

Supporting Information

Formal [4 + 2] Cycloaddition of Donor–Acceptor Cyclobutanes and Aldehydes: Stereoselective Access to Substituted Tetrahydropyrans

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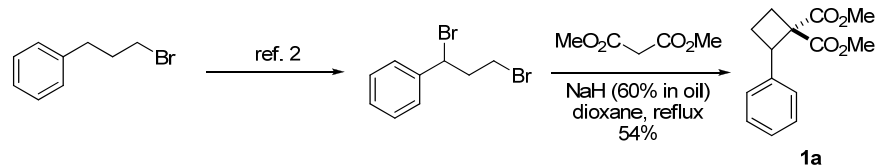
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Methods. Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Proton and carbon nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded on a Bruker model DRX 400 or 500 (^1H NMR at 400 MHz or 500 MHz and ^{13}C NMR at 100 or 125 MHz) spectrometer with solvent resonance as the internal standard (^1H NMR: CDCl_3 at 7.26 ppm, DMSO-d_6 at 2.54 ppm, and C_6D_6 at 7.15 ppm; ^{13}C NMR: CDCl_3 at 77.0 ppm, DMSO-d_6 at 40.45 ppm, and C_6D_6 at 128.6 ppm). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddd = doublet of doublet of doublet, ddt = doublet of doublet of triplet, dtd = doublet of triplet of doublet, t = triplet, bt = broad triplet, td = triplet of doublet, q = quartet, qd = quartet of doublet, qn = quintet, m = multiplet), coupling constants (Hz), and integration. GLC analysis was performed on an Agilent 6890N Network GC System equipped with a Chiradex B-DM column (30 m x 0.250 mm, pressure = 80 kPa, flow = 0.6 mL/min, detector = FID, 250 °C) with helium gas as carrier. Supercritical fluid chromatography was performed on a Berger SFC system equipped with a Chiralpack WO column (modifier = 2.0% MeOH, flow = 2.0 mL/min, pressure = 200 bar, detector = UV, 210 nm, temperature = 40 °C). Optical rotations were measured using a 2.0 mL cell with a 1.0 dm path length on a Jasco DIP 1000 digital polarimeter. Mass spectra were obtained using a Micromass Quattro II (triple quad) instrument with nanoelectrospray ionization. Elemental analysis was performed by Atlantic Microlab, Inc. Analytical thin layer chromatography (TLC) was performed on Sorbent Technologies Silica G 0.20 mm silica gel plates. Visualization was accomplished with UV light, aqueous basic potassium permanganate solution, or aqueous ceric ammonium molybdate solution followed by heating. Flash chromatography was performed using Silia-P flash silica gel (40-63 μm) purchased from Silicycle. Yield refers to isolated yield of analytically pure material unless otherwise noted. Yields and diastereomeric ratios (dr) are reported for a specific experiment and as a result may differ slightly from those found in the tables, which are averages of at least two experiments.

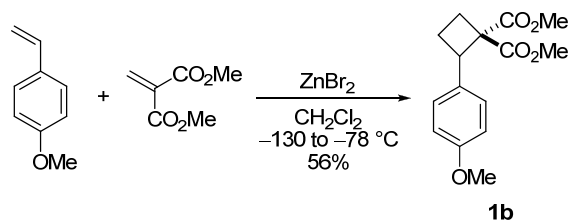
Materials. Tetrahydrofuran, toluene, and dichloromethane were dried by passage through a column of neutral alumina under nitrogen prior to use. 1,4-Dioxane was distilled from a sodium/benzophenone ketyl under N_2 and stored in a Schlenk flask. 1,2-Dichloroethane was purified by distillation from calcium hydride under N_2 prior to use. Benzaldehyde, *p*-anisaldehyde, 4-methylbenzaldehyde, 2-chlorobenzaldehyde, 2-fluorobenzaldehyde, and *trans*-cinnamaldehyde were purified by the following procedure: The neat aldehydes were washed sequentially with a 1 M sodium hydroxide solution and a saturated aqueous sodium bicarbonate solution, dried with magnesium sulfate, and distilled under reduced pressure. 4-Chlorobenzaldehyde was sublimed under reduced pressure. Isobutyraldehyde, cyclohexanecarboxaldehyde, and hexanal were dried over CaSO_4 and distilled under N_2 prior to use. Dimethyl 2,2-methylidene malonate was prepared according to the method of De Keyser¹ and was stored at -30 °C. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted.

Preparation of dimethyl 2-phenylcyclobutane-1,1-dicarboxylate (**1a**):



Under N_2 , a flame dried 500-mL 2-neck round-bottomed flask containing a magnetic stir bar was charged with (1,3-dibromopropyl)benzene² (13.95 g, 50.2 mmol, 1.0 equiv), dimethyl malonate (7.3 g, 55.3 mmol, 1.1 equiv), and 161 mL anhydrous 1,4-dioxane. The flask was affixed with a reflux condenser and the solution was heated to reflux. Sodium hydride (2.06 g (60% in mineral oil), 51.7 mmol, 1.03 equiv) was added in small portions over approximately 10 minutes. The reaction was allowed to reflux for 1 h, at which point additional sodium hydride [2.06 g (60% in mineral oil), 51.7 mmol, 1.03 equiv] was added in an analogous manner. The reaction was heated at reflux for an additional 12 h, at which point it was slowly cooled to room temperature. The resulting heterogeneous mixture was filtered through celite. The filter cake was washed with copious Et_2O and the filtrate was concentrated. Flash chromatography (2.5 – 3.3 – 5.0% EtOAc /hexanes) provided **1a** (6.67 g, 26.87 mmol, 54% yield) as a slightly yellow clear oil. Unreacted (1,3-dibromopropyl)benzene was also recovered (2.5 g, 8.99 mmol, 18%). Analytical data for **1a**: **IR** (thin film, cm^{-1}) 3030, 3000, 2952, 1732, 1496, 1435, 1275, 1201, 1107, 791, 699; **¹H NMR** (400 MHz, CDCl_3) δ 7.29 – 7.28 (m, 4H), 7.22 – 7.18 (m, 1H), 4.37 (t, $J = 9.2$ Hz, 1H), 3.77 (s, 3H), 3.23 (s, 3H), 2.28 (qd, $J = 9.2, 2.4$ Hz, 1H), 2.17 (qd, $J = 8.8, 2.0$ Hz, 1H); **¹³C NMR** (100 MHz, CDCl_3) δ 172.0, 169.6, 139.1, 128.0, 127.5, 126.9, 59.7, 52.4, 51.7, 45.1, 25.6, 20.7; **TLC** (10% EtOAc /hexanes) R_f 0.31; **Anal.** Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_4$: C, 67.73; H, 6.50. Found: C, 67.45; H, 6.60.

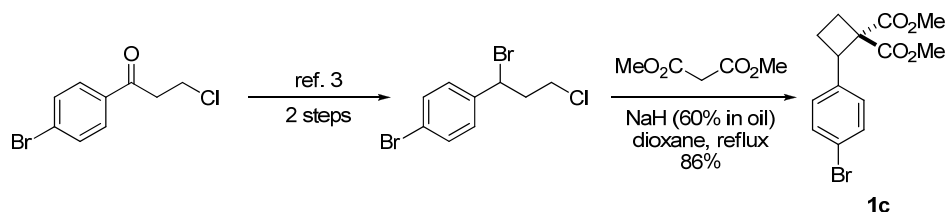
Preparation of dimethyl 2-(4-methoxyphenyl)cyclobutane-1,1-dicarboxylate (**1b**):



In an inert atmosphere glove box, a 100-mL round-bottomed flask was charged with ZnBr_2 (1.32 g, 5.9 mmol, 1.0 equiv), a magnetic stir bar, and was fitted with a rubber septum. A scintillation vial was charged with dimethyl 2,2-methylidene malonate¹ (DMM, 0.85 g, 5.9 mmol, 1.0 equiv) and fitted with a rubber septum. Both vessels were removed from the glove box and placed under N_2 . Outside of the glove box, a flame scintillation vial under N_2 was charged with 1-methoxy-4-vinylbenzene (0.933 g, 0.933 mL, 6.9 mmol, 1.2 equiv). All vials were charged with CH_2Cl_2 (13.5 mL, 40.5 mL total). The flask containing ZnBr_2 was cooled to -130 °C in a pentane/liquid N_2 bath. To the ZnBr_2 was added DMM followed by 1-methoxy-4-vinylbenzene (both added via canula over approximately 5 min). The reaction was warmed to -78 °C in an isopropanol/dry ice bath and was allowed to stir for 1 h. A solution of pyridine (1.82 g, 1.85 mL, 23.1 mmol, 4.3 equiv) in CH_2Cl_2 (13.0 mL) pre-cooled to -78 °C was added to the reaction via syringe. The reaction was allowed to warm to room temperature, washed with saturated aq.

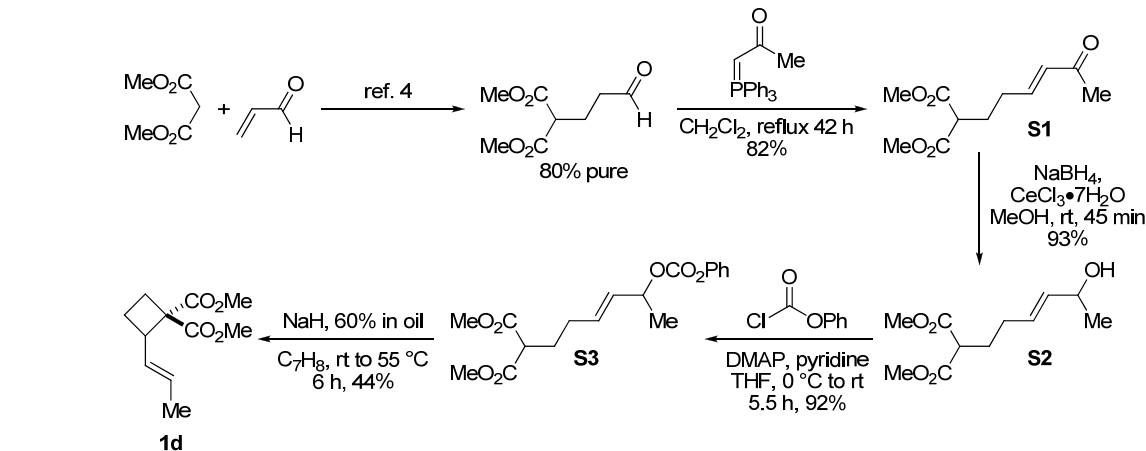
Na₂EDTA (2 x 60 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Flash chromatography (7.5% EtOAc/hexanes) afforded **1b** (0.926 g, 3.33 mmol, 56% yield) as a white solid. Analytical data for **1b**: mp 55-56 °C; IR (thin film, cm⁻¹) 3000, 2952, 2839, 1732, 1612, 1515, 1435, 1275, 1253, 1107, 1037, 835; ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 9.6 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.27 (s, 3H), 2.71 – 2.65 (m, 1H), 2.57 (qn, *J* = 10.0 Hz, 1H), 2.28 – 2.19 (m, 1H), 2.18 – 2.11 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 172.1, 169.8, 158.6, 131.3, 128.7, 113.4, 59.8, 55.2, 52.4, 51.8, 44.7, 25.5, 21.0; TLC (15% EtOAc/hexanes) R_f 0.18; Anal. Calcd. for C₁₅H₁₈O₅: C, 64.74; H, 6.52. Found: C, 64.90; H, 6.58.

Preparation of dimethyl 2-(4-bromophenyl)cyclobutane-1,1-dicarboxylate (**1c**):



Dimethyl 2-(4-bromophenyl)cyclobutane-1,1-dicarboxylate (**1c**) was prepared from 1-bromo-4-(1-bromo-3-chloropropyl)benzene³ (1.13 g, 2.6 mmol, 1.0 equiv), dimethyl malonate (0.530 g, 4.01 mmol, 1.1 equiv), sodium hydride [0.36 g (60% in oil), 9.0 mmol], and 1,4-dioxane (14 mL) in an analogous manner to the synthesis of **1a**. The product was purified by flash chromatography (10% EtOAc/hexanes) to afford **1c** (1.01 g, 3.10 mmol, 86% yield) as a slightly yellow oil. Analytical data for **1c**: IR (thin film, cm⁻¹) 3000, 2952, 1732, 1489, 1435, 1281, 1201, 1107, 1073, 1011, 831; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 4.29 (t, *J* = 9.6 Hz, 1H), 3.77 (s, 3H), 3.29 (s, 3H), 2.75 – 2.62 (m, 1H), 2.62 – 2.48 (m, 1H), 2.28 (dd, *J* = 20.1, 9.1 Hz, 1H), 2.22 – 2.10 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 169.5, 138.2, 131.1, 129.3, 120.9, 59.8, 59.5, 52.5, 52.0, 44.6, 25.7, 20.7; TLC (10% EtOAc/hexanes) R_f 0.18; Anal. Calcd. for C₁₄H₁₅O₄: C, 51.40; H, 4.62. Found: C, 51.58; H, 4.54.

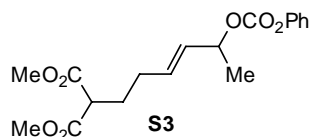
Preparation of (*E*)-dimethyl 2-(prop-1-enyl)cyclobutane-1,1-dicarboxylate (**1d**):



(*E*)-Dimethyl 2-(5-oxohex-3-enyl)malonate (S1**):** A 250-mL round-bottomed flask containing a magnetic stir bar was charged with dimethyl 2-(3-oxopropyl)malonate⁴ (9.9 g, 52.6 mmol, 1.0 equiv, 80% pure), 1-(triphenylphosphoranylidene)-2-propanone, and CH₂Cl₂ (111 mL). The flask was affixed with a reflux condenser and was heated to reflux for 42 h. The reaction was allowed to cool to room temperature and was concentrated *in vacuo*. The resulting residue was suspended in 30% EtOAc/hexanes and stirred for 2 h and was filtered through celite and concentrated. Flash chromatography (40% EtOAc/hexanes) afforded (*E*)-dimethyl 2-(5-oxohex-3-enyl)malonate (**S1**) (7.84 g, 82% yield based on 80% pure starting material) as a clear colorless oil. Analytical data for **S1**: **IR** (thin film, cm⁻¹) 3006, 2956, 1735, 1675, 1437, 1361, 1157, 980; **¹H NMR** (400 MHz, CDCl₃) δ 6.71 (dt, *J* = 16.0, 6.8 Hz, 1H), 6.06 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 6H), 3.36 (t, *J* = 7.6 Hz, 1H), 2.28 – 2.23 (m, 2H), 2.22 (s, 3H), 2.06 (q, *J* = 8.0 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 198.1, 169.3, 145.5, 132.1, 52.5, 50.8, 29.8, 27.0, 26.9; **TLC** (40% EtOAc/hexanes) *R_f* 0.28; **Anal.** Calcd. for C₁₁H₁₆O₅: C, 57.88; H, 7.07. Found: C, 57.73; H, 7.04.

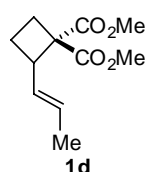
(*E*)-Dimethyl 2-(5-hydroxyhex-3-enyl)malonate (S2**):** A 250-mL round-bottomed flask containing a magnetic stir bar was charged with CeCl₃•7H₂O (1.75 g, 35.19 mmol, 1.75 equiv) and MeOH (50 mL). The suspension was stirred vigorously until homogeneous (approximately 5 min), at which point (*E*)-dimethyl 2-(5-oxohex-3-enyl)malonate (**S1**) (4.59 g, 20.01 mmol, 1.0 equiv) in MeOH (50 mL) was added. The resulting solution was stirred for 5 min and NaBH₄ (0.837 g, 22.12 mmol, 1.1 equiv) was added in 10 portions over 15 min. The reaction mixture was allowed to stir for 1.5 h and was then diluted with CH₂Cl₂ (100 mL) and poured into a 2 M aq. HCl solution (150 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 75 mL). The combined CH₂Cl₂ extracts were washed with 2 M aq. HCl (75 mL), brine (75 mL), dried over Na₂SO₄ and concentrated. The product was purified by flash chromatography (20% EtOAc/hexanes) to afford (*E*)-dimethyl 2-(5-hydroxyhex-3-enyl)malonate (**S2**) (4.28 g, 18.59 mmol, 93%) as a clear colorless oil. Analytical data for **S2**: **IR** (thin film, cm⁻¹) 3421, 2957, 1734, 1438, 1287, 1245, 1158, 1062, 971; **¹H NMR** (400 MHz, CDCl₃) δ 5.62 – 5.41 (m, 2H), 4.29 – 4.13 (m, 1H), 3.70 (s, 6H), 3.34 (t, *J* = 7.2 Hz, 1H), 2.03 (dt, *J* = 9.9, 3.8 Hz,

2H), 1.99 – 1.91 (m, 2H), 1.88 (s, 1H), 1.20 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 135.9, 128.3, 68.4, 52.3, 50.9, 29.6, 28.1, 23.3; TLC (40% EtOAc/hexanes) R_f 0.19; **Anal.** Calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_5$: C, 57.38; H, 7.88. Found: C, 57.35; H, 7.85.



(E)-Dimethyl 2-(5-(phenoxycarbonyloxy)hex-3-enyl)malonate (S3):

A flame-dried 250-mL round-bottomed flask was charged with a solution of (*E*)-dimethyl 2-(5-hydroxyhex-3-enyl)malonate (**S2**) (4.18 g, 18.15 mmol, 1.0 equiv) in tetrahydrofuran (74 mL). The flask was purged with N_2 and cooled to 0 °C in an ice-water bath. 4-Dimethylaminopyridine (0.22 g, 1.82 mmol, 0.10 equiv) was added in one portion followed by dropwise addition of pyridine (3.59 g, 3.66 mL, 45.38 mmol, 2.5 equiv) via syringe over 10 min. Phenyl chloroformate (5.68 g, 4.55 mL, 36.31 mmol, 2.0 equiv) was added via syringe over 10 min. The reaction was allowed to stir for 30 min at 0 °C and was then warmed to room temperature and was stirred for an additional 4.5 h. The reaction was cooled to 0 °C and quenched with 2 M aq. HCl (75 mL). The organic layer was separated and the aqueous layer extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with 2 M aq. HCl (2 x 75 mL), 2 M aq. NaOH (2 x 75 mL), dried over MgSO_4 , and concentrated *in vacuo* to afford pure (*E*)-dimethyl 2-(5-(phenoxycarbonyloxy)hex-3-enyl)malonate (**S3**) (5.88 g, 16.79 mmol, 92%) as a clear colorless oil. Analytical data for **S3**: IR (thin film, cm^{-1}) 2954, 1756, 1496, 1437, 1250, 1210, 1154, 1044, 970, 780, 688; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (td, $J = 7.7, 1.8$ Hz, 2H), 7.25 – 7.19 (m, 1H), 7.17 (dd, $J = 8.6, 1.0$ Hz, 2H), 5.76 (dt, $J = 13.6, 6.6$ Hz, 1H), 5.56 (dd, $J = 15.5, 7.1$ Hz, 1H), 5.23 (qn, $J = 6.5$ Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.38 (t, $J = 7.3$ Hz, 1H), 2.10 (dd, $J = 14.5, 6.7$ Hz, 2H), 2.00 (dt, $J = 7.4, 4.4$ Hz, 2H), 1.42 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 152.9, 151.2, 132.4, 130.1, 129.3, 125.8, 121.0, 75.9, 52.3, 50.8, 29.6, 27.8, 29.6, 27.8, 20.2; TLC (20% EtOAc/hexanes) R_f 0.21; **Anal.** Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_7$: C, 61.71; H, 6.33. Found: C, 61.79; H, 6.45.

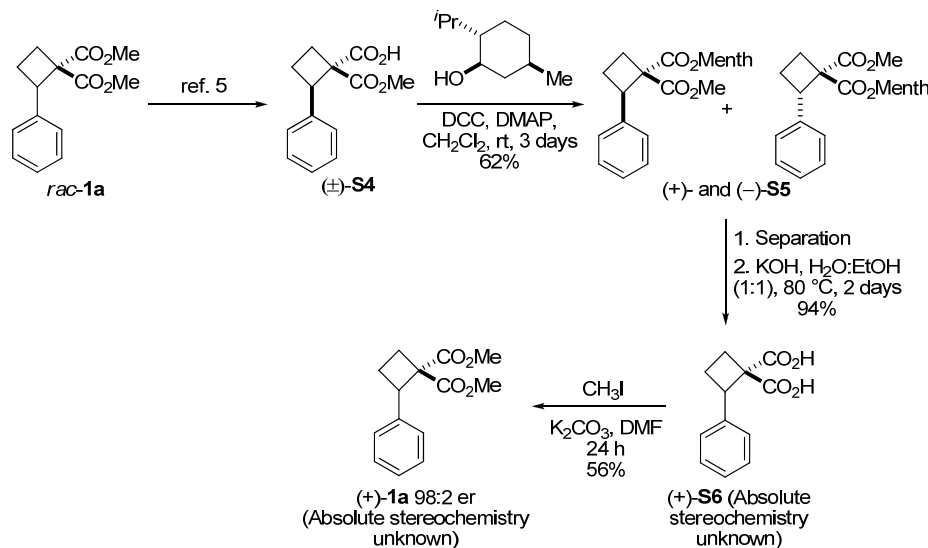


(E)-Dimethyl 2-(prop-1-enyl)cyclobutane-1,1-dicarboxylate (1d):

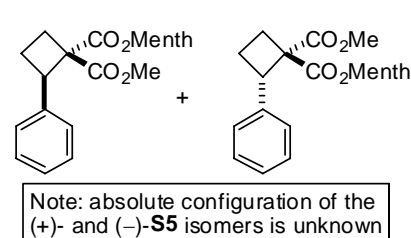
A flame-dried 100 mL round-bottomed flask containing a magnetic stir bar was charged with sodium hydride (0.285 g (60% in oil), 7.13 mmol, 2.0 equiv) under N_2 . The sodium hydride was washed with hexanes to remove the oil and was suspended in C_7H_8 (7.0 mL). To this suspension was added a solution of (*E*)-dimethyl 2-(5-(phenoxycarbonyloxy)hex-3-enyl)malonate (**S3**) (1.25 g, 3.57 mmol, 1.0 equiv) in C_7H_8 (10 mL) via canula over 20 min followed by a C_7H_8 wash (4 mL). The reaction was stirred at room temperature for 30 min and then warmed to 55 °C for an additional 5 h. The reaction was then cooled to room temperature and poured into 50 mL H_2O . The organic layer was separated and the aqueous layer extracted with Et_2O (3 x 25 mL). The combined organic layers were washed with 2 M aq. NaOH (2 x 25 mL), dried over MgSO_4 , and concentrated *in vacuo*. Purification by flash chromatography (7.5% EtOAc/hexanes) afforded **1d** (0.33 g, 1.55 mmol, 44% yield) as a volatile clear colorless oil. (Note: While analyzing the flash column fractions using thin layer chromatography, it is necessary to elute the TLC plate twice in 7.5% EtOAc/hexanes to visualize an undesired impurity). Analytical data for **S3**: IR (thin film, cm^{-1}) 2998, 2953, 1733, 1436, 1275, 1256, 1201, 1115, 970; ^1H NMR (400 MHz, CDCl_3) δ 5.60 – 5.49 (m, 1H), 5.44 (dd, $J = 15.8, 6.6$ Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.60 (dd, $J = 16.0, 8.1$ Hz, 1H), 2.61 – 2.55 (m, 1H), 2.21 – 2.10 (m, 1H), 2.10 – 1.95 (m, 2H), 1.65 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.0, 170.2, 129.5, 127.6, 58.2, 52.3, 52.0, 43.2, 25.7, 22.1,

17.8; **TLC** (7.5% EtOAc/hexanes) R_f 0.16; **LRMS** (ESI) Calcd. for $C_{11}H_{16}O_4+Na$: 235.1, Found: 235.1.

Preparation of (+)-dimethyl 2-phenylcyclobutane-1,1-dicarboxylate ((+)-1a):



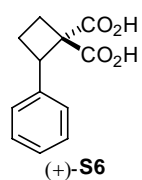
(±)-1-(Methoxycarbonyl)-2-phenylcyclobutanecarboxylic acid (S4): This compound was prepared from *rac-1a* according to the protocol reported by Burger and Coyne⁵ and was of sufficient purity for subsequent transformations. Analytical data for **S4**: **mp** 139-141 °C; **IR** (thin film, cm^{-1}) 3005, 2952, 1743, 1706, 1496, 1419, 1287, 1204, 1122, 943, 792, 700; **^1H NMR** (500 MHz, CDCl_3) δ 7.32 – 7.30 (m, 4H), 7.25 – 7.22 (m, 1H), 4.37 (t, J = 9.5 Hz, 1H), 3.32 (s, 3H), 2.76 – 2.64 (m, 2H), 2.48 – 2.42 (m, 1H), 2.24 – 2.19 (m, 1H); **^{13}C NMR** (125 MHz, CDCl_3) δ 177.2, 169.8, 138.6, 128.1, 127.4, 127.1, 59.5, 52.1, 45.6, 25.5, 20.6; **LRMS** (ESI) Calcd. for $C_{13}H_{14}O_4+Na$: 257.1, Found: 257.1.



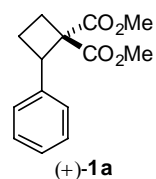
(+)- and (-)-1-Methyl 2-phenylcyclobutane-1,1-dicarboxylate (S5): A 100-mL round-bottomed flask was charged with (±)-(methoxycarbonyl)-2-phenylcyclobutanecarboxylic acid (**S4**) (0.900 g, 3.84 mmol, 1.0 equiv), dicyclohexylcarbodiimide (1.02 g, 4.95 mmol, 1.3 equiv), 4-dimethylaminopyridine (0.469 g, 3.84 mmol, 1.0 equiv), and CH_2Cl_2 (20 mL). The resulting solution was

allowed to stir for 30 min, at which time finely ground (–)-menthol (0.650 g, 4.27 mmol, 1.10 equiv) was added in one portion. The flask was sealed with a polypropylene stopper and was allowed to stir for 3 days. The reaction was filtered through celite and the filtrate was washed with saturated aq. NH_4Cl (2 x 20 mL), H_2O (2 x 20 mL), and brine (1 x 20 mL), dried over Na_2SO_4 , and concentrated *in vacuo*. Partial separation of the isomers was achieved by flash chromatography (30-60% CH_2Cl_2 /hexanes) to afford (–)-1-methyl 2-phenylcyclobutane-1,1-dicarboxylate (0.200 g, 0.537 mmol), (+)-1-methyl 2-phenylcyclobutane-1,1-dicarboxylate (0.174 g, 0.467 mmol), and a mixture of the two isomers (0.560 g, 1.503 mmol), all present as clear slightly yellow oils (total combined yield: 0.934 g, 2.504 mmol, 65%). Analytical data for

(-)-**S5**: $[\alpha]_{\text{D}}^{29} = -115.2$ ($c = 0.440$, CHCl_3); **IR** (thin film, cm^{-1}) 2953, 2871, 1726, 1435, 1198, 1182, 1109, 1037, 956, 757, 698; **^1H NMR** (400 MHz, CDCl_3) δ 7.29 – 7.26 (m, 4H), 7.24 – 7.16 (m, 1H), 4.70 (td, $J = 10.9, 4.3$ Hz, 1H), 4.36 (t, $J = 8.7$ Hz, 1H), 3.20 (s, 3H), 2.72 (t, $J = 8.8$ Hz, 1H), 2.58 (dd, $J = 17.6, 10.5$ Hz, 1H), 2.27 – 2.12 (m, 2H), 2.07 (d, $J = 11.5$ Hz, 1H), 1.86 – 1.74 (m, 1H), 1.74 – 1.62 (m, 2H), 1.57 – 1.45 (m, 1H), 1.43 – 1.32 (m, 1H), 1.13 – 0.79 (m, 3H), 0.93 (d, $J = 6.5$ Hz, 3H), 0.84 (d, $J = 7.1$ Hz, 3H), 0.72 (d, $J = 6.9$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 171.1, 169.9, 139.3, 128.0, 127.7, 126.8, 75.4, 59.9, 51.4, 47.0, 45.0, 40.5, 34.3, 31.4, 25.9, 25.7, 23.3, 22.0, 20.7, 20.7, 16.0; **TLC** (60% CH_2Cl_2 /hexanes) R_f 0.39; **LRMS** (ESI) Calcd. for $\text{C}_{23}\text{H}_{32}\text{O}_4 + \text{Na}$: 395.2, Found: 395.2. Analytical data for (+)-**S5**: $[\alpha]_{\text{D}}^{29} = +24.9$ ($c = 0.400$, CHCl_3); **IR** (thin film, cm^{-1}) 2953, 2871, 1726, 1456, 1435, 1271, 1199, 1109, 1037, 957, 757; **^1H NMR** (400 MHz, CDCl_3) δ 7.34 – 7.22 (m, 4H), 7.20 (t, $J = 6.5$ Hz, 1H), 4.75 (td, $J = 10.9, 4.3$ Hz, 1H), 4.35 (t, $J = 9.4$ Hz, 1H), 3.23 (s, 3H), 2.75 – 2.55 (m, 2H), 2.31 – 2.11 (m, 2H), 2.02 (d, $J = 11.9$ Hz, 1H), 1.91 (dq, $J = 6.6, 4.3$ Hz, 1H), 1.69 (d, $J = 11.4$ Hz, 2H), 1.58 – 1.47 (m, 1H), 1.40 (dd, $J = 23.8, 12.4$ Hz, 1H), 1.08 (dd, $J = 23.0, 12.7$ Hz, 1H), 1.00 – 0.83 (m, 9H), 0.79 (d, $J = 6.9$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 171.2, 170.0, 139.2, 127.9, 127.6, 126.8, 75.2, 60.1, 51.6, 47.0, 45.1, 40.3, 34.2, 31.4, 26.1, 25.6, 23.4, 22.0, 20.7, 20.6, 16.1; **TLC** (60% CH_2Cl_2 /hexanes) R_f 0.35; **LRMS** (ESI) Calcd. for $\text{C}_{23}\text{H}_{32}\text{O}_4 + \text{Na}$: 395.2, Found: 395.2.



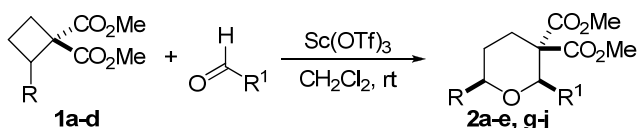
(+)-2-Phenylcyclobutane-1,1-dicarboxylic acid (S6): Potassium hydroxide pellets (0.203 g, 3.62 mmol, 9.0 equiv) were dissolved in H_2O (3.25 mL) and diluted with EtOH (3.25 mL). This KOH solution was added to a 25-mL round-bottomed flask containing a magnetic stir bar and (+)-methyl 2-phenylcyclobutane-1,1-dicarboxylate (**S5**) (0.150 g, 0.403 mmol, 1.0 equiv). The flask was affixed with a reflux condenser and the reaction was heated at reflux for 2 d at which point the reaction was cooled to room temperature and the majority of the ethanol was removed by rotary evaporation. The resulting solution was diluted with H_2O (20 mL) and washed with Et₂O (4 x 20 mL). The aqueous solution was brought to pH = 1 by addition of concentrated HCl. The acidic solution was extracted with Et₂O (4 x 15 mL) and the combined organic extracts were dried over MgSO_4 and concentrated to afford pure (+)-2-phenylcyclobutane-1,1-dicarboxylic acid (**S6**) (0.083 g, 0.381 mmol, 94%) as a white powder. Analytical data for (+)-**S6**: $[\alpha]_{\text{D}}^{27} = +65.5$ ($c = 0.300$, CHCl_3); **mp** 125–128 °C (dec.); **IR** (thin film, cm^{-1}) 2953, 2688, 2573, 1699, 1419, 1290, 1222, 1116, 928, 785, 697; **^1H NMR** (400 MHz, DMSO) δ 12.56 (bs, 2H), 7.31 – 7.28 (m, 4H), 7.22 – 7.17 (m, 1H), 4.18 (t, $J = 9.6$ Hz, 1H), 2.50 – 2.40 (m, 2H), 2.25 – 2.19 (m, 1H), 2.12 – 2.06 (m, 1H); **^{13}C NMR** (100 MHz, DMSO) δ 174.0, 171.7, 140.9, 128.7, 128.4, 127.3, 60.0, 45.1, 26.4, 21.4; **LRMS** (ESI) Calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_4 + \text{Na}$: 243.1, Found: 243.1.



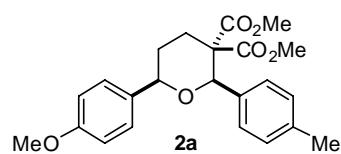
(+)-Dimethyl 2-phenylcyclobutane-1,1-dicarboxylate (1a): A flame-dried 1-dram vial containing a magnetic stir bar was charged with (+)-2-phenylcyclobutane-1,1-dicarboxylic acid (**S6**) (0.083 g, 0.381 mmol, 1.0 equiv), potassium carbonate (0.208 g, 0.151 mmol, 4.0 equiv), and *N,N*-dimethylformamide (1.75 mL). The resulting suspension was stirred for 30 min and then iodomethane (0.321 g, 0.141 mL, 2.26 mmol, 6.0 equiv) was added in one portion. The reaction was allowed to stir for 24 h and was then poured into a separatory funnel containing H_2O (10 mL). The resulting solution was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were washed with H_2O (3 x 15 mL) and 50% saturated aq. NaCl solution (15 mL), dried over Na_2SO_4 , and concentrated *in vacuo*. The product was purified by flash

chromatography (10% EtOAc/hexanes) to afford (+)-**1a** (0.052 g, 0.209 mmol, 56%) as a slightly yellow clear oil in 98:2 er as determined by GC analysis (Chiradex B-DM column, 30 m x 0.250 mm, pressure = 80 kPa, flow = 0.6 mL/min, detector = FID, 250 °C). $[\alpha]_D^{27} = +93.9$ ($c = 0.360$, CHCl_3).

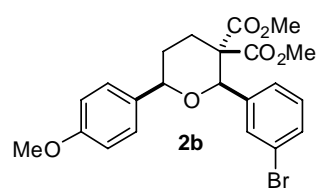
General Procedure A for the $\text{Sc}(\text{OTf})_3$ -catalyzed [4 + 2] cycloaddition of cyclobutanes **1a-d with aryl aldehydes to afford tetrahydropyrans **2a-e, g-j**:**



In an inert atmosphere glove box, a 1-dram vial containing a magnetic stir bar was charged with $\text{Sc}(\text{OTf})_3$ (0.02 equiv). To this vial was added a solution of the cyclobutane (1.0 equiv) and aldehyde (3.0 equiv) in CH_2Cl_2 ($[\mathbf{1}]_0 = 0.25 \text{ M}$). The vial was sealed with a PTFE-lined screw cap, removed from the glove box, and allowed to stir. Upon disappearance of the cyclobutane as indicated by TLC analysis (with 25% EtOAc/hexanes or CH_2Cl_2 as the mobile phase), the reaction was filtered through a 1-inch Monstr-Pette plug of silica with CH_2Cl_2 (12 mL) and concentrated. The resulting tetrahydropyrans **2a-e, g-j** were purified by flash chromatography using the indicated solvent system.

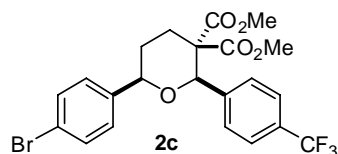


Dimethyl 6-(4-methoxyphenyl)-2-p-tolyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2a**):** The title compound was prepared according to General Procedure A using **1b** (0.090 g, 0.322 mmol, 1.0 equiv), 4-methylbenzaldehyde (0.116 g, 0.967 mmol, 3.0 equiv), $\text{Sc}(\text{OTf})_3$ (0.0032 g, 0.0064 mmol, 0.02 equiv) and CH_2Cl_2 (1.28 mL). After stirring for 15 min, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2a** (0.120 g, 0.301 mmol, 93% yield) as colorless crystals in 96:4 dr. Analytical data for **2a**: mp 126-127 °C; IR (thin film, cm^{-1}) 3003, 2952, 2839, 1728, 1515, 1435, 1250, 1083, 1035, 826; ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 8.0 \text{ Hz}$, 4H), 7.10 (d, $J = 7.7 \text{ Hz}$, 2H), 6.88 (d, $J = 8.4 \text{ Hz}$, 2H), 5.11 (s, 1H), 4.62 (d, $J = 10.0 \text{ Hz}$, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 3.58 (s, 3H), 2.68 (d, $J = 13.3 \text{ Hz}$, 1H), 2.36 – 2.28 (m, 1H), 2.32 (s, 3H), 2.09 (dq, $J = 13.6, 3.8 \text{ Hz}$, 1H), 1.91 (d, $J = 12.0 \text{ Hz}$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 169.2, 159.0, 137.0, 136.5, 134.7, 127.9, 127.3, 127.1, 113.7, 82.4, 80.3, 58.6, 55.2, 52.3, 51.5, 32.8, 29.9, 21.1; TLC (15% EtOAc/hexanes) R_f 0.16; Anal. Calcd. for $\text{C}_{23}\text{H}_{26}\text{O}_6$: C, 69.33; H, 6.58. Found: C, 69.10; H, 6.61.

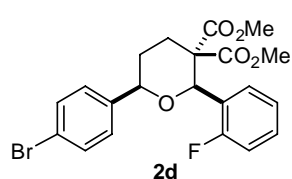


Dimethyl 6-(4-methoxyphenyl)-2-(3-bromophenyl)dihydro-2H-pyran-3,3(4H)-dicarboxylate (2b**):** The title compound was prepared according to General Procedure A using **1b** (0.090 g, 0.322 mmol, 1.0 equiv), 3-bromobenzaldehyde (0.179 g, 0.967 mmol, 3.0 equiv), $\text{Sc}(\text{OTf})_3$ (0.0032 g, 0.0064 mmol, 0.02 equiv) and CH_2Cl_2 (1.28 mL). After stirring for 15 min, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2b** (0.118 g, 0.255 mmol, 79% yield) as a clear colorless oil in 97:3 dr.

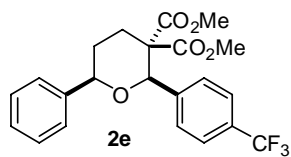
Analytical data for **2b**: **IR** (thin film, cm^{-1}) 3002, 2952, 2838, 1730, 1614, 1515, 1434, 1250, 1082, 1035, 829, 776; **^1H NMR** (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.43 – 7.29 (m, 4H), 7.15 (t, J = 7.9 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 5.11 (s, 1H), 4.61 (dd, J = 11.5, 2.2 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.58 (s, 3H), 2.69 (dt, J = 13.2, 3.1 Hz, 1H), 2.30 (td, J = 13.3, 4.2 Hz, 1H), 2.20 – 2.04 (m, 1H), 1.96 – 1.85 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 171.1, 168.8, 159.2, 141.8, 134.2, 130.6, 130.5, 128.7, 127.1, 126.2, 121.3, 113.8, 81.6, 80.5, 58.5, 55.2, 52.4, 51.6, 32.7, 29.7; **TLC** (15% EtOAc/hexanes) R_f 0.13; **LRMS** (ESI) Calcd. for $\text{C}_{22}\text{H}_{23}\text{BrO}_6 + \text{Na}$: 485.1, Found: 485.1.



Dimethyl 6-(4-bromophenyl)-2-(4-(trifluoromethyl)phenyl) dihydro-2H-pyran-3,3(4H)-dicarboxylate (2c): The title compound was prepared according to General Procedure A using **1c** (0.105 g, 0.322 mmol, 1.0 equiv), 4-trifluoromethylbenzaldehyde (0.168 g, 0.967 mmol, 3.0 equiv), $\text{Sc}(\text{OTf})_3$ (0.0032 g, 0.0064 mmol, 0.02 equiv) and CH_2Cl_2 (1.28 mL). After stirring for 15 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2c** (0.146 g, 0.291 mmol, 90% yield) as a yellow powder in 98:2 dr. Analytical data for **2c**: **mp** 107–109 $^\circ\text{C}$; **IR** (thin film, cm^{-1}) 3003 2954, 2858, 1731, 1436, 1327, 1166, 1122, 1068, 1011, 856, 815; **^1H NMR** (400 MHz, CDCl_3) δ 7.57 (q, J = 8.5 Hz, 4H), 7.48 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.20 (s, 1H), 4.64 (dd, J = 11.4, 2.3 Hz, 1H), 3.70 (s, 3H), 3.54 (s, 3H), 2.71 (dt, J = 13.3, 3.1 Hz, 1H), 2.31 (td, J = 13.3, 4.4 Hz, 1H), 2.08 (ddd, J = 16.8, 13.4, 4.0 Hz, 1H), 2.00 – 1.88 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 171.0, 168.6, 143.3, 140.8, 131.5, 129.7 (q, J = 32.0 Hz), 127.8, 127.5, 124.2 (d, J = 270.0 Hz), 125.6 – 122.7 (m), 121.5, 81.7, 80.0, 58.3, 52.6, 51.7, 32.5, 29.7; **TLC** (15% EtOAc/hexanes) R_f 0.23; **Anal.** Calcd. for $\text{C}_{22}\text{H}_{20}\text{BrF}_3\text{O}_5$: C, 52.71; H, 4.02. Found: C, 52.78; H, 4.05.

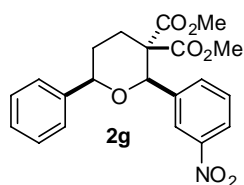


Dimethyl 6-(4-bromophenyl)-2-(2-fluorophenyl) dihydro-2H-pyran-3,3(4H)-dicarboxylate (2d): The title compound was prepared according to General Procedure A using **1c** (0.105 g, 0.322 mmol, 1.0 equiv), 2-fluorobenzaldehyde (0.120 g, 0.967 mmol, 3.0 equiv), $\text{Sc}(\text{OTf})_3$ (0.0032 g, 0.0064 mmol, 0.02 equiv) and CH_2Cl_2 (1.28 mL). After stirring for 16.5 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **2d** (0.136 g, 0.301 mmol, 94% yield) as a clear colorless oil in 99:1 dr. Analytical data for **2d**: **IR** (thin film, cm^{-1}) 2953, 2857, 1735, 1490, 1274, 1255, 1086, 1011, 764; **^1H NMR** (400 MHz, CDCl_3) δ 7.88 (t, J = 7.0 Hz, 1H), 7.47 (d, J = 8.3 Hz, 2H), 7.38 – 7.21 (m, 3H), 7.17 (t, J = 7.4 Hz, 1H), 7.02 – 6.88 (m, 1H), 5.17 (s, 1H), 4.62 (dd, J = 11.2, 2.0 Hz, 1H), 3.66 (s, 6H), 2.65 (dd, J = 10.6, 3.1 Hz, 1H), 2.52 (td, J = 13.7, 4.0 Hz, 1H), 1.95 (dd, J = 13.6, 2.9 Hz, 1H), 1.82 (ddd, J = 25.6, 13.8, 3.9 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.6, 168.7, 161.0, 158.6, 141.1, 131.4, 131.1 (d, J = 3.7 Hz), 129.3 (d, J = 8.7 Hz), 127.5, 125.8 (d, J = 12.6 Hz), 123.3 (d, J = 3.1 Hz), 121.4, 114.2, 113.9, 80.2, 76.8, 57.7, 52.5, 51.8, 32.1, 30.3; **TLC** (20% EtOAc/hexanes) R_f 0.24; **LRMS** (ESI) Calcd. for $\text{C}_{21}\text{H}_{20}\text{BrFO}_5 + \text{Na}$: 473.1, Found: 473.0.



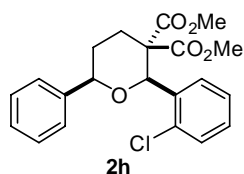
Dimethyl 6-phenyl-2-(4-(trifluoromethyl)phenyl)dihydro-2H-pyran-3,3(4H)-dicarboxylate (2e): The title compound was prepared according to General Procedure A using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), 4-trifluoromethylbenzaldehyde (0.168 g, 0.967 mmol, 3.0 equiv), Sc(OTf)₃ (0.0032 g, 0.0064 mmol, 0.02 equiv) and CH₂Cl₂ (1.28 mL).

After stirring for 4.5 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2e** (0.126 g, 0.298 mmol, 92% yield) as a clear colorless oil in 99:1 dr. Analytical data for **2e**: **IR** (thin film, cm⁻¹) 2954, 2858, 1731, 1436, 1327, 1166, 1121, 1068, 1019, 856; **¹H NMR** (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 5.22 (s, 1H), 4.70 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.71 (s, 3H), 3.56 (s, 3H), 2.73 (dt, *J* = 13.4, 3.2 Hz, 1H), 2.35 (td, *J* = 13.4, 4.4 Hz, 1H), 2.21 – 2.06 (m, 1H), 2.03 – 1.93 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.1, 168.7, 143.6, 141.9, 129.7 (q, *J* = 32.3 Hz), 128.4, 127.9, 127.7, 125.8, 124.3 (q, *J* = 271.5 Hz), 124.15 (q, *J* = 4.0 Hz), 81.7, 80.8, 58.6, 52.5, 51.6, 32.7, 29.8; **TLC** (15% EtOAc/hexanes) *R_f* 0.15; **Anal.** Calcd. for C₂₂H₂₁F₃O₅: C, 62.56; H, 5.01. Found: C, 62.81; H, 5.12.



Dimethyl 2-(3-nitrophenyl)-6-phenyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2g): The title compound was prepared according to General Procedure A using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), 3-nitrobenzaldehyde (0.146 g, 0.967 mmol, 3.0 equiv), Sc(OTf)₃ (0.0032 g, 0.0064 mmol, 0.02 equiv) and CH₂Cl₂ (1.28 mL). After stirring for 6.0 h, the reaction was complete as determined by TLC analysis. The reaction was

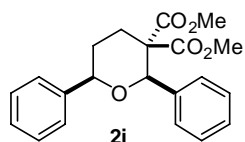
worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **2g** (0.116 g, 0.290 mmol, 90% yield) as yellow crystals in 98:2 dr. Analytical data for **2g**: **mp** 122–123 °C; **IR** (thin film, cm⁻¹) 3032, 2953, 2860, 1731, 1530, 1349, 1275, 1256, 1092, 1069, 806, 699; **¹H NMR** (400 MHz, CDCl₃) δ 8.30 (s, 1H), 8.17 – 8.08 (m, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.44 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 5.24 (s, 1H), 4.71 (dd, *J* = 11.5, 2.7 Hz, 1H), 3.73 (s, 3H), 3.58 (s, 3H), 2.78 – 2.70 (m, 1H), 2.36 (td, *J* = 13.4, 4.5 Hz, 1H), 2.17 – 2.05 (m, 1H), 1.99 (ddt, *J* = 13.9, 4.5, 2.8 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.0, 168.6, 147.7, 141.6 (two overlapping resonances), 133.8, 128.5, 128.1, 127.8, 125.8, 122.6, 122.5, 81.4, 81.1, 58.6, 52.7, 51.9, 32.6, 29.9; **TLC** (20% EtOAc/hexanes) *R_f* 0.19; **Anal.** Calcd. for C₂₁H₂₁NO₇: C, 63.15; H, 5.30; N, 3.51. Found: C, 63.08; H, 5.30; N, 3.51.



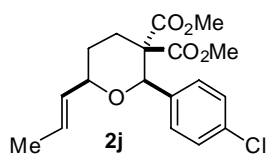
Dimethyl 2-(4-chlorophenyl)-6-phenyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2h): The title compound was prepared according to General Procedure A using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), 2-chlorobenzaldehyde (0.136 g, 0.967 mmol, 3.0 equiv), Sc(OTf)₃ (0.0032 g, 0.0064 mmol, 0.02 equiv) and CH₂Cl₂ (1.28 mL). After stirring for 7.0 h, the reaction was complete as determined by TLC analysis. The reaction was

worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2h** (0.122 g, 0.314 mmol, 97% yield) as a white solid in 92:8 dr. Analytical data for **2h**: **mp** 90–92 °C; **IR** (thin film, cm⁻¹) 3031, 2952, 2856, 1735, 1437, 1276, 1254, 1166, 1092, 1032, 759, 701; **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.24 (m, 5H), 7.23 – 7.17 (m, 1H), 5.31 (s, 1H), 4.69 (dd, *J* = 11.4, 2.7 Hz, 1H), 3.68 (s, 3H), 3.63 (s, 3H), 2.65 – 2.55 (m, 2H), 1.99 (ddd, *J* = 13.9, 6.6, 3.5 Hz, 1H), 1.82 (dtd, *J* = 14.0, 11.5, 6.1 Hz,

1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.5, 168.8, 142.2, 136.4, 133.2, 131.8, 128.9, 128.3, 128.2, 127.6, 126.1, 125.8, 81.0, 78.9, 57.5, 52.7, 51.9, 32.4, 30.6; **TLC** (15% EtOAc/hexanes) R_f 0.21; **Anal.** Calcd. for C₂₁H₂₁ClO₅: C, 64.87; H, 5.44. Found: C, 65.15; H, 5.49.

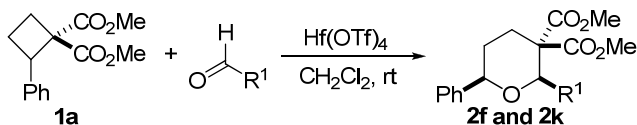


Dimethyl 2,6-diphenyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2i): The title compound was prepared according to General Procedure A using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), benzaldehyde (0.103 g, 0.967 mmol, 3.0 equiv), Sc(OTf)₃ (0.0032 g, 0.0064 mmol, 0.02 equiv) and CH₂Cl₂ (1.28 mL). After stirring for 6.5 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2i** (0.111 g, 0.313 mmol, 97% yield) as a white waxy solid in 96:4 dr. Analytical data for **2i**: **IR** (thin film, cm⁻¹) 3032, 2952, 2857, 1729, 1452, 1435, 1257, 1091, 1068, 700; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.20 (m, 4H), 5.17 (s, 1H), 4.69 (dd, *J* = 11.4, 2.2 Hz, 1H), 3.69 (s, 3H), 3.56 (s, 3H), 2.77 – 2.62 (m, 1H), 2.34 (td, *J* = 13.3, 4.3 Hz, 1H), 2.12 (ddd, *J* = 17.0, 13.5, 4.0 Hz, 1H), 2.01 – 1.89 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 142.3, 139.5, 128.3, 127.5, 127.4, 127.2, 125.8, 82.3, 80.7, 58.6, 52.4, 51.5, 32.8, 30.0; **TLC** (15% EtOAc/hexanes) R_f 0.18; **Anal.** Calcd. for C₂₁H₂₂O₅: C, 71.17; H, 6.26. Found: C, 71.16; H, 6.32.



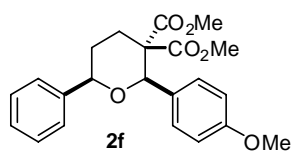
Dimethyl 2-(4-chlorophenyl)-6-((E)-prop-1-enyl)dihydro-2H-pyran-3,3(4H)-dicarboxylate (2j): The title compound was prepared according to General Procedure A using **1d** (0.040 g, 0.188 mmol, 1.0 equiv), 4-chlorobenzaldehyde (0.079 g, 0.564 mmol, 3.0 equiv), Sc(OTf)₃ (0.0018 g, 0.0037 mmol, 0.02 equiv) and CH₂Cl₂ (0.75 mL). After stirring for 6.5 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (60% CH₂Cl₂/hexanes) to afford **2j** (0.047 g, 0.133 mmol, 70% yield) as a clear colorless oil in 94:6 dr. Analytical data for **2j**: **IR** (thin film, cm⁻¹) 2953, 2360, 2342, 1731, 1492, 1436, 1090, 1014, 846, 808; ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.74 (dq, *J* = 12.9, 6.3 Hz, 1H), 5.55 (dd, *J* = 15.4, 6.1 Hz, 1H), 4.96 (s, 1H), 4.16 – 3.97 (m, 1H), 3.65 (s, 3H), 3.53 (s, 3H), 2.68 – 2.50 (m, 1H), 2.14 (td, *J* = 13.4, 4.4 Hz, 1H), 1.95 – 1.79 (m, 1H), 1.70 – 1.65 (m, 1H), 1.69 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 168.9, 138.2, 133.2, 131.3, 128.9, 127.4, 127.3, 81.4, 79.4, 58.5, 52.4, 51.6, 32.3, 28.0, 17.7; **TLC** (60% CH₂Cl₂/hexanes) R_f 0.28; **Anal.** Calcd. for C₁₈H₂₁ClO₅: C, 61.28; H, 6.00. Found: C, 61.51; H, 6.04.

General Procedure B for the Hf(OTf)₄-catalyzed [4 + 2] cycloaddition of cyclobutane **1a with 4-methoxybenzaldehyde and cinnamaldehyde to afford tetrahydropyrans **2f** and **2k**:**



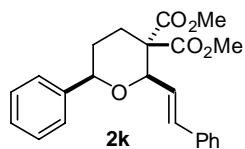
In an inert atmosphere glove box, a 1-dram vial containing a magnetic stir bar was charged with Hf(OTf)₄ (0.0050 g, 0.0064 mmol, 0.02 equiv). To this vial was added a solution of cyclobutane **1a** (0.080 g, 0.322 mmol, 1.0 equiv) and the aldehyde (0.967 mmol, 3.0 equiv) in CH₂Cl₂ (1.28 mL). The vial was sealed with a PTFE-lined screw cap, removed from the glove box, and

allowed to stir. After disappearance of the cyclobutane was confirmed by TLC analysis, the reaction was filtered through a 1-inch Monstr-Pette plug of silica with CH₂Cl₂ (12 mL) and concentrated. The resulting tetrahydropyran products were purified by flash chromatography using the indicated solvent system.



Dimethyl 2-(4-methoxyphenyl)-6-phenyltetrahydropyran-3,3-dicarboxylate (2f): The title compound was prepared according to General Procedure B using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), 4-methoxybenzaldehyde (0.132 g, 0.967 mmol, 3.0 equiv), Hf(OTf)₄ (0.0050 g, 0.0064 mmol, 0.02 equiv) and CH₂Cl₂ (1.28 mL). After

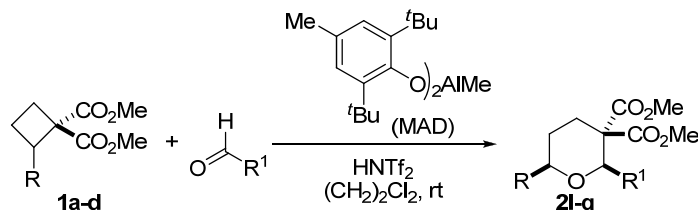
stirring for 11 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (80 – 90 – 100% CH₂Cl₂/hexanes gradient) to afford **2f** (0.084 g, 0.219 mmol, 68% yield) as a clear colorless oil in 96:4 dr. Analytical data for **2f**: **IR** (thin film, cm⁻¹) 2952, 2930, 1851, 1729, 1613, 1514, 1453, 1435, 1250, 1177, 1069, 1033, 700; **¹H NMR** (400 MHz, CDCl₃) δ 7.41 (dd, *J* = 7.6, 6.1 Hz, 4H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.23 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.11 (s, 1H), 4.67 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.59 (s, 3H), 2.76 – 2.58 (m, 1H), 2.32 (td, *J* = 13.3, 4.3 Hz, 1H), 2.19 – 2.02 (m, 1H), 2.02 – 1.88 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.3, 169.2, 159.0, 142.4, 131.7, 128.6, 128.2, 127.5, 125.8, 112.7, 82.1, 80.7, 58.6, 55.1, 52.3, 51.6, 32.7, 30.0; **TLC** (80% CH₂Cl₂/hexanes) *R_f* 0.18; **Anal.** Calcd. for C₂₂H₂₄O₆: C, 68.74; H, 6.29. Found: C, 69.00; H, 6.28.



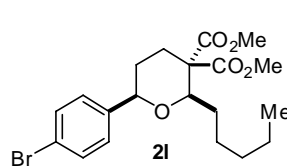
Dimethyl 6-phenyl-2-styryldihydro-2H-pyran-3,3(4H)-dicarboxylate (2k): The title compound was prepared according to General Procedure B using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), *trans*-cinnamaldehyde (0.128 g, 0.967 mmol, 3.0 equiv), Hf(OTf)₄ (0.0050 g, 0.0064 mmol, 0.02 equiv) and CH₂Cl₂ (1.28 mL). After stirring for 22 h, the reaction was complete as

determined by TLC analysis. The reaction was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2k** (0.095 g, 0.264 mmol, 82% yield) as a clear colorless oil in 79:21 dr. Analytical data for **2k**: **IR** (thin film, cm⁻¹) 3030, 2953, 1732, 1451, 1435, 1236, 1171, 1066, 1026, 696; **¹H NMR** (400 MHz, C₆D₆) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.12 – 6.97 (m, 5H), 6.86 (d, *J* = 16.1 Hz, 1H), 4.73 (d, *J* = 5.7 Hz, 1H), 4.32 (dd, *J* = 11.6, 2.2 Hz, 1H), 3.36 (s, 3H), 3.25 (s, 3H), 2.71 – 2.58 (m, 1H), 2.15 (ddd, *J* = 25.2, 13.4, 4.0 Hz, 1H), 1.95 (td, *J* = 13.3, 4.2 Hz, 1H), 1.62 – 1.50 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.9, 169.2, 142.0, 137.1, 131.3, 128.4, 128.3, 127.6, 127.4, 127.4, 126.6, 125.9, 82.2, 80.4, 58.1, 52.5, 52.1, 32.0, 29.9; **TLC** (15% EtOAc/hexanes) *R_f* 0.23; **Anal.** Calcd. for C₂₂H₂₄O₆: C, 72.61; H, 6.36. Found: C, 72.67; H, 6.44.

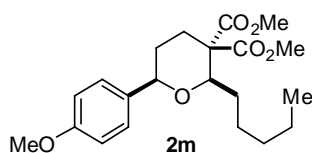
General Procedure C for the MADNTf₂-catalyzed [4 + 2] cycloaddition of cyclobutanes 1a-d with alkyl aldehydes to afford tetrahydropyrans 2l-q:



In an inert atmosphere glove box, a 1-dram vial containing a magnetic stir bar was charged with methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide)⁶ (MAD, 0.07 equiv), HNTf₂ (0.05 equiv) and (CH₂)₂Cl₂ (0.180 mL). The resulting solution was stirred until the evolution of methane gas ceases, approximately 5 min. To this vial is added a solution of the cyclobutane (0.322 mmol, 1.0 equiv) and aldehyde (0.967 mmol, 3.0 equiv) in (CH₂)₂Cl₂ (1.00 mL). The vial was sealed with a PTFE-lined screw cap, removed from the glove box, and stirred. Upon disappearance of the cyclobutane as indicated by TLC analysis (with 25% EtOAc/hexanes or CH₂Cl₂ as the mobile phase), the reaction was filtered through a 1-inch Monstr-Pette plug of silica with CH₂Cl₂ (12 mL) and concentrated. The resulting tetrahydropyrans **2l-q** were purified by flash chromatography using the indicated solvent system.

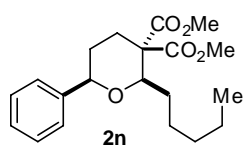


Dimethyl 6-(4-bromophenyl)-2-pentyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2l): The title compound was prepared according to General Procedure C using **1c** (0.105 g, 0.322 mmol, 1.0 equiv), hexanal (0.097 g, 0.967 mmol, 3.0 equiv), MAD (0.011 g, 0.023 mmol, 0.07 equiv), HNTf₂ (0.0045 g, 0.0161 mmol, 0.05 equiv), and 1,2-dichloroethane (1.28 mL). After stirring for 20 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (10% EtOAc/hexanes) to afford **2l** (0.116 g, 0.271 mmol, 84% yield) as a clear colorless oil in 87:13 dr. Analytical data for **2l**: **IR** (thin film, cm⁻¹) 2953, 2928, 2859, 1732, 1489, 1435, 1255, 1233, 1083, 1011, 804; **¹H NMR** (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 4.48 – 4.34 (m, 1H), 3.84 (dd, *J* = 9.7, 1.3 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 2.66 – 2.53 (m, 1H), 2.08 – 1.89 (m, 2H), 1.89 – 1.75 (m, 2H), 1.75 – 1.62 (m, 1H), 1.62 – 1.48 (m, 1H), 1.40 – 1.19 (m, 5H), 0.87 (bt, *J* = 5.9 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.5, 169.6, 141.4, 131.3, 127.6, 121.2, 82.1, 79.5, 56.6, 52.4, 52.0, 32.5, 32.4, 31.6, 29.7, 26.9, 22.5, 14.0; **TLC** (10% EtOAc/hexanes) *R_f* 0.23; **Anal.** Calcd. For C₂₀H₂₇BrO₅: C, 56.21; H, 6.37. Found: C, 56.51; H, 6.47.



Dimethyl 6-(4-methoxyphenyl)-2-pentyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2m): Note: This reaction was run at 0 °C. The title compound was prepared according to General Procedure C using **1b** (0.090 g, 0.322 mmol, 1.0 equiv), hexanal (0.097 g, 0.967 mmol, 3.0 equiv), MAD (0.011 g, 0.023 mmol, 0.07 equiv), HNTf₂ (0.0045 g, 0.0161 mmol, 0.05 equiv), and 1,2-dichloroethane (1.28 mL). After stirring for 3.5 h at 0 °C, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2m** (0.081 g, 0.214 mmol, 66% yield) as a clear colorless oil in 78:22 dr. Analytical data for **2m**: **IR** (thin film, cm⁻¹) 2954, 2930,

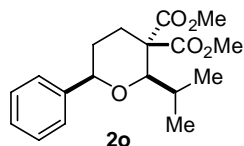
2858, 1731, 1614, 1515, 1436, 1249, 1175, 1081, 1034, 825; **¹H NMR** (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.48 – 4.34 (m, 1H), 3.90 – 3.82 (m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.74 (s, 3H), 2.67 – 2.51 (m, 1H), 2.11 – 1.94 (m, 2H), 1.92 – 1.75 (m, 2H), 1.73 – 1.48 (m, 2H), 1.29 (m, *J* = 3.1 Hz, 5H), 0.87 (bs, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.7, 169.7, 159.1, 134.6, 127.2, 113.7, 82.2, 79.9, 56.9, 55.3, 52.3, 51.9, 32.6, 31.6, 29.4, 27.0, 22.6, 14.0; **TLC** (15% EtOAc/hexanes) *R_f* 0.22; **Anal.** Calcd. For C₂₁H₃₀O₆: C, 66.65; H, 7.99. Found: C, 66.81; H, 8.02.



Dimethyl 2-pentyl-6-phenyldihydro-2H-pyran-3,3(4H)-dicarboxylate

(2n): The title compound was prepared according to General Procedure C using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), hexanal (0.097 g, 0.967 mmol, 3.0 equiv), MAD (0.011 g, 0.023 mmol, 0.07 equiv), HNTf₂ (0.0045 g, 0.0161 mmol, 0.05 equiv), and 1,2-dichloroethane (1.28 mL). After stirring

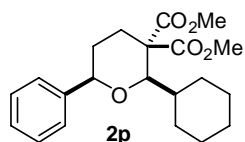
for 6.0 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (10% EtOAc/hexanes) to afford **2n** (0.103 g, 0.296 mmol, 92% yield) as a clear colorless oil in 85:15 dr. Analytical data for **2n**: **IR** (thin film, cm⁻¹) 2954, 2929, 2859, 1732, 1452, 1435, 1256, 1092, 1068, 698; **¹H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.30 (m, 4H), 7.28 (dd, *J* = 7.7, 4.5 Hz, 1H), 4.55 – 4.37 (m, 1H), 3.87 (d, *J* = 9.0 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 2.73 – 2.52 (m, 1H), 2.14 – 1.95 (m, 2H), 1.95 – 1.77 (m, 2H), 1.77 – 1.49 (m, 2H), 1.30 (d, *J* = 3.4 Hz, 5H), 0.88 (bs, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.6, 169.7, 142.4, 128.2, 127.4, 125.9, 82.2, 80.2, 56.8, 52.4, 51.9, 32.6, 31.6, 29.7, 26.9, 22.6, 14.0; **TLC** (10% EtOAc/hexanes) *R_f* 0.25; **Anal.** Calcd. For C₂₀H₂₈O₅: C, 68.94; H, 8.10. Found: C, 69.17; H, 8.06.



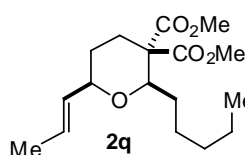
Dimethyl 2-isopropyl-6-phenyldihydro-2H-pyran-3,3(4H)-dicarboxylate

(2o): The title compound was prepared according to General Procedure C using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), isobutyraldehyde (0.070 g, 0.967 mmol, 3.0 equiv), MAD (0.011 g, 0.023 mmol, 0.07 equiv), HNTf₂ (0.0045 g, 0.0161 mmol, 0.05 equiv), and 1,2-dichloroethane (1.28 mL). After

stirring for 22.0 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (7.5% EtOAc/hexanes) to afford **2o** (0.091 g, 0.284 mmol, 88% yield) as a clear colorless oil in 91:9 dr. Analytical data for **2o**: **IR** (thin film, cm⁻¹) 2953, 2871, 1731, 1450, 1435, 1254, 1092, 1068, 1013, 698; **¹H NMR** (400 MHz, CDCl₃) δ 7.38 – 7.30 (m, 4H), 7.30 – 7.22 (m, 1H), 4.48 (dd, *J* = 10.9, 3.1 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.72 – 3.66 (m, 1H), 2.62 (dt, *J* = 12.8, 3.1 Hz, 1H), 2.51 – 2.28 (m, 1H), 2.07 (td, *J* = 12.8, 4.8 Hz, 1H), 2.01 – 1.80 (m, 2H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.2, 169.7, 142.6, 128.2, 127.3, 125.7, 86.9, 80.1, 56.2, 52.3, 52.0, 33.6, 31.7, 29.7, 20.2, 19.8; **TLC** (7.5% EtOAc/hexanes) *R_f* 0.16; **Anal.** Calcd. For C₁₈H₂₄O₅: C, 67.48; H, 7.55. Found: C, 67.44; H, 7.67.

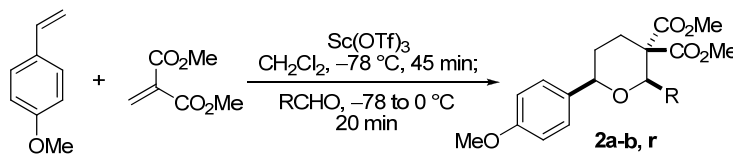


Dimethyl 2-cyclohexyl-6-phenyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2p): The title compound was prepared according to General Procedure C using **1a** (0.080 g, 0.322 mmol, 1.0 equiv), cyclohexanecarboxaldehyde (0.108 g, 0.967 mmol, 3.0 equiv), MAD (0.011 g, 0.023 mmol, 0.07 equiv), HNTf₂ (0.0045 g, 0.0161 mmol, 0.05 equiv), and 1,2-dichloroethane (1.28 mL). After stirring for 24.0 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (10% EtOAc/hexanes) to afford **2p** (0.109 g, 0.302 mmol, 94% yield) as a clear colorless oil in 96:4 dr. Analytical data for **2p**: **IR** (thin film, cm⁻¹) 2927, 2852, 1730, 1450, 1435, 1093, 1068, 1029, 1009; **¹H NMR** (400 MHz, CDCl₃) δ 7.37 – 7.29 (m, 4H), 7.29 – 7.22 (m, 1H), 4.45 (dd, *J* = 10.7, 3.0 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.72 – 3.61 (m, 1H), 2.69 – 2.51 (m, 1H), 2.05 (td, *J* = 12.6, 4.8 Hz, 3H), 1.99 – 1.80 (m, 2H), 1.76 – 1.53 (m, 4H), 1.35 – 1.09 (m, 3H), 1.09 – 0.91 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.3, 169.7, 142.6, 128.2, 127.3, 125.7, 86.2, 80.2, 56.1, 52.3, 52.0, 41.6, 33.7, 30.4, 30.1, 29.8, 26.8, 26.6, 26.3; **TLC** (10% EtOAc/hexanes) *R_f* 0.32; **Anal.** Calcd. For C₁₈H₂₄O₅: C, 69.98; H, 7.83. Found: C, 69.80; H, 7.99.



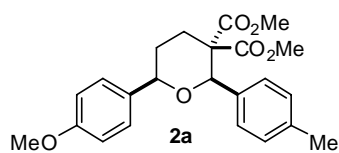
Dimethyl 2-pentyl-6-((E)-prop-1-enyl)dihydro-2H-pyran-3,3(4H)-dicarboxylate (2q): The title compound was prepared according to General Procedure C using **1d** (0.040 g, 0.188 mmol, 1.0 equiv), hexanal (0.056 g, 0.564 mmol, 3.0 equiv), MAD (0.0063 g, 0.013 mmol, 0.07 equiv), HNTf₂ (0.0027 g, 0.0094 mmol, 0.05 equiv), and 1,2-dichloroethane (0.75 mL). After stirring for 3.5 h, the reaction was complete as determined by TLC analysis. The reaction was worked up and purified by flash chromatography (10% EtOAc/hexanes) to afford **2q** (0.050 g, 0.156 mmol, 85% yield) as a clear colorless oil in 77:23 dr containing an inseparable cyclobutane decomposition product (16%, by mass). Corrected yield: 0.042 g, 0.134 mmol, 72%. Analytically pure material was obtained by HPLC purification. Analytical data for **2q**: **IR** (thin film, cm⁻¹) 2955, 2929, 2858, 1733, 1436, 1256, 1230, 1085, 1068, 1016, 966; **¹H NMR** (400 MHz, C₆D₆) δ 5.68 – 5.56 (m, 1H), 5.52 (dd, *J* = 15.6, 4.6 Hz, 1H), 4.00 – 3.83 (m, 1H), 3.74 (d, *J* = 6.4 Hz, 1H), 3.38 (s, 3H), 3.27 (s, 3H), 2.71 – 2.52 (m, 1H), 2.17 (dtd, *J* = 14.5, 9.8, 4.9 Hz, 1H), 2.10 – 1.93 (m, 2H), 1.92 – 1.70 (m, 2H), 1.54 (m, 1H), 1.48 (d, *J* = 6.0 Hz, 3H), 1.44 – 1.20 (m, 5H), 0.86 (t, *J* = 7.0 Hz, 3H); **¹³C NMR** (100 MHz, C₆D₆) δ 172.4, 170.2, 133.4, 126.6, 82.8, 79.7, 57.7, 52.4, 52.1, 33.9, 33.3, 32.7, 29.4, 28.2, 23.6, 18.3, 14.8; **TLC** (10% EtOAc/hexanes) *R_f* 0.27; **LRMS** (ESI) Calcd. For C₁₇H₂₈O₅+Na: 335.2, Found: 335.2.

General Procedure D for the Sc(OTf)₃-catalyzed [[2 + 2] + 2] cycloaddition of 1-methoxy-4-vinylbenzene, dimethyl 2,2-methyldiene malonate, and aldehydes to afford tetrahydropyrans 2a-b, r:



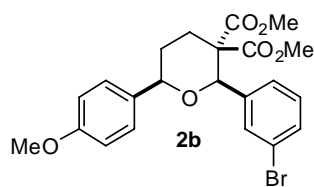
In an inert atmosphere glove box, a 1-dram shell vial containing a magnetic stir bar was charged with Sc(OTf)₃ (0.0171 g, 0.0347 mmol, 0.10 equiv). A second shell vial was charged with dimethyl 2,2-methyldiene malonate¹ (DMM, 0.50 g, 0.347 mmol, 1.0 equiv) and fitted with a

rubber septum. Both vessels were removed from the glove box and placed under N₂. The Sc(OTf)₃ was suspended in CH₂Cl₂ (0.25 mL) and cooled to -78 °C in an isopropanol/dry ice bath. The DMM was dissolved in CH₂Cl₂ (2.0 mL) and 1-methoxy-4-vinylbenzene (0.061 g, 0.061 mL, 1.3 equiv) was added via syringe. The resulting solution was drawn into a syringe and added to the Sc(OTf)₃ by syringe pump over 45 min. When the disappearance of DMM was confirmed by TLC (using 20% EtOAc/hexanes, approx 5-10 min), the aldehyde (1.04 mmol, 3.0 equiv) was added neat via syringe. The reaction was held at -78 °C for 20 min and was then warmed to 0 °C for an additional 20 min at which point disappearance of **1b** can be observed by TLC (20% EtOAc/hexanes). The reaction was filtered through a 1-inch Monstr-Pette plug of silica with CH₂Cl₂ (12 mL) and concentrated. The resulting tetrahydropyrans **2a-b, r** were purified by flash chromatography using the indicated solvent system.



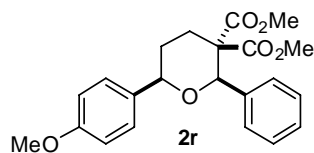
Dimethyl 6-(4-methoxyphenyl)-2-p-tolyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2a):

The title compound was prepared according to General Procedure D using Sc(OTf)₃ (0.0171 g, 0.0347 mmol, 0.10 equiv), DMM (0.50 g, 0.347 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (0.061 g, 0.061 mL, 1.3 equiv), 4-methylbenzaldehyde (0.125 g, 0.124 mL, 1.04 mmol, 3.0 equiv), and CH₂Cl₂ (2.25 mL). After work up and purification by flash chromatography (15% EtOAc/hexanes), **2a** (0.096 g, 0.241 mmol, 69% yield) was afforded as colorless crystals in 99:1 dr.



Dimethyl 6-(4-methoxyphenyl)-2-(3-bromophenyl)dihydro-2H-pyran-3,3(4H)-dicarboxylate (2b):

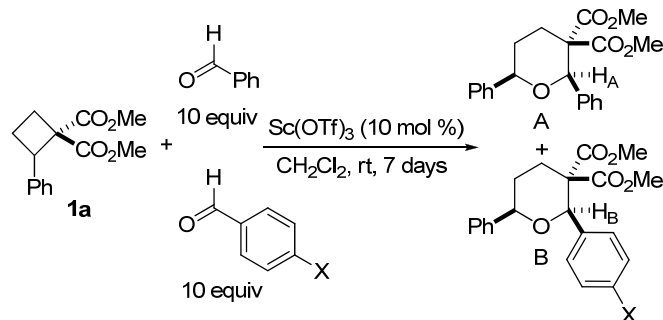
The title compound was prepared according to General Procedure D using Sc(OTf)₃ (0.0171 g, 0.0347 mmol, 0.10 equiv), DMM (0.50 g, 0.347 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (0.061 g, 0.061 mL, 1.3 equiv), 3-bromobenzaldehyde (0.192 g, 0.122 mL, 1.04 mmol, 3.0 equiv), and CH₂Cl₂ (2.25 mL). After work up and purification by flash chromatography (15% EtOAc/hexanes), **2b** (0.076 g, 0.164 mmol, 47% yield) was afforded as a clear colorless oil in 97:3 dr.



Dimethyl 6-(4-methoxyphenyl)-2-phenyldihydro-2H-pyran-3,3(4H)-dicarboxylate (2r):

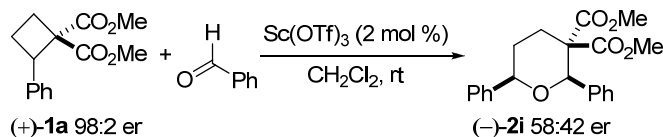
The title compound was prepared according to General Procedure D using Sc(OTf)₃ (0.0171 g, 0.0347 mmol, 0.10 equiv), DMM (0.50 g, 0.347 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (0.061 g, 0.061 mL, 1.3 equiv), benzaldehyde (0.110 g, 0.105 mL, 1.04 mmol, 3.0 equiv), and CH₂Cl₂ (2.25 mL). After work up and purification by flash chromatography (20% EtOAc/hexanes), **2r** (0.079 g, 0.205 mmol, 59% yield) was afforded as a clear colorless oil in 98:2 dr. Analytical data for **2r**: IR (thin film, cm⁻¹) 2952, 2838, 1730, 1614, 1515, 1435, 1250, 1176, 1082, 1033, 828, 700; ¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, *J* = 7.5 Hz, 4H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.29 (m, 3H), 7.29 – 7.24 (m, 2H), 5.18 (s, 1H), 4.66 (m, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.57 (s, 3H), 2.72 – 2.70 (m, 1H), 2.34 (dt, *J* = 13.5, 4.5 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.96 – 1.93 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.3, 169.1, 159.0, 139.4, 134.5, 127.5, 127.4, 127.2, 127.1, 113.6, 82.3, 80.3, 58.5, 55.2, 52.4, 51.6, 32.7, 29.9; TLC (20% EtOAc/hexanes) R_f 0.23; LRMS (ESI) Calcd. For C₂₂H₂₄O₆+Na: 407.2, Found: 407.2.

Procedure for the competition experiment (Equation 3):



In an inert atmosphere glove box, a 1-dram vial containing a magnetic stir bar was charged with the $\text{Sc}(\text{OTf})_3$ (0.0079 g, 0.0161 mmol, 0.10 equiv). To this vial was added a solution of cyclobutane **1a** (0.040 g, 0.161 mmol, 1.0 equiv), benzaldehyde (0.171 g, 1.61 mmol, 10 equiv), and 4-X-PhCHO (1.61 mmol, 10 equiv) in CH_2Cl_2 (0.640 mL). The vial was sealed with a PTFE-lined screw cap, removed from the box, and allowed to stir. After 7 days, the contents of the vial were passed through a 1-inch Monstr-Pette plug of silica with CH_2Cl_2 (12 mL) and concentrated *in vacuo*. The relative abundance of each product was determined by comparison of the ^1H NMR resonances of H_A and H_B .

Cycloaddition of (+)-**1a** with benzaldehyde (Figure 1):



In the glove box, a 1-dram vial containing a magnetic stir bar was charged with $\text{Sc}(\text{OTf})_3$ (0.001 g, 0.002 mmol, 0.02 equiv) (Vial #1). A solution of cyclobutane (+)-**1a** (0.025 g, 0.101 mmol, 1.0 equiv, 98:2 er), benzaldehyde (0.032 g, 0.302 mmol, 3.0 equiv), hexadecane (approx 0.025 g, GC internal standard) in CH_2Cl_2 (0.50 mL) was mixed in a 1-dram vial (Vial #2). A 0.050 mL aliquot was removed ($t = 0.0$ min) and the remaining contents of Vial #2 were transferred to Vial #1 by pipette, which was then sealed with a PTFE-lined screw cap, removed from the glove box, and allowed to stir. Periodically, 0.050 mL aliquots were removed from the reaction via syringe and quenched with 3.0 M NH_4OH and dried over Na_2SO_4 . The er of remaining (+)-**1a** was determined by GC analysis (Chiradex B-DM column, 30 m x 0.250 mm, pressure = 80 kPa, flow = 0.6 mL/min, detector = FID, 250 $^\circ\text{C}$) and conversion was determined by comparison to the reference sample taken at $t = 0.0$ min. SFC analysis (Chiralpack, WO, 2.0% MeOH, 2.0 mL/min, 200 bar, 210 nm, 40 $^\circ\text{C}$) was used to determine the er of (-)-**2i**. Analytical data for (-)-**2i**: SFC analysis: er 58:42, $t_{\text{r-major}}$ 6.89 min, $t_{\text{r-minor}}$ 7.59 min; $[\alpha]_{\text{D}}^{27} = -14.1$ ($c = 0.100$, CHCl_3).

Table S1: Stereochemical Analysis of the $\text{Sc}(\text{OTf})_3$ -Catalyzed Formal [4 + 2] Cycloaddition of (+)-**1a** and Benzaldehyde.

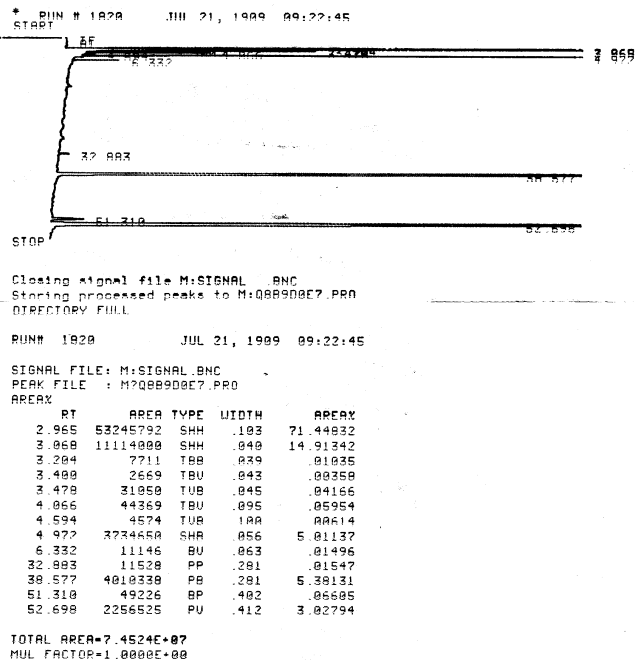
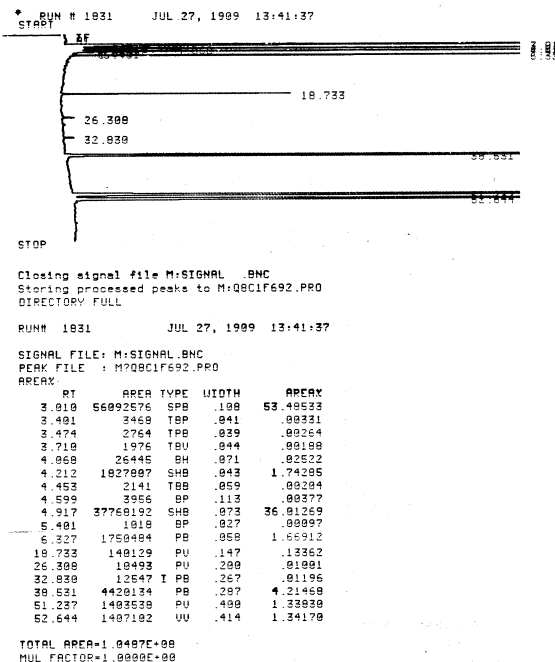
Conversion (%)	0	12	23	32	42	45
(+)- 1a er (%)	98	93	88.5	84.5	80.5	79
(-)- 2i er (%)	-	59.5	59	58.5	58	58

GC data used to determine conversion and er of (+)-1a using a hexadecane internal standard:

rac-1a and hexadecane

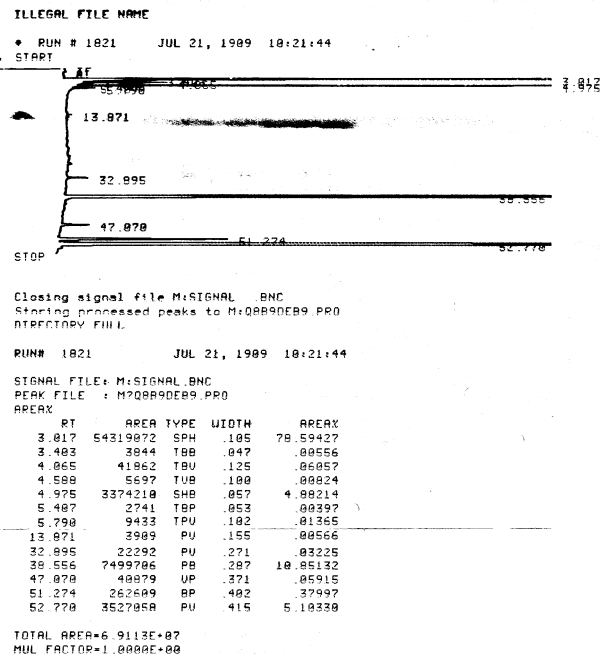
t = 0.0 min

Conversion: 0%, er: 98:2



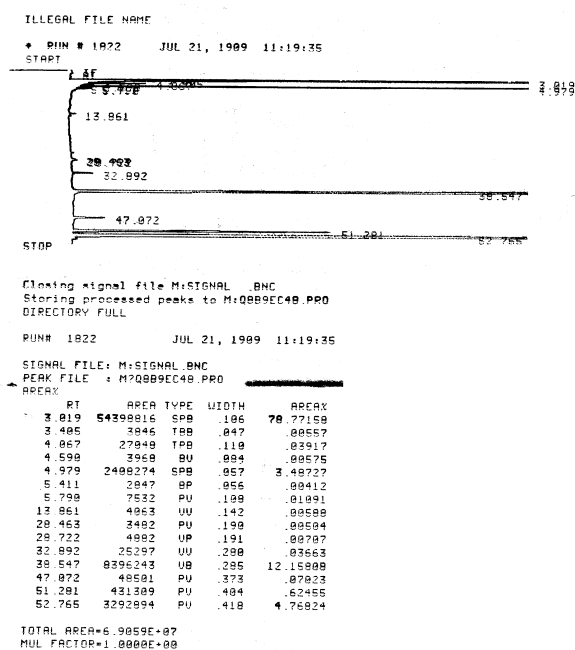
t = 20 min

Conversion: 12%, er: 93:7

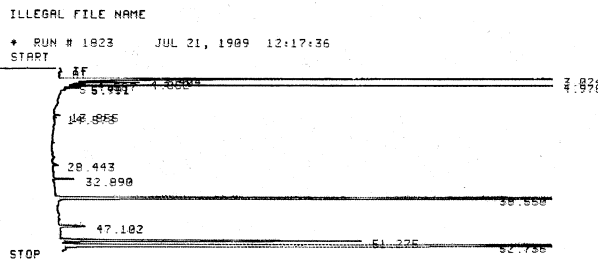


t = 40 min

Conversion: 23%, er: 88.5:11.5



t = 60 min
Conversion: 32%, er: 84.5:15.5



Closing signal file M:SIGNAL .BNC
Storing processed peaks to M:Q8B9F9E1.PRO
DIRECTORY FULL

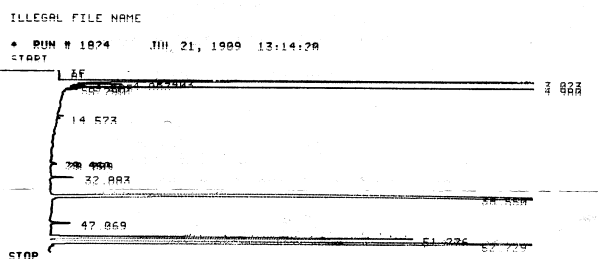
RUN# 1823 JUL 21, 1989 12:17:35

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M:Q8B9F9E1.PRO

RT	AREA	TYPE	WIDTH	AREAX
3.024	54126272	SPB	.105	79.65910
3.404	3799	TBB	.048	.00559
4.052	28624	TBB	.119	.04213
4.507	5337	BP	.101	.00785
4.978	2892677	SPB	.056	4.25723
5.411	2595	BP	.051	.00382
5.791	6332	PV	.099	.00932
13.855	2935	BP	.123	.00432
14.573	1938	PV	.131	.00204
28.443	4045	PV	.241	.00595
32.898	22048	UP	.269	.03244
38.550	7765098	PV	.286	11.42810
47.102	37861	UP	.301	.05572
51.275	471653	PV	.408	.69414
52.735	2576226	UU	.412	3.79150

TOTAL AREA=6.7947E+07
MUL FACTOR=1.0000E+00

t = 100 min
Conversion: 42%, er: 80.5:19.5



Closing signal file M:SIGNAL .BNC
Storing processed peaks to M:Q8B8072D.PRO
DIRECTORY FULL

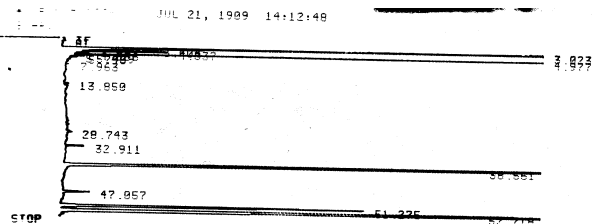
RUN# 1824 JUL 21, 1989 13:14:28

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M:Q8B8072D.PRO

RT	AREA	TYPE	WIDTH	AREAX
3.023	54179808	SPB	.105	79.25434
3.403	3393	TBB	.047	.00496
4.053	21019	TBB	.117	.03075
4.505	3995	BP	.077	.00584
4.980	2189158	SPB	.057	3.28231
5.410	2864	BP	.053	.00419
5.790	5307	PP	.102	.00776
14.573	3398	UP	.198	.00496
28.450	3357	BU	.178	.00491
28.709	5611	UU	.212	.00821
32.883	25658	PP	.278	.03755
38.550	8985946	UU	.286	13.02764
47.069	31051	UU	.378	.04542
51.276	583682	PV	.403	.05381
52.729	2397757	UU	.411	3.58744

TOTAL AREA=6.8362E+07
MUL FACTOR=1.0000E+00

t = 140 min
Conversion: 45%, er: 79:21



Closing signal file M:SIGNAL .BNC
Storing processed peaks to M:Q8B814E1.PRO
DIRECTORY FULL

RUN# 1825 JUL 21, 1989 14:12:48

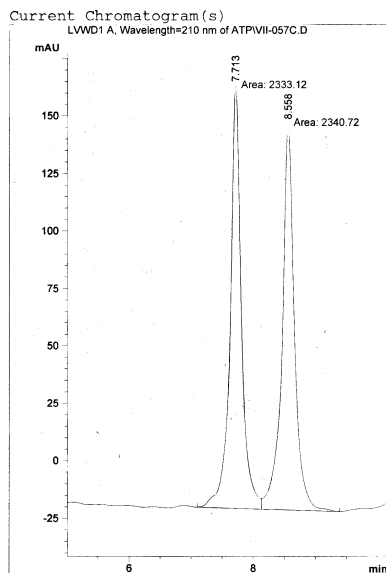
SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M:Q8B814E1.PRO

RT	AREA	TYPE	WIDTH	AREAX
3.023	54233856	SPB	.105	80.75862
3.404	3404	TBB	.045	.00507
4.037	27574	TBB	.082	.04121
4.505	4798	PP	.083	.00713
4.977	3190629	SPB	.056	4.75111
5.409	2802	BP	.054	.00417
5.795	3669	PV	.106	.00546
13.858	3379	PP	.135	.00593
28.743	4983	UP	.209	.00742
32.911	19895	BP	.255	.02854
38.561	7301475	PB	.286	10.87249
47.057	41846	PV	.379	.06231
51.275	487061	UU	.406	.72526
52.718	1830156	UU	.411	2.72525

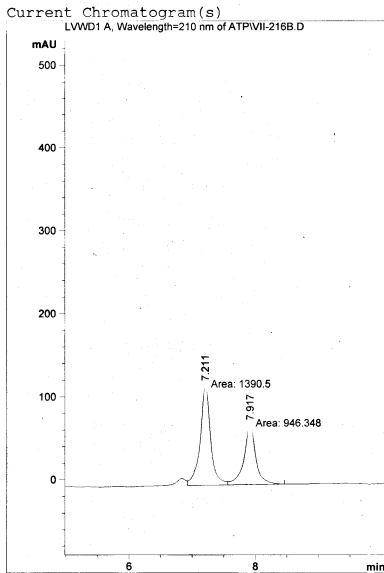
TOTAL AREA=6.7155E+07
MUL FACTOR=1.0000E+00

SFC data used to determine the er of (–)-2i:

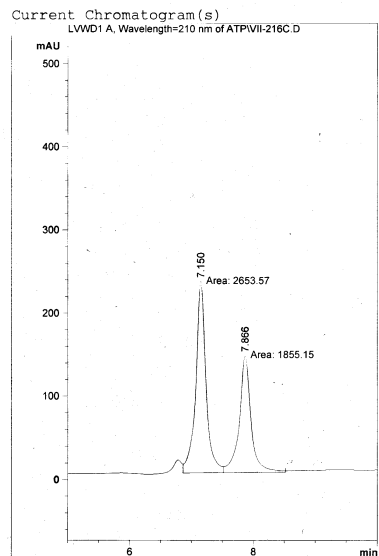
***rac*-2i**



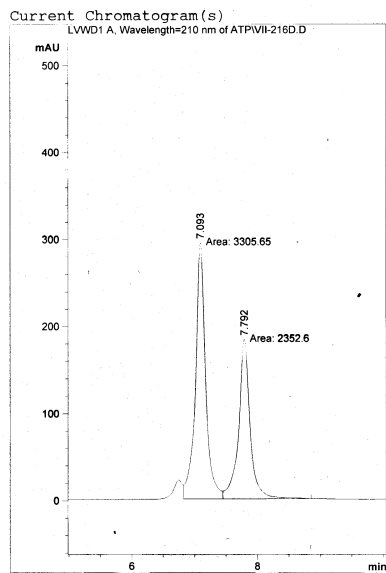
t = 20 min
Conversion: 12%, er: 59.5:40.5



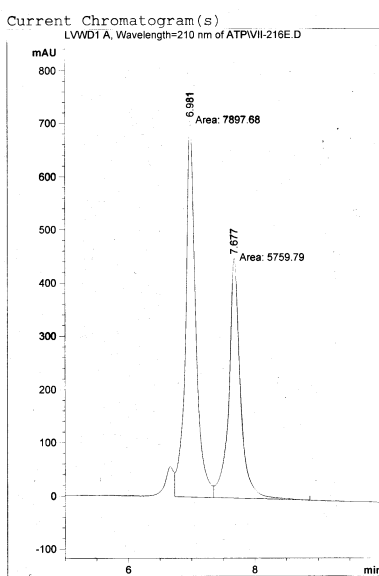
t = 40 min
Conversion: 23%, er: 59:41



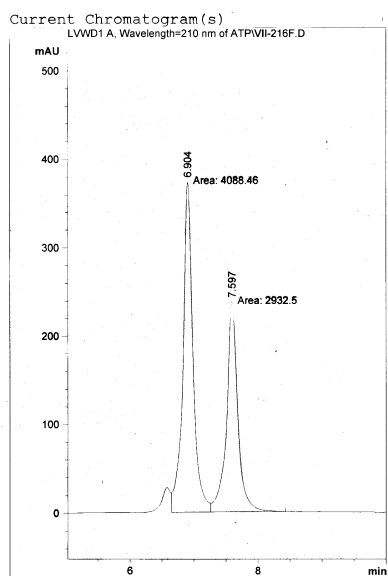
t = 60 min
Conversion: 32%, er: 58.5:41.5



t = 100 min
Conversion: 42%, er: 58:42



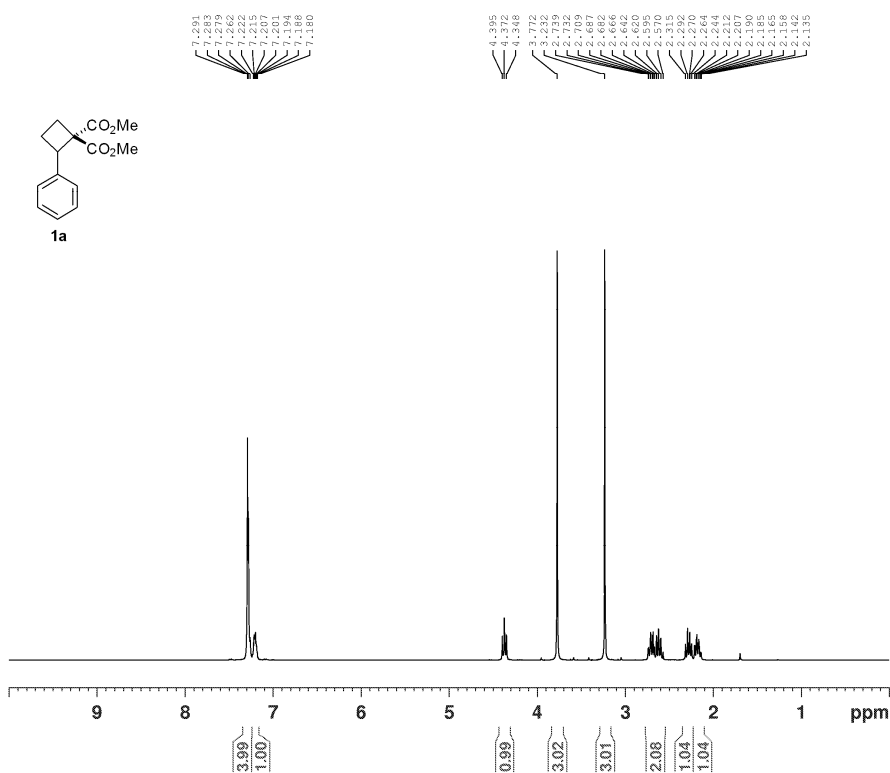
t = 140 min
Conversion: 45%, er: 58:42



References:

- (1) De Keyser, J.-L.; De Cock, C. J. C.; Poupaert, J. H.; Dumont, P. *J. Org. Chem.* **1988**, *53*, 4859–4862.
- (2) Corbin, T. F.; Hahn, R. C.; Shechter, H. *Org. Synth.* **1964**, *44*, 30–33.
- (3) Varney, M. D.; Romines, W. H., III.; Boritzki, T.; Margosiak, S. A.; Bartlett, C.; Howland, E. J. *J. Heterocyclic Chem.* **1995**, 1493–1498.
- (4) Stevens, R. V.; Lee, A. W. M. *J. Am. Chem. Soc.* **1979**, *101*, 7032–7035.
- (5) Burger, A.; Coyne, W. E. *J. Org. Chem.* **1964**, *29*, 3079–3082.
- (6) Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588–3597.

ATP-VI-254C 400 MHz WB



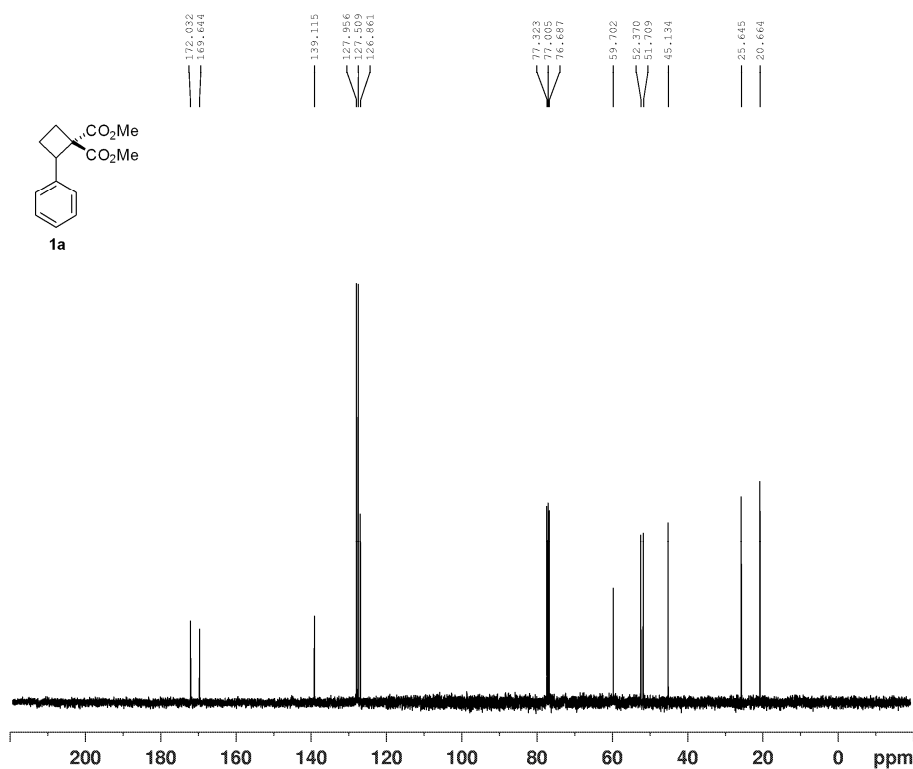
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PROCNO 1

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PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 9
DS 0
SWH 6219.965 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 64
DW 80.400 usec
DB 6.90 usec
TR 300.0 K
D1 1.00000000 sec
TD0 1

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NUC1 1H
P1 9.10 usec
PL1 3.00 dB
SFO1 399.8424924 MHz

F2 - Processing parameters
SI 32768
SF 399.840070 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ATP-VI-254C exp 2 13C 400 MHz WB



Current Data Parameters
NAME ATP-VI-254C
EXPNO 2
PROCNO 1

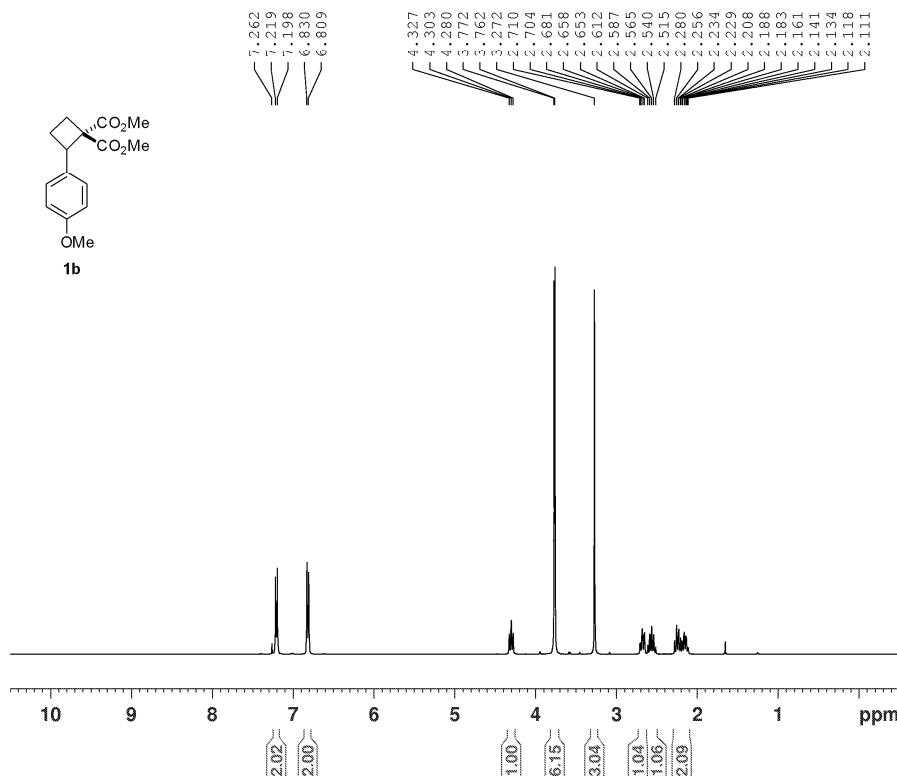
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NS 1035
DS 2
SWH 23980.814 Hz
FIDRES 0.731836 Hz
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RG 16384
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DB 6.00 usec
TR 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999999 sec
TD0 1

----- CHANNEL f1 -----
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P1 7.25 usec
PL1 0.00 dB
SFO1 100.5499020 MHz

----- CHANNEL f2 -----
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NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.50 dB
SFO2 399.8415994 MHz

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ATP-VI-270C 400 MHz WB



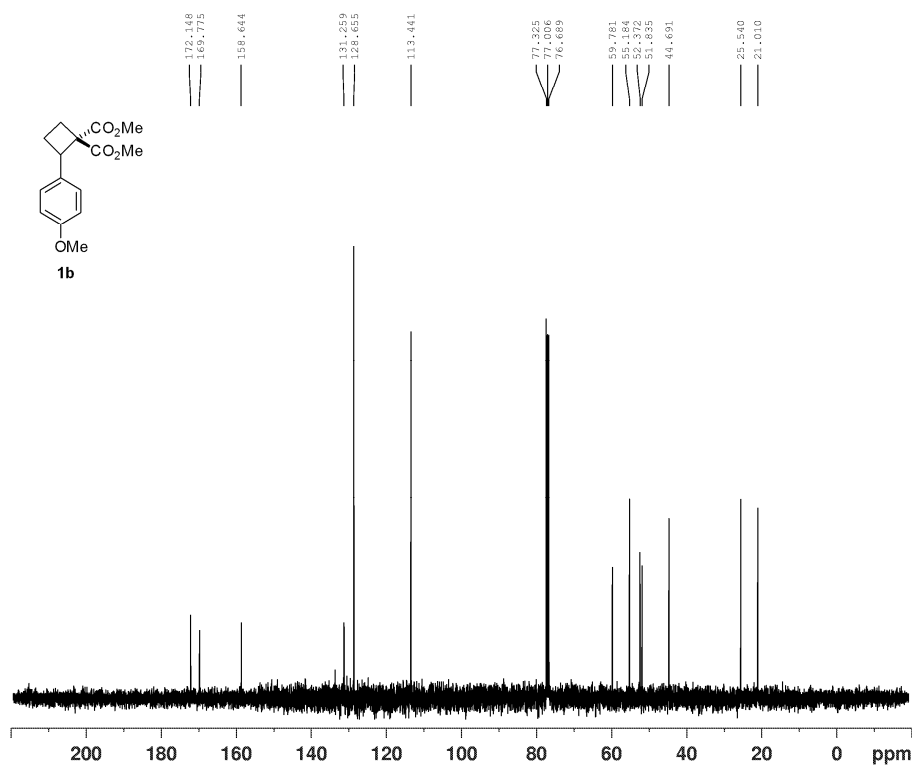
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 SOLVENT CDCl3
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 FIDRES 0.189786 Hz
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 RG 101.6
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 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

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 PL1 -3.00 dB
 SFO1 399.8424924 MHz

F2 - Processing parameters
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 SF 399.8400070 MHz
 WDW EM
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ATP-VI-270C exp 2 13C 400 MHz WB



Current Data Parameters
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 PROCNO 1

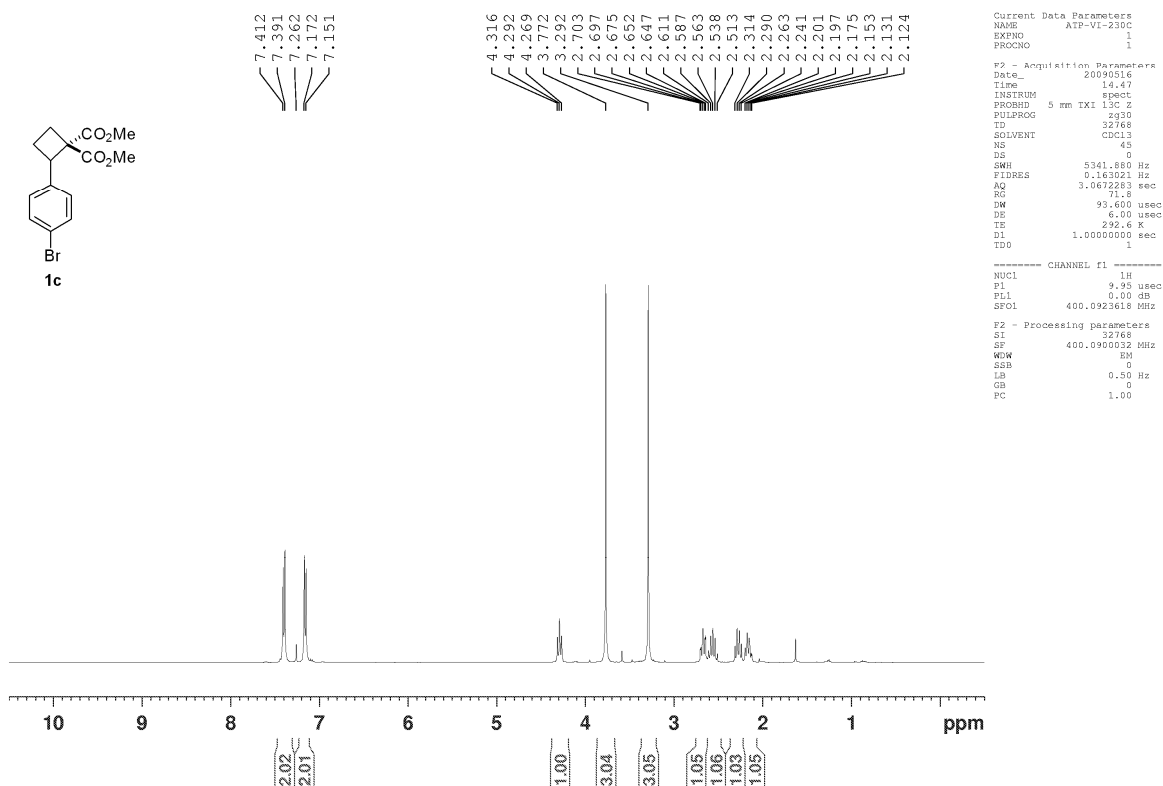
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 NS 828
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 SWH 23980.814 Hz
 FIDRES 0.731836 Hz
 AQ 0.6832628 sec
 RG 16384
 DW 20.850 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 DELTA 0.89999999 sec
 TD0 1

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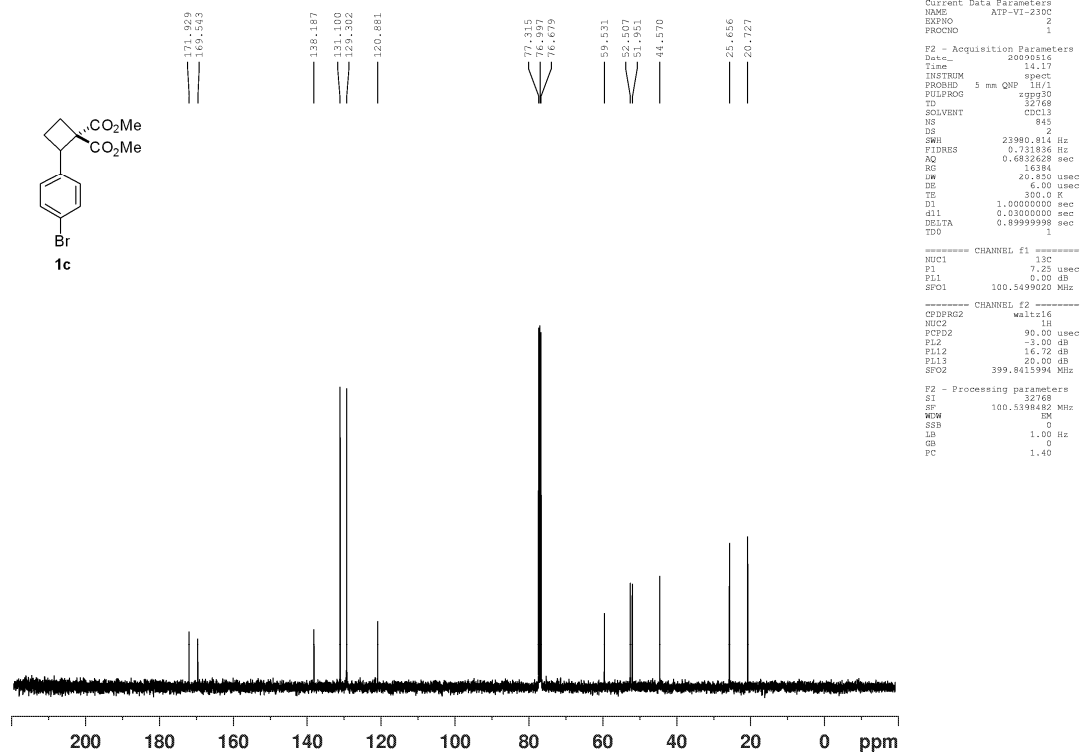
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 PL12 16.72 dB
 PL13 20.00 dB
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F2 - Processing parameters
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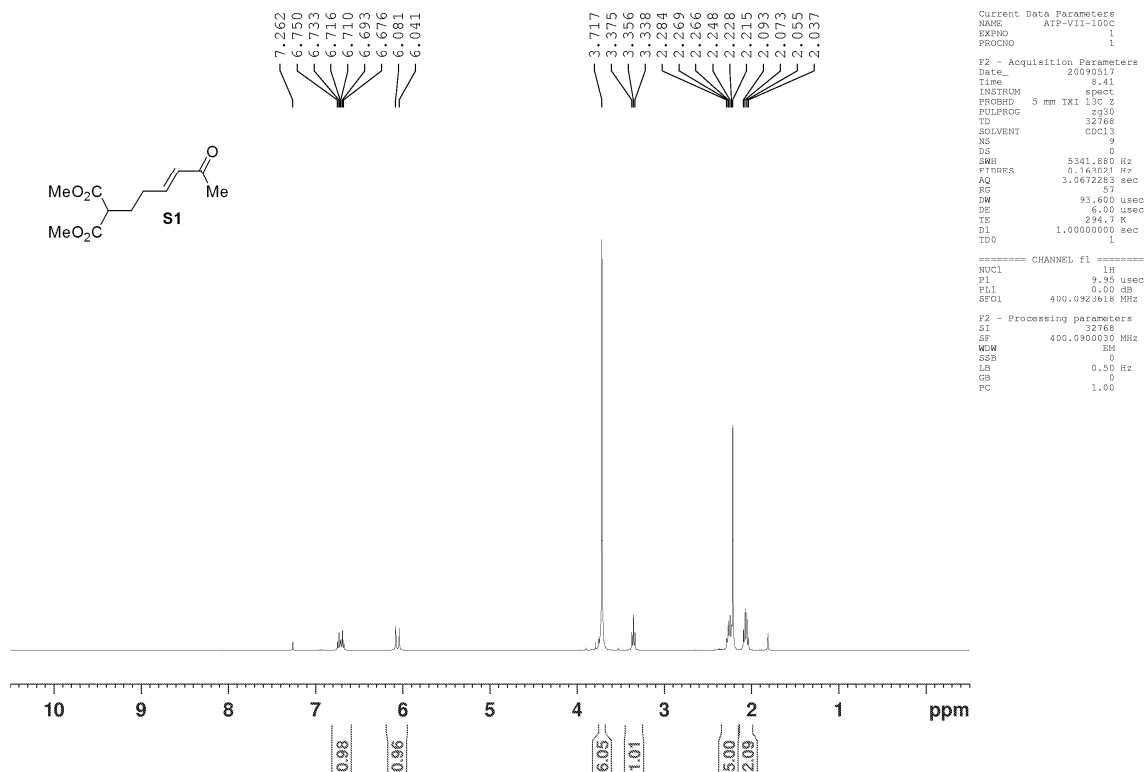
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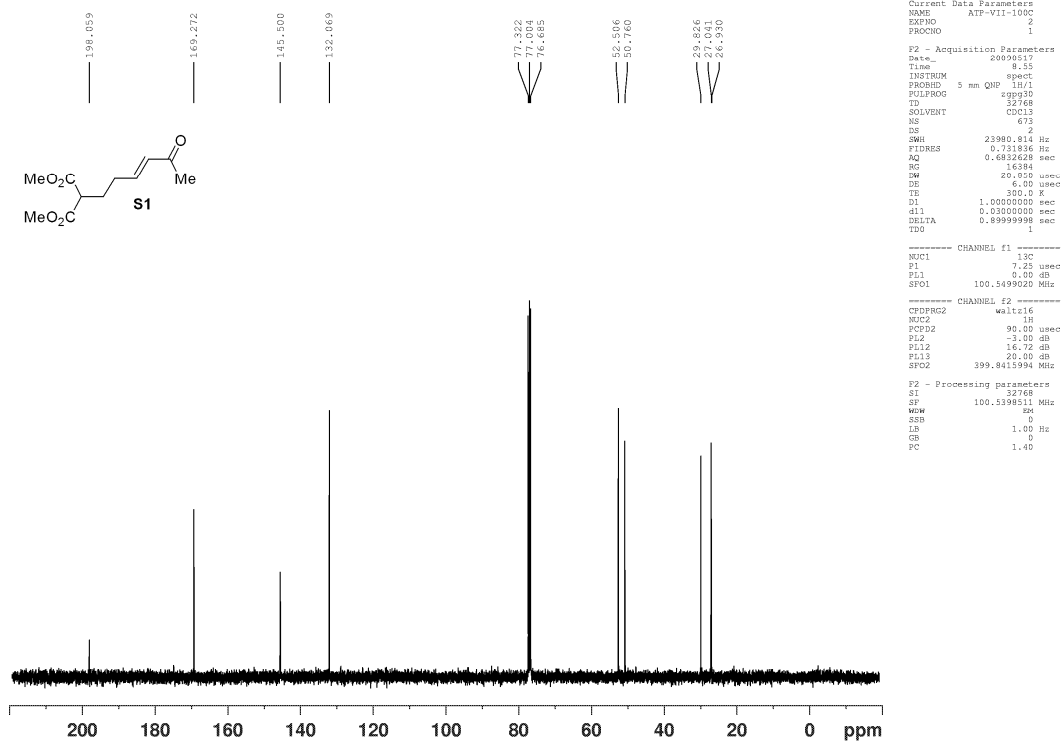
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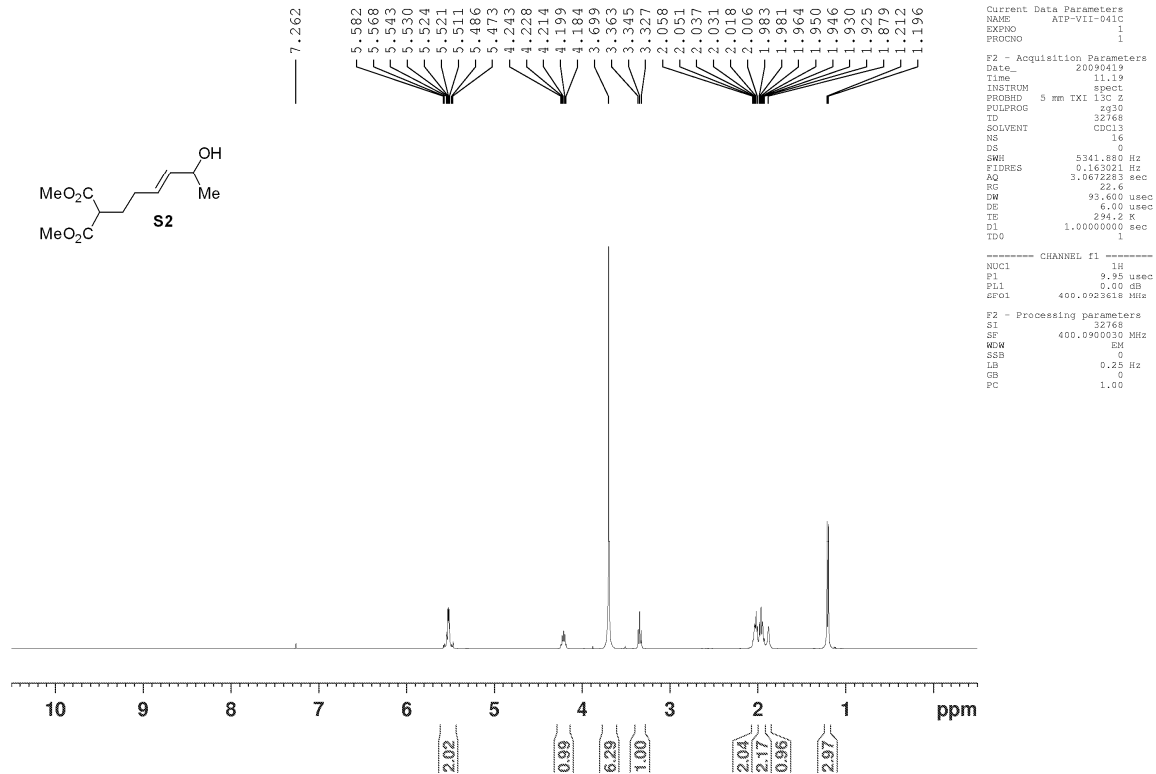
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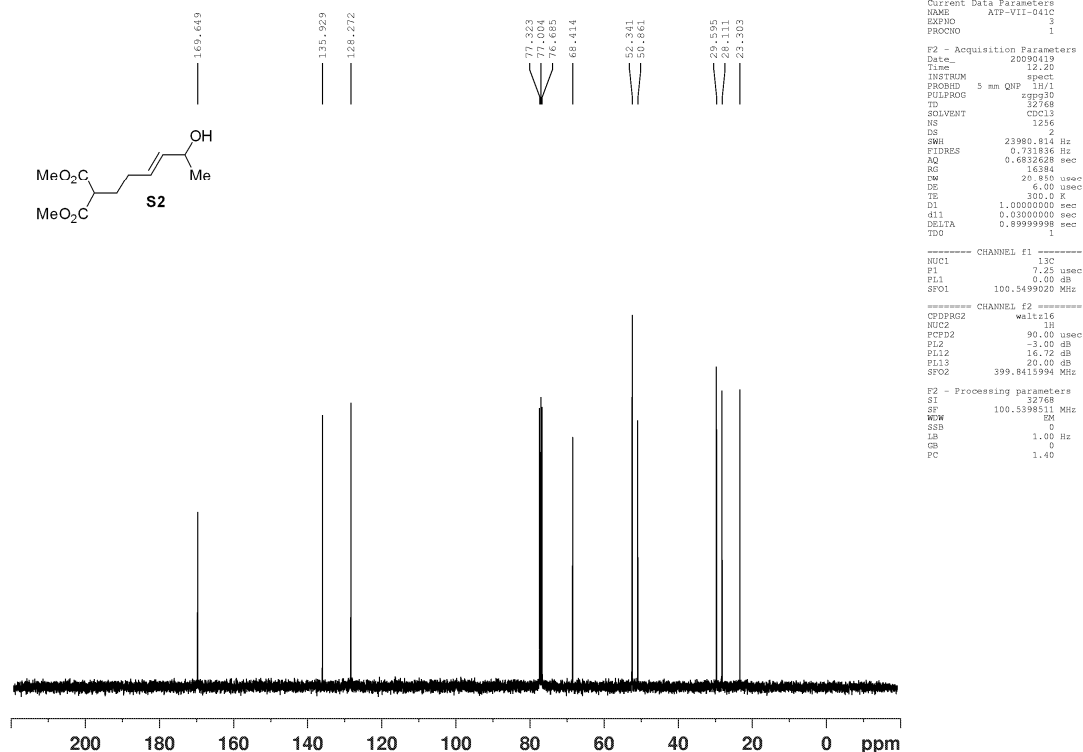
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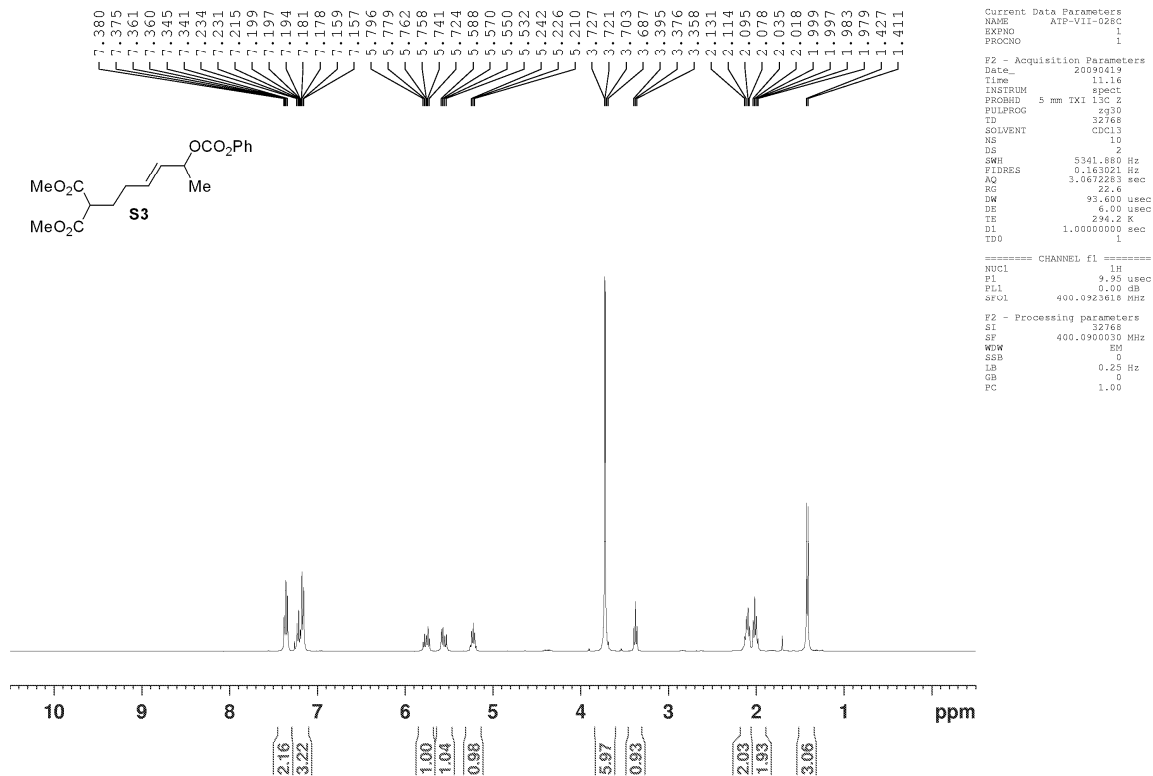
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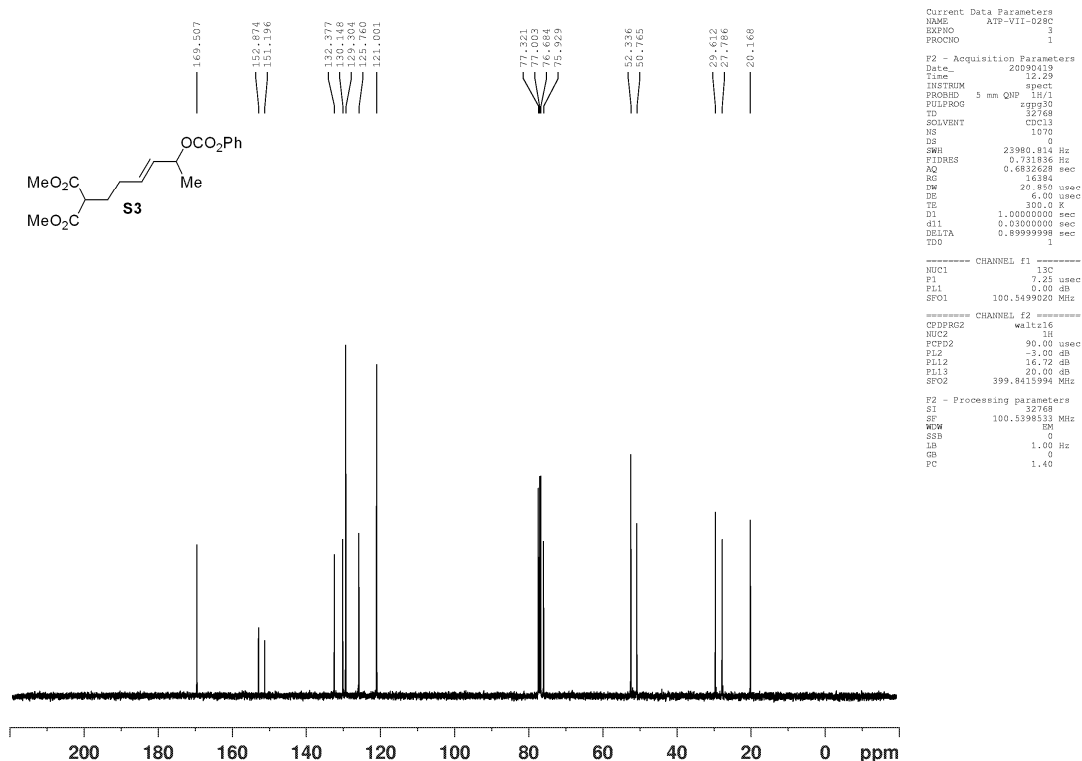
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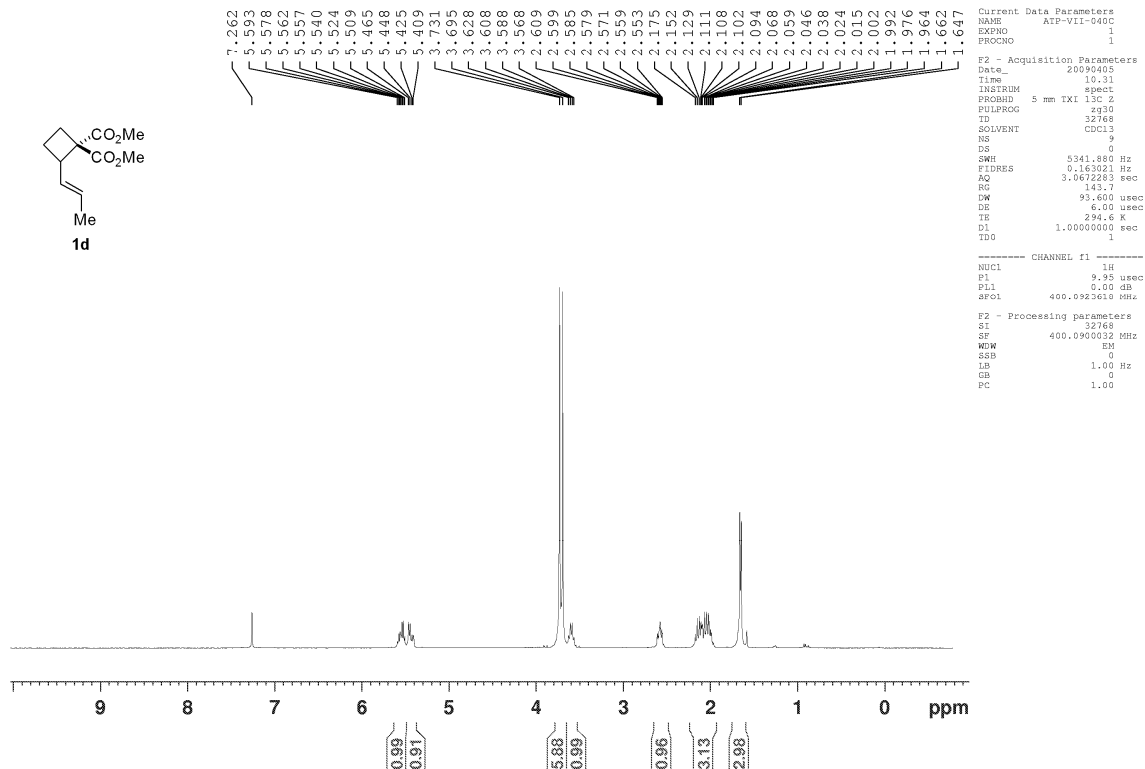
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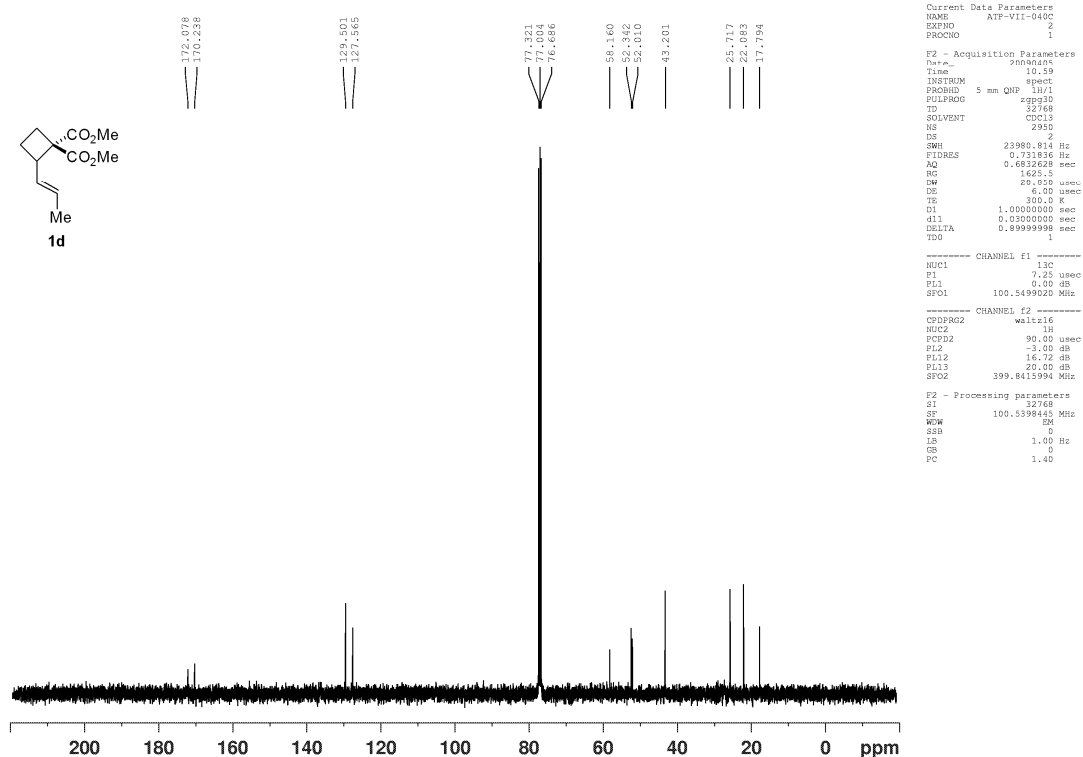
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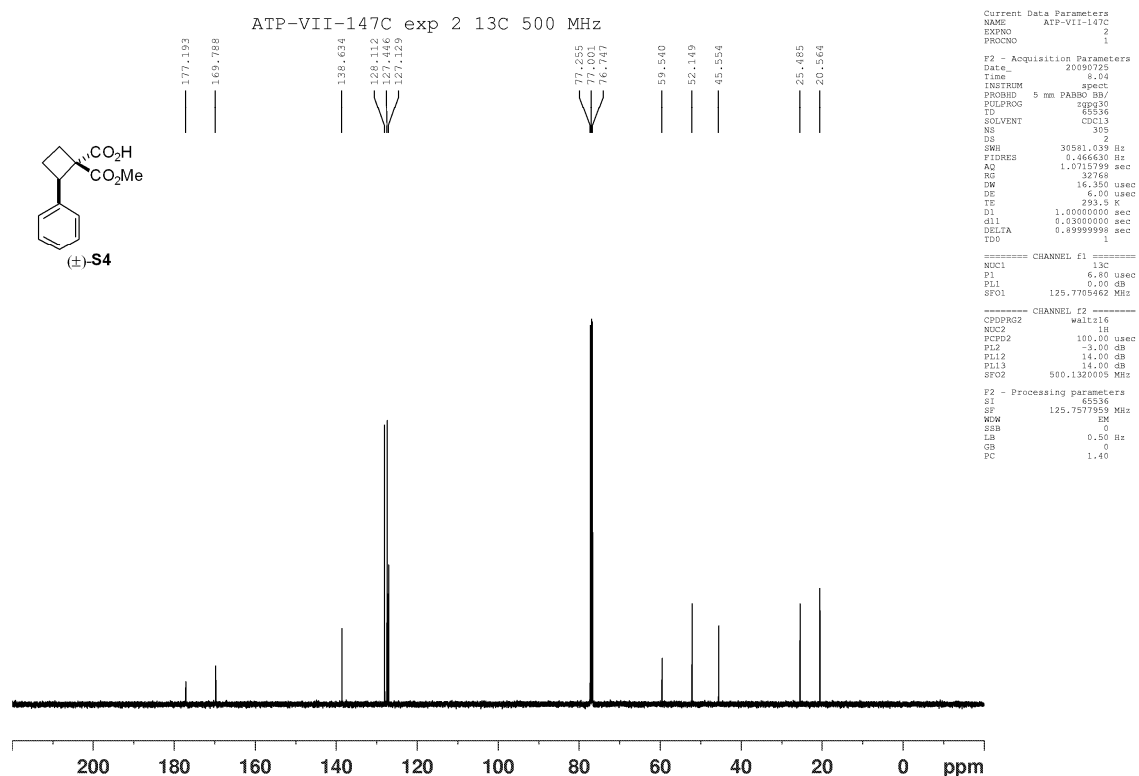
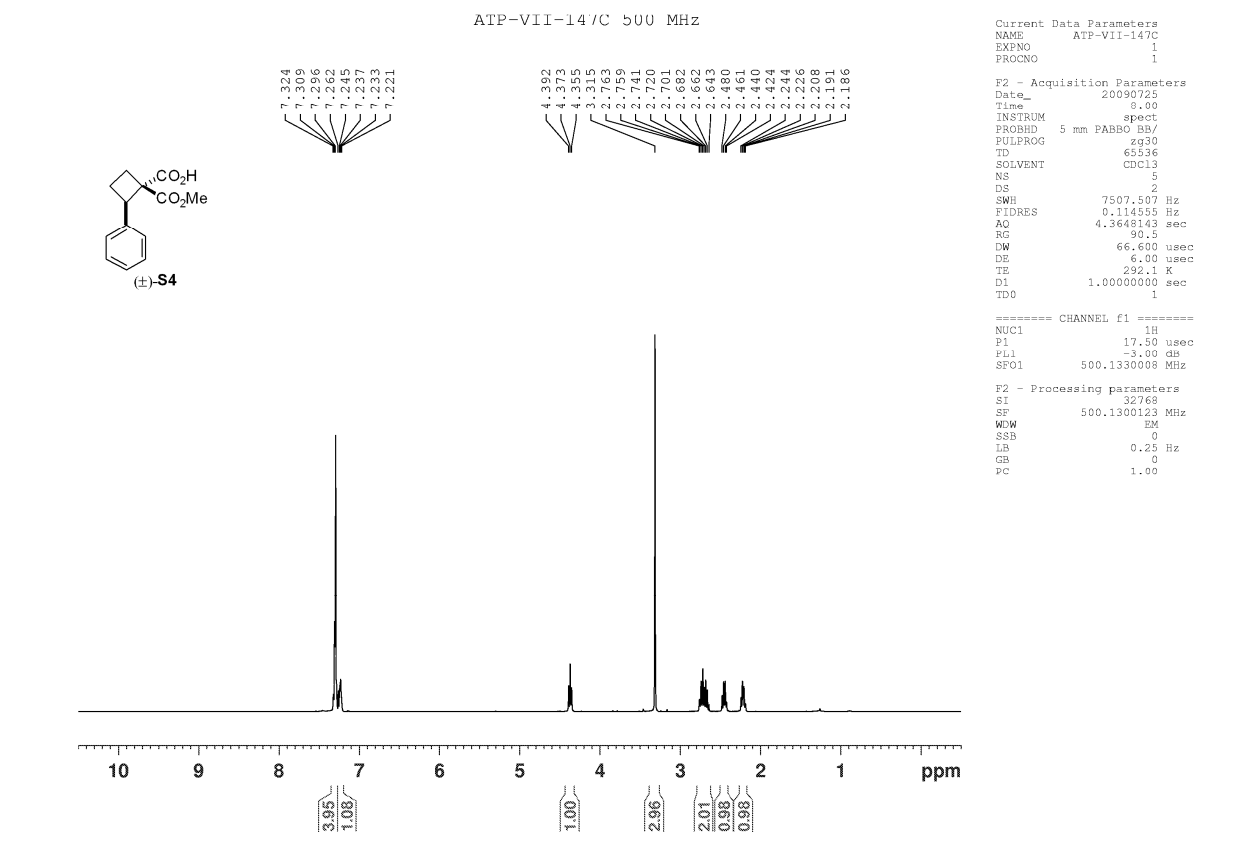


ATP-VII-040C 400 MHz NB

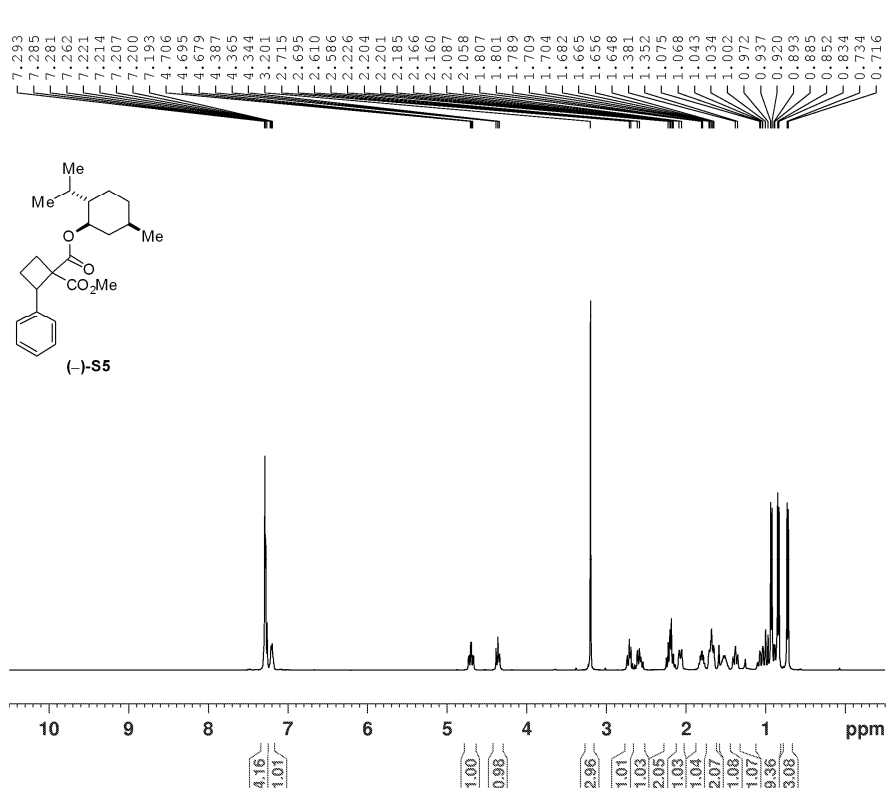


ATP-VII-040C exp 2 13C 400 MHz WB





ATP-VII-153B exp 2 400 MHz WB



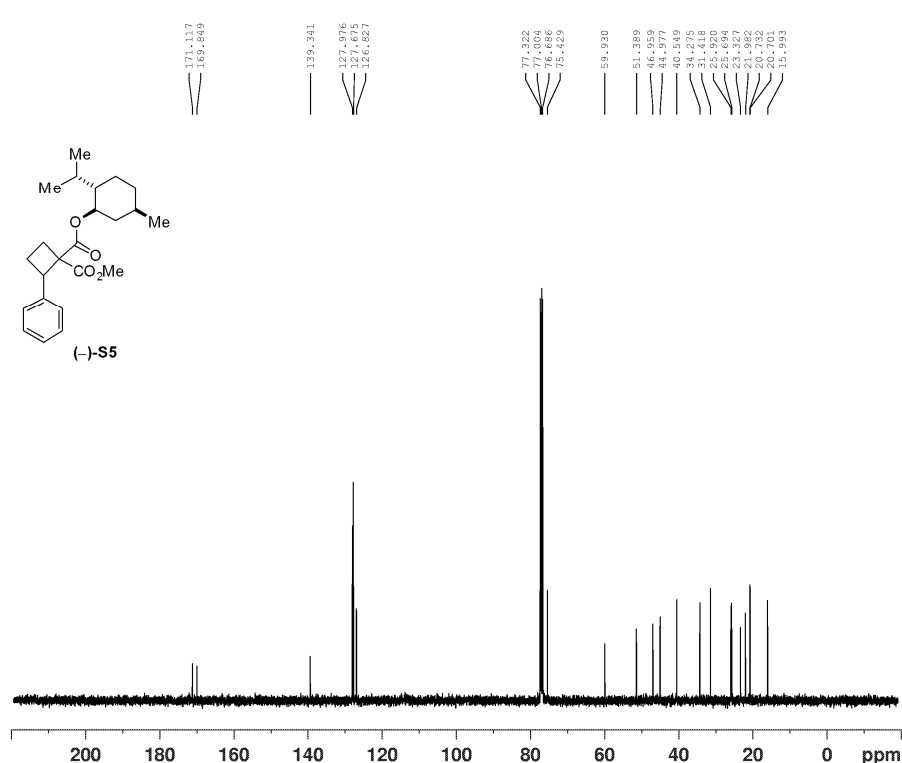
Current Data Parameters
NAME ATP-VII-153B
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090629
Time 6.24
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 14
DS 0
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 101.6
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -5.00 dB
SFO1 399.8424924 MHz

F2 - Processing parameters
SI 32768
SF 399.8400069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ATP-VII-153B 13C exp 4 400 MHz WB



Current Data Parameters
NAME ATP-VII-153B
EXPNO 4
PROCNO 1

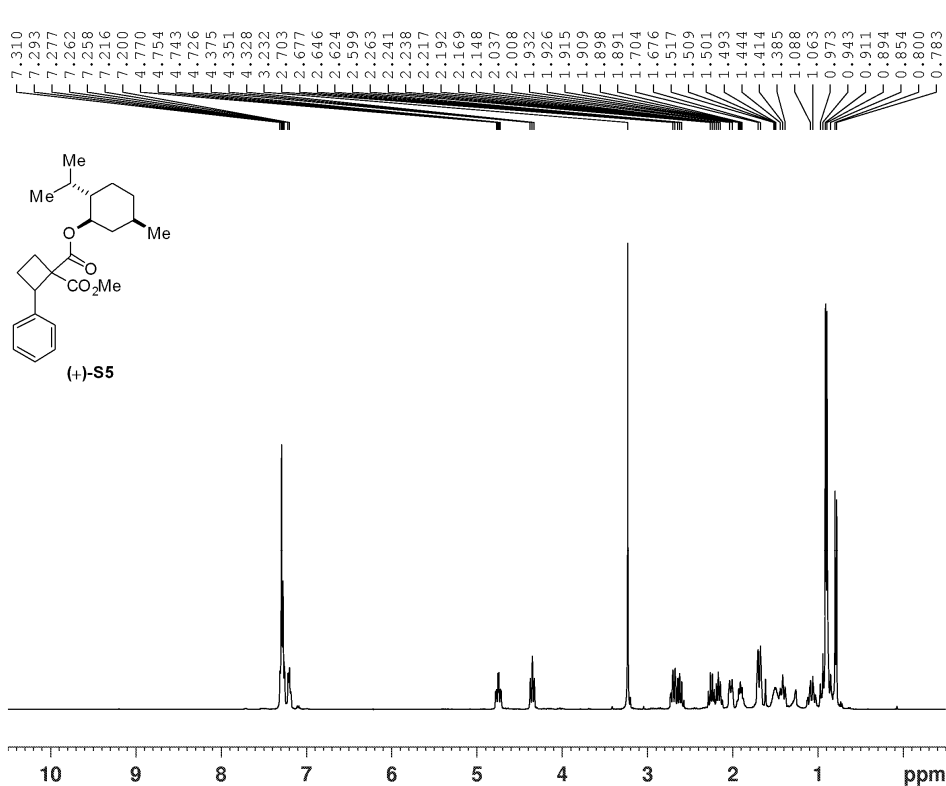
F2 - Acquisition Parameters
Date_ 20090629
Time 6.32
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 1385
DS 2
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 0.683228 sec
RG 16384
DW 20.480 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec
d11 0.0300000 sec
DELTA 0.8999999 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 100.5499020 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.00 dB
SFO2 399.8415994 MHz

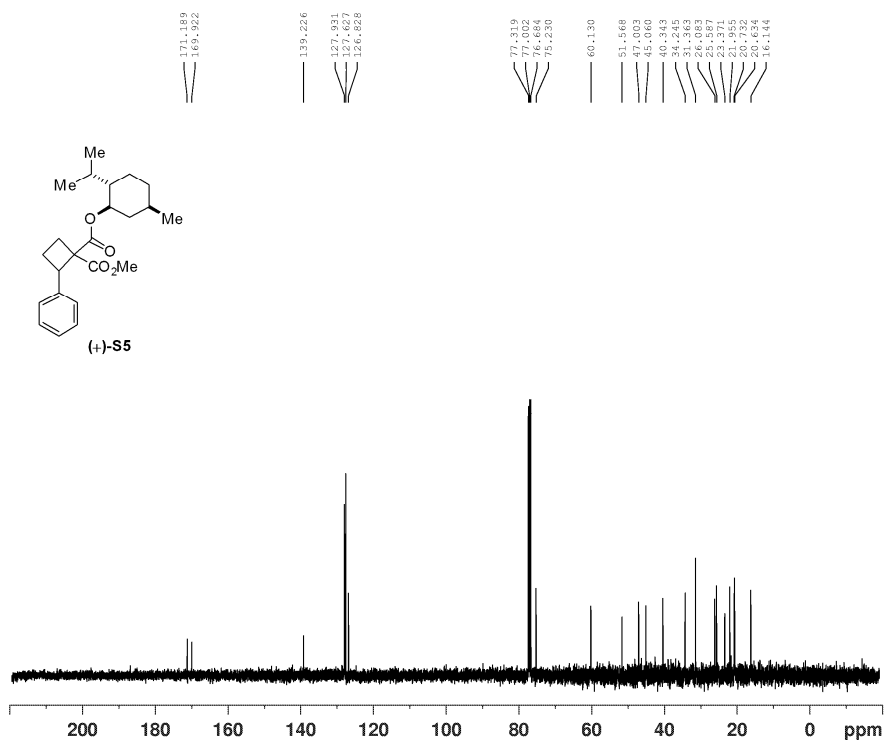
F2 - Processing parameters
SI 32768
SF 100.5398460 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

ATP-VII-161C exp 4 400 MHz WB

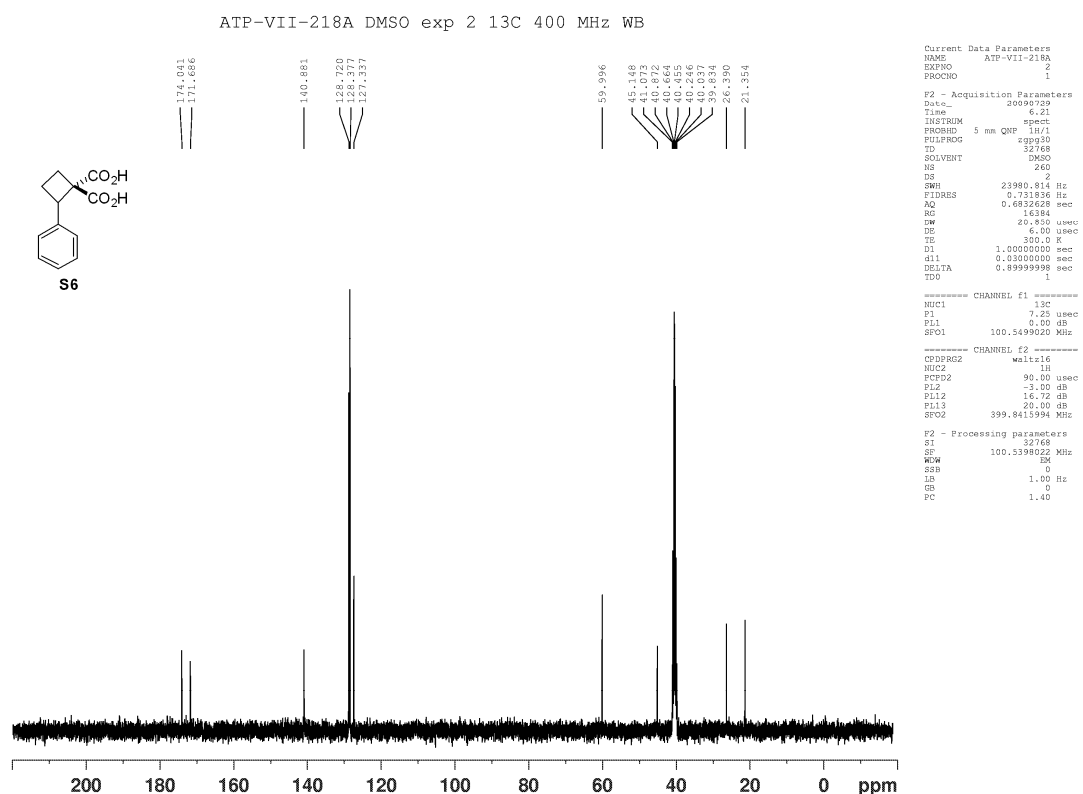
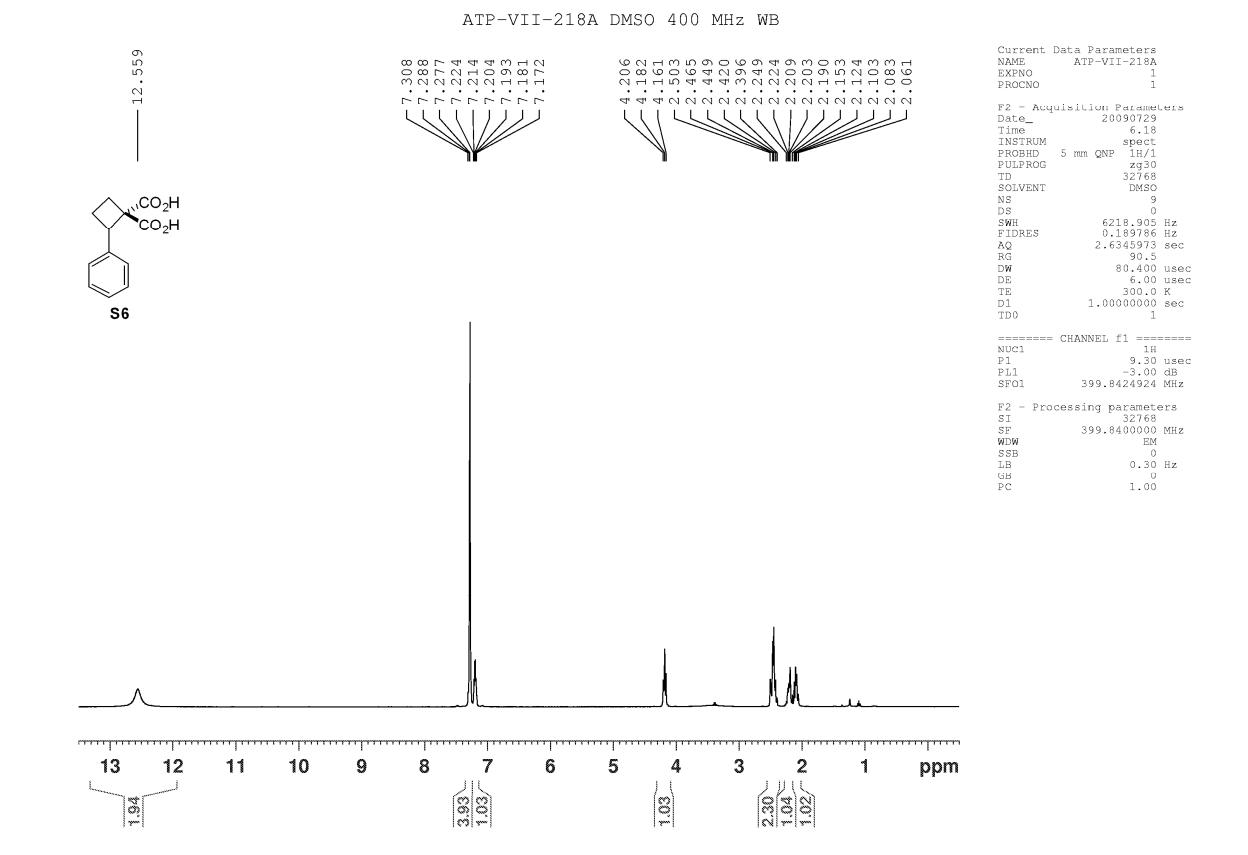


Current Data Parameters
NAME ATP-VII-161C
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090708
Time 8.16
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 6
DS 0
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 80.6
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 399.8424924 MHz
F2 - Processing parameters
SI 32768
SF 399.8400067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

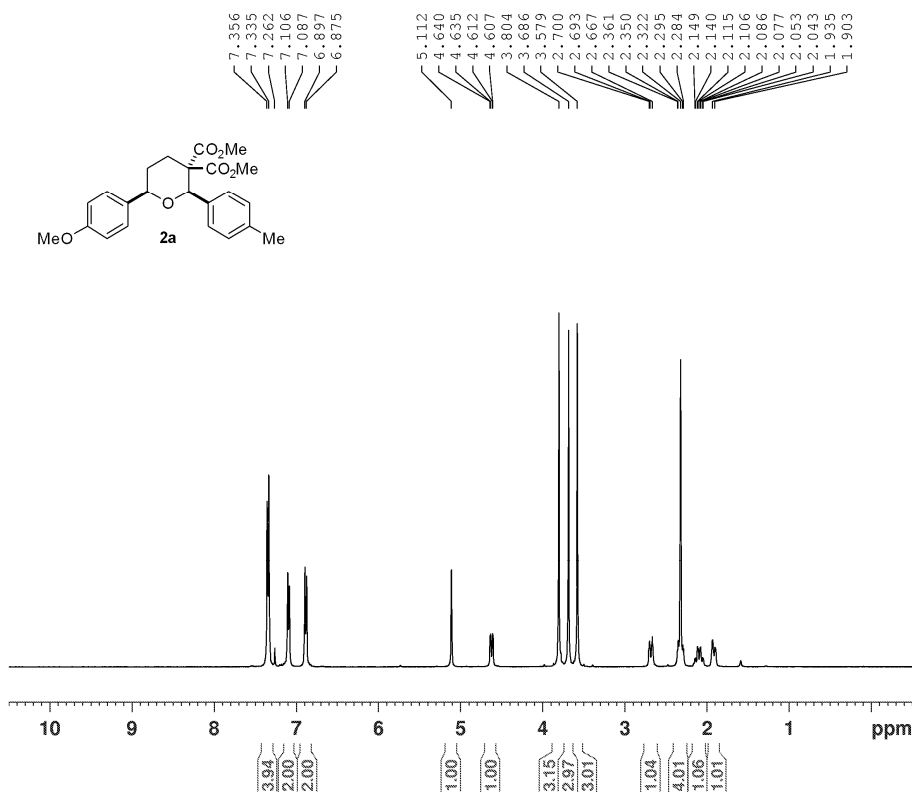
ATP-VII-161C exp 6 13 C 400 MHz WB



Current Data Parameters
NAME ATP-VII-161C
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090708
Time 8.18
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 638
DS 0
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 0.6832628 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999999 sec
TD0
===== CHANNEL f1 =====
NUC1 13C
P1 7.25 usec
PL1 -3.00 dB
SFO1 100.5499020 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.00 dB
SFO2 399.8411994 MHz
F2 - Processing parameters
SI 32768
SF 100.5398489 MHz
WDW DM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



ATP-VII-094C 400 MHz WB



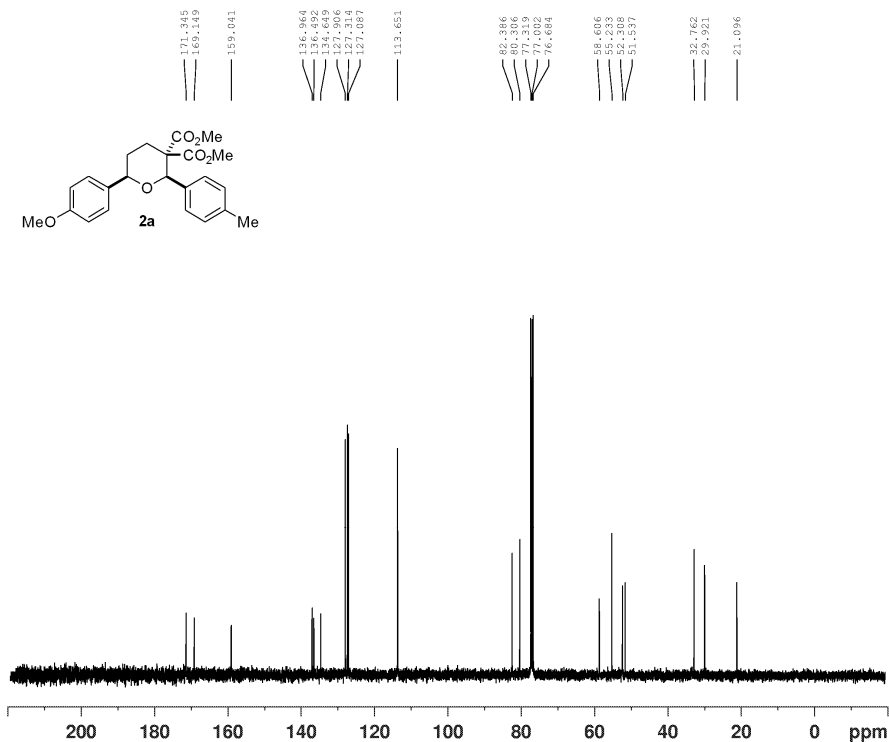
Current Data Parameters
NAME ATP-VII-094C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090427
Time 7.37
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
DS 0
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 90.5
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 399.8424924 MHz

F2 - Processing parameters
SI 32768
SF 399.8400068 MHz
WDW EM
SSB 0
LB 0.05 Hz
GB 0
PC 1.00

ATP-VII-094C exp 3 13C 400 MHz WB



Current Data Parameters
NAME ATP-VII-094C
EXPNO 3
PROCNO 1

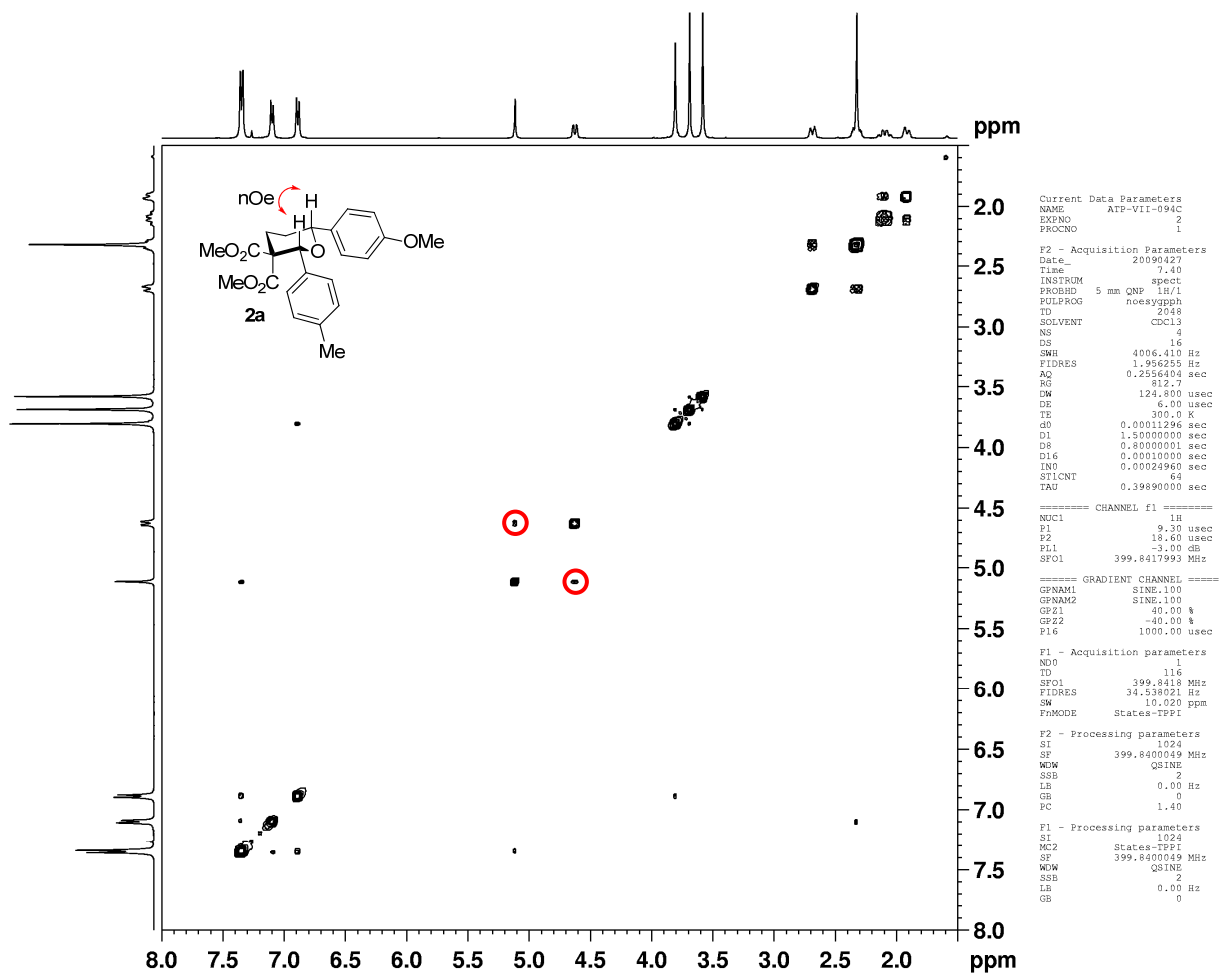
F2 - Acquisition Parameters
Date_ 20090427
Time 8.03
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1019
DS 2
SWH 23980.812 Hz
FIDRES 0.731836 Hz
AQ 0.6812628 sec
RG 16384
DW 20.840 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 100.5499020 MHz

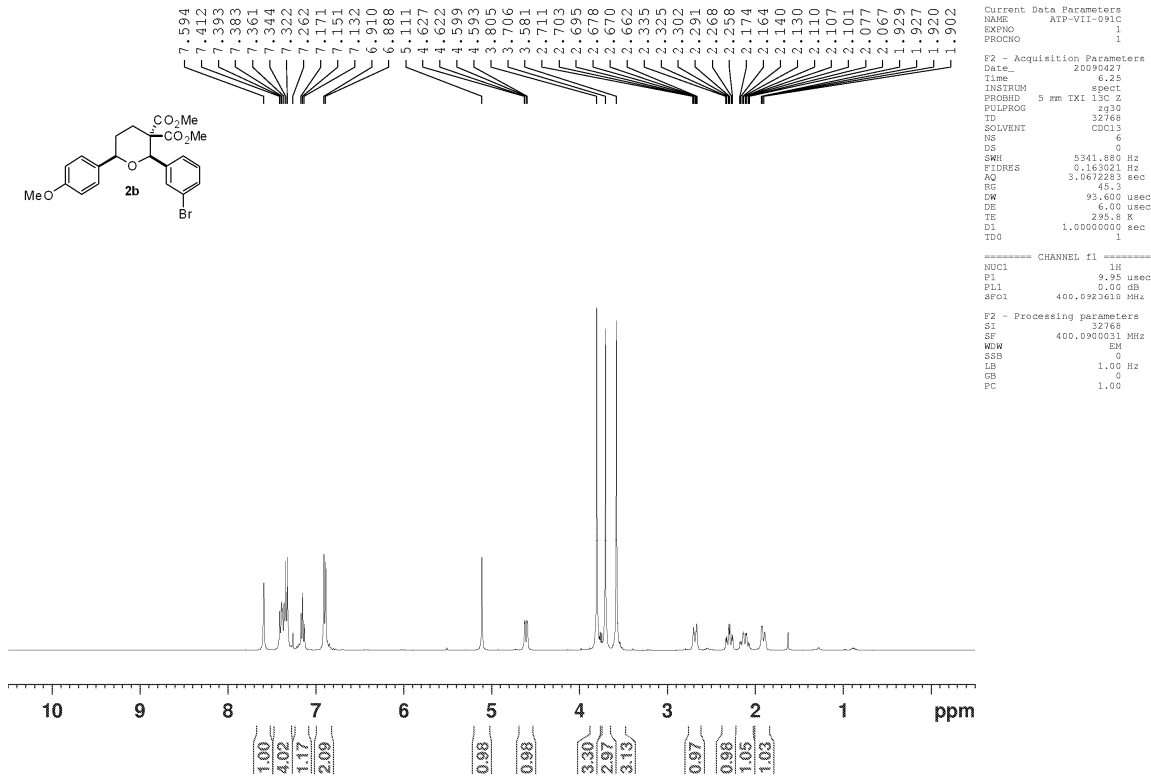
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
F2F22 90.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.00 dB
SFO2 399.8413994 MHz

F2 - Processing parameters
SI 32768
SF 100.5398518 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

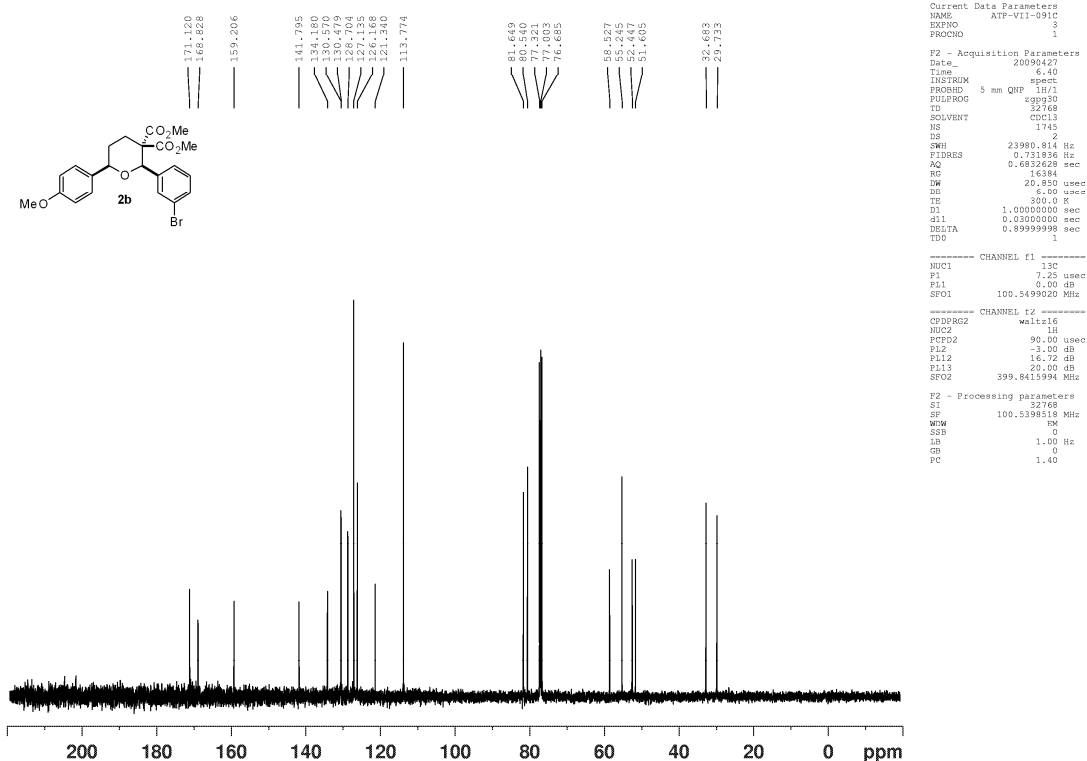
ATP-VII-094C exp 2 NOESY 400 MHz WB



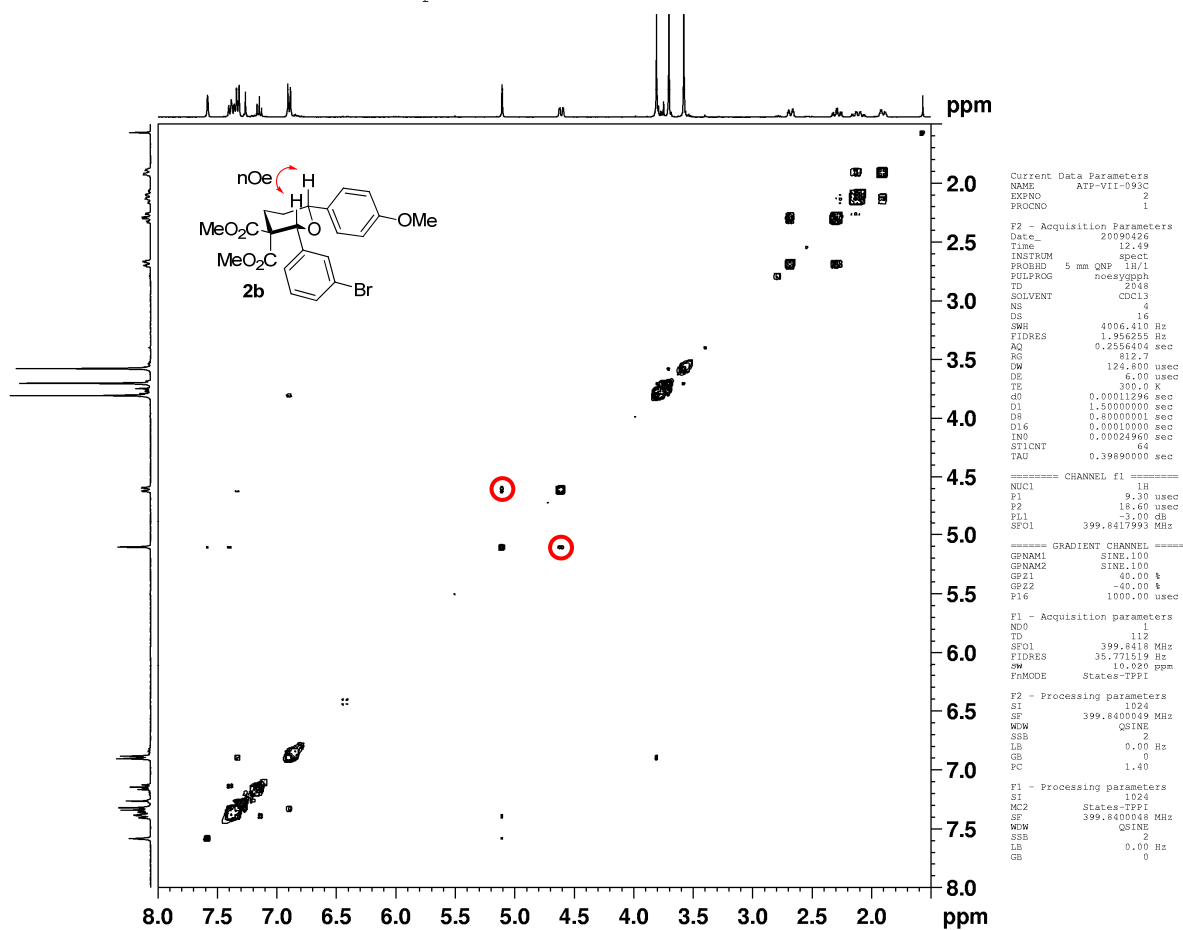
ATP-VII-091C 400 MHz NB



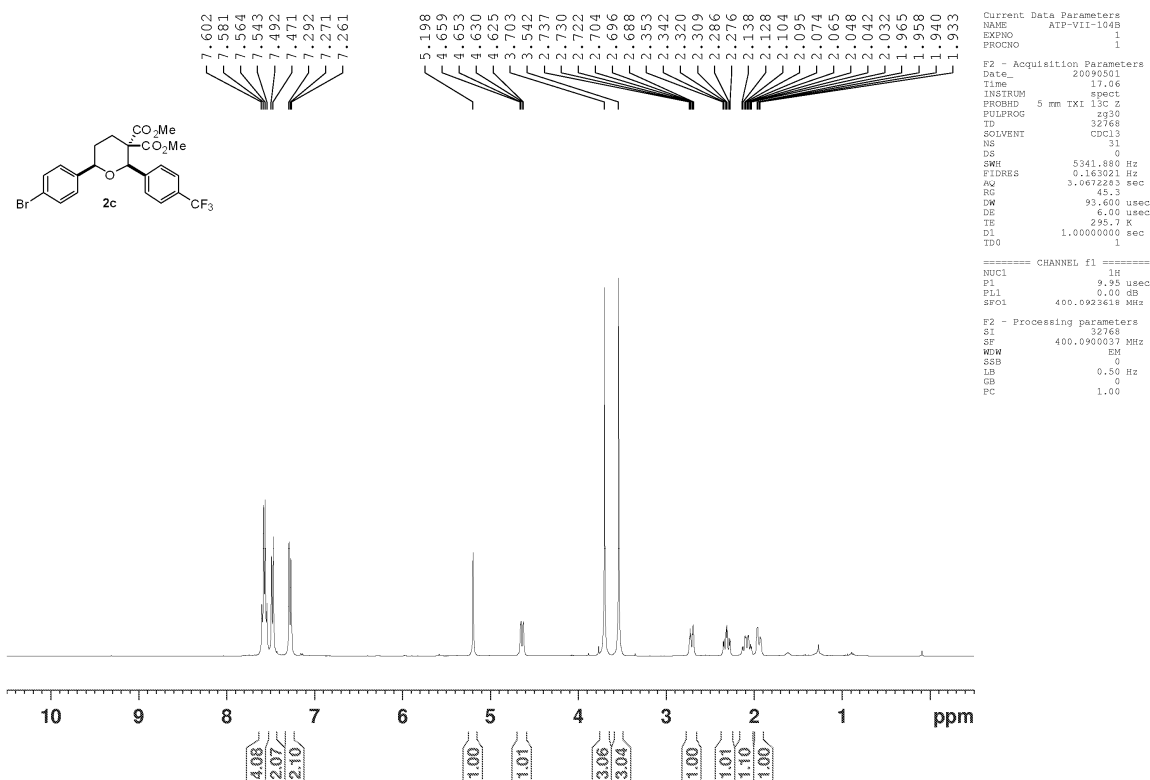
ATP-VII-091C exp 3 13C 400 MHz WB



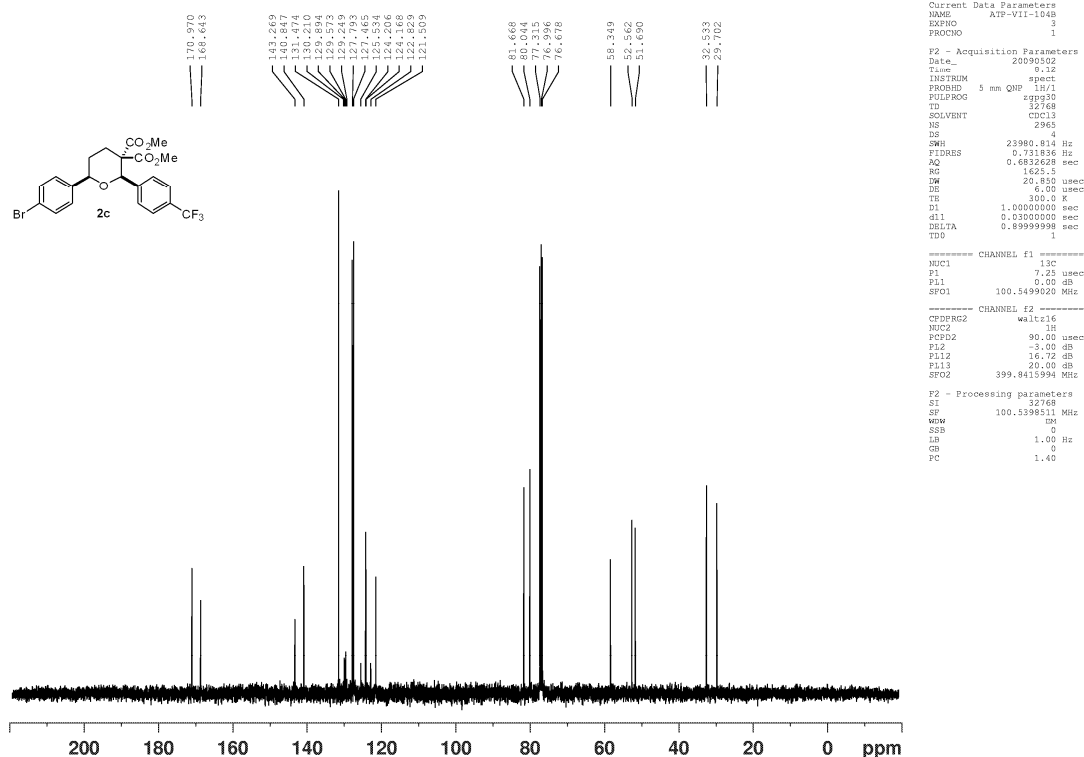
ATP-VII-093C exp 2 NOESY 400 MHz WB



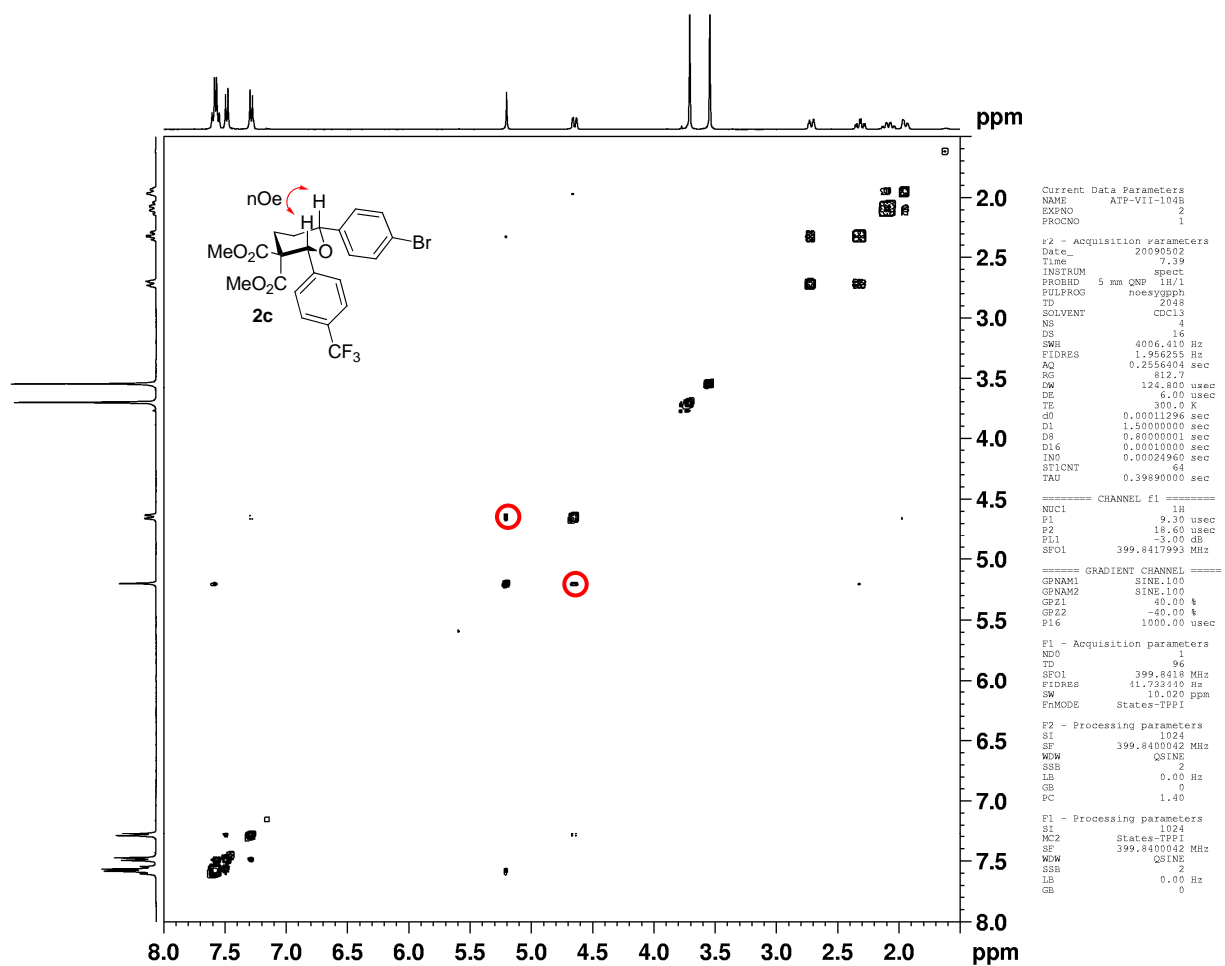
ATP-VII-104B 400 MHz NB



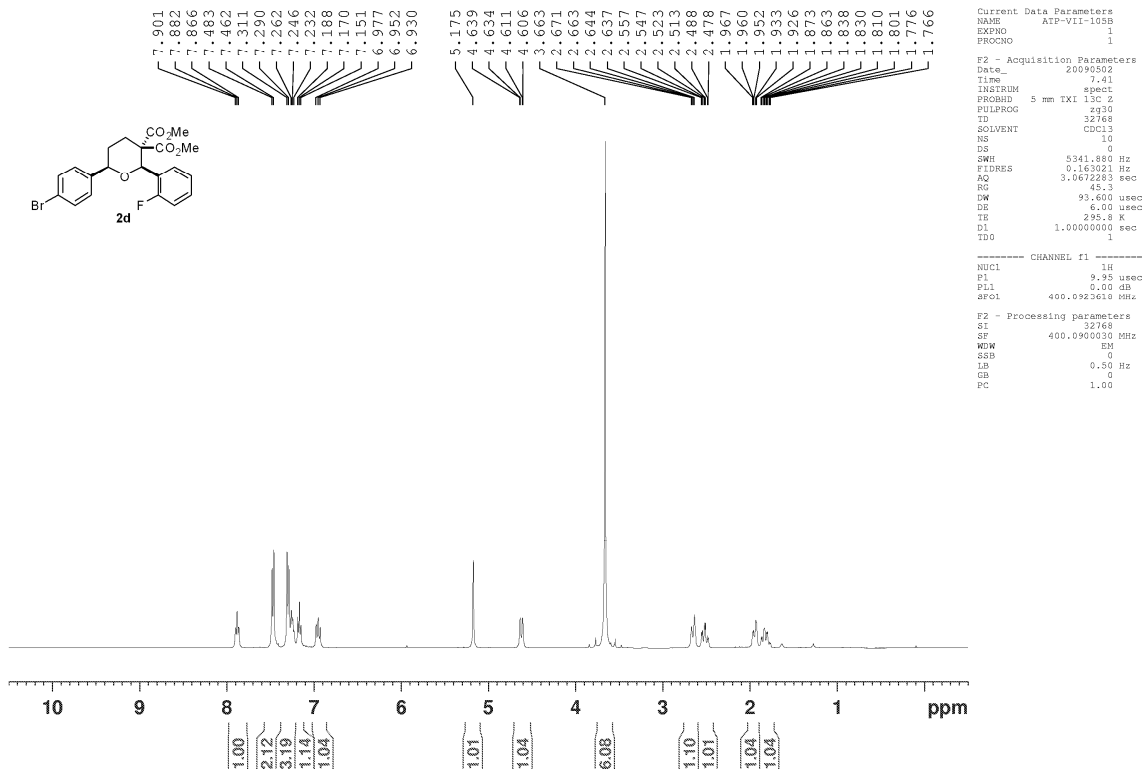
ATP-VII-104B exp 3 13C 400 MHz WB



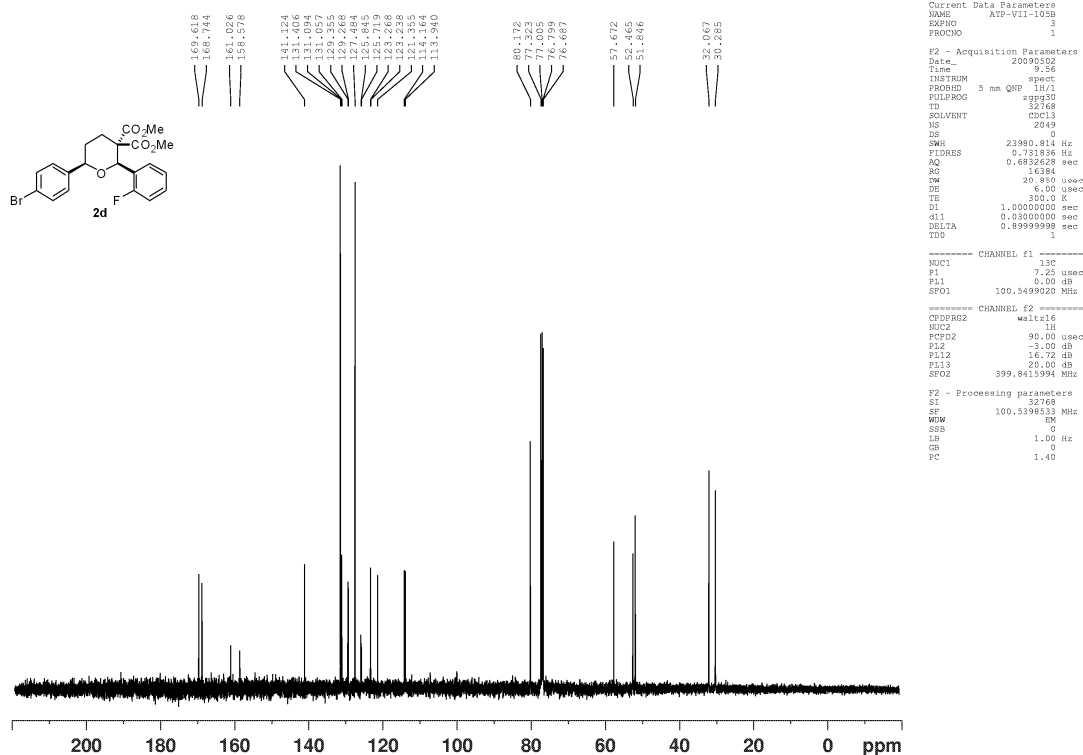
ATP-VII-104B exp 2 NOESY 400 MHz WB



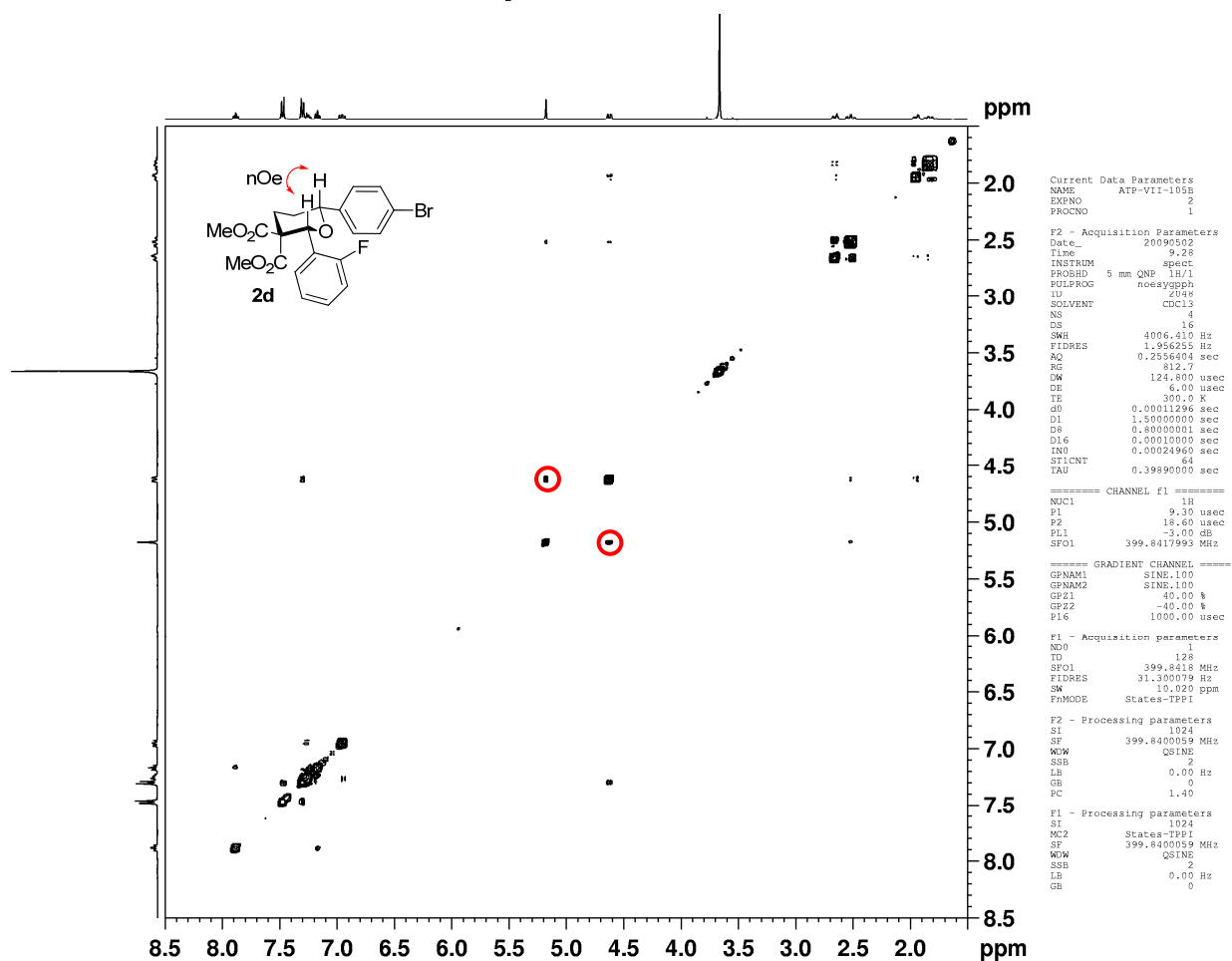
ATP-VII-105B 400 MHz NB



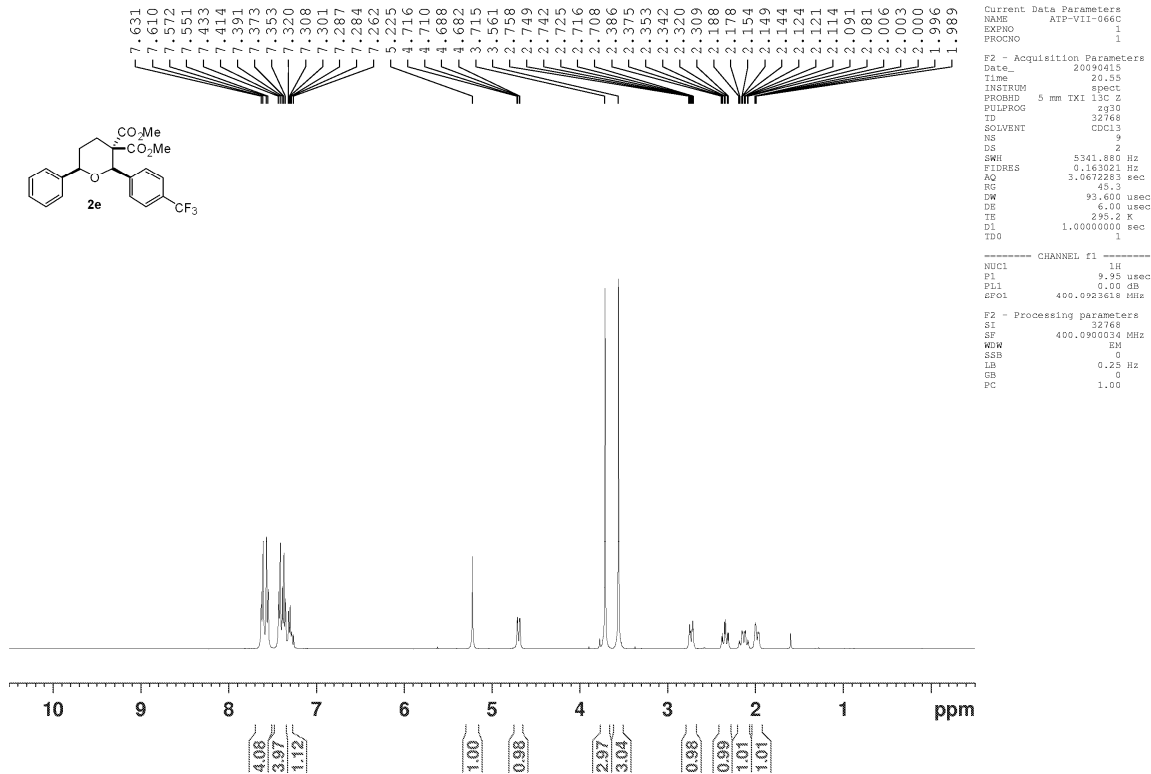
ATP-VII-105B exp 3 13C 400 MHz WB



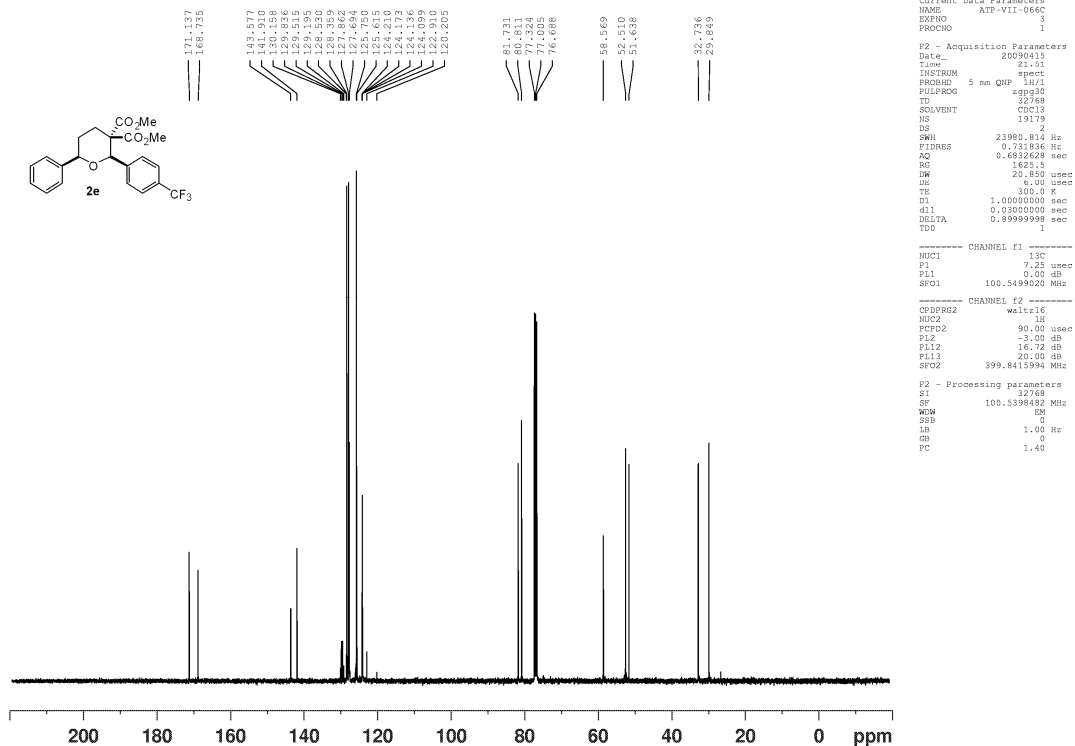
ATP-VII-105B exp 2 NOESY 400 MHz WB



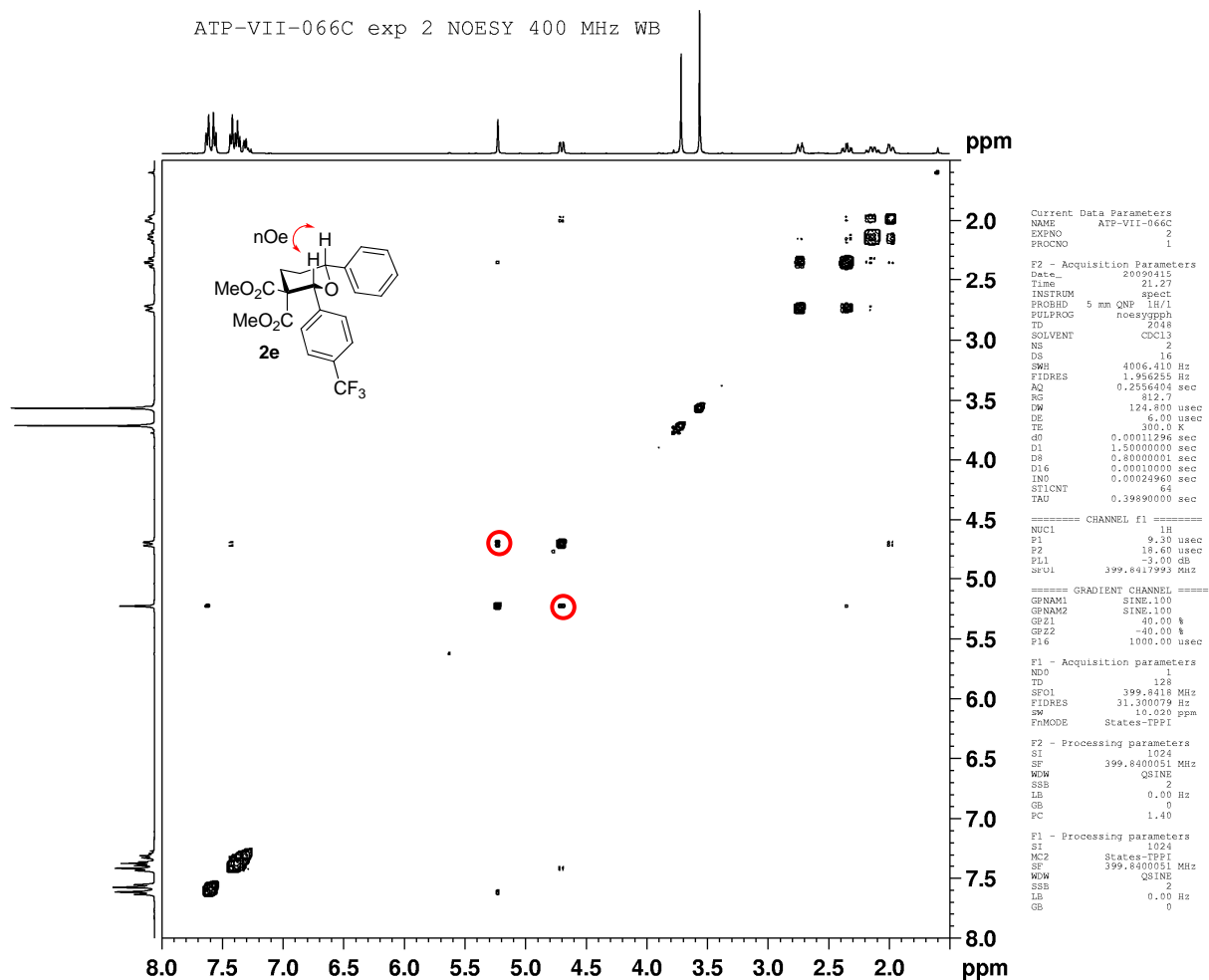
ATP-VII-066C 400 MHz NB



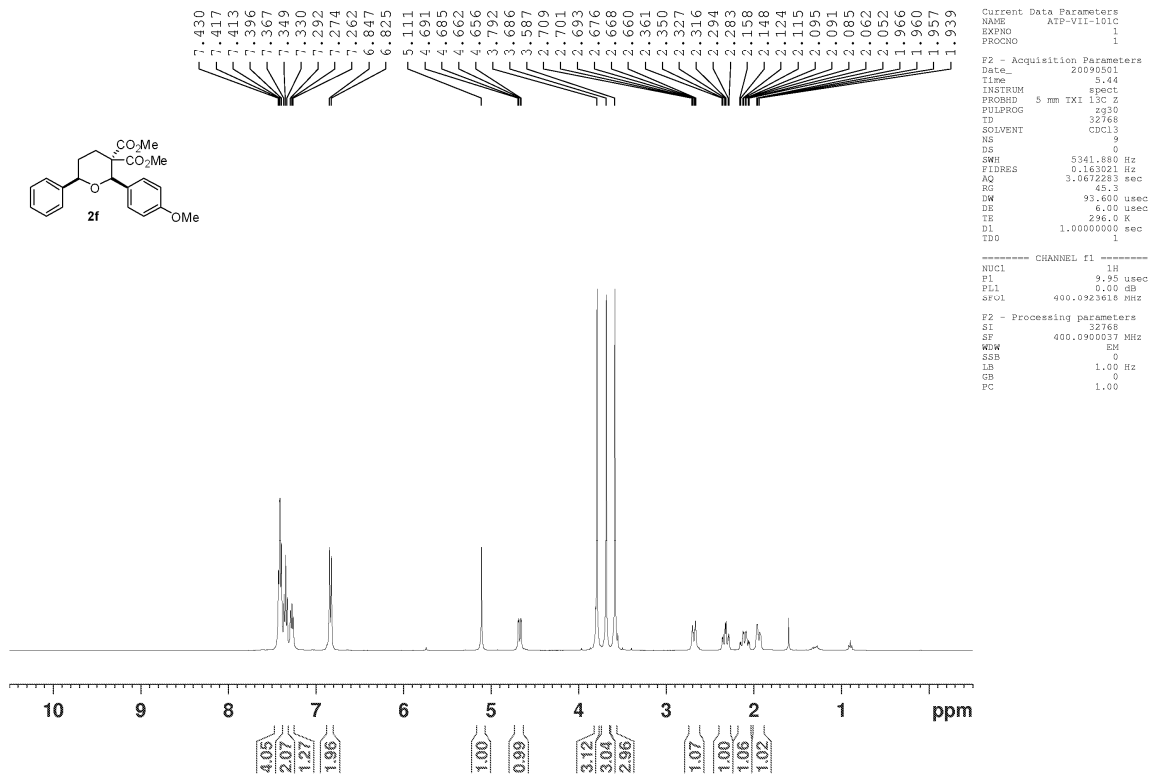
ATP-VII-066C exp 3 13C 400 MHz WB



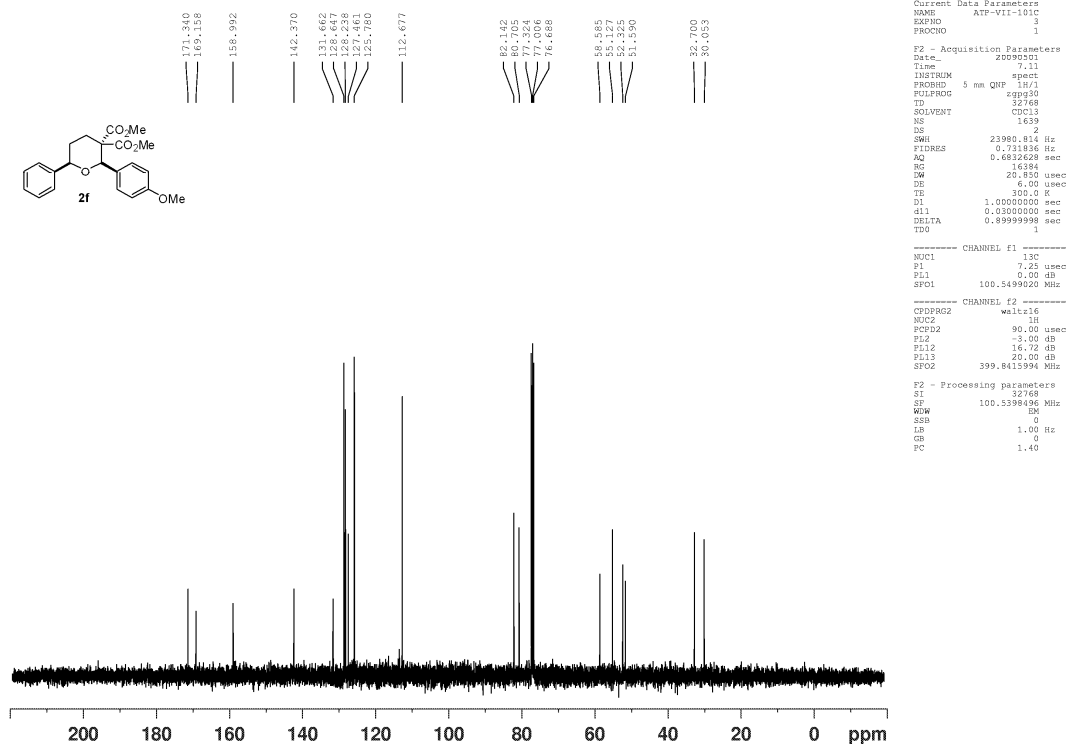
ATP-VII-066C exp 2 NOESY 400 MHz WB



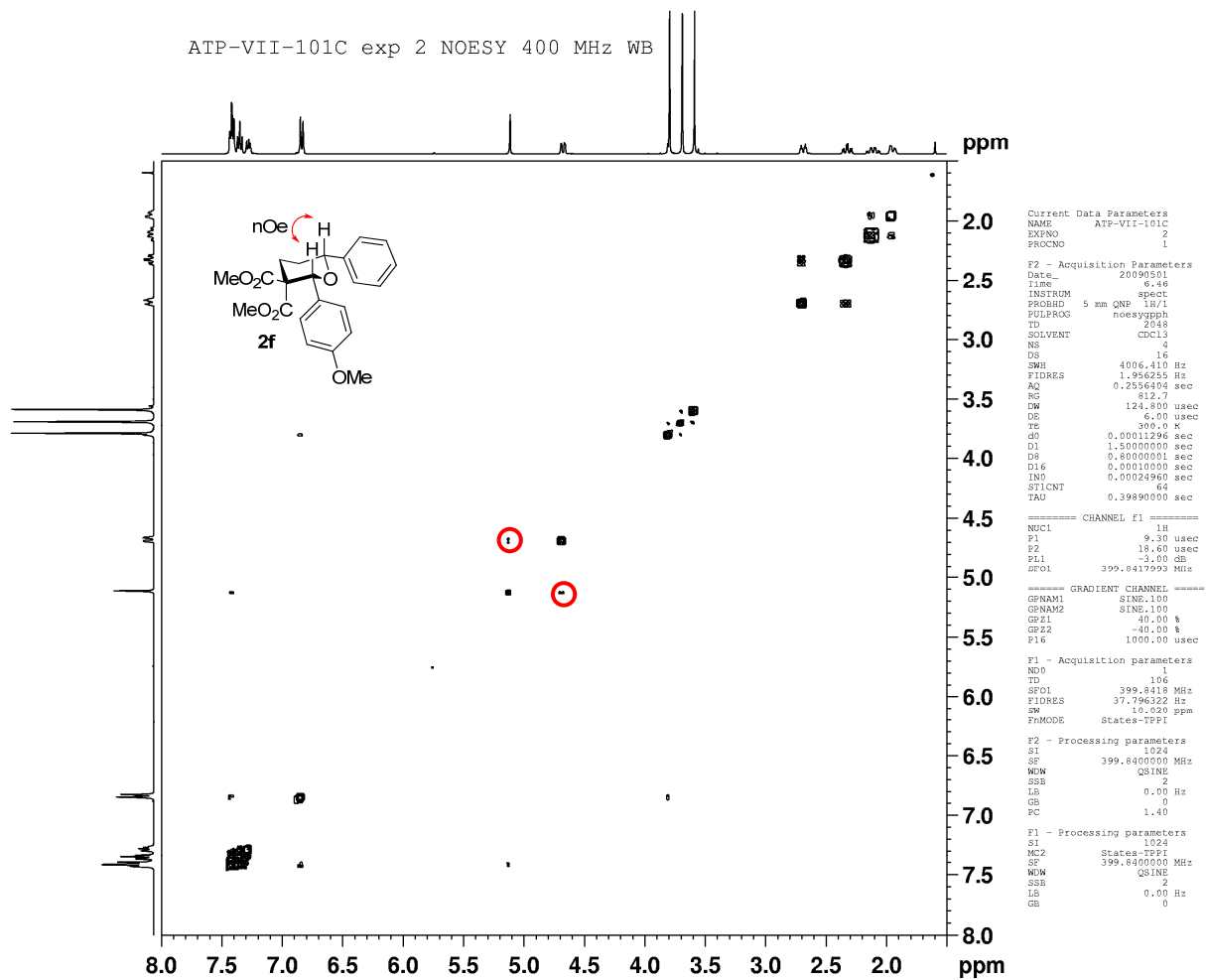
ATP-VII-101C 400 MHz NB



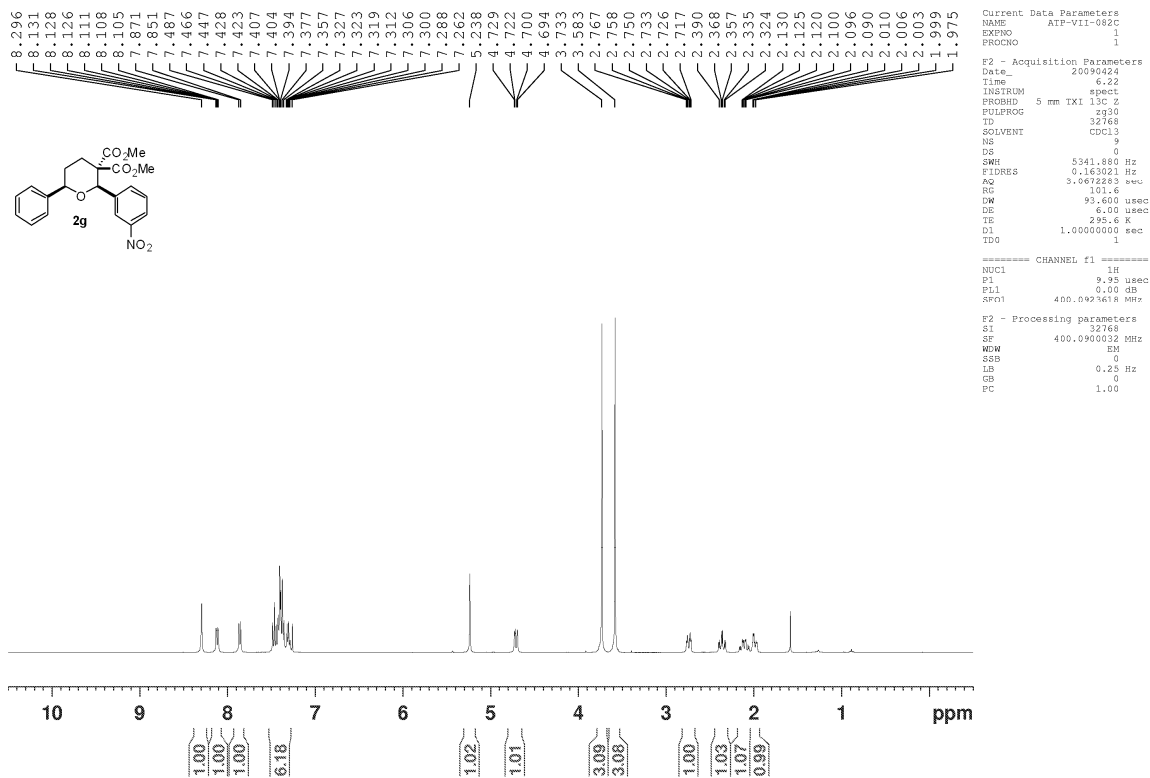
ATP-VII-101C exp 3 13C 400 MHz WB



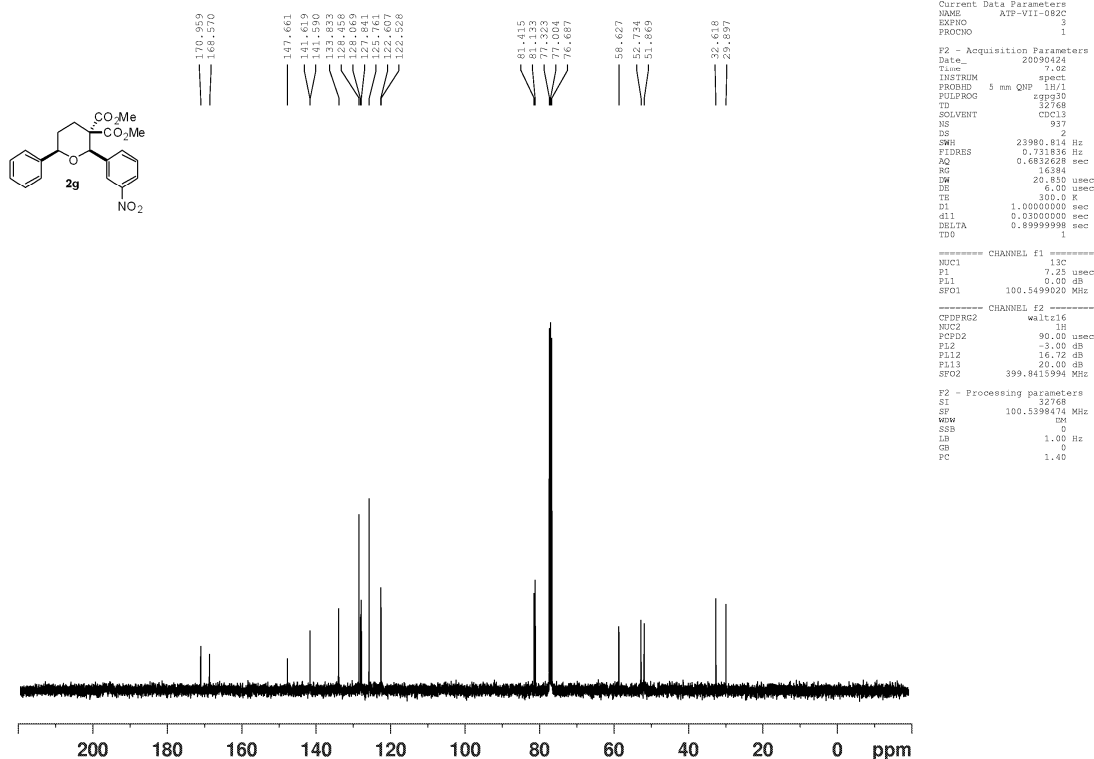
ATP-VII-101C exp 2 NOESY 400 MHz WB



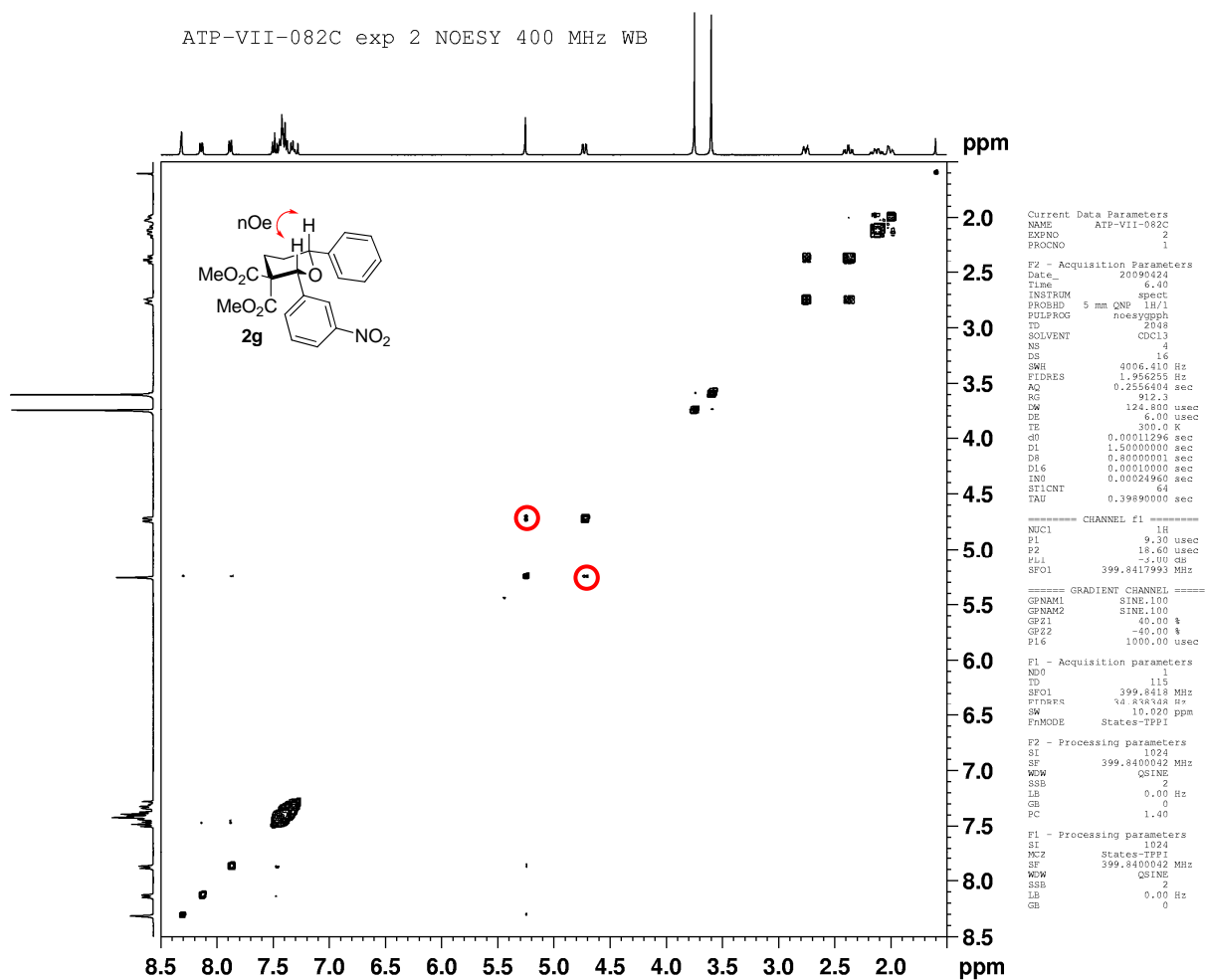
ATP-VII-082C 400 MHz NB



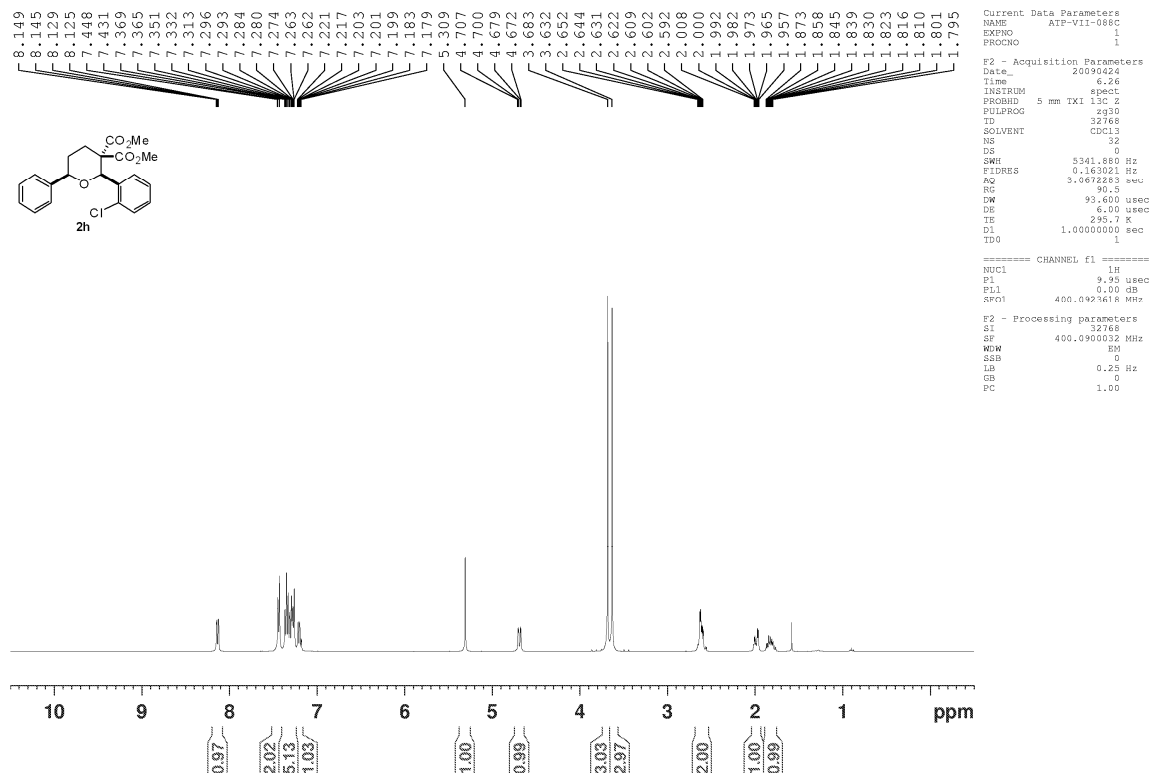
ATP-VII-082C exp 3 13C 400 MHz WB



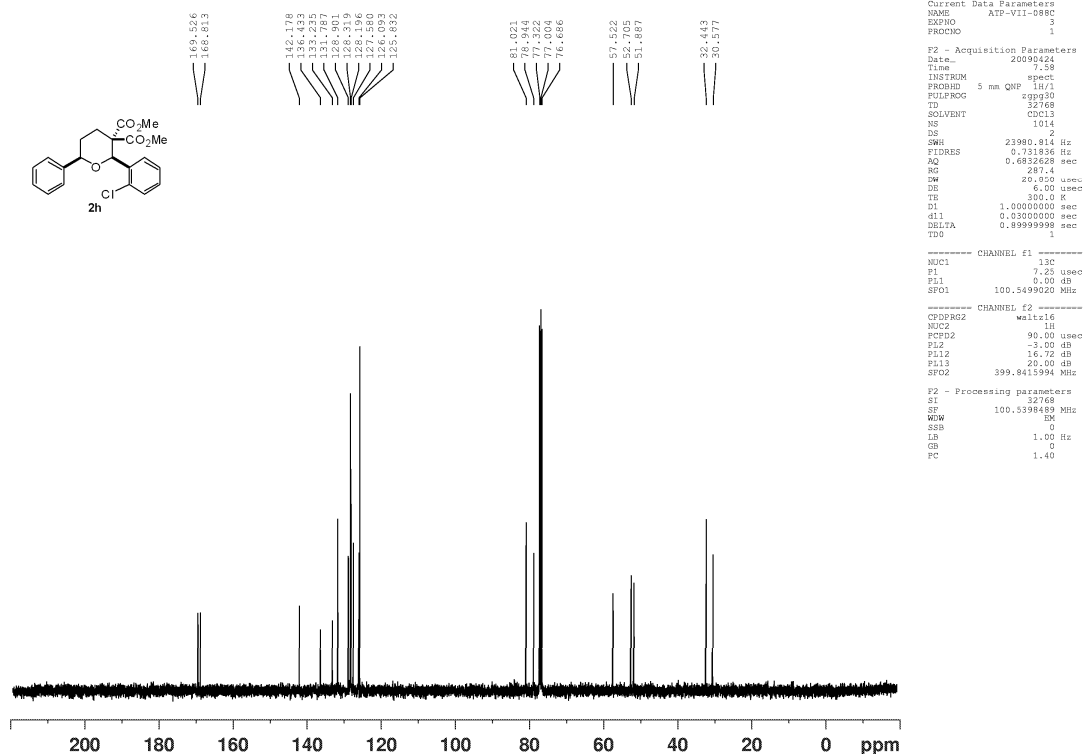
ATP-VII-082C exp 2 NOESY 400 MHz WB



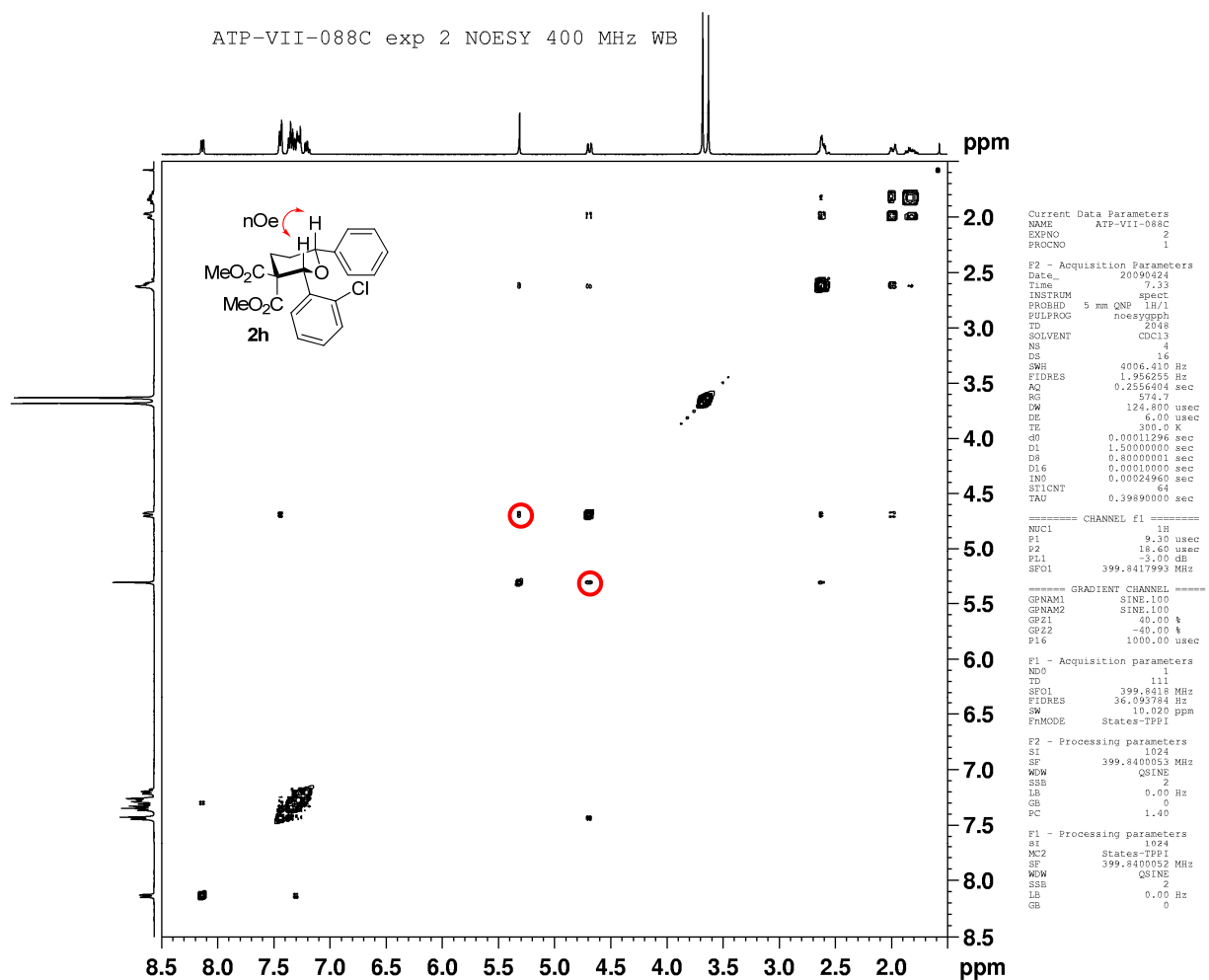
ATP-VII-088C 400 MHz NB



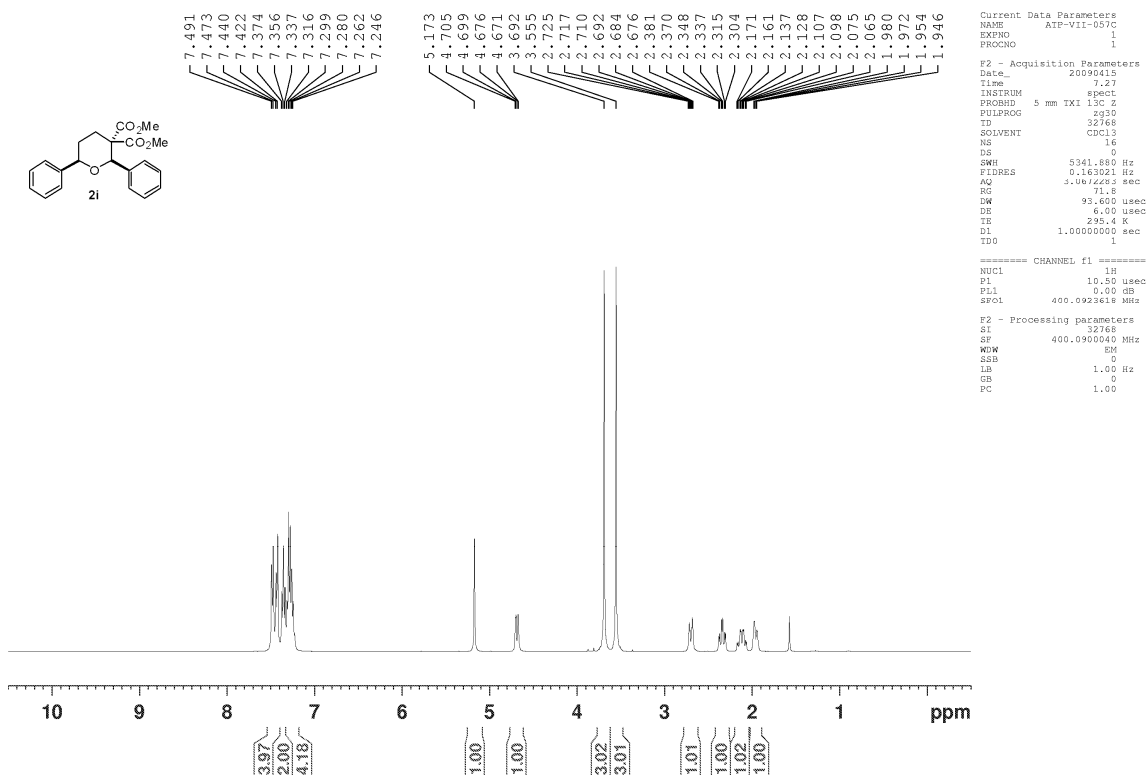
ATP-VII-088C exp 3 13C 400 MHz WB



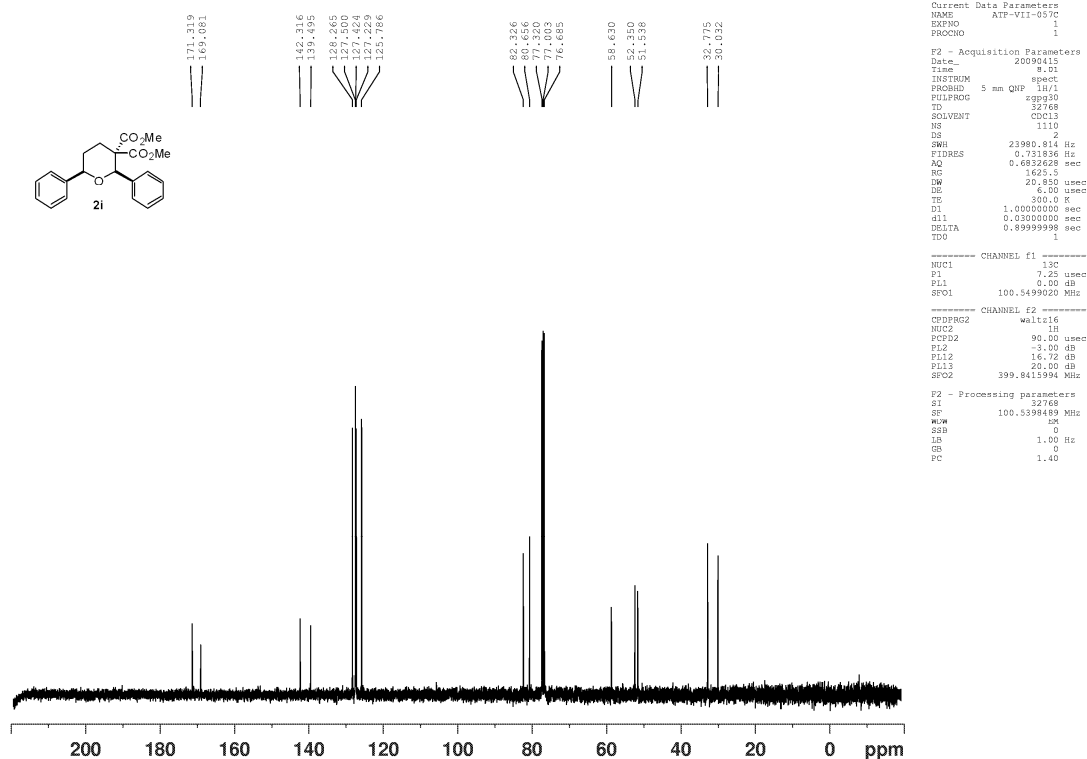
ATP-VII-088C exp 2 NOESY 400 MHz WB

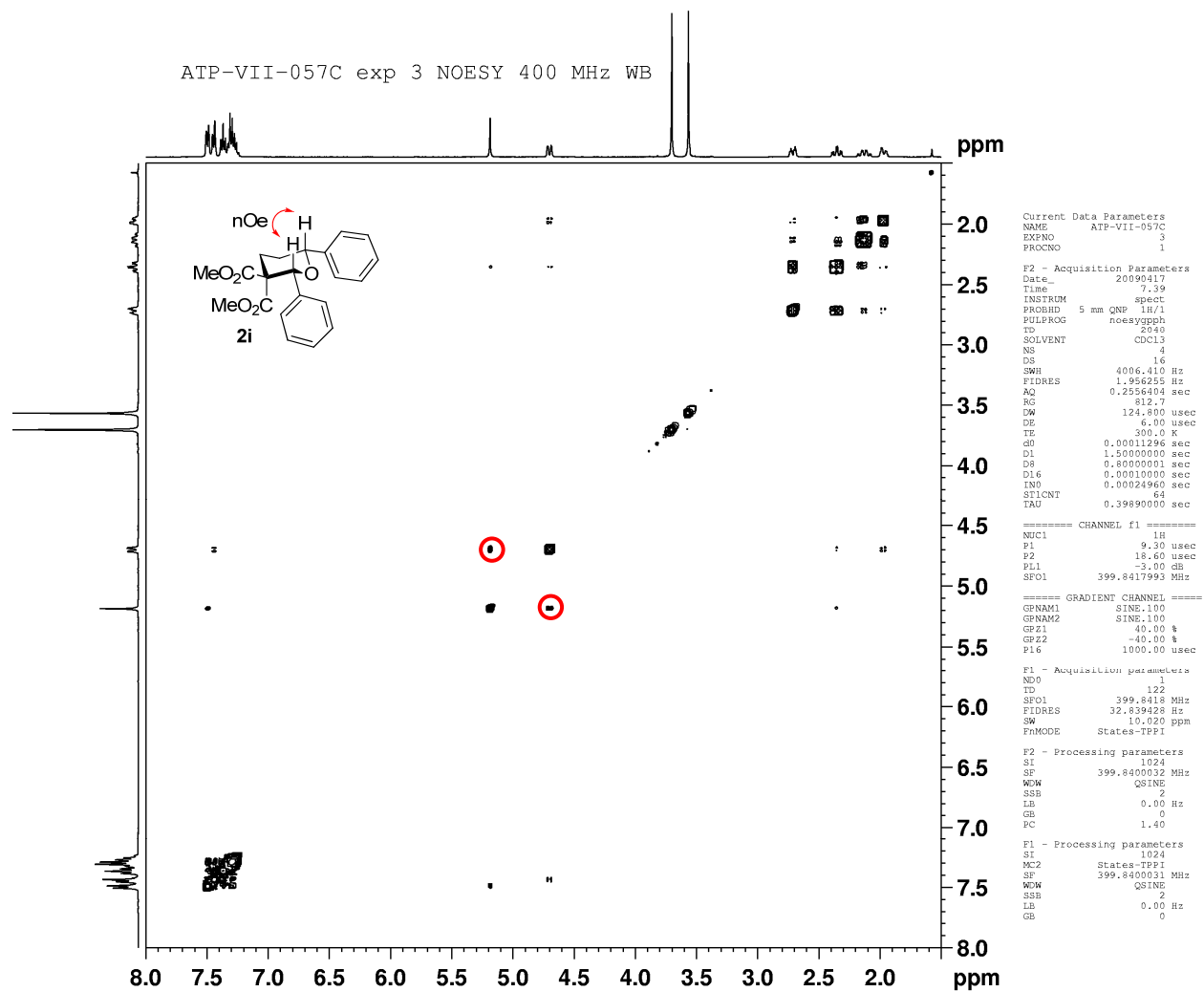


ATP-VII-057C 400 MHz NB



ATP-VII-057C exp 1 13C 400 MHz WB





Chemical structure of **2j**: CC(=C)OC1C(C(=O)OC)C(C(=O)OC)C1c2ccc(Cl)cc2

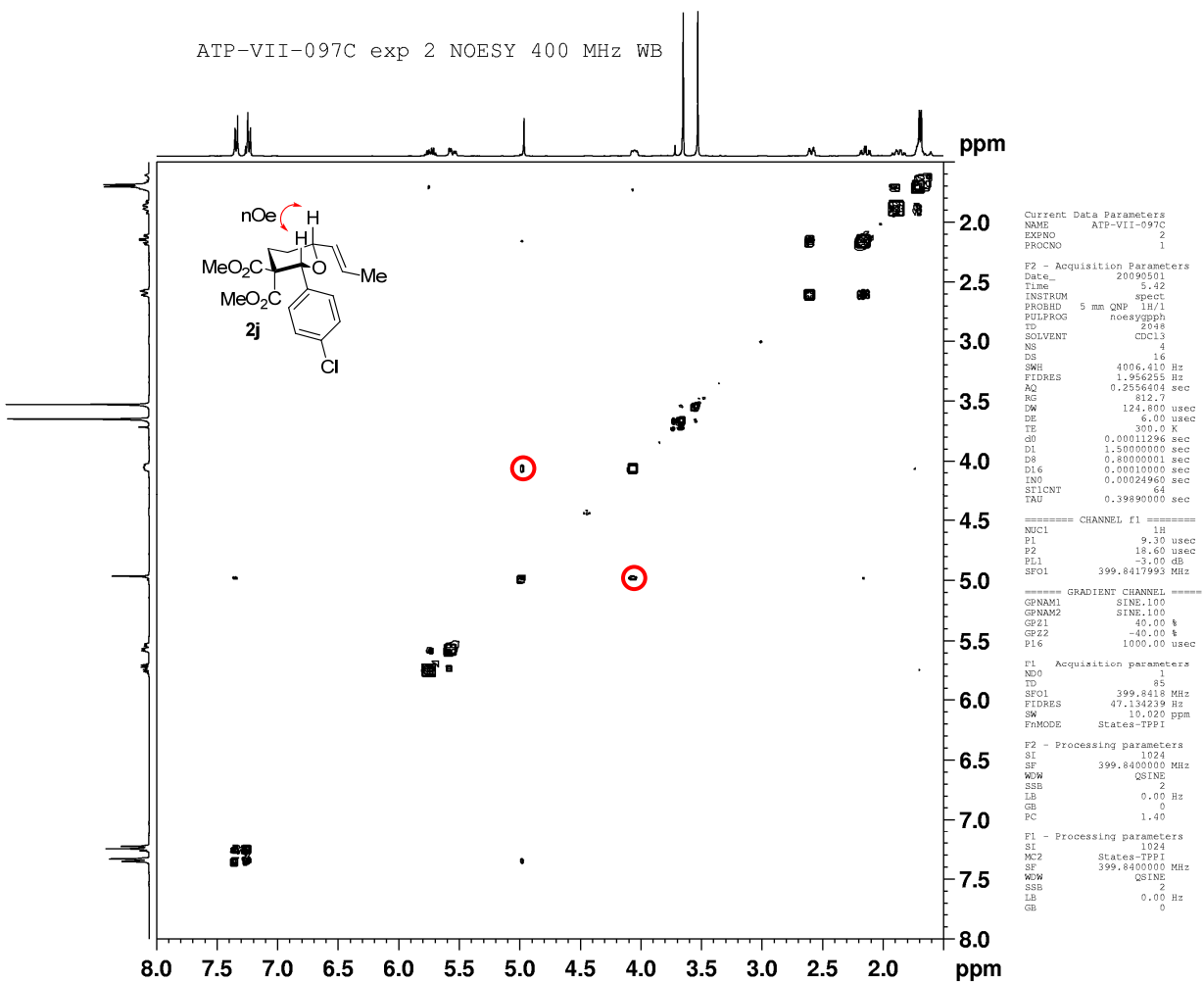
¹H NMR spectrum (CDCl₃) of compound **2j**. The x-axis represents the chemical shift in ppm, ranging from 10 to 0. The spectrum shows several multiplets and singlets. Integration values are provided below the baseline for each major peak group.

Chemical shifts (ppm) listed on the right side of the spectrum:

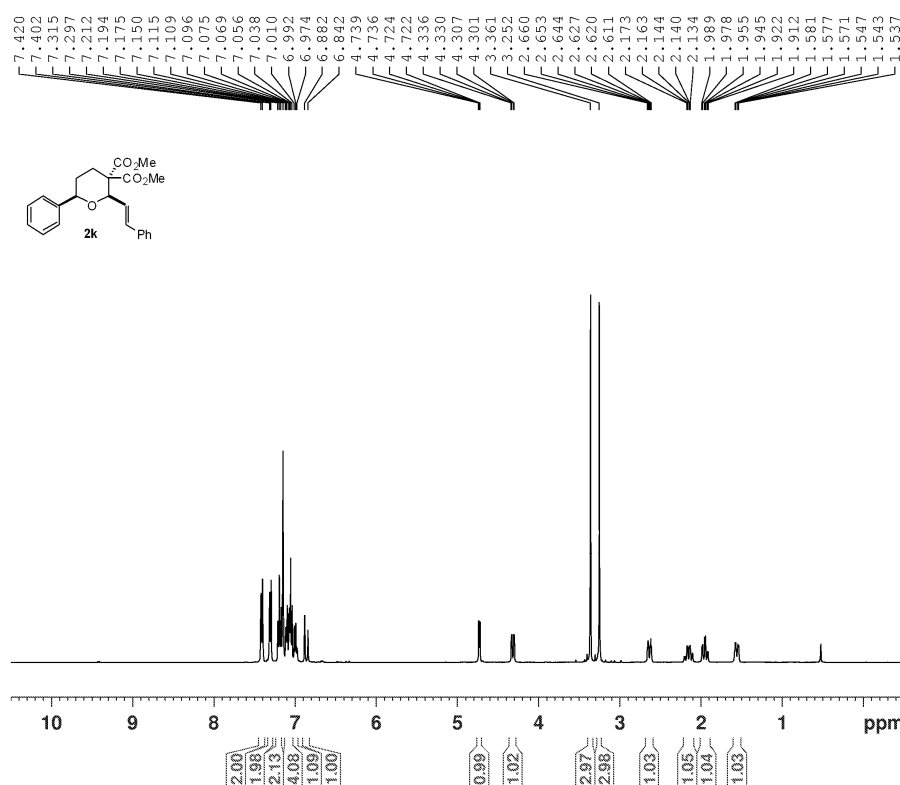
- 7.350, 7.329, 7.262, 7.243, 7.223, 7.179, 7.163, 5.747, 5.725, 5.709, 5.693, 5.581, 5.578, 5.566, 5.563, 5.543, 5.540, 5.528, 5.524, 4.963, 4.069, 4.051, 4.030, 2.614, 2.606, 2.597, 2.580, 2.572, 2.564, 2.183, 2.172, 2.150, 2.139, 2.116, 2.105, 1.926, 1.915, 1.912, 1.892, 1.882, 1.863, 1.853, 1.829, 1.819, 1.787, 1.687

Integration values (from left to right): 2.03, 2.14, 0.98, 1.04, 1.00, 0.98, 3.09, 3.05, 1.01, 1.08, 1.12, 4.11.

[illegible]



ATP-VII-126D C6D6 400 MHz WB



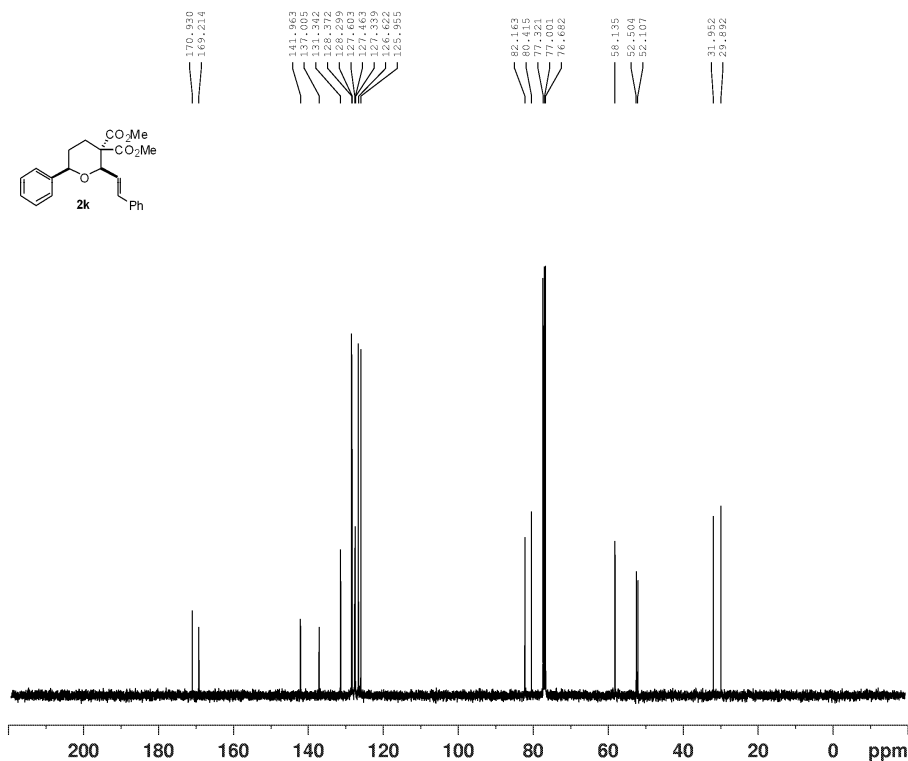
Current Data Parameters
 NAME ATP-VII-126D
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20090525
 Time 7.08
 INSTRUM spect
 PROBHD 5 mm QNP
 PULPROG zg30
 TD 32768
 SOLVENT C6D6
 NS 11
 DS 0
 SWH 6218.905 Hz
 FTHRR 0.184344 Hz
 AQ 2.6345973 sec
 RG 512
 DW 80.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.30 usec
 PL1 -3.00 dB
 SFO1 399.8424924 MHz

F2 - Processing parameters
 SI 32768
 SF 399.8400467 MHz
 WDW EM
 SSB 0
 LB 0.50 Hz
 GB 0
 PC 1.00

ATP-VII-126C exp 3 13C 400 MHz WB



Current Data Parameters
 NAME ATP-VII-126C
 EXPNO 3
 PROCNO 1

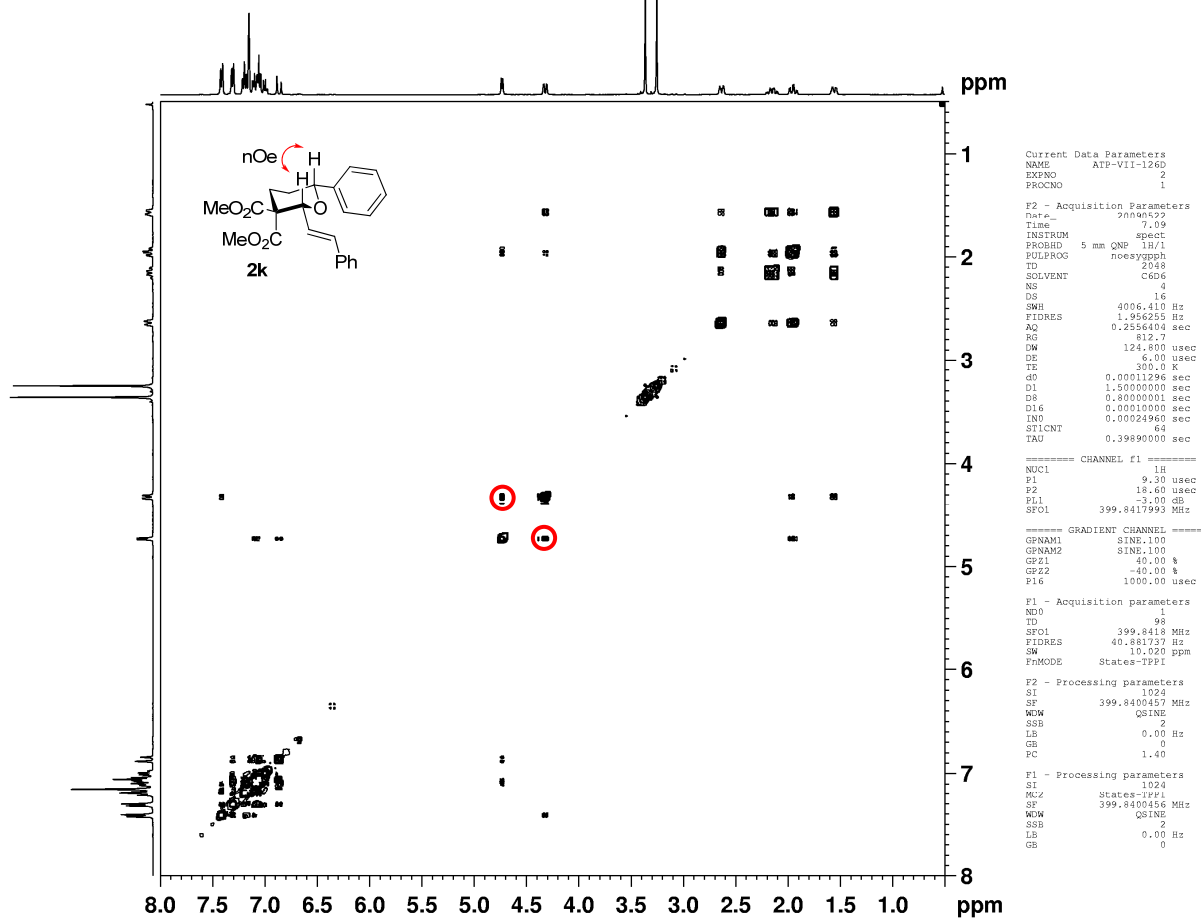
F2 - Acquisition Parameters
 Date_ 20090518
 Time 6.55
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 1416
 DS 2
 SWH 23980.814 Hz
 FIDRES 0.731836 Hz
 AQ 0.6822628 sec
 RG 16384
 DW 20.850 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 DELTA 0.89999999 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 7.25 usec
 PL1 0.00 dB
 SFO1 100.5499020 MHz

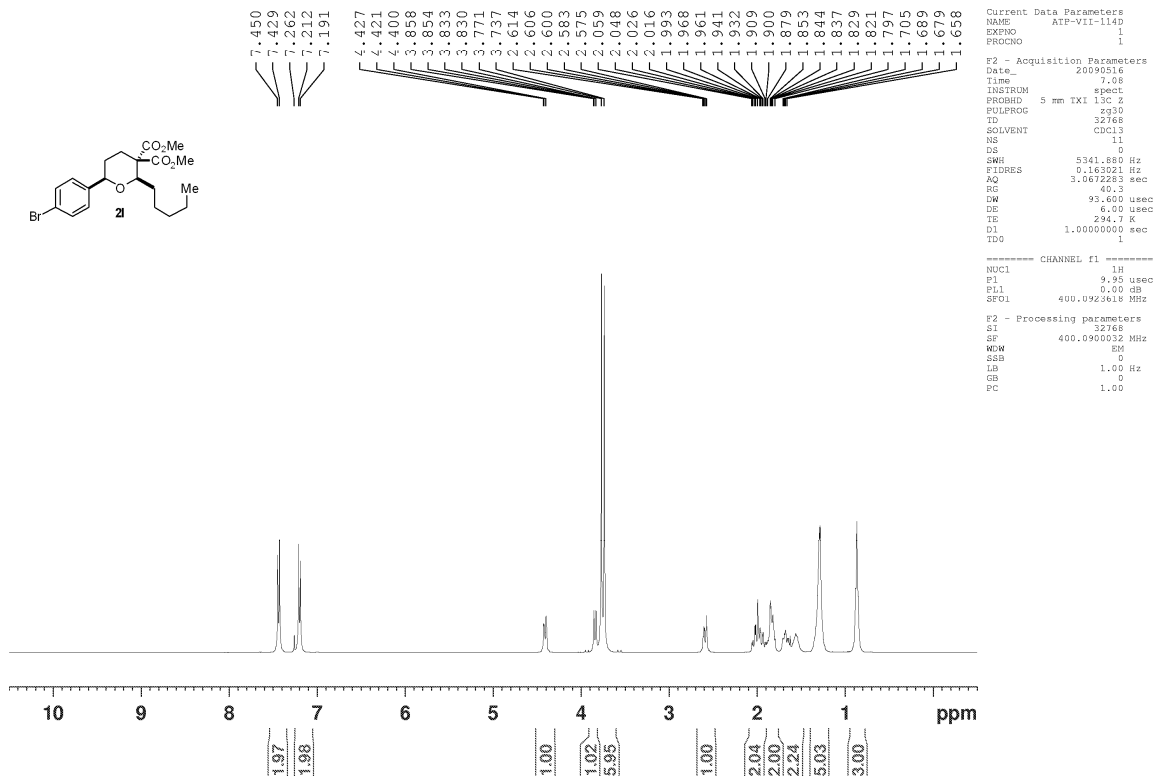
===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 P2 90.00 usec
 F2 90.00 dB
 PL2 16.72 dB
 PL13 20.00 dB
 SFO2 399.8413994 MHz

F2 - Processing parameters
 SI 32768
 SF 100.5398540 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

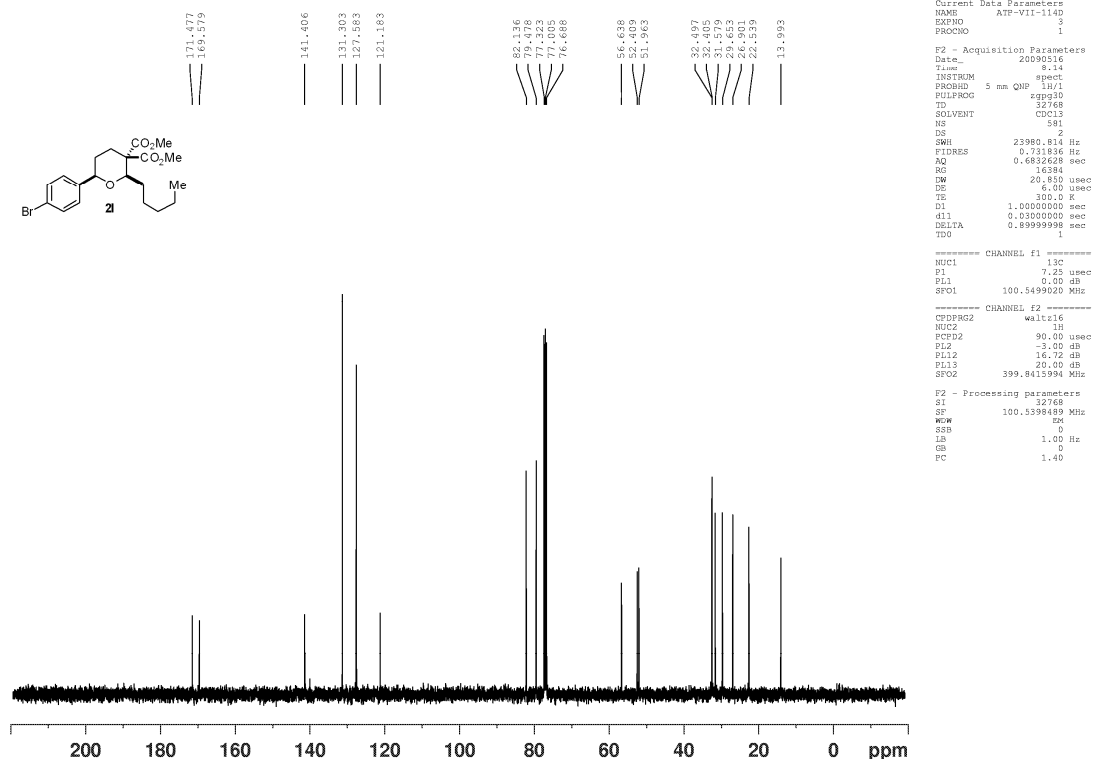
ATP-VII-126D exp 2 NOESY C6D6 400 MHz WB



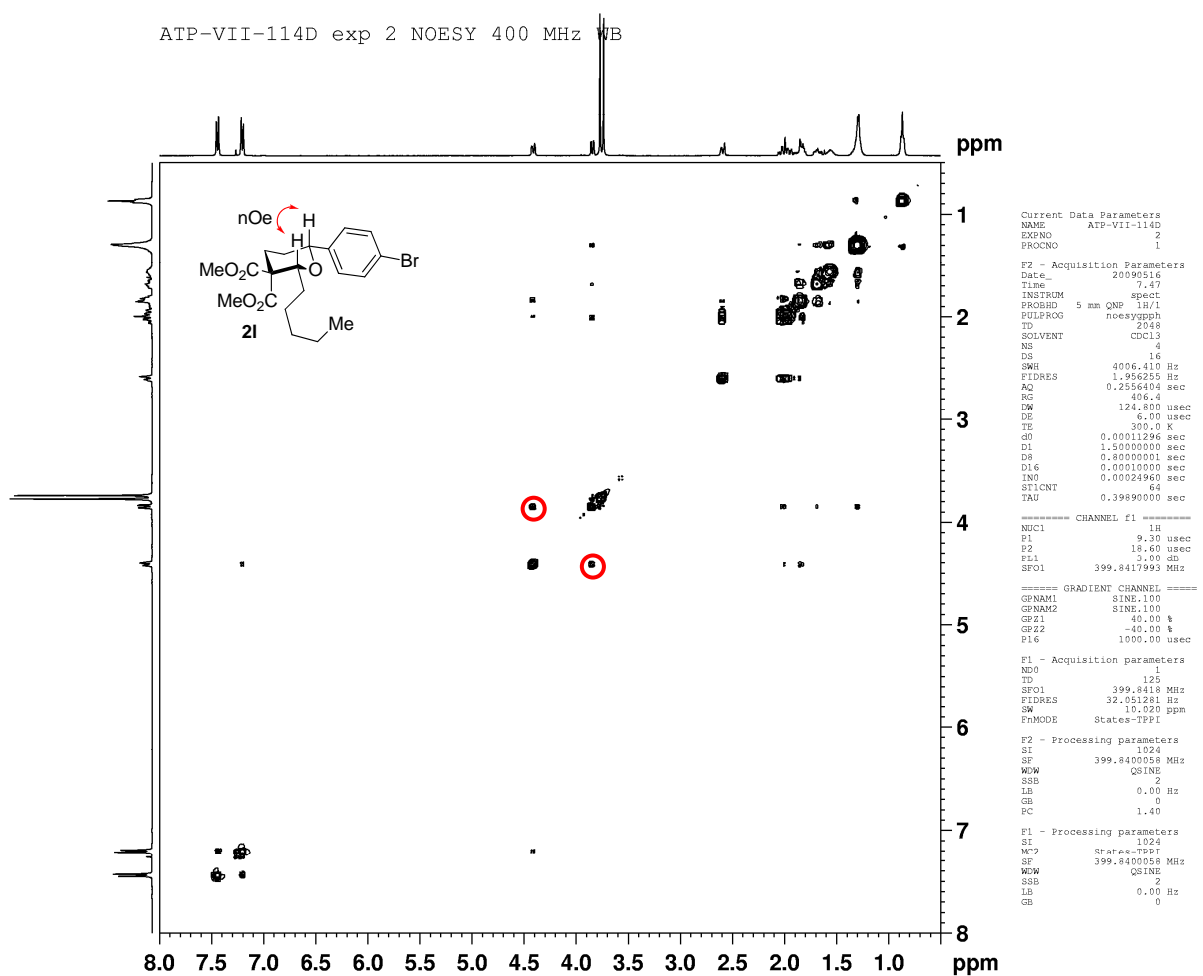
ATP-VII-114D 400 MHz NB



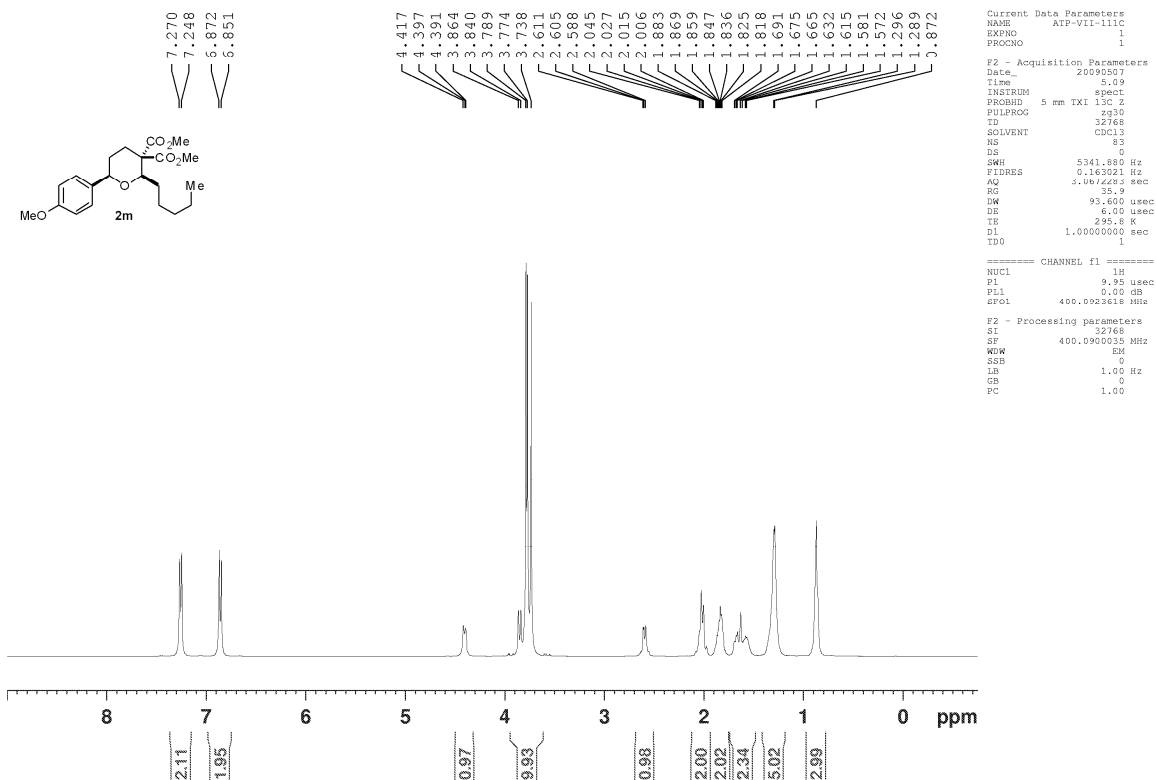
ATP-VII-114D exp 3 13C 400 MHz WB



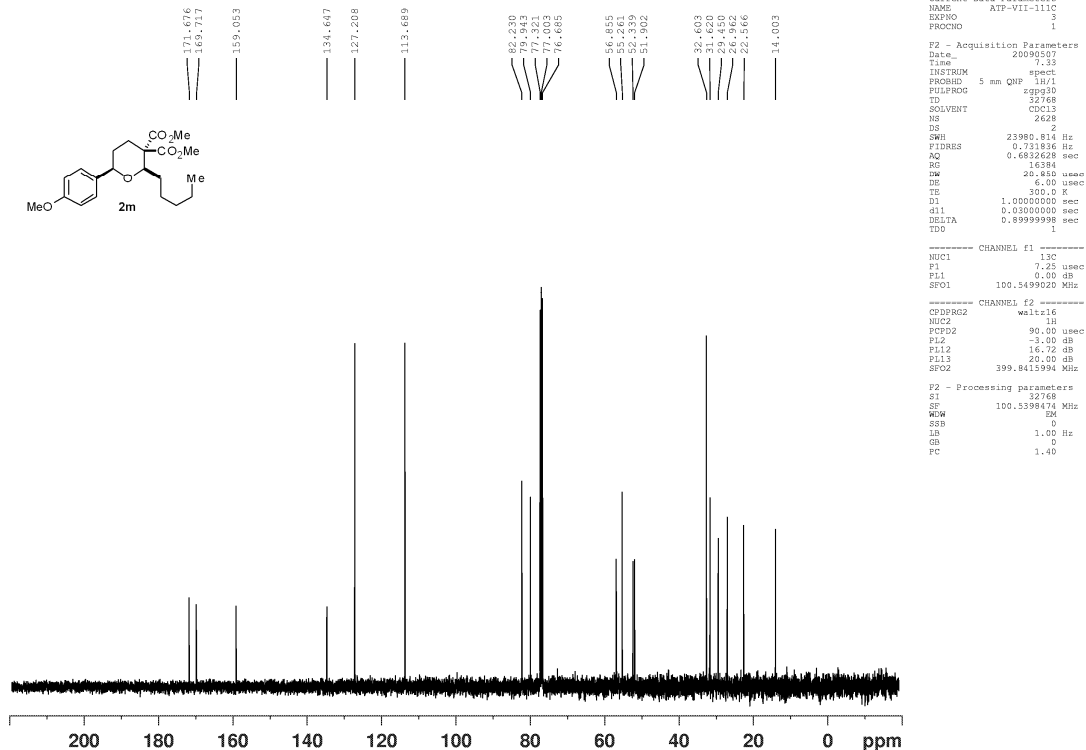
ATP-VII-114D exp 2 NOESY 400 MHz WB



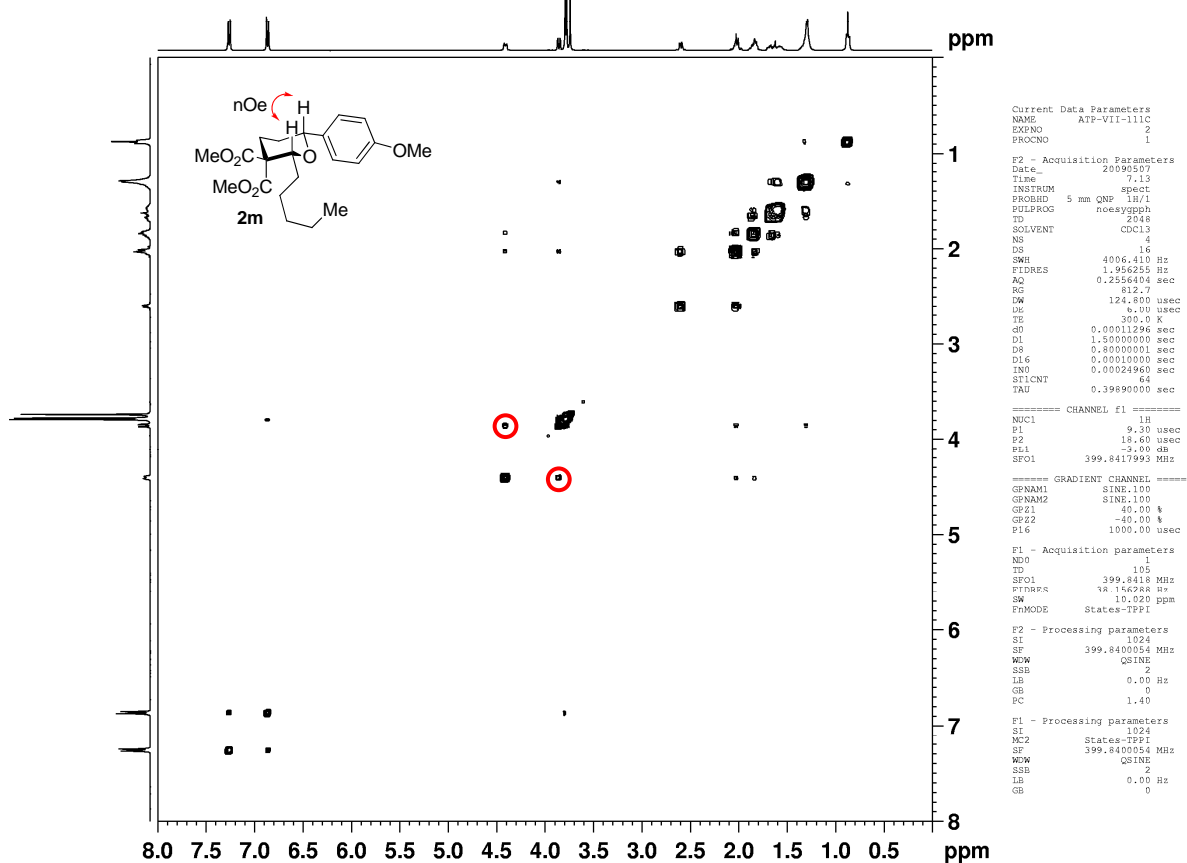
ATP-VII-111C 400 MHz NB



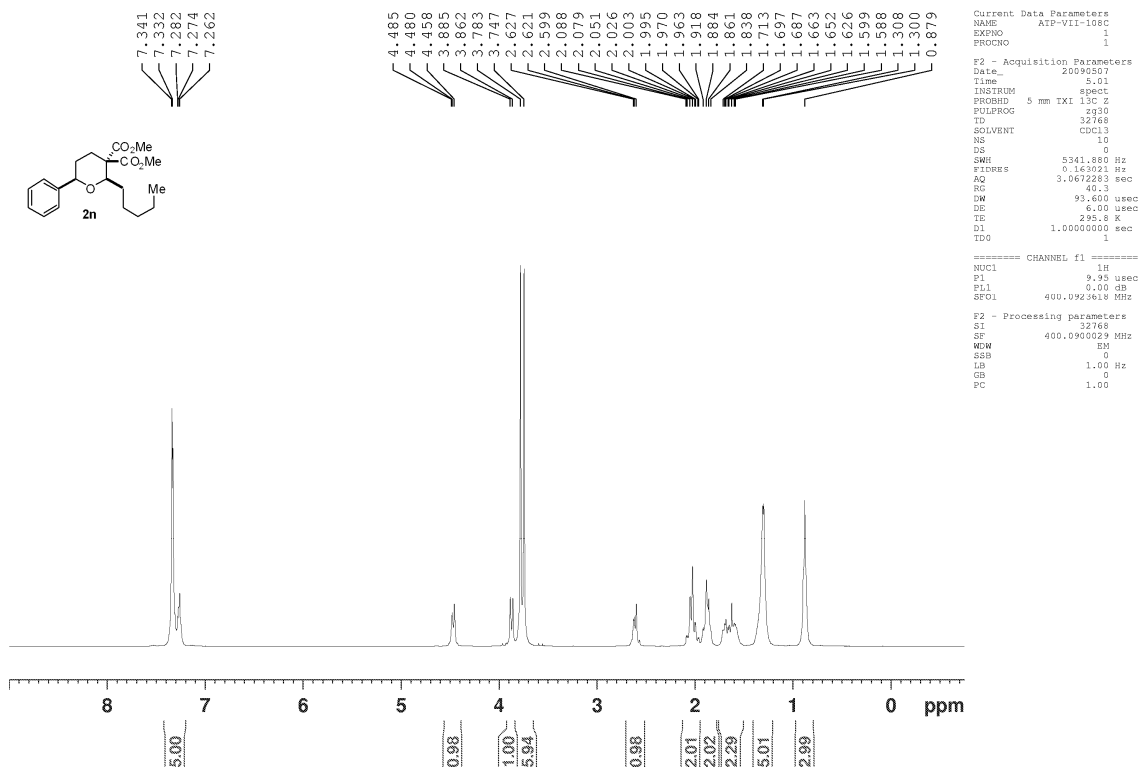
ATP-VII-111C exp 3 13C 400 MHz WB



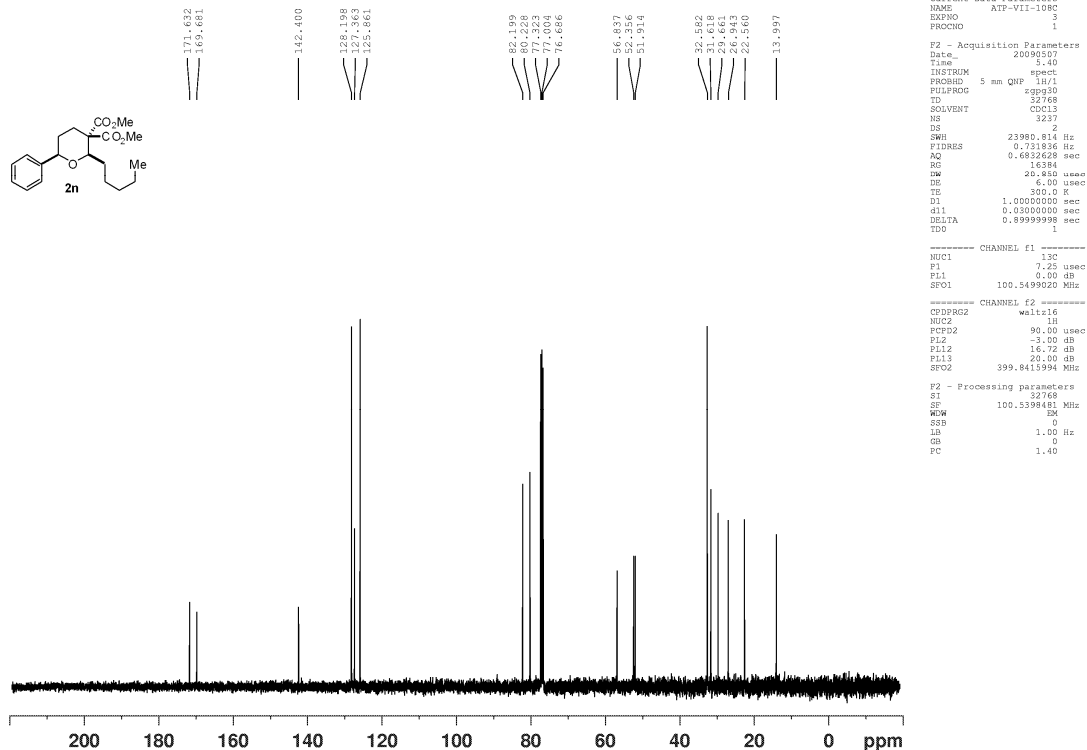
ATP-VII-111C exp 2 NOESY 400 MHz WB



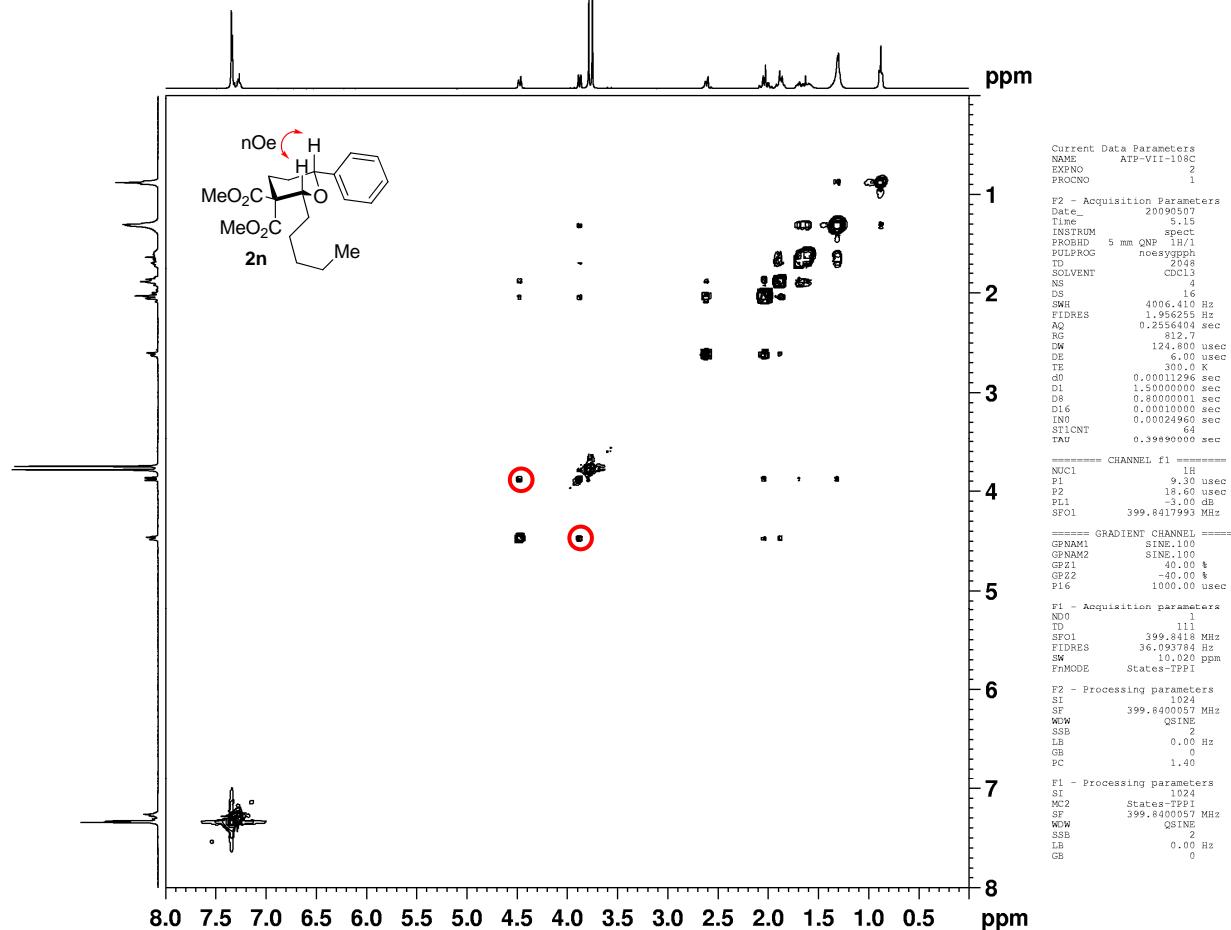
ATP-VII-108C 400 MHz NB



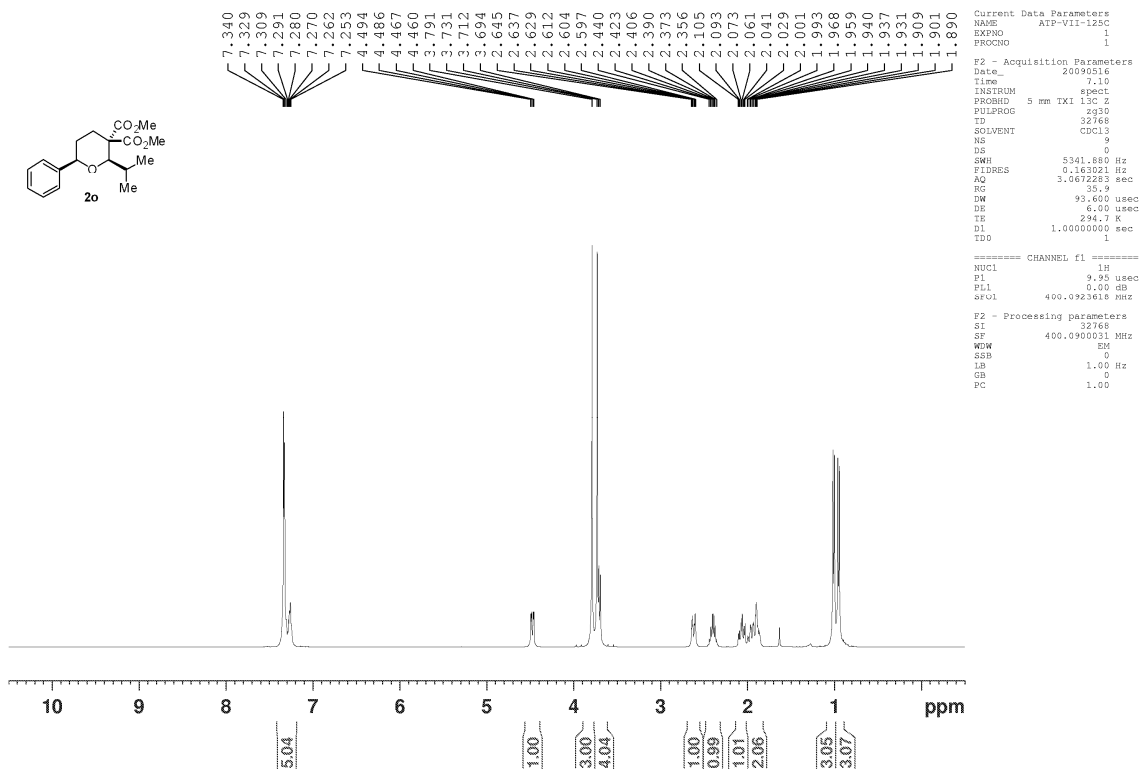
ATP-VII-108C exp 3 13C 400 MHz WB



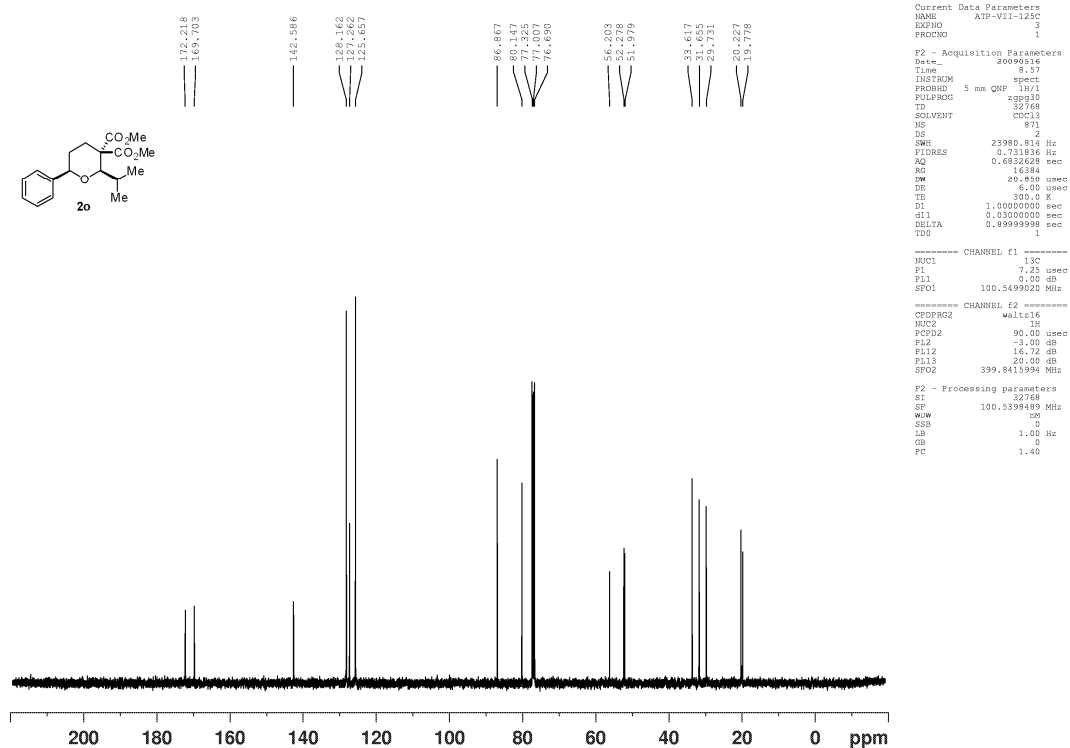
ATP-VII-108C exp 2 NOESY 400 MHz WB



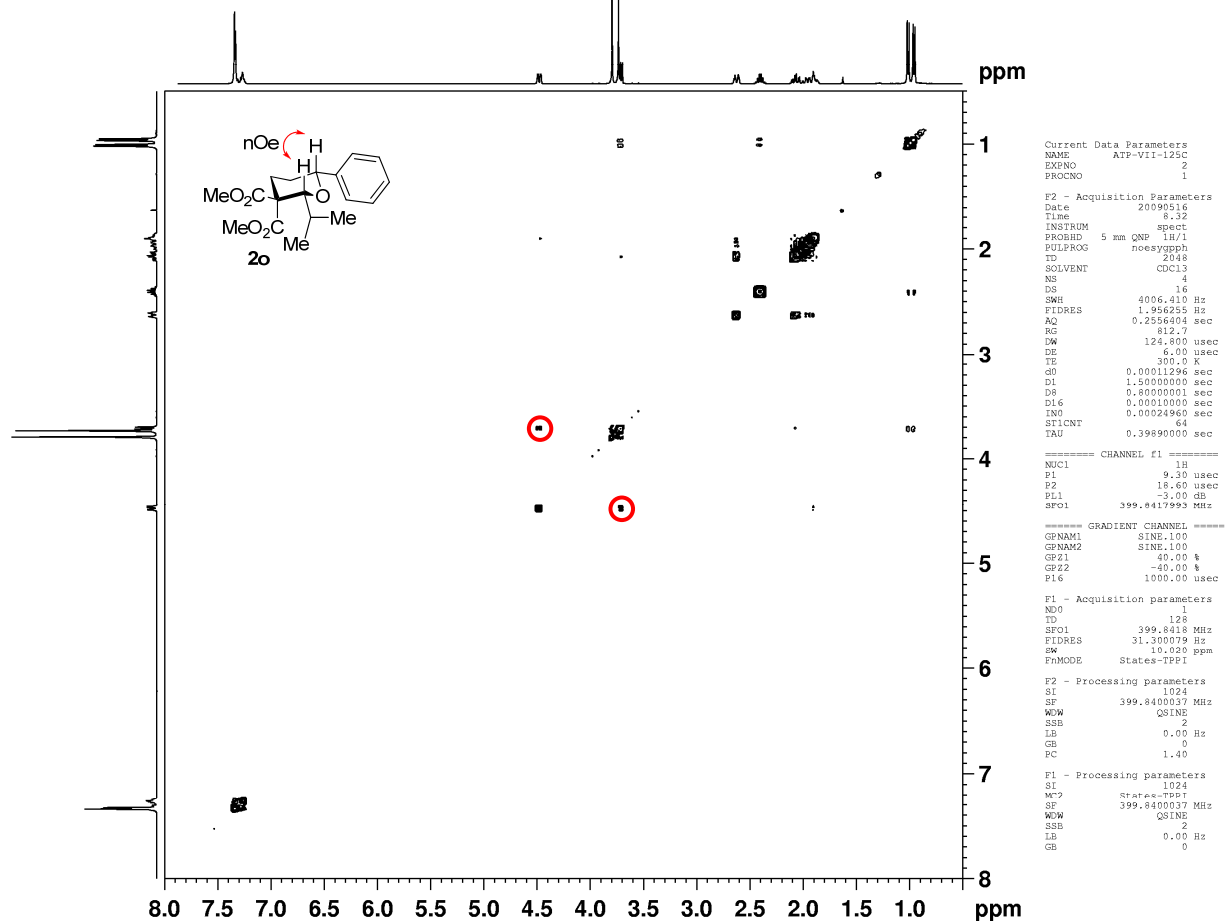
ATP-VII-125C 400 MHz NB



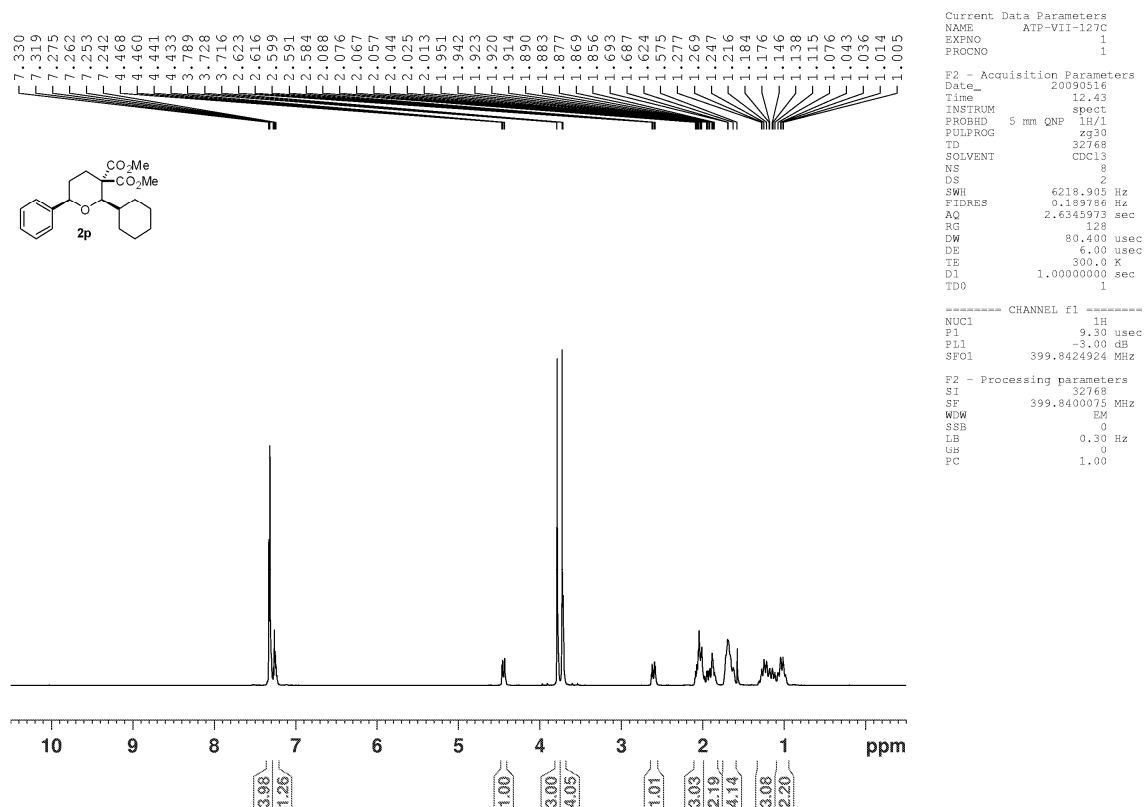
ATP-VII-125C exp 3 13C 400 MHz WB



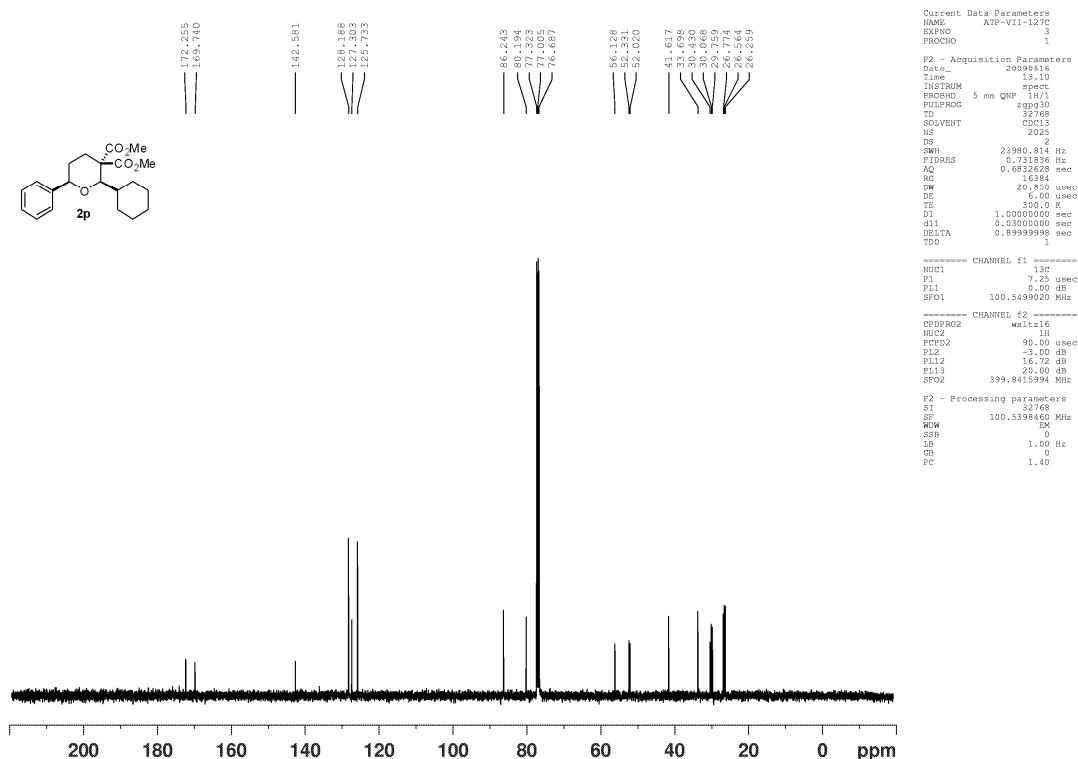
ATP-VII-125C exp 2 NOESY 400 MHz WB



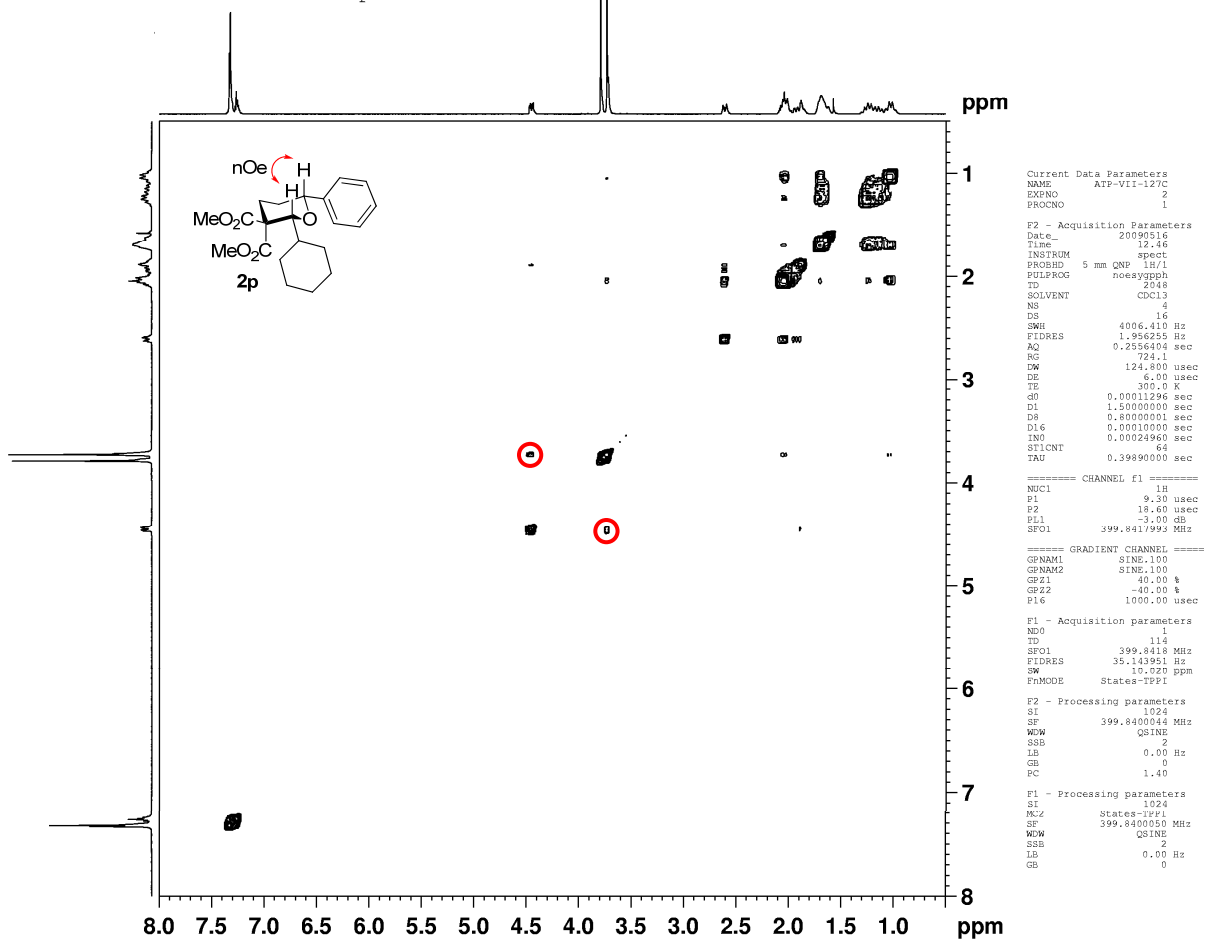
ATP-VII-127C 400 MHz WB



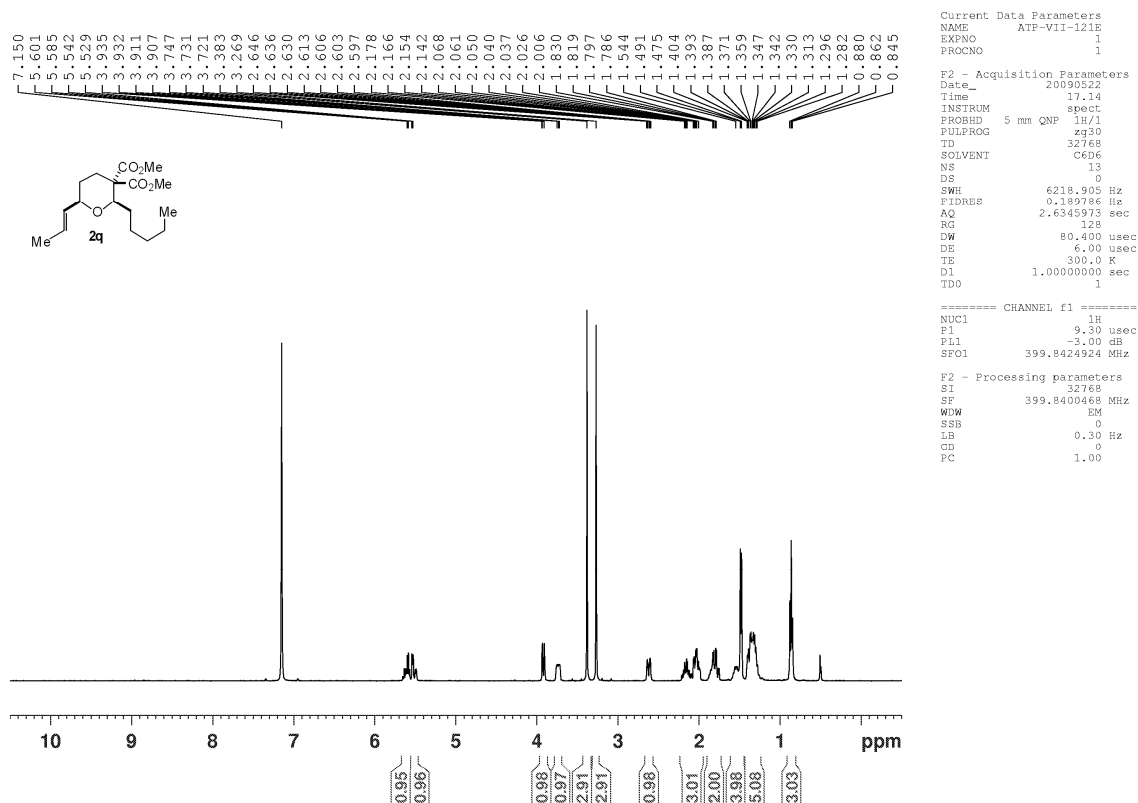
ATP-VII-127C exp 3 13C 400 MHz WB



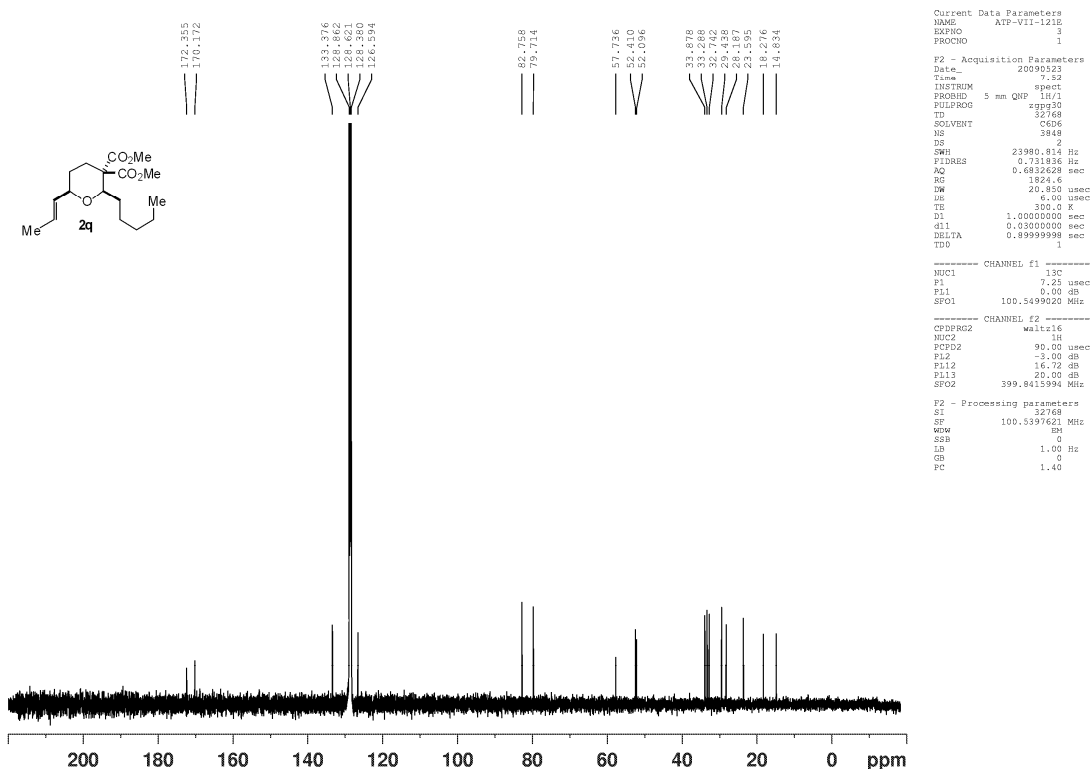
ATP-VII-127C exp 2 NOESY 400 MHz WB



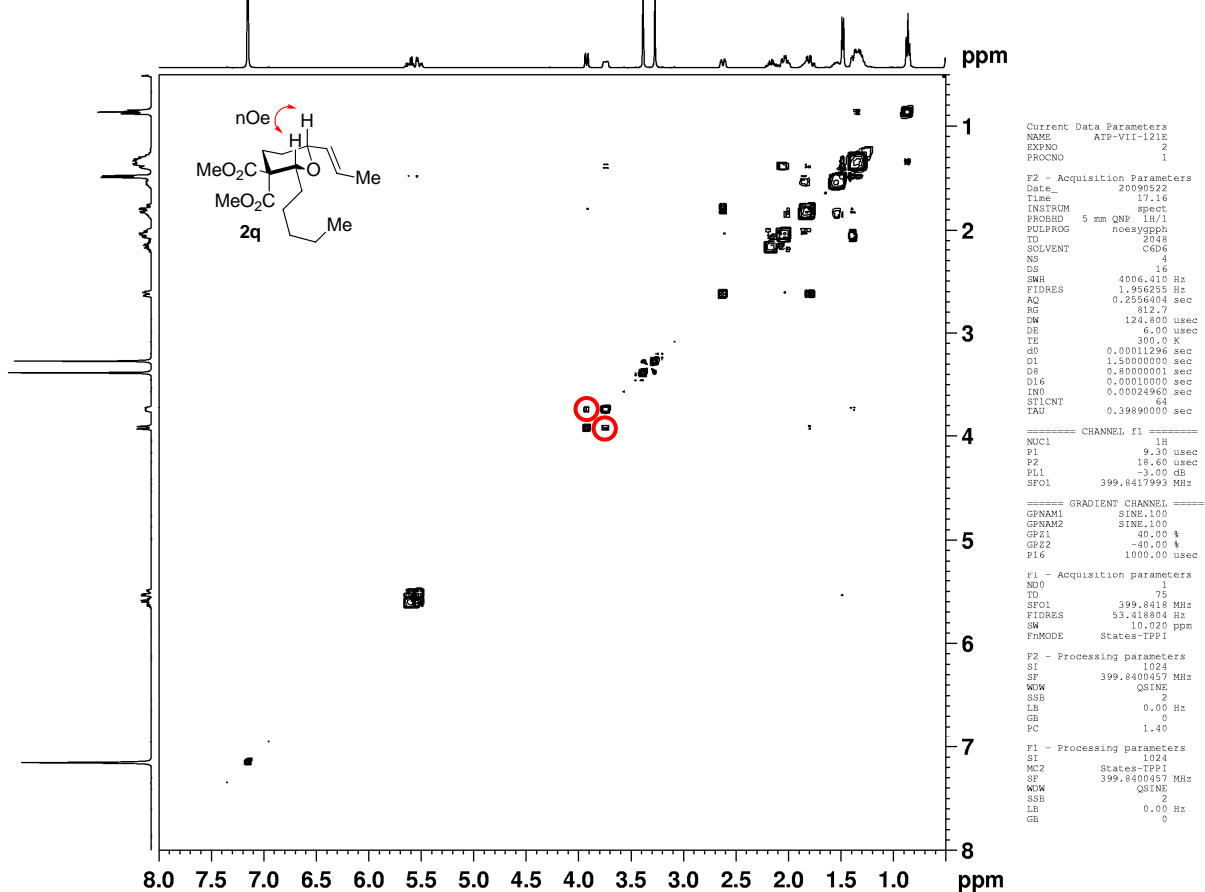
ATP-VII-121E C6D6 400 MHz WB

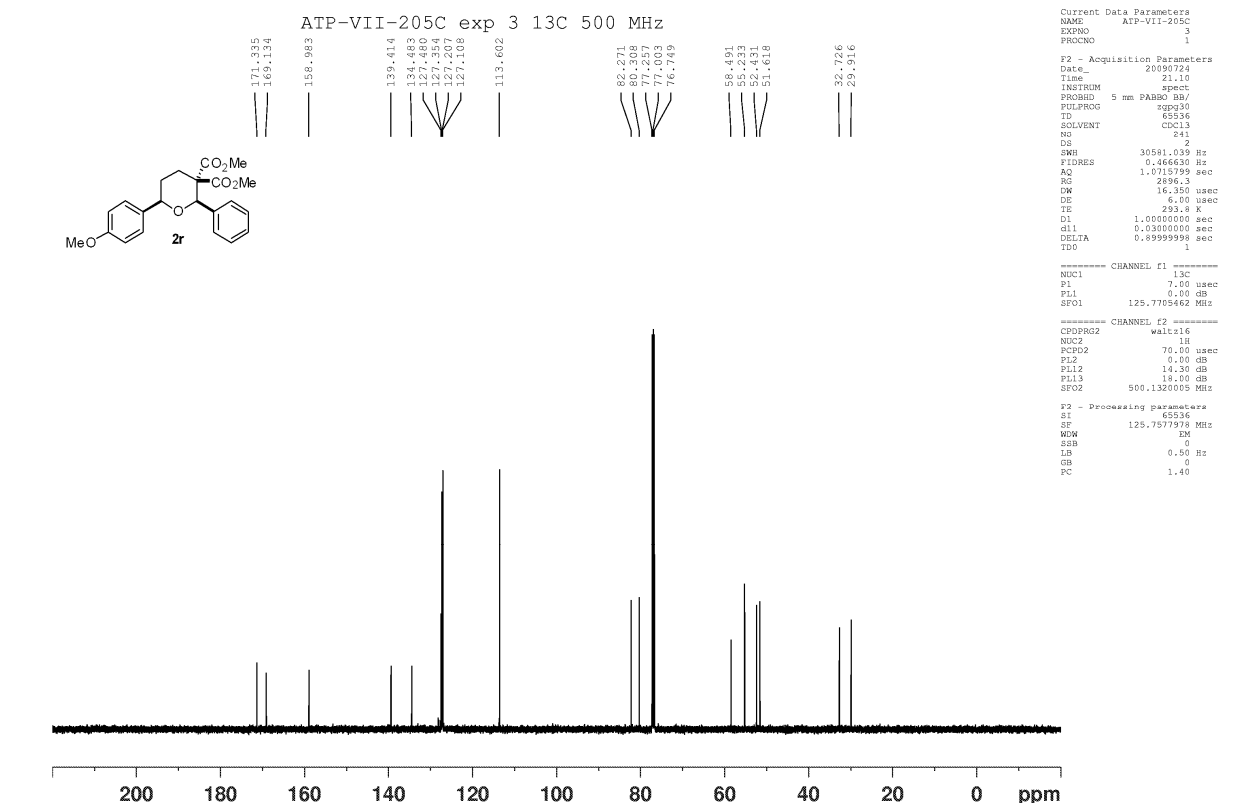
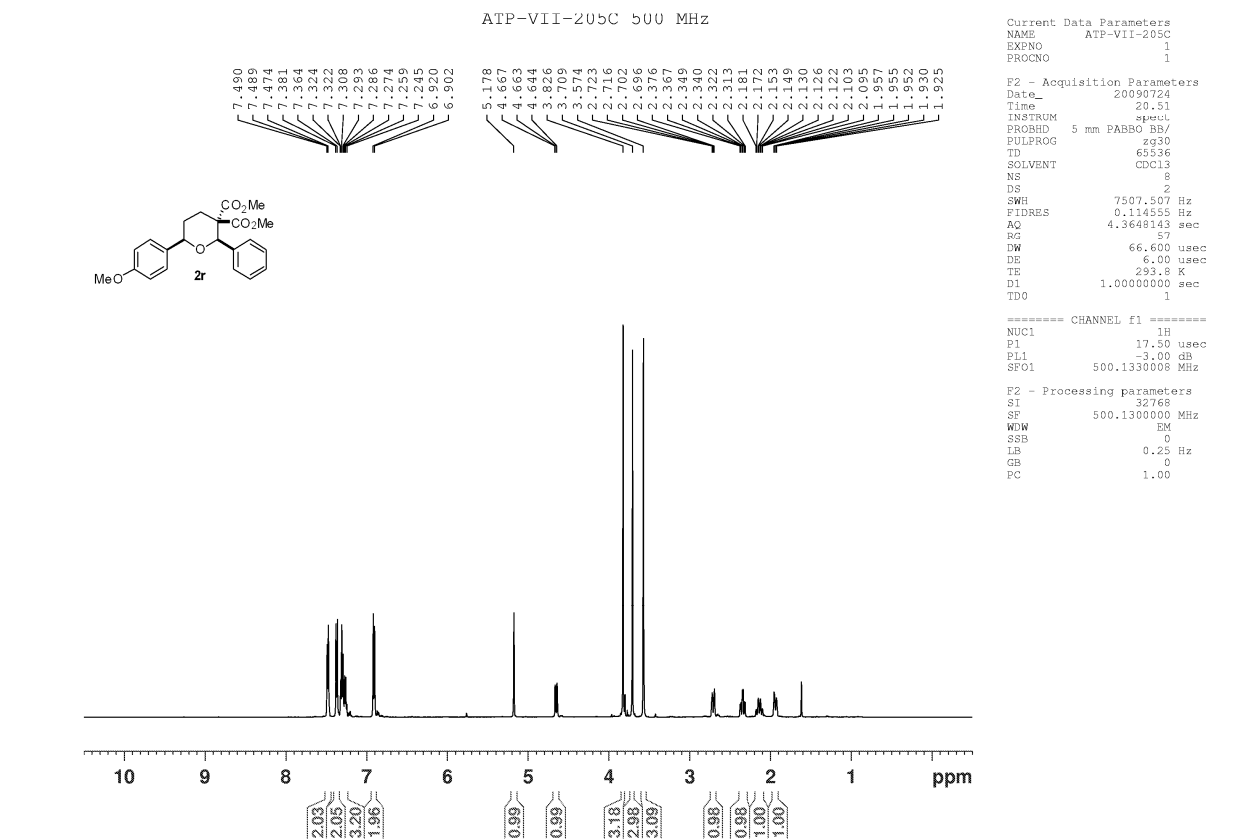


ATP-VII-121E exp 3 13C C6D6 400 MHz WB



ATP-VII-121E exp 2 NOESY 400 MHz WB





ATP-VII-205C exp 2 NOESY 500 MHz

