Highly Selective Synthesis of Tetra-substituted Furans and Cyclopropenes:
Copper(I)-catalyzed Formal Cycloadditions of Internal Aryl Alkynes and
Diazooacetates

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1. General Methods: Chemicals and Instrumentation

All organic chemicals were ordered from Sigma-Aldrich. Transition metal catalysts were obtained from STREM. Proper storage and handling was followed when they were not in use. Bulk chemicals were obtained from the College of Science at Rochester Institute of Technology. Diethyl ether and hexanes were obtained from Fisher Scientific (20 L) for column chromatography. All chemicals and solvents were used from the storage vessel as is, unless otherwise indicated. All reactions were conducted under dry argon gas. Infrared spectroscopic analyses were performed neat on a Shimadzu IRPrestige-21 Fourier Transform Infrared Spectrometer. High resolution mass spectral (HRMS) samples (<1mg) were dissolved in dichloromethane and sent for analysis on the Thermo Finnigan MAT 95XL Mass Spectrometer at State University of New York at Buffalo’s Mass Spectrometry Facility. Nuclear Magnetic Resonance Spectroscopic data was collected on RIT’s Bruker Avance DRX-300 MHz NMR spectrometer, or 500MHz as indicated. All samples were dissolved in CDCl₃ with a TMS internal standard prior to analysis. Spectra are reported in ppm relative to CDCl₃ at 7.26 for ¹H and 77.2 for ¹³C. X-ray crystallography samples were sent for analysis on a Bruker-AXS SMART Platform diffractometer equipped with an APEX II CCD detector at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester.

2. Diazoacetate Synthesis

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\text{Methyl 2-diazo-3-oxobutanoate (1a) To a solution of \textit{p}-acetamidobenzenesulfonyl azide (30.1 g, 126 mmol), methyl acetoacetate (12.4 mL, 115 mmol), and ACN (500mL) was added Et₃N (17.6 mL, 126 mmol) dropwise via syringe (13.0 mL/hr). The mixture was stirred at 0°C. After addition was complete, stirred mixture at room temperature overnight. The crude was then concentrated in vacuo on a rotary evaporator then dissolved in 100mL of 50% Et₂O/hexanes. The mixture was then filtered through celite, washed with 50% Et₂O/hexanes (5 x 50 mL), and reduced in vacuo on a rotary evaporator. Purified by column chromatography (SiO₂, 1/1 : Et₂O/hexanes) to afford 1a (15.2 g, 107 mmol, 92.7 % yield) as a yellow oil. ¹H NMR (CDCl₃, 300MHz): δ 3.85 (s, 3H), 2.49 (s, 3H). Compound 1a is a known compound and the analytical data is consistent with the literature.}^1
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Methyl 2-diazo-2-phenylacetate (1b) To a solution of p-acetamidobenzenesulfonyl azide (19.5 g, 81.2 mmol), methyl phenylacetate (10 mL, 62.5 mmol) and ACN (200 mL) was added DBU (12.1 mL) dropwise over 1 hour, then stirred at room temperature overnight. The crude was diluted with Et₂O (200 mL) and washed with saturated NH₄Cl (3 x 100 mL), dried with MgSO₄, filtered, and reduced in vacuo on a rotary evaporator. Purified by column chromatography (SiO₂, 1/5 : Et₂O/hexanes) to afford 1b (7.06 g, 40.1 mmol, 64.2 % yield) as a red oil. ¹H NMR (CDCl₃, 300 MHz): δ 7.49 (d, J= 7.5 Hz, 2H), 7.39 (t, 2H), 7.19 (t, 1H), 3.87 (s, 3H). Compound 1b is a known compound and the analytical data is consistent with the literature.²

Dimethyl 2-diazopropanedioate (1d) To a solution of p-acetamidobenzenesulfonyl azide (10.0 g, 41.6 mmol), methyl malonate (5.00 g, 37.8 mmol), and ACN (95.0 mL) was added Et₃N (5.80 mL, 41.6 mmol) dropwise via syringe. The reaction mixture was stirred at 0°C and allowed to stir to room temperature overnight. The crude was then reduced in vacuo on a rotary evaporator and dissolved in 100 mL of 50% Et₂O/hexanes. The mixture was then filtered through a plug of celite and washed with 50% Et₂O/hexanes (3 x 100 mL). Subsequently, the solvent removed in vacuo on a rotary evaporator and purified by column chromatography (SiO₂, 2/3 : Et₂O/hexanes) to afford 1c (2.59 g, 16.4 mmol, 39.4% yield) as a yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 3.85 (s, 6H). Compound 1c is a known compound and the analytical data is consistent with the literature.³

Methyl 2-diazo-3,3,3-trifluoropropanoate (1e) A solution of methyl 3,3,3-trifluoropropionate (6.54 mL, 64.1 mmol), tosyl hydrazide (11.9 g, 64.1 mmol), and DCM (120 mL) was heated to reflux (15 minutes) then stirred at room temperature 16 hours. Pyridine was added (30 mL) followed by a slow addition of POCl₃ (5.97 mL, 64.1 mmol) to allow a gentle reflux. The solution was stirred 20 minutes then H₂O (100

mL) was added at which point the phases separated. The aqueous layer was washed with Et₂O (3 x 100 mL). The organic layers were combined and washed with 1M HCl (150 mL), saturated NaHCO₃ (100 mL), and then followed by a brine solution (100 mL). The organic phase was dried with (MgSO₄). The resultant solution was filtered, reduced in vacuo on a rotary evaporator, and distilled by Kugelrohr apparatus (50°C, < 5 mm Hg) to give 1e (2.17 g, 12.9 mmol, 20.1% yield) as a yellow oil. ¹H NMR (CDCl₃, 300MHz): δ 3.86 (s, 3H).

3. Synthetic Procedure and Characterization of Internal Alkynes

(4-methoxyphenyl)prop-2-yn-1-ol (26) A solution of THF (18.0 mL, degassed) and 4-ethynylanisole (5.0 mL, 37.8 mmol) was cooled to -78°C to which was added 2.0M n-BuLi (19.9 mL, 39.7 mmol) dropwise over a 40 minute period after which the reaction stirred 2 hours at -78°C. The reaction was allowed to warm to 0°C. Paraformaldehyde (4.77 g, 30.0 mmol) was added and the reaction was allowed to stir for an additional 2.5 hours. The crude reaction mixture was diluted with Et₂O (50mL) and washed with H₂O and the organic phase was collected. The solvent was removed in vacuo on a rotary evaporator and purified by column chromatography (SiO₂, 1/5 - 2/3 : Et₂O/hexanes) to afford 26 (4.33 g, 26.7 mmol, 70.6% yield) as tan solid. ¹H NMR (CDCl₃, 300MHz): δ 7.37 (d, J= 8.8 Hz, 2H), 6.82 (d, J= 8.8 Hz, 2H), 4.47 (s, 2H), 3.79 (s, 3H), 2.35 (s, 1H); ¹³C NMR (CDCl₃, 300MHz): δ 159.8, 133.3, 114.7, 114.0, 86.0, 85.7, 55.4, 51.7. Compound 26 is a known compound and the analytical data is consistent with the literature.⁴

Methoxy-4-prop-1-ynyl-benzene (7) To a -78°C solution of 4-ethynylanisole (5.00 g, 36.7 mmol) in THF (100 mL) was added 2.0M n-BuLi (20.2 mL, 40.4 mmol) dropwise. The reaction was allowed to stir for an additional 1 hour at -78°C. Methyl iodide (22.9 mL, 367 mmol) was added dropwise via syringe pump over 1 hour. The reaction was allowed to stir to room temperature overnight. The reaction mixture was diluted with Et₂O (50mL) washed with saturated aqueous solutions of NH₄Cl (50 mL), NaHCO₃ (50 mL), and brine (50 mL). The solvent was removed in vacuo on a rotary evaporator and the

resultant oil was purified by Kugelrohr apparatus (115°C, < 5 mm Hg) to afford 7 (4.22 g, 28.9 mmol, 79.0 % yield) as a clear oil. $^1$H NMR (CDCl$_3$, 500MHz): δ 7.32 (d, $J = 8.9$ Hz, 2H), 6.81 (d, $J = 8.9$ Hz, 2H), 3.79 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (CDCl$_3$, 500MHz): δ 159.2, 133.0, 116.4, 114.0, 84.3, 79.6, 55.4, 4.5. Compound 7 is a known compound and the analytical data is consistent with the literature.$^6$

**Methoxy-2-prop-1-ynyl-benzene (10)** A solution of 2-ethylanisole (1.00 g, 7.34 mmol) and THF (75 mL) was cooled to -78°C to which was added 2.0M BuLi (4.04 mL, 8.07 mmol) dropwise. The reaction was stirred 30 minutes at -78°C and methyl iodide (4.56 mL, 73.4 mmol) and stirred reaction to room temperature overnight. The solvent was removed in vacuo on a rotary evaporator and the crude oil was distilled by Kugelrohr apparatus (100°C, < 5 mm Hg) to afford 10 (0.931 g, 6.37 mmol, 87 % yield) as translucent oil. $^1$H NMR (CDCl$_3$, 500MHz): δ 7.38 – 7.36 (m, 1H), 7.24 – 7.23 (m, 1H), 6.90 – 6.85 (m, 2H), 3.88 (s, 3H), 2.12 (s, 3H); $^{13}$C NMR (CDCl$_3$, 300MHz): δ 160.0, 133.8, 129.1, 113.3, 110.7, 90.2, 76.0, 56.0, 5.0. Compound 10 is a known compound and the analytical data is consistent with the literature.$^7$

**Tert-butyl-[3-(4-methoxyphenyl)prop-2-ynoxy]-dimethyl-silane (11)** To a solution of 26 (1.00 g, 6.17 mmol), Et$_3$N (1.72 mL, 12.3 mmol), and DCM (12.5 mL) was added a solution of TBS-Cl (1.21 g, 8.02 mmol) in DCM (3 mL) dropwise. The reaction was allowed to stir overnight to room temperature. The reaction mixture was concentrated in vacuo on a rotary evaporator and purified by column chromatography (SiO$_2$, 1/10 - 1/5 : Et$_2$O/hexanes) to afford 11 (1.29 g, 4.66 mmol, 75.5 % yield) as a yellow oil. IR (film) 2932 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500MHz): δ 7.36 (d, $J = 8.9$ Hz, 2H), 6.83 (d, $J = 8.9$ Hz, 2H), 4.53 (s, 2H), 3.80 (s, 3H), 0.94 (s, 9H), 0.16 (s, 6H); $^{13}$C NMR (CDCl$_3$, 500MHz): δ 159.8, 133.3, 115.3, 114.1, 86.7, 84.9, 55.5, 52.5, 26.1, 18.6, 0.19, -4.8. Compound 11 is a known compound and the analytical data is consistent with the literature.$^8$

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**Phenoxypropynylbenzene (15)** A solution of 1-ethynyl-4-phenoxy- benzene (1.00 g, 5.15 mmol) in THF (20 mL) was cooled to -78°C. 2.0M BuLi (3.08 mL, 6.18 mmol) was added dropwise and allowed to stir at -78°C for an additional hour. Methyl iodide (3.2 mL, 51.5 mmol) was added dropwise and the reaction was allowed to overnight to room temperature. The reaction was quenched with H₂O (30
and then the organic phase was separated and dried with MgSO₄. The solvent was removed from the crude reaction and concentrated in vacuo on the rotary evaporator. The residue was distilled on a Kugelrohr apparatus (170°C, < 5 mm Hg) to give 15 (0.793 g, 3.81 mmol, 74.0% yield) as a translucent oil. ¹H NMR (CDCl₃, 500MHz): δ 7.36 - 7.32 (m, 4H), 7.13 – 7.10 (m, 1H), 7.02 – 7.00 (m, 2H), 6.90 (d, J= 8.8 Hz, 2H), 2.04 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 157.1, 156.9, 133.2, 130.0, 123.8, 119.4, 118.9, 118.6, 85.2, 79.4, 4.5. HRMS (ESI) m/z calcd for C₁₅H₁₂O, 208.0883, found 208.0890 [M]+.

Compound 15 is a known compound and the ¹H NMR analytical data are consistent with those in the literature.⁹

4. General Procedure for CuI-Catalyzed Cycloaddition

A flame-dried 25-mL one-necked round bottom flask equipped with a Teflon-coated stir bar and reflux condenser was purged with argon gas. Catalyst was quickly added (0.103 mmol, 0.05 eq) and all joints were parafilmed. Internal alkyne (2.05 mmol, 1.00 eq) was added via syringe with a long needle through the reflux condenser. The reaction was heated to 110°C and stirred for 15 minutes. Diazooacetate (13.1 mmol, 6.39 eq) was then added dropwise via syring pump (0.167 mL/hr). The reaction was heated overnight and the crude reaction mixture was purified using column chromatography.

5. Compound Characterization of Furans and Cyclopropenes

Methyl 5(4-methoxyphenyl)-2,4-dimethyl-furan-3-carboxylate (8a) Purified by column chromatography (SiO₂, 1/10 : Et₂O/hexanes) to afford 8a as a clear oil (267 mg, 1.0 mmol, 50% yield, 61% conversion). Rf=0.64; 2/3 : Et₂O/hexane. mp = 58 - 61°C; IR (film) 1713 cm⁻¹; ¹H NMR (CDCl₃, 500MHz): δ 7.50 (d, J= 9.0 Hz, 2H), 6.95 (d, J= 8.9 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.59 (s, 3H), 2.35 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 165.5, 159.0, 158.2, 148.0, 127.8, 123.9, 115.5, 115.1, 114.2, 5.5, 1.2, 14.6, 11.0. HRMS (ESI) m/z calcd for C₁₅H₁₆O₄, 260.1043, found 260.1042 [M]+.

Methyl 2,4-dimethyl-5-phenyl-furan-3-carboxylate (16a) Purified by column chromatography (SiO₂, 1/10 : Et₂O/hexanes) to afford a 5:1 regioisomeric mixture of 16a as a clear oil (40 mg, 0.17 mmol, 8.5% yield). Major isomer: Rf = 0.75; 2/3 : Et₂O/hexane. IR (film) 1715 cm⁻¹; ¹H NMR (CDCl₃, 500MHz): δ 7.59 - 7.57 (m, 2H), 7.41 (t, 2H), 7.29 (t, 1H), 3.86 (s, 3H), 2.61 (s, 3H), 2.40 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 165.3, 158.6, 147.8, 131.0, 128.5, 127.2, 126.1, 116.9, 115.2, 51.1, 14.5, 10.9. HRMS (ESI) m/z calcd for C₁₄H₁₄O₃, 230.0937, found 230.0948 [M⁺].

Methyl 5-(2-methoxyphenyl)-2,4-dimethyl-furan-3-carboxylate (17a) Purified by column chromatography (SiO₂, 1/20 - 1/10 : Et₂O/hexanes) to afford 17a as a clear oil (101 mg, 0.39 mmol, 19% yield, 35% conversion). Rf = 0.60; 1/4 : EtOAc/hexane. IR (film) 1715 cm⁻¹; ¹H NMR (CDCl₃, 500MHz): δ 7.37 - 7.32 (m, 2H), 7.03 - 6.96 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 2.59 (s, 3H), 2.13 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 165.6, 159.2, 157.3, 145.6, 131.3, 130.1, 120.6, 120.0, 118.7, 114.7, 111.5, 55.7, 51.2, 14.7, 11.2. HRMS (ESI) m/z calcd for C₁₅H₁₆O₄, 260.1043, found 260.1031 [M⁺].

Methyl 4-[[tert-butyl(dimethyl)silyl]oxy]-5-(4-methoxyphenyl)-2-methyl-furan-3-carboxylate (18a) Purified by column chromatography (SiO₂, 1/35 - 1/20 : Et₂O/hexanes) to afford 18a as a clear oil (306 mg, 0.78 mmol, 38% yield, 59% conversion). Rf = 0.60; 1/4 : Et₂O/hexane. mp = 44 - 47°C; IR (film) 2932, 1713 cm⁻¹; ¹H NMR (CDCl₃, 500MHz): δ 7.68 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9, 2H), 4.79 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.60 (s, 3H), 0.93 (s, 9H), 0.12 (s, 6H); ¹³C NMR (CDCl₃, 500MHz): δ
Methyl 4-(methoxycarbonyloxymethyl)-5-(4-methoxyphenyl)-2-methyl-furan-3-carboxylate (19a) Purified by column chromatography (SiO$_2$, 1/10 - 1/5 : Et$_2$O/hexanes) to afford 19a as a clear oil (163 mg, 0.49 mmol, 24% yield, 35% conversion). $R_f$ = 0.58 in 3/2 : Et$_2$O/hexane. mp = 71 - 74°C; IR (film) 2980, 2970, 2957, 1749, 1717 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500MHz): $\delta$ 7.51 (d, $J$ = 8.7 Hz, 2H), 6.97 (d, $J$ = 8.7 Hz, 2H), 5.32 (s, 2H), 3.85 (s, 6H), 3.81 (s, 3H), 2.62 (s, 3H); $^{13}$C NMR (CDCl$_3$, 500MHz): $\delta$ 164.3, 160.0, 158.8, 155.6, 152.5, 128.4, 121.9, 114.2, 114.0, 113.0, 61.0, 55.3, 54.7, 51.3, 14.1. HRMS (ESI) m/z calcd for C$_{21}$H$_{30}$O$_5$Si, 390.1857, found 390.1859 [M]$^+$.

Methyl 4-(acetoxymethyl)-5-(4-methoxyphenyl)-2-methyl-furan-3-carboxylate (20a) Purified by column chromatography (SiO$_2$, 1/10 - 1/5 : Et$_2$O/hexanes) to afford 20a as a yellow oil in (116 mg, 0.36 mmol, 18% yield, 29% conversion). $R_f$ = 0.48 in 1/1 : Et$_2$O/hexane. mp = 84 - 86°C; IR (film) 1740, 1717 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500MHz): $\delta$ 7.49 (d, $J$ = 8.9 Hz, 2H), 6.96 (d, $J$ = 9.0, 2H), 5.25 (s, 2H), 3.85 (s, 3H), 2.62 (s, 3H), 2.09 (s, 3H); $^{13}$C NMR (CDCl$_3$, 500MHz): $\delta$ 171.1, 164.6, 160.1, 159.0, 152.2, 128.5, 122.3, 114.4, 114.3, 113.7, 58.0, 55.5, 51.5, 21.2, 14.4. HRMS (ESI) m/z calcd for C$_{17}$H$_{18}$O$_6$Na, 341.0996, found 341.0994 [M+Na]$^+$. 

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Methyl 5-(4-methoxyphenyl)-2-methyl-4-trimethylsilyl-furan-3-carboxylate (21a) Purified by column chromatography (SiO₂, 1/20 - 1/5 : Et₂O/hexanes) to afford 21a as a clear oil (124 mg, 0.39 mmol, 19% yield, 32% conversion). Rf = 0.79 in 2/3 : Et₂O/hexane. mp = 66 - 70°C; IR (film) 1717 cm⁻¹; ¹H NMR (CDCl₃, 500MHz): δ 7.33 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H), 3.84 (s, 3H), 2.56 (s, 3H), 0.09 (s, 9H); ¹³C NMR (CDCl₃, 500MHz): δ 165.8, 160.3, 158.8, 158.5, 131.4, 125.1, 118.8, 114.4, 113.5, 55.5, 51.2, 13.9, 0.75. HRMS (ESI) m/z calcld for C₁₇H₂₂O₄Si, 318.1282, found 318.1288 [M⁺].

Methyl 2,4-dimethyl-5-(4-phenoxyphe)nyl)furan-3-carboxylate (22a) Purified by column chromatography (SiO₂, 1/20 - 1/5 : Et₂O/hexanes) to afford 22a as a clear oil (132 mg, 0.41 mmol, 39% yield, 58% conversion). Rf = 0.78 in 2/3 : Et₂O/hexane). IR (film) 1713 cm⁻¹; ¹H NMR (CDCl₃, 500MHz): δ 7.53 (d, J = 8.7 Hz, 2H), 7.34 (t, 2H), 7.11 (t, 1H), 7.05-7.03 (m, 4H), 3.85 (s, 3H), 2.59 (s, 3H), 2.37 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 165.4, 158.5, 157.1, 156.7, 147.6, 130.0, 127.8, 126.3, 123.7, 119.2, 118.9, 116.3, 115.3, 51.2, 14.6, 11.0. HRMS (ESI) m/z calcld for C₂₀H₁₉O₄, 323.1278, found 323.1272 [M+H⁺].

Methyl 2-methoxy-5-(4-methoxyphenyl)- 4-methyl-furan-3-carboxylate (23c) Purified by column chromatography (SiO₂, 1/5 - 1/3 : Et₂O/hexanes) to afford 23c as a clear oil (79.6 mg, 0.29 mmol, 23% yield, 23% conversion). Rf = 0.49; 1/1 : Et₂O/hexane. IR (film) 2947, 1705 cm⁻¹. ¹H NMR (CDCl₃, 500MHz): δ 7.44 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 4.14 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H) 2.36 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 164.5, 161.9, 158.8, 139.9, 127.4, 123.5, 116.5, 114.2, 93.1, 57.8,
Methoxy-5-(4-methoxyphenyl)-4-methyl-3-(trifluoromethyl)furan (23d) Purified by column chromatography (SiO₂, 1/30 : Et₂O/hexanes) to afford 23d as a yellow oil (135 mg, 0.47 mmol, 23% yield, 23% conversion). Rₙ = 0.64; 2/3 : Et₂O/hexane. IR (film) 1649, 1622, 1601 cm⁻¹. ¹H NMR (CDCl₃, 500MHz): δ 7.42 (d, J = 9.0 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 4.05 (s, 3H), 3.94 (s, 3H), 2.21 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 159.0, 156.7, 140.5, 127.4, 124.4, 123.3, 114.3, 114.0, 58.5, 55.5, 10.0. HRMS (ESI) m/z calcd for C_{14}H_{14}O₃F₃, 287.0890, found 287.0884 [M+H]+.

Methyl 2-(4-methoxyphenyl)-3-methyl-1-phenyl-cycloprop-2-ene-1-carboxylate (23b) Purified by column chromatography (SiO₂, 1/20 - 3/20 : Et₂O/hexanes) to afford 23b as a pale yellow solid (353 mg, 1.2 mmol, 59% yield, 65% conversion). Rₙ = 0.53; 2/3 : Et₂O/hexane. mp = 69 - 73°C; IR (film) 2947, 1713, 1605 cm⁻¹. ¹H NMR (CDCl₃, 500MHz): δ 7.47 (d, J = 8.8 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.27 – 7.24 (m, 2H), 7.19 – 7.16 (m, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 3.69 (s, 3H), 2.35 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 175.5, 160.2, 141.5, 130.9, 128.3, 128.2, 126.3, 119.4, 114.6, 108.6, 108.1, 55.5, 52.0, 35.4, 9.7. HRMS (ESI) m/z calcd for C_{19}H_{18}O₃Na, 317.1148, found 317.1153 [M+Na]⁺.

Methyl 2-(2-methoxyphenyl)-3-methyl-1-phenyl-cycloprop-2-ene-1-carboxylate (24b) Purified by column chromatography (SiO₂, 3/20 - 1/3 : Et₂O/hexanes) to afford 24b as a pale yellow solid (407 mg,
1.4 mmol, 67% yield, 73% conversion). Rf= 0.51; 2/3 : Et2O/hexane. mp = 100 - 101°C; IR (film) 1717 cm⁻¹; ¹H NMR (CDCl₃, 500MHz): δ 7.39 - 7.24 (m, 6H), 7.17 (t, 1H), 6.97 – 6.92 (m, 2H), 3.93 (s, 3H), 3.69 (s, 3H), 2.38 (s, 3H); ¹³C NMR (CDCl₃, 500MHz): δ 175.6, 158.5, 141.7, 130.5, 130.2, 128.4, 128.1, 126.3, 120.8, 116.0, 112.7, 110.6, 105.2, 55.7, 55.2, 34.6, 10.2. HRMS (ESI) m/z calcd for C₁₉H₁₈O₃, 294.1250, found 294.1254 [M⁺].

2-(4-Methoxy-phenyl)-1-phenyl-3-trimethylsilyl-cycloprop-2-enecarboxylic acid methyl ester (25b) Purified by column chromatography (SiO₂, 1/20 - 1/5 : Et₂O/hexanes) to afford 25b as a yellow solid (331 mg, 0.94 mmol, 46% yield, 49% conversion). Rf= 0.63; 2/3 : Et₂O/hexane. mp =  95 - 97°C; IR (film) 2955, 1713, 1605 cm⁻¹; ¹H NMR (CDCl₃, 500MHz): δ 7.53 (d, J= 8.8 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.25 – 7.21 (m, 2 H), 7.14 (t, 1H), 6.94 (d, J=  8.8 Hz, 2H), 3.83 (s, 3H), 3.67 (s, 3H), 0.27 (s, 9H); - ¹³C NMR (CDCl₃, 500MHz): δ 175.8, 161.0, 142.4, 131.6, 128.2, 128.0, 126.0, 125.7, 119.9, 114.6, 110.6, 55.6, 51.9, 34.7, -0.8. HRMS (ESI) m/z calcd C₂₁H₂₅O₃Si, 353.1567, found 353.1562 [M+H]⁺.