Electronic Supplementary Information

For

Efficient Carbene Transfer Reactivity Mediated by Fe(II) Complexes Supported by Bulky Alkoxides

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1. Compounds synthesis, characterization, and catalytic procedures.

   General methods and characterization. All air-sensitive reactions were carried out in a nitrogen-filled glovebox or by standard Schlenk line procedures. Styrene, 4-tert-butylstyrene, 4-trifluoromethylstyrene, α-methylstyrene, trans-β-methylstyrene, 1-decene, methyl acrylate, dimethyl malonate, diacetoxyiodo benzene, potassium hydroxide, 5,5-dimethyl-1,3-cyclohexanedione 2,6-dimethylphenyl (xylyl) isocyanide, 1-adamantyl isocyanide reagents were purchased from Sigma-Aldrich and used as received. Diphenyl malonate, 4-methoxystyrene and 4-cyanostyrene were purchased from A2B Chem and used as received. Deuterated solvents including benzene-d_6 and dichloromethane-d_2 were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. HPLC-grade nondeuterated solvents were purchased from Sigma-Aldrich and purified using an MBRAUN solvent purification system. NMR, HRMS and GC-MS spectra were recorded at the Lumigen Instrument Center (Wayne State University). NMR was performed on a Varian Mercury or Agilent 400 MHz Spectrometer in C_6D_6 at room temperature. Chemical shifts and coupling constants (J) were reported in parts per million (δ) and hertz (Hz), respectively. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. GC-MS analysis was done using an Agilent 6890N spectrometer, a Thermo TG5MS 30 m×0.32 mm×0.25μmcolumn, a 7683 series injector, and an Agilent 5973 detector. A Thermo Fisher Scientific LTQ Orbittrap XL mass spectrometer at the Lumigen Instrument Center was used for high resolution mass spectra. Fe(OR)$_2$(THF)$_2$ (**1**, OR = OC^{r}Bu$_2$Ph), Fe(OR')$_2$(THF)$_2$ (**2**, OR' = OC^{r}Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)), Fe[OO]^{Ph}(THF)$_2$ (**3**), and Fe(OR)$_2$(CNXyl)$_2$ (**10**) were synthesized as described previously.[1-3, 10] Ylide precursors were synthesized using previously reported procedures.[4-6]

General procedure for catalytic formation of cyclopropanes. Catalytic reactions were performed by adding 1 equiv of each styrene, a C_6D_6 solution of the corresponding iron-alkoxide catalyst (5 mol%) and mesitylene as an internal standard solution in benzene to the stirred 2 equiv of ylide in C_6D_6 in the N$_2$-filled glovebox. The reaction mixture was stirred at room temperature for 24 h. Yields of cyclopropanes were calculated by ^{1}H NMR; the spectra were compared to the previously published NMR spectra of the corresponding cyclopropanes.[7-9]

Catalytic synthesis of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate by 1. A C_6D_6 solution of **1** (10 mg, 0.016 mmol) was reacted with styrene 32 mg (0.32 mmol) and ylide (210 mg, 0.64 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 57% yield. (Remaining styrene is 43%)

Catalytic synthesis of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate by 1. A C_6D_6 solution of **1** (10 mg, 0.016 mmol) was reacted with 4-tert-butylstyrene (50 mg, 0.32 mmol) and ylide (210 mg, 0.64 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 78% yield. (Remaining 4-tert-butylstyrene is 21%)

Catalytic synthesis of dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate by 1. A C_6D_6 solution of **1** (10 mg, 0.016 mmol) was reacted with 4-trifluoromethylstyrene (54 mg, 0.32 mmol) and ylide (210 mg, 0.64 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 52% yield. (Remaining 4-trifluoromethylstyrene is 48%).

Catalytic synthesis of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate by 1. A C_6D_6 solution of **1** (10 mg, 0.016 mmol) was reacted with 4-methoxystyrene (42 mg, 0.32 mmol) and ylide (210 mg, 0.64 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the product in 100% yield.

Catalytic synthesis of dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate by 1. A C_6D_6 solution of **1** (10 mg, 0.016 mmol) was reacted with 4-cyanostyrene (40 mg, 0.32 mmol) and ylide (210 mg, 0.64 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 78% yield. (Remaining 4-cyanostyrene is 22%).

Catalytic synthesis of dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate by 1. A C_6D_6 solution of **1** (10 mg, 0.016 mmol) was reacted with α-methylstyrene (37 mg, 0.32 mmol) and ylide (210 mg, 0.64 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 60% yield. (Remaining α-methylstyrene is 40%).

Catalytic synthesis of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate by 2. A C_6D_6 solution of **2** (10 mg, 0.011 mmol) was reacted with styrene (22 mg, 0.21 mmol) and ylide (144 mg, 0.44 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 69% yield. (Remaining styrene is 31%)

Catalytic synthesis of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate by 2. A C_6D_6 solution of **2** (10 mg, 0.011 mmol) was reacted with 4-tert-butylstyrene (34 mg, 0.22 mmol) and ylide (144 mg, 0.44 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 66% yield. (Remaining 4-tert-butylstyrene is 34%)

Catalytic synthesis of dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate by 2. A C_6D_6 solution of **2** (10 mg, 0.011 mmol) was reacted with 4-trifluoromethylstyrene (36 mg, 0.22 mmol) and ylide (144 mg, 0.44 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 40% yield. (Remaining 4-trifluoromethylstyrene is 60%).

Catalytic synthesis of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate by 2. A C_6D_6 solution of **2** (10 mg, 0.011 mmol) was reacted with 4-methoxystyrene (28 mg, 0.22 mmol) and ylide (144 mg, 0.44 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 100% yield.

Catalytic synthesis of dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate by 2. A C_6D_6 solution of **2** (10 mg, 0.011 mmol) was reacted with 4-cyanostyrene (26 mg, 0.22 mmol) and ylide (144 mg, 0.44 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 50% yield. (Remaining 4-cyanostyrene is 50%).

Catalytic synthesis of dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate by 2. A C_6D_6 solution of **2** (10 mg, 0.011 mmol) was reacted with α-methylstyrene (26 mg, 0.22 mmol) and ylide (144 mg, 0.44 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 65% yield. (Remaining α-methylstyrene is 33%).

Catalytic synthesis of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate by 3. A C_6D_6 solution of **3** (10 mg, 0.013 mmol) was reacted with styrene (26 mg, 0.26 mmol) and ylide (170 mg, 0.52 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 95% yield. (Remaining styrene is 5%)

Catalytic synthesis of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate by 3. A C_6D_6 solution of **3** (10 mg, 0.013 mmol) was reacted with 4-tert-butylstyrene (40 mg, 0.26 mmol) and ylide (170 mg, 0.52 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GCMS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 58% yield. (Remaining 4-tert-butylstyrene is 42%).

Catalytic synthesis of dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate by 3. A C_6D_6 solution of **3** (10 mg, 0.013 mmol) was reacted with 4-trifluoromethylstyrene (43 mg, 0.26 mmol) and ylide (170 mg, 0.52 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 44% yield. (Remaining 4-trifluoromethylstyrene is 56%).

Catalytic synthesis of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate by 3. A C_6D_6 solution of **3** (10 mg, 0.013 mmol) was reacted with 4-methoxystyrene (34 mg, 0.26 mmol) and ylide (170 mg, 0.52 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 100% yield.

Catalytic synthesis of dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate by 3. A C_6D_6 solution of **3** (10 mg, 0.013 mmol) was reacted with 4-cyanostyrene (32 mg, 0.26 mmol) and ylide (170 mg, 0.52 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 49% yield. (Remaining 4-cyanostyrene is 48%)

Catalytic synthesis of dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate by 3. A C_6D_6 solution of **3** (10 mg, 0.013 mmol) was reacted with α-methylstyrene (30 mg, 0.26 mmol) and ylide (170 mg, 0.52 mmol) in the presence of mesitylene as the internal standard. The reaction mixture was stirred at room temperature for 24 h. The product was characterized by ^{1}H NMR and GC-MS. ^{1}H NMR spectrum indicated formation of the cyclopropane in 85% yield. (Remaining α-methylstyrene is 14%).

Synthesis of diphenyl 2-(phenyl-l,3-iodaneylidene)malonate. Diphenyl 2-(phenyl-l3-iodaneylidene)malonate was prepared similarly to the Charette's literature procedure on preparation of dimethyl 2-(phenyl-l3-iodaneylidene)malonate.[4] Diphenyl malonate (2.00 g, 0.0078 mmol, 1 equiv) and acetonitrile (50 mL) were stirred in a round bottom flask cooled to 5 °C with an ice/water bath. Then potassium hydroxide (2.58 g, 0.0390 mmol, 5 equiv) was added to the stirred solution forming a viscous slurry. Diacetoxyiodo benzene (2.76 g, 0.0086 mmol, 1.1 equiv) was added to the slurry and the mixture was stirred vigorously for 2 h at 0 °C. Water (30 mL) was added in one portion, and the mixture was stirred for 2 min. Suction filtration resulted in a beige color solid (1.15 g, 32% yield). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz) δ 7.95 – 7.88 (m, 2H), 7.66 – 7.57 (m, 1H), 7.49 (dd, $J = 8.4, 7.2$ Hz, 2H), 7.40 – 7.26 (m, 4H), 7.23 – 7.15 (m, 2H), 7.15 – 7.05 (m, 4H) ppm. ^{13}C NMR (CD$_2$Cl$_2$, 150 MHz) δ 152.53, 132.86, 132.07, 129.40, 125.29, 122.46, 114.99, 112.40, 111.24 ppm. IR (cm^{-1}): 3055 (w), 2337 (w), 1690 (s, C=O), 1605 (s), 1490 (m), 1335 (m), 1180 (s), 1158 (m), 957 (s), 833 (m), 725 (m), 687 (m). HRMS (m/z): Calcd, [C$_{30}$H$_{20}$O$_8$]NH$_4^+$ 526.15, found 526.1477.

Formation of tetramethyl ethene-1,1,2,2-tetracarboxylate. A THF solution of dimethyl 2-(phenyl-l3-iodaneylidene)malonate (31 mg, 0.093 mmol) was added to a golden THF solution of **1** (60 mg, 0.093 mmol). The reaction color turned red immediately. The reaction was stirred for 2 hours, and the volatiles were removed in vacuo. A reddish brown oil resulted which was dissolved in diethyl ether. The solution was filtered and placed in the freezer at -35 °C to produce colorless crystals overnight (10 mg, 78% yield) The product was characterized by X-ray crystallography and ^{1}H NMR, which was consistent with reported literature.[4]

Formation of tetraphenyl ethene-1,1,2,2-tetracarboxylate. A THF solution of diphenyl 2-(phenyl-l3-iodaneylidene)malonate (43 mg, 0.093 mmol) was added to a golden THF solution of **1** (60 mg, 0.093 mmol). The reaction color turned brown immediately. The reaction was stirred for 2 hours, and the volatiles were removed in vacuo. A dark brown oil resulted which was dissolved in diethyl ether. The solution was filtered and placed in the 6lovebox freezer at -35 °C to produce colorless crystals overnight (18 mg, 74% yield) ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz) δ 7.46 (t, $J = 7.8$ Hz, 8H), 7.34 (d, $J = 7.4$ Hz, 4H), 7.28 (m, 8H) ppm. ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz) δ 161.05, 150.62, 136.85, 130.36, 127.51, 121.75 ppm. HRMS (m/z): Calcd, [C$_{21}$H$_{15}$IO$_4$]Cl$^-$ 492.97, found 492.9709.

Catalytic reaction in the presence of 1,4-cyclohexadiene. A C_6D_6 solution of the **1** (10 mg, 0.016 mmol, 5 mol%) and mesitylene as an internal standard solution in C_6D_6 was added to a C_6D_6 solution containing styrene (32 mg, 0.31 mmol) and 1,4-cyclohexadiene (125 mg, 1.6 mmol). This mixture was added to a stirred solution of dimethyl 2-(phenyl-l3-iodaneylidene)malonate (210 mg, 0.63 mmol) in C_6D_6 in the N_2-filled glovebox. The reaction mixture was stirred at room temperature for 24 h. The reactions were characterized by ^{1}H NMR spectroscopy (**Figure S49**). The integration of the spectral data suggests 3% yield of dimerized carbene and 4% yield of cyclopropane formation.

Catalytic reaction with 3-(phenyl-l3-iodaneylidene)pentane-2,4-dione. 2,4-pentadione (acac) ylide was synthesized similarly to a previously reported procedure.[5] A C_6D_6 solution of **1** (10 mg, 0.016 mmol, 5 mol%), and styrene (32 mg, 0.031 mmol) was added to stirred acac ylide (190 mg, 0.063 mmol) in the presence of mesitylene as an internal standardand stirred for 24 hours. GC-MS confirmed the formation of 1,1'-(2-phenylcyclopropane-1,1-diyl)bis(ethan-1-one).

Catalytic reaction with dimedone ylide. Dimedone ylide was synthesized similarly to a previously reported procedure.[6] A C_6D_6 solution of **1** (10 mg, 0.016 mmol, 5 mol%) and mesitylene as an internal standard solution in C_6D_6 was added to styrene (32 mg, 0.031 mmol). This mixture was added to the stirred dimedone ylide (214 mg, 0.063 mmol) in C_6D_6 in the N_2-filled glovebox. The reaction mixture was stirred at room temperature for 24 h. The reactions were characterized by ^{1}H NMR spectroscopy. Spectral data suggest no formation of dimerized carbene or cyclopropane.

Synthesis of Fe(OR)₂(CNAd)₂ (11). A THF solution of adamantyl isocyanide (75 mg, 0.46 mmol) was added to a stirred golden THF solution of **1** (75 mg, 0.12 mmol). The color of the reaction turned into red immediately. The reaction was stirred for 2 hours, and the volatiles were removed in vacuo. The resulted orange oily solid was washed with hexanes. The remaining green solid was dissolved in ether, filtered, and placed in the freezer at -35 °C to give green crystals after 1 hour (81 mg, 84% yield). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 20.61 (2H, $\Delta v_{1/2}$ 60 Hz, OC^{t}Bu₂Ph), 13.16 (36H, $\Delta v_{1/2}$ 1080 Hz, OC^{t}Bu₂Ph), 10.26 (2H, $\Delta v_{1/2}$ 240 Hz, OC^{t}Bu₂Ph), 9.61 (2H, $\Delta v_{1/2}$ 60 Hz, OC^{t}Bu₂Ph), 4.58 (2H, $\Delta v_{1/2}$ 240 Hz, OC^{t}Bu₂Ph), 2.34 (12H, $\Delta v_{1/2}$ 180 Hz, Ad), 1.72 (6H, $\Delta v_{1/2}$ 30 Hz, Ad), 0.70 (6H, $\Delta v_{1/2}$ 60 Hz, Ad), 0.31 (6H, $\Delta v_{1/2}$ 60 Hz, Ad) ppm. IR (cm^{-1}) 2920 (m), 2840 (m), 2122 (s, C≡NAd), 1436 (s), 1360 (m), 1342(m), 1084 (s), 1040 (m), 1018 (s), 881 (m), 840 (m), 724 (m), 680 (m), 642 (m). Anal. Calcd for $C_{52}H_{76}N_2O_2Fe$: C, 76.44; H, 9.38. Found: C, 75.87; H, 9.06. The compound was also characterized by X-ray crystallography.

General procedure for the catalytic reactions between dimethyl 2-(phenyl-l3-iodaneylidene)malonate and isocyanides. A CD_2Cl_2 solution of **1** (5 mol%) and mesitylene as an internal standard solution in CD_2Cl_2 was added to dimethyl 2-(phenyl-l3-iodaneylidene)malonate (1 equiv). Then this mixture was added to the stirred solution of corresponding isocyanide (1 equiv) in CD_2Cl_2 in the N_2-filled glovebox. The reaction mixture was stirred at room temperature for 24 h. The reactions were characterized by ^{1}H NMR spectroscopy and GC-MS analysis.

Stoichiometric reaction between Fe(OR)$_2$(CNAd)$_2$ (11) and dimethyl 2-(phenyl-l3-iodaneylidene)malonate. A CD$_2$Cl$_2$ solution of **11** (31 mg, 0.038 mmol) and mesitylene as an internal standard solution in CD$_2$Cl$_2$ was added to a stirred solution of dimethyl 2-(phenyl-l3-iodaneylidene)malonate (13 mg, 0.038 mmol). The reaction mixture was stirred at room temperature for 2 h. The reactions were characterized by ^{1}H NMR spectroscopy and GC-MS analysis.

Stoichiometric reaction between Fe(OR)$_2$(CNXyl)$_2$ (10) and dimethyl 2-(phenyl-l3-iodaneylidene)malonate. Fe(OR)$_2$(CNXyl)$_2$ (**10**) was synthesized according to a previously reported procedure.[10] A CD$_2$Cl$_2$ solution of the Fe(OR)$_2$(CNXyl)$_2$ (30 mg, 0.040 mmol) and mesitylene as an internal standard solution in CD$_2$Cl$_2$ was added to a stirred solution of dimethyl 2-(phenyl-l3-iodaneylidene)malonate (14 mg, 0.042 mmol) in CD$_2$Cl$_2$. The reaction mixture was stirred at room temperature for 2 h, after which it was characterized by ^{1}H NMR spectroscopy and GC-MS.

X-ray crystallographic details

The structures of olefins $(MeO_2C)_2C=C(CO_2Me)_2$ and $(PhO_2C)_2C=C(CO_2Ph)_2$, and complex $Fe_2(OR)_2(CNAd)_2$ (**11**) were determined by X-ray crystallography. A Bruker Kappa APEX-II CCD diffractometer was used for data collection. A graphic monochromator was employed for the wavelength selection (MoKα radiation, λ = 0.71073 Å). The data was processed using the APEX-2/3 software. The structures were solved and refined using SHELXT[11] and difference Fourier (ΔF) maps, as embedded in SHELXL-2018[12] running under Olex2[13] The carbon hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically. The crystal structure of $(PhO_2C)_2C=C(CO_2Ph)_2$ was found to be incommensurately modulated. We have revised the average structure by modeling it with disordered phenyl groups and by modeling the toluene as disordered by symmetry. The crystals of **11** diffracted very poorly, due to twinning and a highly sensitive nature of crystals. The crystal was determined to be a two-component non-merohedral twin related to each other by a 180° rotation around the reciprocal [0 0 1] rotation vector. Refinement was performed using the HKLF-5 using reflections from both domains, which lead to batch scale factor (BASF) parameter of 0.469(3). The crystal diffraction was very weak. Many attempts to recrystallize in different solvents did not lead to better diffraction quality. Cu radiation was also tried and did not result in a better structure result. The crystals were very fragile and sensitive. They degraded very quickly despite using paratone oil and quick transportation to the diffractometer. The extra density peak near C45 must be a result of the degradation and/or twinning. The peak makes no chemical sense. The compound has been characterized by several other methods.

Table S1. Experimental crystallographic parameters for (MeO$_2$C)$_2$C=C(CO$_2$Me)$_2$ (**5**), (PhO$_2$C)$_2$C=C(CO$_2$Ph)$_2$ (**6**), and (Fe(OR)$_2$(CNAd)$_2$ (**11**).

complex	(MeO$_2$C)$_2$C=C(CO$_2$Me)$_2$ (**5**)	(PhO$_2$C)$_2$C=C(CO$_2$Ph)$_2$ (**6**)	Fe(OR)$_2$(CNAd)$_2$ (**11**)
formula	C$_{10}$H$_{12}$O$_8$	C$_{30}$H$_{20}$O$_8$ • C$_7$H$_8$	C$_{52}$H$_{76}$FeN$_2$O$_2$
Fw, g/mol	260.20	600.59	816.99
temperature (K)	110(2)	100(2)	110(2)
cryst syst	triclinic	monoclinic	triclinic
space group	P-1	$P2_1$/c	P-1
color	yellow	yellow	green
Z	1	2	2
a, Å	5.0060(4)	10.3230(7)	9.5346(8)
b, Å	7.2628(8)	19.0774(14)	13.1604(12)
c, Å	8.6451(8)	8.7024(5)	18.8315(15)
α, deg	106.710(4)	90	91.840(3)
β, deg	102.405(3)	114.576(2)	90.463(3)
γ, deg	92.116(3)	90	91.367(3)
V, Å^3	292.37(5)	1558.56(18)	2361.0(3)
d_{calcd}, g/cm^3	1.478	1.280	1.149
μ, mm^{-1}	0.131	0.090	0.359
$R_1{}^a$ (all data)	0.0616	0.0625	0.2119
$wR_2{}^b$ (all data)	0.1077	0.1325	0.4283
$R_1{}^a$ [(I>2σ)]	0.0417	0.0460	0.1598
$wR_2{}^b$ [(I>2σ)]	0.0996	0.1178	0.3966
GOF (F^2)	1.0019	1.035	1.435

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = (\sum (w(F_o{}^2 - F_c{}^2)^2)/\sum(w(F_o{}^2)^2))^{1/2}$. [c] GOF $= (\sum w(F_o{}^2 - F_c{}^2)^2/(n - p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

3. NMR spectra
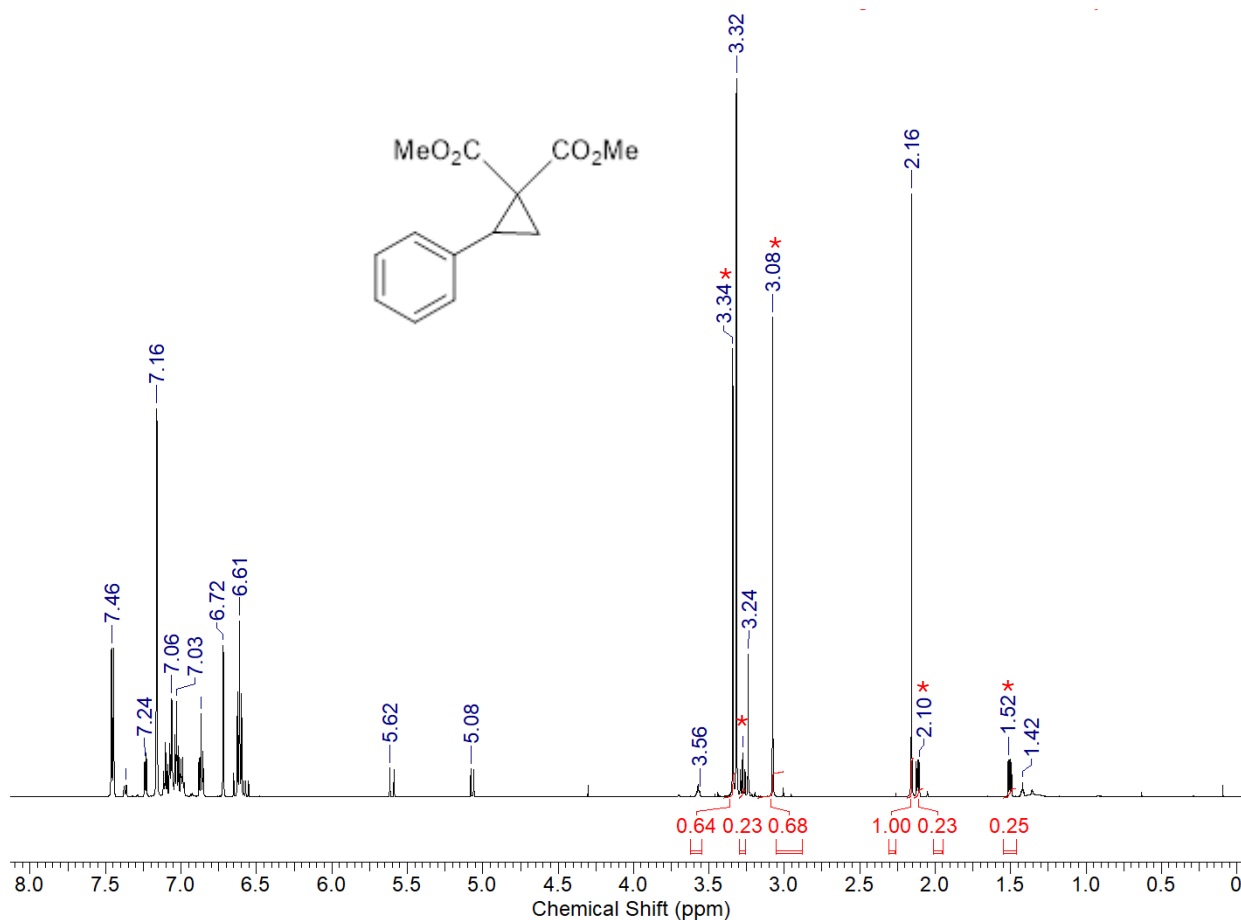
Figure S1. ^{1}H NMR (C$_6$D$_6$) demonstrating catalytic formation of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate using **1** and styrene. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The p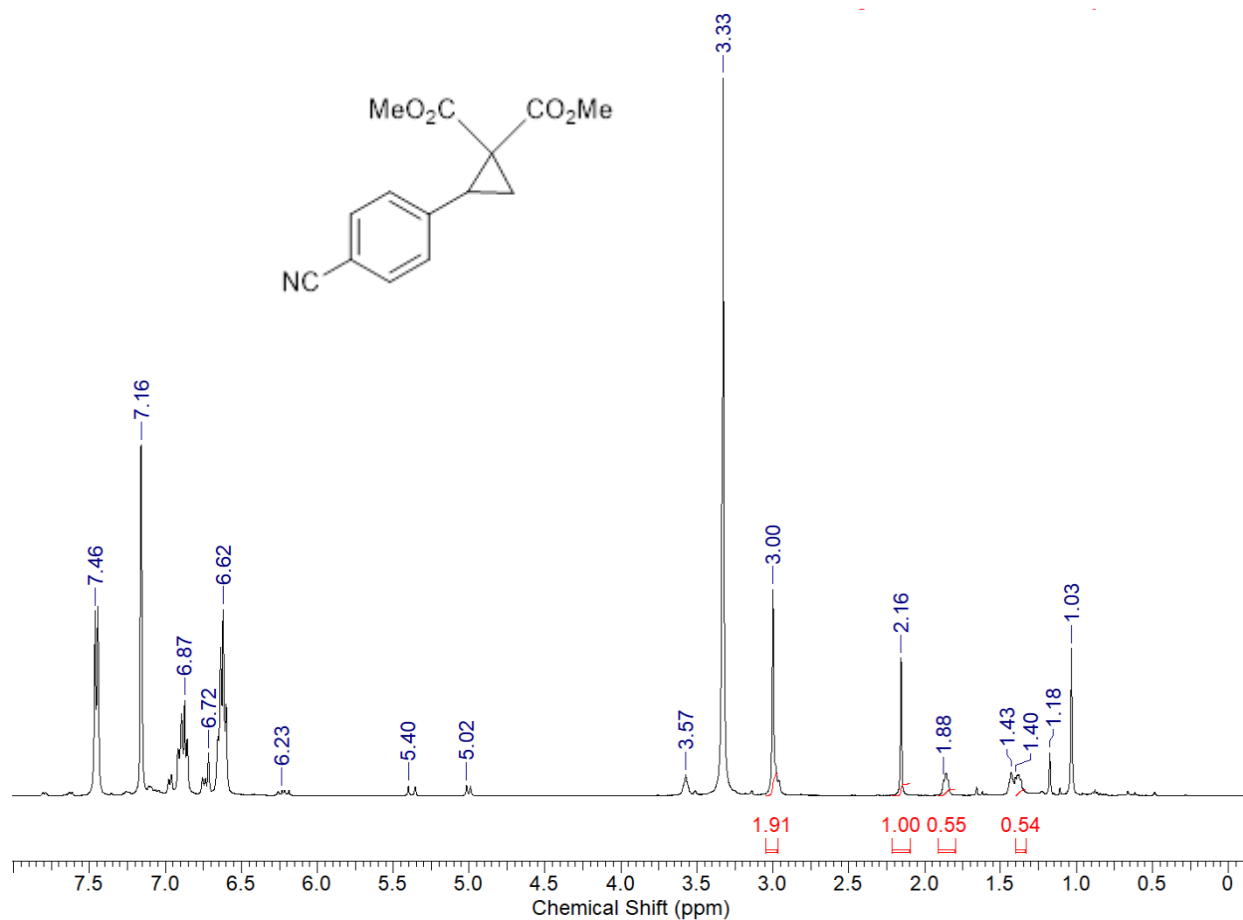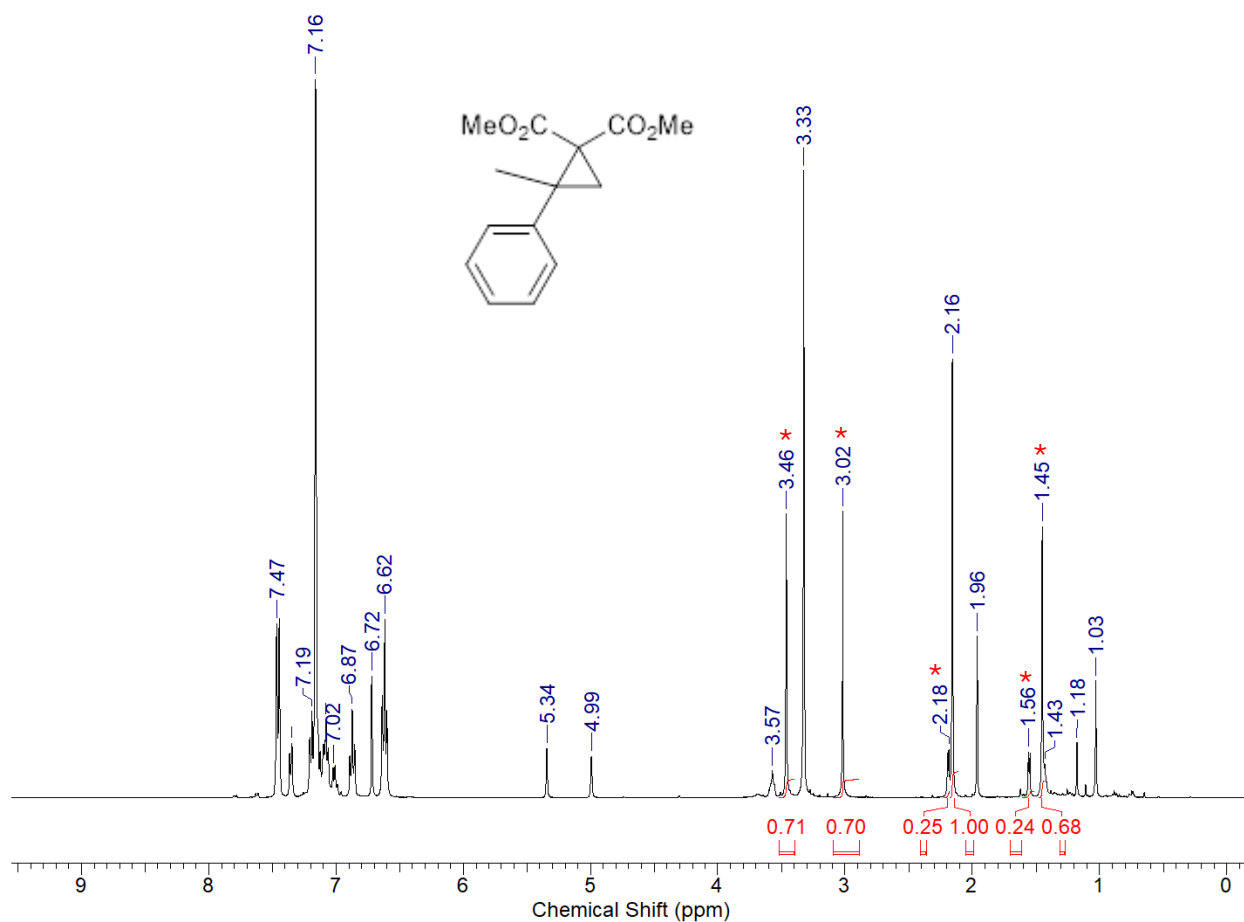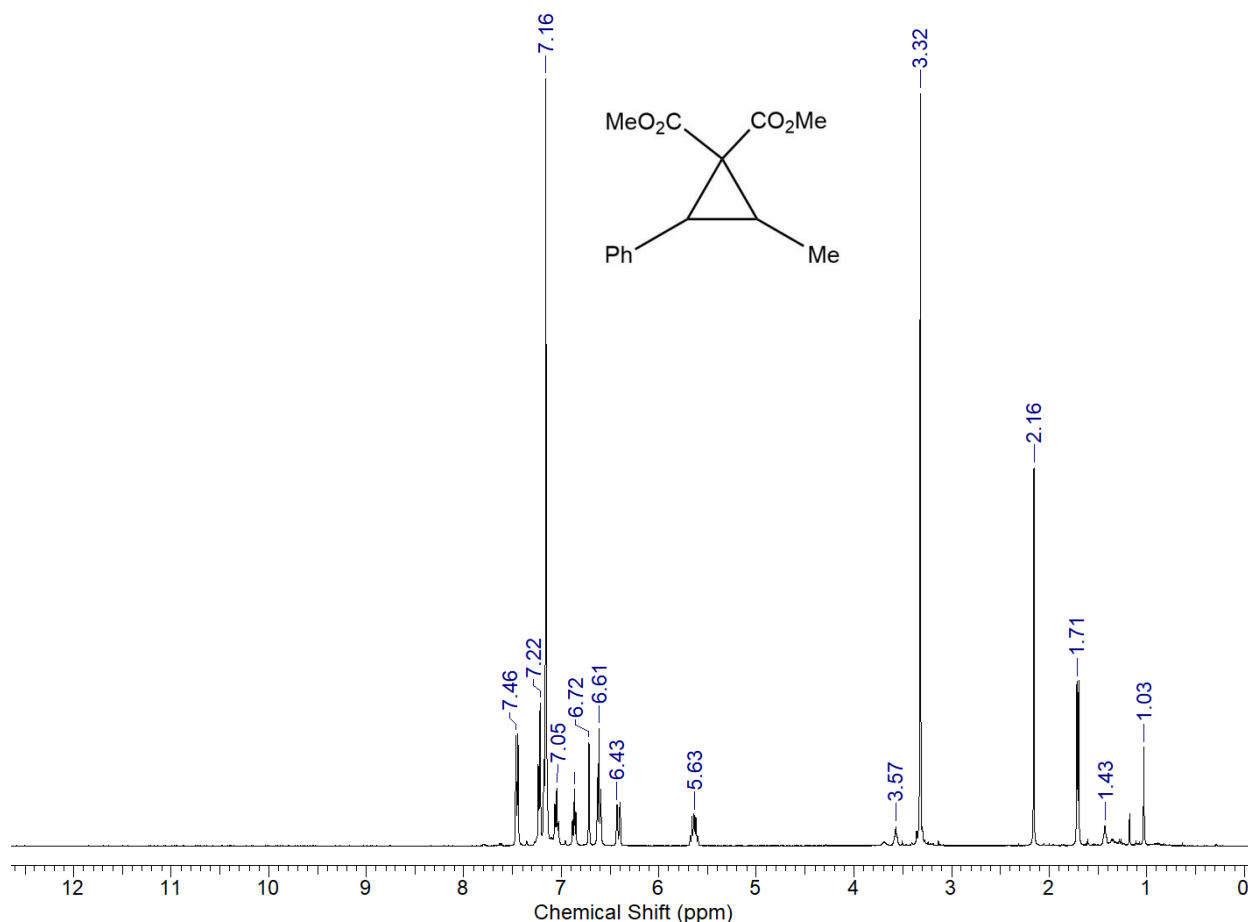eaks at 1.42 ppm and 3.56 ppm correspond to tetrahydrofuran. The peaks at 5.62 ppm and 5.08 ppm correspond to the remaining styrene.

11
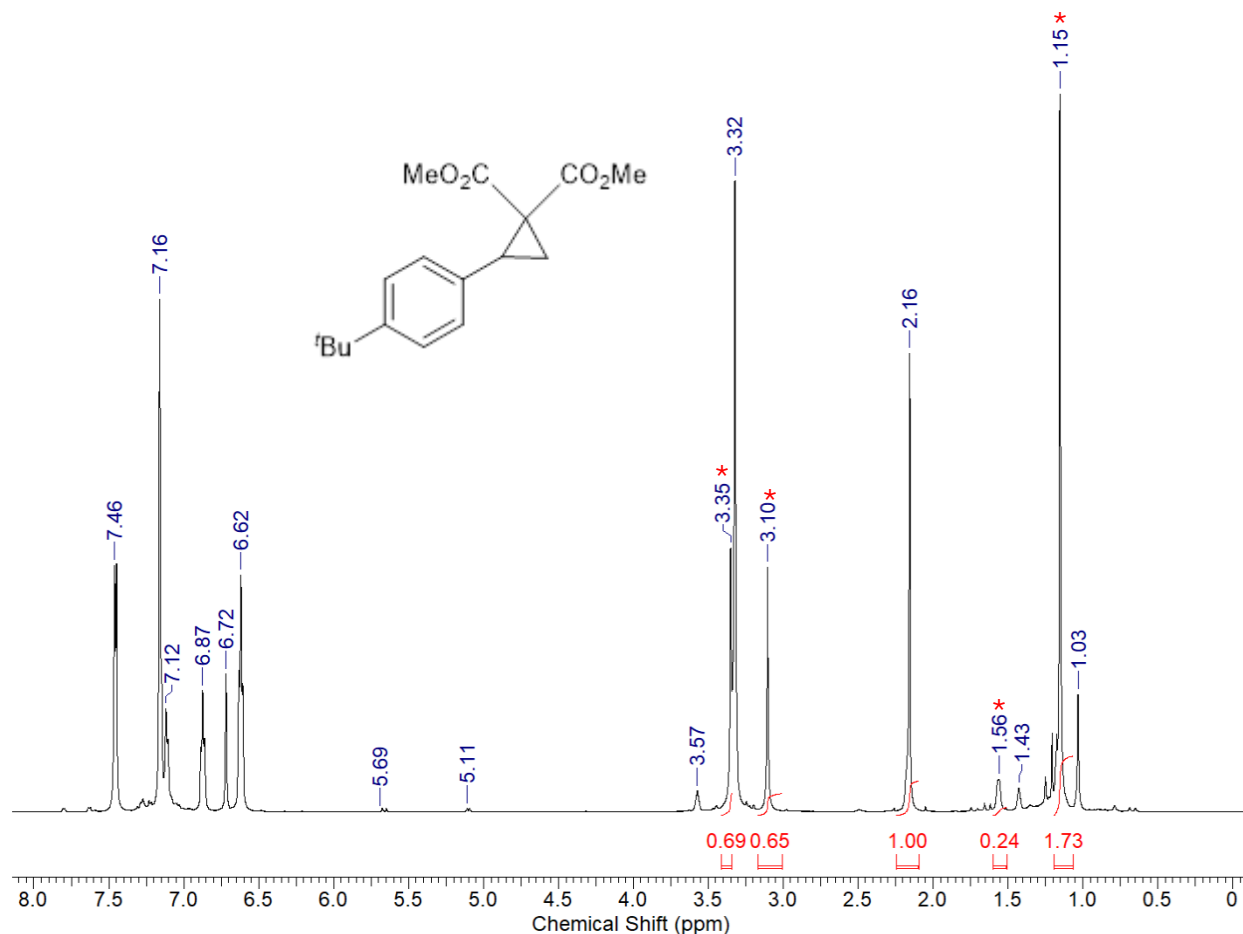
Figure S2. ^{1}H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate using **1** and 4-tert-butylstyrene substrate. The signals belonging to cyclopropane are marked with *. Two cyclopropane protons are obstructed by peaks corresponding to tert-butyl group, by-products or solvents. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.69 ppm and 5.11 ppm correspond to the remaining 4-tert-butylstyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.
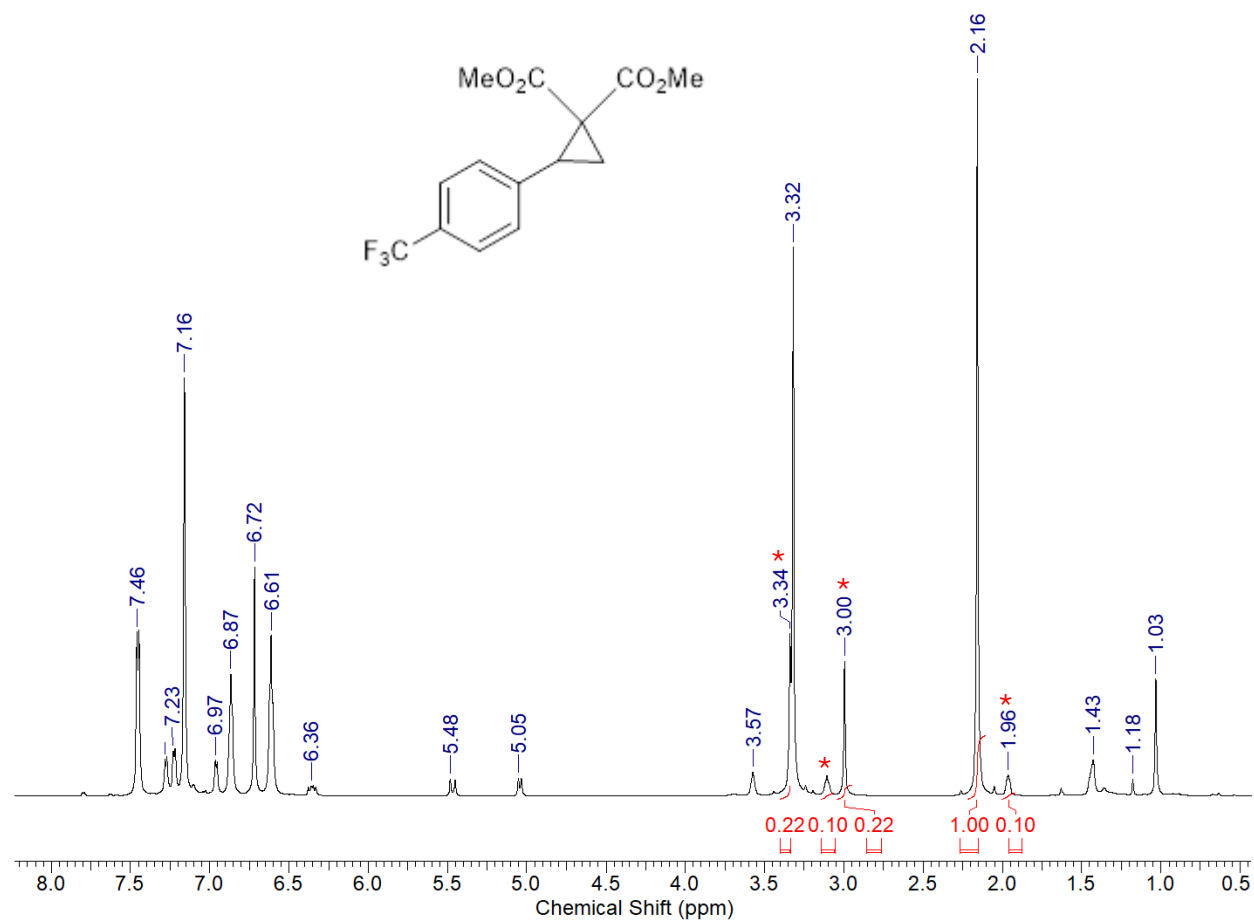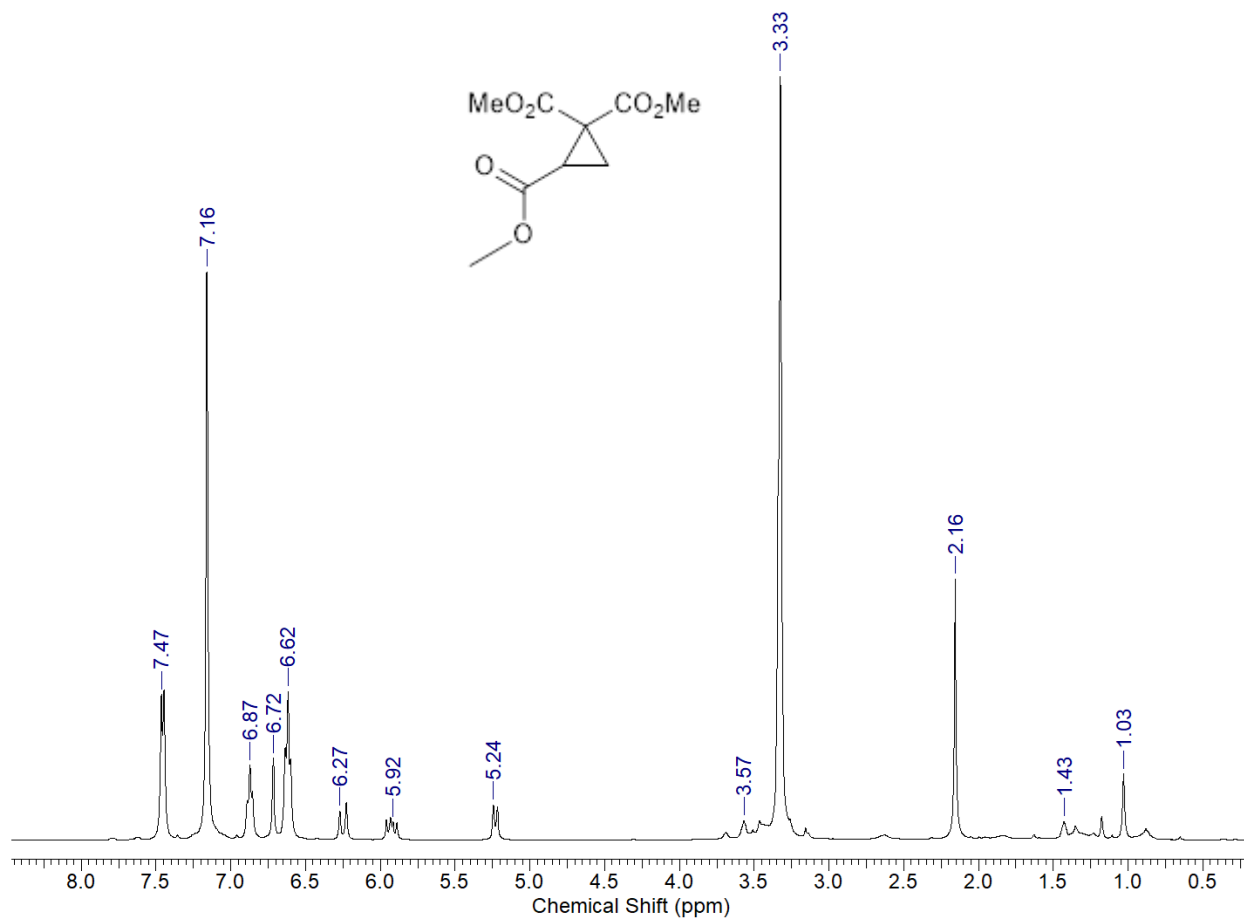
Figure S3. ^{1}H NMR (C$_6$D$_6$) demonstrating catalytic formation of dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate using **1** and 4-CF$_3$-styrene substrate. The signals belonging to cyclopropane are marked with *. One methine cyclopropane proton is obstructed by peaks corresponding to solvents or by-products. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.48 ppm and 5.05 ppm correspond to the remaining 4-CF$_3$-styrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.
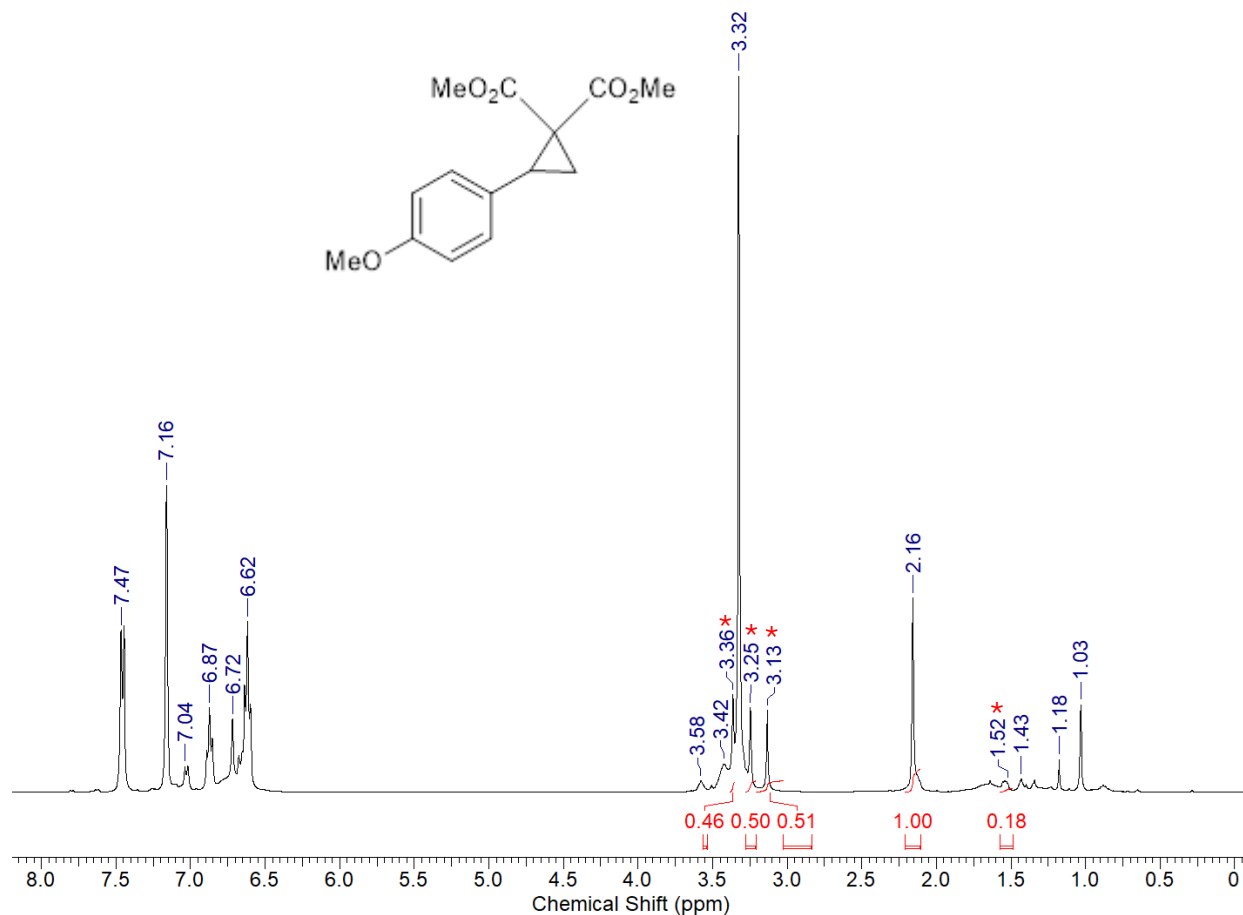
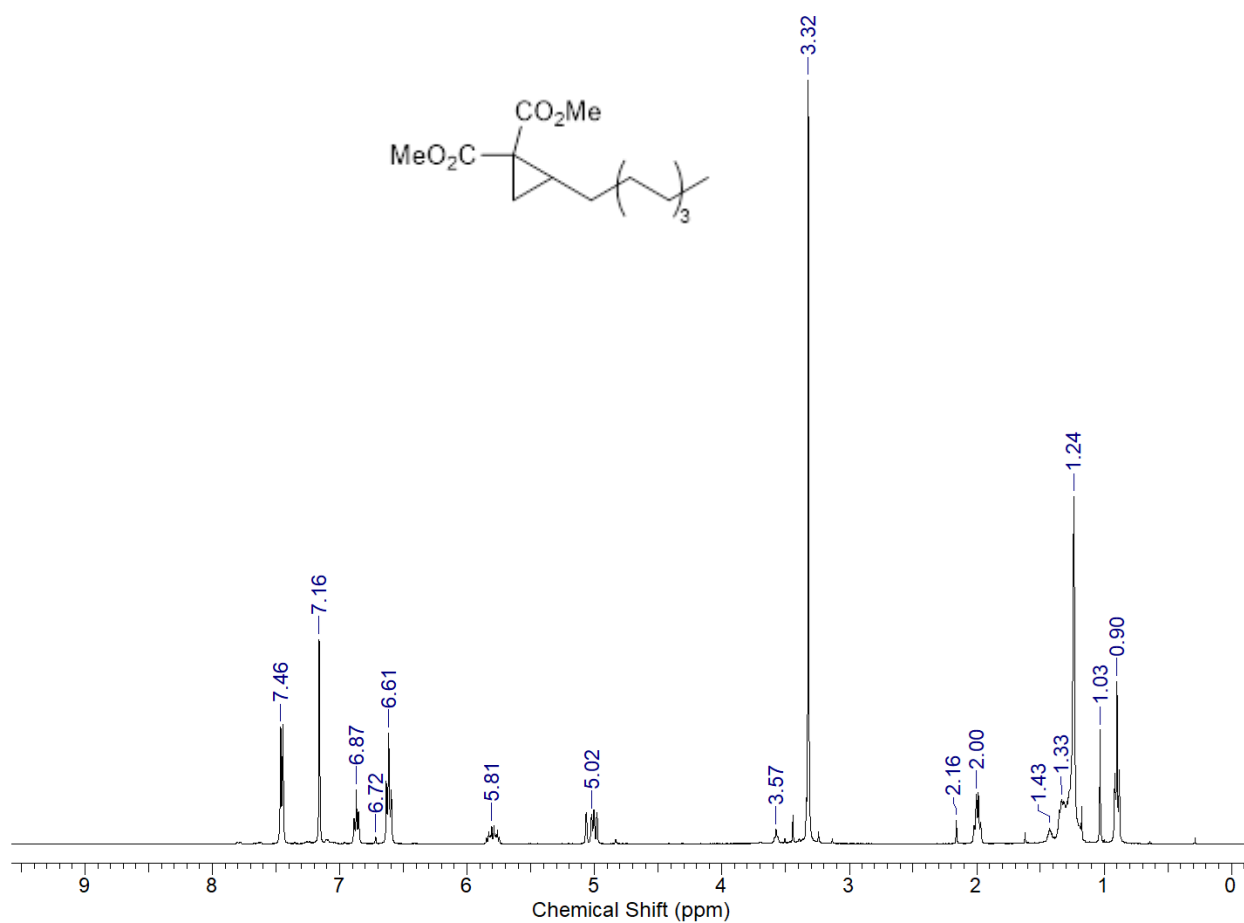**Figure S4.** ^1H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate using **1** and 4-methoxystyrene substrate. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. Two methine cyclopropane protons are obstructed by peaks corresponding to solvents or tetramethyl ethene-1,1,2,2-tetracarboxylate by-product. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.58 ppm correspond to tetrahydrofuran.
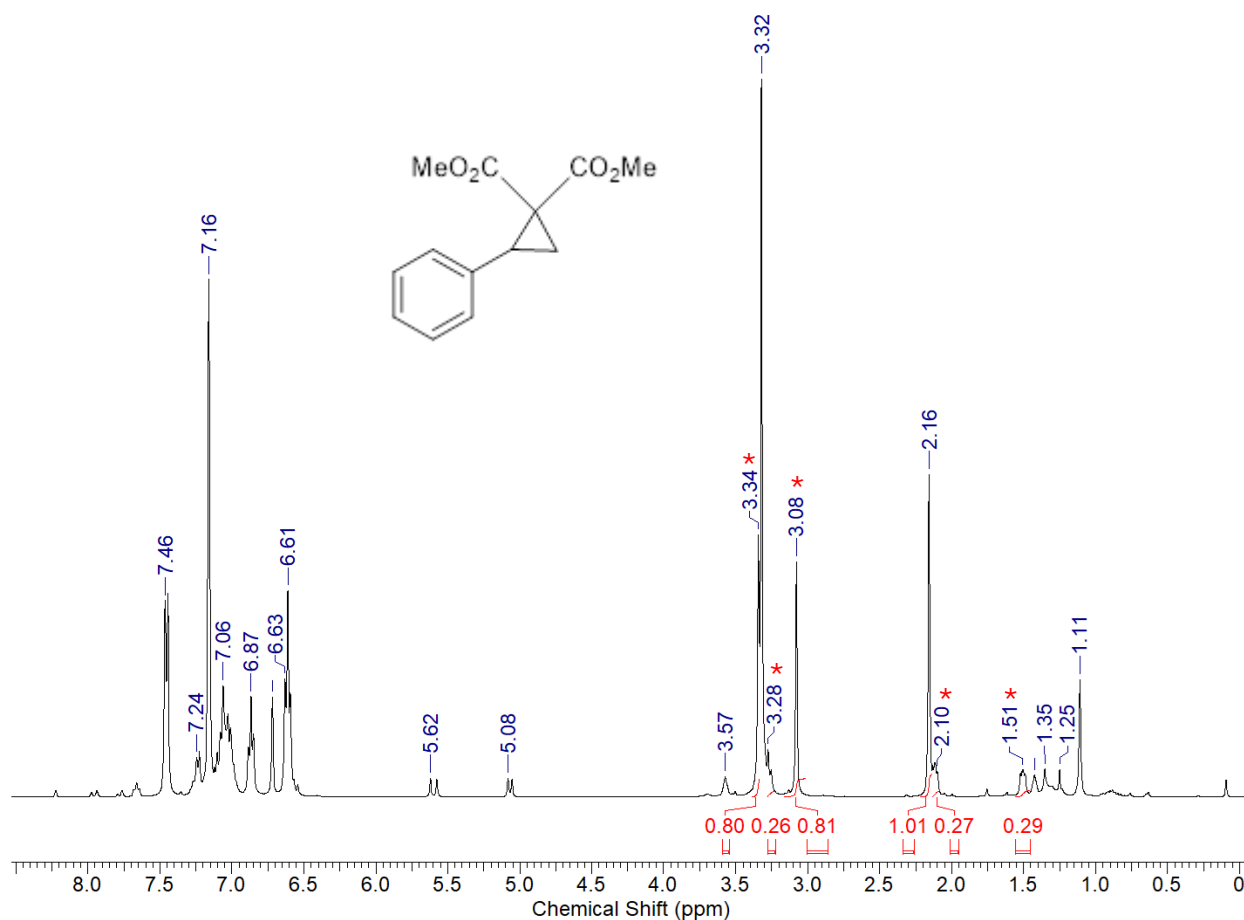
Figure S5. ^{1}H NMR (C$_6$D$_6$) demonstrating catalytic formation of dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate, using **1** and 4-cyanostyrene substrate. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. Two cyclopropane protons are obstructed by peaks corresponding to solvents or tetramethyl ethene-1,1,2,2-tetracarboxylate by-product. The peaks at 5.40 ppm and 5.02 ppm correspond to the remaining 4-cyanostyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.
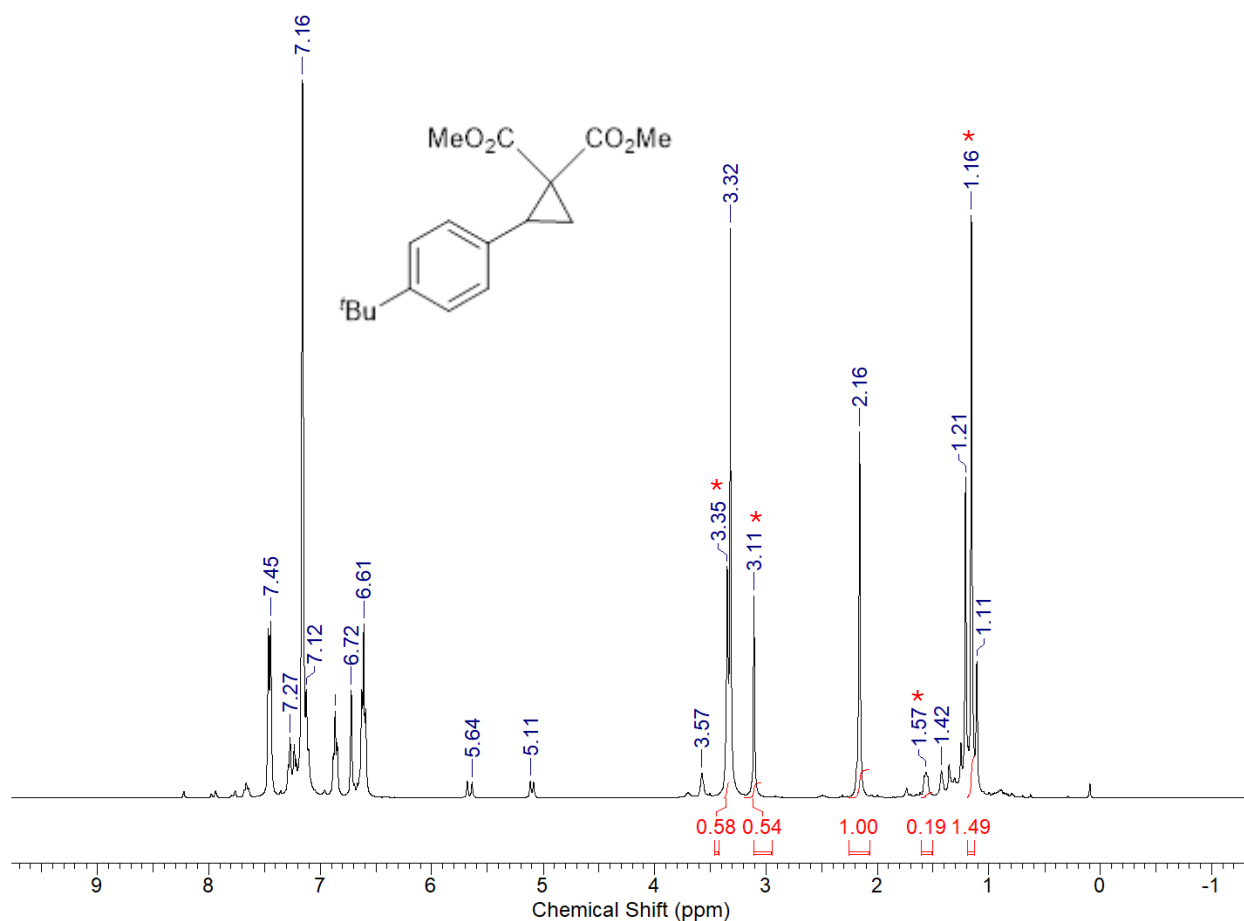
Figure S6. ^{1}H NMR (C$_6$D$_6$) demonstrating catalytic formation of dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate, by **1** and α-methylstyrene. The signals belonging to cyclopropane are marked with *. The peak at 3.33 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.34 ppm, 4.99 ppm, and 1.96 ppm correspond to the remaining α-methylstyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.
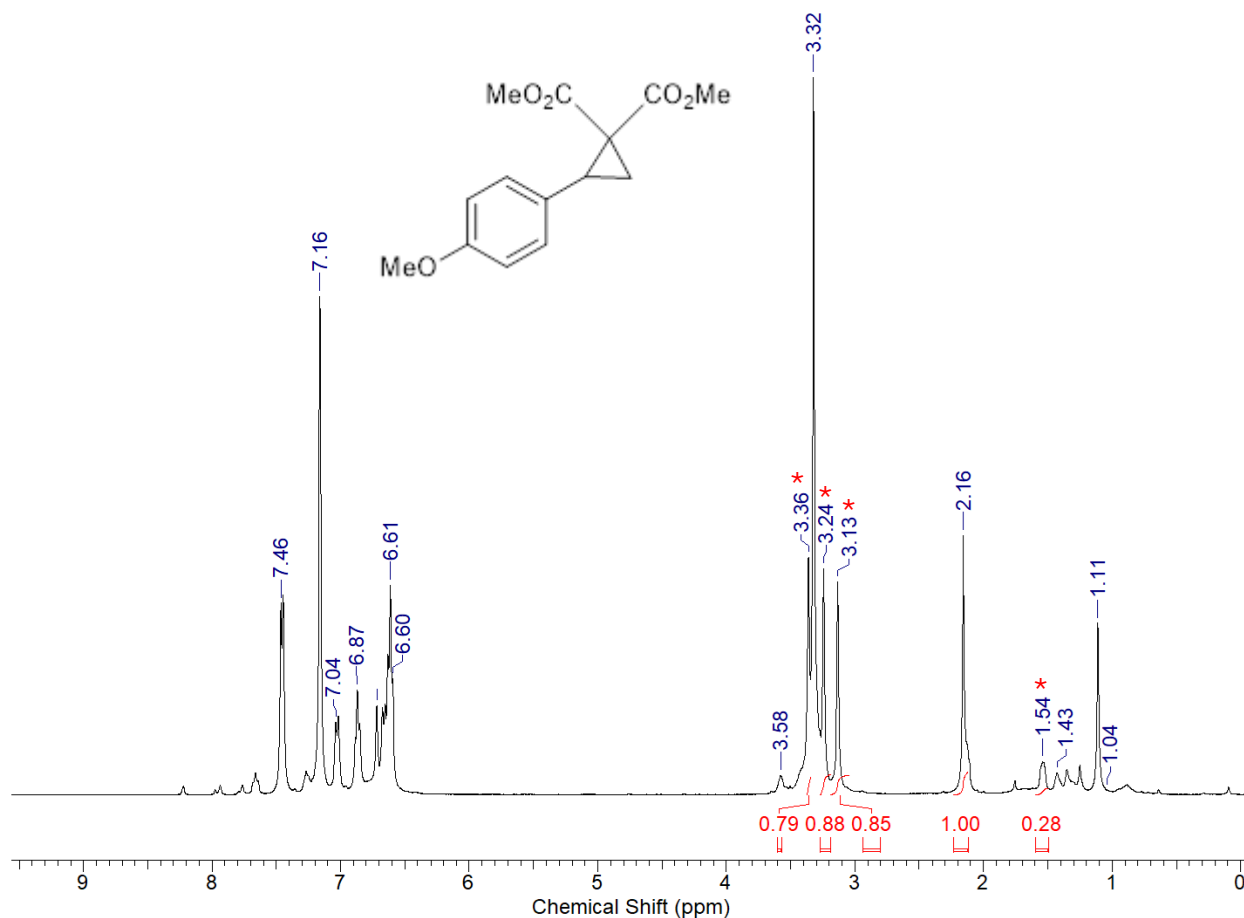
Figure S7. ^1H NMR (C_6D_6) demonstrating no catalytic formation of dimethyl 2-methyl-3-phenylcyclopropane-1,1-dicarboxylate, using **1** with cis-β-methylylstyrene. The peaks at 1.71 ppm, 5.63 ppm, 6.43 ppm, 7.05 ppm, and 7.22 ppm correspond to the remaining cis-β-methylylstyrene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.56 ppm correspond to tetrahydrofuran.
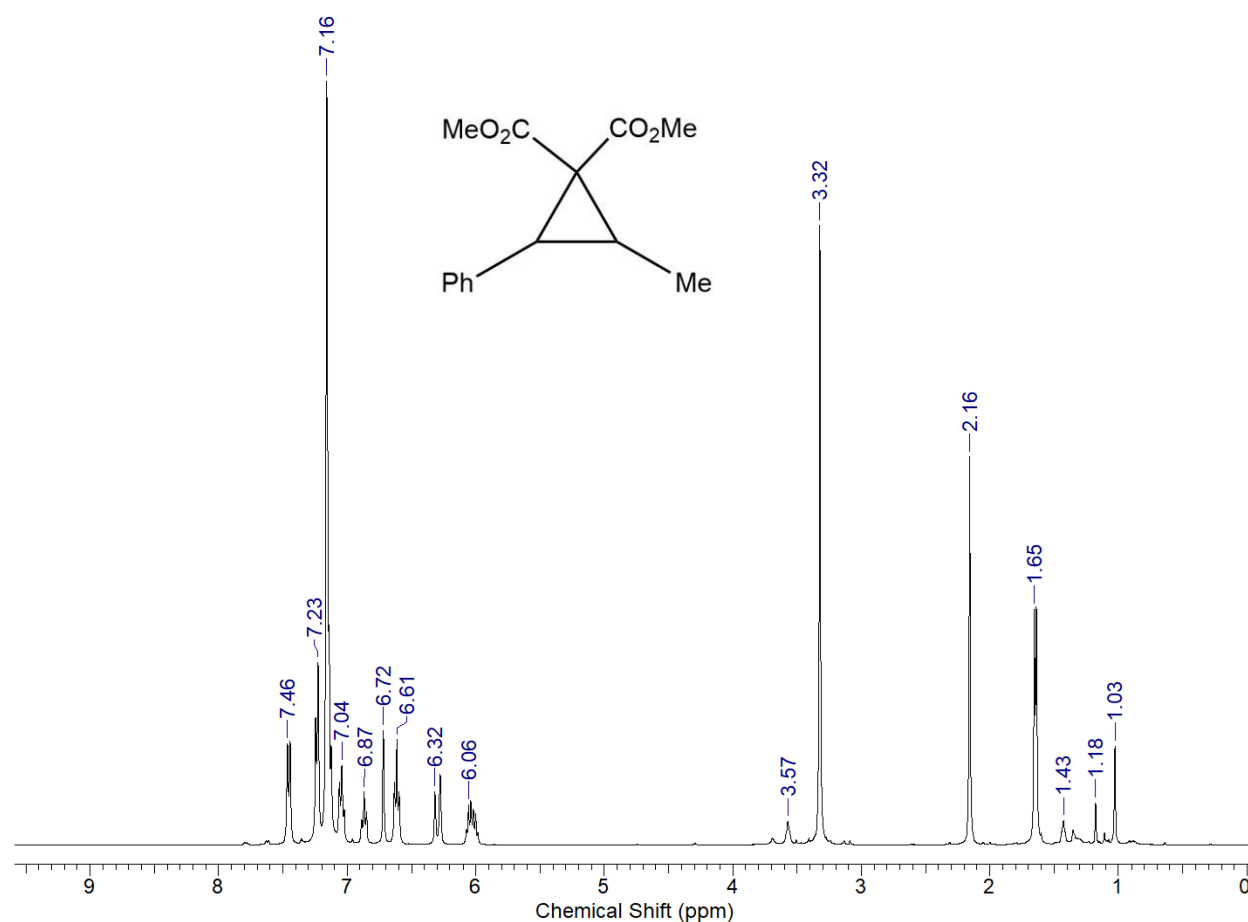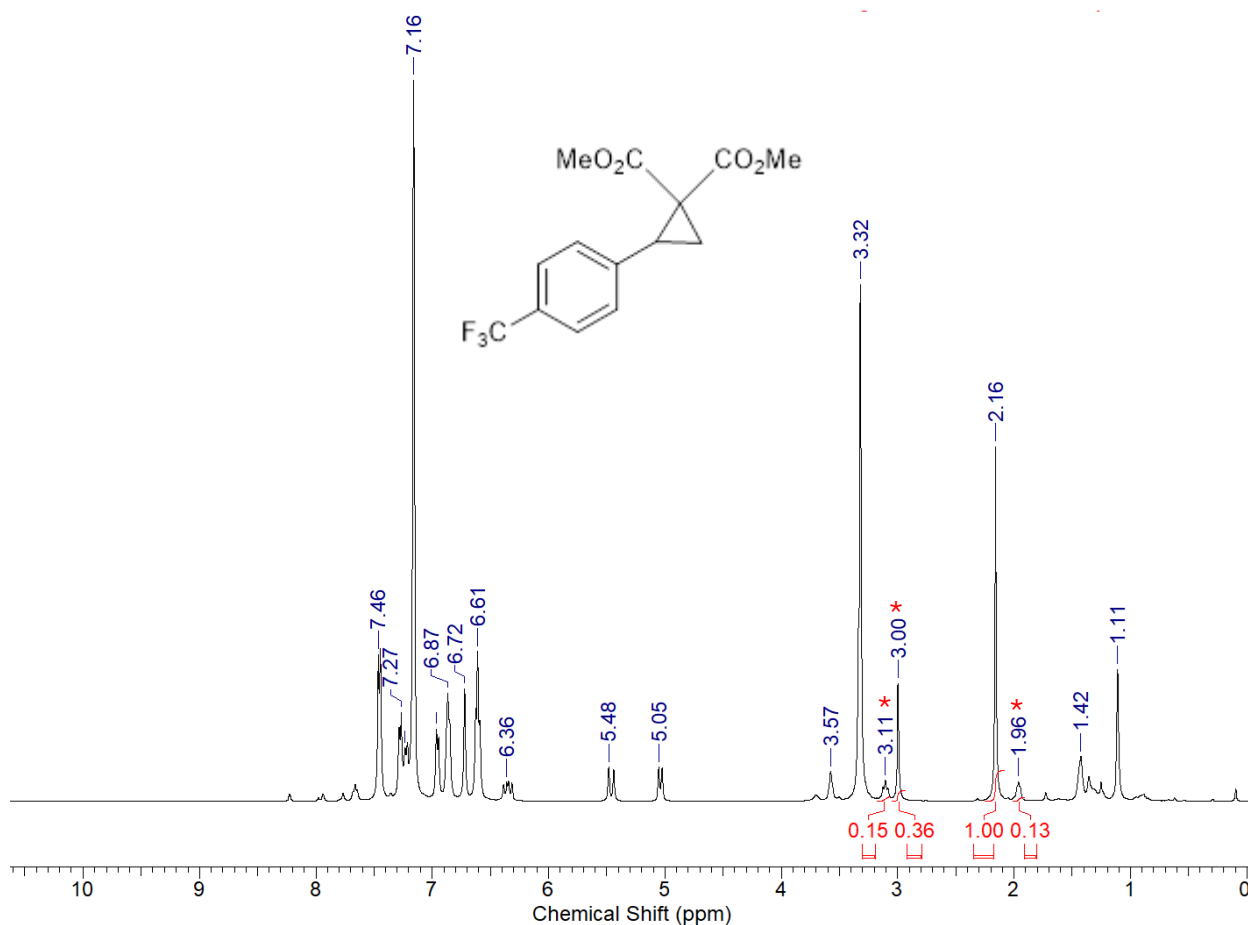
Figure S8. ^{1}H NMR (C_6D_6) demonstrating no catalytic formation of dimethyl 2-methyl-3-phenylcyclopropane-1,1-dicarboxylate, with **1** with trans-β-methylylstyrene. The peaks at 1.65 ppm, 6.06 ppm, 6.32 ppm, 7.04 ppm, and 7.23 ppm correspond to the remaining trans-β-methylylstyrene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.

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Figure S9. ^{1}H NMR (C$_6$D$_6$) demonstrating no catalytic formation of trimethyl cyclopropane-1,1,2-tricarboxylate with **1** and methyl acrylate substrate. The peaks at 5.24 ppm, 5.92 ppm, and 6.27 ppm correspond to the remaining methyl acrylate. The peak at 3.33 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. Three methyl acrylate protons are obstructed by the peak corresponding to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.

Figure S10. ^{1}H NMR (C$_6$D$_6$) demonstrating no catalytic formation of dimethyl 2-octylcyclopropane-1,1-dicarboxylate, with **1** and 1-decene. The peaks at 0.90 ppm, 1.24 ppm, 1.33 ppm, 2.00 ppm, 5.02 ppm, and 5.81 ppm correspond to the remaining 1-decene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.
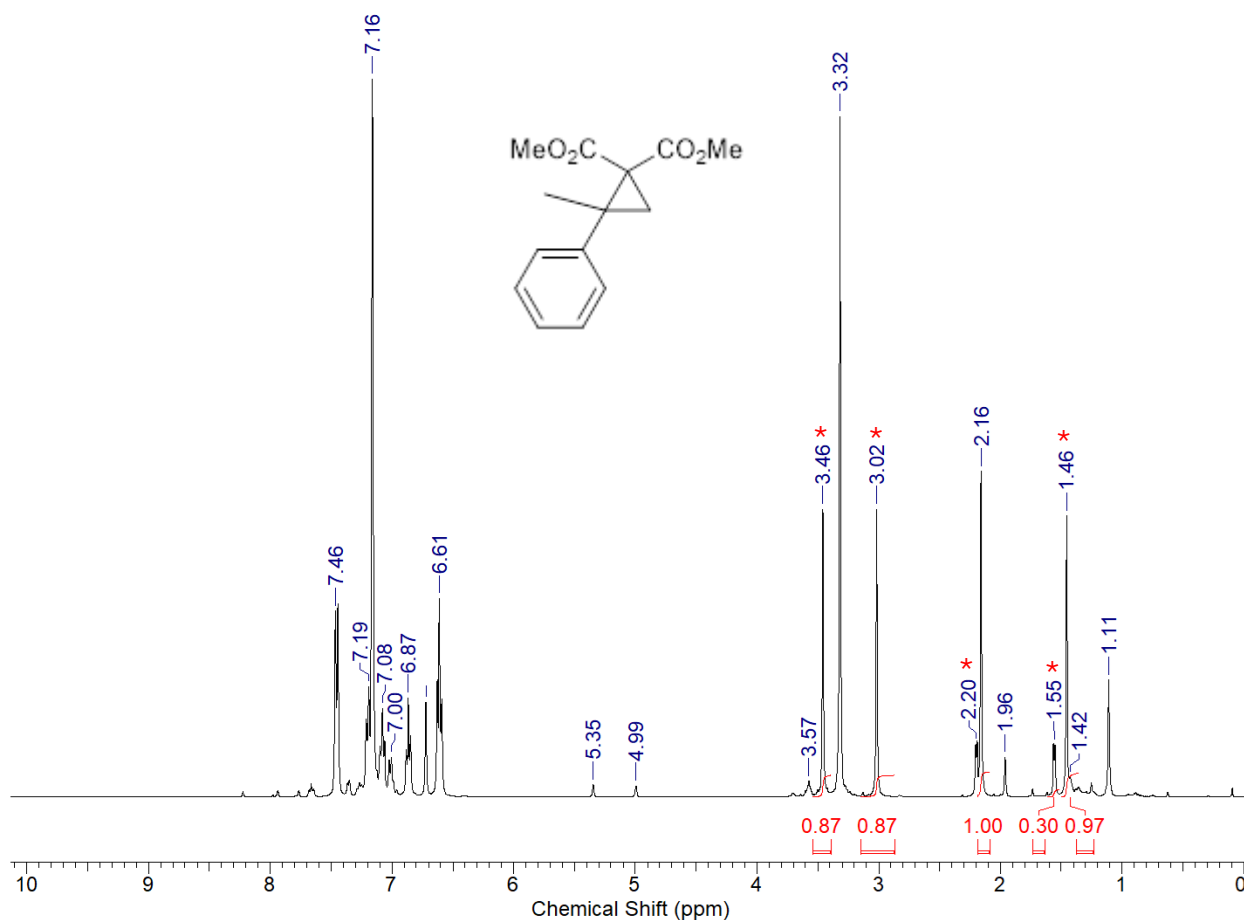
Figure S11. ^{1}H NMR (C$_6$D$_6$) demonstrating catalytic formation of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate using **2** and styrene. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.08 ppm and 5.62 ppm correspond to the remaining styrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.
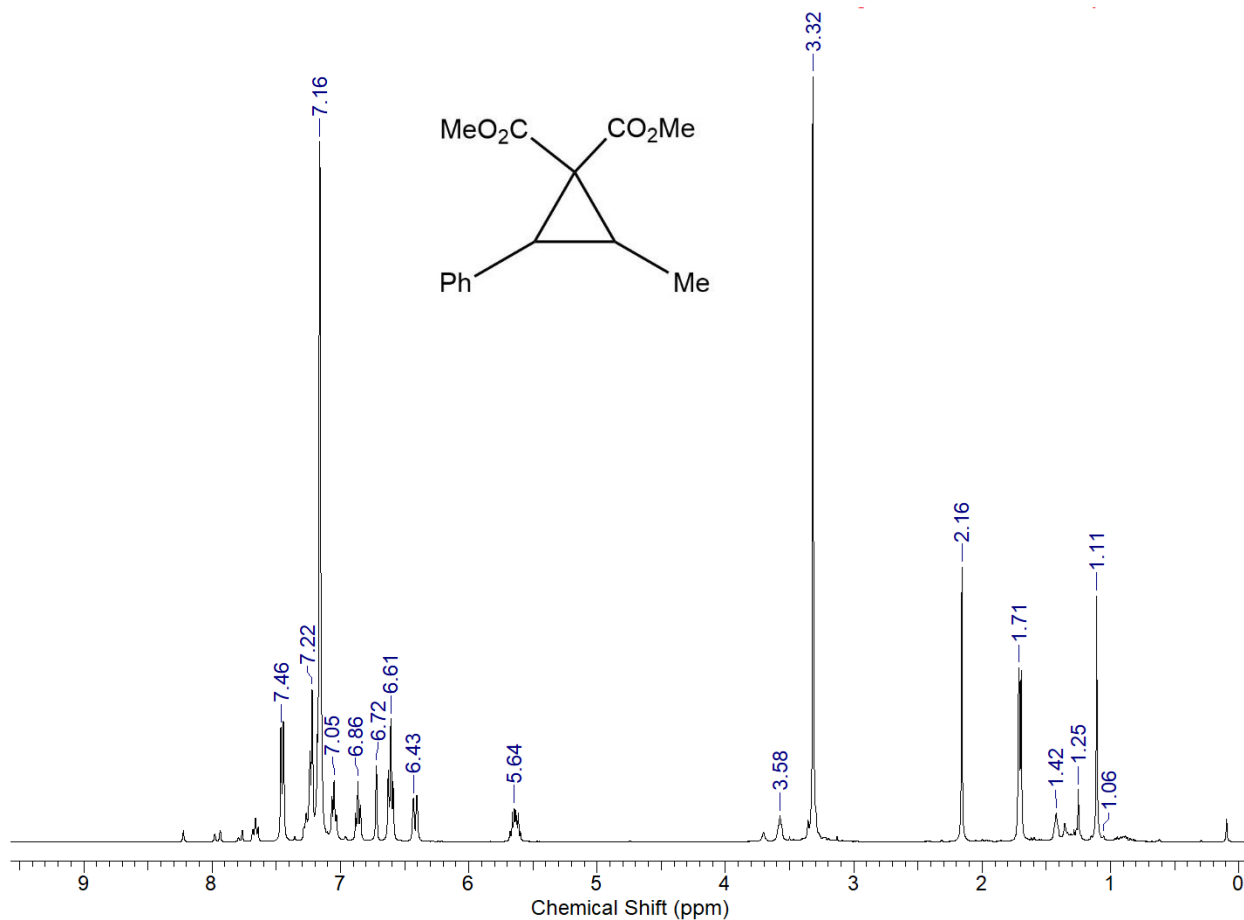
Figure S12. ^1H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate using **2** and 4-tert-butylstyrene substrate. The signals belonging to cyclopropane are marked with *. Two cyclopropane protons are obstructed by peaks corresponding to tert-butyl group, by-product or solvents. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.64 ppm and 5.11 ppm correspond to the remaining 4-tert-butylstyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.57 ppm correspond to tetrahydrofuran.
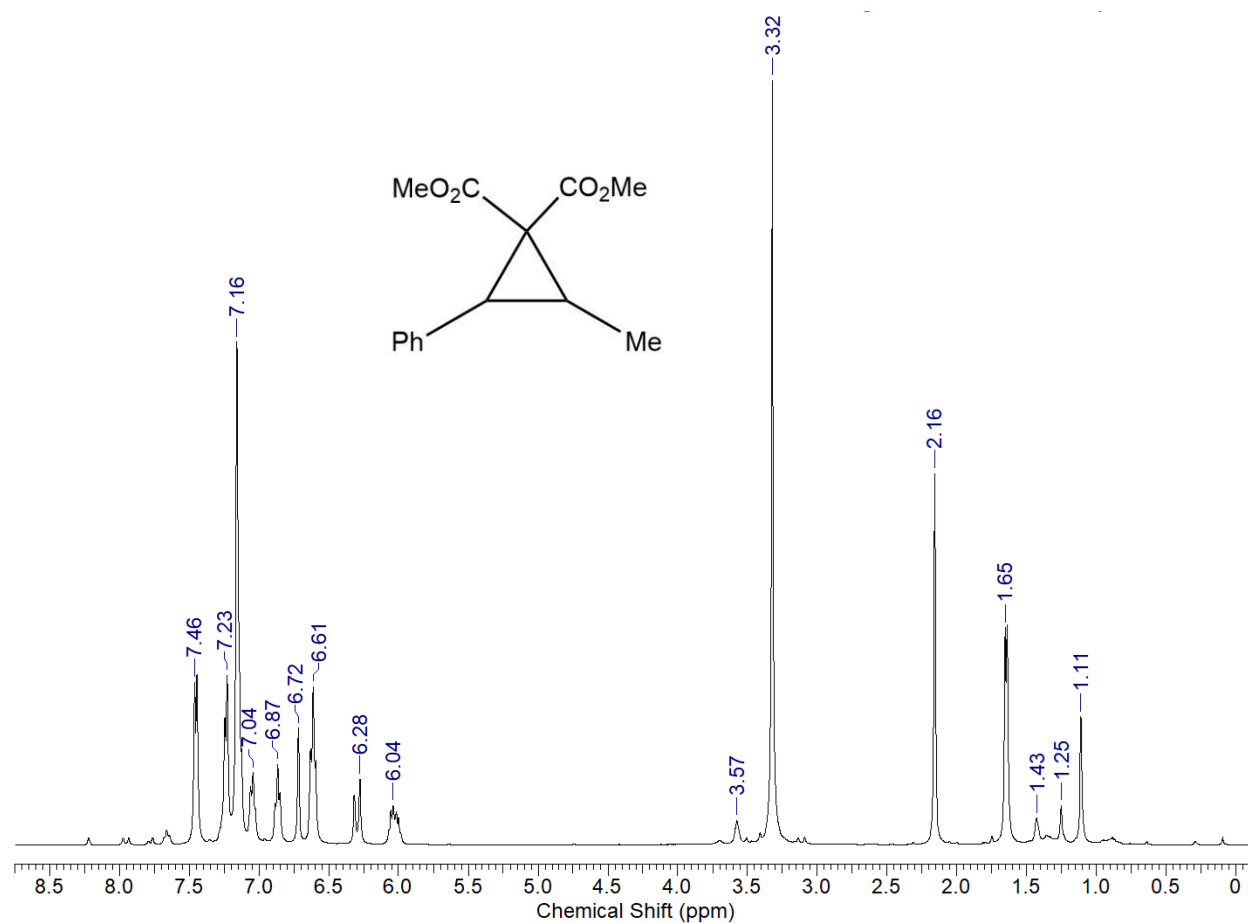
Figure S13. ^{1}H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate using **2** and 4-methoxystyrene substrate. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. Two methine cyclopropane protons are obstructed by peaks corresponding to solvents, internal standard (2.16 ppm), or tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.58 ppm correspond to tetrahydrofuran.
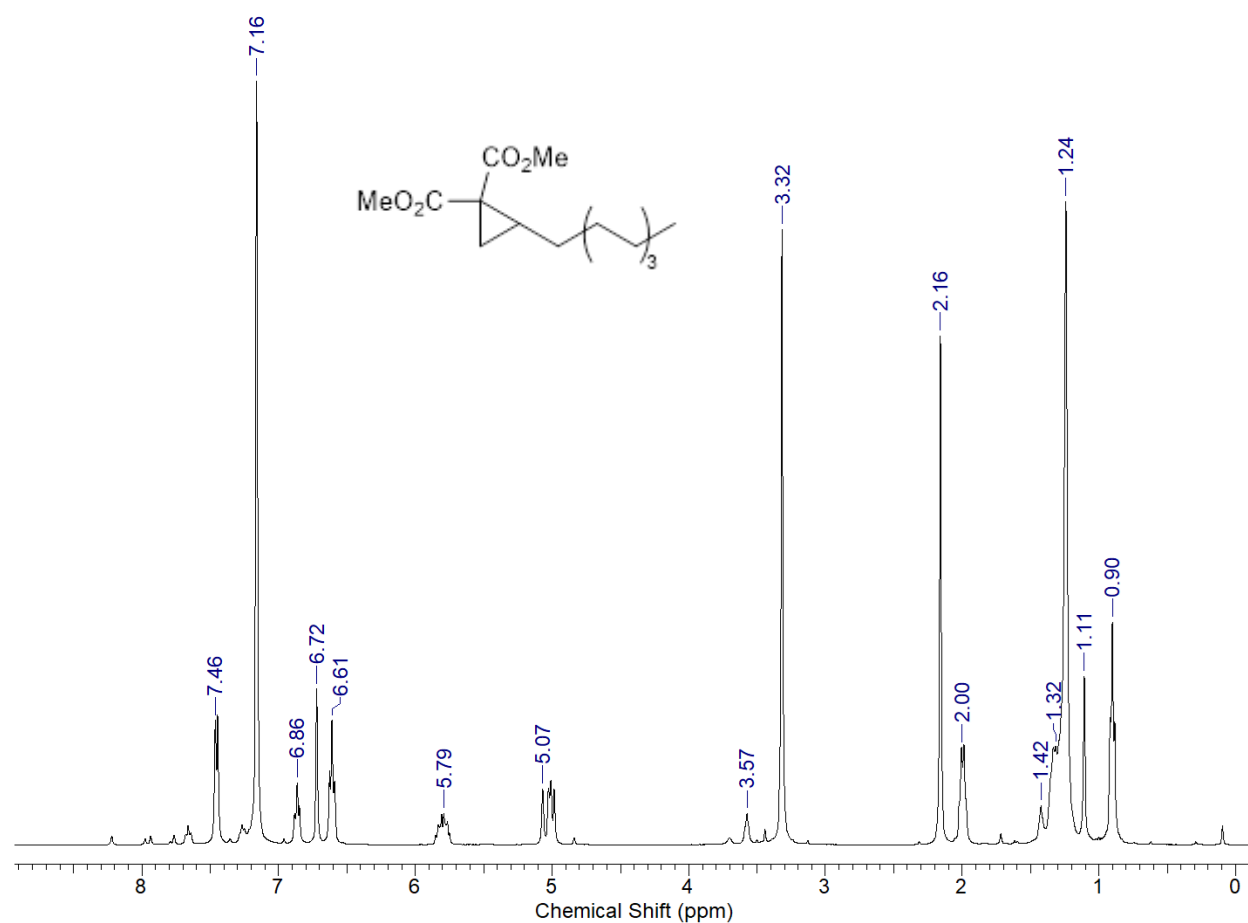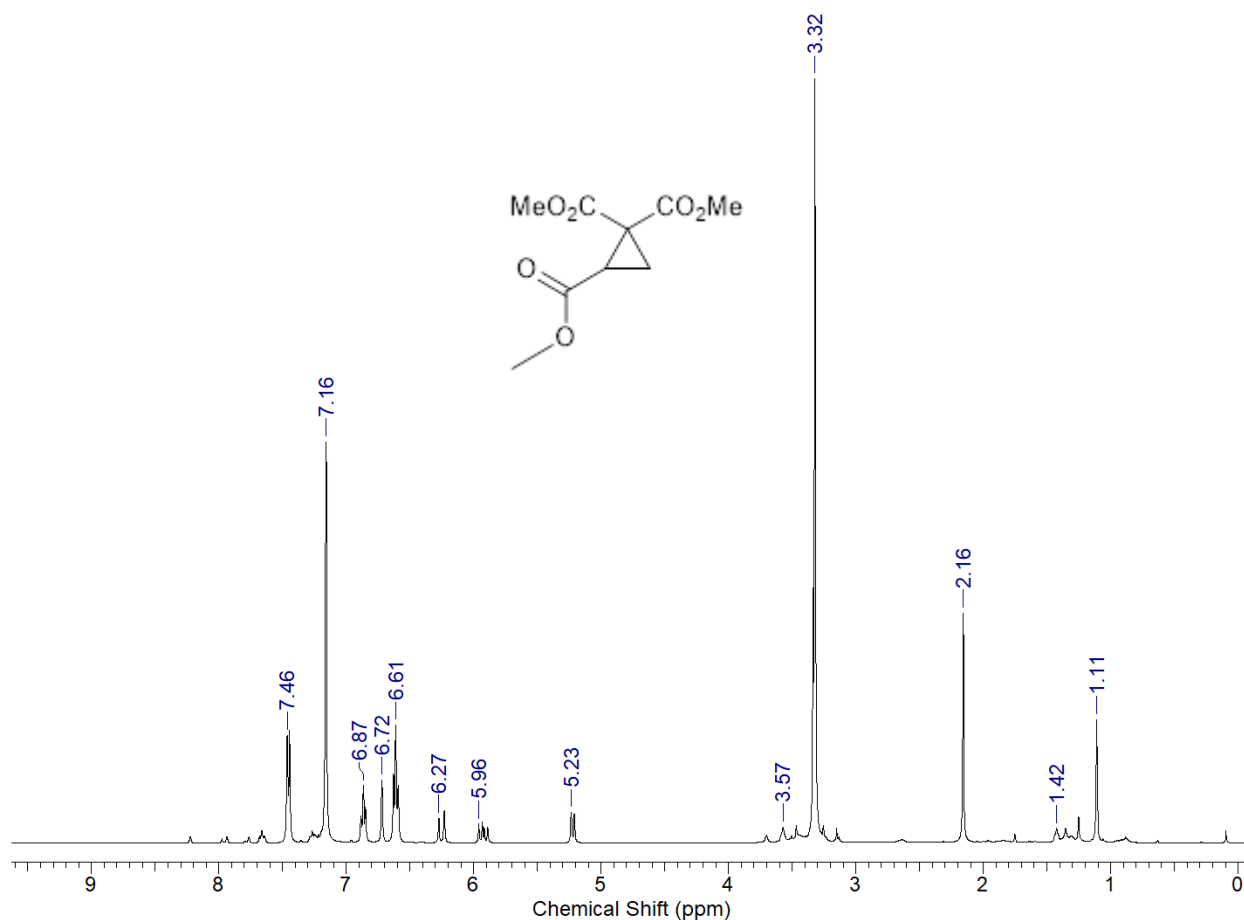
Figure S14. ^{1}H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate using **2** and 4-CF$_3$-styrene substrate. The signals belonging to cyclopropane are marked with *. One cyclopropane methine proton s obstructed by peaks corresponding to solvents or tetramethyl ethene-1,1,2,2-tetracarboxylate. In addition, one of the methyl groups of cyclopropanes is likely under the peak at 3.32 ppm, which corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.48 ppm and 5.05 ppm correspond to the remaining 4-CF$_3$-styrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.57 ppm correspond to tetrahydrofuran.
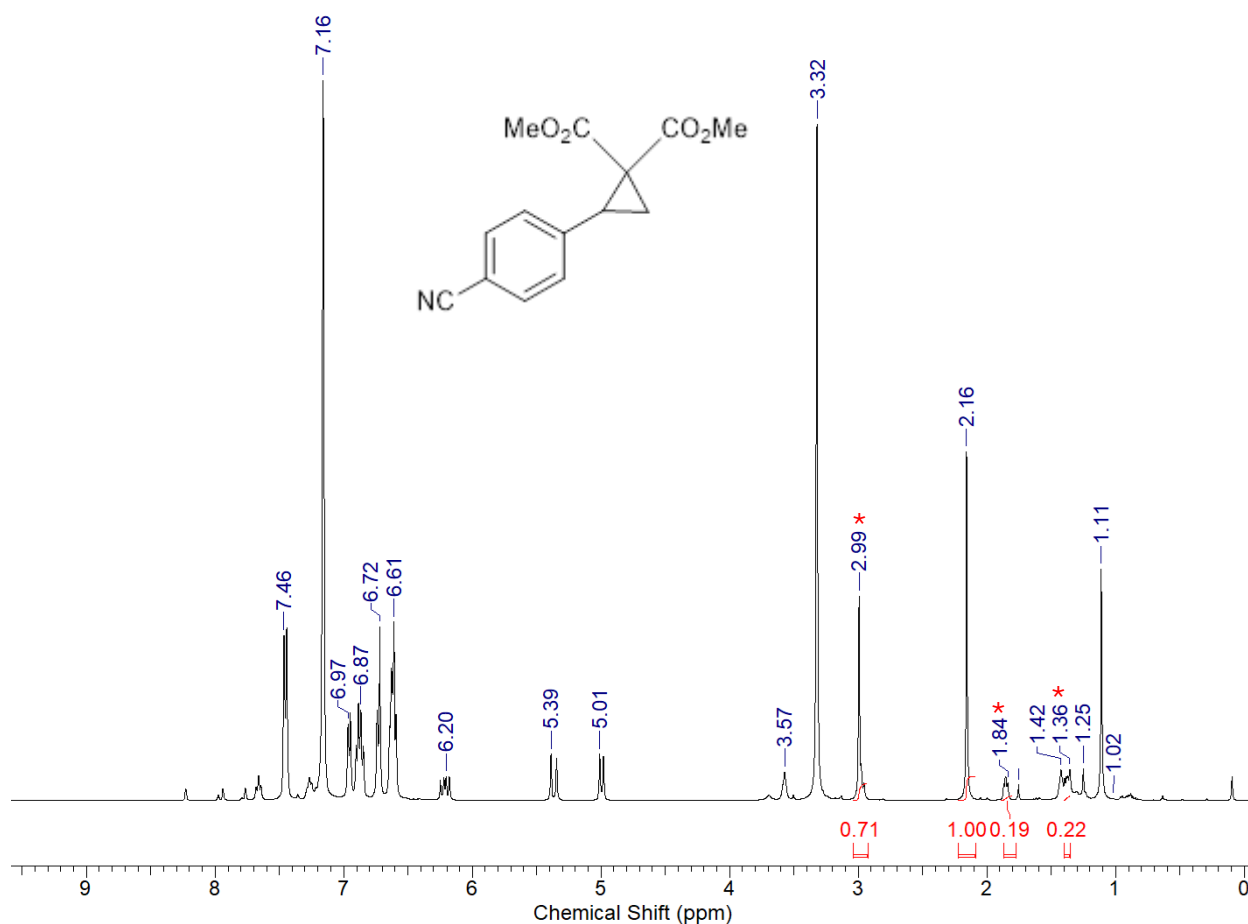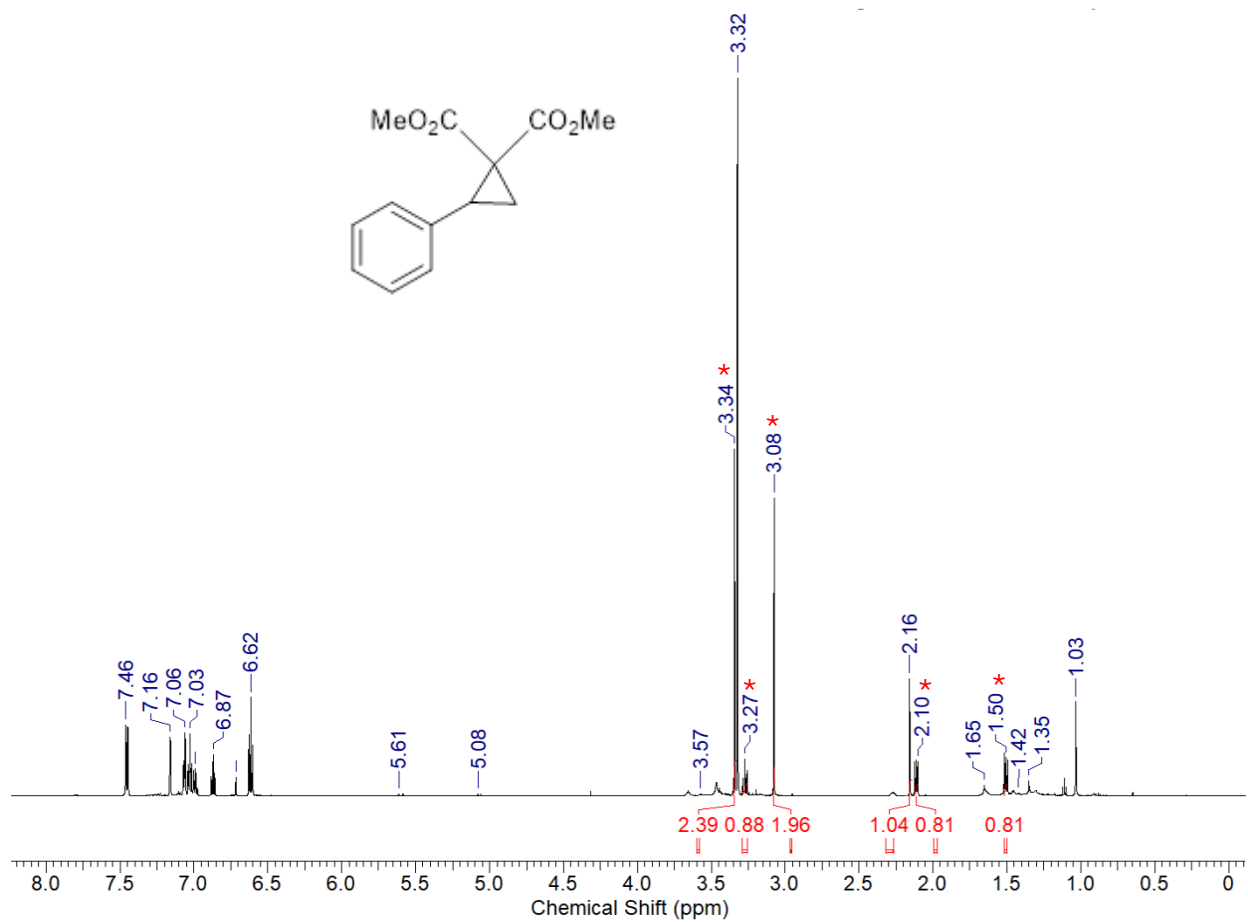
Figure S15. ^{1}H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate, using **2** and 4-cyanostyrene substrate. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate; this peak contained also one of the cyclopropanes methyl groups. The peaks at 5.39 ppm and 5.01 ppm correspond to the remaining 4-cyanostyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.57 ppm correspond to tetrahydrofuran.
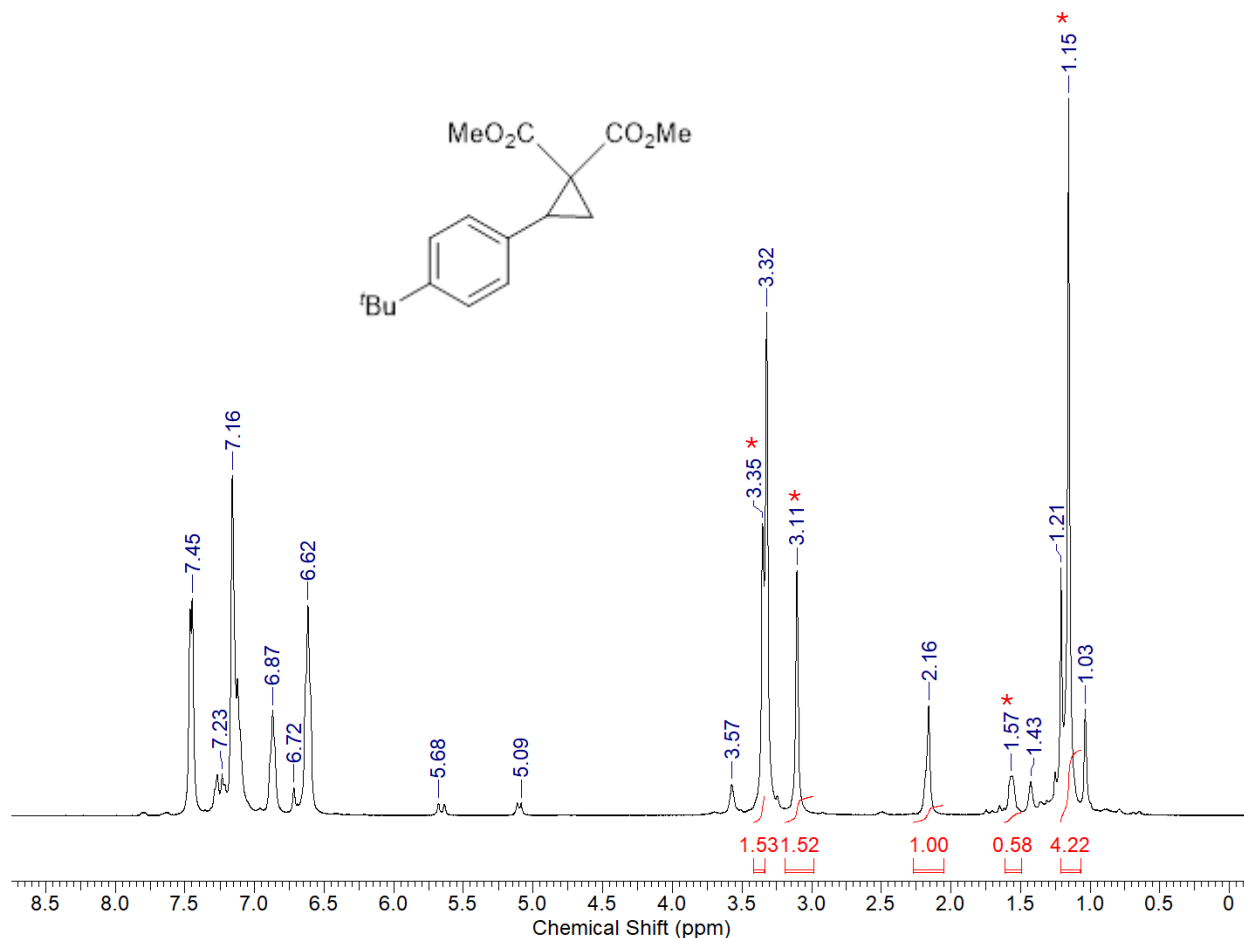
Figure S16. ^{1}H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate, by **2** and α-methylstyrene. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.35 ppm, 4.99 ppm, and 1.96 ppm correspond to the remaining α-methylstyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.57 ppm correspond to tetrahydrofuran.

Figure S17. ^{1}H NMR (C_6D_6) demonstrating no catalytic formation of dimethyl 2-methyl-3-phenylcyclopropane-1,1-dicarboxylate, using **2** with cis-β-methylylstyrene. The peaks at 1.71 ppm, 5.64 ppm, 6.43 ppm, 7.05 ppm, and 7.22 ppm correspond to the remaining cis-β-methylylstyrene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.58 ppm correspond to tetrahydrofuran.
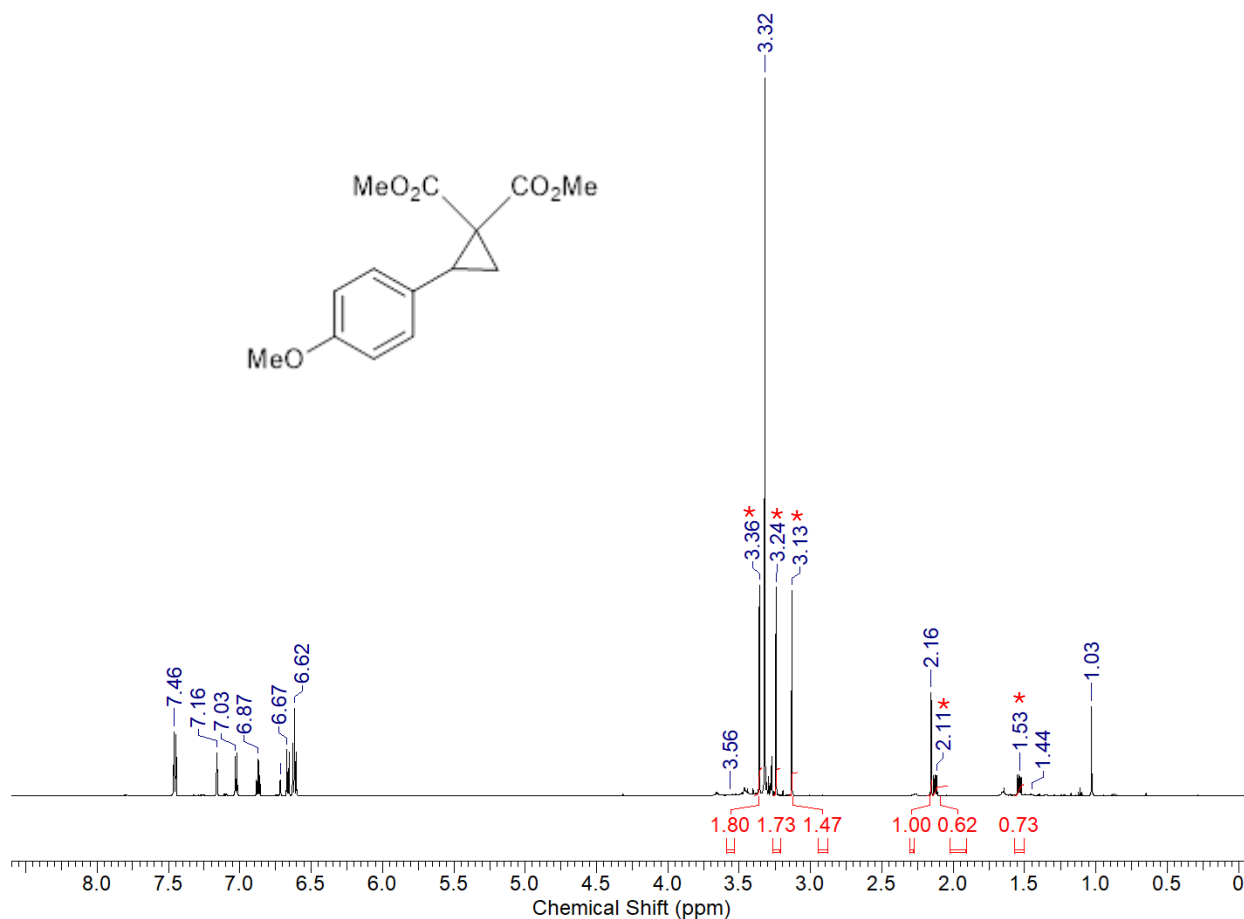
Figure S18. ^{1}H NMR (C$_6$D$_6$) demonstrating no catalytic formation of dimethyl 2-methyl-3-phenylcyclopropane-1,1-dicarboxylate, using **2** with trans-β-methylylstyrene. The peaks at 1.65 ppm, 6.04 ppm, 6.28 ppm, 7.04 ppm, and 7.23 ppm correspond to the remaining trans-β-methylylstyrene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.

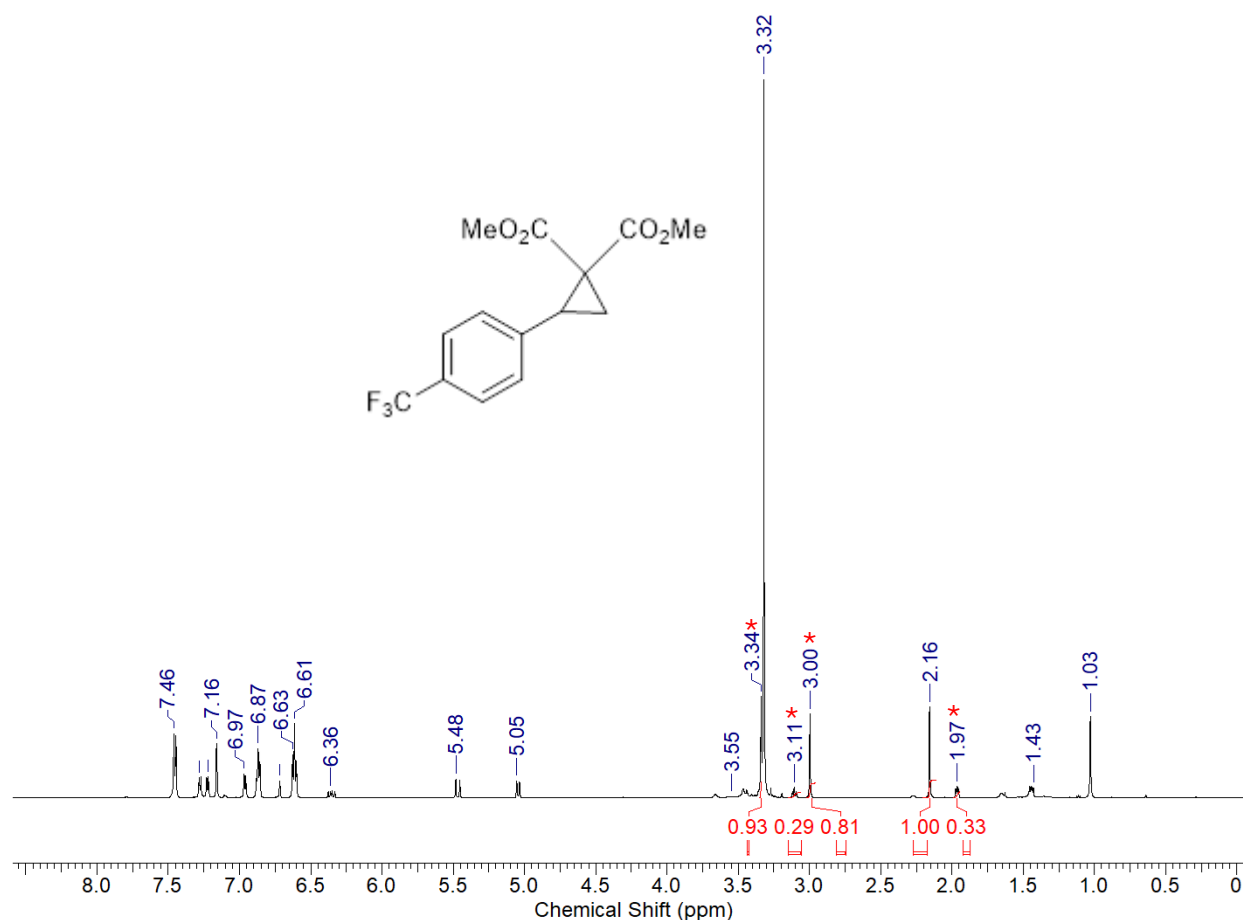**Figure S19.** ^{1}H NMR (C_6D_6) demonstrating no catalytic formation of dimethyl 2-octylcyclopropane-1,1-dicarboxylate, with **2** and 1-decene. The peaks at 0.90 ppm, 1.24 ppm, 1.32 ppm, 2.00 ppm, 5.07 ppm, and 5.79 ppm correspond to the remaining 1-decene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.57 ppm correspond to tetrahydrofuran.
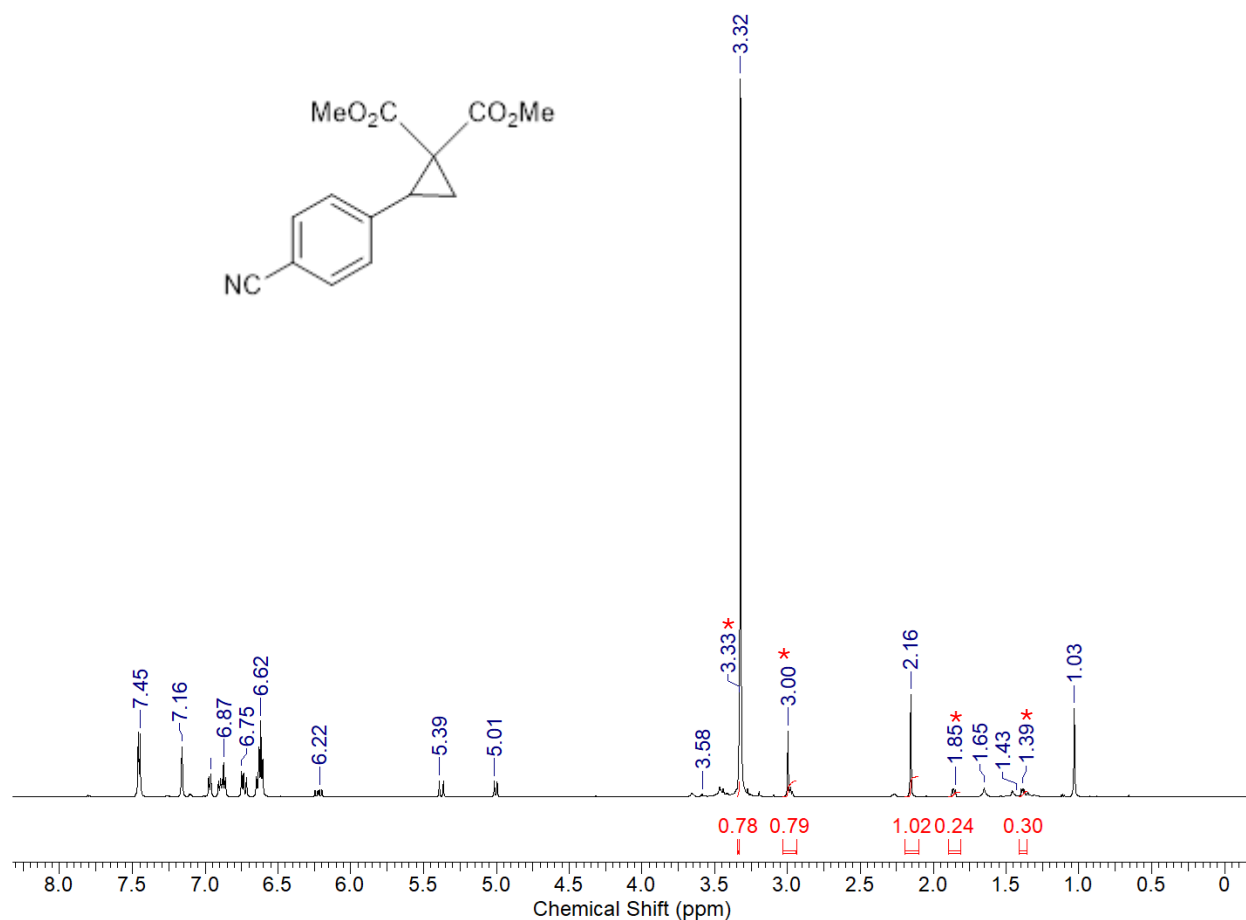
Figure S20. ^{1}H NMR (C$_6$D$_6$) demonstrating no catalytic formation of trimethyl cyclopropane-1,1,2-tricarboxylate with **2** and methyl acrylate substrate. The peaks at 5.23 ppm, 5.96 ppm, and 6.27 ppm correspond to the remaining methyl acrylate. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. Three methyl acrylate protons are obstructed by the peak corresponding to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.57 ppm correspond to tetrahydrofuran.
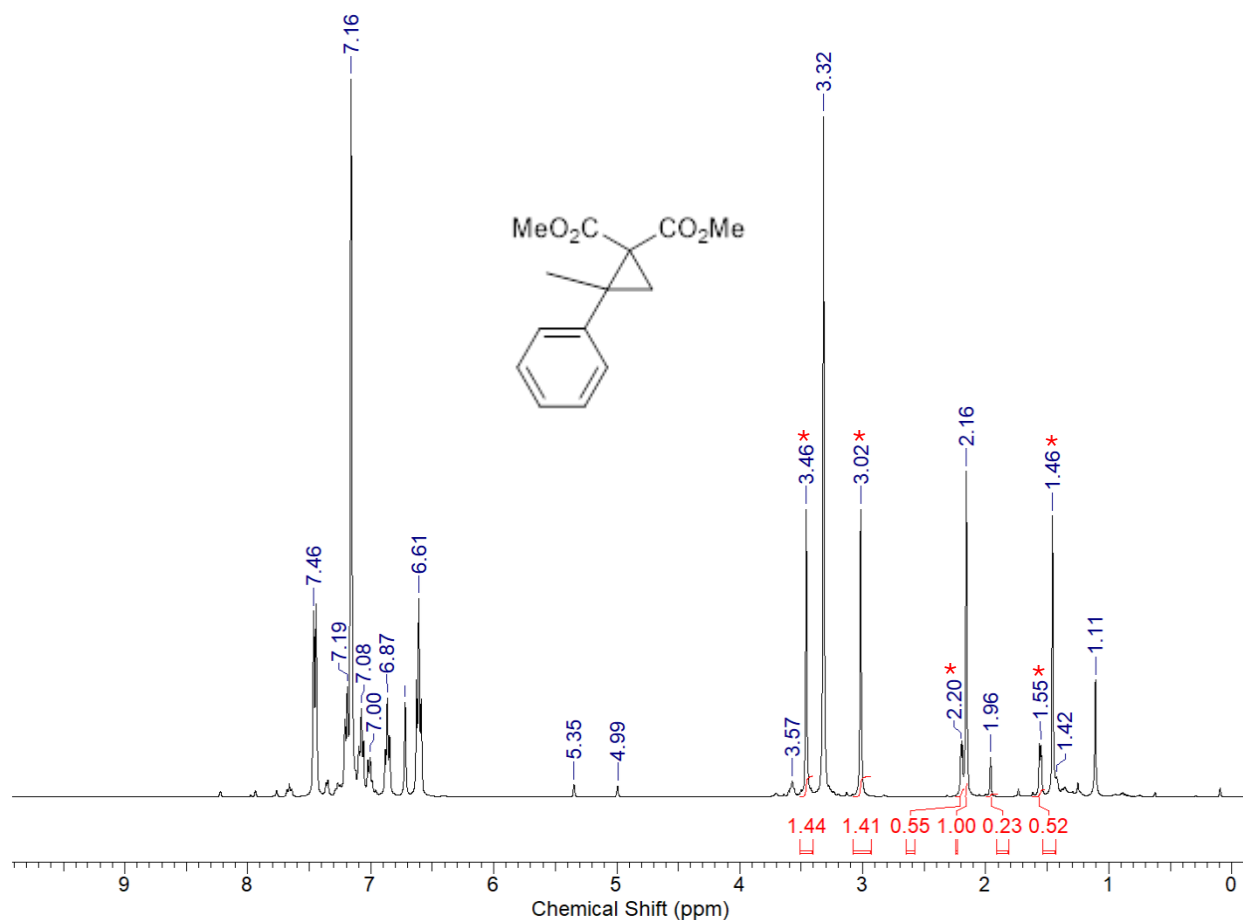
Figure S21. ^{1}H NMR (C$_6$D$_6$) demonstrating catalytic formation of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate using **3** and styrene. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.08 ppm and 5.61 ppm correspond to the remaining styrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.57 ppm correspond to tetrahydrofuran.
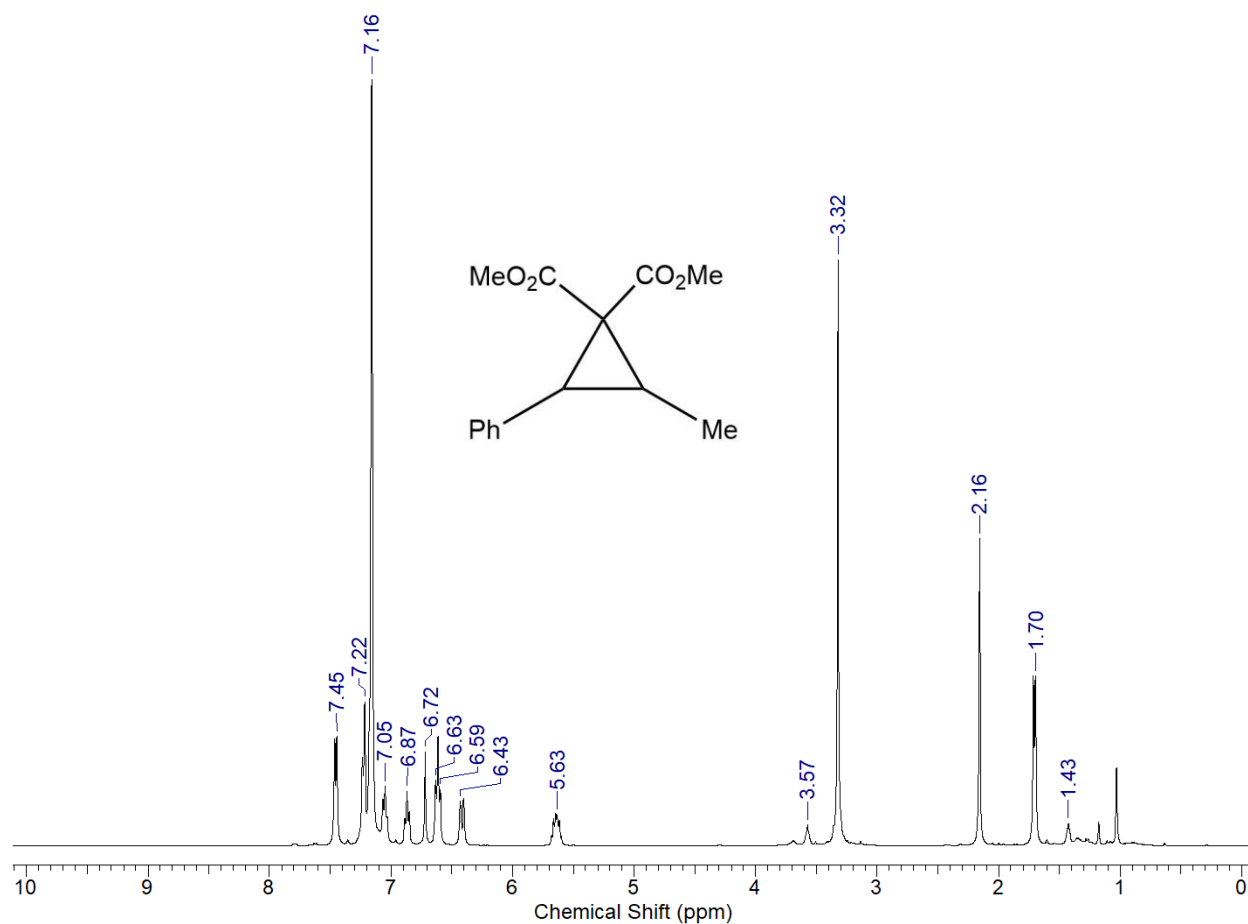
Figure S22. ^1H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate using **3** and 4-tert-butylstyrene substrate. The signals belonging to cyclopropane are marked with *. One the cyclopropane protons (methine) is likely obstructed by the mesytilene peak (2.16 ppm). The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.68 ppm and 5.09 ppm correspond to the remaining 4-tert-butylstyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.

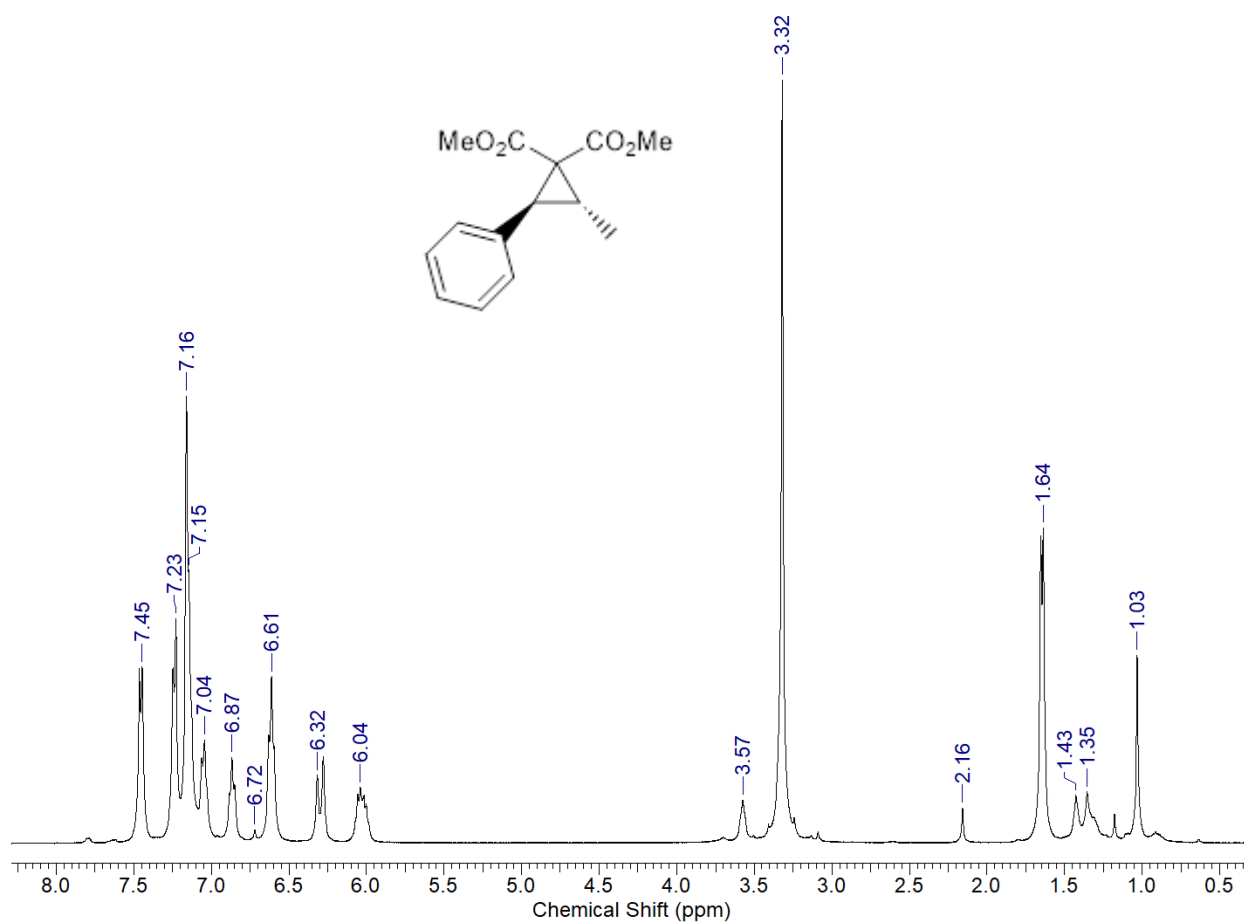**Figure S23.** ^1H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate using **3** and 4-methoxystyrene substrate. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. One of the cyclopropane methines is obstructed by peaks corresponding to tetramethyl ethene-1,1,2,2-tetracarboxylate (3.32 ppm). The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.44 ppm and 3.56 ppm correspond to tetrahydrofuran.

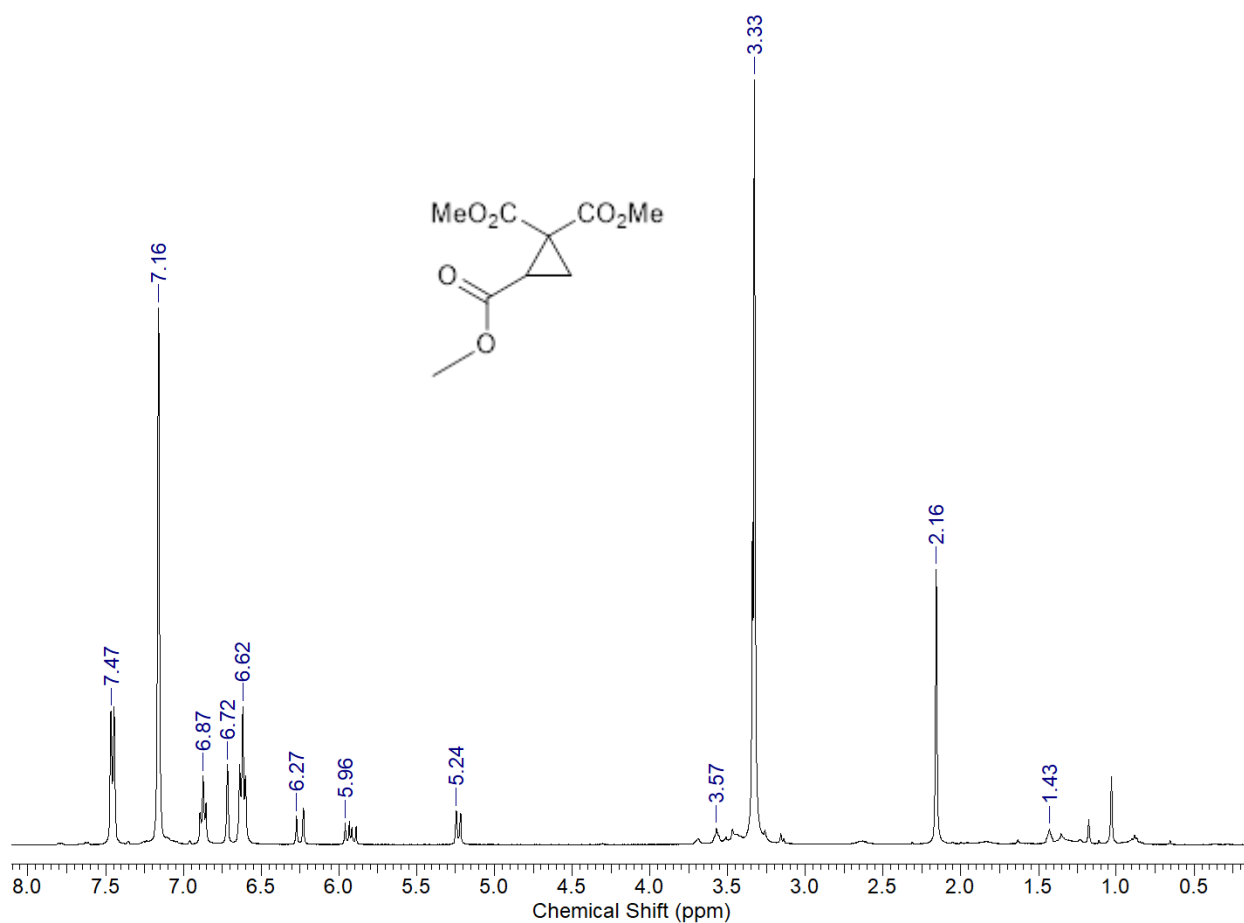**Figure S24.** ¹H NMR (C₆D₆) demonstrating catalytic formation of dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate using **3** and 4-CF₃-styrene substrate. The signals belonging to cyclopropane are marked with *. One cyclopropane methine is likely obstructed by peak corresponding to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.48 ppm and 5.05 ppm correspond to the remaining 4-CF₃-styrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.55 ppm correspond to tetrahydrofuran.
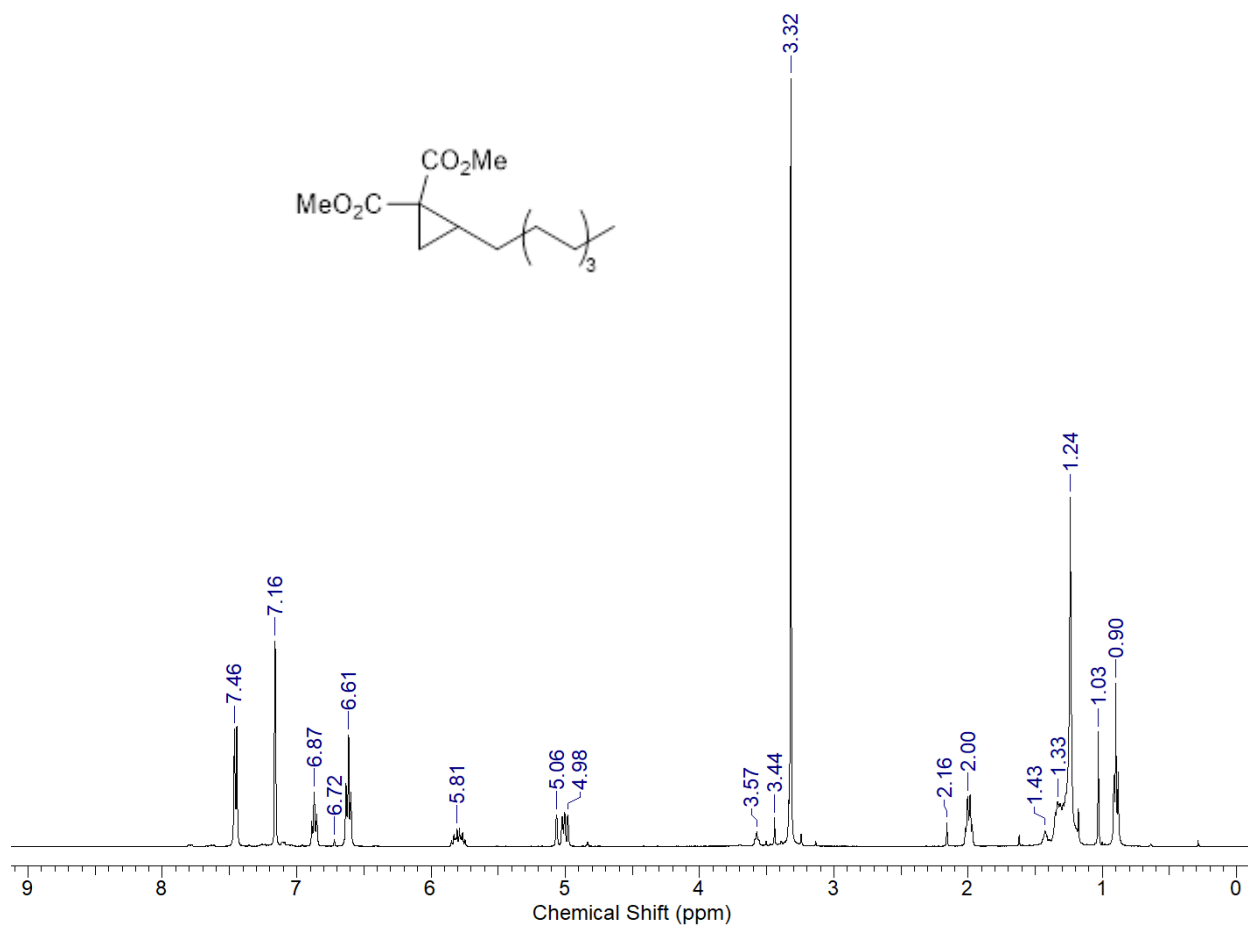
Figure S25. ^{1}H NMR (C$_6$D$_6$) demonstrating catalytic formation of dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate, using **3** and 4-cyanostyrene substrate. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate; this peak likely obscures of the cyclopropane methines. The peaks at 5.39 ppm and 5.01 ppm correspond to the remaining 4-cyanostyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.58 ppm correspond to tetrahydrofuran.

Figure S26. ^{1}H NMR (C_6D_6) demonstrating catalytic formation of dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate, by **3** and α-methylstyrene. The signals belonging to cyclopropane are marked with *. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 5.35 ppm, 4.99 ppm, and 1.96 ppm correspond to the remaining α-methylstyrene. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.42 ppm and 3.57 ppm correspond to tetrahydrofuran.

Figure S27. ^{1}H NMR (C_6D_6) demonstrating no catalytic formation of dimethyl 2-methyl-3-phenylcyclopropane-1,1-dicarboxylate, using **3** with cis-β-methylylstyrene. The peaks at 1.70 ppm, 5.63 ppm, 6.43 ppm, 7.05 ppm, and 7.22 ppm correspond to the remaining cis-β-methylylstyrene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.

Figure S28. ^1H NMR (C_6D_6) demonstrating NO catalytic formation of dimethyl (2S,3R)-2-methyl-3-phenylcyclopropane-1,1-dicarboxylate, with **3** with trans-β-methylylstyrene. The peaks at 1.64 ppm, 6.04 ppm, 6.32 ppm, 7.04 ppm, and 7.23 ppm correspond to the remaining trans-β-methylylstyrene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.

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Figure S29. ^{1}H NMR (C$_6$D$_6$) demonstrating NO catalytic formation of trimethyl cyclopropane-1,1,2-tricarboxylate with **3** and methyl acrylate substrate. The peaks at 5.24 ppm, 5.96 ppm, and 6.27 ppm correspond to the remaining methyl acrylate. The peak at 3.33 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. Three methyl acrylate protons are obstructed by the peak corresponding to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.

Figure S30. ^{1}H NMR (C$_6$D$_6$) demonstrating NO catalytic formation of dimethyl 2-octylcyclopropane-1,1-dicarboxylate, with **3** and 1-decene. The peaks at 0.90 ppm, 1.24 ppm, 1.33 ppm, 2.00 ppm, 5.06 ppm, and 5.81 ppm correspond to the remaining 1-decene. The peak at 3.32 ppm corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.16 ppm and 6.72 ppm correspond to the mesitylene standard. The peaks at 1.43 ppm and 3.57 ppm correspond to tetrahydrofuran.
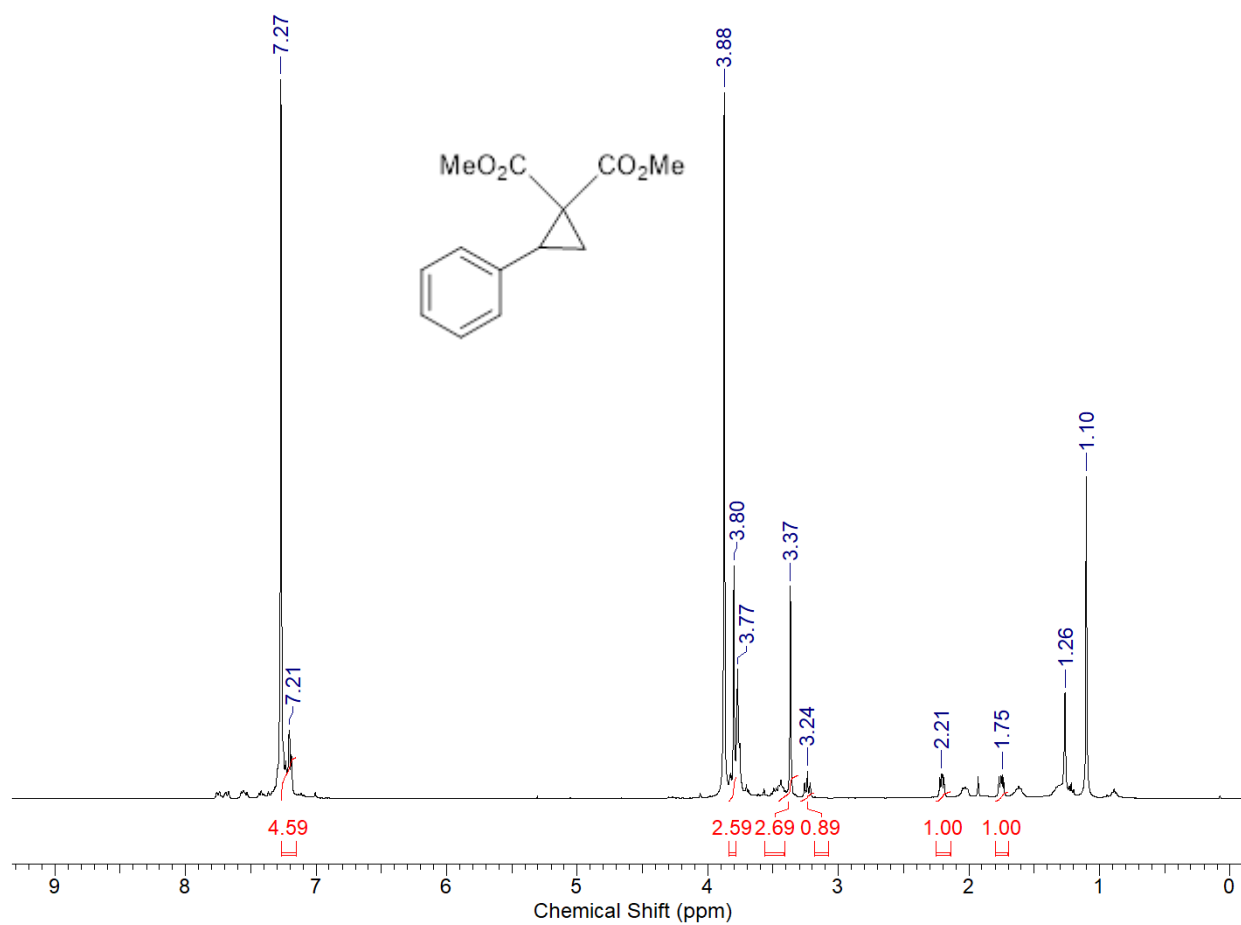
Figure S31. ^{1}H NMR (CDCl$_3$, 400 MHz) of crude reaction mixture indicating the formation of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate, tetramethyl ethene-1,1,2,2-tetracarboxylate, and PhI by **1**.
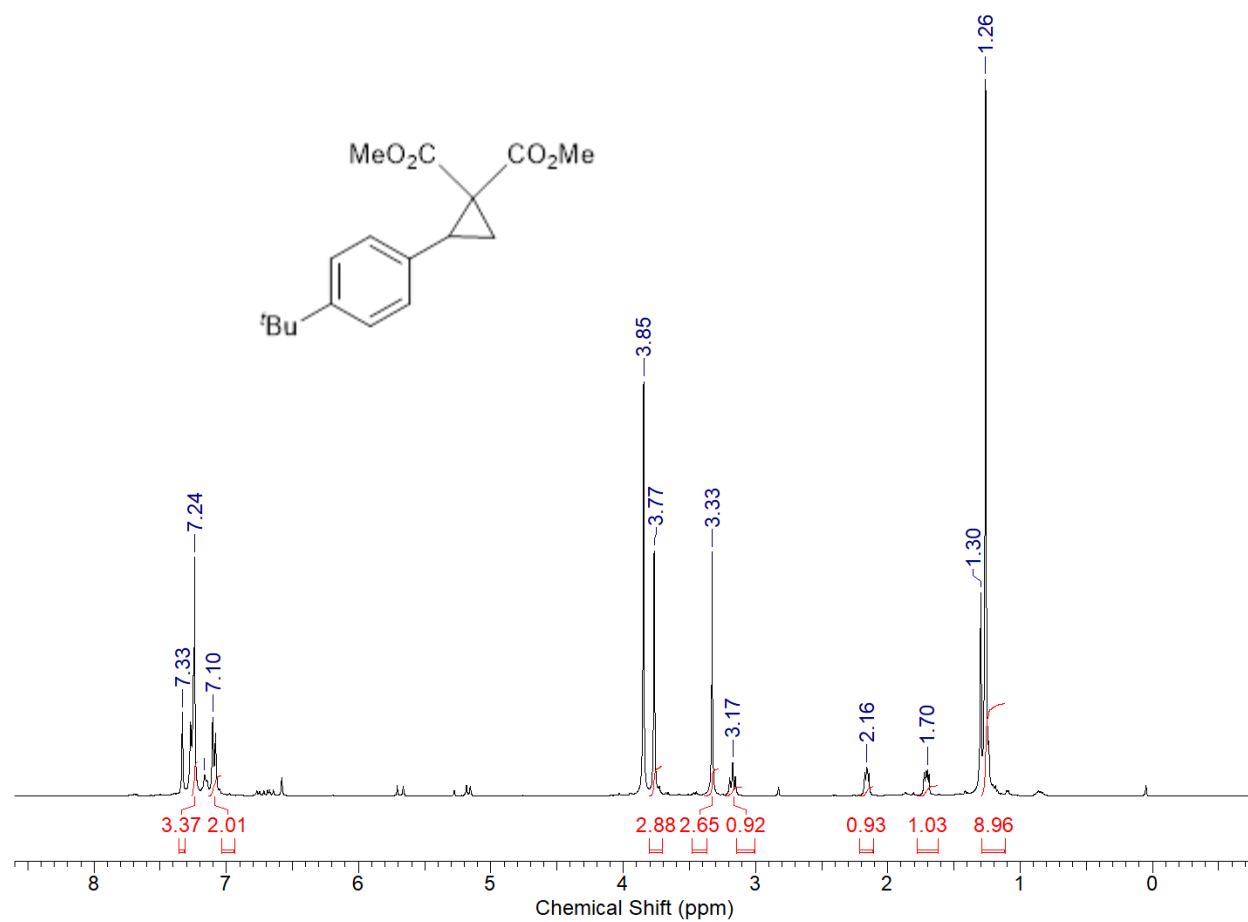
Figure S32. ^{1}H NMR (CDCl$_3$, 400 MHz) of crude reaction mixture indicating the formation of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate, tetramethyl ethene-1,1,2,2-tetracarboxylate, and PhI by **1**.
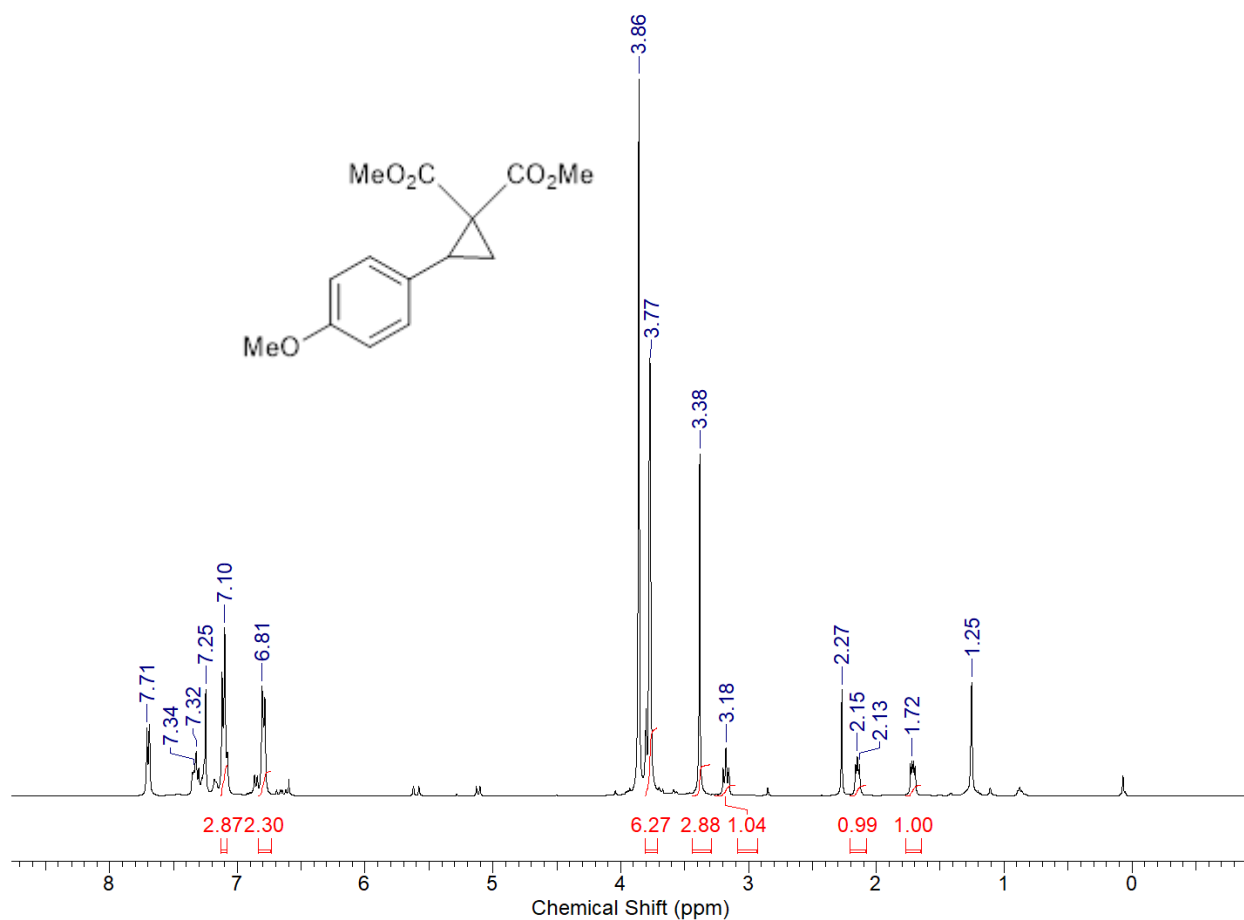
Figure S33. ^{1}H NMR (CDCl$_3$, 400 MHz) of crude reaction mixture indicating the formation of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate, tetramethyl ethene-1,1,2,2-tetracarboxylate, and PhI produced by **1**.
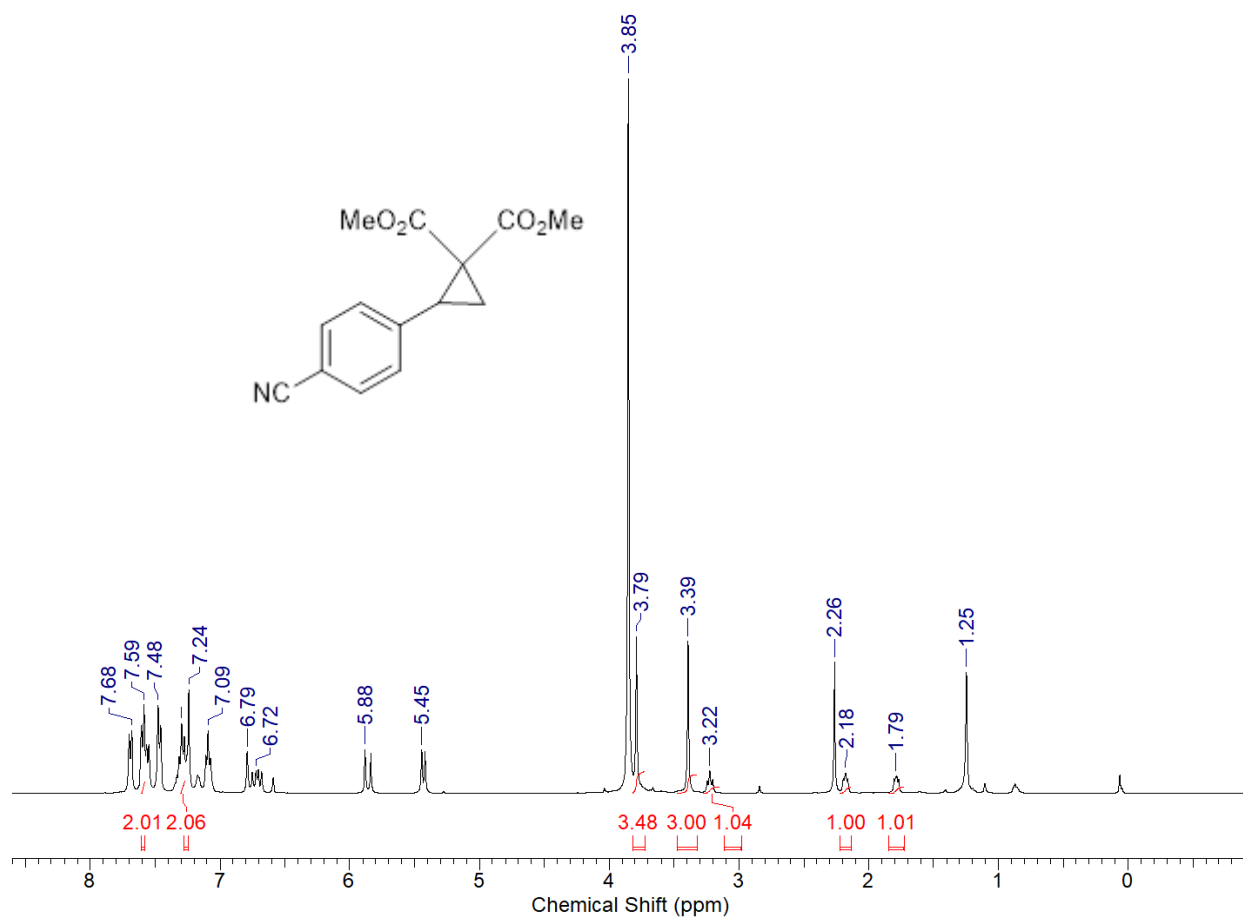
Figure 34. ^{1}H NMR (CDCl$_3$, 400 MHz) of crude reaction mixture indicating the formation of 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate, tetramethyl ethene-1,1,2,2-tetracarboxylate, and PhI produced by **1**.
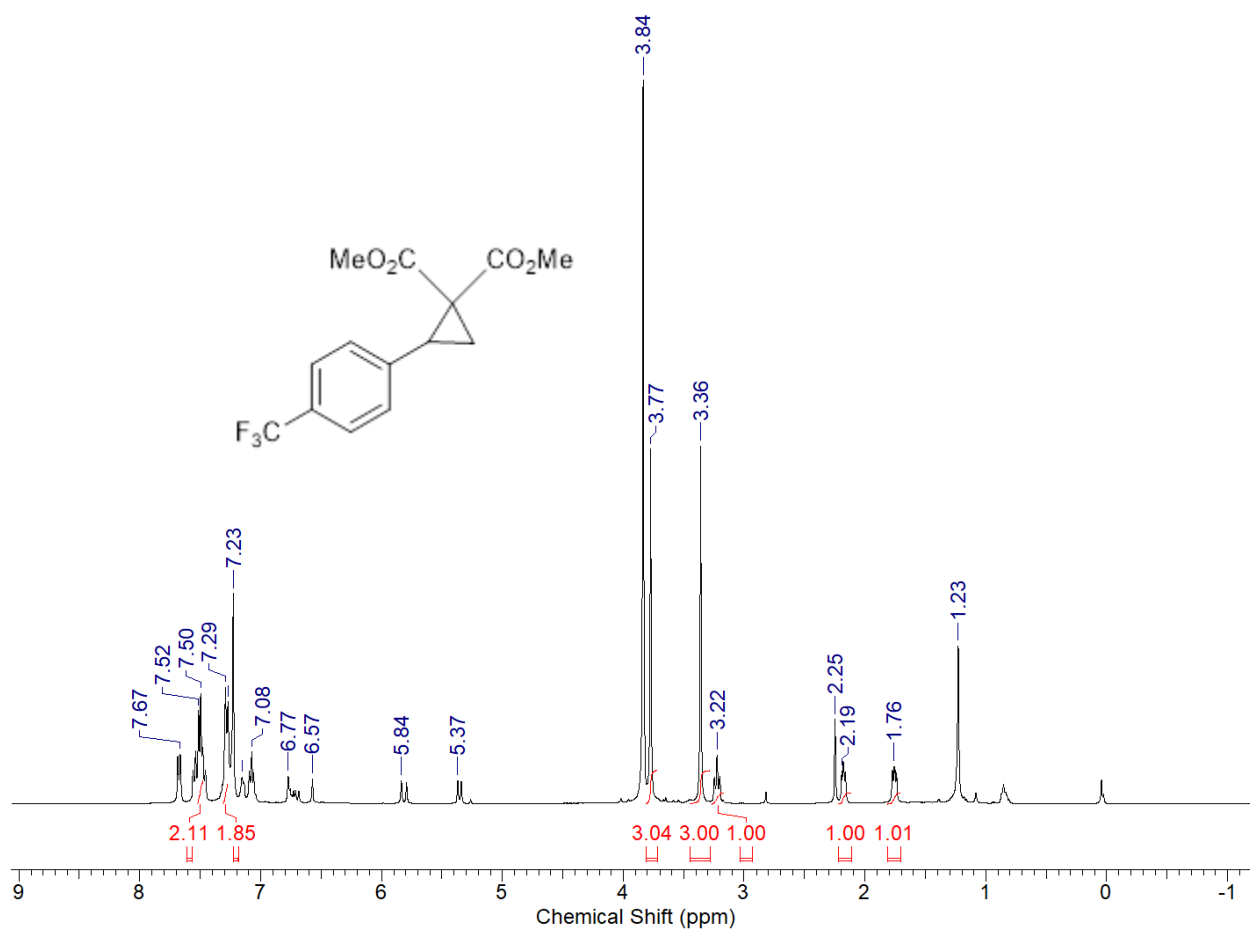
Figure S35. ^{1}H NMR (CDCl₃, 400 MHz) of crude reaction mixture indicating the formation of 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate, tetramethyl ethene-1,1,2,2-tetracarboxylate, and PhI produced by **1**.
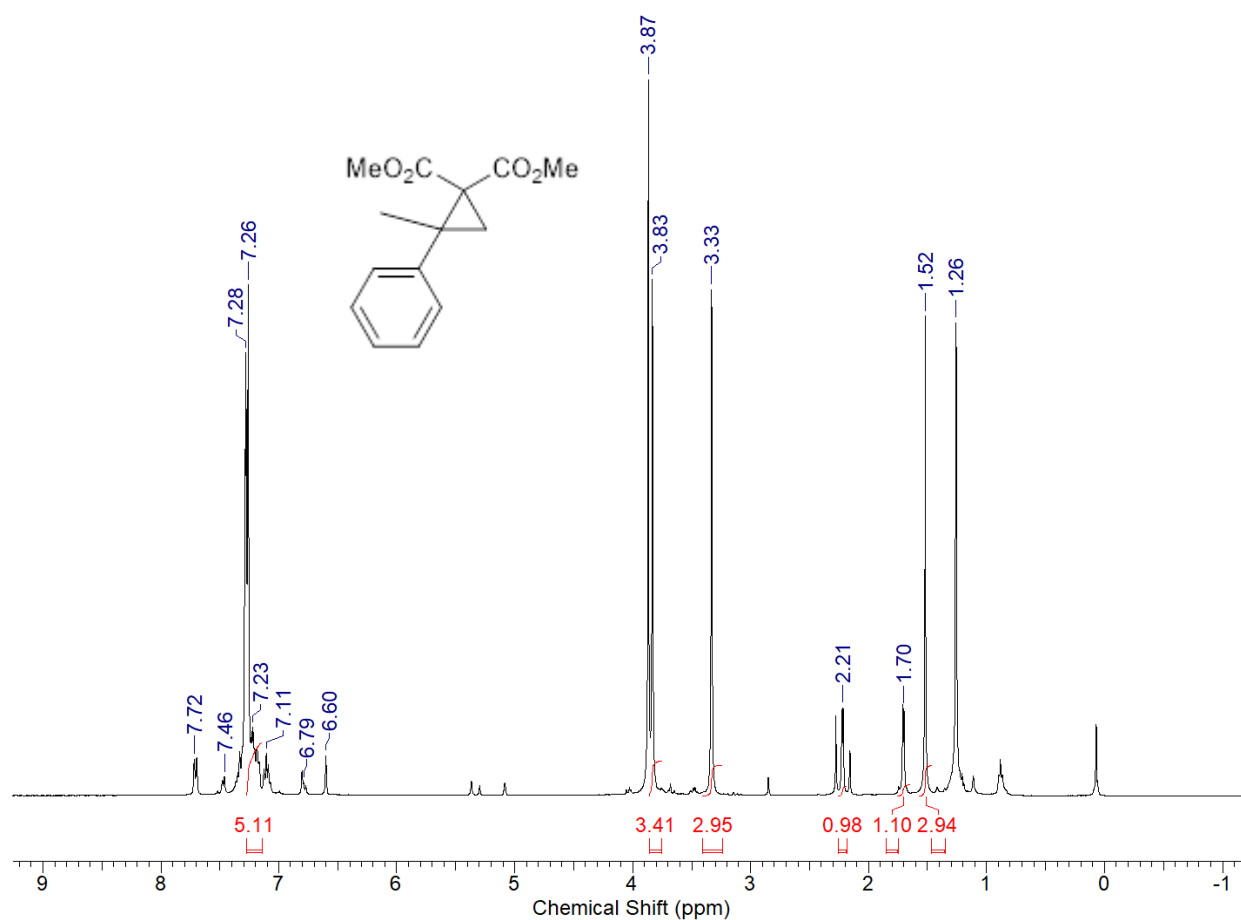
Figure S36. ^{1}H NMR (CDCl$_3$, 400 MHz) of crude reaction mixture indicating the formation of dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate, tetramethyl ethene-1,1,2,2-tetracarboxylate, and PhI produced by **1**.
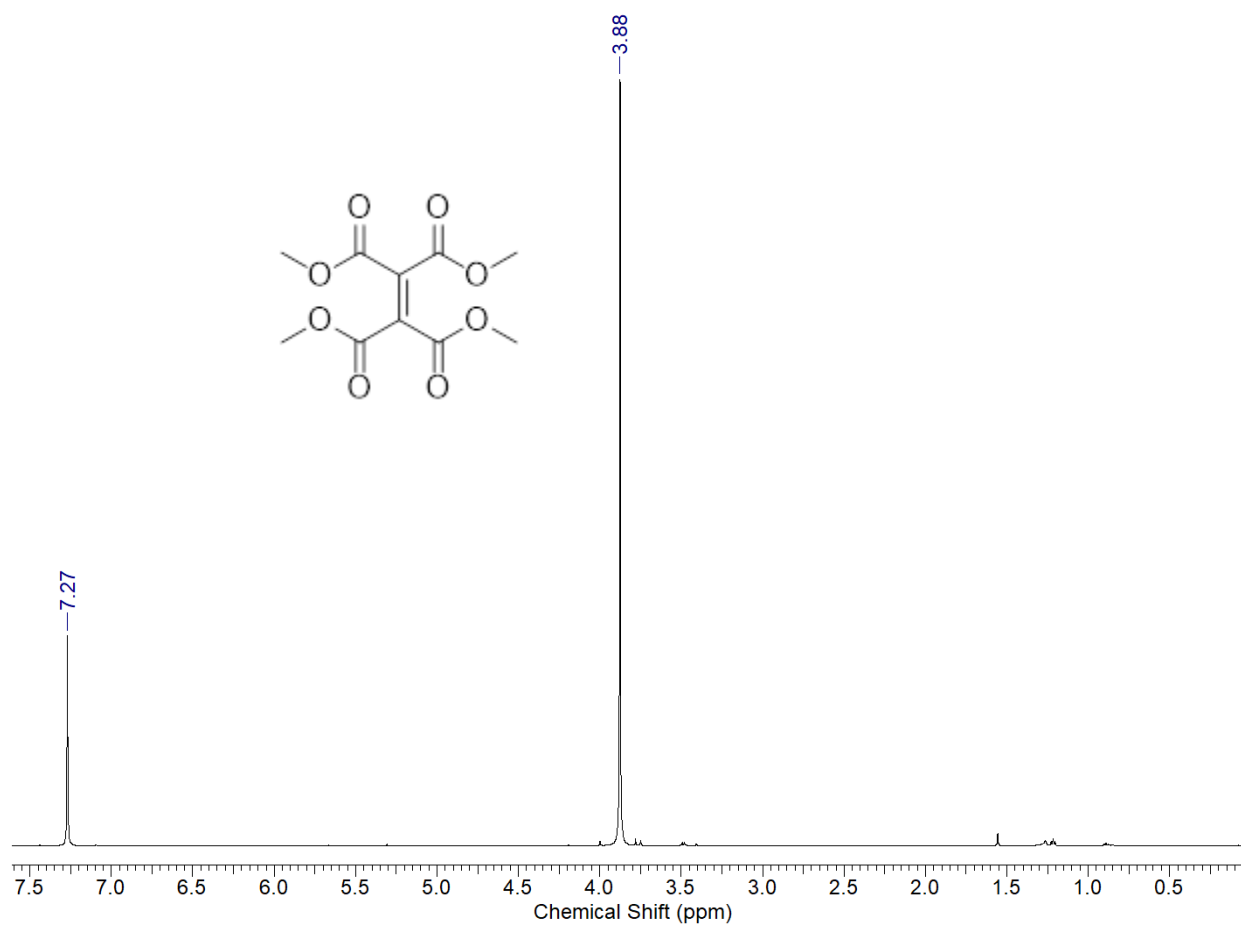
Figure S37. ^{1}H NMR of tetramethyl ethene-1,1,2,2-tetracarboxylate in CDCl$_3$ (purified by column chromatography; 20% ethyl acetate in hexanes).
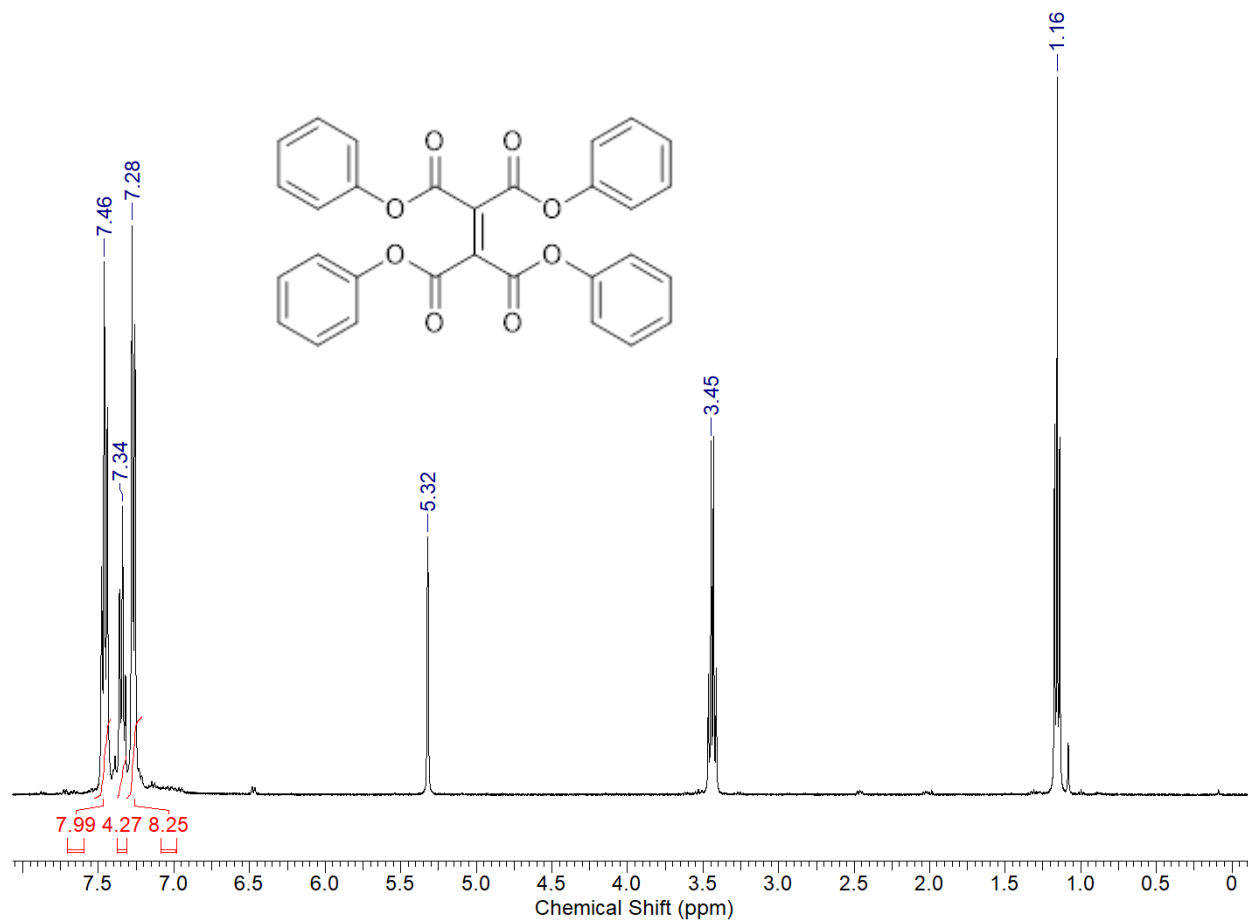
Figure S38. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz) of tetraphenyl ethene-1,1,2,2-tetracarboxylate.
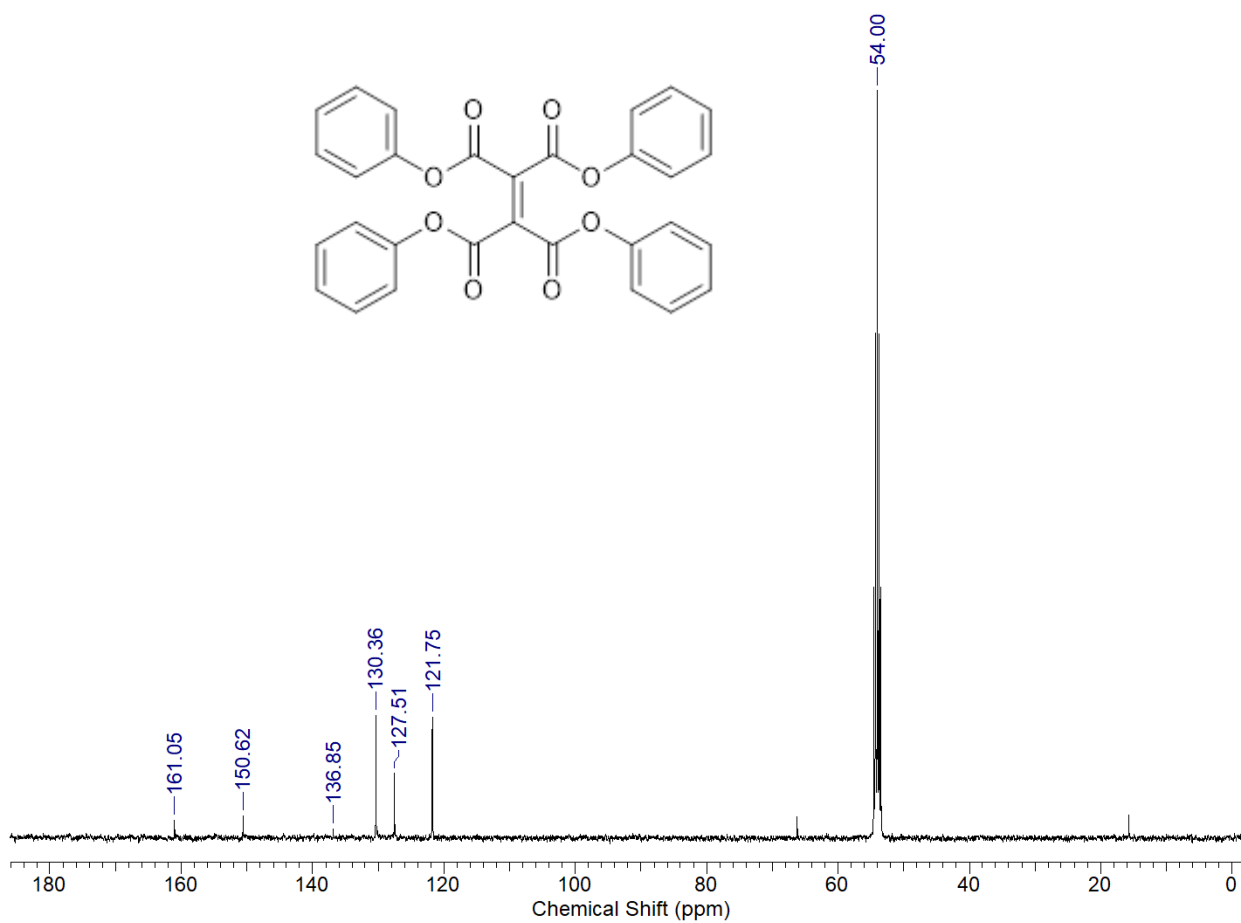
Figure S39. ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz) of tetraphenyl ethene-1,1,2,2-tetracarboxylate.
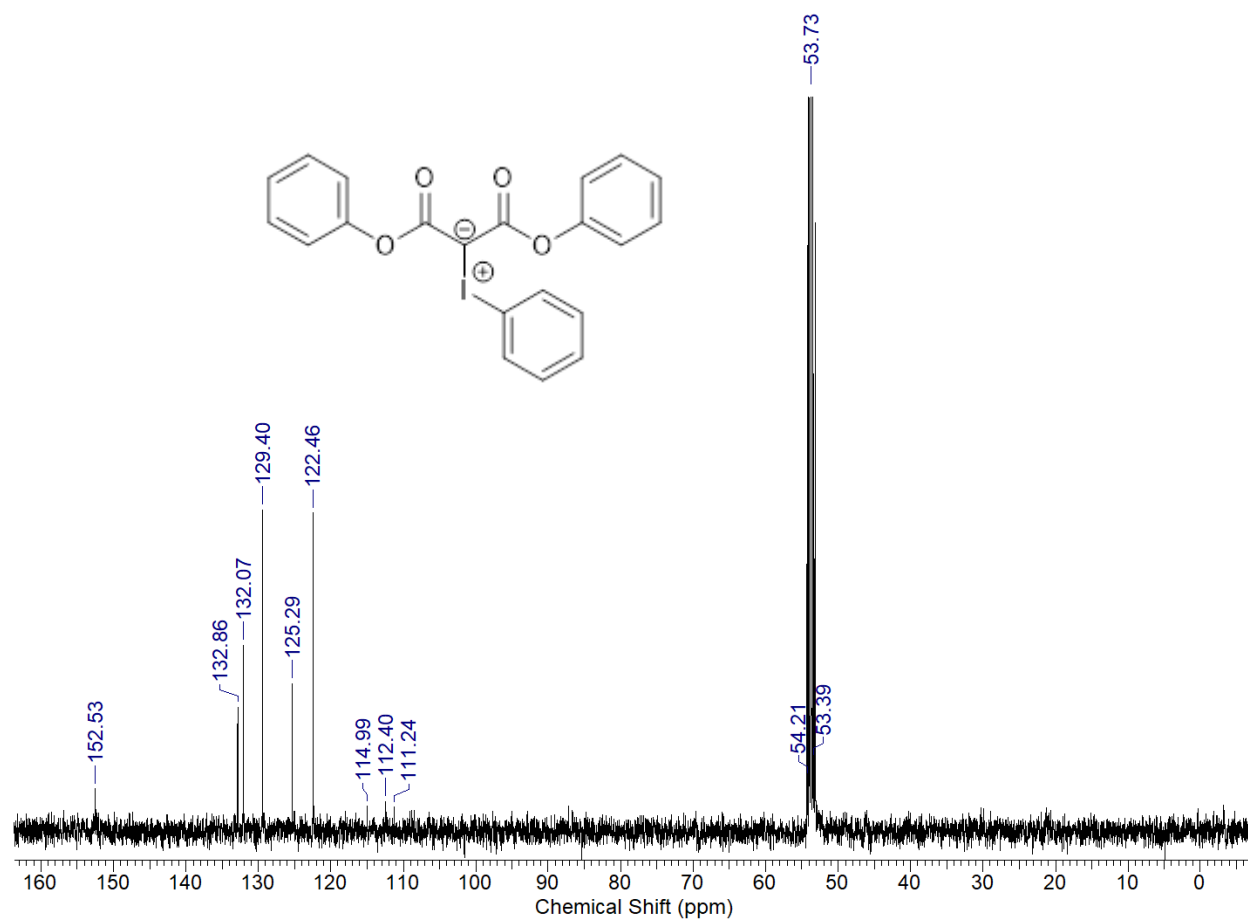
Figure S40. ^{13}C NMR (CD$_2$Cl$_2$, 150 MHz) of diphenyl 2-(phenyl-l3-iodaneylidene)malonate.
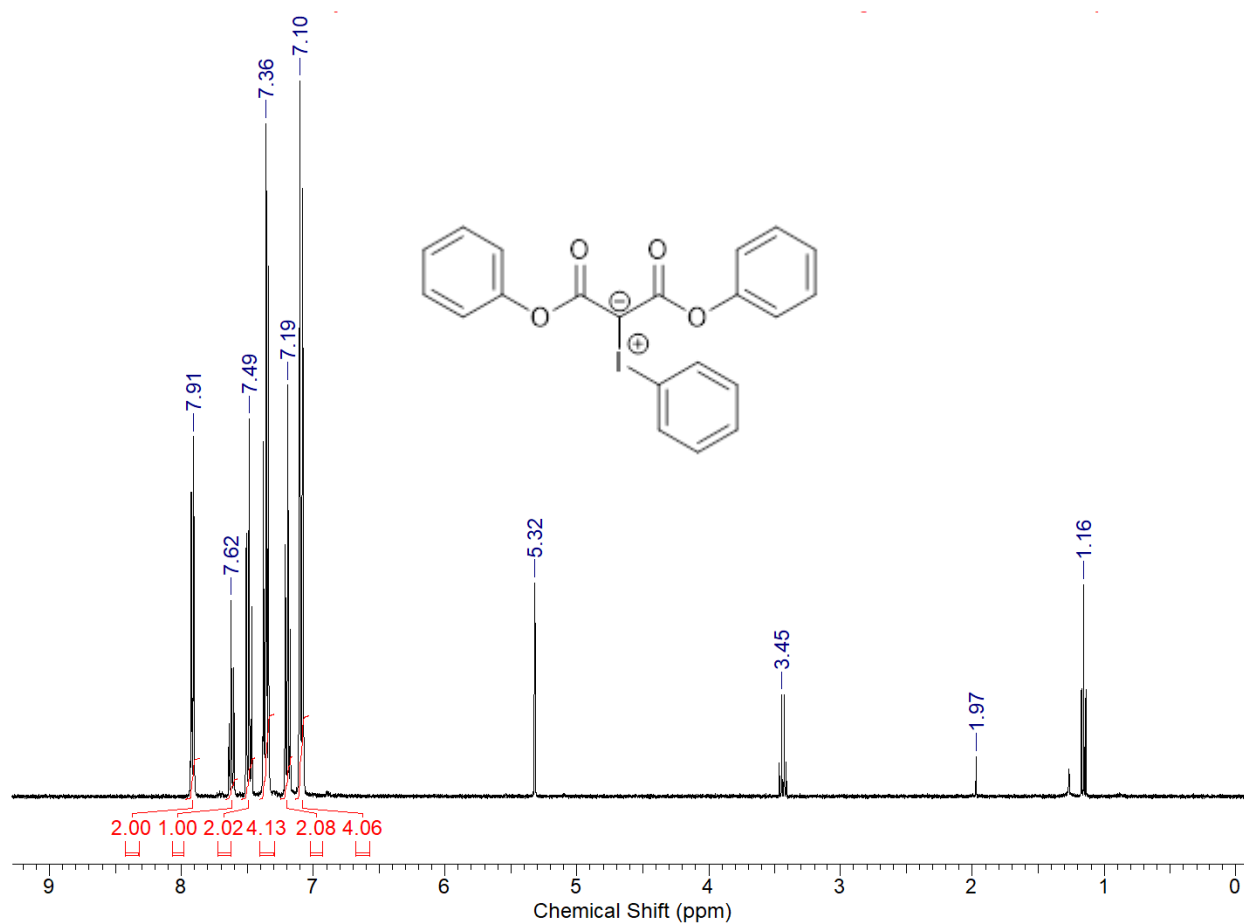
Figure S41. ^{13}C NMR (CD_2Cl_2, 150 MHz) of diphenyl 2-(phenyl-l3-iodaneylidene)malonate.
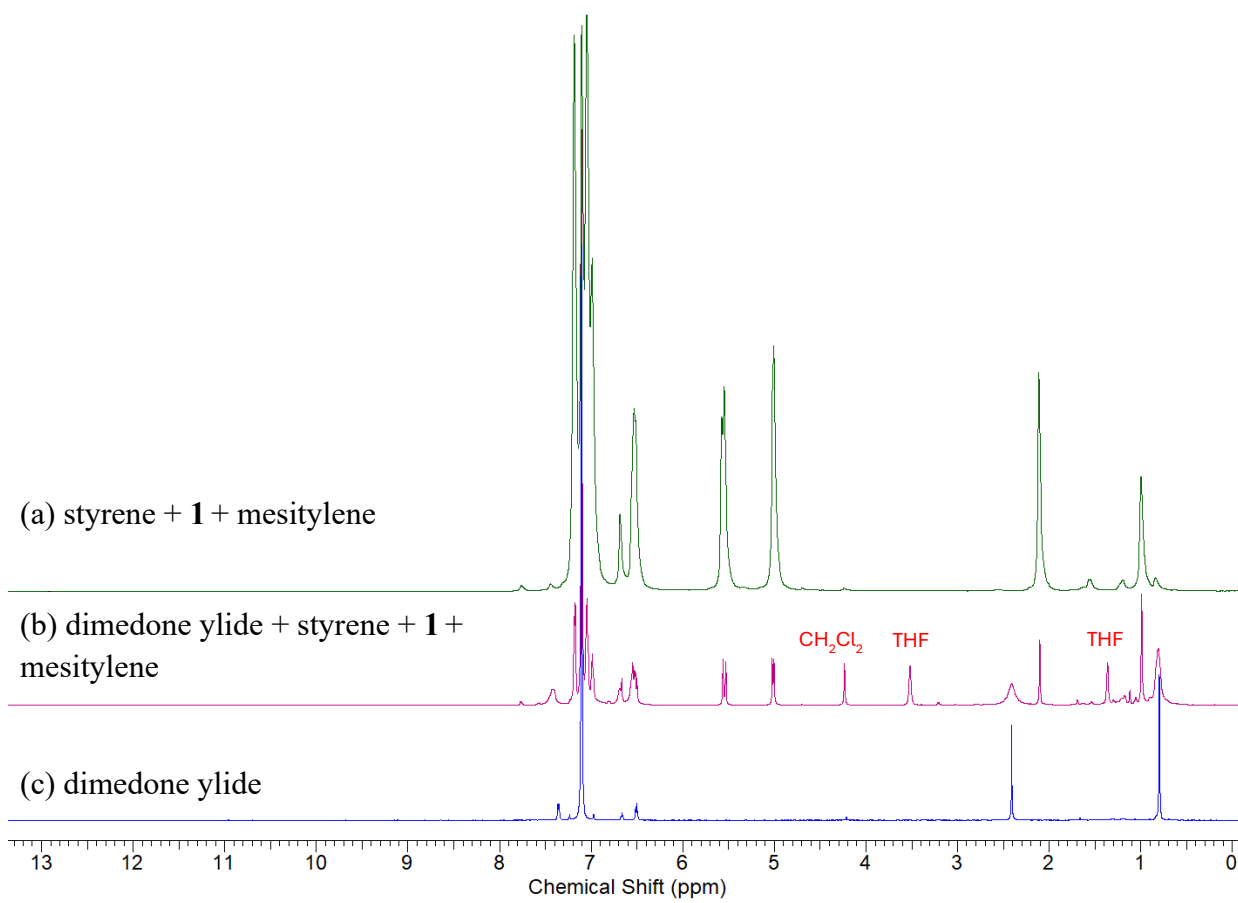
Figure S42. Stacked 1H NMR (C_6D_6, 600 MHz) spectra of: (a) initial reaction of styrene with **1** in the presence of mesitylene; (b) the reaction after adding dimedone ylide (c) dimedone ylide.
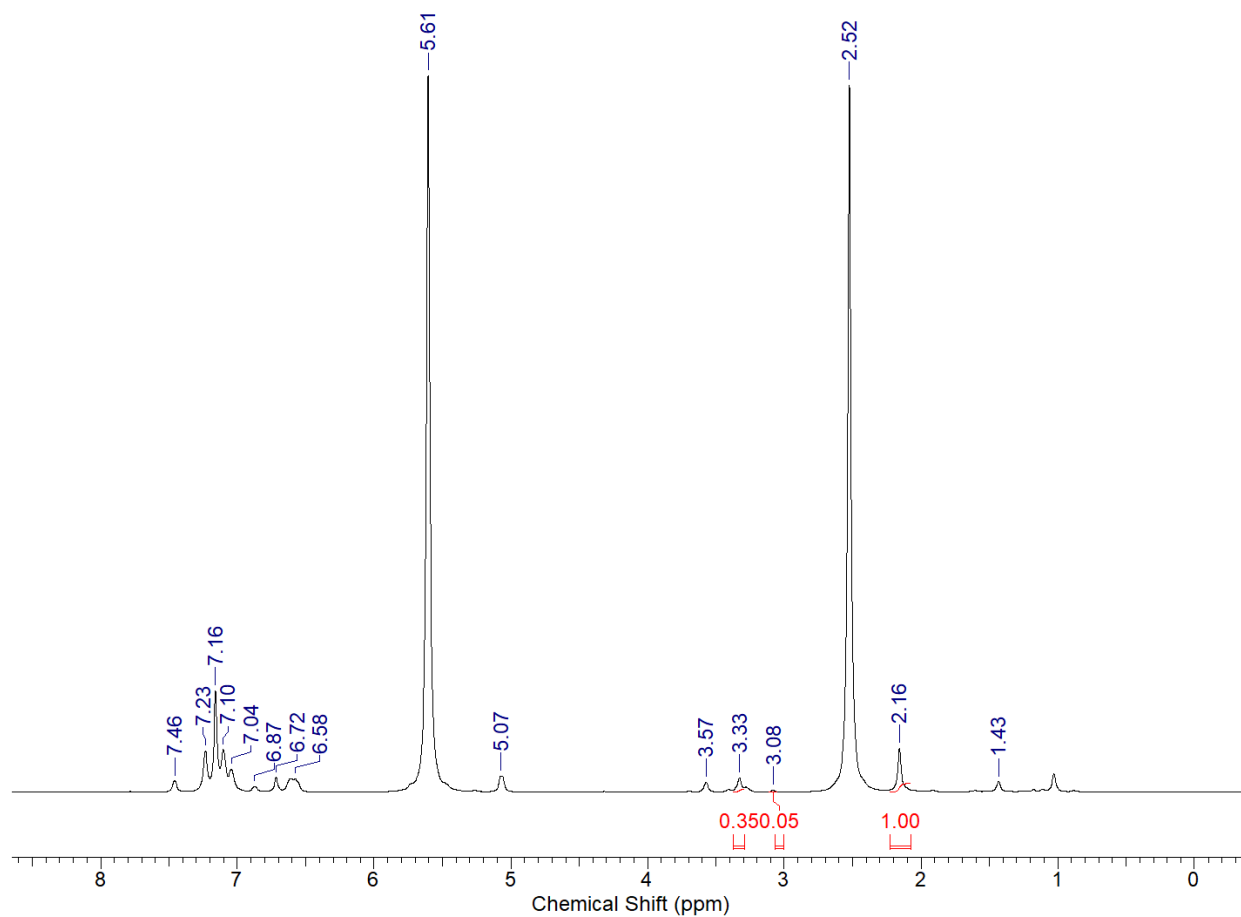
Figure S43. ^{1}H NMR (C$_6$D$_6$, 400 MHz) of the reaction of **1** with styrene, 1,4-cyclohexadiene, and ylide.
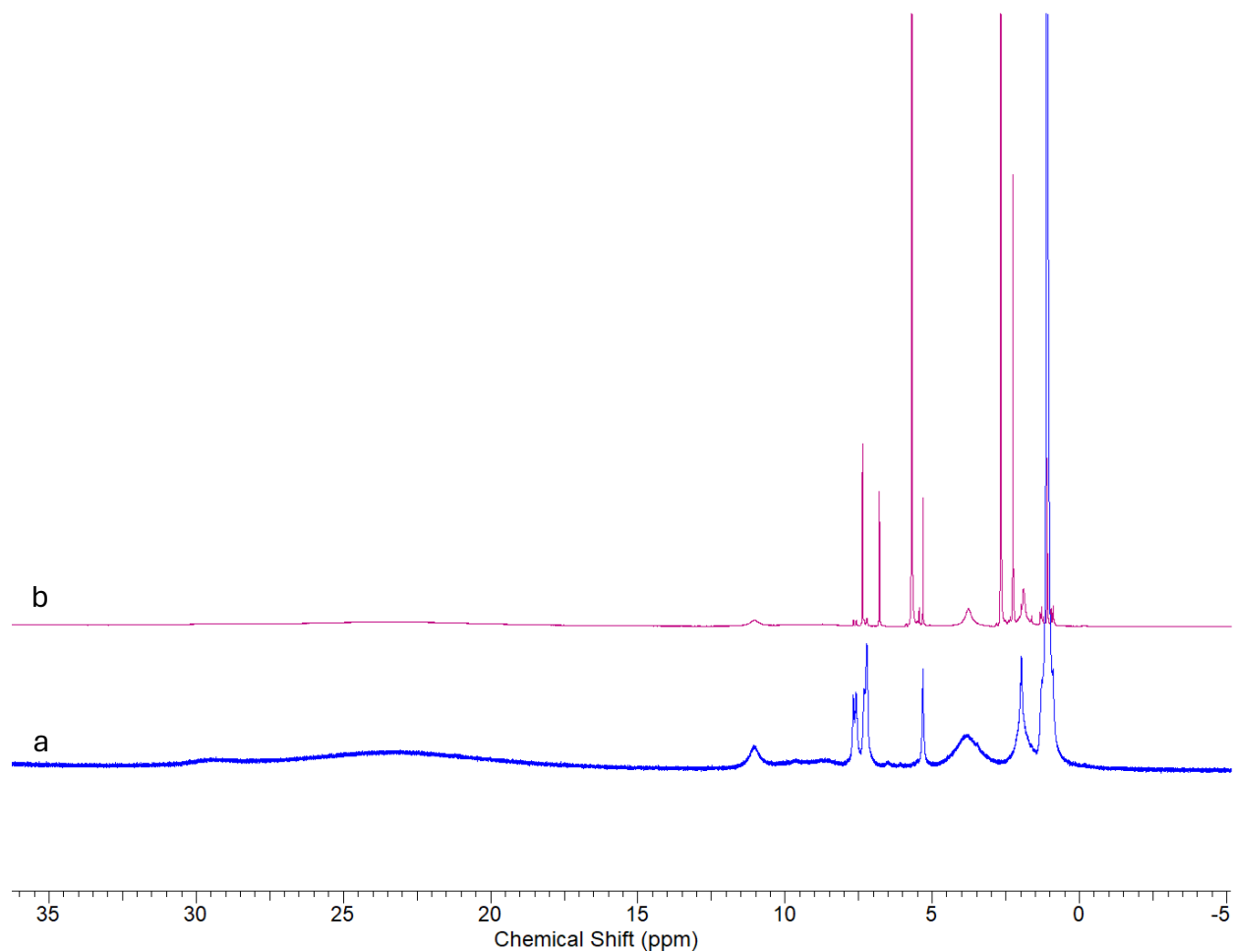
Figure S44. Stacked ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz) spectra of (a) compound **1** before the reaction and (b) 1 with 1,4-cyclohexadiene in the presence of mesitylene. Peaks corresponding to compound **1** can be observed in both cases, suggesting that **1** does not react with 1,4-cyclohexadiene by itself.
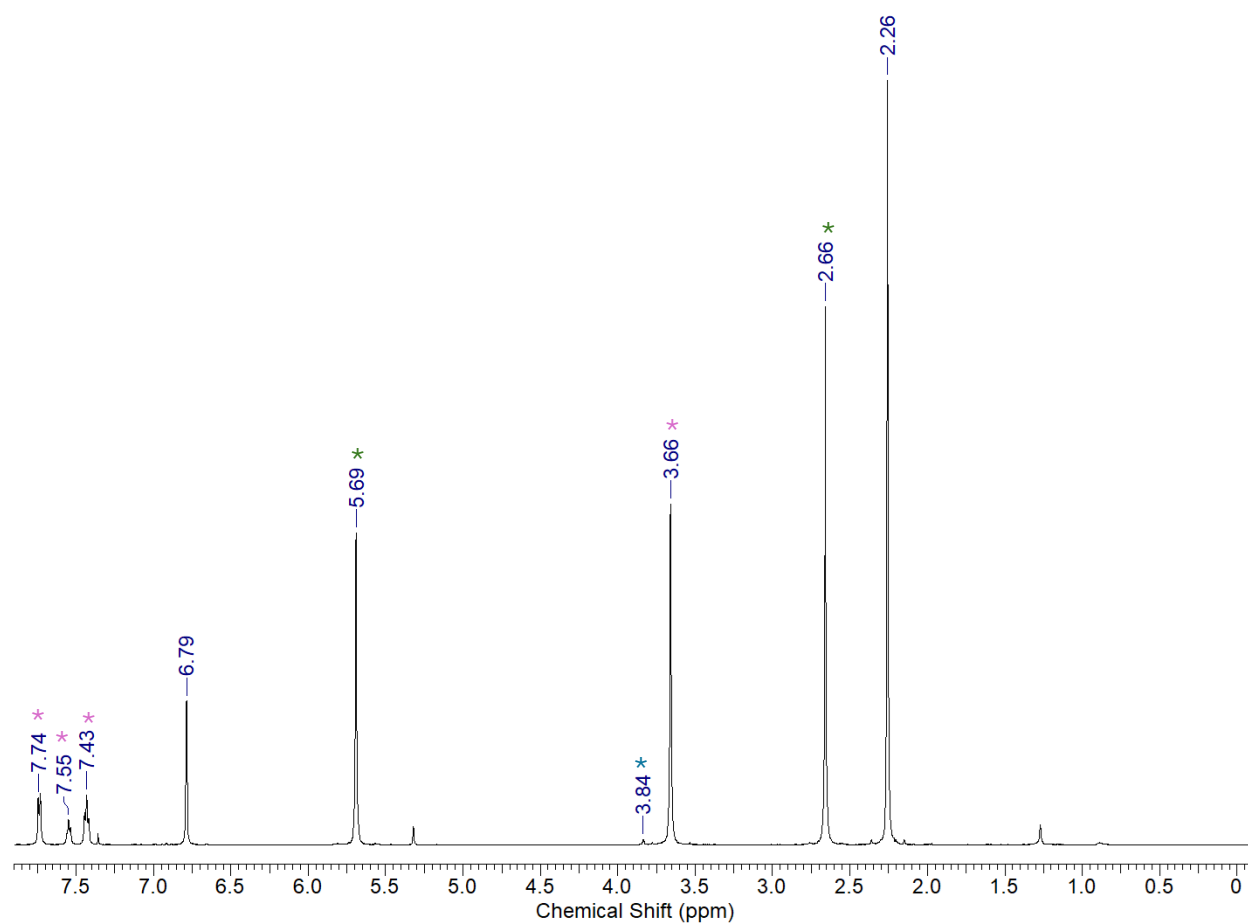
Figure S45. ^{1}H NMR (CD$_2$Cl$_2$, 600 MHz) spectrum of the reaction of 1,4-cyclohexadiene and dimethyl 2-(phenyl-l3-iodaneylidene)malonate in the presence of mesitylene. The remaining dimethyl 2-(phenyl-l3-iodaneylidene)malonate peaks are indicated with *. The peak at 3.84 ppm indicated with * corresponds to tetramethyl ethene-1,1,2,2-tetracarboxylate. The peaks at 2.26 ppm and 6.79 ppm correspond to the mesitylene standard. The peaks at 2.66 ppm and 5.69 ppm indicated with * correspond to 1,4-cyclohexadiene.
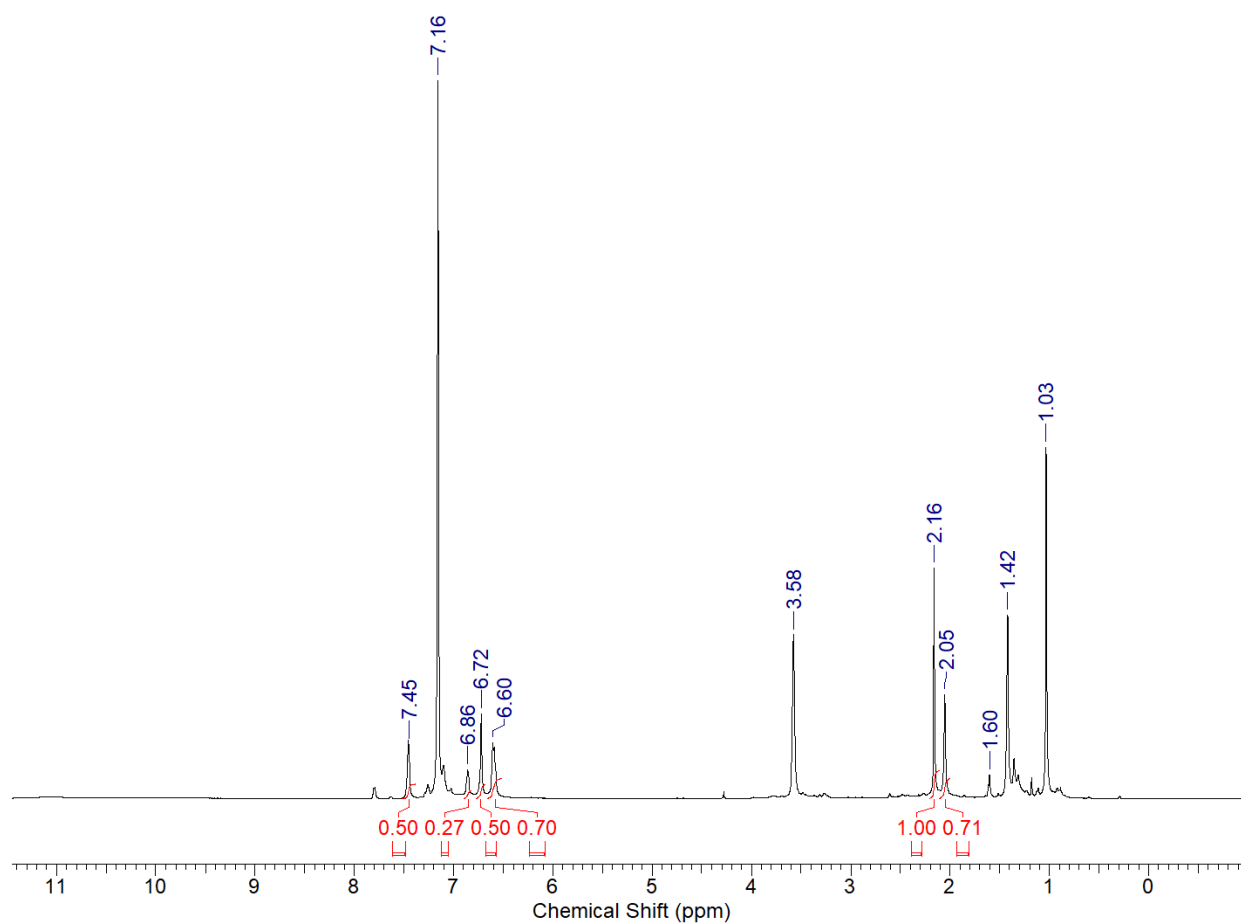
Figure S46. ^{1}H NMR demonstrating no catalytic formation of ketenimine by **1** with 2,6-dimethylphenyl isocyanide (CNXyl, C_6D_6, 400 MHz).
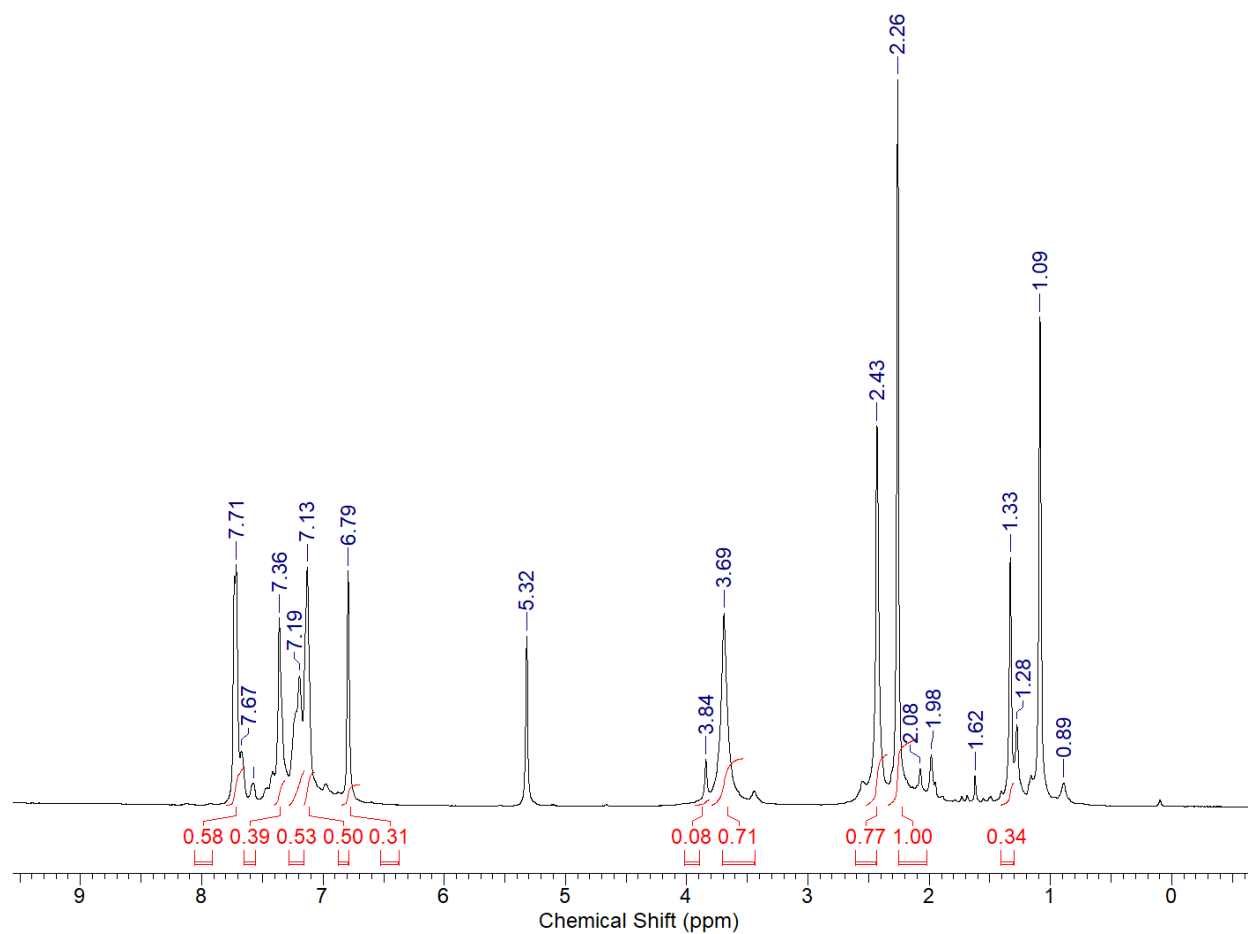
Figure S47. ^{1}H NMR demonstrating no catalytic formation of ketenimine in stoichiometric reaction of Fe(OR)$_2$(CNXyl)$_2$ (**10**) and dimethyl 2-(phenyl-l3-iodaneylidene)malonate (CD$_2$Cl$_2$, 400 MHz).
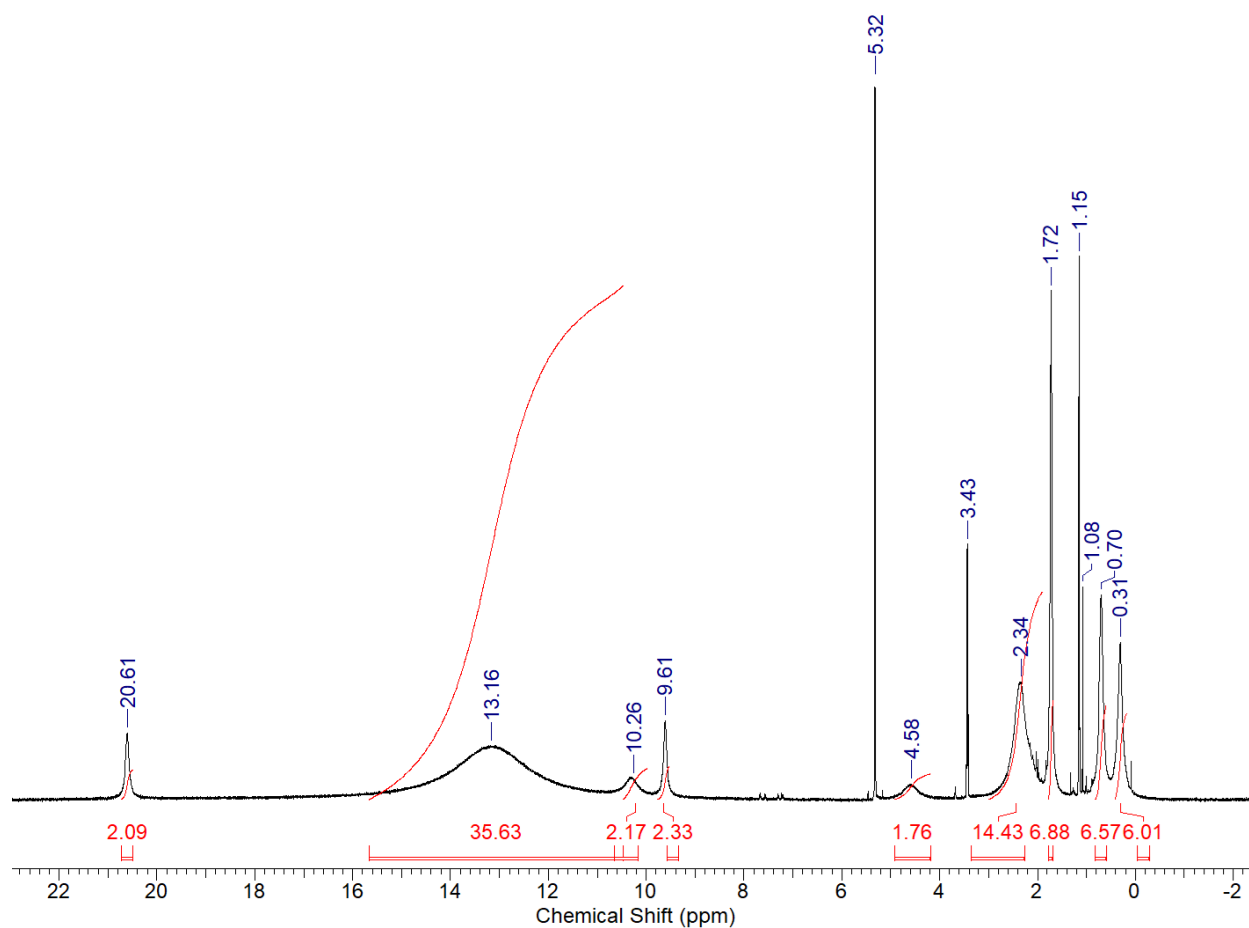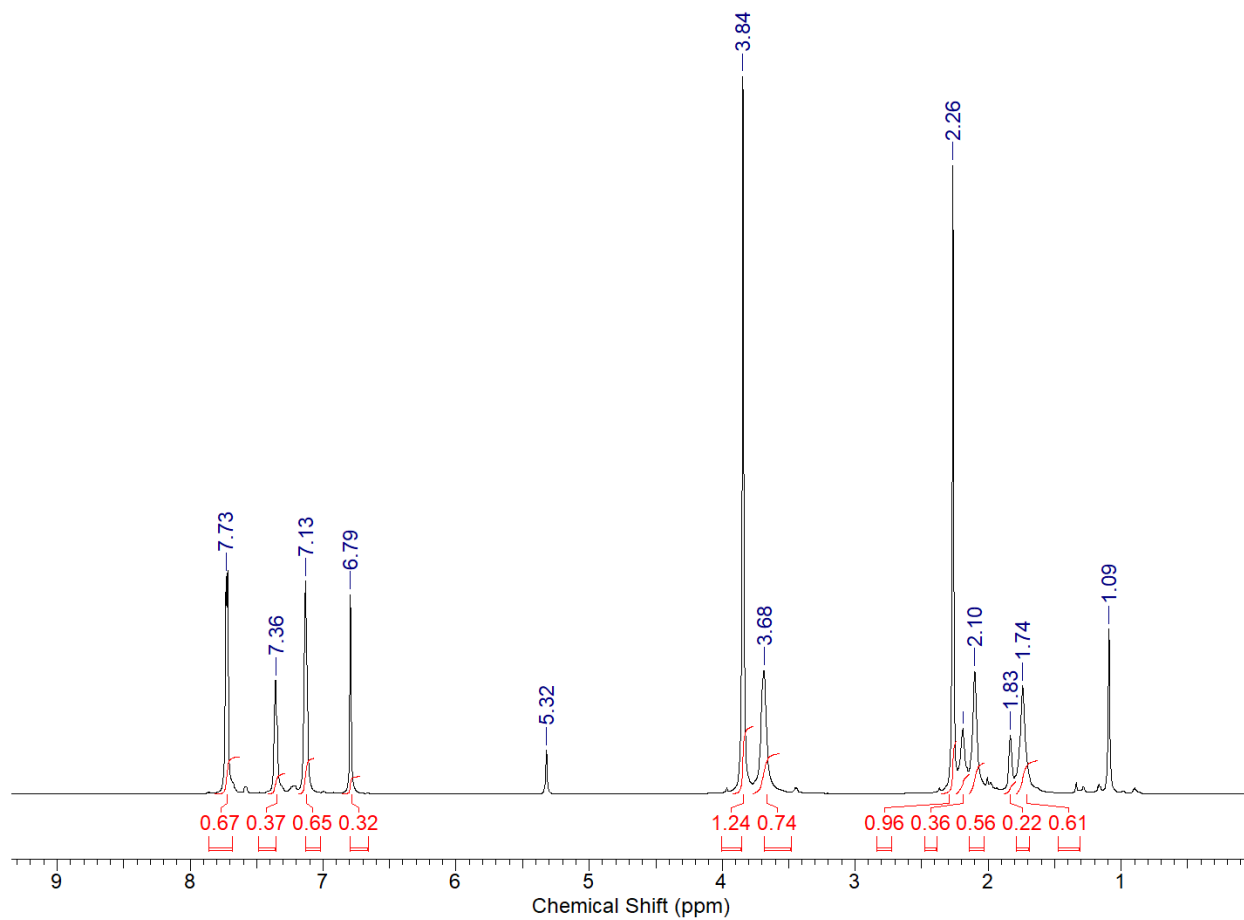
Figure S48. ^{1}H NMR spectrum of Fe(OR)$_2$(CNAd)$_2$ (**11**) (CD$_2$Cl$_2$, 600 MHz). One remaining OR-Ph proton is likely obstructed by peaks corresponding to adamantyl peaks or solvents.
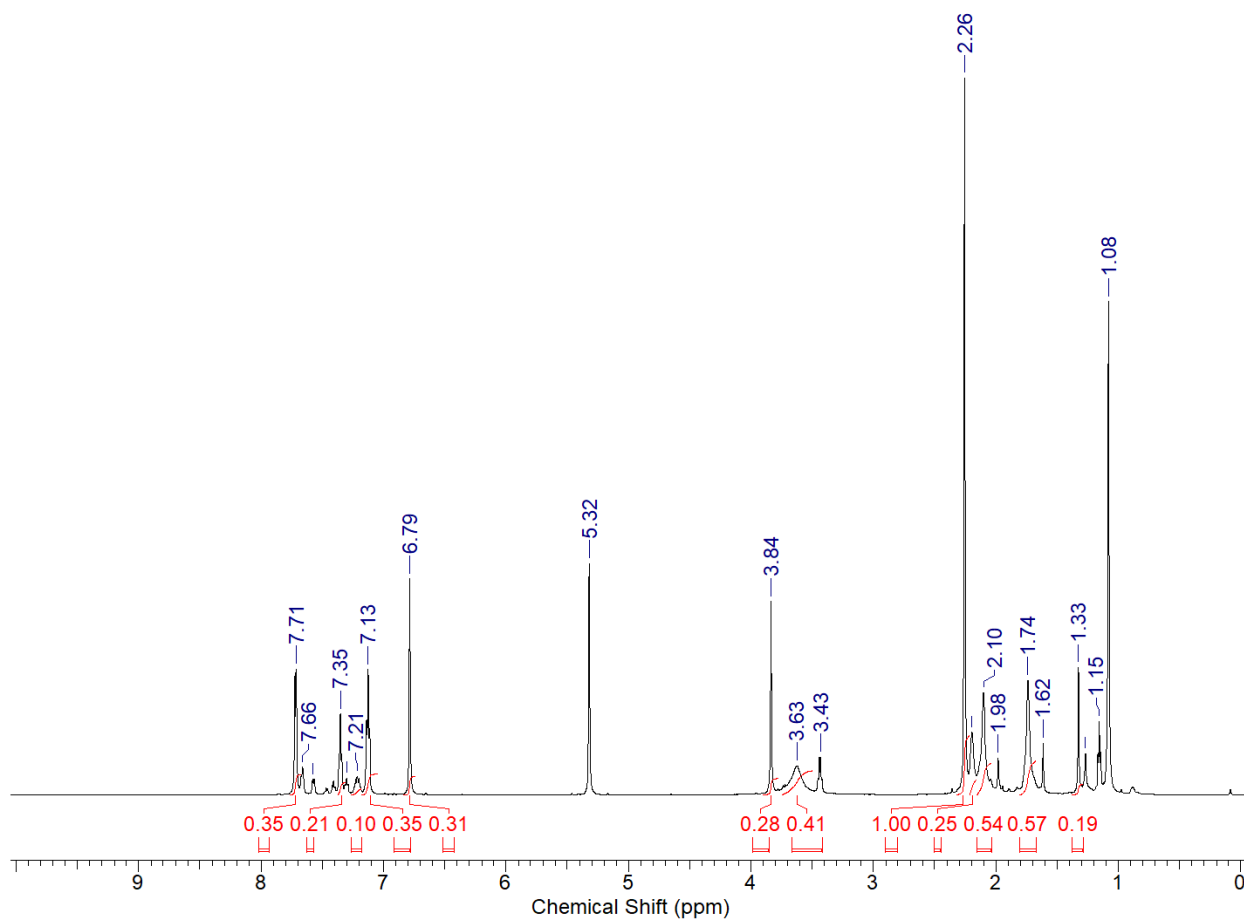
Figure S49. ^{1}H NMR demonstrating no formation of ketenimine in the stoichiometric reaction of Fe(OR)$_2$(CNAd)$_2$ (**11**) and dimethyl 2-(phenyl-l3-iodaneylidene)malonate.

Figure S50. ^{1}H NMR demonstrating no formation of ketenimine in the catalytic reaction of **1**, 1-adamantyl isocyanide and dimethyl 2-(phenyl-l3-iodaneylidene)malonate.

4. GCMS and HRMS spectra
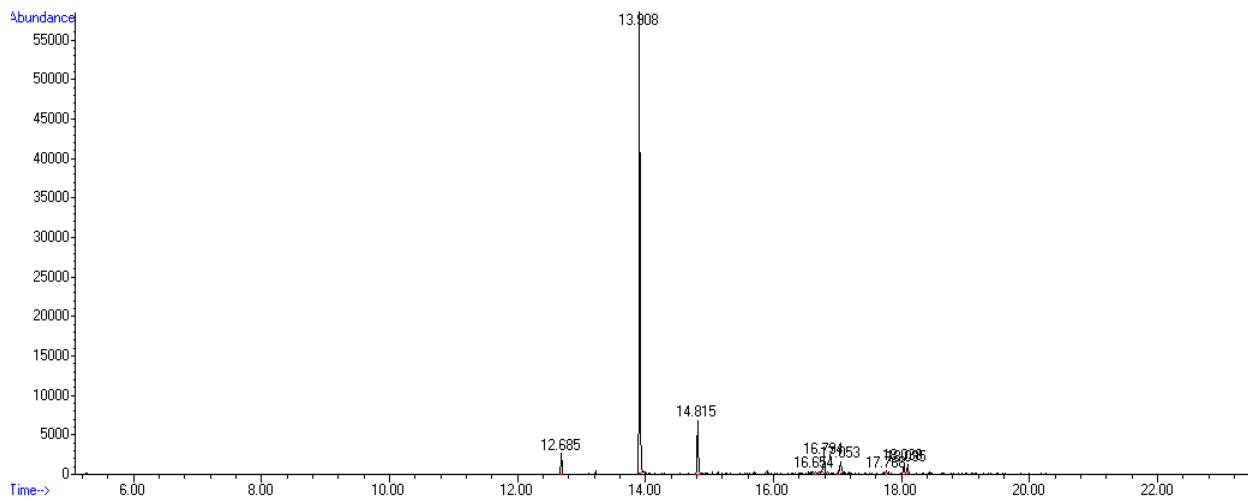
Figure S51. GC-MS of the crude product obtained in the catalytic reaction of styrene with 3-(phenyl-l3-iodaneylidene)pentane-2,4-dione by **1**. The cyclopropane is at 13.908 and the remaining 2,4-pentadione (acac) ylide is at 14.815.
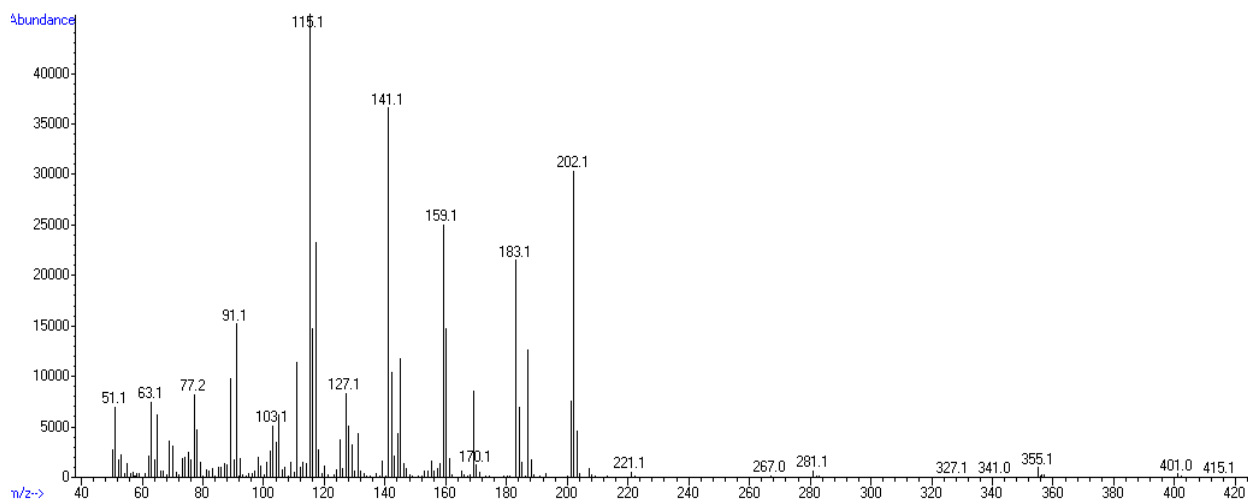

Figure S52. Retention time of 13.908: m/z = 202.1 indicates 1,1'-(2-phenylcyclopropane-1,1-diyl)bis(ethan-1-one) (expected m/z = 202.10).
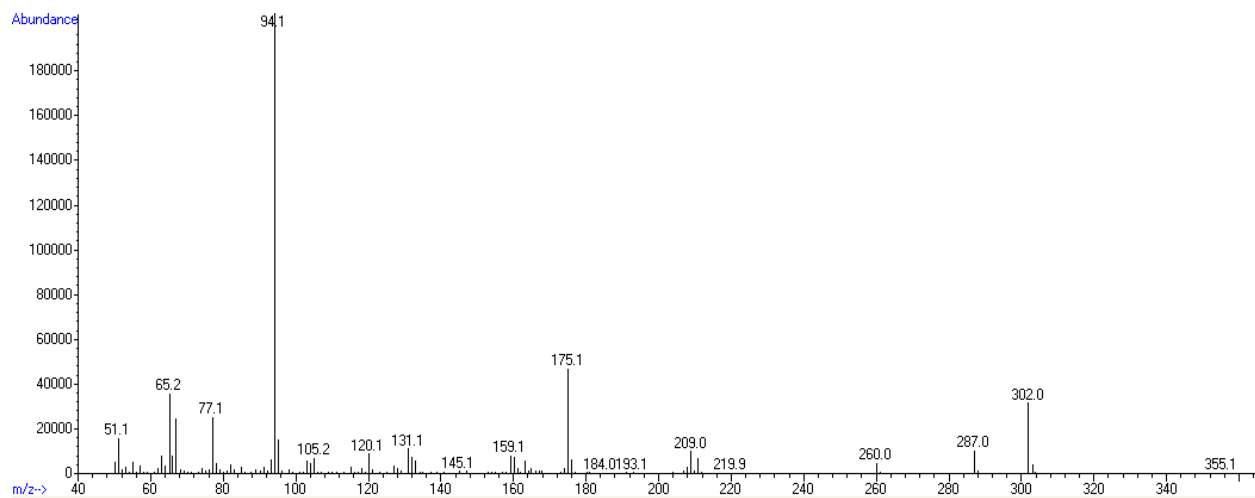
Figure S53. Retention time of 14.815: m/z = 302.0 indicates 2,4-pentadione (acac) ylide (expected m/z = 301.98).
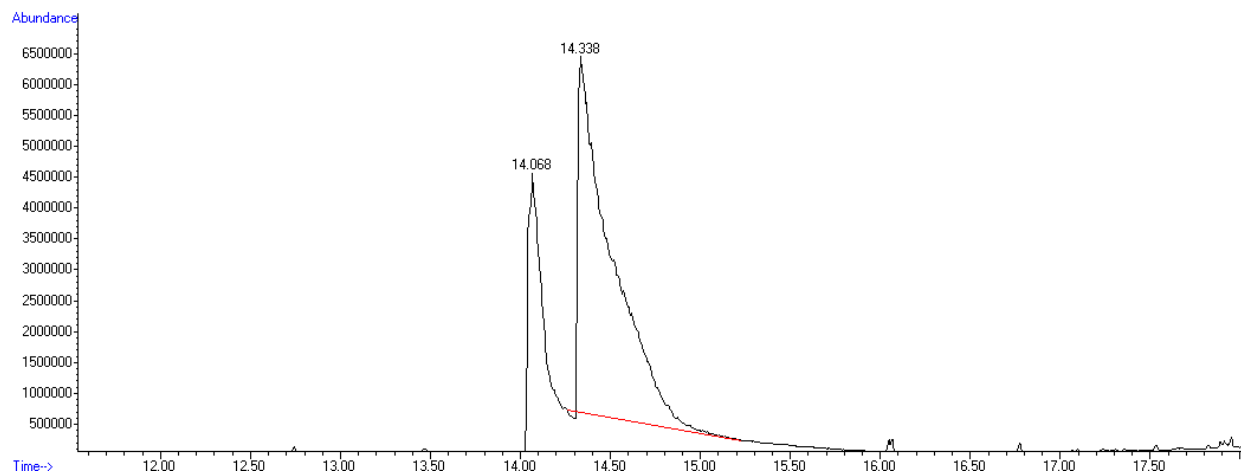
Figure S54. GC-MS of the crude product obtained in the catalytic synthesis of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate by **1**. The cyclopropane is at 16.001 and tetramethyl ethene-1,1,2,2-tetracarboxylate is at 15.387.
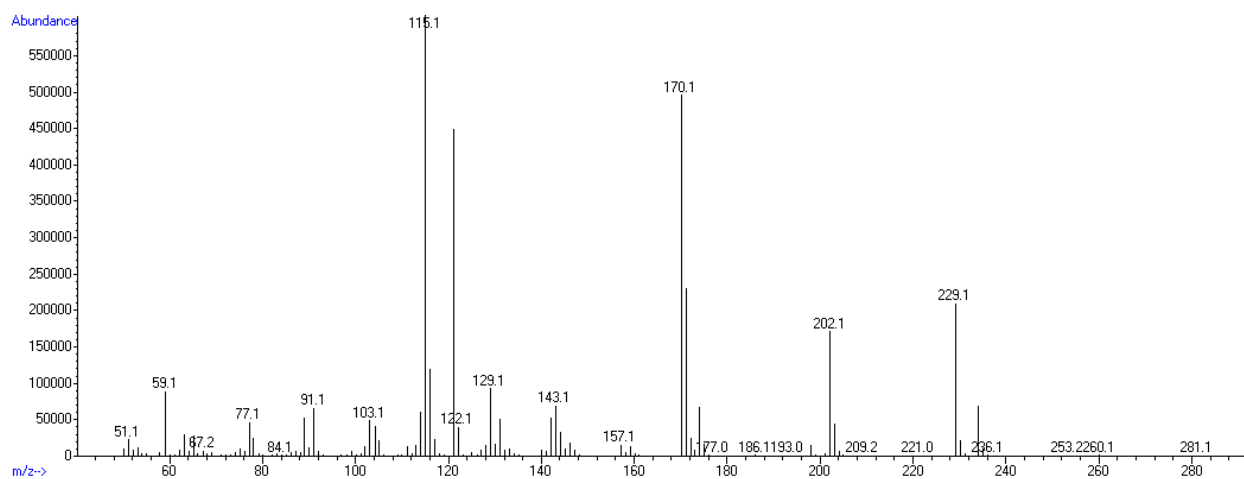

Figure S55. Retention time of 14.338: m/z = 236.1 indicates dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (expected m/z = 236.10).
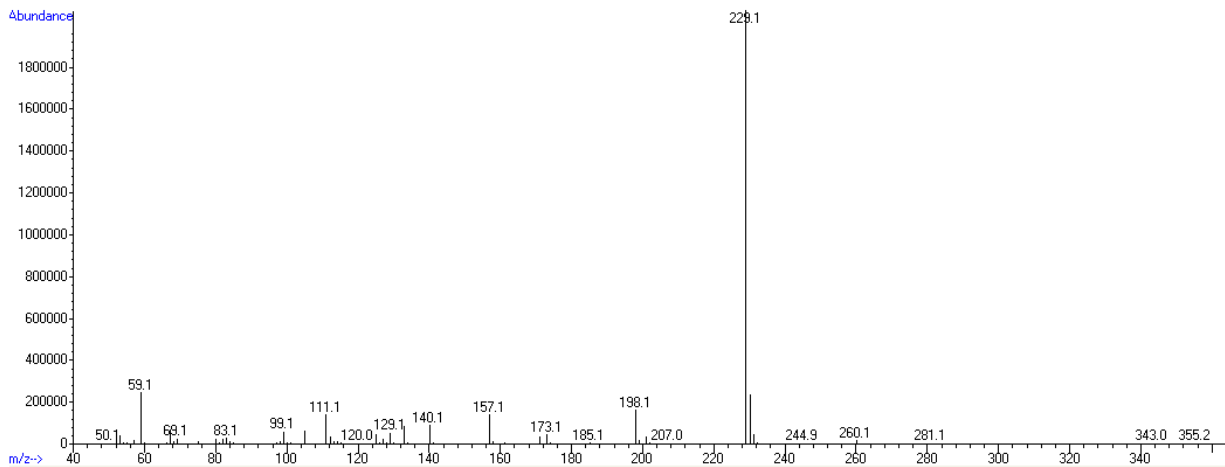
Figure S56. Retention time of 14.068: m/z = 260.1 indicates tetramethyl ethene-1,1,2,2-tetracarboxylate (expected m/z = 260.05).
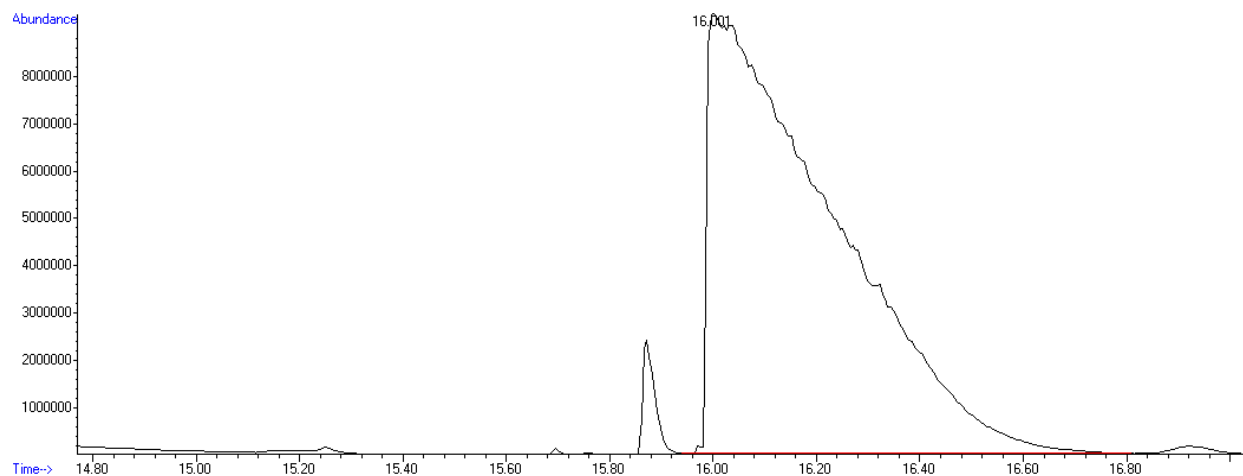
Figure S57. GC-MS of the crude product obtained in the catalytic synthesis of dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate by **1**. The cyclopropane is at 16.001 and tetramethyl ethene-1,1,2,2-tetracarboxylate is at 15.387.
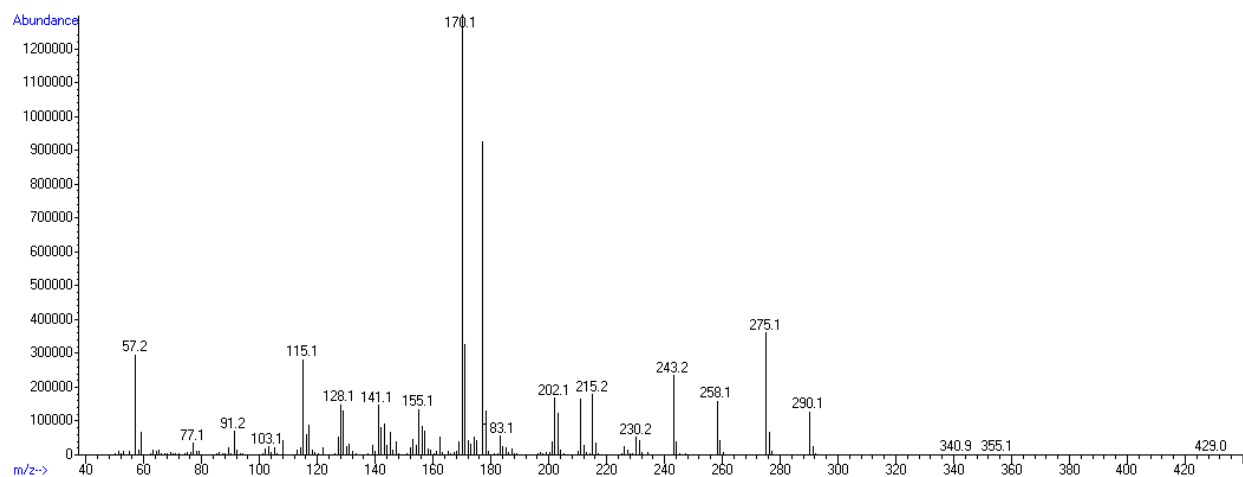

Figure S58. Retention time of 16.001: $m/z = 290.1$ indicates dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate (expected $m/z = 290.15$).
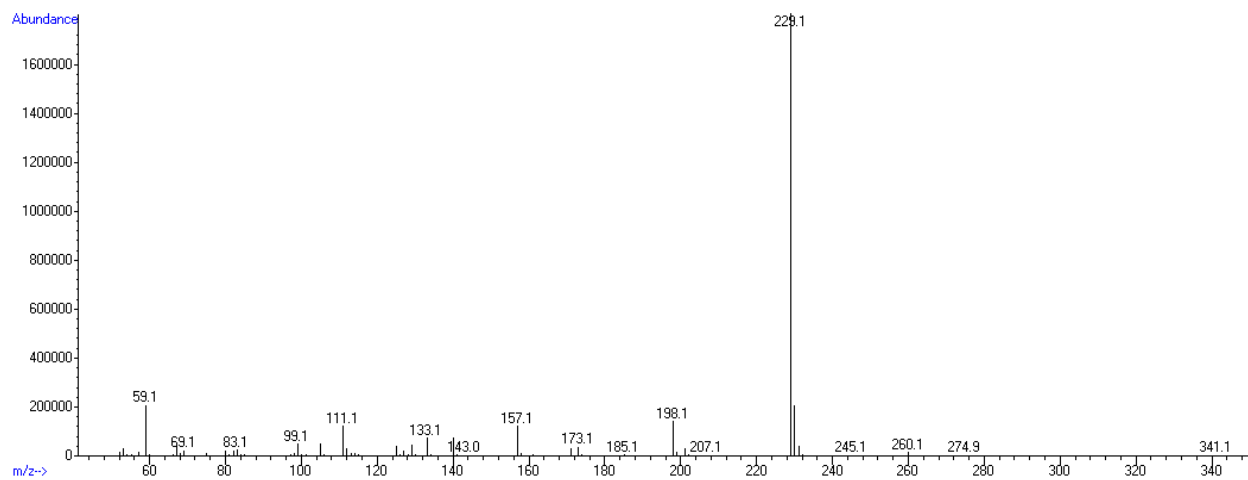
Figure S59. Retention time of 15.387: m/z = 260.1 indicates tetramethyl ethene-1,1,2,2-tetracarboxylate (expected m/z = 260.05).
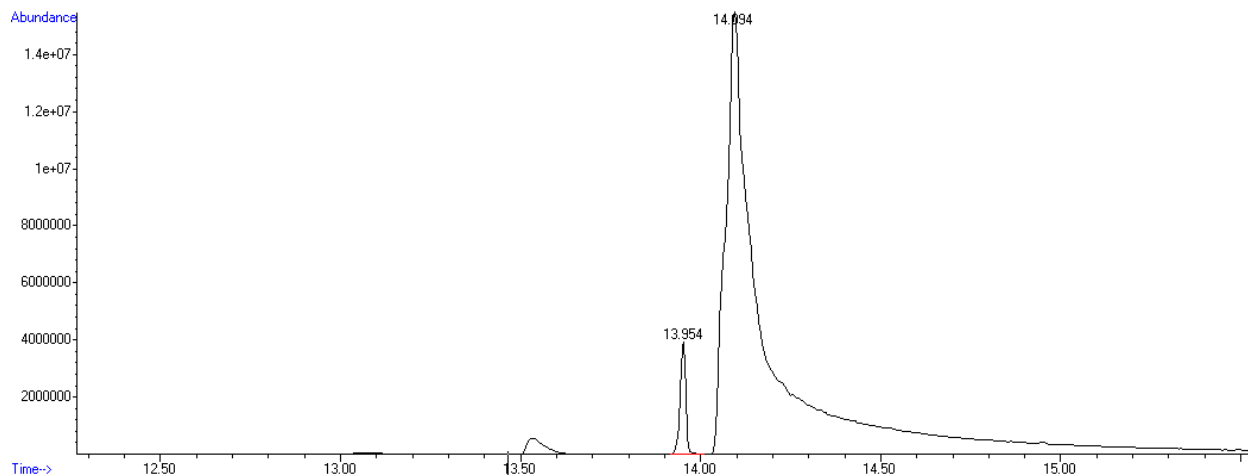
Figure S60. GC-MS of the crude product obtained in the catalytic synthesis of 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate by **1**. The cyclopropane is at 14.094 and tetramethyl ethene-1,1,2,2-tetracarboxylate is at 13.954.
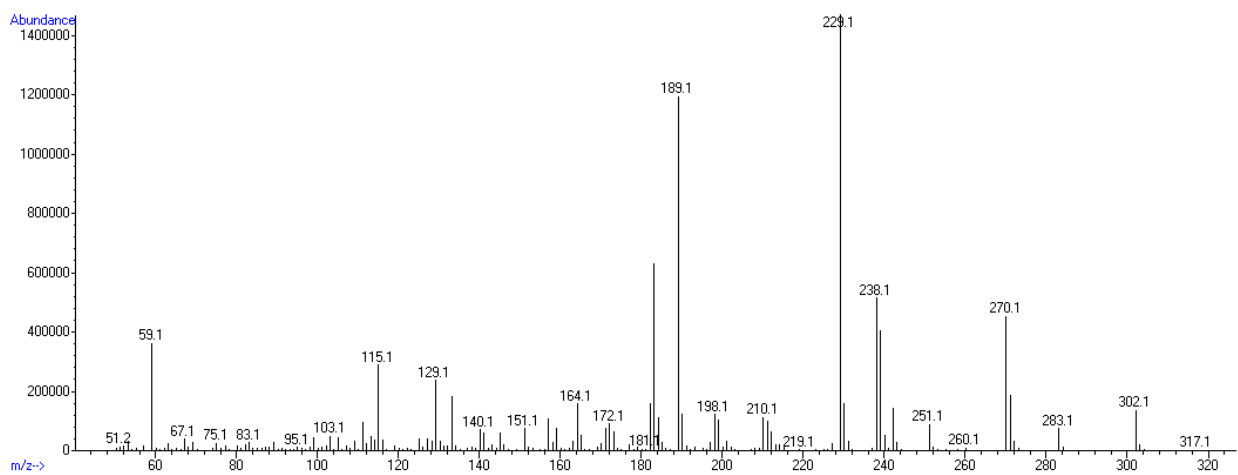

Figure S61. Retention time of 14.094: m/z = 302.1.1 indicates 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate (expected m/z = 302.08).

Figure S62. Retention time of 13.954: m/z = 260.1, indicates tetramethyl ethene-1,1,2,2-tetracarboxylate (expected m/z = 260.05).

Figure S63. GC-MS of the crude product obtained in the catalytic synthesis of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate by **1**. The cyclopropane is at 16.006 and tetramethyl ethene-1,1,2,2-tetracarboxylate is at 14.218.
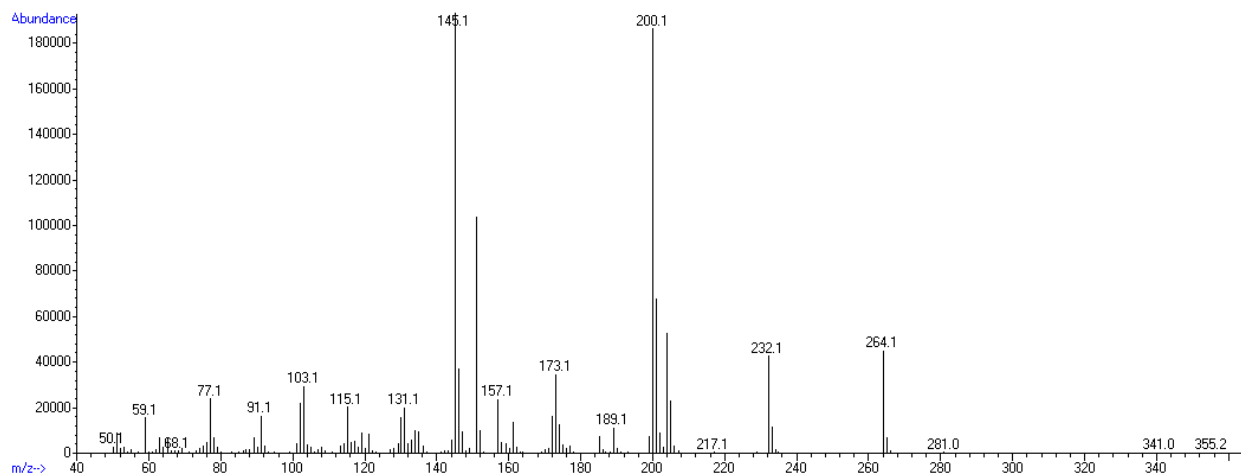
Figure S64. Retention time of 16.001: m/z = 264.1 indicates -(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (expected m/z = 264.10).
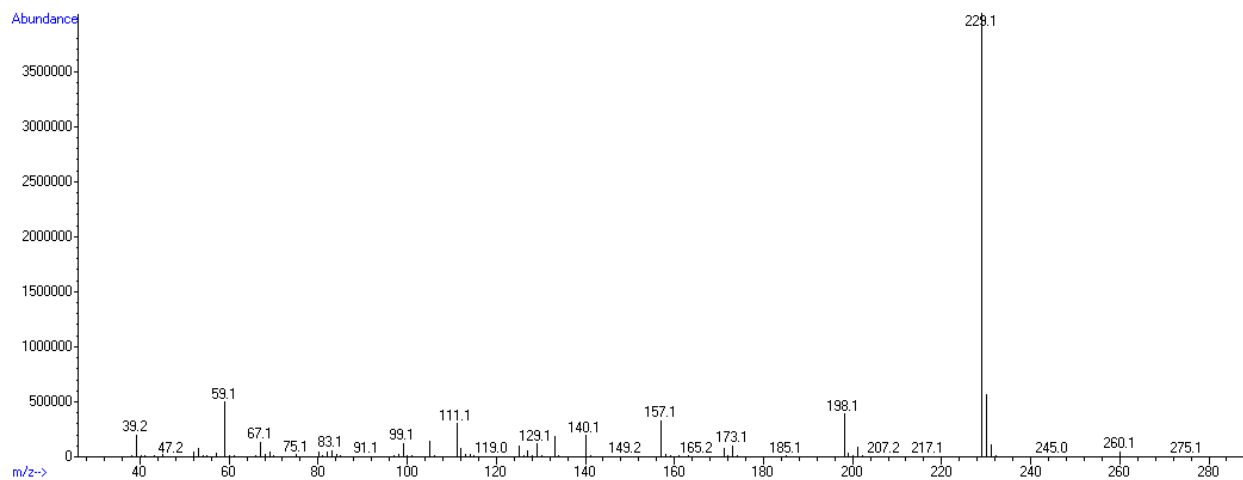
Figure S65. Retention time of 14.218: m/z = 260.1 indicates tetramethyl ethene-1,1,2,2-tetracarboxylate (expected m/z = 260.05).
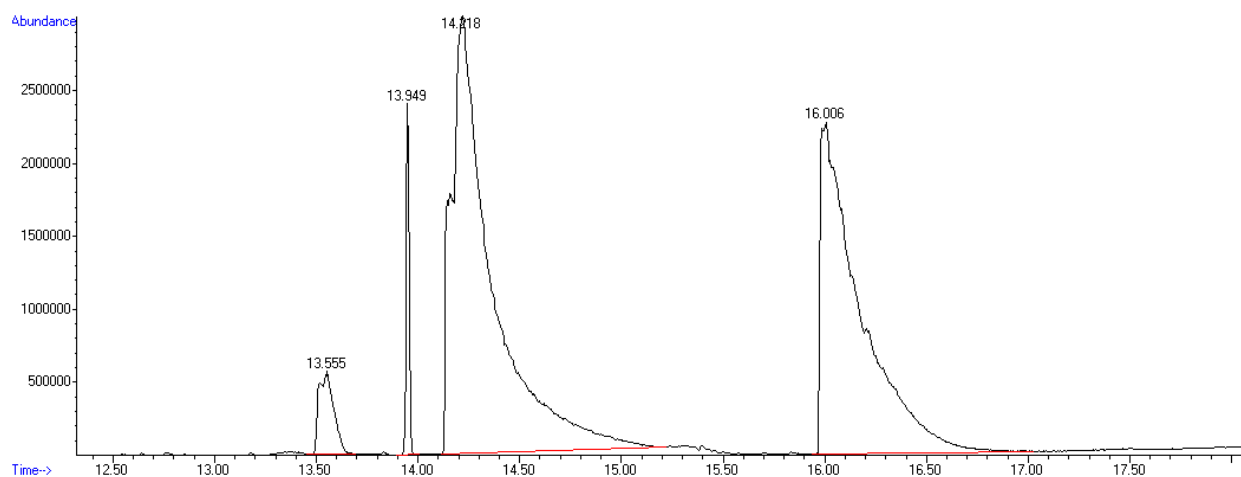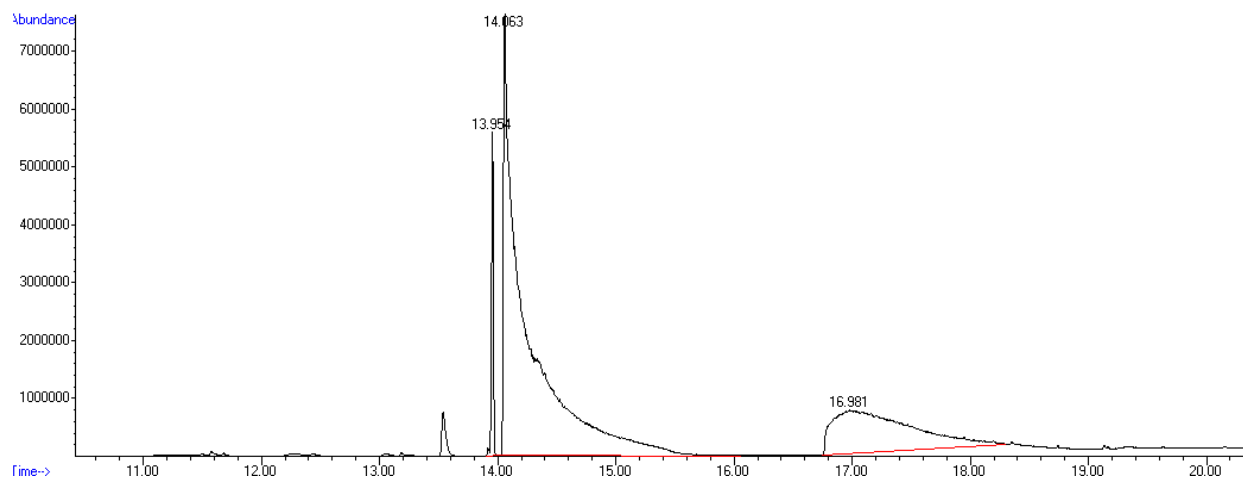
Figure S66. GC-MS of the crude product obtained in the catalytic synthesis of 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate by **1**. The cyclopropane is at 16.981 and tetramethyl ethene-1,1,2,2-tetracarboxylate is at 14.063.
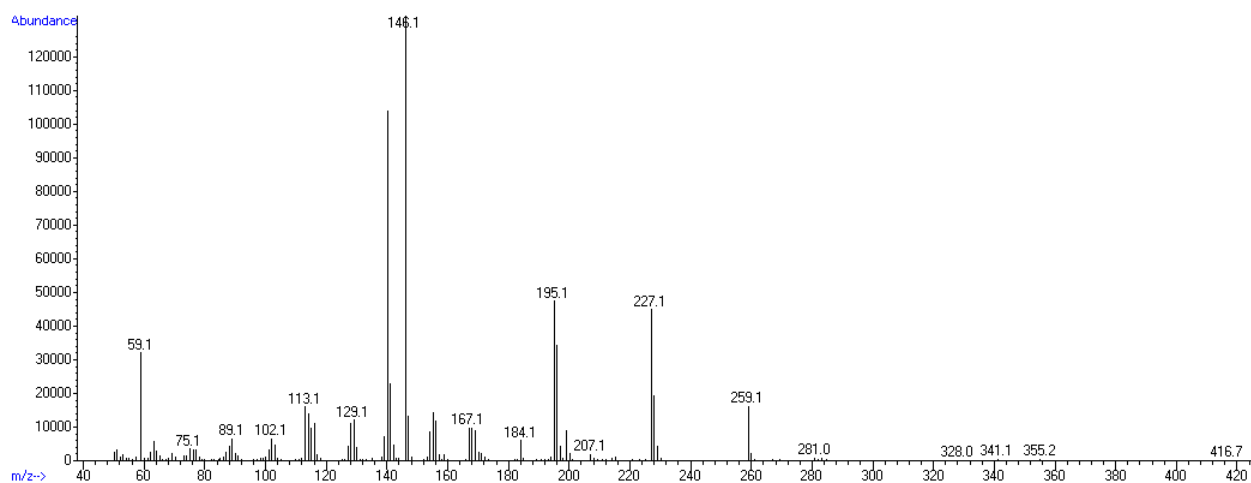
Figure S67. Retention time of 16.981: m/z = 259.1; indicates 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate (expected m/z = 259.08).
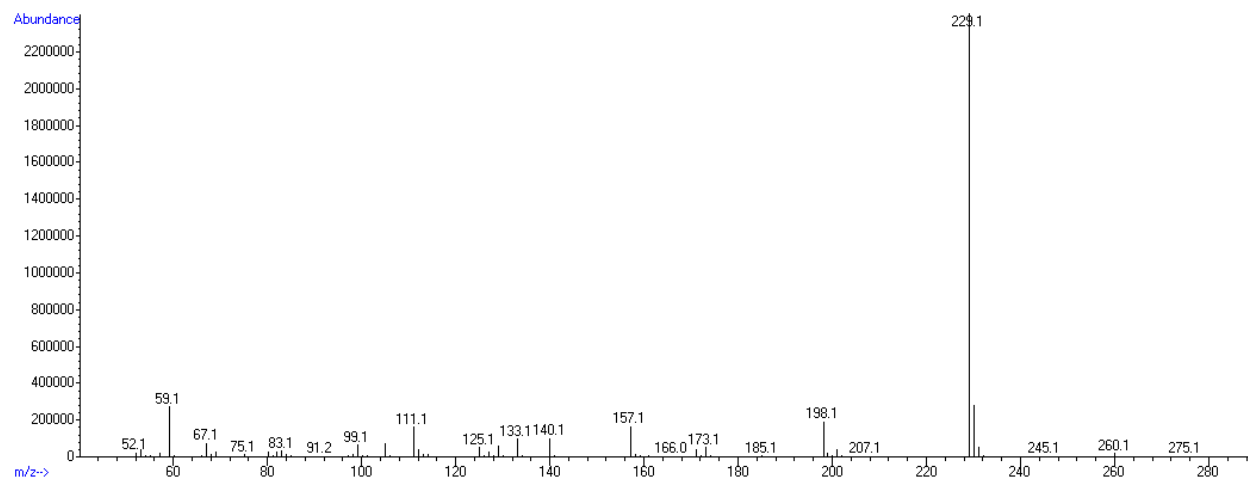
Figure S68. Retention time of 14.063: m/z = 260.1; indicates tetramethyl ethene-1,1,2,2-tetracarboxylate (expected m/z = 260.05).
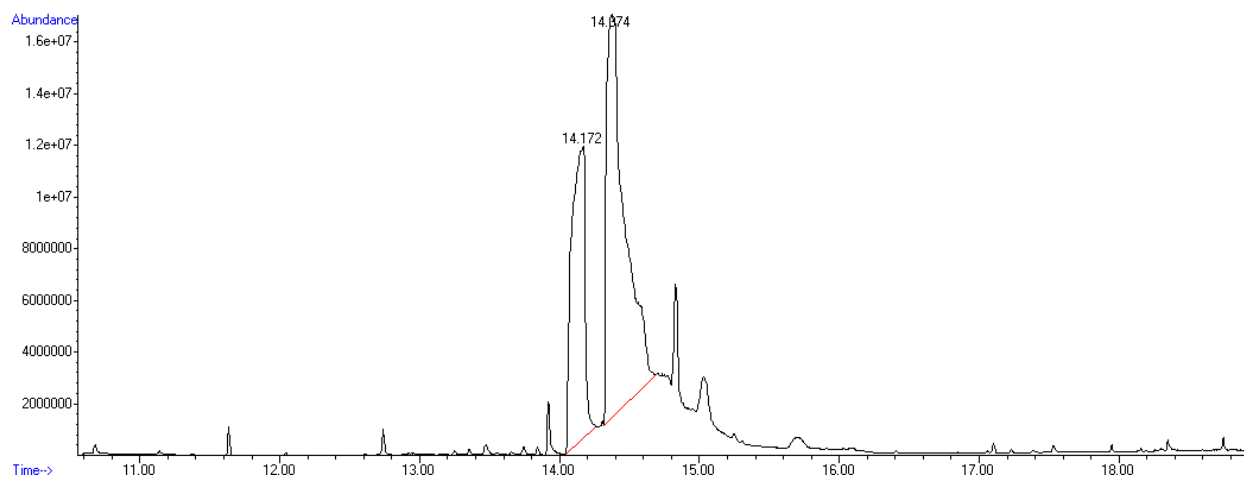
Figure S69. GC-MS of the crude product obtained in the catalytic synthesis of dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate. The cyclopropane is at 14.374 and tetramethyl ethene-1,1,2,2-tetracarboxylate is at 14.172.
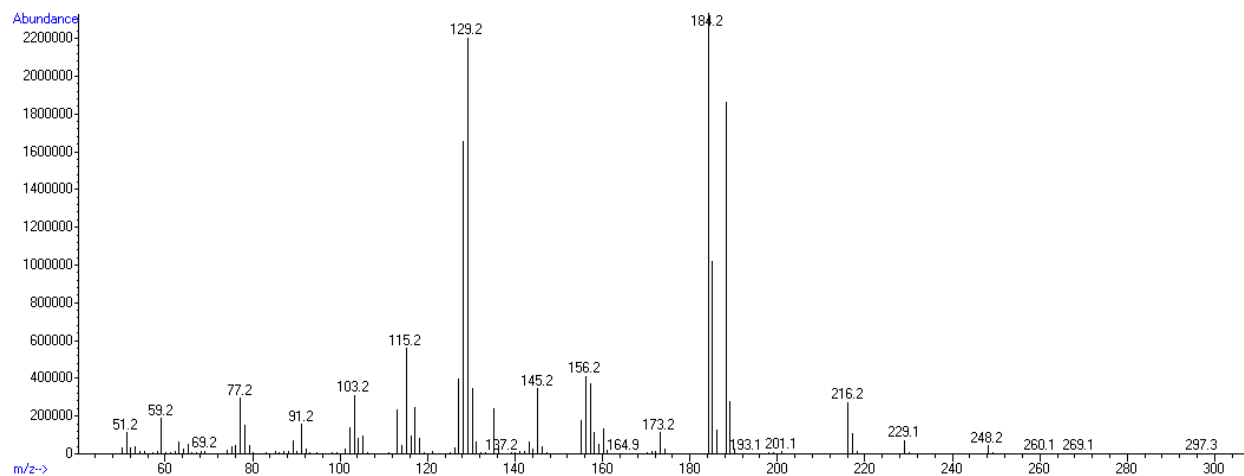
**Figure S70.** Retention time of 14.374: m/z = 248.2; indicates dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate (expected m/z = 248.1).
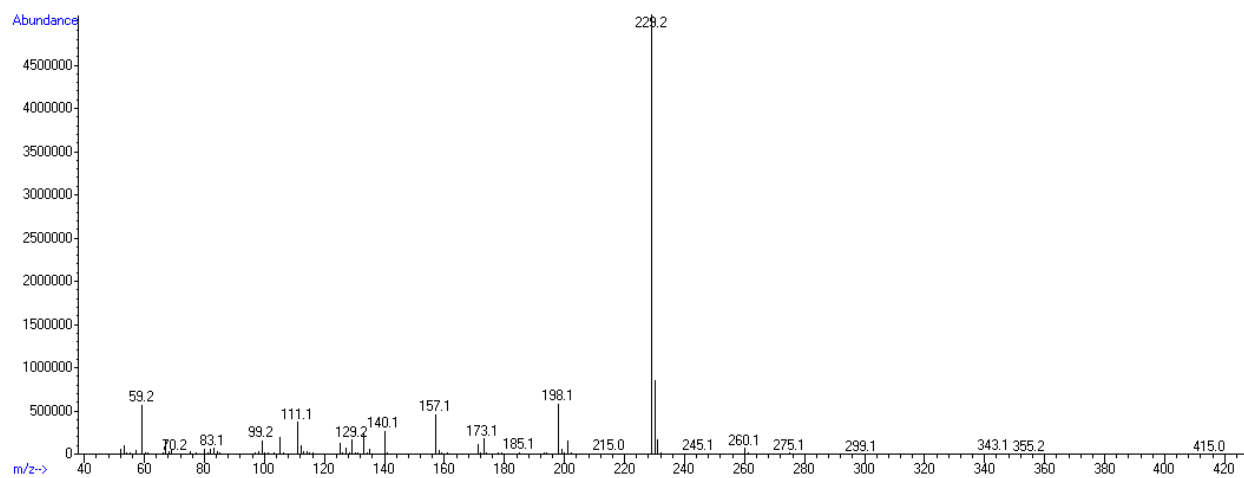
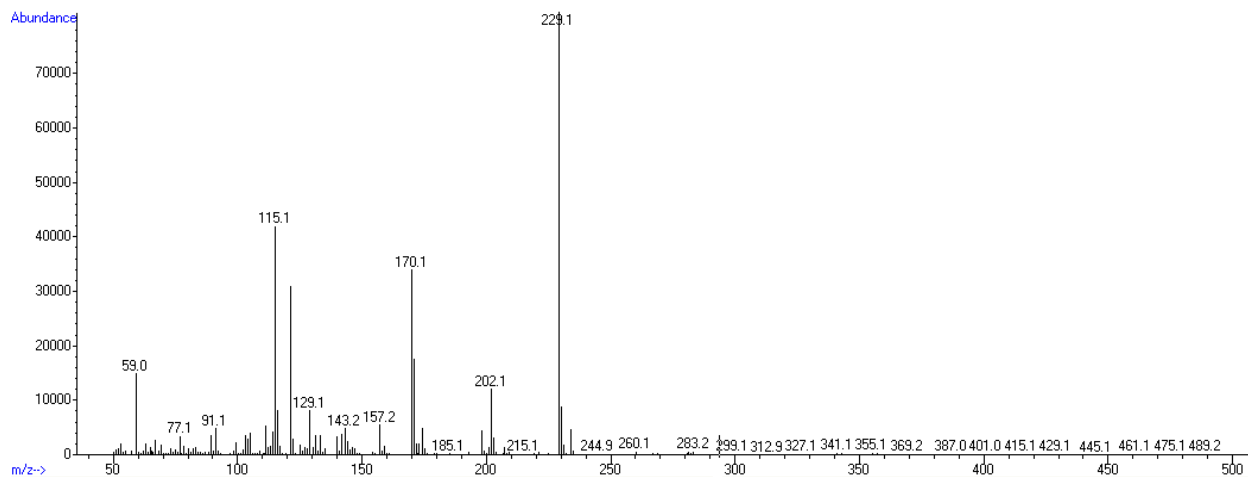**Figure S71.** Retention time of 14.172: m/z = 260.1; indicates tetramethyl ethene-1,1,2,2-tetracarboxylate (expected m/z = 260.05).

492.9709
$C_{21}H_{15}O_4CII = 492.9709$
0.0644 ppm

494.9683
$C_{30}H_4O_6CI = 494.9702$
-3.9025 ppm

493.9744

495.9714
$C_{24}H_{14}O_2CII = 495.9732$
-3.7712 ppm

492.4453   492.7826   493.1594   493.3806   493.7855   494.1637   494.4890   494.7789   495.5363   496.0280   496.9733

492.5   493.0   493.5   494.0   494.5   495.0   495.5   496.0   496.5   497.0

m/z

Figure S72. High resolution mass spectrum of diphenyl 2-(phenyl-l,3-iodaneylidene)malonate.

Figure S73. High resolution mass spectrum of tetraphenyl ethene-1,1,2,2-tetracarboxylate.

5. IR spectra
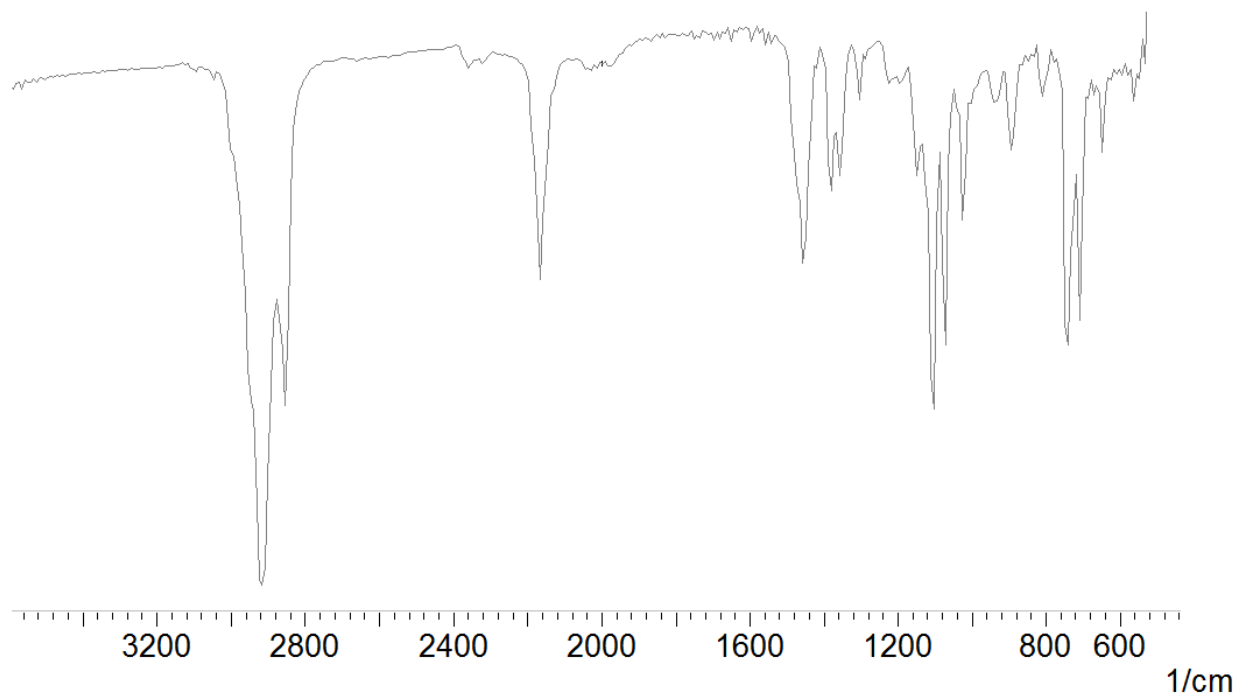
Figure S74. IR spectrum of Fe(OR)$_2$(CNAd)$_2$ (**6**).
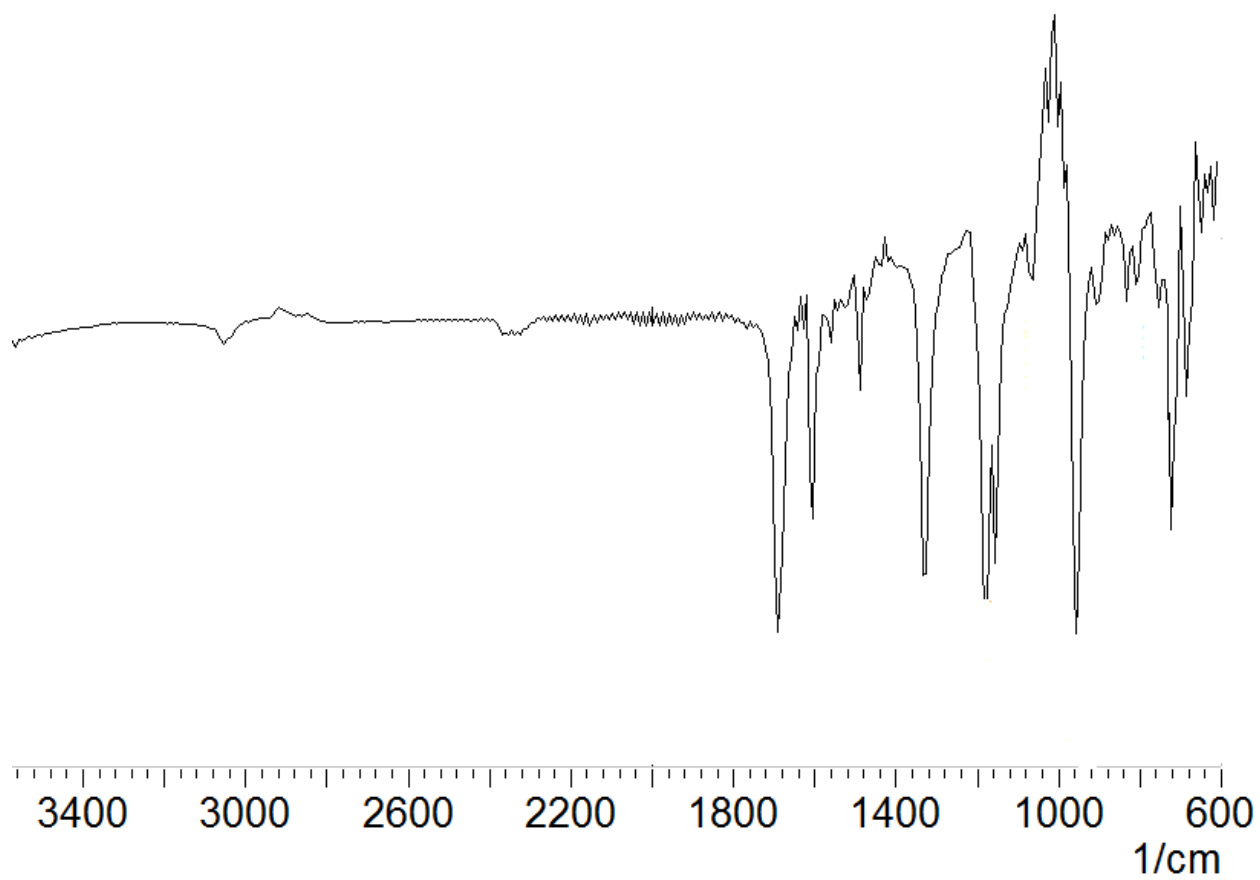
Figure S75. IR spectrum of diphenyl 2-(phenyl-l3-iodaneylidene)malonate.

6. Computational Details

Geometry optimizations were performed in Gaussian09[14] at the BP86-D3(BJ)/def2-SVP level of theory.[15-18] Structures were optimized with multiple starting structures and spin multiplicities to allow the redox/spin flexibility this system provides (see separate file ESI_OptimizedStructures.xyz). Stationary points were confirmed as minima or first-order saddle points by analyzing the harmonic frequencies and wavefunctions were tested for stability at each optimized structure. Those frequencies were used to estimate thermodynamic corrections using standard approximations at room temperature (**Table S1**).[19] Electronic energy refinemen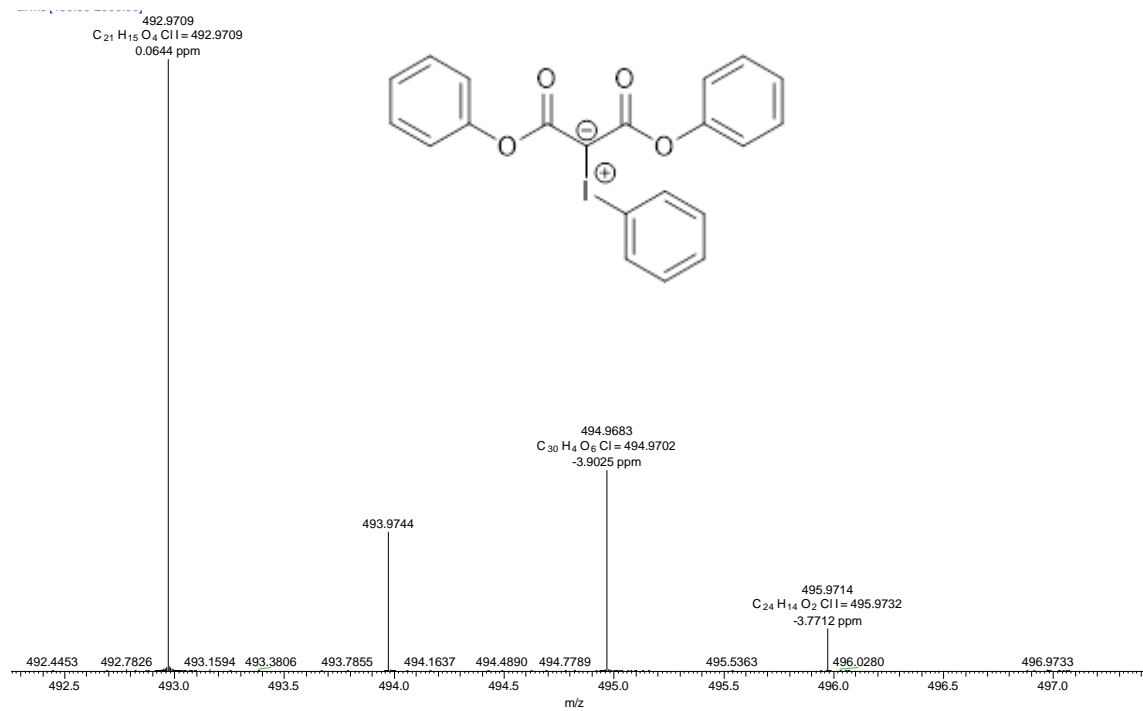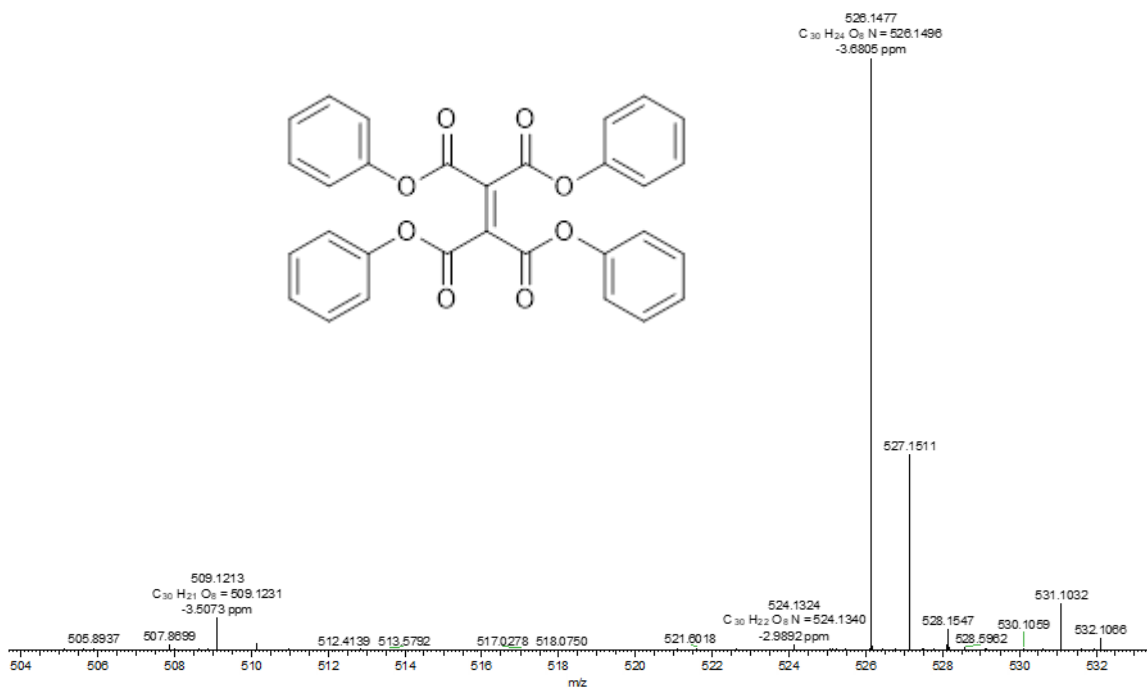ts were done at the B3LYP-D3(BJ)/def2-TZVP/SMD(benzene) level of theory.[17,20-24] Triple-zeta free energies were estimated as $G_{TZ} \approx G_{DZ} + (E_{TZ} - E_{DZ})$. Electronic and geometric structure analyses were done in GaussView 6.[25]

Carbon-bound carbene analogues of **4** were optimized with multiple starting methyl ester orientations (denoted **4'**, **4"**, **4'''**, and **4''''**; see **Fig. S67**) as a singlet, triplet, quintet, and septet. **4''' quintet** was lowest in free energy (see **Table S1**).

Figure S76. Methyl ester orientations probed for the carbon-bound carbene analogues of **4**.

| 4' | 4" | 4''' | 4'''' |
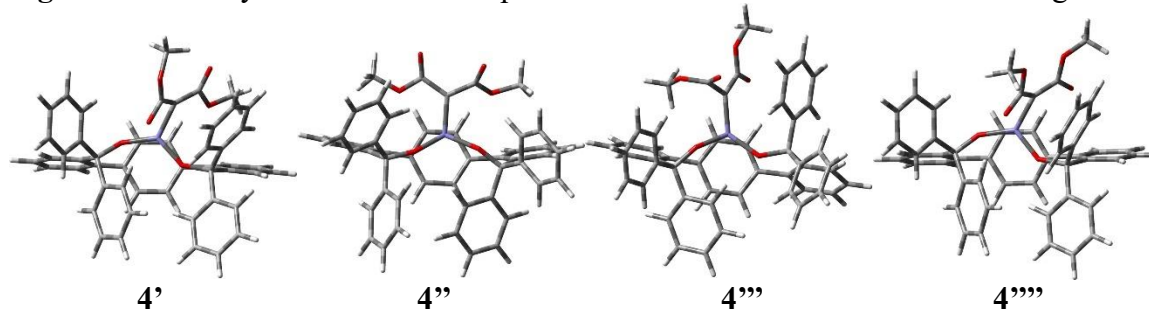
Four initial regioisomers were probed for the starting structures of quintet and septet **ii** (**Fig. S68**). These quintet and septet states were nearly isoenergetic. Because ring closing to form the cyclopropane adduct bound to Fe through the ester groups must be a quintet because it produces high-spin Fe^{II}, we opted to focus on the quintet states of **ii** in the proposed mechanism. We cannot, however, rule out involvement of the septet state for these intermediates.

Figure S77. Orientations of styrene after addition to **4**. In orientation shown, **ii'**, **ii"**, **ii'''**, and **ii''''** correspond to phenyl oriented to the top right, top left, bottom right, and bottom left, respectively.

| ii' | ii" | ii''' | ii'''' |
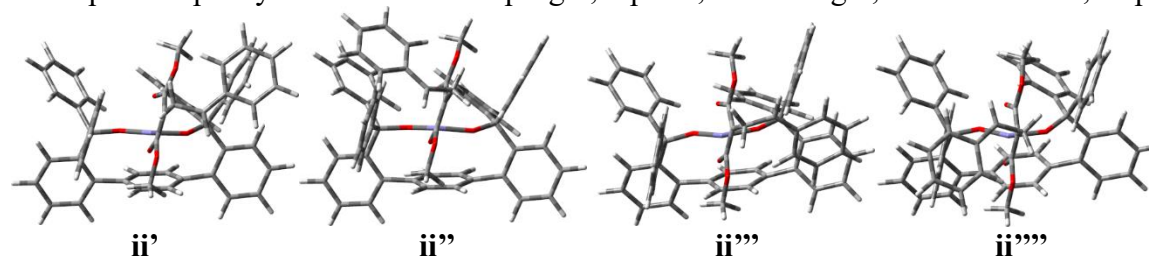
Figure S78. Constrained optimization along the C-IPh bond in **4-IPh** showing the absence of a significant electronic barrier for loss of PhI. Performed by starting with quintet **4-IPh** and elongating the bond. All attempts to optimize a transition state (constrained, QST, etc.) near 2.8 Å failed. Because the bond is already functionally broken upon binding to the metal center, these small energy changes are due to different weak interactions between IPh and the metal complex rather than significant electronic reorganization.
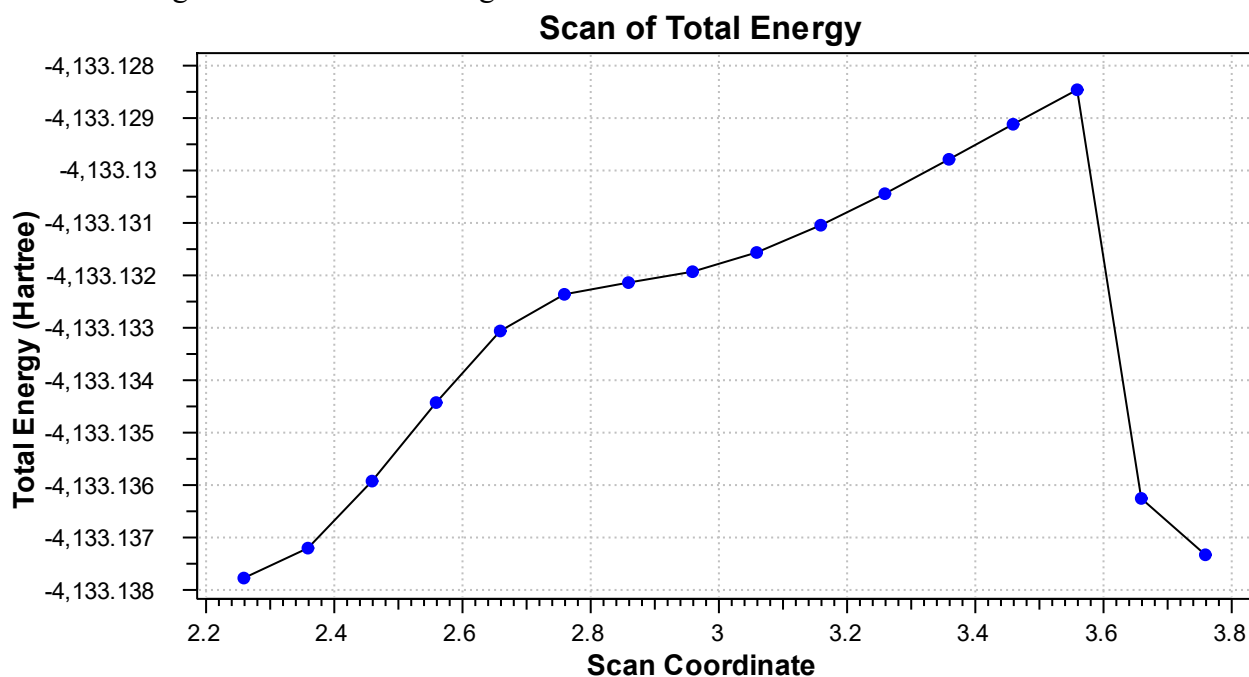
Figure S79. Constrained optimizations along the C-C bond formed when **4** and styrene react to form **ii**. Done starting with **ii"** quintet (top) and **ii"** septet (bottom) working backward toward **4** and styrene (similar plots were seen for other conformers). Both scans show the absence of a significant electronic barrier for C-C bond breaking.
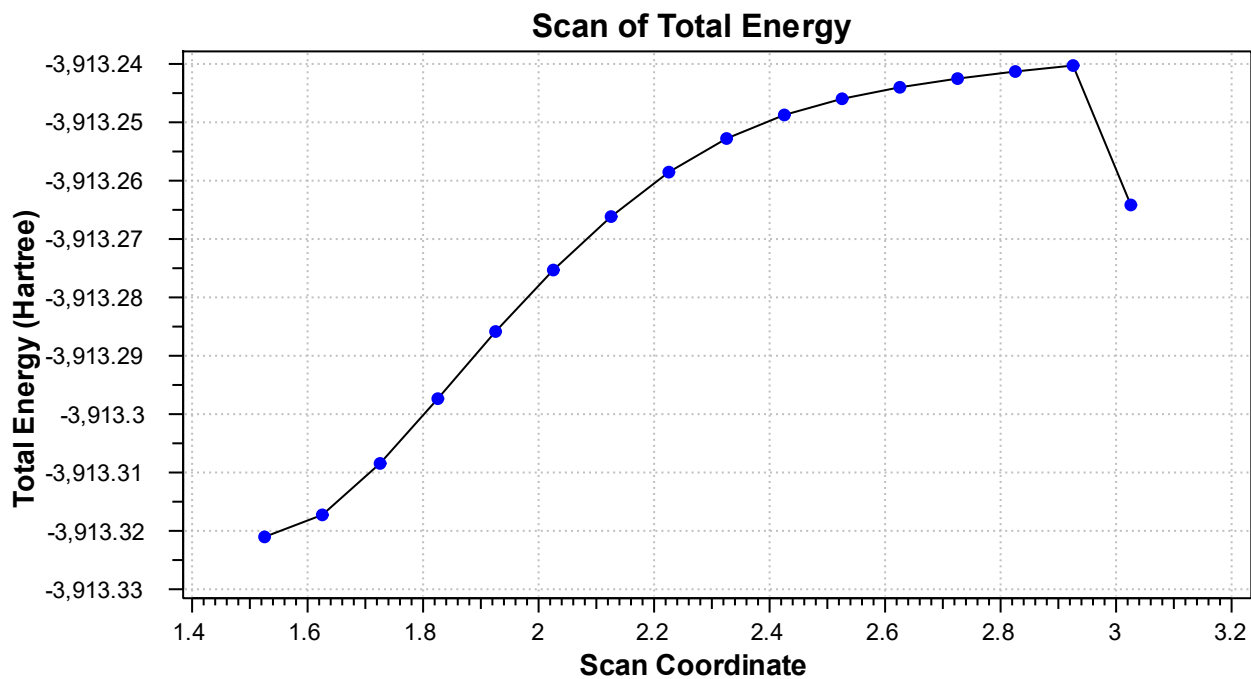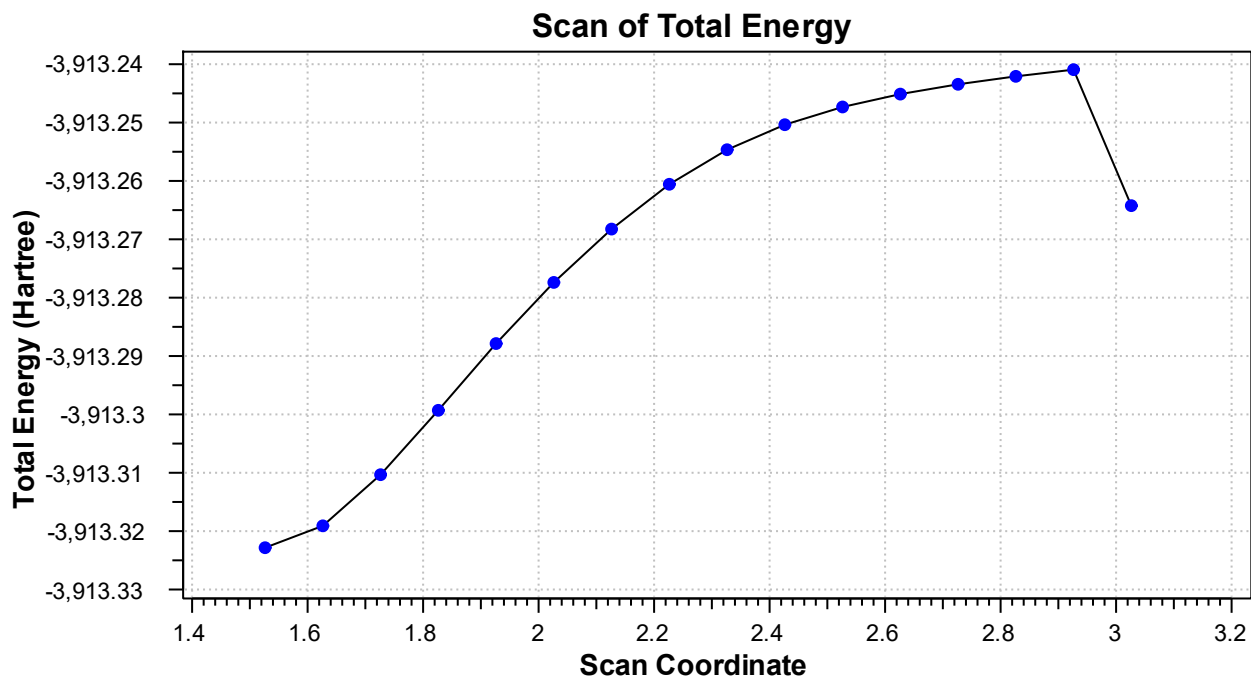
Spin densities show that the quintet states from the time of binding the iodonium ylide up until the ring-closing C-C bond formation occurs are all best described as high-spin Fe^{III} antiferromagnetically coupled to a ligand radical (Mulliken spins show ~5 spin up at Fe and ~1 spin down at ligand (specific locus depends on intermediate). The cyclopropane adduct only shows spin up at Fe and corresponds to 4 unpaired electrons (based on Mulliken spins), confirming reduction to high-spin Fe^{II} accompanies this last mechanistic step. This is reminiscent of the stepwise mechanism previously observed in nitrene reactivity with styrene to form substituted aziridines.[26-27]

Figure S80. Spin density isosurface plots (iso = 0.002 au, blue = spin up, white = spin down) of important intermediates along the proposed mechanism: **4''' quintet** (top left), **ylide i quintet** (top right), **4 quintet** (middle left), **ii''' quintet** (middle right), and **iii'''** (bottom).

Table S2. Thermodynamics (E_h) of all optimized species. SVP denotes BP86-D3(BJ)/def2-SVP, TZVP denoted B3LYP-D3(BJ)/def2-TZVP/SMD(benzene). * indicates a TS we could not locate.

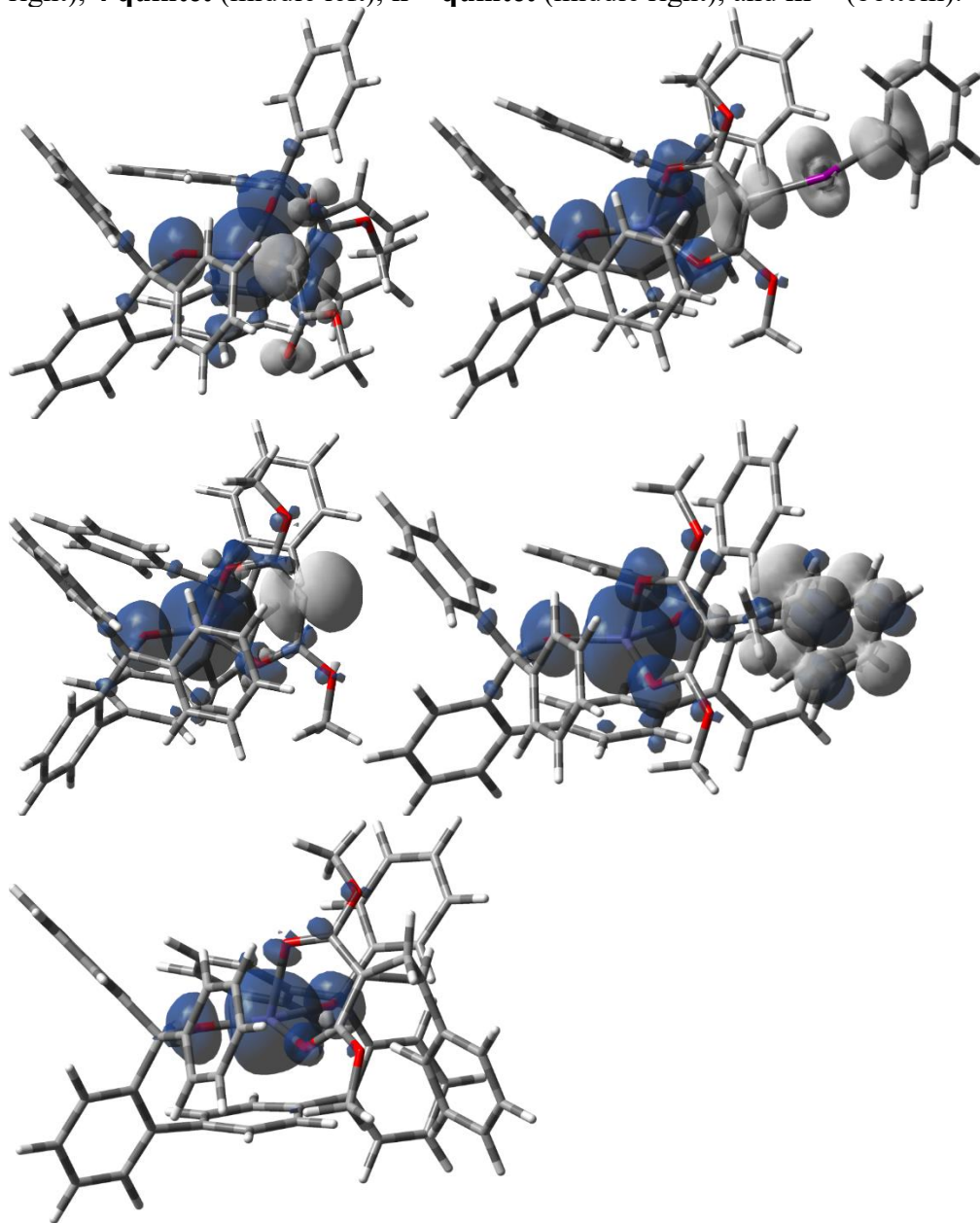| Species	S	E_{SVP}	H_{SVP}	G_{SVP}	E_{TZVP}
4'	0	-3603.783740	-3603.015050	-3603.147070	-3606.310372
4''	0	-3603.766950	-3602.999313	-3603.131435	-3606.287234
4'''	0	-3603.784112	-3603.015890	-3603.143696	-3606.289967
4''''	0	-3603.795263	-3603.024503	-3603.151798	-3606.313790
4'	1	-3603.792266	-3603.023040	-3603.157875	-3606.334631
4''	1	-3603.791856	-3603.022551	-3603.158790	-3606.339114
4'''	1	-3603.789804	-3603.022060	-3603.153396	-3606.334424
4''''	1	-3603.795141	-3603.026949	-3603.161305	-3606.340006
4'	2	-3603.786835	-3603.019019	-3603.154764	-3606.333741
4''	2	-3603.788295	-3603.019447	-3603.156252	-3606.340453
4'''	2	-3603.784127	-3603.016922	-3603.151097	-3606.344840
4''''	2	-3603.788533	-3603.020738	-3603.154485	-3606.337777
4'	3	-3603.765483	-3602.997967	-3603.132158	-3606.331686
4''	3	-3603.762698	-3602.995139	-3603.129683	-3606.333240
4'''	3	-3603.766840	-3602.999788	-3603.133963	-3606.335451
4''''	3	-3603.772687	-3603.005217	-3603.139993	-3606.341723
4	0	-3603.743999	-3602.975108	-3603.105986	-3606.290084
4	1	-3603.757881	-3602.988989	-3603.124077	-3606.314031
4	2	-3603.779378	-3603.011508	-3603.143582	-3606.351654
4	3	-3603.779037	-3603.011135	-3603.143439	-3606.351598
4-IPh	0	-4133.099648	-4132.237630	-4132.379842	-4135.862082
4-IPh	1	-4133.115133	-4132.252271	-4132.401088	-4135.885927
4-IPh	2	-4133.137774	-4132.274891	-4132.425628	-4135.922503
4-IPh	3	-4133.133837	-4132.271848	-4132.419053	-4135.922320
ii'	2	-3913.322838	-3912.414040	-3912.562470	-3916.232794
ii''	2	-3913.321943	-3912.413144	-3912.561440	-3916.232920
ii'''	2	-3913.324352	-3912.415719	-3912.563714	-3916.232775
ii''''	2	-3913.321969	-3912.413273	-3912.561685	-3916.232208
ii'	3	-3913.321031	-3912.412234	-3912.561239	-3916.233231
ii''	3	-3913.321789	-3912.412933	-3912.561318	-3916.232841
ii'''	3	-3913.323571	-3912.414955	-3912.562969	-3916.232768
ii''''	3	-3913.321610	-3912.412803	-3912.561514	-3916.233055
iii'	2	-3913.317213	-3912.406856	-3912.558634	-3916.234367
iii''	2	-3913.319770	-3912.410397	-3912.560777	-3916.238846
iii'''	2	-3913.332598	-3912.422806	-3912.569580	-3916.246078
iii''''	2	-3913.318434	-3912.408744	-3912.557088	-3916.234240
ii-iii-TS'	2	*	*	*	*
ii-iii-TS''	2	-3913.310043	-3912.40246	-3912.550425	-3916.218374
ii-iii-TS'''	2	-3913.312852	-3912.405162	-3912.553923	-3916.222217
ii-iii-TS''''	2	-3913.313675	-3912.404955	-3912.557021	-3916.222351
PhI	0	-529.331579	-529.237123	-529.275943	-529.5633061
styrene	0	-309.443171	-309.305842	-309.345082	-309.7986914

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