729, 1640, 1591, 1479, 1447, 1368, 1301, 1240, 1188, 1140, 1033, 911, 809, 733, 649; ^1H NMR (400 MHz, CDCl_3) δ 7.24 (dd, $J = 2.0, 8.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 1H), 5.70 (dd, $J = 9.2, 17.6$, 1H), 5.19 (dd, $J = 2.8, 14.0$ Hz, 2H), 4.20-4.09 (m, 4H), 3.46 (dd, $J = 10.4, 16.4$ Hz, 1H), 3.34 (dd, $J = 2.0, 16.4$ Hz, 1H), 3.07 (d, $J = 16.4$ Hz, 1H), 2.55 (ddd, $J = 2.4, 6.4, 14.0$ Hz, 1H), 1.95 (dd, $J = 11.2, 13.6$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 170.7, 140.5, 138.9, 132.7, 131.5, 130.6, 129.8, 120.3, 117.5, 61.9, 61.7, 53.5, 41.6, 34.9, 34.7, 14.2, 14.2; HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{BrNaO}_4$ ($M + \text{Na}^+$): 403.0521, found 403.0528.

R-4-177
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-177
INOVA-500 "delta5"
PULSE SEQUENCE
Relax: delay 0.300 sec
Pulse 45.0 degrees
Acq: time 0.334 sec
Width 4662.8 Hz
4 repetitions
OBSERVE H1: 399.9356384 MHz
DATA PROCESSING
FT size 262144
Total time 0 min, 14 sec

0280099
Pulse Sequence: s2pul
Solvent: CDCl_3
Temp: 25.0 C / 298.1 K
File: R-4-177
INOVA-500 "delta5"
PULSE SEQUENCE
Relax: delay 0.300 sec
Pulse 45.0 degrees
Acq: time 0.728 sec
Width 2222.2 Hz
328 repetitions
OBSERVE C13: 100.6238733 MHz
DECOUPLE H1: 399.9356384 MHz
Power: 35 dB
on during acquisition
off during delay
VOLTAGE modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 0 min, 49 sec

4-Vinyl-3,4-dihydro-1 *H*-naphthalene-2,2-dicarboxylic acid diethyl ester (4l). IR (neat) cm^{-1} : 2981, 1732, 1640, 1463, 1390, 1190, 1095, 919, 861, 742, 692; ^1H NMR (400 MHz, CDCl_3) δ 7.18- 7.08 (m, 4H), 5.75 (ddd, $J = 8.4, 16.8, 18.4$ Hz, 1H), 5.16 (ddt, $J = 2.0, 5.2, 16.8$ Hz, 2H), 4.21-4.10 (m, 4H), 3.46 (dd, $J = 9.6, 16.0$ Hz, 1H), 3.40 (dd, $J = 2.0, 16.4$ Hz, 1H), 3.17 (d, $J = 16.4$ Hz, 1H), 2.57 (ddd, $J = 2.0, 6.0, 13.6$ Hz, 1H), 1.99 (dd, $J = 11.2, 13.6$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.15 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.0, 170.9, 141.4, 136.5, 133.7, 129.0, 128.6, 126.7, 126.5, 116.7, 61.8, 61.5, 53.7, 41.6, 35.2, 14.2, 14.2; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{NaO}_4$ ($\text{M} + \text{Na}^+$): 325.1416, found 325.1415.

5,7-Dimethoxy-2-(toluene-4-sulfonyl)-4-vinyl-1,2,3,4-tetrahydro-isoquinoline (4m).

IR (neat) cm^{-1} : 3056, 2961, 2841, 1611, 1462, 1350, 1267, 1165, 1089, 1052, 944, 810, 739, 652; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 6.27 (d, $J = 2.4$ Hz, 1H), 6.14 (d, $J = 2.4$ Hz, 1H), 5.95 (ddd, $J = 6.4, 10.0, 16.8$ Hz, 1H), 5.01 (m, 2H), 4.56 (d, $J = 14.8$ Hz, 1H), 3.90 (dt, $J = 2.0, 12.0$ Hz, 1H), 3.74-3.70 (m, 8H), 3.64 (d, $J = 3.2$ Hz, 1H), 2.69 (dd, $J = 3.6, 11.6$ Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 158.5, 143.8, 138.8, 133.4, 133.3, 129.8, 128.0, 116.8, 115.5, 101.7, 97.4, 55.6, 55.5, 48.5, 47.7, 36.7, 21.7; HRMS Calcd for $\text{C}_{20}\text{H}_{23}\text{NNaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 396.1245, found 396.1249.

R-4-1
Pulse Sequence: zgpg30
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
F1: 400.136
INNOVA-500 "delat5"
PULSE SEQUENCE
Relax. delay 8.300 sec
Pulse 45.0 degrees
Acq. time 3.334 sec
Width 4662.5 Hz
4 repetitions
OBSERVE F1: 399.9356384 MHz
DATA PROCESSING
F1 size 262144
Total time 0 min, 14 sec

R-4-1
Pulse Sequence: zgpg30
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
F1: 400.136
INNOVA-500 "delat5"
PULSE SEQUENCE
Relax. delay 8.300 sec
Pulse 45.0 degrees
Acq. time 3.334 sec
Width 4662.5 Hz
4 repetitions
OBSERVE F1: 399.9356384 MHz
DATA PROCESSING
F1 size 262144
Total time 0 min, 14 sec

Mixutre of 7-methoxy-2-(toluene-4-sulfonyl)-4-vinyl-1,2,3,4-tetrahydro-isoquinoline and 5-methoxy-2-(toluene-4-sulfonyl)-4-vinyl-1,2,3,4-tetrahydro-isoquinoline (para-, ortho-4n). IR (neat) cm^{-1} : 3060, 2978, 2838, 1613, 1503, 1460, 1350, 1266, 1165, 1091, 1055, 958, 816, 736, 661; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.4$

Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.04 ($J = 8.8$ Hz, 1H), 6.73 (dd, $J = 2.8, 8.8$ Hz, 1H), 6.54 (d, $J = 2.8$ Hz, 1H), 5.76 (ddd, $J = 8.4, 10.0, 17.2$ Hz, 1H), 5.16 (dd, $J = 3.2, 10.0$ Hz, 2H), 4.20 (q, $J = 15.2$ Hz, 2H), 3.73 (s, 3H), 3.55 (dd, $J = 7.2, 12.8$ Hz, 1H), 3.42 (dd, $J = 4.8, 11.6$ Hz, 1H), 3.08 (dd, $J = 7.2, 11.6$ Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 143.9, 139.0, 133.4, 132.6, 130.2, 129.9, 129.8, 128.0, 128.0, 117.5, 115.8, 113.6, 111.0, 55.5, 49.0, 48.3, 48.1, 47.4, 42.0, 21.7; HRMS Calcd for $\text{C}_{19}\text{H}_{21}\text{NNaO}_3\text{S}$ ($\text{M} + \text{Na}^+$): 366.1140, found 366.1147.

Mixture of 7-methyl-2-(toluene-4-sulfonyl)-4-vinyl-1,2,3,4-tetrahydroisoquinoline and 5-methyl-2-(toluene-4-sulfonyl)-4-vinyl-1,2,3,4-tetrahydroisoquinoline (para-, ortho-4o). IR (neat) cm^{-1} : 3055, 2980, 2923, 2857, 1639, 1460, 1350, 1266, 1165, 1091, 1048, 958, 816, 736, 660; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 6.8$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.09-6.83 (m, 3H), 5.78 (ddd, $J = 8.4, 10.0, 16.8$ Hz, 1H), 5.16 (m, 2H), 4.19 (q, $J = 14.8$ Hz, 2H), 3.56 (dd, $J = 7.2, 13.6$ Hz, 1H), 3.41 (dd, $J = 4.8, 11.6$ Hz, 1H), 3.10 (dd, $J = 6.8, 11.6$ Hz, 1H), 2.40 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 138.9, 136.6, 132.3, 131.3, 129.9, 129.9, 129.0, 128.9, 128.0, 126.9, 126.9, 124.4, 117.6, 117.0, 49.1, 48.8, 48.0, 47.8, 43.3, 40.6, 21.7, 21.2, 19.1; HRMS Calcd for $\text{C}_{19}\text{H}_{21}\text{NNaO}_2\text{S}$ ($M + \text{Na}^+$): 350.1191, found 350.1184.

2-(Toluene-4-sulfonyl)-4-vinyl-1,2,3,4-tetrahydro-isoquinoline (4p). IR (neat) cm^{-1} : 3065, 2256, 1640, 1598, 1493, 1452, 1353, 1167, 1091, 1053, 994, 957, 814, 775, 710; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.15 (dd, $J = 5.6, 9.2$ Hz, 3H), 7.01 (t, $J = 4.4$ Hz, 1H), 5.78 (ddd, $J = 8.0, 10.0, 16.8$ Hz, 1H), 5.19 (dt, $J = 1.2, 10.4$ Hz, 2H), 4.23 (q, $J = 14.8$ Hz, 2H), 3.62 (dd, $J = 7.2, 13.6$ Hz, 1H), 3.42 (dd, $J = 4.8, 11.6$ Hz, 1H), 3.12 (dd, $J = 6.8, 11.6$ Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0, 138.7, 135.2, 133.2, 131.5, 129.9, 129.1, 128.0, 127.1, 127.0, 126.5, 117.9, 48.7, 48.0, 43.6, 21.8; HRMS Calcd for $\text{C}_{18}\text{H}_{19}\text{NNaO}_2\text{S}$ ($\text{M} + \text{Na}^+$): 336.1034, found 336.1030.